Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for "Conjunctive Functionalization of Vinyl Boronate Complexes with Electrophiles: A Diastereoselective Three-Component Coupling"

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Contents

1. General Information

Reactions were carried out in flame-dried glassware under an atmosphere of nitrogen unless stated otherwise. Room temperature refers to 20-25 °C. Temperatures of 0 °C were obtained using an ice/water bath. Temperatures of –78 °C were obtained using a dry ice/acetone bath. Temperatures of –45 °C were obtained using a dry ice/acetonitrile bath. Reflux conditions were obtained using an oil bath equipped with a contact thermometer.

Dichloromethane, diethyl ether and tetrahydrofuran were purified by filtration through activated alumina columns employing the method of Grubbs *et al*.[1] All other solvents were used as supplied without prior purification. *n*-Butyllithium was purchased from Acros Organics as a 1.6 M solution in hexane and the molarity was established by titration against *N*-benzylbenzamide.[2] *tert*-Butyllithium was purchased from Sigma Aldrich as a 1.7 M solution in pentane and the molarity was established by titration against *N*-benzylbenzamide.[1] Isopropyl lithium was purchased from Sigma Aldrich as a 0.7 M solution in pentane and the molarity was established by titration against *N*-benzylbenzamide.[2] Methyl lithium was purchased from Sigma Aldrich as a 1.6 M solution in diethyl ether and the molarity was established by titration against *N*-benzylbenzamide.[2] Phenyl lithium was purchased as a 1.9 M solution in dibutyl ether and the molarity was established by titration against *N*-benzylbenzamide.[2] All other reagents were used directly as supplied by major chemical suppliers, or following purification procedures described by Perrin and Armarego.[3]

Thin layer chromatography was performed on Merck Kieselgel 60 F_{254} 0.25 mm precoated aluminium plates. Product spots were visualized under UV light (λ = 254 nm) and/or by staining with potassium permanganate solution. Flash chromatography was performed using VWR silica gel 60 (40-63 μm particle size) using head pressure by means of a nitrogen line.

NMR spectroscopy was carried out using Joel Lambda 300, Joel ECP 400, Varian 400-MR, VNMRS500a or Bruker Cryo 500 MHz spectrometers in the deuterated solvent stated, using the residual non-deuterated solvent signal as an internal reference. Chemical shifts are quoted in ppm with signal splittings recorded as singlet (s), doublet (d), triplet (t), quartet (q), quintet (qn), sextet (sex), septet (sept), octet (oct), nonet (non) and multiplet (m). The abbreviation br. denotes broad. Coupling constants, *J*, are measured to the nearest 0.1 Hz and are presented as observed.

Infrared spectra were recorded neat on a PerkinElmer Spectrum One FT-IR spectrometer equipped with an attenuated total reflectance attachment with internal calibration. Absorption maxima (λ_{max}) are quoted in wavenumbers (cm^{-1}).

Mass spectra were recorded by the University of Bristol, School of Chemistry departmental mass spectrometry service using electron impact ionisation (EI), chemical ionisation (CI) or electrospray ionisation (ESI) techniques for low- and high-resolution mass spectra. HRMS EI and CI were performed on a VG Analytical Autospec mass spectrometer at 70 eV. HRMS ESI was performed on either a Bruker Daltonics Apex IV, 7-Tesla FT-ICR or microTOF II. Nanospray was performed on a Synapt G2S mass spectrometer. Samples were submitted in CH_2Cl_2.

GC-MS was performed on an Agilent 7820A using a HP-5MS UI column (30 m x 0.25 mm x 0.25 µm).

2. Optimization

2.1 Solvent Screen for Synthesis of 25

A stirred solution of **24** (39 mg, 0.20 mmol) in *the appropriate solvent* (2.0 mL) was cooled to –78 °C and a solution of phenyl lithium (1.8 M in dibutyl ether, 0.12 mL, 0.22 mmol) was added dropwise.* The resulting solution was stirred at –78 °C for 1 hour. Phenylselenyl chloride (46 mg, 0.24 mmol) was added (either as a solid or dissolved in 0.3 mL of *the appropriate solvent*). The resulting solution was stirred at –78 °C for 1 hour and then warmed to room temperature and stirred for 15 minutes and then filtered through a short plug of silica gel washing with diethyl ether. The filtrate was concentrated under reduced pressure. The residue was dissolved in $CDCl_3$ and 1,4-dimethoxybenzene (0.1 mmol) was added as an internal standard. This solution was analysed by ^1H NMR to determine the ratio of **25**:**26** and an NMR yield of **25**. For characterization of **25** and **26** see experimental procedures section.

Solvent	Temp.	Ratio **25**:**26** (NMR)	Yield **25**
THF	–78 °C	43:57	34 % (NMR)
TBME	–78 °C	29:71	23 % (NMR)
Et_2O	–78 °C	24:76	18 % (NMR)
PhMe	–78 °C	10:90	7 % (NMR)
1 : 1 THF/CF_3CH_2OH	–78 °C	21:79	15 % (NMR)
1 : 1 THF/CH_2Cl_2	–78 °C	32:68	18 % (NMR)
1 : 1 THF/MeCN	–78 °C	42:58	31 % (NMR)
1 : 1 THF/DME	–78 °C	48:52	44 % (NMR)
DMF	–60 °C	42:58	33 % (NMR)
1:1 THF/DMF	–78 °C	71 : 29	58 % (NMR)
1 : 9 THF/DMF	–78 °C	42 : 58	34 % (NMR)
3:1 THF/DMF	–78 °C	85 : 15	61 % (isolated)

* For solvents that are compatible with PhLi (e.g. THF, TBME, Et_2O, PhMe, 1:1 THF/DME), boronate complex formation was carried out directly in the required solvent. When a mixture of THF with a solvent that could react with PhLi was required (e.g. 1:1 THF/CF_3CH_2OH, 1:1 THF/CH_2Cl_2, 1:1 THF:MeCN, 1:1 THF:DMF or 3:1 THF/DMF), boronate complex formation was carried out in THF and after one hour the other solvent was added to achieve the desired solvent ratio. For reactions carried out in a single solvent that would be incompatible with PhLi (e.g. DMF or 1:9 THF:DMF), boronate complex formation was carried out in THF and after 1 hour the reaction mixture was warmed to room temperature and concentrated to dryness. The residue was then redissolved in the desired solvent and cooled to the appropriate temperature.

2.2 Solvent Screen for Synthesis of 29

A stirred solution of **10** (36 mg, 0.20 mmol) in *the appropriate solvent* (2.0 mL) was cooled to –78 °C and a solution of isopropyl lithium (0.58 M in pentane, 0.36 mL, 0.21 mmol) was added dropwise.[*] The resulting solution was stirred at –78 °C for 1 hour. Phenylselenyl chloride (46 mg, 0.24 mmol) was added (either as a solid or dissolved in 0.3 mL of *the appropriate solvent*). The resulting solution was stirred at –78 °C for 1 hour and then warmed to room temperature and stirred for 15 minutes and then filtered through a short plug of silica gel washing with diethyl ether. The filtrate was concentrated under reduced pressure. The residue was analysed by GCMS to determine the d.r. of the product **29**. For characterization of **29** (and the minor diastereoisomer **30**) see experimental procedures section.

Solvent	d.r. (GCMS)	Yield	d.r. (NMR)
THF	88:12	88 % (isolated)	88:12
3:1 THF:DMF	68:32	-	-
Et_2O	97:3	-	-
PhMe	91:9	-	-
CH_2Cl_2	91:9	-	-
MeOH	97:3	-	-
1:1 THF/CF_3CH_2OH	98:2	85 % (isolated)	>95:5

[*] For solvents that are compatible with ^{i}PrLi (e.g. THF, Et_2O or PhMe), boronate complex formation was carried out directly in the required solvent. When a mixture of THF with a solvent that could react with ^{i}PrLi was required (e.g. 3:1 THF:DMF or 1:1 THF/CF_3CH_2OH), boronate complex formation was carried out in THF and after one hour the other solvent was added to achieve the desired solvent ratio. For reactions carried out in a single solvent that would be incompatible with ^{i}PrLi (e.g. CH_2Cl_2 or MeOH), boronate complex formation was carried out in THF and after 1 hour the reaction mixture was warmed to room temperature and concentrated to dryness. The residue was then redissolved in the desired solvent and cooled to the appropriate temperature.

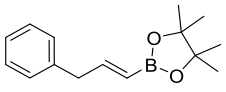
3. General Procedure for Conjunctive Three-Component Coupling

A stirred solution of vinyl boronic ester (1 eq.) in THF (10 mL/mmol vinyl boronic ester) was cooled to –78 ^{o}C and a solution of commercially available organolithium reagent (1.05 eq.) was added dropwise. The resulting solution was stirred at –78 ^{o}C for 1 hour. After this time a solution of electrophile (1 M in THF, 1.2 eq.) was added dropwise and the resulting solution was stirred at –78 ^{o}C for 1 hour and then warmed to room temperature and stirred for 15 minutes. The mixture was filtered through a short plug of silica gel washing with diethyl ether and the filtrate was concentrated under reduced pressure. Purification of the residue *via* column chromatography (see experimental methods section for specific details) afforded the corresponding product.

4. Experimental Procedures

4.1. Starting Material Synthesis

(*E*)-4,4,5,5-Tetramethyl-2-(3-phenylprop-1-en-1-yl)-1,3,2-dioxaborolane, 1



1

3-Phenyl-1-propyne (2.84 g, 24.4 mmol) was stirred neat in a room temperature water bath and freshly distilled catecholborane (2.80 mL, 26.3 mmol) was added dropwise. The resulting solution was heated to 70 ^{o}C for 2 hours and then cooled to room temperature and diluted with THF (60 mL). Pinacol (3.40 g, 28.8 mmol) was added and the resulting solution was stirred at room temperature for 16 hours. After this time, the reaction mixture was diluted with ethyl acetate and water. The organic layer was separated and the aqueous layer was extracted twice with ethyl acetate. The combined organic extracts were washed with brine and then dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure. Purification of the residue *via* column chromatography eluting with 98:2 petrol 40-60/ethyl acetate afforded the title compound **1** as a colourless oil (2.72 g, 46 %, >95:5 *E*/*Z*). The spectral data matched that previously reported in the literature.[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.31 – 7.24 (m, 2H), 7.21 – 7.13 (m, 3H), 6.76 (dt, J = 17.9, 6.3 Hz, 1H), 5.45 (dt, J = 17.9, 1.7 Hz, 1H), 3.47 (dd, J = 6.4, 1.6 Hz, 2H), 1.25 (s, 12H);

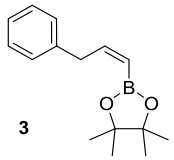
^{13}C NMR (101 MHz, $CDCl_3$) δ_C = 152.5, 139.2, 129.0, 128.5, 126.2, 83.2, 42.4, 24.9. [*N.B. The carbon attached to boron was not observed due to quadrupolar relaxation*];

^{11}B NMR (96 MHz, $CDCl_3$) δ_B = 28.6;

FTIR (neat) ν/cm^{-1} = 2978, 1636, 1359, 1320, 1143, 997, 971, 851;

LRMS (EI^+): calculated for $C_{15}H_{21}BO_2$ = 244, mass found = 244.

(*Z*)-4,4,5,5-Tetramethyl-2-(3-phenylprop-1-en-1-yl)-1,3,2-dioxaborolane, 3



3

According to a modified literature procedure,[5] a flame dried Schlenk tube was charged with chloro(1,5-cyclooctadiene)rhodium(I) dimer (18 mg, 0.037 mmol) and the atmosphere was evacuated and backfilled with nitrogen three times. Anhydrous cyclohexane (7.5 mL), triisopropylphosphine (28 μL, 0.015 mmol), trimethylamine (340 μL, 2.4 mmol) and freshly distilled catechol borane (260 μL, 2.43 mmol) were added sequentially. The resulting mixture was stirred for 30 minutes at room temperature and then 3-phenyl-1-propyne (360 mL, 2.92 mmol) was added in a single portion. The resulting mixture was stirred at room temperature for 2 hours and then diluted with anhydrous cyclohexane (2.5 mL). Pinacol (431 mg, 3.65 mmol) was added in a single portion and the resulting mixture was stirred at room temperature for 16 hours and then concentrated under reduced pressure. Purification of the residue *via* column chromatography eluting with 98:2 pentane/diethyl ether afforded the title compound **3** as a colourless oil (376 mg, 63 %, >95:5 *Z*/*E*). The spectral data matched that previously reported in the literature.[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.31 – 7.16 (m, 5H), 6.55 (dt, J = 13.2, 7.6 Hz, 1H), 5.43 (dt, J = 13.3, 1.4 Hz, 1H), 3.76 (dd, J = 7.6, 1.2 Hz, 2H), 1.30 (s, 12H);

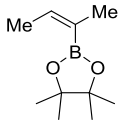
^{13}C NMR (101 MHz, $CDCl_3$) δ_C = 152.8, 140.7, 128.7, 128.5, 126.0, 83.1, 38.8, 25.0. [*N.B. The carbon attached to boron was not observed due to quadrupolar relaxation*];

^{11}B NMR (128 MHz, $CDCl_3$) δ_B = 29.1;

FTIR (neat) ν/cm^{-1} = 2978, 1626, 1419, 1323, 1259, 1142, 967, 746, 699;

LRMS (EI$^+$): calculated for $C_{15}H_{21}BO_2$ = 244, mass found = 244.

(*E*)-2-(But-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 10



10

A stirred solution of (*Z*)-2-Bromo-2-butene (1.00 mL, 9.86 mmol) in THF (20 mL) was cooled to –78 °C and *tert*-butyl lithium (1.7 M in pentane, 10.4 mL, 17.8 mmol) was added dropwise. The resulting mixture was stirred at –78 °C for 30 minutes and then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.41 mL, 11.8 mmol) was added dropwise. The resulting mixture was stirred at –78 °C for 15 minutes and then warmed to room temperature and stirred for 30 minutes. After this time, the reaction mixture was diluted with diethyl ether and water. The organic layer was separated and the aqueous layer was extracted twice with diethyl ether. The combined organic extracts were washed with brine and then dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure. Purification of the residue *via* column chromatography eluting with a gradient from pentane to 99:1 pentane/diethyl ether afforded the title compound **10** as a colourless oil (1.06 g, 59 %, >95:5 *E*/*Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 6.13 (q, J = 7.3 Hz, 1H), 1.89 – 1.84 (m, 3H), 1.75 – 1.71 (m, 3H), 1.26 (s, 12H);

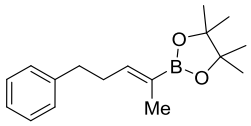
^{13}C NMR (101 MHz, $CDCl_3$) δ_C = 141.7, 82.9, 24.9, 22.4, 17.3. [*N.B. The carbon attached to boron was not observed due to quadrupolar relaxation*];

^{11}B NMR (128 MHz, $CDCl_3$) δ_B = 29.5;

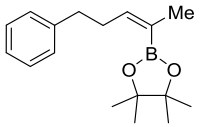
FTIR (neat) ν/cm^{-1} = 2979, 1638, 1457, 1400, 1299, 1265, 1140, 1037, 967, 859, 839;

HRMS (EI$^+$): calculated for $C_9H_{16}BO_2$ = 167.1238, mass found = 167.1237 [M^+-CH_3].

(*Z*)- and (*E*)- 4,4,5,5-Tetramethyl-2-(5-phenylpent-2-en-2-yl)-1,3,2-dioxaborolane, 14 and 16



14



16

A stirred solution of 4-phenyl-1-butene (200 mg, 0.23 mL, 1.5 mmol) and isopropenyl boronic acid pinacol ester (1.4 mL, 7.6 mmol) in degassed dichloromethane (0.6 mL) was stirred at room temperature. A solution of 2,6-dichlorobenzoquinone (27 mg, 0.15 mmol) in degassed dichloromethane (0.8 mL) was then added. A solution of Hoveyda-Grubbs 2nd generation catalyst (0.2 M in degassed dichloromethane, 0.27 mL, 0.050 mmol) was added. The resulting solution was heated to 40 °C under nitrogen for 1 hour and then the solution was freeze-pump-thawed (liquid nitrogen) to remove solvated ethylene. A further portion of HG-II catalyst solution (0.2 M in degassed dichloromethane, 0.27 mL, 0.050 mmol) was added and the reaction mixture was heated to 40 °C for 1 hour. The mixture was freeze-pump-thawed (liquid nitrogen) and then a final portion of HG-II catalyst solution (0.2 M in degassed dichloromethane, 0.27 mL, 0.050 mmol) was added. The reaction mixture was then heated to 40 °C for 2 hours and was then diluted with a mixture of hexanes:Et_2O (10:1) and then passed through a short plug of silica gel, washing with diethyl ether. The filtrate was concentrated under reduced pressure (c.a. 0.2 mmHg) to remove excess isopropenyl boronic acid pinacol ester. Purification of the residue *via* column chromatography eluting with 1:1 toluene/pentane afforded **14** as a colourless oil (280 mg, 68%) along with **16** as a colourless oil (40 mg, 10%).

Data for **14**:

The spectral data matched that previously reported in the literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ_H = δ 7.33 – 7.28 (m, 2H), 7.25 – 7.18 (m, 3H), 6.43 (tq, *J* = 6.9, 1.7 Hz, 1H), 2.77 – 2.68 (m, 2H), 2.52 – 2.41 (m, 2H), 1.69 (dt, *J* = 1.7, 0.8 Hz, 3H), 1.29 (s, 12H);

^{13}C NMR (101 MHz, $CDCl_3$) δ_C = 145.2, 142.2, 128.3, 128.3, 125.8, 83.1, 35.1, 30.8, 24.8, 24.8, 13.9. [*N.B. The carbon attached to boron was not observed due to quadrupolar relaxation*];

^{11}B NMR (128 MHz, $CDCl_3$) δ_B = 29.0;

FTIR (neat) ν/cm^{-1} = 2977, 2927, 2858, 1631, 1453, 1369, 1343, 1302, 1272, 1214, 1145, 1113, 1075, 859, 747;

LRMS (EI^+): calculated for $C_{17}H_{25}BO_2$ = 272, mass found = 272.

Data for **16**:

The spectral data matched that previously reported in the literature.[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.30 – 7.24 (m, 2H), 7.22 – 7.13 (m, 3H), 6.17 – 6.07 (m, 1H), 2.71 – 2.60 (m, 4H), 1.77 (s, 3H), 1.26 (s, 12H);

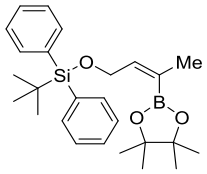
^{13}C NMR (101 MHz, $CDCl_3$) δ_C = 146.3, 142.5, 128.6, 128.3, 125.7, 82.9, 36.7, 33.1, 25.0, 22.4. [*N.B. The carbon attached to boron was not observed due to quadrupolar relaxation*];

^{11}B NMR (128 MHz, $CDCl_3$) δ_B = 29.3;

FTIR (neat) ν/cm^{-1} = 2981, 2933, 2850, 1633, 1492, 1452, 1399, 1373, 1312, 1287, 1241, 1143, 1120, 856, 757, 703;

HRMS (EI^+): calculated for $C_{17}H_{25}BO_2$ = 272, mass found = 272.

(*E*)-*tert*-Butyldiphenyl((3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)oxy)silane, 18



18

A stirred solution of (*Z*)-*tert*-butyl((3-iodobut-2-en-1-yl)oxy)diphenylsilane[8] (200 mg, 0.46 mmol) and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (94 μL, 0.46 mmol) in THF (4.6 mL) was cooled to –78 °C and *tert*-butyl lithium (1.7 M in pentane, 0.54 mL, 0.92 mmol) was added dropwise. The resulting mixture was stirred at –78 °C for 30 minutes and warmed to room temperature and stirred for 15 minutes. After this time, the reaction mixture was diluted with diethyl ether and water. The organic layer was separated and the aqueous layer was extracted twice with diethyl ether. The combined organic extracts were washed with brine and then dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure. Purification of the residue *via* column chromatography eluting with 98:2 pentane/diethyl ether afforded the title compound **18** as a colourless oil (137 mg, 69 %, >95:5 *E*/*Z*).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.71 – 7.66 (m, 4H), 7.42 – 7.33 (m, 6H), 6.25 (t, J = 5.8 Hz, 1H), 4.52 – 4.48 (m, 2H), 1.78 – 1.76 (m, 3H), 1.15 – 1.12 (m, 12H), 1.05 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$) δ_C = 146.2, 135.7, 134.3, 129.5, 127.6, 83.1, 63.6, 27.0, 24.8, 22.1, 19.3. [*N.B. The carbon attached to boron was not observed due to quadrupolar relaxation*];

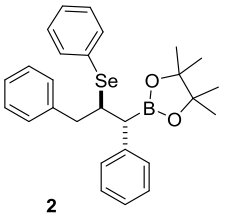
^{11}B NMR (128 MHz, $CDCl_3$) δ_B = 29.4;

FTIR (neat) ν/cm^{-1} = 2978, 2931, 2857, 1638, 1428, 1390, 1306, 1140, 1109, 1089, 823;

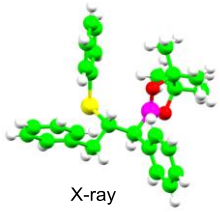
HRMS (ESI$^+$): calculated for $C_{26}H_{37}BNaO_3Si$ = 459.2502, mass found = 459.2498.

4.2 *Conjunctive Three Component Coupling*

(±)-2-((1*R*,2*R*)-1,3-Diphenyl-2-(phenylselanyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 2



2



According to the **General Procedure** with **1** (50 mg, 0.20 mmol), phenyl lithium (1.8 M in dibutyl ether, 0.12 mL, 0.22 mmol) and phenylselenyl chloride (1 M in THF, 0.25 mL, 0.25 mmol). Purification *via* column chromatography eluting with 97:3 pentane/diethyl ether afforded the title compound **2** as a white solid (80 mg, 82 %, >95:5 d.r.).

Melting point 92-93 °C (pentane/diethyl ether);

^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.49 – 7.44 (m, 2H), 7.37 – 7.09 (m, 11H), 7.04 (d, J = 7.0 Hz, 2H), 3.75 (ddd, J = 11.8, 10.3, 3.5 Hz, 1H), 2.95 (dd, J = 14.6, 3.5 Hz, 1H), 2.75 (d, J = 11.7 Hz, 1H), 2.50 (dd, J = 14.5, 10.3 Hz, 1H), 1.25 (s, 6H), 1.23 (s, 6H);

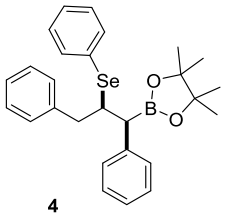
^{13}C NMR (101 MHz, $CDCl_3$) δ_C = 140.8, 140.1, 135.8, 129.3, 129.0, 128.8, 128.6, 128.5, 127.9, 127.4, 126.0, 125.9, 83.7, 49.8, 40.3, 24.9, 24.4. [*N.B. The carbon attached to boron was not observed due to quadrupolar relaxation*];

^{11}B NMR (128 MHz, $CDCl_3$) δ_B = 31.3;

FTIR (neat) ν/cm^{-1} = 2976, 1560, 1578, 1492, 1477, 1453, 1437, 1356, 1322, 1138, 967, 849, 740;

HRMS (ESI^+): calculated for $C_{27}H_{31}BNaO_2Se$ = 501.1481, mass found = 501.1478.

(±)-2-((1*S*,2*R*)-1,3-Diphenyl-2-(phenylselanyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 4



4

According to the **General Procedure** with **3** (50 mg, 0.20 mmol), phenyl lithium (1.8 M in dibutyl ether, 0.12 mL, 0.22 mmol) and phenylselenyl chloride (1 M in THF, 0.25 mL, 0.25 mmol). Purification *via* column chromatography eluting with 97:3 pentane/diethyl ether afforded the title compound **4** as a white solid (68 mg, 70 %, >95:5 d.r.).

Melting point 88-90 ^{o}C (pentane/diethyl ether);

^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.29 – 7.13 (m, 13H), 7.12 – 7.07 (m, 2H), 3.83 (td, J = 9.1, 4.5 Hz, 1H), 3.17 (dd, J = 14.3, 4.5 Hz, 1H), 2.94 (dd, J = 14.3, 9.0 Hz, 1H), 2.78 (d, J = 9.4 Hz, 1H), 1.23 (s, 6H), 1.21 (s, 6H);

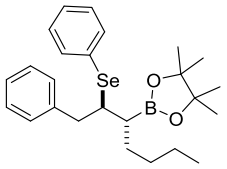
^{13}C NMR (101 MHz, $CDCl_3$) δ_C = 140.4, 140.2, 135.2, 130.3, 129.8, 129.7, 128.6, 128.2, 128.2, 127.2, 126.3, 126.1, 83.9, 52.2, 42.0, 24.8, 24.7. [*N.B. The carbon attached to boron was not observed due to quadrupolar relaxation*];

^{11}B NMR (128 MHz, $CDCl_3$) δ_B = 32.0;

FTIR (neat) ν/cm^{-1} = 2977, 1601, 1579, 1495, 1476, 1453, 1437, 1379, 1371, 1351, 1323, 1140, 967, 850, 741, 699;

HRMS (ESI^{+}): calculated for $C_{27}H_{31}BNaO_2Se$ = 501.1481, mass found = 501.1485.

(±)-4,4,5,5-tetramethyl-2-((2*R*,3*R*)-1-phenyl-2-(phenylselanyl)heptan-3-yl)-1,3,2-dioxaborolane, 5



5

According to the **General Procedure** with **1** (50 mg, 0.20 mmol), *n*-butyl lithium (1.6 M in hexanes, 0.14 mL, 0.22 mmol) and phenylselenyl chloride (1 M in THF, 0.25 mL, 0.25 mmol). Purification *via* column chromatography eluting with 97:3 pentane/diethyl ether afforded the title compound **5** as a colourless oil (85 mg, 91 %, >95:5 d.r.).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.46 – 7.40 (m, 2H), 7.27 – 7.13 (m, 8H), 3.47 (ddd, J = 8.0, 6.9, 5.6 Hz, 1H), 3.18 (dd, J = 14.0, 6.9 Hz, 1H), 2.95 (dd, J = 14.0, 8.0 Hz, 1H), 1.72 – 1.54 (m, 2H), 1.41 (dt, J = 9.2, 5.6 Hz, 1H), 1.31 (s, 12H), 1.29 – 1.13 (m, 4H), 0.85 (t, J = 6.8 Hz, 3H);

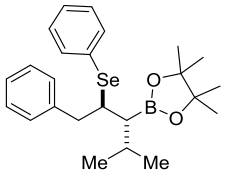
^{13}C NMR (101 MHz, $CDCl_3$) δ_C = 140.5, 134.6, 131.0, 129.3, 128.7, 128.1, 126.9, 126.0, 83.4, 51.6, 42.1, 31.3, 29.5, 25.1, 24.8, 22.8, 14.1. [*N.B. The carbon attached to boron was not observed due to quadrupolar relaxation*];

^{11}B NMR (128 MHz, $CDCl_3$) δ_B = 32.2;

FTIR (neat) ν/cm^{-1} = 2977, 2927, 1579, 1477, 1454, 1437, 1379, 1319, 1143, 739, 696;

HRMS (ESI$^+$): calculated for $C_{25}H_{35}BNaO_2Se$ = 481.1793, mass found = 481.1774.

(±)-4,4,5,5-Tetramethyl-2-((2*R*,3*R*)-4-methyl-1-phenyl-2-(phenylselanyl)pentan-3-yl)-1,3,2-dioxaborolane, 6



6

According to the **General Procedure** with **1** (50 mg, 0.20 mmol), isopropyl lithium (0.58 M in pentane, 0.37 mL, 0.22 mmol) and phenylselenyl chloride (1 M in THF, 0.25 mL, 0.25 mmol). Purification *via* column chromatography eluting with 97:3 pentane/diethyl ether afforded the title compound **6** as a colourless gum (76 mg, 84 %, >95:5 d.r.).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.48 – 7.42 (m, 2H), 7.23 – 7.09 (m, 8H), 3.49 (q, J = 7.2 Hz, 1H), 3.14 (dd, J = 13.9, 7.7 Hz, 1H), 2.91 (dd, J = 14.0, 7.1 Hz, 1H), 2.19 – 2.04 (d sept, J = 8.1, 6.6 Hz, 1H), 1.34 (s, 6H), 1.33 (s, 6H), 1.27 – 1.19 (m, 1H), 0.95 (d, J = 6.7 Hz, 3H), 0.89 (d, J = 6.6 Hz, 3H);

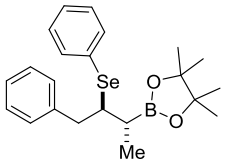
^{13}C NMR (101 MHz, $CDCl_3$) δ_C = 140.5, 134.7, 131.0, 129.4, 128.8, 128.1, 127.0, 126.1, 83.6, 49.4, 42.6, 27.9, 25.4, 25.1, 22.4, 21.5. [*N.B. The carbon attached to boron was not observed due to quadrupolar relaxation*];

^{11}B NMR (128 MHz, $CDCl_3$) δ_B = 31.6;

FTIR (neat) ν/cm^{-1} = 2976, 1258, 1602, 1579, 1477, 1372, 1141, 969, 848, 739;

HRMS (ESI$^+$): calculated for $C_{24}H_{33}BNaO_2Se$ = 467.1637, mass found = 467.1627.

(±)-4,4,5,5-Tetramethyl-2-((2*R*,3*R*)-4-phenyl-3-(phenylselanyl)butan-2-yl)-1,3,2-dioxaborolane, 7



7

According to the **General Procedure** with **1** (50 mg, 0.20 mmol), methyl lithium (1.6 M in diethyl ether, 0.14 mL, 0.22 mmol) and phenylselenyl chloride (1 M in THF, 0.25 mL, 0.25 mmol). Purification *via* column chromatography eluting with 97:3 pentane/diethyl ether afforded the title compound **7** as a colourless oil (67 mg, 79 %, >95:5 d.r.).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.43 – 7.37 (m, 2H), 7.27 – 7.13 (m, 8H), 3.51 (ddd, J = 8.6, 6.2, 4.9 Hz, 1H), 3.16 (dd, J = 14.1, 6.2 Hz, 1H), 2.93 (dd, J = 14.1, 8.6 Hz, 1H), 1.52 (qd, J = 7.3, 4.8 Hz, 1H), 1.27 (s, 12H), 1.14 (d, J = 7.4 Hz, 3H);

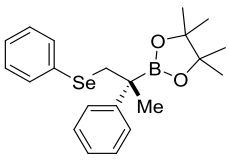
^{13}C NMR (101 MHz, $CDCl_3$) δ_C = 140.7, 134.6, 131.0, 129.4, 128.8, 128.2, 127.0, 126.2, 83.4, 53.1, 41.5, 25.1, 24.9, 13.9. [*N.B. The carbon attached to boron was not observed due to quadrupolar relaxation*];

^{11}B NMR (128 MHz, $CDCl_3$) δ_B = 32.7;

FTIR (neat) ν/cm^{-1} = 2976, 1597, 1456, 1379, 1371, 1319, 1142, 740;

HRMS (ESI$^+$): calculated for $C_{22}H_{29}BNaO_2Se$ = 439.1323, mass found = 439.1326.

(±)-4,4,5,5-tetramethyl-2-(2-phenyl-1-(phenylselanyl)propan-2-yl)-1,3,2-dioxaborolane, 9



9

According to the **General Procedure** with **8** (35 mg, 0.21 mmol), Phenyl lithium (1.8 M in dibutyl ether, 0.12 mL, 0.22 mmol) and phenylselenyl chloride (1 M in THF, 0.25 mL, 0.25 mmol). Purification *via*

column chromatography eluting with 97:3 pentane/diethyl ether afforded the title compound **9** as a colourless oil (65 mg, 78 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.53 – 7.45 (m, 2H), 7.40 – 7.33 (m, 2H), 7.33 – 7.26 (m, 2H), 7.24 – 7.14 (m, 4H), 3.49 (d, J = 11.3 Hz, 1H), 3.45 (d, J = 11.3 Hz, 1H), 1.51 (s, 3H), 1.24 (s, 6H), 1.22 (s, 6H);

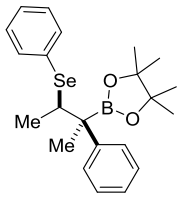
^{13}C NMR (101 MHz, $CDCl_3$) δ_C = 145.5, 132.9, 132.2, 128.8, 128.3, 126.8, 126.5, 125.8, 83.9, 40.8, 24.7, 24.6, 21.9. [*N.B. The carbon attached to boron was not observed due to quadrupolar relaxation*];

^{11}B NMR (128 MHz, $CDCl_3$) δ_B = 32.9;

FTIR (neat) ν/cm^{-1} = 2976, 1578, 1494, 1477, 1437, 1371, 1318, 1150, 851, 736, 698;

HRMS (ESI$^+$): calculated for $C_{21}H_{27}BNaO_2Se$ = 425.1166, mass found = 425.1164.

(±)-4,4,5,5-Tetramethyl-2-((2*R*,3*R*)-2-phenyl-3-(phenylselanyl)butan-2-yl)-1,3,2-dioxaborolane, 11



11

According to the **General Procedure** with **10** (46 mg, 0.25 mmol), phenyl lithium (1.9 M in dibutyl ether, 0.14 mL, 0.26 mmol) and phenylselenyl chloride (1 M in THF, 0.30 mL, 0.30 mmol). Purification *via* column chromatography eluting with 97:3 pentane/diethyl ether afforded the title compound **11** as a white solid (98 mg, 93 %, >95:5 d.r.).

Melting point 66-68 ^{o}C (pentane/diethyl ether);

^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.42 – 7.38 (m, 2H), 7.38 – 7.33 (m, 2H), 7.29 – 7.23 (m, 2H), 7.21 – 7.11 (m, 4H), 3.95 (q, J = 7.0 Hz, 1H), 1.57 (d, J = 7.0 Hz, 3H), 1.48 (s, 3H), 1.19 (s, 6H), 1.15 (s, 6H);

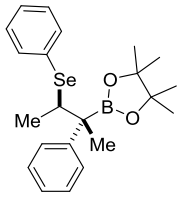
^{13}C NMR (101 MHz, $CDCl_3$) δ_C = 144.8, 135.2, 130.7, 128.6, 128.0, 127.3, 127.0, 125.9, 83.8, 52.2, 24.6, 24.6, 21.7, 16.6. [*N.B. The carbon attached to boron was not observed due to quadrupolar relaxation*];

^{11}B NMR (128 MHz, $CDCl_3$) δ_B = 32.9;

FTIR (neat) ν/cm^{-1} = 2976, 1578, 1475, 1379, 1371, 1357, 1313, 1143, 1084, 1071, 853, 740, 694;

HRMS (ESI$^+$): calculated for $C_{22}H_{29}BNaO_2Se$ = 439.1323, mass found = 439.1318.

(±)-4,4,5,5-Tetramethyl-2-((2*S*,3*R*)-2-phenyl-3-(phenylselanyl)butan-2-yl)-1,3,2-dioxaborolane, 13



13

According to the **General Procedure** with **12**[9] (46 mg, 0.25 mmol), phenyl lithium (1.9 M in dibutyl ether, 0.14 mL, 0.26 mmol) and phenylselenyl chloride (1 M in THF, 0.30 mL, 0.30 mmol). Purification *via* column chromatography eluting with 97:3 pentane/diethyl ether afforded the title compound **13** as a white solid (98 mg, 93 %, >95:5 d.r.).

Melting point 65-69 ^{o}C (pentane/diethyl ether);

^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.74 – 7.68 (m, 2H), 7.45 – 7.40 (m, 2H), 7.31 – 7.24 (m, 5H), 7.17 – 7.12 (m, 1H), 3.96 (q, J = 7.0 Hz, 1H), 1.49 (s, 3H), 1.21 (s, 6H), 1.20 (s, 6H), 1.18 (d, J = 7.0 Hz, 3H).;

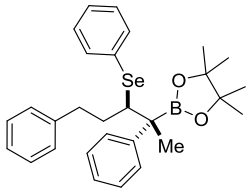
^{13}C NMR (101 MHz, $CDCl_3$) δ_C = 144.2, 134.6, 131.4, 128.9, 128.1, 127.4, 127.2, 125.6, 83.8, 50.3, 24.9, 24.4, 17.8, 16.3. [*N.B. The carbon attached to boron was not observed due to quadrupolar relaxation*];

^{11}B NMR (128 MHz, $CDCl_3$) δ_B = 32.8;

FTIR (neat) ν/cm^{-1} = 2975, 1599, 1579, 1477, 1380, 1371, 1337, 1311, 1146, 1111, 853, 844, 738, 694;

HRMS (ESI$^+$): calculated for $C_{22}H_{29}BNaO_2Se$ = 439.1323, mass found = 439.1328.

(±)-2-((2*S*,3*R*)-2,5-Diphenyl-3-(phenylselanyl)pentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 15



15

According to the **General Procedure** with **14** (54 mg, 0.20 mmol), phenyl lithium (1.9 M in dibutyl ether, 0.11 mL, 0.21 mmol) and phenylselenyl chloride (1 M in THF, 0.24 mL, 0.24 mmol). Purification *via* column chromatography eluting with 98:2 pentane/diethyl ether afforded the title compound **15** as a white solid (89 mg, 89 %, >95:5 d.r.).

Melting point 133-135 ^{o}C (pentane/diethyl ether);

^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.85 – 7.80 (m, 2H), 7.35 – 7.21 (m, 7H), 7.17 – 7.12 (m, 1H), 7.10 – 7.05 (m, 3H), 6.67 – 6.62 (m, 2H), 3.84 (dd, J = 11.1, 2.3 Hz, 1H), 2.76 (ddd, J = 13.8, 9.0, 4.7 Hz, 1H), 2.28 (dt, J = 13.9, 8.3 Hz, 1H), 1.97 – 1.85 (m, 1H), 1.86 – 1.73 (m, 1H), 1.51 (s, 3 H), 1.14 (s, 6H), 1.12 (s, 6H);

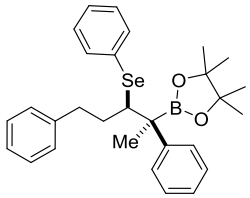
^{13}C NMR (101 MHz, $CDCl_3$) δ_C = 144.1, 141.7, 133.6, 132.7, 128.9, 128.6, 128.1, 128.1, 127.4, 126.8, 125.5, 125.5, 83.9, 55.8, 34.6, 34.3, 25.0, 24.1, 17.0. [*N.B. The carbon attached to boron was not observed due to quadrupolar relaxation*];

^{11}B NMR (128 MHz, $CDCl_3$) δ_B = 31.2;

FTIR (neat) ν/cm^{-1} = 2972, 1578, 1480, 1452, 1439, 1373, 1315, 1144, 1099, 850, 746, 695;

HRMS (EI^{+}): calculated for $C_{29}H_{35}BO_2Se$ = 506.1895, mass found = 506.1893.

(±)-2-((2*R*,3*R*)-2,5-Diphenyl-3-(phenylselanyl)pentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 17



17

According to the **General Procedure** with **16** (54 mg, 0.20 mmol), phenyl lithium (1.9 M in dibutyl ether, 0.11 mL, 0.21 mmol) and phenylselenyl chloride (1 M in THF, 0.24 mL, 0.24 mmol). Purification *via* column chromatography eluting with 98:2 pentane/diethyl ether afforded the title compound **17** as a white solid (71 mg, 71 %, >95:5 d.r.).

Melting point 82-84 °C (pentane/diethyl ether);

^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.34 – 7.29 (m, 2H), 7.28 – 7.22 (m, 2H), 7.21 – 7.02 (m, 11H), 3.67 (dd, J = 10.6, 2.3 Hz, 1H), 3.15 (ddd, J = 13.3, 10.5, 4.8 Hz, 1H), 2.72 (ddd, J = 13.4, 10.6, 6.1 Hz, 1H), 2.16 – 1.96 (m, 2H), 1.44 (s, 3H), 1.20 (s, 6H), 1.17 (s, 6H);

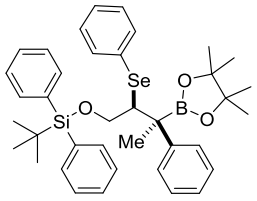
^{13}C NMR (101 MHz, $CDCl_3$) δ_C = 144.6, 142.4, 135.0, 131.6, 128.6, 128.5, 128.4, 127.9, 127.7, 126.8, 125.8, 125.8, 83.8, 61.2, 39.4, 35.7, 24.7, 24.6, 17.3. [*N.B. The carbon attached to boron was not observed due to quadrupolar relaxation*];

^{11}B NMR (128 MHz, $CDCl_3$) δ_B = 32.9;

FTIR (neat) ν/cm^{-1} = 2976, 1601, 1579, 1496, 1475, 1454, 1379, 1371, 1357, 1317, 1143, 1091, 848, 739, 698;

HRMS (ESI$^+$): calculated for $C_{29}H_{35}BNaO_2Se$ = 529.1794, mass found = 529.1793.

(±)-*tert*-Butyldiphenyl((2*S*,3*R*)-3-phenyl-2-(phenylselanyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butoxy)silane, 19



19

According to the **General Procedure** with **18** (87 mg, 0.20 mmol), phenyl lithium (1.9 M in dibutyl ether, 0.11 mL, 0.21 mmol) and phenylselenyl chloride (1 M in THF, 0.24 mL, 0.24 mmol). Purification *via* column chromatography eluting with 97:3 pentane/diethyl ether afforded the title compound **19** as a colourless oil (98 mg, 73 %, >95:5 d.r.).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.74 – 7.68 (m, 4H), 7.44 – 7.32 (m, 6H), 7.31 – 7.26 (m, 4H), 7.20 – 7.00 (m, 6H), 4.08 (dd, J = 10.7, 4.2 Hz, 1H), 3.99 (dd, J = 10.7, 7.1 Hz, 1H), 3.88 (dd, J = 7.0, 4.1 Hz, 1H), 1.49 (s, 3H), 1.08 (s, 6H), 1.05 (s, 9H), 1.05 (s, 6H);

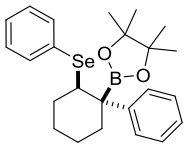
^{13}C NMR (101 MHz, $CDCl_3$) δ_C = 144.2, 135.9, 135.9, 134.4, 133.7, 133.7, 132.2, 129.6, 128.4, 127.8, 127.7, 127.6, 126.5, 125.8, 83.8, 68.0, 62.1, 27.0, 24.6, 24.4, 19.4, 18.9. [*N.B. The carbon attached to boron was not observed due to quadrupolar relaxation*];

^{11}B NMR (128 MHz, $CDCl_3$) δ_B = 32.1;

FTIR (neat) ν/cm^{-1} = 2976, 2857, 1474, 1319, 1143, 1107, 823, 737;

HRMS (ESI$^+$): calculated for $C_{38}H_{47}BNaO_3SeSi$ = 693.2455, mass found = 693.2451.

(±)-4,4,5,5-Tetramethyl-2-((1*S*,2*R*)-1-phenyl-2-(phenylselanyl)cyclohexyl)-1,3,2-dioxaborolane, 21



21

According to the **General Procedure** with **20** (36 mg, 0.17 mmol), phenyl lithium (1.8 M in dibutyl ether, 0.10 mL, 0.18 mmol) and phenylselenyl chloride (1 M in THF, 0.21 mL, 0.21 mmol). Purification *via* column chromatography eluting with 98:2 pentane/diethyl ether afforded the title compound **21** as a white solid (70 mg, 92 %, >95:5 d.r.).

