Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Synthesis of Functionalized Cyclopropylboronic Esters Based on a 1,2-Metallate Rearrangement of Cyclopropenylboronate

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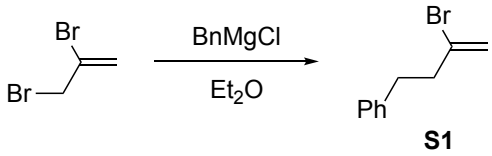
General Methods

IR spectra were recorded on a SHIMADZU FTIR-8400 spectrometer. UV/Vis spectrum was recorded on a Shimadzu UV-2500PC spectrophotometer. ^{1}H NMR spectra were measured on a Varian NMR System 600 PS600 spectrometer (600 MHz), a Varian 400-MR ASW spectrometer (400 MHz), and a Varian Mercury-300 spectrometer (300 MHz) at ambient temperature. Data were recorded as follows: chemical shift in ppm from the solvent resonance employed as the internal standard ($CHCl_3$ at 7.26 ppm) on the δ scale, multiplicity (s = singlet; d = doublet; t = triplet; m = multiplet), coupling constant (Hz), and integration. ^{13}C NMR spectra were measured on a Varian NMR System 600 PS600 spectrometer (150 MHz) and a Varian 400-MR ASW spectrometer (100 MHz) at ambient temperature. Chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard ($CDCl_3$ at 77.16 ppm). For TLC analysis, Merck precoated TLC plates (silica gel 60 F_{254} 0.25 mm) were used. For preparative column chromatography, Kanto Chemical Co., Inc. silica gel 60 N (spherical, neutral), Fuji Silysia Chemical PSQ100B, and Kanto Chemical Co., Inc. silica gel 60 (spherical) NH_2 were used. High- and low-resolution mass spectral analysis (HRMS) was measured on a JEOL JMS-700 Mstation (FAB) and a Bruker micrOTOF II (ESI) at Chemical Instrument Facility, Okayama University. Dry toluene, tetrahydrofuran (THF), dichloromethane (CH_2Cl_2), toluene, dimethyl sulfoxide (DMSO), methanol (MeOH), diethyl ether (Et_2O), ethyl acetate (EtOAc) and chloroform ($CHCl_3$) were purchased from Kanto Chemical Co., Inc. or Wako Pure Chemical Industries Ltd. as the “anhydrous” and stored under nitrogen. Other materials were obtained from commercial supplies and used without further purification. All reactions were conducted in a flame dried glassware under nitrogen atmosphere, otherwise noted.

Preparation of substrates

Synthesis of tribromocyclopropanes

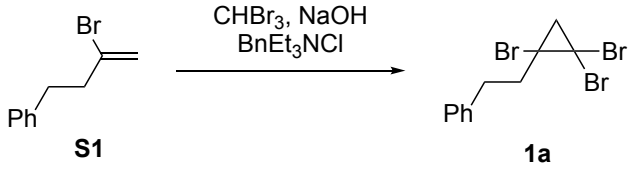
2-bromo-4-phenylbut-1-ene (S1)[2]



S1

Mg turning (770 mg, 30 mmol, 1.25 eq.) was added to the flame-dried flask and dried under vacuum with heat-gun. After cooling down to rt, the flask was added small crystal iodine. This mixture was then added benzyl chloride (a few drops) to initiate the reaction. When the solution became warm, benzyl chloride (3.45 mL, 30 mmol, 1.25 eq.) in Et_2O (10 ml) was added dropwise to this solution at 0 °C and stirred for 2 h at the same temperature. After the period of time, obtained Grignard reagent was added to a solution of 2,3-dibromoprop-1-ene (2.35 mL, 24 mmol, 1.0 eq.) in Et_2O (20 ml) at 0 °C. After being stirred for 2 h, the reaction was quenched with 6 M HCl, and the mixture was extracted Et_2O. The organic layer was washed by brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (hexane) on silica gel to obtain **S1** (3.95 g, 18.7 mmol, 78%) as a colorless oil.

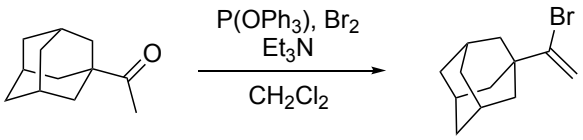
1,1,2-2-(2-phenylethyl)tribromocyclopropane (1a)[1]



S1 **1a**

To a mixture of 2-bromo-4-phenylbut-1-ene (**S1**) (1.39 g, 6.57 mmol, 1.0 eq.), bromoform (1.8 mL, 20.7 mmol, 3.14 eq.) and benzyltriethylammonium chloride (168 mg, 0.738 mmol, 0.11 eq.) was added NaOH (1.3 g, 32.5 mmol, 5.0 eq.) and CH_2Cl_2 (2 ml). The reaction mixture was sonicated in ultrasound bath for 5 h. The mixture was filtrated through Celite and washed with CH_2Cl_2. The combined filtrates were concentrated under reduced pressure. The crude product was purified by column chromatography (hexane) on silica gel to obtain tribromocyclopropane **1a** (1.08 g, 2.82 mmol, 43%) as a yellow oil. The spectral data of obtained material was identical to literature data.[1]

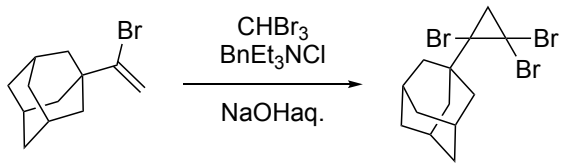
***rac*-(1*S*,3*S*)-1-(1-bromovinyl)adamantane (S2)**[3]



S2

S2 was synthesized from 1-adamantyl methyl ketone following a reported procedure.[4] To a solution of $P(OPh)_3$ (2.9 mL, 11 mmol, 1.1 eq.) in dry CH_2Cl_2 (100 mL) was slowly added Br_2 (0.57 mL, 11 mmol, 1.2 eq.) at –78 °C. After being stirred for 15 min, Et_3N (1.67 mL, 12 mmol, 1.2 eq.) was added to this solution and stirred for 10 minutes. To the solution, 1-Adamantyl methyl ketone (1.78 g, 10 mmol, 1.0 eq) was added. The reaction mixture was gradually warmed to rt and stirring was continued overnight. The reaction was then heated at reflux for 2 hours, before being quenched with saturated sodium sulfite at rt. The mixture was extracted with CH_2Cl_2. The organic layers were washed by brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (hexane) on silica gel to obtain **S2** (1.04 g, 4.33 mmol, 43%) as an oil. The spectral data of obtained material was identical to literature data.

***rac*-(1*S*,3*S*)-1-(1,2,2-tribromocyclopropyl)adamantane (S3)**

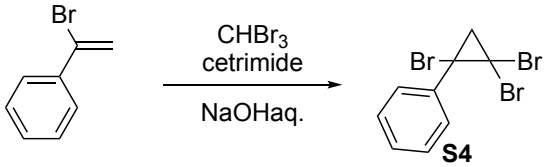


S2 **S3**

To a mixture of **S2** (1.03 g, 4.26 mmol, 1.0 eq.), bromoform (3.0 mL, 34.4 mmol, 8.0 eq.) and benzyltriethylammonium chloride (102 mg, 0.45 mmol, 0.11 eq.) was added 50% NaOH aq. (1.0 g, 25.0 mmol, 5.9 eq.). After being stirred for 4 days, the reaction was quenched with 6 M HCl, and the mixture were extracted with Et_2O and washed by brine. The organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (hexane) on silica gel to obtain tribromocyclopropane **49** (363 mg, 0.88 mmol, 21%) as a colorless oil.

Rf 0.70 (hexane); IR (film) 2905, 2849, 1449, 1410, 1360, 1343, 1310, 1099, 1061, 993, 673, 627 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 2.26 (d, *J* = 9.6 Hz, 1H), 2.09 (br d, *J* = 12.0 Hz, 3H), 2.05-2.02 (m, 3H), 1.96 (br d, *J* = 12.0 Hz, 3H), 1.86 (d, *J* = 9.6 Hz, 1H) 1.66 (s, 6H); ^{13}CNMR (150 MHz, $CDCl_3$) δ 56.9, 40.7, 40.0, 36.6, 33.8, 30.4, 29.2; LRMS (FAB) *m/z* calcd for $C_{13}H_{17}Br_2^+$ $[M–Br^-]^+$ 331.0, found 331.0

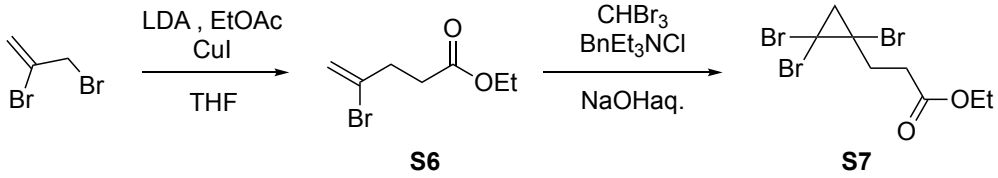
(1,2,2-tribromocyclopropyl)benzene (S4)[5]



S4

Following the procedure described for the synthesis of 1-(1,2,2-tribromocyclopropyl)adamantane (**S3**), (1-bromovinyl)benzene (643 mg, 3.51 mmol) was converted to tribromocyclopropane **S4** (217.4 mg, 0.61 mmol, 17%) using cetrimide as a catalyst instead of $BnEt_3NCl$, which was obtained as a colorless oil. The spectral data of obtained material was identical to literature data.

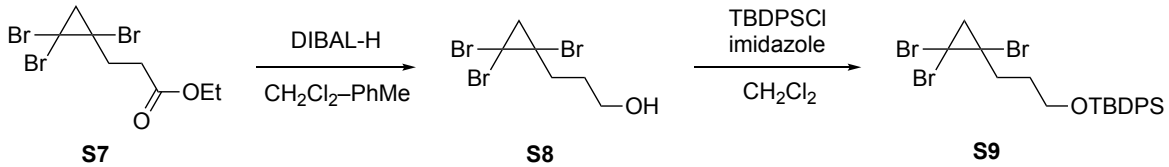
***tert*-butyldiphenyl(3-(1,2,2-tribromocyclopropyl)propoxy)silane (S9)**[6]



S6 **S7**

LDA was prepared with treating a solution of diisopropylamine (5.8 mL, 41.3 mmol, 2.0 eq.) in THF (15 mL) with *n*-BuLi (26 mL, 41.6 mmol, 1.6 M in hexanes) at –78 °C, and gradually warming up to rt over for 2 h. In the separate flask, CuI (16 g, 84.0 mmol, 4.0 equiv.) and EtOAc (6.0 mL, 61.3 mmol, 3.0 eq.) were suspended in THF (40 mL). The mixture was cooled to –40 °C and treated with LDA. The reaction mixture was warmed up to –30 °C before adding a solution of 2,3-dibromopropene (3.88 mL, 37.5 mmol, 1 eq.) in THF (10 mL). After being stirred at same temperature for 2.5 hours, the reaction was quenched with aqueous saturated NH_4Cl (100 mL). The mixture was extracted with Et_2O and the organic layers were dried over $MgSO_4$. After removing the solvent under reduced pressure, the crude product was purified by column chromatography (hexane:Et_2O = 10:1) on silica gel to obtain ethyl 4-bromopent-4-enoate **S7** (2.9516 g) containing some impurities.

A part of **S7** (968 mg) was subjected to the procedure described for the synthesis of tribromocyclopropane **S4** described above. Because the separation of the tribromocyclopropane **S7** from starting material **S6** by column chromatography was difficult, relatively pure fraction (595 mg, ca 10% of **S6** was contaminated) was collected and used for next reaction.



S7 **S8** **S9**

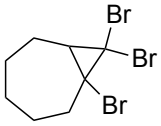
To a solution of ester **S7** (589 mg contains impurity) in CH_2Cl_2 (3 mL) was added a DIBAL-H (1.01 M in toluene, 3.1 mL, 3.1 mmol) at –78 °C. The reaction mixture was removed from the cooling bath and

stirred for 2 h. Because the starting material was still remaining at this point, the mixture was cooled back to –78 °C and additional DIBAL-H (1.01 M in toluene, 3.1 mL, 3.1 mmol) was added. After being stirred for 2 h, another DIBAL-H (1.01 M in toluene, 3.1 mL, 3.1 mmol) was added to complete the reaction. After 1 h, the reaction was quenched with saturated aqueous Rochelle's salt at –78 °C. The mixture was stirred vigorously at rt overnight and then extracted with CH_2Cl_2. The organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (CH_2Cl_2) on silica gel to obtain **S8** (224.3 mg) as a mixture with reduced **S6**.

The alcohol **S8** obtained above was dissolved in CH_2Cl_2 (1 mL) and treated with imidazole (107 mg, 1.57 mmol) and *tert*-Butyl(chloro)diphenylsilane (200 mL, 0.924 mmol) at rt. After being stirred at rt for 1 h, the mixture was quenched with aqueous saturated $NaHCO_3$ at 0 °C. The mixture was extracted with CH_2Cl_2 and the organic layers were dried over $MgSO_4$. After removing the solvent under reduced pressure, the crude product was purified by column chromatography (hexane) on silica gel to afford **S9** (315.0 mg, 0.548 mmol) as a colorless oil.

Rf 0.25 (hexane); IR (film) 3071, 3046, 2957, 2930, 2857, 1472, 1427, 1200, 1111, 1017, 980, 824, 741, 700, 691, 613 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.67–7.64 (m, 4H), 7.44–7.41 (m, 2H), 7.39–7.36 (m, 4H), 3.77–3.70 (m, 2H), 2.26 (ddd, *J* = 14.4, 10.8, 5.4 Hz, 1H), 2.11 (ddd, *J* = 14.4, 10.8, 4.2 Hz, 1H), 2.04–1.97 (m, 1H), 1.94 (dd, *J* = 9.0, 0.6 Hz, 1H), 1.92–1.87 (m, 1H), 1.86 (d, *J* = 9.0, 1H), 1.04 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 135.72, 135.71, 133.91, 133.85, 129.8, 127.8, 127.8, 62.8, 45.7, 38.5, 38.1, 33.2, 30.9, 27.0, 19.4; HRMS (ESI) *m/z* calcd for $C_{22}H_{27}Br_3NaOSi^+$ $[M+Na]^+$ 596.9253, found 596.9252.

1,8,8-tribromobicyclo[5.1.0]octane (S10)[7]



S10

Tribromocyclopropane **S10** was prepared according to the literature procedure.[6]

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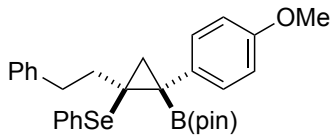
1. L. K. Sydnes, K. L. S. Alnes, N. Erdogan, *Monatshefte Für Chemie.* 2005*,* **136***,* 1737.
2. H. Gilman, W. E. Catlin, *Org. Synth*. 1925, **4**, 59.
3. J. L. Hofstra, K. E. Poremba, A. M. Shimozono, S. E. Reisman, *Angew. Chem. Int. Ed.* 2019, **58**, 14901.
4. C. –C. Xi, Z.–M. Chen, S.–Y. Zang, Y.–Q. Tu, *Org. Lett.* 2018, **20**, 4227.
5. G. -A. Lee, C. -Y. Chang, *J. Org. Chem.* 2004, **69**, 8949.
6. R. E. Ruscoe, N. J. Fazakerley, H. Huang, S. Flitsch, D. J. Procter*, Chem. Eur. J.* 2016, **22**, 116.
7. G. -A. Lee, C. P. -K. Chen, M. -Y. Chen, *J. Chin. Chem. Soc.* 1998, **45**, 381.

Synthesis of cyclopropylboronic esters via 1,2-metallate rearrangement

General procedure for the synthesis of β-selenocyclopropylboronic ester

The solution of tribromocyclopropane **1a** (100 mg, 0.261 mmol, 1.0 eq.) in Et_2O (3 mL) was cooled to –78 °C and treated with *n*-BuLi (1.5 M in hexanes, 0.39 mL, 0.59 mmol, 2.2 eq.). After being stirred for 15 min, the mixture was added a solution of boronic ester (0.39 mmol, 1.5 eq.) in Et_2O (1 mL) via cannular and stirred for 1 h at the same temperature. To the solution was then added a solution of PhSeCl (70.0 mg, 0.365 mmol, 1.4 eq.) and stirred at the same temperature for 30 min. After the period of time, cooling bath (acetone-dry ice bath) was removed and the mixture was gradually warmed up. After being stirred for additional 30 min (the temperature was reached to approximately 0 °C), the reaction was quenched with aqueous saturated $NaHCO_3$ and extracted with Et_2O. The organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel.

***rac*-2-((1*R*,2*S*)-1-(4-methoxyphenyl)-2-phenethyl-2-(phenylselanyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2a)**

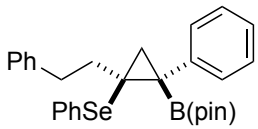


2a

Following the general procedure, tribromocyclopropane **1a** (101 mg, 0.264 mmol) was converted to the corresponding cyclopropane. Purification of the crude mixture by flash chromatography (hexane:Et_2O = 60:1) gave **2a** (111 mg, 0.208 mmol, 79%) as a colorless solid.

Rf 0.48 (hexane:Et_2O = 5:1); IR (film) 2978, 2930, 1510, 1371, 1246,1144, 851, 745, 698 cm^{-1}.; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85–7.79 (m, 2H), 7.37–7.25 (m, 5H), 7.12–7.03 (m, 3H), 6.78–6.76 (m, 4H), 3.77 (s, 3H), 2.87 (app td, *J* = 12.6, 4.4 Hz, 1H), 2.64 (ddd, *J* = 13.2, 12.0, 5.6 Hz, 1H), 1.60 (dd, *J* = 5.2, 0.8 Hz, 1H), 1.42 (dddd, *J* = 15.2, 12.0, 4.4, 0.8 Hz, 1H), 1.30 (d, *J* = 5.2 Hz, 1H), 1.24–1.15 (m, 1H), 1.23 (s, 6H), 1.22 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 142.4, 134.0, 131.5, 131.1, 130.3, 129.1, 128.5, 128.2, 127.4, 125.6, 113.5, 84.1, 55.3, 37.2, 34.3, 34.2, 25.3, 24.8, 22.0; HRMS (ESI) *m/z* calcd for $C_{30}H_{35}BNaO_3Se^+$ $[M+Na]^+$ 557.1737, found 557.1735.

