MODULAR AND DIVERSITY-ORIENTED SYNTHETIC APPROACHES TO BENZOHETEROLES AND DIBENZOHETEROLES

NANYANG TECHNOLOGICAL UNIVERSITY

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WU BIN

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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List of Abbreviations

δ	chemical shift (ppm)
℃	degree centigrade
Ac	acetyl
aq	aqueous
Ar	aryl (substituted aromatic ring)
Bn	benzyl
Boc	*Tert*-butyloxycarbonyl
*t*Bu	*tert*-butyl
d	doublet
DBU	1,8-diazabicyclo(5.4.0)undec-7-ene
DMF	*N*,*N*-dimethylformamide
DMSO	dimethyl sulfoxide
Et	ethyl
h	hour
H	hydrogen
HRMS	High Resolution Mass Spectrometry
Hz	hertz
J	coupling constants
LA	Lewis acid
m	multiplet
M	concentration (mol/L)
M^+	parent ion peak (mass spectrum)
Me	methyl
mg	milligram

min	minute(s)
mL	milliliter
mmol	millimole
mol %	mole percent
m.p.	melting point
MPHT	*N*-Methylpyrrolidin-2-one hydrotribromide
NBS	*N-Bromosuccinimide*
NMP	*N*-Methylpyrrolidone
NMR	nuclear magnetic resonance
Ph	phenyl
PMP	*p*-methoxyphenyl
ppm	parts per million
*i*Pr	isopropyl
q	quartet
rt	room temperature
s	singlet
t	triplet
TBHP	tert-Butyl hydroperoxide
TBS	*tert*-butyldimethylsilyl
THF	tetrahydrofuran
TLC	thin layer chromatography
TMS	Trimethylsilyl
PTSA	*p*-toluenesulfonic acid
Xantphos	4,5-bis(diphenylphosphino)-9,9-dimethylxanthene

Abstract

Benzo[*b*]heterole represents an important class of heterocycles that is comprised of a variety of functional molecules. For example, indole and benzofuran are ubiquitously present in biologically active natural and unnatural compounds. As such, a number of methods have been developed for their synthesis. On the other hand, benzoheteroles containing other Group 13–16 elements are now gaining interested, especially for their unique optical and electronic properties that warrant their applications in various areas including electronics, imaging, and sensing. Nevertheless, synthetic methods for these heterocycles have been relatively limited.

This thesis describes the development of new synthetic approaches that enable expedient, modular, and divergent synthesis of benzoheteroles and related heterocycles from readily available starting materials. Our main approach capitalizes on the cobalt-catalyzed "migratory arylzincation" reaction of an alkyne, which affords an *ortho*-alkenylarylzinc species as a key intermediate. It has been demonstrated that this common intermediate can be readily transformed into several members of the benzoheterole family such as benzothiophene, benzoselenophene, benzotellurophene, and benzophosphole, in a one-pot manner for some cases. Besides benzoheteroles, we have also established a new synthetic route to dibenzoheteroles based on the facile two-step conversion of 2-iodobiaryls into 2,2'-diiodobiaryls via a sequence of oxidative cyclization–iodinative ring opening. Collectively, the new approaches developed in this study have opened access to a diverse set of hitherto inaccessible or difficult-to-access functionalized benzoheteroles and related heterocycles, which may hold promise for applications as functional materials.

Chapter 1. Introduction

1.1 Brief introduction to benzo[*b*]heteroles

Indole and benzofuran represent classes of benzo-fused five-membered heterocyclic compounds that are widely found in natural products. They are also common structural elements in pharmaceutical drugs and other functional molecules. [1] Consequently, many elegant methods have been developed for their synthesis over the years.[2] On the other hand, their analogous benzoheteroles containing other Group 13-16 heteroatom elements have also attracted significant attention in recent years (Figure 1.1). For example, benzothiophene frequently occurs in a wide variety of pharmaceuticals and natural products possessing useful biological activities.[3] Besides this, a major reason for the increasing interest in benzoheteroles, many of which do not exist in nature, resides in their unique optoelectronic properties. From the structure point of view, a benzoheterole can be considered as a heteroatom-bridged styrene. Hence, the orbital interaction between the heteroatom and the π-conjugated framework is expected to endow each benzoheterole with unique electronic properties including the energy levels and gaps of the frontier orbitals. [4] Furthermore, the electronic properties may further be fine-tuned by the peripheral substituents for potential applications in material science.

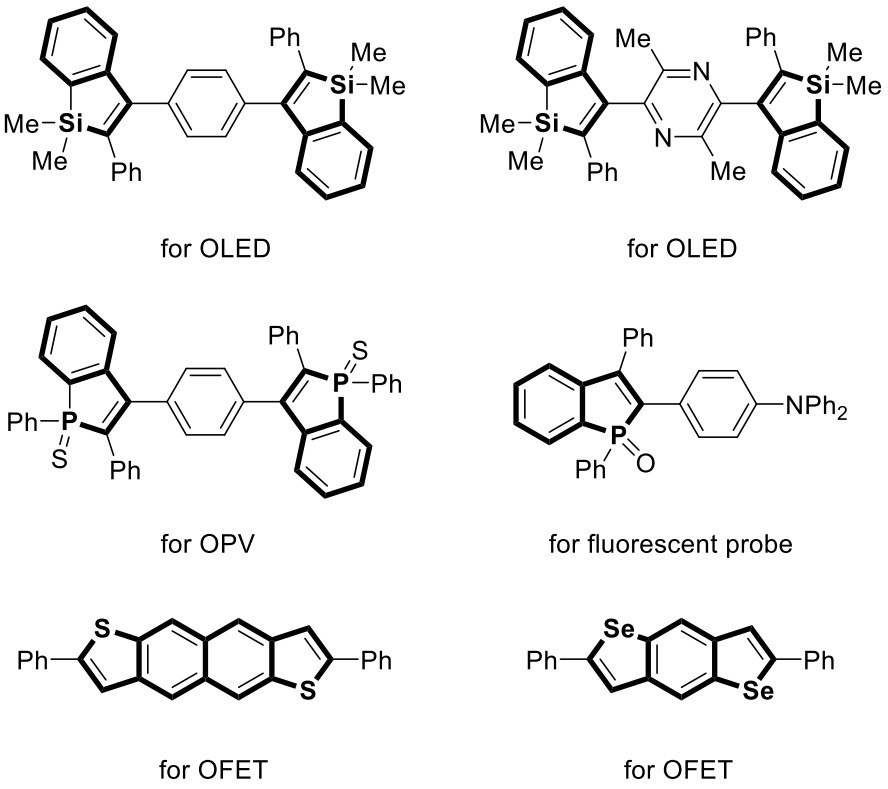


Figure 1.1. Examples of benzoheterole-containing functional molecules.

Over the last few decades, chemists have extensively studied optical and electronic properties of a series of unnatural benzoheteroles and explored their applications in material and biological sciences. [5] While more detailed introduction to each of the benzoheteroles will be given in the ensuing chapters, the following examples are illustrative: Benzosilole derivatives have proved to exhibit high electron drift mobility and thus can serve as hole-blocking materials for organic light-emitting diode (OLED).[6] Benzophosphole-containing molecules have been applied as materials for organic electronics, including OLED[7] and organic photovoltaics (OPV)[8] and also as environment-sensitive fluorescent probes for the imaging of biological process.[9] Benzoselenophene derivatives have been reported to be stable semiconductors for high-performance organic field-effect transistors (OFET) with excellent hole mobilities.[10] Certain benzotellurophene derivatives have been found to exhibit phosphorescence in the solid state under ambient conditions.[11]

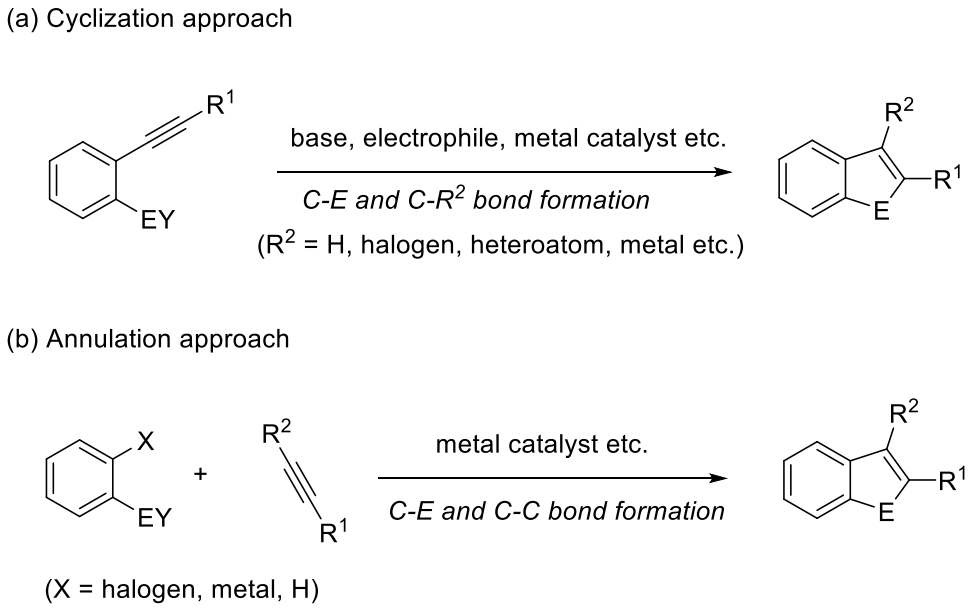
1.2 Common synthetic approaches to benzo[*b*]heteroles

Owing to the unique properties and the potential utility of benzoheteroles, methods for the efficient and selective synthesis of these heterocycles have been actively pursued over the last decades.[12] While the synthesis of indoles and benzofurans is achieved by a multitude of different approaches,[2] many of the existing synthetic methods for other benzoheteroles may be classified into two common conceptual approaches (Scheme 1.1).

One approach involves intramolecular 5-*endo*-*dig* cyclization of heteroatom-functionalized arenes bearing an *ortho*-alkynyl group, which is achieved through the activation of either the heteroatom or the alkyne moiety by a reagent or a catalyst (e.g., base, electrophile, transition metal) (Scheme 1.1a).[13] The Castro indole synthesis from *ortho*-alkynylaniline is a representative example of this approach.[14]

The other approach features annulation of a heteroatom-functionalized arene containing an *ortho*-halogen atom and an internal alkyne with the aid of a transition metal catalyst or other appropriate reaction conditions (Scheme 1.1b).[15] Note that in some cases the halogen atom could be replaced by other functional groups or even by a hydrogen atom,[16] the latter cases attracting much interest in the context of the emerging field of direct C–H bond functionalization. The Larock indole synthesis using *ortho*-haloaniline is a prototypical example of this approach.[17]

Scheme 1.1. Two common approaches to benzoheteroles (E and EY denote heteroatoms or heteroatom-containing groups).



The above two common approaches have indeed been successful for the synthesis of a series of benzoheteroles including benzosiloles, benzophospholes, and benzochalcogenophenes, as discussed in detail in the following chapters. However, they suffer a few significant limitations and drawbacks. First, a multistep preparation of each starting material is required always in the cyclization approach and quite often in the annulation approach. This problem becomes worse for the synthesis of a benzoheterole bearing substituent(s) on the benzene ring moiety, because the regiocontrolled synthesis of tri- or more-substituted benzene derivatives is not trivial. Second, in both of the approaches, the heteroatom has to be installed in the early stage, which makes diversification of a common precursor to different benzoheteroles difficult. Owing to these requirements, rapid construction of benzoheteroles containing different substituents and heteroatoms is difficult with either of the cyclization and the annulation approaches.

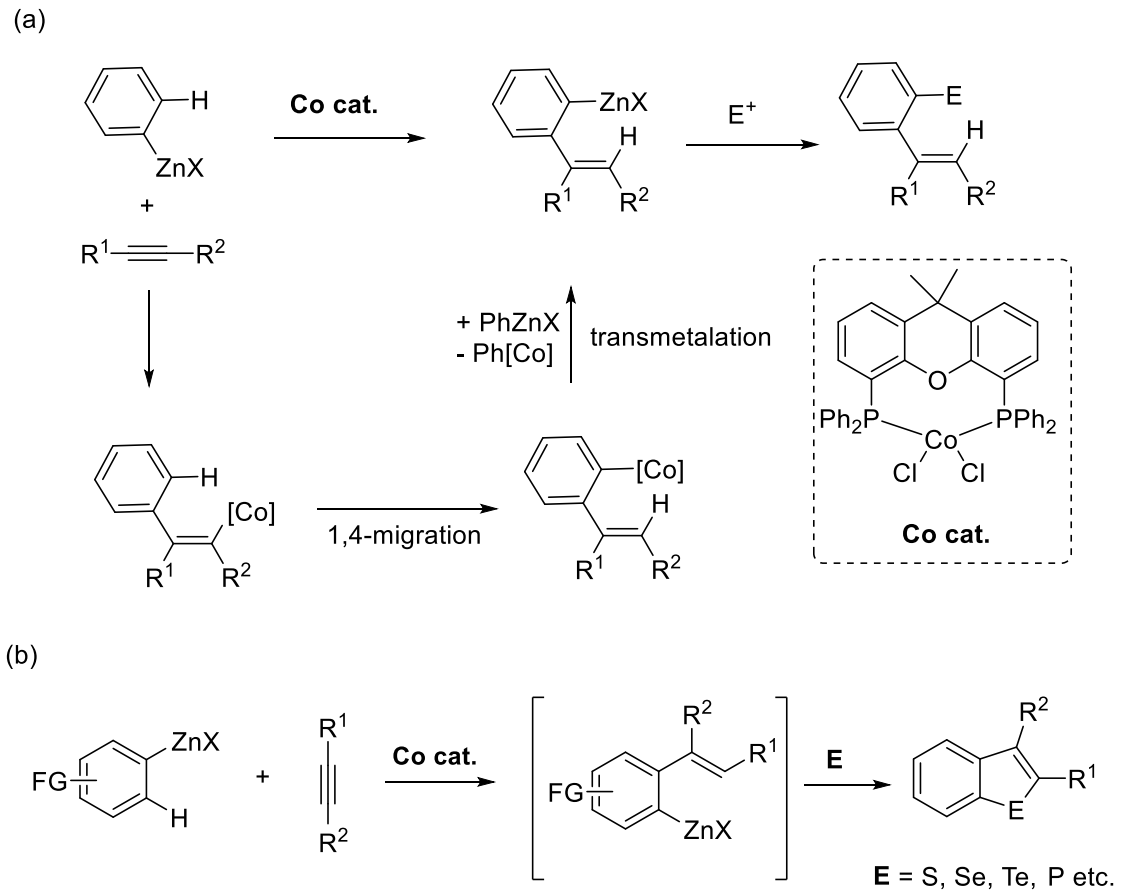
1.3 Design and summary of thesis research

The purpose of this thesis research is to develop new synthetic methods for benzoheteroles and related compounds that can potentially unlock the above-discussed limitations associated with the existing cyclization and annulation approaches. Thus, the new methods should allow for the conversion of common intermediates, which are readily accessible in a structurally diverse manner, into different benzoheteroles. Toward this goal, we designed a few conceptually new approaches capitalizing on catalytic activities of base metals such as cobalt, nickel, and copper, as described below.

Our group has recently reported a cobalt-catalyzed addition reaction of an arylzinc reagent to an internal alkyne that involves 1,4-cobalt migration followed by cobalt-to-zinc transmetalation to afford an *ortho*-alkenylarylzinc species, which can be readily trapped by common electrophiles (e.g., I_2) or subjected to transition metal-catalyzed cross-couplings (e.g., Negishi coupling) (Scheme 1.2a).[18] We conjectured that interception of the *ortho*-alkenylarylzinc species with an appropriate source of heteroatom and subsequent intramolecular cyclization would lead to the desired benzoheterole product (Scheme 1.2b). This approach, if established, appears attractive for the following reasons: (1) different benzoheteroles can be synthesized from the same starting materials just by changing the source of heteroatom, while the existing methods often require preparation of different starting materials; (2) the benzene ring moiety of each benzoheterole can be diversified simply by using differently substituted arylzinc reagents, many of which can be readily prepared from commercially available aryl halides; (3) the approach offers a possibility of one-pot synthesis of the benzoheterole from simple starting materials, which makes the operation and purification more convenient compared with the existing methods. With this proposed hypothesis, we embarked on a series of research projects on the construction of benzoheterole derivatives based on the cobalt-

catalyzed migratory arylzincation, which will be discussed in detail in the following chapters.

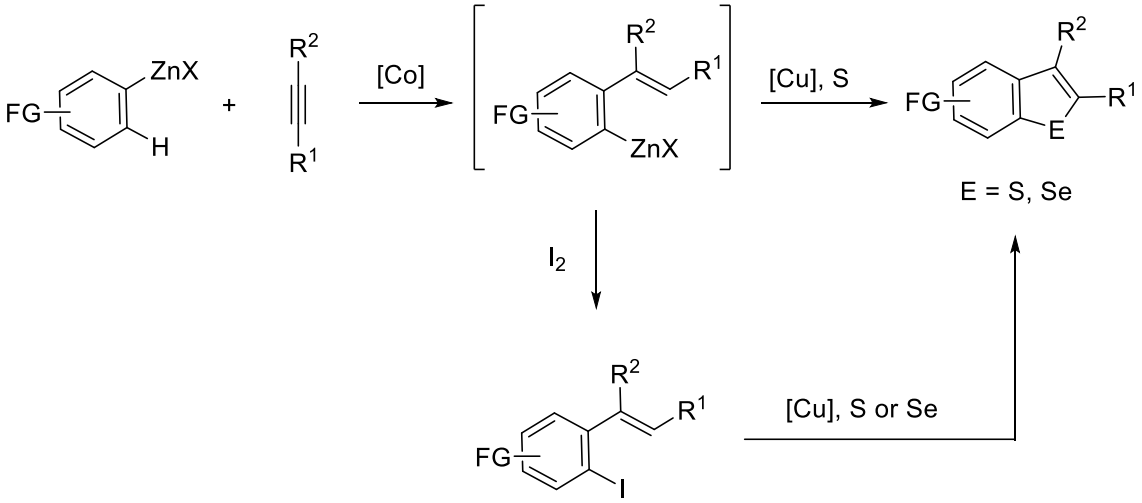
Scheme 1.2. Hypothesis for benzoheterole synthesis based on cobalt-catalyzed migratory arylzincation.



In Chapter 2, we report a new synthetic method for obtaining benzothiophenes and benzoselenophenes based on the assembly of arylzinc reagents, alkynes, and elemental sulfur or selenium with the aid of cobalt and copper catalysts (Scheme 1.3). Thus, a cobalt-catalyzed migratory arylzincation reaction of alkyne was combined with a copper-mediated or catalyzed chalcogenative cyclization reaction of the resulting *ortho*-alkenylaryl zinc or iodide to allow for the expedient synthesis of a wide variety of

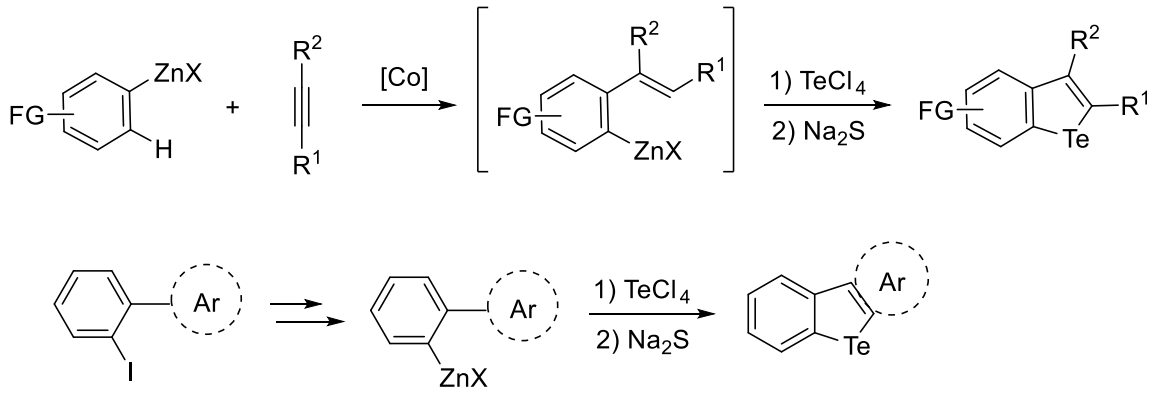
functionalized benzothiophenes and benzoselenophenes, which are not easily accessible by existing synthetic methods.

Scheme 1.3. Benzothiophene and benzoselenophene synthesis based on cobalt-catalyzed migratory arylzincation.



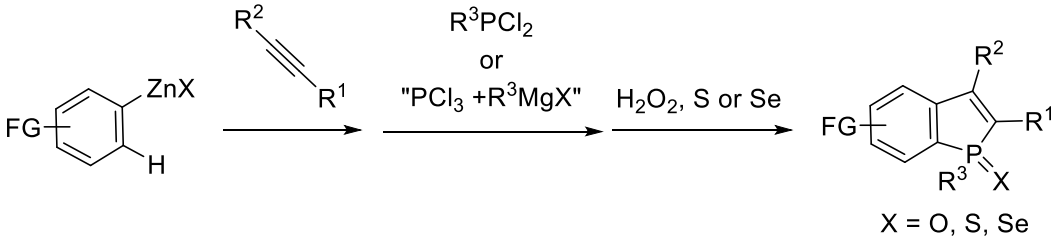
In Chapter 3, we describe a one-pot protocol for the synthesis of benzotellurophene through the combination of the cobalt-catalyzed 1,4-migration chemistry and sequential electrophilic telluration of the aryl–Zn and the alkenyl–H bonds using $TeCl_4$ as a suitable tellurium source (Scheme 1.4). The scope of the sequential electrophilic telluration has been further extended to achieve expedient and versatile synthesis of tellurium-bridged heterobiaryls from 2-iodoheterobiaryls.

Scheme 1.4. Synthesis of benzotellurophene and tellurium-bridged heterobiaryls.



In Chapter 4, we report on a highly modular, one-pot multicomponent approach for the construction of benzophospholes based on the sequential combination of cobalt-catalyzed migratory arylzincation reaction of alkyne, copper-catalyzed P–C coupling, intramolecular electrophilic phosphacyclization, and oxidation (Scheme 1.5). Thus, readily available starting materials, that is, an arylzinc reagent, an alkyne, dichlorophenylphosphine (or phosphorus trichloride and a Grignard reagent), and an oxidant (hydrogen peroxide, sulfur, or selenium) can be sequentially coupled to furnish a benzophosphole derivative in an expedient manner. Absorption and fluorescence behaviors of some of the novel benzophosphole derivatives are also reported.

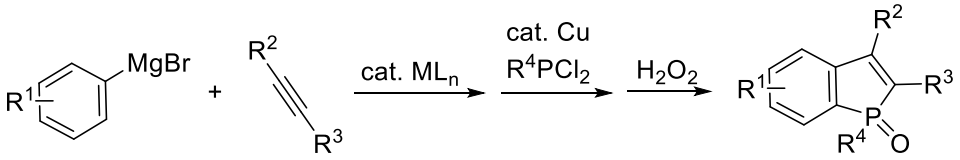
Scheme 1.5. A multicomponent approach to benzophospholes.



In Chapter 5, we report on an alternative method for the sequential one-pot multicomponent synthesis of a highly substituted benzophosphole derivative from an aryl Grignard reagents, an alkyne, and a dichloroorganophosphine (Scheme 1.6). The method

features an integration of transition metal-catalyzed arylmagnesiation of the alkyne, electrophilic trapping of the resulting alkenylmagnesium species with $RPCl_2$, and subsequent intramolecular phospha-Friedel–Crafts-type cyclization. By choosing appropriate arylmagnesiation and P–C bond forming conditions, the method allows for the modular synthesis of benzophospholes bearing a variety of substituents on the phosphorus atom, the C2 and C3 positions, and the "benzo" moiety, many of which are new compounds and are not easily accessible by existing synthetic methods. This method is particularly effective for the expedient preparation of 2,3-diarylbenzophospholes, which cannot be synthesized by the method based on the cobalt-catalyzed migratory arylzincation.

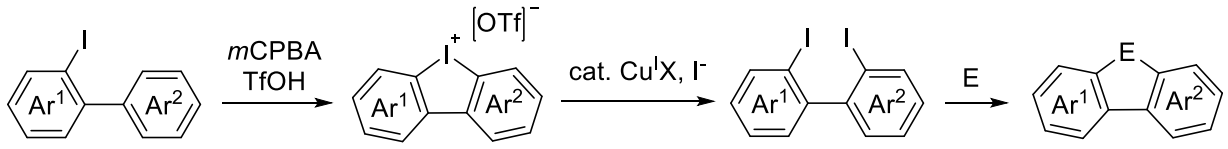
Scheme 1.6. Benzophosphole synthesis from aryl Grignard reagents, alkynes, and phosphorus electrophiles.



Chapter 6 describes the development of a new synthetic approach to dibenzoheteroles, which is conceptually distinct from the approaches discussed in the previous chapters. Thus, we have developed a two-step protocol for the conversion of a 2-iodobiaryl into a 2,2'-diiodobiaryl, which is achieved through oxidation of the 2-iodobiaryl into a cyclic diaryliodonium salt followed by copper-catalyzed iodinative ring-opening (Scheme 1.7). This new approach allows facile conversion of readily accessible 2-iodobiaryls into a variety of unsymmetrical 2,2'-diiodobiaryls, which should serve as versatile precursors to heteroatom-bridged fluorenes. The utility of the method has been

demonstrated by the synthesis of tetraiodoteraryls and their conversion to ladder-shaped heteroatom-bridged teraryls.

Scheme 1.7. Conversion of 2-iodobiaryls into 2,2'-diiodobiaryls via oxidation and iodinative ring-opening.



To summarize, we have developed new synthetic approaches towards benzothiophene, benzoselenophene, benzotellurophene as well as benzophosphole derivatives based on the cobalt-catalyzed migratory arylzincation of alkynes. For benzophospholes, we have also developed an alternative synthetic method based on other transition metal-catalyzed alkyne arylmagnesiation as the key step. Furthermore, we have established a convenient method for the preparation of 2,2'-diiodobiaryls from easily available 2-iodobiaryls, which are useful starting materials for the construction of heterofluorenes. Collectively, the methods developed here should provide opportunities for chemists to access a wide range of functionalized benzoheteroles and related heteroatom-containing cyclic scaffolds and explore their applications in material science.

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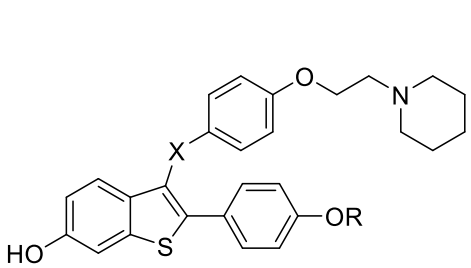
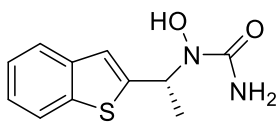
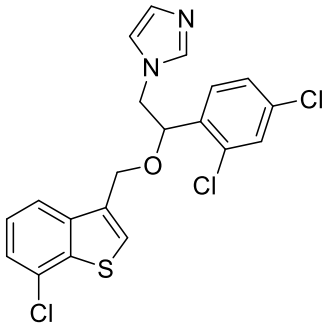
Chapter 2. Synthesis of Benzothiophenes and Benzoselenophenes from Arylzinc Reagents, Alkynes and Elemental Chalcogens

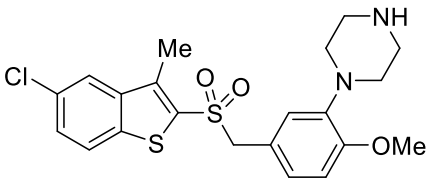
2.1 Introduction

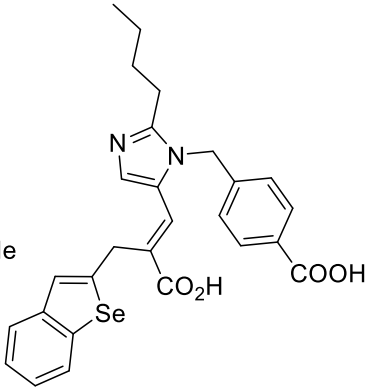
Benzothiophene not only exists in natural products but also forms the core of a number of medicinally important man-made molecules, such as arzoxifene,[1] raloxifene,[2] zileuton,[3] SB-271046[4] and sertaconazole[5] (Figure 2.1). Selenium is known as a fundamental element in life science, and its derivative, benzoselenophene, has also played an important role in the field of medicinal chemistry as well as biological science.[6]











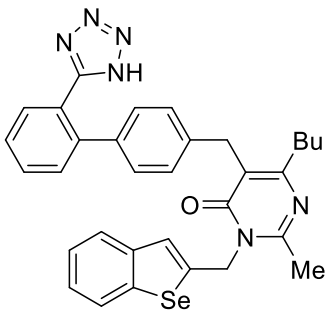
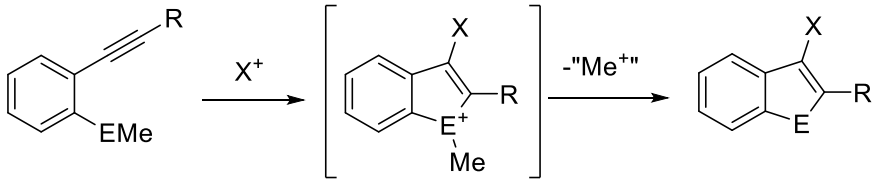


Figure 2.1. Biologically active compounds containing benzothiophene and benzoselenophene moieties.

A number of synthetic methods for the preparation of benzothiophenes and benzoselenophenes have been developed in the last decade. One of representative methods based on the cyclization approach (*cf*. Chapter 1), pioneered by Larock[7] and Flynn,[8] capitalizes on the electrophilic activation of an *ortho*-alkynylaryl methyl sulfide or selenide (Scheme 2.1). Thus, activation of the alkynyl moiety by an electrophile such as I_2, *N*-bromosuccinimide (NBS),[9] ICl,[10] PhSeCl,[11] cupric halides,[12] *N*-methylpyrrolidin-2-one hydrotribromide (MPHT), [13] *p*-toluenesulfonic acid (PTSA) [14] or trifluoromethanesulfanyl cation (CF_3S^+) [15] is followed by intramolecular nucleophilic addition of the methylthio (or methylseleno) group and subsequent demethylation, allowing preparation of benzothiophenes and benzoselenophenes bearing different substituents on the C3 position.

Scheme 2.1. Benzothiophene and benzoselenophene synthesis through electrophile-mediated 5-*endo* cyclization.

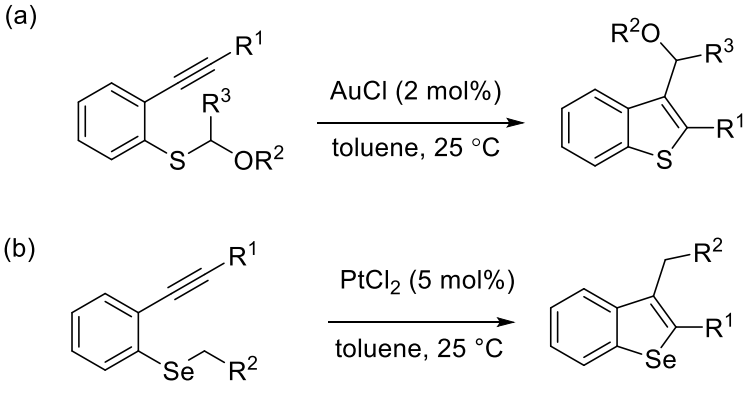


E = S, Se; X^+ = I_2, Br_2, NBS, ICl, PhSeCl, CuX_2 etc

Transition metal catalysis also allows for the conversion of similar *ortho*-difunctionalized benzene derivatives into benzothiophenes and benzoselenophenes. In 2006, Nakamura and co-workers reported the synthesis of 2,3-disubstituted benzothiophenes via gold-catalyzed cyclization of *ortho*-alkynylaryl sulfides (Scheme 2.2a). Migration of the substituent on the sulfur atom to the C3-position takes place readily to give the corresponding 2,3-disubstituted benzothiophenes in good yields.[16]

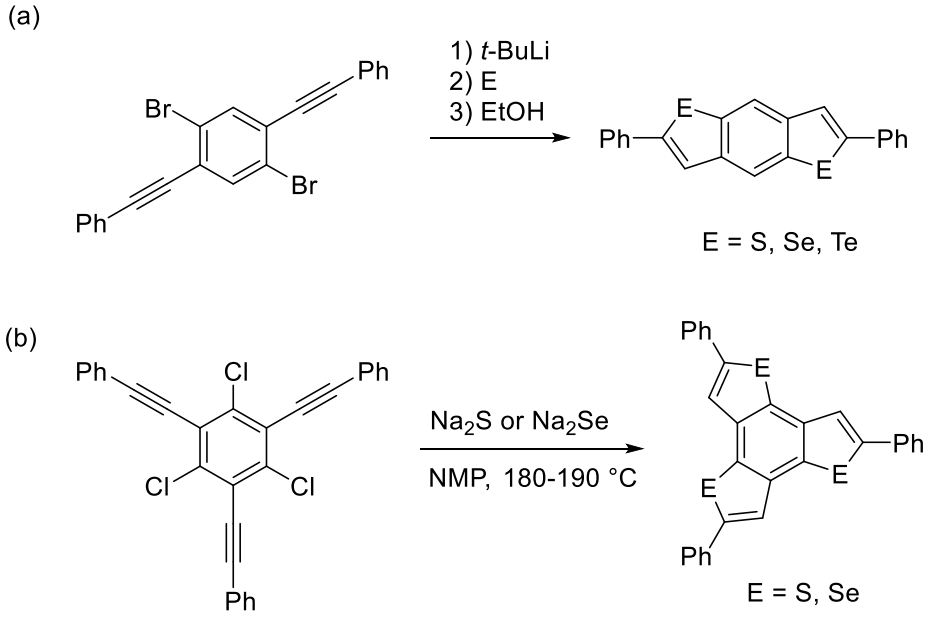
Later, Nakamura extended this approach for the synthesis of benzoselenophene using $PtCl_2$ as the catalyst (Scheme 2.2b).[17]

Scheme 2.2. Benzothiophene and benzoselenophene synthesis through gold- or platinum-catalyzed cyclization.



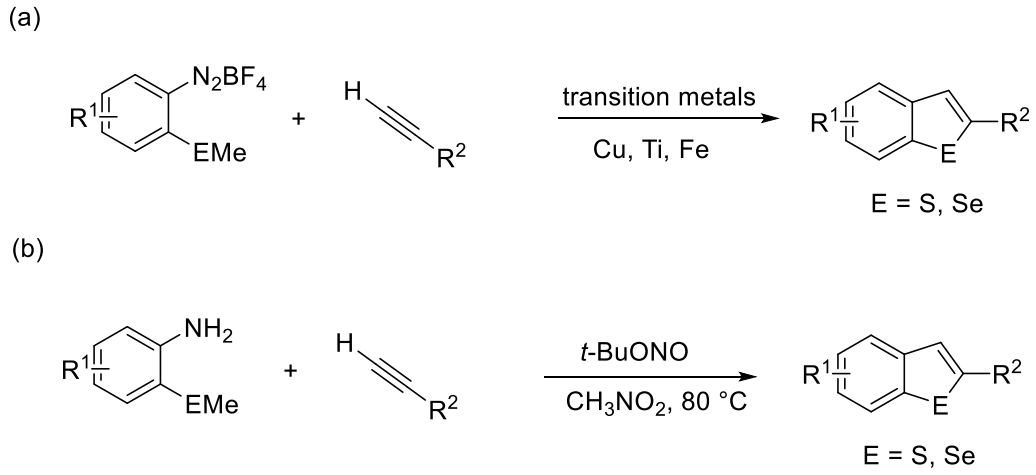
Besides the preformed *ortho*-alkynylaryl sulfides or selenides, *ortho*-alkynylaryl bromides have also been frequently used as precursors for the synthesis of benzothiophenes and benzoselenophenes via sequential aryl–chalcogen bond formation followed by intramolecular cyclization. Early work on such a transformation was reported by Sashida and coworkers in 1998, employing bromine–lithium exchange followed by electrophilic trapping with elemental chalcogens.[18] This reaction was utilized by Takimiya for the construction of benzodichalcogenophenes, which displayed promising performances as OFET materials (Scheme 2.3a).[19] Later, the Takimiya group developed a more convenient approach for the synthesis of benzothiophenes and benzoselenophenes using the same type of starting materials. Thus, treatment of *ortho*-alkynylaryl bromides (or even chlorides) with sodium sulfide or -selenide at high temperature in NMP led to the formation of the corresponding benzochalcogenophenes in good yields (Scheme 2.3b).[20]

Scheme 2.3. Chalcogenative cyclization of *ortho*-alkynylaryl halides.



The annulation approach has also proved feasible for the synthesis of benzothiophenes and benzoselenophenes. For example, the groups of Zanardi, [21] Mcdonald[22] and Schiesser[6b] independently reported the synthesis of such compounds through stoichiometric transition metal-mediated annulation of *ortho*-methylthio-(or seleno-) aryldiazonium salt and terminal alkyne (Scheme 2.4a). The proposed mechanism involves an aryl radical generated from the diazonium salt. Recently, a one-pot synthesis of benzothiophenes and benzoselenophenes through diazotization and intramolecular radical cyclization of *o*-methylthio-(or seleno-) arylamines using *t*-BuONO as a nitrosating agent was achieved by Li and Zhang and coworkers (Scheme 2.4b).[23]

Scheme 2.4. Benzothiophene and benzoselenophene synthesis via radical cascade annulations.

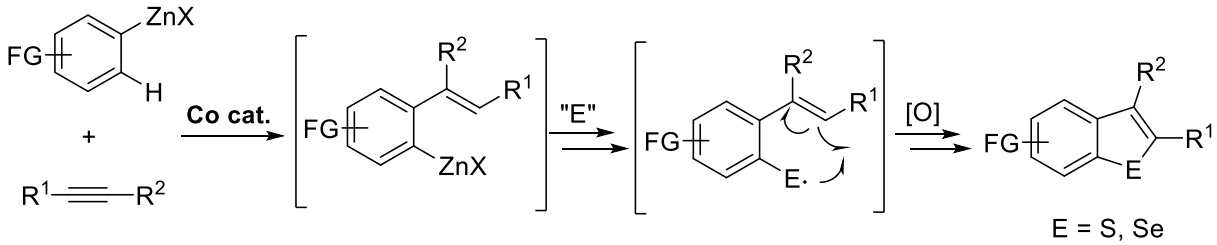


In addition to the above cyclization and annulation reactions, a couple of new methods for benzothiophene synthesis employing unique precursors and cyclization conditions have been reported in the last several years.[24] However, these existing methods have their own problems. First, they often require preparation of different starting materials (e.g., alkynylarenes bearing *ortho*-chalcogen substituents) for benzothiophene and benzoselenophene. Furthermore, specific reaction conditions and approaches for benzothiophene synthesis may not always be extended to benzoselenophene synthesis. Second, the preparation of *ortho*-disubstituted benzene precursors for the existing methods requires multiple steps (e.g., Sonogashira coupling) and becomes increasingly tedious when additional substituents on the benzene ring are required. This makes preparation of benzothiophenes and benzoselenophenes bearing diverse substituents on the benzene ring moiety difficult.

With the development of the cobalt-catalyzed migratory arylzincation reaction (Chapter 1), we envisioned that interception of the *ortho*-alkenylarylzinc species with

elemental chalcogen and subsequent intramolecular cyclization would lead to a benzochalcogenophene (Scheme 2.5). A possible mechanistic scenario for this transformation may involve formation of an *ortho*-alkenylaryl chalcogenide anion, its oxidation to the corresponding chalcogenide radical, intramolecular radical cyclization, and oxidative aromatization of the resulting radical. This initial hypothesis has led us to develop new one- or two-step methods for benzothiophene and benzoselenophene synthesis, which are described herein. The new methods enable expedient synthesis of diversely substituted benzothiophenes and benzoselenophenes from readily available starting materials.

Scheme 2.5. Hypothesis for benzochalcogenophene synthesis from *ortho*-alkenylarylzinc species.

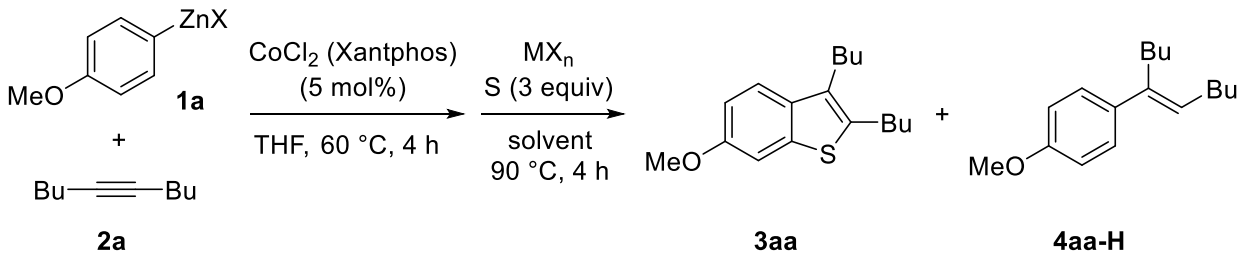


2.2 Results and discussion

Along with the above idea, our initial study started with benzothiophene synthesis by the sequential reaction of 4-methoxyphenylzinc reagent **1a**, 5-decyne **2a**, and elemental sulfur (Table 1). Upon the formation of the *ortho*-alkenylarylzinc reagent under the cobalt–Xantphos catalysis, elemental sulfur (3 equiv) was added and the reaction was stirred at 90 ℃ for 60 h. To our delight, the desired benzothiophene **3aa** was formed in 54% GC yield, accompanied by a small amount (8%) of the protonation product **4aa-H** (entry

1). Replacement of THF with other solvents such as DMSO, DMF or 1,4-dioxane did not improve the reaction (entries 2-4). In order to facilitate the thiolative cyclization process, we screened various transition metal salts as potential catalysts. The addition of CuI (20 mol%) resulted in the formation of **3aa** in 49% yield within 4 h with almost complete suppression of **4aa-H** (entry 5). Other copper(I) salts such as CuBr, CuCl and CuCN gave similar results (entries 6-8), while increase of **4aa-H** was observed using $CuBr_2$ (entry 9). Other metal salts such as $Ni(acac)_2$, $FeCl_3$, and $PdCl_2$ were less effective and failed to suppress **4aa-H** (entries 10-12). Thus, CuI was chosen to be the best catalyst for further screening. The use of a stoichiometric amount (1 equiv) of CuI improved the yield of **3aa** to 59% (entry 13). An additional improvement was observed using 1.5 equiv of CuI (66% GC yield and 63% isolated yield, entry 14), while no further improvement was achieved using 2 equiv of CuI (entry 15).

Table 2.1. Screening of reaction conditions (Protocol **A**).[a]



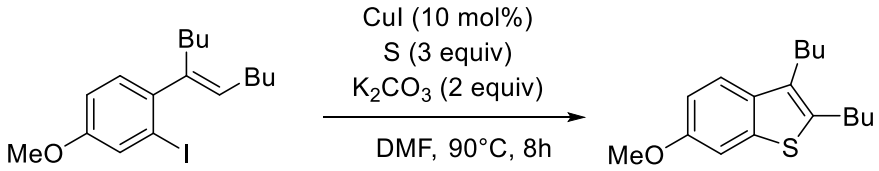
Entry	MXn (equiv)	Solvent	Yield (%)[b]	
			3aa	**4aa-H**
1[c]	None	THF	54	8
2[c]	None	DMSO	48	20
3[c]	None	DMF	53	14
4[c]	None	1,4-Dioxane	33	31
5	CuI (0.2)	THF	49	<1
6	CuBr (0.2)	THF	49	<1
7	CuCl (0.2)	THF	45	<1
8	CuCN•2LiCl (0.2)	THF	44	5
9	$CuBr_2$ (0.2)	THF	42	7
10	$Ni(acac)_2$ (0.2)	THF	33	20
11	$FeCl_3$ (0.2)	THF	42	10
12	$PdCl_2$ (0.2)	THF	38	11
13	CuI (1.0)	THF	59	<1
14	CuI (1.5)	THF	66 (63)[d]	<1
15	CuI (2.0)	THF	60	<1

[a] The reaction was performed using 0.5 mmol of 5-decyne (**2a**) and 1.1 equiv of 4-methoxyphenylzinc reagent (**1a**) prepared from $ZnCl_2$•TMEDA and 4-methoxyphenylmagnesium

bromide. [b] Determined by GC using *n*-tridecane as an internal standard. [c] The reaction time was 60 h. [d] Isolated yield.

The above one-pot protocol (protocol **A**), while being applicable to arylzinc reagents bearing electron-donating groups (vide infra), proved to work poorly with those bearing electron-withdrawing groups (e.g., trifluoromethyl, ester) and produce a large amount of the corresponding protonation products. Thus, we explored an alternative route to benzothiophene based on thiolative cyclization of an *ortho*-alkenylaryl iodide, which can be readily prepared by iodination of the *ortho*-alkenylarylzinc species (Table 2.2). Inspired by Ma's report on copper-catalyzed thiolation of aryl iodide, [25] the substrate **4aa** was treated with 10 mol% of CuI, 3 equiv of sulfur, and 2 equiv of K_2CO_3 in DMF at 90 ℃ for 8 h, which resulted in the desired product **3aa** in 90% yield (protocol **B**, entry 1). A comparable result was obtained using DMSO instead of DMF (entry 2), while no desired transformation was observed in THF (entry 3). An increased loading of CuI (20 mol%) did not lead to an apparent improvement (entry 4). Control experiments showed that both the copper catalyst and the base were essential for this reaction (entries 5 and 6).

Table 2.2. Screening of reaction conditions (Protocol **B**).[a]



4aa **3aa**

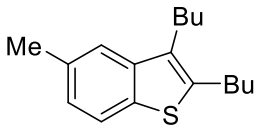
entry	change from the standard conditions	yield (%)[b]
1	None	83 (90)[c]
2	DMSO instead of DMF	82
3	THF instead of DMF	0
4	20 mol% of CuI	76
5	Without CuI	0
6	Without K_2CO_3	0

[a] The reaction was performed on a 0.2 mmol scale. [b] Determined by GC using *n*-tridecane as an internal standard. [c] Isolated yield.

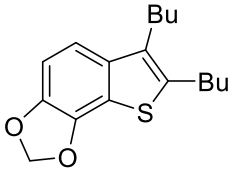
Having established the one-step and two-step protocols (protocols **A** and **B**), we explored the scope of benzothiophene synthesis using different arylzinc reagents and 5-decyne (Scheme 2.1). Protocol **A** allowed the synthesis of benzothiophenes from electron-rich or -neutral arylzinc reagents in moderate to good yields (see the products **3aa**–**3ca** and **3ka**–**3la**). On the other hand, protocol **B** was suitable for *ortho*-alkenylaryl iodides bearing a variety of electron-withdrawing groups such as fluoro, trifluoromethyl, ethoxycarbonyl, formyl, and acetyl groups (see the products **3ea**–**3ia**). It is noted that the synthesis of **3ha** could be performed on a 2 mmol scale in 85% yield. The reaction of *ortho*-alkenylaryl iodide substrate bearing an OBoc group resulted in a complete loss of the Boc group, affording the 6-hydroxybenzothiophene derivative **3na** in 45% yield.

Thieno[2,3-*b*]quinolone **3ma** was also synthesized according to protocol **B**. The reaction of *meta*-tolylzinc reagent according to protocol **A** exclusively afforded 5-methyl benzothiophene **3ja** albeit in a modest yield, as a result of regioselective 1,4-cobalt migration to the less hindered position. On the other hand, a methylenedioxy group directed the migration to take place at the proximal position due to coordination effect, affording 6,7-disubstituted benzothiophene **3ka** in a good yield. 6-Aminobenzothiophene **3oa** was obtained from *p*-bromoaniline protected in the form of the acetophenone imine in 42% yield through a sequence comprising cobalt-catalyzed zinc insertion,[26] migratory arylzincation to 5-decyne, iodination, copper-catalyzed C-S coupling/cyclization, and acidic hydrolysis.

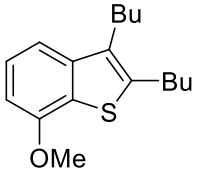
Scheme 2.1. Benzo[*b*]thiophenes synthesized from different arylzinc reagents and 5-decyne.[a]



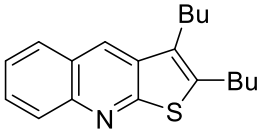
3ja: 38% **(A)**



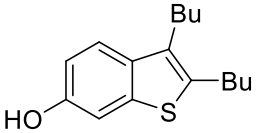
3ka: 70% **(A)**, 97% (**B**)



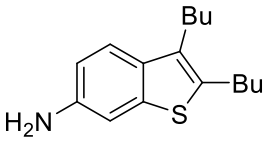
3la: 45% **(A)**



3ma: 78% **(B)**



3na: 45% **(B)**[b]

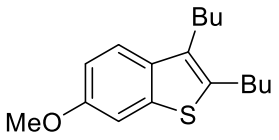


3oa: 42% **(B)**[c]

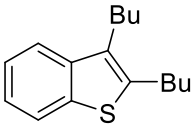
[a] The yields for protocols **A** and **B** are based on 5- decyne and the *ortho*-alkenylaryl iodide, respectively. [b] The starting material was protected with a Boc group, which was removed during the reaction. [c] Yield is based on 5-decyne.

Next, we explored different alkynes to form a variety of 2,3-substituted benzothiophenes (Scheme 2.2). The 3,4-methylenedioxyphenylzinc reagent reacted with other symmetric dialkylalkynes such as 3-hexyne or 4-octyne using protocol **A**, thus producing the desired products **3kb** and **3kc**, respectively, in moderate yields. The reactions of alkylarylalkynes with 3,4-methylenedioxyphenylzinc or 4-methoxyphenylzinc reagent using protocol **A** led to exclusive formation of the corresponding 2-aryl-3-alkylbenzothiophene derivatives **3kd**–**3kf** and **3ag**, reflecting the regioselectivity of the migratory arylzincation reaction. Alkylarylalkynes bearing sterically hindered aryl groups could also be used as the starting materials, using the stepwise protocol **B** (**3ah** and **3ai**). The reaction of 1-trimethylsilyl-1-propyne by using protocol **A** caused partial loss of TMS group, which could be totally removed under basic conditions to give 3-substituted benzothiophene (**3aj**).

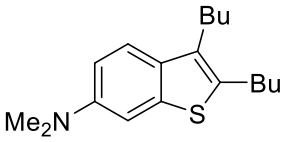
Scheme 2.2. Benzo[*b*]thiophenes synthesized from different alkynes.[a]



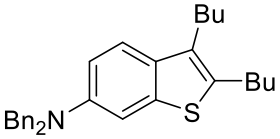
3aa: 63% **(A)**, 90% **(B)**



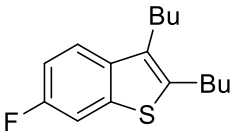
3ba: 40% **(A)**, 82% **(B)**



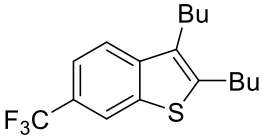
3ca: 76% **(A)**



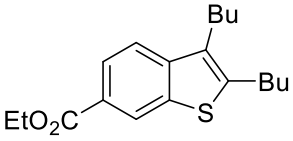
3da: 96% **(B)**



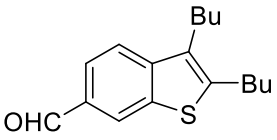
3ea: 67% **(B)**



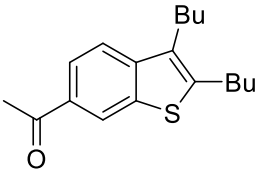
3fa: 85% **(B)**



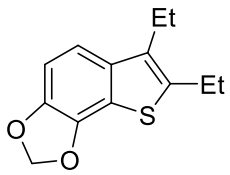
3ga: 84% **(B)**



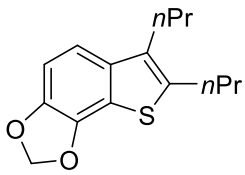
3ha: 94% **(B)**



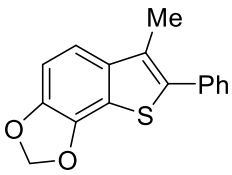
3ia: 83% **(B)**



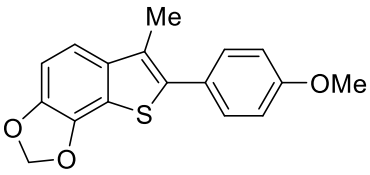
3kb: 64% (**A**)



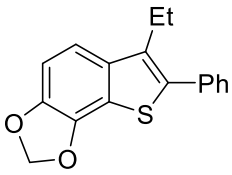
3kc: 71% **(A)**



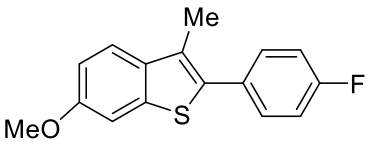
3kd: 54% **(A)**



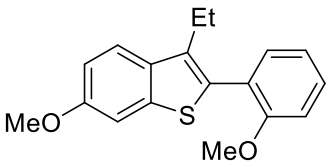
3ke: 58% **(A)**



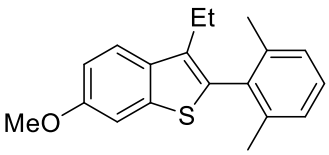
3kf: 52% **(A)**



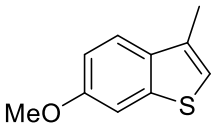
3ag: 58% **(A)**



3ah: 89% **(B)**



3ai: 93% **(B)**



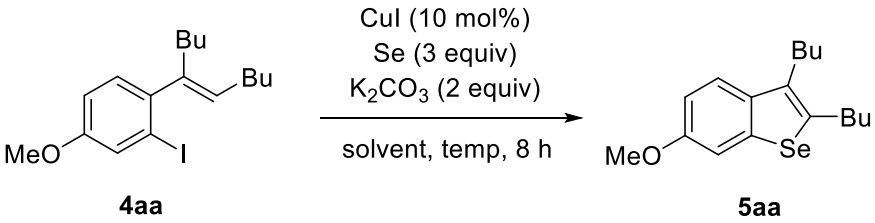
3aj: 50% **(A)**[b]

[a] The yields for protocols A and B are based on the alkyne and the *ortho*-alkenylaryl iodide, respectively. [b] The reaction was performed using 1-trimethylsilyl-1-propyne, and the $SiMe_3$ group was removed by treatment with KOH/MeOH.

With the success of benzothiophene synthesis, we attempted extension of the above approaches to benzoselenophene synthesis. Unfortunately, the extension of the one-pot protocol **A** was unsuccessful. Regardless of many attempts, the reaction always became complicated with no indication of the formation of the desired benzoselenophene. Next, we examined selenative cyclization of the aryl iodide **4aa** into benzoselenophene **5aa** (Table 2.3). Simple replacement of elemental sulfur with elemental selenium in protocol **B** did not afford **5aa** at all (entry 1). No or little amount of **5aa** was observed by changing the solvent to DMSO or increasing the reaction temperature to 120 ℃ (entries 2

and 3). However, to our delight, the use of NMP as the solvent at 120 ℃ promoted the desired transformation to afford **5aa** in 85% yield (entry 4).

Table 2.3. Screening reaction conditions for benzoselenophene synthesis.[a]



4aa **5aa**

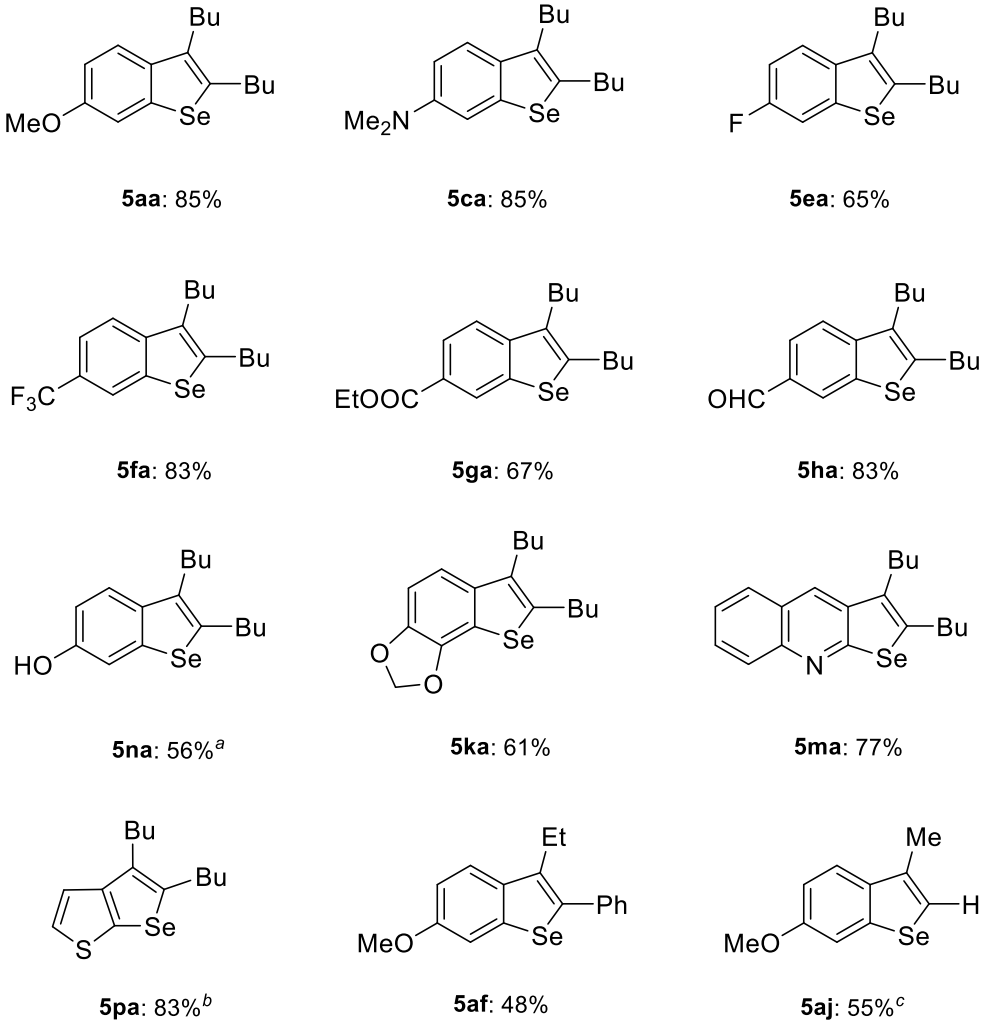
Entry	Solvent	Temp	Yield (%)[b]
1	DMF	90 °C	0
2	DMSO	90 °C	0
3	DMF	120 °C	< 5
4	NMP	120 °C	85

[a] The reaction was performed on a 0.2 mmol scale. [b] Isolated yield.

Having established the optimal reaction conditions, we explored the scope of the benzoselenophene synthesis (Scheme 2.3). The reactions of *ortho*-alkenylaryl iodides bearing a variety of electron-donating or electron-withdrawing groups (e.g., OMe, NMe_2, F, CO_2Et, CHO, CF_3) proceed smoothly, affording the corresponding cyclization products **5aa**–**5ka** in moderate to good yields. The reaction of 2-iodo-3-alkenylquinoline afforded selenophenoquinoline **5ma** in 77% yield. Interestingly, the reaction of 2-iodo-3-alkenylthiophene also took place to afford the selenopheno[2,3-*b*]thiophene **5pa** in 83% yield, while an attempt on thiolative cyclization of the same substrate was unsuccessful for unknown reasons. The *ortho*-alkenylaryl iodide prepared from 1-phenyl-1-butyne

afforded 2-phenyl-3-ethyl benzoselenophene in 48% yield (**5af**). As was the case with the benzothiophene synthesis, 3-methylbenzoselenophene **5aj** was synthesized by the reaction of *ortho*-alkenylaryl iodide derived from 1-silyl-1-propyne.

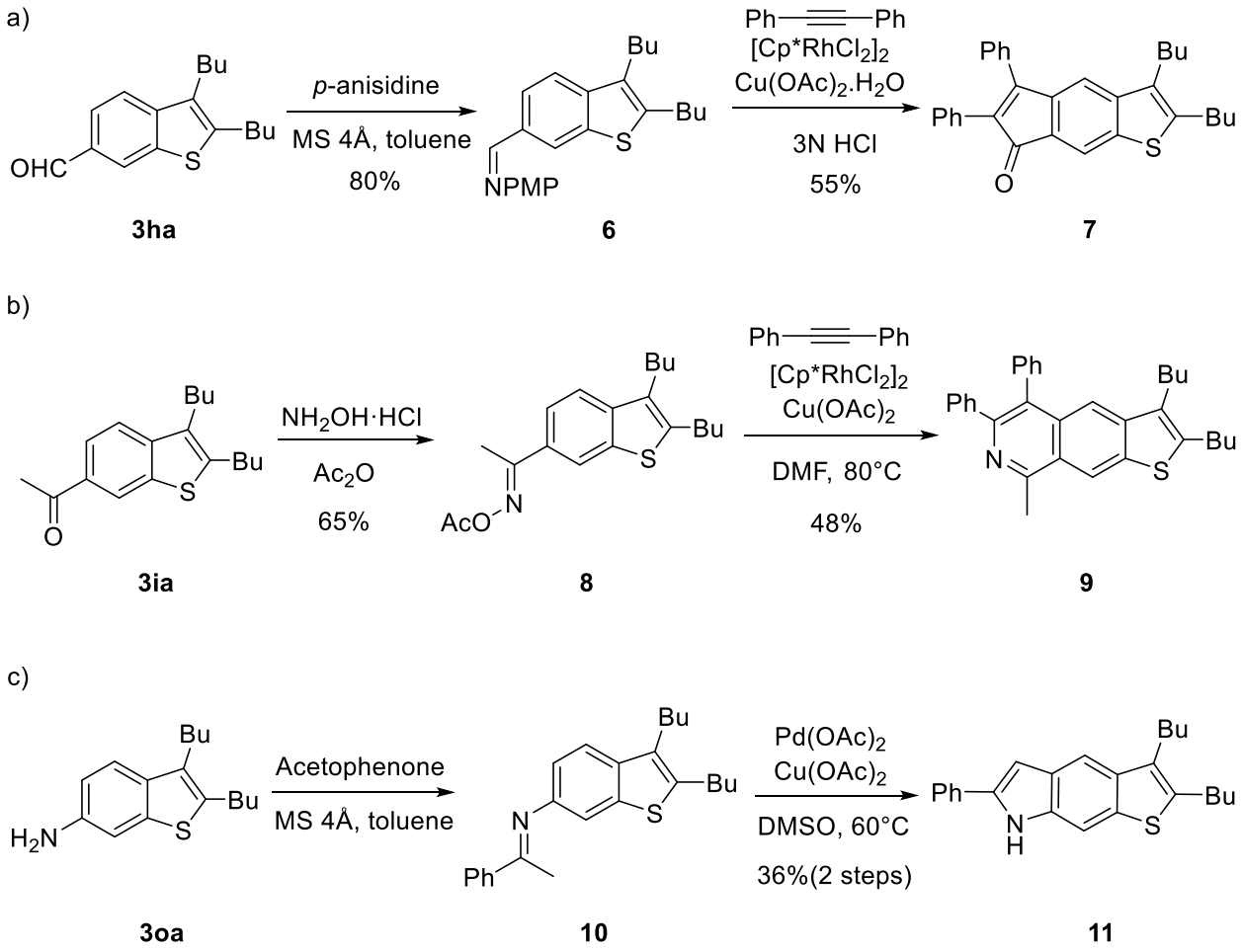
Scheme 2.3. Synthesis of benzoselenophenes.



[a] The starting material was protected with a Boc group, which was removed during the reaction. [b] The reaction time was 36 h. [c] The starting material was (*E*)-(2-(2-iodo-4-methoxyphenyl)prop-1-en-1-yl)trimethylsilane, and the $SiMe_3$ group was removed during the reaction.

The facile preparation of functionalized benzothiophenes and benzoselenophenes enabled by the present methods allows us to explore a variety of directing group-assisted C–H functionalizations on these heterocyclic scaffolds. To illustrate this point, benzothiophene-containing extended π-conjugated compounds were synthesized from functionalized benzothiophenes (Scheme 2.4). First, condensation of benzothiophene-6-carbaldehyde **3ha** with *p*-anisidine was followed by rhodium(III)-catalyzed aldimine-directed annulation reaction with diphenylacetylene [27] to afford 7*H*-indeno[5,6-*b*]thiophen-7-one **7** (Scheme 2.4a). Second, 6-acetylbenzothiophene **3ia** was transformed to *O*-acetyloxime **8** and then subjected to rhodium(III)-catalyzed redox-neutral annulation with diphenylacetylene[28] to afford thieno[3,2-*g*]isoquinoline **9** (Scheme 2.4b). Finally, condensation of 6-aminobenzothiophene **3oa** with acetophenone was followed by palladium-catalyzed dehydrogenative cyclization reaction[29] of the resulting imine **10** to afford 7*H*-thieno[3,2-*f*]indole **11** (Scheme 2.4c).

Scheme 2.4. Transformations of functionalized benzothiophenes through C–H bond functionalization.



2.3 Conclusion

In summary, we have developed versatile and flexible synthetic methods for the construction of benzothiophenes and benzoselenophenes through the combination of cobalt-catalyzed migratory arylzincation and copper-mediated or catalyzed chalcogenative cyclization reactions. Thus, arylzinc reagents, alkynes, and elemental sulfur or selenium can be assembled into a variety of functionalized benzothiophenes and

benzoselenophenes, which are not readily accessible by existing synthetic methods. The facile accessibility to such functionalized benzothiophenes offers us opportunities to exercise a variety of contemporary directing group-assisted C–H functionalization reactions on the benzothiophene scaffold.

2.4 Experimental section

Materials and methods

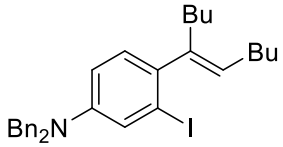
General. All reactions dealing with air- or moisture-sensitive compound were performed by standard Schlenk techniques in oven-dried reaction vessels under nitrogen atmosphere. Analytical thin-layer chromatography (TLC) was performed on Merck 60 F254 silica gel plates. Flash chromatography was performed as described by Still et al., using 40–63 μm silica gel (Si 60, Merck). ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on JEOL ECA-400 (400 MHz), Bruker AV-300 (300 MHz), or AV-500 (500 MHz) NMR spectrometers. ^{1}H and ^{13}C NMR spectra are reported in parts per million (ppm) downfield from an internal standard, tetramethylsilane (0 ppm) and $CHCl_3$ (77.0 ppm), respectively. Gas chromatographic (GC) analysis was performed on a Shimadzu GC-2010 system equipped with an FID detector and a capillary column, DB-5 (Agilent J&W, 0.25 mm i.d. x 30 m, 0.25 μm film thickness). High resolution mass spectra (HRMS) were obtained with a Q-Tof Premier LC HR mass spectrometer. Melting points were determined using a capillary melting point apparatus and are uncorrected.

Materials. Unless otherwise noted, commercial reagents were purchased from Aldrich, Alfa Aesar, and other commercial suppliers and were used as received. Anhydrous $CoCl_2$ (97%) was purchased from Alfa Aesar and was used as received. THF was distilled over

Na/benzophenone. Grignard reagents were prepared from the corresponding halides and magnesium turnings in anhydrous THF and titrated before use. Anhydrous DMSO and DMF were purchased from Aldrich or Alfa Aesar.

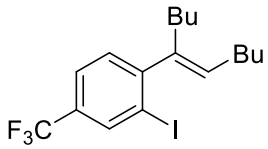
Preparation of *ortho*-alkenylaryl iodides

All *ortho*-alkenylaryl iodides, including the following known compounds, were synthesized from the corresponding arylzinc reagents, alkynes, and iodine according to the cobalt catalyzed procedure. Their spectral data showed good agreement with the literature data: (*E*)-1-(dec-5-en-5-yl)-2-iodo-4-methoxybenzene (**4aa**), (*E*)-1-(dec-5-en-5-yl)-2-iodobenzene (**4ba**), (*E*)-4-(dec-5-en-5-yl)-3-iodo-*N*,*N*-dimethylaniline (**4ca**), (*E*)-1-(dec-5-en-5-yl)-4-fluoro-2-iodobenzene (**4ea**), (*E*)-ethyl 4-(dec-5-en-5-yl)-3-iodobenzoate (**4ga**), (*E*)-4-(dec-5-en-5-yl)-3-iodobenzaldehyde (**4ha**), (*E*)-5-(dec-5-en-5-yl)-4-iodobenzo[*d*][1,3]dioxole (**4ka**), (*E*)-3-(dec-5-en-5-yl)-2-iodoquinoline (**4ma**), (*E*)-*tert*-butyl (4-(dec-5-en-5-yl)phenyl) carbonate (**4na**), (*E*)-3-(dec-5-en-5-yl)-2-iodothiophene (**4pa**). Below are summarized characterization data for newly synthesized *ortho*-alkenylaryl iodides.

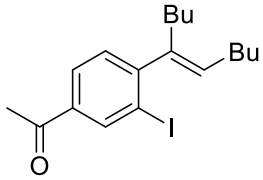


(*E*)-*N*,*N*-dibenzyl-4-(dec-5-en-5-yl)-3-iodoaniline (4da): Yellow oil (94% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.30 (m, 4H), 7.27 – 7.20 (m, 7H), 6.84 (d, *J* = 8.4 Hz, 1H), 6.62 (dd, *J* = 8.4, 2.0 Hz, 1H), 5.23 (t, *J* = 7.2 Hz, 1H), 4.57 (s, 4H), 2.33 (t, *J* = 7.2 Hz, 2H), 2.13 (q, *J* = 6.8 Hz, 2H), 1.42 – 1.36 (m, 4H), 1.32 – 1.26 (m, 4H), 0.91 (t, *J* = 6.8 Hz, 3H), 0.86 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.7, 143.0, 138.2,

137.7, 131.3, 129.7, 128.8, 127.1, 126.8, 122.5, 112.1, 100.6, 54.1, 31.9, 31.8, 30.5, 27.9, 23.0, 22.6, 14.2 (two signals overlapped); HRMS (ESI) Calcd for $C_{30}H_{37}NI$ $[M + H]^+$ 538.1971, found 538.1970.

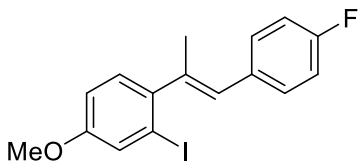


(*E*)-1-(Dec-5-en-5-yl)-2-iodo-4-(trifluoromethyl)benzene (4fa): Yellow oil (94% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.52 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 5.29 (t, *J* = 7.2 Hz, 1H), 2.40 (t, *J* = 7.6 Hz, 2H), 2.19 (q, *J* = 7.2 Hz, 2H), 1.42 – 1.39 (m, 4H), 1.34 – 1.22 (m, 4H), 0.94 (t, *J* = 7.2 Hz, 3H), 0.87 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.0, 142.5, 136.0 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 132.3, 130.0 (q, $^2J_{C\text{-}F}$ = 32.6 Hz), 129.5, 124.6 (q, $^3J_{C\text{-}F}$ = 3.6 Hz), 123.0 (q, $^1J_{C\text{-}F}$ = 270.9 Hz), 99.0, 31.6, 31.0, 30.2, 27.7, 22.8, 22.5, 14.0, 13.9 ; HRMS (ESI) Calcd for $C_{17}H_{23}F_3I$ $[M + H]^+$ 411.0797, found 411.0800.



(*E*)-1-(4-(Dec-5-en-5-yl)-3-iodophenyl)ethanone (4ia): Yellow oil (82% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 5.28 (t, *J* = 7.2 Hz, 1H), 2.55 (s, 3H), 2.39 (t, *J* = 7.2 Hz, 2H), 2.17 (q, *J* = 7.2 Hz, 2H), 1.45 – 1.38 (m, 4H), 1.30 – 1.20 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 3H), 0.84 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.3, 154.1, 142.7, 139.3, 136.7, 132.1, 129.7, 127.6,

99.5, 31.7, 31.1, 30.4, 27.8, 26.6, 22.9, 22.6, 14.1 (two signals overlapped); HRMS (ESI) Calcd for $C_{18}H_{26}IO$ $[M + H]^+$ 385.1028, found 385.1024.

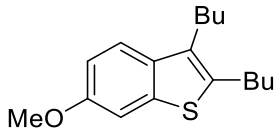


(*E*)-1-(1-(4-Fluorophenyl)prop-1-en-2-yl)-2-iodo-4-methoxybenzene (4ag): Yellow oil (79% yield), with an *E*/*Z* ratio of 84:16 (determined by ^{1}H NMR); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (m, 1H), 7.41 – 7.37 (m, 2H) 7.20 (d, *J* = 8.4 Hz, 1H), 7.13 – 7.09 (m, 2H), 6.96 – 6.92 (m, 1H), 6.36 (s, 1H), 3.84 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 142.7, 141.1, 133.7 (d, $^4J_{C\text{-}F}$ = 3.4 Hz), 130.5 (d, $^3J_{C\text{-}F}$ = 7.8 Hz), 129.6, 128.8, 125.8 (d, $^1J_{C\text{-}F}$ = 250.3 Hz), 124.2, 115.1 (d, $^2J_{C\text{-}F}$ = 21.1 Hz), 114.3, 97.9, 55.6, 20.0; HRMS (ESI) Calcd for $C_{16}H_{15}FIO$ $[M + H]^+$ 369.0152, found 369.0135.

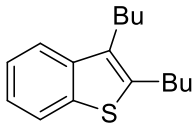
General procedure for protocol A: In an oven-dried 10 mL Schlenk tube was placed $ZnCl_2$·TMEDA (139 mg, 0.55 mmol). The Schlenk tube was submerged in an ice bath for 15 min, followed by dropwise addition of a THF solution of an aryl Grignard reagent (0.575 mmol). The resulting mixture was stirred for 1 h at 0 ℃ and then allowed to room temperature. To the arylzinc reagent was added $CoCl_2$ (3.3 mg, 0.025 mmol), Xantphos (14.5 mg, 0.025 mmol), followed by stirring for 5 min and addition of an alkyne (0.50 mmol). The resulting mixture was stirred at 60 ℃ for 4-12 h and cooled to room temperature, followed by addition of sulfur powder (50 mg, 1.5 mmol) and CuI (142 mg, 0.75 mmol). The reaction mixture was stirred at 90 ℃ (bath temp) for 4-12 h, and then quenched with H_2O and extracted with ethyl acetate (15 mL). The organic extracts were

dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by silica gel chromatography to afford the desired product.

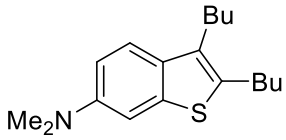
General procedure for protocol B: An oven-dried Schlenk tube was charged with CuI (4.0 mg, 0.021 mmol), 1-iodo-2-alkenylarene (0.20 mmol), sulfur powder (20 mg, 0.62 mmol) and K_2CO_3 (56 mg, 0.41 mmol). The Schlenk tube was evacuated and backfilled with N_2, followed by addition of DMF (1 mL). The reaction mixture was stirred at 90 ℃ until the starting material was fully consumed as monitored by TLC. Upon cooling to room temperature, the reaction mixture was diluted with ethyl acetate (5 mL) and filtered through a pad of silica gel with additional ethyl acetate (15 mL) as the eluent. The filtrate was washed with water (10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product.



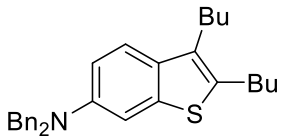
2,3-Dibutyl-6-methoxybenzo[*b*]thiophene (3aa): Yellow oil (63% and 90% yields with protocols A and B, respectively, eluent = hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 8.8 Hz, 1H), 7.24 (d, *J* = 2.4 Hz, 1H), 6.94 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.82 (s, 3H), 2.80 (t, *J* = 8.0 Hz, 2H), 2.72 (t, *J* = 8.0 Hz, 2H), 1.74 – 1.61 (m, 2H), 1.61 – 1.50 (m, 2H), 1.44 – 1.35 (m, 4H), 0.95 (t, *J* = 7.2 Hz, 3H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.8, 139.7, 137.5, 134.5, 131.1, 121.9, 113.3, 105.2, 55.6, 33.8, 32.4, 28.2, 26.4, 22.9, 22.5, 14.1, 14.0; HRMS (ESI) Calcd for $C_{17}H_{25}OS$ $[M + H]^+$ 277.1626, found 277.1611.



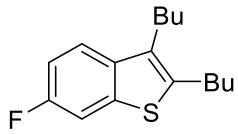
2,3-Dibutylbenzo[*b*]thiophene (3ba): Colourless oil (40% and 82% yields with protocols A and B, respectively , eluent = hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.33 – 7.29 (m, 1H), 7.27 – 7.21 (m, 1H), 2.85 (t, *J* = 8.0 Hz, 2H), 2.77 (t, *J* = 8.0 Hz, 2H), 1.73 – 1.65 (m, 2H), 1.62 – 1.54 (m, 2H), 1.46 – 1.39 (m, 4H), 0.96 (t, *J* = 7.6 Hz, 3H), 0.95 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.4, 140.3, 138.5, 131.6, 123.6, 123.2, 122.2, 121.3, 33.8, 32.3, 28.2, 26.3, 22.9, 22.5, 14.0, 13.9; HRMS (ESI) Calcd for $C_{16}H_{23}S$ $[M + H]^+$ 247.1520, found 247.1513.



