

## Supporting Information

### Synthesis of (2,2-Diborylvinyl)arenes by Rhodium-Catalyzed Desulfanylative *gem*-Diborylation of 2-Arylvinyl Sulfides

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## Instrumentation and chemicals

All reactions were performed under argon atmosphere unless otherwise indicated. All manipulations of air- and/or moisture-sensitive compounds were performed either using standard Schlenk techniques or in a MIWA DBO-1KH-NYWS glovebox under an atmosphere of argon. Unless otherwise noted, rhodium-catalyzed 1,1-diborylation reactions were conducted in a 4 mL (15 × 45 mm) screw-thread clear vial (Thermo Scientific, Cat. No. C4015-1) with a cap assembled with a septum (Thermo Scientific, Cat. No. C4015-75A).

Analytical thin-layer chromatography (TLC) was performed on precoated (0.25 mm) silica-gel plates (Merck, Merck Silica Gel 60 F<sub>254</sub>). Preparative TLC (PTLC) was carried out using precoated silica-gel plates (for 0.50 mm, 1.0 mm and 2.0 mm: Merck, Merck Silica Gel 60 F<sub>254</sub>). Column chromatography was conducted by hand using silica-gel (SiliCycle Inc., SiliaFlash) or on a YAMAZEN Automated Flash Chromatography System that consists of AI-580 and Parallel Frac FR-360 with silica-gel-packed column (Biotage Zip cartridge). Recycling preparative high-performance liquid chromatography (HPLC) was performed by LC-Forte/R (YMC Co., Ltd.) with high-resolution gel permeation chromatography (GPC) column (Japan Analytical Industry Co., Ltd., JAIGEL-1H).

Gas chromatography (GC) analysis was carried out on a Shimadzu GC-2014 using an DB-WAX (Agilent Technologies Japan, Ltd., 30 m, 0.53 mm I.D., 0.5 µm df) column and helium as the carrier gas.

Melting points (mp) were measured with an OptiMelt automated melting point apparatus (Stanford Research Systems, Inc.) and were uncorrected.

<sup>1</sup>H NMR (400 MHz), <sup>13</sup>C NMR (100 MHz), <sup>19</sup>F NMR (373 MHz), and <sup>11</sup>B NMR (127 MHz) spectra were obtained from measurements at ambient temperature on a JEOL 400SS spectrometer. Chloroform-*d*<sub>1</sub> (CDCl<sub>3</sub>) containing 0.05% tetramethylsilane (TMS) (99.8%D, Cambridge Isotope Laboratories, Inc.) or toluene-*d*<sub>8</sub> (99.5%D, Cambridge Isotope Laboratories, Inc.) was used as a solvent for NMR measurements at room temperature. Chemical shifts (δ) for are given in parts per million (ppm) downfield from signal of residual CHCl<sub>3</sub> (δ 7.26 ppm for <sup>1</sup>H NMR), residual toluene (δ 2.09 ppm for <sup>1</sup>H NMR) or CDCl<sub>3</sub> (δ 77.2 ppm for <sup>13</sup>C NMR) as an internal standard, or α,α,α-trifluorotoluene (δ -62.6 ppm for <sup>19</sup>F NMR) or BF<sub>3</sub>·OEt<sub>2</sub> (δ 0.00 ppm for <sup>11</sup>B NMR) as an external standard with coupling constants (*J*) in hertz (Hz). The abbreviations s, d, t, q, sept, m, and br signify singlet, doublet, triplet, quartet, septet, multiplet, and broad, respectively.

Infrared (IR) spectra were measured by diffuse reflectance method on a Shimadzu IRPrestige-21 spectrometer with the absorption band given in cm<sup>-1</sup>.

High-resolution mass spectra (HRMS) were measured on a Thermo Fisher Scientific Exactive™ Plus Orbitrap mass spectrometer under positive electrospray ionization (ESI<sup>+</sup>) conditions.

4-Formylphenyl 4-methylbenzenesulfonate,<sup>S1</sup> methylthio(1,5-cyclooctadiene)rhodium(I) dimer ([Rh(SMe)(cod)]<sub>2</sub>),<sup>S2</sup> (*E*)-styryl acetate (**8**),<sup>S3</sup> (*E*)-(2-bromovinyl)benzene (**10**),<sup>S4</sup> and (*Z*)-(2-bromovinyl)benzene<sup>S4</sup> were prepared according to the reported procedure.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

Tricyclohexylphosphine (PCy<sub>3</sub>) was purchased from Frontier Scientific Inc.

Bis(pinacolato)diboron ((Bpin)<sub>2</sub>), toluene (deoxygenated), benzene (super dehydrated), tetrahydrofuran (THF, deoxygenated), cyclopentyl methyl ether (CPME, super dehydrated), dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>, deoxygenated), *n*-hexane (deoxygenated), 1,4-dioxane (super dehydrated), *N,N*-dimethylformamide (DMF, deoxygenated), acetonitrile (MeCN, super dehydrated), diethyl ether (Et<sub>2</sub>O, super dehydrated), cyclohexane (super dehydrated), 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (Xantphos), 4-(methylthio)benzaldehyde, and sodium methanethiolate (NaSMe, 50%, containing water) were purchased from Wako Pure Chemical Industries, Ltd.

1,2-Dicyclohexylphosphinoethane (dcpe), cesium acetate (CsOAc), cesium carbonate (Cs<sub>2</sub>CO<sub>3</sub>), cesium pivalate (CsOPiv), hydroxy(1,5-cyclooctadiene)rhodium(I) dimer ([Rh(OH)(cod)]<sub>2</sub>), methoxy(1,5-cyclooctadiene)rhodium(I) dimer ([Rh(OMe)(cod)]<sub>2</sub>), chloro(1,5-cyclooctadiene)-rhodium(I) dimer ([RhCl(cod)]<sub>2</sub>), chlorobis(cyclooctene)rhodium(I) dimer ([RhCl(coe)<sub>2</sub>]<sub>2</sub>), 4-methoxybenzyl chloride, 4-methylbenzyl bromide,  $\alpha,\alpha,\alpha$ -trifluorotoluene (PhCF<sub>3</sub>), triethylphosphine (PEt<sub>3</sub>, 1.0 M in THF), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (dtbpy), 2,6-dimethylbenzaldehyde, sodium thiophenoxide, and methyl styryl ether (**7**) were purchased from Sigma–Aldrich Japan Inc.

1,1,2,2-Tetrachloroethane, potassium *tert*-butoxide (*t*-BuOK), sodium *tert*-butoxide, tri(4-methoxyphenyl)phosphine (P(4-MeO-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>), tri(4-fluorophenyl)phosphine (P(4-F-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>), 4-(trifluoromethyl)benzyl bromide, 4-chlorobenzyl bromide, 4-bromobenzyl bromide, 4-fluorobenzyl bromide, 2-methylbenzyl bromide, 4-phenylbenzyl bromide, *N*-(4-formylphenyl)acetamide, 1-(bromomethyl)naphthalene, benzo[*b*]thiophene-2-carbaldehyde, methyl 4-formylbenzoate, methyl (methylsulfinyl)methyl sulfide (FAMSO), hexamethylphosphoric triamide (HMPA), styrene (**9**), diethyl ((methylthio)methyl)phosphonate, 1-dodecanethiol, 2-propanethiol, and pinacol borane (HBpin) were purchased from Tokyo Chemical Industry Co., Ltd.

Ethyl acetate (EtOAc), potassium carbonate (K<sub>2</sub>CO<sub>3</sub>), diethyl ether (Et<sub>2</sub>O), chloroform (CHCl<sub>3</sub>), tri(*n*-butyl)phosphine (P(*n*-Bu)<sub>3</sub>), triphenylphosphine (PPh<sub>3</sub>), cesium fluoride (CsF), potassium acetate (KOAc), sodium acetate (NaOAc), sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), ammonium chloride, triethylamine (Et<sub>3</sub>N), *N,N*-diisopropylethylamine ((*i*-Pr)<sub>2</sub>EtN), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,4-diazabicyclo[2.2.2]octane (DABCO), *N,N*-dimethyl-4-aminopyridine (DMAP), *m*-chloroperoxybenzoic acid (*m*CPBA, 70%, containing water), benzyl bromide, 4-(dimethyl-

amino)benzaldehyde, 4-hydroxybenzaldehyde, sodium hydride (NaH), 1,2-bis(diphenylphosphino)ethane (dppe), sodium periodate, sodium hydrogen carbonate, sodium thiosulfate, and *n*-dodecane were purchased from Nacalai Tesque, Inc.

*n*-Butyllithium (1.6 M in *n*-hexane) was purchased from Kanto Chemical Co.

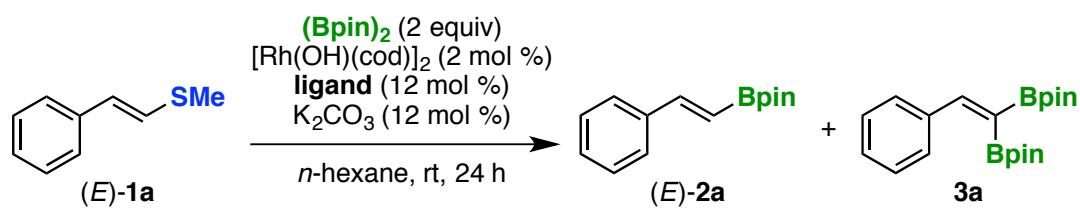


## Optimization study of rhodium-catalyzed 1,1-diborylation of (*E*)-**1a**

### General procedure for optimization study

To a capped vial equipped with a magnetic stir bar were added a rhodium source, a base, a ligand and a solvent (1.0 mL) in a glovebox filled with argon gas, and the solution was stirred for 1 h at room temperature. To the mixture were added bis(pinacolato)diboron ((Bpin)<sub>2</sub>) (102 mg, 0.402 mmol, 2.0 equiv) as a solid and a solution of (*E*)-methyl styryl sulfide ((*E*)-**1a**, 30.0 mg, 0.200 mmol, 1 equiv) dissolved in a solvent (0.5 mL). After stirring the mixture for 24 h at room temperature, the reaction vial was taken out from the glovebox. To the reaction mixture was added saturated aqueous ammonium chloride (ca. 1 mL), and the mixture was extracted with EtOAc (ca. 1 mL × 3). The combined organic extract was dried over Na<sub>2</sub>SO<sub>4</sub>. After filtration, the filtrate was concentrated under reduced pressure. To the residue were added 1,1,2,2-tetrachloroethane (21.0 μL, 0.200 mmol) and CDCl<sub>3</sub> (ca. 1 mL), and then <sup>1</sup>H NMR analysis was conducted using a portion of this solution. The yields were determined by comparison of integrated values of the signals that correspond to vinylic protons of (*E*)-**2a** (δ 6.17 ppm) and **3a** (δ 7.71 ppm) with that corresponds to two protons of 1,1,2,2-tetrachloroethane (δ 5.98 ppm).

**Table S1. Optimization of ligand**



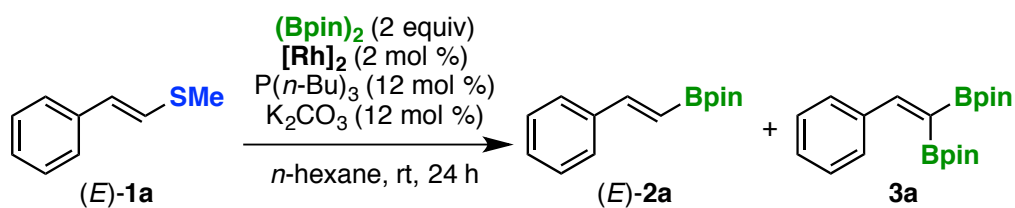
entry	ligand	yield of (E)-2a (%) <sup>a</sup>	yield of 3a (%) <sup>a</sup>
1	$\text{P}(n\text{-Bu})_3$	0	86 [80] <sup>b</sup>
2	$\text{PEt}_3$ (1.0 M in THF)	0	80 [73] <sup>b</sup>
3	$\text{PCy}_3$	0	0
4	$\text{PPh}_3$	0	0
5	$\text{P}(4\text{-MeO-C}_6\text{H}_4)_3$	0	0
6	$\text{P}(4\text{-F-C}_6\text{H}_4)_3$	0	0
7 <sup>c</sup>	dppe	0	0
8 <sup>c</sup>	dcpe	0	0
9 <sup>c</sup>	Xantphos	0	0
10 <sup>c</sup>	dtbpy	0	0

<sup>a</sup>Determined by  $^1\text{H}$  NMR analysis.

<sup>b</sup>Isolated yield in brackets.

<sup>c</sup>6 mol % of ligand was used.

**Table S2. Optimization of rhodium source**

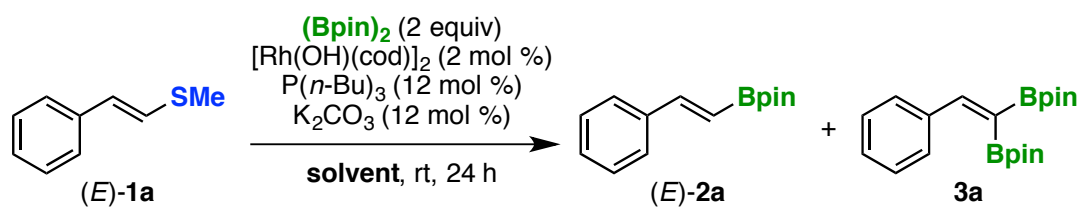


entry	$[\text{Rh}]_2$	yield of (E)-2a (%) <sup>a</sup>	yield of 3a (%) <sup>a</sup>
1	$[\text{Rh}(\text{OH})(\text{cod})]_2$	0	86 [80] <sup>b</sup>
2	$[\text{Rh}(\text{OMe})(\text{cod})]_2$	0	88
3	$[\text{RhCl}(\text{cod})]_2$	12	0
4	$[\text{RhCl}(\text{coe})_2]_2$	19	49
5	$[\text{Rh}(\text{SMe})(\text{cod})]_2$	0	96

<sup>a</sup>Determined by  $^1\text{H}$  NMR analysis.

<sup>b</sup>Isolated yield in brackets.

**Table S3. Optimization of solvent**

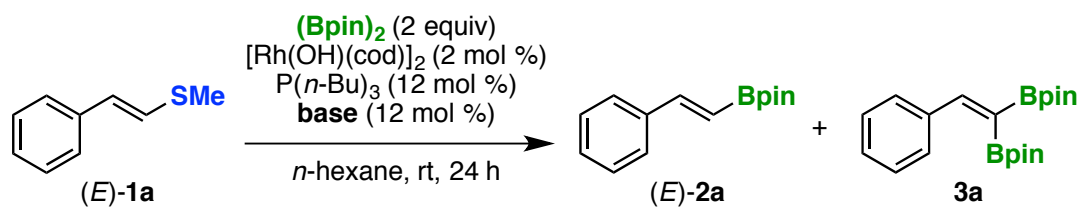


entry	solvent	yield of $(E)\text{-2a}$ (%) <sup>a</sup>	yield of $\text{3a}$ (%) <sup>a</sup>
1	<i>n</i> -hexane	0	86 [80] <sup>b</sup>
2	cyclohexane	0	65
3	benzene	9	83
4	toluene	6	84
5	PhCF <sub>3</sub>	17	73
6	CH <sub>2</sub> Cl <sub>2</sub>	0	0
7	Et <sub>2</sub> O	0	72
8	CPME	41	48
9	1,4-dioxane	17	79
10	THF	16	70
11	MeCN	64	11
12	DMF	21	0

<sup>a</sup>Determined by <sup>1</sup>H NMR analysis.

<sup>b</sup>Isolated yield in brackets.

**Table S4. Optimization of base**

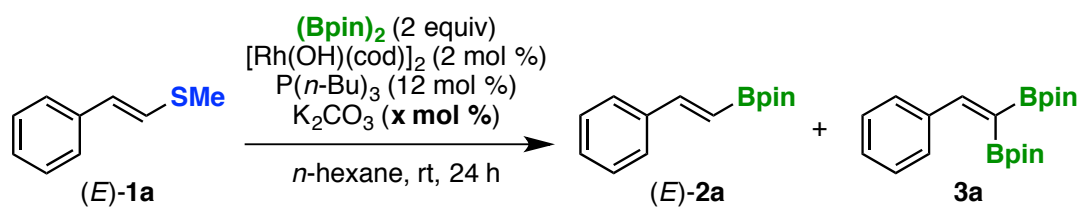


entry	base	yield of <b>(E)-2a</b> (%) <sup>a</sup>	yield of <b>3a</b> (%) <sup>a</sup>
1	CsF	21	12
2	NaOAc	61	14
3	KOAc	8	0
4	CsOAc	38	24
5	CsOPiv	49	7
6	Na <sub>2</sub> CO <sub>3</sub>	43	0
7	K <sub>2</sub> CO <sub>3</sub>	0	86 [80] <sup>b</sup>
8	Cs <sub>2</sub> CO <sub>3</sub>	0	83
9	<i>t</i> -BuOK	0	0
10	Et <sub>3</sub> N	2	71
11	( <i>i</i> -Pr) <sub>2</sub> EtN	2	66
12	DBU	2	65
13	DABCO	0	64
14	DMAP	1	70

<sup>a</sup>Determined by <sup>1</sup>H NMR analysis.

<sup>b</sup>Isolated yield in brackets.

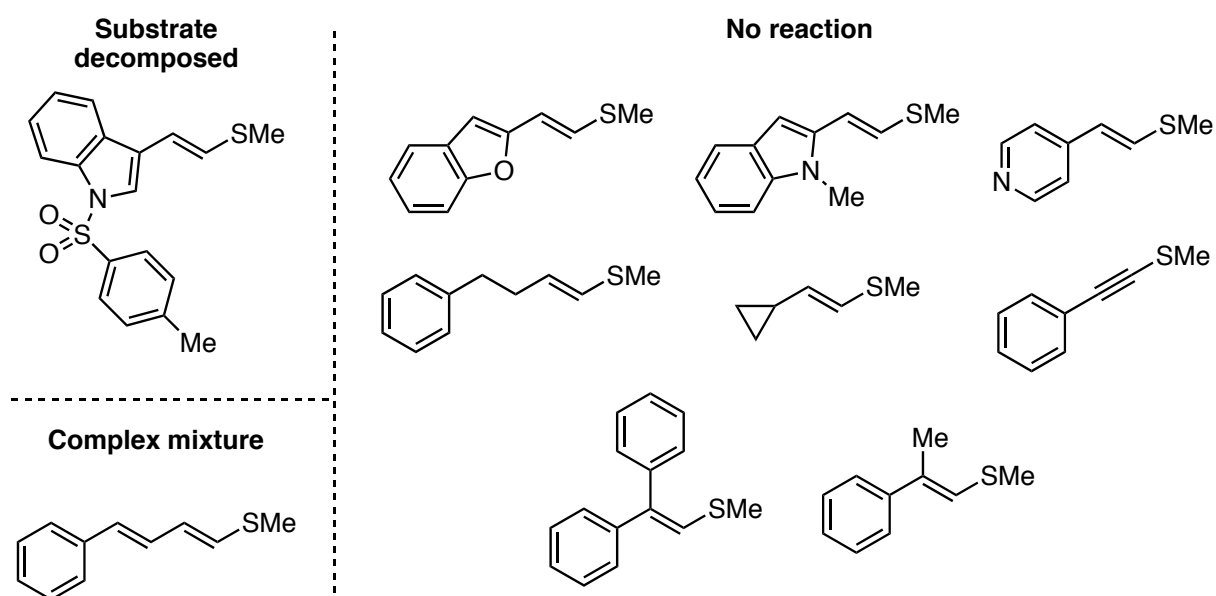
**Table S5. Optimization of the amount of K<sub>2</sub>CO<sub>3</sub>**



entry	x (mol %)	yield of ( <i>E</i> )- <b>2a</b> (%) <sup>a</sup>	yield of <b>3a</b> (%) <sup>a</sup>
1	100	41	50
2	75	33	63
3	50	11	70
4	25	0	81
5	12	0	86 [80] <sup>b</sup>
6	8	0	72
7	4	4	70
8	none	0	0

<sup>a</sup>Determined by <sup>1</sup>H NMR analysis.

<sup>b</sup>Isolated yield in brackets.

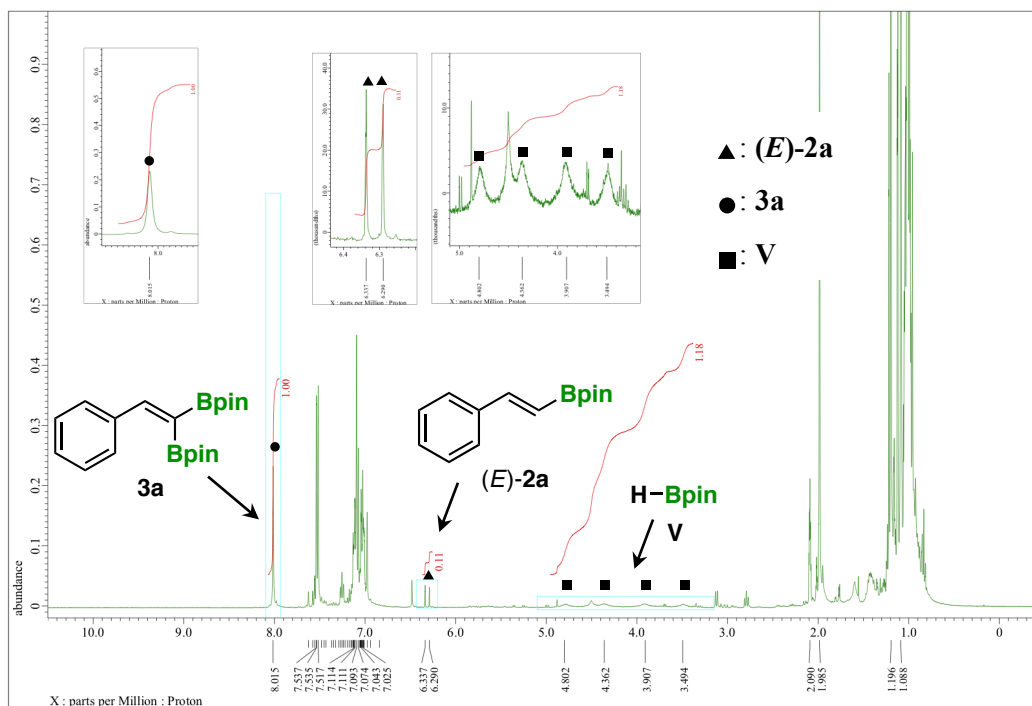


**Figure S1. Examples of unsuccessful substrates.**

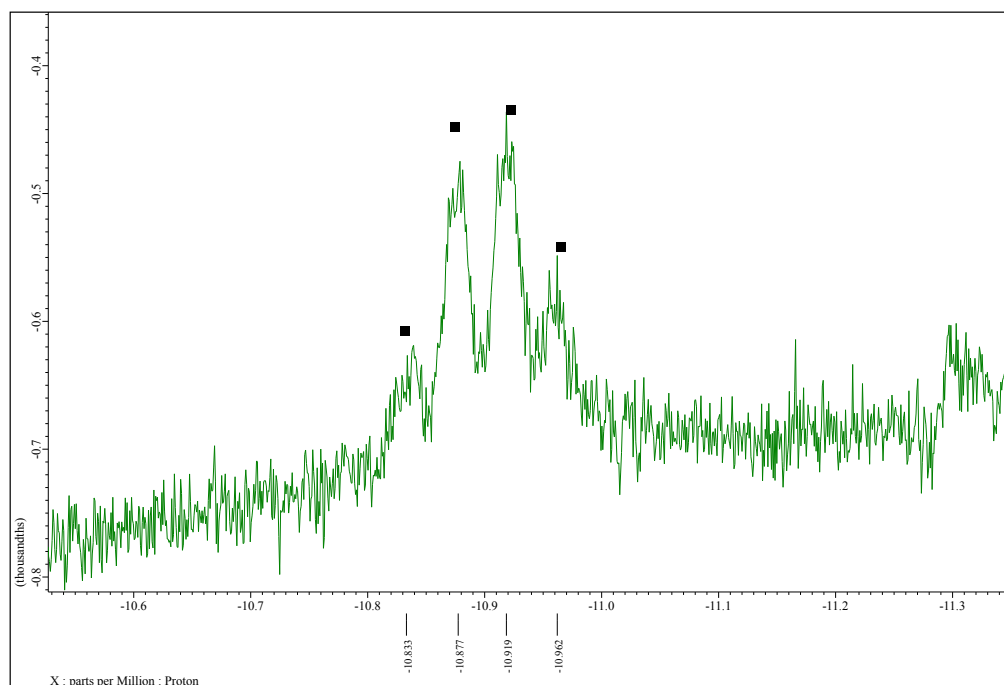
### NMR study to observe pinacol borane (**V**) in the reaction mixture (Figures S2–S4)

To a capped vial equipped with a magnetic stir bar were added [Rh(OH)(cod)]<sub>2</sub> (1.8 mg, 3.9 μmol, 2 mol %), K<sub>2</sub>CO<sub>3</sub> (3.4 mg, 25 μmol, 12 mol %), P(*n*-Bu)<sub>3</sub> (5.9 μL, 24 μmol, 12 mol %), and toluene-*d*<sub>8</sub> (1.0 mL) in a glovebox filled with argon gas, and the solution was stirred for 1 h at room temperature. To the mixture were added bis(pinacolato)diboron ((Bpin)<sub>2</sub>) (102 mg, 0.402 mmol, 2.0 equiv) as a solid and a solution of (*E*)-methyl styryl sulfide ((*E*)-**1a**, 30.0 mg, 0.200 mmol, 1 equiv) dissolved in toluene-*d*<sub>8</sub> (0.5 mL). After stirring the mixture for 6 h at 80 °C, the resulting solution was cooled to room temperature and transferred into an NMR tube in glovebox.

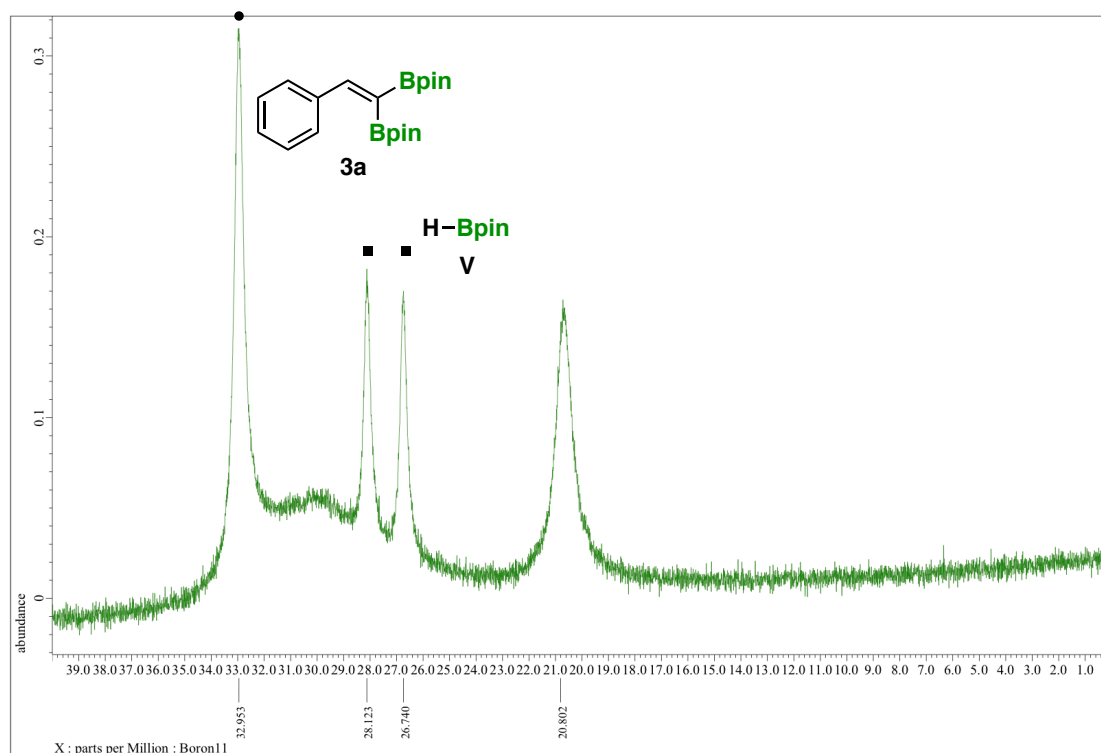
<sup>1</sup>H NMR spectrum (δ −0.5 to 10.5 ppm) obtained from the analysis of the mixture at room temperature is shown in Figure S2. The broad quartet signal observed at δ 4.13 (*J*<sub>H-B</sub> = 171 Hz) indicated the presence of pinacol borane (**V**) and the signals observed at δ 8.02 (s, 1H) and δ 6.31 (d, *J*<sub>H-H</sub> = 18.6 Hz, 1H) indicated the presence of **3a** and (*E*)-**2a**, respectively. The ratio of the integral value for **3a** and **V** was approximately 1:1, indicating that almost the same amounts of **3a** and **V** were generated. <sup>1</sup>H NMR measurement at −70 °C showed a quartet-shaped signal at δ −10.9 ppm (Figure S3). This signal indicated the presence of a rhodium hydride species such as **IV**, although it was difficult to characterize the valency of the rhodium center or other ligand in this complex. <sup>11</sup>B NMR measurement at room temperature also showed the generation of the products. The doublet signal observed at δ 27.4 ppm (*J*<sub>B-H</sub> = 177 Hz) corresponded to pinacol borane (**V**) and the singlet signal observed at δ 33.0 ppm corresponded to **3a**, respectively (Figure S4). Assignments of these signals were performed by comparison of these spectra to each spectrum separately measured using the isolated compounds.



**Figure S2.**  $^1\text{H}$  NMR spectrum ( $\delta$  –0.5 to 10.5 ppm) of the reaction mixture measured in toluene- $d_8$  at room temperature.



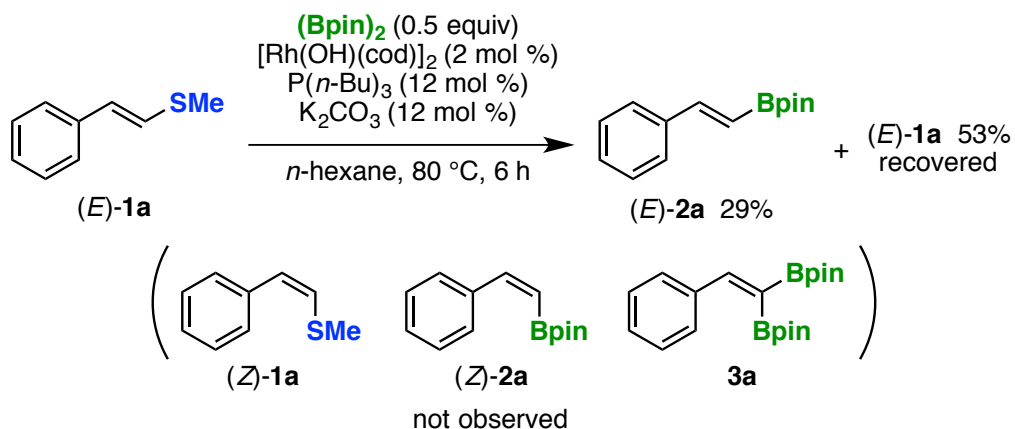
**Figure S3.**  $^1\text{H}$  NMR spectrum ( $\delta$  –11.4 to –10.7 ppm) of the reaction mixture measured in toluene- $d_8$  at –70 °C.



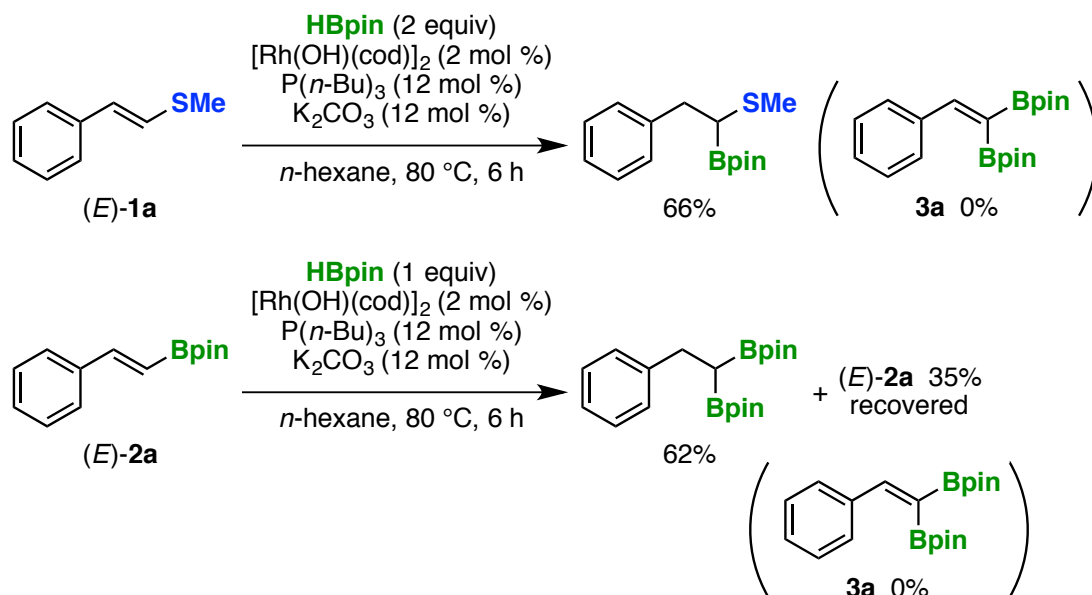
**Figure S4.**  $^{11}\text{B}$  NMR spectrum of the reaction mixture measured in  $\text{toluene-}d_8$  at room temperature.



**Scheme S1. An attempt to observe isomerization of (*E*)-1a**



**Scheme S2. Borylation of (*E*)-1a and (*E*)-2a with HBpin**



### **Monitoring the time-dependent changes in the contents of 1,1-diborylation of (*E*)-1a by GC analysis (Figure 2A)**

To a capped vial equipped with a magnetic stir bar were added [Rh(OH)(cod)]<sub>2</sub> (1.8 mg, 3.9 μmol, 2 mol %), P(*n*-Bu)<sub>3</sub> (5.9 μL, 36 μmol, 12 mol %) and toluene (1.0 mL) in a glovebox filled with argon gas, and the mixture was stirred for 1 h at room temperature. To the mixture were added bis(pinacolato)diboron ((Bpin)<sub>2</sub>) (102 mg, 0.402 mmol, 2.0 equiv) as a solid, a solution of (*E*)-1a (30.0 mg, 0.200 mmol, 1 equiv) in toluene (0.5 mL), and *n*-dodecane (45.5 μL, 0.200 mmol) as an internal standard. The reaction vial was heated at 80 °C. Portions (ca. 10 μL) of this mixture were collected every 15 min, to each of which were added EtOAc (ca. 1 mL) and saturated aqueous ammonium chloride (ca. 1 mL) immediately. After stirring the mixture vigorously, GC analysis was conducted using a portion of the resulting organic phase to evaluate the amount of the products (*E*)-2a and 3a along with the remaining (*E*)-1a.

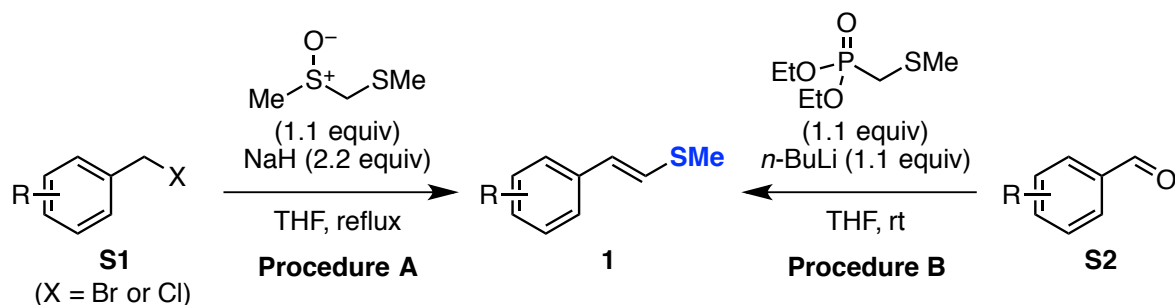
### **Monitoring the time-dependent changes in the contents of 1,1-diborylation of (*E*)-1a conducted in the presence of pinacol borane by GC analysis (Figure 2B)**

To a capped vial equipped with a magnetic stir bar were added [Rh(OH)(cod)]<sub>2</sub> (1.8 mg, 3.9 μmol, 2 mol %), P(*n*-Bu)<sub>3</sub> (5.9 μL, 36 μmol, 12 mol %) and toluene (1.0 mL) in a glovebox filled with argon gas, and the mixture was stirred for 1 h at room temperature. To the mixture were added bis(pinacolato)diboron ((Bpin)<sub>2</sub>) (102 mg, 0.402 mmol, 2.0 equiv) as a solid, a solution of (*E*)-1a (30.0 mg, 0.200 mmol, 1 equiv) in toluene (0.5 mL), pinacol borane (2.9 μL, 20 μmol, 10 mol %), and *n*-dodecane (45.5 μL, 0.200 mmol) as an internal standard. The reaction vial was heated at 80 °C. Portions (ca. 10 μL) of this mixture were collected every 15 min, to each of which were added EtOAc (ca. 1 mL) and saturated aqueous ammonium chloride (ca. 1 mL) immediately. After stirring the mixture vigorously, GC analysis was conducted using a portion of the resulting organic phase to evaluate the amount of the products (*E*)-2a and 3a along with the remaining (*E*)-1a.

GC conditions for analyses of the products: Constant linear column flow was adjusted to 30 cm/sec. Temperatures of the injector and the detector were held at 300 °C, and the GC oven temperature program was set as follows: initially held at 75 °C for 4 min, heated to 220 °C at the rate of 15 °C/min, and held at 220 °C for 11 min. Retention times: *n*-dodecane (8.6 min, internal standard), (Bpin)<sub>2</sub> (12.2 min), (*E*)-1a (*E*-isomer: 13.4 min, *Z*-isomer: 13.8 min), (*E*)-2a (15.1 min), and 3a (22.5 min).

## Synthetic procedures and characterization data

### General procedures for preparation of styryl sulfides **1**



#### Procedure A

Preparations of **1** from benzyl bromide or chloride derivatives **S1** and FAMSOMe were conducted according to the reported procedure with a minor modification.<sup>S5</sup>

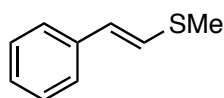
To a round-bottom flask equipped with a magnetic stir bar and charged with NaH (60% purity in mineral oil, 2.2 equiv) and THF (0.44 mol/L for **S1**) was added FAMSOMe (1.1 equiv) at 0 °C via syringe, and then warmed up to room temperature. After stirring for 30 min at the same temperature, to the mixture was added **S1** (1 equiv) at room temperature and refluxed for 16 h. After cooling to room temperature, the reaction mixture was poured into ice water and extracted with EtOAc. The combined organic extract was washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography to give the corresponding styryl sulfide **1**.

#### Procedure B

Preparations of **1** from benzaldehyde derivatives **S2** and diethyl ((methylthio)methyl)-phosphonate were conducted according to the reported procedure with a minor modification.<sup>S6</sup>

To a round-bottom flask equipped with a magnetic stir bar and charged with diethyl ((methylthio)methyl)phosphonate (1.1 equiv) and THF (0.5 mol/L for **S2**) was added *n*-butyllithium (1.1 equiv) at 0 °C via a syringe. After stirring for 30 min at the same temperature, to the mixture was added **S2** (1 equiv) and then warmed up to room temperature. After stirring for 16 h at the same temperature, to the mixture was added saturated aqueous ammonium chloride and extracted with EtOAc. The combined organic extract was washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography to give the corresponding styryl sulfide **1**.

**(*E*)-Methyl styryl sulfide ((*E*)-1a)**



Prepared from benzyl bromide (1.71 g, 9.94 mmol) by Procedure A.