Melting point 95-97 ^{o}C (pentane/diethyl ether);

^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.63 – 7.55 (m, 2H), 7.37 – 7.32 (m, 2H), 7.31 – 7.21 (m, 5H), 7.16 – 7.09 (m, 1H), 3.96 (br s, 1H), 2.27 – 2.16 (m, 1H), 2.15 – 2.04 (m, 1H), 2.02 – 1.81 (m, 3H), 1.53 – 1.37 (m, 3H), 1.19 (s, 6H), 1.14 (s, 6H);

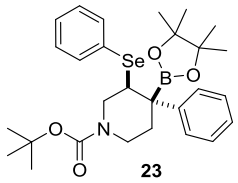
^{13}C NMR (101 MHz, $CDCl_3$) δ_C = 144.1, 133.9, 132.8, 128.8, 128.3, 127.6, 127.0, 125.2, 83.7, 53.4, 32.0, 30.5, 24.8, 24.5, 24.4, 22.1. [*N.B. The carbon attached to boron was not observed due to quadrupolar relaxation*];

^{11}B NMR (128 MHz, $CDCl_3$) δ_B = 32.0;

FTIR (neat) ν/cm^{-1} = 2976, 2930, 1578, 1477, 1378, 1371, 1347, 1317, 1144, 853, 737, 695;

HRMS (ESI^{+}): calculated for $C_{24}H_{31}BNaO_2Se$ = 465.1480, mass found = 465.1486.

(±)-*tert*-Butyl (3*S*,4*S*)-4-phenyl-3-(phenylselanyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine-1-carboxylate, 23



23

According to the **General Procedure** with **22** (63 mg, 0.20 mmol), phenyl lithium (1.8 M in dibutyl ether, 0.12 mL, 0.21 mmol) and phenylselenyl chloride (1 M in THF, 0.25 mL, 0.25 mmol). Purification *via* column chromatography eluting with 85:15 pentane/diethyl ether afforded the title compound **23** as a white foam (95 mg, 86 %, >95:5 d.r.).

Melting point 54-55 ^{o}C (pentane/diethyl ether);

^{1}H NMR (500 MHz, d_6-benzene, 70 ^{o}C) δ_H = 7.74 (br d, J = 7.3 Hz, 2H), 7.26 (d, J = 7.7 Hz, 2H), 7.12 – 7.09 (m, 2H), 7.07 – 6.96 (m, 4H), 4.06 – 3.79 (m, 3H), 3.74 – 3.64 (m, 1H), 3.38 (br s, 1H), 2.22 (ddd, J = 14.4, 8.5, 3.7 Hz, 1H), 2.14 (ddd, J = 14.4, 6.7, 3.6 Hz, 1H), 1.45 (s, 9H), 1.00 (s, 6H), 0.96 (s, 6H);

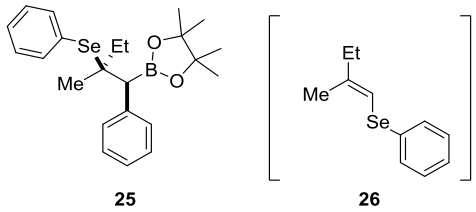
^{13}C NMR (126 MHz, d_6-benzene, 70 ^{o}C) δ_C = 154.4, 142.9, 134.2, 132.1, 128.7, 128.2, 127.6, 127.1, 125.4, 83.6, 78.5, 51.4, 46.9, 40.8, 32.3, 28.2, 24.4, 24.1. [*N.B. The carbon attached to boron was not observed due to quadrupolar relaxation*];

^{11}B NMR (160 MHz, d_6-benzene, 70 ^{o}C) δ_B = 33.1;

FTIR (neat) ν/cm^{-1} = 2976, 2929, 1692, 1477, 1422, 1365, 1321, 1166, 1129, 851, 739, 695;

HRMS (ESI^{+}): calculated for $C_{28}H_{38}BNNaO_4Se$ = 566.1958, mass found = 566.1956.

(±)-4,4,5,5-Tetramethyl-2-((1*S*,2*S*)-2-methyl-1-phenyl-2-(phenylselanyl)butyl)-1,3,2-dioxaborolane, 25



25 **26**

A stirred solution of **24**[10] (40 mg, 0.20 mmol) in THF (1.63 mL) was cooled to –78 °C and a solution of phenyl lithium (1.8 M in dibutyl ether, 0.12 mL, 0.21 mmol) was added dropwise. The resulting solution was stirred at –78 °C for 1 hour. After this time anhydrous DMF (0.63 mL) was added dropwise. A solution of phenylselenyl chloride (1 M in THF, 0.25 mL, 0.25 mmol) was added dropwise and the resulting solution was stirred at –78 °C for 1 hour and then warmed to room temperature and stirred for 15 minutes. The mixture was filtered through a short plug of silica gel washing with diethyl ether and the filtrate was concentrated under reduced pressure. NMR of the crude reaction mixture ($CDCl_3$) indicated that a 85:15 mixture of **25**:**26** was present. Purification of the residue *via* column chromatography afforded the title compound **25** as a colourless oil (53 mg, 61 % yield, >95:5 d.r.) along with an analytical quantity of **26** as a yellow oil.

Data for **25**

^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.78 – 7.72 (m, 2H), 7.43 – 7.10 (m, 8H), 2.85 (s, 1H), 1.46 (s, 3H), 1.31 (s, 6H), 1.30 – 1.20 (m, 7H), 1.19 – 1.08 (m, 1H), 0.95 (t, J = 7.3 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ_C = 138.5, 138.3, 131.4, 128.7, 128.5, 128.3, 127.8, 126.0, 83.4, 55.6, 32.2, 25.0, 24.8, 21.8, 10.1. [*N.B. The carbon attached to boron was not observed due to quadrupolar relaxation*];

^{11}B NMR (128 MHz, $CDCl_3$) δ_B = 29.9;

FTIR (neat) ν/cm^{-1} = 2975, 2929, 1599, 1578, 1493, 1477, 1452, 1437, 1378, 1372, 1354, 1320, 1143, 969, 854, 741, 705;

HRMS (ESI$^+$): calculated for $C_{23}H_{31}BNaO_2Se$ = 453.1480, mass found = 453.1484.

Data for **26** ((*E*)-(2-methylbut-1-en-1-yl)(phenyl)selane)

This double bond geometry of this compound was determined to be *E* by nOe – see NMR spectra.

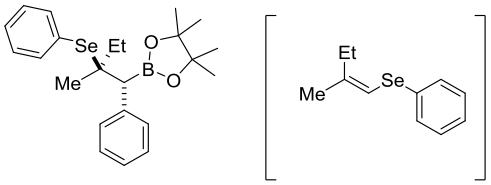
^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 7.51 – 7.44 (m, 2H), 7.32 – 7.20 (m, 3H), 6.26 – 6.09 (m, 1H), 2.22 (qd, J = 7.4, 1.2 Hz, 2H), 1.87 (d, J = 1.0 Hz, 3H), 1.10 (t, J = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 145.5, 132.0, 131.0, 129.1, 126.4, 111.6, 32.7, 19.9, 12.6;

FTIR (neat) ν/cm^{-1} = 2967, 1579, 1477, 1437, 1375, 1294, 1069, 1023, 816, 735;

HRMS (EI$^+$): calculated for $C_{11}H_{14}Se$ = 226.0261, mass found = 226.0258.

(±)-4,4,5,5-Tetramethyl-2-((1*R*,2*S*)-2-methyl-1-phenyl-2-(phenylselanyl)butyl)-1,3,2-dioxaborolane, 28



28 **42**

A stirred solution of **27**[10] (40 mg, 0.20 mmol) in THF (1.63 mL) was cooled to –78 °C and a solution of phenyl lithium (1.8 M in dibutyl ether, 0.12 mL, 0.21 mmol) was added dropwise. The resulting solution was stirred at –78 °C for 1 hour. After this time anhydrous DMF (0.63 mL) was added dropwise. A solution of phenylselenyl chloride (1 M in THF, 0.25 mL, 0.25 mmol) was added dropwise and the resulting solution was stirred at –78 °C for 1 hour and then warmed to room temperature and stirred for 15 minutes. The mixture was filtered through a short plug of silica gel washing with diethyl ether and the filtrate was concentrated under reduced pressure. NMR of the crude reaction mixture ($CDCl_3$)

indicated that a 50:50 mixture of **28**:**42** was present. Purification of the residue *via* column chromatography afforded the title compound **28** as a colourless oil (31 mg, 35 % yield, >95:5 d.r.) along with an analytical quantity of **42** as a yellow oil.

Data for **28**

^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.63 – 7.55 (m, 2H), 7.38 – 7.16 (m, 8H), 2.93 (s, 1H), 1.95 (dq, J = 14.7, 7.3 Hz, 1H), 1.57 (dq, J = 14.8, 7.5 Hz, 1H), 1.31 (s, 3H), 1.28 (s, 6H), 1.23 (s, 6H), 1.10 (t, J = 7.4 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ_C = 138.5, 138.5, 131.5, 128.5, 128.2, 128.2, 127.7, 126.1, 83.3, 55.7, 32.1, 26.3, 24.8, 24.6, 10.2. [*N.B. The carbon attached to boron was not observed due to quadrupolar relaxation*];

^{11}B NMR (128 MHz, $CDCl_3$) δ_B = 31.2;

FTIR (neat) ν/cm^{-1} = 2975, 1599, 1578, 1493, 1476, 1452, 1437, 1379, 1371, 1350, 1318, 1142, 968, 852, 740, 703, 695;

HRMS (ESI$^+$): calculated for $C_{23}H_{31}BNaO_2Se$ = 453.1480, mass found = 453.1477.

Data for **42** ((*Z*)-(2-methylbut-1-en-1-yl)(phenyl)selane)

This double bond geometry of this compound was determined to be *Z* by nOe – see NMR spectra.

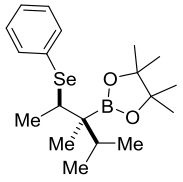
^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 7.48 – 7.43 (m, 2H), 7.30 – 7.24 (m, 2H), 7.24 – 7.20 (m, 1H), 6.13 – 6.10 (m, 1H), 2.28 (q, J = 7.6 Hz, 2H), 1.90 (d, J = 1.4 Hz, 3H), 1.05 (t, J = 7.6 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 145.9, 132.1, 131.0, 129.0, 126.3, 111.8, 28.7, 23.1, 12.3;

FTIR (neat) ν/cm^{-1} = 2965, 2932, 1579, 1477, 1461, 1438, 1069, 1022, 789, 735, 639;

HRMS (EI^+): calculated for $C_{11}H_{14}Se$ = 226.0261, mass found = 226.0262.

(±)-2-((3*R*,4*R*)-2,3-Dimethyl-4-(phenylselanyl)pentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 29



29

A stirred solution of **10** (36 mg, 0.20 mmol) in THF (1.0 mL) was cooled to –78 °C and a solution of isopropyl lithium (0.58 M in pentane, 0.36 mL, 0.21 mmol) was added dropwise. The resulting solution was stirred at –78 °C for 1 hour. After this time 2,2,2-trifluoroethanol (1.0 mL) was added dropwise. Phenylselenyl chloride (46 mg, 0.24 mmol) was added in a single portion and the resulting solution was stirred at –78 °C for 1 hour and then warmed to room temperature and stirred for 15 minutes. The mixture was concentrated under reduced pressure. The residue was diluted with diethyl ether and filtered through a short plug of silica gel washing with diethyl ether and the filtrate was concentrated under reduced pressure. Purification of the residue *via* column chromatography eluting with 98:2 pentane/diethyl ether afforded the title compound **29** as a white solid (65 mg, 85 % yield, >95:5 d.r.).

Melting point 76-80 °C (pentane/diethyl ether);

^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.62-7.56 (m, 2H), 7.28 – 7.22 (m, 3H), 3.62 (q, J = 6.9 Hz, 1H), 1.95 (hept, J = 6.8 Hz, 1H), 1.50 (d, J = 6.9 Hz, 3H), 1.26 (s, 6H), 1.26 (s, 6H), 1.07 (s, 3H), 1.04 (d, J = 6.8 Hz, 3H), 0.93 (d, J = 6.9 Hz, 3H);

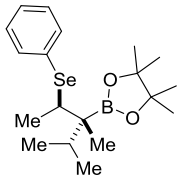
^{13}C NMR (101 MHz, $CDCl_3$) δ_C = 134.9, 130.5, 128.8, 127.0, 83.4, 49.8, 34.6, 25.1, 21.2, 19.4, 18.8, 16.8. [*N.B. The carbon attached to boron was not observed due to quadrupolar relaxation*];

^{11}B NMR (128 MHz, $CDCl_3$) δ_B = 32.7;

FTIR (neat) ν/cm^{-1} = 2977, 1579, 1475, 1379, 1305, 1141, 1090, 851, 738;

HRMS (ESI^+): calculated for $C_{19}H_{31}BNaO_2Se$ = 405.1479, mass found = 405.1472.

(±)-2-((3*S*,4*R*)-2,3-Dimethyl-4-(phenylselanyl)pentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 30



30

A stirred solution of **12**[9] (36 mg, 0.20 mmol) in THF (1.0 mL) was cooled to –78 °C and a solution of isopropyl lithium (0.58 M in pentane, 0.36 mL, 0.21 mmol) was added dropwise. The resulting solution was stirred at –78 °C for 1 hour. After this time 2,2,2-trifluoroethanol (1.0 mL) was added dropwise. Phenylselenyl chloride (46 mg, 0.24 mmol) was added in a single portion and the resulting solution was stirred at –78 °C for 1 hour and then warmed to room temperature and stirred for 15 minutes. The mixture was concentrated under reduced pressure. The residue was diluted with diethyl ether and filtered through a short plug of silica gel washing with diethyl ether and the filtrate was concentrated under reduced pressure. Purification of the residue *via* column chromatography eluting with 98:2 pentane/diethyl ether afforded the title compound **30** as a white gum (57 mg, 75 % yield, 95:5 d.r.). The data for the minor diastereoisomer was identical to that described above.

^1H NMR (400 MHz, $CDCl_3$) δ_H = 7.65 – 7.59 (m, 2H), 7.28 – 7.20 (m, 3H), 3.60 (q, J = 6.9 Hz, 1H), 1.67 (sept, J = 6.9 Hz, 1H), 1.42 (d, J = 7.0 Hz, 3H), 1.29 (s, 6H), 1.28 (s, 6H), 1.03 (s, 3H), 0.98 (d, J = 6.8 Hz, 3H), 0.92 (d, J = 6.9 Hz, 3H);

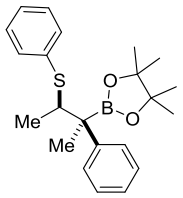
^{13}C NMR (101 MHz, $CDCl_3$) δ_C = 134.1, 131.7, 128.8, 126.9, 83.5, 49.0, 34.5, 25.5, 25.1, 19.7, 19.0, 17.3, 16.9. [*N.B. The carbon attached to boron was not observed due to quadrupolar relaxation*];

^{11}B NMR (128 MHz, $CDCl_3$) δ_B = 32.9;

FTIR (neat) ν/cm^{-1} = 2976, 1579, 1477, 1387, 1371, 1308, 1141, 852, 739;

HRMS (ESI$^+$): calculated for $C_{19}H_{31}BNaO_2Se$ = 405.1479, mass found = 405.1477.

(±)-4,4,5,5-Tetramethyl-2-((2*R*,3*R*)-2-phenyl-3-(phenylthio)butan-2-yl)-1,3,2-dioxaborolane, 31



31

According to the **General Procedure** with **10** (46 mg, 0.25 mmol), phenyl lithium (1.9 M in dibutyl ether, 0.14 mL, 0.26 mmol) and phenylsulfenyl chloride[11] (1 M in THF, 0.30 mL, 0.30 mmol). Purification *via* column chromatography eluting with 97:3 pentane/diethyl ether afforded the title compound **31** as a white solid (92 mg, 99 %, >95:5 d.r.).

Melting point 72-75 ^{o}C (pentane/diethyl ether);

^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.46 – 7.41 (m, 2H), 7.30 – 7.21 (m, 4H), 7.19 – 7.10 (m, 4H), 3.87 (q, J = 6.8 Hz, 1H), 1.49 (s, 3H), 1.42 (d, J = 6.8 Hz, 3H), 1.19 (s, 6H), 1.16 (s, 6H);

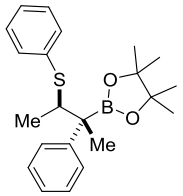
^{13}C NMR (101 MHz, $CDCl_3$) δ_C = 144.3, 136.9, 132.3, 128.6, 128.0, 127.4, 126.4, 125.8, 83.8, 54.0, 24.6, 20.5, 15.7. [*N.B. The carbon attached to boron was not observed due to quadrupolar relaxation*];

^{11}B NMR (128 MHz, $CDCl_3$) δ_B = 32.8;

FTIR (neat) ν/cm^{-1} = 2976, 1583, 1479, 1356, 1372, 1312, 1142, 1096, 852, 747, 695, 672;

HRMS (EI$^+$): calculated for $C_{22}H_{29}BO_2S$ = 368.1981, mass found = 368.1988.

(±)-4,4,5,5-Tetramethyl-2-((2*S*,3*R*)-2-phenyl-3-(phenylthio)butan-2-yl)-1,3,2-dioxaborolane, 32



32

According to the **General Procedure** with **12**[9] (46 mg, 0.25 mmol), phenyl lithium (1.9 M in dibutyl ether, 0.14 mL, 0.26 mmol) and phenylsulfenyl chloride[11] (1 M in THF, 0.30 mL, 0.30 mmol). Purification *via* column chromatography eluting with 97:3 pentane/diethyl ether afforded the title compound **32** as a white solid (85 mg, 91 %, >95:5 d.r.).

Melting point 78-80 ^{o}C (pentane/diethyl ether);

^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.58 (d, J = 7.9 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H), 7.34 – 7.19 (m, 5H), 7.15 (t, J = 7.2 Hz, 1H), 3.90 (q, J = 6.5 Hz, 1H), 1.48 (s, 3H), 1.21 (s, 6H), 1.18 (s, 6H), 0.99 (d, J = 6.7 Hz, 3H);

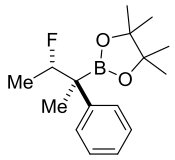
^{13}C NMR (101 MHz, $CDCl_3$) δ_C = 144.1, 137.2, 132.2, 128.8, 128.1, 127.4, 126.8, 125.6, 83.8, 53.4, 24.9, 24.4, 16.4, 15.0. [*N.B. The carbon attached to boron was not observed due to quadrupolar relaxation*];

^{11}B NMR (128 MHz, $CDCl_3$) δ_B = 32.6;

FTIR (neat) ν/cm^{-1} = 2975, 1583, 1479, 1380, 1340, 1312, 1146, 1114, 1024, 845, 741, 700;

HRMS (EI$^+$): calculated for $C_{22}H_{29}BO_2S$ = 368.1981, mass found = 368.1973.

(±)-2-((2*R*,3*S*)-3-Fluoro-2-phenylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 33



33

A stirred solution of **10** (46 mg, 0.25 mmol) in THF (2.5 mL) was cooled to 0 °C and a solution of phenyl lithium (1.9 M in dibutyl ether, 0.15 mL, 0.29 mmol) was added dropwise. The resulting solution was then stirred for 30 minutes at 0 °C, and then warmed to room temperature and stirred for 30 minutes. MeCN (0.50 mL) was added, and the reaction mixture was concentrated under reduced pressure (using a Schlenk line). The residue was redissolved in MeCN/THF (5:1 v/v, 3.0 mL) and the resulting solution was stirred at room temperature. Selectfluor I (106 mg, 0.300 mmol) was added and the mixture was stirred at room temperature for 1 hour and then diethyl ether and aqueous pH 6.0 buffer (formed by mixing 3.69 mL 0.1 M aqueous citric acid with 6.31 mL 0.2 M aqueous Na_2HPO_4) were added. The organic layer was separated and the aqueous phase was extracted twice with diethyl ether. The combined organic phases were washed with brine, dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure. A ^{19}F NMR yield of 72 % and 89:11 d.r. was measured using $PhCF_3$ (10.2 µL, 0.083 mmol) as an internal standard. **33** was found to decompose upon standing in $CDCl_3$, and was unstable to column chromatography. Characterisation of the compound was therefore achieved from the crude reaction mixture (the ^1H and ^{13}C NMR data below are for the major diastereomer).

^1H NMR (400 MHz, $CDCl_3$) δ_H = 7.39 – 7.34 (m, 2H), 7.34 – 7.28 (m, 2H), 7.20 (m, 1H), 5.22 (dq, J = 46.0, 6.5 Hz, 1H), 1.45 (s, 3H), 1.25 (s, 6H), 1.23 (s, 6H), 1.10 (dd, J = 24.0, 6.5 Hz, 3H);

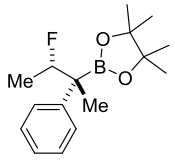
^{13}C NMR (101 MHz, $CDCl_3$) δ_C = 141.9 (d, J_{CF} = 9.0 Hz), 128.3, 127.7 (d, J_{CF} = 1.0 Hz), 126.0, 95.3 (d, J_{CF} = 170.0 Hz), 83.8, 24.7, 24.6, 15.7 (d, J_{CF} = 24.0 Hz), 14.6 (d, J_{CF} = 4.0 Hz). [*N.B. The carbon attached to boron was not observed due to quadrupolar relaxation*];

^{19}F NMR (470 MHz, $CDCl_3$) δ_F = –174.7 (dq, J = 46.0, 24.0 Hz, major diastereomer), –179.0 (dq, J = 47.5, 23.5 Hz, minor diastereoisomer);

^{11}B NMR (128 MHz, $CDCl_3$) δ_B = 33.3;

HRMS (ESI^+): calculated for $C_{16}H_{24}BFNaO_2$ = 301.1746, mass found = 301.1734.

(±)-2-((2*S*,3*S*)-3-Fluoro-2-phenylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 34



34

A stirred solution of **12** (46 mg, 0.25 mmol) in THF (2.5 mL) was cooled to 0 °C and a solution of phenyl lithium (1.9 M in dibutyl ether, 0.15 mL, 0.29 mmol) was added dropwise. The resulting solution was then stirred for 30 minutes at 0 °C, and then warmed to room temperature and stirred for 30 minutes. MeCN (0.50 mL) was added, and the reaction mixture was concentrated under reduced pressure (using a Schlenk line). The residue was redissolved in MeCN/THF (5:1 v/v, 3.0 mL) and the resulting solution was stirred at room temperature. Selectfluor I (106 mg, 0.300 mmol) was added and the mixture was stirred at room temperature for 1 hour and then diethyl ether and aqueous pH 6.0 buffer (formed by mixing 3.69 mL 0.1 M aqueous citric acid with 6.31 mL 0.2 M aqueous Na_2HPO_4) were added. The organic layer was separated and the aqueous phase was extracted twice with diethyl ether. The combined organic phases were washed with brine, dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure. A ^{19}F NMR yield of 66 % and 91:9 d.r. was measured using $PhCF_3$ (10.2 μL, 0.083 mmol) as an internal standard. **34** was found to decompose upon standing in $CDCl_3$, and was unstable to column chromatography. Characterisation of the compound was therefore achieved from the crude reaction mixture (the ^{1}H and ^{13}C NMR data below are for the major diastereomer).

^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 7.41 – 7.37 (m, 2H), 7.34 – 7.29 (m, 2H), 7.20 (m, 1H), 5.16 (dq, J = 47.5, 6.5 Hz, 1H), 1.43 (s, 3H), 1.33 (dd, J = 23.5, 6.5 Hz, 3H), 1.24 (s, 6H), 1.21 (s, 6H);

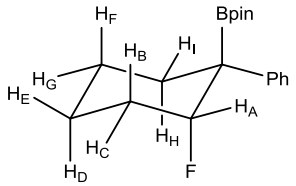
^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 143.2 (d, J_{CF} = 2.5 Hz), 128.1, 127.5, 125.8, 95.2 (d, J_{CF} = 173.0), 83.6, 24.5, 24.4, 17.7 (d, J_{CF} = 24.0 Hz), 15.0 (d, J_{CF} = 6.5 Hz). [*N.B. The carbon attached to boron was not observed due to quadrupolar relaxation*];

^{19}F NMR (470 MHz, $CDCl_3$) δ_F = –174.7 (dq, J = 46.0, 24.0 Hz, minor diastereoisomer), –179.0 (dq, J = 47.5, 23.5 Hz, major diastereoisomer);

^{11}B NMR (128 MHz, $CDCl_3$) δ_B = 33.3;

HRMS (ESI^+): calculated for $C_{16}H_{24}BFNaO_2$ = 301.1746, mass found = 301.1749.

(±)-2-((1*S*,2*R*)-2-Fluoro-1-phenylcyclohexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 41



41

A stirred solution of **20** (52 mg, 0.25 mmol) in THF (2.5 mL) was cooled to 0 °C and a solution of phenyl lithium (1.9 M in dibutyl ether, 0.15 mL, 0.29 mmol) was added dropwise. The resulting solution was then stirred for 30 minutes at 0 °C, and then warmed to room temperature and stirred for 30 minutes. MeCN (0.50 mL) was added, and the reaction mixture was concentrated under reduced pressure (using a Schlenk line). The residue was redissolved in MeCN/THF (5:1 v/v, 3.0 mL) and the resulting solution was stirred at room temperature. Selectfluor I (106 mg, 0.300 mmol) was added and the mixture was stirred at room temperature for 1 hour and then diethyl ether and aqueous pH 6.0 buffer (formed by mixing 3.69 mL 0.1 M aqueous citric acid with 6.31 mL 0.2 M aqueous Na_2HPO_4) were added. The organic layer was separated and the aqueous phase was extracted twice with diethyl ether. The combined organic phases were washed with brine, dried over anhydrous magnesium sulfate,

filtered and concentrated under reduced pressure. A ^{19}F NMR yield of 33 % and >95:5 d.r. was measured using $PhCF_3$ (30.6 µL, 0.25 mmol) as an internal standard. Purification of the crude material *via* column chromatography eluting with a gradient from pentane to 5:95 diethyl ether/pentane afforded the title compound **41** as a colourless solid (16 mg, 21 % yield, >95:5 d.r.). The relative stereochemistry was assigned by NOE and HOESY experiments – see NMR spectra for details.

Melting point 82 ^{o}C (pentane/diethyl ether);

^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.41 – 7.36 (m, 2H, ArH_{ortho}), 7.34 – 7.29 (m, 2H, ArH_{meta}), 7.18 (m, 1H, ArH_{para}), 5.40 (dd, J = 49.0, 4.0 Hz, 1H, H_A), 2.23 (m, 1H, H_I), 2.17 (m, 1H, H_C), 1.98 (m, 1H, H_H), 1.91 (m, 1H, H_G), 1.77 (ddddd, J = 44.0, 14.5, 13.5, 5.0, 2.0 Hz, 1H, H_B), 1.71 – 1.54 (m, 2H, H_D and H_E), 1.43 (qt, J = 13.3, 3.2 Hz, 1H, H_F), 1.19 (s, 6H, Bpin), 1.15 (s, 6H, Bpin);

^{13}C NMR (101 MHz, $CDCl_3$) δ_C = 143.0 (d, J_{CF} = 3.0 Hz), 128.4, 126.6, 125.7, 93.5 (d, J_{CF} = 175.0 Hz), 83.7, 30.8 (d, J_{CF} = 22.5 Hz), 26.9 (d, J_{CF} = 2.5 Hz), 25.1, 24.5, 24.5, 19.8 [*N.B. The carbon attached to boron was not observed due to quadrupolar relaxation*];

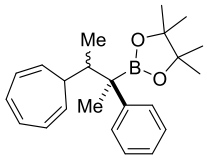
^{19}F NMR ($CDCl_3$, 470 MHz) δ_F = –194.1 (t, J = 49.0, 44.0 Hz);

^{11}B NMR (128 MHz, $CDCl_3$) δ_B = 33.2;

FTIR (neat) ν/cm^{-1} = 2937, 1372, 1349, 1318, 1268, 1140, 952, 871, 853, 744;

HRMS (ESI^+): calculated for $C_{18}H_{26}BFNaO_2$ = 327.1902, mass found = 327.1902.

(±)-2-(3-(Cyclohepta-2,4,6-trien-1-yl)-2-phenylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 35



35

A stirred solution of **10** (46 mg, 0.25 mmol) in THF (2.5 mL) was cooled to 0 °C and a solution of phenyl lithium (1.9 M in dibutyl ether, 0.15 mL, 0.29 mmol) was added dropwise. The resulting solution was then stirred for 30 minutes at 0 °C, and then warmed to room temperature and stirred for 30 minutes. Tropylium tetrafluoroborate (53 mg, 0.30 mmol) was added and the mixture was stirred at room temperature for 1 hour and then diethyl ether and water were added. The organic layer was separated and the aqueous phase was extracted twice with diethyl ether. The combined organic phases were washed with brine, dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure. Purification of the residue *via* column chromatography eluting with a gradient from pentane to 5:95 diethyl ether/pentane afforded the title compound **35** as a yellow oil (79 mg, 90 % yield, 52:48 d.r.).

^{11}B NMR (128 MHz, $CDCl_3$) δ_B = 32.8;

FTIR (neat) ν/cm^{-1} = 2976, 1371, 1343, 1306, 1145, 965, 852, 745;

HRMS (ESI$^+$): calculated for $C_{23}H_{31}BNaO_2$ = 373.2309, mass found = 373.2314.

<u>NMR data for major diastereoisomer, **35**</u>:

^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.36 – 7.31 (m, 2H), 7.23 – 7.17 (m, 2H), 7.06 (m, 1H), 6.67 – 6.54 (m, 2H), 6.15 – 6.05 (m, 2H), 5.32 (dd, J = 9.0, 6.0 Hz, 1H), 5.26 (dd, J = 9.0, 6.0 Hz, 1H), 2.82 – 2.61 (m, 1H), 1.19 (s, 3H), 1.38 – 1.10 (m, 1H), 1.03 (s, 6H), 0.98 (s, 6H), 0.62 (d, J = 7.0 Hz, 3H);

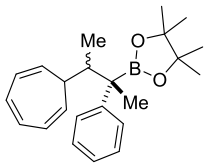
^{13}C NMR (101 MHz, $CDCl_3$) δ_C = 145.5, 130.9, 130.3, 127.9, 127.4, 125.0, 124.5, 123.7, 123.4, 123.2, 83.3, 43.7, 41.5, 24.5, 24.4, 14.3, 10.9. [*N.B. The carbon attached to boron was not observed due to quadrupolar relaxation*];

NMR data for minor diastereoisomer, **36**:

^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.31 – 7.25 (m, 2H), 7.15 – 7.10 (m, 2H), 7.01 (m, 1H), 6.44 (dd, J = 11.0, 5.5 Hz, 1H), 6.37 (dd, J = 11.0, 5.5 Hz, 1H), 5.98 (dd, J = 9.5, 5.5 Hz, 1H), 5.81 (dd, J = 9.5, 5.5 Hz, 1H), 5.14 (dd, J = 9.0, 6.0 Hz, 1H), 4.72 (dd, J = 9.0, 6.0 Hz, 1H), 2.82 – 2.61 (m, 1H), 1.29 (s, 3H), 1.17 (d, J = 7.0 Hz, 3H), 1.38 – 1.10 (m, 1H), 1.09 (s, 6H), 1.07 (s, 6H);

^{13}C NMR (101 MHz, $CDCl_3$) δ_C = 145.5, 130.4, 130.2, 127.8, 127.5, 125.1, 124.0, 123.2, 123.1, 121.8, 83.3, 41.5, 40.2, 24.6, 24.5, 15.5, 14.7. [*N.B. The carbon attached to boron was not observed due to quadrupolar relaxation*];

(±)-2-(3-(Cyclohepta-2,4,6-trien-1-yl)-2-phenylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 36

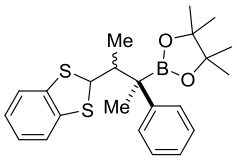


36

A stirred solution of **12** (46 mg, 0.25 mmol) in THF (2.5 mL) was cooled to 0 °C and a solution of phenyl lithium (1.9 M in dibutyl ether, 0.15 mL, 0.29 mmol) was added dropwise. The resulting solution was then stirred for 30 minutes at 0 °C, and then warmed to room temperature and stirred for 30 minutes. Tropylium tetrafluoroborate (53 mg, 0.30 mmol) was added and the mixture was stirred at room temperature for 1 hour and then diethyl ether and water were added. The organic layer was separated and the aqueous phase was extracted twice with diethyl ether. The combined organic phases were washed with brine, dried over anhydrous magnesium sulfate, filtered and concentrated under

reduced pressure. Purification of the residue *via* column chromatography eluting with a gradient from pentane to 5:95 diethyl ether/pentane afforded the title compound **36** as a yellow oil (76 mg, 86 % yield, 67:33 d.r.). [*N.B. the major diastereoisomer formed in this reaction (***36***) was opposite to that obtained in the experiment described above beginning with* **10**]. The spectral data for both diastereoisomers (**35** and **36**) matched that described above.

(±)-2-(3-(Benzo[*d*][1,3]dithiol-2-yl)-2-phenylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 37



37

Preparation of 37 from 10: A stirred solution of **10** (46 mg, 0.25 mmol) in THF (2.5 mL) was cooled to 0 ^{o}C and a solution of phenyl lithium (1.9 M in dibutyl ether, 0.15 mL, 0.29 mmol) was added dropwise. The resulting solution was then stirred for 30 minutes at 0 °C, and then warmed to room temperature and stirred for 30 minutes. 1,3-Benzodithiolylium tetrafluoroborate (72 mg, 0.30 mmol) was added and the mixture was stirred at room temperature for 1 hour and then diethyl ether and water were added. The organic layer was separated and the aqueous phase was extracted twice with diethyl ether. The combined organic phases were washed with brine, dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure. Purification of the residue *via* column chromatography eluting with a gradient from pentane to 5:95 diethyl ether/pentane afforded the title compound **37** as a yellow oil (51 mg, 50 % yield, 53:47 d.r.).

^{11}B NMR (128 MHz, $CDCl_3$) δ_B = 33.5;

FTIR (neat) ν/cm^{-1} = 2975, 1445, 1339, 1307, 1144, 1118, 964, 849, 738;

HRMS (ESI$^+$): calculated for $C_{23}H_{29}BNaO_2S_2$ = 435.1594, mass found = 435.1584.

NMR data for major diastereoisomer:

^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.38 (m, 1H), 7.35 – 7.28 (m, 2H), 7.25 (m, 1H), 7.20 – 7.10 (m, 2H), 7.06 (m, 1H), 6.98 (m, 2H), 5.11 (d, J = 6.0 Hz, 1H), 2.79 (qd, J = 7.0, 6.0 Hz, 1H), 1.32 (s, 3H), 1.15 (s, 6H), 1.13 (s, 6H), 0.74 (d, J = 7.0 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ_C = 144.6, 138.7, 137.7, 128.0, 127.5, 125.4, 125.2, 125.0, 121.8, 121.7, 83.5, 59.2, 47.3, 24.7, 24.3, 14.5, 11.4. [*N.B. The carbon attached to boron was not observed due to quadrupolar relaxation*];

NMR data for minor diastereoisomer:

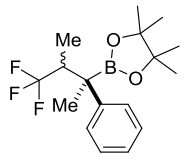
^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.38 (m, 1H), 7.35 – 7.28 (m, 2H), 7.25 (m, 1H), 7.20 – 7.10 (m, 2H), 7.06 (m, 1H), 6.89 (m, 2H), 4.90 (d, J = 2.5 Hz, 1H), 2.85 (qd, J = 7.0, 2.5 Hz, 1H), 1.34 (s, 3H), 1.30 (d, J = 7.0 Hz, 3H), 1.16 (s, 6H), 1.12 (s, 6H);

^{13}C NMR (101 MHz, $CDCl_3$) δ_C = 143.9, 139.2, 138.2, 128.4, 127.2, 125.8, 124.9, 124.9, 121.6, 121.3, 83.6, 56.7, 45.9, 24.4, 24.4, 14.4, 13.5. [*N.B. The carbon attached to boron was not observed due to quadrupolar relaxation*].

Alternative preparation of 37 from 12: A stirred solution of **12** (46 mg, 0.25 mmol) in THF (2.5 mL) was cooled to 0 °C and a solution of phenyl lithium (1.9 M in dibutyl ether, 0.15 mL, 0.29 mmol) was added dropwise. The resulting solution was then stirred for 30 minutes at 0 °C, and then warmed to room temperature and stirred for 30 minutes. 1,3-Benzodithiolylium tetrafluoroborate (72 mg, 0.30 mmol) was added and the mixture was stirred at room temperature for 1 hour and then diethyl ether and water were added. The organic layer was separated and the aqueous phase was extracted twice with diethyl ether. The combined organic phases were washed with brine, dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure. Purification of the residue *via* column chromatography eluting with a gradient from pentane to 5:95 diethyl ether/pentane afforded the title compound **37** as a colourless amorphous solid (29 mg, 28 % yield, 60:40 d.r.). [*N.B. the same*

major diastereoisomer was obtained compared with the above procedure, beginning with **10**]. The spectral data for both diastereoisomers matched that described above.

(±)-4,4,5,5-Tetramethyl-2-(4,4,4-trifluoro-3-methyl-2-phenylbutan-2-yl)-1,3,2-dioxaborolane, 38



38

Preparation of 38 from 10: A stirred solution of **10** (46 mg, 0.25 mmol) in THF (2.5 mL) was cooled to 0 °C and a solution of phenyl lithium (1.9 M in dibutyl ether, 0.15 mL, 0.29 mmol) was added dropwise. The resulting solution was then stirred for 30 minutes at 0 °C, and then warmed to room temperature and stirred for 30 minutes. The reaction mixture was concentrated under reduced pressure (using a Schlenk line) and the residue was redissolved in anhydrous dimethylformamide (2.5 mL). (5-(trifluoromethyl)dibenzothiophenium trifluoromethanesulfonate (121 mg, 0.30 mmol) was added and the mixture was stirred at room temperature for 1 hour and then diethyl ether and water were added. $PhCF_3$ (30.7 µL, 0.25 mmol) was added, and the organic phase was analysed by ^{19}F NMR indicating the product to be formed in 40 % NMR yield, 53:47 d.r. The organic layer was separated and the aqueous phase was extracted twice with diethyl ether. The combined organic phases were washed with brine, dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure. Purification of the residue *via* column chromatography eluting with a gradient from pentane to 4:96 diethyl ether/pernane followed by preparative TLC (5:95 diethyl ether/hexane) afforded the title compound **38** as a yellow oil (25 mg, 26 % yield, 60:40 d.r.).*

^{11}B NMR (128 MHz, $CDCl_3$) δ_B = 33.6;

* Changes in diastereomeric ratio upon concentration were observed, suggesting that the minor diastereomer is marginally more volatile. The diastereomeric ratio of the crude reaction mixture by ^{19}F NMR provides a better measure of the control in the reaction.

FTIR (neat) ν/cm^{-1} = 2980, 1372, 1325, 1259, 1168, 1141, 1083, 847;

HRMS (ESI$^+$): calculated for $C_{17}H_{24}BF_3NaO_2$ = 351.1714, mass found = 351.1721.

NMR data for major diastereoisomer:

^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 7.43 – 7.39 (m, 2H), 7.33 – 7.27 (m, 2H), 7.17 (m, 1H), 3.09 (m, 1H), 1.47 (q, J = 1.5 Hz, 3H), 1.26 (d, J = 7.0 Hz, 3H), 1.19 (s, 6H), 1.14 (s, 6H);

^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 143.4, 127.9, 127.1, 128.9 (q, J_{CF} = 283.5 Hz), 125.6, 83.8, 44.0 (q, J_{CF} = 23.5 Hz), 24.4, 24.4, 15.4, 12.0 (q, J_{CF} = 3.0 Hz). [*N.B. The carbon attached to boron was not observed due to quadrupolar relaxation*];

NMR data for minor diastereoisomer:

^{1}H NMR (500 MHz, $CDCl_3$) δ_H = 7.43 – 7.39 (m, 2H), 7.33 – 7.27 (m, 2H), 7.17 (m, 1H), 3.15 (m, 1H), 1.38 (q, J = 1.5 Hz, 3H), 1.15 (s, 6H), 1.12 (s, 6H), 0.70 (d, J = 7.0 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ_C = 142.6, 128.7 (q, J_{CF} = 283.5 Hz), 128.2, 127.2, 125.7, 83.7, 43.6 (q, J_{CF} = 24.0 Hz), 24.4, 24.2, 13.5, 7.9 (q, J_{CF} = 3.0 Hz). [*N.B. The carbon attached to boron was not observed due to quadrupolar relaxation*].

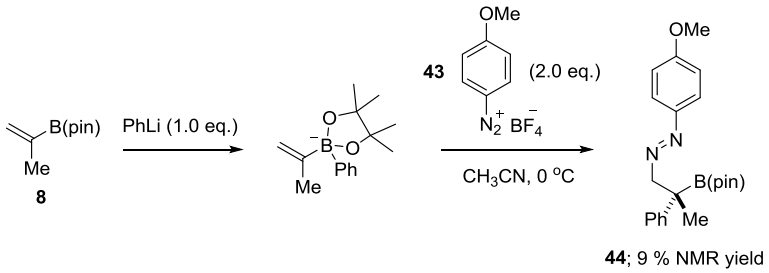
Alternative preparation of 38 from 12: A stirred solution of **12** (46 mg, 0.25 mmol) in THF (2.5 mL) was cooled to 0 °C and a solution of phenyl lithium (1.9 M in dibutyl ether, 0.15 mL, 0.29 mmol) was added dropwise. The resulting solution was then stirred for 30 minutes at 0 °C, and then warmed to room temperature and stirred for 30 minutes. The reaction mixture was concentrated under reduced pressure (using a Schlenk line) and the residue was redissolved in anhydrous dimethylformamide (2.5 mL). (5-(trifluoromethyl)dibenzothiophenium trifluoromethanesulfonate (121 mg, 0.30 mmol) was added and the mixture was stirred at room temperature for 1 hour and then diethyl ether and water were added. $PhCF_3$ (30.7 µL, 0.25 mmol) was added, and the organic phase was analysed by ^{19}F NMR indicating the product to be formed in 43 % NMR yield, 55:45 d.r. The organic layer was

separated and the aqueous phase was extracted twice with diethyl ether. The combined organic phases were washed with brine, dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure. Purification of the residue *via* column chromatography eluting with a gradient from pentane to 4:96 diethyl ether/pernane followed by preparative TLC (5:95 diethyl ether/hexane) afforded the title compound **38** as a yellow oil (25 mg, 20 % yield, 67:33 d.r.).[*] [*N.B. the same major diastereoisomer was obtained compared with the above procedure, beginning with* **10**]. The spectral data for both diastereoisomers matched that described above.

[*] Changes in diastereomeric ratio upon concentration were observed, suggesting that the minor diastereomer is marginally more volatile. The diastereomeric ratio of the crude reaction mixture by ^{19}F NMR provides a better measure of the control in the reaction.