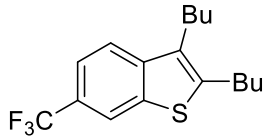
2,3-Dibutyl-*N*,*N*-dimethylbenzo[*b*]thiophen-6-amine (3ca): Yellow oil (76% yield with protocol A , eluent = hexane/Et_2O (100:1)); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.8 Hz, 1H), 7.09 (d, *J* = 2.4 Hz, 1H), 6.87 (dd, *J* = 8.8, 2.4 Hz, 1H), 2.95 (s, 6H), 2.78 (t, *J* = 7.6 Hz, 2H), 2.70 (t, *J* = 7.6 Hz, 2H), 1.69 – 1.62 (m, 4H), 1.44 – 1.37 (m, 4H), 0.94 (t, *J* = 7.2 Hz, 3H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 140.3, 135.6, 132.0, 131.0, 121.5, 112.0, 105.4, 41.4, 33.8, 32.4, 26.3, 22.9, 22.5, 14.1, 14.0; HRMS (ESI) Calcd for $C_{18}H_{28}NS$ $[M + H]^+$ 290.1942, found 290.1942.



***N,N*-dibenzyl-2,3-dibutylbenzo[*b*]thiophen-6-amine (3da):** Yellow oil (96% yield with protocol B , eluent = hexane/Et_2O (100:1)); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.8 Hz, 1H), 7.40 – 7.33 (m, 10H), 7.20 (d, *J* = 2.4 Hz, 1H), 6.94 (dd, *J* = 8.8, 2.4 Hz, 1H), 4.78 (s, 4H), 2.88 (t, *J* = 7.6 Hz, 2H), 2.78 (t, *J* = 7.6 Hz, 2H), 1.76 – 1.64 (m, 4H), 1.53 – 1.48 (m, 4H), 1.04 (t, *J* = 7.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.4, 140.5, 138.8, 135.5, 132.0, 131.0, 128.7, 127.0, 126.8, 121.8, 111.4, 105.0, 54.7, 33.9, 32.4, 28.1, 26.3, 23.0, 22.5, 14.1, 14.0; HRMS (ESI) Calcd for $C_{30}H_{36}NS$ $[M + H]^+$ 442.2568, found 442.2560.

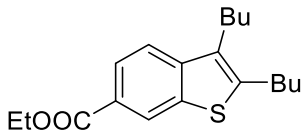


2,3-Dibutyl-6-fluorobenzo[*b*]thiophene (3ea): Yellow oil (67% yield with protocol B , eluent = hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (dd, *J* = 8.8, 4.8 Hz, 1H), 7.46 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.12 – 7.07 (m, 1H), 2.86 (t, *J* = 7.6 Hz, 2H), 2.77 (t, *J* = 7.6 Hz, 2H), 1.74 – 1.67 (m, 2H), 1.61 – 1.55 (m, 2H), 1.50 – 1.41 (m, 4H), 0.98 (t, *J* = 7.2 Hz, 3H), 0.97 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0 (d, $^1J_{C\text{-}F}$ = 241.1 Hz), 139.7 (d, $^4J_{C\text{-}F}$ = 3.7 Hz), 139.2 (d, $^3J_{C\text{-}F}$ = 9.9 Hz), 136.9, 131.1, 122.3 (d, $^2J_{C\text{-}F}$ = 23.7 Hz), 122.1 (d, $^3J_{C\text{-}F}$ = 8.9 Hz), 108.3 (d, $^2J_{C\text{-}F}$ =24.9 Hz), 33.6, 32.2, 28.2, 26.3, 22.9, 22.5, 14.0, 13.9; HRMS (ESI) Calcd for $C_{16}H_{22}FS$ $[M + H]^+$ 265.1426, found 265.1421.

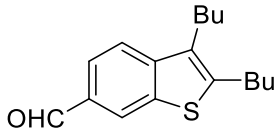


2,3-Dibutyl-6-(trifluoromethyl)benzo[*b*]selenophene (3fa): Yellow oil (85% yield with protocol B , eluent = hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 1.2 Hz, 1H),

7.72 (d, *J* = 8.8 Hz, 1H), 7.57 (dd, *J* = 8.8, 1.2 Hz, 1H), 2.92 (t, *J* = 7.6 Hz, 2H), 2.82 (t, *J* = 7.6 Hz, 2H), 1.78 – 1.70 (m, 2H), 1.64 – 1.57 (m, 2H), 1.52 – 1.42 (m, 4H), 1.00 (t, *J* = 7.2 Hz, 3H), 0.99 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.2, 142.8, 138.2, 131.7, 126.6, 125.4 (q, $^{2}J_{C\text{-}F}$ = 32.1 Hz), 124.7 (q, $^{1}J_{C\text{-}F}$ = 270.2 Hz), 120.4 (q, $^{3}J_{C\text{-}F}$ = 3.5 Hz), 119.6 (q, $^{3}J_{C\text{-}F}$ = 4.3 Hz), 33.6, 32.2, 28.4, 26.2, 22.8, 22.5, 14.0, 13.9; HRMS (ESI) Calcd for $C_{17}H_{22}F_3S$ $[M + H]^+$ 315.1394, found 315.1400.

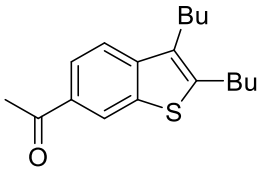


Ethyl 2,3-dibutylbenzo[*b*]thiophene-6-carboxylate (3ga): Yellow oil (84% yield with protocol B, eluent = hexane/Et_2O (50:1)); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, *J* = 1.2 Hz, 1H), 7.99 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 4.40 (q, *J* = 7.2 Hz, 2H), 2.87 (q, *J* = 7.6 Hz, 2H), 2.78 (q, *J* = 7.6 Hz, 2H), 1.75 – 1.67 (m, 2H), 1.61 – 1.53 (m, 2H), 1.49 – 1.37 (m, 7H), 0.96 (t, *J* = 7.2 Hz, 3H), 0.95 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 145.0, 143.8, 138.0, 131.9, 125.3, 124.7, 124.2, 120.9, 60.9, 33.6, 32.2, 28.5, 26.2, 22.8, 22.5, 14.4, 14.0, 13.9; HRMS (ESI) Calcd for $C_{19}H_{27}O_2S$ $[M + H]^+$ 319.1732, found 319.1729.

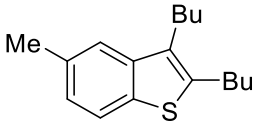


2,3-Dibutylbenzo[b]thiophene-6-carbaldehyde (3ha): Light yellow oil (94% yield with protocol B, eluent = hexane/Et_2O (50:1)); ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.08 (s, 1H), 8.28 (d, *J* = 0.8 Hz, 1H), 7.86 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 2.93 (t, *J* = 7.6 Hz, 2H), 2.83 (t, *J* = 7.6 Hz, 2H), 1.79 – 1.72 (m, 2H), 1.71 – 1.57 (m, 2H), 1.48 –

1.42 (m, 4H), 1.00 (t, *J* = 7.6 Hz, 3H), 0.99 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.9, 146.9, 145.1, 138.5, 132.3, 132.0, 125.6, 124.1, 121.7, 33.6, 32.2, 28.6, 26.2, 22.8, 22.5, 14.0, 13.9; HRMS (ESI) Calcd for $C_{17}H_{23}OS$ $[M + H]^+$ 275.1470, found 275.1474.

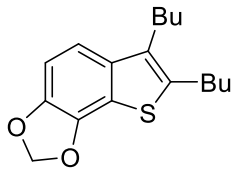


1-(2,3-Dibutylbenzo[*b*]thiophen-6-yl)ethanone (3ia): Yellow oil (83% yield with protocol B, eluent = hexane/EtOAc (50:1)); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (d, *J* = 1.2 Hz, 1H), 7.96 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 2.92 (t, *J* = 7.6 Hz, 2H), 2.82 (t, *J* = 7.6 Hz, 2H), 2.68 (s, 3H), 1.78 – 1.71 (m, 2H), 1.65 – 1.57 (m, 2H), 1.52 – 1.40 (m, 4H), 1.00 (t, *J* = 7.6 Hz, 3H), 0.99 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.7, 145.7, 143.9, 138.3, 132.4, 132.0, 123.6, 123.3, 121.1, 33.6, 32.2, 28.6, 26.7, 26.2, 22.8, 22.5, 14.0, 13.9; HRMS (ESI) Calcd for $C_{18}H_{25}OS$ $[M + H]^+$ 289.1626, found 289.1623.

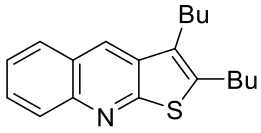


2,3-Dibutyl-5-methylbenzo[*b*]thiophene (3ja): Colourless oil (38% yield with protocol A , eluent = hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.4 Hz, 1H), 7.40 (s, 1H), 7.07 (dd, *J* = 8.4, 1.2 Hz, 1H), 2.83 (t, *J* = 7.6 Hz, 2H), 2.74 (t, *J* = 7.6 Hz, 2H), 2.46 (s, 3H), 1.71 – 1.53 (m, 4H), 1.47 – 1.37 (m, 4H), 0.95 (t, *J* = 7.6 Hz, 3H), 0.94 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.7, 140.4, 135.6, 133.3, 131.3, 124.9, 121.9,

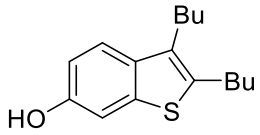
121.4, 33.8, 32.3, 28.3, 26.3, 22.9, 22.5, 21.6, 14.1, 13.9; HRMS (ESI) Calcd for $C_{17}H_{15}S$ $[M + H]^+$ 261.1677, found 261.1674.



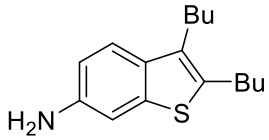
6,7-Methylenedioxy-2,3-dibutyl benzo[*b*]thiophene (3ka): Yellow oil (70% and 97% yields with protocols A and B, respectively , eluent = hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (d, *J* = 8.4 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 6.09 (s, 2H), 2.87 (t, *J* = 8.0 Hz, 2H), 2.77 (t, *J* = 8.0 Hz, 2H), 1.76 – 1.72 (m, 2H), 1.64 – 1.60 (m, 2H), 1.51 – 1.44 (m, 4H), 1.12 (t, *J* = 7.2 Hz, 3H), 1.01 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.4, 141.1, 138.3, 138.1, 131.8, 119.2, 114.2, 106.4, 101.4, 33.6, 32.2, 28.3, 26.5, 22.9, 22.5, 14.0, 13.9; HRMS (ESI) Calcd for $C_{17}H_{23}O_2S$ $[M + H]^+$ 291.1419, found 291.1426.



2,3-Dibutylthieno[2,3-*b*]quinolone (3ma): Yellow oil (78% yield with protocol B, eluent = hexane/Et_2O (30:1)); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (s, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.70 – 7.66 (m, 1H), 7.52 – 7.48 (m, 1H), 2.91 (t, *J* = 7.6 Hz, 2H), 2.84 (t, *J* = 7.6 Hz, 2H), 1.78 – 1.71 (m, 2H), 1.66 – 1.60 (m, 2H), 1.51 – 1.40 (m, 4H), 0.98 (t, *J* = 7.2 Hz, 3H), 0.97 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.0, 146.1, 142.1, 133.4, 128.7, 128.6, 128.2, 128.2, 127.0, 125.6, 125.1, 33.2, 32.1, 28.8, 26.1, 22.9, 22.6, 14.0, 13.9; HRMS (ESI) Calcd for $C_{19}H_{24}NS$ $[M + H]^+$ 298.1629, found 298.1628.

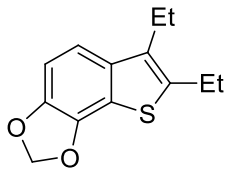


2,3-Dibutylbenzo[*b*]thiophen-6-ol (3na): (*E*)-*tert*-butyl (4-(dec-5-en-5-yl)-3-iodophenyl) carbonate was subjected to the copper-catalyzed reaction according to protocol B. The C–S coupling/cyclization coincided with the deprotection of the OBoc group to afford the title compound as a yellow oil (45% yield with protocol B, eluent = hexane/EtOAc (10:1)); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.8 Hz, 1H), 7.23 (d, *J* = 2.4 Hz, 1H), 6.89 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.94 (s, 1H), 2.83 (t, *J* = 7.6 Hz, 2H), 2.75 (t, *J* = 7.6 Hz, 2H), 1.73 – 1.67 (m, 2H), 1.59 – 1.55 (m, 2H), 1.51 – 1.39 (m, 4H), 0.98 (t, *J* = 7.6 Hz, 3H), 0.97 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.3, 139.7, 137.5, 134.7, 131.0, 122.1, 113.3, 107.8, 33.7, 32.3, 28.1, 26.3, 22.9, 22.5, 14.0, 13.9; HRMS (ESI) Calcd for $C_{16}H_{23}OS$ $[M + H]^+$ 263.1470, found 263.1471.

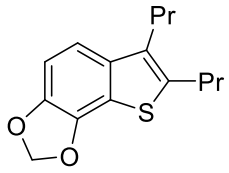


2,3-Dibutylbenzo[*b*]thiophen-6-amine (3oa): (*E*)-4-bromo-*N*-(1-phenylethylidene)aniline was subjected to the $CoCl_2$(Xantphos)-catalyzed zinc insertion, followed by addition of the resulting arylzinc reagent to 5-decyne and quenching with iodine, to afford (*E*)-4-((*E*)-dec-5-en-5-yl)-3-iodo-*N*-(1-phenylethylidene)aniline (**4oa**) with impurities that could not be removed by silica gel chromatography. Without further puritication, **4oa** was subjected to the copper-catalyzed reaction (protocol B), followed by hydrolysis with 1N HCl at room temperature to afford the title compound as a yellow oil (42% yield based on 5-decyne , eluent = hexane/EtOAc (10:1)); ^{1}H NMR (400 MHz,

$CDCl_3$): δ 7.44 (d, *J* = 8.4 Hz, 1H), 7.08 (d, *J* = 2.0 Hz, 1H), 6.76 (dd, *J* = 8.4, 2.0 Hz, 1H), 3.59 (brs, 2H), 2.84 (t, *J* = 7.6 Hz, 2H), 2.75 (t, *J* = 7.6 Hz, 2H), 1.75 – 1.67 (m, 2H), 1.65 – 1.57 (m, 2H), 1.52 – 1.41 (m, 4H), 1.00 (t, *J* = 7.2 Hz, 3H), 0.99 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.9, 140.0, 135.9, 133.3, 131.1, 121.9, 113.7, 107.5, 33.8, 32.3, 28.1, 26.3, 22.9, 22.5, 14.1, 14.0; HRMS (ESI) Calcd for $C_{16}H_{24}NS$ $[M + H]^+$ 262.1629, found 262.1628.

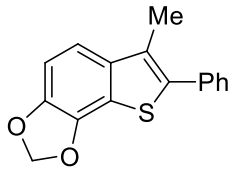


6,7-Methylenedioxy-2,3-diethylbenzo[*b*]thiophene (3kb): Yellow oil (64% yield with protocol A , eluent = hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (d, *J* = 8.4 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 6.09 (s, 2H), 2.89 (q, *J* = 7.6 Hz, 2H), 2.79 (q, *J* = 7.6 Hz, 2H), 1.37 (t, *J* = 7.6 Hz, 3H), 1.24 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5, 141.2, 139.4, 137.8, 132.7, 119.2, 114.1, 106.5, 101.4, 21.8, 19.9, 16.1, 14.6; HRMS (ESI) Calcd for $C_{13}H_{15}O_2S$ $[M + H]^+$ 235.0793, found 235.0782.

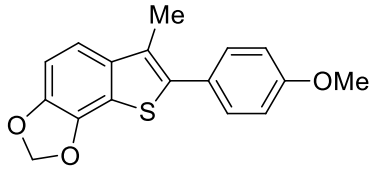


6,7-Methylenedioxy-2,3-dipropylbenzo[*b*]thiophene (3kc): Yellow oil (71% yield with protocol A , eluent = hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10 (d, *J* = 8.0 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.03 (s, 2H), 2.79 (t, *J* = 7.6 Hz, 2H), 2.69 (t, *J* = 7.6 Hz, 2H), 1.74 – 1.69 (m, 2H), 1.64 – 1.55 (m, 2H), 1.00 (t, *J* = 7.2 Hz, 3H), 0.97 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.4, 141.1, 138.3, 138.1, 131.7, 119.3, 114.3, 106.4,

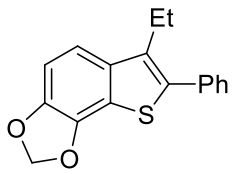
101.4, 30.6, 28.8, 24.7, 23.2, 14.3, 13.9; HRMS (ESI) Calcd for $C_{15}H_{19}O_2S$ $[M + H]^+$ 263.1106, found 263.1118.



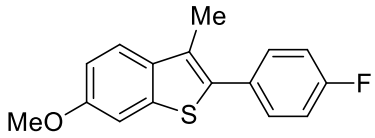
6,7-Methylenedioxy-3-methyl-2-phenylbenzo[*b*]thiophene (3kd): White solid (54% yield with protocol A , eluent = hexane); MP =105-106 ℃ ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 – 7.51 (m, 2H), 7.46 – 7.42 (m, 2H), 7.38 – 7.34 (m, 1H), 7.21 (d, *J* = 8.4 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.09 (s, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.2, 141.0, 138.9, 136.2, 134.6, 129.7, 128.6, 127.8, 127.7, 119.7, 115.3, 107.0, 101.6, 13.0; HRMS (ESI) Calcd for $C_{16}H_{13}O_2S$ $[M + H]^+$ 269.0636, found 269.0651.



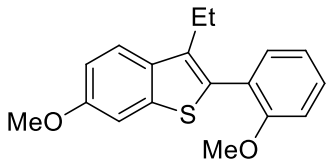
6,7-Methylenedioxy-3-methyl-2-(4-methoxyphenyl)benzo[*b*]thiophene (3ke): Yellow solid (58% yield with protocol A, eluent = hexane/Et_2O (30:1)); MP =133-134 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.06 – 7.02 (m, 3H), 6.13 (s, 2H), 3.90 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 144.0, 140.8, 138.9, 136.0, 130.7 (2C), 126.9, 119.4, 115.0, 114.0, 106.8, 101.4, 55.3, 12.8; HRMS (ESI) Calcd for $C_{17}H_{15}O_3S$ $[M + H]^+$ 299.0742, found 299.0744.



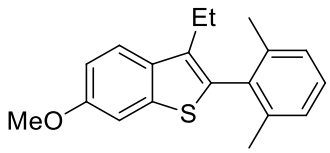
6,7-Methylenedioxy-3-ethyl-2-phenylbenzo[*b*]thiophene (3kf): Yellow solid (52% yield with protocol A , eluent = hexane); MP = 87-88 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 – 7.49 (m, 2H), 7.48 – 7.41 (m, 2H), 7.38 (m, 1H), 7.27 (d, *J* = 8.4 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 1H), 6.09 (s, 2H), 2.85 (q, J = 7.6 Hz, 2H), 1.29 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.0, 141.0, 137.8, 136.1, 134.7, 134.2, 129.5, 128.6, 127.9, 120.2, 115.4, 107.0, 101.5, 20.4, 14.9; HRMS (ESI) Calcd for $C_{17}H_{15}O_2S$ $[M + H]^+$ 283.0793, found 283.0795.



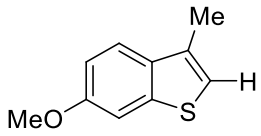
2-(4-Fluorophenyl)-6-methoxy-3-methylbenzo[*b*]thiophene (3ag): Yellow solid (74% yield with protocol B, eluent = hexane/EtOAc (50:1)); MP =76-77 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.8 Hz, 1H), 7.54 – 7.51 (m, 2H), 7.35 (d, *J* = 2.0 Hz, 1H), 7.20 – 7.16 (m, 2H), 7.08 (dd, *J* = 8.8, 2.0 Hz, 1H), 3.93 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.3 (d, $^{1}J_{C\text{-}F}$ = 246.0 Hz), 157.6, 140.1, 135.3, 134.2, 131.3 (d, $^{3}J_{C\text{-}F}$ = 8.1 Hz), 130.9 (d, $^{4}J_{C\text{-}F}$ = 3.3 Hz), 127.2, 122.8, 115.6 (d, $^{2}J_{C\text{-}F}$ = 21.5 Hz), 114.1, 104.8, 55.7, 12.6; HRMS (ESI) Calcd for $C_{16}H_{14}OSF$ $[M + H]^+$ 273.0749, found 273.0754.



3-ethyl-6-methoxy-2-(2-methoxyphenyl)benzo[*b*]thiophene (3ah): Light yellow solid (89% yield with protocol B, eluent = hexane/Et_2O (30:1)); MP =85-86 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.8 Hz, 1H), 7.46 – 7.40 (m, 2H), 7.38 (d, *J* = 2.4 Hz, 1H), 7.10 – 7.04 (m, 3H), 3.93 (s, 3H), 3.86 (s, 3H), 2.76 (q, *J* = 7.6 Hz, 2H), 1.26 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.6, 157.2, 141.4, 135.1, 133.8, 132.6, 131.2, 129.7, 123.5, 122.8, 120.4, 113.7, 111.2, 105.0, 55.7, 55.6, 20.7, 14.4; HRMS (ESI) Calcd for $C_{18}H_{19}O_2S$ $[M + H]^+$ 299.1106, found 299.1103.



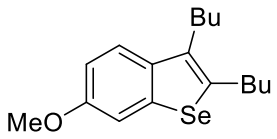
2-(2,6-Dimethylphenyl)-3-ethyl-6-methoxybenzo[*b*]thiophene (3ai): Yellow solid (93% yield with protocol B, eluent = hexane/Et_2O (100:1)); MP =98-99 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.8 Hz, 1H), 7.42 (d, *J* = 2.4 Hz, 1H), 7.31 – 7.28 (m, 1H), 7.20 (d, *J* = 7.6 Hz, 2H), 7.11 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.95 (s, 3H), 2.60 (q, *J* = 7.6 Hz, 2H), 2.23 (s, 6H), 1.19 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.1, 141.7, 138.6, 134.0, 133.8, 133.5, 133.4, 128.4, 127.4, 122.7, 113.7, 105.3, 55.7, 20.5, 20.4, 13.9; HRMS (ESI) Calcd for $C_{19}H_{21}OS$ $[M + H]^+$ 297.1313, found 297.1312.



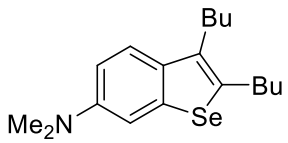
6-Methoxy-3-methylbenzo[*b*]thiophene (3aj): Yellow oil (50% yield with protocol A , eluent = hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.8 Hz, 1H), 7.36 (d, *J* = 2.4 Hz, 1H), 7.06 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.93 (d, *J* = 0.8 Hz, 1H), 3.91 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.7, 139.7, 137.5, 134.6, 131.1, 122.0, 113.3,

105.2, 55.6, 30.5, 28.6, 24.9, 23.3, 14.3, 14.0; HRMS (ESI) Calcd for $C_{10}H_{11}OS$ $[M + H]^+$ 179.0531, found 179.0532.

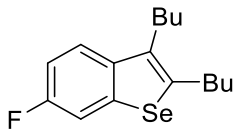
General Procedure for Benzoselenophene Synthesis: An oven-dried Schlenk tube was charged with CuI (4.0 mg, 0.020 mmol), 1-iodo-2-alkenylarene (0.20 mmol), selenium powder (47 mg, 0.60 mmol) and K_2CO_3 (56 mg, 0.40 mmol). The Schlenk tube was evacuated and backfilled with N_2, followed by addition of NMP (1 mL). The reaction mixture was stirred at 120 ℃ until the starting material was fully consumed (typically 8–12 h) as monitored by TLC. Upon cooling to room temperature, the reaction mixture was diluted with ethyl acetate (5 mL) and filtered through a pad of silica gel with additional ethyl acetate (15 mL) as the eluent. The filtrate was washed with water (10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product.



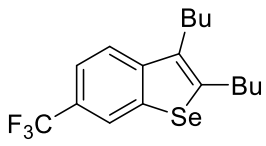
2,3-Dibutyl-6-methoxybenzo[*b*]selenophene (5aa): Yellow oil (85% yield, eluent = hexane/Et_2O (20:1)); ^1H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.4 Hz, 1H), 7.38 (d, *J* = 2.4 Hz, 1H), 6.98 (dd, *J* = 8.4, 2.4 Hz, 1H), 3.88 (s, 3H), 2.90 (t, *J* = 7.6 Hz, 2H), 2.72 (t, *J* = 7.6 Hz, 2H), 1.74 – 1.66 (m, 2H), 1.62 – 1.55 (m, 2H), 152 – 1.40 (m, 4H), 0.99 (t, *J* = 7.2 Hz, 3H), 0.98 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.7, 141.6, 140.8, 136.8, 133.7, 123.7, 113.0, 109.0, 55.6, 34.7, 32.0, 30.2, 27.5, 22.9, 22.5, 14.0, 14.0; HRMS (ESI) Calcd for $C_{17}H_{25}OSe$ $[M + H]^+$ 325.1071, found 325.1078.



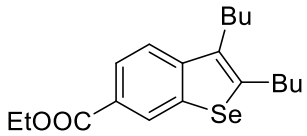
2,3-Dibutyl-N,N-dimethylbenzo[*b*]selenophen-6-amine (5ca): Yellow oil (85% yield, eluent = hexane/Et_2O (50:1)); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 8.8 Hz, 1H), 7.22 (d, *J* = 2.4 Hz, 1H), 6.88 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.00 (s, 6H), 2.87 (t, *J* = 7.6 Hz, 2H), 2.69 (t, *J* = 7.6 Hz, 2H), 1.72 – 1.65 (m, 2H), 1.62 – 1.55 (m, 2H), 1.49 – 1.41 (m, 4H), 0.98 (t, *J* = 7.2 Hz, 3H), 0.97 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 141.3, 139.4, 133.9, 133.6, 123.3, 111.6, 108.8, 41.2, 34.8, 32.1, 30.1, 27.4, 22.9, 22.5, 14.1, 14.0; HRMS (ESI) Calcd for $C_{18}H_{28}NSe$ $[M + H]^+$ 338.1387, found 338.1389.



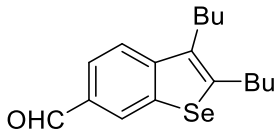
2,3-Dibutyl-6-fluorobenzo[*b*]selenophene (5ea): Yellow oil (65% yield, eluent = hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 – 7.43 (m, 2H), 7.12 – 7.07 (m, 1H), 2.90 (t, *J* = 7.6 Hz, 2H), 2.73 (t, *J* = 7.6 Hz, 2H), 1.73 – 1.66 (m, 2H), 1.61 – 1.54 (m, 2H), 1.52 – 1.40 (m, 4H), 0.99 (t, *J* = 7.6 Hz, 3H), 0.98 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0 (d, $^1J_{C\text{-}F}$ = 243.1 Hz), 143.9 (d, $^4J_{C\text{-}F}$ = 3.5 Hz), 140.4 (d, $^3J_{C\text{-}F}$ = 8.9 Hz), 139.3, 133.5, 123.9 (d, $^3J_{C\text{-}F}$ = 8.5 Hz), 112.5 (d, $^2J_{C\text{-}F}$ =23.2 Hz), 111.8 (d, $^2J_{C\text{-}F}$ =24.1 Hz), 34.6, 31.9, 30.3, 27.5, 22.9, 22.5, 14.0, 13.9; HRMS (ESI) Calcd for $C_{16}H_{22}FSe$ $[M + H]^+$ 313.0871, found 313.0843.



2,3-Dibutyl-6-(trifluoromethyl)benzo[*b*]selenophene (5fa): Yellow oil (83% yield, eluent = hexane/Et_2O (100:1)); ^1H NMR (400 MHz, $CDCl_3$): δ 8.11 (s, 1H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.60 (dd, *J* = 8.4, 1.6 Hz, 1H), 2.97 (t, *J* = 7.6 Hz, 2H), 2.79 (t, *J* = 7.6 Hz, 2H), 1.78 – 1.70 (m, 2H), 1.62 – 1.57 (m, 2H), .1.54 – 1.41 (m, 4H), 1.01 (t, *J* = 7.2 Hz, 3H), 1.00 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.8, 145.5, 139.6, 134.2, 129.2 (q, $^1J_{C\text{-}F}$ = 268.2 Hz), 125.5 (q, $^2J_{C\text{-}F}$ = 32.0 Hz), 123.3, 122.7 (q, $^3J_{C\text{-}F}$ = 4.2 Hz), 121.0 (q, $^3J_{C\text{-}F}$ = 3.5 Hz), 34.6, 31.9, 30.5, 27.4, 22.8, 22.5, 14.0, 13.9; HRMS (ESI) Calcd for $C_{17}H_{22}F_3Se$ $[M + H]^+$ 363.0839, found 363.0855.

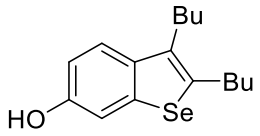


Ethyl 2,3-dibutylbenzo[*b*]selenophene-6-carboxylate (5ga): Colourless oil (67% yield, eluent = hexane/Et_2O (50:1)); ^1H NMR (400 MHz, $CDCl_3$): δ 8.54 (d, *J* = 0.8 Hz, 1H), 8.03 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 4.43 (q, *J* = 7.2 Hz, 2H), 2.96 (t, *J* = 7.6 Hz, 2H), 2.78 (t, *J* = 7.6 Hz, 2H), 1.77 – 1.70 (m, 2H), 1.62 – 1.53 (m, 2H), 1.51 – 1.40 (m, 7H), 1.02 – 0.96 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 149.6, 146.4, 139.3, 134.5, 127.3, 125.5, 125.3, 122.8, 60.9, 34.6, 32.0, 30.6, 27.4, 22.9, 22.6, 14.4, 14.0, 13.9; HRMS (ESI) Calcd for $C_{19}H_{27}O_2Se$ $[M + H]^+$ 367.1176, found 367.1178.

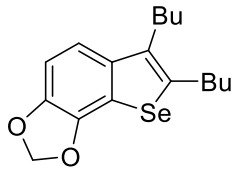


2,3-Dibutylbenzo[*b*]selenophene-6-carbaldehyde (5ha): Yellow oil (83% yield, eluent = hexane/Et_2O (100:1)); ^1H NMR (400 MHz, $CDCl_3$): δ 10.08 (s, 1H), 8.33 (d, *J* = 1.6 Hz, 1H), 7.87 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 2.97 (t, *J* = 7.6 Hz, 2H), 2.79

(t, *J* = 7.6 Hz, 2H), 1.78 – 1.71 (m, 2H), 1.59 – 1.54 (m, 2H), 1.52 – 1.41 (m, 4H), 1.00 (t, *J* = 7.6 Hz, 3H), 0.99 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.9, 151.7, 147.8, 139.9, 134.8, 132.0, 128.4, 124.8, 123.5, 34.6, 32.0, 30.8, 27.4, 22.9, 22.5, 14.0, 13.9; HRMS (ESI) Calcd for $C_{17}H_{23}OSe$ $[M + H]^+$ 323.0914, found 323.0913.

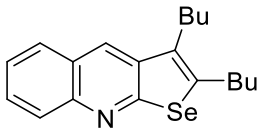


2,3-Dibutylbenzo[*b*]selenophen-6-ol (5na): Yellow oil (56% yield, eluent = hexane/EtOAc (10:1)); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 8.4 Hz, 1H), 7.30 (d, *J* = 2.4 Hz, 1H), 6.89 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.94 (s, 1H), 2.88 (t, *J* = 7.6 Hz, 2H), 2.70 (t, *J* = 7.6 Hz, 2H), 1.73 – 1.65 (m, 2H), 1.61 – 1.53 (m, 2H), 1.46 – 1.39 (m, 4H), 0.99 (t, *J* = 7.6 Hz, 3H), 0.98 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.4, 141.6, 140.8, 137.0, 133.6, 123.9, 113.3, 111.5, 34.7, 32.0, 30.2, 27.5, 22.9, 22.5, 14.0 (two signals overlapped); HRMS (ESI) Calcd for $C_{16}H_{23}OSe$ $[M + H]^+$ 311.0914, found 311.0920.

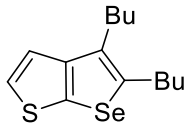


6,7-Methylenedioxy-2,3-dibutylbenzo[*b*]selenophene (5ka): Light yellow oil (61% yield, eluent = hexane/Et_2O (50:1)); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13 (d, *J* = 8.4 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 6.07 (s, 2H), 2.89 (t, *J* = 7.6 Hz, 2H), 2.70 (t, *J* = 7.6 Hz, 2H), 1.74 – 1.66 (m, 2H), 1.61 – 1.54 (m, 2H), 1.50 – 1.41 (m, 4H), 0.99 (t, *J* = 7.6 Hz, 3H), 0.98 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.1, 143.2, 142.1, 140.1,

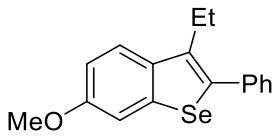
134.2, 118.2, 116.2, 106.5, 101.2, 34.6, 32.0, 30.3, 27.7, 22.9, 22.5, 14.0, 13.9; HRMS (ESI) Calcd for $C_{17}H_{23}O_2Se$ $[M + H]^+$ 339.0863, found 339.0862.



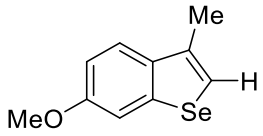
2,3-Dibutylselenopheno[2,3-*b*]quinoline (5ma): Yellow oil (77% yield, eluent = hexane/Et_2O (25:1)); ^1H NMR (400 MHz, $CDCl_3$): δ 8.17 (s, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 7.6 Hz, 1H), 7.72 – 7.68 (m, 1H), 7.55 – 7.51 (m, 1H), 2.96 (t, *J* = 7.6 Hz, 2H), 2.82 (t, *J* = 7.6 Hz, 2H), 1.80 – 1.72 (m, 2H), 1.65 – 1.60 (m, 2H), 1.55 – 1.43 (m, 4H), 1.01 (t, *J* = 7.6 Hz, 3H), 1.00 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4, 146.0, 136.6, 131.1, 128.7, 128.3 (two signals overlapped), 128.1, 128.0, 125.8, 125.3, 34.1, 31.9, 30.8, 27.0, 22.8, 22.6, 14.0, 13.9; HRMS (ESI) Calcd for $C_{19}H_{24}NSe$ $[M + H]^+$ 346.1074, found 346.1080.



4,5-Dibutylselenopheno[2,3-*b*]thiophene (5pa): Yellow oil (83% yield, eluent = hexane/Et_2O (100:1)); ^1H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 5.2 Hz, 1H), 7.17 (d, *J* = 5.2 Hz, 1H), 2.90 (t, *J* = 7.6 Hz, 2H), 2.72 (t, *J* = 7.6 Hz, 2H), 1.74 – 1.57 (m, 4H), 1.54 – 1.40 (m, 4H), 1.00 (t, *J* = 7.6 Hz, 3H), 0.99 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.1, 147.1, 131.9, 131.1, 127.6, 121.0, 35.0, 32.3, 30.5, 28.6, 22.8, 22.5, 14.0 (two signals overlapped); HRMS (ESI) Calcd for $C_{14}H_{21}SSe$ $[M + H]^+$ 301.0529, found 301.0521.

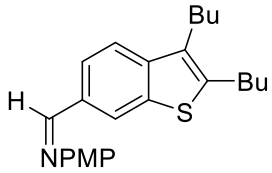


3-Ethyl-6-methoxy-2-phenylbenzo[*b*]selenophene (5af): Light yellow oil (48% yield, eluent = hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 8.8 Hz, 1H), 7.52 – 7.50 (m, 2H), 7.47 – 7.43 (m, 3H), 7.40 – 7.36 (m, 1H), 7.05 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.91 (s, 3H), 2.82 (q, *J* = 7.2 Hz, 2H), 1.31 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.3, 142.2, 138.0, 136.7, 136.5, 136.1, 129.6, 128.5, 127.5, 124.7, 113.6, 108.8, 55.6, 21.4, 14.9; HRMS (ESI) Calcd for $C_{17}H_{17}OSe$ $[M + H]^+$ 317.0445, found 317.0442.



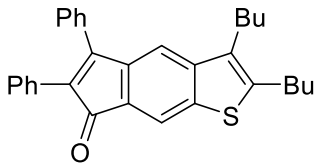
6-Methoxy-3-methylbenzo[*b*]selenophene (5aj): Yellow oil (55% yield, eluent = hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 8.8 Hz, 1H), 7.44 (d, *J* = 2.4 Hz, 1H), 7.39 (d, *J* = 1.2 Hz, 1H), 7.04 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.90 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.4, 142.7, 135.5, 134.7, 124.1, 120.3, 113.5, 109.2, 55.6, 16.1; HRMS (ESI) Calcd for $C_{10}H_{11}OSe$ $[M + H]^+$ 226.9975, found 226.9978.

Transformation of functionalized benzothiophenes



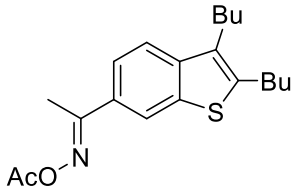
(*E*)-*N*-((2,3-dibutylbenzo[b]thiophen-6-yl)methylene)-4-methoxyaniline (6): A mixture of 2,3-dibutylbenzo[*b*]thiophene-6-carbaldehyde (**3ha**, 0.33 g, 1.2 mmol), *p*-anisidine (0.155 g, 1.26 mmol), and MS 4Å (1.5 g) in toluene (5 mL) was stirred at room temperature for 12 h. The solvent was removed under reduced pressure, and the residue

was extracted with ethyl acetate. The combined organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. Silica gel chromatography (eluent = hexane/Et_3N (10:1)) of the crude product afforded the title compound as a yellow oil (0.36 g, 80 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.57 (s, 1H), 8.27 (s, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.29 (d, *J* = 8.7 Hz, 2H), 6.97 (d, *J* = 8.7 Hz, 2H), 3.86 (s, 3H), 2.92 (t, *J* = 7.6 Hz, 2H), 2.83 (t, *J* = 7.6 Hz, 2H), 1.78 – 1.70 (m, 2H), 1.66 – 1.58 (m, 2H), 1.52 – 1.42 (m, 4H), 1.01 (t, *J* = 7.2 Hz, 3H). 1.00 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.5, 158.2, 145.1, 143.7, 142.7, 138.7, 132.0, 131.9, 123.8, 123.2, 122.2, 121.5, 114.4, 55.5, 33.6, 32.3, 28.5, 26.3, 22.9, 22.6, 14.0, 13.9; HRMS (ESI) Calcd for $C_{24}H_{30}NOS$ $[M + H]^+$ 380.2048, found 380.2043.



2,3-Dibutyl-5,6-diphenyl-7*H*-indeno[5,6-*b*]thiophen-7-one (7): To a 10 mL Schlenk tube were added (*E*)-*N*-((2,3-dibutylbenzo[*b*]thiophen-6-yl)methylene)- 4-methoxyaniline (**6**, 114 mg, 0.30 mmol), diphenylacetylene (26.7 mg, 0.15 mmol), $[Cp^*RhCl_2]_2$ (4.5 mg, 0.0073 mmol), $Cu(OAc)_2{\cdot}H_2O$ (59.7 mg, 0.30 mmol), and DMF (1 mL) was added. The resulting mixture was stirred under N_2 at 80 ℃ for 10 h, and then cooled to room temperature and extracted with EtOAc (30 mL). The organic layer was washed with water (20 mL x 3), dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was subjected to flash chromatography on silica gel (eluent = hexane/EtOAc (100:1)) to afford the product with the imine moiety, which was dissolved in EtOAc (3 mL) and hydrolyzed with 3 N HCl (2 mL) at room temperature for 30 min. The aqueous

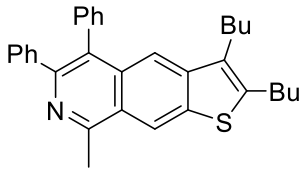
mixture was extracted with EtOAc (10 mL x 3), dried over Na_2SO_4, and concentrated under reduced pressure to afford the title compound as an orange solid (37.1 mg, 55%). MP =117-118 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (s, 1H), 7.48 – 7.44 (m, 5H), 7.31 – 7.28 (m, 6H), 3.92 (s, 3H), 2.88 (t, *J* = 7.6 Hz, 2H), 2.73 (t, *J* = 7.6 Hz, 2H), 1.77 – 1.69 (m, 2H), 1.57 – 1.50 (m, 2H), 1.47 – 1.37 (m, 4H), 0.98 (t, *J* = 7.2 Hz, 3H). 0.97 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.6, 155.8, 145.6, 143.7, 140.7, 138.0, 133.8, 133.5, 133.1, 131.1, 130.0, 129.2, 128.8, 128.6, 128.0, 127.6, 127.3, 118.3, 114.7, 33.6, 32.3, 28.5, 25.9, 22.6, 22.5, 13.9, 13.9 (two signals overlapped); HRMS (ESI) Calcd for $C_{31}H_{31}OS$ $[M + H]^+$ 451.2096, found 451.2090.



(*E*)-1-(2,3-dibutylbenzo[*b*]thiophen-6-yl)ethanone *O*-acetyl oxime (8): To a solution of 1-(2,3- dibutylbenzo[*b*]thiophen-6-yl)ethanone (**3ia**, 288 mg, 1.0 mmol) and pyridine (0.20 mL, 2.8 mmol) in EtOH (1 mL) was added $NH_2OH{\cdot}HCl$ (104 mg, 1.5 mmol) in one portion, and the resulting mixture was stirred at 60 ℃ for 2 h. The reaction was quenched by addition of water, followed by extraction with ethyl acetate. The combined extracts were washed with 1N aqueous HCl and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude residue was treated with Ac_2O (0.20 mL, 2.0 mmol) and DMAP (12 mg, 0.10 mmol) in pyridine (0.5 mL), and the resulting mixture was stirred at room temperature for 2 h. The reaction mixture was extracted with EtOAc. The organic layer was washed with 1N aqueous HCl and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was subjected to flash chromatography on

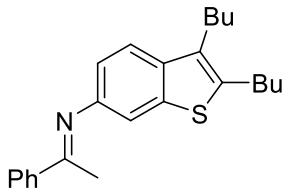
silica gel (eluent = hexane/EtOAc (100:1)) to afford the title compound as a light yellow oil (224.3 mg, 65%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 1.2 Hz, 1H), 7.73 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 2.85 (t, *J* = 7.6 Hz, 2H), 2.76 (t, *J* = 7.6 Hz, 2H), 2.42 (s, 3H), 2.27 (s, 3H), 1.73 – 1.65 (m, 2H), 1.60 – 1.52 (m, 2H), 1.47 – 1.35 (m, 4H), 0.96 (t, *J* = 7.6 Hz, 3H), 0.94 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.1, 162.5, 143.4, 142.2, 138.6, 131.8, 129.8, 122.5, 121.3, 121.2, 33.7, 32.4, 28.5, 26.3, 22.9, 22.6, 20.0, 14.5, 14.1, 14.0; HRMS (ESI) Calcd for $C_{20}H_{28}NO_2S$ $[M + H]^+$ 346.1841, found 346.1851.

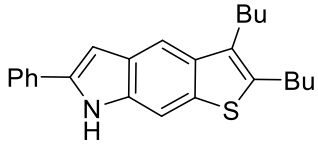


2,3-Dibutyl-8-methyl-5,6-diphenylthieno[3,2-*g*]isoquinoline (9): A Schlenk tube equipped with a stirrer bar was charged with (*E*)-1-(2,3- dibutylbenzo[*b*]thiophen-6-yl)ethanone *O*-acetyl oxime (**8**, 82.8 mg, 0.24 mmol), diphenylacetylene (51.4 mg, 0.29 mmol), $[Cp^*RhCl_2]_2$ (7.4 mg, 0.012 mmol) and $Cu(OAc)_2$ (4.3 mg, 0.024 mmol). The Schlenk tube was evacuated and refilled with N_2 for three times, followed by addition of DMF (1.2 mL). The Schlenk tube was sealed with a Teflon screwcap, and then the reaction mixture was stirred at 80 ℃ for 12 h. Upon cooling to room temperature, the reaction mixture was diluted with ethyl acetate (5 mL) and filtered through a pad of silica gel. The filtrate was washed with water (10 mL), dried over Na_2SO_4, and then concentrated under reduced pressure. The crude product was subjected to flash chromatography on silica gel (eluent = hexane/EtOAc (25:1)) to afford the title compound as a light yellow solid (53.8 mg, 48%).

MP =116-117 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (s, 1H), 7.26 (s, 1H), 6.94 – 6.87 (m, 5H), 6.83 – 6.82 (m, 2H), 6.78 – 6.73 (m, 3H), 3.50 (s, 3H), 3.31 (t, *J* = 6.4 Hz, 2H), 3.11 (t, *J* = 6.4 Hz, 2H), 2.41 – 2.34 (m, 2H), 2.18 – 2.13 (m, 4H), 2.04 – 2.00 (m, 2H), 1.77 (t, *J* = 6.0 Hz, 3H), 1.67 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.2, 147.3, 144.9, 143.1, 141.3, 138.1, 138.0, 132.9, 131.5, 131.3, 130.4, 129.0, 128.2, 127.6, 127.1, 126.7, 123.4, 118.4, 117.9, 33.4, 31.7, 28.7, 26.0, 23.1, 22.6, 22.5, 13.9, 13.8; HRMS (ESI) Calcd for $C_{32}H_{34}NS$ $[M + H]^+$ 464.2412, found 464.2412.



(*E*)-2,3-dibutyl-*N*-(1-phenylethylidene)benzo[*b*]thiophen-6-amine (10): A mixture of 2,3-dibutylbenzo[*b*]thiophen-6-amine (**3oa**, 109.6 mg, 0.42 mmol), acetophenone (48 μL, 0.4 mmol), and MS 4Å (0.5 g) in toluene (2 mL) was stirred at room temperature for 12 h. The solvent was removed under reduced pressure, and the residue was extracted with ethyl acetate. The combined organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. Silica gel chromatography (eluent = hexane/Et_3N (100:1)) of the crude product afforded the title compound containing inseparable impurities (72.6 mg), which was used for the next step without further purification.



2,3-Dibutyl-7-phenyl-6*H*-thieno[2,3-*e*]indole (11): A Schlenk tube equipped with a stirrer bar was charged with (*E*)-2,3-dibutyl-*N*-(1-phenylethylidene)benzo[*b*]thiophen-6-

amine (**10**, 72.6 mg, ca. 0.2 mmol containing impurities), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and $Cu(OAc)_2$ (109 mg, 0.6 mmol). The Schlenk tube was evacuated and refilled with N_2 for three times, followed by addition of DMSO (1 mL). The Schlenk tube was sealed with a Teflon screwcap and then the reaction mixture was stirred at 60 ℃ for 36 h. Upon cooling to room temperature, the reaction mixture was diluted with 5 mL of ethyl acetate, followed by filtration through a pad of silica gel. The filtrate was washed with water (10 mL), dried over Na_2SO_4, and then concentrated under reduced pressure. The crude product was subjected to flash chromatography on silica gel (eluent = hexane/EtOAc (50:1)) to afford the title compound as a brown oil (51.3 mg, 36% in two steps).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (s, 1H), 7.73 (d, *J* = 1.2 Hz, 1H), 7.71 (s, 1H), 7.50 – 7.47 (m, 3H), 7.41 – 7.34 (m, 2H), 7.00 (d, *J* = 1.6 Hz, 1H), 2.95 (t, *J* = 7.6 Hz, 2H), 2.87 (t, *J* = 7.6 Hz, 2H), 1.83 – 1.75 (m, 2H), 1.72 – 1.65 (m, 2H), 1.57 – 1.45 (m, 4H), 1.03 (t, *J* = 7.2 Hz, 3H). 1.02 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.2, 136.0, 134.4, 133.6, 132.4, 132.4 (two signals overlapped), 130.1, 129.1, 127.6, 125.0, 123.5, 116.5, 108.4, 98.3, 34.1, 32.6, 28.2, 26.7, 23.0, 22.5, 14.1, 14.0; HRMS (ESI) Calcd for $C_{24}H_{28}NS$ $[M + H]^+$ 362.1942, found 362.1944.

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Chapter 3. Expedient Synthesis of Benzotellurophenes and Tellurium-Bridged Heterobiaryls

3.1 Introduction

Tellurophenes and their benzo-fused analogues have attracted significant attention in recent years owing to their unique electronic properties.[1] Compared with their thiophene counterparts, they often exhibit lower optical band gaps, deeper LUMO levels and potentially higher charge carrier mobilities.[2]

In 2010, Seferos and coworkers reported the first synthesis of poly(bitellurophene-alt-9,9'-dihexylfluorene) copolymers (Figure 3.1, **A**).[3] These polytellurophenes are stable, processable materials with distinct optoelectronic properties that can be reversibly controlled by treatment with a coordinating species at their tellurium centers. Later, they synthesized a series of poly(3-alkyltellurophenes), which exhibit many interesting properties including regio-regularity, solid state organizing ability and a narrow electrochemical HOMO-LUMO gaps (Figure 3.1, **B**).[4] They also demonstrated that these tellurium-containing polymers have unique solid-state microstructures and phase morphologies, which are suitable for studying structure-property-function relationships as semiconductor materials.[5] In 2013, Rivard and coworkers reported the synthesis of conjugated polymers containing five-membered chalcogenophene rings containing S, Se and Te, and demonstrated that the optoelectronic properties can be readily tuned via controlled atom substitution chemistry (Figure 3.1, **C**).[6] Recently, they prepared a series of tellurophene bearing pinacolboronate (BPin) side groups and discovered their unusual solid- or aggregation-state phosphorescence under ambient conditions (Figure 3.1, **D**).[7]

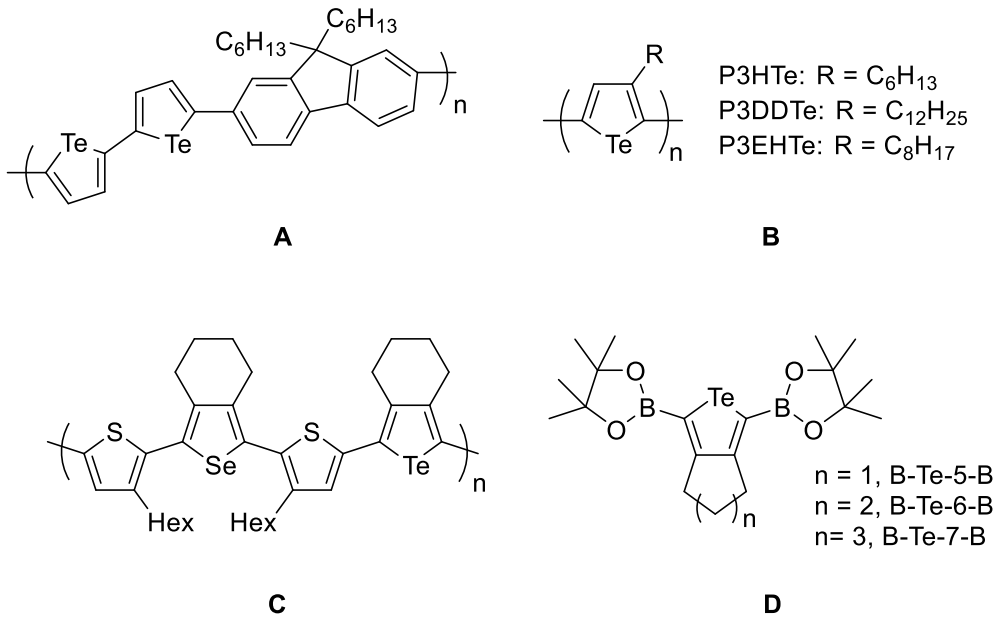
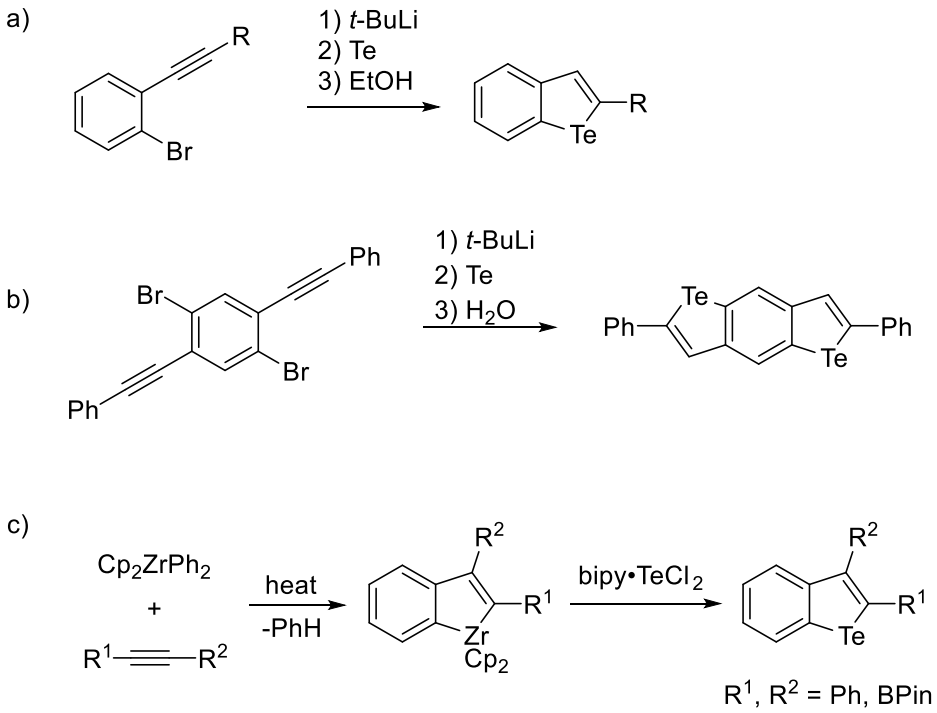


Figure 3.1. Tellurium-containing compounds as functional molecules.

Synthetic methods for tellurophenes have been reasonably established and one representative approach is the tellurative cyclization of 1,3-diynes and reductive coupling-cyclization of alkynes.[8] However, when it comes to benzotellurophene, only a few methods have been reported to date. For example, Sashida and co-workers demonstrated conversion of an *ortho*-alkynylaryl bromides into a benzotellurophene through Br/Li exchange, electrophilic trapping with elemental tellurium, and intramolecular cyclization of the resulting *ortho*-alkynylaryl telluride anion (Scheme 3.1a).[9] This reaction was later adopted by Takimiya and coworkers for the synthesis of benzoditellurophene (Scheme 3.1b). [10] Recently, Rivard and coworkers achieved the synthesis of a few benzotellurophenes through Zr/Te exchange of benzozirconocenes (generated from Cp_2ZrPh_2 and alkyne) with bipy-$TeCl_2$ (bipy = 2,2'-bipyridine) (Scheme 3.1c). [11] Regardless of their success in the synthesis of specific benzotellurophenes, both of these

approaches may not be suited for the expedient construction of benzotellurophenes bearing various substituents on the benzene ring moiety.

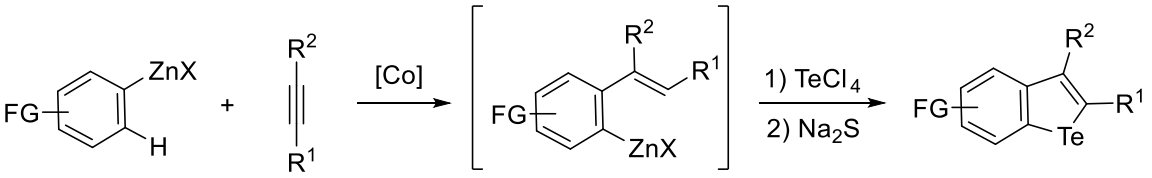
Scheme 3.1. Previous reports on the synthesis of Benzotellurophene.



Given the successful development of the synthetic methods for benzothiophenes and benzoselenophenes capitalizing on the cobalt-catalyzed migratory arylzincation (Chapter 2),[12] we reasoned that benzotellurophene synthesis could also be achieved directly or indirectly from the same key intermediate, that is, *ortho*-alkenylarylzinc species. Unlike the benzothiophene and benzoselenophene synthesis, the attempt to use elemental tellurium as the tellurium source has been unsuccessful. Nevertheless, we have been able to establish a one-pot protocol for benzotellurophene synthesis employing $TeCl_4$. The new protocol likely involves a Friedel–Crafts-like electrophilic telluration of the olefinic moiety as the key ring-closure step. This rationale has allowed us to extend

the scope of the present telluration to achieve the synthesis of a variety of tellurophenes fused with electron-rich heteroarenes.

Scheme 3.2. Benzotellurophene synthesis from arylzinc reagents, alkynes and $TeCl_4$.



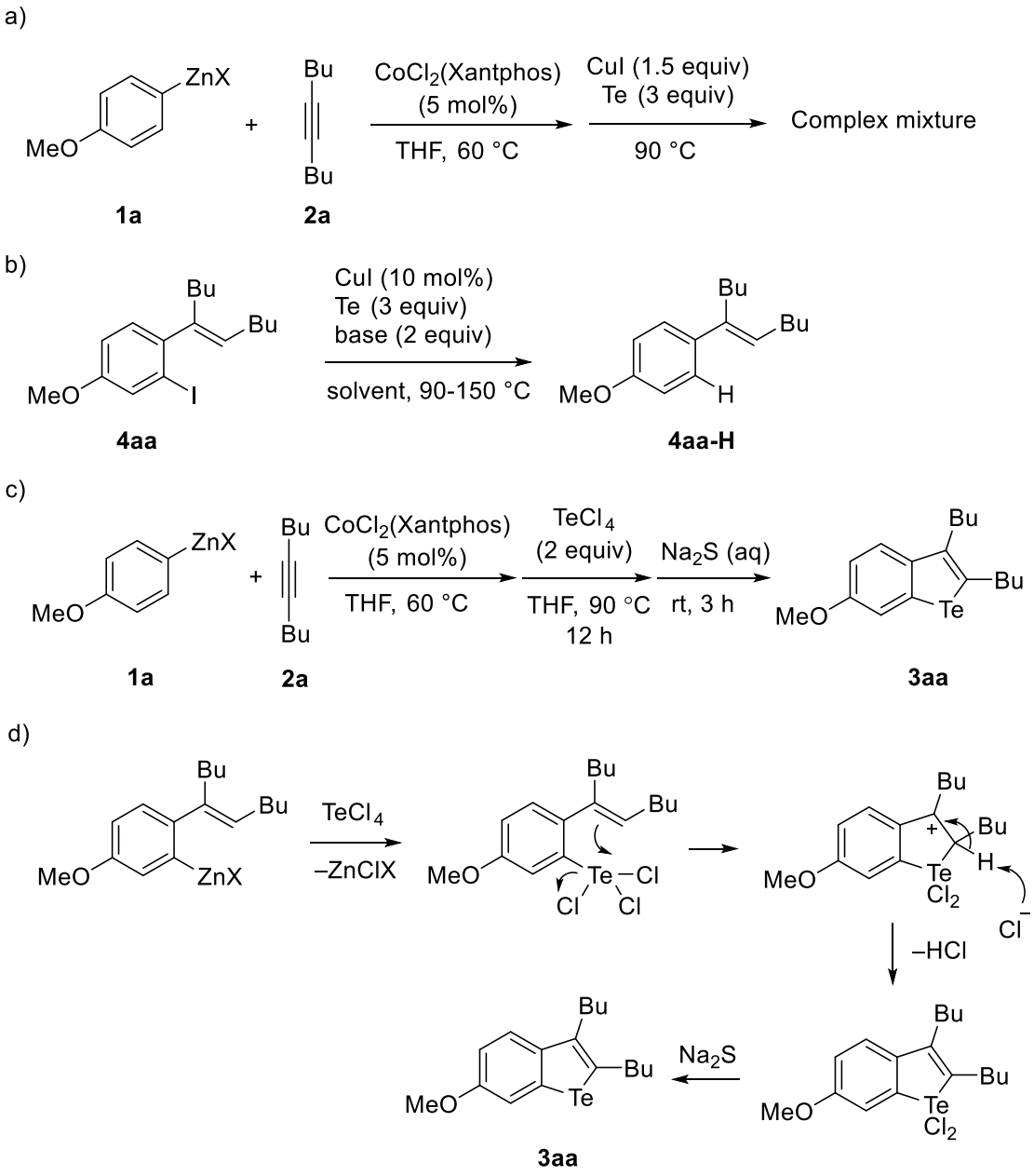
3.2 Results and discussion

We initially attempted benzotellurophene synthesis by trapping of *ortho*-alkenylarylzinc species generated by the [$CoCl_2$(Xantphos)]-catalyzed addition of 4-methoxyphenylzinc reagent **1a** to 5-decyne **2a** with elemental tellurium (Scheme 3.3a). However, regardless of an extensive screening of reaction conditions, we could not obtain the desired benzotellurophene. We next explored copper-catalyzed tellurative cyclization of *ortho*-alkenylaryl iodide **4aa** with elemental tellurium, as we demonstrated for the benzothiophene and benzoselenophene synthesis (Scheme 3.3b). Although the formation of the desired benzotellurophene was indicated by GCMS analysis, the reaction also produced a significant amount of the deiodination product **4aa-H**, which was inseparable from the desired product. The failure of these two approaches may be ascribed to the low electrophilicity and solubility of tellurium compared with sulfur and selenium.

Subsequently we turned our attention to $TeCl_4$ as an electrophile to intercept the *ortho*-alkenylarylzinc species, in light of the report of Sashida and coworkers on the use of $TeCl_4$ for the synthesis of tellurium heterocycles via tin-tellurium exchange.[13] To our delight, exposure of the *ortho*-alkenylarylzinc species generated from **1a** and **2a** to a THF

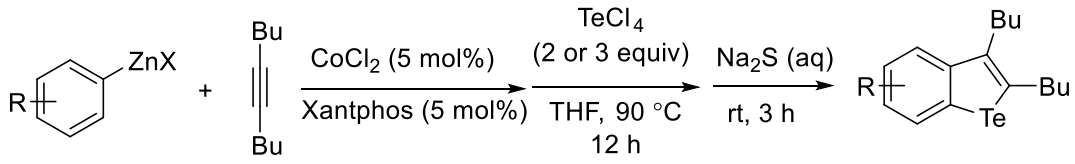
solution of $TeCl_4$ at 90 ℃ for 12 h, followed by reduction with sodium sulfide, afforded the desired benzotellurophene **3aa** in 58% yield (Scheme 3.3c). We consider that the tellurative cyclization of the *ortho*-alkenylarylzinc species proceeds via electrophilic trapping of the aryl–Zn bond with $TeCl_4$, intramolecular electrophilic attack of the Te(IV) center to the alkenyl group, and loss of HCl (Scheme 3.3d).

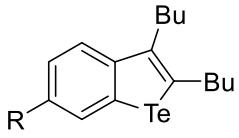
Scheme 3.3. Initial attempts on benzotellurophene synthesis.



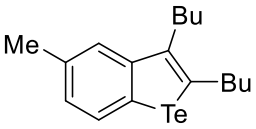
We then explored the scope and limitations of the present benzotellurophene synthesis. First, a variety of arylzinc reagents were subjected to the one-pot protocol using 5-decyne as the coupling partner (Scheme 3.4). Various *para*-substituted arylzinc reagents, including those bearing electron-neutral, electron-donating, and electron-withdrawing substituents furnished the corresponding benzotellurophenes **3aa**–**3la** in moderate to good yields. The hydroxy- and acetyl substituted derivatives **3ka** and **3la** could be synthesized in one-pot from arylzinc reagents bearing protected hydroxy and acetyl groups, respectively. *meta*-Tolylzinc reagent exclusively afforded 5-methylbenzotellurophene **3ma** due to regioselective 1,4-cobalt migration to the less hindered position. One the other hand, the reactions of 3,4-methylenedioxyphenyl and 3,4-difluorophenylzinc reagents led to 6,7-methylenedioxy- and 6,7-difluorobenzotellurophenes **3na** and **3pa**, respectively, due to oxygen- or fluorine-directed 1,4-cobalt migration. The naphtho[2,3-*b*]tellurophene (**3qa**), telluropheno[2,3-*b*]thiophene (**3ra**) and telluropheno[2,3-*b*]quinolone (**3sa**) could also be synthesized with exclusive regioselectivity, albeit in modest yields.

Scheme 3.4. Scope of different arylzinc reagents.[a]

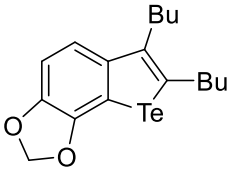




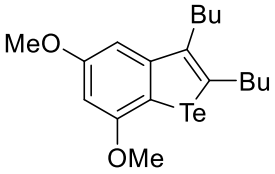
3aa (R = OMe), 58%
3ba (R = H), 62%
3ca (R = NMe_2), 54%
3da (R = Me), 55%,
3ea (R = Ph), 52%
3fa (R = F), 48%
3ga (R = $SiMe_3$), 52%
3ha (R = OTBS), 41%
3ia (R = OH), 47%[b]
3ja (R = CO_2Et), 47%
3ka (R = CF_3), 53%
3la (R = Ac), 50%[c]



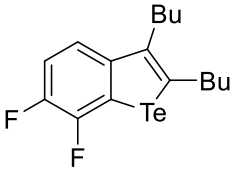
3ma, 51%



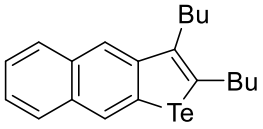
3na, 66%



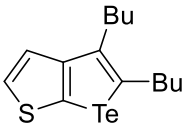
3oa, 46%



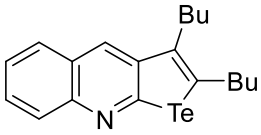
3pa, 55%



3qa, 38%



3ra, 34%



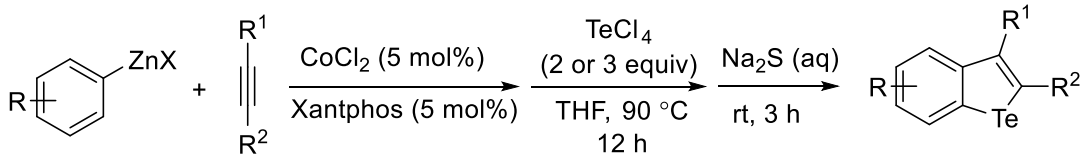
3sa, 46%

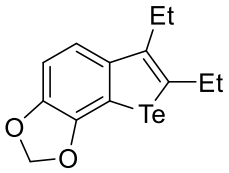
[a] The reactions were performed on a 0.5 mmol scale. See the experimental section for detailed reaction conditions. [b] The starting material was protected with a Boc group, which was removed during the reaction. [c] The acetyl moiety of the arylzinc reagent was protected in the form of *p*-anisidine imine.

Next, we explored the scope of alkynes for the present benzotellurophene synthesis (Scheme 3.5). As was the case with the benzothiophene and benzoselenophene synthesis, the reaction of 1-trimethylsilyl-1-propyne caused partial loss of the silyl group, which could be totally removed under basic conditions to give 3-substituted benzotellurophene (**3ac and 3bc**). Besides dialkylalkynes, the reactions using aryl(alkyl)alkynes also took place smoothly to afford a variety of 2-aryl-3-alkyl-

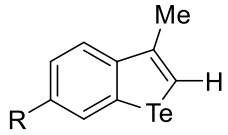
substituted benzotellurophenes. Both electron-donating (**3nf** and **3nh**) and electron-withdrawing (**3nk**-**3nm**) aryl groups were well tolerated as the substituents on the alkyne substrates. A sterically hindered alkyl(aryl)alkyne bearing a xylyl group also participated in this reaction to afford the desired product **3ni** in a reasonable yield. Thienyl- or naphthyl-substituted alkyne was also amenable to this reaction to produce **3nj** and **3nn** in moderate yields.

Scheme 3.5. Scope of different alkynes.[a]

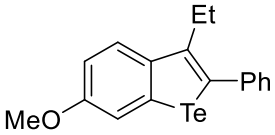




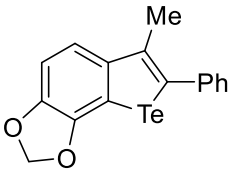
3nb, 60%



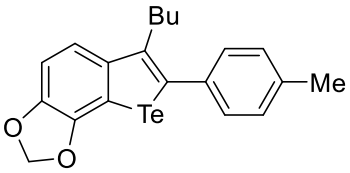
3ac (R = OMe), 53%[b]
3bc (R = H), 52%[b]



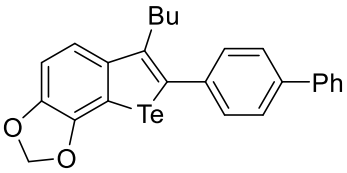
3ad, 50%



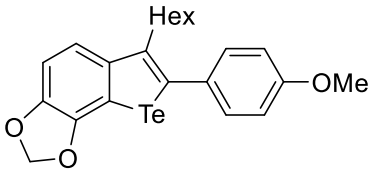
3ne, 56%



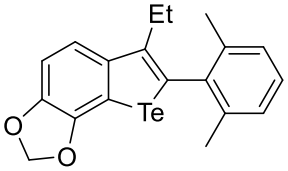
3nf, 47%



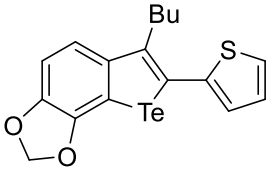
3ng, 58%



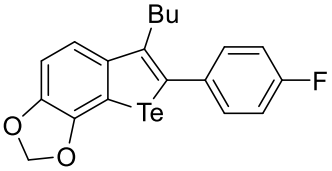
3nh, 46%



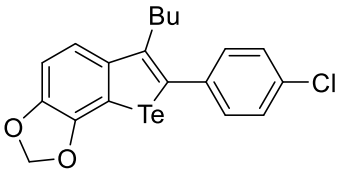
3ni, 40%



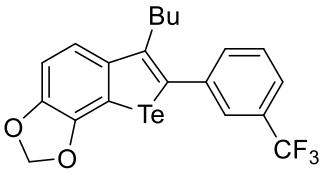
3nj, 38%



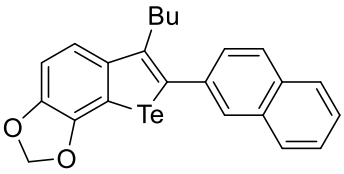
3nk, 46%



3nl, 40%



3nm, 52%

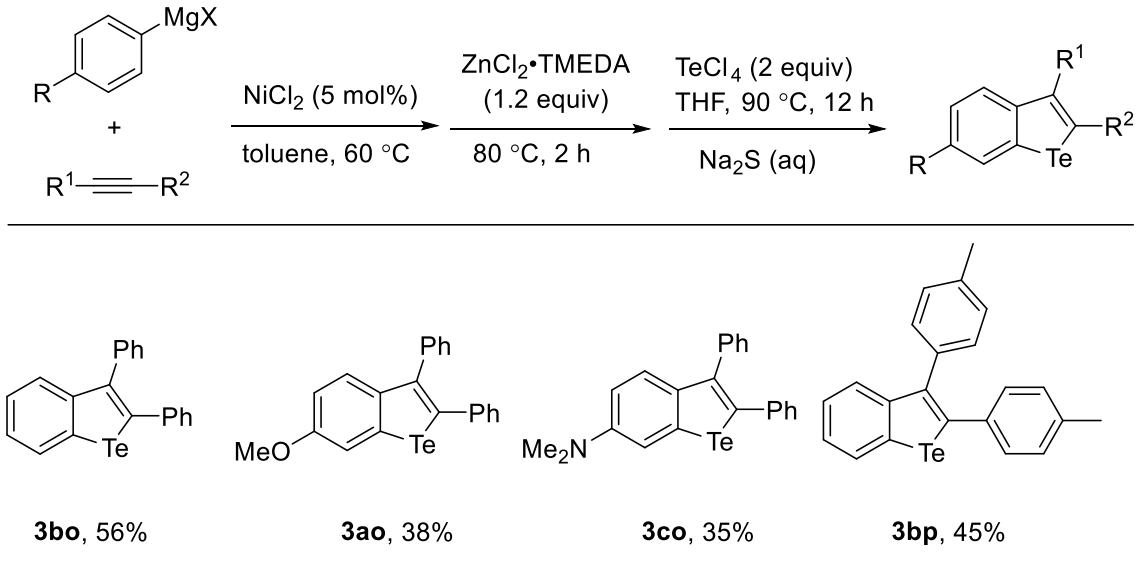


3nn, 41%

[a] The reaction was performed on a 0.5 mmol scale. See the experimental section for detailed reaction conditions. [b] The reaction was performed using 1-trimethylsilyl-1-propyne, and the $SiMe_3$ group was removed by treatment with KOH/MeOH.

Due to the intrinsic limitation of the migratory arylzincation, the above protocol is not applicable to diarylalkynes. We conjectured that this limitation would be compensated by utilizing *cis*-*β*-styrylmetal species, generated by transition metal-catalyzed arylmetalation of diarylalkyne, as an intermediate for the tellurative cyclization. Indeed, a sequential combination of the Ni-catalyzed phenylmagnesiation of diphenylacetylene,[14] transmetallation with $ZnCl_2$, and the tellurative cyclization protocol allowed preparation of 2,3-diphenylbenzotellurophene **3bo** in a moderate yield of 56% (Scheme 3.6). Note that transmetallation of the *cis*-*β*-styrylmagnesium to organozinc species was crucial for the success of the desired cyclization as the direct trapping of *cis*-*β*-styrylmagnesium- or lithium species with $TeCl_4$ always accompanied with side reactions. The applicability of this protocol to different aryl Grignard reagents and alkynes was briefly demonstrated by the synthesis of analogous compounds **3ao**, **3co**, and **3bp**, albeit in modest yields.

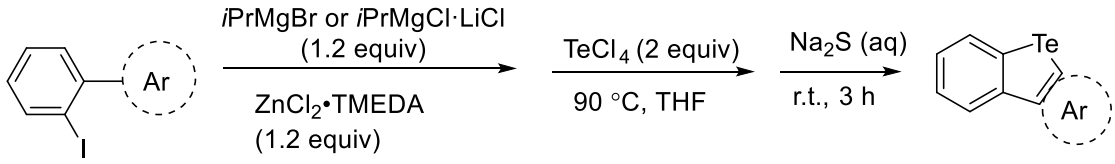
Scheme 3.6. Synthesis of 2,3-diarylbenzotellurophenes based on Ni-catalyzed arylmagnesiation of diarylalkynes. [a]

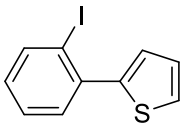
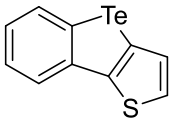
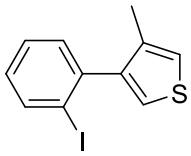
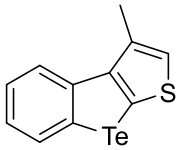
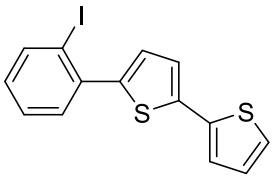
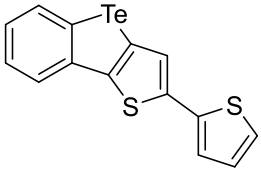
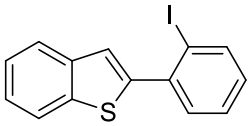
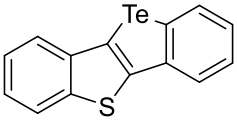
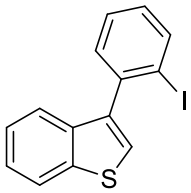
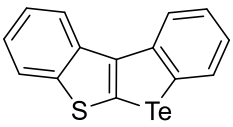
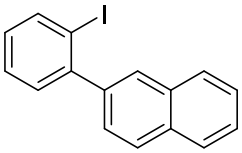
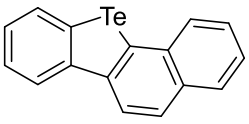


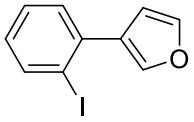
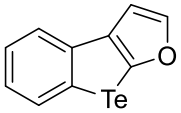
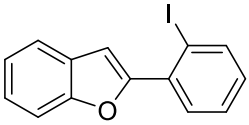
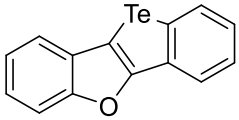
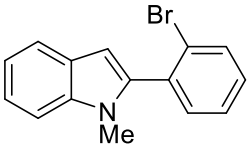
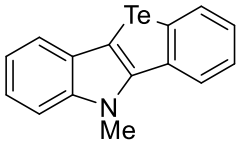
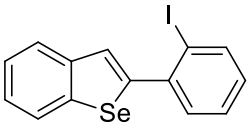
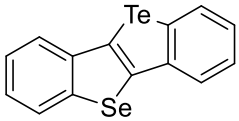
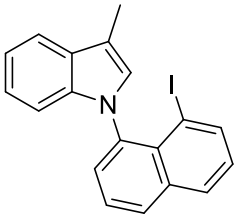
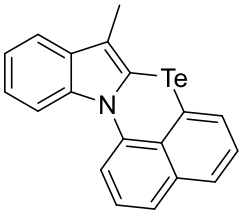
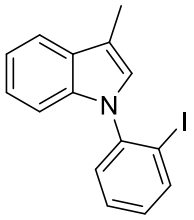
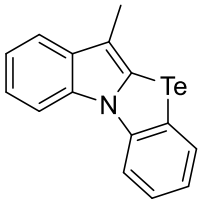
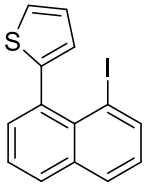
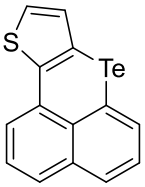
[a] The reaction was performed on a 0.5 mmol scale. See the experimental section for detailed reaction conditions.

