Catalyst Free Annulative Thioboration of Unfunctionalized Olefins

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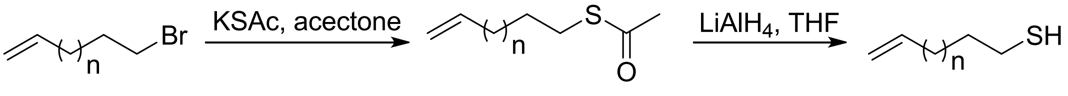
1. General Information

All organic reagents were purchased from Energy Chemical, if not noted otherwise. Column chromatography was performed with 200-300 mesh silica gel unless otherwise noted. Thin layer chromatography (TLC) was performed on silica gel GF254. ^{1}H, ^{13}C and ^{11}B NMR spectra were recorded on a Bruker DRX 400 spectrometer at 298 K using deuterated chloroform as solvent and TMS as internal reference. All chemical shifts in nmr experiments are reported as ppm downfield from TMS. HRMS experiments were performed on a Waters LCT PremierxeTM (USA). Structures, schemes and figures of the supporting information are marked with "S".

2. Synthesis of Olefins

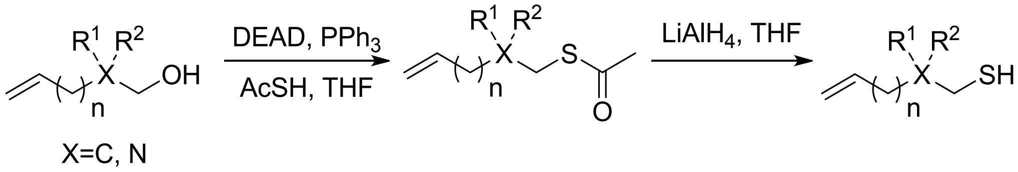
General procedure A



To a suspension of potassium thioacetate (7.5 mmol, 1.5 equiv.) in acetone (10 mL) was added bromoalkene (5 mmol, 1.0 equiv.) under nitrogen atmosphere. The reaction mixture was kept stirring overnight. The solvent was evaporated and the solid residue was dissolved in CH_2Cl_2 (20 mL). The organic solution was extracted with water (5 x 20 mL), dried with Na_2SO_4, and concentrated to get a residue. The residue was purified by flash column chromatography.

To a cooled (0°C) solution of S-alkyl thioacetate in THF (10 mL) was added $LiAlH_4$ (1.1 equiv.) portionwise, and the reaction mixture was kept stirring for 30 min at 0°C. The reaction mixture was carefully quenched with saturated aqueous $NaHSO_4$ solution at 0 °C, and then extracted with Et_2O (3 x 30 mL). The organic extracts were dried over $MgSO_4$, filtered and evaporated under reduced pressure to afford the crude product. The crude product was purified by flash column chromatography to give the thiols.

General procedure B

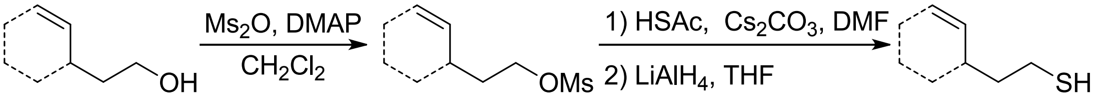


The starting material was prepared according to literature procedure.[1]

To a cooled (0°C) solution of PPh_3 (2 equiv.) in anhydrous THF was added DEAD (2 equiv.) dropwise, and the resulting mixture was allowed to stir at 0°C until the formation of a white solid was observed (typically 15-30 min). A solution of alcohol (1 equiv.) and thioacetic acid (2 equiv.) in anhydrous THF was added dropwise at 0°C followed by stirring at 0°C for 1 h and at 25°C for 1 h. The solvent was evaporated under reduced pressure and the residue was purified with column chromatography.

To a cooled (0°C) solution of S-alkyl thioacetate in THF was added $LiAlH_4$ (1.1 equiv.) portionwise, and the reaction mixture was kept stirring for 30 min at 0°C. The reaction mixture was carefully quenched with saturated aqueous $NaHSO_4$ solution at 0 °C, and then extracted with Et_2O (3 x 20 mL). The organic extracts were dried over $MgSO_4$, filtered and evaporated under reduced pressure to afford the crude product. The crude product was purified by flash column chromatography to give the thiols.

General procedure C



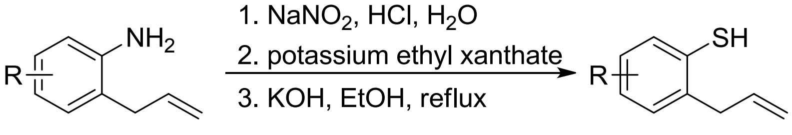
The starting material was prepared according to literature procedure.[1a, 2]

The alcohol (5 mmol) was dissolved in CH_2Cl_2 (30 mL) and pyridine (10 mmol, 2 equiv.), DMAP (0.5 mmol, 0.1 equiv.) and Ms_2O (7.5 mmol, 1.5 equiv.) was added and the resultant suspension was stirred for 45 min. Saturated aqueous $CuSO_4$ was added and the organic phase was separated and washed with $CuSO_4$ and brine. The aqueous layer was extracted with ethyl acetate (3 x 30 mL). The ethyl acetate solution was washed with $CuSO_4$ and brine. The combined organic layers were dried over $MgSO_4$, filtered and evaporated under reduced pressure to afford the residue. The residue was purified with column chromatography.

Under an nitrogen atmosphere, thioacetic acid (1.25 equiv.) was added to a suspension of Cs_2CO_3 (0.65 equiv.) in DMF. After stirring for 30 min at room temperature, methanesulfonate was added at once and the mixture was stirred at 80°C for 12 h. After the reaction solution was cooled to room temperature, water and ethyl acetate was added. The organic layer was separated and the aqueous solution was extracted with ethyl acetate (3 x 30 mL). The combined organic layer was washed with brine, dried over $MgSO_4$, filtered and evaporated under reduced pressure to afford the residue. The residue was purified with column chromatography.

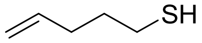
To a cooled (0°C) solution of S-alkyl thioacetate in THF (10 mL) was added $LiAlH_4$ (1.1 equiv.) portionwise, and the reaction mixture was kept stirring for 30 min at 0°C. The reaction mixture was carefully quenched with saturated aqueous $NaHSO_4$ solution at 0 °C, and then extracted with Et_2O (3 x 20 mL). The organic extracts were dried over $MgSO_4$, filtered and evaporated under reduced pressure to afford the crude product. The crude product was purified by flash column chromatography to give the thiols.

General procedure D



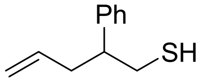
The substituted 2-allylaniline was prepared according to literature procedure.[3]

To a solution of 1 equiv. of substituted 2-allylaniline (2 mmol) in water (5.4 mL) at 0 °C was added concentrated hydrochloric acid (0.3 mL). A cold solution of 1 equiv. of sodium nitrite (138 mg, 2 mmol) in water (1.1 mL) was added slowly and stirred for 15 minutes. The cold diazonium solution was added slowly to a solution of 1.3 equiv. of potassium ethyl xanthate (416 mg, 2.6 mmol) in water (0.5 mL) at 45 °C. The reaction mixture was stirred for an additional 30 minutes at 45 °C and then cooled to room temperature. The reaction mixture was extracted with ethyl acetate (3 x 20 mL). The combined organic extracts were washed with 10 % NaOH solution (75 mL), water (3 x 20 mL), brine (20 mL), dried over $MgSO_4$, filtered and evaporated under reduced pressure. The resulting crude aryl xanthate product was dissolved in ethanol (6 mL) and heated to reflux. Potassium hydroxide pellets (484 mg, 8.6 mmol) were added and refluxing continued overnight. The solution was cooled to room temperature and the ethanol was evaporated under reduced pressure. The residue was dissolved in water and washed with diethyl ether (75 mL). The aqueous layer was acidified with 2 N HCl and extracted with ethyl acetate (3 x 20 mL). The organic extracts were washed with water (20 mL), brine (20 mL), dried over $MgSO_4$, filtered and evaporated under reduced pressure to afford the crude product (overall, 3 steps). The crude product was purified with a short column chromatography.



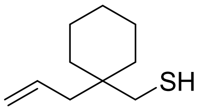
pent-4-ene-1-thiol (**1a**)

Prepared according to general procedure A. **1a** (180 mg, 83%) was obtained as a yellow oil through a short column chromatography (petroleum). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 – 5.64 (m, 1H), 5.09 – 4.89 (m, 2H), 2.56 – 2.47 (m, 2H), 2.22 – 2.10 (m, 2H), 1.78 – 1.64 (m, 2H), 1.33 (t, J = 7.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 115.4, 33.1, 32.4, 24.0. Data is in accordance with the literature.[4]



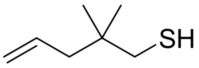
2-phenylpent-4-ene-1-thiol (**1b**)

Prepared according to general procedure B. **1b** (180 mg, 51%) was obtained as a yellow oil through a short column chromatography (petroleum). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.16 (m, 5H), 5.85 – 5.57 (m, 1H), 5.15 – 4.95 (m, 2H), 3.14 – 2.80 (m, 3H), 2.65 – 2.54 (m, 1H), 2.51 – 2.38 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 136.0, 128.5, 127.9, 126.8, 116.8, 45.1, 39.6, 29.8. Data is in accordance with the literature.[5]



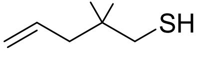
(1-allylcyclohexyl)methanethiol (**1d**)

Prepared according to general procedure B. **1d** (240 mg, 70%) was obtained as a yellow oil through a short column chromatography (petroleum). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89 – 5.68 (m, 1H), 5.16 – 5.01 (m, 2H), 2.50 (d, J = 8.6 Hz, 2H), 2.14 (d, J = 7.5 Hz, 2H), 1.50 – 1.32 (m, 10H), 1.11 (t, J = 8.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.4, 117.7, 36.5, 34.4, 32.8, 29.8, 26.3, 21.7. HRMS–ESI (m/z): $[M+H]^+$ calcd for $C_{10}H_{19}S$, 171.1207; found: 171.1214.



2,2-dimethylpent-4-ene-1-thiol (**1e**)

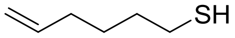
Prepared according to general procedure B. **1e** (180 mg, 70%) was obtained as a yellow oil through a short column chromatography (petroleum). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87 – 5.70 (m, 1H), 5.08 – 4.92 (m, 2H), 2.77 (t, J = 6.0 Hz, 1H), 2.45 – 2.37 (m, 2H), 2.08 – 1.95 (m, 2H), 0.94 (s, 3H), 0.93 (s, 3H). HRMS–ESI (m/z): $[M+H]^+$ calcd for $C_7H_{15}S$, 131.0894; found: 131.0889.



2-ethyl-2-methylpent-4-ene-1-thiol (**1f**)

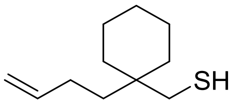
Prepared according to general procedure B. **1f** (180 mg, 74%) was obtained as a yellow oil through a short column chromatography (petroleum). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89 – 5.64 (m, 1H), 5.13 – 4.95 (m, 2H), 2.43 (d, J = 8.5 Hz, 2H), 2.07 (d, J = 6.7 Hz, 2H), 1.40 – 1.27 (m, 2H), 1.01 – 0.94 (m, 1H), 0.88 – 0.78 (m, 6H). ^{13}C

NMR (100 MHz, $CDCl_3$) δ 134.8, 117.6, 42.1, 34.0, 30.4, 29.9, 23.1, 8.0. HRMS–ESI (m/z): $[M+H]^+$ calcd for $C_8H_{17}S$, 145.1051; found: 145.1036.



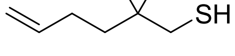
hex-5-ene-1-thiol (**1g**)

Prepared according to general procedure A. **1g** (195 mg, 84%) was obtained as a yellow oil through a short column chromatography (petroleum). ^1H NMR (400 MHz, $CDCl_3$) δ 5.88 – 5.70 (m, 1H), 5.13 – 4.88 (m, 2H), 2.59 – 2.48 (m, 2H), 2.18 – 1.99 (m, 2H), 1.71 – 1.56 (m, 2H), 1.55 – 1.42 (m, 2H), 1.34 (t, J = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 114.8, 33.6, 33.3, 27.7, 24.6. HRMS–ESI (m/z): $[M+H]^+$ calcd for $C_6H_{13}S$, 117.0738; found: 117.0723. Data is in accordance with the literature.[6]



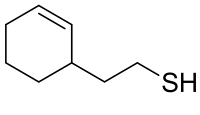
(1-(but-3-en-1-yl)cyclohexyl)methanethiol (**1h**)

Prepared according to general procedure B. **1h** (270 mg, 74%) was obtained as a yellow oil through a short column chromatography (petroleum). ^1H NMR (400 MHz, $CDCl_3$) δ 5.93 – 5.74 (m, 1H), 5.12 – 4.89 (m, 2H), 2.53 (d, J = 8.4 Hz, 2H), 1.99 – 1.83 (m, 2H), 1.49 – 1.35 (m, 12H), 1.08 (t, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4, 114.3, 36.0, 34.6, 33.3, 32.7, 29.8, 27.4, 26.4, 21.7. HRMS–ESI (m/z): $[M+H]^+$ calcd for $C_{11}H_{21}S$, 185.1364; found: 185.1358.



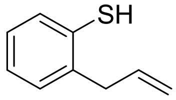
2,2-dimethylhex-5-ene-1-thiol (**1i**)

Prepared according to general procedure B. **1i** (180 mg, 63%) was obtained as a yellow oil through a short column chromatography (petroleum). ^1H NMR (400 MHz, $CDCl_3$) δ 5.92 – 5.69 (m, 1H), 4.98 (m, 2H), 3.48 (m, 2H), 2.43 (d, 2H), 2.01 – 1.95 (m, 2H), 0.94 (s, 6H). HRMS–ESI (m/z): $[M+H]^+$ calcd for $C_8H_{17}S$, 145.1051; found: 145.1036.



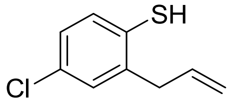
2-(cyclohex-2-en-1-yl)ethanethiol (**1j**)

Prepared according to general procedure C. **1j** (170 mg, 60%) was obtained as a yellow oil through a short column chromatography (petroleum). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.64 – 5.50 (m, 1H), 5.51 – 5.38 (m, 1H), 2.55 – 2.39 (m, 2H), 2.14 (m, 1H),1.91 – 1.87 (m, 2H) 1.73 – 1.38 (m, 6H), 1.26 (t, J = 7.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 130.7, 127.3, 40.6, 33.9, 28.5, 25.1, 22.0, 21.2. HRMS–ESI (m/z): $[M+H]^+$ calcd for $C_8H_{15}S$, 143.0894; found: 143.0891. Data is in accordance with the literature.[2]



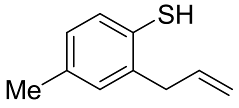
2-allylbenzenethiol **(4a)**

Prepared according to general procedure D. 4a (180 mg, 60%) was obtained as a yellow oil through a short column chromatography (petroleum). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 1H), 7.24 – 7.07 (m, 3H), 5.98 (m, 1H), 5.10 (m, 2H), 3.53 – 3.43 (m, 2H). Data is in accordance with the literature.[7]



2-allyl-4-chlorobenzenethiol (**4b**)

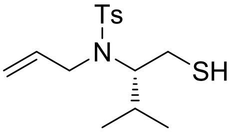
Prepared according to general procedure D. **4b** (160 mg, 43%) was obtained as a yellow oil through a short column chromatography (petroleum). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.22 (m, 1H), 7.20 – 7.17 (m, 1H), 7.11 – 7.07 (m, 1H), 6.01 – 5.89 (m, 1H), 5.21 – 5.05 (m, 2H), 3.44 (d, *J* = 6.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.0, 134.7, 132.1, 132.0, 131.9, 129.8, 127.0, 117.3, 38.6. HRMS–ESI (m/z): $[M+H]^+$ calcd for $C_9H_{10}ClS$, 185.0192; found: 185.0171.



2-allyl-4-methylbenzenethiol (**4c**)

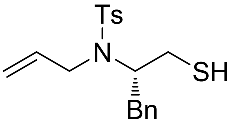
Prepared according to general procedure D. **4c** (170 mg, 52%) was obtained as a yellow oil through a short column chromatography (petroleum). ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.25 (d, *J* = 7.8 Hz, 1H), 7.03 (s, 1H), 6.96 (d, *J* = 7.9 Hz, 1H), 6.06 – 5.93 (m, 1H), 5.23 – 5.03 (m, 2H), 3.48 (d, *J* = 6.3 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 136.4, 135.9, 131.5, 130.8, 127.9, 126.7, 116.5, 39.0, 21.0. HRMS–ESI (m/z): $[M+H]^+$ calcd for $C_{10}H_{13}S$, 165.0738; found: 165.0741.



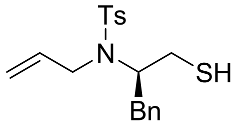
(*S*)-2-(allylamino)-3-methylbutane-1-thiol (**7a**)

Prepared according to general procedure B. **7a** (180 mg, 58%) was obtained as a yellow oil through column chromatography (EtOH:petroleum=1:20).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 9.0 Hz, 2H), 5.96 – 5.80 (m, 1H), 5.14 (m, 2H), 3.94 – 3.73 (m, 2H), 3.68 – 3.58 (m, 1H), 2.82 – 2.73 (m, 1H), 2.71 – 2.58 (m, 1H), 2.43 (s, 3H), 1.99 – 1.84 (m, 1H), 1.36 – 1.32 (m, 1H) 0.99 (d, *J* = 6.6 Hz, 3H), 0.89 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 138.4, 135.8, 129.5, 128.0, 117.8, 68.1, 47.7, 31.5, 29.8, 26.6, 21.0, 20.6. HRMS–ESI (m/z): $[M+H]^+$ calcd for $C_{15}H_{23}NO_2S_2$, 314.1248; found: 314.1247. Data is in accordance with the literature.[8]



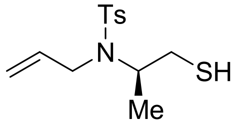
(*S*)-2-(allylamino)-3-phenylpropane-1-thiol (**7b**)

Prepared according to general procedure B. **7b** (180 mg, 50%) was obtained as a yellow oil through column chromatography (EtOH:petroleum=1:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.29 – 7.19 (m, 5H), 7.13 (d, *J* = 6.6 Hz, 2H), 6.00 – 5.79 (m, 1H), 5.21 (m, 2H), 4.11 – 3.98 (m, 1H), 3.96 – 3.81 (m, 2H), 2.93 (m, 2H), 2.84 – 2.71 (m, 1H), 2.67 – 2.57 (m, 1H), 2.41 (s, 3H), 1.41 – 1.37 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 138.1, 138.1, 135.9, 129.7, 129.3, 128.8, 127.6, 126.8, 118.1, 63.9, 48.0, 40.0, 27.4, 21.6. Data is in accordance with the literature[8].



(*R*)-2-(allylamino)-3-phenylpropane-1-thiol (**7c**)

Prepared according to general procedure B. **7c** (160 mg, 44%) was obtained as a yellow oil through column chromatography (EtOH:petroleum=1:20).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.1 Hz, 2H), 7.30 – 7.21 (m, 5H), 7.13 (d, *J* = 7.0 Hz, 2H), 5.98 – 5.75 (m, 1H), 5.21 (m, 2H), 4.14 – 4.01 (m, 1H), 3.96 – 3.77 (m, 2H), 2.98 – 2.87 (m, 2H), 2.87 – 2.75 (m, 1H), 2.66 – 2.57 (m, 1H), 2.41 (s, 3H) 1.45 – 1.36 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 138.0, 137.9, 135.8, 129.6, 129.2, 128.7, 127.4, 126.7, 118.0, 63.8, 47.8, 39.4, 27.2, 21.6. HRMS–ESI (m/z): $[M+H]^+$ calcd for $C_{19}H_{24}NO_2S_2$, 362.1248; found: 362.1262.