Eluent for column chromatographic purification: *n*-hexane/EtOAc = 49/1;

Yield: 43.7% (652 mg, 4.34 mmol);

Yellow oil;

TLC  $R_f$  = 0.72 (*n*-hexane/EtOAc = 9/1);

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.39 (s, 3H), 6.31 (d,  $J$  = 15.4 Hz, 1H), 6.79 (d,  $J$  = 15.4 Hz, 1H), 7.16–7.21 (AA'BB'C, 1H), 7.29–7.30 (AA'BB'C, 4H);

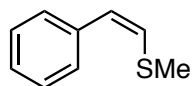
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  15.0 (1C), 124.9 (1C), 125.6 (2C), 126.0 (1C), 126.8 (1C), 128.8 (2C), 137.3 (1C);

The chemical shifts were consistent with those reported in the literature.<sup>S7</sup>

**(*E/Z*)-Methyl styryl sulfide (*E/Z*-mixture of 1a)**

An *E/Z*-mixture of **1a** was prepared by mixing (*E*)-**1a** and (*Z*)-**1a** in the ratio of 1:1. A procedure for the preparation of (*Z*)-**1a** is shown below.

**(*Z*)-Methyl styryl sulfide ((*Z*)-1a)**



Preparations of (*Z*)-**1a** was conducted according to the reported procedure with a minor modification.<sup>S8</sup>

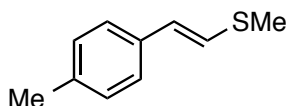
To a 100 mL round-bottom flask equipped with a magnetic stir bar and charged with NaSMe (50%, 1.16 g, 8.28 mmol, 1.5 equiv) in HMPA (10 mL) was added (*Z*)-(2-bromovinyl)benzene (1.01 g, 5.52 mmol, 1 equiv) in HMPA (5 mL) at room temperature. After stirring for 12 h at the same temperature, to the reaction mixture was added water (ca. 20 mL) and extracted with Et<sub>2</sub>O (ca. 10 mL  $\times$  3). The combined organic extract was washed with brine (ca. 20 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (*n*-hexane) to give (*Z*)-**1a** (708 mg, 4.71 mmol, 85.4%, *Z/E* = >25:1) as a colorless oil; TLC  $R_f$  = 0.72 (*n*-hexane/EtOAc = 10/1);

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.41 (s, 3H), 6.22 (d,  $J$  = 10.9 Hz, 1H), 6.44 (d,  $J$  = 10.9 Hz, 1H), 7.19–7.24 (AA'BB'C, 1H), 7.33–7.39 (AA'BB'C, 2H), 7.45–7.49 (AA'BB'C, 2H);

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  19.1 (1C), 125.5 (1C), 126.8 (1C), 128.4 (2C), 128.8 (2C), 129.2 (1C), 137.1 (1C);

The chemical shifts were consistent with those reported in the literature.<sup>S8</sup>

**Methyl 4-methylstyryl sulfide (1b, *E/Z* = 7.8:1)**



Prepared from 4-methylbenzyl bromide (1.85 g, 10.0 mmol) by Procedure A.

Eluent for column chromatographic purification: *n*-hexane/EtOAc = 49/1;

Yield: 36.0% (591 mg, 3.60 mmol, *E/Z* = 7.8:1);

Colorless oil;

TLC  $R_f$  = 0.62 (*n*-hexane/EtOAc = 9/1);

for *E*-isomer:

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.31 (s, 3H), 2.36 (s, 3H), 6.29 (d,  $J$  = 15.4 Hz, 1H), 6.71 (d,  $J$  = 15.4 Hz, 1H), 7.07–7.10 (AA'BB', 2H), 7.17–7.19 (AA'BB', 2H);

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  15.0 (1C), 21.3 (1C), 124.7 (1C), 125.0 (1C), 125.5 (2C), 129.5 (2C), 134.5 (1C), 136.6 (1C);

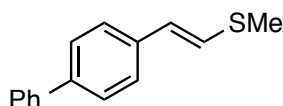
for *Z*-isomer:

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.33 (s, 3H), 2.38 (s, 3H), 6.13 (d,  $J$  = 10.6 Hz, 1H), 6.40 (d,  $J$  = 10.6 Hz, 1H), 7.14–7.16 (AA'BB', 2H), 7.35–7.37 (AA'BB', 2H);

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  19.0 (1C), 21.4 (1C), 126.5 (1C), 127.8 (1C), 128.0 (1C), 128.7 (2C), 129.1 (2C), 134.3 (1C);

The chemical shifts were consistent with those reported in the literature.<sup>S9</sup>

**(*E*)-2-(Biphenyl-4-yl)ethenyl methyl sulfide (1c)**



Prepared from 4-phenylbenzyl bromide (2.47 g, 9.99 mmol) by Procedure A.

Eluent for column chromatographic purification: *n*-hexane/EtOAc = 49/1;

Yield: 29.4% (666 mg, 2.94 mmol);

Colorless solid;

mp: 155–156 °C;

TLC  $R_f$  = 0.45 (*n*-hexane/EtOAc = 9/1);

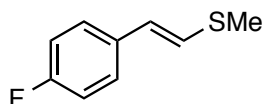
$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.41 (s, 3H), 6.35 (d,  $J$  = 15.4 Hz, 1H), 6.84 (d,  $J$  = 15.4 Hz, 1H), 7.31–7.38 (m, 3H), 7.41–7.45 (AA'BB', 2H), 7.52–7.56 (AA'BB', 2H), 7.58–7.62 (AA'BB', 2H);

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  15.1 (1C), 124.4 (1C), 126.0 (2C), 126.1 (1C), 127.0 (2C), 127.4 (1C), 127.5 (2C), 129.0 (2C), 136.4 (1C), 139.5 (1C), 140.9 (1C);

IR (ZnSe,  $\text{cm}^{-1}$ ) 688, 756, 931, 1487, 1591, 2317, 3026;

HRMS ( $\text{ESI}^+$ )  $m/z$  227.0883 (227.0889 calcd for  $\text{C}_{15}\text{H}_{15}\text{S}^+$ ,  $[\text{M}+\text{H}]^+$ ).

#### 4-Fluorostyryl methyl sulfide (**1d**, $E/Z = 6.5:1$ )



Prepared from 4-fluorobenzyl bromide (1.89 g, 10.0 mmol) by Procedure A.

Eluent for column chromatographic purification: *n*-hexane/EtOAc = 49/1;

Yield: 51.5% (866 mg, 5.15 mmol,  $E/Z = 6.5:1$ );

Colorless oil;

TLC  $R_f = 0.51$  (*n*-hexane/EtOAc = 9/1);

For *E*-isomer:

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.37 (s, 3H), 6.27 (d,  $J = 15.4$  Hz, 1H), 6.69 (d,  $J = 15.4$  Hz, 1H), 6.94–7.01 (AA'BB'X, 2H), 7.23–7.27 (AA'BB'X, 2H);

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  15.0 (1C), 115.7 (d,  $^2J_{\text{C-F}} = 21.0$  Hz, 2C), 123.8 (1C), 125.7 (d,  $^5J_{\text{C-F}} = 1.9$  Hz, 1C), 126.9 (d,  $^3J_{\text{C-F}} = 7.6$  Hz, 2C), 133.5 (d,  $^4J_{\text{C-F}} = 2.9$  Hz, 1C), 161.9 (d,  $^1J_{\text{C-F}} = 246.1$  Hz, 1C);

$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -115.6 (m);

For *Z*-isomer:

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.40 (s, 3H), 6.18 (d,  $J = 10.6$  Hz, 1H), 6.39 (d,  $J = 10.6$  Hz, 1H), 7.01–7.06 (AA'BB'X, 2H), 7.42–7.46 (AA'BB'X, 2H);

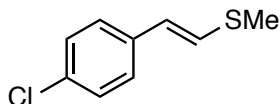
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  18.9 (1C), 115.2 (d,  $^2J_{\text{C-F}} = 21.9$  Hz, 2C), 124.3 (1C), 128.6 (d,  $^5J_{\text{C-F}} = 1.9$  Hz, 1C), 130.4 (d,  $^3J_{\text{C-F}} = 8.6$  Hz, 2C), 133.3 (d,  $^4J_{\text{C-F}} = 2.9$  Hz, 1C), 161.5 (d,  $^1J_{\text{C-F}} = 247.0$  Hz, 1C);

$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -114.7 (m);

IR (ZnSe,  $\text{cm}^{-1}$ ) 835, 925, 1224, 1503, 1581, 1601, 3036;

HRMS ( $\text{ESI}^+$ )  $m/z$  169.0480 (169.0482 calcd for  $\text{C}_9\text{H}_{10}\text{FS}^+$ ,  $[\text{M}+\text{H}]^+$ ).

#### (*E*)-4-Chlorostyryl methyl sulfide (**1e**)



Prepared from 4-chlorobenzyl bromide (2.05 g, 9.97 mmol) by Procedure A.

Eluent for column chromatographic purification: *n*-hexane/EtOAc = 50/1;

Yield: 33.6% (619 mg, 3.35 mmol);

Colorless solid;

mp: 55–56 °C;

TLC  $R_f$  = 0.51 (*n*-hexane/EtOAc = 10/1);

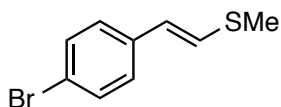
$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.38 (s, 3H), 6.24 (d,  $J$  = 15.4 Hz, 1H), 6.78 (d,  $J$  = 15.4 Hz, 1H), 7.19–7.22 (AA'BB', 2H), 7.24–7.27 (AA'BB', 2H);

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  15.0 (1C), 123.5 (1C), 126.7 (2C), 126.9 (1C), 129.0 (2C), 132.3 (1C), 135.8 (1C);

IR (ZnSe,  $\text{cm}^{-1}$ ) 783, 930, 1088, 1487, 1557, 1593, 2914;

HRMS ( $\text{ESI}^+$ )  $m/z$  185.0182 (185.0186 calcd  $\text{C}_9\text{H}_{10}^{35}\text{ClS}^+$ ,  $[\text{M}+\text{H}]^+$ ).

#### (*E*)-4-Bromostyryl methyl sulfide (1f)



Prepared from 4-bromobenzyl bromide (1.85 g, 7.40 mmol) by Procedure A.

Eluent for column chromatographic purification: *n*-hexane/EtOAc = 49/1;

Yield: 75.5% (1.28 g, 5.59 mmol);

Colorless solid;

mp: 72–73 °C;

TLC  $R_f$  = 0.51 (*n*-hexane/EtOAc = 9/1);

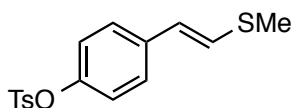
$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.38 (s, 3H), 6.22 (d,  $J$  = 15.4 Hz, 1H), 6.80 (d,  $J$  = 15.4 Hz, 1H), 7.13–7.17 (AA'BB', 2H), 7.39–7.42 (AA'BB', 2H);

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  14.9 (1C), 120.4 (1C), 123.4 (1C), 127.0 (2C), 127.1 (1C), 131.9 (2C), 136.2 (1C);

IR (ZnSe,  $\text{cm}^{-1}$ ) 832, 930, 1487, 1593, 3015, 3744;

HRMS ( $\text{ESI}^+$ )  $m/z$  228.9677 (228.9681 calcd for  $\text{C}_9\text{H}_{10}^{79}\text{BrS}^+$ ,  $[\text{M}+\text{H}]^+$ ).

#### (2-(Methylthio)vinyl)phenyl 4-methylbenzenesulfonate (1g, *E/Z* = 18:1)



Prepared from 4-formylphenyl 4-methylbenzenesulfonate (2.76 g, 9.99 mmol) by Procedure B.

Purified by recrystallization from *n*-hexane/EtOAc = 9/1;

Yield: 40.6% (1.30 g, 4.06 mmol, *E/Z* = 18:1);

Colorless solid;

mp: 88–89 °C;

TLC  $R_f$  = 0.16 (*n*-hexane/EtOAc = 9/1);

For *E*-isomer:

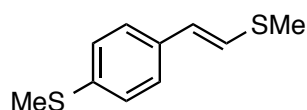
$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.37 (s, 3H), 2.45 (s, 3H), 6.22 (d,  $J = 15.4$  Hz, 1H), 6.75 (d,  $J = 15.4$  Hz, 1H), 6.87–6.91 (AA' BB', 2H), 7.16–7.20 (AA' BB', 2H), 7.29–7.31 (AA' BB', 2H), 7.68–7.71 (AA' BB', 2H);

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  14.9 (1C), 21.9 (1C), 122.8 (2C), 123.2 (1C), 126.4 (2C), 127.4 (1C), 128.7 (2C), 129.9 (2C), 132.5 (1C), 136.3 (1C), 145.5 (1C), 148.2 (1C);

IR (ZnSe,  $\text{cm}^{-1}$ ) 814, 845, 1175, 1366, 1596, 1748, 2311, 3746;

HRMS ( $\text{ESI}^+$ )  $m/z$  343.0430 (343.0433 calcd for  $\text{C}_{16}\text{H}_{16}\text{NaO}_3\text{S}_2^+$ ,  $[\text{M}+\text{Na}]^+$ ).

### (*E*)-Methyl 4-(methylthio)styryl sulfide (1h)



Prepared from 4-(methylthio)benzaldehyde (1.52 g, 9.99 mmol) by Procedure B.

Eluent for column chromatographic purification: *n*-hexane/EtOAc = 49/1;

Yield: 13.9% (273 mg, 1.39 mmol);

Pale yellow solid;

mp: 102–103 °C;

TLC  $R_f$  = 0.54 (*n*-hexane/EtOAc = 4/1);

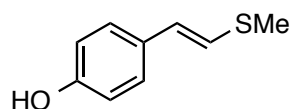
$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.38 (s, 3H), 2.47 (s, 3H), 6.26 (d,  $J = 15.4$  Hz, 1H), 6.74 (d,  $J = 15.4$  Hz, 1H), 7.17–7.23 (AA'BB', 2H+2H, two signals overlapped);

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  15.1 (1C), 16.2 (1C), 124.3 (1C), 125.4 (1C), 126.0 (2C), 127.1 (2C), 134.4 (1C), 136.8 (1C);

IR (ZnSe,  $\text{cm}^{-1}$ ) 783, 928, 1314, 1489, 1589, 2313, 2913;

HRMS ( $\text{ESI}^+$ )  $m/z$  197.0450 (197.0453 calcd for  $\text{C}_{10}\text{H}_{13}\text{S}_2^+$ ,  $[\text{M}+\text{H}]^+$ ).

### (*E*)-4-(2-(Methylthio)vinyl)phenol (1i)



Prepared from 4-hydroxybenzaldehyde (611 mg, 5.00 mmol) by Procedure B.

Purified by recrystallization: *n*-hexane/EtOAc = 9/1;

Yield: 16.1% (134 mg, 0.806 mmol);

Colorless solid;

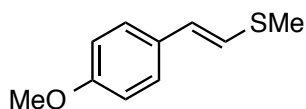
mp: 125–126 °C;

TLC  $R_f$  = 0.51 (*n*-hexane/EtOAc = 1/1);



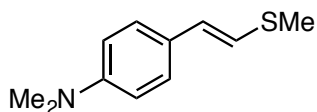
$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.36 (s, 3H), 4.85 (s, 1H), 6.28 (d,  $J = 15.4$  Hz, 1H), 6.60 (d,  $J = 15.4$  Hz, 1H), 6.75–6.78 (AA'BB', 2H), 7.17–7.19 (AA'BB', 2H);  
 $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  15.3 (1C), 115.7 (2C), 123.5 (1C), 124.9 (1C), 126.9 (2C), 130.4 (1C), 154.6 (1C);  
IR (ZnSe,  $\text{cm}^{-1}$ ) 789, 835, 925, 1240, 1508, 1579, 1598, 3394;  
HRMS ( $\text{ESI}^+$ )  $m/z$  167.0524 (167.0525 calcd for  $\text{C}_9\text{H}_{11}\text{OS}^+$ ,  $[\text{M}+\text{H}]^+$ ).

**(*E*)-4-Methoxystyryl methyl sulfide (1j)**



Prepared from 4-methoxybenzyl chloride (1.56 g, 9.96 mmol) by Procedure A.  
Eluent for column chromatographic purification: *n*-hexane/EtOAc = 49/1;  
Yield: 40.8% (731 mg, 4.06 mmol);  
Pale yellow solid;  
mp: 70–71 °C;  
TLC  $R_f$  = 0.72 (*n*-hexane/EtOAc = 9/1);  
 $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.37 (s, 3H), 3.80 (s, 3H), 6.29 (d,  $J = 15.4$  Hz, 1H), 6.61 (d,  $J = 15.4$  Hz, 1H), 6.82–6.86 (AA'BB', 2H), 7.21–7.25 (AA'BB', 2H);  
 $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  15.2 (1C), 55.5 (1C), 114.3 (2C), 123.4 (1C), 125.0 (1C), 126.7 (2C), 130.3 (1C), 158.6 (1C);  
IR (ZnSe,  $\text{cm}^{-1}$ ) 785, 837, 928, 1032, 1256, 1510, 1593, 2999;  
HRMS ( $\text{ESI}^+$ )  $m/z$  181.0679 (181.0682 calcd for  $\text{C}_{10}\text{H}_{13}\text{OS}^+$ ,  $[\text{M}+\text{H}]^+$ ).

**(*E*)-*N,N*-Dimethyl-4-(2-(methylthio)vinyl)aniline (1k)**



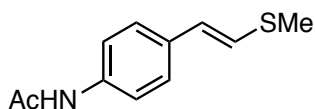
Prepared from 4-(dimethylamino)benzaldehyde (1.49 g, 9.99 mmol) by Procedure B.  
Purified by recrystallization: *n*-hexane/EtOAc = 9/1;  
Yield: 47.9% (925 mg, 4.79 mmol);  
Colorless solid;  
mp: 81–82 °C;  
TLC  $R_f$  = 0.56 (*n*-hexane/EtOAc = 1/1);  
 $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.35 (s, 3H), 2.94 (s, 6H), 6.30 (d,  $J = 15.4$  Hz, 1H), 6.51 (d,  $J = 15.4$  Hz, 1H), 6.64–6.68 (AA'BB', 2H), 7.17–7.21 (AA'BB', 2H);

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  15.5 (1C), 40.7 (2C), 112.8 (2C), 120.8 (1C), 126.1 (1C), 126.2 (1C), 126.6 (2C), 149.7 (1C);

IR (ZnSe,  $\text{cm}^{-1}$ ) 785, 823, 941, 1217, 1337, 1516, 1600, 2793;

HRMS ( $\text{ESI}^+$ )  $m/z$  194.0999 (194.0998 calcd for  $\text{C}_{11}\text{H}_{16}\text{NS}^+$ ,  $[\text{M}+\text{H}]^+$ ).

**(*E*)-*N*-(4-(2-(Methylthio)vinyl)phenyl)acetamide (1l)**



Prepared from *N*-(4-formylphenyl)acetamide (1.63 g, 10.1 mmol) by Procedure B.

Eluent for column chromatographic purification: *n*-hexane/EtOAc = 1/4;

Yield: 10.0% (209 mg, 1.01 mmol);

Colorless solid;

mp: 168–169 °C;

TLC  $R_f$  = 0.45 (*n*-hexane/EtOAc = 1/4);

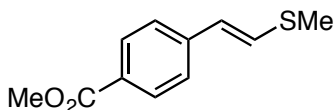
$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.16 (s, 3H), 2.38 (s, 3H), 6.27 (d,  $J$  = 15.4 Hz, 1H), 6.71 (d,  $J$  = 15.4 Hz, 1H), 7.22–7.24 (AA'BB', 2H), 7.34 (br s, 1H), 7.42–7.44 (AA'BB', 2H);

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  15.1 (1C), 24.8 (1C), 120.2 (2C), 124.3 (1C), 125.2 (1C), 126.1 (2C), 133.5 (1C), 136.6 (1C), 168.4 (1C);

IR (ZnSe,  $\text{cm}^{-1}$ ) 762, 844, 937, 1319, 1406, 1504, 1585, 1659, 2311, 3277, 3736;

HRMS ( $\text{ESI}^+$ )  $m/z$  230.0610 (230.0610 calcd for  $\text{C}_{11}\text{H}_{13}\text{NNaOS}^+$ ,  $[\text{M}+\text{Na}]^+$ )

**Methyl (*E*)-4-(2-(methylthio)vinyl)benzoate (1m)**



Prepared from methyl 4-formylbenzoate (1.64 g, 9.99 mmol) by Procedure B.

Eluent for column chromatographic purification: *n*-hexane/EtOAc = 1/1;

Yield: 16.7% (348 mg, 1.67 mmol);

Colorless solid;

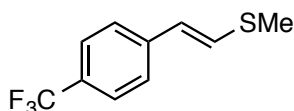
mp: 111–112 °C;

TLC  $R_f$  = 0.14 (*n*-hexane/EtOAc = 9/1);

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.41 (s, 3H), 3.90 (s, 3H), 6.30 (d,  $J$  = 15.4 Hz, 1H), 6.98 (d,  $J$  = 15.4 Hz, 1H), 7.32–7.33 (AA'BB', 2H), 7.94–7.97 (AA'BB', 2H);

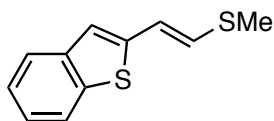
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  14.9 (1C), 52.2 (1C), 123.3 (1C), 125.2 (2C), 128.1 (1C), 129.6 (1C), 130.3 (2C), 141.6 (1C), 167.2 (1C);  
IR (ZnSe,  $\text{cm}^{-1}$ ) 754, 932, 1111, 1280, 1710, 2311, 2945, 3726;  
HRMS ( $\text{ESI}^+$ )  $m/z$  209.0630 (209.0631 calcd for  $\text{C}_{11}\text{H}_{13}\text{O}_2\text{S}^+$ ,  $[\text{M}+\text{H}]^+$ ).

**(*E*)-Methyl 4-(trifluoromethyl)styryl sulfide (1n)**



Prepared from 4-(trifluoromethyl)benzyl bromide (2.39 g, 9.99 mmol) by Procedure A.  
Eluent for column chromatographic purification: *n*-hexane/EtOAc = 49/1;  
Yield: 22.5% (491 mg, 2.25 mmol);  
Colorless solid;  
mp: 55–56 °C;  
TLC  $R_f$  = 0.55 (*n*-hexane/EtOAc = 9/1);  
 $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.41 (s, 3H), 6.29 (d,  $J$  = 15.4 Hz, 1H), 6.94 (d,  $J$  = 15.4 Hz, 1H), 7.36–7.38 (AA'BB', 2H), 7.52–7.55 (AA'BB', 2H);  
 $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  14.8 (1C), 122.9 (1C), 124.5 (q,  $^1J_{\text{C-F}}$  = 241.8 Hz, 1C), 125.5 (2C), 125.8, (q,  $^3J_{\text{C-F}}$  = 3.8 Hz, 2C), 128.4 (q,  $^2J_{\text{C-F}}$  = 34.5 Hz, 1C), 129.4 (1C), 140.6 (1C);  
 $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -62.3 (s);  
IR (ZnSe,  $\text{cm}^{-1}$ ) 829, 1067, 1105, 1163, 1323, 1595, 3744;  
HRMS ( $\text{ESI}^+$ )  $m/z$  219.0447 (219.0450 calcd for  $\text{C}_{10}\text{H}_{10}\text{F}_3\text{S}^+$ ,  $[\text{M}+\text{H}]^+$ ).

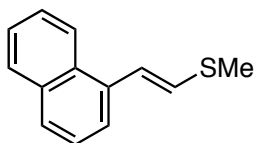
**2-(2-(Methylthio)vinyl)benzo[*b*]thiophene (1o, *E/Z* = 41:1)**



Prepared from benzo[*b*]thiophene-2-carbaldehyde (1.62 g, 9.99 mmol) by Procedure B.  
Eluent for column chromatographic purification: *n*-hexane/EtOAc = 49/1;  
Yield: 70.9% (1.46 g, 7.08 mmol, *E/Z* = 41:1);  
Pale yellow oil;  
TLC  $R_f$  = 0.37 (*n*-hexane/EtOAc = 4/1);  
For *E*-isomer:  
 $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.42 (s, 3H), 6.58–6.63 (m, 1H), 6.86 (d,  $J$  = 15.4 Hz, 1H), 7.30 (s, 1H), 7.34–7.43 (m, 2H), 7.84–7.88 (m, 2H);

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  15.2 (1C), 117.6 (1C), 120.2 (1C), 122.0 (1C), 123.1 (1C), 124.4 (1C), 124.7 (1C), 127.7 (1C), 133.9 (1C), 137.5 (1C), 140.4 (1C);  
IR (ZnSe,  $\text{cm}^{-1}$ ) 725, 752, 926, 1229, 1423, 1587, 3065;  
HRMS ( $\text{ESI}^+$ )  $m/z$  207.0295 (207.0297 calcd for  $\text{C}_{11}\text{H}_{11}\text{S}_2^+$ ,  $[\text{M}+\text{H}]^+$ ).

**(*E*)-Methyl 2-(naphthalen-1-yl)vinyl sulfide (1p)**



Prepared from 1-(bromomethyl)naphthalene (2.21 g, 10.0 mmol) by Procedure A.

Eluent for column chromatographic purification: *n*-hexane/EtOAc = 49/1;

Yield: 16.1% (322 mg, 1.61 mmol);

Colorless oil;

TLC  $R_f$  = 0.61 (*n*-hexane/EtOAc = 9/1);

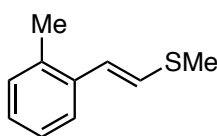
$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.48 (s, 3H), 6.83 (d,  $J$  = 15.0 Hz, 1H), 7.06 (d,  $J$  = 15.0 Hz, 1H), 7.39–7.54 (m, 4H), 7.74 (d,  $J$  = 8.2 Hz, 1H), 7.81–7.85 (m, 1H), 8.07–8.13 (m, 1H);

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  15.3 (1C), 122.1 (1C), 123.3 (1C), 123.9 (1C), 125.9 (1C), 126.0 (1C), 126.1 (1C), 127.5 (1C), 128.7 (1C), 128.8 (1C), 130.8 (1C), 133.9 (1C), 135.0 (1C);

IR (ZnSe,  $\text{cm}^{-1}$ ) 748, 781, 930, 1572, 1582, 3055;

HRMS ( $\text{ESI}^+$ )  $m/z$  201.0731 (201.0732 calcd for  $\text{C}_{13}\text{H}_{13}\text{S}^+$ ,  $[\text{M}+\text{H}]^+$ ).

**(*E*)-Methyl 2-methylstyryl sulfide (1q)**



Prepared from 2-methylbenzyl bromide (1.85 g, 10.0 mmol) by Procedure A.

Eluent for column chromatographic purification: *n*-hexane/EtOAc = 49/1;

Yield: 51.5% (846 mg, 5.15 mmol);

Colorless oil;

TLC  $R_f$  = 0.50 (*n*-hexane/EtOAc = 9/1);

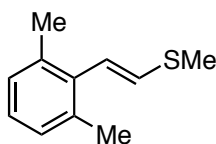
$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.33 (s, 3H), 2.39 (s, 3H), 6.51 (d,  $J$  = 15.4 Hz, 1H), 6.67 (d,  $J$  = 15.4 Hz, 1H), 7.08–7.18 (m, 3H), 7.33–7.36 (m, 1H);

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  15.2 (1C), 20.0 (1C), 123.0 (1C), 125.1 (1C), 126.3 (1C), 126.9 (1C), 127.0 (1C), 130.5 (1C), 134.6 (1C), 136.3 (1C);

IR (ZnSe,  $\text{cm}^{-1}$ ) 740, 930, 1242, 1433, 1587, 2916, 3017;

HRMS (ESI<sup>+</sup>)  $m/z$  165.0732 (165.0732 calcd for C<sub>10</sub>H<sub>13</sub>S<sup>+</sup>, [M+H]<sup>+</sup>).

**(*E*)-Methyl 2,6-dimethylstyryl sulfide (1r)**



Prepared from 2,6-dimethylbenzaldehyde (670 mg, 4.99 mmol) by Procedure B.

Eluent for column chromatographic purification: *n*-hexane/EtOAc = 49/1;

Yield: 45.7% (407 mg, 2.28 mmol);

Colorless oil;

TLC  $R_f$  = 0.38 (*n*-hexane);

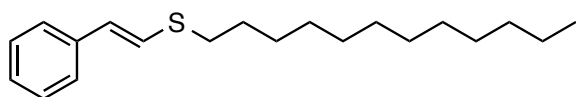
<sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.31 (s, 6H), 2.39 (s, 3H), 6.26 (d,  $J$  = 15.8 Hz, 1H), 6.31 (d,  $J$  = 15.8 Hz, 1H), 7.02–7.04 (m, 3H);

<sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  15.0 (1C), 21.2 (2C), 123.1 (1C), 126.6 (1C), 128.0 (2C), 129.6 (1C), 136.1 (2C), 136.8 (1C);

IR (ZnSe, cm<sup>-1</sup>) 740, 930, 1242, 1433, 1587, 2916, 3017;

HRMS (ESI<sup>+</sup>)  $m/z$  179.0889 (179.0889 calcd for C<sub>11</sub>H<sub>15</sub>S<sup>+</sup>, [M+H]<sup>+</sup>).

**(*E*)-Dodecyl styryl sulfide (4)<sup>S8</sup>**



To a 50 mL round-bottom flask equipped with a magnetic stir bar and charged with sodium *tert*-butoxide (274 mg, 2.85 mmol, 1.5 equiv) in HMPA (5 mL) was added 1-dodecanethiol (0.72 mL, 3.03 mmol, 1.6 equiv) at 0 °C. After stirring for 30 min at the same temperature, to the reaction mixture was added (*E*)-(2-bromovinyl)benzene (348 mg, 1.90 mmol, 1 equiv) in HMPA (5 mL) and warmed up to room temperature. After stirring for 12 h at the same temperature, to the reaction mixture was added water (ca. 10 mL) and extracted with Et<sub>2</sub>O (ca. 10 mL  $\times$  3). The combined organic extract was washed with brine (ca. 20 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (*n*-hexane) to give **4** (516 mg, 1.69 mmol, 89.1%) as a colorless oil;

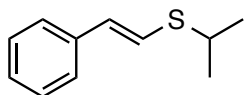
TLC  $R_f$  = 0.74 (*n*-hexane/EtOAc = 10/1);

<sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.88 (t,  $J$  = 6.8 Hz, 3H), 1.20–1.36 (m, 16H), 1.37–1.48 (m, 2H), 1.64–1.74 (m, 2H), 2.80 (t,  $J$  = 7.3 Hz, 2H), 6.46 (d,  $J$  = 15.4 Hz, 1H), 6.73 (d,  $J$  = 15.4 Hz, 1H), 7.15–7.22 (m, 1H), 7.26–7.32 (m, 4H);

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  14.3 (1C), 22.9 (1C), 29.0 (1C), 29.4 (1C), 29.5 (1C), 29.6 (1C), 29.70 (1C), 29.78 (1C), 29.82 (1C), 29.84 (1C), 32.1 (1C), 32.8 (1C), 125.5 (1C), 125.6 (2C), 126.8 (1C), 126.9 (1C), 128.8 (2C), 137.4 (1C);

The chemical shifts were consistent with those reported in the literature.<sup>S10</sup>

**(*E*)-Isopropyl styryl sulfide (**5**)**<sup>S8</sup>



To a 50 mL round-bottom flask equipped with a magnetic stir bar and charged with sodium *tert*-butoxide (256 mg, 2.66 mmol, 1.5 equiv) in HMPA (5 mL) was added 2-propanethiol (0.26 mL, 2.80 mmol, 1.6 equiv) at 0 °C. After stirring for 30 min at the same temperature, to the reaction mixture was added (*E*)-(2-bromovinyl)benzene (325 mg, 1.78 mmol, 1 equiv) in HMPA (5 mL) and warmed up to room temperature. After stirring for 12 h at the same temperature, to the reaction mixture was added water (ca. 10 mL) and extracted with  $\text{Et}_2\text{O}$  (ca. 10 mL  $\times$  3). The combined organic extract was washed with brine (ca. 20 mL) and dried over  $\text{Na}_2\text{SO}_4$ . After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (*n*-hexane) to give **5** (230 mg, 1.29 mmol, 72.7%) as a colorless oil;

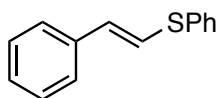
TLC  $R_f$  = 0.73 (*n*-hexane/EtOAc = 10/1);

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.37 (d,  $J$  = 6.8 Hz, 6H), 3.24 (sept,  $J$  = 6.8 Hz, 1H), 6.57 (d,  $J$  = 15.6 Hz, 1H), 6.77 (d,  $J$  = 15.6 Hz, 1H), 7.16–7.24 (m, 1H), 7.27–7.33 (m, 4H);

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  23.6 (2C), 37.0 (1C), 124.2 (1C), 125.8 (2C), 127.1 (1C), 128.8 (2C), 129.0 (1C), 137.3 (1C);

The chemical shifts were consistent with those reported in the literature.<sup>S11</sup>

**Phenyl styryl sulfide (**6**, *E/Z* = 14:1)**<sup>S8</sup>



To a 50 mL round-bottom flask equipped with a magnetic stir bar and charged with sodium thiophenoxide (90%; 635 mg, 4.32 mmol, 1.5 equiv) in HMPA (5 mL) was added (*E*)-(2-bromovinyl)benzene (528 mg, 2.88 mmol, 1 equiv) in HMPA (10 mL) at room temperature and warmed up to room temperature. After stirring for 12 h at the same temperature, to the reaction mixture was added water (ca. 15 mL) and extracted with  $\text{Et}_2\text{O}$  (ca. 10 mL  $\times$  3). The combined organic extract was washed with brine (ca. 20 mL) and dried over  $\text{Na}_2\text{SO}_4$ . After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (*n*-hexane) to give **6** (396 mg, 1.87 mmol, 64.7%, *E/Z* = 14:1) as a colorless solid;

mp: 33–34 °C;

TLC  $R_f$  = 0.72 (*n*-hexane/EtOAc = 10/1);

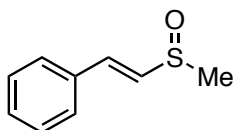
For *E*-isomer:

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  6.74 (d,  $J$  = 15.4 Hz, 1H), 6.89 (d,  $J$  = 15.4 Hz, 1H), 7.21–7.45 (m, 10H);

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  123.6 (1C), 126.2 (2C), 127.1 (1C), 127.8 (1C), 128.9 (2C), 129.3 (2C), 130.0 (2C), 132.0 (1C), 135.4 (1C), 136.7 (1C);

The chemical shifts were consistent with those reported in the literature.<sup>S11</sup>

### **(*E*)-(2-(Methylsulfinyl)vinyl)benzene (11)**



To a 100 mL round-bottom flask equipped with a magnetic stir bar and charged with (*E*)-**1a** (654 mg, 4.35 mmol, 1 equiv) in MeCN (20 mL) was added sodium periodate (1.02 g, 4.77 mmol, 1.1 equiv) in water (10 mL) at –10 °C and warmed up to room temperature. After stirring for 24 h at the same temperature, to the reaction mixture was added water (ca. 20 mL) and extracted with  $\text{CH}_2\text{Cl}_2$  (ca. 30 mL  $\times$  3). The combined organic extract was washed with brine (ca. 40 mL) and dried over  $\text{Na}_2\text{SO}_4$ . After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (*n*-hexane/EtOAc = 1:1 to 0:1) to give **11** (597 mg, 3.59 mmol, 82.5%) as a colorless solid;

mp: 63–64 °C;

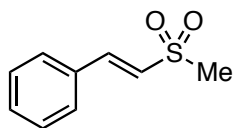
TLC  $R_f$  = 0.10 (*n*-hexane/EtOAc = 1/1);

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.71 (s, 3H), 6.90 (d,  $J$  = 15.6 Hz, 1H), 7.27 (d,  $J$  = 15.6 Hz, 1H), 7.34–7.42 (m, 3H), 7.46–7.50 (m, 2H);

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  41.1 (1C), 127.8 (2C), 129.1 (2C), 129.9 (1C), 132.3 (1C), 133.8 (1C), 136.5 (1C);

The chemical shifts were consistent with those reported in the literature.<sup>S12</sup>

### **(*E*)-(2-(Methylsulfonyl)vinyl)benzene (12)**



To a 100 mL round-bottom flask equipped with a magnetic stir bar and charged with **11** (239 mg, 1.44 mmol, 1 equiv) in  $\text{CH}_2\text{Cl}_2$  (14 mL) was added *m*CPBA (70%, 426 mg, 1.73 mmol, 1.2 equiv) at 0 °C and warmed up to room temperature. After stirring for 22 h at the same temperature, to the reaction mixture were added saturated aqueous sodium hydrogen carbonate (ca. 10 mL) and

saturated aqueous sodium thiosulfate (ca. 10 mL), and then extracted with CH<sub>2</sub>Cl<sub>2</sub> (ca. 30 mL × 3). The combined organic extract was washed with brine (ca. 40 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (*n*-hexane/EtOAc = 4:1 to 1:1) to give **12** (247 mg, 1.36 mmol, 94.3%) as a colorless solid;

mp: 78–79 °C;

TLC *R<sub>f</sub>* = 0.29 (*n*-hexane/EtOAc = 1/1);

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.04 (s, 3H), 6.92 (d, *J* = 15.4 Hz, 1H), 7.40–7.48 (m, 3H), 7.50–7.55 (m, 2H), 7.64 (d, *J* = 15.4 Hz, 1H);

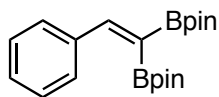
<sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 43.5 (1C), 126.3 (1C), 128.8 (2C), 129.3 (2C), 131.6 (1C), 132.2 (1C), 144.2 (1C);

The chemical shifts were consistent with those reported in the literature.<sup>S13</sup>

### General procedure for 1,1-diborylation of alkenyl sulfide **1**

To a capped vial equipped with a magnetic stir bar were added [Rh(OH)(cod)]<sub>2</sub> (1.8 mg, 3.9 μmol, 2 mol %), K<sub>2</sub>CO<sub>3</sub> (3.4 mg, 25 μmol, 12 mol %), P(*n*-Bu)<sub>3</sub> (5.9 μL, 24 μmol, 12 mol %) and *n*-hexane (1.0 mL) in a glovebox filled with argon gas, and the mixture was stirred for 1 h at room temperature. To the mixture were added bis(pinacolato)diboron ((Bpin)<sub>2</sub>) (102 mg, 0.402 mmol, 2.0 equiv) as a solid and alkenyl sulfide **1** (0.200 mmol, 1 equiv) as a solution or a suspension in *n*-hexane (0.5 mL). After stirring the mixture for 6 h with heating at 80 °C, the reaction vial was cooled to room temperature and taken out from the glovebox. To this was added saturated aqueous ammonium chloride (ca. 1 mL), and the mixture was extracted with EtOAc (ca. 1 mL × 3). The combined organic extract was dried over Na<sub>2</sub>SO<sub>4</sub>. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by PTLC followed by GPC when required for further purification. PTLC purification of **3** was conducted with cooling a developing chamber by a dry ice–acetone bath to avoid severe tailing on PTLC probably due to high affinity of **3** to silica-gel.