We conceived that the application of the present tellurative cyclization to arylzinc species bearing electron-rich (hetero)aryl groups on the ortho position would allow for the synthesis of (hetero)aryl-fused benzotellurophenes. Indeed, a variety of 1-iodo-2-heteroarylbenzenes and related compounds could be converted to novel tellurium-bridged products through iodine–magnesium exchange, transmetallation to zinc chloride, and tellurative cyclization (Scheme 3.7). The tellurative cyclization proved feasible to the 2- and 3-positions of thiophene (**5**–**7**), the 2- and 3-positions of benzothiophene (**8** and **9**), the 2-position of naphthalene (**10**), the 2-position of furan (**11**), and the 3-position of benzofuran, indole and benzoselenophene (**12**–**14**), affording the corresponding fused benzotellurophenes in moderate to good yields. Furthermore, tellurium-bridged heterobiaryls other than tellurophene derivatives could also be synthesized through tellurative cyclization onto the 2-position of indole (**15** and **16**) or the 3-position of thiophene (**17**).

Scheme 3.7. Synthesis of (hetero)aryl-fused benzotellurophenes and related compounds.[a]



Starting Material	Product		Yield
		**5**	66%
		**6**	51%
		**7**	47%
		**8**	54%
		**9**	52%
		**10**	67%

		**11**	47%
		**12**	53%
		**13**	54%[b]
		**14**	50%
		**15**	58%
		**16**	55%
		**17**	62%

[a] The reaction was performed on a 0.3 mmol scale. See the experimental section for detailed reaction conditions. [b] *n*BuLi was used instead of *i*PrMgBr.

3.3 Conclusion

In summary, we have developed a novel synthetic method for the one-pot synthesis of benzotellurophenes based on the sequential combination of cobalt-catalyzed migratory arylzincation of internal alkynes, electrophilic trapping with tellurium tetrachloride and intramolecular cyclization. This protocol allows rapid construction of benzotellurophenes bearing various substituents on the 2- and 3-positions as well as on the benzene ring moiety. The scope of this one-pot protocol was further extended by employing the conventional type of arylmetalation reaction instead of the migratory arylzincation. Furthermore, the tellurative cyclization also allowed facile synthesis of tellurium-bridged heterobiaryls from readily accessible 2-iodoheterobiaryls. Further investigations into the properties and applications of the thus-synthesized tellurium compounds are currently underway.

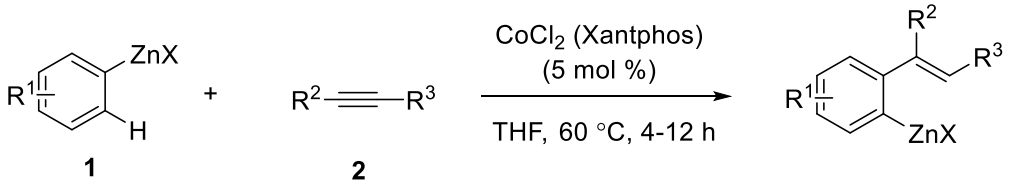
3.4 Experimental section

Preparation of starting materials

1-Butyl-4-(*p*-tolylethynyl) benzene, [15] 4-((4-butylphenyl)ethynyl)-1,1'-biphenyl, [16] 1-methoxy-4-(oct-1-yn-1-yl)benzene, [17] 2-(but-1-yn-1-yl)-1,3-dimethylbenzene, [18] 2-(hex-1-yn-1-yl)thiophene, [19] 1-fluoro-4-(hex-1-yn-1-yl)benzene, [20] 1-chloro-4-(hex-1-yn-1-yl)benzene, [21] 1-(hex-1-yn-1-yl)-3-(trifluoromethyl)benzene, [22] 2-(hex-1-yn-1-yl)naphthalene, [23] 2-(2-iodophenyl)thiophene, [24] 2-(2-iodophenyl)naphthalene, [24] 2-(2-bromophenyl)-1-methyl-1*H*-indole, [25] 1-(2-iodophenyl)-3-methyl-1*H*-indole [26] were prepared according the literature procedures and their ^{1}H and ^{13}C NMR spectra showed good agreement with the literature data.

Procedures for the preparation of arylzinc reagent and its addition to alkyne

An arylzinc reagent was prepared either by transmetalation between $ZnCl_2$•TMEDA and the corresponding aryl Grignard reagent (approx. 1 M, type **I**/**III** reagents) or by Co–Xantphos-catalyzed insertion of Zn•LiCl into the corresponding aryl bromide (type **II** reagent).[27] The resulting arylzinc reagent was subjected to the reaction with an alkyne under Co–Xantphos catalysis as described previously, thus furnishing an *ortho*-alkenylarylzinc reagent.[18] Below are brief descriptions of three different procedures used in the present study.



1 (Type **I-III**) **2**

Type **I**: $ZnCl_2$•TMEDA + ArMgBr
Type **II**: ArBr + Zn•LiCl, 5 mol % $CoCl_2$ (Xantphos)
Type **III**: $ZnCl_2$•TMEDA + 2 ArMgBr

Type I Reagent: In a 10 mL Schlenk tube was placed $ZnCl_2$•TMEDA (138.9 mg, 0.55 mmol). The Schlenk tube was submerged in an ice bath for 15 min, followed by dropwise addition of a THF solution of an aryl Grignard reagent (0.55 mmol). The resulting mixture was stirred for 1 h at 0 ℃ and then allowed to warm to room temperature. To the arylzinc reagent was added Xantphos (14.5 mg, 0.025 mmol), $CoCl_2$ (3.2 mg, 0.025 mmol) followed by stirring for 5 min and addition of an alkyne (0.5 mmol). The resulting mixture was stirred at 60 ℃, monitored by TLC until starting materials were consumed, and then allowed to cool to room temperature.

Type II Reagent: Anhydrous LiCl (42.4 mg, 1 mmol) was placed in a 10 mL Schlenk tube, dried under vacuum (1 mbar) at 150 ℃ for 20 min, and cooled down to room temperature under N_2. To the Schlenk tube was added zinc powder (98.1 mg, 1.5 mmol),

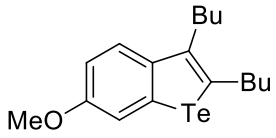
and the heterogeneous mixture of Zn and LiCl was dried under vacuum (1 mbar) at 150 ℃ for 15 min. While cooling to room temperature, the reaction tube was evacuated and backfilled with N_2 for three times. The mixture was suspended with THF (1 mL), followed by the activation of Zn with $BrCH_2CH_2Br$ (5 μL, 0.05 mmol) and Me_3SiCl (1.5 μL, 0.01 mmol) and stirring for 5 min. Then Xantphos (28.9 mg, 0.05 mmol) and $CoCl_2$ (6.5 mg, 0.05 mmol) were added sequentially. After stirring for additional 5 min, an aryl halide (1 mmol) was added in one portion. The reaction was stirred at room temperature. After complete conversion of the starting material, alkyne (0.50 mmol) was added to the arylzinc reagent. The resulting solution was stirred at 60 ℃, monitored by TLC until starting materials were consumed, and then allowed to cool to room temperature.

Type III Reagent: In a 10 mL Schlenk tube was placed $ZnCl_2$•TMEDA (138.9 mg, 0.55 mmol). The Schlenk tube was submerged in an ice bath for 15 min, followed by dropwise addition of a THF solution of an aryl Grignard reagent (1.1 mmol). The resulting mixture was stirred for 1 h at 0 ℃ and then allowed to room temperature. To the arylzinc reagent was added Xantphos (14.5 mg, 0.025 mmol), $CoCl_2$ (3.2 mg, 0.025 mmol) followed by stirring for 5 min and addition of an alkyne (0.5 mmol). The resulting mixture was stirred at 60 ℃, monitored by TLC until starting materials were consumed, and then allowed to cool to room temperature.

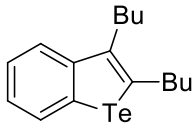
Synthesis of benzotellurophene derivatives

General procedure: To a THF solution (0.2 M) of $TeCl_4$ (269.4 mg, 1 mmol for Type **I** reagent and 403.5 mg, 1.5 mmol for Type **II** and **III** reagent) was added the prepared *ortho*-alkenyl arylzinc reagent at r.t. The resulting solution was stirred at 90 ℃ for 12 h followed by cooling. An saturated aqueous solution of Na_2S (1 mL) was added at 0 ℃,

and the mixture was stirred at room temperature for 3 h; The reaction mixture was diluted with ethyl acetate (5 mL) and filtered through a pad of silica gel with additional ethyl acetate (15 mL) as the eluent. The filtrate was washed with water (10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product.

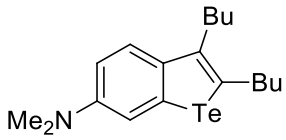


2,3-Dibutyl-6-methoxybenzo[*b*]tellurophene (3aa): Type **I** arylzinc reagent was used; Yellow oil (58% yield, eluent = hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.8 Hz, 1H), 7.45 (d, *J* = 2.4 Hz, 1H), 7.00 (dd, *J* = 8.8, 2.8 Hz, 1H), 3.86 (s, 3H), 2.91 (t, *J* = 7.6 Hz, 2H), 2.74 (t, *J* = 7.6 Hz, 2H), 1.72 – 1.63 (m, 2H), 1.61 – 1.56 (m, 2H), 1.55 – 1.44 (m, 4H), 1.02 (t, *J* = 7.2 Hz, 3H), 1.01 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.5, 142.7, 140.9, 136.9, 131.7, 126.3, 115.9, 113.4, 55.5, 36.8, 33.5, 32.0, 29.6, 23.0, 22.6, 14.1 (two signals overlapped); HRMS (ESI) Calcd for $C_{17}H_{25}OTe$ $[M + H]^+$ 375.0968, found 375.0966.

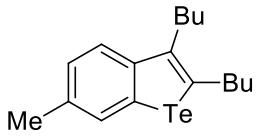


2,3-Dibutylbenzo[*b*]tellurophene (3ba): Type **I** arylzinc reagent was used; Yellow oil (62% yield, eluent = hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 8.0, 0.4 Hz, 1H), 7.61 (dd, *J* = 8.0, 0.4 Hz, 1H), 7.41 – 7.37 (m, 1H), 7.16 – 7.12 (m, 1H), 2.93 (t, *J* = 7.6 Hz, 2H), 2.77 (t, *J* = 7.6 Hz, 2H), 1.71 – 1.67 (m, 2H), 1.61 – 1.56 (m, 2H), 1.54 – 1.45 (m, 4H), 1.01 (t, *J* = 7.2 Hz, 3H), 1.00 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz,

$CDCl_3$): δ 148.8, 141.7, 140.6, 132.2, 130.8, 125.8, 125.0, 123.8, 36.9, 33.7, 31.9, 29.4, 23.0, 22.6, 14.1 (two signals overlapped); HRMS (ESI) Calcd for $C_{16}H_{23}Te$ $[M + H]^+$ 345.0862, found 345.0853.

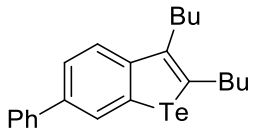


2,3-Dibutyl-*N*,*N*-dimethylbenzo[*b*]tellurophen-6-amine (3ca): Type **I** arylzinc reagent was used; Brown oil (54% yield, eluent = hexane/EtOAc (50:1)); ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.8 Hz, 1H), 7.27 (d, *J* = 2.4 Hz, 1H), 6.84 (dd, *J* = 8.8, 2.4 Hz, 1H), 2.98 (s, 6H), 2.85 (t, *J* = 7.6 Hz, 2H), 2.68 (t, *J* = 7.6 Hz, 2H), 1.68 – 1.60 (m, 2H), 1.58 – 1.53 (m, 2H), 1.49 – 1.40 (m, 4H), 0.98 (t, *J* = 7.2 Hz, 3H), 0.97 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.8, 141.0, 139.5, 134.2, 132.0, 125.9, 115.4, 111.8, 41.0, 36.8, 33.4, 32.0, 29.4, 23.0, 22.6, 14.1 (two signals overlapped); HRMS (ESI) Calcd for $C_{18}H_{28}NTe$ $[M + H]^+$ 388.1284, found 388.1290.

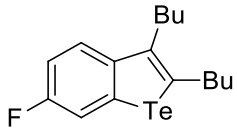


2,3-Dibutyl-6-methylbenzo[*b*]tellurophene (3da): Type **I** arylzinc reagent was used; Yellow oil (55% yield, eluent = hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.18 (dd, *J* = 8.4, 1.2 Hz, 1H), 2.90 (t, *J* = 7.6 Hz, 2H), 2.73 (t, *J* = 7.6 Hz, 2H), 2.40 (s, 3H), 1.71 – 1.63 (m, 2H), 1.60 – 1.56 (m, 2H), 1.54 – 1.43 (m, 4H), 1.00 (t, *J* = 7.2 Hz, 3H), 0.99 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.5, 141.4, 138.9, 133.6, 132.4, 130.9, 126.4, 125.4, 41.0, 36.8, 33.6, 31.9, 29.4, 23.0, 22.6, 14.1 (two

signals overlapped); HRMS (ESI) Calcd for $C_{17}H_{25}Te$ $[M + H]^+$ 359.1019, found 359.1014.

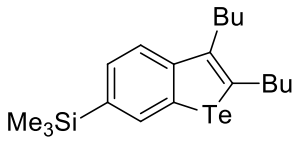


2,3-Dibutyl-6-phenylbenzo[*b*]tellurophene (3ea): Type **I** arylzinc reagent was used; Yellow oil (52% yield, eluent = hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 1.6 Hz, 1H), 7.69 – 7.61 (m, 4H), 7.49 – 7.45 (m, 2H), 7.39 – 7.35 (m, 1H), 2.94 (t, *J* = 7.6 Hz, 2H), 2.79 (t, *J* = 7.6 Hz, 2H), 1.74 – 1.66 (m, 2H), 1.64 – 1.57 (m, 2H), 1.55 – 1.47 (m, 4H), 1.02 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.0, 141.5, 141.1, 141.0, 136.8, 131.5, 130.6, 128.8, 127.2, 127.1, 125.9, 124.4, 36.9, 33.8, 31.9, 29.5, 23.0, 22.6, 14.1 (two signals overlapped); HRMS (ESI) Calcd for $C_{22}H_{27}Te$ $[M + H]^+$ 421.1175, found 421.1176.

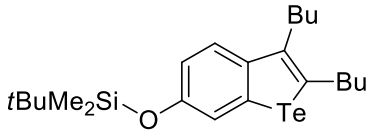


2,3-Dibutyl-6-fluorobenzo[*b*]tellurophene (3fa): Type **I** arylzinc reagent was used; Yellow oil (48% yield, eluent = hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 8.0, 2.4 Hz, 1H), 7.50 – 7.47 (m, 1H), 7.12 – 7.07 (m, 1H), 2.88 (t, *J* = 7.6 Hz, 2H), 2.71 (t, *J* = 7.6 Hz, 2H), 1.69 – 1.61 (m, 2H), 1.57 – 1.53 (m, 2H), 1.51 – 1.42 (m, 4H), 0.98 (t, *J* = 7.2 Hz, 3H), 0.97 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6 (d, $^1J_{C\text{-}F}$ = 245.4 Hz), 145.2 (d, $^4J_{C\text{-}F}$ = 2.1 Hz), 140.7, 139.6, 131.4 (d, $^3J_{C\text{-}F}$ = 7.1 Hz), 126.5 (d, $^3J_{C\text{-}F}$ = 8.0 Hz), 118.3 (d, $^2J_{C\text{-}F}$ = 22.9 Hz), 113.2 (d, $^2J_{C\text{-}F}$ = 22.8 Hz), 36.7, 33.6, 31.8, 29.7,

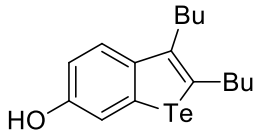
23.0, 22.6, 14.0 (two signals overlapped); HRMS (ESI) Calcd for $C_{16}H_{22}TeF$ $[M + H]^+$ 363.0768, found 363.0765.



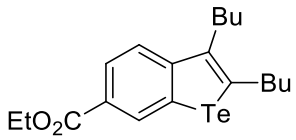
(2,3-Dibutylbenzo[*b*]tellurophen-6-yl)trimethylsilane (3ga): Type **II** arylzinc reagent was used; Yellow oil (52% yield, eluent = hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.48 (dd, *J* = 7.6, 1.2 Hz, 1H), 2.89 (t, *J* = 7.6 Hz, 2H), 2.73 (t, *J* = 7.6 Hz, 2H), 1.67 – 1.61 (m, 2H), 1.57 – 1.53 (m, 2H), 1.51 – 1.41 (m, 4H), 0.97 (t, *J* = 7.2 Hz, 3H), 0.96 (t, *J* = 7.2 Hz, 3H), 0.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.2, 141.8, 141.4, 137.1, 135.6, 131.1, 129.6, 125.3, 36.8, 33.7, 31.8, 29.2, 23.0, 22.5, 14.0 (two signals overlapped), -1.0; HRMS (ESI) Calcd for $C_{19}H_{31}TeSi$ $[M + H]^+$ 417.1257, found 417.1257.



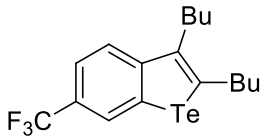
***tert*-Butyl((2,3-dibutylbenzo[*b*]tellurophen-6-yl)oxy)dimethylsilane (3ha):** Type **I** arylzinc reagent was used; Yellow oil (41% yield, eluent = hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.8 Hz, 1H), 7.32 (d, *J* = 2.4 Hz, 1H), 6.86 (dd, *J* = 8.8, 2.4 Hz, 1H), 2.84 (t, *J* = 7.6 Hz, 2H), 2.67 (t, *J* = 7.6 Hz, 2H), 1.66 – 1.58 (m, 2H), 1.55 – 1.51 (m, 2H), 1.49 – 1.40 (m, 4H), 1.00 (s, 9H), 0.96 (t, *J* = 7.2 Hz, 3H), 0.95 (t, *J* = 7.2 Hz, 3H), 0.21 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.3, 143.0, 140.9, 137.0, 131.1, 126.1, 123.0, 118.3, 36.7, 33.5, 31.8, 29.6, 25.7, 23.0, 22.6, 18.2, 14.0 (two signals overlapped), -4.4; HRMS (ESI) Calcd for $C_{22}H_{37}OSiTe$ $[M + H]^+$ 475.1676, found 475.1678.



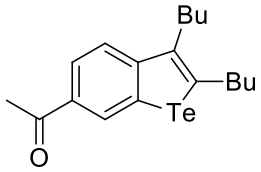
2,3-Dibutylbenzo[*b*]tellurophen-6-ol (3ia): Type II arylzinc reagent prepared from 4-bromophenyl *tert*-butyl carbonate was used. The Boc group was removed during the reaction. Brown oil (47% yield, eluent = hexane/EtOAc (30:1)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.8 Hz, 1H), 7.31 (d, *J* = 2.4 Hz, 1H), 6.87 (dd, *J* = 8.8, 2.4 Hz, 1H), 4.86 (s, 1H), 2.84 (t, *J* = 7.6 Hz, 2H), 2.67 (t, *J* = 7.6 Hz, 2H), 1.68 – 1.58 (m, 2H), 1.55 – 1.51 (m, 2H), 1.49 – 1.40 (m, 4H), 0.96 (t, *J* = 7.2 Hz, 3H), 0.95 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.2, 142.8, 140.8, 136.8, 131.6, 126.4, 118.1, 113.8, 36.7, 33.4, 31.9, 29.5, 23.0, 22.5, 14.0 (two signals overlapped); HRMS (ESI) Calcd for $C_{16}H_{23}OTe$ $[M + H]^+$ 361.0811, found 361.0812.



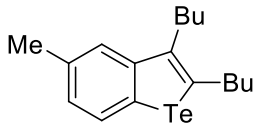
Ethyl 2,3-dibutylbenzo[*b*]tellurophene-6-carboxylate (3ja): Type **II** arylzinc reagent was used; Yellow oil (47% yield, eluent = hexane/EtOAc (50:1)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 1.6 Hz, 1H), 8.02 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 4.40 (q, *J* = 7.2 Hz, 2H), 2.92 (t, *J* = 7.6 Hz, 2H), 2.75 (t, *J* = 7.6 Hz, 2H), 1.71 – 1.63 (m, 2H), 1.61 – 1.45 (m, 6H), 1.41 (t, *J* = 7.2 Hz, 3H), 0.98 (t, *J* = 7.2 Hz, 3H), 0.96 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 152.3, 146.1, 141.7, 133.7, 130.5, 129.5, 126.1, 125.3, 60.9, 36.8, 34.0, 31.8, 29.5, 22.9, 22.6, 14.4, 14.0 (two signals overlapped); HRMS (ESI) Calcd for $C_{19}H_{27}O_2Te$ $[M + H]^+$ 417.1073, found 417.1074.



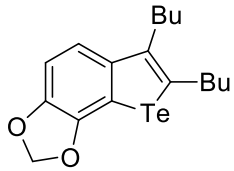
2,3-Dibutyl-6-(trifluoromethyl)benzo[*b*]tellurophene (3ka): Type **II** arylzinc reagent was used; Yellow oil (53% yield, eluent = hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 2.92 (t, *J* = 7.6 Hz, 2H), 2.76 (t, *J* = 7.6 Hz, 2H), 1.69 – 1.63 (m, 2H), 1.55 – 1.41 (m, 6H), 0.98 (t, *J* = 7.2 Hz, 3H), 0.97 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.5, 145.3, 141.3, 130.9, 129.0 (q, $J_{C\text{-}F}$ = 4.0 Hz), 127.6, 127.2 (q, $J_{C\text{-}F}$ = 270.2 Hz), 125.7, 121.8 (d, $J_{C\text{-}F}$ = 3.6 Hz), 36.8, 33.8, 31.8, 29.4, 22.9, 22.6, 14.0 (two signals overlapped); HRMS (ESI) Calcd for $C_{17}H_{22}F_3Te$ $[M + H]^+$ 413.0736, found 413.0754.



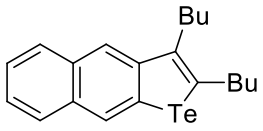
1-(2,3-Dibutylbenzo[*b*]tellurophen-6-yl)ethanone (3la): Type **II** arylzinc reagent was used; Brown oil (50% yield, eluent = hexane/EtOAc (50:1)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 1.6 Hz, 1H), 7.94 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.61 (d, *J* = 8.4Hz, 1H), 2.92 (t, *J* = 7.6 Hz, 2H), 2.76 (t, *J* = 7.6 Hz, 2H), 2.63 (s, 3H), 1.71 – 1.63 (m, 2H), 1.56 – 1.41 (m, 6H), 0.98 (t, *J* = 7.2 Hz, 3H), 0.96 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.7, 152.5, 147.0, 141.7, 132.7, 132.2, 130.9, 125.5, 125.1, 36.8, 34.0, 31.8, 29.4, 26.7, 22.9, 22.6, 14.0 (two signals overlapped); HRMS (ESI) Calcd for $C_{18}H_{25}OTe$ $[M + H]^+$ 387.0968, found 387.0967.



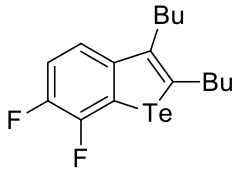
2,3-Dibutyl-5-methylbenzo[*b*]tellurophene (3ma): Type **I** arylzinc reagent was used; Brown oil (51% yield, eluent = hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.6 Hz, 1H), 7.43 (s, 1H), 7.00 (dd, *J* = 7.6, 1.2 Hz, 1H), 2.91 (t, *J* = 7.6 Hz, 2H), 2.75 (t, *J* = 7.6 Hz, 2H), 2.49 (s, 1H), 1.72 – 1.64 (m, 2H), 1.61 – 1.55 (m, 2H), 1.54 – 1.44 (m, 4H), 1.00 (t, *J* = 7.2 Hz, 3H), 0.99 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.1, 141.5, 140.6, 134.6, 131.9, 126.7, 126.3, 125.4, 36.8, 33.7, 31.9, 29.4, 23.0, 22.6, 21.6, 14.1 (two signals overlapped); HRMS (ESI) Calcd for $C_{17}H_{25}Te$ $[M + H]^+$ 359.1019, found 359.1026.



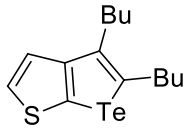
6,7-Dibutyltelluropheno[2',3':3,4]benzo[1,2-*d*][1,3]dioxole (3na): Type **I** arylzinc reagent was used; Yellow oil (66% yield, eluent = hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.0 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.02 (s, 2H) 2.84 (t, *J* = 7.6 Hz, 2H), 2.68 (t, *J* = 7.6 Hz, 2H), 1.67 – 1.59 (m, 2H), 1.55 – 1.50 (m, 2H), 1.48 – 1.40 (m, 4H), 0.97 (t, *J* = 7.2 Hz, 3H), 0.96 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.5, 145.2, 142.3, 141.3, 137.0, 119.1, 107.1, 106.6, 100.9, 36.7, 33.5, 31.9, 29.8, 23.0, 22.6, 14.1 (two signals overlapped); HRMS (ESI) Calcd for $C_{17}H_{23}O_2Te$ $[M + H]^+$ 389.0760, found 389.0768.



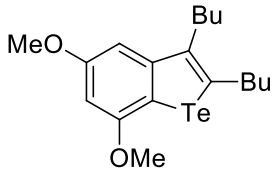
2,3-Dibutylnaphtho[2,3-*b*]tellurophene (3oa): Type **I** arylzinc reagent was used; Orange oil (38% yield, eluent = hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.04 (s, 1H), 7.95 – 7.93 (m, 1H), 7.79 – 7.76 (m, 1H), 7.48 – 7.45 (m, 2H), 2.92 (t, *J* = 7.6 Hz, 2H), 2.85 (t, *J* = 7.6 Hz, 2H), 1.71 – 1.61 (m, 4H), 1.56 – 1.46 (m, 4H), 1.01 (t, *J* = 7.2 Hz, 3H), 1.00 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.8, 140.9, 139.3, 131.4, 131.2, 130.9, 128.4, 126.8, 126.4, 125.3, 125.2, 123.9, 36.4, 34.0, 31.8, 29.4, 23.0, 22.6, 14.1 (two signals overlapped); HRMS (ESI) Calcd for $C_{20}H_{25}Te$ $[M + H]^+$ 395.1019, found 395.1014.



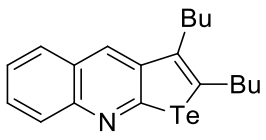
2,3-Dibutyl-6,7-difluorobenzo[*b*]tellurophene (3pa): Type **II** arylzinc reagent was used; Orange oil (55% yield, eluent = hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.27 (m, 1H), 7.25 – 7.18 (m, 1H), 2.90 (t, *J* = 7.6 Hz, 2H), 2.72 (t, *J* = 7.6 Hz, 2H), 1.71 – 1.64 (m, 2H), 1.60 – 1.41 (m, 6H), 1.01 (t, *J* = 7.2 Hz, 3H), 1.00 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.1 (dd, $^{1}J_{C\text{-}F}$ = 240.5 Hz, $^{2}J_{C\text{-}F}$ = 13.7 Hz), 146.7 (dd, $^{3}J_{C\text{-}F}$ = 5.5, 2.6 Hz), 146.0 (dd, $^{1}J_{C\text{-}F}$ = 246.6 Hz, $^{2}J_{C\text{-}F}$ = 13.9 Hz), 141.0, 140.8 (d, $^{4}J_{C\text{-}F}$ = 2.4 Hz), 121.3 (dd, $^{3}J_{C\text{-}F}$ = 6.0 Hz, $^{4}J_{C\text{-}F}$ = 2.9 Hz), 117.9 (d, $^{2}J_{C\text{-}F}$ = 25.7 Hz), 115.5 (d, $^{2}J_{C\text{-}F}$ = 18.9 Hz), 36.7, 33.5, 31.9, 29.8, 22.9, 22.6, 14.0 (two signals overlapped); HRMS (ESI) Calcd for $C_{16}H_{21}TeF_2$ $[M + H]^+$ 381.0674, found 381.0669.



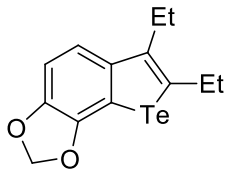
4,5-Dibutyltelluropheno[2,3-*b*]thiophene (3qa): Type **II** arylzinc reagent was used; Brown oil (34% yield, eluent = hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 4.8 Hz, 1H), 7.19 (d, *J* = 4.8 Hz, 1H), 2.87 (t, *J* = 7.6 Hz, 2H), 2.71 (t, *J* = 7.7 Hz, 2H), 1.66 – 1.53 (m, 4H), 1.51 – 1.37 (m, 4H), 0.98 (t, *J* = 7.2 Hz, 3H), 0.96 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.4, 142.5, 137.9, 129.5, 123.9, 115.7, 37.0, 33.3, 32.2, 30.6, 22.8, 22.5, 14.0 (two signals overlapped); HRMS (ESI) Calcd for $C_{14}H_{21}STe$ $[M + H]^+$ 351.0426, found 351.0421.



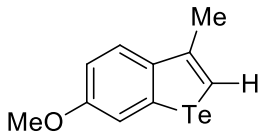
2,3-Dibutyl-5,7-dimethoxybenzo[*b*]tellurophene (3ra): Type **I** arylzinc reagent was used; Yellow oil (46% yield, eluent = hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.79 (d, *J* = 1.6 Hz, 1H), 6.33 (d, *J* = 2.0 Hz, 1H), 3.91 (s, 3H), 3.88 (s, 3H), 2.85 (t, *J* = 7.6 Hz, 2H), 2.68 (t, *J* = 7.6 Hz, 2H), 1.68 – 1.59 (m, 2H), 1.55 – 1.51 (m, 2H), 1.50 – 1.38 (m, 4H), 0.97 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.5, 160.4, 149.9, 142.0, 141.4, 109.7, 102.5, 94.1, 55.8, 55.7, 36.8, 33.7, 31.8, 29.6, 22.9, 22.6, 14.0 (two signals overlapped); HRMS (ESI) Calcd for $C_{18}H_{27}O_2Te$ $[M + H]^+$ 405.1073, found 405.1079.



2,3-Dibutyltelluropheno[2,3-*b*]quinolone (3sa): Type **II** arylzinc reagent was used; Orange oil (46% yield, eluent = hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 8.04 (m, 2H), 7.87 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.70 – 7.66 (m, 1H), 7.52 – 7.48 (m, 1H), 2.92 (t, *J* = 7.6 Hz, 2H), 2.80 (t, *J* = 7.6 Hz, 2H), 1.72 – 1.65 (m, 2H), 1.62 – 1.54 (m, 2H), 1.51 – 1.42 (m, 4H), 0.98 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.7, 146.3, 143.3, 142.0, 137.6, 129.8, 128.7, 128.4, 127.9, 126.1, 125.5, 36.3, 34.1, 31.8, 28.7, 22.9, 22.6, 14.1, 14.0; HRMS (ESI) Calcd for $C_{19}H_{24}NTe$ $[M + H]^+$ 396.0971, found 396.0973.

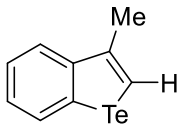


6,7-Diethyltelluropheno[2',3':3,4]benzo[1,2-*d*][1,3]dioxole (3nb): Type **I** arylzinc reagent was used; Yellow oil (60% yield, eluent = hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.4 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.04 (s, 2H), 2.88 (q, *J* = 7.6 Hz, 2H), 2.72 (q, *J* = 7.6 Hz, 2H), 1.32 (t, *J* = 7.6 Hz, 3H), 1.19 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.6, 144.8, 142.3 (2C), 138.3, 119.0, 107.2, 106.6, 100.9, 26.9, 23.1, 18.6, 14.2; HRMS (ESI) Calcd for $C_{13}H_{15}O_2Te$ $[M + H]^+$ 333.0134, found 333.0135.

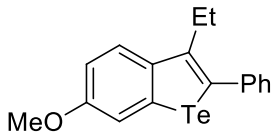


6-Methoxy-3-methylbenzo[*b*]tellurophene (3ac): Type **I** arylzinc reagent was used; Light yellow gum (53% yield, eluent = hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.55 (d, *J* = 8.8 Hz, 1H), 7.48 (s, 1H), 7.02 (d, *J* = 8.8 Hz, 1H), 3.87 (s, 3H), 2.37 (s,

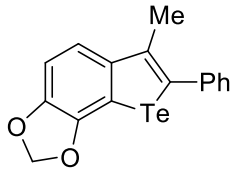
3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157., 142.4, 141.3, 133.5, 126.7, 115.9, 113.6, 111.1, 55.6, 19.9; HRMS (ESI) Calcd for $C_{10}H_{11}OTe$ $[M + H]^+$ 276.9872, found 276.9870.



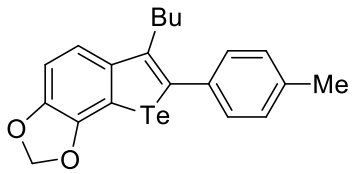
3-Methylbenzo[*b*]tellurophene (3bc): Type **I** arylzinc reagent was used; Light yellow gum (53% yield, eluent = hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.97 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.50 – 7.39 (m, 1H), 7.26 – 7.12 (m, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.3, 143.0, 132.5, 126.3, 125.0, 124.5, 114.7, 19.8 (one carbon missing due to overlap).



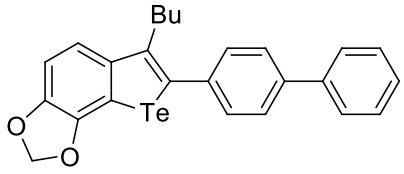
3-Ethyl-6-methoxy-2-phenylbenzo[*b*]tellurophene (3ad): Type **III** arylzinc reagent was used; Yellow solid (50% yield, eluent = hexane); M.p. = 86-87 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.8 Hz, 1H), 7.46 – 7.43 (m, 3H), 7.41 – 7.37 (m, 2H), 7.34 – 7.29 (m, 1H), 7.03 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.88 (s, 3H), 2.73 (q, *J* = 7.6 Hz, 2H), 1.24 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.1, 143.7, 141.8, 140.3, 134.0, 131.7, 129.4, 128.4, 127.4, 127.1, 115.7, 113.8, 55.6, 23.2, 15.1; HRMS (ESI) Calcd for $C_{17}H_{17}OTe$ $[M + H]^+$ 367.0342, found 367.0347.



6-Methyl-7-phenyltelluropheno[2',3':3,4]benzo[1,2-*d*][1,3]dioxole (3ne): Type **III** arylzinc reagent was used; Yellow solid (56% yield, eluent = hexane); M.p. = 104-105 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.38 (m, 4H), 7.34 – 7.30 (m, 1H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.07 (s, 2H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.3, 145.5, 143.2, 140.1, 137.5, 131.6, 129.7, 128.5, 127.2, 120.4, 108.0, 107.5, 101.1, 16.5; HRMS (ESI) Calcd for $C_{16}H_{13}O_2Te$ $[M + H]^+$ 366.9978, found 366.9973.

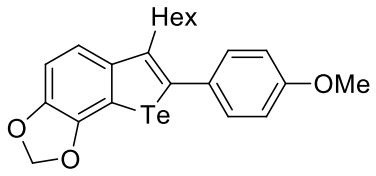


6-Butyl-7-(*p*-tolyl)telluropheno[2',3':3,4]benzo[1,2-*d*][1,3]dioxole (3nf): Type **III** arylzinc reagent was used; Yellow gum (47% yield, eluent = hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.06 (s, 2H), 2.68 (t, *J* = 8.0 Hz, 2H), 2.38 (s, 3H), 1.63 – 1.55 (m, 2H), 1.37 – 1.26 (m, 2H), 0.87 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.3, 144.5, 142.8, 142.7, 137.3, 137.0, 132.1, 129.2, 129.1, 120.4, 108.7, 107.4, 101.0, 32.5, 29.9, 22.8, 21.2, 13.8; HRMS (ESI) Calcd for $C_{20}H_{21}O_2Te$ $[M + H]^+$ 423.0604, found 423.0601.

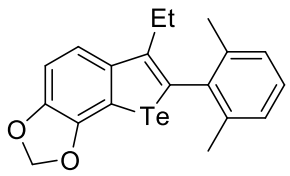


7-([1,1'-Biphenyl]-4-yl)-6-butyltelluropheno[2',3':3,4]benzo[1,2-*d*][1,3]dioxole (3ng): Type **III** arylzinc reagent was used; Yellow solid (58% yield, eluent = hexane); M.p. = 133-134 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.64 (m, 4H), 7.52 – 7.47 (m, 4H),

7.41 – 7.37 (m, 1H), 7.28 (d, *J* = 8.4 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.08 (s, 2H), 2.76 (t, *J* = 7.6 Hz, 2H), 1.70 – 1.62 (m, 2H), 1.42 – 1.33 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.3, 144.5, 143.1, 142.9, 140.6, 140.0, 139.3, 131.5, 129.8, 128.9, 127.5, 127.1, 127.0, 120.6, 108.9, 107.5, 101.1, 32.6, 30.0, 22.9, 13.9; HRMS (ESI) Calcd for $C_{25}H_3O_2Te$ $[M + H]^+$ 485.0760, found 485.0767. Recrystallization from EtOAc/hexane afforded single crystals suitable for X-ray diffraction analysis, which unambiguously confirmed the molecular structure of the compound.[28]

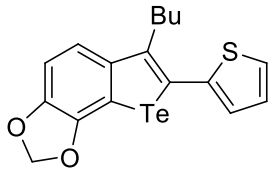


6-Hexyl-7-(4-methoxyphenyl)telluropheno[2',3':3,4]benzo[1,2-*d*][1,3]dioxole (3nh): Type **III** arylzinc reagent was used; Brown solid (46% yield, eluent = hexane); M.p. = 75-76 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.8 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.05 (s, 2H), 3.85 (s, 2H), 2.65 (t, *J* = 7.6 Hz, 2H), 1.63 – 1.56 (m, 2H), 1.33 – 1.20 (m, 6H), 0.86 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 149.3, 144.5, 142.8, 132.6, 131.8, 130.4, 129.9, 120.4, 113.8, 108.7, 107.4, 101.0, 55.4, 31.5, 30.3, 30.2, 29.5, 22.6, 14.1; HRMS (ESI) Calcd for $C_{22}H_{25}O_3Te$ $[M + H]^+$ 467.0866, found 467.0861.

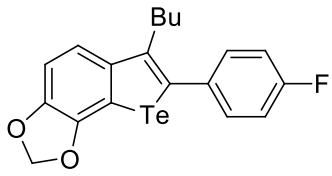


7-(2,6-Dimethylphenyl)-6-ethyltelluropheno[2',3':3,4]benzo[1,2-*d*][1,3]dioxole (3ni): Type **III** arylzinc reagent was used; Yellow gum (40% yield, eluent = hexane); ^{1}H NMR

(400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.4 Hz, 1H), 7.17 – 7.21 (m, 1H), 7.12 (d, *J* = 7.6 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.07 (s, 2H), 2.41 (q, *J* = 7.6 Hz, 2H), 2.20 (s, 6H), 1.08 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.7, 143.8, 143.7, 142.9, 138.3, 136.7, 130.2, 127.7, 127.6, 120.1, 109.3, 107.1, 101.0, 23.7, 20.8, 13.6; HRMS (ESI) Calcd for $C_{19}H_{19}O_2Te$ $[M + H]^+$ 409.0447, found 409.0450.

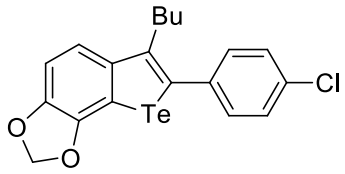


6-Butyl-7-(thiophen-2-yl)telluropheno[2',3':3,4]benzo[1,2-*d*][1,3]dioxole (3nj): Type **III** arylzinc reagent was used; Orange oil (38% yield, eluent = hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 4.4, 2.0 Hz, 1H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.06 – 7.05 (m, 2H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.06 (s, 2H), 2.89 (t, *J* = 8.0 Hz, 2H), 1.70 – 1.63 (m, 2H), 1.52 – 1.39 (m, 2H), 0.97 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.2, 144.6, 144.1, 143.3, 142.3, 127.5, 127.2, 125.9, 122.0, 120.7, 108.5, 107.6, 101.1, 32.3, 30.6, 23.0, 13.9; HRMS (ESI) Calcd for $C_{17}H_{17}O_2STe$ $[M + H]^+$ 415.0012, found 415.0005.

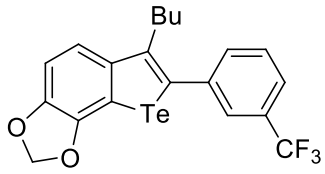


6-Butyl-7-(4-fluorophenyl)telluropheno[2',3':3,4]benzo[1,2-*d*][1,3]dioxole (3nk): Type **III** arylzinc reagent was used; Yellow solid (46% yield, eluent = hexane); M.p. = 101-102 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.36 (m, 2H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.10 – 7.06 (m, 2H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.06 (s, 2H), 2.64 (t, *J* = 8.0 Hz, 2H), 1.60 –

1.54 (m, 2H), 1.35 – 1.26 (m, 2H), 0.85 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.0 (d, $^1J_{C\text{-}F}$ = 245.5 Hz), 149.3, 144.1, 143.4, 143.0,136.2, 130.9 (d, $^3J_{C\text{-}F}$ = 8.0 Hz), 130.3, 120.6, 115.3 (d, $^2J_{C\text{-}F}$ = 21.4 Hz), 108.7, 107.5, 101.0, 32.4, 29.8, 22.8, 13.8; HRMS (ESI) Calcd for $C_{19}H_{18}O_2TeF$ $[M + H]^+$ 427.0353, found 427.0354.

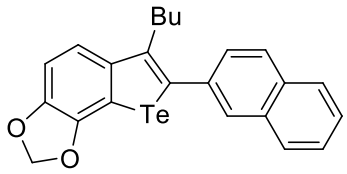


6-Butyl-7-(4-chlorophenyl)telluropheno[2',3':3,4]benzo[1,2-*d*][1,3]dioxole (3nl): Type **III** arylzinc reagent was used; Yellow solid (40% yield, eluent = hexane); M.p. = 106-107 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 4H), 7.24 (d, J = 8.4 Hz, 1H), 7.00 (d, J = 8.4 Hz, 1H), 6.06 (s, 2H), 2.65 (t, J = 8.0 Hz, 2H), 1.61 – 1.53 (m, 2H), 1.36 – 1.27 (m, 2H), 0.86 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.3, 144.1, 143.5, 143.0, 138.8, 133.2, 130.6, 130.0, 128.6, 120.7, 108.8, 107.6, 101.1, 32.5, 29.9, 22.8, 13.8; HRMS (ESI) Calcd for $C_{19}H_{18}O_2ClTe$ $[M + H]^+$ 443.0058, found 443.0053.

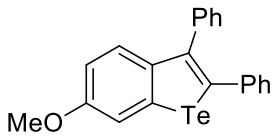


6-Butyl-7-(3-(trifluoromethyl)phenyl)telluropheno[2',3':3,4]benzo[1,2-*d*][1,3]dioxole (3nm): Type **III** arylzinc reagent was used; Yellow solid (52% yield, eluent = hexane); M.p. = 65-66 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.61 – 7.59 (m, 2H), 7.53 (d, J = 7.6 Hz, 1H), 7.28 (d, J = 8.4 Hz, 1H), 7.02 (d, J = 8.4 Hz, 1H), 6.08 (s, 2H), 2.66 (t, J = 8.0 Hz, 2H), 1.65 – 1.58 (m, 2H), 1.38 – 1.29 (m, 2H), 0.87 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.3, 144.2, 143.9, 143.2, 141.2, 132.8, 130.9 (q, $^2J_{C\text{-}F}$ =

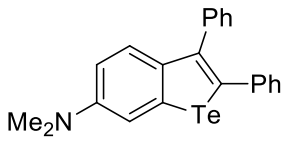
32.1 Hz), 129.2, 129.0, 125.9 (q, $^{3}J_{C\text{-}F}$ = 3.7 Hz), 124.0 (q, $^{1}J_{C\text{-}F}$ = 271.0 Hz), 123.9 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 120.9, 108.8, 107.6, 101.1, 32.5, 29.9, 22.8, 13.7; HRMS (ESI) Calcd for $C_{20}H_{18}O_2TeF_3$ $[M + H]^+$ 477.0321, found 477.0321.



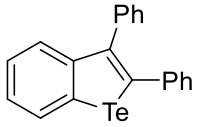
6-Butyl-7-(naphthalen-2-yl)telluropheno[2',3':3,4]benzo[1,2-*d*][1,3]dioxole (3nn): Type **III** arylzinc reagent was used; Yellow solid (41% yield, eluent = hexane); M.p. = 87-89 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.82 (m, 4H), 7.53 – 7.48 (m, 3H), 7.24 (d, *J* = 2.4 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.05 (s, 2H), 2.71 (t, *J* = 8.0 Hz, 2H), 1.64 – 1.58 (m, 2H), 1.31 – 1.23 (m, 2H), 0.81 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.3, 144.4, 143.3, 142.9, 137.7, 133.3, 132.4, 131.8, 128.0(2C), 127.9, 127.7, 127.6, 126.5, 126.1, 120.6, 109.0, 107.5, 101.0, 32.5, 30.0, 22.8, 13.8; HRMS (ESI) Calcd for $C_{23}H_{21}O_2Te$ $[M + H]^+$ 459.0604, found 459.0604.



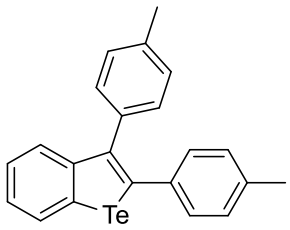
6-Methoxy-2,3-diphenylbenzo[*b*]tellurophene (3ao): Light yellow solid (38% yield, eluent = hexane); M.p. = 150-151 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 2.4 Hz, 1H), 7.40 – 7.33 (m, 3H), 7.29 – 7.25 (m, 3H), 7.20 – 7.14 (m, 5H), 6.93 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.3, 143.7, 143.2, 139.8, 139.1, 134.7, 133.1, 130.8, 130.0, 129.4, 128.4, 128.1, 127.1, 126.7, 115.3, 113.9, 55.6; HRMS (ESI) Calcd for $C_{21}H_{17}OTe$ $[M + H]^+$ 415.0342, found 415.0345.



***N,N*-dimethyl-2,3-diphenylbenzo[*b*]tellurophen-6-amine (3co):** Yellow solid (35% yield, eluent = hexane/EtOAc (30:1)); M.p. = 157-158 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.31 (m, 3H), 7.28 (d, *J* = 2.4 Hz, 1H), 7.25 – 7.23 (m, 2H), 7.19 (d, *J* = 8.8 Hz, 1H), 7.13 – 7.09 (m, 5H), 6.75 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.00 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.5, 143.8, 104.2, 140.0, 139.4, 133.5, 131.5, 130.8, 130.0, 128.9, 128.3, 128.0, 126.9, 126.4, 114.3, 111.8, 40.7; HRMS (ESI) Calcd for $C_{22}H_{20}NTe$ $[M + H]^+$ 428.0658, found 428.0653.



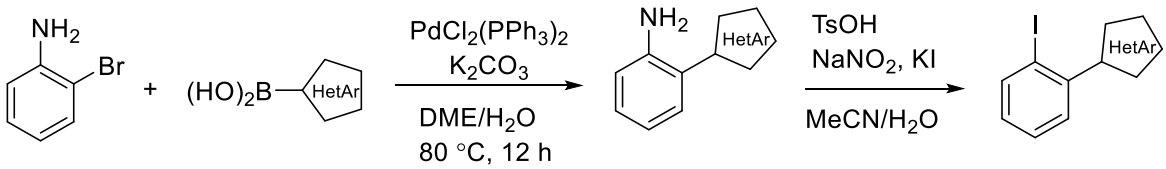
2,3-Diphenylbenzo[*b*]tellurophene (3bo): Yellow solid (58% yield, eluent = hexane); M.p. = 117-118 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.4 Hz, 1H), 7.46 – 7.34 (m, 6H), 7.31 – 7.27 (m, 2H), 7.25 – 7.19 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.3, 144.4, 139.8, 138.9, 138.6, 132.2, 131.8, 130.9, 130.0, 128.9, 128.5, 128.2, 127.2, 127.0, 125.3, 124.9; HRMS (ESI) Calcd for $C_{22}H_{20}NTe$ $[M + H]^+$ 428.0658, found 428.0653.



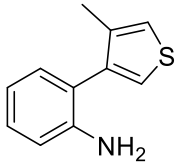
2,3-Di-*p*-tolylbenzo[*b*]tellurophene (3bp): Yellow solid (45% yield, eluent = hexane); M.p. = 117-118 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.0 Hz, 1H), 7.39 – 7.37

(m, 1H), 7.29 – 7.27 (m, 1H), 7.19 – 7.13 (m, 5H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 2.39 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.6, 143.9, 138.5, 137.0, 136.7 (2C), 136.0, 131.8, 131.7, 130.6, 129.9, 129.2, 128.9, 128.8, 125.2, 124.7, 21.3, 21.1; HRMS (ESI) Calcd for $C_{22}H_{19}Te$ $[M + H]^+$ 413.0549, found 413.0554.

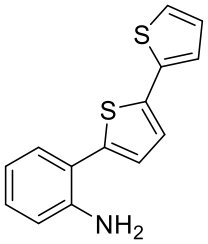
Preparation of 2-iodoaryl-heteroaryl derivatives



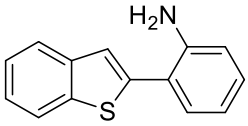
General procedure for the preparation of 2-aminoaryl-heteroaryls: A 50 mL three-necked flask was charged with 2-bromoaniline (0.86 g, 5.0 mmol), heteroaryl boronic acid (7.5 mmol), aqueous solution of K_2CO_3 (2 M, 5 mL), and DME (20 mL) under a gentle stream of nitrogen. The resulting mixture was stirred for 30 min at room temperature, followed by the addition of $PdCl_2(PPh_3)_2$ (109 mg, 0.25 mmol). The reaction mixture was stirred at 80 ℃ for 12 h, cooled to room temperature, and diluted with EtOAc. The organic layer was washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was subjected to flash chromatography on silica gel to afford the desired 2-aminoaryl-heteroaryls. Below are summarized characterization data of newly synthesized substrates.



2-(4-Methylthiophen-3-yl)aniline: Yellow oil (69% yield, eluent = hexane/EtOAc (15:1)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.23 (m, 2H), 7.15 – 7.13 (m, 2H), 6.90 – 6.81 (m, 1H), 6.82 (dd, *J* = 8.0, 1.2 Hz, 1H), 3.63 (s, 2H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.7, 140.1, 137.6, 130.8, 128.8, 123.8, 122.6, 121.9, 118.1, 115.2, 14.8; HRMS (ESI) Calcd for $C_{11}H_{12}NS$ $[M + H]^+$ 190.0690, found 190.0693.

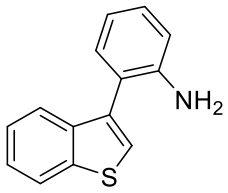


2-([2,2'-Bithiophen]-5-yl)aniline: Yellow gum (54% yield, eluent = hexane/EtOAc (10:1)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.23 (dd, *J* = 5.2, 0.8 Hz, 1H), 7.20 – 7.17 (m, 2H), 7.15 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.12 (d, *J* = 3.6 Hz, 1H), 7.03 (dd, *J* = 4.8, 3.6 Hz, 1H), 6.83 – 6.77 (m, 2H), 4.05 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.1, 140.1, 137.3, 137.1, 130.7, 129.2, 127.9, 126.5, 124.4, 124.1, 123.7, 119.7, 118.7, 116.0; HRMS (ESI) Calcd for $C_{14}H_{12}NS_2$ $[M + H]^+$ 258.0411, found 258.0417.

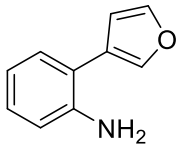


2-(Benzo[*b*]thiophen-2-yl)aniline: Pale yellow solid (85% yield, eluent = hexane/EtOAc (10:1)); M.p. = 129-130 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.44 (s, 1H), 7.42 – 7.34 (m, 3H), 7.23 – 7.19 (m, 1H), 6.87 – 6.80 (m, 2H), 4.12 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.3, 141.6, 140.4, 139.8,

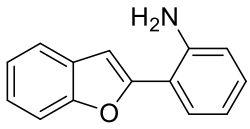
131.2, 129.6, 124.5, 124.3, 123.5, 122.5, 122.2, 119.8, 118.6, 116.1; HRMS (ESI) Calcd for $C_{14}H_{12}NS$ $[M + H]^+$ 226.0690, found 226.0689.



2-(Benzo[*b*]thiophen-3-yl)aniline: Orange gum (89% yield, eluent = hexane/EtOAc (10:1)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 8.00 (m, 1H), 7.74 – 7.72 (m, 1H), 7.50 (s, 1H), 7.49 – 7.42 (m, 2H), 7.34 – 7.30 (m, 2H), 6.97 – 6.93 (m, 1H), 6.90 – 6.87 (m, 1H), 3.73 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.8, 140.4, 138.3, 135.0, 131.2, 129.2, 124.8, 124.7, 124.4, 123.5, 122.9, 121.0, 118.4, 115.6; HRMS (ESI) Calcd for $C_{14}H_{12}NS$ $[M + H]^+$ 226.0690, found 226.0690.

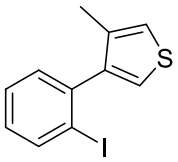


2-(Furan-3-yl)aniline: Light yellow oil (65% yield, eluent = hexane/EtOAc (15:1)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.59 (t, *J* = 1.6 Hz, 1H), 7.28 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.22 – 7.18 (m, 1H), 6.90 – 6.86 (m, 1H), 6.81 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.71 – 6.70 (m, 1H), 3.90 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.1, 143.3, 139.8, 129.8, 128.4, 123.5, 118.8, 118.4, 115.8, 110.9; HRMS (ESI) Calcd for $C_{10}H_{10}NO$ $[M + H]^+$ 160.0762, found 160.0762.



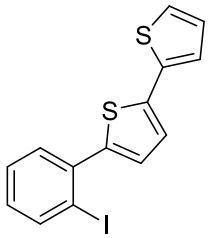
2-(Benzofuran-2-yl)aniline: Orange solid (64% yield, eluent = hexane/EtOAc (15:1)); m.p. = 67-68 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.35 – 7.27 (m, 2H), 7.25 – 7.21 (m, 1H), 6.98 (d, *J* = 0.8 Hz, 1H), 6.91 – 6.86 (m, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 4.52 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.7, 154.3, 144.2, 129.9, 128.9, 128.6, 124.0, 123.0, 120.7, 118.5, 116.9, 115.5, 111.0, 103.0; HRMS (ESI) Calcd for $C_{14}H_{12}NO$ $[M + H]^+$ 210.0919, found 201.0923.

General procedure for the preparation of 2-iodoaryl-heteroaryls: To a solution of *p*-TsOH (1.15 g, 6.0 mmol) in MeCN (15 mL) was added 2-aminoaryl-heteroaryls (2.0 mmol). The resulting suspension was cooled to 10-15 ℃, followed by the slow addition of a solution of $NaNO_2$ (272 mg, 4.0 mmol) and KI (830 mg, 5.0 mmol) in H_2O (5 mL). The mixture was stirred for 10 min, allowed to room temperature for 4 h. An aqueous solution of $NaHCO_3$ was added until the pH of the mixture reached 9, and then $Na_2S_2O_3$ was added until complete reduction of the residual iodine. The crude mixture was extracted with EtOAc, and the extracts were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired 2-iodoaryl-heteroaryls. Below are summarized characterization data for newly synthesized substrates

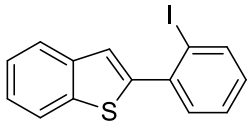


3-(2-Iodophenyl)-4-methylthiophene: Colourless oil (65% yield, eluent = hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 6.4 Hz, 1H), 6.91 – 6.88 (m, 1H), 6.81 – 6.78 (m,

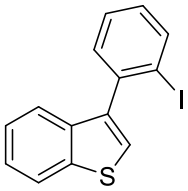
1H), 6.68 – 6.61 (m, 3H), 2.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.5, 142.5, 139.0, 136.7, 130.5, 129.1, 128.0, 123.8, 121.2, 100.7, 15.1; HRMS (ESI) Calcd for $C_{11}H_{10}SI$ $[M + H]^+$ 300.9548, found 300.9548.



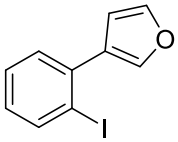
5-(2-Iodophenyl)-2,2'-bithiophene: Colourless oil (63% yield, eluent = hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.46 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.40 – 7.36 (m, 1H), 7.24 – 7.22 (m, 2H), 7.18 (d, *J* = 3.6 Hz, 1H), 7.12 (d, *J* = 3.6 Hz, 1H), 7.06 – 7.01 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.7, 140.3, 139.0, 138.1, 137.3, 131.3, 129.5, 128.6, 128.3, 128.0, 124.6, 123.9, 123.6, 99.2; HRMS (ESI) Calcd for $C_{14}H_{10}S_2I$ $[M + H]^+$ 368.9269, found 368.9266.



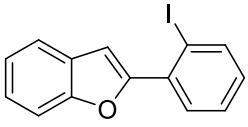
2-(2-Iodophenyl)benzo[*b*]thiophene: Yellow solid (76% yield, eluent = hexane); M.p. = 43-44 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.92 – 7.87 (m, 2H), 7.54 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.46 – 7.39 (m, 4H), 7.12 – 7.08 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.2, 140.3, 140.1, 139.8, 139.5, 131.5, 129.9, 128.2, 124.6, 124.4, 124.0, 122.3, 99.2 (one carbon missing due to overlap); HRMS (ESI) Calcd for $C_{14}H_{10}SI$ $[M + H]^+$ 336.9548, found 336.9563.



3-(2-Iodophenyl)benzo[*b*]thiophene: Pale yellow oil (73% yield, eluent = hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 8.0, 0.8 Hz, 1H), 8.15 (dd, *J* = 7.2, 2.0 Hz, 1H), 7.62 (dd, *J* = 6.8, 2.0 Hz, 1H), 7.56 – 7.46 (m, 5H), 7.24 – 7.20 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.0, 139.9, 139.8, 139.7, 138.4, 131.3, 129.7, 128.3, 125.4, 124.7, 124.5, 123.5, 122.9, 100.4; HRMS (ESI) Calcd for $C_{14}H_{10}SI$ $[M + H]^+$ 336.9548, found 336.9543.



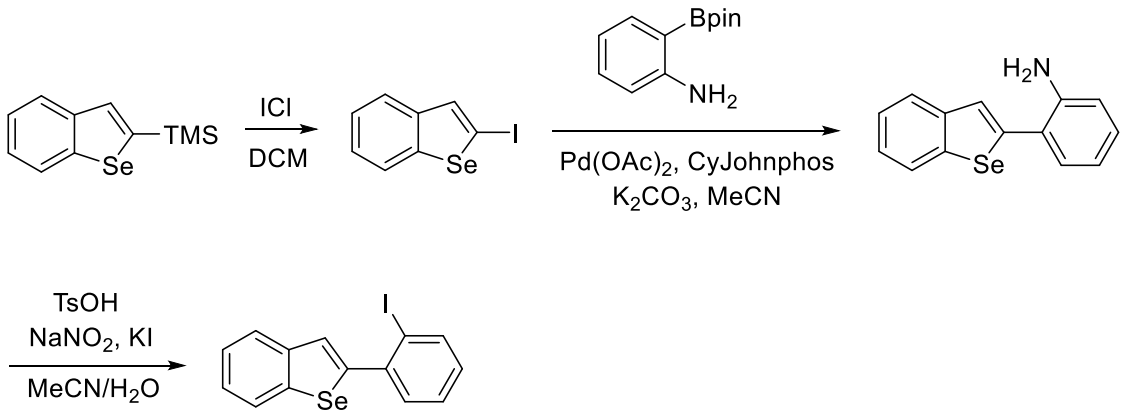
3-(2-Iodophenyl)furan: Colourless oil (48% yield, eluent = hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.6 Hz, 1H), 7.73 (s, 1H), 7.50 (t, *J* = 1.6 Hz, 1H), 7.39 – 7.33 (m, 2H), 7.03 – 6.99 (m, 1H), 6.67 – 6.66 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.4, 140.5, 140.0, 137.9, 130.4, 128.8, 128.2, 128.1, 111.9, 98.5; HRMS (ESI) Calcd for $C_{10}H_8OI$ $[M + H]^+$ 270.9620, found 270.9625.



2-(2-Iodophenyl)benzofuran: Orange oil (81% yield, eluent = hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.89 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.77 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.68 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.53 – 7.52 (m, 1H), 7.51 – 7.38 (m, 3H), 7.14 – 7.09 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.7, 154.7, 141.1, 135.2,

130.3, 130.0, 128.7, 128.3, 124.9, 123.2, 121.6, 111.4, 106.4, 95.5; HRMS (ESI) Calcd for $C_{14}H_{10}OI$ $[M + H]^+$ 320.9776, found 320.9783.

Preparation of 2-(2-iodophenyl)benzo[*b*]selenophene



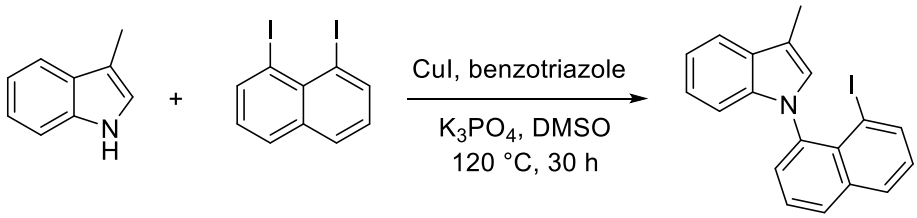
2-Iodobenzo[*b*]selenophene: A 50 mL three-necked flask equipped with a stirrer bar was charged with benzo[*b*]selenophen-2-yltrimethylsilane[9] (1.27 g, 5.0 mmol) and purged with nitrogen. Dry CH_2Cl_2 (20 mL) was added, and the resulting suspension was cooled to -30 ℃. To the suspension was added iodine monochloride in CH_2Cl_2 solution (1M, 5.0 mL) *via* syringe. The mixture was stirred at -30 ℃ for 1 h and then warmed up to r.t. for further 12 h. Saturated $Na_2S_2O_3$ solution was added until the colour did not change. The mixture was extracted with CH_2Cl_2 and the organic phase was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was subjected to flash chromatography on silica gel (eluent = hexane) to afford the title compound as a light yellow solid (1.32 g, 86%). M.p. = 70-71 ℃; ^{1}H NMR (400 MHz, acetone-d_6) δ 8.00 (dd, J = 8.0, 0.8 Hz, 1H), 7.96 (s, 1H), 7.82 (dd, J = 8.0, 0.8 Hz, 1H), 7.36 – 7.27 (m, 2H); ^{13}C NMR (100 MHz, acetone-d_6): δ 146.5, 143.5, 138.4, 125.0,

124.9, 124.8, 124.2, 77.3; HRMS (ESI) Calcd for C_8H_6ISe $[M + H]^+$ 308.8679, found 308.8678.

2-(Benzo[*b*]selenophen-2-yl)aniline: A mixture of 2-iodobenzo[*b*]selenophene (0.92 g, 3.0 mmol), 2-aminophenylboronic acid pinacol ester (0.99 g, 4.5 mmol), (2-biphenyl)-dicyclohexylphosphine [CyJohnPhos] (210.3 mg, 0.6 mmol), $Pd(OAc)_2$ (67.4 mg, 0.3 mmol), K_2CO_3 (1.24 g, 9.0 mmol), MeCN (15 mL) and H_2O (10 mL) was heated at 80 ℃ for 12 h. The mixture was diluted with water, and the aqueous layer was separated and then extracted with EtOAc. The combined organic extracts were washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure. The residue was subjected to flash chromatography on silica gel (eluent = hexane/EtOAc (15:1)) to afford the title compound as a yellow solid (0.42 g, 52%). M.p. = 124-125 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.57 (s, 1H), 7.41 – 7.33 (m, 2H), 7.30 – 7.28 (m, 1H), 7.21 – 7.17 (m, 1H), 6.85 – 6.78 (m, 2H), 4.11 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.7, 143.9, 142.8, 141.8, 131.2, 129.5, 126.3, 125.4, 125.3, 124.8, 124.4, 121.9, 118.6, 116.0; HRMS (ESI) Calcd for $C_{14}H_{12}NSe$ $[M + H]^+$ 274.0135, found 274.0131.

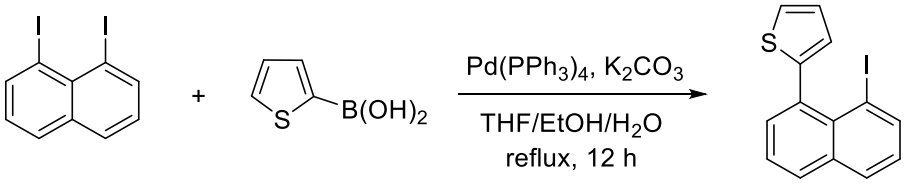
2-(2-Iodophenyl)benzo[*b*]selenophene: The title compound was obtained by using a similar procedure as described above. Colourless oil (73% yield, eluent = hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.53 – 7.50 (m, 2H), 7.43 – 7.38 (m, 2H), 7.33 – 7.29 (m, 1H), 7.09 – 7.04 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.7, 142.5, 142.1, 141.4, 140.0, 131.2, 129.7, 128.1, 128.0, 125.8, 125.4, 124.8, 124.7, 99.0; HRMS (ESI) Calcd for $C_{14}H_{10}SeI$ $[M + H]^+$ 384.8992, found 384.9000.

Preparation of 1-(8-iodonaphthalen-1-yl)-3-methyl-1*H*-indole



1-(8-Iodonaphthalen-1-yl)-3-methyl-1*H*-indole: The reaction was performed according to the literature procedure.[26] A mixture of 3-methyl-1*H*-indole (288.4 mg, 2.2 mmol), 1,8-diiodonaphthalene (759.9 mg, 2.0 mmol), CuI (38.0 mg, 0.2 mmol), benzotriazole (47.6 mg, 0.4 mmol), K_3PO_4 (849.1 mg, 4.0 mmol) and DMSO (8 mL) was heated at 120 ℃ for 30 h. The reaction mixture was washed with ethyl acetate and water. The organic layer was then washed with brine and dried over $MgSO_4$ and evaporated under reduced pressure. The residue was subjected to flash chromatography on silica gel (eluent = hexane/EtOAc (20:1)) to afford the title compound as a yellow solid (306.4 mg, 40%). M.p. = 92-93 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 7.2 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.63 – 7.55 (m, 2H), 7.30 – 7.19 (m, 3H), 7.05 (s, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.9, 140.6, 136.5, 136.0, 130.3, 130.2, 129.8, 129.4, 129.3, 128.8, 127.2, 125.9, 122.3, 119.5, 118.9, 112.9, 111.0, 87.2, 9.9; HRMS (ESI) Calcd for $C_{19}H_{15}NI$ $[M + H]^+$ 384.0249, found 384.0251.

Preparation of 2-(8-iodonaphthalen-1-yl)thiophene

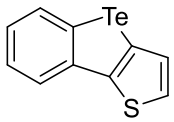


2-(8-Iodonaphthalen-1-yl)thiophene: To a 25 mL three-necked bottom flask, equipped with a magnetic stir bar, 1,8-diiodonaphthalene (417.9 mg, 1.1 mmol), thiophen-2-ylboronic acid (128 mg, 1 mmol), K_2CO_3 (828 mg, 6.0 mmol), and $Pd(PPh_3)_4$ (115.5 mg, 0.1 mmol) were dissolved in 8 mL of THF followed by the addition of 3 mL of H_2O and 3 mL of EtOH. The resulting mixture was refluxed for 12 h. After cooling to room temperature, the biphasic solution was diluted with 10 mL of saturated aqueous NH_4Cl and 15 mL of EtOAc. The aqueous phase was extracted with EtOAc, and the combined organic layers were washed with water and brine. The organic phase was dried over $MgSO_4$ and filtered. The filtrate was concentrated in vacuo and purified by column chromatography to afford the desired product as a yellow gum (100.1 mg, 30%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.92 – 7.88 (m, 2H), 7.66 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.51 – 7.47 (m, 2H), 7.15 – 7.10 (m, 2H), 7.03 (dd, *J* = 3.6, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.8, 141.4, 135.4, 133.3, 132.5, 132.2, 130.9, 130.3, 129.8, 127.0, 126.7, 126.3, 124.9, 91.6; HRMS (ESI) Calcd for $C_{14}H_9IS$ $[M + H]^+$ 336.9548, found 336.9536.

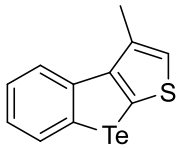
Synthesis of heteroatom-bridged tellurophenes

General procedure: An oven-dried Schlenk tube equipped with a magnetic stirrer bar was charged with 2-iodoaryl-heteroaryl (0.3 mmol). *i*PrMgBr or *i*PrMgCl·LiCl in THF (0.26 mmol, 1.2 equiv) was slowly added at 0 ℃ and the resulting mixture was stirred at

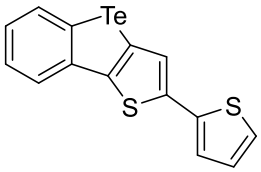
0 ℃ for 2 h. $ZnCl_2$•TMEDA was added at 0 ℃ and the mixture was stirred for further 30 min. The mixture was added to a solution of $TeCl_4$ (161.4 mg, 0.6 mmol) in THF (4 mL) *via* syringe and the resulting mixture was stirred at 90 ℃ for 12 h. The mixture was diluted with ethyl acetate (5 mL) and filtered through a pad of silica gel with additional ethyl acetate (15 mL) as the eluent. The filtrate was washed with water (10 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product.



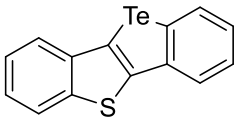
Benzo[4,5]telluropheno[3,2-*b*]thiophene (5): Yellow solid (66% yield, eluent = hexane); M.p. = 70-71 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.86 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.43 – 7.39 (m, 2H), 7.34 – 7.32 (m, 1H), 7.18 – 7.14 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.7, 139.4, 133.1, 131.1, 128.3, 126.0, 125.8, 124.8, 124.4, 120.3; HRMS (ESI) Calcd for $C_{10}H_7STe$ $[M + H]^+$ 288.9331, found 288.9328.



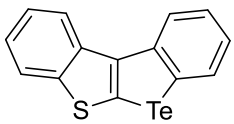
3-Methylbenzo[4,5]telluropheno[2,3-*b*]thiophene (6): Yellow solid (51% yield, eluent = hexane); M.p. = 72-73 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.14 (s, 1H), 2.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.3, 140.9, 135.4, 133.2, 132.8, 127.6, 125.6, 124.9, 124.2, 117.8, 16.9; HRMS (ESI) Calcd for $C_{11}H_9STe$ $[M + H]^+$ 302.9487, found 302.9487.



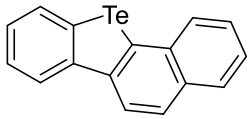
2-(Thiophen-2-yl)benzo[4,5]telluropheno[3,2-*b*]thiophene (7): Yellow solid (47% yield, eluent = hexane); M.p. = 97-98 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.42 – 7.38 (m, 2H), 7.28 – 7.26 (m, 2H), 7.17 – 7.13 (m, 1H), 7.07 – 7.05 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.2, 139.4, 138.0, 137.1, 133.0, 131.1, 128.0, 126.1, 124.9, 124.8, 124.6, 124.2, 124.1, 121.2; HRMS (ESI) Calcd for $C_{14}H_9S_2Te$ $[M + H]^+$ 370.9208, found 370.9202.



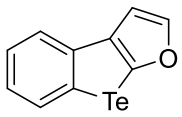
Benzo[*b*]benzo[4,5]telluropheno[2,3-*d*]thiophene (8)[29]: Pale yellow solid (54% yield, eluent = hexane); M.p. = 158-159 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 1H), 7.94 – 7.89 (m, 2H), 7.69 – 7.67 (m, 1H), 7.48 – 7.38 (m, 3H), 7.23 – 7.19 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.9, 140.2, 139.9, 139.7, 133.1, 130.9, 130.8, 126.1, 125.3, 125.2, 125.0, 124.9, 123.5, 123.4; HRMS (ESI) Calcd for $C_{14}H_9STe$ $[M + H]^+$ 338.9487, found 338.9482. Recrystallization from EtOAc/hexane afforded single crystals suitable for X-ray diffraction analysis, which unambiguously confirmed the molecular structure of the compound.[30]



Benzo[*b*]benzo[4,5]telluropheno[3,2-*d*]thiophene (9): Pale yellow solid (52% yield, eluent = hexane); M.p. = 171-172 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (dd, *J* = 8.0, 0.8 Hz, 1H), 8.50 (d, *J* = 8.0 Hz, 1H), 7.95 – 7.92 (m, 2H), 7.55 – 7.48 (m, 2H), 7.39 – 7.35 (m, 1H), 7.25 – 7.21 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.3, 142.7, 140.9, 136.4, 133.5, 132.8, 126.0, 124.8, 124.4, 123.8, 123.4, 122.6, 120.9 (one carbon missing due to overlap); HRMS (ESI) Calcd for $C_{14}H_9STe$ $[M + H]^+$ 338.9487, found 338.9491. Recrystallization from EtOAc/hexane afforded single crystals suitable for X-ray diffraction analysis, which unambiguously confirmed the molecular structure of the compound.[31]

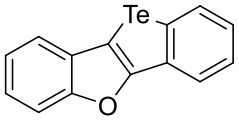


Benzo[*b*]naphtho[2,1-*d*]tellurophene (10): Pale yellow solid (67% yield, eluent = hexane); M.p. = 194-195 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.0 Hz, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.94 – 7.89 (m, 2H), 7.63 – 7.61 (m, 1H), 7.56 – 7.49 (m, 3H), 7.34 – 7.30 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.4, 142.0, 135.7, 132.6, 132.5, 132.2, 129.5, 129.1, 128.9, 127.0, 126.9, 126.6, 126.5, 125.8, 125.1, 122.6; HRMS (ESI) Calcd for $C_{16}H_{11}Te$ $[M + H]^+$ 332.9923, found 332.9929.

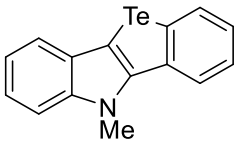


Benzo[4,5]telluropheno[2,3-*b*]furan (11): Yellow oil (47% yield, eluent = hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.77 (m, 2H), 7.77 (d, *J* = 2.0 Hz, 1H), 7.41 – 7.36 (m, 1H), 7.12 – 7.08 (m, 1H), 6.96 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.2,

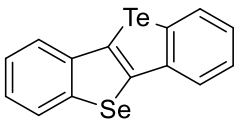
136.2, 135.6 (2C), 132.9, 131.6, 126.2, 124.4, 124.2, 107.5; HRMS (ESI) Calcd for $C_{10}H_7OTe$ $[M + H]^+$ 272.9559, found 272.9564.



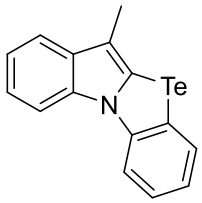
Benzo[4,5]telluropheno[3,2-*b*]benzofuran (12): Light yellow solid (53% yield, eluent = hexane); M.p. = 105-106 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.60 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.40 – 7.32 (m, 2H), 7.24 – 7.20 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 156.5, 133.1, 131.4, 130.1, 129.1, 126.1, 125.6, 124.9, 123.7, 123.3, 120.7, 112.1, 99.7; HRMS (ESI) Calcd for $C_{14}H_9OTe$ $[M + H]^+$ 322.9716, found 322.9712.



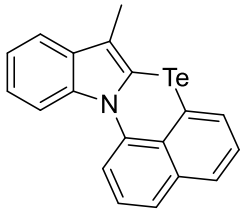
10-Methyl-10*H*-benzo[4,5]telluropheno[3,2-*b*]indole (13): Brown solid (54% yield, eluent = hexane/EtOAc (20:1)); M.p. = 174-175 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 8.0, 0.4 Hz, 1H), 7.99 (dd, *J* = 7.6, 0.4 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.48 – 7.42 (m, 2H), 7.38 – 7.33 (m, 1H), 7.22 – 7.14 (m, 2H), 4.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.0, 140.9, 134.7, 134.1, 130.7, 128.6, 125.6, 124.3, 123.8, 123.0, 120.6, 119.7, 109.6, 96.5, 32.2; HRMS (ESI) Calcd for $C_{15}H_{12}NTe$ $[M + H]^+$ 336.0032, found 336.0037.



