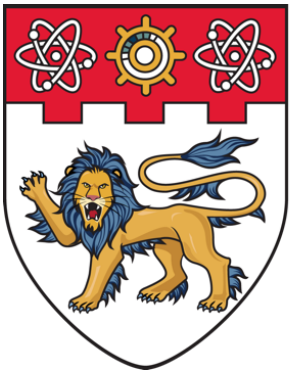
DEVELOPMENT OF NEW CARBON–CARBON BOND FORMING REACTIONS THROUGH 1,4-MIGRATION OF RHODIUM



NANYANG TECHNOLOGICAL UNIVERSITY

SINGAPORE

# DEVELOPMENT OF NEW CARBON–CARBON BOND FORMING REACTIONS THROUGH 1,4-MIGRATION OF RHODIUM

**MING JIALIN**

**SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES**

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A thesis submitted to the Nanyang Technological University in partial fulfilment of the requirement for the degree of Doctor of Philosophy

**2018**

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Ming Jialin

04 Jul 2018

# Table of Contents

**List of abbreviations**

| | |
|---|---|
| δ | chemical shift (ppm) |
| °C | degree centigrade |
| Ac | acetyl |
| acac | acetylacetonate |
| Ar | aryl (substituted aromatic ring) or argon atmosphere |
| BBN | 9-borabicyclo[3.3.1]nonane |
| binap | 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl |
| biphep | 2,2'-bis(diphenylphosphino)-1,1'-biphenyl |
| Bn | benzyl |
| Boc | *tert*-butyloxycarbonyl |
| brs | broad singlet |
| Bu | butyl |
| Bz | benzoyl |
| cat. | catalytic |
| cod | 1,5-cyclooctadiene |
| coe | cyclooctene |
| $cm^{-1}$ | wave number |
| Cy | cyclohexyl |
| d | doublet |
| DBU | 1,8-diazabicyclo[5.4.0]undec-7-ene |
| DCE | 1,2-dichloroethane |
| DFT | density functional theory |
| DME | 1,2-dimethoxyethane |

| | |
|---|---|
| DMF | *N*,*N*-dimethylformamide |
| DMSO | dimethyl sulfoxide |
| dppb | 1,4-bis(diphenylphosphino)butane |
| dppe | 1,2-bis(diphenylphosphino)ethane |
| dppp | 1,3-bis(diphenylphosphino)propane |
| dppf | 1,1’-bis(diphenylphosphino)ferrocene |
| dr | diastereomeric ratio |
| EDG | electron donating group |
| ee | enantiomeric excess |
| Eq | equation |
| equiv | equivalent |
| Et | ethyl |
| EWG | electron withdrawing group |
| FTIR | Fourier Transform Infrared Spectroscopy |
| Fc | ferrocenyl |
| g | gram |
| h | hour |
| Hz | hertz |
| *J* | coupling constants |
| k | reaction rate |
| kcal | kilocalorie |
| LDA | lithium diisopropylamide |
| LG | leaving group |
| LHMDS | lithium bis(trimethylsilyl)amide |

| | |
|---|---|
| M | concentration (N, mol/$dm^{-3}$) |
| $M^+$ | parent ion peak (mass spectrum) |
| m | multiplet |
| Me | methyl |
| mg | milligram |
| MHz | megahertz |
| min | minutes |
| mL | milliliters |
| mmol | millimole |
| MOP | 2-(Diphenylphosphino)-2’-methoxy-1,1’-binaphthyl |
| Ms | methanesulfonyl |
| NBS | *N*-bromosuccinimide |
| NMR | nuclear magnetic resonance |
| Ns | 4-nitrobenzenesulfonyl |
| OTf | trifluoromethanesulfonate |
| Ph | phenyl |
| ppm | parts per million |
| Pr | propyl |
| q | quartet |
| quient | quientet |
| Rh | rhodium |
| rt | room temperature |
| s | singlet |
| segphos | 4,4’-Bi-1,3-benzodioxole-5,5’-diylbis(diphenylphosphane) |

| | |
|---|---|
| sept | septet |
| sext | sextet |
| t | triplet |
| Tf | trifluoromethanesulfonyl |
| tfb | tetrafluorobenzobarrelenes |
| TFA | trifluoroacetic acid |
| THF | tetrahydrofuran |
| TLC | thin layer chromatography |
| TMEDA | *N*,*N*,*N*',*N*'-tetramethylethylenediamine |
| TMS | trimethylsilyl |
| Ts | *para*-toluenesulfonyl |

**Abstract**

This thesis documents our attempts to advance the chemistry of C–C bond forming reactions via 1,4-Rh shift.

Chapter 1 is an introduction of rhodium-catalyzed C–C bond forming reactions and 1,4-migration of rhodium. In the first section of Chapter 1, catalytic reactions of rhodium with organometallics are discussed. This section has been further divided into three subsections: 1,4-additions to alkenes, 1,2-additions to carbonyl and imine compounds, and additions to alkynes. The second section is an introduction of 1,4-migration of rhodium and its applications to catalytic C–C bonds forming reactions.

Chapter 2 describes our discovery of a reaction of potassium aryloxymethyltrifluoroborates with α,β-unsaturated carbonyl compounds in the presence of a chiral diene–rhodium catalyst, which introduces 2-methoxyaryl groups at the β-position of the α,β-unsaturated carbonyl compounds with high enantioselectivity in high yields. It may be surprising that these alkylboron reagents gave the hydroarylation products. The reaction is assumed to proceed through 1,4-Rh shift from aryloxymethyl–Rh intermediate to 2-methoxyaryl–Rh. The wide availability of phenol derivatives makes this asymmetric conjugate arylation synthetically useful.

Chapter 3 describes the first example of catalytic arylstannylation of alkynes. The reaction of arylstannanes $ArSnR_3$ with unfunctionalized alkynes was found to proceed in the presence of a rhodium catalyst and a catalytic amount of zinc chloride to give *ortho*-alkenylarylstannanes with high selectivity in high yields. The catalytic cycle is very unique, consisting of three transmetalation steps, from Sn to Rh, Rh to

Zn, and Zn to Sn, in addition to arylrhodation of the alkyne followed by 1,4-migration of Rh from the 2-arylalkenyl carbon to the *ortho*-alkenylaryl carbon.

Chapter 4 describes the first example of carbozincation of unfunctionalized alkynes using Rh catalysis. The addition of arylzinc reagents ArZnCl to alkynes was found to be catalyzed by rhodium complexes in the presence of a catalytic amount of zinc chloride. The selectivity in giving 2-arylalkenylzinc species or *ortho*-alkenylarylzinc species, the latter of which is generated through 1,4-Rh migration from alkenyl to aryl in the catalytic cycle, is controlled by the ligand on rhodium. Ligands cod and binap gave 2-arylalkenylzinc species and *ortho*-alkenylarylzinc species, respectively, with high selectivity.

# CHAPTER 1

## Introduction of Rhodium-Catalyzed Carbon–Carbon Bond Forming Reactions and 1,4-Migration of Rhodium

## 1.1 Introduction of the rhodium-catalyzed carbon–carbon bond forming reactions

The carbon–carbon bond is viewed as the heart of organic chemistry, and considerable attention has been paid to develop new synthetic methods for forming new carbon–carbon bonds over the last several decades. The transition metal-catalyzed reactions in this regard have become fashionable since application of palladium complexes to catalytic cross-coupling reactions. Specifically, Kumada,[1a] Stille,[1b] Mirozoki-Heck,[1c] Suzuki-Miyaura,[1d] Sonogashira[1e], Hiyama,[1f] and Tsuji-Trost[1g] are the famous examples of Pd-catalyzed coupling reactions. Like these cross-coupling reactions, transition-metal catalysts have proved to be extremely powerful tools for C–C bond formation.

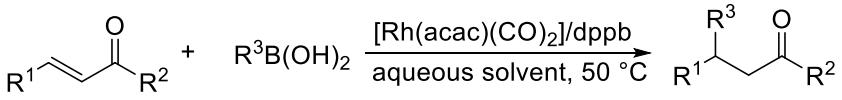
The rhodium complexes have also been frequently used in combination with the organometallic reagents to construct new carbon–carbon bonds. In this section, such addition reactions are discussed according to the following classification: 1,4-addition to electron-deficient olefins, 1,2-addition to carbonyl and imine compounds, and addition to alkynes.

### 1.1.1 Rhodium-catalyzed 1,4-addition to electron-deficient olefins

The copper-catalyzed conjugate addition reaction[2] was most commonly used before the discovery of the rhodium-catalyzed conjugate addition. Copper complexes can catalyze the 1,4-addition reaction in good yields with high chemoselectivities using Grignard reagents, organolithium reagents, or organozinc reagents as organometallics, at a very low temperature under anhydrous conditions. The strict reaction conditions have restricted its application.

As a milestone of rhodium catalysis, Miyaura reported in 1997 that a Rh(I) complex can catalyze the 1,4-addition of aryl/alkenylboronic acids to enones in high yields (Scheme 1.1).[3a] In this report, a wide range of aromatic and vinylic groups can be introduced to enones at the β-position using [Rh(acac)$(CO)_2$]/dppb as the catalyst in aqueous solvent at 50 °C. It is worth noting that bisphosphine ligands with a lager bite angle had better catalytic activity under the same reaction conditions. The absence of water led to low conversion of the substrate, since water in this reaction might accelerate the hydrolysis step. No 1,2-addition to the enone was observed, which is ascribed to the relatively low reactivity of organoboron reagents. Obviously, the mildness of the reaction conditions makes it more attractive than the copper-catalyzed 1,4-addition.

**Scheme 1.1. First Example of Rhodium-Catalyzed Hydroarylation/Alkenylaion of Enones**

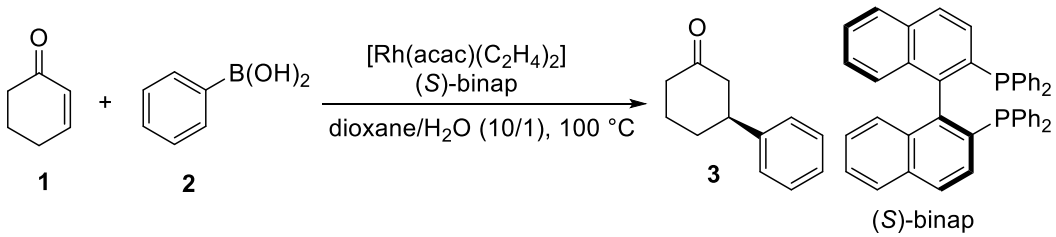



$R^1$ = H, Me, Ph; $R^2$ = H, Me, Bu, Ph; $R^3$ = aryl, alkenyl
aqueous solvent: DMF/$H_2O$ (6/1), cyclohexane/$H_2O$ (6/1), or MeOH/$H_2O$ (6/1)
Ligand effect on reactivity: dppb > dppp > TFP > dppe > $PPh_3$

Hayashi and Miyaura reported the first asymmetric arylation/alkenylation reaction of enones with arylboron reagents in 1998.[3b] In this reaction, the β-arylated ketones were produced in high yields with excellent enantioselectivities by treating the enones with arylboronic acid in dioxane/$H_2O$ (10/1) at 100 °C under the catalysis of a Rh(I) complex generated in situ from (*S*)-binap and [Rh(acac)$(C_2H_4)_2$]. Compared with the initial report by Miyaura in 1997,[3a] the rhodium precursor was changed from [Rh(acac)$(CO)_2$] to [Rh(acac)$(C_2H_4)_2$] due to the selective in situ generation of a Rh–(*S*)-binap species. For instance, 2-cyclohexenone (**1**) reacted with phenylboronic acid (**2**) to give the desired hydroarylation product **3** in only 43%

ee and 15% yield with [Rh(acac)$(CO)_2$] as the rhodium source (entry 2, Scheme 1.2). On the contrary, the use of [Rh(acac)$(C_2H_4)_2$] led to a 64% yield and 97% ee (entry 1, Scheme 1.2). Consistently, the use of isolated [Rh(acac)((*S*)-binap)] led to exactly the same results (64% yield and 97% ee) (entry 3, Scheme 1.2), suggesting that Rh–(*S*)-binap species is a key intermediate in the catalytic cycle. A main side reaction is hydrolysis of the arylboronic acids catalyzed by the rhodium complex, rather than 1,2-addition to the enone. The authors found that the yield was improved by using a large excess amount of $PhB(OH)_2$ (**2**) (entry 4, Scheme 1.2).

**Scheme 1.2. Rhodium-Catalyzed Asymmetric Hydroarylation of Enones**

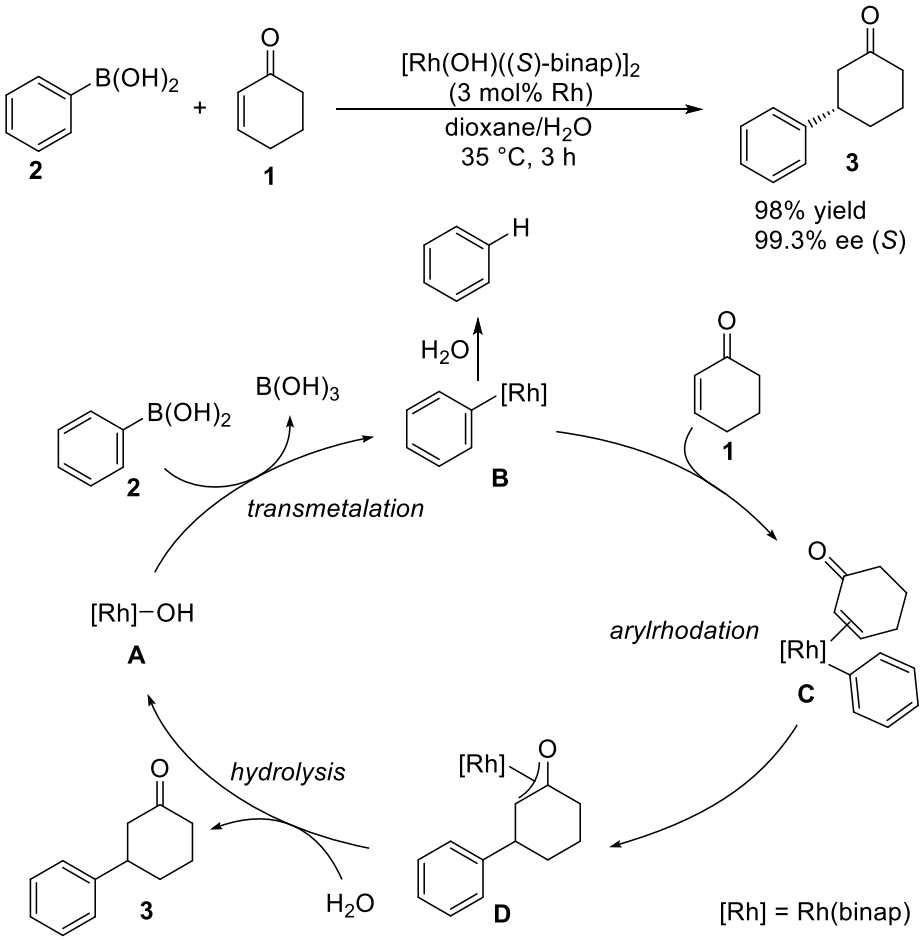



| entry | Rh complex | equiv of $PhB(OH)_2$ | yield (%) | ee (%) |
|---|---|---|---|---|
| 1 | [Rh(acac)$(C_2H_4)_2$] | 1.4 | 64 | 97 |
| 2 | [Rh(acac)$(CO)_2$] | 1.4 | 15 | 43 |
| 3 | [Rh(acac)((*S*)-binap)][a] | 1.4 | 64 | 97 |
| 4 | [Rh(acac)$(C_2H_4)_2$] | 2.5 | 93 | 97 |

[a] without additional binap added

In 2002, Hayashi reported a mechanism generally accepted for the rhodium-catalyzed hydroarylation of enones under aqueous conditions.[3c] Scheme 1.3 displays a catalytic cycle for the asymmetric arylation reaction of 2-cyclohexenone with phenylboronic acid catalyzed by Rh/(*S*)-binap complex. The reaction involves three steps, that is, transmetalation, phenylrhodation (π-coordination and insertion), and hydrolysis. It is interesting that rhodium in the catalytic cycle maintains the oxidation state of +1.

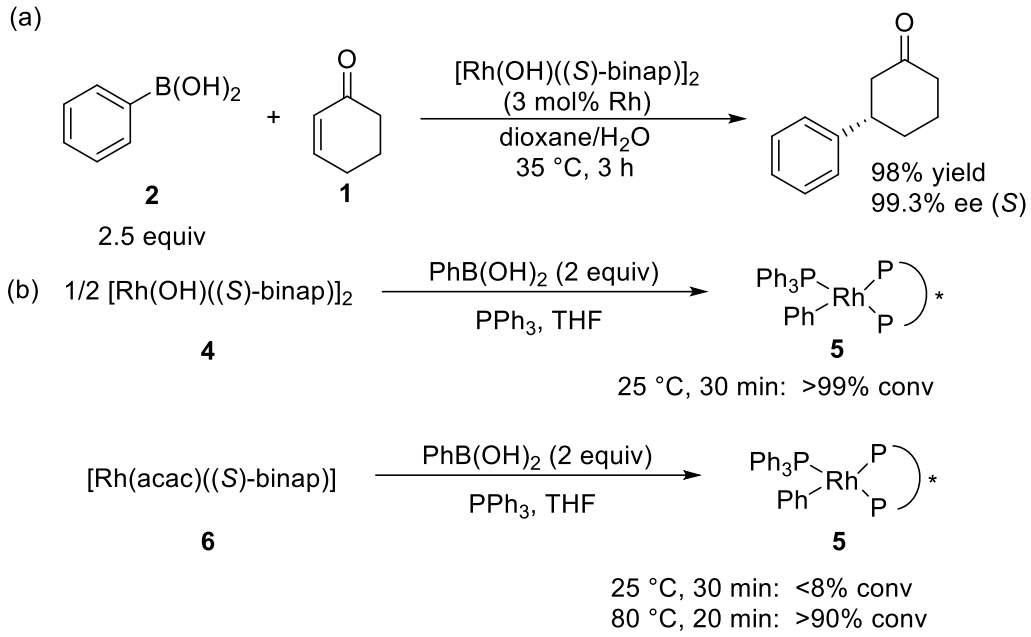
**Scheme 1.3. A Catalytic Cycle for Rhodium-Catalyzed Hydrophenylation of 2-Cyclohexenone**




Thus, phenylboronic acid (**2**) undergoes transmetalation with a HO–Rh species **A** to generate the Ph–Rh intermediate **B** and $B(OH)_3$ (Scheme 1.3).[3c] The carborhodation of 2-cyclohexenone (**3**) with the Ph–Rh intermediate **B** provides the oxa-π-allylrhodium intermediate **D**, along with the generation of a new stereogenic carbon center. The intermediate **D** undergoes protonolysis to produce the 1,4-addition product and to regenerate the HO–Rh species in the presence of a protic solvent (usually water or alcohols). The Ph–Rh species **B** also undergoes hydrolysis with a proton source to give benzene as the side product. Thus, an excess amount of arylboron reagent is necessary to achieve acceptable yields of arylation products. Finding a more active catalyst is a way to minimize the amount of arylboron reagents.

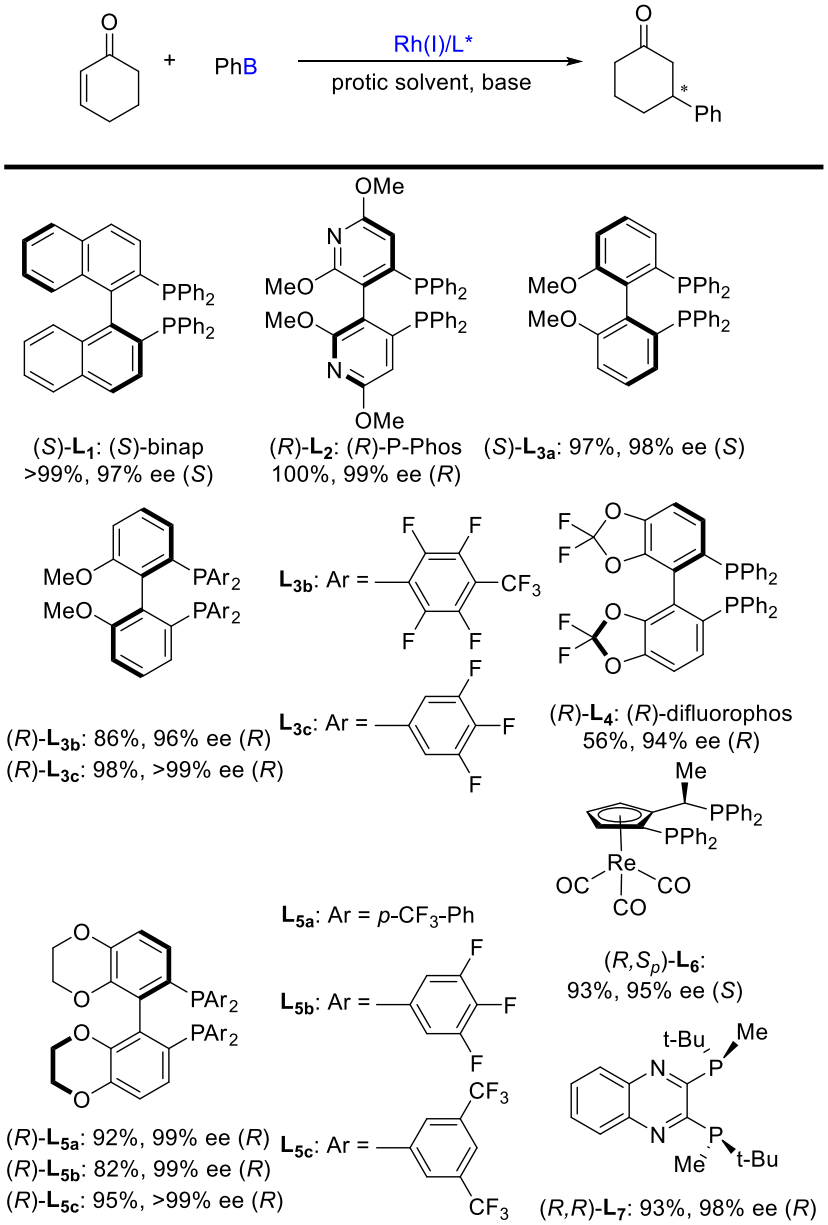
[Rh(OH)((*S*)-binap)]$_2$, which is prepared from [RhCl((*S*)-binap)]$_2$, was used as a more active catalyst for these arylation reactions in 2002.[3c] For instance, the use of [Rh(OH)((*S*)-binap)]$_2$ instead of [Rh(acac)((*S*)-binap)] realized the 1,4-addition reaction of phenylboron reagent **2** to 2-cyclohexenone (**1**) in the presence of 2.5 equiv of the boron reagent at a much lower temperature (35 °C) (Scheme 1.4a). At this low temperature, both the isolated yield and enantioselectivity of the product were increased. Some stoichiometric reactions were performed to explain the enhanced reactivity of [Rh(OH)((*S*)-binap)]$_2$. As is shown in Scheme 1.4b, the rhodium–hydroxide complex **4** is rapidly transmetalated with phenylboronic acid, which produces the phenylrhodium complex **5** in >99% conversion at ambient temperature within 30 min. In contrast, the conversion is <8% for the rhodium–acac complex **6** under the same conditions (Scheme 1.4b). A higher temperature (80 °C) is required for the transmetalation on [Rh(acac)((*S*)-binap)]. These experimental results indicate that the transmetalation of organoboronic acids takes place at a higher rate on [Rh(OH)((*S*)-binap)]$_2$ (**4**) than on the corresponding acac complex **6**. Since then, the rhodium–acac complexes have been rarely employed in the rhodium-catalyzed addition reactions.

**Scheme 1.4. [Rh(OH)((*S*)-binap)]$_2$-Catalyzed Asymmetric Arylation Reaction**




Undeniably, the choice of ligands is another fundamental issue for the Rh-catalyzed 1,4-addition reaction and is based on three criteria, namely, catalytic activity, enantioselectivity, and ease of synthesis. Recently, much attention has been paid to the design and synthesis of chiral ligands for enantioselective variant of Rh-catalyzed hydroarylation reactions. The chiral ligands in these reactions can be classified into two families, bidentate phosphorus and diene ligands. Some of these chiral ligands are compared for their enantioselectivity in the rhodium-catalyzed enantioselective 1,4-addition of phenylboron reagents to 2-cyclohexenone as a model system, which is illustrated in Schemes 1.5 and 1.6. Notably, this limited comparison is not sufficient enough to predict which ligand works better for the rhodium-catalyzed 1,4-addition of specific enones, since some ligands may show higher enantioselectivity for other substrates such as linear enones.

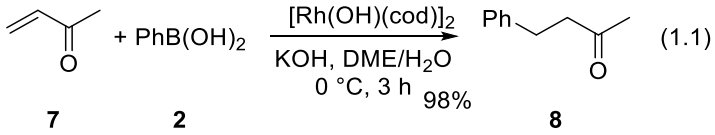
**Scheme 1.5. Selected Bidentate Phosphorous Ligands**




Hayashi and Miyaura reported the first example of Rh(I)-catalyzed asymmetric 1,4-addition of arylboronic acids to enones, where (*S*)-binap worked as the chiral ligand in 1998.[3b] Similar to (*S*)-binap, many other bisphosphine ligands with an axially-chiral biaryl backbone, including (*R*)-P-Phos (**L2**), MeO-biphep (**L3a**, **L3b**, and **L3c**), difluorophos (**L4**), and synphos (**L5a**, **L5b**, and **L5c**) (Scheme 1.5), were successfully employed to the model reaction in >90% ee.[4] The bisphosphine ligand

**L6**[5] with the planar-chiral cyrhetren and P-chiral bisphosphine ligand (*R*,*R*)-QuinoxP* **L7**[6] are reported to produce the hydroarylation product in high yield with high selectivity.

Notably, in 2003, Miyaura disclosed that $[Rh(OH)(cod)]_2$ (cod = 1,5-cyclooctadiene) can smoothly catalyze the hydroarylation reaction of $PhB(OH)_2$ (**2**) to methyl vinyl ketone (**7**) in DME/$H_2O$ even at 0 °C (Eq 1.1).[7]

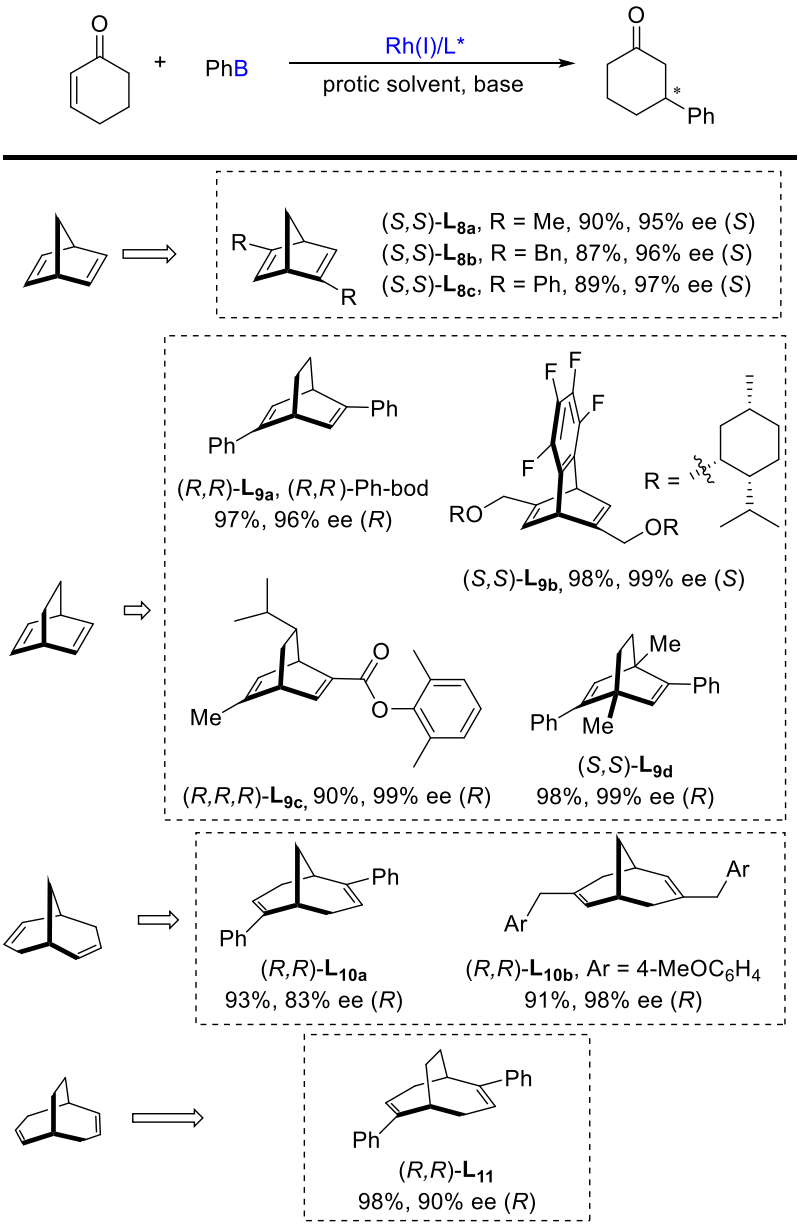



**7** **2** **8** (1.1)

In 2003, Bn-nbd, a chiral diene ligand based on a $C_2$-symmetric norbornadiene, was firstly employed to the rhodium-catalyzed asymmetric 1,4-addition.[8a] The model reaction gave rise to the arylation product in 87% yield and 96% ee, with $[RhCl((S,S)\text{-}\mathbf{L_{8b}})]_2$ as the catalyst (Scheme 1.6). In 2006, Hayashi and his coworkers disclosed that the transmetalation of arylboron reagents took place at a faster rate on the Rh/cod complex than on the Rh/binap complex under the same conditions.[9] The higher catalytic activity of the Rh/diene system for these reactions has encouraged organic chemists to develop diene ligands. Since then, the use of chiral diene ligands has been dramatically developed for rhodium-catalyzed asymmetric 1,4-addition during the past 16 years.[10] A variety of bicyclic diene scaffolds have been successfully employed as ligands to generate the target arylation product in high yield and enantioselectivity. They are bicyclo[2,2,1]heptadiene variations (**L8a**, **L8b**, and **L8c**),[8] bicyclo[2,2,2]octadiene variations (**L9a**, **L9b**, **L9c**, and **L9d**),[11a-11d] bicyclo[3,3,1]nonadiene variations (**L10a** and **L10b**),[12] and bicyclo[3,3,2]decadiene variation **L11**.[12b] Although many reported diene ligands have been applied to the transition metal-catalyzed reactions, they are still not as

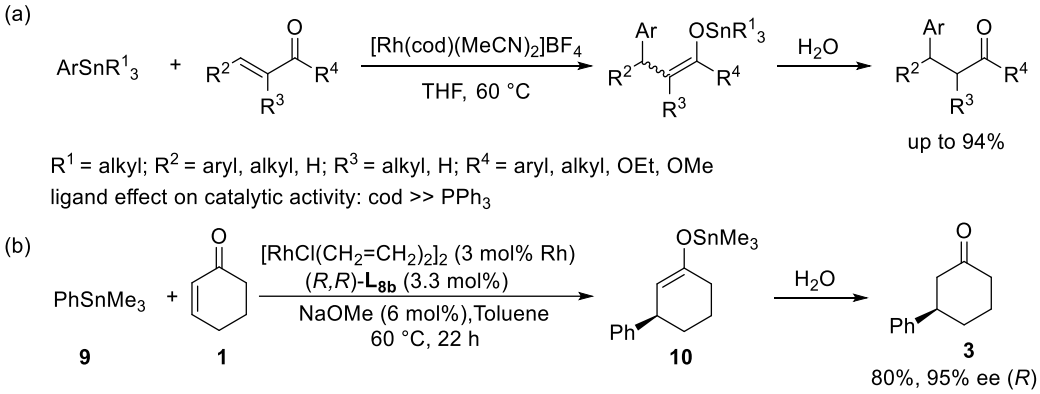
popular as bisphosphines ligands. One of the reasons is that their synthetic methods have not been developed well. Therefore, searching for the novel enantioselective synthesis of chiral diene ligands is attractive and challenging. Another drawback of diene ligands is their relatively weak coordination ability towards the transition metals. However, diene ligands are undeniably the 'rising stars' thanks to their high catalytic activity and selectivity for the rhodium-catalyzed 1,4-addition reactions.

**Scheme 1.6. Selected Examples of Chiral Diene Ligands**



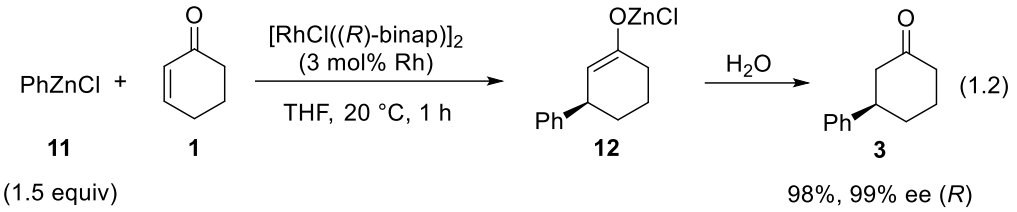
In addition to organoborons, organostannanes were successfully used for the rhodium-catalyzed 1,4-addition reactions in 1998 by Oi and his coworkers (Scheme 1.7a).[13a] The addition products were formed in high yields by treating enones with a slight excess amount of $ArSnMe_3$ in the presence of a Rh/cod catalyst in THF at 60 °C. The yields were low with bulkier organostannanes $ArSnBu_3$ and $Ar_4Sn$. The authors also reported that the presence of water in the reaction system enhanced the yields of some difficult substrates.[13c] Interestingly, the phosphorus ligands showed very low catalytic activity for this catalytic reaction, while the cod ligand showed very high catalytic ability. Hayashi successfully employed the Rh/chiral diene system to catalyze these reactions, which resulted in very high yields and enantioselectivities (Scheme 1.7b).[13d] For instance, the reaction of $PhSnMe_3$ (**9**) with 2-cyclohexenone (**2**) in the presence of Rh/(*R,R*)-**L$_{8b}$** catalyst and 0.06 equiv of NaOMe in toluene at 60 °C gave a high yield of the arylation product **3** after acidic workup. The use of binap instead of Bn-nbd led to a yield of less than 10% for the arylation product **3**.

**Scheme 1.7. Rh-Catalyzed Arylation of Enones/Enonates with Arylstannanes**



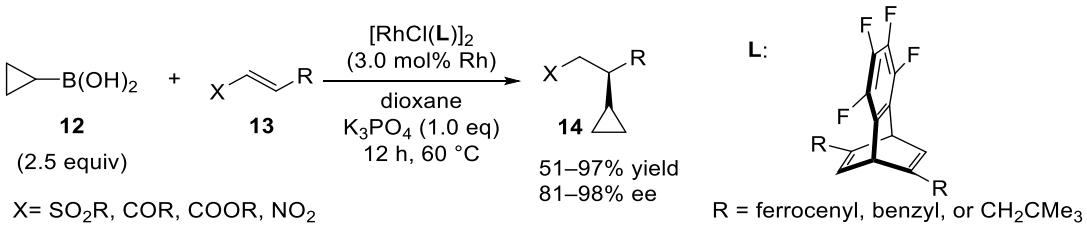

Compared with organoborons and organostannanes, organozinc reagents are considered as more reactive organometallic reagents for the transition metal-

catalyzed C–C bond formation reactions. In 2004, arylzinc chlorides were used as nucleophiles in the rhodium-catalyzed 1,4-addition reactions, which produced the desired arylation products in good yields with high enantioselectivities.[14a] For example, a high yield of zinc enolate **12** was generated by treating PhZnCl (**11**) with 2-cyclohexenone (**1**) in the presence of catalyst $[RhCl((R)\text{-binap})]_2$ in tetrahydrofuran at ambient temperature for 1 h (Eq 1.2). Hydrolysis of **12** gave the β-chiral ketone **3** with 99% ee in a yield of 98%. Since then, arylzinc reagents have been successfully applied to the addition reactions to some other activated alkenes.[14]



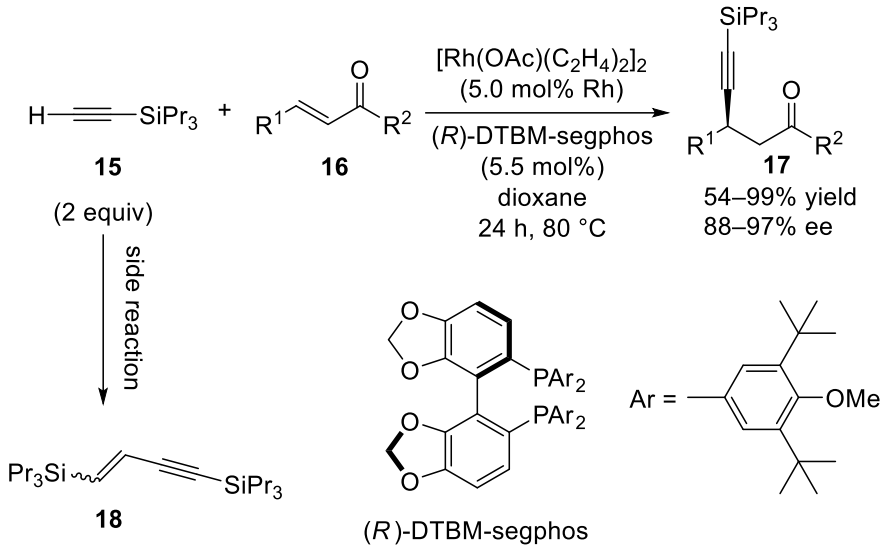

Alkylmetal reagents have been widely used in the alkylation reactions in the presence of copper catalysts.[2] However, only a few examples of rhodium-catalyzed alkylation of α,β-unsaturated carbonyl compounds are available, which may be ascribed to the low reactivity of alkyl–Rh intermediates to α,β-unsaturated carbonyl compounds. In 2015, Nishimura found that the reaction of cyclopropylboronic acid (**12**) with electron-deficient alkenes **13** (such as enones, enoates, and alkenylsulfones) gave high yields of alkylation products **14** with good enantioselectivities in the presence of a chiral diene–rhodium catalyst (Scheme 1.8).[15] It should be noted that the cyclopropyl group can avoid β-hydrogen elimination of the alkyl–Rh(I) intermediate since the formation of strained cyclopropene is relatively difficult.

**Scheme 1.8. Rhodium-Catalyzed Cyclopropylation of Activated Alkenes.**



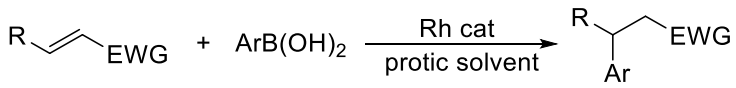

In 2008, Hayashi reported the first example of rhodium-catalyzed conjugate alkynylation of enones.[16a] New Csp–Csp$^3$ bonds were formed in high yields by the 1,4-addition of (triisopropylsilyl)acetylene (**15**) to enones **16** in the presence of a Rh/DTBM-segphos catalyst in dioxane at 80 °C for 24 h (Scheme 1.9). A main side product **18** was formed by the rhodium-catalyzed dimerization of the acetylene, even though the bulky triisopropylsilyl group was used. Alkynylsilanol[16b] and diphenyl[(triisopropylsilyl)ethynyl]methanol,[16c] which were relatively unreactive toward the dimerization under the reaction conditions, were successfully applied as the alkynylation reagents for the rhodium-catalyzed conjugate alkynylation. However, all acetylenes for the alkynylation of enones must be substituted with bulky trialkylsilyl groups on one side. There are still some problems remaining to be solved.

**Scheme 1.9. Rhodium-Catalyzed Alkynylation of α,β-Unsaturated Carbonyl Compounds.**




Not only enones and enoates but many other alkenes activated by adjacent electron-withdrawing groups were successfully applied to the rhodium-catalyzed conjugate addition reactions.[3d-3l] For example, α,β-unsaturated aldehydes,[17] α,β-unsaturated amides,[18] nitroalkenes,[19] alkenyl sulfones,[20] and alkenyl phosphonates,[21] were successfully hydroarylated in good yields in the presence of the rhodium catalyst and proton source (Scheme 1.10).

**Scheme 1.10. Selected Examples of Rhodium-Catalyzed Conjugate Addition**




EWG = COR, COOR, CHO, $CONR_2$, $NO_2$, $SO_2R$, $P(O)(OR)_2$

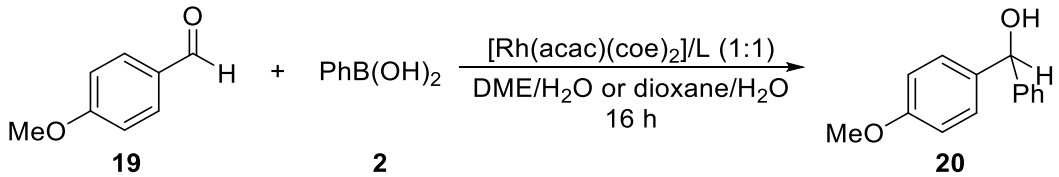
### 1.1.2 Rhodium-catalyzed 1,2-addition to carbonyl and imine compounds

The addition of organometallic reagents to carbon–oxygen or carbon–nitrogen double bonds is a commonly used method to form new carbon–carbon bonds in organic synthesis. For instance, the Barbier-Grignard type reactions can

give rise to products in moderate to high yields. Rhodium(I) complexes have also been extensively used as catalysts for the 1,2-addition to carbonyl and imine compounds.[3d-3l]

In 1998, Miyaura first reported the Rh(I)-catalyzed addition of alkenyl/aryl boronic acids to aldehydes producing the corresponding secondary alcohols in high yields.[22] The authors observed that electron-withdrawing groups on aldehydes and electron-donating groups on arylboronic acids accelerate the reaction, suggesting that the nucleophilic attack of aryl–Rh on the carbonyl group is involved in the catalytic cycle. In 2000, the authors reported the effects of phosphine ligands on the 1,2-addition of phenylboron reagent **2** to 4-$MeOC_6H_4CHO$ (**19**) (Scheme 1.11).[23] Their results suggested that the Rh/bisphosphine complexes with a large P–Rh–P (such as dppf) accelerate the reaction and that the bulky and electron-donating ligands (like $^tBu_3P$) show good catalytic activity when several monophosphines are employed. Typically, at the ligand-to-Rh ratio of 1:1, a quantitative yield of the alcohol **20** was obtained in the presence of a rhodium(I) catalyst generated in situ from $^tBu_3P$ and $[Rh(acac)(coe)_2]$ in $DME/H_2O$ at 25 °C for 16 h.

**Scheme 1.11. Rhodium-Catalyzed Addition of $PhB(OH)_2$ (2) to 4-$MeOC_6H_4CHO$ (19)**




**19** **2** **20**

**Effect of bite angle (at 80 °C):**

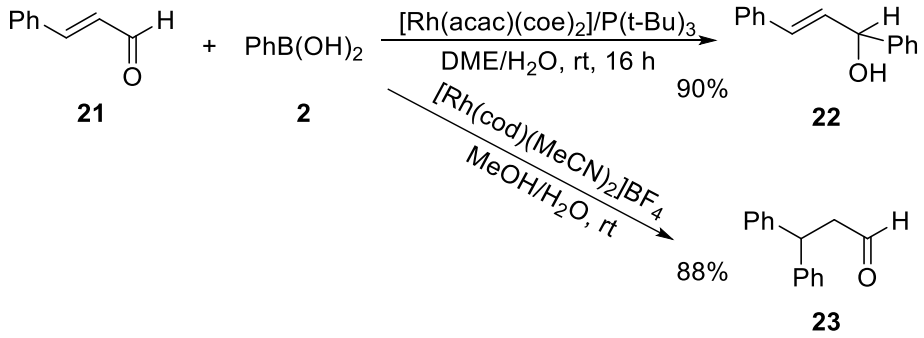
dppe (6%) dppp (71%) dppf (85%) dppf at 50 °C (20%)

**Effect of cone angle (at 50 °C):**

$Ph_3P$ (33%) $Me_3P$ (24%) $^iPr_3P$ (88%) $^tBu_3P$ at 20 °C (99%)

The addition to α,β-unsaturated aldehydes is special because it may proceed through either 1,2-addition or 1,4-addition. Particularly, Miyaura discovered that such competitive process is well controlled by the ligand on the rhodium catalyst.[23] In the addition reaction of phenylboronic acid (**2**) to cinnamaldehyde (**21**), the Rh/diene catalytic system gave the 1,4-addition product **23** in 88% yield without any 1,2-addition product **22**, whereas the Rh/ $^{t}Bu_3P$ system gave rise to the 1,2-adduct **22** in 90% yield (Scheme 1.12).

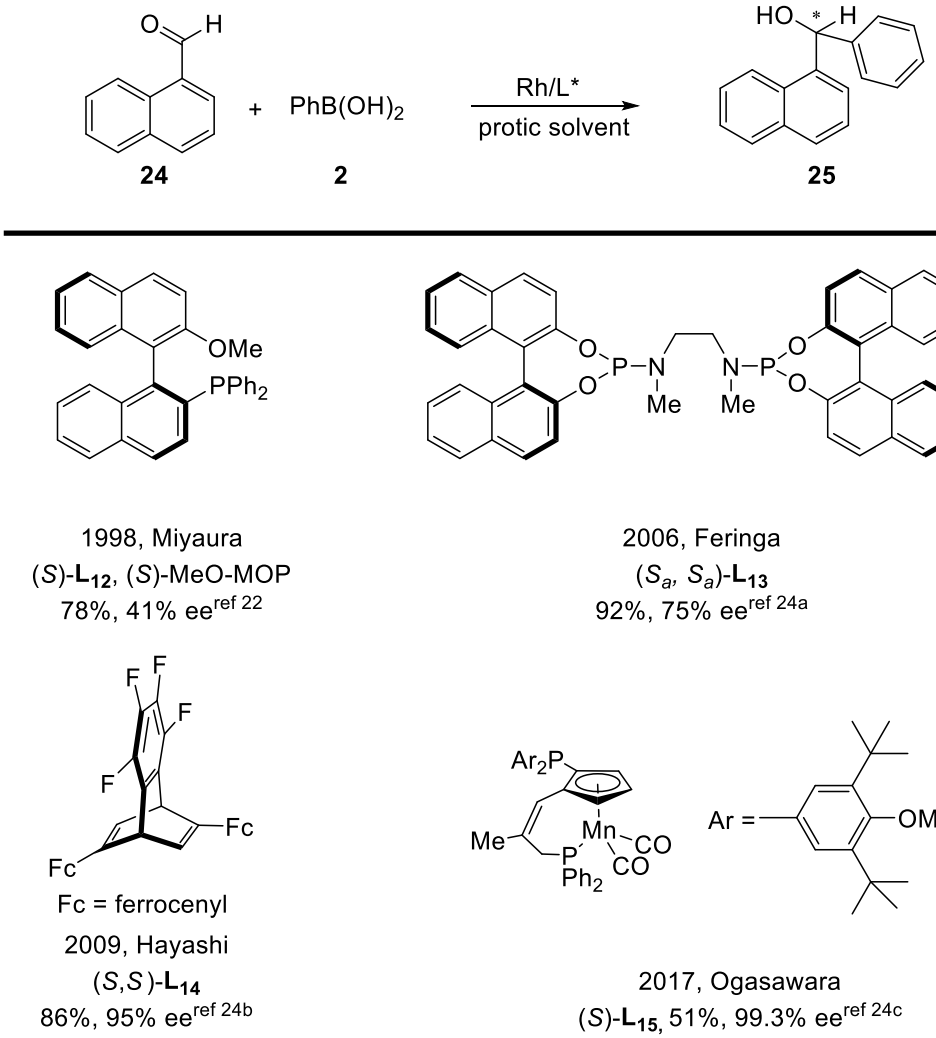
**Scheme 1.12. Ligand Control of 1,2-Addition or 1,4-Addition to Cinnamaldehyde**




Compared with the dramatic growth of rhodium-catalyzed asymmetric 1,4-addition, the enantioselective arylation of aldehydes is still associated with some challenges. In 1998, Miyaura and his coworkers reported that the hydroarylation product **25** was obtained in 78% yield with only 41% ee by the reaction of aromatic aldehyde **24** with phenylboronic acid (**2**) under the catalysis of a rhodium complex generated in situ from [Rh(acac)($CH_2$=$CH_2$)$_2$] and (*S*)-MeO-MOP in aqueous solvent at 60 °C (Scheme 1.13).[22] Since then, various ligand systems have been developed for such reactions. For example, some selected chiral ligands shown in Scheme 1.13 were successfully applied to the Rh-catalyzed addition of phenylboronic acid (**2**) to aldehyde **24**.[24] Of these ligands, Ogasawara's planar

chiral P-olefin ligand **$L_{15}$** is the best ligand in terms of enantioselectivity, although the yield of the arylation product is low.[24c]

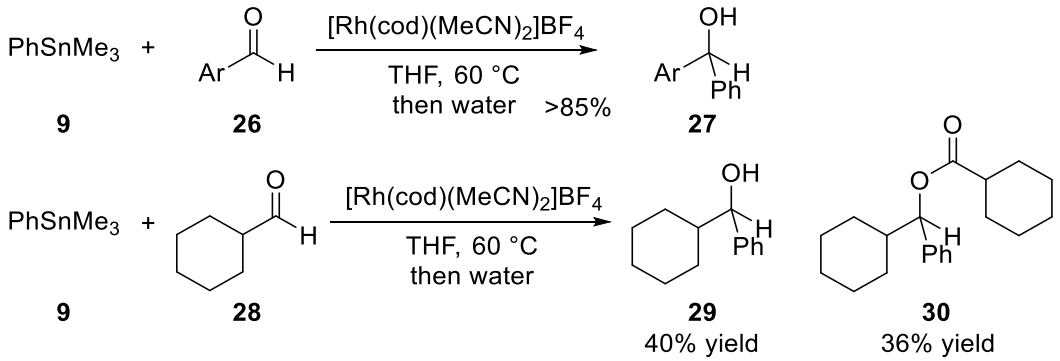
**Scheme 1.13. Selected Ligands for Rhodium-Catalyzed Asymmetric Hydroarylation of Aldehydes**




Before arylboron reagents, arylstannanes were employed in the rhodium-catalyzed arylation of aldehydes in 1997.[25] As shown in Scheme 1.14, the addition of phenyltrimethylstannane (**9**) to arylaldehydes **26** was catalyzed by Rh/cod complex in THF at 60 °C. The hydroarylation product **27** was isolated after hydrolysis in the yield of over 85%. When cyclohexanecarboxaldehyde (**28)** was used, the yield of the product **29** was much lower because of the byproduct **30**. The

authors proposed that the bypoduct **30** was formed by the insertion of another aldehyde **28** into the rhodium–oxygen bond of intermediate **D**, which is shown in Scheme 1.20. Later, Li carried out these reactions in the degassed boiling water under the catalysis of $[Rh(cod)_2]BF_4$.[26] Under these modified conditions, aromatic aldehydes gave the hydroarylation products in the yield of over 70%, and aliphatic aldehydes produced the 1,2-adducts in the yield of over 52%.

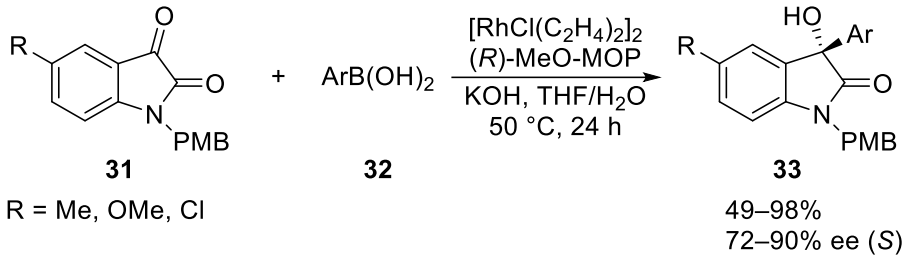
**Scheme 1.14. First Example of Rhodium-Catalyzed Hydroarylation of Aldehydes with Arylstannanes**




Ketones are less reactive than aldehydes in the rhodium-catalyzed 1,2-addition, which can be attributed to their steric hindrance. In 2006, Hayashi and his coworkers reported that the arylation products **33** were formed in high yields by treatment of isatins **31** with arylboronic acids **32** at 50 °C in the presence of a catalyst in situ generated from $[RhCl(C_2H_4)_2]_2$ and (*R*)-MeO-MOP ((*R*)-**L12**), with THF/$H_2O$ being used as the solvent, and the reaction showed moderate to high enantioselectivities (Scheme 1.15).[27a] A key point for this reaction lies in that the carbonyl group of isatins **31** is activated by the adjacent electron-withdrawing group. Similarly, 2,2,2-trifluoroacetophenones[27b] and α-ketoesters[27c] are reactive toward Rh-catalyzed 1,2-addition with organoboron reagents. In 2016, Tang and his coworkers reported the rhodium-catalyzed enantioselective hydroarylation of simple

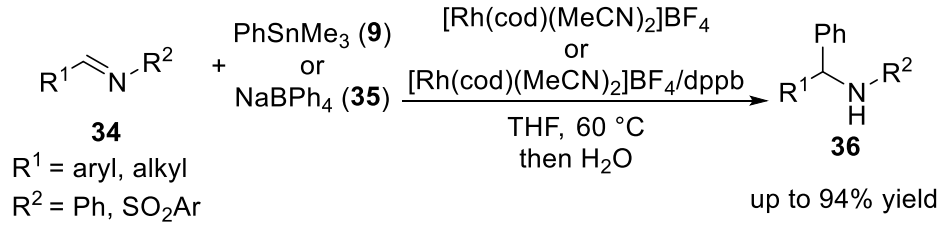
aryl ketones.[27d] The high yield and enantioselectivty were achieved with (*R*,*R*,*R*,*R*)-WingPhos as the ligand.

**Scheme 1.15. Rhodium-Catalyzed Hydroarylation of Isatins**



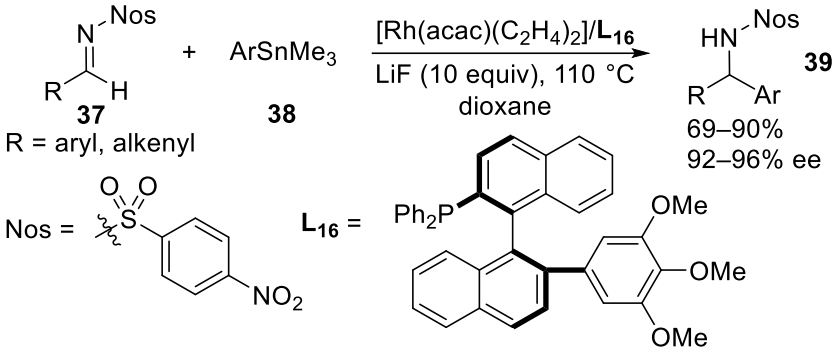

In 2000, Miyaura reported that the addition of phenyltrimethylstannane (**9**) or sodium tetraphenylborate (**35**) to *N*-sulfonyl aldimines **34** is catalyzed by rhodium complex, $[Rh(cod)(MeCN)_2]BF_4$ or $[Rh(cod)(MeCN)_2]BF_4$/dppb, to give high yields of the corresponding 1,2-addition products (Scheme 1.16).[28]

**Scheme 1.16. Rhodium-Catalyzed Hydroarylation of Aldimines**



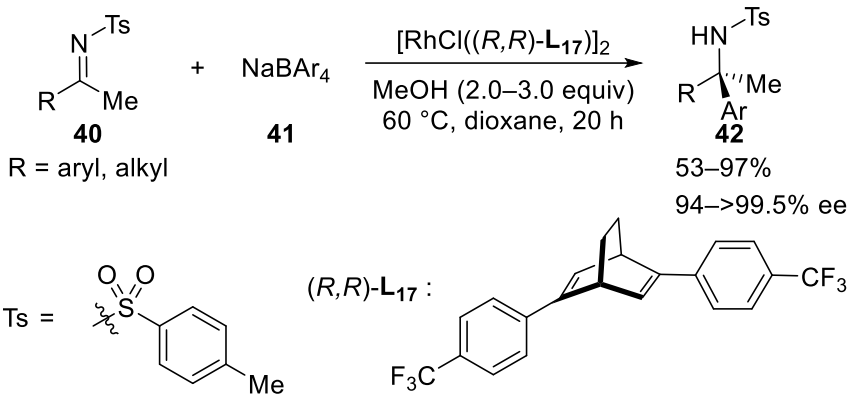

In 2000, Hayashi reported the first example of enantioselective arylation of imines.[29] The reaction of *N*-(4-nitrobenzene)sulfonyl aldimines **37** with aryl/alkenylstannanes **38** in the presence of a catalyst generated in situ from $[Rh(acac)(CH_2{=}CH_2)_2]$ and **L16** in refluxed dioxane for 12 h produced the diarylmethylamines **39** in moderate to high yields and >92% ee (Scheme 1.17). The addition of 10 equiv of LiF was necessary for high reproducibility of these reactions.

**Scheme 1.17. Rhodium-Catalyzed Asymmetric Hydroarylation of Imines**




Ketimines are less reactive than aldimines, which could be ascribed to the steric hindrance. Hayashi successfully developed the Rh-catalyzed 1,2-addition reaction to *N*-tosyl ketimines **40** in 2010, with chiral diene–rhodium complex as a catalyst and sodium tetraarylborates **41** as organometalic reagents (Scheme 1.18).[30] High yields were achieved using methanolic dioxane as the solvent.

**Scheme 1.18. Rhodium-Catalyzed Asymmetric Hydroarylation of Ketimines**

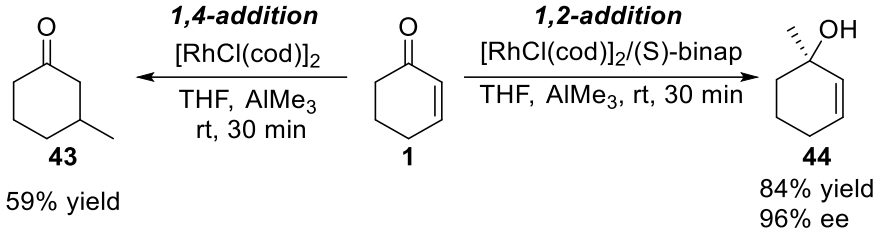



In addition to the arylation of imines, the rhodium-catalyzed methylation of imines has been developed.[31] The reaction was not applicable to the addition of the alkyl groups which possess β-hydrogen.

Von Zezschwitz and his coworkers developed the Rh-catalyzed 1,2-methylation of cyclic enones with $AlMe_3$.[32] For instance, the 1,2-methylation product **44** was produced in 84% yield by the addition reaction of $AlMe_3$ to

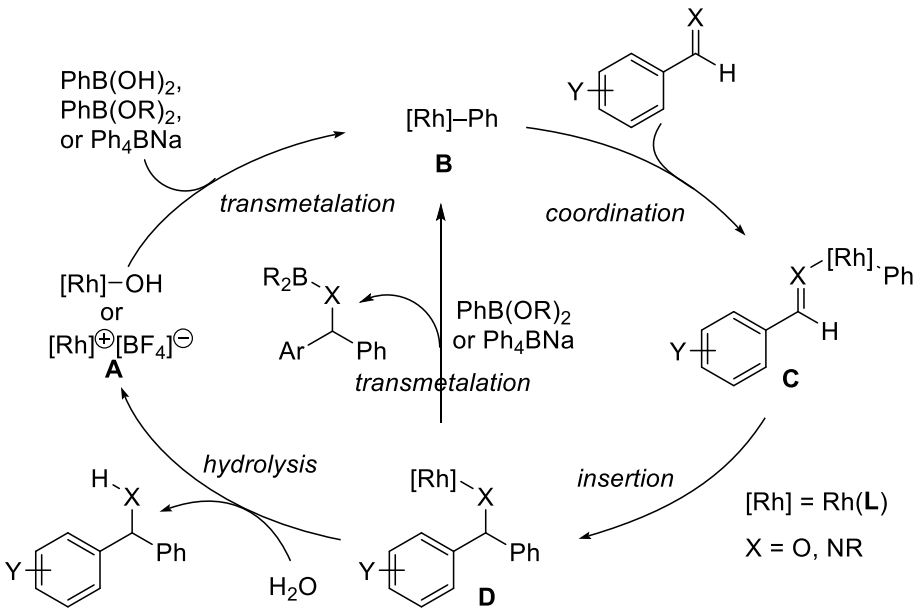
cyclohex-2-enone (**1**) using [RhCl((*S*)-binap)]$_2$ prepared in situ as a catalyst in THF at ambient temperature (Scheme 1.19).[32c] On the other hand, the 1,4-methylation product **43** was the main product when [RhCl(cod)]$_2$ was used instead of [RhCl((*S*)-binap)]$_2$. This is a typical example of ligand control of chemoselectivity of the reaction.

**Scheme 1.19. Rhodium-Catalyzed Addition of AlMe$_3$ to Cyclohex-2-enone**




The catalytic cycle for these Rh-catalyzed 1,2-addition reactions is almost the same as that for 1,4-addition reaction. For example, the addition of PhB(OH)$_2$ to aromatic aldehydes can be illustrated with three steps – transmetalation, phenylrhodation (coordination and insertion), and hydrolysis (Scheme 1.20).[22,23] Starting with the rhodium(I) complex **A**, the transmetalation generates the phenylrhodium species **B**. The next step is coordination of C=N or C=O to rhodium. Then, the C=N or C=O bond inserts into the rhodium–carbon bond, which generates a rhodium alkoxide/amide intermediate **D**. Hydrolysis of the rhodium alkoxide/amide **D** releases the hydroarylation product and regenerates HO–Rh /$[Rh]^+[BF_4]^-$. In the reaction of tetraphenylborate or arylboronic esters in an anhydrous environment, the direct transmetalation of rhodium alkoxide/amide **D** takes place to regenerate aryl/alkenyl rhodium **B**, not by way of HO–Rh/$[Rh]^+[BF_4]^-$ species **A**.

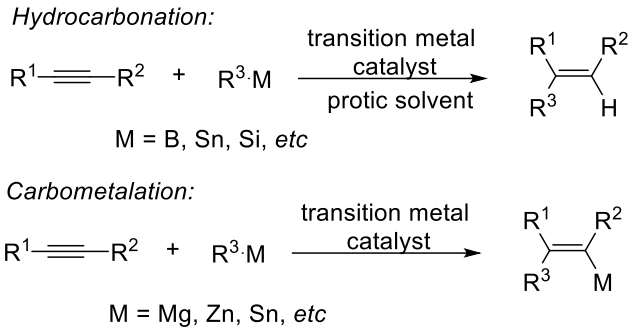
**Scheme 1.20. Catalytic Cycle for Rh-Catalyzed 1,2-Addition**




### 1.1.3 Rhodium-catalyzed addition to alkynes

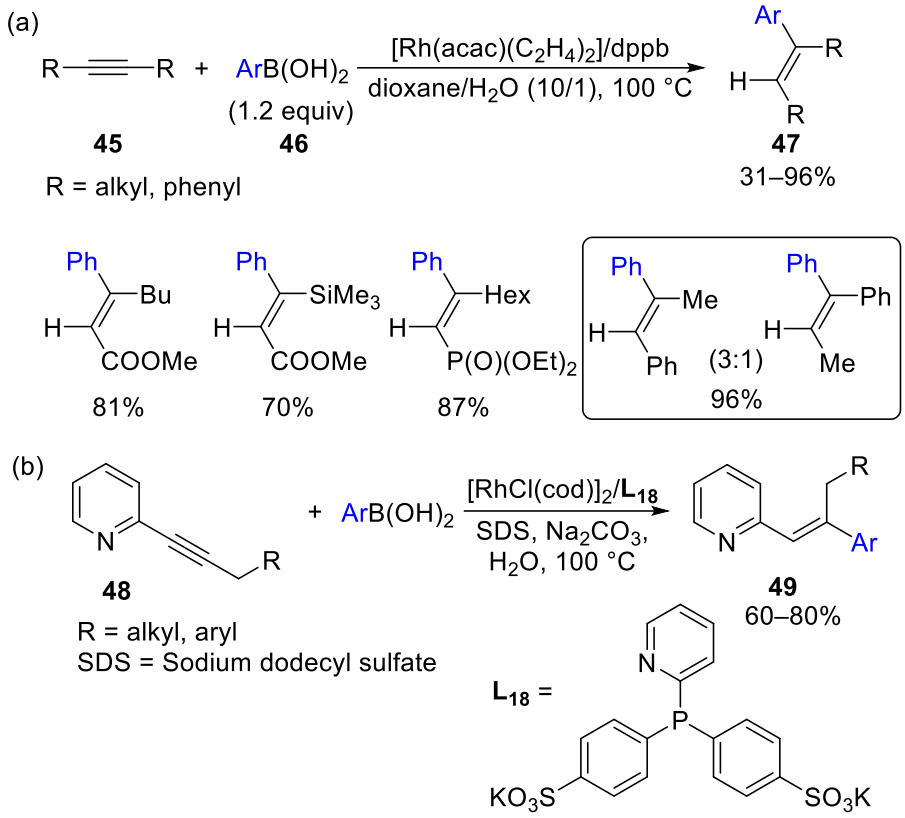
Compared with carbonyl compounds, alkynes are unreactive toward some organometallic reagents like Grignard reagents and organozinc reagents. However, the transition metal-catalyzed addition of organometallic reagents to triple bonds has received much attention and evolved as a convenient and reliable approach to functionalized alkenes. Particularly, hydrocarbonation[33] and carbometalation[34] of alkynes are two major subjects in this research area (Scheme 1.21). Notably, a rhodium complex is one of the best metals to selectively produce the *cis*-addition product without E/Z isomerization.

**Scheme 1.21. Transition Metal-Catalyzed Addition of Organometallic Reagents to Alkynes to Form C–C Bond**



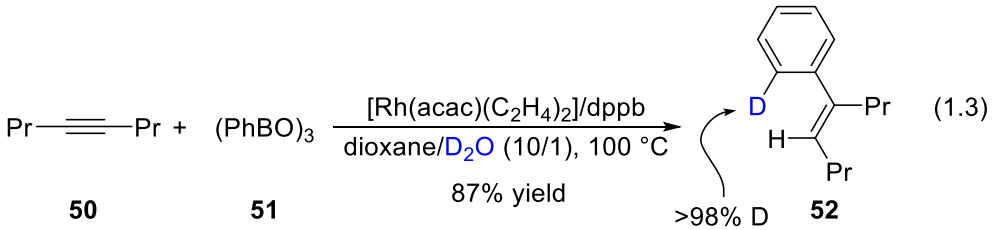

In 2002, Hayashi reported the first example of Rh-catalyzed hydroarylation reaction of internal acetylenes.[35] Trisubstituted alkenes **47** were produced in high yields with perfect *E* geometry by the addition of arylboron reagents **46** to internal alkynes **45** in dioxane/$H_2O$ at 100 °C, using an in situ generated dppb–Rh complex as the catalyst (Scheme 1.22a). Although the regioselectivity was low in the addition to alkyl(aryl)alkynes, the alkynes substituted with electron-withdrawing groups (such as ester and phosphonate) produced the β-arylation products with high regioselectivities. Lautens and his coworkers found in 2002 that the addition of arylboronic acids to 2-alkynylpyridines **48** proceeded with high stereo- and regioselectivity to give the hydroarylation products **49** in 60–80% yield. They proposed that the pyridyl group coordinates to rhodium to control the regioselectivity as a directing group (Scheme 1.22b).[36]

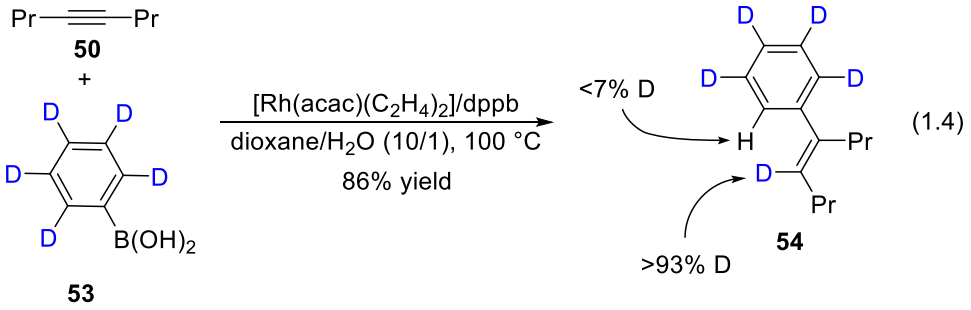
**Scheme 1.22. Rhodium-Catalyzed Hydroarylation of Alkynes**



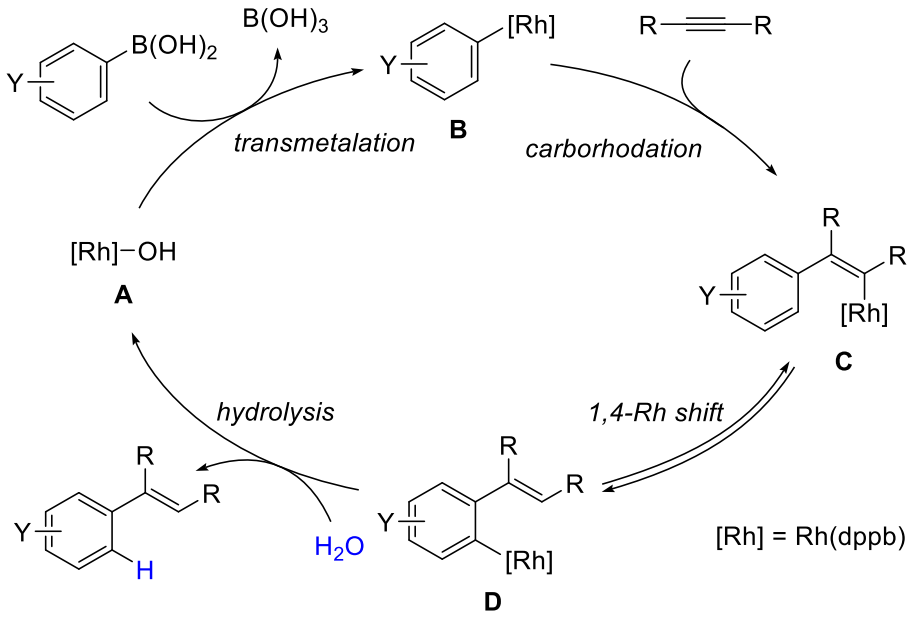

Hayashi also found that the addition of phenylboroxine (**51**) to 4-octyne (**50**) with $D_2O$ as a proton source gave the arylation product **52**, where the deuterium was incorporated into the *ortho*-position of the phenyl ring (Eq 1.3). The arylation product **54** formed by the reaction of $C_6D_5B(OH)_2$ (**53**) with 4-octyne (**50**) in $H_2O$ was found to have one deuterium at the vinylic position (Eq 1.4). These deuterium labeling studies suggest that the 1,4-migration of rhodium from the alkenyl carbon to the phenyl carbon takes place in the catalytic cycle. After careful mechanistic studies, the authors proposed the mechanism of this reaction, which is presented in Scheme 1.23. Thus, the transmetalation of aryl group from B (boron) to Rh takes place in the reaction of the arylboronic acid with a HO–Rh species **A** to generate an Ar–Rh intermediate **B**, and the syn-addition of the aryl–Rh intermediate **B** to the alkyne gives a 2-arylalkenyl–Rh species **C**. The next step is 1,4-migration of Rh

from the alkenyl position to the aryl position to generate an *ortho*-alkenylphenyl–Rh intermediate **D**. Finally, the product is released by the hydrolysis of the *ortho*-alkenylphenyl–Rh intermediate **D**, and the HO–Rh species **A** is regenerated. In Section 1.2.2, the 1,4-migration process is discussed in detail.



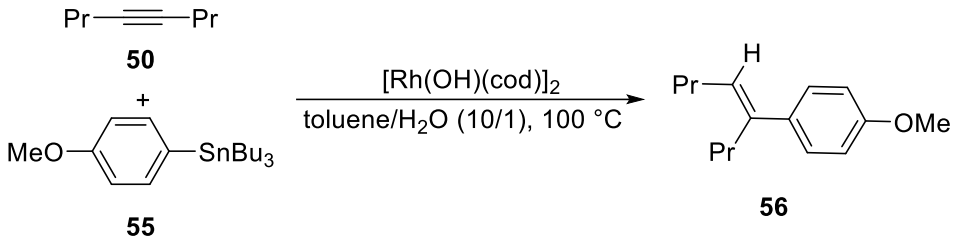




**Scheme 1.23. Catalytic Cycle of Rhodium-Catalyzed Hydroarylation of Alkynes**



In 2002, Mori reported the use of organotin reagents for the rhodium-catalyzed addition to alkynes.[37] For instance, the reaction of 4-octyne (**50**) with *p*-$MeOC_6H_4SnBu_3$ (**55**) in the presence of a catalyst $[Rh(OH)(cod)]_2$ and 1 equiv of phenol in toluene/$H_2O$ at 100 °C gave the hydroarylation product **56** in 72% yield (Scheme 1.24). The phenol is proposed to accelerate the hydrolysis step.

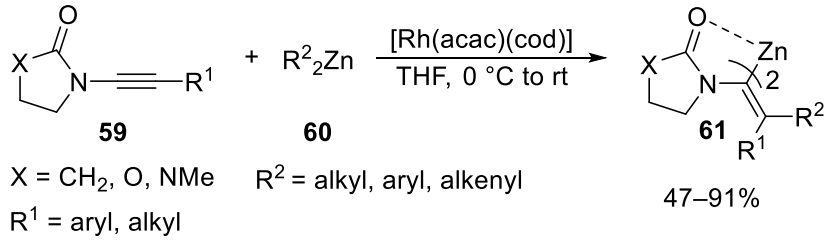
**Scheme 1.24. Rhodium-Catalyzed Hydroarylation of 4-Octyne (50) with Arylstannane 55**




| Entry | Additive (equiv) | Time (h) | Yield (%) |
|---|---|---|---|
| 1 | none | 4 | <5 |
| 2 | $Et_3SiOH$ (3) | 4 | 40 |
| 3 | PhOH (1) | 14 | 72 |

Carbometalation of alkynes is one of the most efficient methods of generating substituted alkenyl–metals that are useful synthetic intermediates for multisubstituted alkenes.[34] Recently, Lam reported the carbozincation of ynamides **59** using alkyl- and arylzinc reagents **60** as nucleophiles in the presence of [Rh(acac)(cod)] under mild conditions, which produced the corresponding alkenylzincs **61** with high regioselectivities (Scheme 1.25).[39] However, the rhodium-catalyzed addition of arylmetals to simple unfunctionalized alkynes remains to be a challenging reaction because of their low reactivity. In Chapters 3 and 4, the rhodium-catalyzed arylstannylation and arylzincation of the unfunctionalized alkynes will be reported as new discoveries to fill in this blank.

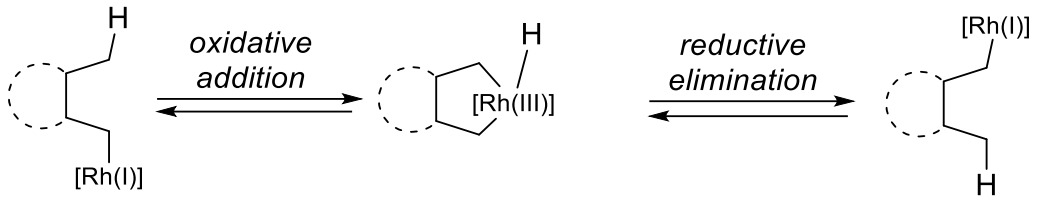
**Scheme 1.25. Rhodium-Catalyzed Carbozincation of Ynamides**




## 1.2 Introduction of 1,4-migration of rhodium and its application to carbon–carbon bond forming reactions

The 1,4-metal shift is involved in several interesting metal-catalyzed reactions as a key step.[40] In most cases, the metal intramolecularly exchanges its position with a hydrogen. Thus, the 1,4-metal shift is also viewed as a unique way to functionalize the remote C–H bond. The 1,4-migration of rhodium is sometimes involved in the catalytic cycle of rhodium-catalyzed C–C bond forming reactions. Typically, the mechanism of 1,4-Rh(I) shift is proposed to be composed of two steps, oxidative addition and reductive elimination (Scheme 1.26). In the catalytic cycle, the five-membered ring metallacycle intermediate is formed by oxidative addition to the carbon–hydrogen bond, and then undergoes reductive elimination to yield the rearranged intermediate with higher thermodynamic stability. However, solid evidence proving the existence of such a five-membered ring metallacycle is still lacking. A more stable carbon–rhodium bond accounts for the major driving force for these shifts. Here, the reported studies on 1,4-migration of rhodium are introduced in the order of 1) 1,4-rhodium shift from alkyl to aryl carbon, 2) from alkenyl to aryl carbon, and 3) from alkyl to alkyl carbon.

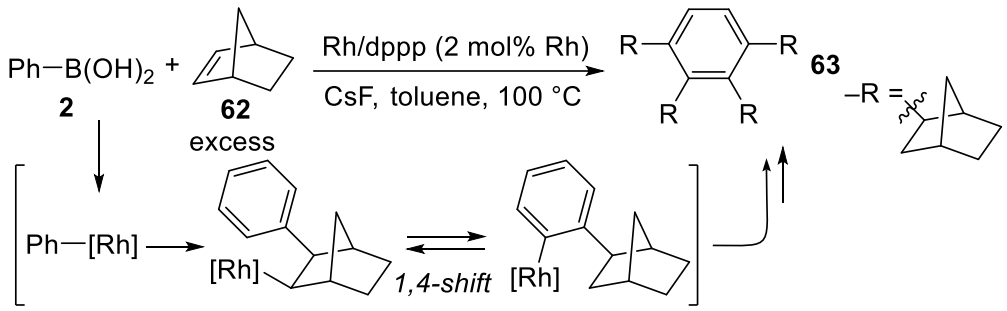
**Scheme 1.26. Proposed Pathway of 1,4-Migartion of Rhodium(I)**




### 1.2.1 1,4-Migration of rhodium from alkyl to aryl carbons and its application to carbon–carbon bond forming reactions

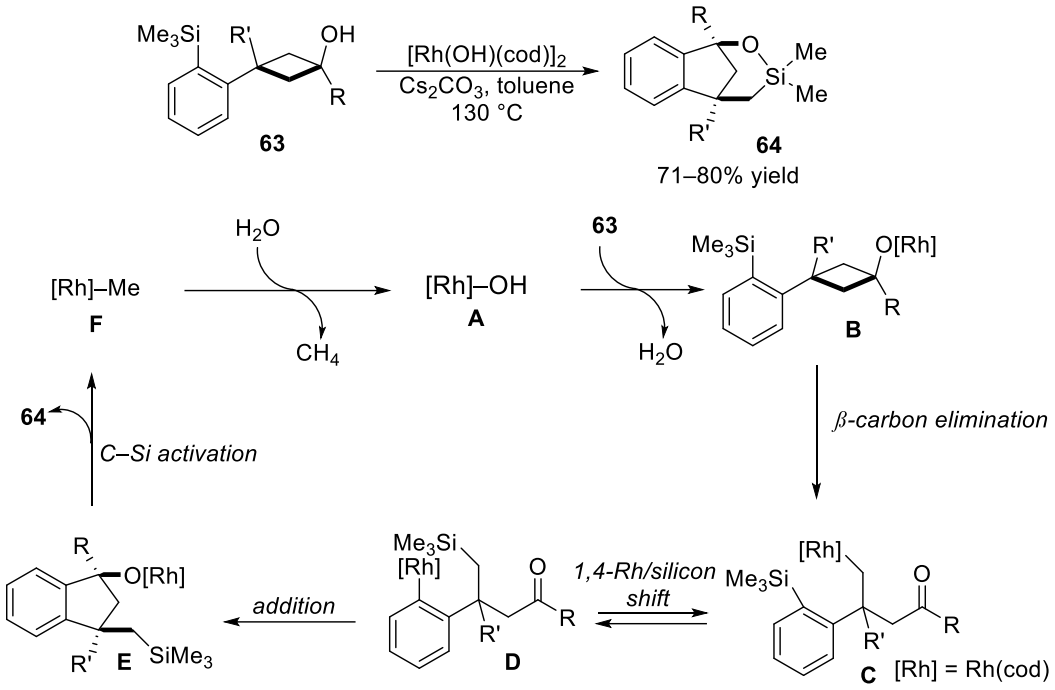
Migration of rhodium from alkyl to aryl carbon is a frequently used strategy to form an aryl–Rh intermediate, which subsequently undergoes the next reactions in the catalytic cycle.[41] This 1,4-migration is reversible, while an aryl–Rh species is thermodynamically preferred to an alkyl–Rh species. Moreover, aryl–Rh species are more reactive than alkyl–Rh species in almost all rhodium-catalyzed reactions, which accounts for another important driving force for these reactions. In 2000, Miura reported the first example of 1,4-rhodium shift from alkyl to aryl carbon (Scheme 1.27).[41a] The treatment of phenylboronic acid (**2**) with 7 equiv of norbornene (**62**) in the presence of a Rh/dppp catalyst in toluene at 100 °C gave the tetraalkylated benzene **63** as a main product. The key step in this reaction is the Rh shift from alkyl to aryl to form a new aryl–Rh intermediate, which undergoes addition to **62** again. It is noted that there is no β-hydrogen available for β-elimination in the alkyl–Rh intermediate and that the alkyl–Rh species is relatively unreactive towards the addition to the C=C bonds.

**Scheme 1.27. 1,4-Migration of Rh from $sp^3$ Carbon to $sp^2$ Carbon (Miura)**



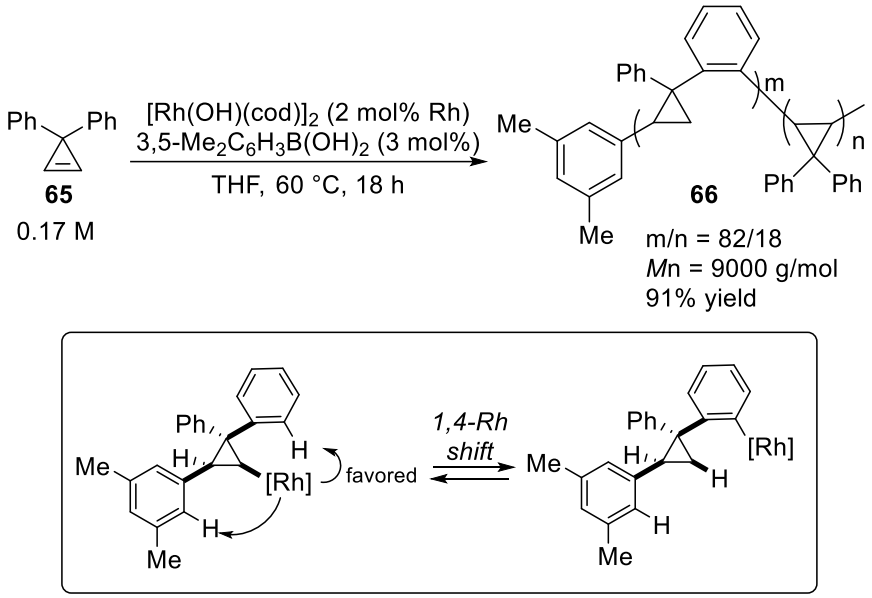

Since Miura's report in 2000, the alkyl-to-aryl 1,4-Rh shift has been reported to be involved as a key step in the catalytic cycle of several types of rhodium-catalyzed reactions.[41] Most of them are 1,4-hydrogen-rhodium shifts. In 2010, Cramer and his coworkers reported a rhodium-catalyzed isomerization/cyclization of a *tert*-cyclobutanol **63** through a 1,4-Rh/Si shift (Scheme 1.28).[41g] As shown in the scheme, an alkyl–Rh intermediate **C** is generated by β-carbon elimination from a RO–Rh species **B**. Then, the alkylrhodium species **C** undergoes the 1,4-Rh/Si shift to generate an arylrhodium species **D**. The intramolecular addition of the arylrhodium species **D** to the carbonyl group generates another rhodium alkoxide **E**. The intramolecular Rh-catalyzed C–Si activation[42] produces a tricyclic product **64** and releases a Me–Rh species **F**, while the latter can be further hydrolyzed into HO–Rh and $CH_4$. The silicon/rhodium positional switch is the key step for the proposed pathway. It was also shown that the selectivity between 1,4-Rh/Si and 1,4-Rh/H shifts can be controlled mainly by the ligand on the rhodium complex. Notably, the 1,4-silicon shift, rather than the 1,4-hydrogen shift, is more synthetically useful in some cases.

**Scheme 1.28. Rhodium-Catalyzed 1,4-Si Shift from $sp^2$ Carbon to $sp^3$ Carbon (Cramer)**



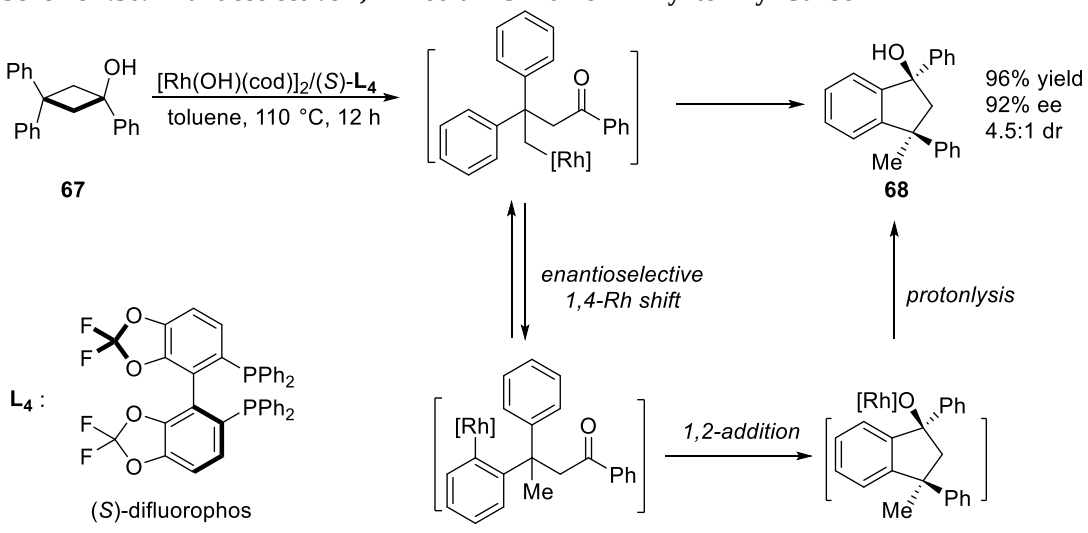

The 1,4-rhodium shift was also employed in the polymerization of 3,3-diphenylcyclopropene (**65**) (Scheme 1.29).[41j] The polymerization is initiated by the addition of a 3,5-$Me_2C_6H_3$–Rh species to the alkene **65**. The continuous arylrhodation/1,4-Rh shift would generate the final polymer **66** at the molar mass of up to 9000 g/mol. Importantly, the choice of the initiator would also affect the molar mass of the polymer. Obviously, 3,5-$Me_2C_6H_3B(OH)_2$ attained the best results, since the relatively bulky structure forced rhodium shift from alkyl group to the phenyl group rather than the 3,5-$Me_2C_6H_3$ group.

**Scheme 1.29. Polymerization of 3,3-Diarylcyclopropenes through 1,4-Rh Shift**




In 2009, Cramer reported the first example of enantioselective 1,4-migration of rhodium.[41d] As shown in Scheme 1.30, treatment of a cyclobutanol **67** bearing two phenyl groups at the 3-position with a Rh/(*S*)-**L4** catalyst in refluxed toluene for 12 h gave the desired isomerization product **68** in 92% ee. This asymmetric reaction is unique in that the key step is enantioselective 1,4-shift of rhodium.

**Scheme 1.30. Enantioselective 1,4-Rhodium Shift from Alkyl to Aryl Carbon**

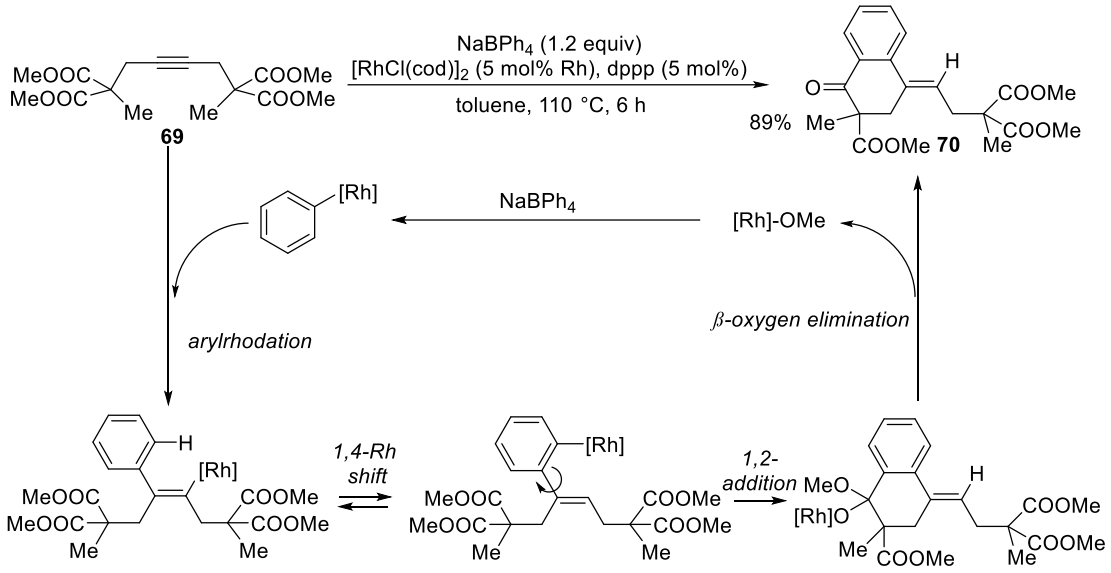


### 1.2.2 1,4-Migration of rhodium from alkenyl to aryl carbons and its application to carbon–carbon bond forming reactions

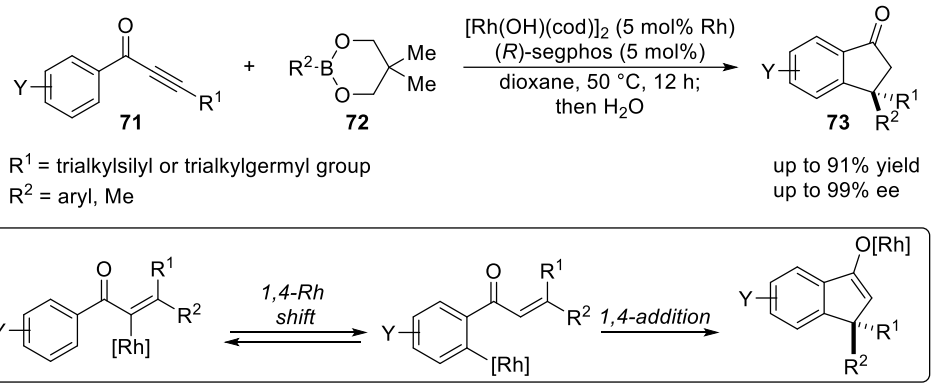
Hayashi and his coworkers reported the first example of alkenyl to aryl rhodium migration in the rhodium-catalyzed reaction of arylboron reagents with alkynes under aqueous conditions (Scheme1.22), which was supported by the deuterium-labeling experiments (Eq 1.3 and 1.4).[35] Thereafter, the 1,4-migration of rhodium from alkenyl to aryl carbon has been frequently used in tandem reactions, since the Ar–Rh species generated by 1,4-Rh shift is reactive enough towards addition to unsaturated bonds (such as carbonyl and vinyl groups).[43a–f] For instance, in 2005, Murakami reported that the arylation of an internal alkyne **69** equipped with ester groups is catalyzed by a rhodium(I) complex to produce a cyclic ketone **70** as the main product, which results from the 1,4-Rh shift and the subsequent intramolecular 1,2-addition of the arylrhodium species to the ester (Scheme 1.31a).[43a] Notably, the aprotic solvent is necessary for the high yield of the desirable cyclization product; otherwise, the aryl rhodium may undergo protonolysis in protic solvent. Using the same strategy, in 2007, Hayashi and his coworkers reported that the cyclic products **73** are obtained through the rhodium-catalyzed addition of aryl/methyl boronates **72** to aryl ethynyl ketones **71**, which was achieved through 1,4-Rh shift/1,4-addition sequence (Scheme 1.31b).[43c]

**Scheme 1.31. Catalytic Tandem Reaction via 1,4-Rh Shift from Alkenyl to Aryl**

(a) Rhodium-catalyzed cyclization via addition/1,4-Rh shift/1,2-addtion



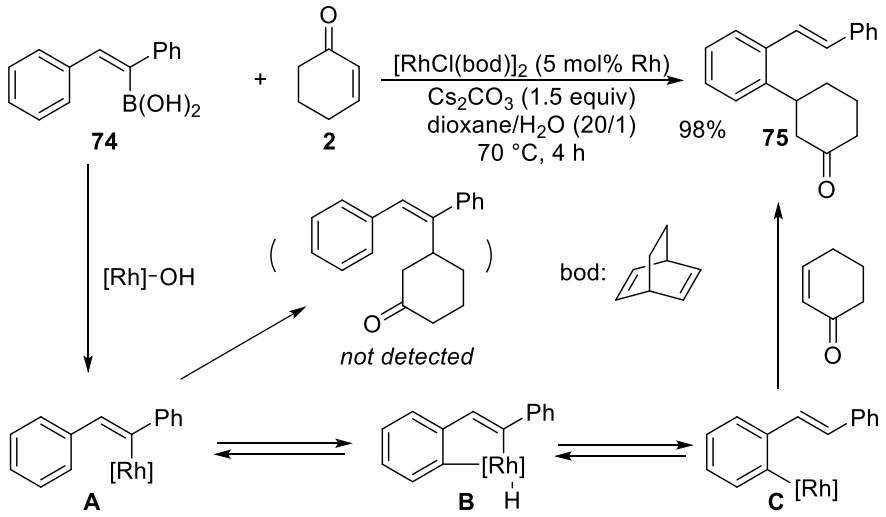

(b) Rhodium-catalyzed cyclization via addition/1,4-Rh shift/intramolecular 1,4-addtion




In 2012, Hayashi and his coworkers further reported the asymmetric hydroarylation of enone **2** with (*E*)-1,2-diphenylethenylboronic acid (**74**) in the presence of a Rh/diene complex, which produced a hydroarylation product **75** rather than an alkenylation product (Scheme 1.32).[43e] They proposed a catalytic cycle involving the 1,4-migration of rhodium from the vinylic carbon to the aromatic carbon followed by 1,4-addition as the key steps. DFT calculations proved that five-membered ring rhoda(III)cycle **B** is an intermediate during the 1,4-shift of rhodium, and the *ortho*-alkenylphenyl–Rh intermediate **A** is more thermodynamically stable

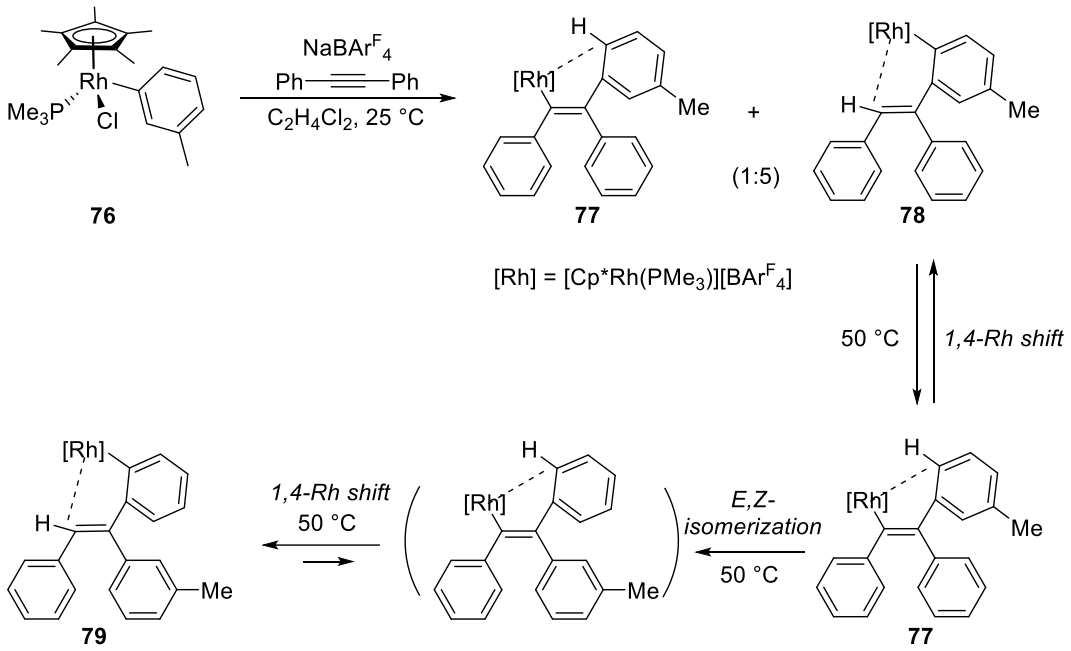
than the 2-arylalkenyl–Rh species **C**. However, more experimental evidence still remains to be obtained for the detailed mechanism.

**Scheme 1.32. Rhodium-Catalyzed Tandem Reaction via 1,4-Rh Shift/Intermolecular 1,4-Addition ([Rh] = Rh(bod))**




In most cases, the 1,4-rhodium migration has been reported for Rh(I) complexes. By contrast, much little is known about 1,4-Rh(III) shift, even though Cp*Rh(III) complex is one of the best catalysts for C–H activation.[44] In 2013, Ishii and his coworkers reported the first example of 1,4-migration of Rh(III).[43g,43h] Thus, treating [Cp*Rh(III)Cl(3-$MeC_6H_4$)($PMe_3$)] (**76**) with 5 equiv of diphenylacetylene in the presence of 1.1 equiv of $NaBAr^F_4$ ($Ar^F$ = 3,5-$(CF_3)_2C_6H_3$) in 1,2-dichloroethane at 25 °C for 1 h gave a mixture of arylrhodium(III) complex **78** and alkenylrhodium(III) complex **77** in a ratio of 5:1 (Scheme 1.33). The reversibility of 1,4-Rh shift was proved through the isomerization of the arylrhodium(III) complex **78** to the more thermodynamically stable **79** at 50 °C.

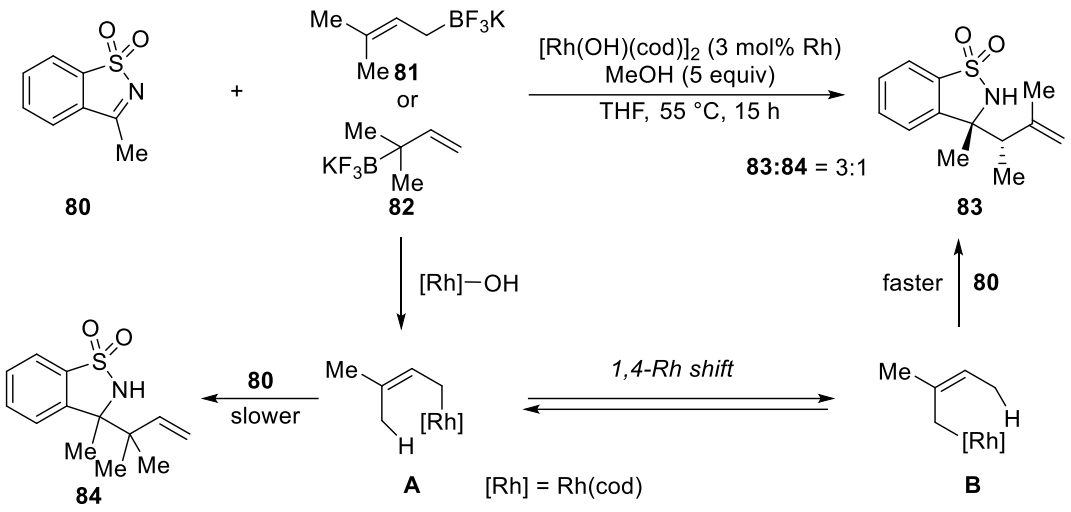
**Scheme 1.33. 1,4-Metal Migration in a Cp*Rh(III) Complex and Its Reversibility**




### 1.2.3 1,4-Migration of rhodium from alkyl to alkyl carbons and its application to carbon–carbon bond forming reactions

The 1,4-shift of rhodium from alkyl/alkenyl to aryl carbon is a well-known step, which has been found in many catalytic reactions. In contrast, much less is known regarding the 1,4-rhodium/hydrogen exchange between two alkyl carbons. In 2014, Lam and his coworkers found the isomerization of allylrhodium intermediates through 1,4-Rh shift during the allylation of cyclic imines (Scheme 1.34).[45] As shown in the scheme, the authors proposed that a more reactive allylrhodium **B** with less steric congestion at the γ-position was generated from the intermediate **A** through 1,4-Rh shift from the allylic carbon to another allylic carbon. The allylation of imine **80** with the allylrhodium **B** leads to the production of the main product **83**.

**Scheme 1.34. 1,4-Rhodium Shift from an Allyl Carbon to Another Allyl Carbon**




## 1.3 Conclusion and outlook

Ever since Miyaura made his inspirational report in the year of 1997, the research on carbon–carbon bond forming reactions involving rhodium complexes as catalysts has significantly progressed. Addition reactions of organoboron and related reagents to various unsaturated substrates have been developed, often with high enatioselectivity. Furthermore, the 1,4-Rh migration has offered a unique twist to the organorhodium chemistry. The combination of 1,4-Rh shift and other elementary steps has enabled a variety of mechanistically intriguing and synthetically attractive cascade transformations. It is desirable to extend the rhodium migration chemistry to some other reactions such as carbometalation and hydroarylation. Here, the project of mine is to focus on the development of new C–C bond forming reactions through 1,4-migration of rhodium.

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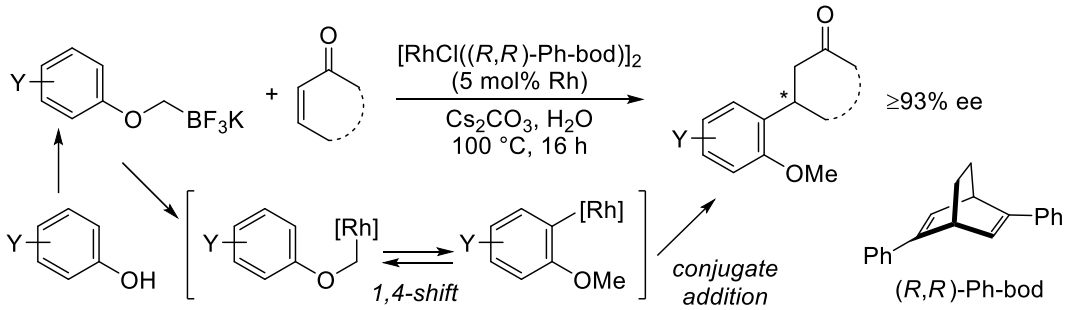
# CHAPTER 2

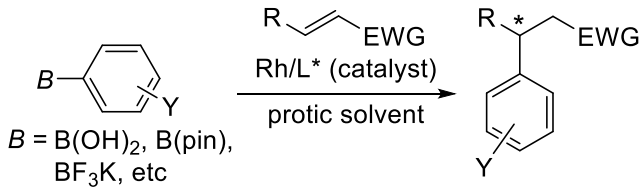
## Aryloxymethyltrifluoroborates for Rhodium-Catalyzed Asymmetric Arylation of Enones. 1,4-Rhodium Shift from $sp^3$ to $sp^2$ Carbons



## 2.1 Introduction

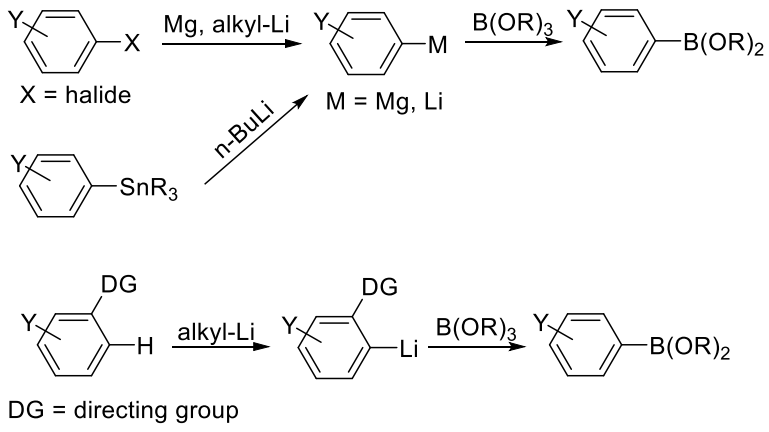
Rhodium-catalyzed asymmetric conjugate arylation of electron-deficient alkenes has attracted considerable attention as one of the most convenient and reliable methods of creating benzylic stereocenters with high enantioselectivity (Scheme 2.1).[1,2] Among various arylating agents, arylboron compounds such as boronic acids, boronates, and trifluoroborates, are by far the most commonly used because of their easy handling in air and moisture.

**Scheme 2.1. Rh-Catalyzed Asymmetric Arylation of Alkenes with Arylboron Reagents**



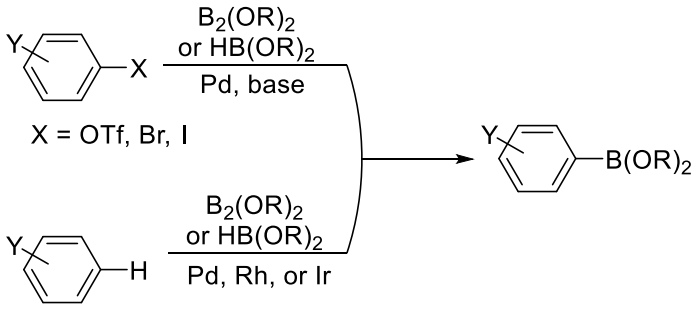

The arylboron reagents[3] are prepared by the borylation of aryllithium or aryl Grignard reagents at low temperature in most cases (Scheme 2.2).[4a,4b] These reactive arylmetals are prepared from the corresponding halides or tin compounds, or arenes bearing appropriate directing groups. However, this method is incompatible with base-sensitive functional groups such as carbonyl groups and nitrile.

**Scheme 2.2. Electrophilic Borate Trapping of Hard Arylmetal Reagents**



Borylation of Ar–X (X = halides, triflate) and Ar–H by transition metal-catalyzed reaction with diboron reagents is another preparation method, which has been developed recently (Scheme 2.3).[4a,4b] The relatively mild conditions allow us to prepare a wider scope of arylboron reagents, while the use of expensive transition metal (palladium, iridium, *et al.*) limits the application.

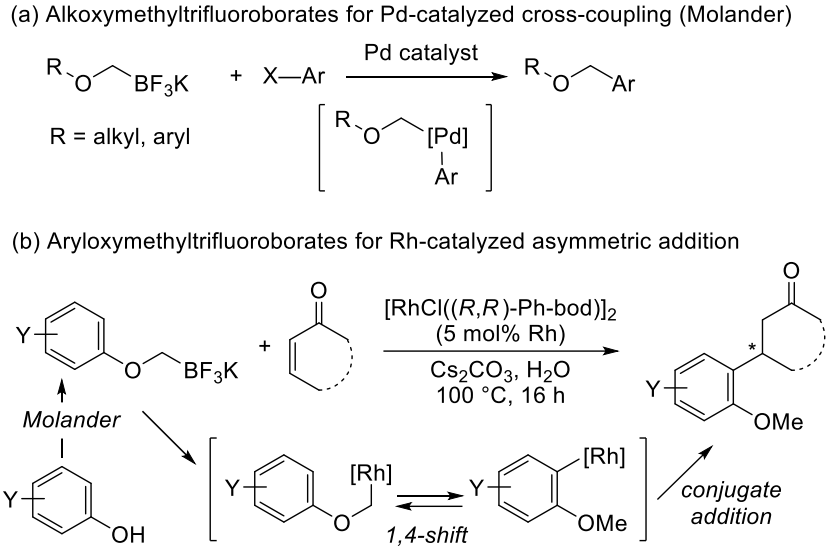
**Scheme 2.3 Direct Boronylation By Transition Metal-Catalyzed Coupling or C–H Functionalization**




On the other hand, Molander reported synthesis of alkoxymethyltrifluoroborates ($ROCH_2BF_3K$) from alcohols (ROH) and their use as alkoxymethyl nucleophiles in the palladium-catalyzed cross-coupling reactions[6,7] (Scheme 2.4a). In this Chapter, we report that the reaction of aryloxymethyltrifluoroborates ($ArOCH_2BF_3K$) with α,β-unsaturated carbonyl compounds in the presence of a chiral diene–rhodium catalyst introduces *ortho*-methoxyaryl groups at the β-position in high yields with high enantioselectivity, where the reaction proceeds through the 1,4-shift of rhodium[8,9] from aryloxymethyl to *ortho*-methoxyaryl intermediates (Scheme 2.4b). Considering the very wide availability of substituted phenols and their easy conversion into aryloxymethyltrifluoroborates,[6,7] this 1,4-shift/arylation sequential reaction is of great advantage over the reaction of *ortho*-methoxyarylboron reagents. The 1,4-Rh

shift from alkyl–Rh to aryl–Rh intermediates[8] has been reported to be involved as a key step in the catalytic cycle of several types of rhodium-catalyzed reactions, which have been developed since Miura's report in 2000.[8a] As a reaction related to the present study, there has been a report where the Rh shift between aryloxymethyl and *ortho*-methoxyaryl is proposed to explain a methoxy-directed aryl-to-aryl 1,3-Rh migration.[10]

**Scheme 2.4. Rh-Catalyzed Conjugate Arylation, Aryloxymethyl Intermediates, and 1,4-Rh Shift**

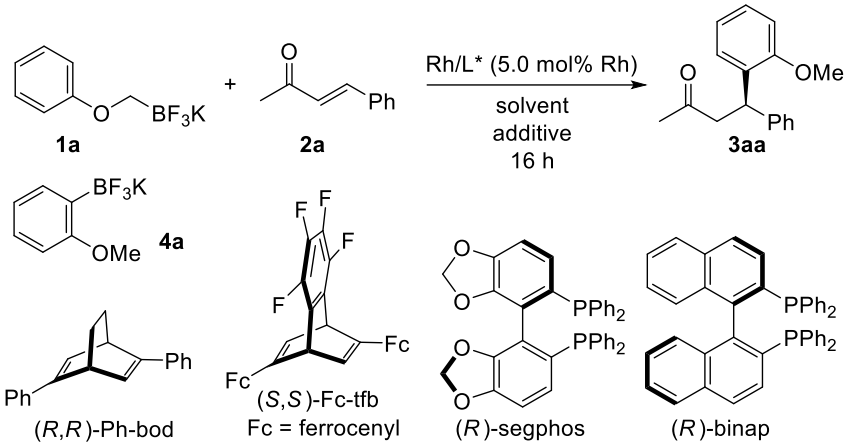


## 2.2 Results and discussion

In the first set of experiments, benzalacetone (**2a**) was allowed to react with phenoxymethyltrifluoroborate **1a** (1.2 equiv to **2a**) in the presence of 5 mol% of a rhodium catalyst coordinated with (*R,R*)-Ph-bod,[13] which is one of the most commonly used chiral diene ligands.[12] The reaction with $Cs_2CO_3$ (2.0 equiv) as a base in dioxane/$H_2O$ (10/1) at 60 °C for 16 h, which is one of the standard conditions for rhodium-catalyzed asymmetric conjugate arylation,[1] did not give any addition products (Table 2.1, entry 1). This is expected because the rhodium-catalyzed conjugate addition of organoboron reagents is known to work well for the introduction of aryl and alkenyl groups but not for that of alkyl groups.[1] On heating the reaction to 100 °C, formation of the addition product **3aa**, where a 2-methoxyphenyl group rather than a phenoxymethyl group was introduced at the β-position, was observed albeit in a low yield (19%) (entry 3). The yield of **3aa** was improved with a higher ratio of water (entries 4 and 5), and the reaction in pure water[13] gave the highest yield (86%) of **3aa**, which was an *R* isomer of 98% ee (entry 6). A more amount (2.0 equiv to **2a**) of the boron reagent **1a** increased the yield of **3aa** to 96% (entry 7). The use of 2-methoxyphenyltrifluoroborate **4a** in place of **1a** gave essentially the same result (91% yield, 98% ee) (entry 8), which may well suggest that the reaction proceeds through a 2-methoxyphenyl–Rh intermediate (*vide infra*). The yield of **3aa** was slightly lower with $K_3PO_4$ as a base (entry 9), and KOH was not an appropriate base for the present reaction (entry 10). Another choice of chiral diene ligand is Fc-tfb, whose enantioselectivity is higher than that of Ph-bod in most of the rhodium-catalyzed asymmetric arylation reactions.[14] Although Fc-tfb ligand was not better than Ph-bod for the addition to enone **2a** due to the lower

yield (entry 11), Fc-tfb ligand showed higher performance for some other enone substrates (see Table 2.2). The yields were low with bisphosphine ligands such as binap and segphos (entries 12 and 13).

**Table 2.1. Rhodium-Catalyzed Asymmetric Arylation of Benzalacetone (2a) with Phenoxymethylborate 1a**[a]

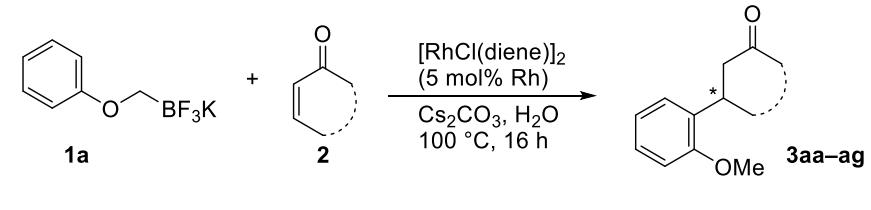


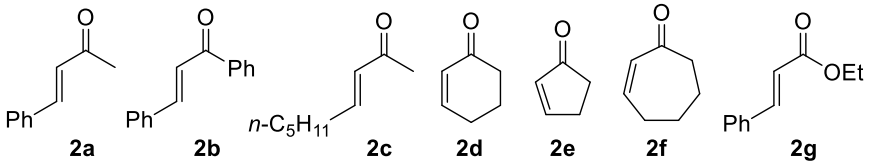

| entry | ligand on Rh | additive (equiv) | solvent (mL) | temp (°C) | yield (%)[b] **3aa** | % ee[c] **3aa** |
|---|---|---|---|---|---|---|
| 1 | (*R*,*R*)-Ph-bod[d] | $Cs_2CO_3$ (2) | dioxane/$H_2O$ (1.0/0.1) | 60 | 0 | — |
| 2 | (*R*,*R*)-Ph-bod[d] | $Cs_2CO_3$ (2) | dioxane/$H_2O$ (1.0/0.1) | 80 | 3 | — |
| 3 | (*R*,*R*)-Ph-bod[d] | $Cs_2CO_3$ (2) | dioxane/$H_2O$ (1.0/0.1) | 100 | 19 | — |
| 4 | (*R*,*R*)-Ph-bod[d] | $Cs_2CO_3$ (2) | dioxane/$H_2O$ (0.5/0.5) | 100 | 57 | 98 |
| 5 | (*R*,*R*)-Ph-bod[d] | $Cs_2CO_3$ (2) | toluene/$H_2O$ (0.5/0.5) | 100 | 70 | 98 |
| 6 | (*R*,*R*)-Ph-bod[d] | $Cs_2CO_3$ (2) | $H_2O$ (1.1) | 100 | 84 | 98 |
| 7[e] | (*R*,*R*)-Ph-bod[d] | $Cs_2CO_3$ (4) | $H_2O$ (1.1) | 100 | 96 | 98 |
| 8[f] | (*R*,*R*)-Ph-bod[d] | $Cs_2CO_3$ (2) | $H_2O$ (1.1) | 100 | 91 | 98 |
| 9 | (*R*,*R*)-Ph-bod[d] | $K_3PO_4$ (2) | $H_2O$ (1.1) | 100 | 76 | 98 |
| 10 | (*R*,*R*)-Ph-bod[d] | KOH (2) | $H_2O$ (1.1) | 100 | <3 | — |
| 11 | (*S*,*S*)-Fc-tfb[g] | $Cs_2CO_3$ (2) | $H_2O$ (1.1) | 100 | 42 | >99 |
| 12 | (*R*)-binap[h] | $Cs_2CO_3$ (2) | $H_2O$ (1.1) | 100 | 39 | 99 |
| 13 | (*R*)-segphos[i] | $Cs_2CO_3$ (2) | $H_2O$ (1.1) | 100 | <3 | — |

[a] Reaction conditions: **1a** (0.24 mmol), **2a** (0.20 mmol), Rh catalyst (5 mol% Rh), at 100 °C for 16 h. [b] Isolated yield. [c] The % ee was determined by HPLC on a chiral stationary phase column. [d] $[RhCl((R,R)\text{-Ph-bod})]_2$. [e] With **1a** (0.40 mmol). [f] Reaction with **4a** (0.24 mmol) instead of **1a**. [g] $[RhCl((S,S)\text{-Fc-tfb})]_2$. [h] $[RhCl(coe)_2]_2$/(*R*)-binap. [i] $[RhCl(coe)_2]_2$/(*R*)-segphos.

The results for the 1,4-shift/arylation reaction of **1a** with several other α,β-unsaturated carbonyl compounds are summarized in Table 2.2. The yields and enatioselectivies of the products are high for linear enones, such as chalcone (**2b**) and 3-nonen-2-one (**2c**), under the conditions using 1.2 equiv of **1a** in the presence of [RhCl((*R*,*R*)-Ph-bod)]$_2$ (5 mol% Rh) catalyst (entries 2 and 3). For 2-cyclohexenone (**2d**), the yield and % ee were not satisfactory (67% yield, 87% ee) under the same conditions (entry 4). The yield was improved from 67% to 82% by the use of 2.0 equiv of boron reagent **1a** (entry 5), and % ee was increased to 94% ee by changing the diene ligand to (*S,S*)-Fc-tfb (entry 6). The reaction of 2-cycloheptenone (**2f**) was also improved by the use of (*S,S*)-Fc-tfb ligand and an excess amount of **1a** (entries 8 and 9). α,β-Unsaturated ester **2g** is also a suitable substrate for the 1,4-shift/arylation reaction (entry 10).

**Table 2.2. Rhodium-Catalyzed Asymmetric Arylation of Enones 2 with Phenoxymethylborate 1a**[a]




| entry | **2** | diene ligand | yield (%)[b] | ee (%)[c] |
|---|---|---|---|---|
| 1 | **2a** | (*R*,*R*)-Ph-bod | **3aa**: 84 | 98 (*R*) |
| 2 | **2b** | (*R*,*R*)-Ph-bod | **3ab**: 94 | >99 (*R*) |
| 3 | **2c** | (*R*,*R*)-Ph-bod | **3ac**: 84 | 97 (*S*) |
| 4 | **2d** | (*R*,*R*)-Ph-bod | **3ad**: 67 | 87 (*R*) |
| 5[d] | **2d** | (*R*,*R*)-Ph-bod | **3ad**: 82 | 88 (*R*) |
| 6[d] | **2d** | (*S*,*S*)-Fc-tfb | **3ad**: 77 | 94 (*R*) |
| 7 | **2e** | (*R*,*R*)-Ph-bod | **3ae**: 76 | 96 (*R*) |

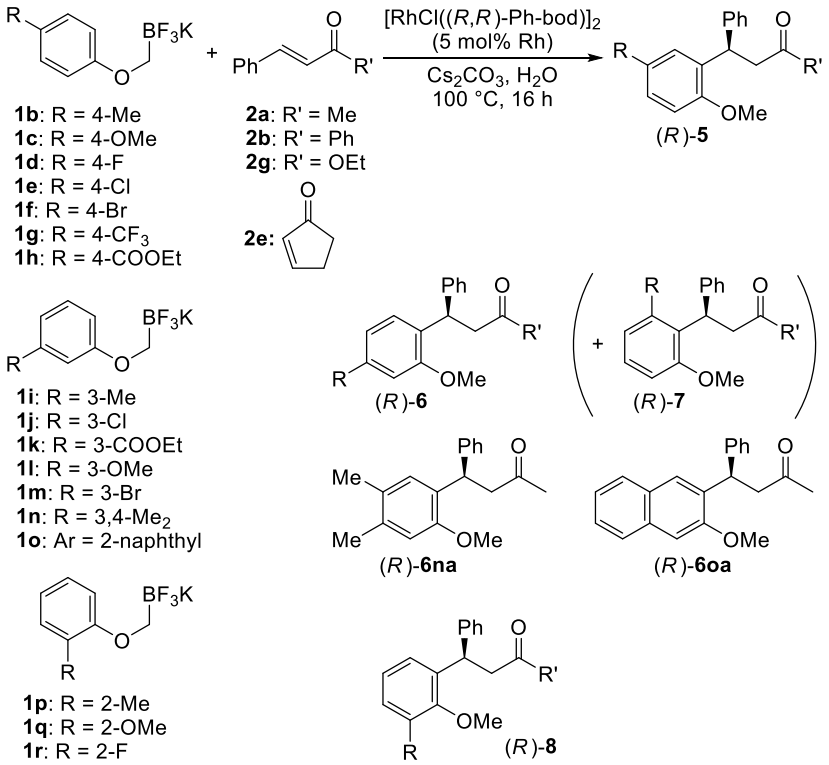
| | | | | |
|---|---|---|---|---|
| 8 | **2f** | (*R*,*R*)-Ph-bod | **3af**: 75 | 88 (*R*) |
| 9[d] | **2f** | (*S*,*S*)-Fc-tfb | **3af**: 81 | 93 (*R*) |
| 10[d] | **2g** | (*R*,*R*)-Ph-bod | **3ag**: 87 | 97 (*R*) |

[a] Reaction conditions: **1a** (0.24 mmol), enone **2** (0.20 mmol), $Cs_2CO_3$ (0.40 mmol), $[RhCl((R,R)\text{-Ph-bod})]_2$ (5 mol% of Rh), $H_2O$ (1.1 mL) at 100 °C for 16 h. [b] Isolated yield. [c] The % ee was determined by HPLC on chiral stationary phase columns. The absolute configurations were estimated by stereochemical similarity to those reported for asymmetric arylation with Rh/(*R*,*R*)-Ph-bod catalyst. [d] With **1a** (0.40 mmol) and $Cs_2CO_3$ (0.80 mmol).

Aryloxymethylborates bearing substituents on the phenyl group, which were prepared from the corresponding phenol derivatives according to the Molander's procedures,[6] were subjected to the present 1,4-shift/arylation reaction (Table 2.3). Those substituted with Me (**1b**), MeO (**1c**), F (**1d**), Cl (**1e**), Br (**1f**), $CF_3$ (**1g**), and COOEt (**1h**) at the *para*-position gave high yields of the arylation products **5** with high % ee in the reaction with **2a** and/or **2b** in the presence of $[RhCl((R,R)\text{-Ph-bod})]_2$ (5 mol% Rh) catalyst (entries 1–8). The introduced aromatic groups in **5** are all substituted at the 5-position in addition to the MeO group at the 2-position, as expected from the 1,4-Rh shift mechanism. In the reaction of aryloxymethylborates with substituents at the *meta*-position, the regioselectivity of the 1,4-Rh shift in giving 2,4-disubstituted isomer **6** or 2,6-disubstituted isomer **7** is an interesting subject of study. With Me (**1i**), Cl (**1j**), and COOEt (**1k**) at the 3-position, the regioselectivity was very high to give the less hindered isomers **6** exclusively (entries 9–12). With OMe (**1l**) and Br (**1m**) as 3-substituents, the regiochemistry was not perfect, the **6**/**7** ratio ranging between 12/1 and 6/1 (entries 13–17). It is notable that the selectivity is not strongly dependent on the enone/enoate substrates. The regioselective 1,4-shift leading to less hindered isomers **6na** and **6oa** was also observed in the reaction of aryloxymethylborates where the aryl groups are 3,4-dimethylphenyl (**1n**) and 2-naphthyl (**1o**) (entries 18 and 19). The 1,4-shift/arylation reaction is also applicable to the ortho substituted borates **1p**, **1q**, and **1r**, which gave

the corresponding arylation products **8** although the yields are somewhat lower (entries 20–22).

**Table 2.3. Rhodium-Catalyzed Asymmetric Arylation of Enones 2 with Substituted Aryloxymethylborates 1**[a]



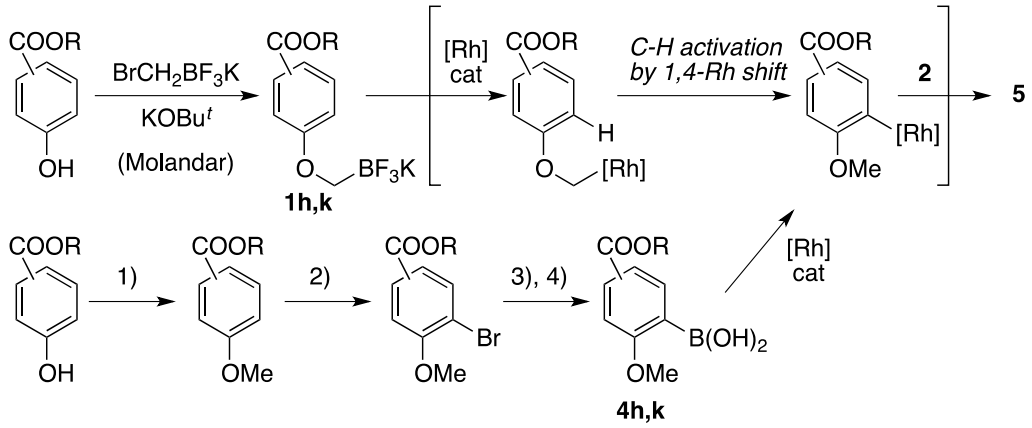

| entry | 1 | 2 | regioselectivity[b] | yield (%)[c] | ee (%)[d] |
|---|---|---|---|---|---|
| 1 | **1b** | **2a** | — | **5ba**: 90 | 99 |
| 2 | **1c** | **2a** | — | **5ca**: 92 | 98 |
| 3 | **1d** | **2b** | — | **5db**: 83 | >99.5 |
| 4 | **1e** | **2b** | — | **5eb**: 86 | >99.5 |
| 5[e] | **1f** | **2a** | — | **5fa**: 85 | 98 |
| 6 | **1f** | **2b** | — | **5fb**: 84 | 99 |
| 7 | **1g** | **2b** | — | **5gb**: 90 | 99 |
| 8 | **1h** | **2b** | — | **5hb**: 87 | >99.5 |
| 9 | **1i** | **2a** | **6/7** = >50/1 | **6ia**: 89 | 99 |
| 10 | **1i** | **2b** | **6/7** = >50/1 | **6ib**: 97 | 99 |
| 11[e] | **1j** | **2b** | **6/7** = >50/1 | **6jb**: 91 | 99 |
| 12[e] | **1k** | **2b** | **6/7** = >50/1 | **6kb**: 87 | 99 |
| 13 | **1l** | **2a** | **6/7** = 7/1 | **6la**: 92[f] | 99 |
| 14 | **1l** | **2b** | **6/7** = 12/1 | **6lb**: 94[f] | >99.5 |
| 15 | **1l** | **2e** | **6/7** = 11/1 | **6le**: 77[f] | 96 |
| 16 | **1l** | **2g** | **6/7** = 9/1 | **6lg**: 92[f] | 98 |
| 17[e] | **1m** | **2b** | **6/7** = 6/1 | **6mb**: 86[f] | >99.5 |

| | | | | | |
|---|---|---|---|---|---|
| 18 | **1n** | **2a** | **6/7** = >50/1 | **6na**: 91 | 99 |
| 19 | **1o** | **2a** | **6/7** = >50/1 | **6oa**: 80 | 98 |
| 20[e] | **1p** | **2a** | — | **8pa**: 72 | 99 |
| 21[e] | **1q** | **2a** | — | **8qa**: 78 | 97 |
| 22[e] | **1r** | **2a** | — | **8ra**: 74 | 97 |

[a] Reaction conditions: **1** (0.24 mmol), enone **2** (0.20 mmol), $Cs_2CO_3$ (0.40 mmol), [RhCl((*R*,*R*)-Ph-bod)]$_2$ (5 mol% of Rh), $H_2O$ (1.1 mL) at 100 °C for 16 h. [b] Determined by $^1$H NMR. [c] Isolated yield. [d] The % ee was determined by HPLC on chiral columns. The absolute configuration of **5fb** was determined to be *R* by X-ray analysis (CCDC 1500570) and others are estimated by stereochemical similarity to those reported for asymmetric arylation with Rh/(*R*,*R*)-Ph-bod catalyst. [e] With **1** (0.40 mmol) and $Cs_2CO_3$ (0.80 mmol). [f] Yield of a mixture of **6** and **7**.

The 1,4-shift/arylation products **5**–**8** shown in Table 2.3 are expected to be also obtainable by use of the corresponding *ortho*-methoxyarylboronic acids (see, entry 8 in Table 2.1). However, the synthesis of aryloxymethylborates from phenol derivatives is generally much more straightforward than that of the *ortho*-methoxyarylboronic acids. As an example, the reported synthetic scheme for ester-substituted 2-methoxyphenylboronic acids **4h,k**[15] is shown in Scheme 2.5, where an ester-substituted phenols were converted into the boronic acids by multiple step reactions including *ortho*-bromination and palladium-catalyzed borylation. To the contrary, the aryloxymethylborates **1h,k** are prepared by one step from the phenols by Molander's method.[6] It should be noted that the present rhodium catalysis can skip the ortho C–H functionalization steps required for the synthesis of *ortho*-methoxyarylboron reagents.

**Scheme 2.5. Comparison of Synthesis and Reaction of Aryloxymethylborates 1 with *ortho*-Methoxyphenylboronic Acids 4**



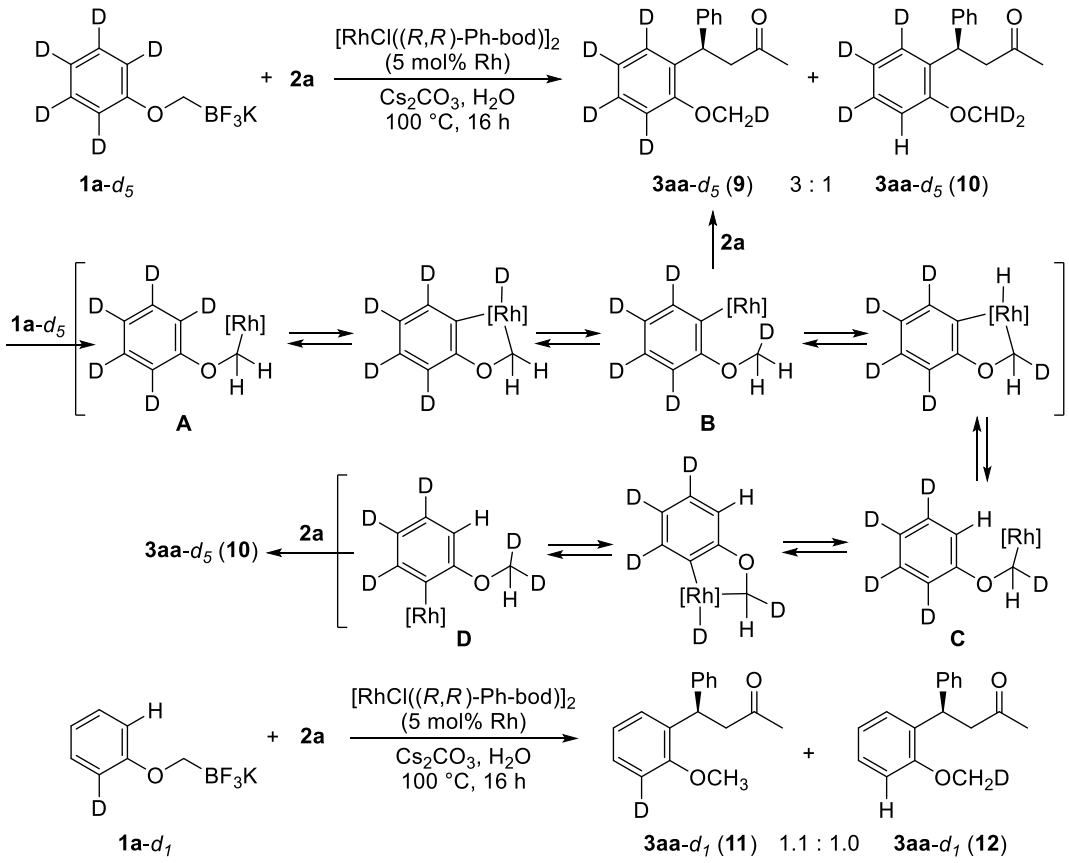

1) $(MeO)_2SO_2/K_2CO_3$. 2) $NBS/HBF_4 \cdot Et_2O$. 3) $(Bpin)_2/KOAc$, $[PdCl_2(dppf)]$. 4) $NaIO_4$.

Deuterium labeling studies provided us with some information on the mechanism of 1,4-Rh shift from the phenoxymethyl carbon to the 2-methoxyphenyl carbon (Scheme 2.6). The product **3aa**-$d_5$ formed by the reaction of pentadeuterio-phenoxymethylborate **1a**-$d_5$ with benzalacetone (**2a**) was found to be a mixture of deuterium-regioisomers **3aa**-$d_5$ (**9**) and **3aa**-$d_5$ (**10**) in a ratio of 3 to 1. The reaction pathway to produce isomer **9**, which is substituted with $OCH_2D$ group at 2-position and with $D_4$ at other positions, is simple. Transmetallation of the phenoxymethyl group from boron to rhodium generates alkyl–Rh intermediate **A**, which is not reactive towards the addition to enone[16] but undergoes the 1,4-Rh shift by way of a Rh(III) species[17] to form a 2-methoxyphenyl–Rh intermediate **B**. Addition of the aryl–Rh **B** to the enone **2a** produces the isomer **9**. The reversibility of 1,4-Rh shift between $sp^3$ carbon and $sp^2$ carbon is demonstrated by the formation of the isomer **10**, where the methoxy group at the 2-position is $OCHD_2$ and H is at the 3-position.

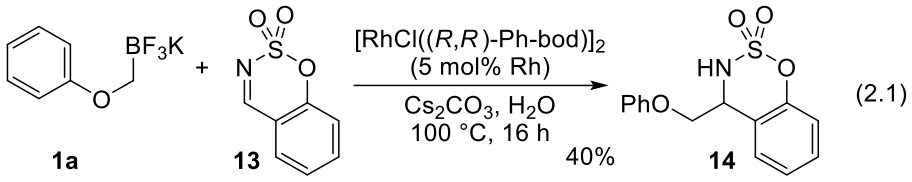
The 1,4-shift from the 2-methoxyphenyl–Rh intermediate **B** goes back to **A** or generates a new alkyl–Rh **C** where H and D are exchanged. The 1,4-Rh shift to the other side of the ortho carbon forms an aryl–Rh intermediate **D**, which finally leads to the isomer **10** by addition to the enone **2a**.

Deuterium kinetic isotope effects (KIE) were studied for intramolecular competition[18,19] in the reaction of 2-deuteriophenoxymethylborate **1a**-*d*$_1$. In the product **3aa**-*d*$_1$, deuterium was incorporated at the aromatic carbon (**11**) and at the methoxy carbon (**12**) in a ratio of 1.1 to 1.0. This small KIE ($k_H/k_D$ = 1.1) may suggest that the C–H bond breaking is not a turnover limiting step in the present reaction.

**Scheme 2.6. Deuterium-Labeling Studies on the 1,4-Rh Shift during the Rhodium-Catalyzed Hydroarylation**



The reaction of *N*-sulfonylimine **13** with phenoxymethylborate **1a** proceeded in a different way (equation 2.1). It gave phenoxymethylation product **14** instead of 1,4-shift/arylation product. The yield is not high (40%) under the standard conditions used for α,β-unsaturated carbonyl compounds **2**. The addition of alkyl–Rh intermediate to imine **13** before the 1,4-shift is consistent with the report[20] that *N*-sulfonylimines undergoes methylation with a methylboron reagent in the presence of a diene/rhodium catalyst.



(2.1)

## 2.3 Conclusion

In summary, a new type of rhodium-catalyzed conjugate arylation using aryloxymethyltrifluoroborates as nucleophiles was developed. In the catalytic cycle, an aryloxymethyl–Rh intermediate generated by transmetallation from the boron reagent undergoes C–H activation by 1,4-Rh shift to form an *ortho*-methoxyaryl–Rh intermediate, which is reactive towards α,β-unsaturated carbonyl compounds. The asymmetric conjugate addition is efficiently catalyzed by a chiral diene–rhodium catalyst in $H_2O$ with high enantioselectivity (≥93% ee).

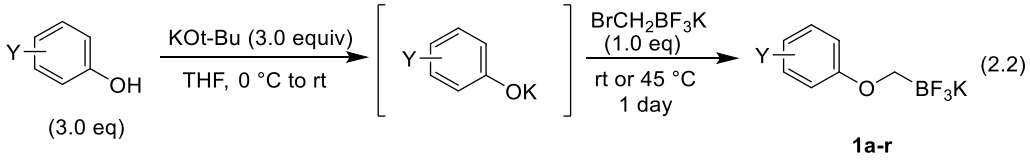
## 2.4 Experimental section

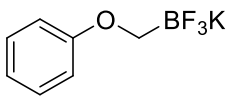
### 2.4.1 Materials

The α,β-unsaturated carbonyl compounds, phenols, $Cs_2CO_3$, dibromomethane, methanesulfonic acid, HPLC grade water, $KHF_2$, potassium t-butoxide, and n-BuLi were purchased and used as received. 1,4-Dioxane, toluene, and THF were distilled over benzophenone ketyl under nitrogen. Rhodium complexes, $[RhCl(coe)_2]_2$,[21] $[RhCl((R,R)\text{-Ph-bod})]_2$,[22] and $[RhCl((S,S)\text{-Fc-tfb})]_2$[23] were prepared according to the reported procedures. Potassium bromomethyltrifluoroborate[6b] was prepared according to the reported procedure.