(*R*)-2-(allylamino)propane-1-thiol (**7d**)

Prepared according to general procedure B. **7b** (190 mg, 67%) was obtained as a yellow oil through column chromatography (EtOH:petroleum=1:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 5.96 – 5.72 (m, 1H), 5.37 – 5.03 (m, 2H), 4.05 – 3.84 (m, 2H), 3.84 – 3.60 (m, 1H), 2.85 – 2.64 (m, 1H), 2.63 – 2.44 (m, 1H), 2.43 (s, 3H), 1.57 – 1.34 (m, 1H), 1.15 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 138.0, 135.9, 129.7, 127.1, 117.5, 57.2, 46.7, 29.8, 21.5, 17.3. HRMS–ESI (m/z): $[M+H]^+$ calcd for $C_{13}H_{20}NO_2S_2$, 286.0935; found: 286.0952.

3. Typical procedure for thioboration

3.1 Typical procedure for the thioboration reaction

A sealed tube was flushed with nitrogen and was charged with substrate (0.2 mmol, 1.0 equiv.), Na_2CO_3 (0.21 mmol, 1.05 equiv.) and 1,2-dichloroethane (2 mL). A solution of BCl_3 (1 M in dichloramethane, 0.24 mL, 1.2 equiv.) was added under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 3 h and was then quenched with water (2 mL). The organic layer was separated. The aqueous layer was extracted with dichloromethane. The organic layers were combined, dried ($MgSO_4$) and concentrated to give a crude product which was purified by flash column chromatography to give the corresponding product.

4.2 General procedure for esterification of boronic acids

To a mixture of pinacol (1.1 equiv.) and NEt_3 (approx. 15 equiv.) was added a solution boronic acid in DCM at 0 °C. After 5 hours' stirring at room temperature, the reaction mixture was concentrated in vacuo. The crude product was purified by flash column chromatography to give pure boronic ester.

4. NMR studies

NMR experiments were carried out to study the interaction between thiol and BCl_3. The following Figure S1 refers to the ^{1}H NMR spectrum of substrate **1g**. After the addition of BCl_3, signal for the S-H was disappeared, and signals for thioboration products appeared (Figure S1).

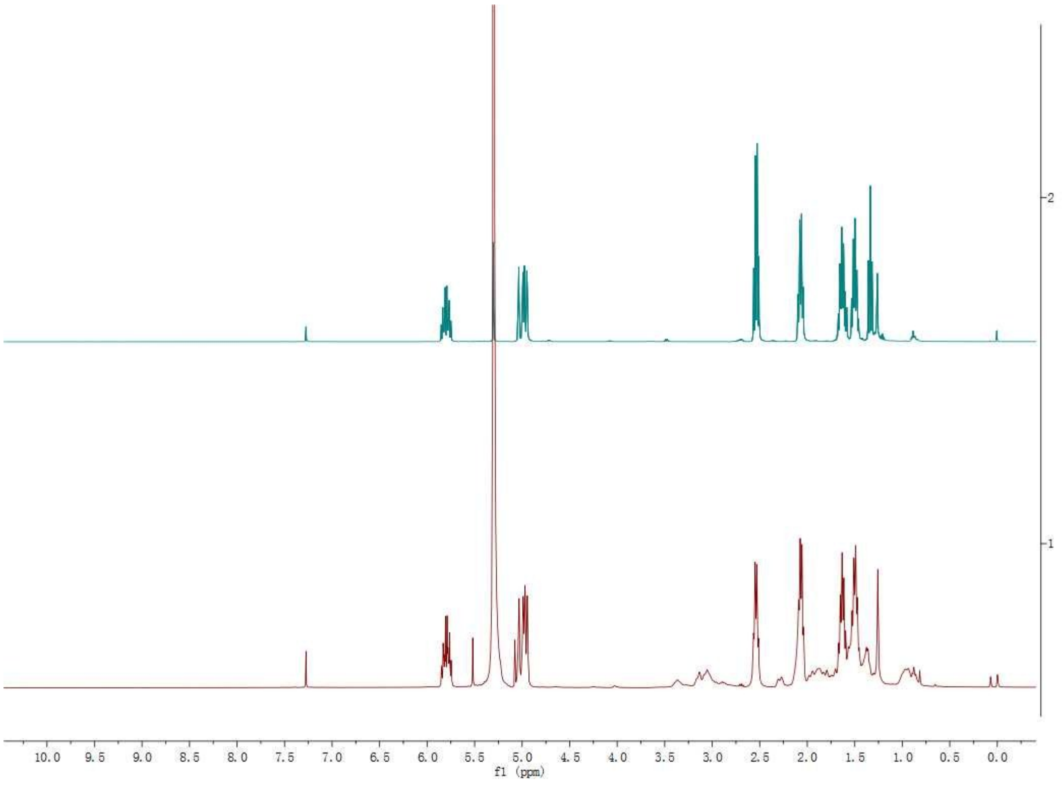


Figure S1. The superimposed ^{1}H NMR spectra of substrate **1g** before (cyan) and after (maroon) the addition of BCl_3

^{11}B NMR was also carried out to study the interaction between BCl_3 and the substrate. The following stacked NMR spectrum refers to the BCl_3 signal changes upon mixing with substrate **1g**. BCl_3 showed a signal at 46.6 ppm. After the addition of BCl_3, the peak at 5.0 ppm took the place of the peak at 46.6 ppm (Figure S2).

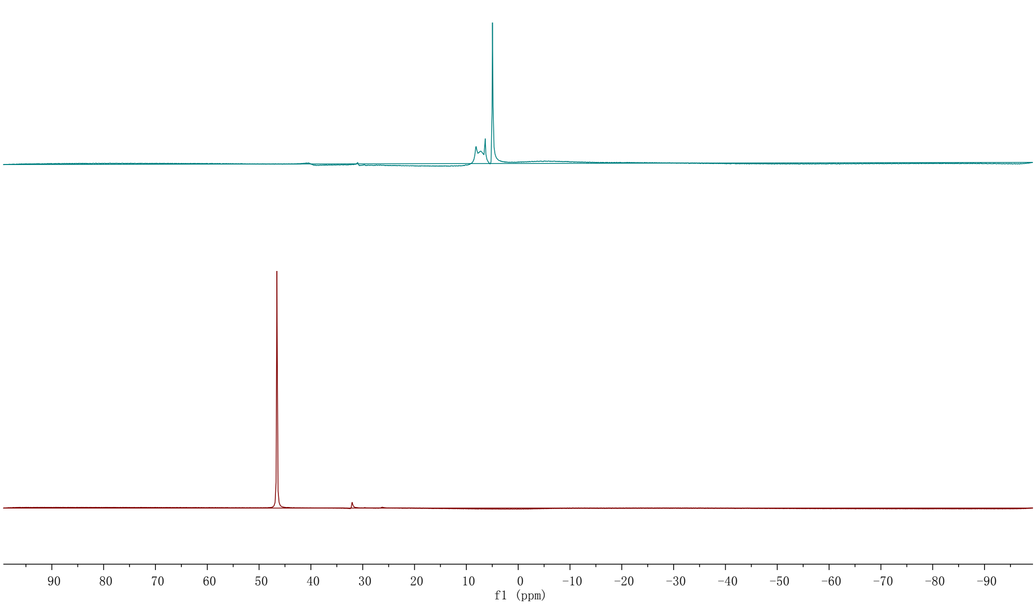
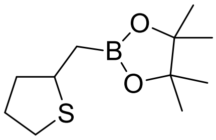


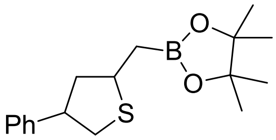
Figure S2. The superimposed ^{11}B NMR spectra of substrate **1g** before (maroon) and after (cyan) the addition of BCl_3

5. Spectral data of products



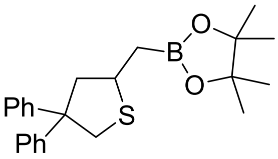
4,4,5,5-tetramethyl-2-((tetrahydrothiophen-2-yl)methyl)-1,3,2-dioxaborolane (**3a**)

Compound **3a** was prepared according to the general procedure and was isolated as a colorless oil (36 mg, 80%) after flash chromatography (EtOAc/Petroleum 2%). ^1H NMR (400 MHz, $CDCl_3$) δ 3.62 – 3.55 (m, 1H), 2.97 – 2.90 (m, 1H), 2.85 – 2.78 (m, 1H), 2.16 – 2.06 (m, 2H), 1.95 – 1.83 (m, 1H), 1.60 – 1.48 (m, 1H), 1.41 – 1.21 (m, 14H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 83.4, 45.2, 39.9, 33.0, 30.5, 25.0, 24.9. ^{11}B NMR (128 MHz, CDCl$_3$) δ 33.0. HRMS–ESI (m/z): [M+H]$^+$ calcd for $C_{11}H_{22}BO_2S$, 229.1434; found: 229.1434.



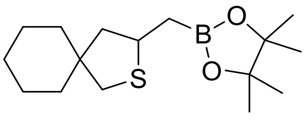
4,4,5,5-tetramethyl-2-((4-phenyltetrahydrothiophen-2-yl)methyl)-1,3,2-dioxaborolane (**3b**)

Compound **3b** was prepared according to the general procedure and was isolated as a yellow oil (30 mg, 50%) after flash chromatography (EtOAc/Petroleum 2%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.27 – 7.16 (m, 5H), 3.73 – 3.60 (m, 1H), 3.34 – 3.18 (m, 1H), 3.06 – 3.00 (m, 1H), 2.97 – 2.89 (m, 1H), 2.49 – 2.36 (m, 1H), 1.79 – 1.65 (m, 1H), 1.25 – 1.22 (m, 2H), 1.17 (s, 12H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 142.19, 128.57, 127.08, 126.77, 83.38, 50.46, 46.83, 44.74, 39.18, 24.87, 24.86. ^{11}B NMR (128 MHz, CDCl$_3$) δ 33.1. HRMS–ESI (m/z): [M+H]$^+$ calcd for $C_{17}H_{26}BO_2S$, 305.1747; found: 305.1735.



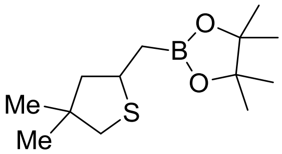
2-((4,4-diphenyltetrahydrothiophen-2-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3c)**

Compound **3c** was prepared according to the general procedure and was isolated as a yellow oil (46 mg, 60%) after flash chromatography (EtOAc/Petroleum 2%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.57 (d, J = 7.4 Hz, 2H), 7.38 (t, J = 7.6 Hz, 2H), 7.30 – 7.26 (m, 2H), 7.21 – 7.12 (m, 3H), 6.84 (s, 1H), 3.32 – 3.22 (m, 1H), 2.91 (dd, J = 16.3, 6.4 Hz, 1H), 2.69 (dd, J = 16.3, 6.6 Hz, 1H), 1.33 – 1.13 (m, 16H). ^{11}B NMR (128 MHz, CDCl$_3$) δ 33.9. HRMS–ESI (m/z): [M+H]$^+$ calcd for $C_{23}H_{30}BO_2S$, 381.2060; found: 381.2060.



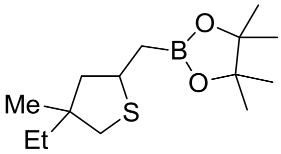
2-(2-thiaspiro[4.5]decan-3-ylmethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3d**)

Compound **3d** was prepared according to the general procedure and was isolated as a colorless oil (46 mg, 78%) after flash chromatography (EtOAc/Petroleum 2%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.67 – 3.51 (m, 1H), 2.70 (q, *J* = 10.5 Hz, 2H), 2.09 (dd, *J* = 12.4, 5.7 Hz, 1H), 1.62 – 1.56 (m, 1H), 1.49 – 1.28 (m, 10H), 1.25 (s, 12H), 1.23 – 1.18 (m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 83.4, 47.7, 42.9, 42.4, 38.2, 34.0, 26.6, 24.9, 24.4, 22.9. ^{11}B NMR (128 MHz, CDCl$_3$) δ 33.0. HRMS–ESI (m/z): [M+H]$^+$ calcd for $C_{16}H_{30}BO_2S$, 297.2060; found: 297.2064.



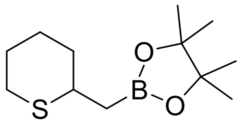
2-((4,4-dimethyltetrahydrothiophen-2-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3e**)

Compound **3e** was prepared according to the general procedure and was isolated as a yellow oil (39 mg, 70%) after flash chromatography (EtOAc/Petroleum 2%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.85 – 2.75 (m, 1H), 2.61 (d, *J* = 13.4 Hz, 1H), 2.18 (dd, *J* = 13.4, 2.0 Hz, 1H), 1.85 – 1.75 (m, 1H), 1.63 – 1.49 (m, 1H), 1.49 – 1.38 (m, 1H), 1.31 – 1.17 (m, 13H), 1.07 (s, 3H), 0.96 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 83.3, 41.7, 39.5, 38.7, 32.9, 31.6, 29.1, 25.0, 24.9, 24.5. ^{11}B NMR (128 MHz, CDCl$_3$) δ 33.1. HRMS–ESI (m/z): [M+H]$^+$ calcd for $C_{13}H_{26}BO_2S$, 257.1747; found: 257.1765.



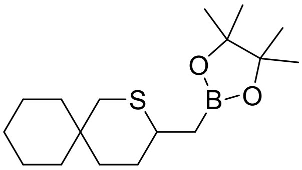
2-((4-ethyl-4-methyltetrahydrothiophen-2-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3f**)

Compound **3f** was prepared according to the general procedure and was isolated as a yellow oil (26 mg, 48%) after flash chromatography (EtOAc/Petroleum 2%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.68 – 3.61 (m, 1H), 3.61 – 3.52 (m, 1H), 2.78 (d, *J* = 10.2 Hz, 1H), 2.71 (d, *J* = 10.5 Hz, 1H), 2.56 (d, *J* = 10.5 Hz, 1H), 2.44 (d, *J* = 10.2 Hz, 1H), 2.02 (dd, *J* = 12.5, 5.6 Hz, 1H), 1.89 (dd, *J* = 12.2, 5.5 Hz, 1H), 1.49 – 1.40 (m, 4H), 1.38 – 1.28 (m, 4H), 1.24 (s, 24H), 1.21 – 1.20 (m, 1H), 1.20 – 1.18 (m, 1H), 1.05 (s, 3H), 1.04 (s, 3H), 0.88 (t, *J* = 7.5 Hz, 3H), 0.84 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 83.3, 51.9, 51.2, 47.6, 47.1, 43.9, 43.8, 43.6, 43.6, 34.4, 30.1, 24.9, 24.4, 22.8, 9.9, 8.8. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.0. HRMS–ESI (m/z): $[M+H]^+$ calcd for $C_{14}H_{28}BO_2S$, 271.1903; found: 271.1904.



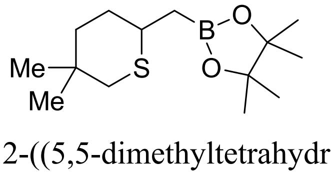
4,4,5,5-tetramethyl-2-((tetrahydro-2H-thiopyran-2-yl)methyl)-1,3,2-dioxaborolane (**3g**)

Compound **3g** was prepared according to the general procedure and was isolated as a coloeless oil (40 mg, 83%) after flash chromatography (EtOAc/Petroleum 2%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.98 – 2.88 (m, 1H), 2.74 – 2.63 (m, 1H), 2.58 – 2.49 (m, 1H), 2.08 – 1.97 (m, 1H), 1.86 (m, 2H), 1.60 – 1.47 (m, 1H), 1.42 – 1.34 (m, 2H), 1.25 (s, 12H), 1.12 – 0.94 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 83.4, 38.8, 36.9, 29.7, 27.0, 26.5, 25.0, 24.9. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.2. HRMS–ESI (m/z): $[M+H]^+$ calcd for $C_{12}H_{24}BO_2S$, 243.1590; found: 243.1592.



2-(2-thiaspiro[5.5]undecan-3-ylmethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3h**)

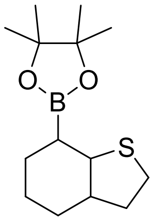
Compound **3h** was prepared according to the general procedure and was isolated as a yellow oil (48 mg, 77%) after flash chromatography (EtOAc/Petroleum 2%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.90 – 2.81 (m, 1H), 2.50 (s, 2H), 1.87 – 1.73 (m, 2H), 1.68 – 1.53 (m, 2H), 1.49 – 1.32 (m, 7H), 1.30 – 1.19 (m, 14H), 1.17 – 0.97 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 83.4, 40.2, 39.2, 32.0, 32.0, 31.0, 26.9, 25.0, 24.9, 21.7, 21.4. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.1. HRMS–ESI (m/z): $[M+H]^+$ calcd for $C_{17}H_{32}BO_2S$, 311.2216; found: 311.2216.



2-((5,5-dimethyltetrahydro-2H-thiopyran-2-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-

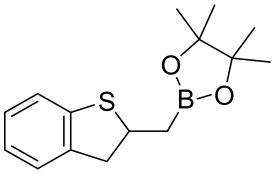
dioxaborolane (**3i**)

Compound **3i** was prepared according to the general procedure and was isolated as a yellow oil (33 mg, 62%) after flash chromatography (EtOAc/Petroleum 2%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.87 – 2.75 (m, 1H), 2.62 (d, *J* = 13.4 Hz, 1H), 2.18 (dd, *J* = 13.4, 2.1 Hz, 1H), 1.85 – 1.77 (m, 1H), 1.63 – 1.57 (m, 1H), 1.49 – 1.40 (m, 1H), 1.32 – 1.29 (m, 1H), 1.25 (s, 12H), 1.07 (s, 3H), 1.12 – 1.00 (m, 2H), 0.96 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 83.4, 41.8, 39.6, 38.7, 33.0, 31.6, 29.8, 29.1, 25.0, 24.9, 24.5. ^{11}B NMR (128 MHz, CDCl$_3$) δ 33.3. HRMS–ESI (m/z): [M+H]$^+$ calcd for $C_{14}H_{28}BO_2S$, 271.1903; found: 271.1906.



4,4,5,5-tetramethyl-2-(octahydrobenzo[b]thiophen-7-yl)-1,3,2-dioxaborolane (**3j**)

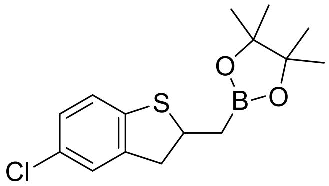
Compound **3j** was prepared according to the general procedure and was isolated as a yellow oil (43 mg, 80%) after flash chromatography (EtOAc/Petroleum 2%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.53 – 3.42 (m, 1H), 2.99 – 2.88 (m, 1H), 2.87 – 2.77 (m, 1H), 2.23 (tt, *J* = 10.1, 5.0 Hz, 1H), 2.03 – 1.82 (m, 2H), 1.71 (dd, *J* = 14.7, 5.8 Hz, 2H), 1.57 (m, 1H), 1.48 – 1.31 (m, 4H), 1.25 (s, 6H), 1.24 (s, 6H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 83.3, 48.9, 42.7, 32.9, 30.1, 26.8, 25.6, 25.0, 24.7, 22.5. ^{11}B NMR (128 MHz, CDCl$_3$) δ 33.6. HRMS–ESI (m/z): [M+H]$^+$ calcd for $C_{14}H_{26}BO_2S$, 269.1747; found: 269.1742.



2-((2,3-dihydrobenzo[b]thiophen-2-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6a**)

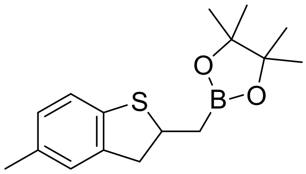
Compound **6a** was prepared according to the general procedure and was isolated as a yellow oil (28 mg, 50%) after flash chromatography (EtOAc/Petroleum 2%). ^{1}H NMR

(400 MHz, $CDCl_3$) δ 7.16 (t, *J* = 6.8 Hz, 2H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.99 (t, *J* = 7.3 Hz, 1H), 4.19 – 4.06 (m, 1H), 3.43 (dd, *J* = 15.2, 7.3 Hz, 1H), 2.99 (dd, *J* = 15.3, 6.8 Hz, 1H), 1.44 – 1.33 (m, 2H), 1.27 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 139.8, 127.3, 124.7, 124.0, 122.3, 83.6, 47.3, 44.8, 25.0, 24.9. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.0. HRMS–ESI (m/z): $[M+H]^+$ calcd for $C_{15}H_{22}BO_2S$, 277.1434; found: 277.1434.



