Transition metal-catalyzed functionalization of alkynes and arenes

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**NANYANG
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Arenes**

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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DEDICATION

I would like to dedicate this thesis to my father late B. Brahma Chary, mother B. Sathya laxmi, my brother B. Ravindra Chary, my wife B. Shailaja, and my kids B. Rahul, B. Adharsh for their encouragement and support.

I would also like to dedicate this to my Prof. Kim Sunggak for his constant support for my entire Ph.D study.

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ABSTRACT

Transition metal-catalyzed reactions are one of the most powerful and direct approaches for the synthesis of organic molecules. During the past several decades, new synthetic methodologies come out continuously. The work of the thesis has been directed towards establishing transition metal-catalyzed functionalization of alkynes and arenes. This thesis is divided into two parts.

Part I: Au(I)-catalyzed addition of diphenyl phosphate, Brønsted acids to alkynes and their further applications.

Part II: Pd- and Rh-catalyzed functionalization of arenes using organophosphoryl directing groups

In Part I, we demonstrated Au(I)-catalyzed regio- and stereo-selective addition of diphenyl phosphate to alkynes to furnish kinetically controlled the Markovnikov products and their isomerization to thermodynamically stable enolates. This methodology also extended to other Brønsted acids like carboxylic acids and sulfonic acids.

To extend this approach, application of this methodology on haloalkynes provided Z-halo vinyl phosphates in a regio- and stereo-selective manner, whereas consecutive Pd-catalyzed cross-coupling reaction of Z-halo vinyl phosphates gave stereodefined trisubstituted olefins. In addition, alkynyl hydrogen phosphate in an *endo*- or *exo-dig* ring closure provided a variety of cyclic vinyl phosphates under very mild conditions.

In Part II, due to importance of organophosphates in biological and organic chemistry, we aimed to explore C-H activation reactions of arenes using phosphoryl related directing groups. In Chapter V, we developed a novel Pd(II)-catalyzed protocol for C-H arylation at room temperature in which the phosphoramidate group was utilized as a directing

group for the first time. Diaryliodonium triflates were used as an aryl source for these reactions.

In Chapter VI, Rh(III)-catalyzed *ortho*-olefination reactions of dialkyl arylphosphonates were studied. In this mild and efficient process, the phosphonic ester was utilized successfully as a new directing group. In addition, mono-selectivity for unsubstituted substrates using a phosphonic diamide directing group was also achieved.

PUBLICATIONS

1. “Rh(III)-Catalyzed *ortho*-olefination of arylphosphonate derivatives”

Bathoju Chandra Chary.; Sunggak Kim. *Org. Biomol. Chem.* **2013**, *11*, 6879.
2. "Palladium-Catalyzed C–H Arylation Using Phosphoramidate as a Directing Group at Room Temperature"

Bathoju Chandra Chary.; Sunggak Kim, Youngchul, Jinsik Kim, Phil Ho Lee. *Org. Lett.* **2013**, *15*, 2692.
3. “A regio- and stereoselective synthesis of trisubstituted alkenes *via* gold(I)-catalyzed hydrophosphoryloxylation of haloalkynes”

Bathoju Chandra Chary.; Sunggak Kim.; Doosup Shin.; Phil Ho Lee. *Chem. Commun.* **2011**, *47*, 7851.
4. “Gold(I)-Catalyzed Cyclization of Alkynyl Hydrogen Phosphates”

Bathoju Chandra Chary.; Wee Suan Low.; Sunggak Kim.; Hyunseok Kim.; Phil Ho Lee. *Chem.Asian.J.* **2011**, *6*, 1970.
5. “Gold(I)-Catalyzed Addition of Carboxylic Acids to Alkynes”

Bathoju Chandra Chary.; Sunggak Kim. *J. Org. Chem.* **2010**, *75*, 7928.
6. “Gold(I)-Catalyzed Addition of Diphenyl Phosphate to Alkynes: Isomerization of Kinetic Enol Phosphates to the Thermodynamically Favored Isomers”

Phil Ho Lee.; Sundae Kim.; Aeri Park.; **Bathoju Chandra Chary.**; Sunggak Kim. *Angew. Chem. Int. Ed.* **2010**, *49*, 6806.

Conferences

1. “Palladium-Catalyzed C–H Arylation of *N*-Aryl Phosphoramidates”

Bathoju Chandra Chary.; Sunggak Kim. *18th European Symposium on Organic Chemistry (ESOC2013) held in july 07-12, 2013*, marseille, France.

2. “Gold(I)-Catalyzed Addition of Carboxylic Acids to Alkynes”

Bathoju Chandra Chary.; Sunggak Kim. *6th Asian-European Symposium*, June 2010, Nanayang Technological University, Singapore.

ABBREVIATIONS

δ	chemical shift (ppm)
$^{\circ}\text{C}$	degree centigrade
Ac	acetyl
AcOH	acetic acid
Ar	aryl (substituted aromatic ring)
ACN	acetonitrile
Boc	<i>tert</i> -butyloxycarbonyl
BQ	benzoquinone
Bu	butyl
conv.	conversion
Cp*	1,2,3,4,5-pentamethylcyclopentadiene
DMF	dimethylformamide
DCM	dichloromethane
DCE	dichloroethane
DMF	<i>N,N</i> -dimethylformamide
DMSO	dimethyl sulfoxide
EA	ethyl acetate
eq /equiv.	equivalent
Et	ethyl
h	hour
H	hydrogen
HRMS	High Resolution Mass Spectrometry
Hz	hertz
<i>i</i> -Pr	<i>iso</i> -propyl

<i>J</i>	coupling constants
M^+	parent ion peak (mass spectrum)
Me	methyl
mg	milligram
MHz	megahertz
mmol	millimole
m.p.	melting point
NMR	nuclear magnetic resonance
NBS	<i>N</i> -bromosuccinimide
NIS	<i>N</i> -iodosuccinimide
OTf	trifluoromethane sulfonate
OAc	acetate
OMe	methoxyl
Ph	phenyl
<i>p</i> -TsOH	toluenesulfonic acid
rt/r.t.	room temperature
<i>t</i> -AmylOH	2-methyl-2-butanol
<i>t</i> -Bu/ ^{<i>t</i>} Bu	<i>tert</i> -butyl
temp.	temperature
TLC	thin layer chromatography
TFA	trifluoroacetic acid
α	alpha
β	beta
γ	gamma

Chapter I. Gold-Catalyzed Nucleophilic Addition to Alkynes

1.1 Introduction

Gold catalyzed organic transformations have emerged as a powerful tool in organic synthesis.¹ Gold is a precious metal for coinage, jewellery and art work used by all the civilizations. It is also used in dental medicine and treatment of arthritis. Recently, gold has been recognized as a soft Lewis acid, which allows activation of soft electrophiles such as the unsaturated system alkynes, alkenes, and allenes, to build carbon–carbon and carbon–heteroatom bonds under mild conditions. The recent enormous interest on gold catalysis has been reflected in excellent reviews and publications in the literature over the past two decades. During the past ten years, several research groups have developed gold-catalyzed homogeneous catalytic reactions. Gold exhibits +0, +1 and +3 oxidation states in organic solvents. In the absence of stabilizing ligands, gold(I) spontaneously disproportionates to gold(III) and gold(0) in aqueous solution. Gold catalysts are simple, operationally safe and exhibits high tolerance to oxygen in contrast to other metals. The apparent redox stability of gold(I) species allows new modes of reactivity. Gold is naturally abundant and the cost is also comparable to the palladium, platinum and rhodium, which are used in industrial applications.

In 1973, a milestone work reported by G. C. Bond involved silica or alumina supported gold catalyzed hydrogenation.² In 1986, Ito–Hayashi reported a gold catalyzed asymmetric aldol reaction for the first time.³ Subsequently, Utimoto⁴ and Teles⁵ initiated an impressive growth of activities on homogeneous gold catalysis. In the field of total synthesis, gold catalysis turned out to be useful for the synthesis of many natural products as the methods have mild reaction conditions and high functional group tolerance. Most of the retrosynthetic disconnections of natural product include the formation of furans,

pyrans, esters, ketones and acetals from alkynes. Figure 1.1 highlights a list of selected natural products involving gold catalysis in the field of total synthesis.⁶

Figure 1.1 Gold-catalysis involved in the area of total synthesis

1.2 Importance and Properties of Gold

1.2.1 Characteristics of Gold

Gold represented as Au derived from Aurum (Latin name) and the atomic number 79. The electronic configuration of gold is $\text{Xe } 4f^{14} 5d^{10} 6s^1$. According to orbital diagram, the bond between metal and π ligands depends on four components, in which two of them are important in bond energy. The in-plane π orbital make σ symmetric $L \rightarrow M$ donation and π -symmetric $M \rightarrow L$ back donation. As per high level computational method the parent Au^+ acetylene and Au^+ ethylene accounted about 65% σ interaction and 27% π interaction. It was established that the back bonding observed was of higher percentage. In gold carbonyls, the back donation was found negligible by characterizing spectroscopic method as the $(\nu_{\text{C-O}})$ frequency was observed greater than that of free CO. These observations clearly demonstrate high reactivity of gold towards π ligands.

Alkynophilicity dominates over alkenophilicity because alkynes have lower LUMO than alkenes. Alkenes are more electrophilic and less nucleophilic than alkynes.

1.2.2 Relativistic Effect

Alkynophilicity of gold can be explained by strong relativistic effects.⁷ For heavy metals, relativistic effects are crucial to understand the electronic structure. Heavy transition metals have highly positive nucleus where by the electrons is liable to have heavier consequences contraction of orbitals closer to nucleus. Strong Lewis acidity of gold is due to the relativistic contraction of s and p orbitals towards nucleus and the expansion of the 5d and f orbital is due to the shielding effect of contracted core. All these will lead to the decrease of bond length and lower the nucleophilicity (lower affinity for oxidative addition). The LUMO of the s orbital is the first acceptor to receive electron density from the HOMO π system causing an increase in the π acidity. The electronegativity of gold is higher in 11th group elements (copper 1.9, Ag 1.9, Au 2.4) and is comparable to iodine (2.2).

1.2. 3 Pull-Push Reactivity

Gold catalyzed acetylenic Schmidt reaction is the best example to explain the pull-push reactivity of gold.⁸ Gold is considered to be a π acid which depletes electron density. Gold can also back-donate electron density in which creates both nucleophilic and electrophilic character on vicinyl carbon of an alkyne. Azide **1** will undergo 5-*endo-dig* cyclization followed by back donation of electron density from gold. This leads to the liberation of nitrogen and gold carbene **1b** which is then stabilized by 1,2-alkyl shift. Finally, protodemetalation of gold and aromatization give the heterocycle **2** (Scheme 1.1).

Scheme 1.1 Gold-catalyzed acetylenic Schmidt reaction

1.2.4 Gold Catalysis (between 1970-2000)

Gold catalyzed organic transformations are atom economic. It usually has mild reaction conditions, different reaction scope and high tolerance to functional groups. In 1976, pioneering work from Thomas *et al.* reported the first gold catalyzed addition of aqueous methanol to alkynes. When the alkyne is treated with aqueous methanol in the presence of a catalytic amount of tetrachloroauric acid, the corresponding ketone was obtained as a major product together with methyl vinyl ether and vinyl chloride as the minor products ($\leq 5\%$) (Scheme 1.2).⁹

Scheme 1.2 Gold-catalyzed nucleophilic addition to alkynes

Scheme 1.3 Gold-catalyzed nucleophilic hydroamination to alkynes

In 1987, Utimoto *et al.* demonstrated intramolecular hydroamination of alkynes in the presence of 5 mol% $\text{Na}(\text{AuCl})_4$ catalyst to give cyclic imine *via* enamine intermediate.^{4a}

In 1986, Ito-Hayashi reported the gold catalyzed aldol reaction for the first time. Treatment of an aldehyde with methyl isocyanoacetate in the presence of generated bis(cyclohexylisocyanide)gold(I)tetrafluoroborate insitu catalyst afford the product (**3** : **4** ratio 89:11) in 95% yield at room temperature in dichloromethane.³

Scheme 1.4 Gold(I)-catalyzed asymmetric aldol reaction of alkynes

In 1998, Teles first introduced the new class of air and water sensitive cationic gold(I) complexes for the addition of alcohol to alkynes. They used methyl(triphenylphosphane)gold(I) as a gold source and methanesulfonic acid as cocatalyst which gave addition products. These gold(I) catalysts are water and air sensitive and the reactions can be performed under neat condition.^{5a, b}

Scheme 1.5 Gold(I)-catalyzed addition of alcohol to alkynes

In 2000, Hashmi demonstrated gold-catalyzed synthesis of phenol from furanyl alkyne derivatives.^{10a, b}

Scheme 1.6 Gold-catalyzed synthesis of phenol

1.3 Gold-Catalyzed Nucleophilic Additions

Transition metal mediated nucleophilic addition onto the alkyne is atom economic, thus fulfilling the requirement of green chemistry. Gold(I) and gold(III) are highly efficient Lewis acids to catalyze nucleophilic addition reactions onto alkynes. Au(I) and Au(III) homogeneous catalysis has emerged as an efficient tool to activate triple bonds for the addition of various nucleophiles. The most generally and extensively used chemical transformation of carbon-carbon multiple bonds is the addition of E-Nu (E= H, BR₂, Si, Sn, and the Nu = halogen, CN, CHO, OH, CO, COOR, NR₂ etc.) across the multiple bond. Alkynes are frequently used as reactive partners in gold catalysis. In addition to its ability to activate alkynes and related substrates, the catalysis of nucleophilic addition by gold complexes for the formation of carbon-carbon and carbon-heteroatom bonds has been one of the most investigated reactions in organometallic catalysis.

Scheme 1.7 General mechanism for gold-catalyzed nucleophilic addition to C-C multiple bond

The general mechanism for nucleophilic addition involves the coordination of gold catalyst with alkyne to form an $Au-\pi$ -alkyne complex. The nucleophilic attack on triple bond *anti* to the gold which then forms a vinyl gold complex. Finally, protodemetalation of gold will give the nucleophilic addition product (Scheme 1.7).

In this chapter, we mainly focused on gold-catalyzed nucleophilic additions associated with alkynes as substrates. Nucleophile can be hetero atom which consists of nitrogen and oxygen. My research focused on *O*-nucleophilic addition and its corresponding transformation.

1.3.1 Gold Catalyzed Addition of *N*-Nucleophiles

Gold catalyzed *N*-nucleophile addition on C-C multiple bonds is an efficient method to prepare nitrogencontaining compounds. Nitrogen heterocycles are important structural units in many drugs and materials. After the finding of gold catalyzed intramolecular hydroamination by Utimoto in 2003,^{4a} the first intermolecular hydroamination was reported by Tanaka and his coworkers.¹¹ They reported addition of aromatic amines to alkynes under solvent free conditions using methyl triphenylphosphine gold(I) and H₃PW₁₂O₄₀ (phosphotungstic acid) as a acidic promoter, which affords ketimines in good yields (Scheme 1.8).

Scheme 1.8 Gold(I)-catalyzed intermolecular hydroamination of alkynes

To prepare *N*-Heterocycles, Li and coworkers reported double hydroamination of *o*-alkynylaniline with terminal alkynes using 5 mol % of AuCl₃ and 5 mol % AgOTf (Scheme 1.9). The corresponding *N*-Vinylindoles were obtained up to 17-88% yields. Mechanistic studies revealed that it follow through an intermediate before of C-N bond formation.¹²

Scheme 1.9 Gold(I)-catalyzed double hydroamination of *o*-alkynylaniline

1.3.2 Gold-Catalyzed Addition of *O*-Nucleophiles

Gold-catalyzed addition of *O*-nucleophiles to non-activated C-C triple bond is considered an attractive method to prepare functionalized ketones, ethers, acetals, lactams, vinyl esters and mainly *O*-heterocycles. Hydration of alkynes leads to ketones is a useful transformation in organic synthesis. Previously, hydration of alkynes known with mercury salts requires harsh acidic conditions.¹³ Utimoto then developed a method where by treatment of an alkyne with 2 mol % sodium tetrachloroaurate in methanolic water which affords the corresponding ketones in excellent yield (Scheme 1.10).

Scheme 1.10 Gold(I)-catalyzed hydration and MeOH addition to alkynes

Later Hayashi and Tanaka hypothesized high turnover frequency in hydration of alkynes using PPh_3AuMe and AgSbF_6 as a cocatalyst in the presence of acidic promoter.¹⁴ Higher catalyst loading and the requirement of concentrated solution of strong acids are required to achieve higher yields are the major drawbacks of this reaction. Recently Nolan reported improved hydration of alkynes using gold carbene as catalyst under acid free conditions.¹⁵

Gold-catalyzed preparation of oxygen-containing heterocycles can be achieved using alkynes as substrates. Furan and dihydrofuran derivatives are synthetically valuable in pharmaceuticals and the key subunit in many natural products.

Scheme 1.11 Various approaches towards synthesis of furan derivatives under gold conditions

Many groups have thus reported gold catalyzed synthesis of furan derivatives. Furan moiety can be constructed by intramolecular attack of alcohol on to alkynes or allenes. The alcohol can be present in the starting material **7**, **8** or formed *insitu* from epoxides **3**, **4**, **5**, carbonyls **6**, **7** or acetates **6** (Scheme 1.11).¹⁶

Scheme 1.12 Aldehyde involved gold(I)-catalyzed cyclization

Belot reported Au(I)-catalyzed tandem acetalization and subsequent cyclization of 3-nitro-2-alkynyl aldehyde. The reaction can also proceed in the absence of the Brønsted acid (Scheme 1.12).¹⁷

In 2000, Hashmi reported cycloisomerization of **9** using gold(III) catalyst under ambient condition in acetonitrile. Encouraged from this work, Liu reported in 2005, the gold catalyzed synthesis of substituted dihydrofurans **10** and furans **11** using common intermediate (Z) enynols **9**. Gold(I) and gold(III) gave comparable yields and the cyclization proceeded in a 5-*exo-dig* fashion with high regioselectivity (Scheme 1.13).¹⁸

Scheme 1.13 Gold-catalyzed stereo selective cyclization and cycloisomerization

Acetals are used as protecting groups in organic synthesis. The conventionally preparation involves the addition of alcohol to aldehyde or ketone under acidic conditions. The removal of water is necessary to obtain acetals in good yields. A variety of acetals including spiroketals, monocyclic, and bicyclic ketals are obtained *via* gold catalysis under mild conditions. Gold catalyzed synthesis of strained bicyclic ketals **13** was reported by Michelet and Genêt whereby two intramolecular hydroxyl groups **12** were utilized as nucleophiles for double cycloisomerization in methanol.¹⁹

Scheme 1.14 Gold-catalyzed cycloisomerisation of homopropargylic diols

After this, Krause claimed that gold catalyst is able to mediate cycloisomerization–hydroalkoxylation. Mechanistic studies provide evidence that tetrahydrofuranyl ether is

obtained with 10 mol % Brønsted acid.²⁰ At about the same time, Barluenga also reported similar type of cycloisomerization.²¹

Recently, Sheppard described the formation of boron enolate from gold catalysis under mild conditions. Enolates are carbanionic sources for C-C bond forming reactions.²² The corresponding *O*-alkynyl boronic acid **14** underwent cyclization in 6-*endo dig* mode to give boran enolate **14a** using 1 mol % PPh₃AuNTf₂ in dichloromethane. Further trapping of the boron enolate with various aldehydes affords aldol product **15** in excellent yields. Instead of boron, silicon was also utilized in the similar gold catalytic system.²³

Scheme 1.15 Gold-catalyzed enolate formation / aldol reaction

Another classical gold mediated reaction is the rearrangement of esters group.²⁴ Classically 1,2- or 1,3- migrations observed with propargylic esters. Furthermore, rearrangement extended not only to esters but also observed with phosphates and halogen.²⁵

Scheme 1.16 Migration of an ester under gold conditions

Despite the lower nucleophilicity of carboxylic acids, acids can also be added to alkynes. It was reported that intermolecular version of gold(I)-catalyzed addition of carboxylic acid to terminal alkynes afford lactones.²⁶ In 2006, J. P. Genet and V. Michelet reported gold(I)-catalyzed intramolecular cyclization of acetylenic acid at room temperature leading to γ -lactones (Scheme 1.17).^{26a} Furthermore, the reusable gold deposited on zeolite is used efficiently for this transformation.²⁷

Scheme 1.17 Gold(I)-catalyzed cycloisomerization of alkynes

Fürstner reported seven membered lactones by using enynyl esters through gold cycloisomerization process.²⁸ Inspired from the above works, intermolecular addition of acid to alkynes generate vinyl esters has been extensively studied with several transition metals other than gold. High reactivity, alkynophilicity and chemo-selective nature of gold would give a variety of the modifications to alkynes under gold catalysis.

Proposed work

The work of this thesis is directed towards the gold catalyzed nucleophilic additions on to alkynes. Addition of nucleophiles to alkynes is perfectly atom economic, mild and fulfils the requirement of green chemistry. However, the nucleophilic additions are known to suffer from regio- and stereo selectivity issues. Enol phosphates and enol esters are versatile building blocks for many organic transformations in organic synthesis. Therefore, the most straight forward technique to prepare enol phosphates and enol esters involves metal catalyzed addition of acid to alkynes. In the literature, we found that an enol phosphate was used as coupling partner in cross coupling reactions.

The aim of this project is to develop stereo- and regio-selective addition of diphenyl phosphate to alkynes using gold catalyst. We envisioned that upon addition of diphenyl phosphate to alkynes will provide the corresponding enol phosphates. However, there is a possible competition between kinetic and thermodynamic isomers. The selective preparation of kinetically controlled Markovnikov addition product and thermodynamical stable enolates will be one of the subjects we plan. Furthermore, this methodology will be extended to investigate other Brønsted acids resembling carboxylic acids. The behavior of sulfonic acids will be investigated in the area of stereo and regio- selectivity of addition reactions.

Extension of this approach will be expanded to intermolecular addition of diphenyl phosphate to haloalkynes. Although halides are used as a cross coupling partner, vinyl phosphates also proved as a electrophiles in cross coupling reactions. We will explore palladium-mediated cross coupling reactions of the addition products derived from alkynes and halo alkynes. Furthermore, cyclic vinyl phosphates formed from intramolecular cyclization of alkynyl hydrogen phosphate are also interesting intermediates for further functionalization.

Scheme 1.18 Gold(I)-catalyzed functionalization of alkynes and halo alkynes

Chapter II. Gold(I)-Catalyzed Hydrophosphoryloxylation of Alkynes

2.1 Introduction

Enol phosphates are synthetically versatile intermediates due to the importance in various organic transformations.²⁹ Enol phosphates are stable, readily accessible, and used as versatile electrophiles. Synthesis of enol phosphates is simple and involves quenching of lithium enolates with the corresponding phosphorochloridates.³⁰ Enol phosphates are used as cross coupling partners in many cross coupling reactions like Suzuki³¹, Heck³², Kumada³³ and Stille³⁴ reaction. However, the selectivity is the main drawback of this transformation. It is difficult to get the selectivity (kinetic and thermodynamic) of the formed products. Even under equilibrium conditions for unsymmetrical ketones, thermodynamic enol phosphates predominate but cannot get exclusively.

In 1998, Tanaka demonstrated ruthenium-catalyzed addition of diphenylphosphinic acid to terminal alkynes for the first time.³⁵ As far as we know, it was the only report described the metal catalyzed preparation of enol phosphosphinates. The Markovnikov addition products were achieved with high regioselectivity using 2.5 mol % of $\text{Ru}(\text{CO})_{12}$ in toluene at 140 °C for 5 h. These reactions required harsh conditions to obtain the desired products. Moreover, it was noteworthy that the reaction was unsuccessful with the addition of diphenyl phosphate to alkynes.

Scheme 2.1 Ruthenium mediated Phosphinic acid addition to alkynes

Due to the wide variety of applications of enol phosphates in organic synthesis, there is a need to develop a new efficient metal catalytic system for the regioselective synthesis of

enol phosphates. The high alkynophilic character of gold drove us to study the regioselective preparation of enol phosphates using gold as a catalytic system.

2.2 Intermolecular Addition of Diphenyl Phosphate to Alkynes

2.2.1 Results and Discussion

To examine the feasibility of hydrophosphoryloxylation, 1-octyne (**16a**) was used as a model substrate. The reaction did not occur with gold(III) catalysts and when gold(I) catalyst was used alone (Table 2.1, entries 1, 2). Non-coordinating counter ions like Ag salts were added to determine whether it would generate active cationic Au catalyst. Interestingly, when the reaction was carried out using 5 mol % PPh₃AuCl and 5 mol % AgPF₆, the kinetically controlled Markovnikov addition product **17a** was obtained in 88%

Table 2.1 Optimization of reaction condition

Entry	Catalyst	Yield (%) ^a
1	AuCl ₃	<1
2	PPh ₃ AuCl	No reaction
3	AuCl ₃ / AgOTf	<1
4	AuCl ₃ / AgPF ₆	<1
5	PPh ₃ AuCl / AgSbF ₆	<1
6	PPh ₃ AuCl / AgBF ₄	72
7	PPh ₃ AuCl / AgPF ₆	88
8	PPh ₃ AuCl / AgNTf ₂	<1
9	TfOH	No reaction

^a Yields of isolated product.

yield in 9 h at room temperature (Table 2.1, entry 7). AgBF₄ is less effective and afforded the corresponding addition product in 72% yield (Table 2.1, entry 6). Combination of

gold(I) with AgSbF₆ and AgNTf₂ was ineffective as well (Table 2.1, entry 5, 8). The reaction did not work in presence of protic acids like TfOH (Table 2.1, entry 9). The reaction did not proceed in solvents like dichloromethane, acetonitrile, nitromethane and ethanol. Toluene was found to be the solvent of choice for the reaction.

Table 2.2 Effect of Solvent

Entry	Solvent	Yield (%)
1	CH ₂ Cl ₂	No reaction
2	CH ₃ CN	No reaction
3	CH ₃ NO ₂	No reaction
4	toluene	88
5	EtOH	No reaction

Table 2.3 Preparation of Kinetic Enol Phosphates^a

^areaction was heated at 60 °C. ^breaction was carried out at 110 °C.

This catalytic system was also successful for the addition of diphenyl phosphinic acid to alkynes to obtain the corresponding vinyl phosphinates **17g** and **17h** in 90% and 70%

yield respectively (Table 2.3). Hydrophosphoryloxylation of phenyl acetylene did not proceed at room temperature and required heating at 60 °C for 12 h (Table 2.3). Addition of diphenyl phosphate to activated alkynes such as ethyl propiolate and phenyl propiolate took place *via trans* addition in a stereo- and regioselective manner to afford enol phosphates **17c** and **17e** with 84% and 78%, respectively (Table 2.3). After successive addition of diphenyl phosphate to terminal alkynes, we tried to add diphenyl phosphate to symmetrical alkynes. Symmetrical alkynes are less reactive than terminal alkynes thus needing to reflux to 110 °C in toluene for 15 h to obtain addition product **17f** in 72% yield (Table 2.3).

2.2.2 Addition of Diphenyl Phosphate to Haloalkynes

We next studied the addition of diphenyl phosphate to haloalkynes. Since the regio- and stereo-selective hydrophosphoryloxylation would provide alkenyl halophosphates, this approach would provide an easy access to stereodefined trisubstituted alkenes *via* sequential transition metal catalyzed cross coupling reactions.

Scheme 2.2 Gold-catalyzed regio- and stereoselective synthesis of alkenyl halophosphate

Haloalkyne **18** was prepared by the treatment of terminal alkyne with *N*-iodosuccinimide or *N*-bromosuccinimide in the presence of a catalytic quantity of silver nitrate in acetone at room temperature for 3 h. The initial experiment was carried out with diphenyl phosphate and 1-iodooctyne in the presence of 5 mol % PPh₃AuCl and 5 mol % AgPF₆ in toluene at room temperature for 6 h. Reaction proceeds cleanly, yielding 80% of product.

The same experiment was then repeated with the replacement of AgPF_6 with AgOTf and it was found to proceed smoothly at room temperature in 4 h to yield **19a** at 90% yield (Scheme 2.3). The geometry of the product formed was determined by NOESY analysis which clearly showed that the product was (Z)-alkenyl iodophosphate. There is a correlation between alkyl group and hydrogen. The hydrophosphoryloxylation of iodoctyne was regio- and stereo-selective and afforded a single product.

2.1 Figure NOE correlation of alkenyliodophosphate

When hydrophosphoryloxylation of several iodo- and bromoalkynes was carried out under the same conditions, the corresponding (Z)-alkenyl halophosphates were isolated in high

Scheme 2.3 Stereoselective preparation of (Z)-alkenyl halophosphates

yields. The addition of diphenyl phosphate to 1-bromodecyne and 1-iodohexyne gave the corresponding (Z)-alkenyl halophosphates **19c** and **19b** in 82% and 88% yield (Scheme

2.3). The reaction equally worked well with aliphatic haloalkynes as well as aromatic haloalkynes.

Hydrophosphorylation of iodophenylacetylene and phenethyliodoacetylene also gave alkenyl iodophosphate **19d** and **19f** in 80% and 76% yield (Scheme 2.3). The electron-withdrawing groups did not influence the addition, giving the (*Z*)-alkenyl halophosphate **19g** and **19h** in 85% and 72%, respectively (Scheme 2.3). The regioselectivity was controlled by the electron-withdrawing effect of the iodo group rather than the resonance effect, although the regioselectivity is normally governed by the resonance effect. In addition, the stereoselectivity is attributed to the *trans*-addition of nucleophiles to vinyl gold complex (Scheme 2.4).³⁶

Scheme 2.4 Plausible mechanism for addition of diphenylphosphate to haloalkynes

2.2.3 Stereoselective Synthesis of Trisubstituted Alkenes

The synthesis of stereodefined trisubstituted alkenes is very important in organic synthesis. The skeleton of the trisubstituted alkene is seen in many biologically active compounds and many ingenious approaches have been reported.³⁷ Among various approaches, one of the most attractive approaches is to utilize the transition metal-mediated cross-coupling reactions of stereodefined alkenyl derivatives and depends very much on the regio- and stereospecific synthesis of alkenyl derivatives from alkynes.³⁸

In 1988, H. C. Brown reported highly regio- and stereoselective synthesis of trisubstituted alkenes using boration of alkynyl halide followed by treatment of alkyl lithium or Grignard reagents.³⁹ Following this seminal work, Negishi utilized alkenyl boranes prepared from the bromoboration of alkyne followed by tandem Pd-catalyzed cross coupling reactions to achieve (*Z*)-trisubstituted alkenes.⁴⁰

Scheme 2.5 Previous approaches towards synthesis of trisubstituted alkenes

Recently, Huanfeng reported trisubstituted alkenes *via* iodination of alkynyl halides using potassium iodide as iodine source.⁴¹ The above reports inspired us to prepare stereo- and regio-selective trisubstituted alkenes from alkenyl iodophosphate which prepared from gold(I)-catalyzed addition of diphenyl phosphate to haloalkynes.

To develop a stereoselective synthesis of trisubstituted alkenes using alkenyl halophosphates, first we focused on the Sonogashira coupling reaction using alkenyl iodophosphate **19a**. Among several palladium catalysts screened for this reaction, $\text{Pd}(\text{PPh}_3)_4$ was the best catalyst for the Sonogashira reaction. The best result was obtained

by treatment of **19a** with phenylacetylene in the presence of 2 mol % of Pd(PPh₃)₄, 10 mol % of CuI and 3 equiv of triethylamine in 1,4-dioxane (Table 2.4, entry 5). The reaction proceeded at room temperature for 2 h and the iodo group underwent the preferential and clean coupling reaction in the presence of a phosphate group.

Table 2.4 Reaction optimization^a

Entry	Catalyst	Solvent	Base	Temp (°C)	Time (h)	Yield (%)
1 ^b	Pd ₂ dba ₃ CHCl ₃	DMF	Et ₃ N	80	3	51
2	PdCl ₂ (PPh ₃) ₂	DMF	Et ₃ N	80	3	64
3	Pd(PPh ₃) ₄	DMF	Et ₃ N	80	2	76
4 ^b	Pd ₂ (OAc) ₂	DMF	Et ₃ N	80	3	51
5	Pd(PPh₃)₄	Dioxane	Et₃N	25	2	81
6 ^c	Pd(PPh ₃) ₄	Dioxane	Et ₃ N	25	2	84
7	Pd(PPh ₃) ₄	THF	Et ₃ N	60	2	67
8	Pd(PPh ₃) ₄	Toluene	Et ₃ N	40	2	65
9	Pd(PPh ₃) ₄	DCE	Et ₃ N	60	3	60
10 ^b	Pd ₂ dba ₃ CHCl ₃	Dioxane	Et ₃ N	40	2	78
11	Pd(PPh ₃) ₄	Dioxane	Na ₂ CO ₃	90	6	30
12	Pd(PPh ₃) ₄	Dioxane	K ₂ CO ₃	90	3	60

^a 2 mol % Pd(PPh₃)₄, 10 mol % CuI and 3 equiv of Et₃N were used. ^b PPh₃ used as a ligand.

^c 4 mol % Pd(PPh₃)₄ was used.

Use of other solvents like THF, toluene, DCE, and DMF afforded the corresponding Sonogashira coupled product **20a** in moderate yield (Table 2.4, entry 7-9). In contrast, 1,4-dioxane is the solvent choice of this reaction. Increment of the catalyst loading to 4 mol % of Pd(PPh₃)₄, slightly increased the yield of the product to 84% (Table 2.4, entry

6). The addition of Na_2CO_3 and K_2CO_3 did not improve the yield (Table 2.4, entry 11, 12) and triethylamine was the most effective among the bases used.

Having the optimum condition in hand, we investigated the scope of the Sonogashira coupling of alkenyl iodo phosphates with other alkynes. Several alkenyl iodophosphates worked well with phenyl acetylene using the standard condition to obtain the corresponding Sonogashira products **20b** and **20e** in good yields (Table 2.5). Different nucleophiles like bromo phenylacetylene and 4-methoxy phenylacetylene underwent the Sonogashira reaction to give the corresponding coupled products **20c** and **20d** in 80% and 88% yield (Table 2.5). But alkyl substituted alkynes gave product **20f** and **20g** in lower yields (Table 2.5).

Table 2.5 Sonagashira coupling^a

^aReaction was carried out using 4 mol % $\text{Pd}(\text{PPh}_3)_4$, 3 equiv of Et_3N , and 10 mol % CuI in dioxane at room temperature for 2-3 h

The success of the Sonogashira reaction by using the alkenyl iodophosphate prompted us to extend the functional modification through other cross coupling reactions like the Suzuki, Stille reactions etc. When **19a** was treated with phenylboronic acid in the presence of 5 mol% $\text{Pd}(\text{PPh}_3)_4$, 2 equiv of triethylamine and 3 equiv of K_3PO_4 in THF, the reaction was complete in 16 h, yielding the desired coupling product in 51% yield at 70 °C (Table 2.6, entry 2). The Suzuki coupling in DMF shortened the reaction time to

1.5 h but the yield was reduced to 40% (Table 2.6, entry 1). Similarly, low yields were obtained using toluene and dichloroethane as the solvent (Table 2.6, entry 4, 5). The best solvent for this Suzuki reaction found out to be 1,4-dioxane (Table 2.6, entry 3).

Scheme 2.6 The Suzuki reaction of (*Z*)-alkenyl iodophosphate using palladium as catalyst

Table 2.6 Solvent screening

Entry	Solvent	Temp (°C)	Time (h)	Yield (%)
1	DMF	90	1.5	40
2	THF	70	16	51
3	1,4-Dioxane	70	1	63
4 ^a	Toulene	100	20	25
5 ^a	DCE	70	20	20

^a 50% starting material was recovered.

The Suzuki reaction of **19b** furnished the coupled product **21b** in 65% yield (Scheme 2.6).

Similar results were observed with vinylboronic acid pinacol ester as coupling partner (Scheme 2.7).

Scheme 2.7 Suzuki cross-coupling reaction of (*Z*)-alkenyl iodophosphate

After the success of the Sonogashira and Suzuki coupling reactions involving alkenyl iodophosphate, we also tried the Stille coupling reaction. When the alkenyl iodophosphate **19** was treated with vinyltributyltin in the presence of 4 mol % of $\text{Pd}(\text{PPh}_3)_4$ in 1,4-dioxane at 100 °C for 12 h, the Stille coupled product **22** was isolated in 54% yield. The yield was improved to 61% by performing the reaction in toluene. Alteration of Pd catalyst from $\text{Pd}(\text{PPh}_3)_4$ to $\text{PdCl}_2(\text{PPh}_3)_4$ gave much better results. The alkenyl iodophosphate **8a** was treated with 5 mol % $\text{PdCl}_2(\text{PPh}_3)_4$ in DMF with vinyl tributyltin to yield **22a** in 93% yield at room temperature.

Scheme 2.8 Pd-catalyzed Stille reaction of alkenyl iodophosphate

2.2.4 Synthesis of Trisubstituted Olefins

To complete the stereoselective synthesis of trisubstituted olefins, we turned our attention to the cross coupling reactions using vinyl phosphates. It was documented that vinyl phosphates were used as electrophiles in many cross coupling reactions. However, we found only few reports using unactivated vinyl phosphates with Grignard reagents. In 2009, Skrydstrup reported ligandless Pd-catalyzed Kumada-Corriu coupling reactions using vinyl phosphate. This attracted us to complete the stereoselective synthesis of trisubstituted olefins.^{5a} Treatment of vinyl phosphate with aryl magnesium halide in the presence of 2 mol % PdCl_2 in THF afforded 1,1-disubstituted alkenes. This reaction is simple, economic and does not require any phosphine ligands.

Scheme 2.9 Kumada-Corriu coupling of vinyl phosphates

When Sonogashira coupled products **20** was subjected to the Kumada-Corriu condition with PhMgBr using 5 mol % of PdCl₂ in THF, the desired trisubstituted product **25** was obtained in good yields. The reaction was fast and could complete within 10 min at room temperature. The ligandless condition is appropriate to a variety of alkenyl and aryl phosphates which afford the corresponding trisubstituted alkenes **25a-25d** in better yields (Scheme 2.10). When we treated Suzuki coupled product **21** with PhMgBr in the presence of 2 mol% PdCl₂ as a catalyst in THF, the reaction proceeded at room temperature and afforded **23a** and **23b** in 72% and 62% yield, respectively (Scheme 2.10). In the case of **23a**, a small amount of (*E*)-isomer was observed. Finally, Stille coupled products **22** equally furnished (*Z*)-trisubstituted alkenes **24a** and **24b** in 65%, 70% yield under the similar conditions (Scheme 2.10). We developed a highly efficient method for a stereodefined synthesis of trisubstituted alkenes *via* hydrophosphoryloxylation of iodo alkynes and subsequent consecutive pd-catalyzed cross coupling reactions.