### 2.4.2 Preparation of Potassium Aryloxymethyltrifluoroborates 1a-r

They were prepared from phenols and potassium bromomethyltrifluoroborate ($BrCH_2BF_3K$) according to the procedure reported by Molander (equation 2.2).[6a]

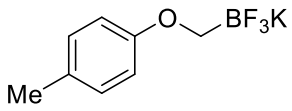



**1a**

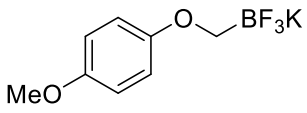
**Preparation of Potassium Phenoxymethyltrifluoroborate (1a) [1027642-30-3].** It was synthesized according to the reported procedure.[25] To a 100 mL 2-neck round-bottom-flask was added potassium tert-butoxide (3.37 g, 30 mmol) and dry THF (50 mL). Phenol (2.82 g, 30 mmol) was added to the suspension via syringe at 0 °C under $N_2$. The mixture was stirred at 0 °C for 15 min and allowed to warm to

room temperature over 30 min. Potassium bromomethyltrifluoroborate (2.00 g, 10 mmol) was added in one portion at 0 °C. The reaction mixture was stirred at room temperature for 1 day, and 4.5 M $KHF_2$ (4.5 mL) was added. The mixture was kept stirring at room temperature for 30 min, and the suspension was concentrated and dried overnight in vacuo. The crude solid was suspended in $Et_2O$ (25 mL) and filtered to remove the organic impurities. The crude solid was purified by continuous Soxhlet extraction with acetonitrile (60 mL). The extract was concentrated and then cooled using an ice-water bath. The white precipitates were collected and dried to give 84% yield (1.80 g, 8.4 mmol) of the target compound **1a**. **$^1$H NMR** (500 MHz, DMSO-*d*$_6$) δ 2.94 (q, $J_{H,^{19}F}$ = 5.2 Hz, 2H), 6.75 (tt, $J_{H,H}$ = 7.3 Hz, 1.2 Hz, 1H), 6.83 (d, $J_{H,H}$ = 7.7 Hz, 2H), 7.18 (dd, $J_{H,H}$ = 8.5 Hz, 7.3 Hz, 2H); **$^{13}$C NMR** (125 MHz, DMSO-*d*$_6$,) δ 113.8, 118.3, 128.9, 162.1. The $OCH_2B$ carbon was not observed in $^{13}$C NMR of compounds **1**. The spectral data are in agreement with reported literature values.[6a]



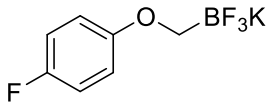

**1b**

**Preparation of Potassium (4-Methylphenoxy)methyltrifluoroborate (1b).** Similarly to the preparation of **1a**, **1b** was prepared with 4-methylphenol (0.65 g, 6.0 mmol) and $BrCH_2BF_3K$ (0.40 g, 2.0 mmol). The product was obtained in 70% yield (0.32 g, 1.4 mmol) as a white crystalline solid. **$^1$H NMR** (500 MHz, DMSO-*d*$_6$) δ 2.19 (s, 3H), δ 2.90 (q, $J_{H,^{19}F}$ = 5.2 Hz, 2H), 6.72 (d, $J_{H,H}$ = 8.5 Hz, 2H), 6.98 (d, $J_{H,H}$ = 8.6 Hz, 2H); **$^{13}$C NMR** (125 MHz, DMSO-*d*$_6$) δ 20.0, 113.5, 126.6, 129.3, 160.0. **HRMS** (APCI) m/z calcd. For $C_8H_9BF_3O$ (M-K) 189.0706; found, 189.0702.



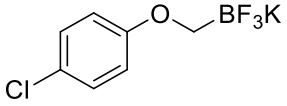

**1c**

**Preparation of Potassium (4-Methoxyphenoxy)methyltrifluoroborate (1c) [1448675-13-5].** Similarly to the preparation of **1a**, **1c** was prepared with 4-methoxylphenol (0.74 g, 6.0 mmol) and $BrCH_2BF_3K$ (0.40 g, 2.0 mmol). The product was obtained in 82% yield (0.40 g, 1.6 mmol) as a white crystalline solid. **$^1$H NMR** (500 MHz, DMSO-$d_6$) δ 2.88 (q, $J_{H,^{19}F}$ = 5.2 Hz, 2H), 3.66 (s, 3H), 6.75 (d, $J_{H,H}$ = 9.0 Hz, 2H), 6.77 (d, $J_{H,H}$ = 9.2 Hz, 2H); **$^{13}$C NMR** (125 MHz, DMSO-$d_6$) δ 55.2, 114.1, 114.2, 151.8, 156.2. **HRMS** (APCI) m/z calcd. For $C_8H_9BF_3O_2$ (M-K) 205.0655; found, 205.0653. The spectral data are in agreement with reported literature values.[6a]



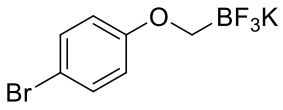

**1d**

**Preparation of Potassium (4-Fluorophenoxy)methyltrifluoroborate (1d).** The potassium aryloxide generated from 4-fluorophenol (0.67 g, 6.0 mmol) was treated with $BrCH_2BF_3K$ (0.40 g, 2.0 mmol) at 45 °C for 1 day. The product was obtained in 87% yield (0.40 g, 1.7 mmol) as a light yellow crystalline solid. **$^1$H NMR** (500 MHz, DMSO-$d_6$) δ 2.93 (q, $J_{H,^{19}F}$ = 5.2 Hz, 2H), 6.82 (dd, $J_{H,H}$ = 9.2 Hz, $J_{H,^{19}F}$ = 4.6 Hz, 2H), 6.99 (t, $J_{H,H}$ = $J_{H,^{19}F}$ = 8.9 Hz, 2H); **$^{13}$C NMR** (100 MHz, DMSO-$d_6$**)** δ 114.5 (d, $J_{C,^{19}F}$ = 7.8 Hz), 115.2 (d, $J_{C,^{19}F}$ = 22.4 Hz), 155.3 (d, $J_{C,^{19}F}$ = 231.6 Hz), 158.4. **HRMS** (APCI) m/z calcd. For $C_7H_6BF_4O$ (M-K) 193.0455; found, 193.0460.



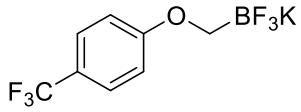

**1d**

**Preparation of Potassium (4-Chlorophenoxy)methyltrifluoroborate (1e).** The potassium aryloxide generated from 4-chlorophenol (0.77 g, 6.0 mmol) was treated with $BrCH_2BF_3K$ (0.40 g, 2.0 mmol) at 45 °C for 1 day. The product was obtained in 91% yield (0.45 g, 1.8 mmol) as a white crystalline solid. **$^1$H NMR** (500 MHz, DMSO-$d_6$) δ 2.95 (q, $J_{H,^{19}F}$ = 5.1 Hz, 2H), 6.85 (d, $J_{H,H}$ = 9.0 Hz, 2H), 6.99 (d, $J_{H,H}$ = 9.1 Hz, 2H); **$^{13}$C NMR** (125 MHz, DMSO-$d_6$**)** δ 115.5, 121.9, 128.6, 160.9. **HRMS** (APCI) m/z calcd. For $C_7H_6BClF_3O$ (M-K) 209.0159; found, 209.0157.




**1f**

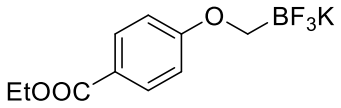
**Preparation of Potassium (4-Bromophenoxy)methyltrifluoroborate (1f).** The potassium aryloxide generated from 4-bromophenol (5.2 g, 30 mmol) was treated with $BrCH_2BF_3K$ (2.0 g, 10 mmol) at 45 °C for 1 day. The product was obtained in 85% yield (2.49 g, 8.5 mmol) as a white crystalline solid. **$^1$H NMR** (500 MHz, DMSO-$d_6$) δ 2.95 (q, $J_{H,^{19}F}$ = 5.2 Hz, 2H), 6.69 (d, $J_{H,H}$ = 9.0 Hz, 2H), 7.47 (d, $J_{H,H}$ = 9.1 Hz, 2H); **$^{13}$C NMR** (125 MHz, DMSO-$d_6$**)** δ 109.5, 116.1, 131.5, 161.4. **HRMS** (APCI) m/z calcd. For $C_7H_6BBrF_3O$ (M-K) 252.9654; found, 252.9651.




**1g**

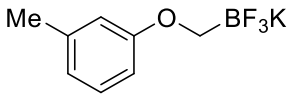
**Preparation of Potassium (4-Trifluoromethylphenoxy)methyltrifluoroborate (1g).** The potassium aryloxide generated from 4-trifluoromethylphenol (0.97 g, 6.0 mmol) was treated with $BrCH_2BF_3K$ (0.40 g, 2.0 mmol) at 45 C for 1 day. The product was obtained in 74% yield (0.42 g, 1.5 mmol) as a yellow crystalline solid. **$^1$H NMR** (500 MHz, DMSO-$d_6$) δ 3.01 (q, $J_{H,^{19}F}$ = 5.0 Hz, 2H), 7.03 (d, $J_{H,H}$ =

8.6 Hz, 2H), 7.54 (d, $J_{H,H}$ = 8.6 Hz, 2H); **$^{13}$C NMR** (125 MHz, DMSO-$d_6$**)** δ 114.4, 119.1 (q, $J_{C,^{19}F}$ = 31.7 Hz), 124.9 (q, $J_{C,^{19}F}$ = 268.9 Hz), 126.4 (q, $J_{C,^{19}F}$ = 15.0 Hz), 165.0. **HRMS** (APCI) m/z calcd. For $C_8H_6BF_6O$ (M-K) 243.0423; found, 243.0418.




**1h**

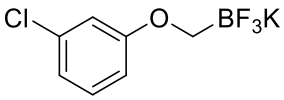
**Preparation of Potassium (4-Ethoxycarbonylphenoxy)methyltrifluoroborate (1h).** The potassium aryloxide generated from 4-ethoxycarbonylphenol (5.0 g, 30 mmol) was treated with $BrCH_2BF_3K$ (2.0 g, 10 mmol) at 45 °C for 1 day. The product was obtained in 62% yield (1.77 g, 6.2 mmol) as a white crystalline solid. **$^1$H NMR** (500 MHz, DMSO-$d_6$) δ 1.30 (t, $J_{H,H}$ = 7.1 Hz, 3H), 3.07 (q, $J_{H,^{19}F}$ = 5.1 Hz, 2H), 4.25 (q, $J_{H,H}$ = 7.1 Hz, 2H), 6.93 (d, $J_{H,H}$ = 8.9 Hz, 2H), 7.82 (d, $J_{H,H}$ = 8.9 Hz, 2H); **$^{13}$C NMR** (125 MHz, DMSO-$d_6$) δ 14.2, 59.9, 113.9, 120.0, 130.8, 165.6, 166.0. **HRMS** (APCI) m/z calcd. For $C_{10}H_{11}BF_3O_3$ (M-K) 247.0761; found, 247.0758.




**1i**

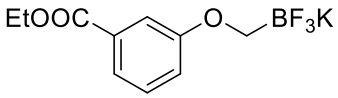
**Preparation of Potassium (3-Methylphenoxy)methyltrifluoroborate (1i).** Similarly to the preparation of **1a**, **1i** was prepared with 3-methylphenol (0.65 g, 6.0 mmol) and $BrCH_2BF_3K$ (0.40 g, 2.0 mmol). The product was obtained in 80% yield (0.36 g, 1.6 mmol) as a white crystalline solid. **$^1$H NMR** (500 MHz, DMSO-$d_6$) δ 2.23 (s, 3H), 2.92 (q, $J_{H,^{19}F}$ = 5.0 Hz, 2H), 6.57 (d, $J_{H,H}$ = 7.4 Hz, 1H), 6.62 (d, $J_{H,H}$ = 7.9 Hz, 1H), 6.65 (s, 1H), 7.05 (t, $J_{H,H}$ = 7.8 Hz, 1H); **$^{13}$C NMR** (75 MHz, DMSO-

*d*$_6$**)** δ 21.2, 110.9, 114.4, 119.2, 128.6, 138.1, 162.1. **HRMS** (APCI) m/z calcd. For $C_8H_9BF_3O$ (M-K) 189.0706; found, 189.0708.




**1j**

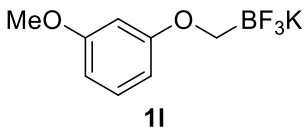
**Preparation of Potassium (3-Chlorophenoxy)methyltrifluoroborate (1j).** The potassium aryloxide generated from 3-chlorophenol (0.77 g, 6.0 mmol) was treated with $BrCH_2BF_3K$ (0.40 g, 2.0 mmol) at 45 °C for 1 day. The product was obtained in 89% yield (0.44 g, 1.8 mmol) as a white crystalline solid. **$^1$H NMR** (500 MHz, DMSO-*d*$_6$) δ 2.98 (q, $J_{H,^{19}F}$ = 5.2 Hz, 2H), 6.81 (d, $J_{H,H}$ = 8.2 Hz, 2H), 6.86 (s, 1H), 7.20 (t, $J_{H,H}$ = 8.2 Hz, 1H); **$^{13}$C NMR** (125 MHz, DMSO-*d*$_6$**)** δ 113.2, 113.6, 118.3, 130.2, 133.2, 163.1. **HRMS** (APCI) m/z calcd. For $C_7H_6BClF_3O$ (M-K) 209.0159; found, 209.0158.




**1k**

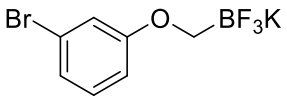
**Preparation of Potassium (3-Ethoxycarbonylphenoxy)methyltrifluoroborate (1k).** The potassium aryloxide generated from 3-ethoxycarbonylphenol (5.0 g, 30 mmol) was treated with $BrCH_2BF_3K$ (2.0 g, 10 mmol) at 45 °C for 2 days. The product was obtained in 87% yield (2.49 g, 8.7 mmol) as a white crystalline solid. **$^1$H NMR** (500 MHz, DMSO-*d*$_6$) δ 1.31 (t, $J_{H,H}$ = 7.1 Hz, 3H), 3.01 (q, $J_{H,^{19}F}$ = 5.1 Hz, 2H), 4.29 (q, $J_{H,H}$ = 7.1 Hz, 2H), 7.12 (ddd, $J_{H,H}$ = 8.2 Hz, 2.6 Hz, 1.3 Hz, 1H), 7.33 (t, $J_{H,H}$ = 8.0 Hz, 1H), 7.40 (dt, $J_{H,H}$ = 8.1 Hz, 1.3 Hz, 1H), 7.41 (s, 1H); **$^{13}$C NMR** (125 MHz, DMSO-*d*$_6$) δ 14.1, 60.5, 113.8, 119.3, 119.4, 129.2, 130.8, 162.1,

165.9. **HRMS** (APCI) m/z calcd. For $C_{10}H_{11}BF_3O_3$ (M-K) 247.0761; found, 247.0760.



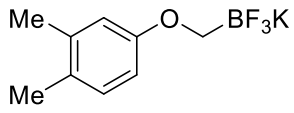

**1l**

**Preparation of Potassium (3-Methoxyphenoxy)methyltrifluoroborate (1l).** Similarly to the preparation of **1a**, **1l** was prepared with 3-methoxylphenol (3.7 g, 30 mmol) and $BrCH_2BF_3K$ (2.0 g, 10 mmol). The product was obtained in 84% yield (2.05 g, 8.4 mmol) as a white crystalline solid. **$^1$H NMR** (300 MHz, DMSO-$d_6$) δ 2.92 (q, $J_{H,^{19}F}$ = 5.1 Hz, 2H), 3.70 (s, 3H), 6.35 (d, $J_{H,H}$ = 8.0 Hz, 1H), 6.39 (s, 1H), 6.42 (d, $J_{H,H}$ = 8.1 Hz, 1H), 7.07 (t, $J_{H,H}$ = 8.1 Hz, 1H); **$^{13}$C NMR** (75 MHz, DMSO-$d_6$**)** δ 54.7, 99.8, 104.2, 106.3, 129.3, 160.2, 163.5. **HRMS** (APCI) m/z calcd. For $C_8H_9BF_3O_2$ (M-K) 205.0655; found, 205.0653.



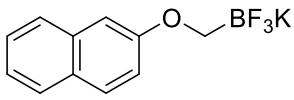

**1m**

**Preparation of Potassium (3-Bromophenoxy)methyltrifluoroborate (1m).** The potassium aryloxide generated from 3-bromophenol (2.6 g, 15 mmol) was treated with $BrCH_2BF_3K$ (1.0 g, 5.0 mmol) at 45 °C for 1 day The product was obtained in 95% yield (1.39 g, 4.8 mmol) as a white crystalline solid. **$^1$H NMR** (400 MHz, DMSO-$d_6$) δ 2.97 (q, $J_{H,^{19}F}$ = 5.1 Hz, 2H), 6.85 (dd, $J_{H,H}$ = 8.4 Hz, 2.3 Hz, 1H), 6.94 (d, $J_{H,H}$ = 8.0 Hz, 1H), 7.01 (s, 1H), 7.14 (t, $J_{H,H}$ = 8.1 Hz, 1H); **$^{13}$C NMR** (125 MHz, DMSO-$d_6$**)** δ 113.5, 116.5, 121.2, 121.7, 130.6, 163.2. **HRMS** (APCI) m/z calcd. For $C_7H_6BBrF_3O$ (M-K) 252.9654; found, 252.9648.



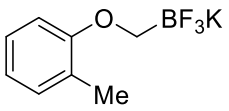

**1n**

**Preparation of Potassium (3,4-Dimethylphenoxy)methyltrifluoroborate (1n).** Similarly to the preparation of **1a**, **1n** was prepared with 3,4-dimethylphenol (3.7 g, 30 mmol) and $BrCH_2BF_3K$ (2.0 g, 10 mmol). The product was obtained in 84% yield (2.03 g, 8.4 mmol) as a white crystalline solid. **$^1$H NMR** (500 MHz, DMSO-$d_6$) δ 2.10 (s, 3H), 2.14 (s, 3H), 2.88 (q, $J_{H,^{19}F}$ = 5.1 Hz, 2H), 6.54 (dd, $J_{H,H}$ = 8.2 Hz, 2.7Hz, 1H), 6.63 (d, $J_{H,H}$ = 2.7 Hz, 1H), 6.91 (d, $J_{H,H}$ = 8.2 Hz, 1H); **$^{13}$C NMR** (125 MHz, DMSO-$d_6$**)** δ 18.3, 19.7, 110.7, 115.2, 125.4, 129.7, 136.3, 160.2. **HRMS** (APCI) m/z calcd. For $C_9H_{11}BF_3O$ (M-K) 203.0862; found, 203.0865.



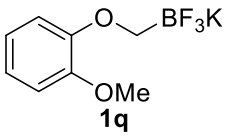

**1o**

**Preparation of Potassium (2-Naphthoxy)methyltrifluoroborate (1o).** The potassium aryloxide generated from 2-naphthol (4.3 g, 30 mmol) was treated with $BrCH_2BF_3K$ (2.0 g, 10 mmol) at 45 °C for 1 day. The product was obtained in 56% yield (1.48 g, 5.6 mmol) as a pink crystalline solid. **$^1$H NMR** (500 MHz, DMSO-$d_6$) δ 3.09 (q, $J_{H,^{19}F}$ = 5.2 Hz, 2H), 7.08 (dd, $J_{H,H}$ = 8.9 Hz, 2.5 Hz, 1H), 7.20 (d, $J_{H,H}$ = 2.5 Hz, 1H), 7.25 (t, $J_{H,H}$ = 7.7 Hz, 1H), 7.38 (t, $J_{H,H}$ = 7.5 Hz, 1H), 7.71 (d, $J_{H,H}$ = 8.8 Hz, 1H), 7.74 (d, $J_{H,H}$ = 7.3 Hz, 1H), 7.75 (d, $J_{H,H}$ = 7.6 Hz, 1H); **$^{13}$C NMR** (125 MHz, DMSO-$d_6$**)** δ 105.2, 119.5, 122.4, 125.7, 126.4, 127.2, 127.7, 128.4, 134.7, 160.2. **HRMS** (APCI) m/z calcd. For $C_{11}H_9BF_3O$ (M-K) 225.0706; found, 225.0699.



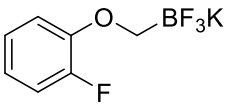

**1p**

**Preparation of Potassium (2-Methylphenoxy)methyltrifluoroborate (1p).** Similarly to the preparation of **1a**, **1p** was prepared with 2-methylphenol (3.2 g, 30 mmol) and $BrCH_2BF_3K$ (2.0 g, 10 mmol). The product was obtained in 72% yield (1.64 g, 7.2 mmol) as a white crystalline solid. **$^1$H NMR** (500 MHz, DMSO-$d_6$) δ 2.09 (s, 3H), 2.96 (q, $J_{H,^{19}F}$ = 5.2 Hz, 2H), 6.65 (t, $J_{H,H}$ = 7.3 Hz, 1H), 6.86 (d, $J_{H,H}$ = 8.1 Hz, 1H), 7.00 (d, $J_{H,H}$ = 7.3 Hz, 1H), 7.05 (t, $J_{H,H}$ = 7.7 Hz, 1H); **$^{13}$C NMR** (125 MHz, DMSO-$d_6$**)** δ 16.1, 110.2, 117.9, 125.1, 126.5, 129.5, 160.1. **HRMS** (APCI) m/z calcd. For $C_8H_9BF_3O$ (M-K) 189.0706; found, 189.0703.



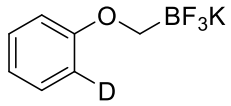

**1q**

**Preparation of Potassium (2-Methoxyphenoxy)methyltrifluoroborate (1q).** Similarly to the preparation of **1a**, **1q** was prepared with 2-methoxylphenol (3.7 g, 30 mmol) and $BrCH_2BF_3K$ (2.0 g, 10 mmol). The product was obtained in 70% yield (1.7 g, 7.0 mmol) as a white crystalline solid. $^1$H NMR (500 MHz, DMSO-$d_6$) δ 2.93 (q, $J_{H,^{19}F}$ = 5.1 Hz, 2H), 3.71 (s, 3H), 6.71 (t, $J_{H,H}$ = 7.6 Hz, 1H), 6.81 (d, $J_{H,H}$ = 7.8 Hz, 1H), 6.83 (d, $J_{H,H}$ = 7.7 Hz, 1H), 6.90 (t, $J_{H,H}$ = 7.9 Hz, 1H); **$^{13}$C NMR** (75 MHz, DMSO-$d_6$**)** δ 55.2, 111.1, 111.4, 118.3, 120.7, 148.6, 151.8. **HRMS** (APCI) m/z calcd. For $C_8H_9BF_3O_2$ (M-K) 205.0655; found, 205.0654.




**1r**

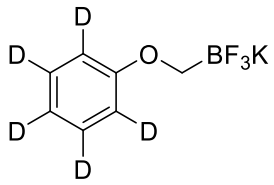
**Preparation of Potassium (2-Fluorophenoxy)methyltrifluoroborate (1r).** The potassium aryloxide generated from 2-fluorophenol (3.4 g, 30 mmol) was treated with $BrCH_2BF_3K$ (2.0 g, 10 mmol) at 45 °C for 2 days. The product was obtained in 81% yield (1.87 g, 8.1 mmol) as a yellow crystalline solid. **$^1$H NMR** (300 MHz, DMSO-$d_6$) δ 3.03 (q, $J_{H,^{19}F}$ = 5.0 Hz, 2H), 6.68-6.82 (m, 1H), 6.94-7.14 (m, 3H); **$^{13}$C NMR** (75 MHz, DMSO-$d_6$) δ 113.5 (d, $J_{C,^{19}F}$ = 1.4 Hz), 114.9 (d, $J_{C,^{19}F}$ = 17.9 Hz), 118.3 (d, $J_{C,^{19}F}$ = 6.7 Hz), 124.4 (d, $J_{C,^{19}F}$ = 3.5 Hz), 150.0 (d, $J_{C,^{19}F}$ = 10.3 Hz), 151.7 (d, $J_{C,^{19}F}$ = 240.7 Hz). **HRMS** (APCI) m/z calcd. For $C_7H_6BF_4O$ (M-K) 193.0455; found, 193.0451.




**1a-*d*$_1$**

**Preparation of Potassium (2-Deuteriophenoxy)methyltrifluoroborate (1a-*d*$_1$).** The *o*-deuteriophenol was synthesized according to a known procedure.[24] Treatment of an ethereal solution of *o*-bromophenol with 2 equiv of n-butyllithium at 0 °C for 2-3 h afforded the dianionic lithium intermediate. Quenching the dianion with $D_2O$ produced *o*-deuteriophenol in 90% isolated yield.

The procedure for preparation of phenoxymethylborate **1a** was followed by employing *o*-deuteriophenol (3.4 g, 30 mmol). The product was obtained in 89% yield (1.91 g, 8.9 mmol) as a white crystalline solid. **$^1$H NMR** (500 MHz, DMSO-$d_6$) δ 2.94 (q, $J_{H,^{19}F}$ = 5.3 Hz, 2H), 6.76 (t, $J_{H,H}$ = 7.3 Hz, 1H), 6.83 (d, $J_{H,H}$ = 8.9 Hz, 1H), 7.15–7.21 (m, 2H); **$^{13}$C NMR** (125 MHz, DMSO-$d_6$) δ 113.5 (t, $J_{C,^2H}$ = 24.1 Hz), 113.8, 118.4, 128.8, 128.9, 162.0. **HRMS** (APCI) m/z calcd. For $C_7H_5BDF_3O$ (M-K) 176.0612; found, 176.0614.




**1a-*d*$_5$**

**Preparation of Potassium (Pentadeuteriophenoxy)methyltrifluoroborate (1a-*d*$_5$).** Similarly to the preparation of **1a**, **1a-***d*$_5$ was prepared with phenol-*d*$_6$ (0.60 g, 6.0 mmol) and $BrCH_2BF_3K$ (0.40 g, 2.0 mmol). The product was obtained in 90% yield (0.39 g, 1.8 mmol) as a white crystalline solid. **$^1$H NMR** (500 MHz, DMSO-*d*$_6$) δ 2.99 (q, $J_{H,}{}^{19}{}_F$ = 5.4 Hz, 2H); **$^{13}$C NMR** (125 MHz, DMSO-*d*$_6$**)** δ 113.5 (t, $J_{C,}{}^2{}_H$ = 24.2 Hz), 118.1 (t, $J_{C,}{}^2{}_H$ = 24.4 Hz), 128,5 (t, $J_{C,}{}^2{}_H$ = 24.1 Hz), 161.9. **HRMS** (APCI) m/z calcd. For $C_7H_2BD_5F_3O$ (M-K) 180.0863; found, 180.0866.

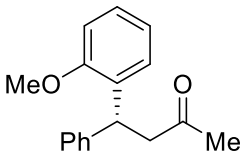
### 2.4.3 A Typical Procedure for Rhodium-Catalyzed Asymmetric Arylation of 2 with 1 (entry 6 in Table 2.1 and entry 1 in Table 2.2)

In an oven-dried Schlenk tube, were placed [RhCl((*R*,*R*)-Ph-bod)]$_2$ (3.97 mg, 0.005 mmol, 5 mol% of Rh), $Cs_2CO_3$ (130 mg, 0.40 mmol, 2.0 equiv), benzalacetone (**2a**) (29.2 mg, 0.20 mmol), and potassium phenoxymethyltrifluoroborate (**1a**) (51.4 mg, 0.24 mmol, 1.2 equiv) under argon. Degassed water (1.1 mL) was added, and the mixture was stirred at 100 °C for 16 h. The reaction mixture was passed through a short column of silica gel with EtOAc as eluent and the water stayed in silica gel. The solvent was removed on a rotary evaporator. After $^1$H NMR analysis of the residue, the crude product was subjected to silica gel chromatography with EtOAc/hexane (1/10) to give **3aa** (43.6 mg, 0.17 mmol, 86% yield) as a colorless oil.

In entry 7 in Table 2.1, 2 equiv of potassium phenoxymethyltrifluoroborate (**1a)** (85.7 mg, 0.40 mmol) and $Cs_2CO_3$ (260 mg, 0.80 mmol, 4.0 equiv) were used.

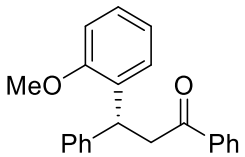
In entries 11 and 12 in Table 2.1, $[RhCl((R)\text{-binap})]_2$ and $[RhCl((R)\text{-segphos})]_2$ were generated in situ from $[RhCl(coe)_2]_2$ (3.59 mg, 0.010 mmol of Rh) and the corresponding bisphosphine ligands (0.011 mmol).

### 2.4.3 Characterization of the products



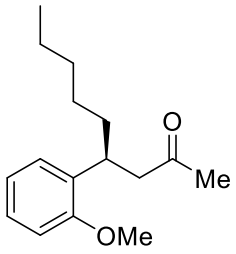

**3aa**

**Compound 3aa [1005497-30-2]**. (86% yield, 98% ee (*R*), Table 2.1, entry 6). The crude product was subjected to silica gel chromatography with EtOAc/hexane (1/10) to give **3aa** (43.6 mg, 0.17 mmol, 86% yield) as a colorless oil. The ee was measured by HPLC (Chiralpak IE column, 0.6 mL/min, hexane/2-propanol = 98/2, 230 nm, $t_{major}$ = 22.9 min (*R*), $t_{minor}$ = 21.9 min (*S*)); $[\alpha]^{25}_D$ +35.8 (*c* 0.963, $CHCl_3$) for 98% ee. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 2.10 (s, 3H), 3.14 (dd, $J_{H,H}$ = 16.5 Hz, 7.3 Hz, 1H), 3.17 (dd, $J_{H,H}$ = 16.3 Hz, 8.1 Hz, 1H), 3.80 (s, 3H), 4.99 (t, $J_{H,H}$ = 7.6 Hz, 1H), 6.85 (d, $J_{H,H}$ = 8.2 Hz, 1H), 6.89 (t, $J_{H,H}$ = 7.5 Hz, 1H), 7.11 (dd, $J_{H,H}$ = 7.6 Hz, 1.7 Hz, 1H), 7.14–7.21 (m, 2H), 7.23–7.29 (m, 4H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 30.2, 39.5, 48.9, 55.4, 110.8, 120.5, 126.1, 127.5, 127.8, 127.9, 128.3, 132.1, 143.4, 156.7, 207.3. **HRMS** (ESI) calcd for $C_{17}H_{18}NaO_2$ $[M+Na]^+$ 277.1199, found 277.1192. The spectral data are in agreement with reported literature values.[25]




**3ab**

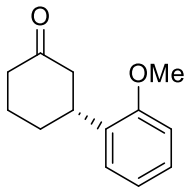
**Compound 3ab [6402-59-5].** (94% yield, >99.5% ee (*R*), Table 2.2, entry 2). The crude product was subjected to silica gel chromatography to give **3ab** (59.4 mg, 0.19 mmol, 94% yield) as a pale yellow oil. The ee was measured by HPLC (Chiralpak IB column, 1.0 mL/min, hexane/2-propanol = 97/3, 280 nm, $t_{major}$ = 8.1 min (*R*), $t_{minor}$ = 9.2 min (*S*)); $[\alpha]^{25}_{D}$ +25.4 (*c* 1.32, $CHCl_3$) for >99.5% ee. **$^1$H NMR** (300 MHz, $CDCl_3$) δ 3.72 (d, $J_{H,H}$ = 7.4 Hz, 2H), 3.77 (s, 3H), 5.18 (t, $J_{H,H}$ = 7.4 Hz, 1H), 6.86 (t, $J_{H,H}$ = 7.8 Hz, 1H), 6.93 (d, $J_{H,H}$ = 7.5 Hz, 1H), 7.07–7.33 (m, 7H), 7.43 (t, $J_{H,H}$ = 7.2 Hz, 2H), 7.54 (tt, $J_{H,H}$ = 7.3 Hz, 2.5 Hz, 1H), 7.95 (d, $J_{H,H}$ = 7.1 Hz, 2H); **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 39.8, 43.8, 55.4, 110.9, 120.5, 126.1, 127.5, 128.06, 128.09, 128.12, 128.2, 128.5, 132.6, 132.8, 137.2, 143.6, 156.9, 198.4. **HRMS** (ESI) calcd for $C_{22}H_{20}NaO_2$ $[M+Na]^+$ 339.1356, found 339.1359. The spectral data were in agreement with reported literature values.[26]



**3ac**

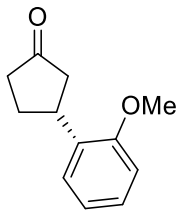
**Compound 3ac [603984-43-6].** (84% yield, 97% ee (*S*), Table 2.2, entry 3). The crude product was subjected to silica gel chromatography to give **3ac** (41.6 mg, 0.17 mmol, 84% yield) as a colorless oil. The ee was measured by HPLC (Chiralcel OJ-H column, 0.4 mL/min, hexane/2-propanol = 98/2, 280 nm, $t_{major}$ = 18.7 min (*S*), $t_{minor}$ = 20.1 min (*R*)); $[\alpha]^{25}_{D}$ +2.4 (*c* 1.27, $CHCl_3$) for 97% ee. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.83 (t, $J_{H,H}$ = 6.8 Hz, 3H), 1.05–1.30 (m, 6H), 1.51–1.70 (m, 2H), 2.04 (s, 3H), 2.68 (dd, $J_{H,H}$ = 15.6 Hz, 7.3 Hz, 1H), 2.72 (dd, $J_{H,H}$ = 15.6 Hz, 7.2 Hz, 1H), 3.56 (quint, $J_{H,H}$ = 7.2 Hz, 1H), 3.82 (s, 3H), 6.85 (d, $J_{H,H}$ = 8.2 Hz, 1H), 6.90 (td,

$J_{H,H}$ = 7.4 Hz, 1.0 Hz, 1H), 7.12 (dd, $J_{H,H}$ = 7.6 Hz, 1.6 Hz, 1H), 7.16 (t, $J_{H,H}$ = 7.8 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 14.0, 22.5, 27.0, 30.1, 31.8, 34.8, 34.9, 49.9, 55.3, 110.7, 120.6, 127.1, 127.9, 132.5, 157.3, 208.6. The spectral data are in agreement with reported literature values.[27]



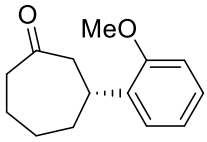

**3ad**

**Compound 3ad [869540-81-8]**. (77% yield, 94% ee (*R*), Table 2.2, entry 6). The crude product was subjected to silica gel chromatography to give **3ad** (31.5 mg, 0.15 mmol, 77% yield) as a colorless oil. The ee was measured by HPLC (Chiralpak IA column, 0.7 mL/min, hexane/2-propanol = 97/3, 230 nm, $t_{major}$ = 11.2 min (*R*), $t_{minor}$ = 10.7 min (*S*)); $[\alpha]^{25}_D$ +37.6 (*c* 1.31, $CHCl_3$) for 94% ee ($[\alpha]^{25}_D$ –36.3 (*c* 1.02, $CHCl_3$) was reported for (*S*)-3-(2-methoxyphenyl)- cyclohexanone (94% ee)).[28] **$^1$H NMR** (500 MHz, $CDCl_3$) δ 1.79 (qdd, $J_{H,H}$ = 12.5 Hz, 4.5 Hz, 3.2 Hz, 1H), 1.87 (qd, $J_{H,H}$ = 12.3 Hz, 2.9 Hz, 1H), 2.02 (br d, $J_{H,H}$ = 13.1 Hz, 1H), 2.13 (ddt, $J_{H,H}$ = 13.1 Hz, 6.4 Hz, 3.5 Hz, 1H), 2.38 (td, $J_{H,H}$ = 12.7 Hz, 6.2 Hz, 1H), 2.46 (br d, $J_{H,H}$ = 14.3 Hz, 1H), 2.50 (t, $J_{H,H}$ = 13.0 Hz, 1H), 2.58 (ddt, $J_{H,H}$ = 14.0 Hz, 4.4 Hz, 2.0 Hz, 1H), 3.42 (tt, $J_{H,H}$ = 11.8 Hz, 4.1 Hz, 1H), 3.82 (s, 3H), 6.87 (dd, $J_{H,H}$ = 8.2 Hz, 1.1 Hz, 1H), 6.94 (td, $J_{H,H}$ =7.6 Hz, 1.3 Hz, 1H), 7.18 (dd, $J_{H,H}$ = 7.6 Hz, 1.7 Hz, 1H), 7.22 (td, $J_{H,H}$ = 7.8 Hz, 1.8 Hz, 1H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 25.6, 31.0, 37.9, 41.4, 47.5, 55.2, 110.5, 120.6, 126.5, 127.5, 132.5, 156.7, 211.6. The spectral data are in agreement with reported literature values.[29]




**3ae**

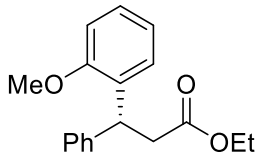
**Compound 3ae [155325-52-3]**. (76% yield, 96% ee (*R*), Table 2.2, entry 7). The crude product was subjected to silica gel chromatography to give **3ae** (28.9 mg, 0.15 mmol, 76% yield) as a colorless oil. The ee was measured by HPLC (Chiralpak IC column, 0.6 mL/min, hexane/2-propanol = 99/1, 230 nm, $t_{major}$ = 42.2 min (*R*), $t_{minor}$ = 44.8 min (*S*)); $[\alpha]^{25}_{D}$ +76.5 (*c* 1.43, $CHCl_3$) for 96% ee. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 2.00–2.10 (m, 1H), 2.25–2.49 (m, 4H), 2.64 (dd, $J_{H,H}$ = 18.3 Hz, 7.8 Hz, 1H), 3.69 (tt, $J_{H,H}$ = 10.2 Hz, 7.2 Hz, 1H), 3.84 (s, 3H), 6.89 (dd, $J_{H,H}$ = 8.2 Hz, 1.1 Hz, 1H), 6.94 (td, $J_{H,H}$ =7.5 Hz, 1.2 Hz, 1H), 7.18 (dd, $J_{H,H}$ = 7.5 Hz, 1.8 Hz, 1H), 7.24 (td, $J_{H,H}$ = 7.8 Hz, 1.7 Hz, 1H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 29.1, 36.8, 38.7, 44.6, 55.2, 110.5, 120.6, 126.6, 127.7, 131.2, 157.4, 219.4. The spectral data are in agreement with reported literature values.[30]




**3af**

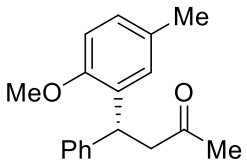
**Compound 3af**. (81% yield, 93% ee (*R*), Table 2.2, entry 9). The crude product was subjected to silica gel chromatography to give **3af** (35.3 mg, 0.16 mmol, 81% yield) as a colorless oil. The ee was measured by HPLC (Chiralpak IC column, 1.0 mL/min, hexane/2-propanol = 97/3, 254 nm, $t_{major}$ = 18.9 min (*R*), $t_{minor}$ = 17.3 min (*S*)); $[\alpha]^{25}_{D}$ +66.7 (*c* 1.09, $CHCl_3$) for 93% ee. **$^1$H NMR** (500 MHz, $CDCl_3$) δ

1.54 (q, $J_{H,H}$ = 13.1 Hz, 1H), 1.68 (qdt, $J_{H,H}$ = 12.2 Hz, 3.6 Hz, 2.0 Hz, 1H), 1.72 (q, $J_{H,H}$ = 12.5 Hz, 1H), 1.94–2.08 (m, 3H), 2.55–2.69 (m, 3H), 2.88 (dd, $J_{H,H}$ = 14.9 Hz, 11.2 Hz, 1H), 3.36 (tt, $J_{H,H}$ = 11.6 Hz, 2.4 Hz, 1H), 3.83 (s, 3H), 6.85 (dd, $J_{H,H}$ = 8.2 Hz, 1.1 Hz, 1H), 6.91 (td, $J_{H,H}$ =7.5 Hz, 1.4 Hz, 1H), 7.12 (dd, $J_{H,H}$ = 7.6 Hz, 1.8 Hz, 1H), 7.18 (t, $J_{H,H}$ = 7.8 Hz, 1H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 24.5, 29.7, 35.4, 37.5, 43.9, 50.2, 55.3, 110.5, 120.6, 126.5, 127.1, 135.1, 156.1, 214.2. **HRMS** (ESI) calcd for $C_{14}H_{18}NaO_2$ $[M+Na]^+$ 241.1199, found 241.1194.



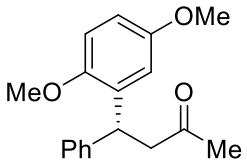

**3ag**

**Compound 3ag**. (87% yield, 97% ee (*R*), Table 2.2, entry 10). The crude product was subjected to silica gel chromatography to give **3ag** (49.4 mg, 0.17 mmol, 87% yield) as a colorless oil. The ee was measured by HPLC (Chiralpak IC column, 1.0 mL/min, hexane/2-propanol = 97/3, 230 nm, $t_{major}$ = 8.9 min (*R*), $t_{minor}$ = 7.3 min (*S*)); $[\alpha]^{25}_D$ +25.8 (*c* 1.06, $CHCl_3$) for 97% ee. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 1.10 (t, $J_{H,H}$ = 7.1 Hz, 3H), 3.02 (dd, $J_{H,H}$ = 15.4 Hz, 8.7 Hz, 1H), 3.06 (dd, $J_{H,H}$ = 15.4 Hz, 7.5 Hz, 1H), 3.79 (s, 3H), 4.03 (q, $J_{H,H}$ = 7.1 Hz, 2H), 4.94 (t, $J_{H,H}$ = 7.7 Hz, 1H), 6.84 (d, $J_{H,H}$ = 8.1 Hz, 1H), 6.90 (td, $J_{H,H}$ = 7.5 Hz, 1.1 Hz, 1H), 7.13–7.21 (m, 3H), 7.23–7.29 (m, 4H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 14.0, 39.7, 40.5, 55.4, 60.2, 110.8, 120.5, 126.1, 127.6, 127.8, 127.9, 128.2, 131.9, 143.3, 156.9, 172.1. **HRMS** (ESI) calcd for $C_{18}H_{20}NaO_3$ $[M+Na]^+$ 307.1305, found 307.1310.




**5ba**

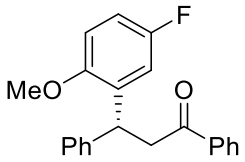
**Compound 5ba**. (90% yield, 99% ee (*R*), Table 2.3, entry 1). The crude product was subjected to silica gel chromatography to give **5ba** (48.2 mg, 0.18 mmol, 90% yield) as a pale orange oil. The ee was measured by HPLC (Chiralpak IC column, 0.7 mL/min, hexane/2-propanol = 97/3, 280 nm, $t_{major}$ = 16.2 min (*R*), $t_{minor}$ = 17.5 min (*S*)); $[\alpha]^{25}_{D}$ +12.1 (*c* 1.29, $CHCl_3$) for 99% ee. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 2.08 (s, 3H), 2.24 (s, 3H), 3.11 (dd, $J_{H,H}$ = 16.2 Hz, 7.2 Hz, 1H), 3.16 (dd, $J_{H,H}$ = 16.3 Hz, 8.4 Hz, 1H), 3.76 (s, 3H), 4.94 (t, $J_{H,H}$ = 7.6 Hz, 1H), 6.73 (d, $J_{H,H}$ = 8.2 Hz, 1H), 6.90 (d, $J_{H,H}$ = 2.2 Hz, 1H), 6.96 (d, $J_{H,H}$ = 8.3 Hz, 1H), 7.12–7.18 (m, 1H), 7.20–7.28 (m, 4H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 20.7, 30.1, 39.6, 48.9, 55.6, 110.9, 126.1, 127.8, 127.9, 128.3, 128.7, 129.6, 131.9, 143.5, 154.7, 207.4. **HRMS** (ESI) calcd for $C_{18}H_{20}NaO_2$ $[M+Na]^+$ 291.1356, found 291.1362.




**5ca**

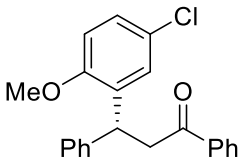
**Compound 5ca**. (92% yield, 98% ee (*R*), Table 2.3, entry 2). The crude product was subjected to silica gel chromatography to give **5ca** (52.3 mg, 0.18 mmol, 92% yield) as a pale yellow oil. The ee was measured by HPLC (Chiralpak IC column, 1.2 mL/min, hexane/2-propanol = 95/5, 230 nm, $t_{major}$ = 15.3 min (*R*), $t_{minor}$ = 19.8 min (*S*)); $[\alpha]^{25}_{D}$ +5.2 (*c* 0.92, $CHCl_3$) for 98% ee. **$^1$H NMR** (500 MHz, $CDCl_3$)

δ 2.10 (s, 3H), 3.14 (d, $J_{H,H}$ = 7.5 Hz, 2H), 3.72 (s, 3H), 3.74 (s, 3H), 4.96 (t, $J_{H,H}$ = 7.7 Hz, 1H), 6.69 (d, $J_{H,H}$ = 8.2 Hz, 1H), 6.70 (s, 1H), 6.77 (d, $J_{H,H}$ = 8.4 Hz, 1H), 7.14–7.20 (m, 1H), 7.22–7.28 (m, 4H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 30.2, 39.7, 48.9, 55.6, 56.1, 111.0, 111.9, 115.0, 126.2, 127.9, 128.3, 133.6, 143.2, 151.1, 153.6, 207.1. **HRMS** (ESI) calcd for $C_{18}H_{20}NaO_3$ $[M+Na]^+$ 307.1305, found 307.1311.



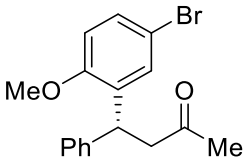

**5db**

**Compound 5db**. (83% yield, >99.5% ee (*R*), Table 2.3, entry 3). The crude product was subjected to silica gel chromatography to give **5db** (55.5 mg, 0.17 mmol, 83% yield) as a white solid. The ee was measured by HPLC (Chiralpak IE column, 0.7 mL/min, hexane/2-propanol = 99/1, 230 nm, $t_{major}$ = 28.0 min (*R*), $t_{minor}$ = 27.3 min (*S*)); $[\alpha]^{25}_D$ +22.5 (*c* 0.926, $CHCl_3$) for >99.5% ee. $^1$H NMR (500 MHz, $CDCl_3$) δ 3.67 (dd, $J_{H,H}$ = 17.1 Hz, 7.1 Hz, 1H), 3.70 (dd, $J_{H,H}$ = 17.1 Hz, 7.7 Hz, 1H), 3.75 (s, 3H), 5.16 (t, $J_{H,H}$ = 7.4 Hz, 1H), 6.74–6.79 (m, 1H), 6.82–6.88 (m, 2H), 7.15–7.22 (m, 1H), 7.25–7.30 (m, 4H), 7.45 (t, $J_{H,H}$ = 8.0 Hz, 2H), 7.55 (t, $J_{H,H}$ = 7.4 Hz, 1H), 7.95 (d, $J_{H,H}$ = 7.8 Hz, 2H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 39.6, 43.6, 56.0, 111.7 (d, $J_{C,}{}^{19}_F$ = 8.2 Hz), 113.1 (d, $J_{C,}{}^{19}_F$ = 22.6 Hz), 115.0 (d, $J_{C,}{}^{19}_F$ = 23.6 Hz), 126.4, 128.0, 128.1, 128.4, 128.6, 133.0, 134.5 (d, $J_{C,}{}^{19}_F$ = 6.4 Hz), 137.0, 142.9, 153.0 (d, $J_{C,}{}^{19}_F$ = 2.2 Hz), 157.1 (d, $J_{C,}{}^{19}_F$ = 236.1 Hz), 197.9. **HRMS** (ESI) calcd for $C_{22}H_{19}FNaO_2$ $[M+Na]^+$ 357.1261, found 357.1268.




**5eb**

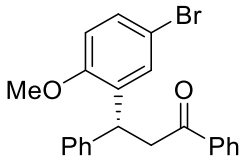
**Compound 5eb**. (86% yield, >99.5% ee (*R*), Table 2.3, entry 4). The crude product was subjected to silica gel chromatography to give **5eb** (60.3 mg, 0.17 mmol, 86% yield) as a pale yellow solid. The ee was measured by HPLC (Chiralpak IC column, 0.6 mL/min, hexane/2-propanol = 98/2, 230 nm, $t_{major}$ = 17.3 min (*R*), $t_{minor}$ = 18.7 min (*S*)); $[\alpha]^{25}_{D}$ –8.0 (*c* 0.94, $CHCl_3$) for >99.5% ee. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 3.64 (dd, $J_{H,H}$ = 17.0 Hz, 6.8 Hz, 1H), 3.70 (dd, $J_{H,H}$ = 17.0 Hz, 8.0 Hz, 1H), 3.74 (s, 3H), 5.14 (t, $J_{H,H}$ = 7.5 Hz, 1H), 6.74 (d, $J_{H,H}$ = 8.6 Hz, 1H), 7.08 (d, $J_{H,H}$ = 2.6 Hz, 1H), 7.11 (dd, $J_{H,H}$ = 8.7 Hz, 2.7 Hz, 1H), 7.14–7.19 (m, 1H), 7.23–7.28 (m, 4H), 7.43 (t, $J_{H,H}$ = 8.0 Hz, 2H), 7.50 (t, $J_{H,H}$ = 7.4 Hz, 1H), 7.93 (d, $J_{H,H}$ = 7.8 Hz, 2H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 39.5, 43.5, 55.7, 112.1, 125.5, 126.3, 127.1, 127.99, 128.03, 128.1, 128.4, 128.5, 133.0, 134.6, 137.0, 142.9, 155.5, 197.9. **HRMS** (ESI) calcd for $C_{22}H_{19}ClNaO_2$ $[M+Na]^+$ 373.0966, found 373.0973.




**5fa**

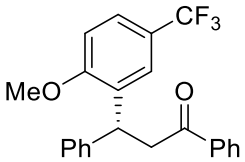
**Compound 5fa**. (85% yield, 98% ee (*R*), Table 2.3, entry 5). The crude product was subjected to silica gel chromatography to give **5fa** (56.5 mg, 0.17 mmol, 85% yield) as a pale yellow oil. The ee was measured by HPLC (Chiralpak IE column, 1.0 mL/min, hexane/2-propanol = 99/1, 230 nm, $t_{major}$ = 15.5 min (*R*), $t_{minor}$ = 14.7 min (*S*)); $[\alpha]^{25}_{D}$ –36.9 (*c* 1.34, $CHCl_3$) for 98% ee. **$^1$H NMR** (500 MHz,

$CDCl_3$) δ 2.10 (s, 3H), 3.09 (dd, $J_{H,H}$ = 16.6 Hz, 6.9 Hz, 1H), 3.16 (dd, $J_{H,H}$ = 16.6 Hz, 8.5 Hz, 1H), 3.77 (s, 3H), 4.94 (t, $J_{H,H}$ = 7.6 Hz, 1H), 6.71 (d, $J_{H,H}$ = 8.6 Hz, 1H), 7.16–7.30 (m, 7H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 30.3, 39.2, 48.5, 55.7, 112.6, 112.9, 126.4, 127.9, 128.4, 130.2, 130.6, 134.7, 142.6, 155.9, 206.6. **HRMS** (ESI) calcd for $C_{17}H_{17}BrNaO_2$ $[M+Na]^+$ 355.0304, found 355.0301.



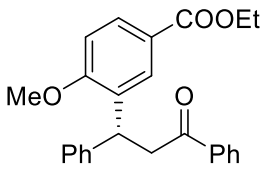

**5fb**

**Compound 5fb**. (84% yield, 99% ee (*R*), Table 2.3, entry 6). The crude product was subjected to silica gel chromatography to give **5fb** (66.3 mg, 0.17 mmol, 84% yield) as a pale orange solid. The ee was measured by HPLC (Chiralpak IE column, 0.6 mL/min, hexane/2-propanol = 99/1, 230 nm, $t_{major}$ = 35.1 min (*R*), $t_{minor}$ = 33.2 min (*S*)); $[\alpha]^{25}_D$ –11.6 (*c* 1.04, $CHCl_3$) for 99% ee. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 3.65 (dd, $J_{H,H}$ = 17.1 Hz, 6.7 Hz, 1H), 3.73 (dd, $J_{H,H}$ = 17.1 Hz, 8.0 Hz, 1H), 3.76 (s, 3H), 5.15 (t, $J_{H,H}$ = 7.4 Hz, 1H), 6.71 (d, $J_{H,H}$ = 8.6 Hz, 1H), 7.18 (t, $J_{H,H}$ = 8.8 Hz, 1H), 7.23 (d, $J_{H,H}$ = 2.6 Hz, 1H), 7.25–7.30 (m, 5H), 7.45 (t, $J_{H,H}$ = 7.7 Hz, 2H), 7.55 (t, $J_{H,H}$ = 7.1 Hz, 1H), 7.95 (d, $J_{H,H}$ = 7.4 Hz, 2H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 39.4, 43.5, 55.6, 112.5, 112.9, 126.3, 127.9, 128.0, 128.3, 128.5, 130.1, 130.8, 132.9, 135.0, 137.0, 142.8, 155.9, 197.8. **HRMS** (ESI) calcd for $C_{22}H_{19}BrNaO_2$ $[M+Na]^+$ 417.0461, found 417.0456.




**5gb**

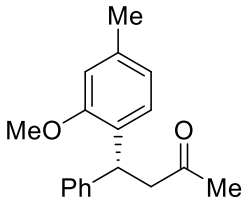
**Compound 5gb**. (90% yield, 99% ee (*R*), Table 2.3, entry 7). The crude product was subjected to silica gel chromatography to give **5gb** (69.3 mg, 0.18 mmol, 90% yield) as a pale yellow oil. The ee was measured by HPLC (Chiralpak IE column, 1.0 mL/min, hexane/2-propanol = 98/2, 254 nm, $t_{major}$ = 15.7 min (*R*), $t_{minor}$ = 14.7 min (*S*)); $[\alpha]^{25}_D$ –1.2 (*c* 1.26, $CHCl_3$) for 99% ee. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 3.69 (dd, $J_{H,H}$ = 17.0 Hz, 6.9 Hz, 1H), 3.76 (dd, $J_{H,H}$ = 17.1 Hz, 7.9 Hz, 1H), 3.82 (s, 3H), 5.21 (t, $J_{H,H}$ = 7.4 Hz, 1H), 6.89 (d, $J_{H,H}$ = 8.5 Hz, 1H), 7.27 (t, $J_{H,H}$ = 8.8 Hz, 1H), 7.25–7.30 (m, 4H), 7.40 (s, 1H), 7.45 (t, $J_{H,H}$ = 7.6 Hz, 2H), 7.47 (d, $J_{H,H}$ = 7.6 Hz, 1H), 7.55 (t, $J_{H,H}$ = 7.3 Hz, 1H), 7.94 (d, $J_{H,H}$ = 7.3 Hz, 2H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 39.5, 43.5, 55.7, 110.5, 122.6 (q, $J_{C,}{}^{19}_F$ = 32.3 Hz), 124.4 (q, $J_{C,}{}^{19}_F$ = 269.6 Hz), 124.9 (q, $J_{C,}{}^{19}_F$ = 3.7 Hz), 125.0 (q, $J_{C,}{}^{19}_F$ = 4.0 Hz), 126.4, 127.95, 128.01, 128.4, 128.6, 133.0, 133.3, 137.0, 142.7, 159.3, 197.9. **HRMS** (ESI) calcd for $C_{22}H_{19}F_3NaO_2$ $[M+Na]^+$ 407.1229, found 407.1234.



**5hb**

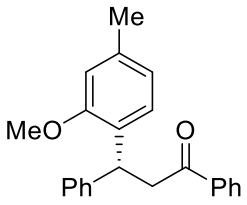
**Compound 5hb**. (87% yield, >99.5% ee (*R*), Table 2.3, entry 8). The crude product was subjected to silica gel chromatography to give **5hb** (67.5 mg, 0.18 mmol, 87% yield) as a pale yellow solid. The ee was measured by HPLC (Chiralpak ID column, 0.8 mL/min, hexane/2–propanol = 97/3, 254 nm, $t_{major}$ = 40.9 min (*R*), $t_{minor}$ = 45.8 min (*S*)); $[\alpha]^{25}_D$ –73.5 (*c* 1.14, $CHCl_3$) for >99.5% ee. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 1,34 (t, $J_{H,H}$ = 7.2 Hz, 3H), 3.75 (d, $J_{H,H}$ = 7.4 Hz, 2H), 3.83 (s, 3H), 4.31 (q, $J_{H,H}$ = 7.1 Hz, 2H), 5.19 (t, $J_{H,H}$ = 7.5 Hz, 1H), 6.84 (d, $J_{H,H}$ = 8.5 Hz, 1H), 7.16 (tt, $J_{H,H}$ = 7.2 Hz, 1.4 Hz, 1H), 7.25 (t, $J_{H,H}$ = 7.9 Hz, 2H), 7.29 (d, $J_{H,H}$ = 7.7 Hz,

2H), 7.44 (t, $J_{H,H}$ = 8.0 Hz, 2H), 7.54 (t, $J_{H,H}$ = 7.4 Hz, 1H), 7.90 (dd, $J_{H,H}$ = 8.5 Hz, 2.2 Hz, 1H), 7.93 (d, $J_{H,H}$ = 2.1 Hz, 1H), 7.95 (d, $J_{H,H}$ = 7.1 Hz, 2H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 14.3, 39.3, 43.7, 55.6, 60.6, 110.2, 122.6, 126.2, 127.97, 128.04, 128.3, 128.5, 129.2, 129.8, 132.5, 133.0, 137.1, 143.3, 160.6, 166.5, 198.1. **HRMS** (ESI) calcd for $C_{25}H_{24}NaO_4$ $[M+Na]^+$ 411.1567, found 411.1575.



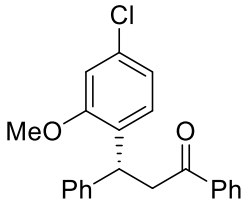
**6ia**

**Compound 6ia**. (89% yield, 99% ee (*R*), Table 2.3, entry 9). The crude product was subjected to silica gel chromatography to give 6ia (47.9 mg, 0.18 mmol, 89% yield) as a yellow oil. The ee was measured by HPLC (Chiralpak IE column, 0.6 mL/min, hexane/2-propanol = 99/1, 230 nm, $t_{major}$ = 33.0 min (*R*), $t_{minor}$ = 30.5 min (*S*)); $[\alpha]^{25}_D$ +29.4 (*c* 1.47, $CHCl_3$) for 99% ee. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 2.09 (s, 3H), 2.31 (s, 3H), 3.13 (d, $J_{H,H}$ = 7.7 Hz, 2H), 3.78 (s, 3H), 4.93 (t, $J_{H,H}$ = 7.8 Hz, 1H), 6.66 (s, 1H), 6.70 (d, $J_{H,H}$ = 7.7 Hz, 1H), 6.98 (d, $J_{H,H}$ = 7.7 Hz, 1H), 7.13–7.18 (m, 1H), 7.22–7.27 (m, 4H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 21.4, 30.1, 39.3, 49.0, 55.4, 111.8, 121.1, 126.1, 127.7, 127.9, 128.3, 129.2, 137.4, 143.6, 156.6, 207.5. **HRMS** (ESI) calcd for $C_{18}H_{20}NaO_4$ $[M+Na]^+$ 291.1356, found 291.1361.




**6ib**

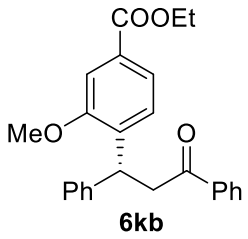
**Compound 6ib.** (97% yield, 99% ee (*R*), Table 2.3, entry 10). The crude product was subjected to silica gel chromatography to give **6ib** (64.1 mg, 0.19 mmol, 97% yield) as a yellow solid. The ee was measured by HPLC (Chiralpak IE column, 0.8 mL/min, hexane/2-propanol = 98/2, 230 nm, $t_{major}$ = 21.4 min (*R*), $t_{minor}$ = 20.1 min (*S*)); $[\alpha]^{25}_{D}$ +24.6 (*c* 1.19, $CHCl_3$) for 99% ee. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 2.31 (s, 3H), 3.70 (d, $J_{H,H}$ = 7.6 Hz, 2H), 3.75 (s, 3H), 5.13 (t, $J_{H,H}$ = 7.4 Hz, 1H), 6.67 (s, 1H), 6.69 (d, $J_{H,H}$ = 7.7 Hz, 1H), 7.00 (d, $J_{H,H}$ = 7.6 Hz, 1H), 7.15 (t, $J_{H,H}$ = 7.2 Hz, 1H), 7.25 (t, $J_{H,H}$ = 8.0 Hz, 2H), 7.28 (d, $J_{H,H}$ = 8.0 Hz, 2H), 7.43 (t, $J_{H,H}$ = 7.6 Hz, 2H), 7.54 (t, $J_{H,H}$ = 7.4 Hz, 1H), 7.95 (d, $J_{H,H}$ = 7.2 Hz, 2H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 21.3, 39.5, 43.8, 55.3, 111.8, 121.0, 125.0, 127.8, 127.99, 128.03, 128.2, 128.4, 129.6, 132.8, 137.1, 137.3, 143.8, 156.6, 198.4. **HRMS** (ESI) calcd for $C_{23}H_{22}NaO_2$ $[M+Na]^+$ 353.1512, found 353.1518.




**6jb**

**Compound 6jb.** (91% yield, 99% ee (*R*), Table 2.3, entry 11). The crude product was subjected to silica gel chromatography to give **6jb** (63.7 mg, 0.18 mmol, 91% yield) as a pale yellow oil. The ee was measured by HPLC (Chiralpak ID

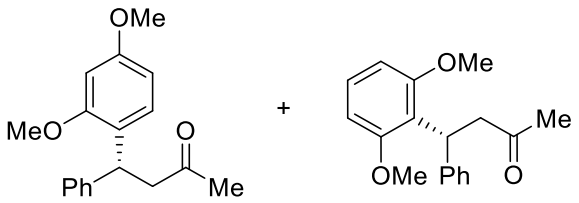
column, 0.6 mL/min, hexane/2-propanol = 98/2, 254 nm, $t_{major}$ = 20.0 min (*R*), $t_{minor}$ = 19.1 min (*S*)); $[\alpha]^{25}_D$ +11.6 (*c* 1.15, $CHCl_3$) for 99% ee. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 3.69 (d, $J_{H,H}$ = 7.4 Hz, 2H), 3.77 (s, 3H), 5.12 (t, $J_{H,H}$ = 7.5 Hz, 1H), 6.83 (s, 1H), 6.87 (d, $J_{H,H}$ = 8.1 Hz, 1H), 7.05 (d, $J_{H,H}$ = 8.2 Hz, 1H), 7.15–7.20 (m, 1H), 7.24–7.28 (m, 4H), 7.45 (t, $J_{H,H}$ = 7.8 Hz, 2H), 7.56 (t, $J_{H,H}$ = 7.3 Hz, 1H), 7.95 (d, $J_{H,H}$ = 7.4 Hz, 2H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 39.4, 43.5, 55.6, 111.6, 120.5, 126.3, 127.94, 127.95, 128.02, 128.3, 128.5, 128.9, 131.2, 133.0, 137.0, 143.1, 157.4, 198.0. **HRMS** (ESI) calcd for $C_{22}H_{19}ClNaO_2$ $[M+Na]^+$ 373.0966, found 373.0972.




**6kb**

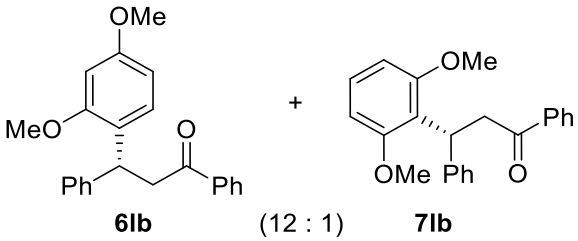
**Compound 6kb.** (87% yield, 99% ee (*R*), Table 2.3, entry 12). The crude product was subjected to silica gel chromatography to give **6kb** (67.4 mg, 0.17 mmol, 87% yield) as a pale-yellow solid. The ee was measured by HPLC (Chiralpak IC column, 1.0 mL/min, hexane/2-propanol = 97/3, 254 nm, $t_{major}$ = 35.0 min (*R*), $t_{minor}$ = 28.7 min (*S*)); $[\alpha]^{25}_D$ –9.3 (*c* 0.910, $CHCl_3$) for 99% ee. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 1.37 (t, $J_{H,H}$ = 7.2 Hz, 3H), 3.72 (dd, $J_{H,H}$ = 17.1 Hz, 7.7 Hz, 1H), 3.75 (dd, $J_{H,H}$ = 17.1 Hz, 7.1 Hz, 1H), 3.83 (s, 3H), 4.36 (q, $J_{H,H}$ = 7.2 Hz, 2H), 5.22 (t, $J_{H,H}$ = 7.4 Hz, 1H), 7.15–7.19 (m, 1H), 7.21 (d, $J_{H,H}$ = 7.7 Hz, 1H), 7.24–7.28 (m, 4H), 7.44 (t, $J_{H,H}$ = 8.1 Hz, 2H), 7.52 (d, $J_{H,H}$ = 1.7 Hz, 1H), 7.54 (tt, $J_{H,H}$ = 7.4 Hz, 1,9 Hz, 1H), 7.59 (dd, $J_{H,H}$ = 8.0 Hz, 1,6 Hz, 1H), 7.95 (d, $J_{H,H}$ = 7.0 Hz, 2H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 14.3, 39.8, 43.4, 55.6, 60.9, 111.5, 122.0, 126.3, 127.8, 127.98,

128.00. 128.3, 128.5, 129.8, 133.0, 137.0, 137.8, 142.9, 156.7, 166.4, 197.9. **HRMS** (ESI) calcd for $C_{25}H_{24}NaO_4$ $[M+Na]^+$ 411.1567, found 411.1574.



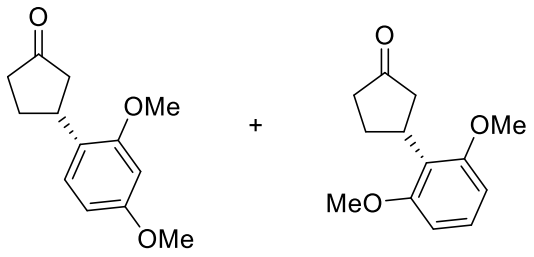

**6la** (7 : 1) **7la**

**Compounds 6la and 7la (7:1).** (92% yield, 99% ee (*R*), Table 2.3, entry 13). The crude product was subjected to silica gel chromatography to give the mixture (52.3 mg, 0.18 mmol, 92% yield) as a yellow oil. The ee for **compound 6la** was measured by HPLC (Chiralpak IE column, 1.0 mL/min, hexane/2-propanol = 95/5, 230 nm, $t_{major}$ = 13.7 min (*R*), $t_{minor}$ = 13.0 min (*S*) (**7la** $t_{major}$ = 11.5 min (*R*), $t_{minor}$ = 11.3 min (*S*)); $[\alpha]^{25}_D$ +28.7 (*c* 0.942, $CHCl_3$) for this mixture. **$^1$H NMR** (500 MHz, $CDCl_3$) for **compound 6la** δ 2.08 (s, 3H), 3.11 (d, $J_{H,H}$ = 7.8 Hz, 2H), 3.77 (s, 6H), 4.88 (t, $J_{H,H}$ = 7.7 Hz, 1H), 6.41 (d, $J_{H,H}$ = 8.1 Hz, 1H), 6.43 (s, 1H), 7.00 (d, $J_{H,H}$ = 8.1 Hz, 1H), 7.10–7.18 (m, 1H), 7.20–7.30 (m, 4H); **$^1$H NMR** (500 MHz, $CDCl_3$) for **compound 7la** δ 2.09 (s, 3H), 3.32 (dd, $J_{H,H}$ = 16.3, 7.7 Hz, 1H), 3.40 (dd, $J_{H,H}$ = 16.3, 7.7 Hz, 1H), 3.80 (s, 6H), 5.29 (t, $J_{H,H}$ = 7.7 Hz, 1H), 6.53 (d, $J_{H,H}$ = 8.3 Hz, 2H), 7.10–7.18 (m, 2H), 7.20–7.30 (m, 4H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) for **compound 6la** δ 30.2, 39.2, 49.1, 55.3, 55.4, 98.9, 104.1, 124.7, 126.1, 127.8, 128.29, 128.32, 143.8, 157.7, 159.4, 207.6, (**7la** δ 55.7). **HRMS** (ESI) calcd for $C_{18}H_{20}NaO_3$ $[M+Na]^+$ 307.1305, found 307.1309.



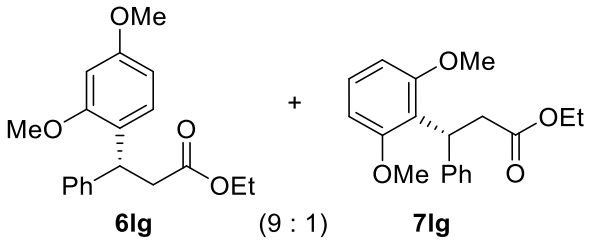

**6lb** (12 : 1) **7lb**

**Compounds 6lb and 7lb (12:1).** (94% yield, >99.5% ee (*R*), Table 2.3, entry 14). The crude product was subjected to silica gel chromatography to give the mixture (65.1 mg, 0.19 mmol, 94% yield) as a yellow oil. The ee for **Compound 6lb** was measured by HPLC (Chiralpak IE column, 0.5 mL/min, hexane/2-propanol = 98/2, 230 nm, $t_{major}$ = 57.7 min (*R*), $t_{minor}$ = 54.6 min (*S*) (**7lb** $t_{major}$ = 61.9 min (*R*), $t_{minor}$ = 64.6 min (*S*)); $[\alpha]^{25}_{D}$ +21.4 (*c* 1.24, $CHCl_3$) for this mixture. **$^1$H NMR** (500 MHz, $CDCl_3$) for **compound 6lb** δ 3.70 (d, $J_{H,H}$ = 7.5 Hz, 2H), 3.75 (s, 3H), 3.77 (s, 3H), 5.10 (t, $J_{H,H}$ = 7.5 Hz, 1H), 6.42 (dd, $J_{H,H}$ = 8.4 Hz, 2.5 Hz, 1H), 6.44 (d, $J_{H,H}$ = 2.5 Hz, 1H), 7.03 (d, $J_{H,H}$ = 8.3 Hz, 1H), 7.10–7.18 (m, 1H), 7.20–7.30 (m, 4H), 7.44 (t, $J_{H,H}$ = 7.5 Hz, 2H), 7.55 (t, $J_{H,H}$ = 7.4 Hz, 1H), 7.97 (d, $J_{H,H}$ = 7.1 Hz, 2H); **$^1$H NMR** (500 MHz, $CDCl_3$) for **compound 7lb** δ 3.70 (d, $J_{H,H}$ = 7.5 Hz, 2H), 3.73 (s, 6H), 5.51 (t, $J_{H,H}$ = 7.5 Hz, 1H), 6.53 (d, $J_{H,H}$ = 8.3 Hz, 2H), 7.08–7.18 (m, 2H), 7.20–7.30 (m, 4H), 7.44 (t, $J_{H,H}$ = 7.5 Hz, 2H), 7.55 (t, $J_{H,H}$ = 7.4 Hz, 1H), 7.97 (d, $J_{H,H}$ = 7.1 Hz, 2H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) for **compound 6lb** δ 38.4, 42.8, 54.2, 54.3, 97.8, 103.0, 124.1, 125.0, 126.95, 127.03, 127.2, 127.4, 127.5, 131.8, 136.1, 142.9, 156.7, 158.3, 197.5, (**7lb** δ 54.7). **HRMS** (ESI) calcd for $C_{23}H_{22}NaO_3$ $[M+Na]^+$ 369.1461, found 369.1465.



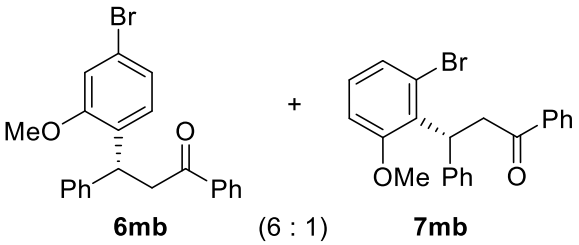

**6le** (11:1) **7le**

**Compounds 6le and 7le (11:1).** (77% yield, 96% ee (*R*), Table 2.3, entry 15). The crude product was subjected to silica gel chromatography to give the mixture (34.0 mg, 0.15 mmol, 77% yield) as a pale yellow oil. The ee for **Compound 6le** was measured by HPLC (Chiralpak IB column, 1.0 mL/min, hexane/2-propanol = 98/2, 280 nm, $t_{major}$ = 17.5 min (*R*), $t_{minor}$ = 19.9 min (*S*) (**7le** $t_{major}$ = 14.7 min (*R*), $t_{minor}$ = 16.3 min (*S*)). $[\alpha]^{25}_{D}$ +64.5 (*c* 1.56, $CHCl_3$) for this mixture. **$^1$H NMR** (400 MHz, $CDCl_3$) for **compound 6le** δ 1.95–2.10 (m, 1H), 2.20–2.50 (m, 4H), 2.60 (dd, $J_{H,H}$ = 18.2 Hz, 7.6 Hz, 1H), 3.59 (tt, $J_{H,H}$ = 10.0 Hz, 7.2 Hz, 1H), 3.80 (s, 3H), 3.81 (s, 3H), 6.46 (d, $J_{H,H}$ = 7.6 Hz, 1H), 6.47 (s, 1H), 7.06 (d, $J_{H,H}$ = 8.0 Hz, 1H), (**7le** δ 3.76 (s, 6H), 6.56 (d, $J_{H,H}$ = 7.3 Hz, 2H), 7.16 (t, $J_{H,H}$ = 8.2 Hz, 1H)); **$^{13}$C NMR** (100 MHz, $CDCl_3$) for **compound 6le** δ 28.3, 35.4, 37.7, 43.7, 54.2, 54.4, 97.8, 102.8, 122.6, 126.0, 157.4, 158.5, 218.7, (**7le** δ 54.0). **HRMS** (ESI) calcd for $C_{19}H_{22}NaO_4$ $[M+Na]^+$ 243.0997, found 243.0995.



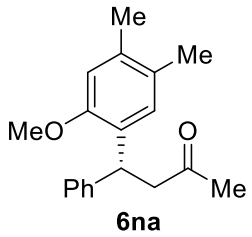

**6lg** (9 : 1) **7lg**

**Compounds 6lg and 7lg (9:1).** (92% yield, 98% ee (*R*), Table 2.3, entry 16). The crude product was subjected to silica gel chromatography to give the mixture (57.8 mg, 0.18 mmol, 92% yield) as a pale yellow oil. The ee for **Compound 6lg** was measured by HPLC (Chiralpak IE column, 0.7 mL/min, hexane/2-propanol = 98.5/1.5, 230 nm, $t_{major}$ = 34.0 min (*R*), $t_{minor}$ = 32.0 min (*S*) (**7lg** $t_{major}$ = 25.8 min (*R*), $t_{minor}$ = 24.7 min (*S*)). $[\alpha]^{25}_{D}$ +17.6 (*c* 0.936, $CHCl_3$) for this mixture. **$^1$H NMR** (400 MHz, $CDCl_3$) for **compound 6lg** δ 1.09 (t, $J_{H,H}$ = 7.1 Hz, 3H), 2.97 (dd, $J_{H,H}$ = 15.3 Hz, 8.6 Hz, 1H), 3.03 (dd, $J_{H,H}$ = 15.3 Hz, 7.6 Hz, 1H), 3.74 (s, 3H), 3.76 (s, 3H), 4.01 (q, $J_{H,H}$ = 7.1 Hz, 2H), 4.84 (t, $J_{H,H}$ = 8.0 Hz, 1H), 6.38–6.44 (m, 1H), 6.40 (s, 1H), 7.04 (d, $J_{H,H}$ = 8.7 Hz, 1H), 7.10–7.25 (m, 5H); **$^1$H NMR** (400 MHz, $CDCl_3$) for **compound 7lg** δ 1.09 (t, $J_{H,H}$ = 7.1 Hz, 3H), 3.19 (dd, $J_{H,H}$ = 15.5 Hz, 7.8 Hz, 1H), 3.31 (dd, $J_{H,H}$ = 15.5 Hz, 8.1 Hz, 1H), 3.76 (s, 6H), 4.01 (q, $J_{H,H}$ = 7.1 Hz, 2H), 5.26 (t, $J_{H,H}$ = 8.0 Hz, 1H), 6.51 (d, $J_{H,H}$ = 8.3 Hz, 2H), 7.10–7.25 (m, 5H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) for **compound 6lg** δ 14.0, 39.8, 40.0, 55.2, 55.4, 60.2, 98.8, 103.9, 124.5, 126.0, 127.8, 128.1, 128.2, 143.6, 157.8, 159.4, 172.1, (**7lg** δ 55.7, 127.7, 104.5). **HRMS** (ESI) calcd for $C_{19}H_{22}NaO_4$ $[M+Na]^+$ 337.1416, found 337.1414.



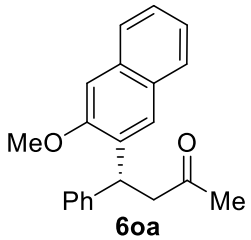

**6mb** (6 : 1) **7mb**

**Compounds 6mb and 7mb (6:1).** (86% yield, >99.5% ee (*R*), Table 2.3, entry 17). The crude product was subjected to silica gel chromatography to give the mixture (67.9 mg, 0.19 mmol, 86% yield) as a pale yellow oil. The ee for **Compound 6mb** was measured by HPLC (Chiralpak ID column, 0.8 mL/min, hexane/2-propanol = 97/3, 230 nm, $t_{major}$ = 14.7 min (*R*), $t_{minor}$ = 13.3 min (*S*) (**7mb** $t_{major}$ = 29.2 min (*R*), $t_{minor}$ = 28.6 min (*S*)); $[\alpha]^{25}_{D}$ +9.49 (*c* 1.09, $CHCl_3$) for this mixture. **$^1$H NMR** (500 MHz, $CDCl_3$) for **compound 6mb** δ 3.69 (d, $J_{H,H}$ = 7.4 Hz, 2H), 3.76 (s, 3H), 5.11 (t, $J_{H,H}$ = 7.4 Hz, 1H), 6.96 (d, $J_{H,H}$ = 1.6 Hz, 1H), 6.98 (d, $J_{H,H}$ = 8.2 Hz, 1H), 7.01 (dd, $J_{H,H}$ = 8.3 Hz, 1.5 Hz, 1H), 7.15–7.22 (m, 1H), 7.25–7.30 (m, 4H), 7.44 (t, $J_{H,H}$ = 7.7 Hz, 2H), 7.56 (t, $J_{H,H}$ = 7.2 Hz, 1H), 7.95 (d, $J_{H,H}$ = 7.4 Hz, 2H); **$^1$H NMR** (500 MHz, $CDCl_3$) for **compound 7mb** δ 3.72 (d, $J_{H,H}$ = 7.4 Hz, 2H), 3.77 (s, 3H), 5.19 (t, $J_{H,H}$ = 7.4 Hz, 1H), 6.85 (d, $J_{H,H}$ = 8.1 Hz, 1H), 6.88 (t, $J_{H,H}$ = 7.5 Hz, 1H), 7.12 (d, $J_{H,H}$ = 7.6 Hz, 1H), 7.15–7.22 (m, 1H), 7.25–7.30 (m, 4H), 7.44 (t, $J_{H,H}$ = 7.7 Hz, 2H), 7.56 (t, $J_{H,H}$ = 7.2 Hz, 1H), 7.95 (d, $J_{H,H}$ = 7.4 Hz, 2H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) for **compound 6mb** δ 39.4, 43.4, 55.6, 114.4, 120.6, 123.4, 126.2, 127.9, 128.0, 128.3, 128.5, 129.2, 131.7, 132.9, 137.0, 143.0, 157.5, 197.9, (**7mb** δ 55.5). **HRMS** (ESI) calcd for $C_{22}H_{19}BrNaO_3$ $[M+Na]^+$ 417.0461, found 417.0469.




**6na**

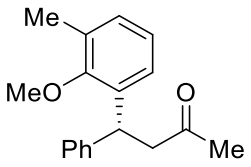
**Compound 6na.** (91% yield, 99% ee (*R*), Table 2.3, entry 18). The crude product was subjected to silica gel chromatography to give **6na** (51.5 mg, 0.18 mmol, 91% yield) as a pale yellow oil. The ee was measured by HPLC (Chiralpak IE column, 1.0 mL/min, hexane/2-propanol = 99/1, 230 nm, $t_{major}$ = 16.8 min (*R*), $t_{minor}$ = 16.0 min (*S*)); $[\alpha]^{25}_{D}$ +12.1 (*c* 0.901, $CHCl_3$) for 99% ee. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 2.10 (s, 3H), 2.15 (s, 3H), 2.22 (s, 3H), 3.11 (dd, $J_{H,H}$ = 16.2 Hz, 7.3 Hz, 1H), 3.16 (dd, $J_{H,H}$ = 16.2 Hz, 8.2 Hz, 1H), 3.77 (s, 3H), 4.92 (t, $J_{H,H}$ = 7.9 Hz, 1H), 6.65 (s, 1H), 6.85 (s, 1H), 7.14–7.17 (m, 1H), 7.24–7.28 (m, 4H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 18.9, 19.8, 30.1, 39.3, 49.0, 55.6, 112.7, 126.0, 127.8, 128.1, 128.2, 129.2, 129.3, 135.5, 143.7, 154.7, 207.5. **HRMS** (ESI) calcd for $C_{19}H_{22}NaO_2$ $[M+Na]^+$ 305.1512, found 305.1514.




**6oa**

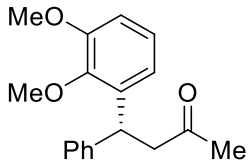
**Compound 6oa.** (80% yield, 98% ee (*R*), Table 2.3, entry 19). The crude product was subjected to silica gel chromatography to give **6oa** (48.7 mg, 0.16 mmol, 80% yield) as a pale yellow oil. The ee was measured by HPLC (Chiralpak IB column, 1.0 mL/min, hexane/2-propanol = 97/3, 230 nm, $t_{major}$ = 14.6 min (*R*), $t_{minor}$

= 17.7 min (*S*)); $[\alpha]^{25}_{D}$ –91.1 (*c* 0.921, $CHCl_3$) for 98% ee. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 2.12 (s, 3H), 3.21 (dd, $J_{H,H}$ = 16.3 Hz, 7.4 Hz, 1H), 3.26 (dd, $J_{H,H}$ = 16.2 Hz, 8.0 Hz, 1H), 3.89 (s, 3H), 5.09 (t, $J_{H,H}$ = 7.6 Hz, 1H), 7.09 (s, 1H), 7.18 (t, $J_{H,H}$ = 6.7 Hz, 1H), 7.25–7.33 (m, 5H), 7.39 (t, $J_{H,H}$ = 7.6 Hz, 1H), 7.53 (s, 1H), 7.69 (d, $J_{H,H}$ = 7.9 Hz, 1H), 7.70 (d, $J_{H,H}$ = 8.0 Hz, 1H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 30.3, 40.0, 49.1, 55.4, 105.5, 123.7, 125.9, 126.18, 126.23, 126.8, 127.4, 128.1, 128.3, 128.6, 133.4, 133.9, 143.2, 155.7, 207.1 **HRMS** (ESI) calcd for $C_{21}H_{20}NaO_2$ $[M+Na]^+$ 327.1356, found 327.1358.



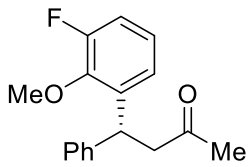

**8pa**

**Compound 8pa**. (72% yield, 99% ee (*R*), Table 2.3, entry 20). The crude product was subjected to silica gel chromatography to give 8pa (38.6 mg, 0.14 mmol, 72% yield) as a pale yellow oil. The ee was measured by HPLC (Chiralpak ID column, 0.8 mL/min, hexane/2-propanol = 98/2, 230 nm, $t_{major}$ = 8.1 min (*R*), $t_{minor}$ = 8.8 min (*S*)); $[\alpha]^{25}_{D}$ +23.5 (*c* 0.994, $CHCl_3$) for 99% ee. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 2.09 (s, 3H), 2.28 (s, 3H), 3.14 (d, $J_{H,H}$ = 7.7 Hz, 2H), 3.63 (s, 3H), 4.98 (t, $J_{H,H}$ = 7.7 Hz, 1H), 6.98 (t, $J_{H,H}$ = 7.5, 1H), 7.04 (d, $J_{H,H}$ = 7.4 Hz, 1H), 7.05 (d, $J_{H,H}$ = 7.5 Hz, 1H), 7.13–7.18 (m, 1H), 7.22–7.28 (m, 4H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 16.4, 30.4, 39.5, 49.7, 60.4, 123.9, 125.5, 126.2, 127.8, 128.4, 129.8, 131.4, 136.6, 143.9, 156.4, 206.9. **HRMS** (ESI) calcd for $C_{18}H_{20}NaO_2$ $[M+Na]^+$ 291.1356, found 291.1361.




**8qa**

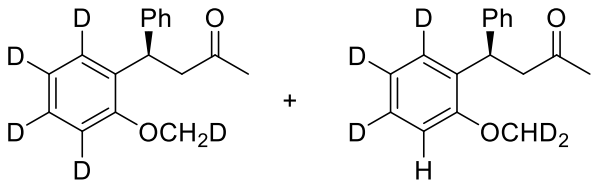
**Compound 8qa.** (78% yield, 97% ee (*R*), Table 2.3, entry 21). The crude product was subjected to silica gel chromatography to give **8qa** (44.4 mg, 0.16 mmol, 78% yield) as a pale yellow oil. The ee was measured by HPLC (Chiralpak IC column, 0.8 mL/min, hexane/2-propanol = 95/5, 230 nm, $t_{major}$ = 27.2 min (*R*), $t_{minor}$ = 23.9 min (*S*)); $[\alpha]^{25}_{D}$ +40.2 (*c* 1.01, $CHCl_3$) for 97% ee. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 2.10 (s, 3H), 3.16 (d, $J_{H,H}$ = 7.7 Hz, 2H), 3.67 (s, 3H), 3.83 (s, 3H), 4.98 (t, $J_{H,H}$ = 7.7 Hz, 1H), 6.76 (d, $J_{H,H}$ = 8.2 Hz, 1H), 6.80 (d, $J_{H,H}$ = 8.1 Hz, 1H), 7.00 (t, $J_{H,H}$ = 7.9 Hz, 1H), 7.12–7.18 (m, 1H), 7.22–7.28 (m, 4H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 30.3, 39.7, 49.1, 55.6, 60.3, 110.8, 119.7, 123.8, 126.2, 127.8, 128.3, 137.6, 143.7, 146.7, 152.9, 207.0. **HRMS** (ESI) calcd for $C_{18}H_{20}NaO_2$ $[M+Na]^+$ 307.1305, found 307.1309.



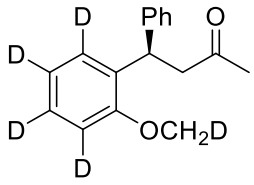

**8ra**

**Compound 8ra.** (74 % yield, 97% ee (*R*), Table 2.3, entry 22). The crude product was subjected to silica gel chromatography to give **8ra** (40.4 mg, 0.15 mmol, 74% yield) as a pale yellow oil. The ee was measured by HPLC (Chiralpak IC column, 0.7 mL/min, hexane/2-propanol = 99/1, 230 nm, $t_{major}$ = 23.7 min (*R*), $t_{minor}$ = 22.4 min (*S*)); $[\alpha]^{25}_{D}$ +10.7 (*c* 0.935, $CHCl_3$) for 97% ee. **$^1$H NMR** (500 MHz,

$CDCl_3$) δ 2.10 (s, 3H), 3.17 (d, $J_{H,H}$ = 7.7 Hz, 2H), 3.74 (s, 3H), 4.95 (t, $J_{H,H}$ = 7.7 Hz, 1H), 6.91–6.98 (m, 3H), 7.17 (t, $J_{H,H}$ = 7.1 Hz, 1H), 7.22 (d, $J_{H,H}$ = 6.8 Hz, 2H), 7.26 (t, $J_{H,H}$ = 7.0 Hz, 2H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 30.3, 39.7, 48.8, 61.0 115.1 (d, $J_{C,}{}^{19}{}_F$ = 19.2 Hz), 122.9 (d, $J_{C,}{}^{19}{}_F$ = 3.1 Hz), 123.4 (d, $J_{C,}{}^{19}{}_F$ = 7.8 Hz), 126.4, 127.7, 128.4, 138.5 (d, $J_{C,}{}^{19}{}_F$ = 2.1 Hz), 143.3, 145.3 (d, $J_{C,}{}^{19}{}_F$ = 10.3 Hz), 155.8 (d, $J_{C,}{}^{19}{}_F$ = 245.8 Hz), 206.6. **HRMS** (ESI) calcd for $C_{17}H_{17}FNaO_2$ $[M+Na]^+$ 295.1105, found 295.1109.

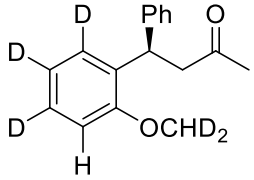



**Compound 3aa-*d*$_5$.** (82%, Scheme 2.6). The crude product was subjected to silica gel chromatography to give **3aa-*d*$_5$** (43.2 mg, 0.16 mmol, 82% yield) as a colorless oil. The ratio is determined by $^1$H and $^2$H NMR. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 2.07 (s, 3H), 3.14 (dd, $J_{H,H}$ = 16.5 Hz, 7.3 Hz, 1H), 3.17 (dd, $J_{H,H}$ = 16.3 Hz, 8.1 Hz, 1H), 3.70–3.80 (m, 1.75H), 4.99 (t, $J_{H,H}$ = 7.6 Hz, 1H), 6.85 (s, 0.25H), 7.14–7.21 (m, 1H), 7.23–7.29 (m, 4H); **$^2$H NMR** (77 MHz, acetone) δ 3.79 (br s, 1.2H), 6.5–7.5 (m, 3.8H); **HRMS** (ESI) calcd for $C_{17}H_{13}D_5NaO_2$ $[M+Na]^+$ 286.1513, found 286.1516.



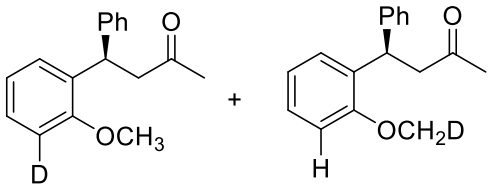

**3aa-*d*$_5$ (9)**

**Compound 3aa-*d*$_5$ (9). $^{13}$C NMR** (125 MHz, $CDCl_3$) δ 30.1, 39.6, 48.9, 55.1 (t, $J_{C,^2H}$ = 21.9 Hz), 110.5 (t, $J_{C,^2H}$ = 23.4 Hz), 120.0 (t, $J_{C,^2H}$ = 24.6 Hz), 126.1, 127.0 (t, $J_{C,^2H}$ = 24.2 Hz), 127.5 (t, $J_{C,^2H}$ = 23.5 Hz), 127.9, 128.2, 132.2, 143.5, 156.6, 207.1.




**3aa-*d*$_5$ (10)**

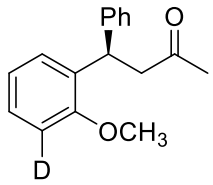
**Compound 3aa-*d*$_5$ (10).$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 30.1, 39.6, 48.9, 54.8 (quint, $J_{C,^2H}$ = 21.7 Hz), 110.8, 120.0 (t, $J_{C,^2H}$ = 24.6 Hz), 126.1, 127.0 (t, $J_{C,^2H}$ = 24.2 Hz), 127.5 (t, $J_{C,^2H}$ = 23.5 Hz), 127.9, 128.2, 132.2, 143.5, 156.6, 207.1.




**3aa-*d*$_1$ (11)** (1.1 : 1) **3aa-*d*$_1$ (12)**

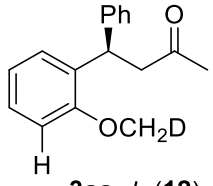
**Compound 3aa-*d*$_1$.** (87%, Scheme 2.6). The crude product was subjected to silica gel chromatography to give **3aa-*d*$_1$** (44.4 mg, 0.17 mmol, 87% yield) as a colorless oil. The ratio is determined by $^1$H and $^2$H NMR. **$^1$H NMR** (500 MHz, acetone-$d_6$) δ 2.06 (s, 3H), 3.17 (dd, $J_{H,H}$ = 16.5 Hz, 7.3 Hz, 1H), 3.20 (dd, $J_{H,H}$ =

16.3 Hz, 8.1 Hz, 1H), 3.78 (t, $J_{H,H}$ = 1.5 Hz, 0.98H), 3.80 (s, 1.68H), 4.97 (t, $J_{H,H}$ = 7.6 Hz, 1H), 6.88 (t, $J_{H,H}$ = 7.5 Hz, 1H), 6.92 (d, $J_{H,H}$ = 8.2 Hz, 0.46H), 7.08–7.14 (m, 2H), 7.16–7.22 (m, 3H), 7.28 (d, $J_{H,H}$ = 7.9 Hz, 2H); **$^2$H NMR** (77 MHz, acetone) δ 3.79 (s, 0.47H), 6.95 (s, 0.53H); **HRMS** (ESI) calcd for $C_{17}H_{17}D_1NaO_2$ $[M+Na]^+$ 278.1262, found 278.1260.



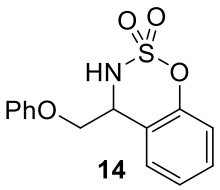

**3aa-*d*$_1$ (11)**

**Compound 3aa-*d*$_1$ (11). $^{13}$C NMR** (75 MHz, $CDCl_3$) δ 30.1, 39.5, 48.9, 55.4, 110.6 (t, $J_{C,^2H}$ = 23.8 Hz), 120.5, 126.1, 127.5, 127.8, 127.9, 128.2, 132.2, 143.5, 156.7, 207.2.




**3aa-*d*$_1$ (12)**

**Compound 3aa-*d*$_1$ (12).$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 30.1, 39.5, 48.9, 55.1 (t, $J_{C,^2H}$ = 21.9 Hz), 110.8, 120.5, 126.1, 127.4, 127.8, 127.9, 128.2, 132.2, 143.5, 156.7, 207.2.




**14**

**Compound 14. $^{1}$H NMR** (500 MHz, acetone-$d_6$) δ 4.00 (dd, $J_{H,H}$ = 10.0 Hz, 8.3 Hz, 1H), 4.22 (dd, $J_{H,H}$ = 10.0 Hz, 3.1 Hz, 1H), 5.03 (d, $J_{H,H}$ = 4.1 Hz, 1H), 5.39 (dt, $J_{H,H}$ = 8.2 Hz, 3.4 Hz, 1H), 6.86 (d, $J_{H,H}$ = 7.6 Hz, 1H), 6.87 (t, $J_{H,H}$ = 7.7 Hz, 1H), 6.91 (tt, $J_{H,H}$ = 7.4 Hz, 1.0 Hz, 1H), 6.98 (d, $J_{H,H}$ = 7.8 Hz, 2H), 7.13 (td, $J_{H,H}$ = 7.7 Hz, 1.7 Hz, 1H), 7.26 (t, $J_{H,H}$ = 8.1 Hz, 1.0 Hz, 2H), 7.43 (d, $J_{H,H}$ = 7.3 Hz, 1H); **$^{13}$C NMR** (500 MHz, $CDCl_3$) δ 70.3, 73.2, 113.7, 116.6, 119.1, 120.7, 121.1, 126.7, 128.66, 128.71, 155.2, 157.0. **HRMS** (ESI) calcd for $C_{14}H_{12}NO_4S$ $[M+H]^+$ 290.0493, found 290.0494.

### 2.4.5 Single crystal X-ray diffraction data for 5fb

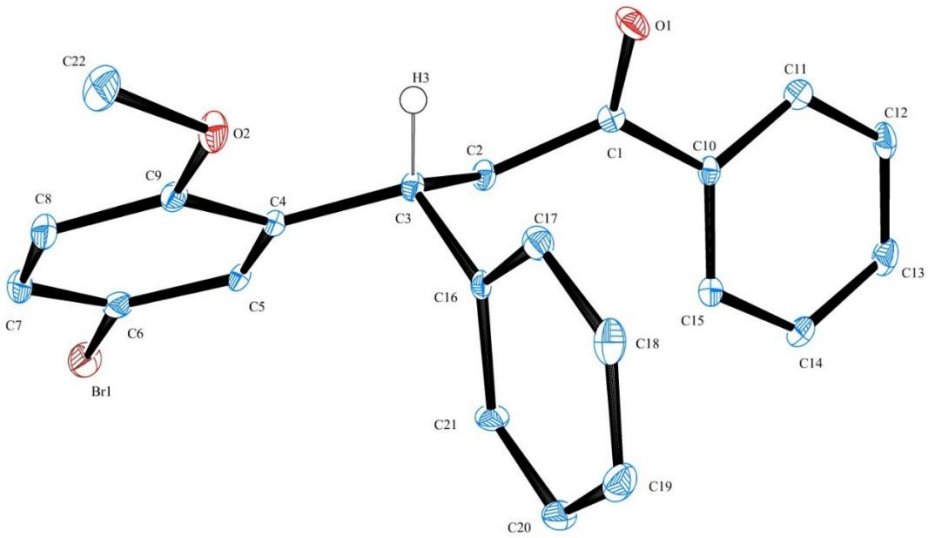



Figure 2.6.1. ORTEP illustration of compound **5fb.**

**Table 2.4. Crystal Data and Structure Refinement for Compound 5fb**

| | | |
|---|---|---|
| Empirical formula | $C_{22}H_{19}BrO_2$ | |
| Formula weight | 395.28 g/mol | |
| Temperature | 100(2) K | |
| Wavelength | 1.54178 Å | |
| Crystal size | 0.086 × 0.146 × 0.376 mm | |
| Crystal habit | clear pale yellow plate | |
| Crystal system | Monoclinic | |
| Space group | P 1 2(1) 1 | |
| Unit cell dimensions | a = 11.8971(6) Å | α = 90° |
| | b = 5.9845(3) Å | β = 95.961(2)° |
| | c = 12.3079(7) Å | γ = 90° |
| Volume | 871.56(8) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.506 $g/cm^3$ | |
| Absorption coefficient | 3.304 $mm^{-1}$ | |
| F(000) | 404 | |
| Theta range for data collection | 3.61 to 72.43° | |

| | |
|---|---|
| Index ranges | –14<=h<=14, –7<=k<=7, –15<=l<=15 |
| Reflections collected | 13071 |
| Independent reflections | 3380 [R(int) = 0.0365] |
| Coverage of independent reflections | 99.8% |
| Absorption correction | Multi-Scan |
| Max. and min. transmission | 0.764 and 0.370 |
| Structure solution technique | direct methods |
| Structure solution program | SHELXT, Acta Cryst., Sect. A 2015, A71, 3-8. |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Refinement program | SHELXL-2014/6 (Sheldrick, 2014) |
| Function minimized | $\Sigma\ w(F_o^2 - F_c^2)^2$ |
| Data / restraints / parameters | 3380 / 1 / 227 |
| Goodness-of-fit on $F^2$ | 1.090 |
| Final R indices = 0.0694 | 3347 data; I>2σ(I) R1 = 0.0264, wR2 |
| | all data R1 = 0.0267, wR2 = 0.0696 |
| Weighting scheme | $w=1/[\sigma^2(F_o^2)+(0.0685P)^2]$ where $P=(F_o^2+2F_c^2)/3$ |
| Largest diff. peak and hole | 0.326 and – 0.658 eÅ$^{-3}$ |
| R.M.S. deviation from mean | 0.068 eÅ$^{-3}$ |

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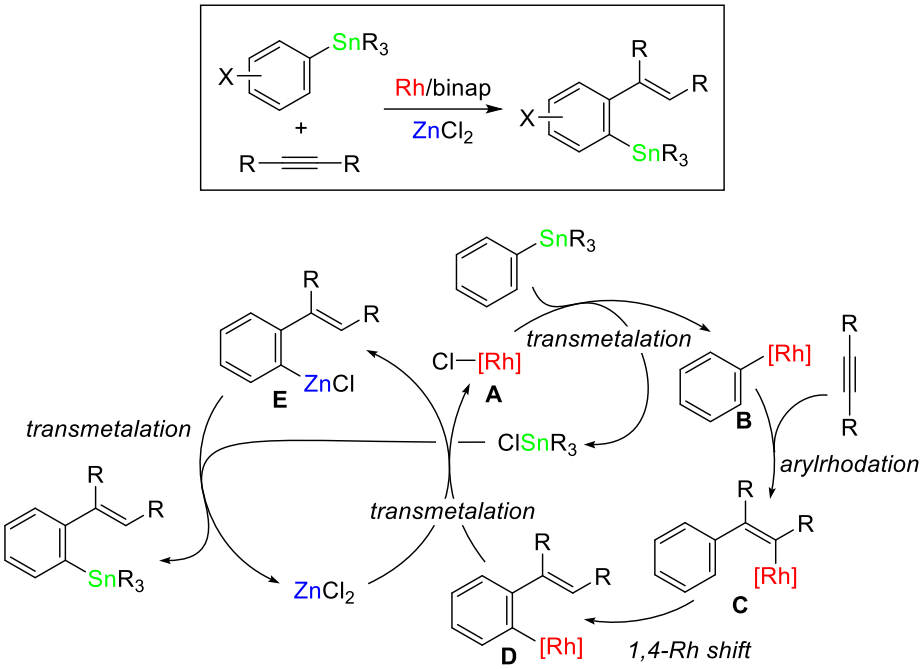
# Chapter 3

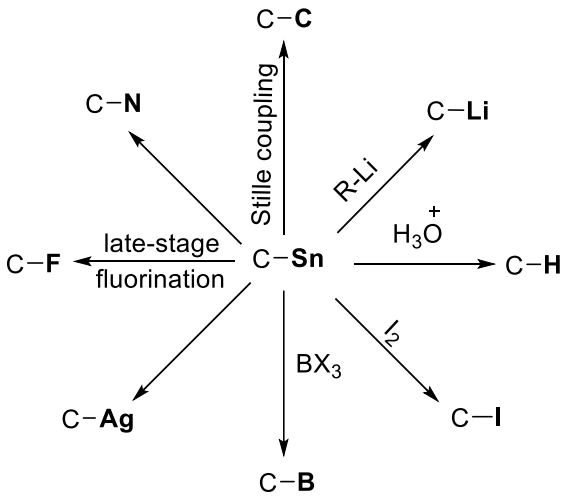
## Migratory Arylstannylation of Alkynes Catalyzed Cooperatively by a Rhodium Complex and Zinc Chloride



## 3.1 Introduction

Organostannanes are the organometallic reagents that have been extensively used for organic synthesis.[1] They can be easily handled, which can be ascribed to their inertness towards oxygen and moisture due to the low polarity of the C–Sn bonds. In addition, organostannanes are reactive with various electrophiles in the presence of appropriate activators (Scheme 3.1). The palladium-catalyzed cross-coupling reaction (Stille coupling) is a classical example.[2] Compared with the more popular organoboron reagents for Suzuki coupling, organostannanes can generally be more easily transmetalated with the transition metal catalyst. The tin-lithium exchange is an invaluable method to prepare organolithium reagents, which will not produce lithium halides as byproduct.[3] The Chan-Lam-Evans-type coupling[4] is also a useful reaction to convert C–Sn bonds to C–N or C–O bonds in a chemoselective manner. Moreover, halodemetallation and protonolysis of organotin reagents are the conventional methods to form carbon–heteroatom and carbon–hydrogen bonds.[5]

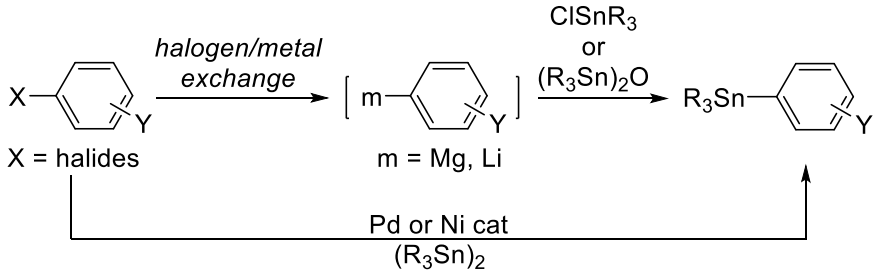
**Scheme 3.1. Selected Examples of Transformations of Organostannanes**




The organostannanes have been most commonly prepared by the reaction of highly reactive organometallic reagents (RLi, RMgX) with tin electrophiles.

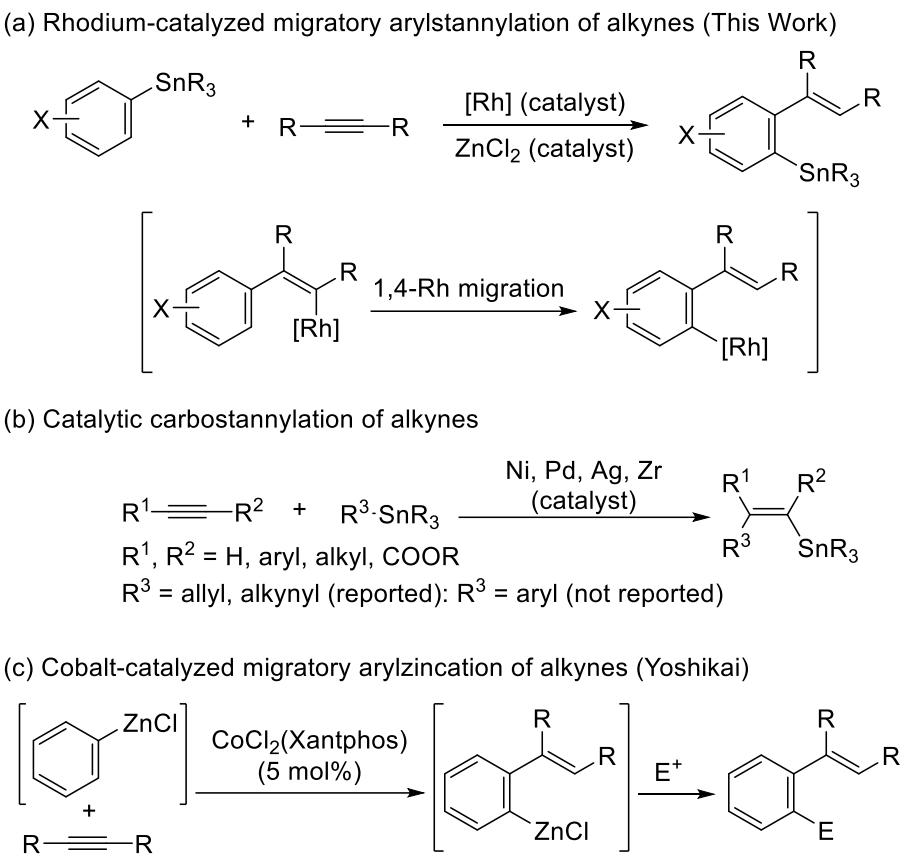
Meanwhile, considerable attention has been paid to the development of their new synthetic methods due to the synthetic utility of organotin reagents (Scheme 3.2). Palladium- or nickel-catalyzed stannylation of organic electrophiles with distannanes is one of such examples.[6]

**Scheme 3.2. Typical Method to Prepare Arylstannanes**




Here, we show our new findings that migratory arylstannylation of unfunctionalized alkynes is catalyzed by Rh complexes in the presence of a catalytic amount of $ZnCl_2$ to give *ortho*-alkenylarylstannanes in high yields. The reaction is proposed to proceed through 1,4-migration of Rh from the alkenyl carbon to the aryl carbon[7–9] (Scheme 3.3a). The detailed discussion of 1,4-migration of Rh is shown in Chapter 1. Carbostannylation of alkynes with allyl- and alkynylstannanes has been achieved using transition metals such as Pd and Ni.[10,11] However, the addition of arylstannanes has not been reported, to the best of our knowledge (Scheme 3.3b). In addition, the rhodium-catalyzed carbometalation of unfunctionalized alkynes has also not been reported. This type of arylmetalation reaction that is accompanied by the 1,4-migration of the metal has been reported by Yoshikai for arylzincation catalyzed by a cobalt complex (Scheme 3.3c).[12]

**Scheme 3.3. Arylstannylation of Alkynes and 1,4-Migration**

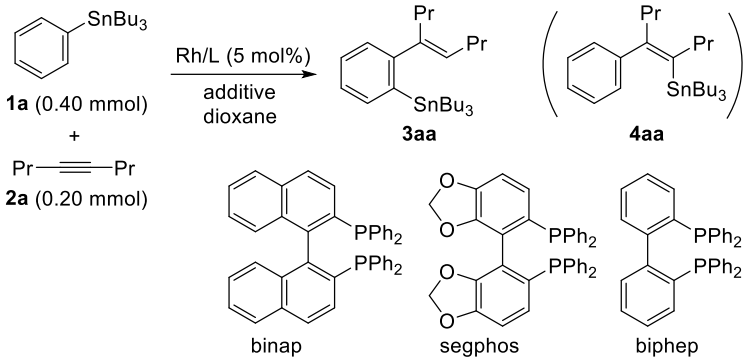



## 3.2 Results and discussion

The results obtained for the reaction of 4-octyne (**2a**) with $PhSnBu_3$ (**1a**, 2.0 equiv to **2a**) under various conditions are summarized in Table 3.1. The migratory arylstannylation was found to proceed in the presence of $ZnCl_2$ (1.0 equiv to **2a**) and a rhodium catalyst generated from $[RhCl(coe)_2]_2$ (5.0 mol % of Rh) and binap[13] (5.5 mol%) in dioxane at 130 °C for 16 h to give 4-(2-stannylphenyl)-4-octene (**3aa**) in 85% yield with perfect *E* geometry[14] (entry 1). The direct arylstannylation product **4aa** was not formed in a detectable amount under these reaction conditions. The yield of **3aa** was dependent on the amount of $ZnCl_2$ to some extent. With 2.0 equiv of $ZnCl_2$, the yield was slightly increased (89%) (entry 2). The yields were lower

with less amount of $ZnCl_2$, being 73%, 71%, and 27%, with 0.50, 0.25, and 0.10 equiv of $ZnCl_2$, respectively (entries 3–5). It is noted that $ZnCl_2$ is working as a catalyst though a substoichiometric amount is necessary for a high yield of **3aa**. The presence of $ZnCl_2$ is essential for the present arylstannylation, **3aa** being not formed at all in its absence (entry 6). At a lower reaction temperature (100 °C), the yield of **3aa** was lower by 10% (entry 7). Other zinc halides such as $ZnBr_2$ and $ZnI_2$ were less catalytically active than $ZnCl_2$ (entries 8 and 9). It was difficult to find a substitute of $ZnCl_2$ from other metal salts. For example, CuCl[15] gave a trace amount of **3aa** (entry 10). The binap ligand on Rh can be replaced by other biaryldiphosphine such as segphos or biphep. The yields with segphos[16] and biphep were slightly lower (73% and 71%, respectively) than that with binap for the reaction of $PhSnBu_3$ (**1a**) (entries 11 and 12), while segphos performed better for the reactions of some other arylstannanes (see Table 3.2). The catalytic activity of other phosphine–Rh complexes were much lower. While dppf ligand gave a low yield (16%) of **3aa** (entry 13), the reaction did not take place with dppe, dppp, xantphos, or $PPh_3$ (entries 14–17). Rh complex with cyclooctadiene (cod) ligand or Ir/binap complex did not catalyze the reaction either (entries 18 and 19). The cobalt complex, $CoCl_2$(xantphos), which has been reported to be an effective catalyst for the migratory arylzincation,[12] is not a catalyst of choice for the present arylstannylation (entry 20).

**Table 3.1. Rhodium-Catalyzed Phenylstannylation of 4-Octyne (2a) with $PhSnBu_3$ (1a)[a]**



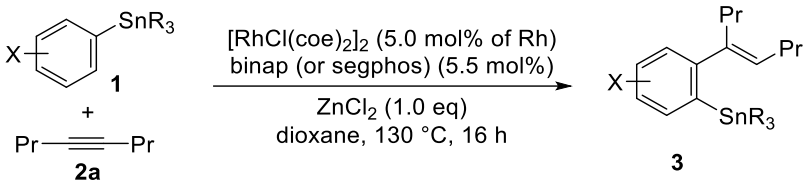

| Entry | Rh catalyst[b] (5 mol%) | Additive (equiv to **2a**) | Yield (%)[c] of **3aa** |
|---|---|---|---|
| 1 | Rh/binap | $ZnCl_2$ (1.0) | 85 |
| 2 | Rh/binap | $ZnCl_2$ (2.0) | 89 |
| 3 | Rh/binap | $ZnCl_2$ (0.50) | 73 |
| 4 | Rh/binap | $ZnCl_2$ (0.25) | 71 |
| 5 | Rh/binap | $ZnCl_2$ (0.10) | 27 |
| 6 | Rh/binap | — | 0 |
| 7[d] | Rh/binap | $ZnCl_2$ (1.0) | 75 |
| 8 | Rh/binap | $ZnBr_2$ (1.0) | 43 |
| 9 | Rh/binap | $ZnI_2$ (1.0) | 18 |
| 10 | Rh/binap | CuCl (1.0) | <3 |
| 11 | Rh/segphos | $ZnCl_2$ (1.0) | 73 |
| 12 | Rh/biphep | $ZnCl_2$ (1.0) | 71 |
| 13 | Rh/dppf | $ZnCl_2$ (1.0) | 16 |
| 14 | Rh/dppe | $ZnCl_2$ (1.0) | 0 |
| 15 | Rh/dppp | $ZnCl_2$ (1.0) | 0 |
| 16 | Rh/xantphos | $ZnCl_2$ (1.0) | 0 |
| 17 | Rh/$PPh_3$[e] | $ZnCl_2$ (1.0) | <3 |
| 18 | Rh/cod[f] | $ZnCl_2$ (1.0) | 0 |
| 19 | Ir/binap[g] | $ZnCl_2$ (1.0) | 0 |
| 20 | Co/xantphos[h] | $ZnCl_2$ (1.0) | 7 |

[a] Reaction conditions: 4-Octyne (**2a**) (0.20 mmol), $PhSnBu_3$ (**1a**) (0.40 mmol), and $ZnCl_2$ (0.20 mmol) in dioxane (1.0 mL) at 130 °C (bath temp) for 16 h. [b] Rh catalyst (5 mol% of Rh) was generated in situ from $[RhCl(coe)_2]_2$ (10 μmol of Rh) and bisphosphine (11 μmol). [c] Isolated yield. [d] At 100 °C. [e] $RhCl(PPh_3)_3$ (10 μmol). [f] $[RhCl(cod)]_2$ (10 μmol of Rh). [g] $[IrCl(coe)_2]_2$ (10 μmol of Ir) + binap (11 μmol). [h] $CoCl_2$(xantphos) (10 μmol).

The reaction conditions optimized for the phenylstannylation with $PhSnBu_3$ (**1a**), that is, Rh/binap (5 mol%) and $ZnCl_2$ (1.0 equiv) at 130 °C (entry 1 in Table 3.1), were successfully applied to the reaction of several other aryltin reagents

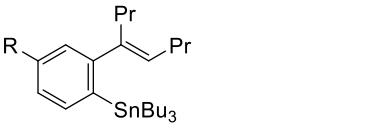
$ArSnR_3$ with 4-octyne (**2a**) (Table 3.2). The phenyltin reagents $PhSnR_3$, where R is methyl (**1b**), propyl (**1c**), or octyl (**1d**), all gave the corresponding phenylstannylation products **3ba**–**3da** in high yields (entries 2–4). It should be noted that trioctylarylstannanes are almost non-toxic. The yields are generally high for *para*-substituted aryltin reagents, those substituted with Me, Ph, $Me_3Si$, and $CF_3O$ groups giving the corresponding products in 83–91% yields (entries 5–8). The lower yield (65%) for MeO-substituted one **1i** is mainly due to the instability of the product **3ia** under the reaction conditions (entry 9). For the reaction of aryltin reagents substituted with electron-withdrawing groups at the *para*-position, Cl (**1k**), Br (**1l**), CN (**1m**), and COOMe (**1n**), the Rh/binap catalyst was not very effective resulting in lower yields of the corresponding arylstannylation products. The use of Rh/segphos as a catalyst instead of Rh/binap improved the reaction for these aryltin reagents (entries 11–18). A typical example is the reaction of $4\text{-}BrC_6H_4SnBu_3$, where the yields of the product **3la** are 47% and 78% with binap and segphos ligands, respectively (entries 13 and 14). In the arylstannylation with *meta*-substituted aryltin reagents, perfect regioselectivity of the 1,4-migration was observed. Thus, the reaction of those substituted with Me (**1p**), $Me_3Si$ (**1q**), and $CF_3$ (**1r**) exclusively gave the corresponding 2,4-disubstituted aryltins **3pa**–**3ra**, which are the less hindered isomers (entries 20–22). The regioselectivity was also high for the reaction of 2-naphthyltin **1s**, where the 1,4-migration took place to the less hindered 3-position selectively (entry 23). Unfortunately, the migratory arylstannylation did not take place for *ortho*-substituted tin reagent **1t** under the present conditions (entry 24).

**Table 3.2. Rhodium-Catalyzed Arylstannylation of 4-Octyne (2a) with $ArSnR_3$ 1**[a]

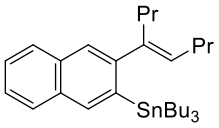



| Entry | $ArSnR_3$ **1** | L on Rh[b] | yield (%)[c] of **3** |
|---|---|---|---|
| 1 | $PhSnBu_3$ (**1a**) | binap | 85 (**3aa**) |
| 2 | $PhSnMe_3$ (**1b**) | binap[d] | 77 (**3ba**) |
| 3 | $PhSnPr_3$ (**1c**) | binap | 89 (**3ca**) |
| 4 | $PhSnOct_3$ (**1d**) | binap | 78 (**3da**) |
| 5 | 4-$MeC_6H_4SnBu_3$ (**1e**) | binap | 87 (**3ea**) |
| 6 | 4-$PhC_6H_4SnBu_3$ (**1f**) | binap | 91 (**3fa**) |
| 7 | 4-$Me_3SiC_6H_4SnBu_3$ (**1g**) | binap | 83 (**3ga**) |
| 8 | 4-$CF_3OC_6H_4SnBu_3$ (**1h**) | binap | 83 (**3ha**) |
| 9 | 4-$MeOC_6H_4SnBu_3$ (**1i**) | binap[d] | 65 (**3ia**) |
| 10 | 4-$FC_6H_4SnBu_3$ (**1j**) | binap | 77 (**3ja**) |
| 11 | 4-$ClC_6H_4SnBu_3$ (**1k**) | binap | 73 (**3ka**) |
| 12 | 4-$ClC_6H_4SnBu_3$ (**1k**) | segphos | 84 (**3ka**) |
| 13 | 4-$BrC_6H_4SnBu_3$ (**1l**) | binap | 47 (**3la**) |
| 14 | 4-$BrC_6H_4SnBu_3$ (**1l**) | segphos | 78 (**3la**) |
| 15 | 4-$NCC_6H_4SnBu_3$ (**1m**) | binap | 51 (**3ma**) |
| 16 | 4-$NCC_6H_4SnBu_3$ (**1m**) | segphos | 67 (**3ma**) |
| 17 | 4-$MeOOCC_6H_4SnBu_3$ (**1n**) | binap | 61 (**3na**) |
| 18 | 4-$MeOOCC_6H_4SnBu_3$ (**1n**) | segphos | 82 (**3na**) |
| 19 | 4-$CF_3C_6H_4SnBu_3$ (**1o**) | segphos | 69 (**3oa**) |
| 20 | 3-$MeC_6H_4SnBu_3$ (**1p**) | binap | 77 (**3pa**)[e] |
| 21 | 3-$Me_3SiC_6H_4SnBu_3$ (**1q**) | binap | 84 (**3qa**)[e] |
| 22 | 3-$CF_3C_6H_4SnBu_3$ (**1r**) | binap | 67 (**3ra**)[e] |
| 23 | 2-naphthyl$SnBu_3$ (**1s**) | binap | 83 (**3sa**)[e] |
| 24 | 2-$MeC_6H_4SnBu_3$ (**1t**) | binap | <3 (**3ta**) |

[a] Reaction conditions: 4-Octyne (**2a**) (0.20 mmol), $ArSnR_3$ **1** (0.40 mmol), $ZnCl_2$ (0.20 mmol), and Rh catalyst (5 mol% of Rh) in dioxane (1.0 mL) at 130 °C (bath temp) for 16 h. [b] Rh catalyst (5 mol% of Rh) was generated in situ from $[RhCl(coe)_2]_2$ (10 μmol of Rh) and binap or segphos (11 μmol). [c] Isolated yield. [d] In THF at 90 °C. [e] Regioselective 1,4-shift giving the products **3** shown below.



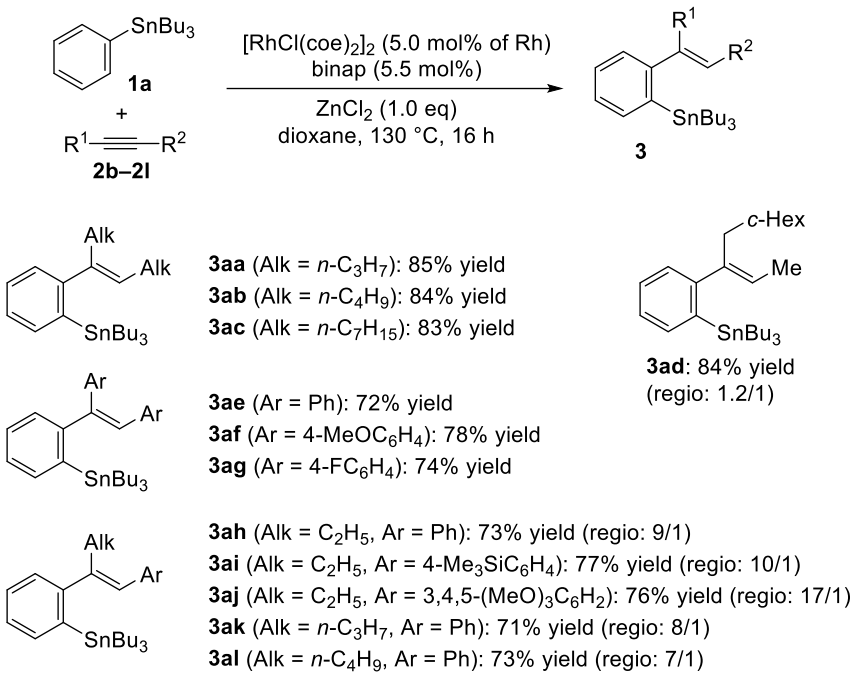

R = Me (**3pa**), $Me_3Si$ (**3qa**), $CF_3$ (**3ra**)




**3sa**

The results obtained for the reaction of $PhSnBu_3$ (**1a**) with several unfunctionalized alkynes substituted with alkyl and aryl groups are summarized in Table 3.3. The migratory arylstannylation proceeded well for longer-chain dialkylacetylenes, 5-decyne (**2b**) and 8-hexadecyne (**2c**), to give high yields of the corresponding products, **3ab** and **3ac**, respectively. In the reaction of unsymmetrically substituted dialkylacetylene **2d**, the regioselectivity was low, resulting in the formation of a mixture of **3ad** and its regioisomer in a ratio of 1.2/1.0. Diarylacetylenes also underwent the migratory arylstannylation, although the yields are generally lower than those for dialkylacetylenes.[17] The reaction of alkyl(aryl)alkynes **2h**–**2l**, proceeded with high regioselectivity for the bond formation between the phenyl group of phenyltin **1a** and the alkyl-substituted alkyne carbon. This selectivity is as expected from the reported regiochemistry of carbometalation of alkyl(aryl)alkynes.[18]

**Table 3.3. Rhodium-Catalyzed Arylstannylation of Alkynes 2 with $PhSnBu_3$ (1a)**[a]

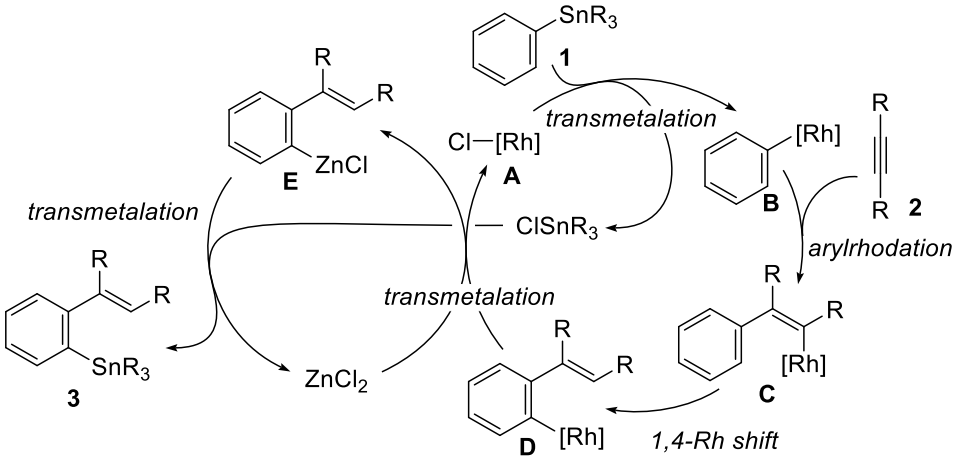



[a] Reaction conditions: Alkyne **2** (0.20 mmol), $PhSnBu_3$ **1a** (0.40 mmol), $ZnCl_2$ (0.20 mmol), and Rh catalyst (5 mol% of Rh), generated in situ from $[RhCl(coe)_2]_2$ (10 μmol of Rh) and binap (11 μmol), in dioxane (1.0 mL) at 130 °C (bath temp) for 16 h. The structures of main regioisomers are shown for the products from unsymmetrically substituted alkynes.

The reaction pathway of the present migratory arylstannylation of alkynes, which is catalyzed cooperatively by Rh complex and $ZnCl_2$, is proposed as shown in Scheme 3.4. Thus, the transmetalation of the aryl group from Sn to Rh takes place in the reaction of $PhSnR_3$ **1** with a Cl–Rh species **A** to generate a Ph–Rh intermediate **B** and $ClSnR_3$,[19] the latter being to be involved in the final step leading to the stannylation product **3**. The syn-addition of the Ph–Rh **B** to the alkyne **2** generates a 2-arylalkenyl–Rh **C**, and 1,4-migration of Rh from alkenyl to aryl[7,8] gives an *ortho*-alkenylphenyl–Rh intermediate **D**, which has been reported to be thermodynamically more stable than **C**.[8e] Transmetalation between the *ortho*-alkenylphenyl–Rh **D** and $ZnCl_2$ takes place to give an arylzinc chloride **E** and the Cl–Rh species **A**. Finally, the reaction of the arylzinc chloride **E** with $ClSnR_3$,[20] which was formed in the initial step, leads to the *ortho*-alkenylphenylstannane **3**,

with regeneration of $ZnCl_2$. Direct transmetalation between the aryl–Rh intermediate **D** and $ArSnR_3$ **1** giving Ar–Rh **B** and the product **3** is less likely because a catalytic amount of $ZnCl_2$ is essential for the present arylstannylation (see entries 1–6 in Table 3.1).

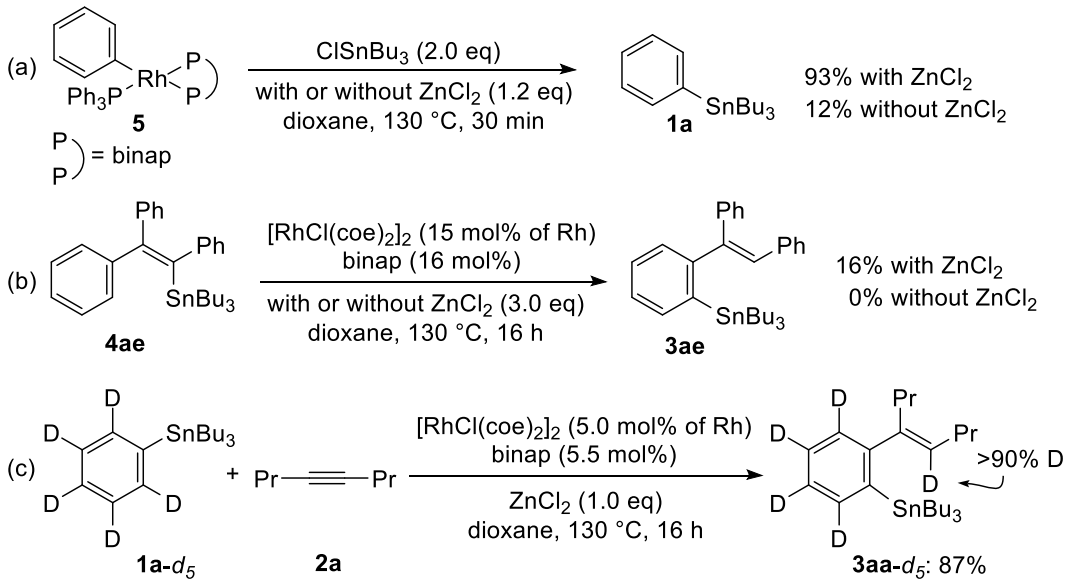
**Scheme 3.4. A Catalytic Cycle Proposed for Migratory Arylstannylation of Alkynes Catalyzed by Rh Complex and $ZnCl_2$**




The reactions shown in Scheme 3.5 gave us further information on the catalytic cycle. Stoichiometric reactions of a Ph–Rh complex, $RhPh(PPh_3)(binap)$ (**5**),[21] with $ClSnBu_3$ (2.0 eq) in the presence of $ZnCl_2$ (1.2 eq) in dioxane at 130 °C gave 93% yield of $PhSnBu_3$ (**1a**), while the yield of **1a** is very low (12%) in the absence of $ZnCl_2$ under otherwise the same conditions (Scheme 3.5a). These reactions are related to the last transmetalation step producing the *ortho*-alkenylphenylstannane **3** from the Ar–Rh intermediate **D** in the catalytic cycle. The results show that the direct transmetalation between the intermediate **D** and $ClSnR_3$ is slow and that $ZnCl_2$ greatly accelerates the transmetalation. The fast transmetalation in the presence of $ZnCl_2$ is probably because of a lower energy caused by the double transmetalations from Rh to Zn and from Zn to Sn by the way

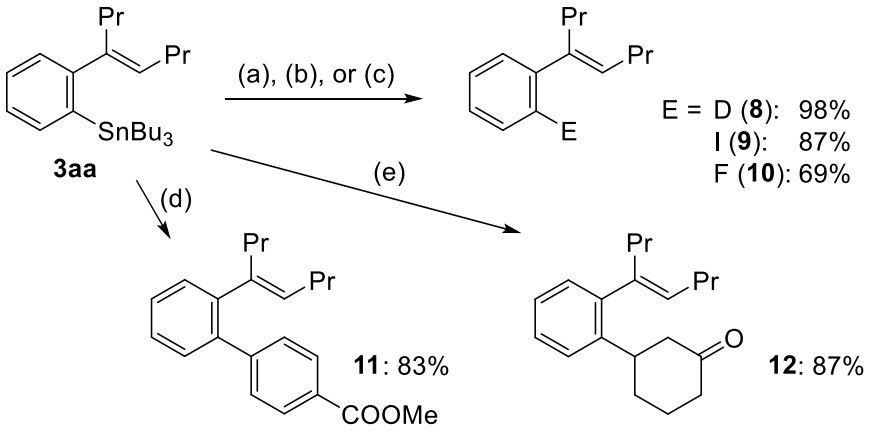
of the arylzinc species **E**. Rhodium-catalyzed 1,4-migration of Sn from an alkenylstannane **4ae** to an arylstannane **3ae** was observed in the presence of $ZnCl_2$, albeit in a low yield (16%).[22] The 1,4-migration of Sn did not take place in the absence of $ZnCl_2$ (Scheme 3.5b). The catalytic cycle involving the 1,4-Rh shift from the intermediates **C** to **D** is supported by these results. The deuterium-labeling study using $C_6D_5SnBu_3$ (**1a**-$d_5$) (Scheme 3.5c), where the deuterium is incorporated at olefinic carbon in **3aa**-$d_5$, further supports this catalytic cycle involving the 1,4-Rh shift.

**Scheme 3.5. Reactions to Support the Catalytic Cycle**




The synthetic utility of arylstannanes has been well established.[1] According to the reported procedures,[23–25] tributylstannyl group in **3aa** was converted into deuterio (**8**), iodo (**9**), and fluoro (**10**) successfully (Scheme 3.6). The palladium-catalyzed cross-coupling with an aryl iodide[2] and the rhodium-catalyzed conjugate addition to 2-cyclohexenone[19] gave high yields of the corresponding products, **11** and **12**, respectively, as expected.

**Scheme 3.6. Transformation of *ortho*-Alkenylarylstannane 3aa**




(a) $(CF_3CO)_2O$, $D_2O$. (b) $I_2$, $CH_2Cl_2$. (c) selectfluor, AgOTf, acetone. (d) 4-$IC_6H_4COOMe$, $PdCl_2(PPh_3)_2$ (10 mol%), CuI, DMF. (e) 2-cyclohexenone, $[RhCl(cod)]_2$ (5 mol% Rh), KOH, dioxane/$H_2O$.

## 3.3 Conclusion

To summarize, migratory arylstannylation was found to take place in the reaction of arylstannanes $ArSnR_3$ with unfunctionalized alkynes in the presence of a bisphosphine–rhodium catalyst and a catalytic amount of zinc chloride to produce *ortho*-alkenylarylstannanes in high yields. A catalytic cycle involving three transmetalation steps, that is, transmetalation of aryl groups from Sn to Rh, Rh to Zn, and Zn to Sn, is proposed.

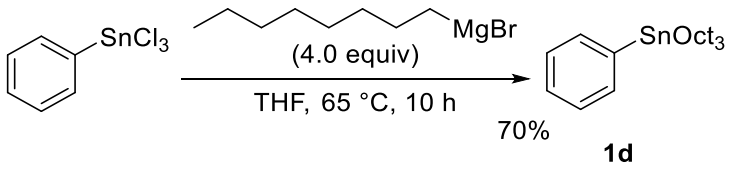
## 3.4 Experimental section

### 3.4.1 Materials

Alkynes (**2a**–**2c**, **2e**–**2h**, **2k**, and **2l**), aryl halides, bisphosphine ligands, n-BuLi, $D_2O$, CuI, CuCl, AgOTf, KOH, Mg, $ZnCl_2$, $ZnBr_2$, $ZnI_2$, cyclohex-2-enone, trifluoroacetic anhydride, tributyltin chloride, $PhSnCl_3$, $PhSnBu_3$ (**1a**), $PhSnMe_3$ (**1b**), $4\text{-}MeOC_6H_4SnBu_3$ (**1i**), $4\text{-}FC_6H_4SnBu_3$ (**1j**), $4\text{-}ClC_6H_4SnBu_3$ (**1k**), 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate), 1-bromooctane, 1-bromopropane, $[IrCl(coe)_2]_2$, $CoCl_2$(xantphos), $PdCl_2(PPh_3)_2$, $RhCl(PPh_3)_3$ and iodine were purchased and used as received. Dioxane and THF were distilled over benzophenone ketyl under $N_2$.

$[RhCl(coe)_2]_2$,[26] $[RhCl(cod)]_2$,[27] $4\text{-}BrC_6H_4SnBu_3$ (**1l**) [17151-49-4],[28] $4\text{-}NCC_6H_4SnBu_3$ (**1m**) [79048-30-9],[28] $4\text{-}MeOOCC_6H_4SnBu_3$ (**1n**) [91734-76-8],[29] and but-2-yn-1-ylcyclohexane (**2d**) [57497-07-1][30] were prepared according to the reported procedures.