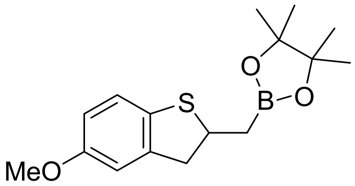
2-((5-chloro-2,3-dihydrobenzo[b]thiophen-2-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6b**)

Compound **6b** was prepared according to the general procedure and was isolated as a yellow oil (32 mg, 52%) after flash chromatography (EtOAc/Petroleum 2%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.14 – 7.10 (m, 1H), 7.08 – 7.04 (m, 2H), 4.23 – 4.07 (m, 1H), 3.40 (dd, *J* = 16.1, 7.3 Hz, 1H), 2.96 (dd, *J* = 15.8, 6.6 Hz, 1H), 1.53 – 1.32 (m, 2H), 1.27 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 140.2, 129.6, 127.3, 124.9, 123.1, 83.7, 47.9, 44.6, 25.0, 24.9. ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.9. HRMS–ESI (m/z): $[M+H]^+$ calcd for $C_{15}H_{21}BClO_2S$, 311.1044; found: 311.1041.



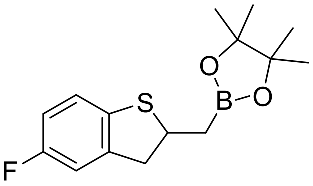
4,4,5,5-tetramethyl-2-((5-methyl-2,3-dihydrobenzo[b]thiophen-2-yl)methyl)-1,3,2-dioxaborolane (**6c**)

Compound **6c** was prepared according to the general procedure and was isolated as a yellow oil (27 mg, 46%) after flash chromatography (EtOAc/Petroleum 2%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, *J* = 7.8 Hz, 1H), 6.96 (s, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 4.09 (p, *J* = 7.4 Hz, 1H), 3.36 (dd, *J* = 15.3, 7.3 Hz, 1H), 2.93 (dd, *J* = 15.3, 6.9 Hz, 1H), 2.26 (s, 3H), 1.36 (m, 2H), 1.25 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.9, 138.0, 133.7, 128.0, 125.6, 122.0, 83.5, 47.5, 44.8, 25.0, 24.9, 21.1. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.0. HRMS–ESI (m/z): $[M+H]^+$ calcd for $C_{16}H_{24}BO_2S$, 291.1590; found: 291.1590.



2-((5-methoxy-2,3-dihydrobenzo[b]thiophen-2-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6d**)

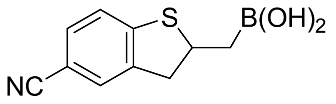
Compound **6e** was prepared according to the general procedure and was isolated as a yellow oil (27 mg, 45%) after flash chromatography (EtOAc/Petroleum 10%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (d, *J* = 8.4 Hz, 1H), 6.76 (d, *J* = 2.3 Hz, 1H), 6.68 (dd, *J* = 8.4, 2.5 Hz, 1H), 4.16 – 4.06 (m, 1H), 3.76 (s, 3H), 3.38 (dd, *J* = 15.4, 7.2 Hz, 1H), 2.95 (dd, *J* = 15.4, 7.0 Hz, 1H), 1.43 – 1.33 (m, 2H), 1.27 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 141.2, 128.8, 122.5, 112.8, 111.3, 83.4, 55.5, 47.7, 45.1 24.8, 24.7. ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.9. HRMS–ESI (m/z): $[M+H]^+$ calcd for $C_{16}H_{24}BO_3S$, 307.1539; found: 307.1547.



2-((5-fluoro-2,3-dihydrobenzo[b]thiophen-2-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6e**)

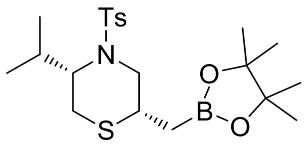
Compound **6e** was prepared according to the general procedure and was isolated as a yellow oil (35 mg, 60%) after flash chromatography (EtOAc/Petroleum 10%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 – 7.03 (m, 1H), 6.90 – 6.85 (m, 1H), 6.83 – 6.77 (m, 1H), 4.20 – 4.08 (m, 1H), 3.40 (dd, *J* = 15.5, 7.3 Hz, 1H), 2.96 (dd, *J* = 15.5, 6.9 Hz, 1H), 1.49 – 1.32 (m, 2H), 1.27 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 159.6, 141.8, 141.8, 136.5, 122.8, 122.7, 114.2, 114.0, 112.4, 112.2, 83.7, 48.1, 44.9, 25.0, 24.9. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.0. HRMS–ESI (m/z): $[M+H]^+$ calcd for

$C_{15}H_{21}BFO_2S$, 295.1339; found: 295.1353.



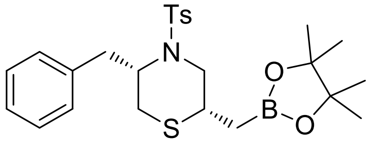
((5-cyano-2,3-dihydrobenzo[b]thiophen-2-yl)methyl)boronic acid (**5f**)

Compound **5f** was prepared according to the general procedure and was isolated as a yellow oil (31 mg, 70%) after flash chromatography (EtOAc/Petroleum 20% - EtOAc). ^{1}H NMR (400 MHz, MeOD) δ 7.48 (s, 1H), 7.43 (d, *J* = 8.1 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 4.19 – 4.06 (m, 1H), 3.49 (dd, *J* = 15.9, 7.6 Hz, 1H), 3.03 (dd, *J* = 15.9, 6.2 Hz, 1H), 1.41 – 1.34 (m, 2H). ^{13}C NMR (100 MHz, MeOD) δ 149.5, 141.3, 130.9, 127.2, 122.1, 118.9, 106.5, 47.7, 43.6. ^{11}B NMR (128 MHz, MeOD) δ 30.5. HRMS–ESI (m/z): $[M+H]^+$ calcd for $C_{10}H_{11}BNO_2S$, 220.0604; found: 220.0624.



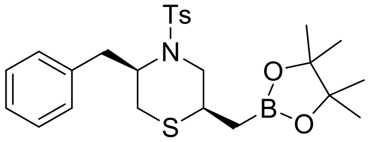
(2*S*,5*S*)-5-isopropyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-4-tosylthiomorpholine (**9a**)

Compound **9a** was prepared according to the general procedure and was isolated as a yellow oil (77 mg, 42%) after flash chromatography (EtOAc/Petroleum 10%). $[\alpha]^{25}_{D}$ =-24.4, (*c* 2.7, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 4.09 (dd, *J* = 14.7, 2.6 Hz, 1H), 3.63 – 3.54 (m, 1H), 2.85 – 2.75 (m, 1H), 2.71 – 2.62 (m, 1H), 2.59 (dd, *J* = 14.1, 3.5 Hz, 1H), 2.52 – 2.41 (m, 1H), 2.38 (dd, *J* = 14.2, 2.0 Hz, 1H), 2.34 (s, 3H), 1.22 (s, 12H), 1.19 – 1.17 (m, 1H), 0.84 (d, *J* = 6.8 Hz, 3H), 0.81 (d, *J* = 6.7 Hz, 3H), 0.79 – 0.73 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 139.1, 129.7, 127.1, 83.7, 57.4, 48.4, 34.7, 29.3, 25.0, 24.8, 24.8, 21.5, 19.6, 19.4. ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.9. HRMS–ESI (m/z): $[M+H]^+$ calcd for $C_{21}H_{35}BNO_4S_2$, 440.2101; found: 440.2101.



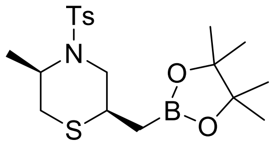
(2*S*,5*S*)-5-benzyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-4-tosylthiomorpholine (**9b**)

Compound **9b** was prepared according to the general procedure and was isolated as a yellow oil (66 mg, 68%) after flash chromatography (EtOAc/Petroleum 10%). $[\alpha]_D^{25}$ =54.2 , (*c* 0.5, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.2 Hz, 2H), 7.33 – 7.14 (m, 7H), 4.43 – 4.35 (m, 1H), 4.10 (dd, *J* = 13.9, 2.5 Hz, 1H), 3.37 (dd, *J* = 13.2, 9.9 Hz, 1H), 3.06 (dd, *J* = 13.8, 11.3 Hz, 1H), 3.00 – 2.88 (m, 1H), 2.86 – 2.74 (m, 2H), 2.40 (s, 3H), 2.26 (dd, *J* = 13.9, 2.0 Hz, 1H), 1.29 (s, 12H), 1.28 – 1.26 (m, 1H) 1.08 – 0.94 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 138.3, 138.1, 129.7, 129.4, 128.7, 127.1, 126.6, 83.7, 52.4, 48.2, 36.3, 34.8, 30.4, 25.0, 24.8, 21.5. ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.9. HRMS–ESI (m/z): $[M+H]^+$ calcd for $C_{25}H_{35}BNO_4S_2$, 488.2101; found: 488.2103.



(2*R*,5*R*)-5-benzyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-4-tosylthiomorpholine (**9c**)

Compound **9c** was prepared according to the general procedure and was isolated as a yellow oil (73 mg, 75%) after flash chromatography (EtOAc/Petroleum 10%). $[\alpha]_D^{25}$ =-43.2 , (*c* 0.2, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.2 Hz, 2H), 7.28 – 7.22 (m, 5H), 7.18 (d, *J* = 6.8 Hz, 2H), 4.43 – 4.34 (m, 1H), 4.09 (dd, *J* = 13.8, 2.6 Hz, 1H), 3.38 (dd, *J* = 13.2, 10.0 Hz, 1H), 3.05 (dd, *J* = 13.8, 11.3 Hz, 1H), 2.99 – 2.89 (m, 1H), 2.85 – 2.72 (m, 2H), 2.41 (s, 3H), 2.26 (dd, *J* = 13.9, 2.1 Hz, 1H), 1.30 (s, 12H), 1.28 – 1.27 (m, 1H), 1.01 – 0.98 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 138.3, 138.2, 129.9, 129.5, 128.8, 127.2, 126.7, 83.9, 52.1, 48.3, 36.4, 34.8, 30.5, 25.1, 24.9, 21.6. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.0. HRMS–ESI (m/z): $[M+H]^+$ calcd for $C_{25}H_{35}BNO_4S_2$, 488.2101; found: 488.2102.

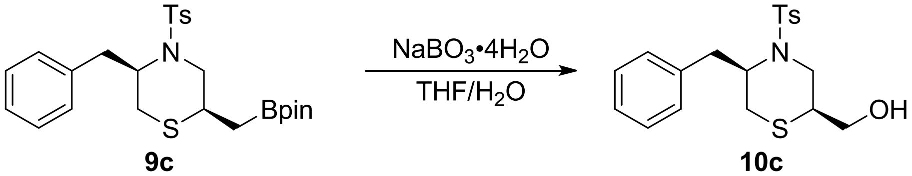


(2*R*,5*R*)-5-methyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-4-

tosylthiomorpholine (**9d**)

Compound **9d** was prepared according to the general procedure and was isolated as a yellow oil (49 mg, 60%) after flash chromatography (EtOAc/Petroleum 2%). $[\alpha]_{D}^{25}$ =-96.8, (*c* 1.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 4.42 – 4.31 (m, 1H), 4.02 (d, *J* = 11.3 Hz, 1H), 3.01 – 2.79 (m, 3H), 2.40 (s, 3H), 2.20 (dd, *J* = 13.6, 2.3 Hz, 1H), 1.25 (s, 12H), 1.20 (d, *J* = 6.7 Hz, 3H), 0.93 – 0.86 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 138.4, 129.8, 127.0, 83.7, 47.5, 46.4, 36.7, 34.3, 29.7, 25.0, 24.7, 21.5, 14.9. ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.9. HRMS–ESI (m/z): $[M+H]^+$ calcd for $C_{19}H_{31}BNO_4S_2$, 412.1788; found: 412.1786.

6. Derivatization of thioboration products

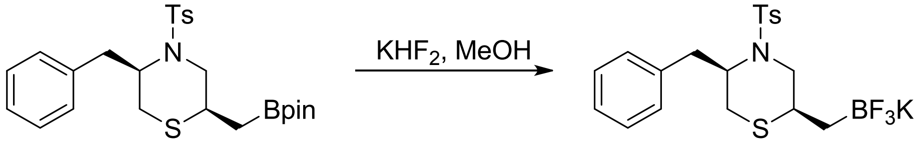


9c **10c**

((2*S*,5*R*)-5-benzyl-4-tosylthiomorpholin-2-yl)methanol (**10c**)

The titled product was prepared according to a reported procedure.[9] To the solution of **9c** (60 mg, 0.12 mmol) in THF (1.5 mL) was added water (0.75 mL) and $NaBO_3 \cdot 4H_2O$ (256 mg, 2.2 mmol). The resulting mixture was stirred at ambient temperature for 5 h. The resulting mixture was quenched with sat. aq. $Na_2S_2O_3$. The mixture was extracted with EtOAc, and the combined organic layer was dried over sodium sulfate and concentrated in vacuo. The crude product was purified by silica gel column chromatography with petroleum/ethyl acetate (EtOAc/Petroleum 20%) as an eluent to give ((2S,5R)-5-benzyl-4-tosylthiomorpholin-2-yl)methanol (40 mg, 86%) as a colorless oil. $[\alpha]_{D}^{25}$ =-23.0, (*c* 0.7, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.30 – 7.21 (m, 5H), 7.15 (d, *J* = 6.8 Hz, 2H), 4.47 – 4.39 (m, 1H), 4.12 (dd, *J* = 13.8, 2.6 Hz, 1H), 3.75 – 3.62 (m, 2H), 3.29 (dd, *J* = 13.2, 9.9 Hz, 1H), 3.16 (dd, *J* = 13.7, 11.4 Hz, 1H), 3.11 – 3.01 (m, 1H), 2.91 (dd, *J* = 13.8, 3.7 Hz, 1H), 2.73 (dd, *J* = 13.2, 5.2 Hz, 1H), 2.44 – 2.38 (m, 1H), 2.41 (s, 3H), 2.14 (s, 1H). ^{13}C

NMR (100 MHz, CDCl$_3$) δ 143.6, 137.9, 137.7, 130.0, 129.4, 128.8, 127.1, 126.8, 63.8, 53.2, 44.2, 42.5, 34.6, 29.8, 21.6. HRMS–ESI (m/z): [M+H]$^+$ calcd for $C_{19}H_{24}NO_3S_2$, 378.1198; found: 378.1219.



9c **11c**

Potassium (((2*R*,5*R*)-5-benzyl-4-tosylthiomorpholin-2-yl)methyl)trifluoroborate (**11c**) The titled product was prepared according to a reported procedure.[10] To a solution of boronic ester **9c** (49 mg, 0.1 mmol) in methanol (0.5 mL) was added KHF$_2$ (0.02 mL, 4.5 M saturated aqueous solution, 4.5 mmol, 1.0 equiv) dropwise. The reaction mixture stirred at room temperature for 30 min. The solvent was then removed under vacuum and the solid residue the solid residue was triturated with dry acetone (0.5 mL). The liquid phase was carefully decanted, and the residual inorganic salts were washed with additional acetone (3×0.2mL). The combined solution was concentrated in vacuo to give white solids. The solids was washed with ether (3×0.5 mL) to remove pinacol and dried under vacuum, affording the desired product **11c** as a white solid (40 mg, 85%). $[\alpha]^{25}_{D}$ =-52.8, (*c* 0.3, DMSO). ^{1}H NMR (400 MHz, DMSO) δ 7.56 (d, *J* = 7.8 Hz, 2H), 7.36 – 7.18 (m, 5H), 7.14 (d, *J* = 7.0 Hz, 2H), 4.36 – 4.12 (m, 2H), 3.17 (dd, *J* = 12.9, 8.8 Hz, 1H), 2.85 – 2.70 (m, 2H), 2.66 – 2.47 (m, 3H), 2.37 (s, 3H), 2.11 (d, *J* = 13.5 Hz, 1H), 0.15 – 0.02 (m, 1H). ^{13}C NMR (100 MHz, DMSO) δ 143.1, 138.8, 138.7, 130.2, 129.6, 128.9, 127.2, 126.8, 52.4, 48.7, 38.1, 34.7, 30.6, 21.4. ^{19}F NMR (376 MHz, DMSO) δ -135.0. ^{11}B NMR (128 MHz, DMSO) δ 4.5. HRMS–ESI (m/z): [M−K]$^-$calcd for $C_{19}H_{22}BF_3NO_2S_2$, 428.1143; found: 428.1136.

7. References

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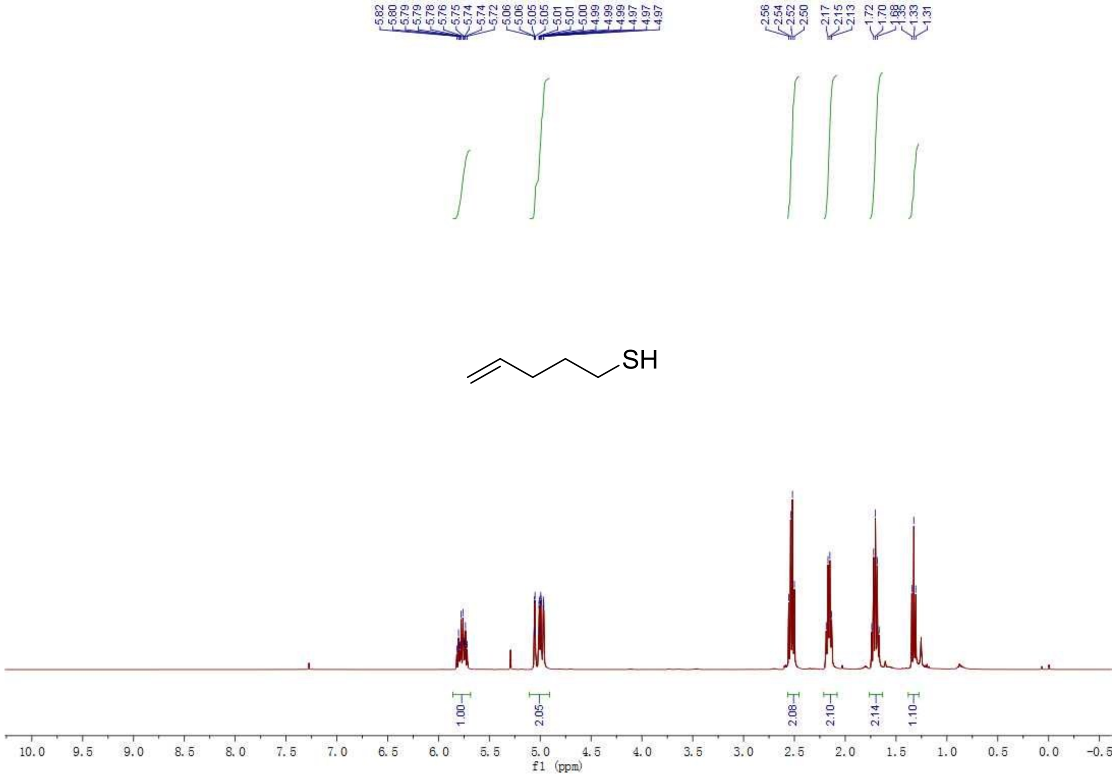
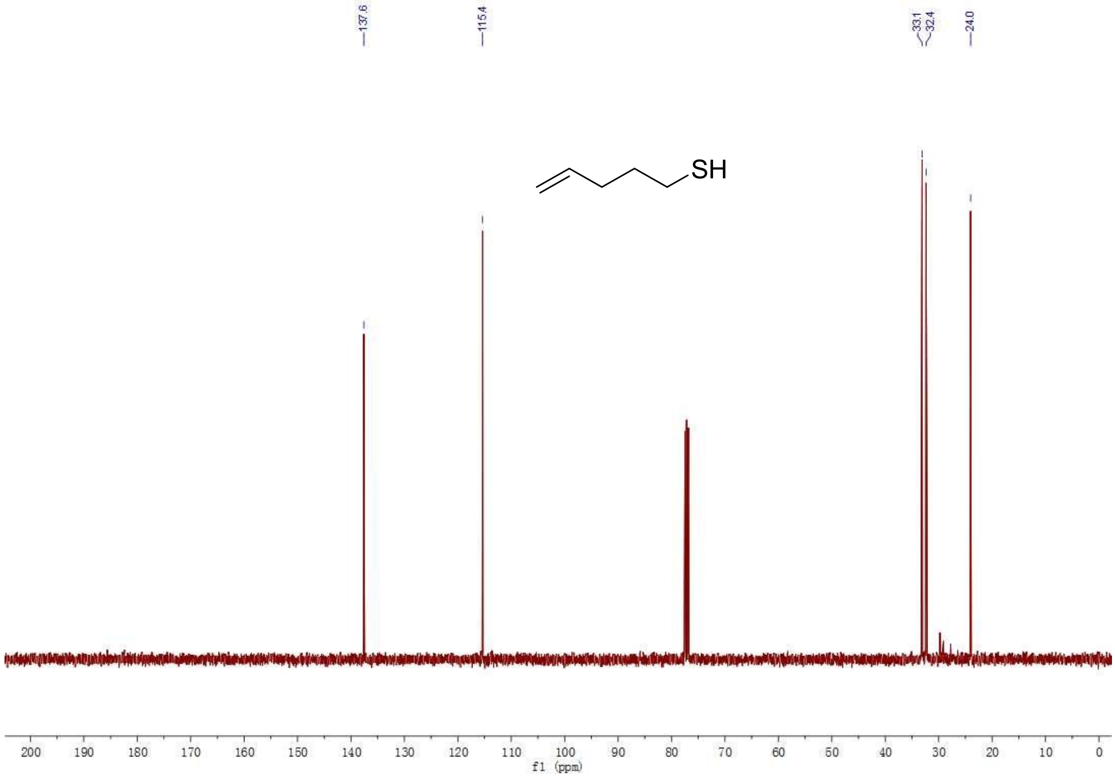
8. Copies of NMR Spectra