5. Conjunctive Coupling With an Aryldiazonium Salt

(±)-1-(4-Methoxyphenyl)-2-(2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)diazene, 44



44; 9 % NMR yield

A stirred solution of **8** (43 mg, 0.25 mmol) in THF (2.0 mL) was cooled to 0 °C and a solution of phenyl lithium (1.9 M in dibutyl ether, 0.13 mL, 0.25 mmol) was added dropwise. The resulting solution was then stirred for 30 minutes at 0 °C, and then warmed to room temperature and stirred for 30 minutes. The reaction mixture was concentrated under reduced pressure (using a Schlenk line) and the residue was redissolved in anhydrous acetonitrile (2.0 mL) and cooled to 0 °C. A solution of aryldiazonium salt **43**[12] (114 mg, 0.51 mmol) in acetonitrile (2 mL) was added dropwise and the reaction mixture was stirred at 0 °C for 1 h and then water and diethyl ether were added. The organic layer was separated and the aqueous phase was extracted twice with diethyl ether. The combined organic phases were washed with brine, dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure. Crude ^{1}H NMR ($CDCl_3$, 400 MHz) *vs* 1,4-dimethoxybenznene (0.25 eq.) showed a pair of roofed doublets: 4.57 ppm (d, J = 13.1 Hz) & 4.09 ppm (d, J = 13.1 Hz) which we tentatively assign to correspond to the diastereotopic methylene protons of **44** (9 % NMR yield). The spectrum is shown below. Attempts to purify **44** by silica gel chromatography were not successful.

6. β-Elimination Studies

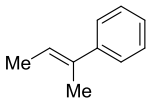
General procedure for β-elimination: β-functionalized boronic ester (1 eq.) was dissolved in THF/MeOH (10 mL/mmol boronic ester) and NaOMe (10.0 eq.) was added. The reaction mixture was stirred at room temperature for 1 h, and then diethyl ether and water were added. The aqueous phase was extracted twice with diethyl ether and the combined organic phase washed with brine, dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure [*N.B. the styrene products are volatile and must be concentrated carefully]*. The residue was either purified *via* column chromatography eluting with hexane, *or* was dissolved in $CDCl_3$ and an NMR yield *vs* 1,4-dimethoxybenzene (0.5 eq.) was measured. Analytical data for alkene products is given below.

Results:

Entry	substrate	d.r. substrate	Major product	E/Z selectivity[b]	Alkene yield
1	**11** (E = SePh)	>95:5	**39**	>95:5	45[c]
2	**13** (E = SePh)	>95:5	**40**	<5:95	57[c]
3	**31** (E = SPh)	>95:5	**39**	96:4	45[c]
4	**32** (E = SPh)	>95:5	**40**	29:71	24[c]
5	**33** (E = F)[a]	89:11	**40**	17:83	15[d]
6	**34** (E = F)[a]	91:9	**39**	92:8	21[d]

Results of β-elimination experiments. [a] crude β-fluoroboronic esters were employed. [b] Determined from crude ^{1}H NMR spectrum. [c] ^{1}H NMR yield vs 1,4-dimethoxybenzene (0.5 eq.), [d] isolated yield

(*E*)-but-2-en-2-ylbenzene, 39



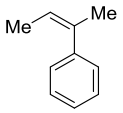
39

The spectral data matched that previously reported in the literature.[13]

^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.41 – 7.35 (m, 2H), 7.34 – 7.28 (m, 2H), 7.22 (m, 1H), 5.87 (qq, J = 7.0, 1.0 Hz, 1H), 2.04 (qd, *J* = 1.0, 1.0 Hz, 3H), 1.81 (dq, J = 7.0, 1.0 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ_C = 144.2, 135.7, 128.3, 126.5, 125.7, 122.6, 15.6, 14.5.

(*Z*)-but-2-en-2-ylbenzene, 40



40

The spectral data matched that previously reported in the literature.[14]

^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.40 – 7.28 (m, 3H), 7.27 – 7.18 (m, 2H), 5.57 (qq, J = 7.0, 1.5 Hz, 1H), 2.03 (qd, J = 1.5, 1.5 Hz, 3H), 1.60 (dq, J = 7.0, 1.5 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ_C = 142.1, 137.0, 128.2, 128.2, 126.5, 121.7, 25.6, 15.0.

7. X-ray crystallographic analysis of 2

The product **2** was recrystallized from hexane/ethyl acetate. An X-ray diffraction experiment on **2** was carried out at 100(2) K on a Bruker APEX II CCD diffractometer using Mo-K_α radiation (λ = 0.71073 Å). Intensities were integrated[15] and absorption corrections were based on equivalent reflections using SADABS.[16] The structure was solved using Superflip[17,18] and refined against F^2 in SHELXL[19,20] using Olex2[21]. All of the non-hydrogen atoms were refined anisotropically. While all of the hydrogen atoms were located geometrically and refined using a riding model. Crystal structure and refinement data are given in Table 1. Crystallographic data for compound **2** has been deposited with the Cambridge Crystallographic Data Centre CCDC 1534237. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax(+44) 1223 336033, e-mail: deposit@ccdc.cam.ac.uk].

Structure of compound **2** with atomic numbering shown. Ellipsoids depicted at the 50% probability level and hydrogen atoms omitted for clarity:

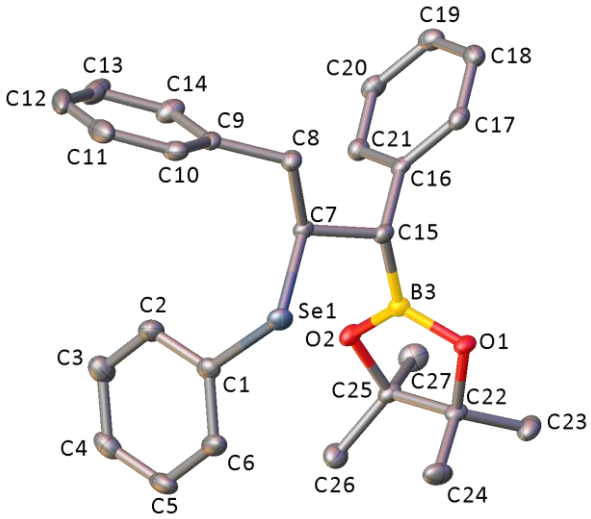


Table 1 Crystal data and structure refinement for 2.

Identification code	rja131_RC
Empirical formula	$C_{27}H_{31}BO_2Se$
Formula weight	477.29
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.4862(5)
b/Å	11.7144(5)
c/Å	20.1408(9)
β/°	102.032(3)
Volume/Å^3	2419.74(19)
Z	4
ρ_{calc}g/cm^3	1.310
μ/mm^{-1}	1.572
F(000)	992.0
Crystal size/mm^3	0.498 × 0.275 × 0.15
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.046 to 60.498
Index ranges	-14 ≤ h ≤ 14, -13 ≤ k ≤ 16, -28 ≤ l ≤ 28
Reflections collected	53076
R_{int} / R_{sigma}	0.0576 / 0.0364]
Data/restraints/parameters	7168/0/284
Goodness-of-fit on F^2	1.014
Final R indexes [I>=2σ (I)]	R_1 = 0.0328, wR_2 = 0.0697
Final R indexes [all data]	R_1 = 0.0494, wR_2 = 0.0754
Largest diff. peak/hole / e Å^{-3}	0.72/-0.34

8. References

[1] A. B. Pangborn, M. A. Gairdello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics*, **1996**, *15*, 1518.

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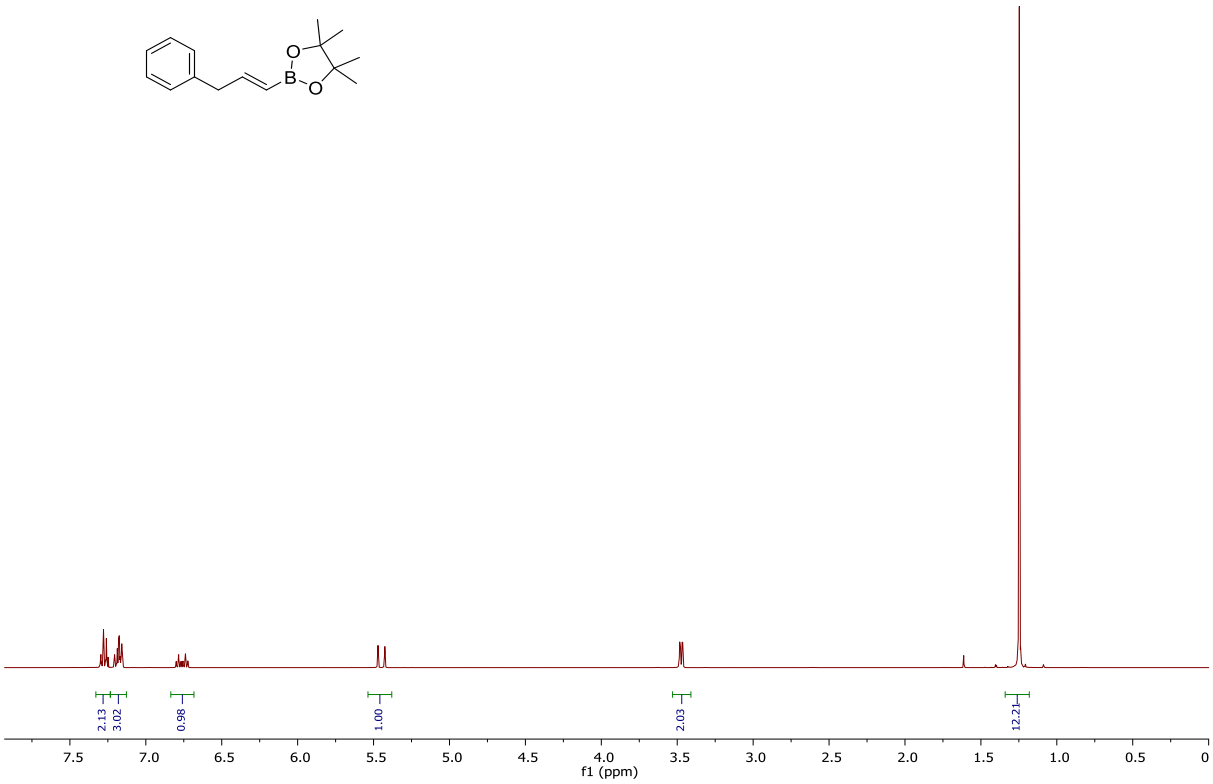
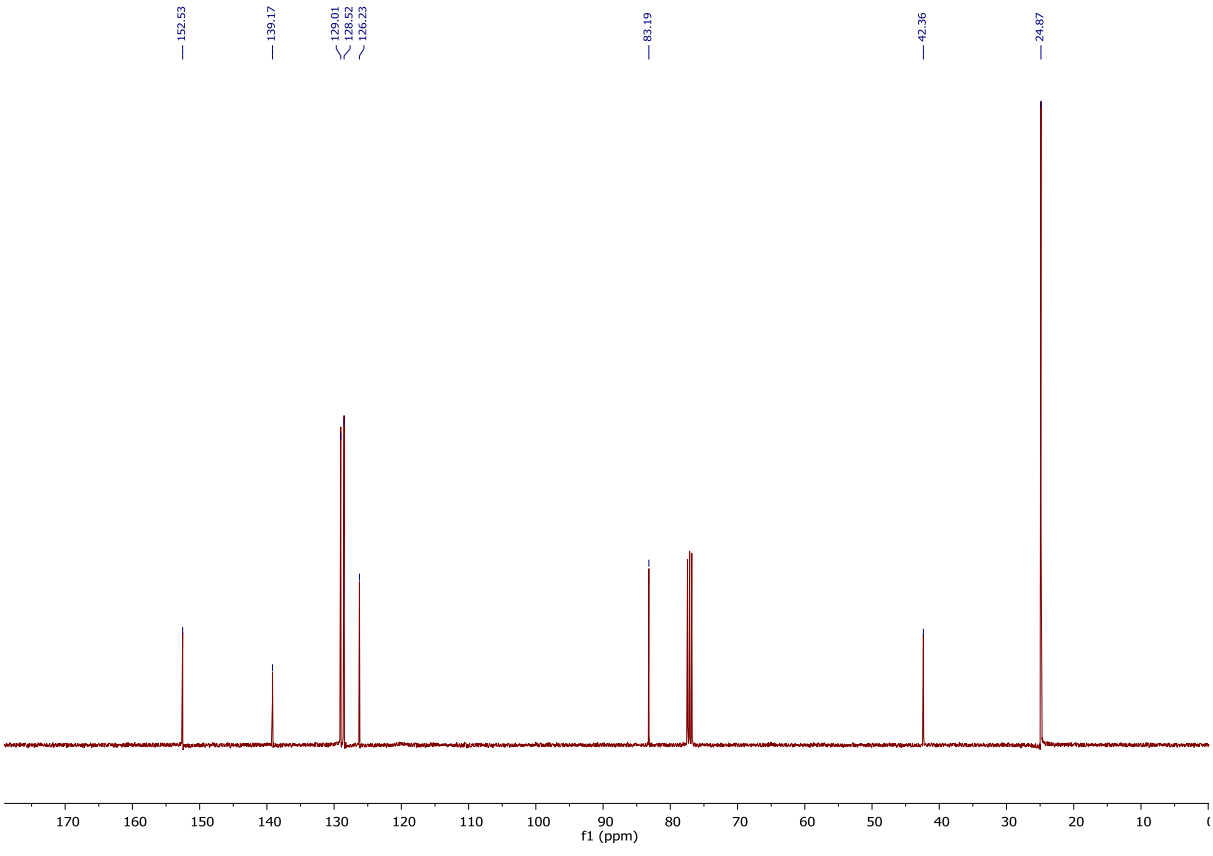
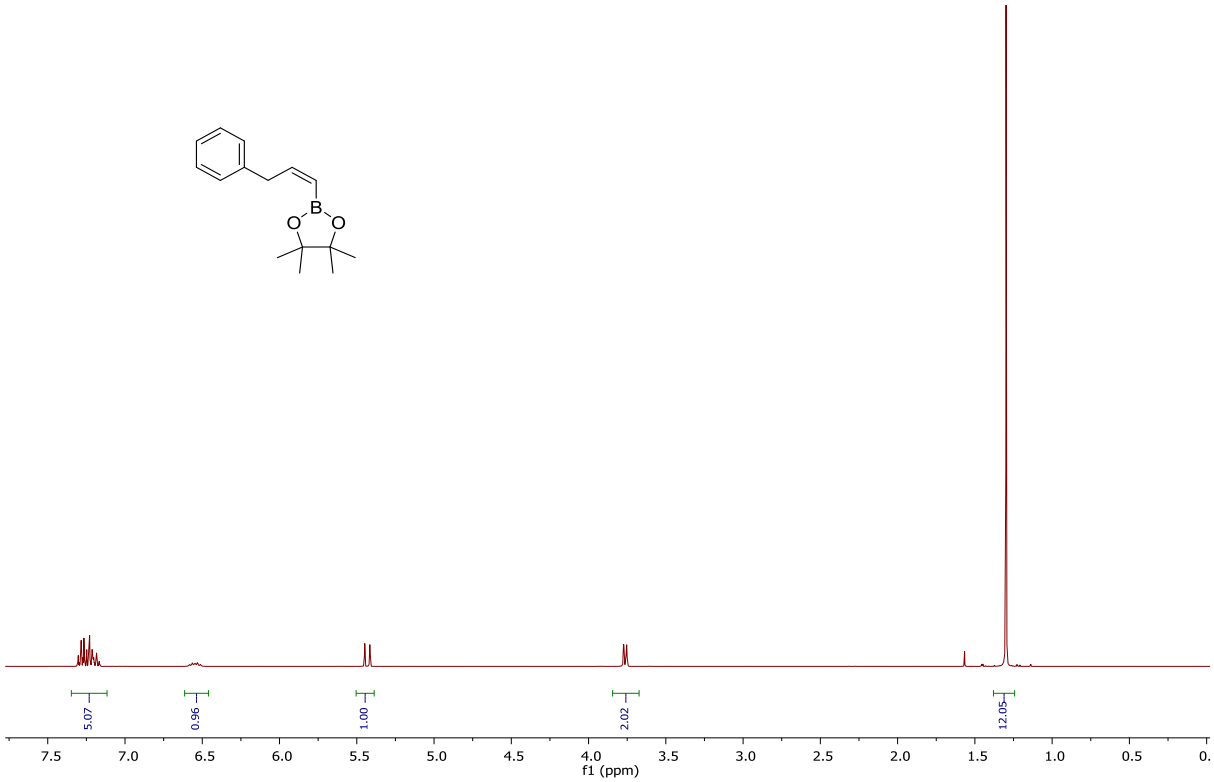
9. NMR Spectra



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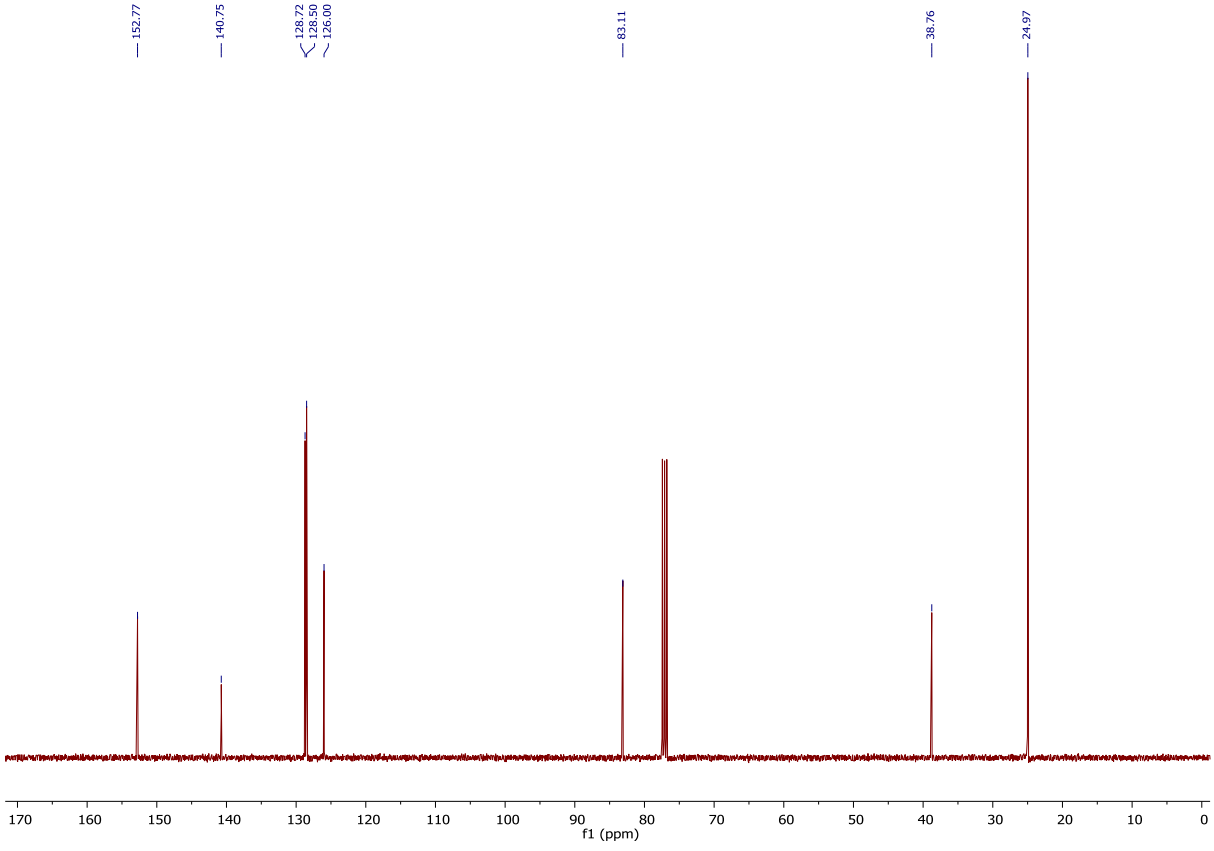
O
O
5.07
0.96
1.00
2.02
12.05
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)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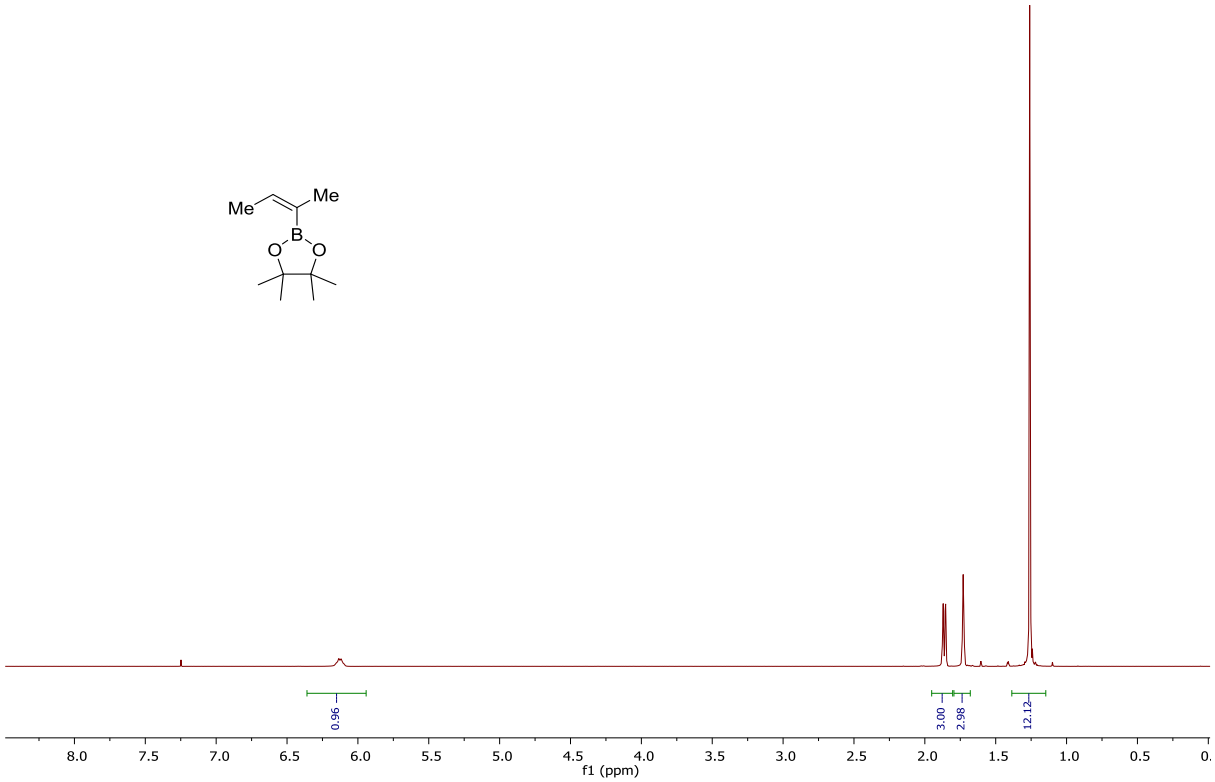
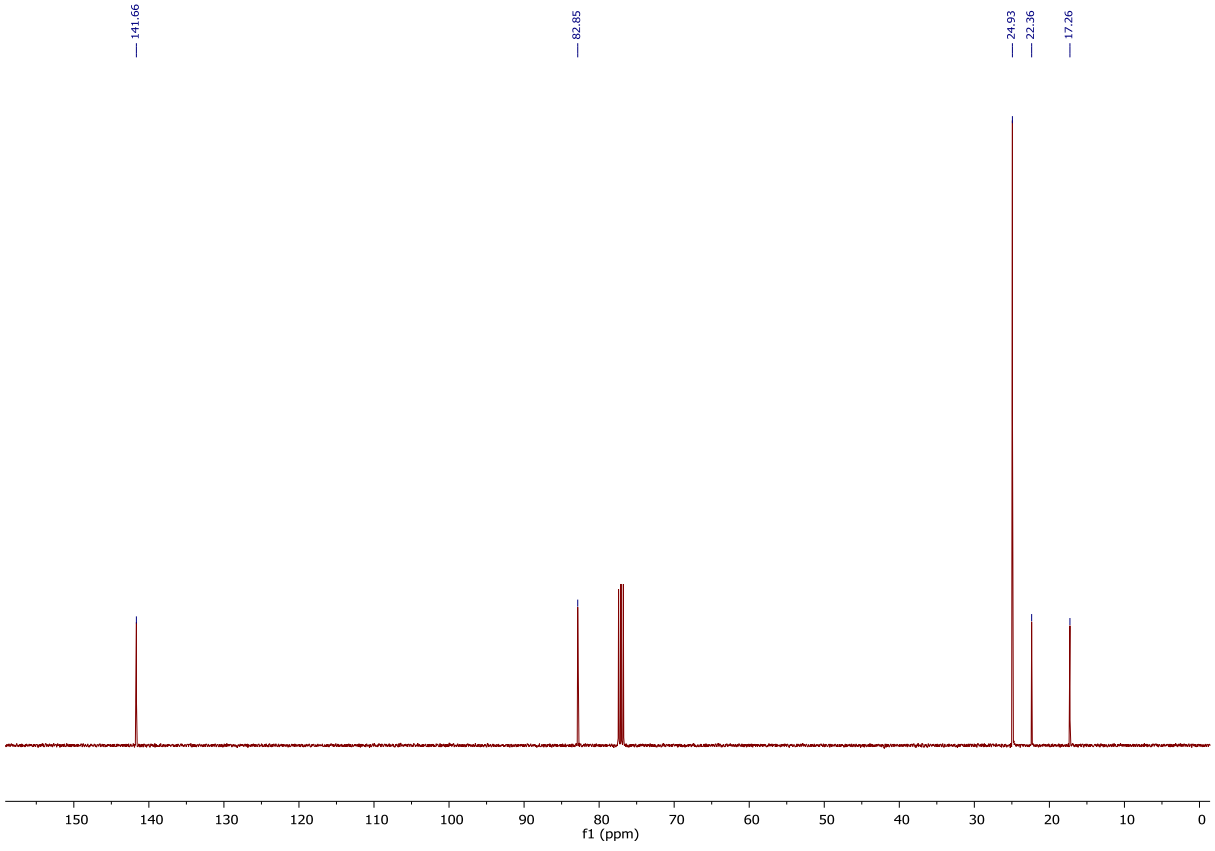
140.75
128.72
128.50
126.00
83.11
38.76
24.97
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Me
Me
B
O
O
0.96
3.00
2.98
12.12
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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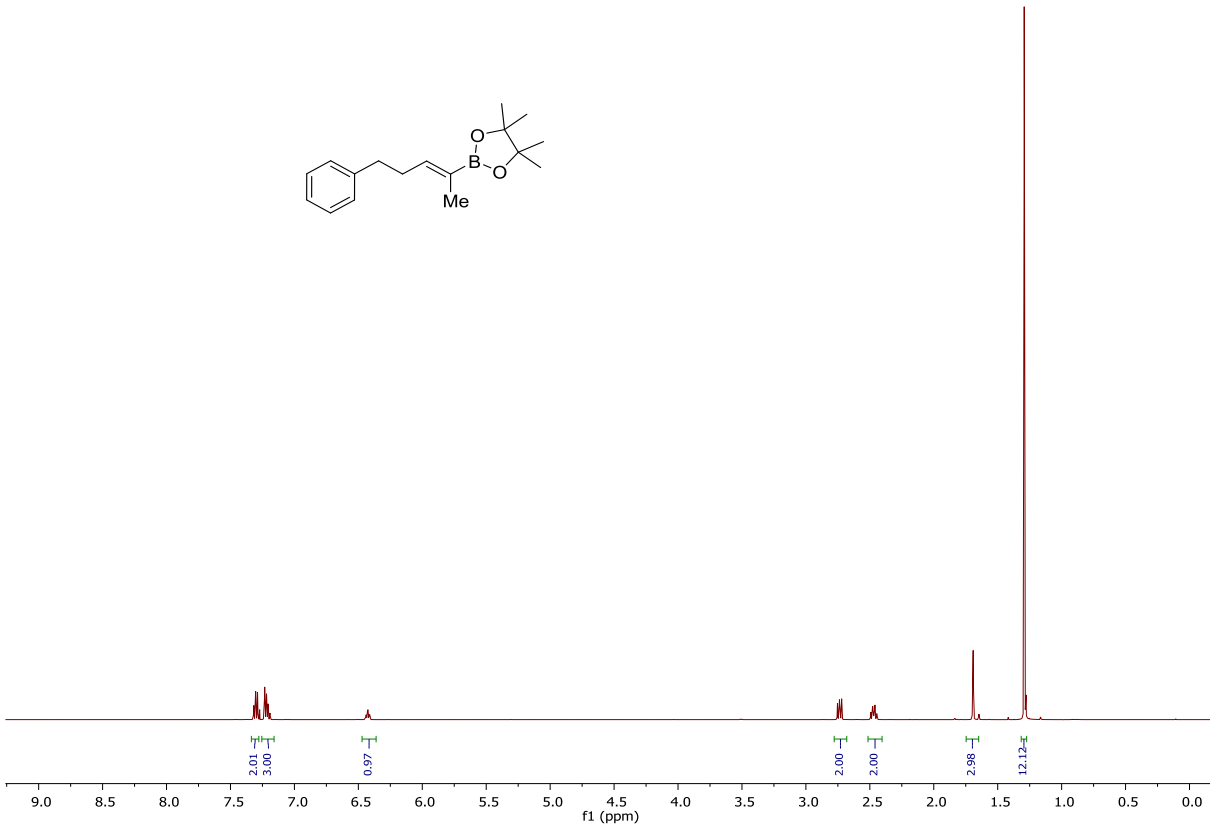
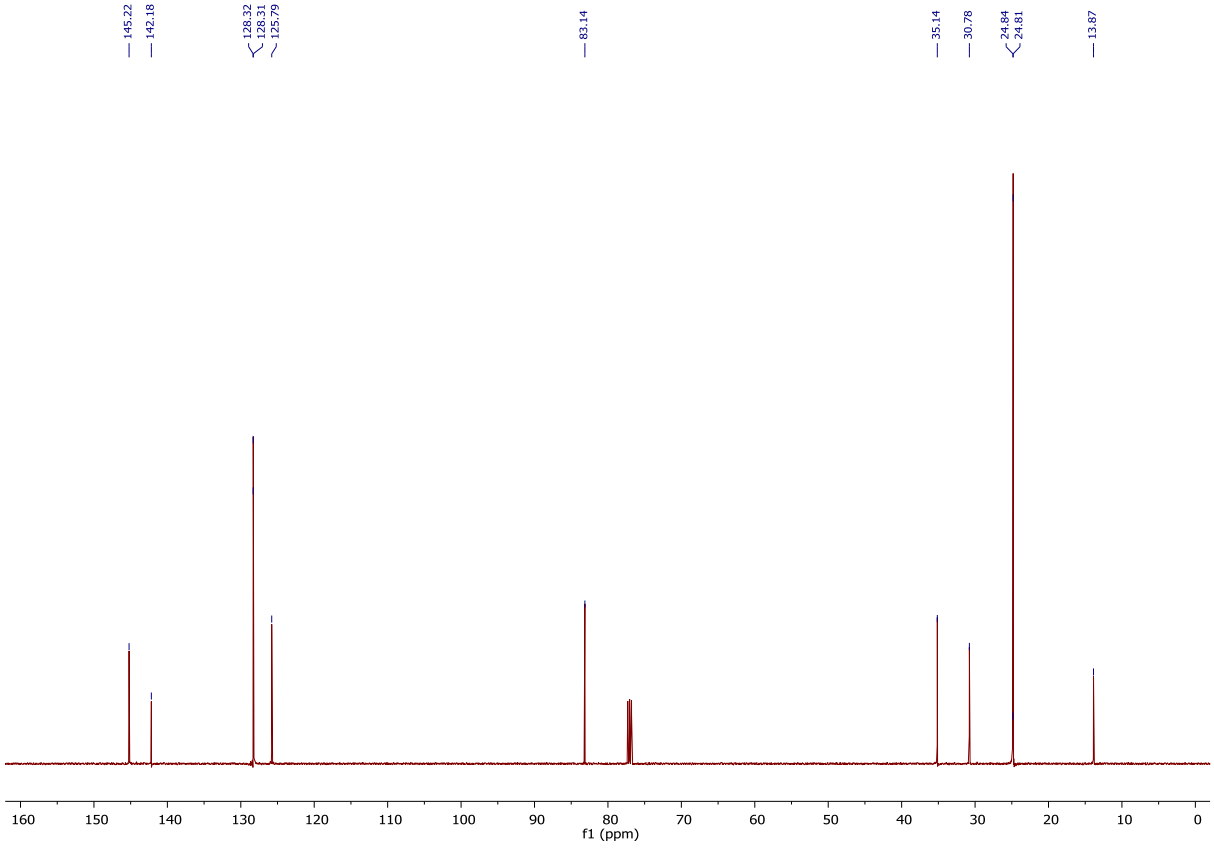
82.85
24.93
22.36
17.26
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
B
O
Me
2.01
3.00
0.97
2.00
2.00
2.98
12.12
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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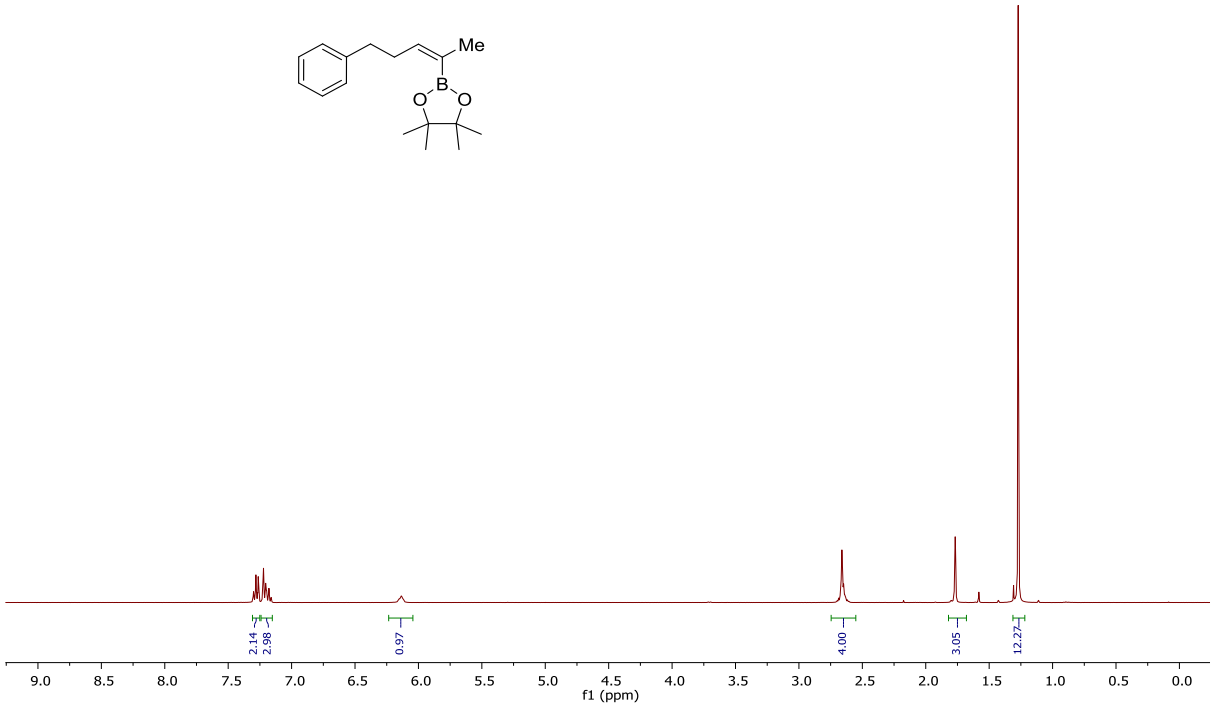
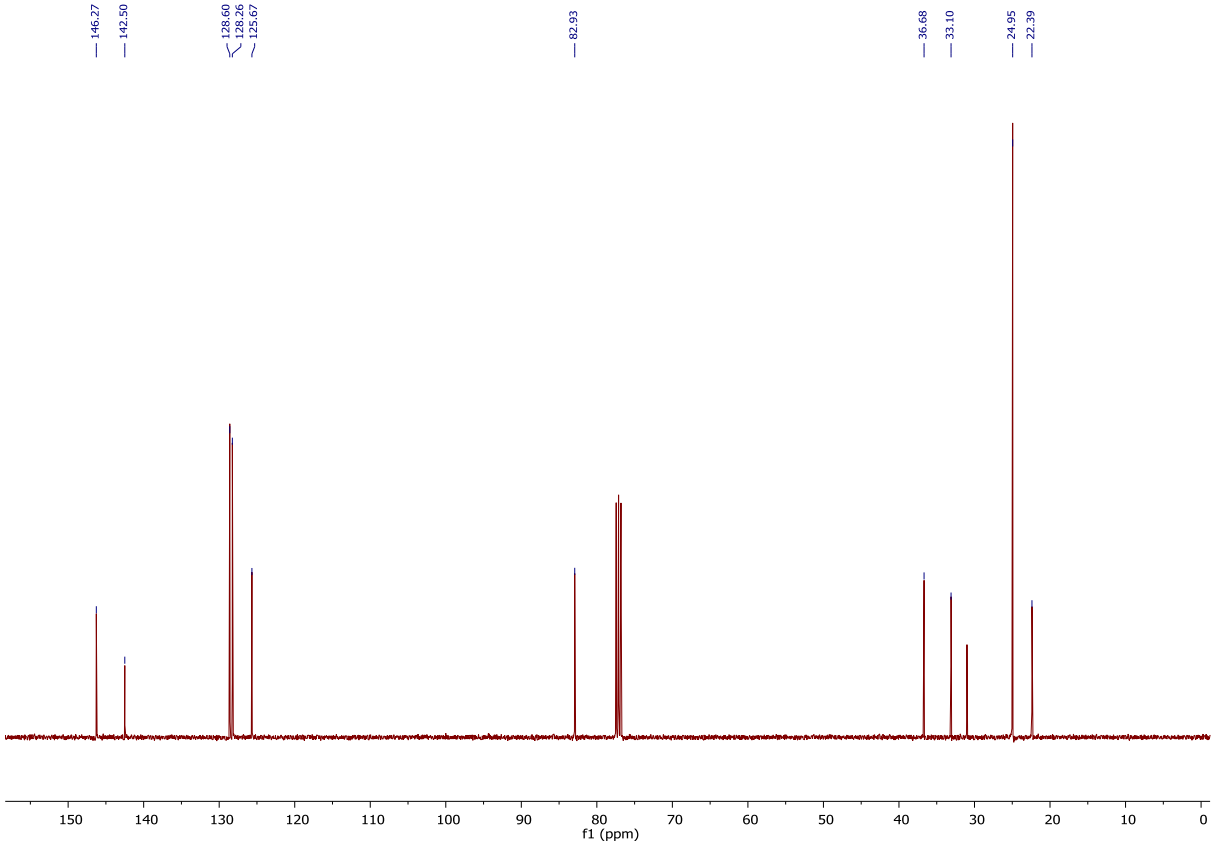
142.18
128.32
128.31
125.79
83.14
35.14
30.78
24.84
24.81
13.87
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Me
B
O
O
2.14
2.98
0.97
4.00
3.05
12.27
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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142.50
128.60
128.26
125.67
82.93
36.68
33.10
24.95
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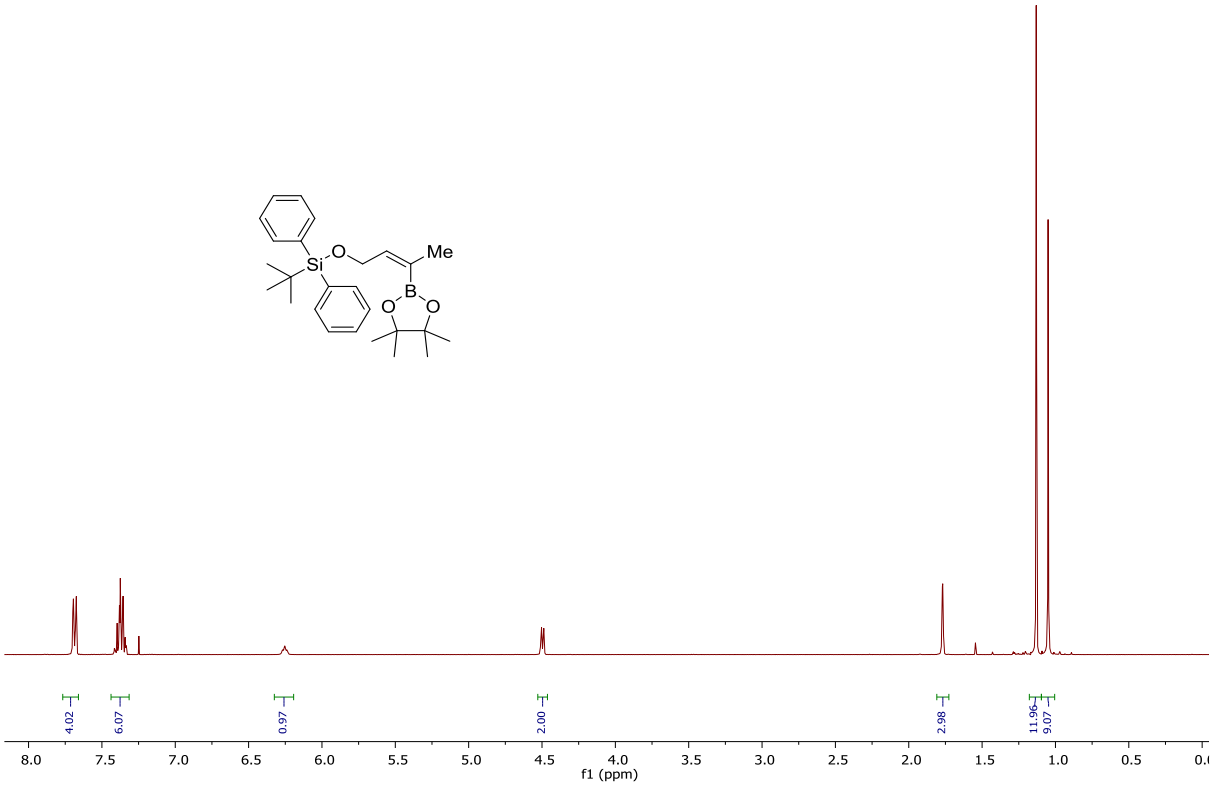
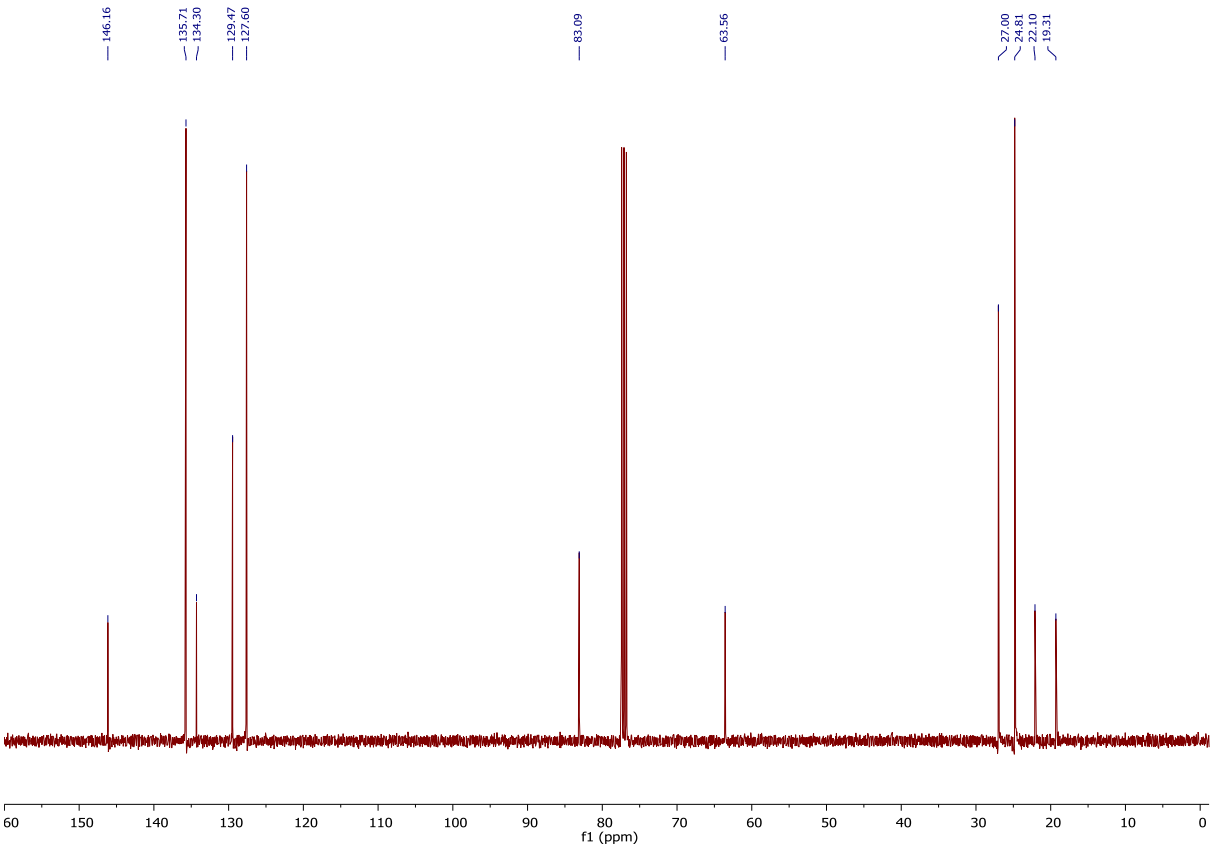
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Si
O
Me
B
O
O
4.02
6.07
0.97
2.00
2.98
11.96
9.07
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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134.30
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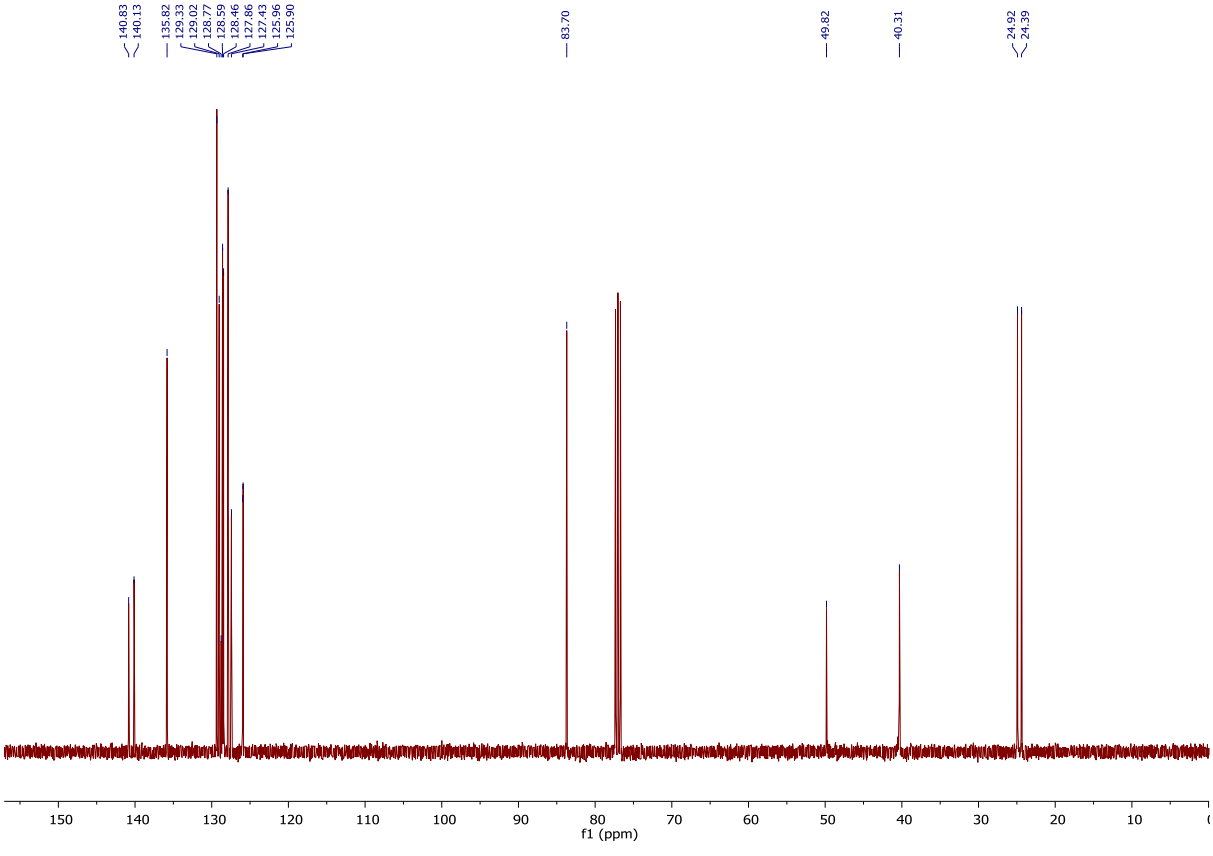
83.09
63.56
27.00
24.81
22.10
19.31
60
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Se
O
B
O