Scheme 2.10 Preparation of trisubstituted olefins using Kumada-Corriu coupling

2.3 Intramolecular Addition of Diphenyl Phosphate to Alkynes

2.3.1 Introduction

After the successful regioselective addition of diphenyl phosphate to alkynes and haloalkynes, we turned our attention towards intramolecular addition of P-OH bond to alkynes. Intramolecular addition of P-OH to the alkyne leads to a new class of phosphorous containing heterocycles, which is more precious in biologically active natural products as well as synthetic intermediates.⁴² Synthesis of these phosphorous heterocycles has not been studied actively in the recent years. In 2003, Ding reported Cu-catalyzed cyclization of *o*-ethynyl phenylphosphonic acid monoester at 90 °C in DMF. The reaction afforded phosphaisocoumarins in excellent yields (Scheme 2.11). This method was useful for the preparation of variety of 3- and 7- substituted phosphaisocoumarins.⁴³ The same research group also studied silver-catalyzed cyclization of **27** (Scheme 2.11).⁴⁴

Scheme 2.11 Intramolecular cyclization of alkynyl phosphonic acid monoester

In our studies, we investigated the possibility of using phosphates not only as a tether linker but utilizing the cyclic phosphate for transition metal catalyzed cross coupling reactions.

The ensuing project will enlighten the possibility of cyclization of P-OH groups to alkynes using gold catalysis for the synthesis of new cyclic phosphates.

2.2 Figure New class of cyclic phosphates

2.3.2 Results and Discussion

Alkynyl hydrogen phosphate was used as the starting material for this cyclization. Intramolecular attack phosphoryl P-OH onto gold activated triple bond will afford the cyclized product. The major concern for this cyclization is the regioselectivity. Cyclization can undergo either cyclized 5-*exo-dig* or 6-*exo-dig* fashion to give a five-membered cyclic phosphate **30** and/or a six-membered cyclic phosphates **31**, respectively (Scheme 2.12).

Scheme 2.12 Possible products from cyclization of alkynyl hydrogen phosphate

The alkynyl hydrogen phosphate can be prepared by treating of an alkynol with phosphorodichloridate using triethylamine in THF. Subsequent hydrolysis of corresponding Chloroalkynyl hydrogen phosphate gave the alkynyl hydrogen phosphate **29** in good yields. Previously, phosphoryl transfer reaction was mainly achieved by using Lewis acids, particularly by TiCl_4 .⁴⁵

Scheme 2.13 Preparation of alkynyl hydrogen phosphate

We tried this reaction in the absence of the Lewis acid. Treatment of propargyl alcohol with 1.2 equiv phosphorodichloridate in the presence of 1.2 equiv of triethylamine followed by the addition of water to afford the desired product **29** in 66% yield with 20% of dialkylated product **32**. The yield could be improved to 75% by adding an excess amount of phosphorodichloridate to propargyl alcohol. Triethylamine was added slowly at 0 °C for 30 mins, followed by the addition of excess water at room temperature for 3 h (Table 2.7). Several alkynyl hydrogen phosphates could be prepared under the standard condition.

Table 2.7 Alkynyl hydrogen phosphates

29a (75%)	29b (84%)	29c (78%)	29d (85%)
29e (86%)	29f (78%)	29g (85%)	29h (82%)
29i (80%)	29j (76%)		

Secondary alcohols also worked well. However, the method was not useful in preparing tertiary alkynyl hydrogen phosphate.

Initially **29a** was used as a model substrate for the cyclization reaction under various conditions. Dichloromethane was chosen as a solvent for this cyclization. This reaction also proceeded in toluene, but needed longer reaction time with comparable yield achieved with dichloromethane. No reaction was observed with silver catalyst alone (Table 2.8, entry 1, 2). Surprisingly, the reaction did not proceed using gold(I) and silver hexafluorophosphate under the standard condition (Table 2.8, entry 4). Furthermore the combination of triphenylphosphine gold(I) chloride and silver tetrafluoroborate was effective in affording cyclized product **31a** in 62% yield (Table 2.8, entry 3). The triphenylphosphine gold(I) chloride and AgOTf catalytic system was most effective and proceeded exclusively by 6-*endo dig* to give the cyclisation product **31a** in 94% yield,

Table 2.8 Reaction Optimization of Au-Catalyzed cyclization

entry	catalyst	T [°C]	T [h]	Yield [%] ^a
1	AgOTf	rt	12	0
2	AgBF ₄	rt	12	<5
3	PPh ₃ AuCl / AgBF ₄	rt	1	62
4	PPh ₃ AuCl / AgPF ₆	rt	1	<5
5	PPh ₃ AuCl / AgOTf	rt	0.1	94
6	FeCl ₃	reflux	12	0
7	FeCl ₃ / AgOTf	reflux	2	63
8	PtCl ₂	rt	12	0
9	InBr ₃	rt	12	0
10	Sc(OTf) ₃	rt	12	0
11	<i>p</i> -TsOH	rt	12	0
12	TfOH	rt	12	0

^a Yields of isolated product.

indicating that 6-*endo-ring* closure was favoured over the 5-*exo-dig* closure (Table 2.8, entry 5).

The reaction did not proceed with protic acids like PTSA and TfOH (Table 2.8, entry 11, 12). Similarly, the cyclization did not proceed with other transition metal catalysts like FeCl₃, PtCl₂, InBr₃, and Sc(OTf)₃ (Table 2.8, entry 6, 8, 9, 10). The active catalyst Fe(OTf)₃ formed with the combination of FeCl₃ and AgOTf, also afforded cyclised product in 63% yield under reflux conditions (Table 2.8, entry 7).

Having the optimum condition in our hand, we investigated the scope and limitation of various alkynyl hydrogen phosphates for gold catalyzed cyclizaion. This strategy was very useful to synthesize a new class of cyclic phosphates. Propargyl derived alkynyl hydrogen phosphate **29b** and **29e** undergo 6-*end- dig* cyclization to give 6 membered cyclic phosphates **31b** and **31c** in very good yields. 6-*endo-dig* is more favourable than 5-*exo-dig* cyclization. Homopropargyl derived alkynyl hydrogen phosphate **29d** (Table 2.7) undergo 6-*exo dig* cyclisation to obtain 6-membered cyclic phosphate **31d** with exomethelene double bond (Table 2.9). This methodology is also useful in preparing 7-membered cyclic phosphates. When **29h** (Table 2.7) was subjected for cyclisation, the reaction proceeded smoothly *via* 7-*exo-dig* ring closure to afford **31h** in 82% yield (Table 2.9).

Table 2.9 Au(I)-catalyzed Cyclic Vinylphosphates^a

31b, 4 h (78%)	31c, 4 h (86%)	31d, 0.5 h (90%)	31e, 4 h (85%)

31f, 4 h (85%)	31g, 12 h (0%)	31h, 8 h (82%)	31i, 8 h (78%)

31j, 0.5 h (82%) (1:1.7) ^a			

^a diastereomeric ratio

It would be possible to further functionalizing the cyclic phosphate by placing an iodo group at the vinylic position to C-C bond forming reaction. The cyclization of **29g** and **29i** (Table 2.7) was regio- and stereoselective and afforded the corresponding cyclic phosphates **31f** and **31i** in 85% and 78% yield, respectively (Table 2.9). For the cyclization of **29f** (Table 2.7), two compounds **29e** were isolated in 1:1.2 ratio of the *E-Z* isomers. These structures were confirmed by NOESY NMR analysis.

The cyclization didn't occur to the secondary alkynyl hydrogen phosphate **29c** (Table 2.7), even at reflux in dichloromethane for 12 h. The reason why the cyclization did not proceed is not clear and may be due to the steric hindrance between adjacent CH₃ group and gold complex. The bulkiness may have hindered the gold complex from approaching the alkynyl group in a close enough proximity to coordinate to the alkynyl group and to activate it, thus vinyl gold could not be formed.

Figure 2.2 Steric hindrance between gold and CH₃ group

29j (Table 2.6) undergone cyclization reaction, and two isomers of **31j** were isolated in 80% total yield (Table 2.9, 1.7:1 diastereomeric ratio).

Mechanism of this cyclisation may involve intramolecular attack of P-OH to the gold activated alkyne to form vinyl gold complex, which would under protodeauration to give the desired cyclic phosphate (Scheme 2.14).

Scheme 2.14 Plausible mechanism for gold-catalyzed 6-*endo-dig* cyclization

2.3.4 Application of Cyclic Phosphates in Cross-coupling Reactions

We successfully utilized vinyl phosphates as a coupling partners in cross coupling reactions in the initial part of this chapter. We briefly studied the use of this cyclic phosphate for C-C bond formation.

Scheme 2.6 Cross coupling reactions of **31f**

When **31f** subjected to Stille coupling condition, the reaction proceeded at room temperature with 5 mol % of $\text{Cl}_2\text{Pd(PPh}_3)_2$ in DMF and afforded the Stille coupled product **33** in 84% yield. When the same substrate applied for the Sonogashira condition, gave the coupled product **27** was isolated in 78% yield. Cyclic vinyl phosphates **31d** and **31h** did not react under the Sonogashira and the Stille reactions conditions (Table 2.9).

When cyclic vinyl phosphates **31d** and **31h** were treated with PhMgBr and 2 mol % PdCl_2 , we were curious whether the cleavage would occur at vinylic C-O or at $\text{sp}^3\text{C-O}$ bond. After reduction with lithium aluminium hydride gave the **36a** in 77% yield. Similarly, seven-membered cyclic phosphates also worked well gave the **36b** in 85% yield.

Scheme 2.7 Kumada-Corriu coupling of cyclic vinyl phosphate

2.4 Conclusion

We have developed a gold(I)-catalytic system for inter- and intramolecular addition of phosphoric acid to alkynes and haloalkynes. Intermolecular hydrophosphoryloxylation of alkynes provided the kinetically controlled Markovnikov addition products in excellent yields. Application of this methodology on haloalkynes provided *Z*-halo vinyl phosphates in a regio- and stereo-selective manner and consecutive Pd-catalyzed cross-coupling reaction of *Z*-iodo vinyl phosphates gave stereodefined trisubstituted olefins. In addition, cyclization of alkynyl hydrogen phosphate in an *endo*- or *exo-dig* ring closure provided a variety of cyclic vinyl phosphates under very mild conditions.

Chapter III. Gold(I)-Catalyzed Addition of Brønsted Acids to Alkynes

3.1 Introduction

Despite the apparent simplicity of addition reactions to alkynes, it is still an important goal to control the regioselectivity of such processes. In chapter II we demonstrated that inter- and intramolecular additions of phosphoric acids to alkynes could be successfully achieved by using gold(I) catalyst. Subsequently, we wanted to expand this strategy to other Brønsted acids like carboxylic acids and sulfonic acids. The resulting enol-esters are valuable intermediates in organic synthesis for carbon-carbon and carbon-heteroatom bond formation. They have been used for the selective generation of enolates⁴⁶, acylating agents⁴⁷ under mild conditions. They are also suitable substrates for the access to α -haloketones⁴⁸, and enzyme-catalyzed kinetic resolution of chiral alcohols.⁴⁹ Alkenyl esters have been involved in cyclopropanation,⁵⁰ Diels-Alder reactions,⁵¹ [2+2] cycloaddition,⁵² and 1,3-dipolar cycloaddition.⁵³ Vinyl acetate, acetoxy styrenes, and vinyl haloacetates are important industrial monomers for the preparation of various polymers and copolymers.⁵⁴ We have been interested in finding out if there are similarities in the mode of action as in the addition of diphenyl phosphate to alkynes and to distinguish any differences in the stereo and regioselectivity of the formed products.

Transition metal-catalyzed addition of carboxylic acids to terminal alkynes is an efficient, atom economic method for the synthesis of 1-alkenyl esters. The electrophilic activation of terminal alkynes by suitable metal catalysts with carboxylic acids provide an easy access of three possible 1-alkenyl esters (one Markovnikov-type adduct **37** and two anti-Markovnikov-type *E* and *Z* adducts **38** and **39**). Therefore, it is interesting and crucial to develop catalyst systems that could induce high regioselectivity and stereoselectivity in the addition reactions. Even now in some reactions it is not possible to get the desired regioselectivity at all.

Scheme 3.1 Possible isomers from the metal mediated addition of carboxylic acid to alkynes

Preparation of enol esters can be achieved by quenching the corresponding aldehyde or ketone with a suitable acid anhydride or acid chloride.⁵⁵ The drawback of this method is poor selectivity. Another straight forward method involves the addition of acids to alkynes. Initially the addition of carboxylic acid to alkynes was carried out with mercury salts.⁵⁶ However the method is not viable due to the toxicity of mercury. Henceforth several groups extensively studied the addition of carboxylic acids to alkyne with ruthenium as the catalyst.

Scheme 3.2 Ru-catalyzed addition of acid to alkynes

In 1983, Shvo and his co-workers reported $\text{Ru}_3(\text{CO})_{12}$ catalyzed addition of acetic acid to symmetrical alkynes to afford vinyl esters **40** as a major product along with some rearranged product **41**.⁵⁷ Following this work Mitsudo-Watanabe described the selective addition of carboxylic acid in the presence of ruthenium complex, triphenyl phosphine and maleic anhydride to give the Markovnikov addition product as the major.⁵⁸

Scheme 3.3 Ruthenium and ligand based selective preparation of Markovnikov and *anti*-Markovnikov products

Later Dixineuf further developed an active catalyst for the regio- and stereo-selective *anti*-Markovnikov addition of carboxylic acids to terminal alkynes. It was clearly demonstrated that nature of the chelating phosphine ligand on the ruthenium centre control the regio-selectivity of the addition reaction.⁵⁹ Afterwards, Gossen developed efficient catalytic systems for the both Markovnikov and *anti*-Markovnikov addition of carboxylic acids to alkynes with readily available ruthenium complexes.⁶⁰

Addition of carboxylic acids to the terminal alkynes giving enolesters is extensively studied by Ru complexes while is also explored with rhenium,⁶¹ iridium⁶² and rhodium complexes.⁶³ We wanted to study hydroacyloxylation in the presence of gold(I)-catalysts in line with our recent interest in the functionalization of alkynes. The aim of our study is to develop a simple, efficient way to catalyze the addition of carboxylic acids to alkynes with high selectivity. Hubert reported intermolecular addition of acetic acid to 3-hexyne in THF at 60 °C using (triphenylphosphine)gold(I) pentafluoropropionate and boron trifluoride etherate as a cocatalyst which afforded 3-hexene-3-acetate **42** in a very low yield of 6.2% along with 3-hexanone **43** in 12.3% yield.⁶⁴ We sought to improve this

unsatisfactory result and to determine the scope and limitation of hydroacyloxylation, by investigating the addition of carboxylic acids to alkynes using gold(I) complexes.

Scheme 3.4 First report used gold(I) for the addition of AcOH to 1-hexyne

3.2 Gold Catalyzed Addition of Carboxylic Acids to Alkynes

3.2.1 Results and Discussion

We initially applied the standard catalyst PPh_3AuCl system using 1-hexyne and benzoic acid in toluene as the solvent. The addition of the acid to alkyne did not proceed with gold alone. However, reaction proceeded after the addition of a silver cocatalyst. The same was true for silver metal catalyst where the reaction did not proceed in the absence of a gold catalyst.

With the standard condition using 5 mol % PPh_3AuCl and 5 mol % AgPF_6 the reaction did not proceed at room temperature. Heating upto 60 °C afforded the kinetically controlled Markovnikov addition product **44** in excellent yields without any isomerisation of the double bond.

Scheme 3.5 Au(I)-catalyzed addition of benzoic acid to alkynes

Table 3.1 Optimization of reaction^a

entry	Cat.	Temp (°C)	44a (%)	45a (%)
1	PPh ₃ AuCl / AgOTf	rt	0	87
2	PPh ₃ AuCl / AgBF ₄	80	50	25
3	PPh ₃ AuCl / AgPF ₆	60	82	0
4 ^b	PPh ₃ AuCl / AgPF ₆	60	76	0
5	PPh ₃ AuCl / AgSbF ₆	110	0	0
6	PPh ₃ AuCl / AgNO ₃	110	0	0
7	PPh ₃ AuCl	110	0	0
8	AgPF ₆	110	0	0
9	TfOH	60	0	0
10	PhSO ₂ OH	60	0	0

^a reaction was carried out in to for 15 h using 5 mol % catalyst. ^b in the presence of 10 mol % of allyltrimethylsilane.

The spectral data of vinyl benzoate **44a** clearly shows the exo-methelene at δ 4.83 (s, 1H) and 4.82 ppm (s, 1H).

The efficiency of the coordinating anion AgPF₆ was studied with several cocatalysts such as AgOTf, AgBF₄, AgSbF₆ and AgNO₃ under the same conditions. While changing AgPF₆ to AgOTf, surprisingly instead of the Markovnikoc addition product, thermodynamically more stable enolester was observed in good yields (Table 3.1, entry 1, diastereomeric ratio 1:3.1). The spectral data clearly shows that alkenyl protons of more stable isomerised product **45a** appears at 5.23 ppm (t, $J = 7.8 \text{ Hz}$, 1H) and 5.09 ppm (t, $J = 7.3 \text{ Hz}$, 1H). But 5 mol % PP₃PAuCl/AgBF₄ catalytic system was less reactive

compared to 5 mol % PPh_3AuCl / AgPF_6 system and took 80 °C for 8 h resulting in 2:1 mixture of kinetically controlled Markovnikov product and thermodynamically stable isomerised product was observed in good yields (Table 3.1, entry 2). However, the reaction did not occur in the case of AgSbF_6 and AgNO_3 under reflux conditions (Table 3.1, entry 5, 6). The reaction was also carried out in the presence of protic acids like triflic acid and benzenesulfonic acid at 60 °C for 15 h but the formation of the desired product was not observed (Table 3.1, entry 9, 10).

Scheme 3.6 Gold(I) mediated isomerisation

The complete inverse of regioselectivity observed with the AgOTf cocatalyst may be attributed to the isomerisation of the initially formed Markovnikov addition product **44** to the more stable enol benzoate **45**. To check whether protic acid participates in the isomerization, the Markovnikov addition product **44a** subjected to the standard condition in the presence of 10 mol % of allyltrimethylsilane. Enol benzoate **45a** was afforded in 3 h, indicative of the sole participation of PPh_3AuOTf .

Scheme 3.1 Proposed mechanism for gold(I)-catalyzed isomerization

The effect of solvent was briefly studied using $\text{Ph}_3\text{PAuCl}/\text{AgPF}_6$ catalyst. The examination of solvent effects revealed that toluene is the solvent choice in this reaction. When the reaction was carried out with dichloromethane, acetonitrile, ethanol, and trifluoroethanol using $\text{Ph}_3\text{PAuCl}/\text{AgPF}_6$ catalyst at 60 °C for 15 h, the reaction did not proceed even at reflux to give any desired products. Traces of the product were observed, when 1, 2-dichloroethane was used as a solvent (Table 3.2, entry 2). The effectiveness of toluene could be due to stabilization of the cationic complex by the formation of arene-gold complex.⁶⁵

Table 3.2 Effect of solvent^a

$\text{C}_4\text{H}_9\text{C}\equiv\text{CH}$ (16c) + PhCO_2H
 $\xrightarrow[\text{solvent (0.25M), temp, 15 h}]{\begin{smallmatrix} 5 \text{ mol \% } \text{PPh}_3\text{AuCl} \\ 5 \text{ mol \% } \text{AgPF}_6 \end{smallmatrix}}$
 $\text{Ph-C(=O)-O-C(=CH-C}_4\text{H}_9\text{)-CH=CH}_2$ (44a)

entry	solvent	temp (°C)	Yield (%)
1	CH_2Cl_2	110	No reaction
2	1,2-DCE	110	<5
3	CH_3CN	110	No reaction
4	toluene	60	82
5	EtOH	110	No reaction
6	$\text{CF}_3\text{CH}_2\text{OH}$	110	No reaction

^a reaction was carried out with 1 equiv of alkyne, 1.2 equiv of acid and 1 ml solvent.

In order to determine the scope and limitations of the method, structurally different alkynes and carboxylic acids using a standard condition of 5 mol% $\text{Ph}_3\text{PAuCl}/\text{AgPF}_6$ catalyst at 60 °C was employed and the experimental results are summarised in table 3.3.

Both aliphatic and aromatic alkynes were used as substrates to be reacted with the different kinds of aromatic and aliphatic acids. Various vinyl carboxylates were obtained in good to excellent yields. It was observed that the addition of acid to phenylacetylene led to a significant amount of *anti*-Markovnikov product **44m** and **44n** (Table 3.3).

Table 3.3 Gold(I)-catalyzed Markovnikov addition^a

$\text{R}^1\text{—}\equiv\text{C} + \text{R}^2\text{CO}_2\text{H} \xrightarrow[\text{toluene, 60 }^\circ\text{C, 15 h}]{\begin{matrix} 5 \text{ mol } \% \text{ PPh}_3\text{AuCl} \\ 5 \text{ mol } \% \text{ AgPF}_6 \end{matrix}} \text{R}^2\text{C(=O)OC(R}^1\text{)=C(R}^2\text{)}$			
$\text{n-C}_8\text{H}_{17}\text{C(=CH}_2\text{)OCOPh}$ <p>44b, 90%</p>	$\text{n-C}_8\text{H}_{17}\text{C(=CH}_2\text{)OAc}$ <p>44c, 82%</p>	$\text{n-C}_8\text{H}_{17}\text{C(=CH}_2\text{)OCHO}$ <p>44d, 80% (3 h)</p>	$\text{n-C}_8\text{H}_{17}\text{C(=CH}_2\text{)OCOC}_6\text{H}_4\text{-NO}_2\text{-4}$ <p>44e, 65% (12 h)</p>
$\text{n-C}_4\text{H}_9\text{C(=CH}_2\text{)OCOC}_6\text{H}_4\text{-F-3}$ <p>44f, 75% (15 h)</p>	$\text{n-C}_4\text{H}_9\text{C(=CH}_2\text{)OCOC}_6\text{H}_4\text{-OMe-4}$ <p>44g, 63% (24 h)</p>	$\text{n-C}_4\text{H}_9\text{C(=CH}_2\text{)OCOCF}_3$ <p>44h, 82% (6 h)^b</p>	$\text{PhCH}_2\text{CH}_2\text{C(=CH}_2\text{)OAc}$ <p>44i, 75%</p>
$\text{PhCH}_2\text{CH}_2\text{C(=CH}_2\text{)OCOPh}$ <p>44j, 77%</p>	$\text{n-C}_6\text{H}_{13}\text{C(=CH}_2\text{)OCOC(=CHPh)CH=CHPh}$ <p>44k, 78%</p>	$\text{n-C}_6\text{H}_{13}\text{C(=CH}_2\text{)OCOC(=CHPh)CH=CH_2}$ <p>44l, 88%</p>	$\text{PhC(=CH}_2\text{)OCOPh}$ <p>44m, 86% (4.9:1)^c</p>
$\text{PhC(=CH}_2\text{)OCOCH}_2\text{Ph}$ <p>44n, 72% (2.5:1)^c</p>	$\text{EtO}_2\text{CCH=CHOCOPh}$ <p>44o, 80%</p>	$\text{EtO}_2\text{CCH=CH(Ph)OAc}$ <p>44p, 78%</p>	PhCH=CH(Ph)OCOPh <p>44q, 62% (20 h)^d</p>
$\text{H}_3\text{CCH=CH(Ph)OCOPh}$ <p>44r, 72% (20 h)</p>	EtCH=CH(Et)OCOPh <p>44s, 65% (18 h)</p>		

^a reaction carried out with 1.2 equiv alkyne, 1 equiv of carboxylic acid. ^b reaction proceed at room temperature. ^c ratio of Markovnikov and anti-Markovnikov products. ^d need 110 °C and 20% starting material was recovered.

It was observed that the acidity had a pronounced effect on the reactivity of the acids. Acids with lower pK_a reacted at lower temperature. When trifluoroacetic acid was treated with terminal alkyne, the reaction proceeded at room temperature (Table 3.3 entry **44h**) in 6 h. Even under strongly acidic conditions, vinyl trifluoroacetates did not undergo further rearrangement to stable isomers. In the case of **44d**, the reaction was complete within 3 h. Furthermore, when benzoic acid is replaced with 4-methoxybenzoic acid (Table 3.3, entry **44g**), the reaction was incomplete after 24 h. It clearly shows that the reaction rate would depend very much on the acidity of carboxylic acids. Addition of α,β -unsaturated carboxylic acids to alkynes affords the Markovnikov addition product **44k**, **44l** in good yields (Table 3.3). As shown in the table, acrylic acid and *trans*-cinnamic acid underwent

the Markovnikov addition products **44k** and **44l** in high yields of 78% and 88% respectively (Table 3.3).

Besides terminal alkynes, internal alkynes were also included in this experimental study. Internal alkynes such as phenyl ethyl propiolate, symmetrical diphenylacetylene were also reacted successfully with acetic acid yielding products **44p**, **44q** in reasonably good yields (Table 3.3). Addition of acetic acid to diphenylacetylene required higher temperature of 110 °C and longer reaction time to yield the product in 62% yield together with recovery of the starting material (20%). This is due to the steric hindrance of symmetrical alkyne which makes nucleophilic addition harder. Hydroacyloxylation occurred regioselectively

Table 3.4 Gold(I)-catalyzed isomerisation of alkynes

and stereoselectively *via* conjugative *trans*-addition in case of conjugated alkyne esters **44o** and **44p** (Table 3.3). As for AgOTf as the cocatalyst instead of AgPF₆ with gold(1) catalyst, 1-hexyne was reacted with benzoic acid and phenylacetic acid at room temperature for 15 h to give the rearranged thermodynamically stable enol benzoate product **45a**, **45c** in 87% and 86%, respectively. 4-Phenyl 1-butyne was reacted with acetic acid at room temperature for 15 h to give **45d** in 82% yield. Treatment with acrylic acid at room temperature for 15 h produced the corresponding product **45b** in 68% yield.

When AgOTf is used as the cocatalyst, for all the above reactions, the kinetically favoured Markonikov product was first formed and then it isomerized to give final thermodynamically stable rearranged enol benzoate.

We briefly investigated the reaction by using NMR studies. 1-Hexyne was treated with benzoic acid in the presence of 5 mol% PPh_3AuCl and 5 mol % of AgOTf catalytic system in deuterated toluene. Although the reaction was incomplete after 2 h, The Markovnikov addition product was not observed. No reaction was occurred even in 6 h when we used deuteriochloroform as the solvent. When the reaction was carried out by using Markovnikov addition product, the isomerisation proceeded very rapidly at ambient temperature. The Markovnikov product (<10%) was observed after 3 h, this clearly shows that isomerization occurs very rapidly.

Interestingly when acetic acid was added to propargyl benzoate under the similar conditions, a mixture of two products was obtained in equal ratio (1:1). During the reaction, the allene benzoate was observed by NMR but the propargyl benzoate was not completely converted to allene benzoate. Spectral data clearly shows that one is the Markonikov addition product **46** and another one is *cis*-isomer of coupled product **47** (structure was determined by NOESY NMR analysis).

Scheme 3.7 Addition of AcOH to propargyl benzoate

We also studied the addition of carboxylic acids to electron rich substrates like alkynyl sulfides. Previously Braga reported the regioselective addition of TsOH and TFA to alkynyl sulphide to obtain (*Z*) vinyl tosylates or (*Z*) vinyl trifluoroacetates in good yields.⁶⁶

Table 3.5 Gold (I)-catalyzed addition of acid to alkynyl sulfide

Treatment of phenyl thioalkyne with carboxylic acids in the presence of 5 mol% $\text{Ph}_3\text{PAuCl}/\text{AgPF}_6$ in toluene at 60 °C for 15 h afforded ketene thioacetal **48** in moderate yields. Addition of carboxylic acid to phenylthioalkynes **17** was also regio- and stereo-selective but it occurred via *syn* addition. It is assumed that the reaction propagates through the formation of the allene intermediate **50** before the nucleophilic carboxylate attack from the less hindered side ensue the product (*Z*) thiovinyl acetate **48b**.

Scheme 3.8 Plausible mechanism of addition of acetic acid to alkynyl sulfide

The addition of benzoic acid and acetic acid to the alkynyl sulphides in presence of gold catalyst yields single products **48a**, **48b** in reasonable yields. The addition of formic acid on the other hand, did not give any desired addition product but produced thioester **49** as a result of the hydrolysis of water on the alkynyl sulphide.

3.3 Gold-Catalyzed Addition of Sulfonic Acids to Alkynes

3.3.1 Introduction

Based on our successful gold(I)-catalyzed addition of diphenyl phosphates and carboxylic acids to alkynes, we attempted our catalytic system for the addition of sulfonic acids to alkynes. Most of the existing methods follow the sulfonylation of the ketone enolate with sulfonic anhydride by base.⁶⁷ Like vinyl phosphates, vinyl sulfonates are also used as an important building blocks in organic synthesis, as electrophiles for cross-coupling reactions.⁶⁸ Vinyl sulfonates are more stable to water than triflates. In literature it was found that Hirsch et al. demonstrated the addition of methanesulfonic acid to tert-butylacetylene catalyzed by HgO with one example.⁶⁹

3.3.2 Results and Discussion

Treatment of 1-decyne with benzenesulfonic acid in the presence of 5 mol % PPh_3AuCl and 5 mol % AgPF_6 in toluene at room temperature for 12 h afforded a roughly equimolar mixture of **51** and **52** in 78% yield. Apparently, the Markovnikov product **51** was isomerized to the thermodynamically more stable isomer **52** under the present condition.

Scheme 3.9 Gold(I)-catalyzed addition of benzenesulfonic acid to 1-decyne

To avoid the isomerization and to get exclusively the Markovnikov addition product under strong acidic conditions, we tried to perform the same reaction in the presence of a base such as triethylamine and Na_2CO_3 . When the reaction was repeated in the presence of 2 equiv triethylamine in toluene, the reaction did not occur to an observable extent, probably due to deactivation of the gold catalyst by triethylamine.

Table 3.6 Effect of base on the sulfonic acid addition^a

Entry	Base	Yield
1	Et_3N	< 5
2	Na_2CO_3	86
3	K_2CO_3	62

^a used 5 mol % PPh_3AuCl and 5 mol % AgPF_6 in toluene.

However, when the reaction was performed in the presence of 2 equiv Na_2CO_3 , the reaction proceeded cleanly at room temperature and was completed within 5 h, yielding the desired vinyl sulfonate **51** in 86% yield. Several noteworthy features are apparent. First, the reaction was cleaner and faster. Second, the isomerisation of the Markovnikov product to the thermodynamic isomer did not occur. The use of potassium carbonate was less effective and the desired product was obtained only in 62% yield. Unfortunately, during our studies we realized that the reaction appeared in *Chem. Commun.*, in which a catalytic amount of $\text{PPh}_3\text{AuNO}_3$ and phthalimide were employed in dichloroethane as solvent at 100 °C for 4 h.⁷⁰

Table 3.7 Preparation of Vinyl Sulfonates^a

51a, 82% (3 h)	51b, 76% (3 h)	51c, (67:3) ^a (3 h)	51d, (77:8) ^a (3 h)

51e, 80% (5 h)	51f, 55% (1 h)	51g, 90% (10 h)	51h, 85% (2 h) ^b

51i, (46:29) ^c (2 h) ^b	51j, (63:7) ^c (2 h) ^b		

^a ratio of Markovnikov and anti-Markovnikov products. ^b heated at 60 °C. ^c ratio of trans and cis isomers.

Compared to their condition, our condition is much milder and faster because the reaction occurs at room temperature with high regioselectivity. The addition of methanesulfonic acid to but-3-ynylbenzene under the standard condition afforded the Markonikov addition product **51b** in 76% yield and the reaction was completed at room temperature for 3 h.

We successfully added sulfonic acids to terminal aliphatic alkynes in presence of gold catalyst. Then we moved to aromatic terminal alkynes with methanesulfonic acid and benzenesulfonic acid. When the methanesulfonic acid was added to phenylacetylene in presence of 5 mol % PPh_3AuCl and 5 mole % AgPF_6 and 2 equiv of Na_2CO_3 at room temperature, the reaction was complete in 3 h and afforded the desired Markonikov product **51c** in 67% yield and anti-Markovnikov product in 3% yield. Treatment of phenylacetylene with benzenesulfonic acid gave the Markovnikov addition product **51d** in 77% and the *anti*-Markovnikov product in 8% yield. In addition, a small amount of acetophenone was observed due to hydrolysis of phenylacetylene under the present condition with methane sulfonic acid, the hydration product was observed in 15% yield.

For instance, methanesulfonic acid underwent a clean addition to ethyl propiolate and phenylpropiolate **51e** and **51g** to yield *cis*-vinyl mesylate in 80% and 90% yield, respectively. Furthermore, methanesulfonic acid underwent addition to propargy alcohol to give the corresponding vinyl sulfonate **51f** without influence of the hydroxyl group. In the cases of conjugated alkynes having electron-withdrawing groups, the addition was regio- and stereo-specific via *trans*-addition. Prop-1-ynylbenzene did not react with methanesulfonic acid in the presence of Na₂CO₃ but reacted very slowly at 60 °C without Na₂CO₃ to afford **51i** in 75% yield.

3.4 Conclusion

In summary, we developed gold(I)-catalyzed hydroacyloxylation and hydrosulfonyloxylation of carboxylic acids and sulfonic acids to alkynes to provide enol esters and vinyl sulfonates in high yields. The gold(I)- AgPF₆ catalyst system provides the Markonikov addition product in good yields while in presence of AgOTf cocatalyst, the Markovnikov addition product underwent isomerization to thermodynamically stable enol benzoate in good yields.

Chapter IV. Transition Metal-Catalyzed C-H Activation of Arenes

4.1 Introduction

Transition metal-catalyzed specific inert C-H bonds functionalization has emerged as a powerful tool in organic synthesis. The development of new C-C and C-heteroatom bond formation is a critical challenge in organic chemistry and, in this regard, C-H bond activation reaction represents one of the most promising approaches in recent years.⁷¹ Activation of arene C-H bonds has been demonstrated using several transition-metals like Pd, Rh and Ru. C-H bond activation processes brought a revolution in production of pharmaceuticals, materials and polymers and are already proven to be valuable in natural product synthesis. Several C-H bond strategies have been exploited in the total synthesis of natural products and Figure 4.1 highlights a list of selected natural products involving C-H activation strategies.⁷²

Figure 4.1 Total synthesis involving C-H activation

Table 4.1 Directing groups in C-H activation

<p>Shi, Z. <i>et al.</i> <i>J. Am. Chem. Soc.</i> 2007, 129, 7666.</p>	<p>Yu, J.-Q. <i>et al.</i> <i>J. Am. Chem. Soc.</i> 2009, 131, 7520.</p>	<p>Yu, J.-Q. <i>et al.</i> <i>J. Am. Chem. Soc.</i> 2010, 132, 12203.</p>	<p>Ge, H. <i>et al.</i> <i>Chem. Eur. J.</i> 2011, 17, 14371.</p>	<p>Yu, J.-Q. <i>et al.</i> <i>Science</i> 2010, 327, 315. <i>J. Am. Chem. Soc.</i> 2010, 132, 14137.</p>
<p>Yu, J.-Q. <i>et al.</i> <i>J. Am. Chem. Soc.</i> 2011, 133, 7222.</p>	<p>Glorius, F. <i>et al.</i> 2011 <i>Angew. Chem. Int. Ed.</i> 2011, 50, 1064.</p>	<p>Chang, S. <i>et al.</i> 2011 <i>Org. Lett.</i> 2011, 13, 2372.</p>	<p>Shi, Z. <i>et al.</i> <i>J. Am. Chem. Soc.</i> 2006, 128, 7416.</p>	<p>Booker-Milburn, K. I. <i>et al.</i> <i>Angew. Chem. Int. Ed.</i> 2009, 48, 1830. <i>J. Am. Chem. Soc.</i> 2008, 130, 10065.</p>
<p>Yu, W.-Y. <i>et al.</i> <i>J. Am. Chem. Soc.</i> 2012, 134, 13565.</p>	<p>Gaunt, M. J. <i>et al.</i> <i>Angew. Chem. Int. Ed.</i> 2011, 50, 1076.</p>	<p>Wang, G.-W. <i>et al.</i> <i>Angew. Chem. Int. Ed.</i> 2011, 123, 1416.</p>	<p>Huang, Y. <i>et al.</i> <i>Angew. Chem. Int. Ed.</i> 2012, 124, 7354.</p>	<p>Sanford, M. S. <i>et al.</i> <i>J. Am. Chem. Soc.</i> 2006, 128, 14047. <i>Org. Lett.</i> 2006, 8, 2523.</p>
<p>Dixneuf, P. H. <i>et al.</i> <i>Green Chem.</i> 2013, 15, 67. <i>Angew. Chem. Int. Ed.</i> 2010, 49, 6629.</p>	<p>Loh, T. P. <i>et al.</i> <i>Chem. Commun.</i> 2011, 47, 10458.</p>	<p>Liu, L. <i>et al.</i> <i>J. Am. Chem. Soc.</i> 2010, 132, 468.</p>	<p>Gevorgyan, V. <i>et al.</i> <i>J. Am. Chem. Soc.</i> 2011, 133, 12406. Gevorgyan, V. <i>et al.</i> <i>J. Am. Chem. Soc.</i> 2011, 133, 17630.</p>	<p>P. H. Lee. <i>et al.</i> 2013 <i>Org. Lett.</i> 2013, 15, 3986. Glorius, F. <i>et al.</i> 2013 <i>Org. Lett.</i> 2013, 15, 4504.</p>
<p>C. Bolm. <i>et al.</i> <i>Angew. Chem.</i> 2013, 125, 11787.</p>				

Generally, the directing group strategy has been instrumental in enabling array of metal catalyzed C-H activation reactions during the past several decades. Directing groups usually can be a hetero atom. Directing element coordinates to the metal and brings the metal centre into close proximity of specific C-H bond to form cyclometallated intermediates. As shown in table 4.1, a variety of directing groups have been developed. To develop synthetically useful the C-H bond activation reactions, the desired C-H bond in an organic molecule must be selectively activated over all the C-H bonds present in the molecule. Especially in benzene derivatives, because there is a slight difference in the reactivity between the C-H bonds, a system to control regioselectivity is highly necessary. To overcome uncontrolled site selectivity, a number of examples of C-C and C-heteroatom bond forming reaction have been reported through introduction of a directing group in recent years. Although the use of the directing group has become the practical strategy for allowing selective functionalization, this approach, in most cases, leads to increase reactivity of *ortho* C-H bond on the arene to the directing group.

In this chapter, we mainly focused on palladium and rhodium-catalyzed C-H arylation and C-H alkenylation.

4.2 Pd and Rh-Catalyzed C-H Arylation of Arenes

Biaryl scaffolds are an important structural motif in natural products, pharmaceuticals and materials.⁷³ Biaryl motifs can be prepared by using classical cross coupling reactions as well as C-H activation processes. For the green and sustainable, transition metal-catalyzed C-H activation of arenes is the best alternative over the traditional cross coupling reactions.

Scheme 4.1 Arylation of C-H bonds

Chealation assisted C-H arylation of unactivated arenes is regio- and stereo-selective. The directing group is essential for C-H functionalization of unactivated arenes to achieve selectivity and broad substrate scope.