***rac*-4,4,5,5-tetramethyl-2-((1*R*,2*S*)-2-phenethyl-1-phenyl-2-(phenylselanyl)cyclopropyl)-1,3,2-dioxaborolane (2b)**



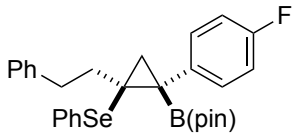
2b

Following the general procedure, tribromocyclopropane **1a** (102 mg, 0.267 mmol) was converted to corresponding cyclopropane. Purification of the crude mixture by flash chromatography (hexane:Et_2O = 80:1) gave **2b** (105 mg, 0.209 mmol, 78%) as a colorless solid.

For the large-scale reaction, tribromocyclopropane **1a** (1.01 g, 2.64 mmol) was converted to **2b** (1.12 g, 2.23 mmol, 84%) following the same procedure and purification method.

Rf 0.63 (hexane:Et_2O = 5:1); IR (film) 3057, 2980, 2930, 1597, 1578, 1489, 1371, 1314, 1202, 1165, 1142, 1045, 1022, 964, 854, 745, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85–7.80 (m, 2H), 7.40–7.28 (m, 5H), 7.28–7.22 (m, 2H), 7.18–7.13 (m, 1H), 7.18–7.01 (m, 3H), 6.77–6.73 (m, 2H), 2.86 (app td, *J* = 12.8, 4.4 Hz, 1H), 2.64 (ddd, *J* = 13.2, 11.6, 5.6 Hz, 1H), 1.63 (dd, *J* = 5.2, 0.8 Hz, 1H), 1.43 (dddd, *J* = 15.6, 11.6, 4.4, 0.8 Hz, 1H), 1.35 (dd, *J* = 5.2, 0.8 Hz, 1H), 1.35 (d, *J* = 5.6 Hz, 1H), 1.24–1.14 (m, 1H), 1.24 (s, 6H), 1.22 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 139.5, 134.1, 130.24, 130.17, 129.1, 128.5, 128.2, 128.1, 127.5, 126.0, 125.6, 84.2, 37.4, 34.4, 34.2, 25.3, 24.8, 22.0; HRMS (ESI) *m/z* calcd for $C_{29}H_{33}BNaO_2Se^+$ $[M+Na]^+$ 527.1631, found 527.1631.

***rac* -2-((1*R*,2*S*)-1-(4-fluorophenyl)-2-phenethyl-2-(phenylselanyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2c)**



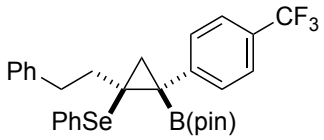
2c

Following the general procedure, tribromocyclopropane **1a** (100 mg, 0.261 mmol) was converted to the corresponding cyclopropane. Purification of the crude mixture by flash chromatography (hexane:Et_2O = 100:1) gave **2c** (91.6 mg, 0.176 mmol, 67%) as a colorless solid.

Rf 0.50 (hexane:Et_2O = 5:1); IR (film) 3057, 2980, 2930, 1601, 1506, 1371, 1323, 1220, 1144, 853, 745, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.84–7.80 (m, 2H), 7.38–7.28 (m, 5H), 7.14–7.08 (m, 2H), 7.08–7.03 (m, 1H), 6.97–6.90 (m, 2H), 6.81–6.76 (m, 2H), 2.87 (app td, *J* = 12.4, 4.4 Hz, 1H), 2.64 (ddd, *J* = 13.2, 11.6, 5.6 Hz, 1H), 1.63 (dd, *J* = 5.2, 0.8 Hz, 1H), 1.41 (dddd, *J* = 14.4, 11.6, 4.4, 0.8 Hz, 1H), 1.27 (d, *J* = 5.2 Hz, 1H), 1.24 (s, 6H), 1.22 (s, 6H), 1.13 (ddd, *J* = 14.4, 12.0, 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4 (d, *J* = 242.7 Hz), 142.2, 135.3 (d, *J* = 3.2 Hz), 134.2, 131.6 (d, *J* = 7.9 Hz), 130.0, 129.1, 128.5, 128.3, 127.6,

125.7, 114.9 (d, *J* = 21.2 Hz), 84.3, 37.4, 34.3, 34.1, 25.3, 24.8, 22.1; HRMS (ESI) *m/z* calcd for $C_{29}H_{32}BFNaO_2Se^+$ $[M+Na]^+$ 545.1537, found 545.1537.

***rac*-4,4,5,5-tetramethyl-2-((1*R*,2*S*)-2-phenethyl-2-(phenylselanyl)-1-(4-(trifluoromethyl)phenyl)cyclopropyl)-1,3,2-dioxaborolane (2d)**

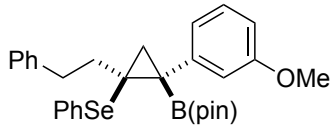


2d

Following the general procedure, tribromocyclopropane **1a** (103 mg, 0.269 mmol) was converted to the corresponding cyclopropane. Purification of the crude mixture by flash chromatography (hexane:Et_2O = 50:1) gave **2d** (109 mg, 0.190 mmol, 71%) as a white amorphous.

Rf 0.55 (hexane:Et_2O = 5:1); IR (film) 3059, 3026, 2980, 2930, 1614, 1371, 1325, 1215, 1165, 1144, 1125, 1071, 1017, 853, 745, 694 cm^{-1}.; ^1H NMR (600 MHz, $CDCl_3$) δ 7.86–7.82 (m, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.39–7.32 (m, 3H), 7.11 (app t, *J* = 7.2 Hz, 2H), 7.08–7.04 (m, 1H), 6.76 (d, *J* = 7.2 Hz, 2H), 2.87 (app td, *J* = 12.6, 3.6 Hz, 1H), 2.64 (ddd, *J* = 12.8, 12.0, 6.0 Hz, 1H), 1.69 (d, *J* = 5.4, 1H), 1.41 (ddd, *J* = 14.4, 12.0, 3.6 Hz, 1H), 1.33 (d, *J* = 5.4 Hz, 1H), 1.25 (s, 6H), 1.23 (s, 6H), 1.06 (ddd, *J* =14.4, 12.0, 6.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.07 (app d, *J* = 1.0 Hz), 142.0, 134.4, 130.5, 129.7, 129.2, 128.5, 128.3, 128.2 (q, *J* = 31.5 Hz) 127.8, 125.8, 125.0 (q, *J* = 3.0 Hz), 124.5 (q, *J* = 270.0 Hz), 84.5, 37.6, 34.5, 34.1, 25.3, 24.8, 22.0; HRMS (ESI) *m/z* calcd for $C_{30}H_{32}BF_3NaO_2Se^+$ $[M+Na]^+$ 595.1505, found 595.1505.

***rac*-2-((1*R*,2*S*)-1-(3-methoxyphenyl)-2-phenethyl-2-(phenylselanyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2e)**



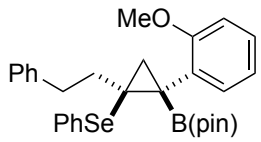
2e

Following the general procedure, tribromocyclopropane **1a** (102 mg, 0.265 mmol) was converted to the corresponding cyclopropane. Purification of the crude mixture by flash chromatography (hexane:Et_2O = 60:1) gave **2e** (92.7 mg, 0.174 mmol, 66%) as a colorless solid.

Rf 0.48 (hexane:Et_2O = 5:1); IR (film) 3057, 2980, 2930, 1371, 1323, 1311, 1215, 1144, 773, 748, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.86–7.82 (m, 2H), 7.38–7.29 (m, 3H), 7.17 (t, *J* = 8.0 Hz, 1H), 7.14–7.03 (m,

3H), 6.99–6.95 (m, 2H), 6.79 (d, *J* = 5.2 Hz, 2H), 6.72 (ddd, *J* = 8.0, 2.4, 1.2 Hz, 1H), 3.79 (s, 3H), 2.90 (app td, *J* = 12.8, 4.0 Hz, 1H), 2.66 (app td, *J* = 12.4, 5.6 Hz, 1H), 1.63 (d, *J* = 7.2 Hz, 1H), 1.43 (ddd, *J* = 14.4, 11.6, 4.0 Hz, 1H), 1.35 (d, *J* = 5.6 Hz, 1H), 1.25–1.16 (m, 1H), 1.25 (s, 6H), 1.24 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 142.3, 141.1, 134.1, 130.2, 129.1, 128.9, 128.5, 128.2, 127.5, 125.6, 122.7, 115.9, 111.6, 84.2, 55.2, 37.3, 34.5, 34.2, 25.3, 24.8, 22.1; HRMS (ESI) *m/z* calcd for $C_{30}H_{35}BNaO_3Se^+$ $[M+Na]^+$ 557.1737, found 557.1737.

***rac*-2-((1*R*,2*S*)-1-(2-methoxyphenyl)-2-phenethyl-2-(phenylselanyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2f)**

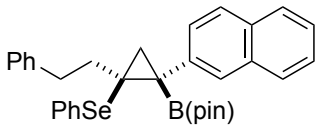


2f

Following the general procedure, tribromocyclopropane **1a** (102 mg, 0.267 mmol) was converted to the corresponding cyclopropane. Purification of the crude mixture by flash chromatography (hexane:Et_2O = 50:1) gave **2f** (104 mg, 0.195 mmol, 73%) as a colorless solid.

Rf 0.48 (hexane:Et_2O = 5:1); IR (film) 3057, 2980, 2932, 2833, 1580, 1489, 1370, 1316, 1242, 1146, 1028, 847, 750, 694 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95–7.91 (m, 2H), 7.36–7.28 (m, 3H), 7.16–7.02 (m, 5H), 6.85–6.79 (m, 4H), 3.76 (s, 3H), 3.00 (app td, *J* = 12.8, 4.0 Hz, 1H), 2.56 (ddd, *J* = 13.2, 12.0, 5.6 Hz, 1H), 1.80–1.70 (m, 1H), 1.65 (dd, *J* = 7.8, 1.2 Hz, 1H), 1.23–1.11 (m, 1H), 1.20 (s, 6H), 1.18 (s, 6H), 1.15 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 142.6, 134.9, 131.3, 130.2, 129.5, 128.8, 128.6, 128.1, 127.4, 127.2, 125.5, 120.4, 110.8, 83.6, 55.3, 37.4, 34.8, 34.4, 25.0, 24.8, 23.0; HRMS (ESI) *m/z* calcd for $C_{30}H_{35}BNaO_3Se^+$ $[M+Na]^+$ 557.1737, found 557.1737.

***rac*-4,4,5,5-tetramethyl-2-((1*R*,2*S*)-1-(naphthalen-2-yl)-2-phenethyl-2-(phenylselanyl)cyclopropyl)-1,3,2-dioxaborolanene (2g)**

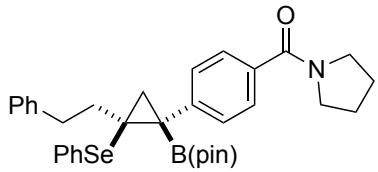


2g

Following the general procedure, tribromocyclopropane **1a** (103 mg, 0.269 mmol) was converted to the corresponding cyclopropane. Purification of the crude mixture by flash chromatography (hexane:Et_2O = 50:1) gave **2g** (119 mg, 0.216 mmol, 81%) as a colorless solid.

Rf 0.63 (hexane:Et_2O = 5:1); IR (film) 3057, 3021, 2980, 2930, 1630, 1599, 1580, 1371,1319,1142, 858, 750, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.92–7.88 (m, 2H), 7.81–7.75 (m, 2H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.70 (br s, 1H), 7.63 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.46–7.32 (m, 5H), 7.06–6.97 (m, 3H), 6.75–6.70 (m, 2H), 2.93 (ddd, *J* = 13.2, 12.0, 4.0 Hz, 1H), 2.66 (ddd, *J* = 13.2, 11.6, 5.6 Hz, 1H), 1.74 (dd, *J* = 5.2, 0.8 Hz, 1H), 1.55–1.45 (m, 1H), 1.47 (d, *J* = 5.2 Hz, 1H), 1.25 (s, 6H), 1.22 (s, 6H), 1.14 (ddd, *J* = 14.4, 12.0, 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 137.6, 134.3, 133.5, 132.2, 130.1, 129.3, 129.1, 128.5, 128.1, 127.8, 127.7, 127.6, 127.5, 125.8, 125.6, 125.4, 84.2, 37.3, 34.6, 34.3, 25.3, 24.8, 22.2; HRMS (ESI) *m/z* calcd for $C_{33}H_{35}BNaO_2Se^+$ $[M+Na]^+$ 577.1788, found 577.1787.

rac-(4-((1*R*,2*S*)-2-phenethyl-2-(phenylselanyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)phenyl)(pyrrolidin-1-yl)methanone (2h)

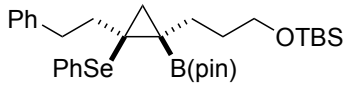


2h

Following the general procedure, tribromocyclopropane **1a** (99 mg, 0.259 mmol) was converted to the corresponding cyclopropane. Purification of the crude mixture by flash chromatography (CH_2Cl_2:EtOAc = 20:1) gave **2h** (96.7 mg, 0.161 mmol, 62%) as a yellow oil.

Rf 0.53 (CH_2Cl_2:EtOAc = 5:1); IR (film) 2978, 2930, 1616, 1418, 1371, 1323, 1141, 750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.84–7.79 (m, 2H), 7.45–7.38 (m, 4H), 7.38–7.28 (m, 3H) 7.11–7.01 (m, 3H), 6.78–6.74 (m, 2H), 3.63 (br s, 2H), 3.40 (br s, 1H), 2.85 (ddd, *J* = 13.2, 12.0, 4.0 Hz, 1H), 2.67 (ddd, *J* = 13.2, 11.6, 5.6 Hz, 1H), 1.93 (br s, 2H), 1.86 (br s, 2H), 1.67 (d, *J* = 5.2 Hz, 1H), 1.44–1.32 (m, 1H), 1.34 (d, *J* = 5.2 Hz, 1H), 1.29–1.15 (m, 1H), 1.24 (s, 6H), 1.22 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 142.2, 141.7, 134.8, 134.1, 130.1, 129.9, 129.1, 128.5, 128.2, 127.6, 127.1, 125.6, 84.3, 49.8, 46.3, 37.4, 34.4, 34.1, 26.6, 25.3, 24.8, 24.6, 22.2; HRMS (ESI) *m/z* calcd for $C_{34}H_{40}BNNaO_3Se^+$ $[M+Na]^+$ 624.2159, found 624.2162.

rac-tert-butyldimethyl(3-((1*S*,2*S*)-2-phenethyl-2-(phenylselanyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)propoxy)silane (2i)

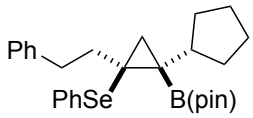


2i

Following the general procedure, tribromocyclopropane **1a** (101 mg, 0.264 mmol) was converted to the corresponding cyclopropane. Purification of the crude mixture by flash chromatography (hexane:toluene = 1:1) gave **2i** (86.3 mg, 0.144 mmol, 55%) as a yellow oil.

Rf 0.25 (toluene: hexane = 5:1); IR (film) 3057, 3026, 2978, 2953, 2928, 2857, 1389, 1316, 1254, 1144, 1099, 835, 775, 739, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.64–7.59 (m, 2H), 7.31–7.19 (m, 5H), 7.16–7.11 (m, 1H), 7.08 (d, *J* = 7.6 Hz, 2H), 3.67–3.55 (m, 2H), 3.00–2.82 (m, 2H), 1.99–1.79 (m, 3H), 1.74–1.56 (m, 2H), 1.34 (d, *J* = 4.8 Hz, 1H), 1.28 (s, 6H), 1.25 (s, 6H), 0.89–0.87 (m, 10H), 0.60 (d, *J* = 5.2 Hz, 1H), 0.05–0.03 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 132.9, 130.9, 128.9, 128.6, 128.3, 126.8, 125.7, 83.9, 63.1, 37.1, 34.9, 32.6, 28.4, 26.1, 25.4, 25.0, 23.5, 18.4, –5.1; HRMS (ESI) *m/z* calcd for $C_{32}H_{49}BNaO_3SeSi^+$ $[M+Na]^+$ 623.2601, found 623.2544.

rac-2-((1*R*,2*S*)-1-cyclopentyl-2-phenethyl-2-(phenylselanyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2j)

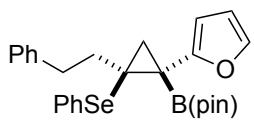


2j

Following the general procedure, tribromocyclopropane **1a** (101 mg, 0.265 mmol) was converted to the corresponding cyclopropane. Purification of the crude mixture by flash chromatography (hexane:toluene = 3:1) gave **2j** (95.0 mg, 0.184 mmol, 69%) as a yellow oil.