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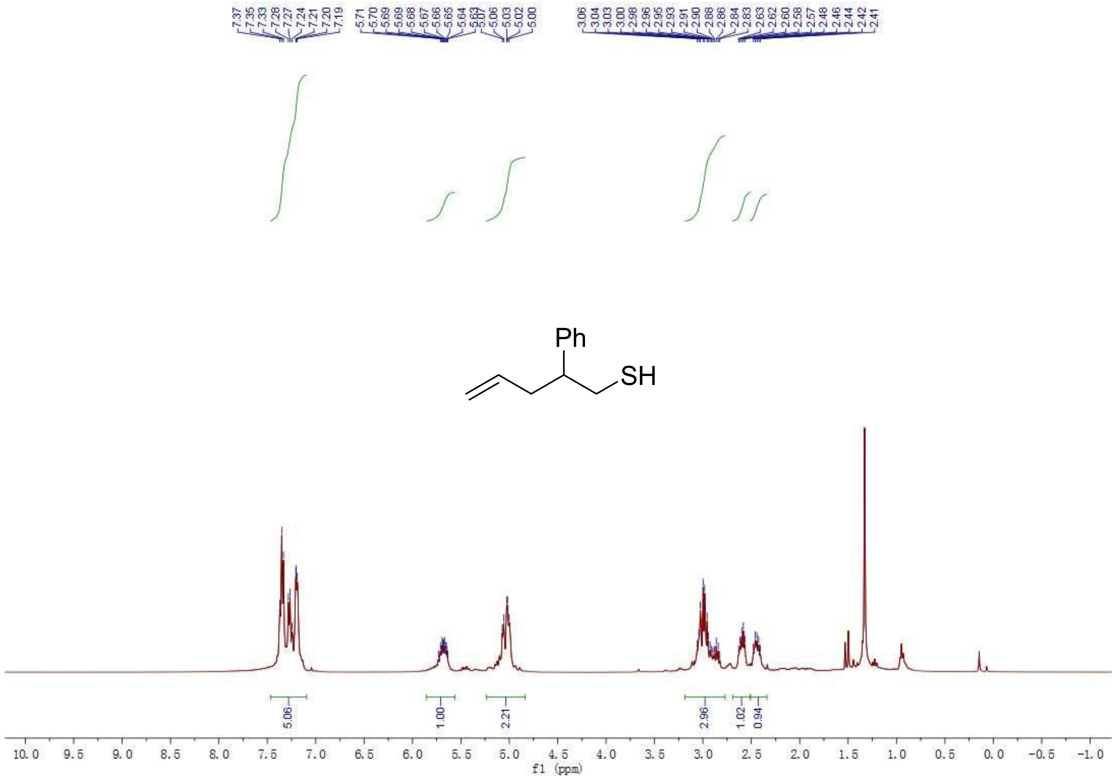
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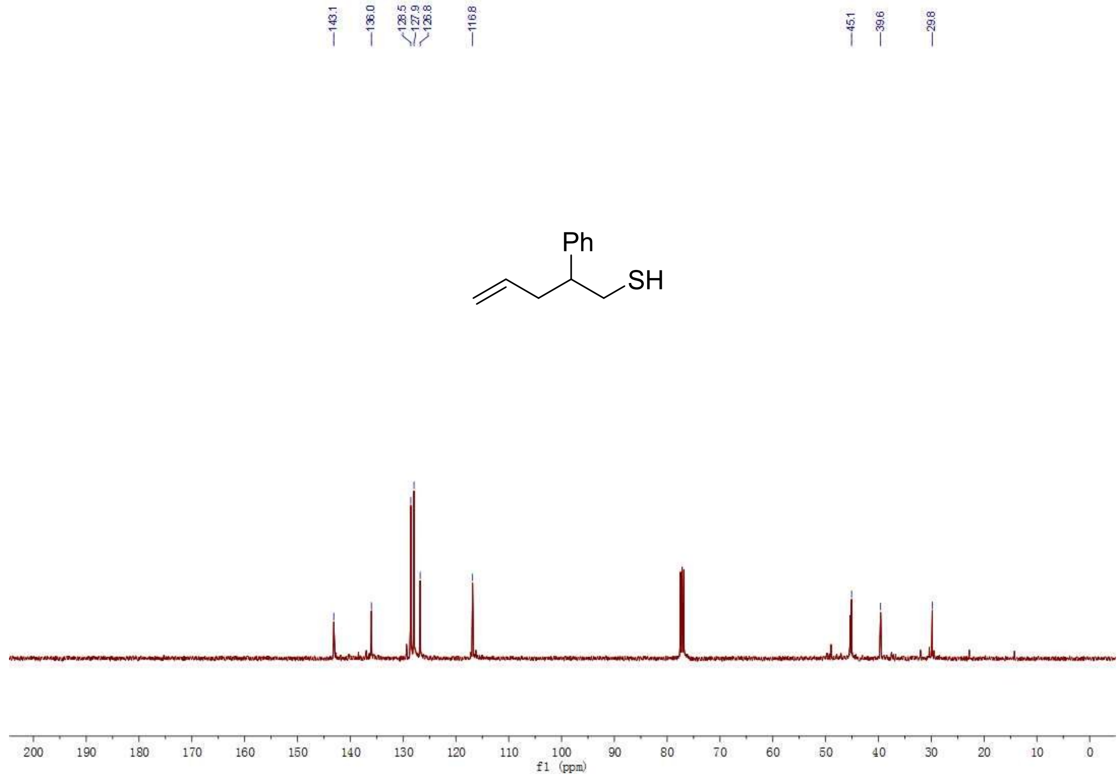
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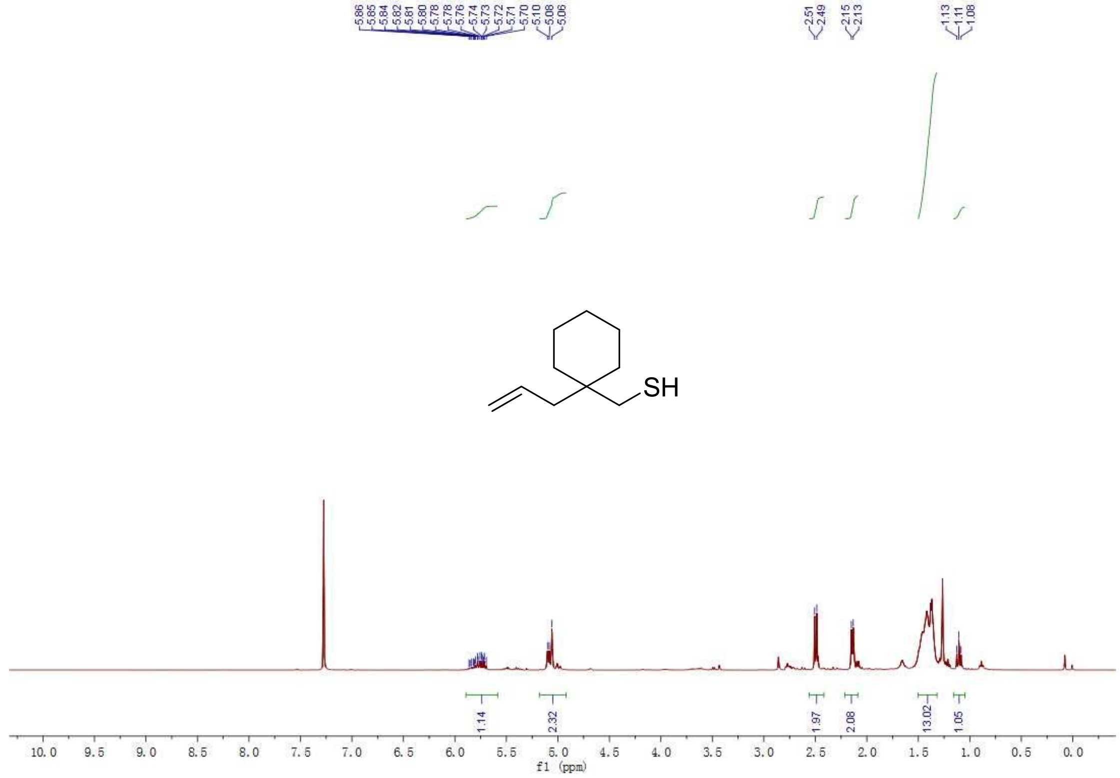
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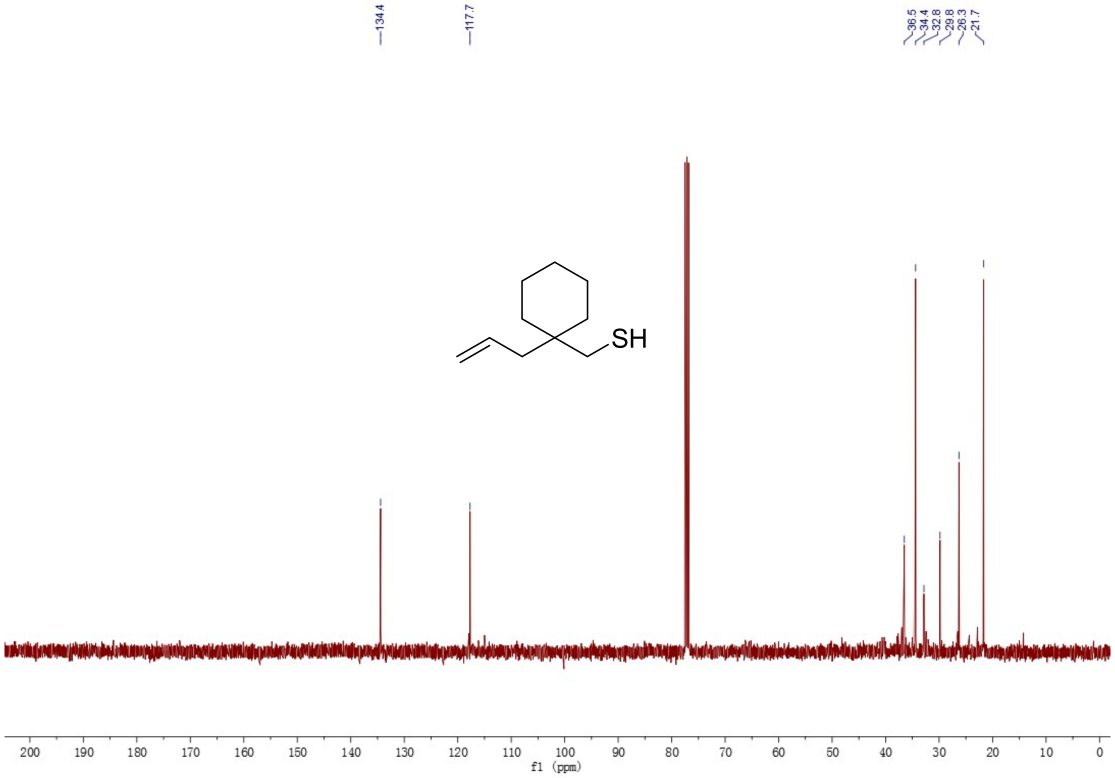
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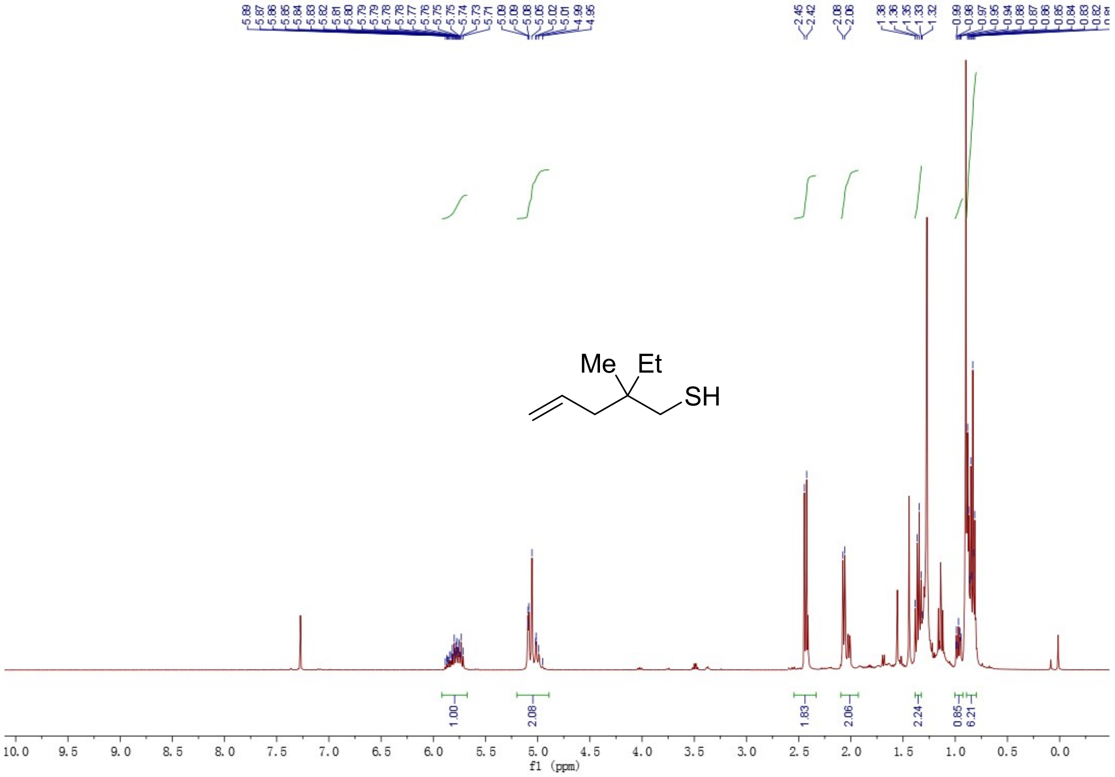
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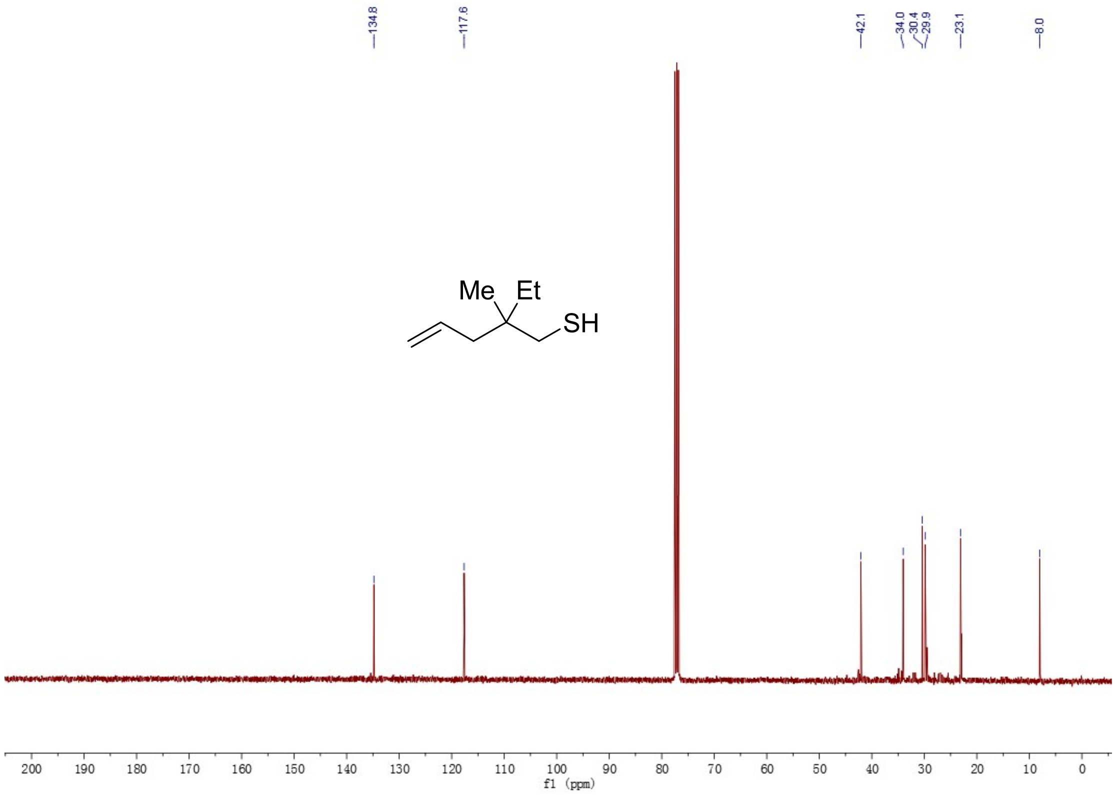
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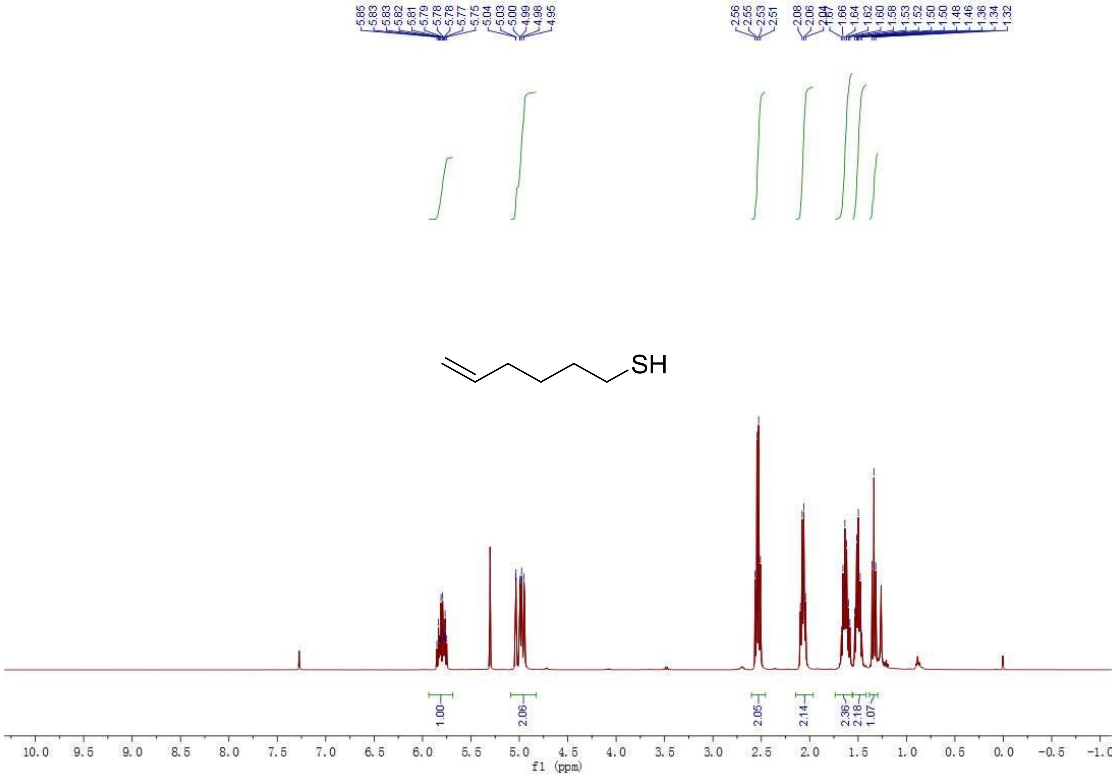
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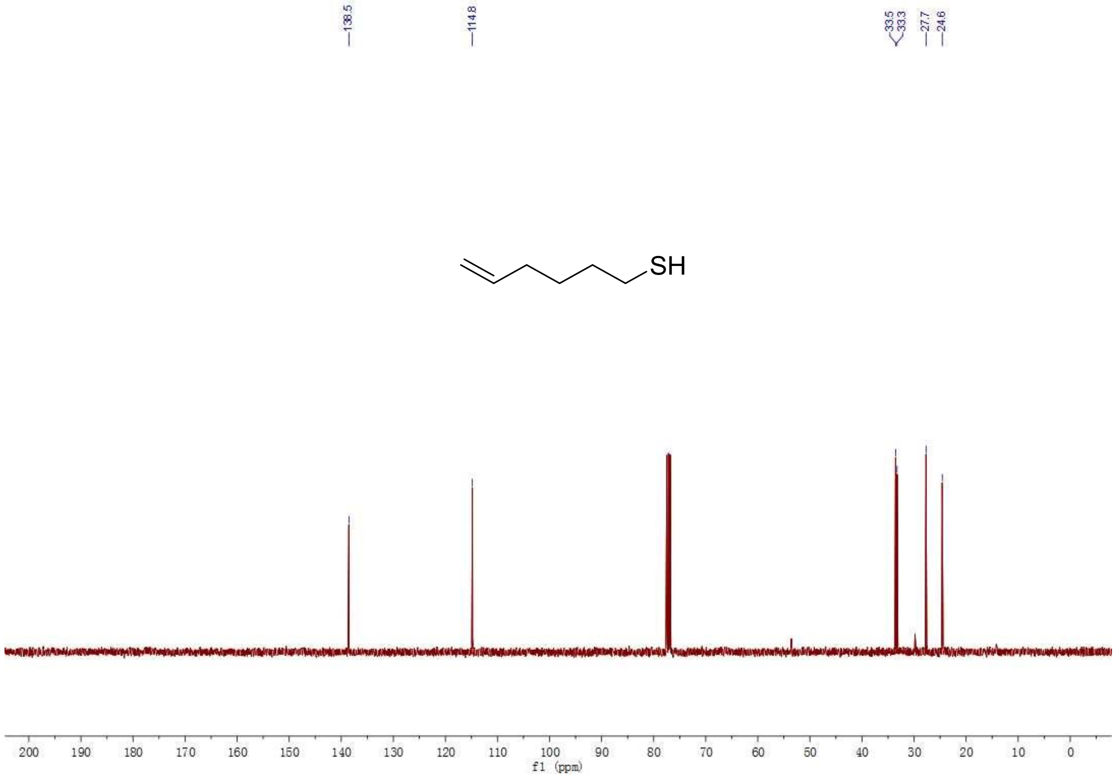
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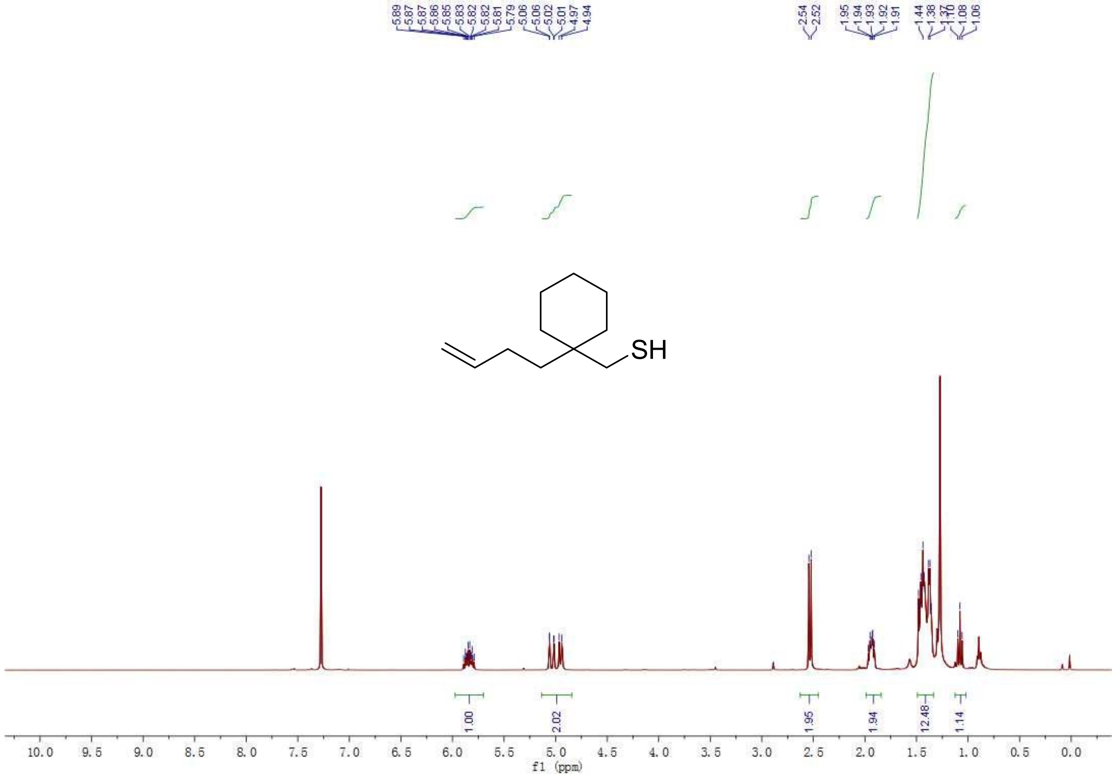
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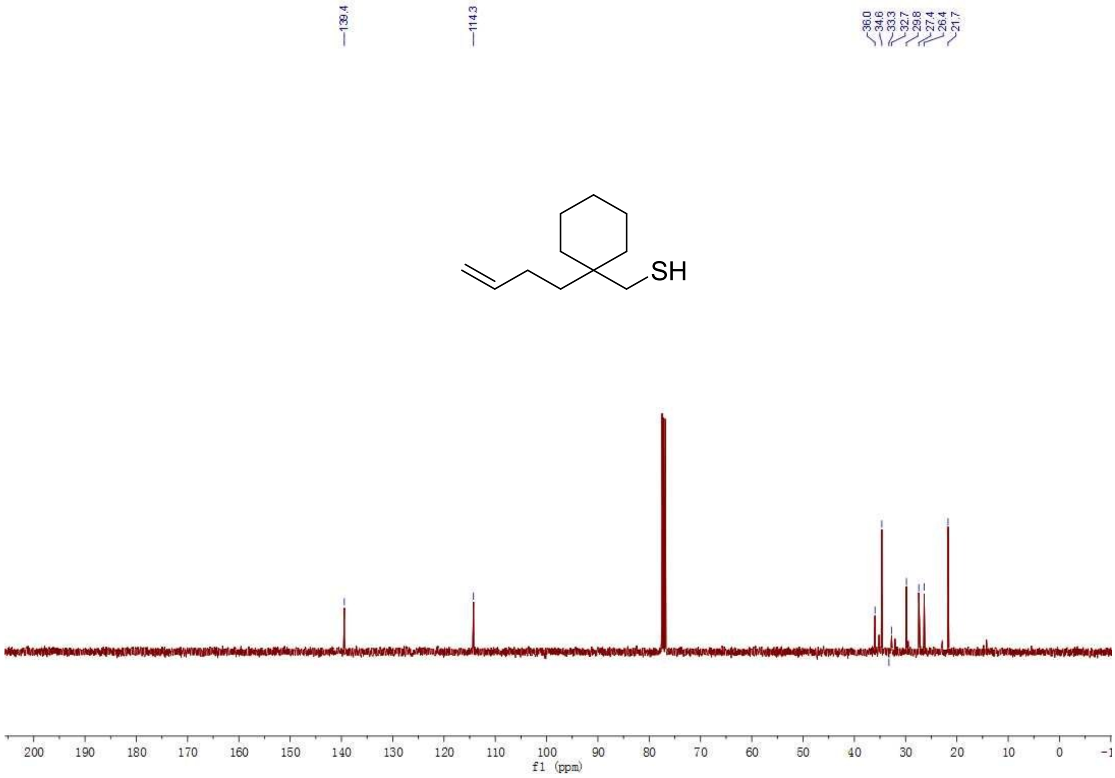
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180
170
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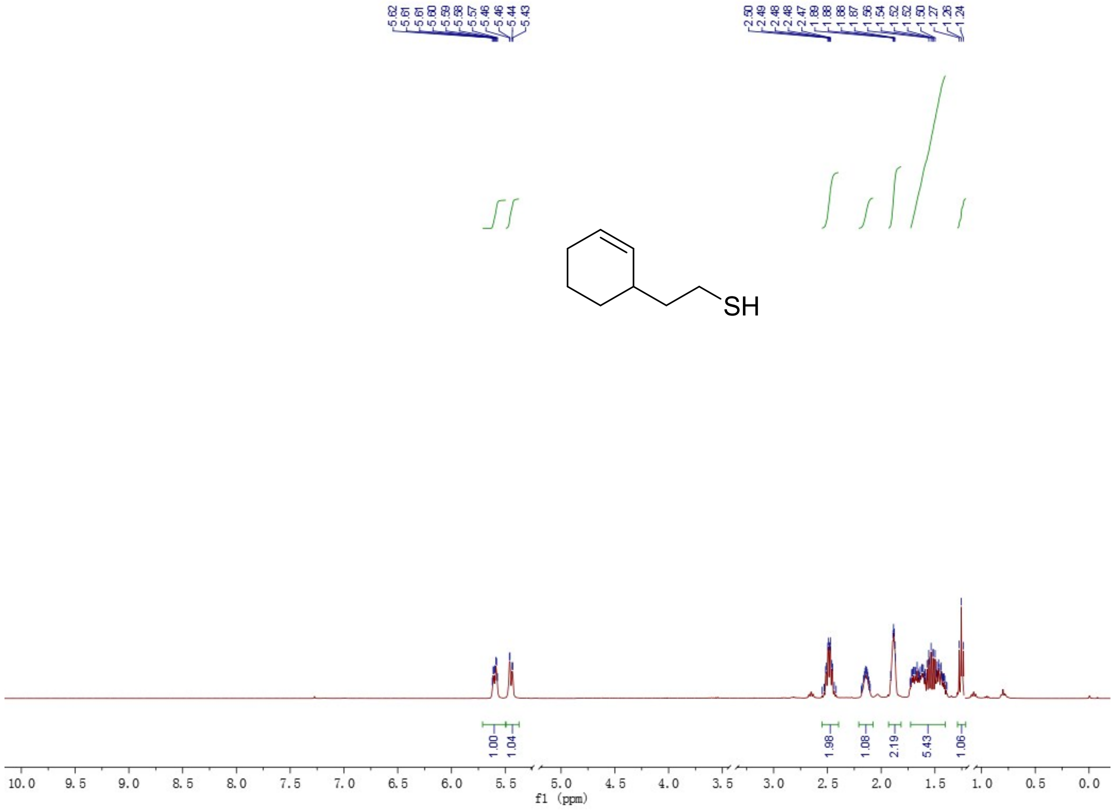
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2.48
2.47
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1.08
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8.0
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7.0
6.5
6.0
5.5
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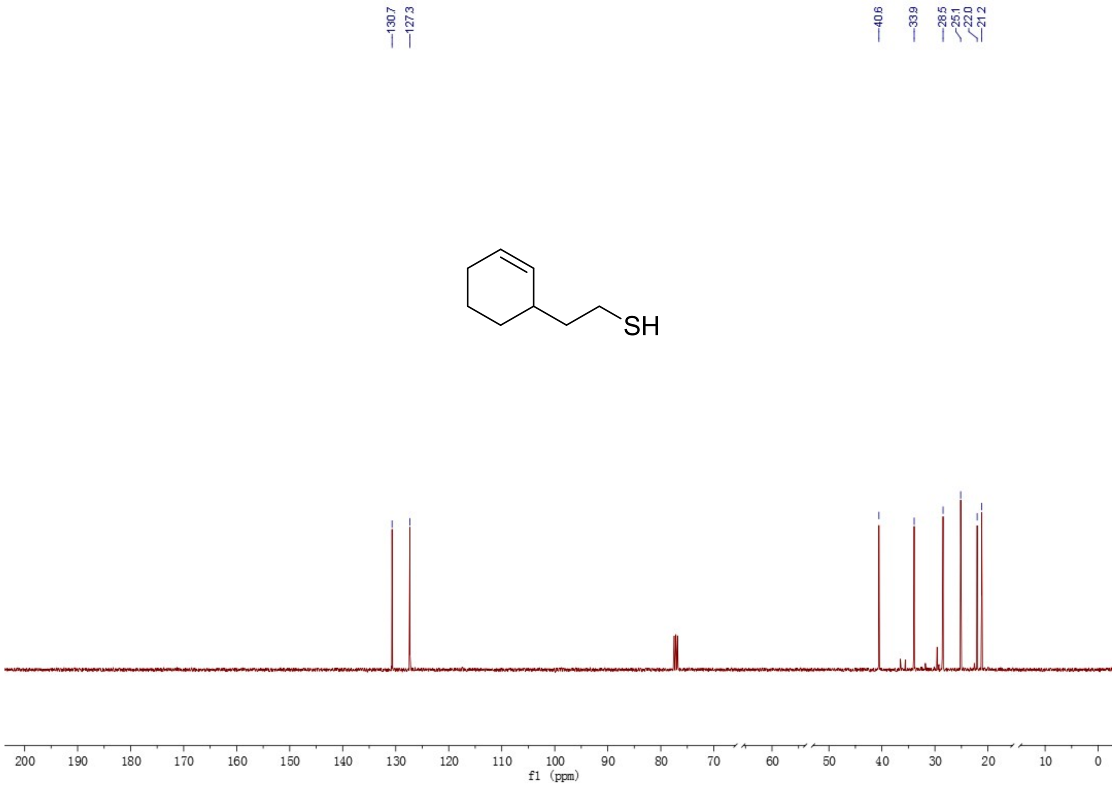
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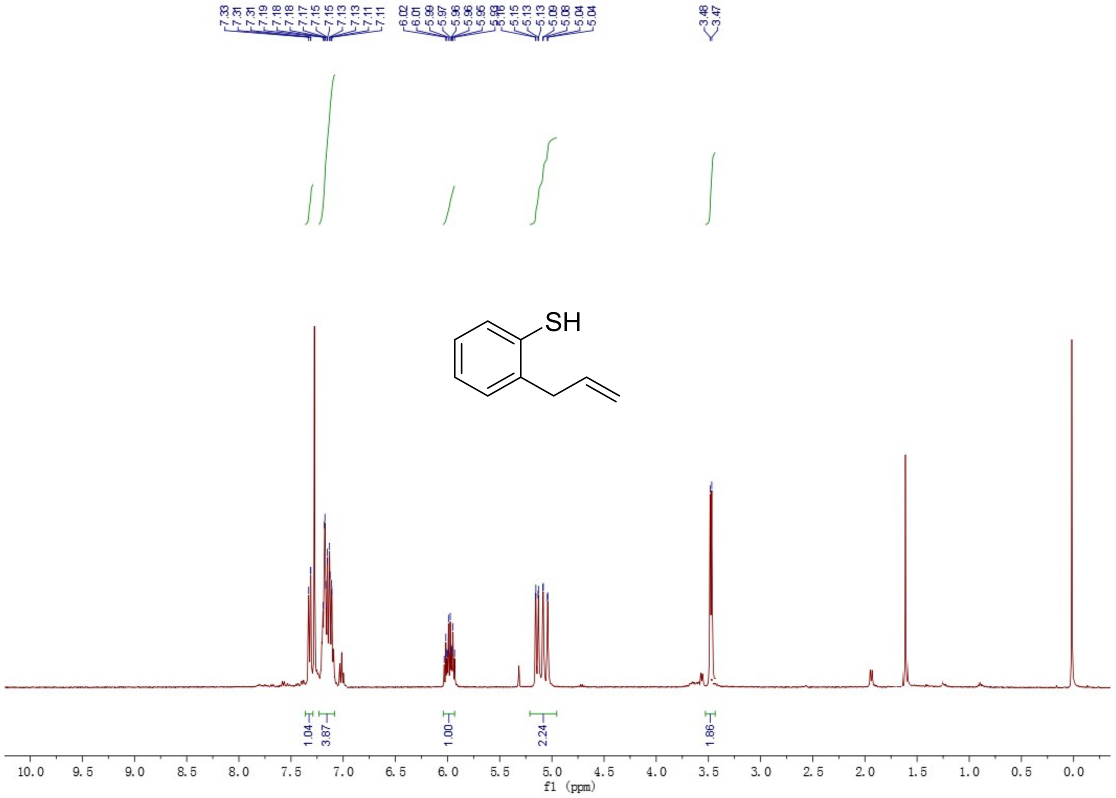
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7.11
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6.01
5.99
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5.96
5.96
5.95
5.93
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5.15
5.13
5.13
5.09
5.08
5.04
5.04
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SH
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9.0
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8.0
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7.0
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6.0
5.5
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0.0
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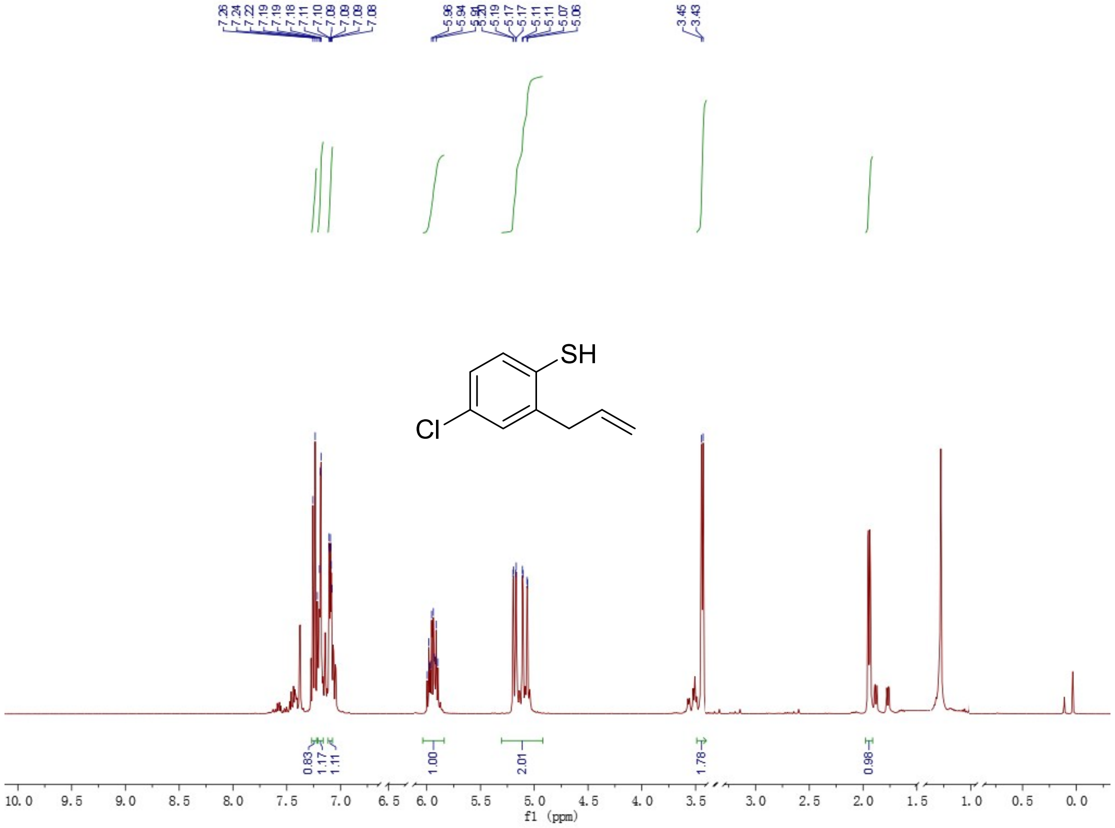
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5.91
5.20
5.19
5.17
5.17
5.11
5.11
5.07
5.06
3.45
3.43
SH
Cl
0.83
1.17
1.11
1.00
2.01
1.78
0.98
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9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
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2.5
2.0
1.5
1.0
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0.0
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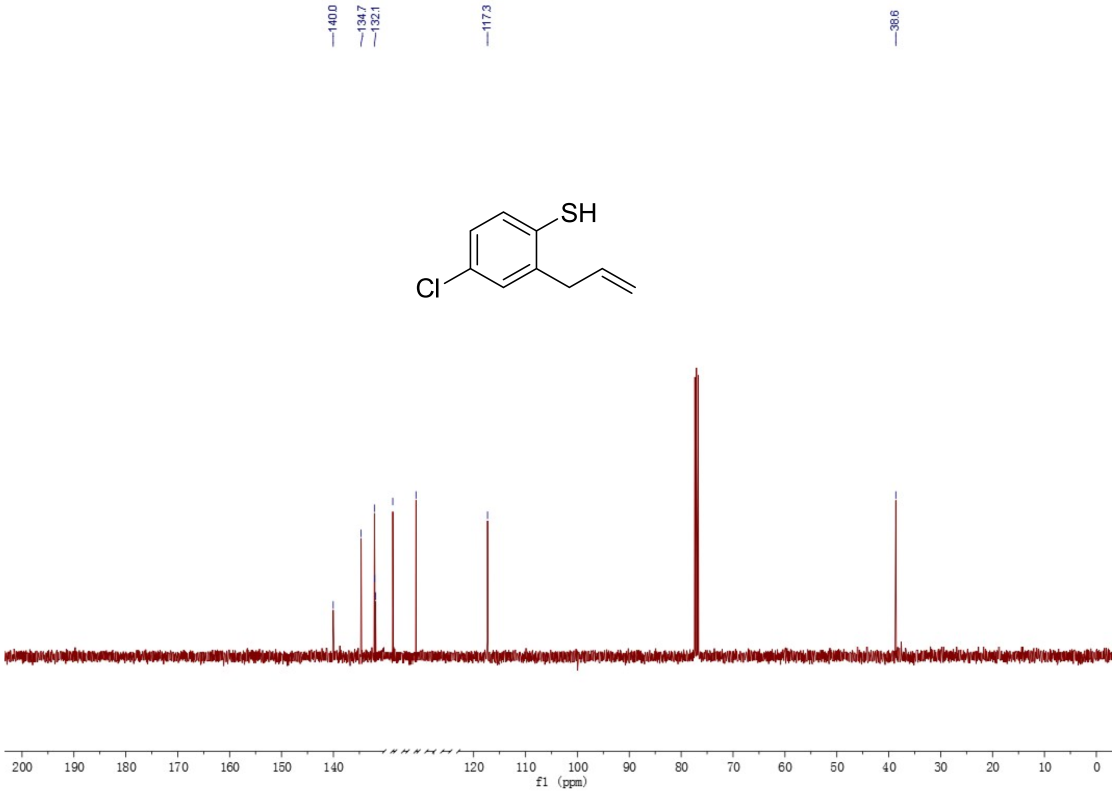
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Cl
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190
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10
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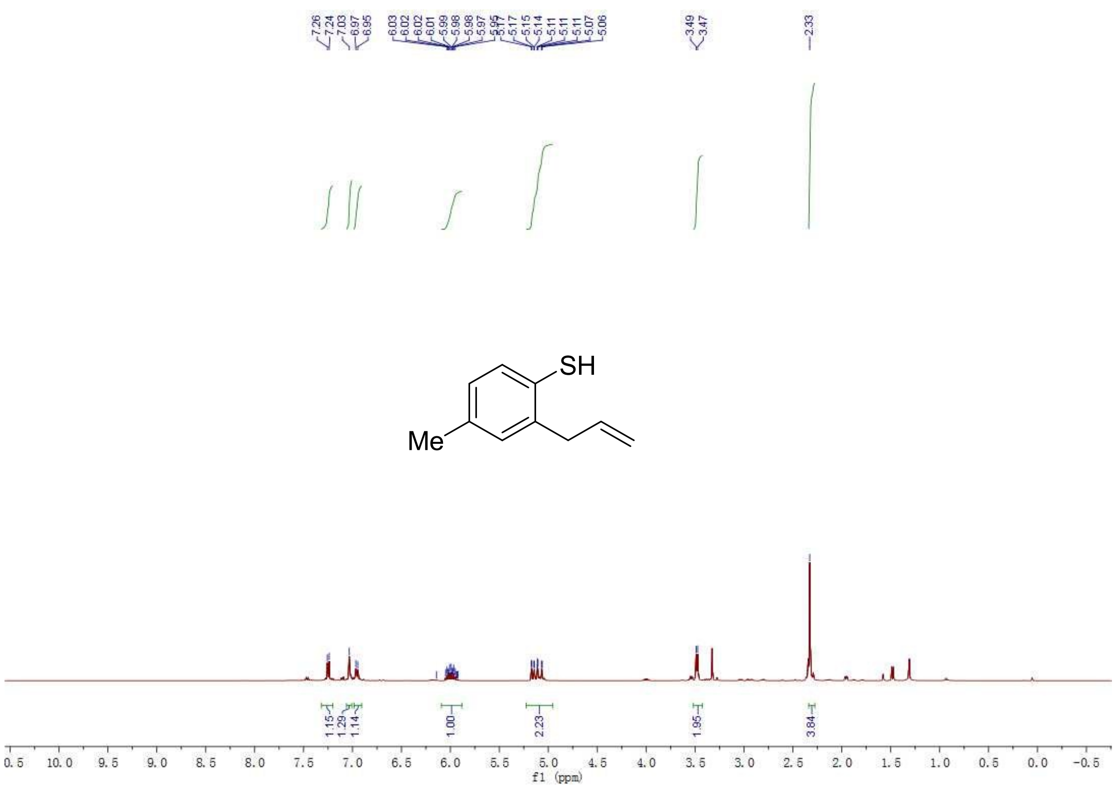
f1 (ppm)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6.02
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5.98
5.97
5.95
5.17
5.17
5.15
5.14
5.11
5.11
5.11
5.07
5.06
3.49
3.47
2.33
SH
Me
1.15
1.29
1.14
1.00
2.23
1.95
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9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
2.5
2.0
1.5
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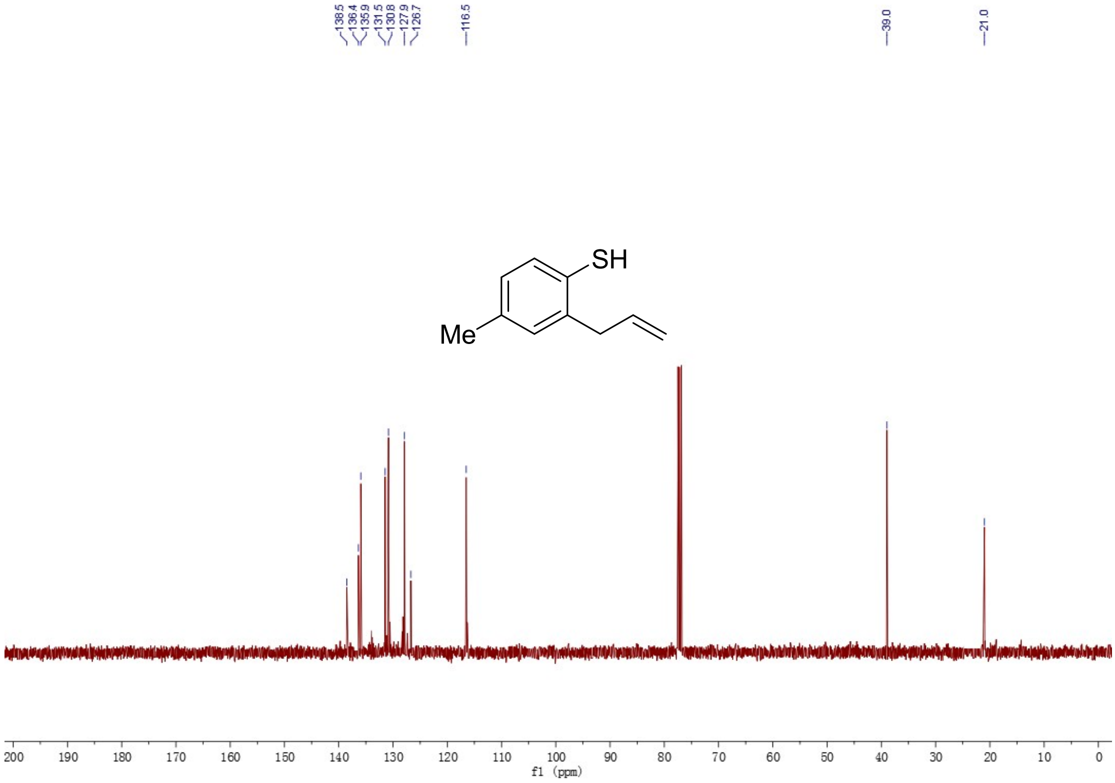
f1 (ppm)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126.7
116.5
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21.0
SH
Me
200
190
180