Reductive functionalization pathway: Pd(II)/Pd(0) catalytic cycle

Oxidative functionalization pathway: Pd(II)/Pd(IV) catalytic cycle

Scheme 4.2 Mechanistic manifolds of Pd-catalyzed C-H functionalization

Mechanistic aspects of palladium catalyzed C-H activation can be explained two pathways. First one is reductive functionalization pathway, in which follows Pd(II)/Pd(0)

catalytic cycle. Functionalization will occur via reductive elimination or β -hydride elimination. The second is oxidative functionalization pathway. Functionalization proceeds with electrophilic reagent. The electrophile can be cleaved *via* distinct mechanisms which include one-electron oxidation of palladacycle (Pd(II)/Pd(I)), two-electro oxidation of palladacycle (Pd(II)/Pd(III) or Pd(IV)) or without disturbing the oxidation state of metal centre (Scheme 4.2).

In 1992, Dyker reported Pd(II)-catalyzed C-H arylation using 2-Iodoanisole. In 1997, Miura reported regioselective arylation of 2-phenyl phenols and naphthols using Pd(II) catalyst. The treatment of 2-phenyl phenol with aryl iodide in the presence of Pd(OAc)₂, 1 equiv of Cs₂CO₃ at 100 °C in DMF furnished the arylated product (Scheme 4.3).⁷⁴

Scheme 4.3 Pd(II)-catalyzed C-H arylation

In 2005, Sanford utilized hypervalent iodonium sources like aryliodonium tetrafluoroborate and aryl iodonium triflate. Iodonium salts play a dual role as both aryl sources and oxidants. The reactions proceeded faster and high yields were obtained under mild reaction conditions. The reaction mechanism follows Pd(II)/Pd(IV) catalytic pathway (Scheme 4.4).⁷⁵

Scheme 4.4 Arylation with hypervalent phenyl iodonium sources

Daugulis reported Pd-catalyzed C-H arylation using readily available carboxylic acids as substrates. Carboxylate directed *ortho*-arylation of arenes was accomplished using aryl halides. After that, Yu group demonstrated C-H arylation of benzoic acid using aryltrifluoroborates and organoboron reagents. Furthermore, it was noteworthy that the same group reported for the first time arylation of sp³ C-H bonds in aliphatic carboxylic acids. When the reaction was carried out aliphatic acids with 2 equiv of aryl iodide in presence of 10 mol % Pd(OAc)₂, 2 equiv of Ag₂CO₃, 1 equiv K₂HPO₄, 2 equiv NaOAc in *t*-Butanol at 130 °C afforded a mixture of monoarylated and diarylated products in good yields. Low yields were obtained using organoboron reagent instead of aryl iodide (Scheme 4.5).⁷⁶

Scheme 4.5 Pd-catalyzed C-H arylation of sp² and sp³ C-H bonds

Shi and coworkers described acetanilide assisted Pd-catalyzed C-H arylation using (trialkoxyl)phenylsilane as coupling partner. Treatment of acetanilide with trimethoxy phenylsilane in the presence of 5 mol % Pd(OAc)₂, 2 equiv Cu(OTf)₂ and 2 equiv of AgF in 1,4-dioxane under reflux condition furnished mono arylation product in excellent

yields (Scheme 4.6). C-H arylation of acetanilide can also be accomplished using aryl boronic acids as arylating agent.⁷⁷

Scheme 4.6 *Ortho* arylation of acetanilide C-H bonds

Recently, Dong and coworkers reported C-H arylation of phenylcarbamates with benzene and 1,2- substituted benzenes. Reaction was carried out with 10 mol % Pd(OAc)_2 and sodium persulfate oxidant in excess TFA at 70 °C and afforded the corresponding C-H arylated products (Scheme 4.7).⁷⁸

Scheme 4.7 Oxidative arylation of phenylcarbamates

In 2008, Booker-Milburn introduced an urea directing group, which is a more active coupling partner in C-H functionalization than other anilides. Lipshutz also utilized this directing group for Pd(II)-catalyzed C-H arylation reaction. Biaryl derivatives were obtained at room temperature using water as solvent (Scheme 4.8).⁷⁹

Scheme 4.8 C-H arylation of urea in water

More recently, Glorius reported Rh(III)-catalyzed dehydrogenative cross-coupling between benzamides with halogen-substituted benzene derivatives. The treatment of

benzamides with aryl halides using 2.5 mol % $(\text{RhCp}^*\text{Cl}_2)_2$, 10 mol % AgSbF_6 , 2.2 mol % $\text{Cu}(\text{OAc})_2$ oxidant and additives like PivOH , CsOPiv furnished biarylated product in excellent yields. Harsh reaction conditions are required to achieve two fold C-H activation (Scheme 4.9).⁸⁰

Scheme 4.9 Rh-catalyzed aryl-aryl bond formation

4.2 Pd and Rh-Catalyzed C-H Alkenylation of Arenes

Transition metal catalyzed oxidative Mizoroki-Heck reaction is straight forward reaction in organic chemistry. Pioneering work from Murai showed *ortho*-directing group assisted C-H olefination using Ru catalyst.⁸¹ After that a milestone work from Fujiwara⁸², a lot of efforts have been made in the arylation of alkenes using Pd, Rh, and Ru.

In 2002, Leeuwen demonstrated C-H olefination of acetanilide under mild reaction conditions. The reaction proceeded at room temperature and afforded the desired olefinated products in good yields (Scheme 4.10).⁸³

Scheme 4.10 Pd-catalyzed oxidative coupling of anilides with olefins

Recently, Yu group reported carboxylate directed Pd(II)-catalyzed C-H olefination of substituted phenylacetic acid. Treatment of phenylacetic acid with ethylacrylate using 5 mol % $\text{Pd}(\text{OAc})_2$, 1 atm O_2 as terminal oxidant afforded the corresponding alkenylation

product in excellent yields. Benzoquinone used as a ligand for the selective alkenylation. Selectivity is tuned by introducing amino acid derivatives as ligands. This methodology also applied to commercially available drugs NSAIDs (ibuprofen, naproxen, ketoprofen and flubiprofen). Furthermore, C-H alkenylation of benzenesulfonamide using sulfonamide as a directing group explained by the same group (Scheme 4.11).⁸⁴

Scheme 4.11 C-H Olefination of phenylacetic acid and benzenesulfonamides

The same research group extended to sp^3 C-H bonds. Amide directed Pd(II)-catalyzed C-H olefination of β -C-H bond and subsequent 1,4-conjugate addition gave the corresponding lactum compounds (Scheme 4.12).⁸⁵

Scheme 4.12 Amide directed olefination of sp^3 C-H bond

More recently, Gevorgyan reported that Pd(II)-catalyzed *o*-alkenylation using silanol as a temporary directing group. It is noteworthy that the directing group can be easily removed after C-H olefination reaction (Scheme 4.13).⁸⁶

Scheme 4.13 Silanol directed Pd-catalyzed C-H olefination

On the other hand, Rh is also known to be suitable in C-H activation reactions. Rhodium was less explored compared to palladium. Specifically rhodium will allow low catalyst loading, high selectivity and broad olefin scope. In 2000, Matsumoto and Yoshida described rhodium-catalyzed oxidative coupling of benzene with ethylene.⁸⁷ Last four years, many groups extensively investigated rhodium-catalyzed C-H activation of arenes with alkenes and alkynes.

Glorius reported Rh(III)-catalyzed C-H olefination using directing groups like acetanilide⁸⁸, acetophenone⁸⁹ and benzamides.⁹⁰ He also demonstrated C-H alkenylation with modified directing group having internal oxidant. In the presence of internal oxidants within the molecule, the C-H olefination occurred regio- and mono-selectively under mild reaction conditions. *N*-Methoxy benzamides underwent clean monoolefination with a variety of styrene derivatives using 1 mol % of $(\text{RhCp}^*\text{Cl}_2)_2$, 30 mol % CsOAc in methanol at 60 °C to afford olefinated benzamides in excellent yields (Scheme 4.14).

Scheme 4.14 Rh(III)-catalyzed C-H olefination using various directing groups

In 2011, Chang developed rhodium-catalyzed olefination using ester as directing group. Thus, treatment of arene esters with acrylates using 2.5 mol % $(\text{RhCp}^*\text{Cl}_2)_2$, 10 mol % AgSbF_6 and 20 mol % $\text{Cu}(\text{OAc})_2$ in dichloroethane under aerobic condition affords selective olefinated products in good yields (Scheme 4.15).⁹¹

Scheme 4.15 Ester group directed Rh(III)-catalyzed *ortho*-olefination

Very recently, Huang and coworkers reported triazene as removable directing group for Rh(III)-catalyzed C-H olefination reaction. Triazene substituted arenes undergo oxidative coupling with various olefins using 1 mol % $(\text{RhCp}^*\text{Cl}_2)_2$, 2 equiv of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ and 30 mol % AgOAc in methanol at 90 °C furnished the corresponding olefinated products in excellent yields (Scheme 4.16).⁹²

Scheme 4.16 Triazene directed Rh(III)-catalyzed C-H olefination

Among a wide range of directing groups in C-H activation, ketones⁹³, carbamates⁹⁴, and carboxylic esters⁹⁵ are less commonly used due to their weak coordinating properties toward metals and may be more challenging directing groups for further development. Furthermore, many directing groups are restricted within pyridines⁹⁶, carboxylic acids⁹⁷, or their derivatives⁹⁸, thus development of new practical directing groups is still a significant issue in the field of straightforward reactions.

Proposed Work

The work of this thesis is directed towards introduction of new phosphoryl directing group in the field of C-H activation. Transition metal-catalyzed C-H bond activation and functionalization is atom economic and emerged as powerful tool in organic synthesis. Organophosphorous compounds are very important in numerous biological functions. Organophosphorous derivatives are already proved in organic chemistry as cross coupling partners. Since there is a remarkable similarity in reactivity and bioactivity between the carbon species and their phosphorus counterparts⁹⁹, we imagined that functionalization of organophosphorous compounds *via* C-H bond activation would be advantageous over previously reported methods.

The aim of this project is to develop phosphoryl-derived directing groups for selective functionalization. This directing group can be utilized for the functionalization of arenes using C-H activation strategy. We choose aryl phosphoramidates and aryl phosphonates, which are synthetically more useful building blocks in organic chemistry. We envisioned that C-H activation of these organophosphorous derivatives using appropriate transition metal could lead to selective C-H functionalizations and have explored these substrates for Pd and Rh- catalyzed C-H arylations and C-H alkenylations strategies.

Scheme 4.10 P=O directed metal-catalyzed C-H functionalization of arenes

Chapter V. Pd-Catalyzed C-H Arylation of Phosphoramidates

5.1 Introduction

Organophosphorus compounds continue to receive widespread attention due to their ubiquity in biological systems.¹⁰⁰ Organophosphonates are essential for human, animal and plant life. They are main building blocks in DNA, RNA, skeletal structure and cell membranes. Organophosphorous compounds are not only used in agrochemicals as insecticides, herbicides and also have potential to serve as novel drugs in pharmaceutical industry.¹⁰¹ Moreover phosphorous compounds also play a significant role in the field of organic synthesis.¹⁰²

Organophosphorous compounds have attracted considerable interest owing to their broad applications in medicinal chemistry¹⁰³ and materials.¹⁰⁴ Particularly, in the field of organic synthesis, organophosphorous derivatives are used as ligands in organic catalysis¹⁰⁵ and organometallic catalysis.¹⁰⁶ Many chiral based phosphorous catalysts developed for enantioselective transformations include phosphinic acid derivatives (Fig. 5.1).

Figure 5.1 Binol derived monophosphinic acid catalysts for enantioselective transformations

In addition, organophosphorous compounds are also used for the preparation of olefins by the Horner-Wadsworth-Emmons reaction.¹⁰⁷ This approach is very useful for the selective

preparation of *trans* olefins. The reaction was carried out with the phosphonate stabilized carbanion attack on the corresponding aldehydes or ketones under basic conditions.

Scheme 5.1 Preparation of alkenes from Wittig-Horner reaction

Furthermore, tremendous efforts have been made for cleavage of the C-P bond as well as construction of the C-P bond. Organophosphates already proved several synthetic applications, especially as good electrophiles in the area of transition metal-catalyzed cross coupling reactions. K. Oshima reported palladium catalyzed oxidative Heck reaction using cleavage of aryl phosphinic acids C-P bond.¹⁰⁸

Scheme 5.2 Cross coupling reactions of organo phosphorous compounds

5.1.2 Whether an Organo Phosphorous Derivative Serves as Directing Group?

Scheme 5.3 *ortho* C-H activation of organophosphates

Organophosphorous compounds are useful in a variety of organic transformations. Now the question is whether phosphoryl oxygen (P=O) can be used as a directing group for the C-H activation process. Since the C-H activation is a hot topic in the field of current organic chemistry, we have been interested in using organophorous derivatives as directing groups for C-H activation processes. To extend the utility of organophosphates and also considering the interest in functionalization of arenes, we contemplated the possibility of P=O directed Pd insertion onto the C-H bond of arenes. Since *N*-aryl phosphoramidates are utilized as synthetic derivatives for many organic transformations, we chose the phosphoramidate as the model directing group for C-H arylation reactions. As far as we know *N*-aryl phosphoramidate have not been utilized for the C-H activation reactions.¹⁰⁹

In addition, *N*-aryl phosphoramidates are among the most prominent synthetic derivatives due to versatile functionalities for further transformations (Scheme 5.4).¹¹⁰ For example, *N*-aryl phosphoramidates could be used for the preparation of imines **52** by aza-Witting reaction.^{110e, g} Other applications include synthesis of heterocyclic compounds *via* stabilized anion of *N*-aryl phosphoramidates.^{110b} Recently it was reported that functionalized aziridines **53** were obtained by nucleophile-induced cyclization of readily available anion of *N*-aryl phosphoramidates.^{110b} *N*-Aryl phosphoramidates have also been used to afford 1,2-disubstituted azetidines and 1,2,4-trisubstituted azetidines **54** by means of reactions with Bayliss-Hillman adduct and aza-Michael adduct respectively.^{110c,f,h}

Furthermore, treatment of isatoic anhydride with *N*-aryl phosphoramidates yielded various **55** quinazolinedione derivatives.^{110g}

Scheme 5.4 Various Synthetic Transformations of *N*-Aryl Phosphoramidates

Strategy using *N*-aryl phosphoramidates as the directing group for C–H bond activation, therefore, represents a relevant example for efficient synthesis of functional molecules which can be transformed into useful building blocks as well.

5.1 Results and Discussion

N-Aryl phosphoramidates can be easily prepared by two different methods using the known procedure. First, treatment of aniline and diethyl phosphite with Idoform in presence of triethylamine in diethyl ether at room temperature afforded phosphoramidates in high yields.¹¹¹ Second, treatment of aniline with diethyl phosphorochloridate in presence of triethylamine as a base would also furnished the product in high yields.

Scheme 5.5 Preparation of Phosphoramidate and Diphenyl iodonium triflate

Most commonly used arylating agents could be aryl halides and benzene boronic acids for the C-H arylation reactions. Recent studies revealed that hypervalent iodine salts of aryliodonium triflates and aryl iodonium tetrafluoroborate proved very effective aryl source to achieve C-H arylation reaction under mild conditions.¹¹² Inspired from the report from Liu on palladium(II)-catalyzed arylation of phenol esters with diphenyl iodonium triflate at room temperature,¹¹³ we studied C-H arylation of *N*-aryl phosphoramidate using Ph₂IOTf as the arylating agent. Diphenyl iodonium triflate can also prepared by known procedure.¹¹⁴

O-Tolyl phosphoramidate was selected as a model substrate for initial investigation of Pd(II)-catalyzed arylation reaction using Ph₂IOTf. To begin with, the reaction was carried out at 60 °C using 1,4-dioxane as a solvent for 16 h (Table 5.1). When the reaction was performed in the absence of additives, the reaction did not give any observable amount of desired product (Table 5.1, entry 1). Unfortunately, arylation of **56a** did not progress under both basic and solely acidic condition at all and the starting material was remained quantitatively (Table 5.1, entry 2, 4). To elicit the reaction, we extensively tested various additives which were known to positively influence palladium-catalyzed C–H activation reactions. Several additives like Ag₂CO₃ and Cu(OAc)₂ were tested to be incompatible and AgO, Cu(OTf)₂ gave untidy reaction mixtures with the present reaction conditions (Table 5.1, entry 5, 8, 6 and 9). The use of additives like Na₂S₂O₈ was also unsuccessful

(Table 5.1, entry 7). Gratifyingly, we observed that arylation of *N*-aryl phosphoramidate proceeded in the presence of both catalytic amount of TfOH and 3 equiv of Cu₂O in 1,4 dioxane after heating at 60 °C for 16 h to yield the corresponding arylated product **57a** in 25% yield (Table 5.1, entry 10).

Table 5.1 Optimization of reaction conditions^a

Entry	Additive	Temp (°C)	Yield (%)
1	-	60	<1
2	NaOAc	60	<1
3	AcOH	60	<1
4	TfOH	60	No reaction
5	TfOH, Ag ₂ CO ₃	60	<1
6	TfOH, AgO	60	messy
7	TfOH, Na ₂ S ₂ O ₈	60	messy
8	TfOH, Cu(OAc) ₂	60	<1
9	TfOH, Cu(OTf) ₂	60	messy
10	TfOH, Cu ₂ O	60	25
11 ^b	TfOH, CuO	60	37
12	TfOH, CuO	100	71
13	TfOH, CuO	60	78
14 ^c	TfOH, CuO	25	84
15 ^d	TfOH, CuO	25	<1
16 ^e	TfOH, CuO	25	22

^a 5 mol % Pd(OAc)₂, 1.2 equiv of Ph₂IOTf, 20 mol % of NaOAc, AcOH and TfOH used and

3 equiv of oxidant in 1,4-dioxane for 16 h. ^b 20 mol % Pd(OAc)₂ used. ^c reaction carried out

for 3 h. ^d without Pd catalyst. ^e 20 mol % of CuO used and 69% *o*-tolyl phosphoramidate recovered.

Encouraged by the result, we tried the reaction with different copper salts to improve the C-H arylation turnover. CuO turned out to be best additive and accomplished C-H arylated product **57a** in 78% yield (Table 5.1, entry 13). Prompted by the literature reports on the C-H arylation by copper, we performed the reaction in the absence of Pd(OAc)₂ but found the recovery of the starting material (Table 5.1, entry 15). To push the reaction condition to even lower temperature, we increased the catalyst loading from 5 mol % to 20 mol % of Pd(OAc)₂ but somewhat surprisingly the yield was dropped to 37% and compound **58** was isolated in 29% yield.

Table 5.2 Screening of different aryl source

Entry	Arylating agent	Yield (%)
1	C ₆ H ₆	No reaction
2	PhI	No reaction
3	PhB(OH) ₂	No reaction
4	Ph ₂ IOTf	84

The best result was obtained by using 5 mol % of Pd(OAc)₂, 20 mol % of TfOH and 3 equiv of CuO in 1,4-dioxane at room temperature for 3 h (Table 5.1, entry 14). Especially, it was also discovered that reaction carried out at higher temperature provided a slightly lower yield (Table 5.1, entries 12–14). Notably we also observed that a stoichiometric amount of CuO was required to complete the reaction (Table 5.1, entry 14).

Other aryl sources were also screened, like benzene, iodobenzene, phenyl boronic acid under the standard conditions. However, the reaction did not proceed to give the desired product.

Table 5.3 Solvent screening^a

Entry	Solvent	Yield (%)
1	DCE	<5
2 ^b	DCE	<5
3	Toluene	<5
4	CH ₂ Cl ₂	<5
5	Benzene	<5
6	AcOH	No reaction

^a 20 mol % Pd(OAc)₂ used. ^b 10 mol % Pd(OAc)₂ used and 1 equiv of TfOH used.

To establish the optimum condition, we next examined the effect of solvent for this arylation process. As shown in table 5.3, all the solvents examined were ineffective for the arylation. Thus, 1,4-dioxane found out to be the best solvent for this C-H arylation reaction with Ph₂IOTf by using phosphoramidate directing group.

Having optimum condition in our hand, the scope of the present method was examined under the standard condition. Arylation of unsubstituted phosphoramidate afforded the desired mono-phenylated product **57b** selectively. However, 10 mol % Pd(OAc)₂ was required for the completion of the reaction. High selectivity was accomplished in case of phosphoramidate having *ortho* benzyl group. It was observed that C–H phenylated compound **57c** was isolated in 80% yield (Scheme 5.6). C-H arylation of phosphoramidate having electron-donating methyl and methoxy groups at *meta* position of phenyl ring proceeded smoothly to give the corresponding products **57d** and **57f** in 86% and 84%, yields respectively (Scheme 5.6). Interestingly, *para* substituted phosphoramidates equally worked well with mono-phenylation products in excellent

yields. Substrates bearing *tert*-butyl and methoxy at *para* position, the C-H arylation proceeded selectively and afforded the corresponding mono arylated products **57e** and **57g** in 76% and 80% yields (Scheme 5.6).

Scheme 5.6 Synthesis of *N*-Aryl Phosphoramidates^a

Conditions: ^a 5 mol % $\text{Pd}(\text{OAc})_2$, 1.2 equiv of Ph_2IOTf , 20 mol % of TfOH and 3 equiv of CuO in 1,4-dioxane.
^b 10 mol % $\text{Pd}(\text{OAc})_2$ was used. ^c Reaction was carried out at 60 °C.

Furthermore, dimethoxy-substituted *N*-aryl phosphoramidate underwent clean arylation to obtain C-H phenylated product **57i** in 82% yield. In addition, phosphoramidates having both bromo and methyl group also underwent efficient C-H arylation which provided **57j** and **57k** in 70% and 75% yield. The tolerance of bromo group is especially useful for further functionalization.

Scheme 5.7 Arylation of *N*-Alkyl Phosphoramidates^a

Conditions: ^a 5 mol % Pd(OAc)₂, 1.2 equiv of Ph₂IOTf, 20 mol % of TfOH and 3 equiv of CuO in 1,4-dioxane.
^b 10 mol % Pd(OAc)₂ was used. ^c Reaction was carried out at 60 °C.

With these results in hand, we examined palladium-catalyzed arylation of *N*-alkyl-*N*-aryl phosphoramidates (Scheme 5.7). When *N*-alkyl-*N*-aryl phosphoramidate was subjected to C-H arylation under the standard condition, mono selective *ortho* phenylated product **60a** was accomplished in high yield. The electron-donating groups like methyl and methoxy at *para* position proceeded smoothly to give the corresponding products **60b** and **60d** in 75% and 75% yield, respectively (Scheme 5.7).

The phosphoramidates having methoxy at *meta* position also worked well (**60c**). *N*-aryl-*N*-methyl phosphoramidates with chloride or bromide as a substituent on the phenyl ring also afforded desired products **60e** and **60f** in good yields (Scheme 5.7). The presence of halide can be utilized to introduce other functionalities by cross-coupling reactions. Naphthalene derived substrate needed heating 60 °C to furnish **60g** in 75% yield. In the same way, **59h** also gave the arylated product **60h** in 86% yield. These results suggested

that the present methodology can be applied in not only *N*-aryl phosphoramidates but also *N*-alkyl-*N*-phenyl phosphoramidates.

Scheme 5.8 Arylation of Phosphoramidates using Various Ar₂IOTf

Furthermore, we also examined the generality of our methodology for other hypervalent iodine aryl source. Ar₂IOTf containing electron-donating methyl substituent turned out to be compatible with the Pd-catalyzed C–H arylation of *N*-aryl phosphoramidates and *N*-alkyl-*N*-aryl phosphoramidates. Treatment of *N*-alkyl-*N*-aryl phosphoramidates with di(4-methylphenyl) iodonium triflate under optimized condition afforded **61b** and **61c** in 80% and 81% yields respectively (Scheme 5.8). A similar result was obtained with the phosphoramidate having *ortho* ethyl group **61a**. Remarkably, electron withdrawing chloride also tolerated on the oxidant to provide **61d** in 53% yield together with recovery of the starting material (32%) (Scheme 5.8).

Scheme 5.9 Plausible mechanism for Pd(II)-catalyzed C-H arylation of *N*-arylphosphoramidate

Based on results,¹³ the mechanism of this C-H arylation would involve Pd(II)/Pd(IV) catalytic cycle as shown in scheme 5.6. Initial coordination of Pd(II) catalyst to the *N*-aryl phosphoramidates and the successive C-H insertion would form the six-membered palladacycle **52x**. Here diphenyl iodonium triflate serves as arylating agent as well as oxidizing agent. Subsequently, aryl palladacycle(II) **52x** might be oxidized to the Pd(IV) species **52y** by Ph₂IOTf. The specific role of Cu(II) is still unclear and remains to be elucidated. During optimization the reaction needs a stoichiometric amount of CuO to obtain excellent yields. It clearly shows that CuO play a crucial role as a base for regeneration of palladacycle **52x**.

5.3 Conclusion

We have developed a novel protocol to effect C-H arylation at room temperature in which the phosphoramidate group was utilized as a directing group for the first time. The present methodology also could be applied in *N*-alkyl-*N*-phenyl phosphoramidates. Stoichiometric amount of CuO was essential for efficient Pd(II)-catalysis for arylation of

phosphoramidates. This transformation offers a new synthetic tool for construction of complex phosphoramidates from simple ones for the diverse synthesis of industrially and medicinally important molecules.

VI. Rhodium(III)-Catalyzed *ortho*-Olefination of Aryl Phosphonates

6.1 Introduction

Transition metal-catalyzed C-H alkenylation is an atom economical and straight-forward reaction in organic synthesis. Palladium catalysts have been already used to promote arylation of alkenes, in parallel with rhodium also allowed oxidative addition to arenes and heteroarenes. Rhodium-catalyzed *ortho*-functionalization of arenes have been actively studied in recent years and has proved to be a highly effective for the formation of C-C and C-hetero atom bonds.^{115, 116} In achieving *ortho* C-H activation, directing groups play a vital role to enhance and to control the reaction. Directing groups like carboxylate esters¹¹⁷, carbamates¹¹⁸, and ketones¹¹⁹ are less commonly used due to weak coordination towards metal catalysts.

In the previous chapter, we have demonstrated the possibility of insertion of a metal catalyst into C-H bond through weak coordination of P=O bond with a metal catalyst rather than P-OH bond.¹²⁰ Concerning P-OH directing group, our group demonstrated Pd(II)-catalyzed *ortho*-olefination of aryl phosphoric monoacids and benzylic phosphonic monoacids using mono-phosphoric acid.^{121,122}

6.2 Results and Discussion

The palladium-catalyzed oxidative Heck reactions involving *N*-aryl phosphoramidate **62a** as a substrate was futile. Furthermore, our attempts towards Rh(III)-catalyzed *ortho*-olefination of **62b** and **62c** were also unsuccessful. We next studied the reaction with arylphosphonates, which are served as important intermediates in organic synthesis. Aryl phosphonates have various applications in medicinal, polymers and materials.

Scheme 6.1 *Ortho* olefination of **62a**, **62b** and **62c**

Aryl phosphonates can be easily prepared by the palladium-catalyzed cross-coupling reaction of aryl halides with diaryl and dialkyl phosphites.¹²³ The choice of metals have been explored and expanded to other metals such as Ni and Cu.^{124, 125}

Scheme 6.2 Pd-catalyzed preparation of aryl phosphonates

Diethyl *o*-tolylphosphonate was used as a model substrate for the metal-catalyzed C-H olefination under various conditions (Table 6.1). We studied the possibility of Pd-catalyzed C-H olefination using an aryl phosphonate ester as the directing group. When **64a** was treated with 2 equiv of ethyl acrylate using 5 mol % Pd(OAc)₂ and 1 equiv of Cu(OAc)₂ oxidant in 1,2-dichloroethane at 110 °C for 15 h, the reaction did not proceed (Table 6.1, entry 1). Pd(II)-catalyzed C-H olefination was unsuccessful by changing oxidants and solvents (Table 6.1, entry 2, 3).

Based on recent work on Rh(III)-catalyzed *ortho* C-H olefination using a carboxylic ester¹²⁶, we next turned our attention to Rh(III)-catalyzed olefination reaction. Poor results were obtained in the absence of additive or oxidant (Table 6.1, entry 5, 6). In addition, Rh(III)-catalyst was necessary for the C-H alkenylation reaction (Table 6.1, entry 4).

Table 6.1 Optimization of reaction conditions^a

Entry	Additive (mol %)	Oxidant (equiv)	Solvent	Yield (%)
1 ^b	None	Cu(OAc) ₂ (1)	1,2-DCE	0
2 ^b	None	AgOAc (2)	1,4-dioxane	0
3 ^b	AgSbF ₆ (10)	Cu(OAc) ₂ (1)	1,2-DCE	0
4 ^c	None	Cu(OAc) ₂ (1)	1,2-DCE	0
5	None	Cu(OAc) ₂ (0.2)	1,2-DCE	<5
6	AgSbF ₆ (10)	None	1,2-DCE	28
7	AgSbF ₆ (10)	Cu(OAc) ₂ (1)	1,4-dioxane	28
8	AgSbF ₆ (10)	Cu(OAc) ₂ (1)	1,2-DCE	85
9	AgSbF ₆ (10)	Cu(OAc) ₂ (0.2)	1,2-DCE	82
10	AgSbF ₆ (10)	Cu(OAc) ₂ (0.2)	toluene	0
11	AgSbF ₆ (10)	Cu(OAc) ₂ (0.2)	acetonitrile	0
12	AgSbF ₆ (10)	Cu(OAc) ₂ (0.2)	^t AmOH	34
13	AgSbF ₆ (10)	CuO	1,2-DCE	10
14	AgSbF ₆ (10)	AgOAc (0.2)	1,2-DCE	32
15	AgSbF ₆ (10)	Ag ₂ O	1,2-DCE	24

^a Reaction was carried out in presence of O₂. ^b 5 mol % Pd(OAc)₂ was used. ^c with out Rh catalyst.

Interestingly, treatment of **64a** with 2 equiv of ethyl acrylate in the presence of 2.5 mol % Rh(III)-catalyst and 10 mol % AgSbF₆ together with 1 equiv of Cu(OAc)₂ as an oxidant in 1,4-dioxane at 110 °C for 15 h afforded 28% of the olefinated product **65a** (Table 6.1, entry 7). When the reaction was carried out in 1,2-dichloroethane, the yield drastically improved to 85% (Table 6.1, entry 8). Furthermore, the reaction proceeded smoothly with a catalytic amount of 20 mol % Cu(OAc)₂ in the presence of oxygen to furnish the product in 82% yield (Table 6.1, entry 9). Different oxidants were also screened for this reaction. CuO and silver based oxidants like AgOAc and Ag₂O gave inferior results (Table 6.1, entries 13 - 15). Furthermore, dichloroethane was found out to be the solvent

of choice. The reaction did not proceed in toluene, acetonitrile (Table 6.1, entries 10 and 11), whereas low yields were obtained in 1,4-dioxane and ^tAmOH with 34% and 28%, respectively (Table 6.1, entry 7, 12).

Table 6.2 Alkenylation of aryl phosphonates^a

^a 2.5 mol % of $[\text{RhCp}^*\text{Cl}_2]_2$, 10 mol % AgSbF_6 , and 20 mol % $\text{Cu}(\text{OAc})_2$ in dichloroethane for 15 h at 110 °C in a screw-caped vial; yields of isolated products.

Thus, the subsequent reactions were carried out with 20 mol % of $\text{Cu}(\text{OAc})_2$ in the presence of oxygen using Rh(III)-catalyst in 1,2-dichloroethane at 110 °C for 15 h.

Having the optimized condition in our hand, we investigated the scope of various aryl phosphonates for Rh-catalyzed olefination reaction using ethyl acrylate as counterpart and the results are summarized in table 6.2. Aryl phosphonates bearing different functional groups were olefinated under the standard condition (Table 6.2, entry **65b -65l**). Electron-poor and electron-rich groups like chloro, phenyl, methoxy and methyl were tolerated

(**65c**, **65d**, **65e**, **65f**). The results clearly demonstrate that electronic nature of the substituents on aryl phosphonates play a marginal role in the olefination reaction. *Meta*-substituted aryl phosphonates underwent regioselective olefination, which occurred at sterically less hindered position (**65h**). As expected, for unsubstituted and *para*-substituted phosphonates, the regioselectivity of the mono-olefination was not well-controlled, giving a mixture of mono-olefinated product (**65i**, **65j**) and di-olefinated product (**66i**, **66j**). On the other hand, in case of naphthyl derivatives C-H olefination occurred regioselectively and afforded the corresponding olefination products in good yields (**65k**, **65l**).

To improve the mono-olefination, we modified the structure of aryl phosphonates changing the alkoxy part with bulkier substituents. When a more bulky di-isopropyl phosphonate **64m** was subjected to the optimum condition using 1.2 equiv of ethyl acrylate, a mixture of **65m** and **66m** was obtained in a ratio of 60:15 in favor of **66n** (Scheme 6.2).

Scheme 6.2 Rh(III)-catalyzed C-H olefination of **64m** and **64n**

We next turned our attention to a phosphonic dialkylamino group. When the reaction was repeated with **64n**, di-olefinated product **66n** was not observed under the present condition, albeit with recovery of starting material **64n** (30%). A similar result was also obtained with 2 equiv of ethyl acrylate. Mono selectivity was observed in case of **64o**, **64p**, **64q** in moderate yields.

Scheme 6.3 *Ortho*-olefination of diethyl tolylphosphonate

To broaden the scope of the olefination, tolyl phosphonate **64a** was treated with several electron-deficient olefins and styrene derivatives (Scheme 6.3). Reaction of vinyl sulfone with tolyl phosphonate under the standard condition furnished the corresponding olefinated product **67c** in 78% yield (Scheme 6.3). The olefination of electron-deficient *n*-butyl and benzyl acrylate proceeded cleanly to give the corresponding products **67a** and **67b** in 85% and 75% yields, respectively. Similarly, the olefination reaction with styrene derivatives worked equally well to afford the olefinated products **67d**, **67e**, **67f** in moderate yields. However, the reaction failed to give olefinated products with ethyl crotonate and allyl benzene.

The efficiency of the phosphonate directing group in C-H alkenylation was investigated by competitive study between aryl phosphonate **64a** and ethyl benzoate **68**. When reaction was carried out with 1.2 equiv of ethyl acrylate a 1:2 mixture of **65a** and **68a** was isolated, the products indicating that the ester directing group was somewhat more effective than the phosphonate group.

Scheme 6.4 Competitive *ortho* olefination between **64a** and **68**

Based on experimental results, a plausible reaction mechanism for the Rh(III)-catalyzed C-H olefination reaction is shown in scheme 6.5. Coordination of highly cationic rhodium species **A** to phosphoryl oxygen and subsequent cleavage of C-H bond would form a five-membered rhodocycle **C**. Then olefin insertion gives the seven-membered intermediate **D** followed by the subsequent β -hydride elimination would provide the olefination product as

Scheme 6.5 Plausible mechanism for Rh(III)-catalyzed C-H olefination

well as the regeneration of Rh(I) catalyst. Rh(I) is then reoxidised to Rh(III) in the presence of Cu(OAc)₂.

6.3 Conclusion

A new and efficient Rh(III)-catalyzed *ortho*-alkenylation of aryl phosphonates is developed. The phosphonate group is utilized as the directing group in Rh(III)-catalyzed olefination. The present approach feature broad scope of olefins, good functional group tolerance, and high efficiency. Furthermore, the approach could be applied to further functionalization using alkynes, aldehydes, and other reactive functional groups.

Chapter VII. Experimental Section

Supporting information

7.1 General remarks

Reactions were carried out in oven-dried glassware under nitrogen atmosphere. All commercial reagents were used without purification, and all solvents were reaction grade. All reaction mixtures were stirred magnetically and were monitored by thin-layer chromatography using Merck silica gel 60 F₂₅₄ precoated glass plates, which were visualized with UV light and then developed using either iodine or a solution of anisaldehyde. Flash column chromatography was carried out using Merck silica gel 60 (0.040-0.063 mm, 230-400 mesh) and gradient solvent system (EtOAc : *n*-hexane as a eluant). ¹H NMR(400MHz) and ¹³C NMR spectra were recorded on a ECA 400 MHz and ECA 400SL) spectrometer. Deuterated chloroform was used as the solvent, and chemical shift values (δ) are reported in parts per million relative to the residual signals of this solvent (δ 7.24 for ¹H and δ 77.2 for ¹³C). Infrared spectra were recorded on a FTIR spectrometer as either a thin film pressed between two sodium chloride plates or as a solid suspended in a potassium bromide disk. High-resolution mass spectra were recorded on a LC/ HRMS mass spectrometer.

7.2.1 Gold (I)-Catalyzed Addition of Diphenyl Phosphate to Alkynes: Isomerization of Kinetic Enol Phosphates to Thermodynamic Isomers

General procedure of Au-catalyzed addition reactions

Oct-1-en-2-yl diphenyl phosphate (17a)¹: To a suspension of Ph_3PAuCl (12.37 mg, 0.025 mmol), AgPF_6 (6.32 mg, 0.025 mmol) and diphenyl phosphate (125.1 mg, 0.5 mmol) in toluene (2 mL) was added 1-octyne (66.12 mg, 0.6 mmol) at room temperature using v-vial. After being stirred for 9 h, the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (EtOAc:hexane = 1:5) to give oct-1-en-2-yl diphenyl phosphate (159 mg, 88%) as a colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.37-7.33 (m, 4H), 7.25-7.19 (m, 6H), 4.93 (t, $J = 2.2$ Hz, 1H), 4.59 (t, $J = 2.0$ Hz, 1H), 2.19 (t, $J = 7.6$ Hz, 2H), 1.44 (quint, $J = 7.4$ Hz, 2H), 1.31-1.19 (m, 6H), 0.87 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.9 (d, $J_{cp} = 9.5$ Hz), 150.5 (d, $J_{cp} = 7$ Hz), 129.8, 125.5, 120.1 (d, $J_{cp} = 5$ Hz), 98.0 (d, $J_{cp} = 4$ Hz), 34.3 (d, $J_{cp} = 5.4$ Hz), 31.5, 28.4, 26.1, 22.5, 14.1; IR (film) 3071, 2931, 2859, 1940, 1864, 1783, 1726, 1659, 1560, 1591, 1490, 958, 688 cm^{-1} ; HRMS (EI) calcd. for $\text{C}_{20}\text{H}_{25}\text{O}_4\text{P}$: m/z 360.1490 $[\text{M}^+]$, found: m/z 360.1488.

1-Phenyl-1-ethen-1-yl diphenyl phosphate (17b)^{1,2}: a pale yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.49-7.51 (m, 2H), 7.30-7.36 (m, 7H), 7.23-7.26 (m, 4H), 7.18-7.22 (m, 2H), 5.38 (t, $J = 2.9$ Hz, 1H), 5.34 (t, $J = 2.7$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.8 (d, $J_{cp} = 8.4$ Hz), 150.9 (d, $J_{cp} = 7.5$ Hz), 134.0 (d, $J_{cp} = 6.6$ Hz), 130.2, 129.7,

128.8, 126.0, 125.7, 120.6 (d, $J_{cp} = 5.5$ Hz), 98.7 (d, $J_{cp} = 3.8$ Hz); IR (film) 1943, 1889, 1792, 1749, 1733, 1717, 1670, 1636, 1590, 1301, 960, 770, 687 cm^{-1} ; HRMS (EI) calcd. for $\text{C}_{20}\text{H}_{17}\text{O}_4\text{P}$: m/z 375.0762 [M^+], found: m/z 375.0766.