Rf 0.83 (toluene); IR (film) 2976, 2934, 2866, 1580, 1478, 1393, 1312, 1312, 1140, 1022, 966, 854, 760, 739, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.75–7.70 (m, 2H), 7.32–7.18 (m, 5H), 7.16–7.11 (m, 1H), 7.07–7.03 (m, 2H), 3.09 (app td, *J* = 13.2, 4.4 Hz, 1H), 2.74 (ddd, *J* = 13.6, 12.0, 5.2 Hz, 1H), 2.06–1.89 (m, 2H), 1.85–1.60 (m, 5H), 1.54–1.37 (m, 3H), 1.30 (d, *J* = 5.2 Hz, 1H), 1.37–1.20 (m, 1H), 1.27 (s, 6H), 1.23 (s, 6H), 0.56 (d, *J* = 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 133.4, 130.6, 128.8, 128.6, 128.3, 126.9, 125.7, 83.7, 45.2, 36.0, 34.9, 33.0, 32.7, 30.4, 26.0, 25.7, 25.6, 25.1, 23.0; HRMS (ESI) *m/z* calcd for $C_{28}H_{37}BNaO_2Se^+$ $[M+Na]^+$ 519.1944, found 519.1944.

rac-2-((1*R*,2*S*)-1-(furan-2-yl)-2-phenethyl-2-(phenylselanyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2k)

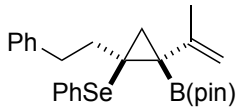


2k

Following the general procedure, tribromocyclopropane **1a** (102 mg, 0.266 mmol) was converted to the corresponding cyclopropane. Purification of the crude mixture by flash chromatography (hexane:Et_2O = 50:1) gave **2k** (52.9 mg, 0.107 mmol, 40%) as a yellow oil.

Rf 0.50 (hexane:Et_2O = 5:1); IR (film) 3057, 3024, 2930, 1578, 1497, 1478, 1454, 1437, 1390, 1363, 1325, 1225, 1213, 1144, 1007, 739, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.71–7.66 (m, 2H), 7.35–7.25 (m, 3H), 7.19–7.13 (m, 2H), 7.13–7.05 (m, 2H), 6.92–6.87 (m, 2H), 6.33 (dd, *J* = 3.2, 1.6 Hz, 1H), 6.31 (dd, *J* = 3.2, 0.8 Hz, 1H), 2.81 (ddd, *J* = 13.2, 8.0, 6.8 Hz, 1H), 2.72 (ddd, *J* = 13.2, 9.6, 6.0 Hz, 1H), 1.71 (d, *J* = 5.2 Hz, 1H), 1.66–1.60 (m, 2H), 1.63 (d, *J* = 5.2 Hz, 1H), 1.30 (s, 6H), 1.28 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 142.4, 141.0, 133.1, 130.4, 129.1, 128.6, 128.2, 127.1, 125.6, 110.7, 108.4, 84.3, 37.4, 35.2, 34.3, 25.3, 24.8, 23.2; HRMS (ESI) *m/z* calcd for $C_{27}H_{31}BNaO_3Se^+$ $[M+Na]^+$ 517.1424, found 517.1424.

***rac*-4,4,5,5-tetramethyl-2-((1*R*,2*S*)-2-phenethyl-2-(phenylselanyl)-1-(prop-1-en-2-yl)cyclopropyl)-1,3,2-dioxaborolane (2l)**

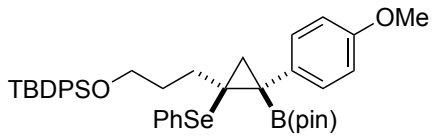


2l

Following the general procedure, tribromocyclopropane **1a** (102 mg, 0.266 mmol) was converted to the corresponding cyclopropane. Purification of the crude mixture by flash chromatography (hexane:Et_2O = 100:1) gave **2l** (38.3 mg, 0.0822 mmol, 31%) as a colorless oil.

Rf 0.58 (hexane:Et_2O = 5:1); IR (film) 3057, 3026, 2978, 2928, 1371, 1636, 1364, 1323, 1147, 1086, 849, 741, 694 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.84–7.79 (m, 2H), 7.34–7.27 (m, 3H), 7.22–7.17 (m, 2H), 7.14–7.09 (m, 1H), 7.04–7.00 (m, 2H), 4.86 (dd, *J* = 2.0, 1.2 Hz, 1H), 4.73 (dd, *J* = 2.0, 0.8 Hz, 1H), 3.01 (ddd, *J* = 13.6, 12.0, 4.0 Hz, 1H), 2.61 (ddd, *J* = 13.6, 11.6, 5.6 Hz, 1H), 1.91 (s, 3H), 1.84–1.76 (m, 1H), 1.45–1.37 (m, 2H), 1.27 (s, 6H), 1.25 (s, 6H), 0.98 (d, *J* = 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 142.5, 134.2, 130.0, 128.9, 128.6, 128.3, 127.4, 125.7, 113.7, 83.9, 35.6, 34.7, 33.6, 25.3, 24.8, 23.4, 21.3; HRMS (ESI) *m/z* calcd for $C_{26}H_{33}BNaO_2Se^+$ $[M+Na]^+$ 491.1631, found 491.1631.

***rac-tert*-butyl(3-((1S,2R)-2-(4-methoxyphenyl)-1-(phenylselanyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)propoxy)diphenylsilane (2m)**

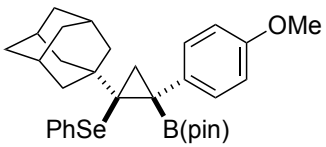


2m

Following the general procedure, tribromocyclopropane **S9** (103 mg, 0.179 mmol) was converted to the corresponding cyclopropane. Purification of the crude mixture by flash chromatography (hexane:Et_2O = 20:1) gave **2m** (87.0 mg, 0.120 mmol, 67%) as a colorless oil.

Rf 0.58 (hexane:Et_2O = 5:1); IR (film) 3071, 3051, 2994, 2976, 2930, 2857, 1609, 1558, 1510, 1371, 1246, 1144, 1109, 851, 758, 702, 613 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.76–7.73 (m, 2H), 7.52–7.48 (m, 4H), 7.40–7.36 (m, 2H), 7.33–7.30 (m, 4H), 7.30–7.24 (m, 5H), 6.78 (app dd, *J* = 9.0, 1.2, 2H), 3.75 (s, 3H), 3.44 (dtd, *J* = 9.6, 6.0, 1.2 Hz, 1H), 3.34 (app td, *J* = 9.6, 6.0 Hz, 1H), 1.84–1.77 (m, 1H), 1.67–1.56 (m, 1H), 1.58 (d, *J* = 4.8 Hz, 1H), 1.30 (dd, *J* = 4.8, 1.2 Hz, 1H), 1.30–1.23 (m, 1H), 1.21 (s, 6H), 1.20 (s, 6H), 1.02–0.96 (m, 1H), 0.89–0.88 (m, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.7, 135.6 (2C), 134.14, 134.09, 133.9, 131.9, 131.1, 130.4, 129.52, 129.51, 128.9, 127.63, 127.60, 127.2, 113.4, 84.0, 63.4, 55.2, 34.2, 31.4, 30.9, 26.9, 25.3, 24.8, 21.8, 19.2 ; HRMS (ESI) *m/z* calcd for $C_{41}H_{51}BNaO_4SeSi^+$ $[M+Na]^+$ 749.2707, found 749.2707.

rac-2-((1*R*,2*S*)-2-((3*S*,5*S*,7*S*)-adamantan-1-yl)-1-(4-methoxyphenyl)-2-(phenylselanyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2n)



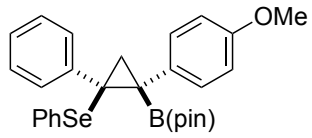
2n

Following the general procedure, tribromocyclopropane **S3** (54.8 mg, 0.133 mmol) was converted to the corresponding cyclopropane. Purification of the crude mixture by flash chromatography (hexane:Et_2O = 50:1) gave **2n** (30.2 mg, 0.0536 mmol, 40%) as a colorless solid.

Rf 0.40 (hexane:Et_2O = 5:1); IR (film) 2903, 2847, 1508, 1356, 1244, 1142, 1024, 849 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.72 (br d, *J* = 7.8 Hz, 1H), 7.61–7.57 (m, 2H), 7.28–7.21 (m, 3H), 7.05 (br d, *J* = 7.8 Hz, 1H), 6.81 (br d, *J* = 7.8 Hz, 1H), 6.71 (br d, *J* = 7.8 Hz, 1H), 3.79 (s, 3H), 1.79–1.75 (m, 4H), 1.69 (app d, *J* = 12.0 Hz, 3H), 1.51–1.46 (m, 4H), 1.40 (app d, *J* = 12.0 Hz, 3H), 1.54 (d, *J* = 12.0 Hz, 3H), 1.18 (s, 6H), 1.13 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.8, 134.4 (br), 133.8, 132.6, 132.3, 129.8 (br), 128.7, 126.9, 113.0, 83.7, 55.3, 47.8, 40.6, 39.8, 36.8, 28.8, 25.0, 24.7, 16.6; HRMS (ESI) *m/z* calcd for $C_{32}H_{41}BNaO_3Se^+$ $[M+Na]^+$ 587.2206, found 587.2209.

* Probably because adamantly group and 4-methoxyphenyl group are arranged in close proximity, proton- and carbon-peaks of 4-methoxyphenyl group are observed as broad and non-equivalent peaks, and one carbon peak is missing in the spectrum.

rac-2-((1*R*,2*S*)-1-(4-methoxyphenyl)-2-phenyl-2-(phenylselanyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2o)

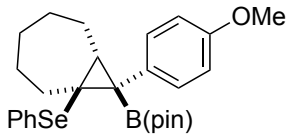


2o

Following the general procedure (THF was used as a solvent instead of Et_2O, and the reaction was conducted at –98 °C), tribromocyclopropane **S4** (67.9 mg, 0.191 mmol) was converted to the corresponding cyclopropane. Purification of the crude mixture by flash chromatography (hexane:Et_2O = 25:1) gave **2o** (38.0 mg, 0.0752 mmol, 39%) as a colorless oil.

Rf 0.40 (hexane:Et_2O = 5:1); IR (film) 3057, 2980, 2955, 2930, 1530, 1371, 1246, 1142, 1032, 1020, 851, 741 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.37–7.34 (m, 2H), 7.22–7.19 (m, 1H), 7.18–7.15 (m, 2H), 7.11–7.07 (m, 2H), 7.07–7.04 (m, 2H), 6.96–6.92 (m, 2H), 6.90–6.87 (m, 1H), 6.58–6.54 (m, 2H), 3.65 (s, 3H), 2.23 (d, *J* = 5.4 Hz, 1H), 1.90 (d, *J* = 5.4 Hz, 1H), 1.32 (s, 6H), 1.30 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.5, 141.2, 133.99, 131.0, 130.8, 130.43, 130.40, 128.8, 127.4, 127.3, 126.0, 113.1, 84.3, 55.1, 36.8, 25.3, 24.8, 23.3; HRMS (ESI) *m/z* calcd for $C_{28}H_{31}BNaO_3Se^+$ $[M+Na]^+$ 529.1424, found 529.1424.

***rac*-2-((1*S*,7*R*,8*R*)-8-(4-methoxyphenyl)-1-(phenylselanyl)bicyclo[5.1.0]octan-8-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2p)**

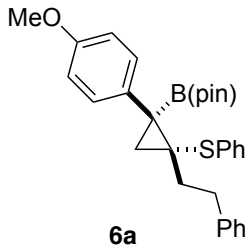


2p

Following the general procedure, tribromocyclopropane **S10** (101 mg, 0.292 mmol) was converted to the corresponding cyclopropane. Purification of the crude mixture by flash chromatography (hexane:Et_2O = 40:1) gave **2p** (97.3 mg, 0.195 mmol, 67%) as a colorless solid.

Rf 0.48 (hexane:Et_2O = 5:1); IR (film) 2976, 2920, 2853, 1508, 1344, 1244, 1144, 1171, 1111, 1036, 974, 854, 758, 743, 694 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.88–7.85 (m, 2H), 7.36–7.29 (m, 3H), 7.02–6.98 (m, 2H), 6.82–6.80 (m, 2H), 3.78 (s, 3H), 2.10 (app. dt, *J* = 14.4, 6.6 Hz, 1H), 2.06–1.99 (m, 1H), 1.82–1.69 (m, 4H), 1.48–1.42 (m, 1H), 1.40–1.34 (m, 1H), 1.33–1.24 (m, 1H), 1.16 (s, 6H), 1.13 (s, 6H), 0.94 (app. tt, *J* = 8.8, 2.4 Hz, 1H), 0.84–0.81 (app. tt, *J* = 13.8, 11.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.6, 134.6, 132.0, 130.9, 130.5, 129.0, 127.4, 113.8, 83.8, 55.3, 39.1, 31.9, 31.3, 31.2, 28.5, 27.4, 25.9, 25.0, 24.7; HRMS (ESI) *m/z* calcd for $C_{27}H_{35}BNaO_3Se^+$ $[M+Na]^+$ 521.1737, found 521.1737.

***rac*-2-((1S,2R)-1-(4-methoxyphenyl)-2-phenethyl-2-(phenylthio)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane**



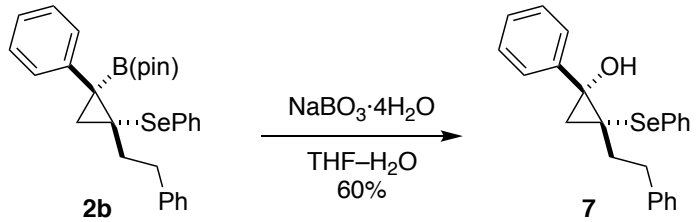
6a

Following the general procedure, tribromocyclopropane **1a** (100 mg, 0.261 mmol) was converted to the corresponding cyclopropane. Purification of the crude mixture by flash chromatography (hexane:Et_2O = 50:1) gave **6a** (45.8 mg, 0.0941 mmol, 36%) as a white solid.

Rf 0.38 (hexane:Et_2O = 5:1); IR (film) 2978, 2930, 1607, 1584, 1510, 1371, 1246, 1144, 1035, 851, 749, 700 cm–1.; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68–7.65 (m, 2H), 7.37–7.31 (m, 4H), 7.26–7.22 (m, 1H), 7.11 (app t, *J* = 7.2 Hz, 2H), 7.06–7.03 (m, 1H), 6.82 (d, *J* = 8.4 Hz, 2H), 6.79 (d, *J* = 7.8 Hz, 2H), 3.79 (s, 3H), 2.83 (app td, *J* = 13.2, 4.2 Hz, 1H), 2.67 (ddd, *J* = 13.2, 12.0, 5.4 Hz, 1H), 1.60 (d, *J* = 4.8 Hz, 1H), 1.49 (ddd, *J* = 13.8, 11.4, 4.2 Hz, 1H), 1.33 (d, *J* = 4.8, 1H), 1.29–1.23 (m, 1H), 1.19 (s, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.9, 142.4, 135.9, 131.3, 131.1, 130.6, 128.8, 128.5, 128.2, 126.4, 125.6, 113.6, 84.1, 55.3, 37.0, 35.5, 33.2, 25.2, 24.7, 22.3; HRMS (ESI) m/z calcd for $C_{30}H_{35}BNaO_3S^+$ $[M+Na]^+$ 509.2292, found 509.2292.

Oxidation of the cyclopropylboronic ester

(1R,2R)-2-phenethyl-1-phenyl-2-(phenylselanyl)cyclopropan-1-ol



To a solution of cyclopropylboronic ester **2b** (50.0 mg, 0.099 mmol) in THF–water (1:1, 2 mL) was added $NaBO_3 \cdot 4H_2O$ (45.8 mg, 0.298 mmol) at room temperature. After being stirred at same temperature for 4 h, $NaBO_3 \cdot 4H_2O$ (45.8 mg, 0.298 mmol) was added, and the mixture and further stirred for 1 h. The mixture was then extracted with CH_2Cl_2 and dried over Na_2SO_4. Purification of the crude mixture by flash chromatography (hexane:Et_2O = 20:1) gave alcohol **7** (23.5 mg, 0.060 mmol, 60%) as a yellow oil.

Rf 0.38 (hexane:Et_2O = 5:1); IR (film) 3408, 3399, 3387, 3059, 3024, 2924, 2853, 1603, 1578, 1495, 1476, 1451, 1437, 1231, 1022, 770, 741, 698 cm^{-1};
^1H NMR (400 MHz, $CDCl_3$) δ 7.77–7.72 (m, 2H), 7.41–7.34 (m, 5H), 7.34–7.31 (m, 2H), 7.29–7.24 (m, 1H), 7.18–7.13 (m, 2H), 7.12–7.07 (m, 1H), 6.91–6.87 (m, 2H), 3.69 (s, 1H), 2.92 (ddd, *J* = 13.6, 11.2, 4.4 Hz, 1H), 2.67 (ddd, *J* = 13.6, 11.2, 6.0 Hz, 1H), 1.61 (dddd, *J* = 14.4, 11.2, 4.0, 1.6 Hz, 1H), 1.56 (d, *J* = 7.6 Hz 1H), 1.20–1.11 (m, 1H), 1.14 (dd, *J* = 7.6, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 138.2, 134.6, 129.5, 128.48, 128.47, 128.45, 128.34, 128.33, 128.1, 127.9, 125.9, 64.1, 41.8, 36.7, 34.3, 24.9;
HRMS (ESI) m/z calcd for $C_{23}H_{22}OSeNa^+$ $[M+Na]^+$ 417.0728, found 417.0727.

DFT calculations for the reaction mechanism

Density functional theory (DFT) calculations were performed using Gaussian 09 program.[7] Geometries were optimized at the B3LYP-D3BJ[8] with 6-31G(d) basis set. Tight convergence criteria and an ultrafine integration grid were applied. Thermochemical corrections were obtained from frequency calculations at the same level of theory. The single point energies were computed at the B3LYP-D3(BJ)/6-311+G(d,p) basis set by using SMD[9] solvation model in diethyl ether (Et_2O). Enthalpy and free energies in solution were computed by adding the gas phase thermochemical corrections to the solution phase single point energy. The data were summarized in Figure S1. Calculated structures are illustrated using ChemDraw and CYLView.[10]

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7. Gaussian 09, Revision E.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

8. (a) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104–15419. (b) Grimme, S.; Ehrlich, S.; Goerigk, L. *J. Comp. Chem.* **2011**, *32*, 1456–1465. (c) Phys, J. C.; Becke, A. D.; Johnson, E. R. A Density-Functional Model of the Dispersion Interaction. *J. Chem. Phys.* **2005**, *123*, 154101–154109.

9. Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2009**, *113*, 6378–6396.

10. Legault, C. Y. CYLView, 1.0b; Université de Sherbrooke, Canada, 2009; http://www.cylview.org.

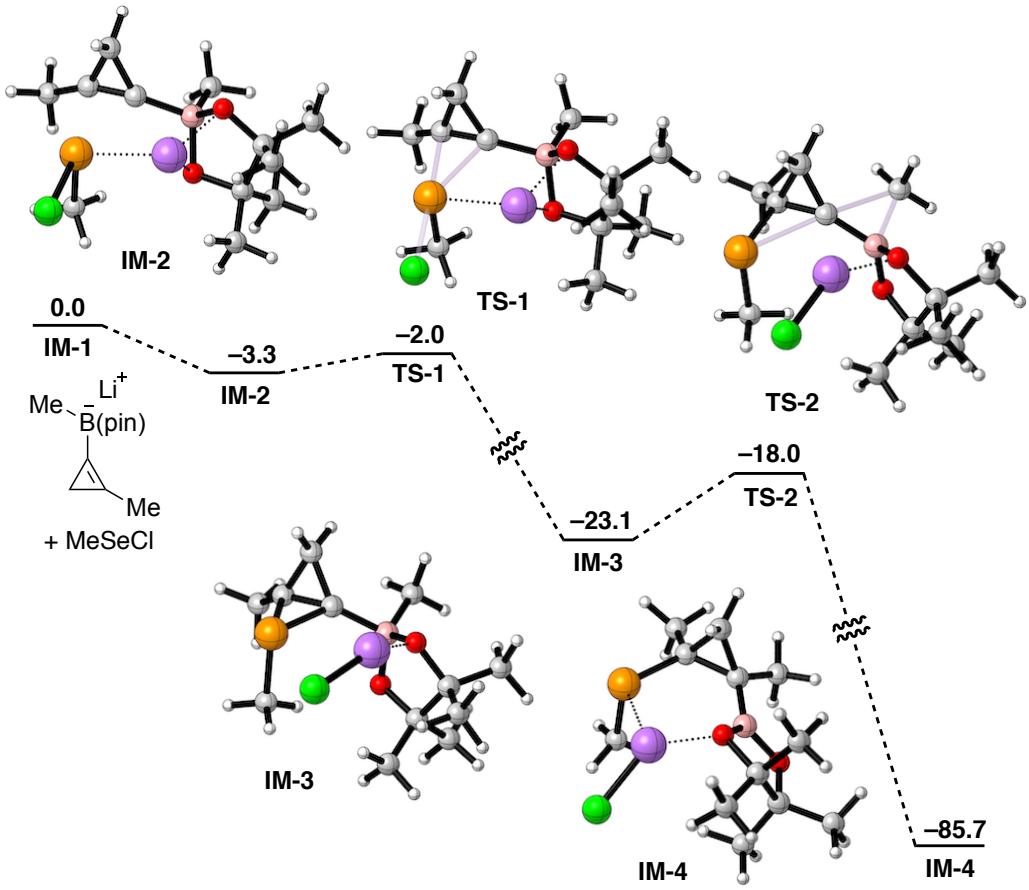


Figure S1. Calculated reaction coordinate for the selenenyl chloride induced 1,2-metallate rearrangement. Optimized geometry calculated using DFT (B3LYP-D3BJ/6-31G(d)). ΔG values are in kcal/mol, calculated using DFT (B3LYP-D3BJ/6-311+G(d,p); SMD solvation model with Et_2O). Calculated structures were shown with following color code: grey: carbon, red: oxygen, pink: boron, orange: selenium, purple: lithium, green: chloride

Underneath the Cartesian coordinates for the optimized geometries are listed the following gas phase energies:

B3LYP-D3BJ/6-31G(d) electronic energy ($E_{6\text{-}31G}$)

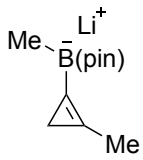
B3LYP-D3BJ/ 6-31G(d) Gibbs free energy ($G_{6\text{-}31G}$),

along with the solution-phase single-point energies at the B3LYP-D3BJ/6-311+G(d,p) of theory in Et_2O:

B3LYP-D3BJ/6-311+G(d,p) electronic energy ($E_{6\text{-}311+G}$)

B3LYP-D3BJ/ 6-311+G(d,p) Gibbs free energy ($G_{6\text{-}311+G}$)

Otherwise noted, all energies are given in Hartree.



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MeSeCl

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0 imaginary frequencies

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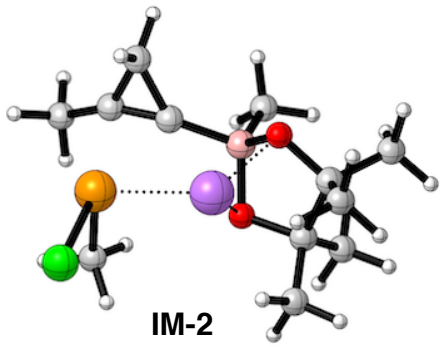

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0 imaginary frequencies

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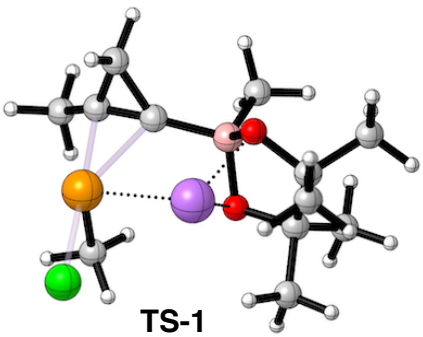

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O	-1.135517506409	0.010270379710	1.027200019106
C	-2.326431290973	-0.784459010929	0.849459299929
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O	-1.563225615226	0.212358227459	-1.204438232762
C	-3.984677686770	-0.086471336745	-1.108875188121
C	-2.450725966212	-1.990650265783	-1.514060468043
C	-1.988696050534	-2.206413410762	1.331961401758
C	-3.456428029211	-0.248830290116	1.741943147000
H	0.681322906065	3.158735554437	-1.862986614829
H	1.689083521762	1.686553474981	-2.268498441689
H	3.425394153976	3.029499159853	0.688696481414
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H	-1.119323755282	-2.645815829872	0.826410692223
H	-1.750577241522	-2.173344851257	2.399527829479
H	-2.830774605927	-2.892193237272	1.191159461530
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H	-3.129114198819	-0.289353381516	2.785802228022
H	-3.712383028379	0.786087297144	1.515314693308
Li	-0.140011334353	-0.903494710028	-0.491100441301
C	1.993453691258	-0.224619523338	1.795719595617
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H	1.767996427404	-1.261791005506	2.034300610751
Se	2.124069380504	-0.100109895108	-0.176627336760
Cl	2.752927631247	-2.509052488247	-0.231562280430

1 imaginary frequencies

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$G_{6\text{-}31G}$ = -3513.445743

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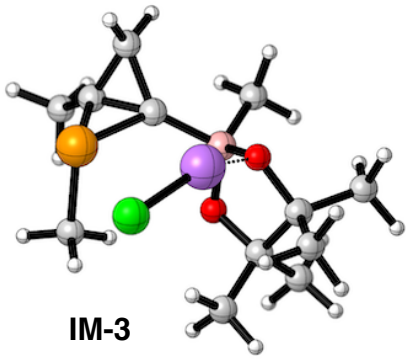
$G_{6\text{-}311+G}$ = -3515.816682



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B	-1.329338965372	1.197328249768	-0.050424412146
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O	-1.340583620566	0.126405672193	1.018728177290
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H	-1.879878398941	-2.081752156285	2.376335721558
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Li	-0.299901072078	-0.649442571460	-0.502017355390
C	1.861470310583	-0.290973251746	1.828692485416
H	2.782785285507	0.066021177816	2.288953851325
H	1.002346255853	0.323133161397	2.096568967352
H	1.680156492801	-1.330910228513	2.097300165098
Se	2.076021972528	-0.217709794263	-0.140297066346
Cl	3.144633301440	-2.290291274557	-0.185205875913

0 imaginary frequencies

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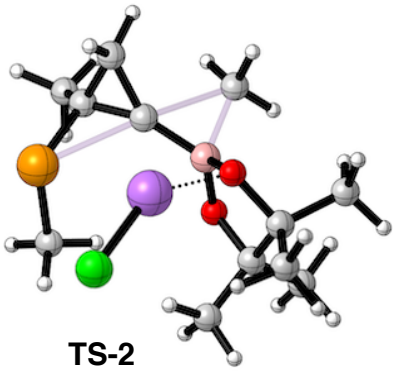
$G_{6\text{-}31G}$ = -3513.474337

$E_{6\text{-}311+G}$ = -3516.140961

$G_{6\text{-}311+G}$ = -3515.850283



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C	2.764091948798	2.603355171489	0.720834361597
B	-0.590987200579	1.009648463699	-0.377697925386
C	-0.565403444583	2.641383030500	-1.150114326977
O	-1.188136705046	1.080672479299	0.911772305863
C	-2.316168173319	0.177941075749	0.990463603531
C	-2.573358520507	-0.241690261412	-0.518265883988
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C	-2.990639658908	-1.699047294805	-0.721317081642

C	-1.927043091228	-1.001391930181	1.895558999072
C	-3.480768607798	0.936248180865	1.636632330534
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H	2.471415126333	0.581720359022	-2.189051484066
H	3.858695410421	2.602748155017	0.721670592798
H	2.422238628809	3.552864512952	0.292314229361
H	2.413501542167	2.555958374413	1.756627712629
H	0.192118198009	3.389095965160	-0.902011105013
H	-0.644601354249	2.537782578538	-2.233707728848
H	-1.504992085621	2.986973811595	-0.710803774139
H	-3.529995535551	0.427877264637	-2.328467808562
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H	-1.105512426305	-1.603088765973	1.493149217810
H	-1.615400153590	-0.605414828937	2.868179018304
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H	-3.207193258946	1.215076667420	2.659373542432
H	-3.721951735452	1.853316077763	1.093705639598
Li	0.138835353967	-1.399364527228	-0.850145085866
Se	2.548025692862	-0.431497316384	0.412478172733
C	1.755366435220	-0.434017076661	2.210664424801

H	0.862032986438	0.191483491140	2.206652555964
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Cl	0.555891651340	-3.352642170885	-0.053088131432

1 imaginary frequencies

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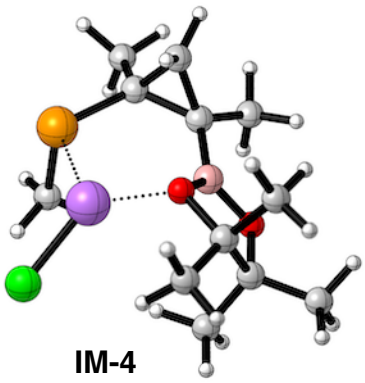
$G_{6\text{-}31G}$ = -3513.460782

$E_{6\text{-}311+G}$ = -3516.131678

$G_{6\text{-}311+G}$ = -3515.842066



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C	2.876977507011	2.393302048439	-0.138301230073
B	-0.945566533738	1.028754476820	-0.139985971008
C	0.012103318710	3.402612630789	0.115249908693

O	-1.963482634463	1.399671467879	0.687489562601
C	-2.947934412159	0.318538548602	0.739402269199
C	-2.680529698207	-0.422195090997	-0.615274950628
O	-1.215481114399	-0.192912972351	-0.775502057069
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C	-2.970242313724	-1.917918012267	-0.615741826941
C	-2.624303852588	-0.532135796407	1.972739230685
C	-4.333929135969	0.945286644936	0.866227193514
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H	0.593372020295	1.045635143380	-2.446034917319
H	3.787092172959	2.070626409853	-0.654507490017
H	2.706734698417	3.445472747393	-0.383671299860
H	3.063628241983	2.330616759089	0.939870227439
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H	-2.614477586571	0.116048607880	2.854639078312
H	-3.379782586386	-1.308907171684	2.127102135411

H	-5.111362200517	0.174223764875	0.827503462042
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H	-4.525650471079	1.676369326054	0.077304206017
Li	0.013203897628	-1.676451655119	-0.458786572721
Se	2.146421053497	-0.388545347216	-0.314495893480
C	2.134268860660	-0.478687721480	1.658243517855
H	1.305163614394	0.118139662656	2.044255273995
H	1.973617650069	-1.529417111543	1.907585130011
H	3.085284565322	-0.120680119281	2.054474347789
Cl	0.051724225438	-3.425039517756	0.782403904020

0 imaginary frequencies

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$G_{6\text{-}31G}$ = -3513.571641