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150
140
130
120
110
100
90
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50
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10
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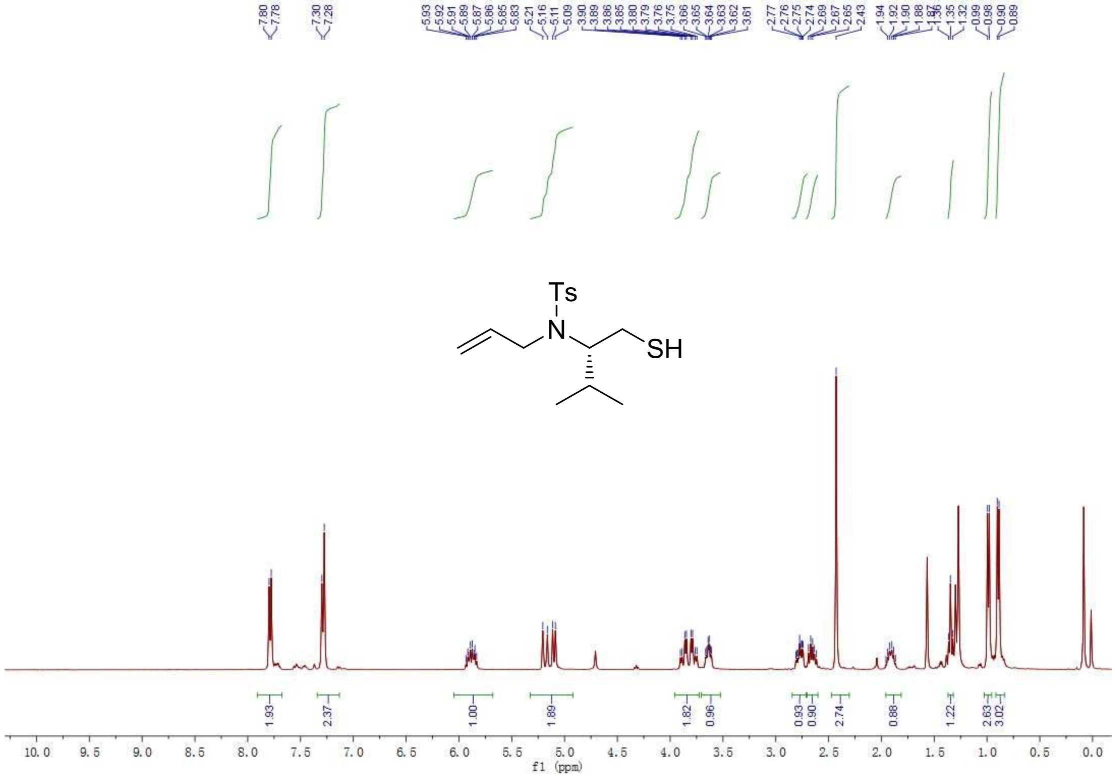
f1 (ppm)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5.16
5.11
5.09
3.90
3.89
3.86
3.85
3.80
3.79
3.76
3.75
3.66
3.65
3.64
3.63
3.62
3.61
2.77
2.76
2.75
2.74
2.69
2.67
2.65
2.43
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1.92
1.90
1.88
1.35
1.32
0.99
0.98
0.90
0.89
Ts
N
SH
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1.00
1.89
1.82
0.96
0.93
0.90
2.74
0.88
1.22
2.63
3.02
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9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.0
2.5
2.0
1.5
1.0
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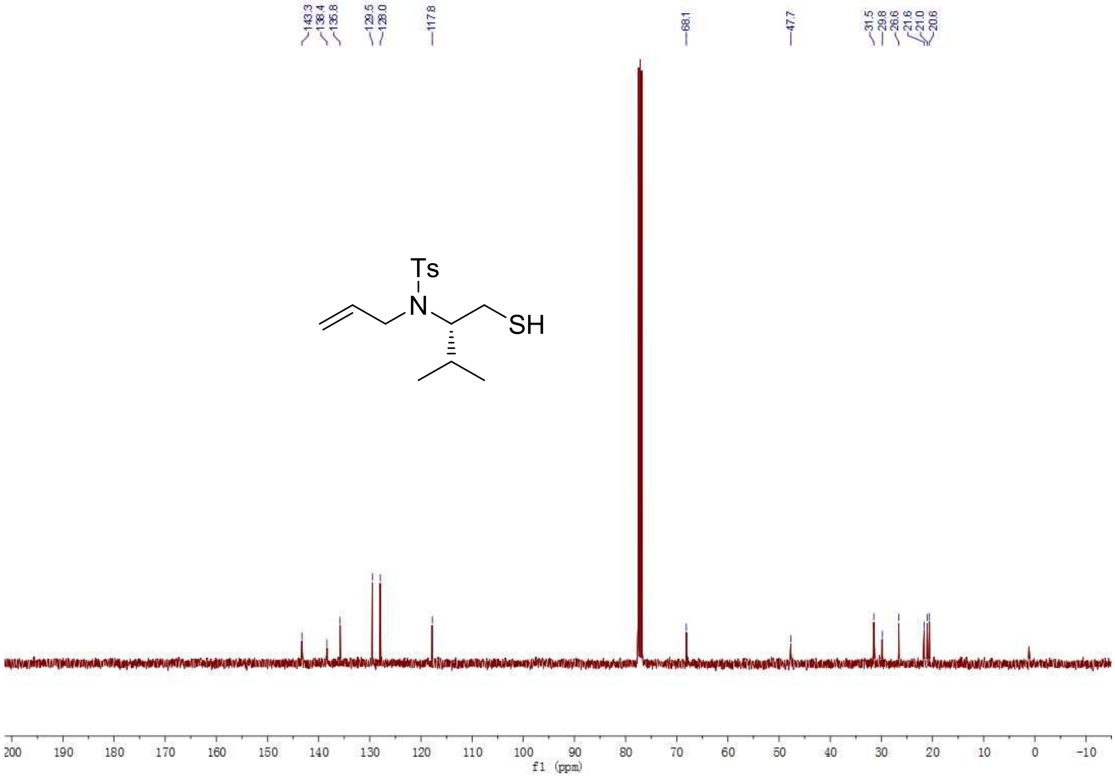
0.0
f1 (ppm)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26.6
21.6
21.0
20.6
Ts
N
SH
200
190
180
170
160
150
140
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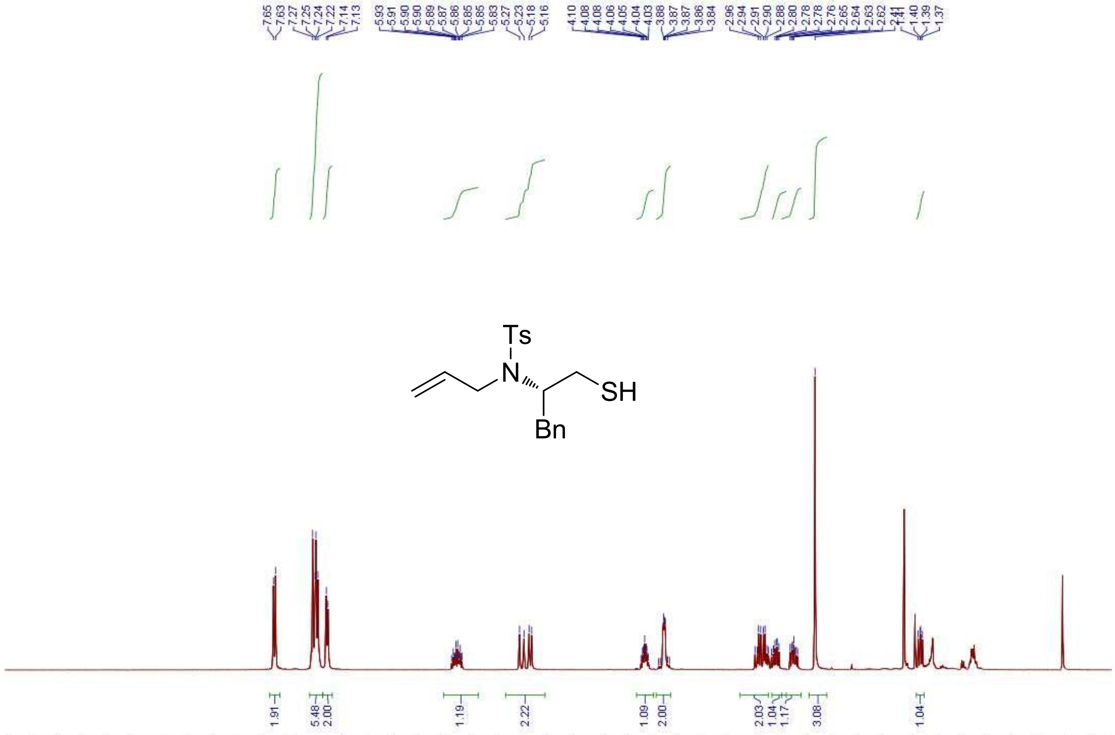
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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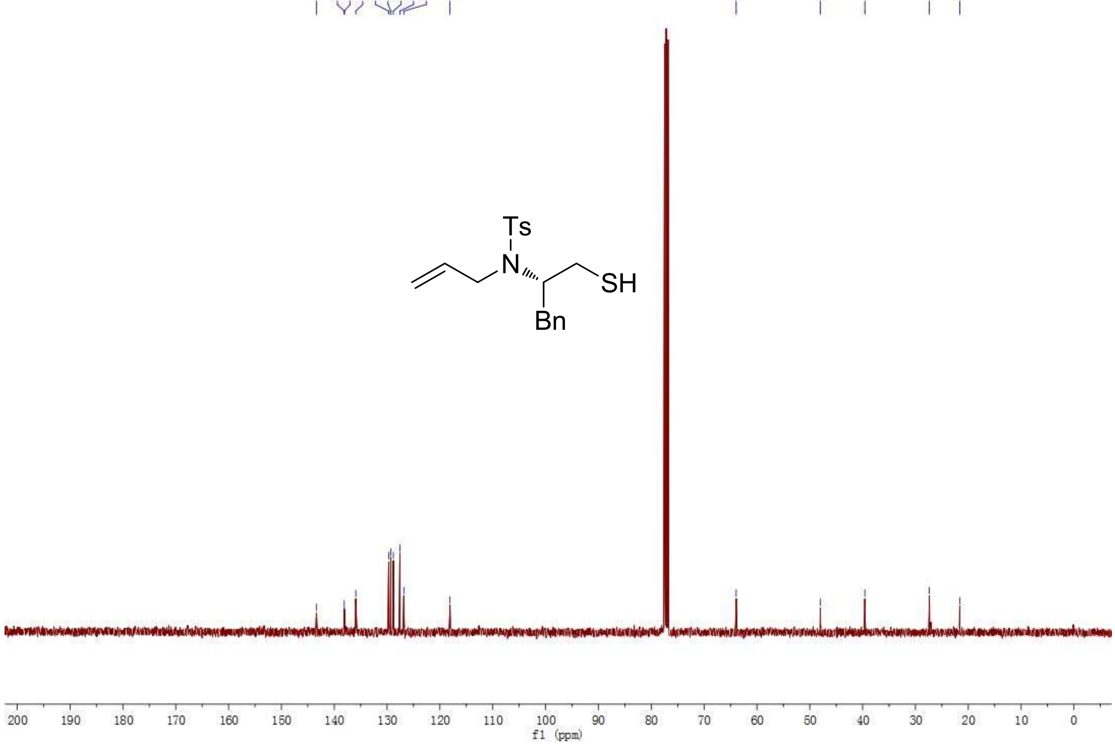
5.90
5.89
5.87
5.86
5.85
5.85
5.83
5.27
5.23
5.18
5.16
4.10
4.08
4.08
4.06
4.05
4.04
4.03
3.88
3.87
3.87
3.86
3.84
2.96
2.94
2.91
2.90
2.88
2.80
2.78
2.78
2.76
2.65
2.64
2.63
2.62
2.41
1.41
1.40
1.39
1.37
Ts
N
SH
Bn
1.91
5.48
2.00
1.19
2.22
1.09
2.00
2.03
1.04
1.17
3.08
1.04
10.0 9.5 9.0 8.5 8.0 7.5 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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127.6
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118.1
63.9
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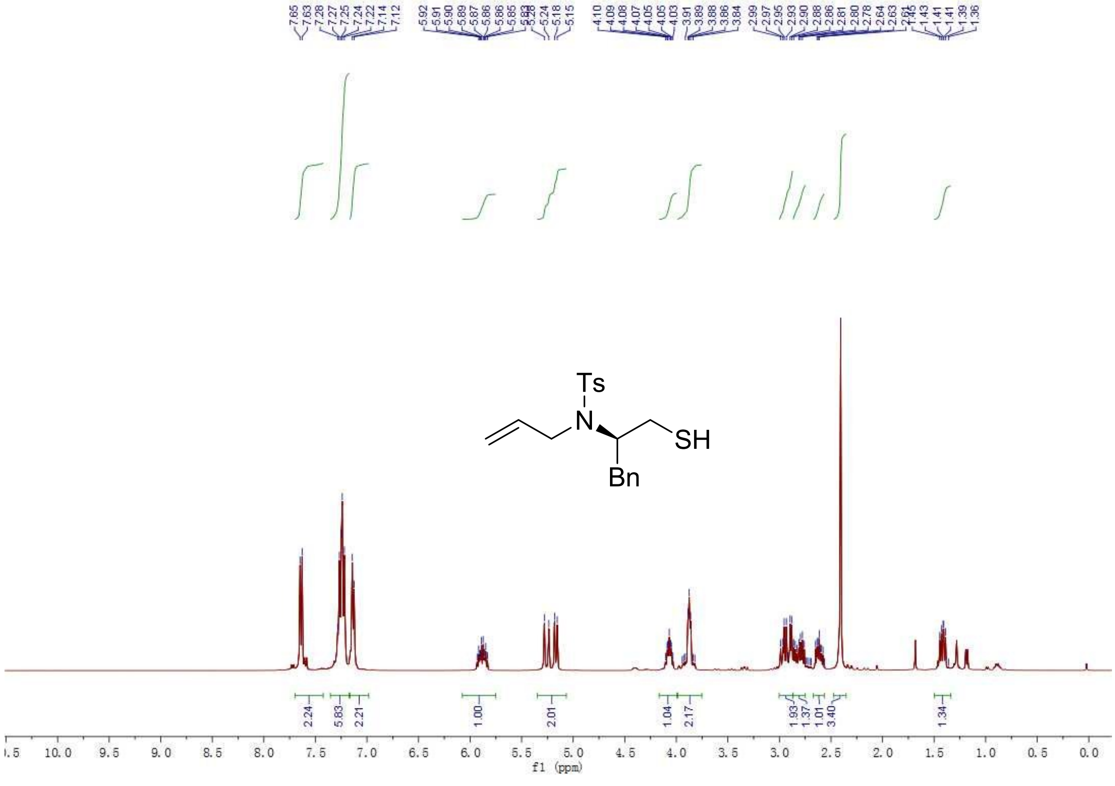
21.6
Ts
N
SH
Bn
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.14
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5.90
5.89
5.87
5.86
5.86
5.85
5.83
5.28
5.24
5.18
5.15
4.10
4.09
4.08
4.07
4.05
4.05
4.03
3.91
3.89
3.88
3.86
3.84
2.99
2.97
2.95
2.93
2.90
2.88
2.86
2.81
2.80
2.78
2.64
2.63
2.61
1.45
1.43
1.41
1.39
1.36
Ts
N
SH
Bn
2.24
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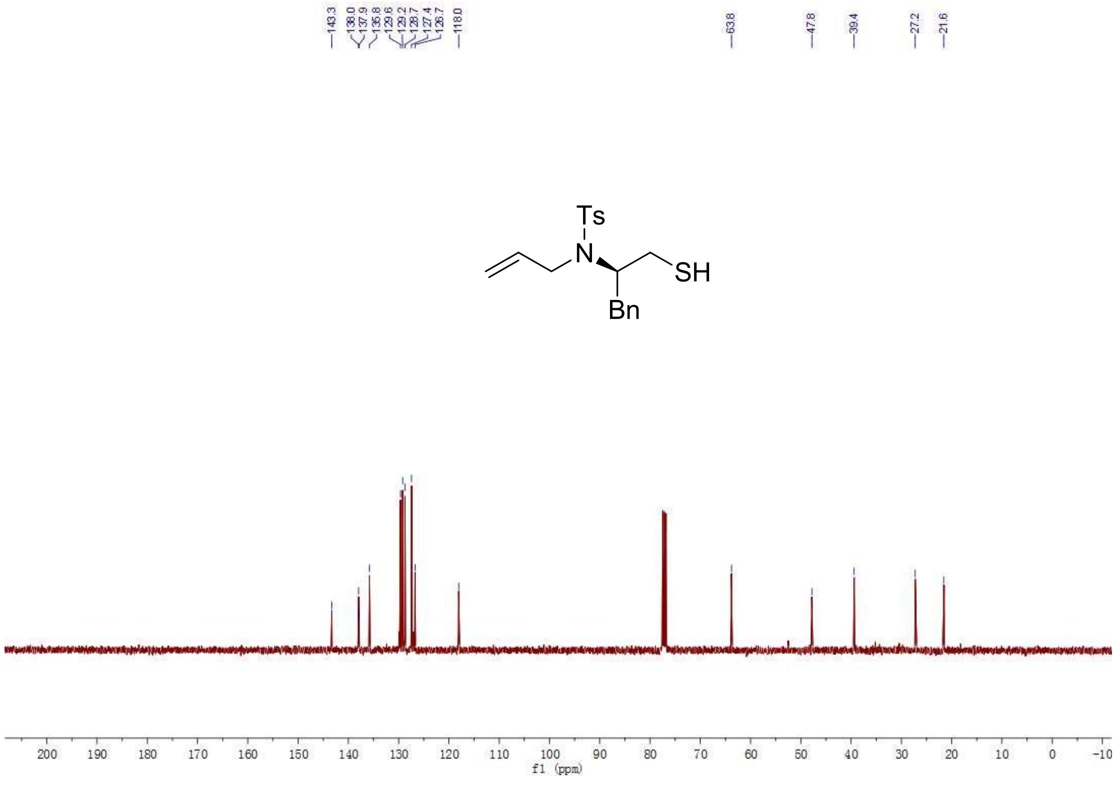
2.01
1.04
2.17
1.93
1.37
1.01
3.40
1.34
f1 (ppm)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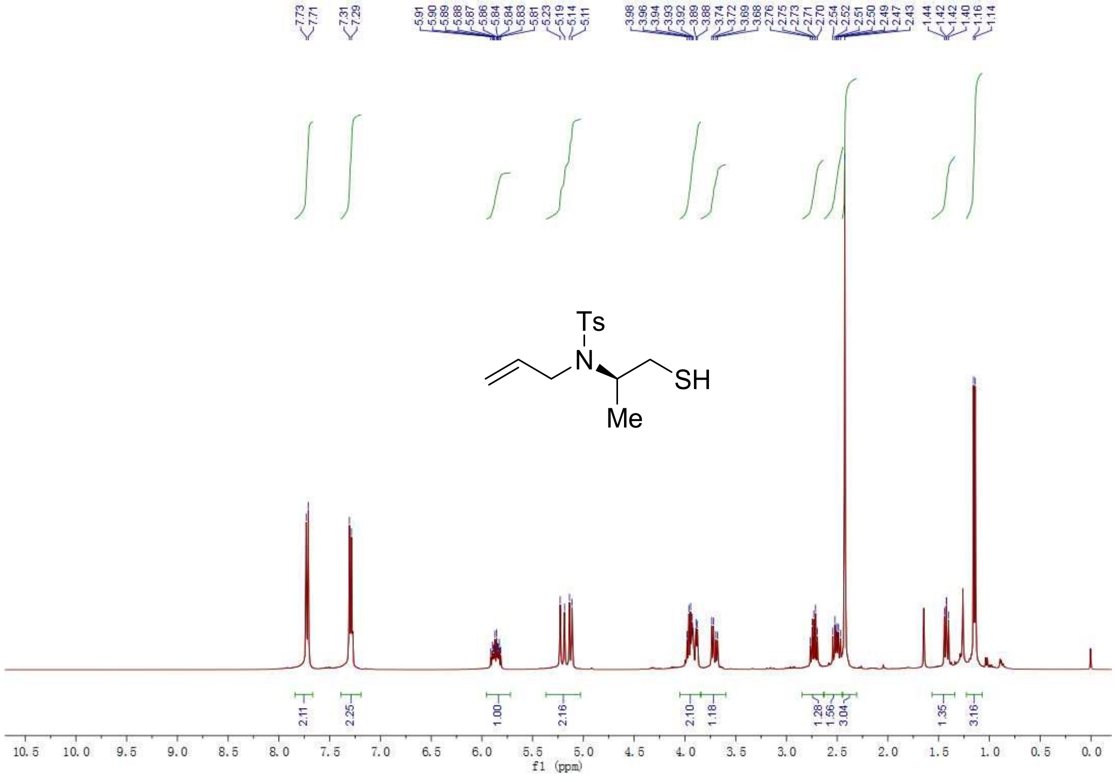
39.4
27.2
21.6
Ts
N
SH
Bn
f1 (ppm)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5.88
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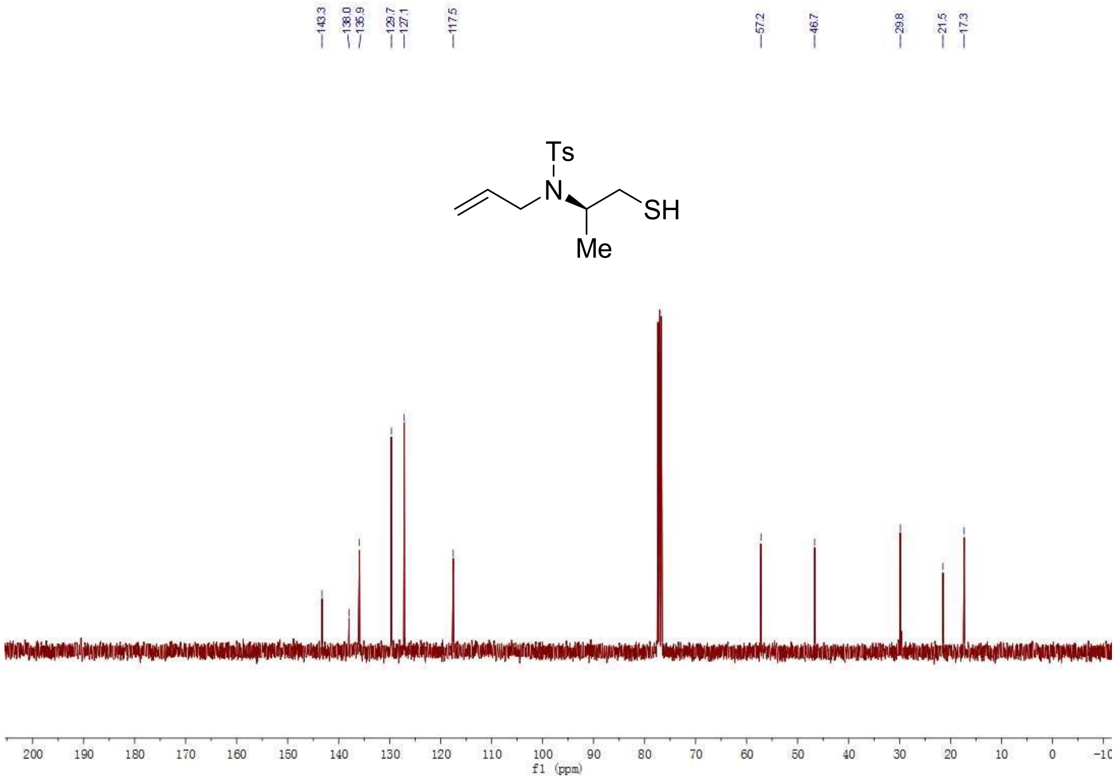
5.84
5.83
5.81
5.23
5.19
5.14
5.11
3.98
3.96
3.94
3.93
3.92
3.89
3.88
3.74
3.72
3.69
3.68
2.76
2.75
2.73
2.71
2.70
2.54
2.52
2.51
2.50
2.49
2.47
2.43
1.44
1.42
1.42
1.40
1.16
1.14
Ts
N
SH
Me
2.11
2.25
1.00
2.16
2.10
1.18
1.28
1.56
3.04
1.35
3.16
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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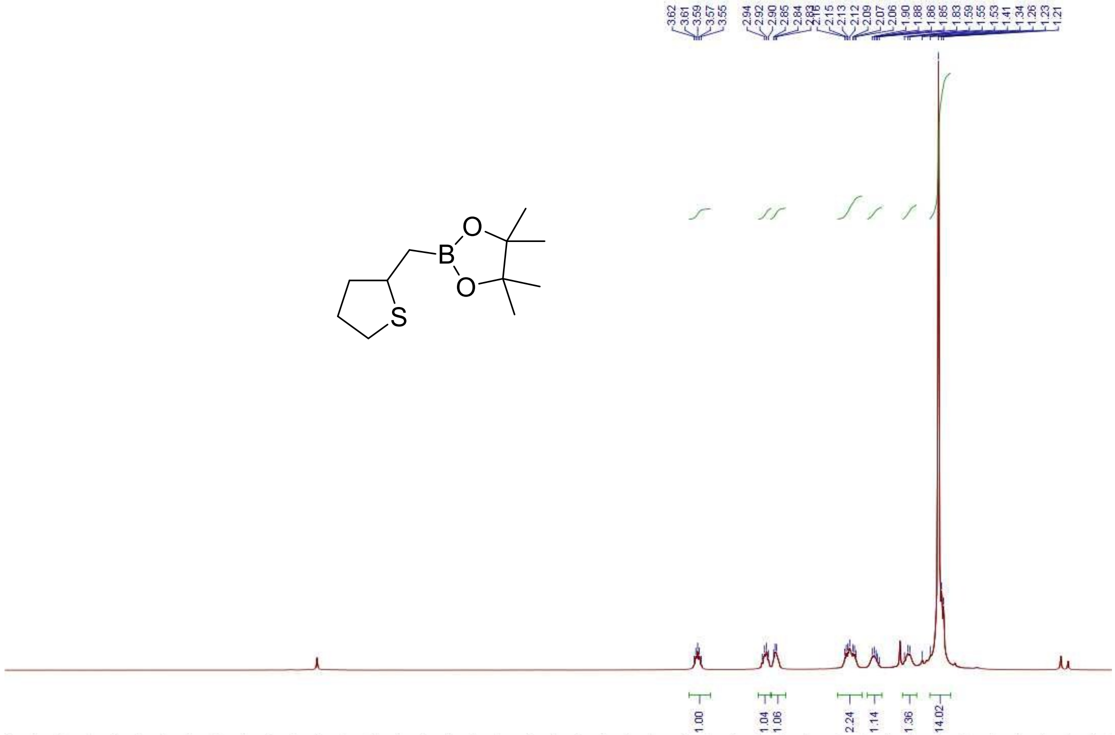
127.1
117.5
57.2
46.7
29.8
21.5
17.3
Ts
N
SH
Me
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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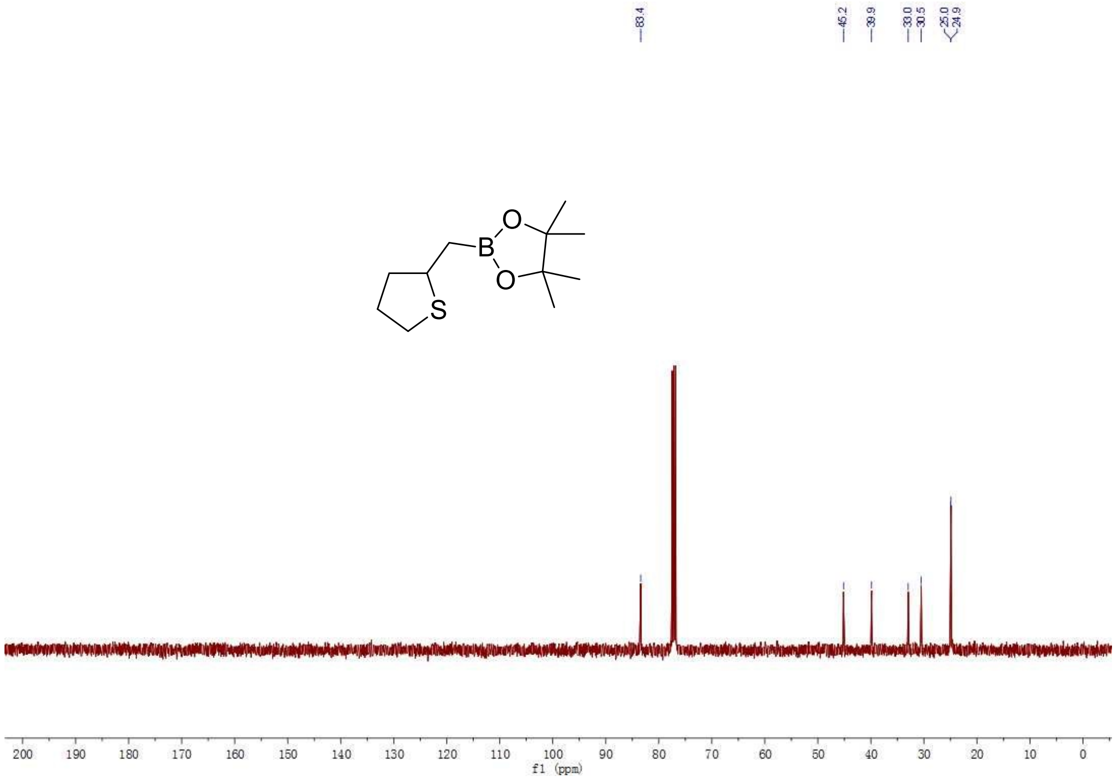
2.85
2.84
2.83
2.16
2.15
2.13
2.12
2.09
2.07
2.06
1.90
1.88
1.86
1.85
1.83
1.59
1.55
1.53
1.41
1.34
1.26
1.23
1.21
O
B
O
S
1.00
1.04
1.06
2.24
1.14
1.36
14.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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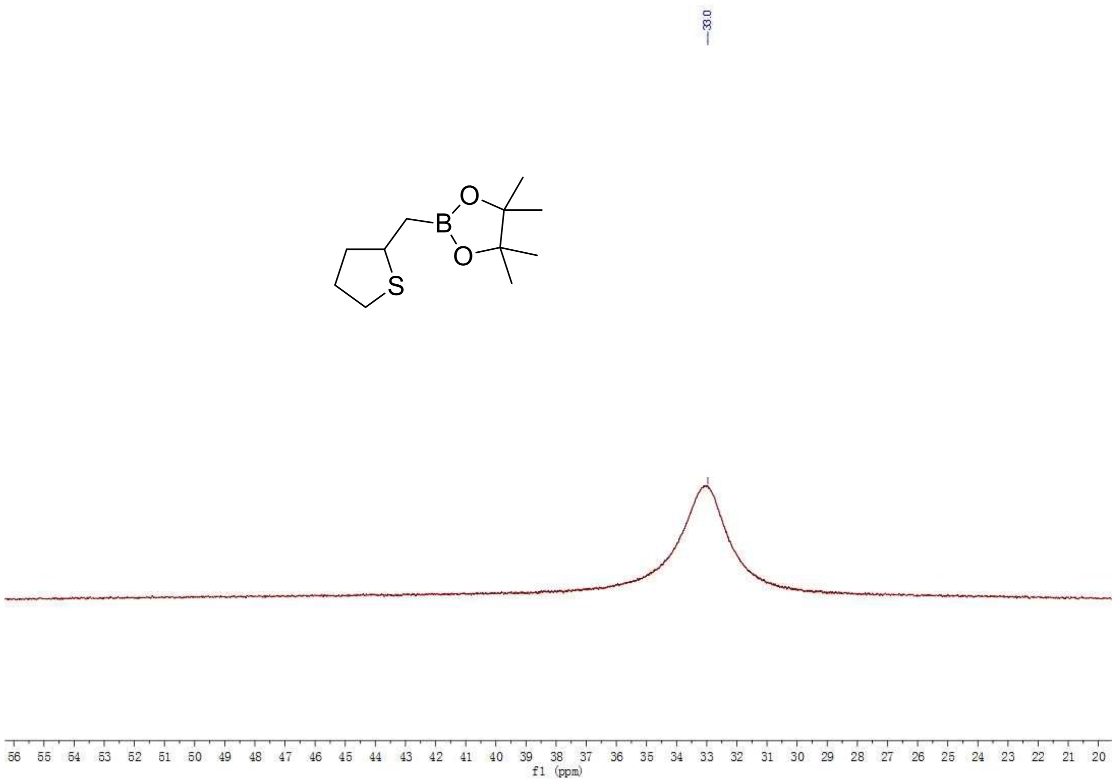
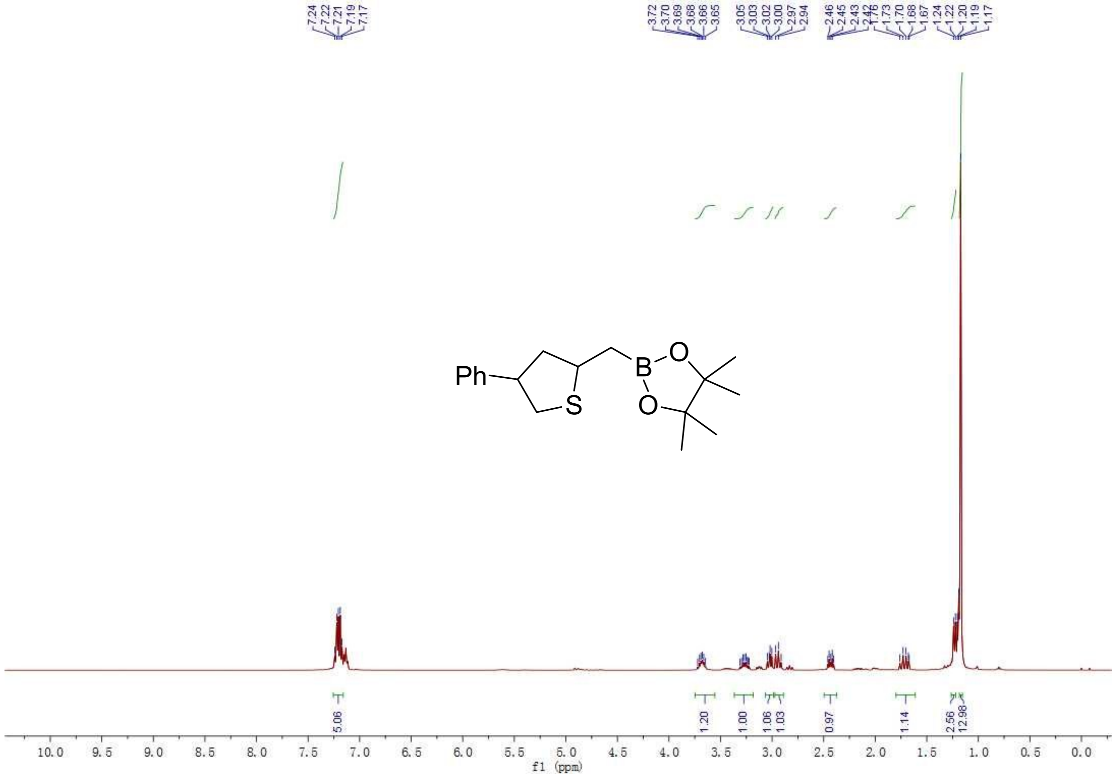
45.2
39.9
33.0
30.5
25.0
24.9
O
B
O
S
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