### 3.4.2 Preparation of trioctyl(phenyl)stannane (1d) [143363-50-2]

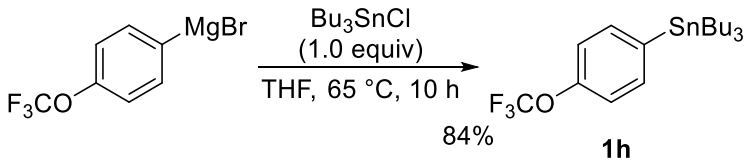



To a solution of octylmagnesium bromide in THF (25.0 mL), prepared from magnesium turnings (593 mg, 24 mmol) and 1-bromooctane (3.86 g, 20.0 mmol), $PhSnCl_3$ (1.51 g, 5.0 mmol) was added dropwise over 15 min at room temperature. The mixture was stirred at 65 °C for 10 h before $H_2O$ (10.0 mL) was added. The mixture was extracted with ethyl acetate, and the combined organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was subjected to

chromatography on silica gel (pre-treated with 1% $Et_3N$ in hexanes) to give trioctyl(phenyl)stannane (**1d**) [143363-50-2] (70%, 1.87 g, 3.5 mmol) as colorless oil. The spectral data are in agreement with reported literature values.[31]

$PhSnPr_3$ (**1c**) [55335-05-2] was prepared in the same manner as above using propylmagnesium bromide, and the spectral data are in agreement with reported literature values.[32]

### 3.4.3 Preparation of tributyl(4-(trifluoromethoxy)phenyl)stannane (1h) and tributyl(pentadeuterophenyl)stannane (1a-$d_5$)



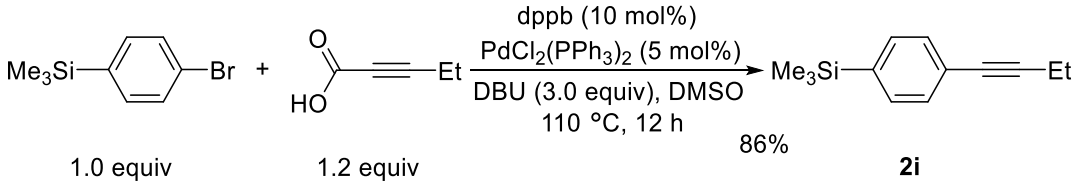

To a solution of 4-(trifluoromethoxy)phenylmagnesium bromide in THF (10.0 mL), prepared from magnesium turnings (288 mg, 12 mmol) and 4-bromotrifluoromethoxybenzene (2.41 g, 10.0 mmol), $Bu_3SnCl$ (3.26 g, 10.0 mmol) was added dropwise over 15 min at room temperature. The mixture was stirred at 65 °C for 10 h before $H_2O$ (5.0 mL) was added. The mixture was extracted with ethyl acetate, and the combined organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was subjected to chromatography on silica gel (pre-treated with 1% $Et_3N$ in hexanes) to give tributyl(4-(trifluoromethoxy)phenyl)stannane (**1h**) (84%, 3.79 g, 8.4 mmol) as colorless oil. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.92 (t, $J_{H,H}$ = 7.3 Hz, 9H), 1.09 (t, $J_{H,H}$ = 8.1 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 51.2 Hz, 6H), 1.36 (sext, $J_{H,H}$ = 7.3 Hz, 6H), 1.45–1.65 (m, 6H), 7.19 (d, $J_{H,H}$ = 7.6 Hz, 2H), 7.50 (d, $J_{H,H}$ = 8.1 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 35.7 Hz, 2H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 9.7 ($J_{C,}{}^{119}{}_{Sn}$ = 343.4 Hz, $J_{C,}{}^{117}{}_{Sn}$ = 328.2 Hz), 13.6, 27.4 ($J_{C,}{}^{119}{}_{Sn}$ =

55.9 Hz), 29.0 ($J_{C,}{}^{119}_{Sn}$ = 20.3 Hz), 120.3 ($J_{C,}{}^{119}_{Sn}$ = 41.7 Hz), 120.6 (q, $J_{C,}{}^{19}_{F}$ = 256.8 Hz), 137.6 ($J_{C,}{}^{119}_{Sn}$ = 33.5 Hz), 140.6 ($J_{C,}{}^{119}_{Sn}$ = 368.7 Hz, $J_{C,}{}^{117}_{Sn}$ = 352.7 Hz), 149.5 (q, $J_{C,}{}^{19}_{F}$ = 1.4 Hz). **HRMS** (ESI) calcd for $C_{19}H_{31}OF_3Na^{120}Sn$ $[M+Na]^+$ 475.1247, found 475.1272.

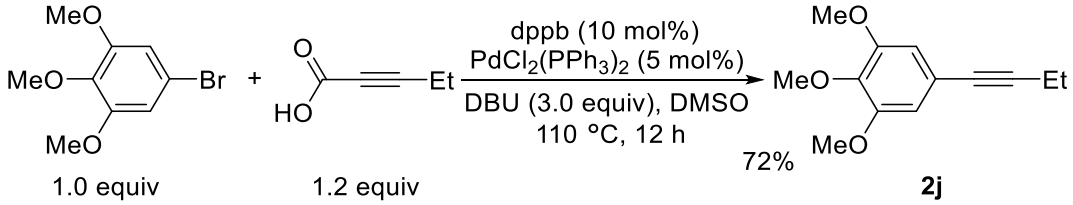
$C_6D_5SnBu_3$ (**1a**-$d_5$) was prepared in the same manner as above using pentadeuterophenylmagnesium bromide and $Bu_3SnCl$. Thus, the reaction of a solution of pentadeuterophenylmagnesium bromides in THF (10.0 mL), prepared from magnesium turnings (299 mg, 12 mmol) and pentadeuterophenyl bromide (1.62 g, 10.0 mmol), with $Bu_3SnCl$ (3.26 g, 10.0 mmol) at 65 °C for 10 h gave tributyl(pentadeuterophenyl)stannane (**1a**-$d_5$) (83% yield, 3.09 g, 8.3 mmol) as colorless oil. **$^1$H NMR** (300 MHz, $CDCl_3$) δ 0.93 (t, $J_{H,H}$ = 7.3 Hz, 9H), 1.10 (t, $J_{H,H}$ = 8.1 Hz, $J_{H,}{}^{119}_{Sn}$ = 51.1 Hz, 6H), 1.37 (sext, $J_{H,H}$ = 7.3 Hz, 6H), 1.44–1.75 (m, 6H); **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 9.5 ($J_{C,}{}^{119}_{Sn}$ = 339.6 Hz, $J_{C,}{}^{117}_{Sn}$ = 324.6 Hz), 13.7, 27.4 ($J_{C,}{}^{119}_{Sn}$ = 56.6 Hz), 29.1 ($J_{C,}{}^{119}_{Sn}$ = 20.1 Hz), 127.4 (t, $J_{C,}{}^{2}_{H}$ = 24.1 Hz), 136.0 (t, $J_{C,}{}^{2}_{H}$ = 24.0 Hz), 141.7. **HRMS** (ESI) calcd for $C_{18}H_{27}D_5Na^{120}Sn$ $[M+Na]^+$ 396.1738, found 396.1733.

4-$MeC_6H_4SnBu_3$ (**1e**) [31614-66-1],[31] 4-$PhC_6H_4SnBu_3$ (**1f**) [51533-89-2],[32] 4-$Me_3SiC_6H_4SnBu_3$ (**1g**) [38860-01-4],[33] 4-$CF_3C_6H_4SnBu_3$ (**1o**) [86487-19-6],[29] 3-$MeC_6H_4SnBu_3$ (**1p**) [68971-88-0],[30] 3-$Me_3SiC_6H_4SnBu_3$ (**1q**) [1026787-60-9],[34] 3-$CF_3C_6H_4SnBu_3$ (**1r**) [53566-38-4],[24] 2-naphthylSnBu$_3$ (**1s**) [972-11-2],[24] and 2-$MeC_6H_4SnBu_3$ (**1t**) [68971-87-9][29] were prepared in the same manner as above from the corresponding arylmagnesium bromides and $Bu_3SnCl$. Their spectral data are in agreement with reported literature values.

### 3.4.4 Preparation of 1-(4-trimethylsilylphenyl)but-1-yne (2i) and 1-(3,4,5-trimethoxyphenyl)but-1-yne (2j)




$PdCl_2(PPh_3)_2$ (351.0 mg, 0.50 mmol, 5.0 mol%) and 1,4-bis(diphenylphosphino)butane (426.5 mg, 1.0 mmol, 10.0 mol%) were placed in a 100 mL flask under nitrogen. DMSO (25 mL) was added and the mixture was stirred at room temperature for 10 min. To the mixure, 1-bromo-4-(trimethylsilyl)benzene (2.29 g, 10.0 mmol), 2-pentynoic acid (1.18 g, 12.0 mmol), and DBU (4.58 g, 30.0 mmol) were added. The mixture was heated at 110 °C for 12 h. The mixture was diluted with 20.0 mL of diethyl ether, and it was passed through a short pad of silica gel with ethyl acetate as an eluent. The solution was washed with $H_2O$ and brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was subjected to chromatography on silica gel to give 1-(4-trimethylsilylphenyl)but-1-yne (**2i**) (86%, 1.74 g, 8.6 mmol) as pale yellow oil. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.25 (s, 9H), 1.24 (t, $J_{H,H}$ = 7.5 Hz, 3H), 2.42 (q, $J_{H,H}$ = 7.5 Hz, 2H), 7.36 (d, $J_{H,H}$ = 8.1 Hz, 2H), 7.43 (d, $J_{H,H}$ = 8.1 Hz, 2H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ –1.2, 13.1, 13.9, 80.0, 92.1, 124.3, 130.6, 133.1, 139.9. **HRMS** (ESI) calcd for $C_{13}H_{19}Si$ $[M+H]^+$ 203.1256, found 203.1218.




The alkyne, 1-(3,4,5-trimethoxyphenyl)but-1-yne (**2j**), was prepared in the same manner as above using 5-bromo-1,2,3-trimethoxybenzene. Thus, the reaction of $PdCl_2(PPh_3)_2$ (351.0 mg, 0.50 mmol, 5.0 mol%), 1,4-bis(diphenylphosphino)butane (426.5 mg, 1.0 mmol, 10.0 mol%), 5-bromo-1,2,3-trimethoxybenzene (2.47 g, 10.0 mmol), 2-pentynoic acid (1.18 g, 12.0 mmol), and DBU (4.58 g, 30.0 mmol) at 110 °C for 12 h gave **2j** (72% yield, 1.59 g, 7.2 mmol) as colorless solid. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 1.24 (t, $J_{H,H}$ = 7.5 Hz, 3H), 2.41 (q, $J_{H,H}$ = 7.5 Hz, 2H), 3.83 (s, 3H), 3.84 (s, 6H), 6.63 (s, 2H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 12.9, 13.8, 55.9, 60.8, 79.7, 90.6, 108.6, 119.0, 138.1, 152.8. **HRMS** (ESI) calcd for $C_{13}H_{17}O_3$ $[M+H]^+$ 221.1178, found 221.1190.

### 3.4.5 A typical procedure for migratory arylstannylation of alkynes catalyzed by rhodium complex and zinc chloride (Table 3.1, entry 1)

$[RhCl(coe)_2]_2$ (3.58 mg, 0.0050 mmol, 5.0 mol% of Rh), binap (6.85 mg, 0.0055 mmol, 5.5 mol%), $ZnCl_2$ (27.3 mg, 0.20 mmol), and $PhSnBu_3$ (**1a**) (146.9 mg, 0.40 mmol) were placed in a 10 mL Schlenk tube under nitrogen. Dioxane (1.0 mL) was added and the mixture was stirred at room temperature for 10 min. Before the tube was sealed, 4-octyne (**2a**) (22.0 mg, 0.20 mmol) was added. The tube was placed in a preheated oil bath at 130 °C and the mixture was stirred for 16 h. The reaction mixture was passed through a short pad of basic aluminum oxide with ethyl acetate as the eluent. The solvent was removed on a rotary

evaporator. The residue was subjected to chromatography on silica gel (pre-treated with 1% $Et_3N$ in hexanes) to give (*E*)-4-(2-tributylstannylphenyl)oct-4-ene (**3aa**) (85%, 81.2 mg, 0.17 mmol) as colorless oil.

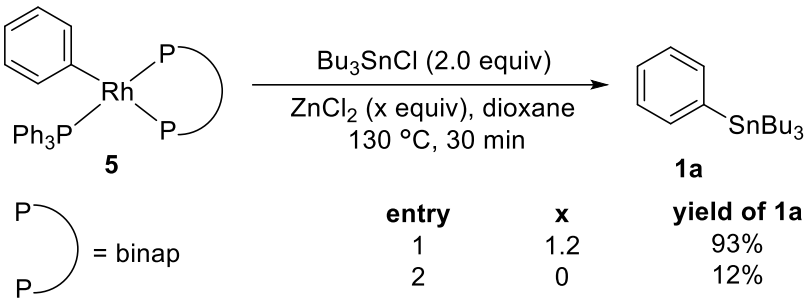
The procedures shown above in Section 3.4.5 for the reaction of $PhSnBu_3$ (**1a**) with 4-octyne (**2a**) (Table 3.1, entry 1) were used for the reaction of $ArSnR_3$ (**1c**–**1h**, **1j**–**1n**, and **1p**–**1t**) with 4-octyne (**2a**) (Table 3.2, entries 3–8, 10, 11, 13, 15, 17, and 20–24), and that of $PhSnBu_3$ (**1a**) with unfunctionalized alkynes (**2b**–**2l**) (Table 3.3).

In the reaction of $ArSnR_3$ (**1k**–**1o**) with 4-octyne (**2a**) (Table 3.2, entries 12, 14, 16, 18, and 19), the procedures shown in Section 3.4.5 were modified by use of segphos instead of binap.

In Table 3.2 entry 2, the procedures shown in Section 3.4.5 were modified by using THF as solvent and decreasing the reaction temperature to 90 °C. Thus, the reaction of $[RhCl(coe)_2]_2$ (3.58 mg, 0.0050 mmol, 5.0 mol% of Rh), binap (6.85 mg, 0.0055 mmol, 5.5 mol%), $ZnCl_2$ (27.3 mg, 0.20 mmol), $PhSnMe_3$ (**1b**) (96.4 mg, 0.40 mmol), and 4-octyne (**2a**, 22.0 mg, 0.20 mmol) in THF (1.0 mL) at 90 °C for 16 h gave (*E*)-4-(2-trimethylstannylphenyl)oct-4-ene (**3ba**) (77% yield, 54.1 mg, 0.15 mmol) as colorless oil. The same procedures for the reaction of $PhSnMe_3$ (**1b**) with 4-octyne (**2a**) were also applied to the reaction of $4\text{-}MeOC_6H_4SnBu_3$ (**1i**) with 4-octyne (**2a**) (Table 3.2, entry 9).

### 3.4.6 Reactions to support the catalytic cycle (Scheme 3.5)

**Scheme 3.5a**

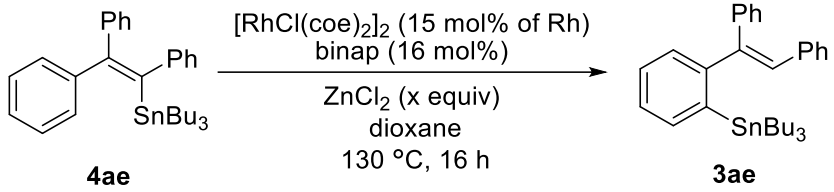



| entry | x | yield of 1a |
|---|---|---|
| 1 | 1.2 | 93% |
| 2 | 0 | 12% |

**Scheme 3.5a, entry 1**: In an oven-dried Schlenk tube, $RhPh(PPh_3)$(binap) (**5**)[21] (106.0 mg, 0.10 mmol) and $ZnCl_2$ (16.4 mg, 0.12 mmol) were placed under nitrogen. Dioxane (1.0 mL) and $Bu_3SnCl$ (65.3 mg, 0.20 mmol) were added and the mixture was heated at 130 °C for 30 min. The reaction was quenched with saturated aqueous solution of $Na_2CO_3$ (1.0 mL). The mixture was extracted with diethyl ether, and the combined organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was subjected to short chromatography on silica gel (pre-treated with 1% $Et_3N$ in hexanes) to give tributyl(phenyl)stannane (**1a**) (93%, 34.5 mg, 0.09 mmol) as colorless oil. $R_f$ = 0.9 (hexanes). The spectral data are in agreement with reported literature values.[25]

**Scheme 3.5a, entry 2**: The procedures for entry 1 in Scheme 3.5a were modified by removing $ZnCl_2$. The reaction of $RhPh(PPh_3)$(binap) (107.1 mg, 0.10 mmol) and $Bu_3SnCl$ (66.0 mg, 0.20 mmol) in dioxane (1.0 mL) at 130 °C for 30 min gave tributyl(phenyl)stannane (**1a**) (12%, 4.5 mg, 0.01 mmol) as colorless oil.

**Scheme 3.5b**




**4ae** **3ae**

| entry | x | yield of 3ae |
|---|---|---|
| 1 | 3 | 16% |
| 2 | 0 | 0% |

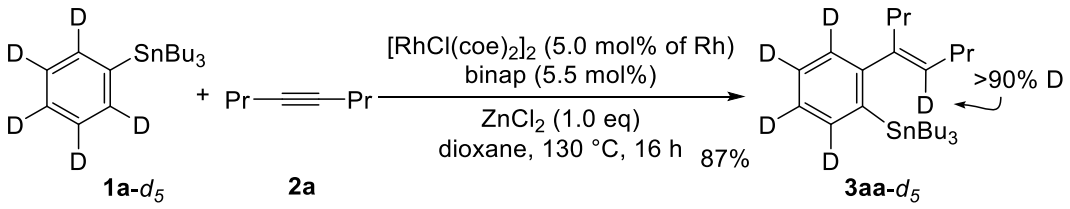
**Preparation of compound 4ae:** To a solution of 2-bromo-1,1,2-triphenylethylene (3.35 g, 10.0 mmol) in diethyl ether (20.0 mL), n-BuLi (5.0 mL, 10.0 mmol, 2.0 M in cyclohexane) was added dropwise at –78 °C over 30 min. The mixture was allowed to warm to 0 °C and stirred for 2 h. $Bu_3SnCl$ (3.30 g, 10.1 mmol) was added to the mixture at 0 °C. The mixture was stirred at room temperature for 12 h before $H_2O$ (5.0 mL) was added. The mixture was extracted with ethyl acetate, and the combined organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was subjected to chromatography on silica gel (pre-treated with 1% $Et_3N$ in hexanes) to give **4ae** (88%, 4.78 g, 8.8 mmol) as pale yellow oil. $R_f$ = 0.8 (hexanes). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.53 (t, $J_{H,H}$ = 8.2 Hz, $J_{H,^{119}Sn}$ = 50.8 Hz, 6H), 0.80 (t, $J_{H,H}$ = 7.2 Hz, 9H), 1.16 (sext, $J_{H,H}$ = 7.2 Hz, 6H), 1.21–1.32 (m, 6H), 6.87–7.03 (m, 8H), 7.12 (t, $J_{H,H}$ = 7.6 Hz, 2H), 7.28–7.35 (m, 5H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 11.6 ($J_{C,^{119}Sn}$ = 334.2 Hz, $J_{C,^{117}Sn}$ = 319.6 Hz), 13.6, 27.3 ($J_{C,^{119}Sn}$ = 61.6 Hz), 29.0 ($J_{C,^{119}Sn}$ = 19.3 Hz), 124.4, 125.9, 127.1, 127.2, 127.6, 128.0 ($J_{C,^{119}Sn}$ = 15.6 Hz), 128.1, 129.4, 130.0, 142.5 ($J_{C,^{119}Sn}$ = 49.2 Hz), 145.9 ($J_{C,^{119}Sn}$ = 26.0 Hz), 146.2 ($J_{C,^{119}Sn}$ = 25.4 Hz), 148.3, 152.7 ($J_{C,^{119}Sn}$ = 24.7 Hz). **HRMS** (ESI) calcd for $C_{32}H_{42}Na^{120}Sn$ $[M+Na]^+$ 569.2206, found 569.2206.

**Scheme 3.5b, entry 1**: In an oven-dried Schlenk tube, $[RhCl(coe)_2]_2$ (10.9 mg, 0.015 mmol, 15 mol% of Rh), binap (19.9 mg, 0.032 mmol, 16 mol%), $ZnCl_2$

(81.5 mg, 0.60 mmol) and compound **4ae** (110.2 mg, 0.20 mmol) were placed under nitrogen. Before the tube was sealed, dioxane (1.0 mL) was added. The reaction mixture was heated at 130 °C for 16 h. The reaction mixture was passed through a short pad of basic aluminum oxide with ethyl acetate as the eluent. The solvent was removed on a rotary evaporator. The residue was subjected to chromatography on silica gel (pre-treated with 1% $Et_3N$ in hexanes) to give **3ae** (16%, 17.6 mg, 0.32 mmol) as colorless oil.

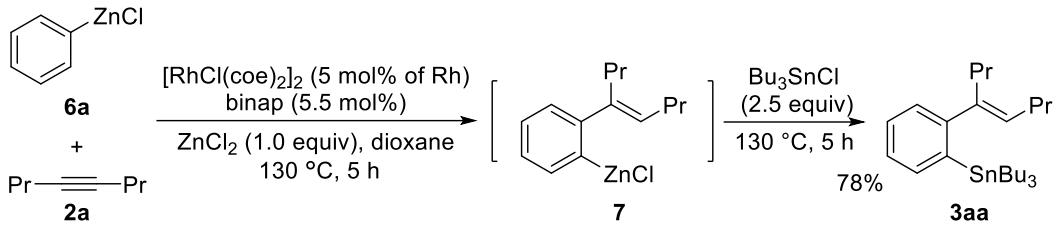
**Scheme 3.5b, entry 2:** The procedures for entry 1 in Scheme 3.5b were modified by removing $ZnCl_2$. The reaction of compound **4ae** (112.2 mg, 0.21 mmol), $[RhCl(coe)_2]_2$ (10.5 mg, 0.015 mmol, 15 mol% of Rh) and binap (19.5 mg, 0.032 mmol, 16 mol%) in dioxane (1.0 mL) at 130 °C for 16 h did not give **3ae**. Compound **3ae** was not detected by $^1H$ NMR or GC.

**Scheme 3.5c**




**Scheme 3.5c**: The procedures for the reaction of $PhSnBu_3$ (**1a**) with 4-octyne (**2a**) (Table 3.1, entry 1) were used for the reaction of $C_6D_5SnBu_3$ (**1a**-*d*$_5$) with 4-octyne (**2a**). Thus, the reaction of $[RhCl(coe)_2]_2$ (3.61 mg, 0.0050 mmol, 5.0 mol% of Rh), binap (6.92 mg, 0.0110 mmol, 5.5 mol%), $ZnCl_2$ (27.6 mg, 0.20 mmol), $C_6D_5SnBu_3$ (**1a**-*d*$_5$) (148.9 mg, 0.40 mmol) and 4-octyne (**2a**) ( 22.3 mg, 0.20 mmol) in dioxane (1.0 mL) at 130 °C for 16 h gave **3aa**-*d*$_5$ (87% yield, 83.9 mg, 0.17 mmol) as colorless oil.

**Scheme 3.5d**

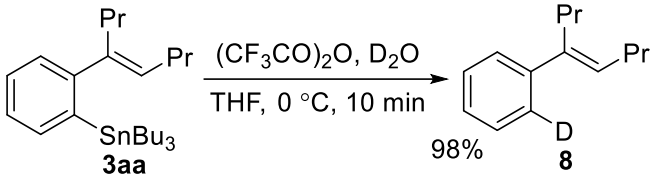



**Preparation of PhZnCl (6a):** An oven-dried Schlenk flask equipped with a stir bar was charged with a solution of bromobenzene (3.39 g, 22.0 mmol) in THF (12.0 mL). The solution was cooled down to –80 °C and n-BuLi (7.4 mL, 20.0 mmol, 2.69 M in hexanes) was added dropwise over 30 min. Precipitates were formed immediately. The reaction mixture was stirred at –80 °C for 90 min. To the THF solution of phenyllithium thus generated, the THF solution of $ZnCl_2$ (30.0 mL, 30 mmol, 1.0 M) was added dropwise at –80 °C. The reaction mixture was allowed to warm to room temperature to give a solution of phenylzinc chloride (**6a**) (0.4 M) and $ZnCl_2$ (0.2 M) in THF.

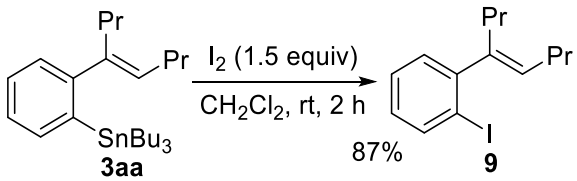
**Scheme 3.5d**: In an oven-dried Schlenk tube, $[RhCl(coe)_2]_2$ (3.58 mg, 0.0050 mmol, 5.0 mol% of Rh) and binap (6.85 mg, 0.0110 mmol, 5.5 mol%) were placed under nitrogen. Dioxane (1.2 mL) was added and the mixture was stirred at room temperature for 10 min. To the mixture, 4-octyne (**2a**) (22.3 mg, 0.20 mmol) and 1.0 mL of the THF solution containing phenylzinc chloride (**6a**) (0.40 mmol, 0.4 M) and $ZnCl_2$ (0.4 mmol, 0.2 M), whose preparation is shown above, were added at room temperature. After the mixture was concentrated to *ca.* 1.0 mL under the flow of dry $N_2$, the reaction mixture was heated at 130 °C for 5 h. $Bu_3SnCl$ (163.1 mg, 0.50 mmol) was added to the mixture at room temperature and the mixture was heated at 130 °C for another 5 h. The reaction mixture was passed through a short pad of basic aluminum oxide with ethyl acetate as the eluent. The solvent was

removed on a rotary evaporator. The residue was subjected to chromatography on silica gel (pre-treated with 1% $Et_3N$ in hexanes) to give (*E*)-4-(2-tributylstannylphenyl)oct-4-ene (**3aa**) (78%, 74.6 mg, 0.16 mmol) as colorless oil.

### 3.4.7 Transformations of (*E*)-4-(2-tributylstannylphenyl)oct-4-ene (3aa) (Scheme 3.6)

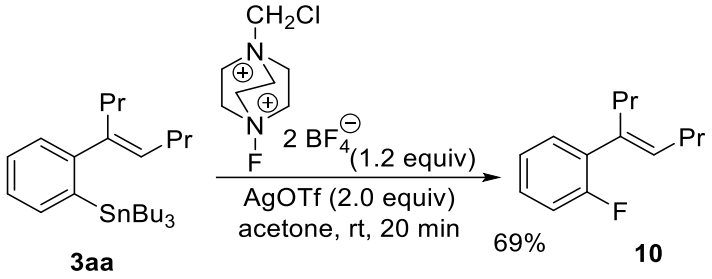



Deuterodestannylation of **3aa** was carried out according to a reported procedure.[23] To a mixture of trifluoroacetic anhydride (3.02g, 14.4 mmol) and **3aa** (85.9 mg, 0.18 mmol) in THF (1.0 mL) at 0 °C was added deuterium oxide (0.27 g, 13.5 mmol). The mixture was stired at 0 °C for 10 min and was neutralized by addition of 6 N aqueous sodium hydroxide. The mixture was extracted with $Et_2O$, and the combined organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was subjected to chromatography on silica gel to give (*E*)-4-(2-deuteriophenyl)oct-4-ene (**8**) (98%, 33.5 mg, 0.18 mmol) as colorless oil.

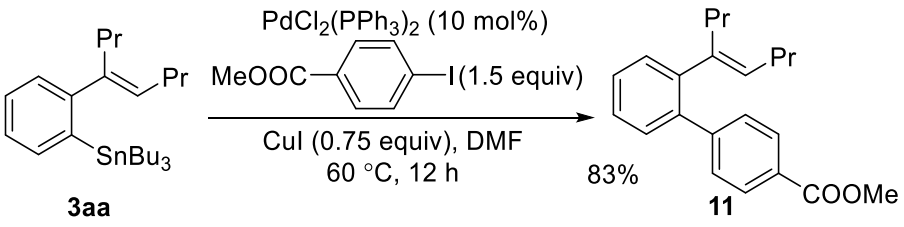



Iododestannylation of **3aa** was carried out according to a reported procedure[24] with minor modifications. An oven-dried flask was charged with **3aa** (114.7 mg, 0.24 mmol), $I_2$ (91.4 mg, 0.36 mmol), and $CH_2Cl_2$ (5.0 mL). The

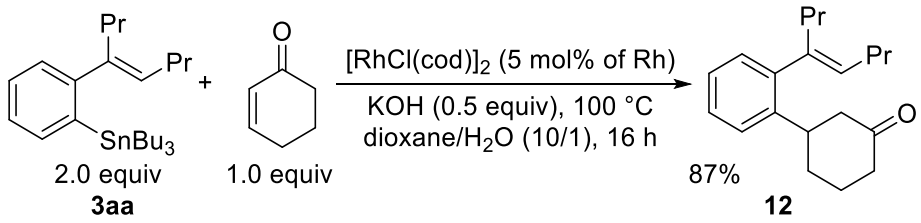
mixture was stirred at room temperatue for 2 h before saturated aqueous solution of $Na_2S_2O_3$ (3.0 mL) was added. The mixture was extracted with $Et_2O$, and the combined organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was subjected to chromatography on silica gel (pre-treated with 1% $Et_3N$ in hexanes) to give (*E*)-4-(2-iodophenyl)oct-4-ene (**9**) (87%, 65.5 mg, 0.21 mmol) as colorless oil.




Fluorodestannylation of **3aa** was carried out according to a reported procedure.[25] Under nitrogen at room temperature, to a solution of **3aa** (90.6 mg, 0.19 mmol) in dry acetone (2.0 mL) was added silver triflate (97.6 mg, 0.38 mmol) and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (80.9 mg, 0.23 mmol). The mixture was stirred at room temperature for 20 min, and it was passed through a short pad of silica gel with ethyl acetate as the eluent. The solvent was removed on a rotary evaporator. The residue was subjected to chromatography on silica gel to give (*E*)-4-(2-fluorophenyl)oct-4-ene (**10**) (69%, 27.1 mg, 0.13 mmol) as colorless oil.

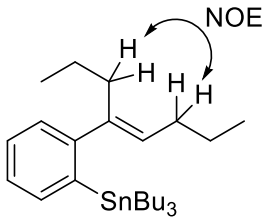


The cross-coupling of **3aa** was performed according to a reported procedure[35] with some modifications. Under nitrogen, **3aa** (95.5 mg, 0.20 mmol), methyl 4-iodobenzoate (78.6 mg, 0.30 mmol), $PdCl_2(PPh_3)_2$ (14.0 mg, 0.020 mmol, 10 mol%), and CuI (28.6 mg, 0.15 mmol) were placed in a 10 mL Schlenk tube. DMF (4.0 mL) was added by syringe and the mixture was allowed to stir at 60 °C for 12 h. The mixture was passed through a short pad of silica gel with ethyl acetate as the eluent. The solvent was removed on a rotary evaporator. The residue was subjected to chromatography on silica gel to give (*E*)-4-(2-(4-methoxycarbonylphenyl)phenyl)oct-4-ene (**11**) (83%, 53.5 mg, 0.17 mmol) as pale yellow oil.



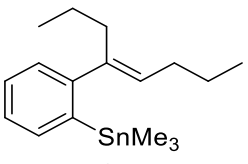

$[RhCl(cod)]_2$ (2.46 mg, 0.0050 mmol, 5 mol% of Rh), **3aa** (190.9 mg, 0.40 mmol), 2-cyclohexenone (19.2 mg, 0.20 mmol), and KOH (5.61 mg, 0.10 mmol) were placed in a 10 mL Schlenk tube under nitrogen. Dioxane (1.0 mL) and water (0.1 mL) were added by syringe, and the mixture was heated at 100 °C for 16 h. The mixture was passed through a short pad of silica gel with ethyl acetate as the eluent. The solvent was removed on a rotary evaporator. The residue was subjected to chromatography on silica gel to give the product **12** (87%, 49.5 mg, 0.17 mmol) as colorless oil.

### 3.4.8 Characterization of the products




**3aa**

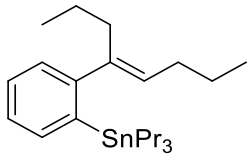
**Compound 3aa.** (Table 3.2, entry 1, 85% yield, colorless oil). The *E* geometry was assigned by NOESY NMR study. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 0.88 (t, $J_{H,H}$ = 7.3 Hz, 9H), 0.90 (t, $J_{H,H}$ = 7.2 Hz, 3H), 0.97 (t, $J_{H,H}$ = 7.3 Hz, 3H), 0.99 (t, $J_{H,H}$ = 8.0 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 51.4 Hz, 6H), 1.32 (sext, $J_{H,H}$ = 7.2 Hz, 6H+2H), 1.42–1.54 (m, 8H), 2.14 (q, $J_{H,H}$ = 7.5 Hz, 2H), 2.32 (t, $J_{H,H}$ = 8.0 Hz, 2H), 5.27 (t, $J_{H,H}$ = 7.0 Hz, 1H), 7.15 (d, $J_{H,H}$ = 7.4 Hz, 1H), 7.18 (td, $J_{H,H}$ = 7.1 Hz, 1.5 Hz, 1H), 7.23 (td, $J_{H,H}$ = 7.3 Hz, 1.6 Hz, 1H), 7.42 (dd, $J_{H,H}$ = 7.0 Hz, 1.2 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 42.9 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 10.9 ($J_{C,}{}^{119}{}_{Sn}$ = 339.7 Hz, $J_{C,}{}^{117}{}_{Sn}$ = 324.5 Hz), 13.6, 14.1, 14.4, 21.6, 22.9, 27.5 ($J_{C,}{}^{119}{}_{Sn}$ = 60.9 Hz), 29.2 ($J_{C,}{}^{119}{}_{Sn}$ = 18.9 Hz), 30.6, 34.9, 125.6 ($J_{C,}{}^{119}{}_{Sn}$ = 42.4 Hz), 127.4 ($J_{C,}{}^{119}{}_{Sn}$ = 9.6 Hz), 127.9 ($J_{C,}{}^{119}{}_{Sn}$ = 35.0 Hz), 129.5, 136.9 ($J_{C,}{}^{119}{}_{Sn}$ = 32.7 Hz), 140.7 ($J_{C,}{}^{119}{}_{Sn}$ = 412.3 Hz, $J_{C,}{}^{117}{}_{Sn}$ = 393.8 Hz), 144.3 ($J_{C,}{}^{119}{}_{Sn}$ = 14.6 Hz), 152.7 ($J_{C,}{}^{119}{}_{Sn}$ = 28.4 Hz). **HRMS** (ESI) calcd for $C_{26}H_{46}Na^{120}Sn$ $[M+Na]^+$ 501.2519, found 501.2537.




**3ba**

**Compound 3ba.** (Table 3.2, entry 2, 77% yield, colorless oil). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 0.24 (t, $J_{H,}{}^{119}{}_{Sn}$ = 53.0 Hz, 9H), 0.91 (t, $J_{H,H}$ = 7.3 Hz, 3H),

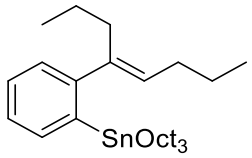
0.97 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.37 (sext, $J_{H,H}$ = 7.8 Hz, 2H), 1.46 (sext, $J_{H,H}$ = 7.4 Hz, 2H), 2.15 (q, $J_{H,H}$ = 7.4 Hz, 2H), 2.34 (t, $J_{H,H}$ = 8.1 Hz, 2H), 5.31 (t, $J_{H,H}$ = 7.1 Hz, 1H), 7.19 (d, $J_{H,H}$ = 7.5 Hz, 1H), 7.22 (t, $J_{H,H}$ = 6.9 Hz, 1H), 7.24–7.28 (m, 1H), 7.47 (d, $J_{H,H}$ = 6.9 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 49.4 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ –7.4 ($J_{C,}{}^{119}{}_{Sn}$ = 350.4 Hz, $J_{C,}{}^{117}{}_{Sn}$ = 334.8 Hz), 14.1, 14.5, 21.6, 22.9, 30.5, 34.8, 125.9 ($J_{C,}{}^{119}{}_{Sn}$ = 47.8 Hz), 127.6 ($J_{C,}{}^{119}{}_{Sn}$ = 38.2 Hz), 127.8 ($J_{C,}{}^{119}{}_{Sn}$ = 9.5 Hz), 130.0, 136.3 ($J_{C,}{}^{119}{}_{Sn}$ = 38.6 Hz), 141.0 ($J_{C,}{}^{119}{}_{Sn}$ = 497.6 Hz, $J_{C,}{}^{117}{}_{Sn}$ = 475.1 Hz), 144.2 ($J_{C,}{}^{119}{}_{Sn}$ = 16.4 Hz), 152.4 ($J_{C,}{}^{119}{}_{Sn}$ = 31.1 Hz). **HRMS** (ESI) calcd for $C_{17}H_{28}Na^{120}Sn$ $[M+Na]^+$ 375.1111, found 375.1118.




**3ca**

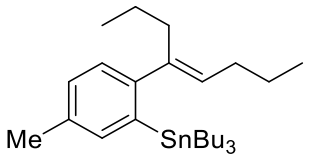
**Compound 3ca.** (Table 3.2, entry 3, 89% yield, colorless oil). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.90 (t, $J_{H,H}$ = 7.3 Hz, 3H), 0.96 (t, $J_{H,H}$ = 7.2 Hz, 9H), 0.98 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.00 (t, $J_{H,H}$ = 8.3 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 50.8 Hz, 6H),1.36 (sext, $J_{H,H}$ = 7.6 Hz, 2H), 1.47 (sext, $J_{H,H}$ = 7.5 Hz, 2H), 1.55 (sext, $J_{H,H}$ = 7.7 Hz, 6H), 2.14 (q, $J_{H,H}$ = 7.4 Hz, 2H), 2.32 (t, $J_{H,H}$ = 8.0 Hz, 2H), 5.27 (t, $J_{H,H}$ = 7.0 Hz, 1H), 7.16 (dd, $J_{H,H}$ = 7.6 Hz, 1.3 Hz, 1H), 7.18 (td, $J_{H,H}$ = 7.1 Hz, 1.6 Hz, 1H), 7.23 (td, $J_{H,H}$ = 7.3 Hz, 1.6 Hz, 1H), 7.43 (dd, $J_{H,H}$ = 7.0 Hz, 1.4 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 43.0 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 13.9 ($J_{C,}{}^{119}{}_{Sn}$ = 339.0 Hz, $J_{C,}{}^{117}{}_{Sn}$ = 323.8 Hz), 14.1, 14.4, 19.1 ($J_{C,}{}^{119}{}_{Sn}$ = 62.6 Hz, $J_{C,}{}^{117}{}_{Sn}$ = 59.2 Hz), 20.4 ($J_{C,}{}^{119}{}_{Sn}$ = 18.6 Hz), 21.6, 22.9, 30.6, 34.9, 125.6 ($J_{C,}{}^{119}{}_{Sn}$ = 41.0 Hz), 127.5 ($J_{C,}{}^{119}{}_{Sn}$ = 9.5 Hz), 128.0 ($J_{C,}{}^{119}{}_{Sn}$ = 35.1 Hz), 129.5, 136.9 ($J_{C,}{}^{119}{}_{Sn}$ = 32.4 Hz), 140.7 ($J_{C,}{}^{119}{}_{Sn}$ = 412.6 Hz, $J_{C,}{}^{117}{}_{Sn}$ = 394.1 Hz), 144.3 ($J_{C,}{}^{119}{}_{Sn}$ = 14.7 Hz), 152.7 ($J_{C,}{}^{119}{}_{Sn}$ = 27.7 Hz). **HRMS** (ESI)

calcd for $C_{23}H_{40}Na^{120}Sn$ $[M+Na]^+$ 459.2059, found 459.2050.




**3da**

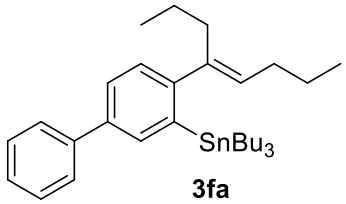
**Compound 3da.** (Table 3.2, entry 4, 78% yield, colorless oil). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.88 (t, $J_{H,H}$ = 7.0 Hz, 9H), 0.90 (t, $J_{H,H}$ = 7.2 Hz, 3H), 0.97 (t, $J_{H,H}$ = 7.2 Hz, 3H), 0.98 (t, $J_{H,H}$ = 8.3 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 50.7 Hz, 6H), 1.20–1.40 (br m, 32H), 1.41–1.60 (m, 8H), 2.14 (q, $J_{H,H}$ = 7.4 Hz, 2H), 2.31 (t, $J_{H,H}$ = 8.0 Hz, 2H), 5.26 (t, $J_{H,H}$ = 7.0 Hz, 1H), 7.15 (d, $J_{H,H}$ = 7.6 Hz, 1H), 7.17 (td, $J_{H,H}$ = 7.1 Hz, 1.5 Hz, 1H), 7.22 (td, $J_{H,H}$ = 7.3 Hz, 1.6 Hz, 1H), 7.41 (dd, $J_{H,H}$ = 7.0 Hz, 1.3 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 42.8 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 11.2 ($J_{C,}{}^{119}{}_{Sn}$ = 339.2 Hz, $J_{C,}{}^{117}{}_{Sn}$ = 323.0 Hz), 14.09, 14.13, 14.4, 21.6, 22.7, 23.0, 26.9 ($J_{C,}{}^{119}{}_{Sn}$ = 18.6 Hz), 29.2, 29.3, 30.6, 31.9, 34.5 ($J_{C,}{}^{119}{}_{Sn}$ = 58.1 Hz), 34.9, 125.6 ($J_{C,}{}^{119}{}_{Sn}$ = 41.7 Hz), 127.4, 127.9, 129.5, 136.9 ($J_{C,}{}^{119}{}_{Sn}$ = 32.9 Hz), 140.8, 144.3, 152.7. **HRMS** (ESI) calcd for $C_{38}H_{71}{}^{120}Sn$ $[M+H]^+$ 647.4578, found 647.4565.




**3ea**

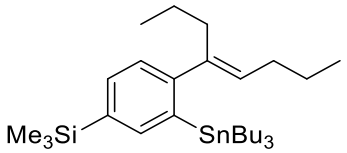
**Compound 3ea.** (Table 3.2, entry 5, 87% yield, colorless oil). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.88 (t, $J_{H,H}$ = 7.3 Hz, 9H), 0.89 (t, $J_{H,H}$ = 7.3 Hz, 3H), 0.96 (t, $J_{H,H}$ = 7.3 Hz, 3H), 0.98 (t, $J_{H,H}$ = 7.8 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 49.6 Hz, 6H), 1.32 (sext, $J_{H,H}$ = 7.3 Hz, 6H), 1.28–1.40 (m, 2H), 1.41–1.54 (m, 8H), 2.12 (q, $J_{H,H}$ = 7.4 Hz, 2H), 2.30 (t, $J_{H,H}$ = 8.2 Hz, 2H), 2.32 (s, 3H), 5.25 (t, $J_{H,H}$ = 7.0 Hz, 1H), 7.02–7.08

(m, 2H), 7.21 (s, $J_{H,}{}^{119}{}_{Sn}$ = 44.3 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 10.8 ($J_{C,}{}^{119}{}_{Sn}$ = 338.7 Hz, $J_{C,}{}^{117}{}_{Sn}$ = 323.7 Hz), 13.6, 14.1, 14.4, 21.1, 21.6, 23.0, 27.5 ($J_{C,}{}^{119}{}_{Sn}$ = 62.3 Hz, $J_{C,}{}^{117}{}_{Sn}$ = 59.4 Hz), 29.2 ($J_{C,}{}^{119}{}_{Sn}$ = 18.7 Hz), 30.6, 35.0, 127.7 ($J_{C,}{}^{119}{}_{Sn}$ = 37.0 Hz), 128.3, 129.4, 134.8, 137.6, 140.5, 144.1, 149.8. **HRMS** (ESI) calcd for $C_{27}H_{48}Na^{120}Sn$ $[M+Na]^+$ 515.2676, found 515.2684.



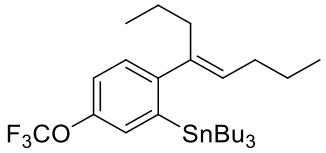

**3fa**

**Compound 3fa.** (Table 3.2, entry 6, 91% yield, colorless oil). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 0.89 (t, $J_{H,H}$ = 7.3 Hz, 9H), 0.92 (t, $J_{H,H}$ = 7.4 Hz, 3H), 0.98 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.02 (t, $J_{H,H}$ = 8.3 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 47.2 Hz, 6H), 1.33 (sext, $J_{H,H}$ = 7.3 Hz, 6H), 1.32–1.42 (m, 2H), 1.44–1.55 (m, 8H), 2.16 (q, $J_{H,H}$ = 7.4 Hz, 2H), 2.35 (t, $J_{H,H}$ = 8.0 Hz, 2H), 5.32 (t, $J_{H,H}$ = 7.0 Hz, 1H), 7.23 (d, $J_{H,H}$ = 8.0 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 16.0 Hz, 1H), 7.32 (t, $J_{H,H}$ = 7.3 Hz, 1H), 7.43 (t, $J_{H,H}$ = 7.7 Hz, 2H), 7.45 (d, $J_{H,H}$ = 8.0 Hz, 1H), 7.58 (d, $J_{H,H}$ = 7.1 Hz, 2H), 7.63 (d, $J_{H,H}$ = 1.9 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 43.6 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 11.0 ($J_{C,}{}^{119}{}_{Sn}$ = 339.7 Hz, $J_{C,}{}^{117}{}_{Sn}$ = 324.9 Hz), 13.7, 14.1, 14.5, 21.7, 23.0, 27.5 ($J_{C,}{}^{119}{}_{Sn}$ = 61.4 Hz), 29.2 ($J_{C,}{}^{119}{}_{Sn}$ = 18.7 Hz), 30.6, 34.9, 126.4 ($J_{C,}{}^{119}{}_{Sn}$ = 9.7 Hz), 126.9, 127.1, 128.1 ($J_{C,}{}^{119}{}_{Sn}$ = 36.1 Hz), 128.7, 129.7, 135.6 ($J_{C,}{}^{119}{}_{Sn}$ = 32.9 Hz), 138.2, 141.3, 141.5, 144.0 ($J_{C,}{}^{119}{}_{Sn}$ = 13.9 Hz), 151.8. **HRMS** (ESI) calcd for $C_{32}H_{50}Na^{120}Sn$ $[M+Na]^+$ 577.2832, found 577.2823.




**3ga**

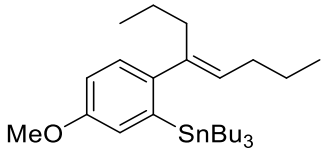
**Compound 3ga.** (Table 3.2, entry 7, 83% yield, colorless oil). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 0.26 (s, 9H), 0.89 (t, $J_{H,H}$ = 7.2 Hz, 9H+3H), 0.96 (t, $J_{H,H}$ = 7.4 Hz, 3H), 0.99 (t, $J_{H,H}$ = 8.4 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 48.8 Hz, 6H), 1.33 (sext, $J_{H,H}$ = 7.3 Hz, 6H+2H), 1.43–1.53 (m, 8H), 2.14 (q, $J_{H,H}$ = 7.4 Hz, 2H), 2.32 (t, $J_{H,H}$ = 8.0 Hz, 2H), 5.27 (t, $J_{H,H}$ = 7.0 Hz, 1H), 7.15 (d, $J_{H,H}$ = 7.5 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 15.0 Hz, 1H), 7.39 (dd, $J_{H,H}$ = 7.5 Hz, 1.4 Hz, 1H), 7.58 (s, $J_{H,}{}^{119}{}_{Sn}$ = 42.3 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ –1.0, 11.0 ($J_{C,}{}^{119}{}_{Sn}$ = 337.9 Hz, $J_{C,}{}^{117}{}_{Sn}$ = 322.1 Hz), 13.7, 14.1, 14.4, 21.7, 22.9, 27.5 ($J_{C,}{}^{119}{}_{Sn}$ = 60.1 Hz), 29.2 ($J_{C,}{}^{119}{}_{Sn}$ = 19.5 Hz), 30.6, 34.8, 127.2, 129.7, 132.6, 136.7, 139.7, 142.2, 144.3, 153.1. **HRMS** (ESI) calcd for $C_{29}H_{54}NaSi^{120}Sn$ $[M+Na]^+$ 573.2914, found 573.2903.




**3ha**

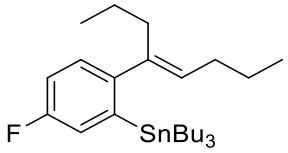
**Compound 3ha.** (Table 3.2, entry 8, 83% yield, colorless oil). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 0.88 (t, $J_{H,H}$ = 7.2 Hz, 9H), 0.90 (t, $J_{H,H}$ = 7.1 Hz, 3H), 0.97 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.01 (t, $J_{H,H}$ = 8.2 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 49.9 Hz, 6H), 1.32 (sext, $J_{H,H}$ = 7.2 Hz, 6H+2H), 1.43–1.54 (m, 8H), 2.13 (q, $J_{H,H}$ = 7.4 Hz, 2H), 2.30 (t, $J_{H,H}$ = 8.0 Hz, 2H), 5.27 (t, $J_{H,H}$ = 7.1 Hz, 1H), 7.04 (dd, $J_{H,H}$ = 8.4 Hz, 1.4 Hz, 1H), 7.14 (d, $J_{H,H}$ = 8.4 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 16.5 Hz, 1H), 7.23 (d, $J_{H,H}$ = 1.5 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 43.4 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 11.0 ($J_{C,}{}^{119}{}_{Sn}$ = 343.7 Hz, $J_{C,}{}^{117}{}_{Sn}$ = 328.4

Hz), 13.6, 14.1, 14.3, 21.5, 22.9, 27.4 ($J_{C,}^{119}_{Sn}$ = 62.7 Hz, $J_{C,}^{117}_{Sn}$ = 59.2 Hz), 29.0 ($J_{C,}^{119}_{Sn}$ = 19.2 Hz), 30.6, 34.9, 119.7, 120.6 (q, $J_{C,}^{19}_{F}$ = 256.5 Hz), 128.6 ($J_{C,}^{119}_{Sn}$ = 34.4 Hz), 128.9 ($J_{C,}^{119}_{Sn}$ = 37.0 Hz), 130.2, 143.3 ($J_{C,}^{119}_{Sn}$ = 13.1 Hz), 143.4 ($J_{C,}^{119}_{Sn}$ = 380.6 Hz, $J_{C,}^{117}_{Sn}$ = 343.7 Hz), 147.3, 151.2 ($J_{C,}^{119}_{Sn}$ = 25.0 Hz). **HRMS** (ESI) calcd for $C_{27}H_{45}F_3ONa^{120}Sn$ $[M+Na]^+$ 585.2342, found 585.2335.




**3ia**

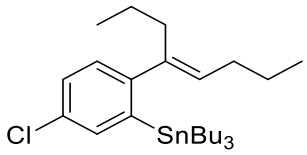
**Compound 3ia.** (Table 3.2, entry 9, 65% yield, colorless oil). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.88 (t, $J_{H,H}$ = 7.3 Hz, 9H), 0.89 (t, $J_{H,H}$ = 7.3 Hz, 3H), 0.96 (t, $J_{H,H}$ = 7.4 Hz, 3H), 0.98 (t, $J_{H,H}$ = 8.4 Hz, $J_{H,}^{119}_{Sn}$ = 50.5 Hz, 6H), 1.32 (sext, $J_{H,H}$ = 7.3 Hz, 6H+2H), 1.42–1.52 (m, 8H), 2.11 (q, $J_{H,H}$ = 7.4 Hz, 2H), 2.29 (t, $J_{H,H}$ = 8.0 Hz, 2H), 3.80 (s, 3H), 5.24 (t, $J_{H,H}$ = 7.0 Hz, 1H), 6.76 (dd, $J_{H,H}$ = 8.4 Hz, 2.8 Hz, 1H), 6.97 (d, $J_{H,H}$ = 2.8 Hz, $J_{H,}^{119}_{Sn}$ = 46.6 Hz, 1H), 7.09 (d, $J_{H,H}$ = 8.4 Hz, $J_{H,}^{119}_{Sn}$ = 17.6 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 10.9 ($J_{C,}^{119}_{Sn}$ = 340.5 Hz, $J_{C,}^{117}_{Sn}$ = 325.5 Hz), 13.6, 14.1, 14.4, 21.6, 23.0, 27.5 ($J_{C,}^{119}_{Sn}$ = 60.6 Hz), 29.1 ($J_{C,}^{119}_{Sn}$ = 18.9 Hz), 30.6, 35.0, 55.1, 112.2, 122.4, 128.6, 129.3, 142.2, 143.8, 145.2, 157.2. **HRMS** (ESI) calcd for $C_{27}H_{48}ONa^{120}Sn$ $[M+Na]^+$ 531.2625, found 531.2617.




**3ja**

**Compound 3ja.** (Table 3.2, entry 10, 77% yield, colorless oil). **$^1$H NMR**

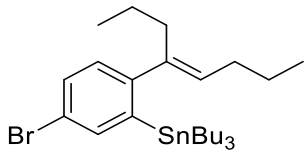
(400 MHz, $CDCl_3$) δ 0.886 (t, $J_{H,H}$ = 7.3 Hz, 9H), 0.894 (t, $J_{H,H}$ = 7.3 Hz, 3H), 0.97 (t, $J_{H,H}$ = 7.4 Hz, 3H), 0.99 (t, $J_{H,H}$ = 8.3 Hz, $J_{H,}{}^{119}_{Sn}$ = 50.9 Hz, 6H), 1.32 (sext, $J_{H,H}$ = 7.3 Hz, 6H), 1.27–1.37 (m, 2H), 1.41–1.53 (m, 8H), 2.12 (q, $J_{H,H}$ = 7.4 Hz, 2H), 2.28 (t, $J_{H,H}$ = 8.0 Hz, 2H), 5.24 (t, $J_{H,H}$ = 7.0 Hz, 1H), 6.88 (td, $J_{H,H}$ = $J_{H,}{}^{19}_{F}$ = 8.6 Hz, 2.8 Hz, 1H), 7.09 (dd, $J_{H,H}$ = 2.0 Hz, $J_{H,}{}^{19}_{F}$ = 8.4 Hz, $J_{H,}{}^{119}_{Sn}$ = 43.6 Hz, 1H), 7.10 (d, $J_{H,H}$ = 8.3 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 10.9 ($J_{C,}{}^{119}_{Sn}$ = 343.0 Hz, $J_{C,}{}^{117}_{Sn}$ = 327.7 Hz), 13.6, 14.1, 14.4, 21.5, 22.9, 27.4 ($J_{C,}{}^{119}_{Sn}$ = 61.7 Hz), 29.1 ($J_{C,}{}^{119}_{Sn}$ = 19.1 Hz), 30.6, 35.0, 114.0 (d, $J_{C,}{}^{19}_{F}$ = 20.9 Hz, $J_{C,}{}^{119}_{Sn}$ = 8.7 Hz), 122.7 (d, $J_{C,}{}^{19}_{F}$ = 17.5 Hz, $J_{C,}{}^{119}_{Sn}$ = 34.1 Hz), 129.2 (d, $J_{C,}{}^{19}_{F}$ = 6.5 Hz, $J_{C,}{}^{119}_{Sn}$ = 39.4 Hz), 129.9, 143.4 ($J_{C,}{}^{119}_{Sn}$ = 13.2 Hz), 143.6 (d, $J_{C,}{}^{19}_{F}$ = 2.1 Hz), 148.4 (d, $J_{C,}{}^{19}_{F}$ = 3.1 Hz, $J_{C,}{}^{119}_{Sn}$ = 25.8 Hz), 161.1 (d, $J_{C,}{}^{19}_{F}$ = 248.6 Hz). **HRMS** (ESI) calcd for $C_{26}H_{45}FNa^{120}Sn$ $[M+Na]^+$ 519.2425, found 519.2407.




**3ka**

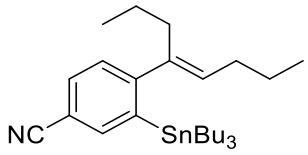
**Compound 3ka.** (Table 3.2, entry 12, 84% yield, colorless oil). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.89 (t, $J_{H,H}$ = 7.3 Hz, 9H+3H), 0.96 (t, $J_{H,H}$ = 7.3 Hz, 3H), 1.00 (t, $J_{H,H}$ = 8.3 Hz, $J_{H,}{}^{119}_{Sn}$ = 51.7 Hz, 6H), 1.32 (sext, $J_{H,H}$ = 7.3 Hz, 6H+2H), 1.42–1.51 (m, 8H), 2.12 (q, $J_{H,H}$ = 7.4 Hz, 2H), 2.28 (t, $J_{H,H}$ = 8.0 Hz, 2H), 5.25 (t, $J_{H,H}$ = 7.0 Hz, 1H), 7.06 (d, $J_{H,H}$ = 8.2 Hz, $J_{H,}{}^{119}_{Sn}$ = 16.2 Hz, 1H), 7.18 (dd, $J_{H,H}$ = 8.2 Hz, 2.3 Hz, 1H), 7.34 (d, $J_{H,H}$ = 2.3 Hz, $J_{H,}{}^{119}_{Sn}$ = 42.1 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 10.9 ($J_{C,}{}^{119}_{Sn}$ = 342.6 Hz, $J_{C,}{}^{117}_{Sn}$ = 327.6 Hz), 13.6, 14.1, 14.4, 21.5, 22.9, 27.4 ($J_{C,}{}^{119}_{Sn}$ = 62.1 Hz), 29.1 ($J_{C,}{}^{119}_{Sn}$ = 19.0 Hz), 30.5, 34.8, 127.4 ($J_{C,}{}^{119}_{Sn}$ = 8.5 Hz), 129.2 ($J_{C,}{}^{119}_{Sn}$ = 35.7 Hz), 130.0, 132.0 ($J_{C,}{}^{119}_{Sn}$ = 53.4 Hz),

136.1 ($J_{C,}^{119}{}_{Sn}$ = 34.6 Hz), 143.3($J_{C,}^{119}{}_{Sn}$ = 13.0 H), 143.4, 150.8 ($J_{C,}^{119}{}_{Sn}$ = 25.4 Hz). **HRMS** (ESI) calcd for $C_{26}H_{45}NaCl^{120}Sn$ $[M+Na]^+$ 535.2129, found 535.2140.




**3la**

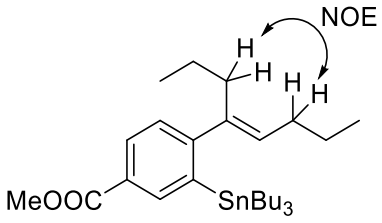
**Compound 3la.** (Table 3.2, entry 14, 78% yield, colorless oil). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.89 (t, $J_{H,H}$ = 7.3 Hz, 9H+3H), 0.96 (t, $J_{H,H}$ = 7.3 Hz, 3H), 1.00 (t, $J_{H,H}$ = 8.3 Hz, $J_{H,}^{119}{}_{Sn}$ = 51.2 Hz, 6H), 1.32 (sext, $J_{H,H}$ = 7.3 Hz, 6H+2H), 1.42–1.51 (m, 8H), 2.12 (q, $J_{H,H}$ = 7.3 Hz, 2H), 2.28 (t, $J_{H,H}$ = 8.0 Hz, 2H), 5.26 (t, $J_{H,H}$ = 7.0 Hz, 1H), 7.00 (d, $J_{H,H}$ = 8.1 Hz, $J_{H,}^{119}{}_{Sn}$ = 16.1 Hz, 1H), 7.32 (dd, $J_{H,H}$ = 8.2 Hz, 2.2 Hz, 1H), 7.48 (d, $J_{H,H}$ = 2.1 Hz, $J_{H,}^{119}{}_{Sn}$ = 41.4 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 11.0 ($J_{C,}^{119}{}_{Sn}$ = 343.0 Hz, $J_{C,}^{117}{}_{Sn}$ = 327.1 Hz), 13.6, 14.1, 14.4, 21.5, 22.9, 27.4 ($J_{C,}^{119}{}_{Sn}$ = 61.5 Hz), 29.1 ($J_{C,}^{119}{}_{Sn}$ = 19.2 Hz), 30.5, 34.8, 120.7, 129.7, 130.0, 130.3, 139.0, 143.3, 144.1, 151.2. **HRMS** (ESI) calcd for $C_{26}H_{45}NaBr^{120}Sn$ $[M+Na]^+$ 579.1624, found 579.1625.




**3ma**

**Compound 3ma.** (Table 3.2, entry 16, 67% yield, colorless oil). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.886 (t, $J_{H,H}$ = 7.3 Hz, 9H), 0.892 (t, $J_{H,H}$ = 7.3 Hz, 3H), 0.97 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.01 (t, $J_{H,H}$ = 8.3 Hz, $J_{H,}^{119}{}_{Sn}$ = 51.2 Hz, 6H), 1.31 (sext, $J_{H,H}$ = 7.3 Hz, 6H), 1.25–1.36 (m, 2H), 1.41–1.50 (m, 8H), 2.14 (q, $J_{H,H}$ = 7.4 Hz,

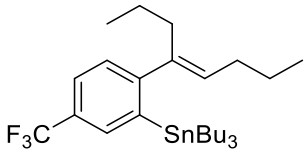
2H), 2.31 (t, $J_{H,H}$ = 8.0 Hz, 2H), 5.28 (t, $J_{H,H}$ = 7.1 Hz, 1H), 7.20 (d, $J_{H,H}$ = 7.9 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 14.4 Hz, 1H), 7.50 (dd, $J_{H,H}$ = 7.9 Hz, 1.8 Hz, 1H), 7.66 (d, $J_{H,H}$ = 1.7 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 39.2 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 11.0 ($J_{C,}{}^{119}{}_{Sn}$ = 345.3 Hz, $J_{C,}{}^{117}{}_{Sn}$ = 329.8 Hz), 13.6, 14.1, 14.3, 21.6, 22.8, 27.3 ($J_{C,}{}^{119}{}_{Sn}$ = 62.3 Hz), 29.0 ($J_{C,}{}^{119}{}_{Sn}$ = 19.3 Hz), 30.5, 34.5, 109.6 ($J_{C,}{}^{119}{}_{Sn}$ = 44.8 Hz), 119.8, 128.2 ($J_{C,}{}^{119}{}_{Sn}$ = 30.9 Hz), 131.0, 131.1 ($J_{C,}{}^{119}{}_{Sn}$ = 8.5 Hz), 140.3 ($J_{C,}{}^{119}{}_{Sn}$ = 35.6 Hz), 142.9, 143.5 ($J_{C,}{}^{119}{}_{Sn}$ = 12.2 H), 157.2 ($J_{C,}{}^{119}{}_{Sn}$ = 24.8 Hz). **HRMS** (ESI) calcd for $C_{27}H_{45}NNa^{120}Sn$ $[M+Na]^+$ 526.2472, found 526.2480.




**3na**

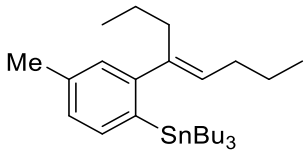
**Compound 3na.** (Table 3.2, entry 18, 82% yield, colorless oil). The *E* geometry was assigned by NOESY NMR study. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 0.88 (t, $J_{H,H}$ = 7.3 Hz, 9H), 0.89 (t, $J_{H,H}$ = 7.3 Hz, 3H), 0.97 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.02 (t, $J_{H,H}$ = 8.3 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 49.9 Hz, 6H), 1.32 (sext, $J_{H,H}$ = 7.3 Hz, 6H+2H), 1.42–1.53 (m, 8H), 2.14 (q, $J_{H,H}$ = 7.4 Hz, 2H), 2.33 (t, $J_{H,H}$ = 8.0 Hz, 2H), 3.90 (s, 3H), 5.30 (t, $J_{H,H}$ = 7.0 Hz, 1H), 7.20 (d, $J_{H,H}$ = 8.0 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 15.0 Hz, 1H), 7.87 (dd, $J_{H,H}$ = 8.0 Hz, 1.8 Hz, 1H), 8.09 (d, $J_{H,H}$ = 1.8 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 43.2 Hz, 1H); **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 10.9 ($J_{C,}{}^{119}{}_{Sn}$ = 342.4 Hz, $J_{C,}{}^{117}{}_{Sn}$ = 327.3 Hz), 13.6, 14.1, 14.3, 21.6, 22.9, 27.4 ($J_{C,}{}^{119}{}_{Sn}$ = 62.3 Hz, $J_{C,}{}^{117}{}_{Sn}$ = 59.6 Hz), 29.1 ($J_{C,}{}^{119}{}_{Sn}$ = 19.1 Hz), 30.6, 34.6, 51.9, 127.1 ($J_{C,}{}^{119}{}_{Sn}$ = 41.3 Hz), 127.8 ($J_{C,}{}^{119}{}_{Sn}$ = 32.9 Hz), 128.8 ($J_{C,}{}^{119}{}_{Sn}$ = 8.8 Hz), 130.3, 138.1 ($J_{C,}{}^{119}{}_{Sn}$ = 35.4 Hz), 141.2, 143.9 ($J_{C,}{}^{119}{}_{Sn}$ = 13.1 Hz), 157.5 ($J_{C,}{}^{119}{}_{Sn}$ = 27.5 Hz), 167.6. **HRMS** (ESI) calcd for

$C_{28}H_{48}O_2Na^{120}Sn$ $[M+Na]^+$ 559.2574, found 559.2605.




**3oa**

**Compound 3oa.** (Table 3.2, entry 19, 69% yield, colorless oil). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.89 (t, $J_{H,H}$ = 7.3 Hz, 9H), 0.90 (t, $J_{H,H}$ = 7.2 Hz, 3H), 0.97 (t, $J_{H,H}$ = 7.3 Hz, 3H), 1.02 (t, $J_{H,H}$ = 8.3 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 52.2 Hz, 6H), 1.32 (sext, $J_{H,H}$ = 7.3 Hz, 6H), 1.27–1.37 (m, 2H), 1.42–1.52 (m, 8H), 2.15 (q, $J_{H,H}$ = 7.4 Hz, 2H), 2.32 (t, $J_{H,H}$ = 8.0 Hz, 2H), 5.29 (t, $J_{H,H}$ = 7.1 Hz, 1H), 7.23 (d, $J_{H,H}$ = 7.9 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 14.5 Hz, 1H), 7.46 (dd, $J_{H,H}$ = 8.0 Hz, 1.5 Hz, 1H), 7.63 (s, $J_{H,}{}^{119}{}_{Sn}$ = 42.4 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 10.9 ($J_{C,}{}^{119}{}_{Sn}$ = 343.6 Hz, $J_{C,}{}^{117}{}_{Sn}$ = 328.7 Hz), 13.6, 14.1, 14.4, 21.6, 22.9, 27.4 ($J_{C,}{}^{119}{}_{Sn}$ = 62.0 Hz), 29.1 ($J_{C,}{}^{119}{}_{Sn}$ = 19.2 Hz), 30.5, 34.7, 124.4 (q, $J_{C,}{}^{19}{}_{F}$ = 3.8 Hz), 124.7 (q, $J_{C,}{}^{19}{}_{F}$ = 272.2 Hz), 127.5 (q, $J_{C,}{}^{19}{}_{F}$ = 31.6 Hz), 127.9, 130.5, 133.2 (q, $J_{C,}{}^{19}{}_{F}$ = 3.4 Hz), 142.0, 143.6, 156.2. **HRMS** (ESI) calcd for $C_{27}H_{45}F_3Na^{120}Sn$ $[M+Na]^+$ 569.2393, found 569.2371.



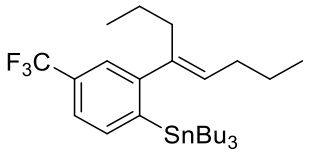

**3pa**

**Compound 3pa.** (Table 3.2, entry 20, 77% yield, colorless oil). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.88 (t, $J_{H,H}$ = 7.3 Hz, 9H+3H), 0.97 (t, $J_{H,H}$ = 8.2 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 50.2 Hz, 6H), 0.97 (t, $J_{H,H}$ = 8.2 Hz, 3H), 1.32 (sext, $J_{H,H}$ = 7.4 Hz, 6H), 1.29–1.38 (m, 2H) 1.43–1.53 (m, 8H), 2.13 (q, $J_{H,H}$ = 7.4 Hz, 2H), 2.31 (t, $J_{H,H}$ = 8.2 Hz, 2H), 2.32 (s, 3H), 5.26 (t, $J_{H,H}$ = 7.0 Hz, 1H), 6.99 (s, 1H), 7.02 (d, $J_{H,H}$ = 7.5 Hz,

1H), 7.31 (d, $J_{H,H}$ = 7.4 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 42.9 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 10.8 ($J_{C,}{}^{119}{}_{Sn}$ = 339.9 Hz, $J_{C,}{}^{117}{}_{Sn}$ = 324.5 Hz), 13.6, 14.1, 14.4, 21.3, 21.7, 23.0, 27.5 ($J_{C,}{}^{119}{}_{Sn}$ = 61.0 Hz), 29.2 ($J_{C,}{}^{119}{}_{Sn}$ = 18.6 Hz), 30.6, 34.9, 126.6 ($J_{C,}{}^{119}{}_{Sn}$ = 44.5 Hz), 128.8 ($J_{C,}{}^{119}{}_{Sn}$ = 36.6 Hz), 129.4, 136.7, 136.9, 137.1, 144.4 ($J_{C,}{}^{119}{}_{Sn}$ = 14.5 Hz), 152.7 ($J_{C,}{}^{119}{}_{Sn}$ = 29.1 Hz). **HRMS** (ESI) calcd for $C_{27}H_{48}Na^{120}Sn$ $[M+Na]^+$ 515.2676, found 515.2698.

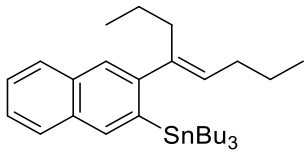

**3qa**

**Compound 3qa.** (Table 3.2, entry 21, 84% yield, colorless oil). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 0.27 (s, 9H), 0.90 (t, $J_{H,H}$ = 7.3 Hz, 9H), 0.92 (t, $J_{H,H}$ = 7.4 Hz, 3H), 0.987 (t, $J_{H,H}$ = 7.2 Hz, 3H), 0.993 (t, $J_{H,H}$ = 8.4 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 50.7 Hz, 6H), 1.33 (sext, $J_{H,H}$ = 7.3 Hz, 6H), 1.33–1.41 (m, 2H), 1.44–1.52 (m, 8H), 2.15 (q, $J_{H,H}$ = 7.4 Hz, 2H), 2.33 (t, $J_{H,H}$ = 8.0 Hz, 2H), 5.28 (t, $J_{H,H}$ = 7.0 Hz, 1H), 7.28 (s, $J_{H,}{}^{119}{}_{Sn}$ = 16.4 Hz, 1H), 7.34 (d, $J_{H,H}$ = 7.2 Hz, 1H), 7.43 (d, $J_{H,H}$ = 7.1 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 43.0 Hz, 1H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ –1.1, 10.8 ($J_{C,}{}^{119}{}_{Sn}$ = 339.0 Hz, $J_{C,}{}^{117}{}_{Sn}$ = 323.9 Hz), 13.6, 14.2, 14.4, 21.6, 23.0, 27.5 ($J_{C,}{}^{119}{}_{Sn}$ = 60.4 Hz), 29.2 ($J_{C,}{}^{119}{}_{Sn}$ = 18.5 Hz), 30.6, 35.0, 129.5, 130.5, 132.6, 136.3, 139.1, 141.6, 144.5, 151.8. **HRMS** (ESI) calcd for $C_{29}H_{54}NaSi^{120}Sn$ $[M+Na]^+$ 573.2914, found 573.2917.




**3ra**

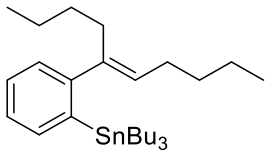
**Compound 3ra.** (Table 3.2, entry 22, 67% yield, colorless oil). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 0.89 (t, $J_{H,H}$ = 7.3 Hz, 9H), 0.91 (t, $J_{H,H}$ = 7.4 Hz, 3H), 0.98 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.02 (t, $J_{H,H}$ = 8.2 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 50.0 Hz, 6H), 1.32 (sext, $J_{H,H}$ = 7.3 Hz, 6H), 1.26–1.42 (m, 2H), 1.42–1.51 (m, 8H), 2.15 (q, $J_{H,H}$ = 7.4 Hz, 2H), 2.32 (t, $J_{H,H}$ = 8.0 Hz, 2H), 5.29 (t, $J_{H,H}$ = 7.0 Hz, 1H), 7.34 (s, 1H), 7.40 (d, $J_{H,H}$ = 7.6 Hz, 1H), 7.53 (d, $J_{H,H}$ = 7.6 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 40.0 Hz, 1H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 10.9 ($J_{C,}{}^{119}{}_{Sn}$ = 343.1 Hz, $J_{C,}{}^{117}{}_{Sn}$ = 328.1 Hz), 13.6, 14.1, 14.4, 21.6, 22.9, 27.4 ($J_{C,}{}^{119}{}_{Sn}$ = 61.7 Hz), 29.1 ($J_{C,}{}^{119}{}_{Sn}$ = 19.2 Hz), 30.6, 34.8, 121.8 (q, $J_{C,}{}^{19}{}_{F}$ = 3.7 Hz, $J_{C,}{}^{119}{}_{Sn}$ = 41.0 Hz), 124.1 (q, $J_{C,}{}^{19}{}_{F}$ = 3.6 Hz, $J_{C,}{}^{119}{}_{Sn}$ = 34.0 Hz), 124.4 (q, $J_{C,}{}^{19}{}_{F}$ = 272.2 Hz), 129.6 (q, $J_{C,}{}^{19}{}_{F}$ = 31.8 Hz), 130.6, 137.1 ($J_{C,}{}^{119}{}_{Sn}$ = 33.0 Hz), 143.4 ($J_{C,}{}^{119}{}_{Sn}$ = 13.0 Hz), 146.3, 153.2 ($J_{C,}{}^{119}{}_{Sn}$ = 28.2 Hz). **HRMS** (ESI) calcd for $C_{27}H_{45}F_3Na^{120}Sn$ $[M+Na]^+$ 569.2393, found 569.2393.




**3sa**

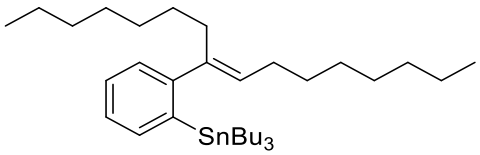
**Compound 3sa.** (Table 3.2, entry 23, 83% yield, colorless oil). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 0.89 (t, $J_{H,H}$ = 7.3 Hz, 9H+3H), 1.00 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.06 (t, $J_{H,H}$ = 8.3 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 50.8 Hz, 6H), 1.34 (sext, $J_{H,H}$ = 7.3 Hz, 6H), 1.25–1.41 (m, 2H), 1.47–1.54 (m, 8H), 2.19 (q, $J_{H,H}$ = 7.4 Hz, 2H), 2.39 (t, $J_{H,H}$ = 7.9 Hz, 2H), 5.38 (t, $J_{H,H}$ = 7.0 Hz, 1H), 7.40–7.45 (m, 2H), 7.56 (s, $J_{H,}{}^{119}{}_{Sn}$ = 14.3 Hz, 1H), 7.73–7.80 (m, 2H), 7.89 (s, $J_{H,}{}^{119}{}_{Sn}$ = 48.3 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 11.0 ($J_{C,}{}^{119}{}_{Sn}$ = 340.0 Hz, $J_{C,}{}^{117}{}_{Sn}$ = 325.2 Hz), 13.7, 14.2, 14.3, 21.6, 23.0, 27.5 ($J_{C,}{}^{119}{}_{Sn}$ = 62.1 Hz), 29.2 ($J_{C,}{}^{119}{}_{Sn}$ = 19.0 Hz), 30.6, 34.8, 125.2, 125.7, 125.9, 127.3, 127.5, 129.9, 131.7, 133.0, 137.1 ($J_{C,}{}^{119}{}_{Sn}$ = 30.6 Hz), 140.0,

144.1($J_{C,}{}^{119}{}_{Sn}$ = 11.6 Hz), 149.3. **HRMS** (ESI) calcd for $C_{30}H_{48}Na^{120}Sn$ $[M+Na]^+$ 551.2676, found 551.2660.




**3ab**

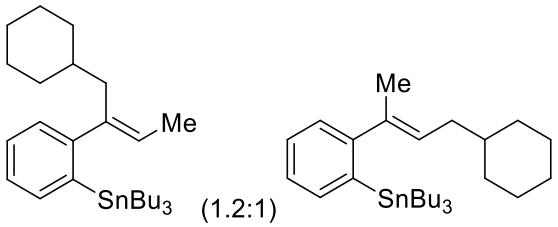
**Compound 3ab.** (Table 3.3, 84% yield, colorless oil). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.88 (t, $J_{H,H}$ = 7.0 Hz, 3H), 0.89 (t, $J_{H,H}$ = 7.3 Hz, 9H), 0.94 (t, $J_{H,H}$ = 7.1 Hz, 3H), 0.99 (t, $J_{H,H}$ = 8.3 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 50.6 Hz, 6H), 1.28–1.52 (m, 20H), 2.16 (q, $J_{H,H}$ = 7.1 Hz, 2H), 2.34 (t, $J_{H,H}$ = 7.5 Hz, 2H), 5.25 (t, $J_{H,H}$ = 7.0 Hz, 1H), 7.16 (d, $J_{H,H}$ = 7.4 Hz, 1.3 Hz, 1H), 7.19 (td, $J_{H,H}$ = 7.1 Hz, 1.6 Hz, 1H), 7.24 (td, $J_{H,H}$ = 7.3 Hz, 1.7 Hz, 1H), 7.42 (dd, $J_{H,H}$ = 7.0 Hz, 1.3 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 43.0 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 10.9 ($J_{C,}{}^{119}{}_{Sn}$ = 339.7 Hz, $J_{C,}{}^{117}{}_{Sn}$ = 324.5 Hz), 13.6, 13.9, 14.0, 22.6, 23.1, 27.5 ($J_{C,}{}^{119}{}_{Sn}$ = 61.0 Hz), 28.1, 29.2 ($J_{C,}{}^{119}{}_{Sn}$ = 18.9 Hz), 30.6, 32.0, 32.5, 125.6 ($J_{C,}{}^{119}{}_{Sn}$ = 42.6 Hz), 127.5 ($J_{C,}{}^{119}{}_{Sn}$ = 9.5 Hz), 127.9 ($J_{C,}{}^{119}{}_{Sn}$ = 34.8 Hz), 129.6, 136.9 ($J_{C,}{}^{119}{}_{Sn}$ = 30.5 Hz), 140.7 ($J_{C,}{}^{119}{}_{Sn}$ = 413.7 Hz, $J_{C,}{}^{117}{}_{Sn}$ = 395.4 Hz), 144.4 ($J_{C,}{}^{119}{}_{Sn}$ = 14.4 Hz), 152.7 ($J_{C,}{}^{119}{}_{Sn}$ = 28.3 Hz). **HRMS** (ESI) calcd for $C_{28}H_{50}Na^{120}Sn$ $[M+Na]^+$ 529.2832, found 529.2819.




**3ac**

**Compound 3ac.** (Table 3.3, 83% yield, colorless oil). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.89 (t, $J_{H,H}$ = 7.2 Hz, 9H), 0.85–0.92 (m, 6H), 0.99 (t, $J_{H,H}$ = 8.3 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 50.8 Hz, 6H), 1.18–1.40 (m, 24H), 1.42–1.54 (m, 8H), 2.15 (q, $J_{H,H}$ = 7.2

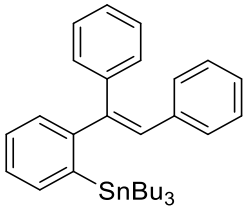
Hz, 2H), 2.33 (t, $J_{H,H}$ = 7.5 Hz, 2H), 5.25 (t, $J_{H,H}$ = 7.0 Hz, 1H), 7.16 (d, $J_{H,H}$ = 7.4 Hz, 1H), 7.19 (td, $J_{H,H}$ = 7.1 Hz, 1.5 Hz, 1H), 7.24 (td, $J_{H,H}$ = 7.3 Hz, 1.6 Hz, 1H), 7.42 (dd, $J_{H,H}$ = 7.0 Hz, 1.5 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 42.8 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 10.9 ($J_{C,}{}^{119}{}_{Sn}$ = 339.6 Hz, $J_{C,}{}^{117}{}_{Sn}$ = 324.6 Hz), 13.7, 14.06, 14.09, 22.6, 22.7, 27.5 ($J_{C,}{}^{119}{}_{Sn}$ = 62.1 Hz), 28.5, 29.16, 29.17, 29.3, 29.6, 29.8, 30.0, 31.9, 32.8, 125.6 ($J_{C,}{}^{119}{}_{Sn}$ = 42.3 Hz), 127.4 ($J_{C,}{}^{119}{}_{Sn}$ = 9.4 Hz), 127.9 ($J_{C,}{}^{119}{}_{Sn}$ = 34.9 Hz), 129.6, 136.9 ($J_{C,}{}^{119}{}_{Sn}$ = 32.4 Hz), 140.7 ($J_{C,}{}^{119}{}_{Sn}$ = 414.0 Hz, $J_{C,}{}^{117}{}_{Sn}$ = 395.7 Hz), 144.4 ($J_{C,}{}^{119}{}_{Sn}$ = 14.5 Hz), 152.7 ($J_{C,}{}^{119}{}_{Sn}$ = 28.1 Hz). **HRMS** (ESI) calcd for $C_{34}H_{62}Na^{120}Sn$ $[M+Na]^+$ 613.3771, found 613.3762.




**3ad** **3ad'**

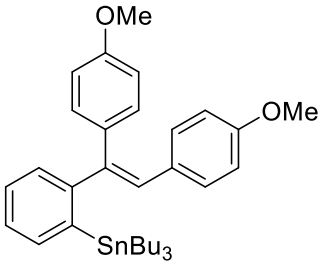
**Compound 3ad:3ad' (1.2:1).** (Table 3.3, 84% yield, colorless oil). **$^1$H NMR** (400 MHz, $CDCl_3$) for **3ad** δ 0.88 (t, $J_{H,H}$ = 7.3 Hz, 9H), 0.83–0.91 (m, 2H), 0.98 (t, $J_{H,H}$ = 8.3 Hz, 6H), 1.32 (sext, $J_{H,H}$ = 7.3 Hz, 6H), 1.10–1.41 (m, 4H), 1.43–1.60 (m, 6H), 1.73 (d, $J_{H,H}$ = 6.8 Hz, 3H), 1.60–1.83 (m, 5H), 2.22 (d, $J_{H,H}$ = 7.1 Hz, 2H), 5.39 (q, $J_{H,H}$ = 6.8 Hz, 1H), 7.10 (dd, $J_{H,H}$ = 7.4 Hz, 1.3 Hz, 1H), 7.16–7.29 (m, 2H), 7.41 (dd, $J_{H,H}$ = 6.9 Hz, 1.6 Hz, 1H); **3ad'** δ 0.89 (t, $J_{H,H}$ = 7.3 Hz, 9H), 0.83–0.91 (m, 2H), 0.97 (t, $J_{H,H}$ = 8.3 Hz, 6H), 1.32 (sext, $J_{H,H}$ = 7.3 Hz, 6H), 1.10–1.40 (m, 4H), 1.43–1.60 (m, 6H), 1.60–1.83 (m, 5H), 1.96 (s, 3H), 2.03 (t, $J_{H,H}$ = 7.0 Hz, 2H), 5.31 (td, $J_{H,H}$ = 7.3 Hz, 1.4 Hz, 1H), 7.16–7.29 (m, 3H), 7.43 (dd, $J_{H,H}$ = 7.0 Hz, 1.4 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) for **3ad** δ 10.7 ($J_{C,}{}^{119}{}_{Sn}$ = 339.4 Hz, $J_{C,}{}^{117}{}_{Sn}$ = 323.9 Hz), 13.6, 14.1, 26.3, 26.6, 27.5 ($J_{C,}{}^{119}{}_{Sn}$ =

60.7 Hz), 29.2 ($J_{C,}^{119}{}_{Sn}$ = 19.0 Hz), 33.6, 36.4, 38.4, 125.5, 127.0, 127.5 ($J_{C,}^{119}{}_{Sn}$ = 10.0 Hz), 128.2, 136.8, 140.5, 143.7, 153.2; **3ad'** δ 10.8 ($J_{C,}^{119}{}_{Sn}$ = 340.9 Hz, $J_{C,}^{117}{}_{Sn}$ = 326.5 Hz), 13.6, 18.9, 26.4, 26.6, 27.5 ($J_{C,}^{119}{}_{Sn}$ = 60.7 Hz), 29.2 ($J_{C,}^{119}{}_{Sn}$ = 19.0 Hz), 33.4, 36.6, 40.1, 124.6, 125.8, 127.6 ($J_{C,}^{119}{}_{Sn}$ = 10.0 Hz), 128.3, 137.0, 140.4, 140.7, 154.0. **HRMS** (ESI) calcd for $C_{28}H_{48}Na^{120}Sn$ $[M+Na]^+$ 527.2676, found 527.2703.



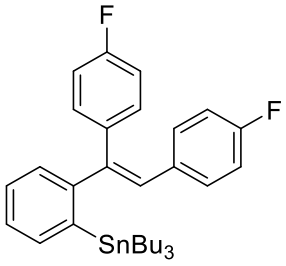

**3ae**

**Compound 3ae.** (Table 3.3, 72% yield, colorless oil). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.83 (t, $J_{H,H}$ = 7.3 Hz, 9H), 0.98 (t, $J_{H,H}$ = 8.3 Hz, $J_{H,}^{119}{}_{Sn}$ = 50.6 Hz, 6H), 1.27 (sext, $J_{H,H}$ = 7.3 Hz, 6H), 1.4–1.5 (m, 6H), 6.58 (s, 1H), 7.01 (dd, $J_{H,H}$ = 7.6 Hz, 1.0 Hz, 1H), 7.05–7.30 (m, 12H), 7.54 (dd, $J_{H,H}$ = 7.2 Hz, 1.1 Hz, $J_{H,}^{119}{}_{Sn}$ = 41.6 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 11.0 ($J_{C,}^{119}{}_{Sn}$ = 342.2 Hz, $J_{C,}^{117}{}_{Sn}$ = 327.0 Hz), 13.6, 27.4 ($J_{C,}^{119}{}_{Sn}$ = 61.6 Hz), 29.2 ($J_{C,}^{119}{}_{Sn}$ = 18.9 Hz), 126.7, 126.8, 127.5, 127.6 ($J_{C,}^{119}{}_{Sn}$ = 9.3 Hz), 128.0, 128.2, 129.4, 129.5, 129.6, 130.6, 137.2, 137.4, 140.8, 142.0, 146.3 ($J_{C,}^{119}{}_{Sn}$ = 14.3 Hz), 152.4 ($J_{C,}^{119}{}_{Sn}$ = 25.1 Hz). **HRMS** (ESI) calcd for $C_{32}H_{42}Na^{120}Sn$ $[M+Na]^+$ 569.2206, found 569.2222.




**3af**

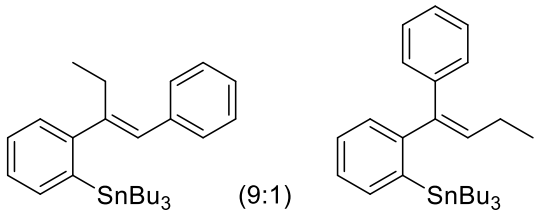
**Compound 3af.** (Table 3.3, 78% yield, colorless oil). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 0.83 (t, $J_{H,H}$ = 7.3 Hz, 9H), 0.96 (t, $J_{H,H}$ = 7.3 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 50.6 Hz, 6H), 1.26 (sext, $J_{H,H}$ = 7.3 Hz, 6H), 1.40–1.48 (m, 6H), 3.78 (s, 3H), 3.81 (s, 3H), 6.43 (s, 1H), 6.72 (d, $J_{H,H}$ = 8.8 Hz, 2H), 6.78 (d, $J_{H,H}$ = 8.8 Hz, 2H), 7.00 (dd, $J_{H,H}$ = 7.6 Hz, 1.1 Hz, 1H), 7.06 (d, $J_{H,H}$ = 8.6 Hz, 2H), 7.11 (d, $J_{H,H}$ = 8.8 Hz, 2H), 7.19 (td, $J_{H,H}$ = 7.4 Hz, 1.5 Hz, 1H), 7.24 (td, $J_{H,H}$ = 7.2 Hz, 1.4 Hz, 1H), 7.52 (dd, $J_{H,H}$ = 7.2 Hz, 1.1 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 41.7 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 11.0 ($J_{C,}{}^{119}{}_{Sn}$ = 341.9 Hz, $J_{C,}{}^{117}{}_{Sn}$ = 326.7 Hz), 13.6, 27.5 ($J_{C,}{}^{119}{}_{Sn}$ = 61.7 Hz), 29.2 ($J_{C,}{}^{119}{}_{Sn}$ = 18.9 Hz), 55.1, 55.2, 113.4, 113.6, 126.5, 127.5 ($J_{C,}{}^{119}{}_{Sn}$ = 9.4 Hz), 128.3, 129.5, 130.2, 130.6, 131.8, 133.3, 137.3 ($J_{C,}{}^{119}{}_{Sn}$ = 32.1 Hz), 142.0, 144.1 ($J_{C,}{}^{119}{}_{Sn}$ = 14.6 Hz), 152.8, 158.3, 158.9. **HRMS** (ESI) calcd for $C_{34}H_{46}O_2Na^{120}Sn$ $[M+Na]^+$ 629.2417, found 629.2411.



**3ag**

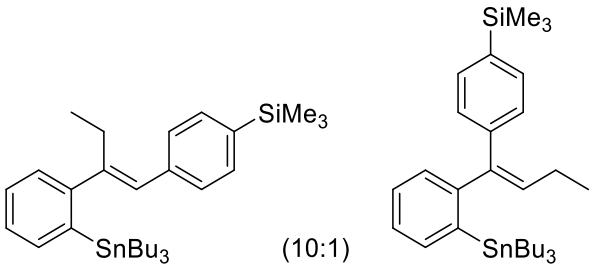
**Compound 3ag.** (Table 3.3, 74% yield, colorless solid). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 0.83 (t, $J_{H,H}$ = 7.3 Hz, 9H), 0.96 (t, $J_{H,H}$ = 8.3 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 52.1 Hz, 6H), 1.26 (sext, $J_{H,H}$ = 7.3 Hz, 6H), 1.40–1.48 (m, 6H), 6.51 (s, 1H), 6.88 (t, $J_{H,H}$ = $J_{H,}{}^{19}{}_{F}$ = 8.7 Hz, 2H), 6.94 (t, $J_{H,H}$ = $J_{H,}{}^{19}{}_{F}$ = 8.7 Hz, 2H), 6.97 (dd, $J_{H,H}$ = 7.1 Hz, 1.0 Hz, 1H), 7.06 (dd, $J_{H,H}$ = 8.6 Hz, $J_{H,}{}^{19}{}_{F}$ = 5.5 Hz, 2H), 7.13 (dd, $J_{H,H}$ = 8.7 Hz, $J_{H,}{}^{19}{}_{F}$ = 5.5 Hz, 2H), 7.20 (td, $J_{H,H}$ = 7.5 Hz, 1.5 Hz, 1H), 7.27 (td, $J_{H,H}$ = 7.3 Hz, 1.4 Hz, 1H), 7.54 (dd, $J_{H,H}$ = 7.2 Hz, 1.2 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 41.5 Hz, 1H); **$^{13}$C NMR**

(100 MHz, $CDCl_3$) δ 11.1 ($J_{C,}{}^{119}{}_{Sn}$ = 343.4 Hz, $J_{C,}{}^{117}{}_{Sn}$ = 326.9 Hz), 13.6, 27.4 ($J_{C,}{}^{119}{}_{Sn}$ = 61.8 Hz), 29.1 ($J_{C,}{}^{119}{}_{Sn}$ = 18.9 Hz), 115.2 (d, $J_{C,}{}^{19}{}_{F}$ = 21.3 Hz), 115.4 (d, $J_{C,}{}^{19}{}_{F}$ = 21.4 Hz), 126.9, 127.7, 128.4, 129.5, 130.9 (d, $J_{C,}{}^{19}{}_{F}$ = 7.9 Hz), 132.3 (d, $J_{C,}{}^{19}{}_{F}$ = 7.9 Hz), 133.2 (d, $J_{C,}{}^{19}{}_{F}$ = 3.2 Hz), 136.4 (d, $J_{C,}{}^{19}{}_{F}$ = 2.6 Hz), 137.5, 142.0, 145.1, 151.9, 161.6 (d, $J_{C,}{}^{19}{}_{F}$ = 247.4 Hz), 162.3 (d, $J_{C,}{}^{19}{}_{F}$ = 247.7 Hz). **HRMS** (ESI) calcd for $C_{32}H_{40}F_2Na^{120}Sn$ $[M+Na]^+$ 605.2018, found 605.2023. The structure of compound **3ag** was confirmed by single crystal X-ray diffraction (Section 3.4.9).



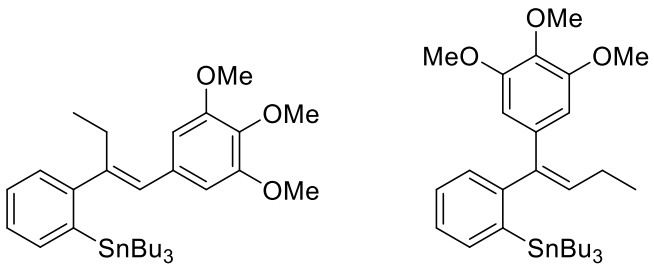

**3ah** **3ah'**

**Compound 3ah:3ah' (9:1).** (Table 3.3, 73% yield, colorless oil). **$^1$H NMR** (400 MHz, $CDCl_3$) for **3ah** δ 0.83 (t, $J_{H,H}$ = 7.3 Hz, 9H), 1.00 (t, $J_{H,H}$ = 8.4 Hz, 6H), 1.04 (t, $J_{H,H}$ = 7.8 Hz, 3H), 1.26 (sext, $J_{H,H}$ = 7.3 Hz, 6H), 1.40–1.50 (m, 6H), 2.68 (q, $J_{H,H}$ = 7.5 Hz, 2H), 6.33 (s, 1H), 7.15–7.38 (m, 8H), 7.49 (d, $J_{H,H}$ = 7.0 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 42.7 Hz, 1H), (**3ah'** δ 1.12 (t, $J_{H,H}$ = 7.5 Hz, 3H), 2.31 (quint, $J_{H,H}$ = 7.5 Hz, 2H), 5.63 (t, $J_{H,H}$ = 7.5 Hz, 1H)); **$^{13}$C NMR** (100 MHz, $CDCl_3$) for **3ah** δ 11.0 ($J_{C,}{}^{119}{}_{Sn}$ = 338.4 Hz, $J_{C,}{}^{117}{}_{Sn}$ = 323.7 Hz), 12.9, 13.6, 25.9, 27.4 ($J_{C,}{}^{119}{}_{Sn}$ = 61.2 Hz), 29.1 ($J_{C,}{}^{119}{}_{Sn}$ = 18.8 Hz), 126.2, 126.5, 127.4, 127.6, 128.2, 128.7, 129.9, 137.3, 137.8, 141.1, 148.4, 151.7. **HRMS** (ESI) calcd for $C_{26}H_{46}Na^{120}Sn$ $[M+Na]^+$ 521.2206, found 521.2206.




**3ai** **3ai'**

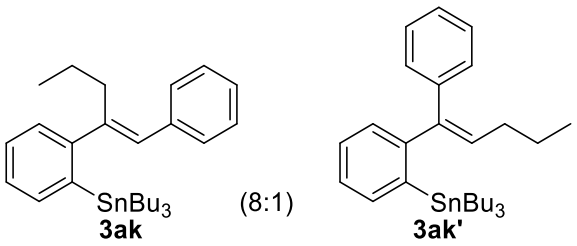
**Compound 3ai:3ai' (10:1).** (Table 3.3, 77% yield, colorless oil). **$^{1}$H NMR** (400 MHz, $CDCl_3$) for **3ai** δ 0.29 (s, 9H), 0.83 (t, $J_{H,H}$ = 7.3 Hz, 9H), 1.01 (t, $J_{H,H}$ = 8.4 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 50.3 Hz, 6H), 1.05 (t, $J_{H,H}$ = 7.5 Hz, 3H), 1.28 (sext, $J_{H,H}$ = 7.3 Hz, 6H), 1.41–1.50 (m, 6H), 2.70 (q, $J_{H,H}$ = 7.5 Hz, 2H), 6.33 (s, 1H), 7.23–7.30 (m, 3H), 7.32 (d, $J_{H,H}$ = 7.8 Hz, 2H), 7.50 (d, $J_{H,H}$ = 7.0 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 41.6 Hz, 1H), 7.53 (d, $J_{H,H}$ = 8.0 Hz, 2H), (**3ai'** δ 0.26 (s, 9H), 1.13 (t, $J_{H,H}$ = 7.5 Hz, 3H), 2.34 (quint, $J_{H,H}$ = 7.5 Hz, 2H), 5.63 (t, $J_{H,H}$ = 7.5 Hz, 1H)); **$^{13}$C NMR** (100 MHz, $CDCl_3$) for **3ai** δ –1.1, 11.1 ($J_{C,}{}^{119}{}_{Sn}$ = 339.9 Hz, $J_{C,}{}^{117}{}_{Sn}$ = 325.0 Hz), 12.9, 13.6, 26.0, 27.4 ($J_{C,}{}^{119}{}_{Sn}$ = 61.9 Hz), 29.1 ($J_{C,}{}^{119}{}_{Sn}$ = 19.0 Hz), 126.2 ($J_{C,}{}^{119}{}_{Sn}$ = 40.5 Hz), 127.4, 127.6 ($J_{C,}{}^{119}{}_{Sn}$ = 9.5 Hz), 128.0, 128.7, 133.3, 137.3 ($J_{C,}{}^{119}{}_{Sn}$ = 31.6 Hz), 138.2, 138.5, 141.1, 148.6 ($J_{C,}{}^{119}{}_{Sn}$ = 13.9 Hz), 151.7. **HRMS** (ESI) calcd for $C_{31}H_{50}NaSi^{120}Sn$ $[M+Na]^+$ 593.2601, found 593.2617.




**3aj** **3aj'**

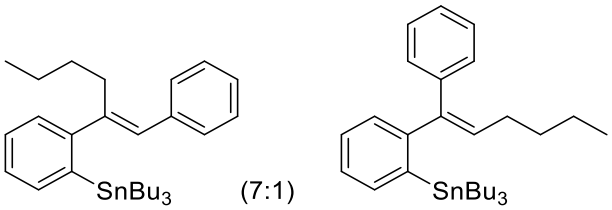
**Compound 3aj:3aj' (17:1).** (Table 3.3, 76% yield, colorless oil). **$^{1}$H NMR** (400 MHz, $CDCl_3$) for **3aj** δ 0.84 (t, $J_{H,H}$ = 7.3 Hz, 9H), 1.02 (t, $J_{H,H}$ = 8.4

Hz, 6H), 1.07 (t, $J_{H,H}$ = 7.5 Hz, 3H), 1.29 (sext, $J_{H,H}$ = 7.3 Hz, 6H), 1.43–1.51 (m, 6H), 2.71 (q, $J_{H,H}$ = 7.6 Hz, 2H), 3.87 (s, 6H), 3.88 (s, 3H), 6.27 (s, 1H), 6.57 (s, 2H), 7.20–7.37 (m, 3H), 7.49 (d, $J_{H,H}$ = 7.0 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 42.5 Hz, 1H), (**3aj'** δ 1.34 (t, $J_{H,H}$ = 7.5 Hz, 3H), 2.33 (quint, $J_{H,H}$ = 7.5 Hz, 2H), 5.60 (t, $J_{H,H}$ = 7.5 Hz, 1H)); **$^{13}$C NMR** (100 MHz, $CDCl_3$) for **3aj** δ 11.1 ($J_{C,}{}^{119}{}_{Sn}$ = 340.4 Hz, $J_{C,}{}^{117}{}_{Sn}$ = 325.2 Hz), 12.9, 13.6, 26.1, 27.5, 29.1 ($J_{C,}{}^{119}{}_{Sn}$ = 18.7 Hz), 56.0, 60.9, 105.9, 126.3, 127.4, 127.6, 128.7, 133.5, 136.9, 137.3, 141.1, 148.1, 151.6, 153.0. **HRMS** (ESI) calcd for $C_{31}H_{48}O_3Na^{120}Sn$ $[M+Na]^+$ 611.2523, found 611.2550.



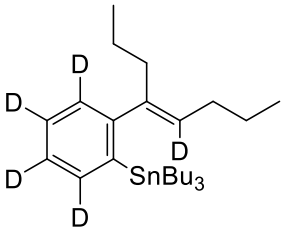

**3ak** **3ak'**

**Compound 3ak:3ak' (8:1).** (Table 3.3, 71% yield, colorless oil). **$^1$H NMR** (400 MHz, $CDCl_3$) for **3ak** δ 0.84 (t, $J_{H,H}$ = 7.3 Hz, 9H), 0.91 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.01 (t, $J_{H,H}$ = 8.4 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 51.4 Hz, 6H), 1.28 (sext, $J_{H,H}$ = 7.3 Hz, 6H), 1.41–1.50 (m, 8H), 2.61 (deformed t, $J_{H,H}$ = 8.2 Hz, 2H), 6.35 (s, 1H), 7.18–7.39 (m, 8H), 7.49 (d, $J_{H,H}$ = 7.0 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 41.8 Hz, 1H), (**3ak'** δ 2.28 (q, $J_{H,H}$ = 7.5 Hz, 2H), 5.68 (t, $J_{H,H}$ = 7.4 Hz, 1H)); **$^{13}$C NMR** (100 MHz, $CDCl_3$) for **3ak** δ 11.0 ($J_{C,}{}^{119}{}_{Sn}$ = 340.1 Hz, $J_{C,}{}^{117}{}_{Sn}$ = 325.1 Hz), 13.6, 14.5, 21.7, 27.4 ($J_{C,}{}^{119}{}_{Sn}$ = 62.1 Hz), 29.1 ($J_{C,}{}^{119}{}_{Sn}$ = 19.1 Hz), 35.3, 126.1, 126.5, 127.5, 127.6, 128.2, 128.7, 129.0, 137.2, 137.9, 140.8, 147.3, 152.2. **HRMS** (ESI) calcd for $C_{29}H_{44}Na^{120}Sn$ $[M+Na]^+$ 535.2363, found 535.2394.




**3al** **3al'**

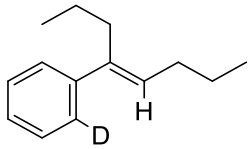
**Compound 3al:3al' (7:1).** (Table 3.3, 73% yield, colorless oil). **$^{1}$H NMR** (400 MHz, $CDCl_3$) for **3al** δ 0.84 (t, $J_{H,H}$ = 7.3 Hz, 9H), 0.87 (t, $J_{H,H}$ = 7.2 Hz, 3H), 1.01 (t, $J_{H,H}$ = 8.4 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 51.2 Hz, 6H), 1.24 (t, $J_{H,H}$ = 7.3 Hz, 6H), 1.27–1.35 (m, 2H), 1.39–1.51 (m, 8H), 2.64 (deformed t, $J_{H,H}$ = 8.1 Hz, 2H), 6.34 (s, 1H), 7.16–7.39 (m, 8H), 7.50 (d, $J_{H,H}$ = 7.0 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 41.9 Hz, 1H), (**3al'** δ 2.30 (q, $J_{H,H}$ = 7.5 Hz, 2H), 5.67 (t, $J_{H,H}$ = 7.4 Hz, 1H)); **$^{13}$C NMR** (100 MHz, $CDCl_3$) for **3al** δ 11.0 ($J_{C,}{}^{119}{}_{Sn}$ = 340.3 Hz, $J_{C,}{}^{117}{}_{Sn}$ = 325.1 Hz), 13.6, 13.9, 23.1, 27.4 ($J_{C,}{}^{119}{}_{Sn}$ = 62.0 Hz), 29.1 ($J_{C,}{}^{119}{}_{Sn}$ = 19.7 Hz), 30.6, 32.9, 126.2, 126.5, 127.5, 127.6, 128.2, 128.7, 128.9, 137.3, 137.9, 140.9, 147.4, 152.2. **HRMS** (ESI) calcd for $C_{26}H_{46}Na^{120}Sn$ $[M+Na]^+$ 549.2519, found 549.2546.




**3aa-*d*$_5$**

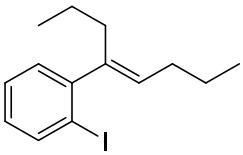
**Compound 3aa-*d*$_5$.** (Scheme 3.5c, 87% yield, colorless oil). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 0.89 (t, $J_{H,H}$ = 7.1 Hz, 9H+3H), 0.96 (t, $J_{H,H}$ = 6.7 Hz, 3H), 0.99 (t, $J_{H,H}$ = 8.1 Hz, $J_{H,}{}^{119}{}_{Sn}$ = 51.0 Hz, 6H), 1.32 (sext, $J_{H,H}$ = 7.1 Hz, 6H+2H), 1.42–1.51 (m, 8H), 2.14 (t, $J_{H,H}$ = 7.5 Hz, 2H), 2.32 (t, $J_{H,H}$ = 8.0 Hz, 2H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 10.8 ($J_{C,}{}^{119}{}_{Sn}$ = 339.6 Hz, $J_{C,}{}^{117}{}_{Sn}$ = 324.7 Hz), 13.6, 14.1, 14.4, 21.6, 22.9, 27.5 ($J_{C,}{}^{119}{}_{Sn}$ = 61.0 Hz), 29.2 ($J_{C,}{}^{119}{}_{Sn}$ = 18.9 Hz), 30.5, 34.9, 125.1 (t, $J_{C,}{}^{2}{}_{H}$ = 23.8

Hz), 126.9 (t, $J_{C,^2H}$ = 23.9 Hz), 127.5 (t, $J_{C,^2H}$ = 23.2 Hz), 129.2 (t, $J_{C,^2H}$ = 22.8 Hz), 136.5 (t, $J_{C,^2H}$ = 23.9 Hz), 140.5, 144.2 ($J_{C,^{119}Sn}$ = 14.6 Hz), 152.6 ($J_{C,^{119}Sn}$ = 28.6 Hz); **$^2$H{$^1$H} NMR** (61 MHz, acetone) δ 5.26 (s, 1H), 7.19 (s, 2H), 7.32 (s, 1H), 7.43 (s, 1H). **HRMS** (ESI) calcd for $C_{26}H_{41}D_5Na^{120}Sn$ $[M+Na]^+$ 506.2833, found 506.2838.




**8**

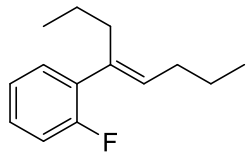
**Compound 8 [374107-00-3]**. (Scheme 3.6, 98% yield, colorless oil). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 0.89 (t, $J_{H,H}$ = 7.4 Hz, 3H), 0.97 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.37 (sext, $J_{H,H}$ = 7.6 Hz, 2H), 1.48 (sext, $J_{H,H}$ = 7.4 Hz, 2H), 2.18 (q, $J_{H,H}$ = 7.3 Hz, 2H), 2.48 (t, $J_{H,H}$ = 7.7 Hz, 2H), 5.67 (t, $J_{H,H}$ = 7.3 Hz, 1H), 7.21 (td, $J_{H,H}$ = 7.4 Hz, 1.3 Hz, 1H), 7.30 (t, $J_{H,H}$ = 6.9 Hz, 1H), 7.30 (d, $J_{H,H}$ = 6.7 Hz, 1H), 7.34 (d, $J_{H,H}$ = 7.7 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 13.9, 14.0, 21.8, 23.1, 30.6, 31.7, 126.0 (t, $J_{C,^2H}$ = 24.1 Hz), 126.3, 128.0, 128.1, 129.2, 140.0, 143.5. The spectral data are in agreement with reported literature values.[8a]




**9**

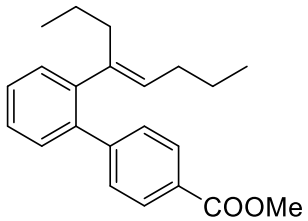
**Compound 9.** (Scheme 3.6, 96% yield, colorless oil). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.98 (t, $J_{H,H}$ = 7.3 Hz, 3H), 1.07 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.39 (sext, $J_{H,H}$ = 7.8 Hz, 2H), 1.57 (sext, $J_{H,H}$ = 7.3 Hz, 2H), 2.25 (q, $J_{H,H}$ = 7.3 Hz, 2H), 2.46 (t, $J_{H,H}$ = 7.8 Hz, 2H), 5.37 (t, $J_{H,H}$ = 7.3 Hz, 1H), 6.95 (td, $J_{H,H}$ = 7.7 Hz, 1.7 Hz, 1H), 7.17 (dd, $J_{H,H}$ = 7.5 Hz, 1.7 Hz, 1H), 7.31 (td, $J_{H,H}$ = 7.5 Hz, 1.2 Hz, 1H), 7.89 (dd,

$J_{H,H}$ = 7.9 Hz, 1.1 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 14.0, 14.2, 21.2, 22.7, 30.0, 33.5, 99.4, 127.5, 127.8, 129.6, 131.3, 139.0, 143.3, 149.1. **HRMS** (ESI) calcd for $C_{14}H_{20}I$ $[M+H]^+$ 315.0610, found 315.0613.




**10**

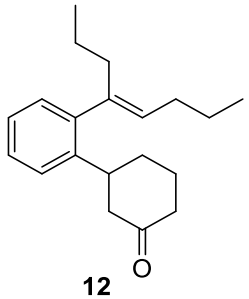
**Compound 10 [1092526-15-2**]. (Scheme 3.6, 69% yield, colorless oil). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.86 (t, $J_{H,H}$ = 7.3 Hz, 3H), 0.96 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.30 (sext, $J_{H,H}$ = 7.4 Hz, 2H), 1.47 (sext, $J_{H,H}$ = 7.4 Hz, 2H), 2.18 (q, $J_{H,H}$ = 7.3 Hz, 2H), 2.44 (t, $J_{H,H}$ = 7.6 Hz, 2H), 5.50 (t, $J_{H,H}$ = 7.2 Hz, 1H), 6.99 (dd, $J_{H,H}$ = 8.4 Hz, $J_{H,}{}^{19}{}_F$ = 10.6 Hz, 1H), 7.06 (dd, $J_{H,H}$ = 7.4 Hz, 1.2 Hz, 1H), 7.17 (d, $J_{H,H}$ = 7.2 Hz, 1H), 7.19–7.23 (m, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 13.8, 21.5, 22.9, 30.3, 32.5, 115.4 (d, $J_{C,}{}^{19}{}_F$ = 23.1 Hz), 123.7 (d, $J_{C,}{}^{19}{}_F$ = 3.2 Hz), 126.4, 127.9 (d, $J_{C,}{}^{19}{}_F$ = 8.0 Hz), 130.6 (d, $J_{C,}{}^{19}{}_F$ = 4.6 Hz), 131.9 (d, $J_{C,}{}^{19}{}_F$ = 14.6 Hz), 136.1, 160.0 (d, $J_{C,}{}^{19}{}_F$ = 245.8 Hz). The spectral data are in agreement with reported literature values.[36]




**11**

**Compound 11**. (Scheme 3.6, 83% yield, pale yellow oil). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.69 (t, $J_{H,H}$ = 7.3 Hz, 3H), 0.91 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.10 (sext, $J_{H,H}$ = 7.5 Hz, 2H), 1.40 (sext, $J_{H,H}$ = 7.3 Hz, 2H), 1.79 (t, $J_{H,H}$ = 7.7 Hz, 2H), 2.06

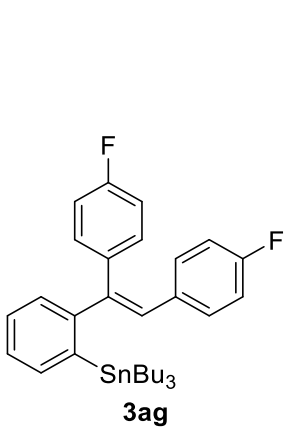
(q, $J_{H,H}$ = 7.3 Hz, 2H), 3.93 (s, 3H), 5.48 (t, $J_{H,H}$ = 7.3 Hz, 1H), 7.20–7.33 (m, 4H), 7.50 (d, $J_{H,H}$ = 8.3 Hz, 2H), 8.01 (d, $J_{H,H}$ = 8.3 Hz, 2H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 13.9, 21.5, 22.8, 30.3, 32.9, 52.0, 126.8, 127.6, 128.3, 129.1, 129.2, 129.7, 130.4, 132.2, 138.6, 141.2, 143.6, 147.2, 167.2. **HRMS** (ESI) calcd for $C_{22}H_{27}O_2$ $[M+H]^+$ 323.2011, found 323.1995.




**12**

**Compound 12**. (Scheme 3.6, 87% yield, colorless oil). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.87 (t, $J_{H,H}$ = 7.3 Hz, 3H), 0.94 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.27 (sext d, $J_{H,H}$ = 7.8 Hz, 2.2 Hz, 2H), 1.43 (sext, $J_{H,H}$ = 7.3 Hz, 2H), 1.69 (qt, $J_{H,H}$ = 12.8 Hz, 4.5 Hz, 1H), 1.82 (qd, $J_{H,H}$ = 12.3 Hz, 3.2 Hz, 1H), 1.91 (br d, $J_{H,H}$ = 13.2 Hz, 1H), 2.14 (q, $J_{H,H}$ = 7.4 Hz, 2H), 2.11–2.20 (m, 1H), 2.22–2.31 (m, 2H), 2.38 (td, $J_{H,H}$ = 14.5 Hz, 6.6 Hz, 1H), 2.4–2.5 (m, 1H), 2.45 (br d, $J_{H,H}$ = 14.1 Hz, 1H), 2.53 (t, $J_{H,H}$ = 13.8 Hz, 1H), 3.23 (tt, $J_{H,H}$ = 12.2 Hz, 3.9 Hz, 1H), 5.21 (t, $J_{H,H}$ = 7.3 Hz, 1H), 7.05 (dd, $J_{H,H}$ = 7.5 Hz, 1.0 Hz, 1H), 7.15 (td, $J_{H,H}$ =7.3 Hz, 1.6 Hz, 1H), 7.25 (td, $J_{H,H}$ = 7.8 Hz, 1.2 Hz, 1H), 7.29 (dd, $J_{H,H}$ = 7.7 Hz, 1.4 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 13.9, 14.2, 21.3, 23.0, 25.9, 30.1, 33.4, 34.9, 40.6, 41.2, 49.3, 125.6, 125.8, 126.8, 129.5, 130.4, 139.6, 141.7, 143.8, 211.1. **HRMS** (ESI) calcd for $C_{20}H_{29}O$ $[M+H]^+$ 285.2218, found 285.2221.

### 3.4.9 Single crystal X-ray diffraction data for compound 3ag (CCDC 1841177)




3ag

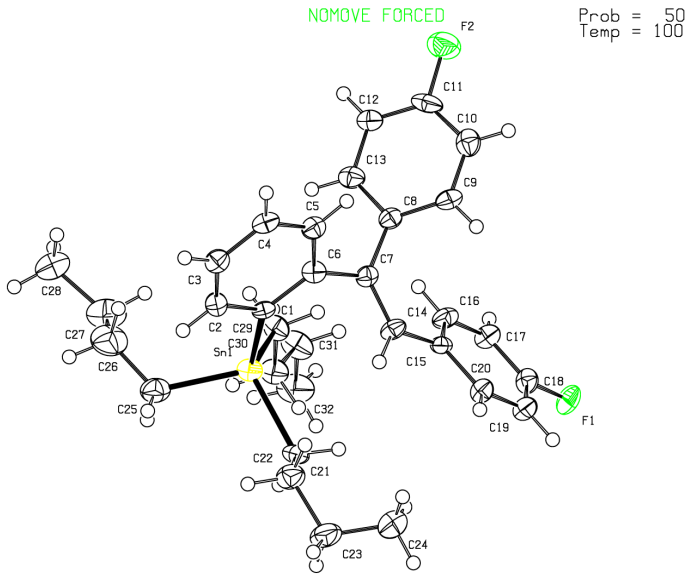



**Table 3.4. Crystal data and structure refinement for compound 3ag**

| | | |
|---|---|---|
| Empirical formula | $C_{32}H_{40}F_2Sn$ | |
| Formula weight | 581.33 g/mol | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal size | 0.020 x 0.040 x 0.320 mm | |
| Crystal habit | colorless needle | |
| Crystal system | Monoclinic | |
| Space group | P 1 21/c 1 | |
| Unit cell dimensions | a = 17.1715(13) Å | α = 90°. |
| | b = 17.8894(14) Å | β = 101.309(3)°. |
| | c = 9.4518(7) Å | γ = 90°. |
| Volume | 2847.1(4) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.356 $g/cm^3$ | |
| Absorption coefficient | 0.928 $mm^{-1}$ | |
| F(000) | 1200 | |
| Theta range for data collection | 2.48 to 27.94°. | |

| | |
|---|---|
| Index ranges | –22<=h<=20, –22<=k<=23, –12<=l<=11 |
| Reflections collected | 16876 |
| Independent reflections | 6610 [R(int) = 0.0945] |
| Coverage of independent reflections | 96.5% |
| Absorption correction | Multi-Scan |
| Max. and min. transmission | 0.9820 and 0.7560 |
| Structure solution technique | direct methods |
| Structure solution program | XT, VERSION 2014/5 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Refinement program | SHELXL-2016/6 (Sheldrick, 2016) |
| Function minimized | $\Sigma\ w(F_o^2 - F_c^2)^2$ |
| Data / restraints / parameters | 6610 / 0 / 319 |
| Goodness-of-fit on $F^2$ | 1.014 |
| Final R indices | 3523 data; I>2σ(I) R1 = 0.0663, wR2 = 0.1362 |
| | all data R1 = 0.1468, wR2 = 0.1726 |
| Weighting scheme | $w=1/[\sigma^2(F_o^2)+(0.0685P)^2]$ where $P=(F_o^2+2F_c^2)/3$ |
| Largest diff. peak and hole | 1.424 and –1.680 eÅ$^{-3}$ |
| R.M.S. deviation from mean | 0.155 eÅ$^{-3}$ |

## 3.5 Refernece

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(15) CuBr has been used as a cocatalyst in Fe-catalyzed arylmagnesiation of alkynes: Shirakawa, E.; Yamagami, T.; Kimura, T.; Yamaguchi, S.; Hayashi, T. *J. Am. Chem. Soc.* **2005**, *127*, 17164.

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(17) The lower yields are due mainly to the formation of higher molecular weight compounds.

(18) For pertinent reviews on catalytic carbometalation of alkynes, see: Chapter 1, Reference 34.

(19) The transmetalation from Sn to Rh has been reported for the conjugate addition of aryl- and alkenylstannanes to α,β-unsaturated carbonyl compounds: (a) Oi, S.; Moro, M.; Ono, S.; Inoue, Y. *Chem. Lett*. **1998**, 83. (b) Venkatraman, S.; Meng, Y.; Li, C.-J. *Tetrahedron Lett*. **2001**, *42*, 4459. (c) Oi, S.; Moro, M.; Ito, H.; Honma, Y.; Miyano, S.; Inoue, Y. *Tetrahedron* **2002**, *58*, 91.