### 2,2'-(2-Phenylethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**3a**)



Yield: 90.0% (64.2 mg, 0.180 mmol);

Pale yellow oil;

Conditions for PTLC purification: *n*-hexane/EtOAc = 4/1 at –78 °C;

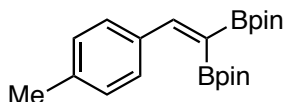
TLC *R<sub>f</sub>* = 0.13 (*n*-hexane/EtOAc = 9/1);

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.28 (s, 12H), 1.31 (s, 12H), 7.24–7.32 (m, 3H), 7.47–7.49 (AA'BB'C, 2H), 7.71 (s, 1H);



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  24.8 (4C), 25.1 (4C), 83.4 (2C), 83.8 (2C), 128.29 (2C), 128.34 (2C), 128.6 (1C), 139.8 (1C), 155.4 (1C) (the signal for the carbon that is attached to the boron atom was not observed);  
 $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ )  $\delta$  31.4 (1B+1B, two signals overlapped);  
The chemical shifts were consistent with those reported in the literature.<sup>S15</sup>

**2,2'-(2-(4-Methylphenyl)ethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3b)**



Yield: 91.1% (67.4 mg, 0.182 mmol);

Pale yellow oil;

Conditions for PTLC purification: *n*-hexane/EtOAc = 4/1 at  $-78\text{ }^\circ\text{C}$ ;

TLC  $R_f$  = 0.26 (*n*-hexane/EtOAc = 9/1);

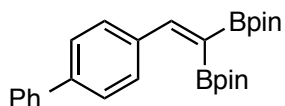
$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.27 (s, 12H), 1.32 (s, 12H), 2.33 (s, 3H), 7.09–7.11 (AA'BB', 2H), 7.38–7.40 (AA'BB', 2H), 7.68 (s, 1H);

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  21.5 (1C), 24.8 (4C), 25.0 (4C), 83.3 (2C), 83.7 (2C), 128.4 (2C), 129.0 (2C), 137.0 (1C), 138.6 (1C), 155.3 (1C) (the signal for the carbon that is attached to the boron atom was not observed);

$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ )  $\delta$  30.4 (1B+1B, two signals overlapped);

The chemical shifts were consistent with those reported in the literature.<sup>S14</sup>

**2,2'-(2-(Biphenyl-4-yl)ethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3c)**



Yield: 65.0% (56.2 mg, 0.130 mmol);

Pale yellow oil;

Conditions for PTLC purification: *n*-hexane/EtOAc = 4/1 at  $-78\text{ }^\circ\text{C}$ ;

TLC  $R_f$  = 0.23 (*n*-hexane/EtOAc = 9/1);

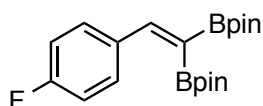
$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.29 (s, 12H), 1.34 (s, 12H), 7.30–7.36 (m, 1H), 7.39–7.48 (m, 2H), 7.52–7.61 (m, 6H), 7.74 (s, 1H);

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  24.9 (4C), 25.1 (4C), 83.4 (2C), 83.8 (2C), 127.0 (2C), 127.2 (2C), 127.6 (1C), 128.87 (2C), 128.93 (2C), 138.7 (1C), 140.9 (1C), 141.3 (1C), 154.8 (1C) (the signal for the carbon that is attached to the boron atom was not observed);

$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ )  $\delta$  29.7 (1B+1B, two signals overlapped);

The chemical shifts were consistent with those reported in the literature.<sup>S14</sup>

**2,2'-(2-(4-Fluorophenyl)ethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3d)**



Yield: 75.1% (56.2 mg, 0.150 mmol);

Pale yellow oil;

Conditions for PTLC purification: *n*-hexane/EtOAc = 4/1 at -78 °C;

TLC  $R_f$  = 0.26 (*n*-hexane/EtOAc = 9/1);

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.28 (s, 12H), 1.31 (s, 12H), 6.95–7.01 (AA'BB'X, 2H), 7.44–7.49 (AA'BB'X, 2H), 7.66 (s, 1H);

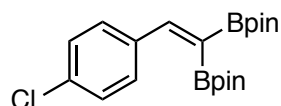
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  24.8 (4C), 25.0 (4C), 83.4 (2C), 83.8 (2C), 115.2 (d,  $^2J_{\text{C-F}}$  = 21.0 Hz, 2C), 130.1 (d,  $^3J_{\text{C-F}}$  = 7.6 Hz, 2C), 136.0 (d,  $^4J_{\text{C-F}}$  = 2.9 Hz, 1C), 154.0 (1C), 163.0 (d,  $^1J_{\text{C-F}}$  = 248.0 Hz, 1C) (the signal for the carbon that is attached to the boron atom was not observed);

$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ )  $\delta$  29.9 (1B+1B, two signals overlapped);

$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -113.0 (m);

The chemical shifts were consistent with those reported in the literature.<sup>S14</sup>

**2,2'-(2-(4-Chlorophenyl)ethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3e)**



Yield: 92.6% (72.3 mg, 0.185 mmol);

Pale yellow oil;

Conditions for PTLC purification: *n*-hexane/EtOAc = 4/1 at -78 °C;

TLC  $R_f$  = 0.25 (*n*-hexane/EtOAc = 9/1);

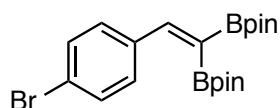
$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.28 (s, 12H), 1.31 (s, 12H), 7.25–7.28 (AA'BB', 2H), 7.40–7.43 (AA'BB', 2H), 7.64 (s, 1H);

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  24.8 (4C), 25.0 (4C), 83.5 (2C), 83.9 (2C), 128.5 (2C), 129.6 (2C), 134.4 (1C), 138.2 (1C), 153.8 (1C) (the signal for the carbon that is attached to the boron atom was not observed);

$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ )  $\delta$  30.2 (1B+1B, two signals overlapped);

The chemical shifts were consistent with those reported in the literature.<sup>S14</sup>

**2,2'-(2-(4-Bromophenyl)ethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3f)**



Yield: 81.2% (70.6 mg, 0.162 mmol);

Pale yellow oil;

Conditions for PTLC purification: *n*-hexane/EtOAc = 4/1 at –78 °C;

TLC  $R_f$  = 0.25 (*n*-hexane/EtOAc = 9/1);

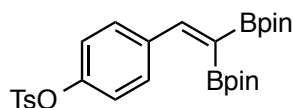
$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.28 (s, 12H), 1.31 (s, 12H), 7.33–7.37 (AA'BB', 2H), 7.41–7.44 (AA'BB', 2H), 7.62 (s, 1H);

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  24.8 (4C), 25.0 (4C), 83.5 (2C), 83.9 (2C), 122.7 (1C), 129.9 (2C), 131.5 (2C), 138.7 (1C), 153.8 (1C) (the signal for the carbon that is attached to the boron atom was not observed);

$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ )  $\delta$  29.2 (1B+1B, two signals overlapped);

The chemical shifts were consistent with those reported in the literature.<sup>S14</sup>

**4-(2,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)phenyl 4-methylbenzenesulfonate (3g)**



Yield: 86.6% (91.1 mg, 0.173 mmol);

Pale yellow oil;

Conditions for PTLC purification: *n*-hexane/EtOAc = 4/1 at –78 °C;

TLC  $R_f$  = 0.26 (*n*-hexane/EtOAc = 4/1);

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.27 (s, 12H), 1.28 (s, 12H), 2.43 (s, 3H), 6.89–6.92 (AA'BB', 2H), 7.26–7.30 (AA'BB', 2H), 7.36–7.40 (AA'BB', 2H), 7.62 (s, 1H), 7.65–7.68 (AA'BB', 2H);

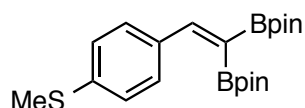
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  21.9 (1C), 24.8 (4C), 25.0 (4C), 83.5 (2C), 83.9 (2C), 122.2 (2C), 128.7 (2C), 129.5 (2C), 129.9 (2C), 132.3 (1C), 138.8 (1C), 145.5 (1C), 149.7 (1C), 153.5 (1C) (the signal for the carbon that is attached to the boron atom was not observed);

$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ )  $\delta$  30.2 (1B+1B, two signals overlapped);

IR (ZnSe,  $\text{cm}^{-1}$ ) 845, 1138, 1331, 1371, 1501, 1599, 2976;

HRMS (ESI<sup>+</sup>)  $m/z$  549.2248 (549.2260 calcd for  $\text{C}_{27}\text{H}_{36}\text{B}_2\text{NaO}_7\text{S}^+$ ,  $[\text{M}+\text{Na}]^+$ ).

**2,2'-(2-(4-(Methylthio)phenyl)ethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3h)**



Yield: 64.8% (52.1 mg, 0.130 mmol);

Pale yellow oil;

Conditions for PTLC purification: *n*-hexane/EtOAc = 4/1 at -78 °C;

TLC  $R_f$  = 0.33 (*n*-hexane/EtOAc = 4/1);

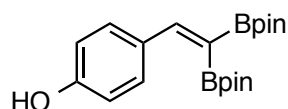
$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.27 (s, 12H), 1.32 (s, 12H), 2.48 (s, 3H), 7.15–7.18 (AA'BB', 2H), 7.40–7.43 (AA'BB', 2H), 7.64 (s, 1H);

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  15.7 (1C), 24.9 (4C), 25.0 (4C), 83.4 (2C), 83.8 (2C), 126.0 (2C), 128.8 (2C), 136.5 (1C), 139.3 (1C), 154.6 (1C) (the signal for the carbon that is attached to the boron atom was not observed);

$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ )  $\delta$  29.5 (1B+1B, two signals overlapped);

The chemical shifts were consistent with those reported in the literature.<sup>S14</sup>

**4-(2,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)phenol (3i)**



Yield: 57.8% (43.0 mg, 0.116 mmol);

Pale yellow oil;

Eluent for GPC purification:  $\text{CHCl}_3$ ;

TLC  $R_f$  = 0.29 (*n*-hexane/EtOAc = 7/3);

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.26 (s, 12H), 1.32 (s, 12H), 5.52 (s, 1H), 6.72–6.74 (AA'BB', 2H), 7.34–7.36 (AA'BB', 2H), 7.64 (s, 1H);

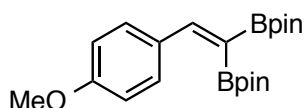
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  24.8 (4C), 25.0 (4C), 83.3 (2C), 83.8 (2C), 115.3 (2C), 130.1 (2C), 132.6 (1C), 155.3 (1C), 156.5 (1C) (the signal for the carbon that is attached to the boron atom was not observed);

$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ )  $\delta$  30.1 (1B+1B, two signals overlapped);

IR (ZnSe,  $\text{cm}^{-1}$ ) 1136, 1601, 2932, 2978, 3352;

HRMS ( $\text{ESI}^+$ )  $m/z$  373.2347 (373.2352 calcd for  $\text{C}_{20}\text{H}_{31}\text{B}_2\text{O}_5^+$ ,  $[\text{M}+\text{H}]^+$ ).

**2,2'-(2-(4-Methoxyphenyl)ethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3j)**



Yield: 88.1% (68.0 mg, 0.176 mmol);

Pale yellow oil;

Conditions for PTLC purification: *n*-hexane/EtOAc = 4/1 at –78 °C;

TLC  $R_f$  = 0.26 (*n*-hexane/EtOAc = 4/1);

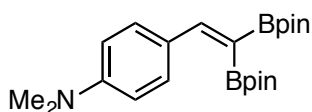
$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.27 (s, 12H), 1.33 (s, 12H), 3.79 (s, 3H), 6.80–6.84 (AA'BB', 2H), 7.43–7.46 (AA'BB', 2H), 7.66 (s, 1H);

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  24.8 (4C), 26.0 (4C), 55.4 (1C), 83.2 (2C), 83.7 (2C), 113.7 (2C), 129.9 (2C), 132.6 (1C), 154.9 (1C), 160.1 (1C) (the signal for the carbon that is attached to the boron atom was not observed);

$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ )  $\delta$  29.7 (1B+1B, two signals overlapped);

The chemical shifts were consistent with those reported in the literature.<sup>S14</sup>

**4-(2,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-*N,N*-dimethylaniline (3k)**



Yield: 85.6% (68.3 mg, 0.171 mmol);

Pale yellow oil;

Conditions for PTLC purification: *n*-hexane/EtOAc = 4/1 at –78 °C;

TLC  $R_f$  = 0.13 (*n*-hexane/EtOAc = 9/1);

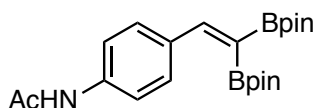
$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.26 (s, 12H), 1.34 (s, 12H), 2.96 (s, 6H), 6.60–6.63 (AA'BB', 2H), 7.39–7.43 (AA'BB', 2H), 7.62 (s, 1H);

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  24.9 (4C), 25.0 (4C), 40.5 (2C), 83.0 (2C), 83.5 (2C), 111.7 (2C), 128.0 (1C), 130.0 (2C), 150.8 (1C), 155.8 (1C) (the signal for the carbon that is attached to the boron atom was not observed);

$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ )  $\delta$  30.1 (1B+1B, two signals overlapped);

The chemical shifts were consistent with those reported in the literature.<sup>S14</sup>

***N*-(4-(2,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)phenyl)acetamide (3l)**



Yield: 50.0% (41.3 mg, 0.100 mmol);

Pale yellow oil;

Eluent for GPC purification: CHCl<sub>3</sub>;

TLC  $R_f$  = 0.13 (*n*-hexane/EtOAc = 3/2);

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.27 (s, 12H), 1.32 (s, 12H), 2.14 (s, 3H), 7.41 (m, 4H), 7.48 (br s, 1H), 7.64 (s, 1H);

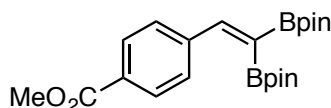
<sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 24.9 (4C+1C, two signals overlapped), 25.0 (4C), 83.4 (2C), 83.9 (2C), 119.2 (2C), 129.1 (2C), 135.6 (1C), 138.5 (1C), 154.7 (1C), 168.5 (1C) (the signal for the carbon that is attached to the boron atom was not observed);

<sup>11</sup>B NMR (CDCl<sub>3</sub>) δ 30.3 (1B+1B, two signals overlapped);

IR (ZnSe, cm<sup>-1</sup>) 839, 1140, 1533, 1589, 1686, 2979, 3333;

HRMS (ESI<sup>+</sup>)  $m/z$  436.2431 (436.2437 calcd for C<sub>22</sub>H<sub>33</sub>B<sub>2</sub>NNaO<sub>5</sub><sup>+</sup>, [M+Na]<sup>+</sup>).

**Methyl 4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzoate (3m)**



Yield: 78.2% (64.8 mg, 0.156 mmol);

Pale yellow oil;

Conditions for PTLC purification: *n*-hexane/EtOAc = 7/3 at -78 °C;

TLC  $R_f$  = 0.33 (*n*-hexane/EtOAc = 4/1);

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.28 (s, 12H), 1.31 (s, 12H), 3.91 (s, 3H), 7.53–7.55 (AA'BB', 2H), 7.71 (s, 1H), 7.96–7.98 (AA'BB', 2H);

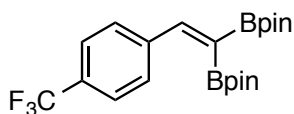
<sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 24.8 (4C), 25.0 (4C), 52.3 (1C), 83.6 (2C), 84.0 (2C), 128.2 (2C), 129.7 (2C), 129.8 (1C), 144.1 (1C), 153.8 (1C), 167.1 (1C) (the signal for the carbon that is attached to the boron atom was not observed);

<sup>11</sup>B NMR (CDCl<sub>3</sub>) δ 28.9 (1B+1B, two signals overlapped);

IR (ZnSe, cm<sup>-1</sup>) 845, 1107, 1138, 1269, 1605, 1721, 2978;

HRMS (ESI<sup>+</sup>)  $m/z$  415.2449 (415.2458 calcd for C<sub>22</sub>H<sub>33</sub>B<sub>2</sub>O<sub>6</sub><sup>+</sup>, [M+H]<sup>+</sup>).

**2,2'-(2-(4-(Trifluoromethyl)phenyl)ethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)**  
**(3n)**



Yield: 83.4% (70.7 mg, 0.167 mmol);

Pale yellow oil;

Conditions for PTLC purification: *n*-hexane/EtOAc = 4/1 at  $-78\text{ }^{\circ}\text{C}$ ;

TLC  $R_f$  = 0.18 (*n*-hexane/EtOAc = 9/1);

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.29 (s, 12H), 1.31 (s, 12H), 7.54–7.59 (AA'BB', 2H+2H, two signals overlapped), 7.70 (s, 1H);

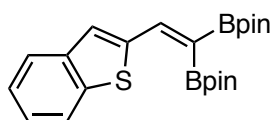
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  24.8 (4C), 25.1 (4C), 83.7 (2C), 84.1 (2C), 124.3 (q,  $^1J_{\text{C-F}}$  = 276.9 Hz, 1C), 125.3 (q,  $^3J_{\text{C-F}}$  = 3.8 Hz, 2C), 128.4 (2C), 130.2 (q,  $^2J_{\text{C-F}}$  = 32.4 Hz, 1C), 143.1 (1C), 153.3 (1C) (the signal for the carbon that is attached to the boron atom was not observed);

$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ )  $\delta$  30.1 (1B+1B, two signals overlapped);

$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ )  $\delta$   $-62.4$  (s);

The chemical shifts were consistent with those reported in the literature.<sup>S14</sup>

**2,2'-(2-(Benzo[*b*]thiophen-2-yl)ethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)**  
**(3o)**



Yield: 61.9% (51.0 mg, 0.124 mmol);

Pale yellow oil;

Conditions for PTLC purification: *n*-hexane/EtOAc = 4/1 at  $-78\text{ }^{\circ}\text{C}$ ;

TLC  $R_f$  = 0.37 (*n*-hexane/EtOAc = 4/1);

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.27 (s, 12H), 1.30 (s, 12H), 7.32–7.40 (m, 2H), 7.75–7.76 (s, 1H), 7.81–7.84 (m, 1H), 7.90–7.92 (m, 2H);

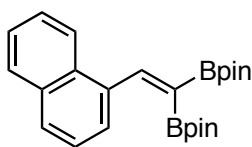
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  24.9 (4C), 25.1 (4C), 83.4 (2C), 83.9 (2C), 122.6 (1C), 122.7 (1C), 124.3 (1C), 124.6 (1C), 124.7 (1C), 137.1 (1C), 138.5 (1C), 140.1 (1C), 146.5 (1C) (the signal for the carbon that is attached to the boron atom was not observed);

$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ )  $\delta$  30.0 (1B+1B, two signals overlapped);

IR (ZnSe,  $\text{cm}^{-1}$ ) 731, 851, 1138, 1300, 1345, 1591, 2976;

HRMS ( $\text{ESI}^+$ )  $m/z$  413.2117 (413.2124 calcd for  $\text{C}_{22}\text{H}_{31}\text{B}_2\text{O}_4\text{S}^+$ ,  $[\text{M}+\text{H}]^+$ ).

**2,2'-(2-(Naphthalen-1-yl)ethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3p)**



Yield: 72.8% (59.1 mg, 0.146 mmol);

Pale yellow oil;

Conditions for PTLC purification: *n*-hexane/EtOAc = 4/1 at –78 °C;

TLC  $R_f$  = 0.32 (*n*-hexane/EtOAc = 9/1);

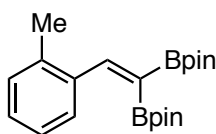
$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.16 (s, 12H), 1.31 (s, 12H), 7.32–7.51 (m, 3H), 7.61–7.63 (m, 1H), 7.76–7.83 (m, 2H), 8.09–8.13 (m, 1H), 8.41 (s, 1H);

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  24.6 (4C), 25.1 (4C), 83.4 (2C), 83.6 (2C), 125.1 (1C), 125.3 (1C), 125.7 (1C), 126.0 (1C), 126.1 (1C), 128.3 (1C), 128.8 (1C), 131.5 (1C), 133.5 (1C), 137.9 (1C), 153.7 (1C) (the signal for the carbon that is attached to the boron atom was not observed);

$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ )  $\delta$  30.3 (1B+1B, two signals overlapped);

The chemical shifts were consistent with those reported in the literature.<sup>S15</sup>

**2,2'-(2-(2-Methylphenyl)ethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3q)**



Yield: 69.4% (51.4 mg, 0.139 mmol);

Pale yellow oil;

Conditions for PTLC purification: *n*-hexane/EtOAc = 4/1 at –78 °C;

TLC  $R_f$  = 0.26 (*n*-hexane/EtOAc = 9/1);

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.24 (s, 12H), 1.28 (s, 12H), 2.35 (s, 3H), 7.02–7.19 (m, 3H), 7.45 (d,  $J$  = 7.2 Hz, 1H), 7.89 (s, 1H);

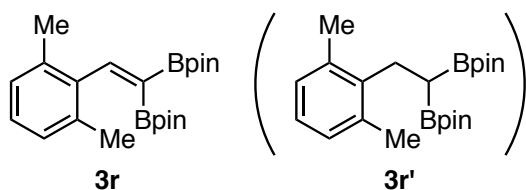
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  20.0 (1C), 24.7 (4C), 25.1 (4C), 83.3 (2C), 83.7 (2C), 125.7 (1C), 127.9 (1C), 128.5 (1C), 130.0 (1C), 136.5 (1C), 139.4 (1C), 154.4 (1C) (the signal for the carbon that is attached to the boron atom was not observed);

$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ )  $\delta$  29.7 (1B+1B, two signals overlapped);

The chemical shifts were consistent with those reported in the literature.<sup>S14</sup>



**2,2'-(2-(2,6-Dimethylphenyl)ethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3r)**



$^1\text{H}$  NMR yield: 38%;

Total weight of the product after the PTLC purification: 15.8 mg (containing the corresponding reduced product **3r'**, although not fully characterized, 94:6 in molar ratio);

Net yield: 19%;

Colorless oil;

Conditions for PTLC purification: *n*-hexane/EtOAc = 8/2 at  $-78\text{ }^\circ\text{C}$ ;

TLC  $R_f$  = 0.31 (*n*-hexane/EtOAc = 9/1);

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.97 (s, 12H), 1.29 (s, 12H), 2.23 (s, 6H), 6.93–7.03 (m, 3H), 7.69 (s, 1H);

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  20.6 (2C), 24.3 (4C), 25.0 (4C), 83.1 (2C), 83.2 (2C), 126.6 (1C), 126.7 (2C), 135.4 (2C), 140.7 (1C), 156.4 (1C) (the signal for the carbon that is attached to the boron atom was not observed);

$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ )  $\delta$  30.1 (1B+1B, two signals overlapped);

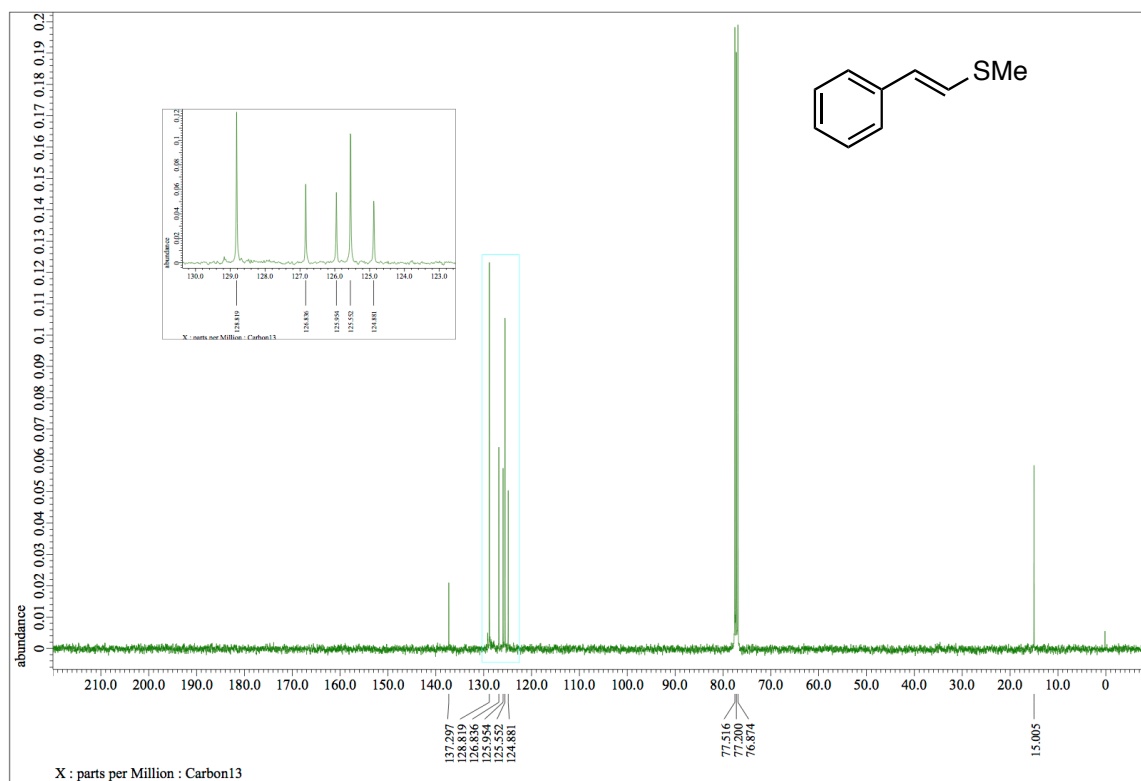
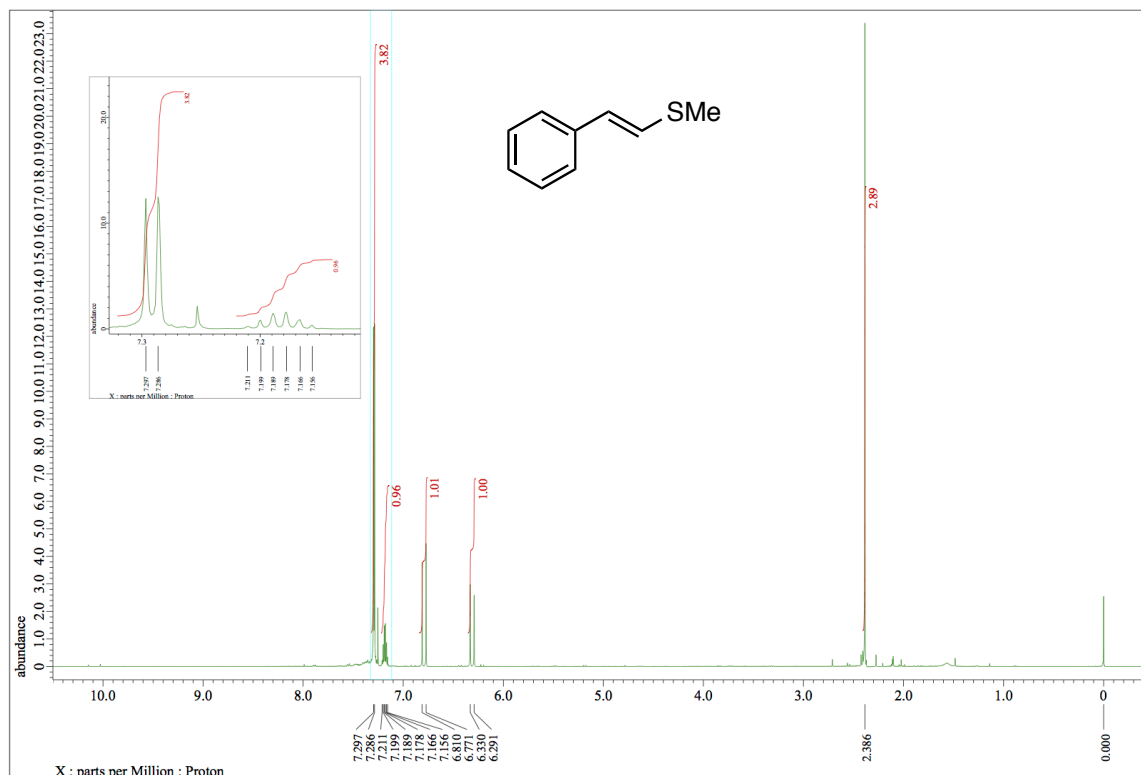
IR (ZnSe,  $\text{cm}^{-1}$ ) 673, 762, 856, 1013, 1140, 1325, 2976;

HRMS ( $\text{ESI}^+$ )  $m/z$  385.2716 (385.2716 calcd for  $\text{C}_{22}\text{H}_{35}\text{B}_2\text{O}_4^+$ ,  $[\text{M}+\text{H}]^+$ ).

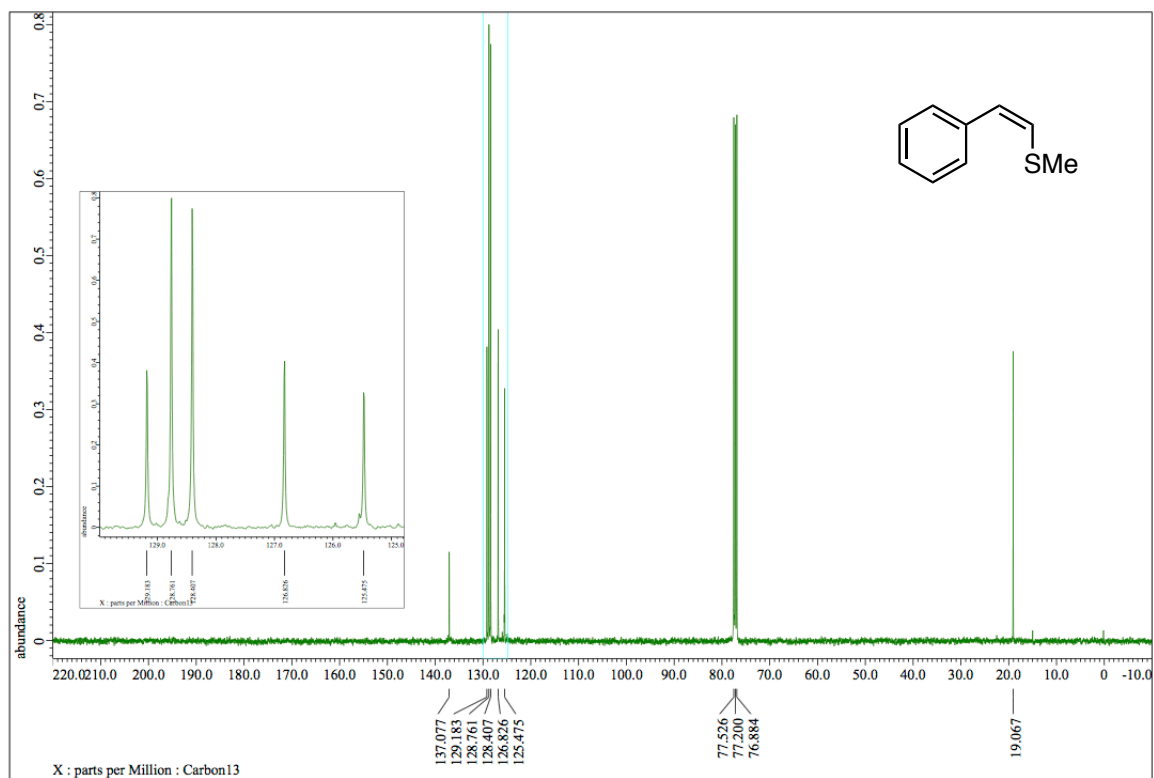
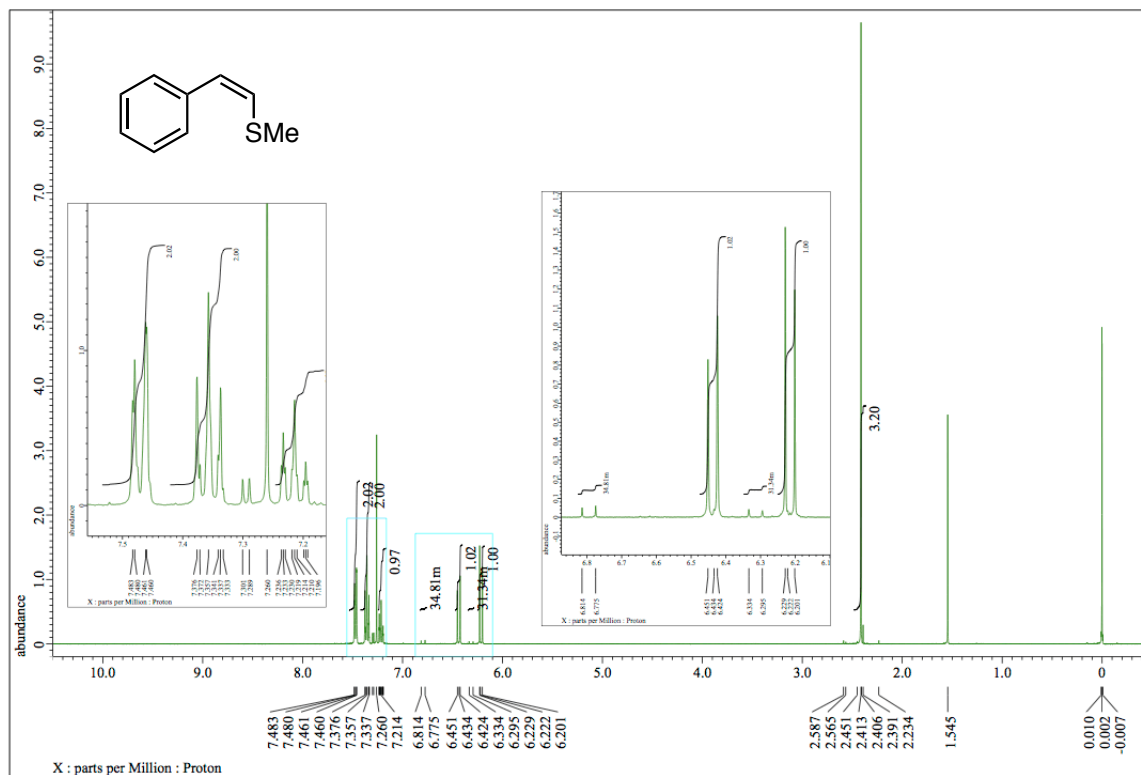
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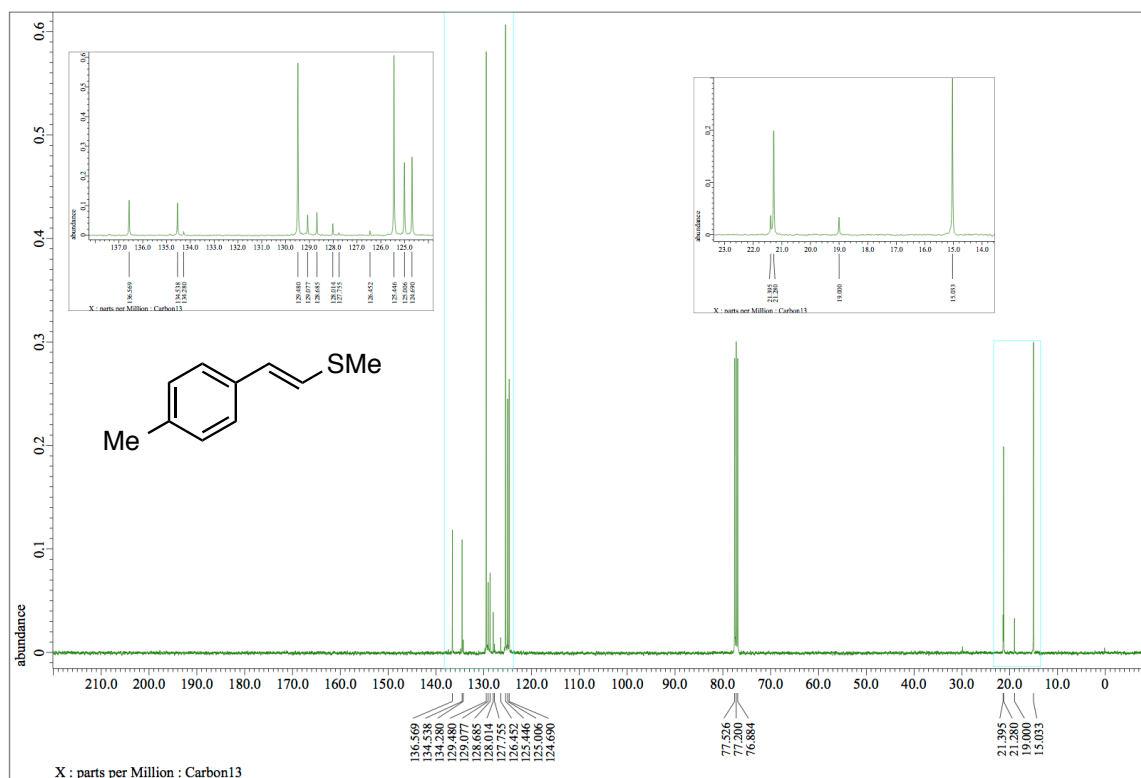
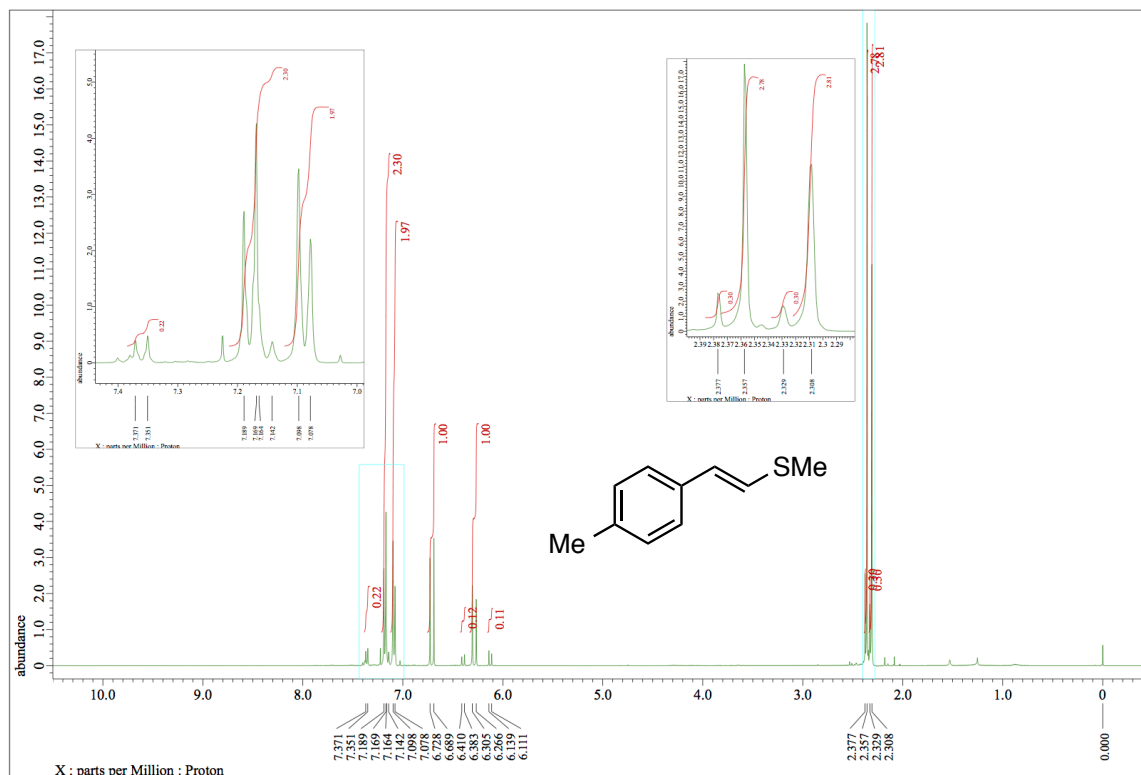
$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra of (*E*)-**1a** ( $\text{CDCl}_3$ )



$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra of (Z)-**1a** ( $\text{CDCl}_3$ )



$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra of **1b** (*E/Z* = 7.8:1,  $\text{CDCl}_3$ )