33.0
S
B
O
O
56 55 54 53 52 51 50 49 48 47 46 45 44 43 42 41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20
f1 (ppm)



7.24
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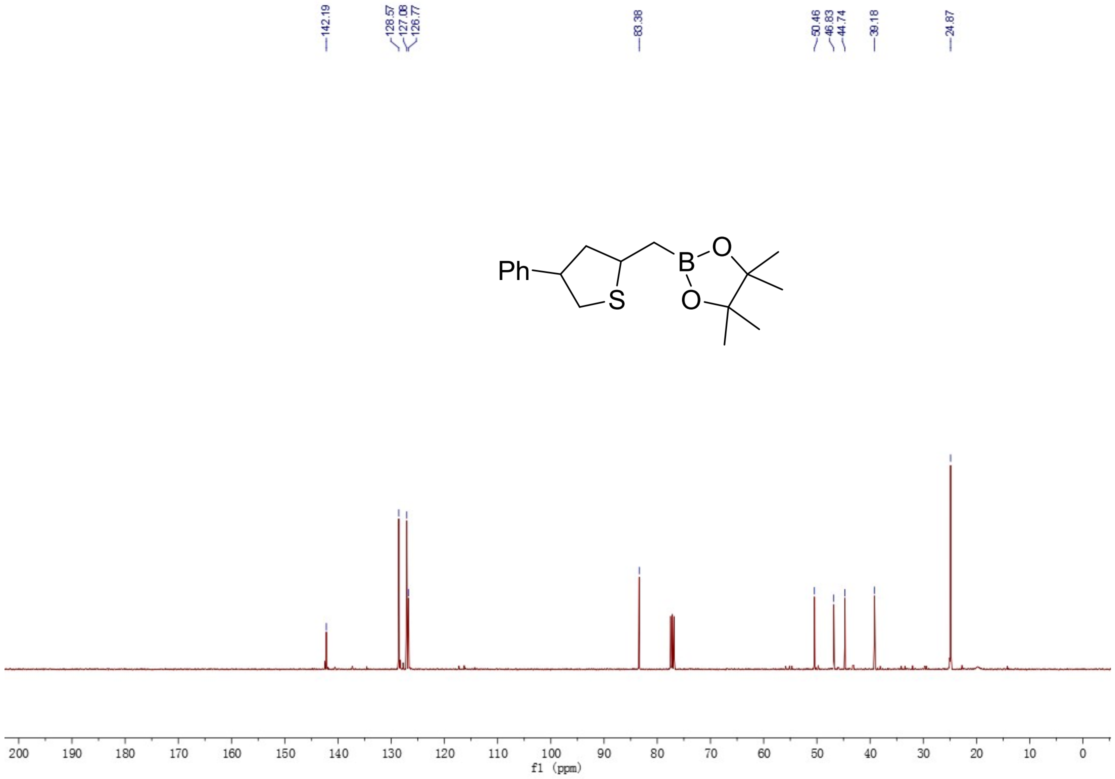
3.66
3.65
3.05
3.03
3.02
3.00
2.97
2.94
2.46
2.45
2.43
2.42
1.76
1.73
1.70
1.68
1.67
1.24
1.22
1.20
1.19
1.17
Ph
S
B
O
O
5.06
1.20
1.00
1.06
1.03
0.97
1.14
2.56
12.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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B
O
O
200
190
180
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130
120
110
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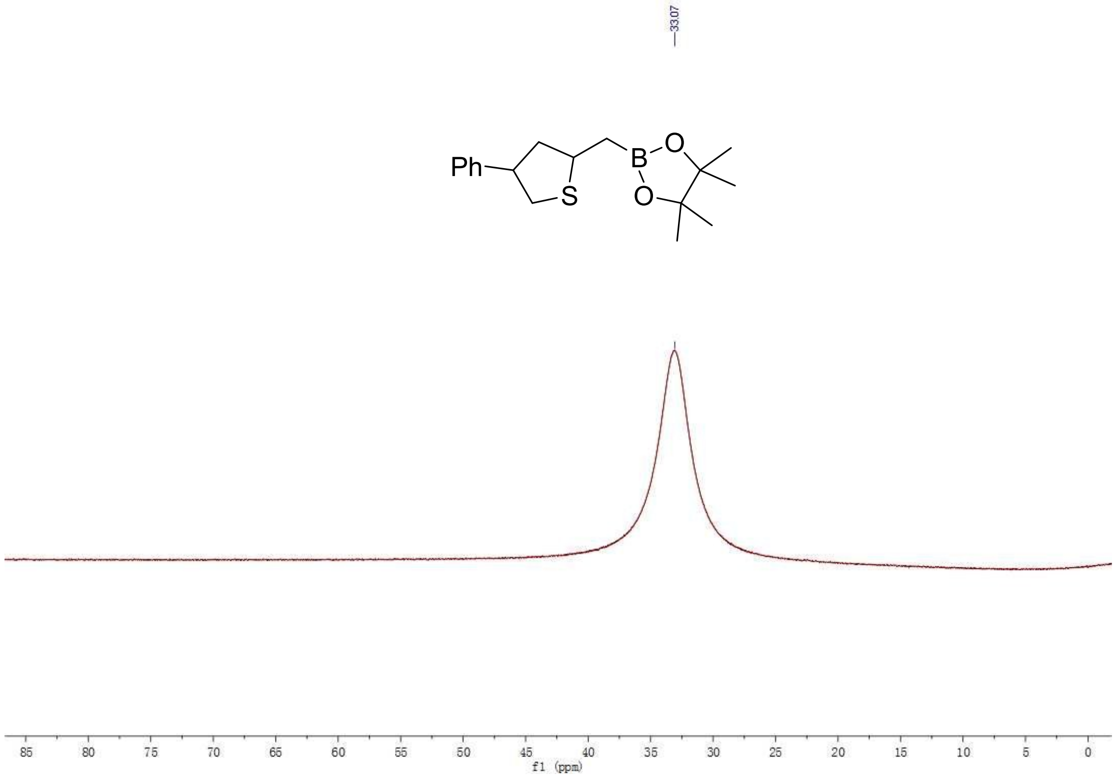
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