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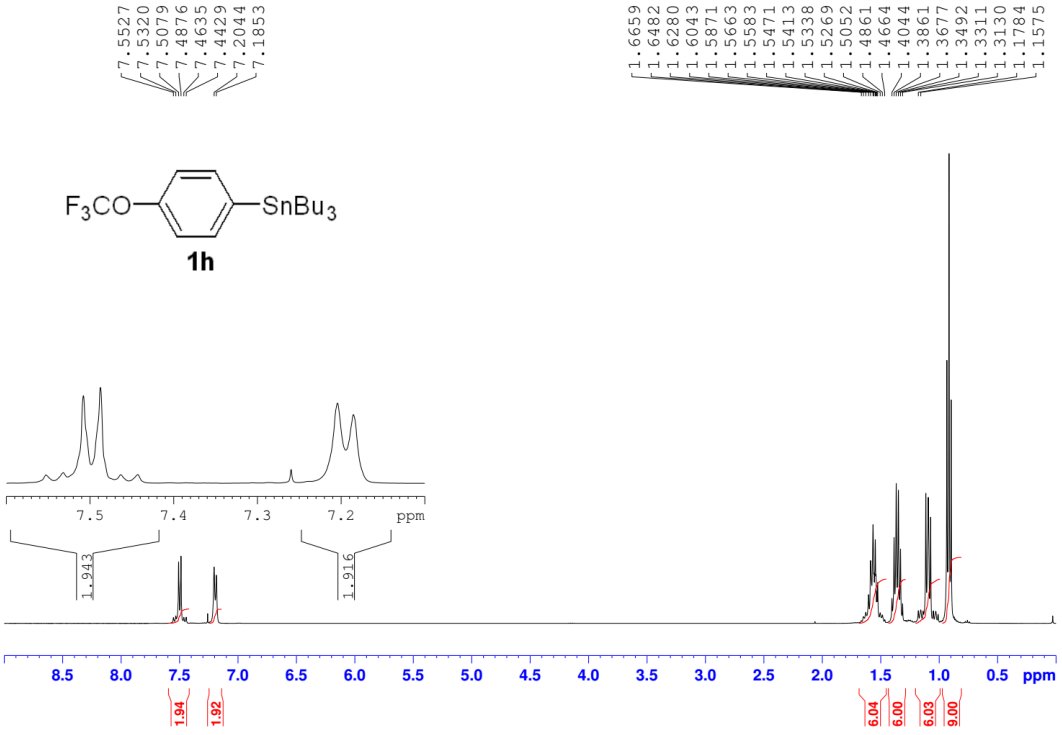
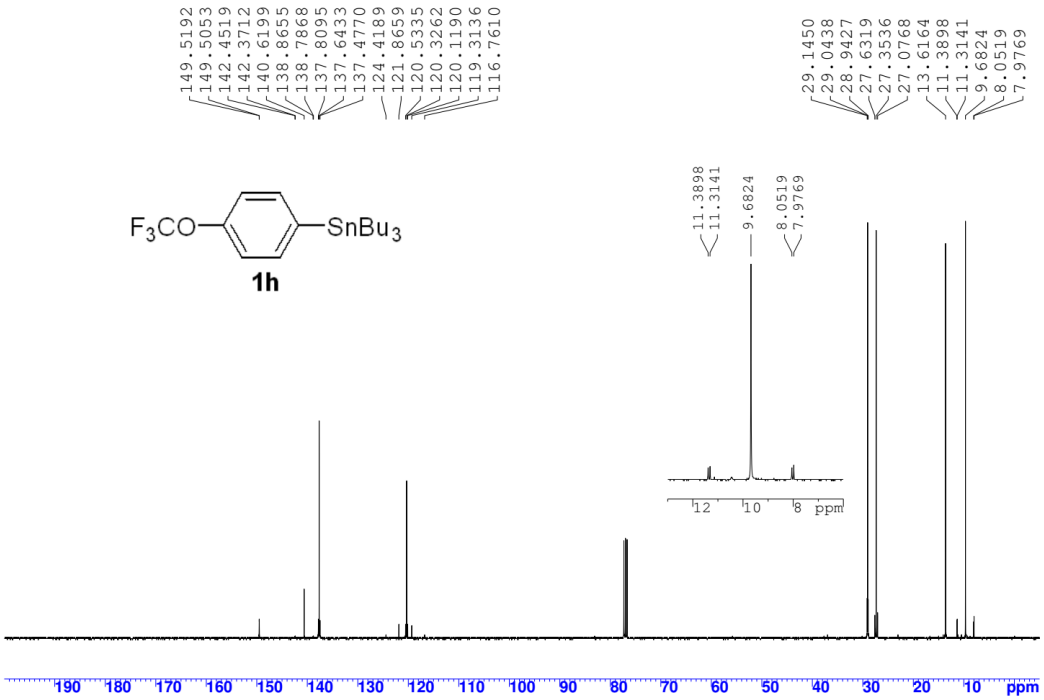
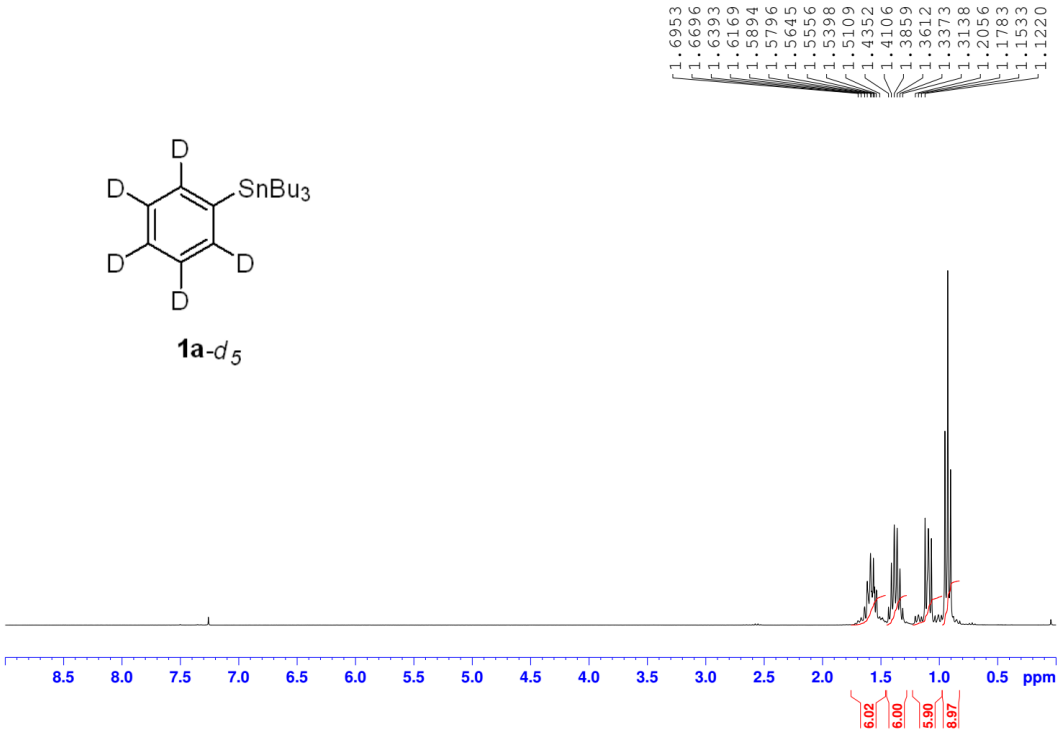
## 3.6 NMR spectra

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1.4106
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1.3373
1.3138
1.2056
1.1783
1.1533
1.1220
D
D
SnBu3
D
D
D
1a-d5
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
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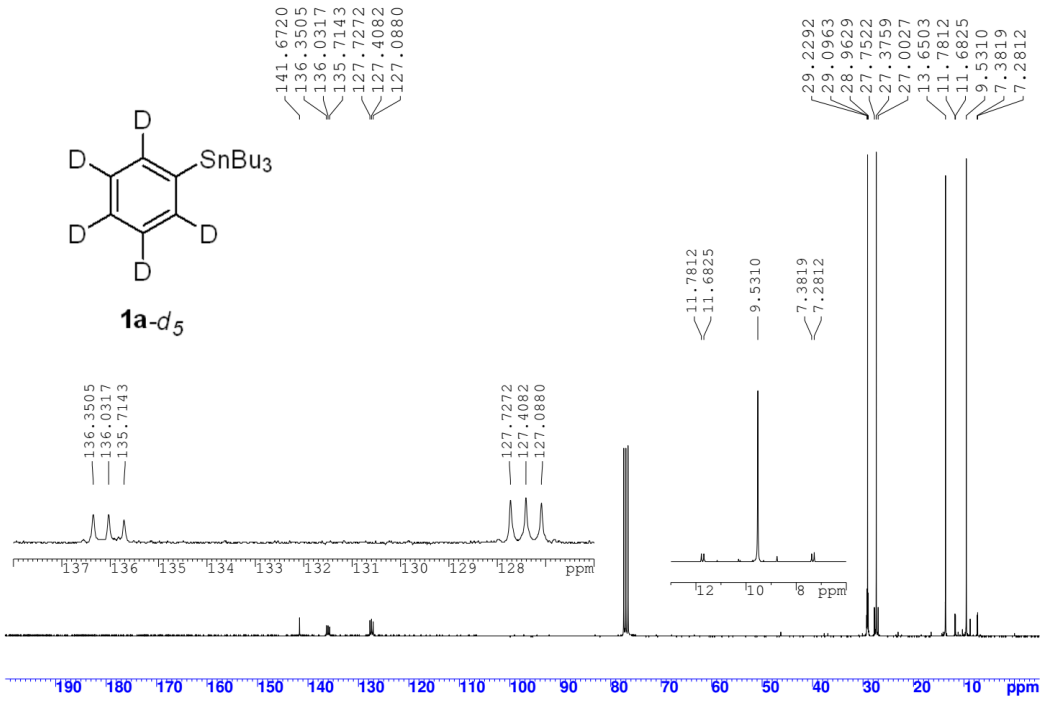
6.00
5.90
8.97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27.3759
27.0027
13.6503
11.7812
11.6825
9.5310
7.3819
7.2812
D
D
SnBu3
D
D
D
1a-d5
11.7812
11.6825
9.5310
7.3819
7.2812
136.3505
136.0317
135.7143
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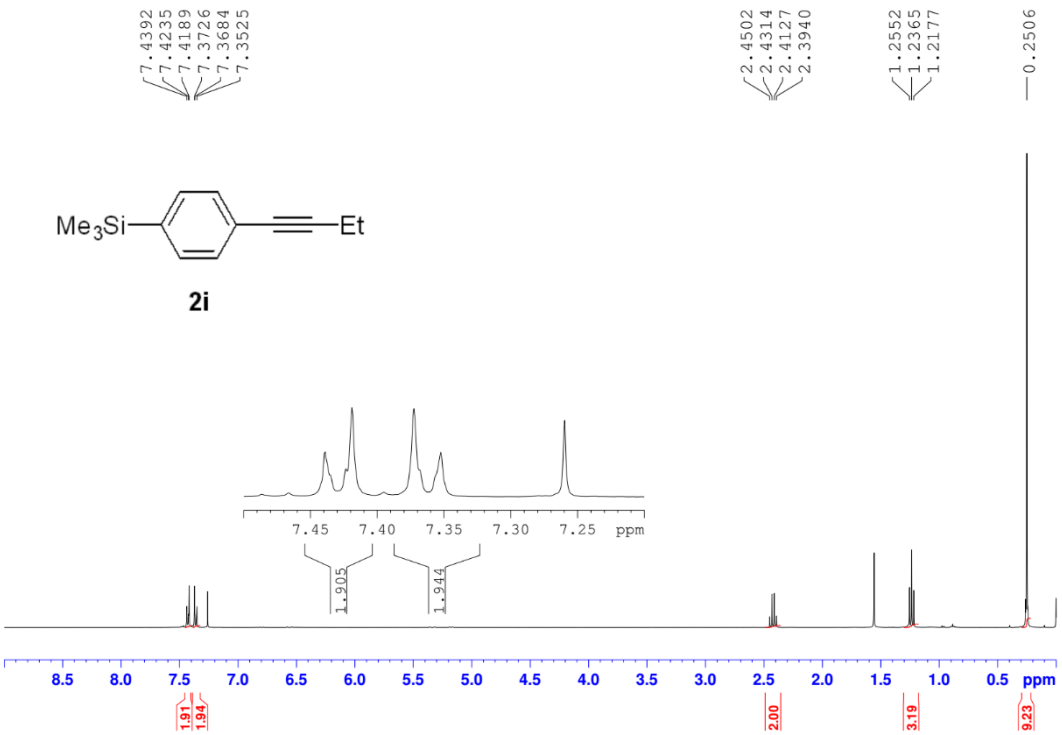
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1.2365
1.2177
0.2506
Me3Si
Et
2i
7.45
7.40
7.35
7.30
7.25
ppm
1.905
1.944
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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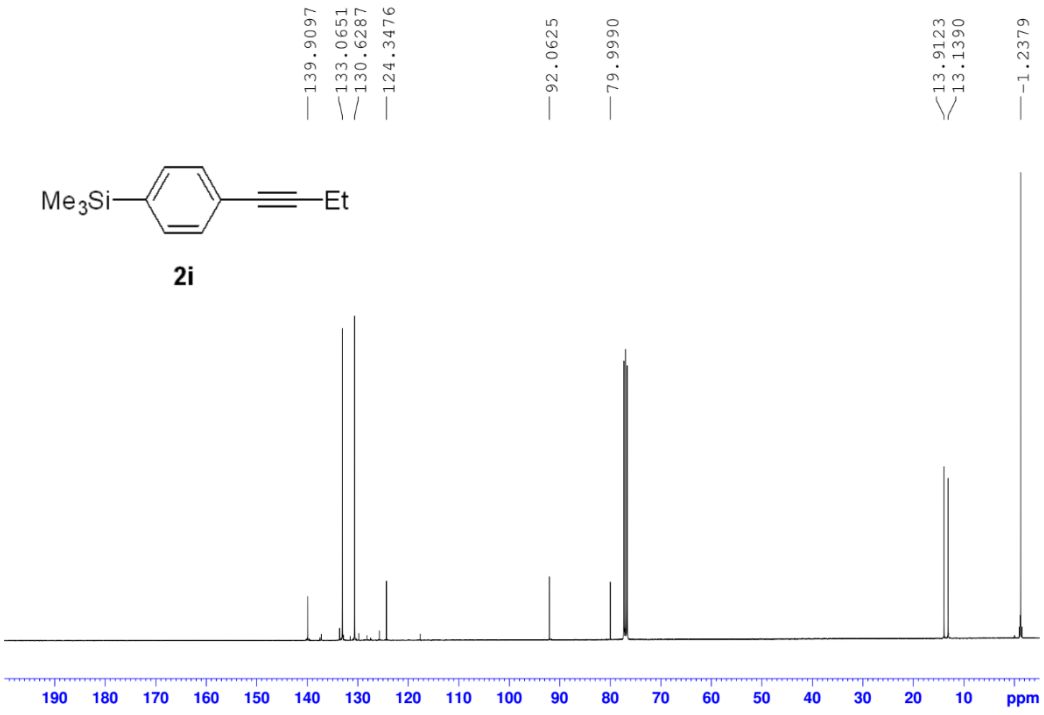
9.23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Et
2i
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150
140
130
120
110
100
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80
70
60
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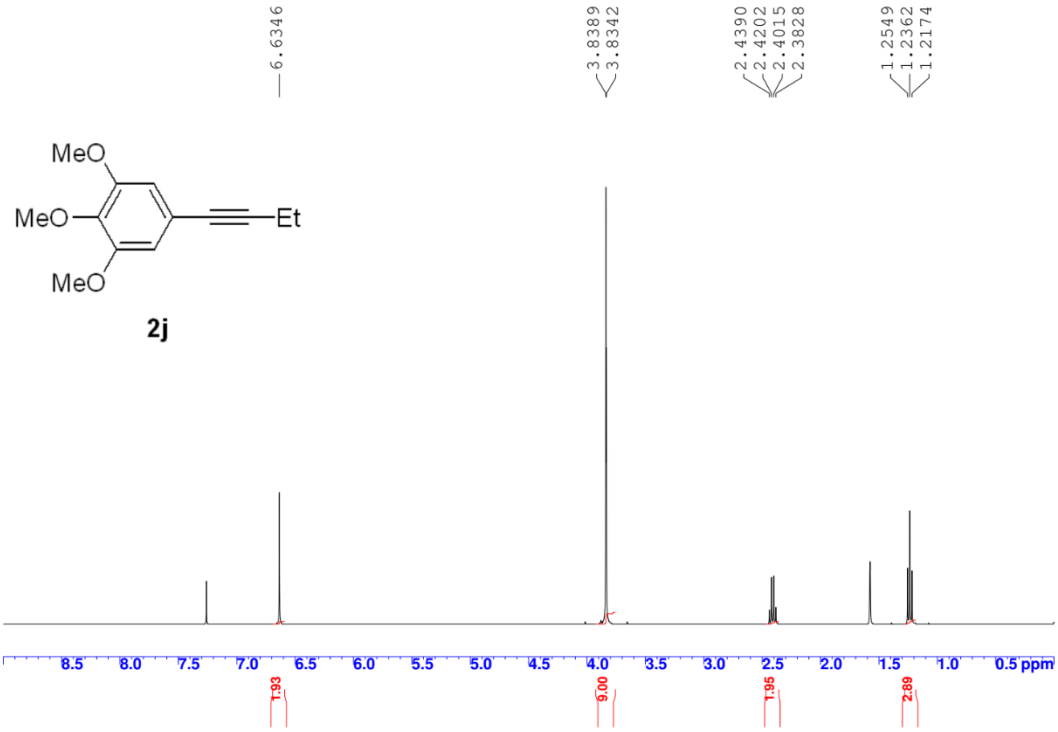
40
30
20
10
ppm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MeO
MeO
MeO
Et
2j
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
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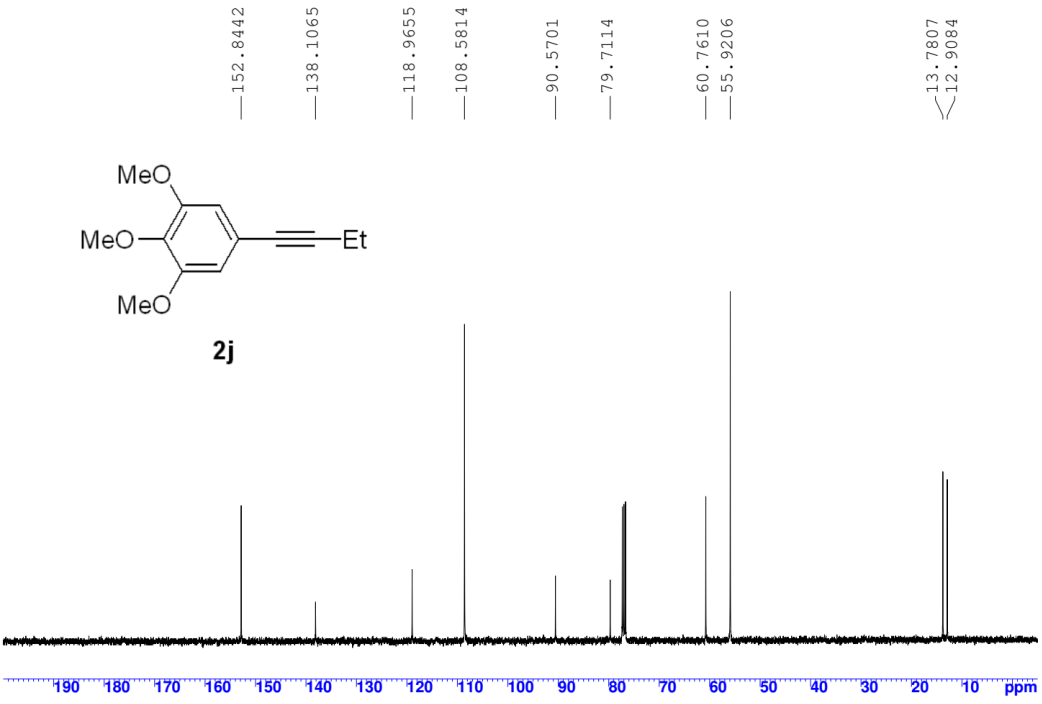
2.89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Et
2j
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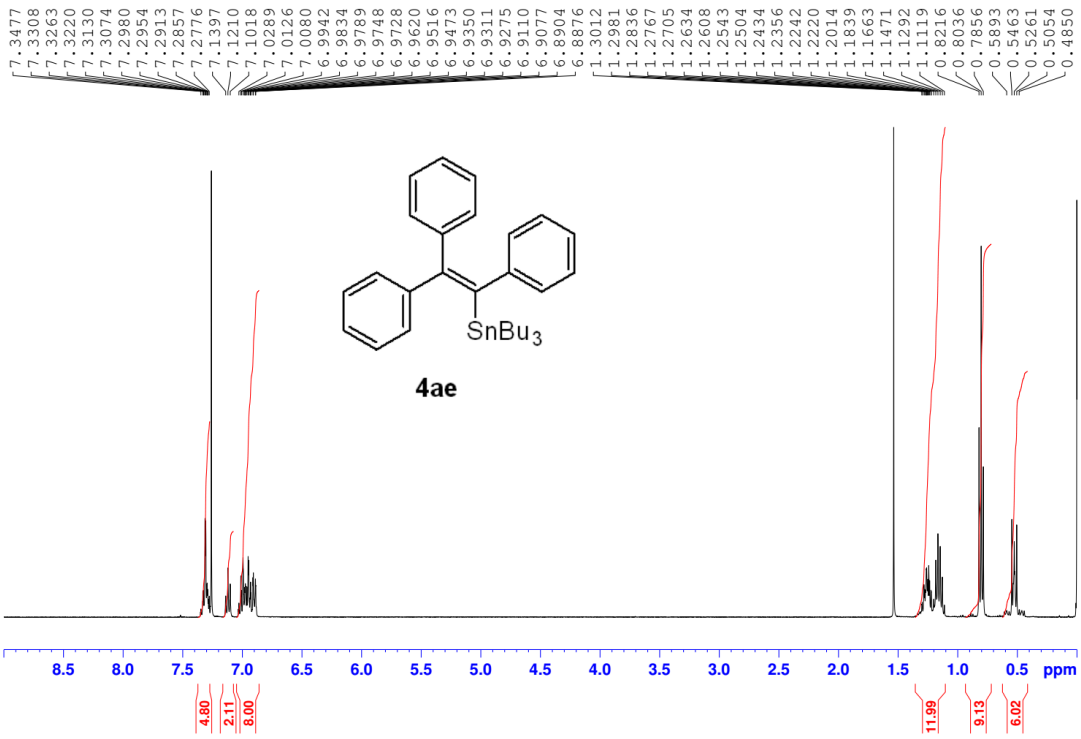
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0.4850
SnBu3
4ae
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
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2.11
8.00
11.99
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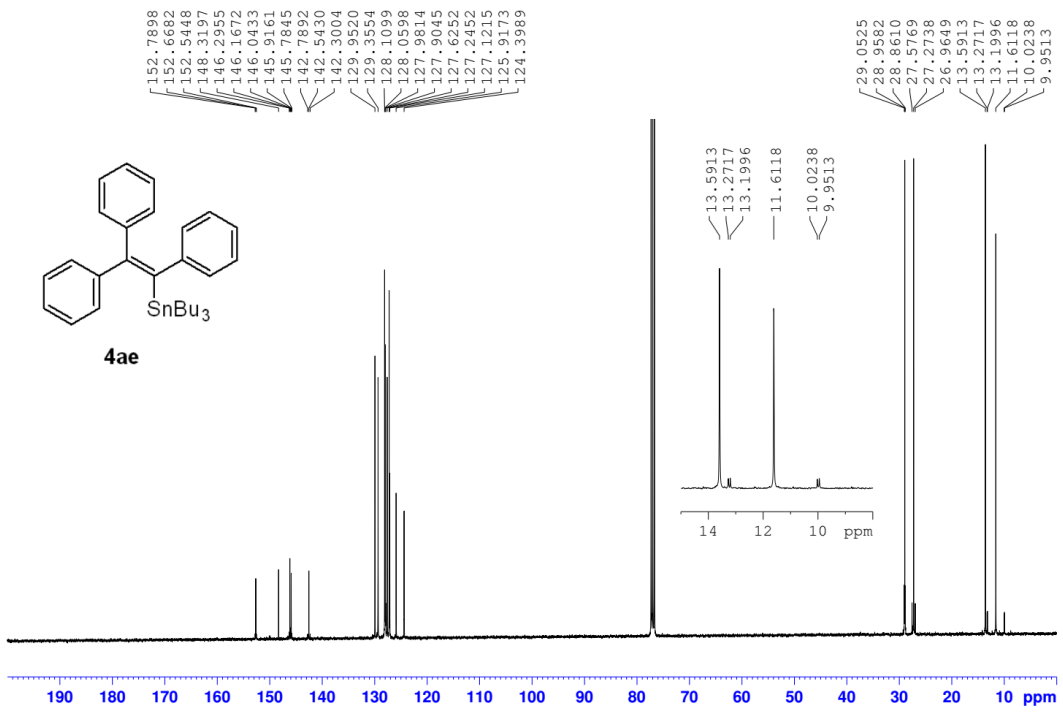
6.02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4ae
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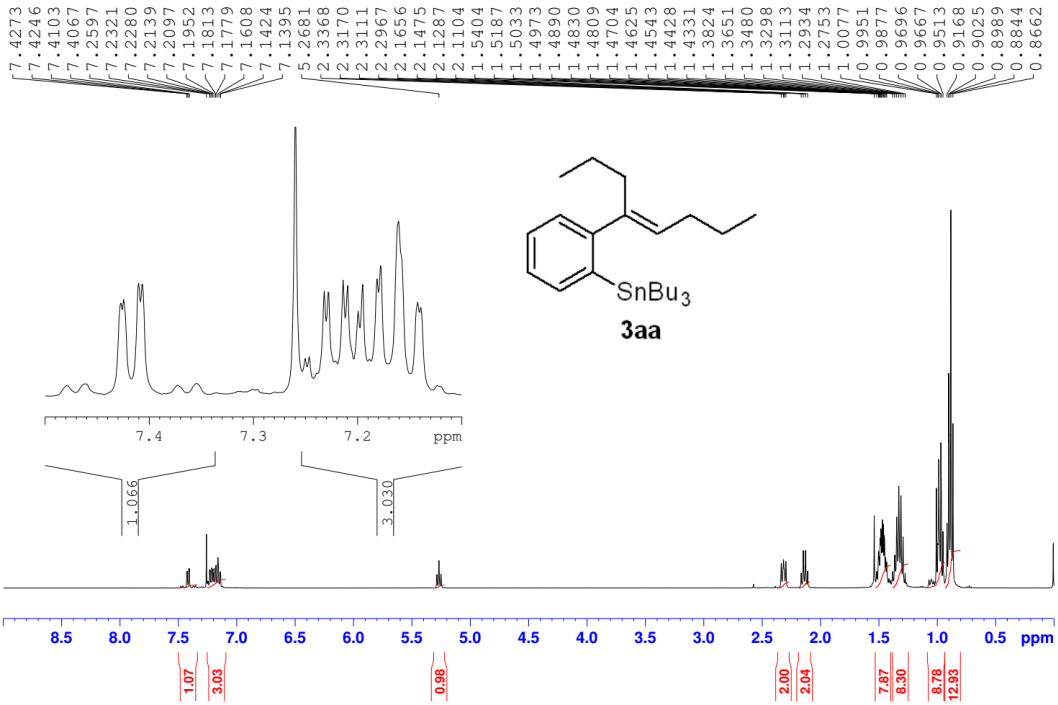
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7.2097
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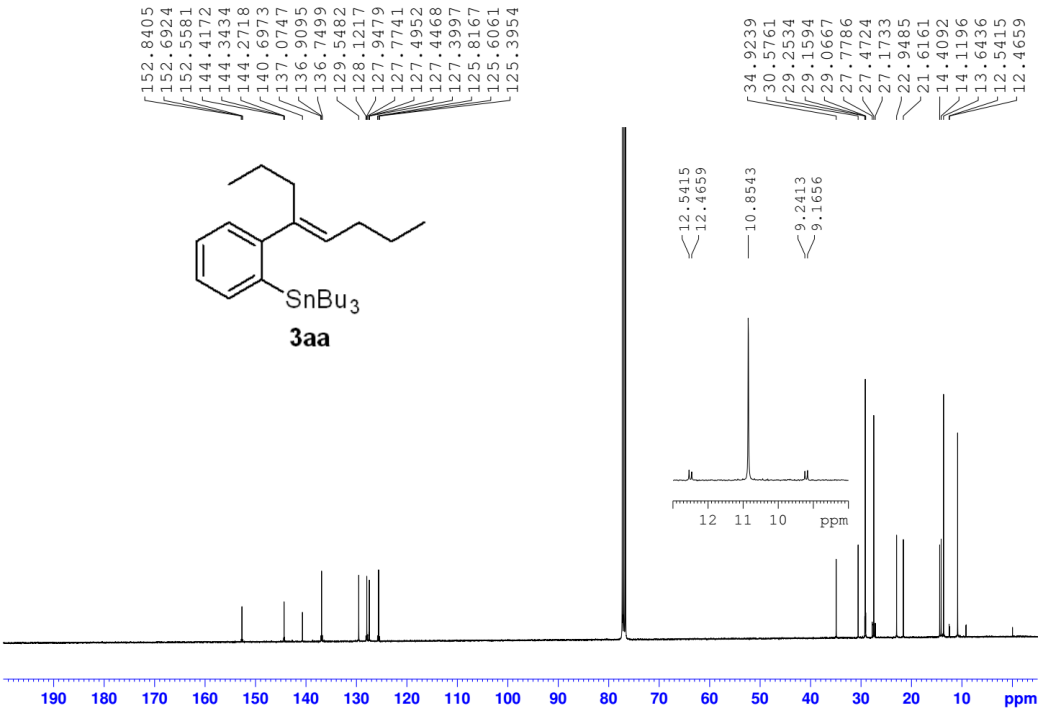
7.1813
7.1779
7.1608
7.1424
7.1395
5.2681
2.3368
2.3170
2.3111
2.2967
2.1656
2.1475
2.1287
2.1104
1.5404
1.5187
1.5033
1.4973
1.4890
1.4830
1.4809
1.4704
1.4625
1.4543
1.4428
1.4331
1.3824
1.3651
1.3480
1.3298
1.3113
1.2934
1.2753
1.0077
0.9951
0.9877
0.9696
0.9667
0.9513
0.9168
0.9025
0.8989
0.8844
0.8662
SnBu3
3aa
7.4
7.3
7.2
ppm
1.066
3.030
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.07
3.03
0.98
2.00
2.04
7.87
8.30
8.78
12.93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127.7741
127.4952
127.4468
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125.6061
125.3954
34.9239
30.5761
29.2534
29.1594
29.0667
27.7786
27.4724
27.1733
22.9485
21.6161
14.4092
14.1196
13.6436
12.5415
12.4659
SnBu3
3aa
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10.8543
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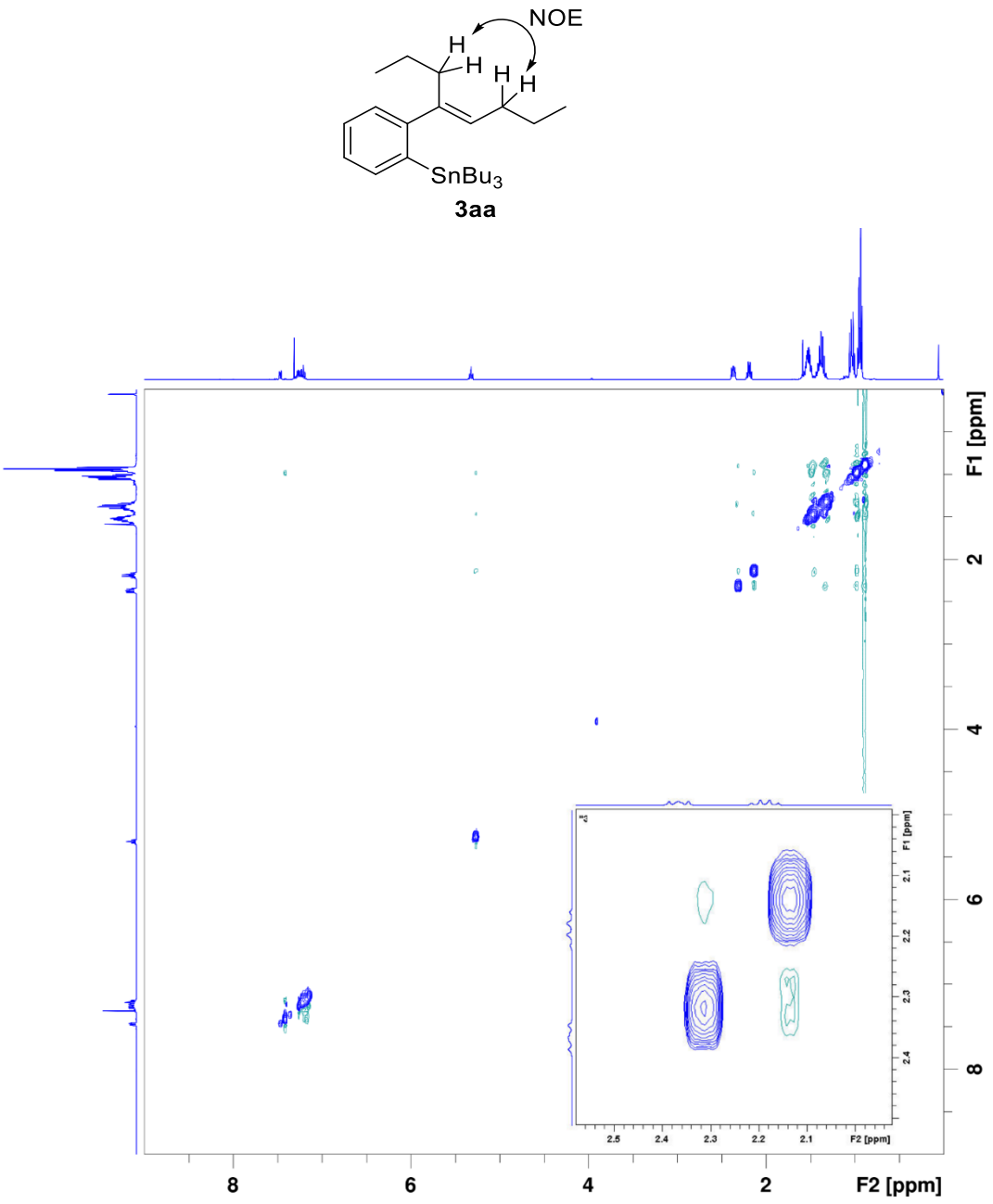
12 11 10 ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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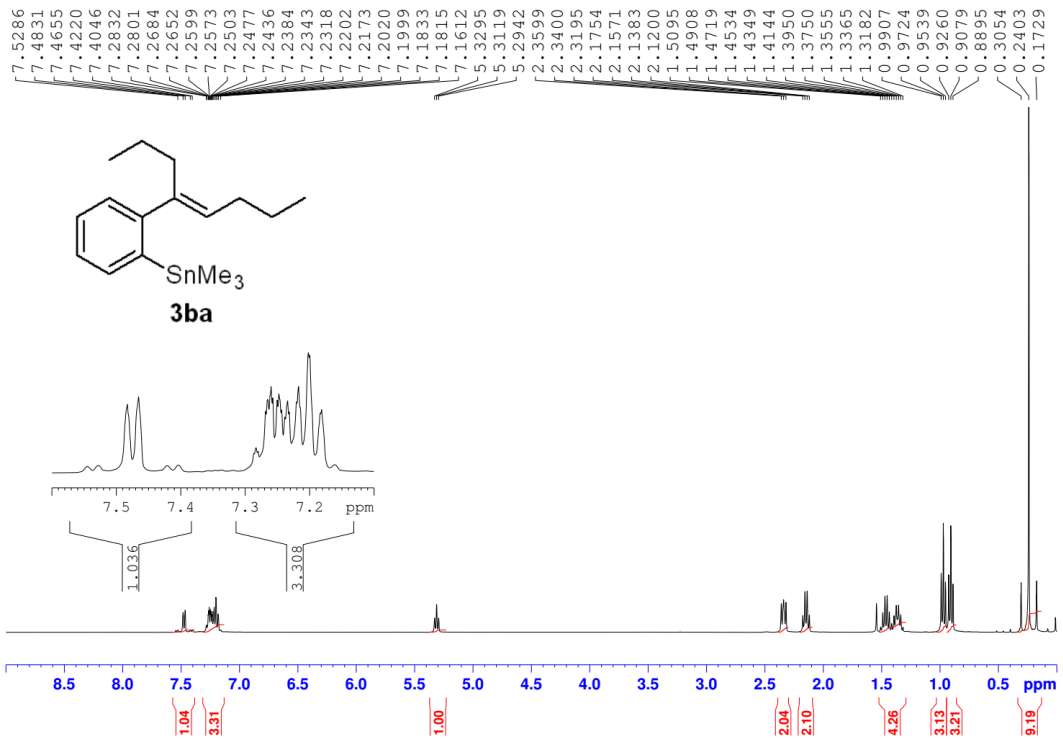
H
H
H
H
SnBu3
3aa
F1 [ppm]
F2 [ppm]
8
6
4
2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3ba
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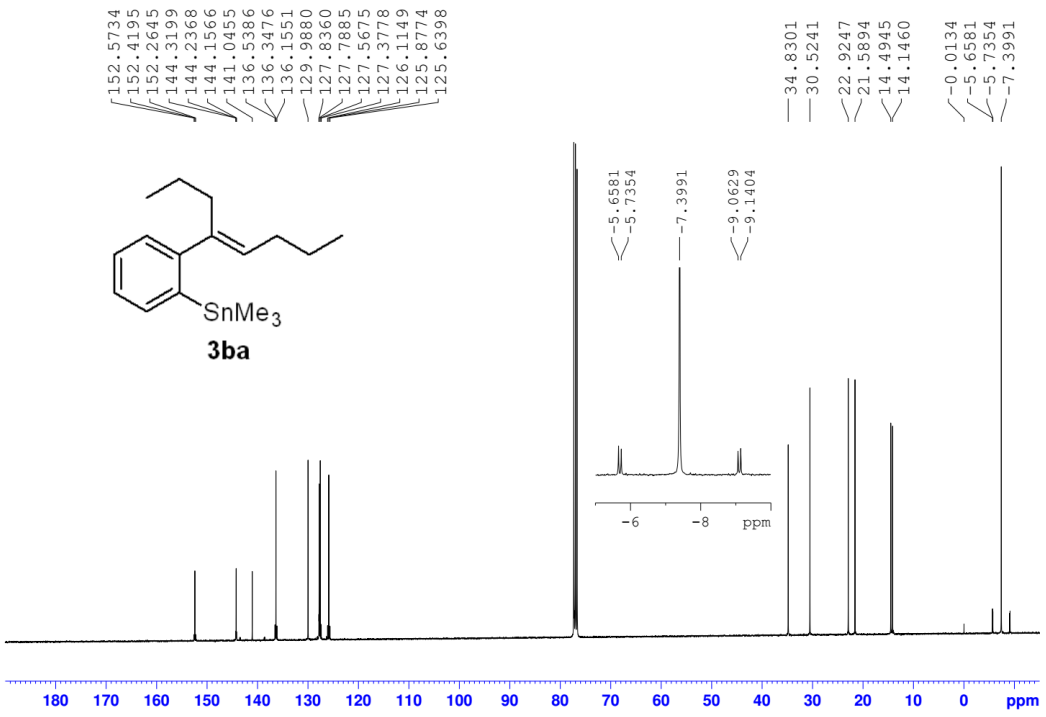
1.036
3.308
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.04
3.31
1.00
2.04
2.10
4.26
3.13
3.21
9.19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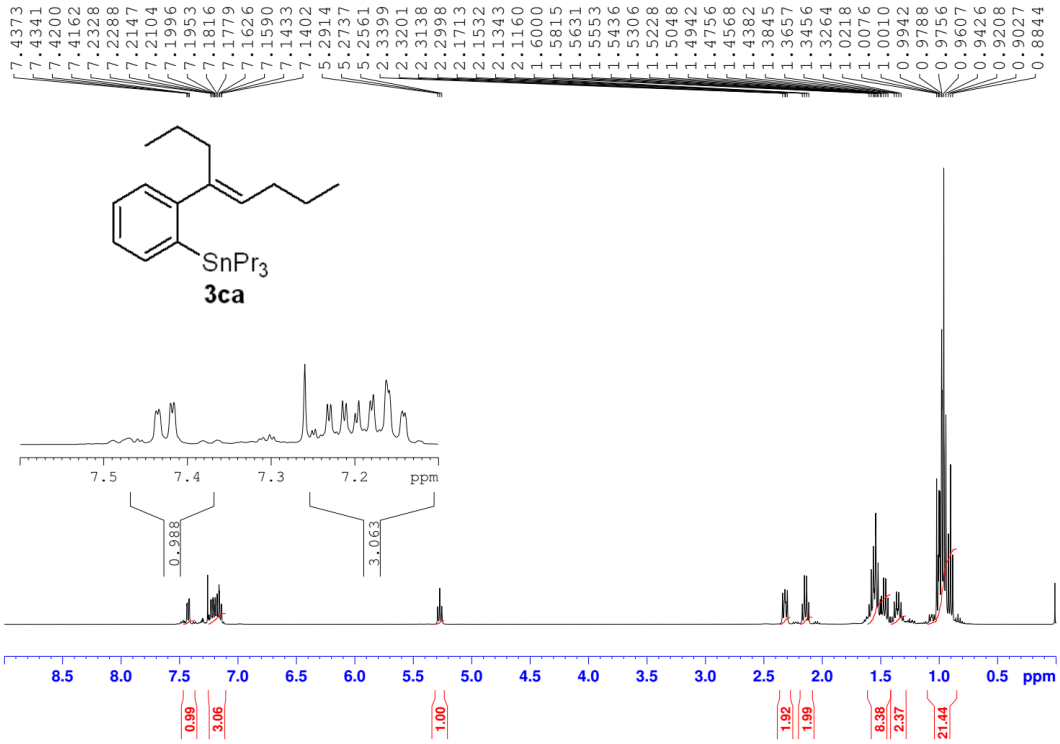
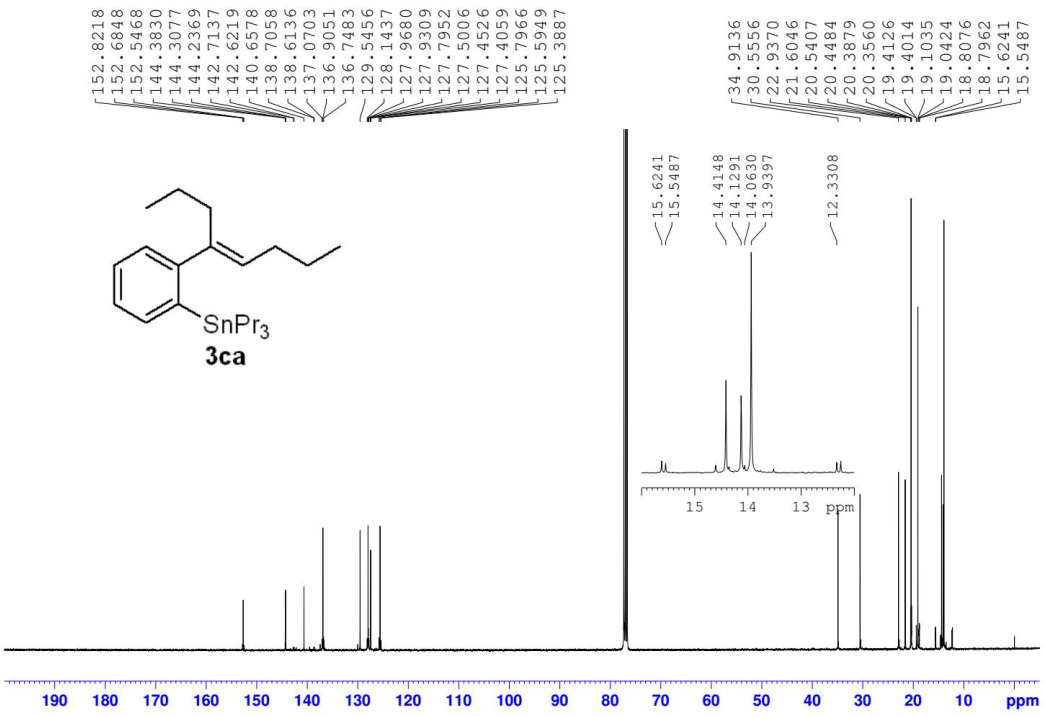
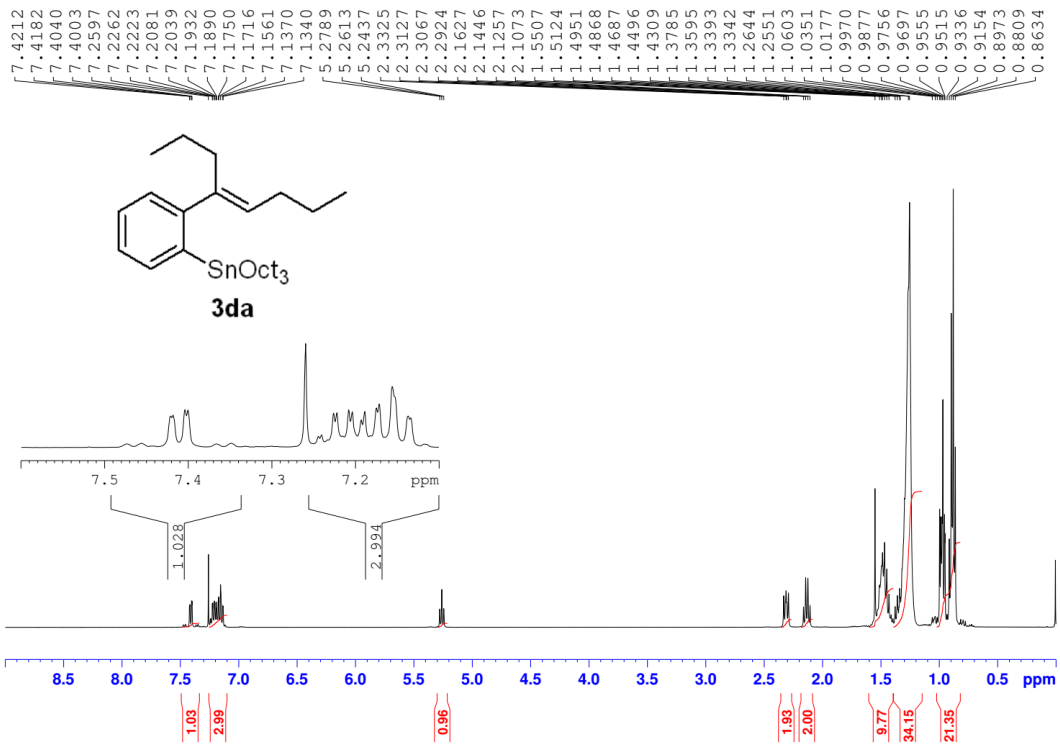
3ba
-6 -8 ppm
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


SnPr3
3ca


SnPr3
3ca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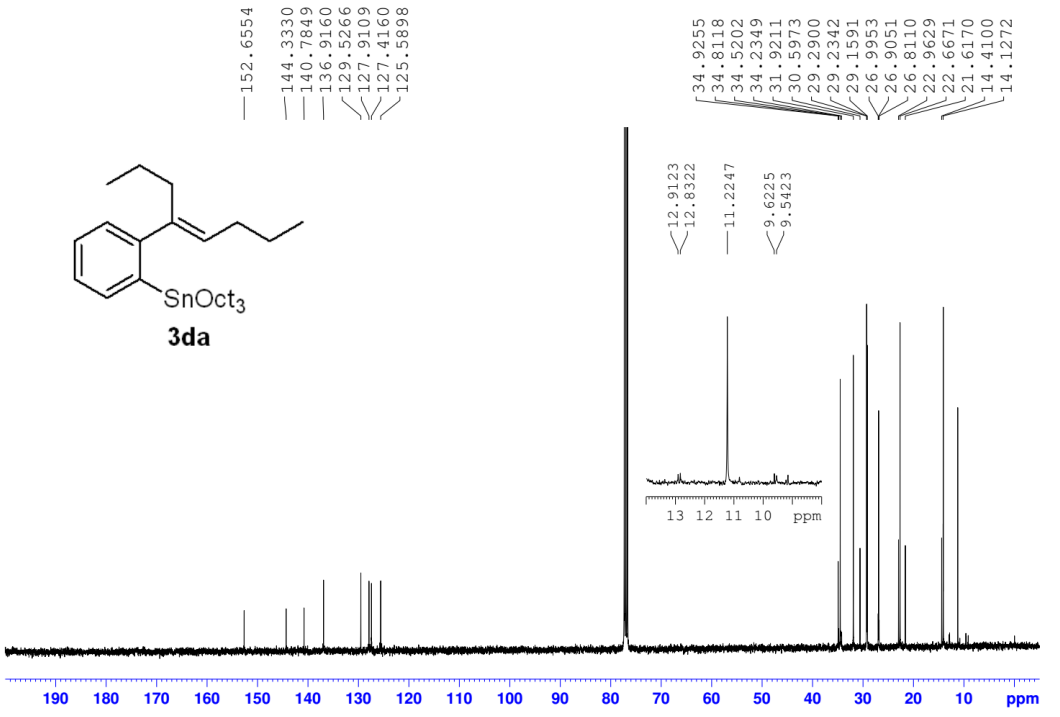
7.2039
7.1932
7.1890
7.1750
7.1716
7.1561
7.1370
7.1340
5.2789
5.2613
5.2437
2.3325
2.3127
2.3067
2.2924
2.1627
2.1446
2.1257
2.1073
1.5507
1.5124
1.4951
1.4868
1.4687
1.4496
1.4309
1.3785
1.3595
1.3393
1.3342
1.2644
1.2551
1.0603
1.0351
1.0177
0.9970
0.9877
0.9756
0.9697
0.9555
0.9515
0.9336
0.9154
0.8973
0.8809
0.8634
SnOct3
3da
7.5
7.4
7.3
7.2
ppm
1.028
2.994
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.03
2.99
0.96
1.93
2.00
9.77
34.15
21.35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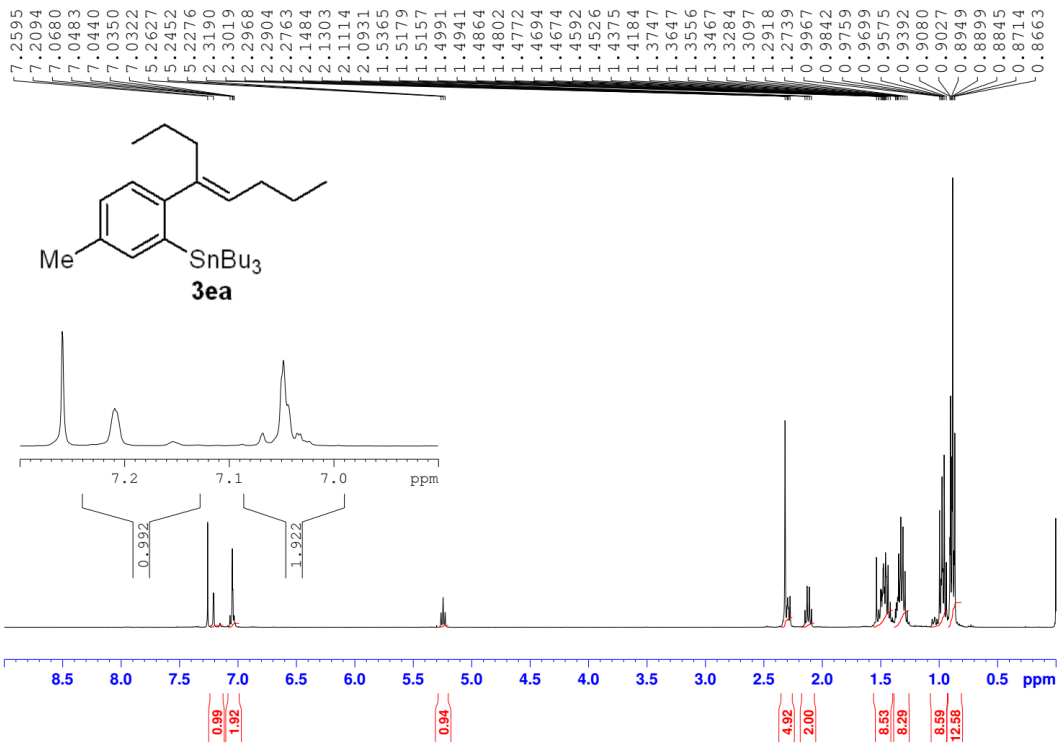
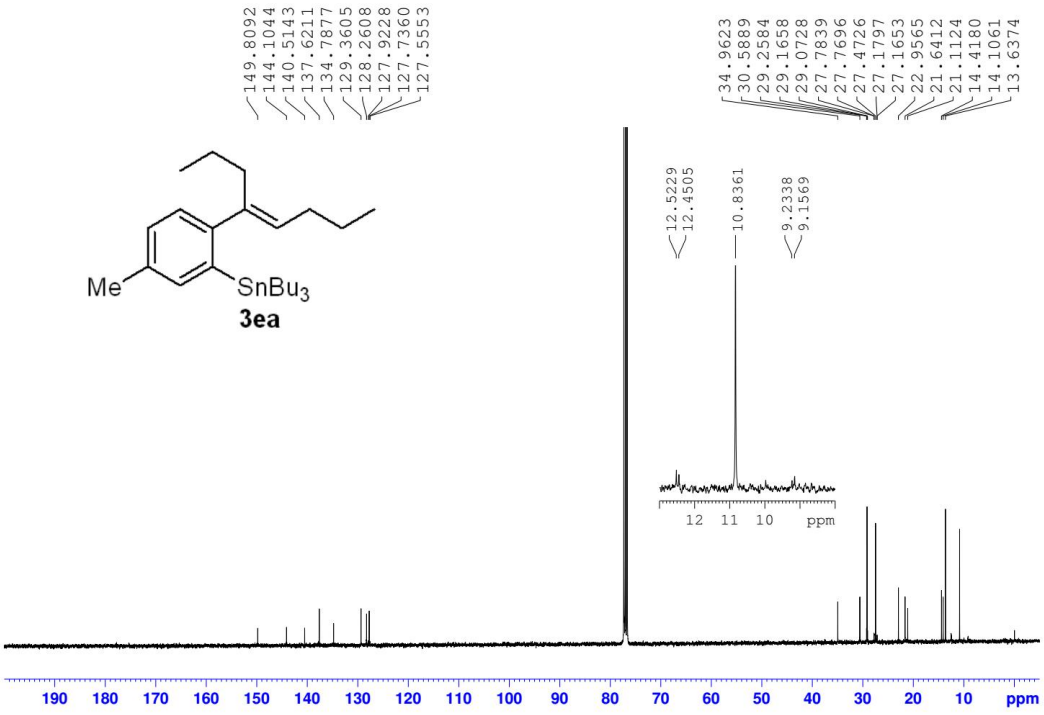
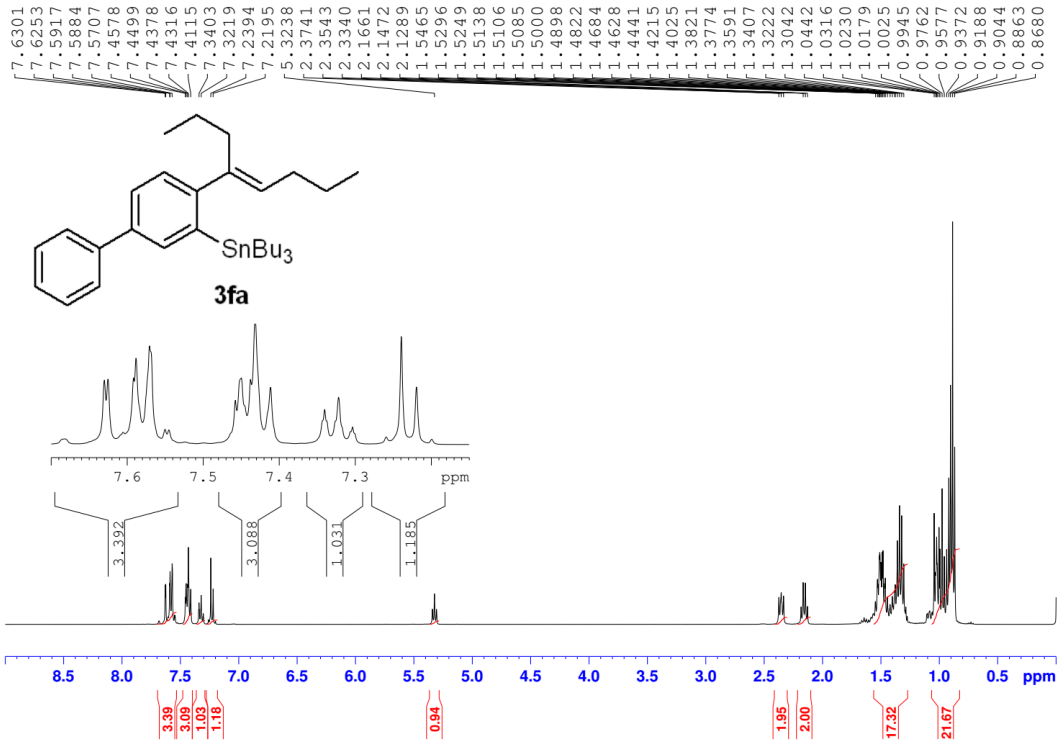
127.4160
125.5898
34.9255
34.8118
34.5202
34.2349
31.9211
30.5973
29.2900
29.2342
29.1591
26.9953
26.9051
26.8110
22.9629
22.6671
21.6170
14.4100
14.1272
12.9123
12.8322
11.2247
9.6225
9.5423
SnOct3
3da
13 12 11 10 ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Me
SnBu3
3ea
7.2
7.1
7.0
ppm
0.992
1.922
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.99
1.92
0.94
4.92
2.00
8.53
8.29
8.59
12.58


Me
SnBu3
3ea
12 11 10 ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.5707
7.4578
7.4499
7.4378
7.4316
7.4115
7.3403
7.3219
7.2394
7.2195
5.3238
2.3741
2.3543
2.3340
2.1661
2.1472
2.1289
1.5465
1.5296
1.5249
1.5138
1.5106
1.5085
1.5000
1.4898
1.4822
1.4684
1.4628
1.4441
1.4215
1.4025
1.3821
1.3774
1.3591
1.3407
1.3222
1.3042
1.0442
1.0316
1.0230
1.0179
1.0025
0.9945
0.9762
0.9577
0.9372
0.9188
0.9044
0.8863
0.8680
SnBu3
3fa
7.6
7.5
7.4
7.3
ppm
3.392
3.088
1.031
1.185
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
3.39
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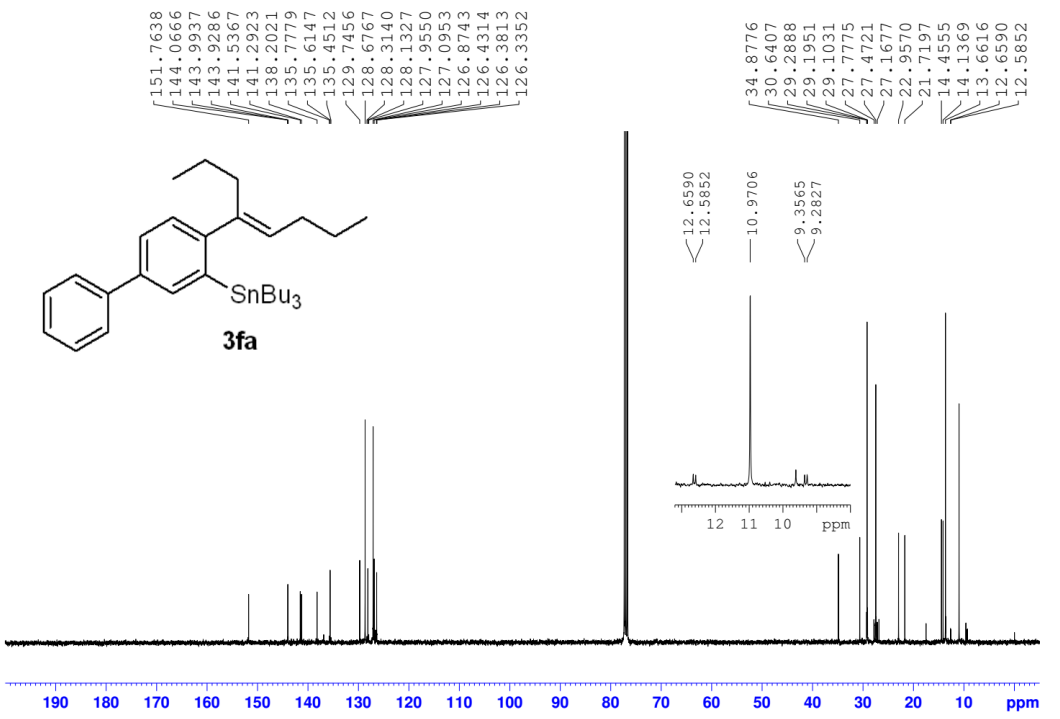
1.03
1.18
0.94
1.95
2.00
17.32
21.67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128.3140
128.1327
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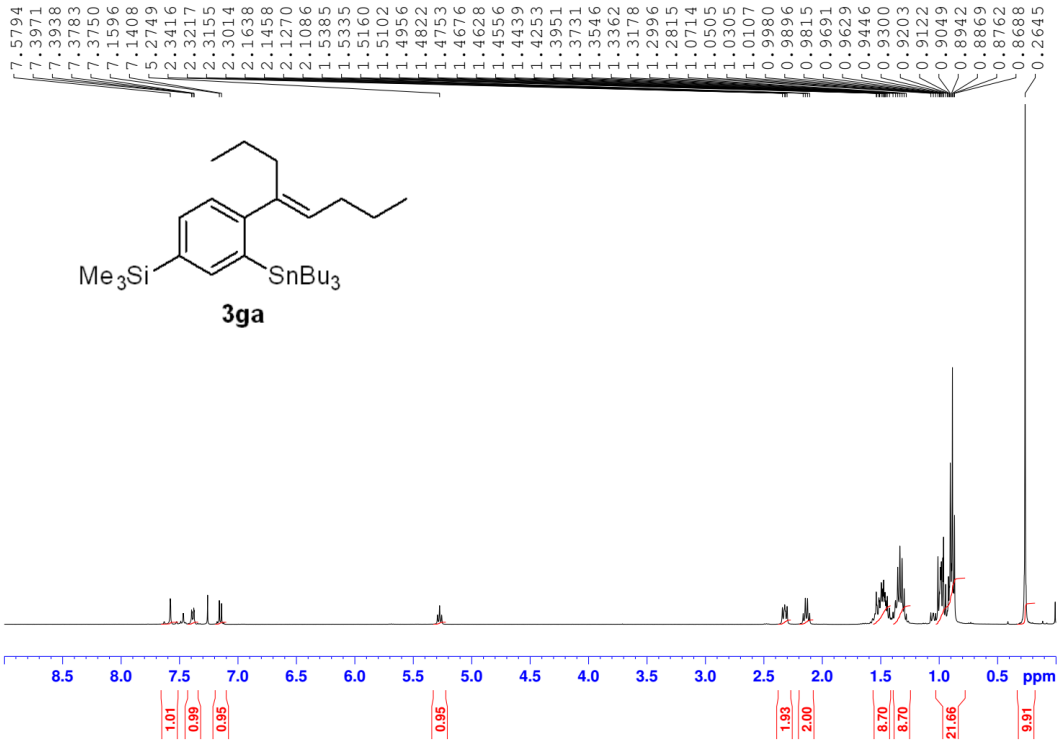
127.0953
126.8743
126.4314
126.3813
126.3352
34.8776
30.6407
29.2888
29.1951
29.1031
27.7775
27.4721
27.1677
22.9570
21.7197
14.4555
14.1369
13.6616
12.6590
12.5852
SnBu3
3fa
12.6590
12.5852
10.9706
9.3565
9.2827
12
11
10
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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2.3416
2.3217
2.3155
2.3014
2.1638
2.1458
2.1270
2.1086
1.5385
1.5335
1.5160
1.5102
1.4956
1.4822
1.4753
1.4676
1.4628
1.4556
1.4439
1.4253
1.3951
1.3731
1.3546
1.3362
1.3178
1.2996
1.2815
1.0714
1.0505
1.0305
1.0107
0.9980
0.9896
0.9815
0.9691
0.9629
0.9446
0.9300
0.9203
0.9122
0.9049
0.8942
0.8869
0.8762
0.8688
0.2645
Me3Si
SnBu3
3ga
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
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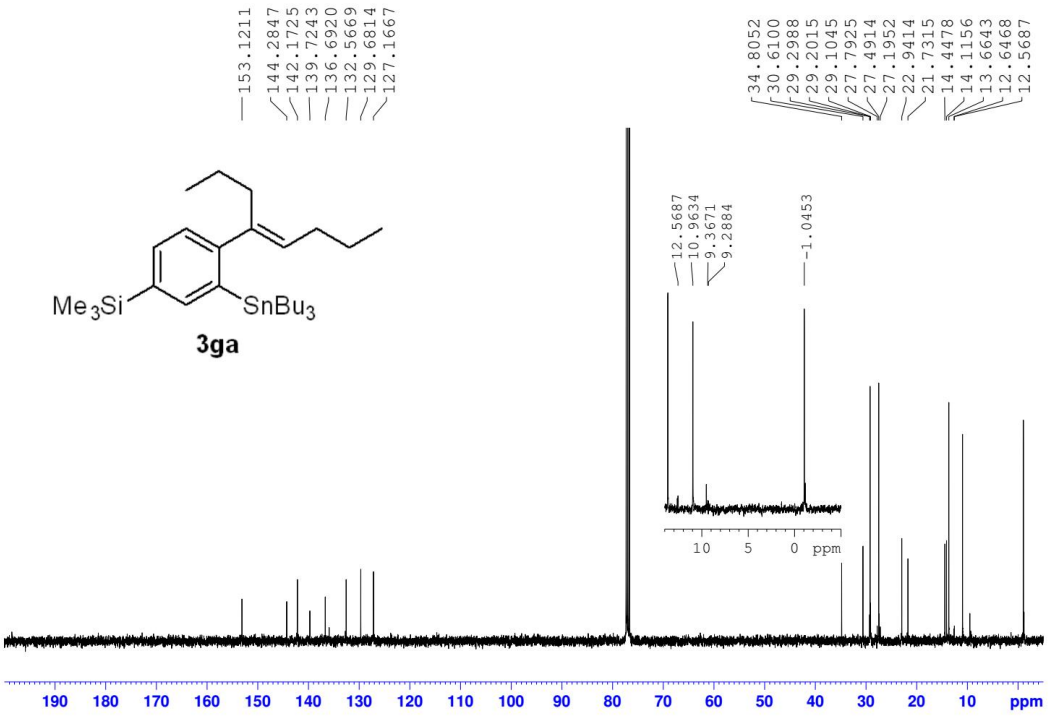
0.99
0.95
0.95
1.93
2.00
8.70
8.70
21.66
9.91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132.5669
129.6814
127.1667
34.8052
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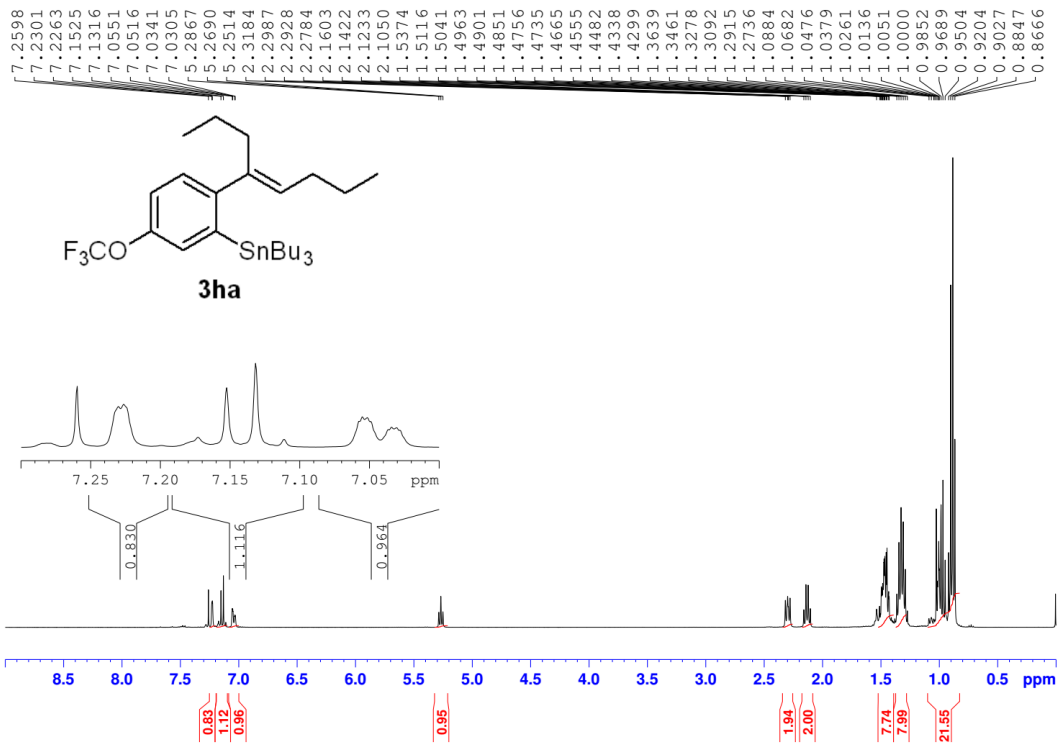
29.2988
29.2015
29.1045
27.7925
27.4914
27.1952
22.9414
21.7315
14.4478
14.1156
13.6643
12.6468
12.5687
12.5687
10.9634
9.3671
9.2884
-1.0453
10 5 0 ppm
Me3Si
SnBu3
3ga
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.0516
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7.0305
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5.2690
5.2514
2.3184
2.2987
2.2928
2.2784
2.1603
2.1422
2.1233
2.1050
1.5374
1.5116
1.5041
1.4963
1.4901
1.4851
1.4756
1.4735
1.4665
1.4555
1.4482
1.4338
1.4299
1.3639
1.3461
1.3278
1.3092
1.2915
1.2736
1.0884
1.0682
1.0476
1.0379
1.0261
1.0136
1.0051
1.0000
0.9852
0.9689
0.9504
0.9204
0.9027
0.8847
0.8666
F3CO
SnBu3
3ha
7.25
7.20
7.15
7.10
7.05
ppm
0.830
1.116
0.964
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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2.00
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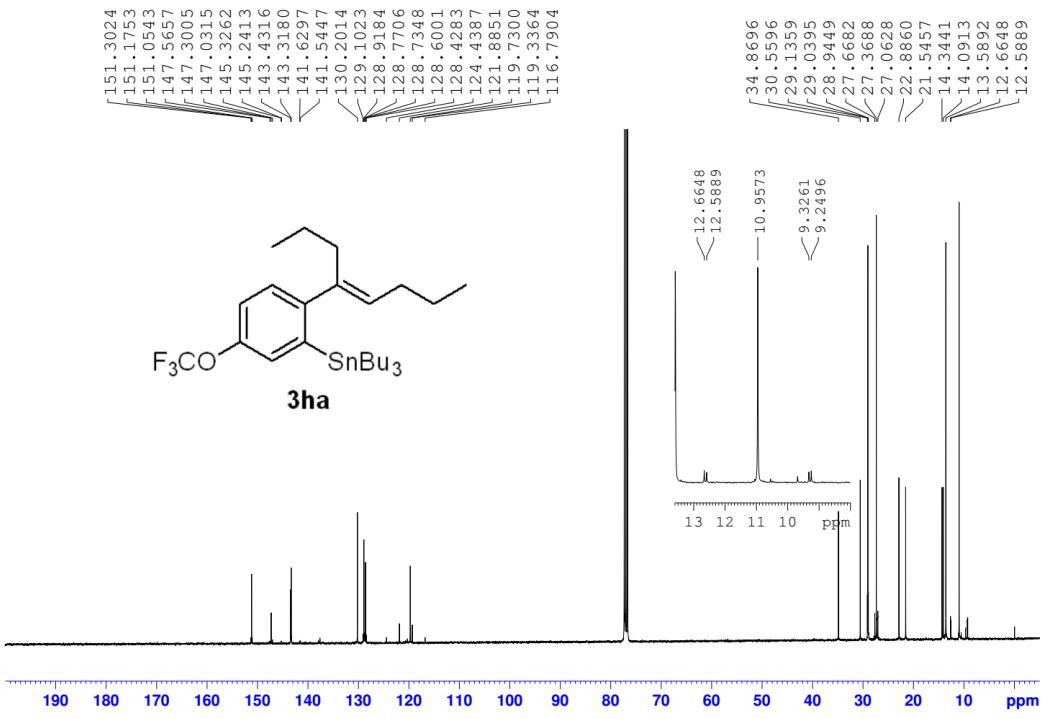
7.99
21.55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141.5447
130.2014
129.1023
128.9184
128.7706
128.7348
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119.7300
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14.3441
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12.6648
12.5889
12.6648
12.5889
10.9573
9.3261
9.2496
F3CO
SnBu3
3ha
13
12
11
10
ppm
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180
170
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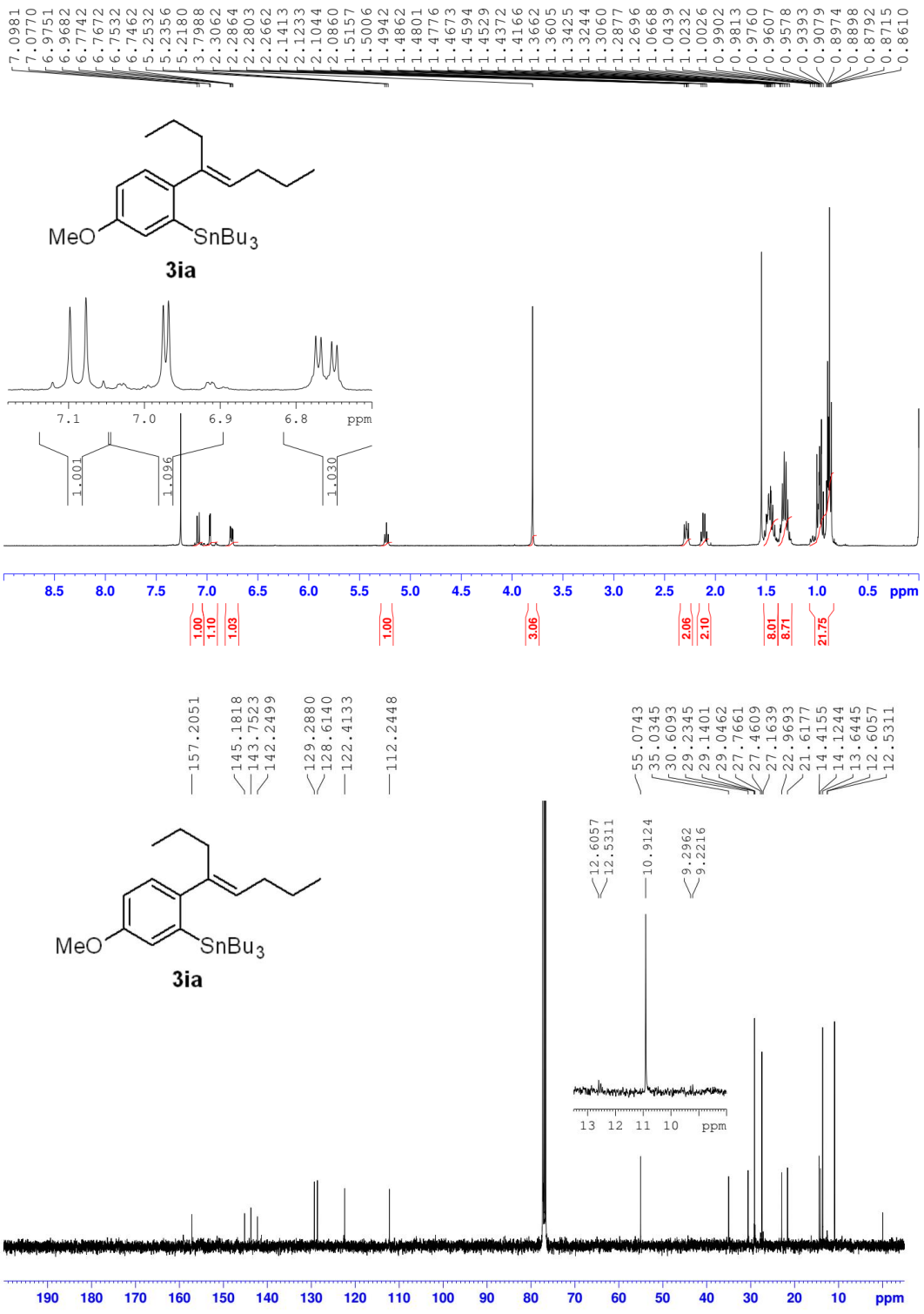
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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5.2532
5.2356
5.2180
3.7988
3.3062
2.2864
2.2803
2.2662
2.1413
2.1233
2.1044
2.0860
1.5157
1.5006
1.4942
1.4862
1.4801
1.4776
1.4673
1.4594
1.4529
1.4372
1.4166
1.3662
1.3605
1.3425
1.3244
1.3060
1.2877
1.2696
1.0668
1.0439
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1.0026
0.9902
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0.8974
0.8898
0.8792
0.8715
0.8610
MeO
SnBu3
3ia
7.1
7.0
6.9
6.8
ppm
1.001
1.096
1.030
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.10
1.03
1.00
3.06
2.06
2.10
8.01
8.71
21.75
157.2051
145.1818
143.7523
142.2499
129.2880
128.6140
122.4133
112.2448
55.0743
35.0345
30.6093
29.2345
29.1401
29.0462
27.7661
27.4609
27.1639
22.9693
21.6177
14.4155
14.1244
13.6445
12.6057
12.5311
12.6057
12.5311
10.9124
9.2962
9.2216
MeO
SnBu3
3ia
13
12
11
10
ppm
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70
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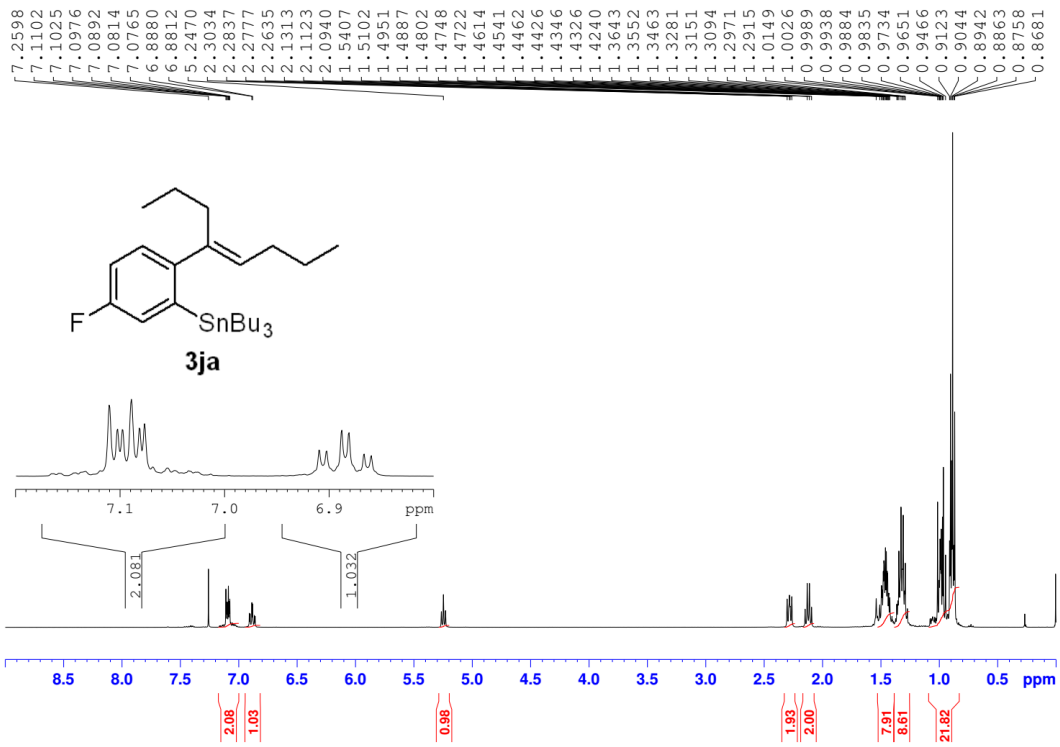
30
20
10
ppm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2.3034
2.2837
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2.1313
2.1123
2.0940
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SnBu3
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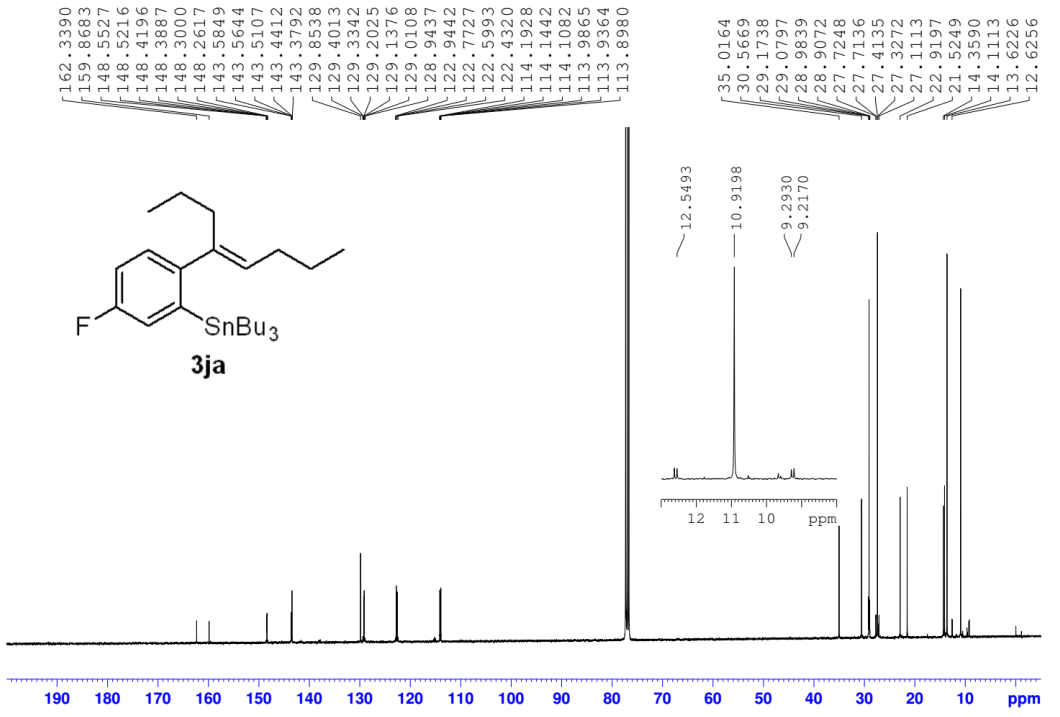
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10
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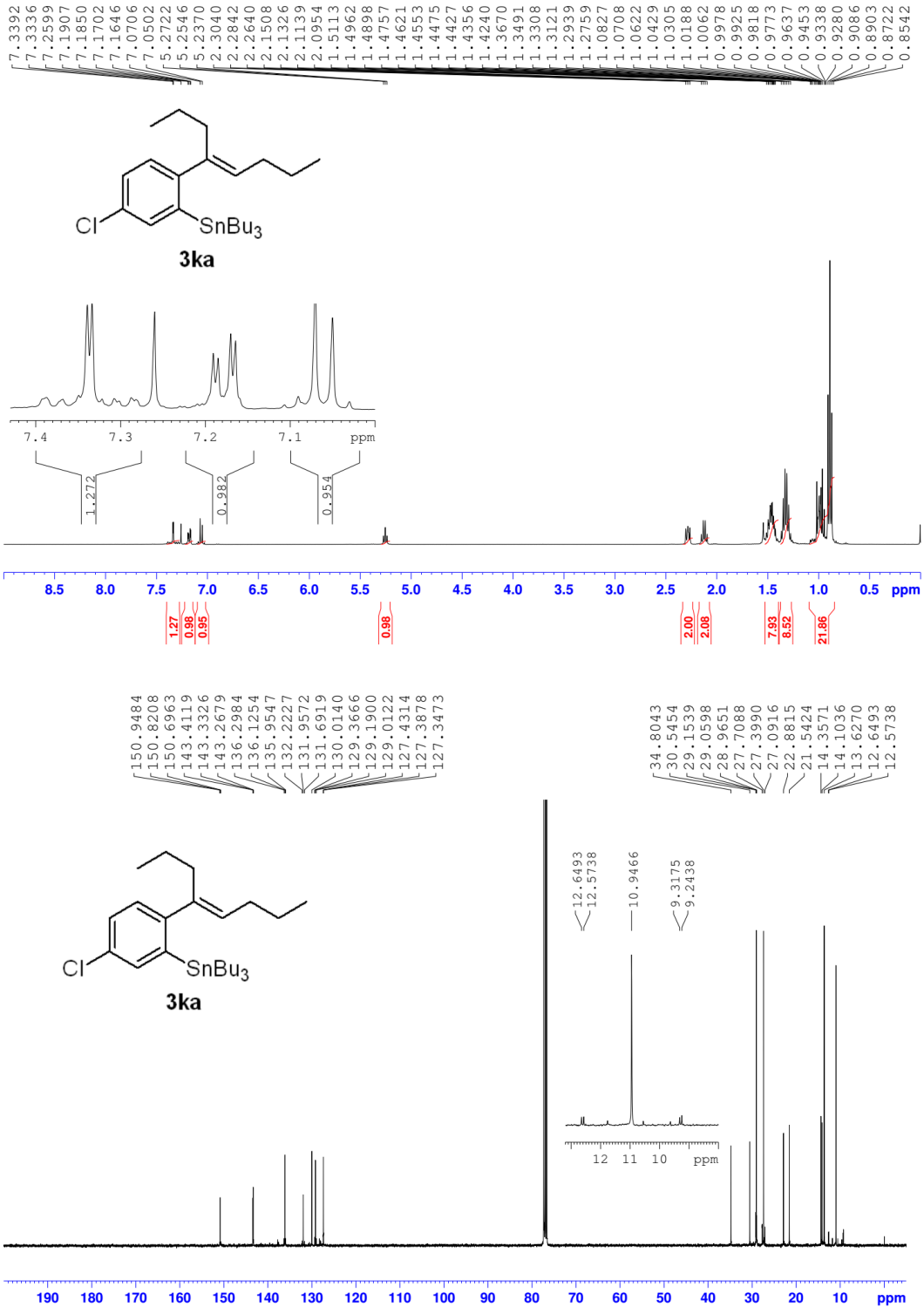
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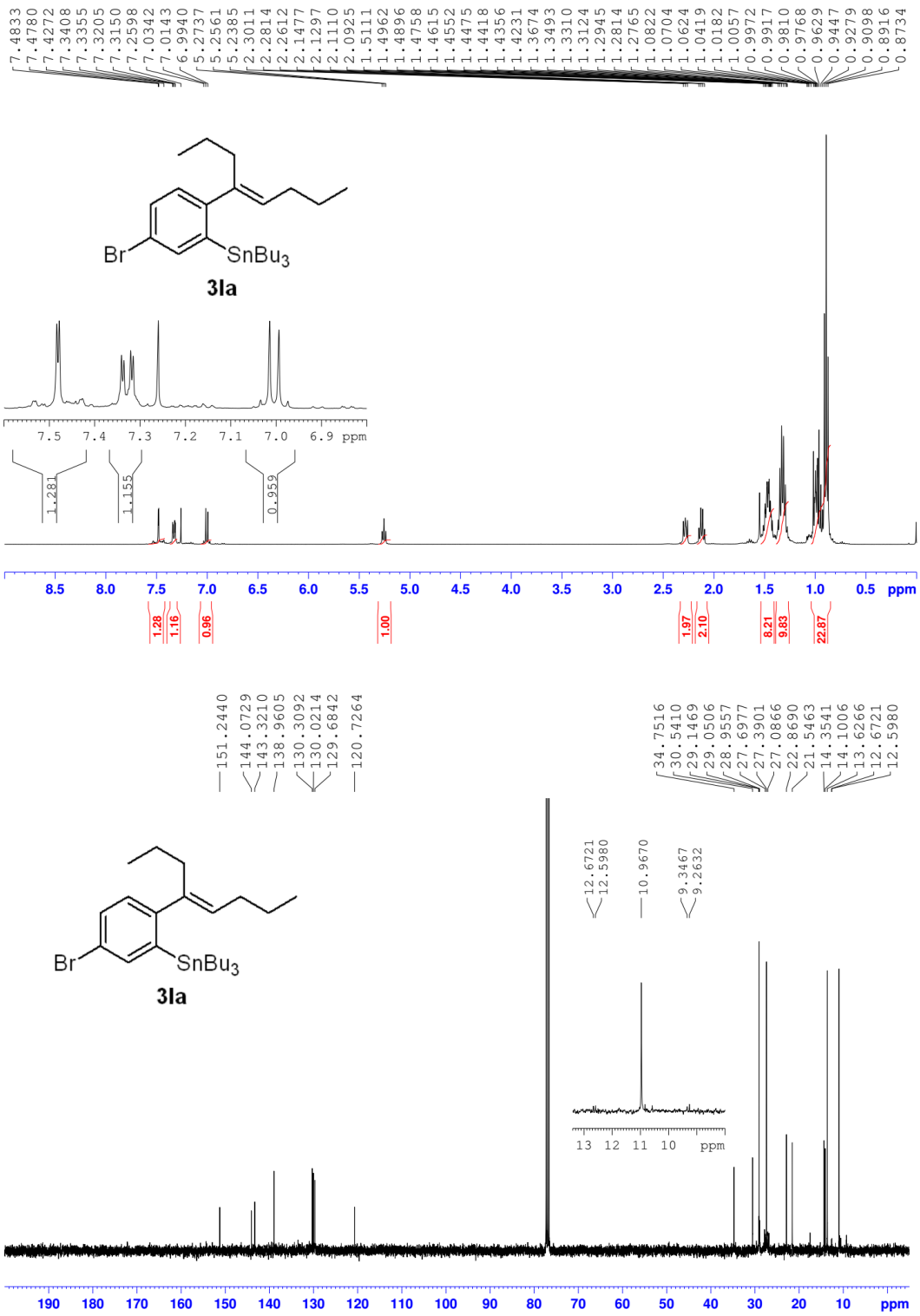
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Br
SnBu3
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1.16
0.96
1.00
1.97
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9.83
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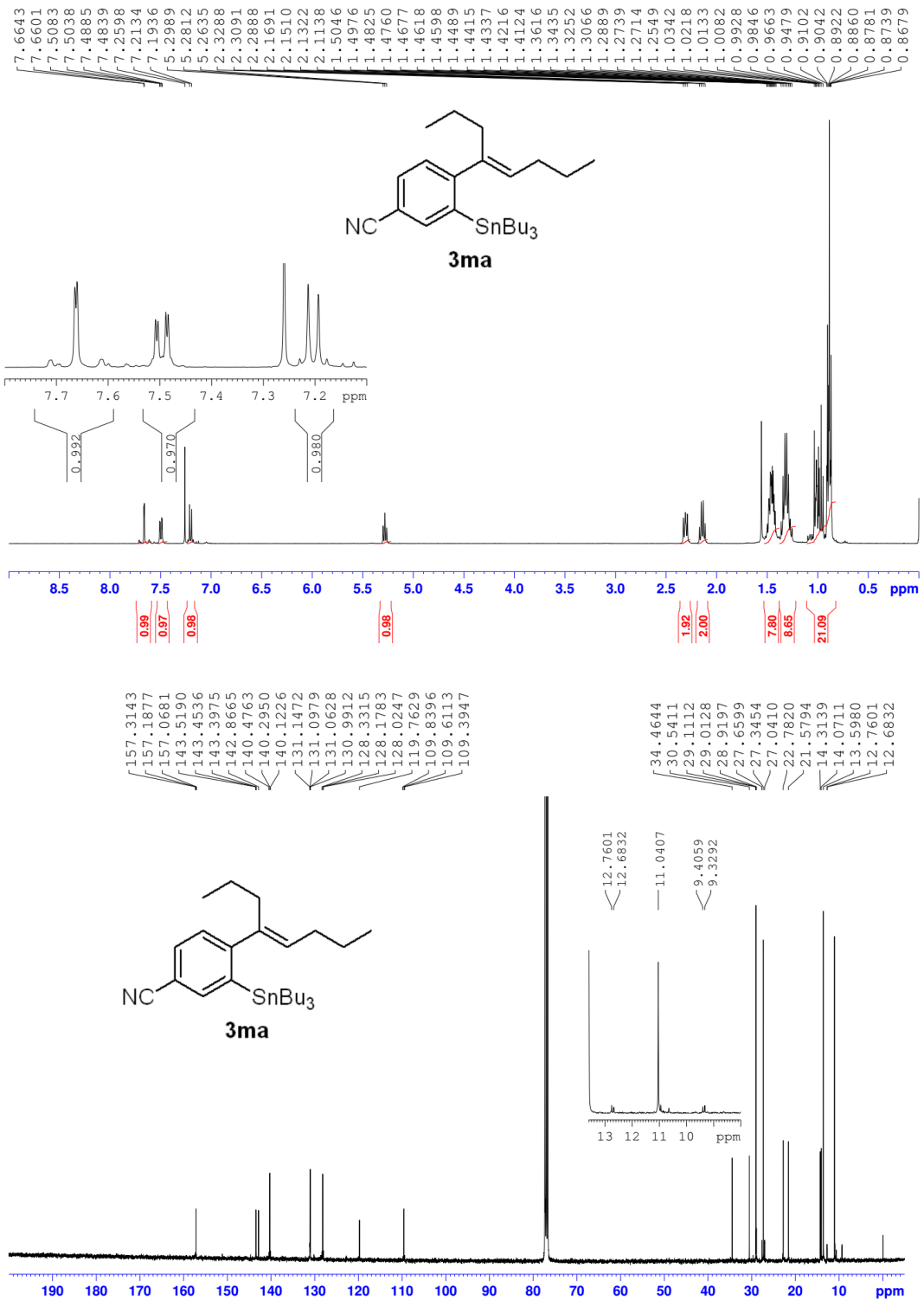
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7.3
7.2
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5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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SnBu3
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13
12
11
10
ppm
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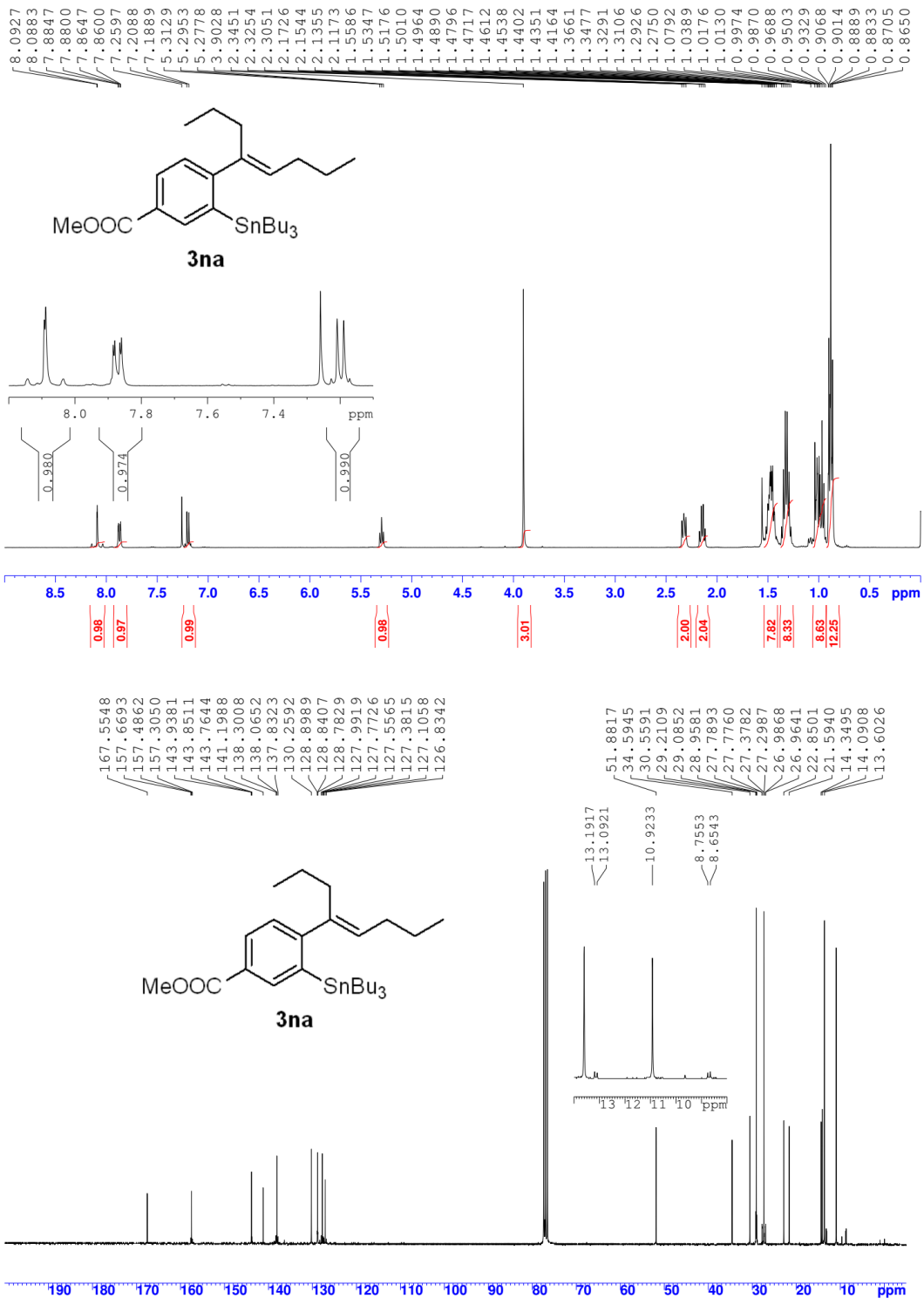
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MeOOC
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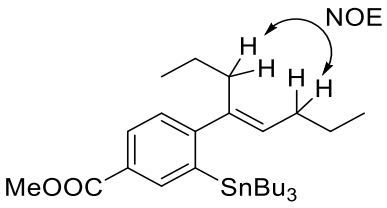


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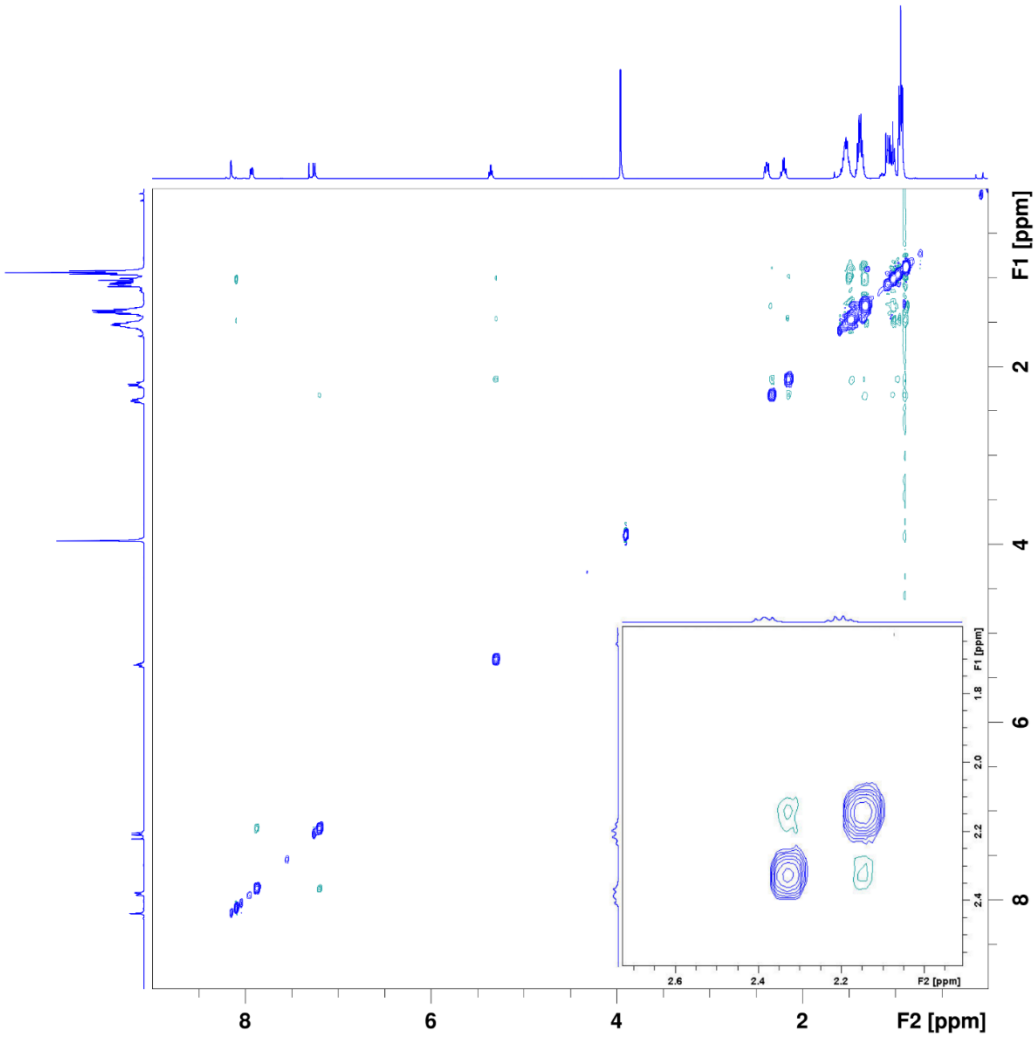

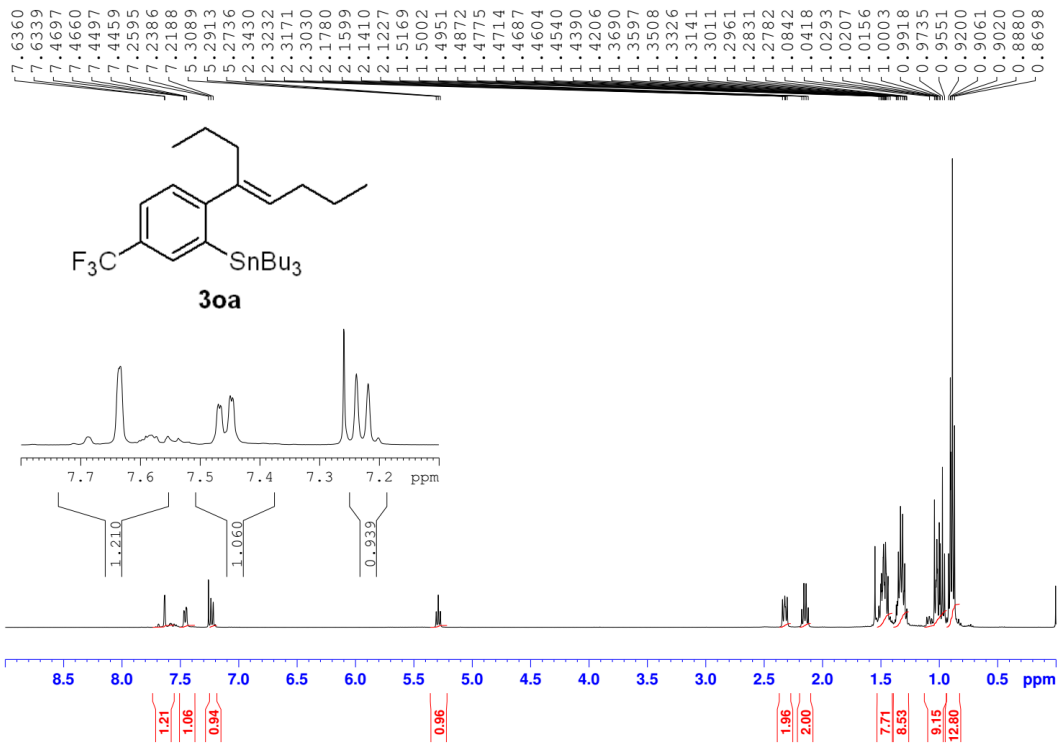
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1.4872
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1.4714
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1.3011
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SnBu3
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3.5
3.0
2.5
2.0
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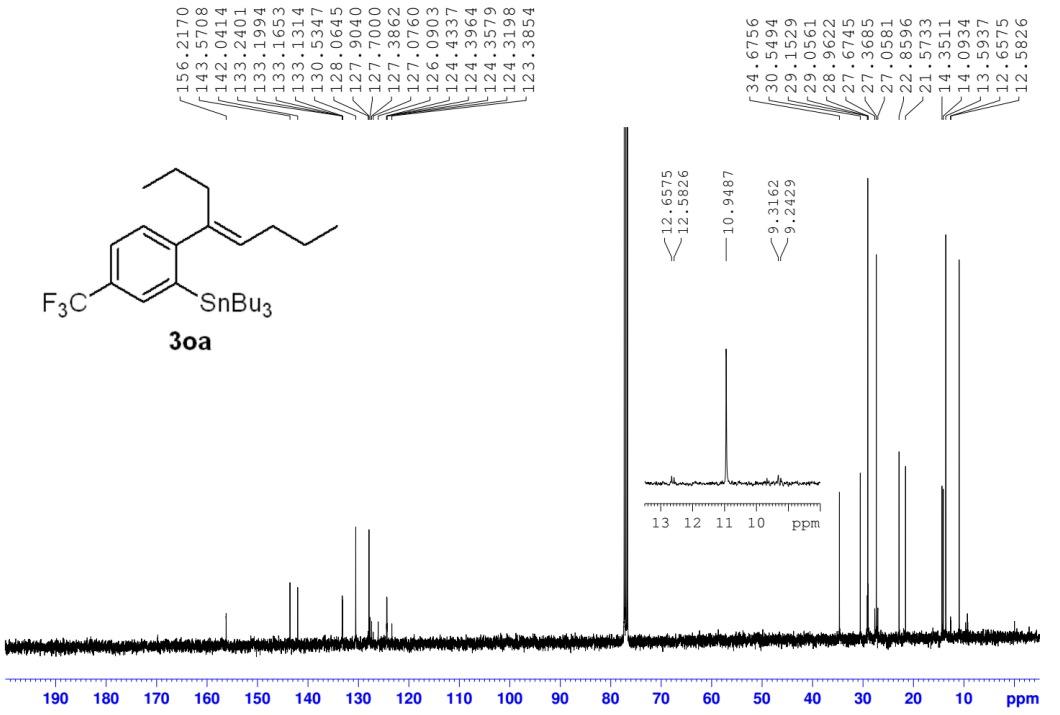
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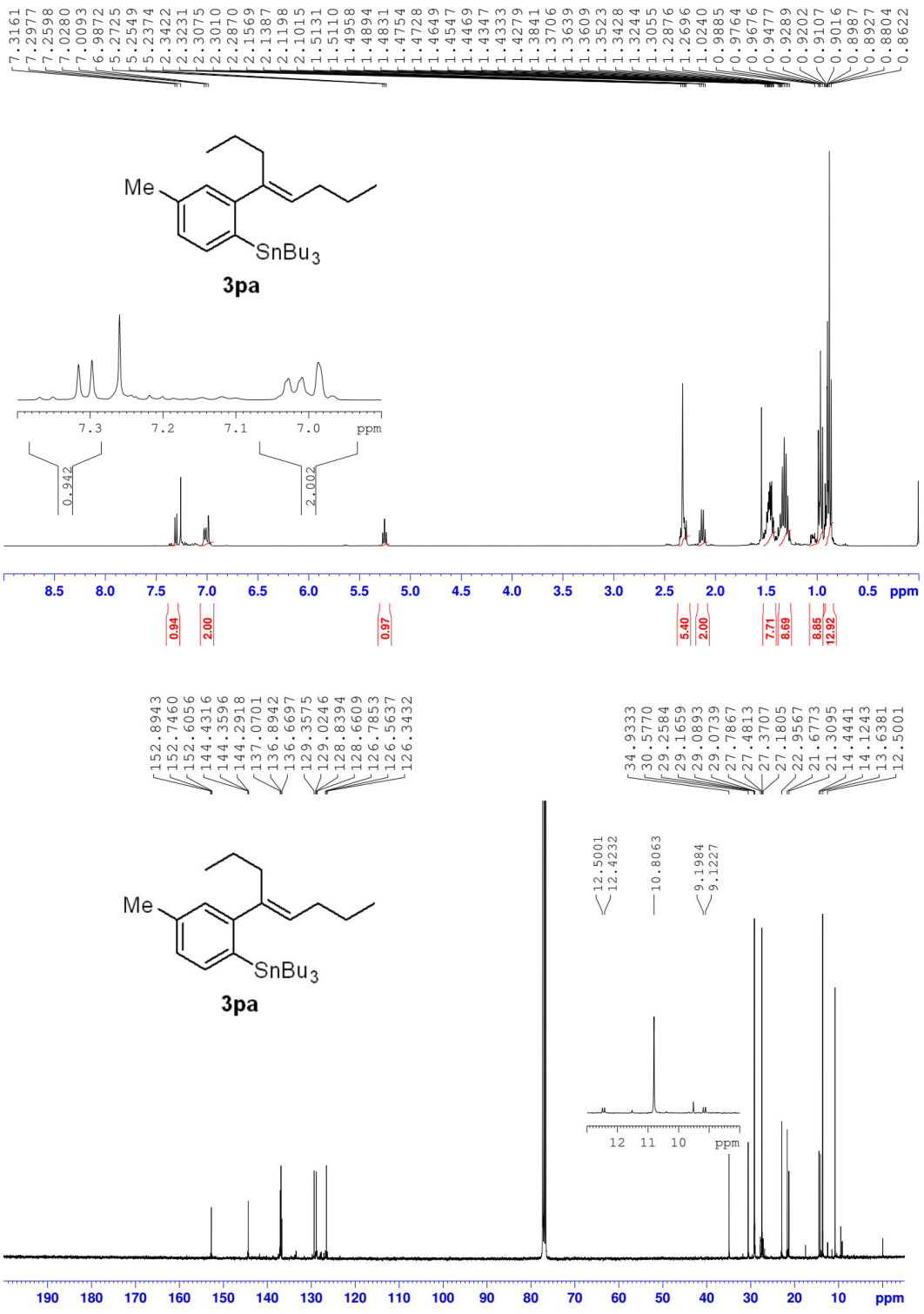
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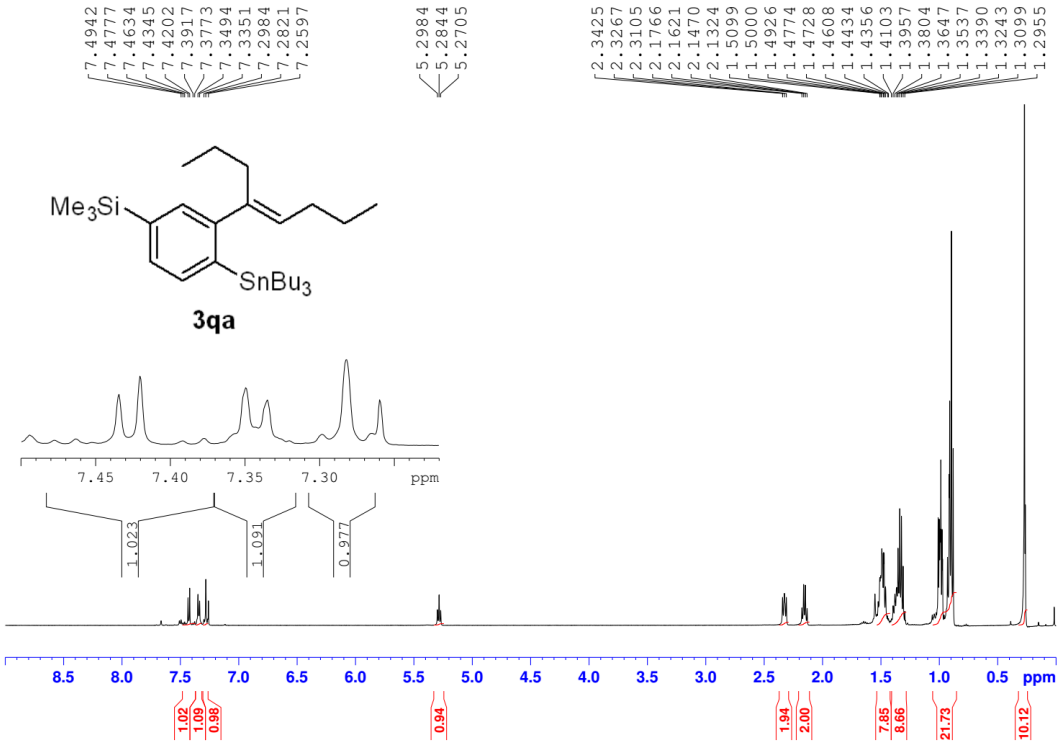
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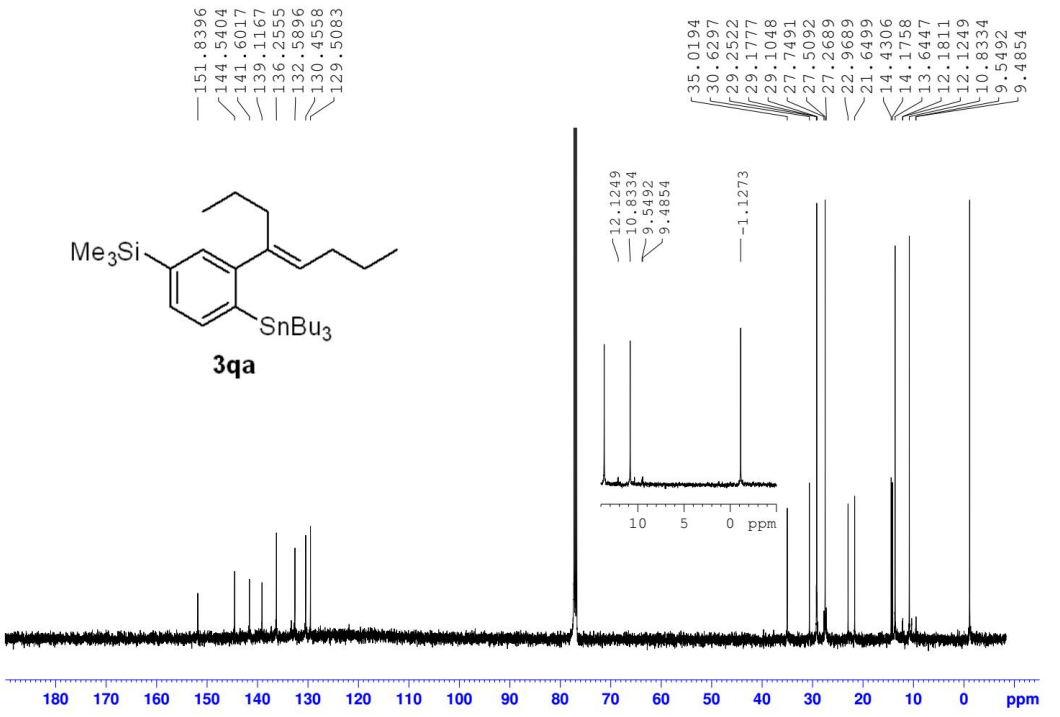
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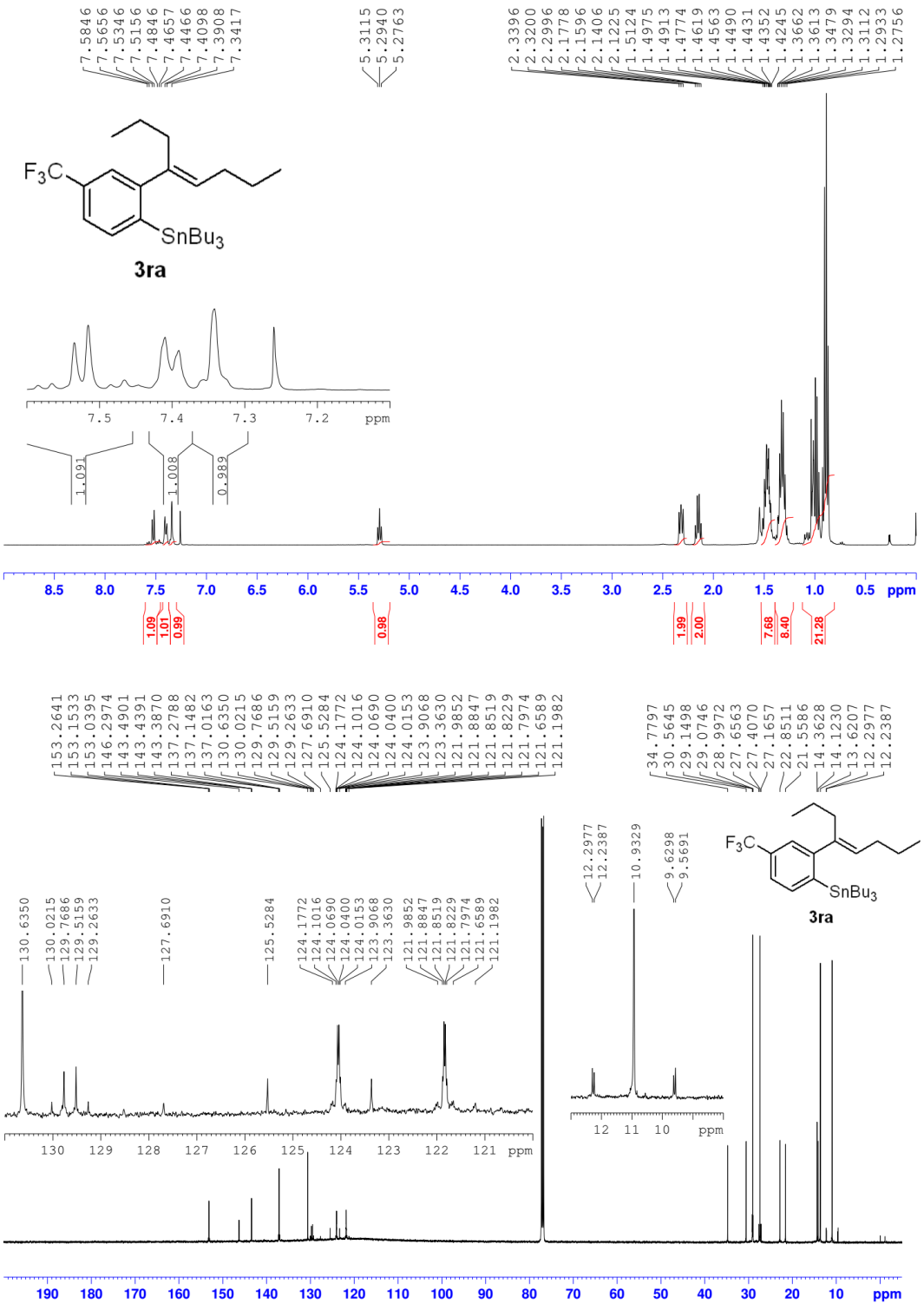
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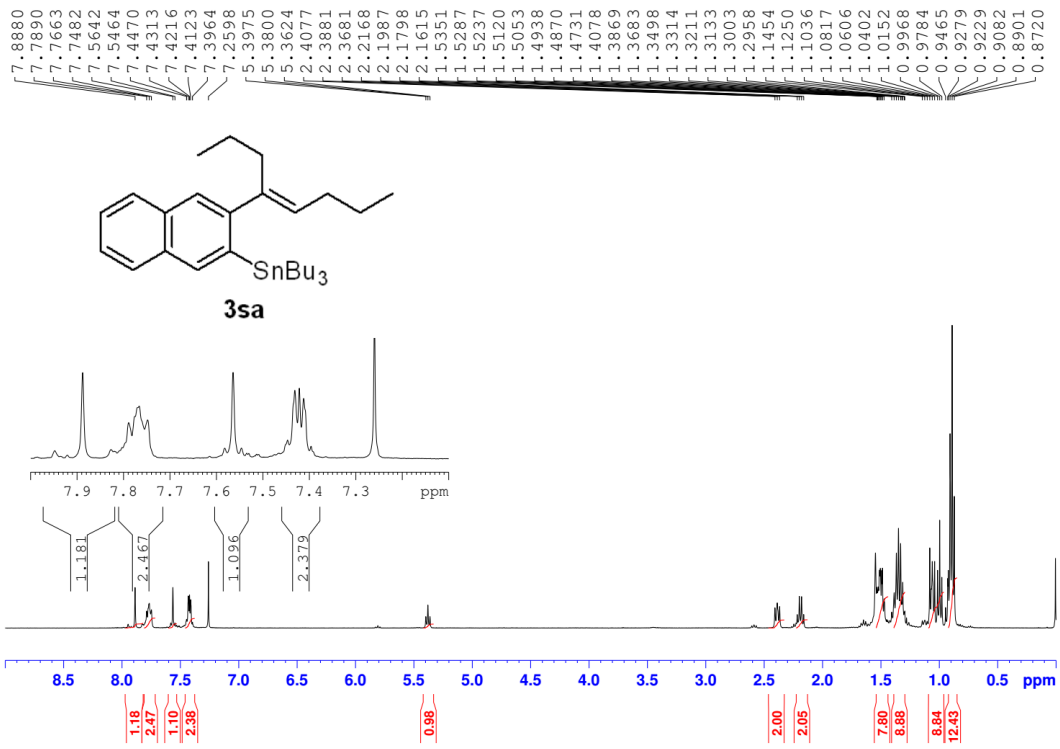
13.6207
12.2977
12.2387
130.6350
130.0215
129.7686
129.5159
129.2633
127.6910
125.5284
124.1772
124.1016
124.0690
124.0400
124.0153
123.9068
123.3630
121.9852
121.8847
121.8519
121.8229
121.7974
121.6589
121.1982
130
129
128
127
126
125
124
123
122
121
ppm
12.2977
12.2387
10.9329
9.6298
9.5691
12
11
10
ppm
F3C
SnBu3
3ra
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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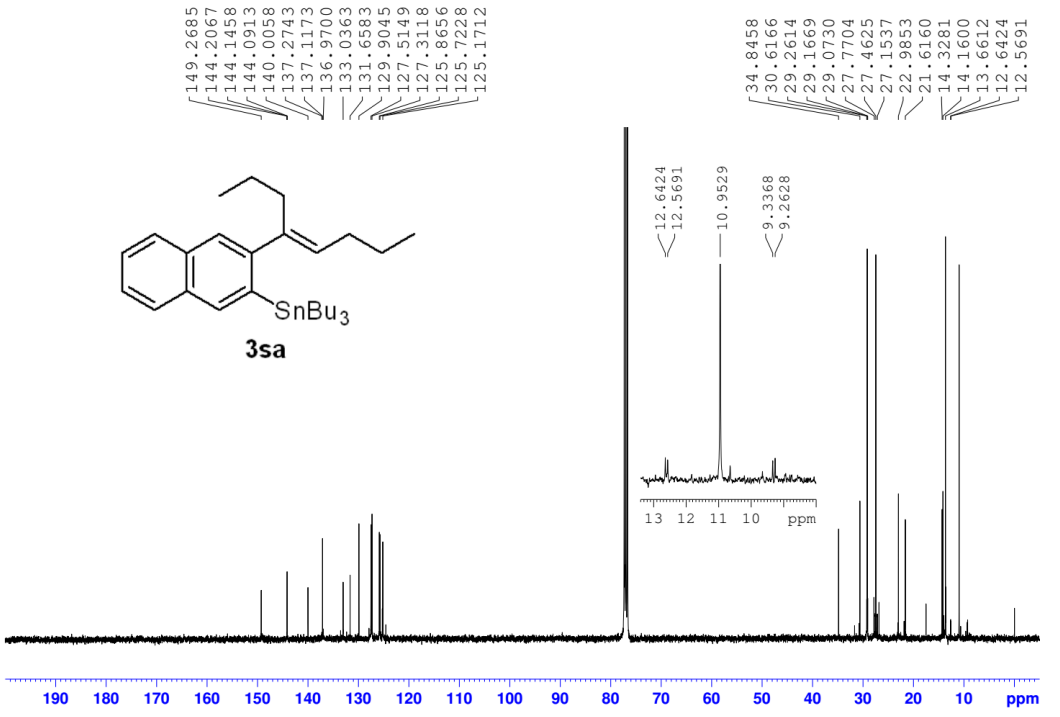
7.7663
7.7482
7.5642
7.5464
7.4470
7.4313
7.4216
7.4123
7.3964
7.2598
5.3975
5.3800
5.3624
2.4077
2.3881
2.3681
2.2168
2.1987
2.1798
2.1615
1.5351
1.5287
1.5237
1.5120
1.5053
1.4938
1.4870
1.4731
1.4078
1.3869
1.3683
1.3498
1.3314
1.3211
1.3133
1.3003
1.2958
1.1454
1.1250
1.1036
1.0817
1.0606
1.0402
1.0152
0.9968
0.9784
0.9465
0.9279
0.9229
0.9082
0.8901
0.8720
SnBu3
3sa
7.9 7.8 7.7 7.6 7.5 7.4 7.3 ppm
1.181
2.467
1.096
2.379
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.18
2.47
1.10
2.38
0.98
2.00
2.05
7.80
8.88
8.84
12.43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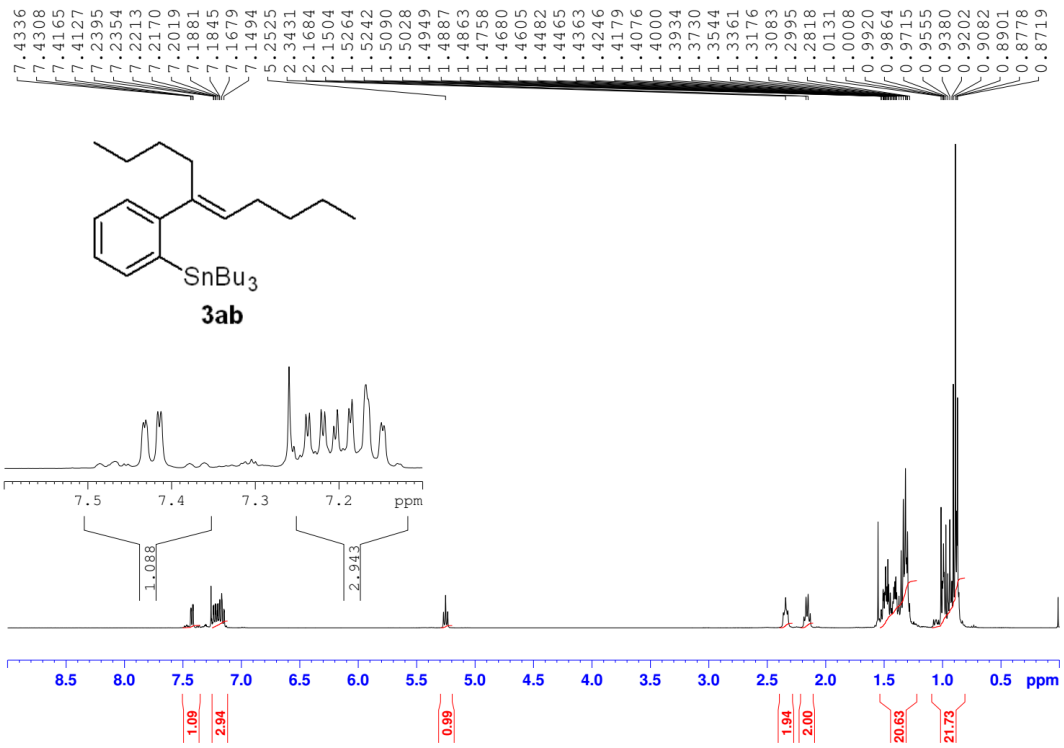
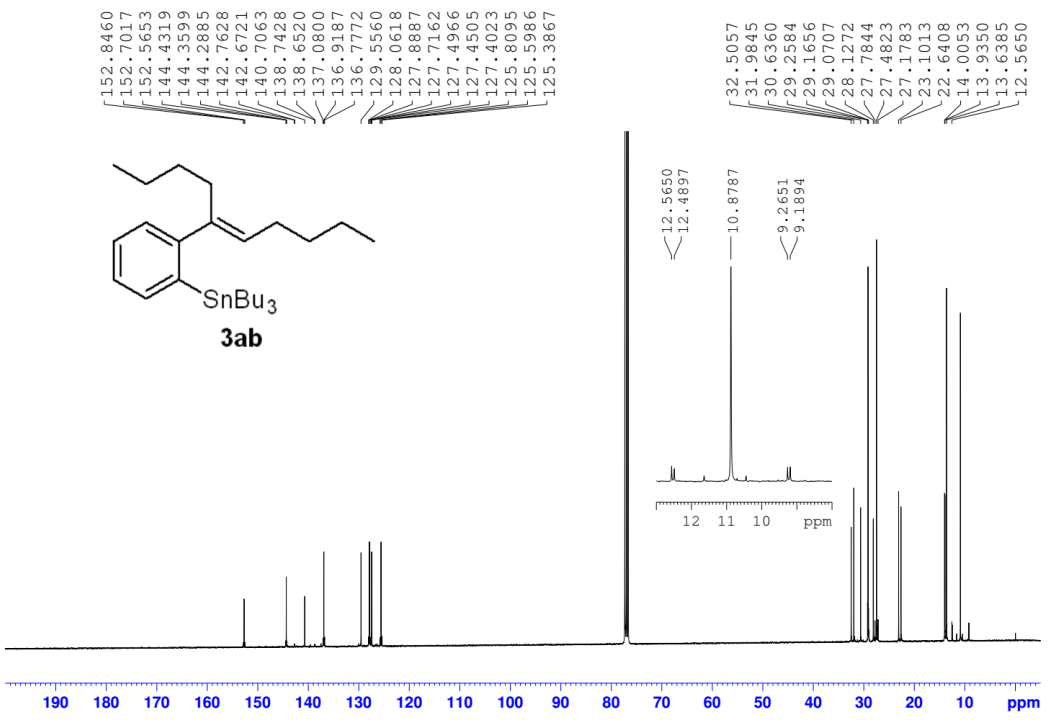
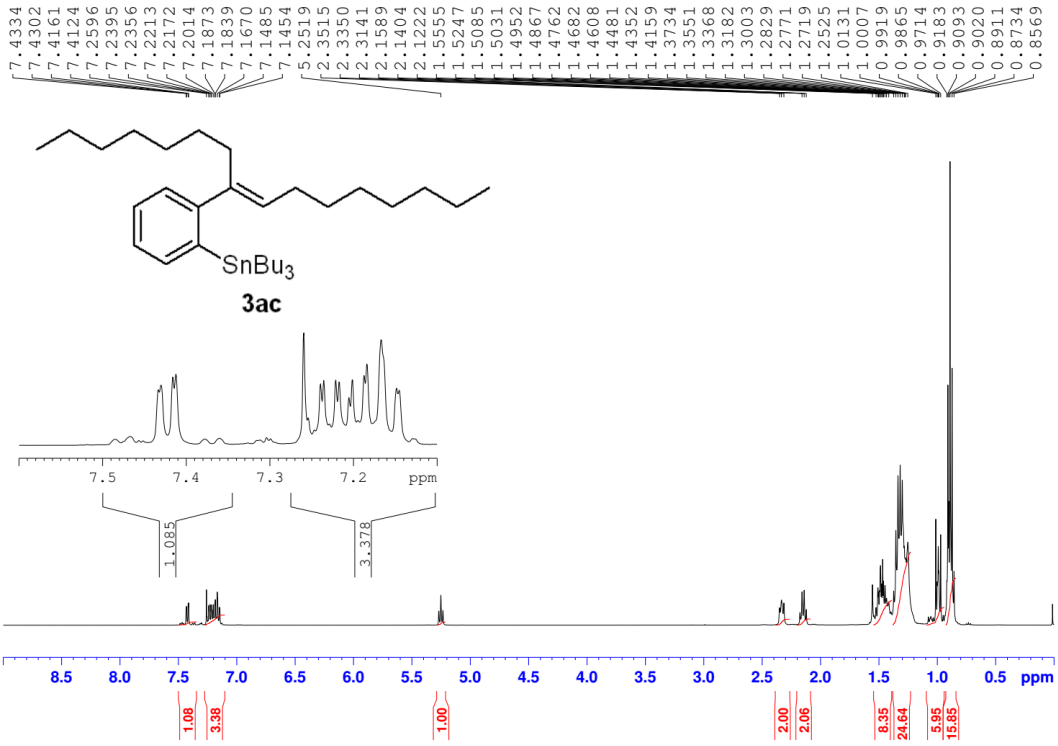
144.1458
144.0913
140.0058
137.2743
137.1173
136.9700
133.0363
131.6583
129.9045
127.5149
127.3118
125.8656
125.7228
125.1712
34.8458
30.6166
29.2614
29.1669
29.0730
27.7704
27.4625
27.1537
22.9853
21.6160
14.3281
14.1600
13.6612
12.6424
12.5691
SnBu3
3sa
12.6424
12.5691
10.9529
9.3368
9.2628
13 12 11 10 ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


SnBu3
3ab


SnBu3
3ab


SnBu3
3ac
7.5
7.4
7.3
7.2
ppm
1.085
3.378
8.5
8.0
7.5
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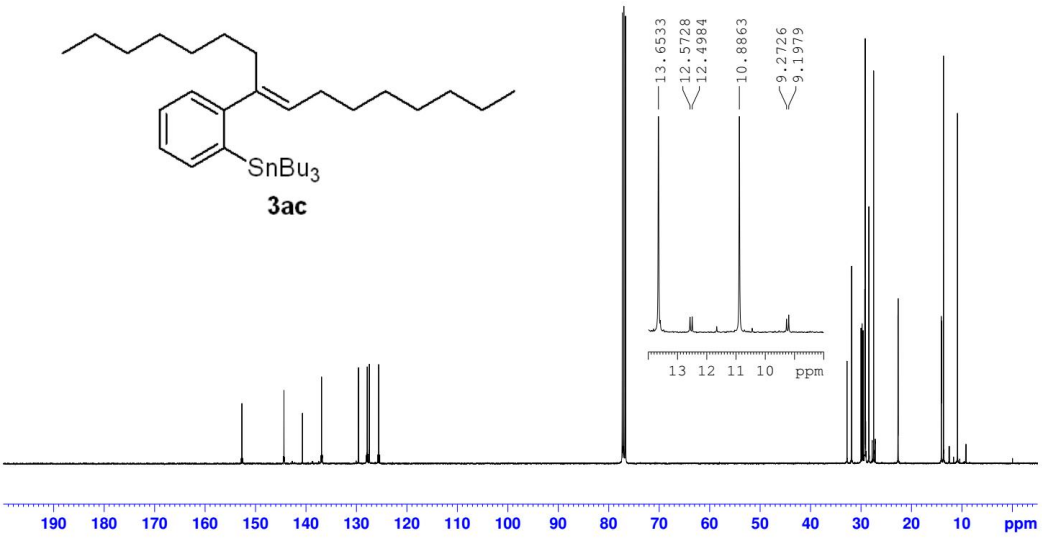
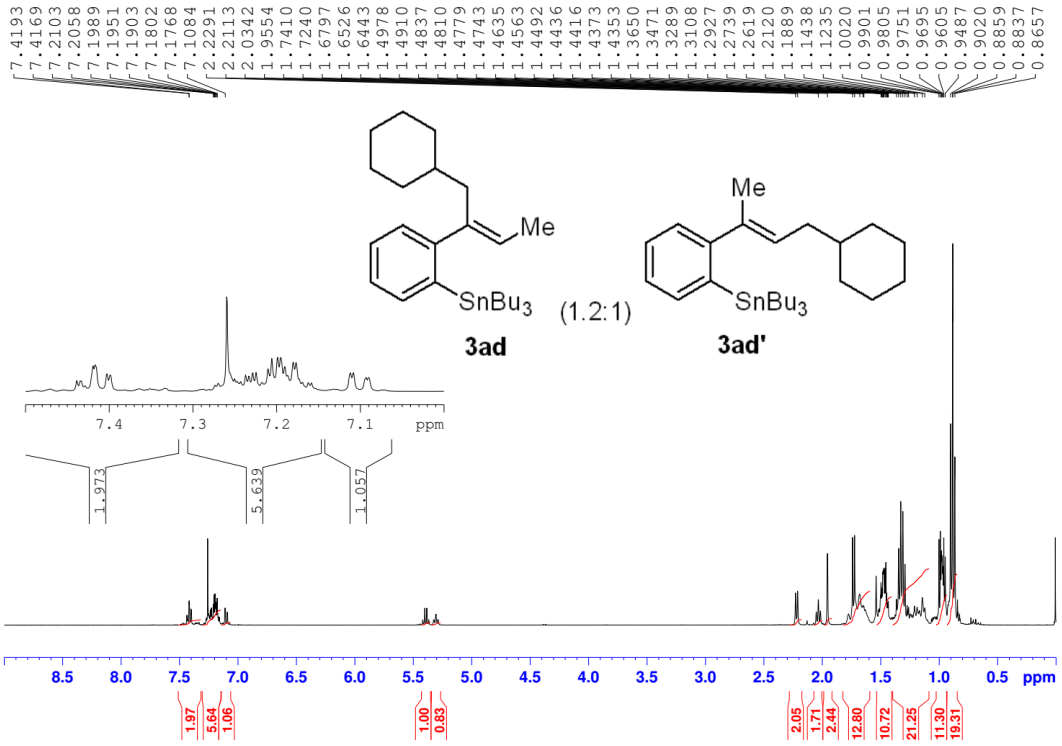
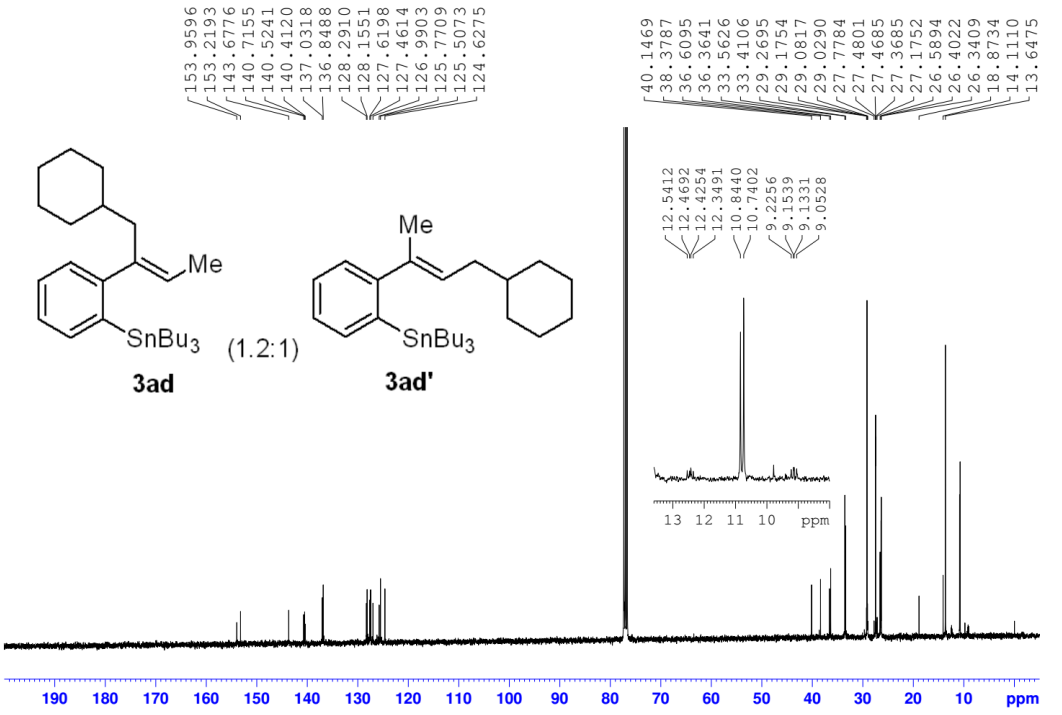
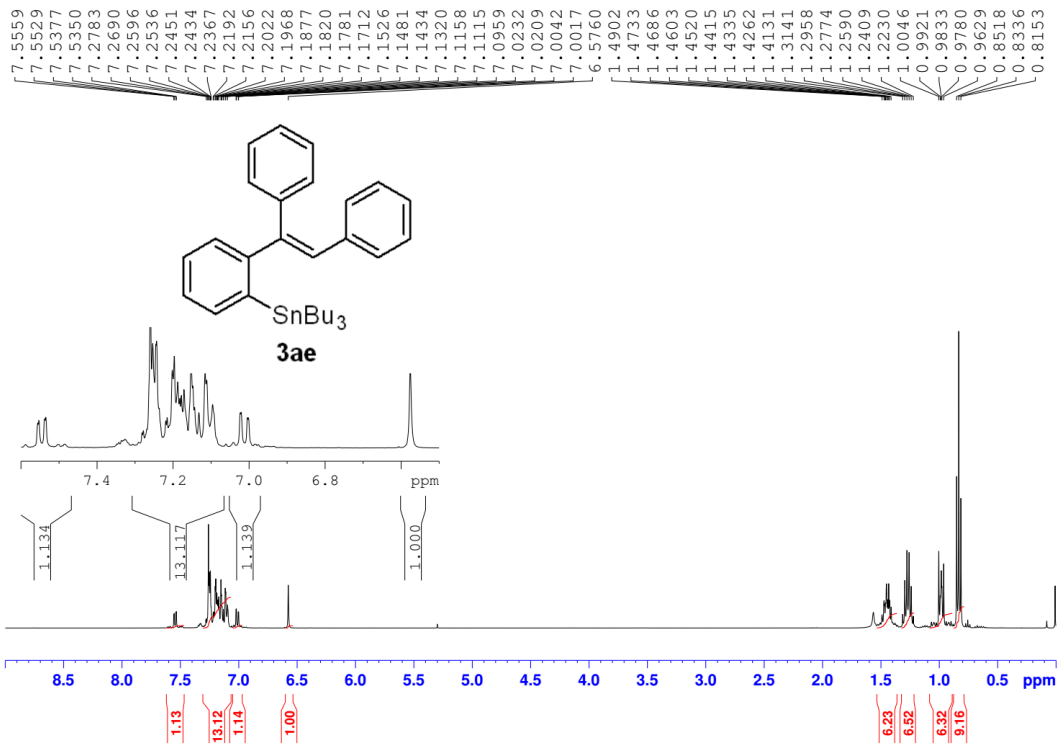
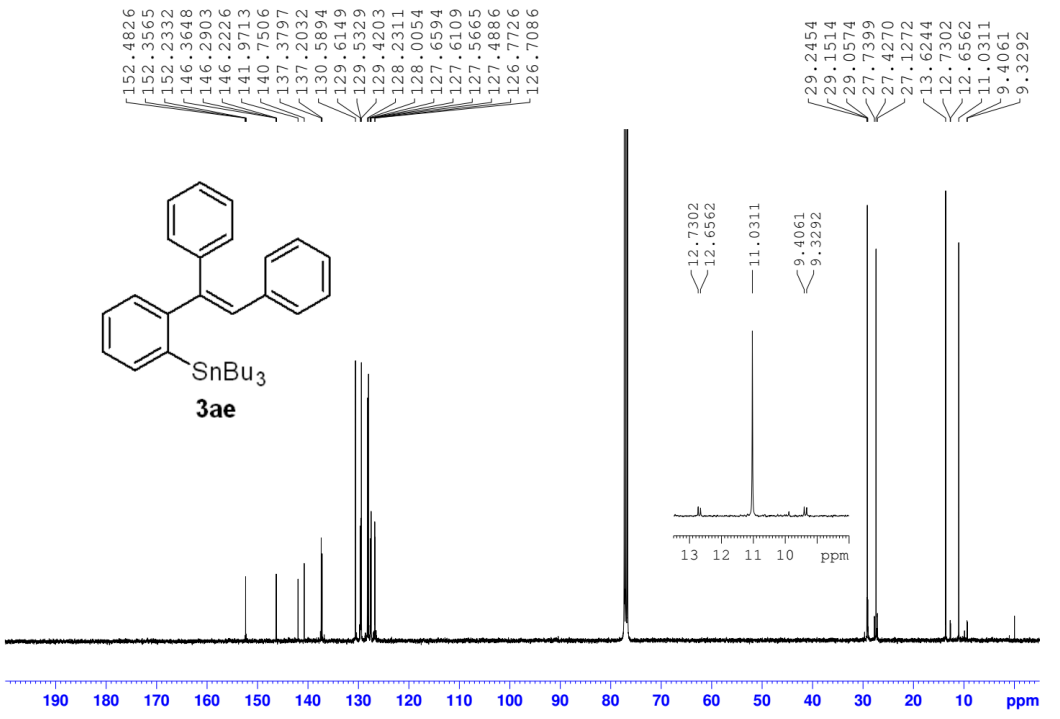
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.08
3.38
1.00
2.00
2.06
8.35
24.64
5.95
15.85

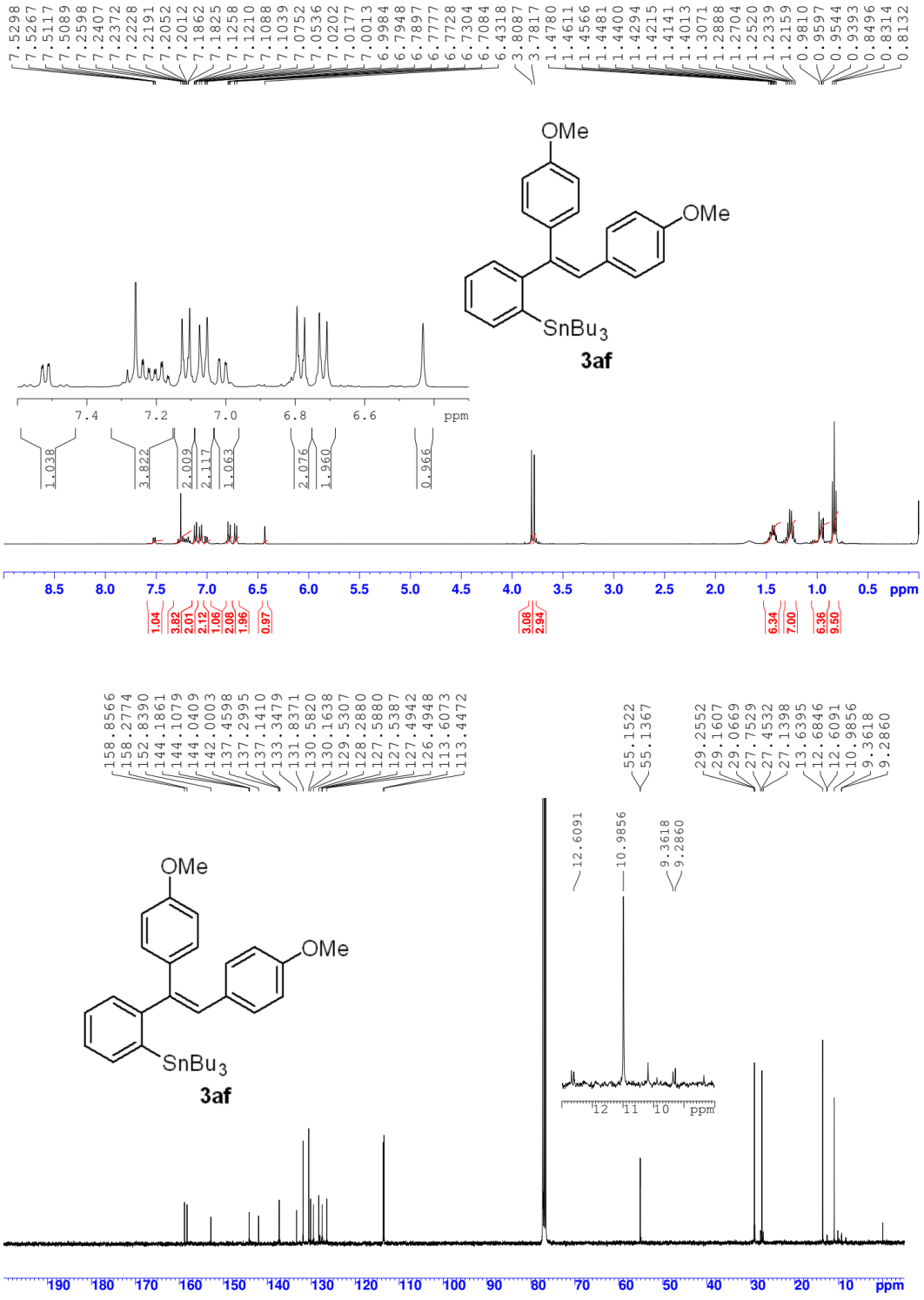

SnBu3
3ac
13 12 11 10 ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

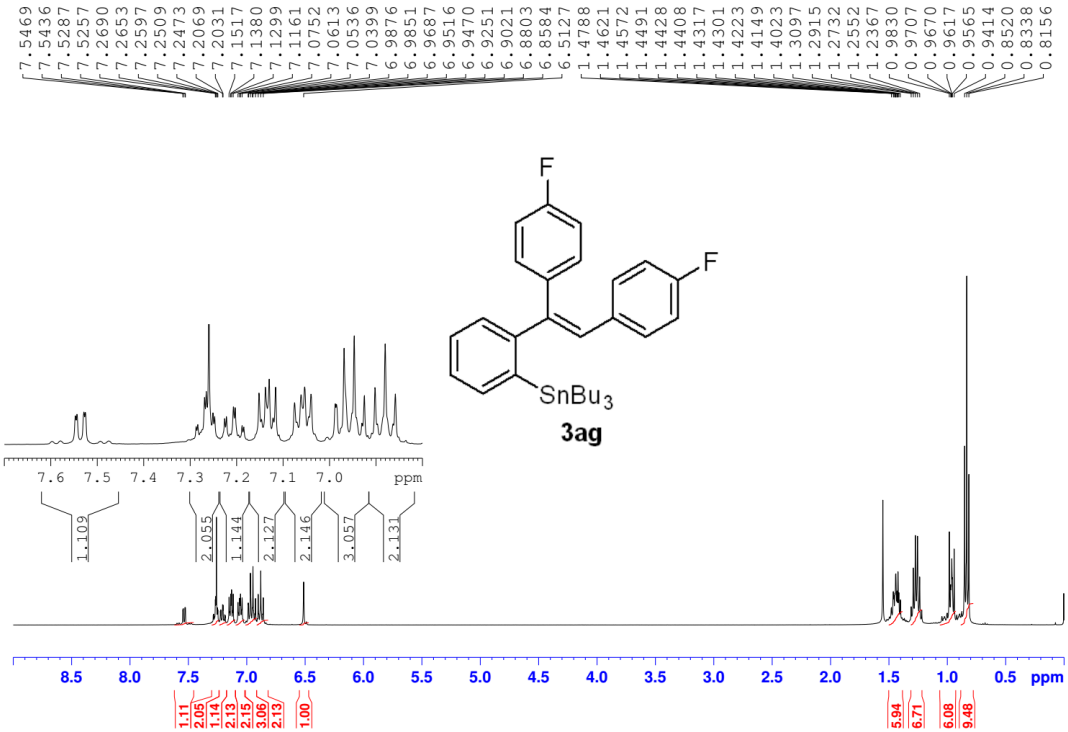

Me
SnBu3
3ad
(1.2:1)
Me
SnBu3
3ad'
ppm


Me
SnBu3
3ad
(1.2:1)
Me
SnBu3
3ad'
ppm


SnBu3
3ae


SnBu3
3ae


OMe
OMe
SnBu3
3af
OMe
OMe
SnBu3
3af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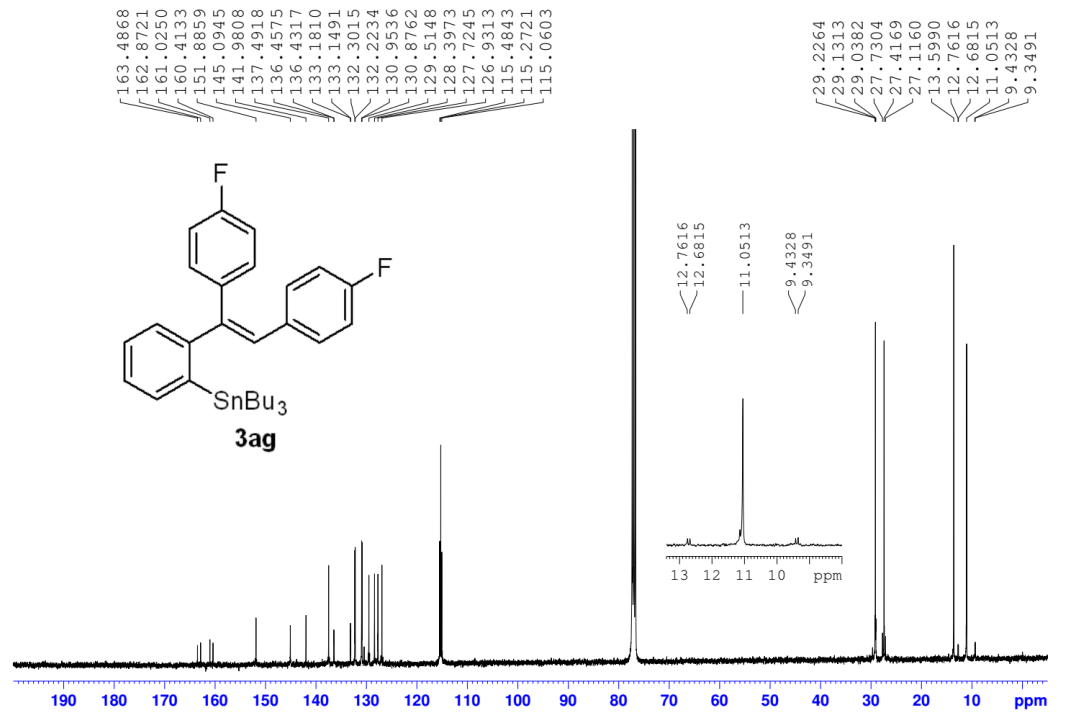
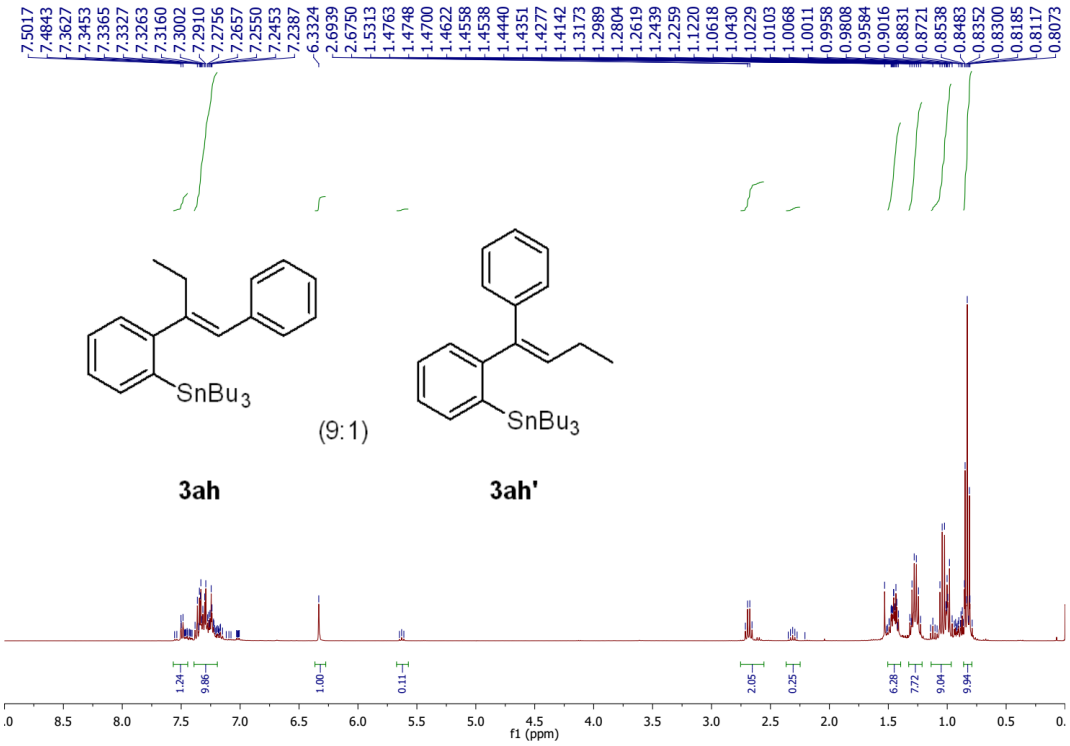
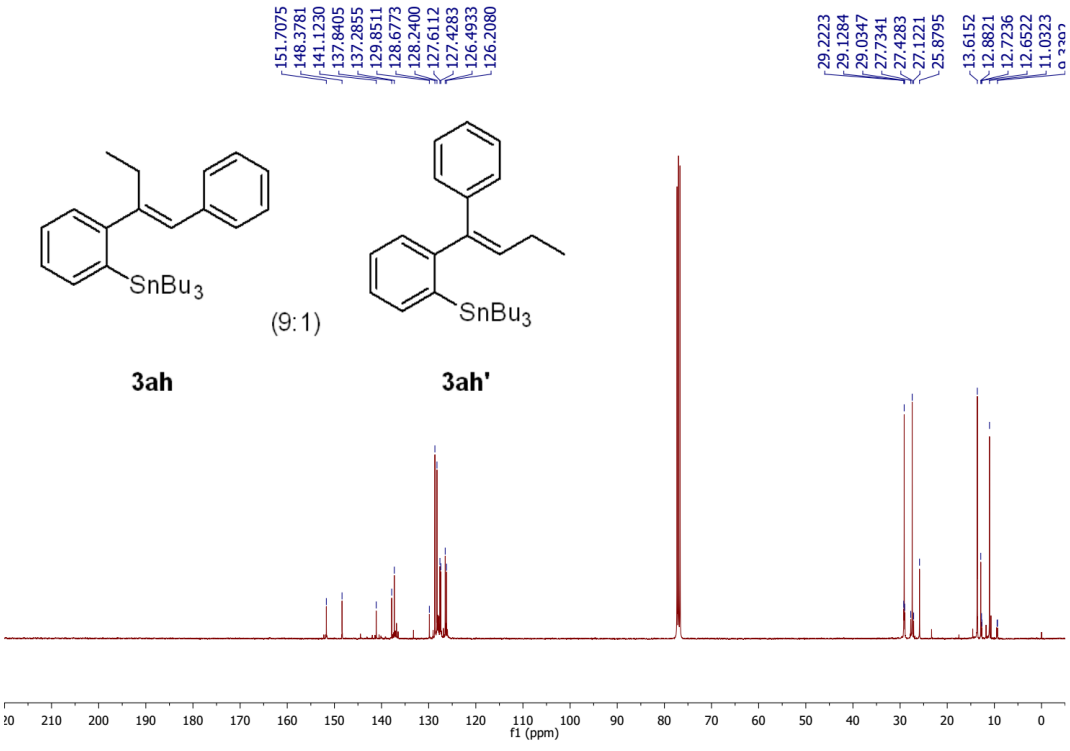
7.5436
7.5287
7.5257
7.2690
7.2653
7.2597
7.2509
7.2473
7.2069
7.2031
7.1517
7.1380
7.1299
7.1161
7.0752
7.0613
7.0536
7.0399
6.9876
6.9851
6.9687
6.9516
6.9470
6.9251
6.9021
6.8803
6.8584
6.5127
1.4788
1.4621
1.4572
1.4491
1.4428
1.4408
1.4317
1.4301
1.4223
1.4149
1.4023
1.3097
1.2915
1.2732
1.2552
1.2367
0.9830
0.9707
0.9670
0.9617
0.9565
0.9414
0.8520
0.8338
0.8156
F
F
SnBu3
3ag
7.6 7.5 7.4 7.3 7.2 7.1 7.0 ppm
1.109
2.055
1.144
2.127
2.146
3.057
2.131
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.11
2.05
1.14
2.13
2.15
3.06
2.13
1.00
5.94
6.71
6.08
9.48