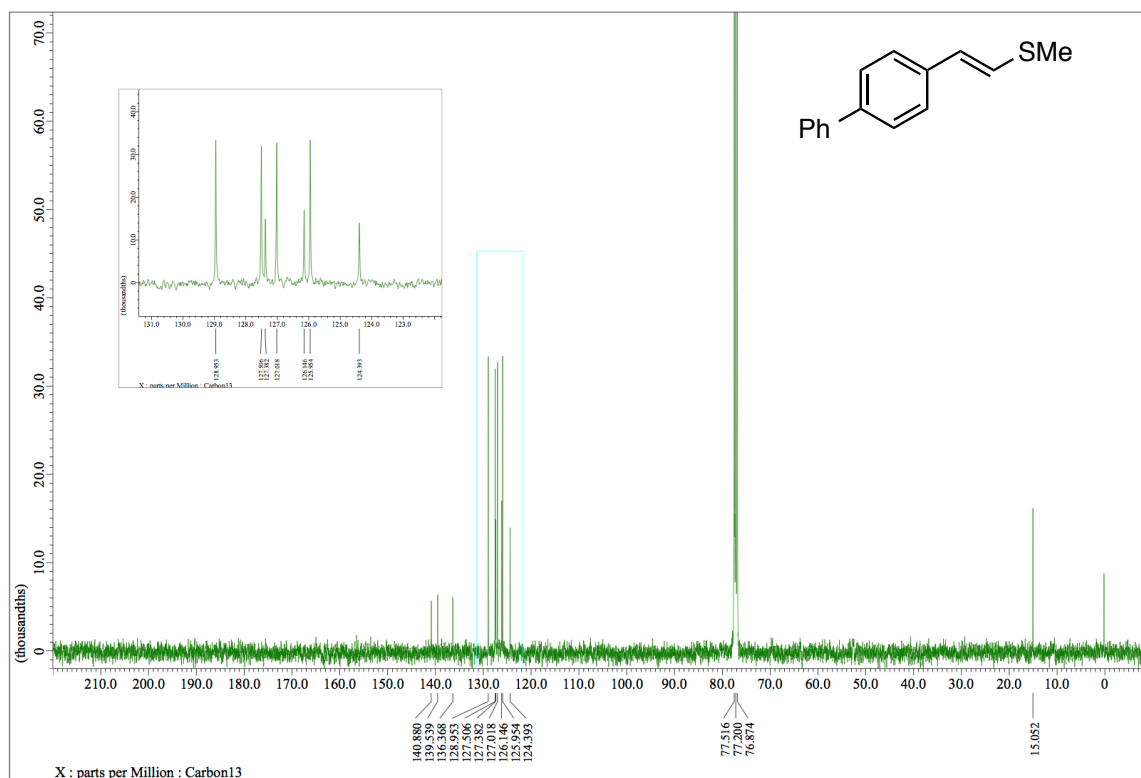


Chemical structure: C=CC1=CC=CC=C1SC

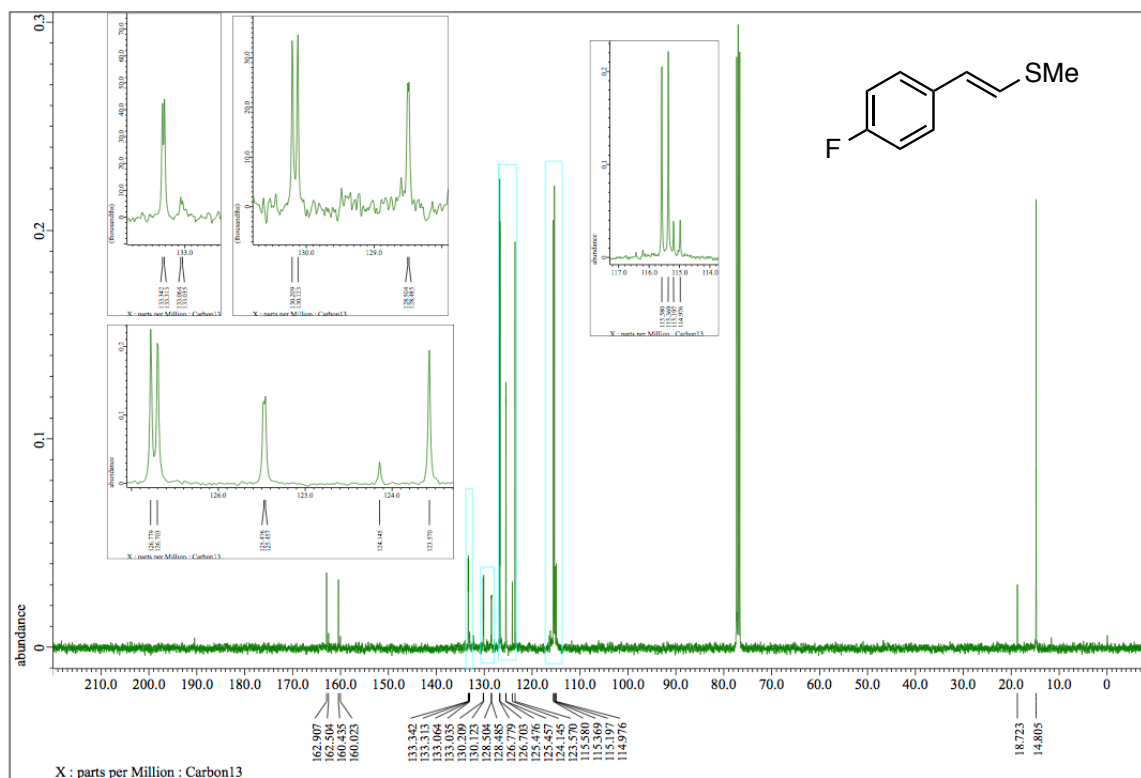
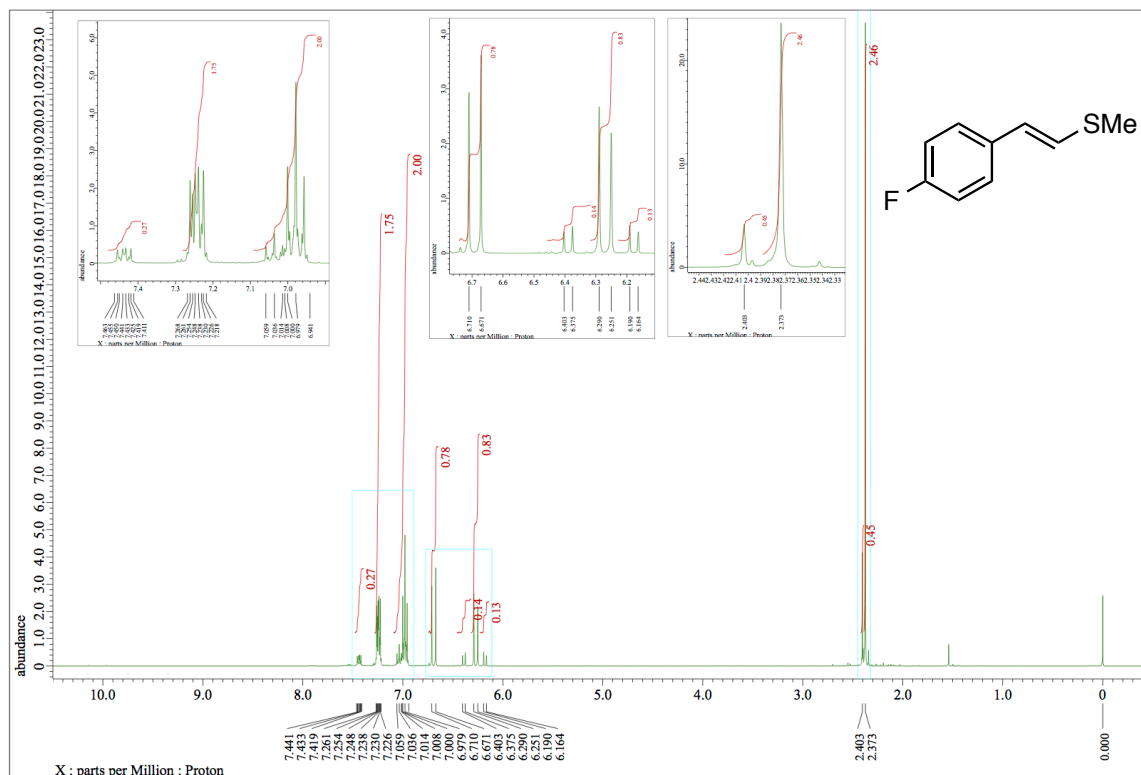
<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) showing the following peaks (ppm):

- 7.606, 7.602, 7.584, 7.583, 7.553, 7.531, 7.432, 7.378, 7.357 (aromatic protons, integration 2.00, 2.06)
- 6.864, 6.855 (aromatic protons, integration 1.00, 1.00)
- 6.366, 6.327 (aromatic protons, integration 1.00, 1.00)
- 2.411 (methyl sulfide, integration 3.00)
- 0.000 (TMS)

Integration values: 2.00, 2.06, 1.00, 1.00, 3.00.

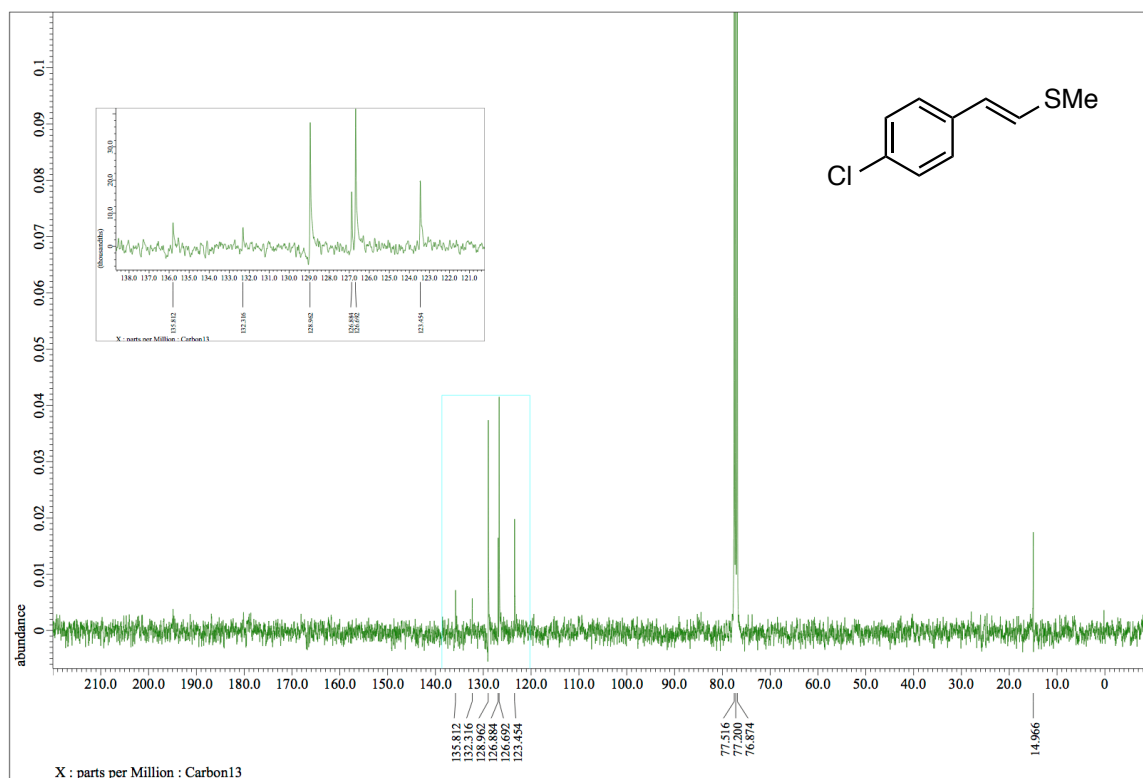


$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra of **1d** ( $E/Z = 6.5:1$ ,  $\text{CDCl}_3$ )



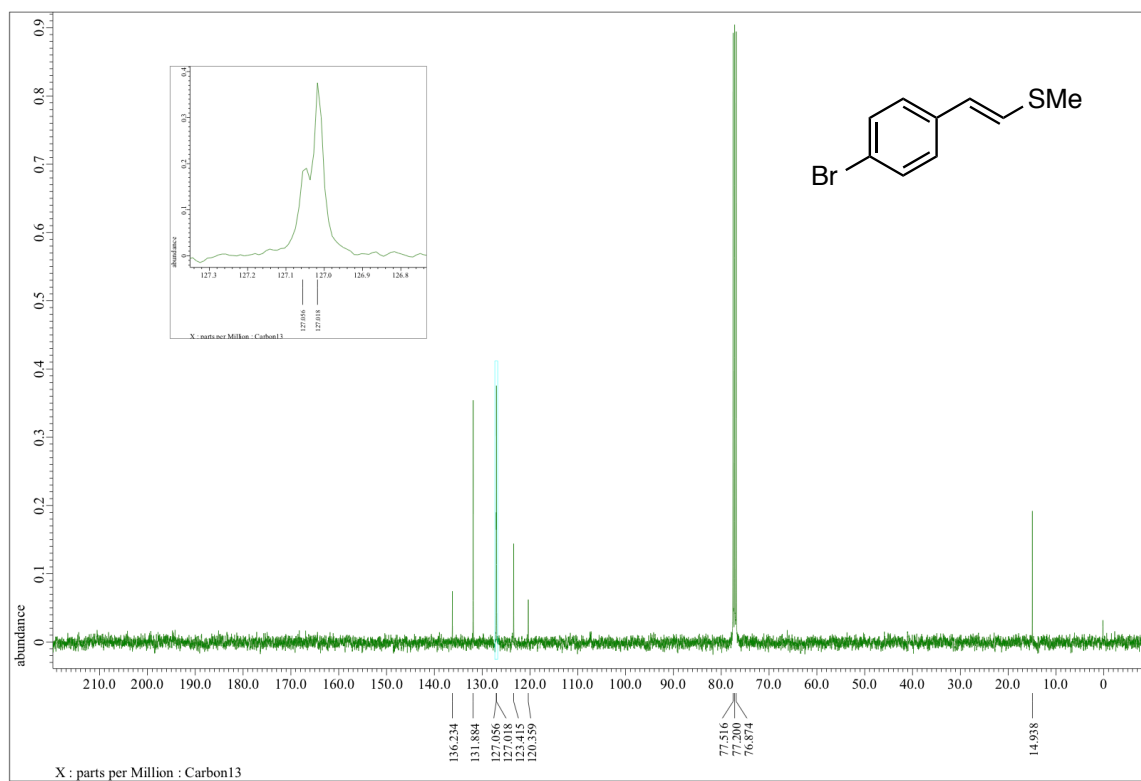
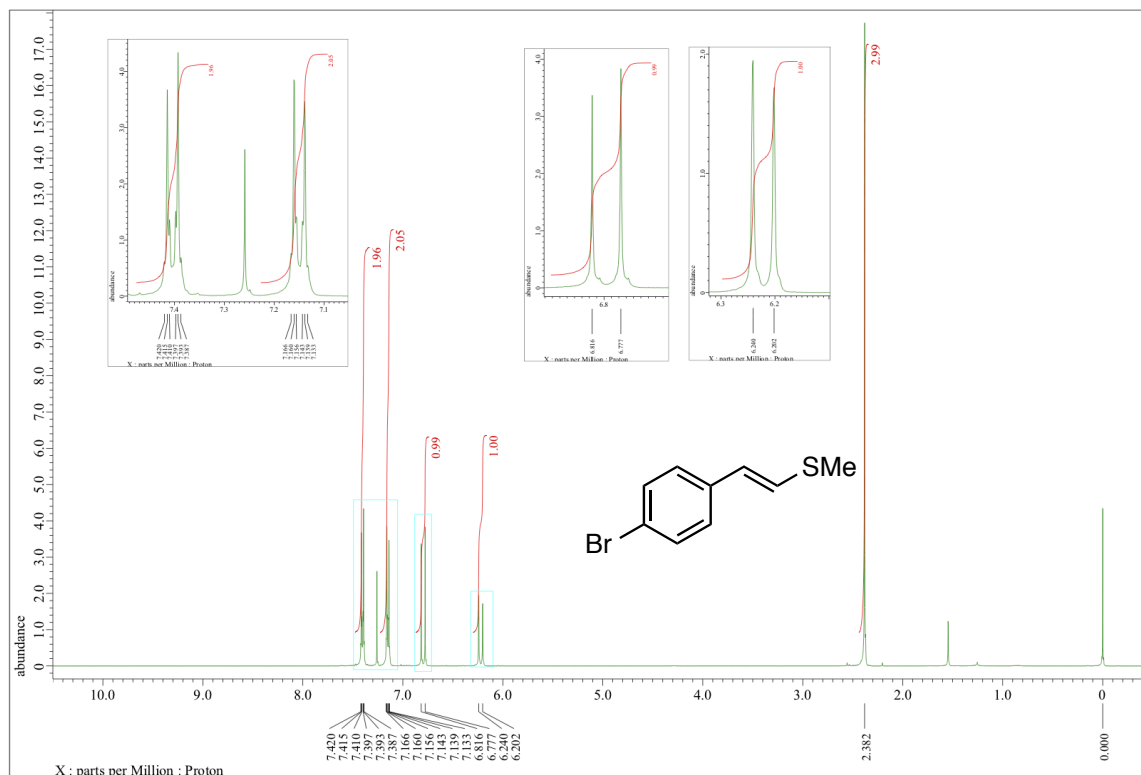
Chemical structure: CSC=Cc1ccc(Cl)cc1

<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) showing peaks at 7.272, 7.266, 7.244, 7.240, 7.223, 7.217, 7.213, 7.202, 7.197, 7.191, 6.577, 6.578, 6.263, 6.224, 2.384, and 0.000 ppm. Integration values are 2.13, 1.68, 0.99, and 1.00.

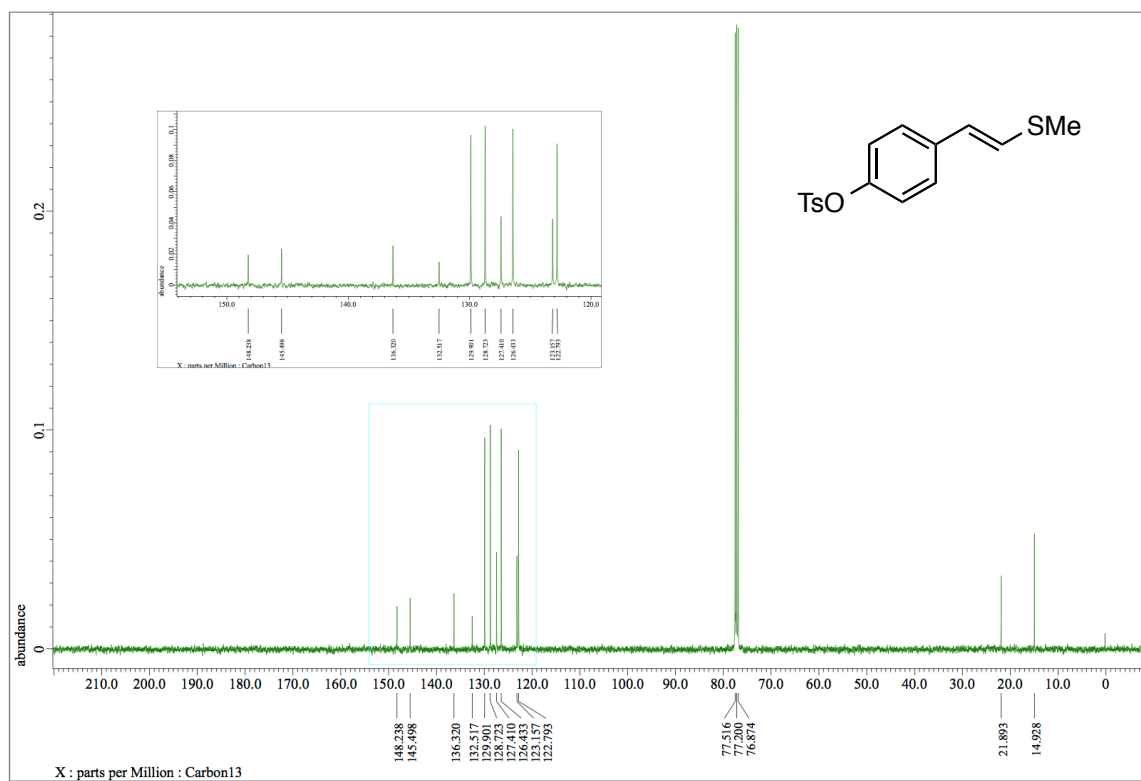
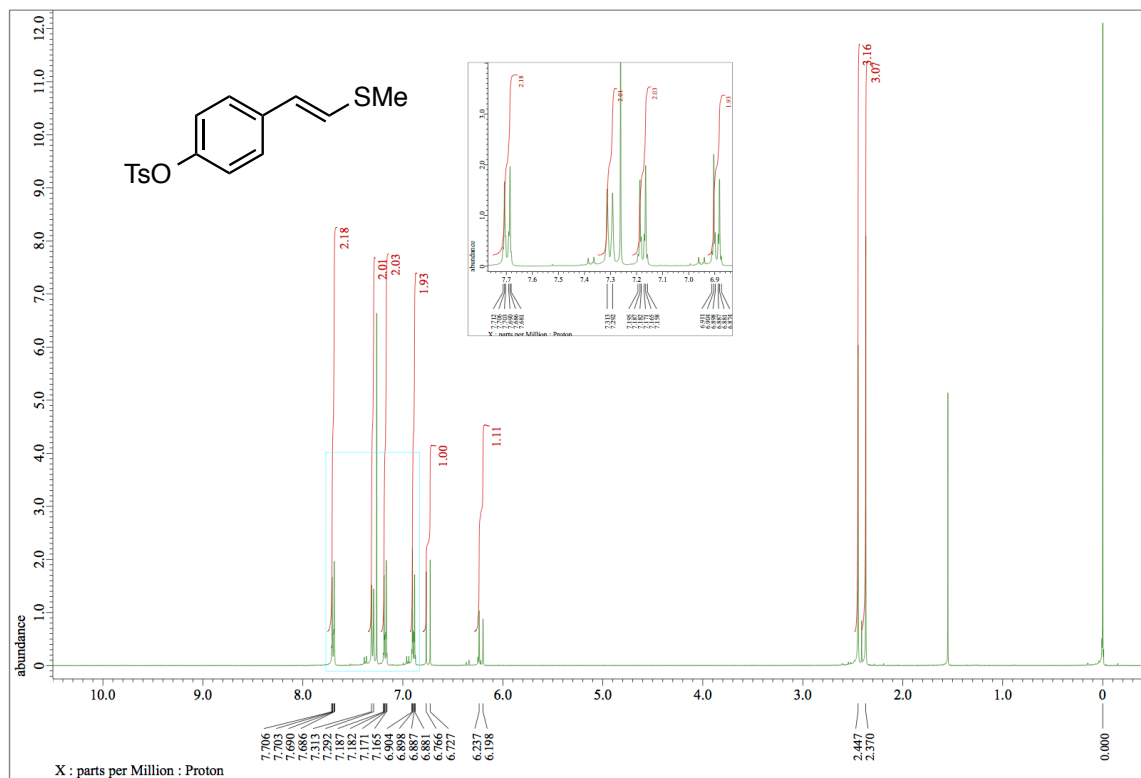




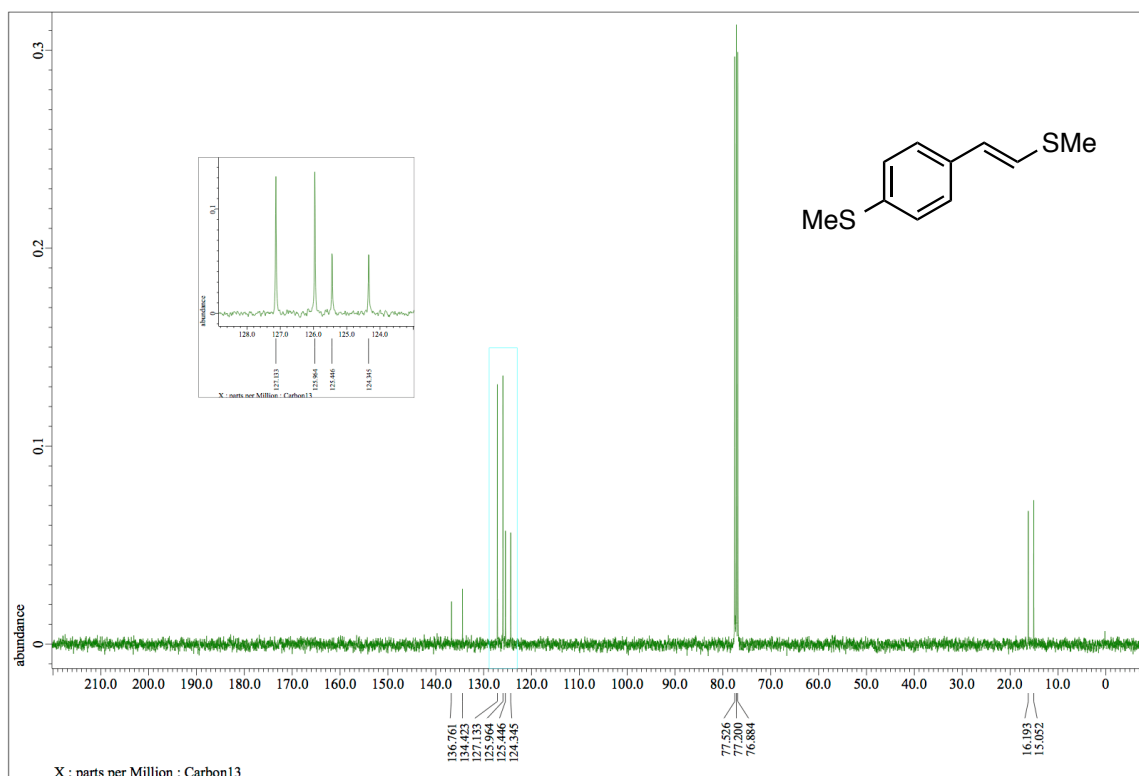
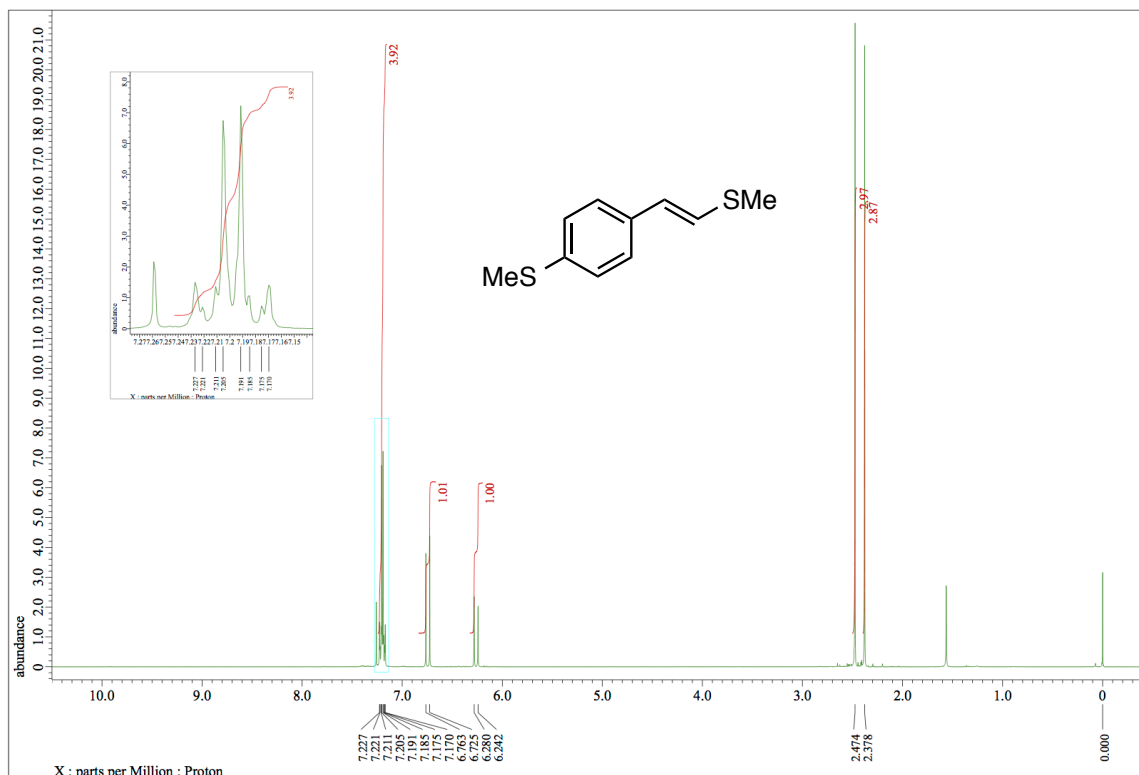
$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra of **1f** ( $\text{CDCl}_3$ )



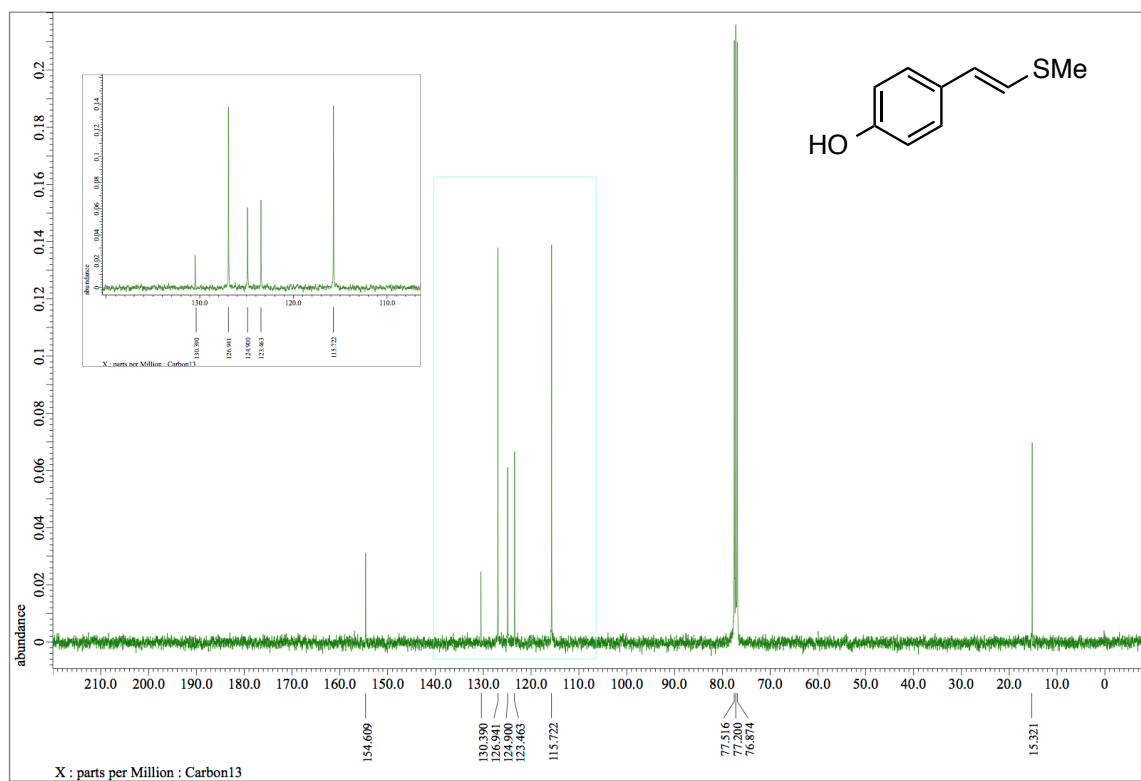
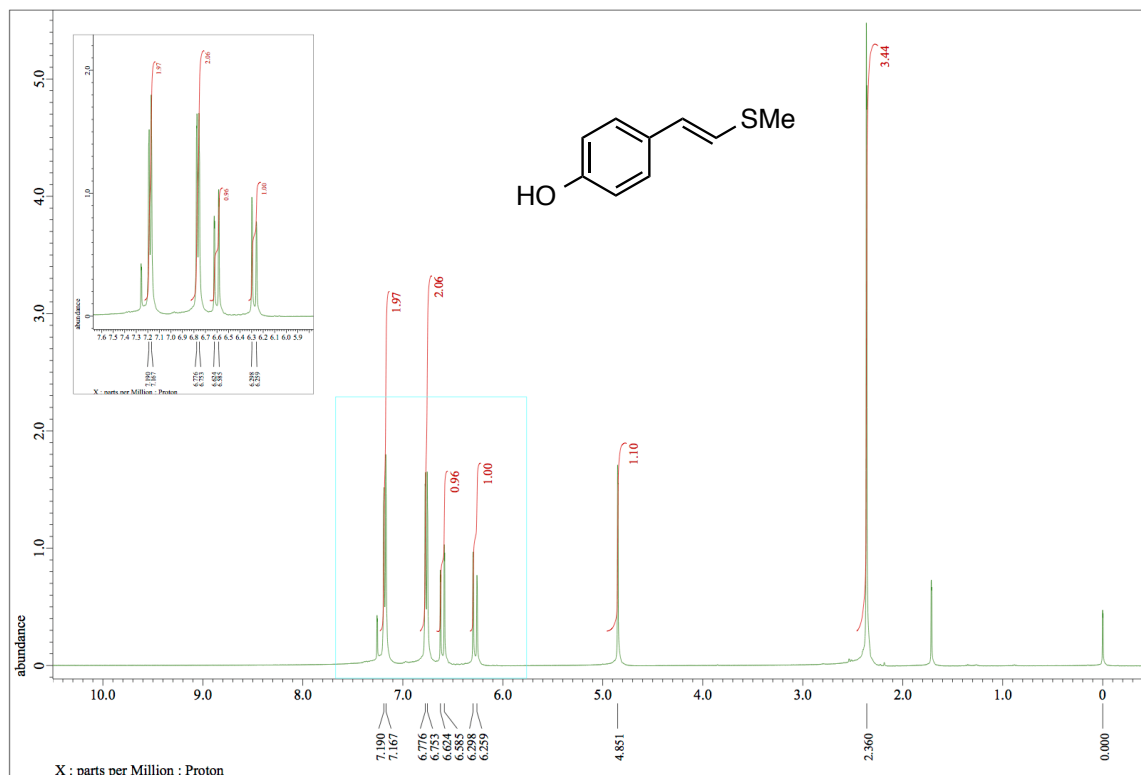
$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra of **1g** (*E/Z* = 18:1,  $\text{CDCl}_3$ )



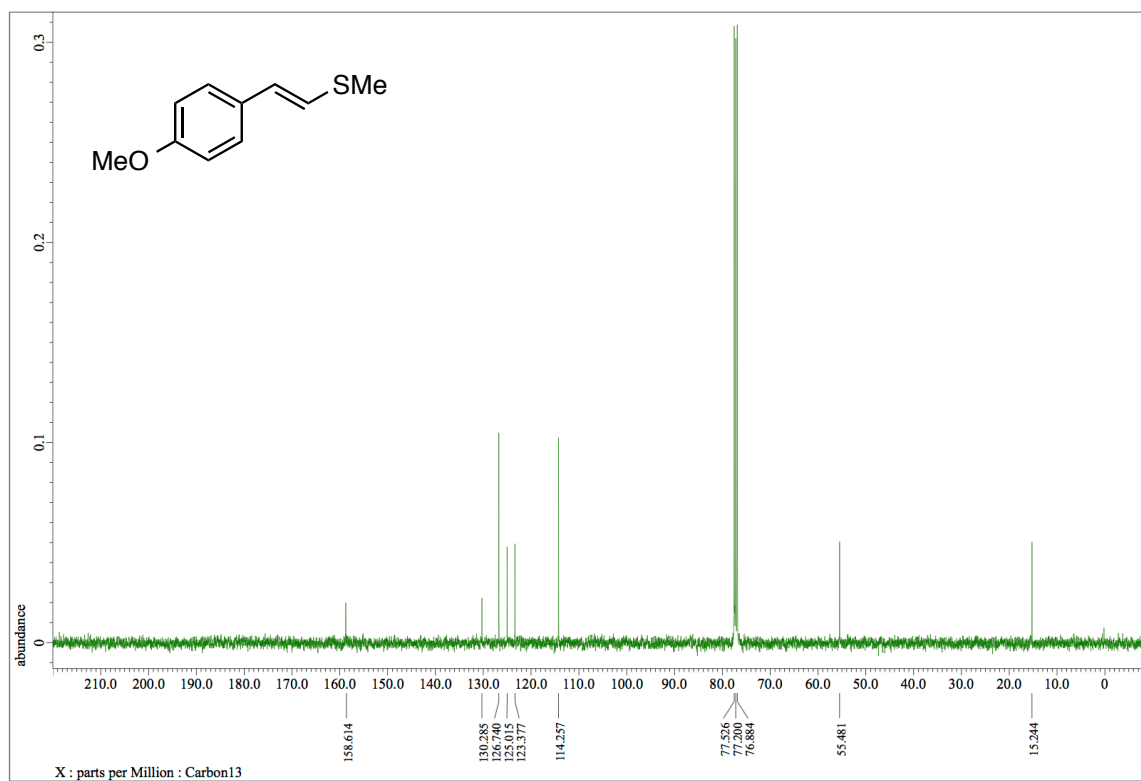
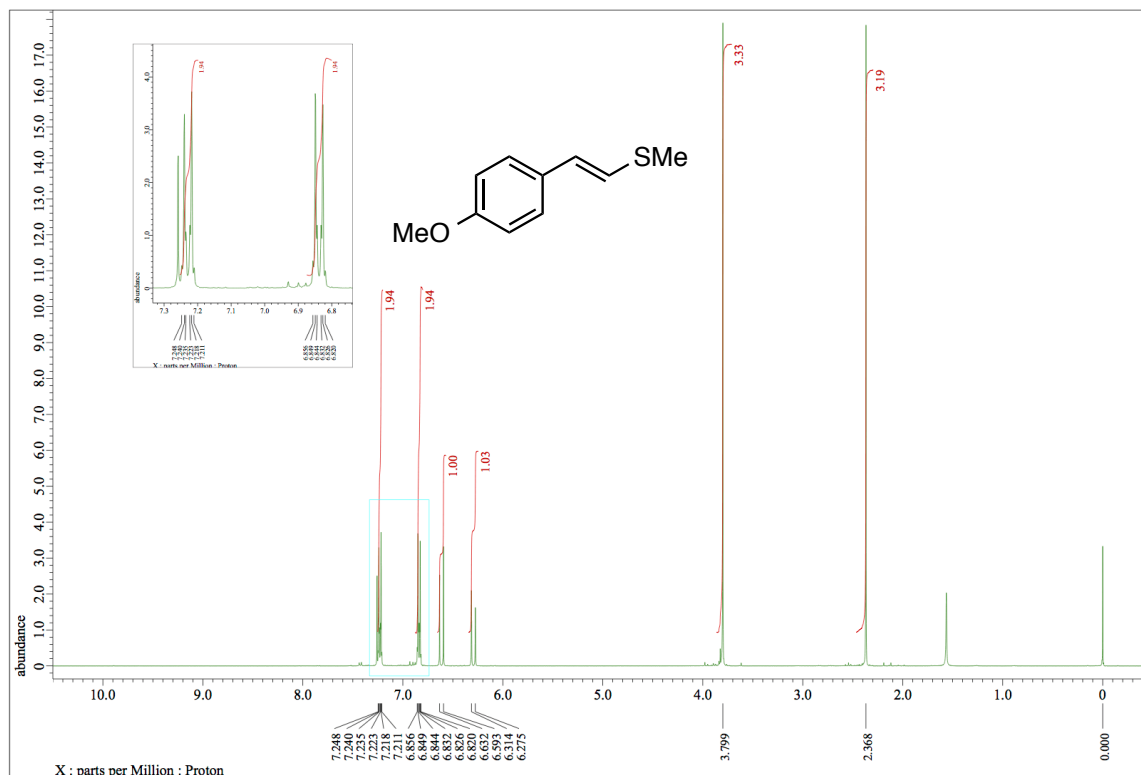
$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra of **1h** ( $\text{CDCl}_3$ )