$E_{6\text{-}311+G}$ = -3516.243471

$G_{6\text{-}311+G}$ = -3515.950003

^{1}H and ^{13}C NMR Spectra of New Compounds

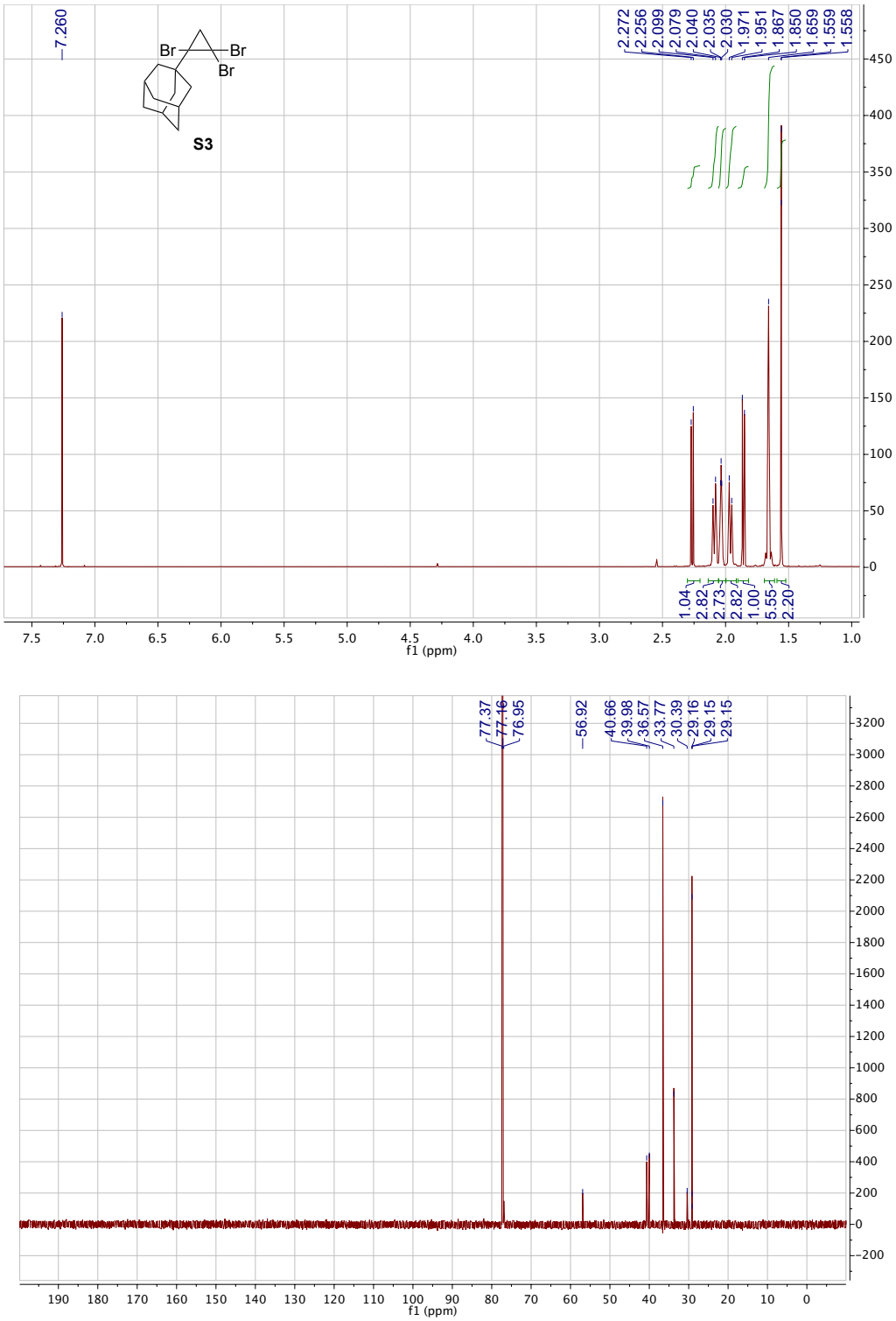

Figure S2. ^{1}H- and ^{13}C-NMR spectra of **S3**

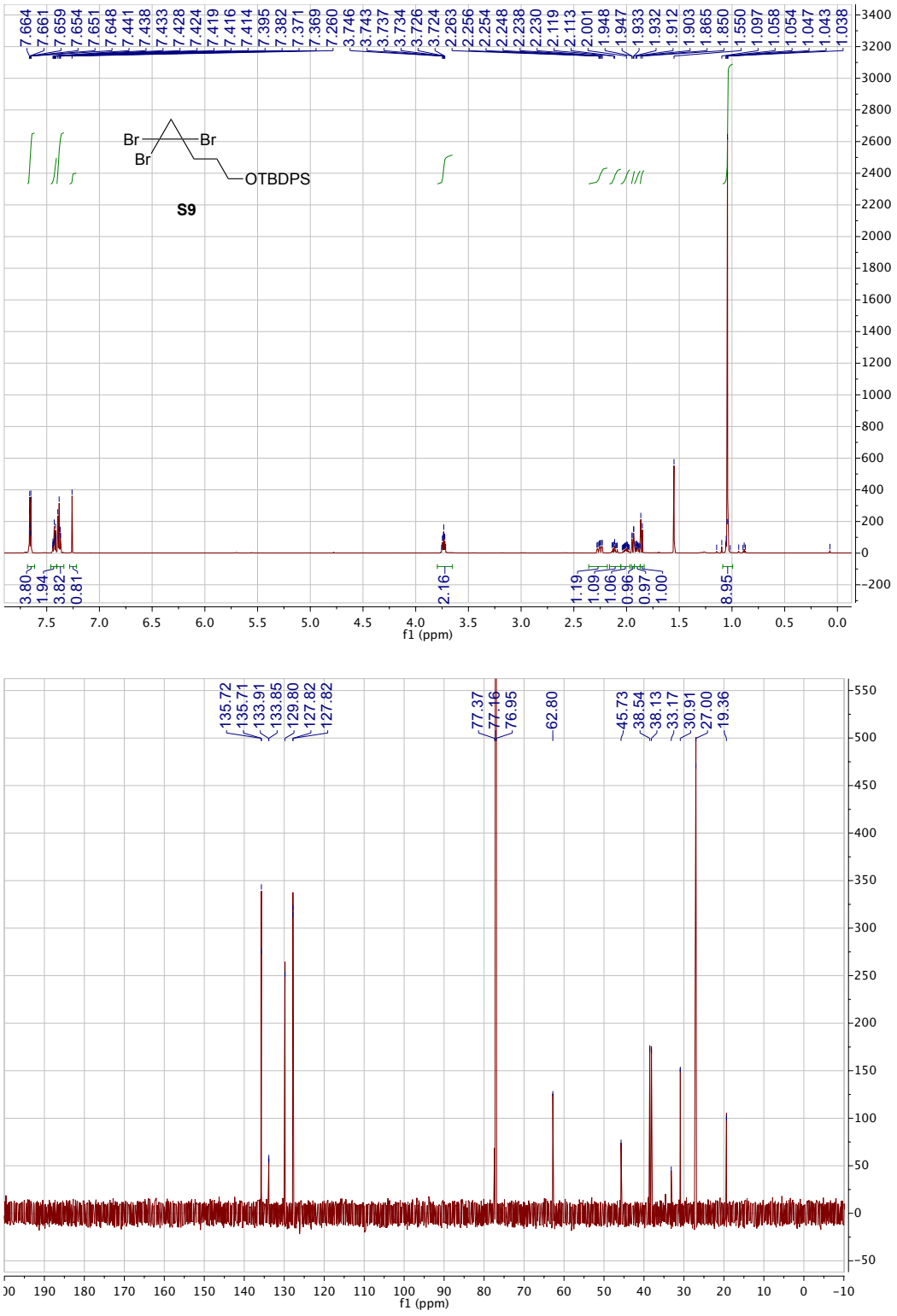

Figure S4. ^{1}H- and ^{13}C-NMR spectra of **S9**

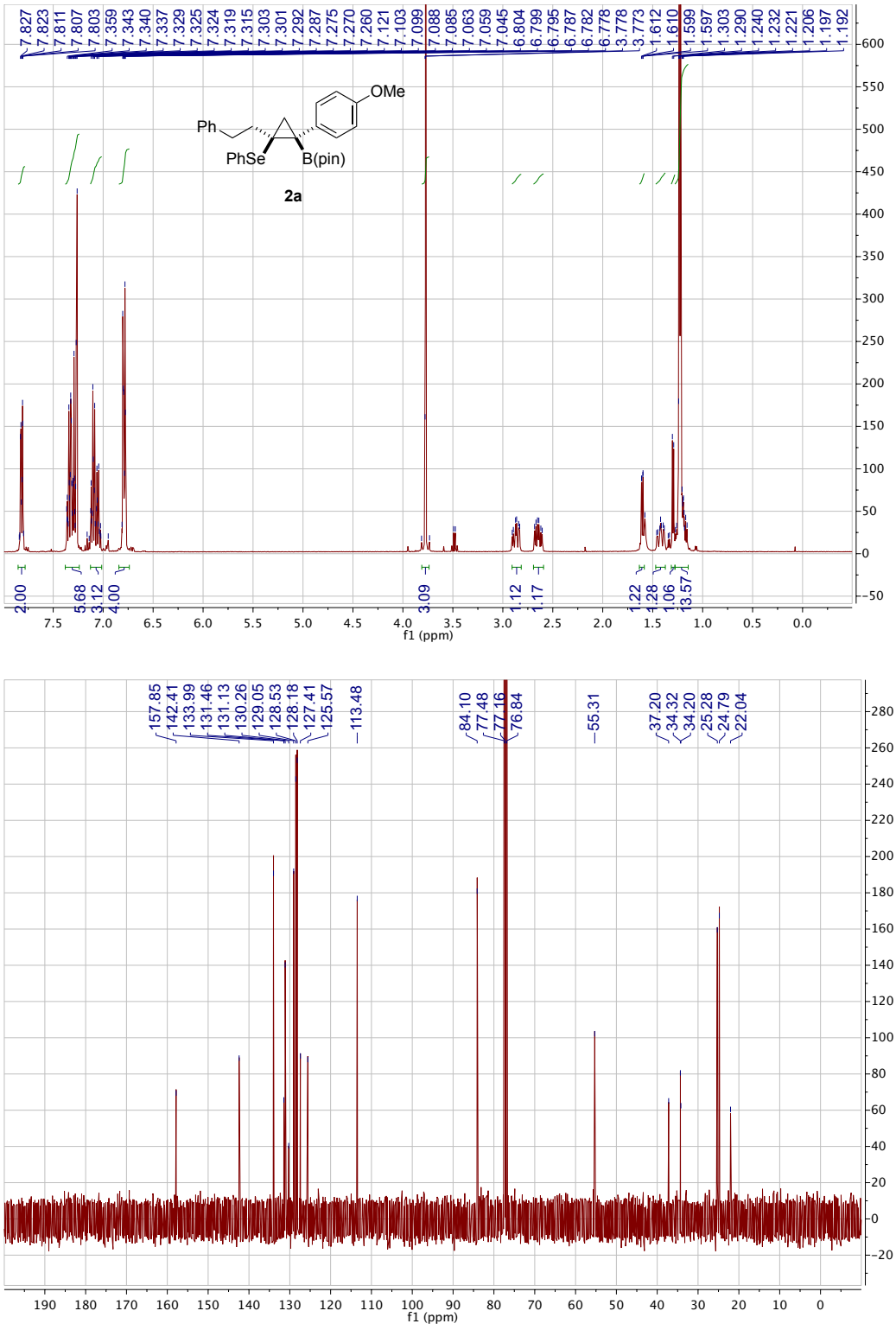

Figure S5. ^{1}H- and ^{13}C-NMR spectra of **2a**

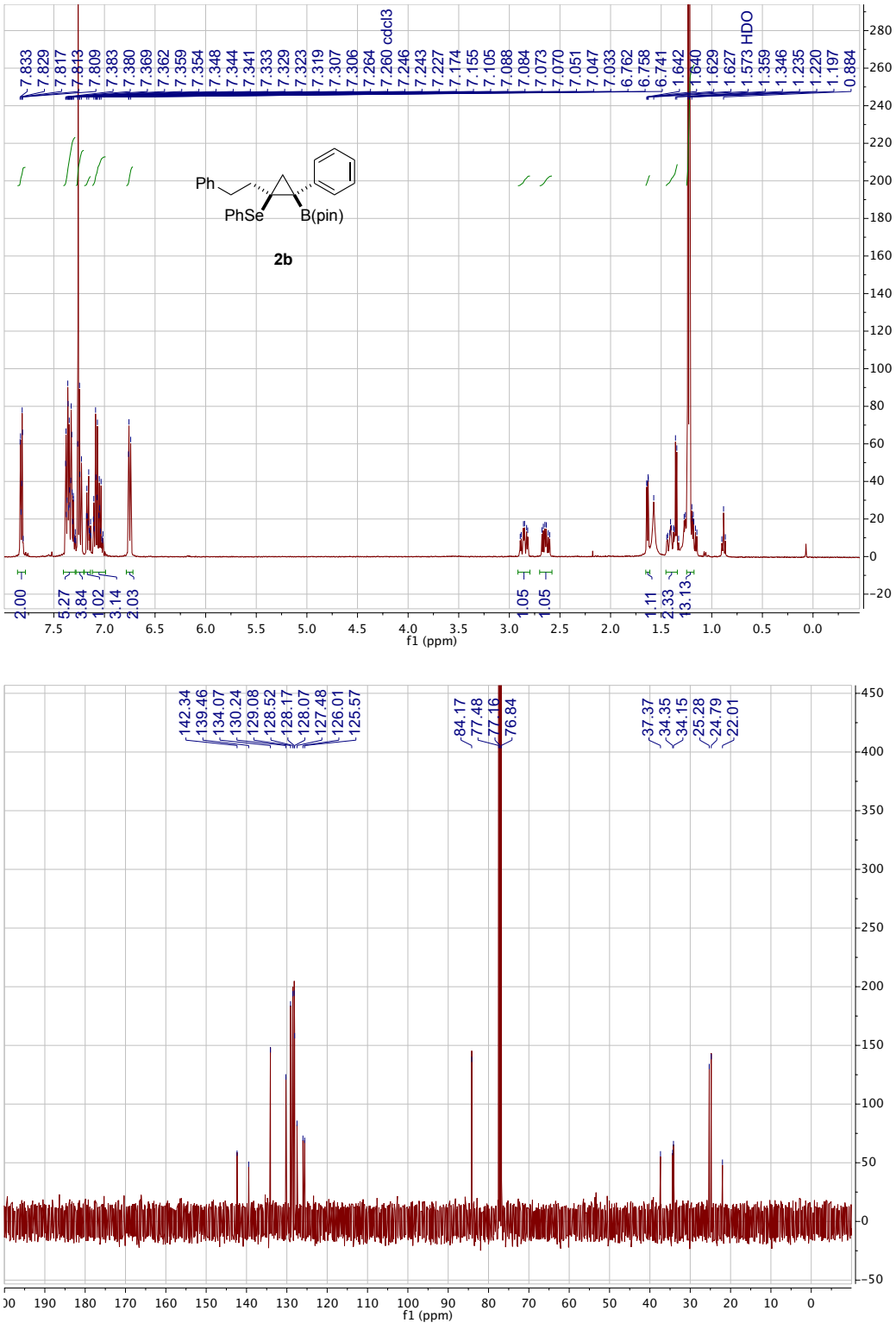

Figure S6. ^{1}H- and ^{13}C-NMR spectra of **2b**