163.4868
162.8721
161.0250
160.4133
151.8859
145.0945
141.9808
137.4918
136.4575
136.4317
133.1810
133.1491
132.3015
132.2234
130.9536
130.8762
129.5148
128.3973
127.7245
126.9313
115.4843
115.2721
115.0603
29.2264
29.1313
29.0382
27.7304
27.4169
27.1160
13.5990
12.7616
12.6815
11.0513
9.4328
9.3491
F
F
SnBu3
3ag
12.7616
12.6815
11.0513
9.4328
9.3491
13 12 11 10 ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.5017
7.4843
7.3627
7.3453
7.3365
7.3327
7.3263
7.3160
7.3002
7.2910
7.2756
7.2657
7.2550
7.2453
7.2387
6.3324
2.6939
2.6750
2.5313
1.4763
1.4748
1.4700
1.4622
1.4558
1.4538
1.4440
1.4351
1.4277
1.4142
1.3173
1.2989
1.2804
1.2619
1.2439
1.2259
1.1220
1.0618
1.0430
1.0229
1.0103
1.0068
1.0011
0.9958
0.9808
0.9584
0.9016
0.8831
0.8721
0.8538
0.8483
0.8352
0.8300
0.8185
0.8117
0.8073
SnBu3
(9:1)
SnBu3
3ah
3ah'
1.24
9.86
1.00
0.11
2.05
0.25
6.28
7.72
9.04
9.94
f1 (ppm)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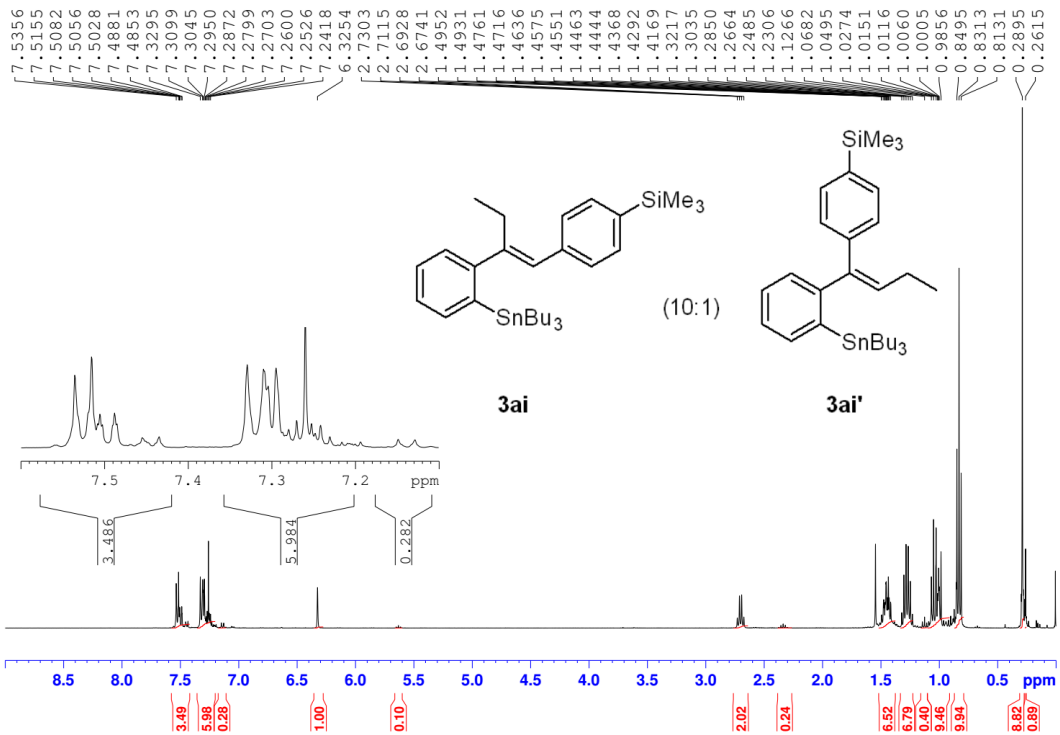
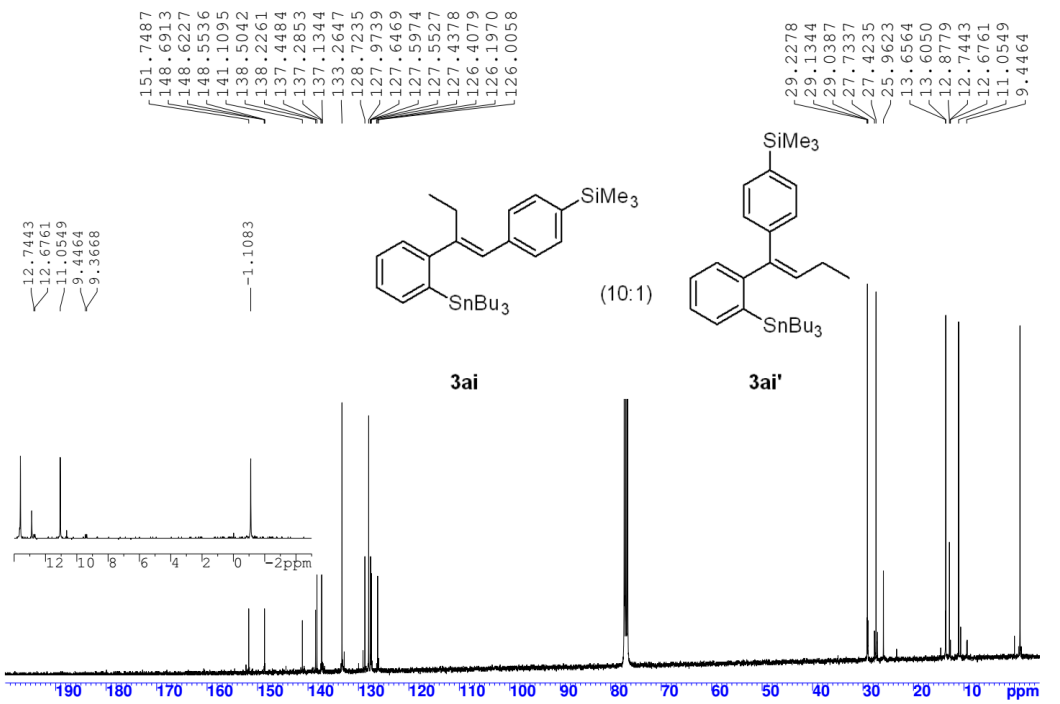
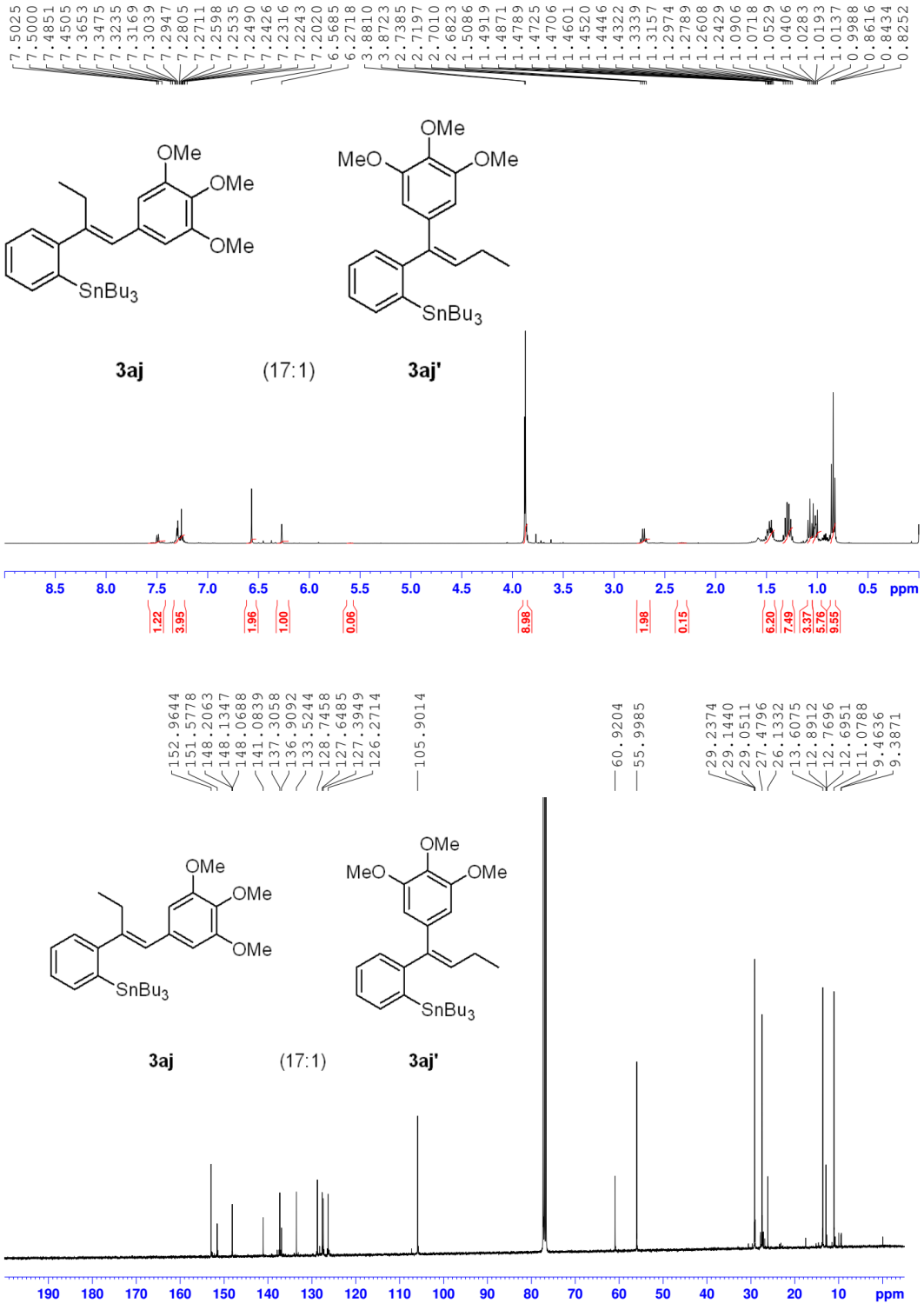
141.1230
137.8405
137.2855
129.8511
128.6773
128.2400
127.6112
127.4283
126.4933
126.2080
29.2223
29.1284
29.0347
27.7341
27.4283
27.1221
25.8795
13.6152
12.8821
12.7236
12.6522
11.0323
SnBu3
(9:1)
SnBu3
3ah
3ah'
f1 (ppm)


SiMe3
SnBu3
(10:1)
3ai
3ai'
ppm


SiMe3
SnBu3
(10:1)
3ai
3ai'
ppm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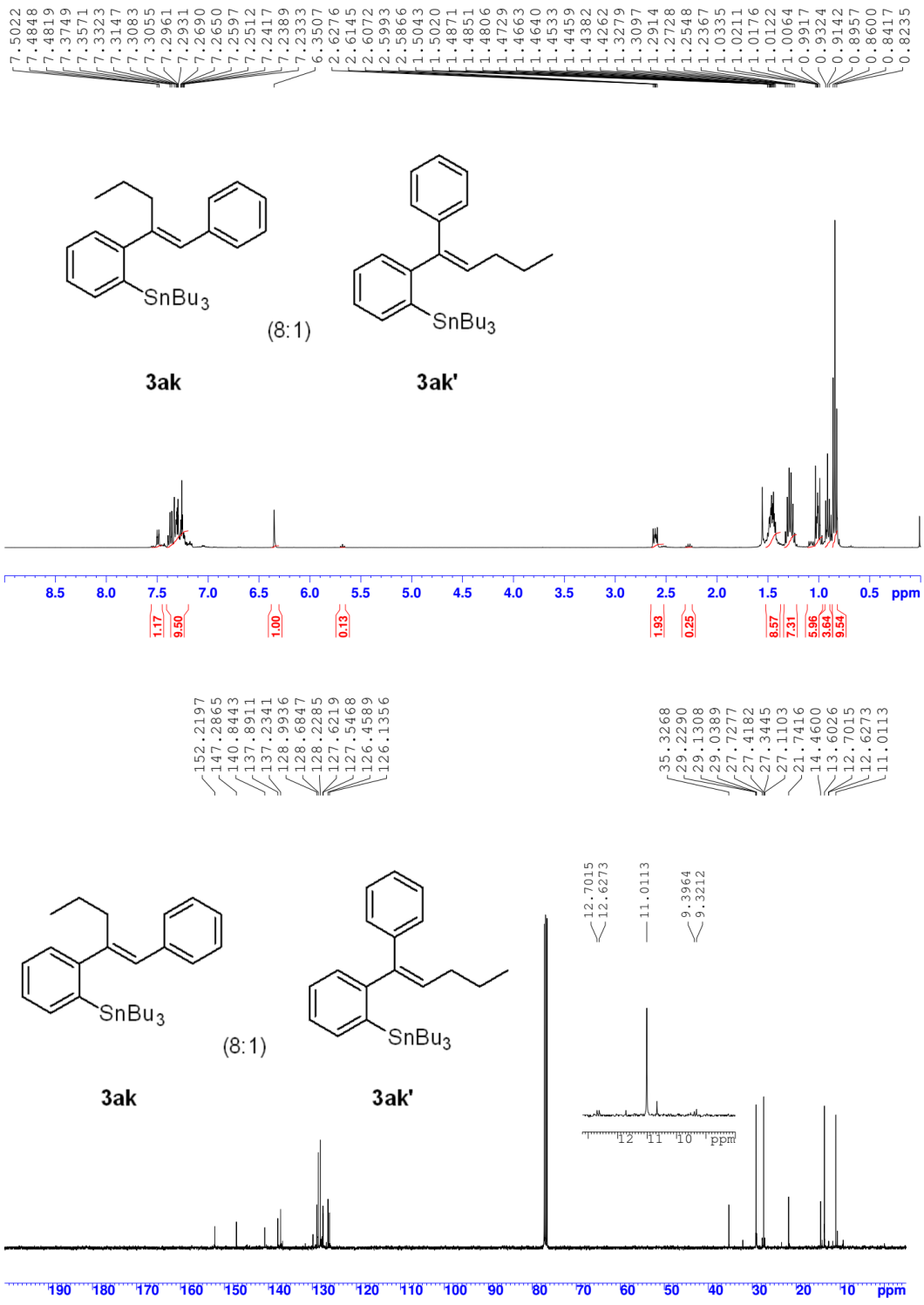
3.8810 3.8723 2.7385 2.7197 2.7010 2.6823 1.5086 1.4919 1.4871 1.4789 1.4725 1.4706 1.4601 1.4520 1.4446 1.4322 1.3339 1.3157 1.2974 1.2789 1.2608 1.2429 1.0906 1.0718 1.0529 1.0406 1.0283 1.0193 1.0137 0.9988 0.8616 0.8434 0.8252
OMe
OMe
OMe
SnBu3
MeO
OMe
OMe
SnBu3
3aj
(17:1)
3aj'
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.22 3.95 1.96 1.00 0.06 8.99 1.98 0.15 6.20 7.49 3.37 5.76 9.55
152.9644 151.5778 148.2063 148.1347 148.0688 141.0839 137.3058 136.9092 133.5244 128.7458 127.6485 127.3949 126.2714
105.9014
60.9204 55.9985
29.2374 29.1440 29.0511 27.4796 26.1332 13.6075 12.8912 12.7696 12.6951 11.0788 9.4636 9.3871
OMe
OMe
OMe
SnBu3
MeO
OMe
OMe
SnBu3
3aj
(17:1)
3aj'
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.4819
7.3749
7.3571
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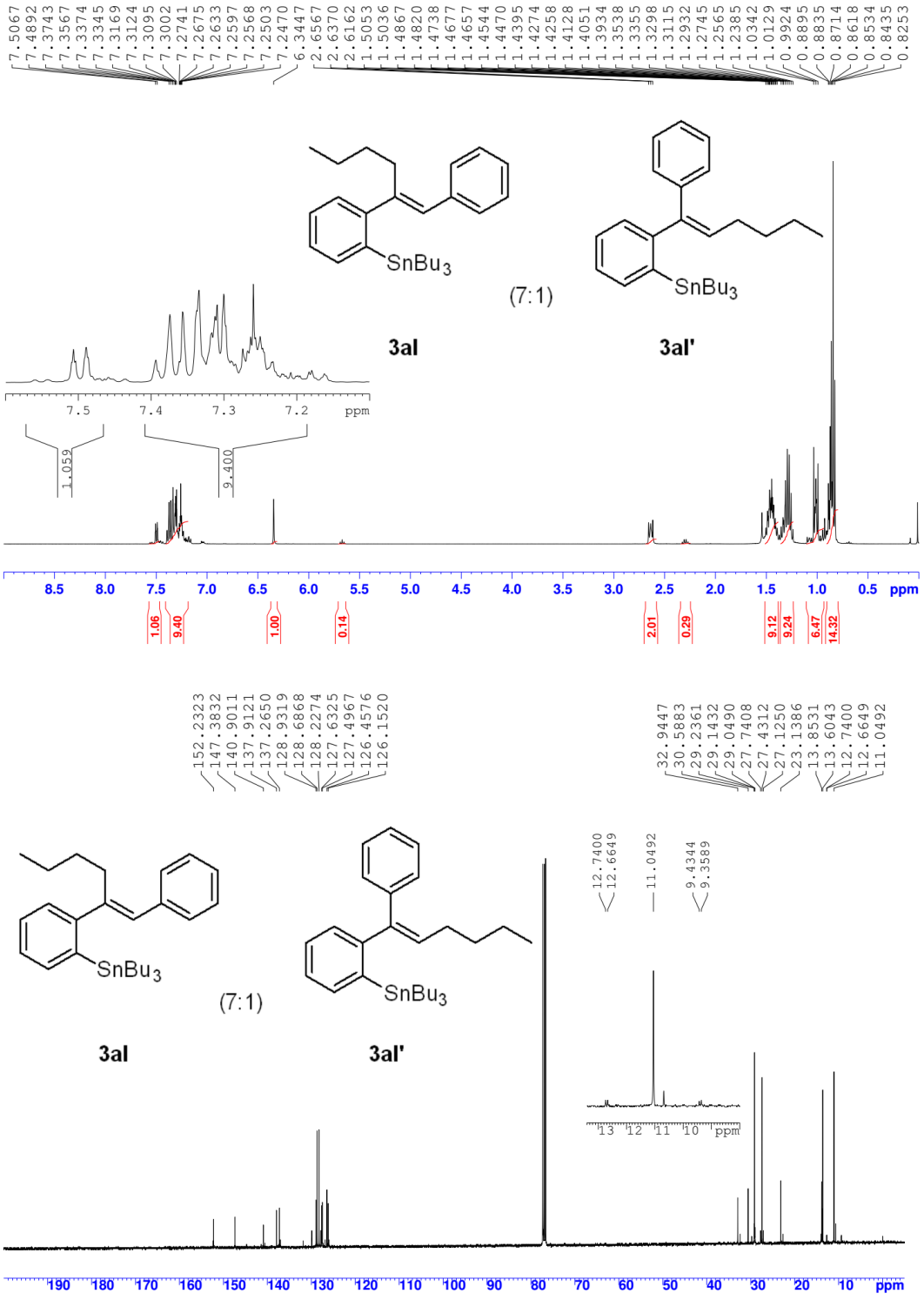
7.3147
7.3083
7.3055
7.2961
7.2931
7.2690
7.2650
7.2597
7.2512
7.2417
7.2389
7.2333
6.3507
2.6276
2.6145
2.6072
2.5993
2.5866
1.5043
1.5020
1.4871
1.4851
1.4806
1.4729
1.4663
1.4640
1.4533
1.4459
1.4382
1.4262
1.3279
1.3097
1.2914
1.2728
1.2548
1.2367
1.0335
1.0211
1.0176
1.0122
1.0064
0.9917
0.9324
0.9142
0.8957
0.8600
0.8417
0.8235
SnBu3
(8:1)
SnBu3
3ak
3ak'
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.17
9.50
1.00
0.13
1.93
0.25
8.57
7.31
5.96
3.64
9.54
152.2197
147.2865
140.8443
137.8911
137.2341
128.9936
128.6847
128.2285
127.6219
127.5468
126.4589
126.1356
35.3268
29.2290
29.1308
29.0389
27.7277
27.4182
27.3445
27.1103
21.7416
14.4600
13.6026
12.7015
12.6273
11.0113
SnBu3
(8:1)
SnBu3
3ak
3ak'
12.7015
12.6273
11.0113
9.3964
9.3212
12 11 10 ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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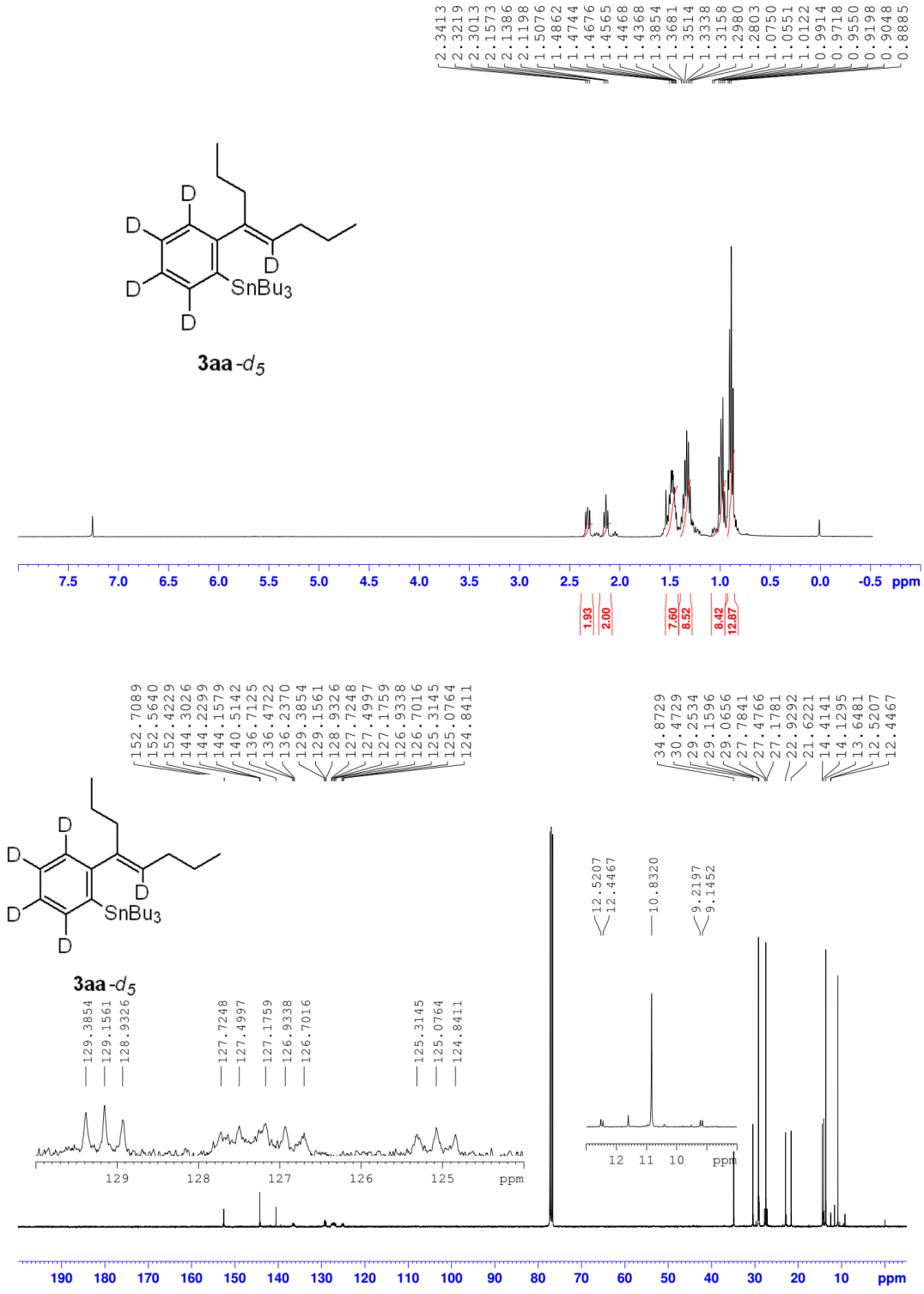
7.3743
7.3567
7.3374
7.3345
7.3169
7.3124
7.3095
7.3002
7.2741
7.2675
7.2633
7.2597
7.2568
7.2503
7.2470
6.3447
2.6567
2.6370
2.6162
1.5053
1.5036
1.4867
1.4820
1.4738
1.4677
1.4657
1.4544
1.4470
1.4395
1.4274
1.4258
1.4128
1.4051
1.3934
1.3538
1.3355
1.3298
1.3115
1.2932
1.2745
1.2565
1.2385
1.0342
1.0129
0.9924
0.8895
0.8835
0.8714
0.8618
0.8534
0.8435
0.8253
SnBu3
(7:1)
SnBu3
3al
3al'
7.5
7.4
7.3
7.2
ppm
1.059
9.400
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.06
9.40
1.00
0.14
2.01
0.29
9.12
9.24
6.47
14.32
152.2323
147.3832
140.9011
137.9121
137.2650
128.9319
128.6868
128.2274
127.6325
127.4967
126.4576
126.1520
32.9447
30.5883
29.2361
29.1432
29.0490
27.7408
27.4312
27.1250
23.1386
13.8531
13.6043
12.7400
12.6649
11.0492
SnBu3
(7:1)
SnBu3
3al
3al'
12.7400
12.6649
11.0492
9.4344
9.3589
13
12
11
10
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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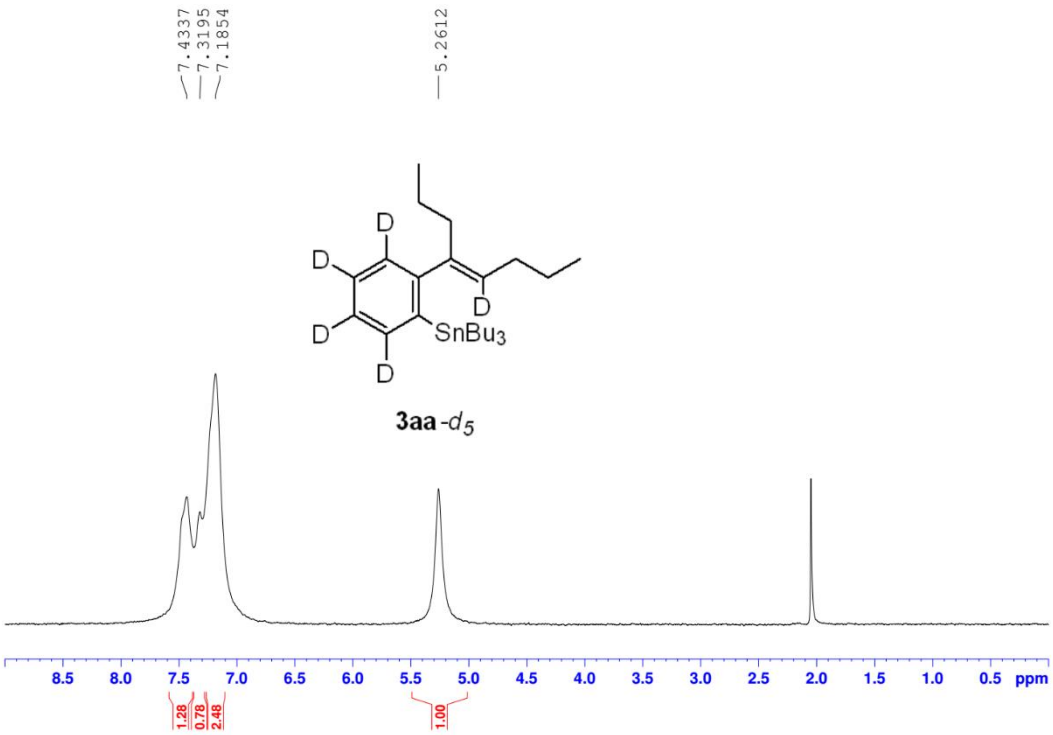
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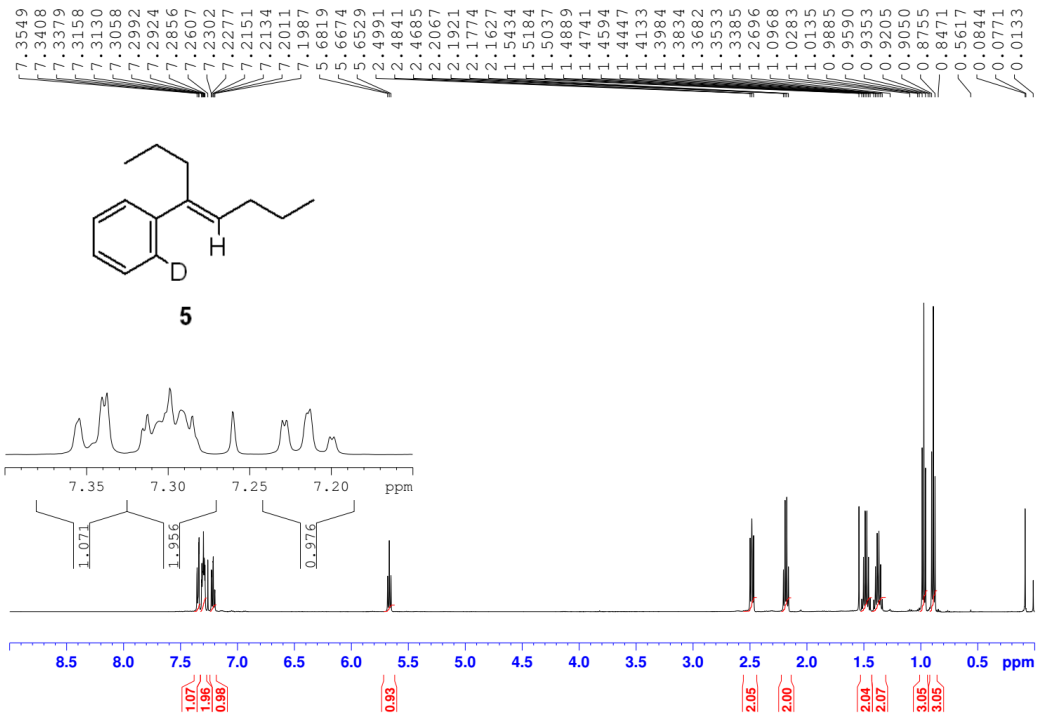
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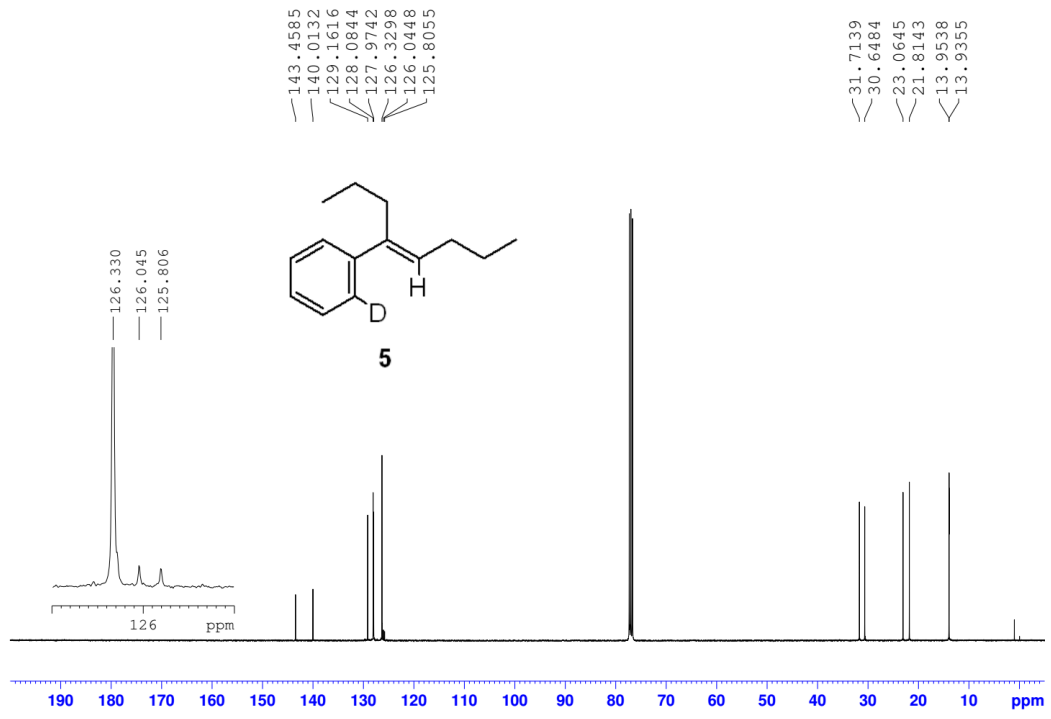
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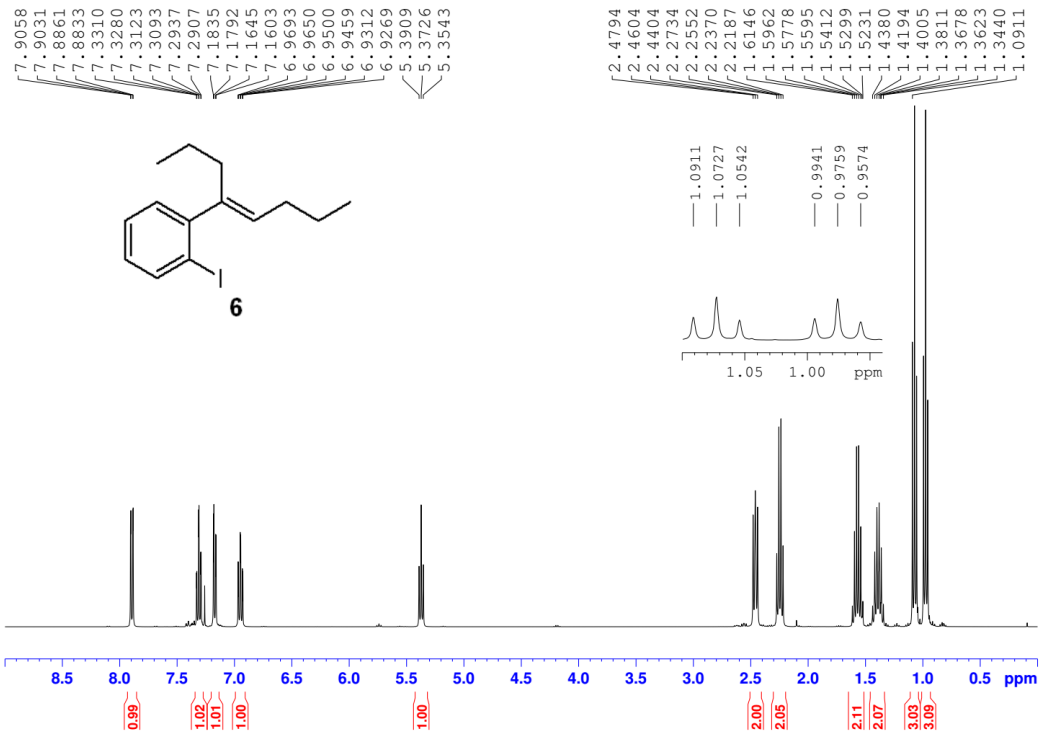
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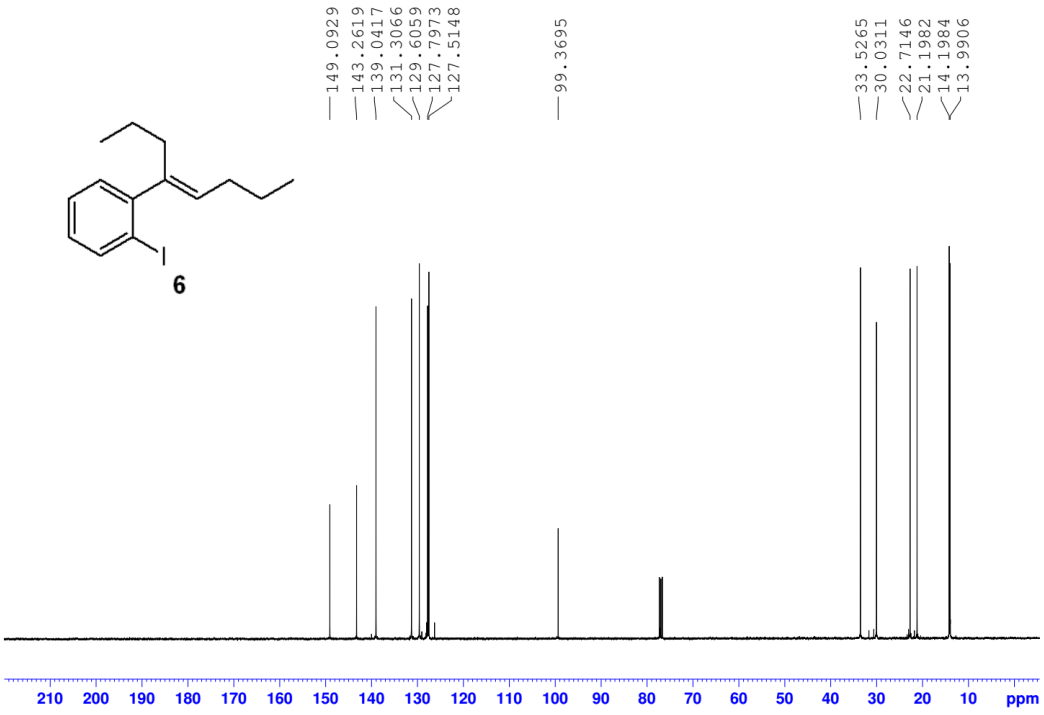
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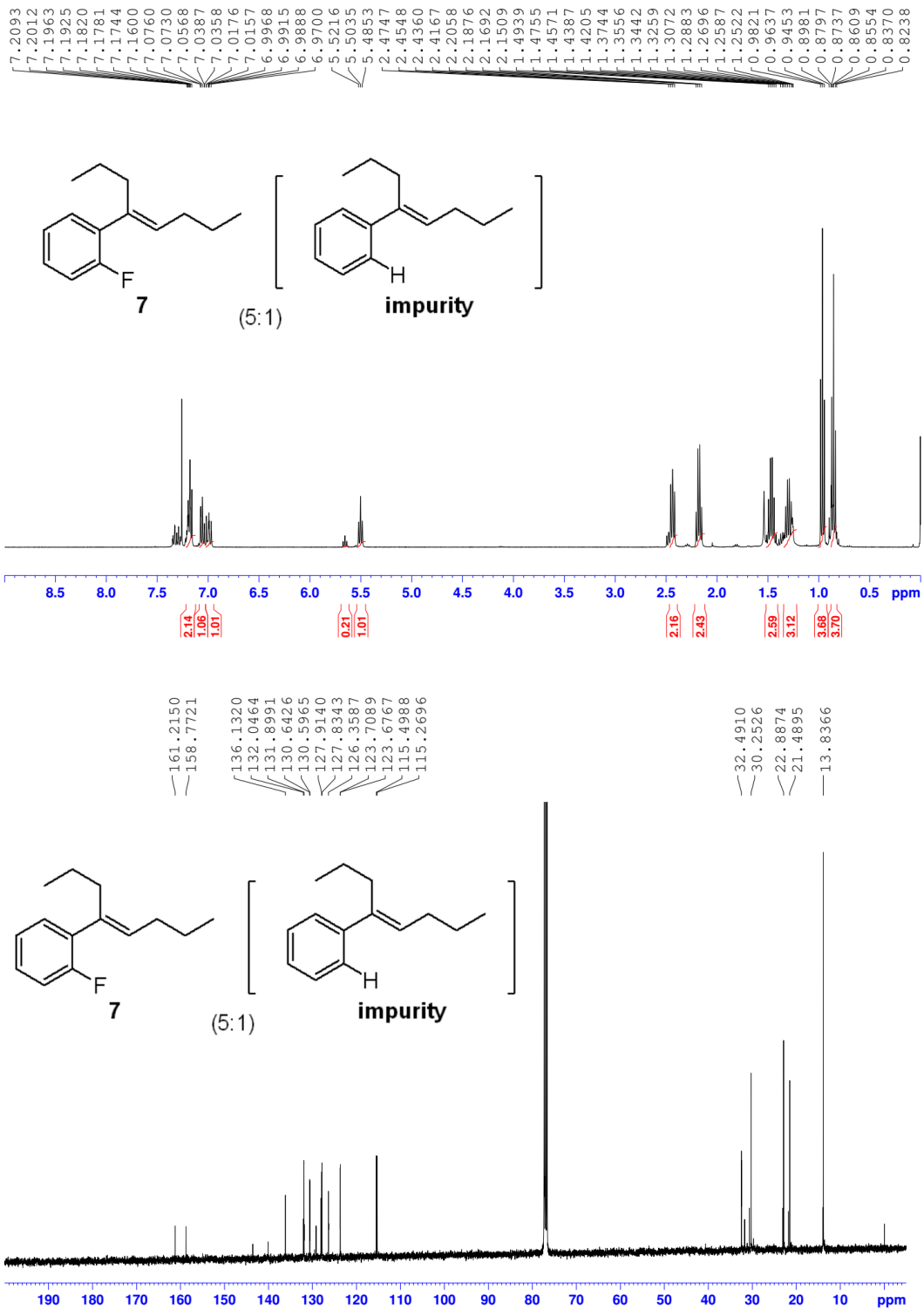
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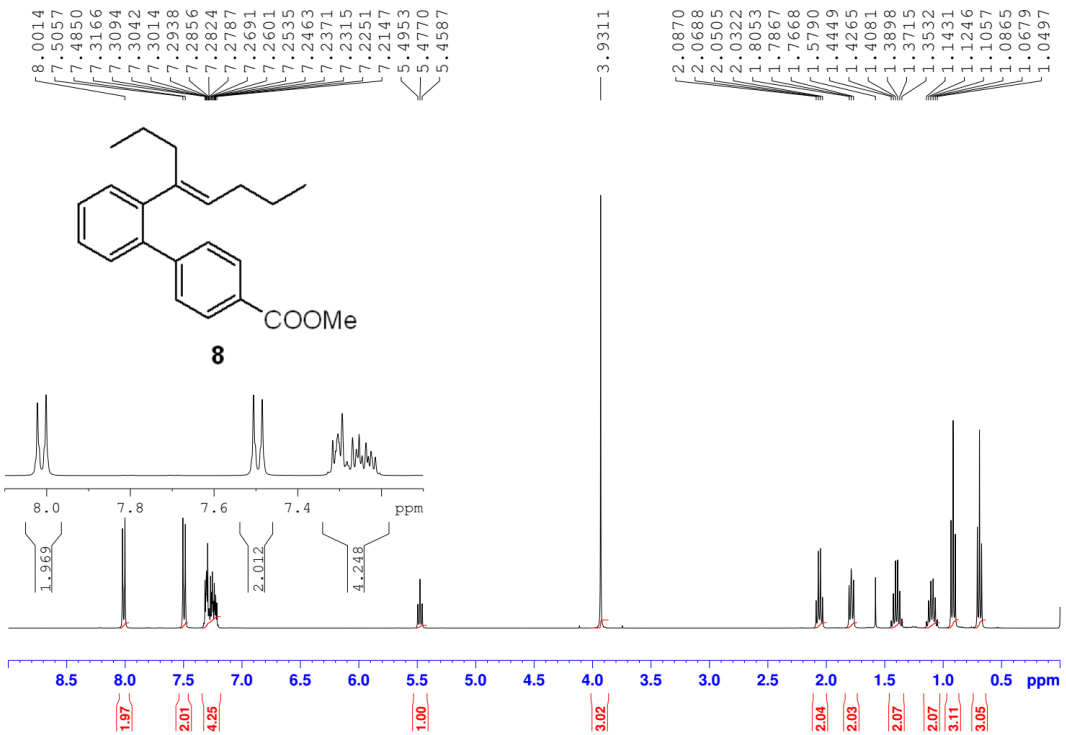
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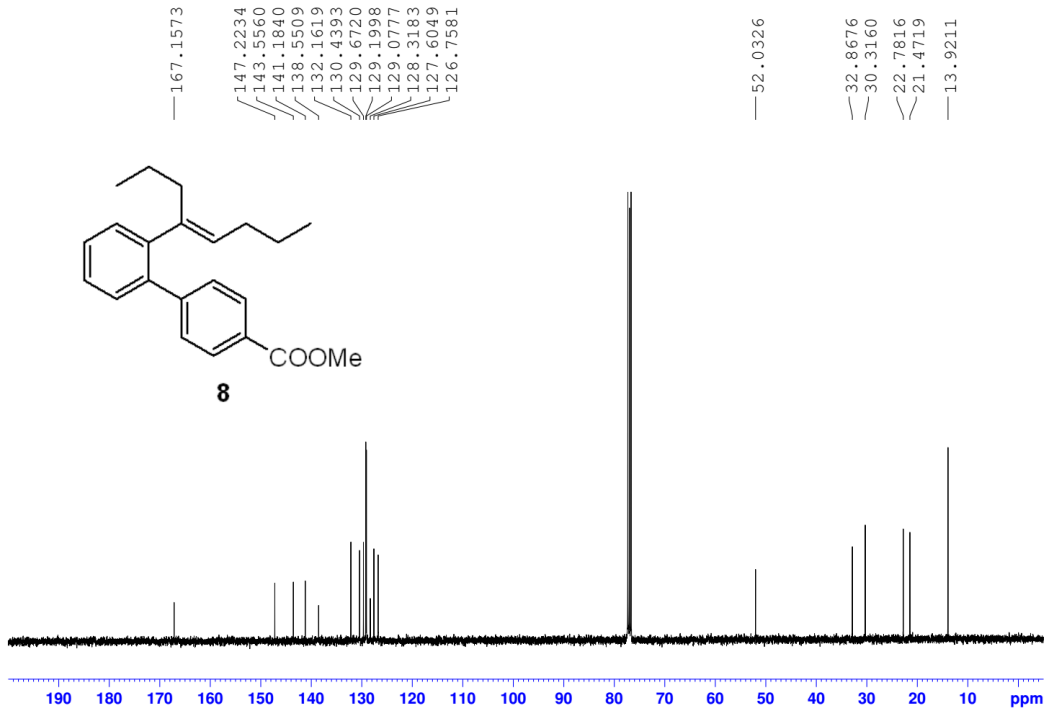
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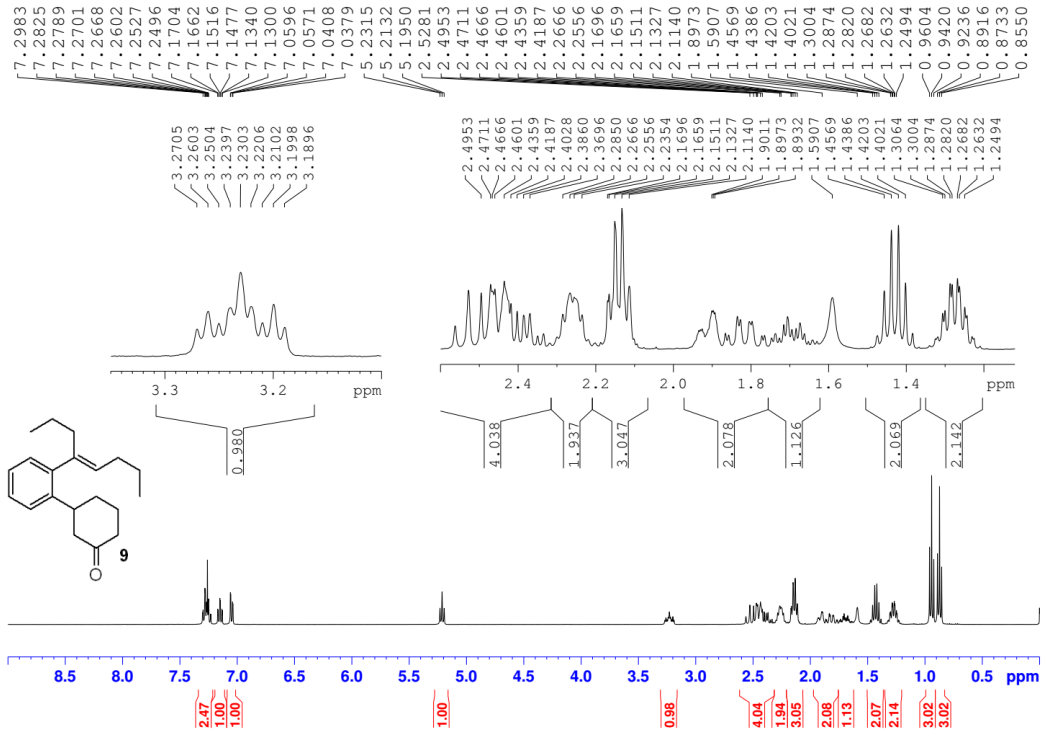
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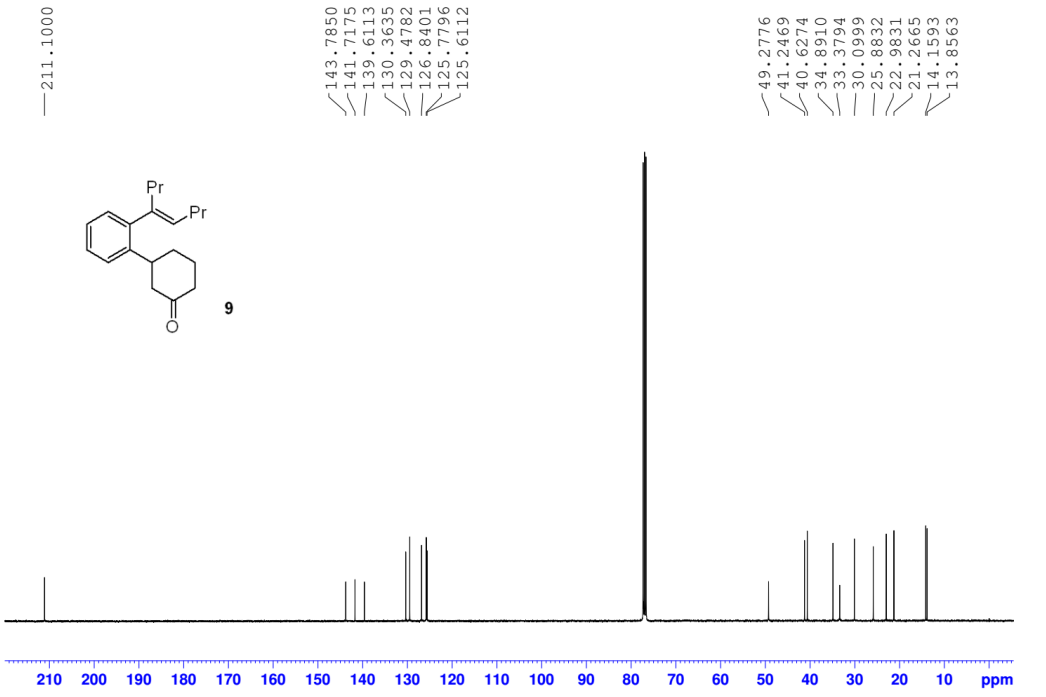
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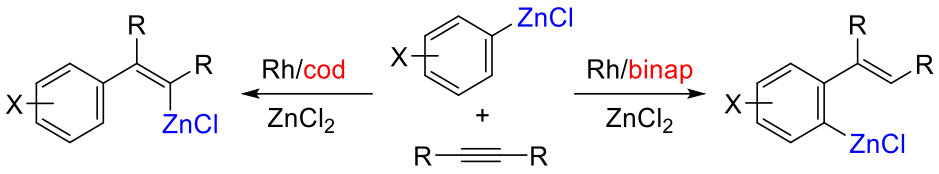
# CHAPTER 4

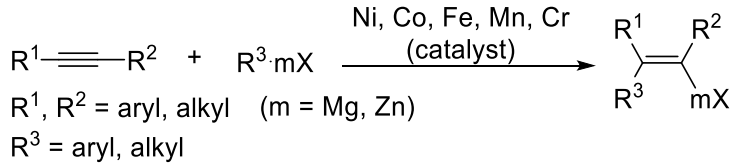
## Rhodium-Catalyzed Arylzincation of Alkynes. Ligand Control of 1,4-Migration Selectivity



## 4.1 Introduction

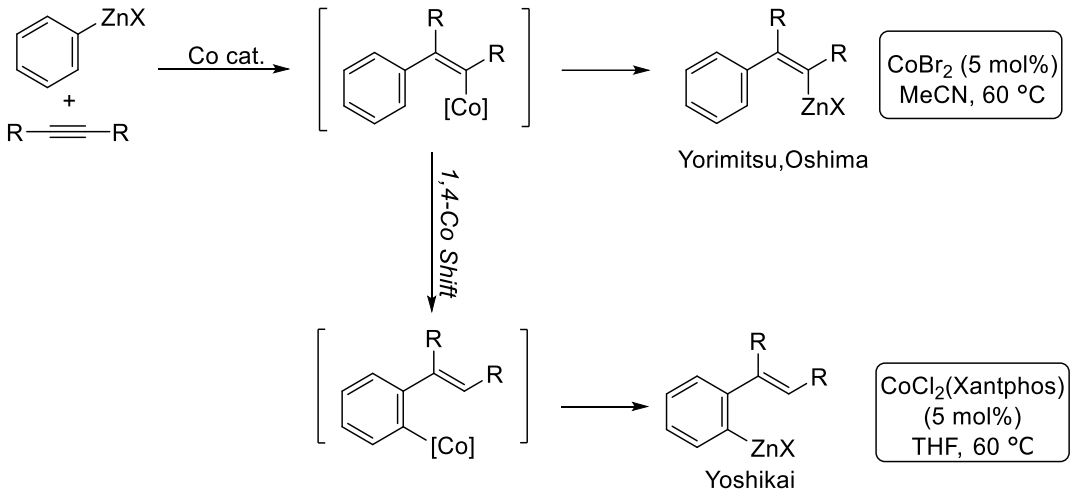
Carbometalation of alkynes is one of the most efficient methods of generating substituted alkenyl–metals which are useful synthetic intermediates for the multisubstituted alkenes. The addition of arylmetals to simple unfunctionalized alkynes has been a reaction of challenge because of their low reactivity.[1] The first-row transition metals including Ni, Co, Fe, Mn, and Cr have been reported to catalyze the addition of arylmagnesium[2] and –zinc[3] reagents to the unfunctionalized alkynes (Scheme 4.1). The detailed discussion on rhodium catalyzed addition of organometals to alkynes is shown in Section 1.1.3.

**Scheme 4.1. Catalytic Carbometalation of Alkynes**



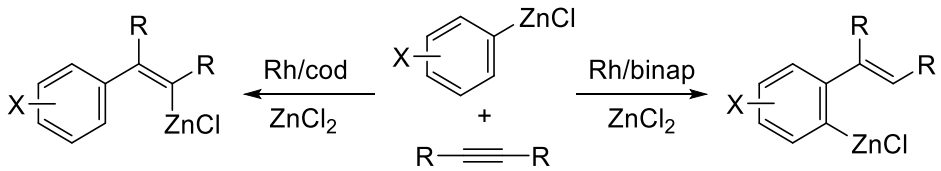

In 2009, Yorimitsu and Oshima reported ligand-free catalytic arylzincation of alkynes in presence of 5 mol% of $CoBr_2$ (Scheme 4.2).[3c] In 2014, Yoshikai reported a new type of Co-catalyzed arylzincation of alkynes where *ortho*-alkenylarylzinc species are formed through 1,4-migration of cobalt from the alkenyl carbon to the aryl carbon.[4] The use of Xantphos as a ligand totally changed the products.

**Scheme 4.2. Cobalt-Catalyzed Arylzincation of Alkynes.**




In this chapter, we introduce our findings that arylzincation of alkynes is catalyzed by Rh complexes in the presence of a catalytic amount of $ZnCl_2$ and the arylzincation with or without 1,4-migration is controlled with high selectivity by the ligands on rhodium (Scheme 4.3). The 1,4-shift of rhodium from alkenyl to aryl carbons has been known as a key step in several Rh-catalyzed multiple carbon–carbon bond forming reactions including asymmetric reactions.[5–7] To the best of our knowledge, it is the first example of the carbozincation of unfunctionalized alkynes using Rh catalysis.

**Scheme 4.3. Rhodium-Catalyzed Arylzincation of Alkynes.**

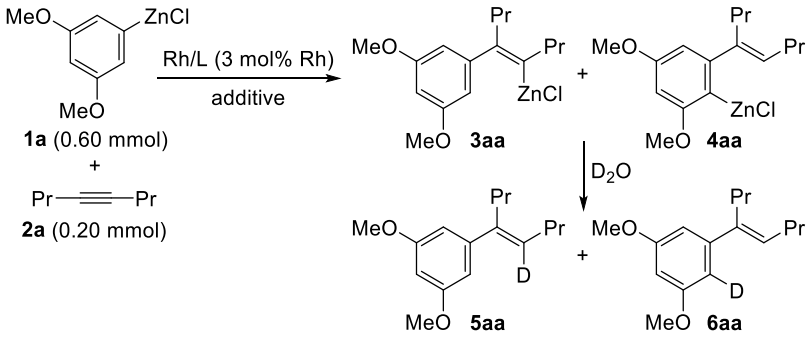


## 4.2 Results and discussion

In our present studies, arylzinc reagents ArZnCl were prepared by lithiation of ArBr with BuLi in THF at –80 °C followed by addition of an excess amount (1.3 equiv) of $ZnCl_2$ to the THF solution of ArLi.[8,9] The results obtained for the reaction of 3,5-$(MeO)_2C_6H_3ZnCl$ (**1a**) with 4-octyne (**2a**) in the presence of several rhodium catalysts are summarized in Table 4.1. The reaction mixture containing 2-arylalkenylzinc **3aa** and/or *ortho*-alkenylarylzinc **4aa** was hydrolyzed with $D_2O$ and the location of D (**5aa**:**6aa**) was analyzed by $^1H$ and $^2H$ NMR spectra. The yield of the arylzincation and the selectivity with or without 1,4-migration are heavily dependent on the ligand on rhodium. The THF solution of ArZnCl (**1a**, 0.60 mmol, 3.0 equiv to **2a**) containing $ZnCl_2$ (0.18 mmol, 0.9 equiv to **2a**) was added to the alkyne (**2a**, 0.20 mmol) in the presence of a rhodium catalyst generated from $[RhCl(coe)_2]_2$ (3 mol% of Rh) and binap[10] (3.3 mol%) in THF, and the mixture was heated at 50 °C for 5 h. The arylzincation accompanied by the 1,4-migration proceeded selectively to give, after the $D_2O$ quenching, 91% yield of **6aa**, where the deuterium is incorporated into the *ortho*-position of the phenyl ring (entry 1). On the other hand, the reaction in the presence of a rhodium catalyst coordinated with cod[10] under otherwise the same conditions gave 82% yield of the arylation product where the deuterium is found mainly at the alkenyl carbon (**5aa**:**6aa** = 92:8) (entry 2). In the Rh/binap-catalyzed reaction, the amounts of ArZnCl **1a** and $ZnCl_2$ were reduced to 1.5 and 0.45 equiv, respectively, without loss of the arylzincation yield or 1,4-migration selectivity (entry 3). The presence of $ZnCl_2$ as a catalyst, which was added in an excess amount (1.3 equiv to ArLi) during the preparation of ArZnCl from ArLi, is essential for the present arylzincation. The yield of arylzincation was much lower

(22%) in the reaction with ArZnCl generated with 1.0 equiv of $ZnCl_2$ (entry 4). Diarylzinc $Ar_2Zn$ generated from ArLi and 0.50 equiv of $ZnCl_2$ did not give the arylzincation products (entry 5). Other zinc salts, $ZnX_2$ (X = Br and I), which were used in an excess amount during the preparation of ArZnX[11] from ArLi, also catalyzed the reaction, but the yields and the migration selectivity were somewhat lower (entries 6 and 7). The lower yield and selectivity were observed with other phosphine ligands such as dppe, dppp, dppf, biphep, and $PPh_3$ (entries 8–12). The arylzincation did not proceed with xantphos ligand (entry 13), which has been reported to be the best ligand in the cobalt-catalyzed migratory arylzincation.[4] Interestingly, the high selectivity in giving **3aa** without the 1,4-migration was observed only with 1,5-cyclooctadiene (cod). Other diene ligands including norbornadiene (nbd) promoted the migratory arylzincation giving **4aa** preferentially (entry 14).

**Table 4.1. Rhodium-Catalyzed Arylzincation of 4-Octyne (2a) with 3,5-$(MeO)_2C_6H_3ZnCl$ (1a)** [a]




| entry | ligand on Rh[b] | additive (mmol)[c] | yield (%)[d] **5aa**+**6aa** | ratio[e] of **5aa**:**6aa** |
|---|---|---|---|---|
| 1 | binap | $ZnCl_2$ (0.18) | 91 | <1:99 |
| 2 | cod | $ZnCl_2$ (0.18) | 82 | 92:8 |
| 3[f] | binap | $ZnCl_2$ (0.09) | 90 | <1:99 |
| 4 | binap | — | 22 | 4:96 |
| 5[g] | binap | — | <3 | — |
| 6[h] | binap | $ZnBr_2$ (0.18) | 81 | 5:95 |
| 7[h] | binap | $ZnI_2$ (0.18) | 87 | 3:97 |
| 8 | dppe | $ZnCl_2$ (0.18) | 23 | 37:63 |

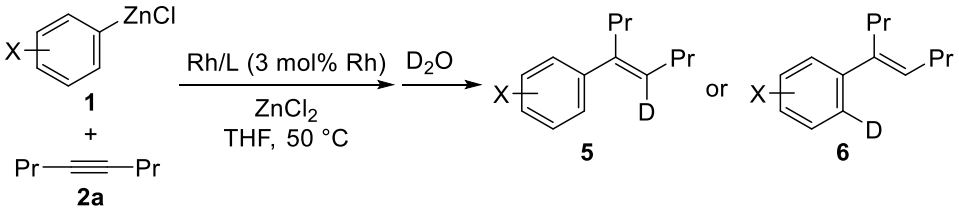
| | | | | |
|---|---|---|---|---|
| 9 | dppp | $ZnCl_2$ (0.18) | 52 | 48:52 |
| 10 | dppf | $ZnCl_2$ (0.18) | 27 | 19:81 |
| 11 | biphep | $ZnCl_2$ (0.18) | 83 | 12:88 |
| 12 | $PPh_3$ | $ZnCl_2$ (0.18) | 78 | 6:94 |
| 13 | xantphos | $ZnCl_2$ (0.18) | <3 | — |
| 14 | nbd | $ZnCl_2$ (0.18) | 83 | 5:95 |

[a] Reaction conditions: 4-Octyne (**2a**) (0.20 mmol), ArZnCl (**1a**) (0.60 mmol), $ZnCl_2$ (0.18 mmol), and Rh catalyst (3 mol% of Rh) in THF (2.0 mL) at 50 °C for 5 h. The reaction was quenched with $D_2O$ (0.2 mL). [b] $[RhCl(coe)_2]_2$ (6.0 μmol of Rh) + bisphosphine (6.6 μmol), $RhCl(PPh_3)_3$ (6.0 μmol), or $([RhCl(diene)]_2$ (diene = cod or nbd, 6 μmol of Rh). [c] The excess amount of $ZnX_2$ used at the generation of ArZnX. [d] Isolated yield. [e] Determined by $^1H$ and $^2H$ NMR spectra. [f] ArZnCl (**1a**) (0.30 mmol), $ZnCl_2$ (0.09 mmol), THF (1.0 mL) for 1 h. [g] Reaction of $Ar_2Zn$ generated from ArLi (0.60 mmol) and $ZnCl_2$ (0.30 mmol). [h] ArZnX was generated from ArLi (0.60 mmol) and $ZnX_2$ (0.78 mmol, X = Br or I).

The rhodium-catalyzed arylzincation was also successful with several other arylzinc reagents ArZnCl and similar selectivity control in giving arylzincation products with or without 1,4-migration was observed in the arylzincation of 4-octyne (**2a**), whose results are summarized in Table 4.2. The selectivity of the addition/1,4-migration sequence giving *ortho*-alkenylphenylzinc **4** with binap as the ligand is very high for all the arylzinc reagents shown in Table 4.2, including unsubstituted phenylzinc (entry 2) and *para*-substituted ones with both electron-donating and -withdrawing groups (entries 3-8). The ratio of **5**:**6** ranges between <1:99 and 6:94. The 1,4-shift was regioselective in the reaction of *meta*-substituted phenylzinc reagents with Me, $NMe_2$, and $SiMe_3$, deuterium being exclusively incorporated into the less hindered position (entries 9, 11, 12). The regioselectivity was low with 3-$MeOC_6H_4ZnCl$ (entry 10). Considering that the size of Me and MeO groups is not so different, it is probably because of the coordination of MeO group to Rh, which promotes the Rh 1,4-shift to the MeO side. Interestingly, the 1,4-migration took place selectively to the position next to MeO group in the reaction of 3-Me-5-$MeOC_6H_3ZnCl$ (entry 13). The selective formation of 2-arylethenylzincs **3** without

1,4-migration was also realized using cod as the ligand of the rhodium catalyst for most of the arylzinc reagents examined, although the selectivity is generally not as high as that for the reaction with migration. The ratio of **5**:**6** after $D_2O$ quenching is higher than 7:3 except for the arylzinc reagents substituted with electron-withdrawing groups. Zinc reagents 4-$FC_6H_4ZnCl$ and 4-$CF_3C_6H_4ZnCl$ gave the corresponding arylation products with **5**:**6** = 49:51 and <1:99, respectively[12] (entries 7 and 8).

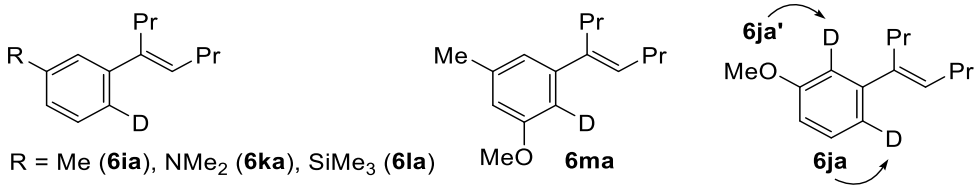
**Table 4.2. Rhodium-Catalyzed Arylzincation of 4-Octyne (2a) with Arylzinc Reagents 1**[a]




| entry | **1**: Ar in ArZnCl | L on Rh[b] (A) or (B)[a] | yield (%)[c] of **5** + **6** | ratio[d] of **5**:**6** |
|---|---|---|---|---|
| 1 | **1a**: 3,5-$(MeO)_2C_6H_3$ | binap (B) | 90 | <1:99 |
| | | cod (A) | 82 | 92:8 |
| 2 | **1b**: Ph | binap (A) | 87 | 2:98 |
| | | cod (A) | 80 | 80:20 |
| 3 | **1c**: 4-$MeC_6H_4$ | binap (B) | 91 | 1:99 |
| | | cod (A) | 68 | 77:23 |
| 4 | **1d**: 4-$MeOC_6H_4$ | binap (A) | 94 | 1:99 |
| | | cod (A) | 84 | 74:26 |
| 5 | **1e**: 4-$Me_2NC_6H_4$ | binap (B) | 87 | 1:99 |
| | | cod (A) | 71 | 94:6 |
| 6 | **1f**: 4-$Me_3SiC_6H_4$ | binap (B) | 85 | 6:94 |
| | | cod (A) | 86 | 81:19 |
| 7 | **1g**: 4-$FC_6H_4$ | binap (B) | 83 | <1:99 |
| | | cod (A) | 52 | 49:51 |
| 8 | **1h**: 4-$CF_3C_6H_4$ | binap (B) | 93 | <1:99 |
| | | cod (A) | 87 | <1:99 |
| 9 | **1i**: 3-$MeC_6H_4$ | binap (B) | 87 | 1:99[e] |
| | | cod (A) | 72 | 86:14[e] |
| 10 | **1j**: 3-$MeOC_6H_4$ | binap (A) | 93 | 1:99[f] |
| | | cod (A) | 82 | 80:20[f] |

| | | | | |
|---|---|---|---|---|
| 11 | **1k**: 3-$Me_2NC_6H_4$ | binap (B) | 95 | 1:99[e] |
| | | cod (A) | 72 | 95:5[e] |
| 12 | **1l**: 3-$Me_3SiC_6H_4$ | binap (B) | 87 | 1:99[e] |
| | | cod (A) | 79 | 83:17[e] |
| 13 | **1m**: 3-Me-5-$MeOC_6H_3$ | binap (B) | 97 | 1:99[e] |
| | | cod (A) | 79 | >99:1 |
| 14 | **1n**: 2-$MeOC_6H_4$ | binap (A) | 88 | 13:87 |
| | | cod (A) | 64 | 94:6 |

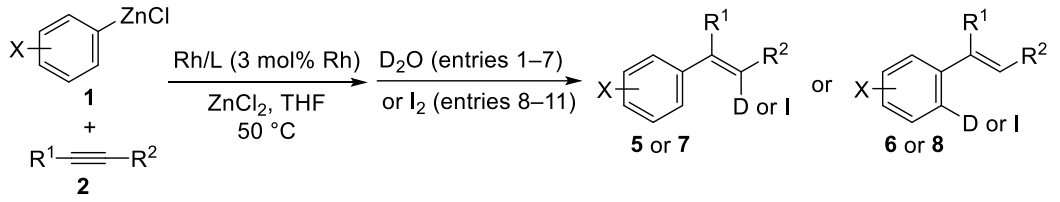
[a] Reaction condition (A): ArZnCl **1** (0.60 mmol), $ZnCl_2$ (0.18 mmol), 4-octyne (**2a**) (0.20 mmol), and Rh catalyst (3 mol% of Rh), THF (total 2.0 mL) at 50 °C for 5 h. The reaction was quenched with $D_2O$ (0.2 mL). (B): ArZnCl **1** (0.30 mmol), $ZnCl_2$ (0.09 mmol), 4-octyne (**2a**) (0.20 mmol), and Rh catalyst (3 mol% of Rh), THF (total 1.0 mL) at 50 °C for 1 h. [b] $[RhCl(coe)_2]_2$ (6 μmol of Rh) + binap (6.6 μmol) or $[RhCl(cod)]_2$ (6 μmol of Rh). [c] Isolated yield. [d] Determined by $^1H$ and $^2H$ NMR. [e] Regioselective 1,4-shift giving the products **6** shown below. [f] A mixture of **6ja** and **6ja'** in a ratio of 2:1 and 4:1 with binap and cod, respectively.




The reaction conditions used for the arylzincation of 4-octyne are applicable to other unfunctionalized alkynes. The results are summarized in Table 4.3, which also contains examples where the generated zinc reagents were used for a few transformations other than the deuteration.[13] The arylzincation with **1a** took place for symmetrically substituted dialkylalkynes **2b**–**2c** and diphenylacetylene (**2d**) to give the corresponding *ortho*-alkenylarylzinc or 2-arylalkenylzinc products with high selectivity using binap or cod (entries 1–4). In the reactions of alkyl(aryl)alkynes **2e**–**2f**, high regioselectivity was observed for the bond formation between the aryl group of the arylzinc and the alkyl-substituted alkyne carbon (entries 5 and 6). This selectivity is expected from the reported regiochemistry of carbometalation of alkyl(aryl)alkynes.[1] A high regioselectivity was also observed in the arylzincation of methyl(alkyl)alkyne **2g**, where the alkyl group is much larger than methyl (entry 7). The iodination of arylzinc reagents, 2-arylalkenylzinc **3** and

*ortho*-alkenylarylzinc **4**, with $I_2$ proceeded smoothly to give the corresponding alkenyl- and aryliodides in high yields (entries 8–11). As another example of transformation of the resulting zinc reagents, Rh-catalyzed conjugate addition of the arylzinc species[14] generated from 4-octyne (**2a**) and PhZnCl (**1b**) is shown in entry 12.[15]

**Table 4.3. Rhodium-Catalyzed Arylzincation of Alkynes 2 with Arylzinc Reagents 1**[a]




entry 1)
**1a** with **2b** ($R^1 = R^2 = n\text{-}C_5H_{11}$)
binap (A): 91%, **5ab**:**6ab** = 1:99
cod (A): 78%, **5ab**:**6ab** = 90:10

entry 2)
**1a** with **2c** ($R^1 = R^2 = n\text{-}C_7H_{15}$)
binap (A): 97%, **5ac**:**6ac** = 4:96
cod (A): 74%, **5ac**:**6ac** = 93:7

entry 3)
**1a** with **2d** ($R^1 = R^2$ = Ph)
binap (B): 98%, **5ad**:**6ad** = 13:87
cod (A): 86%, **5ad**:**6ad** = 97:3

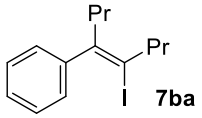
entry 4)
**1b** with **2d** ($R^1 = R^2$ = Ph)
binap (B): 97%, **5bd:6bd =** 10:90
cod (A):[b] 61%, **5bd:6bd =** 92:8

entry 5)
**1a** with **2e** ($R^1$ = Et, $R^2$ = Ph)
binap (B): 93%, **5ae**:**6ae** = 10:90
cod (A):[c] 72%, **5ae**:**6ae** = 94:6

entry 6)
**1a** with **2f** ($R^1$ = *i*-Pr, $R^2$ = *p*-Tol)
binap (B): 93%, **5af**:**6af** = 10:90
cod (A): 89%, **5af**:**6af** = 95:5[d]

entry 7)
**1a** with **2g** ($R^1$ = Me, $R^2 = CH_2CMe(COOEt)_2$)
cod (A): 87%, **5ag**:**6ag** = 97:3

entry 8)
**1b** with **2a**, cod (A)
then $I_2$:[e] 63% **7ba**



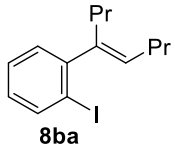
**7ba**

entry 9)
**1b** with **2a**, binap (A)
then $I_2$:[f] 77% **8ba**

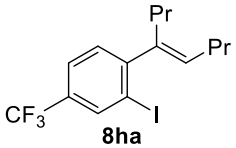
entry 10)
**1h** with **2a**, binap (B)
then $I_2$: 87% **8ha**

entry 11)
**1a** with **2h**
($R^1$ = Me, $R^2 = CH_2SiMe_3$)
cod (A), then $I_2$: 73% **7ah**

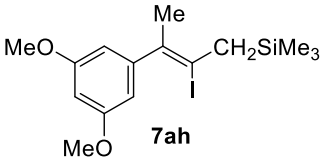
entry 12) 67% **9**
**1b** with **2a**, binap (B)
then cyclohex-2-enone:[g]
67% **9**



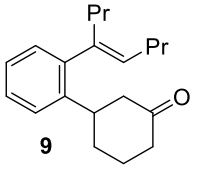
**8ba**



**8ha**



**7ah**



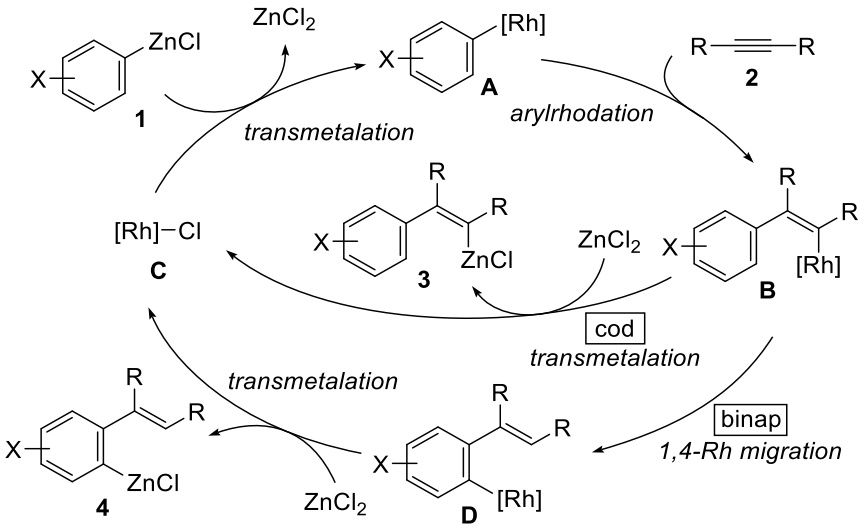
**9**

[a] For reaction conditions (A) and (B), see footnote *a* in Table 4.2. For idodination, $I_2$ (0.60 mmol) was added after the Rh-catalyzed arylzincation. [b] THF solutions of $[RhCl(cod)]_2$ and alkyne **2d** were added dropwise to PhZnCl (**1b**) and $ZnCl_2$ in THF over 40 min. [c] 1.5 mol% of Rh catalyst. [d] Containing 5% of its regioisomer. [e] 5 mmol scale. [f] 20 mmol scale, 1 mol% of Rh catalyst. [g] Cyclohex-2-enone (0.36 mmol) and $[RhCl(cod)]_2$ (15

The catalytic cycle of the present arylzincation of alkynes with/without 1,4-migratory is proposed in Scheme 4.4. Thus, the syn-addition of an aryl–Rh intermediated **A** to the alkyne generates a 2-arylalkenyl–Rh species **B**. Transmetalation of the alkenyl group from Rh to $ZnCl_2$ takes place to produce the

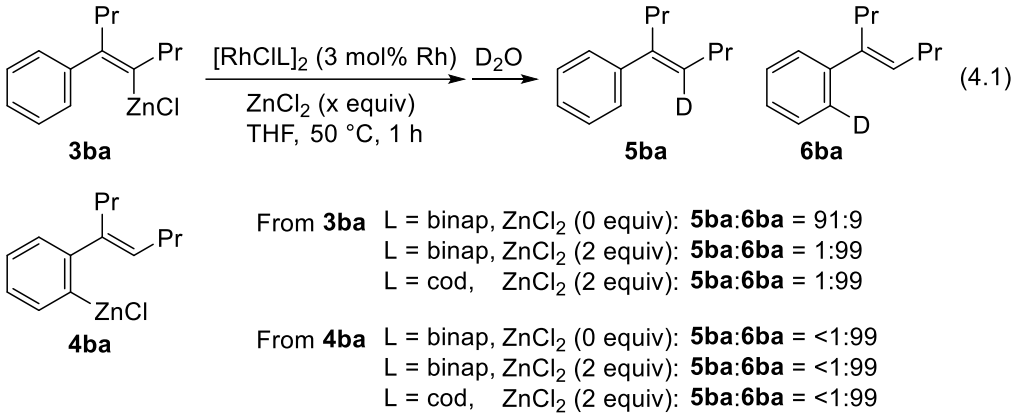
alkenylzinc product **3** and a Cl–Rh species **C**. Arylation of **C** with ArZnCl regenerates the aryl–Rh **A**.[14] Direct transmetalation between the alkenyl–Rh **B** and ArZnCl **2** giving the aryl–Rh **A** and the alkenylzinc **3** is less likely because a catalytic amount of $ZnCl_2$ is necessary for the present arylzincation (see entries 4 and 5 in Table 4.1). When the transmetalation of the alkenyl–Rh intermediate **B** with $ZnCl_2$ is relatively slow, it undergoes 1,4-migration of Rh giving an *ortho*-alkenylphenyl–Rh intermediate **D**, which is thermodynamically more stable than **B**.[6e] Transmetalation with $ZnCl_2$ finally leads to the *ortho*-alkenylarylzinc **4**. The selectivity in producing **3** or **4** is dependent on the reactivity of the alkenyl–Rh intermediate **B** towards transmetalation with $ZnCl_2$. It is our understanding that the transmetalation, which is an intermolecular reaction, is faster with a cod ligand and the Rh 1,4-migration which is an intramolecular event is not strongly affected by the ligands on rhodium. The faster transmetalation with cod ligand than binap ligand has been reported by Hayashi in 2006.[16]

**Scheme 4.4. A Catalytic Cycle Proposed for Arylzincation of Alkynes Catalyzed by Rh Complexes and $ZnCl_2$**




The reactions starting with alkenylzinc **3ba** and *ortho*-alkenylarylzinc **4ba** (equation 4.1) gave us further insight into the reaction mechanism. The isomerization of **3ba** into **4ba** was observed in the presence of $ZnCl_2$ with both Rh/binap and Rh/cod catalysts, while the isomerization is very slow without $ZnCl_2$. The isomerization from **4ba** to **3ba** was not observed under the same conditions with binap or cod ligand. These results demonstrate that $ZnCl_2$ plays a key role in the transmetalation steps in the catalytic cycle and that the *ortho*-alkenylarylzinc **4ba** is thermodynamically more stable than the alkenylzinc **3ba**. It is remarkable that the ratio of the 2-arylalkenylzinc **3** to the *ortho*-alkenylarylzinc **4** is not dependent on the reaction time or conversion. Thus, $D_2O$ quench of the reaction of **1a** with **2a** at 15 min reaction time gave 47% yield of **5aa**/**6aa** (1/99) and 29% yield of **5aa**/**6aa** (93/7) with binap and cod ligands, respectively. The **5aa**/**6aa** ratios are essentially the same as those observed in entries 1 and 2 in Table 4.1. The 1,4-migration selectivity did not change when lower amount of **1a** was used. The organozincs **3**

and **4** generated by the reaction of alkyne **2** with an excess amount of ArZnCl **1** do not go back to the catalytic cycle shown in Scheme 4.4 in the presence of excess **1**, although both Rh/binap and Rh/cod catalyze the isomerization of **3** to **4** in the absence of ArZnCl **1** (equation 4.1).




## 4.3 Conclusion

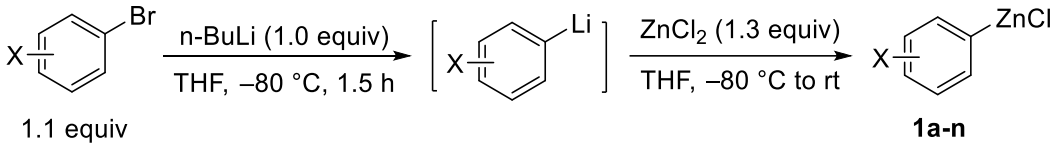
In summary, we have disclosed that the addition of arylzinc reagents ArZnCl to unfunctionalized alkynes is efficiently catalyzed by rhodium complexes in the presence of a catalytic amount of zinc chloride. The selectivity between the 2-arylalkenylzincs and the *ortho*-alkenylarylzinc products, the latter of which is generated through 1,4-Rh migration from alkenyl to aryl, is controlled by the use of the appropriate ligands on rhodium.

## 4.4 Experimental section

### 4.4.1 Materials

Alkynes, aryl bromides, bisphosphine ligands, n-BuLi, $D_2O$, $ZnCl_2$, $ZnBr_2$, $ZnI_2$, 3-methyl-1-butyne, 4-iodotoluene, cyclohex-2-enone, and iodine were purchased and used as received. $Et_2O$ and THF were distilled over benzophenone ketyl under $N_2$. $[RhCl(coe)_2]_2$,[17] $[RhCl(cod)]_2$,[18] Diethyl (2-butynyl)(methyl)malonate (**2g**) [182809-41-2],[19] and but-2-yn-1-yltrimethylsilane (**2h**) [18825-29-1][20] were prepared according to the reported procedures. 1-(4-Methylphenyl)-3-methyl-1-butyne (**2f**) [79756-94-8][21] was prepared from 3-methyl-1-butyne and 4-iodotoluene according to the reported procedure.[22]

### 4.4.2 Preparation of arylzinc chlorides 1 in THF[23]




**Preparation of $ZnCl_2$ Solution (0.87 M in THF):** A Schlenk flask equipped with a stir bar was flame-dried under vacuum and allowed to cool down to room temperature. Under nitrogen, $ZnCl_2$ (3.54 g, 26.0 mmol) was charged, and the flask was heated under vacuum in an oil-bath at 150 °C for 12 h. Then, the flask was cooled to room temperature and THF (anhydrous, 30.0 mL) was added. The mixture was vigorously stirred until all $ZnCl_2$ was dissolved.

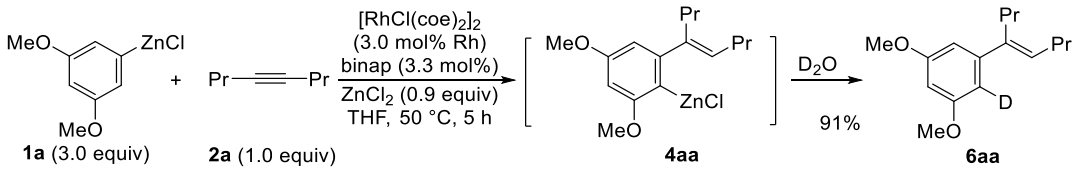
**Preparation of 3,5-$(MeO)_2C_6H_3ZnCl$ (1a, 0.40 M in THF):** An oven-dried Schlenk flask equipped with a stir bar was charged with a solution of 1-bromo-3,5-dimethoxybenzene (4.78 g, 22.0 mmol) in THF (12.0 mL). The solution was cooled down to –80 °C and n-BuLi (7.4 mL, 20.0 mmol, 2.69 M in hexanes) was added dropwise over 30 min. Precipitates were formed immediately. The reaction mixture

was stirred at –80 °C for 90 min. To the THF solution of aryllithium thus generated, the THF solution of $ZnCl_2$ (30.0 mL, 26.0 mmol, 0.87 M) prepared above was added dropwise at –80 °C. The reaction mixture was allowed to warm to room temperature to give a solution of 3,5-$(MeO)_2C_6H_3ZnCl$ (**1a**, 0.40 M) and $ZnCl_2$ (0.12 M) in THF.

All other arylzinc reagents ArZnCl **1** were prepared in the same manner as above from the corresponding aryl bromides.

ArZnX (Ar = 3,5-$(MeO)_2C_6H_3$, X = Br and I) were prepared using $ZnX_2$ (X = Br and I), and $Ar_2Zn$ was prepared with 0.5 equiv of $ZnCl_2$.

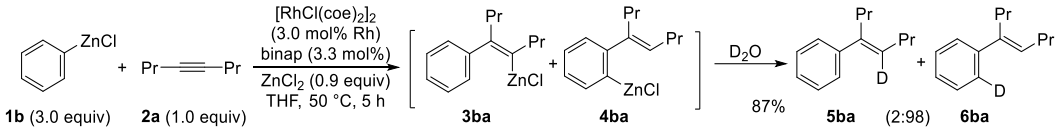
### 4.4.3 A typical procedure for Table 4.1 (entry 1)




In an oven-dried Schlenk tube, $[RhCl(coe)_2]_2$ (2.15 mg, 0.0030 mmol, 3.0 mol% of Rh) and binap (4.11 mg, 0.0066 mmol, 3.3 mol%) were placed under nitrogen. THF (0.50 mL) was added and the mixture was stirred at room temperature for 10 min. 4-Octyne (**2a**) (22.0 mg, 0.20 mmol) was added at room temperature. To the mixture, 1.5 mL of the THF solution containing 3,5-$(MeO)_2C_6H_3ZnCl$ (**1a**) (0.60 mmol, 0.40 M) and $ZnCl_2$ (0.18 mmol, 0.12 M), whose preparation was shown in Section 4.4.2, was added at room temperature. The reaction mixture was heated at 50 °C for 5 h before $D_2O$ (0.2 mL) was added. The reaction mixture was passed through a short silica gel pad with EtOAc as eluent. The solvent was removed on a rotary evaporator. After $^1H$ NMR analysis of the residue, the crude product was subjected to silica gel chromatography with hexane to give **6aa** (91% yield, 45.4 mg, 0.18 mmol) as colorless oil. $^2H$ NMR showed that **6aa** was produced selectively.

### 4.4.4 Typical procedures for Table 4.2 and Table 4.3 (entries 1-7)

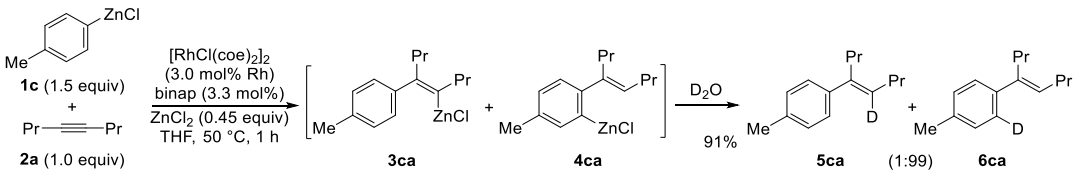
#### 4.4.4-1. Entry 2 in Table 4.2, condition (A) with binap ligand:




According to the procedures shown in Section 4.4.2, THF solution of PhZnCl (**1b**, 0.40 M) and $ZnCl_2$ (0.12 M) was prepared from bromobenzene (3.45 g, 22.0 mmol), n-BuLi (7.4 mL, 20.0 mmol, 2.69 M in hexane), and $ZnCl_2$ (3.54 g, 26.0 mmol). A part of this stock solution was used for the rhodium-catalyzed phenylzincation.

The procedures in Section 4.4.3 for the reaction of entry 1 in Table 4.1 were followed with $[RhCl(coe)_2]_2$ (2.15 mg, 0.0030 mmol, 3.0 mol% of Rh), binap (4.11 mg, 0.0066 mmol, 3.3 mol%), 4-octyne (**2a**, 22.0 mg, 0.20 mmol), and THF solution containing PhZnCl (**1b**) (0.60 mmol, 0.40 M) and $ZnCl_2$ (0.18 mmol, 0.12 M) at 50 °C for 5 h. A mixture of **5ba** and **6ba** (87% yield, 32.9 mg, 0.17 mmol) was obtained as colorless oil. $^2H$ NMR showed that the ratio of **5ba**:**6ba** is 2:98.

#### 4.4.4-2. Entry 3 in Table 4.2, condition (B) with binap ligand:

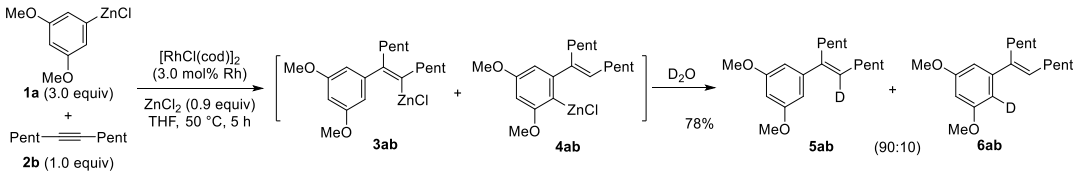



A THF solution of 4-$MeC_6H_4ZnCl$ (**1c**, 0.4 M) and $ZnCl_2$ (0.12 M) was prepared starting with 4-bromotoluene (3.76 g, 22.0 mmol) by otherwise the same procedures described in Section 4.4.2.

The procedures shown in Section 4.4.4-1 were modified by reducing the amount of THF, 4-$MeC_6H_4ZnCl$ (**1c**), and $ZnCl_2$ to (0.25 mL), (0.30 mmol, 0.40 M),

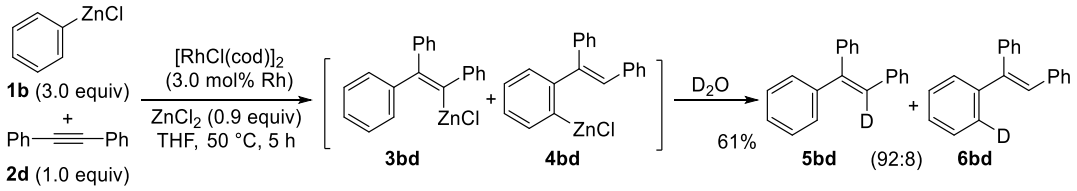
and (0.09 mmol, 0.12 M), respectively, and by shortening the reaction time to 1 h. A mixture of **5ca** and **6ca** (91% yield, 37.0 mg, 0.18 mmol) was obtained as colorless oil. $^2$H NMR showed that the ratio of **5ca**:**6ca** is 1:99.

#### 4.4.4-3. Entry 1 in Table 4.3, condition (A) with cod ligand:




The catalyst used for condition (A) with binap ligand (Section 4.4.4-1) was replaced by [RhCl(cod)]$_2$. Thus, the reaction of [RhCl(cod)]$_2$. (1.48 mg, 0.0030 mmol, 3.0 mol% of Rh), 6-dodecyne (**2b**, 33.3 mg, 0.20 mmol), 3,5-(MeO)$_2$C$_6$H$_3$ZnCl (**1a**) (0.60 mmol, 0.40 M), and $ZnCl_2$ (0.18 mmol, 0.12 M) at 50 °C for 5 h gave a mixture of **5ab** and **6ab** (78% yield, 47.8 mg, 0.16 mmol) as colorless oil. $^2$H NMR showed that the ratio of **5ab**:**6ab** is 90:10.

#### 4.4.4-4. Entry 4 in Table 4.3, modified condition (A) with cod ligand:

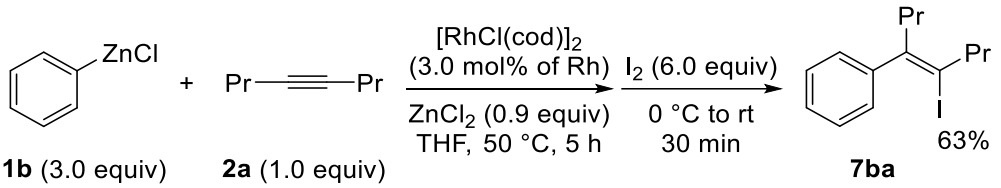



Under nitrogen, an oven-dried Schlenk tube equipped with a stir bar was charged with THF solution (1.5 mL) containing PhZnCl (0.60 mmol) and $ZnCl_2$ (0.18 mmol) at room temperature (see Section 4.4.4-1 for the preparation of PhZnCl solution). A solution of [RhCl(cod)]$_2$ (1.48 mg, 0.0030 mmol, 3.0 mol% of Rh) in THF (1.0 mL) and a solution of diphenylacetylene (**2d**) (35.6 mg, 0.20 mmol) in THF (1.0 mL) were added simultaneously into reaction mixture by syringe at room temperature over 40 min. Then, the mixture was heated at 50 °C for 5 h before $D_2O$

(0.2 mL) was added. The reaction mixture was passed through a short column of silica gel with EtOAc as eluent. The solvent was removed on a rotary evaporator. After $^{1}$H NMR analysis of the residue, it was subjected to silica gel chromatography with pentane to give a mixture of **5bd** and **6bd** (61% yield, 31.5 mg, 0.12 mmol) as a colorless oil. $^{2}$H NMR showed that the ratio of **5bd**:**6bd** is 92:8.

### 4.4.5 Procedures for the syntheses of alkenyl iodides 7 and aryl iodides 8 (Table 4.3, entries 8-11)

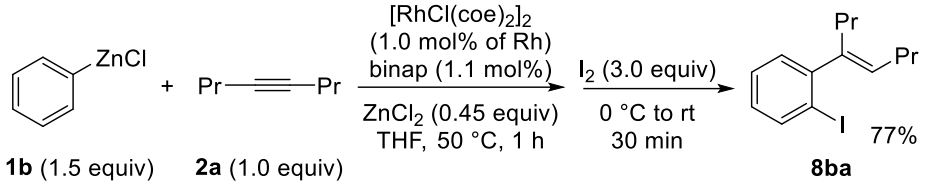
#### 4.4.5-1. 7ba, entry 8 in Table 4.3




In an oven-dried Schlenk flask, $[RhCl(cod)]_2$ (37.0 mg, 0.075 mmol, 3 mol% of Rh) was placed under nitrogen, and it was dissolved in dry THF (12.5 mL). A THF solution (37.5 mL) containing phenylzinc chloride (**1b**) (15 mmol) and $ZnCl_2$ (4.5 mmol), which was prepared from bromobenzene (2.59 g, 16.5 mmol), n-BuLi (15.0 mmol), and $ZnCl_2$ (2.66 g, 19.5 mmol) according to the procedures shown in Section 4.4.4-1, was added at room temperature. Subsequently, 4-octyne (**2a**) (551 mg, 5.0 mmol) was added slowly to the solution over 10 min at 0 °C. The mixture was heated at 50 °C for 5 h, and $I_2$ (7.61 g, 30.0 mmol) was subsequently added at 0 °C. The mixture was stirred at room temperature for 30 min before saturated aqueous solution of $Na_2S_2O_3$ (15 mL) was added. The mixture was extracted with ethyl acetate, and the combined organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was subjected to

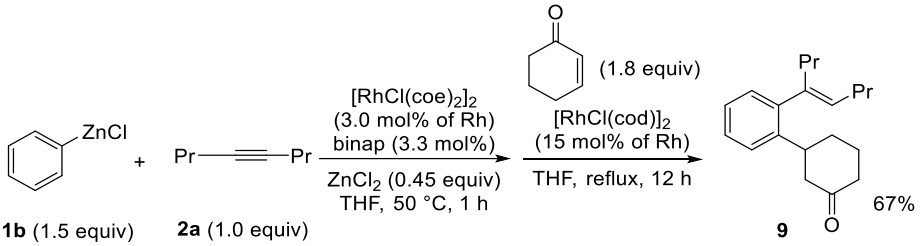
chromatography on silica gel (pre-treated with 1% $Et_3N$ in hexane) to give the product **7ba** (63%, 0.99 g, 3.2 mmol) as colorless oil.

**4.4.5-2. 8ba, entry 9 in Table 4.3**




In an oven-dried Schlenk flask, $[RhCl(coe)_2]_2$ (71.8 mg, 0.10 mmol, 1 mol% of Rh) and binap (137.0 mg, 0.22 mmol, 1.1 mol%) were placed under nitrogen. Dry THF (5.0 mL) was added and the solution was stirred at room temperature for 10 min. A THF solution (45.0 mL) containing phenylzinc chloride (**1b**) (30.0 mmol) and $ZnCl_2$ (9.0 mmol), which was prepared from bromobenzene (5.18 g, 33.0 mmol), n-BuLi (30.0 mmol), and $ZnCl_2$ (5.32 g, 39.0 mmol) according to the procedures shown in Section 4.4.2, was added at room temperature. Then, 4-octyne (**2a**) (2.20 g, 20.0 mmol) was added slowly to the solution over 10 min at 0 °C. The mixture was heated at 50 °C for 1 h, and $I_2$ (15.2 g, 60.0 mmol, 3.0 equiv) was added at 0 °C. The resulting mixture was stirred at room temperature for 30 min before saturated aqueous solution of $Na_2S_2O_3$ (30 mL) was added. The mixture was extracted with ethyl acetate, and the combined organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was subjected to chromatography on silica gel (pre-treated with 1% $Et_3N$ in hexanes) to give the product **8ba** (77%, 4.82 g, 15.4 mmol) as colorless oil.

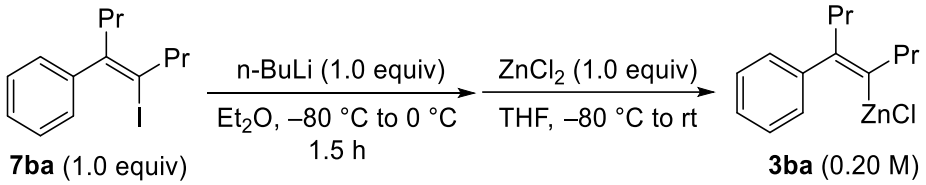
### 4.4.6 Procedures for the Rh-catalyzed arylzincation followed by conjugate addition (Table 4.3, entry 12)




In an oven-dried Schlenk tube, $[RhCl(coe)_2]_2$ (2.15 mg, 0.0030 mmol, 3.0 mol% of Rh) and binap (4.11 mg, 0.0066 mmol, 3.3 mol%) were placed under nitrogen. THF (0.25 mL) was added and the mixture was stirred at room temperature for 10 min. 4-Octyne (**2a**) (22.0 mg, 0.20 mmol) was added at room temperature. To the mixture, 0.75 mL of the THF solution containing PhZnCl (0.30 mmol) and $ZnCl_2$ (0.09 mmol) (see Section 4.4.4-1 for the preparation of PhZnCl solution) was added at room temperature, and the mixture was heated at 50 °C for 1 h. Cyclohex-2-enone (34.6 mg, 0.36 mmol) and $[RhCl(cod)]_2$ (7.40 mg, 0.015 mmol, 15 mol% of Rh) were added. The mixture was refluxed for 12 h before $H_2O$ (2.0 mL) was added. The mixture was extracted with ethyl acetate, and the combined organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was subjected to chromatography on silica gel to give the product **9** (67%, 38.0 mg, 0.13 mmol) as colorless oil.

### 4.4.7 Preparation of alkenylzinc chloride 3ba and arylzinc chloride 4ba in THF

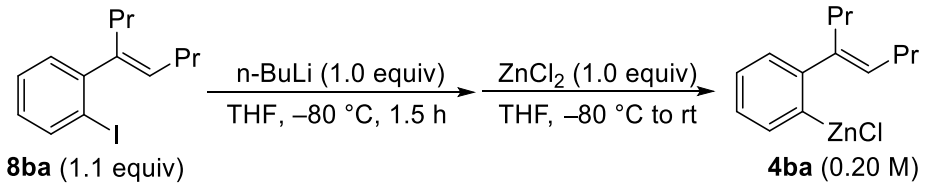
#### 4.4.7-1. Preparation of alkenylzinc chloride 3ba in THF




**7ba** (1.0 equiv) **3ba** (0.20 M)

To a solution of compound **7ba** (0.99 g, 3.2 mmol) in $Et_2O$ (3.0 mL), n-BuLi in hexane (1.2 mL, 3.2 mmol, 2.69 M) was added dropwise over 30 min at –80 °C. The mixture was allowed to warm to 0 °C and stirred for 90 min before it was cooled back to –80 °C. Dry $ZnCl_2$ (436.2 mg, 3.2 mmol) in THF (12.0 mL) was subsequently added and the mixture was allowed to warm to room temperature to give a solution of alkenylzinc chloride **3ba** (0.20 M) in THF.

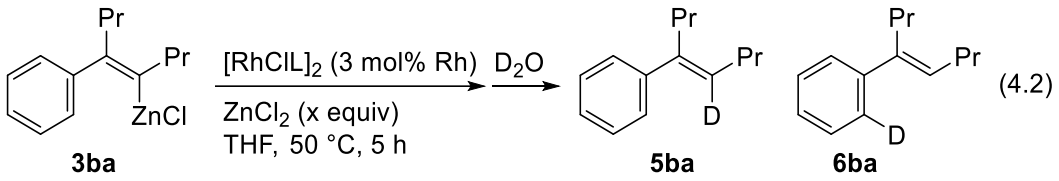
#### 4.4.7-2. Preparation of alkenylzinc chloride 4ba in THF




**8ba** (1.1 equiv) **4ba** (0.20 M)

To a solution of compound **8ba** (3.46 g, 11.0 mmol) in THF (10.0 mL), n-BuLi in hexane (3.7 mL, 10.0 mmol, 2.69 M) was added dropwise over 30 min at –80 °C. The mixture was stirred at –80 °C for 90 min before $ZnCl_2$ (1.36 g, 10 mmol) in THF (36.0 mL) was added. The mixture was allowed to warm to room temperature to give a solution of arylzinc chloride **4ba** (0.20 M) in THF.

### 4.4.8 Isomerization between alkenylzinc 3ba and arylzinc 4ba (equation 4.1)



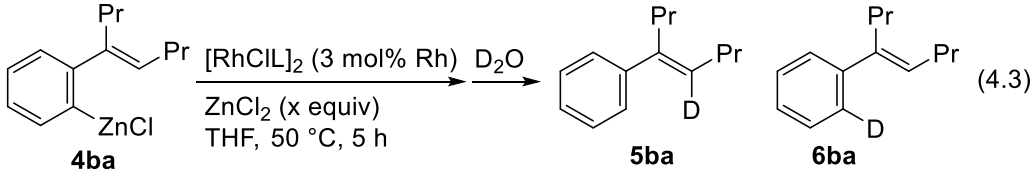

(4.2)

entry 1: L = binap, $ZnCl_2$ (0 equiv): **5ba**:**6ba** = 91:9
entry 2: L = binap, $ZnCl_2$ (2 equiv): **5ba**:**6ba** = 1:99
entry 3: L = cod, $ZnCl_2$ (2 equiv): **5ba**:**6ba** = 1:99

**Entry 1 in equation 4.2**: In an oven-dried Schlenk flask, $[RhCl(coe)_2]_2$ (2.15 mg, 0.0030 mmol, 3.0 mol% of Rh), binap (4.11 mg, 0.0066 mmol, 3.3 mol%) were placed under nitrogen. Anhydrous THF (1.0 mL) was added and the mixture was stirred at room temperature for 10 min. The THF solution of **3ba** (1.0 mL, 0.20 mmol, 0.2 M), which was prepared in Section 4.4.7-1, was added. The mixture was heated at 50 °C for 5 h, and it was quenched with $D_2O$ (0.2 mL). The reaction mixture was passed through a short column of silica gel with EtOAc as eluent. The solvent was removed on a rotary evaporator. After $^1H$ NMR analysis of the residue, the crude product was subjected to silica gel chromatography with pentane.

**Entry 2:** Anhydrous $ZnCl_2$ powder (54.5 mg, 0.40 mmol) and THF (1.0 mL) were added before **3ba** in THF was added.

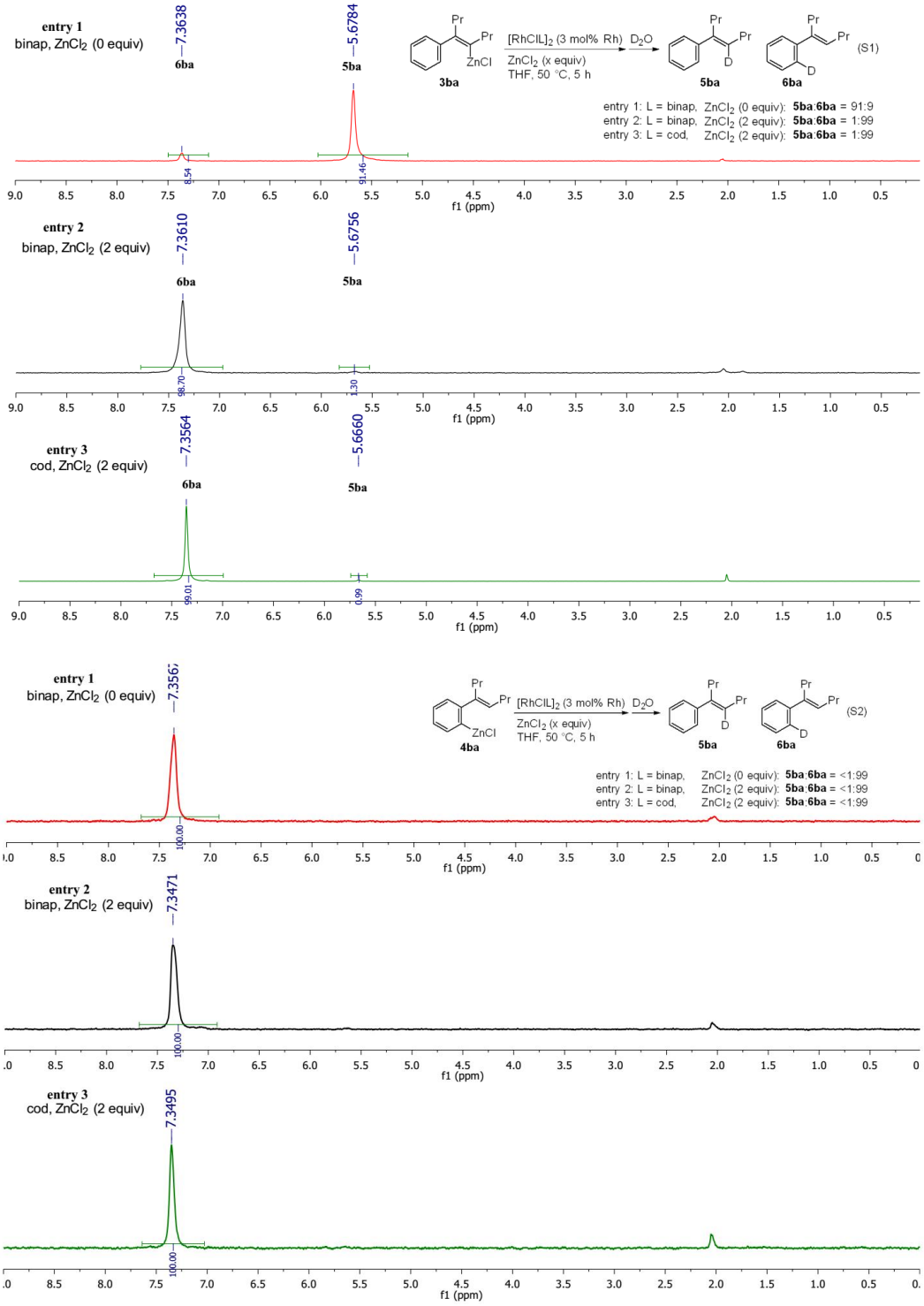
**Entry 3:** $[RhCl(cod)]_2$ (1.48 mg, 0.0030 mmol, 3 mol% of Rh) was used as catalyst instead of $[RhCl(coe)_2]_2$ and binap. Anhydrous $ZnCl_2$ powder (54.5 mg, 0.40 mmol) and THF (1.0 mL) were added before **3ba** in THF was added.




(4.3)

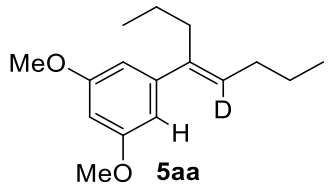
entry 1: L = binap, $ZnCl_2$ (0 equiv): **5ba**:**6ba** = <1:99
entry 2: L = binap, $ZnCl_2$ (2 equiv): **5ba**:**6ba** = <1:99
entry 3: L = cod, $ZnCl_2$ (2 equiv): **5ba**:**6ba** = <1:99

The same procedures as those for equation 4.2 were followed by using a THF solution of **4ba** prepared in Section 4.4.7-2.



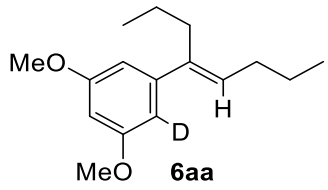
### 4.4.9 Characterization of the products

The ratios of **5** to **6** were determined by $^{2}H$ NMR analysis except for **5ae**/**6ae**, **5af**/**6af**, and **5ag**/**6ag**.



**5aa**

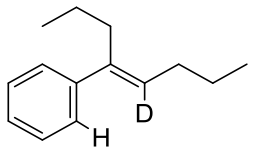
**Compound 5aa**. (Table 4.2, entry 1, cod (A), 82% yield, **5aa**:**6aa** = 92:8). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 0.88 (t, $J_{H,H}$ = 7.4 Hz, 3H), 0.96 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.37 (sext, $J_{H,H}$ = 7.6 Hz, 2H), 1.47 (sext, $J_{H,H}$ = 7.4 Hz, 2H), 2.16 (t, $J_{H,H}$ = 7.3 Hz, 2H), 2.43 (t, $J_{H,H}$ = 7.6 Hz, 2H), 3.80 (s, 6H), 6.35 (t, $J_{H,H}$ = 2.1 Hz, 1H), 6.50 (d, $J_{H,H}$ = 2.2 Hz, 2H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 14.11, 14.15, 22.0, 23.1, 30.6, 32.0, 55.4, 98.4, 105.0, 129.1 (t, $J_{C,^{2}H}$ = 23.0 Hz), 140.1, 146.0, 160.7; $^{2}H$ NMR (61 MHz, acetone) δ 5.68 (s). **HRMS** (ESI) calcd for $C_{16}H_{24}DO_2$ $[M+H]^+$ 250.1917, found 250.1898.



**6aa**

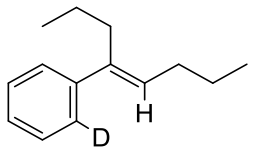
**Compound 6aa**. (Table 4.2, entry 1, binap (B), 90% yield, **5aa**:**6aa** = <1:99). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 0.88 (t, $J_{H,H}$ = 7.3 Hz, 3H), 0.96 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.37 (sext, $J_{H,H}$ = 7.6 Hz, 2H), 1.47 (sext, $J_{H,H}$ = 7.4 Hz, 2H), 2.16 (q, $J_{H,H}$ = 7.3 Hz, 2H), 2.43 (t, $J_{H,H}$ = 7.6 Hz, 2H), 3.80 (s, 6H), 5.67 (t, $J_{H,H}$ = 7.3 Hz, 1H), 6.35 (s, 1H), 6.50 (d, $J_{H,H}$ = 1.7 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 14.09, 14.14, 22.0, 23.2, 30.7, 32.0, 55.4, 98.4, 104.7 (t, $J_{C,^{2}H}$ = 24.1 Hz), 105.0, 129.4, 140.2 (t,

$J_{C,^2H}$ = 4.1 Hz), 146.0 (t, $J_{C,^2H}$ = 8.8 Hz), 160.6, 160.7; **$^2$H NMR** (61 MHz, acetone) δ 6.50 (s). **HRMS** (ESI) calcd for $C_{16}H_{24}DO_2$ $[M+H]^+$ 250.1917, found 250.1940.




**5ba**

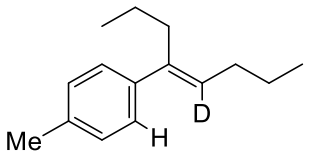
**Compound 5ba [819047-73-9]**. (Table 4.2, entry 2, cod (A), 80% yield, **5ba**:**6ba** = 80:20). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.88 (t, $J_{H,H}$ = 7.3 Hz, 3H), 0.97 (t, $J_{H,H}$ = 7.3 Hz, 3H), 1.37 (sext, $J_{H,H}$ = 7.6 Hz, 2H), 1.48 (sext, $J_{H,H}$ = 7.3 Hz, 2H), 2.17 (t, $J_{H,H}$ = 7.1 Hz, 2H), 2.48 (t, $J_{H,H}$ = 7.6 Hz, 2H), 7.21 (t, $J_{H,H}$ = 6.9 Hz, 1H), 7.29 (t, $J_{H,H}$ =7.2 Hz, 2H), 7.34 (d, $J_{H,H}$ = 8.0 Hz, 2H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 14.10, 14.11, 22.0, 23.2, 30.7, 31.8, 126.5, 128.1, 128.2, 129.0 (t, $J_{C,^2H}$ = 22.8 Hz), 140.1, 143.7; **$^2$H NMR** (61 MHz, acetone) δ 5.66 (s). The spectral data are in agreement with reported literature values.[24]




**6ba**

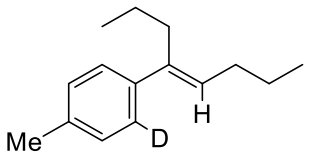
**Compound 6ba [374107-00-3]**. (Table 4.2, entry 2, binap (A), 87% yield, **5ba**:**6ba** = 2:98). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 0.89 (t, $J_{H,H}$ = 7.4 Hz, 3H), 0.97 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.37 (sext, $J_{H,H}$ = 7.6 Hz, 2H), 1.48 (sext, $J_{H,H}$ = 7.4 Hz, 2H), 2.18 (q, $J_{H,H}$ = 7.3 Hz, 2H), 2.48 (t, $J_{H,H}$ = 7.7 Hz, 2H), 5.67 (t, $J_{H,H}$ = 7.3 Hz, 1H), 7.21 (td, $J_{H,H}$ = 7.4 Hz, 1.3 Hz, 1H), 7.30 (t, $J_{H,H}$ = 6.9 Hz, 1H), 7.30 (d, $J_{H,H}$ = 6.7 Hz, 1H), 7.34 (d, $J_{H,H}$ = 7.7 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 14.10, 14.11, 22.0, 23.2, 30.8, 31.9, 126.2 (t, $J_{C,^2H}$ = 24.1 Hz), 126.5, 128.1, 128.2, 129.3, 140.2,

143.6; **$^2$H NMR** (61 MHz, acetone) δ 7.35 (s). The spectral data are in agreement with reported literature values.[6b]



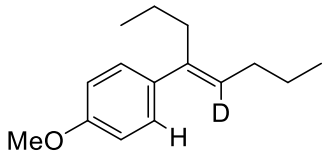

**5ca**

**Compound 5ca**. (Table 4.2, entry 3, cod (A), 68% yield, **5ca**:**6ca** = 77:23). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.89 (t, $J_{H,H}$ = 7.4 Hz, 3H), 0.96 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.35 (sext, $J_{H,H}$ = 7.6 Hz, 2H), 1.47 (sext, $J_{H,H}$ = 7.4 Hz, 2H), 2.16 (t, $J_{H,H}$ = 7.4 Hz, 2H), 2.34 (s, 3H), 2.46 (t, $J_{H,H}$ = 7.6 Hz, 2H), 7.11 (d, $J_{H,H}$ = 7.9 Hz, 2H), 7.24 (d, $J_{H,H}$ = 8.1 Hz, 2H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 13.94, 13.96, 21.0, 21.8, 23.1, 30.6, 31.6, 126.2, 128.1 (t, $J_{C,^2H}$ = 22.8 Hz), 128.8, 135.9, 139.7, 140.6; **$^2$H NMR** (61 MHz, acetone) δ 5.63 (s). **HRMS** (ESI) calcd for $C_{15}H_{22}D$ $[M+H]^+$ 204.1863, found 204.1858.



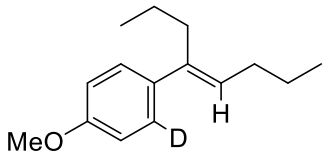

**6ca**

**Compound 6ca**. (Table 4.2, entry 3, binap (B), 91% yield, **5ca**:**6ca** = 1:99). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.88 (t, $J_{H,H}$ = 7.4 Hz, 3H), 0.97 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.37 (sext, $J_{H,H}$ = 7.6 Hz, 2H), 1.48 (sext, $J_{H,H}$ = 7.4 Hz, 2H), 2.17 (q, $J_{H,H}$ = 7.3 Hz, 2H), 2.34 (s, 3H), 2.47 (t, $J_{H,H}$ = 7.6 Hz, 2H), 5.64 (t, $J_{H,H}$ = 7.2 Hz, 1H), 7.06–7.14 (br m, 2H), 7.25 (d, $J_{H,H}$ = 8.5 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 13.9, 14.0, 21.0, 21.8, 23.1, 30.6, 31.7, 125.9 (t, $J_{C,^2H}$ = 23.9 Hz), 126.2, 128.4, 128.7, 128.8, 135.9, 139.8, 140.5; **$^2$H NMR** (61 MHz, acetone) δ 7.24 (s). **HRMS** (ESI) calcd for $C_{15}H_{22}D$ $[M+H]^+$ 204.1863, found 204.1864.



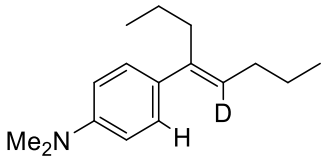

**5da**

**Compound 5da**. (Table 4.2, entry 4, cod (A), 84% yield, **5da**:**6da** = 74:26). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.88 (t, $J_{H,H}$ = 7.4 Hz, 3H), 0.96 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.36 (sext, $J_{H,H}$ = 7.6 Hz, 2H), 1.46 (sext, $J_{H,H}$ = 7.4 Hz, 2H), 2.16 (t, $J_{H,H}$ = 7.3 Hz, 2H), 2.44 (t, $J_{H,H}$ = 7.6 Hz, 2H), 3.80 (s, 3H), 6.84 (d, $J_{H,H}$ = 8.7 Hz, 2H), 7.27 (d, $J_{H,H}$ = 8.6 Hz, 2H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 14.0, 21.8, 23.1, 30.5, 31.7, 55.2, 113.5, 127.3, 127.5 (t, $J_{C,^2H}$ = 22.5 Hz), 136.0, 139.2, 158.3; **$^2$H NMR** (61 MHz, acetone) δ 5.58 (s). **HRMS** (ESI) calcd for $C_{15}H_{22}DO$ $[M+H]^+$ 220.1812, found 220.1818.



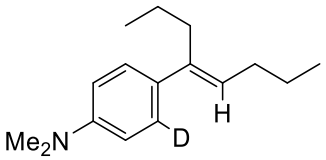

**6da**

**Compound 6da**. (Table 4.2, entry 4, binap (A), 94% yield, **5da**:**6da** = 1:99). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.88 (t, $J_{H,H}$ = 7.4 Hz, 3H), 0.96 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.37 (sext, $J_{H,H}$ = 7.6 Hz, 2H), 1.47 (sext, $J_{H,H}$ = 7.4 Hz, 2H), 2.16 (q, $J_{H,H}$ = 7.3 Hz, 2H), 2.45 (t, $J_{H,H}$ = 7.6 Hz, 2H), 3.81 (s, 3H), 5.60 (t, $J_{H,H}$ = 7.2 Hz, 1H), 6.84–6.86 (br m, 2H), 7.28 (d, $J_{H,H}$ = 9.3 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 13.94, 13.95, 21.8, 23.1, 30.6, 31.7, 55.2, 113.4, 113.5, 127.0 (t, $J_{C,^2H}$ = 23.8 Hz), 127.3, 127.8, 135.9, 139.3, 158.3; **$^2$H NMR** (61 MHz, acetone) δ 7.29 (s). **HRMS** (ESI) calcd for $C_{15}H_{22}DO$ $[M+H]^+$ 220.1812, found 220.1809.



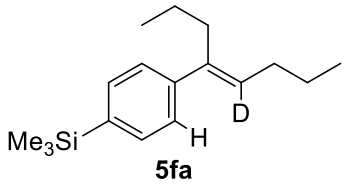

**5ea**

**Compound 5ea**. (Table 4.2, entry 5, cod (A), 71% yield, **5ea**:**6ea** = 94:6). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.88 (t, $J_{H,H}$ = 7.4 Hz, 3H), 0.95 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.38 (sext, $J_{H,H}$ = 7.6 Hz, 2H), 1.46 (sext, $J_{H,H}$ = 7.4 Hz, 2H), 2.15 (t, $J_{H,H}$ = 7.3 Hz, 2H), 2.44 (t, $J_{H,H}$ = 7.7 Hz, 2H), 2.94 (s, 6H), 6.71 (d, $J_{H,H}$ = 8.6 Hz, 2H), 7.25 (d, $J_{H,H}$ = 8.8 Hz, 2H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 13.95, 14.02, 21.9, 23.2, 30.5, 31.5, 40.8, 112.6, 126.1 (t, $J_{C,^2H}$ = 23.0 Hz), 126.9, 131.9 (br s), 139.3, 149.3; **$^2$H NMR** (61 MHz, acetone) δ 5.55 (s). **HRMS** (ESI) calcd for $C_{16}H_{25}DN$ $[M+H]^+$ 233.2128, found 233.2135.



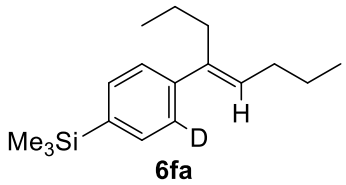

**6ea**

**Compound 6ea**. (Table 4.2, entry 5, binap (B), 87% yield, **5ea**:**6ea** = 1:99). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.89 (t, $J_{H,H}$ = 7.4 Hz, 3H), 0.96 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.39 (sext, $J_{H,H}$ = 7.6 Hz, 2H), 1.47 (sext, $J_{H,H}$ = 7.4 Hz, 2H), 2.16 (q, $J_{H,H}$ = 7.3 Hz, 2H), 2.45 (t, $J_{H,H}$ = 7.6 Hz, 2H), 2.95 (s, 6H), 5.60 (t, $J_{H,H}$ = 7.2 Hz, 1H), 6.70–6.76 (br m, 2H), 7.27 (d, $J_{H,H}$ = 9.3 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 13.9, 14.0, 21.9, 23.2, 30.6, 31.6, 40.9, 112.6, 112.7, 126.5, 126.6 (t, $J_{C,^2H}$ = 23.9 Hz), 126.9, 132.1 (br s), 139.3, 149.1; **$^2$H NMR** (61 MHz, acetone) δ 7.22 (s). **HRMS** (ESI) calcd for $C_{16}H_{25}DN$ $[M+H]^+$ 233.2128, found 233.2128.



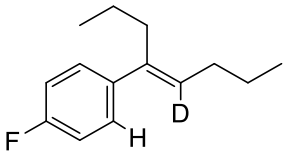

**5fa**

**Compound 5fa**. (Table 4.2, entry 6, cod (A), 86% yield, **5fa**:**6fa** = 81:19). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.26 (s, 9H), 0.89 (t, $J_{H,H}$ = 7.4 Hz, 3H), 0.96 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.38 (sext, $J_{H,H}$ = 7.6 Hz, 2H), 1.47 (sext, $J_{H,H}$ = 7.4 Hz, 2H), 2.17 (t, $J_{H,H}$ = 7.4 Hz, 2H), 2.48 (t, $J_{H,H}$ = 7.7 Hz, 2H), 7.33 (d, $J_{H,H}$ = 8.2 Hz, 2H), 7.46 (d, $J_{H,H}$ = 8.2 Hz, 2H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ –1.1, 13.9, 14.0, 21.9, 23.0, 30.6, 31.6, 125.6, 129.0 (t, $J_{C,^2H}$ = 22.6 Hz), 133.2, 138.1, 139.8, 143.9; **$^2$H NMR** (61 MHz, acetone) δ 5.69 (s). **HRMS** (ESI) calcd for $C_{17}H_{28}DSi$ $[M+H]^+$ 262.2101, found 262.2100.



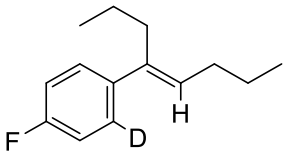

**6fa**

**Compound 6fa**. (Table 4.2, entry 6, binap (B), 85% yield, **5fa**:**6fa** = 6:94). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.26 (s, 9H), 0.89 (t, $J_{H,H}$ = 7.3 Hz, 3H), 0.96 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.37 (sext, $J_{H,H}$ = 7.6 Hz, 2H), 1.47 (sext, $J_{H,H}$ = 7.4 Hz, 2H), 2.18 (q, $J_{H,H}$ = 7.3 Hz, 2H), 2.47 (t, $J_{H,H}$ = 7.7 Hz, 2H), 5.68 (t, $J_{H,H}$ = 7.3 Hz, 1H), 7.33 (d, $J_{H,H}$ = 8.0 Hz, 1H), 7.43–7.48 (br m, 2H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ –1.1, 13.9, 14.0, 21.9, 23.0, 30.7, 31.6, 125.3 (t, $J_{C,^2H}$ = 24.3 Hz), 125.6, 129.3, 133.1, 133.2, 138.1, 139.9, 143.8; **$^2$H NMR** (61 MHz, acetone) δ 7.35 (s). **HRMS** (ESI) calcd for $C_{17}H_{28}DSi$ $[M+H]^+$ 262.2101, found 262.2113.



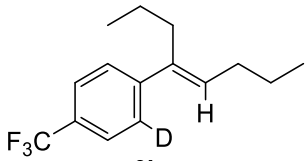

**5ga**

**Compound 5ga**. (Table 4.2, entry 7, cod (A), 52% yield, **5ga**:**6ga** = 49:51). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 0.86 (t, $J_{H,H}$ = 7.4 Hz, 3H), 0.94 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.33 (sext, $J_{H,H}$ = 7.6 Hz, 2H), 1.45 (sext, $J_{H,H}$ = 7.4 Hz, 2H), 2.14 (t, $J_{H,H}$ = 7.3 Hz, 2H), 2.43 (t, $J_{H,H}$ = 7.6 Hz, 2H), 6.92–6.99 (m, 2H), 7.22–7.30 (m, 2H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 13.90, 13.93, 21.7, 23.0, 30.5, 31.8, 114.8 (d, $J_{C,}{}^{19}{}_{F}$ = 21.2 Hz), 127.8 (d, $J_{C,}{}^{19}{}_{F}$ = 7.7 Hz), 128.8 (t, $J_{C,}{}^{2}{}_{H}$ = 23.0 Hz), 139.0, 139.5 (d, $J_{C,}{}^{19}{}_{F}$ = 2.9 Hz), 161.7 (d, $J_{C,}{}^{19}{}_{F}$ = 245.9 Hz); **$^{2}$H NMR** (61 MHz, acetone) δ 5.63 (s). **HRMS** (ESI) calcd for $C_{14}H_{19}DF$ $[M+H]^+$ 208.1612, found 208.1616.



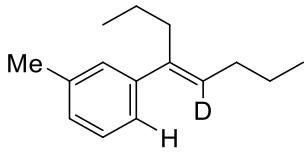

**6ga**

**Compound 6ga**. (Table 4.2, entry 7, binap (B), 83% yield, **5ga**:**6ga** = <1:99). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 0.86 (t, $J_{H,H}$ = 7.4 Hz, 3H), 0.94 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.33 (sext, $J_{H,H}$ = 7.6 Hz, 2H), 1.45 (sext, $J_{H,H}$ = 7.4 Hz, 2H), 2.14 (q, $J_{H,H}$ = 7.3 Hz, 2H), 2.43 (t, $J_{H,H}$ = 7.6 Hz, 2H), 5.58 (t, $J_{H,H}$ = 7.2 Hz, 1H), 6.92–6.99 (m, 2H), 7.23–7.29 (m, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 13.90, 13.93, 21.7, 23.0, 30.6, 31.8, 114.7 (d, $J_{C,}{}^{19}{}_{F}$ = 21.2 Hz), 114.8 (d, $J_{C–F}$ = 21.2 Hz), 127.5 (td, $J_{C,}{}^{2}{}_{H}$ = 24.3 Hz, $J_{C,}{}^{19}{}_{F}$ = 7.9 Hz), 127.8 (d, $J_{C,}{}^{19}{}_{F}$ = 7.7 Hz), 129.2, 139.1, 139.4 (d, $J_{C,}{}^{19}{}_{F}$ = 3.1 Hz), 161.7 (d, $J_{C,}{}^{19}{}_{F}$ = 245.7 Hz); **$^{2}$H NMR** (61 MHz, acetone) δ 7.38 (s). **HRMS** (ESI) calcd for $C_{14}H_{19}DF$ $[M+H]^+$ 208.1612, found 208.1618.



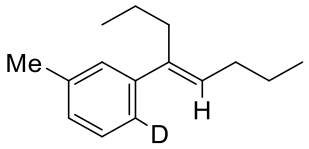

**6ha**

**Compound 6ha**. (Table 4.2, entry 8, binap (B), 93% yield, **5ha**:**6ha** = <1:99). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.88 (t, $J_{H,H}$ = 7.4 Hz, 3H), 0.97 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.35 (sext, $J_{H,H}$ = 7.6 Hz, 2H), 1.49 (sext, $J_{H,H}$ = 7.4 Hz, 2H), 2.20 (q, $J_{H,H}$ = 7.3 Hz, 2H), 2.49 (t, $J_{H,H}$ = 7.6 Hz, 2H), 5.72 (t, $J_{H,H}$ = 7.3 Hz, 1H), 7.43 (d, $J_{H,H}$ = 8.8 Hz, 1H), 7.52–7.56 (br m, 2H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 13.87, 13.92, 21.7, 22.9, 30.7, 31.5, 124.4 (q, $J_{C,}{}^{19}{}_F$ = 273.0 Hz), 124.9 (q, $J_{C,}{}^{19}{}_F$ = 3.8 Hz), 125.1 (q, $J_{C,}{}^{19}{}_F$ = 3.8 Hz), 126.0 (t, $J_{C,}{}^{2}{}_H$ = 25.1 Hz), 126.5, 128.4 (q, $J_{C,}{}^{19}{}_F$ = 32.4 Hz), 131.2, 139.1, 147.0; **$^2$H NMR** (61 MHz, acetone) δ 7.58 (s). **HRMS** (ESI) calcd for $C_{15}H_{19}DF_3$ $[M+H]^+$ 258.1580, found 258.1575.



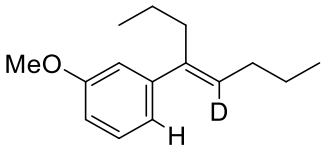

**5ia**

**Compound 5ia**. (Table 4.2, entry 9, cod (A), 72% yield, **5ia**:**6ia** = 86:14). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.88 (t, $J_{H,H}$ = 7.4 Hz, 3H), 0.96 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.36 (sext, $J_{H,H}$ = 7.6 Hz, 2H), 1.47 (sext, $J_{H,H}$ = 7.4 Hz, 2H), 2.17 (t, $J_{H,H}$ = 7.3 Hz, 2H), 2.35 (s, 3H), 2.46 (t, $J_{H,H}$ = 7.6 Hz, 2H), 7.03 (dd, $J_{H,H}$ = 7.1 Hz, 0.4 Hz, 1H), 7.15 (s, 1H), 7.10–7.22 (m, 2H); **$^{13}$C NMR** δ 13.9, 14.0, 21.5, 21.8, 23.1, 30.5, 31.7, 123.5, 127.1, 127.9, 128.0, 128.6 (t, $J_{C,}{}^{2}{}_H$ = 22.8 Hz), 137.5, 140.0, 143.5; **$^2$H NMR** (61 MHz, acetone) δ 5.63 (s). **HRMS** (ESI) calcd for $C_{15}H_{21}DNa$ $[M+Na]^+$ 226.1682, found 226.1684.



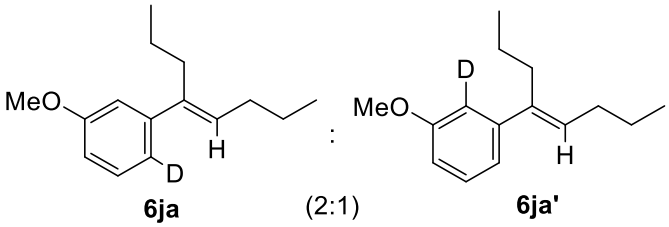

**6ia**

**Compound 6ia**. (Table 4.2, entry 9, binap (B), 87% yield, **5ia**:**6ia** = 1:99). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.88 (t, $J_{H,H}$ = 7.4 Hz, 3H), 0.96 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.36 (sext, $J_{H,H}$ = 7.6 Hz, 2H), 1.47 (sext, $J_{H,H}$ = 7.4 Hz, 2H), 2.17 (q, $J_{H,H}$ = 7.3 Hz, 2H), 2.35 (s, 3H), 2.46 (t, $J_{H,H}$ = 7.6 Hz, 2H), 5.64 (t, $J_{H,H}$ = 7.3 Hz, 1H), 7.03 (d, $J_{H,H}$ = 6.8 Hz, 1H), 7.15 (s, 1H), 7.10–7.22 (m, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 13.9, 14.0, 21.5, 21.8, 23.1, 30.6, 31.8, 123.2 (t, $J_{C,^2H}$ = 24.0 Hz), 127.1, 127.9, 128.0, 129.0, 137.5, 140.1, 143.5; **$^2$H NMR** (61 MHz, acetone) δ 7.13 (s). **HRMS** (ESI) calcd for $C_{15}H_{21}DNa$ $[M+Na]^+$ 226.1682, found 226.1662.

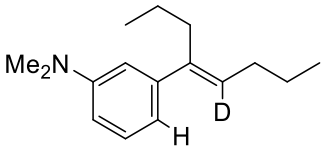



**5ja**

**Compound 5ja**. (Table 4.2, entry 10, cod (A), 82% yield, **5ja**:(**6ja**+**6ja'**) = 80:20). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.88 (t, $J_{H,H}$ = 7.4 Hz, 3H), 0.96 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.37 (sext, $J_{H,H}$ = 7.6 Hz, 2H), 1.47 (sext, $J_{H,H}$ = 7.4 Hz, 2H), 2.17 (t, $J_{H,H}$ = 7.3 Hz, 2H), 2.46 (t, $J_{H,H}$ = 7.6 Hz, 2H), 3.82 (s, 3H), 6.77 (dd, $J_{H,H}$ = 8.2 Hz, 2.5 Hz, 1H), 6.89 (t, $J_{H,H}$ = 2.4 Hz, 1H), 6.94 (dt, $J_{H,H}$ = 8.1 Hz, 1.0 Hz, 1H), 7.21 (t, $J_{H,H}$ = 7.9 Hz, 1H); **$^{13}$C NMR** δ 13.9, 14.0, 21.8, 23.0, 30.5, 31.7, 55.2, 111.4, 112.4, 119.0, 128.9 (t, $J_{C,^2H}$ = 22.9 Hz), 129.0, 139.8, 145.1, 159.5; **$^2$H NMR** (61 MHz, acetone) δ 5.68 (s). **HRMS** (ESI) calcd for $C_{15}H_{21}DONa$ $[M+Na]^+$ 242.1631, found 242.1642.