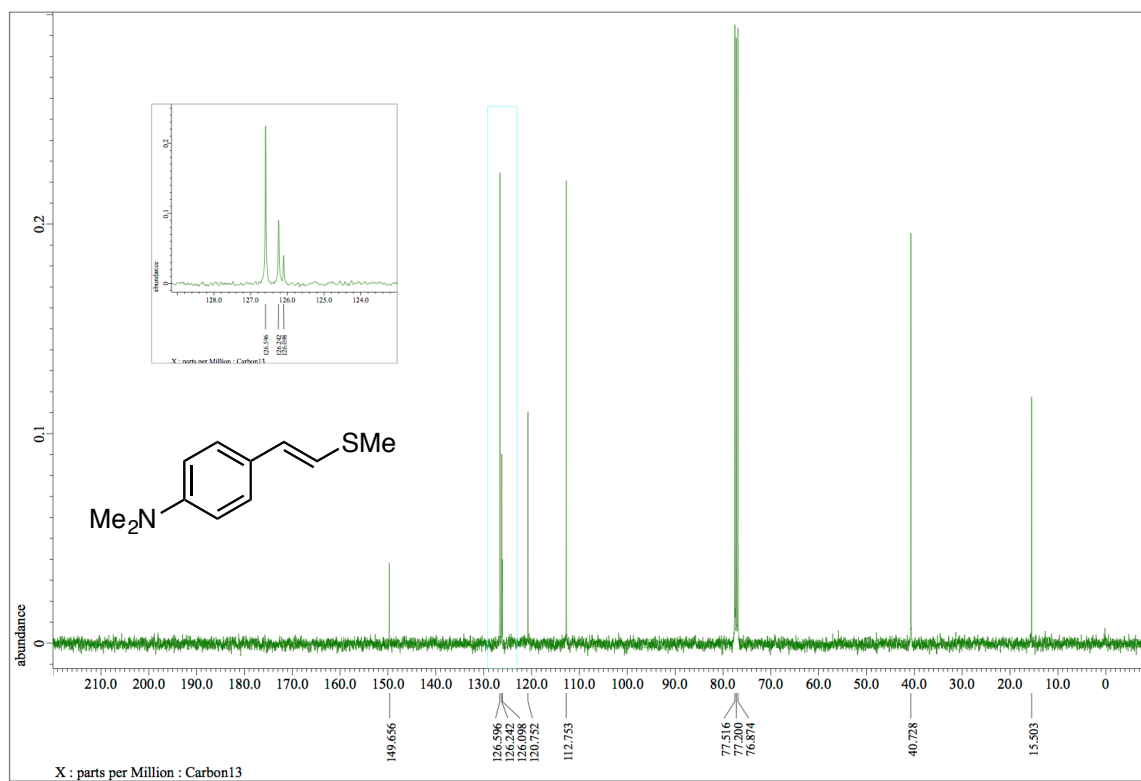
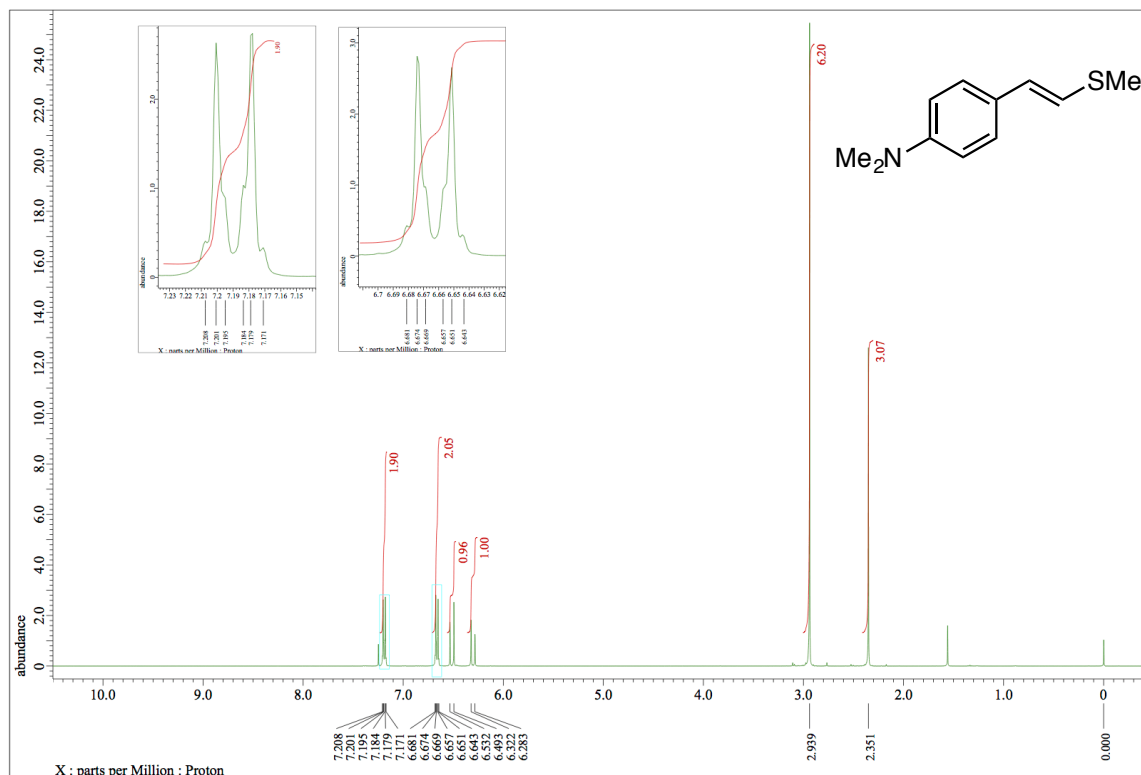
$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra of **1i** ( $\text{CDCl}_3$ )



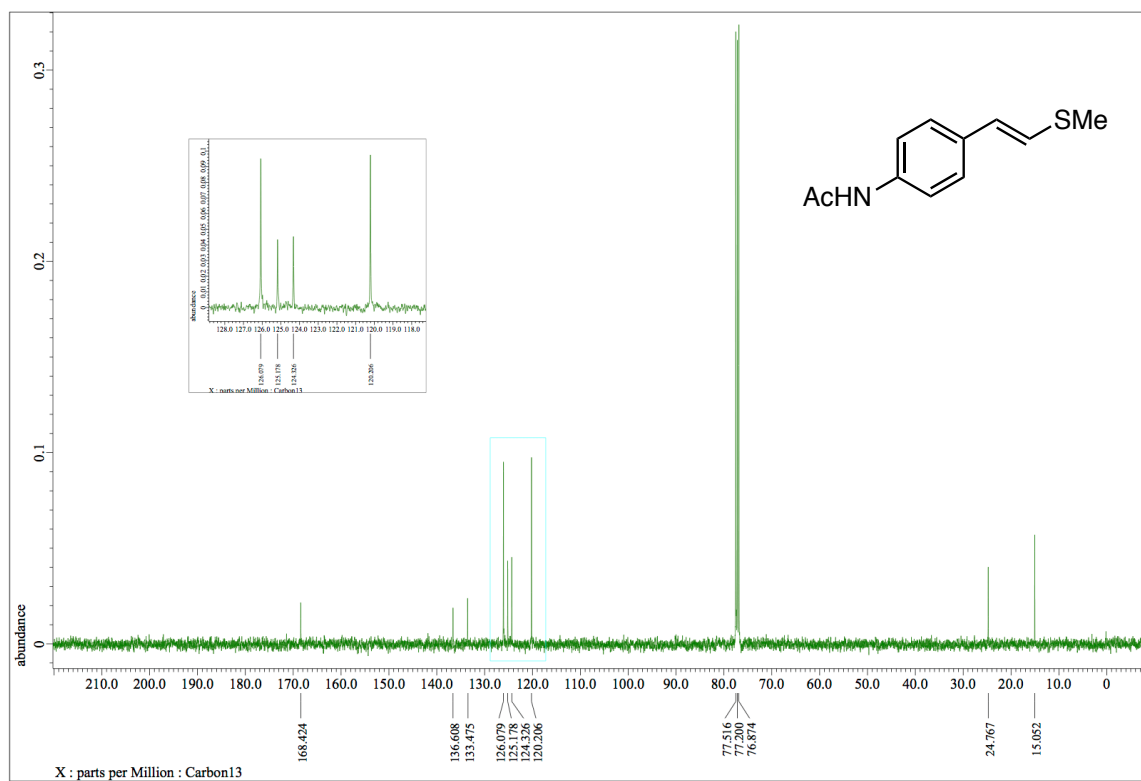
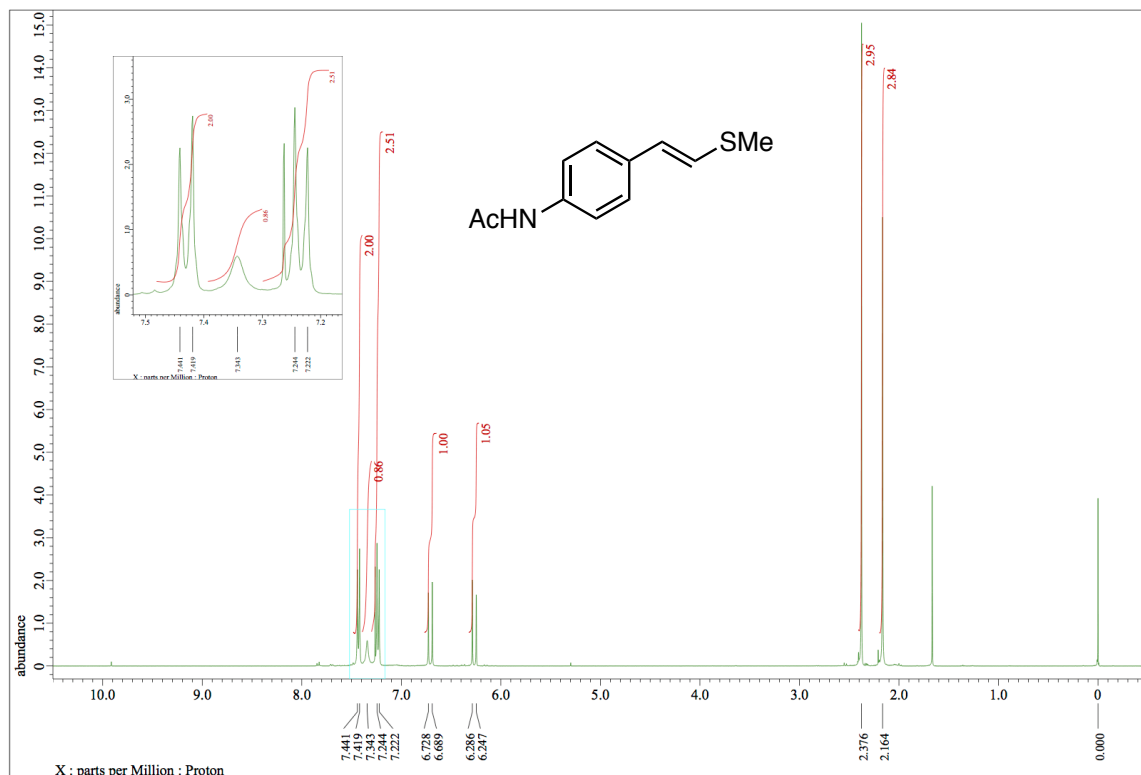
$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra of **1j** ( $\text{CDCl}_3$ )



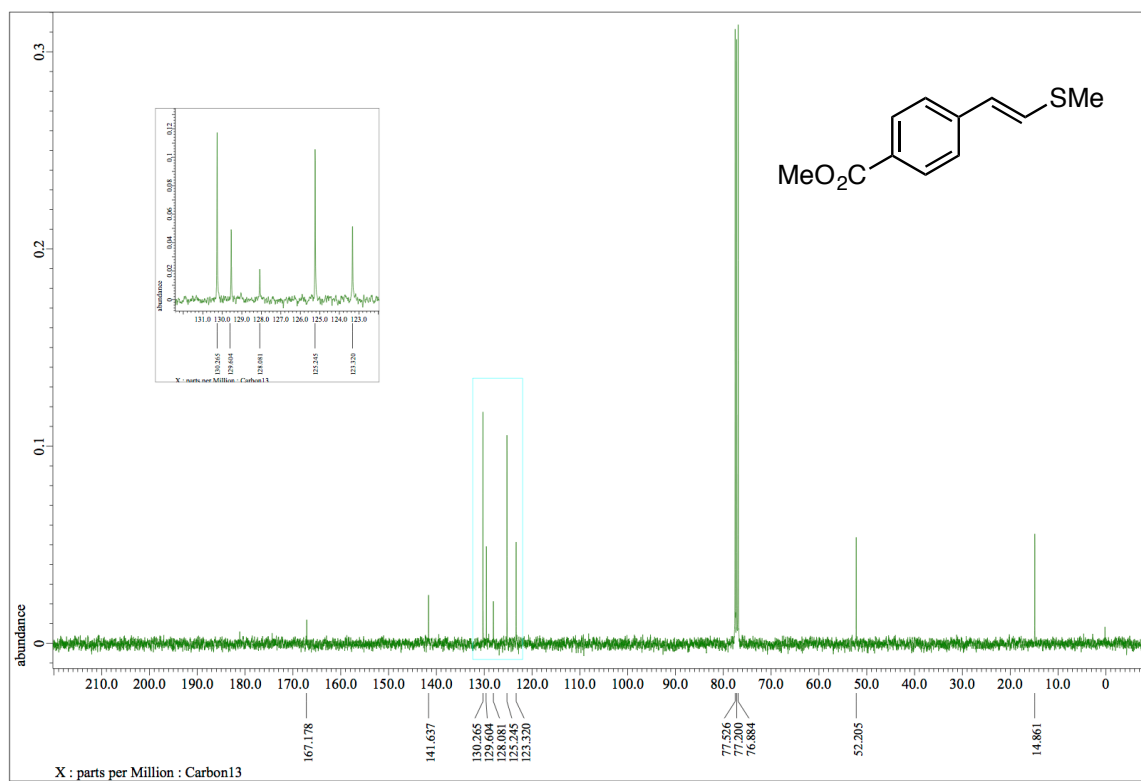
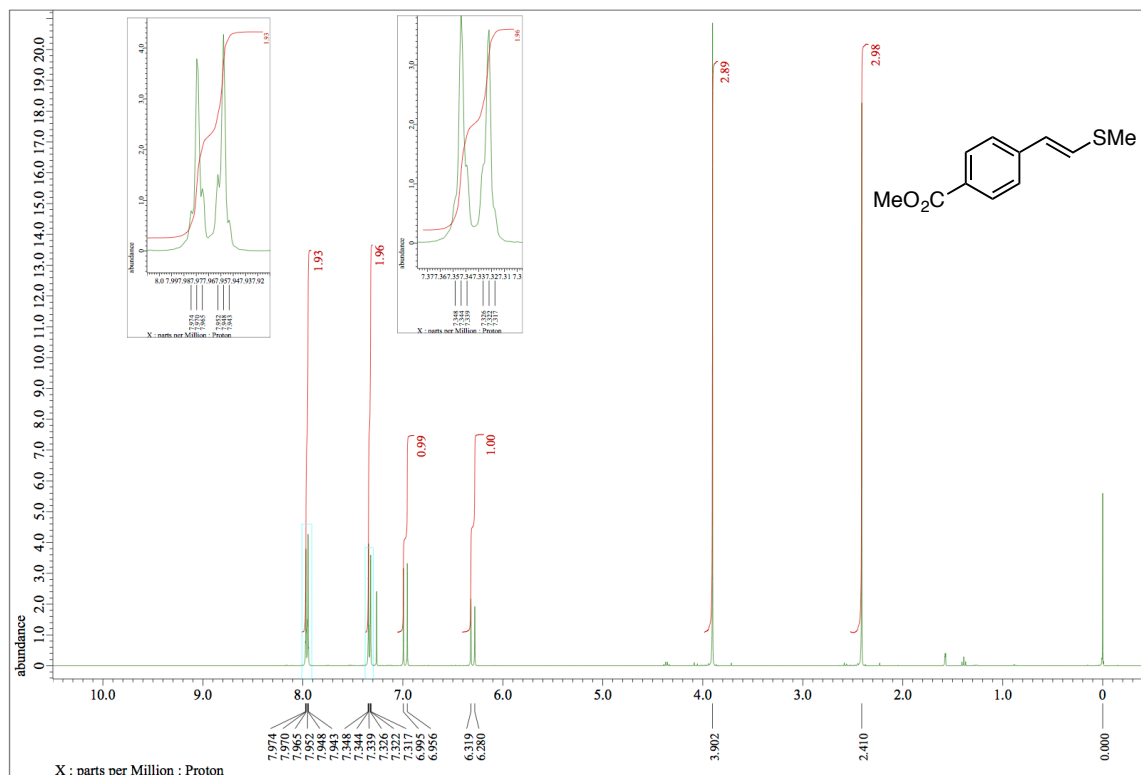
$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra of **1k** ( $\text{CDCl}_3$ )



$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra of **11** ( $\text{CDCl}_3$ )

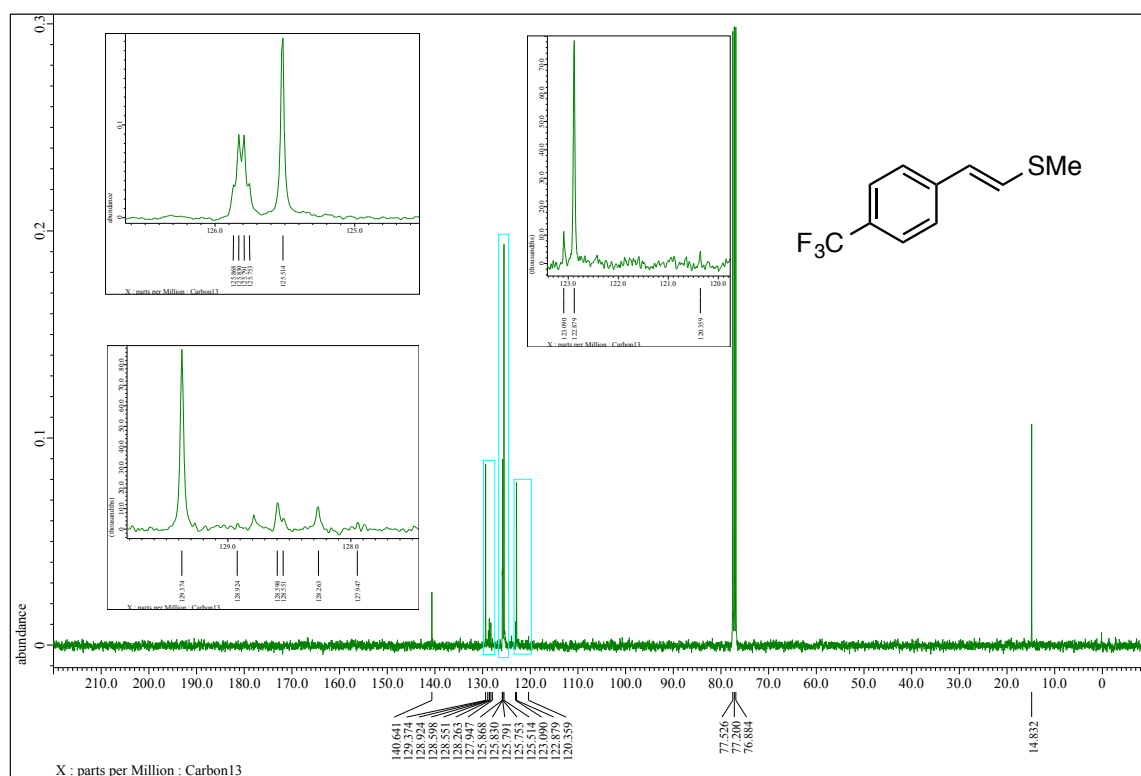
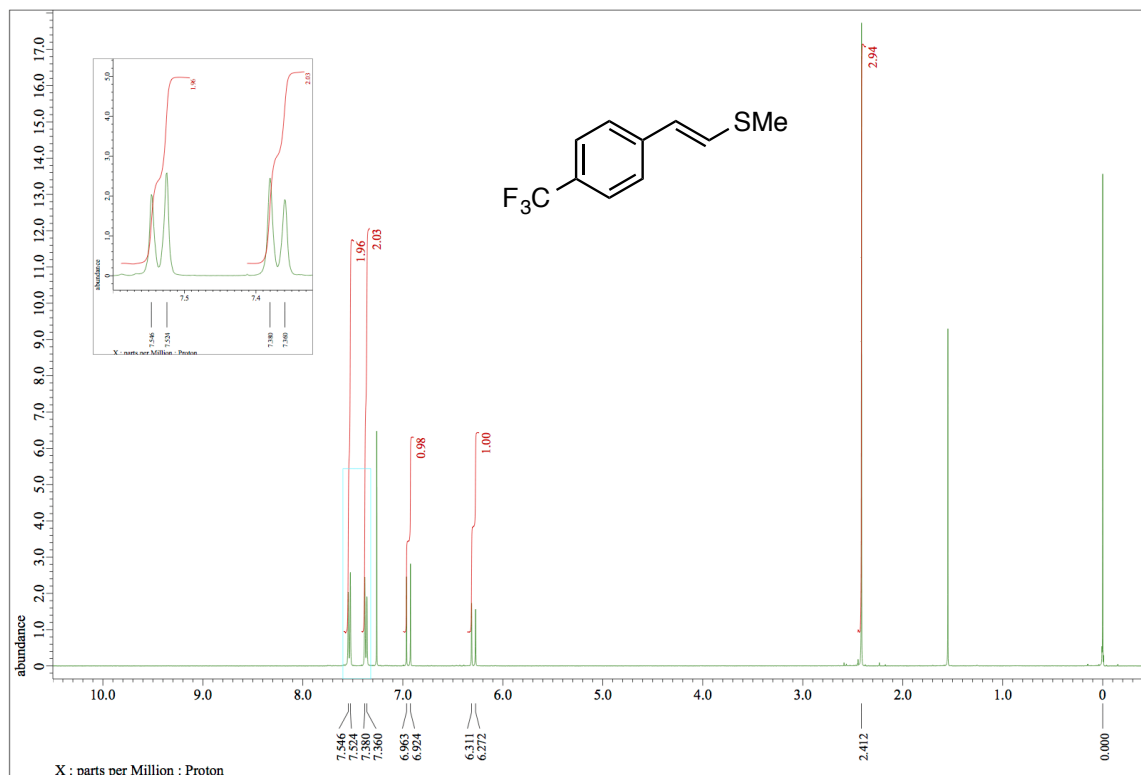


$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra of **1m** ( $\text{CDCl}_3$ )

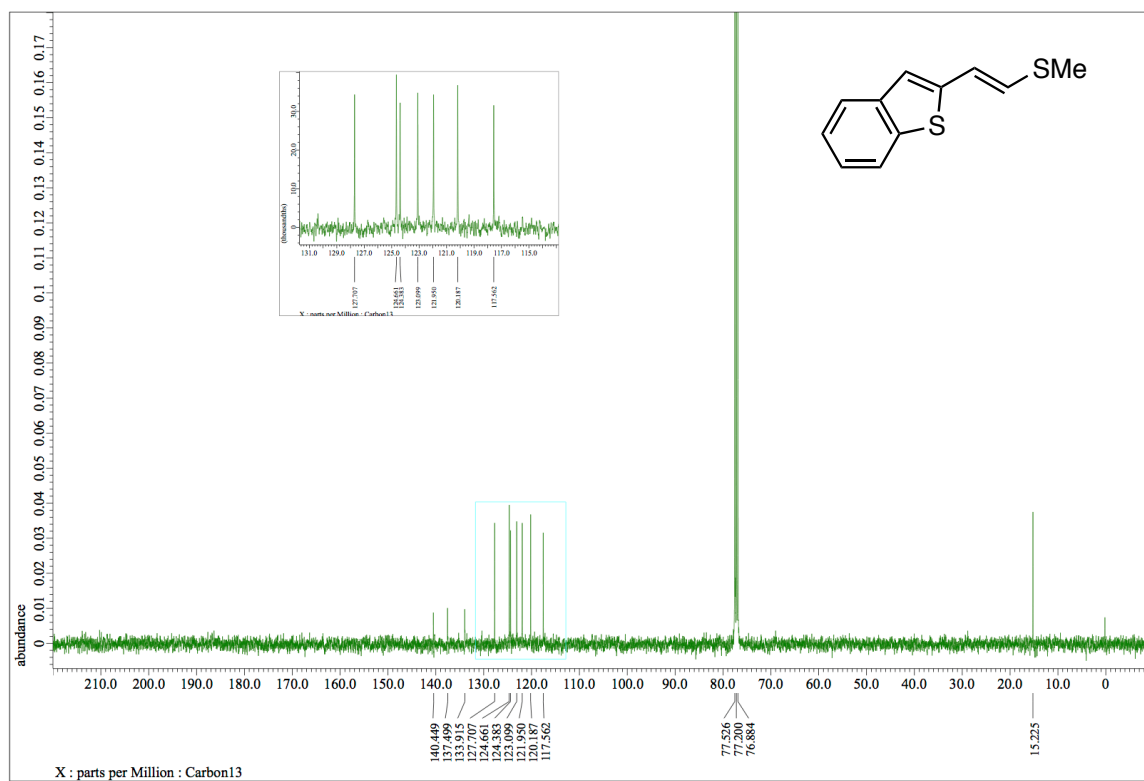
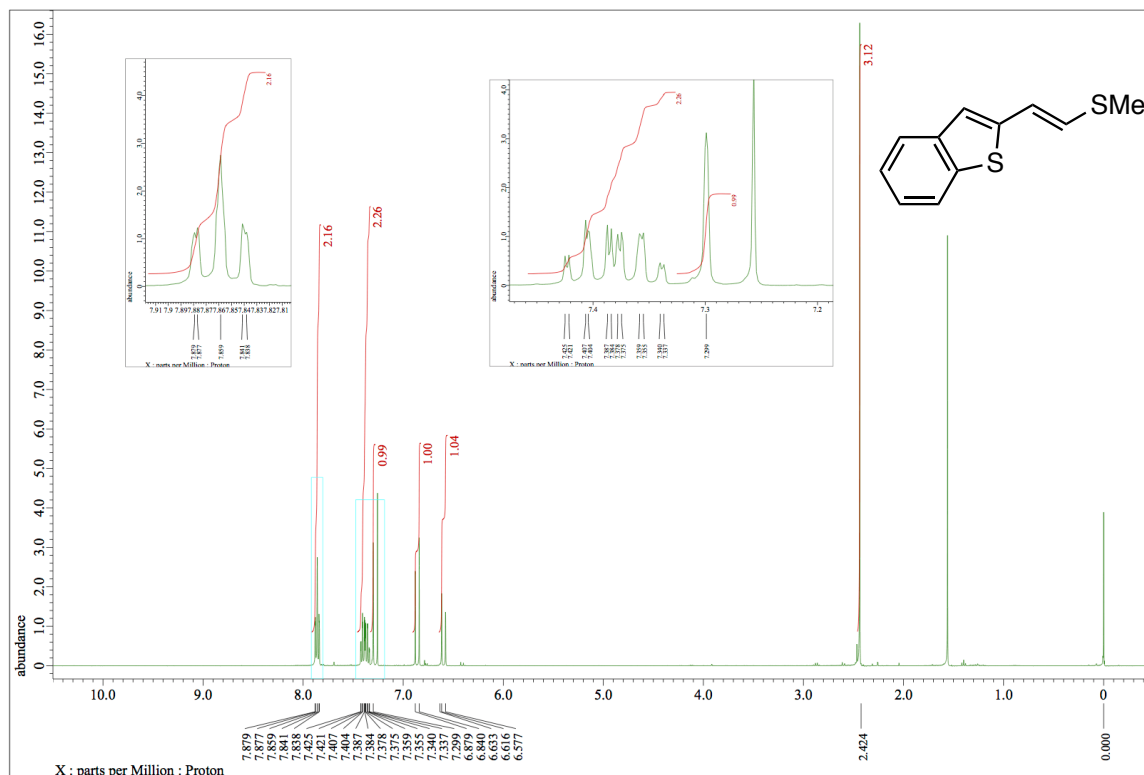




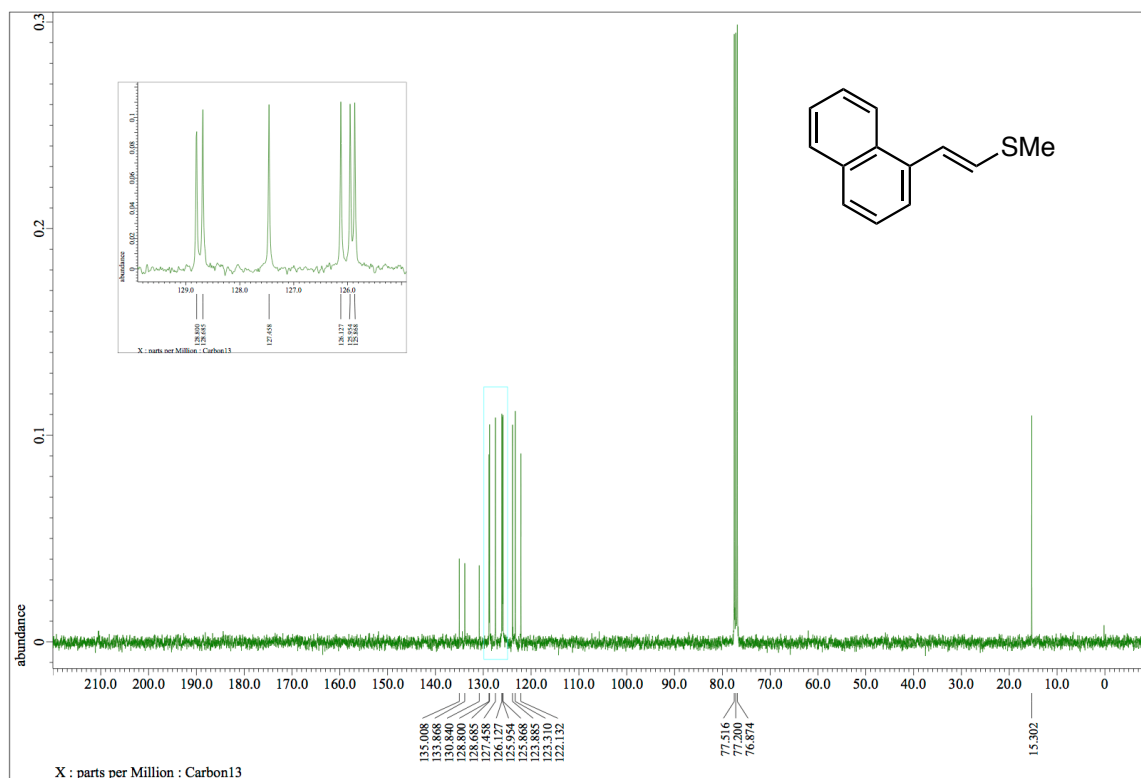
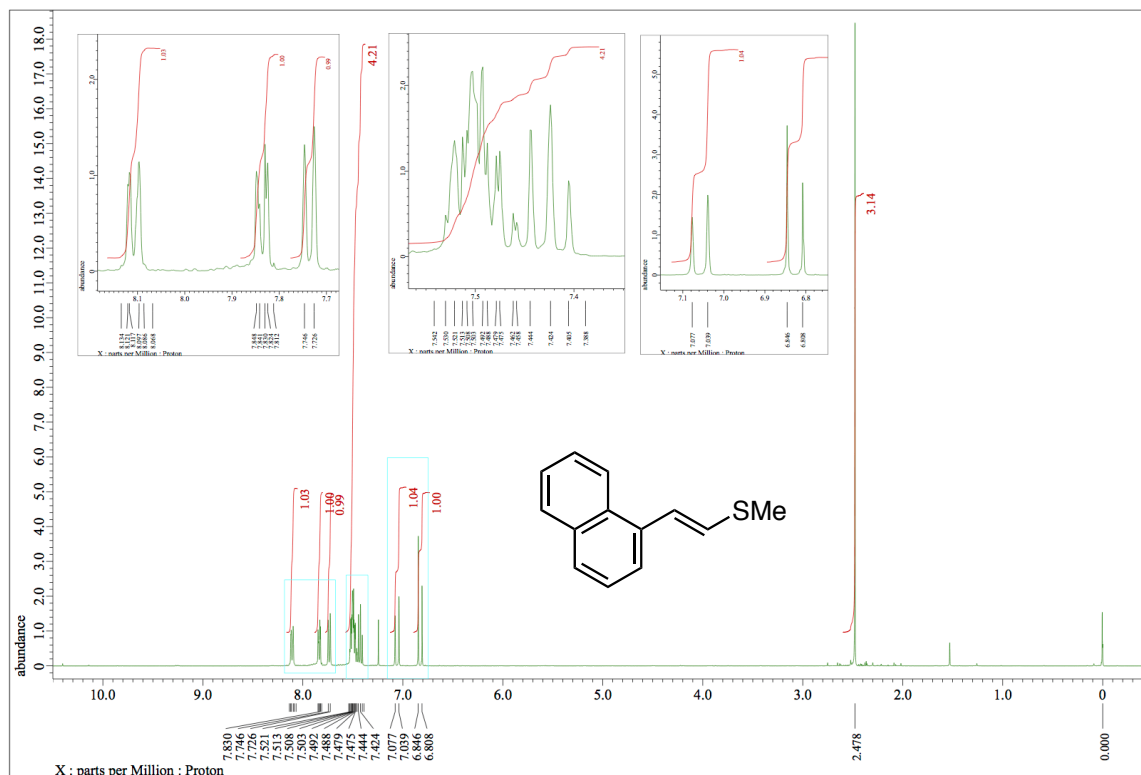
$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra of **1n** ( $\text{CDCl}_3$ )



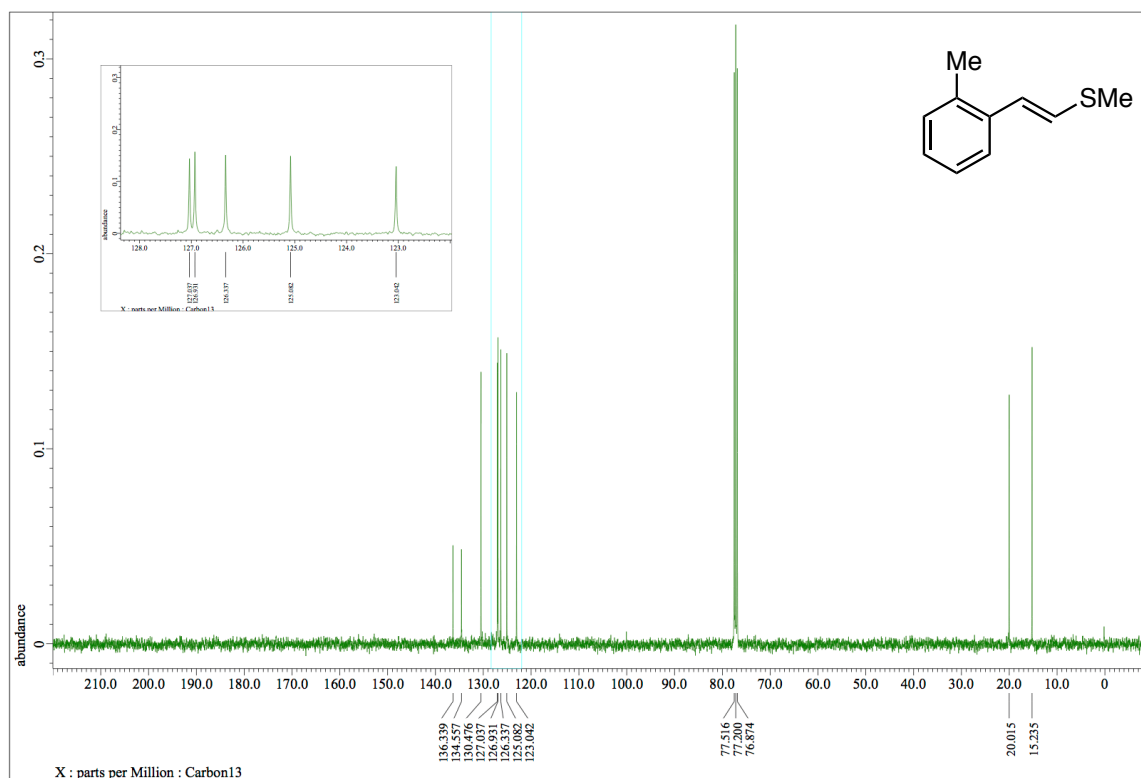
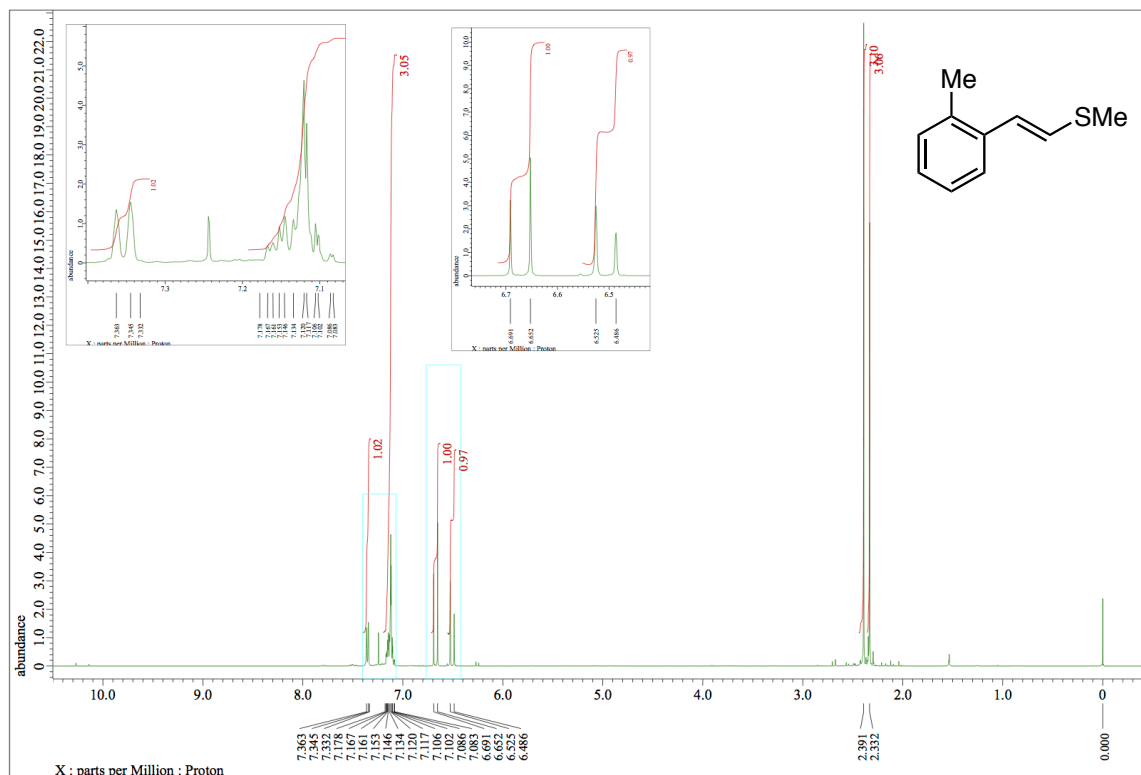
$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra of **1o** (*E/Z* = 41:1,  $\text{CDCl}_3$ )



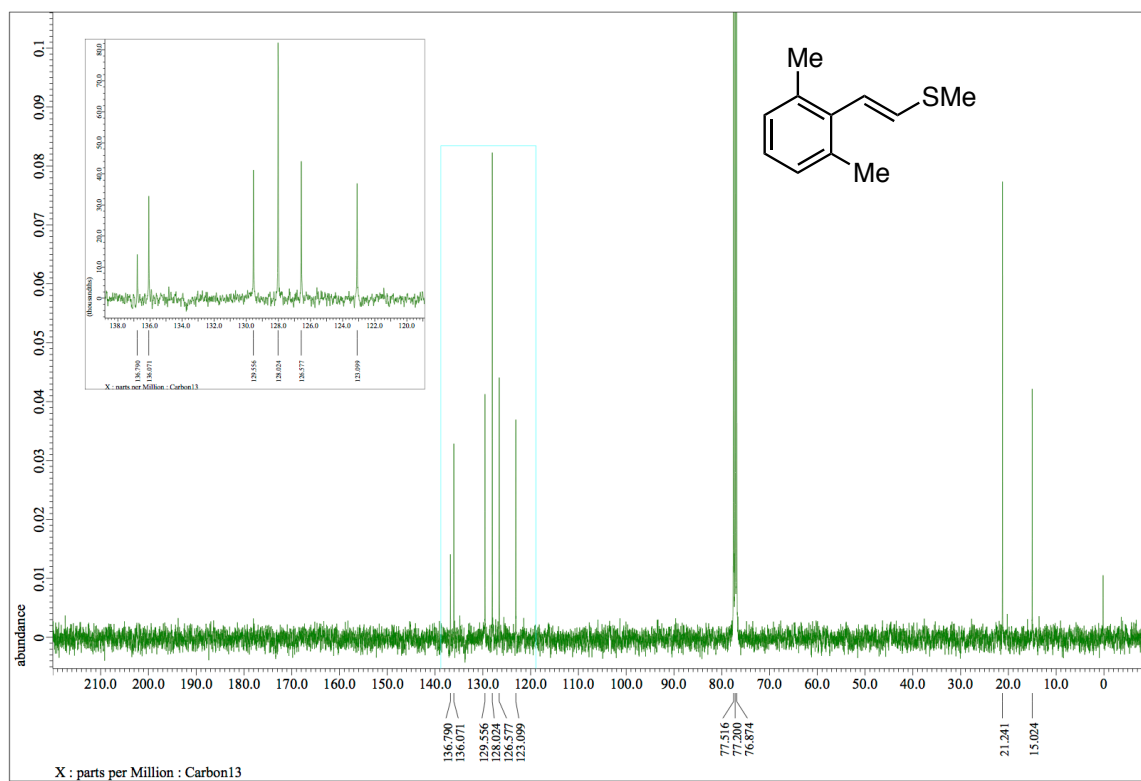
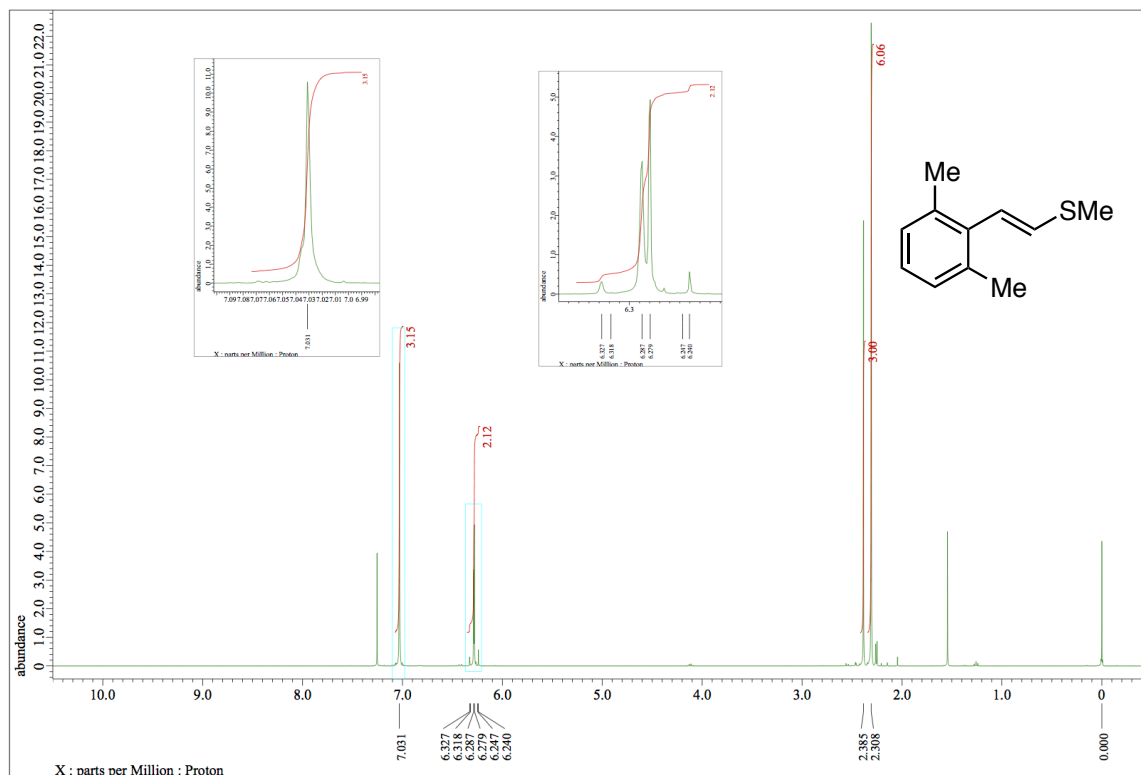
$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra of **1p** ( $\text{CDCl}_3$ )