Benzo[*b*]benzo[4,5]telluropheno[2,3-*d*]selenophene (14): Yellow solid (50% yield, eluent = hexane); M.p. = 139-140 ℃; ^{1}H NMR (400 MHz, THF-d_8) δ 8.07 (d, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.41 – 7.36 (m, 2H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.15 (t, *J* = 7.2 Hz, 1H).; ^{13}C NMR (100 MHz, THF-d_8): δ 143.6, 141.4, 140.9, 133.8, 131.6, 127.1, 126.6, 126.3, 125.9, 125.8, 125.6, 125.5, 124.4 (one carbon missing due to overlap); HRMS (ESI) Calcd for $C_{14}H_9SeTe$ $[M + H]^+$ 386.8932, found 386.8931.

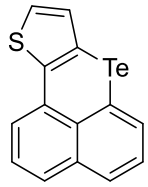


11-Methylbenzo[4,5][1,3]tellurazolo[3,2-*a*]indole (15): Yellow solid (55% yield, eluent = hexane/EtOAc (30:1)); M.p. = 80-81 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.6 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.66 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.55 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.30 – 7.22 (m, 2H), 7.11 – 7.06 (m, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.0, 136.1, 133.6, 132.3, 127.7, 122.8, 120.8, 120.6, 117.3, 115.1, 114.2, 113.0, 111.3, 111.1, 11.8; HRMS (ESI) Calcd for $C_{15}H_{12}NTe$ $[M + H]^+$ 336.0032, found 336.0033.



8-Methylnaphtho[1',8':4,5,6][1,3]tellurazino[3,2-*a*]indole (16): Yellow solid (58% yield, eluent = hexane/EtOAc (30:1)); M.p. = 175-176 ℃; ^{1}H NMR (400 MHz, THF-d_8)

δ 8.09 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.73 – 7.66 (m, 3H), 7.58 (t, *J* = 8.0 Hz, 1H), 7.47 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.29 – 7.25 (m, 1H), 7.13 – 7.03 (m, 2H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, THF-d_8): δ 139.8, 137.6, 136.6, 132.5, 131.8, 129.0, 128.1, 127.1, 126.4, 126.2, 125.9, 121.8, 121.4, 119.2, 118.3, 118.0, 112.1, 104.9, 11.4; HRMS (ESI) Calcd for $C_{19}H_{14}NTe$ $[M + H]^+$ 386.0189, found 386.0195.



Benzo[4,5]tellurochromeno[3,2-*b*]thiophene (17): Pale yellow solid (62% yield, eluent = hexane); M.p. = 74-75 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.59 (dd, *J* = 6.8, 1.2 Hz, 1H), 7.51 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.42 (d, *J* = 5.2 Hz, 1H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.14 (dd, *J* = 8.0, 7.2 Hz, 1H), 6.96 (d, *J* = 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.1, 132.2, 131.3, 130.7, 129.3, 129.0, 127.8, 127.5, 126.5, 126.2, 126.1, 123.1, 110.6, 101.1; HRMS (ESI) Calcd for $C_{14}H_9STe$ $[M + H]^+$ 338.9487, found 338.9483.

3.5 References

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[30] CCDC 1523264 contains the supplementary crystallographic data for compound **8**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.uk/data_request/cif.

[31] CCDC 1523263 contains the supplementary crystallographic data for compound **9**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.uk/data_request/cif.

Chapter 4. One-pot Multicomponent Synthesis of Benzophospholes from Arylzinc Reagents, Alkynes, and Chlorophosphines

4.1 Introduction

The phosphorus analogue of indole, benzo[*b*]phosphole, was first synthesized by Klemann in 1967.[1] While the following synthetic studies have been relatively sporadic for a few decades, this class of heterocycles has attracted increasing attention because of their unique physical and chemical properties.[2] Among benzo[*b*]heterole series of heterocycles, benzo[*b*]phosphole is unique because chemical modification of the phosphorus atom (e.g., oxidation, quaternization[3]) allows modulation of its electronic properties. For example, a number of benzo[*b*]phosphole oxides have been shown to exhibit intense fluorescence,[4] which allow their application as biological imaging probes[5] or materials for organic electronic devices (Figure 4.1).[6] The coordination ability and the nucleophilicity of the phosphorus atom also allow exploration of coordination chemistry and catalysis of benzo[*b*]phospholes. For example, helicene-fused benzophospholes have been studied as chiral ligands[7] and organocatalysts[8] for asymmetric synthesis.

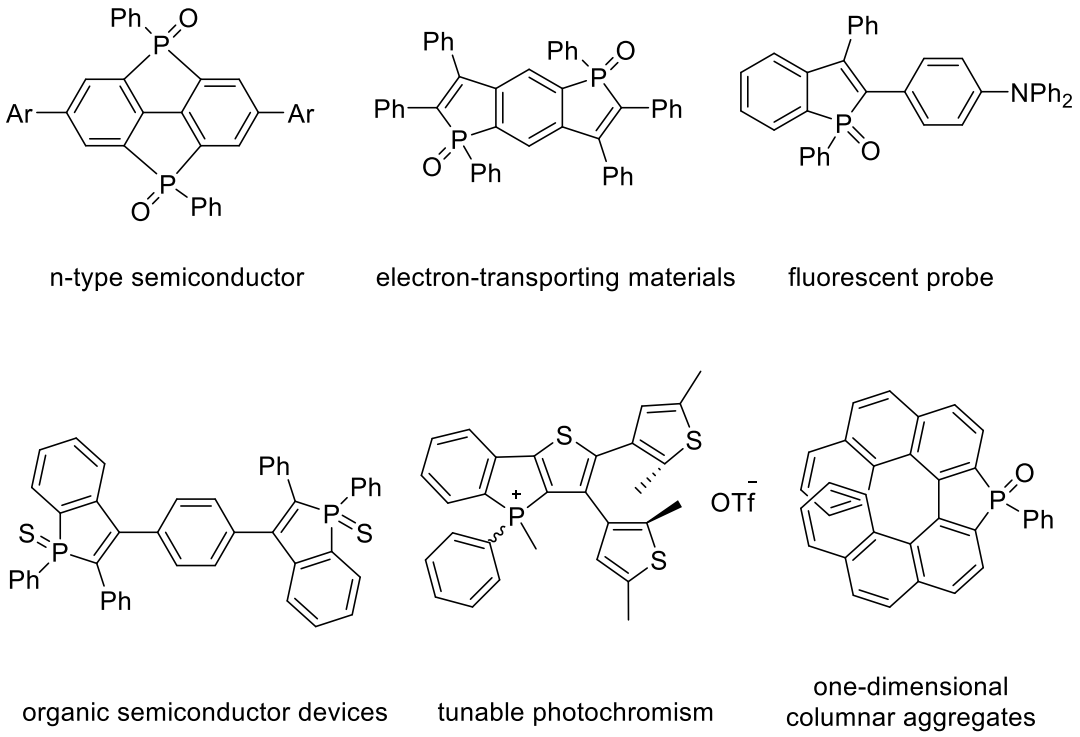
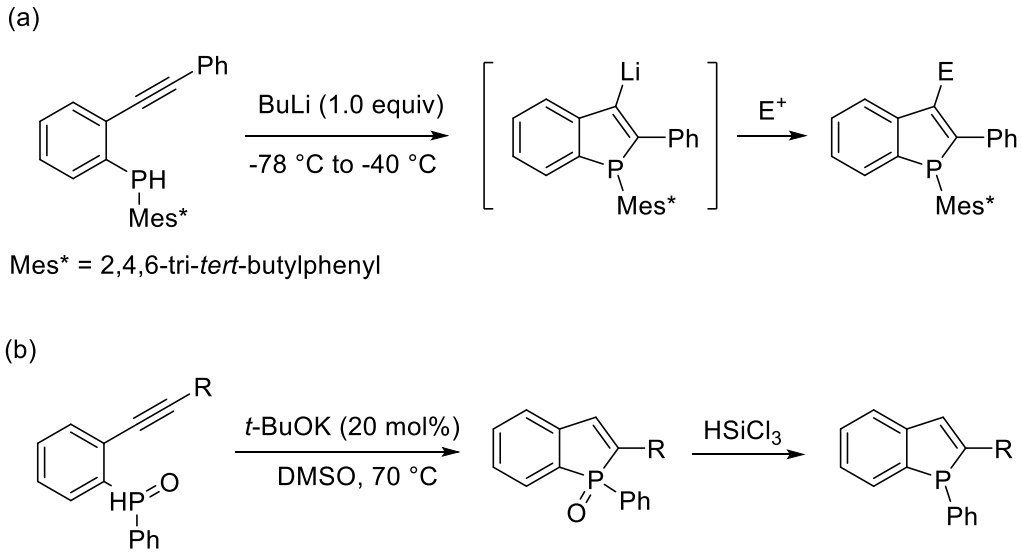


Figure 4.1. Functional materials containing benzophosphole moiety.

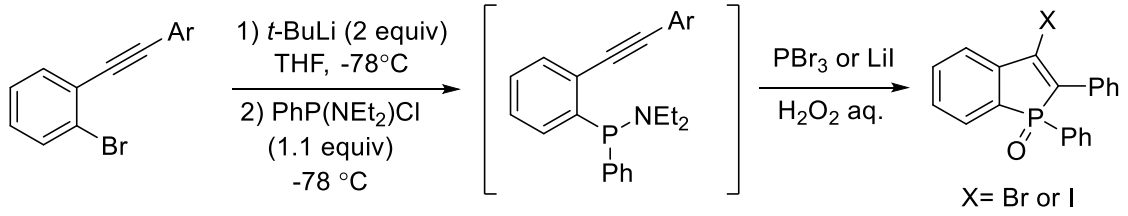
Over the last several years, a series of notable new methods have been developed for benzophosphole synthesis, capitalizing on either "cyclization approach" or "annulation approach" (*cf.* Chapter 1). In 2008, Tsuji, Nakamura and co-workers reported a BuLi-mediated conversion of *ortho*-alkynylaryl phosphine to 3-lithiobenzophosphole, which likely proceeds via P–H deprotonation followed by 5-*endo* cyclization (Scheme 4.1a).[9] The 3-lithiobenzophosphole can be used for a variety of electrophilic trapping reactions including Pd-catalyzed cross-coupling. Sanji and Tanaka reported *t*-BuOK-catalyzed cyclization reaction of 2-alkynylphenylphosphine oxides, affording a variety of benzophosphole oxides, which could be reduced by trichlorosilane to afford the corresponding benzophosphole derivatives (Scheme 4.1b). [10] Furthermore, the photophysical properties of benzophosphole oxide derivatives and related compounds such as fluorescence were investigated as well.

Scheme 4.1. Benzophosphole synthesis via intramolecular cyclization of *ortho*-alkynylarylphosphine.



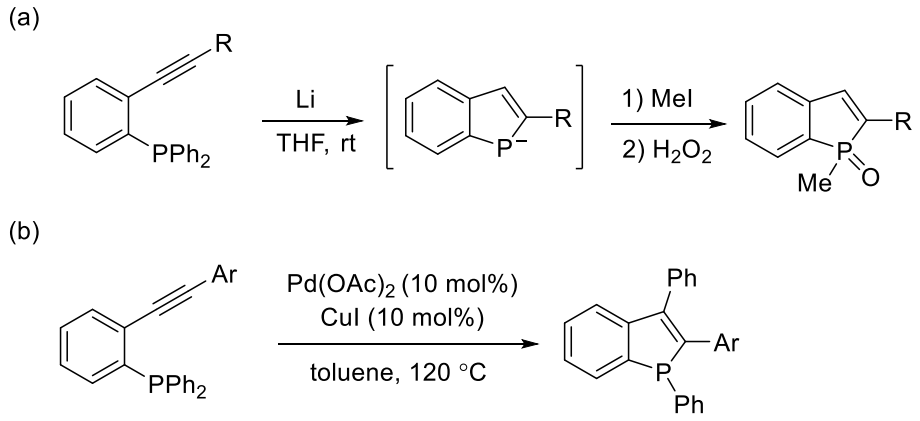
Fukazawa and Yamaguchi reported a benzophosphole synthesis based on intramolecular *trans*-halophosphanylation (Scheme 4.2). [11] Treatment of 2-(aminophosphanyl) phenylacetylenes, generated in situ from a brominated precursor through Br/Li exchange and electrophilic trapping with PBr_3 followed by the oxidation with H_2O_2 afforded 3-bromobenzophosphole oxide derivatives. The 3-iodobenzophosphole oxides could also be obtained in the presence of LiI. The 3-halobenzophosphole oxides provided opportunities for further transformations to various 3-substituted benzophosphole derivatives.

Scheme 4.2. Benzophosphole synthesis through intramolecular *trans*-halophosphanylation.



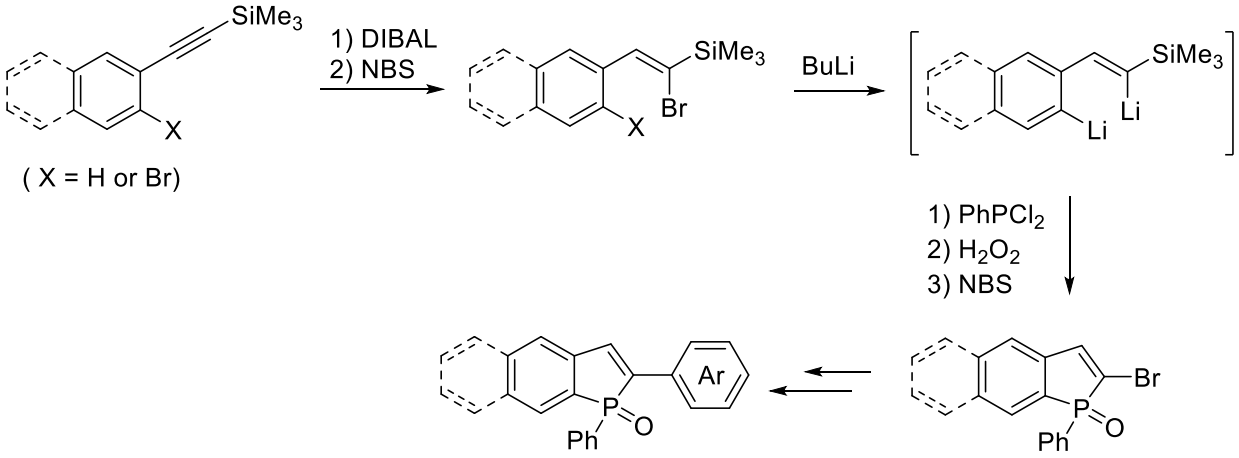
A diarylphosphino group can also be used as a viable phosphorus group leading to benzophospholes by intramolecular cyclization. Duan and Mathey demonstrated conversion of *ortho*-diphenylphosphinophenylalkyne to a benzophospholide anion using excess Li as a reductant, which presumably proceeded through the cleavage of the first P–Ph bond, 5-*endo*-*dig* cyclization, and subsequent reduction of the second P–Ph bond (Scheme 4.3a).[12] Trapping of the benzophospholide with an electrophile such as MeI followed by oxidation with H_2O_2 leads to a 2-substituted benzophosphole oxide. They also developed an intramolecular arylphosphination reaction of *o*-diphenylphosphinophenylalkynes with a $Pd(OAc)_2$/CuI bimetallic catalyst system, which affords 2,3-substituted benzophospholes via P–Ph bond cleavage (Scheme 4.3b).[13]

Scheme 4.3. Benzophospholes synthesis from *ortho*-diphenylphosphinophenylalkynes



Benzophosphole synthesis involving electrophilic trapping of organometallic intermediates with phosphorus electrophiles has been pioneered by Tsuchiya [14] and extended by Matano and co-workers.[15] They demonstrated the synthetic utility of 2-bromobenzophospholes, which are prepared in a few steps from linear precursors via dilithio species as key intermediates (Scheme 4.4). Further transformations using Stille, Suzuki–Miyaura, Heck, and Sonogashira coupling reactions allowed them to access a variety of 2-substituted benzophosphole derivatives. The electronic and steric effects on the optical and photophysical properties of the phospholes have also been investigated.

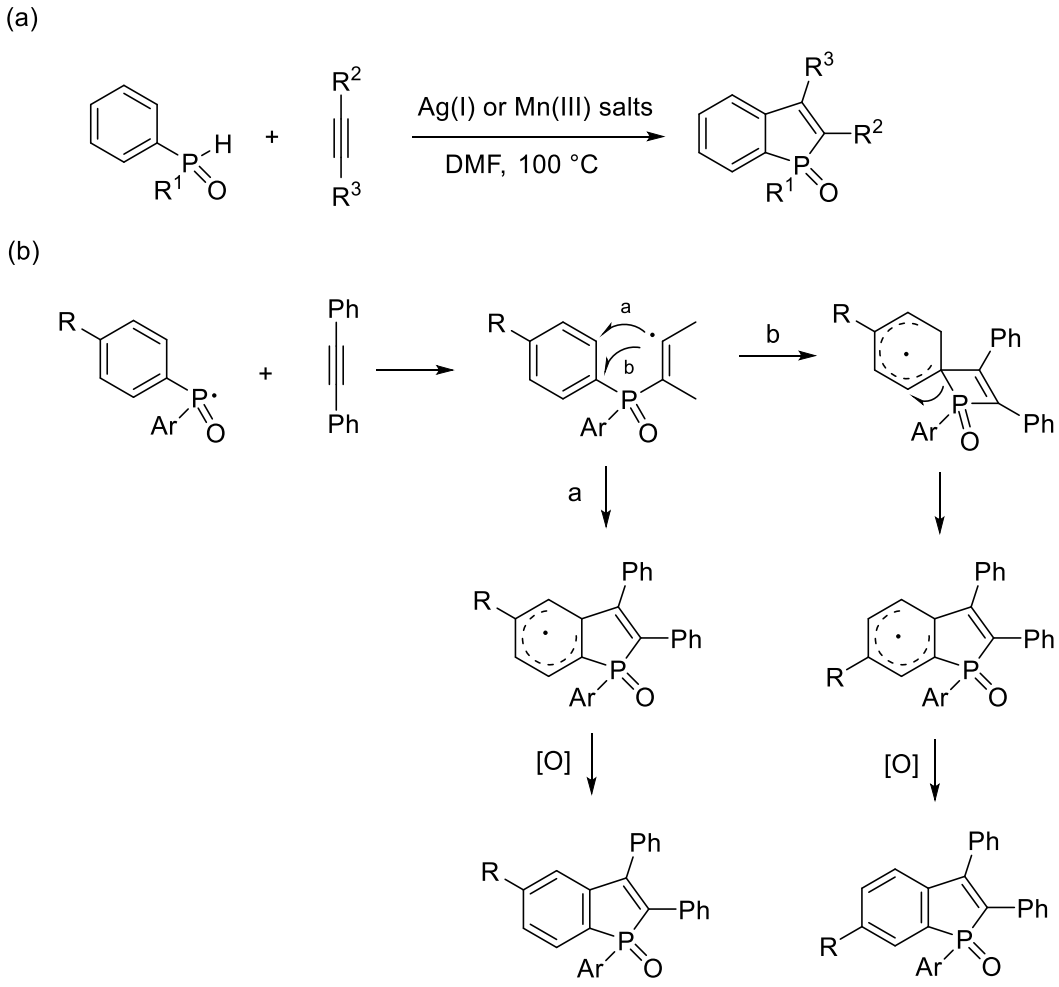
Scheme 4.4. Benzophosphole synthesis from dilithio intermediates.



The feasibility of the intermolecular annulation approach to benzophospholes has also been demonstrated by several research groups. In 2013, Satoh/Miura[16] and Duan[17] independently reported the synthesis of benzophosphole oxides via dehydrogenative coupling of secondary arylphosphine oxides and internal alkynes mediated by silver or manganese salts (Scheme 4.5a). This approach was later extended by Ackermann[18] and Gao. [19] Tang and coworkers demonstrated that the similar reaction could also be promoted

by using copper as catalyst and TBHP as a stoichiometric oxidant.[20] Regardless of the high atom efficiency and the ready availability of the starting materials, this dehydrogenative annulation has an intrinsic limitation with respect to regioselectivity. For example, the reaction of a *para*-substituted arylphosphine oxide results in a mixture of 5- and 6-substituted benzophosphole oxides with moderate and unpredictable ratio (Scheme 4.5b). This observation was rationalized by a mechanism involving radical intermediates. Thus, a P-centered radical generated by oxidation of the P-H bond with Ag(I) or Mn(III) adds to the alkyne to form an alkenyl radical. The alkenyl radical may undergo cyclization to afford a 5-membered fused bicyclic intermediate, which leads to the 5-substituted benzophospholes upon oxidation (Scheme 4.5b). Alternatively, the alkenyl radical may form a 4-membered spirocyclic intermediate, which may undergo rearrangement via P–C bond cleavage, leading to the 6-substituted isomer. Besides this particular problem, the reaction of an unsymmetrical diarylphosphine oxide becomes even more complicated, because both of the aryl groups have chance to participate in the annulation, often with unpredictable regioselectivity.

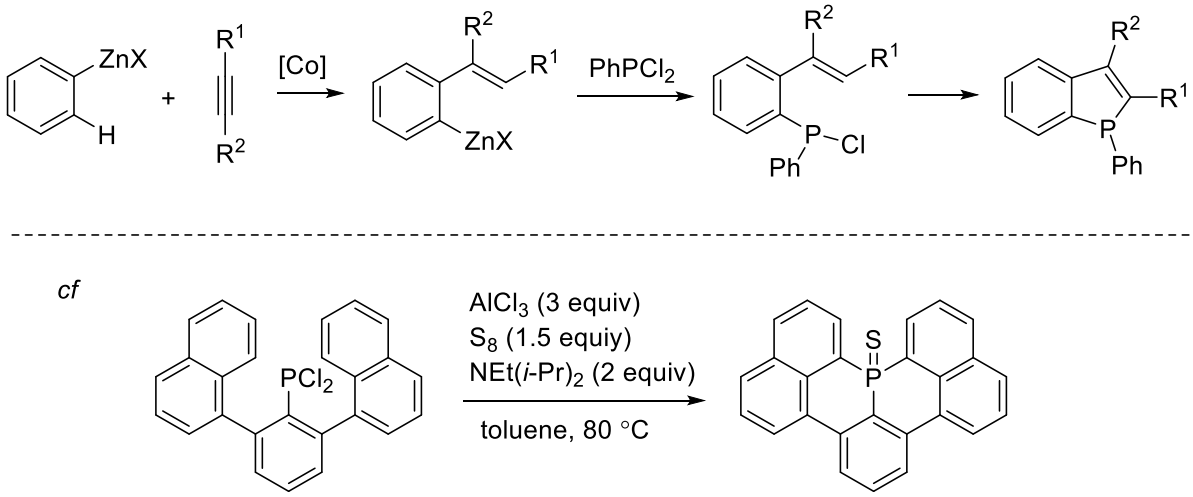
Scheme 4.5. Benzophospholes synthesis via oxidative annulation of arylphosphine oxides with alkynes.



With the above analysis and discussion, it would be fair to conclude that the existing methods do not allow for expedient construction of benzophospholes bearing diverse substituents on the benzo moiety. This is because of the necessity of multistep preparation of each starting material for the cyclization approach, and because of the intrinsic regioselectivity problem for the annulation approach. In addition, many of the existing methods would have difficulty in the modification of the P-substituent of benzophosphole, as the phosphorus moiety is installed in the early stage. In order to address these problems, we conjectured that the *ortho*-alkenylarylzinc species would

serve as a viable and useful intermediate for benzophosphole synthesis (Scheme 4.6). Thus, upon trapping of this species with dichlorophenylphosphine, the resulting intermediate would undergo intramolecular phospha-Friedel–Crafts type cyclization to produce the desired benzophosphole product. This mechanistic scenario appeared feasible in light of literature examples of intramolecular phospha-Friedel cyclization, such as the synthesis of a fused triarylphosphine derivative via cyclization of a dichloroarylphosphine bearing 2-napththyl groups on the *ortho*-positions mediated by a reaction system comprising aluminum chloride, sulfur, and a bulky amine base.[21] We report here the development of modular one-pot methods for benzophosphole synthesis from arylzinc reagents, alkynes, and chlorophosphines.

Scheme 4.6. Proposed transformation of *ortho*-alkenylarylzinc species into benzophosphole.

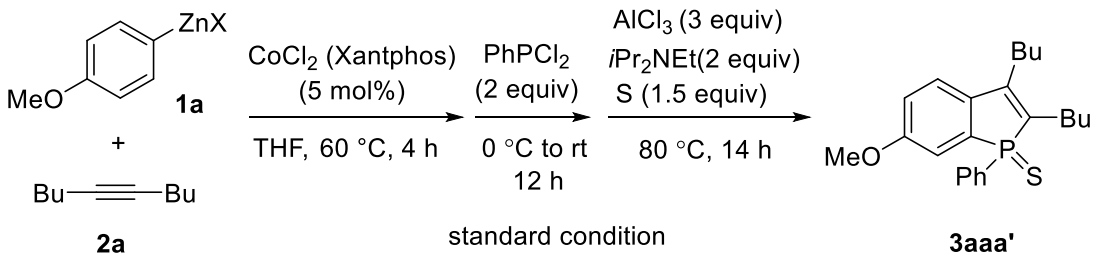


4.2 Results and discussion

Our initial study was focused on the synthesis of a benzophosphole sulfide from *ortho*-alkenylarylzinc reagent generated by [$CoCl_2$(Xantphos)]-catalyzed addition of 4-

methoxyphenylzinc reagent **1a** to 5-decyne **2a** (Table 4.1). The reaction of the zinc species with dichlorophenylphosphine (room temperature, 12 h) was followed by treatment with aluminum trichloride, sulphur and ethyldiisopropylamine in toluene (80 ℃, 14 h), which afforded the desired benzophosphole **3aaa'** in 12% GC yield (entry 1). The addition of a catalytic amount of CuI (20 mol%) together with $PhPCl_2$ improved the yield to 24% (entry 2). Notably, $AlCl_3$ and the amine proved non-essential but rather slightly detrimental to the reaction (entry 3). With 20 mol% of CuI in the absence of $AlCl_3$, the yield was further improved to 38% (entry 4).

Table 4.1. Initial study on the reaction conditions.



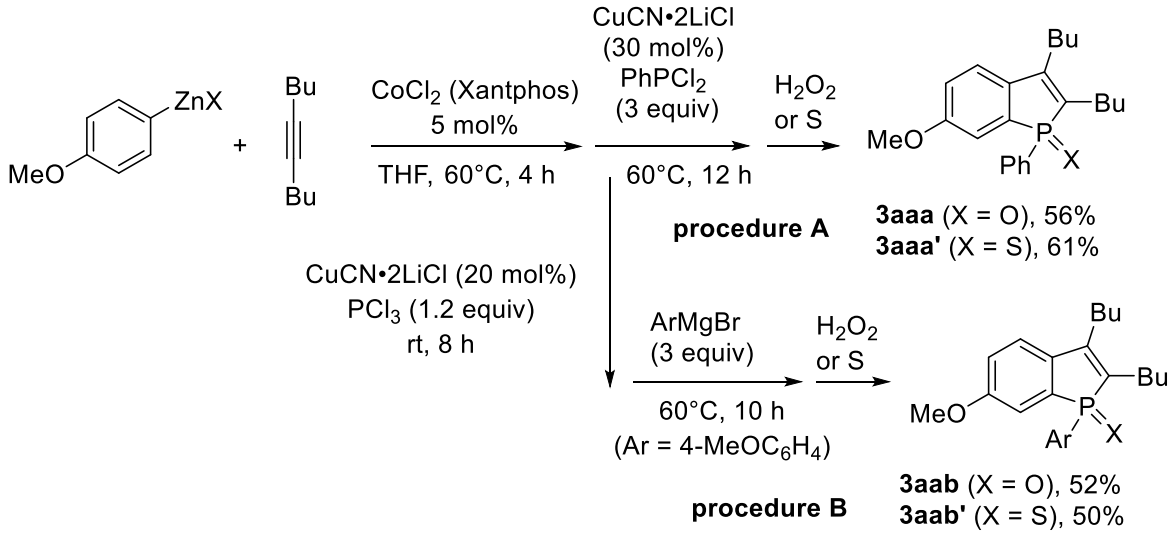
Entry	Deviation from standard condition	Yield[a]
1	None	12
2	CuI (20 mol%) was added with $PPhCl_2$	24
3	Without $AlCl_3$ and iPr_2NEt	26
4	Without $AlCl_3$ and iPr_2NEt, with CuI (20 mol%)	38

[a] The yields was determined by GC using *n*-tridecane as an internal standard.

Further extensive screening of the reaction conditions such as the copper catalyst, the temperature, and the reaction stoichiometry allowed us to determine the optimum conditions as follows: The reaction of the *ortho*-alkenylarylzinc species with 3 equiv of $PhPCl_2$ in the presence of 30 mol% of CuCN•2LiCl (60 ℃, 12 h) was followed by

treatment with hydrogen peroxide or sulfur powder, affordeding benzophosphole oxide **3aaa** or sulfide **3aaa'**, respectively, in ca. 60% yield (Scheme 4.7, procedure A). Furthermore, the same zinc intermediate may also be treated sequentially with PCl_3 (1.2 equiv) in the presence of CuCN•2LiCl (20 mol%) (rt, 8 h), 4-methoxyphenylmagnesium bromide (60 ℃, 10 h), and hydrogen peroxide or sulfur to afford different benzophosphole oxide **3aab** or sulfide **3aab'**, respectively, in a respectable yield of ca. 50% (procedure B). Thus, the latter procedure offers an opportunity to modify the P-substituent on the benzophosphole.

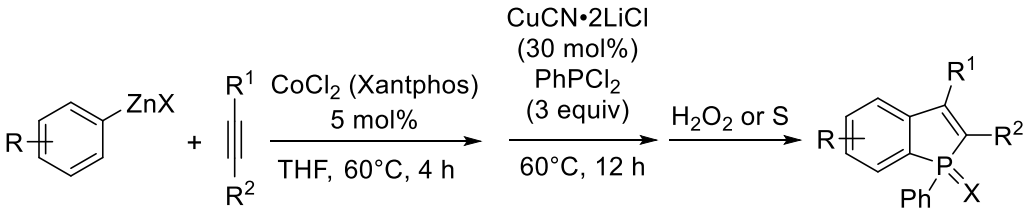
Scheme 4.7. Optimized reaction conditions for benzophosphole synthesis.

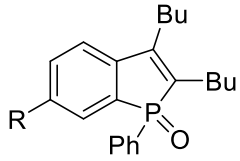


We first explored the scope of the benzophosphole synthesis by using procedure A. A wide variety of aryl and hetero-arylzinc reagents, including those bearing electron-neutral, electron-donating, and electron-withdrawing substituents, could be coupled with 5-decyne and $PhPCl_2$ to furnish the corresponding benzophospholes **3baa**-**3paa** in moderate to good yields. Of note are the hydroxy- and acetyl substituted derivative **3gaa** and **3kaa**, which could be synthesized in one-pot from arylzinc reagents bearing protected

hydroxy and acetyl groups, respectively. The regioselectivity of the product was influenced by the cobalt-catalyzed migratory arylzincation step. For 5-methyl benzophosphole (**3naa**), it was controlled by the steric effect, while for products bearing 6,7-methylenedioxy (**3laa'**, **3laa"**) and 6,7-difluoro groups, the regiochemistry may be explained by the directing effect of the oxygen and fluorine atoms. Note that the benzophosphole selenide **3laa"** was obtained by using selenium in the last step of the multicomponent coupling. Besides 5-decyne, other internal alkynes such as dialkylalkyne, arylalkylalkyne, and alkylsilylalkyne could be coupled with randomly chosen arylzinc reagents and $PhPCl_2$ to afford the corresponding benzophospholes in respectable yields. Note that the reaction of 1-trimethylsilyl-1-propyne was accompanied by spontaneous loss of the trimethylsilyl group, thus affording 2-unsubstituted benzophosphole sulfide **3aga'**. The diphenyl substituted benzophosphole could also be synthesized, albeit in a lower yield (**3bha**).

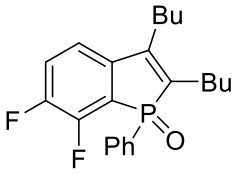
Scheme 4.8. Benzophosphole derivatives synthesized by procedure A.



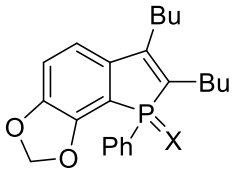


3baa (R = H), 49%
3caa (R = Ph), 68%
3daa (R = $SiMe_3$), 67%
3eaa (R = NPh_2), 41%
3faa (R = NBn_2), 47%

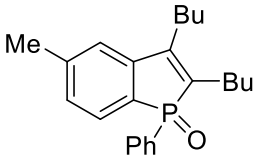
3gaa (R = OH), 45%[a]
3haa (R = F), 67%
3iaa (R = CF_3), 76%
3jaa (R = CO_2Et), 60%
3kaa (R = Ac), 56%[b]



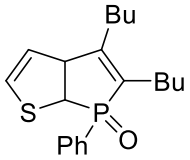
3maa, 56%



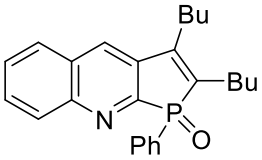
3laa' (X = S), 55%
3laa" (X = Se), 40%



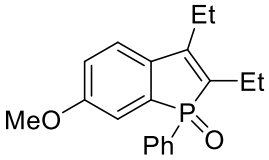
3naa, 60%



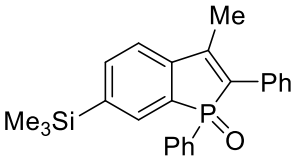
3oaa, 48%



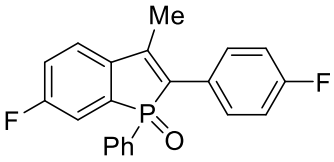
3paa, 52%



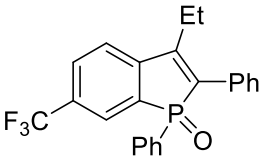
3aba, 52%



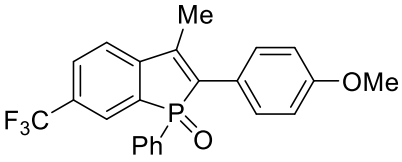
3cca, 37%



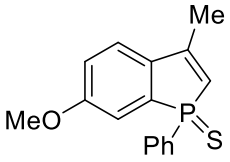
3hda, 38%



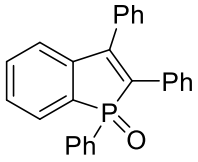
3ifa, 56%



3iea, 36%



3aga', 35%[c]

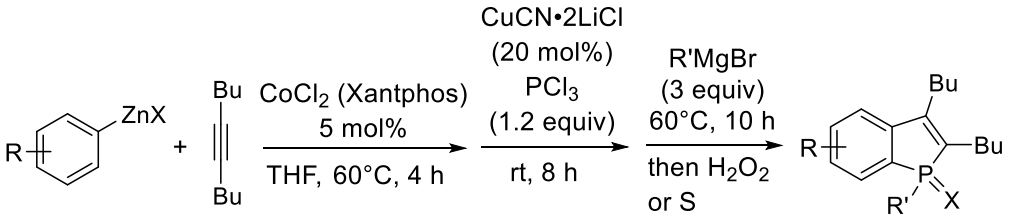


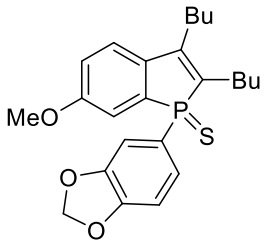
3bha, 39%

[a] The hydroxy group of the arylzinc reagent was protected using a Boc group. [b] The acetyl moiety of the arylzinc reagent was protected in the form of *p*-anisidine imine. [c] 1-trimethylsilyl-1-propyne was used.

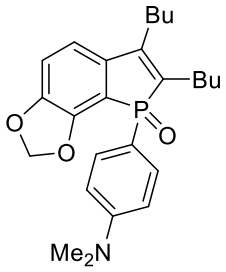
The greatest merit of protocol B is that it allows rapid construction of benzophosphole derivatives bearing a wide variety of substituents on the phosphorus atom (Scheme 4.9). Indeed, the coupling of arylzinc reagent (**1a**, **1h** or **1l**), 5-decyne **2a**, and PCl_3 was followed by the addition of various Grignard reagents and then hydrogen peroxide or sulfur powder, thus furnishing benzophosphole oxides or sulfides bearing electron-rich aryl, electron-poor aryl, bulky aryl, and primary and secondary alkyl groups on the phosphorus atom in decent yields ranging from 25% to 43%.

Scheme 4.9. Benzophosphole derivatives synthesized by procedure B.

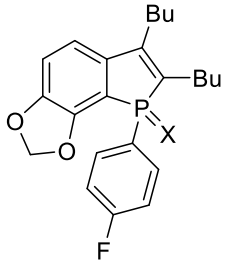




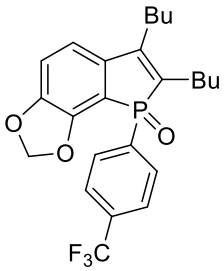
3aac', 41%



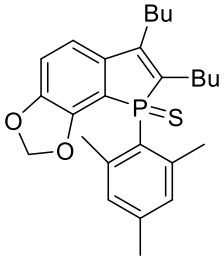
3lad, 40%



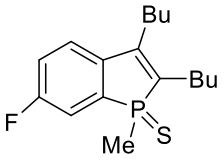
3lae (X = O), 34%
3lae' (X = S), 41%



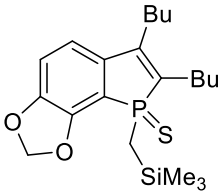
3laf, 25%[a]



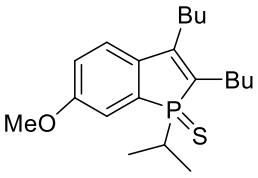
3lag', 43%



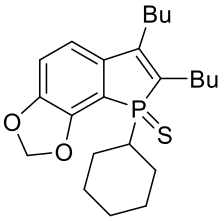
3hah', 43%[b]



3lai', 35%



3aaj', 42%



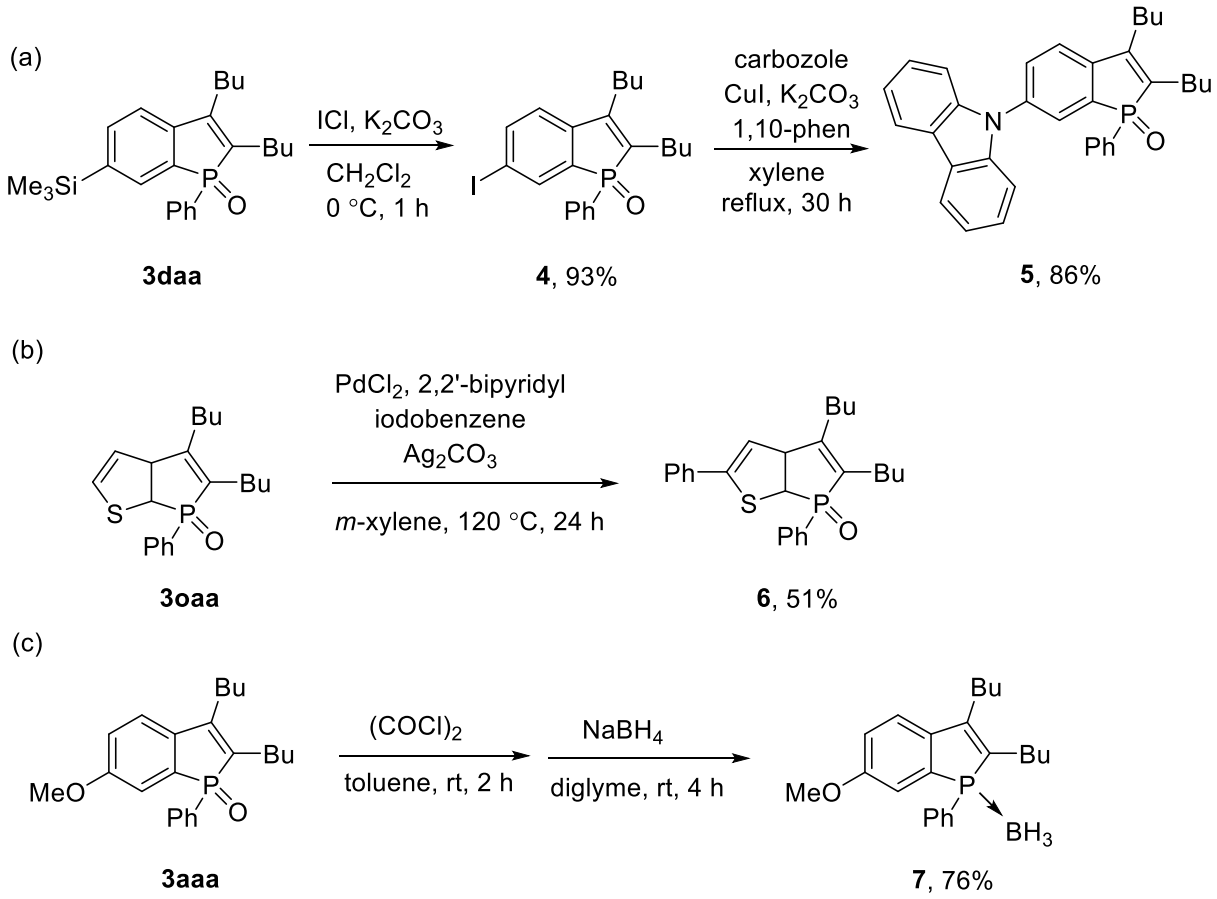
3lak', 40%

[a] 4-Trifluoromethylphenyllithium was used instead of the corresponding Grignard reagent. [b] The reaction with PCl_3 was performed at 60 ℃.

The functional groups on the benzophosphole derivatives synthesized by the present approach serve as footholds for further synthetic manipulation of the π-system as demonstrated by examples shown in Scheme 4.10. The carbazole-conjugated

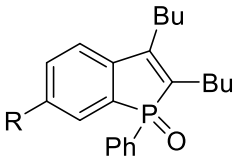
benzophosphole oxide **5** was obtained in two steps via iododesilylation with ICl and copper-catalyzed C–N coupling reaction from trimethylsilyl-substituted derivative **3daa** (Scheme 4.10a).[22] C5-selective direct phenylation of the phosphole-embedded thiophene **3oaa** with iodobenzene was achieved using the palladium/2,2'-bipyridyl catalytic system developed by Itami and coworkers (Scheme 4.10b).[23] The benzophosphole oxide **3aaa** could be directly converted to the corresponding benzophosphole–borane adduct **7** in a good yield by using the conditions reported by Gilheany and coworkers (Scheme 4.10c).[24]

Scheme 4.10. Transformation of benzophosphole derivatives.

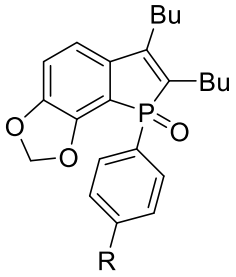


Most of the benzophosphole derivatives (particularly oxides) reported herein showed fluorescence in solution, as was discovered by the earlier studies.[9,10,11] Since the benzophosphole oxides can be regarded as a styrene derivative bridged by an electron-withdrawing phosphoryl group, the substituents on the 6-position and phosphorus atom should have some significant influence on the photophysical properties. With this in mind, we selected some benzophosphole oxides and measured the UV/Vis absorption and emission spectra, which are summarized in Table 4.2. The compounds studied here exhibited longest absorption maxima (λ_{abs}) in a range of 317-394 nm and emission maxima (λ_{em}) in a range of 385-484 nm. Expectedly, the presence of electron-donating dibenzylamino and diphenylamino groups induced a significant red-shifted both on the absorption and emission maxima (entries 4 and 5), while no significant shift was observed with electron-withdrawing trifluoromethyl and ethoxycarbonyl groups (entries 7 and 8). The compounds bearing phenyl, amino, and carbazolyl substituents on the 6-position gave higher fluorescence quantum yields (entries 3-5 and 9). The effect of the substituent on the phosphorus atom was also noteworthy. Weakly fluorescence was observed for **3lad** which bears a 4-dimethylaminophenyl group (entry 10) while **3lae** and **3laf** bearing 4-fluorophenyl and 4-trifluoromethylphenyl groups, exhibited intense blue emission and high quantum yields, respectively (entries 11 and 12). The sulfur analogue **3aaa'** was almost non-fluorescent (entry 13) and the borane adduct 7 was moderately emmisive (entry 14). The diphenyl analogue also exhibited distinct elongation of λ_{abs} and λ_{em} with a good quantum yield (entry 15).

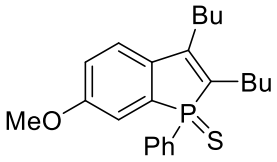
Table 4.2. Photophysical properties of selected benzophosphole derivatives.[a]



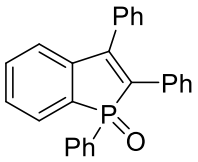
3baa: R = H
3aaa: R = OMe
3caa: R = Ph
3eaa: R = NBn_2
3faa: R = NPh_2
3haa: R = F
3iaa: R = CF_3
3jaa: R = CO_2Et
5: R = carbozolyl



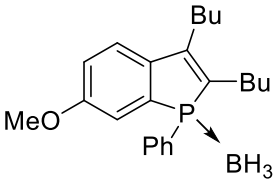
3lad: R = NMe_2
3lae: R = F
3laf: R = CF_3



3aaa'



3bha



7

Entry	Cmpd[b]	λ_{abs} [nm]	ε [$cm^{-1}M^{-1}$]	λ_{em} [nm][c]	Φ_F[d]
1	**3baa**	320	1870	387	0.11[e]
2	**3aaa**	343	2270	434	0.39
3	**3caa**	336	5490	415	0.77
4	**3eaa**	383	3180	479	0.57
5	**3faa**	394	6400	484	0.63
6	**3haa**	329	1170	412	0.15[e]
7	**3iaa**	317	2460	385	0.12[e]
8	**3jaa**	324	4700	388	0.21
9	**5**	340	9250	447	0.94
10	**3lad**	347	5420	447	0.05
11	**3lae**	350	4740	420	0.86
12	**3laf**	350	3870	422	0.93
13	**3aaa'**	344	1310	428	0.001
14	**7**	330	3540	420	0.25
15	**3bha**	344	7733	449	0.66

[a] In CH_2Cl_2. [b] Longest wavelength UV/Vis absorption maxima are shown. [c] Excited at λ=350 nm. [d] Unless otherwise noted, fluorescence quantum yields were determined using quinine sulfate as a standard. [e] Anthracene was used as a standard.

4.3 Conclusion

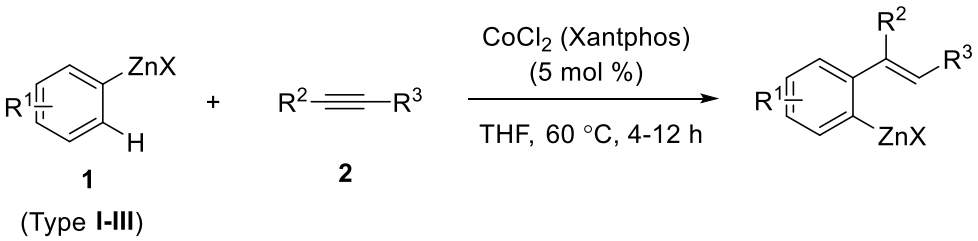
In summary, we have developed a highly modular, one-pot multicomponent approach for the construction of benzophosphole derivatives based on the combination of cobalt-catalyzed migratory arylzincation of alkyne, copper-catalyzed P–C coupling, intramolecular electrophilic phospha-cyclization, and oxidation. Thus, readily available starting materials, that is, an arylzinc reagent, an alkyne, dichlorophenylphosphine (or phosphorus trichloride and a Grignard reagent), and an oxidant (hydrogen peroxide, sulfur, or selenium) can be sequentially coupled to furnish a benzo[*b*]phosphole derivative in an expedient manner. The present method allows us to systematically investigate (and then fine-tune) substituent effects on the optoelectronic properties of these heterocyclic scaffolds.

4.4 Experimental section

Procedures for the preparation of arylzinc reagent and its addition to alkyne

An arylzinc reagent was prepared either by transmetalation between $ZnCl_2$•TMEDA and the corresponding aryl Grignard reagent (type **I** reagent) or by Co–Xantphos-catalyzed insertion of Zn•LiCl into the corresponding aryl bromide (type **II**/**III** reagents).[25] The resulting arylzinc reagent was subjected to the reaction with an alkyne under Co–Xantphos catalysis as described previously,[26] thus furnishing an *ortho*-alkenylarylzinc reagent (Scheme 4.11). Below are brief descriptions of three different procedures used in the present study.

Scheme 4.11. Preparation of *ortho*-alkenylarylzinc reagent.



Type **I**: $ZnCl_2$•TMEDA + ArMgBr
Type **II**: ArBr + Zn•LiCl, 5 mol % $CoCl_2$-Xantphos
Type **III**: ArBr + Zn•LiCl, 5 mol % $CoCl_2$-Xantphos, then Me_3SiCH_2MgCl

Type I Reagent: In a 10 mL Schlenk tube was placed $ZnCl_2$•TMEDA (138.9 mg, 0.55 mmol). The Schlenk tube was submerged in an ice bath for 15 min, followed by dropwise addition of a THF solution of an aryl Grignard reagent (0.55 mmol). The resulting mixture was stirred for 1 h at 0 ℃ and then allowed to room temperature. To the arylzinc reagent was added Xantphos (14.5 mg, 0.025 mmol), $CoCl_2$ (3.2 mg, 0.025 mmol) followed by stirring for 5 min and addition of an alkyne (0.5 mmol). The resulting mixture was stirred at 60 ℃, monitored by TLC until starting materials were consumed, and then allowed to cool to room temperature.

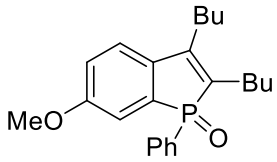
Type II Reagent: Anhydrous LiCl (42.4 mg, 1 mmol) was placed in a 10 mL Schlenk tube, dried under vacuum (1 mbar) at 150 ℃ for 20 min, and cooled down to room temperature under N_2. To the Schlenk tube was added zinc powder (98.1 mg, 1.5 mmol), and the heterogeneous mixture of Zn and LiCl was dried under vacuum (1 mbar) at 150 ℃ for 15 min. While cooling to room temperature, the reaction tube was evacuated and backfilled with N_2 for three times. The mixture was suspended with THF (1 mL), followed by the activation of Zn with $BrCH_2CH_2Br$ (5 μL, 0.05 mmol) and Me_3SiCl (1.5 μL, 0.01 mmol) and stirring for 5 min. Then Xantphos (28.9 mg, 0.05 mmol) and $CoCl_2$ (6.5 mg, 0.05 mmol) were added sequentially. After stirring for additional 5 min, an aryl

halide (1 mmol) was added in one portion. The reaction was stirred at room temperature. After complete conversion of the starting material, alkyne (0.50 mmol) was added to the arylzinc reagent. The resulting solution was stirred at 60 ℃, monitored by TLC until starting materials were consumed, and then allowed to cool to room temperature.

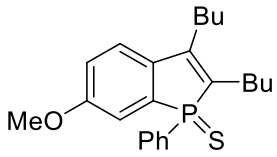
Type III Reagent: To a Type **II** arylzinc reagent (vide supra) was added a THF solution of Me_3SiCH_2MgCl (0.9 mmol) dropwise at 0 ℃. The resulting solution was stirred for 1 h at 0 ℃, followed by addition of an alkyne (0.50 mmol). The resulting solution was stirred at 60 ℃, monitored by TLC until starting materials were consumed, and then allowed to cool to room temperature.

Synthesis of benzophosphole derivatives

General procedure for protocol A: To an *ortho*-alkenylarylzinc reagent prepared on a 0.5 mmol scale according to Scheme 4.11 (vide supra) was added a THF solution of CuCN•2LiCl (0.15 mmol), $PhPCl_2$ (1.5 mmol) at 0 ℃, the resulting solution was stirred at 60 ℃ for 12 h followed by cooling. For benzophosphole oxides, an aqueous solution of H_2O_2 (ca. 30%, a few drops) was added at 0 ℃, and the mixture was stirred at room temperature for 0.5 h; for benzophosphole sulfides and selenides, the mixture was added sulfur powder (64.0 mg, 2 mmol) or selenium powder (156.7 mg, 2 mmol) and was stirred at room temperature for 4 h. The reaction mixture was diluted with ethyl acetate (5 mL) and filtered through a pad of silica gel with additional ethyl acetate (15 mL) as the eluent. The filtrate was washed with water (10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product.

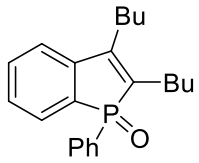


2,3-Dibutyl-6-methoxy-1-phenyl-1*H*-phosphindole 1-oxide (3aaa): Type **I** arylzinc reagent was used; Yellow oil (56% yield, eluent = hexane/EtOAc (2:1)); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 – 7.60 (m, 2H), 7.46 – 7.43 (m, 1H), 7.37 – 7.33 (m, 2H), 7.23 (dd, *J* = 8.4, 3.6 Hz, 1H), 7.09 (d, *J* = 9.6 Hz, 1H), 6.93 (dd, *J* = 8.4, 2.0 Hz, 1H), 3.71 (s, 3H), 2.54 (t, *J* = 7.6 Hz, 2H), 2.48 – 2.38 (m, 1H), 2.26 – 2.16 (m, 1H), 1.56 – 1.49 (m, 2H), 1.47 – 1.38 (m, 2H), 1.36 – 1.28 (m, 2H), 1.26 – 1.16 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H), 0.73 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0 (d, J_{PC} = 13.3 Hz), 150.7 (d, J_{PC} = 19.7 Hz), 136.0 (d, J_{PC} = 28.9 Hz), 134.0 (d, J_{PC} = 104.8 Hz), 131.9 (d, J_{PC} = 97.2 Hz), 131.8 (d, J_{PC} = 2.4 Hz), 131.0 (d, J_{PC} = 10.5 Hz), 129.9 (s), 128.7 (d, J_{PC} = 12.0 Hz), 122.4 (d, J_{PC} = 13.3 Hz), 117.8 (s), 114.4 (d, J_{PC} = 10.7 Hz), 55.6 (s), 31.1 (d, J_{PC} = 1.4 Hz), 30.6 (d, J_{PC} = 1.3 Hz), 26.4 (d, J_{PC} = 13.6 Hz), 25.7 (d, J_{PC} = 10.9 Hz), 23.0 (s), 22.8 (s), 13.9 (s), 13.6 (s); ^{31}P NMR (162 MHz, $CDCl_3$): δ 39.9; HRMS (ESI) Calcd for $C_{23}H_{30}O_2P$ $[M + H]^+$ 369.1983, found 369.1984.

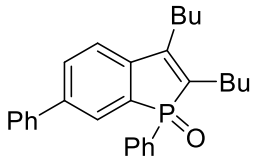


2,3-Dibutyl-6-methoxy-1-phenyl-1*H*-phosphindole 1-sulfide (3aaa'): Type **I** arylzinc reagent was used; Colorless gum (61% yield, eluent = hexane/EtOAc (20:1)); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 – 7.72 (m, 2H), 7.48 – 7.44 (m, 1H), 7.40 – 7.32 (m, 3H), 7.10 (dd, *J* = 11.6, 2.4 Hz, 1H), 7.02 – 6.99 (m, 1H), 3.76 (s, 3H), 2.63 (t, *J* = 7.6 Hz, 2H), 2.59 – 2.51 (m, 1H), 2.38 – 2.26 (m, 1H), 1.67 – 1.57 (m, 2H), 1.54 – 1.43 (m, 2H), 1.31 –

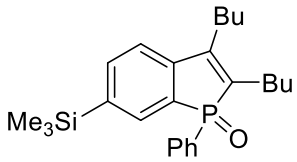
1.17 (m, 4H), 1.00 (t, J = 7.2 Hz, 3H), 0.74 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1 (d, J_{PC} = 14.0 Hz), 149.0 (d, J_{PC} = 16.3 Hz), 137.8 (d, J_{PC} = 88.8 Hz), 136.5 (d, J_{PC} = 25.9 Hz), 134.2 (d, J_{PC} = 78.8 Hz), 131.6 (d, J_{PC} = 3.0 Hz), 130.9 (d, J_{PC} = 11.6 Hz), 130.0 (d, J_{PC} = 75.1 Hz), 128.5 (d, J_{PC} = 12.4 Hz), 122.8 (d, J_{PC} = 12.5 Hz), 117.8 (d, J_{PC} = 18.0 Hz), 113.5 (d, J_{PC} = 12.1 Hz), 55.6 (s), 31.5 (d, J_{PC} = 1.6 Hz), 30.8 (d, J_{PC} = 1.9 Hz), 26.9 (d, J_{PC} = 13.0 Hz), 25.4 (d, J_{PC} = 12.8 Hz), 23.1 (s), 22.8 (s), 14.0 (s), 13.6 (s); ^{31}P NMR (162 MHz, $CDCl_3$): δ 47.8; HRMS (ESI) Calcd for $C_{23}H_{30}OPS$ $[M + H]^+$ 385.1755, found 385.1758.



2,3-Dibutyl-1-phenyl-1*H*-phosphindole 1-oxide (3baa): Type **I** arylzinc reagent was used; Yellow oil (49% yield, eluent = hexane/EtOAc (2:1)); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 – 7.58 (m, 2H), 7.52 – 7.41 (m, 3H), 7.35 – 7.31 (m, 3H), 7.23 – 7.20 (m, 1H), 2.56 (t, J = 7.6 Hz, 2H), 2.51 – 2.41 (m, 1H), 2.29 – 2.18 (m, 1H), 1.58 – 1.50 (m, 2H), 1.48 – 1.37 (m, 2H), 1.33 – 1.28 (m, 2H), 1.25 – 1.13 (m, 2H), 0.94 (t, J = 7.2 Hz, 3H), 0.73 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.6 (d, J_{PC} = 19.8 Hz), 143.6 (d, J_{PC} = 29.1 Hz), 134.3 (d, J_{PC} = 95.7 Hz), 132.8 (s), 132.0 (d, J_{PC} = 96.4 Hz), 131.9 (d, J_{PC} = 2.1 Hz), 130.9 (d, J_{PC} = 10.6 Hz), 130.1 (d, J_{PC} = 100.4 Hz), 128.7 (d, J_{PC} = 12.0 Hz), 128.6 (d, J_{PC} = 9.0 Hz), 128.2 (d, J_{PC} = 10.5 Hz), 121.3 (d, J_{PC} = 11.2 Hz), 30.9 (s), 30.6 (s), 26.3 (d, J_{PC} = 13.2 Hz), 25.8 (d, J_{PC} = 10.6 Hz), 23.0 (s), 22.8 (s), 13.9 (s), 13.6 (s); ^{31}P NMR (162 MHz, $CDCl_3$): δ 40.1; HRMS (ESI) Calcd for $C_{22}H_{28}OP$ $[M + H]^+$ 339.1878, found 339.1873.

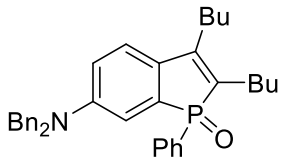


2,3-Dibutyl-1,6-diphenyl-1*H*-phosphindole 1-oxide (3caa): Type **II** arylzinc reagent was used; Yellow oil (68% yield, eluent = hexane/EtOAc (2:1)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 10.4, 1.6 Hz, 1H), 7.76 – 7.68 (m, 3H), 7.57 – 7.55 (m, 2H), 7.52 – 7.39 (m, 6H), 7.35 – 7.31 (m, 1H), 2.67 (t, *J* = 7.6 Hz, 2H), 2.61 – 2.50 (m, 1H), 2.38 – 2.27 (m, 1H), 1.69 – 1.60 (m, 2H), 1.57 – 1.50 (m, 2H), 1.48 – 1.37 (m, 2H), 1.36 – 1.24 (m, 2H), 1.03 (t, *J* = 7.2 Hz, 3H), 0.82 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.3 (d, J_{PC} = 19.6 Hz), 142.6 (d, J_{PC} = 28.9 Hz), 141.2 (d, J_{PC} = 10.4 Hz), 139.8 (s), 134.8 (d, J_{PC} = 95.8 Hz), 133.3 (d, J_{PC} = 103.6 Hz), 131.9 (d, J_{PC} = 2.7 Hz), 131.3 (d, J_{PC} = 1.6 Hz), 131.0 (d, J_{PC} = 10.5 Hz), 130.4 (d, J_{PC} = 95.8 Hz), 128.9 (s), 128.7 (d, J_{PC} = 12.0 Hz), 127.8 (s), 127.3 (d, J_{PC} = 10.0 Hz), 126.9 (s), 121.7 (d, J_{PC} = 11.7 Hz), 31.0 (d, J_{PC} = 1.5 Hz), 30.7 (d, J_{PC} = 1.6 Hz), 26.4 (d, J_{PC} = 13.1 Hz), 26.0 (d, J_{PC} = 10.8 Hz), 23.1 (s), 22.9 (s), 14.0 (s), 13.7 (s); ^{31}P NMR (162 MHz, $CDCl_3$): δ 39.5; HRMS (ESI) Calcd for $C_{28}H_{32}OP$ $[M + H]^+$ 415.2191, found 415.2191.

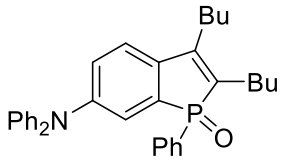


2,3-Dibutyl-1-phenyl-6-(trimethylsilyl)-1*H*-phosphindole 1-oxide (3daa): Type **II** arylzinc reagent was used; Pale yellow oil (67% yield, eluent = hexane/EtOAc (2:1)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.63 (m, 4H), 7.48 – 7.45 (m, 1H), 7.40 – 7.32 (m, 3H), 2.59 (t, *J* = 7.6 Hz, 2H), 2.51 – 2.45 (m, 1H), 2.29 – 2.23 (m, 1H), 1.59 – 1.55 (m, 2H), 1.49 – 1.41 (m, 2H), 1.36 – 1.19 (m, 4H), 0.96 (t, *J* = 7.2 Hz, 3H), 0.76 (t, *J* = 7.2 Hz, 3H),

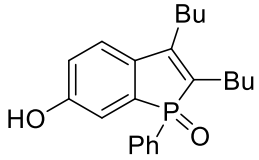
0.20 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.4 (d, J_{PC} = 20.0 Hz), 144.2 (d, J_{PC} = 29.3 Hz), 141.0 (d, J_{PC} = 7.5 Hz), 138.0 (s), 134.9 (d, J_{PC} = 95.1 Hz), 133.1 (d, J_{PC} = 8.6 Hz), 131.8 (d, J_{PC} = 2.3 Hz), 131.0 (d, J_{PC} = 10.5 Hz), 130.8 (s), 130.0 (s), 128.6 (d, J_{PC} = 12.0 Hz), 120.6 (d, J_{PC} = 10.6 Hz), 31.0 (d, J_{PC} = 1.3 Hz), 30.6 (d, J_{PC} = 1.3 Hz), 26.3 (d, J_{PC} = 13.1 Hz), 25.8 (d, J_{PC} = 10.7 Hz), 23.0 (s), 22.8 (s), 13.9 (s), 13.6 (s), -1.2 (s); ^{31}P NMR (162 MHz, $CDCl_3$): δ 40.2; HRMS (ESI) Calcd for $C_{25}H_{36}OPSi$ $[M + H]^+$ 411.2273, found 411.2275.



2,3-Dibutyl-6-(dibenzylamino)-1-phenyl-1*H*-phosphindole 1-oxide (3eaa): Type **II** arylzinc reagent was used; Yellow oil (47% yield, eluent = hexane/EtOAc (2:1)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.60 (m, 2H), 7.50 – 7.46 (m, 1H), 7.40 – 7.35 (m, 2H), 7.31 – 7.21 (m, 6H), 7.18 – 7.13 (m, 5H), 7.07 (dd, *J* = 11.4, 2.4 Hz, 1H), 6.74 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.62 (d, *J* = 4.4 Hz, 4H), 2.54 (t, *J* = 7.6 Hz, 2H), 2.50 – 2.40 (m, 1H), 2.30 – 2.18 (m, 1H), 1.59 – 1.53 (m, 2H), 1.50 – 1.30 (m, 4H), 1.29 – 1.22 (m, 2H), 0.98 (t, *J* = 7.6 Hz, 3H), 0.79 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.9 (d, J_{PC} = 20.2 Hz), 149.4 (d, J_{PC} = 12.5 Hz), 137.6 (s), 134.0 (d, J_{PC} = 103.5 Hz), 132.3 (s), 131.9 (d, J_{PC} = 6.6 Hz), 131.4 (d, J_{PC} = 2.7 Hz), 131.0 (d, J_{PC} = 10.4 Hz), 129.7 (d, J_{PC} = 97.9 Hz), 128.7 (s), 128.5 (d, J_{PC} = 11.8 Hz), 127.1 (s), 126.6 (s), 122.3 (d, J_{PC} = 13.0 Hz), 115.0 (d, J_{PC} = 1.3 Hz), 113.4 (d, J_{PC} = 11.4 Hz), 54.1 (s), 31.4 (d, J_{PC} = 1.5 Hz), 30.7 (d, J_{PC} = 1.6 Hz), 26.4 (d, J_{PC} = 13.6 Hz), 25.6 (d, J_{PC} = 11.0 Hz), 23.1 (s), 22.8 (s), 13.9 (s), 13.7 (s); ^{31}P NMR (162 MHz, $CDCl_3$): δ 40.6; HRMS (ESI) Calcd for $C_{36}H_{41}NOP$ $[M + H]^+$ 534.2926, found 534.2932.

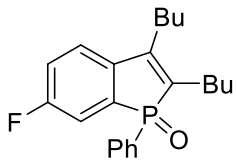


2,3-Dibutyl-6-(diphenylamino)-1-phenyl-1*H*-phosphindole 1-oxide (3faa): Type **II** arylzinc reagent was used; Yellow oil (41% yield, eluent = hexane/EtOAc (2:1)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.63 (m, 2H), 7.53 – 7.49 (m, 1H), 7.44 – 7.39 (m, 2H), 7.31 (dd, *J* = 10.8, 2.0 Hz, 1H), 7.25 – 7.18 (m, 5H), 7.13 – 7.11 (m, 1H), 7.06 – 7.01 (m, 6H), 2.58 (t, *J* = 7.6 Hz, 2H), 2.53 – 2.41 (m, 1H), 2.31 – 2.19 (m, 1H), 1.61 – 1.57 (m, 2H), 1.51 – 1.46 (m, 2H), 1.40 – 1.33 (m, 2H), 1.30 – 1.22 (m, 2H), 1.00(t, *J* = 7.2 Hz, 3H), 0.80 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.4 (d, J_{PC} = 19.8 Hz), 148.4 (d, J_{PC} = 12.8 Hz), 147.2 (s), 137.0 (d, J_{PC} = 29.3 Hz), 133.9 (d, J_{PC} = 104.7 Hz), 132.8 (d, J_{PC} = 97.8 Hz), 131.8 (d, J_{PC} = 2.9 Hz), 130.8 (d, J_{PC} = 97.0 Hz), 131.0 (d, J_{PC} = 10.7 Hz), 129.5 (s), 128.7 (d, J_{PC} = 12.1 Hz), 126.0 (d, J_{PC} = 2.0 Hz), 124.8 (s), 123.6 (s), 123.3 (d, J_{PC} = 10.8 Hz), 122.1 (d, J_{PC} = 12.9 Hz), 31.3 (d, J_{PC} = 1.8 Hz), 30.8 (d, J_{PC} = 1.9 Hz), 26.5 (d, J_{PC} = 13.6 Hz), 25.9 (d, J_{PC} = 11.0 Hz), 23.2 (s), 22.9 (s), 14.0 (s), 13.8 (s); ^{31}P NMR (162 MHz, $CDCl_3$): δ 39.5; HRMS (ESI) Calcd for $C_{34}H_{37}NOP$ $[M + H]^+$ 506.2613, found 506.2617.



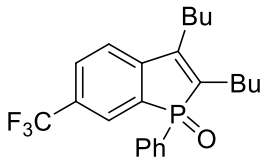
2,3-Dibutyl-6-hydroxy-1-phenyl-1*H*-phosphindole 1-oxide (3gaa): Type **II** arylzinc reagent prepared from 4-bromophenyl *tert*-butyl carbonate was used. The Boc group was removed during the reaction; Pale yellow solid (45% yield, eluent = DCM/EtOAc (2:1)); M. p. = 182-184 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.4 (brs, 1H), 7.58 – 7.53 (m, 2H),

7.47 – 7.39 (m, 2H), 7.35 – 7.31 (m, 2H), 7.19 (dd, *J* = 8.4, 3.6 Hz, 1H), 6.97 (dd, *J* = 8.0, 2.0 Hz, 1H), 2.53 (t, *J* = 7.6 Hz, 2H), 2.47 – 2.35 (m, 1H), 2.22 – 2.11 (m, 1H), 1.60 – 1.54 (m, 2H), 1.52 – 1.33 (m, 4H), 1.31 – 1.16 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H), 0.78 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.9 (d, J_{PC} = 13.3 Hz), 152.0 (d, J_{PC} = 20.7 Hz), 134.4 (d, J_{PC} = 29.4 Hz), 132.3 (d, J_{PC} = 104.6 Hz), 132.0 (d, J_{PC} = 2.8 Hz), 130.8 (d, J_{PC} = 11.0 Hz), 130.2 (d, J_{PC} = 20.9 Hz), 129.2 (d, J_{PC} = 19.4 Hz), 128.8 (d, J_{PC} = 12.2 Hz), 122.9 (d, J_{PC} = 13.6 Hz), 119.9 (d, J_{PC} = 1.6 Hz), 116.9 (d, J_{PC} = 10.7 Hz), 31.1 (d, J_{PC} = 1.6 Hz), 30.7 (d, J_{PC} = 1.6 Hz), 26.5 (d, J_{PC} = 14.0 Hz), 25.6 (d, J_{PC} = 10.9 Hz), 23.1 (s), 22.8 (s), 13.9 (s), 13.7 (s); ^{31}P NMR (162 MHz, $CDCl_3$): δ 42.5; HRMS (ESI) Calcd for $C_{22}H_{28}O_2P$ $[M + H]^+$ 355.1827, found 355.1824.

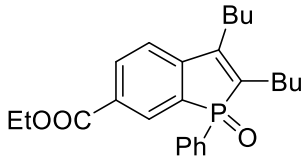


2,3-Dibutyl-6-fluoro-1-phenyl-1*H*-phosphindole 1-oxide (3haa): Type **II** arylzinc reagent was used; Pale yellow oil (67% yield, eluent = hexane/EtOAc (2:1)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.58 (m, 2H), 7.47 – 7.44 (m, 1H), 7.37 – 7.34 (m, 2H), 7.31 – 7.27 (m, 1H), 7.22 – 7.17 (m, 1H), 7.13 – 7.08 (m, 1H), 2.56 (t, *J* = 7.6 Hz, 2H), 2.52 – 2.40 (m, 1H), 2.28 – 2.17 (m, 1H), 1.58 – 1.51 (m, 2H), 1.48 – 1.39 (m, 2H), 1.37 – 1.15 (m, 4H), 0.94 (t, *J* = 7.2 Hz, 3H), 0.74 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8 (dd, J_{CF} = 249.5 Hz, J_{CP} = 14.9 Hz), 149.9 (d, *J* = 18.8 Hz), 139.3 (dd, J_1 = 30.0 Hz, J_2 = 25.5 Hz), 135.1 (dd, J_{CP} = 96.8 Hz, J_{CF} = 6.1 Hz), 134.3 (dd, J_{CP} = 94.2 Hz, J_{CF} = 1.6 Hz), 132.1 (d, *J* = 2.6 Hz), 130.8 (d, *J* = 10.6 Hz), 129.7 (d, *J* = 97.2 Hz), 128.8 (d, *J* = 12.1 Hz), 122.8 (dd, J_1 = 7.5 Hz, J_2 = 5.6 Hz), 119.1 (d, *J* = 22.3 Hz), 116.2 (dd, J_1 = 13.0 Hz, J_2 = 10.5 Hz), 30.9 (d, *J* = 1.6 Hz), 30.5 (d, *J* = 1.6 Hz), 26.4 (d, *J* = 13.4 Hz), 25.9 (d,

J = 10.9 Hz), 23.0 (s), 22.8 (s), 13.8 (s), 13.6 (s); ^{31}P NMR (162 MHz, $CDCl_3$): δ 38.5; HRMS (ESI) Calcd for $C_{22}H_{27}OPF$ $[M + H]^+$ 357.1784, found 357.1786.

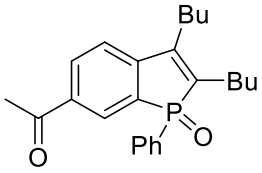


2,3-Dibutyl-1-phenyl-6-(trifluoromethyl)-1*H*-phosphindole 1-oxide (3iaa): Type **II** arylzinc reagent was used; Pale yellow oil (76% yield, eluent = hexane/EtOAc (2:1)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.71 (m, 2H), 7.63 (dd, *J* = 12.8, 7.2 Hz, 2H), 7.51 – 7.44 (m, 2H), 7.42 – 7.37 (m, 2H), 2.62 (t, *J* = 7.6 Hz, 2H), 2.58 – 2.46 (m, 1H), 2.33 – 2.22 (m, 1H), 1.60 – 1.52 (m, 2H), 1.50 – 1.31 (m, 4H), 1.29 – 1.17 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H), 0.75 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6 (d, *J* = 18.5 Hz), 147.7 (d, *J* = 28.9 Hz), 137.7 (d, *J* = 94.9 Hz), 135.5 (d, *J* = 103.5 Hz), 132.3 (d, *J* = 2.6 Hz), 130.8 (d, *J* = 10.6 Hz), 130.5 (d, *J* = 10.9 Hz), 130.1 (qd, $J_{C\text{-}F}$ = 21.7 Hz, $J_{C\text{-}P}$ = 10.8 Hz), 128.9 (d, *J* = 98.0 Hz), 128.8 (d, *J* = 12.3 Hz), 125.2 (qd, $J_{C\text{-}P}$ = 14.3 Hz, $J_{C\text{-}F}$ = 3.6 Hz), 123.7 (qd, $J_{C\text{-}F}$ = 270.8 Hz, $J_{C\text{-}P}$ = 1.9 Hz), 121.5 (d, *J* = 11.0 Hz), 30.7 (d, *J* = 1.3 Hz), 30.4 (d, *J* = 1.6 Hz), 26.3 (d, *J* = 12.9 Hz), 26.1 (d, *J* = 10.7 Hz), 22.9 (s), 22.8 (s), 13.8 (s), 13.5 (s); ^{31}P NMR (162 MHz, $CDCl_3$): δ 38.8; HRMS (ESI) Calcd for $C_{23}H_{27}OF_3P$ $[M + H]^+$ 407.1752, found 407.1750.



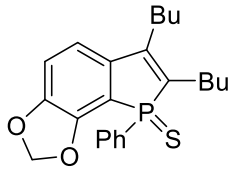
Ethyl 2,3-dibutyl-1-phenyl-1*H*-phosphindole-6-carboxylate 1-oxide (3jaa): Type **II** arylzinc reagent was used; Yellow gum (60% yield, eluent = hexane/EtOAc (1:1)); ^{1}H

NMR (400 MHz, $CDCl_3$): δ 8.16 – 8.13 (m, 2H), 7.62 – 7.57 (m, 2H), 7.45 – 7.43 (m, 1H), 7.39 – 7.33 (m, 3H), 4.33 – 4.18 (m, 2H), 2.58 (t, *J* = 7.6 Hz, 2H), 2.54 – 2.42 (m, 1H), 2.30 – 2.19 (m, 1H), 1.56 – 1.49 (m, 2H), 1.47 – 1.36 (m, 2H), 1.35 – 1.14 (m, 7H), 0.93 (t, *J* = 7.2 Hz, 3H), 0.72 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.5 (d, J_{PC} = 1.9 Hz), 149.8 (d, J_{PC} = 18.8 Hz), 147.7 (d, J_{PC} = 29.2 Hz), 138.1 (d, J_{PC} = 94.7 Hz), 134.6 (s), 133.2 (s), 132.1 (d, J_{PC} = 2.6 Hz), 130.8 (d, J_{PC} = 10.7 Hz), 130.2 (d, J_{PC} = 10.6 Hz), 129.8 (s), 129.4 (d, J_{PC} = 10.6 Hz), 128.8 (d, J_{PC} = 12.1 Hz), 121.2 (d, J_{PC} = 11.2 Hz), 61.2 (s), 30.8 (d, J_{PC} = 1.7 Hz), 30.5 (d, J_{PC} = 1.7 Hz), 26.3 (d, J_{PC} = 12.8 Hz), 26.1 (d, J_{PC} = 10.6 Hz), 23.0 (s), 22.8 (s), 14.2 (s), 13.9 (s), 13.6 (s); ^{31}P NMR (162 MHz, $CDCl_3$): δ 43.6; HRMS (ESI) Calcd for $C_{25}H_{32}O_3P$ $[M + H]^+$ 411.2089, found 411.2086.