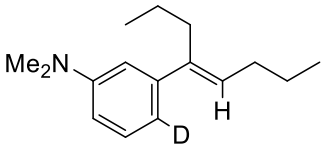



**Compound 6ja:6ja' (2:1)**. (Table 4.2, entry 10, binap (A), 93% yield, **5ja**:(**6ja+6ja'**) = 1:99). The ratio of **6ja:6ja'** was determined by $^{1}$H NMR of crude sample. **Compound 6ja**: **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 0.89 (t, $J_{H,H}$ = 7.4 Hz, 3H), 0.97 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.37 (sext, $J_{H,H}$ = 7.6 Hz, 2H), 1.47 (sext, $J_{H,H}$ = 7.4 Hz, 2H), 2.17 (q, $J_{H,H}$ = 7.3 Hz, 2H), 2.46 (t, $J_{H,H}$ = 7.6 Hz, 2H), 3.82 (s, 3H), 5.68 (t, $J_{H,H}$ = 7.3 Hz, 1H), 6.77 (dd, $J_{H,H}$ = 8.2 Hz, 2.2 Hz, 1H), 6.89 (d, $J_{H,H}$ = 2.5 Hz, 1H), 7.21 (d, $J_{H,H}$ = 8.2 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 13.9, 14.0, 21.8, 23.0, 30.6, 31.8, 55.2, 111.4, 112.4, 118.7 (t, $J_{C,^2H}$ = 24.1 Hz), 128.9, 129.3, 139.9, 145.1, 159.5; **$^{2}$H NMR** (61 MHz, acetone) δ 6.93 (s). **Compound 6ja'**: **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 0.89 (t, $J_{H,H}$ = 7.4 Hz, 3H), 0.97 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.37 (sext, $J_{H,H}$ = 7.6 Hz, 2H), 1.47 (sext, $J_{H,H}$ = 7.4 Hz, 2H), 2.17 (q, $J_{H,H}$ = 7.3 Hz, 2H), 2.46 (t, $J_{H,H}$ = 7.6 Hz, 2H), 3.82 (s, 3H), 5.68 (t, $J_{H,H}$ = 7.3 Hz, 1H), 6.77 (dd, $J_{H,H}$ = 8.2 Hz, 2.2 Hz, 1H), 6.94 (d, $J_{H,H}$ = 7.7 Hz, 1H), 7.22 (t, $J_{H,H}$ = 7.9 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 13.9, 14.0, 21.8, 23.0, 30.6, 31.8, 55.2, 111.5, 112.1 (t, $J_{C,^2H}$ = 23.8 Hz), 118.9, 129.0, 129.3, 139.9, 145.1, 159.4; **$^{2}$H NMR** (61 MHz, acetone) δ 6.90 (s). **HRMS** (ESI) calcd for $C_{15}H_{21}DONa$ $[M+Na]^+$ 242.1631, found 242.1633.



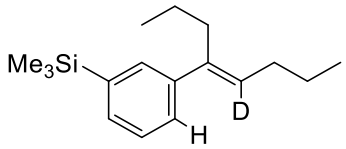

**5ka**

**Compound 5ka**. (Table 4.2, entry 11, cod (A), 72% yield, **5ka**:**6ka** = 95:5). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.89 (t, $J_{H,H}$ = 7.4 Hz, 3H), 0.96 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.38 (sext, $J_{H,H}$ = 7.6 Hz, 2H), 1.47 (sext, $J_{H,H}$ = 7.4 Hz, 2H), 2.16 (t, $J_{H,H}$ = 7.4 Hz, 2H), 2.46 (t, $J_{H,H}$ = 7.6 Hz, 2H), 2.96 (s, 6H), 6.66 (dd, $J_{H,H}$ = 6.9 Hz, 2.4 Hz, 1H), 6.73 (d, $J_{H,H}$ = 6.7 Hz, 1H), 6.75 (s, 1H), 7.18 (t, $J_{H,H}$ = 8.1 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 13.96, 14.04, 21.9, 23.1, 30.5, 32.0, 40.9, 111.2 (br s), 115.6 (br s), 128.3 (t, $J_{C,^2H}$ = 23.5 Hz), 128.7, 140.7, 144.7, 150.5 (br s); **$^2$H NMR** (61 MHz, acetone) δ 5.63 (s). **HRMS** (ESI) calcd for $C_{16}H_{25}DN$ $[M+H]^+$ 233.2128, found 233.2110.



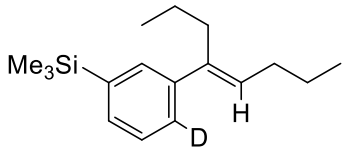

**6ka**

**Compound 6ka**. (Table 4.2, entry 11, binap (B), 95% yield, **5ka**:**6ka** = 1:99). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.90 (t, $J_{H,H}$ = 7.4 Hz, 3H), 0.97 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.39 (sext, $J_{H,H}$ = 7.6 Hz, 2H), 1.48 (sext, $J_{H,H}$ = 7.4 Hz, 2H), 2.18 (q, $J_{H,H}$ = 7.3 Hz, 2H), 2.47 (t, $J_{H,H}$ = 7.6 Hz, 2H), 2.97 (s, 6H), 5.66 (t, $J_{H,H}$ = 7.3 Hz, 1H), 6.68 (dd, $J_{H,H}$ = 6.8 Hz, 2.4 Hz, 1H), 6.76 (d, $J_{H,H}$ = 2.0 Hz, 1H), 7.19 (d, $J_{H,H}$ = 8.2 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 13.95, 14.03, 21.9, 23.1, 30.6, 32.0, 41.0, 111.3, 111.4, 115.5 (br t, $J_{C,^2H}$ = 23.0 Hz), 128.6, 128.7, 140.8, 144.6, 150.3; **$^2$H NMR** (61 MHz, acetone) δ 6.69 (s). **HRMS** (ESI) calcd for $C_{16}H_{25}DN$ $[M+H]^+$ 233.2128, found 233.2150.



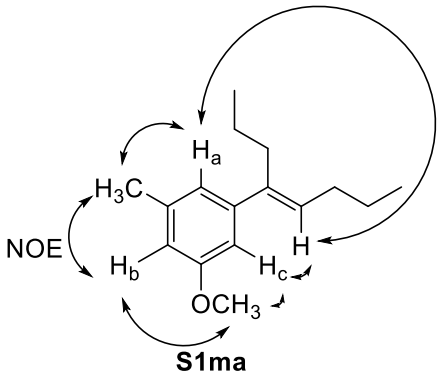

**5la**

**Compound 5la**. (Table 4.2, entry 12, cod (A), 79% yield, **5la**:**6la** = 83:17). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.28 (s, 9H), 0.89 (t, $J_{H,H}$ = 7.4 Hz, 3H), 0.97 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.38 (sext, $J_{H,H}$ = 7.6 Hz, 2H), 1.48 (sext, $J_{H,H}$ = 7.4 Hz, 2H), 2.18 (t, $J_{H,H}$ = 7.3 Hz, 2H), 2.48 (t, $J_{H,H}$ = 7.6 Hz, 2H), 7.29 (td, $J_{H,H}$ = 6.8 Hz, 2.9 Hz, 1H), 7.32 (dt, $J_{H,H}$ = 7.8 Hz, 0.9 Hz, 1H), 7.38 (dt, $J_{H,H}$ = 8.0 Hz, 1.4 Hz, 1H), 7.47 (s, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ –1.1, 13.96, 14.00, 21.8, 23.1, 30.6, 31.8, 126.9, 127.5, 128.8 (t, $J_{C,^2H}$ = 22.9 Hz), 131.1, 131.4, 140.0, 140.2, 142.7; **$^2$H NMR** (61 MHz, acetone) δ 5.66 (s). **HRMS** (ESI) calcd for $C_{17}H_{28}DSi$ $[M+H]^+$ 262.2101, found 262.2107.



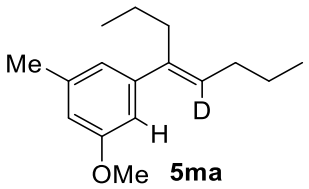

**6la**

**Compound 6la**. (Table 4.2, entry 12, binap (B), 87% yield, **5la**:**6la** = 1:99). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.30 (s, 9H), 0.92 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.00 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.41 (sext, $J_{H,H}$ = 7.6 Hz, 2H), 1.51 (sext, $J_{H,H}$ = 7.4 Hz, 2H), 2.21 (q, $J_{H,H}$ = 7.3 Hz, 2H), 2.51 (t, $J_{H,H}$ = 7.7 Hz, 2H), 5.68 (t, $J_{H,H}$ = 7.3 Hz, 1H), 7.31 (d, $J_{H,H}$ = 7.2 Hz, 1H), 7.41 (dd, $J_{H,H}$ = 7.3 Hz, 1.1 Hz, 1H), 7.50 (s, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ –1.1, 13.96, 14.00, 21.9, 23.1, 30.7, 31.9, 126.6 (t, $J_{C,^2H}$ = 23.7 Hz), 127.4, 129.1, 131.1, 131.4, 140.0, 140.3, 142.7; **$^2$H NMR** (61 MHz, acetone) δ 7.34 (s). **HRMS** (ESI) calcd for $C_{17}H_{28}DSi$ $[M+H]^+$ 262.2101, found 262.2104.




**S1ma**

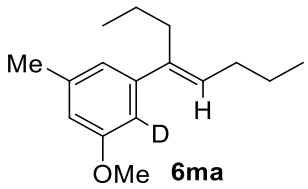
**Compound S1ma**. (Table 4.2, entry 13, quenched with $H_2O$). The E geometry and all aromatic protons were assigned by NOESY NMR study. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.88 (t, $J_{H,H}$ = 7.3 Hz, 3H), 0.96 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.37 (sext, $J_{H,H}$ = 7.6 Hz, 2H), 1.47 (sext, $J_{H,H}$ = 7.4 Hz, 2H), 2.16 (q, $J_{H,H}$ = 7.3 Hz, 2H), 2.33 (s, 3H), 2.48 (t, $J_{H,H}$ = 7.6 Hz, 2H), 3.80 (s, 3H), 5.65 (t, $J_{H,H}$ = 7.2 Hz, 1H), 6.60 (s, *$H_b$,* 1H), 6.69 (s, *$H_c$,* 1H), 6.76 (s, *$H_a$,* 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 13.9, 14.0, 21.7, 21.9, 23.0, 30.6, 31.8, 55.1, 109.5, 112.4, 119.9, 129.1, 138.9, 140.1, 145.0, 159.5. **HRMS** (ESI) calcd for $C_{16}H_{25}O$ $[M+H]^+$ 233.1905, found 233.1913.




**5ma**

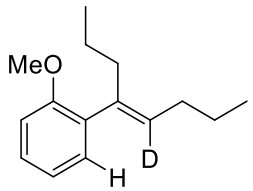
**Compound 5ma**. (Table 4.2, entry 13, cod (A), 79% yield, **5ma**:**6ma** = >99:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.89 (t, $J_{H,H}$ = 7.3 Hz, 3H), 0.97 (t, $J_{H,H}$ = 7.3 Hz, 3H), 1.38 (sext, $J_{H,H}$ = 7.6 Hz, 2H), 1.47 (sext, $J_{H,H}$ = 7.4 Hz, 2H), 2.16 (t, $J_{H,H}$ = 7.4 Hz, 2H), 2.33 (s, 3H), 2.44 (t, $J_{H,H}$ = 7.6 Hz, 2H), 3.80 (s, 3H), 6.60 (s, 1H), 6.69 (s, 1H), 6.76 (s, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 13.9, 14.0, 21.7, 21.8, 23.0, 30.5, 31.8, 55.1, 109.5, 112.4, 119.8, 128.7 (t, $J_{C,^2H}$ = 22.8 Hz), 138.9, 140.0,

145.0, 159.5; **$^{2}$H NMR** (61 MHz, acetone) δ 5.65 (s). **HRMS** (ESI) calcd for $C_{16}H_{24}DO$ $[M+H]^+$ 234.1968, found 234.1965.



**6ma**

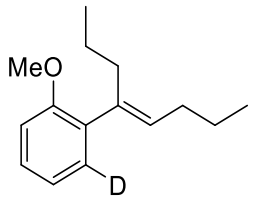
**Compound 6ma**. (Table 4.2, entry 13, binap (B), 97% yield, **5ma**:**6ma** = 1:99). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 0.89 (t, $J_{H,H}$ = 7.3 Hz, 3H), 0.97 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.37 (sext, $J_{H,H}$ = 7.6 Hz, 2H), 1.47 (sext, $J_{H,H}$ = 7.4 Hz, 2H), 2.17 (q, $J_{H,H}$ = 7.3 Hz, 2H), 2.33 (s, 3H), 2.44 (t, $J_{H,H}$ = 7.6 Hz, 2H), 3.80 (s, 3H), 5.66 (t, $J_{H,H}$ = 7.3 Hz, 1H), 6.60 (s, 1H), 6.76 (s, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 13.9, 14.0, 21.7, 21.9, 23.0, 30.6, 31.8, 55.1, 109.2 (t, $J_{C,^2H}$ = 23.9 Hz), 112.4, 119.8, 129.1, 138.8, 140.0, 144.9, 159.4; **$^{2}$H NMR** (61 MHz, acetone) δ 6.68 (s). **HRMS** (ESI) calcd for $C_{16}H_{24}DO$ $[M+H]^+$ 234.1968, found 234.1965.



**5na**

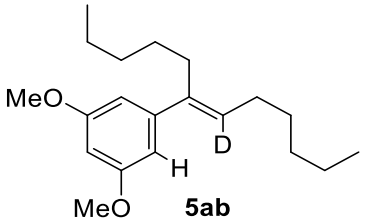
**Compound 5na**. (Table 4.2, entry 14, cod (A), 64% yield, **5na**:**6na** = 94:6). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 0.84 (t, $J_{H,H}$ = 7.3 Hz, 3H), 0.97 (t, $J_{H,H}$ = 7.3 Hz, 3H), 1.25 (sext, $J_{H,H}$ = 7.6 Hz, 2H), 1.46 (sext, $J_{H,H}$ = 7.4 Hz, 2H), 2.17 (t, $J_{H,H}$ = 7.3 Hz, 2H), 2.44 (t, $J_{H,H}$ = 7.7 Hz, 2H), 3.81 (s, 3H), 6.85 (d, $J_{H,H}$ = 8.2 Hz, 1H), 6.89 (td, $J_{H,H}$ = 7.4 Hz, 0.7 Hz, 1H), 7.09 (dd, $J_{H,H}$ = 7.4 Hz, 1.7 Hz, 1H), 7.21 (td, $J_{H,H}$ = 7.8 Hz, 1.1 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 13.9, 14.0, 21.6, 23.0, 30.1, 32.3, 55.4, 110.6, 120.3, 127.6, 129.8 (t, $J_{C,^2H}$ = 23.2 Hz), 130.7, 134.0, 139.7, 156.7; $^{2}$H

NMR (61 MHz, acetone) δ 5.31 (s). HRMS (ESI) calcd for $C_{15}H_{22}DO$ $[M+H]^+$ 220.1812, found 220.1804.




**6na**

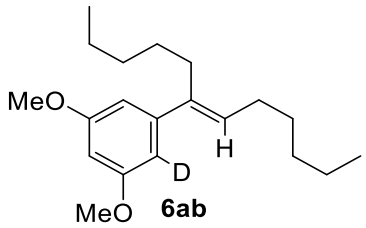
**Compound 6na**. (Table 4.2, entry 14, binap (A), 88% yield, **5na**:**6na** = 13:87). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.84 (t, $J_{H,H}$ = 7.3 Hz, 3H), 0.97 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.25 (sext, $J_{H,H}$ = 7.6 Hz, 2H), 1.46 (sext, $J_{H,H}$ = 7.4 Hz, 2H), 2.17 (q, $J_{H,H}$ = 7.3 Hz, 2H), 2.44 (t, $J_{H,H}$ = 7.7 Hz, 2H), 3.81 (s, 3H), 5.39 (t, $J_{H,H}$ = 7.2 Hz, 1H), 6.85 (d, $J_{H,H}$ = 8.2 Hz, 1H), 6.89 (d, $J_{H,H}$ = 7.4 Hz, 1H), 7.21 (t, $J_{H,H}$ = 7.8 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 13.9, 14.0, 21.6, 23.0, 30.2, 32.3, 55.4, 110.6, 120.2, 127.6, 130.1, 130.4 (t, $J_{C,^2H}$ = 24.1 Hz), 133.9, 139.7, 156.7; **$^2$H NMR** (61 MHz, acetone) δ 7.05 (s). **HRMS** (ESI) calcd for $C_{15}H_{22}DO$ $[M+H]^+$ 220.1812, found 220.1811.




**5ab**

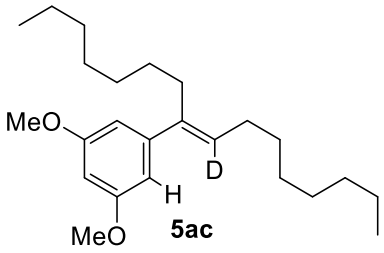
**Compound 5ab**. (Table 4.3, entry 1, cod (A), 78% yield, **5ab**:**6ab** = 90:10). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.86 (t, $J_{H,H}$ = 6.8 Hz, 3H), 0.90 (t, $J_{H,H}$ = 6.9 Hz, 3H), 1.20–1.40 (m, 10H), 1.44 (quint, $J_{H,H}$ = 7.0 Hz, 2H), 2.16 (t, $J_{H,H}$ = 7.3 Hz, 2H), 2.43 (t, $J_{H,H}$ = 7.5 Hz, 2H), 3.80 (s, 6H), 6.35 (t, $J_{H,H}$ = 2.2 Hz, 1H), 6.49 (d, $J_{H,H}$ = 2.2 Hz, 2H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 14.1, 22.5, 22.6, 28.37, 28.43, 29.5, 29.8, 31.6, 31.9, 55.3, 98.3, 104.8, 128.9 (t, $J_{C,^2H}$ = 22.6 Hz), 140.0, 145.9, 160.5;

**$^2$H NMR** (61 MHz, acetone) δ 5.67 (s). **HRMS** (ESI) calcd for $C_{20}H_{32}DO_2$ $[M+H]^+$ 306.2543, found 306.2543.



**6ab**

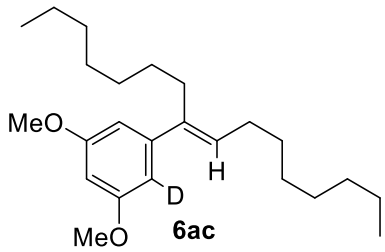
**Compound 6ab**. (Table 4.3, entry 1, binap (A), 91% yield, **5ab**:**6ab** = 1:99). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.86 (t, $J_{H,H}$ = 6.8 Hz, 3H), 0.91 (t, $J_{H,H}$ = 6.9 Hz, 3H), 1.20–1.40 (m, 10H), 1.44 (quint, $J_{H,H}$ = 7.0 Hz, 2H), 2.17 (q, $J_{H,H}$ = 7.3 Hz, 2H), 2.43 (t, $J_{H,H}$ = 7.5 Hz, 2H), 3.80 (s, 6H), 5.66 (t, $J_{H,H}$ = 7.3 Hz, 1H), 6.35 (d, $J_{H,H}$ = 2.2 Hz, 1H), 6.50 (d, $J_{H,H}$ = 2.2 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 14.0, 22.5, 22.6, 28.4, 28.5, 29.5, 29.8, 31.6, 31.8, 55.3, 98.3, 104.5 (t, $J_{C,^2H}$ = 24.0 Hz), 104.8, 129.2, 140.1, 145.8, 160.47, 160.50; **$^2$H NMR** (61 MHz, acetone) δ 6.51 (s). **HRMS** (ESI) calcd for $C_{20}H_{32}DO_2$ $[M+H]^+$ 306.2543, found 306.2545.



**5ac**

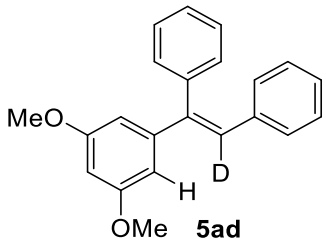
**Compound 5ac**. (Table 4.3, entry 2, cod (A), 74% yield, **5ac**:**6ac** = 93:7). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.87 (t, $J_{H,H}$ = 6.9 Hz, 3H), 0.89 (t, $J_{H,H}$ = 6.7 Hz, 3H), 1.10–1.50 (m, 20H), 2.16 (t, $J_{H,H}$ = 7.3 Hz, 2H), 2.43 (t, $J_{H,H}$ = 7.4 Hz, 2H), 3.80 (s, 6H), 6.35 (t, $J_{H,H}$ = 2.3 Hz, 1H), 6.49 (d, $J_{H,H}$ = 2.2 Hz, 2H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 14.07, 14.09, 22.6, 22.7, 28.4, 28.7, 29.1, 29.2, 29.4, 29.6, 29.8, 31.8, 31.9, 55.3, 98.2, 104.8, 128.9 (t, $J_{C,^2H}$ = 22.6 Hz), 140.0, 145.9, 160.5; **$^2$H NMR** (61

MHz, acetone) δ 5.67 (s). **HRMS** (ESI) calcd for $C_{24}H_{40}DO_2$ $[M+H]^+$ 362.3169, found 362.3163.



**6ac**

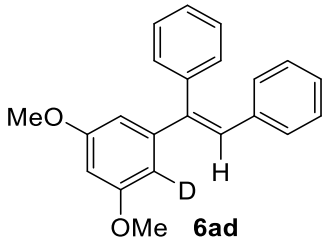
**Compound 6ac**. (Table 4.3, entry 2, binap (A), 97% yield, **5ac**:**6ac** = 4:96). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.88 (t, $J_{H,H}$ = 6.9 Hz, 3H), 0.91 (t, $J_{H,H}$ = 6.7 Hz, 3H), 1.20–1.50 (m, 20H), 2.18 (q, $J_{H,H}$ = 7.3 Hz, 2H), 2.45 (t, $J_{H,H}$ = 7.4 Hz, 2H), 3.81 (s, 6H), 5.67 (t, $J_{H,H}$ = 7.3 Hz, 1H), 6.36 (d, $J_{H,H}$ = 2.2 Hz, 1H), 6.51 (d, $J_{H,H}$ = 2.2 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 14.0, 14.1, 22.6, 22.7, 28.5, 28.7, 29.1, 29.2, 29.4, 29.6, 29.9, 31.8, 31.9, 55.2, 98.3, 104.5 (t, $J_{C,^2H}$ = 23.8 Hz), 104.8, 129.2, 140.1, 145.8, 160.47, 160.49; **$^2$H NMR** (61 MHz, acetone) δ 6.50 (s). **HRMS** (ESI) calcd for $C_{24}H_{40}DO_2$ $[M+H]^+$ 362.3172, found 362.3163.



**5ad**

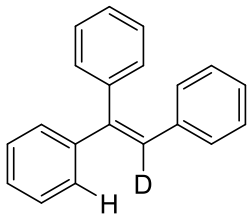
**Compound 5ad**. (Table 4.3, entry 3, cod (A), 86% yield, **5ad**:**6ad** = 97:3). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 3.77 (s, 6H), 6.43 (t, $J_{H,H}$ = 2.3 Hz, 1H), 6.50 (d, $J_{H,H}$ = 2.3 Hz, 2H), 7.03 (dd, $J_{H,H}$ = 7.8 Hz, 2.2 Hz, 2H), 7.05–7.16 (m, 3H), 7.21 (dd, $J_{H,H}$ = 7.6 Hz, 2.3 Hz, 2H), 7.28–7.36 (m, 3H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 55.3, 99.5, 106.1, 126.8, 127.4, 127.9, 128.0 (t, $J_{C,^2H}$ = 22.8 Hz), 128.6, 129.5, 130.3,

137.1, 140.1, 142.4, 145.6, 160.5; **$^{2}$H NMR** (61 MHz, acetone) δ 7.07 (s). **HRMS** (ESI) calcd for $C_{22}H_{20}DO_2$ $[M+H]^+$ 318.1604, found 318.1623.



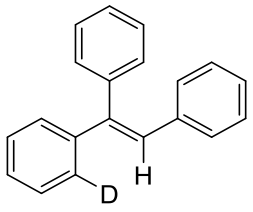

**6ad**

**Compound 6ad**. (Table 4.3, entry 3, binap (B), 98% yield, **5ad**:**6ad** = 13:87). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 3.77 (s, 6H), 6.43 (d, $J_{H,H}$ = 2.2 Hz, 1H), 6.50 (d, $J_{H,H}$ = 2.3 Hz, 1H), 6.99 (s, 1H), 7.03 (dd, $J_{H,H}$ = 7.8 Hz, 2.2 Hz, 2H), 7.05–7.16 (m, 3H), 7.21 (dd, $J_{H,H}$ = 7.6 Hz, 2.3 Hz, 2H), 7.28–7.36 (m, 3H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 55.3, 99.6, 105.8 (t, $J_{C,^2H}$ = 24.4 Hz), 106.1, 126.8, 127.4, 127.9, 128.3, 128.6, 129.6, 130.3, 137.2, 140.1, 142.5, 145.6, 160.49, 160.52; **$^{2}$H NMR** (61 MHz, acetone) δ 6.49 (s). **HRMS** (ESI) calcd for $C_{22}H_{20}DO_2$ $[M+H]^+$ 318.1604, found 318.1606.




**5bd**

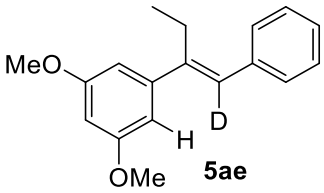
**Compound 5bd [42353-76-4]**. (Table 4.3, entry 4, modified cod (A), 61% yield, **5bd**:**6bd** = 92:8). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.06 (br d, $J_{H,H}$ = 7.8 Hz, 2H), 7.10–7.16 (m 3H), 7.20–7.25 (m, 2H), 7.26–7.38 (m, 8H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 126.7, 127.4, 127.5, 127.6, 127.92 (t, $J_{C,^2H}$ = 27.0 Hz), 127.93, 128.2, 128.6, 129.5, 130.3, 137.3, 140.3, 142.5, 143.4; **$^{2}$H NMR** (61 MHz, acetone) δ 7.04 (s). The spectral data are in agreement with reported literature values.[2b]




**6bd**

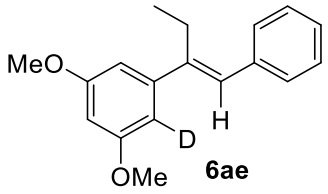
**Compound 6bd**. (Table 4.3, entry 4, binap (B), 97% yield, **5bd**:**6bd** = 10:90). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 6.98 (s, 1H), 7.06 (dd, $J_{H,H}$ = 7.8 Hz, 2.0 Hz, 2H), 7.10–7.16 (m, 3H), 7.20–7.25 (m, 2H), 7.26–7.38 (m, 7H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 126.7, 127.3 (t, $J_{C,^2H}$ = 24.3 Hz), 127.4, 127.5, 127.6, 127.9, 128.07, 128.13, 128.2, 128.6, 129.5, 130.4, 137.4, 140.3, 142.5, 143.3; **$^{2}$H NMR** (61 MHz, acetone) δ 7.33 (s). **HRMS** (ESI) calcd for $C_{20}H_{16}D$ $[M+H]^+$ 258.1393, found 258.1397.

The ratio of **5ae**:**6ae** was determined by $^{1}$H NMR because $^{2}$H NMR peaks are overlapping.




**5ae**

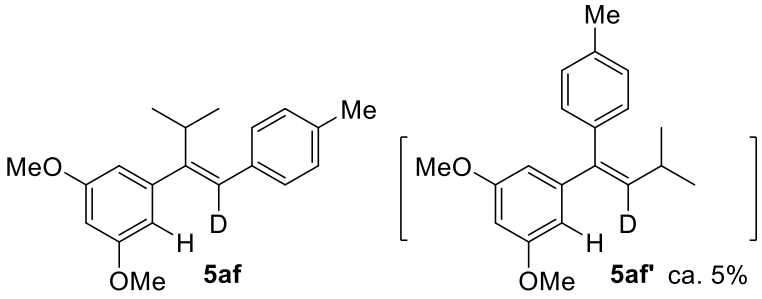
**Compound 5ae**. (Table 4.3, entry 5, cod (A), 72% yield, **5ae**:**6ae** = 94:6). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 1.08 (t, $J_{H,H}$ = 7.5 Hz, 3H), 2.71 (q, $J_{H,H}$ = 7.5 Hz, 2H), 3.83 (s, 6H), 6.43 (t, $J_{H,H}$ = 2.0 Hz, 1H), 6.63 (d, $J_{H,H}$ = 2.3 Hz, 2H), 7.25 (t, $J_{H,H}$ = 7.0 Hz, 1H), 7.34 (d, $J_{H,H}$ = 7.4 Hz, 2H), 7.38 (t, $J_{H,H}$ = 7.1 Hz, 2H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 13.5, 23.4, 55.3, 99.1, 105.1, 126.6, 127.3 (t, $J_{C,^2H}$ = 23.4 Hz), 128.2, 128.7, 138.0, 144.4, 145.1, 160.7; **$^{2}$H NMR** (61 MHz, acetone) δ 6.74 (s). HRMS (ESI) calcd for $C_{18}H_{20}DO_2$ $[M+H]^+$ 270.1604, found 270.1582.




**6ae**

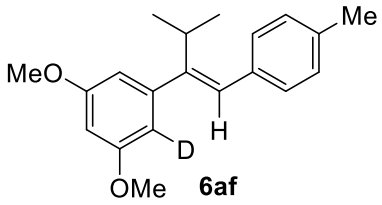
**Compound 6ae**. (Table 4.3, entry 5, binap (B), 93% yield, **5ae**:**6ae** = 10:90). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 1.09 (t, $J_{H,H}$ = 7.5 Hz, 3H), 2.71 (q, $J_{H,H}$ = 7.5 Hz, 2H), 3.84 (s, 6H), 6.44 (d, $J_{H,H}$ = 2.0 Hz, 1H), 6.64 (d, $J_{H,H}$ = 2.1 Hz, 1H), 6.72 (s, 1H), 7.26 (t, $J_{H,H}$ = 7.0 Hz, 1H), 7.34 (d, $J_{H,H}$ = 7.4 Hz, 2H), 7.38 (t, $J_{H,H}$ = 7.1 Hz, 2H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 13.5, 23.4, 55.3, 99.1, 104.7 (t, $J_{C,}{}^{2}{}_{H}$ = 24.4 Hz), 105.0, 126.6, 127.6, 128.2, 128.7, 138.1, 144.5, 145.0, 160.66, 160.69; **$^{2}$H NMR** (61 MHz, acetone) δ 6.67 (s). **HRMS (ESI)** calcd for $C_{18}H_{20}DO_2$ $[M+H]^+$ 270.1604, found 270.1592.

The ratio of **5af**:**6af** was determined by $^{1}$H NMR because $^{2}$H NMR peaks are overlapping.




**Compound 5af and 5af'**. (Table 4.3, entry 6, cod (A), 89% yield, **5af**:**6af** = 95:5). The ratio of **5af:5af'** was determined by $^{1}$H NMR. **Compound 5af**: **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 1.08 (d, $J_{H,H}$ = 6.9 Hz, 6H), 2.37 (s, 3H), 3.28 (sept, $J_{H,H}$ = 6.9 Hz, 1H), 3.82 (s, 6H), 6.42 (t, $J_{H,H}$ = 2.2 Hz, 1H), 6.44 (d, $J_{H,H}$ = 2.2 Hz, 2H), 7.17 (d, $J_{H,H}$ = 8.0 Hz, 2H), 7.22 (d, $J_{H,H}$ = 8.2 Hz, 2H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 21.2, 22.0, 29.2, 55.3, 98.4, 107.4, 127.6 (t, $J_{C,}{}^{2}{}_{H}$ = 23.2 Hz), 128.7, 128.9, 134.8, 136.1, 144.7, 149.0, 160.0; **$^{2}$H NMR** (61 MHz, acetone) δ 6.31 (s). **Compound 5af'**:

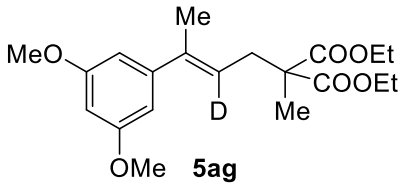
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 1.00 (d, $J_{H,H}$ = 6.6 Hz, 6H), 2.17 (s, 3H), 3.28 (sept, $J_{H,H}$ = 6.9 Hz, 1H), 3.74 (s, 6H), 6.33 (t, $J_{H,H}$ = 2.2 Hz, 1H), 6.38 (d, $J_{H,H}$ = 2.3 Hz, 1H), 7.06 (d, $J_{H,H}$ = 8.0 Hz, 2H), 7.22 (d, $J_{H,H}$ = 8.2 Hz, 2H). **HRMS** (ESI) calcd for $C_{20}H_{24}DO_2$ $[M+H]^+$ 298.1917, found 298.1942.



**6af**

**Compound 6af**. (Table 4.3, entry 6, binap (B), 93% yield, **5af**:**6af** = 10:90). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 1.09 (d, $J_{H,H}$ = 6.9 Hz, 6H), 2.37 (s, 3H), 3.28 (sept, $J_{H,H}$ = 6.9 Hz, 1H), 3.83 (s, 6H), 6.35 (s, 1H), 6.42 (d, $J_{H,H}$ = 2.2 Hz, 1H), 6.45 (d, $J_{H,H}$ = 2.3 Hz, 1H), 7.18 (d, $J_{H,H}$ = 8.1 Hz, 2H), 7.22 (d, $J_{H,H}$ = 8.1 Hz, 2H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 21.1, 22.0, 29.2, 55.3, 98.4, 107.1 (t, $J_{C,^2H}$ = 24.6 Hz), 107.4, 127.9, 128.7, 128.9, 134.9, 136.1, 144.6, 149.0, 159.9, 160.0; **$^2$H NMR** (61 MHz, acetone) δ 6.43 (s). **HRMS** (ESI) calcd for $C_{20}H_{24}DO_2$ $[M+H]^+$ 298.1917, found 298.1888.

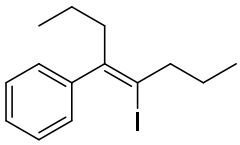
The ratio of **5ag**:**6ag** was determined by $^1$H NMR because of some impurities in $^2$H NMR.



**5ag**

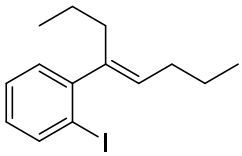
**Compound 5ag**. (Table 4.3, entry 7, cod (A), 87% yield, **5ag**:**6ag** = 97:3). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 1.25 (t, $J_{H,H}$ = 7.1 Hz, 6H), 1.44 (s, 3H), 2.01 (s, 3H), 2.77 (s, 2H), 3.79 (s, 6H), 4.19 (q, $J_{H,H}$ = 7.1 Hz, 4H), 6.36 (t, $J_{H,H}$ = 2.2 Hz, 1H), 6.48 (d, $J_{H,H}$ = 2.3 Hz, 2H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 14.1, 16.3, 19.9, 34.6,

53.9, 55.3, 61.3, 98.7, 104.4, 121.9 (t, $J_{C,^2H}$ = 23.1 Hz), 138.3, 146.1, 160.5, 172.0; **$^2$H NMR** (61 MHz, acetone) δ 5.67 (s). **HRMS** (ESI) calcd for $C_{20}H_{28}DO_6$ $[M+H]^+$ 366.2027, found 366.2026.



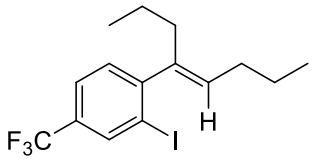
**7ba**

**Compound 7ba**. (Table 4.3, entry 8, 63% yield). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 0.87 (t, $J_{H,H}$ = 7.3 Hz, 3H), 1.00 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.33 (sext, $J_{H,H}$ = 7.7 Hz, 2H), 1.66 (sext, $J_{H,H}$ = 7.4 Hz, 2H), 2.45 (t, $J_{H,H}$ = 7.7 Hz, 2H), 2.66 (t, $J_{H,H}$ = 7.4 Hz, 2H), 7.07 (d, $J_{H,H}$ = 8.4 Hz, 2H), 7.27 (t, $J_{H,H}$ = 8.4 Hz, 1H), 7.34 (t, $J_{H,H}$ = 7.6 Hz, 2H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 13.0, 13.7, 21.4, 23.0, 36.7, 42.9, 106.3, 126.8, 128.0, 128.2, 147.3, 147.6. **HRMS** (ESI) calcd for $C_{14}H_{20}I$ $[M+H]^+$ 315.0610, found 315.0609.



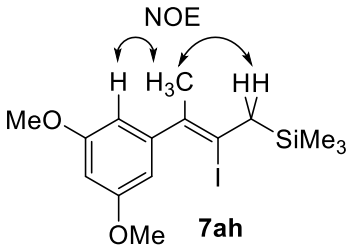
**8ba**

**Compound 8ba**. (Table 4.3, entry 9, 77% yield). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 0.98 (t, $J_{H,H}$ = 7.3 Hz, 3H), 1.07 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.39 (sext, $J_{H,H}$ = 7.8 Hz, 2H), 1.57 (sext, $J_{H,H}$ = 7.3 Hz, 2H), 2.25 (q, $J_{H,H}$ = 7.3 Hz, 2H), 2.46 (t, $J_{H,H}$ = 7.8 Hz, 2H), 5.37 (t, $J_{H,H}$ = 7.3 Hz, 1H), 6.95 (td, $J_{H,H}$ = 7.7 Hz, 1.7 Hz, 1H), 7.17 (dd, $J_{H,H}$ = 7.5 Hz, 1.7 Hz, 1H), 7.31 (td, $J_{H,H}$ = 7.5 Hz, 1.2 Hz, 1H), 7.89 (dd, $J_{H,H}$ = 7.9 Hz, 1.1 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 14.0, 14.2, 21.2, 22.7, 30.0, 33.5, 99.4, 127.5, 127.8, 129.6, 131.3, 139.0, 143.3, 149.1. **HRMS** (ESI) calcd for $C_{14}H_{20}I$ $[M+H]^+$ 315.0610, found 315.0613.



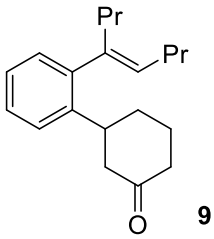

**8ha**

**Compound 8ha**. (Table 4.3, entry 10, 87% yield). **$^1$H NMR** (400 MHz, $CDCl_3$) 0.90 (t, $J_{H,H}$ = 7.3 Hz, 3H), 1.00 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.30 (sext, $J_{H,H}$ = 7.8 Hz, 2H), 1.50 (sext, $J_{H,H}$ = 7.3 Hz, 2H), 2.18 (q, $J_{H,H}$ = 7.3 Hz, 2H), 2.38 (t, $J_{H,H}$ = 7.8 Hz, 2H), 5.32 (t, $J_{H,H}$ = 7.3 Hz, 1H), 7.20 (d, $J_{H,H}$ = 8.0 Hz, 1H), 7.52 (dd, $J_{H,H}$ = 7.9 Hz, 1.0 Hz, 1H), 8.07 (d, $J_{H,H}$ = 0.8 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 14.0, 14.2, 21.2, 22.6, 30.0, 33.3, 98.9, 123.0 (q, $J_{C,}{}^{19}{}_F$ = 270.8 Hz), 124.4 (q, $J_{C,}{}^{19}{}_F$ = 3.6 Hz), 129.7, 129.9 (q, $J_{C,}{}^{19}{}_F$ = 32.6 Hz), 132.3, 135.9 (q, $J_{C,}{}^{19}{}_F$ = 3.8 Hz), 142.5, 152.9. **HRMS** (ESI) calcd for $C_{15}H_{19}F_3I$ $[M+H]^+$ 383.0484, found 383.0484.




**7ah**

**Compound 7ah**. (Table 4.3, entry 11, 73% yield). The regiochemistry and *Z* geometry was determined by NOESY NMR study. **$^1$H NMR** (400 MHz, $CDCl_3$) 0.19 (s, 9H), 2.00 (s, 3H), 2.58 (s, 2H), 3.80 (s, 6H), 6.26 (d, $J_{H,H}$ = 2.3 Hz, 2H), 6.37 (d, $J_{H,H}$ = 2.2 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ –0.6, 20.9, 34.5, 55.3, 97.2, 98.5, 106.2, 138.4, 151.0, 160.5. **HRMS (ESI)** calcd for C15H24IO2Si $[M+H]^+$ 391.0590, found 391.0578.




**9**

**Compound 9**. (Table 4.3, entry 12, 67% yield). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 0.87 (t, $J_{H,H}$ = 7.3 Hz, 3H), 0.94 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.27 (sext d, $J_{H,H}$ = 7.8 Hz, 2.2 Hz, 2H), 1.43 (sext, $J_{H,H}$ = 7.3 Hz, 2H), 1.69 (qt, $J_{H,H}$ = 12.8 Hz, 4.5 Hz, 1H), 1.82 (qd, $J_{H,H}$ = 12.3 Hz, 3.2 Hz, 1H), 1.91 (br d, $J_{H,H}$ = 13.2 Hz, 1H), 2.14 (q, $J_{H,H}$ = 7.4 Hz, 2H), 2.10–2.20 (m, 1H), 2.22–2.31 (m, 2H), 2.38 (td, $J_{H,H}$ = 14.5 Hz, 6.6 Hz, 1H), 2.4–2.5 (m, 1H), 2.45 (br d, $J_{H,H}$ = 14.1 Hz, 1H), 2.53 (t, $J_{H,H}$ = 13.8 Hz, 1H), 3.23 (tt, $J_{H,H}$ = 12.2 Hz, 3.9 Hz, 1H), 5.21 (t, $J_{H,H}$ = 7.3 Hz, 1H), 7.05 (dd, $J_{H,H}$ = 7.5 Hz, 1.0 Hz, 1H), 7.15 (td, $J_{H,H}$ =7.3 Hz, 1.6 Hz, 1H), 7.25 (td, $J_{H,H}$ = 7.8 Hz, 1.2 Hz, 1H), 7.29 (dd, $J_{H,H}$ = 7.7 Hz, 1.4 Hz, 1H);**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 13.9, 14.2, 21.3, 23.0, 25.9, 30.1, 33.4, 34.9, 40.6, 41.2, 49.3, 125.6, 125.8, 126.8, 129.5, 130.4, 139.6, 141.7, 143.8, 211.1. **HRMS** (ESI) calcd for $C_{20}H_{29}O$ $[M+H]^+$ 285.2218, found 285.2221.

## 4.5 Reference

(1) For reviews on catalytic carbometalation of alkynes, see: Chapter 1, Reference 34.

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(3) Ni catalyst: (a) Stüdemann, T.; Knochel, P. *Angew. Chem., Int. Ed.* **1997**, *36,* 93. (b) Stüdemann, T.; Ibrahim-Ouali, M.; Knochel, P. *Tetrahedron* **1998**, *54*, 1299. Co catalyst: (c) Murakami, K.; Yorimitsu, H.; Oshima, K. *Org. Lett.* **2009**, *11*, 2373. (d) Corpet, M.; Gosmini, C. *Chem. Commun.* **2012**, *48,* 11561. (e) Murakami, K.; Yorimitsu, H.; Oshima, K. *Chem.–Eur. J.* **2010**, *16,* 7688. (f) Nishikawa, T.; Yorimitsu, H.; Oshima, K. *Synlett* **2004**, 41573. (g) Yasui, H.; Nishikawa, T.; Yorimitsu, H.; Oshima, K. *Bull. Chem. Soc. Jpn.* **2006**, *79,* 1271.

(4) (a) Tan, B.-H.; Dong, J.; Yoshikai, N. *Angew. Chem., Int. Ed.* **2012**, *51*, 9610. See also: (b) Tan, B.-H.; Yoshikai, N. *Org. Lett*. **2014**, *16,* 3392. (c) Wu, J.; Yoshikai, N. *Angew. Chem., Int. Ed.* **2016**, *55,* 336. (d) Yan, J.; Yoshikai, N. *Org. Chem. Front.* **2017**, *4*, 1972.

(5) For reviews dealing with 1,4-metal shift, see: Chapter 1, Reference 40

(6) For 1,4-Rh shift from alkenyl to aryl, see: Chapter 1, Refernece 43.

(7) For examples of 1,4-Rh shift from alkyl to aryl, see: Chapter 1, Reference 41.

(8) Reviews on organozinc reagents: (a) Knochel, P.; Singer, R. D. *Chem. Rev*. **1993**, *93*, 2117. (b) Negishi, E.-I.; Gagneur, S. In *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E.-I., Ed.; Wiley: New York, 2002; Vol. 1, p 597. (c) Phapale, V. B.; Cárdenas, D. J. *Chem. Soc. Rev*. **2009**, *38*, 1598.

(9) The structure and reactivity of arylzinc reagents are dependent on what they are generated from, ArMgX or ArLi. For example: Jin, L.; Liu, C.; Liu, J.; Hu, F.; Lan, Y.; Batsanov, A. S.; Howard, J. A. K.; Marder, T. B.; Lei, A. *J. Am. Chem. Soc*. **2009**, *131*, 16656.

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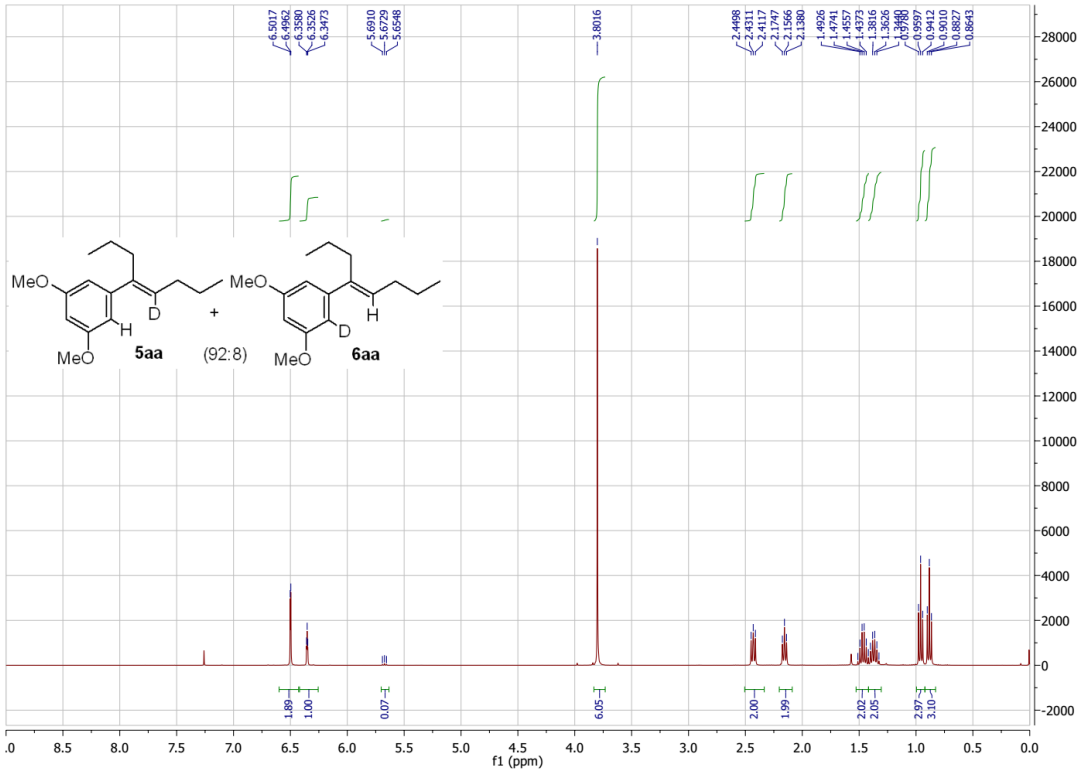
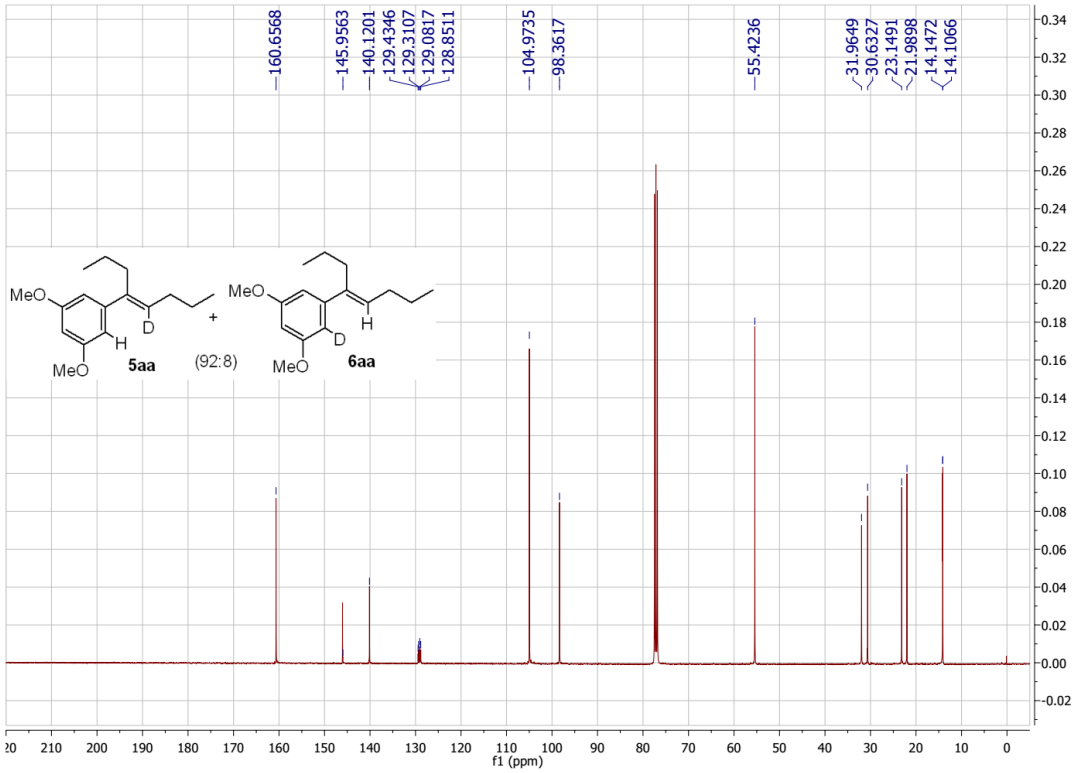
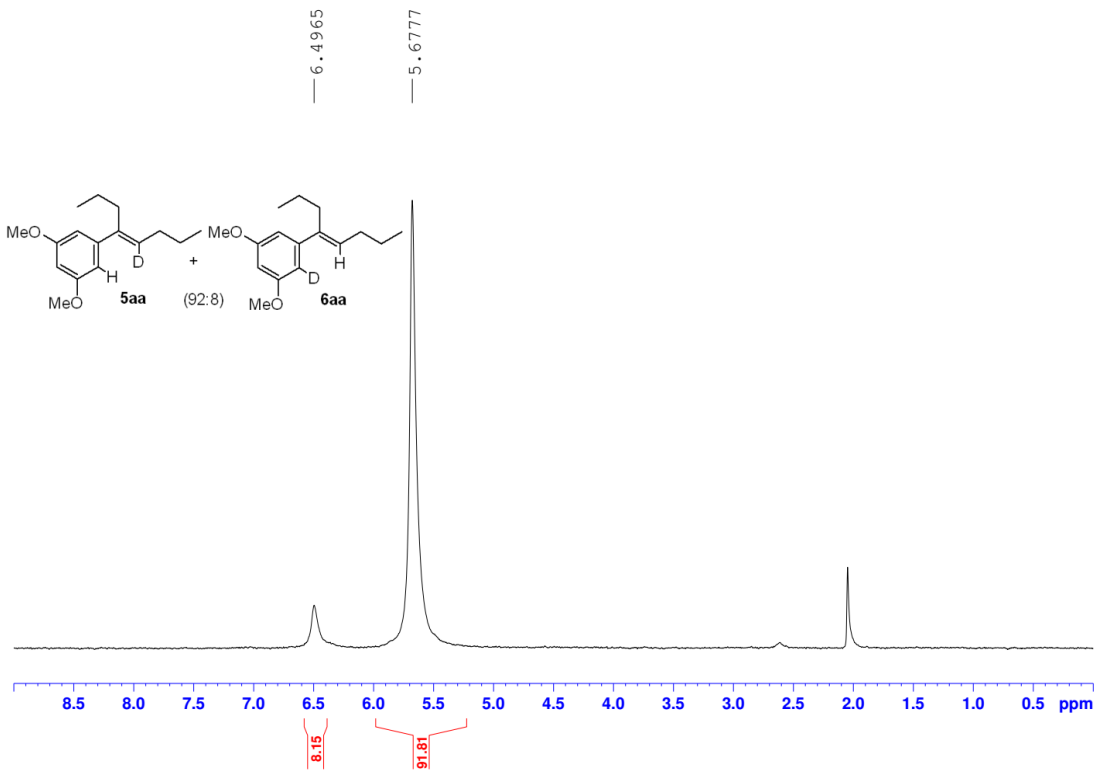
## 4.6 NMR spectra

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7.5
7.0
6.5
6.0
5.5
5.0
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3.0
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ppm
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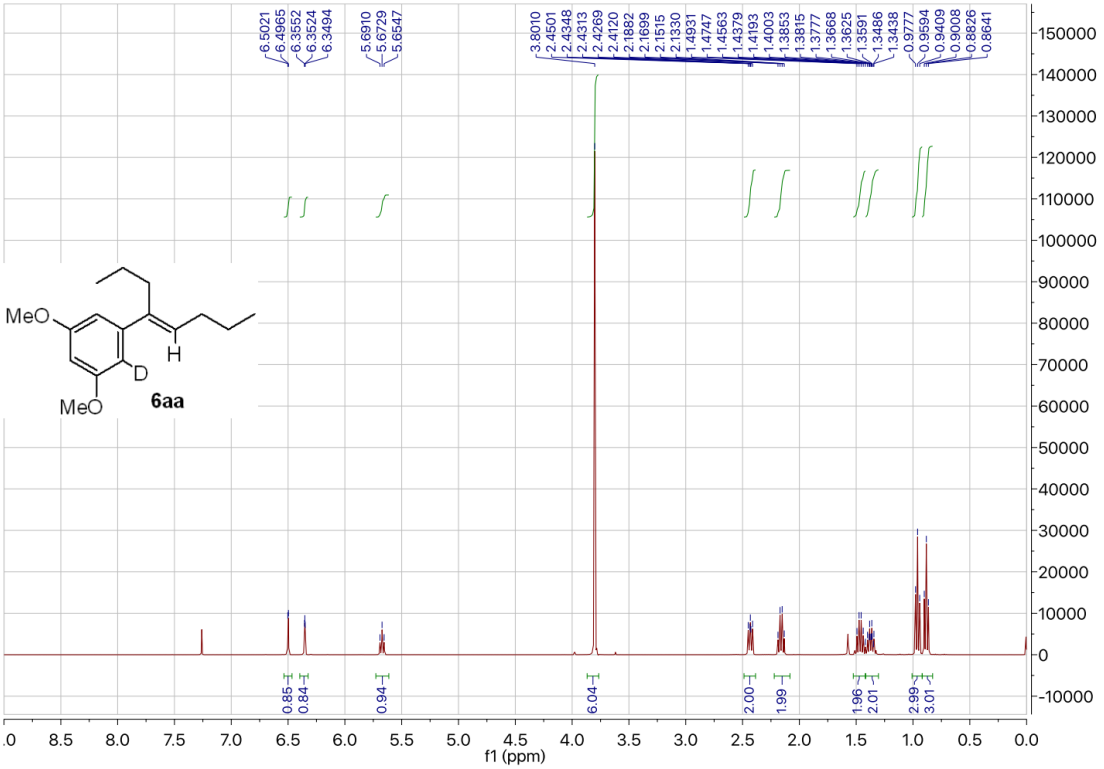
91.81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2.4120
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0.9008
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D
MeO
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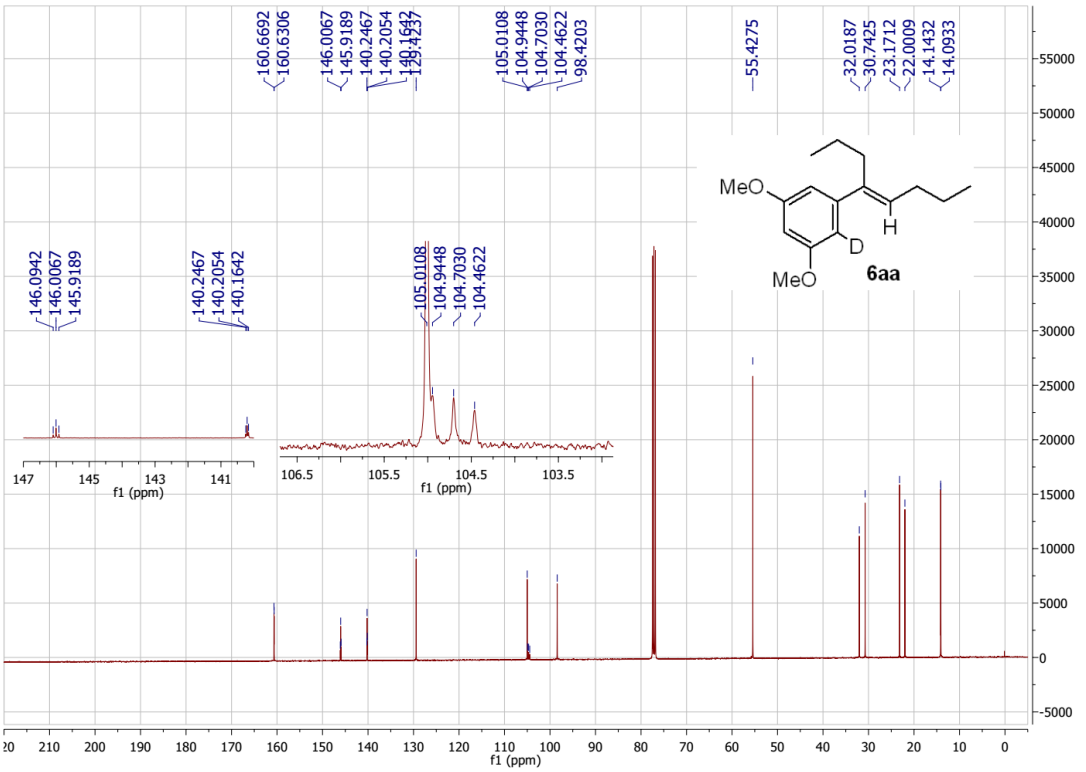
2.01
2.99
3.01
f1 (ppm)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14.0933
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H
D
MeO
6aa
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146.0067
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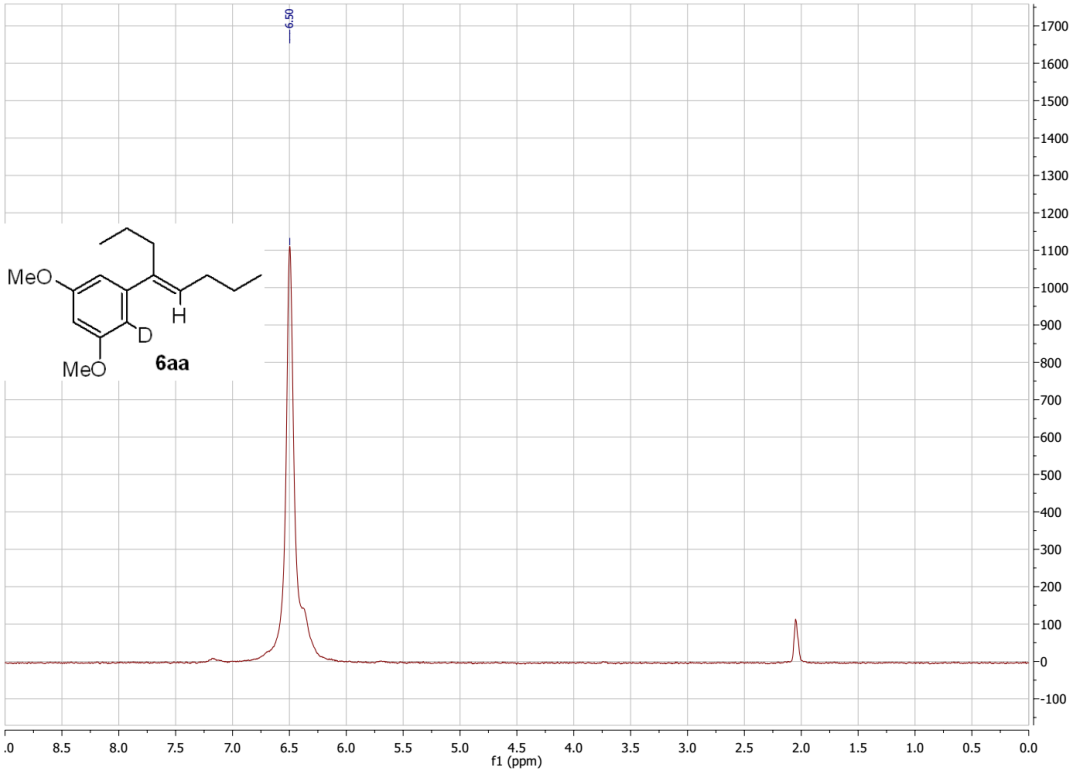
f1 (ppm)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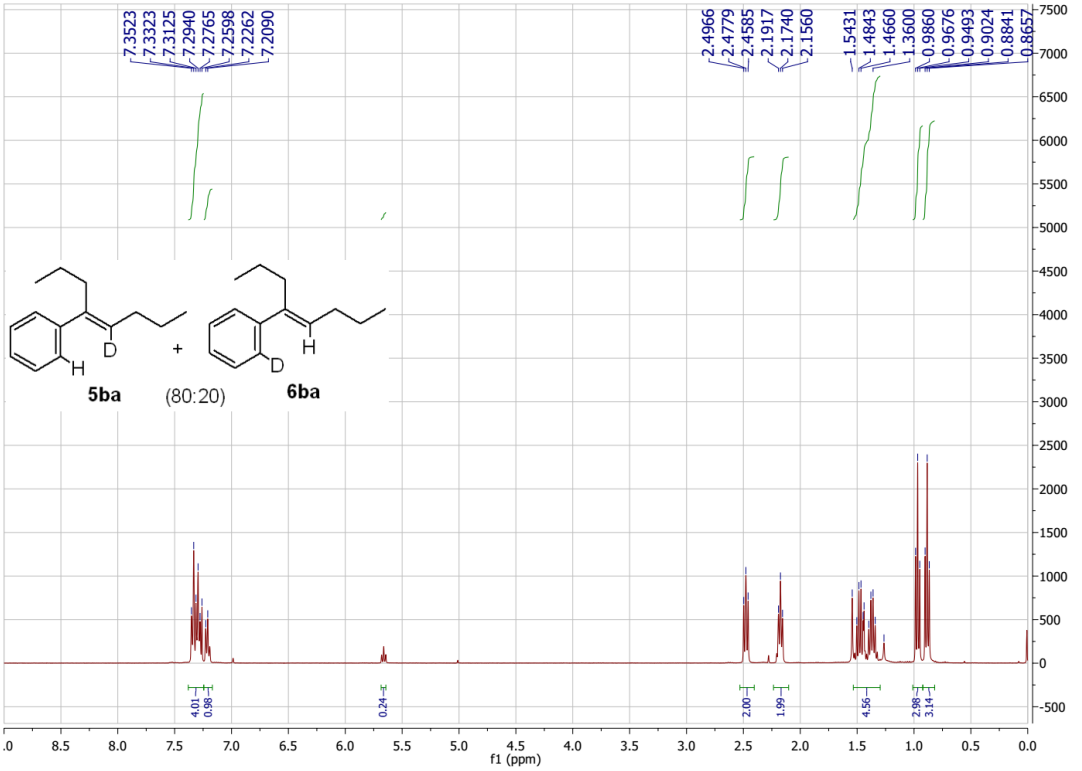
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2.1917
2.1740
2.1560
1.5431
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1.4660
1.3600
0.9860
0.9676
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+
H
D
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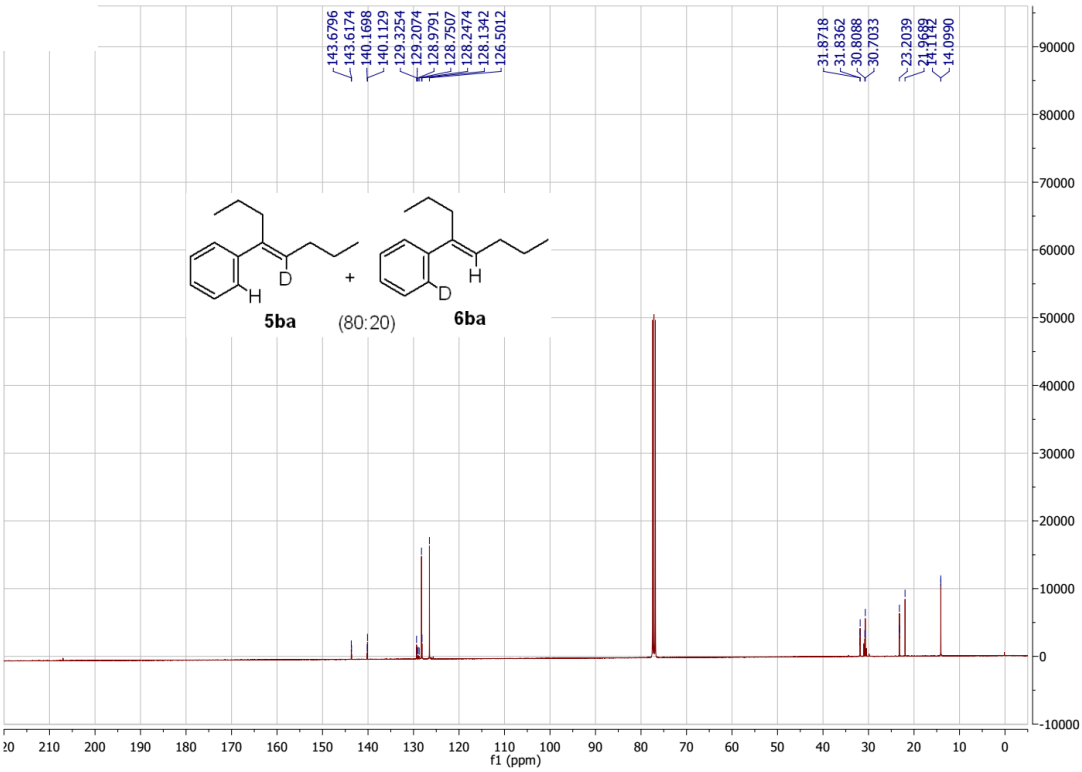
f1 (ppm)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31.8718
31.8362
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+
H
D
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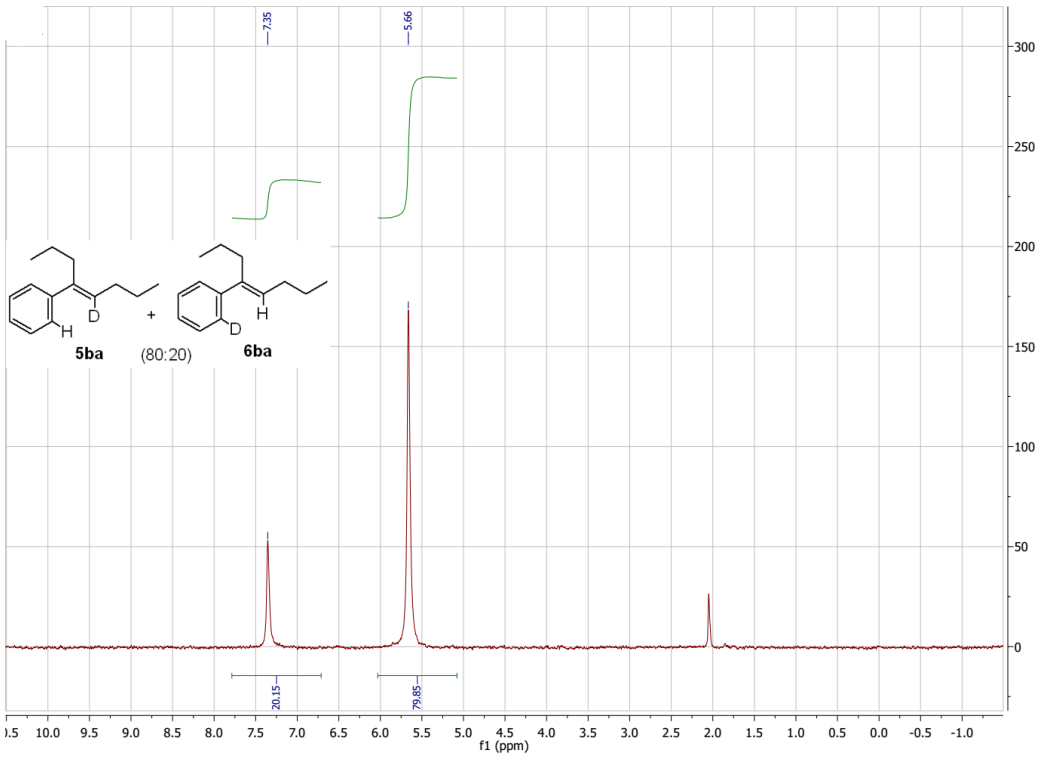
f1 (ppm)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4.0
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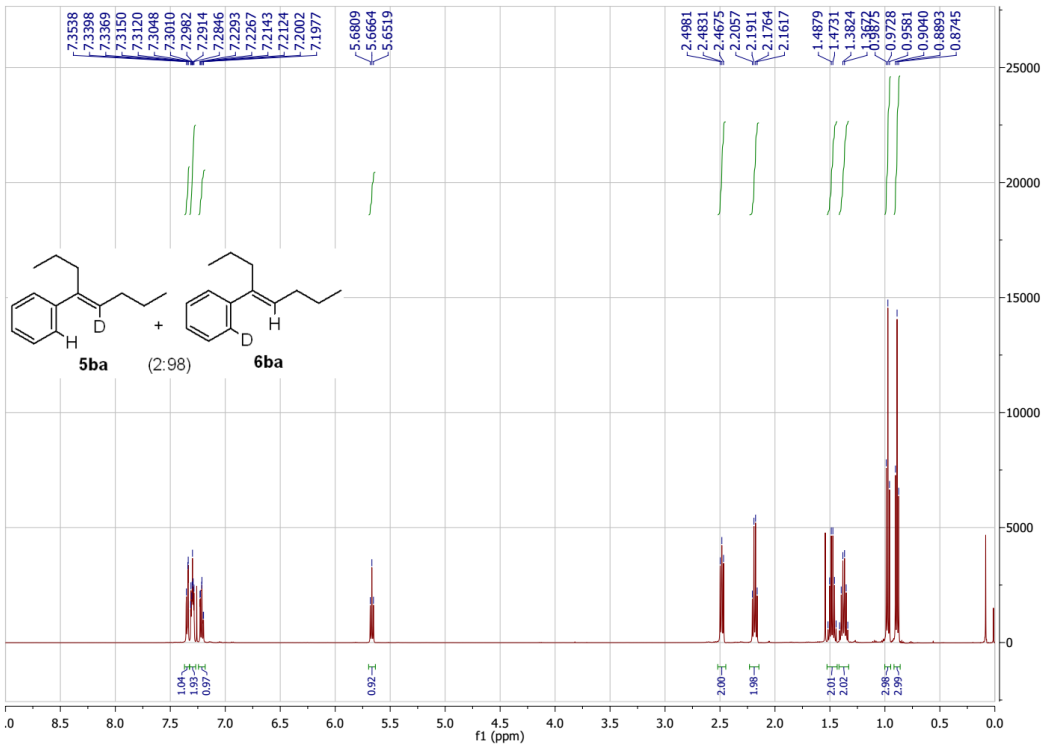
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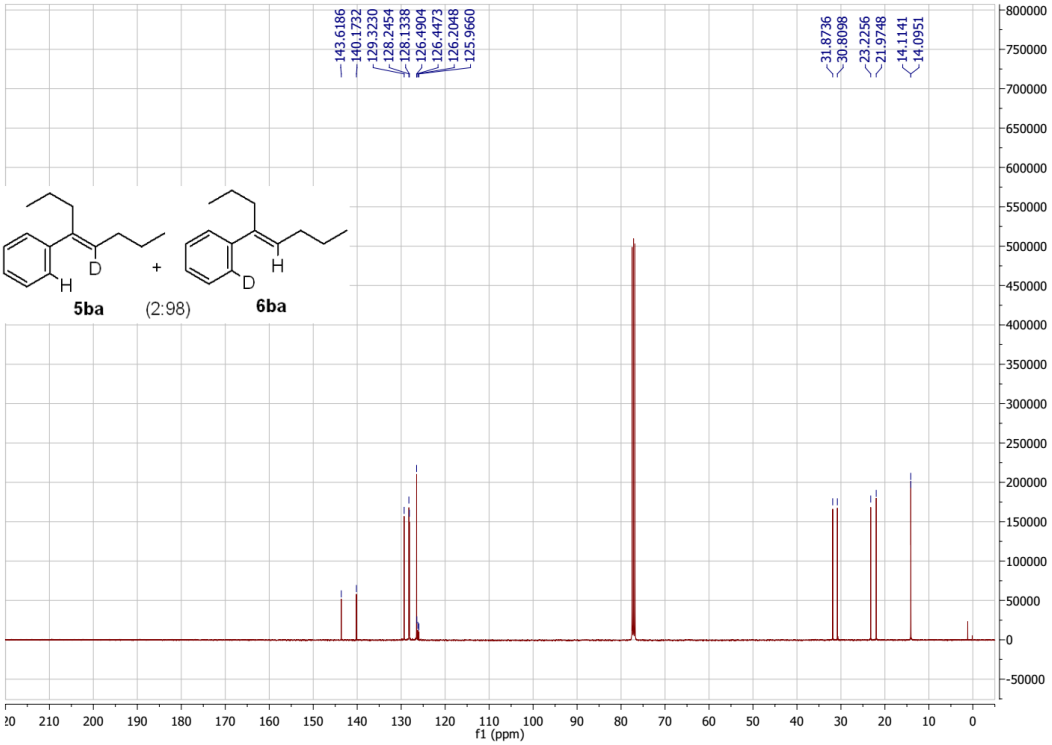
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H
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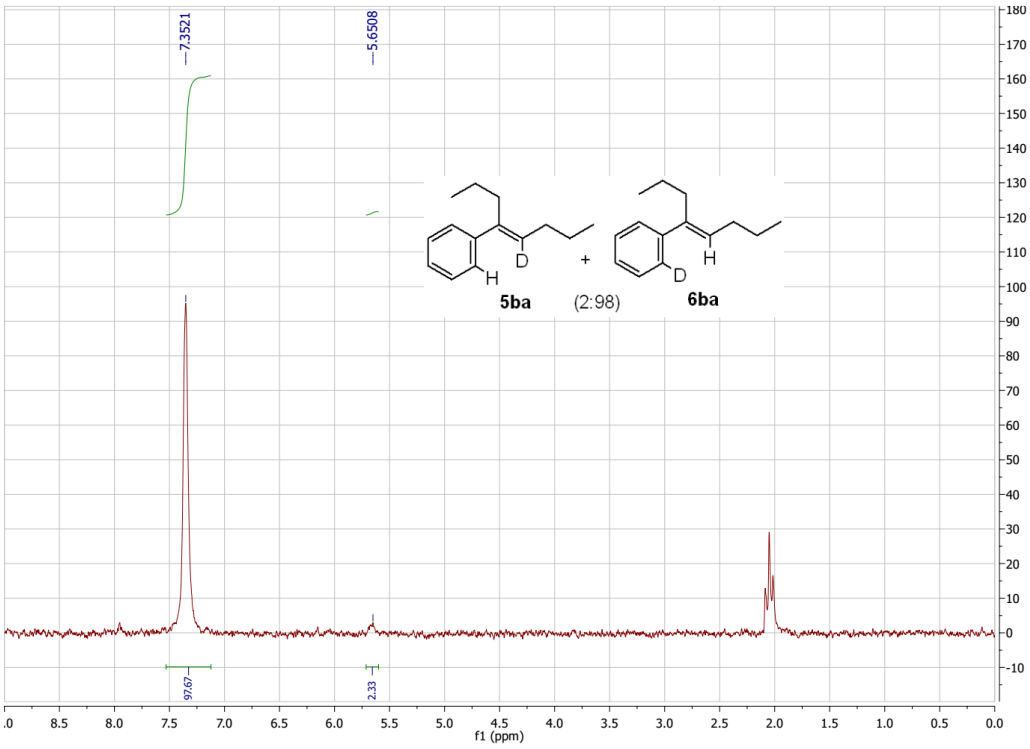
f1 (ppm)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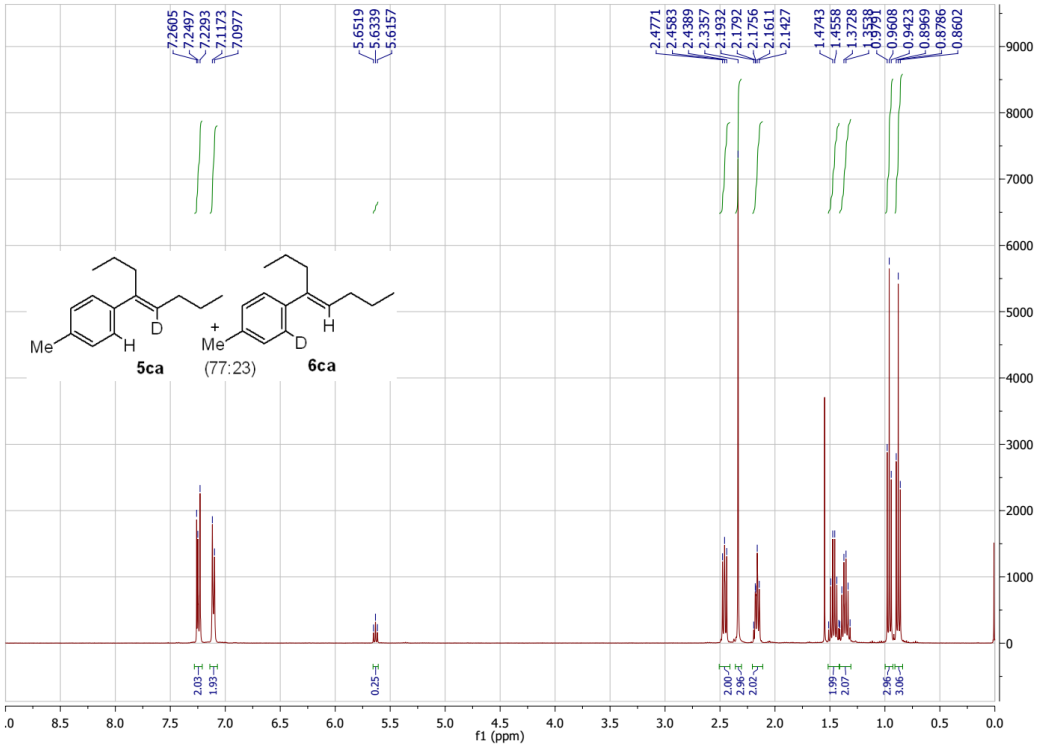
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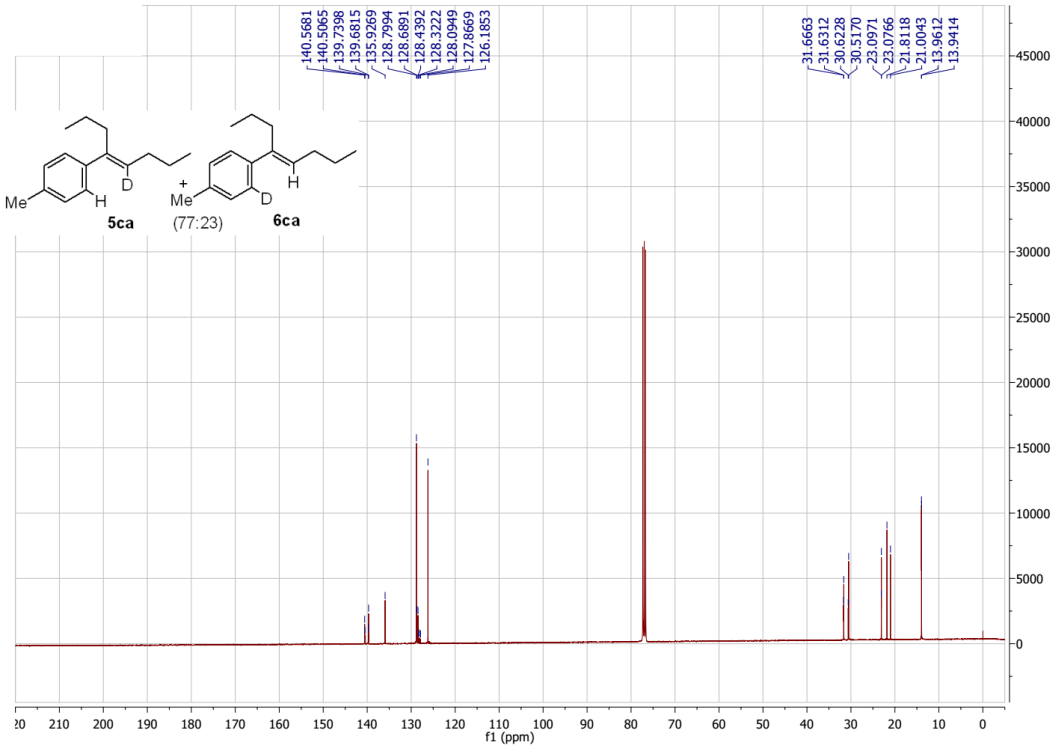
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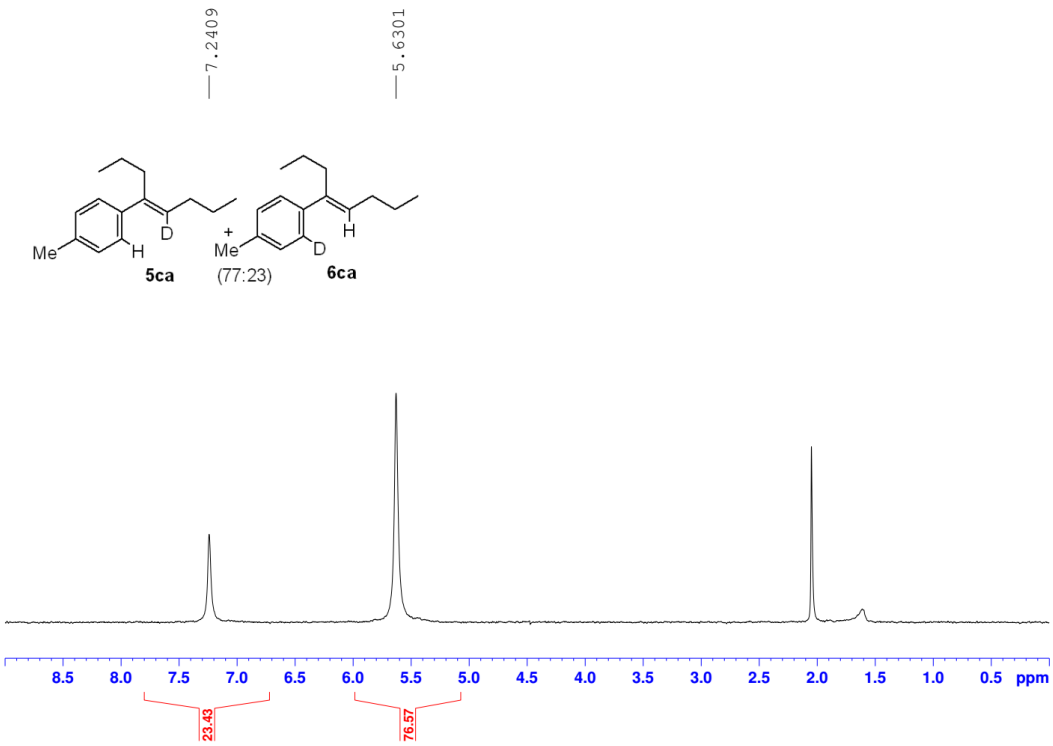
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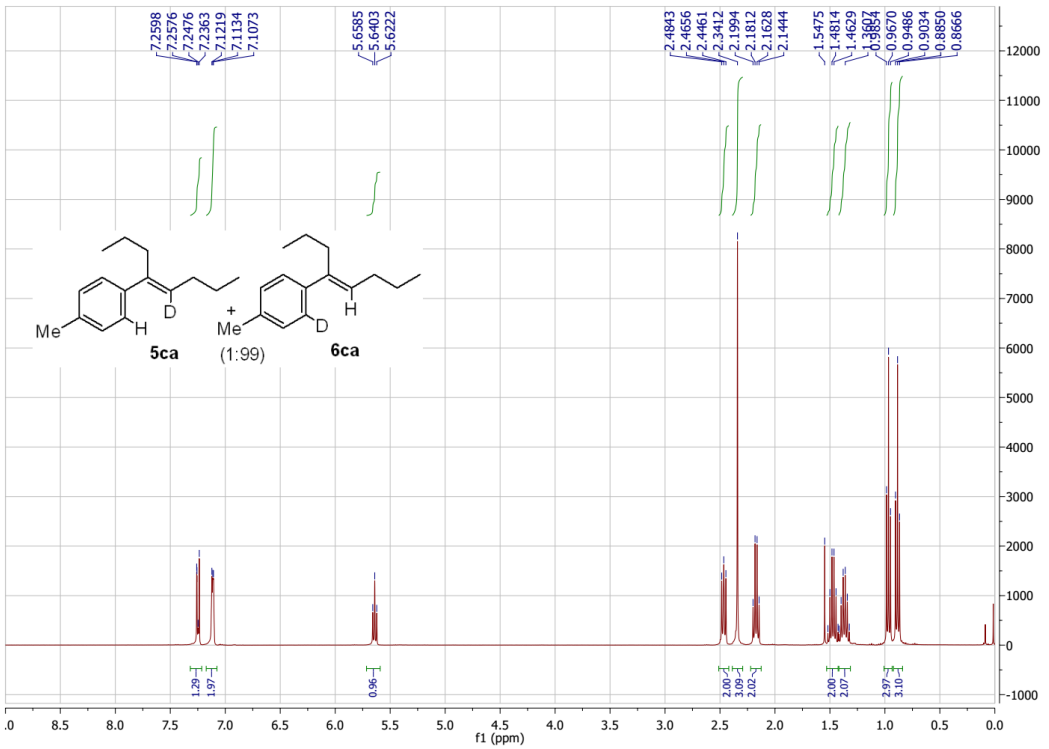
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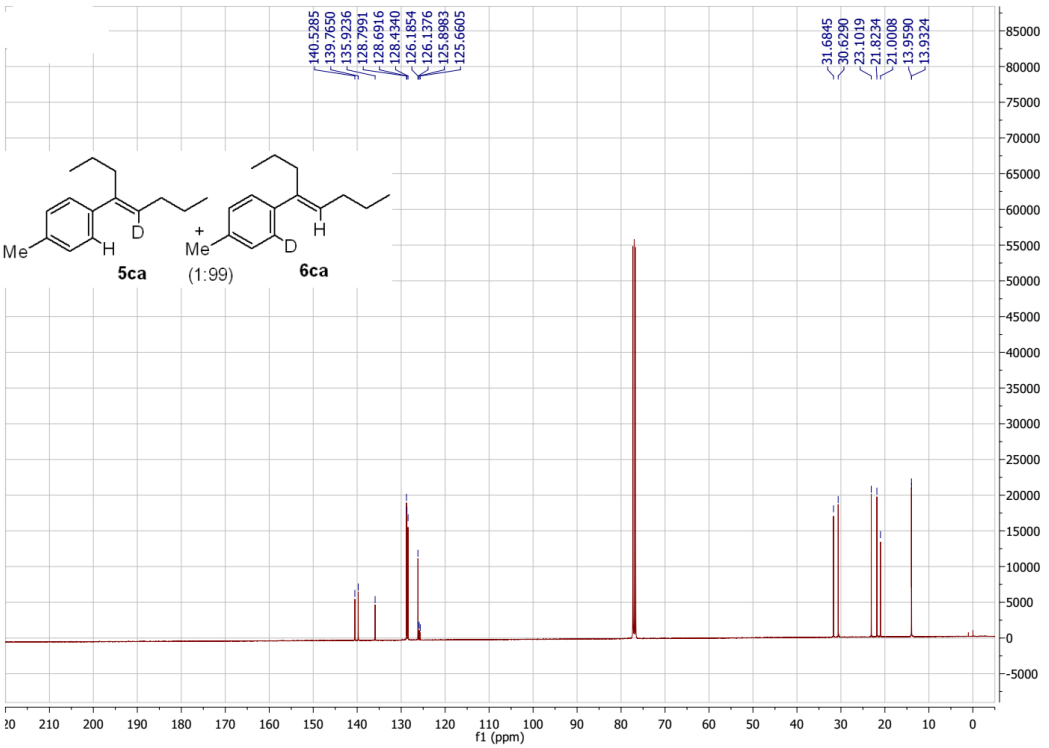
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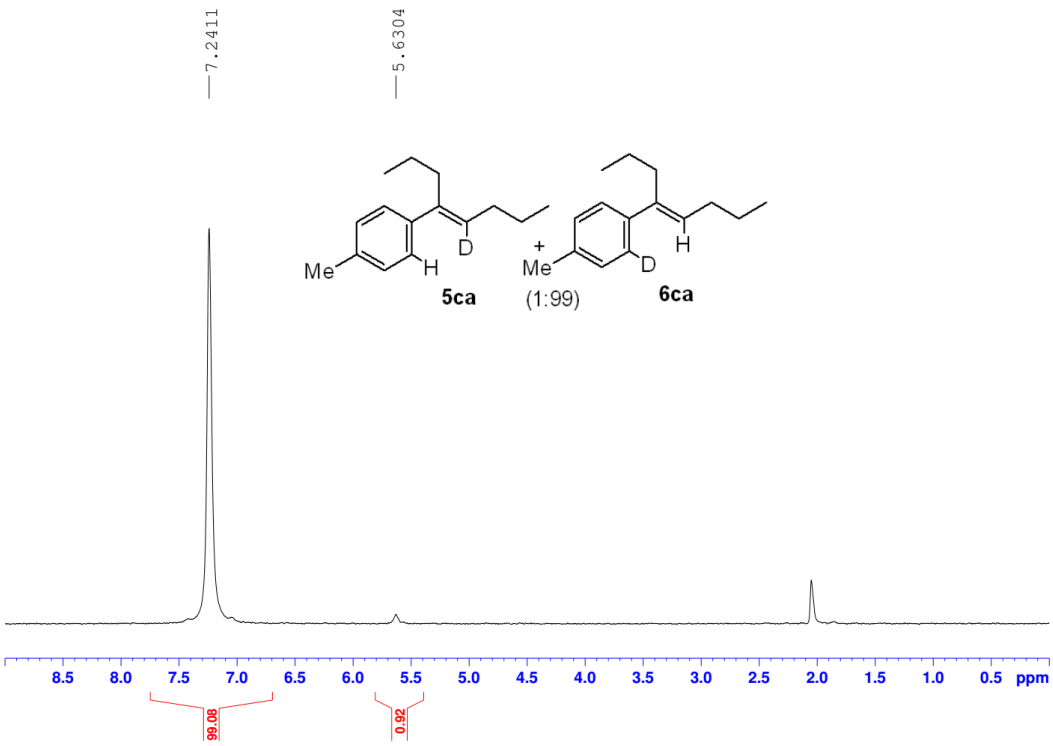
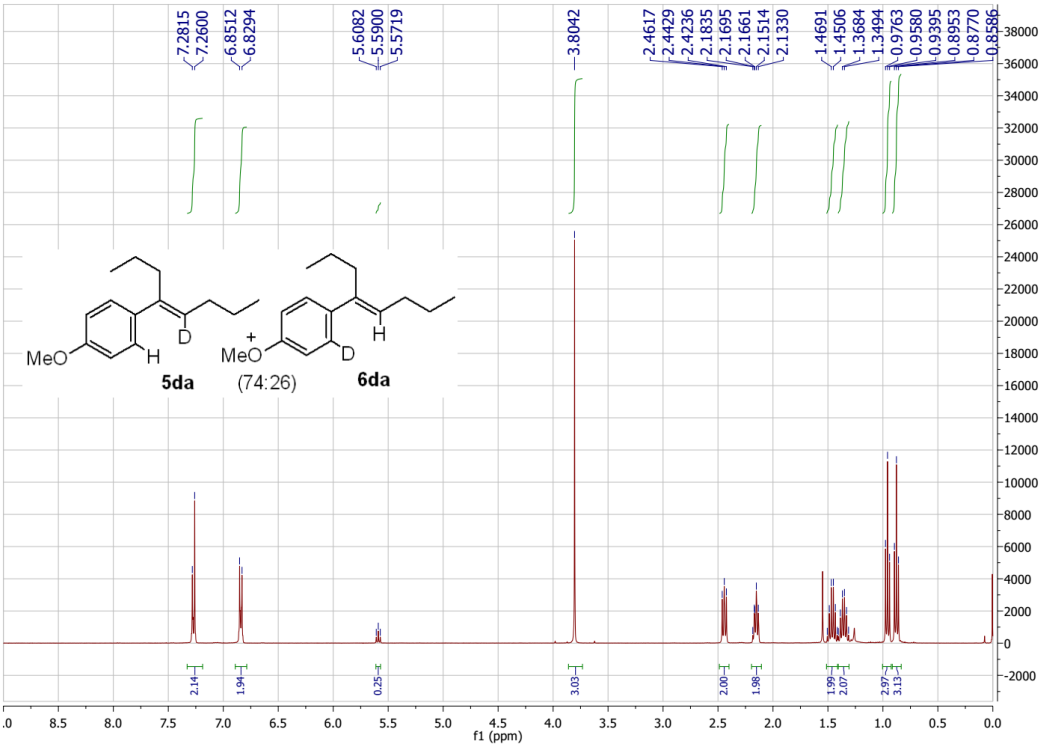
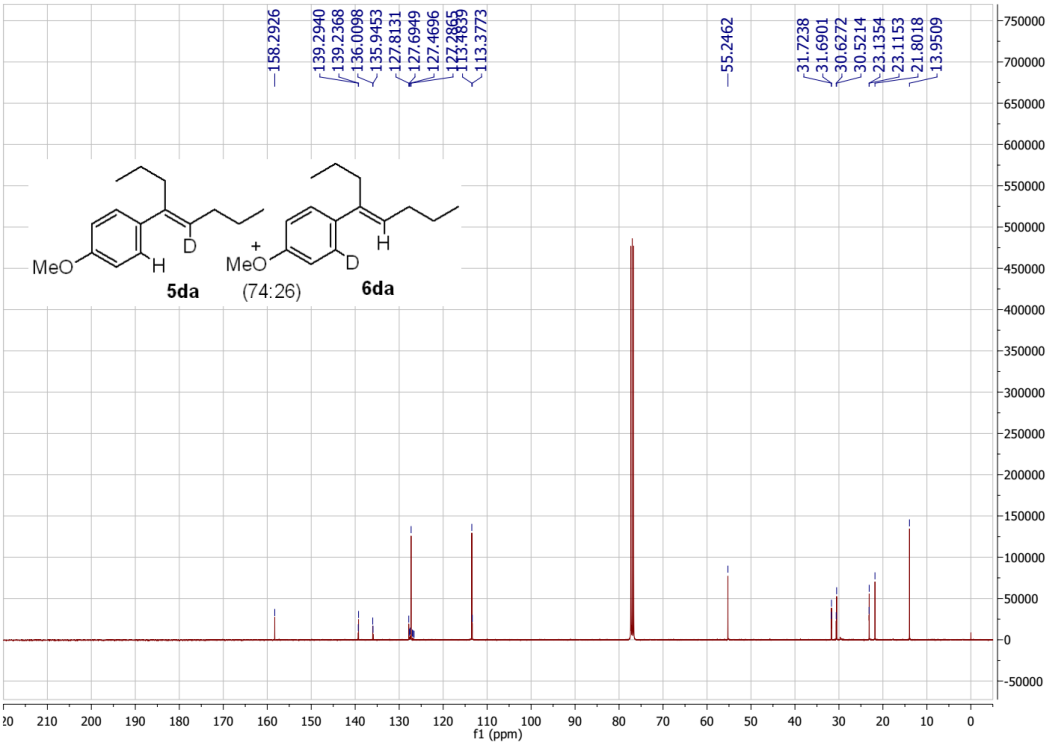
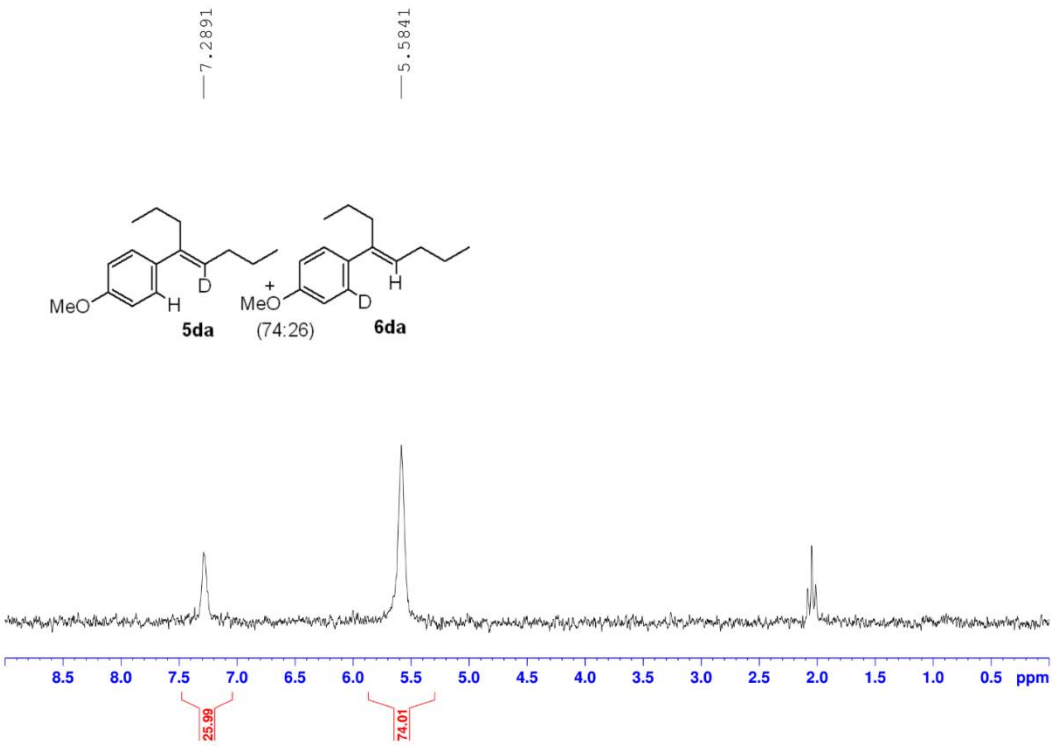
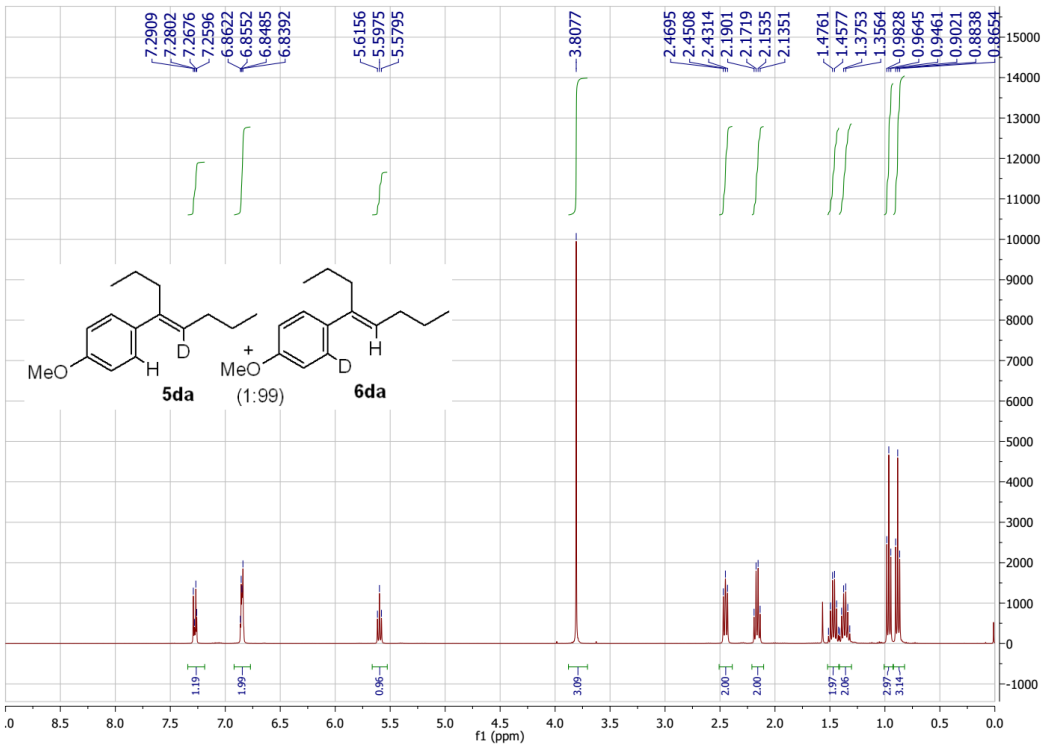
6ca
f1 (ppm)

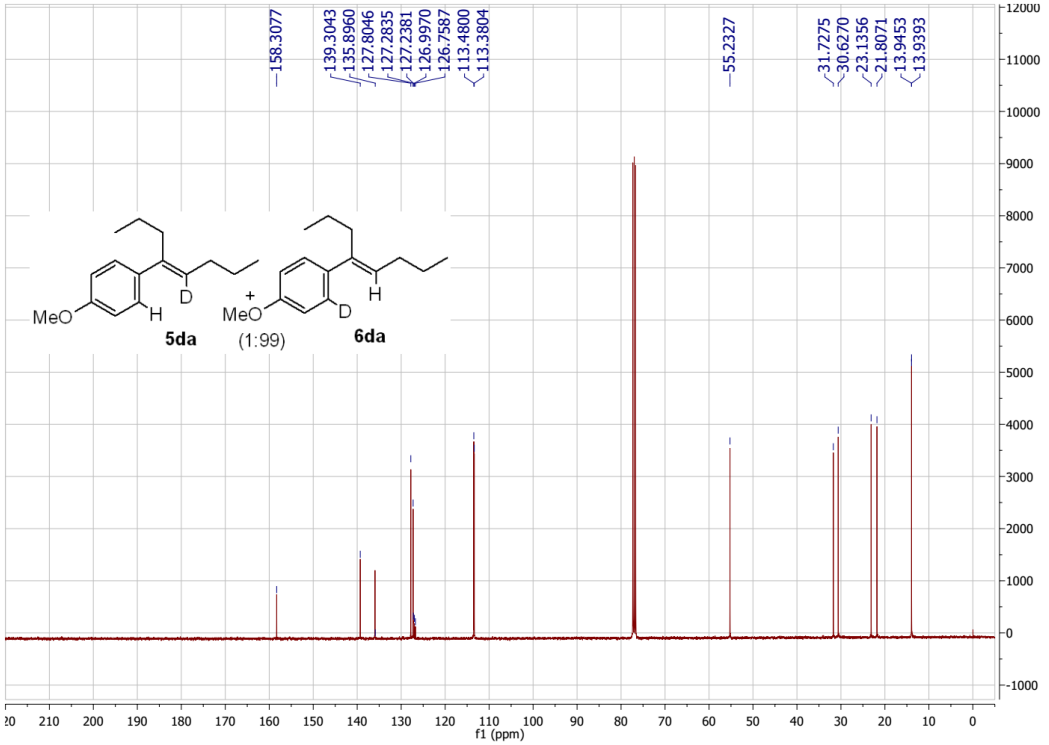

7.2411
5.6304
Me
H
D
5ca
+
Me
D
H
(1:99)
6ca
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
99.08
0.92

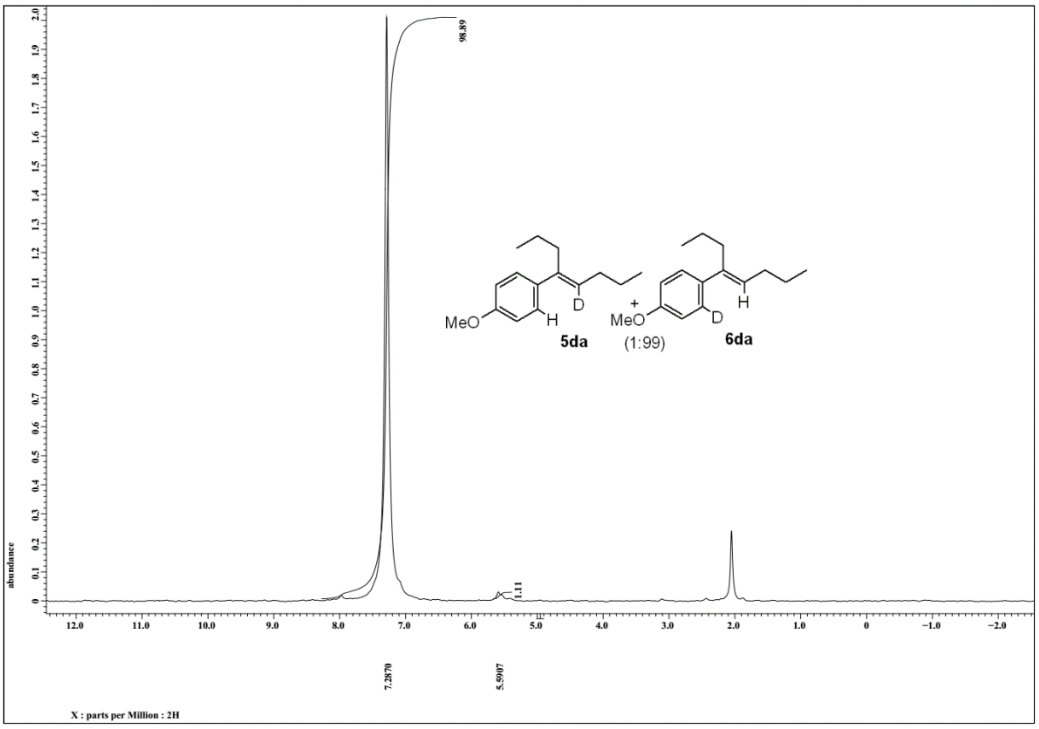

7.2815
7.2600
6.8512
6.8294
5.6082
5.5900
5.5719
3.8042
2.4617
2.4429
2.4236
2.1835
2.1695
2.1661
2.1514
2.1330
1.4691
1.4506
1.3684
1.3494
0.9763
0.9580
0.9395
0.8953
0.8770
0.8586
MeO
D
H
5da
(74:26)
6da
f1 (ppm)

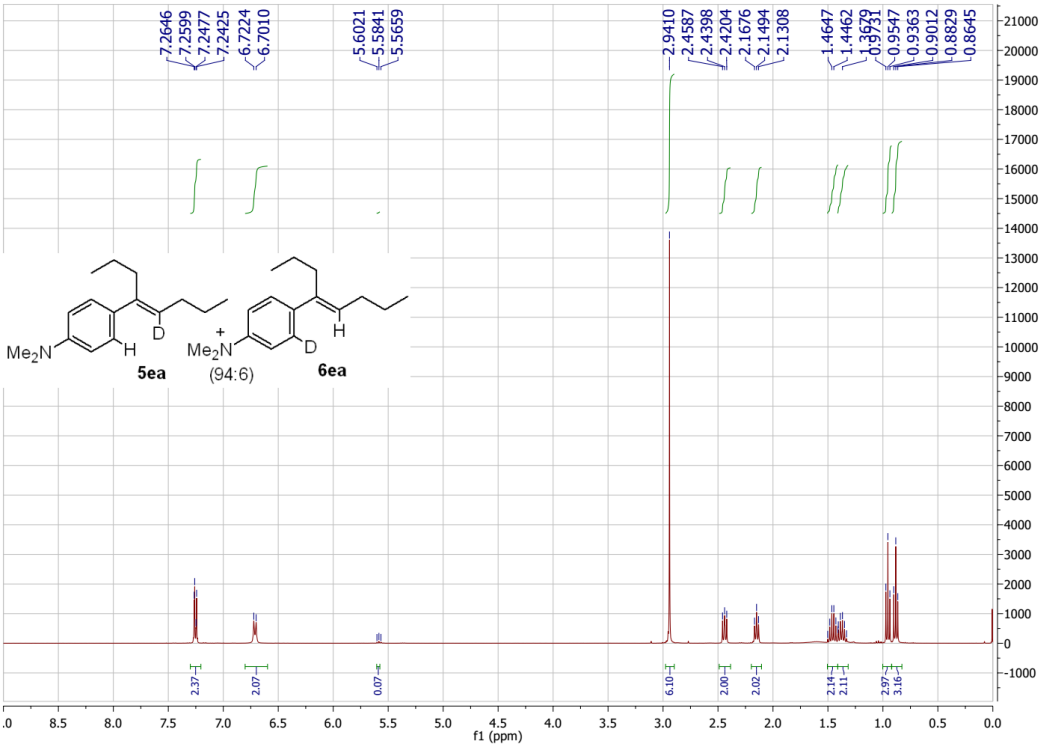

158.2926
139.2940
139.2368
136.0098
135.9453
127.8131
127.6949
127.4696
113.3773
55.2462
31.7238
31.6901
30.6272
30.5214
23.1354
23.1153
21.8018
13.9509
MeO
D
H
5da
(74:26)
6da
f1 (ppm)

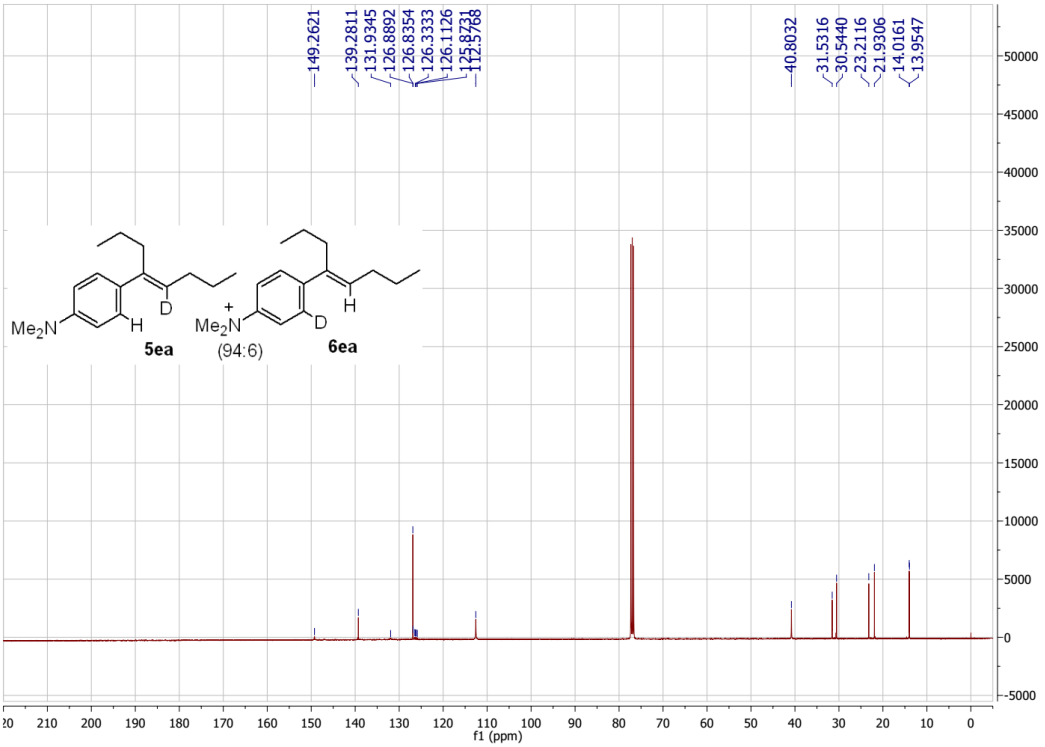

7.2891
5.5841
MeO
H
D
5da
(74:26)
MeO
D
H
6da
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
25.99
74.01

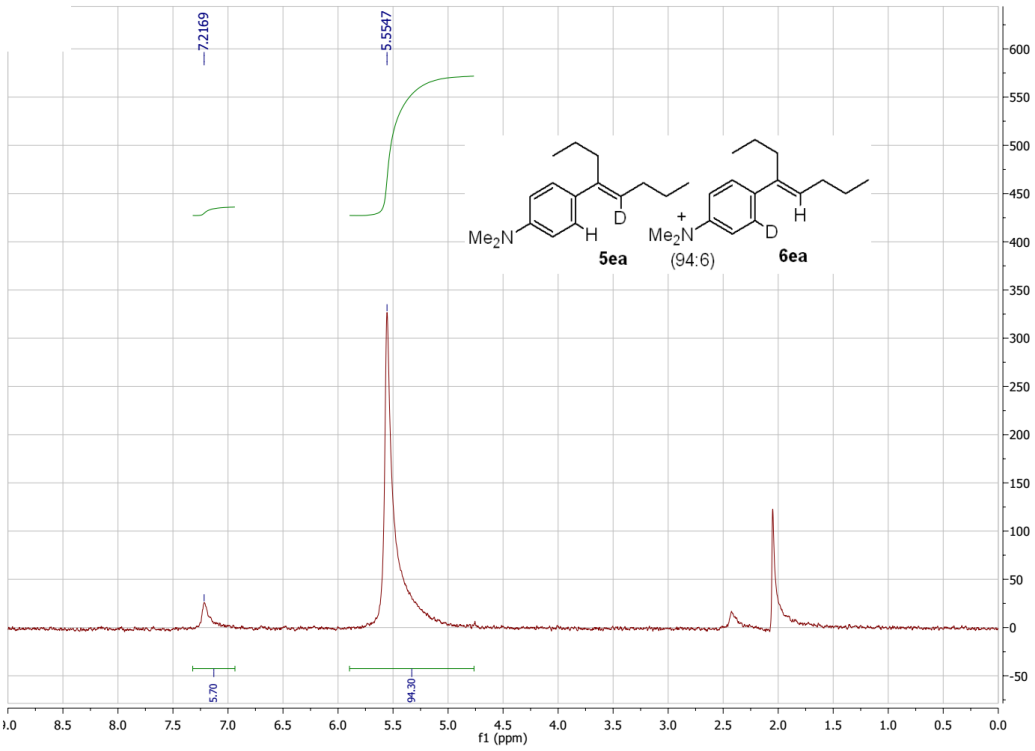

7.2909
7.2802
7.2676
7.2596
6.8622
6.8552
6.8485
6.8392
5.6156
5.5975
5.5795
3.8077
2.4695
2.4508
2.4314
2.1901
2.1719
2.1535
2.1351
1.4761
1.4577
1.3753
1.3564
0.9828
0.9645
0.9461
0.9021
0.8838
0.8654
MeO
H
D
5da
(1:99)
6da
f1 (ppm)

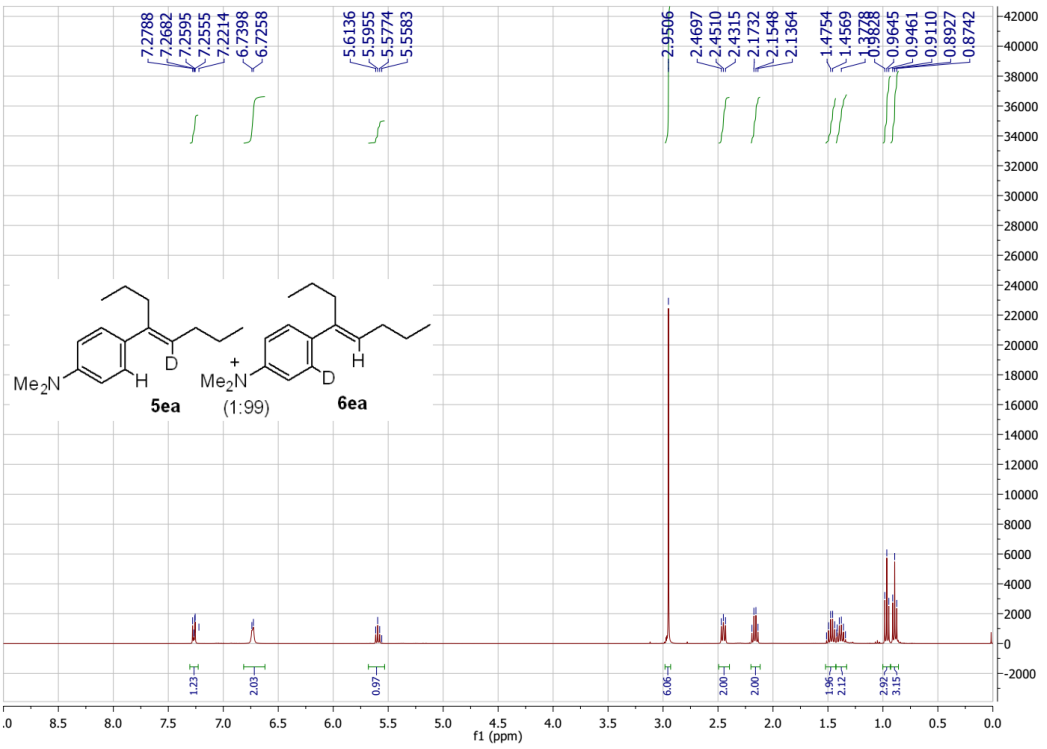

158.3077
139.3043
135.8960
127.8046
127.2835
127.2381
126.9970
126.7587
113.4800
113.3804
55.2327
31.7275
30.6270
23.1356
21.8071
13.9453
13.9393
MeO
H
D
5da
(1:99)
6da
f1 (ppm)

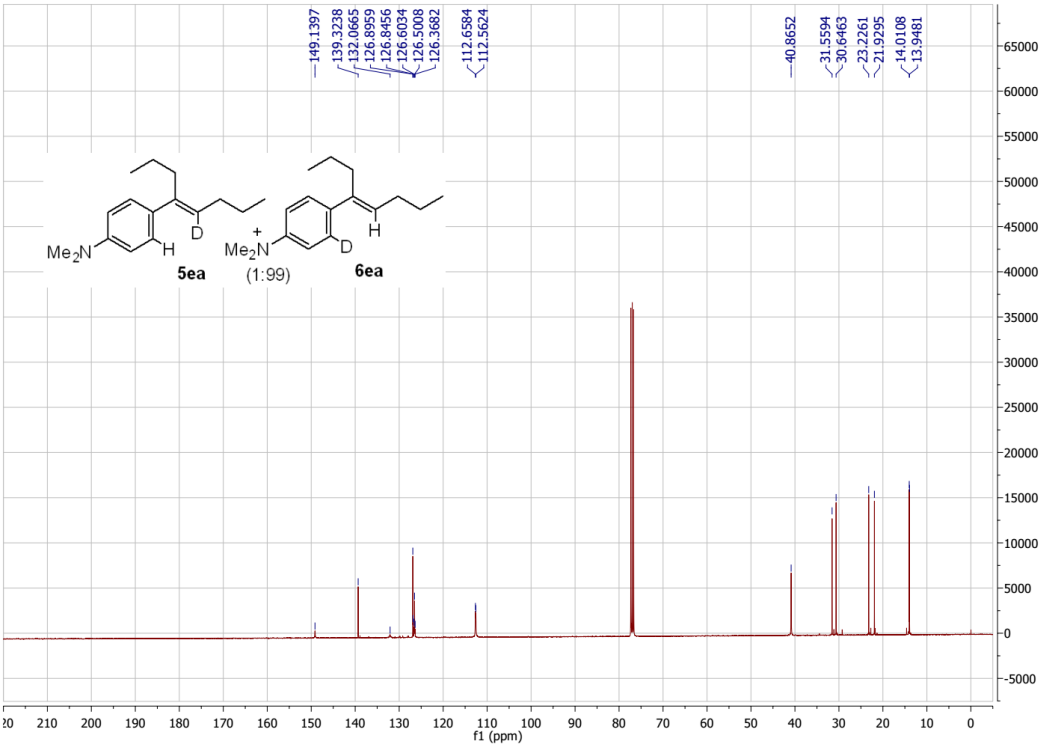

98.89
1.11
abundance
7.2870
5.9097
X : parts per Million : 2H
MeO
H
D
5da
+
MeO
D
H
(1:99)
6da

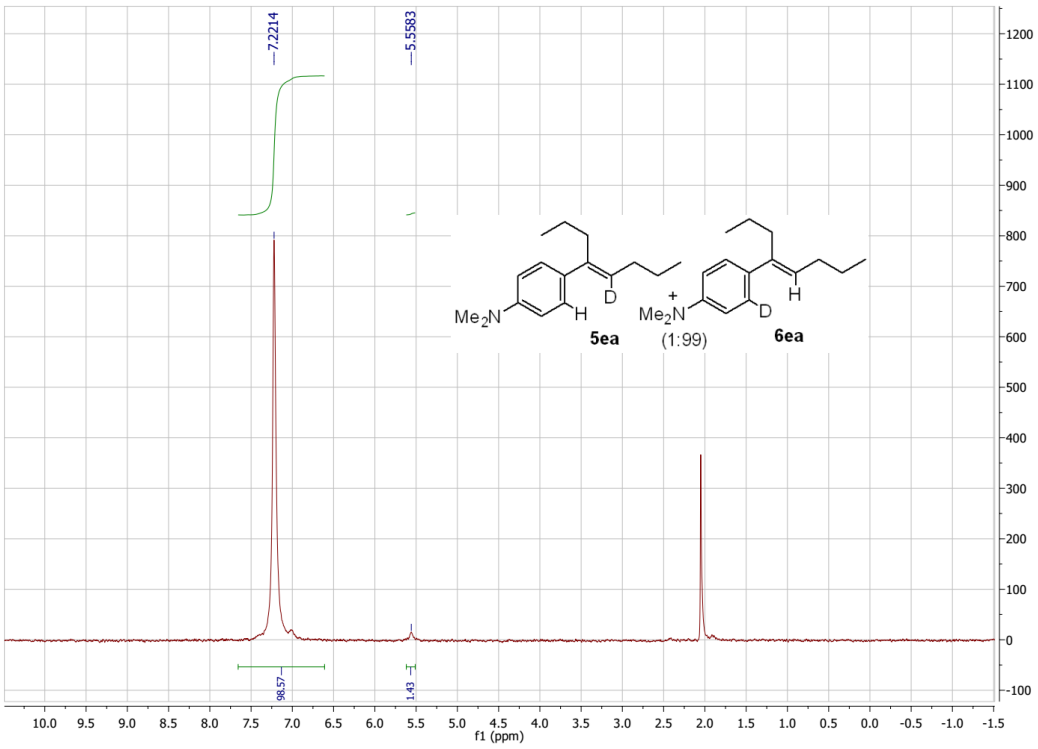

7.2646
7.2599
7.2477
7.2425
6.7224
6.7010
5.6021
5.5841
5.5659
2.9410
2.4587
2.4398
2.4204
2.1676
2.1494
2.1308
1.4647
1.4462
1.3679
0.9731
0.9547
0.9363
0.9012
0.8829
0.8645
Me2N
H
D
5ea
(94:6)
6ea
f1 (ppm)

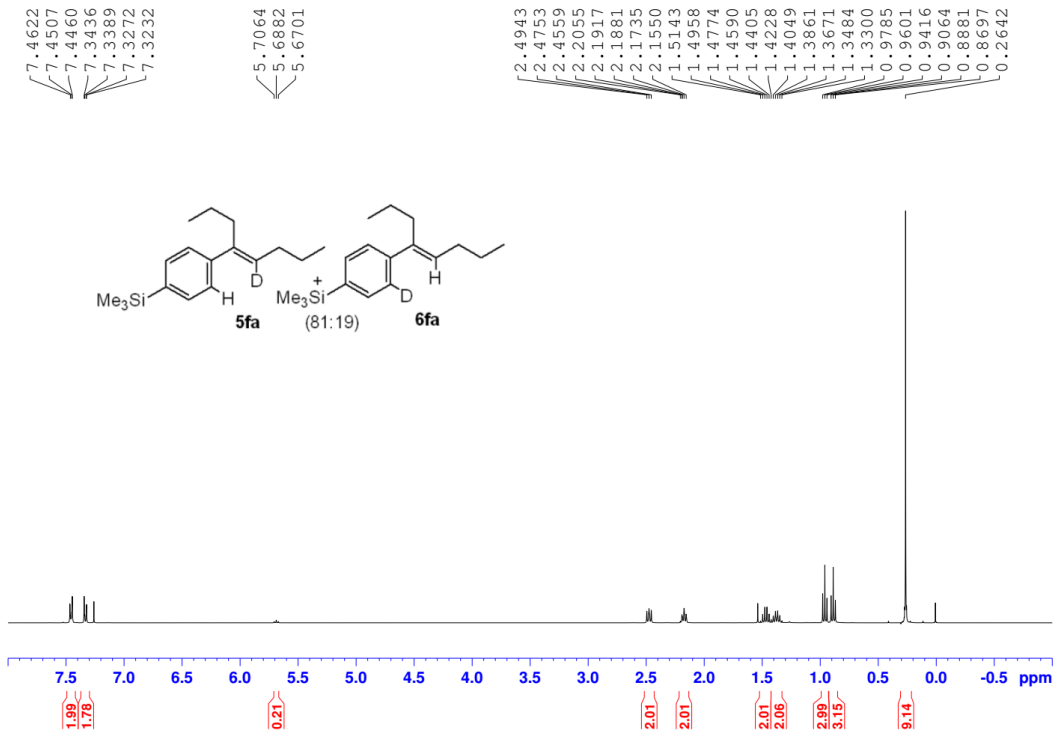

149.2621
139.2811
131.9345
126.8892
126.8354
126.3333
126.1126
125.8731
112.5768
40.8032
31.5316
30.5440
23.2116
21.9306
14.0161
13.9547
Me2N
H
D
5ea
(94:6)
6ea
f1 (ppm)

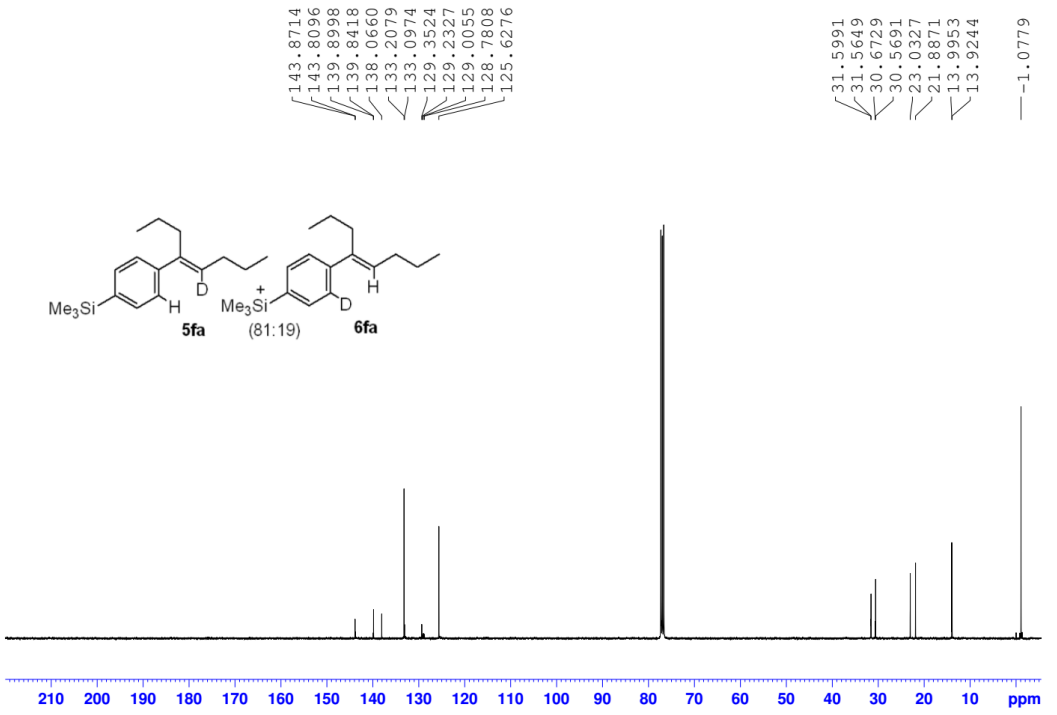

7.2169
5.5547
Me2N
H
D
5ea
+
Me2N
D
H
6ea
(94:6)
5.70
94.30
f1 (ppm)

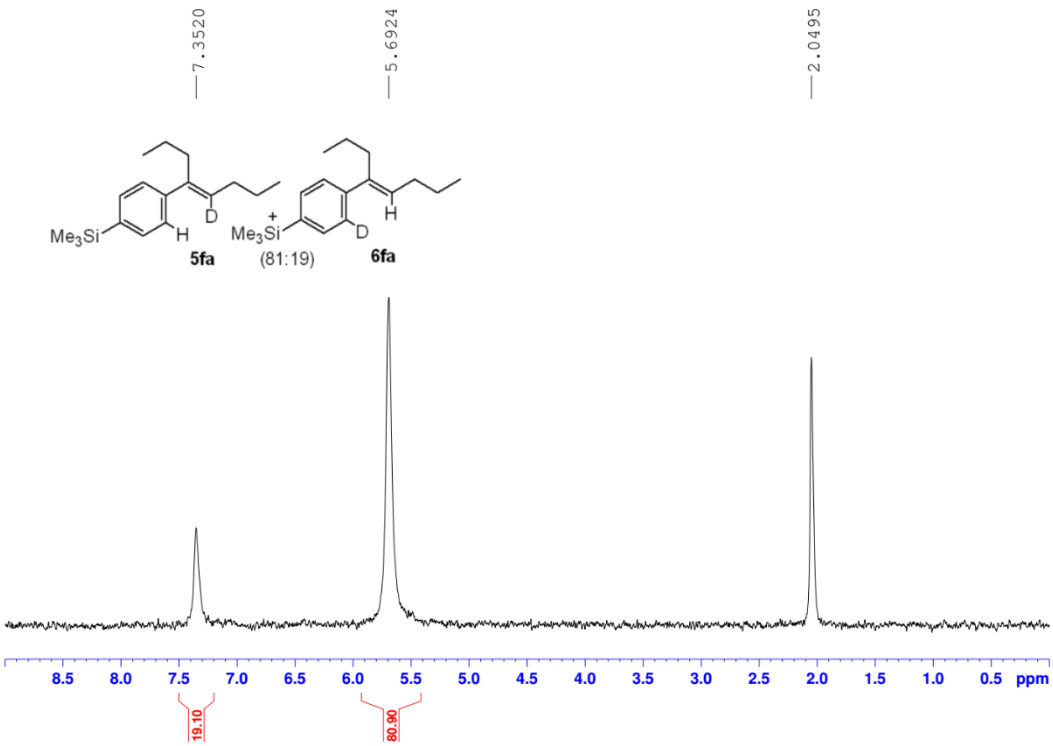

7.2788
7.2682
7.2595
7.2555
7.2214
6.7398
6.7258
5.6136
5.5955
5.5774
5.5583
2.9506
2.4697
2.4510
2.4315
2.1732
2.1548
2.1364
1.4754
1.4569
1.3778
0.9645
0.9461
0.9110
0.8927
0.8742
Me2N
D
H
5ea
+
Me2N
H
D
(1:99)
6ea
1.23
2.03
0.97
6.06
2.00
2.00
1.96
2.12
2.92
3.15
f1 (ppm)

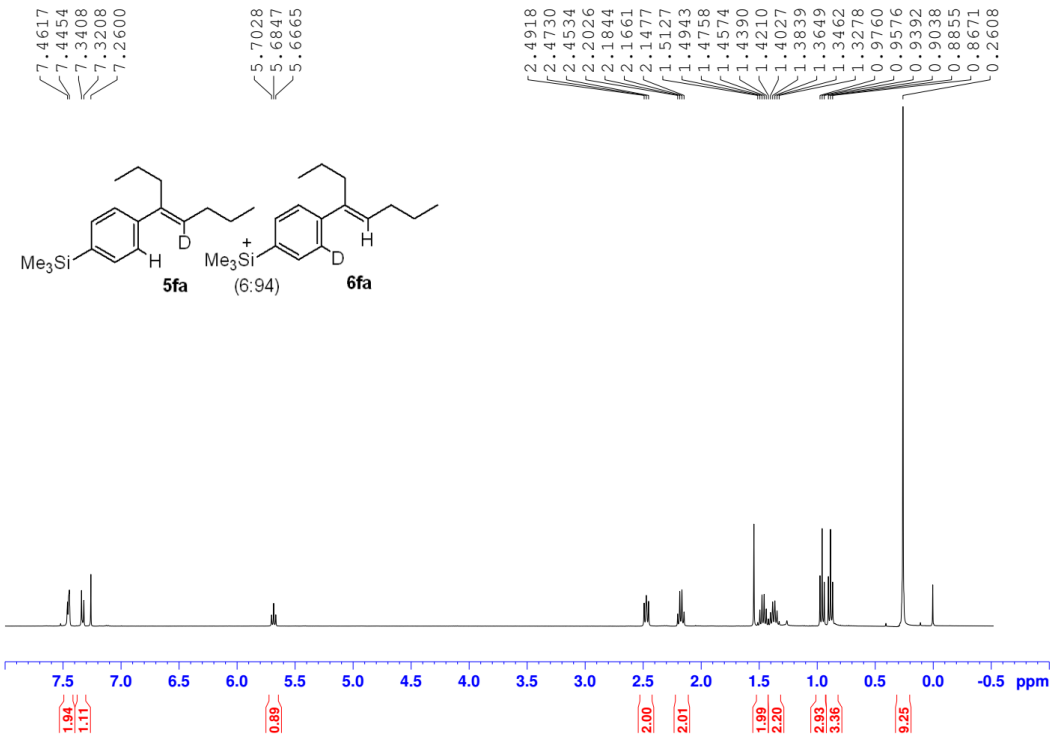

149.1397
139.3238
132.0665
126.8959
126.8456
126.6034
126.5008
126.3682
112.6584
112.5624
40.8652
31.5594
30.6463
23.2261
21.9295
14.0108
13.9481
Me2N
D
H
5ea
+
Me2N
H
D
(1:99)
6ea
f1 (ppm)

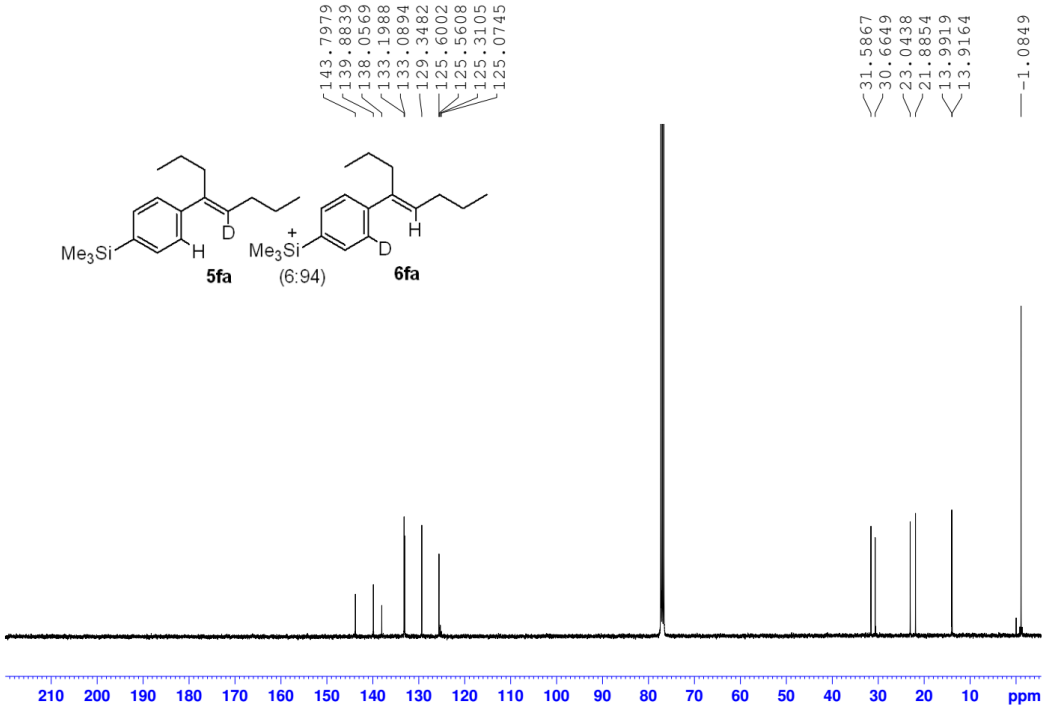

7.2214
5.5583
Me2N
H
D
5ea
(1:99)
Me2N
D
H
6ea
98.57
1.43
f1 (ppm)

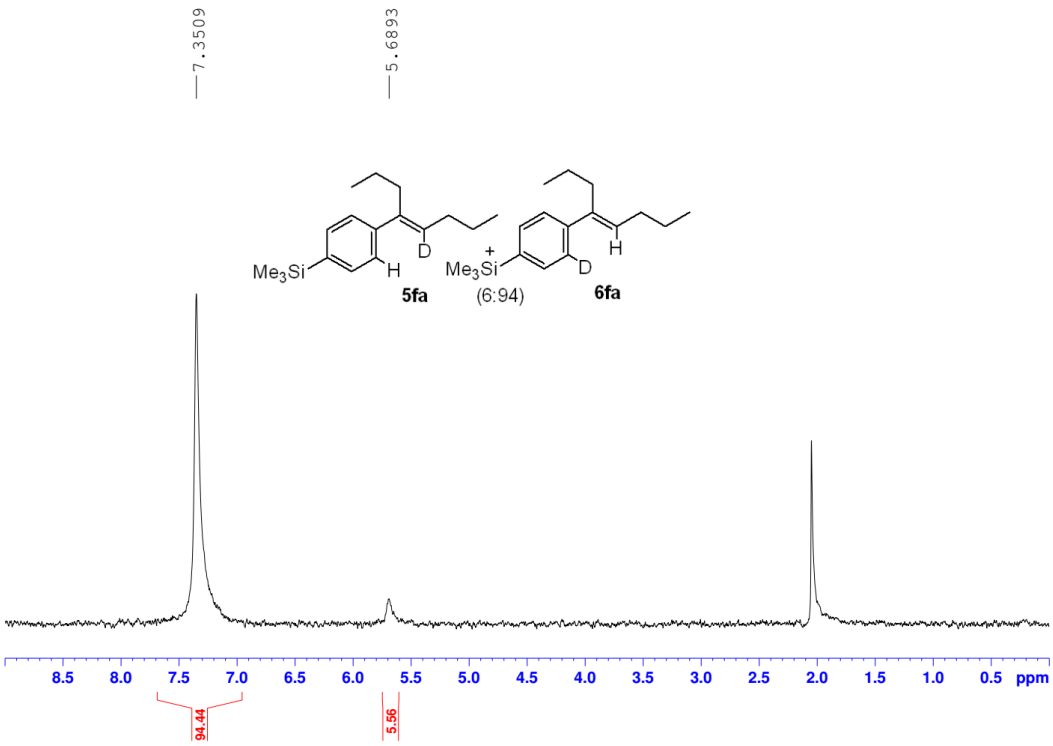

7.4622
7.4507
7.4460
7.3436
7.3389
7.3272
7.3232
5.7064
5.6882
5.6701
2.4943
2.4753
2.4559
2.2055
2.1917
2.1881
2.1735
2.1550
1.5143
1.4958
1.4774
1.4590
1.4405
1.4228
1.4049
1.3861
1.3671
1.3484
1.3300
0.9785
0.9601
0.9416
0.9064
0.8881
0.8697
0.2642
Me3Si
H
D
5fa
(81:19)
6fa
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm
1.99
1.78
0.21
2.01
2.01
2.01
2.06
2.99
3.15
9.14