2.05
11.54
1.99
1.00
0.99
0.98
0.97
12.49
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)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125.96
125.90
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49.82
40.31
24.92
24.39
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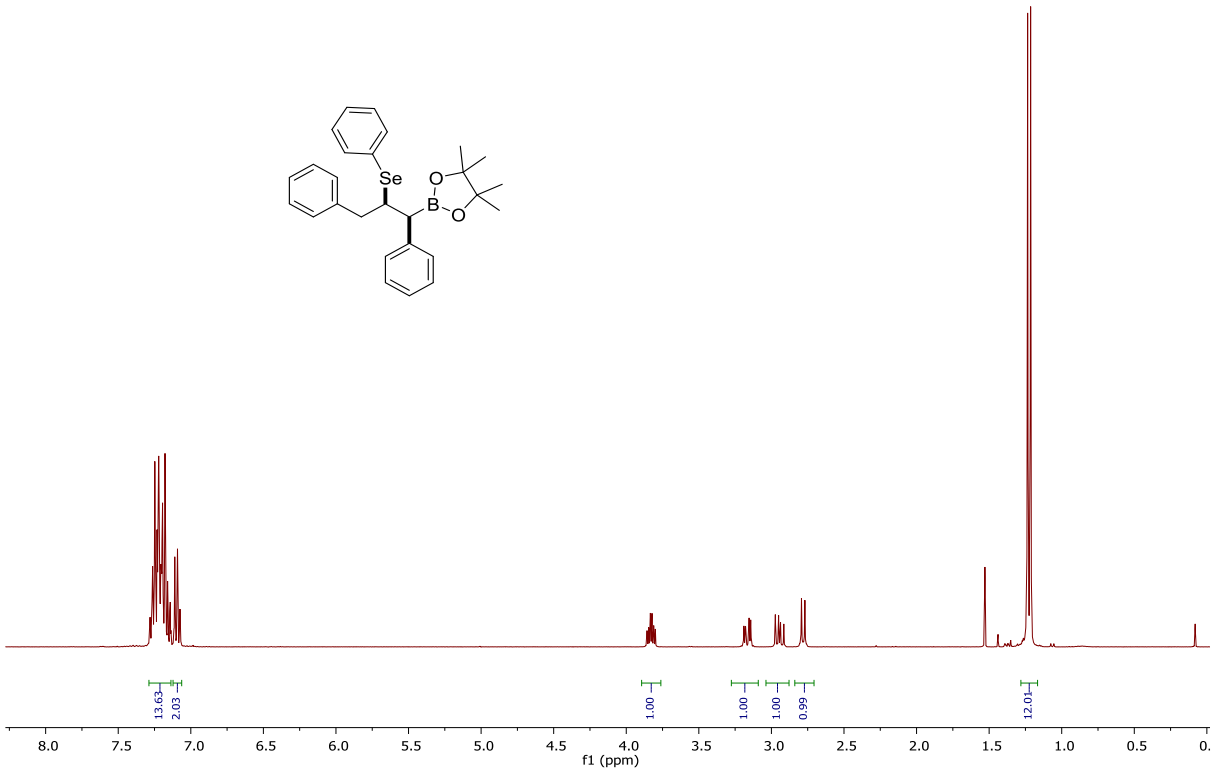
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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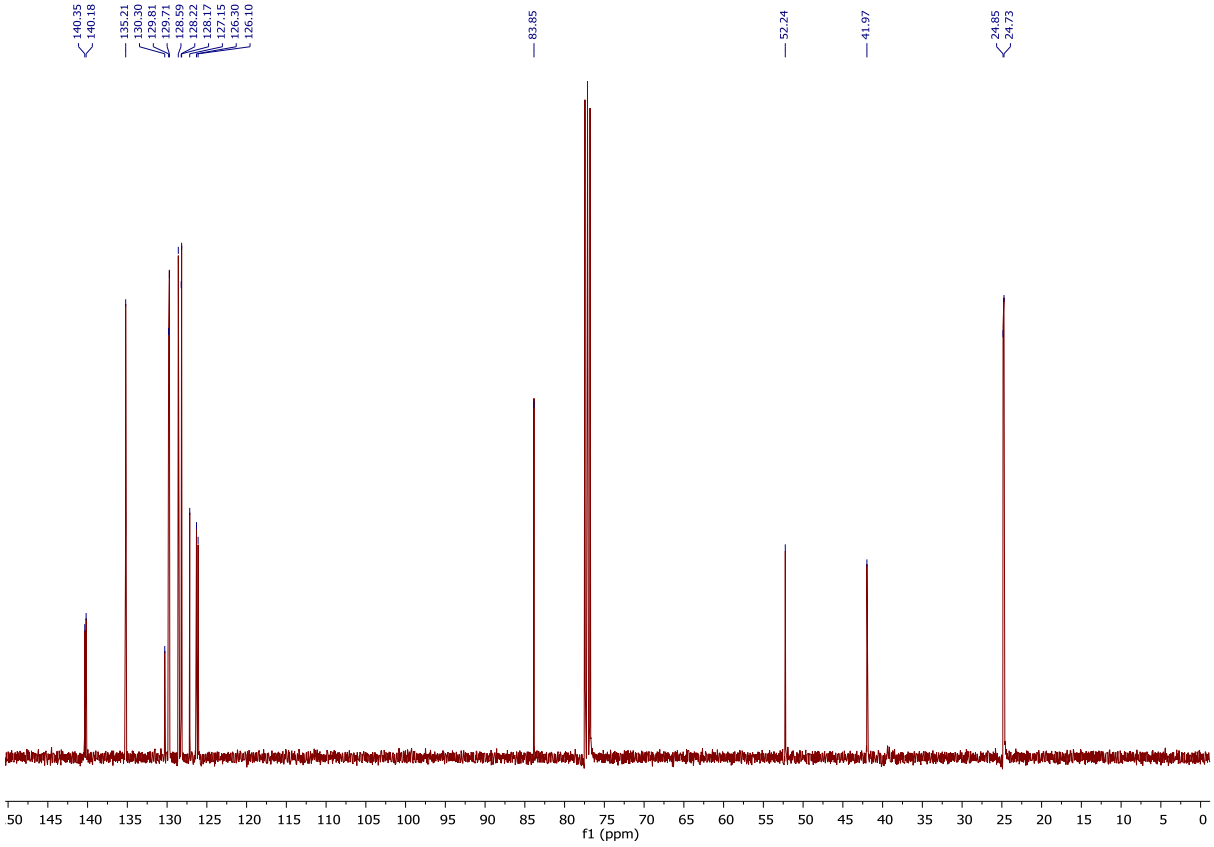
B
O
13.63
2.03
1.00
1.00
1.00
0.99
12.01
f1 (ppm)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129.71
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127.15
126.30
126.10
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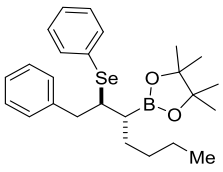
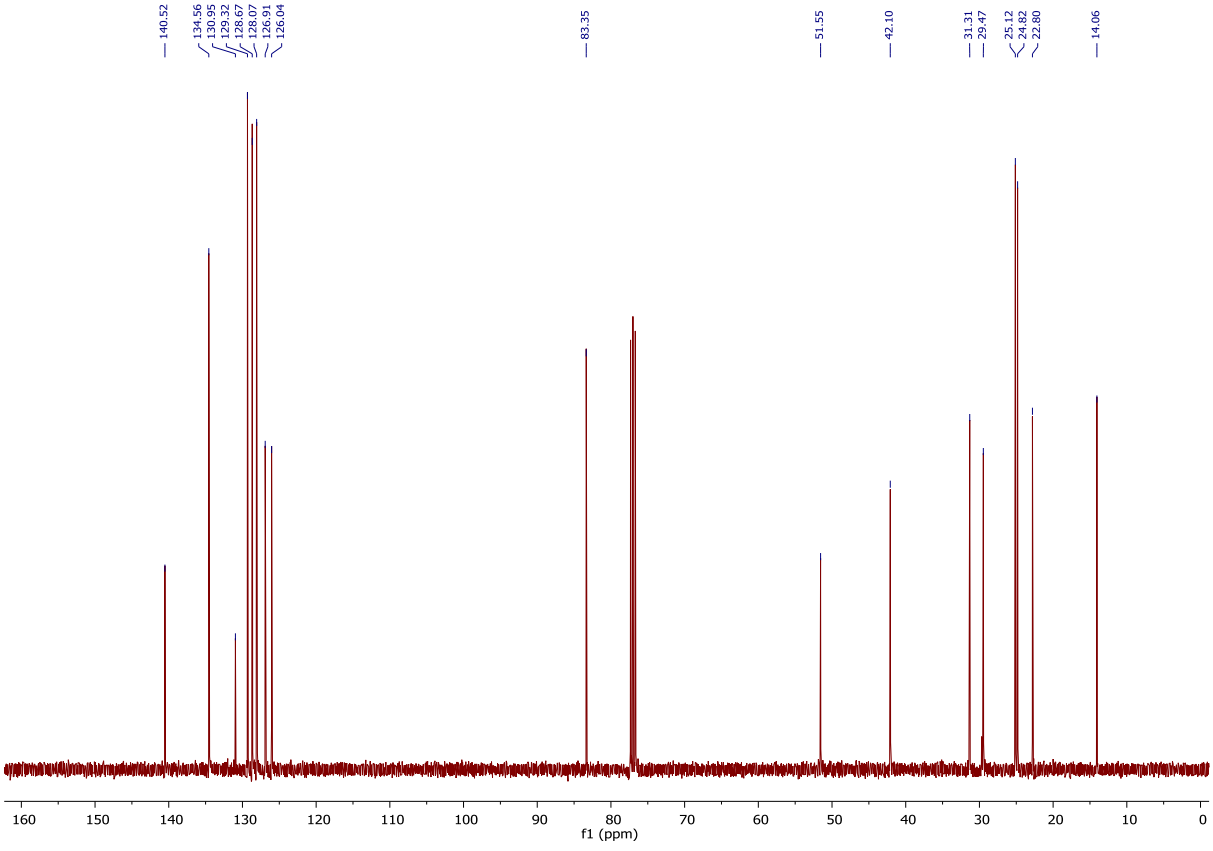
52.24
41.97
24.85
24.73
f1 (ppm)


Se
O
B
O
Me

1.99
8.11
0.98
0.97
0.96
2.08
1.06
16.40
2.93
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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126.04
83.35
51.55
42.10
31.31
29.47
25.12
24.82
22.80
14.06
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140
130
120
110
100
90
80
70
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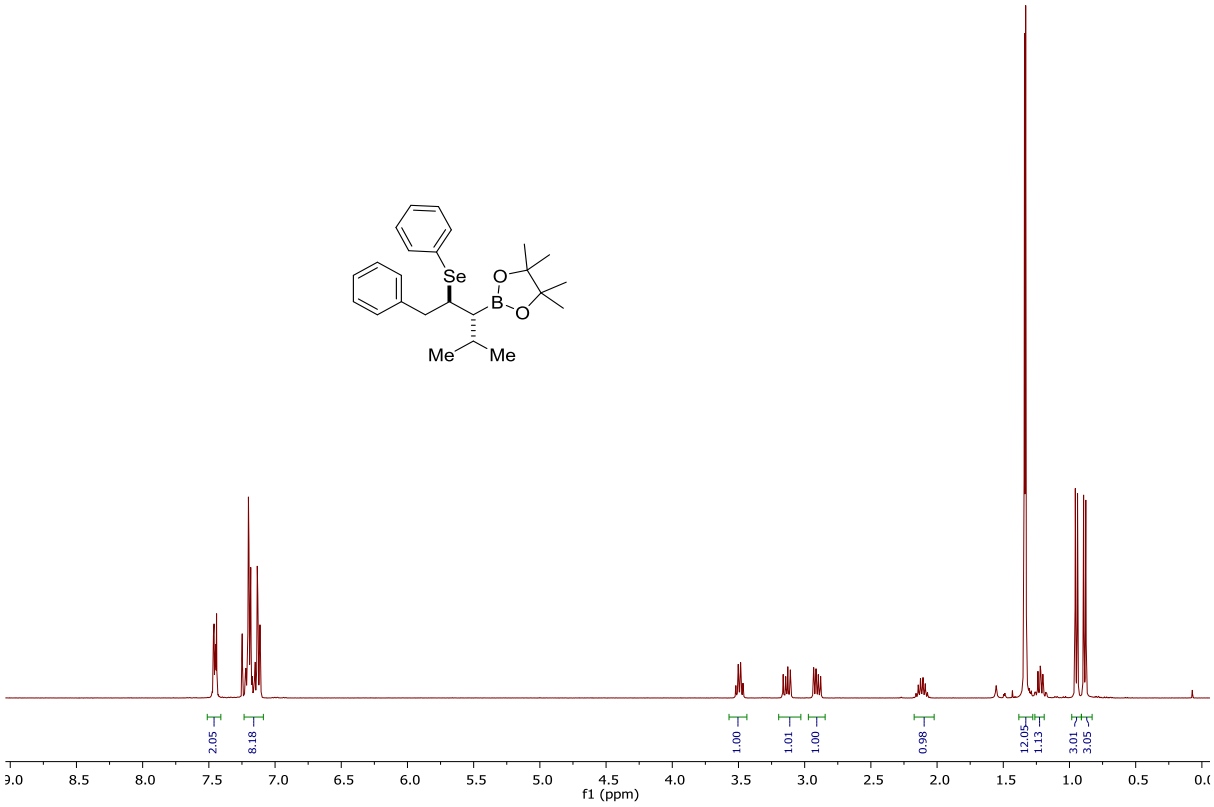
50
40
30
20
10
0
f1 (ppm)


Se
O
B
O
Me
Me
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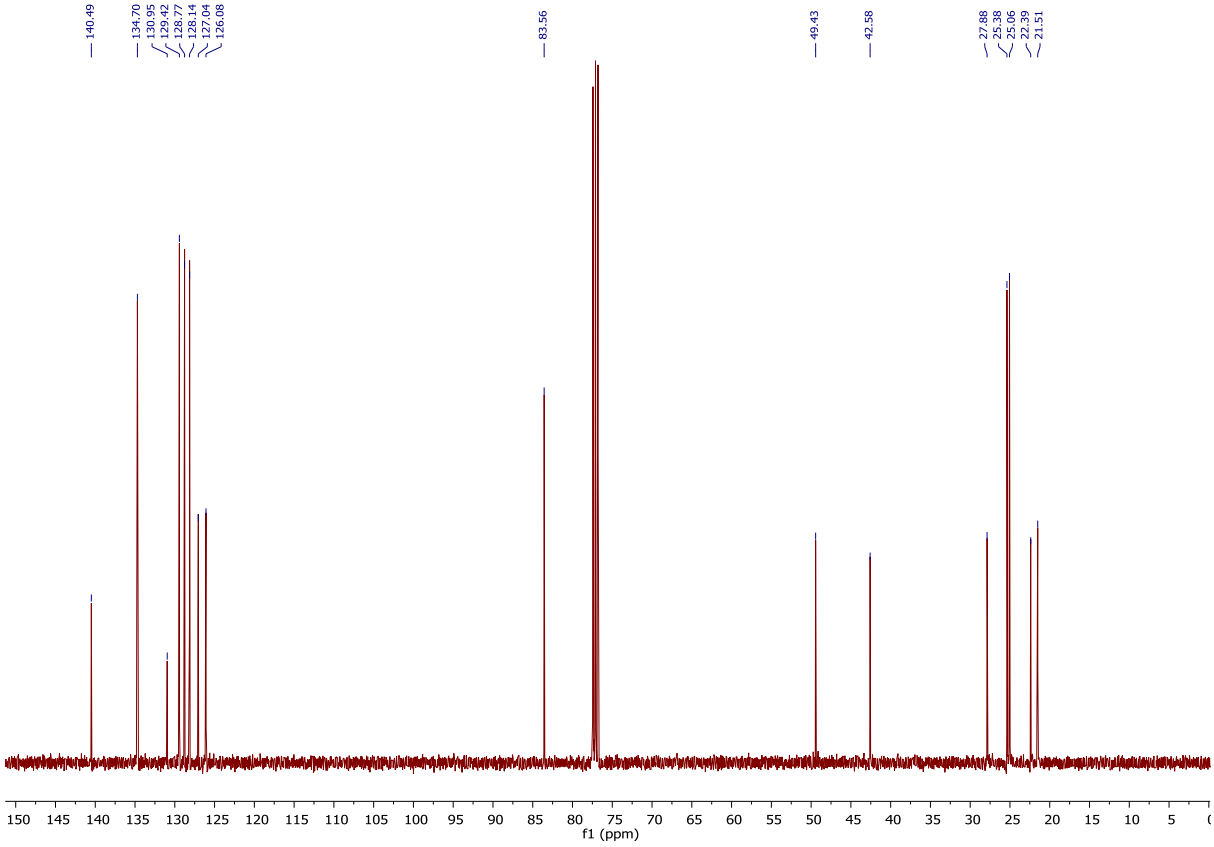
1.01
1.00
0.98
12.05
1.13
3.01
3.05
f1 (ppm)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128.14
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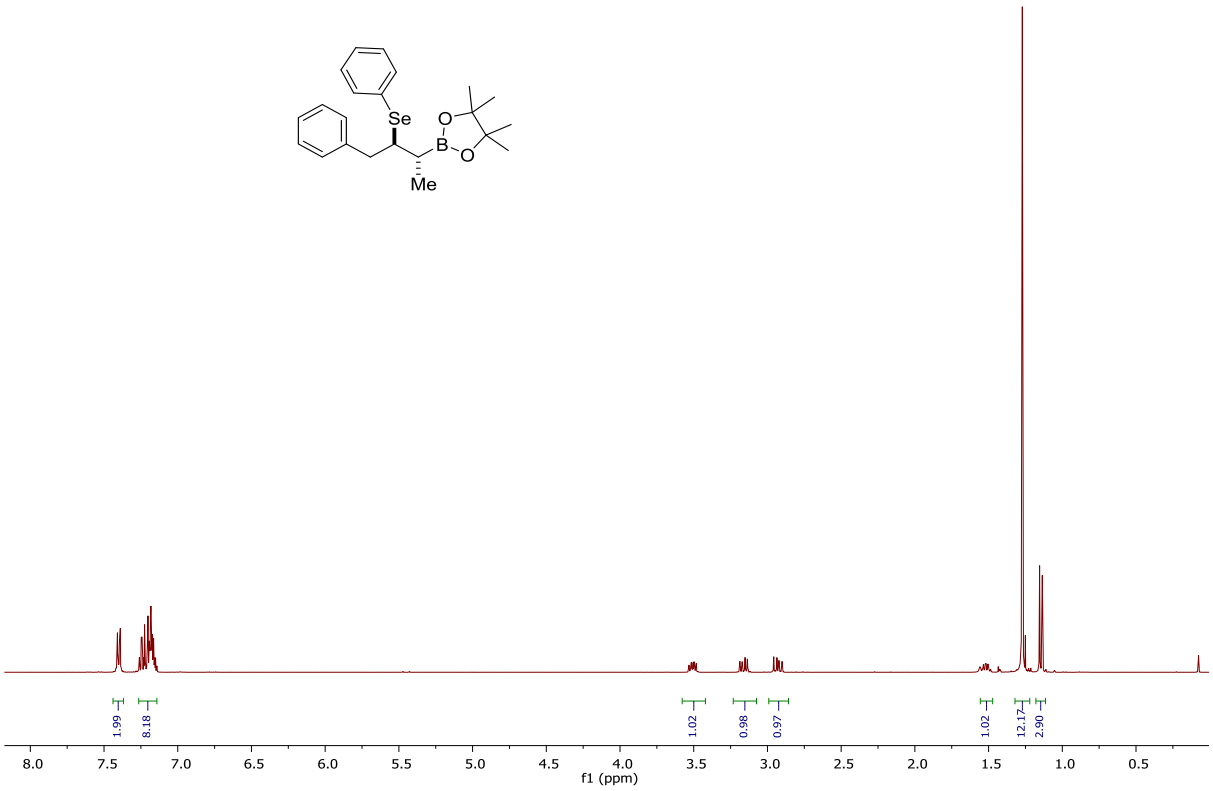
49.43
42.58
27.88
25.38
25.06
22.39
21.51
f1 (ppm)


Se
O
B
O
Me
1.99
8.18
1.02
0.98
0.97
1.02
12.17
2.90
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
3.5
3.0
2.5
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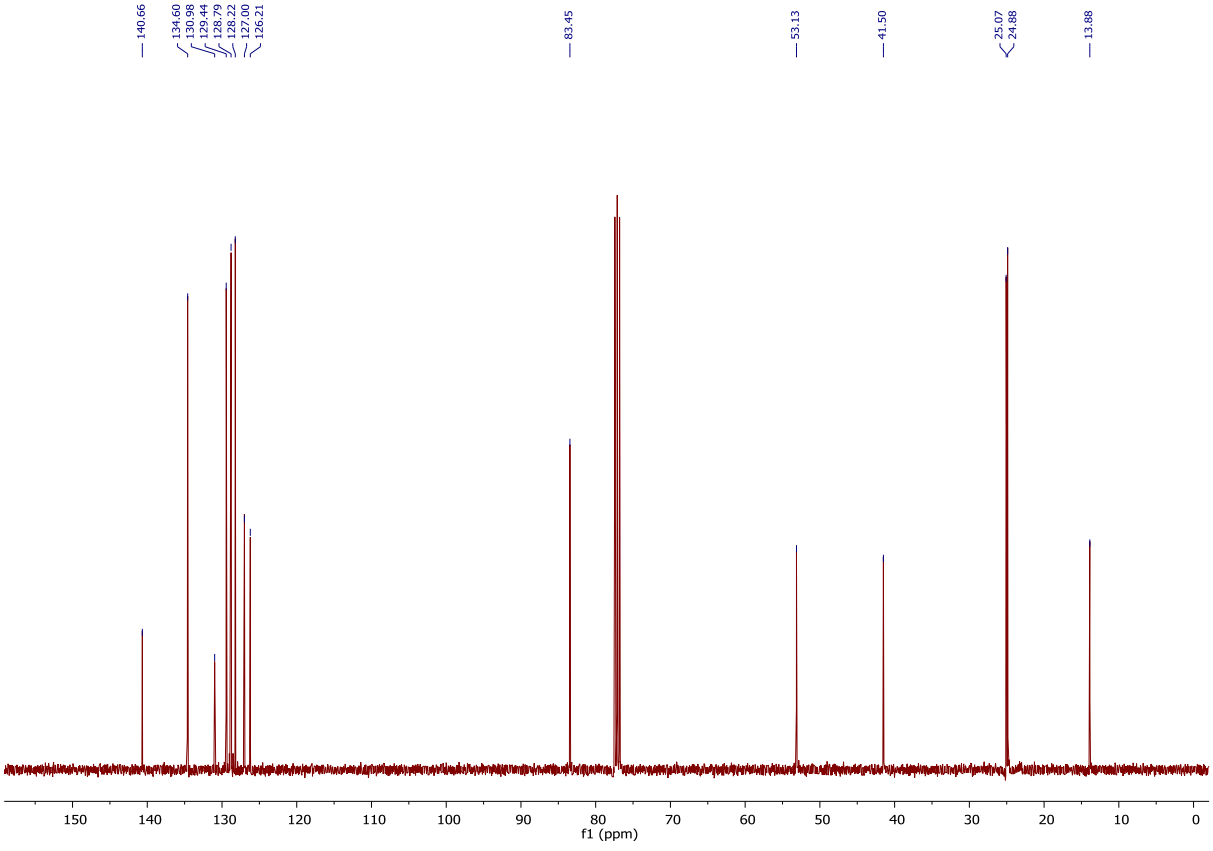
1.5
1.0
0.5
f1 (ppm)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24.88
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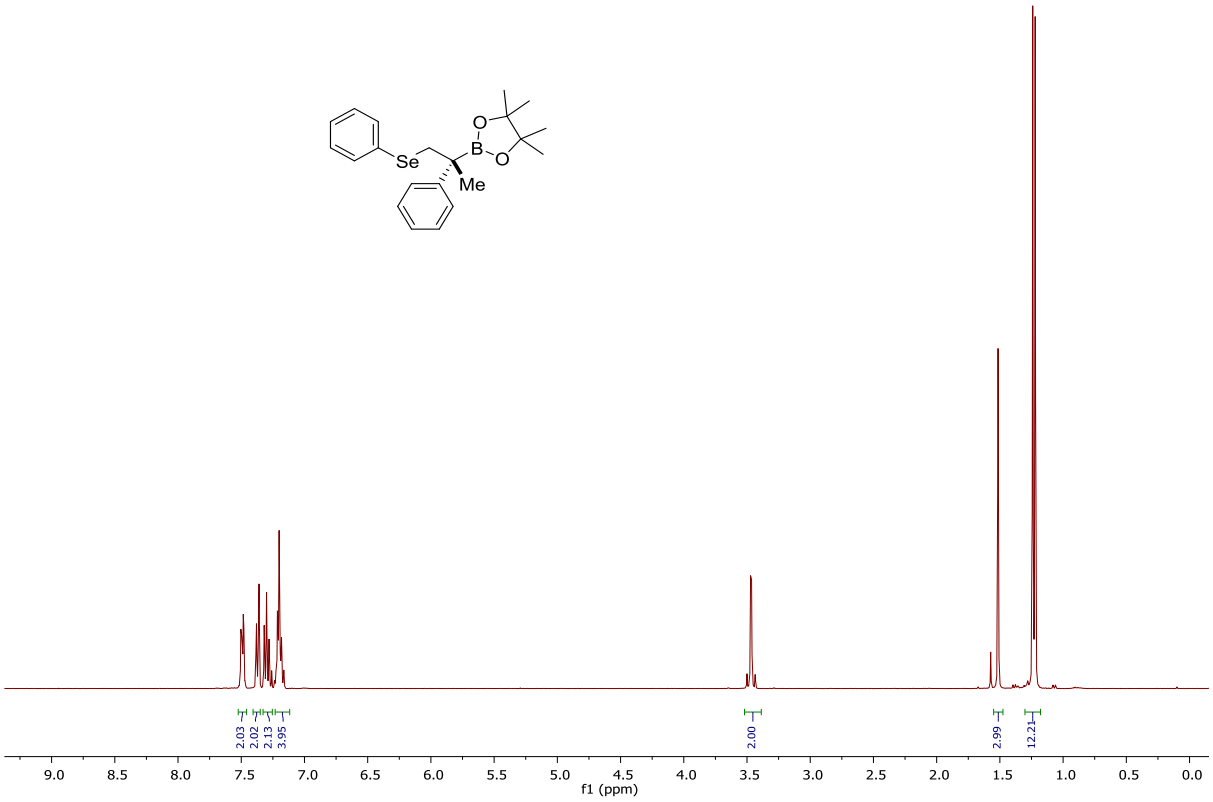
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Se
B
O
O
Me
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2.02
2.13
3.95
2.00
2.99
12.21
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8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.5
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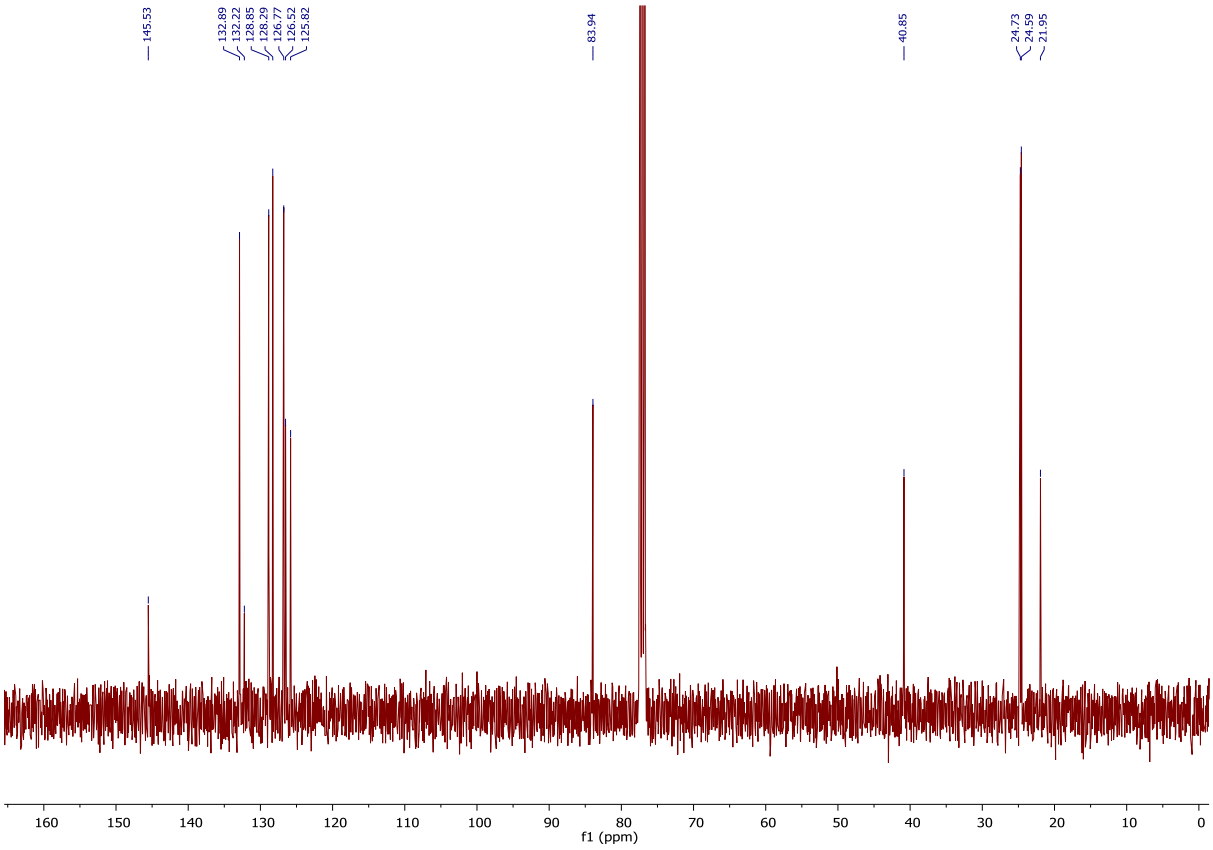
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150
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130
120
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90
80
70
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50
40
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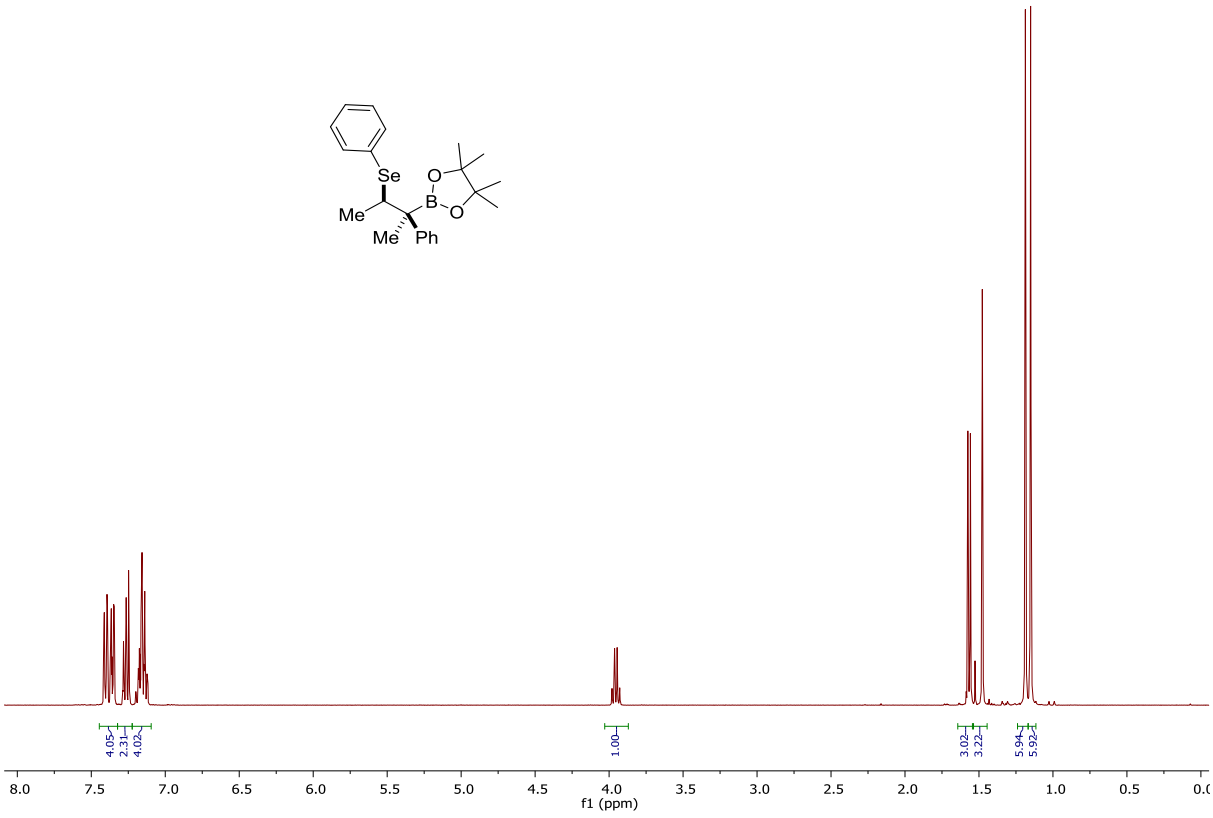
10
0
f1 (ppm)