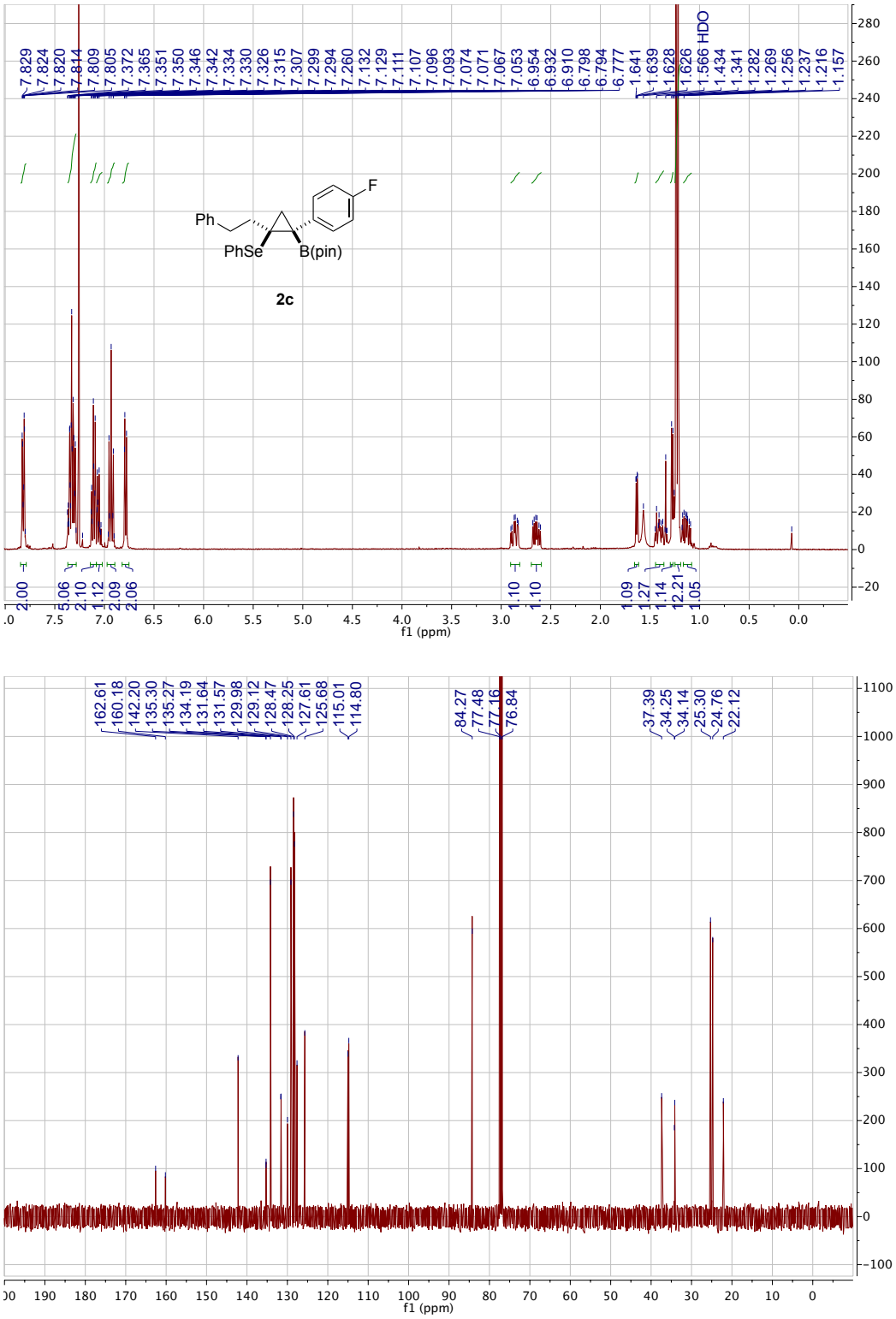

Figure S7. ^{1}H- and ^{13}C-NMR spectra of **2c**

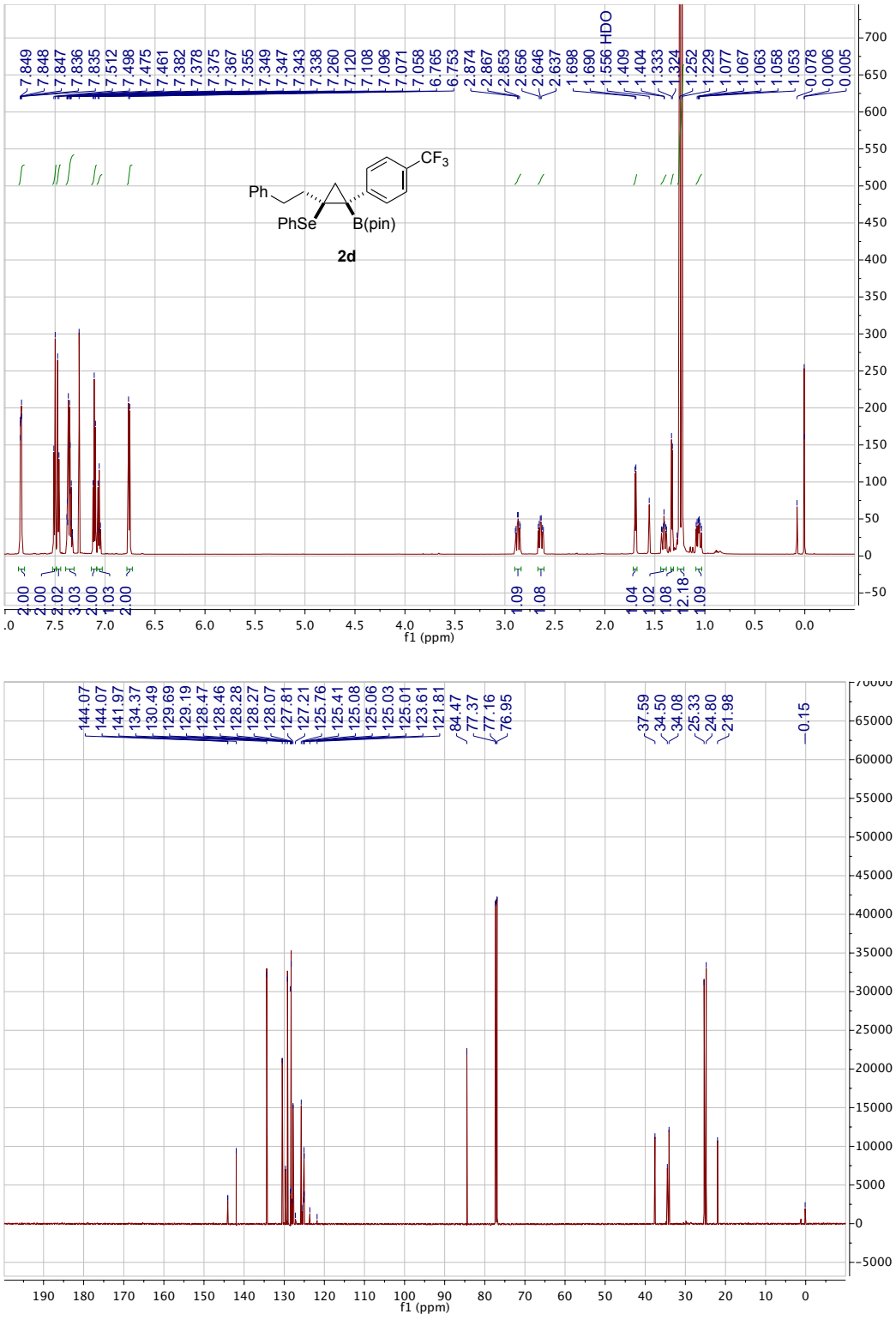

Figure S8. ^{1}H- and ^{13}C-NMR spectra of **2d**

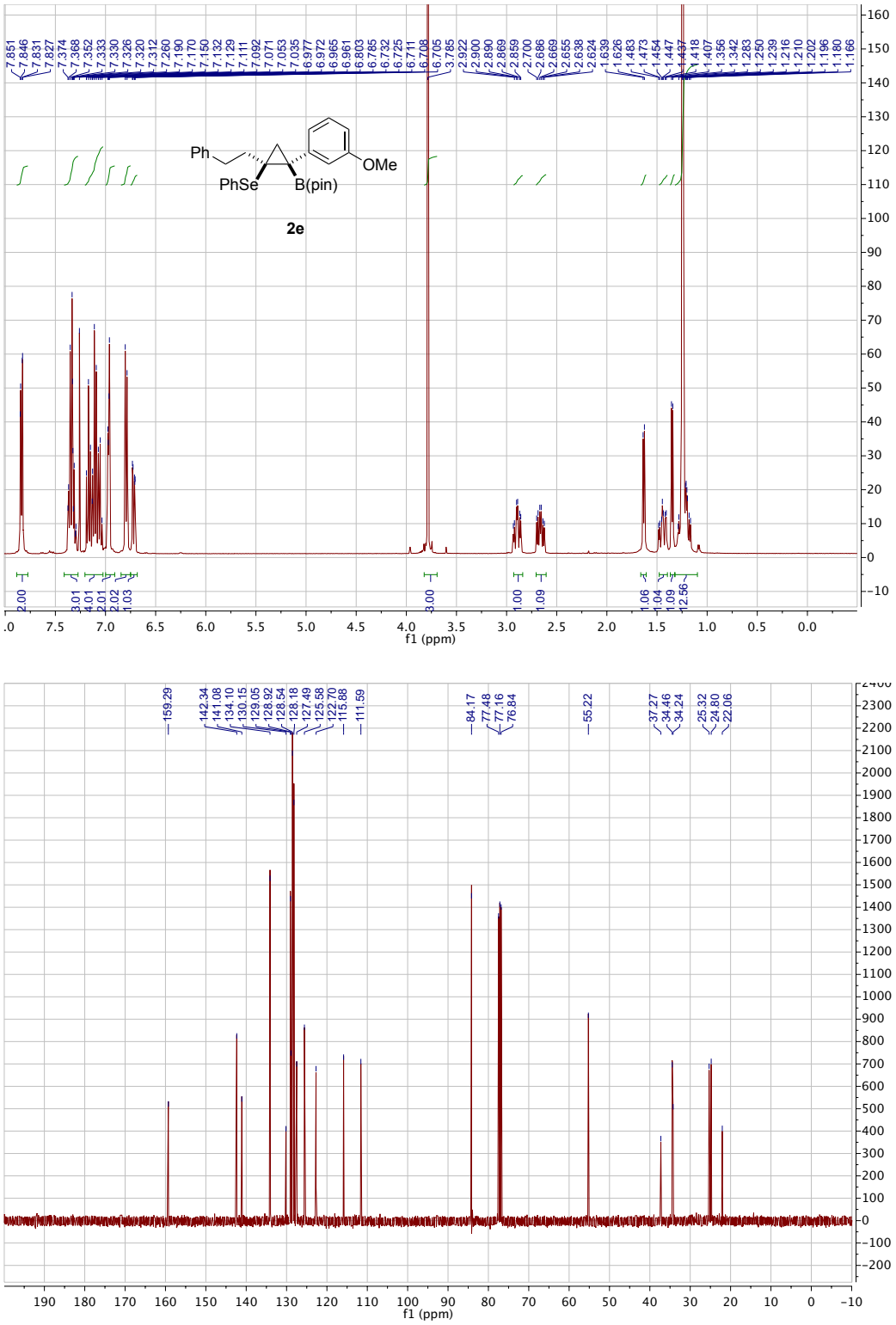

Figure S9. ^{1}H- and ^{13}C-NMR spectra of **2e**

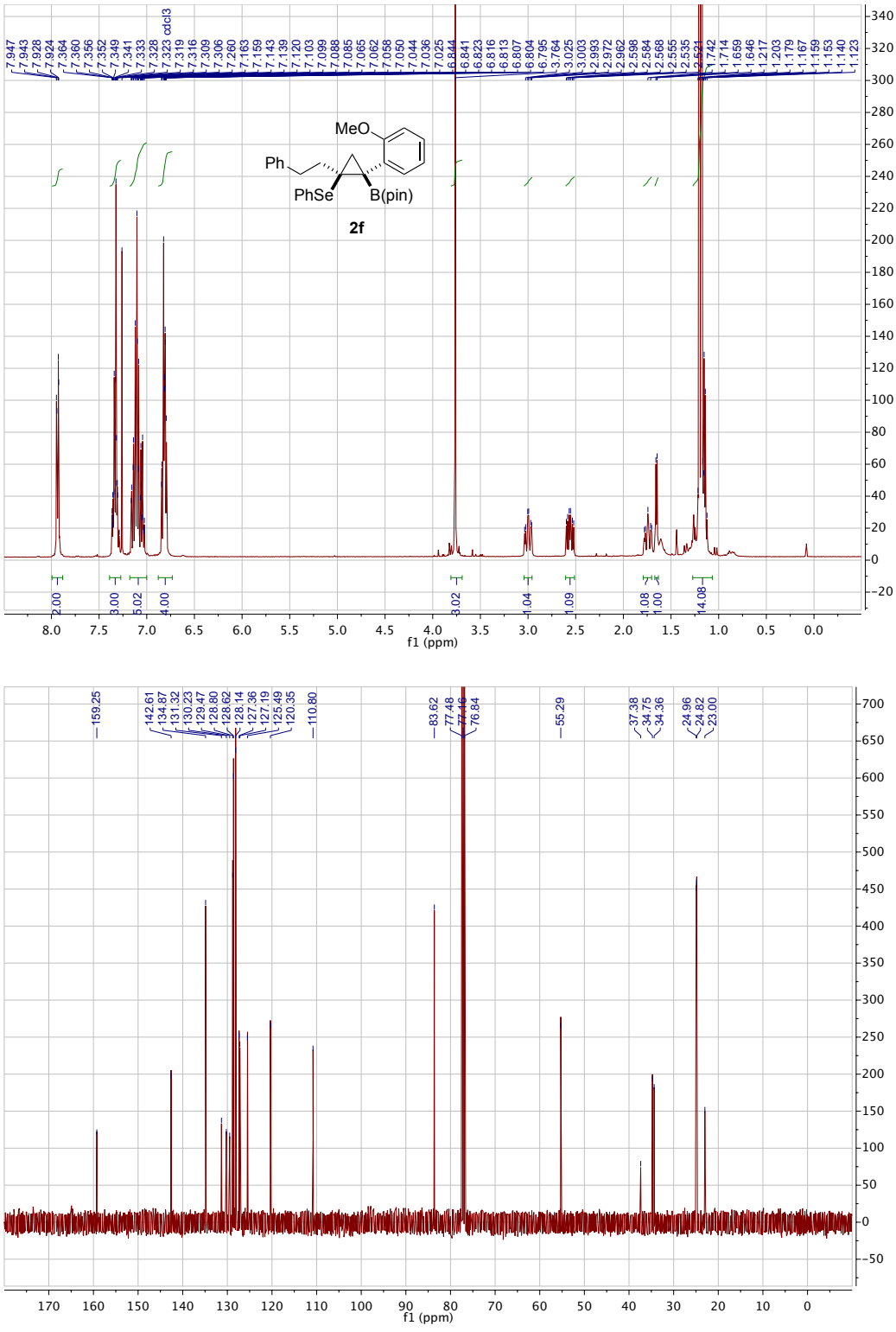

Figure S10. ^{1}H- and ^{13}C-NMR spectra of **2f**

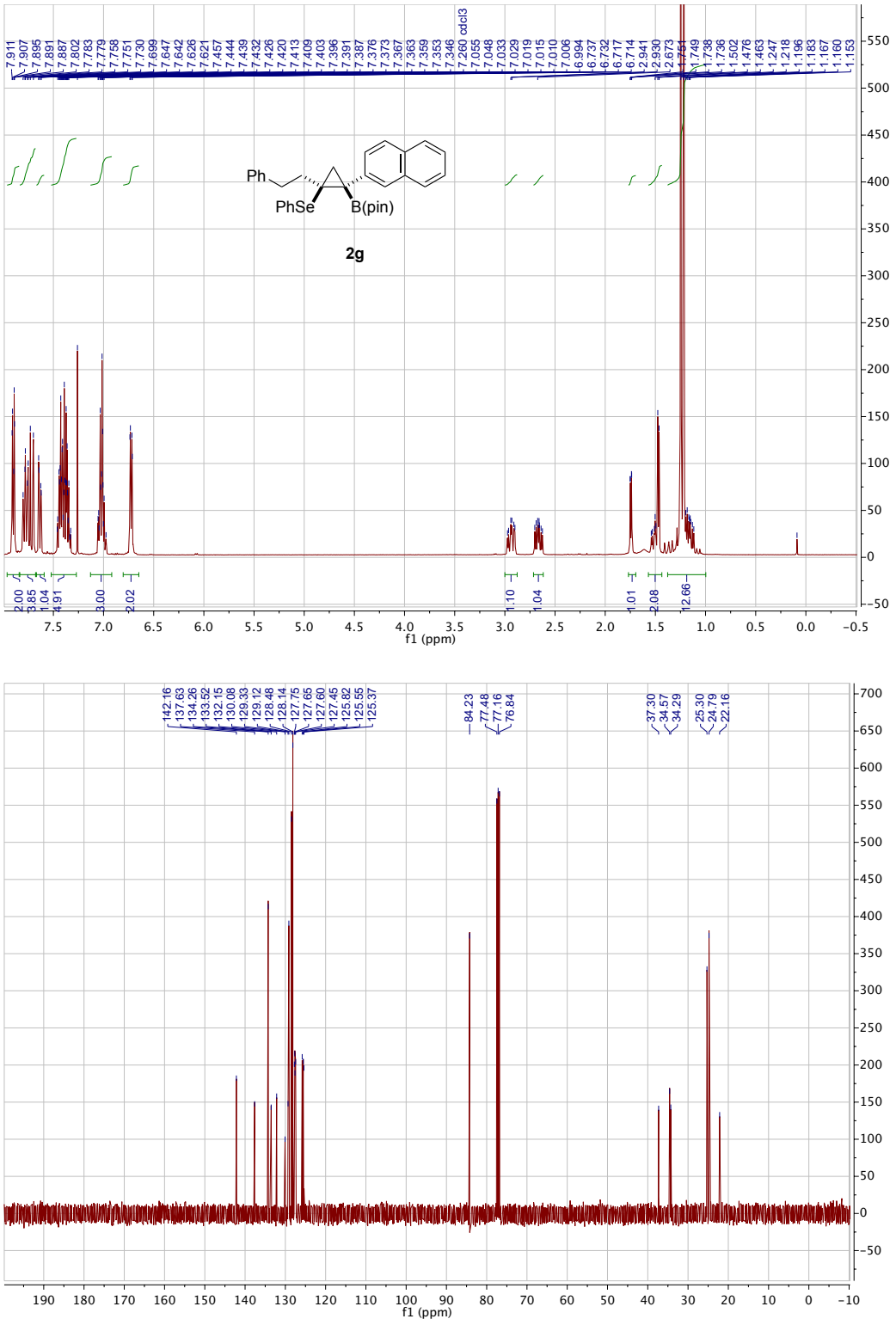

Figure S11. ^{1}H- and ^{13}C-NMR spectra of **2g**

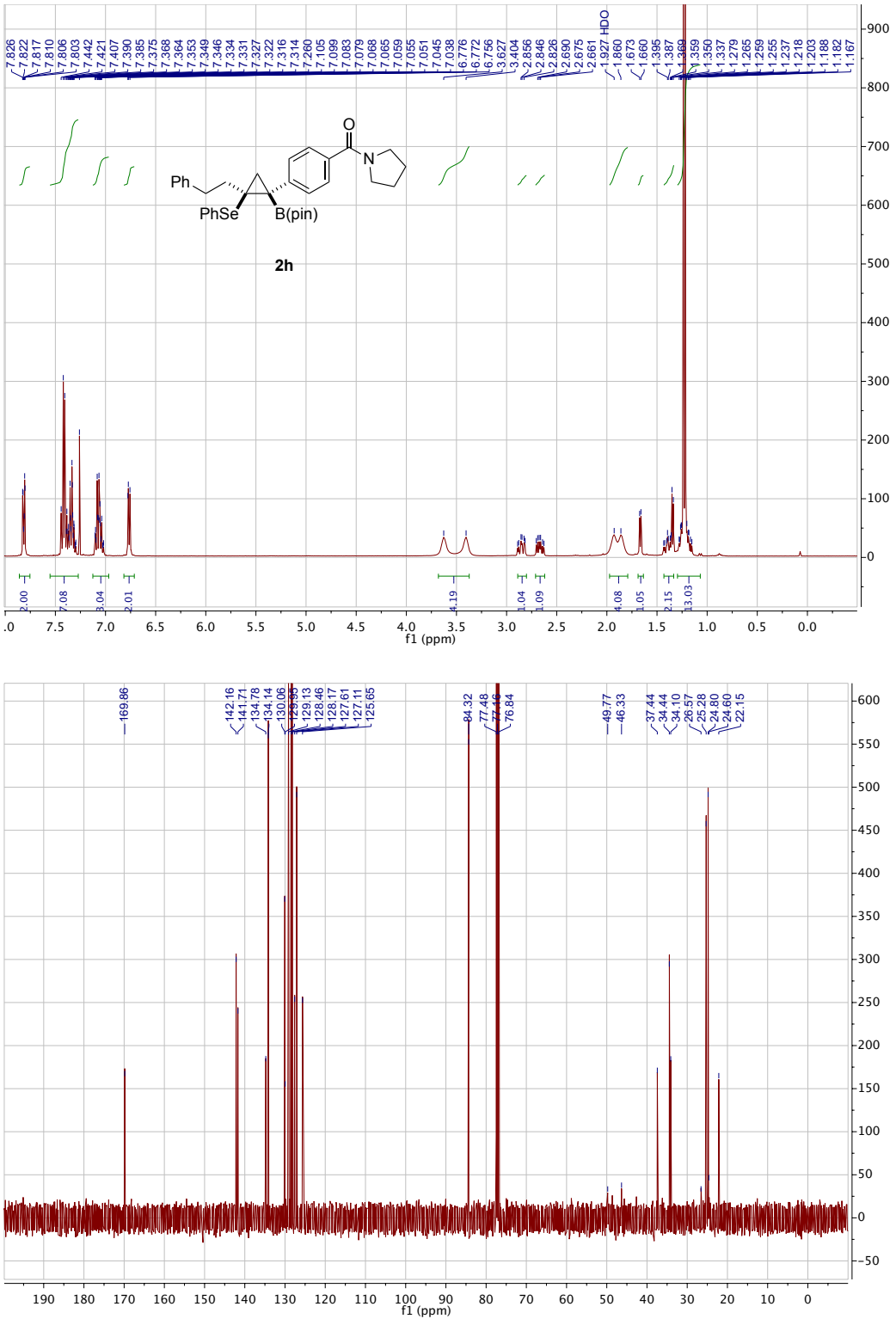