3-Bromo-1-propen-2-yl diphenyl phosphate (17c): colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.26-7.36 (m, 10H), 5.17 (s, 1H), 5.03 (s, 1H), 3.95 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.5 (d, $J_{cp} = 30.5$ Hz), 134.4, 130.1, 125.9, 120.4 (d, $J_{cp} = 19.1$ Hz), 102.9 (d, $J_{cp} = 15.2$ Hz), 30.4 (d, $J_{cp} = 26.7$ Hz); IR (film) 3018, 1651, 1591, 1489, 1296, 1215, 1161, 970 cm^{-1} ; HRMS (EI) calcd. for $\text{C}_{23}\text{H}_{29}\text{ClO}_4\text{P}$: m/z 368.9891 [M^+], found: m/z 368.9890.

(Z)-2-(Ethoxycarbonyl)vinyl diphenyl phosphate (17d): a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.24-7.36 (m, 10H), 6.98 (t, $J = 6.2$ Hz, 1H), 5.31-5.33 (m, 1H), 4.18 (q, $J = 7.34$ Hz, 2H), 1.25 (t, $J = 7.34$ Hz, 3H); ^{13}C NMR (400 MHz, CDCl_3) δ 163.3, 150.1 (d, $J_{cp} = 30.5$ Hz), 145.5 (d, $J_{cp} = 15.3$ Hz), 130.0, 126.0, 120.3 (d, $J_{cp} = 19.1$ Hz), 105.9 (d, $J_{cp} = 45.8$ Hz), 60.5, 14.3; IR (film) 3018, 1720, 1645, 1490, 1215, 1068, 968 cm^{-1} ; HRMS (EI) calcd. for $\text{C}_{17}\text{H}_{27}\text{O}_6\text{P}$: m/z 349.0841 [M^+], found: m/z 349.0839.

Ethyl (Z)-3-(diphenoxyphosphoryloxy)-3-phenylacrylate (17e): colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.12-7.65 (m, 15H), 6.11 (s, 1H), 4.18 (q, $J = 7.3$ Hz, 1H), 1.27 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (400 MHz, CDCl_3) δ 163.9, 156.1 (d, $J_{cp} = 34.4$ Hz), 150.6 (d,

$J_{cp} = 34.4$ Hz), 134.3 (d, $J_{cp} = 52.1$ Hz), 133.4, 132.1, 131.0, 129.8, 129.3 (d, $J_{cp} = 49.6$ Hz), 128.7, 126.9, 125.5, 120.2 (d, $J = 14.6$ Hz), 107.4 (d, $J_{cp} = 26.7$ Hz), 60.7, 14.3; IR (film) 3018, 1720, 1645, 1490, 1215, 1068, 968 cm^{-1} ; HRMS (EI) calcd. for $\text{C}_{23}\text{H}_{21}\text{O}_6\text{P}$: m/z 425.1154 [M^+], found: m/z , 425.1159.

(Z)-Hex-3-en-3-yl diphenyl phosphate (17f): a colorless liquid. ^1H NMR (300 MHz, CDCl_3) δ 7.38-7.30 (m, 4H), 7.27-7.17 (m, 6H), 4.87 (t, $J = 7.3$ Hz, 1H), 2.34 (q, $J = 6.0$ Hz, 2H), 2.05 (q, $J = 7.5$ Hz, 2H), 1.05 (t, $J = 7.4$ Hz, 3H), 0.88 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.1 (d, $J_{cp} = 6.9$ Hz), 149.4 (d, $J_{cp} = 9$ Hz), 130.2, 125.8, 120.6 (d, $J_{cp} = 5.1$ Hz), 116.3 (d, $J_{cp} = 6.7$ Hz), 27.6, 18.9, 14.2, 11.7; IR (film) 2970, 2936, 2875, 1940, 1864, 1785, 1726, 1490, 1191, 953, 756, 688 cm^{-1} ; HRMS (EI) calcd. for $\text{C}_{18}\text{H}_{21}\text{O}_4\text{P}$: m/z 332.1177 [M^+], found: m/z 332.1176.

Oct-1-en-2-yl diphenylphosphinate (17g): a colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.87-7.80 (m, 4H), 7.55-7.43 (m, 6H), 4.76 (s, 1H), 4.39 (s, 1H), 2.17 (t, $J = 7.8$ Hz, 2H), 1.51-1.48 (m, 2H), 1.28-1.22 (m, 6H), 0.88-0.84 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.5, 132.4, 131.9, 131.8, 131.7, 130.9, 128.7, 128.6, 97.8, 35.5, 31.7, 28.7, 26.6, 22.7, 14.2; IR (film) 2954, 1590, 1782, 1120, 953, 756, 688 cm^{-1} ; HRMS (EI) calcd. for $\text{C}_{20}\text{H}_{25}\text{O}_2\text{P}$: m/z 329.1670 [M^+], found: m/z 329.1668.

3-((Diphenylphosphoryl)oxy)but-3-en-1-yl ethyl carbonate (17h): a colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.88-7.82 (m, 4H), 7.57-7.44 (m, 6H), 4.87 (s, 1H), 4.52 (s,

1H), 2.17 (t, $J = 6.6$ Hz, 2H), 2.17 (q, $J = 7.1$ Hz, 2H), 2.58 (t, $J = 6.6$ Hz, 2H), 1.30 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.1, 151.3, 151.2, 132.6, 132.5, 131.8, 131.7, 130.4, 128.8, 128.6, 100.3 (d, $J_{cp} = 4.8$ Hz), 64.4, 64.2, 35.1 (d, $J_{cp} = 3.8$ Hz), 14.4; IR (film) 2970, 2936, 2875, 1940, 1864, 1785, 1726, 1490, 1191, 953, 756, 688 cm^{-1} ; HRMS (EI) calcd. for $\text{C}_{19}\text{H}_{21}\text{O}_5\text{P}$: m/z 361.1205 [M^+], found: m/z 361.1203.

7.2.2 A regio- and stereoselective synthesis of trisubstituted alkenes via gold(I)-catalyzed hydrophosphoryloxylation of haloalkynes

General procedure of Au-catalyzed addition reactions

(Z)-1-iodooct-1-en-2-yl diphenyl phosphate (19a): To a suspension of Ph_3PAuCl (114.0 mg, 0.23 mmol), AgOTf (59.0 mg, 0.23 mmol) and diphenyl phosphate (1373 mg, 5.5 mmol) in toluene (22 mL) was added 1-iodooct-1-yne (1.080 g, 4.57 mmol) at room temperature. After being stirred for 4 h, the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography ($\text{EtOAc}:\text{hexane} = 1:10$) to give **19a** (159.0 mg, 80%) as a yellowish oil. ^1H NMR (400 MHz, CDCl_3) δ 7.19-7.38 (m, 10H), 5.65 (s, 1H), 2.49 (t, $J = 7.6$ Hz, 2H), 1.50-1.47 (m, 2H), 1.29-1.19 (m, 6H), 0.86 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.9, 150.6, 130, 125.8, 120.5 (d, $J_{cp} = 4.8$ Hz), 62.1 (d, $J_{cp} = 10.5$ Hz), 35.3, 31.6, 28.6, 26.7, 22.7, 14.2; IR (film) 2954, 2929, 1591, 1490, 1189, 963, 772, 687, 514 cm^{-1} ; HRMS (EI) calcd. for $\text{C}_{20}\text{H}_{24}\text{IO}_4\text{P}$: m/z 486.0457 [M^+], found: m/z 486.0460.

General procedure of Pd-catalyzed cross-coupling reactions

Diphenyl (Z)-1-phenyldec-3-en-1-yn-4-yl phosphate (20a): To a suspension of $\text{Pd(PPh}_3)_4$ (13.86 mg, 0.012 mmol) and CuI (5.71 mg, 0.03 mmol) in 1,4-dioxane (1.5 mL) was added (Z)-1-iodooct-1-en-2-yl diphenyl phosphate (145.8 mg, 0.3 mmol) at room temperature. After 15 min, Et_3N (91.07 mg, 0.9 mmol) and phenylacetylene (36.76 mg, 0.36 mmol) was added. After being stirred for 2 h at room temperature, the reaction mixture was quenched with saturated aqueous NaHCO_3 . The aqueous layer was extracted with ether (3×20 mL), dried with MgSO_4 , filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography ($\text{EtOAc:hexane} = 1:10$) to give **20a** (116.0 mg, 84%) as a brown oil. ^1H NMR (400 MHz, CDCl_3) δ 7.30-7.19 (m, 13H), 7.16-7.12 (m, 2H), 5.33 (s, 1H), 2.42 (t, $J = 7.6$ Hz, 2H), 1.49 (quint, $J = 7.5$ Hz, 2H), 1.32-1.20 (m, 6H), 0.87 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.0 (d, $J_{\text{cp}} = 8.8$ Hz), 151.0 (d, $J_{\text{cp}} = 7.7$ Hz), 131.9, 130.2, 128.6, 125.8, 123.7, 120.6, 96.7, 96.6, 94.6, 83.6 (d, $J_{\text{cp}} = 2.9$ Hz), 34.8, 31.9, 28.9, 26.8, 22.9, 14.5; IR (film) 3061, 2930, 1489, 1188, 1160, 1010, 961, 689 cm^{-1} ; HRMS (EI) calcd. for $\text{C}_{28}\text{H}_{29}\text{O}_4\text{P}$: m/z 460.1803 [M^+], found: m/z 460.1803.

(Z)-1,4-diphenyldec-3-en-1-yne (25a): To a suspension of PdCl_2 (1.773 mg, 0.010 mmol) and (Z)-diphenyl 1-phenyldec-3-en-1-yn-4-yl phosphate (92.1 mg, 0.2 mmol) in THF (1.0 mL) was added phenyl magnesium bromide 1.0 M in THF (39.9 mg, 0.22 mmol) at room temperature. After being stirred for 15 min at room temperature, the reaction mixture was,

filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane) to give **25a** (37.0 mg, 70%) as a yellowish oil. ^1H NMR (400 MHz, CDCl_3) δ 7.59 (d, $J = 8.0$ Hz, 2H), 7.38 (t, $J = 7.4$ Hz, 2H), 7.33-7.29 (m, 1H), 7.28-7.22 (m, 5H), 5.80 (s, 1H), 2.55 (td, $J = 7.5$ Hz, $J = 1.0$ Hz, 2H), 1.43-1.37 (m, 2H), 1.34-1.22 (m, 6H), 0.86 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.3, 140.0, 131.7, 128.6, 128.5, 128.3, 128.14, 128.11, 124.3, 106.2, 91.5, 89.1, 38.3, 32.0, 29.3, 28.8, 23.0, 14.5; IR (film) 2025, 2855, 1489, 755, 690, 441, 427 cm^{-1} ; HRMS (EI) calcd. for $\text{C}_{22}\text{H}_{24}$: m/z 288.1878 [M^+], found: m/z 288.1880.

Diphenyl (Z)-1-phenyloct-1-en-2-yl phosphate (21a): To a suspension of $\text{Pd}(\text{PPh}_3)_4$ (11.56 mg, 0.010 mmol) in 1,4-dioxane (1.0 mL) was added (Z)-1-iodooct-1-en-2-yl diphenyl phosphate (97.26 mg, 0.2 mmol) at room temperature. After 15 min, Et_3N (40.48 mg, 0.4 mmol), 3.0 M K_3PO_4 (138.6 mg, 0.6 mmol) and phenylboronic acid (29.27 mg, 0.24 mmol) was added. After being stirred for 1 h at 70 $^\circ\text{C}$, the reaction mixture was quenched with saturated aqueous NaHCO_3 . The aqueous layer was extracted with ether (3 $\times$ 20 mL), dried with MgSO_4 , filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (EtOAc :hexane = 1:10) to give **5a** (55.0 mg, 63%) as a brown oil. ^1H NMR (400 MHz, CDCl_3) δ 7.42 (d, $J = 8.4$ Hz, 2H), 7.28 (t, $J = 7.9$ Hz, 4H), 7.22-7.11 (m, 9H), 5.81 (s, 1H), 2.54 (t, $J = 7.5$ Hz, 2H), 1.61 (quint, $J = 7.5$ Hz, 2H), 1.38-1.24 (m, 6H), 0.87 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.9 (d, $J_{\text{cp}} = 6.9$ Hz), 149.3 (d, $J_{\text{cp}} = 8.7$ Hz), 134.2, 130.1, 129.2, 128.6, 127.4, 125.7, 120.4 (d, $J_{\text{cp}} = 4.9$ Hz), 114.5 (d, $J_{\text{cp}} = 8.6$ Hz), 35.4, 32.0, 29.0, 27.4, 22.9, 14.5; IR (film) 2954, 2929, 1591, 1290, 1190, 1010, 776, 402 cm^{-1} ; HRMS (EI) calcd. for $\text{C}_{26}\text{H}_{29}\text{O}_4\text{P}$: m/z 436.1803 [M^+], found: m/z 436.1806.

(Z)-deca-1,3-dien-4-yl diphenyl phosphate (22c): To a suspension of $\text{PdCl}_2(\text{PPh}_3)_2$ (10.52 mg, 0.015 mmol) and (Z)-1-iodooct-1-en-2-yl diphenyl phosphate (145.8 mg, 0.3 mmol) in DMF (1.5 mL) was added tributyl(vinyl)tin (142.6 mg, 0.45 mmol) at room temperature. After being stirred for 16 h at room temperature, the reaction mixture was quenched with saturated aqueous NaHCO_3 . The aqueous layer was extracted with ether (3×20 mL), dried with MgSO_4 , filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (EtOAc:hexane = 1:10) to give **7c** (110.0 mg, 95%) as a yellow oil. ^1H NMR (600 MHz, CDCl_3) δ 7.35 (t, $J = 7.9$ Hz, 4H), 7.25 (d, $J = 7.9$ Hz, 4H), 7.20 (t, $J = 7.4$ Hz, 2H), 6.53 (td, $J = 10.5$ Hz, $J = 7.1$ Hz, 1H), 5.58 (d, $J = 10.7$ Hz, 1H), 5.15 (d, $J = 17.1$ Hz, 1H), 4.97 (d, $J = 10.4$ Hz, 1H), 2.36 (t, $J = 7.5$ Hz, 2H), 1.47 (quint, $J = 7.5$ Hz, 2H), 1.28-1.20 (m, 6H), 0.86 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.0 (d, $J_{\text{cp}} = 7.6$ Hz), 149.6 (d, $J_{\text{cp}} = 9.4$ Hz), 130.2, 130.0, 125.9, 120.6 (d, $J_{\text{cp}} = 4.9$ Hz), 117.3, 116.3 (d, $J_{\text{cp}} = 7.9$ Hz), 34.6, 31.9, 29.0, 26.9, 22.9, 14.4; IR (film) 2956, 2929, 2857, 1490, 1188, 1009, 955, 632 cm^{-1} ; HRMS (EI) calcd. for $\text{C}_{22}\text{H}_{27}\text{O}_4\text{P}$: m/z 386.1647 [M^+], found: m/z 386.1646.

(Z)-1-iodohex-1-en-2-yl diphenyl phosphate (19b): ^1H NMR (400 MHz, CDCl_3) δ 7.37-7.18 (m, 10H), 5.64 (s, 1H), 2.49 (t, $J = 7.8$ Hz, 2H), 1.49-1.43 (m, 2H), 1.31-1.25 (m, 2H), 0.85 (t, $J = 6.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 157 (d, $J_{\text{cp}} = 6.7$ Hz), 150.6 (d, $J_{\text{cp}} = 7.7$ Hz), 129.9, 125.8, 120.4 (d, $J_{\text{cp}} = 4.8$ Hz), 62.1 (d, $J_{\text{cp}} = 11.5$ Hz), 34.9, 28.7, 22.0, 13.8; IR (film) 3012, 2958, 2931, 1637, 1591, 1489, 1296, 1188, 1122, 966; HRMS (EI) calcd for $\text{C}_{18}\text{H}_{20}\text{IO}_4\text{P}$: m/z 459.0222 [M^+], found: m/z 459.0218.

(Z)-1-bromodec-1-en-2-yl diphenyl phosphate (19c): ^1H NMR (400 MHz, CDCl_3) δ 7.37-7.19 (m, 10H), 5.66 (s, 1H), 2.38 (t, $J = 7.6$ Hz, 2H), 1.47-1.44 (m, 2H), 1.27-1.22 (m, 10H), 0.87 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.5, 150.6, 129.9, 125.7 (d, $J_{cp} = 10.5$ Hz), 120.4, 91.79, 34.4, 32.0, 29.3, 28.9, 26.4, 22.8, 14.3; IR (film) 3018, 2927, 2856, 1653, 1591, 1489, 1296, 1215, 1188, 1139, 1010, 968, 756, 667 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{22}\text{H}_{28}\text{BrO}_4\text{P}$: m/z 467.0987 [M^+], found: m/z 467.0981.

(Z)-2-iodo-1-phenylvinyl diphenyl phosphate (19d): ^1H NMR (400 MHz, CDCl_3) δ 7.49-7.47 (m, 2H), 7.35-7.25 (m, 7H), 7.18-7.13 (m, 6H), 6.38 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.0 (d, $J_{cp} = 8.6$ Hz), 150.6 (d, $J_{cp} = 7.7$ Hz), 133.9, 129.9 (d, $J_{cp} = 13.4$ Hz), 128.6, 125.6, 120.3 (d, $J_{cp} = 4.8$ Hz), 66.4 (d, $J_{cp} = 9.6$ Hz); IR (film) 3018, 1591, 1489, 1298, 1215, 1188, 1053, 1024, 966, 756 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{20}\text{H}_{16}\text{IO}_4\text{P}$: m/z 477.9831 [M^+], found: m/z 477.9834.

(Z)-1-(4-bromophenyl)-2-iodovinyl diphenyl phosphate (19e): ^1H NMR (400 MHz, CDCl_3) δ 7.43-7.41 (m, 2H), 7.34-7.19 (m, 6H), 7.18-7.16 (m, 6H), 6.42 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.0 (d, $J_{cp} = 8.6$ Hz), 150.5 (d, $J_{cp} = 7.6$ Hz), 132.9, 131.9, 129.9, 128.0, 125.8, 124.2, 120.3 (d, $J_{cp} = 4.8$ Hz), 67.2 (d, $J_{cp} = 9.5$ Hz); IR (film) 3068, 3014, 1589, 1487, 1394, 1307, 1215, 1188, 1043, 947, 754 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{20}\text{H}_{15}\text{IO}_4\text{PBrNa}$: m/z 578.8834 [M^+], found: m/z 578.8836.

(Z)-1-iodo-4-phenylbut-1-en-2-yl diphenyl phosphate (19f): ^1H NMR (400 MHz, CDCl_3) δ 7.38-7.30 (m, 8H), 7.28-7.17 (m, 5H), 7.10 (d, $J = 6.9$ Hz, 2H), 5.63 (s, 1H), 2.82 (s, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.7 (d, $J_{cp} = 7.1$ Hz), 150.4 (d, $J_{cp} = 7.6$ Hz), 139.9, 129.9, 128.5, 128.4, 126.3, 125.7, 120.3 (d, $J_{cp} = 4.8$ Hz), 63.1 (d, $J_{cp} = 10.5$ Hz), 37.0, 32.9; IR (film) 3075, 1590, 1488, 1297, 1185, 960, 688, 639 cm^{-1} ; HRMS (EI) calcd. for $\text{C}_{22}\text{H}_{20}\text{IO}_4\text{P}$: m/z 506.0144 [M^+], found: m/z 506.0145.

(Z)-3-(diphenoxyphosphoryloxy)-4-iodobut-3-enyl ethyl carbonate (19g): ^1H NMR (400 MHz, CDCl_3) 7.37-7.19 (m, 10H), 5.85 (s, 1H), 4.24-4.15 (m, 4H), 2.90-2.89 (m, 2H), 1.31-1.26 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.9, 152.4 (d, $J_{cp} = 7.6$ Hz), 150.4 (d, $J_{cp} = 7.6$ Hz), 130.0, 125.9, 120.4 (d, $J_{cp} = 4.8$ Hz), 65.2, 64.4, 63.5, 34.7, 14.4; IR (film) 3076, 2981, 1735, 1641, 1589, 1487, 1384, 1367, 1184, 1120, 1070, 763, 638 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{19}\text{H}_{20}\text{IO}_7\text{P}$: m/z 519.0070 [M^+], found: m/z 519.0071.

(Z)-4-(benzoyloxy)-1-bromobut-1-en-2-yl diphenyl phosphate (19h): ^1H NMR (400 MHz, CDCl_3) δ 8.01-7.98 (m, 2H), 7.45-7.19 (m, 15H), 5.85 (s, 1H), 4.39 (t, $J = 6.6$ Hz, 2H), 2.89-2.86 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.7, 151.0, 148.1, 133.3, 130.0, 128.5, 125.9, 120.2, 94.1, 60.6, 33.9; IR (film) 3070, 2962, 1732, 1678, 1589, 1487, 1454, 1382, 1070, 773, 711 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{23}\text{H}_{21}\text{O}_6\text{BrP}$: m/z 503.0259 [M^+], found: m/z 503.0255.

Diphenyl (Z)-1-phenyloct-3-en-1-yn-4-yl phosphate (20b): ^1H NMR (400 MHz, CDCl_3) δ 7.34-7.14 (m, 15H), 5.34 (s, 1H), 2.43 (t, $J = 7.8$ Hz, 2H), 1.49-1.45 (m, 2H), 1.35-1.29 (m, 2H), 0.87 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.6, 150.8, 131.7, 129.9, 128.3, 125.6, 120.4 (d, $J_{cp} = 4.8$ Hz), 96.4, 94.9, 84.1, 34.2, 28.7, 22.2, 13.9; IR (film) 3053, 2958, 2872, 1653, 1591, 1489, 1296, 1265, 1219, 1188, 1161, 1008, 688 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{26}\text{H}_{25}\text{O}_4\text{P}$: m/z 433.1569 [M^+], found: m/z 433.1566.

(Z)-1-(4-bromophenyl)oct-3-en-1-yn-4-yl diphenyl phosphate (20c): ^1H NMR (400 MHz, CDCl_3) δ 7.35-7.09 (m, 14H), 5.31 (s, 1H), 2.40 (t, $J = 7.8$ Hz, 2H), 1.49-1.45 (m, 2H), 1.34-1.28 (m, 2H), 0.87 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.1, 150.6, 133.1, 131.6, 129.9, 125.7, 122.4 (d, $J_{cp} = 14.4$ Hz), 96.3 (d, $J_{cp} = 7.7$ Hz), 93.2, 84.5, 34.3, 28.6, 22.1, 13.9; IR (film) 3018, 2399, 1591, 1489, 1294, 1215, 1161, 1010, 966, 767, 669 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{26}\text{H}_{25}\text{O}_4\text{PBr}$: m/z 511.0674 [M^+], found: m/z 511.0668.

(Z)-1-(4-methoxyphenyl)oct-3-en-1-yn-4-yl diphenyl phosphate (20d): ^1H NMR (400 MHz, CDCl_3) δ 7.31-7.12 (m, 12H), 6.76-6.73 (m, 2H), 5.32 (s, 1H), 3.77 (s, 3H), 2.40 (t, $J = 7.8$ Hz, 2H), 1.49-1.43 (m, 2H), 1.33-1.28 (m, 2H), 0.86 (t, $J = 7.3$ Hz, 3H); ^{13}C

NMR (100 MHz, CDCl_3) δ 159.7, 157.9 (d, $J_{cp} = 9.6$ Hz), 150.7 (d, $J_{cp} = 7.7$ Hz), 133.1, 129.9, 125.6, 120.3 (d, $J_{cp} = 4.8$ Hz), 115.6, 113.9, 96.6 (d, $J_{cp} = 8.6$ Hz), 82.0, 55.4, 34.2, 28.7, 22.1, 13.9; IR (film) 3016, 2960, 2399, 1602, 1508, 1489, 1292, 1247, 1215, 1026, 966, 771, 667 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{27}\text{H}_{28}\text{O}_5\text{P}$: m/z 463.1674 [M^+], found: m/z 463.1666.

Diphenyl (Z)-1,4-diphenylbut-1-en-3-ynyl phosphate (20e): ^1H NMR (400 MHz, CDCl_3) δ 7.57-7.55 (m, 2H), 7.36-7.557.09 (m, 18H), 6.08 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.5, 150.7 (d, $J_{cp} = 7.7$ Hz), 133.6, 131.8, 129.9, 128.7, 128.3, 125.6 (d, $J_{cp} = 16.3$ Hz), 120.3 (d, $J_{cp} = 4.8$ Hz), 97.7 (d, $J_{cp} = 8.6$ Hz), 84.2; IR (film) 3016, 2399, 1593, 1489, 1294, 1215, 1070, 1010, 966, 771, 669 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{28}\text{H}_{22}\text{O}_4\text{P}$: m/z 453.1256 [M^+], found: m/z 453.1262.

Diphenyl (Z)-1,5-diphenylpent-1-en-3-ynyl phosphate (20f): ^1H NMR (400 MHz, CDCl_3) δ 7.52-7.50 (m, 2H), 7.33-7.12 (m, 18H), 5.88 (s, 1H), 3.58 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.0, 150.8 (d, $J_{cp} = 7.6$ Hz), 136.5, 133.8, 129.8 (d, $J_{cp} = 4.8$ Hz), 128.7 (d, $J_{cp} = 5.7$ Hz), 120.3 (d, $J_{cp} = 5.7$ Hz), 98.1 (d, $J_{cp} = 6.7$ Hz), 96.4, 26.2; IR (film) 3053, 2985, 2252, 1489, 1421, 1265, 1219, 910, 771, 650 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{29}\text{H}_{24}\text{O}_4\text{P}$: m/z 467.1412 [M^+], found: m/z 467.1418.

Diphenyl (Z)-1-phenyldodec-5-en-3-yn-6-yl phosphate (20g): ^1H NMR (400 MHz, CDCl_3) δ 7.35-7.24 (m, 10H), 7.18 (t, $J = 6.8$ Hz, 3H), 7.12 (d, $J = 7.1$ Hz, 2H), 5.09 (s, 1H), 2.70 (t, $J = 7.8$ Hz, 2H), 2.43 (t, $J = 7.2$ Hz, 2H), 2.32 (t, $J = 7.6$ Hz, 2H), 1.43 (quint, $J = 7.0$ Hz, 2H), 1.30-1.17 (m, 6H), 0.86 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.6 (d, $J_{cp} = 9.5$ Hz), 150.6 (d, $J_{cp} = 7.5$ Hz), 140.7, 129.8 (d, $J_{cp} = 8.3$ Hz), 128.3 (d, $J_{cp} = 2.7$ Hz), 126.2, 125.4, 120.2 (d, $J_{cp} = 4.9$ Hz), 96.5 (d, $J_{cp} = 7.8$ Hz), 94.7, 74.4, 35.0, 34.2, 31.4, 28.5, 26.3, 22.5, 21.7, 14.0; IR (film) 2953, 2928, 1591, 1490, 1010, 961, 774, 415 cm^{-1} ; HRMS (EI) calcd. for $\text{C}_{30}\text{H}_{33}\text{O}_4\text{P}$: m/z 488.2116 [M^+], found: m/z 488.2115.

(Z)-1,4-diphenyloct-3-en-1-yne (25b): ^1H NMR (400 MHz, CDCl_3) δ 7.61-7.59 (m, 2H), 7.40-7.22 (m, 8H), 5.80 (s, 1H), 2.56 (t, $J = 7.5$ Hz, 2H), 1.42-1.26 (m, 4H), 0.88 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.0, 139.7, 131.4, 128.4, 128.3, 128.0, 127.9, 124.1, 106.0, 91.3, 88.9, 37.8, 30.7, 22.5, 14.1; IR (film) 3078, 3014, 2956, 2194, 1591, 1489, 1440, 1377, 1215, 1068, 914, 839, 767, 690 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{20}\text{H}_{20}$: m/z 261.1643 [M^+], found: m/z 261.1653.

1,1,4-triphenylbut-1-en-3-yne (25c): ^1H NMR (400 MHz, CDCl_3) δ 7.60-7.00 (m, 15H), 6.23 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.9, 141.6, 139.4, 131.6, 130.4, 128.7,

128.5, 128.5, 128.0, 127.5, 107.3, 93.9, 89.4; IR (film) 3053, 2985, 2252, 1265, 1219, 910, 771, 734, 650 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{22}\text{H}_{16}$: m/z 281.1330 [M^+], found: m/z 281.1336.

1-methoxy-4-((Z)-4-phenyloct-3-en-1-ynyl)benzene (22d): ^1H NMR (400MHz, CDCl_3) δ 7.60-7.58 (m, 2H), 7.39-7.19 (m, 6H), 6.79-6.77 (m, 2H), 5.77 (s, 1H), 3.77 (s, 3H), 2.54 (t, $J = 7.5$ Hz, 2H), 1.38-1.26 (m, 4H), 0.88 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.4, 152.9, 139.9, 132.9, 128.3, 128.0, 127.8, 116.3, 114.1, 106.2, 91.5, 87.5, 55.5, 37.7, 30.8, 22.5, 14.1; IR (film) 3012, 2956, 1604, 1508, 1463, 1247, 1170, 1035, 831, 756, 667 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{21}\text{H}_{23}\text{O}$: m/z 291.1749 [M^+], found: m/z 291.1752.

Diphenyl (Z)-1-phenylhex-1-en-2-yl phosphate (21b): ^1H NMR (400 MHz, CDCl_3) δ 7.42-7.39 (m, 2H), 7.29-6.78 (m, 13H), 5.81 (s, 1H), 2.54 (t, $J = 7.3$ Hz, 2H), 1.61-1.57 (m, 2H), 1.39-1.33 (m, 2H), 0.89 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.4, 150.6 (d, $J_{cp} = 7.7$ Hz), 149.0 (d, $J_{cp} = 8.6$ Hz), 133.9, 129.9, 129.6, 129.0, 128.4, 127.2, 125.6, 120.2 (d, $J_{cp} = 4.8$ Hz), 115.5, 114.4 (d, $J_{cp} = 8.6$ Hz), 34.9, 29.3, 22.2, 14.0; IR (film) 3059, 2956, 2870, 1672, 1591, 1489, 1296, 1188, 1095, 960, 754, 688 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{24}\text{H}_{25}\text{O}_4\text{P}$: m/z 409.1569 [M^+], found: m/z 409.1563.

(Z)-1,2-diphenyloct-1-ene (23a): ^1H NMR (400 MHz, CDCl_3) δ 7.59 (d, $J = 7.5$ Hz, 1H), 7.44 (t, $J = 7.5$ Hz, 1H), 7.36-7.21 (m, 3H), 7.14 (d, $J = 6.6$ Hz, 2H), 7.09.-7.01 (m, 2H), 6.91 (d, $J = 6.5$ Hz, 1H), 6.42 (s, 1H), 2.48 (t, $J = 7.2$ Hz, 2H), 1.50-1.21 (m, 8H), 0.87 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (400 MHz, CDCl_3) δ 144.0, 141.9, 138.0, 129.4, 129.0, 128.9, 128.2, 127.6, 127.2, 126.4, 41.2, 32.1, 29.3, 28.3, 23.1, 14.5; IR (film) 2928, 1593, 1439, 1187, 962, 693, 541 cm^{-1} ; HRMS (EI) calcd. for $\text{C}_{20}\text{H}_{24}$: m/z 264.1878 [M^+], found: m/z 264.1874.

(Z)-1,2-diphenylhex-1-ene (23b): ^1H NMR (400 MHz, CDCl_3) δ 7.59 (d, $J = 7.3$ Hz, 1H), 7.42 (t, $J = 7.8$ Hz, 1H), 7.30-7.04 (m, 6H), 6.90 (d, $J = 6.4$ Hz, 2H), 6.43 (s, 1H), 2.49 (t, $J = 6.7$ Hz, 2H), 1.41-1.25 (m, 4H), 0.88 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.6, 141.6, 137.5, 129.0, 128.8, 128.6, 127.9, 127.2, 126.1, 40.5, 30.2, 22.4, 14.0, 139.7, 131.4, 128.4, 128.3, 128.0, 127.9, 124.1, 106.0, 91.3, 88.9, 37.8, 30.7, 22.5, 14.1; IR (film) 3153, 2958, 2252, 1791, 1548, 1379, 1219, 906, 732, 650 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{18}\text{H}_{20}\text{Na}$: m/z 259.1463 [M^+], found: m/z 259.1466.

(Z)-octa-1,3-dien-4-yl diphenyl phosphate (22a): ^1H NMR (400 MHz, CDCl_3) δ 7.36-7.17 (m, 10H), 6.57-6.48 (m, 1H), 5.57 (d, $J = 11$ Hz, 1H), 5.15 (d, $J = 17.4$ Hz, 1H), 4.96 (d, $J = 10.5$ Hz, 1H), 2.36 (t, $J = 7.3$ Hz), 1.49-1.42 (m, 2H), 1.34-1.22 (m, 2H), 0.86 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.7 (d, $J_{cp} = 7.7$ Hz), 149.4, 129.9, 129.8, 125.7, 120.4, 120.3, 117.1, 116.1 (d, $J_{cp} = 7.7$ Hz), 34.0, 28.8, 22.2, 13.9; IR (film) 2956, 2929, 1668, 1591, 1489, 1417, 1290, 1217, 1188, 960, 771, 688 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{20}\text{H}_{23}\text{O}_4\text{PNa}$: m/z 381.1232 [M^+], found: m/z 381.1235.

Diphenyl (Z)-1-phenylbuta-1,3-dienyl phosphate (22b): ^1H NMR (400 MHz, CDCl_3) δ 7.54-7.51 (m, 2H), 7.34-7.11 (m, 13H), 6.86-6.35 (m, 1H), 6.33 (d, $J = 1.8$ Hz, 1H), 5.38 (d, $J = 17.4$ Hz, 1H), 5.19 (d, $J = 10.5$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.7 (d, $J = 6.7$ Hz), 145.9, 134.5, 130.3, 129.9, 129.1, 128.6, 125.7 (d, $J = 10.5$ Hz), 120.3 (d, $J = 4.8$ Hz), 117.6 (d, $J = 6.7$ Hz); IR (film) 3043, 2926, 1732, 1643, 1591, 1487, 1456, 1415, 1296, 1217, 1045, 960, 769, 688, 648 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{22}\text{H}_{19}\text{O}_4\text{P}$: m/z 379.1099 $[\text{M}^+]$, found: m/z 379.1105.

1-((Z)-octa-1,3-dien-4-yl)benzene (24a): ^1H NMR (400 MHz, CDCl_3) δ 7.37-7.18 (m, 5H), 6.38-6.28 (m, 1H), 6.12 (d, $J = 11.4$ Hz, 1H), 5.16 (d, $J = 17.4$ Hz, 1H), 4.94 (d, $J = 10.4$ Hz, 1H), 2.42 (t, $J = 7.1$ Hz, 2H), 1.34-1.25 (m, 4H), 0.88 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.7, 140.9, 134.8, 128.8, 128.4, 127.4, 127.0, 126.8, 116.1, 39.0, 30.5, 22.5, 14.1; IR (film) 2925, 1642, 1415, 1217, 961, 769, 688, 647 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{18}$: m/z 187.1490 $[\text{M}^+]$, found: m/z 187.1490.

1-((Z)-deca-1,3-dien-4-yl)benzene (24b): ^1H NMR (400 MHz, CDCl_3) δ 7.36-7.16 (m, 5H), 6.37-6.28 (m, 1H), 6.12 (d, $J = 10.9$ Hz, 1H), 5.18 (dd, $J = 16.9$ Hz, $J = 1.9$ Hz, 1H), 4.94 (dd, $J = 10.1$ Hz, $J = 1.9$ Hz, 1H), 2.41 (t, $J = 7.1$ Hz, 2H), 1.52-1.21 (m, 8H), 0.85 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.6, 140.8, 134.6, 128.6, 128.0,

127.2, 126.8, 115.9, 39.1, 31.7, 28.9, 28.1, 22.6, 14.1; IR (film) 3061, 3034, 2926, 1477, 1429, 1005, 725, 693 cm^{-1} ; HRMS (EI) calcd. for $\text{C}_{16}\text{H}_{22}$: m/z 214.1722 [M^+], found: m/z 214.1722.

7.2.3 Intramolecular Addition of Diphenyl Phosphate to Alkynes

General procedure for alkynyl hydrogen phosphates

Phenyl phosphorodichloridate (665 mg, 0.47 mL, 3.15 mmol) was stirred in THF (2 mL) at 0 °C under nitrogen. A solution of alkynyl alcohol (3.00 mmol) in THF (2 mL) was added dropwise by syringe over 0.5 h and then a solution of triethylamine (364 mg, 0.50 mL, 3.60 mmol) in THF (2 mL) was also added dropwise to the reaction mixture for another 0.5 h. The white reaction mixture was then stirred for an additional 3 h at 0 °C and then warmed to room temperature for 1 h. Water (1 mL) was subsequently added dropwise over 10 min and the resultant reaction mixture was left to stir for an additional 3 h at room temperature. The resulting mixture was concentrated to remove the THF before extracting with CH_2Cl_2 (3x20 mL). The combined organic extracts were dried over anhydrous MgSO_4 and concentrated under reduced pressure to afford the crude material, which was then purified by silica-gel chromatography ($\text{MeOH}/\text{CH}_2\text{Cl}_2$, 1:9).

General procedure for the cyclization of alkynyl hydrogen phosphates

Chlorotriphenylphosphine gold(I) (5 mol%) and silver trifluoromethanesulfonate (5 mol%) were stirred in CH_2Cl_2 (1 mL) at room temperature under a nitrogen atmosphere. A solution of the alkynyl hydrogen phosphate (0.30 mmol) in CH_2Cl_2 (2 mL) was added. The reaction mixture was then allowed to stir for 0.5 h before extracting with CH_2Cl_2 (3x20 mL). The combined organic phases were dried over anhydrous MgSO_4 , filtered,

and concentrated under reduced pressure to afford the crude material, which was then purified by silica-gel chromatography (EtOAc/hexane, 3:7)

Phenyl prop-2-ynyl hydrogen phosphate (29a): ^1H NMR (400 MHz, CDCl_3) δ 2.55 (1H, t, $J = 2.4$ Hz), 4.68 (2H, dd, $J = 10.1, 2.2$ Hz), 7.16–7.34 (5H, m), 8.32 (1H, bs); ^{13}C NMR (400 MHz, CDCl_3) δ 55.8 (d, $J_{\text{C-P}} = 15.3$ Hz), 76.6, 77.2, 120.4 (d, $J_{\text{C-P}} = 19.2$ Hz), 125.4, 129.9, 150.6 (d, $J_{\text{C-P}} = 26.8$ Hz); IR (NaCl, cm^{-1}): 3632, 3295, 3070, 3045, 2941, 2879, 2850, 2626, 2265, 2133, 1719, 1592, 1491, 1456, 1375, 1246, 1208, 1166, 1044, 1025, 997, 948, 906, 852, 814, 769, 738, 690; HRMS (EI) calcd for $\text{C}_9\text{H}_9\text{O}_4\text{PM}^+$ 213.0317, found 213.0316.