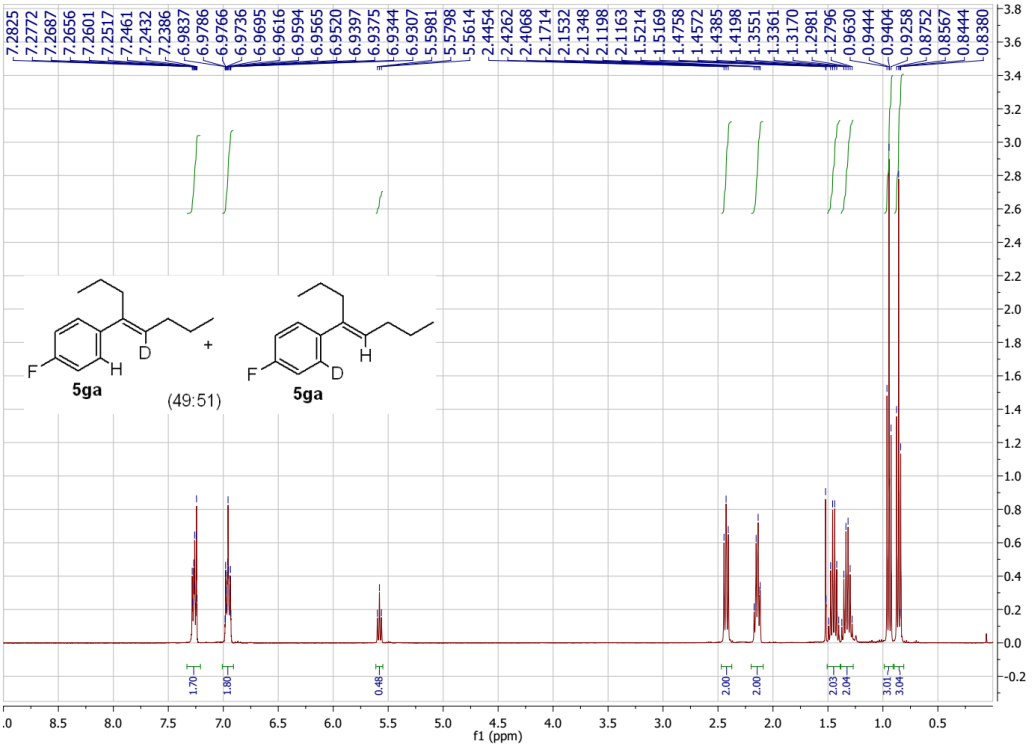

143.8714
143.8096
139.8998
139.8418
138.0660
133.2079
133.0974
129.3524
129.2327
129.0055
128.7808
125.6276
31.5991
31.5649
30.6729
30.5691
23.0327
21.8871
13.9953
13.9244
-1.0779
Me3Si
H
D
5fa
(81:19)
6fa
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

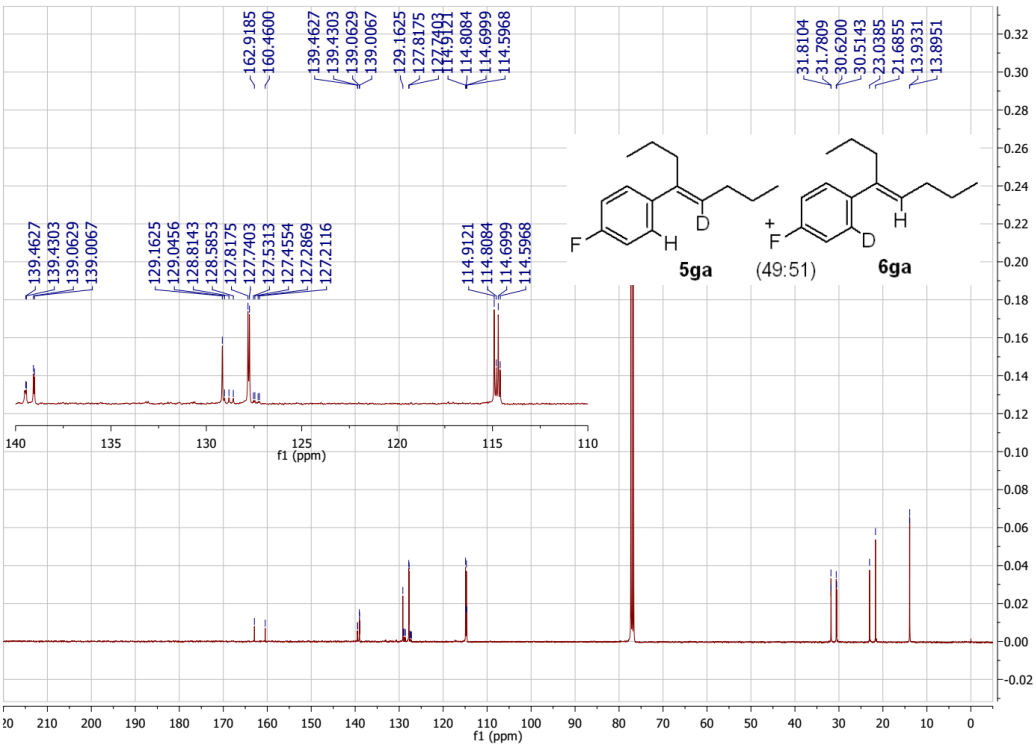

7.3520
5.6924
2.0495
Me3Si
H
D
5fa
(81:19)
Me3Si
D
H
6fa
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
19.10
80.90

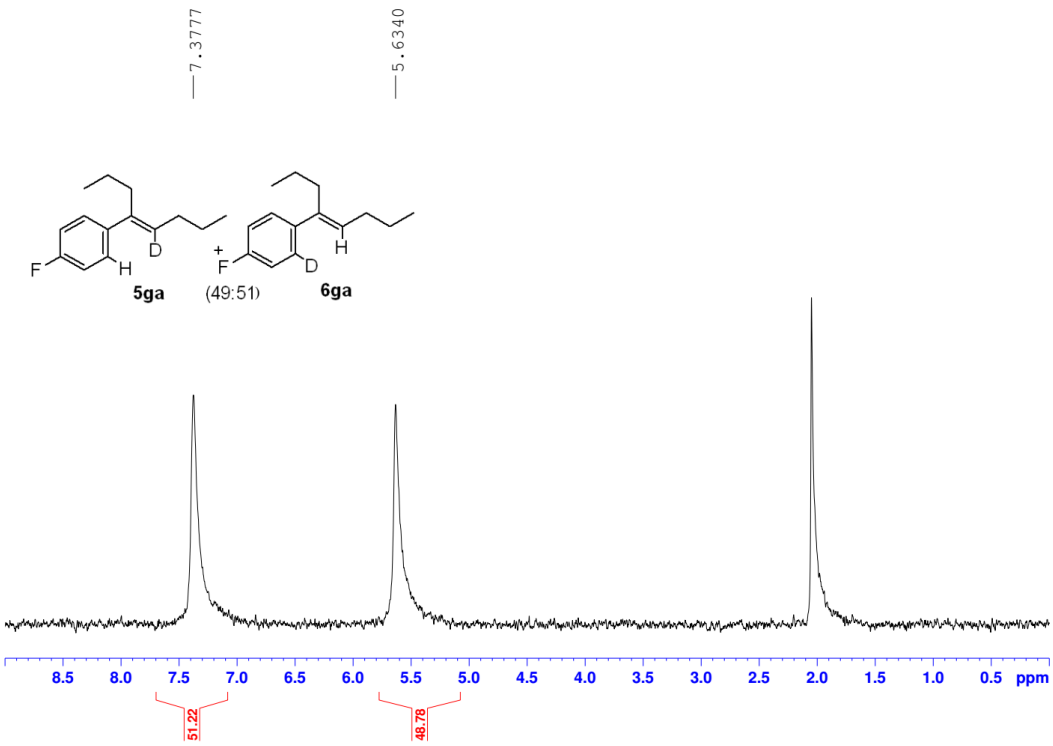

7.4617
7.4454
7.3408
7.3208
7.2600
5.7028
5.6847
5.6665
2.4918
2.4730
2.4534
2.2026
2.1844
2.1661
2.1477
1.5127
1.4943
1.4758
1.4574
1.4390
1.4210
1.4027
1.3839
1.3649
1.3462
1.3278
0.9760
0.9576
0.9392
0.9038
0.8855
0.8671
0.2608
Me3Si
H
D
5fa
+
Me3Si
D
H
(6:94)
6fa
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm
1.94
1.11
0.89
2.00
2.01
1.99
2.20
2.93
3.36
9.25

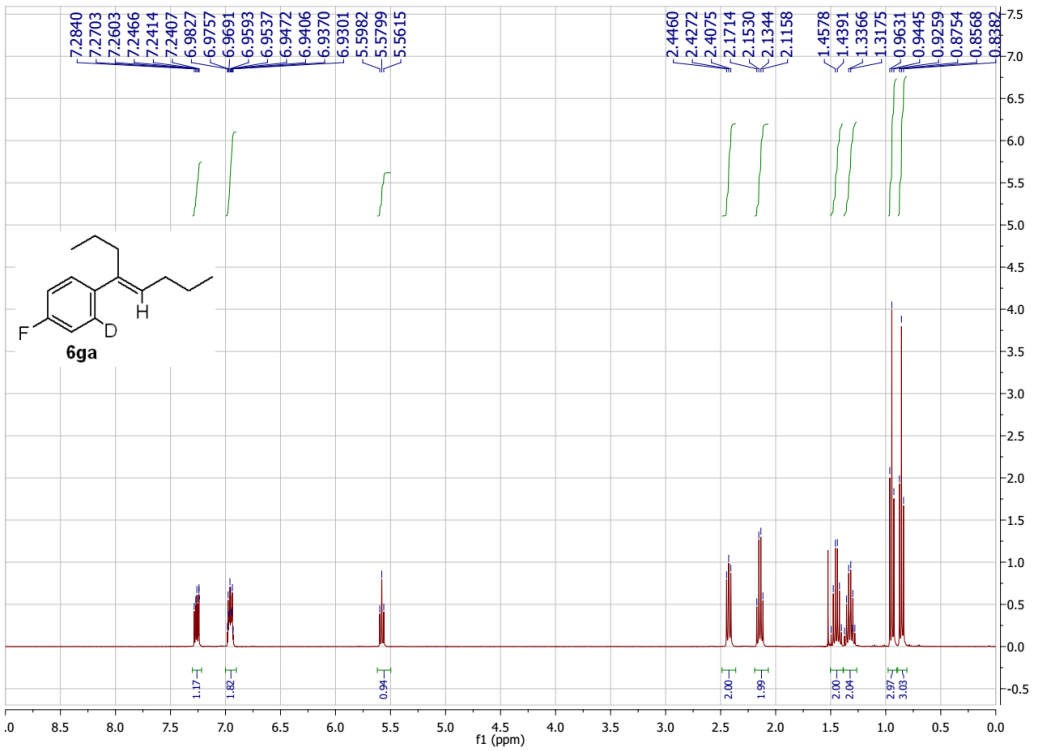

143.7979
139.8839
138.0569
133.1988
133.0894
129.3482
125.6002
125.5608
125.3105
125.0745
31.5867
30.6649
23.0438
21.8854
13.9919
13.9164
1.0849
Me3Si
H
D
5fa
+
Me3Si
D
H
(6:94)
6fa
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

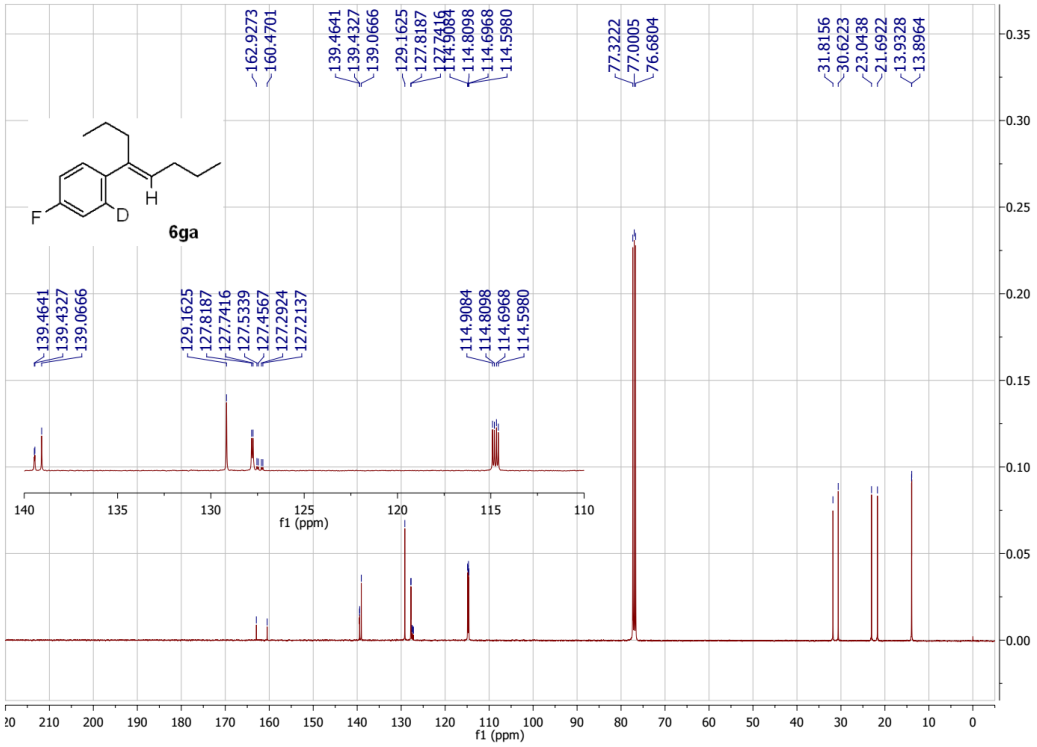

7.3509
5.6893
Me3Si
H
D
5fa
+
Me3Si
D
H
(6:94)
6fa
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
94.44
5.56

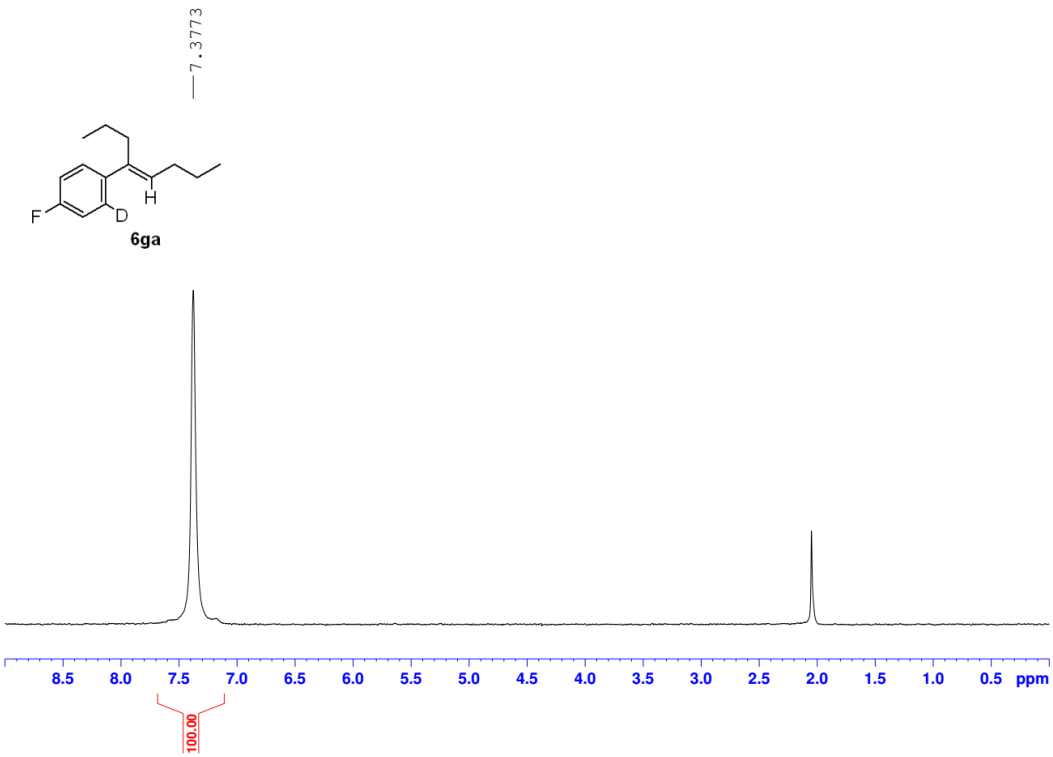

5ga
(49:51)
5ga
f1 (ppm)

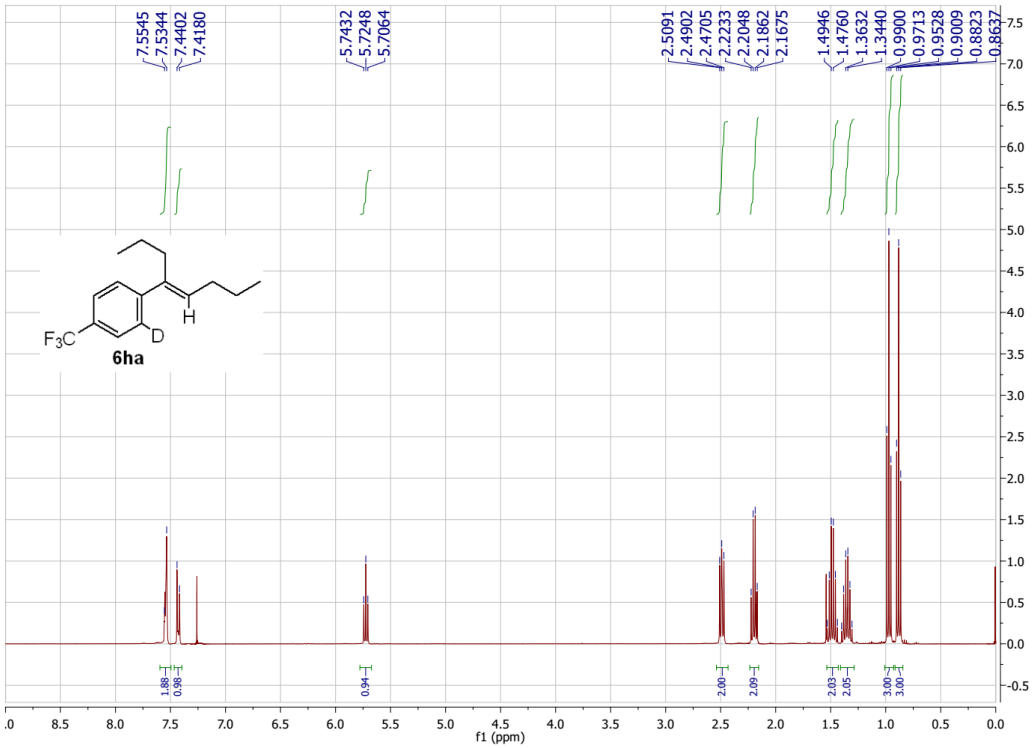

5ga
(49:51)
6ga
f1 (ppm)

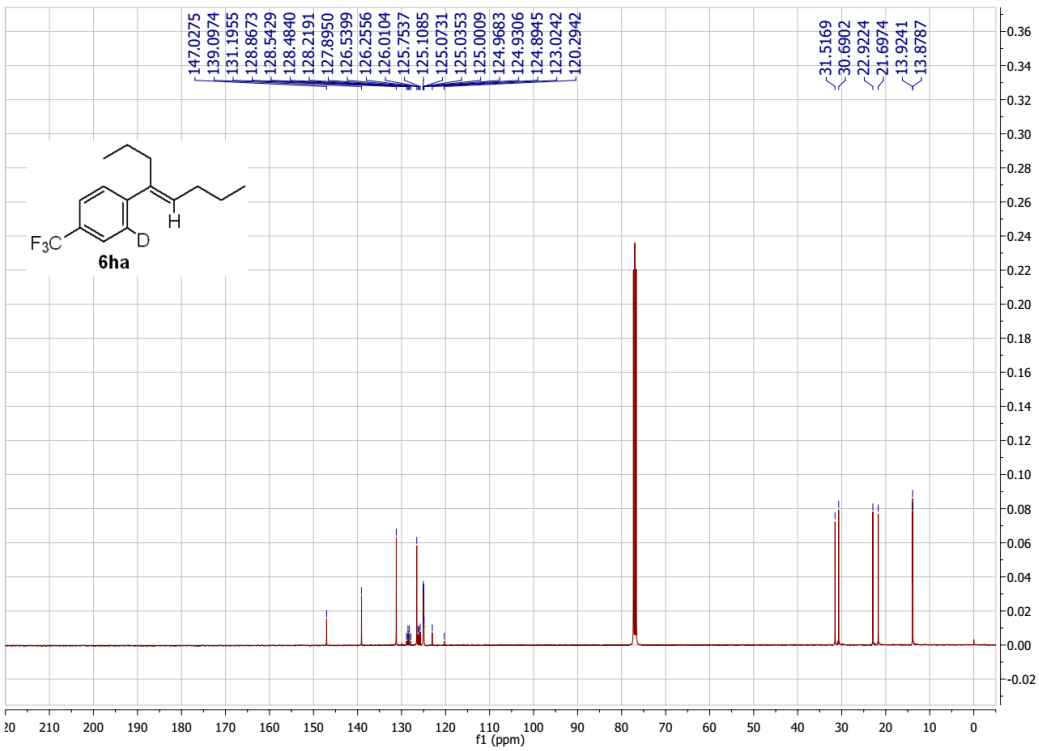

7.3777
5.6340
F
H
D
5ga
(49:51)
F
D
H
6ga
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
51.22
48.78

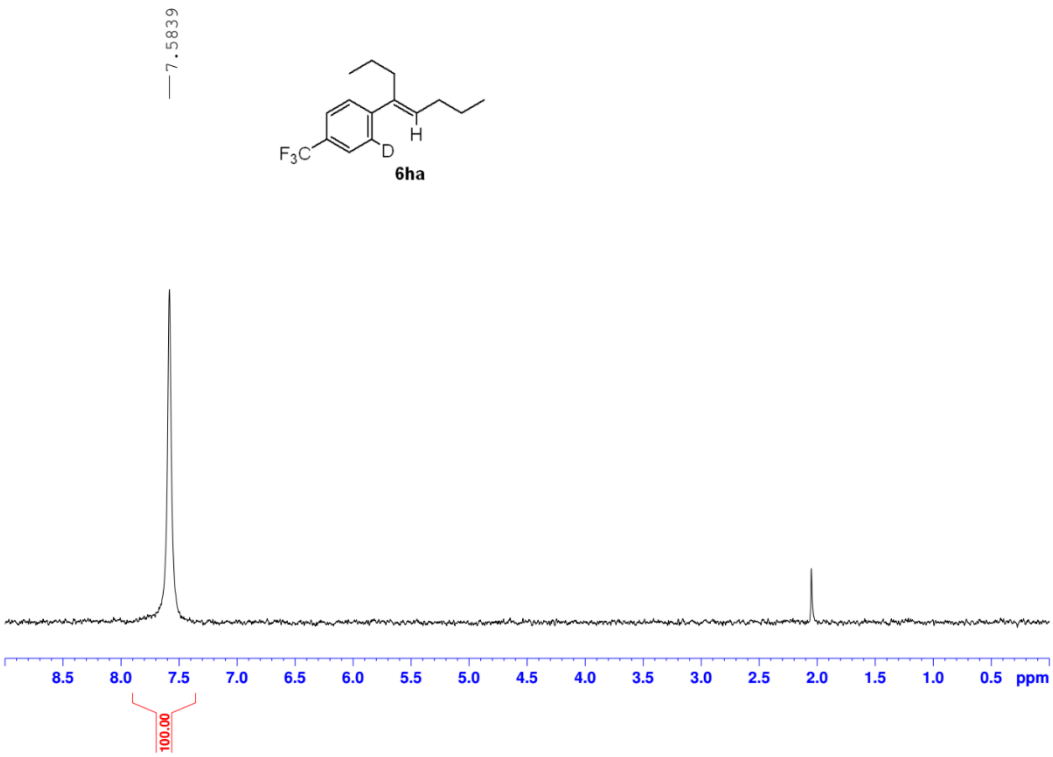

7.2840
7.2703
7.2603
7.2466
7.2414
7.2407
6.9827
6.9757
6.9691
6.9593
6.9537
6.9472
6.9406
6.9370
6.9301
5.5982
5.5799
5.5615
2.4460
2.4272
2.4075
2.1714
2.1530
2.1344
2.1158
1.4578
1.4391
1.3366
1.3175
0.9631
0.9445
0.9259
0.8754
0.8568
0.8382
F
D
H
6ga
1.17
1.82
0.94
2.00
1.99
2.00
2.04
2.97
3.03
f1 (ppm)

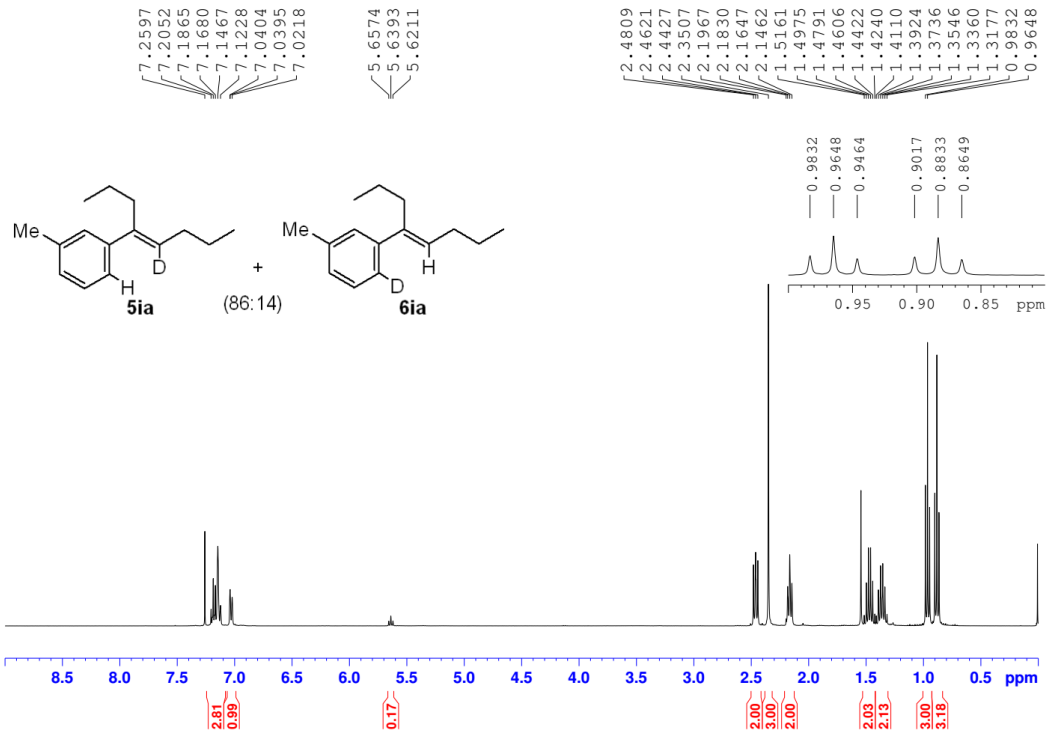

162.9273
160.4701
139.4641
139.4327
139.0666
129.1625
127.8187
127.7416
127.5339
127.4567
127.2924
127.2137
114.9084
114.8098
114.6968
114.5980
77.3222
77.0005
76.6804
31.8156
30.6223
23.0438
21.6922
13.9328
13.8964
F
D
H
6ga
f1 (ppm)

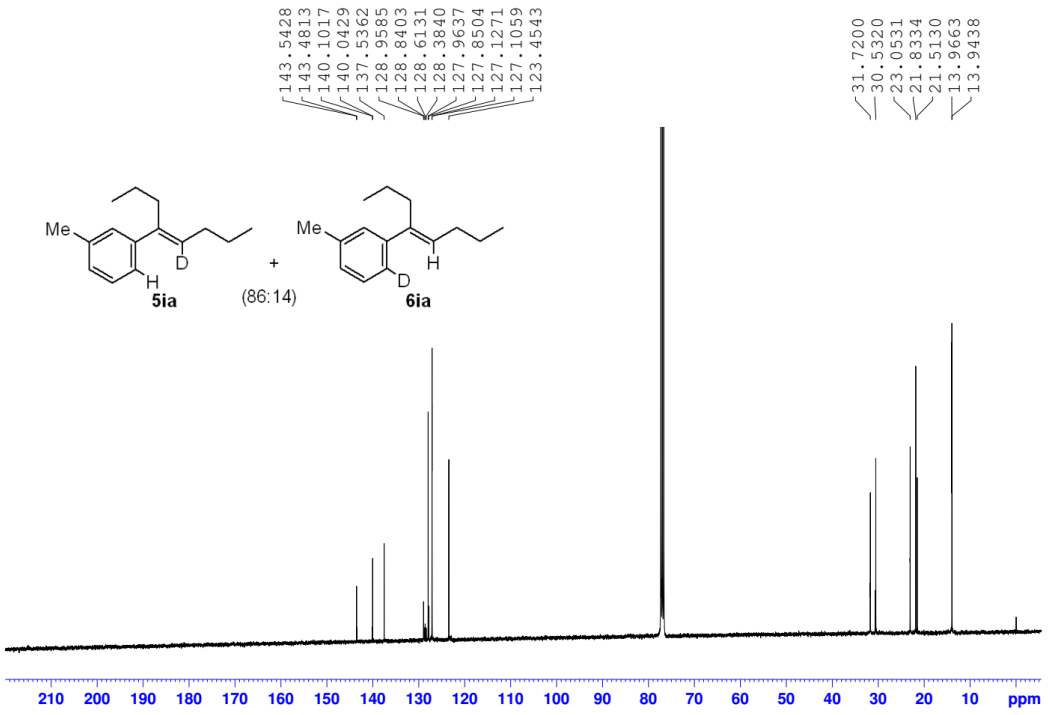

7.3773
F
D
H
6ga
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
100.00

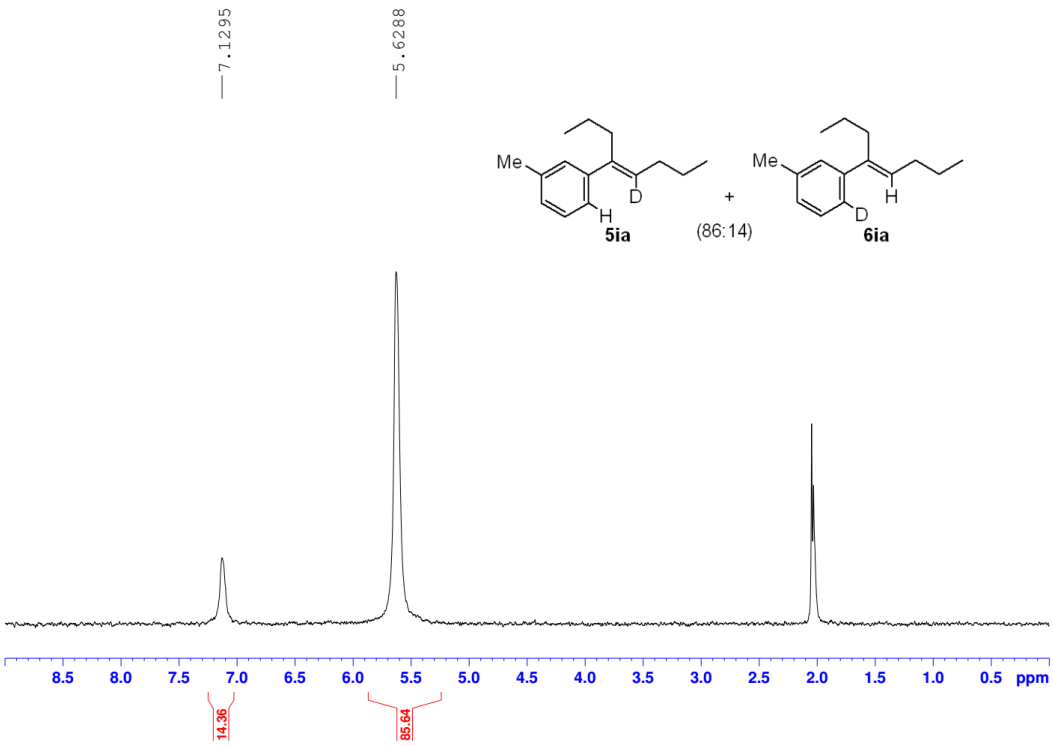

7.5545
7.5344
7.4402
7.4180
5.7432
5.7248
5.7064
2.5091
2.4902
2.4705
2.2233
2.2048
2.1862
2.1675
1.4946
1.4760
1.3632
1.3440
0.9900
0.9713
0.9528
0.9009
0.8823
0.8637
F3C
D
H
6ha
f1 (ppm)

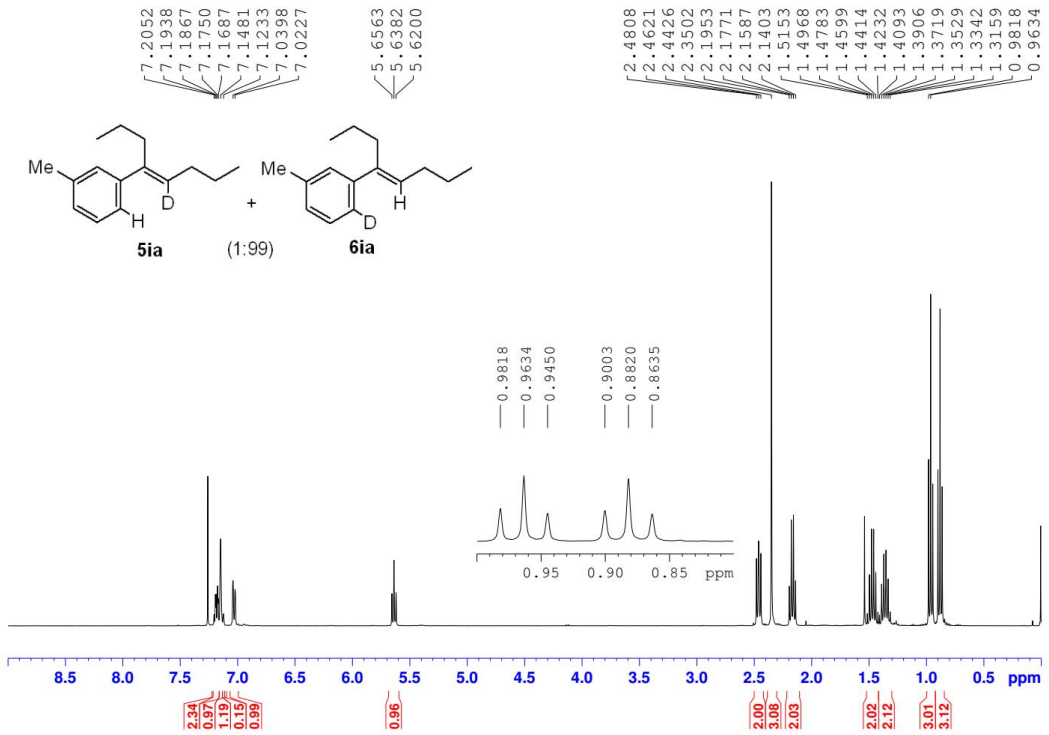

147.0275
139.0974
131.1955
128.8673
128.5429
128.4840
128.2191
127.8950
126.5399
126.2556
126.0104
125.7537
125.1085
125.0731
125.0353
125.0009
124.9683
124.9306
124.8945
123.0242
120.2942
31.5169
30.6902
22.9224
21.6974
13.9241
13.8787
F3C
D
H
6ha
f1 (ppm)

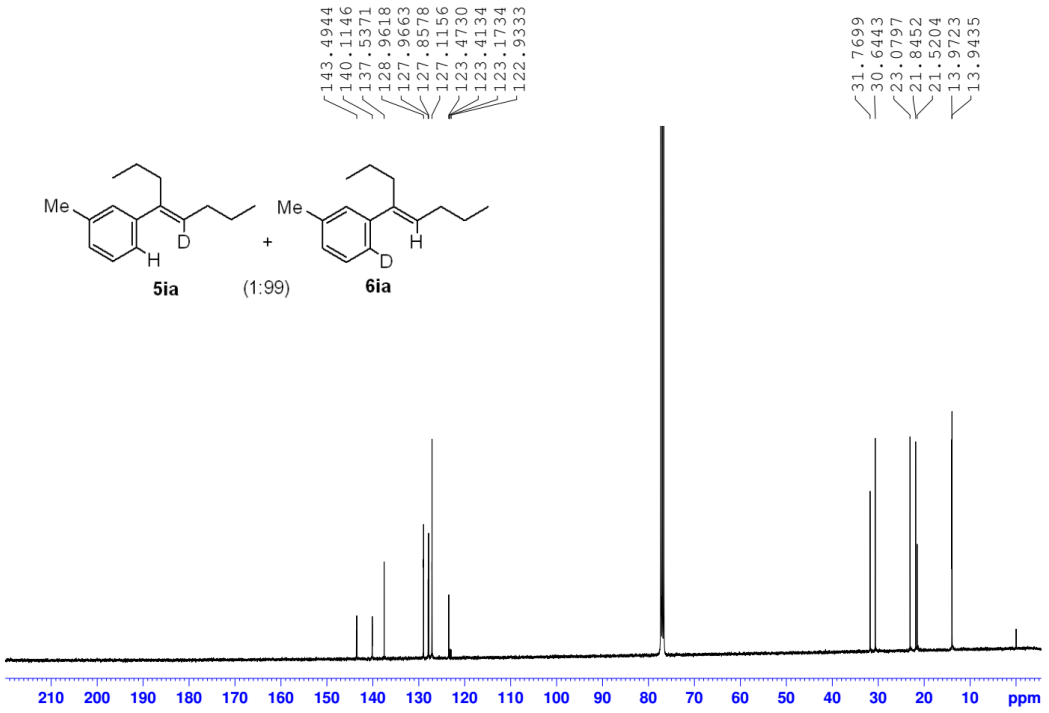

7.5839
F3C
D
H
6ha
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
100.00

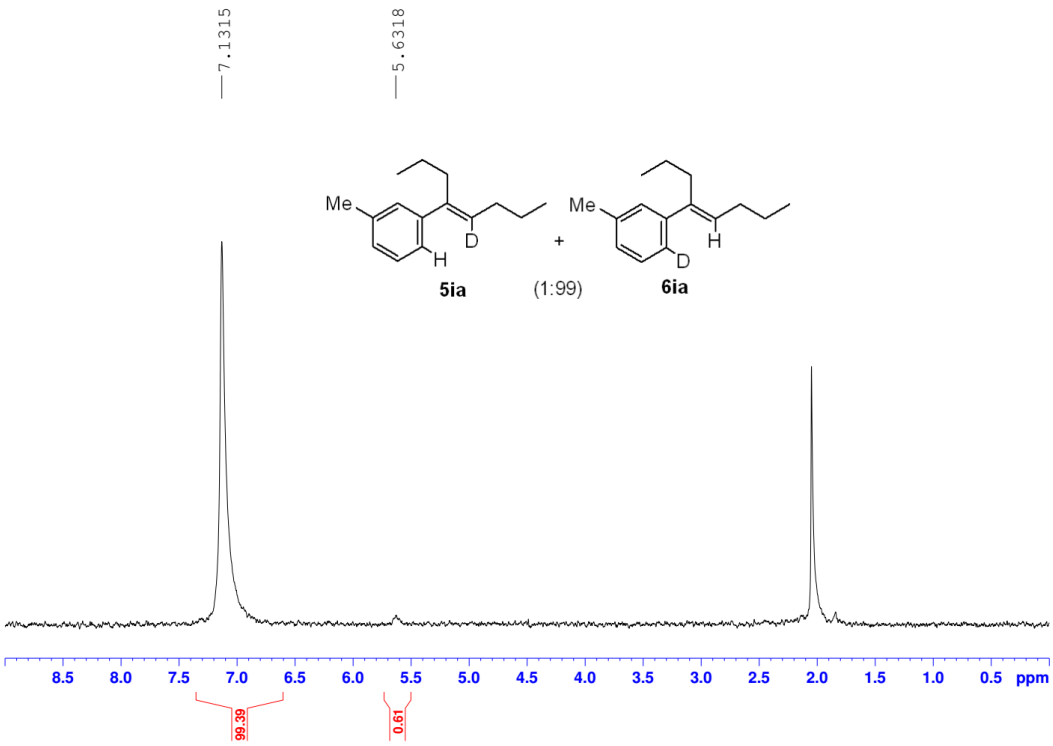

7.2597
7.2052
7.1865
7.1680
7.1467
7.1228
7.0404
7.0395
7.0218
5.6574
5.6393
5.6211
2.4809
2.4621
2.4427
2.3507
2.1967
2.1830
2.1647
2.1462
1.5161
1.4975
1.4791
1.4606
1.4422
1.4240
1.4110
1.3924
1.3736
1.3546
1.3360
1.3177
0.9832
0.9648
0.9832
0.9648
0.9464
0.9017
0.8833
0.8649
0.95
0.90
0.85
ppm
Me
D
H
5ia
+
(86:14)
Me
H
D
6ia
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.81
0.99
0.17
2.00
3.00
2.00
2.03
2.13
3.00
3.18

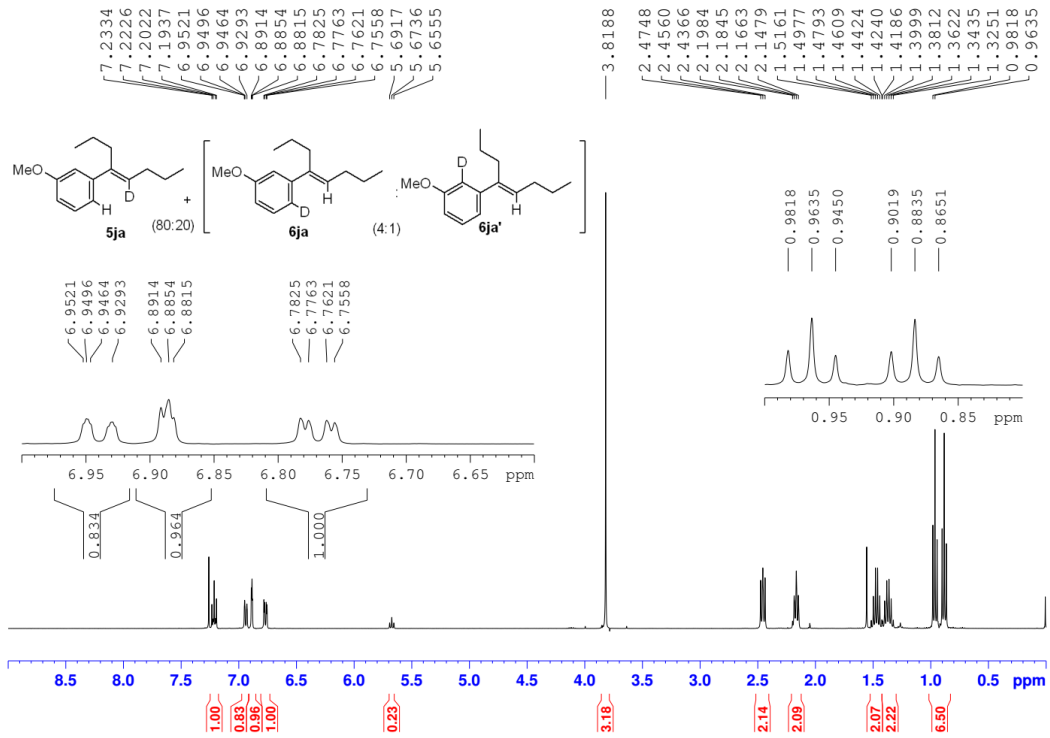

143.5428
143.4813
140.1017
140.0429
137.5362
128.9585
128.8403
128.6131
128.3840
127.9637
127.8504
127.1271
127.1059
123.4543
31.7200
30.5320
23.0531
21.8334
21.5130
13.9663
13.9438
Me
D
H
5ia
+
(86:14)
Me
H
D
6ia
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

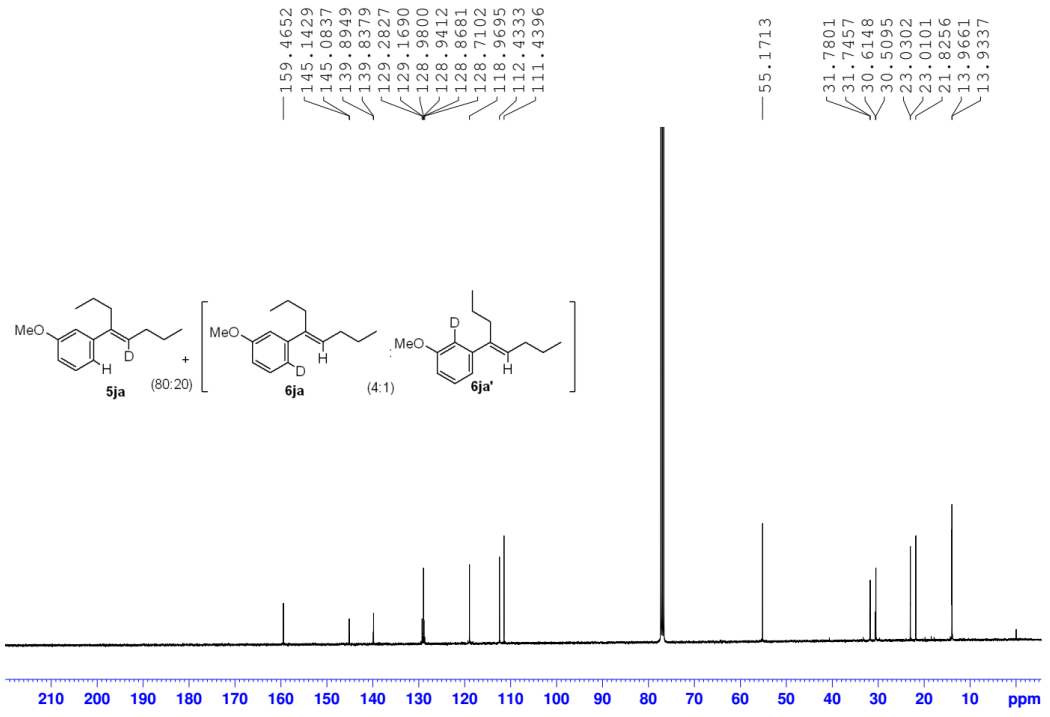

7.1295
5.6288
Me
D
H
5ia
+
(86:14)
Me
H
D
6ia
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
14.36
85.64

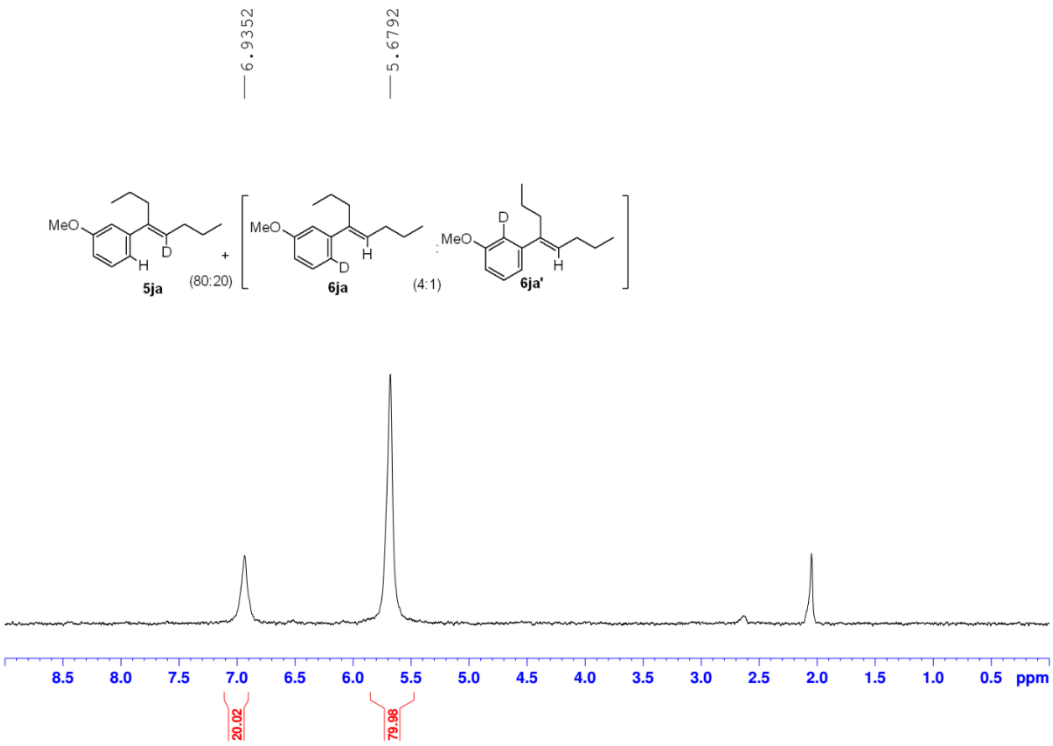

7.2052
7.1938
7.1867
7.1750
7.1687
7.1481
7.1233
7.0398
7.0227
5.6563
5.6382
5.6200
2.4808
2.4621
2.4426
2.3502
2.1953
2.1771
2.1587
2.1403
1.5153
1.4968
1.4783
1.4599
1.4414
1.4232
1.4093
1.3906
1.3719
1.3529
1.3342
1.3159
0.9818
0.9634
Me
D
H
+
Me
H
D
5ia
(1:99)
6ia
0.9818
0.9634
0.9450
0.9003
0.8820
0.8635
0.95
0.90
0.85
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.34
0.97
1.19
0.15
0.99
0.96
2.00
3.08
2.03
2.02
2.12
3.01
3.12

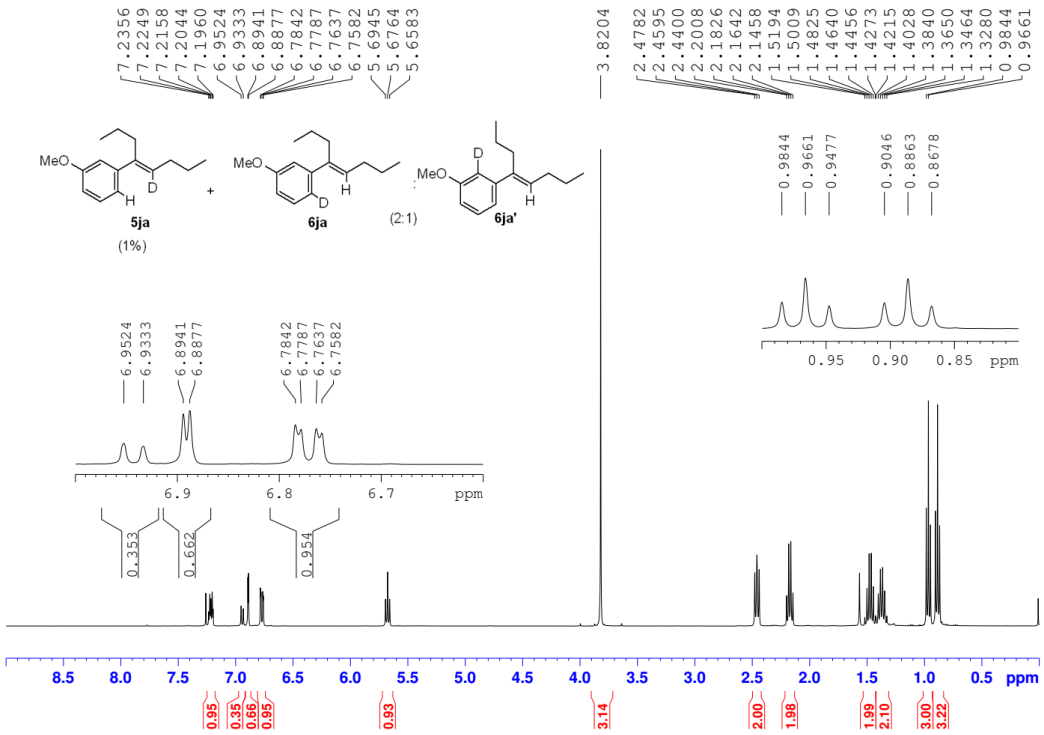

143.4944
140.1146
137.5371
128.9618
127.9663
127.8578
127.1156
123.4730
123.4134
123.1734
122.9333
31.7699
30.6443
23.0797
21.8452
21.5204
13.9723
13.9435
Me
D
H
+
Me
H
D
5ia
(1:99)
6ia
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

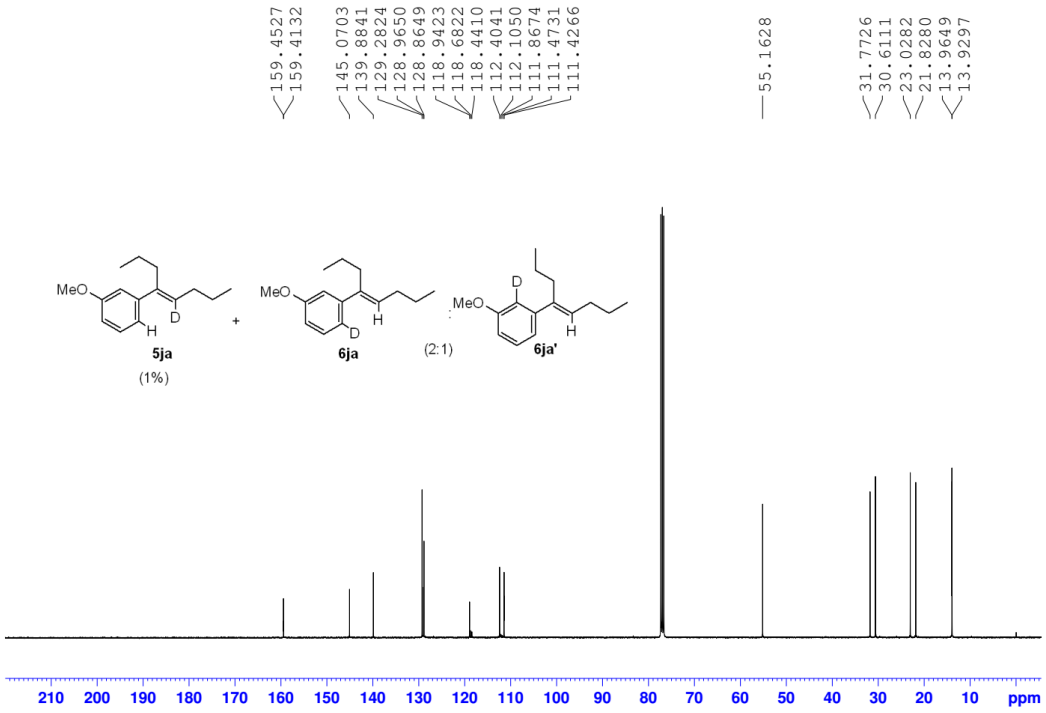

7.1315
5.6318
Me
D
H
5ia
(1:99)
Me
H
D
6ia
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
99.39
0.61

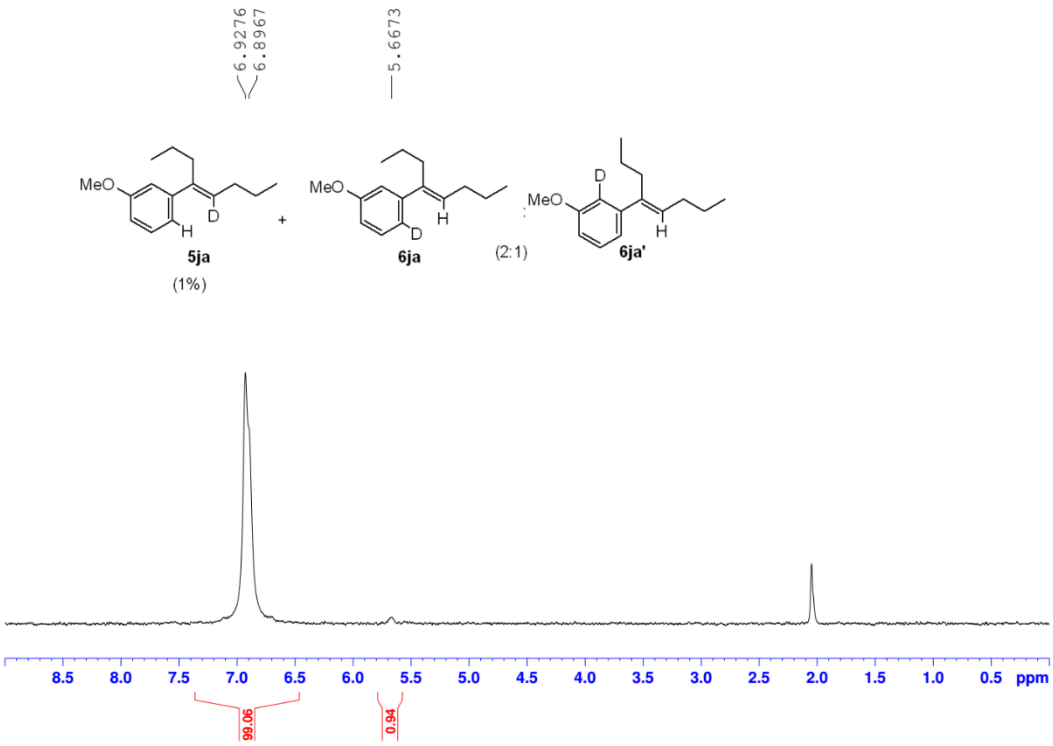

7.2334
7.2226
7.2022
7.1937
6.9521
6.9496
6.9464
6.9293
6.8914
6.8854
6.8815
6.7825
6.7763
6.7621
6.7558
5.6917
5.6736
5.6555
3.8188
2.4748
2.4560
2.4366
2.1984
2.1845
2.1663
2.1479
1.5161
1.4977
1.4793
1.4609
1.4424
1.4240
1.4186
1.3999
1.3812
1.3622
1.3435
1.3251
0.9818
0.9635
MeO
D
H
5ja
(80:20)
6ja
(4:1)
6ja'
0.9818
0.9635
0.9450
0.9019
0.8835
0.8651
0.95
0.90
0.85
ppm
6.95
6.90
6.85
6.80
6.75
6.70
6.65
ppm
0.834
0.964
1.000
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
0.83
0.96
1.00
0.23
3.18
2.14
2.09
2.07
2.22
6.50

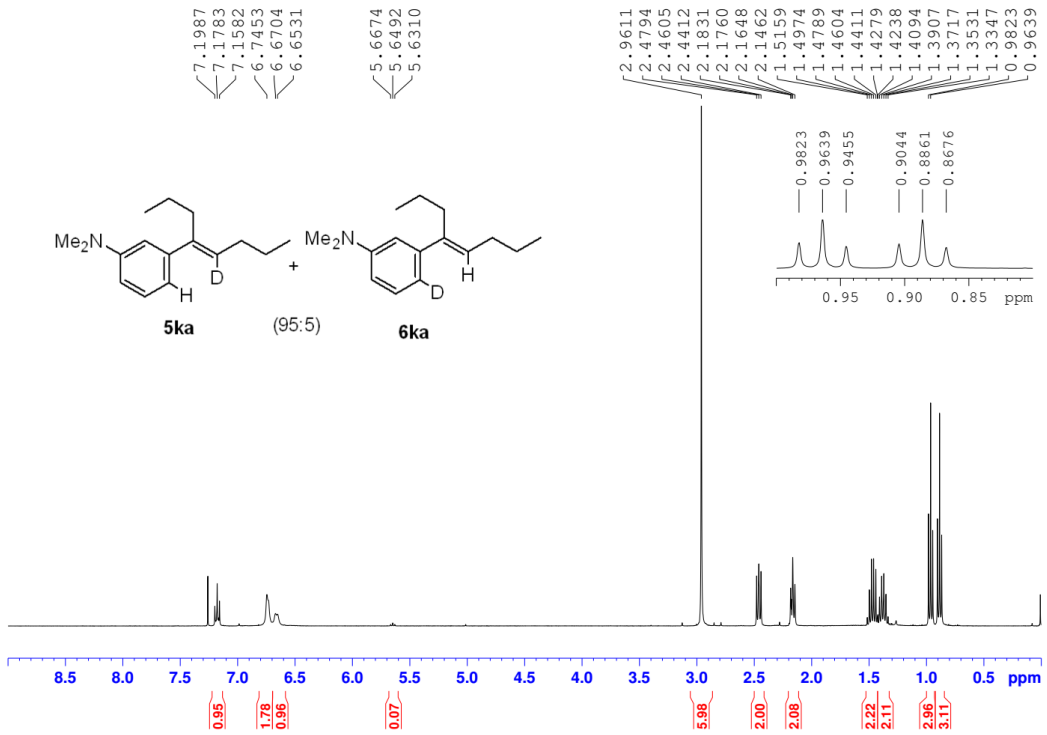

159.4652
145.1429
145.0837
139.8949
139.8379
129.2827
129.1690
128.9800
128.9412
128.8681
128.7102
118.9695
112.4333
111.4396
55.1713
31.7801
31.7457
30.6148
30.5095
23.0302
23.0101
21.8256
13.9661
13.9337
MeO
D
H
5ja
(80:20)
6ja
(4:1)
6ja'
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

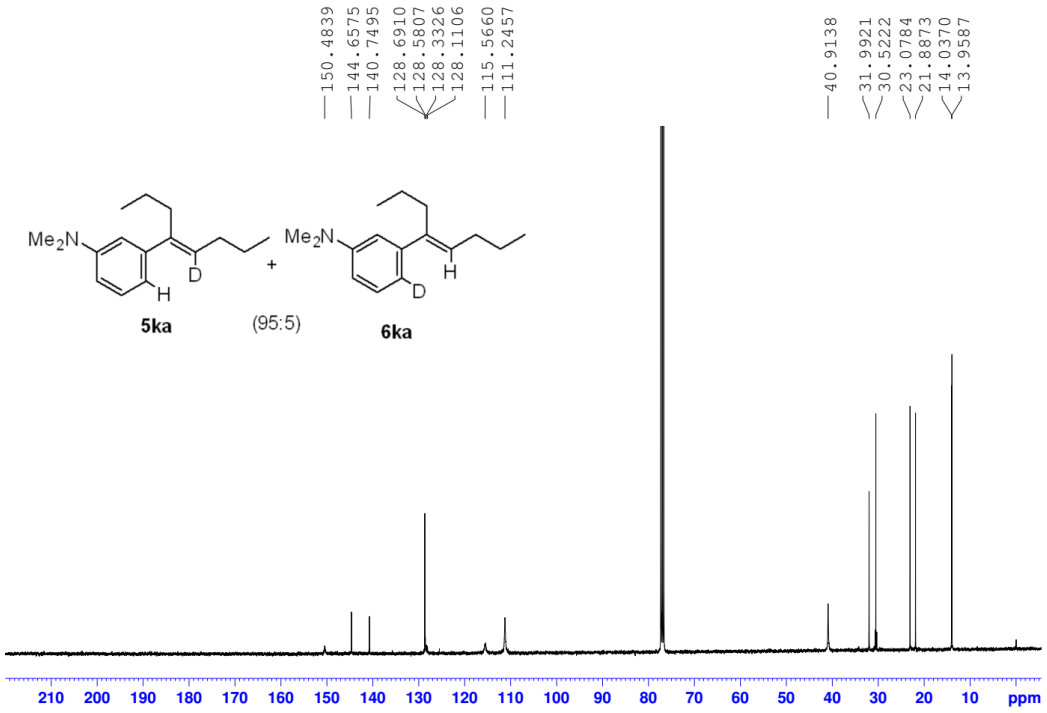

6.9352
5.6792
MeO
D
H
5ja
(80:20)
MeO
H
D
6ja
(4:1)
MeO
D
H
6ja'
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
20.02
79.98

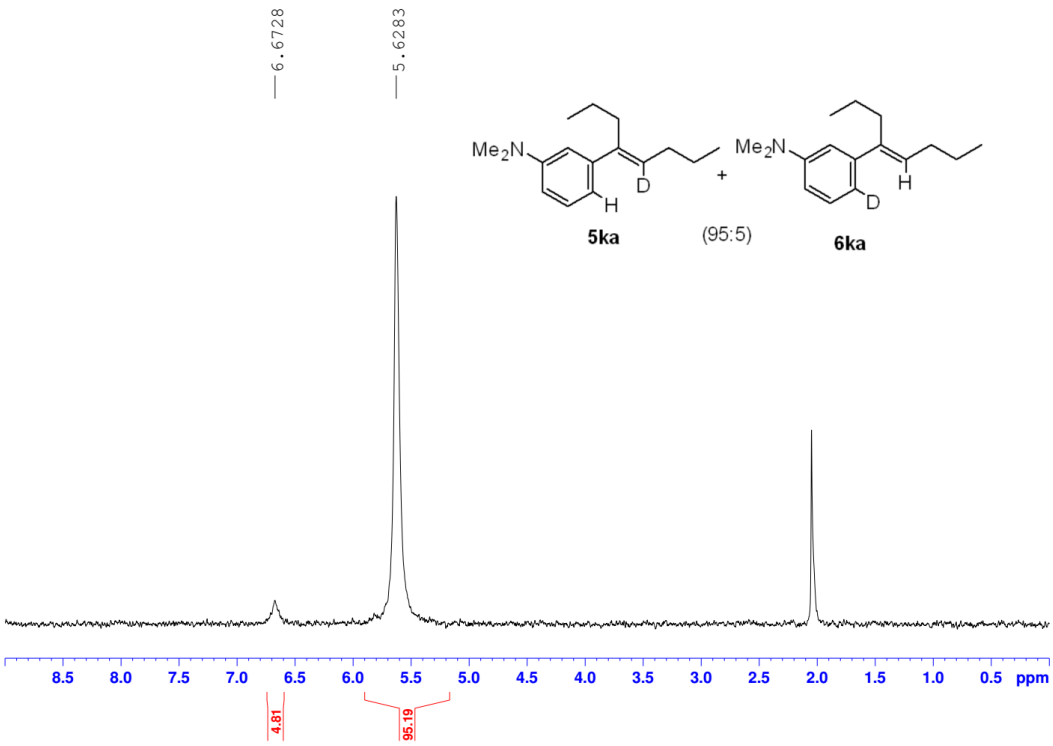

7.2356
7.2249
7.2158
7.2044
7.1960
6.9524
6.9333
6.8941
6.8877
6.7842
6.7787
6.7637
6.7582
5.6945
5.6764
5.6583
3.8204
2.4782
2.4595
2.4400
2.2008
2.1826
2.1642
2.1458
1.5194
1.5009
1.4825
1.4640
1.4456
1.4273
1.4215
1.4028
1.3840
1.3650
1.3464
1.3280
0.9844
0.9661
MeO
D
H
5ja
(1%)
MeO
H
D
6ja
(2:1)
MeO
D
H
6ja'
0.9844
0.9661
0.9477
0.9046
0.8863
0.8678
0.95
0.90
0.85
ppm
6.9524
6.9333
6.8941
6.8877
6.7842
6.7787
6.7637
6.7582
6.9
6.8
6.7
ppm
0.353
0.662
0.954
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.95
0.35
0.66
0.95
0.93
3.14
2.00
1.98
1.99
2.10
3.00
3.22

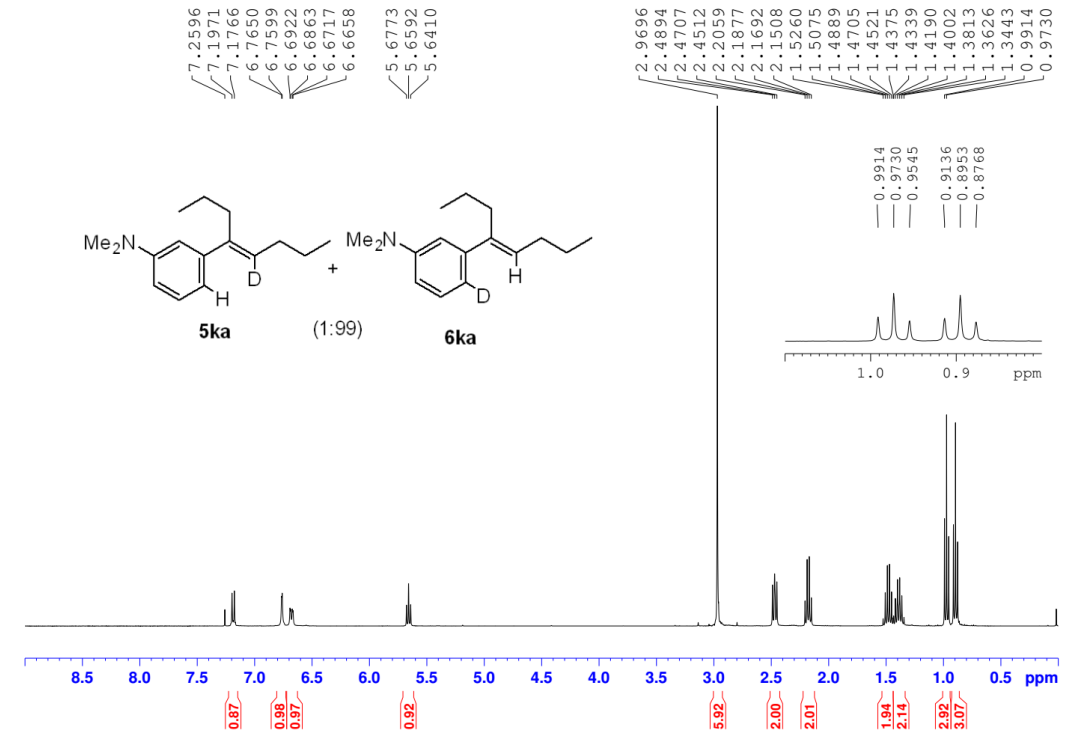

159.4527
159.4132
145.0703
139.8841
129.2824
128.9650
128.8649
118.9423
118.6822
118.4410
112.4041
112.1050
111.8674
111.4731
111.4266
55.1628
31.7726
30.6111
23.0282
21.8280
13.9649
13.9297
MeO
D
H
5ja
(1%)
MeO
H
D
6ja
(2:1)
MeO
D
H
6ja'
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

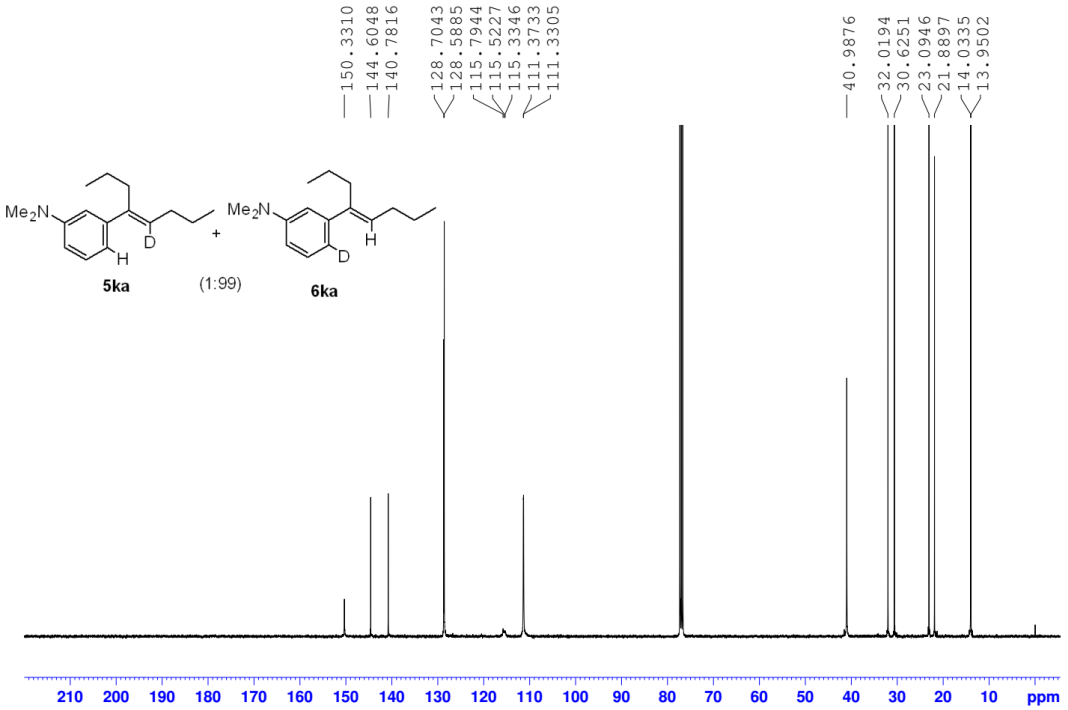

6.9276
6.8967
5.6673
MeO
D
H
5ja
(1%)
+
MeO
H
D
6ja
(2:1)
MeO
D
H
6ja'
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
99.06
0.94

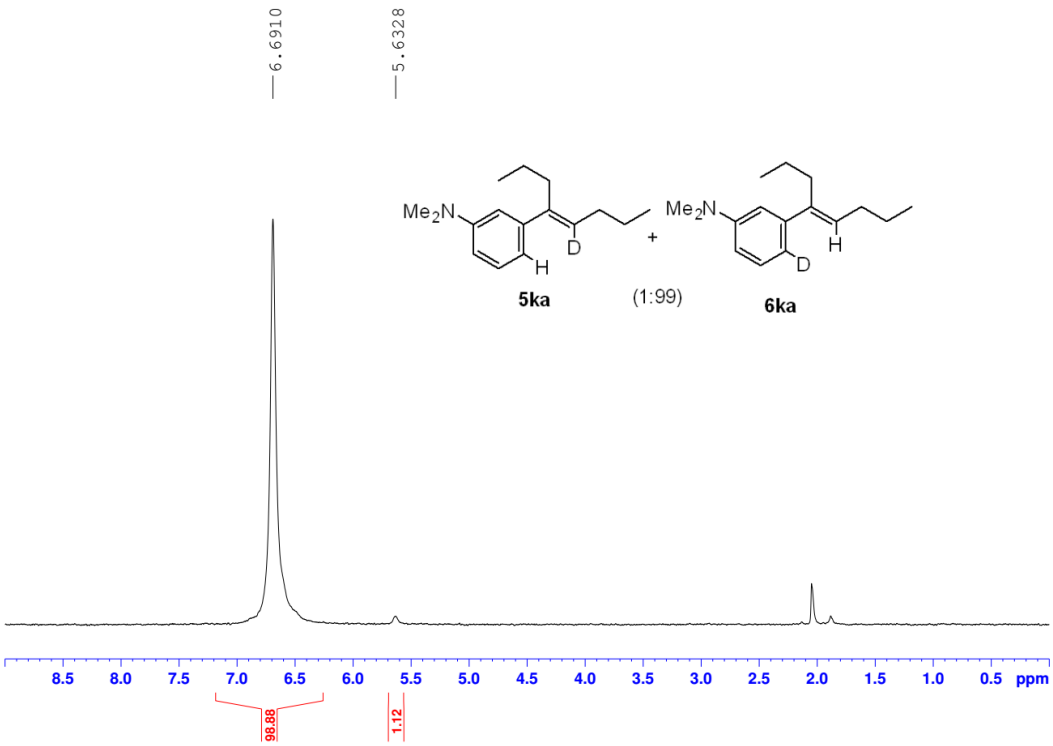

7.1987
7.1783
7.1582
6.7453
6.6704
6.6531
5.6674
5.6492
5.6310
2.9611
2.4794
2.4605
2.4412
2.1831
2.1760
2.1648
2.1462
1.5159
1.4974
1.4789
1.4604
1.4411
1.4279
1.4238
1.4094
1.3907
1.3717
1.3531
1.3347
0.9823
0.9639
0.9823
0.9639
0.9455
0.9044
0.8861
0.8676
0.95
0.90
0.85
ppm
Me2N
D
H
5ka
(95:5)
6ka
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.95
1.78
0.96
0.07
5.98
2.00
2.08
2.22
2.11
2.96
3.11

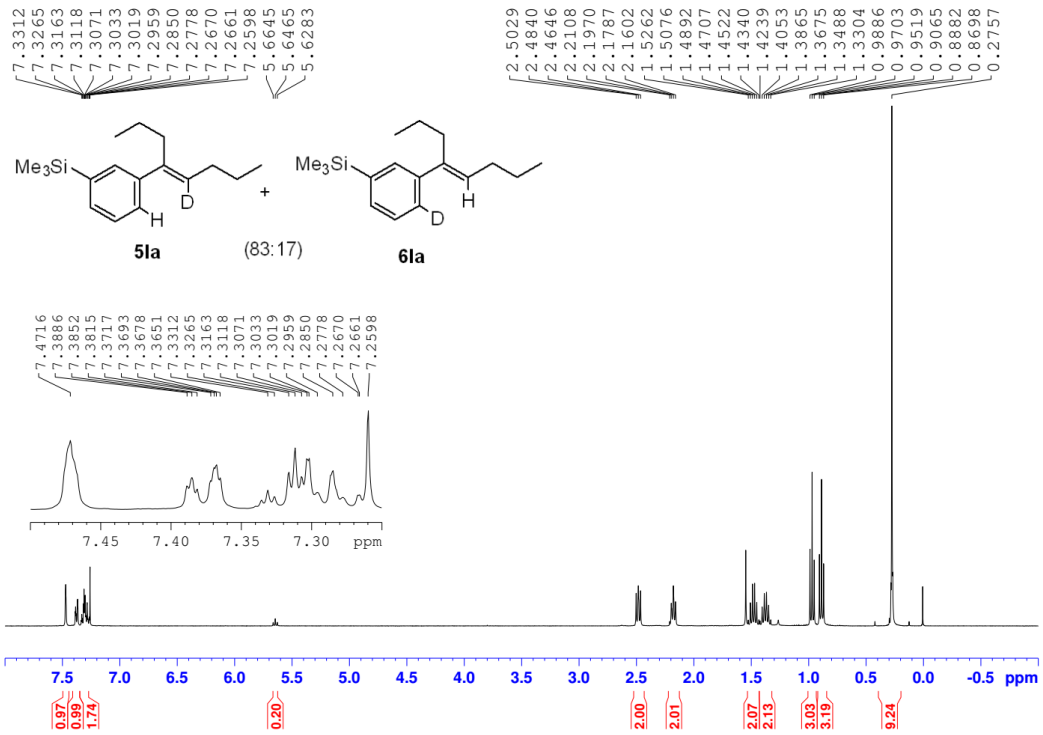

150.4839
144.6575
140.7495
128.6910
128.5807
128.3326
128.1106
115.5660
111.2457
40.9138
31.9921
30.5222
23.0784
21.8873
14.0370
13.9587
Me2N
D
H
5ka
(95:5)
6ka
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

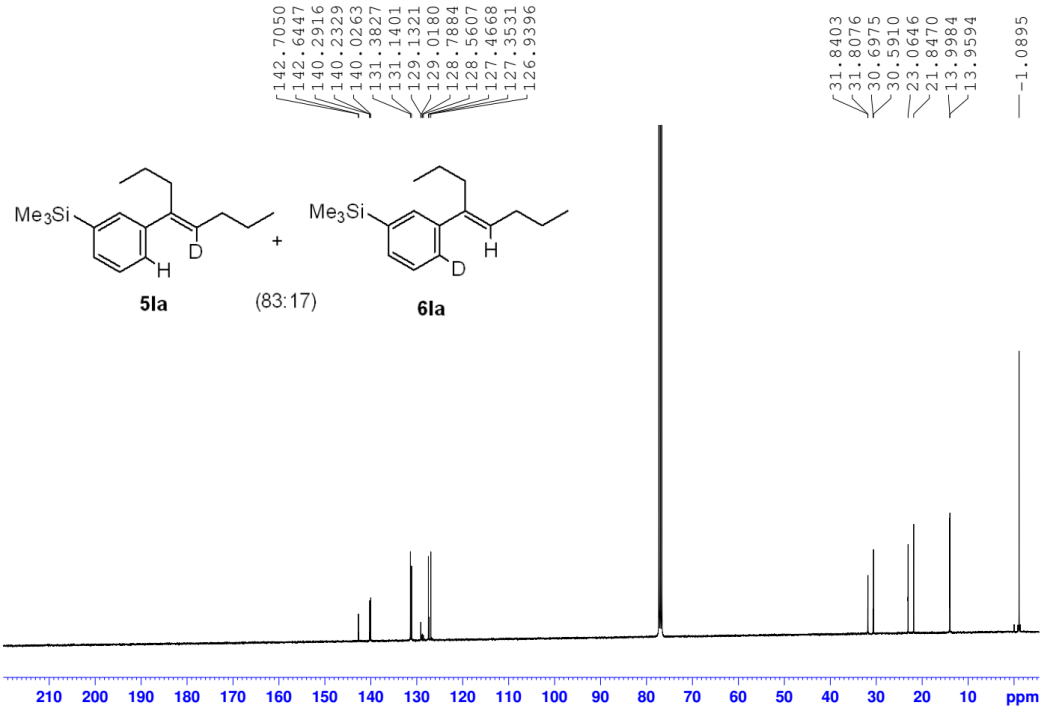

6.6728
5.6283
Me2N
D
H
5ka
(95:5)
Me2N
H
D
6ka
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
4.81
95.19

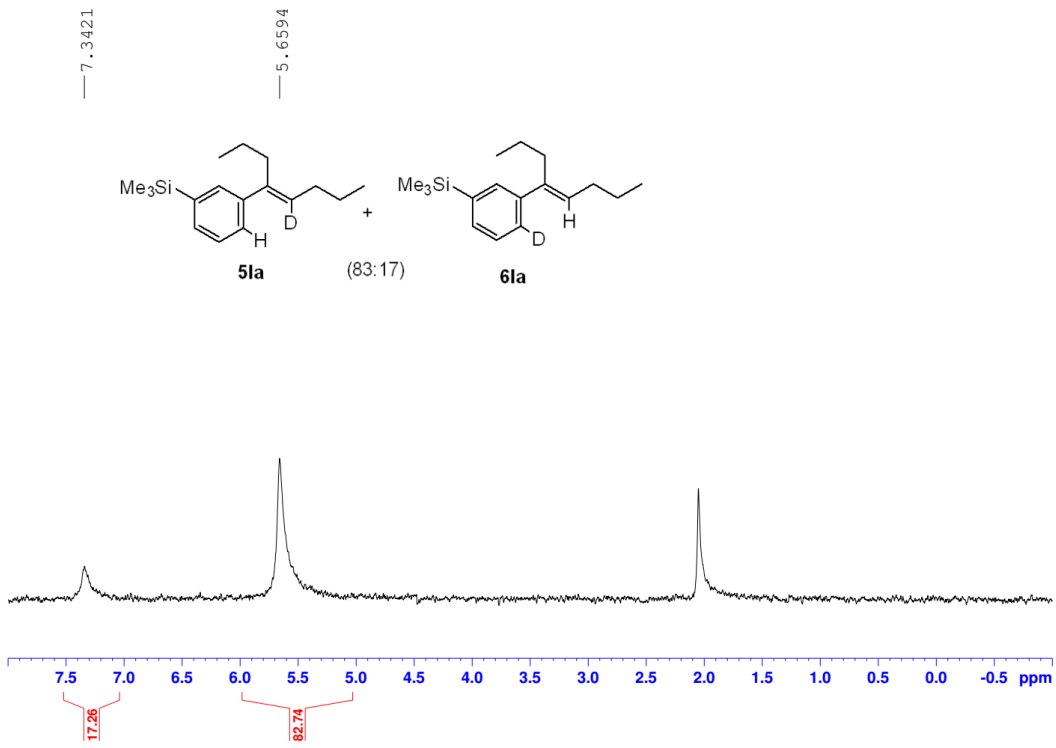

7.2596
7.1971
7.1766
6.7650
6.7599
6.6922
6.6863
6.6717
6.6658
5.6773
5.6592
5.6410
2.9696
2.4894
2.4707
2.4512
2.2059
2.1877
2.1692
2.1508
1.5260
1.5075
1.4889
1.4705
1.4521
1.4375
1.4339
1.4190
1.4002
1.3813
1.3626
1.3443
0.9914
0.9730
0.9914
0.9730
0.9545
0.9136
0.8953
0.8768
Me2N
D
H
5ka
(1:99)
Me2N
H
D
6ka
1.0
0.9
ppm
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.87
0.98
0.97
0.92
5.92
2.00
2.01
1.94
2.14
2.92
3.07

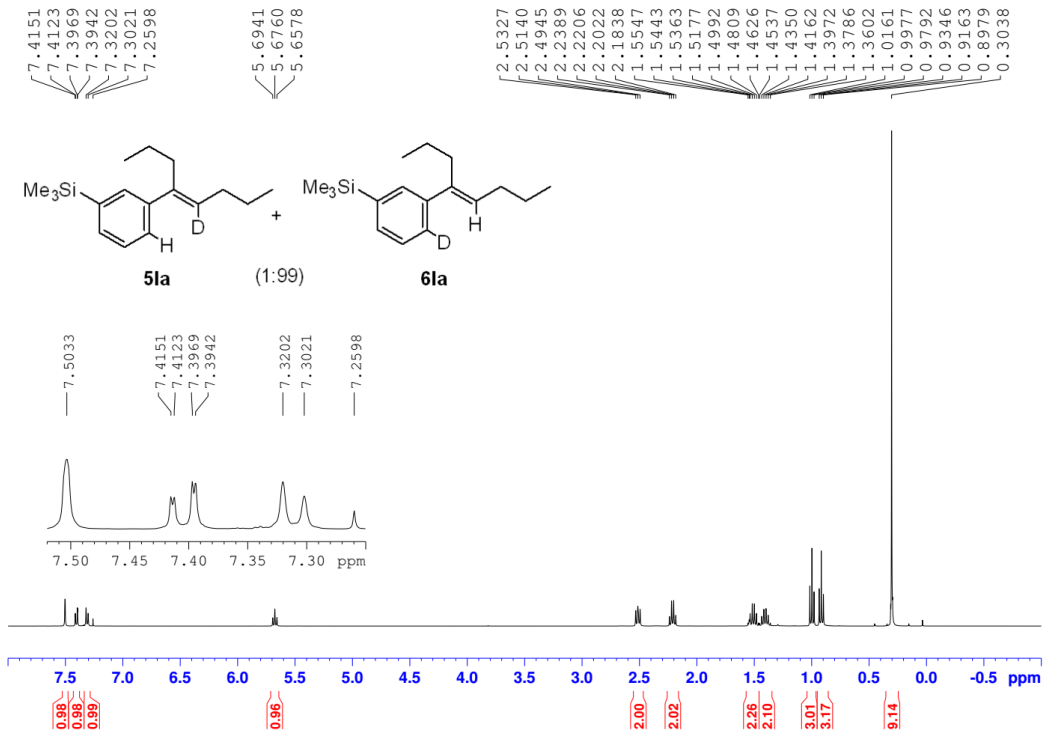

150.3310
144.6048
140.7816
128.7043
128.5885
115.7944
115.5227
115.3346
111.3733
111.3305
40.9876
32.0194
30.6251
23.0946
21.8897
14.0335
13.9502
Me2N
D
H
5ka
(1:99)
Me2N
H
D
6ka
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

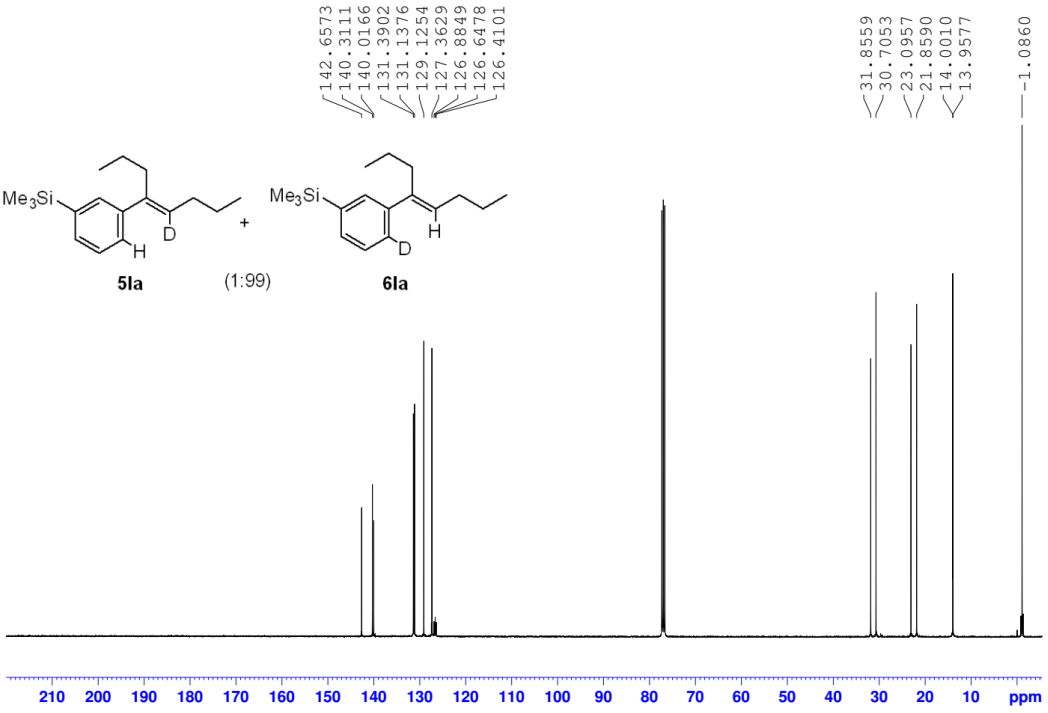

6.6910
5.6328
Me2N
D
H
+
Me2N
H
D
5ka
(1:99)
6ka
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
98.88
1.12

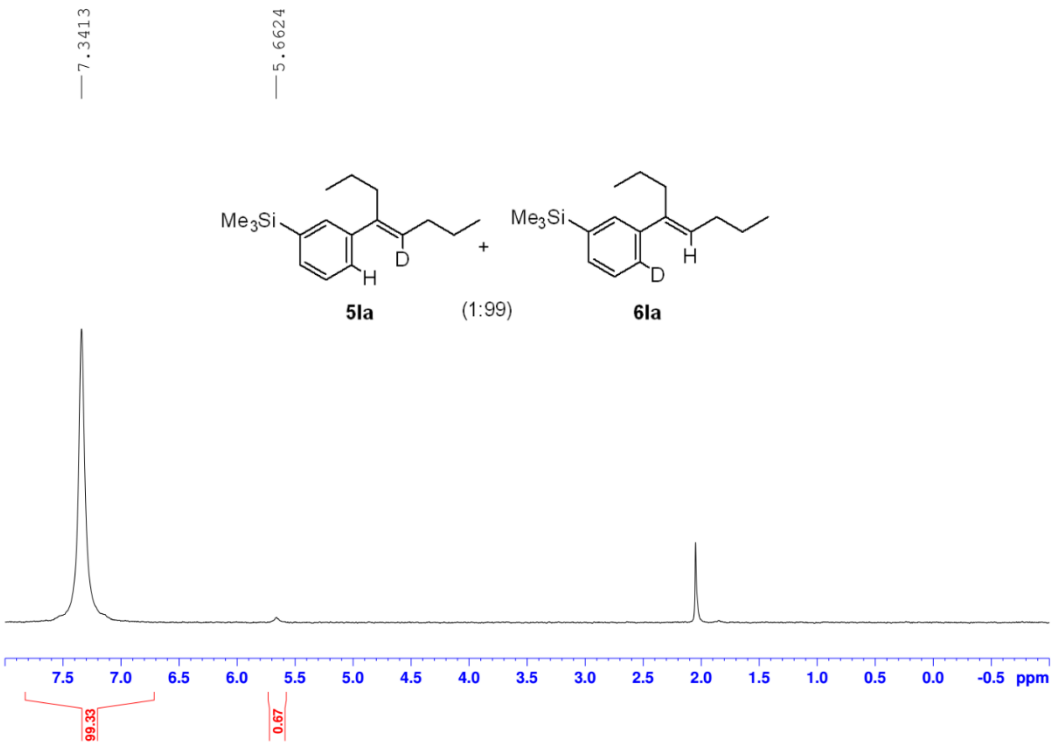

7.3312
7.3265
7.3163
7.3118
7.3071
7.3033
7.3019
7.2959
7.2850
7.2778
7.2670
7.2661
7.2598
5.6645
5.6465
5.6283
2.5029
2.4840
2.4646
2.2108
2.1970
2.1787
2.1602
1.5262
1.5076
1.4892
1.4707
1.4522
1.4340
1.4239
1.4053
1.3865
1.3675
1.3488
1.3304
0.9886
0.9703
0.9519
0.9065
0.8882
0.8698
0.2757
Me3Si
D
H
+
Me3Si
H
D
5la
(83:17)
6la
7.4716
7.3886
7.3852
7.3815
7.3717
7.3693
7.3678
7.3651
7.3312
7.3265
7.3163
7.3118
7.3071
7.3033
7.3019
7.2959
7.2850
7.2778
7.2670
7.2661
7.2598
7.45
7.40
7.35
7.30
ppm
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm
0.97
0.99
1.74
0.20
2.00
2.01
2.07
2.13
3.03
3.19
9.24

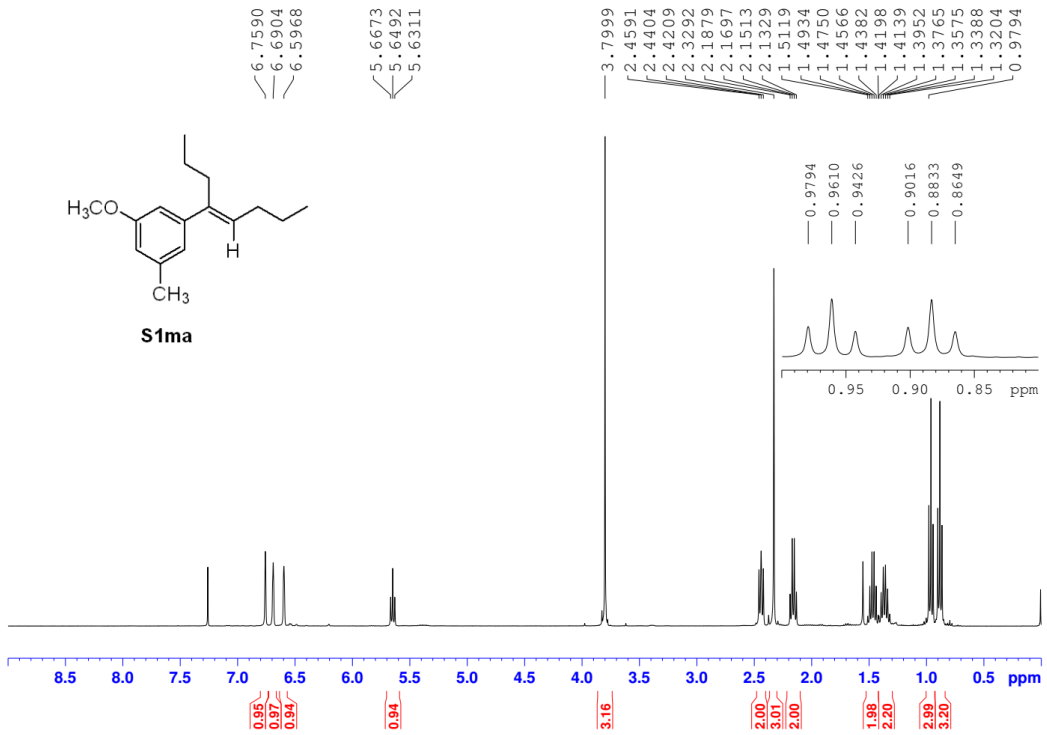

142.7050
142.6447
140.2916
140.2329
140.0263
131.3827
131.1401
129.1321
129.0180
128.7884
128.5607
127.4668
127.3531
126.9396
31.8403
31.8076
30.6975
30.5910
23.0646
21.8470
13.9984
13.9594
-1.0895
Me3Si
D
H
+
Me3Si
H
D
5la
(83:17)
6la
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

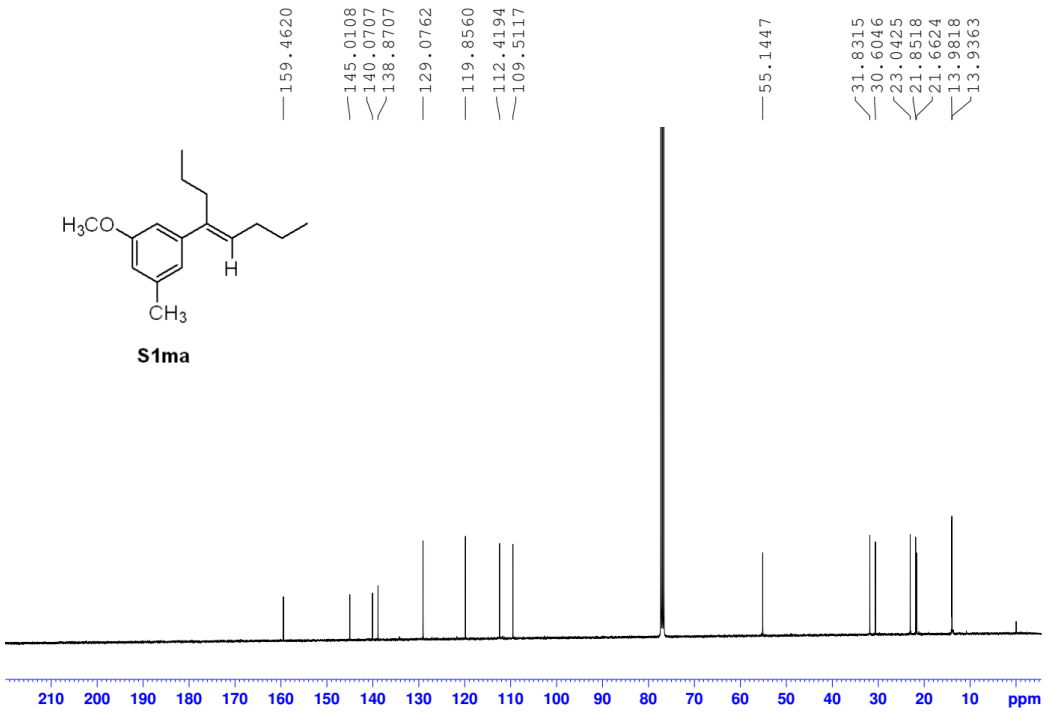

7.3421
5.6594
Me3Si
D
H
+
Me3Si
H
D
5la
(83:17)
6la
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm
17.26
82.74

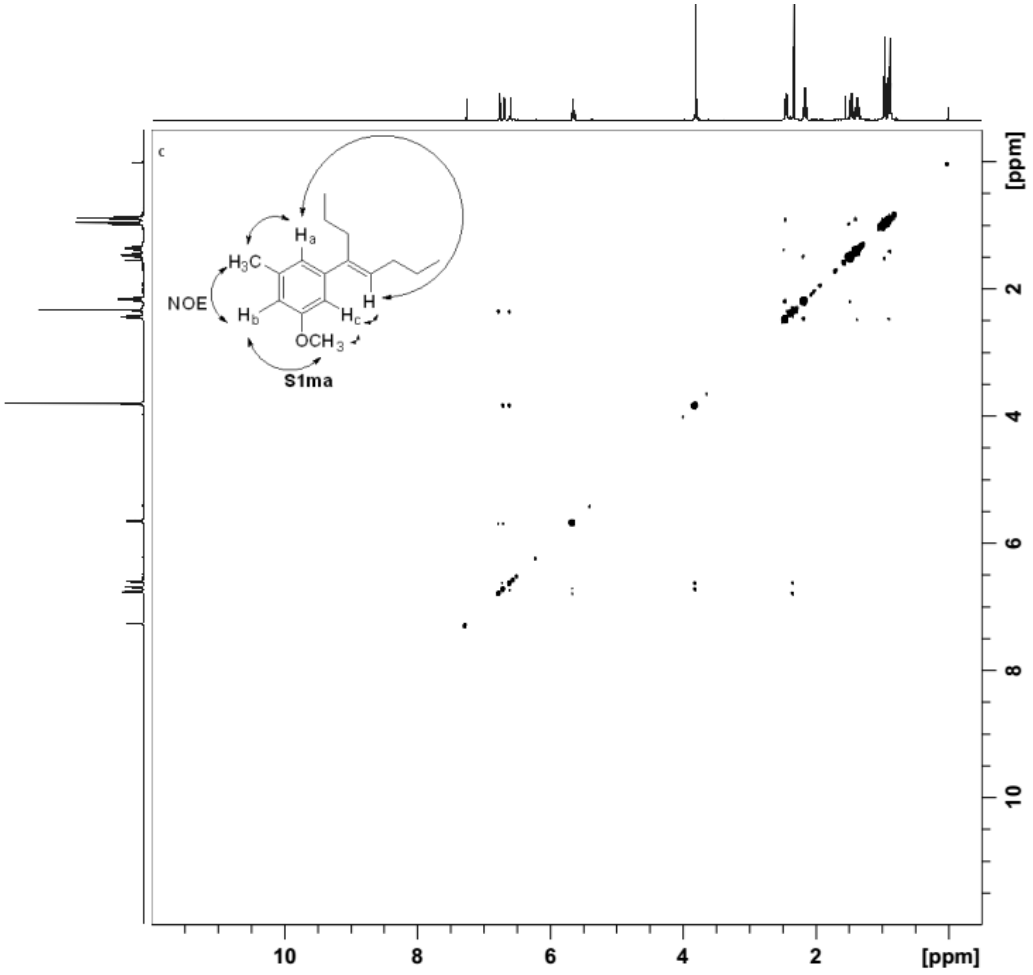

7.4151
7.4123
7.3969
7.3942
7.3202
7.3021
7.2598
5.6941
5.6760
5.6578
2.5327
2.5140
2.4945
2.2389
2.2206
2.2022
2.1838
1.5547
1.5443
1.5363
1.5177
1.4992
1.4809
1.4626
1.4537
1.4350
1.4162
1.3972
1.3786
1.3602
1.0161
0.9977
0.9792
0.9346
0.9163
0.8979
0.3038
Me3Si
D
H
+
Me3Si
H
D
5la
(1:99)
6la
7.5033
7.4151
7.4123
7.3969
7.3942
7.3202
7.3021
7.2598
7.50 7.45 7.40 7.35 7.30 ppm
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
0.98
0.98
0.99
0.96
2.00
2.02
2.26
2.10
3.01
3.17
9.14

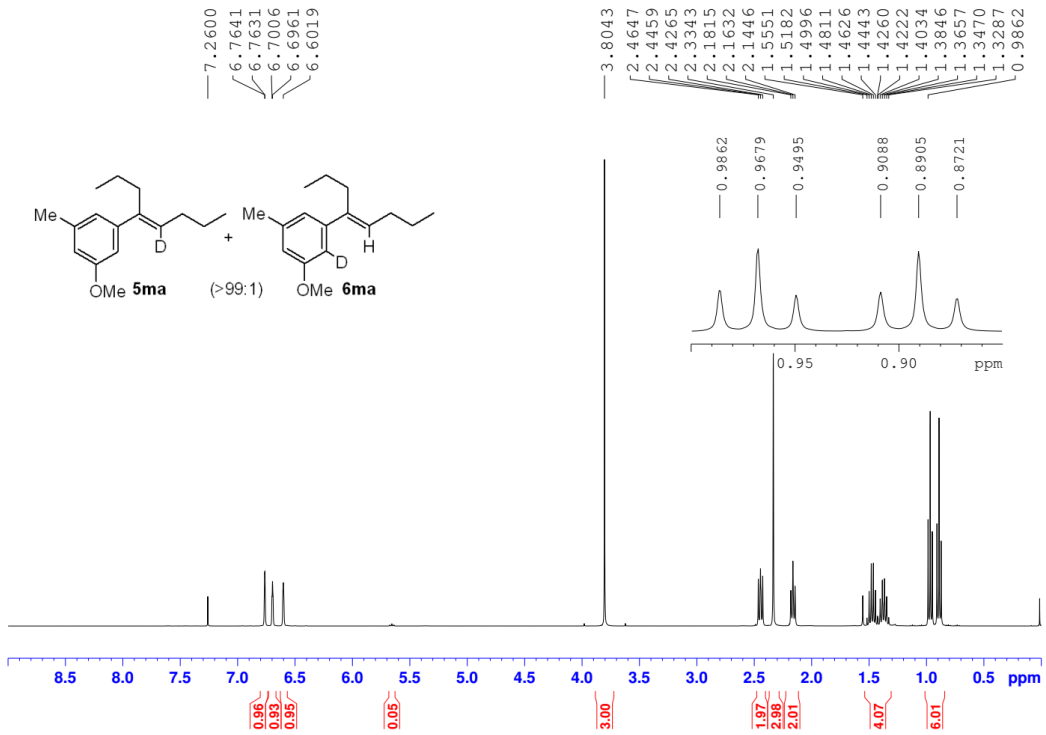

142.6573
140.3111
140.0166
131.3902
131.1376
129.1254
127.3629
126.8849
126.6478
126.4101
31.8559
30.7053
23.0957
21.8590
14.0010
13.9577
-1.0860
Me3Si
D
H
+
Me3Si
H
D
5la
(1:99)
6la
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

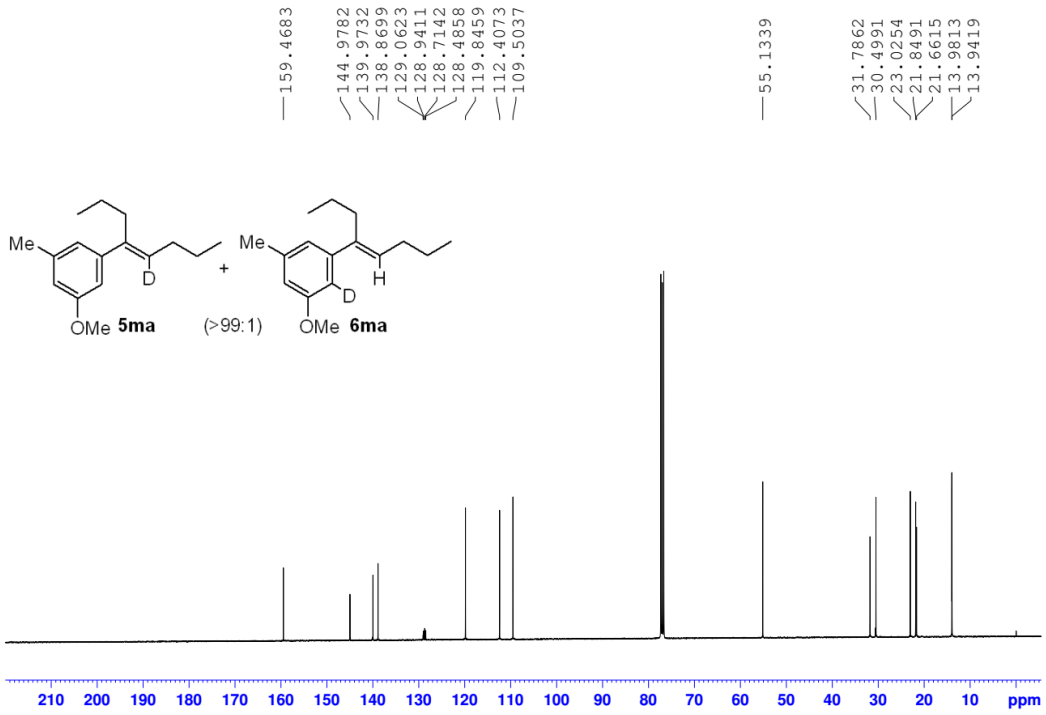

7.3413
5.6624
Me3Si
D
H
+
Me3Si
H
D
5la
(1:99)
6la
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm
99.33
0.67

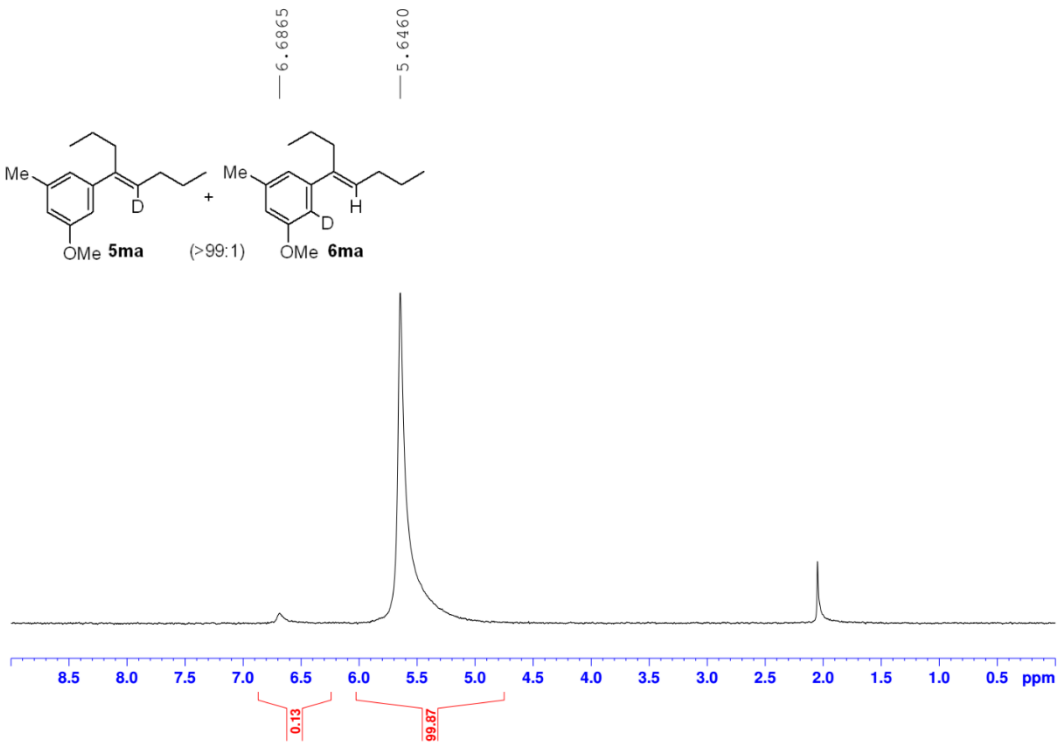

6.7590
6.6904
6.5968
5.6673
5.6492
5.6311
3.7999
2.4591
2.4404
2.4209
2.3292
2.1879
2.1697
2.1513
2.1329
1.5119
1.4934
1.4750
1.4566
1.4382
1.4198
1.4139
1.3952
1.3765
1.3575
1.3388
1.3204
0.9794
0.9794
0.9610
0.9426
0.9016
0.8833
0.8649
0.95
0.90
0.85
ppm
H3CO
H
CH3
S1ma
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.95
0.97
0.94
0.94
3.16
2.00
3.01
2.00
1.98
2.20
2.99
3.20

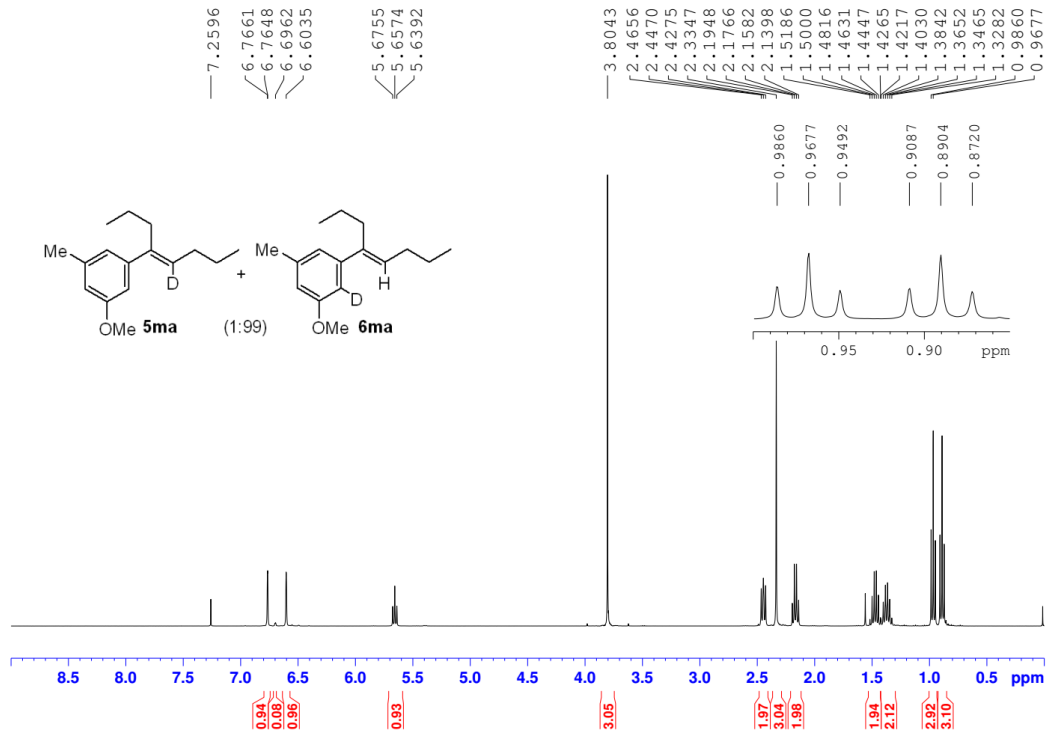

159.4620
145.0108
140.0707
138.8707
129.0762
119.8560
112.4194
109.5117
55.1447
31.8315
30.6046
23.0425
21.8518
21.6624
13.9818
13.9363
H3CO
H
CH3
S1ma
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

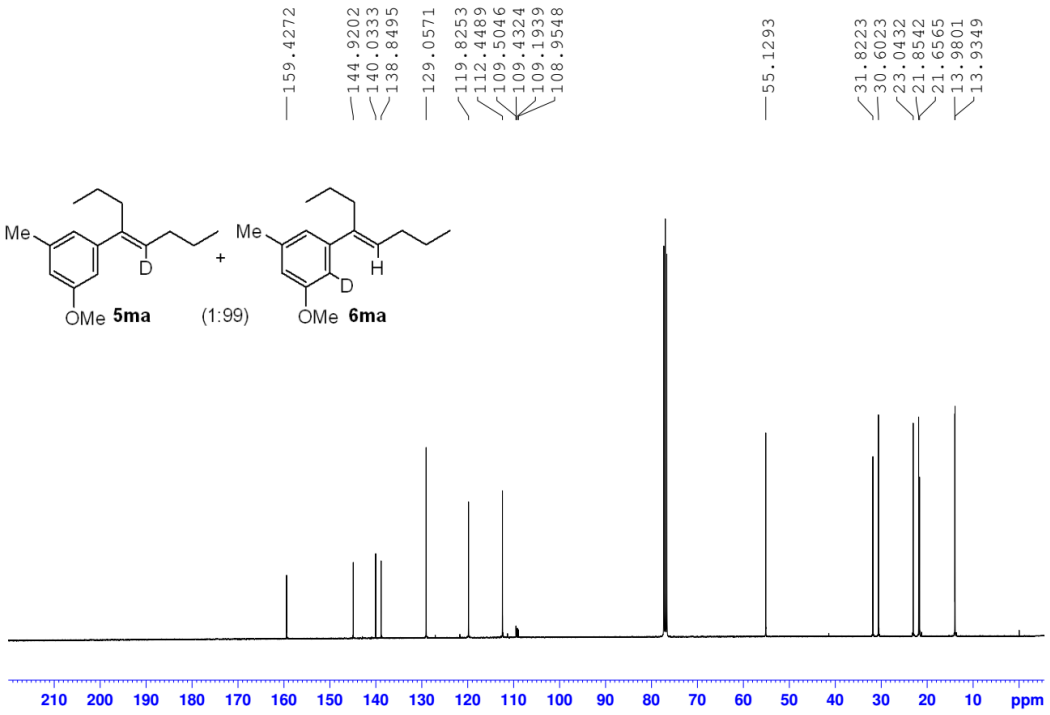

c
$H_a$
$H_3C$
NOE
$H_b$
$H_c$
H
$OCH_3$
S1ma
10
8
6
4
2
[ppm]
2
4
6
8
10
[ppm]

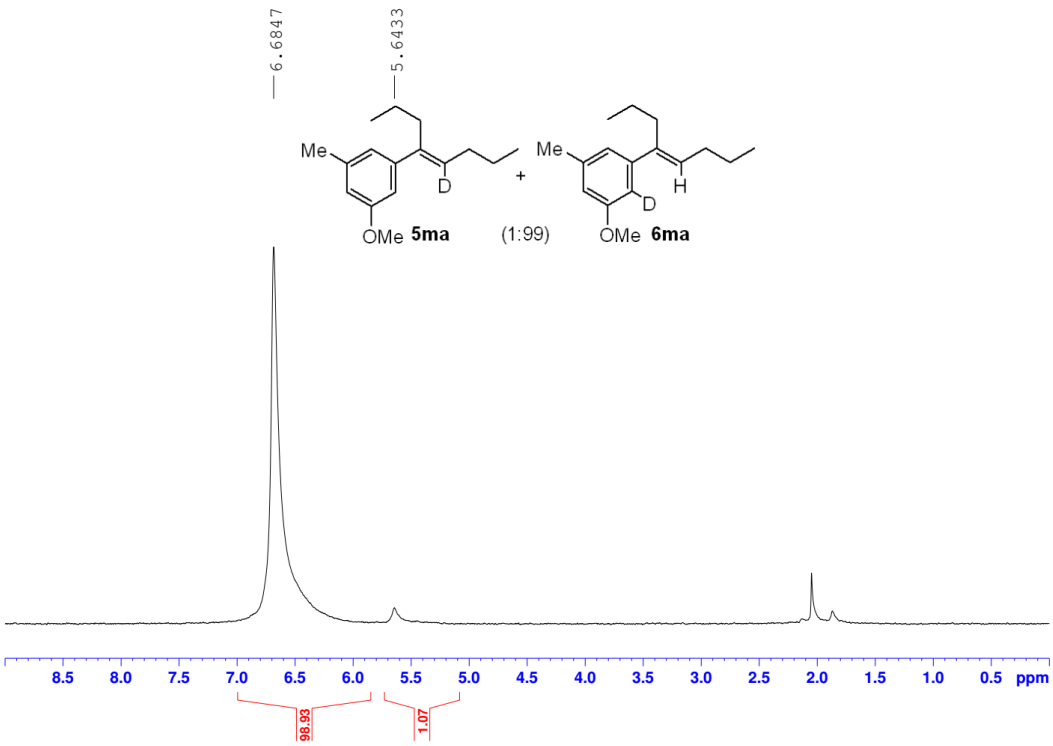

7.2600
6.7641
6.7631
6.7006
6.6961
6.6019
3.8043
2.4647
2.4459
2.4265
2.3343
2.1815
2.1632
2.1446
1.5551
1.5182
1.4996
1.4811
1.4626
1.4443
1.4260
1.4222
1.4034
1.3846
1.3657
1.3470
1.3287
0.9862
0.9862
0.9679
0.9495
0.9088
0.8905
0.8721
0.95
0.90
ppm
Me
D
OMe 5ma
(>99:1)
Me
H
D
OMe 6ma
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.96
0.93
0.95
0.05
3.00
1.97
2.98
2.01
4.07
6.01

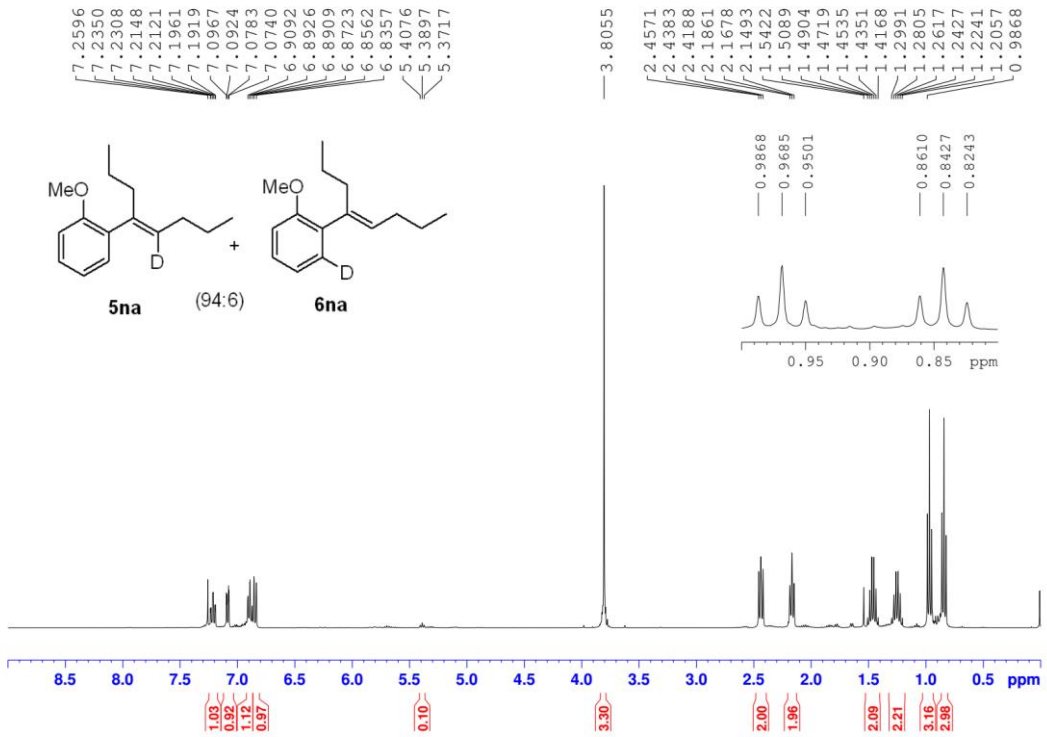

159.4683
144.9782
139.9732
138.8699
129.0623
128.9411
128.7142
128.4858
119.8459
112.4073
109.5037
55.1339
31.7862
30.4991
23.0254
21.8491
21.6615
13.9813
13.9419
Me
D
OMe 5ma
(>99:1)
Me
H
D
OMe 6ma
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

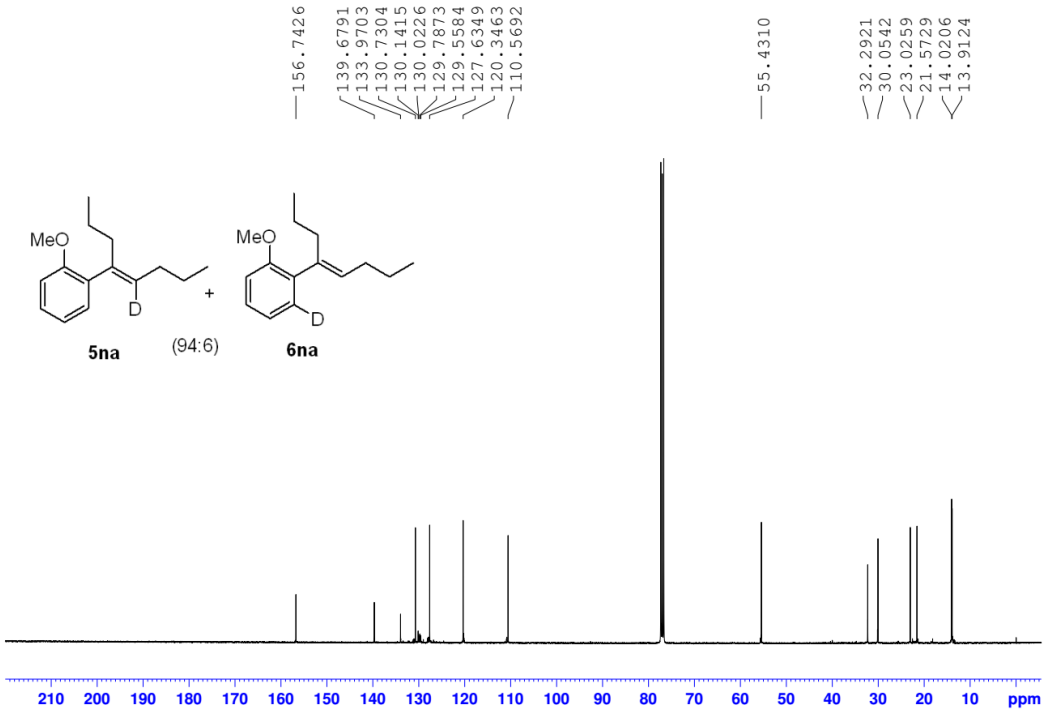

6.6865
5.6460
Me
D
OMe
5ma
(>99:1)
Me
H
D
OMe
6ma
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.13
99.87

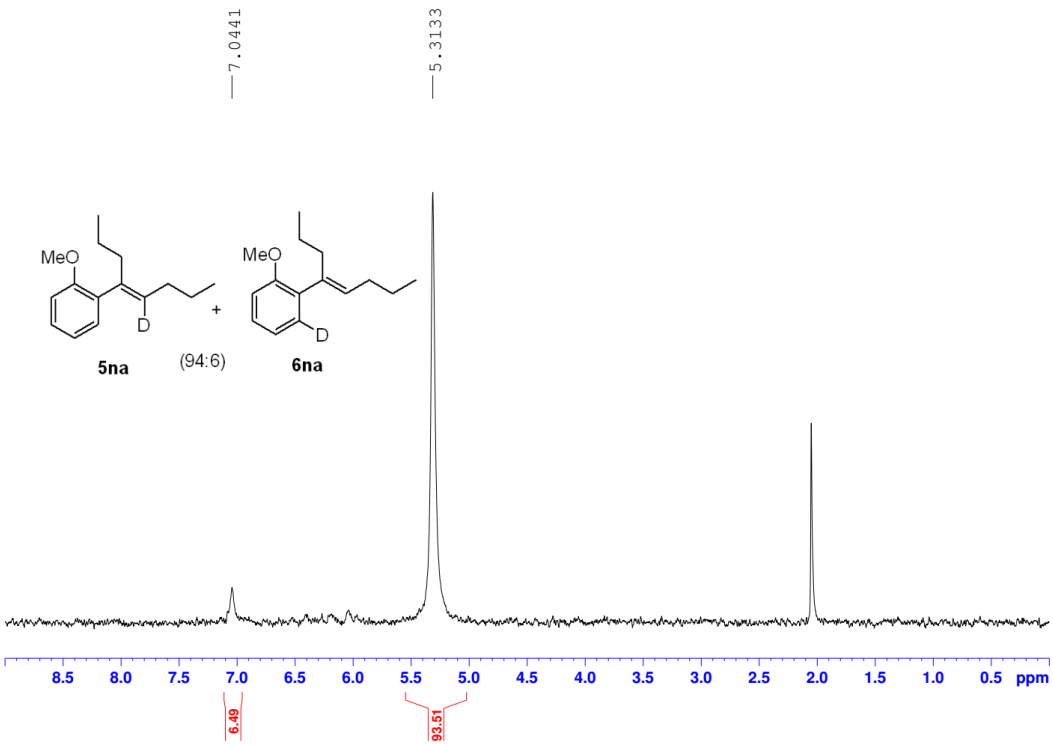

7.2596
6.7661
6.7648
6.6962
6.6035
5.6755
5.6574
5.6392
3.8043
2.4656
2.4470
2.4275
2.3347
2.1948
2.1766
2.1582
2.1398
1.5186
1.5000
1.4816
1.4631
1.4447
1.4265
1.4217
1.4030
1.3842
1.3652
1.3465
1.3282
0.9860
0.9677
0.9860
0.9677
0.9492
0.9087
0.8904
0.8720
Me
D
OMe 5ma
(1:99)
Me
H
D
OMe 6ma
0.95
0.90
ppm
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.94
0.08
0.96
0.93
3.05
1.97
3.04
1.98
1.94
2.12
2.92
3.10

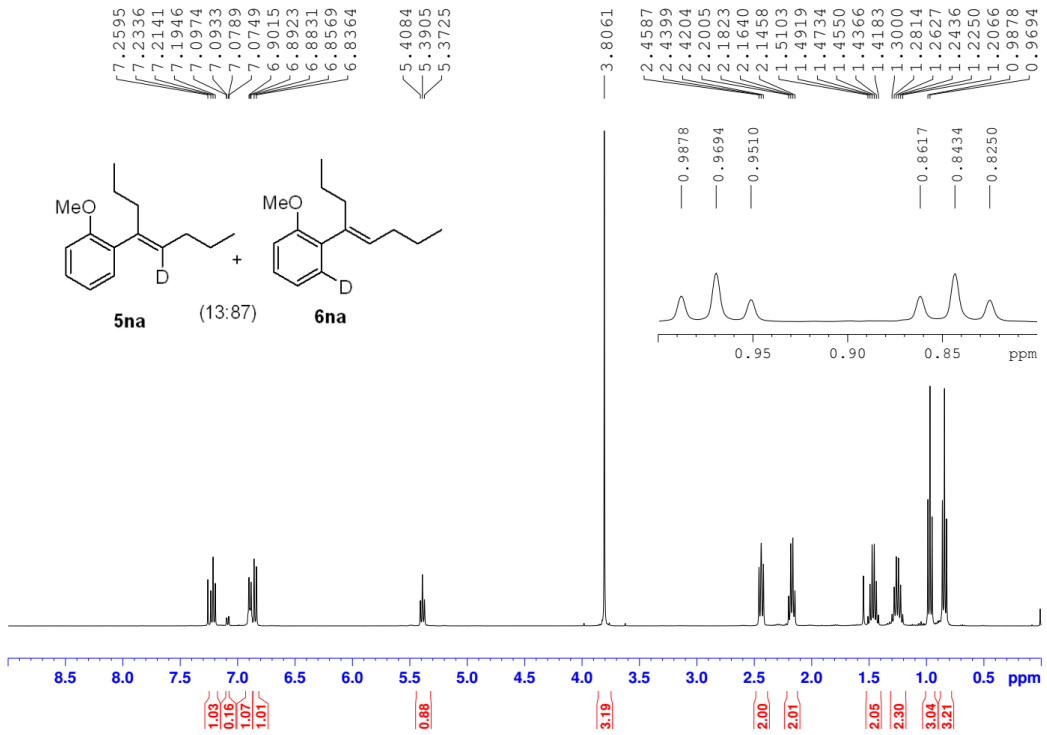

159.4272
144.9202
140.0333
138.8495
129.0571
119.8253
112.4489
109.5046
109.4324
109.1939
108.9548
55.1293
31.8223
30.6023
23.0432
21.8542
21.6565
13.9801
13.9349
Me
D
OMe 5ma
(1:99)
Me
H
D
OMe 6ma
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

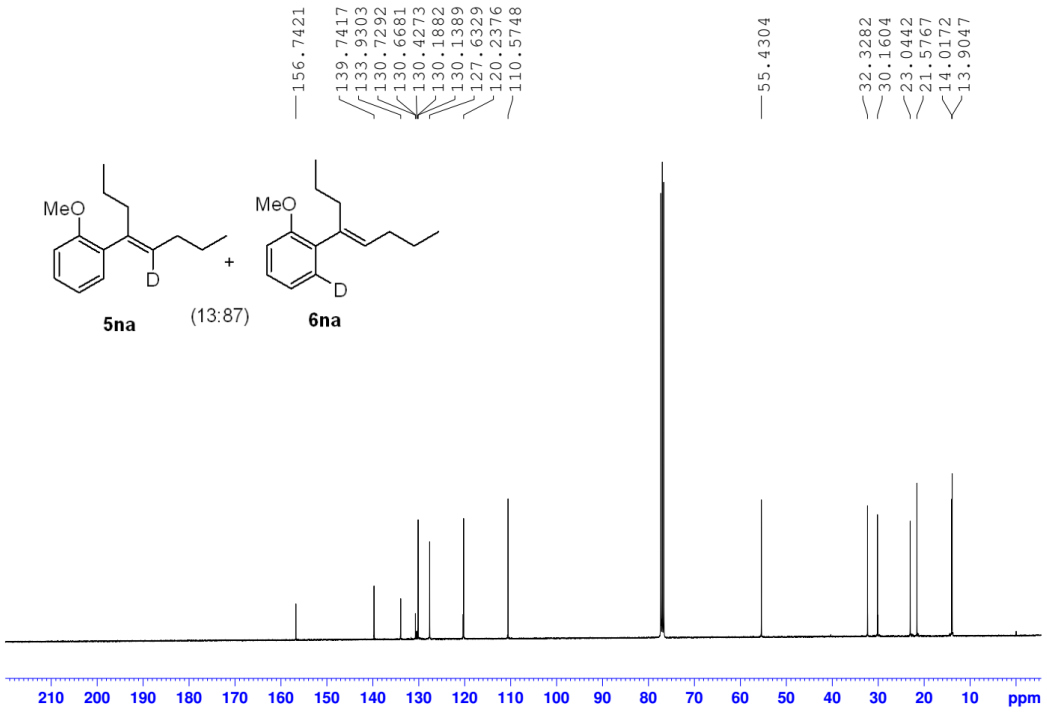

6.6847
5.6433
Me
D
OMe
5ma
+
Me
H
D
OMe
6ma
(1:99)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
98.93
1.07


7.2596
7.2350
7.2308
7.2148
7.2121
7.1961
7.1919
7.0967
7.0924
7.0783
7.0740
6.9092
6.8926
6.8909
6.8723
6.8562
6.8357
5.4076
5.3897
5.3717
3.8055
2.4571
2.4383
2.4188
2.1861
2.1678
2.1493
1.5422
1.5089
1.4904
1.4719
1.4535
1.4351
1.4168
1.2991
1.2805
1.2617
1.2427
1.2241
1.2057
0.9868
MeO
D
+
5na
(94:6)
6na
0.9868
0.9685
0.9501
0.8610
0.8427
0.8243
0.95
0.90
0.85
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.03
0.92
1.12
0.97
0.10
3.30
2.00
1.96
2.09
2.21
3.16
2.96


156.7426
139.6791
133.9703
130.7304
130.1415
130.0226
129.7873
129.5584
127.6349
120.3463
110.5692
55.4310
32.2921
30.0542
23.0259
21.5729
14.0206
13.9124
MeO
D
+
5na
(94:6)
6na
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.0441
5.3133
MeO
D
+
MeO
D
5na
(94:6)
6na
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
6.49
93.51