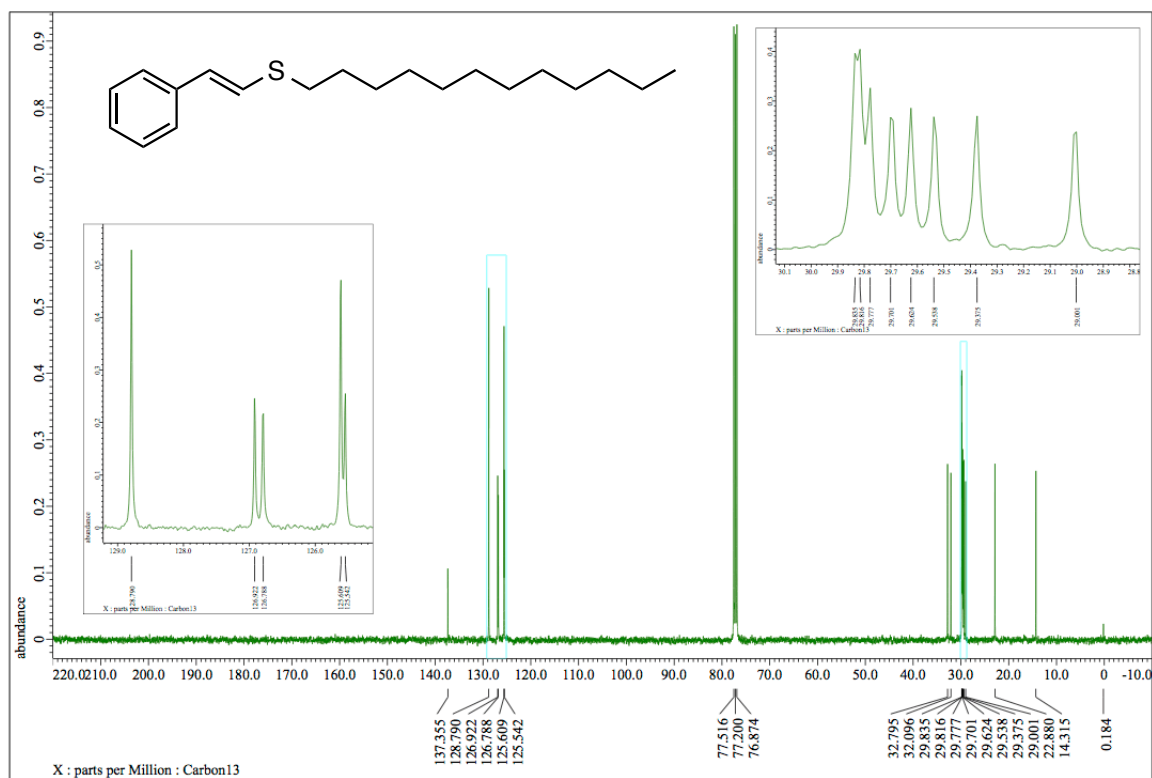
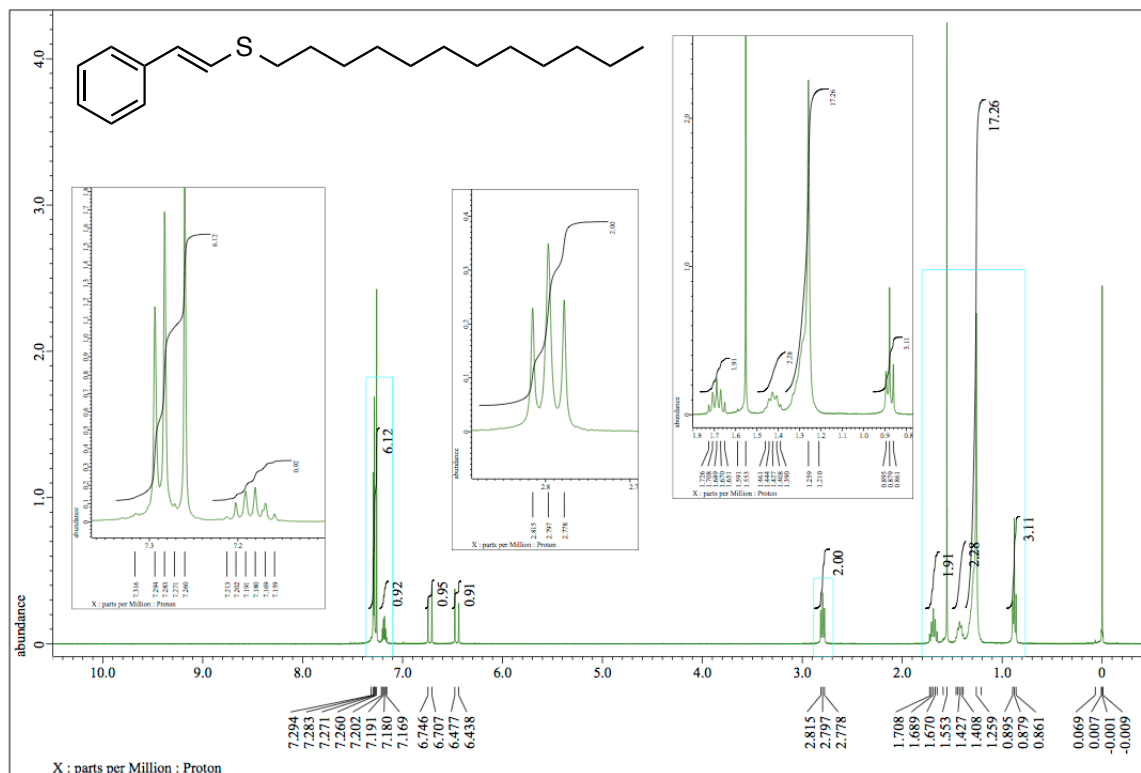
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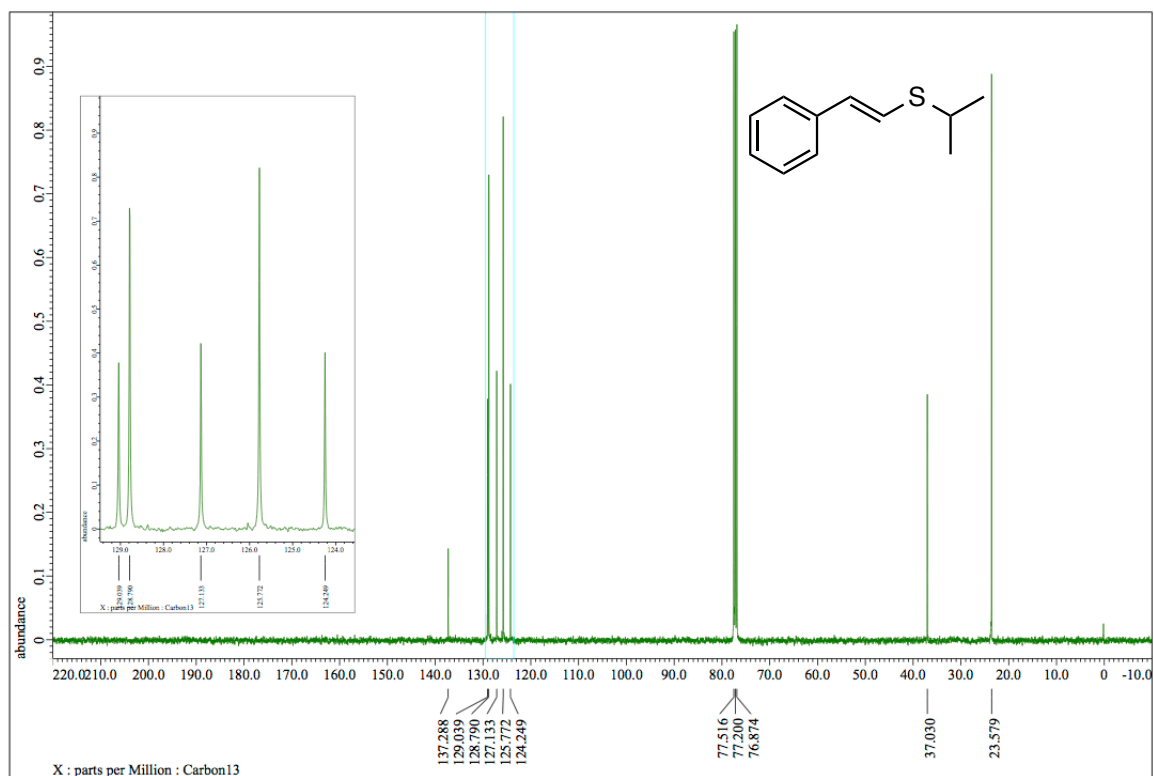
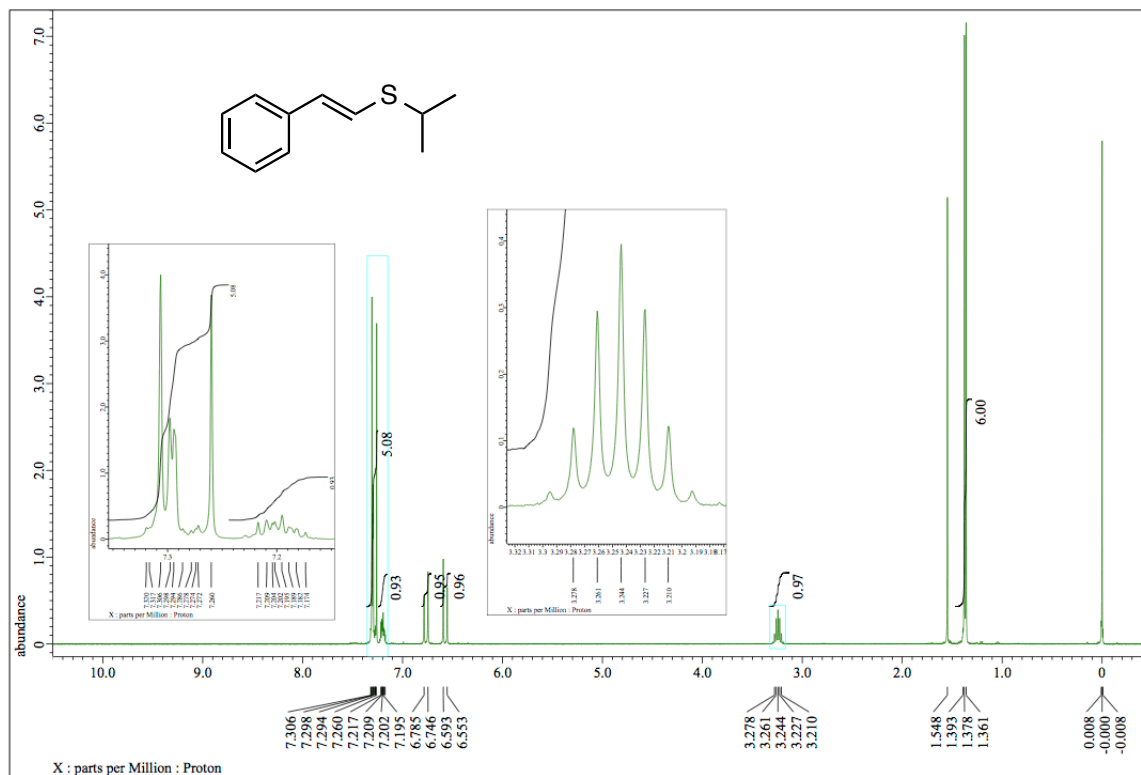
$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra of **1r** ( $\text{CDCl}_3$ )



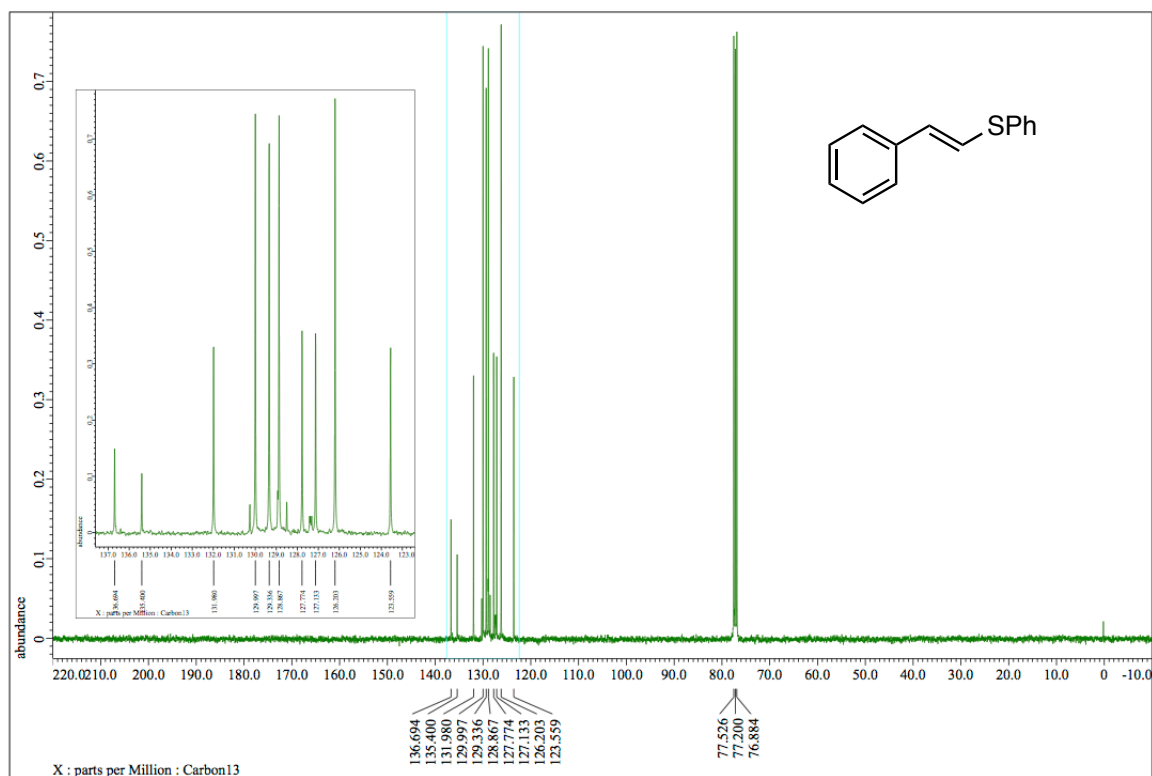
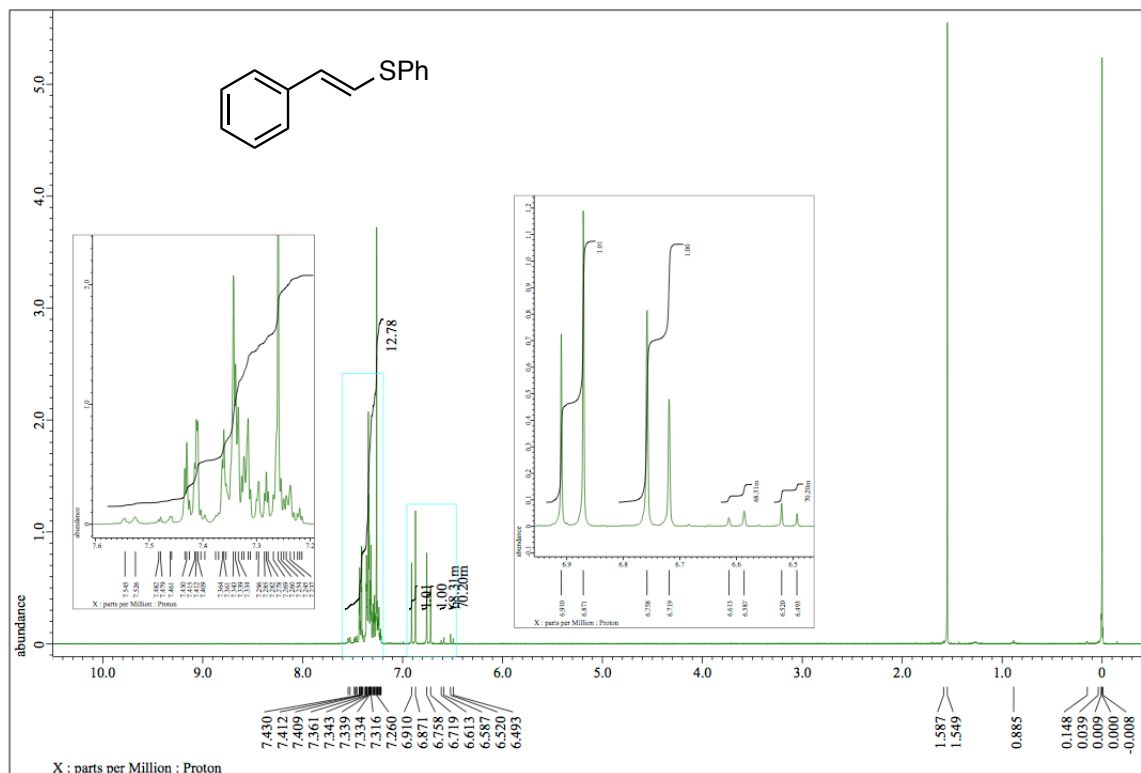
$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra of **4** ( $\text{CDCl}_3$ )



$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra of **5** ( $\text{CDCl}_3$ )

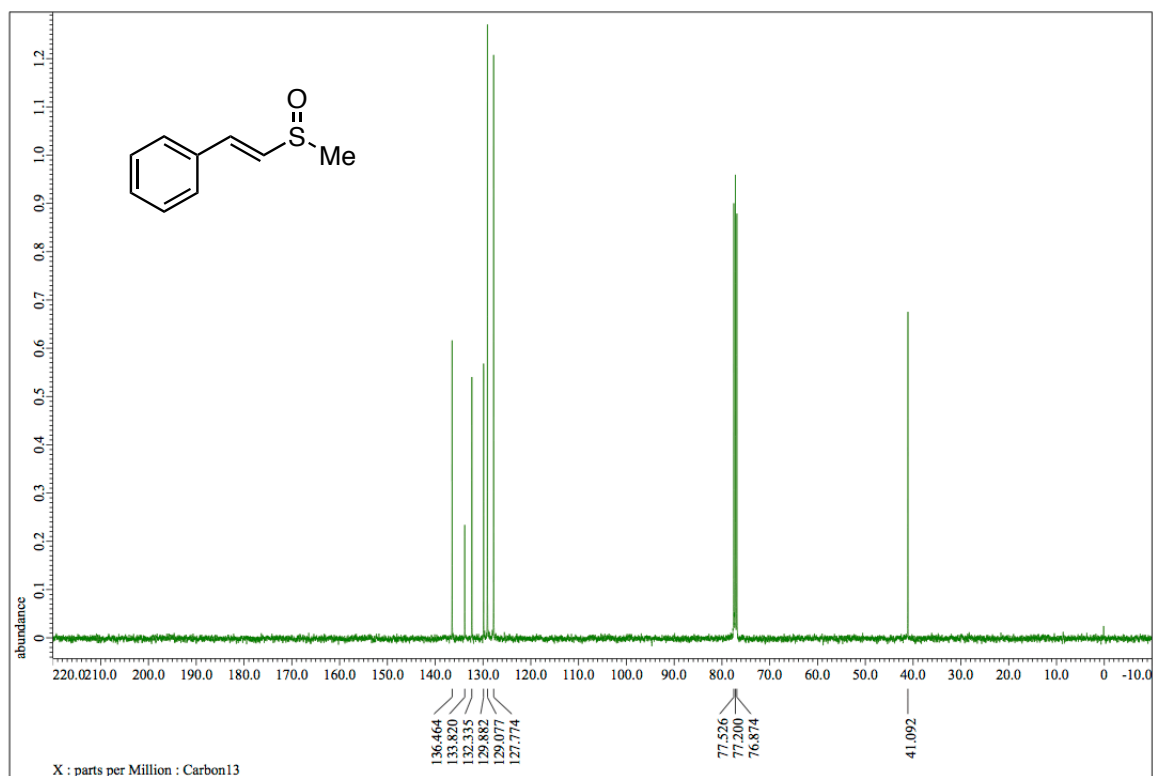
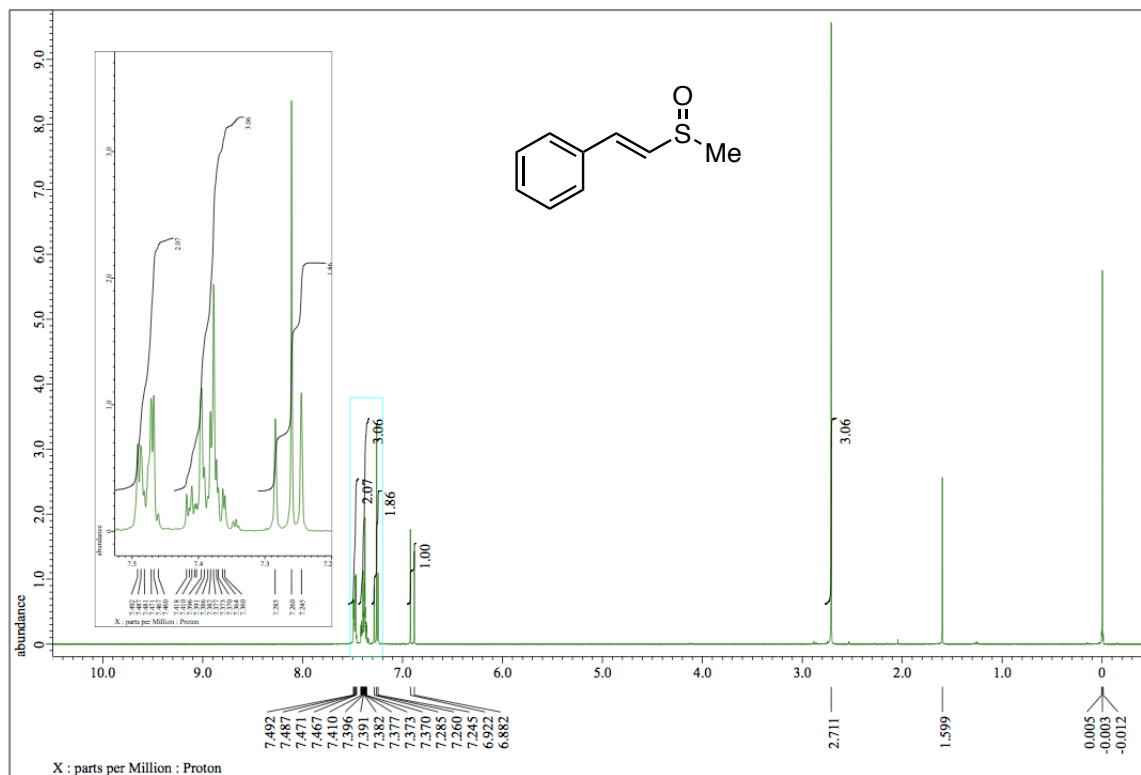


$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra of **6** (*E/Z* = 14:1,  $\text{CDCl}_3$ )

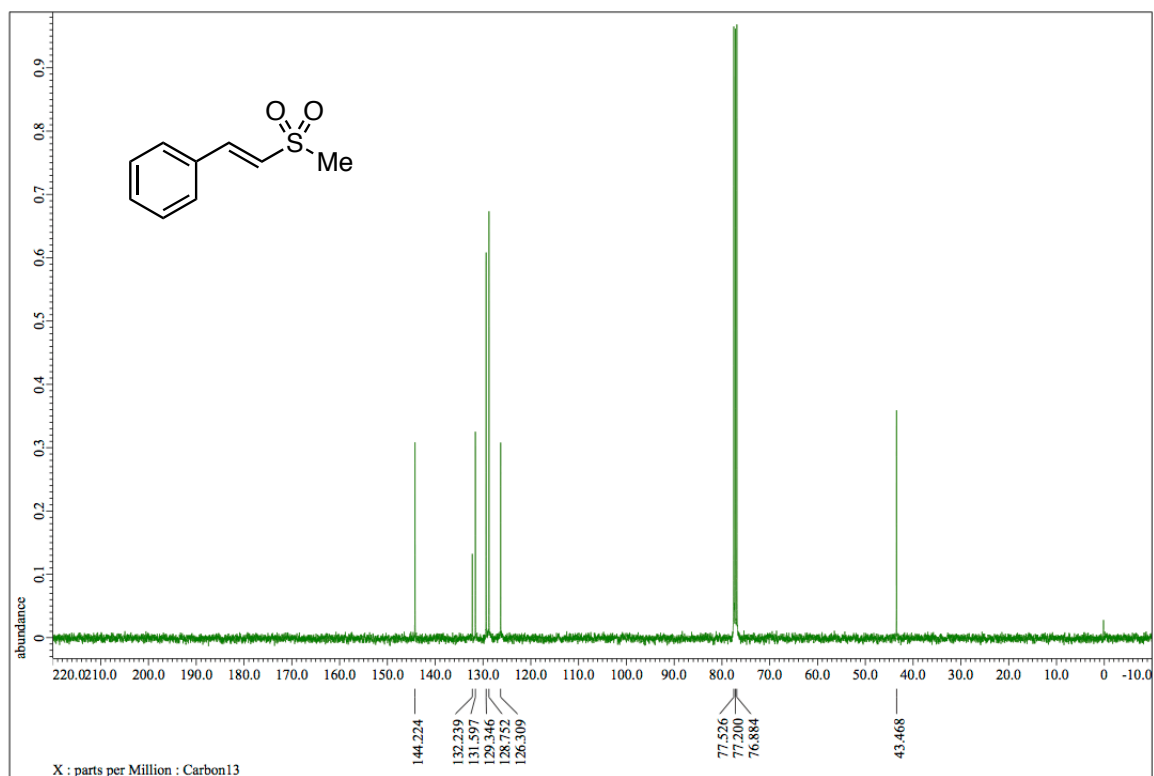
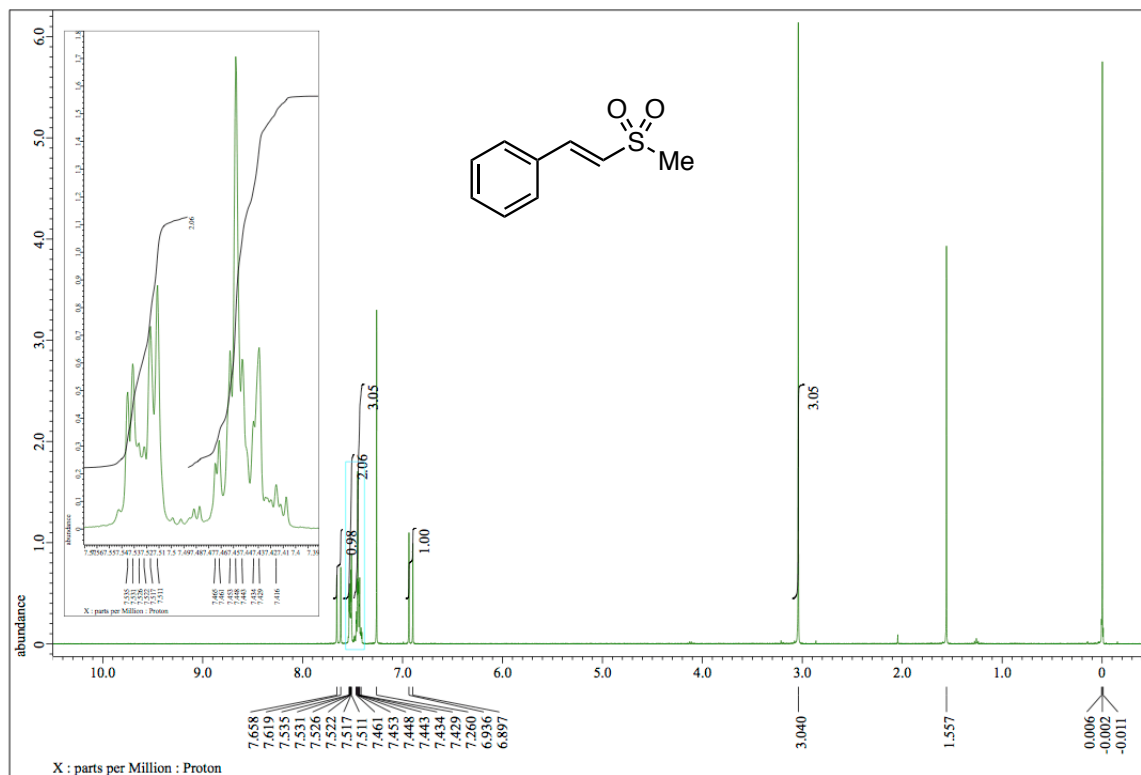




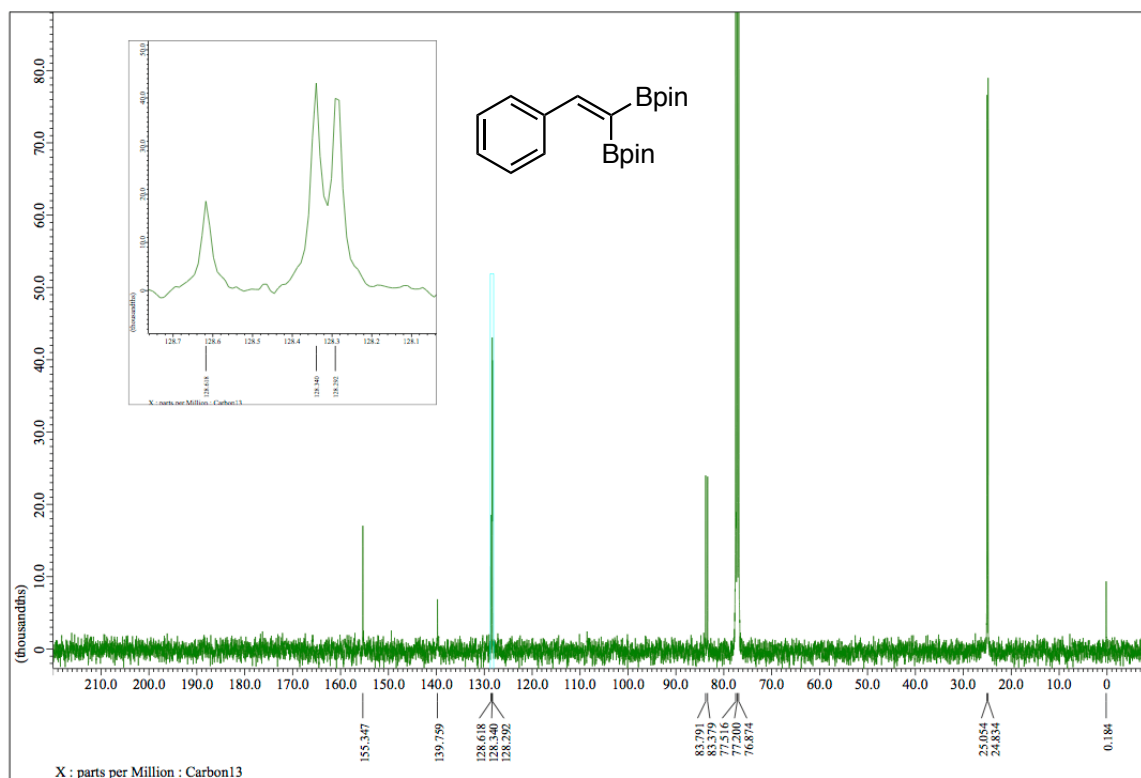
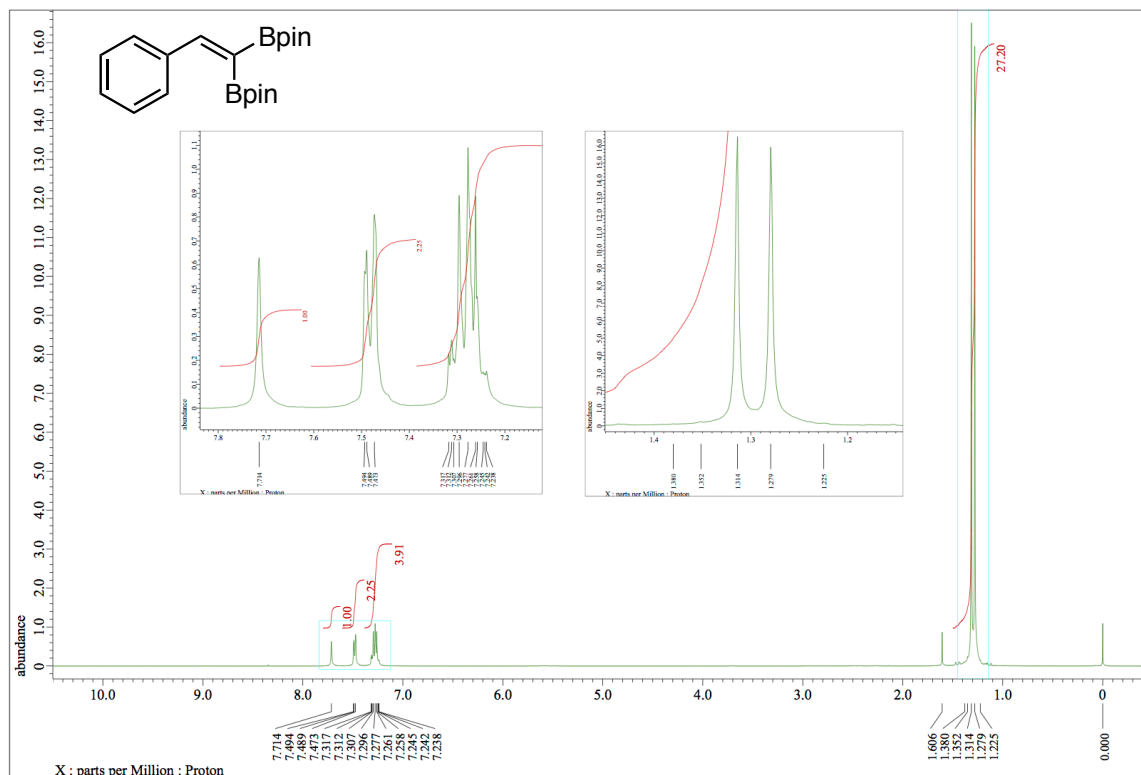
$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra of **11** ( $\text{CDCl}_3$ )



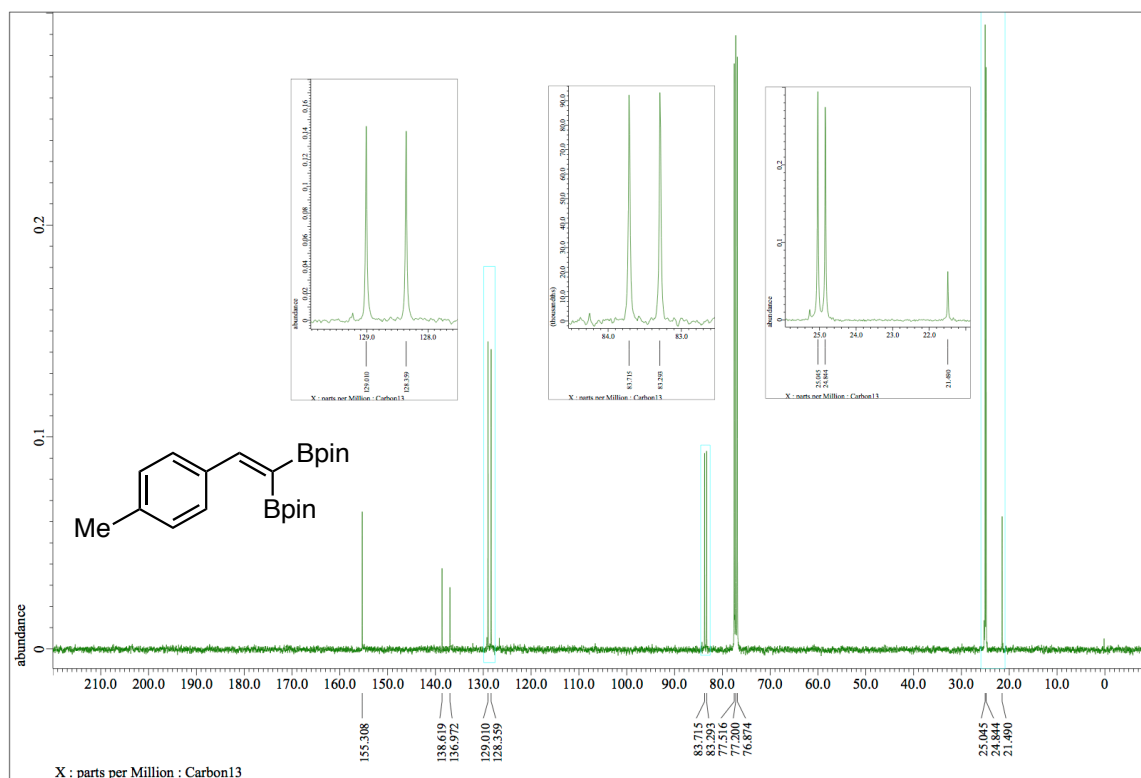
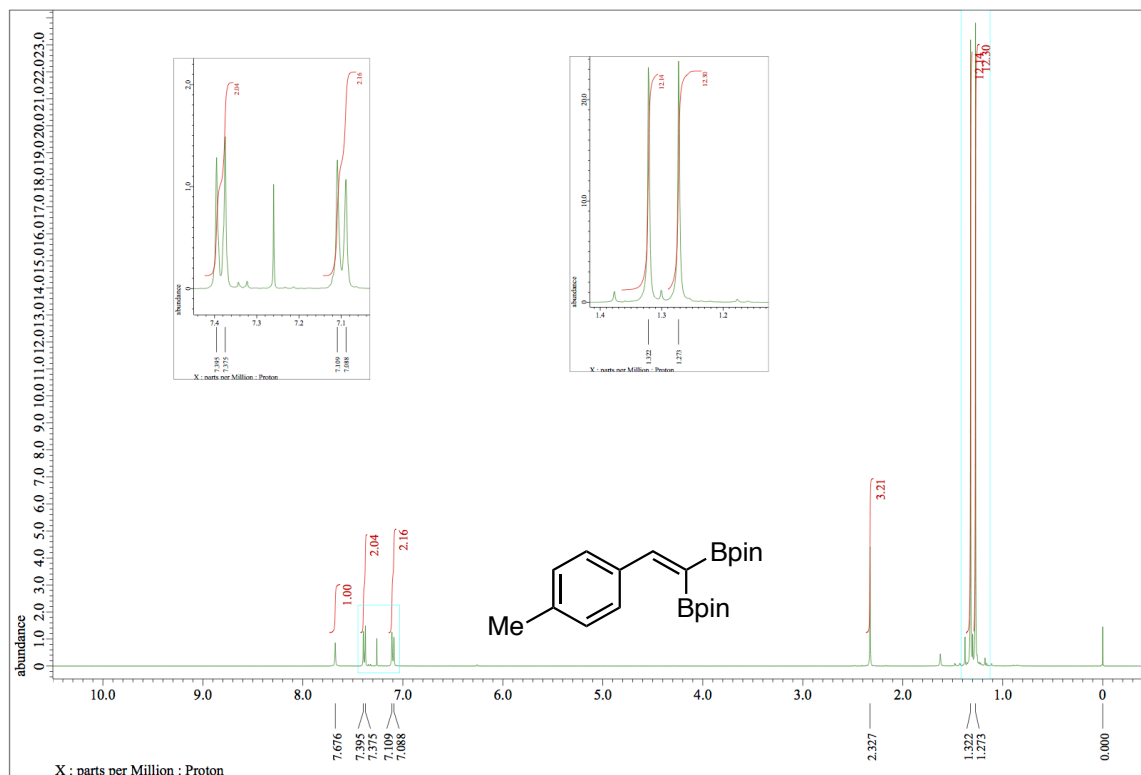
$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra of **12** ( $\text{CDCl}_3$ )