But-2-ynyl phenyl hydrogen phosphate (29b): ^1H NMR (400 MHz, CDCl_3) δ 1.83 (3H, t, $J = 2.4$ Hz), 4.67 (2H, m), 4.86 (1H, bs), 7.16–7.34 (5H, m); ^{13}C NMR (400 MHz, CDCl_3) δ 3.8, 56.8 (d, $J_{\text{C-P}} = 19.2$ Hz), 72.9 (d, $J_{\text{C-P}} = 30.6$ Hz), 85.2, 120.4 (d, $J_{\text{C-P}} = 19.2$ Hz), 125.3, 129.8, 150.7 (d, $J_{\text{C-P}} = 26.8$ Hz); IR (NaCl, cm^{-1}): 3302, 3070, 3044, 2944, 2922, 2883, 2853, 2635, 2325, 2243, 1691, 1592, 1492, 1456, 1381, 1374, 1243, 1205, 1164, 1027, 1003, 988, 948, 906, 850, 815, 768, 739, 690; HRMS (EI) calcd for $\text{C}_{10}\text{H}_{11}\text{O}_4\text{PM}^+$ 227.0473, found 227.0476.

But-3-yn-2-yl phenyl hydrogen phosphate (29c): ^1H NMR (400 MHz, CDCl_3) δ 1.28 (3H, d, $J = 5.5$ Hz), 2.34 (1H, s), 2.64 (1H, bs), 5.07 (1H, m), 6.90–7.26 (5H, m); ^{13}C

NMR (400 MHz, CDCl_3) δ 23.7, 65.3, 74.7, 82.4, 120.9, 125.4, 130.1, 151.4 (d, $J_{\text{C-P}} = 15.4$ Hz); IR (NaCl, cm^{-1}): 3617, 3303, 3055, 2987, 2959, 2928, 2855, 1633, 1595, 1489, 1456, 1377, 1342, 1265, 1228, 1166, 1125, 1105, 1089, 1032, 1005, 979, 923, 900, 853, 795, 739, 704, 693; HRMS (EI) calcd for $\text{C}_{10}\text{H}_{11}\text{O}_4\text{PM}^+$ 227.0473, found 227.0482.

But-3-ynyl phenyl hydrogen phosphate (4e): ^1H NMR (400 MHz, CDCl_3) δ 1.99 (1H, s), 2.52 (2H, td, $J = 14.3, 2.8$ Hz), 4.11 (2H, td, $J = 35.4, 7.3$ Hz), 7.12 – 7.30 (5H, m), 12.73 (1H, bs); ^{13}C NMR (400 MHz, CDCl_3) δ 20.5 (d, $J_{\text{C-P}} = 30.6$ Hz), 65.8 (d, $J_{\text{C-P}} = 23.0$ Hz), 70.7, 79.2, 120.2 (d, $J_{\text{C-P}} = 19.2$ Hz), 125.3, 129.6 (d, $J_{\text{C-P}} = 115.0$ Hz), 150.5 (d, $J_{\text{C-P}} = 26.8$ Hz); IR (NaCl, cm^{-1}): 3620, 3296, 3069, 3046, 2965, 2911, 2852, 2636, 2125, 1652, 1590, 1489, 1340, 1259, 1210, 1164, 1079, 1013, 954, 905, 841, 787, 761, 731, 690; HRMS (EI) calcd for $\text{C}_{10}\text{H}_{11}\text{O}_4\text{PM}^+$ 227.0473, found 227.0477.

4-(hydroxy(phenoxy)phosphoryloxy)but-2-ynyl benzoate (29e): ^1H NMR (400 MHz, CDCl_3): δ 4.70 (1H, s), 4.88 (1H, s), 7.08-7.29 (5H, m), 7.42-7.44 (2H, m), 7.54-7.58 (1H, m), 8.02-8.03 (2H, m), 8.39 (1H, bs); ^{13}C NMR (100 MHz, CDCl_3) δ 52.8, 56.0, 77.7, 80.5, 82.6, 120.4, 125.5, 128.7, 129.5, 129.8, 129.9, 130.1, 133.6, 150.6, 166.1; IR (NaCl, cm^{-1}): 3018, 1718, 1593, 1490, 1273, 1026, 754 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{15}\text{O}_6\text{PM}^+$ 347.0685, found 347.0687.

Pent-3-ynyl phenyl hydrogen phosphate (29f): ^1H NMR (400 MHz, CDCl_3) δ (ppm) 1.72 (3H, t, $J = 2.5$ Hz), 2.46 – 2.50 (2H, m), 4.10 (2H, q, $J = 7.53$ Hz), 7.12 – 7.31 (5H, m), 12.61 (1H, br s); ^{13}C NMR (400 MHz, CDCl_3) δ 3.46, 20.78 (d, $J_{\text{C-P}} = 30.5$ Hz), 66.51 (d, $J_{\text{C-P}} = 22.9$ Hz), 73.99 (d, $J_{\text{C-P}} = 72.5$ Hz), 78.00, 120.25 (d, $J_{\text{C-P}} = 15.2$ Hz), 125.17, 129.59 (d, $J_{\text{C-P}} = 114.5$ Hz), 150.64 (d, $J_{\text{C-P}} = 26.7$ Hz); IR (NaCl, cm^{-1}): 3401, 3070, 3045, 2965, 2922, 2857, 1683, 1594, 1489, 1456, 1386, 1345, 1206, 1165, 1076, 1024, 1000, 953, 910, 786, 764, 691; MS (EI): m/z calcd for $\text{C}_{11}\text{H}_{13}\text{O}_4\text{P}(\text{M}^+)$: 240.06; found: 240.84.

4-iodo but-3-ynyl phenyl hydrogen phosphate (29g): ^1H NMR (400 MHz, CDCl_3): δ 2.62 (t, $J = 6.4$ Hz, 2H), 3.71 (t, $J = 6.4$ Hz, 2H), 4.34 (bs, 1H), 7.17-7.33 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 22.8, 65.8, 70.5, 89.2, 120.3, 125.4, 129.9, 150.6; IR (NaCl, cm^{-1}): 3016, 1591, 1489, 1215, 1024, 954, 756 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{10}\text{H}_{10}\text{O}_4\text{PIM}^+$ 352.9440, found 352.9445.

Pent-4-ynyl phenyl hydrogen phosphate (29h): ^1H NMR (400 MHz, CDCl_3) δ 1.82 (2H, t, $J = 6.4$ Hz), 1.94 (1H, s), 2.23 (2H, m), 4.16 (2H, m), 7.11 – 7.30 (5H, m), 12.51 (1H, bs); ^{13}C NMR (400 MHz, CDCl_3) δ 14.6, 28.9 (d, $J_{\text{C-P}} = 26.8$ Hz), 66.8 (d, $J_{\text{C-P}} = 23.0$ Hz), 69.3, 82.8, 120.2 (d, $J_{\text{C-P}} = 19.2$ Hz), 125.1, 129.7, 150.6 (d, $J_{\text{C-P}} = 26.8$ Hz); IR (NaCl, cm^{-1}): 3298, 3066, 3044, 2965, 2924, 2904, 2848, 2616, 2289, 2179, 2119, 1946, 1865, 1708, 1592, 1490, 1457, 1444, 1434, 1392, 1355, 1327, 1240, 1205, 1165, 1092, 1070,

1036, 990, 944, 906, 857, 829, 771, 729, 690; HRMS (EI) calcd for $C_{11}H_{13}O_4PM^+$ 241.0630, found 241.0633.

5-iodopent-4-ynyl phenyl hydrogen phosphate(29i): 1H NMR (400 MHz, $CDCl_3$): δ 1.81-1.89 (2H, m), 2.23-2.26 (2H, m), 4.15-4.20 (2H, m), 7.13-7.32 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.8, 29.1 (d, $J_{C-P} = 26.8$ Hz), 66.9, 69.4, 82.9, 120.3 (d, $J_{C-P} = 15.3$ Hz), 125.2, 129.8, 150.7 (d, $J_{C-P} = 26.8$ Hz); IR (NaCl, cm^{-1}): 3304, 1591, 1490, 1213, 1024, 756 cm^{-1} ; HRMS (EI) calcd for $C_{11}H_{12}O_4PIM^+$ 366.9596, found 366.9600.

Pent-4-yn-2-yl phenyl hydrogen phosphate (29j): 1H NMR (400 MHz, $CDCl_3$) δ 1.39 (3H, d, $J = 6.1$ Hz), 1.99 (1H, s), 2.40 – 2.55 (2H, m), 4.60 (1H, quintet, $J = 6.1$ Hz), 7.11 – 7.30 (5H, m), 11.9 (1H, bs); ^{13}C NMR (400 MHz, $CDCl_3$) δ 20.7 (d, $J_{C-P} = 11.5$ Hz), 27.2 (d, $J_{C-P} = 23.0$ Hz), 71.3, 74.2, 79.4, 120.4 (d, $J_{C-P} = 15.3$ Hz), 125.1, 129.8, 150.9 (d, $J_{C-P} = 26.8$ Hz); IR (NaCl, cm^{-1}): 3298, 3068, 3045, 2981, 2934, 2878, 2123, 1945, 1713, 1591, 1492, 1450, 1386, 1247, 1212, 1164, 1134, 1087, 1013, 999, 944, 905, 803, 766, 735, 691; HRMS (EI) calcd for $C_{11}H_{13}O_4PM^+$ 241.0630, found 241.0634.

1,2,6-dioxaphosphorin,5-hydro-1-phenoxy,1-oxide (31a): 1H NMR (400 MHz, $CDCl_3$): δ 4.85 – 5.01 (2H, m), 5.19-5.22 (1H, m), 6.38-6.46 (1H, m), 7.19 – 7.38 (5H, m); ^{13}C NMR (400 MHz, $CDCl_3$) δ 68.2 (d, $J_{C-P} = 30.6$ Hz), 105.0 (d, $J_{C-P} = 61.0$ Hz), 119.9 (d,

$J_{C-P} = 22.9$ Hz), 125.6, 130.0, 140.5 (d, $J_{C-P} = 38.2$ Hz), 150.1; IR (NaCl, cm^{-1}): 3076, 2968., 2938, 2890, 1661, 1592, 1458, 1384, 1319, 1307, 1220, 1165, 1099, 1072, 1026, 1008, 982, 906, 871, 835, 792, 764, 735, 722; HRMS (EI) calcd for $\text{C}_9\text{H}_9\text{O}_4\text{PM}^+$ 213.0317, found 213.0315.

1,2,6-dioxaphosphorin-5-hydro-3-methyl-1-phenoxy-1-oxide (31b): ^1H NMR (400 MHz, CDCl_3) δ 1.90 (3H, s), 4.77 – 4.93 (3H, m), 7.18 – 7.38 (5H, m); ^{13}C NMR (400 MHz, CDCl_3) δ 20.1 (d, $J_{C-P} = 30.6$ Hz), 67.7 (d, $J_{C-P} = 30.7$ Hz), 99.2 (d, $J_{C-P} = 49.8$ Hz), 120.0 (d, $J_{C-P} = 19.2$ Hz), 125.6, 130.0, 149.5 (d, $J_{C-P} = 34.5$ Hz), 150.3 (d, $J_{C-P} = 30.6$ Hz); IR (NaCl, cm^{-1}): 3071, 2959, 2925, 2889, 1701, 1593, 1490, 1457, 1446, 1429, 1393, 1374, 1316, 1288, 1208, 1180, 1165, 1089, 1069, 1030, 1007, 946, 911, 797, 766, 691; HRMS (EI) calcd for $\text{C}_{10}\text{H}_{11}\text{O}_4\text{PM}^+$ 227.0473, found 227.0475.

1,2,6-dioxaphosphorinane-3-methylbenzoate-1-phenoxy-1-oxide (31c): ^1H NMR (400 MHz, CDCl_3): δ 4.79-4.94 (m, 2H), 4.94-5.02 (m, 2H), 5.42 (d, $J = 2.8$ Hz, 1H), 7.04-7.7.27 (m, 5H), 7.34-7.49 (2H, m), 7.56-7.65 (1H, m), 7.95-7.98 (1H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 62.9 (d, $J_{C-P} = 30.7$ Hz), 67.8, 103.7 (d, $J_{C-P} = 53.7$ Hz), 119.9 (d, $J_{C-P} = 19.2$ Hz), 125.7, 128.7, 129.3, 130.0 (d, $J_{C-P} = 46.0$ Hz), 133.7, 147.0 (d, $J_{C-P} = 34.5$ Hz), 150.1, 165.9; IR (NaCl, cm^{-1}): 3018, 1722, 1490, 1317, 1271, 1215, 1091, 954 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{15}\text{O}_6\text{PM}^+$ 347.0685, found 347.0685.

1,2,6-dioxaphosphorinane-3-methylene-1-phenoxy-1-oxide (31d): ^1H NMR (400MHz, CDCl_3) δ 2.54 (1H, dq, $J = 15.1, 2.9$ Hz), 2.79 – 2.88 (1H, m), 4.43 – 4.53 (2H, m), 4.56 (1H, s), 4.79 (1H, s), 7.18 – 7.38 (5H, m); ^{13}C NMR (400 MHz, CDCl_3) δ 29.6 (d, $J_{\text{C-P}} = 22.9$ Hz), 68.1 (d, $J_{\text{C-P}} = 30.5$ Hz), 98.8 (d, $J_{\text{C-P}} = 30.5$ Hz), 120.1 (d, $J_{\text{C-P}} = 19.1$ Hz), 125.5, 130.0, 150.4 (d, $J_{\text{C-P}} = 30.6$ Hz), 152.7 (d, $J_{\text{C-P}} = 30.5$ Hz); IR (NaCl, cm^{-1}): 3079, 3009, 2976, 2968, 2913, 2854, 1675, 1597, 1590, 1489, 1460, 1426, 1370, 1306, 1249, 1234, 1201, 1187, 1167, 1161, 1074, 1039, 1024, 1013, 1006, 977, 937, 908, 886, 860, 812, 778; HRMS (EI) calcd for $\text{C}_{10}\text{H}_{11}\text{O}_4\text{P}^+$ 227.0473, found 227.0472.

1,3,2-dioxaphosphorinane,4-ethylidene-2-phenoxy-,2-oxide (31e)

1,3,2-dioxaphosphorinane,4-(*E*)-ethylidene-2-phenoxy-,2-oxide: ^1H NMR (400 MHz, CDCl_3) δ (ppm) 1.87 (3H, s), 2.35 – 2.43 (1H, m), 2.55 – 2.64 (1H, m), 4.27 – 4.43 (2H, m), 5.03 – 5.06 (1H, m), 7.18 – 7.38 (5H, m); ^{13}C NMR (400 MHz, CDCl_3) δ 21.07 (d, $J_{\text{C-P}} = 23.0$ Hz), 27.90, 67.78 (d, $J_{\text{C-P}} = 26.8$ Hz), 107.96, 120.09 (d, $J_{\text{C-P}} = 19.2$ Hz), 125.44, 129.96, 147.62 (d, $J_{\text{C-P}} = 38.3$ Hz), 150.62 (d, $J_{\text{C-P}} = 26.8$ Hz); IR (NaCl, cm^{-1}): 3062, 2991, 2958, 2921, 1697, 1592, 1489, 1456, 1448, 1428, 1385, 1365, 1295, 1209, 1159, 1096, 1066, 1044, 1022, 951, 910, 866, 850, 802, 770, 756, 731, 691; MS (EI): m/z calcd for $\text{C}_{11}\text{H}_{13}\text{O}_4\text{P}(\text{M}^+)$ 240.06; found: 240.96.

1,3,2-dioxaphosphorinane,4-(*Z*)-ethylidene-2-phenoxy-,2-oxide: ^1H NMR (400 MHz, CDCl_3) δ (ppm) 1.48 (3H, dd, $J = 6.9, 0.9$ Hz), 2.43 (1H, dq, $J = 15.1, 2.7$ Hz), 2.76 – 2.85 (1H, m), 4.41 – 4.49 (2H, m), 4.91 (1H, qt, $J = 6.9, 2.0$ Hz), 7.17 – 7.38 (5H, m); ^{13}C NMR (400 MHz, CDCl_3) δ (ppm) 9.67, 30.00 (d, $J_{\text{C-P}} = 23.0$ Hz), 68.80 (d, $J_{\text{C-P}} = 30.7$ Hz), 109.02 (d, $J_{\text{C-P}} = 26.8$ Hz), 120.00 (d, $J_{\text{C-P}} = 19.2$ Hz), 125.40, 129.97, 145.71 (d, $J_{\text{C-P}} =$

34.5 Hz), 150.43 (d, $J_{C-P} = 30.6$ Hz); ^{31}P NMR (400 MHz) δ : -14.80; IR (NaCl, cm^{-1}): 3063, 3044, 2968, 2920, 2864, 1707, 1592, 1488, 1457, 1445, 1422, 1382, 1373, 1319, 1302, 1245, 1208, 1178, 1167, 1092, 1065, 1040, 1026, 1005, 990, 972, 943, 916, 897, 807, 772, 757, 716, 690; MS (EI): m/z calcd for $\text{C}_{11}\text{H}_{13}\text{O}_4\text{P}(\text{M}^+)$: 240.06; found: 240.98.

(Z)-1,2,6-dioxaphosphorinane-3-iodomethylene-1-phenoxy-1-oxide (31f): ^1H NMR (400 MHz, CDCl_3): δ 2.68-2.74 (1H, m), 2.84-2.93 (1H, m), 4.38-4.46 (2H, m), 5.65 (1H, s), 7.17-7.37 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 29.9, 60.3 (d, $J_{C-P} = 34.5$ Hz), 67.9, 77.5, 120.3 (d, $J_{C-P} = 19.1$ Hz), 125.7, 130.1, 151.1, 154.0; IR (NaCl, cm^{-1}): 3016, 2924, 1649, 1490, 1315, 1215, 1120, 954 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{10}\text{H}_{10}\text{O}_4\text{PI}$ M^+ 352.9440, found 352.9443.

1,2,7-dioxaphosphorinane,6-methyl-3-methylene-1-phenoxy-1-oxide (31h): ^1H NMR (400 MHz, CDCl_3) δ 1.98 – 2.09 (2H, m), 2.55 – 2.59 (2H, m), 4.25 – 4.45 (2H, m), 4.63 (1H, s), 4.80 (1H, s), 7.17 – 7.49 (5H, m); ^{13}C NMR (400 MHz, CDCl_3) δ 29.8, 32.5, 68.45 (d, $J_{C-P} = 22.9$ Hz), 101.6 (d, $J_{C-P} = 34.3$ Hz), 120.0 (d, $J_{C-P} = 19.1$ Hz), 125.4, 129.9, 150.7 (d, $J_{C-P} = 22.9$ Hz), 153.9 (d, $J_{C-P} = 30.5$ Hz); IR (NaCl, cm^{-1}): 3063, 3045, 2962, 2924, 2852, 1733, 1663, 1592, 1489, 1456, 1437, 1383, 1356, 1335, 1295, 1249, 1209, 1179, 1166, 1086, 1021, 958, 940, 911, 878, 817, 770, 764; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{13}\text{O}_4\text{P}(\text{M}^+)$ 241.0630, found 241.0630.

(Z)-1,2,7-dioxaphosphorinane-6-iodomethyl-3-methylene-1-phenoxy-1-oxide (31i): ^1H NMR (400 MHz, CDCl_3): δ 1.99-2.06 (m, 2H), 2.86 (t, $J = 5.9$ Hz, 2H), 4.24-4.43 (m, 2H), 5.59 (s, 1H), 7.19-7.39 (5H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 29.1, 33.2, 60.9 (d, $J_{\text{C-P}} = 53.7$ Hz), 68.5 (d, $J_{\text{C-P}} = 23.0$ Hz), 120.4 (d, $J_{\text{C-P}} = 19.1$ Hz), 125.7, 129.9, 151.0, 154.0; IR (NaCl, cm^{-1}): 3014, 1645, 1490, 1284, 1215, 1134, 981, 754 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{12}\text{O}_4\text{PIM}^+$ 366.9596, found 366.9591.

1,2,6-dioxaphosphorinane,5-methyl-3-methylene-1-phenoxy-1-oxide (31j)

Compound A (30%) : ^1H NMR (400 MHz, CDCl_3) δ 1.46 (3H, dd, $J = 6.2, 2.5$ Hz), 2.53 (2H, dd, $J = 6.2, 2.1$ Hz), 4.54 (1H, q, $J = 1.1$ Hz), 4.68 (1H, m), 4.76 (1H, d, $J = 1.8$ Hz), 7.17 – 7.37 (5H, m); ^{13}C NMR (400 MHz, CDCl_3) δ 22.0 (d, $J_{\text{C-P}} = 42.2$ Hz), 36.9 (d, $J_{\text{C-P}} = 15.3$ Hz), 76.7 (d, $J_{\text{C-P}} = 30.6$ Hz), 98.9 (d, $J_{\text{C-P}} = 34.5$ Hz), 120.1 (d, $J_{\text{C-P}} = 19.2$ Hz), 125.5, 130.0, 150.5 (d, $J_{\text{C-P}} = 26.8$ Hz), 152.3 (d, $J_{\text{C-P}} = 30.6$ Hz); IR (NaCl, cm^{-1}): 3068, 3044, 2985, 2936, 2900, 2875, 1673, 1592, 1490, 1456, 1447, 1423, 1387, 1343, 1313, 1285, 1245, 1210, 1191, 1164, 1133, 1072, 1033, 1012, 990, 942, 913, 877, 805, 787; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{13}\text{O}_4\text{PM}^+$ 241.0630, found 241.0626.

1,2,6-dioxaphosphorinane,5-methyl-3-methylene-1-phenoxy-1-oxide (6i) Compound

B (50%): ^1H NMR (400 MHz, CDCl_3) δ 1.44 (3H, dd, $J = 6.4, 1.8$ Hz), 2.47 (1H, qd, $J = 8.2, 1.1$ Hz), 2.69 (1H, dt, $J = 15.6, 2.8$ Hz), 4.48 (1H, dt, $J = 5.0, 1.7$ Hz), 4.74 – 4.80 (1H, m), 4.82 (1H, t, $J = 1.6$ Hz), 7.18 – 7.38 (5H, m); ^{13}C NMR (400 MHz, CDCl_3) δ 21.5 (d, $J_{\text{C-P}} = 23.0$ Hz), 35.9 (d, $J_{\text{C-P}} = 30.6$ Hz), 76.5 (d, $J_{\text{C-P}} = 26.8$ Hz), 97.8 (d, $J_{\text{C-P}} = 34.5$ Hz), 120.4 (d, $J_{\text{C-P}} = 19.2$ Hz), 125.6, 129.9, 150.6 (d, $J_{\text{C-P}} = 30.6$ Hz), 151.3 (d, $J_{\text{C-P}} = 26.8$ Hz); IR (NaCl, cm^{-1}): 3058, 2985, 2936, 2875, 2855, 1673, 1593, 1490, 1457, 1426, 1387, 1349, 1302, 1267, 1245, 1213, 1195, 1164, 1131, 1110, 1087, 1071, 1038, 1020, 1009, 991, 941, 930, 912, 905, 877, 871, 800, 775, 735, 702; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{13}\text{O}_4\text{P}^+$ 241.0630, found 241.0629.

(Z)-4-allylidene-2-phenoxy-1,3,2-dioxaphosphinane 2-oxide (33): ^1H NMR (400 MHz, CDCl_3) δ 7.36 – 7.17 (m, 5H), 6.47 (dt, $J = 17.2, 10.5$ Hz, 1H), 5.52 (d, $J = 10.9$ Hz, 1H), 5.18 (d, $J = 17.2$ Hz, 1H), 5.03 (d, $J = 10.4$ Hz, 1H), 4.51-4.44 (m, 2H), 3.02-2.87 (m, 1H), 2.51-2.45 (m, 1H); ^{13}C NMR (400 MHz, CDCl_3) δ 150.2, 145.6 (d, $J_{\text{C-P}} = 7.6$ Hz), 130.0, 128.4, 125.6, 120.2 (d, $J_{\text{C-P}} = 4.8$ Hz), 117.9, 114.6 (d, $J_{\text{C-P}} = 6.7$ Hz), 68.4 (d, $J_{\text{C-P}} = 8.6$ Hz), 29.8 (d, $J_{\text{C-P}} = 5.7$ Hz); IR (NaCl, cm^{-1}): 3052, 2985, 2855, 1673, 1593, 1490, 1457, 1426, 1382, 1345, 1302, 1225, 1195, 1164, 1131, 1115, 1087, 1071, 1038, 1020, 1009, 991, 941, 930, 912, 905, 877, 871, 800, 775; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{13}\text{O}_4\text{P}^+$ 253.0630, found 253.0625.

(Z)-2-phenoxy-4-(3-phenylprop-2-yn-1-ylidene)-1,3,2-dioxaphosphinane 2-oxide (34):

^1H NMR (400 MHz, CDCl_3) δ 7.35-7.22 (m, 1H), 7.12-7.08 (m, 1H), 5.26 (s, 1H), 4.56-4.48 (m, 2H), 2.99-2.91 (m, 1H), 2.57 (dq, $J = 15.4, 2.7$ Hz, 1H); ^{13}C NMR (400 MHz, CDCl_3) δ 154.6 (d, $J_{\text{C-P}} = 7.7$ Hz), 150.2 (d, $J_{\text{C-P}} = 7.7$ Hz), 131.8, 130.0, 128.7, 128.4, 125.7, 123.0, 120.4, 120.3, 95.6, 94.9 (d, $J_{\text{C-P}} = 7.7$ Hz), 81.8, 68.1 (d, $J_{\text{C-P}} = 7.7$ Hz), 29.7 (d, $J_{\text{C-P}} = 6.7$ Hz); IR (NaCl, cm^{-1}): 3058, 2985, 2936, 2875, 2855, 1673, 1593, 1490, 1457, 1426, 1387, 1349, 1302, 1267, 1245, 1213, 1195, 1164, 1131, 1110, 1087, 1071, 1038, 1020, 1009, 991, 941, 930, 912, 905, 877, 871, 800, 775, 735, 702; HRMS (EI) calcd for $\text{C}_{18}\text{H}_{15}\text{O}_4\text{PM}^+$ 327.0786, found 327.0783.

3-phenylbut-3-en-1-ol (36a): ^1H NMR (400 MHz, CDCl_3): δ 7.43-7.24 (m, 5 H), 5.41 (d, $J = 1.2$ Hz, 1 H), 5.16 (d, $J = 1.2$ Hz, 1 H), 3.73 (t, $J = 6.4$ Hz, 2H), 2.79 (t, $J = 6.4$ Hz, 2 H); ^{13}C NMR (100 MHz, CDCl_3): δ 145.0, 140.6, 129.0, 128, 126.4, 114.9, 61.3, 38.7; IR: 3402, 2927, 2865, 1626, 1445, 1040, 703 cm^{-1} ;

4-phenylpent-4-en-1-ol (36b): ^1H NMR (400 MHz, CDCl_3): δ 1.59 (br, 1H), 1.67-1.73 (m, 2H), 2.57 (t, 2H, $J = 6.5$ Hz), 5.09 (d, 2H, $J = 1.3$ Hz), 5.29 (d, 2H, $J = 1.3$ Hz), 7.26-7.33 (m, 3H), 7.35-7.43 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 31.1, 31.5, 62.3, 112.5, 126.1, 127.3, 128.2, 140.9, 147.9;

7.2.4 Typical procedure for $\text{Ph}_3\text{PAuCl}/\text{AgPF}_6$ -catalyzed addition of carboxylic acids to alkynes. To a suspension of Ph_3PAuCl (10 mg, 0.02 mmol), AgPF_6 (5.1 mg, 0.02 mmol) and benzoic acid (50 mg, 0.41 mmol) in toluene (1 mL) was added 1-hexyne (56 μl 0.49 mmol) at room temperature. After being stirred at 60 $^\circ\text{C}$ for 15 h, the solvent was

removed under reduced pressure and the reaction mixture was purified by silica gel column chromatography (EtOAc:hexane = 1:10) to give the title compound.

Hex-1-en-2-yl benzoate (44a): (69 mg, 82%) as a colorless oil ^1H NMR (CDCl_3 , 400 MHz) δ 8.11-8.03 (m, 2H), 7.59-7.53 (m, 1H), 7.47-7.41 (m, 2H), 4.83 (s, 1H), 4.82 (s, 1H), 2.33 (t, $J = 7.6$ Hz, 2H), 1.55-1.48 (m, 2H), 1.42-1.33 (m, 2H), 0.91 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) 164.9, 156.9, 133.4, 130.0, 128.5, 128.4, 101.4, 33.2, 28.8, 22.2, 13.9; IR (film) 3019.9, 1733.5, 1667.4, 1215.6, 1170.0, 1026.6, 707.4, 665.9 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{13}\text{H}_{16}\text{O}_2$ M^+ 227.1048, found 227.1047.

Dec-1-en-2-yl benzoate (44b) : ^1H NMR (400 MHz, CDCl_3): δ 7.94-7.92 (m, 2H), 7.67-7.63 (m, 1H), 7.56-7.52 (m, 2H), 4.71 (s, 1H), 4.63 (s, 1H), 2.10 (t, $J = 7.6$ Hz, 2H), 1.20-1.40 (m, 12H), 0.86 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.6, 136.6, 134.1, 129.3, 128.5, 102.6, 34.3, 32.0, 29.4, 29.3, 28.9, 26.3, 22.8, 14.3; IR (film) 3019.46, 1749.86, 1215.60, 1135.07 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{24}\text{O}_2\text{M}^+$ 261.1855, found 261.1868.

Dec-1-en-2-yl acetate¹ (44c): ^1H NMR (400 MHz, CDCl_3): δ 4.72 (s, 1H), 4.71 (s, 1H), 2.18 (t, $J = 7.5$ Hz 2H), 2.11 (s, 3H), 1.46-1.48 (m, 2H), 1.27-1.32 (m, 10H), 0.86 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 169.4, 156.8, 101.2, 33.5, 32.0, 29.4, 26.6, 22.9, 21.3, 14.3 ; IR (film) 3019.95, 1742.69, 1608.10, 1495.51, 1451.15, 1371.10, 1216.32, cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{22}\text{O}_2\text{M}^+$ 199.1698, found 199.1699.

Dec-1-en-2-yl formate (44d) : ^1H NMR (400 MHz, CDCl_3): δ 8.12 (s, 1H), 4.72 (s, 1H), 4.69 (s, 1H), 2.19 (t, $J = 7.6$ Hz, 2H) 1.43-1.24 (m, 12H), 0.85 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 159.5, 156.6, 100.8, 33.7, 32.0, 29.5, 29.4, 29.1, 26.4, 22.8, 14.3; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{20}\text{O}_2\text{M}^+$ 185.1542, found 185.1535.

Dec-1-en-2-yl-4-Nitro benzoate (44e) : ^1H NMR (400 MHz, CDCl_3): δ 8.33-8.09 (m, 4H), 4.89 (s, 1H), 4.87 (s, 1H), 2.33 (t, $J = 7.6$ Hz, 2H), 1.25-1.54 (m, 12 H), 0.86 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) : 163.3, 156.4, 135.8, 131.1, 123.7, 101.9, 33.3, 31.9, 29.4, 29.3, 29.0, 26.6, 22.7, 14.2; IR (film) 2962, 1943, 1868, 1784, 1732, 1660, 1300, 1189, 958, 688 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{23}\text{NO}_4\text{M}^+$ 306.1705, found 306.1711.

Hex-1-en-2-yl-3-Fluoro benzoate (44f): ^1H NMR (CDCl_3 , 400 MHz) δ 7.88-7.77 (m, 1H), 7.78-7.74 (m, 1H), 7.47-7.42 (m, 1H), 7.32-7.26 (m, 1H), 4.85 (s, 1H), 4.84 (s, 1H), 2.32 (t, $J = 7.6$ Hz, 2H), 1.54-1.46 (m, 2H), 1.40-1.34 (m, 2H), 0.92 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 161.9, 164.6, 156.9, 132.0, 130.3 ($J_{\text{cf}} = 3.4$ Hz), 125.9, 120.6 ($J_{\text{cf}} = 88.12$ Hz), 117.0 ($J_{\text{cf}} = 91.9$ Hz), 101.7, 33.3, 22.3, 14.0; IR (film) 3019.71, 1730.33, 1594.60, 1445.36, 1290.10, 1214.63, 1097.22 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{13}\text{H}_{15}\text{FO}_2\text{M}^+$ 223.1134, found 223.1143.

Hex-1-en-2-yl-4-methoxy benzoate (44g) : ^1H NMR (CDCl_3 , 400 MHz) δ 8.04 (d, $J = 6.8$ Hz, 2H), 6.94 (d, $J = 6.8$ Hz, 2H), 4.83 (s, 1H), 4.82 (s, 1H), 3.88 (s, 3H), 1.55-1.48

(m, 2H), 1.43-1.34 (m, 2H), 0.92 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) 164.8, 163.8, 157.1, 132.2, 122.5, 113.9, 101.4, 55.7, 33.4, 28.9, 22.3, 14.1; IR (film) 3020.67, 1724.55, 1607.13, 1510.46, 1258.27, 1216.32, 1166.90 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{24}\text{H}_{18}\text{O}_3\text{M}^+$ 235.1334, found 235.1330.

Dec-1-en-2-yl – trifluoroacetate (44h) : ^1H NMR (400 MHz, CDCl_3): δ 4.93 (s, 1H), 4.87 (s, 1H), 2.26 (t, $J = 7.8$ Hz, 2H), 1.25-1.48 (m, 12H), 0.87 (t, $J = 5.7$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 155.7, 102.6, 32.7, 31.9, 29.3, 29.2, 28.8, 26.1, 22.7, 14.1; IR (film) 3019.95, 1792.54, 1711.77 1674.16, 1360.01, 1173.65, 1143.75 ; HRMS (EI) calcd for $\text{C}_{10}\text{H}_{19}\text{O}_2\text{F}_3\text{M}^+$ 253.1415, found 253.1410.

4-Phenyl but-1-en-2-yl acetate² (44i): ^1H NMR (400 MHz, CDCl_3): δ 7.30-7.25 (m, 2H), 7.20-7.17 (m, 3H), 4.74 (s, 1H), 4.73(s,1H), 2.79 (t, $J = 7.9$ Hz, 2H), 2.53 (t, $J = 7.9$ Hz, 2H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 169.4, 155.8, 141.0, 128.6, 128.5, 126.3, 102.0, 35.2, 33.1, 21.2; IR (film) 3019.95, 1743.59, 1608.10, 1495.51, 1451.15, 1371.10, 1216.32, ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{14}\text{O}_2\text{M}^+$ 191.1072, found 191.1063.

4-Phenylprop-1-en-2-yl benzoate (44j) : ^1H NMR (400 MHz, CDCl_3): δ 8.08-8.06 (m, 2H), 7.62-7.58 (m, 1H), 7.49-7.45 (m, 2H), 7.30-7.17 (m, 5H), 4.89 (s, 1H) 4.85(s,1H), 2.87 (t, $J = 7.8$ Hz, 2H), 2.76 (t, $J = 7.8$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 165.2, 156.0, 141.5, 133.6, 130.2, 128.7, 128.6, 128.6, 126.3, 102.3, 35.4, 33.2; IR (film)

3019.46, 1727.44, 1509.49, 1215.60 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{16}\text{O}_2\text{M}^+$ 253.1229, found 253.1224.

Oct-1-en-2-yl cinnamate³ (44k): ^1H NMR (400 MHz, CDCl_3): δ 7.79 (d, $J = 15.9$ Hz, 1H), 7.55-7.53 (m, 2H), 7.39-7.38 (m, 3H), 6.47 (d, $J = 15.9$ Hz, 1H), 4.79 (s, 1H), 4.77 (s, 1H), 2.27 (t, $J = 7.6$ Hz, 2H), 1.52-1.27 (m, 8H), 0.87 (t, $J = 6.7$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 165.3, 156.9, 146.0, 134.4, 130.7, 129.1, 128.4, 117.9, 101.3, 33.6, 31.8, 28.9, 26.6, 22.8, 14.3; IR (film) 3018.98, 2929.30, 1715.63, 1637.99, 1215.60, 1155.32; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{22}\text{O}_2\text{M}^+$ 259.1698, found 259.1702.

Oct-1-en-2-yl acrylate (44l): ^1H NMR (400 MHz, CDCl_3): δ 6.47 (dd, $J = 17.2$ Hz, 1H), 6.16 (dd, $J = 17.2$ Hz, 1H), 5.90 (dd, $J = 10.4$ Hz, 1H), 4.76 (s, 1H), 4.75 (s, 1H), 2.23 (t, $J = 7.5$ Hz, 2H), 1.49-1.24 (m, 8H), 0.87 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 164.4, 156.6, 131.9, 128.4, 101.3, 33.5, 31.7, 28.8, 26.6, 22.7, 14.2; IR (film) 3020.19, 1735.88, 1667.41, 1404.62, 1216.08, 1163.04 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{18}\text{O}_2\text{M}^+$ 183.1385, found 183.1391.

1-Phenylvinyl benzoate (44m): ^1H NMR (400 MHz, CDCl_3): δ 8.16-8.20 (m, 2H), 7.67-7.61 (m, 1H), 7.55-7.49 (m, 4H), 7.42-7.28 (m, 3H), 5.59 (d, $J = 2.3$ Hz, 1H), 5.16 (d, $J =$

2.3 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) ; δ 165.0, 153.3, 134.0, 130.4, 129.2, 128.7, 125.1, 102.5; IR (film) 3019.71, 1733.47, 1452.11, 1215.60, 1103.01 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{12}\text{O}_2\text{M}^+$ 225.0916, found 225.0909.

1-Phenylvinyl 2-phenylacetate (44n): ^1H NMR (400 MHz, CDCl_3): δ 7.23-7.94 (m, 10H), 5.45 (s, 1H), 5.01 (s, 1H), 3.82 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 234.7, 153.1, 134.3, 133.6, 129.6, 129.1, 128.8, 128.6, 128.5, 127.6, 125.0, 41.7; IR (film) 3019.95, 1733.47, 1667.41, 1215.60; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{14}\text{O}_2\text{M}^+$ 239.1072, found 239.1088.

(Z)-Styryl 2-Phenylacetate: ^1H NMR (400 MHz, CDCl_3): δ 7.21-7.7.39 (m, 10H), 5.69 (d, $J = 7.3$ Hz, 1H), ^{13}C NMR (100 MHz, CDCl_3): δ 167.9, 134.1, 129.8, 129.3, 129.0, 128.5, 127.8, 127.5.

(Z)-3-Ethoxy-3-oxoprop-1-enyl benzoate (44o) : ^1H NMR (400 MHz, CDCl_3): δ 8.23-8.21 (m, 2H), 7.79(d, $J = 7.0$ Hz, 1H), 7.63-7.59 (m, 1H), 7.49-7.45 (m, 2H), 5.38 (s, 1H), 4.23 (q, $J = 7.2$ Hz, 2H), 1.32 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 164.3, 162.7, 144.7, 134.5, 130.8, 128.9, 128.0, 103.5, 60.5, 14.5; IR (film) 3021.88, 1743.83, 1715.63, 1654.87, 1453.08, 1215.60, 1023.69 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{12}\text{O}_4\text{M}^+$ 221.0814, found 221.0818.