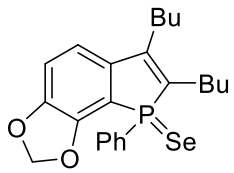


1-(2,3-Dibutyl-1-oxido-1-phenyl-1*H*-phosphindol-6-yl)ethanone (3kaa): Type **II** arylzinc reagent prepared from (*E*)-*N*-(1-(4-bromophenyl)ethylidene)-4-methoxyaniline was used. After the reaction was completed, aqueous HCl (1.5 mL, 1 M) was added, and the resulting mixture was stirred for 1 h. Silica gel chromatography (eluent = hexane/EtOAc (2:1)) of the crude product afforded the title compound as a yellow oil (56% yield);^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.07 (m, 2H), 7.63 (dd, *J* = 12.4, 7.2 Hz, 2H), 7.52 – 7.34 (m, 4H), 2.62 (t, *J* = 7.6 Hz, 2H), 2.58 – 2.46 (m, 4H), 2.34 – 2.23 (m, 1H), 1.61 – 1.53 (m, 2H), 1.51 – 1.42 (m, 2H), 1.39 – 1.30 (m, 2H), 1.29 – 1.18 (m, 2H), 0.97 (t, *J* = 7.2 Hz, 3H), 0.76 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.7 (s), 149.9 (d, J_{PC} = 18.8 Hz), 147.9 (d, J_{PC} = 29.2 Hz), 138.5 (d, J_{PC} = 94.9 Hz), 136.7 (d, J_{PC} = 9.6 Hz), 133.3 (d, J_{PC} = 1.1 Hz), 132.9 (d, J_{PC} = 103.9 Hz), 132.3 (d, J_{PC} = 2.7 Hz),

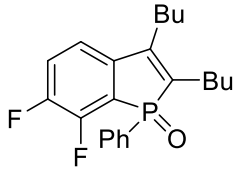
130.9 (d, J_{PC} = 10.6 Hz), 129.1 (d, J_{PC} = 97.3 Hz), 128.9 (d, J_{PC} = 12.2 Hz), 128.3 (d, J_{PC} = 10.1 Hz), 121.5 (d, J_{PC} = 11.1 Hz), 30.7 (d, J_{PC} = 1.4 Hz), 30.5 (d, J_{PC} = 1.4 Hz), 26.6 (s), 26.3 (d, J_{PC} = 12.8 Hz), 26.2 (d, J_{PC} = 10.5 Hz), 23.01 (s), 22.8 (s), 13.9 (s), 13.6 (s); ^{31}P NMR (162 MHz, $CDCl_3$): δ 38.6; HRMS (ESI) Calcd for $C_{24}H_{30}O_2P$ $[M + H]^+$ 381.1983, found 381.1975.



6,7-Dibutyl-8-phenyl-8*H*-phosphindolo[6,7-*d*][1,3]dioxole 8-sulfide (3laa'): Type **I** arylzinc reagent was used; Pale yellow oil (55% yield, eluent = hexane/EtOAc (20:1)); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 – 7.79 (m, 2H), 7.53 – 7.49 (m, 1H), 7.45 – 7.40 (m, 2H), 6.92 – 6.86 (m, 2H), 6.02 (d, *J* = 0.8 Hz, 1H), 5.92 (d, *J* = 1.2 Hz, 1H), 2.61 (t, *J* = 7.6 Hz, 2H), 2.57 – 2.50 (m, 1H), 2.37 – 2.24 (m, 1H), 1.67 – 1.58 (m, 2H), 1.54 – 1.45 (m, 2H), 1.33 – 1.18 (m, 4H), 1.01 (t, *J* = 7.2 Hz, 3H), 0.75 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.5 (d, J_{PC} = 14.9 Hz), 148.7 (d, J_{PC} = 8.3 Hz), 148.1 (d, J_{PC} = 4.7 Hz), 137.9 (d, J_{PC} = 22.8 Hz), 134.2 (d, J_{PC} = 79.4 Hz), 131.8 (d, J_{PC} = 3.0 Hz), 131.0 (d, J_{PC} = 11.9 Hz), 129.4 (d, J_{PC} = 78.7 Hz), 128.6 (d, J_{PC} = 12.7 Hz), 115.4 (d, J_{PC} = 9.5 Hz), 113.9 (d, J_{PC} = 91.9 Hz), 110.4 (d, J_{PC} = 1.3 Hz), 102.5 (s), 31.5 (d, J_{PC} = 1.6 Hz), 31.1 (d, J_{PC} = 1.9 Hz), 27.1 (d, J_{PC} = 13.1 Hz), 25.3 (d, J_{PC} = 13.2 Hz), 23.1 (s), 22.8 (s), 14.0 (s), 13.6 (s); ^{31}P NMR (162 MHz, $CDCl_3$): δ 43.6; HRMS (ESI) Calcd for $C_{23}H_{28}O_2PS$ $[M + H]^+$ 399.1548, found 399.1541.

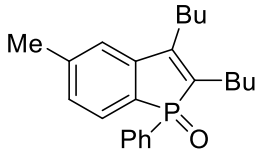


6,7-Dibutyl-8-phenyl-8*H*-phosphindolo[6,7-*d*][1,3]dioxole 8-selenide (3laa''); Type **I** arylzinc reagent was used; Pale yellow solid (40% yield, eluent = hexane/EtOAc (20:1)); M. p. = 135-137 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 – 7.78 (m, 2H), 7.45 – 7.43 (m, 1H), 7.39 – 7.36 (m, 2H), 6.90 – 6.82 (m, 2H), 5.99 (d, *J* = 0.8 Hz, 1H), 5.87 (d, *J* = 1.2 Hz, 1H), 2.63 – 2.52 (m, 1H), 2.59 (t, *J* = 7.6 Hz, 2H), 2.34 – 2.21 (m, 1H), 1.64 – 1.53 (m, 2H), 1.52 – 1.41 (m, 2H), 1.28 – 1.12 (m, 4H), 0.96 (t, *J* = 7.2 Hz, 3H), 0.70 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.2 (d, J_{PC} = 13.3 Hz), 148.7 (d, J_{PC} = 8.4 Hz), 148.3 (d, J_{PC} = 5.0 Hz), 138.1 (d, J_{PC} = 21.6 Hz), 133.6 (d, J_{PC} = 73.1 Hz), 131.9 (d, J_{PC} = 3.0 Hz), 131.5 (d, J_{PC} = 12.2 Hz), 128.6 (d, J_{PC} = 12.7 Hz), 127.9 (d, J_{PC} = 69.3 Hz), 115.6 (d, J_{PC} = 9.1 Hz), 113.4 (d, J_{PC} = 85.1 Hz), 110.4 (d, J_{PC} = 1.2 Hz), 102.6 (s), 31.6 (d, J_{PC} = 1.7 Hz), 31.1 (d, J_{PC} = 2.0 Hz), 27.2 (d, J_{PC} = 12.7 Hz), 25.4 (d, J_{PC} = 14.1 Hz), 23.1 (s), 22.8 (s), 14.0 (s), 13.6 (s); ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.4; HRMS (ESI) Calcd for $C_{23}H_{28}O_2PSe$ $[M + H]^+$ 447.0992, found 447.0997.

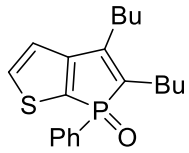


2,3-Dibutyl-6,7-difluoro-1-phenyl-1*H*-phosphindole 1-oxide (3maa): Type **II** arylzinc reagent was used; Yellow oil (51% yield, eluent = hexane/EtOAc (2:1)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.65 (m, 2H), 7.54 – 7.49 (m, 1H), 7.44 – 7.39 (m, 2H), 7.26 – 7.19 (m, 1H), 7.06 – 7.02 (m, 1H), 2.56 (t, *J* = 7.6 Hz, 2H), 2.50 – 2.41 (m, 1H), 2.30 – 2.19 (m, 1H), 1.60 – 1.49 (m, 2H), 1.49 – 1.41 (m, 2H), 1.41 – 1.28 (m, 2H), 1.29 – 1.17

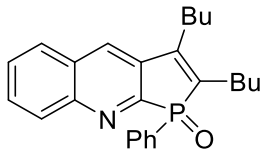
(m, 2H), 0.96 (t, J = 7.2 Hz, 3H), 0.76 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.6 (ddd, J_{CF} = 254.5 Hz, J_2 = 13.9 Hz, J_3 = 8.7 Hz), 150.3 (ddd, J_{CF} = 259.6 Hz, J_2 = 14.8 Hz, J_3 = 2.7 Hz), 150.0 (dd, J_1 = 17.9 Hz, J_2 = 2.1 Hz), 140.4 (dd, J_1 = 24.9 Hz, J_2 = 3.8 Hz), 135.1 (ddd, J_{CP} = 98.6 Hz, J_2 = 3.9 Hz, J_3 = 1.4 Hz), 132.6 (d, J = 3.0 Hz), 130.8 (d, J = 11.1 Hz), 129.0 (d, J = 12.8 Hz), 128.8 (d, J = 102.2 Hz), 121.7 (d, J = 18.5 Hz), 121.0 (dd, J_{CF} = 99.7 Hz, J_{CP} = 19.2 Hz), 117.7 (ddd, J_1 = 12.0 Hz, J_2 = 5.6 Hz, J_3 = 3.3 Hz), 30.9 (d, J = 1.9 Hz), 30.6 (d, J = 2.0 Hz), 26.6 (d, J = 13.9 Hz), 26.1 (d, J = 11.5 Hz), 23.1 (s), 22.9 (s), 14.0 (s), 13.7 (s); ^{31}P NMR (162 MHz, $CDCl_3$): δ 37.4 (d, J_{FP} = 5.7 Hz); HRMS (ESI) Calcd for $C_{22}H_{26}OPF_2$ $[M + H]^+$ 375.1689, found 375.1688.



2,3-Dibutyl-5-methyl-1-phenyl-1*H*-phosphindole 1-oxide (3naa): Type **I** arylzinc reagent was used; Yellow oil (60% yield, eluent = hexane/EtOAc (2:1)); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (dd, J = 12.0, 7.2 Hz, 2H), 7.40 – 7.32 (m, 4H), 7.12 (s, 1H), 7.04 (dd, J = 6.8, 2.8 Hz, 1H), 2.56 (t, J = 7.6 Hz, 2H), 2.48 – 2.40 (m, 1H), 2.37 (s, 3H), 2.86 – 2.17 (m, 1H), 1.59 – 1.51 (m, 2H), 1.49 – 1.42 (m, 2H), 1.33 – 1.24 (m, 2H), 1.20 – 1.14 (m, 2H), 0.95 (t, J = 7.2 Hz, 3H), 0.74 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.3 (d, J_{PC} = 19.8 Hz), 144.0 (d, J_{PC} = 29.4 Hz), 143.3 (d, J_{PC} = 1.2 Hz), 134.9 (d, J_{PC} = 95.2 Hz), 131.7 (d, J_{PC} = 2.4 Hz), 131.2 (s), 130.9 (d, J_{PC} = 10.4 Hz), 130.2 (s), 129.5 (s), 128.6 (d, J_{PC} = 32.0 Hz), 128.5 (d, J_{PC} = 12.0 Hz), 122.3 (d, J_{PC} = 5.8 Hz), 31.0 (s), 30.7 (s), 26.2 (d, J_{PC} = 13.1 Hz), 25.9 (d, J_{PC} = 10.6 Hz), 23.1 (s), 22.8 (s), 22.0 (s), 13.9 (s), 13.6 (s); ^{31}P NMR (162 MHz, $CDCl_3$): δ 39.3; HRMS (ESI) Calcd for $C_{23}H_{30}OP$ $[M + H]^+$ 353.2034, found 353.2038.

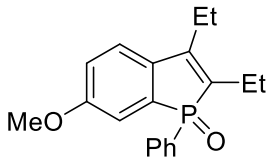


4,5-Dibutyl-6-phenyl-6*H*-phospholo[2,3-*b*]thiophene 6-oxide (3oaa): Type **II** arylzinc reagent was used; Pale yellow oil (48% yield, eluent = hexane/EtOAc (2:1)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.68 (m, 1H), 7.64 – 7.59 (m, 2H), 7.49 – 7.46 (m, 1H), 7.40 – 7.37 (m, 2H), 7.06 (dd, *J* = 4.4, 1.2 Hz, 1H), 2.53 (t, *J* = 7.6 Hz, 2H), 2.46 – 2.35 (m, 1H), 2.26 – 2.15 (m, 1H), 1.61 – 1.53 (m, 2H), 1.47 – 1.39 (m, 2H), 1.32 – 1.26 (m, 2H), 1.25 – 1.16 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H), 0.74 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.2 (d, J_{PC} = 31.0 Hz), 145.6 (d, J_{PC} = 15.9 Hz), 137.2 (d, J_{PC} = 3.6 Hz), 136.9 (d, J_{PC} = 98.6 Hz), 132.0 (d, J_{PC} = 2.9 Hz), 130.8 (d, J_{PC} = 10.7 Hz), 130.5 (d, J_{PC} = 110.3 Hz), 128.7 (d, J_{PC} = 102.5 Hz), 128.3 (d, J_{PC} = 108.1 Hz), 121.1 (d, J_{PC} = 14.3 Hz), 31.1 (d, J_{PC} = 1.6 Hz), 30.6 (d, J_{PC} = 1.8 Hz), 27.9 (d, J_{PC} = 13.3 Hz), 26.1 (d, J_{PC} = 11.8 Hz), 22.9 (s), 22.7 (s), 13.9 (s), 13.6 (s); ^{31}P NMR (162 MHz, $CDCl_3$): δ 31.2; HRMS (ESI) Calcd for $C_{20}H_{26}OPS$ $[M + H]^+$ 345.1442, found 345.1440.

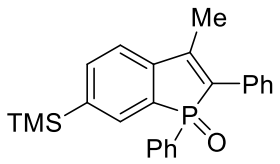


2,3-Dibutyl-1-phenyl-1*H*-phospholo[2,3-*b*]quinoline 1-oxide (3paa): Type **II** arylzinc reagent was used; Pale yellow solid (52% yield, eluent = hexane/EtOAc (2:1)); M. p. = 114-116 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 4.4 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.74 – 7.69 (m, 2H), 7.65 – 7.62 (m, 1H), 7.58 – 7.48 (m, 2H), 7.42 – 7.38 (m, 2H), 2.72 (t, *J* = 7.6 Hz, 2H), 2.67 – 2.55 (m, 1H), 2.43 – 2.31 (m, 1H), 1.68 – 1.62 (m, 2H), 1.58 – 1.39 (m, 4H), 1.34 – 1.24 (m, 2H), 1.01 (t, *J* = 7.2 Hz,

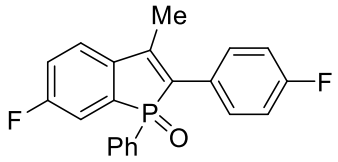
3H), 0.80 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5 (d, J_{PC} = 127.5 Hz), 150.3 (d, J_{PC} = 13.5 Hz), 148.1 (d, J_{PC} = 18.2 Hz), 136.4 (d, J_{PC} = 94.4 Hz), 134.3 (d, J_{PC} = 44.5 Hz), 132.3 (d, J_{PC} = 2.4 Hz), 131.3 (d, J_{PC} = 10.6 Hz), 130.5 (s), 129.7 (s), 129.0 (s), 128.8 (d, J_{PC} = 12.3 Hz), 128.7 (d, J_{PC} = 0.6 Hz), 128.4 (d, J_{PC} = 11.9 Hz), 128.0 (s), 126.3 (d, J_{PC} = 9.0 Hz), 31.0 (d, J_{PC} = 1.3 Hz), 30.4 (d, J_{PC} = 0.5 Hz), 26.5 (d, J_{PC} = 3.0 Hz), 26.4 (d, J_{PC} = 3.0 Hz), 23.1 (s), 23.0 (s), 14.0 (s), 13.6 (s); ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.0; HRMS (ESI) Calcd for $C_{25}H_{29}NOP$ $[M + H]^+$ 390.1987, found 390.1987.



2,3-Diethyl-6-methoxy-1-phenyl-1*H*-phosphindole 1-oxide (3aba): Type **I** arylzinc reagent was used; Yellow oil (52% yield, eluent = hexane/EtOAc (2:1)); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 – 7.63 (m, 2H), 7.49 – 7.45 (m, 1H), 7.40 – 7.37 (m, 2H), 7.28 – 7.25 (m, 1H), 7.12 – 7.09 (m, 1H), 6.95 (dd, J = 8.4, 2.4 Hz, 1H), 3.74 (s, 3H), 2.62 – 2.56 (m, 2H), 2.53 – 2.43 (m, 1H), 2.35 – 2.26 (m, 1H), 1.21 (t, J = 7.2 Hz, 3H), 0.98 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1 (d, J_{PC} = 13.2 Hz), 151.7 (d, J_{PC} = 19.5 Hz), 135.7 (d, J_{PC} = 28.7 Hz), 134.3 (d, J_{PC} = 103.5 Hz), 132.8 (d, J_{PC} = 97.3 Hz), 131.8 (d, J_{PC} = 2.6 Hz), 131.0 (d, J_{PC} = 10.5 Hz), 130.6 (d, J_{PC} = 95.5 Hz), 128.7 (d, J_{PC} = 12.0 Hz), 122.3 (d, J_{PC} = 13.1 Hz), 117.7 (d, J_{PC} = 0.9 Hz), 114.5 (d, J_{PC} = 10.9 Hz), 55.6 (s), 19.7 (d, J_{PC} = 13.8 Hz), 18.9 (d, J_{PC} = 11.1 Hz), 14.1 (s), 13.1 (s); ^{31}P NMR (162 MHz, $CDCl_3$): δ 39.4; HRMS (ESI) Calcd for $C_{19}H_{22}O_2P$ $[M + H]^+$ 313.1357, found 313.1357.

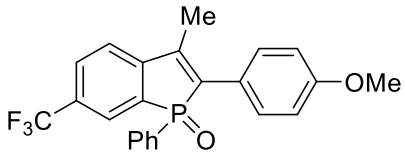


3-Methyl-1,2-diphenyl-6-(trimethylsilyl)-1*H*-phosphindole 1-oxide (3cca): Type **III** arylzinc reagent was used; yellow solid (37% yield, eluent = hexane/EtOAc (2:1)); M. p. = 160-162 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 9.6 Hz, 1H), 7.73 – 7.62 (m, 3H), 7.46 – 7.41 (m, 2H), 7.37 – 7.23 (m, 7H), 2.31 (d, *J* = 2.0 Hz, 3H); 0.25 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.3 (d, *J* = 22.3 Hz), 144.5 (d, *J* = 28.4 Hz), 142.3 (d, J_{PC} = 7.3 Hz), 138.3 (s), 133.8 (s), 133.2 (d, J_{PC} = 9.0 Hz), 133.1 (s), 132.0 (d, J_{PC} = 2.4 Hz), 131.1 (d, J_{PC} = 10.6 Hz), 129.8 (d, J_{PC} = 96.1 Hz), 128.9 (d, J_{PC} = 4.9 Hz), 128.7 (d, J_{PC} = 12.3 Hz), 128.7 (s), 127.9 (s), 126.5 (s), 121.3 (d, J_{PC} = 10.3 Hz), 13.6 (d, J_{PC} = 12.8 Hz), -1.2 (s); ^{31}P NMR (162 MHz, $CDCl_3$): δ 39.0; HRMS (ESI) Calcd for $C_{24}H_{26}OPSi$ $[M + H]^+$ 389.1491, found 389.1491.

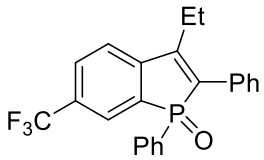


6-Fluoro-2-(4-fluorophenyl)-3-methyl-1-phenyl-1*H*-phosphindole 1-oxide (3hda): Type **III** arylzinc reagent was used; Pale yellow solid (38% yield, eluent = hexane/EtOAc (2:1)); M. p. = 207-209 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.45 (m, 4H), 7.36 – 7.19 (m, 6H), 7.02 – 6.98 (m, 2H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4 (dd, J_{CF} = 250.6 Hz, J_{CP} = 15.4 Hz), 162.4 (d, J_{CF} = 246.7 Hz), 146.8 (d, *J* = 20.2 Hz), 139.7 (dd, J_1 = 28.2 Hz, J_2 = 1.4 Hz), 135.0 (d, *J* = 4.4 Hz), 134.0 (d, *J* = 1.9 Hz), 133.6 (d, *J* = 5.6 Hz), 132.5 (s), 130.9 (d, *J* = 10.0 Hz), 130.6 (d, *J* = 4.6 Hz), 129.0 (d, J_{CP} = 98.8 Hz), 128.9 (d, *J* = 11.5 Hz), 123.8 (dd, J_1 = 11.1 Hz, J_2 = 7.6 Hz), 119.5 (d, *J* = 22.3 Hz), 116.4

(dd, J_1 = 23.5 Hz, J_2 = 10.0 Hz), 115.7 (d, J = 21.4 Hz), 13.7 (d, J = 12.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 36.9; HRMS (ESI) Calcd for $C_{21}H_{16}OF_2P$ $[M + H]^+$ 353.0907, found 353.0908.

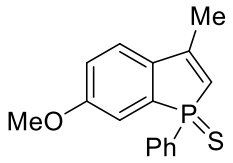


2-(4-Methoxyphenyl)-3-methyl-1-phenyl-6-(trifluoromethyl)-1*H*-phosphindole 1-oxide (3iea): Type **III** arylzinc reagent was used; Pale yellow solid (36% yield, eluent = hexane/EtOAc (2:1)); M. p. = 196-198 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.73 (m, 2H), 7.65 – 7.55 (m, 3H), 7.49 – 7.37 (m, 5H), 6.86 (d, J = 7.6 Hz, 2H), 3.76 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.1 (s), 133.3 (d, J_{CP} = 22.1 Hz), 131.2 (d, J_{PC} = 16.1 Hz), 124.3 (d, J_{PC} = 78.5 Hz), 121.9 (q, J_{CF} = 43.5 Hz), 121.6 (s), 120.1 (d, J_{PC} = 7.7 Hz), 119.6 (s), 119.4 (s), 118.5 (d, J_{PC} = 9.3 Hz), 117.7 (d, J_{PC} = 24.4 Hz), 115.8 (d, J_{PC} = 5.9 Hz), 115.6 (d, J_{PC} = 3.8 Hz), 115.1 (d, J_{PC} = 7.7 Hz), 114.2 (q, J_{CF} = 270.1 Hz), 113.0 (d, J_{PC} = 7.5 Hz), 106.7 (s), 59.5 (s), 26.3 (d, J_{PC} = 9.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 37.0; HRMS (ESI) Calcd for $C_{23}H_{19}O_2PF_3$ $[M + H]^+$ 415.1075, found 415.1077.

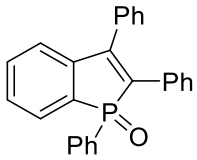


3-Ethyl-1,2-diphenyl-6-(trifluoromethyl)-1*H*-phosphindole 1-oxide (3ifa): Type **III** arylzinc reagent was used; Yellow solid (56% yield, eluent = hexane/EtOAc (2:1)); M. p. = 80-82 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 9.6 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.66 – 7.59 (m, 3H), 7.50 – 7.46 (m, 1H), 7.40 – 7.26 (m, 7H), 2.77 – 2.70 (m, 2H),

1.30 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.9 (d, J = 18.5 Hz), 146.3 (qd, J_{CF} = 26.9 Hz, J_{CP} = 1.3 Hz), 136.6 (d, J_{PC} = 97.4 Hz), 133.8 (d, J_{PC} = 105.1 Hz), 132.6 (d, J_{PC} = 2.9 Hz), 132.5 (d, J_{PC} = 10.0 Hz), 131.1 (d, J_{PC} = 10.8 Hz), 131.0 (d, J_{PC} = 10.9 Hz), 130.3 (qd, J_{CF} = 9.4 Hz, J_{CP} = 2.0 Hz), 129.1 (d, J_{PC} = 12.6 Hz), 128.9 (s), 128.7 (d, J_{PC} = 1.7 Hz), 128.5 (d, J_{PC} = 5.1 Hz), 128.4 (d, J_{PC} = 1.4 Hz), 125.8 (qd, J_{CF} = 14.5 Hz, J_{CP} = 3.7 Hz), 123.7 (qd, J_{CF} = 273.8 Hz, J_{CP} = 2.2 Hz), 122.5 (d, J_{PC} = 11.0 Hz), 20.6 (d, J_{PC} = 12.3 Hz), 13.5 (d, J_{PC} = 1.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 38.0; HRMS (ESI) Calcd for $C_{23}H_{19}OPF_3$ $[M + H]^+$ 399.1126, found 399.1121.



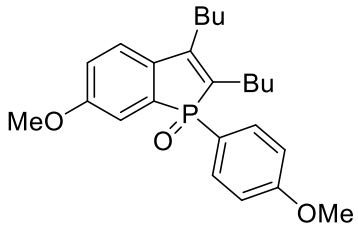
6-Methoxy-3-methyl-1-phenyl-1*H*-phosphindole 1-sulfide (3aga'): Type **I** arylzinc reagent and 1-trimethylsilyl-1-propyne were used. The trimethylsilyl group was removed during the reaction to afford the product as a yellow solid (35% yield, eluent = hexane/EtOAc (20:1)); M. p. = 84-86 ℃;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.75 (m, 2H), 7.47 – 7.44 (m, 1H), 7.40 – 7.33 (m, 3H), 7.12 (dd, J = 12.0, 2.4 Hz, 1H), 7.01 – 6.98 (m, 1H), 6.12 – 6.04 (m, 1H), 3.78 (s, 3H), 2.31 (t, J = 1.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.1 (d, J_{PC} = 14.3 Hz), 153.1 (d, J_{PC} = 10.6 Hz), 139.3 (d, J_{PC} = 88.8 Hz), 136.0 (d, J_{PC} = 26.0 Hz), 132.0 (d, J_{PC} = 3.3 Hz), 130.9 (d, J_{PC} = 12.0 Hz), 129.7 (d, J_{PC} = 80.5 Hz), 128.7 (d, J_{PC} = 12.9 Hz), 123.5 (d, J_{PC} = 12.8 Hz), 122.0 (d, J_{PC} = 86.3 Hz), 117.6 (d, J_{PC} = 2.2 Hz), 113.7 (d, J_{PC} = 12.6 Hz), 55.8 (s), 16.8 (d, J_{PC} = 16.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 44.0; HRMS (ESI) Calcd for $C_{16}H_{16}OPS$ $[M + H]^+$ 287.0660, found 287.0662.



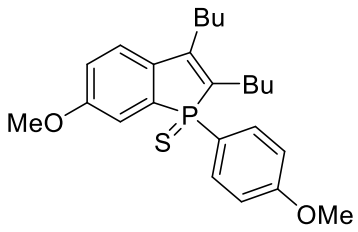
1,2,3-Triphenyl-1*H*-phosphindole 1-oxide (3bha): Modified type **I** arylzinc reagent, that is, diphenylzinc reagent prepared from a 1:2 mixture of $ZnCl_2$•TMEDA and PhMgBr was used; White solid (39% yield, eluent = hexane/EtOAc (1:1)); M.p. = 75-76 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 – 7.77 (m, 2H), 7.74 – 7.70 (m, 1H), 7.50 – 7.34 (m, 10H), 7.28 – 7.21 (m, 3H), 7.12 – 7.50 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.0 (d, J_{PC} = 21.3 Hz), 143.8 (d, J_{PC} = 27.0 Hz), 134.3 (d, J_{PC} = 95.2 Hz), 134.2 (d, J_{PC} = 14.9 Hz), 132.9 (d, J_{PC} = 1.8 Hz), 132.7 (d, J_{PC} = 9.8 Hz), 132.6 (s), 132.2 (d, J_{PC} = 2.8 Hz), 131.5 (s), 131.0 (d, J_{PC} = 10.5 Hz), 129.9 (d, J_{PC} = 99.2 Hz), 129.2 (s), 129.1 (d, J_{PC} = 10.6 Hz), 129.0 (br, 2C, overlapped), 128.9 (s), 128.8 (d, J_{PC} = 11.4 Hz), 128.3 (s), 127.9 (s), 124.1 (d, J_{PC} = 14.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 39.1; HRMS (ESI) Calcd for $C_{26}H_{20}OP$ $[M + H]^+$ 379.1252, found 379.1248.

General procedure for protocol B: To an *ortho*-alkenyl arylzinc reagent prepared on a 0.5 mmol scale according to Scheme 4.11 (vide supra) was added a THF solution of CuCN•2LiCl (0.1 mmol), PCl_3 (0.6 mmol) at 0 ℃, the resulting solution was stirred at rt for 8-12 h. To the mixture was added a THF solution of an aryl Grignard reagent (1.5 mmol) at 0 ℃ and the resulting solution was stirred at 60 ℃ for 10-16 h followed by cooling. For benzophosphole oxides, an aqueous solution of H_2O_2 (ca. 30%, a few drops) was added at 0 ℃, and the mixture was stirred at room temperature for 0.5 h; for benzophosphole sulfides, sulfur powder (64.0 mg, 2 mmol) was added and the mixture was stirred at room temperature for 4 h. The reaction mixture was diluted with ethyl acetate (5 mL) and filtered through a pad of silica gel with additional ethyl acetate (15 mL)

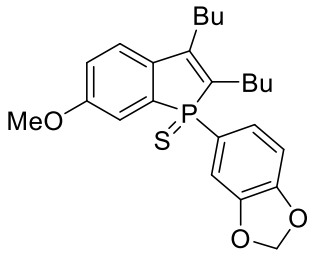
as the eluent. The filtrate was washed with water (10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product.



2,3-Dibutyl-6-methoxy-1-(4-methoxyphenyl)-1*H*-phosphindole 1-oxide (3aab): Type **I** arylzinc reagent was used; Pale yellow oil (52% yield, eluent = hexane/EtOAc (1:1)); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 – 7.54 (m, 2H), 7.22 (dd, *J* = 8.4, 3.6 Hz, 1H), 7.11 (d, *J* = 10.4 Hz, 1H), 6.95 – 6.88 (m, 3H), 3.80 (s, 3H), 3.74 (s, 3H), 2.54 (t, *J* = 7.6 Hz, 2H), 2.49 – 2.38 (m, 1H), 2.27 – 2.15 (m, 1H), 1.57 – 1.49 (m, 2H), 1.47 – 1.40 (m, 2H), 1.38 – 1.28 (m, 2H), 1.26 – 1.17 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H), 0.77 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.6 (d, J_{PC} = 2.8 Hz), 160.0 (d, J_{PC} = 13.3 Hz), 150.3 (d, J_{PC} = 19.9 Hz), 135.9 (d, J_{PC} = 29.1 Hz), 134.2 (d, J_{PC} = 104.2 Hz), 132.8 (d, J_{PC} = 12.0 Hz), 132.0 (d, J_{PC} = 97.9 Hz), 122.3 (d, J_{PC} = 13.3 Hz), 120.7 (d, J_{PC} = 102.5 Hz), 117.7 (s), 114.4 (d, J_{PC} = 13.0 Hz), 114.3 (d, J_{PC} = 10.7 Hz), 55.5 (s), 55.2 (s), 31.1 (d, J_{PC} = 1.4 Hz), 30.6 (d, J_{PC} = 1.6 Hz), 26.4 (d, J_{PC} = 13.6 Hz), 25.7 (d, J_{PC} = 11.0 Hz), 23.0 (s), 22.8 (s), 13.9 (s), 13.6 (s); ^{31}P NMR (162 MHz, $CDCl_3$): δ 40.2; HRMS (ESI) Calcd for $C_{24}H_{32}O_3P$ $[M + H]^+$ 399.2089, found 399.2084.

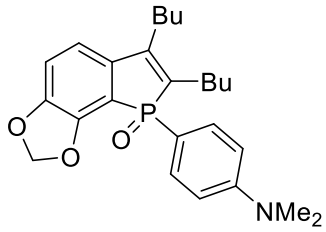


2,3-Dibutyl-6-methoxy-1-(4-methoxyphenyl)-1*H*-phosphindole 1-sulfide (3aab'): Type **I** arylzinc reagent was used; Pale yellow gum (50% yield, eluent = hexane/EtOAc (20:1)); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 – 7.60 (m, 2H), 7.28 (dd, *J* = 8.4, 4.0 Hz, 1H), 7.05 (dd, *J* = 12.0, 2.4 Hz, 1H), 6.95 (m, 1H), 6.86 (dd, *J* = 8.8, 2.0 Hz, 2H), 3.78 (s, 3H), 3.74 (s, 3H), 2.58 (t, *J* = 7.6 Hz, 2H), 2.54 – 2.46 (m, 1H), 2.38 – 2.21 (m, 1H), 1.64 – 1.54 (m, 2H), 1.50 – 1.41 (m, 2H), 1.29 – 1.15 (m, 4H), 0.96 (t, *J* = 7.2 Hz, 3H), 0.74 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.6 (d, J_{PC} = 3.1 Hz), 160.2 (d, J_{PC} = 14.0 Hz), 148.6 (d, J_{PC} = 16.4 Hz), 138.1 (d, J_{PC} = 89.0 Hz), 136.4 (d, J_{PC} = 26.0 Hz), 134.4 (d, J_{PC} = 79.4 Hz), 132.9 (d, J_{PC} = 13.3 Hz), 122.8 (d, J_{PC} = 12.6 Hz), 120.6 (d, J_{PC} = 81.3 Hz), 117.8 (d, J_{PC} = 2.2 Hz), 114.2 (d, J_{PC} = 13.7 Hz), 113.4 (d, J_{PC} = 12.3 Hz), 55.7 (s), 55.4 (s), 31.6 (d, J_{PC} = 2.0 Hz), 30.9 (d, J_{PC} = 2.3 Hz), 26.9 (d, J_{PC} = 13.0 Hz), 25.5 (d, J_{PC} = 13.0 Hz), 23.2 (s), 22.9 (s), 14.1 (s), 13.7 (s); ^{31}P NMR (162 MHz, $CDCl_3$): δ 47.2; HRMS (ESI) Calcd for $C_{24}H_{32}O_2PS$ $[M + H]^+$ 415.1861, found 415.1862.



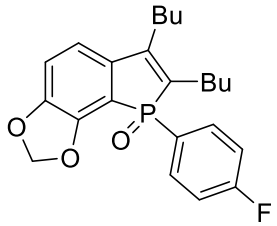
1-(Benzo[*d*][1,3]dioxol-5-yl)-2,3-dibutyl-6-methoxy-1*H*-phosphindole 1-sulfide (3aac'): Type **I** arylzinc reagent was used; Pale yellow gum (41% yield, eluent = hexane/EtOAc (20:1)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (ddd, *J* = 14.8, 8.0, 1.6 Hz,

1H), 7.29 (dd, *J* = 8.4, 4.0 Hz, 1H), 7.06 (dd, *J* = 12.0, 2.8 Hz, 1H), 7.02 – 6.95 (m, 2H), 6.82 (dd, *J* = 8.0, 2.4 Hz, 1H), 5.97 (d, *J* = 1.2 Hz, 1H), 5.96 (d, *J* = 1.2 Hz, 1H), 3.77 (s, 3H), 2.59 (t, *J* = 7.6 Hz, 2H), 2.56 – 2.47 (m, 1H), 2.35 – 2.22 (m, 1H), 1.63 – 1.53 (m, 2H), 1.51 – 1.43 (m, 2H), 1.31 – 1.17 (m, 4H), 0.97 (t, *J* = 7.2 Hz, 3H), 0.78 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2 (d, J_{PC} = 14.0 Hz), 150.9 (d, J_{PC} = 2.9 Hz), 148.8 (d, J_{PC} = 16.5 Hz), 147.9 (d, J_{PC} = 18.6 Hz), 137.8 (d, J_{PC} = 89.3 Hz), 136.2 (d, J_{PC} = 26.2 Hz), 134.0 (d, J_{PC} = 79.6 Hz), 126.8 (d, J_{PC} = 13.1 Hz), 123.0 (d, J_{PC} = 35.5 Hz), 122.5 (d, J_{PC} = 31.2 Hz), 117.8 (d, J_{PC} = 1.8 Hz), 113.3 (d, J_{PC} = 12.1 Hz), 110.1 (d, J_{PC} = 15.1 Hz), 108.6 (d, J_{PC} = 15.8 Hz), 101.7 (s), 55.6 (s), 31.5 (d, J_{PC} = 1.4 Hz), 30.8 (d, J_{PC} = 1.9 Hz), 26.9 (d, J_{PC} = 13.1 Hz), 25.4 (d, J_{PC} = 12.7 Hz), 23.1 (s), 22.8 (s), 14.0 (s), 13.7 (s); ^{31}P NMR (162 MHz, $CDCl_3$): δ 47.3; HRMS (ESI) Calcd for $C_{24}H_{30}O_3PS$ $[M + H]^+$ 429.1653, found 429.1651.

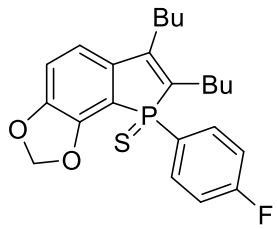


6,7-Dibutyl-8-(4-(dimethylamino)phenyl)-8*H*-phosphindolo[6,7-*d*][1,3]dioxole 8-oxide (3lad): Type **I** arylzinc reagent was used; Pale yellow solid (40% yield, eluent = hexane/EtOAc (1:1)); M. p. = 124-126 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 2H), 6.74 (d, *J* = 1.2 Hz, 2H), 6.66 (dd, *J* = 8.8, 2.0 Hz, 2H), 5.89 (s, 1H), 5.87 (s, 1H), 2.96 (s, 6H), 2.50 (t, *J* = 7.6 Hz, 2H), 2.46 – 2.36 (m, 1H), 2.26 – 2.15 (m, 1H), 1.55 – 1.48 (m, 2H), 1.47 – 1.35 (m, 4H), 1.30 – 1.21 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H), 0.78 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.8 (d, J_{PC} = 2.3 Hz), 150.2 (d, J_{PC} = 18.4 Hz), 148.5 (d, J_{PC} = 7.9 Hz), 148.2 (d, J_{PC} = 4.1 Hz), 137.3 (d, J_{PC} = 25.6 Hz), 132.6

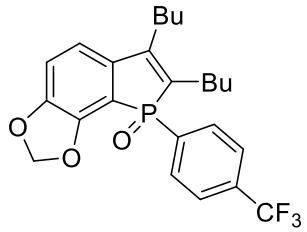
(d, J_{PC} = 98.7 Hz), 132.3 (d, J_{PC} = 12.3 Hz), 114.7 (d, J_{PC} = 10.3 Hz), 112.9 (d, J_{PC} = 112.0 Hz), 111.6 (d, J_{PC} = 106.6 Hz), 111.7 (d, J_{PC} = 13.2 Hz), 110.2 (s), 102.1 (s), 39.9 (s), 31.1 (d, J_{PC} = 1.3 Hz), 31.0 (d, J_{PC} = 1.6 Hz), 26.6 (d, J_{PC} = 13.6 Hz), 25.8 (d, J_{PC} = 11.3 Hz), 23.1 (s), 22.9 (s), 13.9 (s), 13.7 (s); ^{31}P NMR (162 MHz, $CDCl_3$): δ 38.6; HRMS (ESI) Calcd for $C_{25}H_{33}NO_3P$ $[M + H]^+$ 426.2198, found 426.2195.



6,7-Dibutyl-8-(4-fluorophenyl)-8*H*-phosphindolo[6,7-*d*][1,3]dioxole 8-oxide (3lae): Type **I** arylzinc reagent was used; Pale yellow gum (34% yield, eluent = hexane/EtOAc (2:1)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.68 (m, 2H), 7.15 – 7.09 (m, 2H), 6.83 – 6.79 (m, 2H), 5.95 (d, *J* = 0.8 Hz, 1H), 5.92 (d, *J* = 0.8 Hz, 1H), 2.54 (t, *J* = 7.6 Hz, 2H), 2.50 – 2.39 (m, 1H), 2.27 – 2.16 (m, 1H), 1.59 – 1.50 (m, 2H), 1.48 – 1.41 (m, 2H), 1.39 – 1.29 (m, 2H), 1.27 – 1.17 (m, 2H), 0.97 (t, *J* = 7.2 Hz, 3H), 0.78 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3 (dd, J_{CF} = 251.0 Hz, J_{CP} = 6.1 Hz), 151.4 (d, *J* = 18.7 Hz), 148.8 (d, *J* = 8.1 Hz), 148.5 (d, *J* = 4.0 Hz), 137.2 (d, *J* = 26.1 Hz), 134.4 (dd, J_{CP} = 36.3 Hz, J_{CF} = 20.1 Hz), 134.3 (dd, J_{CP} = 36.4 Hz, J_{CF} = 2.6 Hz), 133.4 (dd, J_{CP} = 12.1 Hz, J_{CF} = 8.8 Hz), 131.9 (d, *J* = 99.0 Hz), 116.2 (dd, J_{CF} = 21.3 Hz, J_{CP} = 13.4 Hz), 115.1 (d, *J* = 10.4 Hz), 110.7 (d, *J* = 1.0 Hz), 102.3 (s), 31.2 (d, *J* = 1.8 Hz), 31.0 (d, *J* = 1.8 Hz), 26.6 (d, *J* = 13.9 Hz), 25.8 (d, *J* = 11.3 Hz), 23.1 (s), 22.9 (s), 13.9 (s), 13.7 (s); ^{31}P NMR (162 MHz, $CDCl_3$): δ 35.8; HRMS (ESI) Calcd for $C_{23}H_{27}O_3PF$ $[M + H]^+$ 401.1682, found 401.1683.

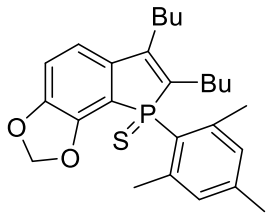


6,7-Dibutyl-8-(4-fluorophenyl)-8*H*-phosphindolo[6,7-*d*][1,3]dioxole 8-sulfide (3lae'): Type **I** arylzinc reagent was used; Pale yellow solid (41% yield, eluent = hexane/EtOAc (20:1)); M. p. = 122-124 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.76 (m, 2H), 7.14 – 7.05 (m, 2H), 6.89 – 6.83 (m, 2H), 6.00 (d, *J* = 1.2 Hz, 1H), 5.90 (d, *J* = 0.8 Hz, 1H), 2.58 (t, *J* = 7.6 Hz, 2H), 2.56 – 2.47 (m, 1H), 2.33 – 2.20 (m, 1H), 1.60 – 1.53 (m, 2H), 1.48 – 1.43 (m, 2H), 1.28 – 1.17 (m, 4H), 0.97 (t, *J* = 7.2 Hz, 3H), 0.74 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3 (dd, J_{CF} = 251.5 Hz, J_{CP} = 3.3 Hz), 149.6 (d, *J* = 15.2 Hz), 148.8 (d, *J* = 8.4 Hz), 148.1 (d, *J* = 4.7 Hz), 137.2 (d, *J* = 23.2 Hz), 134.0 (d, *J* = 79.8 Hz), 133.5 (dd, J_{CP} = 13.7 Hz, J_{CF} = 8.7 Hz), 125.3 (dd, J_{CP} = 81.2 Hz, J_{CF} = 3.0 Hz), 115.9 (dd, J_{CF} = 21.5 Hz, J_{CP} = 14.0 Hz), 115.5 (d, *J* = 9.7 Hz), 113.7 (d, *J* = 92.4 Hz), 110.6 (d, *J* = 1.2 Hz), 102.5 (s), 31.5 (d, *J* = 1.6 Hz), 31.1 (d, *J* = 1.6 Hz), 27.1 (d, *J* = 13.2 Hz), 25.2 (d, *J* = 13.2 Hz), 23.1 (s), 22.8 (s), 13.9 (s), 13.6 (s); ^{31}P NMR (162 MHz, $CDCl_3$): δ 41.9; HRMS (ESI) Calcd for $C_{23}H_{27}O_2PSF$ $[M + H]^+$ 417.1453, found 417.1454.



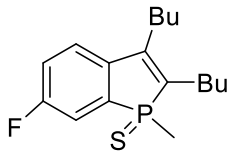
6,7-Dibutyl-8-(4-(trifluoromethyl)phenyl)-8*H*-phosphindolo[6,7-*d*][1,3]dioxole 8-oxide (3laf): Type **I** arylzinc reagent was used. After the addition of PCl_3 and stirring for

12 h, an aryllithium reagent prepared from 1-bromo-4-(trifluoromethyl)benzene and *n*-BuLi in THF was introduced to the reaction vessel, and the resulting mixture was stirred at rt for 6 h; Pale yellow solid (25% yield, eluent = hexane/EtOAc (2:1)); M. p. = 94-96 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.81 (m, 2H), 7.74 – 7.67 (m, 2H), 6.83 (d, *J* = 1.2 Hz, 2H), 5.96 (s, 1H), 5.92 (s, 1H), 2.56 (t, *J* = 7.6 Hz, 2H), 2.49 – 2.41 (m, 1H), 2.27 – 2.16 (m, 1H), 1.60 – 1.53 (m, 2H), 1.50 – 1.43 (m, 2H), 1.40 – 1.27 (m, 2H), 1.30 – 1.20 (m, 2H), 0.98 (t, *J* = 7.2 Hz, 3H), 0.77 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2 (d, *J* = 8.8 Hz), 148.9 (d, *J* = 8.1 Hz), 148.7 (d, *J* = 4.1 Hz), 137.1 (d, *J* = 26.4 Hz), 131.5 (d, *J* = 11.1 Hz), 131.4 (d, *J* = 99.1 Hz), 131.2 (d, *J* = 9.6 Hz), 125.7 (qd, $J_{C\text{-}F}$ = 7.2 Hz, $J_{C\text{-}P}$ = 3.8 Hz), 125.6 (qd, $J_{C\text{-}F}$ = 7.5 Hz, $J_{C\text{-}P}$ = 3.8 Hz), 123.7 (qd, $J_{C\text{-}F}$ = 271.7 Hz, $J_{C\text{-}P}$ = 21.6 Hz), 115.3 (d, *J* = 10.5 Hz), 111.0 (d, *J* = 1.2 Hz), 109.9 (d, *J* = 107.6 Hz), 102.4 (s), 31.2 (d, *J* = 1.8 Hz), 31.0 (d, *J* = 1.7 Hz), 26.7 (d, *J* = 14.0 Hz), 25.8 (d, *J* = 11.3 Hz), 23.1 (s), 22.8 (s), 13.9 (s), 13.6 (s); ^{31}P NMR (162 MHz, $CDCl_3$): δ 35.0; HRMS (ESI) Calcd for $C_{24}H_{27}O_3F_3P$ $[M + H]^+$ 451.1650, found 451.1654.

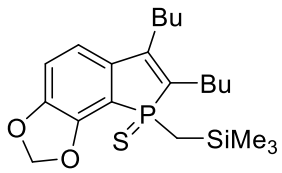


6,7-Dibutyl-8-mesityl-8*H*-phosphindolo[6,7-*d*][1,3]dioxole 8-sulfide (3lag'): Type **I** arylzinc reagent was used; White solid (43% yield, eluent = hexane/EtOAc (20:1)); M. p. = 159-161 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 – 6.83 (m, 4H), 6.02 (s, 1H), 5.98 (s, 1H), 2.68 – 2.62 (m, 1H), 2.60 – 2.56 (m, 1H), 2.52 (s, 6H), 2.48 – 2.36 (m, 2H), 2.27 (s, 3H), 1.64 – 1.46 (m, 5H), 1.44 – 1.30 (m, 3H), 0.99 (t, *J* = 7.2 Hz, 3H), 0.85 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.4 (d, J_{PC} = 8.4 Hz), 147.3 (d, J_{PC} = 4.7 Hz),

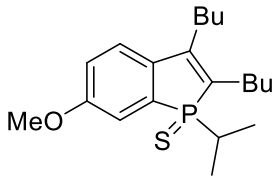
146.5 (d, J_{PC} = 15.1 Hz), 143.9 (d, J_{PC} = 11.2 Hz), 141.1 (d, J_{PC} = 2.9 Hz), 136.8 (d, J_{PC} = 22.8 Hz), 135.9 (d, J_{PC} = 77.2 Hz), 132.0 (d, J_{PC} = 11.1 Hz), 121.5 (d, J_{PC} = 73.7 Hz), 117.1 (d, J_{PC} = 91.1 Hz), 115.9 (d, J_{PC} = 9.6 Hz), 109.9 (d, J_{PC} = 1.1 Hz), 102.3 (s), 31.6 (d, J_{PC} = 1.3 Hz), 30.6 (d, J_{PC} = 1.9 Hz), 26.9 (d, J_{PC} = 12.9 Hz), 26.1 (d, J_{PC} = 13.4 Hz), 24.2 (d, J_{PC} = 5.3 Hz), 23.2 (s), 23.1 (s), 20.9 (d, J_{PC} = 1.1 Hz), 14.0 (s), 13.7 (s); ^{31}P NMR (162 MHz, $CDCl_3$): δ 41.3; HRMS (ESI) Calcd for $C_{26}H_{34}O_2PS$ $[M + H]^+$ 441.2017, found 441.2014.



2,3-Dibutyl-6-fluoro-1-methyl-1*H*-phosphindole 1-sulfide (3hah'): Type **I** arylzinc reagent was used. The reaction with PCl_3 was performed at 60 ℃ (instead of room temperature) for 12 h; Pale yellow oil (38% yield, eluent = hexane/EtOAc (50:1)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 1H), 7.32 – 7.28 (m, 1H), 7.17 – 7.13 (m, 1H), 2.69 – 2.60 (m, 1H), 2.53 (t, J = 7.6 Hz, 2H), 2.49 – 2.39 (m, 1H), 1.87 (d, J = 13.2 Hz, 3H), 1.66 – 1.58 (m, 2H), 1.56 – 1.49 (m, 2H), 1.47 – 1.39 (m, 4H), 0.96 (t, J = 7.2 Hz, 3H), 0.94 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8 (dd, J_{CF} = 249.5 Hz, J_{CP} = 15.4 Hz), 147.0 (d, J = 15.7 Hz), 138.5 (dd, J_{CF} = 25.8 Hz, J_{CP} = 2.9 Hz), 137.6 (dd, J_{CP} = 85.7 Hz, J_{CF} = 6.9 Hz), 135.7 (dd, J_{CP} = 76.1 Hz, J_{CF} = 3.9 Hz), 123.2 (dd, J_{CP} = 12.1 Hz, J_{CF} = 7.7 Hz), 118.8 (dd, J_{CP} = 22.4 Hz, J_{CF} = 1.7 Hz), 115.1 (dd, J_{CF} = 23.7 Hz, J_{CP} = 11.9 Hz), 31.8 (d, J = 1.36 Hz), 30.6 (d, J = 2.0 Hz), 26.7 (d, J = 12.7 Hz), 25.6 (d, J = 12.9 Hz), 23.1 (s), 23.0 (s), 21.4 (d, J_{CP} = 51.6 Hz), 13.9 (s), 13.8 (s); ^{31}P NMR (162 MHz, $CDCl_3$): δ 45.1; HRMS (ESI) Calcd for $C_{17}H_{25}PSF$ $[M + H]^+$ 311.1399, found 311.1398.

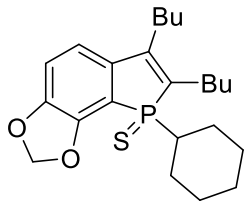


6,7-Dibutyl-8-((trimethylsilyl)methyl)-8*H*-phosphindolo[6,7-*d*][1,3]dioxole 8-sulfide (3lai'): Type **I** arylzinc reagent was used; White solid (35% yield, eluent = hexane/EtOAc (20:1)); M. p. = 96-98 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 – 6.77 (m, 2H), 6.09 (d, *J* = 0.8 Hz, 1H), 6.04 (d, *J* = 1.2 Hz, 1H), 2.60 – 2.51 (m, 1H), 2.46 (t, *J* = 7.6 Hz, 2H), 2.40 – 2.28 (m, 1H), 1.90 – 1.73 (m, 2H), 1.71 – 1.53 (m, 2H), 1.51 – 1.38 (m, 6H), 0.94 (t, *J* = 7.2 Hz, 6H), -0.12 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.3 (d, J_{PC} = 8.2 Hz), 148.1 (d, J_{PC} = 4.9 Hz), 147.3 (d, J_{PC} = 14.8 Hz), 137.2 (d, J_{PC} = 22.7 Hz), 134.3 (d, J_{PC} = 77.0 Hz), 115.3 (d, J_{PC} = 9.2 Hz), 114.0 (d, J_{PC} = 87.9 Hz), 113.4 (d, J_{PC} = 1.3 Hz), 102.3 (s), 32.4 (d, J_{PC} = 1.5 Hz), 30.7 (d, J_{PC} = 1.9 Hz), 26.9 (d, J_{PC} = 12.8 Hz), 25.8 (d, J_{PC} = 13.5 Hz), 23.4 (s), 23.3 (d, J_{PC} = 40.2 Hz), 23.2 (s), 13.9 (s), 13.8 (s), -0.4 (d, J_{PC} = 3.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 45.1; HRMS (ESI) Calcd for $C_{21}H_{34}O_2PSSi$ $[M + H]^+$ 409.1786, found 409.1782.



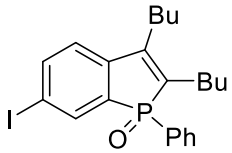
2,3-Dibutyl-1-isopropyl-6-methoxy-1*H*-phosphindole 1-sulfide (3aaj'): Type **I** arylzinc reagent was used; Pale yellow oil (42% yield, eluent = hexane/EtOAc (20:1)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 1H), 7.19 (dd, *J* = 10.0, 2.4 Hz, 1H), 6.98 (dd, *J* = 8.4, 2.0 Hz, 1H), 3.85 (s, 3H), 2.66 – 2.60 (m, 1H), 2.59 – 2.51 (m, 2H), 2.43 – 2.32 (m, 1H), 2.26 – 2.15 (m, 1H), 1.72 – 1.52 (m, 4H), 1.50 – 1.40 (m, 4H), 1.32 (dd, *J* = 18.0, 6.8 Hz, 3H), 0.98 – 0.95 (m, 6H), 0.91 (dd, *J* = 18.8, 7.2 Hz, 3H); ^{13}C NMR (100 MHz,

$CDCl_3$): δ 159.7 (d, J_{PC} = 12.9 Hz), 149.5 (d, J_{PC} = 14.4 Hz), 136.7 (d, J_{PC} = 23.6 Hz), 134.0 (d, J_{PC} = 80.3 Hz), 131.0 (d, J_{PC} = 73.0 Hz), 122.6 (d, J_{PC} = 11.5 Hz), 117.2 (d, J_{PC} = 1.8 Hz), 114.4 (d, J_{PC} = 10.9 Hz), 55.7 (s), 32.0 (d, J_{PC} = 23.8 Hz), 31.7 (d, J_{PC} = 22.8 Hz), 30.9 (d, J_{PC} = 2.0 Hz), 26.9 (d, J_{PC} = 12.1 Hz), 26.0 (d, J_{PC} = 12.4 Hz), 23.2 (s), 23.1 (s), 16.2 (d, J_{PC} = 0.8 Hz), 15.9 (d, J_{PC} = 1.4 Hz), 13.9 (s), 13.8 (s); ^{31}P NMR (162 MHz, $CDCl_3$): δ 62.2; HRMS (ESI) Calcd for $C_{20}H_{32}OPS$ $[M + H]^+$ 351.1912, found 351.1911.



6,7-Dibutyl-8-cyclohexyl-8*H*-phosphindolo[6,7-*d*][1,3]dioxole 8-sulfide (3lak'): Type **I** arylzinc reagent was used; Pale yellow solid (40% yield, eluent = hexane/EtOAc (20:1)); m. p. = 87-89 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 – 6.80 (m, 2H), 6.09 (d, J = 1.2 Hz, 1H), 6.04 (d, J = 1.2 Hz, 1H), 2.58 – 2.49 (m, 3H), 2.47 – 2.31 (m, 2H), 2.01 – 1.96 (m, 1H), 1.93 – 1.86 (m, 1H), 1.72 – 1.63 (m, 4H), 1.59 – 1.49 (m, 3H), 1.47 – 1.38 (m, 4H), 1.36 – 1.08 (m, 5H), 0.95 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.8 (d, J_{PC} = 13.0 Hz), 148.4 (d, J_{PC} = 4.9 Hz), 148.2 (d, J_{PC} = 8.1 Hz), 138.3 (d, J_{PC} = 21.1 Hz), 131.1 (d, J_{PC} = 73.5 Hz), 115.3 (d, J_{PC} = 8.7 Hz), 111.0 (d, J_{PC} = 82.5 Hz), 110.3 (d, J_{PC} = 1.1 Hz), 102.2 (s), 41.4 (d, J_{PC} = 49.9 Hz), 31.8 (d, J_{PC} = 1.4 Hz), 31.1 (d, J_{PC} = 1.9 Hz), 27.2 (d, J_{PC} = 3.0 Hz), 27.0 (d, J_{PC} = 13.0 Hz), 26.9 (d, J_{PC} = 2.1 Hz), 26.7 (d, J_{PC} = 26.1 Hz), 26.4 (d, J_{PC} = 11.5 Hz), 25.8 (d, J_{PC} = 1.6 Hz), 25.9 (d, J_{PC} = 12.8 Hz), 23.2 (s), 23.1 (s), 13.9 (s), 13.8 (s); ^{31}P NMR (162 MHz, $CDCl_3$): δ 58.8; HRMS (ESI) Calcd for $C_{23}H_{34}O_2PS$ $[M + H]^+$ 405.2017, found 405.2020.

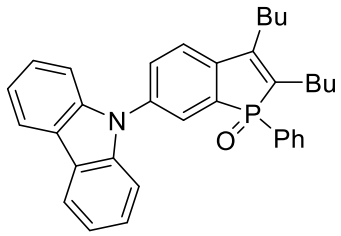
Transformation of functionalized benzophospholes



2,3-Dibutyl-6-iodo-1-phenyl-1*H*-phosphindole 1-oxide (4): A Schlenk tube equipped with a stirrer bar was charged with 2,3-dibutyl-1-phenyl-6-(trimethylsilyl)-1*H*-phosphindole 1-oxide (**3daa**, 82.2 mg, 0.2 mmol), K_2CO_3 (110.3 mg, 0.8 mmol) and purged with nitrogen. Then 1 mL dry methylene chloride was added under nitrogen and the suspension was cooled to 0 ℃. To the suspension was added 130 mg (0.8 mmol) of iodine monochloride in 1 mL of methylene chloride via syringe. The mixture was stirred at 0 ℃ for 1 h and was poured into a solution of 0.3 g of $NaHSO_3$ in 5 mL of water. The mixture was stirred at room temperature for 1 h, diluted with 5 mL of methylene chloride and the organic phase was washed with saturated aqueous $NaHCO_3$ and brine, and then dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was subjected to flash chromatography on silica gel (eluent = hexane/EtOAc (2:1)) to afford the title compound as a yellow gum (86.4 mg, 93%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 – 7.77 (m, 2H), 7.64 – 7.59 (m, 2H), 7.49 – 7.47 (m, 1H), 7.40 – 7.37 (m, 2H), 7.08 (dd, J = 8.0, 2.8 Hz, 1H), 2.55 (t, J = 7.6 Hz, 2H), 2.53 – 2.40 (m, 1H), 2.28 – 2.15 (m, 1H), 1.57 – 1.48 (m, 2H), 1.47 – 1.41 (m, 2H), 1.38 – 1.28 (m, 2H), 1.27 – 1.16 (m, 2H), 0.95 (t, J = 7.2 Hz, 3H), 0.75 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.0 (d, J_{PC} = 19.0 Hz), 142.9 (d, J_{PC} = 28.6 Hz), 141.5 (d, J_{PC} = 1.6 Hz), 137.1 (d, J_{PC} = 10.1 Hz), 135.4 (d, J_{PC} = 19.4 Hz), 134.4 (d, J_{PC} = 13.9 Hz), 132.2 (d, J_{PC} = 2.8 Hz), 130.9 (d, J_{PC} = 10.6 Hz), 129.5 (d, J_{PC} = 97.1 Hz), 128.8 (d, J_{PC} = 12.2 Hz), 123.1 (d, J_{PC} = 11.5 Hz), 93.9 (d, J_{PC} = 12.0 Hz), 30.8 (d, J_{PC} = 1.7 Hz), 30.5 (d, J_{PC} = 1.8 Hz), 26.2 (d, J_{PC} = 13.2 Hz), 25.9 (d, J_{PC} = 10.8 Hz), 23.0 (s), 22.8 (s), 13.9 (s),

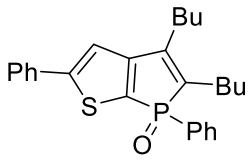
13.6 (s); ^{31}P NMR (162 MHz, $CDCl_3$): δ 38.8; HRMS (ESI) Calcd for $C_{22}H_{27}OPI$ $[M + H]^+$ 465.0844, found 465.0846.



2,3-Dibutyl-6-(9*H*-carbazol-9-yl)-1-phenyl-1H-phosphindole 1-oxide (5): A Schlenk tube equipped with a stirrer bar was charged with CuI (11.5 mg, 0.06 mmol), K_2CO_3 (275.8 mg, 2 mmol), 1,10-phenanthraline (23.8 mg, 0.12 mmol) and carbozole (66.8 mg, 0.4 mmol). The Schlenk tube was evacuated and refilled with N_2 for three times, and then was added 2,3-dibutyl-6-iodo-1-phenyl-1H-phosphindole 1-oxide (**4**, 92.8 mg, 0.2 mmol) and xylene (1 mL) under a stream of nitrogen. The Schlenk tube was sealed with a Teflon screwcap, and then the reaction mixture was refluxed for 30 h. Upon cooling to room temperature, the reaction mixture was diluted with ethyl acetate (5 mL) and filtered through a pad of silica gel. The filtrate was washed with water (10 mL), dried over Na_2SO_4, and then concentrated under reduced pressure. The crude product was subjected to flash chromatography on silica gel (eluent = hexane/EtOAc (5:1)) to afford the title compound as a pale yellow powder (86.6 mg, 86%).

m. p. = 78-79 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.0 Hz, 2H),7.83 – 7.71 (m, 4H), 7.60 (dd, *J* = 8.4, 3.2 Hz, 1H), 7.56 – 7.52 (m, 1H), 7.49 – 7.44 (m, 2H), 7.41 – 7.38 (m, 4H), 7.32 – 7.28 (m, 2H), 2.74 (t, *J* = 7.6 Hz, 2H), 2.65 – 2.57 (m, 1H), 2.43 – 2.37 (m, 1H), 1.75 – 1.70 (m, 2H), 1.61 – 1.47 (m, 4H), 1.39 – 1.29 (m, 2H), 1.09 (t, *J* = 7.2 Hz, 3H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.1 (d, J_{PC} = 18.9 Hz), 142.3 (d, J_{PC} = 28.6 Hz), 140.4 (s), 137.9 (d, J_{PC} = 12.8 Hz), 136.0 (s), 135.2 (d, J_{PC}

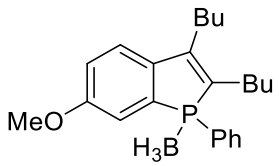
= 29.6 Hz), 134.3 (s), 132.2 (d, J_{PC} = 2.7 Hz), 131.0 (s), 130.9 (s), 129.7 (d, J_{PC} = 97.2 Hz), 128.9 (d, J_{PC} = 12.2 Hz), 127.0 (d, J_{PC} = 10.0 Hz), 126.1 (s), 123.6 (s), 122.6 (d, J_{PC} = 12.3 Hz), 120.3 (d, J_{PC} = 1.8 Hz), 109.7 (s), 31.0 (d, J_{PC} = 1.7 Hz), 30.6 (d, J_{PC} = 1.7 Hz), 26.5 (d, J_{PC} = 13.3 Hz), 26.1 (d, J_{PC} = 10.8 Hz), 23.1 (s), 22.9 (s), 14.0 (s), 13.7 (s); ^{31}P NMR (162 MHz, $CDCl_3$): δ 39.0; HRMS (ESI) Calcd for $C_{34}H_{35}NOP$ $[M + H]^+$ 504.2456, found 504.2455.



4,5-Dibutyl-2,6-diphenyl-6*H*-phospholo[2,3-*b*]thiophene 6-oxide (6): A Schlenk tube equipped with a stirrer bar was charged with $PdCl_2$ (3.5 mg, 0.02 mmol), 2,2'-bipyridyl (6.2 mg, 0.04 mmol), Ag_2CO_3 (55.2 mg, 0.2 mmol) and dry *m*-xylene (0.5 mL) under a stream of nitrogen. The Schlenk tube was headed at 60 ℃ for 20 min. To this Schlenk tube was added 4,5-dibutyl-6-phenyl-6*H*-phospholo[2,3-b]thiophene 6-oxide (**3oaa**, 68.6 mg, 0.2 mmol), iodobenzene (81.1 mg, 0.4 mmol) and dry *m*-xylene (0.5 mL) under a stream of nitrogen. The Schlenk tube was sealed with a Teflon screwcap and then the reaction mixture was stirred at 120 ℃ for 24 h. Upon cooling to room temperature, the reaction mixture was diluted with 5 mL of ethyl acetate, followed by filtration through a pad of silica gel. The filtrate was washed with water (10 mL), dried over Na_2SO_4, and then concentrated under reduced pressure. The crude product was subjected to flash chromatography on silica gel (eluent = hexane/EtOAc (2:1)) to afford the title compound as a yellow oil (42.9 mg, 51%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.65 (m, 2H), 7.61 – 7.59 (m, 2H), 7.52 – 7.48 (m, 1H), 7.44 – 7.31 (m, 5H), 7.25 (d, *J* = 1.2 Hz, 1H), 2.55 (t, *J* = 7.6 Hz, 2H), 2.46 – 2.38

(m, 1H), 2.31 – 2.17 (m, 1H), 1.64 – 1.58 (m, 2H), 1.49 – 1.43 (m, 2H), 1.35 – 1.29 (m, 2H), 1.26 – 1.18 (m, 2H), 0.98 (t, J = 7.2 Hz, 3H), 0.76 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.0 (d, J_{PC} = 3.6 Hz), 156.5 (d, J_{PC} = 29.7 Hz), 145.6 (d, J_{PC} = 16.2 Hz), 136.7 (d, J_{PC} = 98.6 Hz), 133.6 (d, J_{PC} = 0.9 Hz), 132.0 (d, J_{PC} = 2.8 Hz), 130.9 (d, J_{PC} = 10.8 Hz), 130.6 (d, J_{PC} = 101.5 Hz), 129.1 (s), 128.8 (d, J_{PC} = 12.3 Hz), 128.7 (s), 126.8 (d, J_{PC} = 107.9 Hz), 126.0 (s), 117.0 (d, J_{PC} = 13.1 Hz), 31.2 (d, J_{PC} = 1.5 Hz), 30.7 (d, J_{PC} = 1.8 Hz), 27.9 (d, J_{PC} = 13.3 Hz), 26.1 (d, J_{PC} = 11.8 Hz), 22.9 (s), 22.7 (s), 14.0 (s), 13.7 (s); ^{31}P NMR (162 MHz, $CDCl_3$): δ 32.0; HRMS (ESI) Calcd for $C_{26}H_{30}OPS$ $[M + H]^+$ 421.1755, found 421.1757.



2,3-Dibutyl-6-methoxy-1-phenyl-1*H*-phosphindole 1-borane (7): To a stirred solution of 2,3-dibutyl-6-methoxy-1-phenyl-1H-phosphindole 1-oxide (**3aaa**, 220.8 mg, 0.6 mmol) in toluene (1 mL) was added oxalyl chloride (76.2 mg, 0.6 mmol) dissolved in toluene (1 mL) dropwise at room temperature under a nitrogen atmosphere. After 2 h, sodium borohydride (41.8mg, 1.1 mmol) dissolved in diglyme (2 mL) was added dropwise to the reaction mixture. This mixture was stirred for 4 h, diluted with 10 mL of ethyl acetate, washed with deionised water (5 mL) and the isolated organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was subjected to flash chromatography on silica gel (eluent = hexane/EtOAc (10:1)) to afford the title compound as a yellow oil (166.9 mg, 76%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 – 7.53 (m, 2H), 7.49 – 7.43 (m, 1H), 7.39 – 7.33 (m, 3H), 7.07 (dd, J = 12.0, 3.2 Hz, 1H), 7.01 (dd, J = 11.2, 2.4 Hz, 1H), 3.78 (s, 3H), 2.64 (t,

J = 7.6 Hz, 2H), 2.58 – 2.44 (m, 1H), 2.35 – 2.20 (m, 1H), 1.63 – 1.56 (m, 3H), 1.53 – 1.19 (m, 8H), 0.99 (t, *J* = 9.6 Hz, 3H), 0.79 (t, *J* = 9.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.4 (d, J_{PC} = 12.3 Hz), 150.1 (d, J_{PC} = 8.4 Hz), 139.1 (d, J_{PC} = 15.5 Hz), 136.2 (d, J_{PC} = 62.5 Hz), 133.1 (d, J_{PC} = 51.2 Hz), 132.4 (d, J_{PC} = 9.8 Hz), 131.5 (d, J_{PC} = 2.5 Hz), 128.8 (d, J_{PC} = 10.0 Hz), 127.1 (d, J_{PC} = 49.5 Hz), 123.0 (d, J_{PC} = 8.4 Hz), 117.2 (d, J_{PC} = 1.4 Hz), 114.5 (d, J_{PC} = 13.2 Hz), 55.6 (s), 31.5 (d, J_{PC} = 1.5 Hz), 31.1 (d, J_{PC} = 1.3 Hz), 27.0 (d, J_{PC} = 9.0 Hz), 26.8 (d, J_{PC} = 14.1 Hz), 23.0 (s), 22.7 (s), 14.0 (s), 13.7 (s); ^{31}P NMR (162 MHz, $CDCl_3$): δ 31.1; HRMS (ESI) Calcd for $C_{23}H_{30}O_2P$ $[M - BH_3]^+$ 353.2034, found 353.2037.

4.5 References

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Chapter 5. Benzophosphole Synthesis via Alkyne Arylmagnesiation, Electrophilic Trapping and Phospha-Friedel–Crafts Cyclization

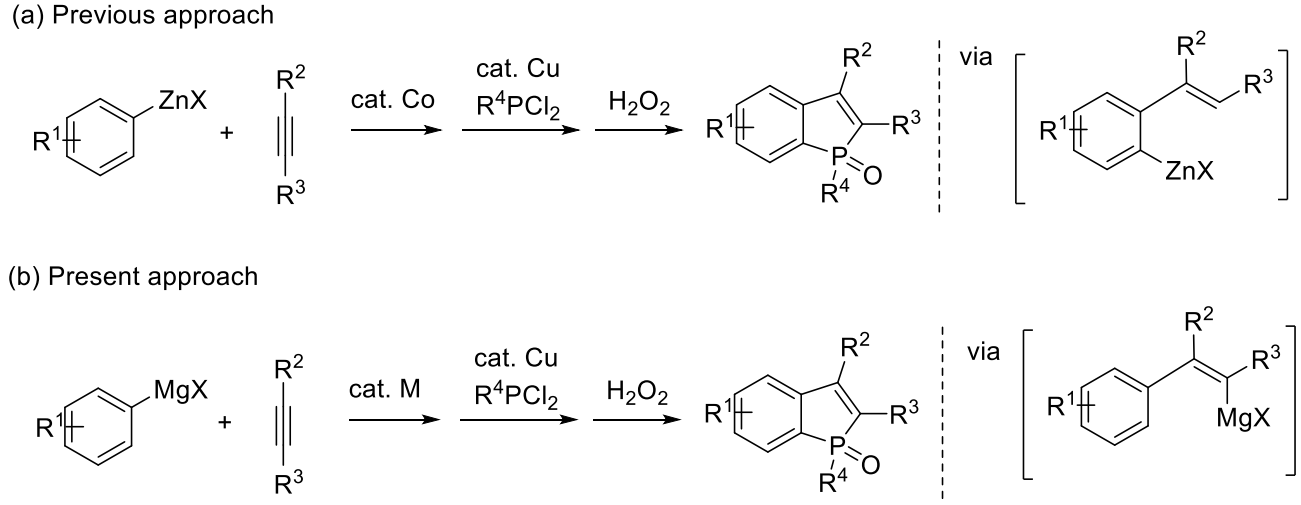
5.1 Introduction

As discussed in the last chapter, the unique properties of benzophospholes have attracted significant attention in the context of organic electronics, imaging, sensing, and catalysis, and thus have stimulated the recent development of methods for their synthesis. [1] The one-pot multicomponent approach based on the cobalt-catalyzed migratory arylzincation of alkynes, described in the last chapter, is notable among others because it enables rapid construction of benzophospholes bearing diverse substituents on the benzo moiety with predictable regioselectivity (Scheme 5.1a). [2] That said, this approach suffers a major limitation with respect to the variation of the substituents on the 2- and 3-position of benzophosphole, which originates from the intrinsic limitation of the cobalt-catalyzed migratory arylzincation. [3] For example, this reaction does not work with diarylalkynes and hence does not allow for the preparation of 2,3-diarylbenzophospholes, regardless of the significant potential utility of such benzophospholes with extended conjugation.

The success of our previous benzophosphole synthesis appears to originate from facile intramolecular P–alkenyl bond formation of the *ortho*-alkenylaryl(chloro)phosphine species, where the alkenyl group serves as a good nucleophile toward the phosphorus(III) center. However, in light of the literature precedents on intramolecular phospha-Friedel–Crafts (PFC) P–aryl bond formation,[4] we reasoned that a *cis*-*β*-styryl(chloro)phosphine species, which could be generated via arylmetalation of alkyne followed by trapping with dichloroorganophosphine, would also serve as a viable precursor to a benzophosphole

(Scheme 5.1). Here, we report that a combination of nickel-catalyzed alkyne arylmagnesiation and PFC cyclization indeed allows for one-pot construction of benzophospholes, especially those bearing aryl groups on the 2- and 3-positions, thus complementing the scope of our previous method based on the migratory arylzincation

Scheme 5.1 Complementary approaches to benzophospholes.

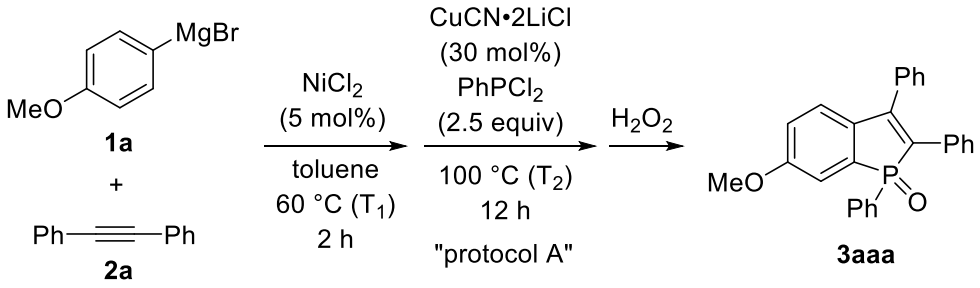


5.2 Results and discussion

At the outset of the present study, we became interested in the use of the Ni-catalyzed alkyne arylmagnesiation reaction, developed by Zhao and Hor,[5] as the initial step of the one-pot benzophosphole synthesis. Compared with other reported catalytic systems for the arylmagnesiation,[6] this catalytic system features several advantages including broad applicability to diarylalkynes, simplicity of catalyst composition, and near stoichiometric ratio of the arylmagnesium reagent and the alkyne. With careful examination of reaction conditions, we were able to achieve the desired multicomponent coupling using 4-methoxyphenylmagnesium bromide (**1a**, 1.2 equiv), diphenylacetylene

(**2a**, 1 equiv), and dichlorophenylphosphine (2.5 equiv) by performing the arylmagnesiation step using 5 mol% of $NiCl_2$ at 60 ℃ and the C–P bond formation step using 30 mol% of CuCN•2LiCl at 100 ℃, which afforded, upon oxidation with H_2O_2, the desired benzophosphole oxide **3aaa** in a respectable isolated yield of 61% (Table 5.1, entry 1; protocol A). While the original arylmagnesiation reaction was performed using 1 mol% of $NiCl_2$•$6H_2O$ at room temperature, such conditions resulted in distinctively lower yields of **3aaa** (entries 2 and 3). The use of 2 equiv of $PhPCl_2$ led to a slightly lower yield (entry 4). An increase in the temperature of the second step did not improve the yield (entry 5), while the yield decreased at lower temperatures (entries 6 and 7). Unlike literature precedents on intramolecular reactions,[4] the addition of a Lewis acid such as $AlCl_3$ did not have a positive influence (entry 8). The yield dropped substantially when CuCN•2LiCl was omitted from the second step (entry 9).

Table 5.1. Screening of reaction conditions (Protocol **A**).[a]



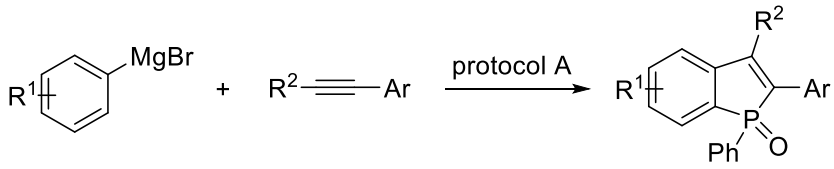
Entry	Deviation from protocol A	Yield (%)[b]
1	None	62 (61)
2	$NiCl_2$ (1 mol%), T_1 = rt	43
3	$NiCl_2$ (1 mol%)	49
4	$PhPCl_2$ (2 equiv)	52
5	T_2 = 120 °C	60
6	T_2 = 80 °C	54
7	T_2 = 60 °C	34
8	$AlCl_3$ (3 equiv) added	49
9	Without CuCN•2LiCl	21

[a] The reaction was performed using 0.6 mmol of **1a** and 0.5 mmol of **2a**. [b] Determined by ^{31}P NMR using triphenylphosphine oxide as an internal standard. Isolated yield is shown in the parentheses.