Se
Me
Me
Ph
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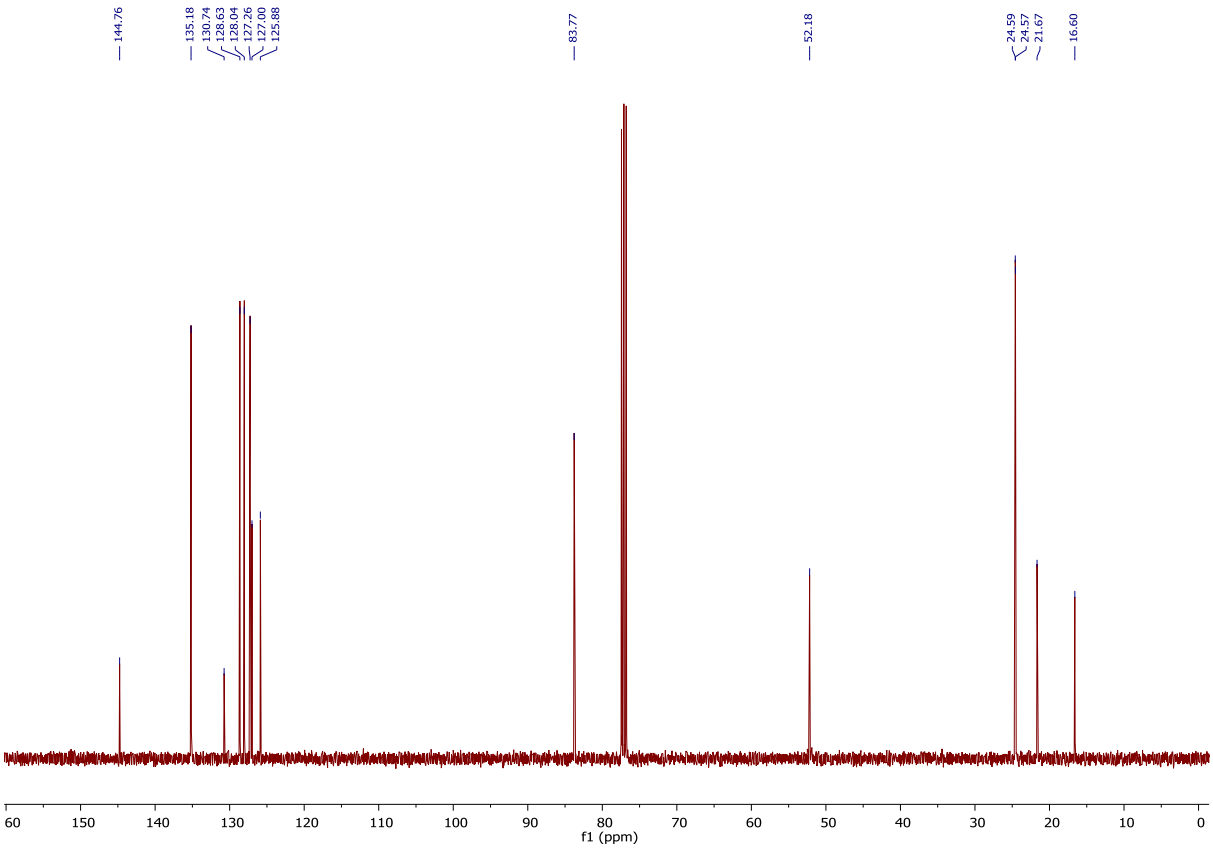
4.02
1.00
3.02
3.22
5.94
5.92
f1 (ppm)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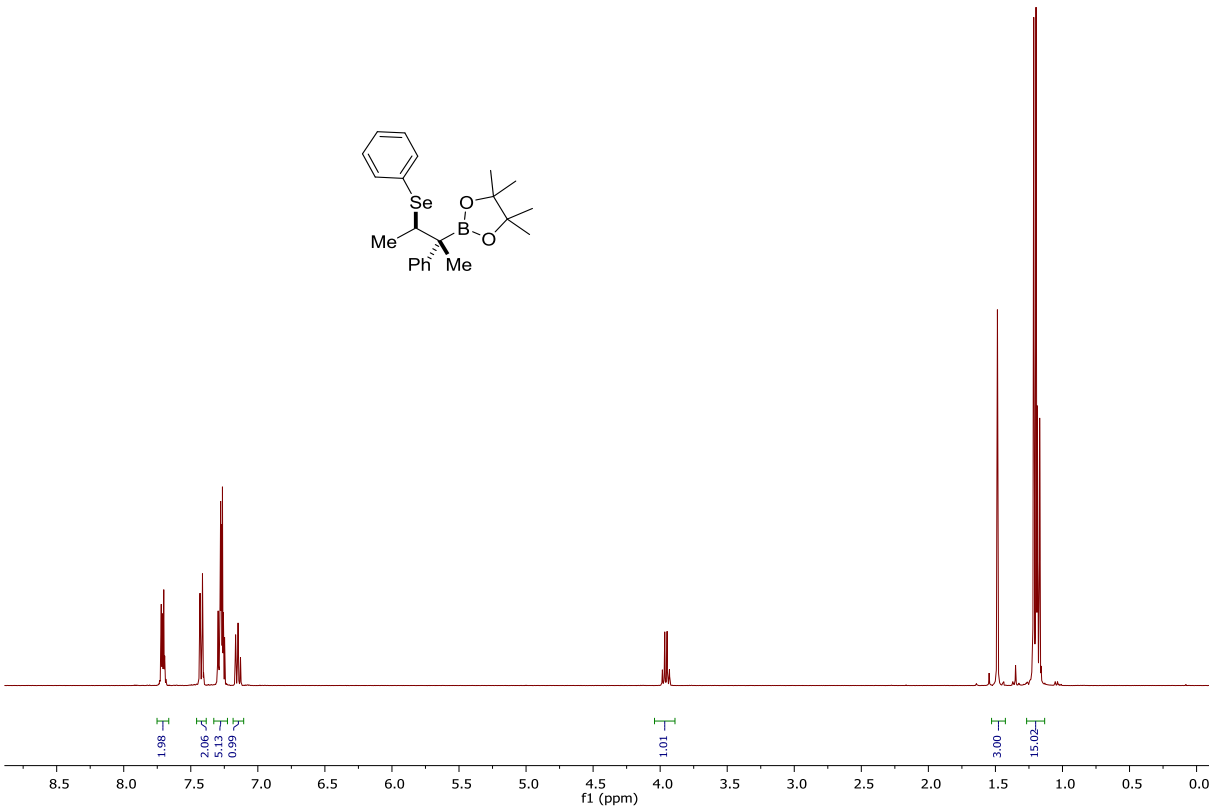
24.57
21.67
16.60
f1 (ppm)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Me
Ph
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B
O
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2.06
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0.99
1.01
3.00
15.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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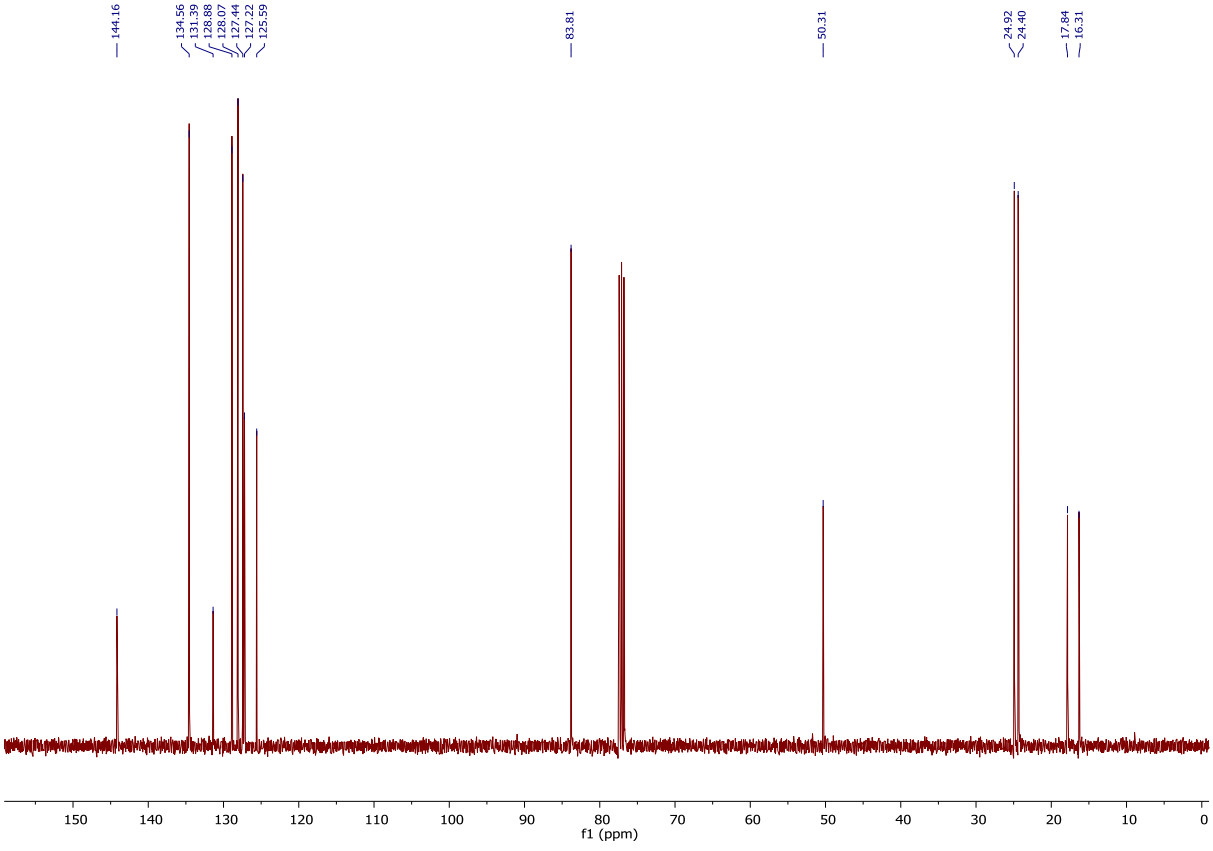
0.0
f1 (ppm)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24.92
24.40
17.84
16.31
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130
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100
90
80
70
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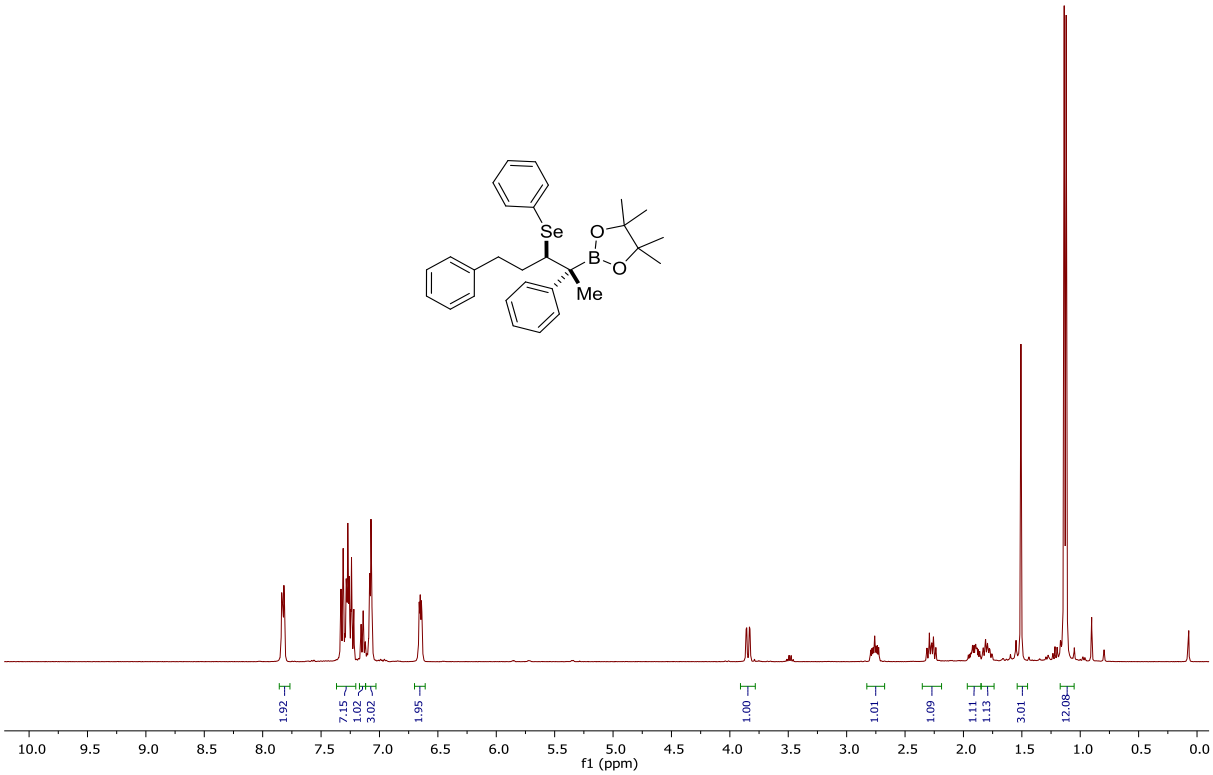
50
40
30
20
10
0
f1 (ppm)


Se
O
B
O
Me
1.92
7.15
1.02
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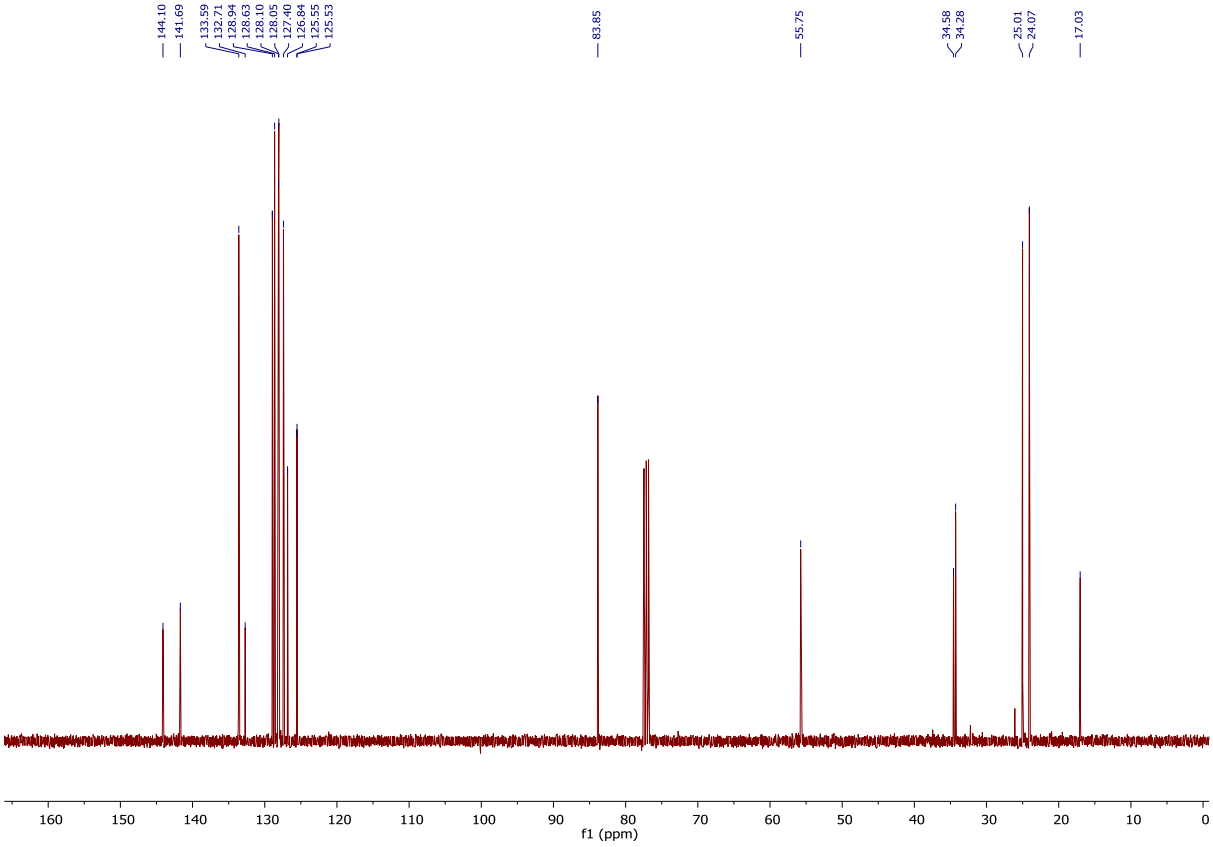
1.95
1.00
1.01
1.09
1.11
1.13
3.01
12.08
f1 (ppm)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133.59
132.71
128.94
128.63
128.10
128.05
127.40
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125.55
125.53
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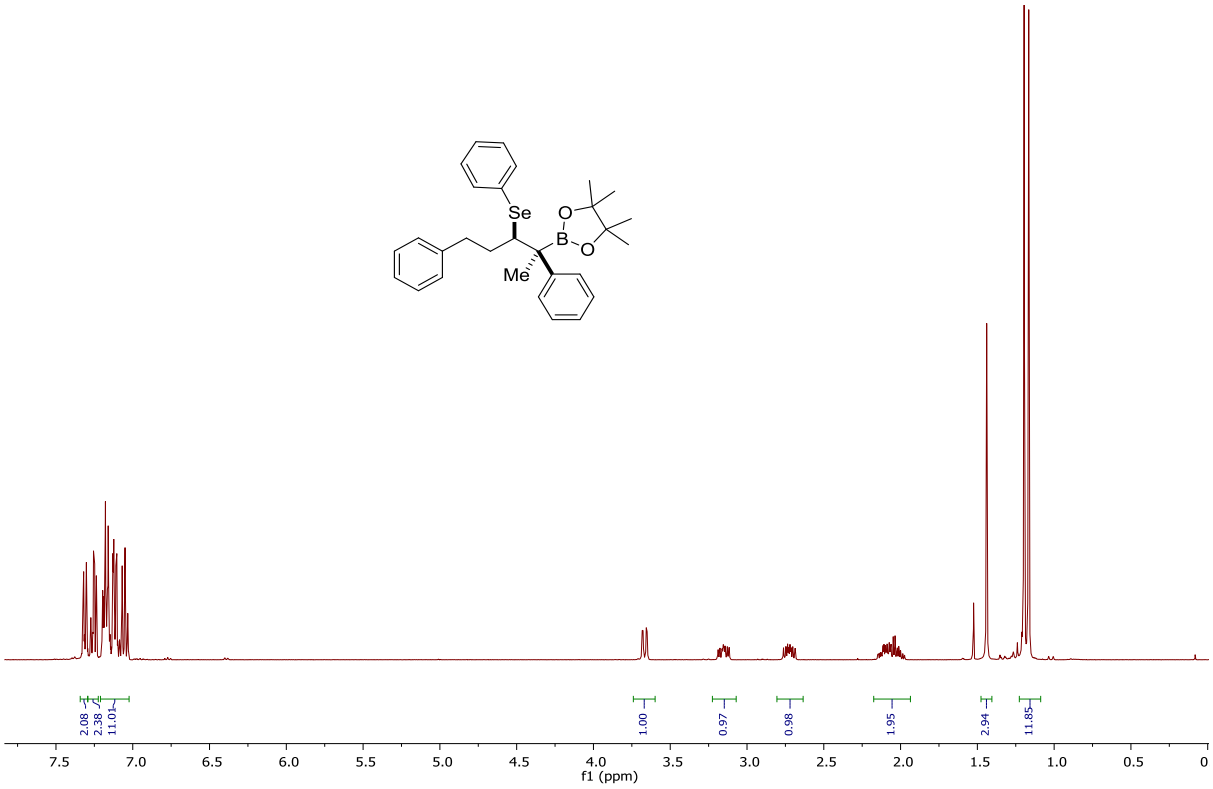
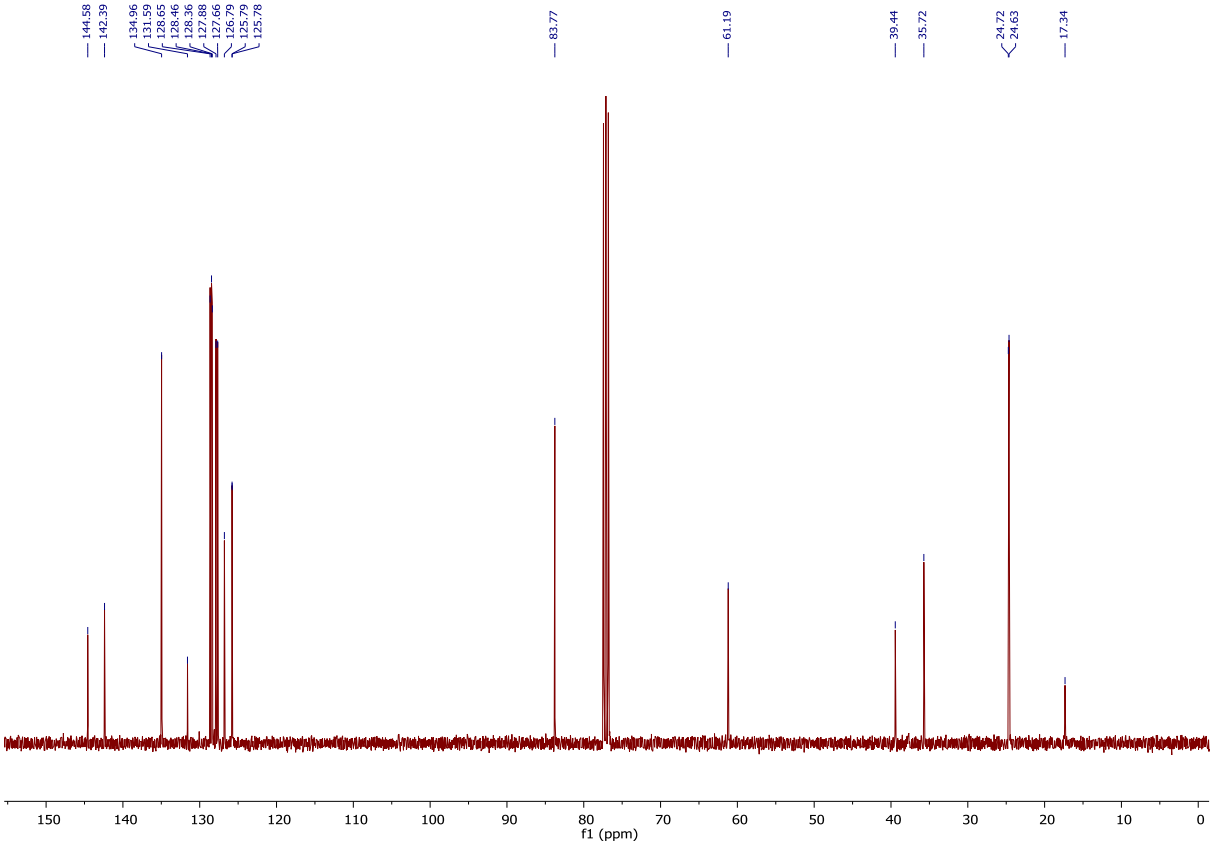
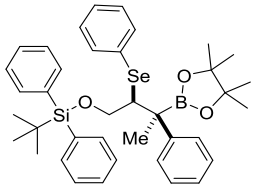
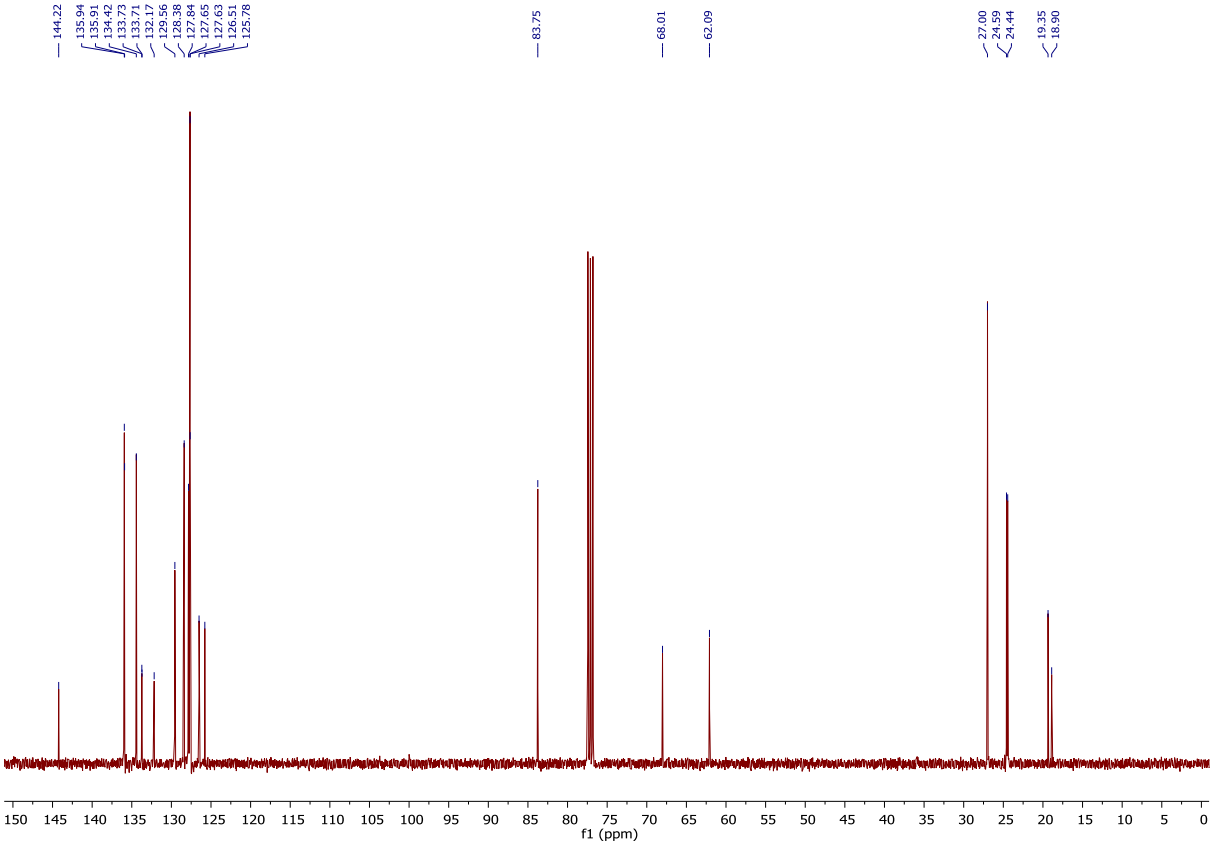
55.75
34.58
34.28
25.01
24.07
17.03
f1 (ppm)

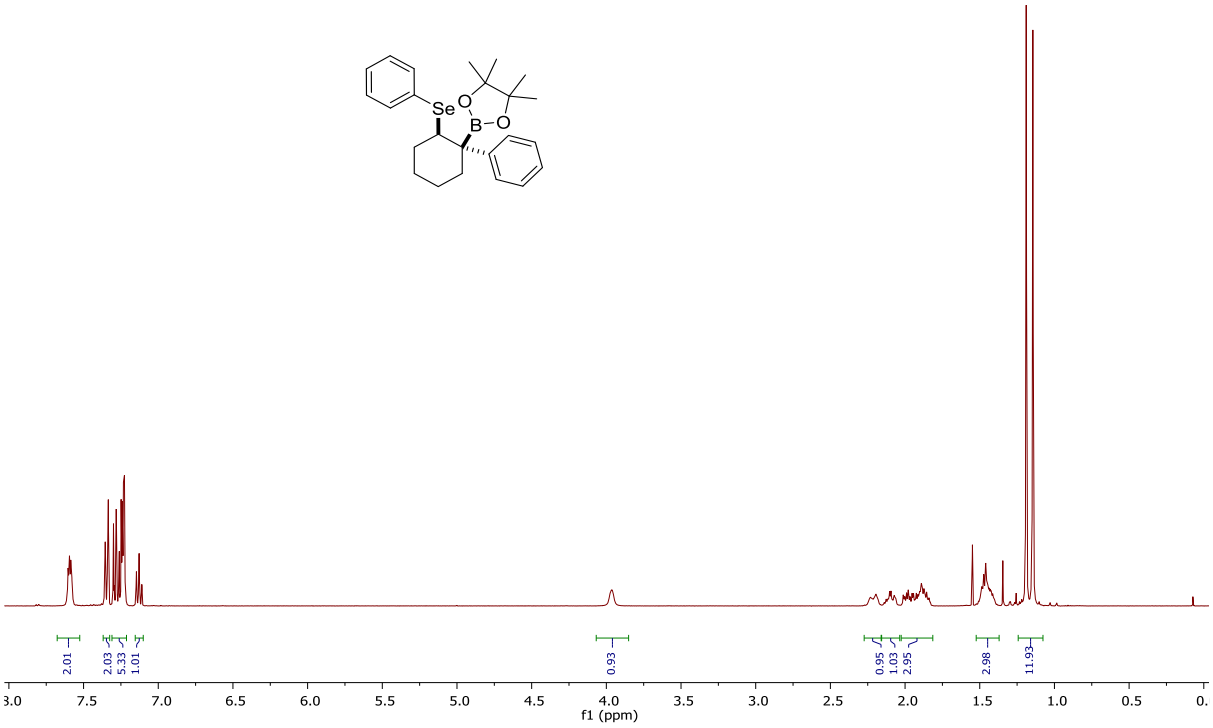

Se
O
B
O
Me
2.08
2.38
11.01
1.00
0.97
0.98
1.95
2.94
11.85
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

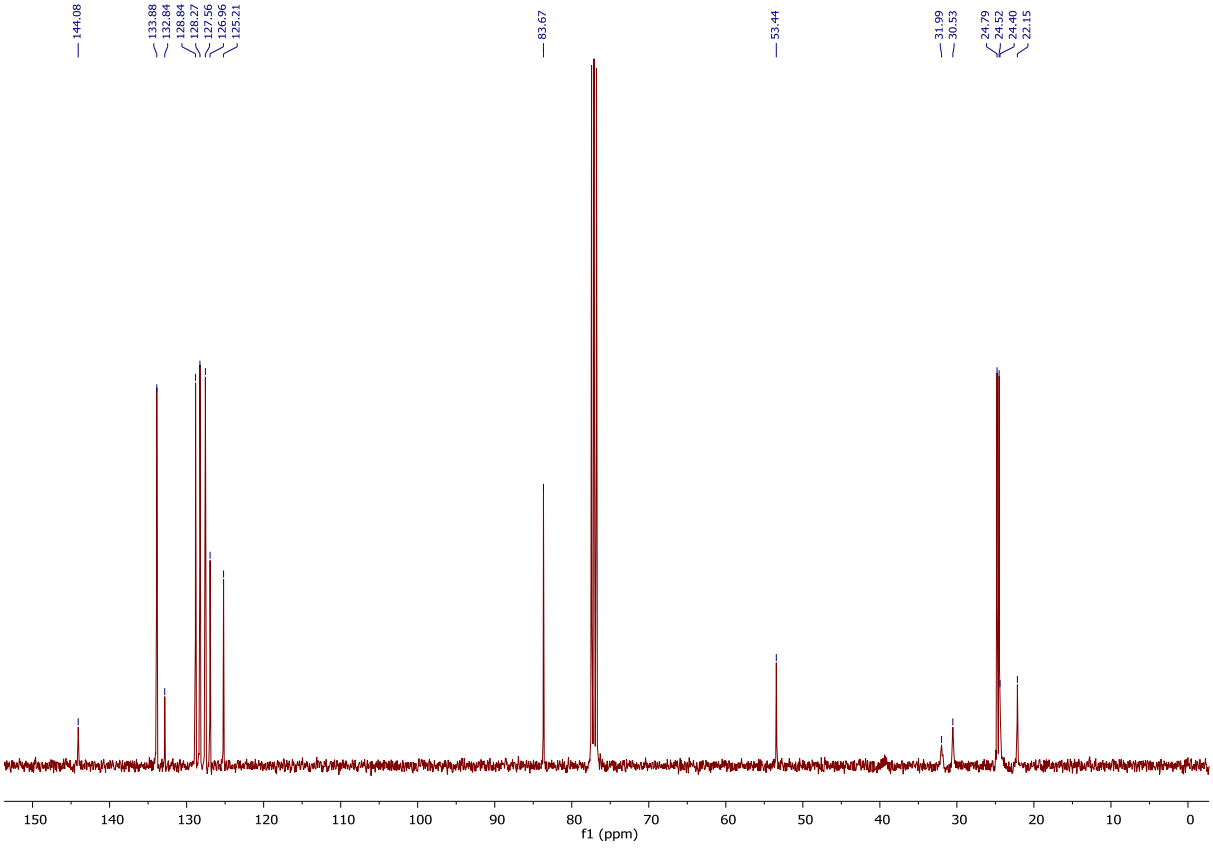

144.58
142.39
134.96
131.59
128.65
128.46
128.36
127.88
127.66
126.79
125.79
125.78
83.77
61.19
39.44
35.72
24.72
24.63
17.34
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

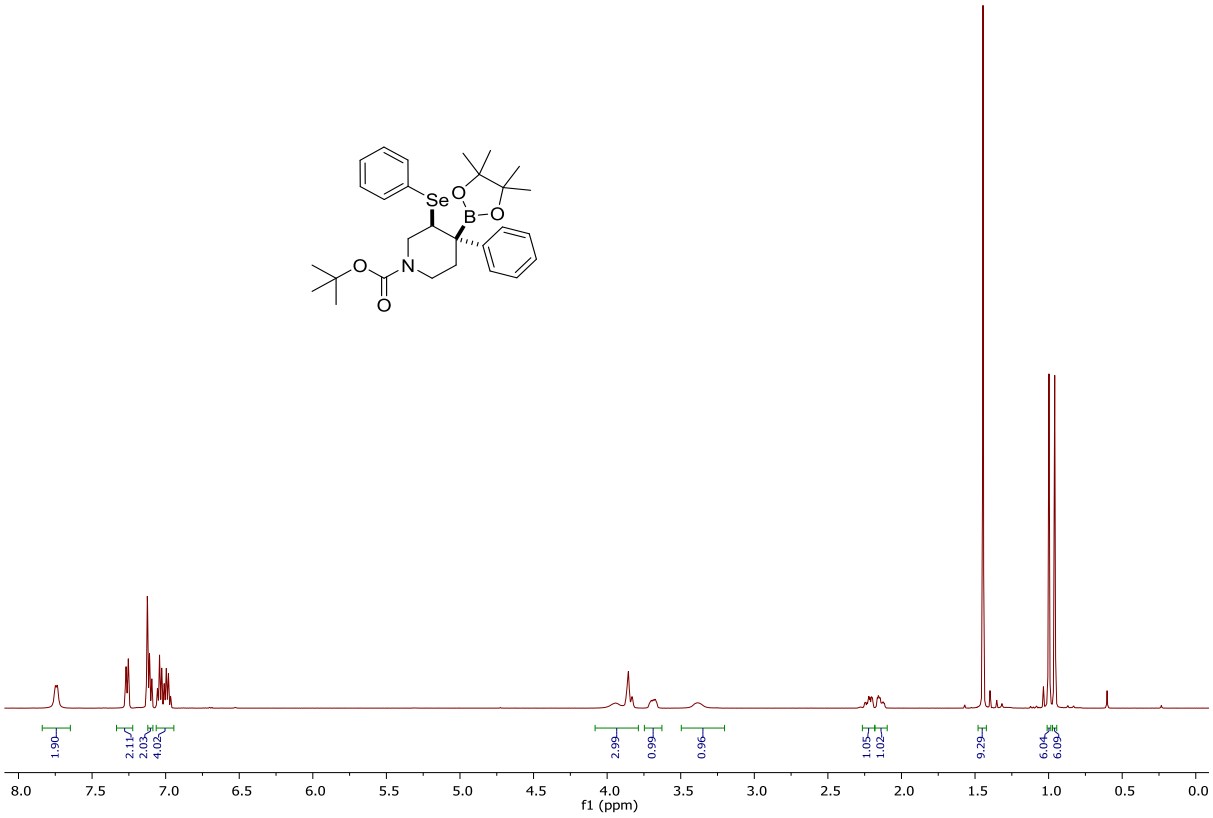

Se
O
B
O
O
Si
Me

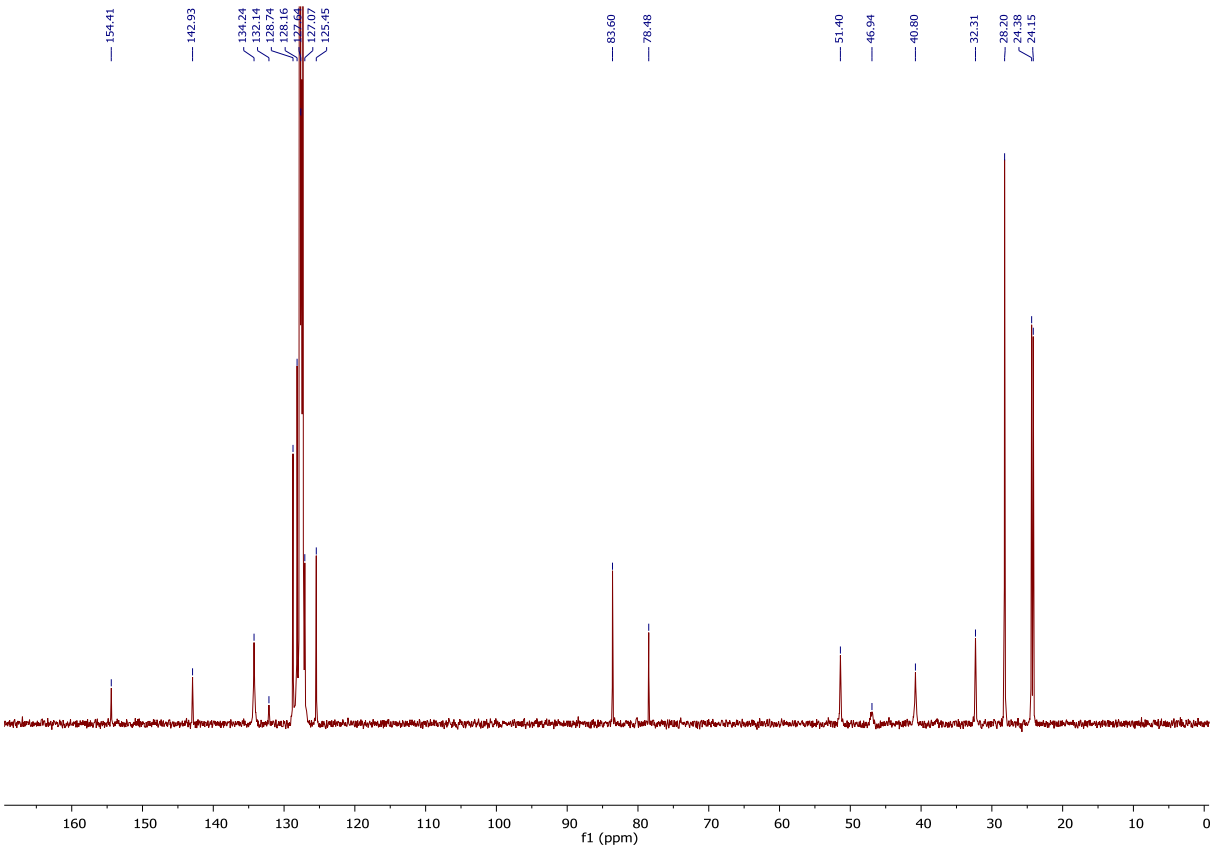
4.02
6.09
3.98
6.01
1.01
0.99
0.99
3.04
20.90
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

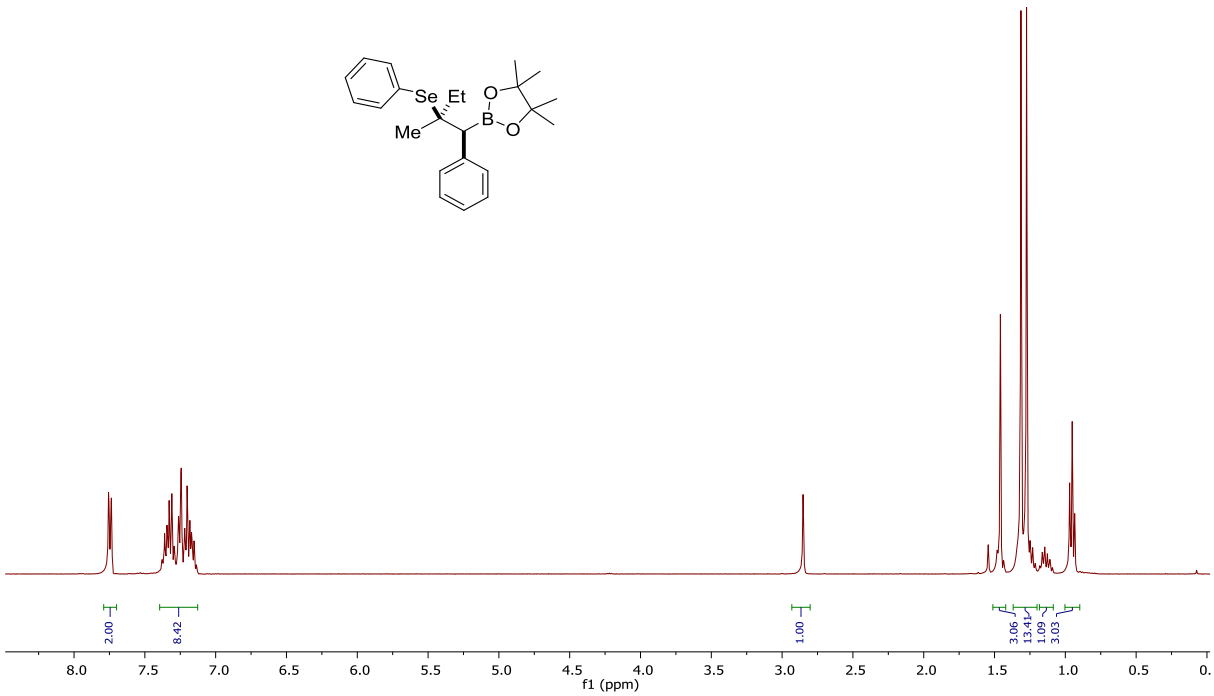

144.22
135.94
135.91
134.42
133.73
133.71
132.17
129.56
128.38
127.84
127.65
127.63
126.51
125.78
83.75
68.01
62.09
27.00
24.59
24.44
19.35
18.90
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

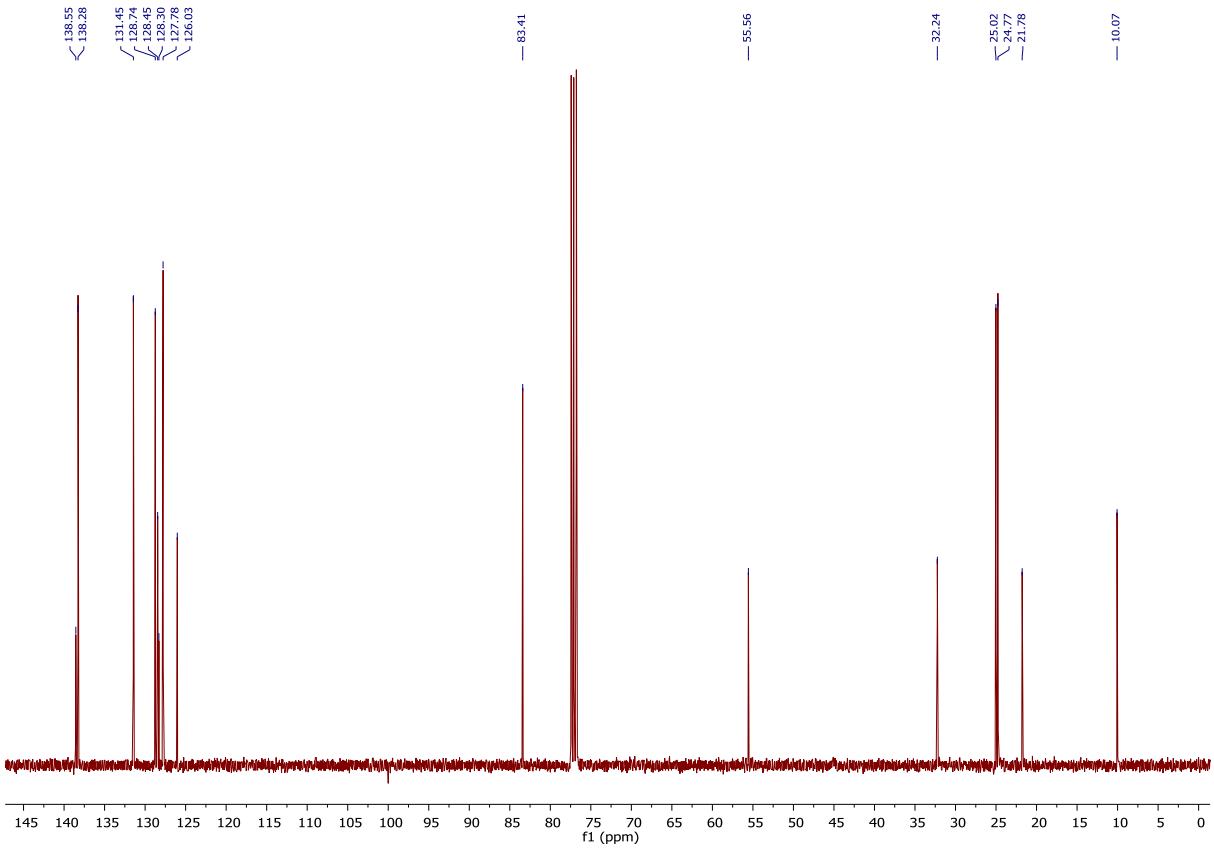

Se
O
B
O
2.01
2.03
5.33
1.01
0.93
0.95
1.03
2.95
2.98
11.93
f1 (ppm)