(Z)-Ethyl 3-acetoxy-3-phenylacrylate (44p): ^1H NMR (400 MHz, CDCl_3): δ 7.57-7.55 (m, 2H), 7.41-7.35 (m, 3H), 6.25 (s, 1H), 4.17 (q, $J = 7.2$ Hz, 2H), 2.37 (s, 3H), 1.27 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 168.3, 164.4, 158.2, 133.5, 131.2, 129.0, 126.1, 106.3, 60.5, 21.1, 14.4; IR (film) 3022.12, 1772.28, 1719.73, 1640.16, 1449.22, 1332.05, 1277.80, 1194.38; HRMS (EI) calcd for $\text{C}_{13}\text{H}_{14}\text{O}_4\text{M}^+$ 235.0970, found 235.0980.

(E)-1,2-Diphenylvinyl acetate⁴ (44q): ^1H NMR (400 MHz, CDCl_3): δ 7.54-7.50 (m, 4H), 7.40-7.24 (m, 6H), 6.70 (s, 1H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 168.8, 146.8, 135.7, 134.5, 128.9, 128.8, 127.9, 124.9, 117.0, 21.3; IR (film) 3021.15, 1758.78, 1445.36, 1369.90, 1212.70; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{14}\text{O}_2\text{M}^+$ 239.1072, found 239.1074.

(Z)-1-Phenylprop-1-enyl benzoate⁵ (44r): ^1H NMR (400 MHz, CDCl_3): δ 8.14-8.12 (m, 2H), 7.65-7.12 (m, 8H), 6.06 (s, 1H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 164.3, 146.5, 133.7, 130.4, 130.3, 128.8, 128.7, 128.4, 128.2, 124.5, 117.1, 21.0; ; IR (film) 3021.15, 1758.78, 1445.36, 1369.90, 1212.70; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{14}\text{O}_2\text{M}^+$ 239.1072, found 239.1068.

(Z)-Hex-3-en-3-yl benzoate (44s): ^1H NMR (400 MHz, CDCl_3): δ 8.11-8.09 (m, 2H), 7.59-7.55 (m, 1H), 7.47-7.43 (m, 2H), 5.09 (t, $J = 7.3$ Hz, 1H), 2.29 (q, $J = 7.4$ Hz, 2H),

1.97 (q, $J = 7.5$ Hz, 2H), 1.07 (t, $J = 7.3$ Hz, 3H), 0.94 (t, $J = 7.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 164.6, 149.6, 133.3, 130.0, 130.0, 128.5, 117.2, 26.6, 18.9, 13.9, 11.4; HRMS (EI) calcd for $\text{C}_{13}\text{H}_{16}\text{O}_2\text{M}^+$ 205.1229, found 205.1232.

Typical procedure for the hydroacyloxylation using $\text{Ph}_3\text{PAuCl}/\text{AgOTf}$ catalyst. To a suspension of Ph_3PAuCl (6.1 mg, 0.01 mmol), AgOTf (3.1 mg, 0.01 mmol) and benzoic acid (30 mg, 0.24 mmol) in toluene (1 mL) was added 1-hexyne (34 μL , 0.29 mmol) at room temperature. After being stirred for 15 h, the solvent was evaporated under reduced pressure and the resulting crude product was separated by silica gel column chromatography (EtOAc:hexane = 1:10) to give hex-2-en-2-yl benzoate (diastereomeric ratio 1:3.1, 44 mg, 87%) as a colorless oil.

Hex-2-en-2-yl benzoate (45a): (diastereomeric ratio 1:3.1, 44 mg, 87%) as a colorless oil.

^1H NMR (CDCl_3 , 400 MHz) δ 8.05-8.12(m, 2H), 7.56-7.59 (m, 1H), 7.25-7.46(m, 2H), 5.23 (t, $J = 7.8$ Hz, 1H), 5.09 (t, $J = 7.3$ Hz, 1H), 1.96-1.99(m, 5H), 1.34-1.40 (m, 2H), 0.91 (t, $J = 6.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 165.5, 164.6, 145.8, 145.2, 133.3, 130.1, 128.6, 128.6, 117.8, 117.4, 28.8, 27.7, 22.9, 22.5, 19.8, 15.5, 13.9; IR (film) 3019.9, 1733.5, 1667.4, 1215.6, 1170.0, 1026.6, 707.4, 665.9 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{13}\text{H}_{16}\text{O}_2\text{M}^+$ 205.1229, found 205.1225.

Oct-1-en-2-yl acrylate (45b) (major A): ^1H NMR (400 MHz, CDCl_3): δ 6.45-6.41 (m, 2H), 6.212-6.106 (m, 2H), 5.91-5.85 (m, 2H), 5.02 (t, $J = 6.8$ Hz, 1H), 1.92-1.87 (m, 3H), 1.38-1.20 (m, 8H), 0.894-0.837 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 164.2,

144.7, 131.7, 128.6, 117.4, 31.6, 31.5, 29.2, 25.4, 22.5, 19.5, 14.1; HRMS (EI) calcd for $C_{13}H_{22}O_2M^+$ 183.0082, found 183.0138. (**minor B**): 1H NMR (400 MHz, $CDCl_3$): δ 6.45-6.41 (m, 2H), 6.212-6.106 (m, 2H), 5.91-5.85 (m, 2H), 5.16-5.12 (m, 1H), 2.02 (t, $J = 7.2$ Hz, 1H), 1.92-1.87 (m, 3H), 1.38-1.20 (m, 8H), 0.894-0.837 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 145.7, 131.3, 128.5, 117.9, 31.4, 29.2, 26.6, 22.6, 19.5, 15.2.

Hex-2-en-2-yl-2-phenylacetate (45c) (major A): 1H NMR (400 MHz, $CDCl_3$) δ 7.35-7.24 (m, 5H), 4.95 (t, $J = 7.4$ Hz, 1H), 3.69 (s, 2H), 1.83 (s, 3H), 1.72 (q, $J = 7.4$ Hz, 2H), 1.29-1.19 (m, 2H), 0.77 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.6, 144.9, 133.93, 129.3, 128.7, 127.3, 117.1, 41.5, 27.4, 22.3, 19.5, 15.1, 13.8, 13.7; HRMS (EI) calcd for $C_{14}H_{18}O_2M^+$ 219.1385, found 219.1380. (**minor B**): 1H NMR (400 MHz, $CDCl_3$) δ 7.35-7.24 (m, 5H), 5.085 (t, $J = 7.7$ Hz, 1H), 3.66 (s, 2H), 1.971 (q, $J = 7.4$ Hz, 1H), 1.80 (s, 3H), 1.37 (q, $J = 7.3$ Hz, 1H), 0.89 (t, $J = 7.4$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.6, 145.0, 133.9, 129.3, 128.7, 127.2, 117.5, 41.4, 28.6, 22.7, 19.5, 15.1.

4-Phenylbut-2-en-2-yl acetate (45d) (major isomer A): 1H NMR (400 MHz, $CDCl_3$): δ 7.30-7.16 (m, 5H), 5.18 (t, $J = 7.6$ Hz, 1H), 3.25 (d, $J = 7.3$ Hz, 2H), 2.17 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.1, 145.7, 140.3, 128.7, 128.6, 128.6, 128.4, 126.3, 126.1, 115.9, 31.9, 21.0, 19.7; HRMS (EI) calcd for $C_{12}H_{14}O_2M^+$ 191.1072, found 191.1069. (**minor isomer B**) 1H NMR (400 MHz, $CDCl_3$): δ 7.30-7.16 (m, 5H), 5.32 (t, $J = 7.9$ Hz, 1H), 3.39 (d, $J = 8.2$ Hz, 2H), 2.10 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.0, 146.0, 140.3, 128.6, 126.3, 116.4, 32.8, 21.3, 19.7.

2-acetoxyallyl benzoate (46): ^1H NMR (400 MHz, CDCl_3): δ 8.08-8.04 (m, 2H), 7.59-7.54 (m, 1H), 7.47-7.27 (m, 2H), 5.18 (s, 1H), 5.07 (s, 1H), 4.87 (s, 2H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 169.0, 165.9, 150.2, 133.3, 130.1, 128.7, 105.65, 63.3, 20.9; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{12}\text{O}_4(\text{M}^+)$ 221.0814, found 221.0810.

(Z)-3-acetoxyprop-1-en-1-yl benzoate (47): ^1H NMR (400 MHz, CDCl_3): δ 8.08-8.04 (m, 2H), 7.59-7.54 (m, 1H), 7.47-7.27 (m, 2H), 7.25 (d, $J = 1.4$ Hz, 1H), 5.23-5.20 (m, 1H), 4.98 (d, $J = 6.9$ Hz, 2H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.5, 166.5, 137.1, 133.1, 129.8, 128.5, 107.6, 58.5, 20.7.

(Z)-1-(phenylthio)oct-1-en-1-yl benzoate (48a): ^1H NMR (400 MHz, CDCl_3): δ 8.14-8.11 (m, 2H), 7.62-7.18 (m, 8H), 5.95 (s, 1H), 2.46 (t, $J = 7.32$ Hz, 2H), 1.58-1.53 (m, 2H), 1.39-1.25 (m, 6H), 0.88 (t, $J = 7.32$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 151.8, 135.9, 133.7, 132.5, 130.2, 129.2, 129.1, 128.6, 126.4, 110.2, 34.4, 31.6, 28.8, 26.6, 22.4, 14.3; HRMS (EI) calcd for $\text{C}_{21}\text{H}_{24}\text{O}_2\text{S}(\text{M}^+)$ 341.1575, found 341.1570.

(Z)-1-(phenylthio)oct-1-en-1-yl acetate (48b): ^1H NMR (400 MHz, CDCl_3): δ 7.37-7.20 (m, 5H), 5.83 (s, 1H), 2.32 (t, $J = 7.32$ Hz, 2H), 2.31 (s, 3H), 1.59-1.29 (m, 8H), 0.89 (t, $J = 6.6$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 168.4, 151.8, 135.7, 129.5, 129.3, 129.2,

126.7, 109.9, 34.2, 31.7, 28.9, 26.6, 22.8, 20.9, 14.3; HRMS (EI) calcd for $C_{16}H_{22}O_2S(M^+)$ 279.1419, found 279.1422.

Dec-1-en-2-yl benzenesulfonate (51): 1H NMR (400 MHz, $CDCl_3$): δ 7.96-7.93 (m, 2H), 7.69-7.54 (m, 3H), 4.73 (s, 1H), 4.64 (s, 1H), 2.11 (t, $J = 7.8$ Hz, 2H), 1.67-1.22 (m, 12H), 0.88 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.4, 134.0, 129.1, 128.3, 102.4, 43.9, 34.1, 31.9, 29.4, 29.3, 29.2, 28.8, 22.7, 14.2; HRMS (EI) calcd for $C_{16}H_{24}O_3S(M^+)$ 297.1524, found 297.1530.

Dec-1-en-2-yl methanesulfonate (51a): 1H NMR (400 MHz, $CDCl_3$): δ 5.01 (s, 1H), 4.78 (s, 1H), 3.11 (s, 3H), 2.28 (t, $J = 7.5$ Hz, 2H), 1.58-1.50 (m, 2H), 1.34-1.27 (m, 10H), 0.88 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.4, 101.9, 44.0, 38.0, 34.5, 32.0, 29.5, 29.5, 29.4, 29.0, 26.5, 22.9, 14.3; HRMS (EI) calcd for $C_{11}H_{22}O_3S(M^+)$ 235.1368, found 235.1360.

4-Phenylbut-1-en-2-yl methanesulfonate (51b): 1H NMR (400 MHz, $CDCl_3$): δ 7.31-7.18 (m, 5H), 5.02 (s, 1H), 4.77 (s, 3H), 3.08 (s, 3H), 2.86 (t, $J = 7.8$ Hz, 2H), 2.61 (t, $J = 7.8$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.2, 140.4, 128.7, 128.6, 126.5, 102.8, 37.9, 36.2, 32.8; HRMS (EI) calcd for $C_{11}H_{14}O_3S(M^+)$ 227.0742, found 227.0738.

1-Phenylvinyl methanesulfonate (51c): ^1H NMR (400 MHz, CDCl_3): δ 7.58-7.37 (m, 5H), 5.53 (s, 1H), 5.37 (s, 3H), 3.10 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 152.6, 129.9, 128.9, 125.6, 103.5, 38.4; HRMS (EI) calcd for $\text{C}_9\text{H}_{10}\text{O}_3\text{S}(\text{M}^+)$ 199.0429, found 199.0428.

1-Phenylvinyl benzenesulfonate (51d): ^1H NMR (400 MHz, CDCl_3): δ 7.94-7.92 (m, 2H), 7.63-7.23 (m, 8H), 5.42 (s, 1H), 5.11 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 153.0, 134.3, 129.5, 129.2, 128.6, 128.1, 125.6, 103.5; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{12}\text{O}_3\text{S}(\text{M}^+)$ 261.0585, found 261.0594.

(Z)-Ethyl 3-((methylsulfonyl)oxy)acrylate (51e): ^1H NMR (400 MHz, CDCl_3): δ 6.97 (d, J = 6.8 Hz, 1H), 5.46 (d, J = 6.9 Hz, 1H), 4.20 (q, J = 6.9 Hz, 2H), 3.21 (s, 3H), 1.30 (t, J = 7.1 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 162.9, 144.2, 107.0, 60.8, 38.8, 14.3; HRMS (EI) calcd for $\text{C}_6\text{H}_{10}\text{O}_5\text{S}(\text{M}^+)$ 195.0327, found 195.0334.

3-Hydroxyprop-1-en-2-yl benzenesulfonate (51f): ^1H NMR (400 MHz, CDCl_3): δ 7.97-7.94 (m, 2H), 7.72-7.67 (m, 1H), 7.60-7.56 (m, 2H), 5.02 (s, 1H), 4.85 (s, 3H), 4.07 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 154.2, 135.7, 134.5, 129.4, 128.5, 104.2, 62.3; HRMS (EI) calcd for $\text{C}_9\text{H}_{10}\text{O}_4\text{S}(\text{M}^+)$ 215.0378, found 215.0377.

(E)-Ethyl 3-((methylsulfonyl)oxy)-3-phenylacrylate (51g): ^1H NMR (400 MHz, CDCl_3): δ 7.71-7.69 (m, 2H), 7.46-7.39 (m, 3H), 6.21 (s, 1H), 4.22 (q, J = 7.3 Hz, 2H),

3.37 (s, 3H), 1.31 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 163.6, 156.3, 133.6, 131.5, 129.0, 127.0, 109.3, 60.8, 40.3, 14.3; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{14}\text{O}_5\text{S}(\text{M}^+)$ 271.0640, found 271.0649.

4-((methylsulfonyl)oxy)pent-4-en-1-yl benzoate (51h): ^1H NMR (400 MHz, CDCl_3): δ 8.05-8.03 (m, 2H), 7.58-7.43 (m, 3H), 5.08 (s, 1H), 4.87 (s, 3H), 4.37 (t, $J = 6.4$ Hz, 2H), 3.13 (s, 3H), 2.49 (t, $J = 7.6$ Hz, 2H), 2.07-2.01 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 166.7, 154.8, 133.2, 130.3, 129.7, 128.6, 102.9, 63.7, 38.1, 31.2, 25.7; HRMS (EI) calcd for $\text{C}_{13}\text{H}_{16}\text{O}_5\text{S}(\text{M}^+)$ 285.0797, found 285.0799.

(E)-1-phenylprop-1-en-1-yl methanesulfonate (51i): ^1H NMR (400 MHz, CDCl_3): δ 7.41-7.24 (m, 5H), 5.84-5.80 (m, 2H), 2.87 (s, 3H), 1.85 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 147.0, 134.9, 132.8, 129.3, 128.9, 128.8, 125.7, 117.9, 39.6, 29.8, 12.7; HRMS (EI) calcd for $\text{C}_9\text{H}_{12}\text{O}_3\text{S}(\text{M}^+)$ 201.0585, found 201.0588.

(E)-1,2-diphenylvinyl methanesulfonate (51j): ^1H NMR (400 MHz, CDCl_3): δ 7.46-7.34 (m, 3H), 7.19-7.14 (m, 2H), 6.80 (s, 1H), 2.89 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 146.7, 133.5, 129.9, 129.6, 129.2, 129.0, 128.5, 128.1, 123.2, 39.3; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{14}\text{O}_3\text{S}(\text{M}^+)$ 275.0742, found 275.0743.

7.2.5 Pd-Catalyzed C-H Arylation of Phosphoramidates

General procedure: To an oven dried test tube were added palladium(II) acetate (3.4 mg, 5 mol %), copper(II) oxide (71.6 mg, 0.9 mmol) and diphenyliodonium trifluoromethanesulfonate (154.9 mg, 0.36 mmol) under nitrogen atmosphere. Diethyl arylphosphoramidate (0.3 mmol) in 1,4-dioxane (1.2 mL) was added to the reaction mixture. After being stirred for 5 min, trifluoromethanesulfonic acid (5.3 μ L, 20 mol %) was added to the reaction mixture. The reaction mixture was stirred at room temperature. The reaction mixture was quenched with H₂O and then, aqueous layer was extracted with dichloromethane (3 x 20 mL). The combined organic phases were washed with NaHCO₃ (sat. aq.), dried with MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography.

Diethyl o-tolylphosphoramidate (56a): ¹H NMR (400 MHz, CDCl₃): δ 7.26-7.11 (m, 3H), 6.92 (t, J = 6.9 Hz, 1H), 4.91 (m, 1H), 4.23-4.03 (m, 4H), 2.23 (s, 3H), 1.33-1.30 (m, 6H); ¹³C NMR (400 MHz, CDCl₃) δ 138.2, 130.8, 127.3, 125.2, 122.1, 117.1, 63.1, 17.9, 16.3 (d, J_{C-P} = 7.7 Hz); ³¹P NMR (400 MHz, CDCl₃): δ = 2.8132; IR(film) 3008.95, 1710.86, 1587.42, 1500.62, 1394.53, 1290.38, 1217.08, 1026.13, 977.91, 773.46 cm⁻¹; HRMS (EI) calcd for C₁₁H₁₈NO₃PM⁺ 244.1103, found 244.1099.

Diethyl (3-methyl-[1,1'-biphenyl]-2-yl)phosphoramidate (57a): ¹H NMR (400 MHz, CDCl₃): δ 7.44-7.357.32 (m, 5H), 7.20 (d, J = 6.8 Hz, 1H), 7.10 (dt, J = 7.6, 6.7 Hz, 2H), 4.36 (d, J = 4.1 Hz, 1H), 3.85-3.79 (m, 2H), 3.67-3.61 (m, 2H), 2.49 (s, 3H), 1.12 (t, J = 7.1 Hz, 3H); ¹³C NMR (400 MHz, CDCl₃) δ 140.7, 139.5, 135.8, 134.4, 130.8, 129.8,

128.5, 127.1, 125.4, 62.6, 19.8, 16.4; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 4.1008$; IR (film) 3018.60, 2399.45, 1471.69, 1442.75, 1215.15, 1029.99, 972.12, 756.10, 669.30 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{22}\text{NO}_3\text{P}^+$ 320.1416, found 320.1415.

Diethyl phenylphosphoramidate (56b): ^1H NMR (400 MHz, CDCl_3): δ 7.26-7.22(m, $J = 13.1, 5.3$ Hz, 1H), 7.02 (d, $J = 8.7$ Hz, 1H), 6.94 (t, $J = 7.3$ Hz, 1H), 6.75 (m, 1H), 4.23-4.03 (m, 4H), 1.31 (q, $J = 7.3$ Hz, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 140.1, 129.4, 121.5, 117.4 (d, $J_{\text{C-P}} = 7.7$ Hz), 62.8 (d, $J_{\text{C-P}} = 3.8$ Hz), 16.2 (d, $J_{\text{C-P}} = 6.7$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 2.8947$; IR (film) 3197.98, 2987.74, 2908.65, 1710.86, 1604.77, 1500.62, 1419.61, 1288.45, 1220.94, 1033.85, 773.46 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{10}\text{H}_{16}\text{NO}_3\text{P}^+$ 230.0946, found 230.0946.

Diethyl [1,1'-biphenyl]-2-ylphosphoramidate (57b): ^1H NMR (400 MHz, CDCl_3): δ 7.48-7.26 (m, 6H), 7.19-7.16 (m, 3H), 5.25 (d, $J = 8.7$ Hz, 1H), 4.19-4.05 (m, 4H), 1.32 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (400 MHz, CDCl_3) δ 147.1, 138.3, 131.6, 130.7, 129.5, 129.4, 128.8, 128.4, 128.2, 121.8, 116.9, 63.1 (d, $J_{\text{C-P}} = 4.8$ Hz), 16.3 (d, $J_{\text{C-P}} = 7.7$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 2.4345$; IR (film) 3018.60, 1712.79, 1361.74, 1224.80, 1089.78, 756.10 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{20}\text{NO}_3\text{P}^+$ 306.1259, found 306.1262.

Diethyl (2-benzylphenyl)phosphoramidate (56c): ^1H NMR (400 MHz, CDCl_3): δ 7.31-7.14 (m, 8H), 6.98 (t, $J = 7.34$ Hz, 1H), 4.88 (d, $J = 8.2$ Hz, 1H), 4.87-3.87 (m, 6H),

1.25-1.21 (m, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 138.7, 138, 131.2, 129, 128.6, 128.3, 128.2, 128, 126.9, 122.3, 118.4, 62.9 (d, $J_{\text{C-P}} = 4.8$ Hz), 38.3, 16.2 (d, $J_{\text{C-P}} = 7.7$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 2.7320$; IR (film) 3203.76, 2981.95, 2243.21, 1496.76, 1392.61, 1290.38, 1232.51, 1026.13, 908.47, 732.95 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{22}\text{NO}_3\text{PM}^+$ 320.1416, found 320.1413.

Diethyl (3-benzyl-[1,1'-biphenyl]-2-yl)phosphoramidate (57c): ^1H NMR (400 MHz, CDCl_3): δ 7.39-7.10 (m, 13H), 4.26 (s, 3H), 3.76-3.69 (m, 2H), 3.56-3.50 (m, 2H), 1.08 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 140.9, 140.8, 140.7, 139.3, 133.9, 130.3, 129.9, 129.5, 129.2, 128.8, 128.5, 128.3, 127.1, 126.4, 126.3, 62.7 (d, $J_{\text{C-P}} = 6.7$ Hz), 38.6, 16.2 (d, $J_{\text{C-P}} = 7.7$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 4.1008$; IR (film) 3018.60, 1710.86, 1433.11, 1217.08, 1029.99, 970.19, 775.38, 702.09, 667.37 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{23}\text{H}_{26}\text{NO}_3\text{PM}^+$ 396.1729, found 396.1728.

Diethyl m-tolylphosphoramidate (56d): ^1H NMR (400 MHz, CDCl_3): δ 7.14-7.10 (m, 1H), 6.85-6.75 (m, 3H), 4.22-4.03 (m, 4H), 2.30 (s, 3H), 1.34-1.29 (m, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 140.3, 139.3, 129.2, 122.5, 118.2, 118.1 (d, $J_{\text{C-P}} = 7.7\text{Hz}$), 114.5 (d, $J_{\text{C-P}} = 6.7\text{Hz}$), 62.8, 21.7, 16.2 (d, $J_{\text{C-P}} = 30.7\text{Hz}$); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 2.1978$; IR (film) 3184.48, 2989.66, 1710.86, 1610.56, 1485.19, 1392.61, 1296.16, 1172.72, 1024.20, 975.98, 881.47 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{18}\text{NO}_3\text{PM}^+$ 244.1103, found 244.1100.

Diethyl (4-methyl-[1,1'-biphenyl]-2-yl)phosphoramidate (57d): ^1H NMR (400 MHz, CDCl_3): δ 7.47-7.39 (m, 2H), 7.39-7.33 (m, 3H), 7.16 (s, 1H), 7.06 (dd, $J = 1.4, 7.4\text{Hz}$, 1H), 6.84 (d, $J = 7.8\text{Hz}$, 1H), 5.17 (d, $J = 8.7\text{Hz}$, 1H), 4.19-4.05 (m, 4H), 2.37 (s, 3H), 1.34-1.31 (m, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 138.7, 138.2, 136.4, 130.4, 129.3, 127.9, 122.5, 117.3, 62.9 (d, $J_{\text{C-P}} = 19.2\text{ Hz}$), 21.6, 16.2 (d, $J_{\text{C-P}} = 26.8\text{ Hz}$); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 2.5194$; IR (film) 3385.07, 2999.31, 1616.35, 1517.98, 1487.12, 1388.75, 1253.73, 1022.27, 977.91, 815.89 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{22}\text{NO}_3\text{PM}^+$ 320.1416, found 320.1419.

Diethyl (4-(tert-butyl)phenyl)phosphoramidate (56e): ^1H NMR (400 MHz, CDCl_3): δ 7.26-7.23 (m, 2H), 6.96-6.94 (m, 2H), 6.44 (m, 1H), 4.20-4.05 (m, 4H), 1.33-1.26 (m, 15H); ^{13}C NMR (400 MHz, CDCl_3) δ 144.3, 137.4, 126.2, 117.1 (d, $J_{\text{C-P}} = 7.7\text{ Hz}$), 62.8 (d, $J_{\text{C-P}} = 4.8\text{ Hz}$), 34.2, 31.6, 16.3 (d, $J_{\text{C-P}} = 6.7\text{ Hz}$); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 3.4039$; IR (film) 2991.59, 1512.19, 1394.53, 1217.08, 1029.99, 979.84, 829.39, 752.24 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{24}\text{NO}_3\text{PM}^+$ 286.1572, found 286.1574.

Diethyl (5-(tert-butyl)-[1,1'-biphenyl]-2-yl)phosphoramidate (57e): ^1H NMR (400 MHz, CDCl_3): δ 7.49-7.15 (m, 8H), 5.13 (d, $J = 8.7\text{Hz}$, 1H), 4.19-4.04 (m, 4H), 1.34-1.27

(m, 15H), 1.33-1.26 (m, 15H); ^{13}C NMR (400 MHz, CDCl_3) δ 144.6, 138.9, 134.1, 130.3, 130.2, 130.1, 129.5, 129.4, 128.4, 128, 127.6, 125.7, 116.5, 63 (d, $J_{\text{C-P}} = 5.7$ Hz), 34.4, 31.6 (d, $J_{\text{C-P}} = 12.4$ Hz), 16.3 (d, $J_{\text{C-P}} = 7.7$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 2.7320$; IR (film) 3016.67, 1710.86, 1506.41, 1489.05, 1363.67, 1215.15, 1026.13, 975.98 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{20}\text{H}_{28}\text{NO}_3\text{PM}^+$ 362.1885, found 362.1882.

Diethyl (3-methoxyphenyl)phosphoramidate (56f): ^1H NMR (400 MHz, CDCl_3): δ 7.15-7.11 (m, 1H), 7.04 (d, $J = 9.6\text{Hz}$, 1H), 6.65-6.63 (m, 2H), 6.49 (dd, $J = 8.2, 2.3\text{Hz}$, 1H), 4.22-4.03 (m, 4H), 3.77 (s, 3H), 1.31 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 160.5, 141.4, 130, 110.1 (d, $J_{\text{C-P}} = 7.7\text{Hz}$), 106.8, 103.5 (d, $J_{\text{C-P}} = 7.7\text{Hz}$), 62.8 (d, $J_{\text{C-P}} = 4.5$ Hz), 55.3, 16.2 (d, $J_{\text{C-P}} = 6.7\text{Hz}$); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 2.8402$; IR (film) 2985.81, 1710.86, 1608.63, 1506.41, 1394.53, 1292.31, 1159.22 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{18}\text{NO}_4\text{PM}^+$ 260.1052, found 260.1048.

Diethyl (4-methoxy-[1,1'-biphenyl]-2-yl)phosphoramidate (57f): ^1H NMR (400 MHz, CDCl_3): δ 7.46-7.32 (m, 5H), 7.10-7.08 (m, 1H), 6.92 (d, $J = 2.3\text{Hz}$, 1H), 6.58 (dd, $J = 8.7, 2.3\text{Hz}$, 1H), 5.13 (d, $J = 9.2\text{Hz}$, 1H), 4.19-4.06 (m, 4H), 3.83 (s, 3H), 1.33 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 160.1, 138.1, 137.7, 131.4, 129.6, 129.5, 127.9, 123.5 (d, $J_{\text{C-P}} = 11.5$ Hz), 107.1, 103, 63.1 (d, $J_{\text{C-P}} = 5.8$ Hz), 55.5, 16.3 (d, $J_{\text{C-P}} = 7.7$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 2.2782$; IR (film) 3388.93, 2995.45, 1712.79, 1614.42, 1517.98, 1487.12, 1392.61, 1253.73, 1168.86, 1024.20, 756.10, 705.95 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{22}\text{NO}_4\text{PM}^+$ 336.1365, found 336.1364.

Diethyl (4-methoxyphenyl)phosphoramidate (56g): ^1H NMR (400 MHz, CDCl_3): δ 6.99-6.96 (m, 2H), 6.82-6.78 (m, 2H), 6.42 (m, 1H), 4.21-4.02 (m, 4H), 3.75 (s, 3H), 1.32-1.28 (m, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 154.7, 133.3, 119 (d, $J_{\text{C-P}} = 7.7$ Hz), 114.7, 62.7 (d, $J_{\text{C-P}} = 4.8$ Hz), 55.7, 16.2 (d, $J_{\text{C-P}} = 7.7$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 3.6452$; IR (film) 3199.91, 2989.66, 2835.36, 1514.12, 1394.53, 1284.59, 1242.16, 1180.44, 1028.06, 829.39, 748.38 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{18}\text{NO}_4\text{P}^+$ 260.1052, found 260.1056.

Diethyl (5-methoxy-[1,1'-biphenyl]-2-yl)phosphoramidate (57g): ^1H NMR (400 MHz, CDCl_3): δ 7.49-7.34 (m, 4H), 7.27-7.25 (m, 2H), 6.87-6.83 (m, 1H), 6.76-6.75 (m, 1H), 4.96 (d, $J = 8.7\text{ Hz}$, 1H), 4.17-4.02 (m, 4H), 3.78 (s, 3H), 1.34-1.29 (m, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 155, 138.6, 129.5, 129.3, 128.2, 120.4, 118.6, 116.2, 114.5, 63.0, 56.0, 16.2; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 3.0025$; IR (film) 2422.59, 2252.86, 1479.40, 1382.96, 912.33 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{22}\text{NO}_4\text{P}^+$ 336.1365, found 336.1365.

Diethyl (4-phenoxyphenyl)phosphoramidate (56h): ^1H NMR (400 MHz, CDCl_3): δ 7.32-7.28 (m, 2H), 7.26-6.92 (m, 7H), 6.36 (d, $J = 6.4\text{ Hz}$, 1H), 4.24-4.06 (m, 4H), 1.32 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 158.3, 151.4, 135.9, 129.8, 122.8, 120.6, 118.9 (d, $J_{\text{C-P}} = 6.7$ Hz), 62.9 (d, $J_{\text{C-P}} = 4.8$ Hz), 16.3 (d, $J_{\text{C-P}} = 6.7$ Hz); ^{31}P NMR (400

MHz, CDCl_3): $\delta = 3.1091$; IR (film) 3178.69, 2991.59, 1589.34, 1506.41, 1487.12, 1394.53, 1217.08, 1026.13, 773.46 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{20}\text{NO}_4\text{PM}^+$ 322.1208, found 322.1209.

Diethyl (5-phenoxy-[1,1'-biphenyl]-2-yl)phosphoramidate (57h): ^1H NMR (400 MHz, CDCl_3): δ 7.47-7.26 (m, 7H), 7.08-6.88 (m, 6H), 5.10 (d, $J = 8.7\text{ Hz}$, 1H), 4.19-4.06 (m, 4H), 1.32 (t, $J = 6.6\text{ Hz}$, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 158, 151.5, 137.8, 132.5, 129.9, 129.5, 129.3, 128.4, 123.1, 121.5, 119.6, 118.4, 63.1 (d, $J_{\text{C-P}} = 4.8\text{ Hz}$), 16.3 (d, $J_{\text{C-P}} = 7.7\text{ Hz}$); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 2.5999$; IR (film) 3387.00, 3016.67, 1593.20, 1487.12, 1386.82, 1219.01, 1024.20, 977.91, 756.10, 667.37 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{22}\text{H}_{24}\text{NO}_4\text{PM}^+$ 398.1521, found 398.1520.

Diethyl (3,4-dimethoxyphenyl)phosphoramidate (56i): ^1H NMR (400 MHz, CDCl_3): δ 6.75 (d, $J = 8.7\text{ Hz}$, 1H), 6.69-6.67 (m, 1H), 6.57 (dd, $J = 8.7, 2.8\text{ Hz}$, 1H), 4.22-4.06 (m, 4H), 3.83 (d, $J = 8.7\text{ Hz}$, 5H), 1.31 (t, $J = 7.1\text{ Hz}$, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 149.5, 144.1, 133.7, 112.3, 109.2 (d, $J_{\text{C-P}} = 6.7\text{ Hz}$), 102.8 (d, $J_{\text{C-P}} = 7.7\text{ Hz}$), 62.7, 56.3, 55.9, 16.2 (d, $J_{\text{C-P}} = 6.7\text{ Hz}$); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 3.8596$; IR (film) 2985.81, 1712.79, 1600.92, 1517.98, 1394.53, 1224.80, 1166.93, 1028.06, 754.17 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{20}\text{NO}_5\text{PM}^+$ 290.1157, found 290.1159.

Diethyl (4,5-dimethoxy-[1,1'-biphenyl]-2-yl)phosphoramidate (57i): ^1H NMR (400 MHz, CDCl_3): δ 7.48-7.44 (m, 2H), 7.39-7.34 (m, 3H), 7.00 (s, 1H), 6.72 (d, $J = 1.0$ Hz, 1H), 5.03 (d, $J = 8.7$ Hz, 1H), 4.19 – 4.05 (m, 4H), 3.90 (d, $J = 4.6$ Hz, 2H), 3.84 (s, 1H), 1.32 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (400 MHz, CDCl_3) δ 149.1, 144.1, 138.2, 130.1, 129.6, 129.5, 127.9, 122.7, 113.9, 102.2, 63.0, 56.5, 56.2, 16.4 (d, $J_{\text{C-P}} = 7.7$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 2.8411$; IR (film) 3018.60, 1710.86, 1517.98, 1490.97, 1442.75, 1215.15, 1024.20, 756.10, 667.37 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{18}\text{H}_{24}\text{NO}_5\text{P}^+$ 366.1470, found 366.1472.

Diethyl (3-bromo-4-methylphenyl)phosphoramidate (56j): ^1H NMR (400 MHz, CDCl_3): δ 7.29-7.25 (m, 1H), 7.11-7.05 (m, 1H), 7.05-7.02 (m, 1H), 6.94-6.91 (m, 1H), 4.25-4.06 (m, 4H), 2.33 (s, 3H), 1.36-1.33 (m, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 139.2, 131.2, 130.7, 125.3, 121.2 (d, $J_{\text{C-P}} = 7.7\text{Hz}$), 116.6 (d, $J_{\text{C-P}} = 7.7\text{Hz}$), 63, 22.1, 16.3 (d, $J_{\text{C-P}} = 26.8$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 2.8673$; IR (film) 3298.66, 1608.63, 1496.76, 1292.31, 1215.15, 1026.13, 983.70, 756.10, 667.37 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{17}\text{NO}_3\text{P}^{79}\text{BrM}^+$ 322.0208, found 322.0201, $\text{C}_{11}\text{H}_{17}\text{NO}_3\text{P}^{81}\text{BrM}^+$ 324.0187, found 324.0183.

Diethyl (4-bromo-5-methyl-[1,1'-biphenyl]-2-yl)phosphoramidate (57j): ^1H NMR (400 MHz, CDCl_3): δ 7.51 (s, 1H), 7.47-7.30 (m, 5H), 7.03 (s, 1H), 5.09 (d, $J = 8.7\text{Hz}$, 1H), 4.19-4.05 (m, 4H), 2.34 (s, 3H), 1.34 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 137, 135.9, 132.4, 131, 129.6, 129.2, 128.4, 124.4, 120.6, 63.3, 22.1, 16.3 (d,

$J_{C-P} = 7.7$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 1.8935$; IR (film) 3016.67, 1730.15, 1606.70, 1564.27, 1483.26, 1367.53, 1215.15, 1026.13, 975.98, 756.10, 669.30 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{21}\text{NO}_3\text{P}^{81}\text{BrM}^+$ 400.0500, found 400.0493.

Diethyl 4-bromo-3-methylphenylphosphoramidate (56k): white solid; m.p = 70.1-71.0 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.36 (d, $J = 8.57$ Hz, 1H), 6.9 (d, $J = 2.7$ Hz, 1H), 6.82 (d, $J = 9.4$ Hz, 1H), 6.75 (dd, $J = 8.6$ Hz, 2.7 Hz, 1H), 4.22-4.02 (m, 4H), 2.34 (s, 3H), 1.31 (td, $J = 7.1$ Hz, 0.7 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 139.4, 138.6, 132.7, 119.6 (d, $J_{C-P} = 8$ Hz), 116.39, 116.38 (d, $J_{C-P} = 7$ Hz), 62.7 (d, $J_{C-P} = 4.8$), 23.0, 16.1 (d, $J_{C-P} = 7.0$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 2.27; IR (film) 3174, 2982, 1602, 1476, 1228, 1028 cm^{-1} ; HRMS (EI) calcd. for $\text{C}_{11}\text{H}_{17}\text{BrNO}_3\text{P}$ (M^+) 321.0129, found 321.0132.

Diethyl 5-bromo-4-methylbiphenyl-2-ylphosphoramidate (57k) $R_f = 0.35$ (EtOAc: Hexane = 1:1); brown oil; ^1H NMR (400 MHz, CDCl_3): 7.49-7.45 (m, 2H), 7.42-7.38 (m, 1H), 7.34-7.31 (m, 3H), 7.22 (s, 1H), 5.12 (d, $J = 8.5$ Hz, 1H), 4.21-4.03 (m, 4H), 2.41 (s, 3H), 1.33 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.0, 136.7, 135.8, 133.6, 130.0 (d, $J_{C-P} = 1.0$ Hz), 129.4, 129.1, 128.3, 118.9, 116.7, 63.0 (d, $J_{C-P} = 5.0$ Hz), 23.0, 16.1 (d, $J_{C-P} = 7.0$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 1.43; IR (film) 3396, 2981, 1556, 1482, 1371, 1252, 1024, 973, 770, 710, 644 cm^{-1} ; HRMS (EI) calcd. for $\text{C}_{17}\text{H}_{21}\text{BrNO}_3\text{P}$ (M^+) 397.0442, found 397.0446.