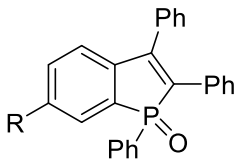
With the protocol A in hand, we explored the scope of aryl Grignard reagents and alkynes for the benzophosphole synthesis (Scheme 5.2). Aryl Grignard reagents bearing electron-donating or electron-withdrawing groups at the *para*-position participated in this reaction with diphenylacetylene to produce 6-substituted benzophosphole oxides **3aaa**-**3gaa** in 38-68% yields. Due to the nonregioselective cyclization, the reaction of *m*-tolylmagnesium bromide resulted in a mixture of 5-methyl and 7-methyl benzophospholes **3haa** and **3haa'** in a nearly 1:1 ratio. Exclusive regioselectivity was

observed for 3,4-methylenedioxyphenylmagnesium bromide, where the cyclization was occurred at less hindered position to furnish 5,6-disubstituted product **3iaa** in 41% yield. 4-Substituted benzophosphole product **3jaa** could also be obtained from *o*-methoxyphenylmagnesium bromide, albeit in a lower yield. A series of diarylalkynes were also examined under the optimized reaction conditions, which afforded the desired products **3aba**-**3aha** in 46-65% yields. Di(2-thienyl)alkyne was also amenable to this reaction, thus producing **3ala** in a moderate yield. Besides diarylalkynes, arylalkylalkynes could also be incorporated into 2-aryl-3-alkyl-benzophosphole derivatives **3aja**-**3ala** with perfect regioselectivity.

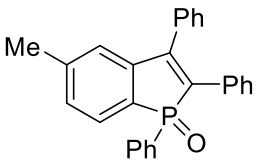
Scheme 5.2. Benzophosphole synthesis using protocol A.[a]



1a-1j **2a-2l** **3**

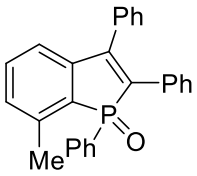


3aaa (R = OMe), 61%
3baa (R = H), 62%
3caa (R = Me), 68%
3daa (R = Ph), 58%
3eaa (R = NMe_2), 56%
3faa (R = $SiMe_3$), 61%
3gaa (R = F), 38%

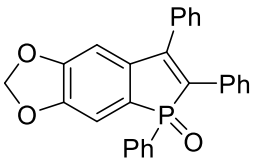


3haa, 35%

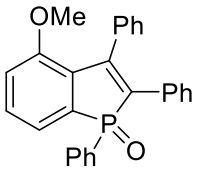
+



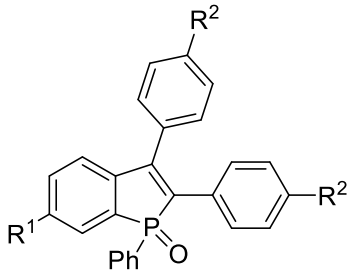
3haa', 40%



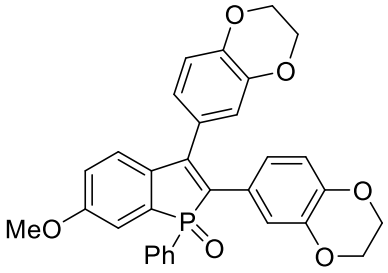
3iaa, 41%



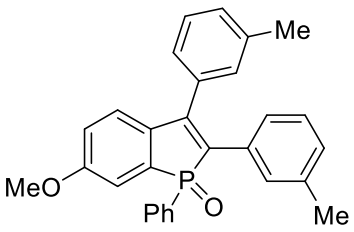
3jaa, 28%



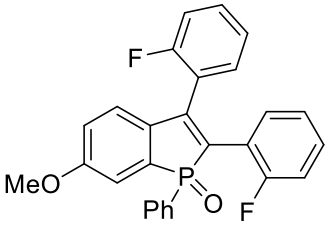
3aba (R^1 = OMe, R^2 = Me), 65%
3aca (R^1 = R^2 = OMe), 57%
3ada (R^1 = OMe, R^2 = F), 51%
3fea (R^1 = R^2 = $SiMe_3$), 60%



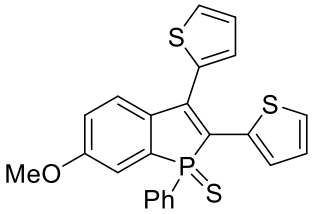
3afa, 58%



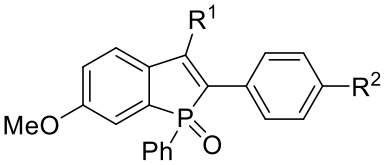
3aga, 61%



3aha, 46%



3aia, 47%[b]



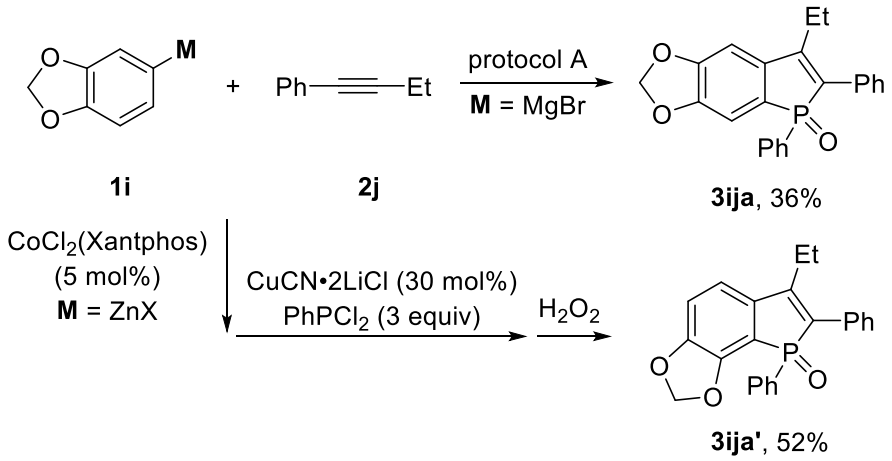
3aja (R^1 = Et, R^2 = H), 37%
3aka (R^1 = Bu, R^2 = Me), 40%
3ala (R^1 = Bu, R^2 = Ph), 41%

[a] The reaction were performed using 0.6 mmol of **1** and 0.5 mmol of **2**. [b] The benzophosphole product was oxidized using sulfur powder instead of H_2O_2.

Interestingly, the present method and our previous protocol based on the cobalt-catalyzed migratory arylzincation allowed us to construct methylenedioxy-substituted benzophosphole derivatives with complementary regioselectivity (Scheme 5.3). The reaction of 3,4-methylenedioxyphenyl Grignard reagent **1i** and 1-phenyl-1-butyne **2j** under the present conditions furnished 5,6-methylenedioxybenzophosphole derivative **3ija**, where the PFC reaction took place on the sterically less hindered aryl carbon atom. By contrast, the application of the corresponding zinc reagent and **2j** to our previous conditions afforded 6,7-methylenedioxybenzophosphole **3ija'** with exclusive

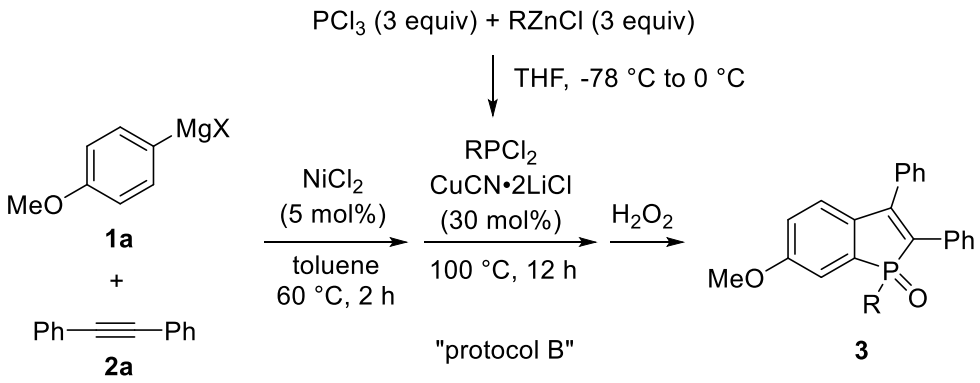
regioselectivity, because the 1,4-cobalt migration occurred on the position proximal to the oxygen atom due to its secondary directing effect.

Scheme 5.3. Benzophospholes synthesis with complementary regioselectivity.



The variation of the substituents on the phosphorus atom was achieved by a slight modification of protocol A (Table 5.2). Thus, to a solution of the alkenylmagnesium species generated by the Ni-catalyzed reaction of **1a** and **2a** was subjected to the reaction with dichloroorganophosphine generated in situ from 1:1 mixture of PCl_3 and the corresponding organozinc reagent under otherwise the same conditions (protocol B). This protocol allowed convenient preparation of benzophospholes bearing different P-aryl and P-alkyl substituents in moderate yields.

Table 5.2. Modified protocol enabling variation of P-substituent.[a]

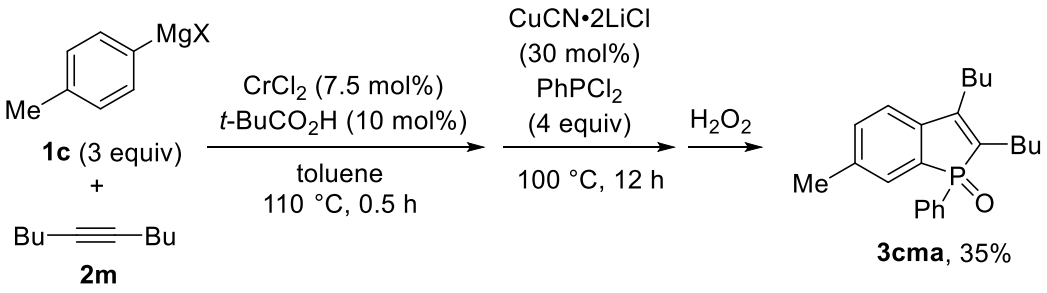


entry	R	product	yield (%)
1	4-$MeOC_6H_4$	**3aab**	47
2	4-$Me_2NC_6H_4$	**3aac**	51
3	4-FC_6H_4	**3aad**	47
4	*i*-Pr	**3aae**	54

[a] The reaction was performed using 0.6 mmol of **1a** and 0.5 mmol of **2a.**

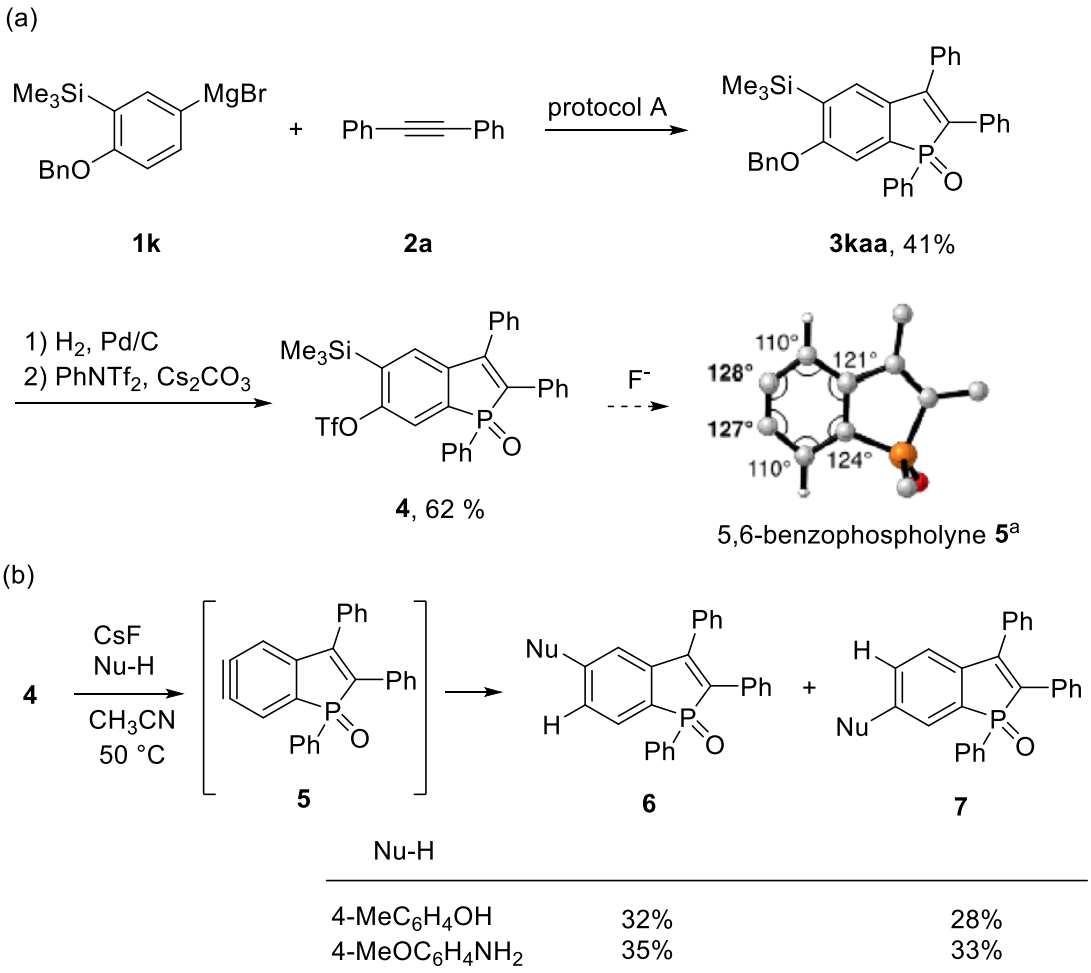
Besides the nickel-catalyzed reaction, other transition metal-catalyzed arylmagnesiation of alkyne could also be applied to the present one-pot approach to benzophosphole. For example, the reaction between *p*-tolyl Grignard reagent **1c** with 5-decyne **2m** in the presence of chromium catalyst developed by Yorimitsu and Oshima[7] followed by the present P–C coupling procedures afforded 2,3-dibutylbenzophosphole **3cma** in a modest yield (Scheme 5.4). This protocol is complementary to the one employing the nickel-catalyzed arylmagnesiation, because the nickel catalysis is not applicable to dialkylalkynes.

Scheme 5.4. Benzophosphole synthesis employing Cr-catalyzed arylmagnesiation.



Compared with existing methods, the present approach enables convenient construction of benzophospholes with various substituents on the benzene ring. Taking this advantage, we investigated the reactivity of hitherto unknown 5,6-benzophospholynes (Scheme 5.5). Treatment of 3-trimethylsilyl-4-benzyloxyphenyl Grignard reagent **1k** with diphenylacetylene under the standard conditions followed by deprotection of benzyl group and subsequently triflation provided the silyl triflate precursor **4** in a reasonable yield. Inspired by the work of Garg and Houk on the chemistry of indolynes,[8] before the reaction experiments using **4**, we examined the structure of the 5,6-benzophospholyne **5** by a DFT calculation (Scheme 5.5a). The internal angles at the C≡C termini of 5,6-benzophospholyne are very close to each other (θ_{CCC} = 128 and 127 °), suggesting similar reactivity of C-5 and C-6 positions toward nucleophilic attack. In accordance with this computational prediction, the reaction of **4** with *p*-cresol or *p*-anisidine in the presence of CsF afforded a nearly equimolar mixture of regioisomeric adducts **6** and **7** (Scheme 5.5b).

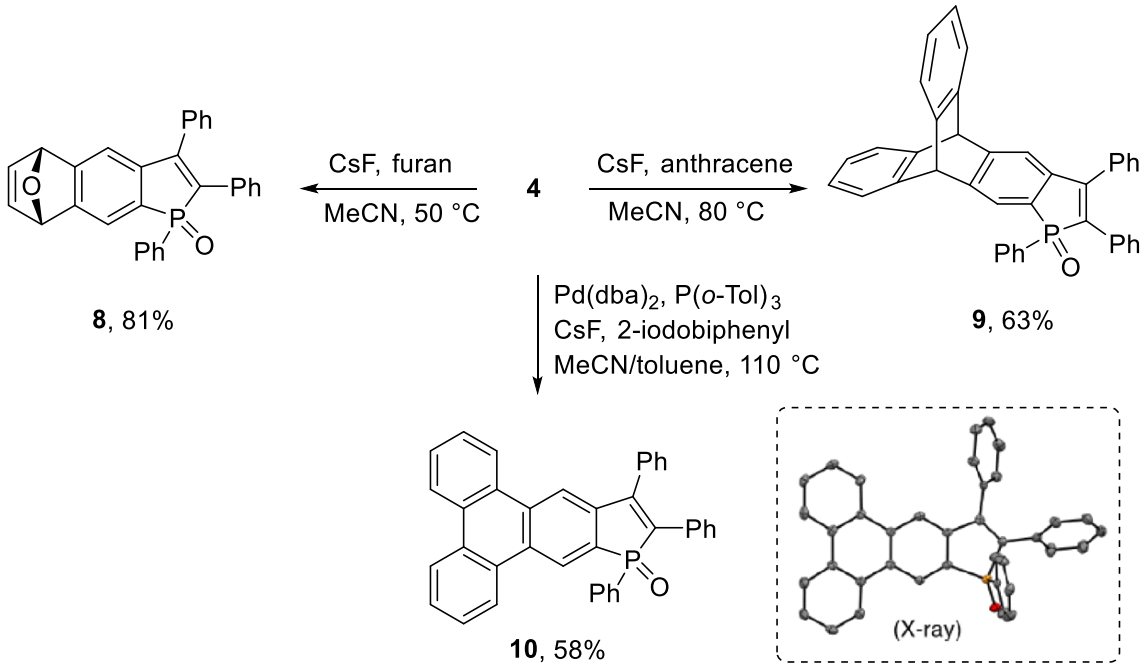
Scheme 5.5. Generation and reactivity of 5,6-benzophospholyne.



[a]B3LYP/6-31G(d)-optimized structure (phenyl groups at the 1-, 2-, and 3-positions have been omitted for clarity).

The 5,6-benzophospholyne **5** could participate in a variety of cycloaddition reactions (Scheme 5.6). Interception with furan afforded the Diels-Alder product **8** in 81% yield. Anthracene could also be used to trap 5,6-benzophospholyne **5**, thus affording phosphole-embedded triptycene **9**. Finally, palladium-catalyzed annulation of **5** and 2-iodobiphenyl under the conditions developed by Larock[9] produced phosphole-embedded triphenylene **10**, the structure of which was confirmed by X-ray crystallographic analysis.

Scheme 5.6. Cycloaddition reaction of 5,6-benzophospholyne.



5.3 Conclusion

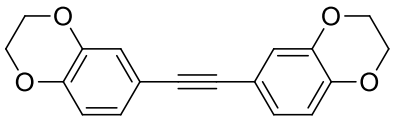
In summary, we have developed a new method for the sequential one-pot multicomponent synthesis of a highly substituted benzophosphole derivative from an aryl Grignard reagent, an alkyne, and a dichloroorganophosphine ($RPCl_2$). The method features an integration of transition metal-catalyzed arylmagnesiation of the alkyne, electrophilic trapping of the resulting alkenylmagnesium species with $RPCl_2$, and subsequent intramolecular phospha-Friedel–Crafts-type cyclization. By choosing appropriate arylmagnesiation and P–C bond forming conditions, this method allows for the modular synthesis of benzophospholes bearing a variety of substituents on the phosphorus atom, the C2 and C3 positions, as well as the "benzo" moiety, which are not easily accessible by existing synthetic methods. In particular, the merit of the flexibility with respect to the benzo moiety has been demonstrated by a facile preparation of a

hitherto unknown 5,6-benzophospholyne precursor and a study of its reactivity in nucleophilic trapping and cycloaddition reactions.

5.4 Experimental section

Preparation of starting materials

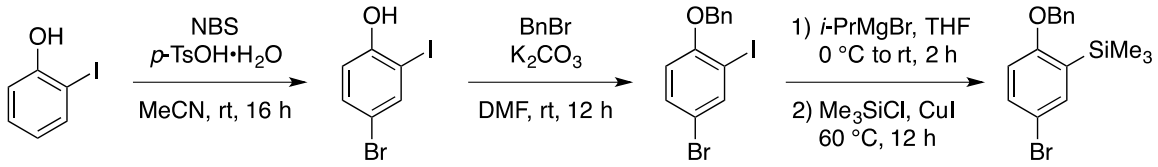
Internal alkynes 1,2-di-*p*-tolylethyne (2b),[10] 1,2-bis(4-methoxyphenyl)ethyne (2c),[1] 1,2-bis(4-fluorophenyl)ethyne (2d),[1] 1,2-bis(4-(trimethylsilyl)phenyl)ethyne (2e),[11] 1,2-di-*m*-tolylethyne (2g),[12] 1,2-bis(2-fluorophenyl)ethyne (2h),[1] 1,2-di(thiophen-2-yl)ethyne (2i)[1], 1-butyl-4-(*p*-tolylethynyl)benzene (2k),[13] 4-((4-butylphenyl)ethynyl)-1,1'-biphenyl (2l),[14] were prepared according the literature procedures. For the known substrates, their ^{1}H and ^{13}C NMR spectra showed good agreement with the literature data. Below are summarized general procedure and characterization data for newly synthesized substrates**.**



1,2-Bis(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)ethyne (2f): A 25 mL round bottom flask with magnetic stir bar was fitted with a rubber septum and dried under vacuum. The flask was purged with N_2, and charged with $PdCl_2(PPh_3)_2$ (105.0 mg, 0.375 mmol), CuI (95.0 mg, 0.625 mmol) and 6-iodo-2,3-dihydrobenzo[*b*][1,4]dioxine (1.3 g, 5.0 mmol). While stirring, dry THF (25 mL), DBU (4.5 mL, 30 mmol) and thrimethylsilylethynylene (0.36 mL, 2.5 mmol) were added by syringe, followed immediately by distilled water (36.3 μL, 2.5 mmol). The reaction flask was covered in aluminum foil and left stirring at a high rate of speed for 18 h, at the end of which the reaction mixture was partitioned in ethyl ether

and water. The organic layer was washed with 10% HCl, saturated aqueous NaCl, dried over $MgSO_4$, gravity-filtered and the solvent removed in vacuo. The crude product was purified by flash chromatography on silica gel (eluent = hexane/EtOAc (30:1)) to afford the product as a white solid (1.1 g, 72% yield). M.p. = 128-129 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 – 6.99 (m, 4H), 6.81 (d, *J* = 8.4 Hz, 2H), 4.27 – 4.24 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.0, 143.3, 125.2, 120.3, 117.3, 116.3, 87.6, 64.5, 64.3; HRMS (ESI) Calcd for $C_{18}H_{15}O_4$ $[M + H]^+$ 295.0970, found 295.0977.

Preparation of (2-(benzyloxy)-5-bromophenyl)trimethylsilane



4-Bromo-2-iodophenol: The title compound was prepared according to the literature procedure.[15] To a solution of 2-iodophenol (11.0 g, 50.0 mmol) in CH_3CN (150 mL) was added *p*-toluenesulfonic acid monohydrate (9.5 g, 50.0 mmol), followed by *N*-bromosuccinimide (7.3 g, 55.0 mmol). The mixture was stirred for 16 h at ambient temperature and then quenched by addition of aqueous Na_2SO_3 solution. It was acidified by addition of aqueous HCl (1 M), the organic solvent was evaporated, and the aqueous layer was extracted with diethyl ether. The combined organic layers were dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica to furnish the desired product as a white solid (9.7g, 65% yield). The ^{1}H and ^{13}C NMR spectra showed good agreement with the literature data.

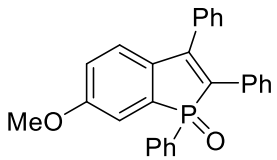
1-(Benzyloxy)-4-bromo-2-iodobenzene: The protection of alcohol group was performed according to the literature procedure.[16] To a solution of 4-bromo-2-iodophenol (6.0 g, 20.0 mmol) in *N*,*N*-dimethylformamide (50.0 ml) was added potassium carbonate (4.1 g, 30.0 mmol) and benzyl bromide (2.9 ml, 24.0 mmol), and the mixture was stirred at room temperature for 12 hours. Water was added to the reaction solution, followed by extraction with diethyl ether. The organic layer was washed with brine, dried over $MgSO_4$, and then concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent = hexane) to give the title compound as a white solid (5.1 g, 85% yield). M.p. = 53-54 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 2.4 Hz, 1H), 7.52 (d, *J* = 7.2 Hz, 2H), 7.47 – 7.37 (m, 4H), 6.75 (d, *J* = 8.8 Hz, 1H), 5.16 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.6, 141.3, 136.1, 132.2, 128.7, 128.1, 127.1, 113.9, 113.8, 87.7, 71.2; HRMS (ESI) Calcd for $C_{13}H_{11}OBrI$ $[M + H]^+$ 388.9038, found 388.9022.

(2-(Benzyloxy)-5-bromophenyl)trimethylsilane: The title compound was prepared from 1-(benzyloxy)-4-bromo-2-iodobenzene through iodine–magnesium exchange[17] followed by copper catalyzed arylation with chlorosilanes.[18] To a solution of 1-(benzyloxy)-4-bromo-2-iodobenzene (5.8 g, 15.0 mmol) in THF (30 mL) was slowly added *i*PrMgBr (18.8 mL, 0.94 M in THF, 17.2 mmol) at 0 ℃. After stirring at room temperature for 2 h, Me_3SiCl (5.7 mL, 45.0 mmol) and CuI (285.0 mg, 1.5 mmol) were added and the mixture was stirred at 60 ℃ for 12 h before a saturated aqueous solution of NH_4Cl was added. The mixture was extracted with ethyl acetate and the combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent = hexane) to give the title compound as a white solid (3.3 g, 65% yield). M.p. = 94-95 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 2.4

Hz, 1H), 7.54 – 7.44 (m, 6H), 6.84 (d, *J* = 8.8 Hz, 1H), 5.14 (s, 2H), 0.40 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.3, 137.6, 136.8, 133.2, 131.5, 128.7, 128.1, 127.5, 113.7, 112.5, 70.3, -0.9; HRMS (ESI) Calcd for $C_{16}H_{20}OSiBr$ $[M + H]^+$ 335.0467, found 335.0475.

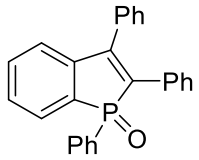
Benzophosphole synthesis through Ni-catalyzed arylmagnesiation of alkyne

Protocol A: A 25 mL Schlenk tube equipped with a stirrer bar was charged with $NiCl_2$ (3.2 mg, 0.025 mmol) and alkyne (0.5 mmol). The Schlenk tube was evacuated and backfilled with N_2 for three times, and followed by the addition of toluene (2 mL) and aryl Grignard reagent (0.6 mmol). The resulting mixture was stirred at 60 ℃ for 2 h and then allowed to cool to room temperature. To the Schlenk tube was added a THF solution of CuCN•2LiCl (0.15 mmol), $PhPCl_2$ (169.6 μL, 1.25 mmol), and the resulting solution was stirred at 100 ℃ for 12 h. The Schlenk tube was cooled in an ice bath and to this was added an aqueous solution of H_2O_2 (ca. 30%, a few drops). After stirring at room temperature for 30 min, the reaction mixture was diluted with ethyl acetate (15 mL). The organic layer was washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product.

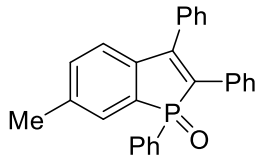


6-Methoxy-1,2,3-triphenyl-1*H*-phosphindole 1-oxide (3aaa): Yellow solid (124.4 mg, 61% yield, eluent = hexane/EtOAc (1:1)); M.p. = 78-79 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.78 (m, 2H), 7.49 – 7.42 (m, 6H), 7.35 – 7.28 (m, 3H), 7.21 – 7.09 (m, 6H), 6.95

(d, J = 7.2 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.8 (d, J_{PC} = 13.5 Hz), 150.4 (d, J_{PC} = 21.2 Hz), 136.1 (d, J_{PC} = 26.9 Hz), 134.5 (d, J_{PC} = 15.3 Hz), 134.4, 133.4, 132.8 (d, J_{PC} = 9.9 Hz), 132.2 (d, J_{PC} = 2.5 Hz), 131.3, 131.0 (d, J_{PC} = 10.6 Hz), 129.9 (d, J_{PC} = 99.2 Hz), 129.0, 128.9, 128.8, 128.7, 128.2, 127.6, 125.3 (d, J_{PC} = 12.7 Hz), 118.0 (d, J_{PC} = 1.5 Hz), 114.8 (d, J_{PC} = 10.7 Hz), 55.7; ^{31}P NMR (162 MHz, $CDCl_3$): δ 39.3; HRMS (ESI) Calcd for $C_{27}H_{22}O_2P$ $[M + H]^+$ 409.1357, found 409.1355.

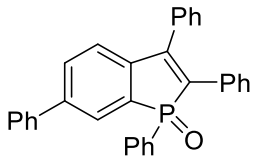


1,2,3-Triphenyl-1*H*-phosphindole 1-oxide (3baa): White solid (117.2 mg, 62% yield, eluent = hexane/EtOAc (2:1)); M.p. = 75-76 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.77 (m, 2H), 7.74 – 7.69 (m, 1H), 7.49 – 7.33 (m, 10H), 7.25 – 7.21 (m, 3H), 7.10 – 7.08 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.1 (d, J_{PC} = 21.3 Hz), 143.7 (d, J_{PC} = 27.0 Hz), 134.7 (d, J_{PC} = 95.1 Hz), 134.2 (d, J_{PC} = 14.9 Hz), 132.9 (d, J_{PC} = 1.8 Hz), 132.7 (d, J_{PC} = 9.8 Hz), 132.5, 132.2 (d, J_{PC} = 2.8 Hz), 131.5, 131.0 (d, J_{PC} = 10.6 Hz), 129.9 (d, J_{PC} = 99.1 Hz), 129.2, 129.1 (d, J_{PC} = 10.6 Hz), 129.0 (br, 2C, overlapped), 128.9, 128.8 (d, J_{PC} = 11.1 Hz), 128.3, 127.9, 124.1 (d, J_{PC} = 10.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 39.2; HRMS (ESI) Calcd for $C_{26}H_{20}OP$ $[M + H]^+$ 379.1252, found 379.1248.

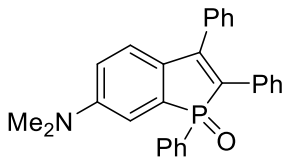


6-Methyl-1,2,3-triphenyl-1*H*-phosphindole 1-oxide (3caa): Yellow oil (133.3 mg, 68% yield, eluent = hexane/EtOAc (2:1)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.75 (m, 2H), 7.50 (d, J = 10.0 Hz, 1H), 7.45 – 7.34 (m, 6H), 7.33 – 7.30 (m, 2H), 7.24 – 7.20 (m, 3H),

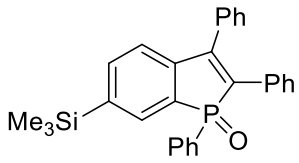
7.08 (dd, J = 8.0, 3.2 Hz, 1H), 7.05 – 7.02 (m, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.3 (d, J_{PC} = 21.4 Hz), 141.1 (d, J_{PC} = 26.9 Hz), 139.5 (d, J_{PC} = 10.5 Hz), 134.4 (d, J_{PC} = 15.0 Hz), 133.4 (d, J_{PC} = 1.7 Hz), 133.1 (d, J_{PC} = 95.8 Hz), 132.8 (d, J_{PC} = 9.8 Hz), 132.7, 132.2 (d, J_{PC} = 2.8 Hz), 131.1 (d, J_{PC} = 107.3 Hz), 130.9 (d, J_{PC} = 10.6 Hz), 129.8 (d, J_{PC} = 9.5 Hz), 129.6 (d, J_{PC} = 13.2 Hz), 129.1, 129.0, 128.9, 128.8 (d, J_{PC} = 14.7 Hz), 128.2, 127.7, 124.0 (d, J_{PC} = 11.5 Hz), 21.3; ^{31}P NMR (162 MHz, $CDCl_3$): δ 39.3; HRMS (ESI) Calcd for $C_{27}H_{22}OP$ $[M + H]^+$ 393.1408, found 393.1411.



1,2,3,6-Tetraphenyl-1*H*-phosphindole 1-oxide (3daa): Yellow solid (131.7 mg, 58% yield, eluent = hexane/EtOAc (2:1)); M.p. = 215-216 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 9.6 Hz, 1H), 7.86 (dd, J = 12.4, 7.2 Hz, 2H), 7.70 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 7.6 Hz, 2H), 7.49 – 7.28 (m, 14H), 7.13 – 7.12 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.9 (d, J_{PC} = 21.1 Hz), 142.7 (d, J_{PC} = 27.0 Hz), 142.2 (d, J_{PC} = 10.6 Hz), 139.6, 134.4 (d, J_{PC} = 95.4 Hz), 134.3 (d, J_{PC} = 14.9 Hz), 133.0 (d, J_{PC} = 104.5 Hz), 132.8 (d, J_{PC} = 9.9 Hz), 132.3 (d, J_{PC} = 2.7 Hz), 131.4 (d, J_{PC} = 7.4 Hz), 131.0 (d, J_{PC} = 10.6 Hz), 129.9 (d, J_{PC} = 99.1 Hz), 129.1 (2C, overlapped), 129.0 (2C, overlapped), 128.9 (d, J_{PC} = 10.1 Hz), 128.3, 128.1, 128.0, 127.9 (d, J_{PC} = 3.5 Hz), 127.8, 127.0, 124.5 (d, J_{PC} = 11.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 38.9; HRMS (ESI) Calcd for $C_{32}H_{24}OP$ $[M + H]^+$ 455.1565, found 455.1561.

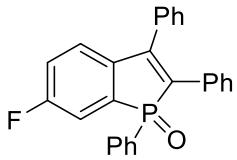


6-(Dimethylamino)-1,2,3-triphenyl-1*H*-phosphindole 1-oxide (3eaa): Yellow solid (117.9 mg, 56% yield, eluent = hexane/EtOAc (1:1)); M.p. = 165-166 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 12.0, 7.2 Hz, 2H), 7.46 – 7.38 (m, 8H), 7.18 – 7.16 (m, 2H), 7.09 – 7.03 (m, 5H), 6.62 (dd, *J* = 8.4, 1.2 Hz, 1H), 2.94 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.3, 151.0 (d, J_{PC} = 12.3 Hz), 135.0 (d, J_{PC} = 15.3 Hz), 134.5, 133.4 (d, J_{PC} = 2.1 Hz), 133.3, 131.9 (d, J_{PC} = 2.6 Hz), 131.4 (d, J_{PC} = 33.1 Hz), 131.0 (d, J_{PC} = 10.6 Hz), 130.0 (d, J_{PC} = 103.8 Hz), 129.0, 128.9, 128.8 (d, J_{PC} = 3.7 Hz), 128.7, 128.6 (d, J_{PC} = 28.7 Hz), 128.1, 127.0, 125.1 (d, J_{PC} = 12.5 Hz), 114.3, 113.0 (d, J_{PC} = 11.4 Hz), 40.4; ^{31}P NMR (162 MHz, $CDCl_3$): δ 39.6; HRMS (ESI) Calcd for $C_{28}H_{25}NOP$ $[M + H]^+$ 422.1674, found 422.1676.

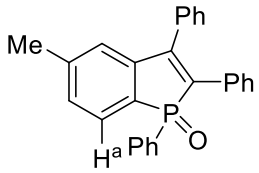


1,2,3-Triphenyl-6-(trimethylsilyl)-1*H*-phosphindole 1-oxide (3faa): Light yellow solid (137.4 mg, 61% yield, eluent = hexane/EtOAc (2:1)); M.p. = 161-162 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 9.6 Hz, 1H), 7.82 – 7.77 (m, 2H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.45 – 7.31 (m, 6H), 7.33 – 7.31 (m, 2H), 7.24 – 7.19 (m, 3H), 7.07 – 7.05 (m, 3H), 0.24 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.2 (d, J_{PC} = 21.7 Hz), 144.3 (d, J_{PC} = 27.3 Hz), 142.5 (d, J_{PC} = 7.6 Hz), 138.2 (d, J_{PC} = 1.5 Hz), 134.3 (d, J_{PC} = 95.0 Hz), 134.2 (d, J_{PC} = 14.8 Hz), 133.6 (d, J_{PC} = 8.7 Hz), 132.7 (d, J_{PC} = 9.7 Hz), 132.2 (d, J_{PC} = 2.9 Hz), 131.5, 131.0 (d, J_{PC} = 10.6 Hz), 130.4 (d, J_{PC} = 15.4 Hz), 129.3, 129.1, 129.0 (d, J_{PC} = 2.1 Hz),

128.8, 128.7 (d, J_{PC} = 13.0 Hz), 128.3, 127.9, 123.3 (d, J_{PC} = 10.1 Hz), -1.2; ^{31}P NMR (162 MHz, $CDCl_3$): δ 40.9; HRMS (ESI) Calcd for $C_{29}H_{28}OPSi$ $[M + H]^+$ 451.1647, found 451.1644.

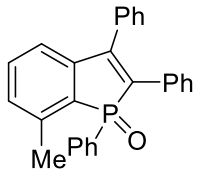


6-Fluoro-1,2,3-triphenyl-1*H*-phosphindole 1-oxide (3gaa): Light yellow gum (75.3 mg, 38% yield, eluent = hexane/EtOAc (2:1)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.74 (m, 2H), 7.53 – 7.49 (m, 1H), 7.45 – 7.38 (m, 6H), 7.33 – 7.31 (m, 2H), 7.22 – 7.16 (m, 3H), 7.13 – 7.07 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4 (dd, J_{CF} = 251.4 Hz, J_{CP} = 15.1 Hz), 149.5 (d, J = 20.4 Hz), 139.6 (d, J = 29.8 Hz), 135.4 (d, J = 6.9 Hz), 134.4 (dd, J_1 = 8.1 Hz, J_2 = 4.0 Hz), 134.0 (d, J = 15.2 Hz), 133.5 (d, J = 3.8 Hz), 132.5 (d, J = 2.9 Hz), 132.4, 130.9 (d, J = 10.7 Hz), 129.2 (d, J = 99.8 Hz), 129.1, 129.0, 128.9 (2C, overlapped), 128.3, 127.9 (d, J = 0.5 Hz), 125.7 (dd, J_{CP} = 12.7 Hz, J_{CF} = 7.7 Hz), 119.4 (d, J = 22.3 Hz), 116.8 (dd, J_{CF} = 23.8 Hz, J_{CP} = 10.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 37.9 (d, J_{FP} = 5.3 Hz) ; HRMS (ESI) Calcd for $C_{26}H_{19}OPF$ $[M + H]^+$ 397.1158, found 397.1161.

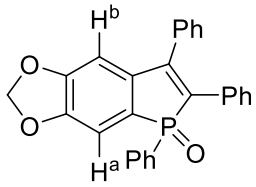


5-Methyl-1,2,3-triphenyl-1*H*-phosphindole 1-oxide (3haa): Yellow gum (68.8 mg, 35% yield, eluent = hexane/EtOAc (2:1)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.73 (m, 2H), 7.59 (dd, J_{PH} = 9.6 Hz, J_{HH} = 7.2 Hz, 1H), 7.48 – 7.34 (m, 6H), 7.33 – 7.31 (m, 2H), 7.23

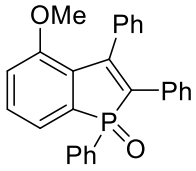
– 7.16 (m, 3H), 7.09 – 7.05 (m, 3H), 7.00 (s, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.1 (d, J_{PC} = 21.4 Hz), 144.1 (d, J_{PC} = 27.2 Hz), 143.7 (d, J_{PC} = 2.0 Hz), 134.6 (d, J_{PC} = 95.1 Hz), 134.4 (d, J_{PC} = 14.9 Hz), 132.8 (d, J_{PC} = 9.8 Hz), 132.1 (d, J_{PC} = 2.8 Hz), 131.0 (d, J_{PC} = 10.5 Hz), 130.7, 129.7 (d, J_{PC} = 11.0 Hz), 129.4 (d, J_{PC} = 8.8 Hz), 129.3, 129.2, 129.1, 129.0 (d, J_{PC} = 2.3 Hz), 128.9, 128.7 (d, J_{PC} = 13.0 Hz), 128.2, 127.8, 125.0 (d, J_{PC} = 11.2 Hz), 21.9; ^{31}P NMR (162 MHz, $CDCl_3$): δ 38.9; HRMS (ESI) Calcd for $C_{27}H_{22}OP$ $[M + H]^+$ 393.1408, found 393.1406. The regiochemistry of this compound was assigned on the basis of the dd signal at 7.59 ppm (H^a) in the ^{1}H NMR spectrum.



7-Methyl-1,2,3-triphenyl-1*H*-phosphindole 1-oxide (3haa'): Yellow solid (72.4 mg, 40% yield, eluent = hexane/EtOAc (2:1)); M.p. = 51-52 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.78 (m, 2H), 7.45 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.39 – 7.36 (m, 5H), 7.34 – 7.30 (m, 3H), 7.23 – 7.20 (m, 2H), 7.12 – 7.06 (m, 4H), 7.01 (dd, *J* = 7.6, 2.8 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.1 (d, J_{PC} = 21.6 Hz), 144.0 (d, J_{PC} = 27.1 Hz), 141.1 (d, J_{PC} = 8.9 Hz), 134.5 (d, J_{PC} = 14.9 Hz), 133.6, 133.0 (d, J_{PC} = 1.6 Hz), 132.8 (d, J_{PC} = 9.8 Hz), 132.0 (d, J_{PC} = 2.9 Hz), 131.0 (d, J_{PC} = 10.6 Hz), 130.7 (d, J_{PC} = 9.3 Hz), 130.1, 130.0 (d, J_{PC} = 104.4 Hz), 129.1, 129.0, 128.9, 128.8, 128.6, 128.2, 127.7, 121.7 (d, J_{PC} = 10.9 Hz), 19.3 (d, J_{PC} = 4.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 39.4; HRMS (ESI) Calcd for $C_{27}H_{22}OP$ $[M + H]^+$ 393.1408, found 393.1408. The regiochemistry of this compound was assigned on the basis of the doublet signal at 19.3 ppm (methyl carbon) in the ^{13}C NMR spectrum.

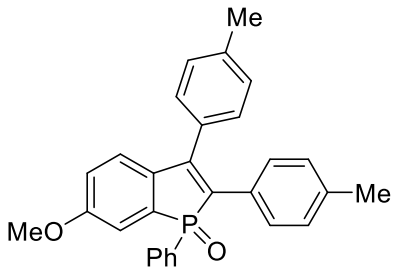


5,6,7-Triphenyl-5*H*-phosphindolo[5,6-*d*][1,3]dioxole 5-oxide (3iaa): Yellow gum (86.5 mg, 41% yield, eluent = hexane/EtOAc (1:1)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.74 (m, 2H), 7.49 – 7.37 (m, 6H), 7.31 – 7.29 (m, 2H), 7.19 – 7.17 (m, 2H), 7.13 (d, J_{PH} = 9.2 Hz, 1H), 7.08 – 7.06 (m, 3H), 6.67 (d, J_{PH} = 2.4 Hz, 1H), 6.00 (d, J = 1.2 Hz, 1H), 5.99 (d, J = 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.7 (d, J_{PC} = 2.0 Hz), 149.3 (d, J_{PC} = 21.3 Hz), 148.7 (d, J_{PC} = 16.6 Hz), 139.6 (d, J_{PC} = 28.5 Hz), 134.4 (d, J_{PC} = 15.4 Hz), 133.4 (d, J_{PC} = 95.8 Hz), 132.7 (d, J_{PC} = 10.0 Hz), 132.1 (d, J_{PC} = 2.8 Hz), 130.9 (d, J_{PC} = 10.5 Hz), 130.2 (d, J_{PC} = 99.5 Hz), 129.1, 129.0, 128.9, 128.8, 128.7, 128.2, 127.7, 125.4 (d, J_{PC} = 109.2 Hz), 109.3 (d, J_{PC} = 12.6 Hz), 105.7 (d, J_{PC} = 13.7 Hz), 102.1; ^{31}P NMR (162 MHz, $CDCl_3$): δ 37.9; HRMS (ESI) Calcd for $C_{27}H_{20}O_3P$ $[M + H]^+$ 423.1150, found 423.1148. The regiochemistry of this compound was assigned on the basis of the doublet signals at 7.13 ppm (H^a) and 6.67 ppm (H^b) in the ^{1}H NMR spectra.

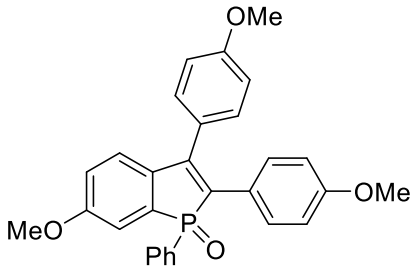


4-Methoxy-1,2,3-triphenyl-*1H*-phosphindole 1-oxide (3jaa): Yellow solid (57.2 mg, 28% yield, eluent = hexane/EtOAc (2:1)); M.p. = 178-179 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.75 (m, 2H), 7.47 (dd, J = 7.2, 1.2 Hz, 1H), 7.41 – 7.36 (m, 3H), 7.35 – 7.26 (m, 6H), 7.13 – 7.11 (m, 2H), 7.05 – 7.03 (m, 3H), 7.00 (d, J = 8.0 Hz, 1H), 3.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.1 (d, J_{PC} = 14.5 Hz), 150.4 (d, J_{PC} = 21.3 Hz), 137.3 (d,

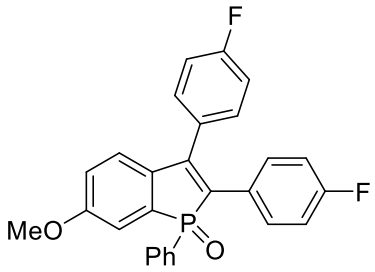
J_{PC} = 15.3 Hz), 134.4 (d, J_{PC} = 102.8 Hz), 134.0 (d, J_{PC} = 94.0 Hz), 132.9 (d, J_{PC} = 9.6 Hz), 132.1 (d, J_{PC} = 2.8 Hz), 131.2 (d, J_{PC} = 12.6 Hz), 131.0 (d, J_{PC} = 10.6 Hz), 130.5, 130.1 (d, J_{PC} = 27.6 Hz), 129.5, 129.2 (d, J_{PC} = 5.5 Hz), 128.8 (d, J_{PC} = 12.2 Hz), 128.6, 128.0, 127.5, 127.4, 121.7 (d, J_{PC} = 9.3 Hz), 117.8 (d, J_{PC} = 1.7 Hz), 55.7; ^{31}P NMR (162 MHz, $CDCl_3$): δ 38.8; HRMS (ESI) Calcd for $C_{27}H_{22}O_2P$ $[M + H]^+$ 409.1357, found 409.1357.



6-Methoxy-1-phenyl-2,3-di-*p*-tolyl-1*H*-phosphindole 1-oxide (3aba): Yellow solid (141.8 mg, 65% yield, eluent = hexane/EtOAc (2:1)); M.p. = 83-84 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.75 (m, 2H), 7.47 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.41 – 7.37 (m, 2H), 7.25 – 7.20 (m, 5H), 7.13 – 7.10 (m, 3H), 6.92 – 6.88 (m, 3H), 3.80 (s, 3H), 2.41 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.6 (d, J_{PC} = 13.3 Hz), 149.6 (d, J_{PC} = 21.4 Hz), 138.4, 137.3, 136.5 (d, J_{PC} = 26.8 Hz), 134.2 (d, J_{PC} = 103.8 Hz), 132.0 (d, J_{PC} = 2.8 Hz), 131.9, 131.7 (d, J_{PC} = 15.6 Hz), 131.0 (d, J_{PC} = 10.5 Hz), 130.1, 130.0 (d, J_{PC} = 9.5 Hz), 129.6, 129.0, 128.9, 128.8, 128.7, 125.1 (d, J_{PC} = 12.8 Hz), 117.9, 114.5 (d, J_{PC} = 10.7 Hz), 55.7, 21.4, 21.2; ^{31}P NMR (162 MHz, $CDCl_3$): δ 38.8; HRMS (ESI) Calcd for $C_{29}H_{26}O_2P$ $[M + H]^+$ 437.1670, found 437.1671.

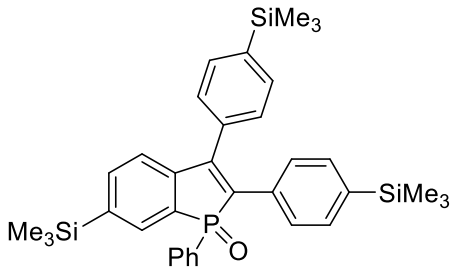


6-Methoxy-2,3-bis(4-methoxyphenyl)-1-phenyl-1*H*-phosphindole 1-oxide (3aca): Yellow solid (133.4 mg, 57% yield, eluent = hexane/EtOAc (1:1)); M.p. = 177-178 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.77 (m, 2H), 7.50 – 7.46 (m, 1H), 7.40 (t, *J* = 7.2 Hz, 2H), 7.29 – 7.27 (m, 3H), 7.20 – 7.16 (m, 3H), 6.97 (d, *J* = 8.8 Hz, 2H), 6.93 (dd, *J* = 8.8, 1.6 Hz, 1H), 6.64 (d, *J* = 8.4 Hz, 2H), 3.86 (s, 1H), 3.79 (s, 3H), 3.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.5 (d, J_{PC} = 13.3 Hz), 159.3 (d, J_{PC} = 91.9 Hz), 148.5 (d, J_{PC} = 22.4 Hz), 136.5 (d, J_{PC} = 27.0 Hz), 133.9 (d, J_{PC} = 104.9 Hz), 132.2, 132.1, 131.0 (d, J_{PC} = 10.3 Hz), 130.5, 130.2 (d, J_{PC} = 5.1 Hz), 128.9 (d, J_{PC} = 11.9 Hz), 127.7, 126.7 (d, J_{PC} = 15.4 Hz), 125.5 (d, J_{PC} = 9.6 Hz), 125.0 (d, J_{PC} = 12.6 Hz), 117.9, 114.6 (d, J_{PC} = 10.7 Hz), 114.4, 114.2, 113.8, 55.7, 55.3, 55.1; ^{31}P NMR (162 MHz, $CDCl_3$): δ 39.7; HRMS (ESI) Calcd for $C_{29}H_{26}O_4P$ $[M + H]^+$ 469.1569, found 469.1567.

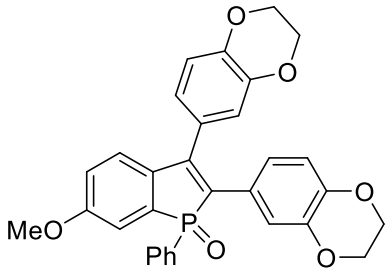


2,3-Bis(4-fluorophenyl)-6-methoxy-1-phenyl-1*H*-phosphindole 1-oxide (3ada): Yellow solid (113.3 mg, 51% yield, eluent = hexane/EtOAc (2:1)); M.p. = 194-195 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 12.4, 7.2 Hz, 2H), 7.55 – 7.51 (m, 1H), 7.46 – 7.42 (m, 2H), 7.34 – 7.28 (m, 3H), 7.21 – 7.13 (m, 5H), 6.98 (dd, *J* = 8.4, 2.4 Hz, 1H),

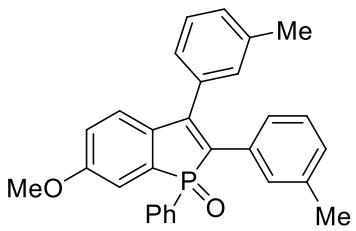
6.85 – 6.80 (m, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8 (d, J_{CF} = 247.5 Hz), 162.1 (d, J_{CF} = 247.9 Hz), 160.9 (d, *J* = 13.5 Hz), 149.0 (d, *J* = 21.7 Hz), 135.8 (d, *J* = 26.4 Hz), 133.9 (d, *J* = 104.3 Hz), 132.3 (d, *J* = 2.8 Hz), 131.6 (d, *J* = 96.9 Hz), 130.9 (d, *J* = 10.4 Hz), 130.7 (d, *J* = 13.7 Hz), 130.6 (d, *J* = 2.4 Hz), 130.2, 130.0 (d, *J* = 3.3 Hz), 129.2, 129.0 (d, *J* = 12.3 Hz), 125.1 (d, *J* = 12.7 Hz), 118.0 (d, *J* = 1.7 Hz), 116.3 (d, *J* = 21.5 Hz), 115.5 (d, *J* = 21.4 Hz), 115.0 (d, *J* = 10.8 Hz), 55.8; ^{31}P NMR (162 MHz, $CDCl_3$): δ 38.5 ; HRMS (ESI) Calcd for $C_{27}H_{20}O_2PF_2$ $[M + H]^+$ 445.1169, found 445.1170.



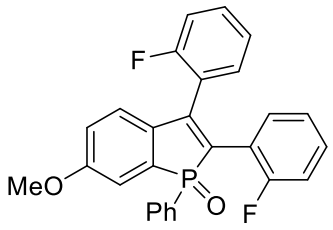
1-Phenyl-6-(trimethylsilyl)-2,3-bis(4-(trimethylsilyl)phenyl)-1*H*-phosphindole 1-oxide (3fea): Light yellow solid (178.2 mg, 60% yield, eluent = hexane/EtOAc (2:1)); M.p. = 185-186 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.83 (m, 3H), 7.64 – 7.61 (m, 3H), 7.51 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.47 – 7.42 (m, 2H) 7.35 (d, *J* = 7.6 Hz, 2H), 7.30 – 7.23 (m, 4H), 7.20 (dd, *J* = 7.2, 2.4 Hz, 1H), 0.36 (s, 9H), 0.27 (s, 9H), 0.19 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.0 (d, J_{PC} = 21.5 Hz), 144.4 (d, J_{PC} = 27.3 Hz), 142.3 (d, J_{PC} = 7.6 Hz), 141.2, 140.2, 138.0, 134.8 (d, J_{PC} = 14.9 Hz), 134.2 (d, J_{PC} = 94.6 Hz), 133.9, 133.4 (d, J_{PC} = 8.6 Hz), 133.2, 133.0 (d, J_{PC} = 9.8 Hz), 132.1 (d, J_{PC} = 2.9 Hz), 131.3 (d, J_{PC} = 91.8 Hz), 131.1 (d, J_{PC} = 10.6 Hz), 130.3 (d, J_{PC} = 86.7 Hz), 128.9 (d, J_{PC} = 12.2 Hz), 128.2, 128.1 (d, J_{PC} = 1.7 Hz), 123.4 (d, J_{PC} = 10.1 Hz), -1.0, -1.1, -1.2; ^{31}P NMR (162 MHz, $CDCl_3$): δ 39.8; HRMS (ESI) Calcd for $C_{35}H_{44}OPSi_3$ $[M + H]^+$ 595.2438, found 595.2437.



2,3-Bis(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)-6-methoxy-1-phenyl-1*H*-phosphindole 1-oxide (3afa): Light yellow solid (152.1 mg, 58% yield, eluent = hexane/EtOAc (1:1)); M.p. = 125-126 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.72(m, 2H), 7.44 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.39 – 7.35(m, 2H), 7.20 (dd, *J* = 10.8, 2.4 Hz, 1H), 7.13 (dd, *J* = 8.4, 3.6 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 1.6 Hz, 1H), 6.76 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.75 – 6.72 (m, 2H), 6.56 (d, *J* = 8.0 Hz, 1H), 4.28 – 4.25 (m, 4H), 4.12 – 4.09 (m, 2H), 4.08 – 4.05 (m, 2H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.5 (d, J_{PC} = 13.4 Hz), 148.5 (d, J_{PC} = 21.7 Hz), 143.9, 143.8, 143.2, 143.1, 136.3 (d, J_{PC} = 26.8 Hz), 133.9 (d, J_{PC} = 104.0 Hz), 132.1 (d, J_{PC} = 2.7 Hz), 130.9 (d, J_{PC} = 10.6 Hz), 130.7 (d, J_{PC} = 97.9 Hz), 130.3, 130.2 (d, J_{PC} = 98.6 Hz), 128.9 (d, J_{PC} = 12.3 Hz), 127.5 (d, J_{PC} = 15.7 Hz), 126.2 (d, J_{PC} = 10.4 Hz), 125.1 (d, J_{PC} = 12.8 Hz), 122.6 (d, J_{PC} = 6.1 Hz), 122.4, 117.9, 117.8, 117.7 (d, J_{PC} = 6.2 Hz), 117.1, 114.5 (d, J_{PC} = 10.8 Hz), 64.4, 64.3, 64.2, 64.0, 55.7; ^{31}P NMR (162 MHz, $CDCl_3$): δ 38.8; HRMS (ESI) Calcd for $C_{31}H_{26}O_6P$ $[M + H]^+$ 525.1467, found 525.1465.

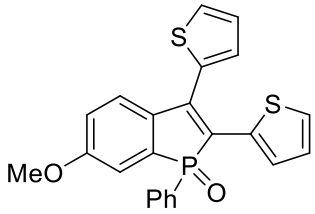


6-Methoxy-1-phenyl-2,3-di-*m*-tolyl-1*H*-phosphindole 1-oxide (3aga): Light yellow oil (133.0 mg, 61% yield, eluent = hexane/EtOAc (2:1)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.79 (m, 2H), 7.49 – 7.45 (m, 1H), 7.41 – 7.29 (m, 2H), 7.33 – 7.25 (m, 2H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.16 – 7.10 (m, 4H), 7.00 – 6.88 (m, 4H), 3.78 (s, 3H), 2.36 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.7 (d, J_{PC} = 13.4 Hz), 150.3 (d, J_{PC} = 21.2 Hz), 138.5, 137.6, 136.3 (d, J_{PC} = 26.9 Hz), 134.6 (d, J_{PC} = 2.0 Hz), 134.0 (d, J_{PC} = 91.1 Hz), 132.8 (d, J_{PC} = 10.0 Hz), 132.1 (d, J_{PC} = 2.9 Hz), 131.0, 131.1 (d, J_{PC} = 10.6 Hz), 130.3 (d, J_{PC} = 98.5 Hz), 129.5 (d, J_{PC} = 5.7 Hz), 129.4, 129.3, 128.9, 128.8, 128.4, 128.0, 126.2, 126.1 (d, J_{PC} = 3.3 Hz), 125.3 (d, J_{PC} = 12.7 Hz), 117.9 (d, J_{PC} = 1.5 Hz), 114.7 (d, J_{PC} = 10.8 Hz), 55.7, 21.5, 21.4; ^{31}P NMR (162 MHz, $CDCl_3$): δ 38.9; HRMS (ESI) Calcd for $C_{29}H_{26}O_2P$ $[M + H]^+$ 437.1670, found 437.1673.

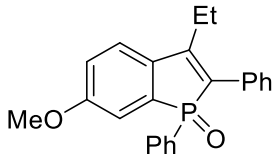


2,3-Bis(2-fluorophenyl)-6-methoxy-1-phenyl-1*H*-phosphindole 1-oxide (3aha): Pale yellow solid (102.2 mg, 46% yield, eluent = hexane/EtOAc (2:1)); M.p. = 160-161 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.78 (m, 2H), 7.59 – 7.47 (m, 2H), 7.41 – 7.31 (m, 3H), 7.29 – 7.24 (m, 2H), 7.19 – 7.06 (m, 4H), 7.05 – 6.99 (m, 1H), 6.95 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.78 – 6.72 (m, 1H), 3.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0 (d, *J* = 13.6 Hz), 159.6 (dd, J_{CF} = 246.6 Hz, J_{CP} = 7.5 Hz), 159.1 (dd, J_{CF} = 247.8 Hz, J_{CP} = 5.4 Hz), 149.0 (d, *J* = 24.4 Hz), 134.5 (d, *J* = 5.6 Hz), 133.5, 132.3 (d, *J* = 2.8 Hz), 131.1 (dd, J_1 = 10.5 Hz, J_2 = 2.8 Hz), 130.8 (d, *J* = 7.1 Hz), 130.4 (dd, J_1 = 8.3 Hz, J_2 = 3.1 Hz), 129.8 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz), 128.6 (d, *J* = 100.5 Hz), 128.9 (dd, J_1 = 12.6 Hz, J_2 = 4.9

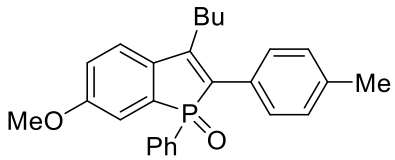
Hz), 125.3 (dd, J_1 = 12.1 Hz, J_2 = 1.6 Hz), 125.1 (d, J = 13.3 Hz), 124.4 (d, J = 3.4 Hz), 124.1 (d, J = 4.4 Hz), 122.4 (dd, J_1= 15.4 Hz, J_2 = 14.1 Hz), 120.2 (dd, J_1= 15.1 Hz, J_2 = 9.5 Hz), 118.0 (dd, J_1= 8.2 Hz, J_2 = 1.6 Hz), 116.2 (d, J = 21.4 Hz), 115.7 (dd, J_1= 21.1 Hz, J_2 = 13.3 Hz), 115.0 (d, J = 11.0 Hz), 114.7 (d, J = 10.9 Hz), 55.7; ^{31}P NMR (162 MHz, $CDCl_3$): δ 38.2 ; HRMS (ESI) Calcd for $C_{27}H_{20}O_2F_2P$ $[M + H]^+$ 445.1169, found 445.1168.



6-Methoxy-1-phenyl-2,3-di(thiophen-2-yl)-1*H*-phosphindole 1-sulfide (3aia): The title compound was obtained with a slight modification to protocol A. Thus, the three-component coupling reaction was followed by the addition of sulfur powder (2 mmol) at room temperature, and the resulting mixture was stirred for 4 h. The workup and purification were performed in the same manner. Brown oil (102.5 mg, 47% yield, eluent = hexane/EtOAc (10:1)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.87 (m, 2H), 7.61 (dd, J = 6.5, 1.2 Hz, 1H), 7.53 – 7.48 (m, 1H), 7.45 – 7.39 (m, 3H), 7.25 – 7.23 (m, 1H), 7.22 – 7.16 (m, 3H), 7.14 – 7.12 (m, 1H), 6.98 – 6.95 (m, 1H), 6.84 (dd, J = 4.8, 4.0 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.9 (d, J_{PC} = 14.6 Hz), 139.1 (d, J_{PC} = 20.1 Hz), 137.1 (d, J_{PC} = 11.3 Hz), 136.5 (d, J_{PC} = 57.4 Hz), 134.5 (d, J_{PC} = 15.2 Hz), 133.8 (d, J_{PC} = 15.9 Hz), 132.2 (d, J_{PC} = 3.0 Hz), 131.2 (d, J_{PC} = 100.7 Hz), 130.9 (d, J_{PC} = 11.9 Hz), 130.3, 130.0, 129.2, 129.1 (d, J_{PC} = 5.5 Hz), 128.9 (d, J_{PC} = 12.8 Hz), 128.2 (d, J_{PC} = 22.8 Hz), 127.2 (d, J_{PC} = 97.4 Hz), 125.3 (d, J_{PC} = 11.7 Hz), 118.4 (d, J_{PC} = 1.9 Hz), 114.7, 113.6 (d, J_{PC} = 12.4 Hz), 55.8; ^{31}P NMR (162 MHz, $CDCl_3$): δ 47.0; HRMS (ESI) Calcd for $C_{23}H_{18}OPS_3$ $[M + H]^+$ 437.0257, found 437.0255.

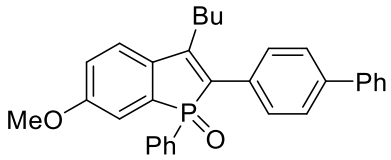


3-Ethyl-6-methoxy-1,2-diphenyl-1*H*-phosphindole 1-oxide (3aja): Yellow solid (66.7 mg, 37% yield, eluent = hexane/EtOAc (1:1)); M.p. = 147-148 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 12.4, 7.6 Hz, 2H), 7.52 – 7.42 (m, 2H), 7.42 – 7.38 (m, 2H), 7.34 – 7.26 (m, 5H), 7.24 (dd, *J* = 10.8, 2.4 Hz, 1H), 7.06 (dd, *J* = 8.4, 2.0 Hz, 1H), 3.83 (s, 3H), 2.72 (q, *J* = 7.6 Hz, 2H), 1.32 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.5 (d, J_{PC} = 13.3 Hz), 153.1 (d, J_{PC} = 19.2 Hz), 135.3, 135.0 (d, J_{PC} = 2.2 Hz), 134.0, 133.3 (d, J_{PC} = 10.3 Hz), 132.0 (d, J_{PC} = 2.5 Hz), 131.0 (d, J_{PC} = 10.5 Hz), 130.0 (d, J_{PC} = 99.5 Hz), 128.8, 128.7 (d, J_{PC} = 1.9 Hz), 128.6, 127.7, 123.5 (d, J_{PC} = 13.0 Hz), 118.1 (d, J_{PC} = 1.1 Hz), 114.6 (d, J_{PC} = 10.8 Hz), 55.7, 20.6 (d, J_{PC} = 12.8 Hz), 13.6; ^{31}P NMR (162 MHz, $CDCl_3$): δ 38.2; HRMS (ESI) Calcd for $C_{23}H_{22}O_2P$ $[M + H]^+$ 361.1357, found 361.1355.

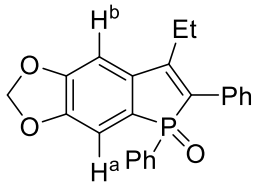


3-Butyl-6-methoxy-1-phenyl-2-(*p*-tolyl)-1*H*-phosphindole 1-oxide (3aka): Yellow solid (80.4 mg, 40% yield, eluent = hexane/EtOAc (1:1)); M.p. = 131-132 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.61 (m, 2H), 7.45 – 7.43 (m, 1H), 7.38 – 7.33 (m, 3H), 7.21 – 7.18 (m, 3H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.01 (ddd, *J* = 8.4, 2.4, 0.8 Hz, 1H), 3.80 (s, 3H), 2.66 (t, *J* = 8.4 Hz, 2H), 2.30 (s, 3H), 1.67 – 1.59 (m, 2H), 1.46 – 1.36 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.4 (d, J_{PC} = 13.4 Hz), 151.4 (d, J_{PC} = 19.8 Hz), 137.4, 135.6 (d, J_{PC} = 28.0 Hz), 134.4 (d, J_{PC} = 103.6 Hz), 131.9 (d, J_{PC} = 2.7

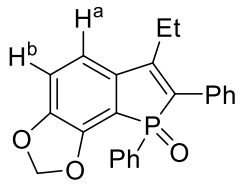
Hz), 131.8 (d, J_{PC} = 98.6 Hz), 131.0 (d, J_{PC} = 10.6 Hz), 130.3 (d, J_{PC} = 10.2 Hz), 130.1 (d, J_{PC} = 98.4 Hz), 129.3, 128.7 (d, J_{PC} = 12.2 Hz), 128.5 (d, J_{PC} = 5.1 Hz), 123.4 (d, J_{PC} = 12.9 Hz), 118.0 (d, J_{PC} = 1.8 Hz), 114.5 (d, J_{PC} = 10.7 Hz), 55.7, 31.0, 27.1 (d, J_{PC} = 12.6 Hz), 23.0, 21.2, 13.8; ^{31}P NMR (162 MHz, $CDCl_3$): δ 38.0; HRMS (ESI) Calcd for $C_{26}H_{28}O_2P$ $[M + H]^+$ 403.1827, found 403.1824.



2-([1,1'-Biphenyl]-4-yl)-3-butyl-6-methoxy-1-phenyl-1*H*-phosphindole 1-oxide (3ala): Yellow solid (95.1 mg, 41% yield, eluent = hexane/EtOAc (1:1)); M.p. = 180-181 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.69 (m, 2H), 7.61 – 7.56 (m, 4H), 7.50 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.46 (d, *J* = 3.2 Hz, 1H), 7.45 – 7.39 (m, 6H), 7.37 – 7.35 (m, 1H), 7.25 (dd, *J* = 10.8, 2.4 Hz, 1H), 7.07 (dd, *J* = 8.4, 2.4 Hz, 1H), 3.84 (s, 3H), 2.75 (t, *J* = 8.0 Hz, 2H), 1.85 – 1.61 (m, 2H), 1.57 – 1.42 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.5 (d, J_{PC} = 13.3 Hz), 152.1 (d, J_{PC} = 19.5 Hz), 140.4 (d, J_{PC} = 28.9 Hz), 135.5 (d, J_{PC} = 27.8 Hz), 134.4 (d, J_{PC} = 103.9 Hz), 132.4 (d, J_{PC} = 10.2 Hz), 132.1 (d, J_{PC} = 2.7 Hz), 132.0, 131.0 (d, J_{PC} = 10.6 Hz), 130.0 (d, J_{PC} = 98.5 Hz), 129.1 (d, J_{PC} = 5.1 Hz), 128.9, 128.8, 128.7, 127.4, 127.3, 127.0, 123.6 (d, J_{PC} = 12.9 Hz), 118.1 (d, J_{PC} = 1.6 Hz), 114.6 (d, J_{PC} = 10.8 Hz), 55.7, 31.1, 27.2 (d, J_{PC} = 12.6 Hz), 23.0, 13.8; ^{31}P NMR (162 MHz, $CDCl_3$): δ 38.3; HRMS (ESI) Calcd for $C_{31}H_{30}O_2P$ $[M + H]^+$ 465.1983, found 465.1985.



7-Ethyl-5,6-diphenyl-5*H*-phosphindolo[5,6-*d*][1,3]dioxole 5-oxide (3ija): This product was prepared according to protocol A but with a slight modification: Before the addition of $PhPCl_2$ and CuCN•2LiCl, $ZnCl_2$•TMEDA (151.5 mg, 0.6 mmol) was added and the mixture was stirred at 60 ℃ for 2 h. Yellow solid (67.4 mg, 36% yield, eluent = hexane/EtOAc (1:1)); M.p. = 127-128 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, J = 12.4, 7.2 Hz, 2H), 7.50 – 7.47 (m, 1H), 7.41 – 7.36 (m, 2H), 7.33 – 7.27 (m, 5H), 7.11 (d, J_{PH} = 9.2 Hz, 1H), 7.02 (d, J_{PH} = 2.0 Hz, 1H), 6.08 (s, 1H), 6.07 (s, 1H), 2.68 (q, J = 7.6 Hz, 2H), 1.31 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.0 (d, J_{PC} = 19.5 Hz), 151.8 (d, J_{PC} = 1.9 Hz), 148.4 (d, J_{PC} = 16.5 Hz), 138.5 (d, J_{PC} = 29.7 Hz), 133.2 (d, J_{PC} = 10.0 Hz), 133.1 (d, J_{PC} = 97.4 Hz), 131.9 (d, J_{PC} = 2.8 Hz), 131.0 (d, J_{PC} = 10.5 Hz), 130.0 (d, J_{PC} = 99.4 Hz), 128.7 (d, J_{PC} = 12.2 Hz), 128.6, 128.5 (d, J_{PC} = 4.9 Hz), 127.8 (d, J_{PC} = 1.0 Hz), 125.8 (d, J_{PC} = 108.9 Hz), 109.3 (d, J_{PC} = 12.5 Hz), 103.9 (d, J_{PC} = 14.1 Hz), 102.1, 20.6 (d, J_{PC} = 12.8 Hz), 13.6; ^{31}P NMR (162 MHz, $CDCl_3$): δ 37.2; HRMS (ESI) Calcd for $C_{23}H_{20}O_3P$ $[M + H]^+$ 375.1150, found 375.1155. The regiochemistry of this compound was assigned on the basis of the doublet signals at 7.11 ppm (H^a) and 7.02 ppm (H^b) in the ^{1}H NMR spectra.



6-Ethyl-7,8-diphenyl-8*H*-phosphindolo[6,7-*d*][1,3]dioxole 8-oxide (3ija'): The title compound was synthesized according to our previous method.[2] A 10 mL Schlenk tube containing $ZnCl_2$•TMEDA (139 mg, 0.55 mmol) was submerged in an ice bath for 15 min, followed by dropwise addition of a THF solution of 3,4-

methylenedioxyphenylmagnesium bromide (0.55 mmol). The resulting mixture was stirred for 1 h at 0 ℃ and then allowed to room temperature. To the arylzinc reagent was added Xantphos (14.5 mg, 0.025 mmol), $CoCl_2$ (3.2 mg, 0.025 mmol). After stirring for 5 min, 1-phenyl-1-butyne (65 mg, 0.5 mmol) was added. The resulting mixture was stirred at 60 ℃, monitored by TLC until the starting materials were consumed. To this Schlenk tube was added a THF solution of CuCN•2LiCl (0.15 mmol) and $PhPCl_2$ (203.5 μL, 1.5 mmol) at 0 ℃, and the resulting solution was stirred at 60 ℃ for 12 h. An aqueous solution of H_2O_2 (ca. 30%, a few drops) was added at 0 ℃, and the resulting mixture was stirred at room temperature for 30 min. The reaction mixture was diluted with ethyl acetate (5 mL) and filtered through a pad of silica gel with additional ethyl acetate (15 mL) as the eluent. The filtrate was washed with water (10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product as a pale yellow solid (97.3 mg, 52% yield, eluent = hexane/EtOAc (1:1)). M.p. = 192-196 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.72 (m, 2H), 7.49 (t, J = 7.6 Hz, 1H), 7.41 – 7.25 (m, 7H), 6.99 (dd, J_{HH} = 8.0 Hz, J_{PH} = 2.4 Hz, 1H), 6.90 (d, J = 8.0 Hz, 1H), 6.02 (s, 1H), 5.98 (s, 1H), 2.68 (q, J = 7.2 Hz, 2H), 1.29 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.7 (d, J_{PC} = 18.0 Hz), 149.2 (d, J_{PC} = 8.1 Hz), 148.8 (d, J_{PC} = 4.1 Hz), 136.4 (d, J_{PC} = 24.7 Hz), 133.2 (d, J_{PC} = 10.4 Hz), 132.1 (d, J_{PC} = 2.9 Hz), 131.0 (d, J_{PC} = 10.8 Hz), 129.6 (d, J_{PC} = 103.4 Hz), 128.8 (d, J_{PC} = 7.1 Hz), 128.7 (br, 2C, overlapped), 128.6, 127.7 (d, J_{PC} = 1.3 Hz), 116.3 (d, J_{PC} = 10.1 Hz), 111.0 (d, J_{PC} = 106.6 Hz), 110.8 (d, J_{PC} = 1.1 Hz), 102.4, 20.7 (d, J_{PC} = 12.7 Hz), 14.0; ^{31}P NMR (162 MHz, $CDCl_3$): δ 35.0; HRMS (ESI) Calcd for $C_{23}H_{20}O_3P$ $[M + H]^+$ 375.1150, found 375.1148. The regiochemistry of this compound was assigned on the

basis of the dd and d signals at 6.99 ppm (H^a) and 6.90 ppm (H^b), respectively, in the ^1H NMR spectra.

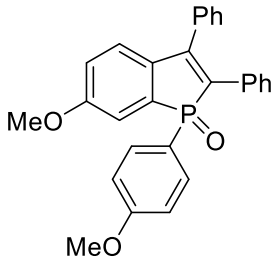
Protocol B:

1. Preparation of dichloroorganophosphine ($RPCl_2$)

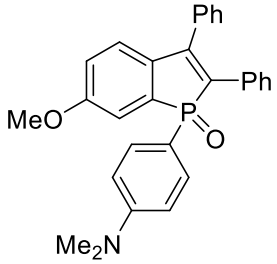
A 10 mL Schlenk tube containing $ZnCl_2$•TMEDA (379 mg, 1.5 mmol) was submerged in an ice bath for 15 min, followed by dropwise addition of a THF solution of a Grignard reagent (1.5 mmol). The resulting mixture was stirred at 0 ℃ for 1 h and then allowed to room temperature. In another 10 mL Schlenk tube was prepared a solution of PCl_3 (131.2 μL, 1.5 mmol) in dry THF (2 mL), which was then cooled to –78 ℃. To this solution was added the above-prepared aryl zinc reagent slowly via cannula at –78 ℃. The resulting mixture was stirred at 0 ℃ for 2 h and then allowed to room temperature to afford a solution containing dichloroorganophosphine ($RPCl_2$), which was directly used in the next step.

2. Multicomponent benzophosphole synthesis

The arylmagnesiation reaction was performed in the same manner as in protocol A. To the Schlenk tube containing the resulting alkenylmagnesium species was added a THF solution of CuCN•2LiCl (0.15 mmol), the above-prepared solution of $RPCl_2$, and the resulting solution was stirred at 100 ℃ for 12 h. The oxidation, workup, and purification steps were performed in the same manner as in protocol A.