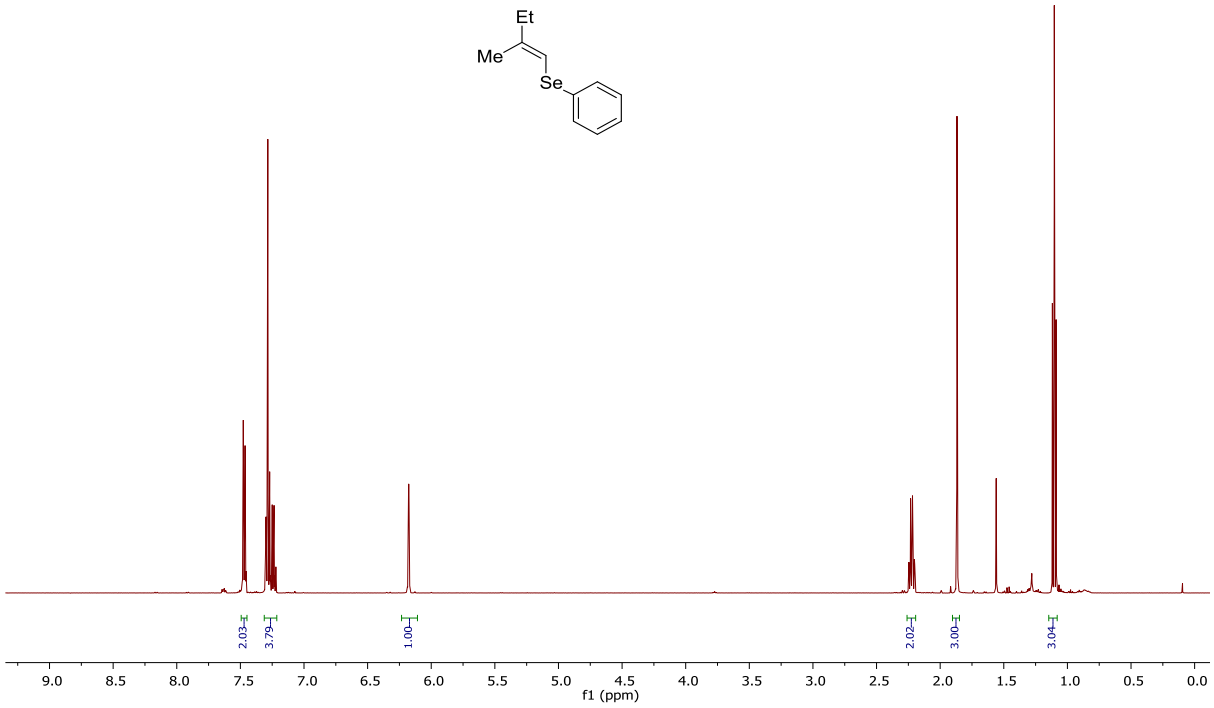

144.08
133.88
132.84
128.84
128.27
127.56
126.96
125.21
83.67
53.44
31.99
30.53
24.79
24.52
24.40
22.15
f1 (ppm)

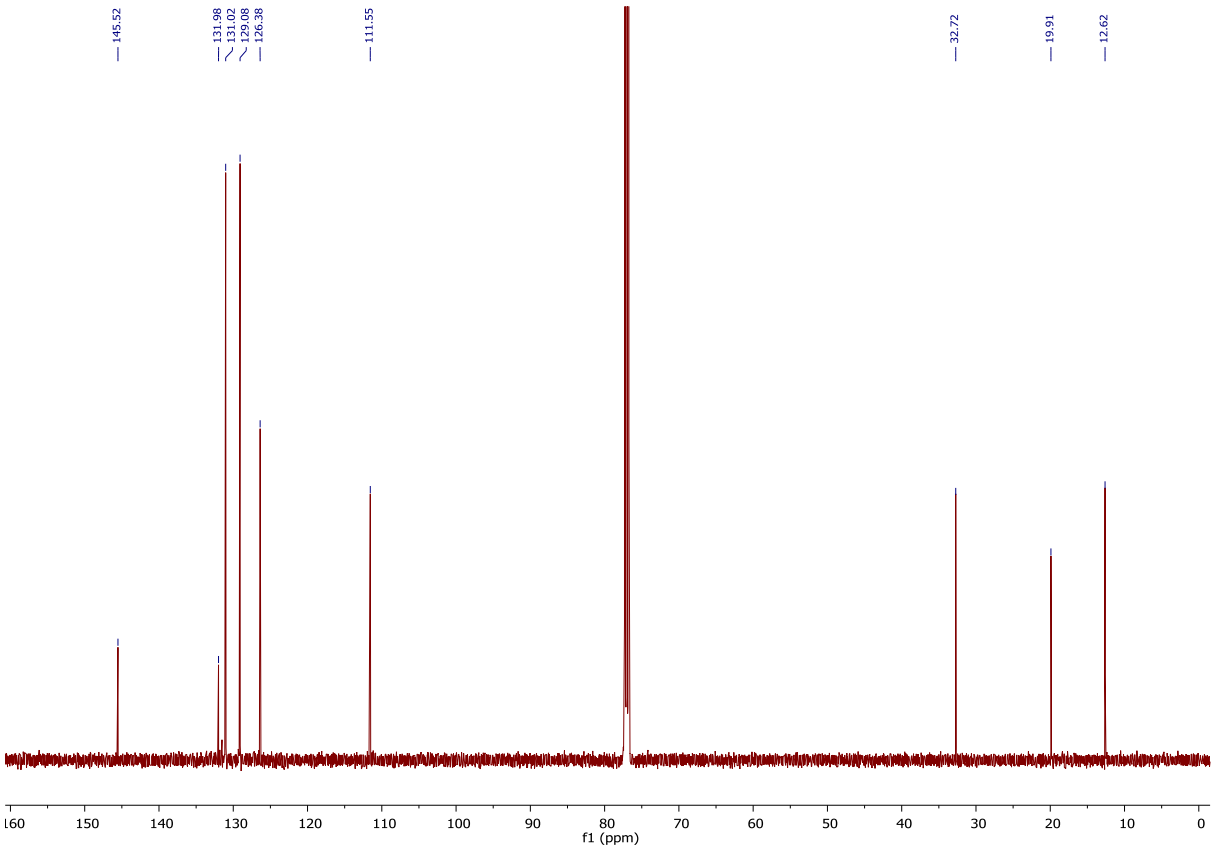

Se
O
B–O
N
O
O
1.90
2.11
2.03
4.02
2.99
0.99
0.96
1.05
1.02
9.29
6.04
6.09
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


154.41
142.93
134.24
132.14
128.74
128.16
127.64
127.07
125.45
83.60
78.48
51.40
46.94
40.80
32.31
28.20
24.38
24.15
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

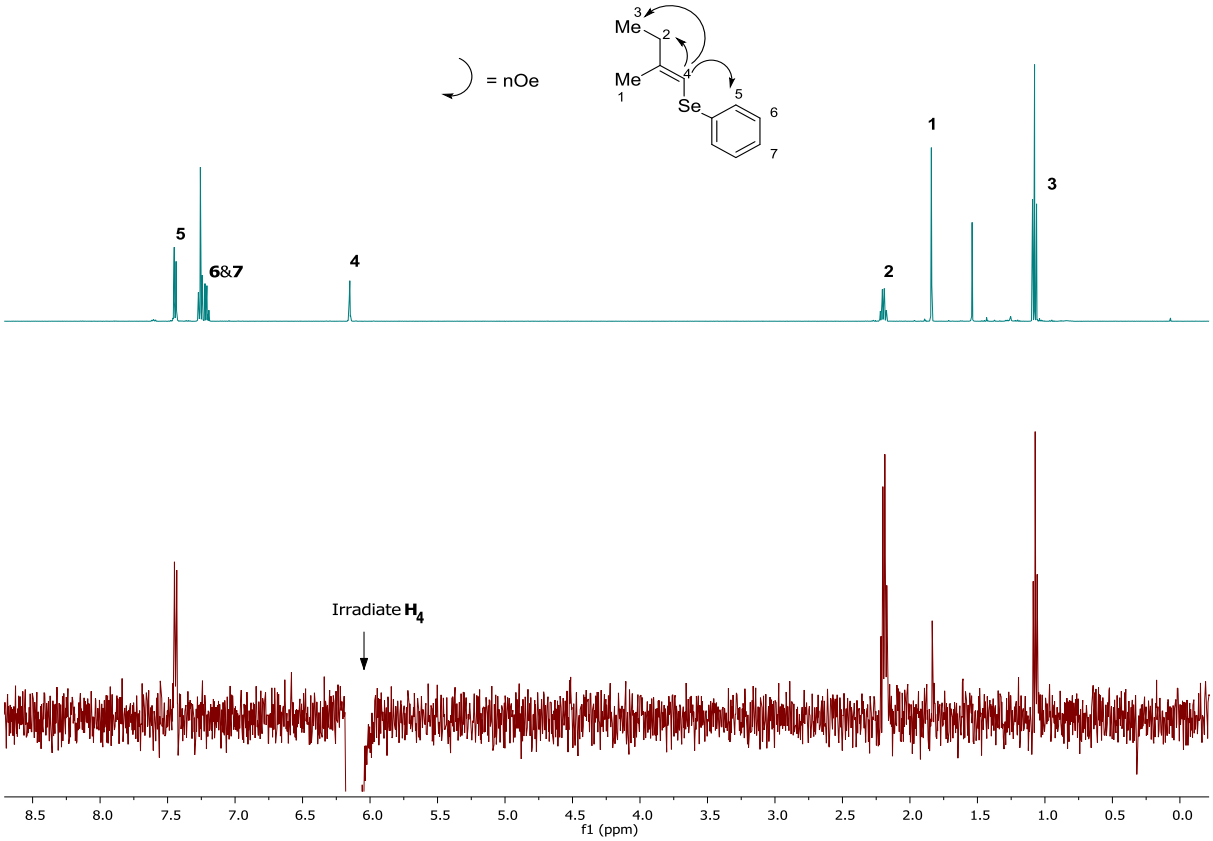

Se
Et
Me
O
B
O
2.00
8.42
1.00
3.06
13.41
1.09
3.03
f1 (ppm)

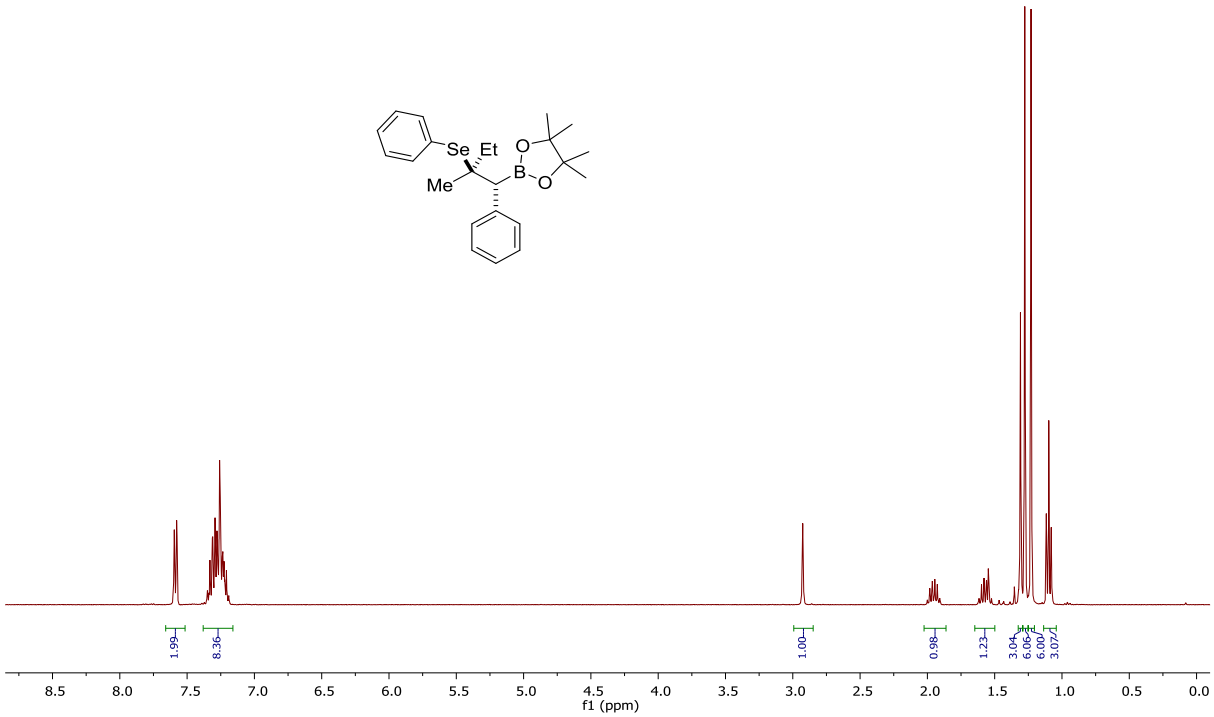

138.55
138.28
131.45
128.74
128.45
128.30
127.78
126.03
83.41
55.56
32.24
25.02
24.77
21.78
10.07
f1 (ppm)

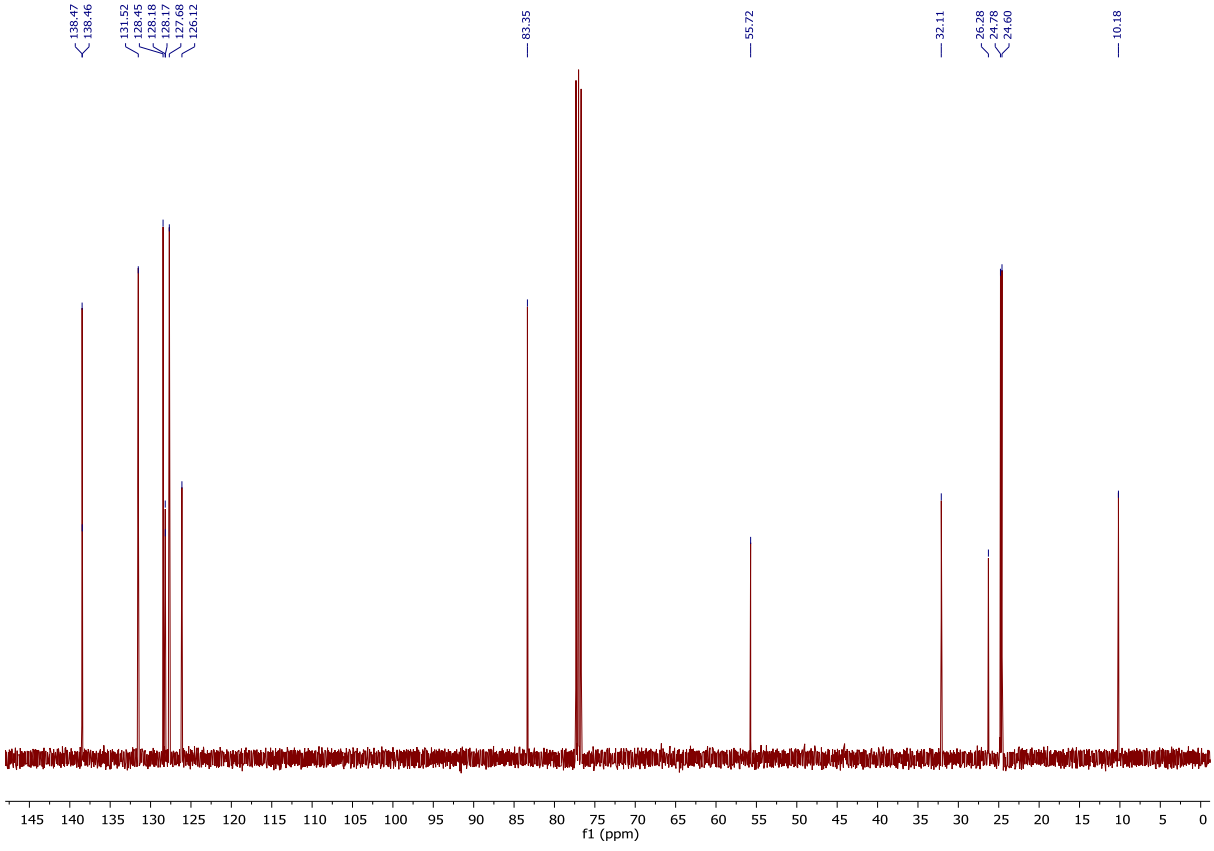

Et
Me
Se
2.03
3.79
1.00
2.02
3.00
3.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

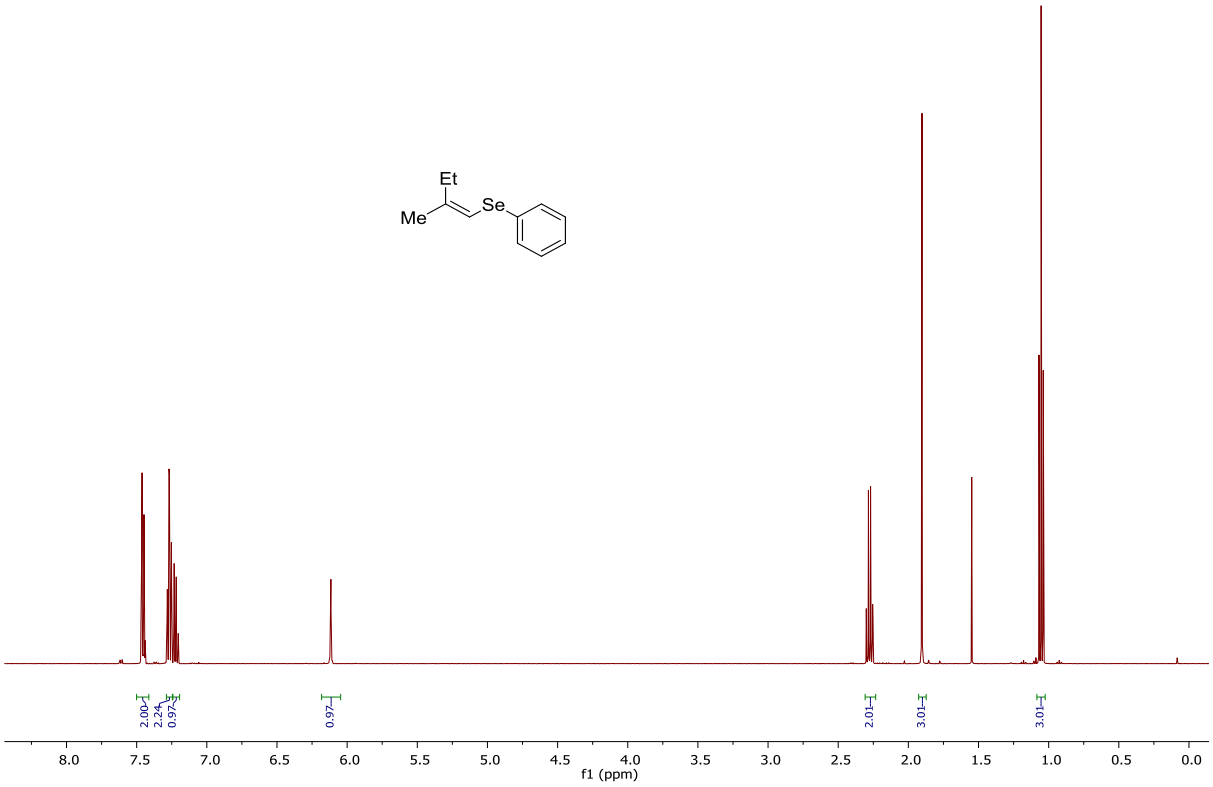

145.52
131.98
131.02
129.08
126.38
111.55
32.72
19.91
12.62
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

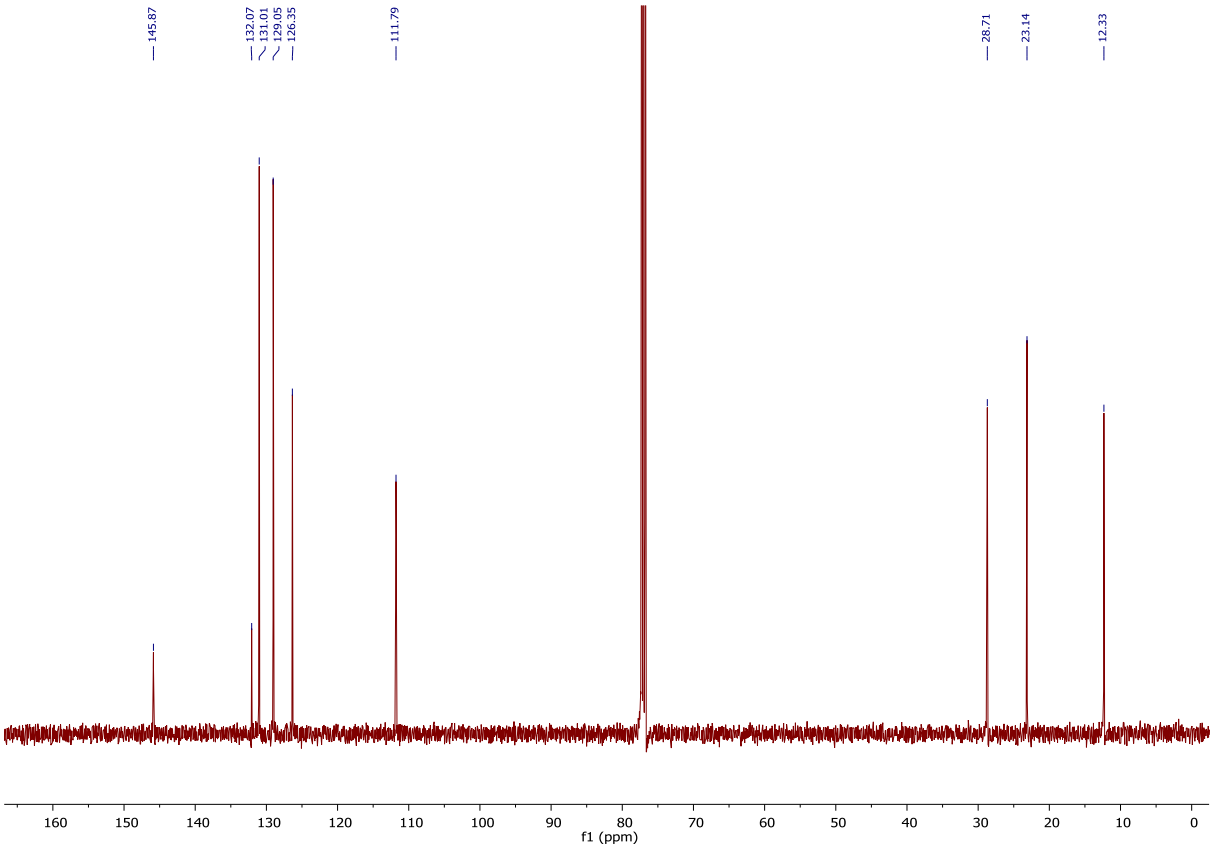
1D nOe data obtained by irradiation of H_4:



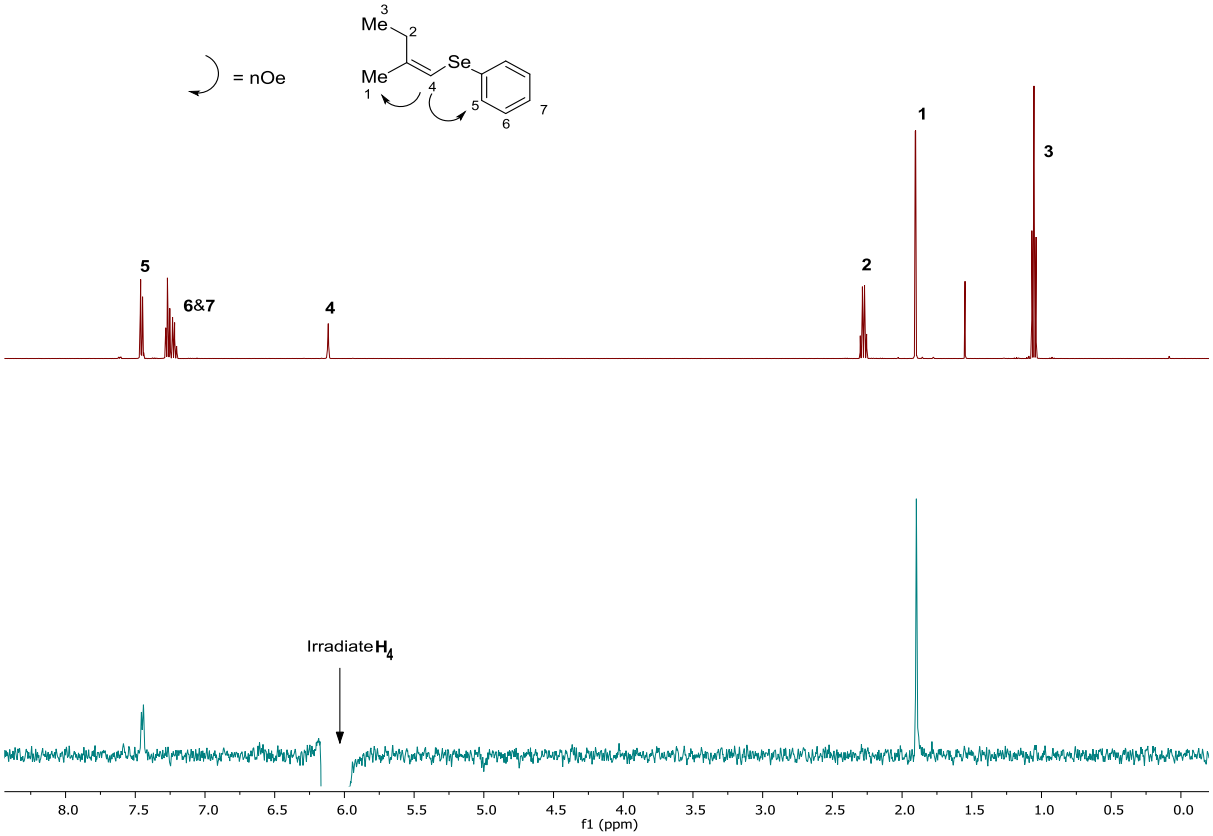

Se
Et
Me
O
B
O
1.99
8.36
1.00
0.98
1.23
3.04
6.06
6.00
3.07
f1 (ppm)

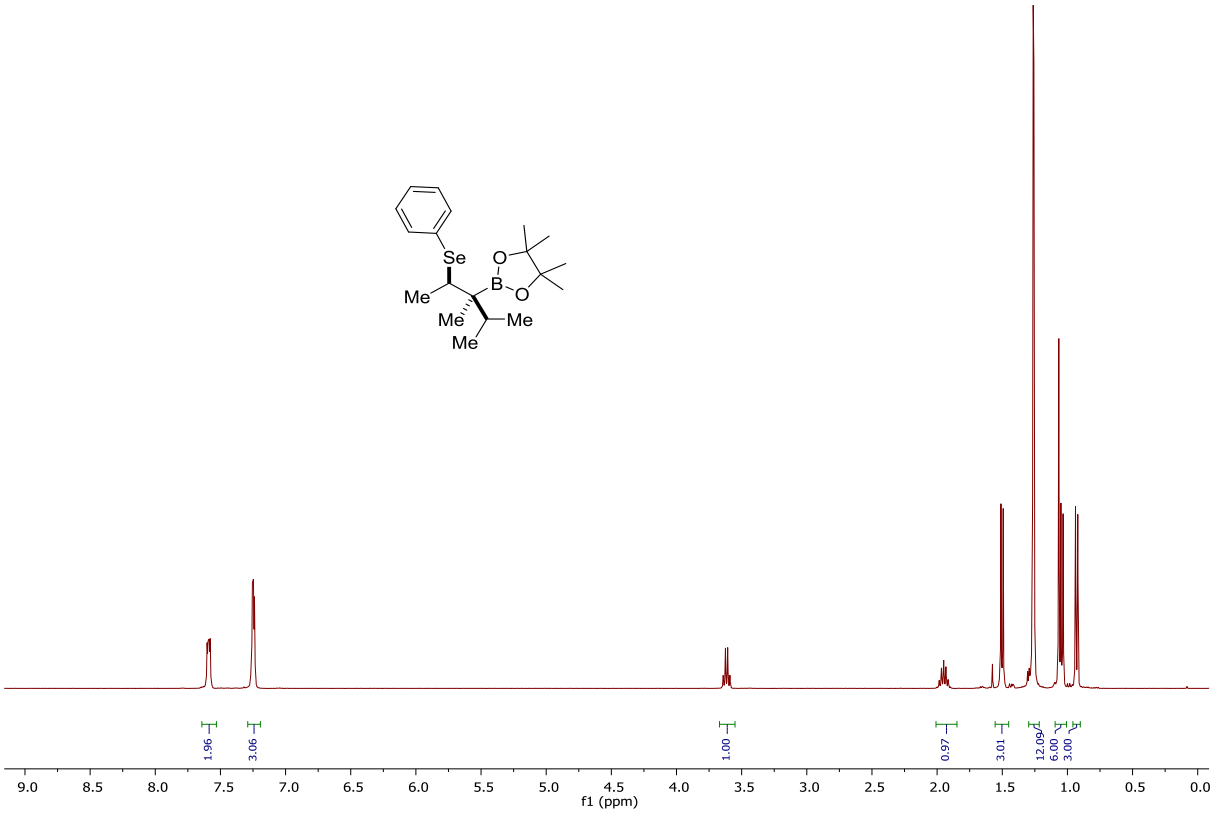

138.47
138.46
131.52
128.45
128.18
128.17
127.68
126.12
83.35
55.72
32.11
26.28
24.78
24.60
10.18
f1 (ppm)

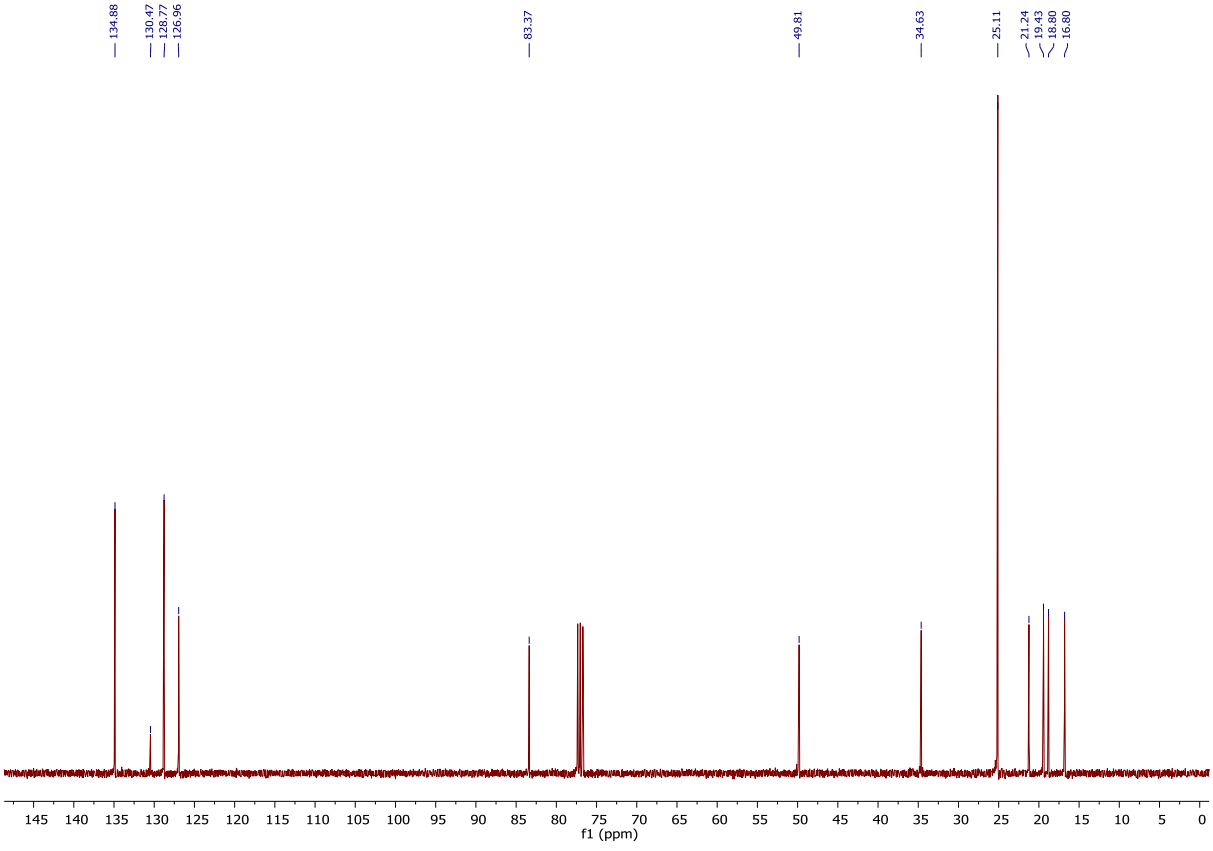

Et
Me
Se
2.00
2.24
0.97
0.97
2.01
3.01
3.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

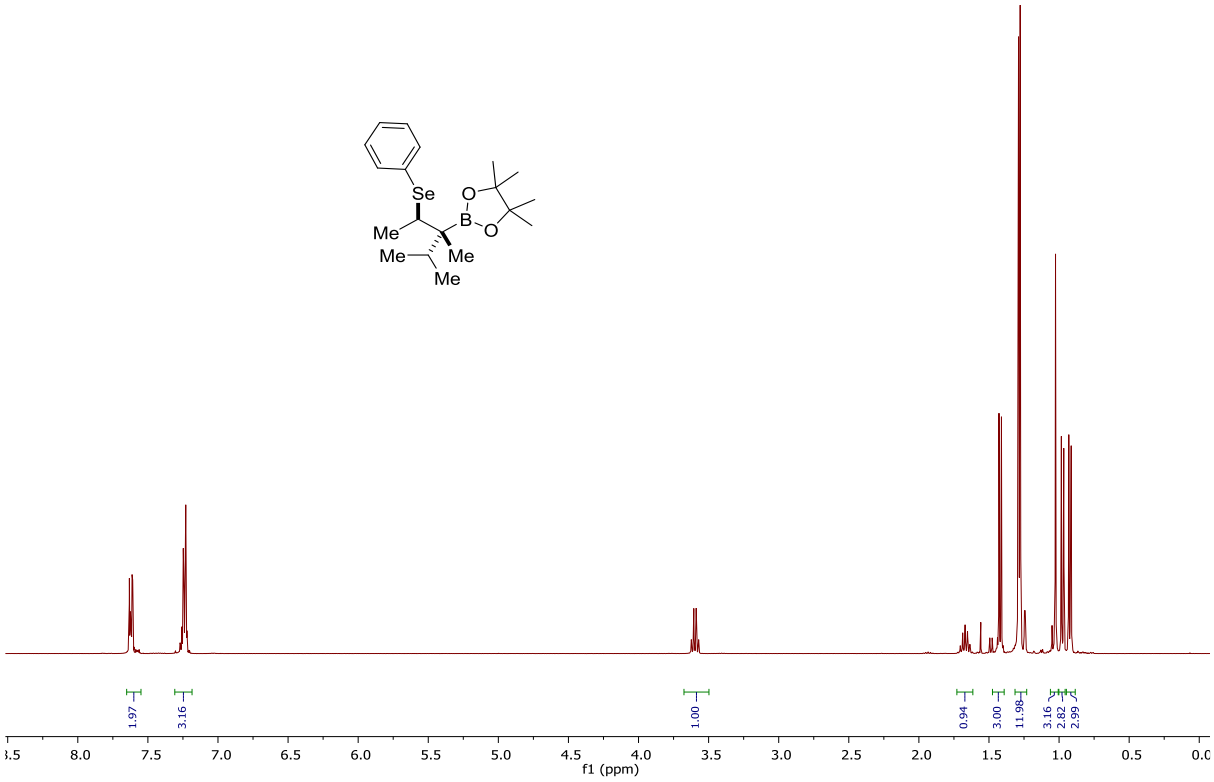

145.87
132.07
131.01
129.05
126.35
111.79
28.71
23.14
12.33
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

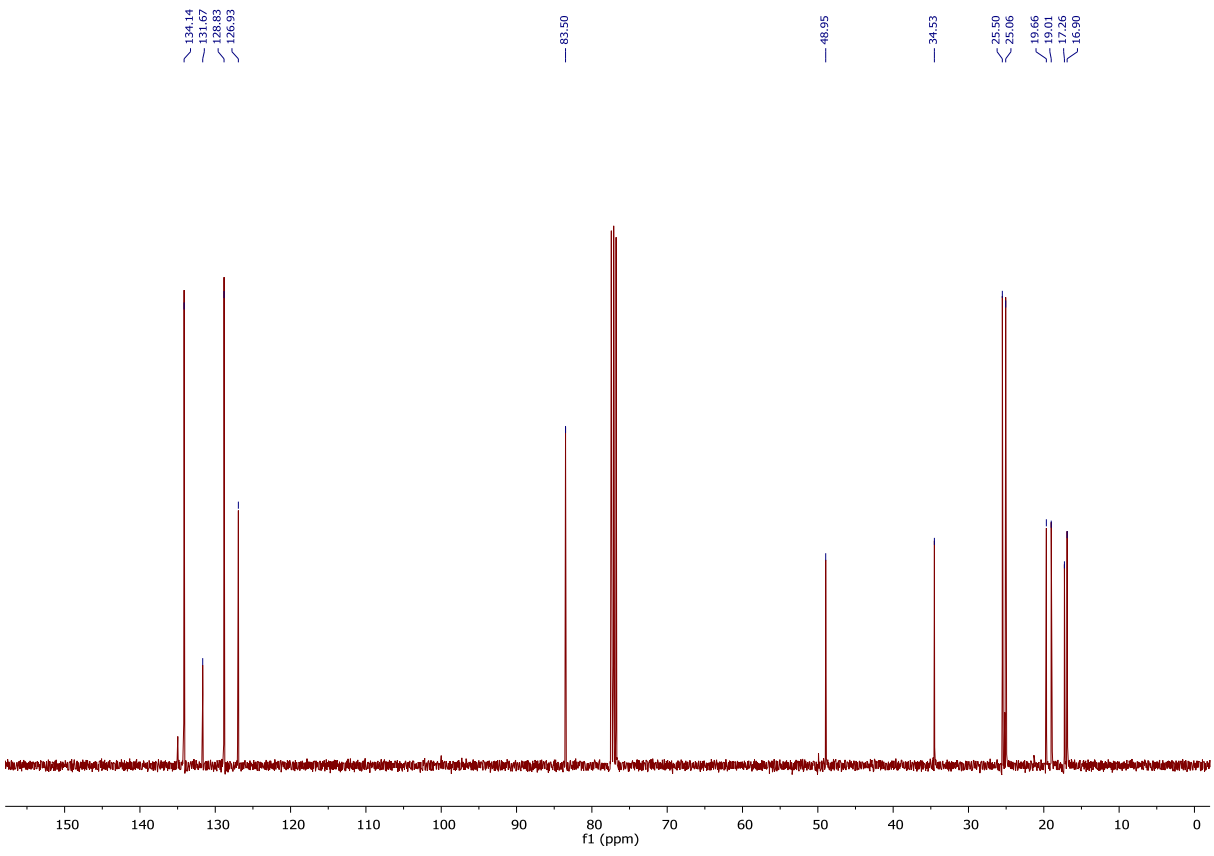
1D nOe data obtained by irradiation of H_4:

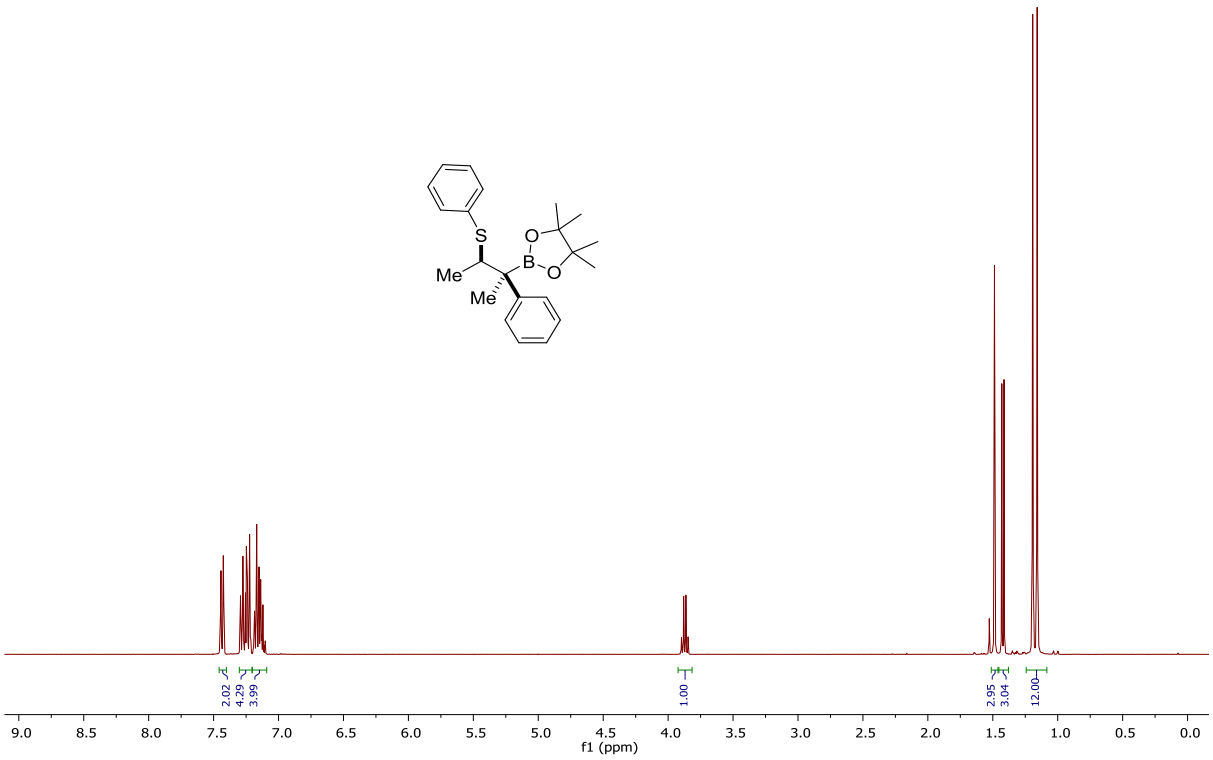


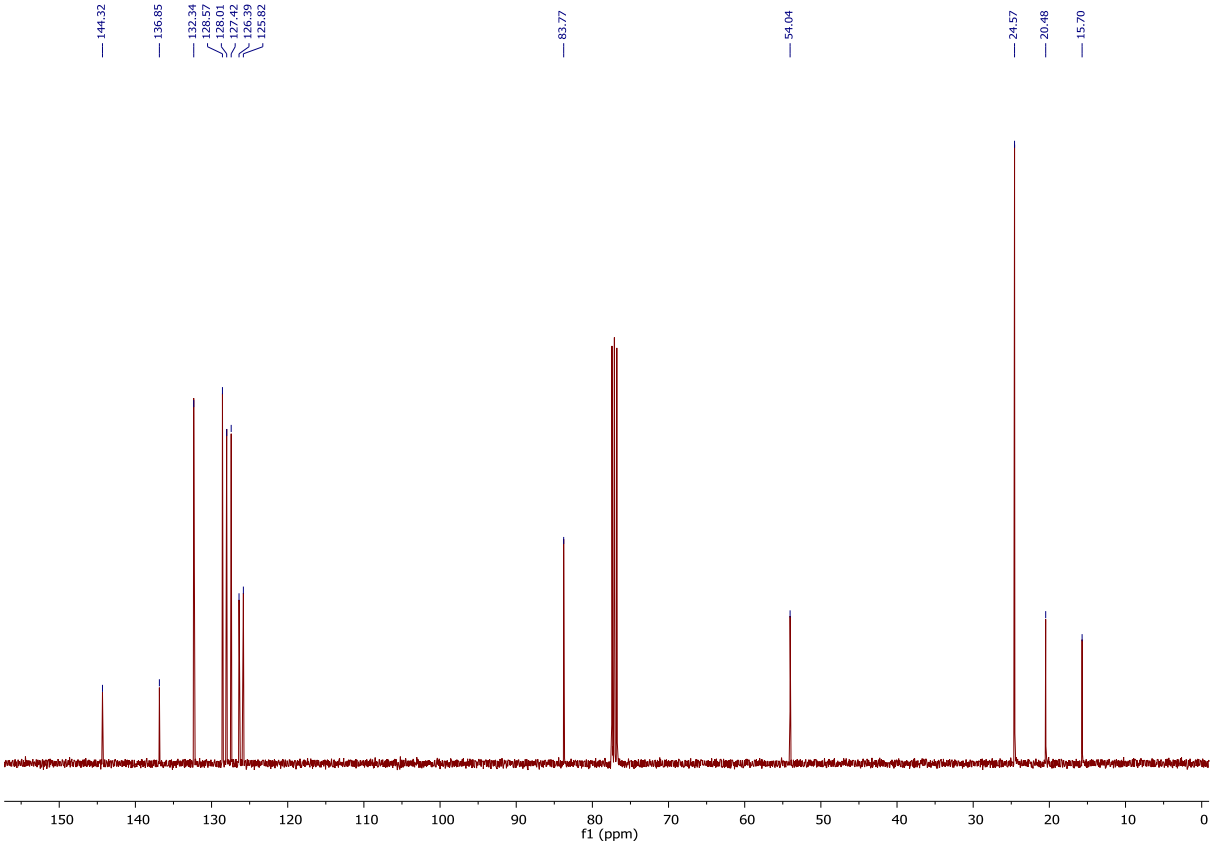

Se
Me
O
B
O
Me
Me
Me
1.96
3.06
1.00
0.97
3.01
12.09
6.00
3.00
f1 (ppm)