7.2595
7.2336
7.2141
7.1946
7.0974
7.0933
7.0789
7.0749
6.9015
6.8923
6.8831
6.8569
6.8364
5.4084
5.3905
5.3725
3.8061
2.4587
2.4399
2.4204
2.2005
2.1823
2.1640
2.1458
1.5103
1.4919
1.4734
1.4550
1.4366
1.4183
1.3000
1.2814
1.2627
1.2436
1.2250
1.2066
0.9878
0.9694
0.9878
0.9694
0.9510
0.8617
0.8434
0.8250
MeO
D
+
MeO
D
5na
(13:87)
6na
0.95
0.90
0.85
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.03
0.16
1.07
1.01
0.88
3.19
2.00
2.01
2.05
2.30
3.04
3.21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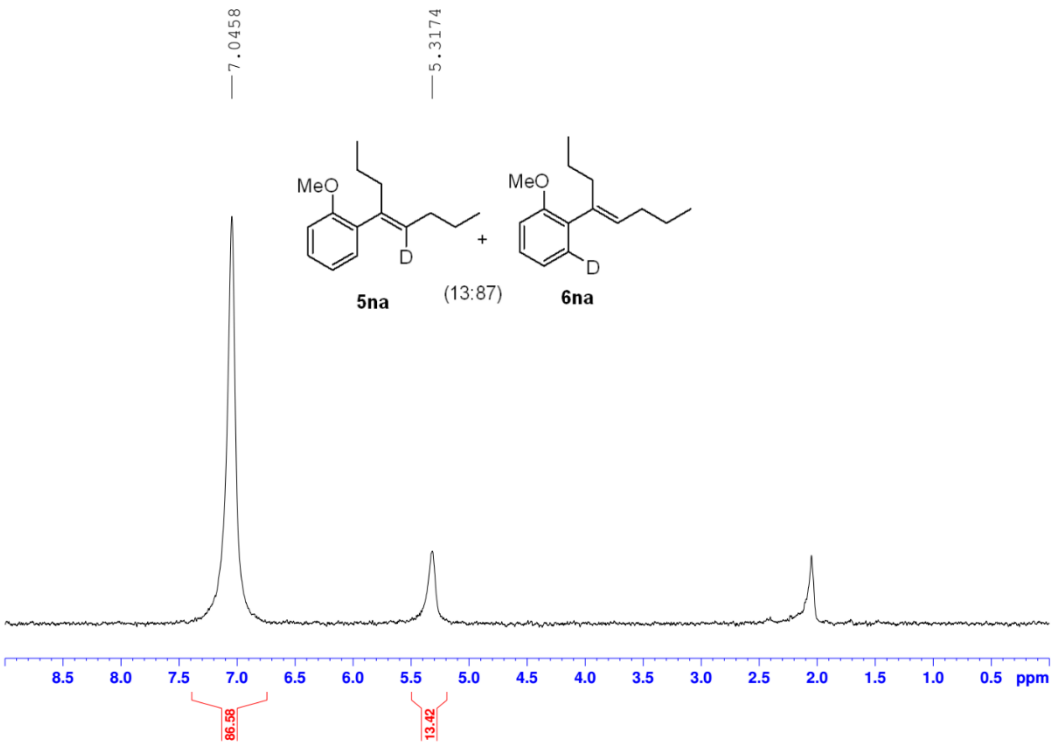
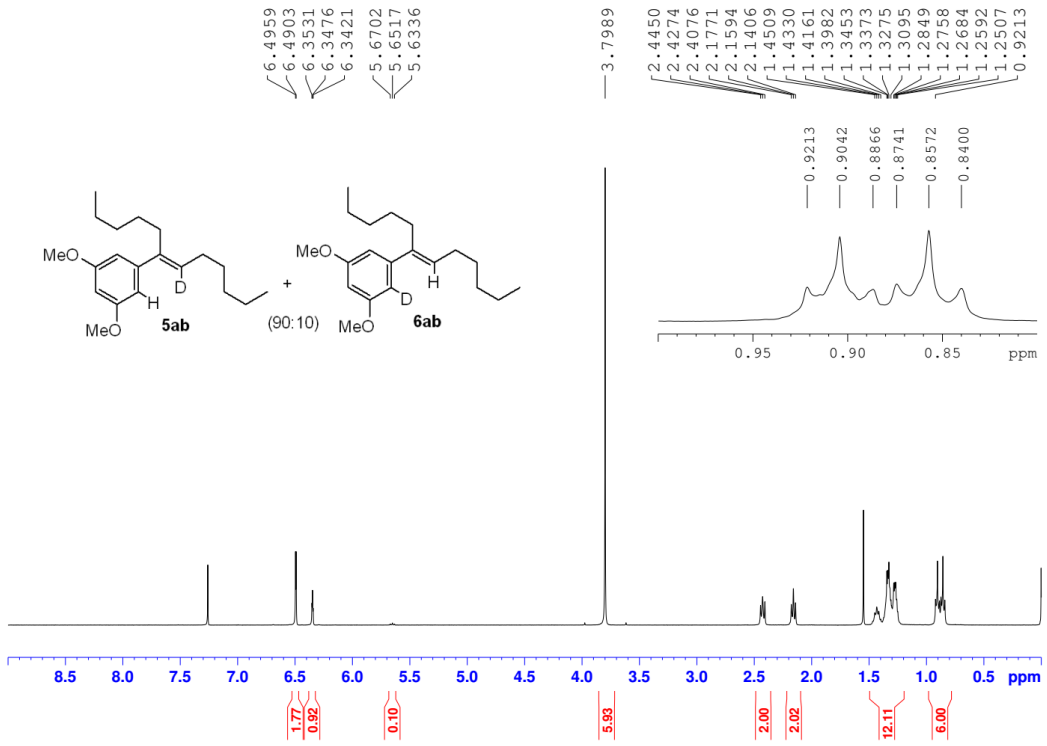
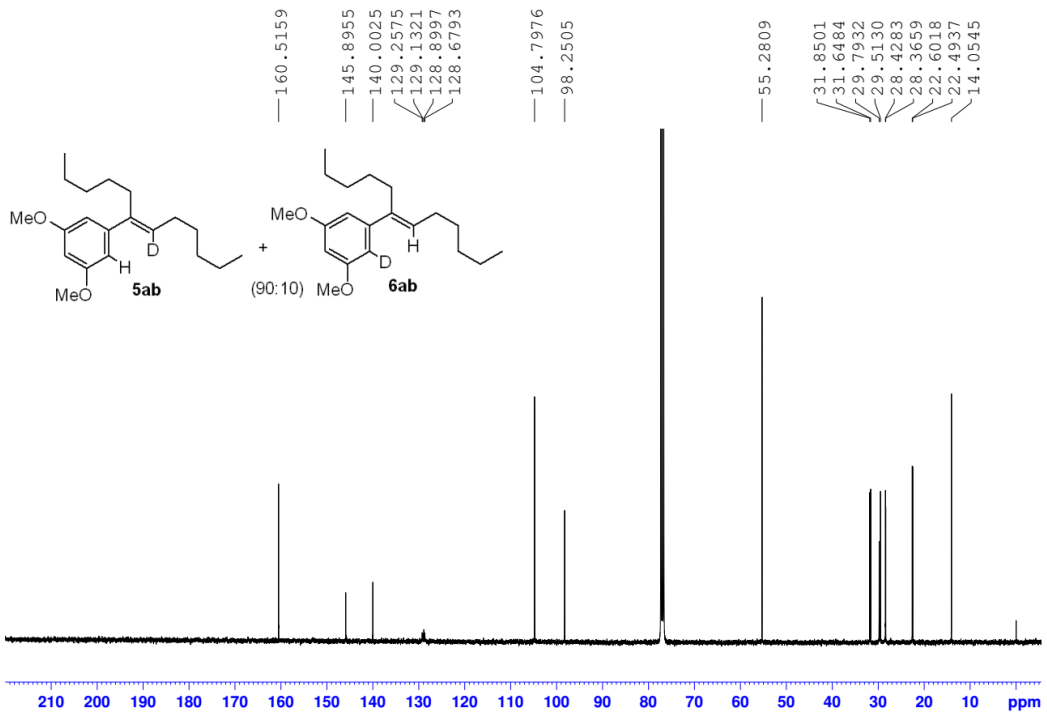
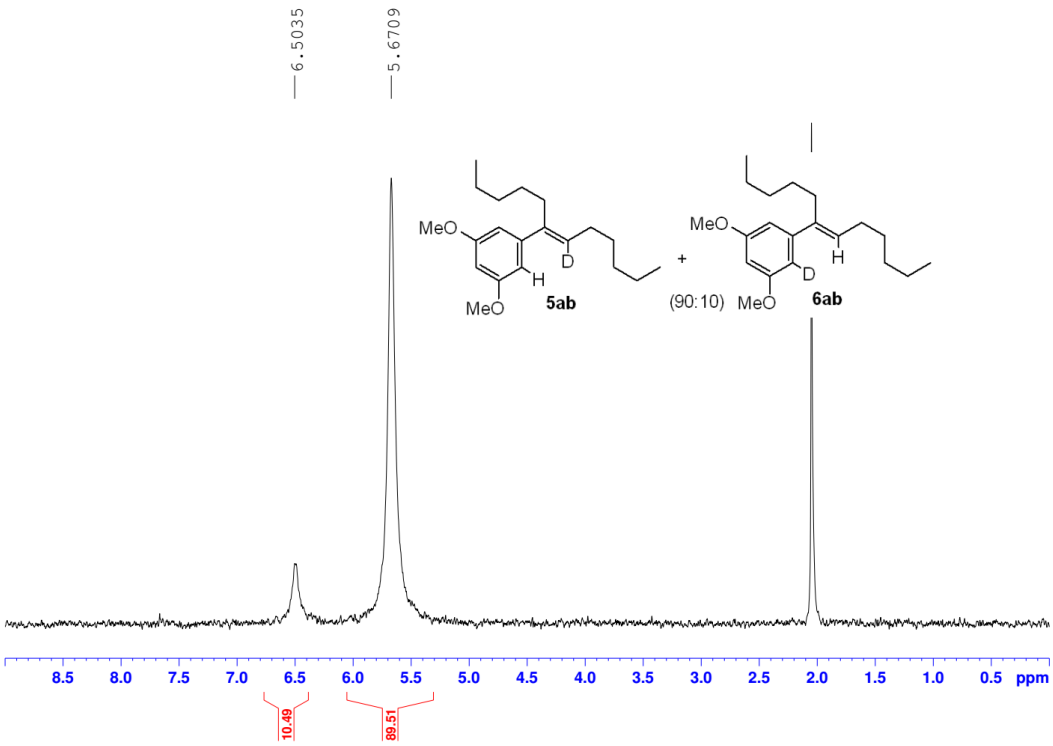
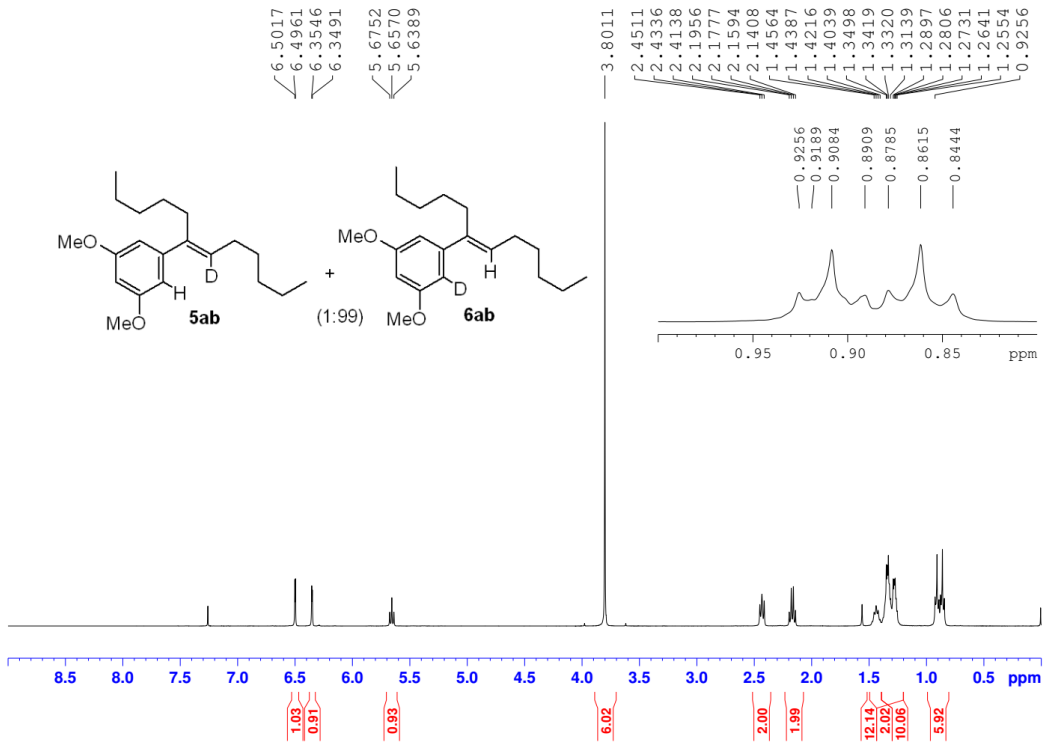
139.7417
133.9303
130.7292
130.6681
130.4273
130.1882
130.1389
127.6329
120.2376
110.5748
55.4304
32.3282
30.1604
23.0442
21.5767
14.0172
13.9047
MeO
D
+
MeO
D
5na
(13:87)
6na
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

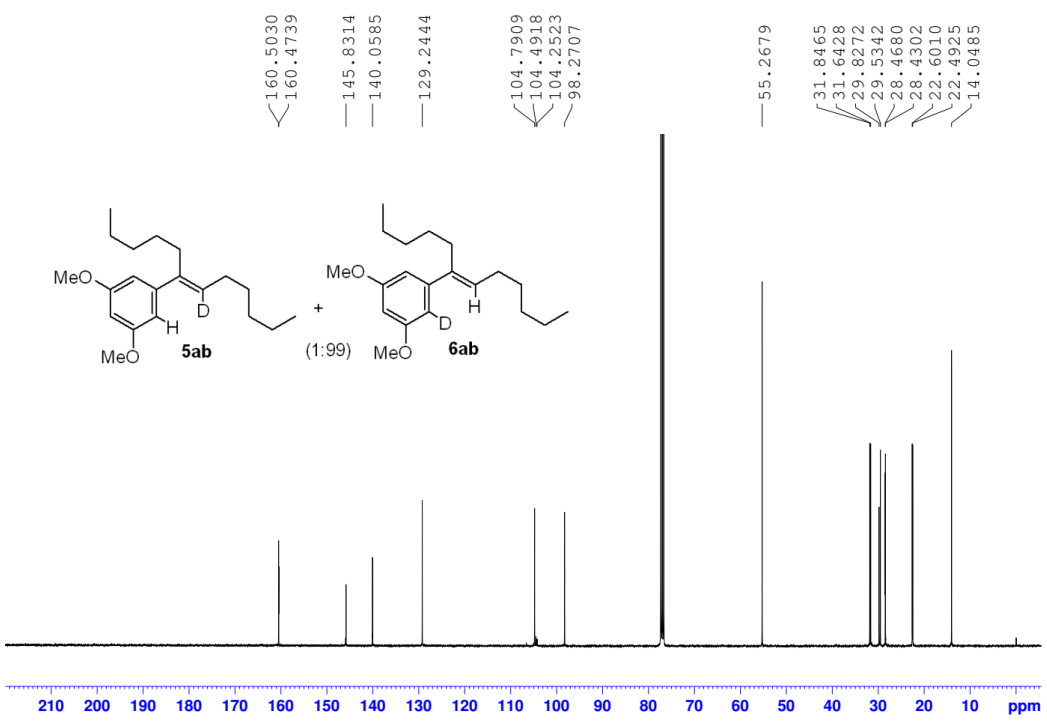

7.0458
5.3174
MeO
D
+
MeO
D
5na
(13:87)
6na
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
86.58
13.42


6.4959
6.4903
6.3531
6.3476
6.3421
5.6702
5.6517
5.6336
3.7989
2.4450
2.4274
2.4076
2.1771
2.1594
2.1406
1.4509
1.4330
1.4161
1.3982
1.3453
1.3373
1.3275
1.3095
1.2849
1.2758
1.2684
1.2592
1.2507
0.9213
0.9213
0.9042
0.8866
0.8741
0.8572
0.8400
MeO
D
H
MeO
5ab
(90:10)
MeO
H
D
MeO
6ab
0.95
0.90
0.85
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.77
0.92
0.10
5.93
2.00
2.02
12.11
6.00


160.5159
145.8955
140.0025
129.2575
129.1321
128.8997
128.6793
104.7976
98.2505
55.2809
31.8501
31.6484
29.7932
29.5130
28.4283
28.3659
22.6018
22.4937
14.0545
MeO
D
H
MeO
5ab
(90:10)
MeO
H
D
MeO
6ab
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


6.5035
5.6709
MeO
D
H
MeO
5ab
+
(90:10)
MeO
H
D
MeO
6ab
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
10.49
89.51


6.5017
6.4961
6.3546
6.3491
5.6752
5.6570
5.6389
3.8011
2.4511
2.4336
2.4138
2.1956
2.1777
2.1594
2.1408
1.4564
1.4387
1.4216
1.4039
1.3498
1.3419
1.3320
1.3139
1.2897
1.2806
1.2731
1.2641
1.2554
0.9256
0.9256
0.9189
0.9084
0.8909
0.8785
0.8615
0.8444
MeO
MeO
H
D
5ab
+
(1:99)
MeO
MeO
H
D
6ab
0.95
0.90
0.85
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.03
0.91
0.93
6.02
2.00
1.99
12.14
2.02
10.06
5.92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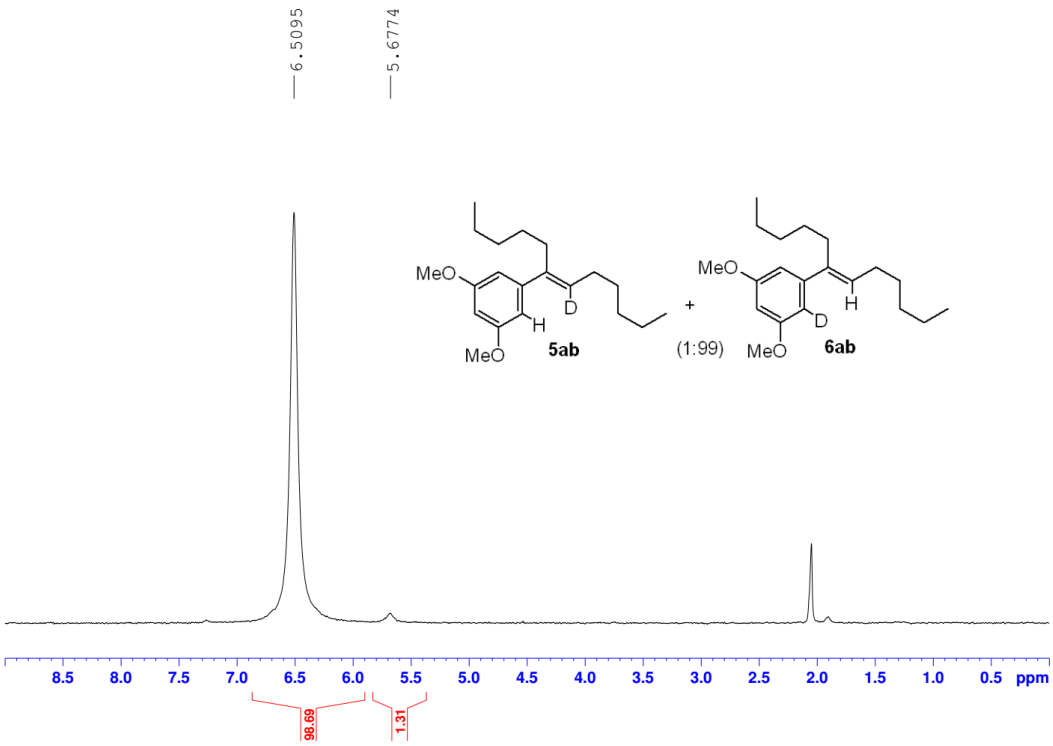
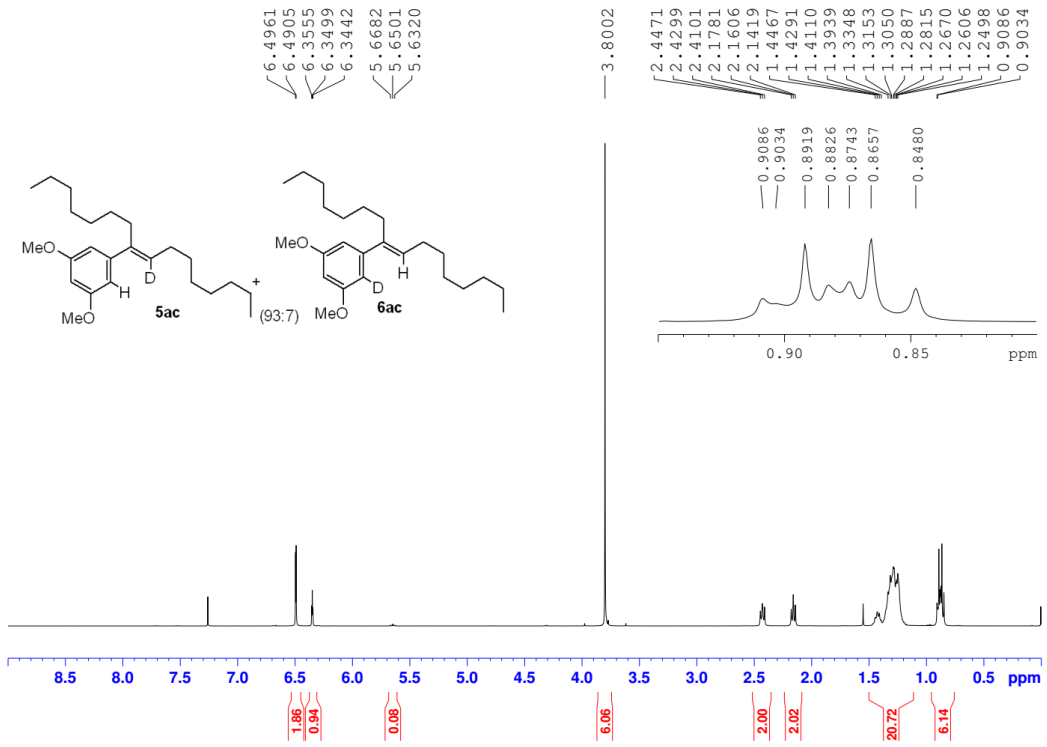
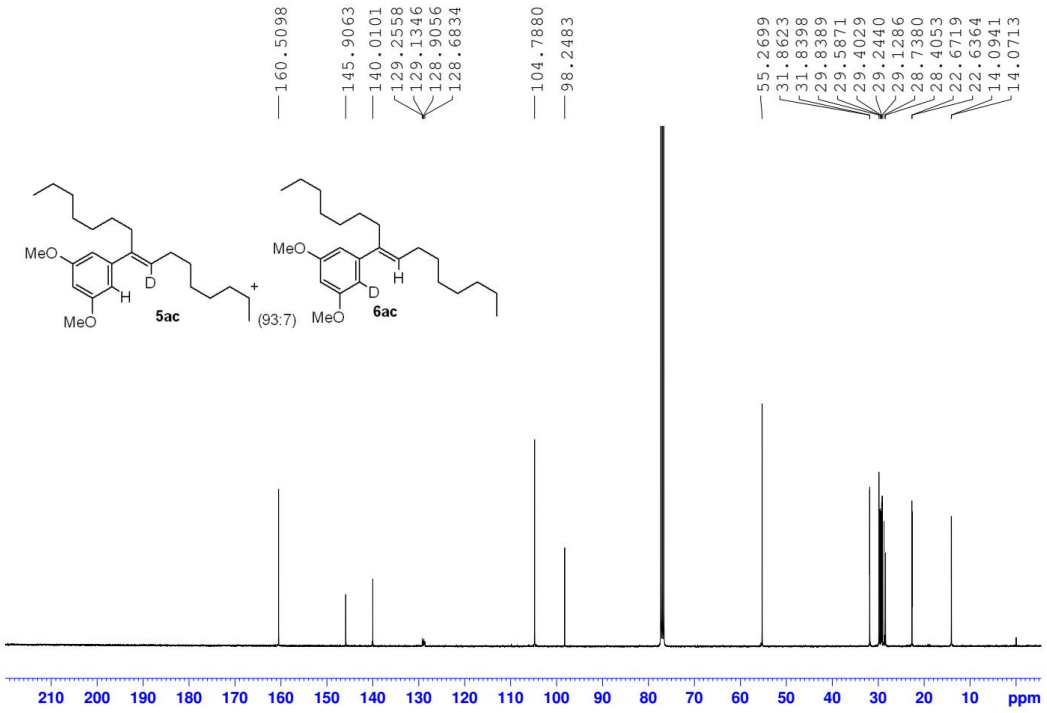
160.4739
145.8314
140.0585
129.2444
104.7909
104.4918
104.2523
98.2707
55.2679
31.8465
31.6428
29.8272
29.5342
28.4680
28.4302
22.6010
22.4925
14.0485
MeO
MeO
H
D
5ab
+
(1:99)
MeO
MeO
H
D
6ab
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


6.5095
5.6774
MeO
D
H
MeO
5ab
+
(1:99)
MeO
H
D
MeO
6ab
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
98.69
1.31


6.4961
6.4905
6.3555
6.3499
6.3442
5.6682
5.6501
5.6320
3.8002
2.4471
2.4299
2.4101
2.1781
2.1606
2.1419
1.4467
1.4291
1.4110
1.3939
1.3348
1.3153
1.3050
1.2887
1.2815
1.2670
1.2606
1.2498
0.9086
0.9034
0.9086
0.9034
0.8919
0.8826
0.8743
0.8657
0.8480
0.90
0.85
ppm
MeO
D
H
MeO
5ac
(93:7)
MeO
H
D
MeO
6ac
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.86
0.94
0.08
6.06
2.00
2.02
20.72
6.14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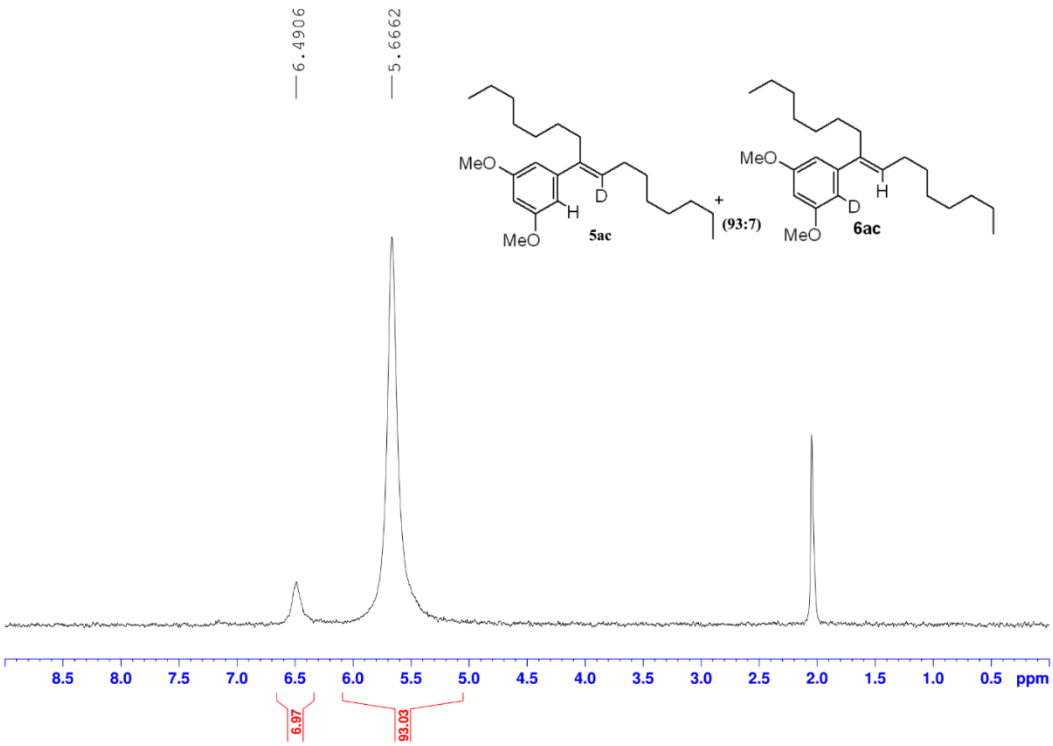
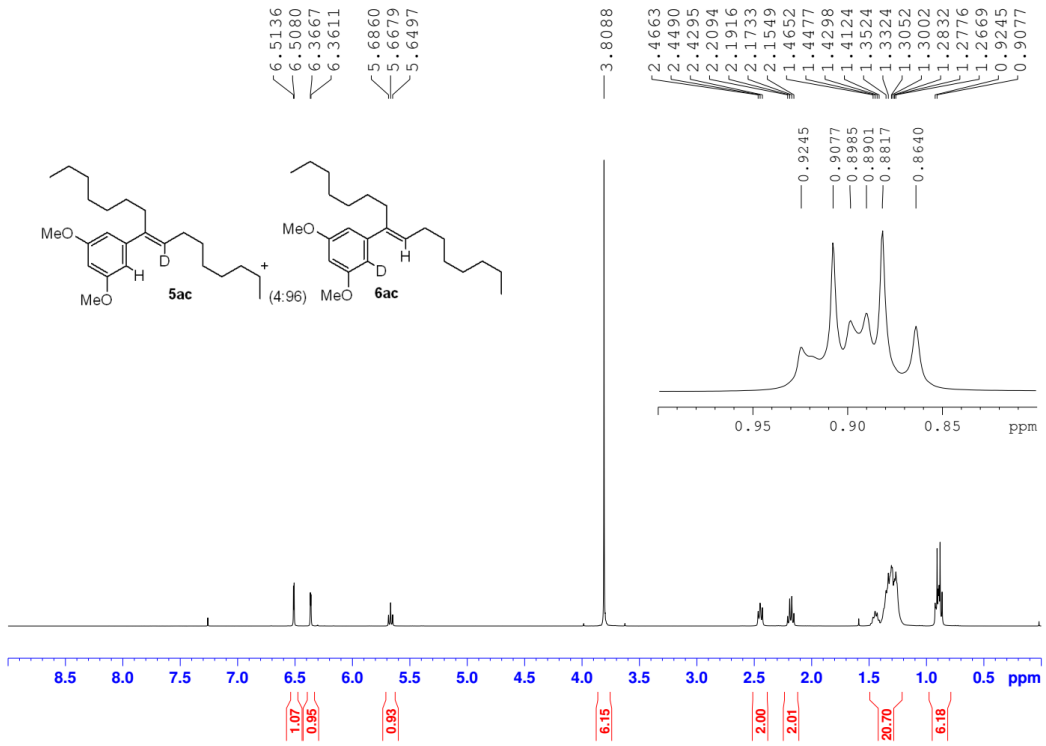
145.9063
140.0101
129.2558
129.1346
128.9056
128.6834
104.7880
98.2483
55.2699
31.8623
31.8398
29.8389
29.5871
29.4029
29.2440
29.1286
28.7380
28.4053
22.6719
22.6364
14.0941
14.0713
MeO
D
H
MeO
5ac
(93:7)
MeO
H
D
MeO
6ac
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


6.4906
5.6662
MeO
D
H
MeO
5ac
(93:7)
MeO
H
D
MeO
6ac
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
6.97
93.03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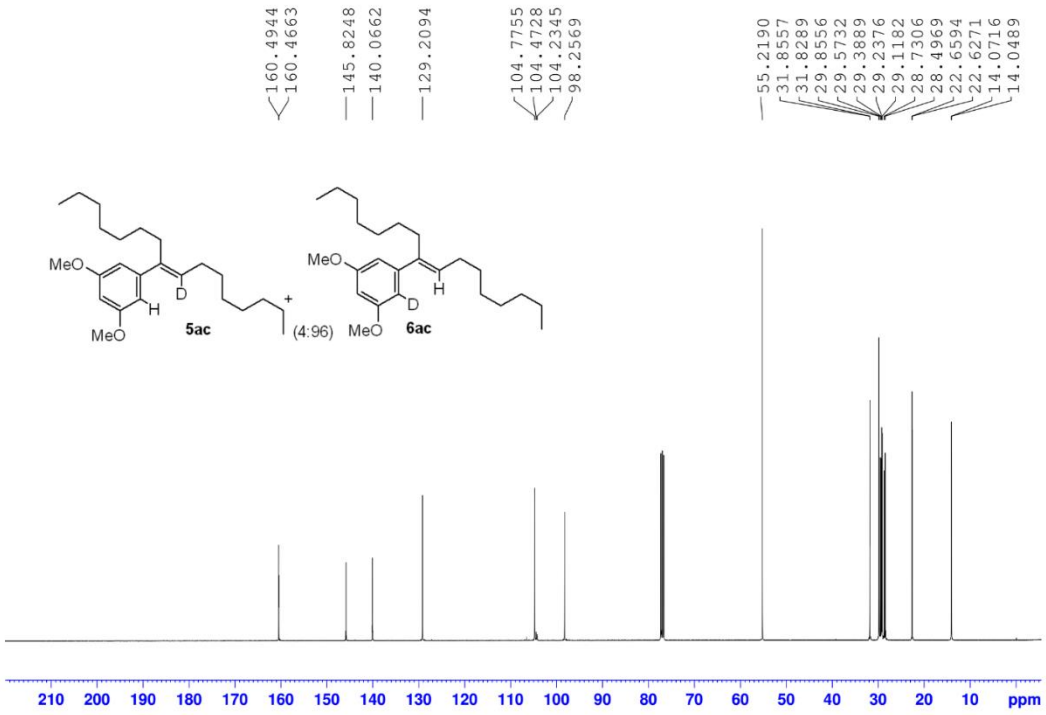
6.5080
6.3667
6.3611
5.6860
5.6679
5.6497
3.8088
2.4663
2.4490
2.4295
2.2094
2.1916
2.1733
2.1549
1.4652
1.4477
1.4298
1.4124
1.3524
1.3324
1.3052
1.3002
1.2832
1.2776
1.2669
0.9245
0.9077
0.9245
0.9077
0.8985
0.8901
0.8817
0.8640
MeO
MeO
D
H
5ac
(4:96)
MeO
D
H
MeO
6ac
0.95
0.90
0.85
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.07
0.95
0.93
6.15
2.00
2.01
20.70
6.18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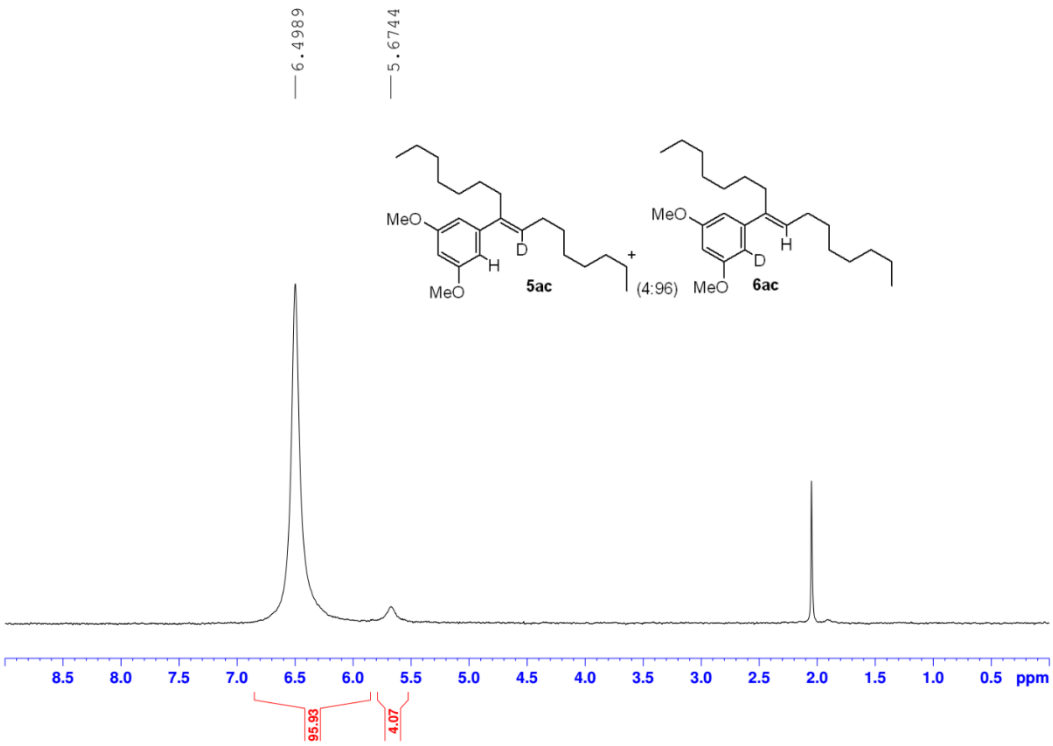
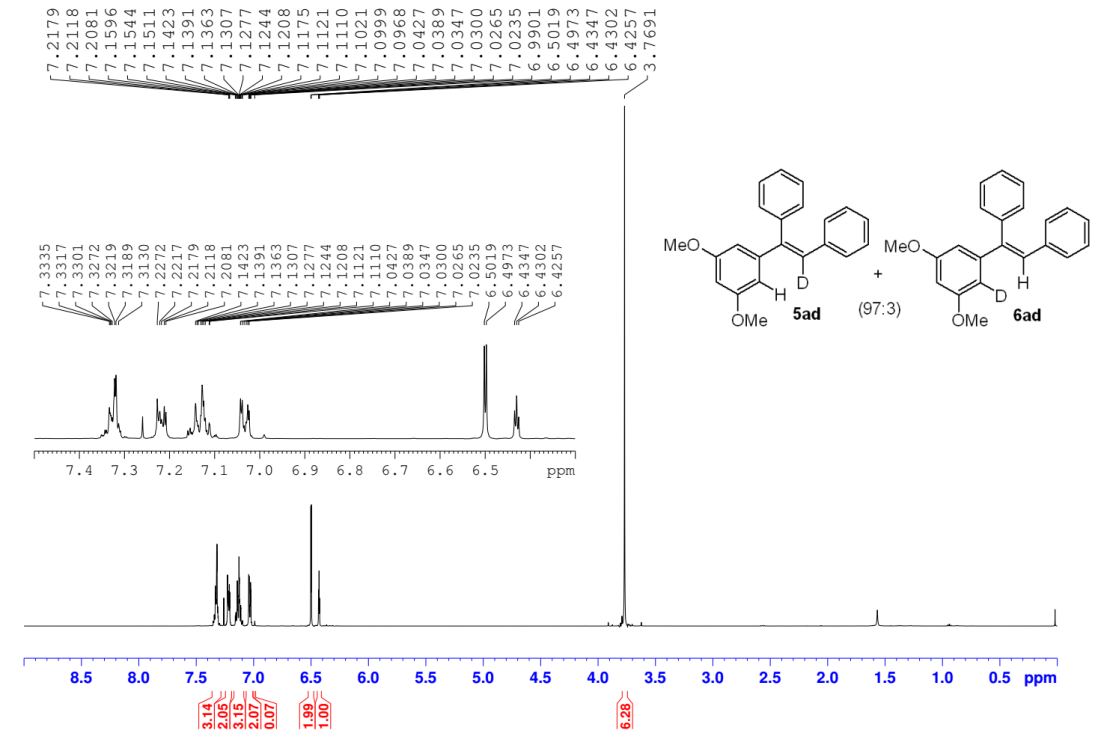
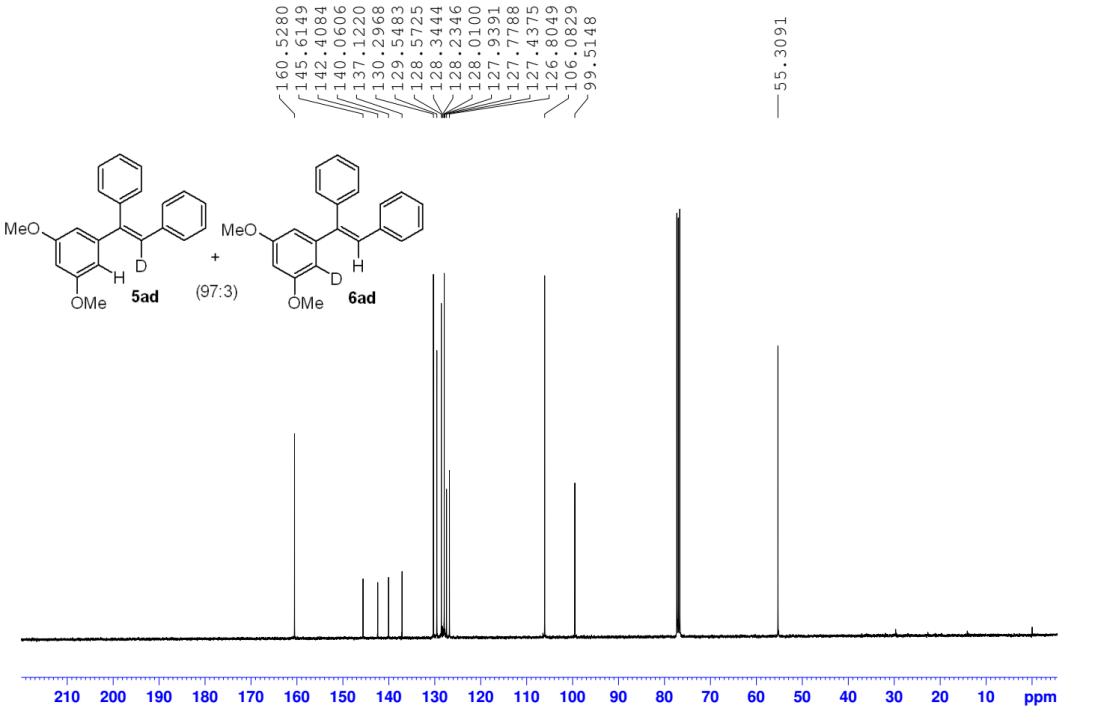
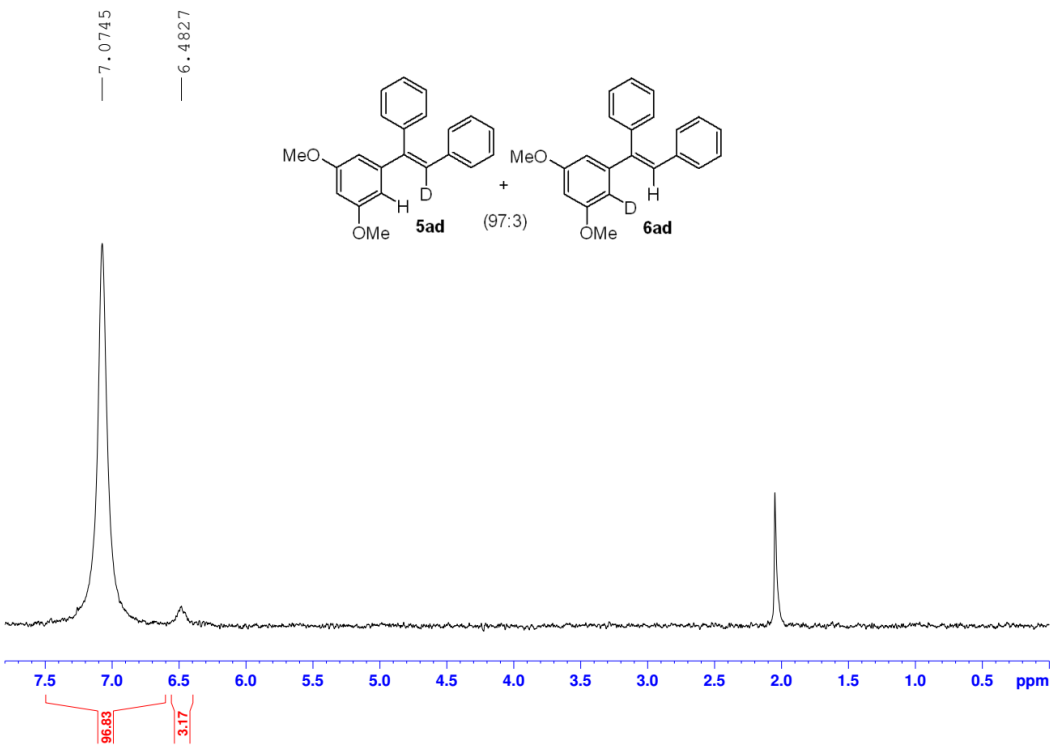
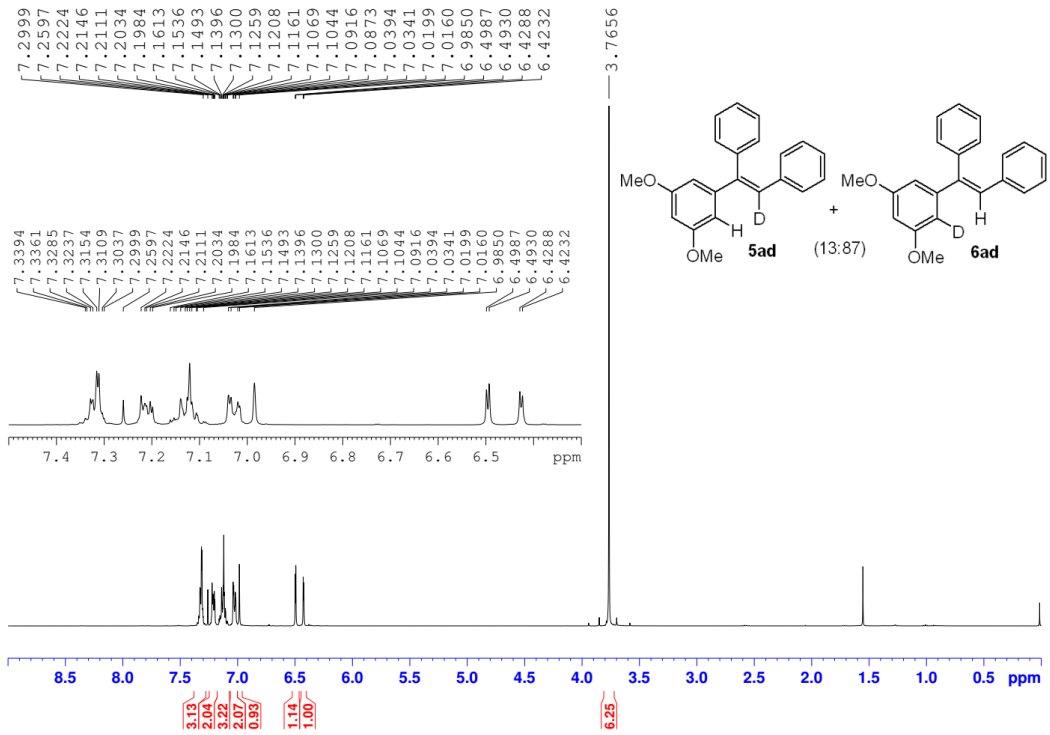
160.4663
145.8248
140.0662
129.2094
104.7755
104.4728
104.2345
98.2569
55.2190
31.8557
31.8289
29.8556
29.5732
29.3889
29.2376
29.1182
28.7306
28.4969
22.6594
22.6271
14.0716
14.0489
MeO
MeO
D
H
5ac
(4:96)
MeO
D
H
MeO
6ac
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

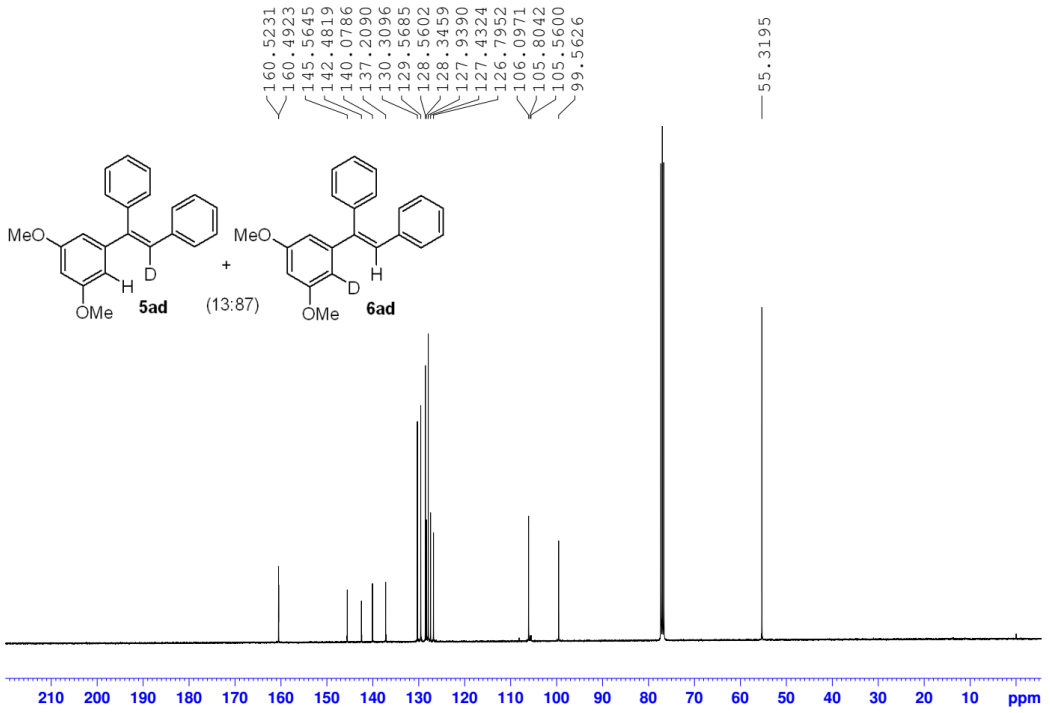

6.4989
5.6744
MeO
D
H
MeO
5ac
(4:96)
MeO
H
D
MeO
6ac
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
95.93
4.07

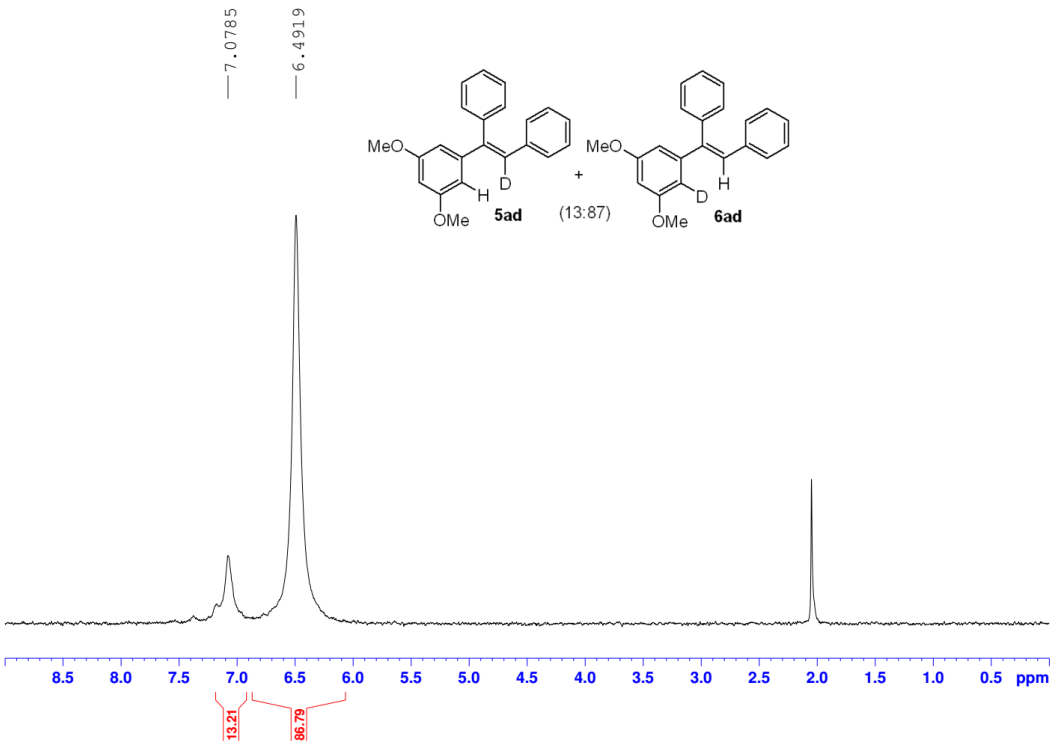

7.2179
7.2118
7.2081
7.1596
7.1544
7.1511
7.1423
7.1391
7.1363
7.1307
7.1277
7.1244
7.1208
7.1175
7.1121
7.1110
7.1021
7.0999
7.0968
7.0427
7.0389
7.0347
7.0300
7.0265
7.0235
6.9901
6.5019
6.4973
6.4347
6.4302
6.4257
3.7691
MeO
D
H
OMe
5ad
(97:3)
6ad
ppm
3.14
2.05
3.15
2.07
0.07
1.99
1.00
6.28

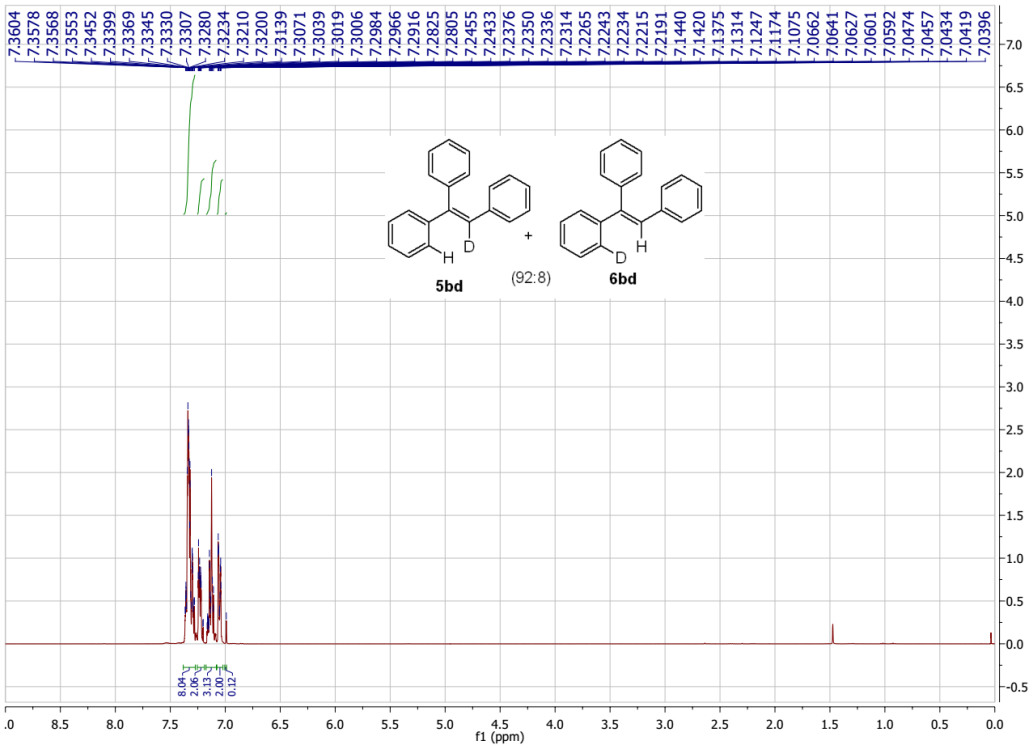

160.5280
145.6149
142.4084
140.0606
137.1220
130.2968
129.5483
128.5725
128.3444
128.2346
128.0100
127.9391
127.7788
127.4375
126.8049
106.0829
99.5148
55.3091
MeO
D
H
OMe
5ad
(97:3)
6ad
ppm

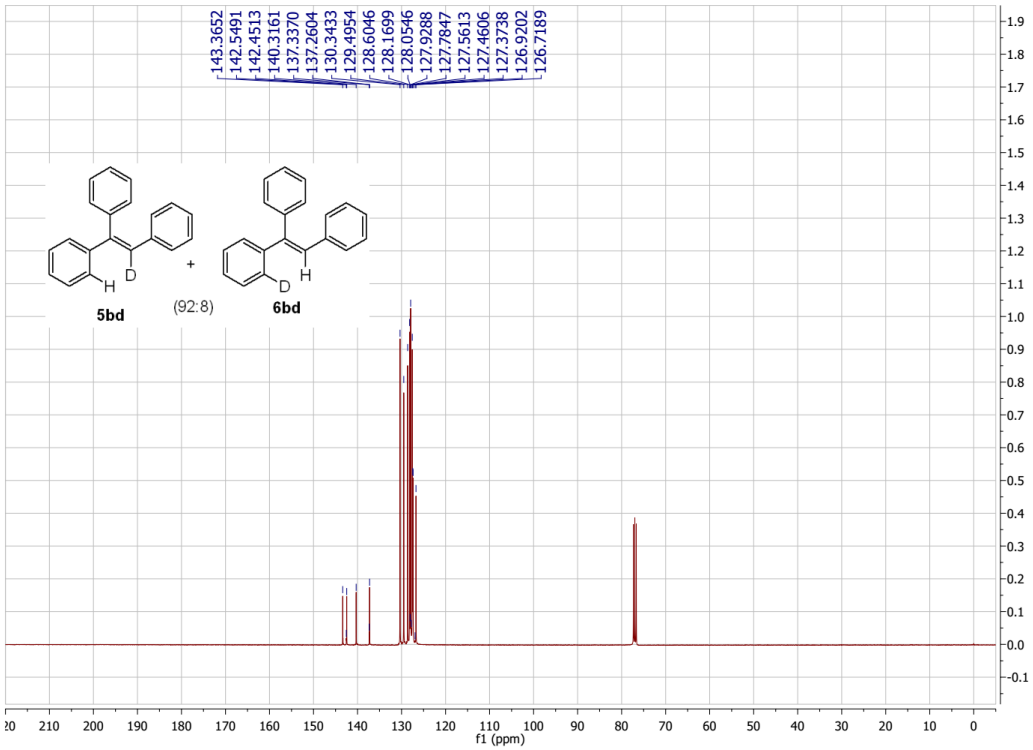

7.0745
6.4827
MeO
D
H
OMe
5ad
+
(97:3)
MeO
H
D
OMe
6ad
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
96.83
3.17

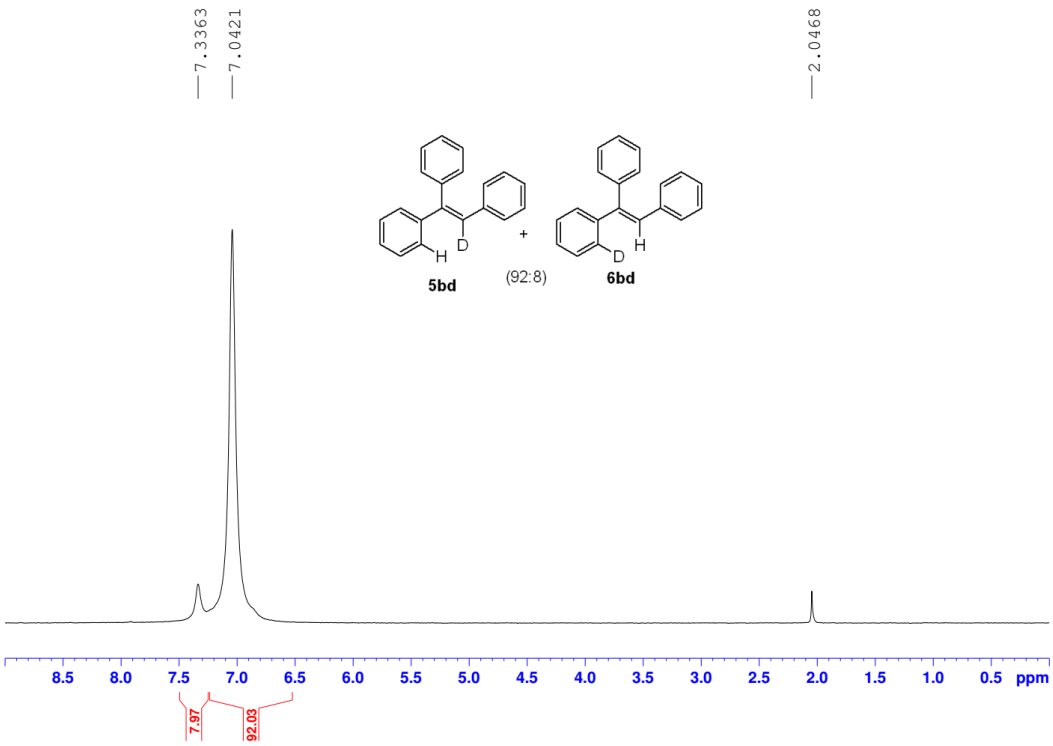

7.2999
7.2597
7.2224
7.2146
7.2111
7.2034
7.1984
7.1613
7.1536
7.1493
7.1396
7.1300
7.1259
7.1208
7.1161
7.1069
7.1044
7.0916
7.0873
7.0394
7.0341
7.0199
7.0160
6.9850
6.4987
6.4930
6.4288
6.4232
3.7656
MeO
H
D
OMe
5ad
(13:87)
6ad
7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 ppm
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
3.13
2.04
3.22
2.07
0.93
1.14
1.00
6.25

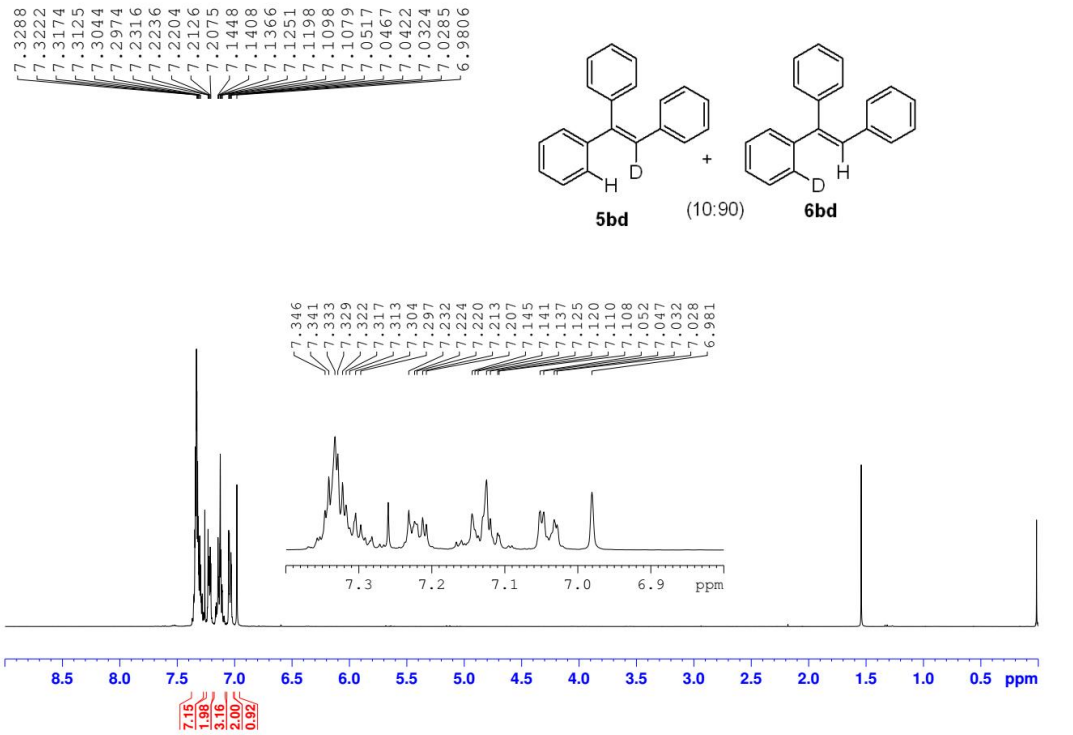

160.5231
160.4923
145.5645
142.4819
140.0786
137.2090
130.3096
129.5685
128.5602
128.3459
127.9390
127.4324
126.7952
106.0971
105.8042
105.5600
99.5626
55.3195
MeO
H
D
OMe
5ad
(13:87)
6ad
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

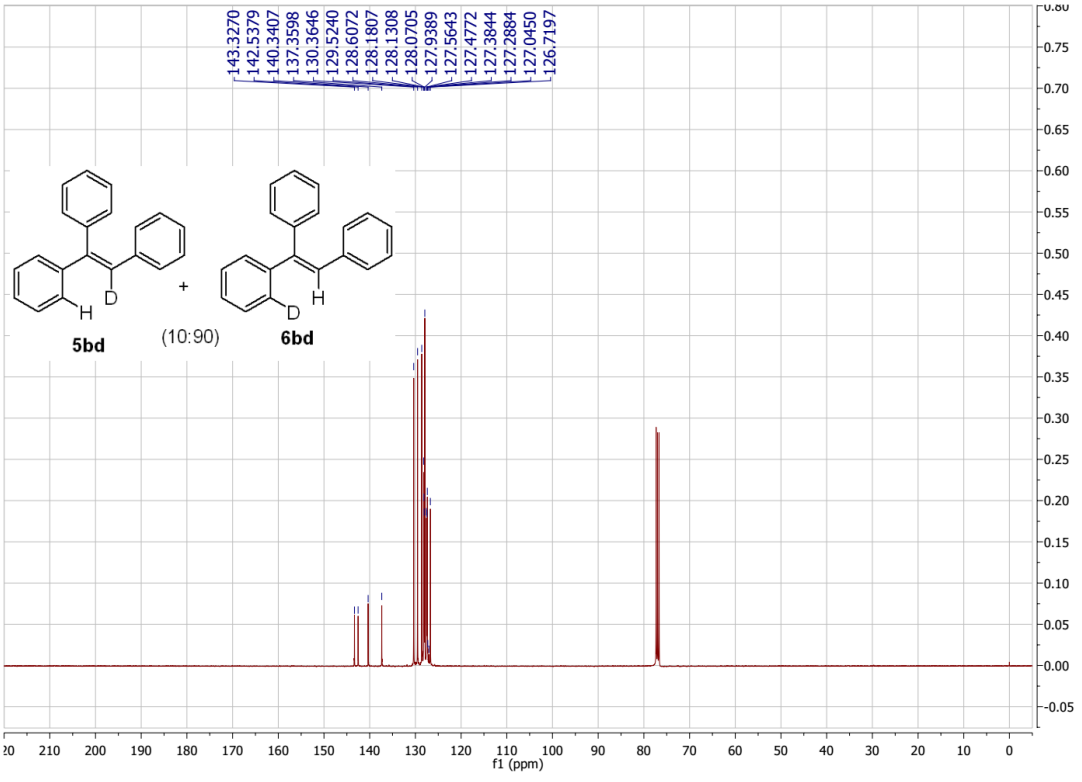

7.0785
6.4919
MeO
D
H
OMe
5ad
+
(13:87)
MeO
H
D
OMe
6ad
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
13.21
86.79

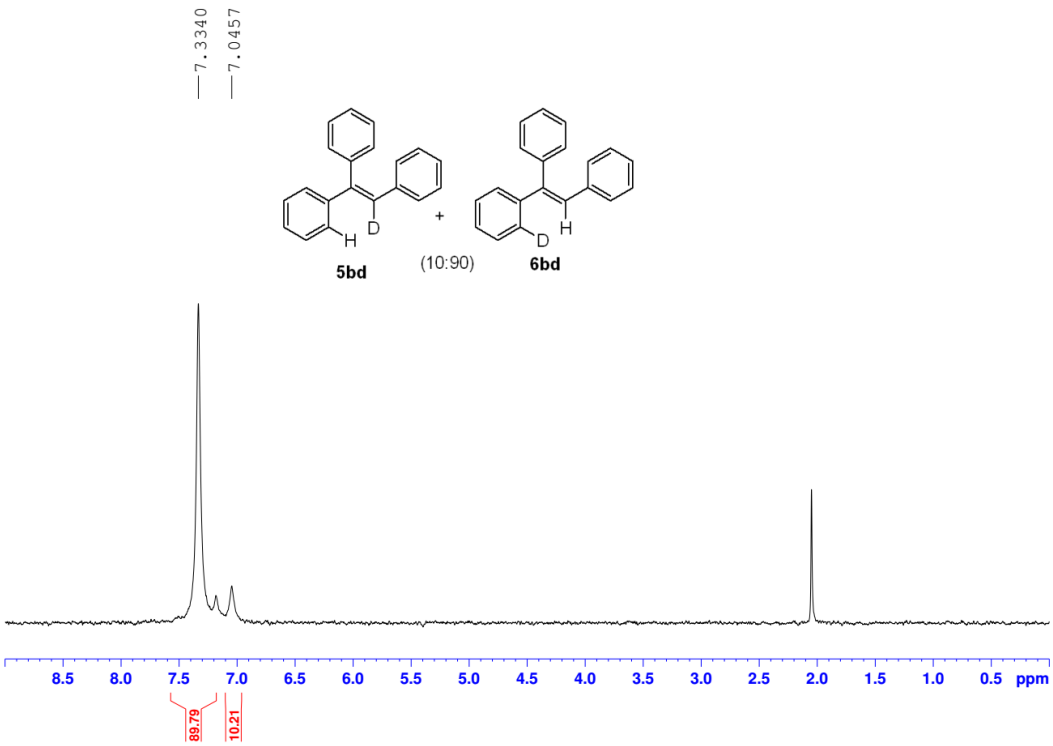

7.3604
7.3578
7.3568
7.3553
7.3452
7.3399
7.3369
7.3345
7.3330
7.3307
7.3280
7.3234
7.3210
7.3200
7.3139
7.3071
7.3039
7.3019
7.3006
7.2984
7.2966
7.2916
7.2825
7.2805
7.2455
7.2433
7.2376
7.2350
7.2336
7.2314
7.2265
7.2243
7.2234
7.2215
7.2191
7.1440
7.1420
7.1375
7.1314
7.1247
7.1174
7.1075
7.0662
7.0641
7.0627
7.0601
7.0592
7.0474
7.0457
7.0434
7.0419
7.0396
H
D
5bd
(92:8)
D
H
6bd
8.04
2.06
3.13
2.00
0.12
f1 (ppm)

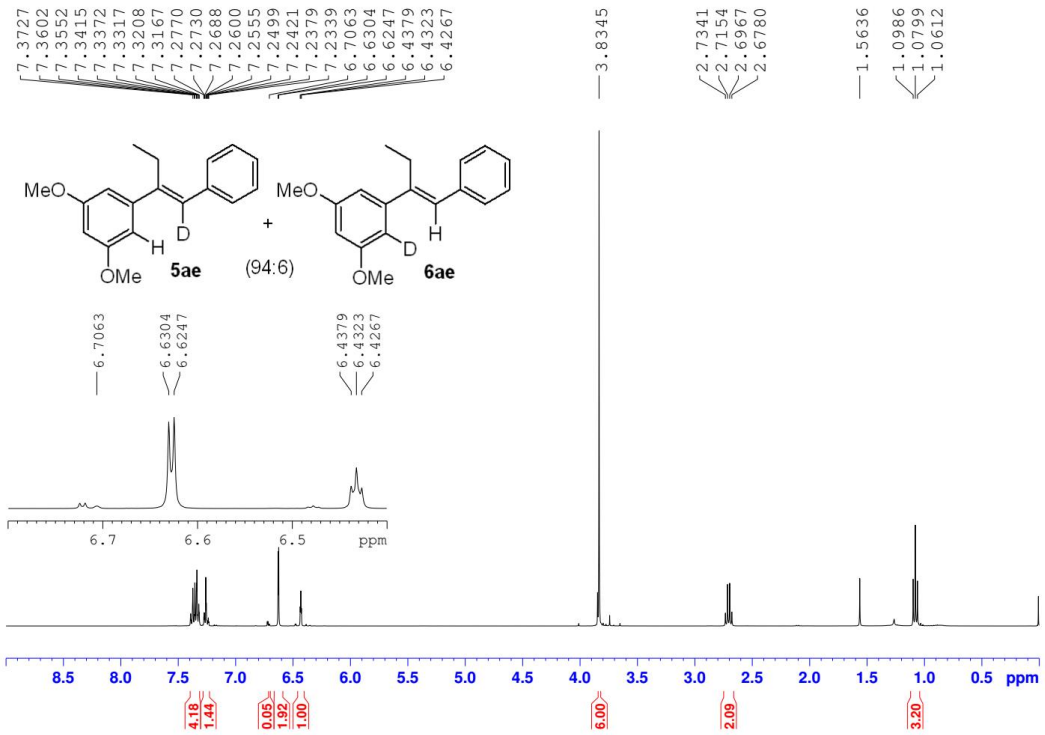

143.3652
142.5491
142.4513
140.3161
137.3370
137.2604
130.3433
129.4954
128.6046
128.1699
128.0546
127.9288
127.7847
127.5613
127.4606
127.3738
126.9202
126.7189
H
D
5bd
(92:8)
D
H
6bd
f1 (ppm)

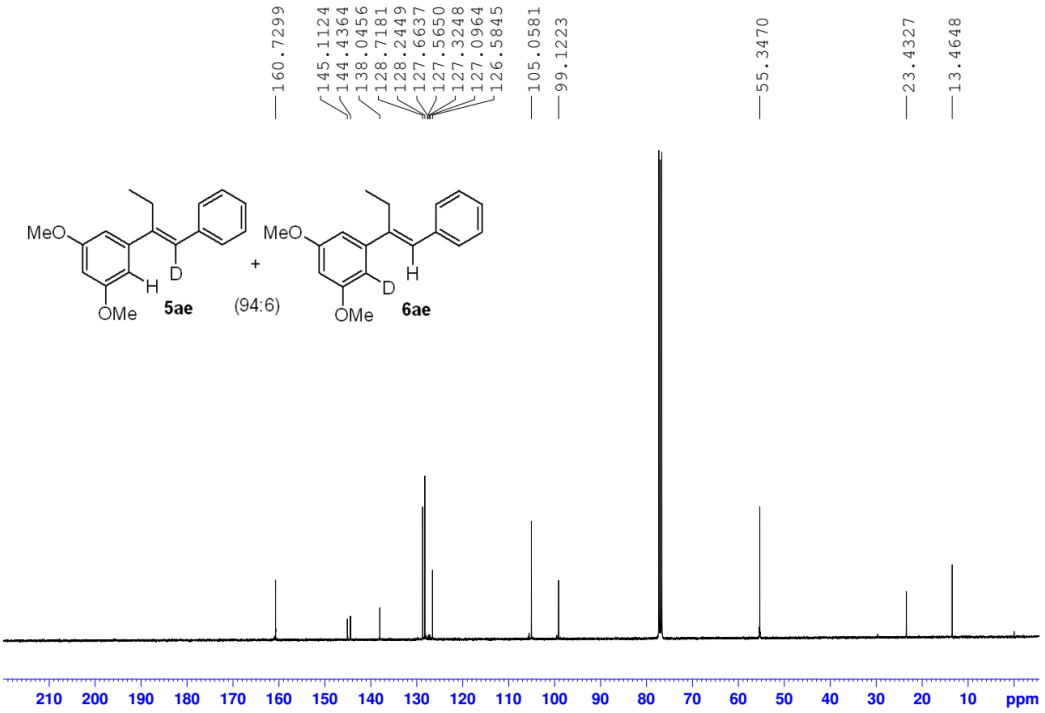

7.3363
7.0421
2.0468
H
D
5bd
(92:8)
D
H
6bd
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
7.97
92.03

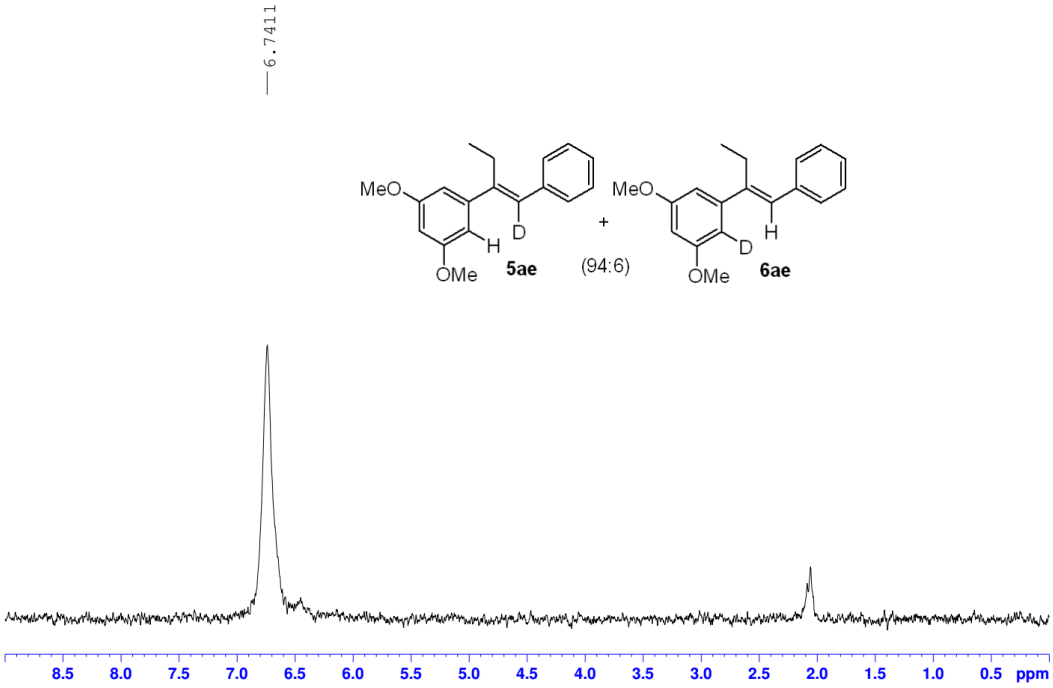

7.3288
7.3222
7.3174
7.3125
7.3044
7.2974
7.2316
7.2236
7.2204
7.2126
7.2075
7.1448
7.1408
7.1366
7.1251
7.1198
7.1098
7.1079
7.0517
7.0467
7.0422
7.0324
7.0285
6.9806
H
D
+
(10:90)
D
H
5bd
6bd
7.346
7.341
7.333
7.329
7.322
7.317
7.313
7.304
7.297
7.232
7.224
7.220
7.213
7.207
7.145
7.141
7.137
7.125
7.120
7.110
7.108
7.052
7.047
7.032
7.028
6.981
7.3
7.2
7.1
7.0
6.9
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
7.15
1.98
3.16
2.00
0.92

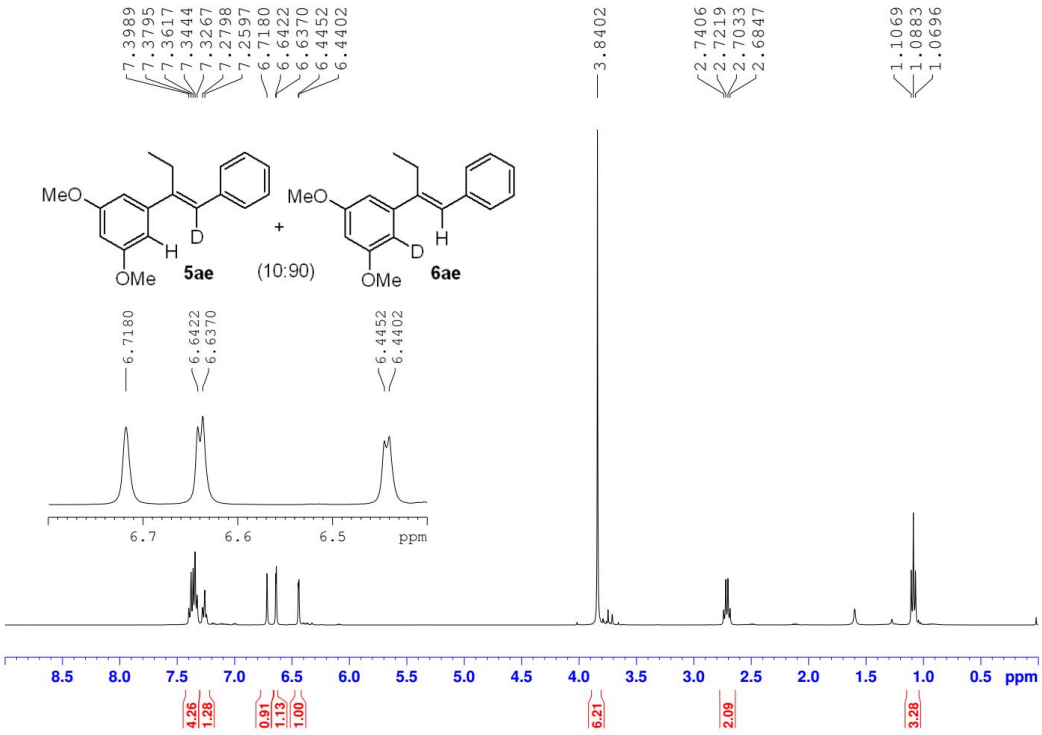

143.3270
142.5379
140.3407
137.3598
130.3646
129.5240
128.6072
128.1807
128.1308
128.0705
127.9389
127.5643
127.4772
127.3844
127.2884
127.0450
126.7197
H
D
+
(10:90)
D
H
5bd
6bd
f1 (ppm)

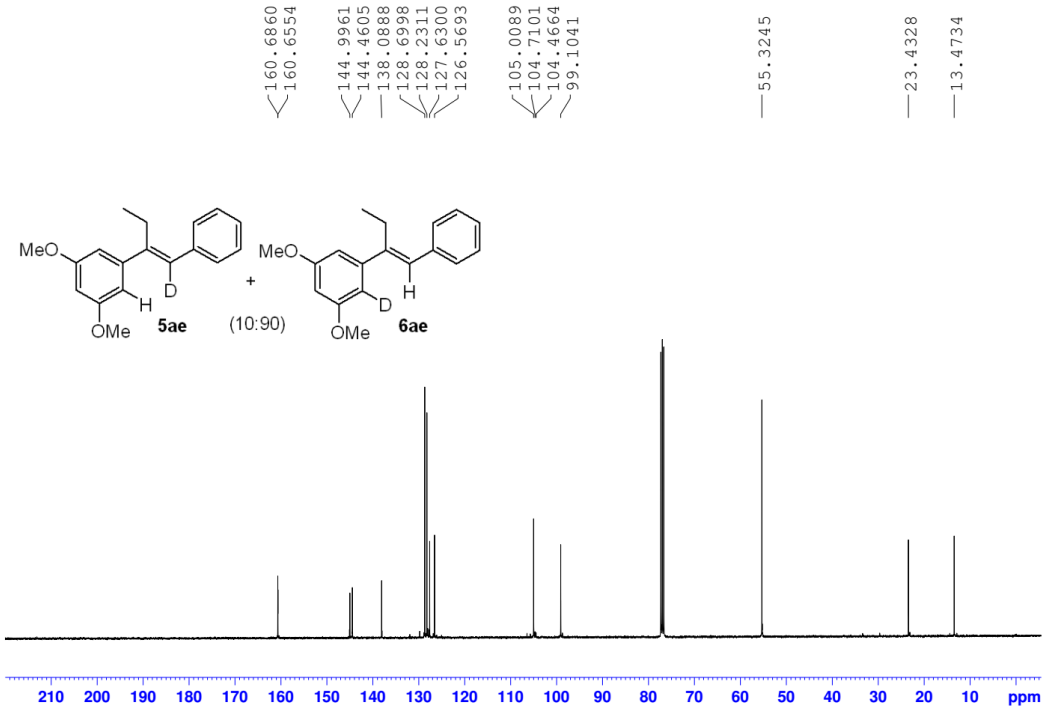

7.3340
7.0457
D
H
+
H
D
5bd
(10:90)
6bd
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
89.79
10.21

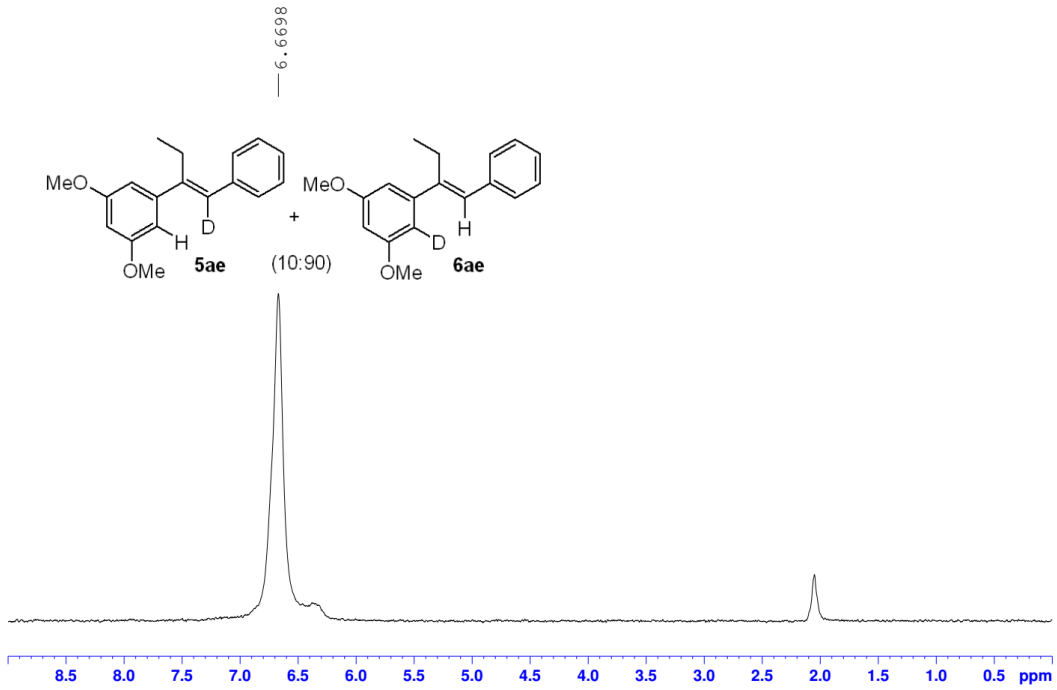

7.3727
7.3602
7.3552
7.3415
7.3372
7.3317
7.3208
7.3167
7.2770
7.2730
7.2688
7.2600
7.2555
7.2499
7.2421
7.2379
7.2339
6.7063
6.6304
6.6247
6.4379
6.4323
6.4267
3.8345
2.7341
2.7154
2.6967
2.6780
1.5636
1.0986
1.0799
1.0612
MeO
D
H
OMe
5ae
(94:6)
6ae
ppm
4.18
1.44
0.05
1.92
1.00
6.00
2.09
3.20

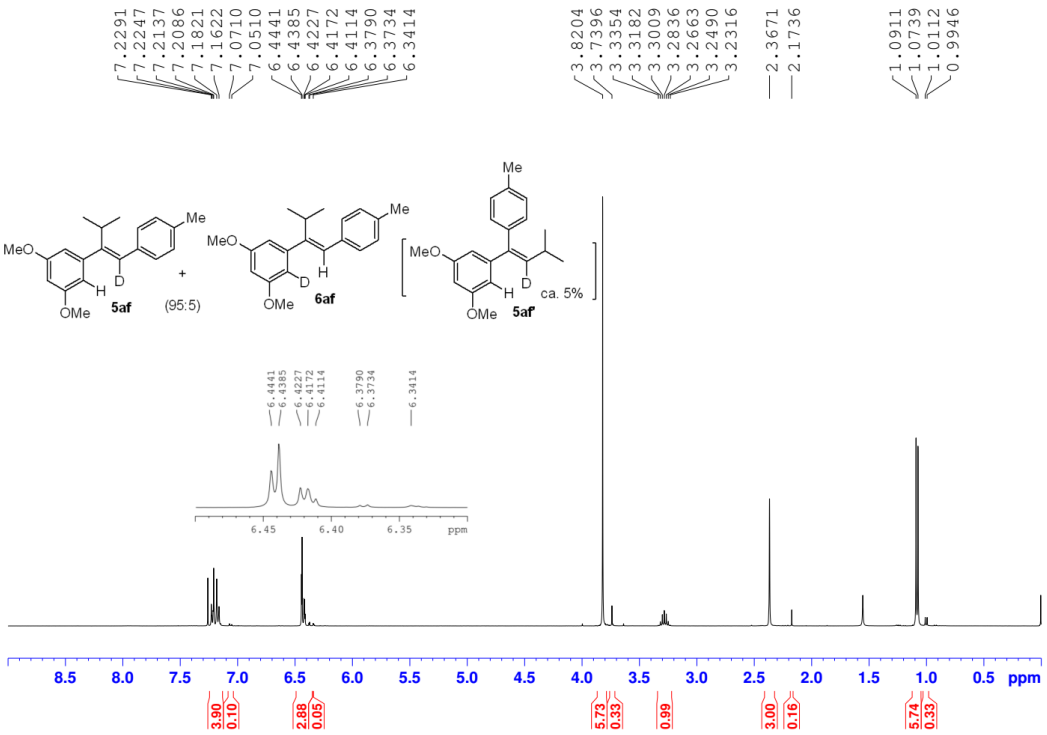

160.7299
145.1124
144.4364
138.0456
128.7181
128.2449
127.6637
127.5650
127.3248
127.0964
126.5845
105.0581
99.1223
55.3470
23.4327
13.4648
MeO
D
H
OMe
5ae
(94:6)
6ae
ppm

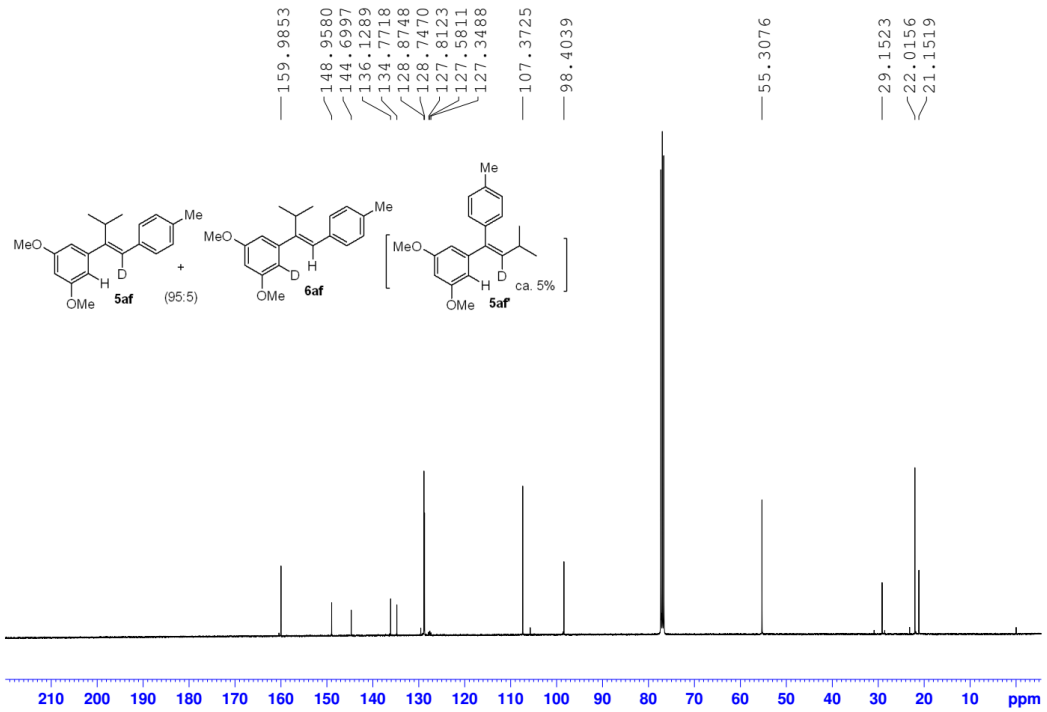

6.7411
MeO
D
H
OMe
5ae
(94:6)
MeO
H
D
OMe
6ae
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

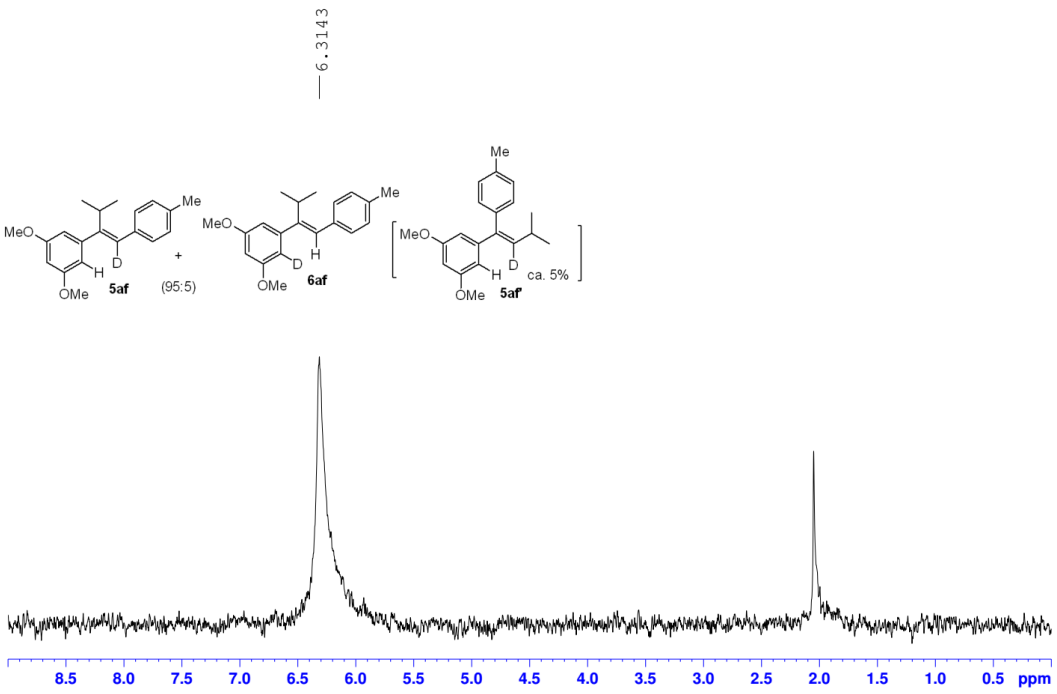

7.3989
7.3795
7.3617
7.3444
7.3267
7.2798
7.2597
6.7180
6.6422
6.6370
6.4452
6.4402
3.8402
2.7406
2.7219
2.7033
2.6847
1.1069
1.0883
1.0696
MeO
D
H
OMe
5ae
(10:90)
MeO
H
D
OMe
6ae
6.7180
6.6422
6.6370
6.4452
6.4402
6.7 6.6 6.5 ppm
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
4.26
1.28
0.91
1.13
1.00
6.21
2.09
3.28

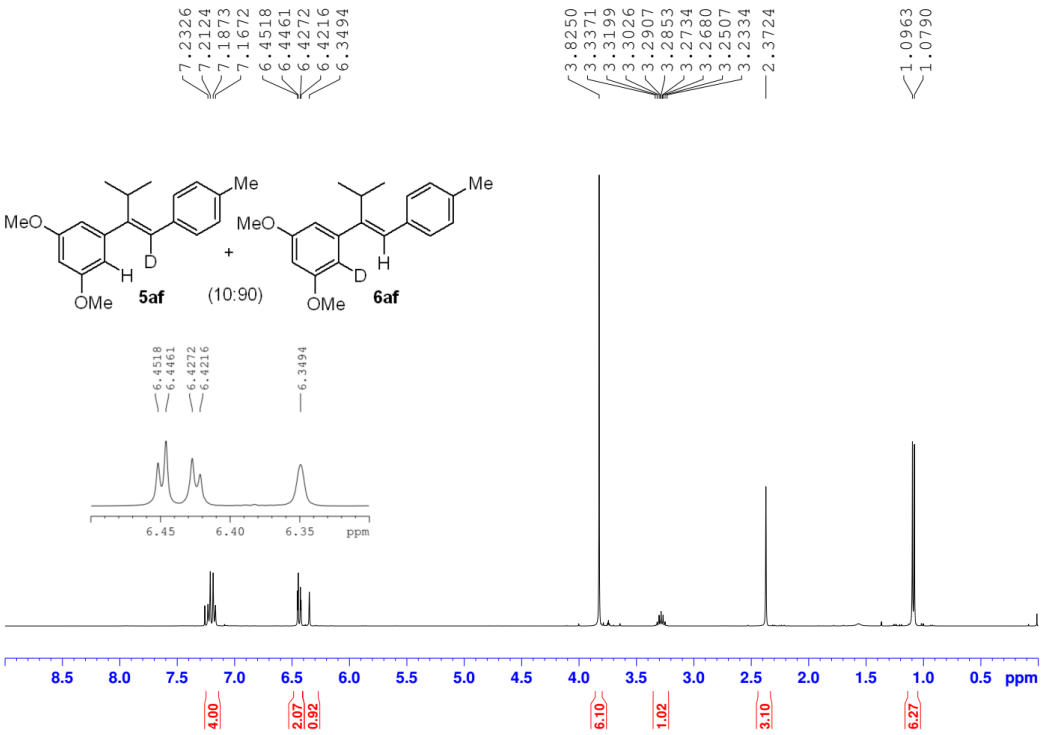

160.6860
160.6554
144.9961
144.4605
138.0888
128.6998
128.2311
127.6300
126.5693
105.0089
104.7101
104.4664
99.1041
55.3245
23.4328
13.4734
MeO
D
H
OMe
5ae
+
(10:90)
MeO
H
D
OMe
6ae
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

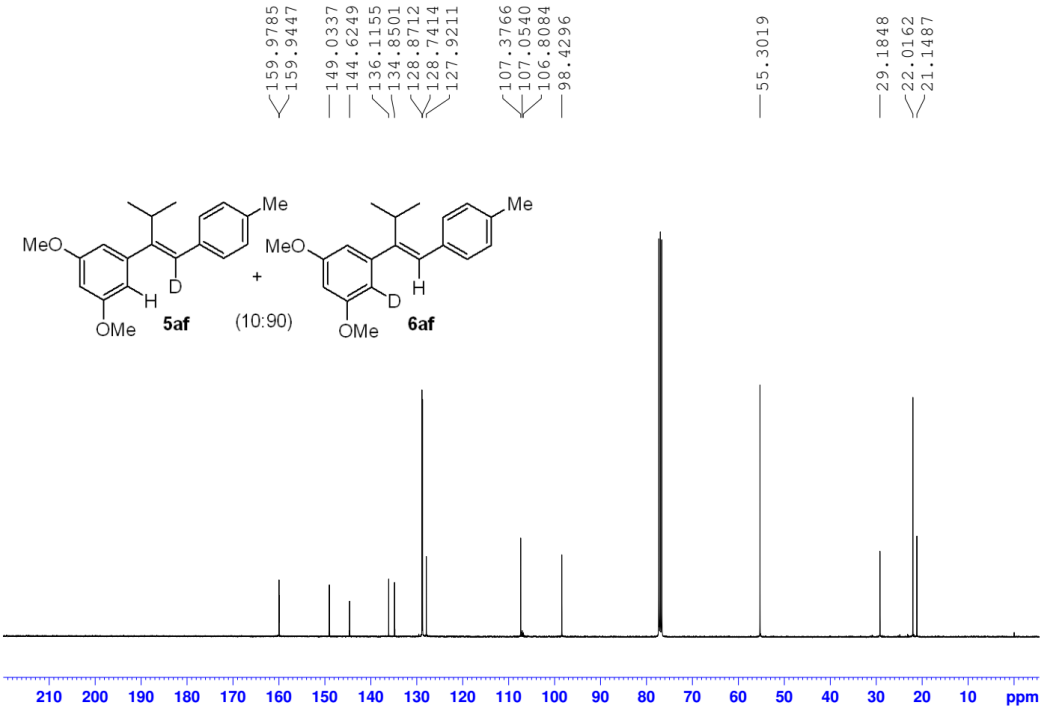

6.6698
MeO
D
H
OMe
5ae
+
(10:90)
MeO
H
D
OMe
6ae
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

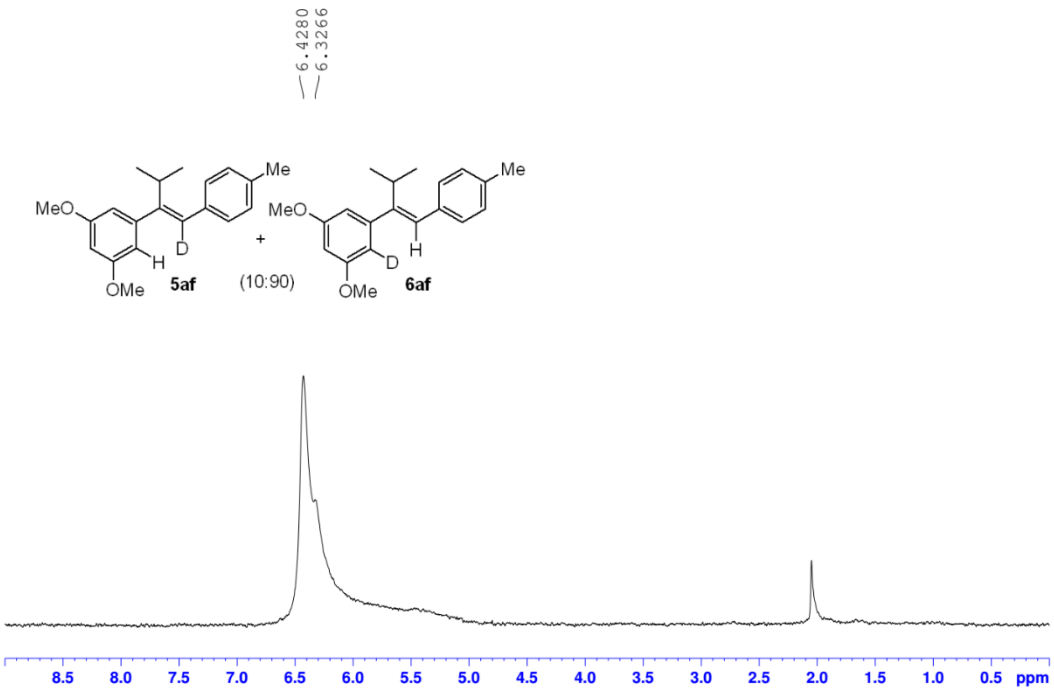

7.2291
7.2247
7.2137
7.2086
7.1821
7.1622
7.0710
7.0510
6.4441
6.4385
6.4227
6.4172
6.4114
6.3790
6.3734
6.3414
3.8204
3.7396
3.3354
3.3182
3.3009
3.2836
3.2663
3.2490
3.2316
2.3671
2.1736
1.0911
1.0739
1.0112
0.9946
MeO
Me
D
H
OMe
5af
(95:5)
6af
ca. 5%
5af'
ppm
3.90
0.10
2.88
0.05
5.73
0.33
0.99
3.00
0.16
5.74
0.33

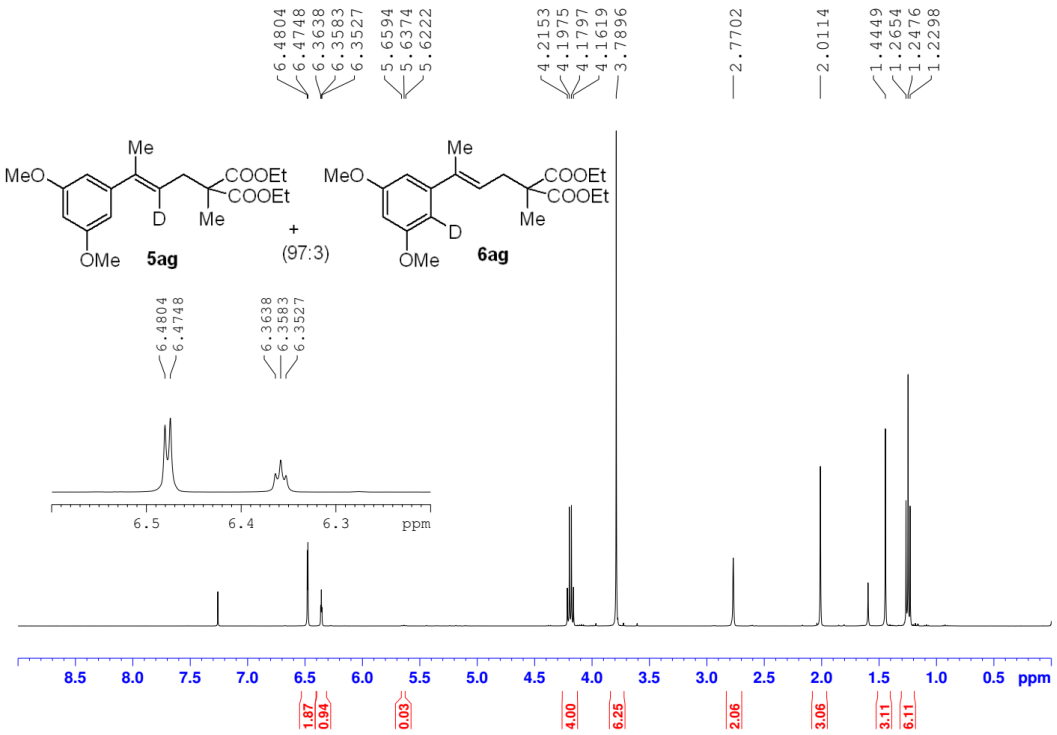

159.9853
148.9580
144.6997
136.1289
134.7718
128.8748
128.7470
127.8123
127.5811
127.3488
107.3725
98.4039
55.3076
29.1523
22.0156
21.1519
MeO
Me
D
H
OMe
5af
(95:5)
6af
ca. 5%
5af'
ppm

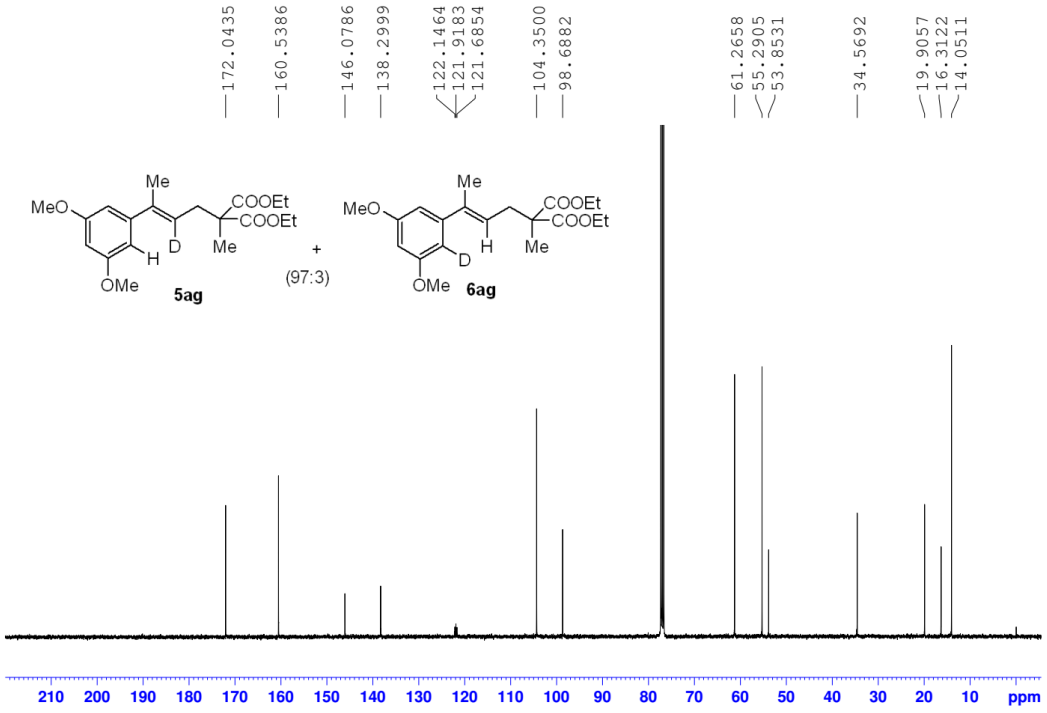

6.3143
MeO
Me
H
D
OMe
5af
(95:5)
6af
ca. 5%
5af'
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

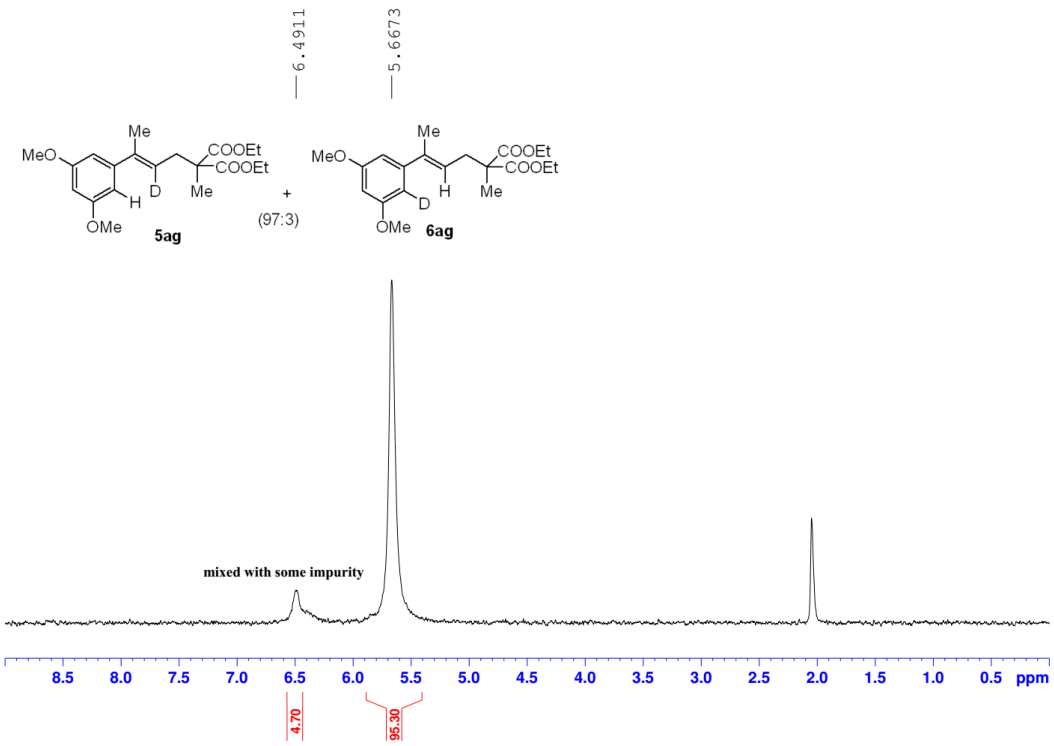

7.2326
7.2124
7.1873
7.1672
6.4518
6.4461
6.4272
6.4216
6.3494
3.8250
3.3371
3.3199
3.3026
3.2907
3.2853
3.2734
3.2680
3.2507
3.2334
2.3724
1.0963
1.0790
MeO
Me
D
H
OMe
5af
(10:90)
6af
6.45
6.40
6.35
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.00
2.07
0.92
6.10
1.02
3.10
6.27

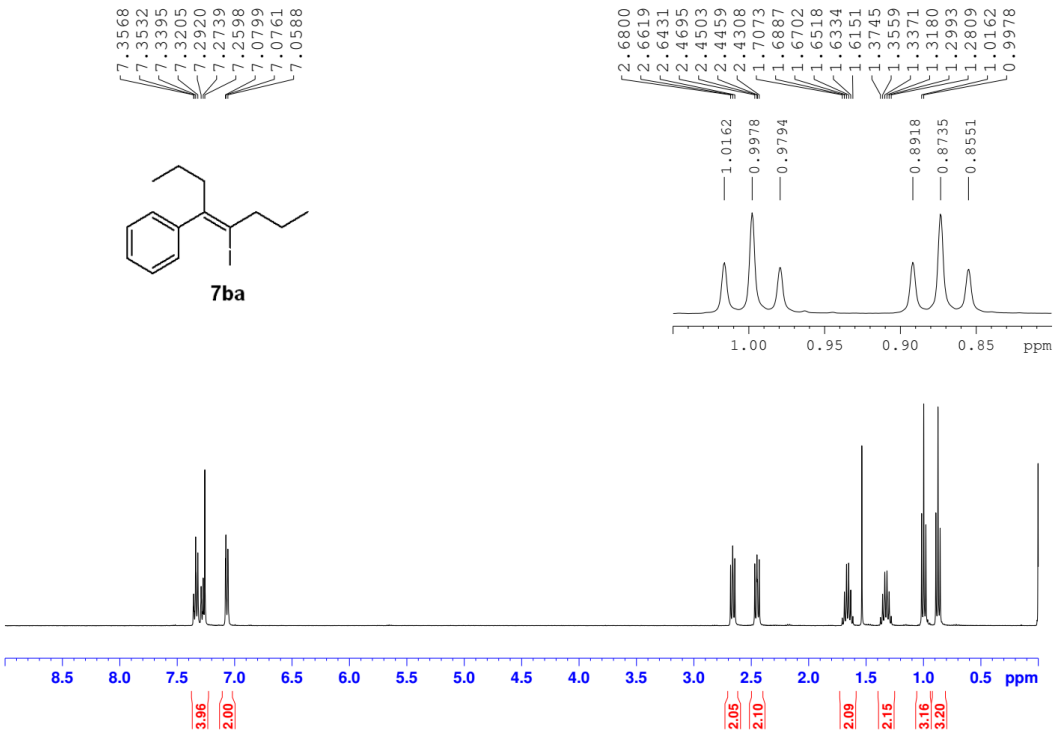

159.9785
159.9447
149.0337
144.6249
136.1155
134.8501
128.8712
128.7414
127.9211
107.3766
107.0540
106.8084
98.4296
55.3019
29.1848
22.0162
21.1487
MeO
Me
D
H
OMe
5af
(10:90)
6af
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

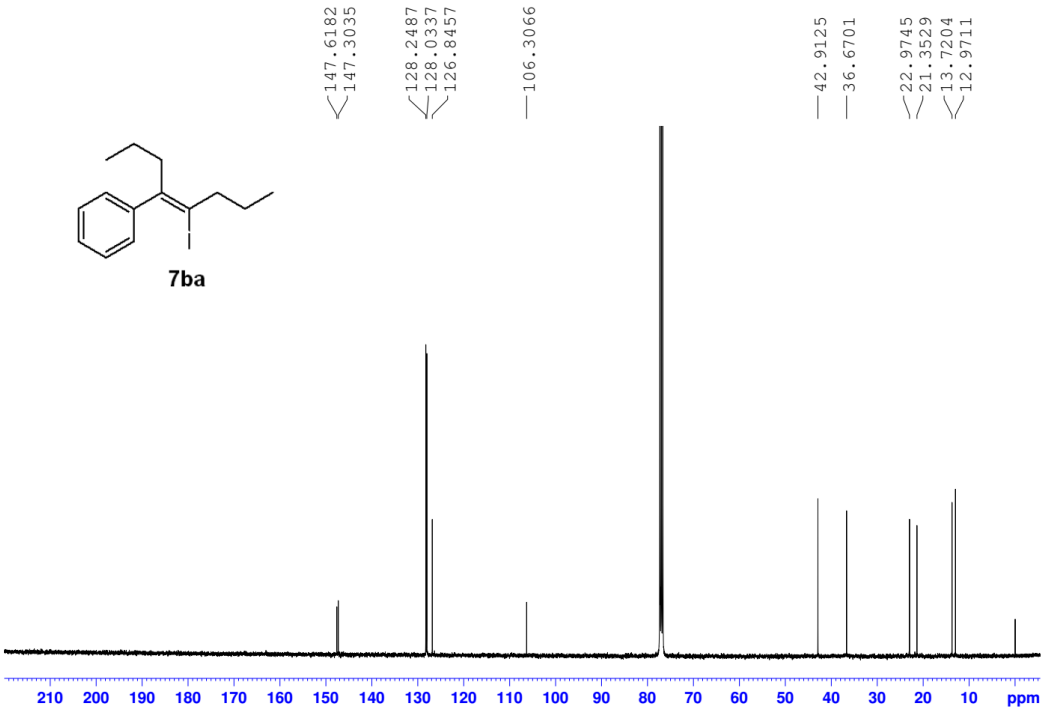

6.4280
6.3266
MeO
Me
D
H
OMe
5af
(10:90)
+
MeO
Me
H
D
OMe
6af
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

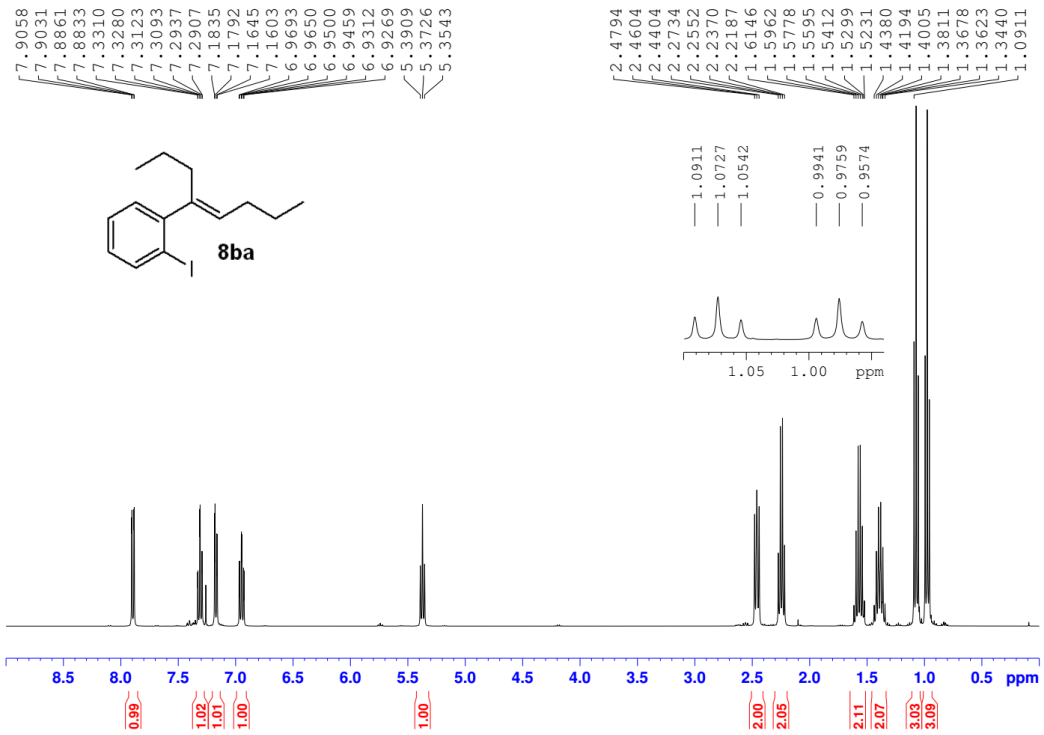

6.4804
6.4748
6.3638
6.3583
6.3527
5.6594
5.6374
5.6222
4.2153
4.1975
4.1797
4.1619
3.7896
2.7702
2.0114
1.4449
1.2654
1.2476
1.2298
MeO
Me
COOEt
COOEt
D
Me
OMe
5ag
+
(97:3)
6ag
6.5
6.4
6.3
ppm
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.87
0.94
0.03
4.00
6.25
2.06
3.06
3.11
6.11


172.0435
160.5386
146.0786
138.2999
122.1464
121.9183
121.6854
104.3500
98.6882
61.2658
55.2905
53.8531
34.5692
19.9057
16.3122
14.0511
MeO
Me
COOEt
COOEt
D
H
Me
OMe
5ag
+
(97:3)
6ag
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


6.4911
5.6673
Me
MeO
COOEt
COOEt
D
Me
H
OMe
5ag
(97:3)
6ag
mixed with some impurity
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.70
95.30


7.3568
7.3532
7.3395
7.3205
7.2920
7.2739
7.2598
7.0799
7.0761
7.0588
2.6800
2.6619
2.6431
2.4695
2.4503
2.4459
2.4308
1.7073
1.6887
1.6702
1.6518
1.6334
1.6151
1.3745
1.3559
1.3371
1.3180
1.2993
1.2809
1.0162
0.9978
1.0162
0.9978
0.9794
0.8918
0.8735
0.8551
1.00
0.95
0.90
0.85
ppm
7ba
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
3.96
2.00
2.05
2.10
2.09
2.15
3.16
3.20


147.6182
147.3035
128.2487
128.0337
126.8457
106.3066
42.9125
36.6701
22.9745
21.3529
13.7204
12.9711
7ba
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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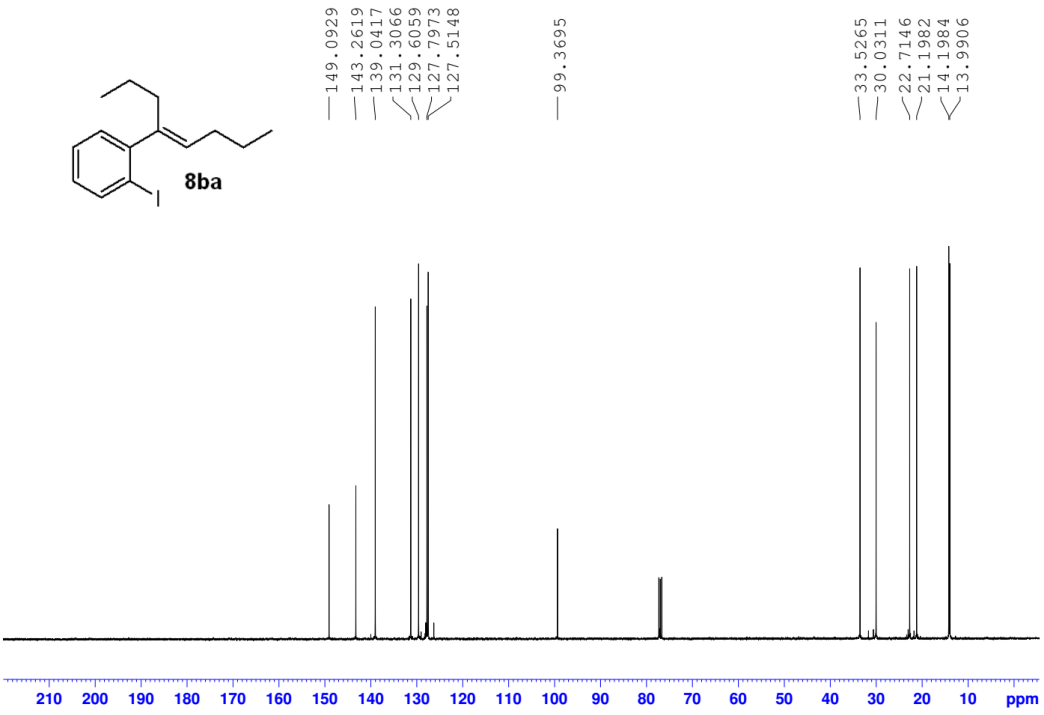
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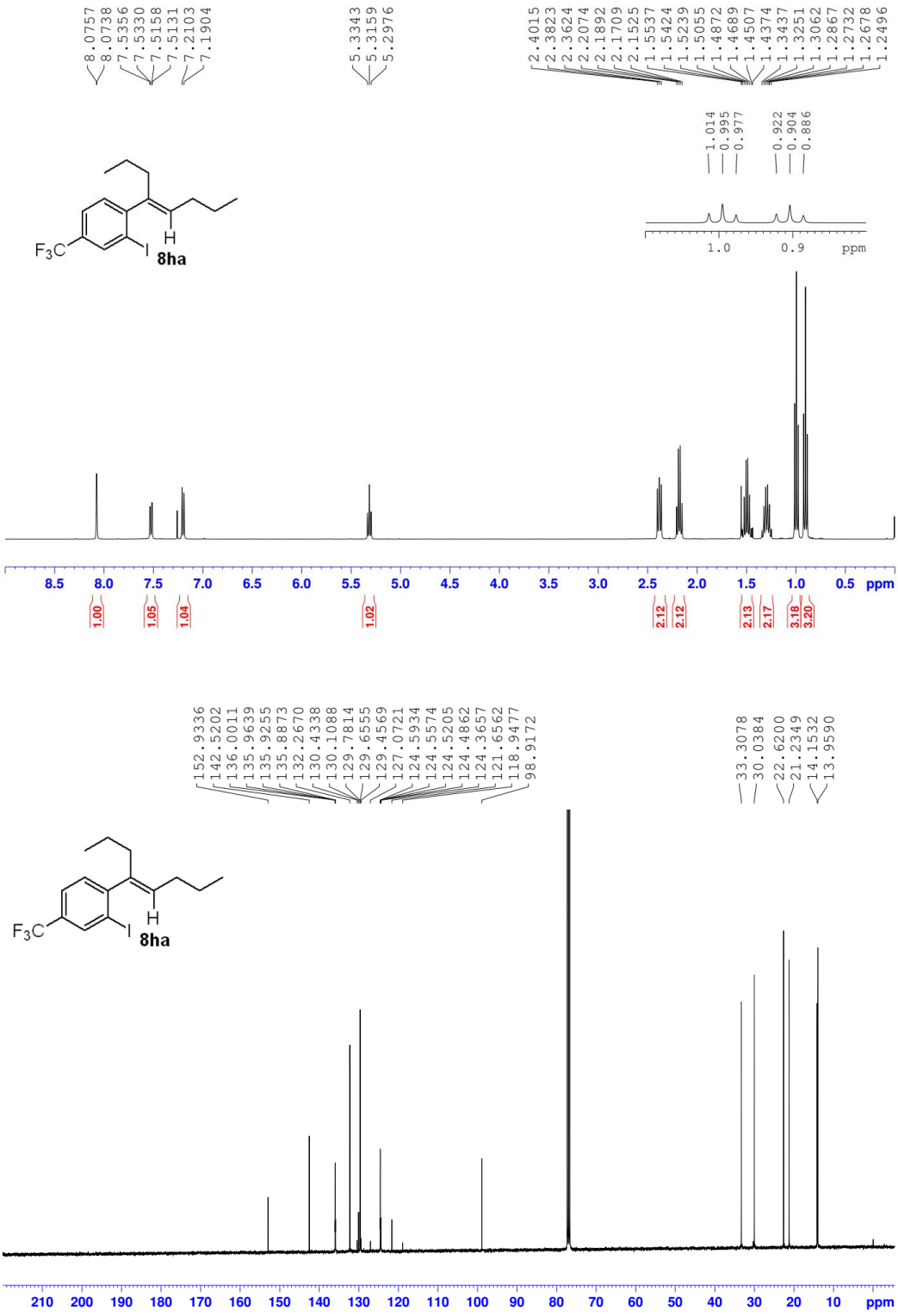
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I
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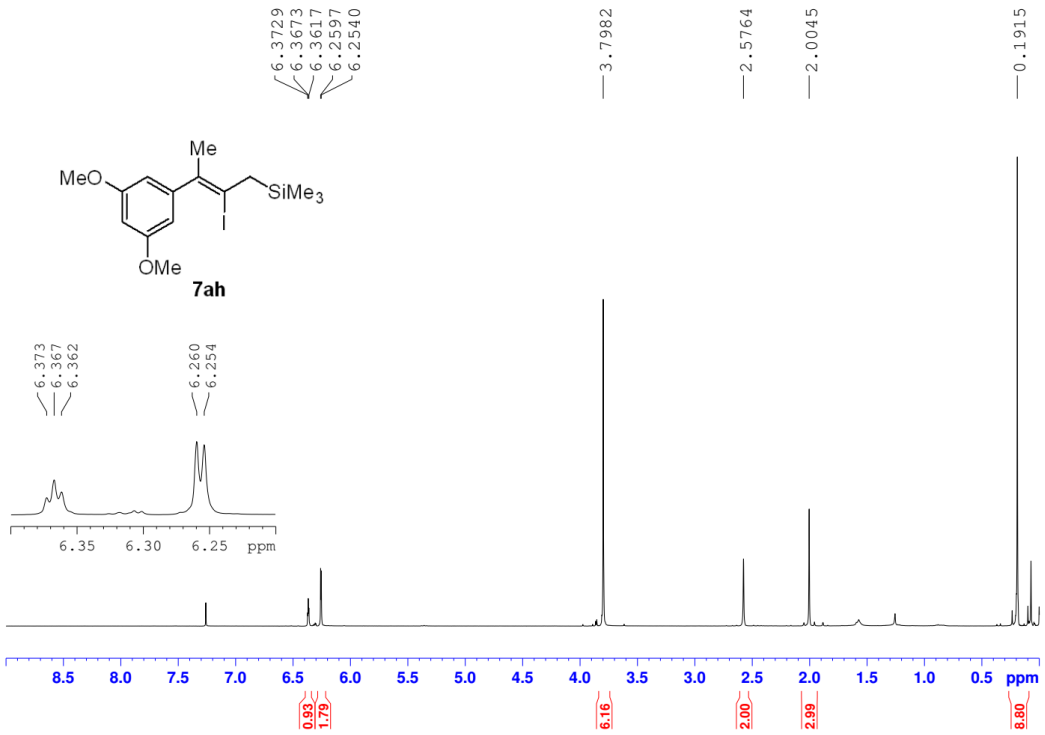
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I
OMe
7ah
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6.30
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6.0
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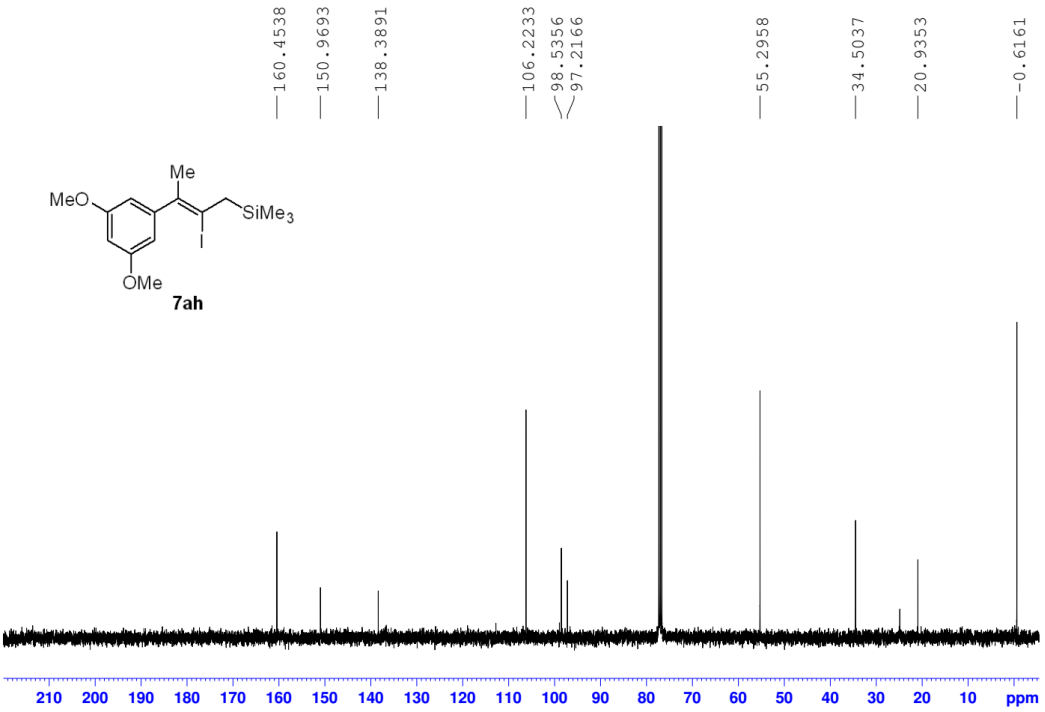
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Me
MeO
SiMe3
I
OMe
7ah
210
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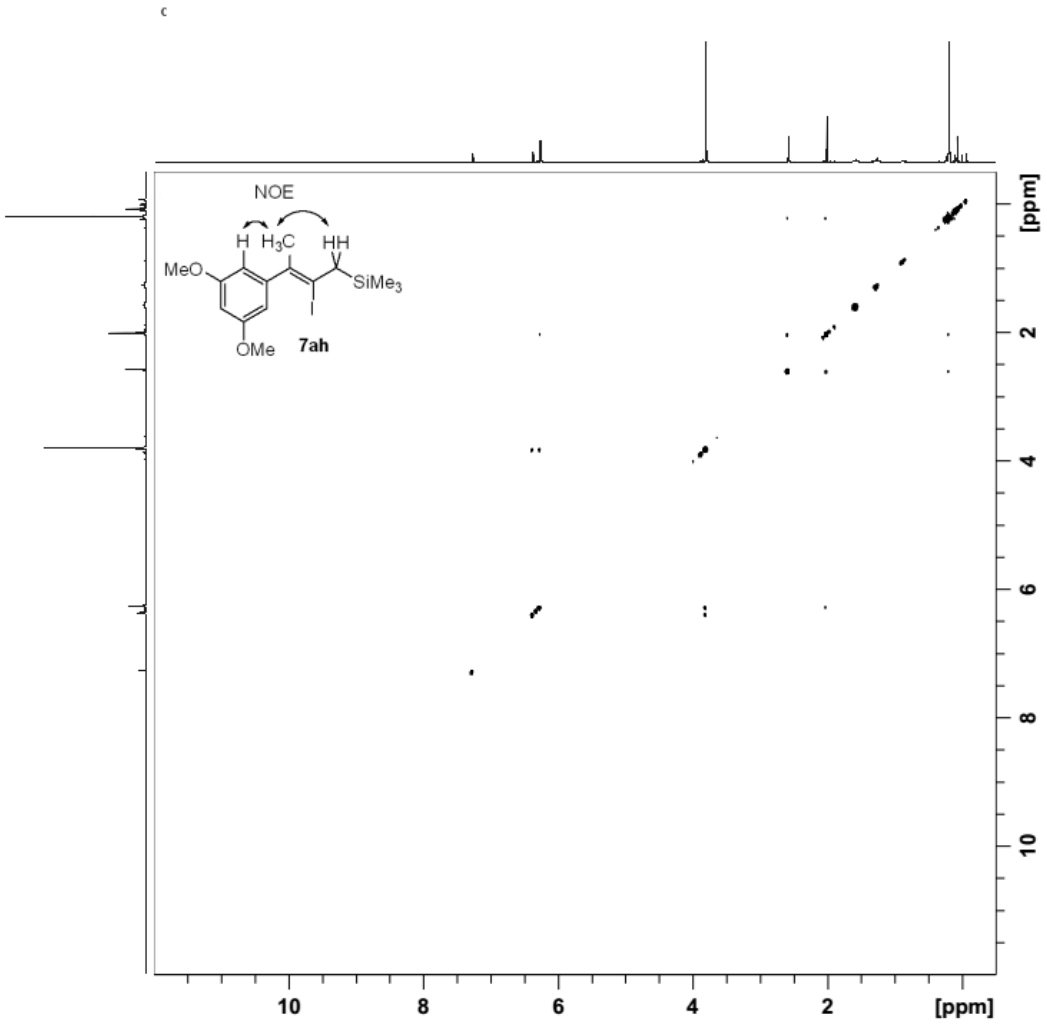
10
ppm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OMe
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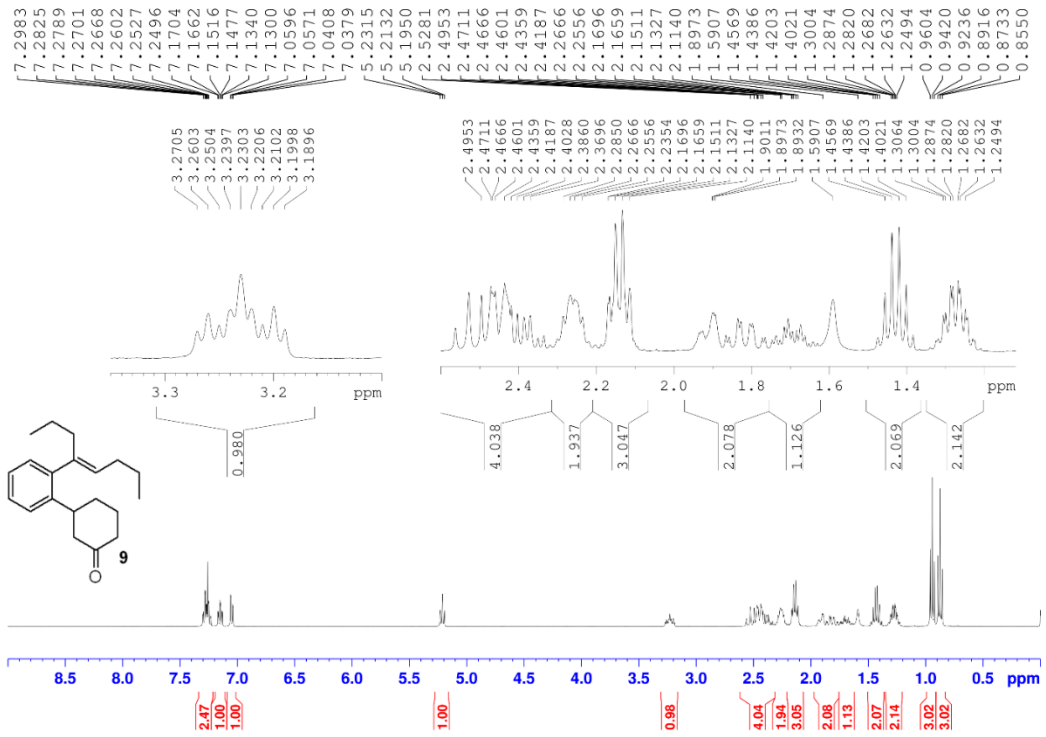
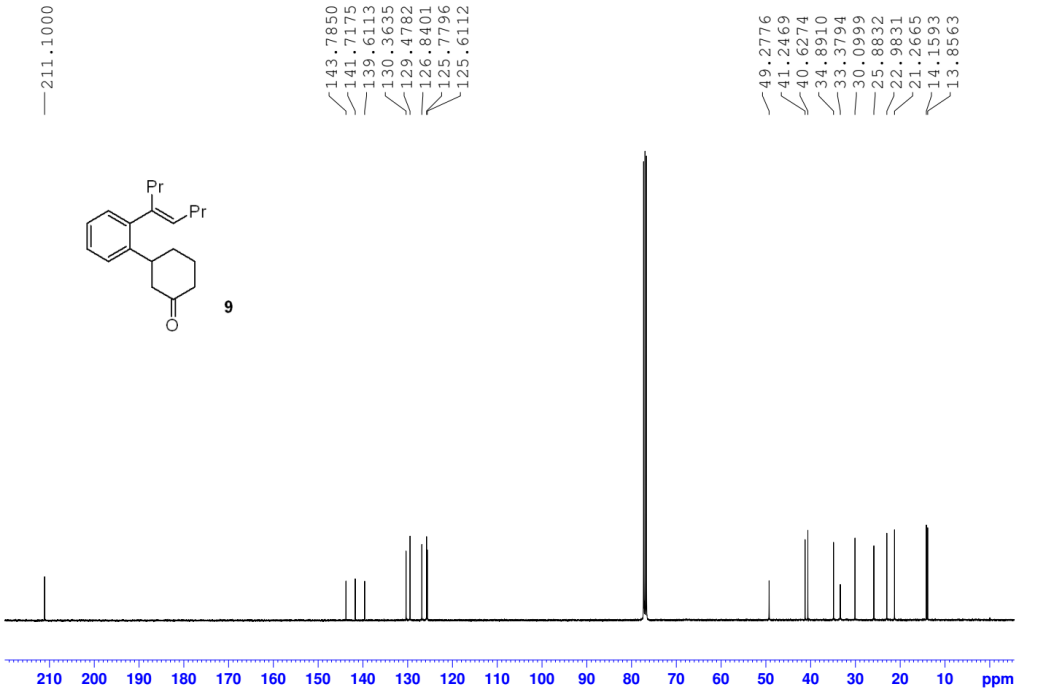

9


Pr
Pr
9

## Conclusions

This thesis presents the development of new Rh-catalyzed reactions that proceed through 1,4-migration of rhodium. Chapter 1 is an introduction of rhodium-catalyed C–C bond forming reactions and 1,4-migration of rhodium. In Chapter 2, a new type of rhodium-catalyzed conjugate arylation using aryloxymethyltrifluoroborates as nucleophiles was developed. The 1,4-Rh shift from alkyl to aryl is the key step to generate an arylrhodium intermediate. The asymmetric conjugate addition is efficiently catalyzed by a chiral diene–rhodium catalyst in $H_2O$ with high enantioselectivity (≥93% ee). In Chapter 3, migratory arylstannylation was found to take place in the reaction of arylstannanes $ArSnR_3$ with unfunctionalized alkynes in the presence of a bisphosphine–rhodium catalyst and a catalytic amount of zinc chloride to produce *ortho*-alkenylarylstannanes in high yields. A catalytic cycle involving three transmetalation steps, that is, transmetalation of aryl groups from Sn to Rh, Rh to Zn, and Zn to Sn is proposed. In Chapter 4, the thesis discloses that the addition of arylzinc reagents ArZnCl to unfunctionalized alkynes is efficiently catalyzed by rhodium complexes in the presence of a catalytic amount of zinc chloride. The selectivity between the 2-arylalkenylzincs and the *ortho*-alkenylarylzinc products, the latter of which is generated through 1,4-Rh migration from alkenyl to aryl, is controlled by the use of appropriate ligands on rhodium.

## List of Publications related to this Thesis

1. **Ming, J**.; Hayashi, T. *Org. Lett*. **2016**, *18*, 6452.