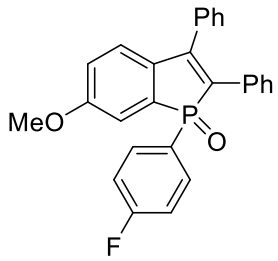


6-Methoxy-1-(4-methoxyphenyl)-2,3-diphenyl-1*H*-phosphindole 1-oxide (3aab): Yellow oil (102.9 mg, 47% yield, eluent = hexane/EtOAc (1:1)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 11.6, 8.8 Hz, 2H), 7.46 – 7.41 (m, 3H), 7.35 – 7.33 (m, 2H), 7.28 (dd, *J* = 11.2, 2.4 Hz, 1H), 7.24 – 7.22 (m, 2H), 7.15 – 7.09 (m, 4H), 6.98 – 6.91 (m, 3H), 3.82 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.8 (d, J_{PC} = 2.9 Hz), 160.7 (d, J_{PC} = 13.3 Hz), 149.8 (d, J_{PC} = 21.2 Hz), 136.1 (d, J_{PC} = 26.6 Hz), 134.6 (d, J_{PC} = 15.3 Hz), 134.5 (d, J_{PC} = 104.3 Hz), 133.1 (d, J_{PC} = 9.9 Hz), 132.9 (d, J_{PC} = 11.9 Hz), 131.2 (d, J_{PC} = 125.7 Hz), 129.0 (d, J_{PC} = 2.6 Hz), 128.9 (d, J_{PC} = 3.2 Hz), 128.6, 128.2, 127.5, 125.2 (d, J_{PC} = 12.7 Hz), 120.6 (d, J_{PC} = 105.1 Hz), 117.8 (d, J_{PC} = 1.6 Hz), 114.7 (d, J_{PC} = 13.4 Hz), 114.6, 113.4, 55.7, 55.3; ^{31}P NMR (162 MHz, $CDCl_3$): δ 39.0; HRMS (ESI) Calcd for $C_{28}H_{24}O_3P$ $[M + H]^+$ 439.1463, found 439.1459.

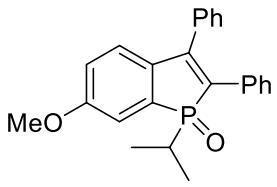


1-(4-(Dimethylamino)phenyl)-6-methoxy-2,3-diphenyl-1*H*-phosphindole 1-oxide (3aac): Yellow solid (115.2 mg, 51% yield, eluent = hexane/EtOAc (1:1)); M.p. = 80-81 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 11.6, 8.4 Hz, 2H), 7.42 – 7.39 (m, 3H), 7.33 (d, *J* = 7.2 Hz, 2H), 7.29 – 7.23 (m, 3H), 7.11 – 7.08 (m, 4H), 6.90 (d, *J* = 8.4 Hz,

1H), 6.67 (d, J = 8.4 Hz, 2H), 3.81 (s, 3H), 2.98 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.6 (d, J_{PC} = 13.2 Hz), 152.7 (d, J_{PC} = 2.4 Hz), 149.2 (d, J_{PC} = 21.0 Hz), 135.6 (d, J_{PC} = 122.8 Hz), 135.4 (d, J_{PC} = 111.7 Hz), 135.2 (d, J_{PC} = 103.7 Hz), 133.4 (d, J_{PC} = 9.9 Hz), 133.3, 132.4 (d, J_{PC} = 11.9 Hz), 129.1 (d, J_{PC} = 1.5 Hz), 129.0, 128.8, 128.4, 128.1, 127.3, 125.0 (d, J_{PC} = 12.6 Hz), 117.6, 114.3 (d, J_{PC} = 10.7 Hz), 113.4 (d, J_{PC} = 109.8 Hz), 111.8 (d, J_{PC} = 13.0 Hz), 55.7, 39.9; ^{31}P NMR (162 MHz, $CDCl_3$): δ 40.1; HRMS (ESI) Calcd for $C_{29}H_{27}NO_2P$ $[M + H]^+$ 452.1779, found 452.1777.

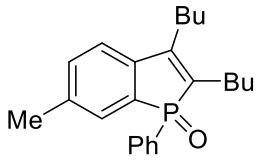


1-(4-Fluorophenyl)-6-methoxy-2,3-diphenyl-1*H*-phosphindole 1-oxide (3aad): Pale yellow oil (100.1 mg, 47% yield, eluent = hexane/EtOAc (2:1)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.76 (m, 2H), 7.44 – 7.42 (m, 3H), 7.34 (d, J = 7.2 Hz, 2H), 7.27 (d, J = 9.2 Hz, 1H), 7.21 – 7.20 (m, 2H), 7.15 (dd, J = 8.4, 3.6 Hz, 1H), 7.12 – 7.08 (m, 5H), 6.96 (d, J = 8.4 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3 (dd, J_{CF} = 251.7 Hz, J_{CP} = 3.2 Hz), 160.9 (d, J = 13.5 Hz), 150.3 (d, J = 21.6 Hz), 136.0 (d, J = 27.1 Hz), 134.4 (d, J = 15.4 Hz), 133.8 (d, J = 104.9 Hz), 133.5 (d, J = 20.8 Hz), 133.4 (d, J = 3.2 Hz), 132.7 (d, J = 9.9 Hz), 131.8 (d, J = 97.8 Hz), 129.0, 128.9, 128.8 (d, J = 12.6 Hz), 128.3, 127.7, 126.4 (d, J = 3.3 Hz), 125.4 (d, J = 12.8 Hz), 118.0 (d, J = 1.7 Hz), 116.3 (dd, J_{CF} = 21.4 Hz, J_{CP} = 13.3 Hz), 114.8 (d, J = 10.8 Hz), 55.7; ^{31}P NMR (162 MHz, $CDCl_3$): δ 37.9 ; HRMS (ESI) Calcd for $C_{27}H_{21}O_2PF$ $[M + H]^+$ 427.1263, found 427.1266.



1-Isopropyl-6-methoxy-2,3-diphenyl-1H-phosphindole 1-oxide (3aae): Yellow oil (101.0 mg, 54% yield, eluent = hexane/EtOAc (2:1)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 6H), 7.20 – 7.14 (m, 5H), 7.05 (dd, *J* = 8.4, 3.2 Hz, 1H), 6.88 (dd, *J* = 8.4, 2.4 Hz, 1H), 3.83 (s, 3H), 2.28 – 2.17 (m, 1H), 1.23 (dd, *J* = 16.4, 7.2 Hz, 3H), 0.90 (dd, *J* = 18.0, 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3 (d, J_{PC} = 12.5 Hz), 149.8 (d, J_{PC} = 18.9 Hz), 136.4 (d, J_{PC} = 24.3 Hz), 134.5 (d, J_{PC} = 14.2 Hz), 133.8 (d, J_{PC} = 9.8 Hz), 131.1 (d, J_{PC} = 95.1 Hz), 130.2 (d, J_{PC} = 44.4 Hz), 129.0, 128.9 (d, J_{PC} = 7.5 Hz), 128.5, 128.4, 127.7 (d, J_{PC} = 17.2 Hz), 125.1 (d, J_{PC} = 11.7 Hz), 117.3 (d, J_{PC} = 1.5 Hz), 115.4 (d, J_{PC} = 9.9 Hz), 114.3, 55.7, 27.6 (d, J_{PC} = 67.6 Hz), 15.5 (d, J_{PC} = 2.6 Hz), 15.1 (d, J_{PC} = 2.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 56.6; HRMS (ESI) Calcd for $C_{24}H_{24}O_2P$ $[M + H]^+$ 375.1514, found 375.1515.

Benzophosphole synthesis through Cr-catalyzed arylmagnesiation of alkyne



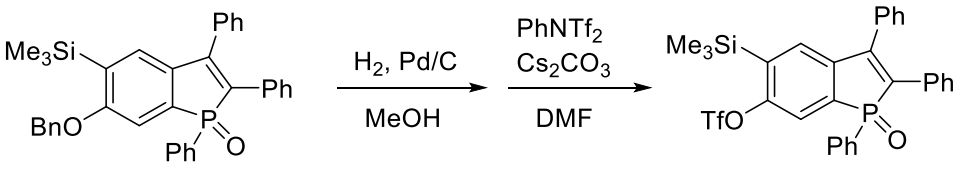
2,3-Dibutyl-6-methyl-1-phenyl-1*H*-phosphindole 1-oxide (3cma): A Schlenk tube equipped with a stirrer bar was charged with $CrCl_2$ (9.2 mg, 0.075 mmol), *t*-BuCOOH (10.2 mg, 0.1 mmol) and 5-decyne (138 mg, 1.0 mmol). The Schlenk tube was evacuated and backfilled with N_2 for three times, followed by the addition of toluene (3 mL) and *p*-tolylmagnesium bromide (3.0 mmol). The resulting mixture was stirred at 110 ℃ for 0.5 h and then allowed to cool to room temperature. To the Schlenk tube was added a THF

solution of CuCN•2LiCl (0.15 mmol) and $PhPCl_2$ (542.7 μL, 4.0 mmol), and the resulting solution was stirred at 100 ℃ for 12 h. The oxidation, workup, and purification steps were performed in the same manner as in protocol A. Light yellow oil (123.2 mg, 35% yield, eluent = hexane/EtOAc (2:1)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.65 (m, 2H), 7.52– 7.48 (m, 1H), 7.42 (dd, *J* = 7.6, 2.8 Hz, 2H), 7.38 (d, *J* = 10.0 Hz, 1H), 7.30 – 7.24 (m, 2H), 2.60 (t, *J* = 7.6 Hz, 2H), 2.52 – 2.44 (m, 1H), 2.32 (s, 3H), 2.29 – 2.21 (m, 1H), 1.64 – 1.56 (m, 2H), 1.55 – 1.43 (m, 2H), 1.42 – 1.31 (m, 2H), 1.29 – 1.20 (m, 2H), 1.00 (t, *J* = 7.6 Hz, 3H), 0.79 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.5 (d, J_{PC} = 20.0 Hz), 141.0 (d, J_{PC} = 29.0 Hz), 138.3 (d, J_{PC} = 10.4 Hz), 133.5 (d, J_{PC} = 96.6 Hz), 133.2 (d, J_{PC} = 1.8 Hz), 131.9, 131.8 (d, J_{PC} = 2.8 Hz), 130.9 (d, J_{PC} = 10.5 Hz), 130.7 (d, J_{PC} = 95.8 Hz), 129.4 (d, J_{PC} = 9.5 Hz), 128.6 (d, J_{PC} = 11.9 Hz), 121.1 (d, J_{PC} = 11.9 Hz), 31.1 (d, J_{PC} = 1.7 Hz), 30.7 (d, J_{PC} = 1.7 Hz), 26.3 (d, J_{PC} = 13.4 Hz), 25.8 (d, J_{PC} = 10.8 Hz), 23.1, 22.9, 21.1, 14.0, 13.7; ^{31}P NMR (162 MHz, $CDCl_3$): δ 39.7; HRMS (ESI) Calcd for $C_{23}H_{30}OP$ $[M + H]^+$ 353.2034, found 353.2032.

Preparation and transformation of 5,6-benzophospholyne precursor

6-(Benzyloxy)-1,2,3-triphenyl-5-(trimethylsilyl)-1*H*-phosphindole 1-oxide (3kaa): The title compound was prepared according to protocol A. Yellow solid (113.9 mg, 41% yield, eluent = hexane/EtOAc (2:1)); M.p. = 90-91 ℃; ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.83 – 7.78 (m, 2H), 7.58 – 7.56 (m, 1H), 7.54 – 7.52 (m, 4H), 7.49 – 7.41 (m, 7H), 7.40 (s, 1H), 7.38 – 7.34 (m, 1H), 7.30 – 7.27 (m, 3H), 7.14 – 7.13 (m, 3H), 5.29 (d, *J* = 11.2 Hz, 1H), 5.24 (d, *J* = 11.2 Hz, 1H), 0.19 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.4 (d, J_{PC} = 12.4 Hz), 150.7 (d, J_{PC} = 21.6 Hz), 136.1, 135.7 (d, J_{PC} = 1.2 Hz), 135.4, 134.7, 134.4 (d, J_{PC} = 15.4 Hz), 133.4 (d, J_{PC} = 1.6 Hz), 133.0 (d, J_{PC} = 10.0 Hz), 132.1 (d, J_{PC} =

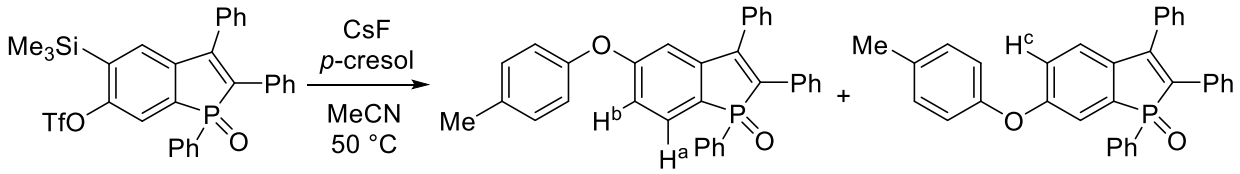
3.0 Hz), 131.1, 131.0 (d, J_{PC} = 10.5 Hz), 130.6 (d, J_{PC} = 12.5 Hz), 130.3 (d, J_{PC} = 98.3 Hz), 129.0, 128.9 (d, J_{PC} = 3.8 Hz), 128.8, 128.7, 128.5, 128.2, 128.1, 127.8, 127.5, 111.0 (d, J_{PC} = 10.7 Hz), 70.5, -1.2; ^{31}P NMR (162 MHz, $CDCl_3$): δ 39.1; HRMS (ESI) Calcd for $C_{36}H_{34}O_2PSi$ $[M + H]^+$ 557.2066, found 557.2064.



1-Oxido-1,2,3-triphenyl-5-(trimethylsilyl)-1*H*-phosphindol-6-yl triflate (4): To a solution of 6-(benzyloxy)-1,2,3-triphenyl-5-(trimethylsilyl)-1*H*-phosphindole 1-oxide (**3kaa**) (278 mg, 0.5 mmol) in MeOH (5 mL) was added 10% Pd/C (104.5 mg, 0.05 mmol, 10 mol% Pd). The mixture was placed under an atmosphere of hydrogen (balloon), stirred at room temperature for 16 h, and then filtered through a pad of celite (MeOH eluent, 10 mL). Evaporation of the solvent under reduced pressure afforded crude 6-hydroxy-1,2,3-triphenyl-5-(trimethylsilyl)-1*H*-phosphindole 1-oxide, which was used in the subsequent step without further purification.

To a solution of the above crude product in DMF (5 mL) was added Cs_2CO_3 (244 mg, 0.75 mmol) and $PhNTf_2$ (214 mg, 0.60 mmol).[19] The solution was stirred at room temperature for 18 h, followed by the addition of a saturated solution of NH_4Cl (3 mL). The aqueous layer was extracted twice with EtOAc (5 mL). The combined organic layer was washed with water, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the title compound as a white solid (185.4 mg, 62% yield for two steps, eluent = hexane/EtOAc (3:1)); M.p. = 78-79 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 12.8, 7.2 Hz, 2H), 7.63 (d, *J* = 10.0 Hz, 1H), 7.50 – 7.49 (m, 1H), 7.47 – 7.39 (m, 5H), 7.37 (d, *J* = 3.6 Hz, 1H), 7.33 – 7.31

(m, 2H), 7.24 – 7.22 (m, 2H), 7.11 – 7.10 (m, 3H), 0.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.2 (d, J_{PC} = 14.2 Hz), 148.9 (d, J_{PC} = 19.9 Hz), 142.2 (d, J_{PC} = 25.9 Hz), 138.6 (d, J_{PC} = 1.2 Hz), 136.0 (d, J_{PC} = 102.9 Hz), 135.8 (d, J_{PC} = 95.9 Hz), 133.5 (d, J_{PC} = 14.9 Hz), 132.7 (d, J_{PC} = 2.8 Hz), 132.3 (d, J_{PC} = 9.9 Hz), 131.1 (d, J_{PC} = 11.7 Hz), 130.9 (d, J_{PC} = 10.7 Hz), 129.2, 129.1 (2C, overlapped), 129.0, 128.9, 128.4, 128.2, 128.1, 120.2 (d, J_{PC} = 11.7 Hz), 118.4 (q, J_{CF} = 318.2 Hz), -1.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.6; ^{31}P NMR (162 MHz, $CDCl_3$): δ 37.6; HRMS (ESI) Calcd for $C_{30}H_{27}O_4F_3PSSi$ [M + H]$^+$ 599.1089, found 599.1086.



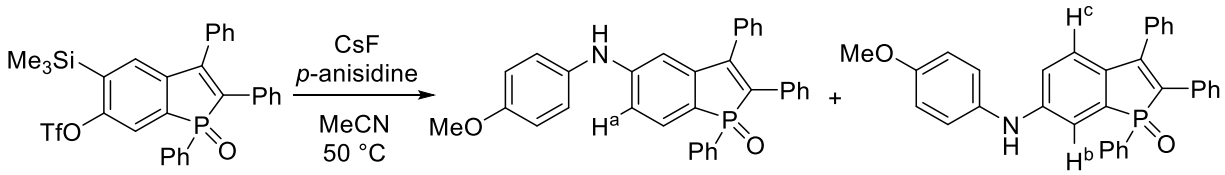
4 **6a** **7a**

1,2,3-triphenyl-5-(*p*-tolyloxy)-1*H*-phosphindole 1-oxide (6a) and 1,2,3-Triphenyl-6-(*p*-tolyloxy)-1*H*-phosphindole 1-oxide (7a): To a stirred solution of **4** (120 mg, 0.20 mmol) and *p*-cresol (32.5 mg, 0.30 mmol) in MeCN (2 mL) was added CsF (91 mg, 0.60 mmol). The resulting mixture was stirred at 50 ℃ for 14 h, and then filtered through silica gel using EtOAc as an eluent. Evaporation of the solvents under reduced pressure was followed by purification of the residue by flash chromatography (eluent = hexane/EtOAc (2:1)) to afford each of the title compounds **6a** and **7a**.

1,2,3-Triphenyl-5-(*p*-tolyloxy)-1*H*-phosphindole 1-oxide (6a): Pale yellow solid (31.1 mg, 32% yield); M.p. = 91-92 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.73 (m, 2H), 7.59 (dd, J_{PH} = 9.2 Hz, J_{HH} = 8.0 Hz, 1H), 7.50 – 7.45 (m, 1H), 7.41 – 7.36 (m, 5H), 7.32 – 7.30 (m, 2H), 7.23 – 7.21 (m, 2H), 7.15 (d, J = 8.0 Hz, 2H), 7.11 – 7.04 (m, 3H), 6.93 –

6.90 (m, 3H), 6.78 (ddd, J = 8.0, 3.2, 2.0 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.6 (d, J_{PC} = 2.1 Hz), 153.2, 149.2 (d, J_{PC} = 20.6 Hz), 146.5 (d, J_{PC} = 28.3 Hz), 135.9 (d, J_{PC} = 94.7 Hz), 134.2, 134.0 (d, J_{PC} = 14.7 Hz), 132.7 (d, J_{PC} = 9.7 Hz), 132.1 (d, J_{PC} = 2.7 Hz), 131.0 (d, J_{PC} = 10.5 Hz), 130.6, 130.5, 130.2 (d, J_{PC} = 100.3 Hz), 129.1, 129.0, 128.9 (2C, overlapped), 128.8 (d, J_{PC} = 5.1 Hz), 128.3, 127.9, 124.9 (d, J_{PC} = 109.7 Hz), 119.8, 116.5 (d, J_{PC} = 11.6 Hz), 114.7 (d, J_{PC} = 11.8 Hz), 20.8; ^{31}P NMR (162 MHz, $CDCl_3$): δ 37.9; HRMS (ESI) Calcd for $C_{33}H_{26}O_2P$ $[M + H]^+$ 485.1670, found 485.1660. The regiochemistry of this compound was assigned on the basis of the dd and ddd signals at 7.59 ppm (H^a) and 6.78 ppm (H^b), respectively, in the ^{1}H NMR spectrum.

1,2,3-Triphenyl-6-(*p*-tolyloxy)-1*H*-phosphindole 1-oxide (7a): Yellow solid (27.1 mg, 28% yield); M.p. = 208-209 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.73 (m, 2H), 7.48 – 7.46 (m, 1H), 7.44 – 7.37 (m, 5H), 7.33 – 7.28 (m, 3H), 7.20 – 7.18 (m, 2H), 7.15 – 7.12 (m, 3H), 7.09 – 7.07 (m, 3H), 7.01 (dd, J = 8.4, 1.6 Hz, 1H), 6.90 (d, J = 8.8 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3 (d, J_{PC} = 13.7 Hz), 153.6, 149.8 (d, J_{PC} = 21.1 Hz), 137.9 (d, J_{PC} = 26.8 Hz), 134.4 (d, J_{PC} = 15.1 Hz), 134.2 (d, J_{PC} = 104.1 Hz), 134.0, 133.0 (d, J_{PC} = 96.5 Hz), 132.8 (d, J_{PC} = 9.9 Hz), 132.2 (d, J_{PC} = 2.8 Hz), 131.0 (d, J_{PC} = 10.5 Hz), 130.5, 129.8 (d, J_{PC} = 99.1 Hz), 129.0 (2C, overlapped), 128.9 (2C, overlapped), 128.7 (d, J_{PC} = 2.5 Hz), 128.2, 127.7, 125.4 (d, J_{PC} = 12.5 Hz), 121.6, 119.6, 118.7 (d, J_{PC} = 10.6 Hz), 20.7; ^{31}P NMR (162 MHz, $CDCl_3$): δ 38.4; HRMS (ESI) Calcd for $C_{33}H_{26}O_2P$ $[M + H]^+$ 485.1670, found 485.1669. The regiochemistry of this compound was assigned on the basis of the dd signal at 7.01 ppm (H^c) in the ^{1}H NMR spectrum.



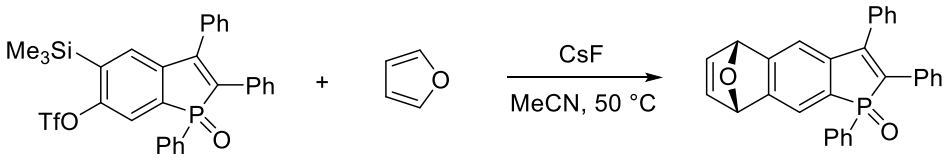
4 **6b** **7b**

5-((4-Methoxyphenyl)amino)-1,2,3-triphenyl-1*H*-phosphindole 1-oxide (6b) and 6-((4-methoxyphenyl)amino)-1,2,3-triphenyl-1*H*-phosphindole 1-oxide (7b): To a stirred solution of **4** (120 mg, 0.20 mmol) and *p*-anisidine (74 mg, 0.60 mmol) in MeCN (2 mL) was added CsF (91 mg, 0.60 mmol). The resulting mixture was stirred at 50 ℃ for 12 h, and then filtered through silica gel using EtOAc as an eluent. Evaporation of the solvents under reduced pressure was followed by purification of the residue by flash chromatography (eluent = hexane/EtOAc (1:1)) to afford each of the title compounds **6b** and **7b**.

5-((4-Methoxyphenyl)amino)-1,2,3-triphenyl-1*H*-phosphindole 1-oxide (6b): Yellow solid (34.9 mg, 35% yield); M.p. = 141-142 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.34 (m, 2H), 7.50 – 7.43 (m, 2H), 7.41 – 7.36 (m, 5H), 7.31 – 7.29 (m, 2H), 7.22 – 7.19 (m, 2H), 7.08 – 7.05 (m, 5H), 6.87 – 6.83 (m, 2H), 6.77 (ddd, J = 8.0, 3.2, 2.0 Hz, 1H), 6.64 – 6.63 (m, 1H), 5.84 (s, 1H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.4, 150.1 (d, J_{PC} = 1.7 Hz), 149.3 (d, J_{PC} = 21.1 Hz), 146.1 (d, J_{PC} = 28.2 Hz), 135.7 (d, J_{PC} = 94.6 Hz), 134.5 (d, J_{PC} = 14.7 Hz), 133.4, 133.0 (d, J_{PC} = 9.6 Hz), 131.8 (d, J_{PC} = 2.8 Hz), 131.7, 131.1 (d, J_{PC} = 10.5 Hz), 130.6 (d, J_{PC} = 11.1 Hz), 129.1 (2C, overlapped), 129.0, 128.9, 128.8, 128.5 (d, J_{PC} = 13.8 Hz), 128.2, 127.7, 124.0, 114.7, 112.7 (d, J_{PC} = 11.5 Hz), 111.1 (d, J_{PC} = 11.8 Hz), 55.5; ^{31}P NMR (162 MHz, $CDCl_3$): δ 38.2; HRMS (ESI) Calcd for $C_{33}H_{27}NO_2P$ $[M + H]^+$ 500.1779, found 500.1778. The regiochemistry of this

compound was assigned on the basis of the ddd signal at 6.77 ppm (H^a) in the ^{1}H NMR spectrum.

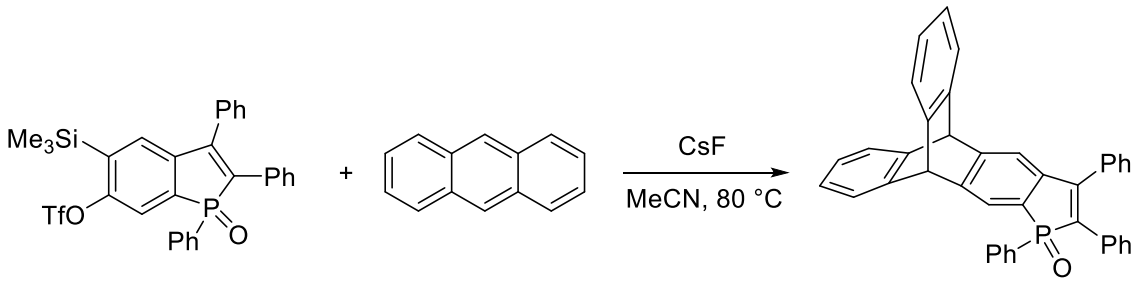
6-((4-Methoxyphenyl)amino)-1,2,3-triphenyl-1*H*-phosphindole 1-oxide (7b): Orange solid (32.9 mg, 33% yield); M.p. = 152-153 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.75 (m, 2H), 7.49 – 7.45 (m, 1H), 7.43 – 7.36 (m, 5H), 7.33 – 7.31 (m, 2H), 7.23 (dd, *J* = 11.0, 2.2 Hz, 1H), 7.18 – 7.16 (m, 2H), 7.07 – 7.05 (m, 5H), 7.00 (dd, *J* = 8.4, 3.6 Hz, 1H), 6.88 – 6.83 (m, 3H), 5.99 (s, 1H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.1, 150.7 (d, J_{PC} = 21.8 Hz), 146.8 (d, J_{PC} = 12.8 Hz), 134.7 (d, J_{PC} = 6.3 Hz), 134.4 (d, J_{PC} = 102.5 Hz), 134.0 (d, J_{PC} = 16.9 Hz), 133.6, 133.2 (d, J_{PC} = 10.0 Hz), 132.0 (d, J_{PC} = 2.7 Hz), 131.0 (d, J_{PC} = 10.5 Hz), 130.6 (d, J_{PC} = 98.3 Hz), 130.1 (d, J_{PC} = 97.9 Hz), 129.0, 128.9 (d, J_{PC} = 5.9 Hz), 128.8 (2C, overlapped), 128.6 (d, J_{PC} = 24.9 Hz), 128.2, 127.2, 125.2 (d, J_{PC} = 12.2 Hz), 123.5, 117.0, 115.9 (d, J_{PC} = 10.6 Hz), 114.8, 55.6; ^{31}P NMR (162 MHz, $CDCl_3$): δ 39.3; HRMS (ESI) Calcd for $C_{33}H_{27}NO_2P$ $[M + H]^+$ 500.1779, found 500.1778. The regiochemistry of this compound was assigned on the basis of the dd signals at 7.23 ppm (H^b) and 7.00 ppm (H^c), respectively, in the ^{1}H NMR spectrum.



4 **8**

1,2,3-Triphenyl-5,8-dihydro-1*H*-5,8-epoxybenzo[*f*]phosphindole 1-oxide (8): To a stirred solution of **4** (89.7 mg, 0.15 mmol) and furan (54.5 μL, 0.75 mmol) in MeCN (1.5 mL) was added CsF (68.4 mg, 0.45 mmol). The solution was stirred at room temperature for 6 h, and then filtered through silica gel (EtOAc as an eluent). Evaporation of the solvents under reduced pressure is followed by purification by flash chromatography

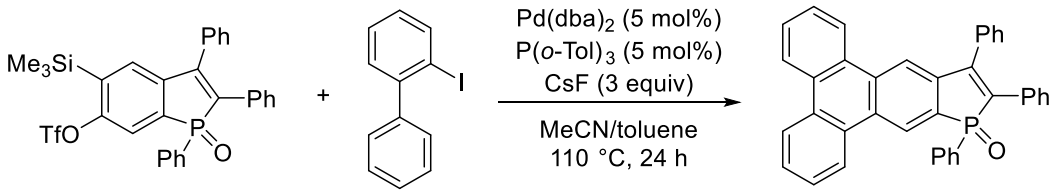
(eluent = hexane/EtOAc (1:1)) to afford the title compound as a pale yellow solid (54.1 mg, 81% yield). ^{1}H NMR (singlet signals around 5.7–5.6 ppm) and ^{31}P NMR (two signals at 38.3, 38.2 ppm of similar intensity) analyses indicated a diastereomer ratio of ca. 1:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.73 (m, 2H), 7.53 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.47 – 7.37 (m, 6H), 7.32 – 7.30 (m, 2H), 7.21 – 7.20 (m, 2H), 7.10 – 7.08 (m, 4H), 7.02 – 6.95 (m, 2H), 5.70 (s, 1H), 5.65 (s, 0.5H), 5.63 (s, 0.5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.6, 151.0 (d, J_{PC} = 11.6 Hz), 149.7 (d, J_{PC} = 21.5 Hz), 149.4 (d, J_{PC} = 21.6 Hz), 143.1 (d, J_{PC} = 11.4 Hz), 142.8, 142.6, 142.5, 142.4, 142.3, 134.5 (d, J_{PC} = 4.6 Hz), 134.4 (d, J_{PC} = 94.8 Hz), 134.2 (d, J_{PC} = 4.4 Hz), 134.3 (d, J_{PC} = 94.8 Hz), 132.7 (d, J_{PC} = 9.1 Hz), 132.2 (d, J_{PC} = 2.6 Hz), 132.1 (d, J_{PC} = 2.8 Hz), 131.0 (d, J_{PC} = 3.5 Hz), 130.9 (d, J_{PC} = 3.6 Hz), 130.5, 130.2, 129.9, 129.8, 129.5, 129.2, 129.1, 129.0 (2C, overlapped), 128.9, 128.8 (2C, overlapped), 128.7, 128.3, 127.8, 120.2 (d, J_{PC} = 10.9 Hz), 120.1 (d, J_{PC} = 11.0 Hz), 116.6 (d, J_{PC} = 7.5 Hz), 116.5 (d, J_{PC} = 7.6 Hz), 82.3 (2C, overlapped), 82.1 (d, J_{PC} = 1.4 Hz), 82.0 (d, J_{PC} = 1.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 38.3, 38.2; HRMS (ESI) Calcd for $C_{30}H_{22}O_2P$ $[M + H]^+$ 445.1357, found 445.1359.



4 **9**

(5*r*,10*r*)-1,2,3-Triphenyl-5,10-dihydro-1*H*-5,10-[1,2]benzenonaphtho[2,3-*f*]phosphindole 1-oxide (9): To a stirred solution of **4** (89.7 mg, 0.15 mmol) and anthracene (53.5 mg, 0.3 mmol) in MeCN (1.5 mL) was added CsF (68.4 mg, 0.45 mmol).

The solution was stirred at 80 ℃ for 48 h, and then filtered through silica gel (EtOAc as an eluent). Evaporation of the solvents under reduced pressure is followed by purification by flash chromatography (eluent = hexane/EtOAc (2:1)) to afford the desired product as a pale yellow solid (52.5 mg, 63% yield). While ^{1}H NMR showed only two signals responsible for the triptycene aliphatic protons (5.43, 5.38 ppm) and ^{31}P NMR showed only one signal at 38.7 ppm, a diastereomer ratio of ca. 1:1 is assumed in light of the above result for **8** and the greater number of ^{13}C NMR signals than expected for a single diastereomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.68 (m, 3H), 7.46 – 7.44 (m, 4H), 7.40 – 7.33 (m, 6H), 7.31 – 7.29 (m, 3H), 7.20 – 7.17 (m, 3H), 7.06 – 7.04 (m, 2H), 7.03 – 7.00 (m, 2H), 6.99 – 6.96 (m, 2H), 5.43 (s, 1H), 5.38 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.0 (d, J_{PC} = 1.8 Hz), 150.0 (d, J_{PC} = 21.4 Hz), 147.0 (d, J_{PC} = 11.3 Hz), 144.5, 144.3, 144.2, 144.0, 141.7 (d, J_{PC} = 27.7 Hz), 134.5 (d, J_{PC} = 15.2 Hz), 134.2 (d, J_{PC} = 95.2 Hz), 132.7 (d, J_{PC} = 9.7 Hz), 132.1 (d, J_{PC} = 2.8 Hz), 131.0 (d, J_{PC} = 10.6 Hz), 130.3, 129.9, 129.5, 129.4, 129.3, 129.2, 129.1 (2C, overlapped), 129.0 (2C, overlapped), 128.9 (2C, overlapped), 128.7 (d, J_{PC} = 10.7 Hz), 128.5, 128.4 (2C, overlapped), 128.3, 128.2, 127.7, 125.6 (d, J_{PC} = 8.7 Hz), 125.4, 124.2 (d, J_{PC} = 10.5 Hz), 123.9, 123.8 (2C, overlapped), 123.7, 119.9 (d, J_{PC} = 11.7 Hz), 55.5, 53.9; ^{31}P NMR (162 MHz, $CDCl_3$): δ 38.7; HRMS (ESI) Calcd for $C_{40}H_{28}OP$ $[M + H]^+$ 555.1878, found 555.1881.



4 **10**

10,11,12-Triphenyl-10*H*-phenanthro[9,10-*f*]phosphindole 10-oxide (10): To a solution of the 2-iodobiphenyl (168 mg, 0.60 mmol), $Pd(dba)_2$ (9.2 mg, 0.01 mmol), P(*o*-tolyl)$_3$

(3.1 mg, 0.01 mmol), and **4** (120 mg, 0.20 mmol) in a mixed solvent system (4.0 mL) consisting of acetonitrile and toluene was added CsF (91 mg, 0.60 mmol). The reaction mixture was allowed to stir at 110 ℃ for 24 h under N_2. The resulting solution was washed with brine, extract with EtOAc, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent = hexane/EtOAc (2:1)) to afford the desired product as a white solid (61.4 mg, 58% yield). M.p. > 300 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (d, J = 11.2 Hz, 1H), 8.67 – 8.61 (m, 3H), 8.46 (d, J = 3.2 Hz, 1H), 8.40 (d, J = 8.0 Hz, 1H), 7.90 – 7.84 (m, 2H), 7.71 – 7.60 (m, 4H), 7.58 – 7.48 (m, 5H), 7.44 – 7.40 (m, 3H), 7.30 – 7.28 (m, 2H), 7.14 – 7.13 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.5 (d, J_{PC} = 20.1 Hz), 141.7 (d, J_{PC} = 27.0 Hz), 136.0, 135.8, 135.0, 134.4, 133.8 (d, J_{PC} = 105.3 Hz), 133.2, 132.8 (d, J_{PC} = 9.7 Hz), 132.3, 132.2, 131.4, 131.2 (d, J_{PC} = 10.5 Hz), 130.7, 130.2 (d, J_{PC} = 11.9 Hz), 130.0, 129.7, 129.3, 129.2 (2C, overlapped), 129.1, 129.0 (2C, overlapped), 128.9, 128.3, 128.0 (2C, overlapped), 127.6 (d, J_{PC} = 26.1 Hz), 125.4 (d, J_{PC} = 10.4 Hz), 123.7 (d, J_{PC} = 6.7 Hz), 123.4 (d, J_{PC} = 14.9 Hz), 118.9 (d, J_{PC} = 10.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 38.7; HRMS (ESI) Calcd for $C_{38}H_{26}OP$ $[M + H]^+$ 529.1721, found 529.1725. Recrystallization from DCM/hexane afforded single crystals suitable for X-ray diffraction analysis, which unambiguously confirmed the molecular structure of the compound.[20]

5.5 References

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[20] CCDC 1412955 contains the supplementary crystallographic data for the compound **10**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.uk/data_request/cif.

Chapter 6. Dibenzoheteroles Synthesis Based on Conversion of 2-Iodobiaryls to 2,2'-Diiodobiaryls via Oxidation–Iodination Sequence

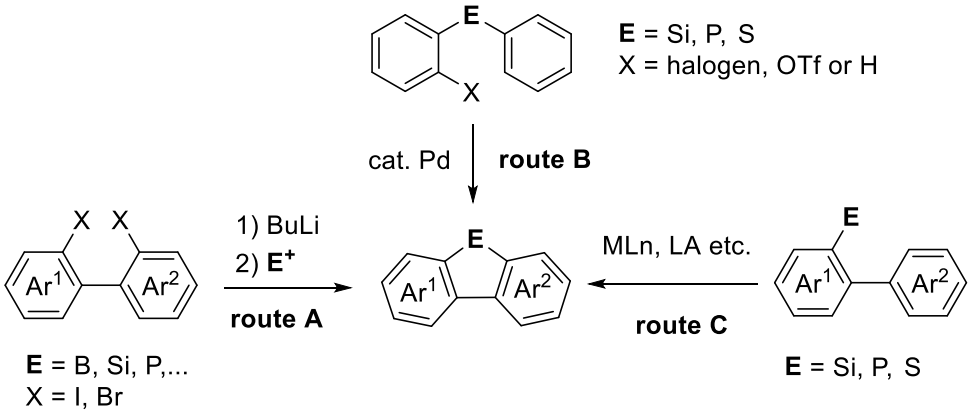
6.1 Introduction

Dibenzoheteroles (or heterofluorenes) containing Group 13-16 heteroatom elements have emerged as important building blocks of organic and polymer materials for various applications such as electronic devices.[1] The interaction between the heteroatom and the π-conjugated phenylene framework[2] determines their electronic structures, which allows for the modulation of the optical and electronic properties of materials containing these building blocks for specific applications. As is the case for indoles and benzofunans, numerous preparative methods have been established for the synthesis of the nitrogen- and oxygen-containing analogues (carbozoles and dibenzofurans).[3] On the other hand, synthetic methods for dibenzoheteroles containing other heteroatom elements remain relatively limited despite their unique and fascinating electronic properties.

Among the most straightforward approaches to construct these dibenzoheteroles is the halogen–lithium exchange of 2,2'-dihalobiaryls (X = Br or I) followed by trapping with boron,[4] silicon,[5] phosphorus,[6] or other heteroatom electrophiles (Scheme 6.1, route A). On the other hand, transition metal-catalyzed C–H functionalization has also emerged as a viable approach to dibenzoheteroles.[7] For example, palladium-catalyzed intramolecular C–X/C–H coupling of heteroatom-tethered arenes has been successfully employed for the synthesis of dibenzosiloles,[8] dibenzophospholes,[9] and dibenzothiophenes[10] (Scheme 6.1, route B). Alternatively, *ortho*-heteroatom-functionalized biaryls may also give rise to dibenzoheteroles via intramolecular heteroatom–aryl bond formation (Scheme 6.1, route C). A variety of dibenzoheteroles

including dibenzosiloles, [11] dibenzogermoles, [12] dibenzophospholes [13] and dibenzothiophenes[14] have been synthesized by this approach.

Scheme 6.1. Common synthetic approaches to dibenzoheteroles.

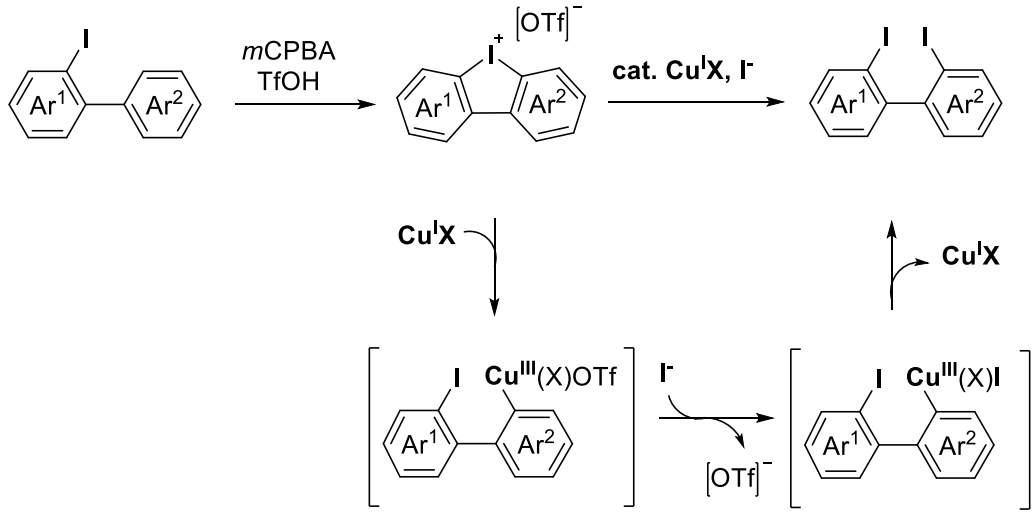


Regardless of their success, each of the aforementioned approaches has its individual limitation. The fatal weakness of route A is the laborious and nontrivial preparation of structurally diverse 2,2'-dihalobiaryl precursors, especially those bearing differently substituted Ar^1 and Ar^2 groups. Because routes B and C require installation of the heteroatom moiety in the early stage of the synthesis, they are not suitable for the expedient synthesis of dibenzoheteroles containing diverse heteroatoms. To remove these limitations, a general, practical and convenient solution to enable diversity of both the central heteroatom and the peripheral substituents is highly desirable.

We reasoned that the development of an efficient and broad-scope method for the preparation of 2,2'-diiodobiaryls would fulfill the above requirement and enhance our capability to access a diverse set of dibenzoheteroles. To achieve this specific goal, we designed a two-step conversion of 2-iodobiaryls, which are readily accessible by conventional cross-coupling, into 2,2'-diiodobiaryls via cyclic diaryliodonium salts as key

intermediates (Scheme 6.2). While the first oxidation step has been well established, the second, iodinative ring-opening reaction has been elusive. In light of the ability of copper(I) catalysts to engage in electrophilic aryl group transfer reactions using diaryliodonium salts, we envisioned that the iodinative ring-opening would be achieved by a combination of a copper(I) catalyst and an iodide anion. Thus, oxidative addition of the cyclic iodonium salt to Cu(I) would generate a 2-iodo-2'-cuprio(III)biaryl intermediate, which would undergo anionic ligand exchange with iodide and C–I bond-forming reductive elimination to afford the desired 2,2'-diiodobiaryl. Herein we describe the feasibility of the proposed two-step conversion and the demonstration of its utility in the synthesis of ladder-shaped dibenzoheteroles.

Scheme 6.2. Working hypothesis for conversion of 2-iodobiaryls to 2,2'-diiodobiaryls.

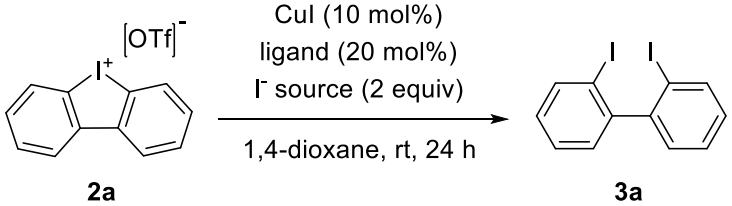


6.2 Results and discussion

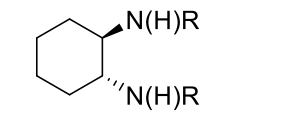
To test the above hypothesis, we initially investigated the iodination of dibenzo[*b*,*d*]iodol-5-ium triflate (**2a**) using CuI as a catalyst and tetrabutylammonium iodide (TBAI) as an iodide source in 1,4-dioxane at 110 ℃ for 24 hours. However, the

desired product 2,2'-diiodobiphenyl (**3a**) was observed only in 10% yield (Table 6.1, entry 1). Inspired by the work of Buchwald and co-workers on the conversion of aryl bromides into the corresponding iodides using a catalyst system comprising CuI and dinitrogen ligands,[15] we performed the reaction using a combination of CuI and *N,N'*-dimethylcyclohexane-1,2-diamine (**L1**, 20 mol%). To our delight, the reaction was clean and the desired product **3a** could be obtained in 95% yield as determined by ^{1}H NMR spectroscopy (89% yield of isolated product, entry 2). Other 1,2-diamine ligands (**L2**-**L4**), 2,2'-bipyridine, and 1,10-phenanthroline also promoted the iodonative ring-opening reaction, albeit in lower yields (entries 3-7). Besides TBAI, other sources of iodide such as NaI and KI could also be used for this transformation (entries 8 and 9). Reducing the loading of CuI and **L1** resulted in a dramatic decrease in the yield (entry 10). The reaction could be readily scaled up to 5 mmol without significant decrease in the yield (entry 11).

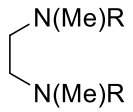
Table 6.1. Optimization of the reaction conditions. [a]



2a **3a**



L1 (R = Me); **L2** (R = H)



L3 (R = Me); **L4** (R = H)

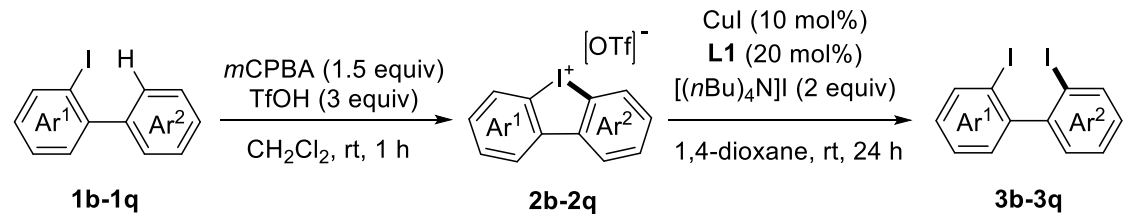
Entry	Ligand	I- source	Yield [%][b]
1	none	[(*n*Bu)$_4$N]I	10
2	**L1**	[(*n*Bu)$_4$N]I	95 (89)
3	**L2**	[(*n*Bu)$_4$N]I	74
4	**L3**	[(*n*Bu)$_4$N]I	64
5	**L4**	[(*n*Bu)$_4$N]I	83
6	2,2'-bipyridyl	[(*n*Bu)$_4$N]I	57
7	1,10-phenantrroline	[(*n*Bu)$_4$N]I	66
8	**L1**	NaI	82
9	**L1**	KI	83
10[c]	**L1**	[(*n*Bu)$_4$N]I	20
11[d]	**L1**	[(*n*Bu)$_4$N]I	(84)

[a] The reaction was performed on 0.2 mmol scale. [b] Determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard; yield of isolated product in parentheses. [c] Reduced loading of CuI (5 mol%) and **L1** (10 mol%). [d] Scale: 5 mmol.

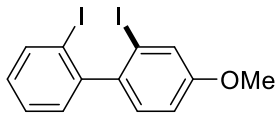
With the optimized conditions in hand, we proceeded to explore the scope of the iodinative ring-opening reaction (Scheme 6.3). The starting cyclic diaryliodonium triflates **2b**–**2q** could be easily obtained by oxidation of 2-iodobiaryls **1b**–**1q** with a combination of *m*CPBA and TfOH in CH_2Cl_2 at room temperature for 1 h. Subsequently, treatment of

2b–**2q** under the present conditions afforded a variety of 2,2'-diiodobiaryls **3b**–**3q** in moderate to good yields. Either electron-donating groups such as methoxy (**3b**, **3i**, **3n**) or electron-withdrawing groups such as fluoro (**3d**), chloro (**3e**), acetyl (**3f**), cyano (**3g**), trifluoromethyl (**3h**, **3n**) and nitro (**3q**) could be well tolerated in this reaction. Moreover, cyclic diaryliodonium triflates bearing polyaryl or heteroaryl groups such as naphthyl (**3k**), phenanthryl (**3l**) and thienyl (**3m**) groups were also suitable substrates for this reaction. Due to the poor solubility of some iodonium triflates (**2l**, **2m**, **2o**-**2q**) in dioxane, a modified reaction using DMSO or DMF at higher temperature was required to achieve the desired reaction.

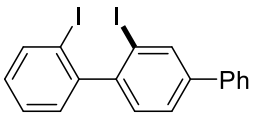
Scheme 6.3. Two step conversion of 2-iodobiaryls to 2,2'-diiodobiaryls.[a]



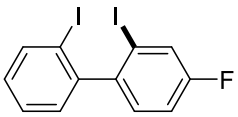
1b-1q **2b-2q** **3b-3q**



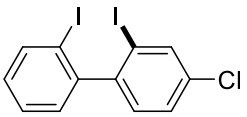
3b, 70% (61%)



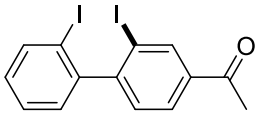
3c, 76% (65%)



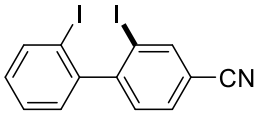
3d, 76% (59%)



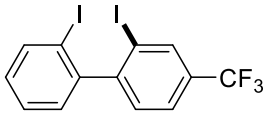
3e, 81% (62%)



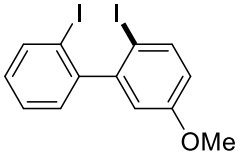
3f, 62% (51%)



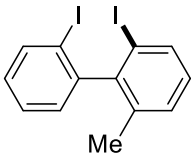
3g, 84% (58%)



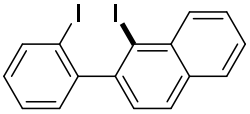
3h, 86% (68%)



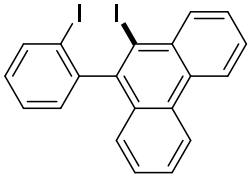
3i, 72% (55%)



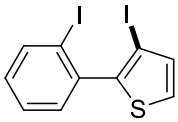
3j, 92% (71%)



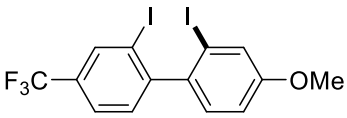
3k, 72% (64%)



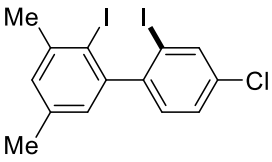
3l, 65% (46%)[b]



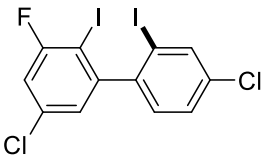
3m, 58% (40%)[c]



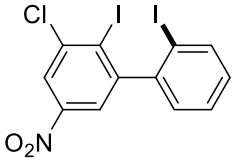
3n, 90% (77%)



3o, 66% (49%)[b]



3p, 70% (52%)[b]



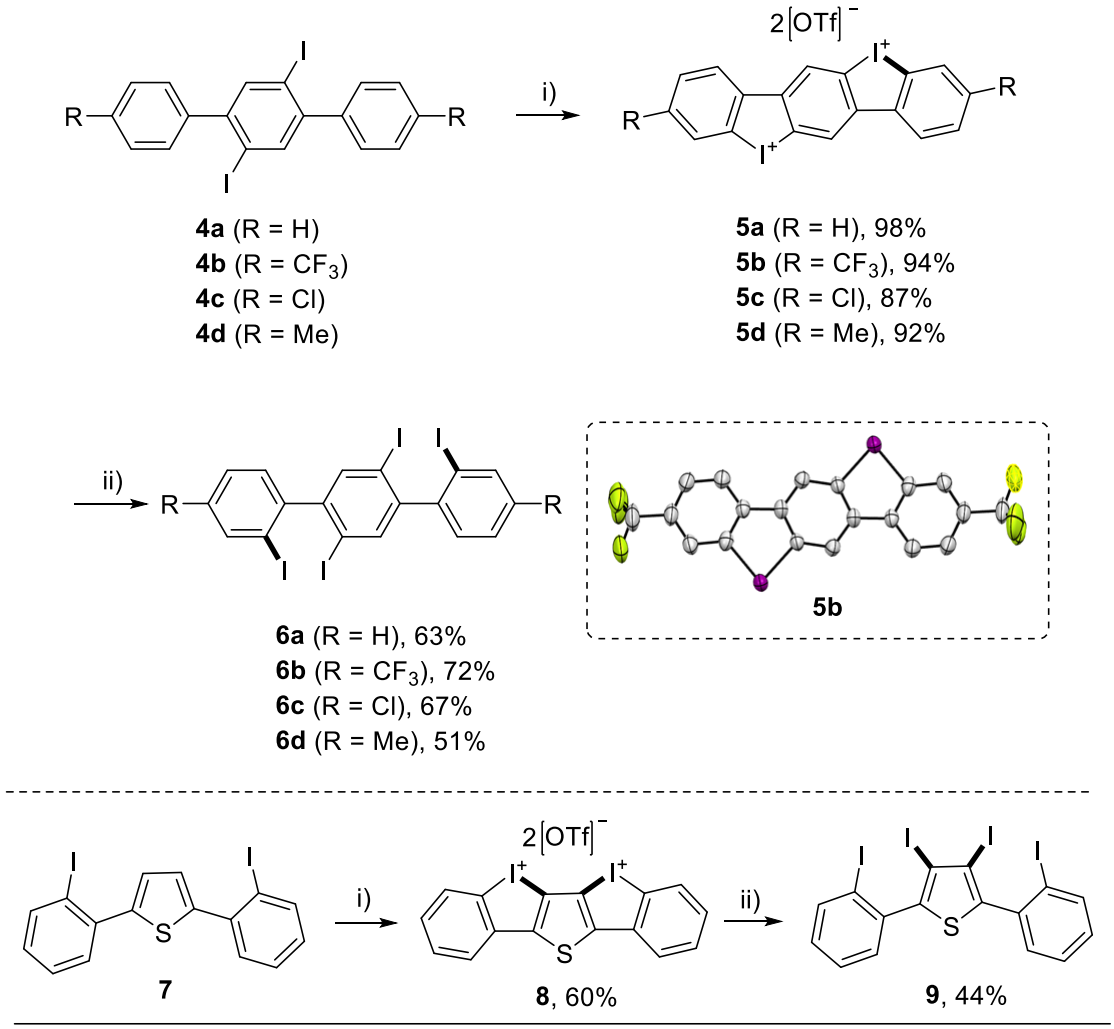
3q, 86% (68%)[b]

[a] The yield refers to that of the second step, and the overall yield over two steps is shown in parentheses. [b] Reaction in DMSO at 60 ℃. [c] Reaction in DMF at 60 ℃.

We were curious about whether the twofold iodinative ring-opening reaction could be achieved by using the present approach. Thus 2',5'-diiodo-1,1':4',1''-terphenyl

(**4a**) was synthesized and subsequently subjected to the oxidative conditions with slight modifications (the amount of *m*CPBA and HOTf were doubled), which cleanly afforded the corresponding bis-iodonium triflate **5a** in excellent yield (Scheme 6.4). Other derivatives bearing electron-withdrawing groups (**5b** and **5c**) and electron-donating group (**5d**) were also prepared in good yields under the same reaction conditions. Note that the structure of **5b** was confirmed by X-ray crystallographic analysis. These bis-iodonium salts showed poor solubility in dioxane, and thus were not amenable to the standard conditions for the iodinative ring-opening. Nevertheless, the desired transformations were achieved under modified conditions with a higher catalyst loading, acetonitrile as the solvent, a higher temperature, and an extended reaction time to afford the 2,2',2'',5'-tetraiodo-*p*-terphenyl derivatives **6a-6d** were obtained in 51-72% yields as light-sensitive solids. Furthermore, 2,5-bis(2-iodophenyl)thiophene (**7**) also underwent this twofold oxidation/iodinative ring-opening reaction, affording 3,4-diiodo-2,5-bis(2-iodophenyl)thiophene (**9**) in moderate yield.

Scheme 6.4. Conversion of 2',5'-diiodo-*p*-terphenyls to 2,2',2'',5'-tetraiodo-*p*-terphenyls.



4a (R = H)
4b (R = CF_3)
4c (R = Cl)
4d (R = Me)

5a (R = H), 98%
5b (R = CF_3), 94%
5c (R = Cl), 87%
5d (R = Me), 92%

5b

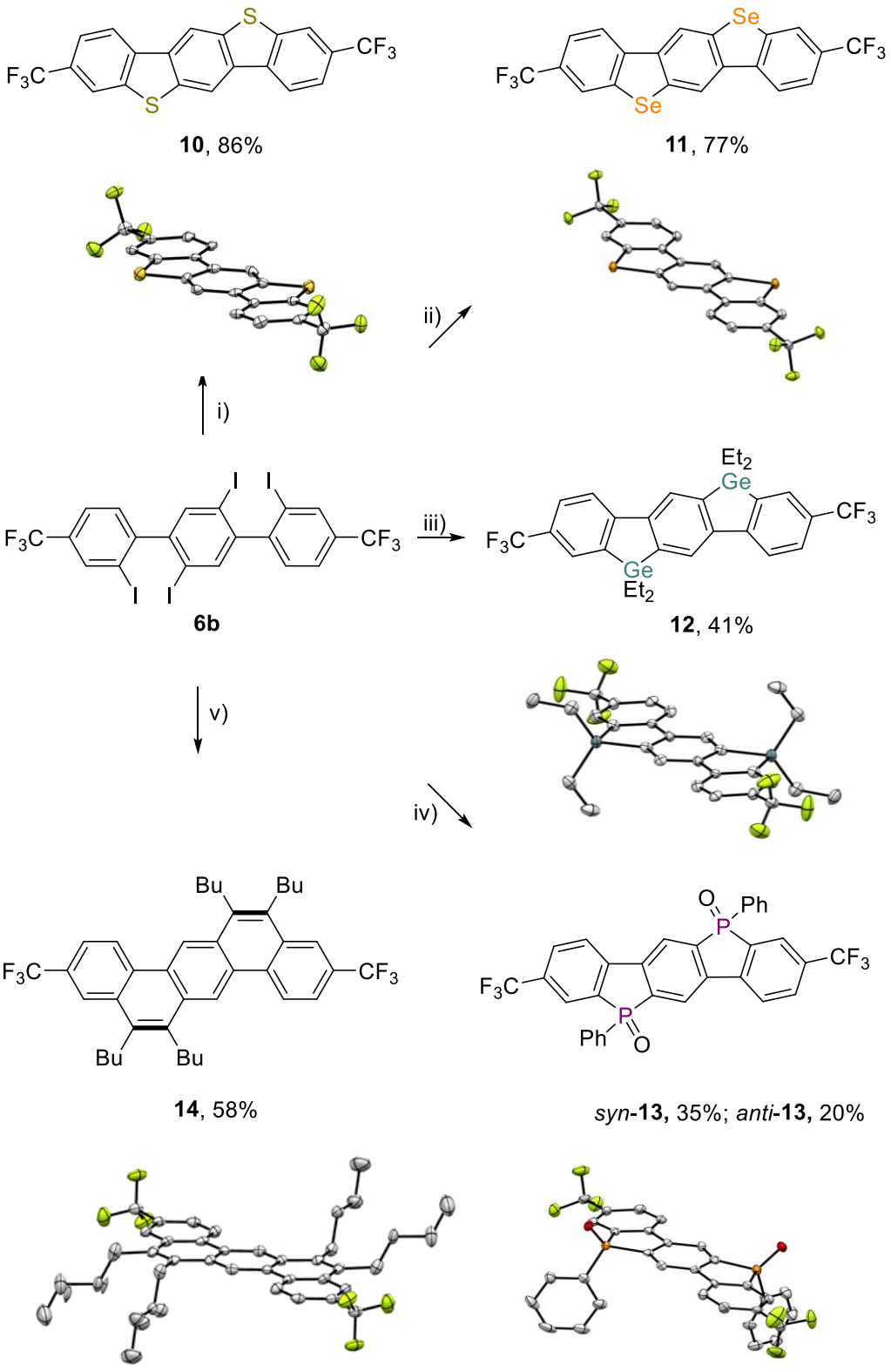
6a (R = H), 63%
6b (R = CF_3), 72%
6c (R = Cl), 67%
6d (R = Me), 51%

Reaction conditions: i) *m*CPBA (3 equiv), TfOH (6 equiv), CH_2Cl_2, rt, 2 h; ii) CuI (20 mol%), **L1** (40 mol%), [$(nBu)_4NI$] (4 equiv); MeCN, 60 ℃, 24 h. Inset: ORTEP drawing of **5b** (thermal ellipsoids set at 50% probability), whereby hydrogen atoms, counter-anions, and solvent molecules were omitted for clarity.

To illustrate the utility of the diiodobiaryls and tetraiodoteraryls as precursors to dibenzoheteroles, we examined transformations of tetraiodoteraryls to ladder-type heterofluorenes (Scheme 6.5). Treatment of tetraiodoteraryls **6b** with sulfur powder using CuI as a catalyst and K_2CO_3 as a base in DMF[16] resulted in a fourfold C-S bond formation

to produce benzo[1,2-*b*:4,5-*b'*]bis[*b*]benzothiophene **10** in 86% yield. The selenium analogue benzo[1,2-*b*:4,5-*b'*]bis[*b*]benzoselenophene **11** could also be achieved by a copper-catalyzed selenation developed by our group,[17] using selenium and NMP instead of sulfur and DMF at higher temperature. The germanium- and phosphorus-bridged teraryls **12** and **13** could be constructed through twofold iodine–lithium exchanges followed by electrophilic trapping with dichlorodiethylgermane and dichlorophenylphosphine, respectively. Finally, employing the palladium-catalyzed annulation reaction of 2,2'-diiodobiaryl with internal alkyne developed by Wu and coworkers,[18] benzo[*k*]tetraphene derivative **14** was obtained in good yield. The structures of all the above compounds were confirmed by single-crystal X-ray diffraction analysis.[19]

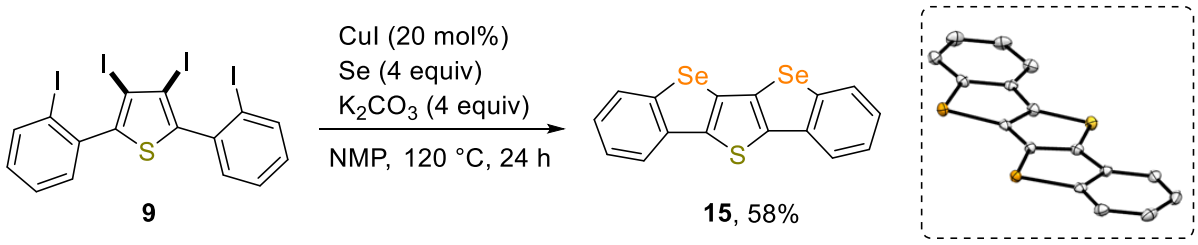
Scheme 6.5. Conversion of tetraiodoteraryls **6b** into ladder-type π-conjugated systems.



Reaction conditions: i) CuI (20 mol%), sulfur powder, K_2CO_3, DMF, 90 ℃; ii) CuI (20 mol%), selenium powder, K_2CO_3, NMP, 120 ℃; iii) 1) *n*BuLi, THF, -78 ℃; 2) Et_2GeCl_2, -78 ℃ to rt; iv) 1) *n*BuLi, THF, -78 ℃; 2) $PhPCl_2$, -78 ℃ to rt; 3) H_2O_2; v) $Pd(OAc)_2$ (20 mol%), IPr·Cl (10 mol%), $P(tBu)_3 \cdot HBF_4$ (10 mol%), AgOAc, *p*-xylene, 130 ℃. ORTEP drawings of **10**, **11**, **12**, *syn*-**13** and **14** (thermal ellipsoids at 50% probability; hydrogen atoms and solvent molecules were omitted for clarity).

In addition to the above heteroatom-bridged teraryls, we were also able to convert 3,4-diiodo-2,5-bis(2-iodophenyl)thiophene (**9**) into dibenzo[*d,d'*]thieno[3,2-*b*;4,5-*b'*]diselenophene (**15**) via copper-catalyzed four-fold C–Se bond formation using selenium powder (Scheme 6.6). Expectedly, the product **15** showed a high level of coplanarity as demonstrated by X-ray diffraction analysis (Scheme 6.6).

Scheme 6.6. Conversion of 3,4-diiodo-2,5-bis(2-iodophenyl)thiophene (**9**) to dibenzo[*d,d'*]thieno[3,2-*b*;4,5-*b'*]diselenophene (**15**).



6.3 Conclusion

In summary, we have demonstrated that a 2-iodobiaryl can be readily converted into a 2,2'-diiodobiaryl in two steps via oxidation into a cyclic diaryliodonium salt followed by subsequent iodinative ring-opening. The latter step is achieved efficiently

with the aid of a copper–diamine catalytic system under mild conditions. The method allows facile conversion of readily accessible 2-iodobiaryls into a variety of unsymmetrical 2,2'-diiodobiaryls, which should serve as useful precursors to heteroatom-bridged fluorenes. The versatility of the present two-step approach is further demonstrated by the preparation of hitherto unexplored tetraiodoteraryls and their conversion into ladder-type π-conjugated systems containing heteroatoms such as sulfur, selenium, germanium, and phosphorus.

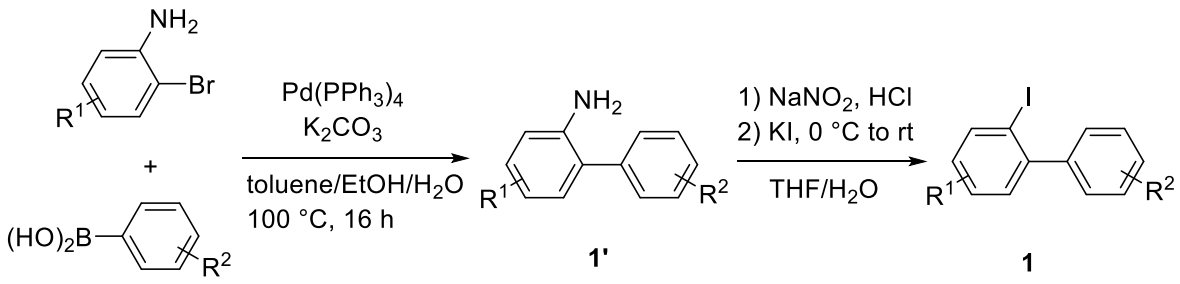
6.4 Experimental section

Preparation of *ortho*-alkenylaryl iodides

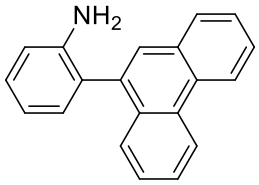
The following known substrates were prepared according the literatures.[20] Their ^{1}H and ^{13}C NMR spectra showed good agreement with the literature data.

2-Iodo-1,1'-biphenyl (**1a**), 2-iodo-4'-methoxy-1,1'-biphenyl (**1b**), 2-iodo-1,1':4',1''-terphenyl (**1c**), 4'-fluoro-2-iodo-1,1'-biphenyl (**1d**), 4'-chloro-2-iodo-1,1'-biphenyl (**1e**), 2-iodo-4'-(trifluoromethyl)-1,1'-biphenyl (**1h**), 2-iodo-3'-methoxy-1,1'-biphenyl (**1i**), 2-iodo-2'-methyl-1,1'-biphenyl (**1j**), and 2-(2-iodophenyl)thiophene (**1m**).

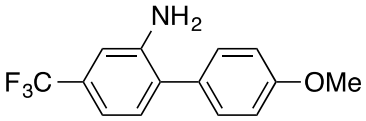
Below are summarized general procedure and characterization data for newly synthesized substrates.



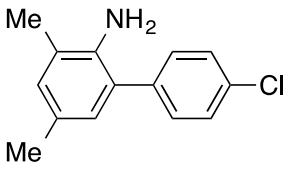
General procedure for the preparation of 2-aminobiaryl derivative:[21] A 250 mL three-necked flask equipped with a magnetic stir bar was charged with an arylboronic acid (7.5 mmol, 1.5 equiv), K_2CO_3 (2.75 g, 20.0 mmol, 4.0 equiv), $Pd(PPh_3)_4$ (577 mg, 0.5 mmol, 0.1 equiv), toluene (40 mL), H_2O (8 mL), and EtOH (10 mL). To the resulting solution was added a 2-bromoaniline derivative (5.0 mmol, 1.0 equiv), and the reaction mixture was heated at 100 ℃ for 16 h. After cooling to room temperature, the biphasic mixture was diluted with saturated aqueous NH_4Cl (30 mL) and CH_2Cl_2 (30 mL). The aqueous phase was extracted with CH_2Cl_2, and the combined organic extracts were washed with water and saturated aqueous $NaHCO_3$, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired 2-aminobiaryl derivative. Below are summarized characterization data of newly synthesized substrates.



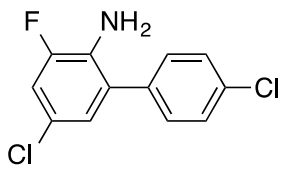
2-(Phenanthren-9-yl)aniline (1l'): White solid (80% yield, eluent = hexane/EtOAc = 10:1); M.p. = 130-131 ℃; IR (neat, cm^{-1}): 3481, 3388, 2922, 2852, 1610, 1458, 1375; ^1H NMR (400 MHz, $CDCl_3$) δ 8.80 (dd, *J* = 14.8, 8.4 Hz, 2H), 7.94 (d, *J* = 7.6 Hz, 1H), 7.83 – 7.63 (m, 5H), 7.64 – 7.54 (m, 1H), 7.37 – 7.28 (m, 2H), 7.00 – 6.95 (m, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 3.56 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.6, 135.6, 131.8, 131.2, 130.8, 130.7, 130.3, 129.0, 128.7, 128.4, 126.9, 126.8 (2C), 126.7 (2C), 125.9, 123.0, 122.6, 118.5, 115.4; HRMS (ESI) Calcd for $C_{20}H_{16}N$ $[M + H]^+$ 270.1277, found 270.1284.



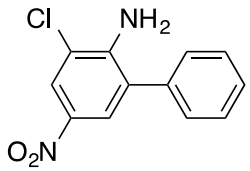
4'-Methoxy-4-(trifluoromethyl)-[1,1'-biphenyl]-2-amine (1n'): White solid (91% yield, eluent = hexane/EtOAc = 10:1); M.p. = 88-89 ℃; IR (neat, cm^{-1}): 3487, 3379, 2922, 2852, 1629, 1462, 1334, 1120; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 1H), 7.07 – 6.93 (m, 4H), 3.92 (s, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 144.2, 130.9, 130.5, 130.4, 130.2, 130.1, 124.4 (q, $^{1}J_{C-F}$ = 273.3 Hz), 115.0 (q, $^{3}J_{C-F}$ = 3.8 Hz), 114.5, 111.8 (q, $^{3}J_{C-F}$ = 3.7 Hz), 55.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6; HRMS (ESI) Calcd for $C_{14}H_{13}NOF_3$ $[M + H]^+$ 268.0944, found 268.0943.



4'-Chloro-3,5-dimethyl-[1,1'-biphenyl]-2-amine (1o'): Pale yellow oil (77% yield, eluent = hexane/EtOAc = 15:1); IR (neat, cm^{-1}): 3477, 3394, 2922, 2852, 1454, 1091; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 4H), 6.94 – 6.93 (m, 1H), 6.82 – 6.81 (m, 1H), 3.55 (s, 2H), 2.28 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.1, 138.5, 133.1, 130.8, 130.7, 129.0, 128.7, 127.5, 126.4, 122.9, 20.5, 18.0; HRMS (ESI) Calcd for $C_{14}H_{15}NCl$ $[M + H]^+$ 232.0888, found 232.0896.



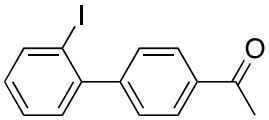
4',5-Dichloro-3-fluoro-[1,1'-biphenyl]-2-amine (1p'): White solid (78% yield, eluent = hexane/EtOAc = 15:1); M.p. = 105-106 ℃; IR (neat, cm^{-1}): 3440, 3360, 2916, 2850, 1454, 1377, 1091; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 2H), 7.39 – 7.35 (m, 2H), 7.03 (dd, *J* = 10.4, 2.4 Hz, 1H), 6.91 – 6.90 (m, 1H), 3.77 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.2 (d, $^{1}J_{C-F}$ = 240.7 Hz), 135.5 (d, $^{4}J_{C-F}$ = 3.3 Hz), 134.1, 131.1 (d, $^{3}J_{C-F}$ = 12.7 Hz), 130.1, 129.3, 128.7 (d, $^{4}J_{C-F}$ = 4.2 Hz), 125.2 (d, $^{4}J_{C-F}$ = 3.1 Hz), 122.0 (d, $^{3}J_{C-F}$ = 10.7 Hz), 114.9 (d, $^{2}J_{C-F}$ = 22.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -131.5; HRMS (ESI) Calcd for $C_{12}H_9NFCl_2$ $[M + H]^+$ 256.0091, found 256.0094.



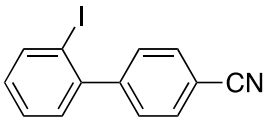
3-Chloro-5-nitro-[1,1'-biphenyl]-2-amine (1q'): The title compound was prepared according to the above general procedure but using 1.0 equiv of phenylboronic acid and 1.5 equiv of 2-bromo-6-chloro-4-nitroaniline. Yellow solid (76% yield, eluent = hexane/EtOAc = 30:1); M.p. = 132-133 ℃; IR (neat, cm^{-1}): 3390, 1458, 1375, 1105; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.96 (s, 1H), 7.53 – 7.41 (m, 5H), 4.93 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.6, 138.3, 136.5, 129.5, 128.8, 128.7, 127.0, 124.9, 124.8, 118.0; HRMS (ESI) Calcd for $C_{12}H_{10}N_2O_2Cl$ $[M + H]^+$ 249.0425, found 249.0426.

General procedure for the preparation of 2-iodobiaryl from 2-aminobiaryl: To a stirred solution of 2-aminobiaryl **1'** (3.0 mmol) in THF (8 mL) was added 4 M aqueous HCl (8 mL), and the solution was cooled in an ice bath. A solution of $NaNO_2$ (248 mg, 3.6 mmol) in H_2O (3 mL) was added dropwise. After 20 min, a solution of KI (1.2 g, 7.2 mmol) in H_2O (5 mL) was added, and upon additional stirring for 10 min, the reaction

mixture was slowly warmed to room temperature and stirred for another 1 h. Then 1M aqueous $Na_2S_2O_3$ was added portionwise until the color of the mixture did not change further. The organic and aqueous phases were separated, and the latter was extracted with EtOAc. The combined organic layers were washed with H_2O and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired 2-iodobiaryl **1**. Below are summarized characterization data for newly synthesized substrates.

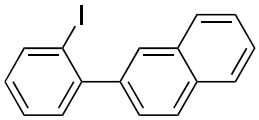


1-(2'-Iodo-[1,1'-biphenyl]-4-yl)ethanone (1f): White solid (65% yield, eluent = hexane/EtOAc = 15:1); M.p. = 103-104 ℃; IR (neat, cm^{-1}): 2953, 2922, 1624, 1463, 1184; ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 – 8.04 (m, 2H), 7.99 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.50 – 7.41 (m, 3H), 7.31 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.09 (td, *J* = 7.6, 1.6 Hz, 1H), 2.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.7, 148.7, 145.5, 139.7, 136.2, 129.9, 129.7, 129.4, 128.3, 128.1, 97.8, 26.8; HRMS (ESI) Calcd for $C_{14}H_{12}OI$ $[M + H]^+$ 322.9927, found 322.9938.

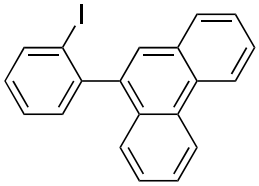


2'-Iodo-[1,1'-biphenyl]-4-carbonitrile (1g): Yellow solid (63% yield, eluent = hexane/EtOAc = 15:1); M.p. = 82-83 ℃; IR (neat, cm^{-1}): 2926, 2852, 2230, 1458, 1377; ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.77 – 7.75 (m, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.45 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.31 – 7.29 (m, 1H), 7.13 (td, *J* = 7.6, 1.6

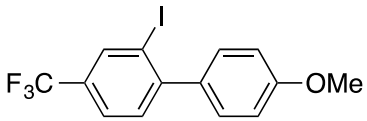
Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.5, 144.7, 139.8, 132.6, 131.9, 129.7, 128.4, 120.0, 118.8, 111.6, 97.5; HRMS (ESI) Calcd for $C_{13}H_9NI$ $[M + H]^+$ 305.9774, found 305.9786.



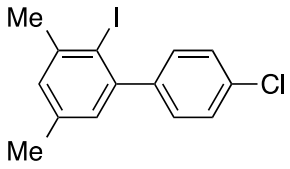
2-(2-Iodophenyl)naphthalene (1k): White solid (86% yield, eluent = hexane); M.p. = 81-82 ℃; IR (neat, cm^{-1}): 2922, 2852, 1458, 1375; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.0 Hz, 1H), 7.96 – 7.92 (m, 3H), 7.86 (s, 1H), 7.59 – 7.55 (m, 3H), 7.49 – 7.44 (m, 2H), 7.13 – 7.09 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.6, 141.7, 139.6, 133.1, 132.8, 130.5, 129.0, 128.3 (2C), 128.2, 127.9, 127.7, 127.5, 126.4, 126.3, 98.8; HRMS (ESI) Calcd for $C_{16}H_{12}I$ $[M + H]^+$ 330.9978, found 330.9985.