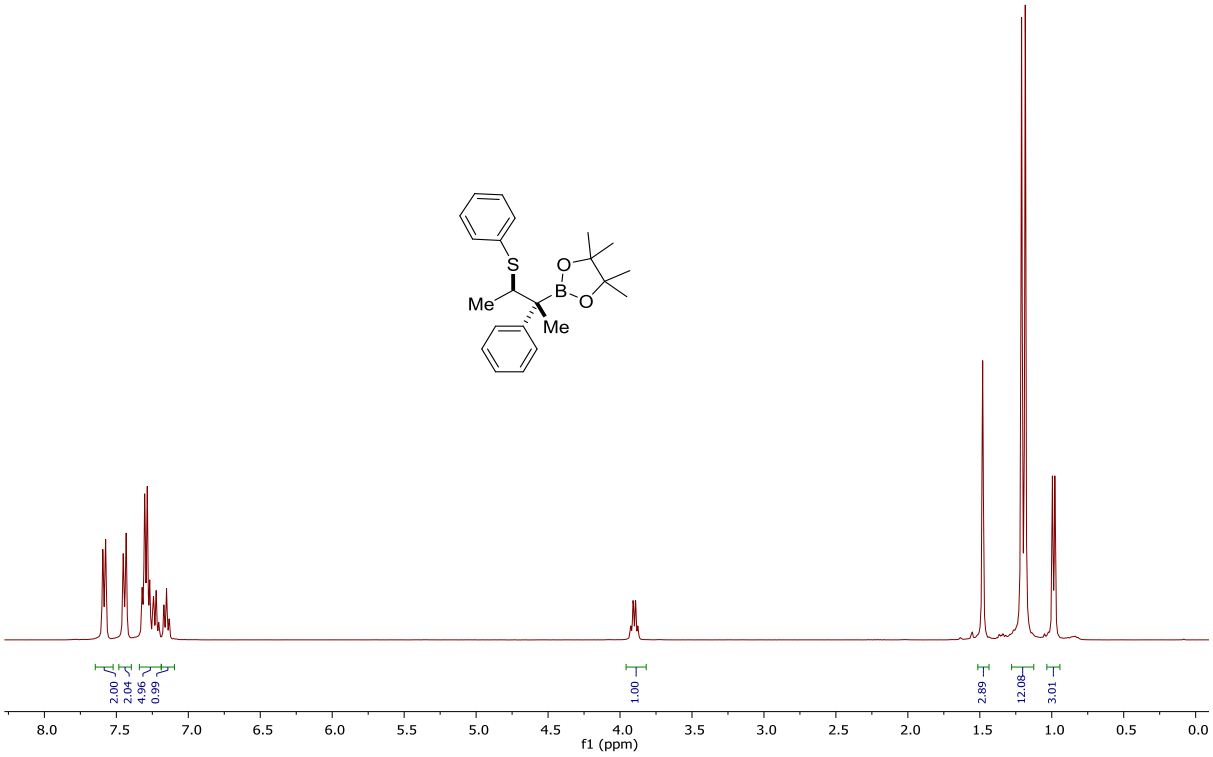

134.88
130.47
128.77
126.96
83.37
49.81
34.63
25.11
21.24
19.43
18.80
16.80
f1 (ppm)

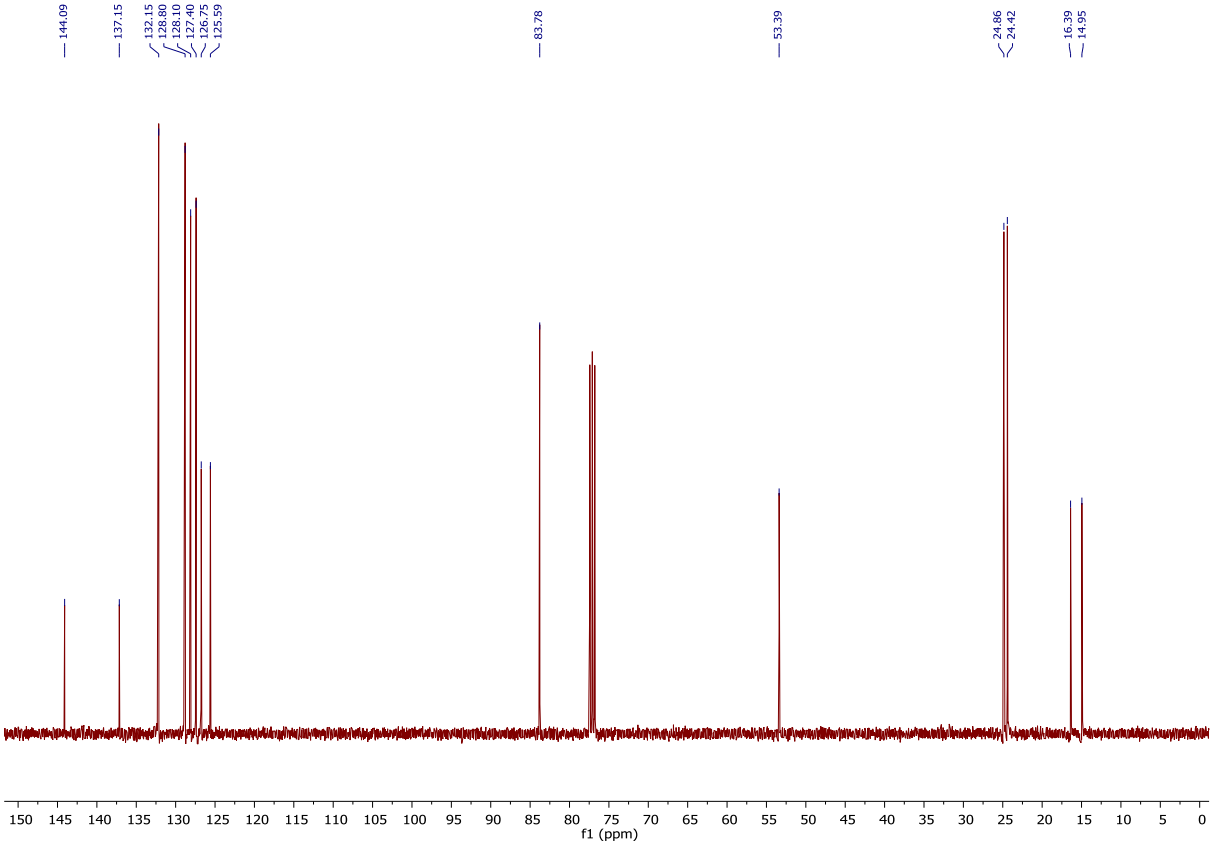

Se
O
B
O
Me
Me
Me
Me
1.97
3.16
1.00
0.94
3.00
11.98
3.16
2.82
2.99
f1 (ppm)

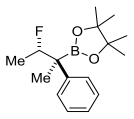

134.14
131.67
128.83
126.93
83.50
48.95
34.53
25.50
25.06
19.66
19.01
17.26
16.90
f1 (ppm)


S
Me
Me
O
B
O
2.02
4.29
3.99
1.00
2.95
3.04
12.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

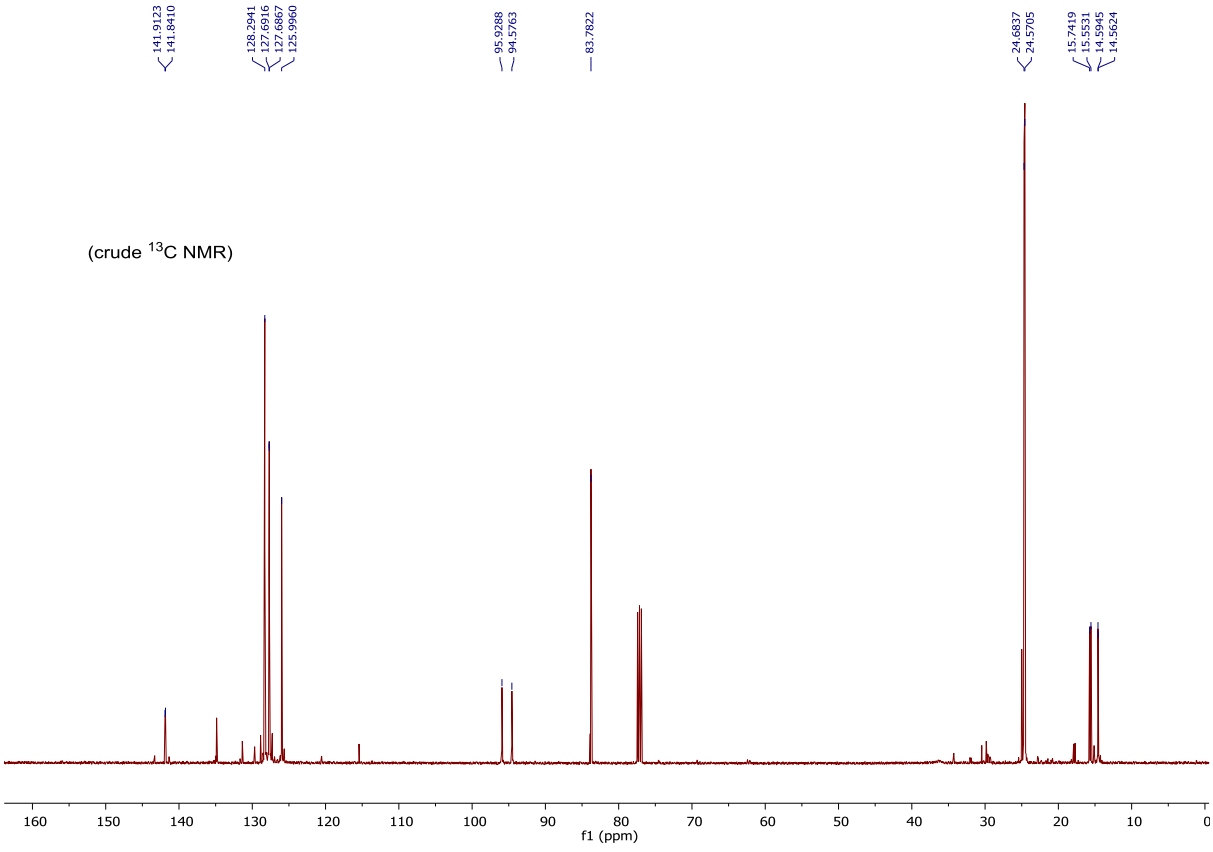

144.32
136.85
132.34
128.57
128.01
127.42
126.39
125.82
83.77
54.04
24.57
20.48
15.70
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


S
O
B
O
Me
Me
2.00
2.04
4.96
0.99
1.00
2.89
12.08
3.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

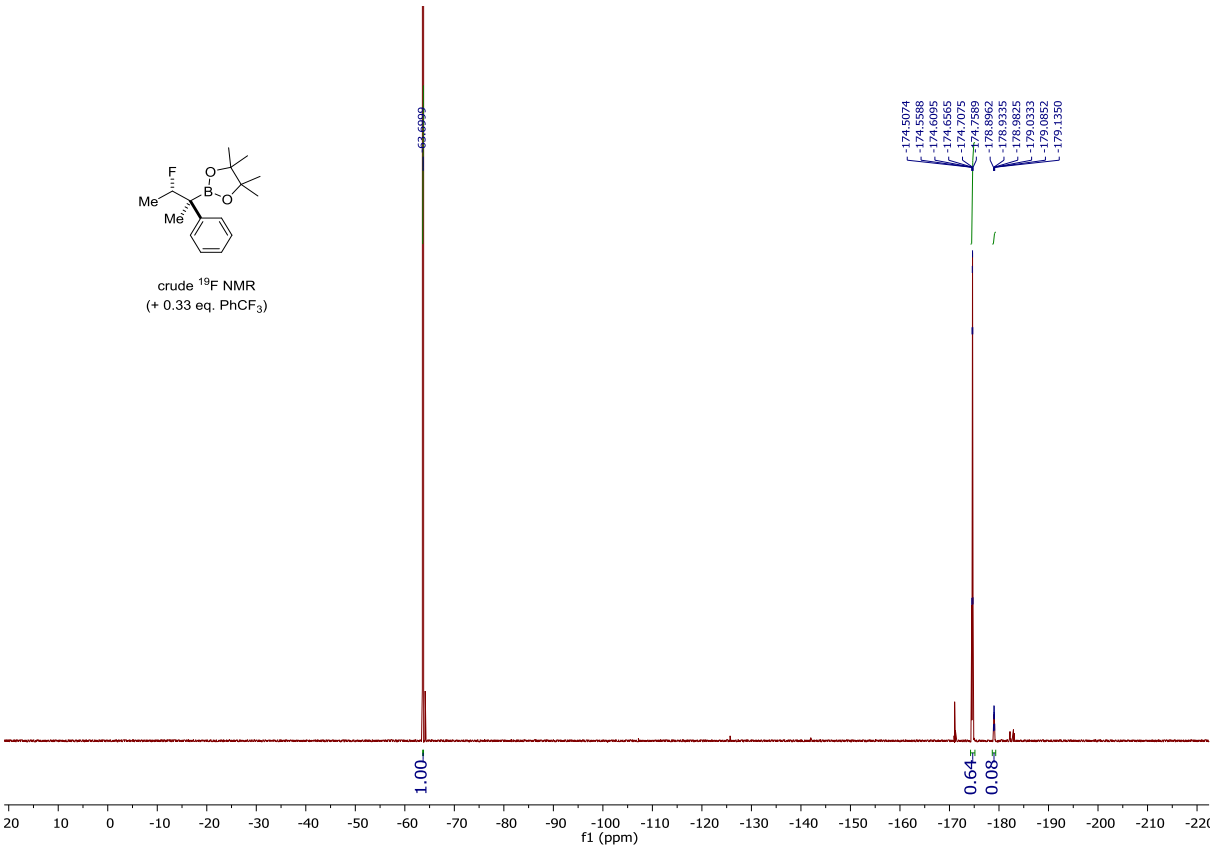

144.09
137.15
132.15
128.80
128.10
127.40
126.75
125.59
83.78
53.39
24.86
24.42
16.39
14.95
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)

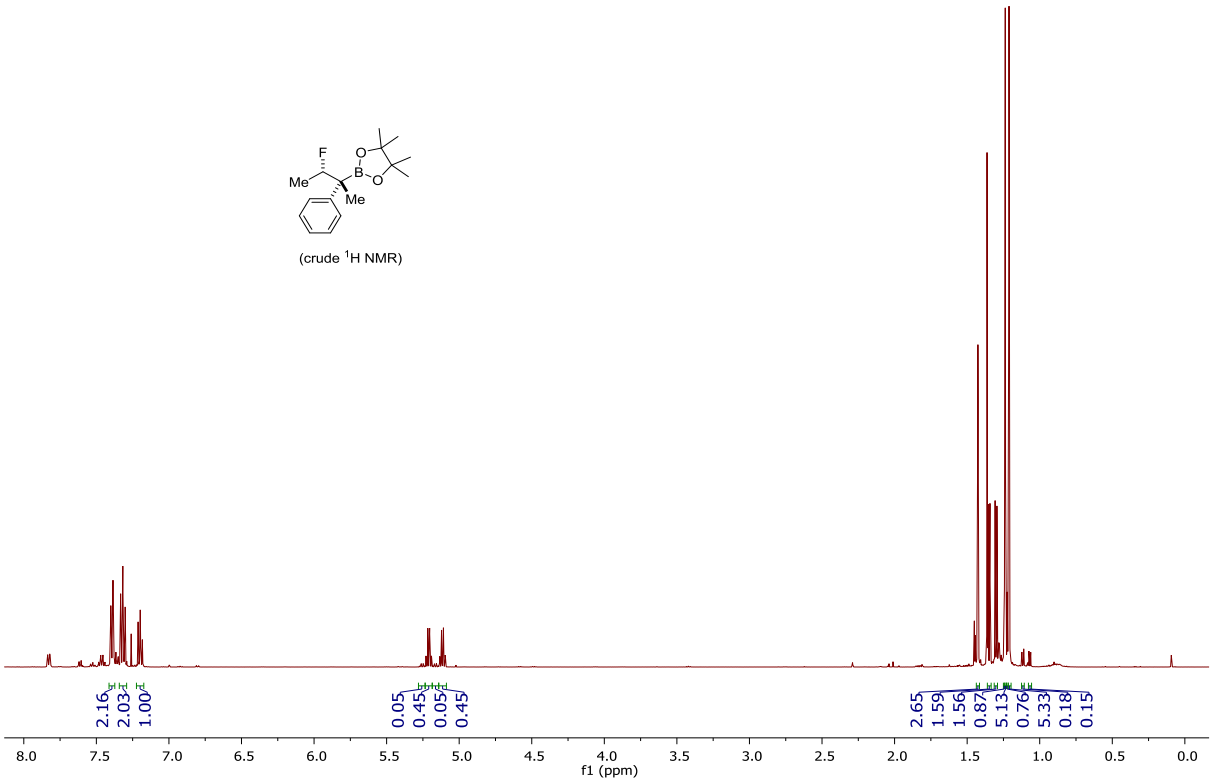


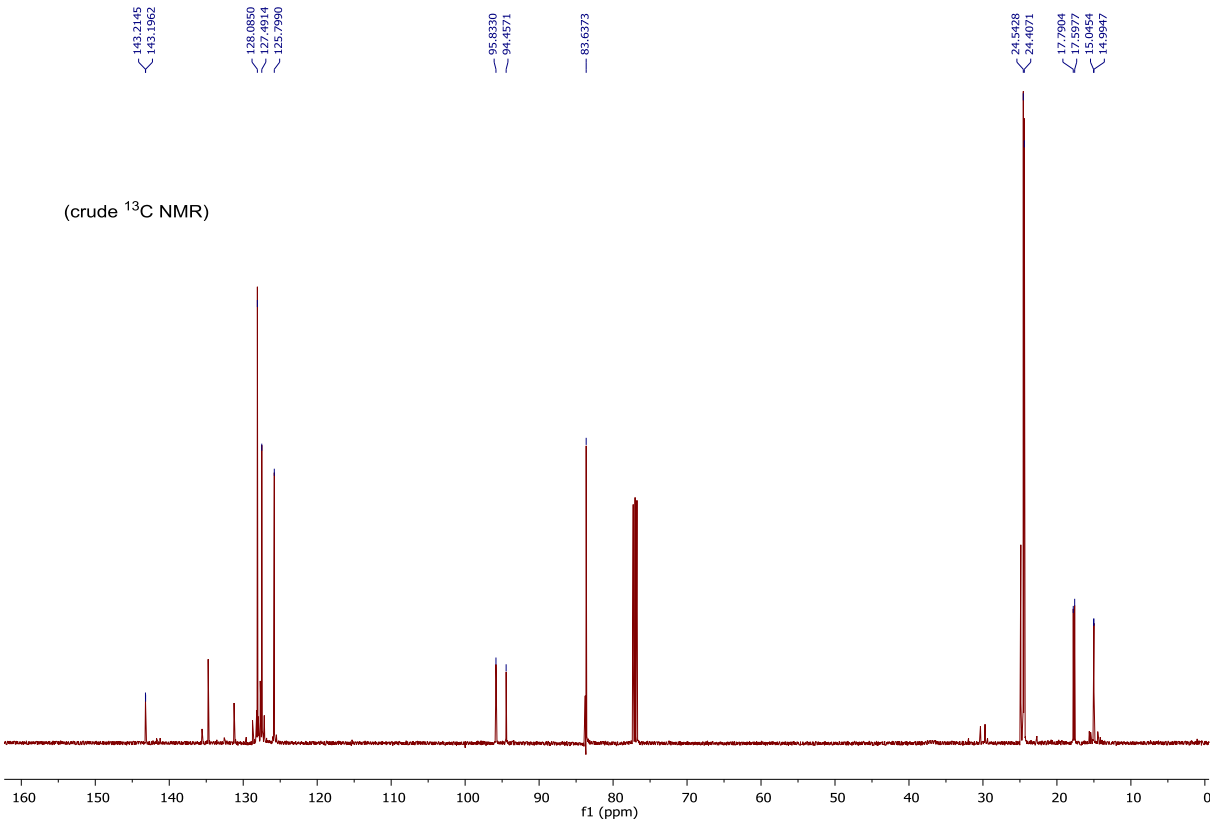
(crude ^{1}H NMR)

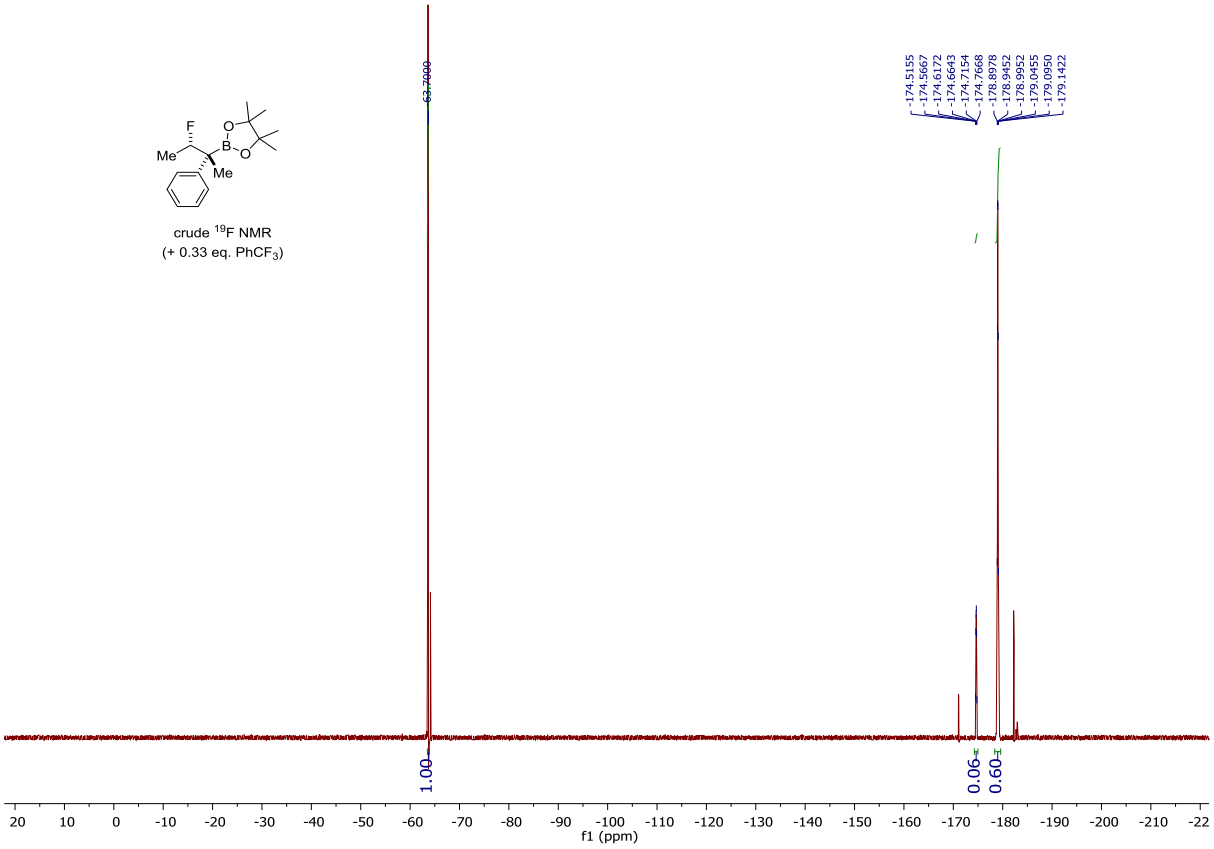


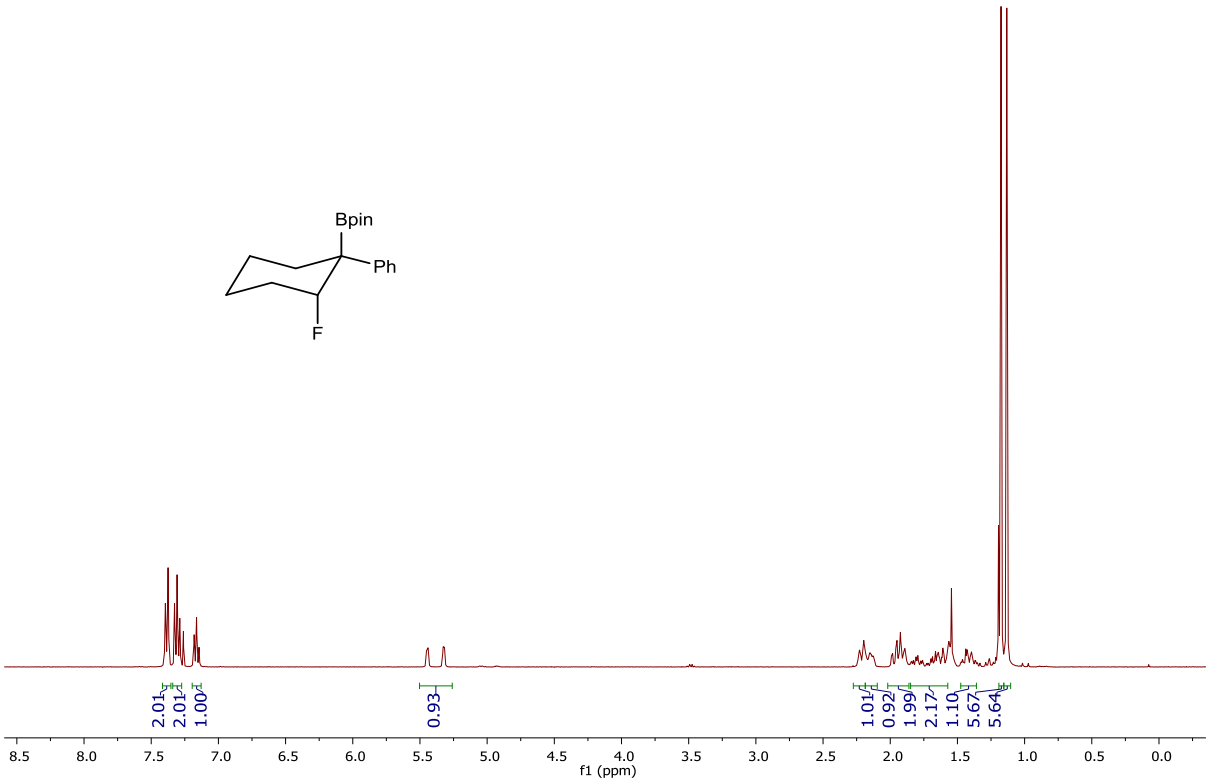
(crude ^{13}C NMR)

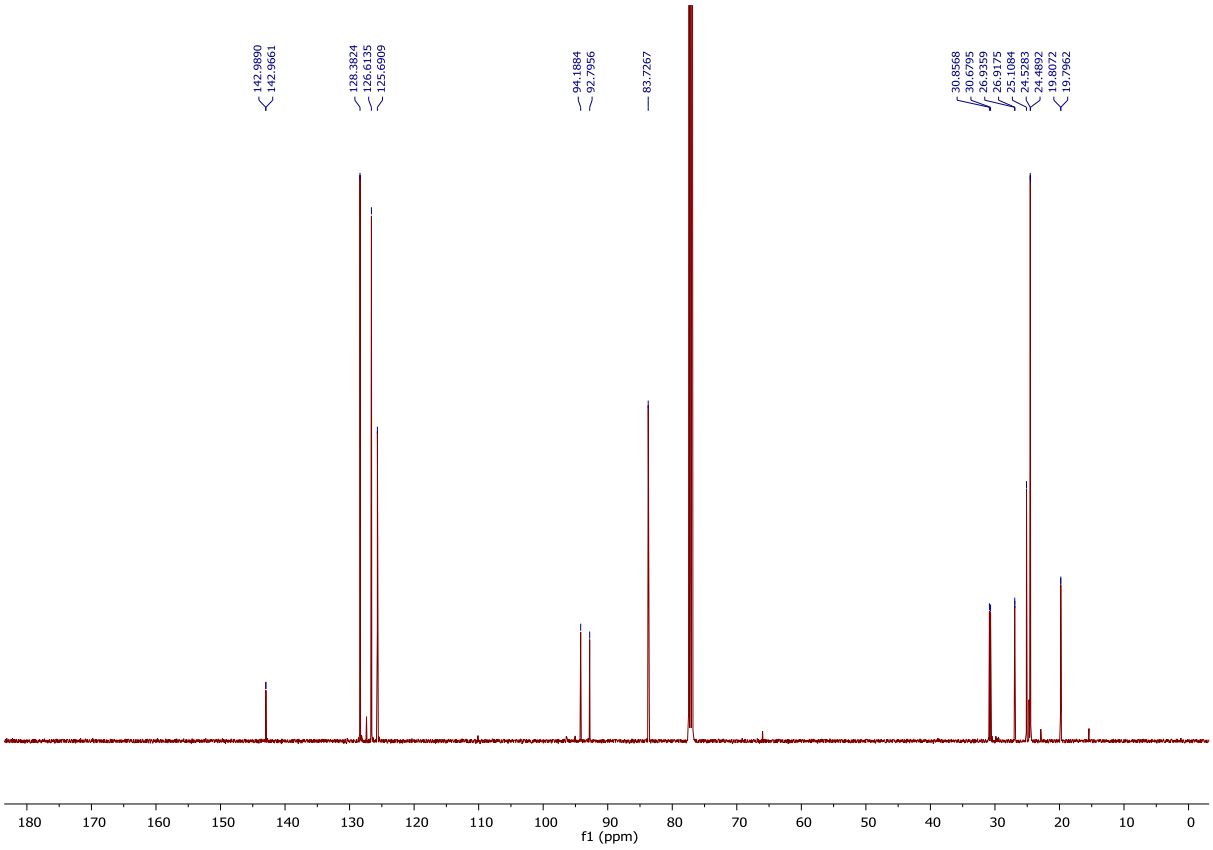

F
Me
Me
O
B
O
crude ^{19}F NMR
(+ 0.33 eq. PhCF$_3$)
-62.6090
-174.5074
-174.5588
-174.6095
-174.6565
-174.7075
-174.7589
-178.8962
-178.9335
-178.9825
-179.0333
-179.0852
-179.1350
1.00
0.64
0.08
f1 (ppm)

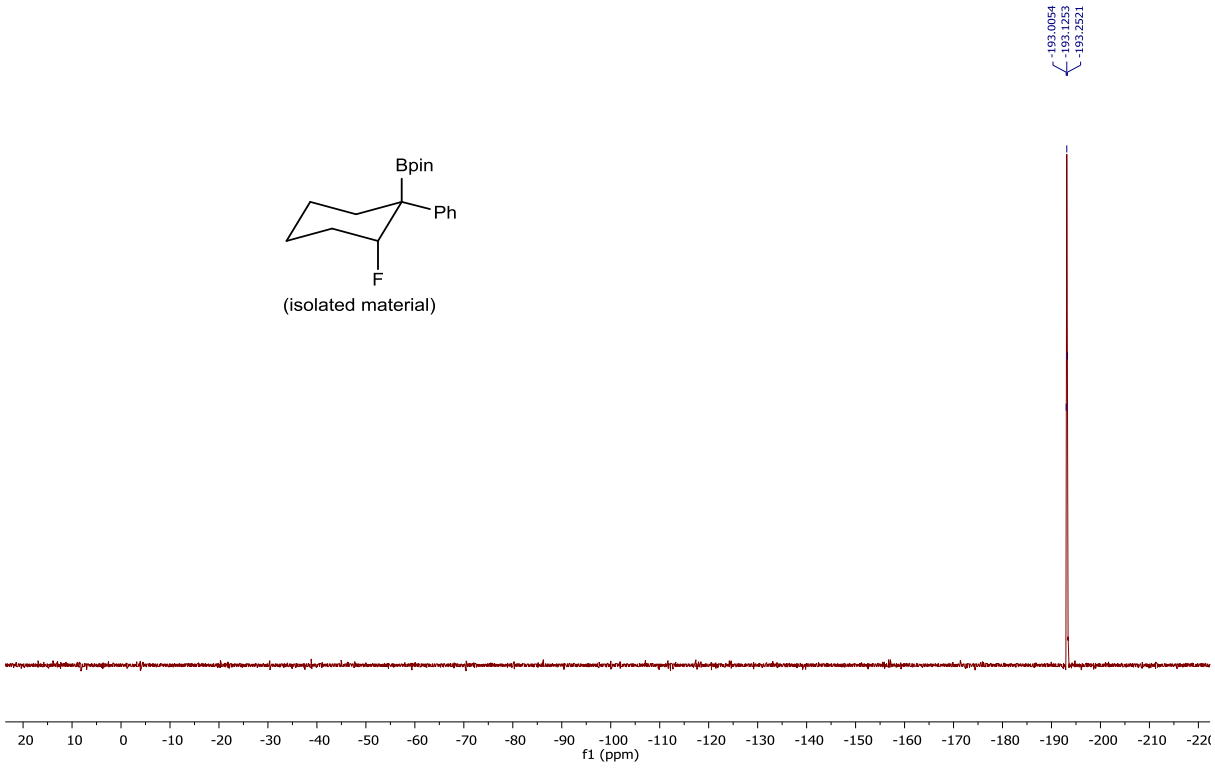

F
O
B
O
Me
Me
(crude 1H NMR)
2.16
2.03
1.00
0.05
0.45
0.05
0.45
2.65
1.59
1.56
0.87
5.13
0.76
5.33
0.18
0.15
f1 (ppm)

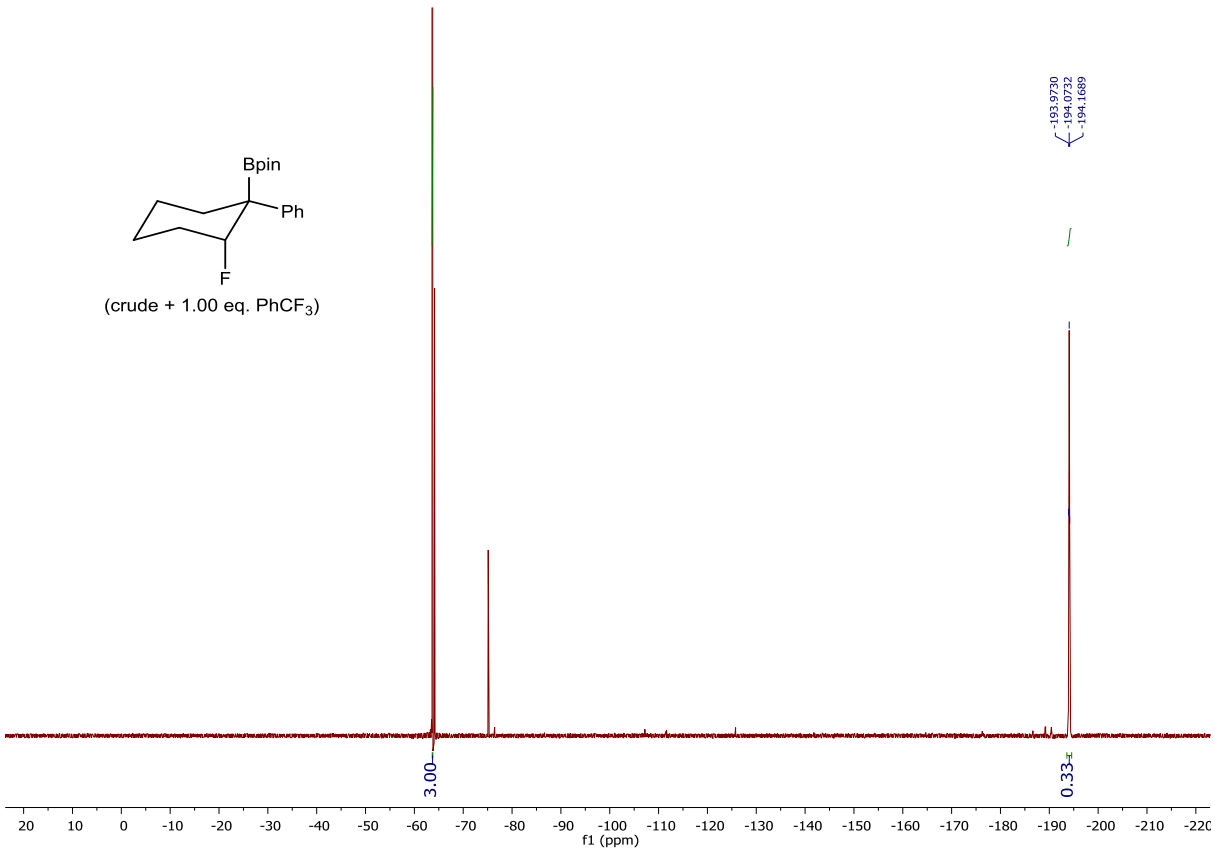

143.2145
143.1962
128.0850
127.4914
125.7990
95.8330
94.4571
83.6373
24.5428
24.4071
17.7904
17.5977
15.0454
14.9947
(crude 13C NMR)
f1 (ppm)


F
Me
O
B
O
Me
crude ^{19}F NMR
(+ 0.33 eq. PhCF$_3$)
-63.7099
-174.5155
-174.5667
-174.6172
-174.6643
-174.7154
-174.7668
-178.8978
-178.9452
-178.9952
-179.0455
-179.0950
-179.1422
1.00
0.06
0.60
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22
f1 (ppm)


Bpin
Ph
F
2.01
2.01
1.00
0.93
1.01
0.92
1.99
2.17
1.10
5.67
5.64
f1 (ppm)

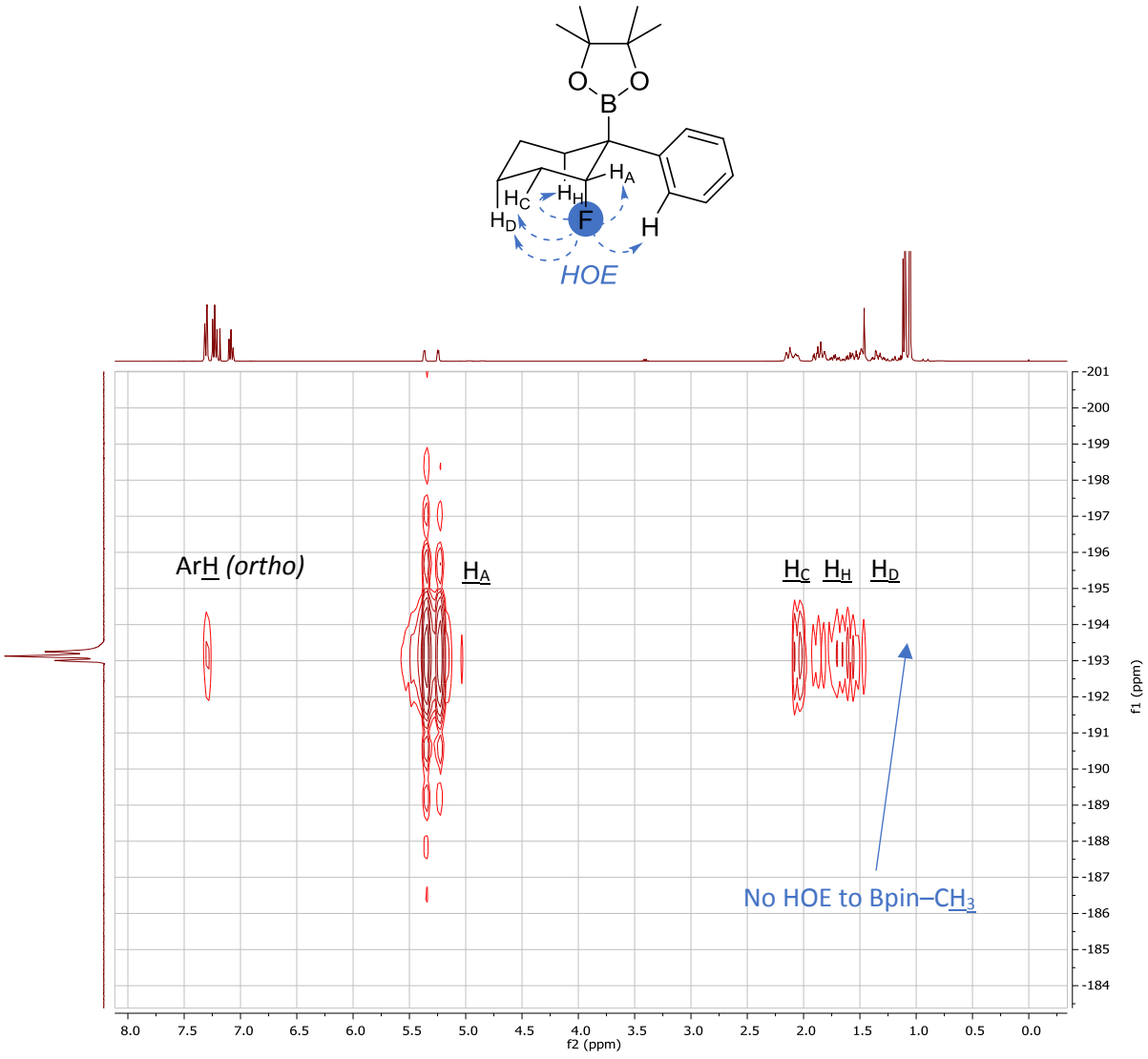

142.9890
142.9661
128.3824
126.6135
125.6909
94.1884
92.7956
83.7267
30.8568
30.6795
26.9359
26.9175
25.1084
24.5283
24.4892
19.8072
19.7962
f1 (ppm)


-193.0054
-193.1253
-193.2521
Bpin
Ph
F
(isolated material)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22(
f1 (ppm)

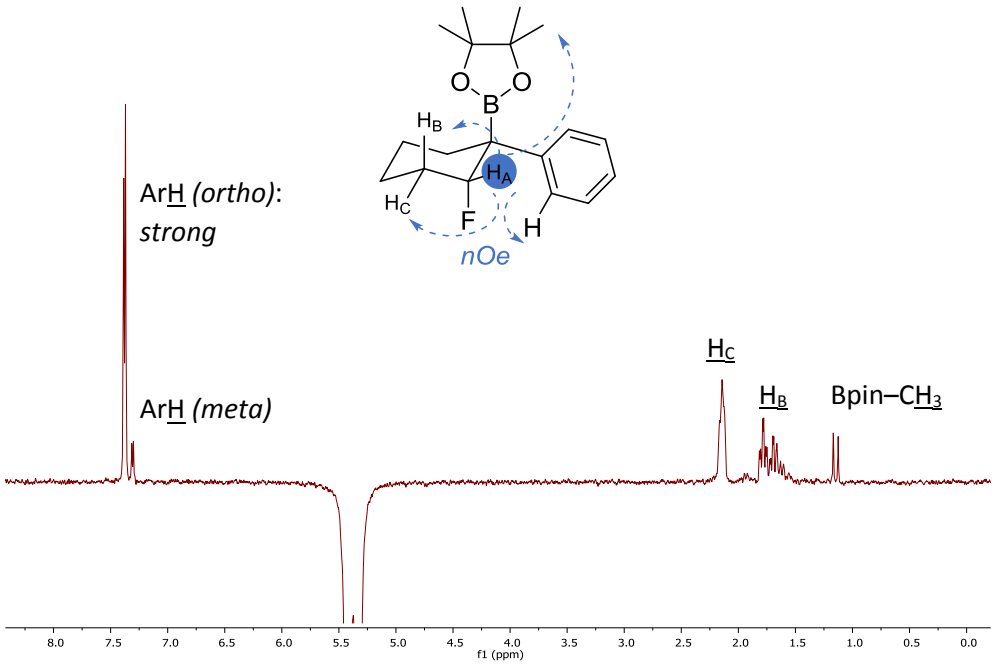

-193.9730
-194.0732
-194.1689
Bpin
Ph
F
(crude + 1.00 eq. PhCF3)
3.00
0.33
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

The configuration of the major diastereomer with fluorine *syn* to the phenyl ring which results from a *syn* migration, was unambiguously proven by 2D HOESY and 1D NOESY experiments, noting that the axial conformation of the fluorine is assigned by chemical shift value [see: Dolbier, W. R., *Guide to Fluorine NMR for Organic Chemists*. John Wiley & Sons, Inc.: Hoboken, New Jersey, 2009] and the triplet coupling pattern (a large geminal $^{2}J_{HF}$ coupling to H_A and a large vicinal *trans*-diaxial $^{3}J_{HF}$ coupling to H_B).