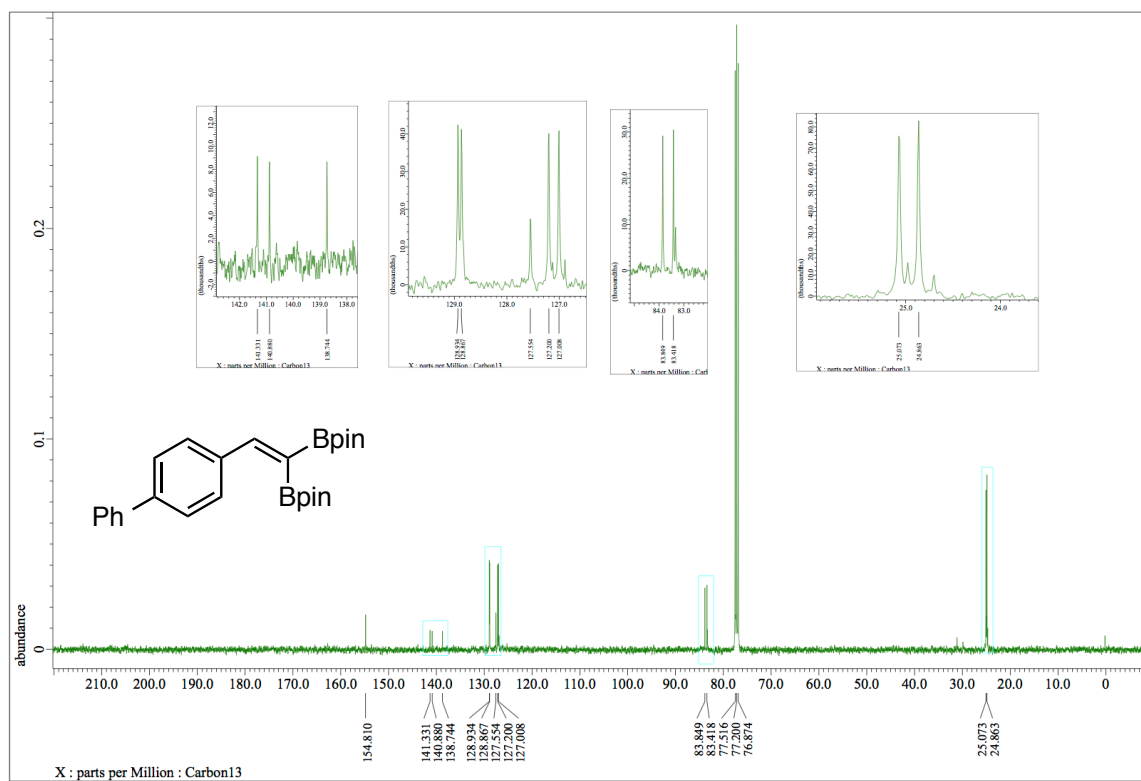
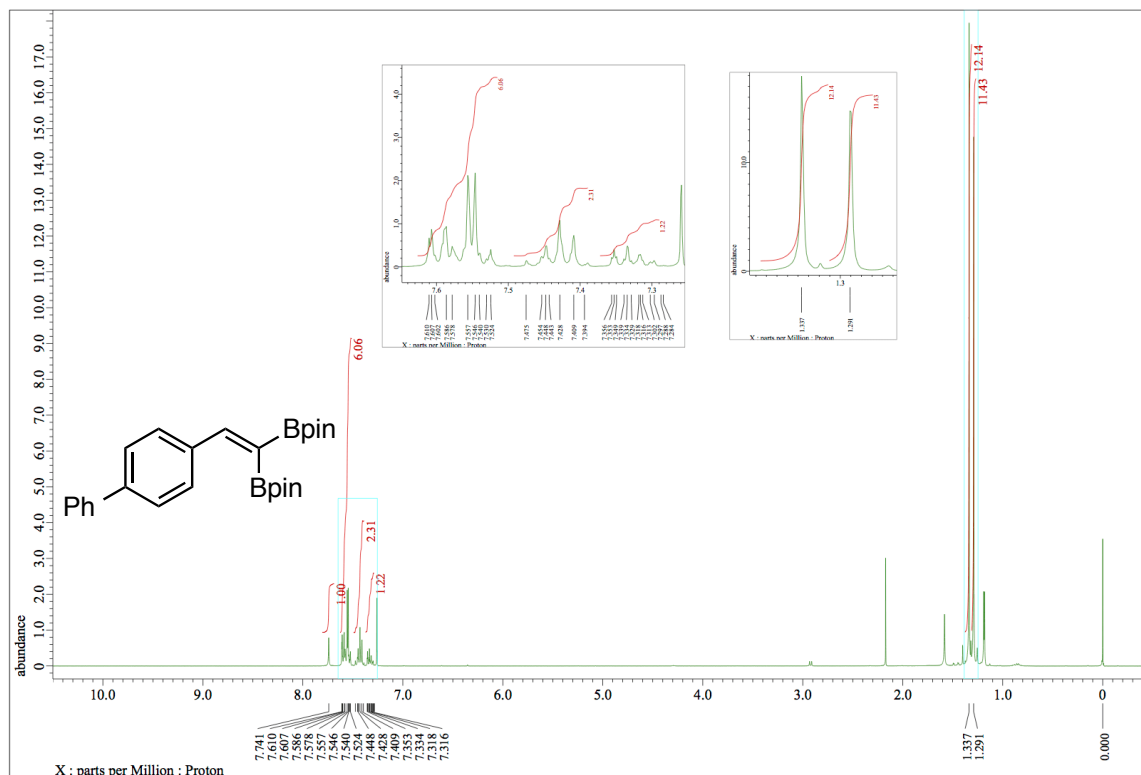
$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra of **3a** ( $\text{CDCl}_3$ )



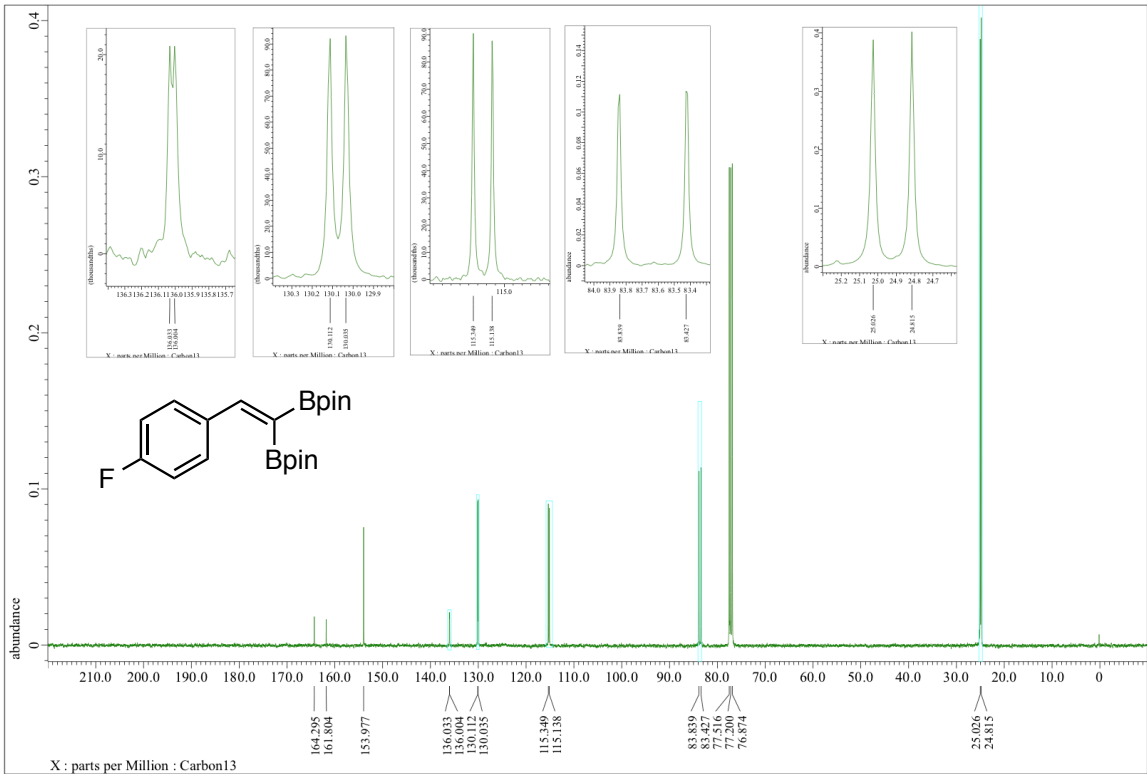
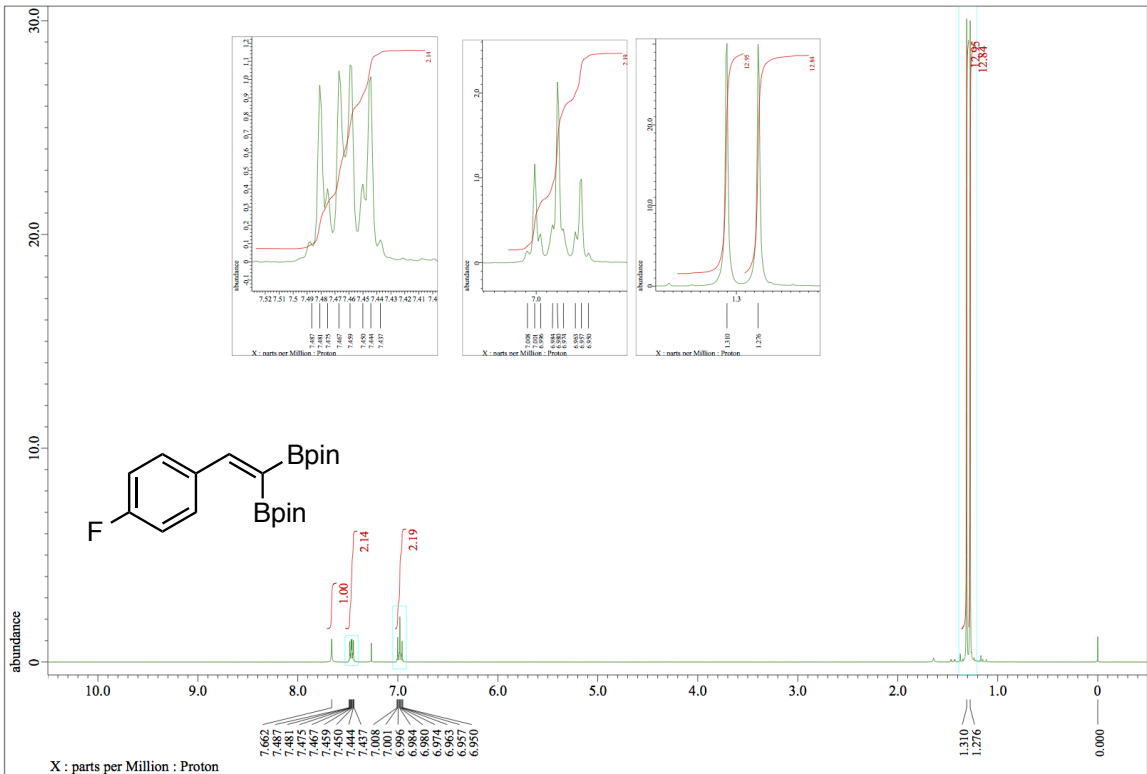
$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra of **3b** ( $\text{CDCl}_3$ )



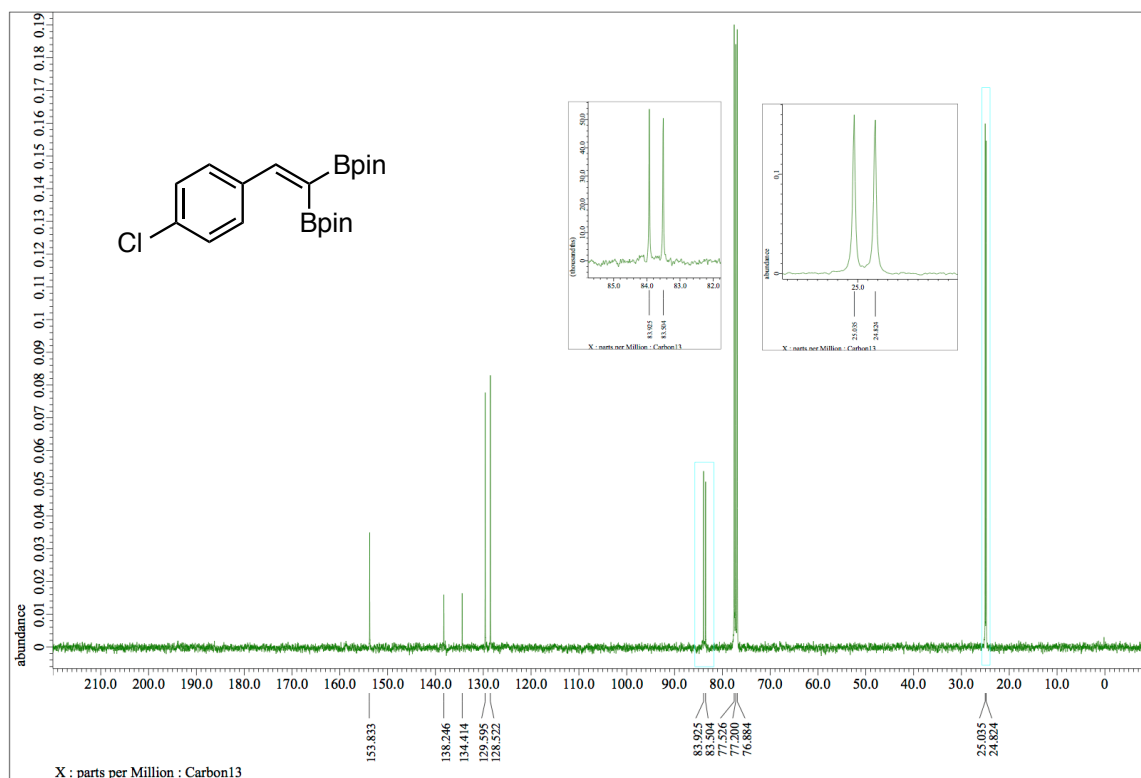
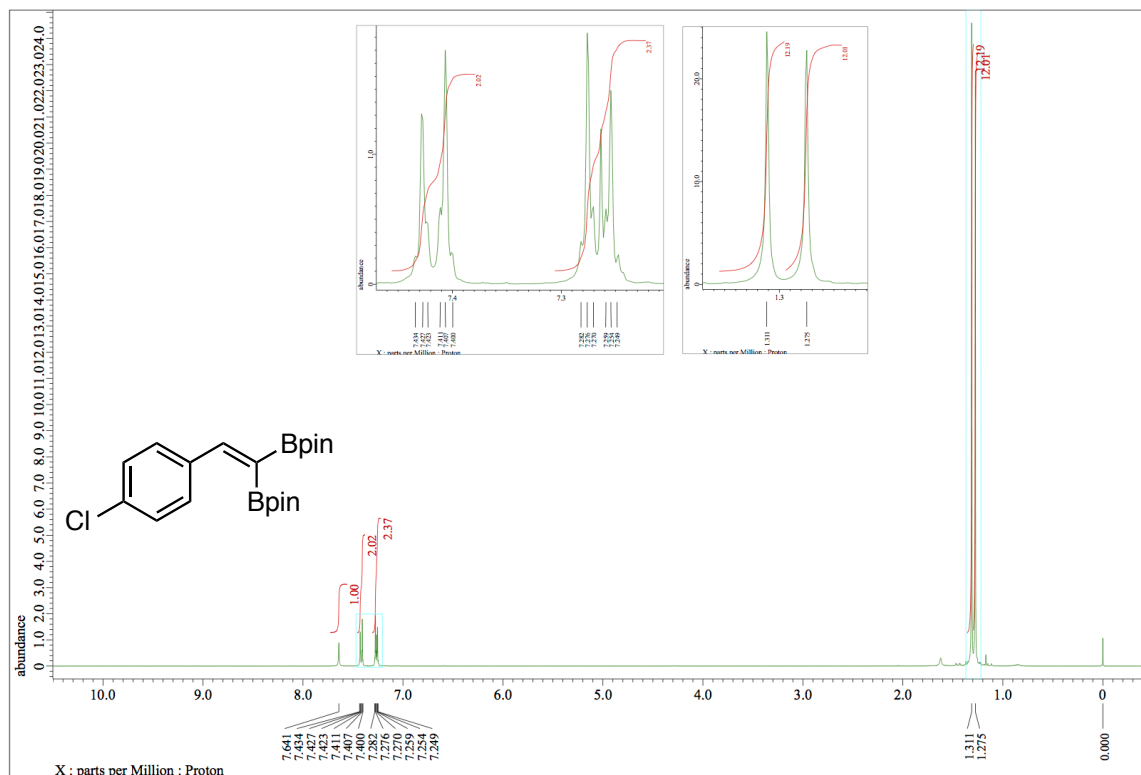
$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra of **3c** ( $\text{CDCl}_3$ )



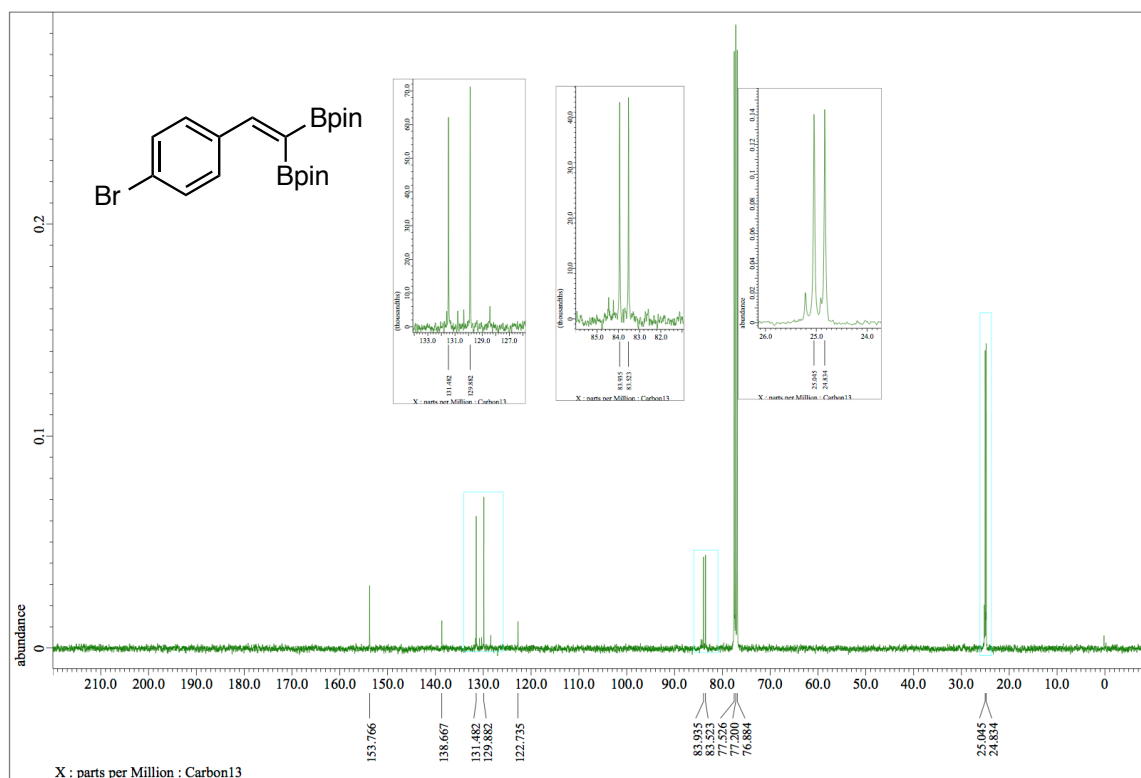
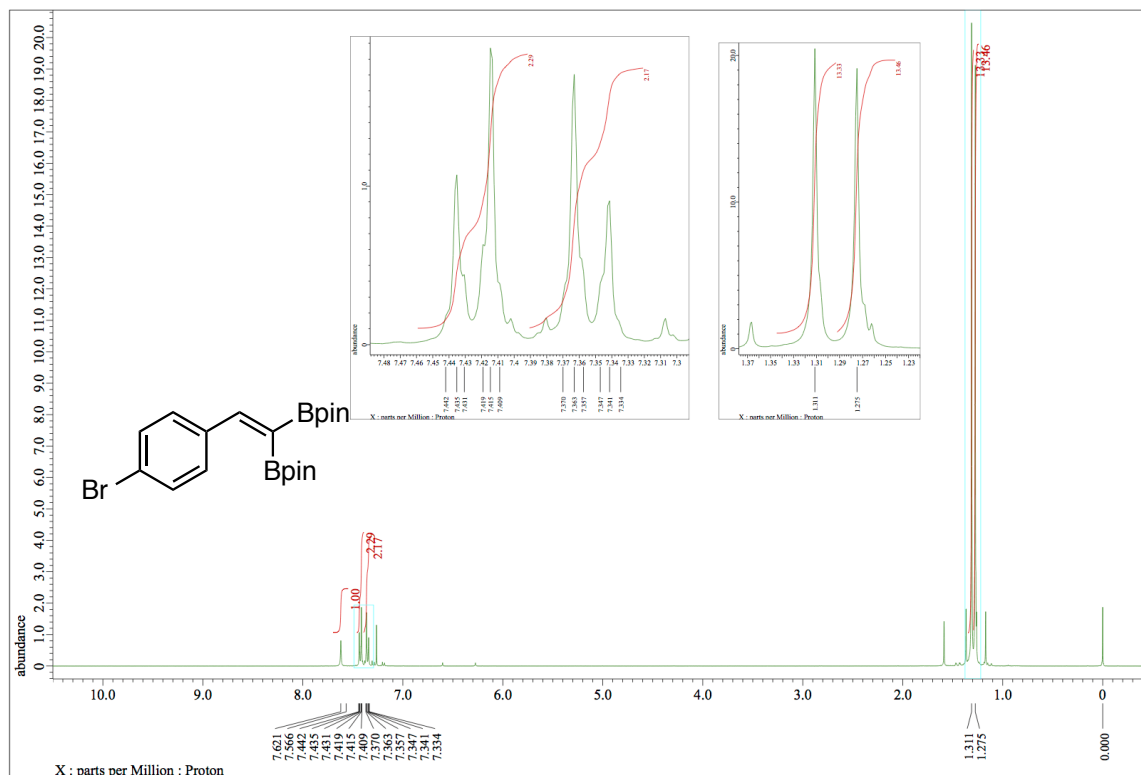
<sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra of **3d** (CDCl<sub>3</sub>)



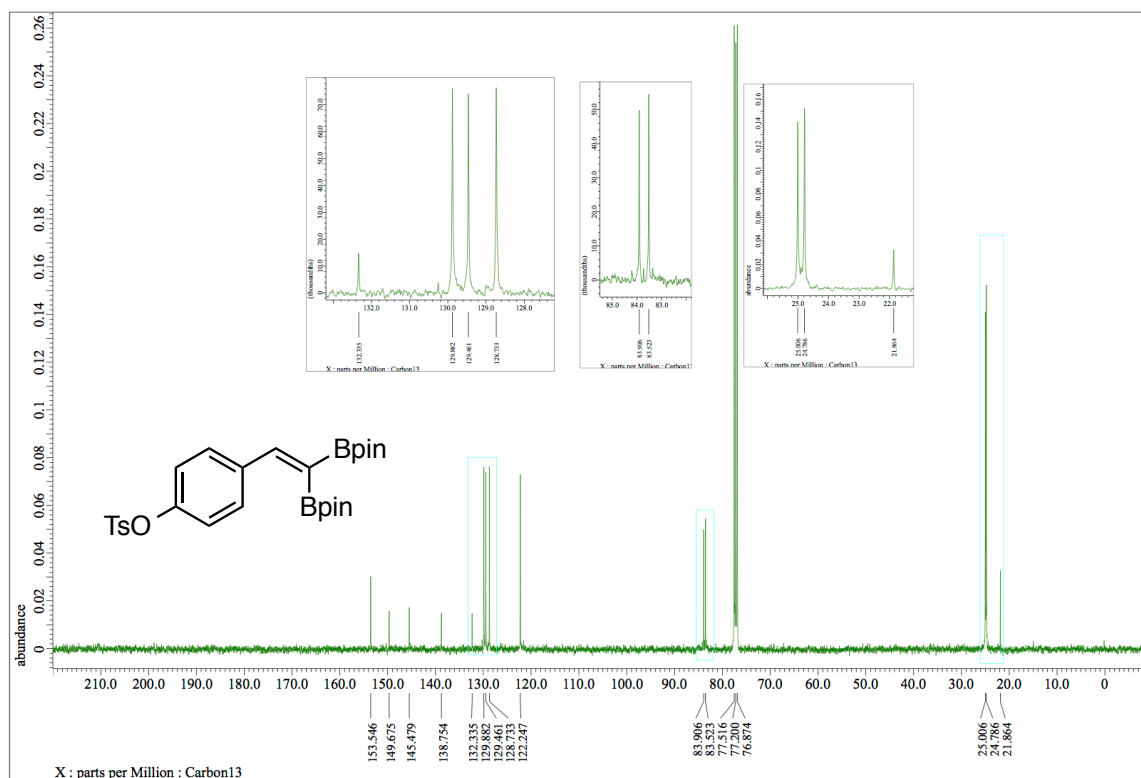
$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra of **3e** ( $\text{CDCl}_3$ )



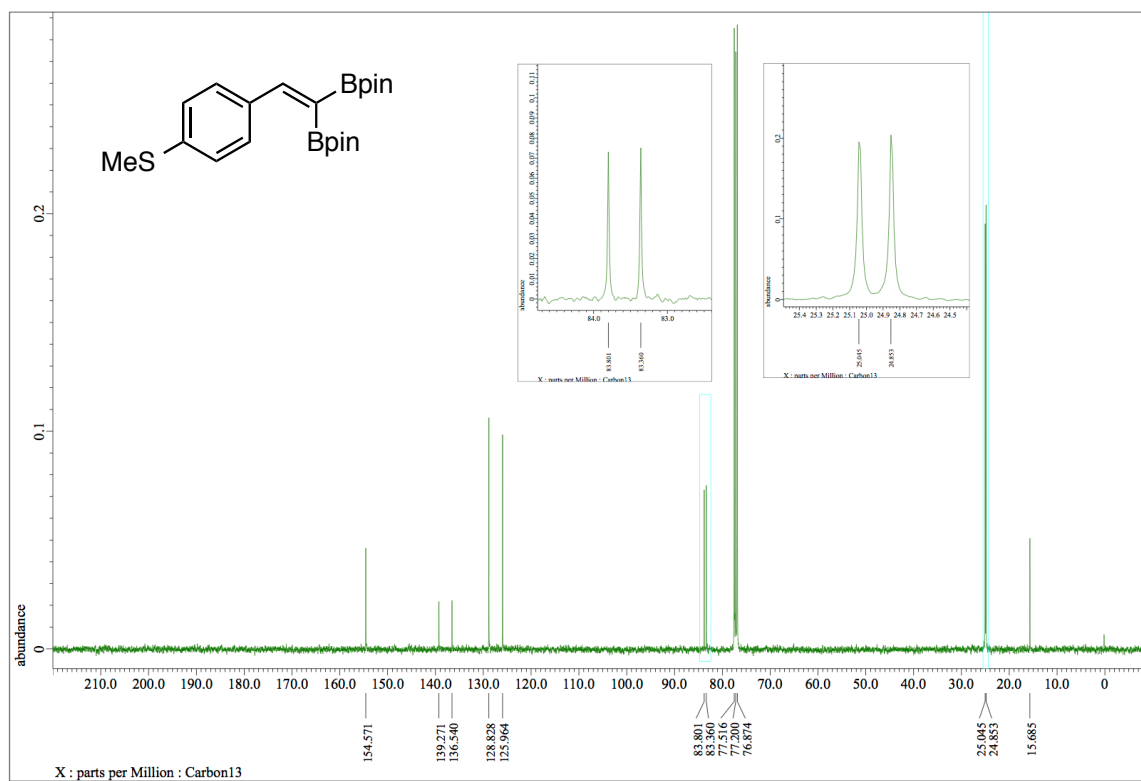
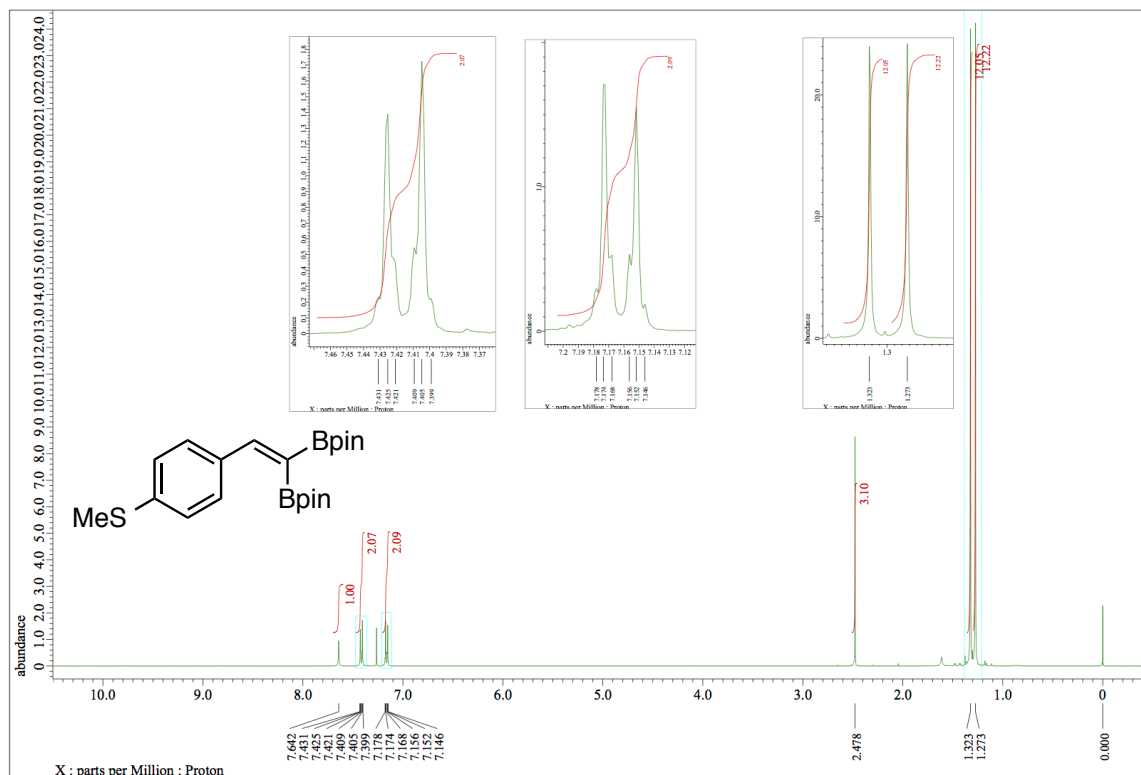
$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra of **3f** ( $\text{CDCl}_3$ )



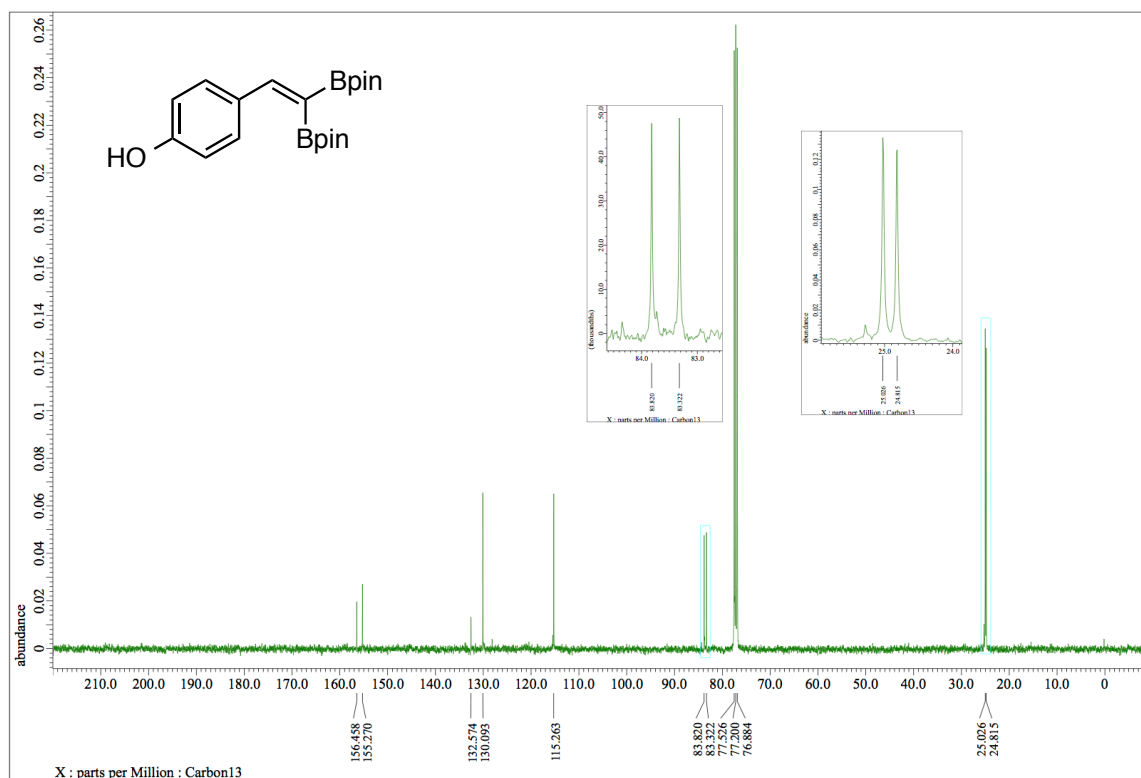
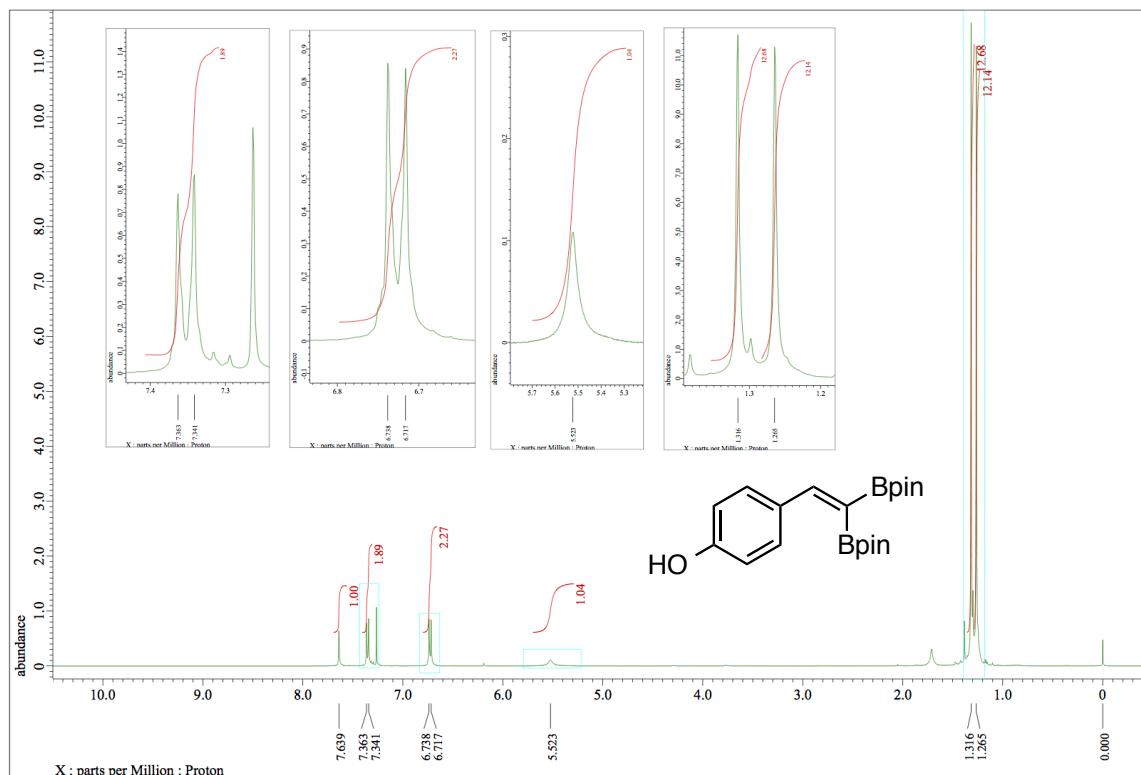


[illegible]