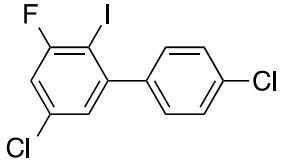
9-(2-Iodophenyl)phenanthrene (1l): Colorless gum (68% yield, eluent = hexane); IR (neat, cm^{-1}): IR (neat, cm^{-1}): 2955, 2850, 1458, 1375; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (dd, *J* = 13.6, 8.4 Hz, 2H), 8.04 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.73 – 7.61 (m, 4H), 7.55 – 7.41 (m, 4H), 7.17 (td, *J* = 8.0, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.5, 140.9, 139.2, 138.3, 131.4, 131.1, 130.5, 130.3, 129.2, 128.9, 128.2, 127.7, 127.4, 127.0, 126.7, 126.6, 123.0, 122.7, 114.1, 100.7; HRMS (ESI) Calcd for $C_{20}H_{14}I$ $[M + H]^+$ 381.0135, found 381.0144.



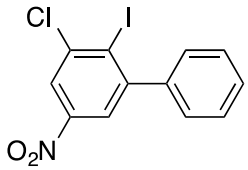
2-Iodo-4'-methoxy-4-(trifluoromethyl)-1,1'-biphenyl (1n): Yellow solid (75% yield, eluent = hexane/EtOAc = 15:1); M.p. = 53-54 ℃; IR (neat, cm^{-1}): 2953, 2922, 1458, 1319, 1136; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 149.9, 136.3 (q, $^{3}J_{C-F}$ = 3.8 Hz),, 135.5, 130.5 (q, $^{2}J_{C-F}$ = 32.7 Hz), 130.3, 130.2, 125.0 (q, $^{3}J_{C-F}$ = 3.6 Hz), 123.0 (q, $^{1}J_{C-F}$ = 271.0 Hz), 113.6, 98.8, 55.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.4; HRMS (ESI) Calcd for $C_{14}H_{11}OF_3I$ $[M + H]^+$ 378.9801, found 378.9800.



4'-Chloro-2-iodo-3,5-dimethyl-1,1'-biphenyl (1o): Yellow oil (58% yield, eluent = hexane); This compound contained the deiodinated byproduct with a 2:1 ratio that could not be removed by chromatographic separation. Without further purification, it was used for the cyclization reaction. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 1.2 Hz, 1H), 6.92 (d, *J* = 1.6 Hz, 1H), 2.55 (s, 3H), 2.34 (s, 3H); HRMS (ESI) Calcd for $C_{14}H_{13}ClI$ $[M + H]^+$ 342.9745, found 342.9759.

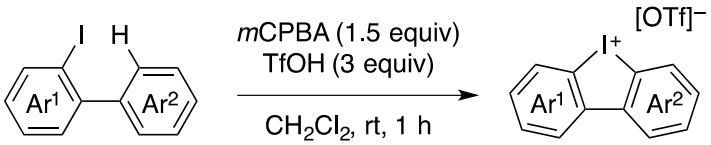


4',5-Dichloro-3-fluoro-2-iodo-1,1'-biphenyl (1p): Colorless oil (63% yield, eluent = hexane); IR (neat, cm^{-1}): 3076, 1307, 1211, 1087; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 6.4, 2.0 Hz, 2H), 7.29 – 7.27 (m, 2H), 7.15 – 7.11 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.8 (d, $^{1}J_{C\text{-}F}$ = 246.4 Hz), 140.3 (d, $^{4}J_{C\text{-}F}$ = 2.3 Hz), 135.2 (d, $^{3}J_{C\text{-}F}$ = 10.9 Hz), 130.5, 129.2, 128.5, 128.3, 125.7 (d, $^{4}J_{C\text{-}F}$ = 3.1 Hz), 115.1 (d, $^{2}J_{C\text{-}F}$ = 28.3 Hz), 84.7 (d, $^{2}J_{C\text{-}F}$ = 25.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.9; HRMS (ESI) Calcd for $C_{12}H_7FCl_2I$ $[M + H]^+$ 366.8948, found 366.8947.



3-Chloro-2-iodo-5-nitro-1,1'-biphenyl (1q): Light yellow solid (66% yield, eluent = hexane/EtOAc = 50:1); M.p. = 130-131 ℃; IR (neat, cm^{-1}): 2953, 2922, 1521, 1458, 1377; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.99 (d, *J* = 2.0 Hz, 1H), 7.49 – 7.47 (m, 3H), 7.32 – 7.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.2, 147.8, 143.3, 141.0, 128.9, 128.8, 128.5, 122.2, 121.5, 112.6; HRMS (ESI) Calcd for $C_{12}H_8ClINO_2$ $[M + H]^+$ 359.9283, found 359.9294.

Preparation of Cyclic Diaryliodonium Salts



General procedure: To a stirred solution of 2-iodobiaryl (5.0 mmol) in anhydrous CH_2Cl_2 (20 mL) was added *m*CPBA (75%, 1.73 g, 7.5 mmol) and TfOH (1.32 mL, 15.0

mmol). The solution was stirred for 1 h at room temperature, followed by removal of CH_2Cl_2 by rotary evaporation. To the solid residue was added Et_2O (15 mL), and the resulting mixture was stirred for 20 min. The solid precipitate was collected by vacuum filtration, washed with Et_2O (ca. 5 mL) for three times, and dried under vacuum to afford the cyclic diaryliodonium triflate in analytically pure form. ^1H and ^{13}C NMR spectra data for the following known substrates showed good agreement with the literature data.[22] Below are summarized newly synthesized substrates.

Diphenyleniodonium trifluoromethanesulfonate (**2a**)

3-Methoxydibenzo[*b*,*d*]iodol-5-ium trifluoromethanesulfonate (**2b**)

3-Phenyldibenzo[*b*,*d*]iodol-5-ium trifluoromethanesulfonate (**2c**)

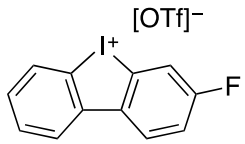
3-Cyanodibenzo[*b*,*d*]iodol-5-ium trifluoromethanesulfonate (**2g**)

3-(Trifluoromethyl)dibenzo[*b*,*d*]iodol-5-ium trifluoromethanesulfonate (**2h**)

2-Methoxydibenzo[*b*,*d*]iodol-5-ium trifluoromethanesulfonate (**2i**)

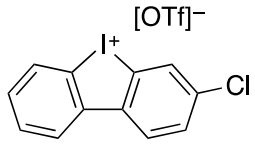
Benzo[*b*]naphtho[2,1-*d*]iodol-11-ium trifluoromethanesulfonate (**2k**).

Below are summarized characterization data for newly synthesized substrates.

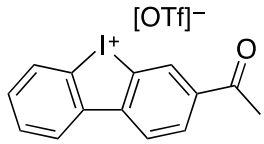


3-Fluorodibenzo[*b*,*d*]iodol-5-ium trifluoromethanesulfonate (2d): Brown solid (78% yield); IR (neat, cm^{-1}): 2924, 2852, 1456, 1377, 1261, 1029; ^1H NMR (400 MHz, $(CD_3)_2SO$) δ 8.47 – 8.37 (m, 2H), 8.15 (dd, J = 8.4, 4.0 Hz, 1H), 7.96 – 7.92 (m, 1H), 7.81 – 7.79 (m, 1H), 7.76 – 7.66 (m, 2H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 162.4 (d, $^1J_{C\text{-}F}$ = 251.0 Hz), 141.0, 138.9, 131.2 (d, $^4J_{C\text{-}F}$ = 4.1 Hz), 130.9, 128.7 (d, $^3J_{C\text{-}F}$ = 8.5 Hz), 127.5, 122.7, 122.3, 119.5, 119.3 (d, $^2J_{C\text{-}F}$ = 22.7 Hz), 118.1 (d, $^2J_{C\text{-}F}$ = 27.3 Hz); ^{19}F

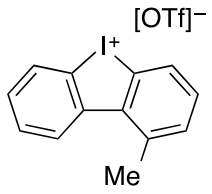
NMR (376 MHz, $CDCl_3$) δ -78.0; HRMS (ESI) Calcd for $C_{12}H_7FI$ [M - OTf]$^+$ 296.9571, found 296.9589.



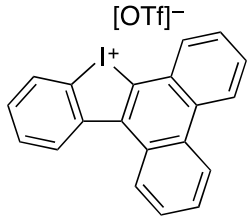
3-Chlorodibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (2e): White solid (77% yield); IR (neat, cm^{-1}): 2922, 2852, 1456, 1377, 1026; ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.49 – 8.47 (m, 2H), 8.23 – 8.21 (m, 2H), 7.94 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.87 (t, *J* = 7.6 Hz, 1H), 7.75 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 141.3, 141.1, 135.0, 131.8, 131.5, 131.3, 131.0, 130.3, 128.4, 127.8, 122.7, 122.5; HRMS (ESI) Calcd for $C_{12}H_7ClI$ [M - OTf]$^+$ 312.9275, found 312.9284.



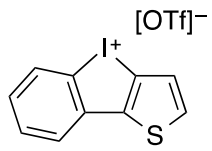
3-Acetyldibenzo[*b,d*]iodol-5-ium trifluoromethanesulfonate (2f): Brown solid (82% yield); IR (neat, cm^{-1}): 2924, 2852, 1685, 1458, 1377, 1022; ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.65 (d, *J* = 1.2 Hz, 1H), 8.49 (d, *J* = 8.0 Hz, 2H), 8.30 (dd, *J* = 8.0, 1.2 Hz, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 7.87 – 7.83 (m, 1H), 7.77 – 7.73 (m, 1H), 2.67 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 196.5, 145.8, 141.0, 138.3, 132.5, 131.3, 131.1, 131.0, 130.6, 128.3, 127.3, 123.1, 122.5, 27.3; HRMS (ESI) Calcd for $C_{14}H_{10}OI$ [M - OTf]$^+$ 320.9771, found 320.9777.



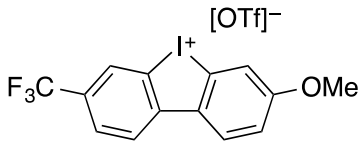
1-Methyldibenzo[*b*,*d*]iodol-5-ium trifluoromethanesulfonate (2j): White solid (77% yield); IR (neat, cm^{-1}): 2922, 2852, 1458, 1377, 1028; ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.54 (dd, *J* = 8.0, 1.2 Hz, 1H), 8.38 (dd, *J* = 8.0, 1.2 Hz, 1H), 8.24 (d, *J* = 8.0 Hz, 1H), 7.91 – 7.87 (m, 1H), 7.71 – 7.67 (m, 2H), 7.56 – 7.52 (m, 1H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$): δ 143.4, 140.6, 140.0, 135.0, 131.3, 131.1, 131.0, 130.5, 130.1, 129.1, 121.3, 119.8, 22.9; HRMS (ESI) Calcd for $C_{13}H_{10}I$ $[M - OTf]^+$ 292.9822, found 292.9821.



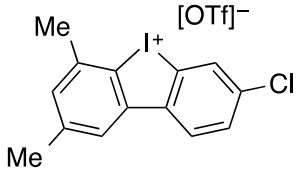
Benzo[*b*]phenanthro[9,10-*d*]iodol-9-ium trifluoromethanesulfonate (2l): Pale brown solid (71% yield); IR (neat, cm^{-1}): 2922, 2852, 1456, 1377, 1282, 1024; ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.89 – 8.67 (m, 4H), 8.43 – 8.34 (m, 1H), 8.19 – 8.07 (m, 1H), 7.91 – 7.72 (m, 6H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 144.0, 138.0, 131.9, 131.3, 130.8, 130.5, 130.3, 130.0, 129.5, 129.3, 129.0, 128.8, 128.7, 128.6, 125.3, 124.9, 124.0, 122.8, 122.3, 119.6; HRMS (ESI) Calcd for $C_{20}H_{12}I$ $[M - OTf]^+$ 378.9978, found 378.9983.



Benzo[*b*]thieno[2,3-*d*]iodol-4-ium trifluoromethanesulfonate (2m): White solid (69% yield); IR (neat, cm^{-1}): 2922, 2852, 1456, 1377, 1024; ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.22 (dd, *J* = 8.4, 0.8 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 5.2 Hz, 1H), 7.76 (t, *J* = 8.0 Hz, 1H), 7.56 – 7.52 (m, 1H), 7.50 (d, *J* = 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 146.0, 137.2, 131.6, 129.9, 127.2, 126.4, 126.0, 122.8, 119.6, 112.8; HRMS (ESI) Calcd for $C_{10}H_6SI$ $[M - OTf]^+$ 284.9229, found 284.9230.

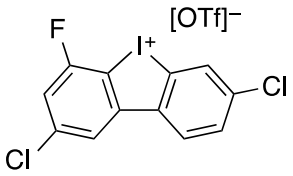


3-Methoxy-7-(trifluoromethyl)dibenzo[*b*,*d*]iodol-5-ium trifluoromethanesulfonate (2n): White solid (86% yield); IR (neat, cm^{-1}): 2922, 2852, 1458, 1377, 1024; ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.56 – 8.47 (m, 3H), 8.17 (d, *J* = 8.0 Hz, 1H), 7.76 – 7.40 (m, 1H) 7.48 (dd, *J* = 8.8, 2.0 Hz, 1H), 3.95 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 162.1, 145.9, 133.2, 129.5, 129.1, 127.9 (q, $^{2}J_{C\text{-}F}$ = 24.2 Hz), 127.2, 124.7 (q, $^{3}J_{C\text{-}F}$ = 2.3 Hz), 123.9 (q, $^{1}J_{C\text{-}F}$ = 270.7 Hz), 122.7, 121.7, 118.5, 115.3 (q, $^{3}J_{C\text{-}F}$ = 6.4 Hz), 56.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.4; HRMS (ESI) Calcd for $C_{14}H_9OIF_3$ $[M - OTf]^+$ 376.9645, found 376.9645.

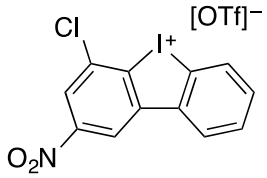


3-Chloro-6,8-dimethyldibenzo[*b*,*d*]iodol-5-ium trifluoromethanesulfonate (2o): White solid (75% yield); IR (neat, cm^{-1}): 2922, 2852, 1458, 1375, 1028; ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.36 (d, *J* = 8.4 Hz, 1H), 8.29 (s, 1H), 8.09 (s, 1H), 7.93 (d, *J* = 8.4 Hz, 1H),

7.41 (s, 1H), 2.63 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 142.0, 141.9, 141.4, 139.3, 134.7, 133.0, 131.8, 130.9, 128.8, 125.8, 123.4, 122.2, 25.1, 21.0; HRMS (ESI) Calcd for $C_{14}H_{11}ClI$ $[M - OTf]^+$ 340.9588, found 340.9599.



2,7-Dichloro-4-fluorodibenzo[*b*,*d*]iodol-5-ium trifluoromethanesulfonate (2p): White solid (74% yield); IR (neat, cm^{-1}): 2922, 2852, 1458, 1377, 1018; ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.59 – 8.48 (m, 2H), 8.26 – 8.22 (m, 1H), 8.01 – 7.97 (m, 1H), 7.92 – 7.88 (m, 1H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 160.7 (d, $^1J_{C\text{-}F}$ = 214.0 Hz), 145.2, 139.6, 138.0 (d, $^3J_{C\text{-}F}$ = 11.2 Hz), 136.1, 131.9, 130.7, 129.5 (d, $^4J_{C\text{-}F}$ = 4.9 Hz), 123.6, 122.7, 119.5, 117.9 (d, $^2J_{C\text{-}F}$ = 28.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.0; HRMS (ESI) Calcd for $C_{12}H_5Cl_2IF$ $[M - OTf]^+$ 364.8792, found 364.8795.

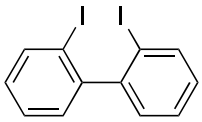


2-Nitro-4-chlorodibenzo[*b*,*d*]iodol-5-ium trifluoromethanesulfonate (2q):White powder (79% yield); IR (neat, cm^{-1}): 2960, 2846, 1539, 1458, 1377, 1020; ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 9.22 (d, *J* = 1.6 Hz, 1H), 8.80 (d, *J* = 8.0 Hz, 1H), 8.64 (d, *J* = 2.0 Hz, 1H), 8.38 (d, *J* = 8.4 Hz, 1H), 7.95 (t, *J* = 7.6 Hz, 1H), 7.85 (t, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 151.1, 145.5, 141.1, 134.5, 133.3, 132.5, 131.7, 129.7, 124.3,

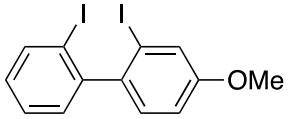
124.1, 122.8, 120.3; HRMS (ESI) Calcd for $C_{12}H_6NO_2ClI$ [M - OTf]$^+$ 357.9126, found 357.9133.

Conversion of cyclic diaryliodonium salts to 2,2'-diiodobiaryls

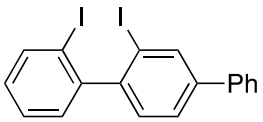
General procedure: An oven-dried Schlenk tube was charged with CuI (3.8 mg, 0.020 mmol), cyclic diaryliodonium triflate (0.20 mmol), and tetrabutylammonium iodide (148 mg, 0.40 mmol). The Schlenk tube was evacuated and backfilled with N_2, followed by the addition of 1,4-dioxane (2 mL) and *trans*-*N*,*N*′-dimethylcyclohexane-1,2-diamine (6.3 μL, 0.040 mmol). The reaction mixture was stirred at room temperature for 24 h, diluted with 5 mL of ethyl acetate, and filtered through a pad of silica gel, using additional ethyl acetate (15 mL) as the eluent. The filtrate was washed with water (10 mL), dried over Na_2SO_4, and concentrated under reduced pressure, before being purified by flash chromatography on silica gel to afford the desired 2,2'-diiodobiaryl.



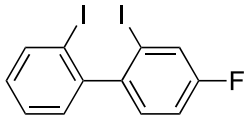
2,2'-Diiodo-1,1'-biphenyl (3a): White solid (89% yield, eluent = hexane); M.p. = 110-111 ℃; IR (neat, cm^{-1}): 2927, 2848, 1456, 1377; ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 8.0, 1.0 Hz, 2H), 7.45 (td, *J* = 7.5, 1.2 Hz, 2H), 7.23 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.12 (td, *J* = 7.7, 1.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.0, 138.9, 129.9, 129.4, 128.0, 99.6; HRMS (ESI) Calcd for $C_{12}H_9I_2$ [M + H]$^+$ 406.8788, found 406.8784. The ^{1}H and ^{13}C NMR spectra showed good agreement with the literature data.[23]



2,2'-Diiodo-4-methoxy-1,1'-biphenyl (3b): Yellow solid (70% yield, eluent = hexane); M.p. = 86-87 ℃; IR (neat, cm^{-1}): 2922, 2852, 1458, 1377, 1026; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.50 (d, *J* = 2.5 Hz, 1H), 7.43 (td, *J* = 7.5, 1.1 Hz, 1H), 7.22 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.13 – 7.08 (m, 2H), 6.99 (dd, *J* = 8.5, 2.6 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 148.6, 141.7, 138.8, 130.4, 130.2, 129.3, 128.0, 123.8, 114.1, 100.8, 99.6, 55.6; HRMS (ESI) Calcd for $C_{13}H_{11}I_2O$ $[M + H]^+$ 436.8894, found 436.8929.

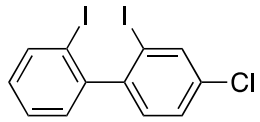


2,2'-Diiodo-1,1':4',1''-terphenyl (3c): White solid (76% yield, eluent = hexane); M.p. = 115-116 ℃; IR (neat, cm^{-1}): 2922, 2852, 1456, 1375; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 1.8 Hz, 1H), 8.01 (dd, *J* = 7.9, 0.8 Hz, 1H), 7.69 – 7.66 (m, 3H), 7.52 – 7.47 (m, 3H), 7.46 – 7.43 (m, 1H), 7.30 – 7.26 (m, 2H), 7.14 (td, *J* = 7.7, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.7, 147.7, 142.4, 139.1, 139.0, 137.4, 130.1, 129.5, 129.0, 128.1, 128.0, 127.2, 126.8, 100.1, 99.8 (one carbon missing due to overlap); HRMS (ESI) Calcd for $C_{18}H_{13}I_2$ $[M + H]^+$ 482.9101, found 482.9103.

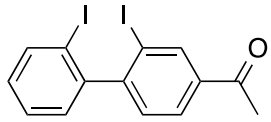


4-Fluoro-2,2'-diiodo-1,1'-biphenyl (3d): Yellow solid (76% yield, eluent = hexane); M.p. = 60-61 ℃; IR (neat, cm^{-1}): 2922, 2852, 1456, 1377; ^{1}H NMR (400 MHz, $CDCl_3$) δ

7.95 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.67 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.43 (td, *J* = 7.6, 1.2 Hz, 1H), 7.20 – 7.14 (m, 3H), 7.10 (td, *J* = 7.6, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.4 (d, $^{1}J_{C\text{-}F}$ = 250.7 Hz), 148.0, 145.2, 139.0, 130.6 (d, $^{3}J_{C\text{-}F}$ = 8.1 Hz), 130.1, 129.6, 128.1, 125.8 (d, $^{2}J_{C\text{-}F}$ = 23.5 Hz), 115.2 (d, $^{2}J_{C\text{-}F}$ = 21.0 Hz), 100.0, 99.1 (d, $^{3}J_{C\text{-}F}$ = 8.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.7; HRMS (ESI) Calcd for $C_{12}H_8FI_2$ $[M + H]^+$ 424.8694, found 424.8697.

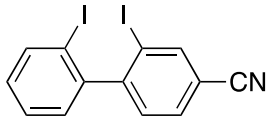


4-Chloro-2,2'-diiodo-1,1'-biphenyl (3e): White solid (81% yield, eluent = hexane); M.p. = 70-71 ℃; IR (neat, cm^{-1}): 2922, 2852, 1454, 1371, 1095; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (td, *J* = 3.4, 0.9 Hz, 2H), 7.47 – 7.42 (m, 2H), 7.19 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.16 – 7.11 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.9. 147.4, 139.1, 138.3, 134.2, 130.5, 129.9, 129.7, 128.4, 128.2, 99.7, 99.5; HRMS (ESI) Calcd for $C_{12}H_8ClI_2$ $[M + H]^+$ 440.8398, found 440.8403.

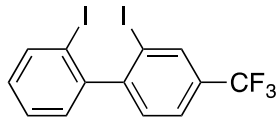


1-(2,2'-Diiodo-[1,1'-biphenyl]-4-yl)ethanone (3f): Pale yellow solid (62% yield, eluent = hexane); M.p. = 105-106 ℃; IR (neat, cm^{-1}): 2922, 2852, 1674, 1458, 1377; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 1.6 Hz, 1H), 7.99 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.95 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.44 (td, *J* = 7.6, 1.2 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.17 – 7.09 (m, 2H), 2.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.2, 153.3, 148.1, 139.0, 138.9,

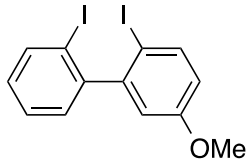
137.7, 130.1, 129.8, 129.5, 128.2, 127.9, 99.9, 98.5, 26.7; HRMS (ESI) Calcd for $C_{14}H_{11}OI_2$ $[M + H]^+$ 448.8894, found 448.8910.



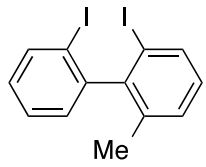
2,2'-Diiodo-[1,1'-biphenyl]-4-carbonitrile (3g): Yellow solid (84% yield, eluent = hexane); M.p. = 132-133 ℃; IR (neat, cm^{-1}): 2920, 2852, 2223, 1462, 1375; ^1H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 1.6 Hz, 1H), 7.98 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.73 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.17 (dd, *J* = 7.6, 2.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.5, 147.5, 142.1, 139.2, 131.6, 130.4, 130.1, 129.3, 128.4, 116.9, 113.3, 99.8, 98.2; HRMS (ESI) Calcd for $C_{13}H_8NI_2$ $[M + H]^+$ 431.8741, found 431.8759.



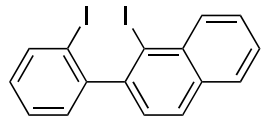
2,2'-Diiodo-4-(trifluoromethyl)-1,1'-biphenyl (3h): Colourless oil (86% yield, eluent = hexane); IR (neat, cm^{-1}): 2924, 2852, 1465, 1319, 1138; ^1H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.48 (td, *J* = 7.6, 0.9 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 1H), 7.24 – 7.10 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.4, 147.8, 139.1, 135.8 (q, $^3J_{C-F}$ = 3.7 Hz), 131.4 (q, $^2J_{C-F}$ = 32.7 Hz), 130.2, 129.9, 129.6, 128.3, 125.0 (q, $^3J_{C-F}$ = 3.5 Hz), 122.9 (q, $^1J_{C-F}$ = 271.2 Hz), 99.5, 98.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.5; HRMS (ESI) Calcd for $C_{13}H_8I_2F_3$ $[M + H]^+$ 474.8662, found 474.8662.



2,2'-Diiodo-5-methoxy-1,1'-biphenyl (3i): Yellow oil (72% yield, eluent = hexane); IR (neat, cm^{-1}): 2956, 2931, 1456, 1016; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.2 Hz, 1H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.42 (td, *J* = 7.6, 1.2 Hz, 1H), 7.20 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.09 (td, *J* = 7.8, 1.6 Hz, 1H), 6.77 (d, *J* = 3.2 Hz, 1H), 6.70 (dd, *J* = 8.8, 3.2 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 149.7, 148.8, 139.4, 138.9, 129.8, 129.4, 128.1, 115.9, 115.7, 99.5, 88.1, 55.5; HRMS (ESI) Calcd for $C_{13}H_{11}OI_2$ $[M + H]^+$ 436.8894, found 436.8894.

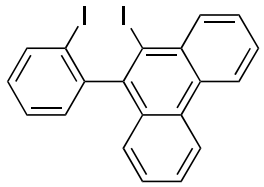


2,2'-Diiodo-6-methyl-1,1'-biphenyl (3j): Pale yellow solid (92% yield, eluent = hexane); M.p. = 98-99 ℃; IR (neat, cm^{-1}): 2920, 2850, 1462, 1377; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.6 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.49 (td, *J* = 7.6, 1.2 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.17 – 7.10 (m, 2H), 7.04 (t, *J* = 7.6 Hz, 1H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.7, 148.0, 139.2, 137.8, 136.5, 129.9, 129.8, 129.6, 129.3, 128.6, 100.7, 100.0, 21.9; HRMS (ESI) Calcd for $C_{13}H_{11}I_2$ $[M + H]^+$ 420.8945, found 420.8963.

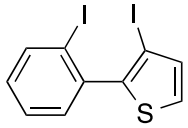


1-Iodo-2-(2-iodophenyl)naphthalene (3k): Yellow solid (72% yield, eluent = hexane); M.p. = 105-106 ℃; IR (neat, cm^{-1}): 2922, 2852, 1456, 1377; ^{1}H NMR (400 MHz, $CDCl_3$)

δ 8.35 (d, *J* = 8.4 Hz, 1H), 8.03 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.93 – 7.87 (m, 2H), 7.69 – 7.64 (m, 1H), 7.62 – 7.58 (m, 1H), 7.50 (td, *J* = 7.6, 1.2 Hz, 1H), 7.34 – 7.29 (m, 2H), 7.16 (td, *J* = 7.6, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.4, 148.2, 138.9, 134.8, 133.2, 133.1, 130.2, 129.4, 128.7, 128.4, 128.2, 128.1, 127.2, 126.9, 105.1, 99.4; HRMS (ESI) Calcd for $C_{16}H_{11}I_2$ $[M + H]^+$ 456.8945, found 456.8932.

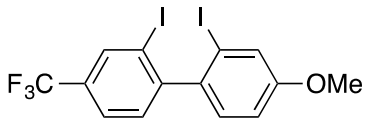


9-Iodo-10-(2-iodophenyl)phenanthrene (3l): Yellow solid (65% yield, eluent = hexane); M.p. = 134-135 ℃; IR (neat, cm^{-1}): 2922, 2852, 1458, 1377; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 8.4 Hz, 1H), 8.74 – 8.69 (m, 1H), 8.51 – 8.48 (m, 1H), 8.08 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.77 – 7.67 (m, 3H), 7.56 (td, *J* = 7.6, 1.2 Hz, 1H), 7.51 – 7.46 (m, 1H), 7.31 – 7.29 (m, 2H),, 7.22 (td, *J* = 8.0, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.5, 146.8, 139.3, 134.6, 132.4, 131.4, 131.0, 130.7, 130.4, 129.5, 128.6, 128.1, 127.1, 127.8, 127.4, 126.9, 122.9, 122.8, 107.1, 100.5; HRMS (ESI) Calcd for $C_{20}H_{13}I_2$ $[M + H]^+$ 506.9101, found 506.9126.

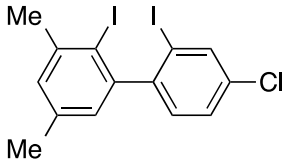


3-Iodo-2-(2-iodophenyl)thiophene (3m): White solid (58% yield, eluent = hexane); M.p. = 106-107 ℃; IR (neat, cm^{-1}): 2943, 2846, 1458, 1377; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.42 (td, *J* = 7.6, 0.8 Hz, 1H), 7.36 – 7.34 (m, 2H), 7.14 – 7.10 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.9, 139.6, 139.2, 134.9, 131.8, 130.4,

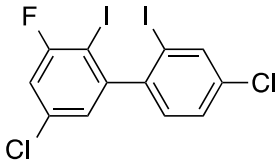
128.0, 127.4, 101.4, 82.6; HRMS (ESI) Calcd for $C_{10}H_7I_2S$ $[M + H]^+$ 412.8352, found 412.8351.



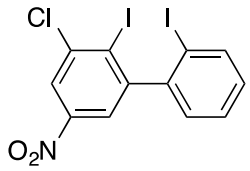
2,2'-Diiodo-4-methoxy-4'-(trifluoromethyl)-1,1'-biphenyl (3n): Yellow oil (90% yield, eluent = hexane); IR (neat, cm^{-1}): 2935, 2835, 1471, 1317; ^1H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.69 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.51 (d, *J* = 2.8 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 7.01 (dd, *J* = 8.4, 2.4 Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 152.2, 140.4, 135.6 (q, $^3J_{C\text{-}F}$ = 3.9 Hz), 131.2 (q, $^2J_{C\text{-}F}$ = 32.7 Hz), 130.7, 129.9, 124.9 (q, $^3J_{C\text{-}F}$ = 3.5 Hz), 124.0, 122.9 (q, $^1J_{C\text{-}F}$ = 271.2 Hz), 114.3, 100.6, 98.7, 55.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.4; HRMS (ESI) Calcd for $C_{14}H_{10}OI_2F_3$ $[M + H]^+$ 504.8768, found 504.8756.



4'-Chloro-2,2'-diiodo-3,5-dimethyl-1,1'-biphenyl (3o): White solid (66% yield, eluent = hexane); M.p. = 82-83 ℃; IR (neat, cm^{-1}): 2922, 2852, 1446, 1377; ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 2.0 Hz, 1H), 7.42 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.14 – 7.10 (m, 2H), 6.80 (d, *J* = 1.2 Hz, 1H), 2.52 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.6, 148.5, 142.1, 138.2, 137.7, 133.8, 130.5, 130.2, 128.3, 127.9, 102.2, 100.0, 29.4, 20.8; HRMS (ESI) Calcd for $C_{14}H_{12}ClI$ $[M + H]^+$ 468.8711, found 468.8701.

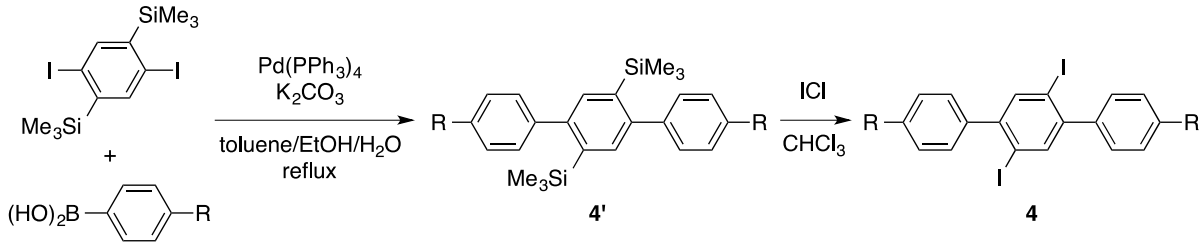


4',5-Dichloro-3-fluoro-2,2'-diiodo-1,1'-biphenyl (3p): White solid (70% yield, eluent = hexane); M.p. = 91-92 ℃; IR (neat, cm^{-1}): 2922, 2852, 1458, 1375, 1095; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 2.0 Hz, 1H), 7.43 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.12 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 7.01 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.8 (d, $^{1}J_{C\text{-}F}$ = 247.6 Hz), 150.6 (d, $^{4}J_{C\text{-}F}$ = 2.5 Hz), 145.1, 138.5, 135.2 (d, $^{3}J_{C\text{-}F}$ = 10.7 Hz), 134.9, 130.2, 128.6, 125.8 (d, $^{4}J_{C\text{-}F}$ = 3.2 Hz), 115.7 (d, $^{2}J_{C\text{-}F}$ = 27.8 Hz), 98.9, 85.5 (d, $^{2}J_{C\text{-}F}$ = 25.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -87.4; HRMS (ESI) Calcd for $C_{12}H_6Cl_2FI_2$ $[M + H]^+$ 492.7914, found 492.7885.

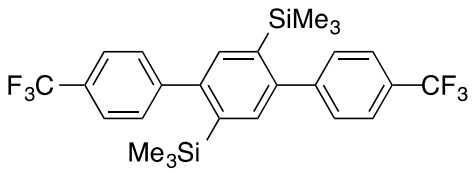


3-Chloro-2,2'-diiodo-5-nitro-1,1'-biphenyl (3q): Yellow solid (86% yield, eluent = hexane); M.p. = 97-98 ℃; IR (neat, cm^{-1}): 2939, 2835, 1525, 1465; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 2.8 Hz, 1H), 7.98 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.91 (d, *J* = 2.4 Hz, 1H), 7.48 (td, *J* = 7.6, 1.2 Hz, 1H), 7.20 – 7.14 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 152.9, 147.9, 147.7, 141.0, 139.3, 130.4, 129.5, 128.6, 122.7, 121.9, 113.7, 98.4; HRMS (ESI) Calcd for $C_{12}H_7ClI_2NO_2$ $[M + H]^+$ 485.8249, found 485.8307.

Preparation of diiodoteraryls

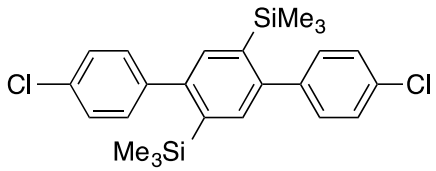


Typical procedure for the preparation of disilylteraryl derivative:[24] A dry round bottom flask was charged with 2,5-diiodo-1,4-phenylenebistrimethylsilane (1.42 g, 3.0 mmol), phenylboronic acid (1.10 g, 9.0 mmol, 3 equiv), K_2CO_3 (2.49 g, 18.0 mmol, 6 equiv), and $Pd(PPh_3)_4$ (346 mg, 0.030 mmol, 0.01 equiv), briefly evacuated and backfilled with nitrogen. To the flask were added THF (30 mL), EtOH (10 mL), and H_2O (10 mL) under nitrogen atmosphere, and the reaction mixture was refluxed for 24 h. The reaction mixture was poured into water and the product was extracted with ethyl acetate. The organic extracts were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica (eluent = hexane) to afford 2',5'-bis(trimethylsilyl)-1,1':4',1''-terphenyl (**4a'**) as a white solid (1.07 g, 96%). ^1H and ^{13}C NMR spectra data showed good agreement with the literature data.[24] The same procedure was applied for the synthesis of **4b'**, **4c',** and **4d'** using (4-(trifluoromethyl)phenyl)boronic acid, (4-chlorophenyl)boronic acid, and *p*-tolylboronic acid, respectively.

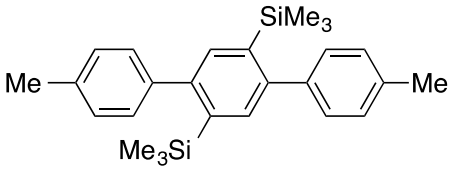


(4,4''-Bis(trifluoromethyl)-[1,1':4',1''-terphenyl]-2',5'-diyl)bis(trimethylsilane) (4b'): White solid (59% yield, eluent = hexane); M.p. = 234-235 ℃; IR (neat, cm^{-1}): 2922, 2852,

1458, 1251; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 4H), 7.51 (d, *J* = 8.0 Hz, 4H), 7.46 (s, 2H), 0.04 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 146.1, 139.1, 135.5, 129.8, 124.8 (2C), 124.3 (q, $^{1}J_{C\text{-}F}$ = 272.8 Hz), 0.51; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.2; HRMS (ESI) Calcd for $C_{26}H_{29}F_6Si_2$ $[M + H]^+$ 511.1706, found 511.1719.



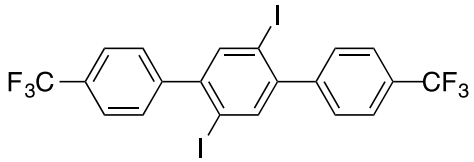
(4,4''-Dichloro-[1,1':4',1''-terphenyl]-2',5'-diyl)bis(trimethylsilane) (4c'): White solid (67% yield, eluent = hexane); M.p. = 255-256 ℃; IR (neat, cm^{-1}): 2922, 2852, 1463, 1377, 1249; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.39 (m, 6H), 7.30 – 7.28 (m, 4H), 0.03 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.9, 142.9, 139.1, 135.6, 133.3, 130.8, 128.0, 0.57; HRMS (ESI) Calcd for $C_{24}H_{29}Si_2Cl_2$ $[M + H]^+$ 443.1185, found 443.1174.



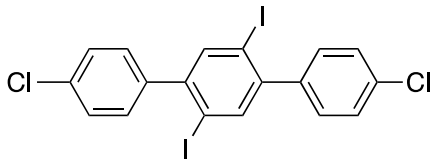
(4,4''-Dimethyl-[1,1':4',1''-terphenyl]-2',5'-diyl)bis(trimethylsilane) (4d'): White solid (82% yield, eluent = hexane); M.p. = 239-240 ℃; IR (neat, cm^{-1}): 2922, 2852, 1458, 1377, 1240; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (s, 2H), 7.28 – 7.25 (m, 8H), 2.46 (s, 6H), 0.04 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.8, 141.8, 138.9, 136.6, 135.7, 129.4, 128.4, 21.2, 0.58; HRMS (ESI) Calcd for $C_{26}H_{35}Si_2$ $[M + H]^+$ 403.2277, found 403.2267.

Typical Procedure for the Preparation of Diiodoteraryl Derivative:[24] A solution of 2',5'-bis(trimethylsilyl)-1,1':4',1''-terphenyl (**4a'**) (1.00 g, 2.67 mmol) in $CHCl_3$ (120 mL)

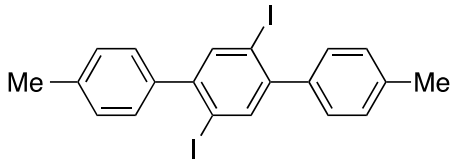
was degassed by bubbling through nitrogen for 20 min, followed by the dropwise addition of a CH_2Cl_2 solution of ICl (1 M, 10.7 mL, 4.0 equiv). After stirring for 1 h, the reaction was quenched with aqueous $Na_2S_2O_3$. Standard workup and purification by flash chromatography on silica gel (eluent = hexane) afforded 2',5'-diiodo-1,1':4',1''-terphenyl (**4a**) as a white solid (1.09 g, 85%). ^{1}H and ^{13}C NMR spectra data showed good agreement with the literature data.[24] The same procedure was applied to synthesize **4b**, **4c** and **4d**, respectively.



2',5'-Diiodo-4,4''-bis(trifluoromethyl)-1,1':4',1''-terphenyl (4b): White solid (89% yield, eluent = hexane); M.p. = 247-248 ℃; IR (neat, cm^{-1}): 2943, 2845, 1458, 1377; ^{1}H NMR (400 MHz, THF-d_8) δ 7.96 (s, 2H), 7.78 (d, J = 8.4 Hz, 4H), 7.58 (d, J = 8.0 Hz, 4H); ^{13}C NMR (100 MHz, THF-d_8): δ 147.4, 147.0, 141.1, 130.9 (q, $^2J_{C\text{-}F}$ = 32.2 Hz), 130.8, 126.0 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 125.3 (q, $^1J_{C\text{-}F}$ = 270.1 Hz), 98.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.5; HRMS (ESI) Calcd for $C_{20}H_{11}F_6I_2$ $[M + H]^+$ 618.8849, found 618.8865.

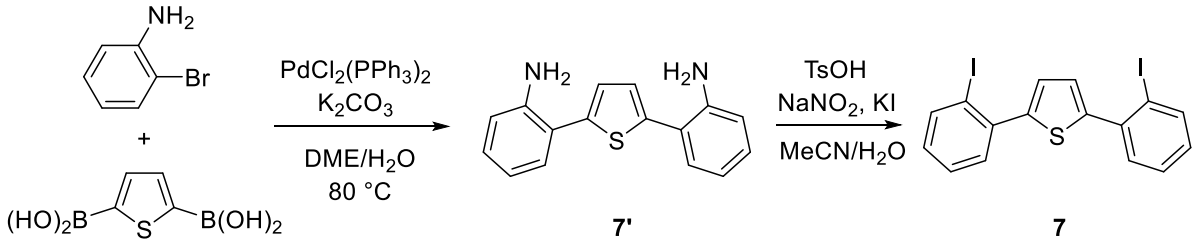


4,4''-Dichloro-2',5'-diiodo-1,1':4',1''-terphenyl (4c): White solid (72% yield, eluent = hexane); M.p. = 256-257 ℃; IR (neat, cm^{-1}): 2922, 2852, 1458, 1377; ^{1}H NMR (400 MHz, THF-d_8) δ 7.89 (s, 2H), 7.45 (d, J = 8.4 Hz, 4H), 7.36 (d, J = 8.0 Hz, 4H); ^{13}C NMR (100 MHz, THF-d_8): δ 147.3, 141.9, 141.1, 134.9, 131.7, 129.1, 98.5; HRMS (ESI) Calcd for $C_{18}H_{11}Cl_2I_2$ $[M + H]^+$ 550.8322, found 550.8308.



2',5'-Diiodo-4,4''-dimethyl-1,1':4',1''-terphenyl (4d): White solid (66% yield, eluent = hexane); M.p. = 212-213 ℃; IR (neat, cm^{-1}): 2933, 2854, 1458, 1377; ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 7.83 (s, 2H), 7.29 (s, 8H), 2.39 (s, 6H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 147.0, 140.2, 139.5, 137.9, 129.4, 129.3, 99.5, 21.4; HRMS (ESI) Calcd for $C_{20}H1_7I_2$ $[M + H]^+$ 510.9414, found 510.9428.

Preparation of diiodoteraryl 7



2,2'-(Thiophene-2,5-diyl)dianiline (7'):[25] A 100 mL three-necked flask was charged with 2-bromoaniline (2.58 g, 15.0 mmol), thiophene-2,5-diyldiboronic acid (0.86 g, 5.0 mmol), aqueous solution of K_2CO_3 (2 M, 10 mL), and DME (20 mL) under a gentle stream of nitrogen. The resulting mixture was stirred for 30 min at room temperature, followed by the addition of $PdCl_2(PPh_3)_2$ (175 mg, 0.40 mmol). The reaction mixture was stirred at 80 ℃ for 12 h, cooled to room temperature, and diluted with EtOAc. The organic layer was washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was subjected to flash chromatography on silica gel (hexane/EtOAc = 5/1) to afford the title compound as a white solid (0.9 g, 68%).

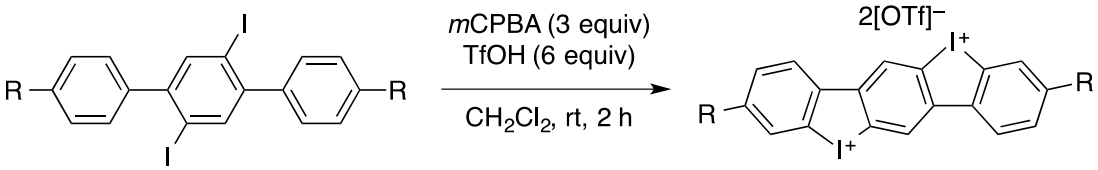
M.p. = 126-127 ℃; IR (neat, cm^{-1}): 3500, 3320, 2939, 2845, 1458, 1377; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 7.6, 1.2 Hz, 2H), 7.23 – 7.16 (m, 4H), 6.87 – 6.79 (m, 4H), 4.11 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.1, 141.0, 130.9, 129.2, 126.4, 120.0, 118.8, 116.2; HRMS (ESI) Calcd for $C_{16}H_{15}N_2S$ $[M + H]^+$ 267.0950, found 267.0952.

2,5-Bis(2-iodophenyl)thiophene (7):[26] To a solution of *p*-TsOH (2.29 g, 12.0 mmol) in MeCN (15 mL) was added **7'** (532 mg, 2.0 mmol). The resulting suspension was cooled to 10-15 ℃, followed by the slow addition of a solution of $NaNO_2$ (543 mg, 8.0 mmol) and KI (1.66 g, 10.0 mmol) in H_2O (10 mL). The mixture was stirred for 10 min, allowed to room temperature for 1 h, and then heated at 60 ℃ for 3 h. An aqueous solution of $NaHCO_3$ was added until the pH of the mixture reached 9, and then $Na_2S_2O_3$ was added until complete reduction of the residual iodine. The crude mixture was extracted with EtOAc, and the extracts were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent = hexane) to afford the title compound as a pale yellow oil (693 mg, 71%).

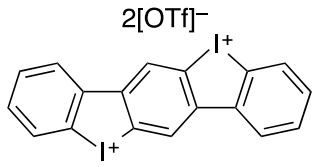
IR (neat, cm^{-1}): 2922, 2852, 1458, 1377; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.21 (s, 2H), 7.07 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.4, 140.2, 139.1, 131.4, 129.5, 128.2, 127.5, 99.3; HRMS (ESI) Calcd for $C_{16}H_{11}I_2S$ $[M + H]^+$ 488.8665, found 488.8676.

Preparation of bis-iodonium salts

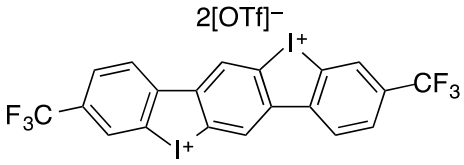
General procedure for the preparation of bis-iodonium salts



To a stirred solution of 2',5'-diiodo-1,1':4',1"-terphenyl derivatives (2.0 mmol) in anhydrous CH_2Cl_2 (30 mL) was added *m*CPBA (75%, 1.37 g, 6.0 mmol) and TfOH (1.06 mL, 12 mmol). A precipitate was formed immediately, and the reaction mixture was stirred at room temperature for 2 h. The precipitate was collected by vacuum filtration, washed with Et_2O (ca. 5 mL) three times, dried under vacuum to afford the pure bis-iodonium ditriflate.

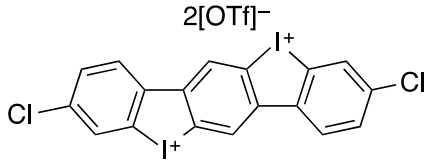


5a: White solid (98% yield); IR (neat, cm^{-1}): 2939, 2839, 1462, 1377, 1031; ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.90 (s, 2H), 8.23 (dd, *J* = 13.2, 8.0 Hz, 4H), 7.94 (t, *J* = 7.6 Hz, 2H), 7.80 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 143.4, 139.9, 132.7, 131.8, 131.3, 128.2, 127.3, 125.1, 122.9; HRMS (ESI) Calcd for $C_{19}H_{10}O_3F_3SI_2$ [M - OTf]$^+$ 628.8387, found 628.8397.

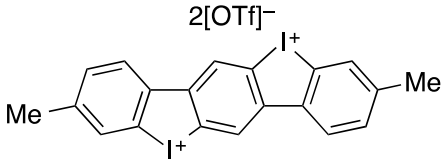


5b: White solid (94% yield); IR (neat, cm^{-1}): 2941, 2845, 1462, 1377, 1022; ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 9.14 (s, 2H), 8.62 (s, 2H), 8.55 (d, *J* = 8.4 Hz, 2H), 8.34 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 143.7, 142.9, 131.5 (q, $^2J_{C\text{-}F}$ = 32.9 Hz), 129.3, 128.7 (q, $^3J_{C\text{-}F}$ = 3.6 Hz), 128.4, 128.1 (q, $^3J_{C\text{-}F}$ = 3.0 Hz), 126.6, 124.0, 123.6 (q, $^1J_{C\text{-}F}$ = 271.5 Hz); ^{19}F NMR (376 MHz, $(CD_3)_2SO$) δ -77.7; HRMS (ESI) Calcd for $C_{21}H_8O_3F_9SF_6I_2$ [M - OTf]$^+$ 764.8134, found 764.8150. Recrystallization from

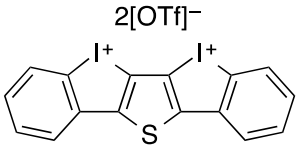
THF/DMSO afforded single crystals of **5b**•2DMSO suitable for X-ray diffraction analysis, which confirmed the regiochemistry of the compound.



5c: White solid (87% yield); IR (neat, cm^{-1}): 2943, 2845, 1458, 1377, 1028; ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.94 (s, 2H), 8.30 – 8.28 (m, 4H), 8.04 (dd, *J* = 8.4, 1.2 Hz, 2H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 142.5, 139.0, 136.3, 132.2, 130.6, 128.4, 125.7, 123.9, 122.7; HRMS (ESI) Calcd for $C_{19}H_8O_3F_3SCl_2I_2$ $[M - OTf]^+$ 696.7607, found 696.7618.



5d: White solid (92% yield); IR (neat, cm^{-1}): 2922, 2852, 1458, 1375, 1242, 1029; ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.80 (s, 2H), 8.06 (d, *J* = 8.0 Hz, 2H), 8.01 (s, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 2.52 (s, 6H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 143.4, 143.0, 137.4, 132.8, 130.9, 127.8, 126.8, 124.8, 122.9, 21.8; HRMS (ESI) Calcd for $C_{21}H_{14}O_3F_3SI_2$ $[M - OTf]^+$ 656.8700, found 656.8712.

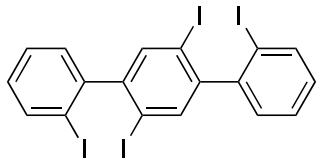


8: White solid (60% yield); IR (neat, cm^{-1}): 2912, 2848, 1458, 1377; ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.28 (d, *J* = 8.4 Hz, 4H), 7.88 (t, *J* = 7.6 Hz, 2H), 7.69 (t, *J* = 7.6 Hz, 2H);

^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 148.5, 136.4, 131.8, 131.4, 131.3, 127.0, 126.5, 111.7; HRMS (ESI) Calcd for $C_{17}H_8O_3F_3S_2I_2$ $[M - OTf]^+$ 634.7951, found 634.7964.

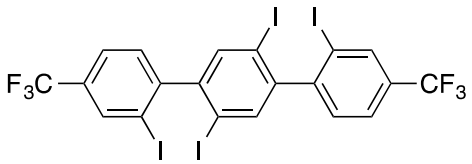
Conversion of bis-iodonium salts to tetraiodoteraryls

General procedure for the synthesis of tetraiodoterphenyls: An oven-dried Schlenk tube was charged with CuI (7.6 mg, 0.040 mmol), a bis-iodonium salt (0.20 mmol), and tetrabutylammonium iodide (295 mg, 0.80 mmol). The Schlenk tube was evacuated and backfilled with N_2, followed by the addition of MeCN (4 mL) and *trans-N,N′*-dimethylcyclohexane-1,2-diamine (13 μL, 0.080 mmol). The reaction mixture was stirred at 80 ℃ under darkness for 24 h, diluted with ethyl acetate (5 mL), and filtered through a pad of silica gel, using additional ethyl acetate (15 mL) as the eluent. The filtrate was concentrated under reduced pressure, and the residue was purified by flash chromatography on silica gel to afford the desired product as a light-sensitive solid (Note: quick workup is crucial for the minimization of the product decomposition and for the reproducibility of the result).

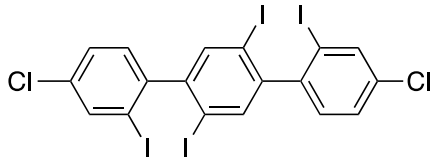


2,2',2'',5'-Tetraiodo-1,1':4',1''-terphenyl (6a): White solid (63% yield); M.p. = 243-244 ℃; IR (neat, cm^{-1}): 2922, 2852, 1456, 1375; ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 7.99 (dd, *J* = 8.0, 0.8 Hz, 2H), 7.73 (d, *J* = 0.8 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 2H), 7.32 – 7.27 (m, 2H), 7.22 – 7.17 (m, 2H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 151.0, 150.9, 148.5, 148.4, 140.5 (2C), 140.0, 139.9, 131.0 (2C), 130.6, 130.5, 129.0 (2C), 100.1, 99.8, 99.6, 99.5

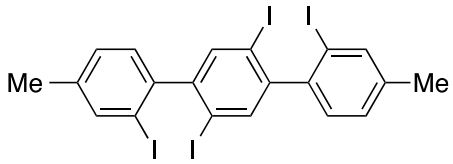
(^{13}C NMR indicates that the compound exist as a mixture of rotamers); HRMS (ESI) Calcd for $C_{18}H_{11}I_4$ $[M + H]^+$ 734.7034, found 734.7042.



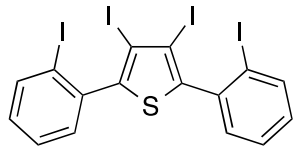
2,2',2'',5'-Tetraiodo-4,4''-bis(trifluoromethyl)-1,1':4',1''-terphenyl (6b): Pale yellow solid (72% yield); M.p. = 198-199 ℃; IR (neat, cm^{-1}): 2943, 2846, 1462, 1377; ^{1}H NMR (400 MHz, THF-d_8) δ 8.30 (s, 2H), 7.85 – 7.82 (m, 4H), 7.48 (dd, J = 16.4, 8.0 Hz, 2H); ^{13}C NMR (100 MHz, THF-d_8): δ 152.1, 152.0, 150.4, 150.3, 140.4 (2C), 136.6 (q, $^3J_{C\text{-}F}$ = 2.4 Hz), 132.3 (q, $^2J_{C\text{-}F}$ = 32.6 Hz), 132.2 (q, $^2J_{C\text{-}F}$ = 32.5 Hz), 131.6, 131.1, 126.0 (q, $^3J_{C\text{-}F}$ = 1.9 Hz), 125.4, 124.0 (q, $^1J_{C\text{-}F}$ = 271.0 Hz), 122.7, 100.4, 100.1, 98.9, 98.8 (^{13}C NMR indicates that the compound exist as a mixture of rotamers); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6; HRMS (ESI) Calcd for $C_{20}H_8F_6I_4$ $[M + H]^+$ 870.6782, found 870.6786.



4,4''-Dichloro-2,2',2'',5'-tetraiodo-1,1':4',1''-terphenyl (6c): Pale yellow solid (67% yield); M.p. = 245-246 ℃; IR (neat, cm^{-1}): 2941, 2852, 1456, 1377; ^{1}H NMR (400 MHz, THF-d_8) δ 8.02 (s, 2H), 7.78 (d, J = 1.6 Hz, 2H), 7.53 – 7.50 (m, 2H), 7.25 (dd, J = 15.2, 8.4 Hz, 2H); ^{13}C NMR (100 MHz, THF-d_8): δ 150.2, 150.1, 147.1, 147.0, 140.6, 140.5, 139.1 (2C), 135.2, 135.1, 131.8, 131.4, 129.3, 129.2, 100.5, 100.2, 99.6, 99.5 (^{13}C NMR indicates that the compound exist as a mixture of rotamers); HRMS (ESI) Calcd for $C_{18}H_9Cl_2I_4$ $[M + H]^+$ 802.6255, found 802.6255.

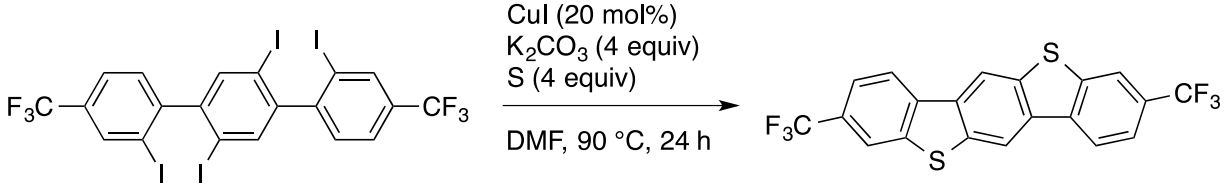


2,2',2'',5'-Tetraiodo-4,4''-dimethyl-1,1':4',1''-terphenyl (6d): White solid (ca. 51% yield); IR (neat, cm^{-1}): 2922, 2852, 1458, 1375; This compound was highly sensitive and degraded during the workup, purification, and NMR analysis; ^{1}H NMR (400 MHz, THF-d_8) δ 7.81 (s, 2H), 7.73 (d, J = 0.8 Hz, 2H), 7.28 – 7.25 (m, 2H), 7.12 (dd, J = 14.8, 8.0 Hz, 2H), 2.36 (s, 6H); ^{13}C NMR (100 MHz, THF-d_8): δ 150.8, 150.7, 145.7, 145.5, 140.8, 140.7, 140.6 (2C), 140.3, 140.2, 130.6, 130.1, 129.8. 129.7, 100.0, 99.9, 99.8, 99.6 (^{13}C NMR indicates that the compound exist as a mixture of rotamers); HRMS (ESI) Calcd for $C_{20}H_{15}I_4$ $[M + H]^+$ 762.7347, found 762.7331.



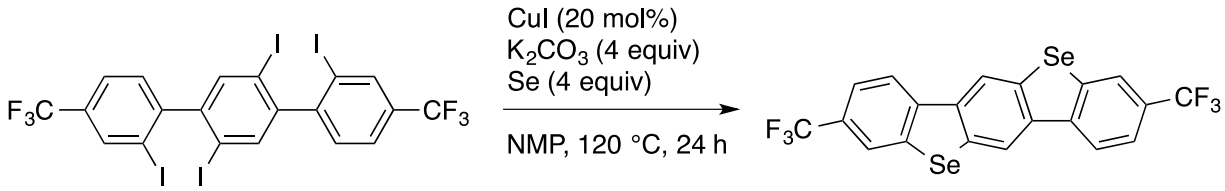
3,4-Diiodo-2,5-bis(2-iodophenyl)thiophene (9): White solid (44% yield); M.p. = 223-224 ℃; IR (neat, cm^{-1}): 2927, 2854, 1462, 1377; ^{1}H NMR (400 MHz, THF-d_8) δ 8.00 (d, J = 8.0 Hz, 2H), 7.47 (t, J = 7.6 Hz, 2H), 7.40 (dd, J = 7.6, 1.6 Hz, 2H), 7.15 (td, J = 7.6, 1.6 Hz, 2H); ^{13}C NMR (100 MHz, THF-d_8): δ 146.9, 141.2, 140.3, 132.4, 131.6, 129.1, 101.7, 97.9; HRMS (ESI) Calcd for $C_{16}H_9I_4S$ $[M + H]^+$ 740.6598, found 740.6605.

Synthesis of ladder-type π-conjugated systems



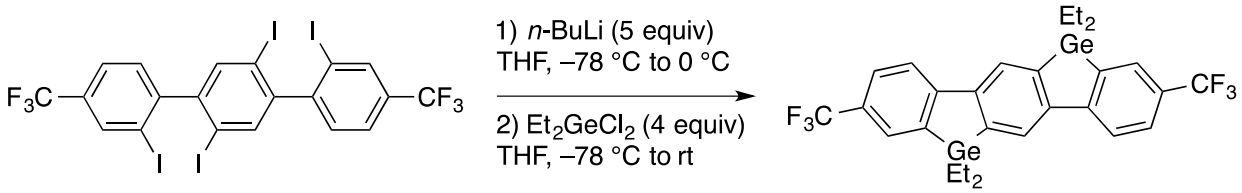
3,9-Bis(trifluoromethyl)benzo[1,2-*b*:4,5-*b*']bis[*b*]benzothiophene (10): An oven-dried Schlenk tube was charged with CuI (4.0 mg, 0.021 mmol), 2,2',2",5'-tetraiodo-4,4"-bis(trifluoromethyl)-1,1':4',1"-terphenyl (174 mg, 0.20 mmol), sulfur powder (25.6 mg, 0.80 mmol), and K_2CO_3 (109 mg, 0.80 mmol). The Schlenk tube was evacuated and backfilled with N_2, followed by the addition of DMF (4 mL). The reaction mixture was stirred at 90 ℃ for 24 h. Upon cooling to room temperature, the reaction mixture was diluted with ethyl acetate (5 mL) and filtered through a pad of silica gel using additional ethyl acetate (15 mL) as the eluent. The filtrate was washed with water (10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent = hexane/EtOAc (10:1)) to afford the title compounds as a pale yellow solid (73.4 mg, 86%).

M.p. = 281-282 ℃; IR (neat, cm^{-1}): 2914, 2848, 1462, 1377; ^{1}H NMR (400 MHz, THF-d_8) δ 8.85 (s, 2H), 8.42 (d, J = 8.0 Hz, 2H), 8.30 (s, 2H), 7.74 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, THF-d_8) δ 141.5, 138.6, 138.5, 135.7, 129.9 (q, $^2J_{C\text{-}F}$ = 32.1 Hz), 125.5 (q, $^1J_{C\text{-}F}$ = 270.3 Hz), 123.3, 122.2 (q, $^3J_{C\text{-}F}$ = 3.6 Hz), 121.2 (q, $^3J_{C\text{-}F}$ = 4.2 Hz), 117.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.7; HRMS (ESI) Calcd for $C_{20}H_9F_6S_2$ $[M + H]^+$ 427.0044, found 427.0051. Recrystallization from THF/pentane afforded single crystals suitable for X-ray diffraction analysis, which unambiguously confirmed the molecular structure of the compound.



3,9-Bis(trifluoromethyl)benzo[1,2-*b*:4,5-*b*']bis[*b*]benzoselenophene (11): An oven-dried Schlenk tube was charged with CuI (4.0 mg, 0.021 mmol), 2,2',2",5'-tetraiodo-4,4"-bis(trifluoromethyl)-1,1':4',1"-terphenyl (174 mg, 0.20 mmol), selenium powder (63.2 mg, 0.80 mmol) and K_2CO_3 (109 mg, 0.80 mmol). The Schlenk tube was evacuated and backfilled with N_2, followed by the addition of NMP (4 mL). The reaction mixture was stirred at 120 ℃ for 24 h. Upon cooling to room temperature, the reaction mixture was diluted with ethyl acetate (5 mL) and filtered through a pad of silica gel using additional ethyl acetate (15 mL) as the eluent. The filtrate was washed with water (10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent = hexane/EtOAc (10:1)) to afford the title compound as a pale yellow solid (80.2 mg, 77%).

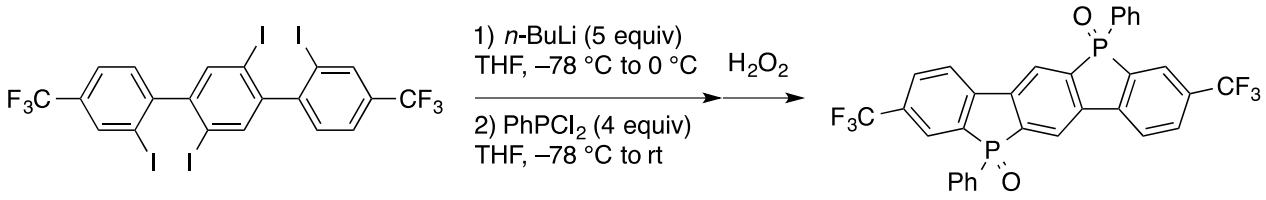
M.p. = 274-275 ℃; IR (neat, cm^{-1}): 2939, 2839, 1456, 1377; ^{1}H NMR (400 MHz, THF-d_8) δ 8.89 (s, 2H), 8.39 – 8.37 (m, 4H), 7.74 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, THF-d_8) δ 141.4, 141.3, 138.5, 138.2, 129.7 (q, $^2J_{C\text{-}F}$ = 31.9 Hz), 125.4 (q, $^1J_{C\text{-}F}$ = 270.4 Hz), 124.4 (q, $^3J_{C\text{-}F}$ = 4.2 Hz), 124.3, 122.7 (q, $^3J_{C\text{-}F}$ = 3.6 Hz), 122.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.7; HRMS (ESI) Calcd for $C_{20}H_9F_6Se_2$ $[M + H]^+$ 520.8953, found 520.8949. Recrystallization from THF afforded single crystals suitable for X-ray diffraction analysis, which unambiguously confirmed the molecular structure of the compound.



2,8-Bis(trifluoromethyl)-6,6,12,12-tetraethyl-6,12-digermaindeno[1,2-*b*]fluorene (12): To a solution of 2,2',2",5'-tetraiodo-4,4"-bis(trifluoromethyl)-1,1':4',1"-terphenyl (174 mg,

0.20 mmol) in THF (2 mL) was added *n*-BuLi (1.6 M in hexane, 0.63 mL, 1.0 mmol) dropwise at –78 ℃. The resulting mixture was stirred for 30 min, allowed to 0 ℃ for 1 h, and then cooled again to –78 ℃. Dichlorodiethylgermane (118 μL, 0.80 mmol) was added, and the reaction mixture was allowed to room temperature and stirred for 12 h. The reaction was quenched with saturated NH_4Cl solution, and then extracted with ethyl acetate. The extracts were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent = hexane/CH_2Cl_2 (10:1)) to afford the title compound as a white solid (51.1 mg, 41%).

M.p. = 199-200 ℃; IR (neat, cm^{-1}): 2922, 2854, 1458, 1377; ^{1}H NMR (400 MHz, THF-d_8) δ 8.16 (s, 2H), 8.02 (d, J = 8.0 Hz, 2H), 7.85 (s, 2H), 7.68 (d, J = 8.0 Hz, 2H), 1.30 (q, J = 8.0 Hz, 8H), 1.13 (t, J = 7.6 Hz, 12H); ^{13}C NMR (100 MHz, THF-d_8) δ 150.3, 145.6, 142.2, 140.9, 129.9 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 128.9 (q, $^2J_{C\text{-}F}$ = 31.6 Hz), 127.0, 126.5 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 124.7 (q, $^1J_{C\text{-}F}$ = 270.6 Hz), 121.4, 9.3, 6.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.0; HRMS (ESI) Calcd for $C_{28}H_{29}F_6Ge_2$ $[M + H]^+$ 625.0592, found 625.0611. Recrystallization from THF afforded single crystals suitable for X-ray diffraction analysis, which unambiguously confirmed the molecular structure of the compound.



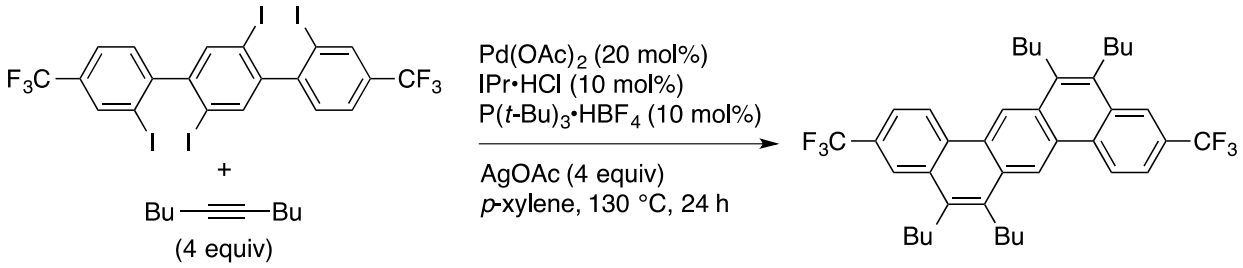
5,11-Diphenyl-3,9-bis(trifluoromethyl)-5,11-dihydrobenzo[1,2-*b*:4,5-*b*']bis(phosphindole) 5,11-dioxide (13): To a solution of 2,2',2",5'-tetraiodo-4,4"-bis(trifluoromethyl)-1,1':4',1"-terphenyl (348 mg, 0.40 mmol) in THF (4 mL) was added *n*-BuLi (1.6 M in hexane, 1.25 mL, 2.0 mmol) dropwise at –78 ℃. The resulting mixture

was stirred for 30 min, allowed to 0 ℃ for 1 h, and then cooled again to –78 ℃. Dichlorophenylphosphine (217 μL, 1.6 mmol) was added, and the reaction mixture was allowed to room temperature and stirred for 12 h. An aqueous solution of H_2O_2 (ca. 30%, a few drops) was added at 0 ℃, and the resulting mixture was stirred at room temperature for 0.5 h. The reaction was quenched with saturated NH_4Cl solution, and then extracted with ethyl acetate. The extracts were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent = EtOAc/hexane/$CHCl_3$ (1:2:2)) to afford ***anti*-13** (48.8 mg, 20%) and ***syn*-13** (85.5 mg, 35%) both as white solids.

***anti*-13:** M.p. > 400 ℃ ; IR (neat, cm^{-1}): 2922, 2852, 1458, 1377, 1195; ^1H NMR (400 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 9.6, 2.4 Hz, 2H), 7.99 – 7.86 (m, 6H), 7.72 – 7.66 (m, 4H), 7.63 – 7.60 (m, 2H), 7.50 (td, *J* = 7.6, 3.2 Hz, 4H); ^{13}C NMR could not be obtained due to the poor solubility of the compound in any solvent; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.8; HRMS (ESI) Calcd for $C_{32}H_{19}O_2F_6P_2$ $[M + H]^+$ 611.0759, found 611.0762.

***syn*-13:** M.p. = 325-326 ℃; IR (neat, cm^{-1}): 2922, 2852, 1462, 1377, 1118; ^1H NMR (400 MHz, $CDCl_3$) δ 8.25 (dd, *J* = 9.6, 2.4 Hz, 2H), 8.02 – 7.92 (m, 4H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.71 – 7.65 (m, 4H), 7.60 (td, *J* = 7.6, 1.2 Hz, 2H), 7.48 (td, *J* = 7.6, 3.2 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7 (d, $J_{C\text{-}P}$ = 21.0 Hz), 142.1 (qd, $J_{C\text{-}P}$ = 10.7 Hz, $J_{C\text{-}F}$ = 3.2 Hz), 140.2 (d, $J_{C\text{-}P}$ = 1.8 Hz), 139.2 (d, $J_{C\text{-}P}$ = 1.7 Hz), 134.3, 133.3, 132.5 (qd, $J_{C\text{-}F}$ = 21.0 Hz, $J_{C\text{-}P}$ = 12.0 Hz), 131.1 (d, $J_{C\text{-}P}$ = 11.4 Hz), 129.3 (d, $J_{C\text{-}P}$ = 13.2 Hz), 128.4 (d, $J_{C\text{-}P}$ = 105.2 Hz), 127.3 (qd, $J_{C\text{-}P}$ = 7.5 Hz, $J_{C\text{-}F}$ = 3.9 Hz), 123.4 (t, $J_{C\text{-}P}$ = 10.2 Hz), 122.4 (d, $J_{C\text{-}P}$ = 10.1 Hz), 123.3 (q, $J_{C\text{-}F}$ = 271.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.8; HRMS (ESI) Calcd for $C_{32}H_{19}O_2F_6P_2$ $[M + H]^+$ 611.0759,

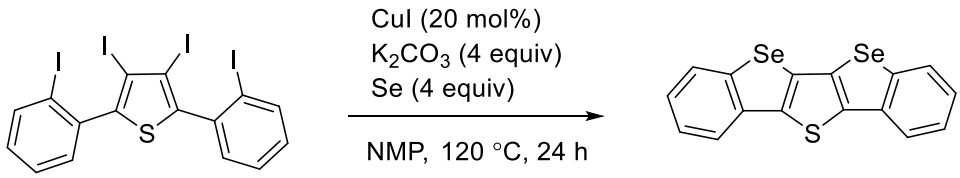
found 611.0751. Recrystallization from pentane/ethyl acetate afforded single crystals of ***syn*-13**•EtOAc suitable for X-ray diffraction analysis, which unambiguously confirmed the molecular structure of the compound.



5,6,12,13-Tetrabutyl-3,10-bis(trifluoromethyl)benzo[*k*]tetraphene (14): An oven-dried Schlenk tube was charged with 2,2',2",5'-tetraiodo-4,4"-bis(trifluoromethyl)-1,1':4',1"-terphenyl (174 mg, 0.20 mmol), 5-decyne (142 μL, 0.80 mmol), $Pd(OAc)_2$ (9.0 mg, 0.040 mmol), IPr•HCl (8.6 mg, 0.020 mmol), P(*t*-Bu)$_3$•HBF_4 (6.0 mg, 0.020 mmol), and AgOAc (132 mg, 0.80 mmol). The Schlenk tube was evacuated and backfilled with N_2, followed by the addition of *p*-xylene (4 mL). The resulting mixture was stirred at 130 ℃ for 24 h. Upon cooling to room temperature, the reaction mixture was diluted with ethyl acetate (5 mL) and filtered through a pad of silica gel using additional ethyl acetate (15 mL) as the eluent. The filtrate was washed with water (10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent = hexane) to afford the title compound as a yellow solid (74.1 mg, 58%).

M.p. = 200-201 ℃; IR (neat, cm^{-1}): 2924, 2854, 1458, 1375; ^{1}H NMR (400 MHz, THF-d_8) δ 198-199 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.43 (s, 2H), 8.93 (d, *J* = 8.8 Hz, 2H), 8.39 (s, 2H), 7.88 (d, *J* = 8.4 Hz, 2H), 3.37 (t, *J* = 8.0 Hz, 4H), 3.21 (t, *J* = 8.0 Hz, 4H), 1.87 – 1.62 (m, 16H), 1.15 (t, *J* = 7.2 Hz, 6H), 1.09 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100

MHz, $CDCl_3$) δ 135.4, 133.9, 132.3, 131.5, 129.7, 128.7 (q, $^2J_{C\text{-}F}$ = 32.0 Hz), 128.5, 124.7 (q, $^1J_{C\text{-}F}$ = 270.1 Hz), 123.6, 122.2 (q, $^3J_{C\text{-}F}$ = 4.1 Hz), 121.7 (q, $^3J_{C\text{-}F}$ = 3.3 Hz), 119.3, 32.8, 32.7, 29.3, 29.0, 23.5, 23.3, 14.1, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.9; HRMS (ESI) Calcd for $C_{40}H_{45}F_6$ $[M + H]^+$ 639.3420, found 639.3422. Recrystallization from EtOAc/hexane afforded single crystals suitable for X-ray diffraction analysis, which unambiguously confirmed the molecular structure of the compound.



Benzo[4,5]selenopheno[3,2-b]benzo[4,5]selenopheno[2,3-d]thiophene (15): The reaction of tetraiodoteraryl **9** was performed under the same conditions used for the conversion of **6b** to **11**. Light yellow solid (58% yield); M.p. = 274-275 ℃ ; IR (neat, cm^{-1}): 2920, 2852, 1462, 1377; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.46 (t, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR could not be obtained due to the poor solubility of the compound in any solvent; HRMS (ESI) Calcd for $C_{16}H_9SSe_2$ $[M + H]^+$ 392.8755, found 392.8736. Recrystallization from EtOAc/hexane afforded single crystals suitable for X-ray diffraction analysis, which unambiguously confirmed the molecular structure of the compound.

6.5 References

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List of Publications

1. Versatile Synthesis of Benzothiophenes and Benzoselenophenes by Rapid Assembly of Arylzinc Reagents, Alkynes, and Elemental Chalcogens, B. Wu, N. Yoshikai, *Angew. Chem. Int. Ed.* **2013**, *52*, 10496.
2. A Highly Modular One-Pot Multicomponent Approach to Functionalized Benzo[*b*]phosphole Derivatives, B. Wu, M. Santra, N. Yoshikai, *Angew. Chem. Int. Ed.* **2014**, *53*, 7546.
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4. Conversion of 2-Iodobiaryls into 2,2'-Diiodobiaryls *via* Oxidation–Iodination Sequences: A Versatile Route to Ladder-Type Heterofluorenes, B. Wu, N. Yoshikai, *Angew. Chem. Int. Ed.* **2015**, *54*, 8736.
5. Recent Development in Synthetic Methods for Benzo[*b*]heteroles, B. Wu, N. Yoshikai, *Org. Biomol. Chem.* **2016**, *14*, 5402.