33.07
Ph
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B
O
O
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80
75
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50
45
40
35
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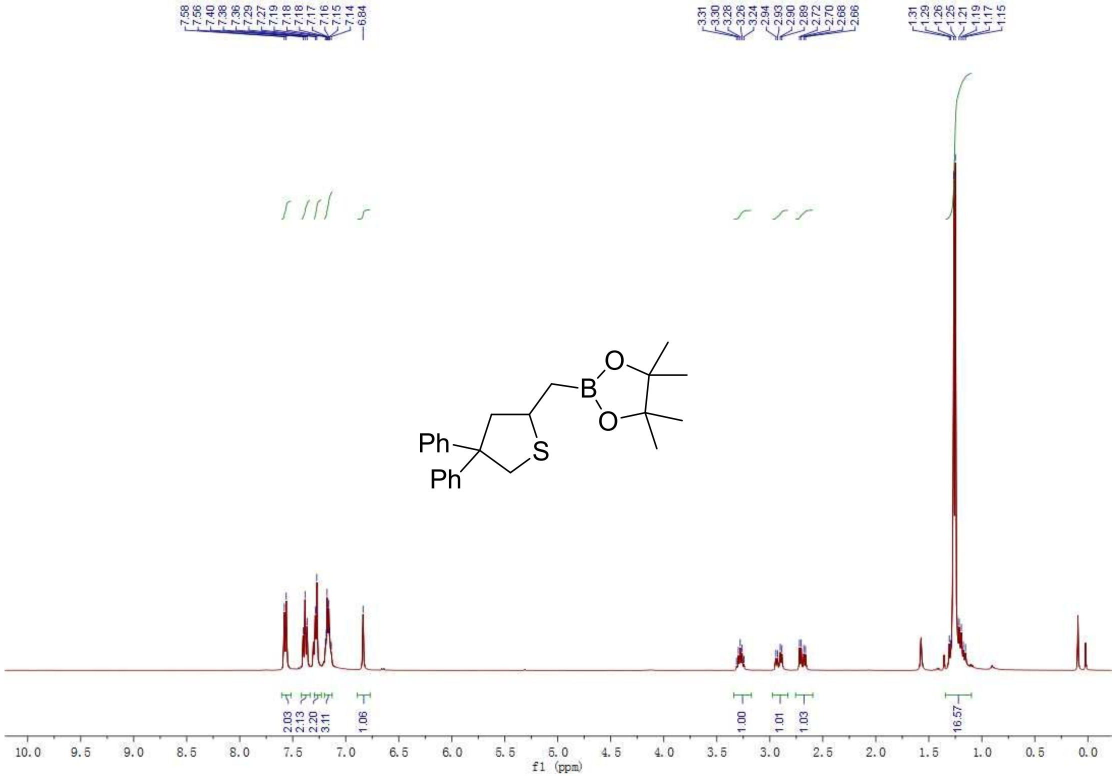
25
20
15
10
5
0
f1 (ppm)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7.19
7.18
7.18
7.17
7.16
7.15
7.14
6.84
3.31
3.30
3.28
3.26
3.24
2.94
2.93
2.90
2.89
2.72
2.70
2.68
2.66
1.31
1.29
1.26
1.25
1.21
1.19
1.17
1.15
Ph
Ph
S
B
O
O
2.03
2.13
2.20
3.11
1.06
1.00
1.01
1.03
16.57
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
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2.5
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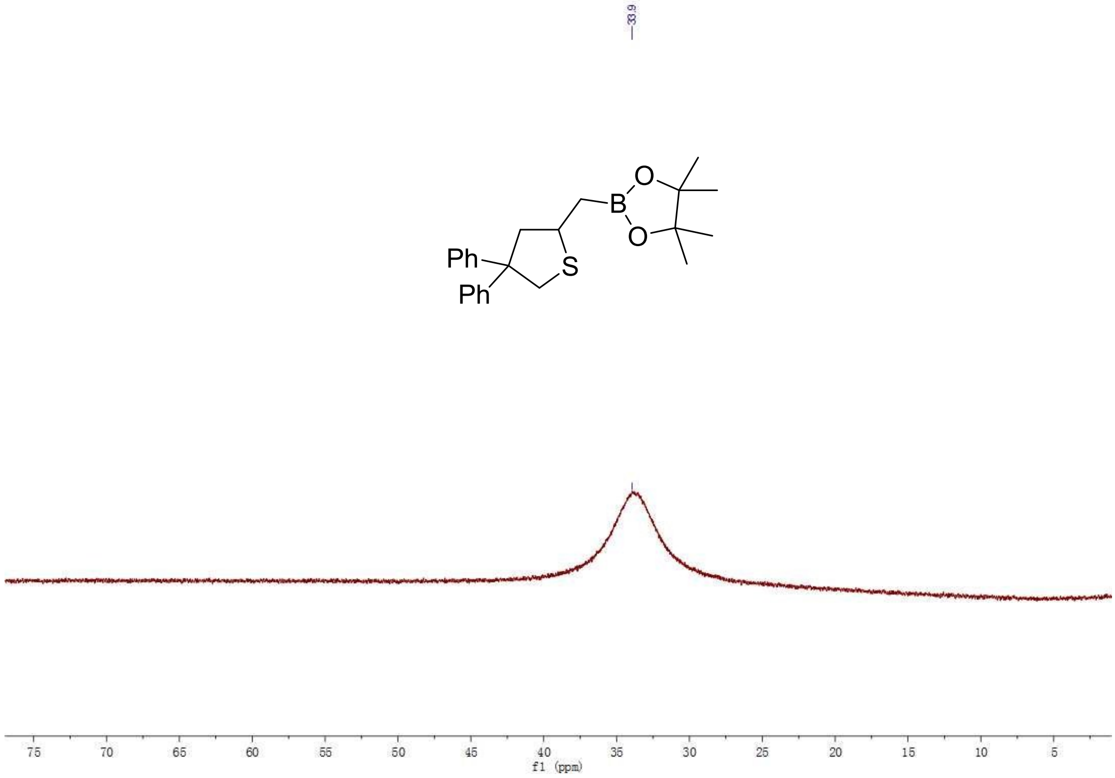
f1 (ppm)