Figure S12. ^{1}H- and ^{13}C-NMR spectra of **2h**

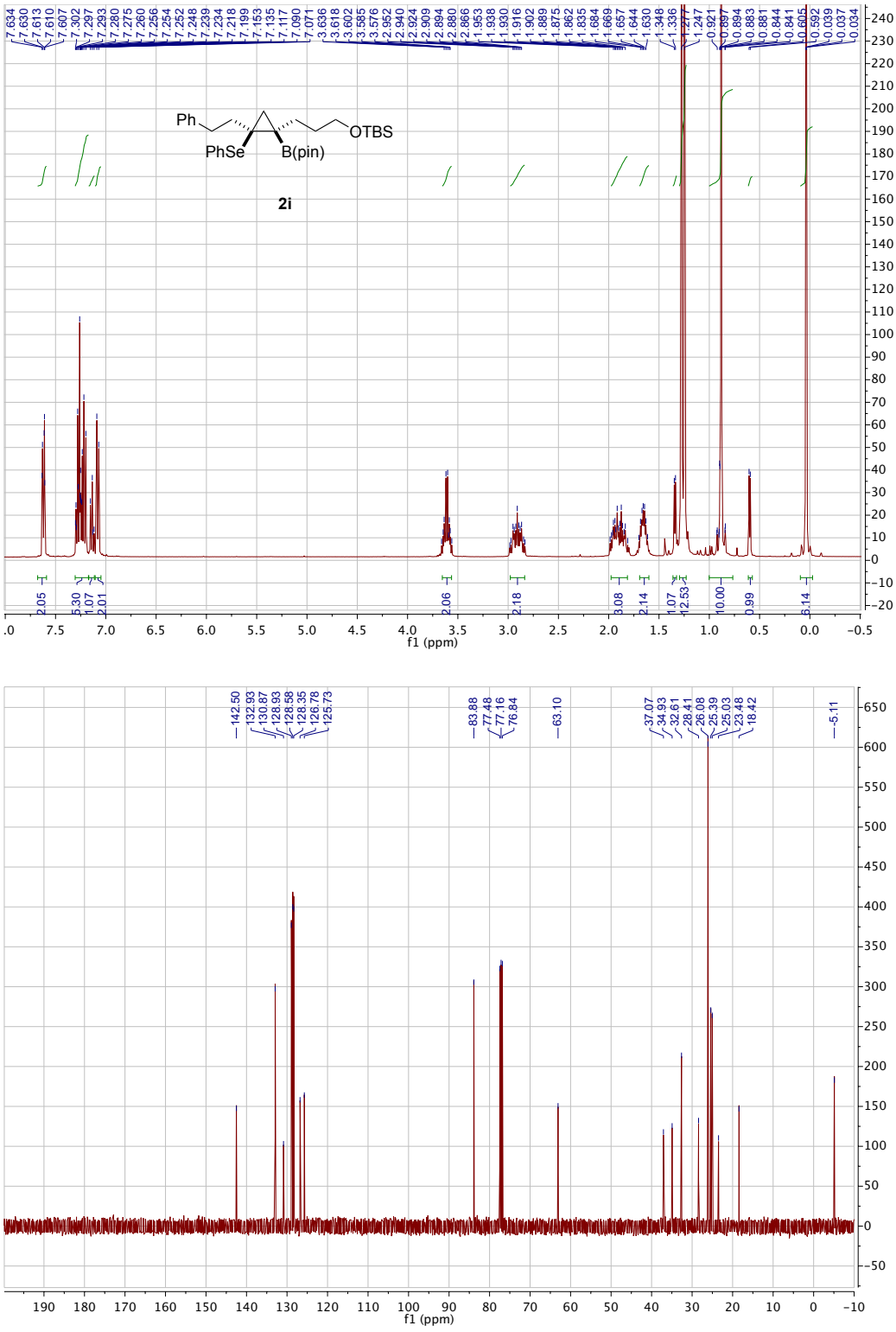

Figure S13. ^{1}H- and ^{13}C-NMR spectra of **2i**

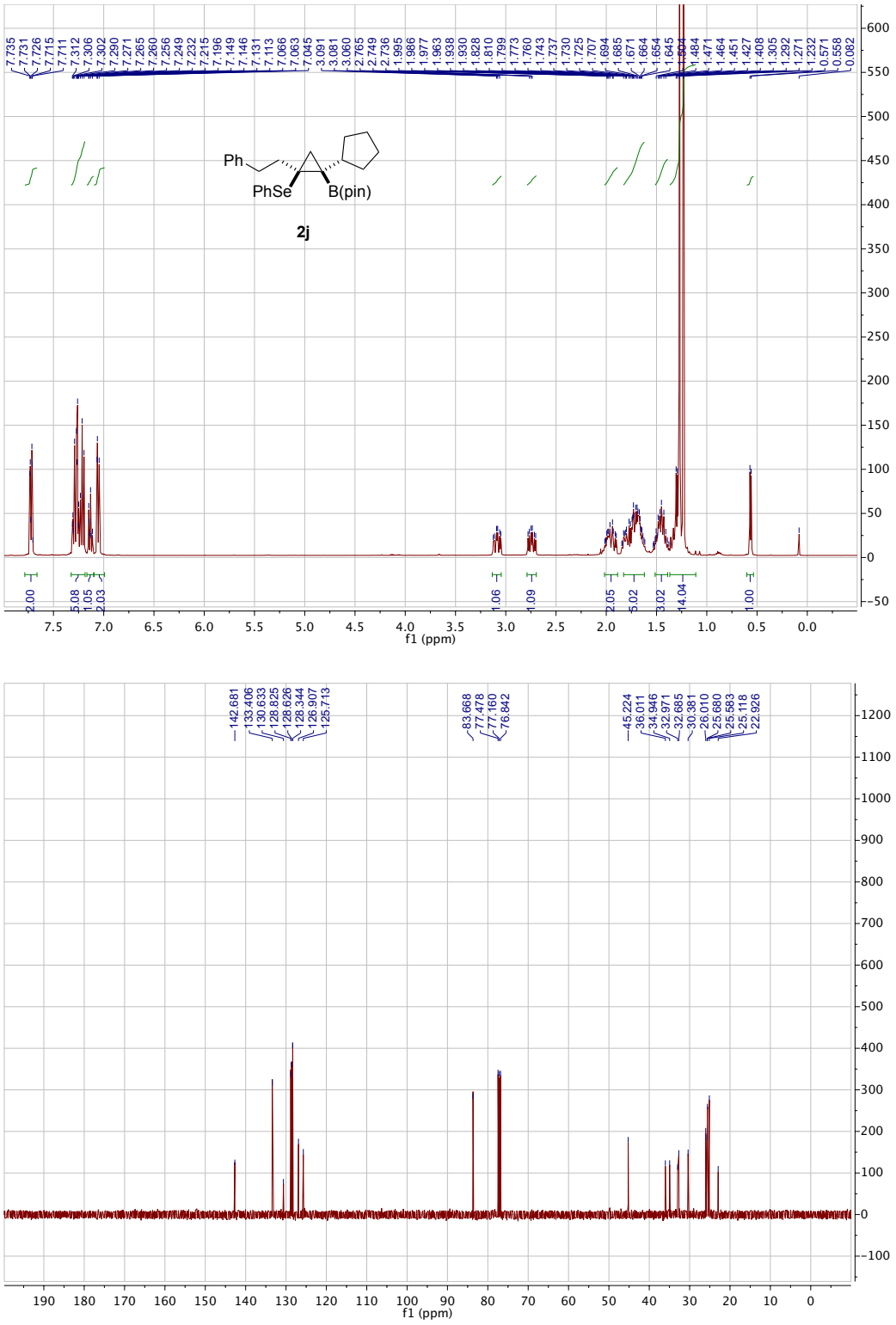

Figure S14. ^{1}H- and ^{13}C-NMR spectra of **2j**

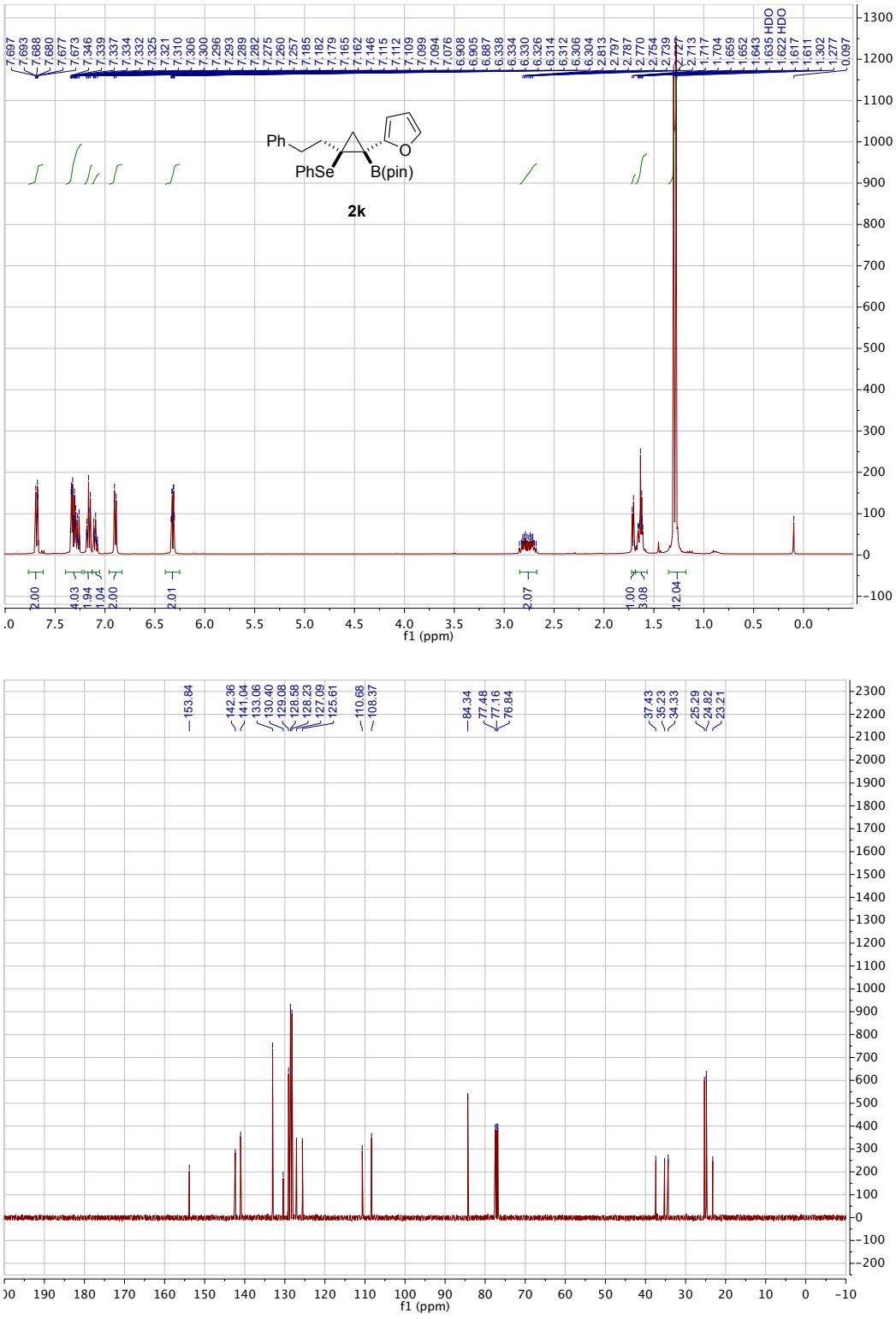

Figure S15. ^{1}H- and ^{13}C-NMR spectra of **2k**

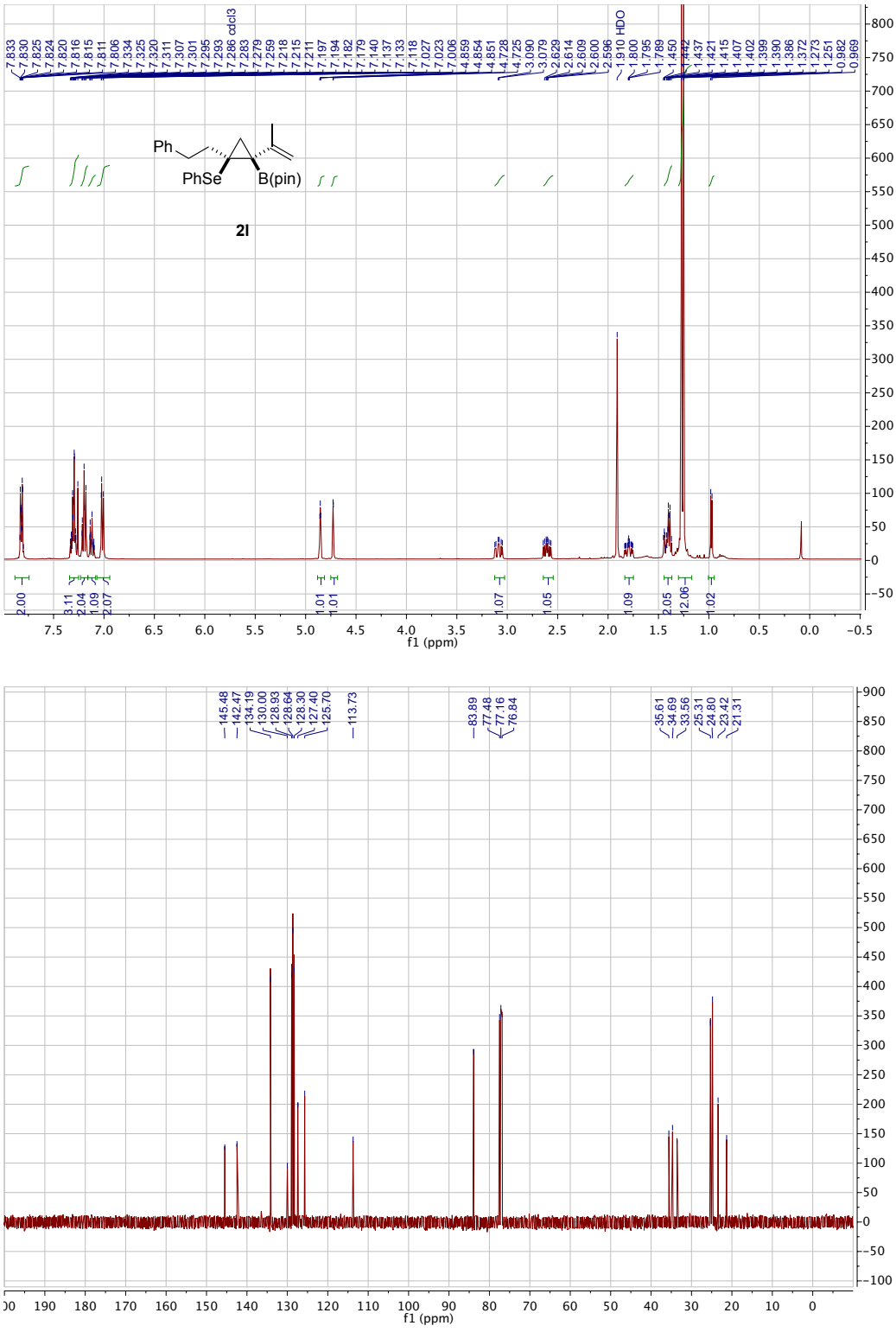

Figure S16. ^{1}H- and ^{13}C-NMR spectra of **2l**

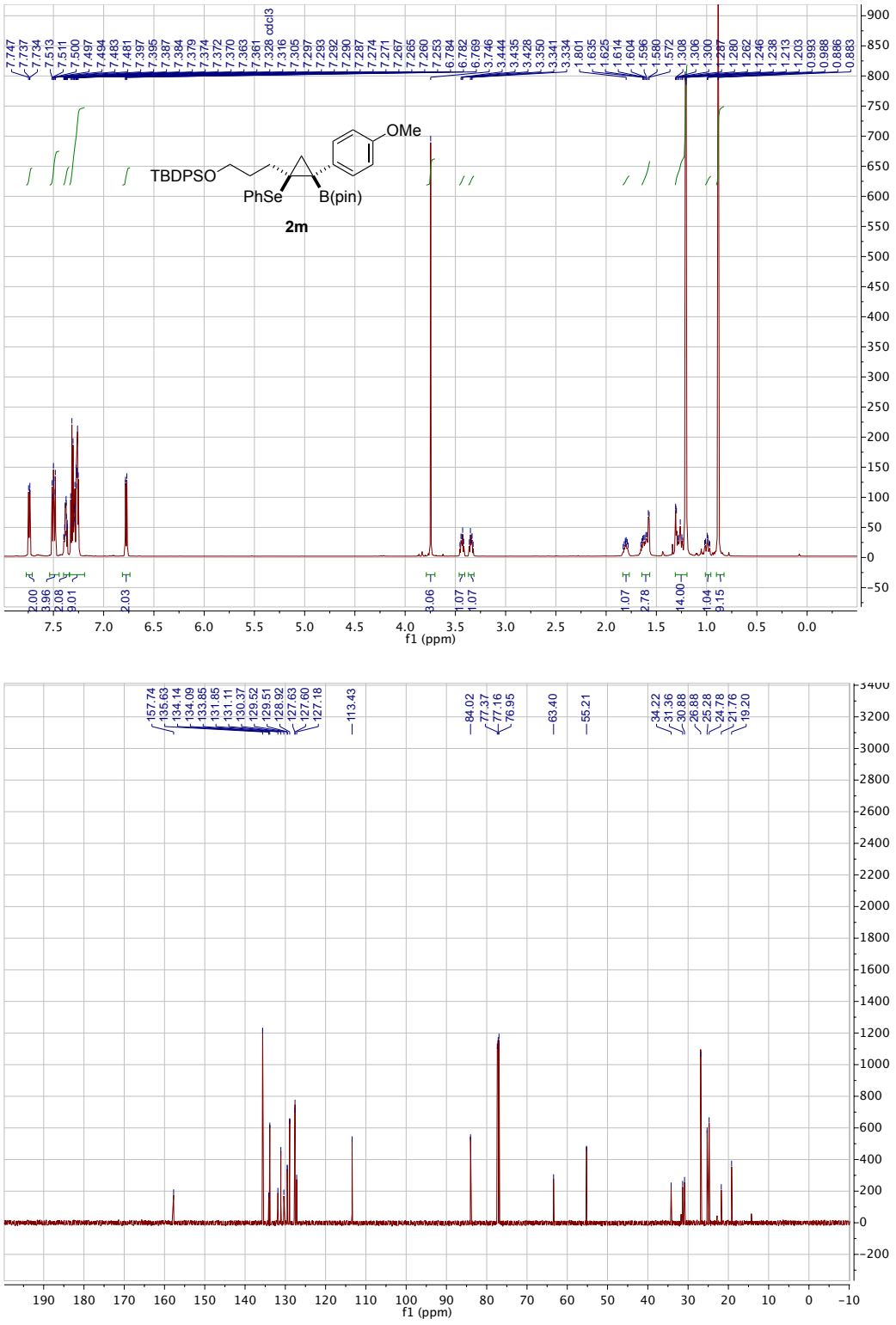