Methyl o-tolyl o-tolylphosphoramidate (56l): ^1H NMR (400 MHz, CDCl_3): δ 7.35 (d, J = 8.2 Hz, 1H), 7.24 (d, J = 8.7 Hz, 1H), 7.17-7.02 (m, 5H), 6.95 (t, J = 7.5 Hz, 1H), 5.16 (d, J = 9.2 Hz, 1H), 3.88 (d, J = 11.9 Hz, 3H), 2.21 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (400 MHz, CDCl_3) δ 149.4, 137.3, 131.6, 130.9, 129.5, 127.4, 127.2, 126.3, 125.2, 122.9, 119.9, 118.3, 53.8 (d, $J_{\text{C-P}}$ = 21.1 Hz), 17.9, 16.5; ^{31}P NMR (400 MHz, CDCl_3): δ = 0.1893; IR (film) 3010.88, 1710.86, 1587.42, 1494.83, 1396.46, 1290.38, 1242.16, 1178.51, 1111.00, 1045.42, 975.98 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{20}\text{NO}_3\text{P}^+$ 306.1259, found 306.1261.

Methyl o-tolyl (3-methyl-[1,1'-biphenyl]-2-yl)phosphoramidate (57l): ^1H NMR (400 MHz, CDCl_3): δ 7.41-6.96 (m, 12H), 4.71 (d, J = 6.0 Hz, 1H), 3.17 (d, J = 11.9 Hz, 3H), 2.49 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (400 MHz, CDCl_3) δ 149.7, 140.7, 136.6, 133.6, 131.3, 130.6, 129.8, 128.9, 128.5, 127.3, 127, 124.7, 120, 53.9, 19.6, 16.1; ^{31}P NMR (400 MHz, CDCl_3): δ = 0.8309; IR (film) 3016.67, 2399.45, 1587.42, 1492.90, 1224.80, 1112.93, 1049.28, 960.55, 756.10, 667.37 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{22}\text{H}_{24}\text{NO}_3\text{P}^+$ 382.1572, found 382.1566.

Diethyl (3-methyl-[1,1':2',1''-terphenyl]-2-yl)phosphoramidate (58): ^1H NMR (400 MHz, CDCl_3): δ 7.45-7.42 (m, 4H), 7.27-7.09 (m, 1H), 3.81-3.75 (m, 2H), 3.65-3.43 (m, 3H), 3.41-3.41 (m, 1H), 2.26 (s, 3H), 1.26-1.10 (m, 3H), 1.04 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (400 MHz, CDCl_3) δ 141.5, 140.5, 139.5, 138.3, 136.8, 133.9, 131.7, 130.2, 129.5, 128.3, 127.8, 127.5, 126.1, 62.4, 19.5, 16.2; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 3.8951$; IR (film) 2985.81, 1940.39, 1712.79, 1494.83, 1392.61, 1292.31, 1192.01, 748.38, 665.44 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{23}\text{H}_{26}\text{NO}_3\text{P}^+$ 396.1729, found 396.1721.

Diethyl methyl(phenyl)phosphoramidate (59a): ^1H NMR (400 MHz, CDCl_3): δ 7.32-7.27 (m, 4H), 7.10-7.05 (m, 1H), 4.15-3.99 (m, 4H), 4.19 (d, $J = 9.2$ Hz, 3H), 1.28 (t, $J = 7.2$ Hz, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 144.2 (d, $J_{\text{C-P}} = 4.8$ Hz), 128.9, 123.7, 122 (d, $J_{\text{C-P}} = 4.8$ Hz), 62.7 (d, $J_{\text{C-P}} = 5.7$ Hz), 36.9 (d, $J_{\text{C-P}} = 4.8$ Hz), 16.1 ((d, $J_{\text{C-P}} = 7.7$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 6.3254$; IR (film) 2985.81, 1940.39, 1712.79, 1600.92, 1494.83, 1392.61, 1292.31, 1192.01, 748.38, 694.37, 665.44 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{18}\text{NO}_3\text{P}^+$ 244.1103, found 244.1105.

Diethyl [1,1'-biphenyl]-2-yl(methyl)phosphoramidate (60a): ^1H NMR (400 MHz, CDCl_3): δ 7.50-7.26 (m, 9H), 3.97-3.81 (m, 4H), 2.72 (d, $J = 9.6$ Hz, 3H), 1.23 (m, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 142.4, 140.4, 131.5, 129.5, 128.6, 128.15, 127.2, 127,

62.8, 38.6, 16.4 (d, $J_{C-P} = 6.7$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 6.5934$; IR (film) 3016.67, 2399.45, 1479.40, 1436.97, 1392.61, 1215.15, 1029.99, 966.34 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{22}\text{NO}_3\text{P}^+$ 320.1416, found 320.1412.

Diethyl methyl(p-tolyl)phosphoramidate (59b): ^1H NMR (400 MHz, CDCl_3): δ 7.16 (d, $J = 8.2\text{Hz}$, 2H), 7.10 (d, $J = 8.7\text{Hz}$, 2H), 4.16-3.97 (m, 4H), 3.16 (d, $J = 8.8\text{Hz}$, 3H), 2.31 (s, 3H), 1.28 (m, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 141.7, 133.6, 129.7, 122.7 (d, $J_{C-P} = 3.8$ Hz), 62.7 (d, $J_{C-P} = 4.8$ Hz), 37.4 (d, $J_{C-P} = 4.8$ Hz), 20.9, 16.2 (d, $J_{C-P} = 7.7$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 6.8615$; IR (film) 2987.74, 1514.12, 1294.24, 1192.01, 1026.13, 968.27, 908.47, 754.17 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{20}\text{NO}_3\text{P}^+$ 258.1259, found 258.1256.

Diethyl methyl(5-methyl-[1,1'-biphenyl]-2-yl)phosphoramidate (60b): ^1H NMR (400 MHz, CDCl_3): δ 7.49-7.47 (m, 2H), 7.40-7.14 (m, 4H), 7.12 (d, $J = 8.2\text{Hz}$, 2H), 3.95-3.78 (m, 4H), 2.72 (d, $J = 9.6\text{Hz}$, 3H), 2.35 (s, 3H), 1.21 (t, $J = 7.3$ Hz, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 140.8, 140.5, 139.5, 136.7, 132.1, 129.5, 129.3, 128.6, 128.1, 127.1, 62.6 (d, $J_{C-P} = 5.7$ Hz), 38.7, 21.2, 16.4 (d, $J_{C-P} = 6.7$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 6.8883$; IR (film) 2991.59, 1710.86, 1363.67, 1217.08, 1028.06, 966.34, 769.60 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{18}\text{H}_{24}\text{NO}_3\text{P}^+$ 334.1572, found 334.1571.

Diethyl (3-methoxyphenyl)(methyl)phosphoramidate (59c): ^1H NMR (400 MHz, CDCl_3): δ 7.20 (t, $J = 8.2$ Hz, 1H), 6.86 (m, 2H), 6.61 (dd, $J = 8.2, 2.3$ Hz, 1H), 4.17-3.97 (m, 4H), 3.79 (s, 1H), 3.20 (d, $J = 8.7$ Hz, 1H), 1.28 (t, $J = 7.3$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.2, 145.6, 129.6, 114.2, 108.7, 108.1 (d, $J = 3.8$ Hz), 62.8 (d, $J = 5.7$ Hz), 55.4, 36.9 (d, $J = 4.8$ Hz), 16.2 (d, $J = 7.7$ Hz); ^{31}P NMR (162 MHz, CDCl_3): $\delta = 6.38$; IR (film) 2989, 1602, 1496, 1284, 1251, 1165, 1026, 833, 752 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{20}\text{NO}_4\text{P}(\text{M}^+)$ 274.1208, found 274.1205.

Diethyl (4-methoxy-[1,1'-biphenyl]-2-yl)(methyl)phosphoramidate (60c) : ^1H NMR (400 MHz, CDCl_3): δ 7.47-7.45 (m, 2H), 7.39-7.35 (m, 2H), 7.31-7.21 (m, 2H), 6.98 (dd, $J = 2.9, 1.0$ Hz, 1H), 6.86-6.83 (m, 1H), 3.97-3.80 (m, 4H), 3.82 (s, 3H), 2.72 (d, $J = 2.3$ Hz, 3H), 1.26-1.21 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.6, 142.9, 140.1, 133.7, 132.1, 129.6, 128.1, 126.9, 114.4, 112.5, 62.7 (d, $J_{\text{C-P}} = 5.7$ Hz), 55.6, 38.6, 16.4 (d, $J_{\text{C-P}} = 6.7$ Hz); ^{31}P NMR (162 MHz, CDCl_3): $\delta = 6.57$; IR (film) 2993, 1710, 1608, 1483, 1215, 1029, 968, 756, 667 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{18}\text{H}_{24}\text{NO}_4\text{P} (9\text{M}^+)$ 350.1521, found 350.1524.

Diethyl (4-methoxyphenyl)(methyl)phosphoramidate (59d): ^1H NMR (400 MHz, CDCl_3): δ 7.19 (m, 2H), 6.84 (m, 2H), 4.13-4.00 (m, 4H), 3.79 (s, 3H), 3.11 (dd, $J = 9.2,$

0.9Hz, 3H), 1.30-1.26 (m, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 156.8, 137.4, 125.3 (d, $J_{\text{C-P}} = 3.8$ Hz), 114.4, 62.7 (d, $J_{\text{C-P}} = 5.7$ Hz), 55.6, 38.1, 16.3 (d, $J_{\text{C-P}} = 7.7$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 7.0223$; IR (film) 2983.88, 2906.73, 1510.26, 1247.94, 1184.29, 1035.77, 968.27, 910.40, 731.02 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{20}\text{NO}_4\text{PM}^+$ 274.1208, found 274.1205.

Diethyl (5-methoxy-[1,1'-biphenyl]-2-yl)(methyl)phosphoramidate (60d): ^1H NMR (400 MHz, CDCl_3): δ 7.50-7.48 (m, 2H), 7.41-7.26 (m, 4H), 6.88-6.83 (m, 2H), 3.93-3.77 (m, 4H), 3.87 (s, 3H), 2.72 (d, $J = 9.6$ Hz, 3H), 1.20 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 158.1, 142.1, 139.7, 134.8, 129.9, 129.4, 128.1, 127.3, 116.4, 114.1, 62.6, 55.7, 38.7, 16.4 (d, $J_{\text{C-P}} = 7.7$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 7.1295$; IR (film) 3018.60, 2399.45, 1600.92, 1485.19, 1219.01, 1033.85, 966.34, 756.10, 669.30 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{18}\text{H}_{24}\text{NO}_4\text{PM}^+$ 350.1521, found 350.1525.

Diethyl (4-chlorophenyl)(methyl)phosphoramidate (59e): ^1H NMR (400 MHz, CDCl_3): δ 7.32-7.20 (m, 4H), 4.17-3.98 (m, 4H), 3.18 (dd, $J = 8.7, 4.6$ Hz, 3H), 1.31-1.27 (m, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 142.9 (d, $J_{\text{C-P}} = 4.8$ Hz), 128.9 (d, $J_{\text{C-P}} = 10.5$ Hz), 123 (d, $J_{\text{C-P}} = 4.8$ Hz), 62.8 (d, $J_{\text{C-P}} = 4.8$ Hz), 36.8 (d, $J_{\text{C-P}} = 4.8$ Hz), 16.1 (d, $J_{\text{C-P}} = 7.7$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 6.0574$; IR (film) 2991.59, 1633.71, 1494.83, 1392.61, 1292.31, 1190.08, 1099.43, 906.54, 825.53, 773.46 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{17}\text{NO}_3\text{PClM}^+$ 278.0713, found 278.0709.

Diethyl (5-chloro-[1,1'-biphenyl]-2-yl)(methyl)phosphoramidate (60e): ^1H NMR (400 MHz, CDCl_3): δ 7.48-7.26 (m, 8H), 3.97-3.80 (m, 4H), 2.68 (d, $J = 9.6\text{ Hz}$, 3H), 1.24-1.21 (m, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 142.7, 141.1, 139.3, 132.7, 131.3, 130.1, 129.3, 128.5, 128.3, 127.7, 62.8 (d, $J_{\text{C-P}} = 5.7\text{ Hz}$), 38.5, 16.4 (d, $J_{\text{C-P}} = 6.7\text{ Hz}$); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 6.2986$; IR (film) 3018.60, 1710.86, 1363.67, 1215.15, 1029.99, 966.34, 756.10, 667.37 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{21}\text{NO}_3\text{P}\text{ClM}^+$ 354.1026, found 354.1029.

Diethyl 3-bromophenyl(methyl)phosphoramidate (59f): (yellow oil) ^1H NMR (400 MHz, CDCl_3) δ 7.41 (s, 1H), 7.24 (app d, $J = 7.7\text{ Hz}$, 1H), 7.20-7.13 (m, 2H), 4.16-3.18 (m, 4H), 3.17 (d, $J = 1.0\text{ Hz}$, 3H), 1.30 (td, $J = 7.1\text{ Hz}$, 1.0 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.6, 130.0, 126.1, 124.1 (d, $J_{\text{C-P}} = 4.7\text{ Hz}$), 122.4, 119.9 (d, $J_{\text{C-P}} = 3.9\text{ Hz}$), 62.8 (d, $J_{\text{C-P}} = 5.3\text{ Hz}$), 36.5 (d, $J_{\text{C-P}} = 4.4\text{ Hz}$), 16.0 (d, $J_{\text{C-P}} = 6.8\text{ Hz}$); ^{31}P NMR (162 MHz, CDCl_3) δ 5.13; IR (film) 2982, 1591, 1271, 1192, 1029, 779 cm^{-1} ; HRMS (EI) $\text{C}_{11}\text{H}_{17}\text{BrNO}_3\text{P}(\text{M}^+)$ calcd for 321.0129; found: 321.0131.

Diethyl 4-bromobiphenyl-2-yl(methyl)phosphoramidate (60f) : brown oil; ^1H NMR (400 MHz, CDCl_3) δ 7.58-7.57 (m, 1H), 7.47-7.32 (m, 6H), 7.18 (dd, $J = 8.2\text{ Hz}$, 0.8 Hz, 1H), 3.99-3.79 (m, 4H), 2.71 (d, $J = 9.3\text{ Hz}$, 3H), 1.24 (td, $J = 7.1\text{ Hz}$, 0.8 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) 143.3 (d, $J_{\text{C-P}} = 4.0\text{ Hz}$), 139.9 (d, $J_{\text{C-P}} = 6.0\text{ Hz}$), 139.1, 132.5,

131.7 (d, $J_{C-P} = 2.0$ Hz), 130.0 (d, $J_{C-P} = 1.0$ Hz), 129.1, 128.1, 127.4, 121.3 (d, $J_{C-P} = 2.0$ Hz), 62.7 (d, $J_{C-P} = 6.0$ Hz), 38.4 (d, $J_{C-P} = 4.0$ Hz), 16.2 (d, $J_{C-P} = 7.0$ Hz); ^{31}P NMR (162 MHz, CDCl_3) $\delta = 5.36$; IR (film) 2981, 2932, 1583, 1477, 1388, 1266, 1026, 962, 791, 701, 647 cm^{-1} ; HRMS (EI) calcd. for $\text{C}_{17}\text{H}_{21}\text{BrNO}_3\text{P}(\text{M}^+)$ 397.0442, found 397.0442.

Diethyl methyl(naphthalen-2-yl)phosphoramidate (59g): ^1H NMR (400 MHz, CDCl_3): δ 7.78-7.75 (m, 3H), 7.75 (s, 1H), 7.56 (d, $J = 8.7\text{ Hz}$, 1H), 7.55-7.36 (m, 2H), 4.20-4.01 (m, 4H), 3.31 (d, $J = 8.7\text{ Hz}$, 3H), 1.29 (t, $J = 7.1\text{ Hz}$, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 142, 134, 130.3, 128.7, 127.6, 127.5, 126.5, 125, 122.3, 118 (d, $J_{C-P} = 5.7$ Hz), 62.9 (d, $J_{C-P} = 5.7$ Hz), 37.2 (d, $J_{C-P} = 4.8\text{ Hz}$), 16.2 (d, $J_{C-P} = 6.7$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 6.5934$; IR (film) 2991.59, 1710.86, 1631.78, 1598.99, 1508.33, 1280.73, 1024.20, 962.48, 756.10 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{20}\text{NO}_3\text{PM}^+$ 294.1259, found 294.1261.

Diethyl methyl(3-phenylnaphthalen-2-yl)phosphoramidate (60g): ^1H NMR (400 MHz, CDCl_3): δ 7.91 (s, 1H), 7.84-7.81 (m, 2H), 7.79 (s, 1H), 7.60-7.58 (m, 2H), 7.48-7.36 (m, 5H), 4.02-3.86 (m, 4H), 2.77 (d, $J = 9.6$ Hz, 3H), 1.25 (t, $J = 7.3$ Hz, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 140.6, 140.3, 139.1, 133.4, 132.3, 130.6, 129.8, 128.1, 127.8, 127.6, 127.3, 126.9, 126.4 (d, $J_{C-P} = 4.8$ Hz), 62.9 (d, $J_{C-P} = 6.7$ Hz), 38.9, 16.4 (d, $J_{C-P} = 6.7$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 6.7007$; IR (film) 33018.60, 1710.86, 1490.97, 1363.67, 1211.30, 966.34, 736.81, 667.37 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{21}\text{H}_{24}\text{NO}_3\text{PM}^+$ 370.1572, found 370.1575.

Diethyl ethyl(*m*-tolyl)phosphoramidate (59h): yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.22-7.18 (m, 1H), 7.07-7.05 (m, 2H), 6.98-6.95 (m, 1H), 4.15- 3.98 (m, 4H), 3.65-3.58 (m, 2H), 2.34 (s, 3H), 1.28 (td, $J = 7.1$ Hz, 0.8 Hz, 6H), 1.10 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) 141.9 (d, $J_{\text{C-P}} = 4.0$ Hz), 138.8, 128.7, 126.4 (d, $J_{\text{C-P}} = 4.0$ Hz), 125.8, 122.8 (d, $J_{\text{C-P}} = 4.0$ Hz), 62.4 (d, $J_{\text{C-P}} = 6.0$ Hz), 44.8 (d, $J_{\text{C-P}} = 5.0$ Hz), 21.5, 16.1 (d, $J_{\text{C-P}} = 7.0$ Hz), 14.6 (d, $J_{\text{C-P}} = 2.0$ Hz); ^{31}P NMR (162 MHz, CDCl_3) $\delta = 1.67$; IR (film) 2980, 2932, 2905, 2871, 1605, 1491, 1390, 1265, 1158, 1019, 963, 786 cm^{-1} ; HRMS (EI) calcd. for $\text{C}_{13}\text{H}_{22}\text{NO}_3\text{P}(\text{M}^+)$ 271.1337, found 271.1339.

Diethyl ethyl(4-methylbiphenyl-2-yl)phosphoramidate (60h): yellow oil; ^1H NMR (400 MHz, CDCl_3) 7.54-7.51 (m, 2H), 7.38-7.28 (m, 3H), 7.19 (d, $J = 7.3$ Hz, 2H), 7.10 (dt, $J = 7.8$ Hz, 0.7 Hz, 1H), 4.06-3.90 (m, 4H), 2.96 (s, 2H), 2.38 (s, 3H), 1.26 (td, $J = 7.1$ Hz, 0.5 Hz, 6H), 0.88 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) 140.2, 138.8 (d, $J_{\text{C-P}} = 5.0$ Hz), 138.2 (d, $J_{\text{C-P}} = 6.0$ Hz), 137.7 (d, $J_{\text{C-P}} = 1.0$ Hz), 131.2, 130.8 (d, $J_{\text{C-P}} = 2.0$ Hz), 129.5, 127.8, 127.6 (d, $J_{\text{C-P}} = 1.0$ Hz), 126.8, 62.5 (d, $J_{\text{C-P}} = 6.0$ Hz), 44.8 (d, $J_{\text{C-P}} = 4.0$ Hz), 21.1, 16.2 (d, $J_{\text{C-P}} = 7.0$ Hz), 13.7; ^{31}P NMR (162 MHz, CDCl_3) $\delta = 6.17$; IR (film) 2979, 2930, 1482, 1443, 1257, 1162, 1054, 1027, 963, 785, 702 cm^{-1} ; HRMS (EI) calcd. for $\text{C}_{19}\text{H}_{26}\text{NO}_3\text{P}(\text{M}^+)$ 347.1650, found 347.1651.

Diethyl butyl(phenyl)phosphoramidate (59i): ^1H NMR (400 MHz, CDCl_3): δ 7.33-7.24 (m, 4H), 7.16-7.12 (m, 1H), 4.12-3.98 (m, 4H), 3.59-3.53 (m, 2H), 1.50-1.43 (m, 2H), 1.34-1.24 (m, 8H), 0.87 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (400 MHz, CDCl_3) δ 142.6, 129.1, 125.8 (d, $J_{\text{C-P}} = 3.8$ Hz), 125.1, 62.7 (d, $J_{\text{C-P}} = 5.7$ Hz), 49.9, 31.2, 20, 16.3 (d, $J_{\text{C-P}} = 6.7$ Hz), 13.9; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 6.6739$; IR (film) 32989.66, 1502.20, 1215.15, 1028.06, 972.12, 777.31 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{24}\text{NO}_3\text{PM}^+$ 286.1572, found 286.1567.

Diethyl [1,1'-biphenyl]-2-yl(butyl)phosphoramidate (60i): ^1H NMR (400 MHz, CDCl_3): δ 7.55-7.52 (m, 1H), 7.41-7.24 (m, 7H), 7.14 (t, $J = 7.3$ Hz, 1H), 4.12-3.96 (m, 4H), 3.95-3.53 (m, 2H), 1.28-1.24 (m, 10H), 0.87 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (400 MHz, CDCl_3) δ 142.4, 140.4, 131.6, 130.3, 129.5, 129.1, 128.1, 127.2, 126.8, 125.8, 125, 62.7, 49.9, 31.2, 30.6, 20.1, 19.9, 16.4, 16.3, 13.9, 13.9; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 6.6542$; IR (film) 32987.74, 1598.99, 1494.83, 1392.61, 1215.15, 1028.06, 970.19, 771.53, 698.23 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{20}\text{H}_{28}\text{NO}_3\text{PM}^+$ 362.1885, found 362.1885.

Diethyl 3-ethyl-4'-methylbiphenyl-2-ylphosphoramidate (61a): pale brown solid; m.p = 99.6-101.0 ; ^1H NMR (400 MHz, CDCl_3) δ 7.30-7.28 (m, 2H), 7.24-7.22 (m, 3H), 7.18

(td, $J = 7.5$ Hz, 1.1 Hz, 1H), 7.09 (d, $J = 7.2$ Hz, 1H), 4.33 (d, $J = 4.1$ Hz, 1H), 3.86-3.76 (m, 2H), 3.68-3.58 (m, 2H), 2.90 (q, $J = 7.5$ Hz, 2H), 2.39 (s, 3H), 1.28 (t, $J = 7.5$ Hz, 3H), 1.12 (td, $J = 7.1$ Hz, 0.9 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) 141.3 (d, $J_{\text{C-P}} = 3.0$ Hz), 139.7 (d, $J_{\text{C-P}} = 4.0$ Hz), 137.7, 136.7, 133.3, 129.5, 128.9, 128.4 (d, $J_{\text{C-P}} = 1.0$ Hz), 128.2 (d, $J_{\text{C-P}} = 1.0$ Hz), 125.8 (d, $J_{\text{C-P}} = 2.0$ Hz), 62.5 (d, $J_{\text{C-P}} = 6.0$ Hz), 24.8, 21.2, 16.1 (d, $J_{\text{C-P}} = 7.0$ Hz), 14.5; ^{31}P NMR (162 MHz, CDCl_3) $\delta = 3.57$; IR (film) 3135, 2977, 2928, 1455, 1234, 1062, 1035, 964, 798; HRMS (EI) calcd. for $\text{C}_{19}\text{H}_{26}\text{NO}_3\text{P}(\text{M}^+)$ 347.1650, found 347.1654.

Diethyl 3-ethyl-4'-methylbiphenyl-2-ylphosphoramidate (61b): brown oil; ^1H NMR (400 MHz, CDCl_3) δ 7.44-7.38 (m, 3H), 7.33-7.26 (m, 3H), 7.20 (d, $J = 7.9$ Hz, 2H), 4.02-3.92 (m, 2H), 3.90-3.82 (m, 2H), 2.71 (d, $J = 9.4$ Hz, 3H), 2.39 (s, 3H), 1.23 (td, $J = 7.1$ Hz, 0.6 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 141.9, 140.7 (d, $J_{\text{C-P}} = 6.0$ Hz), 137.2, 136.7, 131.4, 129.1, 128.7, 128.6 (d, $J_{\text{C-P}} = 2.0$ Hz), 128.2, 126.7, 62.5 (d, $J_{\text{C-P}} = 6.0$ Hz), 38.4 (d, $J_{\text{C-P}} = 4.0$ Hz), 21.2, 16.2 (d, $J_{\text{C-P}} = 7.0$ Hz); ^{31}P NMR (162 MHz, CDCl_3) $\delta = 6.09$; IR (film) 2981, 2929, 1483, 1445, 1267, 1026, 961, 820, 755; HRMS (EI) calcd. For $\text{C}_{18}\text{H}_{24}\text{NO}_3\text{P}(\text{M}^+)$ 333.1494, found 333.1498.

Diethyl 4,4'-dimethylbiphenyl-2-yl(ethyl)phosphoramidate (61c): (brown oil) ^1H NMR (400 MHz, CDCl_3) δ 7.43-7.40 (m, 2H), 7.18-7.16 (m, 4H), 7.08 (dt, $J = 7.8$ Hz,

0.8 Hz, 1H), 4.15-3.92 (m, 4H), 2.96 (s, 2H), 2.37 (d, $J = 2.3$ Hz, 6H), 1.27 (td, $J = 7.1$ Hz, 0.8 Hz, 6H), 0.87 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.8 (d, $J_{\text{C-P}} = 4.0$ Hz), 138.0 (d, $J_{\text{C-P}} = 6.0$ Hz), 137.5, 137.3, 136.4, 131.2, 130.9 (d, $J_{\text{C-P}} = 4.0$ Hz), 129.3, 128.5, 127.6, 62.5 (d, $J_{\text{C-P}} = 6.0$ Hz), 44.6 (d, $J_{\text{C-P}} = 4.0$ Hz), 21.1 (d, $J_{\text{C-P}} = 1.0$ Hz), 16.2 (d, $J_{\text{C-P}} = 7.0$ Hz), 13.8; ^{31}P NMR (162 MHz, CDCl_3) $\delta = 6.20$; IR (film) 2979, 2928, 1493, 1391, 1257, 1054, 1028, 963, 811, 785; HRMS (EI) calcd. for $\text{C}_{20}\text{H}_{28}\text{NO}_3\text{P}(\text{M}^+)$ 361.1807, found 361.1803.

Diethyl 4'-chloro-3-ethylbiphenyl-2-ylphosphoramidate (61d): pale brown solid; m.p = 155.2-158.8 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.40-7.34 (m, 4H), 7.25 (d, $J = 1.48$ Hz, 1H), 7.20 (td, $J = 7.6$ Hz, 1.2 Hz, 1H), 7.08 (d, 7.2 Hz, 1H), 4.20 (d, 4.4 Hz, 1H), 3.87-3.77 (m, 2H), 3.71-3.61 (m, 2H), 2.88 (q, $J = 7.5$ Hz, 2H), 1.28 (t, $J = 7.5$ Hz, 3H), 1.14 (td, $J = 7.1$ Hz, 0.8 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 141.7 (d, $J_{\text{C-P}} = 3.0$ Hz), 139.2, 139.0 (d, $J_{\text{C-P}} = 4.0$ Hz), 131.2, 128.6 (d, $J_{\text{C-P}} = 2.0$ Hz), 128.4, 128.2, 126.2 (d, $J_{\text{C-P}} = 2.0$ Hz), 62.6 (d, $J_{\text{C-P}} = 6.0$ Hz), 24.7, 16.1 (d, $J_{\text{C-P}} = 7.0$ Hz), 14.5; ^{31}P NMR (162 MHz, CDCl_3) δ 3.47; IR (film) 3082, 2977, 2817, 1229, 1059, 1032, 963, 798; HRMS (EI) calcd. for $\text{C}_{18}\text{H}_{23}\text{ClNO}_3\text{P}(\text{M}^+)$ 367.1104, found 367.1105.

7.2.6 General experimental procedure for the preparation of Aryl Phosphonate (64):⁶

To a stirred solution of diethyl phosphite (2.0 mmol) and triethylamine (2.0 mmol) in presence of a catalytic amount of $\text{Pd}(\text{PPh}_3)_4$ (0.08 mmol, 5 mol % equiv), aryl bromide or aryl iodide (1.6 mmol) was added under nitrogen, and the reaction mixture was stirred at 90 °C for 6-15 h. when the aryl halide used was solid, toluene (1 ml) was added as solvent. After the addition of ether, the reaction mixture was filtered. The residue obtained upon evaporation is purified by silica gel column chromatography.

General experimental procedure for the Rh-catalyzed C-H alkenylation (65):

$(\text{RhCp}^*\text{Cl}_2)_2$ (3.4 mg, 0.005 mmol, 2.5mol % equiv), AgSbF_6 (7.5 mg, 0.02 mmol, 10 mol % equiv) and $\text{Cu}(\text{OAc})_2$ (7.9 mg, 0.04 mmol, 20 mol % equiv) was carefully weighed to a vial equipped with a magnetic stirrer bar and a tightly-screwed cap. Aryl phosphonate (0.22 mmol, 1.0 equiv) in dichloroethane (0.5 mL) was then added, followed by ethyl acrylate (0.44 mmol, 2.0 equiv). The reaction mixture was flushed with oxygen for 30 seconds and stirred at 110 °C for 15 h, and cooled to room temperature. The crude product was concentrated *in vacuo* and purified by flash column chromatography (ethyl acetate:hexane = 1:1) to afford the desired alkenylated product.

Diethyl o-tolyl phosphonate (64a): ^1H NMR (400 MHz, CDCl_3): δ 7.94-7.88 (m, 1H), 7.44-7.40 (m, 1H), 7.28-7.24 (m, 2H), 4.18-4.05 (m, 4H), 2.57 (s, 3H), 1.32 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 155.2, 134.1 (d, $J_{\text{C-P}} = 10.5$ Hz), 132.8, 131.5, 131.3, 130.9, 126.8, 125.6, 119.7, 115.1, 62.3, 21.3, 16.4 (d, $J_{\text{C-P}} = 6.8$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 20.1288$; IR (film) 3053.32, 2304.94, 1712.79, 1421.54, 1361.74, 1265.30, 1222.87, 894.97, 727.16 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{17}\text{O}_3\text{P}$ (M^+) 229.0994, found 229.0990.

Diethyl (2-ethylphenyl) phosphonate (64b): ^1H NMR (400 MHz, CDCl_3): δ 7.92-7.86 (m, 1H), 7.49-7.43 (m, 1H), 7.34-7.21 (m, 2H), 4.21-4.04 (m, 4H), 2.97 (q, $J = 7.8$ Hz, 2H), 1.35-1.23 (m, 9H); ^{13}C NMR (400 MHz, CDCl_3) δ 148.4 (d, $J_{\text{C-P}} = 10.5$ Hz), 134.0, 132.8, 129.8 (d, $J_{\text{C-P}} = 15.3$ Hz), 125.5 (d, $J_{\text{C-P}} = 15.3$ Hz), 62.1 (d, $J_{\text{C-P}} = 5.7$ Hz), 27.3, 16.5 (d, $J_{\text{C-P}} = 5.7$ Hz), 15.8; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 20.3413$; IR (film) 2983.88, 1712.79, 1595.13, 1568.13, 1475.54, 1392.61, 1361.74, 1246.02, 1143.79, 964.41 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{19}\text{O}_3\text{P}$ (M^+) 243.1150, found 243.1151.

Diethyl (2-chlorophenyl) phosphonate (64c): ^1H NMR (400 MHz, CDCl_3): δ 8.03-7.97 (m, 1H), 7.50-7.31 (m, 3H), 4.24-4.08 (m, 4H), 1.21-1.29 (m, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 136.9, 136.0 (d, $J_{\text{C-P}} = 7.6$ Hz), 133.7, 130.9 (d, $J_{\text{C-P}} = 10.5$ Hz), 128.3, 126.5 (d,

$J_{C-P} = 13.4$ Hz), 62.7 (d, $J_{C-P} = 5.7$ Hz), 16.4 (d, $J_{C-P} = 6.7$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 15.1435$; IR (film) 2983.88, 1712.79, 1583.56, 1566.20, 1456.26, 1392.61, 1367.53, 1163.08, 1060.85, 758.02 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{10}\text{H}_{14}\text{O}_3\text{PCl}(\text{M}^+)$ 249.0447, found 249.0441.

Diethyl [1,1'-biphenyl]-2-yl phosphonate (64d): ^1H NMR (400 MHz, CDCl_3): δ 8.07-8.01(m, 1H), 7.57-7.26 (m, 8H), 3.96-3.80 (m, 4H), 1.11 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 146.3 (d, $J_{C-P} = 9.6$ Hz), 141.6, 134.0 (d, $J_{C-P} = 9.6$ Hz), 132.1, 131.5 (d, $J_{C-P} = 14.4$ Hz), 129.5 (d, $J_{C-P} = 10.5$ Hz), 127.9, 127.6, 127.5, 127.4, 127.1, 126.9, 126.1, 62.0 (d, $J_{C-P} = 5.7$ Hz), 16.2 (d, $J_{C-P} = 6.7$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 18.7995$; IR (film) 3016.67, 2399.45, 1712.79, 1591.27, 1562.34, 1469.76, 1444.68, 1392.61, 1367.53, 1217.08, 1139.93, 1095.57, 1028.06, 974.05 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{19}\text{O}_3\text{P}(\text{M}^+)$ 291.1150, found 291.1148.

Diethyl (4-methoxy-2-methylphenyl) phosphonate (64e): ^1H NMR (400 MHz, CDCl_3): δ 7.88-7.85 (m, 1H), 6.78-6.75 (m, 2H), 4.13- 4.06 (m, 4H), 2.53 (s, 3H), 1.33-1.30 (m, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 163.4, 144.2, 136.4 (d, $J_{C-P} = 12.4$ Hz), 132.2, 128.6, 117.3 (d, $J_{C-P} = 15.3$ Hz), 61.9 (d, $J_{C-P} = 4.8$ Hz), 55.4, 21.5, 16.4 (d, $J_{C-P} = 6.7$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 21.0401$; IR (film) 3412.08, 2985.81, 1699.29, 1637.56, 1591.27, 1363.67, 1166.93, 1109.07, 1022.27, 530.42 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{19}\text{O}_4\text{P}(\text{M}^+)$ 259.1099, found 259.1097.

Diethyl (2,3-dimethylphenyl) phosphonate (64f): ^1H NMR (400 MHz, CDCl_3): δ 7.79-7.75 (m, 1H), 7.44-7.31 (m, 2H), 4.14-4.09 (m, 4H), 2.49 (s, 3H), 2.31 (s, 3H), 1.32 (t, J = 7.3 Hz, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 140.3 (d, $J_{\text{C-P}}$ = 10.5 Hz), 138.1 (d, $J_{\text{C-P}}$ = 14.4 Hz), 135.0, 134.2, 131.9 (d, $J_{\text{C-P}}$ = 10.5 Hz), 127.9, 126.1, 125.3, 125.2, 61.9 (d, $J_{\text{C-P}}$ = 5.7 Hz), 20.5, 17.7, 16.4 (d, $J_{\text{C-P}}$ = 6.7 Hz); ^{31}P NMR (400 MHz, CDCl_3): δ = 20.0167; IR (film) 3018.60, 2399.45, 1708.93, 1521.84, 1444.68, 1215.15, 1161.15, 1053.13, 1026.13, 968.27, 848.68, 759.95 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{19}\text{O}_3\text{P}(\text{M}^+)$ 243.1150, found 243.1149.

Diethyl (3,4-dimethylphenyl) phosphonate (64g):⁸ ^1H NMR (400 MHz, CDCl_3): δ 7.59-7.46 (m, 2H), 7.24-7.16 (m, 1H), 4.18-4.00 (m, 4H), 2.30-2.23 (m, 6H), 1.35-1.26 (m, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 141.9, 141.5, 137.4, 132.9, 132.3, 130.3, 129.9, 129.6, 126.4, 124.3, 62.2 (d, $J_{\text{C-P}}$ = 5.7 Hz), 20.1, 19.8 (d, $J_{\text{C-P}}$ = 4.8 Hz), 16.5 (d, $J_{\text{C-P}}$ = 13.4 Hz); ^{31}P NMR (400 MHz, CDCl_3): δ = 20.5848; IR (film) 2987.74, 1606.70, 1446.61, 1215.15, 1111.00, 1026.13, 968.27, 754.17, 667.17 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{19}\text{O}_3\text{P}(\text{M}^+)$ 243.1150, found 243.1150.

Diethyl *m*-tolyl phosphonate (64h):⁸ ^1H NMR (400 MHz, CDCl_3): δ 7.66-7.57 (m, 2H), 7.36-7.35 (m, 2H), 4.18-4.04 (m, 4H), 2.39 (s, 3H), 1.34-1.30 (m, 6H); ^{13}C NMR (400

MHz, CDCl_3) δ 138.4 (d, $J_{\text{C-P}} = 15.3$ Hz), 133.3, 132.4 (d, $J_{\text{C-P}} = 10.5$ Hz), 129.0, 128.9, 128.8, 128.6, 128.4, 127.2, 62.1 (d, $J_{\text{C-P}} = 5.7$ Hz), 21.4, 16.4 (d, $J_{\text{C-P}} = 6.7$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 19.9356$; IR (film) 3435.88, 2983.88, 1708.93, 1442.75, 1363.67, 1313.52, 1247.94, 1120.64, 1022.27, 968.27, 569.00, 547.78 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{17}\text{O}_3\text{P}(\text{M}^+)$ 229.0994, found 229.0994.

Dimethyl phenyl phosphonate (64i):^{7, 9} ^1H NMR (400 MHz, CDCl_3): δ 7.77-7.71(m, 2H), 7.71-7.39 (m, 3H), 3.72-3.68 (m, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 132.7, 131.9, 131.9, 128.7, 128.5; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 22.1807$; IR (film) 2953.02, 2850.79, 1714.72, 1593.20, 1438.90, 1234.44, 1134.14, 835.18, 798.53, 752.24 cm^{-1} ; HRMS (EI) calcd for $\text{C}_8\text{H}_{11}\text{O}_3\text{P}(\text{M}^+)$ 187.0524, found 187.0522.

Diethyl (4-methoxyphenyl) phosphonate (64j):⁹ ^1H NMR (400 MHz, CDCl_3): δ 7.79-7.72 (m, 3H), 6.99-6.96 (m, 2H), 4.17-4.02 (m, 4H), 3.85 (d, $J = 9.2$ Hz, 3H), 1.38-1.26 (m, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 162.9, 133.8 (d, $J_{\text{C-P}} = 11.5$ Hz), 132.0, 128.6 (d, $J_{\text{C-P}} = 12.4$ Hz), 114.1 (d, $J_{\text{C-P}} = 16.2$ Hz), 62.0 (d, $J_{\text{C-P}} = 4.8$ Hz), 55.3, 16.3 (d, $J_{\text{C-P}} = 6.7\text{Hz}$); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 20.3684$; IR (film) 2985.81, 1710.86, 1600.92, 1571.99, 1506.41, 1440.83, 1392.61, 1298.09, 1242.16, 1130.29, 968.27, 808.17 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{17}\text{O}_4\text{P}(\text{M}^+)$ 245.0943, found 245.0941.