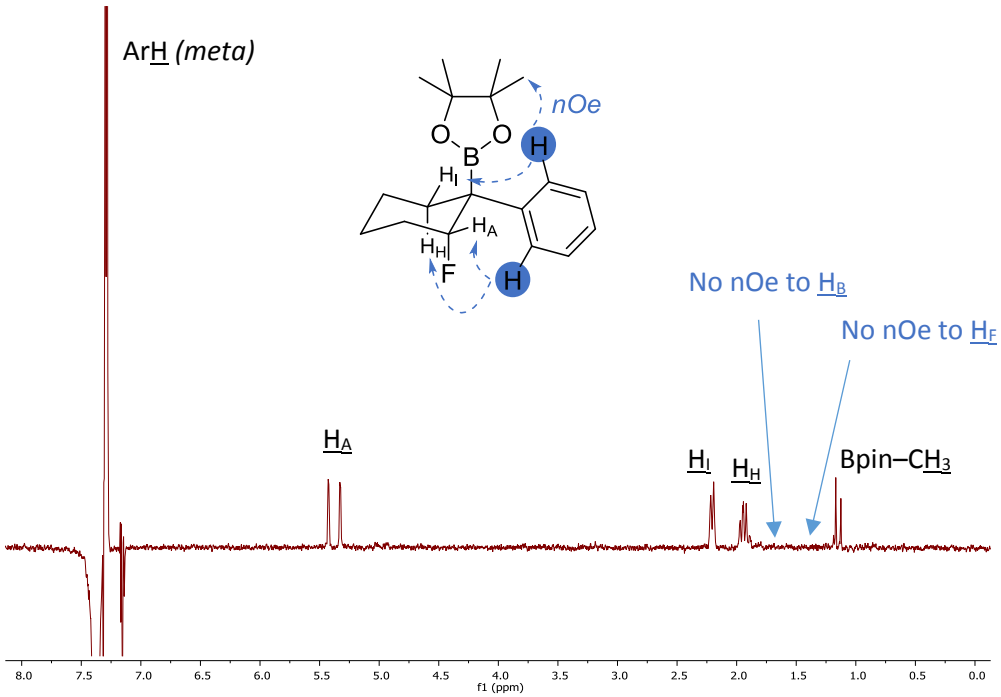
<u>2D HOESY Experiment, irradiation of fluorine:</u>



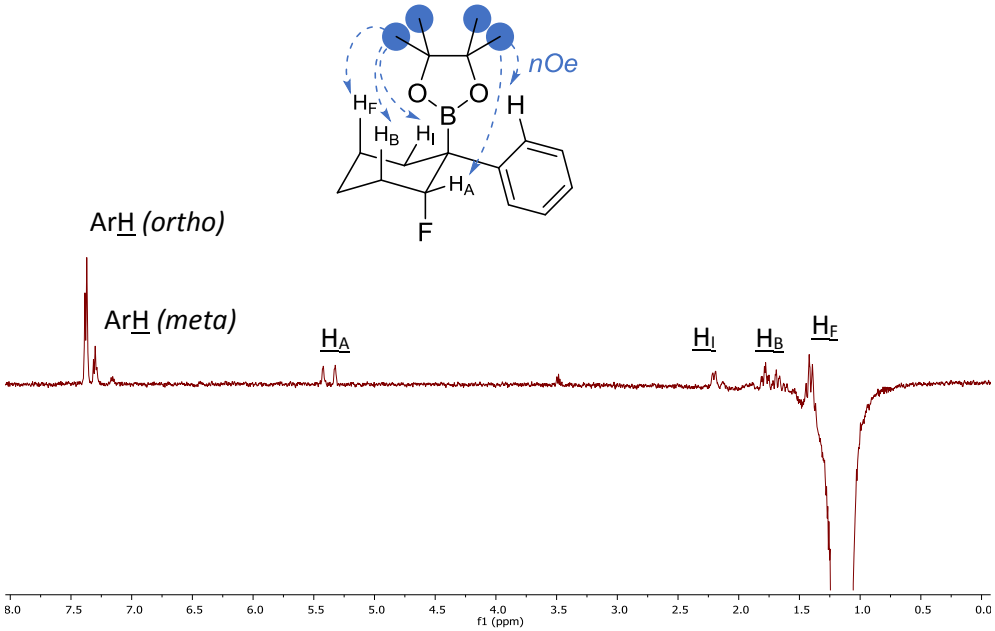
1D NOESY Experiment **A**, irradiation of H_A:

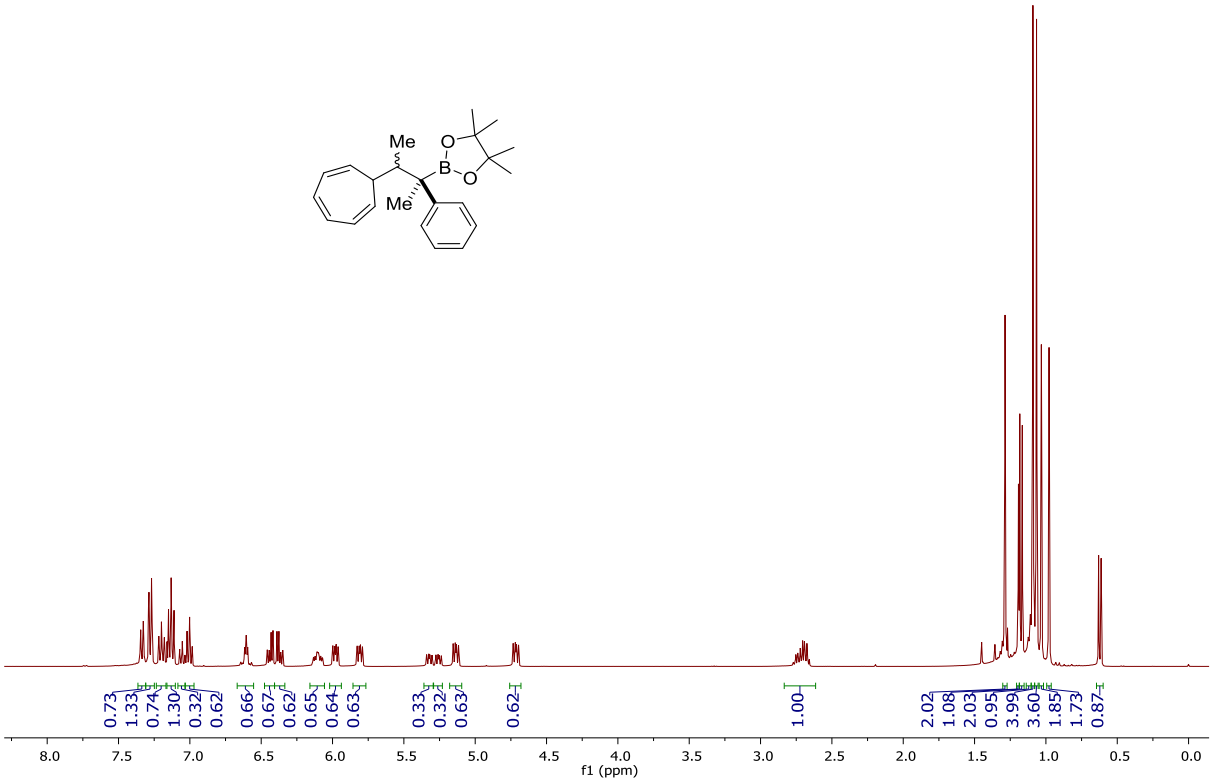


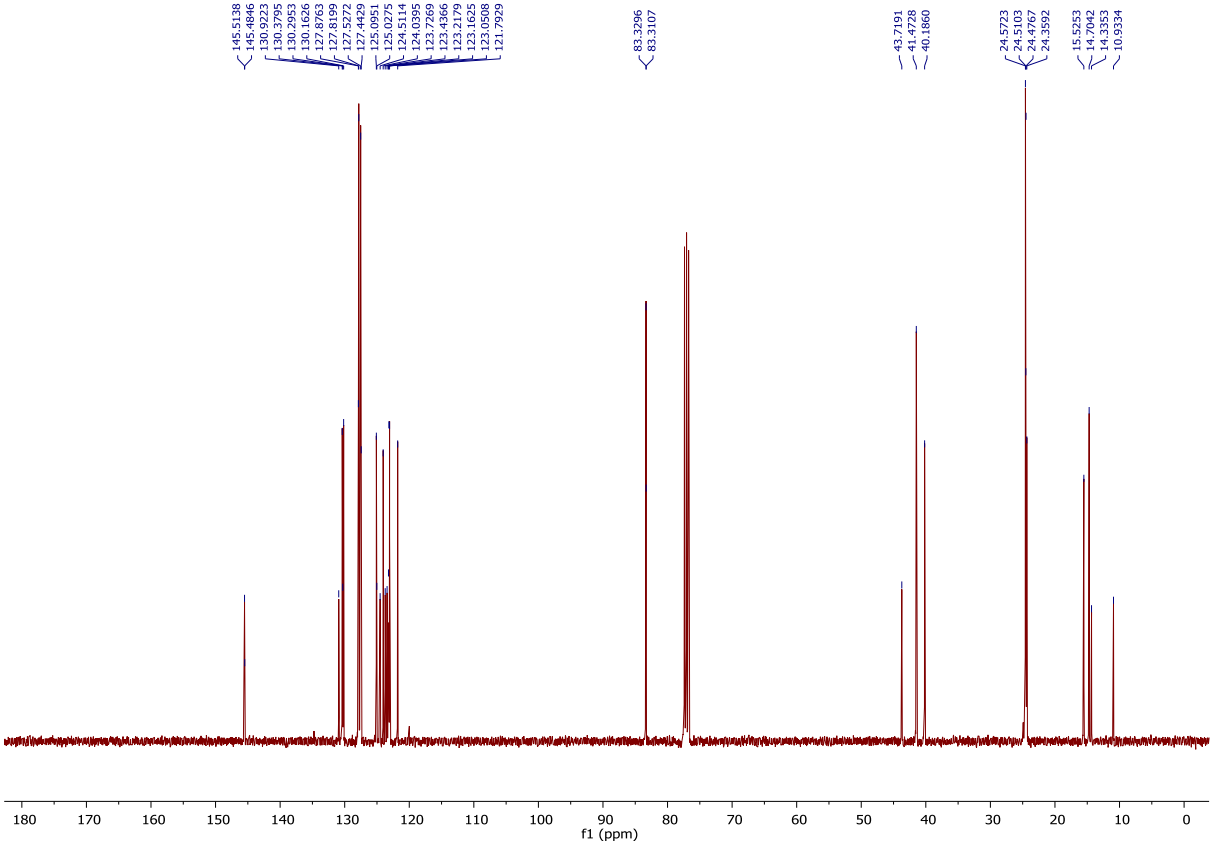
1D NOESY Experiment **B**, irradiation of ArH *(ortho)*:

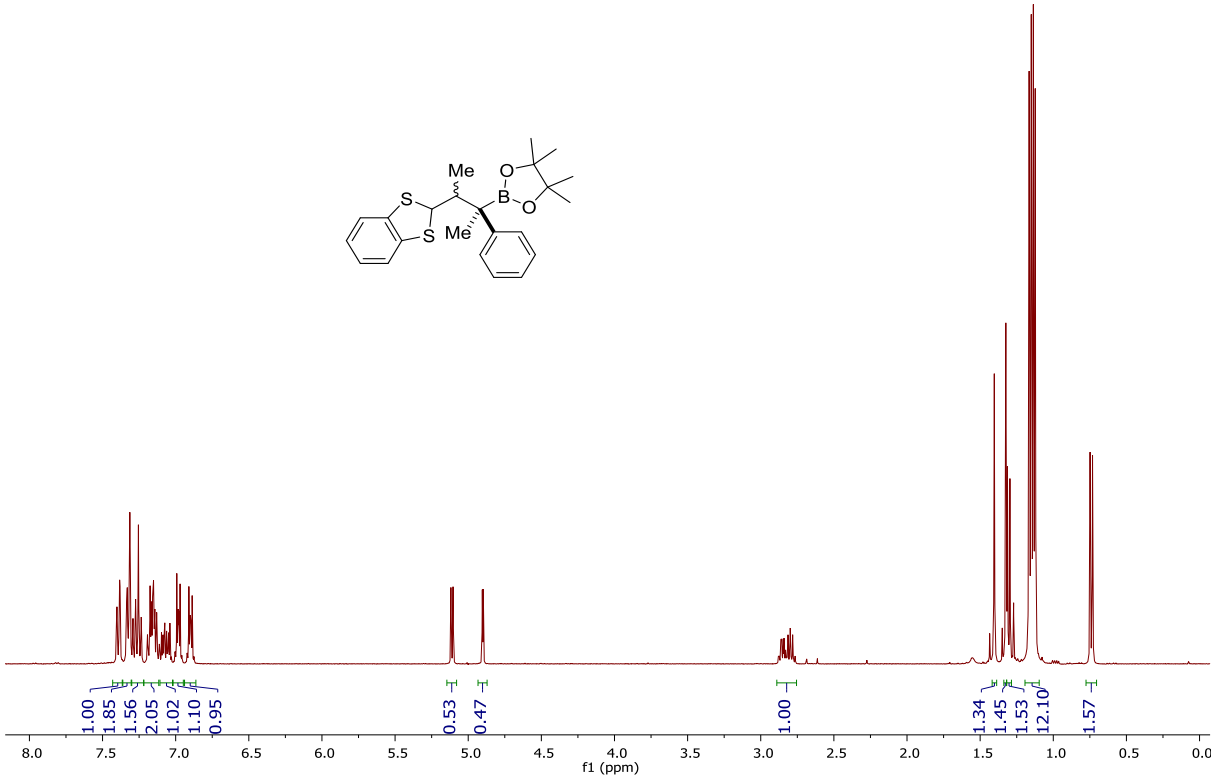


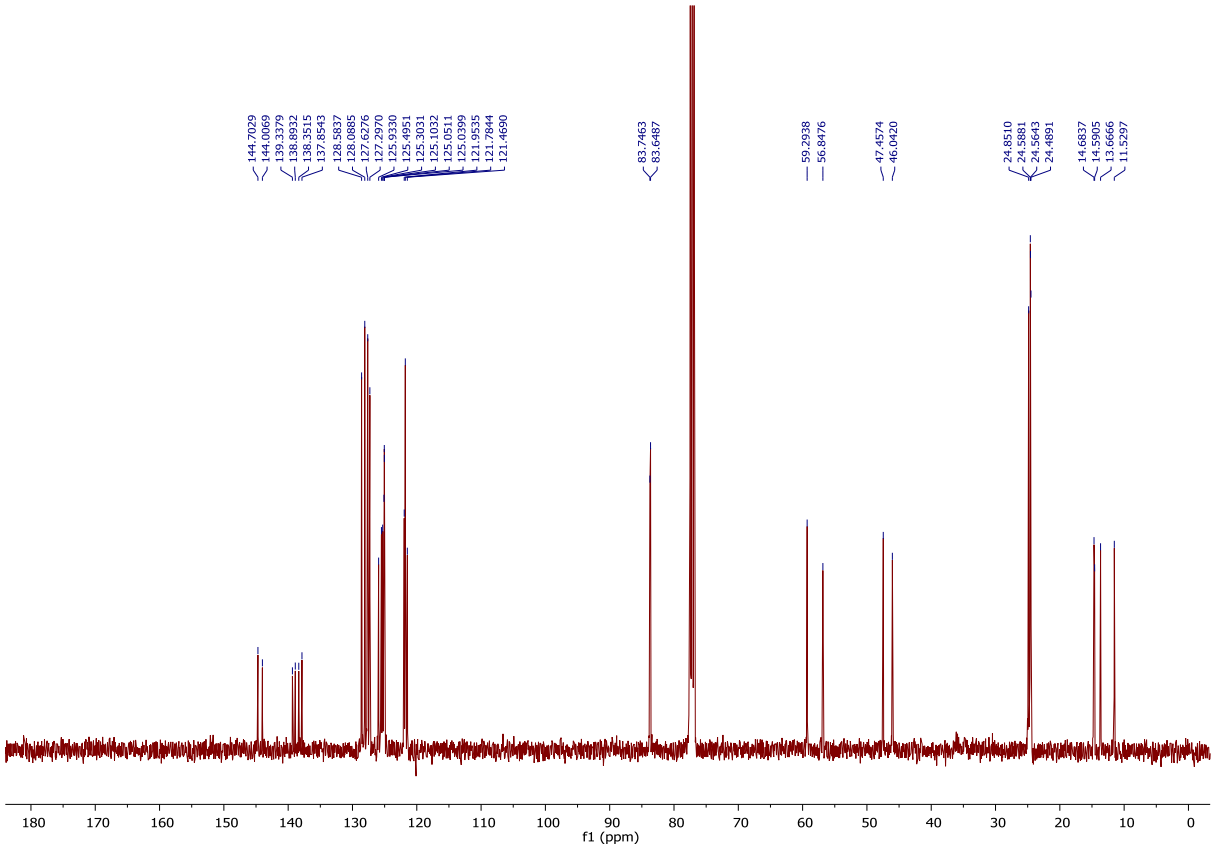
1D NOESY Experiment **C**, irradiation of Bpin–CH_3:

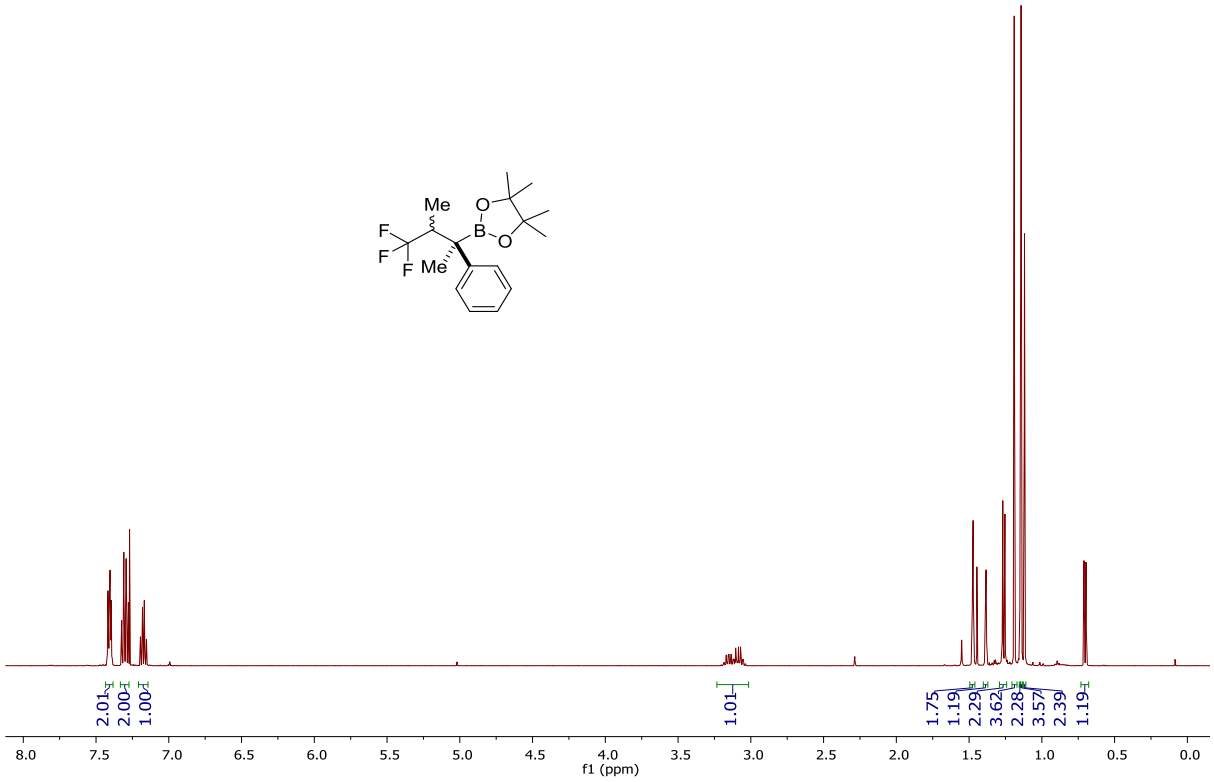


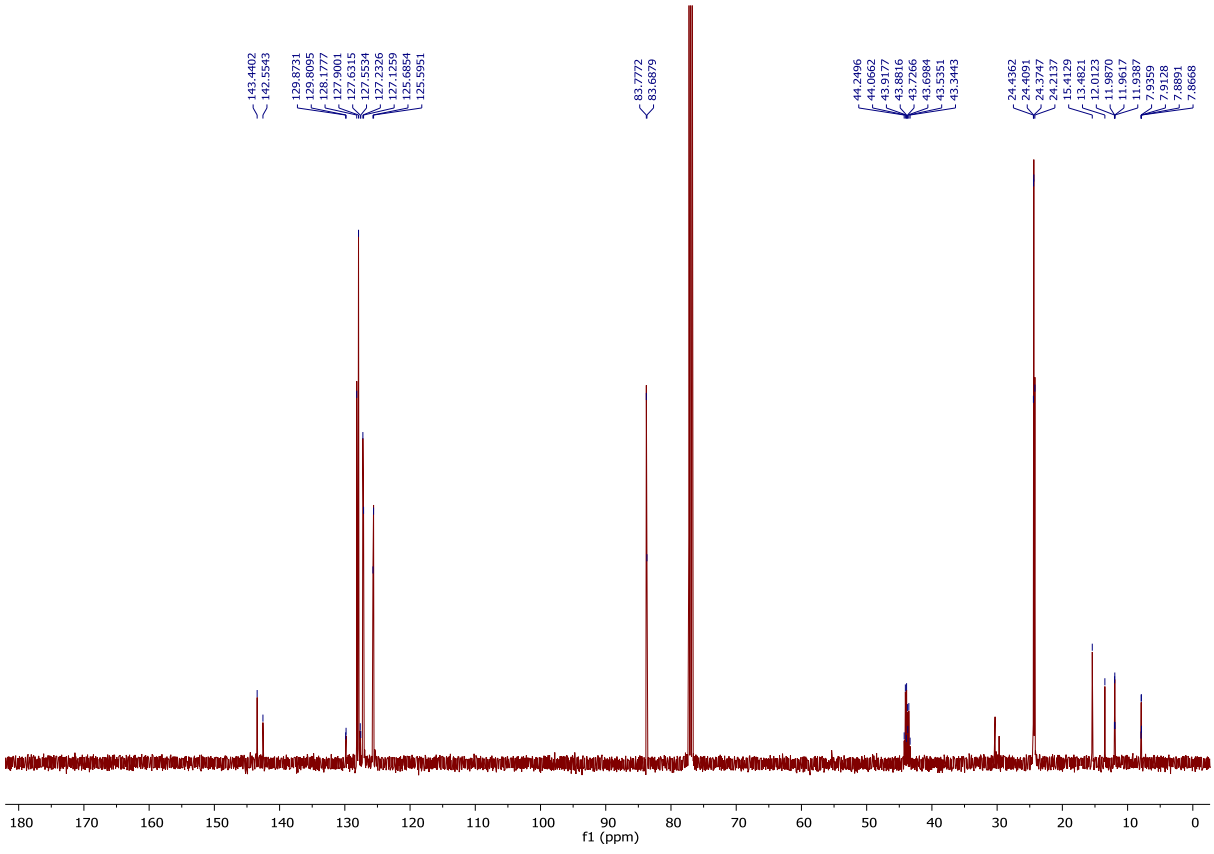

Me
O
B
O
Me
0.73
1.33
0.74
1.30
0.32
0.62
0.66
0.67
0.62
0.65
0.64
0.63
0.33
0.32
0.63
0.62
1.00
2.02
1.08
2.03
0.95
3.99
3.60
1.85
1.73
0.87
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

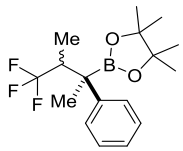

145.5138
145.4846
130.9223
130.3795
130.2953
130.1626
127.8763
127.8199
127.5272
127.4429
125.0951
125.0275
124.5114
124.0395
123.7269
123.4366
123.2179
123.1625
123.0508
121.7929
83.3296
83.3107
43.7191
41.4728
40.1860
24.5723
24.5103
24.4967
24.3592
15.5253
14.7042
14.3353
10.9334
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Me
S
S
S
Me
O
B
O
1.00
1.85
1.56
2.05
1.02
1.10
0.95
0.53
0.47
1.00
1.34
1.45
1.53
12.10
1.57
f1 (ppm)

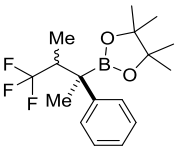

144.7029
144.0069
139.3379
138.8932
138.3515
137.8543
128.5837
128.0885
127.6276
127.2970
125.9330
125.4951
125.3031
125.1032
125.0511
125.0399
121.9535
121.7844
121.4690
83.7463
83.6487
59.2938
56.8476
47.4574
46.0420
24.8510
24.5881
24.5643
24.4891
14.6837
14.5905
13.6666
11.5297
f1 (ppm)


Me
O
B
O
F
F
F
Me
2.01
2.00
1.00
1.01
1.75
1.19
2.29
3.62
2.28
3.57
2.39
1.19
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

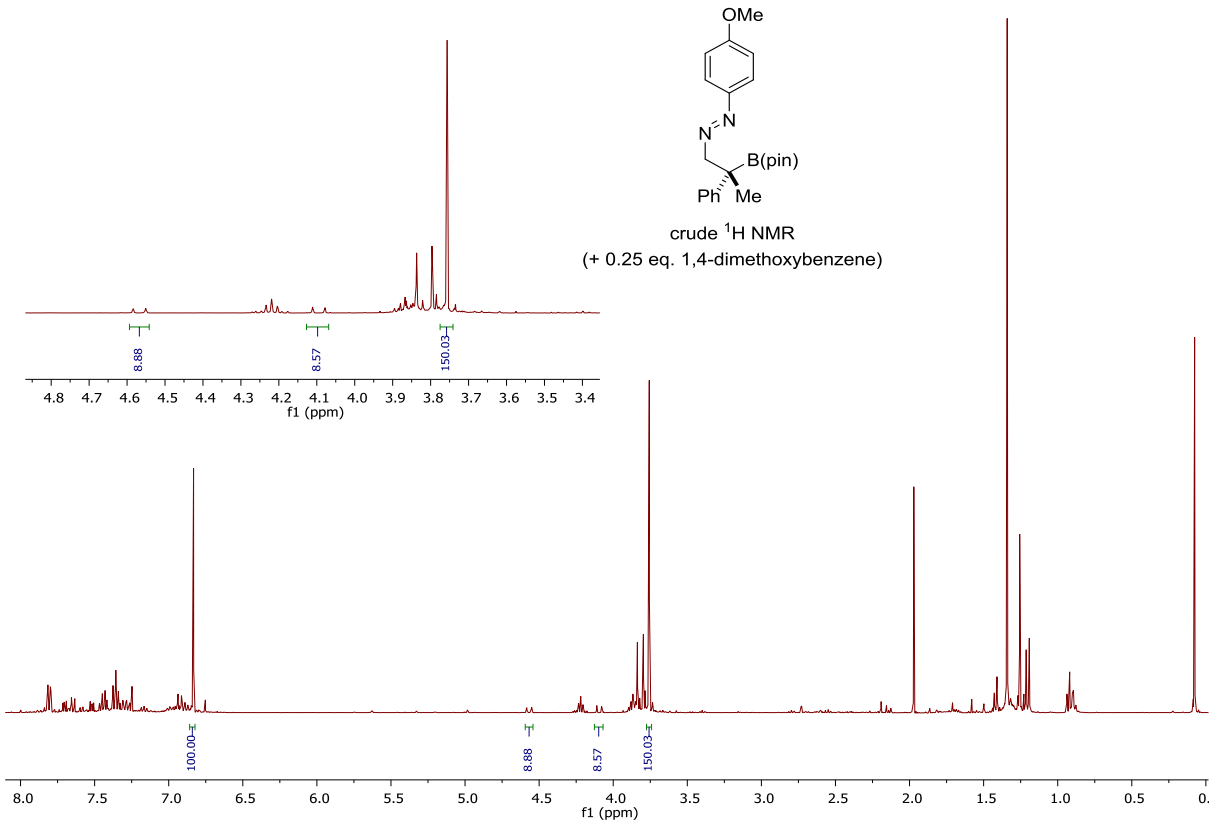

143.4402
142.5543
129.8731
129.8095
128.1777
127.9001
127.6315
127.5534
127.2326
127.1259
125.6854
125.5951
83.7772
83.6879
44.2496
44.0662
43.9177
43.8816
43.7266
43.6984
43.5351
43.3443
24.4362
24.4091
24.3747
24.2137
15.4129
13.4821
12.0123
11.9870
11.9617
11.9387
7.9359
7.9128
7.8891
7.8668
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

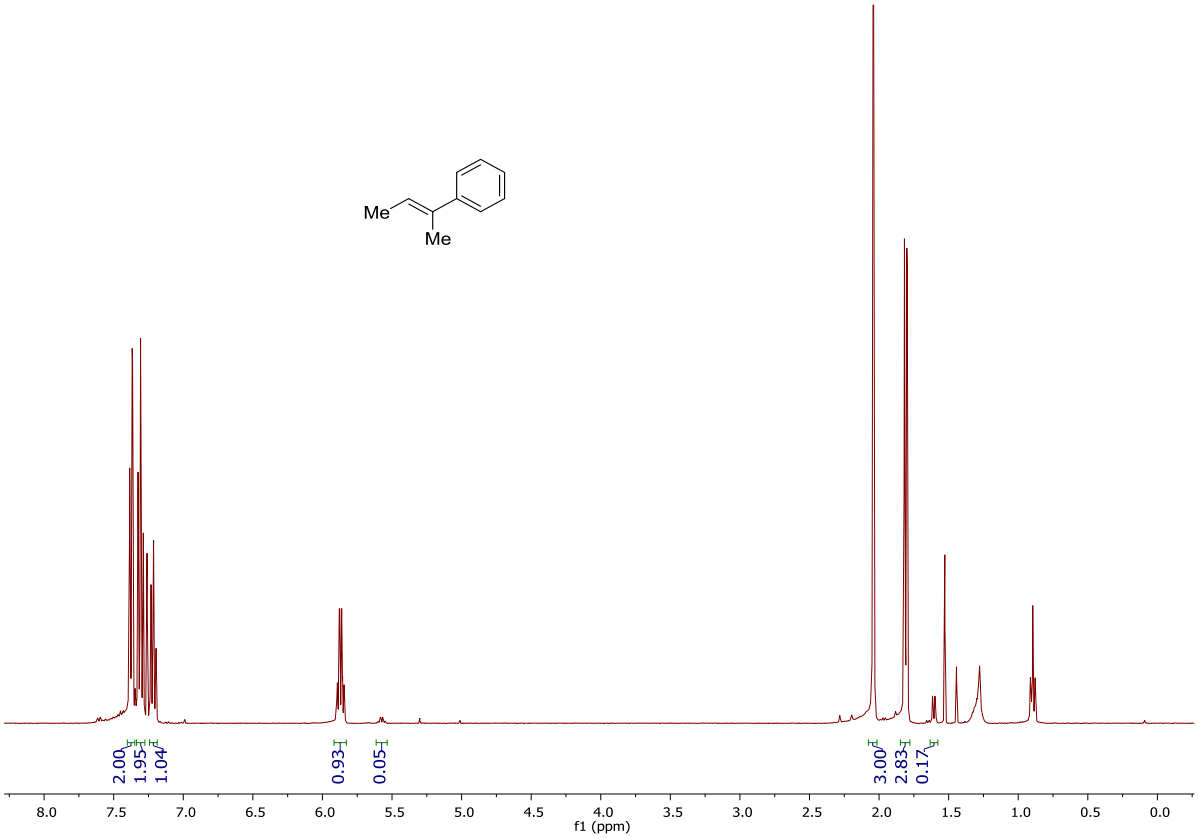


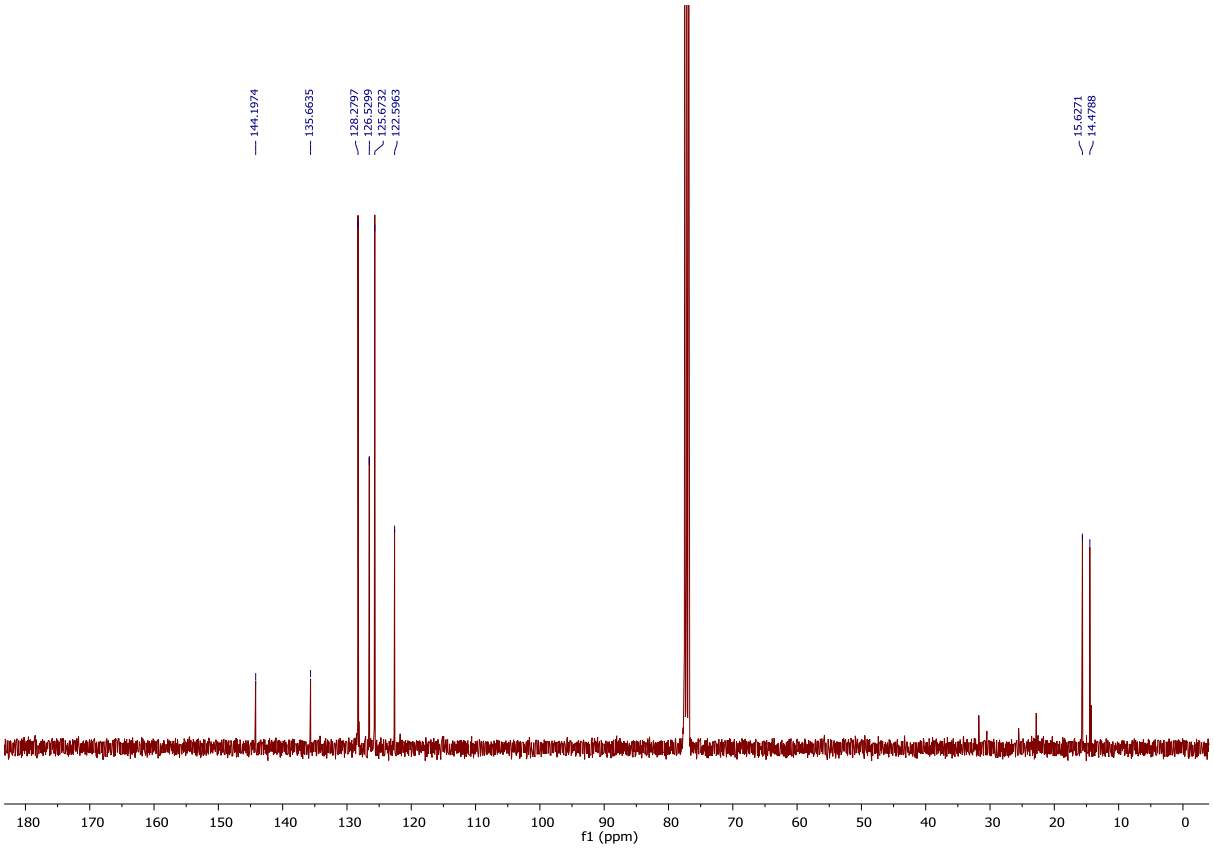
crude ^{19}F NMR
(+ 1.0 eq. $PhCF_3$)

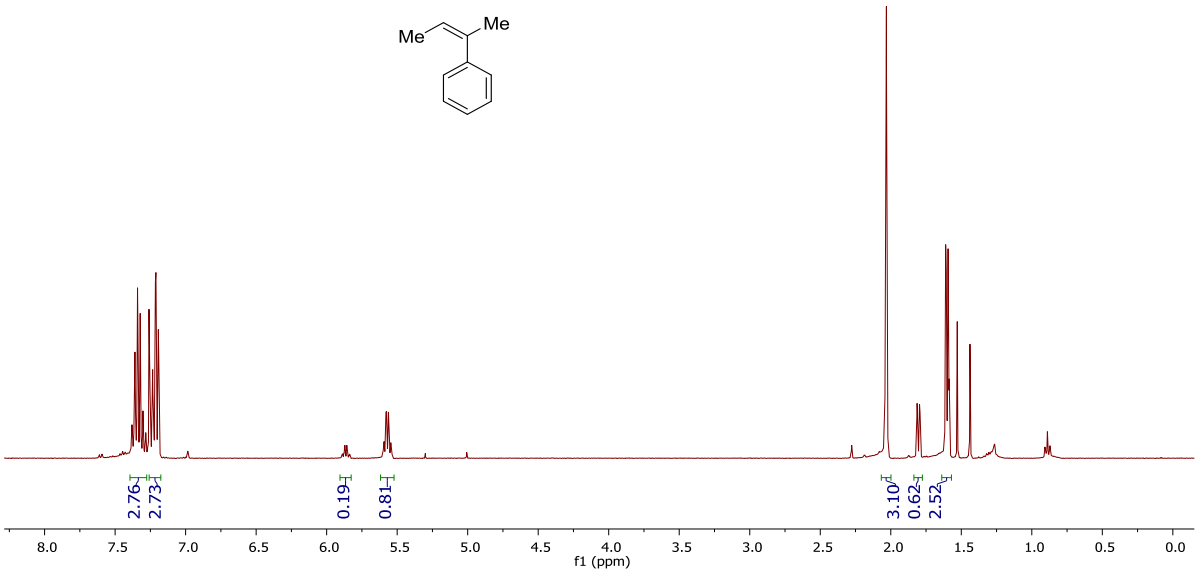


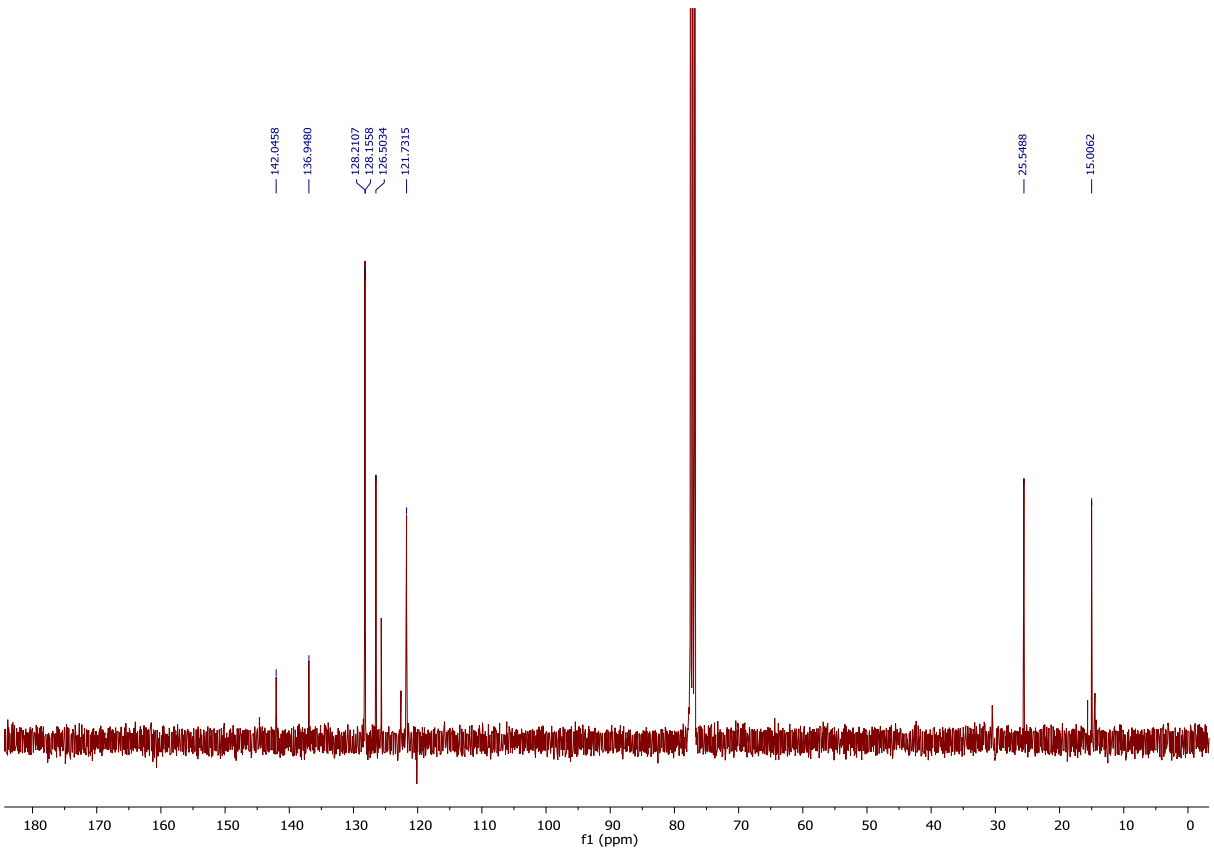
^{19}F NMR after isolation


OMe
N
N
B(pin)
Ph
Me
crude ^{1}H NMR
(+ 0.25 eq. 1,4-dimethoxybenzene)
8.88
8.57
150.03
100.00
f1 (ppm)


Me
Me
2.00
1.95
1.04
0.93
0.05
3.00
2.83
0.17
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


144.1974
135.6635
128.2797
126.5299
125.6732
122.5963
15.6271
14.4788
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Me
Me
2.76
2.73
0.19
0.81
3.10
0.62
2.52
f1 (ppm)


142.0458
136.9480
128.2107
128.1558
126.5034
121.7315
25.5488
15.0062
f1 (ppm)