Figure S17. ^{1}H- and ^{13}C-NMR spectra of **2m**

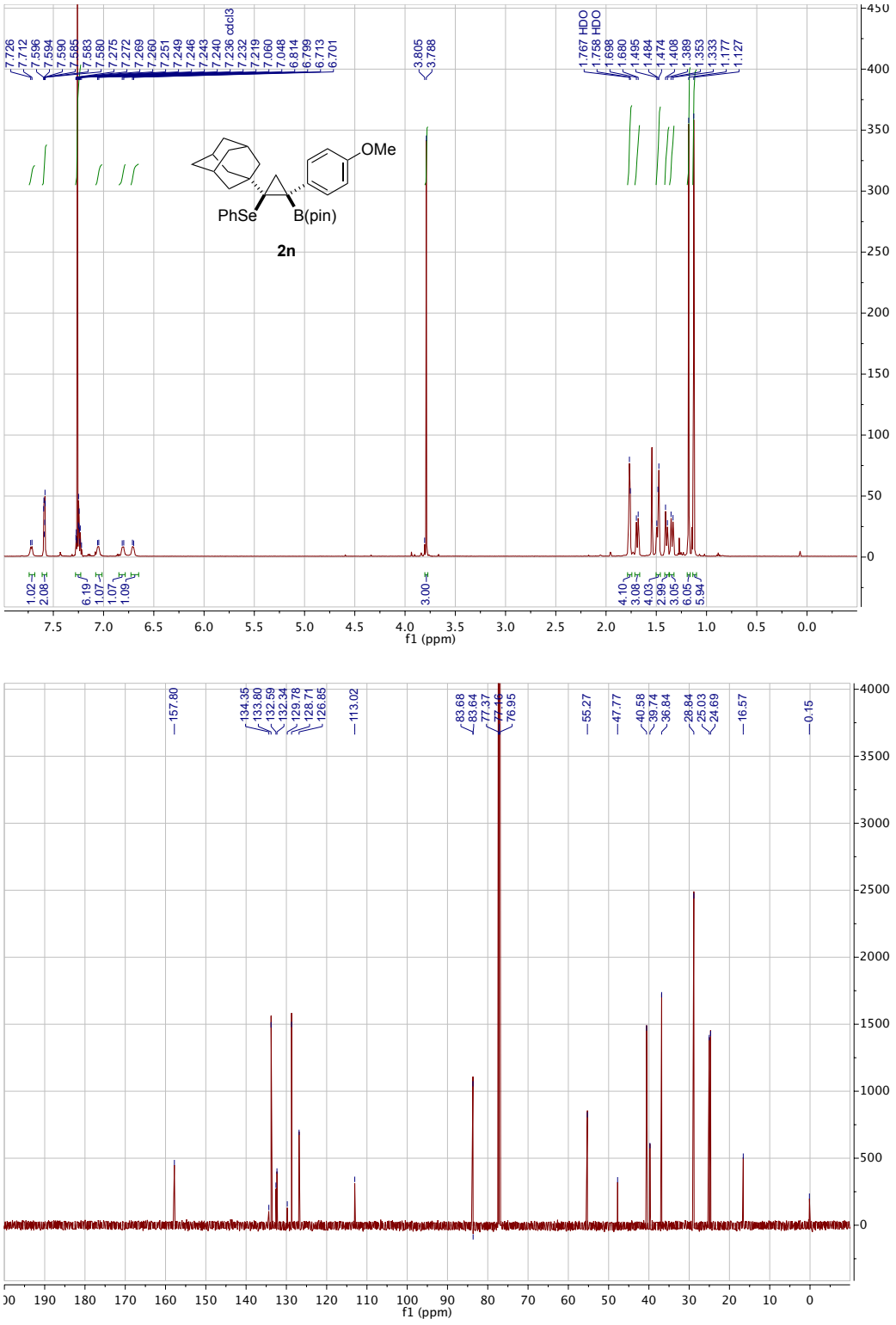

Figure S18. ^{1}H- and ^{13}C-NMR spectra of **2n**

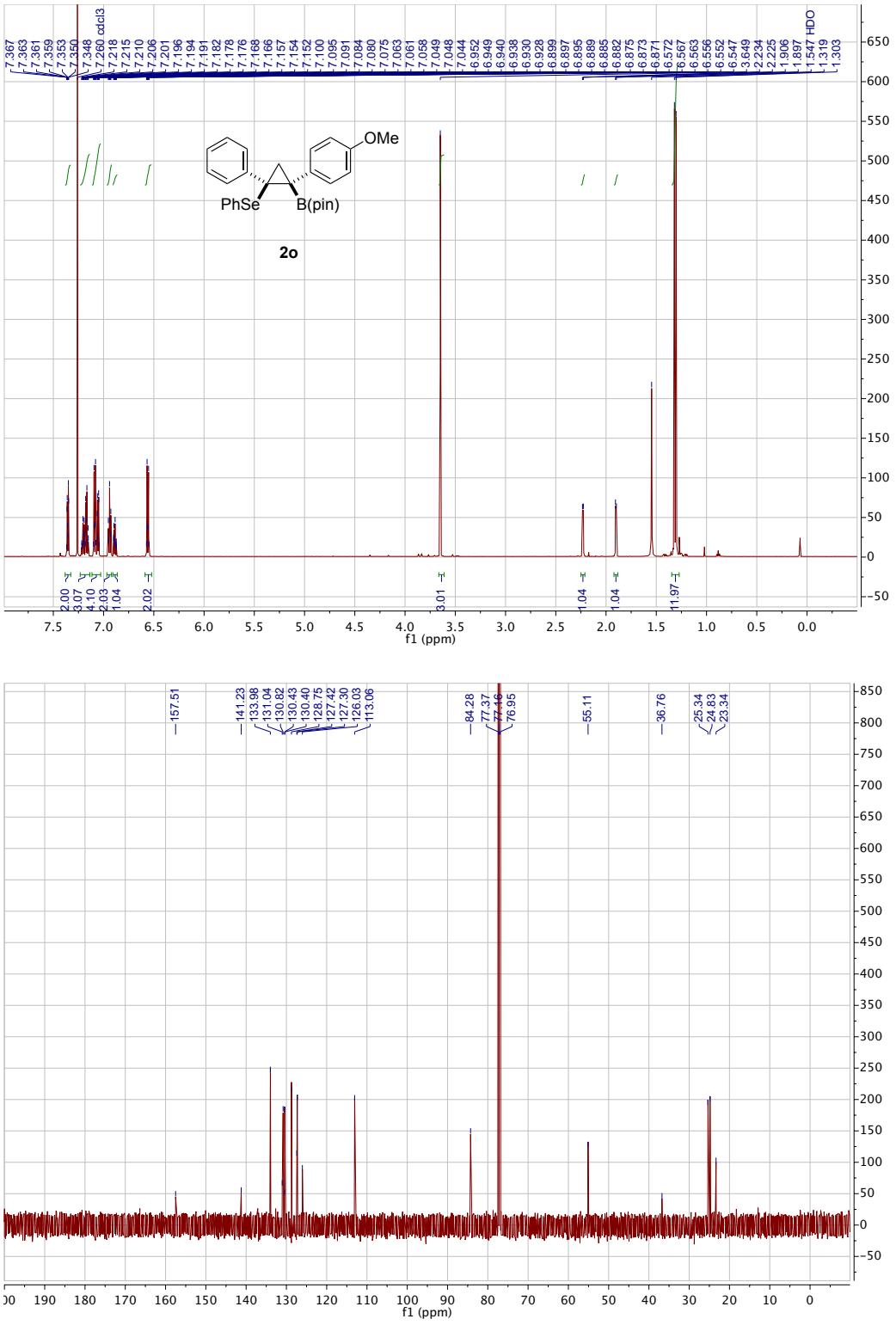

Figure S19. ^{1}H- and ^{13}C-NMR spectra of **2o**

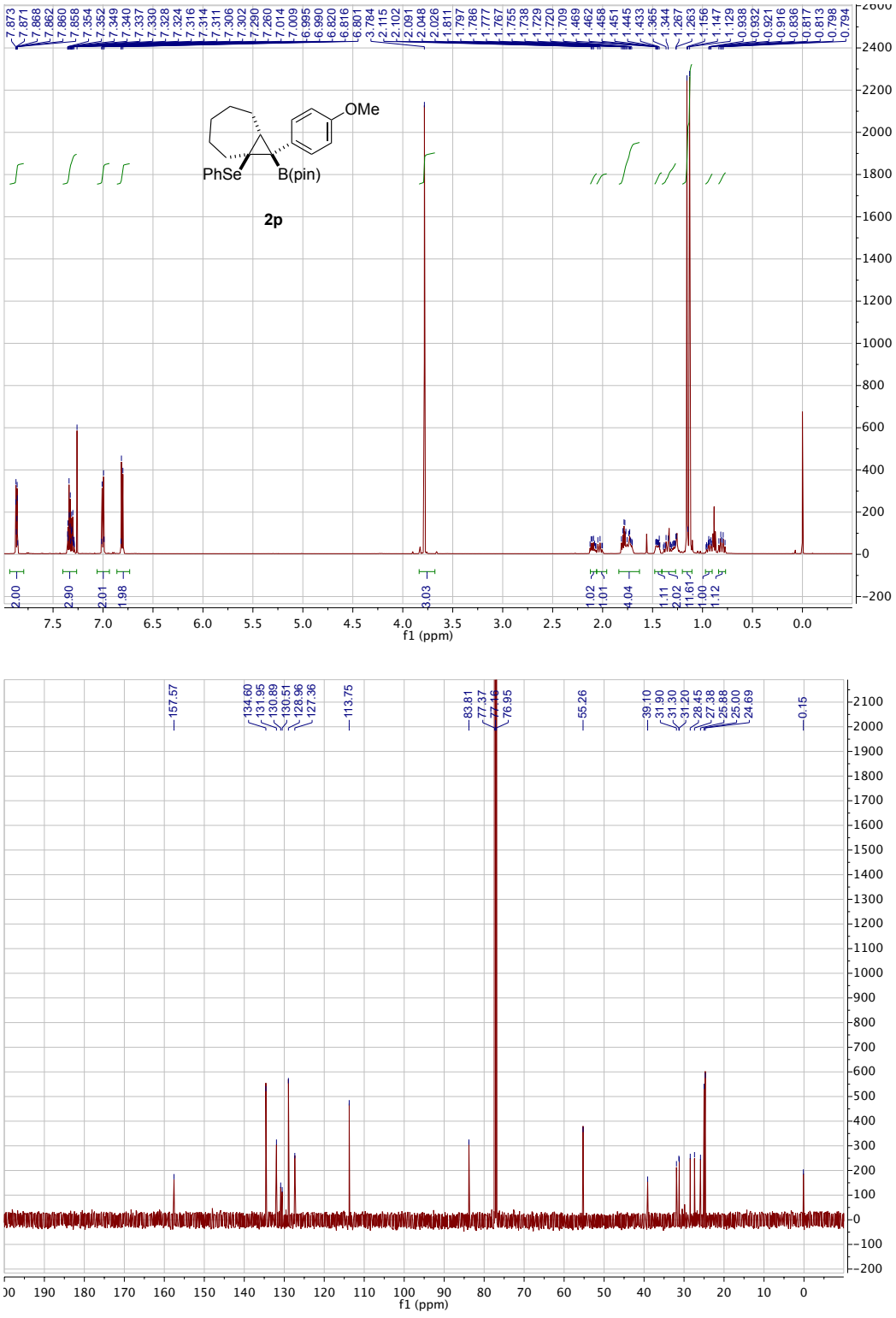

Figure S20. ^{1}H- and ^{13}C-NMR spectra of **2p**

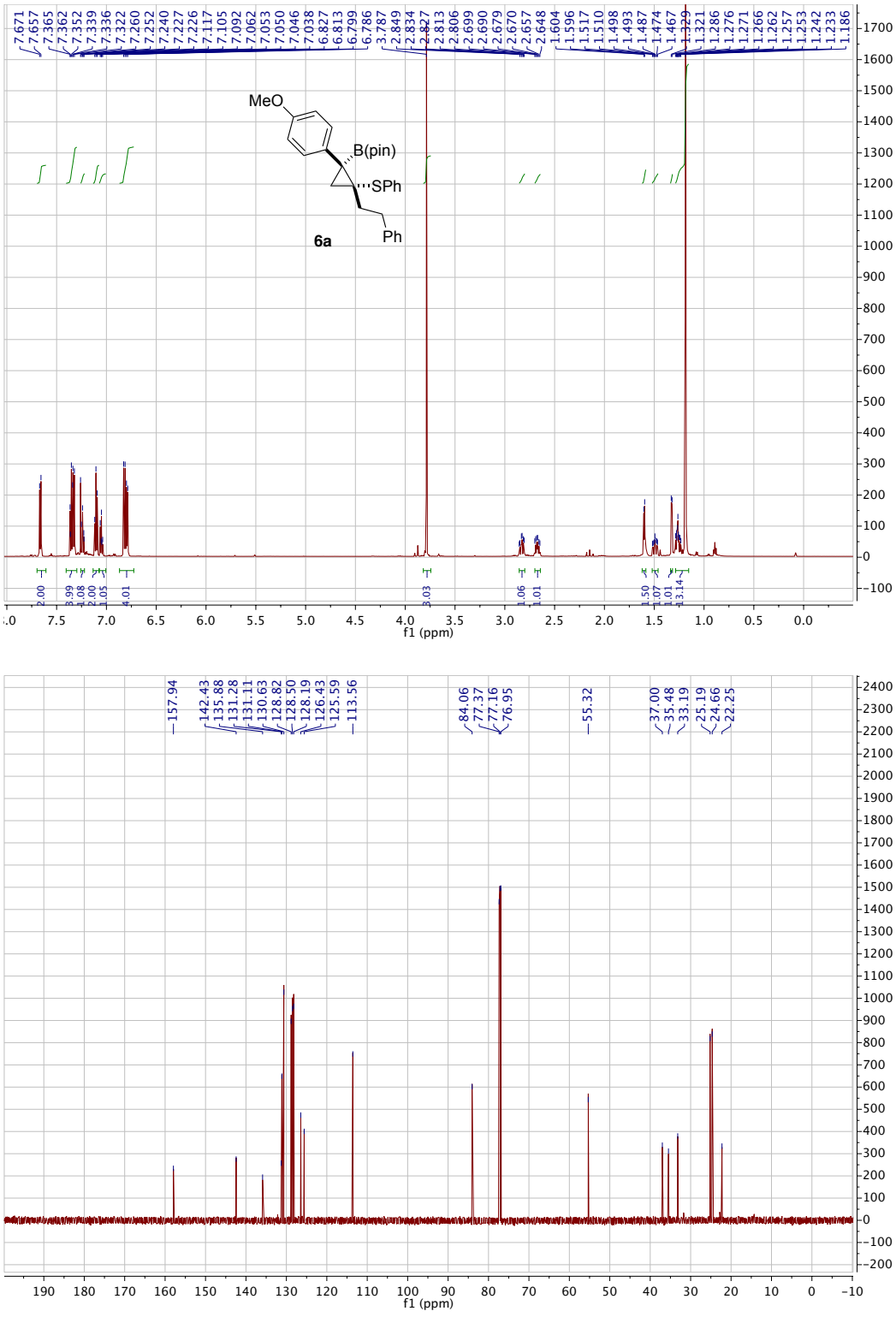

Figure S21. ^{1}H- and ^{13}C-NMR spectra of **6a**

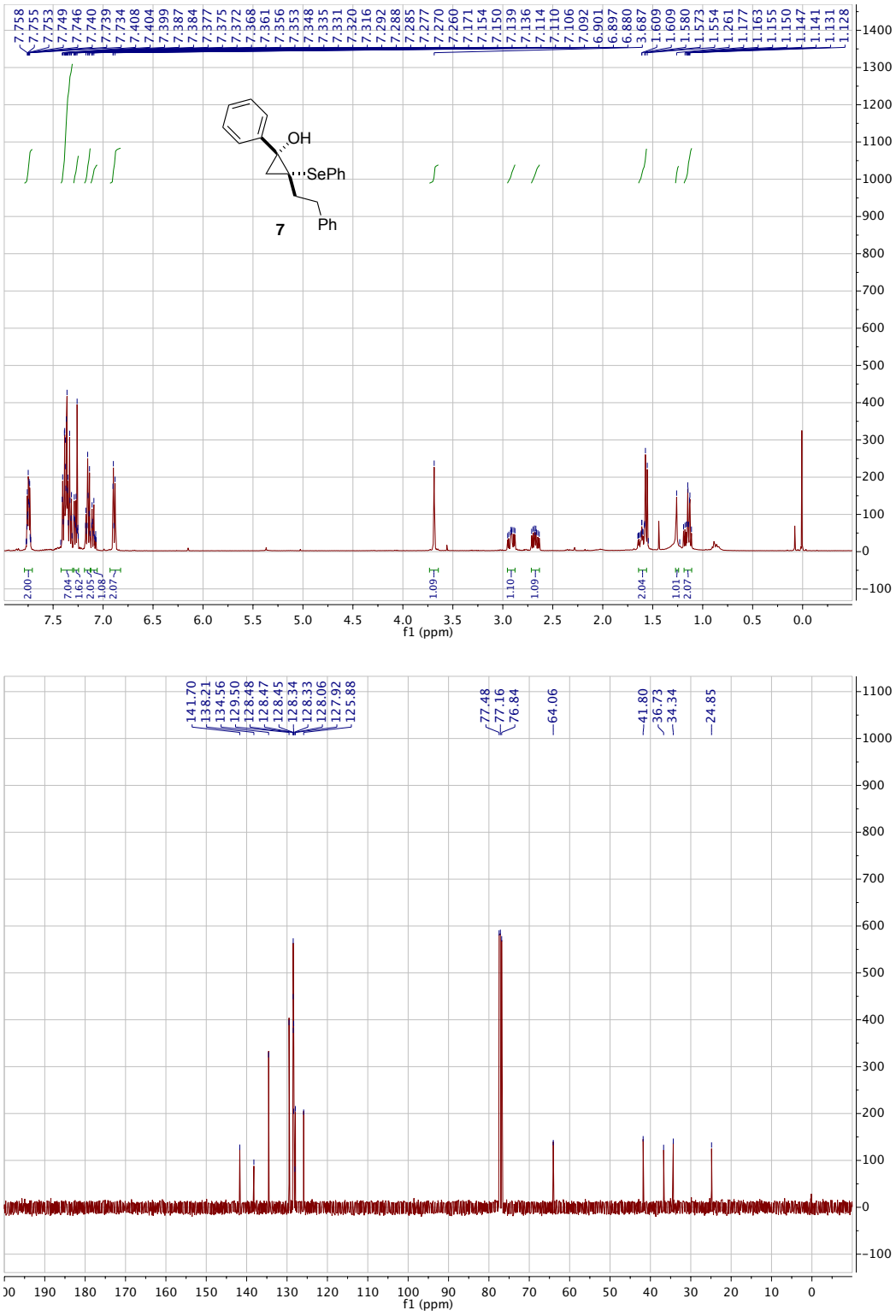

Figure S22. ^{1}H- and ^{13}C-NMR spectra of **7**