Diethyl naphthalen-1-yl phosphonate (64k):⁹ ¹H NMR (400 MHz, CDCl₃): δ 8.55-8.49 (m, 1H), 8.27-8.17 (m, 1H), 8.04-7.84 (m, 2H), 7.63-7.39 (m, 3H), 4.23-4.03 (m, 4H), 1.35-1.21 (m, 6H); ¹³C NMR (400 MHz, CDCl₃) δ 134.9 (d, *J*_{C-P} = 8.6 Hz), 133.7 (d, *J*_{C-P} = 15.3 Hz), 128.8 (d, *J*_{C-P} = 19.2 Hz), 127.6, 127.4, 126.8, 126.4, 124.7 (d, *J*_{C-P} = 16.3 Hz), 62.5, 16.5 (d, *J*_{C-P} = 6.7 Hz); ³¹P NMR (400 MHz, CDCl₃): δ = 19.8274; IR (film) 2983.88, 1712.79, 1508.33, 1363.67, 1222.87, 1045.42, 804.32, 777.31 cm⁻¹; HRMS (EI) calcd for C₁₄H₁₇O₃P(M⁺) 265.0994, found 265.0995.

Diethyl naphthalen-2-yl phosphonate (64l):⁷ ¹H NMR (400 MHz, CDCl₃): δ 8.35 (d, *J* = 16.0 Hz, 1H), 7.86-7.78 (m, 3H), 7.70-7.65 (m, 1H), 7.53-7.45 (m, 3H), 4.14-3.99 (m, 4H), 1.25 (t, *J* = 7.1 Hz, 6H); ¹³C NMR (400 MHz, CDCl₃) δ 135.1, 134.1 (d, *J*_{C-P} = 10.5 Hz), 132.4 (d, *J*_{C-P} = 17.2 Hz), 129.1, 128.6, 128.4, 127.9, 127.0, 126.6, 126.5, 126.4, 124.5, 62.3 (d, *J*_{C-P} = 4.8 Hz), 16.5 (d, *J*_{C-P} = 5.7 Hz); ³¹P NMR (400 MHz, CDCl₃): δ = 19.7462; IR (film) 2987.74, 1710.86, 1627.92, 1438.90, 1392.61, 1236.37, 1163.08, 1097.50, 1024.20, 968.27, 864.11, 819.75, 651.94, 540.07 cm⁻¹; HRMS (EI) calcd for C₁₄H₁₇O₃P(M⁺) 265.0994, found 265.0996.

Diisopropyl phenylphosphonate (64m):^{7,9} ^1H NMR (400 MHz, CDCl_3): δ 7.85-7.79 (m, 2H), 7.55-7.51 (m, 1H), 7.47-7.42 (m, 2H), 4.73-4.65 (m, 2H), 1.38 (s, 3H), 1.37 (s, 3H), 1.23 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (400 MHz, CDCl_3) δ 132.2, 131.9, 128.6, 128.4, 70.9 (d, $J_{\text{C-P}} = 5.7$ Hz), 24.2 (d, $J_{\text{C-P}} = 3.8$ Hz), 24.0 (d, $J_{\text{C-P}} = 4.8$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 17.2847$; IR (film) 2981.95, 1438.90, 1386.82, 1242.16, 1178.51, 1132.21, 1103.28, 987.55, 885.33, 748.38, 694.37, 565.14 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{19}\text{O}_3\text{P}(\text{M}^+)$ 243.1150, found 243.1154.

Aryl phosphinic acid bis (dimethylamide) (64n): ^1H NMR (400 MHz, CDCl_3): δ 7.68-7.64 (m, 2H), 7.40-7.35 (m, 2H), 2.56 (s, 6H), 2.54 (s, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 132.1, 131.9, 131.2, 130.9, 129.4, 128.3, 128.2, 36.2 (d, $J_{\text{C-P}} = 2.9$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 30.4038$; IR (film) 2304.94, 1712.78, 1265.30, 894.97, 727.16 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{10}\text{H}_{17}\text{N}_2\text{OP}(\text{M}^+)$ 213.1157, found 213.1158.

4-Methyl-aryl phosphinic acid bis (dimethylamide) (64o): ^1H NMR (400 MHz, CDCl_3): δ 7.65-7.61 (m, 2H), 7.28-7.23 (m, 2H), 2.64 (s, 6H), 2.62 (s, 6H), 2.39 (s, 3H); ^{13}C NMR (400 MHz, CDCl_3) δ 141.7 (d, $J_{\text{C-P}} = 2.9$ Hz), 132.4, 132.3, 132.2, 132, 130, 129.4, 129.3, 129.2, 120 (d, $J_{\text{C-P}} = 4.8$ Hz), 36.4, 21.6; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 30.8636$; IR

(film) 2376.30, 1734.01, 1602.85, 1456.26, 1217.08, 1114.86, 771.53 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{27}\text{N}_2\text{OP}(\text{M}^+)$ 283.1939, found 283.1933.

2-Ethyl-aryl phosphinic acid bis (diethylamide) (64p): ^1H NMR (400 MHz, CDCl_3): δ 7.49-7.31 (m, 3H), 7.19-7.16 (m, 1H), 3.18-3.04 (m, 10H), 1.27 (t, $J = 3.7$ Hz, 3H), 1.09-1.06 (m, 12H); ^{13}C NMR (400 MHz, CDCl_3) δ 149.9, 132.5 (d, $J_{\text{C-P}} = 10.5$ Hz), 131.3, 129.9 (d, $J_{\text{C-P}} = 13.4$ Hz), 125.1 (d, $J_{\text{C-P}} = 13.4$ Hz), 39.2 (d, $J_{\text{C-P}} = 4.8$ Hz), 26.9, 15.6, 14.2; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 30.9838$; IR (film) 3197.98, 2987.74, 1710.86, 1604.77, 1500.62, 1419.61, 1230.95, 1033.85, 774.46 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{21}\text{N}_2\text{OP}(\text{M}^+)$ 241.1470, found 241.1477.

3-Methyl-aryl phosphinic acid bis (dimethylamide) (64q): ^1H NMR (400 MHz, CDCl_3): δ 7.66-7.62 (m, 1H), 7.54-7.49 (m, 1H), 7.32-7.25 (m, 2H), 3.14-3.03 (m, 8H), 2.38 (s, 3H), 1.04 (t, $J = 7.1$ Hz); ^{13}C NMR (400 MHz, CDCl_3) δ 138.1, 134.3, 132.9, 132.8, 131.7, 128.8, 128.1, 128, 38.4 (d, $J_{\text{C-P}} = 3.8$ Hz), 21.5, 13.8; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 29.0242$; IR (film) 1714.72, 1640.23, 1390.68, 1020.34, 866.04, 655.80 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{27}\text{N}_2\text{OP}(\text{M}^+)$ 283.1939, found 283.1938.

(E)-Ethyl 3-(2-(diethoxyphosphoryl)-3-methylphenyl)acrylate (65a): ^1H NMR (400 MHz, CDCl_3): δ 8.56 (d, $J = 16.0$ Hz, 1H), 7.40-7.38 (m, 2H), 7.28-7.27 (m, 1H), 6.17 (d, $J = 15.6$ Hz, 1H), 4.29-4.04 (m, 6H), 2.69 (s, 3H), 1.35-1.30 (m, 9H); ^{13}C NMR (400 MHz, CDCl_3) δ 166.9, 146.4, 144.4 (d, $J_{\text{C-P}} = 10.5$ Hz), 140.5, 133.1 (d, $J_{\text{C-P}} = 15.3$ Hz), 132.2, 126.4 (d, $J_{\text{C-P}} = 13.4$ Hz), 120.8, 62.1 (d, $J_{\text{C-P}} = 4.8$ Hz), 60.7, 23.2, 16.4 (d, $J_{\text{C-P}} = 6.7$ Hz), 14.5; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 18.3330$; IR (film) 2981.95, 1712.79, 1633.71, 1581.63, 1454.33, 1367.53, 1307.74, 1168.86, 1138.00, 966.34, 867.97 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{23}\text{O}_5\text{P}(\text{M}^+)$ 327.1361, found 327.1368.

(E)-Ethyl 3-(2-(diethoxyphosphoryl)-3-ethylphenyl)acrylate (65b): ^1H NMR (400 MHz, CDCl_3): δ 8.53 (d, $J = 16.0$ Hz, 1H), 7.47-7.28 (m, 3H), 6.16 (d, $J = 15.6$ Hz, 1H), 4.29-3.69 (m, 6H), 3.18-3.13 (m, 2H), 1.36-1.24 (m, 12H); ^{13}C NMR (400 MHz, CDCl_3) δ 166.9, 151.2 (d, $J_{\text{C-P}} = 11.5$ Hz), 146.7, 140.4 (d, $J_{\text{C-P}} = 9.6$ Hz), 132.3, 131.9, 131.8, 126.4 (d, $J_{\text{C-P}} = 14.4$ Hz), 120.5, 62.0 (d, $J_{\text{C-P}} = 5.7$ Hz), 60.6, 28.5, 17.1, 16.4 (d, $J_{\text{C-P}} = 6.7$ Hz), 14.5; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 18.2314$; IR (film) 2983.88, 1708.93, 1635.64, 1581.63, 1454.33, 1392.61, 1367.53, 1309.67, 1172.72, 1138.00, 966.34, 808.17 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{25}\text{O}_5\text{P}(\text{M}^+)$ 341.1518, found 341.1515.

(E)-Ethyl 3-(3-chloro-2-(diethoxyphosphoryl)phenyl)acrylate (65c): ^1H NMR (400 MHz, CDCl_3): δ 8.61 (d, $J = 16.0$ Hz, 1H), 7.749-7.42 (m, 3H), 6.15 (d, $J = 16.0$ Hz, 1H), 4.30-4.11 (m, 6H), 1.37-1.32 (m, 9H); ^{13}C NMR (400 MHz, CDCl_3) δ 166.5, 145.4, 143.0 (d, $J_{\text{C-P}} = 8.6$ Hz), 138.9, 132.9, 132.3, 132.2, 125.4, 121.9, 62.7 (d, $J_{\text{C-P}} = 5.7$ Hz), 60.9, 16.4 (d, $J_{\text{C-P}} = 6.7$ Hz), 14.5; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 13.9576$; IR (film) 2995.45, 1701.22, 1637.56, 1554.63, 1438.90, 1367.53, 1309.67, 1238.30, 1178.51, 1124.50, 1024.20, 974.05, 798.53, 665.44, 621.08, 567.07 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{20}\text{O}_5\text{PCl}(\text{M}^+)$ 347.0816, found 347.0816.

(E)-Ethyl 3-(2-(diethoxyphosphoryl)-[1,1'-biphenyl]-3-yl)acrylate (65d): ^1H NMR (400 MHz, CDCl_3): δ 8.54 (d, $J = 16.0$ Hz, 1H), 7.59-7.26 (m, 8H), 4.32-4.26 (m, 2H), 3.96-3.88 (m, 2H), 3.79-3.72 (m, 2H), 1.37-1.26 (m, 3H), 1.13-1.09 (m, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 166.7, 147.9, 145.7, 142.6, 140.5, 140.4, 132.9, 132.8, 131.5, 129.2, 127.8, 127.6, 127.4, 121.1, 61.9 (d, $J_{\text{C-P}} = 6.7$ Hz), 60.8, 29.9, 16.1 (d, $J_{\text{C-P}} = 6.7$ Hz), 14.5; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 16.8249$; IR (film) 1708.93, 1309.67, 1276.88, 1047.35, 1026.13, 972.12, 557.43 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{21}\text{H}_{25}\text{O}_5\text{P}(\text{M}^+)$ 389.1518, found 389.1520.

(E)-Ethyl 3-(2-(diethoxyphosphoryl)-5-methoxy-3-methylphenyl)acrylate (65e): ^1H NMR (400 MHz, CDCl_3): δ 8.56 (d, $J = 15.6$ Hz, 1H), 6.89-6.87 (m, 1H), 6.79-6.77 (m, 1H), 6.16 (d, $J = 15.6$ Hz, 1H), 4.29-3.84 (m, 6H), 2.66 (s, 3H), 1.35-1.26 (m, 9H); ^{13}C NMR (400 MHz, CDCl_3) δ 166.8, 161.9, 146.5, 142.8, 120.8, 118.3 (d, $J_{\text{C-P}} = 16.3$ Hz), 111.7 (d, $J_{\text{C-P}} = 14.4$ Hz), 61.8 (d, $J_{\text{C-P}} = 5.7$ Hz), 55.5, 23.4, 16.4 (d, $J_{\text{C-P}} = 6.7$ Hz), 14.5; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 19.0700$; IR (film) 2985.81, 1699.29, 1591.27, 1363.67, 1166.93, 1045.42, 966.34, 530.42 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{25}\text{O}_6\text{P}(\text{M}^+)$ 357.1467, found 357.1465.

(E)-Ethyl 3-(2-(diethoxyphosphoryl)-3,4-dimethylphenyl)acrylate (65f): ^1H NMR (400 MHz, CDCl_3): δ 8.56 (d, $J = 15.6$ Hz, 1H), 7.30-7.27 (m, 2H), 6.12 (d, $J = 15.6$ Hz, 1H), 4.28-4.04 (m, 6H), 2.60 (s, 3H), 2.32 (s, 3H), 1.36-1.30 (m, 9H); ^{13}C NMR (400 MHz, CDCl_3) δ 167.0, 146.5 (d, $J_{\text{C-P}} = 3.8$ Hz), 142.9 (d, $J_{\text{C-P}} = 11.4$ Hz), 139.8 (d, $J_{\text{C-P}} = 15.3$ Hz), 138.5 (d, $J_{\text{C-P}} = 10.5$ Hz), 133.8 (d, $J_{\text{C-P}} = 2.9$ Hz), 127.2, 126.3 (d, $J_{\text{C-P}} = 15.2$ Hz), 125.4, 119.7, 62.0 (d, $J_{\text{C-P}} = 5.7$ Hz), 60.6, 21.3, 18.7, 16.4 (d, $J_{\text{C-P}} = 6.7$ Hz), 14.5; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 19.9897$; IR (film) 2985.81, 1712.79, 1633.71, 1444.68, 1365.60, 1307.74, 1226.73, 1166.93, 1022.27, 966.34, 827.46, 761.88, 624.94, 549.71 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{25}\text{O}_5\text{P}(\text{M}^+)$ 341.1518, found 341.1512.

(E)-Ethyl 3-(2-(diethoxyphosphoryl)-4,5-dimethylphenyl)acrylate (65g): ^1H NMR (400 MHz, CDCl_3): δ 8.31 (d, $J = 16.0$ Hz, 1H), 7.81 (d, $J = 14.6$ Hz, 1H), 7.47-7.48 (m, 1H), 6.34 (d, $J = 16.0$ Hz, 1H), 4.28-4.05 (m, 6H), 2.32-2.30 (m, 6H), 1.35-1.30 (m, 9H); ^{13}C NMR (400 MHz, CDCl_3) δ 166.9, 143.1 (d, $J_{\text{C-P}} = 19.1$ Hz), 142.1 (d, $J_{\text{C-P}} = 11.5$ Hz), 138.7 (d, $J_{\text{C-P}} = 10.5$ Hz), 136.0, 135.9, 135.3, 128.6, 125.9, 120.1, 62.3 (d, $J_{\text{C-P}} = 5.7$ Hz), 60.7, 20.1, 19.7, 16.4 (d, $J_{\text{C-P}} = 6.7$ Hz), 14.5; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 19.0429$; IR (film) 2983.88, 1712.79, 1637.56, 1446.61, 1367.53, 1242.16, 1028.06, 765.74 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{25}\text{O}_5\text{P}(\text{M}^+)$ 341.1518, found 341.1521.

(E)-Ethyl 3-(2-(diethoxyphosphoryl)-4-methylphenyl)acrylate (65h): ^1H NMR (400 MHz, CDCl_3): δ 8.31 (d, $J = 16.0$ Hz, 1H), 7.88-7.84 (m, 1H), 7.60-7.58 (m, 1H), 7.35-7.33 (m, 1H), 6.32 (d, $J = 16.0$ Hz, 1H), 4.26-4.08 (m, 4H), 2.39 (s, 3H), 1.33-1.31 (m, 9H); ^{13}C NMR (400 MHz, CDCl_3) δ 166.8, 142.9, 140.0 (d, $J_{\text{C-P}} = 13.4$ Hz), 135.4 (d, $J_{\text{C-P}} = 9.6$ Hz), 133.6, 128.7, 127.3 (d, $J_{\text{C-P}} = 14.4$ Hz), 120.3, 62.4, 60.7, 21.4, 16.4 (d, $J_{\text{C-P}} = 6.7$ Hz), 14.4 (d, $J_{\text{C-P}} = 11.5$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 18.5560$; IR (film) 2981.95, 1438.90, 1242.16, 1132.21, 1008.77, 748.38, 694.37, 565.14, 540.07 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{23}\text{O}_5\text{P}(\text{M}^+)$ 327.1361, found 327.1362.

(E)-Ethyl 3-(2-(diethoxyphosphoryl)phenyl)acrylate (65i): ^1H NMR (400 MHz, CDCl_3): δ 8.30 (d, $J = 16.0$ Hz, 1H), 8.05-7.99 (m, 1H), 7.60-7.56 (m, 1H), 7.50-7.26 (m, 1H), 6.38 (d, $J = 16.0$ Hz, 1H), 4.26 (q, $J = 7.3$ Hz, 2H), 3.80 (s, 3H), 3.78 (s, 3H), 1.34 (t, $J = 7.1$ Hz, 3H), 6.75 (m, 1H), 4.23-4.03 (m, 4H), 1.31 (q, $J = 7.3$ Hz, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 166.6, 142.7, 138.1 (d, $J_{\text{C-P}} = 9.5$ Hz), 134.8 (d, $J_{\text{C-P}} = 9.5$ Hz), 133.0, 132.0 (d, $J_{\text{C-P}} = 9.5$ Hz), 129.3 (d, $J_{\text{C-P}} = 15.3$ Hz), 128.7, 127.6, 127.4 (d, $J_{\text{C-P}} = 13.3$ Hz), 125.8, 121.7, 60.9, 52.9 (d, $J_{\text{C-P}} = 5.7$ Hz), 14.5; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 21.1205$; IR (film) 1710.86, 1315.45, 1247.94, 1182.36, 1138.00, 1033.85, 775.38, 557.43 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{21}\text{O}_5\text{P}(\text{M}^+)$ 313.1205, found 313.1206.

(2E,2'E)-Diethyl 3,3'-(2-(diethoxyphosphoryl)-1,3-phenylene)diacrylate (66i): ^1H NMR (400 MHz, CDCl_3): δ 8.53 (m, $J = 16.0$ Hz, 2H), 7.58-7.57 (m, 3H), 6.23 (d, $J = 16.0$ Hz, 2H), 4.28 (q, $J = 7.1$ Hz, 4H), 3.79 (s, 3H), 3.78 (s, 3H), 1.34 (t, $J = 7.3$ Hz, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 166.6 (d, $J_{\text{C-P}} = 3.8$ Hz), 144.8 (d, $J_{\text{C-P}} = 8.6$ Hz), 141.2 (d, $J_{\text{C-P}} = 9.6$ Hz), 132.9, 129.5 (d, $J_{\text{C-P}} = 14.4$ Hz), 60.7, 52.7, 14.5 (d, $J_{\text{C-P}} = 4.8$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 19.3783$; IR (film) 3410.15, 1708.93, 1629.85, 1363.67, 1273.02, 1028.06, 1028.06, 977.91, 555.50 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{18}\text{H}_{23}\text{O}_7\text{P}(\text{M}^+)$ 383.1260, found 383.1255.

(*E*)-Ethyl 3-(2-(diethoxyphosphoryl)-5-methoxyphenyl)acrylate (65j): ^1H NMR (400 MHz, CDCl_3): δ 8.32 (d, $J = 15.6$ Hz, 1H), 8.01-7.95 (m, 1H), 7.18-7.16 (m, 1H), 6.98-6.94 (m, 1H), 6.34 (d, $J = 16.0$ Hz, 1H), 4.31-4.04 (m, 6H), 3.88 (s, 3H), 1.36-1.30 (m, 9H); ^{13}C NMR (400 MHz, CDCl_3) δ 166.6, 163.1, 143.0, 140.1, 136.9 (d, $J_{\text{C-P}} = 11.5$ Hz), 121.5, 114.5 (d, $J_{\text{C-P}} = 15.3$ Hz), 113.2 (d, $J_{\text{C-P}} = 14.4$ Hz), 62.4 (d, $J_{\text{C-P}} = 5.7$ Hz), 60.8, 55.7, 16.5 (d, $J_{\text{C-P}} = 6.7$ Hz), 14.5; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 18.9495$; IR (film) 2983.88, 1712.79, 1637.56, 1595.13, 1560.41, 1477.47, 1367.53, 1234.44, 966.34 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{23}\text{O}_6\text{P}(\text{M}^+)$ 343.1311, found 343.1310.

(2*E*,2'*E*)-Diethyl3,3'-(2-(diethoxyphosphoryl)-5-methoxy-1,phenylene)diacrylate(66j): ^1H NMR (400 MHz, CDCl_3): δ 8.58 (d, $J = 16.0$ Hz, 2H), 7.06 (d, $J = 3.6$ Hz, 2H), 6.21 (d, $J = 16.0$ Hz, 2H), 4.30-4.02 (m, 8H), 3.89 (s, 3H), 1.39-1.11 (m, 12H); ^{13}C NMR (400 MHz, CDCl_3) δ 166.6, 162.2, 145.3, 143.1 (d, $J_{\text{C-P}} = 10.5$ Hz), 121.8, 114.8 (d, $J_{\text{C-P}} = 14.3$ Hz), 62.3 (d, $J_{\text{C-P}} = 5.7$ Hz), 60.9, 55.8, 16.4 (d, $J_{\text{C-P}} = 6.7$ Hz), 14.5; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 17.1537$; IR (film) 3016.67, 1712.79, 1639.49, 1589.34, 1417.68, 1361.74, 1224.80, 1180.44, 1109.07, 1024.20, 765.74 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{21}\text{H}_{29}\text{O}_8\text{P}(\text{M}^+)$ 441.1678, found 441.1674.

(E)-Ethyl 3-(1-(diethoxyphosphoryl)naphthalen-2-yl)acrylate (65k): ^1H NMR (400 MHz, CDCl_3): δ 9.10 (d, $J = 2.2$ Hz, 1H), 8.90 (d, $J = 16.0$ Hz, 1H), 8.01 (d, $J = 9.2$ Hz, 1H), 7.84 (d, $J = 8.2$ Hz, 1H), 7.67-7.26 (m, 3H), 6.34 (d, $J = 16.0$ Hz, 1H), 4.33-4.22 (m, 4H), 4.12-4.05 (m, 2H), 1.38-1.29 (m, 9H); ^{13}C NMR (400 MHz, CDCl_3) δ 166.7, 146.0, 140.2, 133.8, 133.6, 128.5, 128.0, 127.8, 126.9, 125.1 (d, $J_{\text{C-P}} = 15.3$ Hz), 121.9, 62.2, 60.7, 16.3 (d, $J_{\text{C-P}} = 6.7$ Hz), 14.4; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 17.9880$; IR (film) 3008.95, 1708.93, 1419.61, 1363.67, 1224.80, 1091.71, 1022.27, 765.74, 665.44, 530.42 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{19}\text{H}_{23}\text{O}_5\text{P}(\text{M}^+)$ 363.1361, found 363.1364.

(E)-Ethyl 3-(3-(diethoxyphosphoryl)naphthalen-2-yl)acrylate (65l): ^1H NMR (400 MHz, CDCl_3): δ 8.63 (d, $J = 16.5$ Hz, 1H), 8.42 (d, $J = 15.6$ Hz, 1H), 8.14 (d, $J = 5.0$ Hz, 1H), 7.95-7.87 (m, 2H), 7.63-7.56 (m, 2H), 6.48 (d, $J = 16.0$ Hz, 1H), 4.33-4.09 (m, 6H), 1.36-1.32 (m, 9H); ^{13}C NMR (400 MHz, CDCl_3) δ 166.9, 143.6, 137.2, 134.8, 129.0, 128.4, 127.8, 127.4, 120.9, 62.1, 60.1, 29.7, 16.2, 14.5; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 18.5560$; IR (film) 3005.10, 1712.79, 1363.67, 1222.87, 1180.44, 1024.20, 970.19, 763.81, 530.42 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{19}\text{H}_{23}\text{O}_5\text{P}(\text{M}^+)$ 363.1361, found 363.1360.

(E)-Ethyl 3-(2-(diisopropoxyphosphoryl)phenyl)acrylate (65m): ^1H NMR (400 MHz, CDCl_3): δ 8.40 (d, $J = 16.5$ Hz, 1H), 8.11-8.05 (m, 1H), 7.85-7.57 (m, 1H), 7.48-7.46 (m, 1H), 7.45-7.28 (m, 2H), 6.36 (d, $J = 16$ Hz, 1H), 4.78-4.67 (m, 2H), 4.28 (q, $J = 7.1$ Hz, 2H), 1.42-1.20 (m, 15H); ^{13}C NMR (400 MHz, CDCl_3) δ 166.7, 143.5, 134.6 (d, $J_{\text{C-P}} = 9.5$ Hz), 132.6 (d, $J_{\text{C-P}} = 2.9$ Hz), 131.9 (d, $J_{\text{C-P}} = 10.1$ Hz), 129.4 (d, $J_{\text{C-P}} = 14.3$ Hz), 128.5 (d, $J_{\text{C-P}} = 15.1$ Hz), 127.2 (d, $J_{\text{C-P}} = 13.4$ Hz), 121.0, 71.5 (d, $J_{\text{C-P}} = 6.7$ Hz), 70.9, 60.7, 24.2, 24.0, 23.9, 14.5; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 15.8240$; IR (film) 3018.60, 2983.88, 1710.86, 1467.83, 1386.82, 1313.52, 1242.16, 1103.28, 991.41, 781.17, 736.81, 667.37, 565.14 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{25}\text{O}_5\text{P}(\text{M}^+)$ 341.1518, found 341.1522.

(2E,2'E)-Diethyl 3,3'-(2-(diisopropoxyphosphoryl)-1,3-phenylene)diacrylate (66m): ^1H NMR (400 MHz, CDCl_3): δ 8.67 (d, $J = 16.0$ Hz, 2H), 7.59-7.52 (m, 3H), 6.21 (d, $J = 15.6$ Hz, 2H), 4.82-4.74 (m, 2H), 4.74-4.25 (m, 4H), 1.41-1.32 (m, 12H), 1.27-1.19 (m, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 166.7, 145.6 (d, $J_{\text{C-P}} = 3.8$ Hz), 140.7 (d, $J_{\text{C-P}} = 9.6$ Hz), 132.3, 129.4, 129.3, 121.4, 71.8 (d, $J_{\text{C-P}} = 6.7$ Hz), 60.8, 24.1, 14.5; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 13.8764$; IR (film) 2981.95, 1712.79, 1635.64, 1454.33, 1367.53, 1311.59, 1238.30, 1174.65, 1103.28, 991.41, 650.01, 561.29 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{22}\text{H}_{31}\text{O}_7\text{P}(\text{M}^+)$ 439.1886, found 439.1879.

(E)-ethyl 3-(2-(bis(dimethylamino)phosphoryl)phenyl)acrylate (65n): ^1H NMR (400 MHz, CDCl_3): δ 8.56 (d, $J = 16.0$ Hz, 1H), 7.17-7.42 (m, 4H), 6.34 (d, $J = 16.0$ Hz), 4.25 (q, $J = 7.1$ Hz, 6H), 2.69 (s, 6H), 2.67 (s, 6H), 1.33 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (400 MHz, CDCl_3) δ 166.9, 143.7, 139.2, 133.4 (d, $J_{\text{C-P}} = 8.6$ Hz), 131.9, 129.5, 129.4, 127.8, 127.7, 120.8, 60.8, 36.6 (d, $J_{\text{C-P}} = 4.8$ Hz), 14.5; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 29.9385$; IR (film) 1643.35, 1463.97, 1436.97, 1292.31, 1192.01, 979.84, 786.81 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{23}\text{N}_2\text{O}_3\text{P}(\text{M}^+)$ 311.1525, found 311.1524.

(E)-ethyl 3-(2-(bis(dimethylamino)phosphoryl)-5-methylphenyl)acrylate (65o): ^1H NMR (400 MHz, CDCl_3): δ 8.51 (d, $J = 16.0$ Hz, 1H), 7.58-7.49 (m, 2H), 7.27-7.23 (m, 1H), 6.32 (d, $J = 16.0$ Hz, 1H), 4.25 (q, $J = 7.1$ Hz, 2H), 2.69 (s, 6H), 2.67 (s, 6H), 1.33 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (400 MHz, CDCl_3) δ 166.9, 143.7, 138.6 (d, $J_{\text{C-P}} = 8.6$ Hz), 133.4 (d, $J_{\text{C-P}} = 8.6$ Hz), 130.2 (d, $J_{\text{C-P}} = 13.4$ Hz), 128.4 (d, $J_{\text{C-P}} = 12.4$ Hz), 120.5, 60.6, 36.6 (d, $J_{\text{C-P}} = 4.8$ Hz), 14.3; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 30.1333$; IR (film) 2841.08, 1710.86, 1598.99, 1506.41, 1296.16, 1132.21 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{25}\text{N}_2\text{O}_3\text{P}(\text{M}^+)$ 325.1681, found 325.1673.

(E)-ethyl 3-(2-(bis(diethylamino)phosphoryl)-3-methylphenyl)acrylate (65p): ^1H NMR (400 MHz, CDCl_3): δ 8.30 (d, $J = 16.0$ Hz, 1H), 7.49-7.26 (m, 3H), 6.11 (d, $J = 16.0$ Hz, 1H), 4.24 (q, $J = 7.3$ Hz, 2H), 3.15-2.99 (m, 10H), 1.33-1.24 (m, 3H), 1.14-1.06 (m, 15H); ^{13}C NMR (400 MHz, CDCl_3) δ 167.1, 147.7, 139.8, 132.6 (d, $J_{\text{C-P}} = 9.6$ Hz), 132.1 (d, $J_{\text{C-P}} = 12.4$ Hz), 131.4, 131.1, 129.9 (d, $J_{\text{C-P}} = 12.5$ Hz), 126.7 (d, $J_{\text{C-P}} = 11.5$ Hz), 125.1 (d, $J_{\text{C-P}} = 13.4$ Hz), 119.3, 60.6, 39.9 (d, $J_{\text{C-P}} = 4.8$ Hz), 39.3, 27.9, 16.4, 14.5, 14.3, 14.2; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 28.2939$; IR (film) 2 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{39}\text{N}_2\text{O}_2\text{P}(\text{M}^+)$ 335.2827, found 335.2818.

(E)-ethyl 3-(2-(bis(diethylamino)phosphoryl)-4-methylphenyl)acrylate (65q): ^1H NMR (400 MHz, CDCl_3): δ 8.68 (d, $J = 16$ Hz, 1H), 7.63-7.25 (m, 3H), 6.28 (d, $J = 16.0$ Hz, 1H), 4.25-4.20 (m, 2H), 3.12-3.03 (m, 8H), 2.37 (s, 3H), 1.31-1.28 (m, 3H), 1.09-1.01 (m, 12H); ^{13}C NMR (400 MHz, CDCl_3) δ 167.0, 143.9, 139.4 (d, $J_{\text{C-P}} = 12.4$ Hz), 138.2 (d, $J_{\text{C-P}} = 12.5$ Hz), 132.9, 132.3, 131.8, 128.9, 128.2, 127.7, 119.6, 60.6, 39.4 (d, $J_{\text{C-P}} = 4.8$ Hz), 38.5 (d, $J_{\text{C-P}} = 6.9$ Hz), 21.6 (d, $J_{\text{C-P}} = 5.7$ Hz), 14.2, 13.9, 13.8; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 29.5111$; IR (film) 1712.79, 1583.56, 1456.26, 1242.16, 1022.27, 758.02 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{20}\text{H}_{33}\text{N}_2\text{O}_3\text{P}(\text{M}^+)$ 381.2307, found 381.2303.

(E)-Butyl 3-(2-(diethoxyphosphoryl)-3-methylphenyl)acrylate (67a): ^1H NMR (400 MHz, CDCl_3): δ 8.56 (d, $J = 16.0$ Hz, 1H), 7.40-7.38 (m, 2H), 7.28-7.25 (m, 1H), 6.17 (d, $J = 16.0$ Hz, 1H), 4.23-4.04 (m, 6H), 2.69 (s, 3H), 1.73-1.66 (m, 2H), 1.47-1.42 (m, 2H), 1.31 (t, $J = 7.1$ Hz, 6H), 0.96 (t, $J = 7.6$ Hz, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 166.9, 146.4, 144.5, 140.5 (d, $J_{\text{C-P}} = 10.5$ Hz), 133.2 (d, $J_{\text{C-P}} = 15.3$ Hz), 132.1, 126.3 (d, $J_{\text{C-P}} = 13.4$ Hz), 120.7, 64.6, 62.0 (d, $J_{\text{C-P}} = 4.8$ Hz), 30.9, 23.2, 19.4, 16.4 (d, $J_{\text{C-P}} = 6.7$ Hz), 13.9; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 18.3667$; IR (film) 2962.66, 1712.79, 1635.64, 1581.63, 1454.33, 1390.68, 1309.67, 1238.30, 1168.86, 1138.00, 1022.27, 968.27, 754.17, 640.37, 570.93, 532.35 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{18}\text{H}_{27}\text{O}_5\text{P}(\text{M}^+)$ 355.1674, found 355.1675.

(E)-Benzyl 3-(2-(diethoxyphosphoryl)-3-methylphenyl)acrylate (67b): ^1H NMR (400 MHz, CDCl_3): δ 8.62 (d, $J = 16.0$ Hz, 1H), 7.43-7.26 (m, 8H), 6.22 (d, $J = 16.0$ Hz, 1H), 5.25 (s, 2H), 4.19-4.01 (m, 4H), 2.69 (s, 3H), 1.31-1.26 (m, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 166.6, 146.9, 144.1, 140.5, 136.1, 132.9, 132.0, 129.1, 128.6, 128.3, 127.8, 119.9, 78.4, 77.5, 76.7, 67.7, 66.3, 61.8, 23.0, 16.2 (d, $J_{\text{C-P}} = 6.7$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 18.2585$; IR (film) 3018.60, 1708.93, 1417.68, 1361.74, 1222.87, 1089.78, 1024.20, 966.34, 748.38, 667.37, 530.42 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{21}\text{H}_{25}\text{O}_5\text{P}(\text{M}^+)$ 389.1518, found 389.1495.

(E)-Diethyl (2-methyl-6-(2-(phenylsulfonyl)vinyl)phenyl) phosphonate (67c): ^1H NMR (400 MHz, CDCl_3): δ 8.66 (d, $J = 16.0$ Hz, 1H), 8.02 (d, $J = 7.3$ Hz, 1H), 7.63-7.26 (m, 7H), 6.59 (d, $J = 15.6$ Hz, 1H), 4.19-4.02 (m, 4H), 2.68 (s, 3H), 1.35-1.25 (m, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 145.1, 140.6, 138.2, 133.9, 133.8, 133.5, 132.3, 129.5, 129.4, 129.3, 128.1, 126.6, 62.2, 29.9, 23.0, 16.5 (d, $J_{\text{C-P}} = 5.7$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 17.9068$; IR (film) 2993.52, 1710.86, 1446.61, 1361.74, 1307.74, 1147.65, 1022.27, 970.19, 850.61, 686.66, 594.08 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{19}\text{H}_{23}\text{O}_5\text{PS}(\text{M}^+)$ 395.1082, found 395.1077.

(E)-Diethyl (2-(3-fluorostyryl)-6-methylphenyl) phosphonate (67d): ^1H NMR (400 MHz, CDCl_3): δ 8.63 (d, $J = 16.0$ Hz, 1H), 8.58-7.25 (m, 7H), 6.21 (d, $J = 15.6$ Hz, 1H), 4.21-4.01 (m, 4H), 2.69 (s, 3H), 1.27 (t, $J = 6.2$ Hz, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 166.6, 147.0 (d, $J_{\text{C-P}} = 3.8$ Hz), 144.5 (d, $J_{\text{C-P}} = 11.5$ Hz), 141.4, 140.4 (d, $J_{\text{C-P}} = 9.6$ Hz), 136.3, 133.3, 133.1, 132.1, 128.8, 128.7, 128.6, 128.5, 128.4, 126.4, 126.3, 120.2, 66.5, 62.0 (d, $J_{\text{C-P}} = 5.7$ Hz), 23.1 (d, $J_{\text{C-P}} = 2.9$ Hz), 16.4 (d, $J_{\text{C-P}} = 6.7$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 18.2585$; IR (film) 1712.79, 1419.61, 1363.67, 1224.80, 1165.00, 1091.71, 756.10, 698.23, 530.42 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{19}\text{H}_{22}\text{O}_3\text{PF}(\text{M}^+)$ 349.1369, found 349.1360.

(E)-Diethyl (2-(4-chlorostyryl)-6-methylphenyl) phosphonate (67e): ^1H NMR (400 MHz, CDCl_3): δ 8.19 (d, $J = 16.0$ Hz, 1H), 7.54-7.19 (m, 7H), 6.81 (d, $J = 16.0$ Hz, 1H), 4.21-4.03 (m, 4H), 2.69 (s, 3H), 1.32-1.27 (m, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 144.5, 143.3, 136.7, 132.1, 129.5, 129.0, 128.1 (d, $J_{\text{C-P}} = 4.8$ Hz), 125.4, 123.7, 61.8, 23.5, 16.5 (d, $J_{\text{C-P}} = 6.7$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 19.8815$; IR (film) 2991.59, 1710.86, 1490.97, 1452.40, 1363.67, 1217.08, 1091.71, 1022.27, 970.19, 815.89, 767.67, 665.44 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{19}\text{H}_{23}\text{O}_3\text{PCl}(\text{M}^+)$ 365.1073, found 365.1068.

(E)-Diethyl (2-methyl-6-styrylphenyl) phosphonate (67f): ^1H NMR (400 MHz, CDCl_3): δ 8.16 (d, $J = 16.0$ Hz, 1H), 7.56-7.17 (m, 8H), 6.85 (d, $J = 16.0$ Hz, 1H), 4.21-4.02 (m, 4H), 2.68 (s, 3H), 1.33-1.22 (m, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 138.4, 131.3, 130.9, 130.1, 128.9, 127.8, 127.0, 125.6, 125.4, 61.7, 23.5, 16.5 (d, $J_{\text{C-P}} = 6.7$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 20.0167$; IR (film) 3408.22, 2991.59, 1710.86, 1450.47, 1363.67, 1024.20, 968.27, 596.00, 530.42 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{19}\text{H}_{23}\text{O}_3\text{P}(\text{M}^+)$ 331.1463, found 331.1453.

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