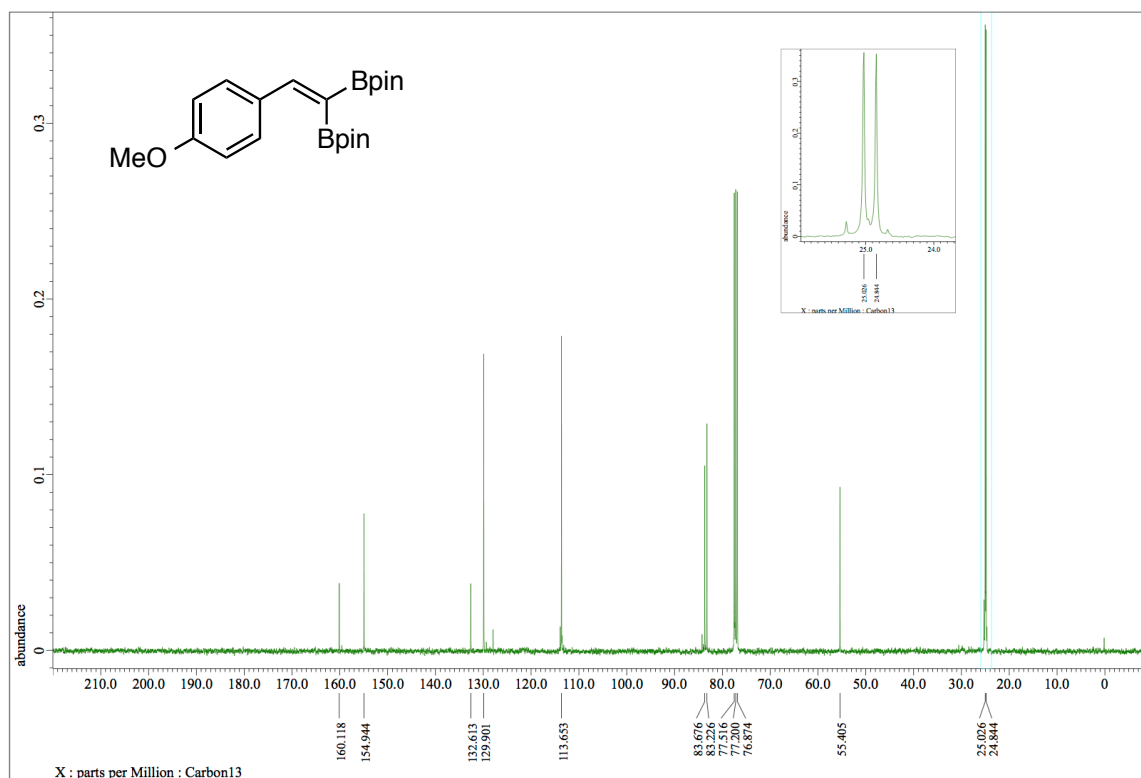
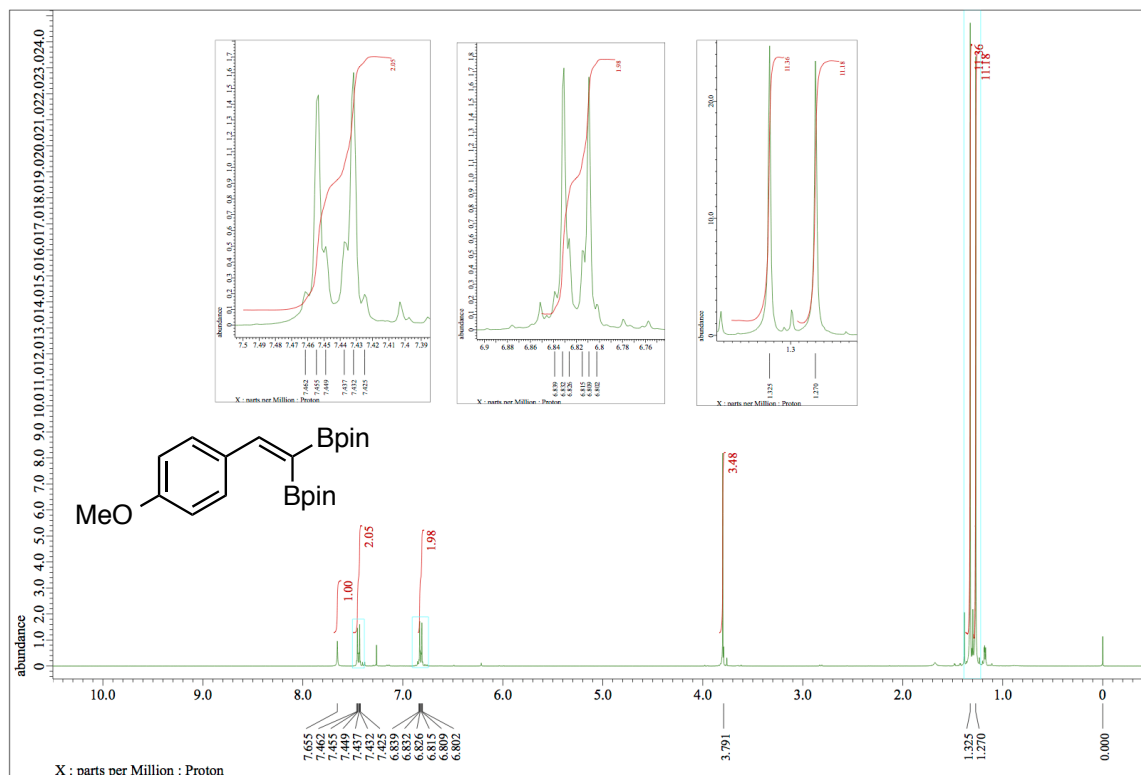
$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra of **3h** ( $\text{CDCl}_3$ )



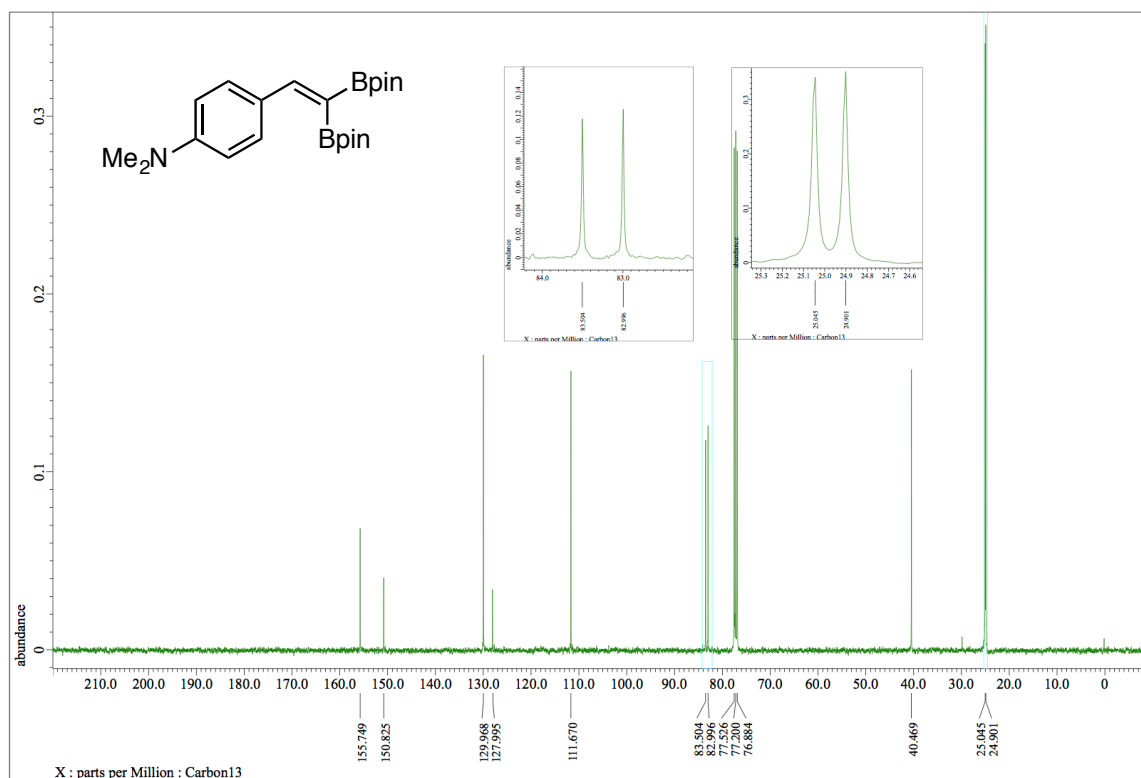
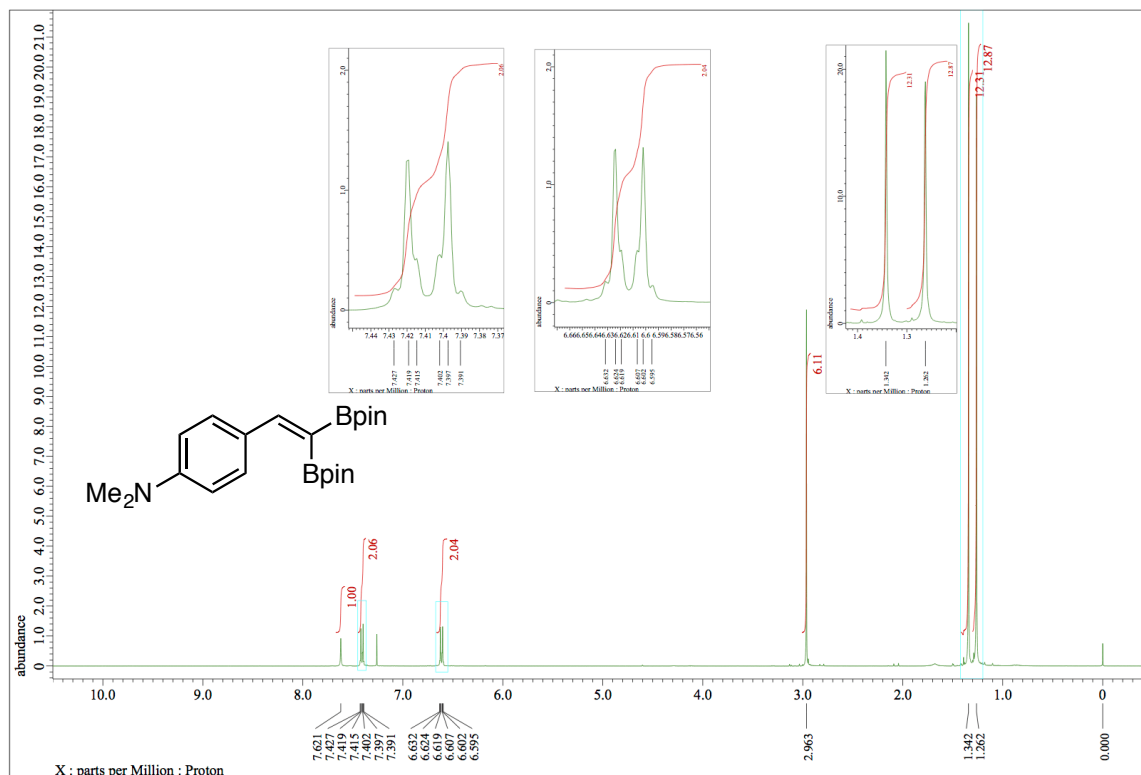
$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra of **3i** ( $\text{CDCl}_3$ )



<sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra of **3j** (CDCl<sub>3</sub>)



<sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra of **3k** (CDCl<sub>3</sub>)



**<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of (E)-N-(4-(benzyloxycarbonylmethyl)phenyl)acetamide.**

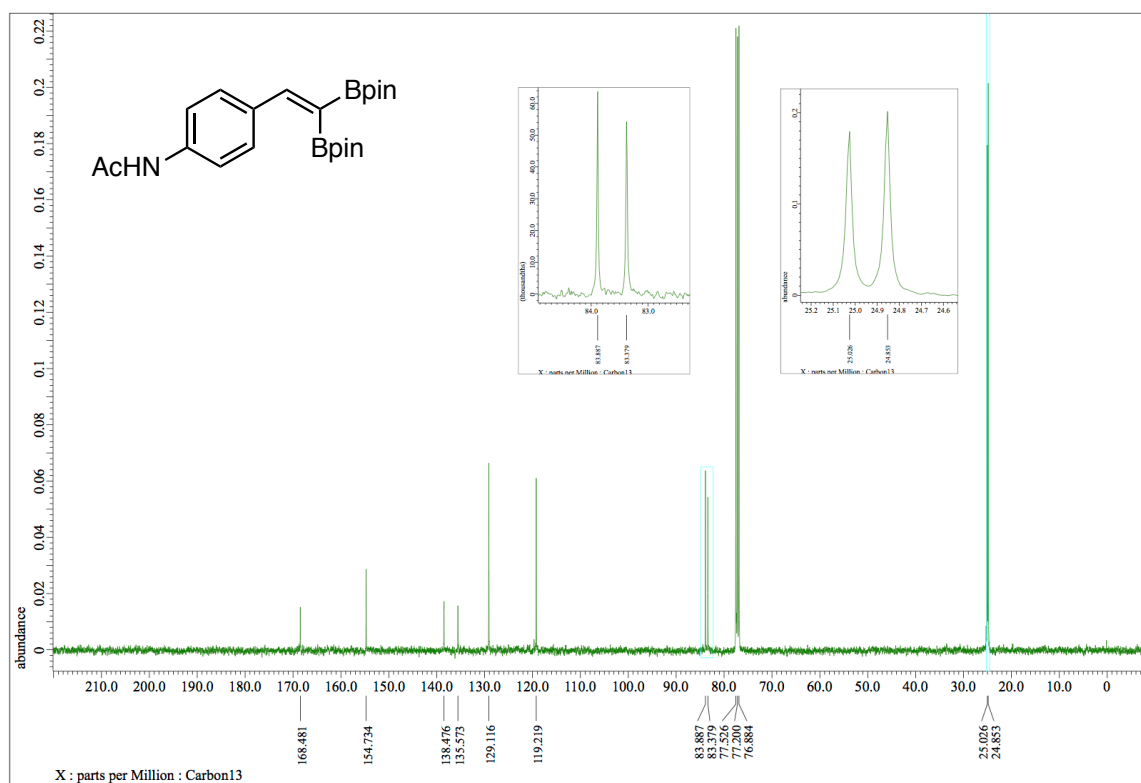
**Chemical structure:** CC(=O)Nc1ccc(cc1)/C=C/c2ccc(cc2)COC(=O)c3ccccc3

**Peak list (ppm):** 7.640, 7.475, 7.411, 3.95, 2.139, 1.354, 1.269, 0.000.

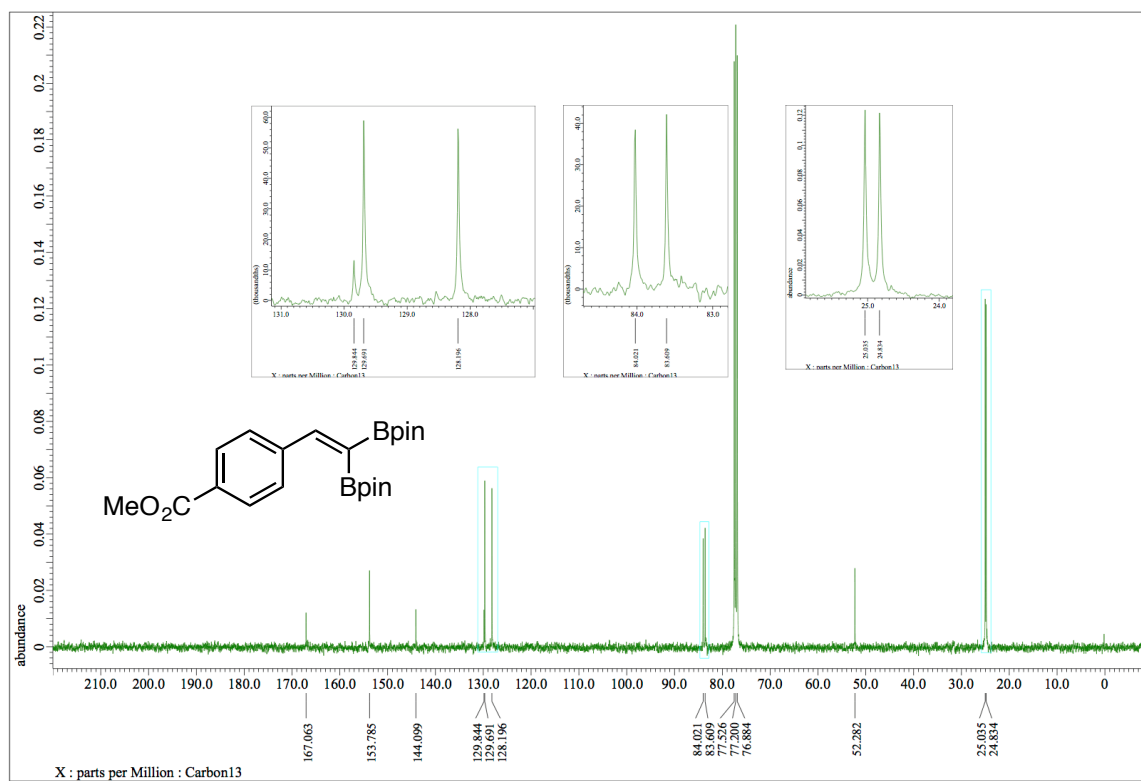
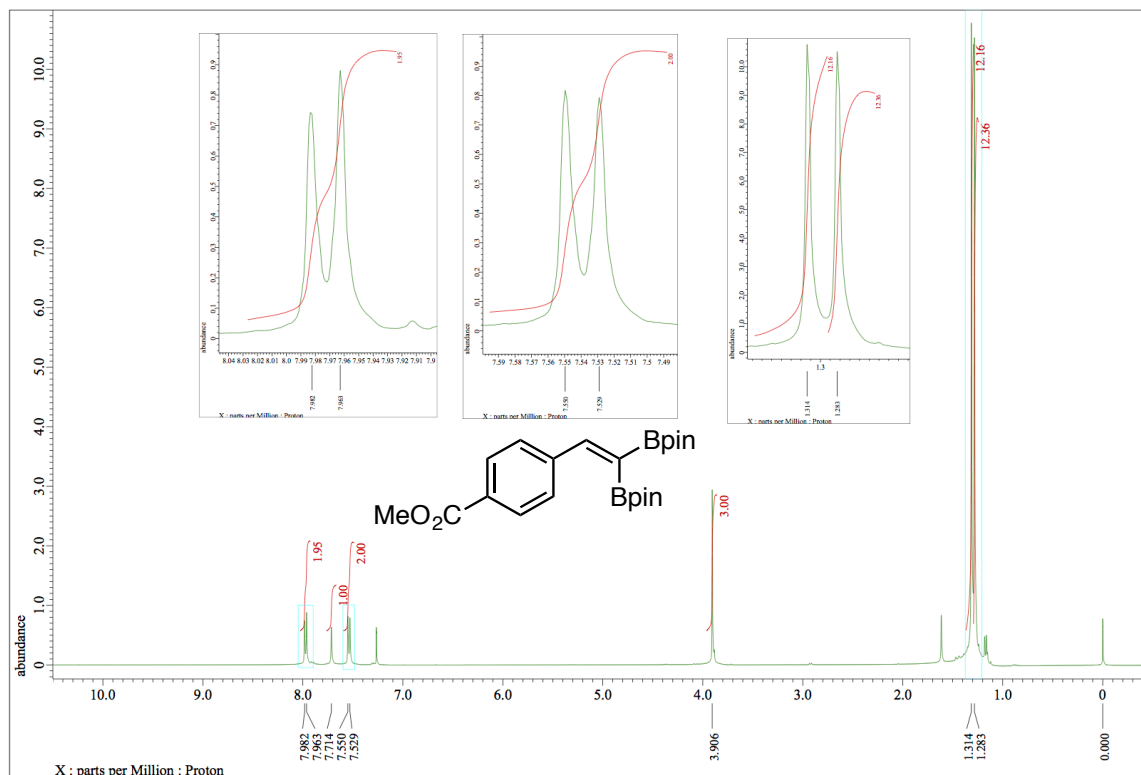
**Integration values:** 1.00, 1.02, 3.95, 1.34, 1.28, 11.99, 11.92.

**Inset 1 (Aromatic region):** Peaks at 7.640 (1.00), 7.475 (1.02), and 7.411 (3.95) ppm.

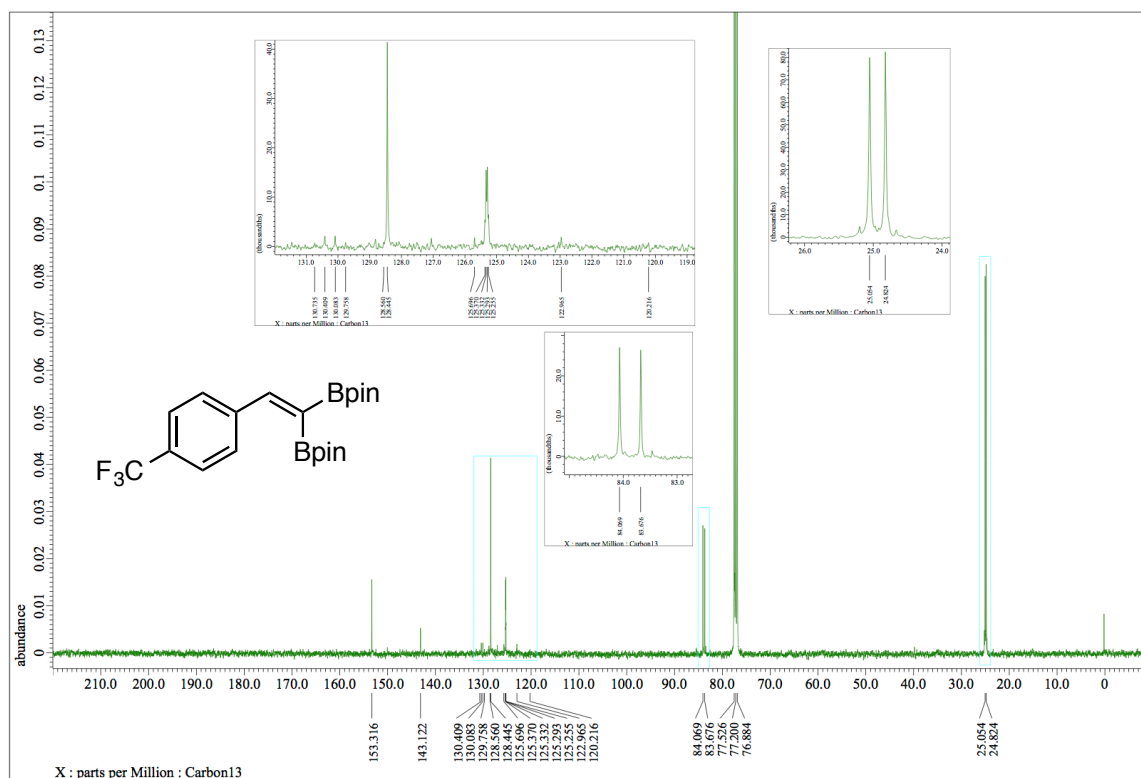
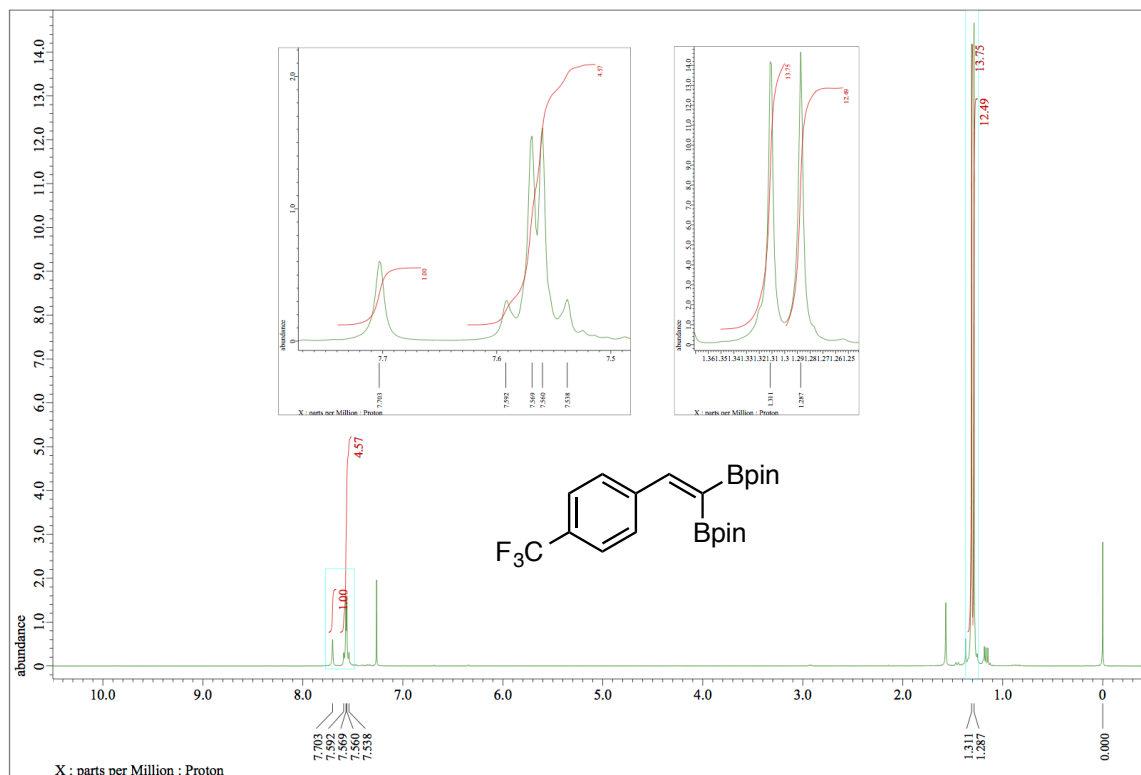
**Inset 2 (Aliphatic region):** Peaks at 1.354 (1.34) and 1.269 (1.28) ppm.



$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra of **3m** ( $\text{CDCl}_3$ )

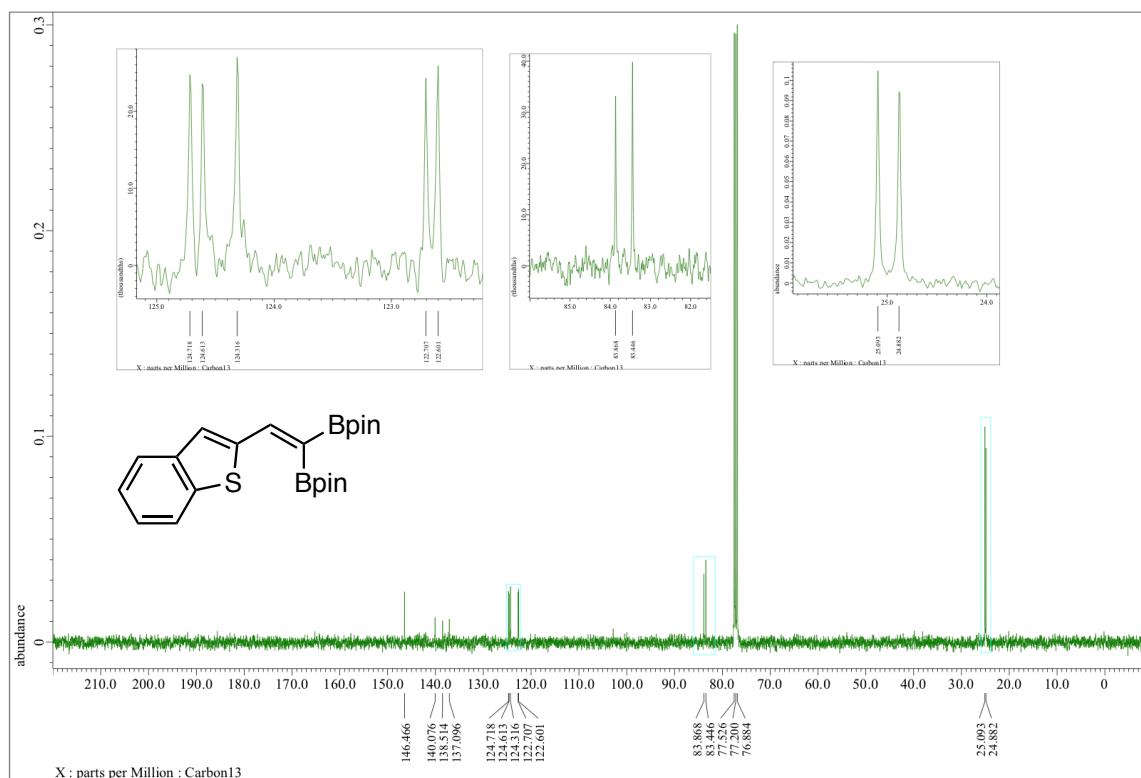
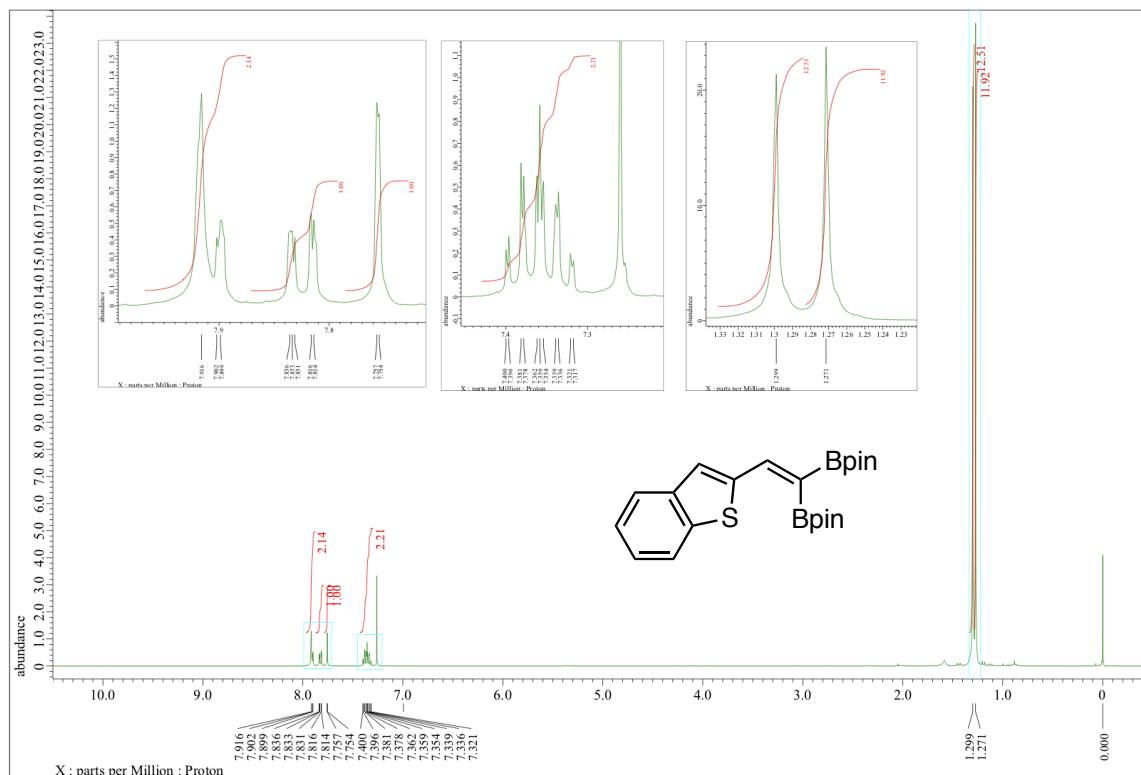


$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra of **3n** ( $\text{CDCl}_3$ )

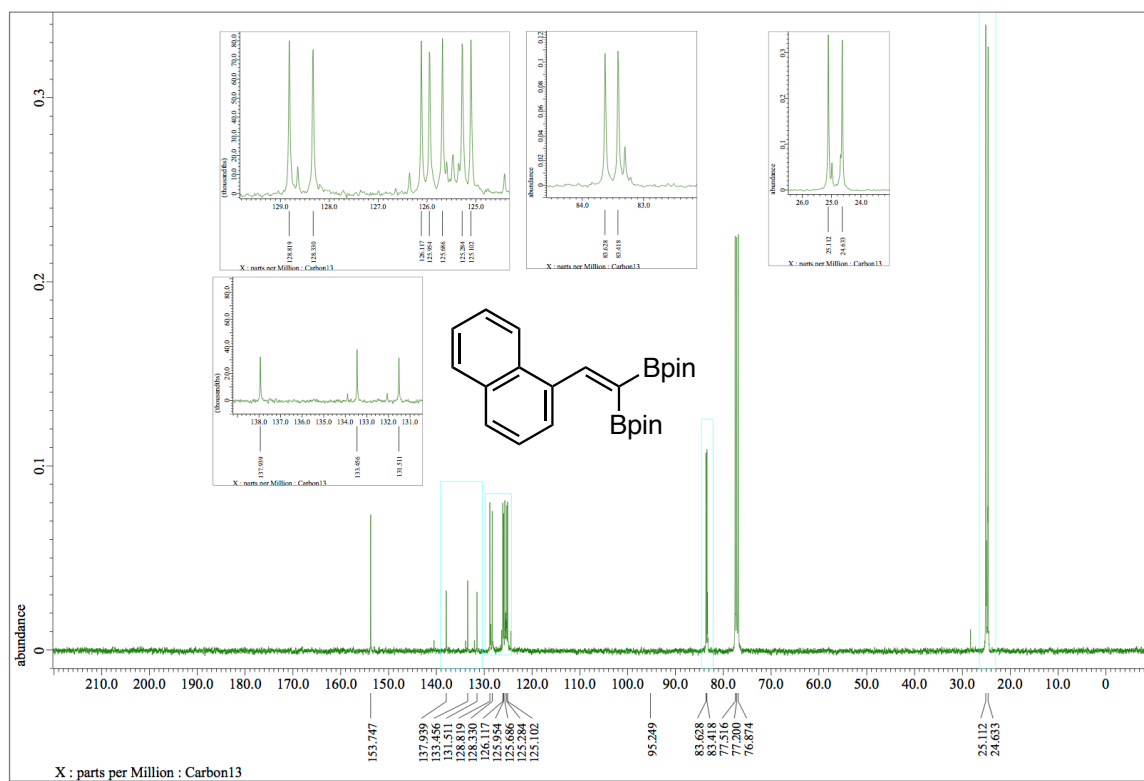
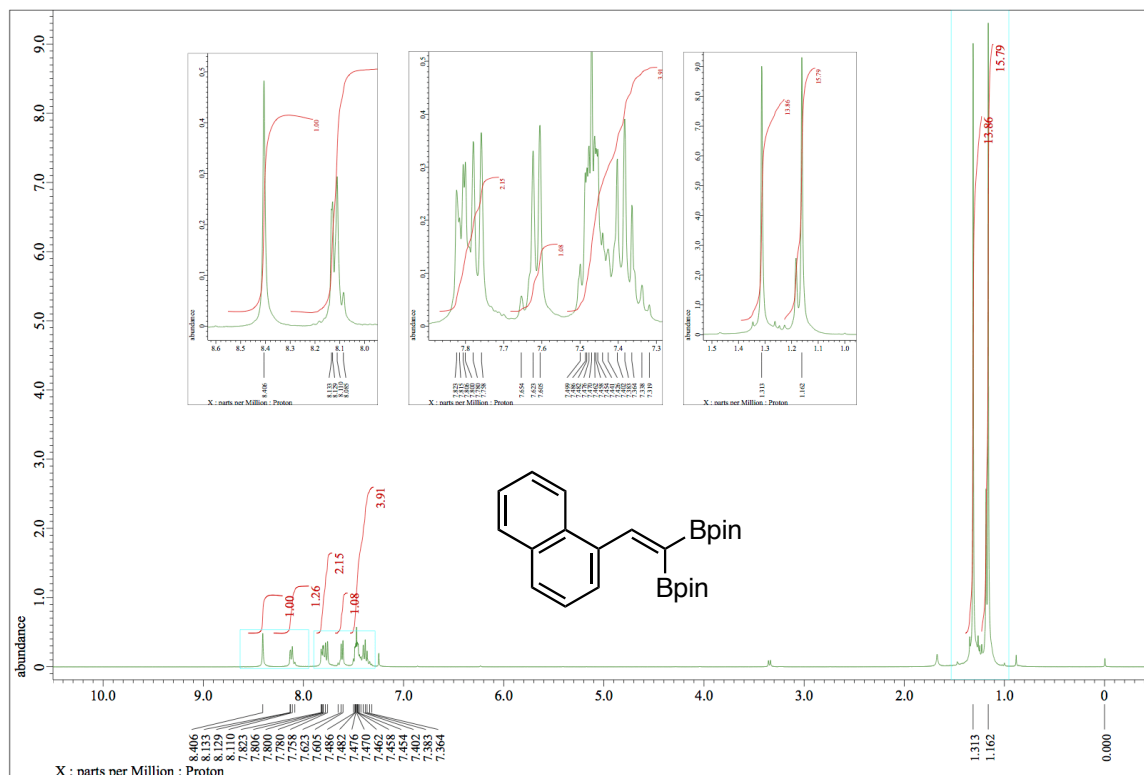




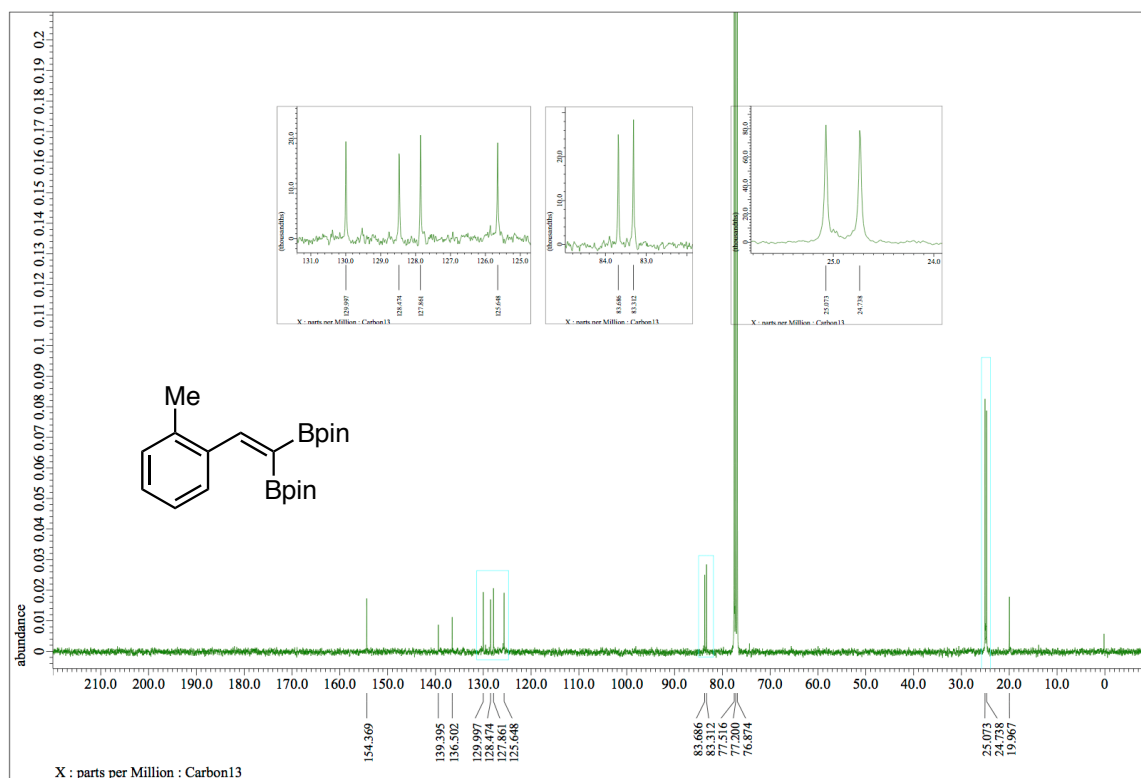
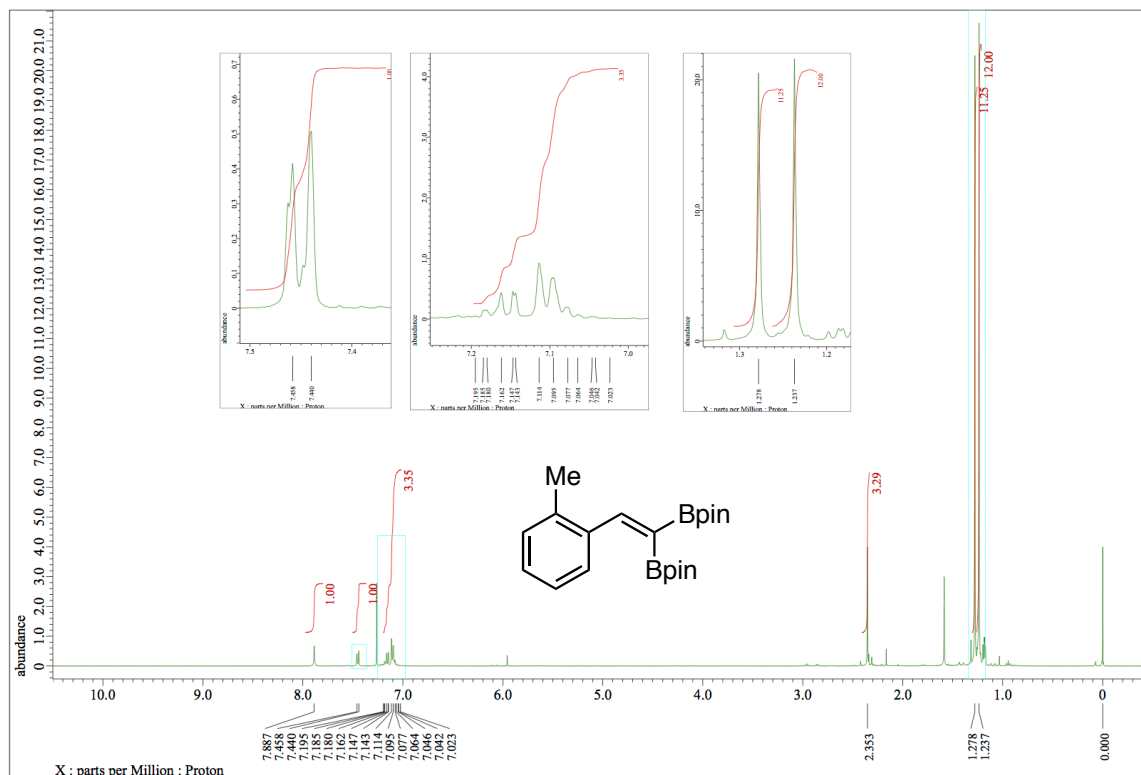
$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra of **3o** ( $\text{CDCl}_3$ )



$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra of **3p** ( $\text{CDCl}_3$ )



$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra of **3q** ( $\text{CDCl}_3$ )



<sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra of **3r** (CDCl<sub>3</sub>)