33.9
Ph
Ph
S
B
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O
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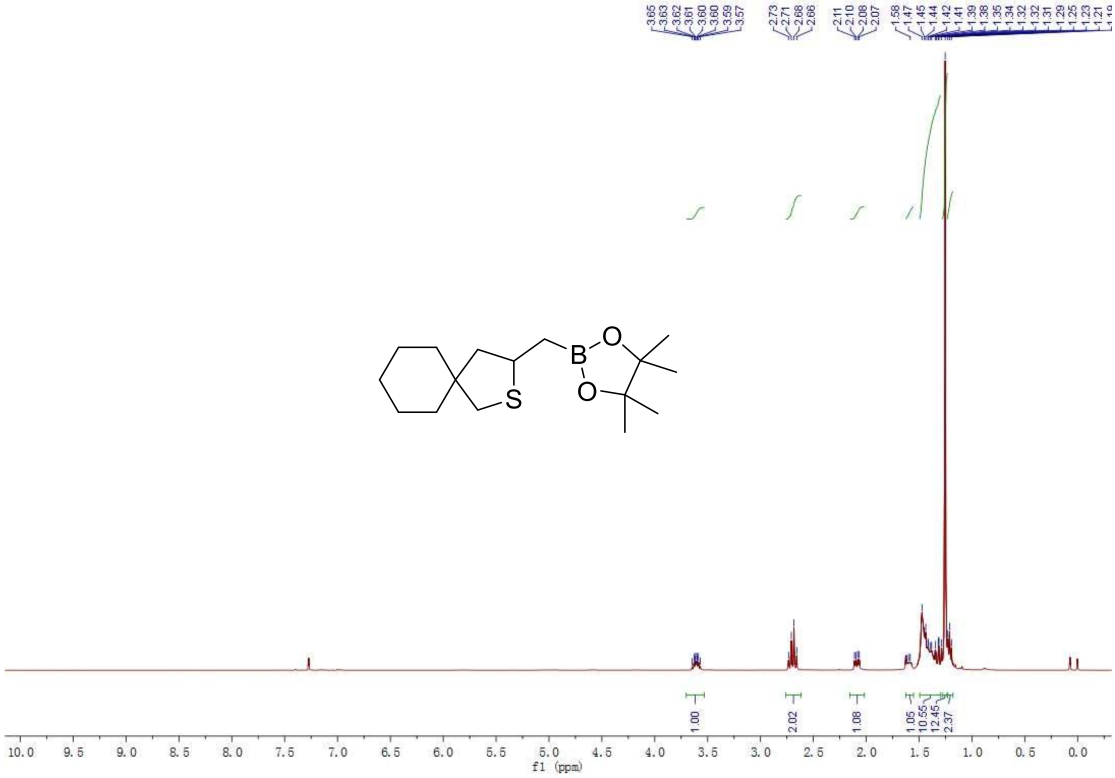
15
10
5
f1 (ppm)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2.10
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2.07
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1.47
1.45
1.44
1.42
1.41
1.39
1.38
1.35
1.34
1.32
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1.21
1.19
B
O
O
S
1.00
2.02
1.08
1.05
10.55
12.45
2.37
10.0
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9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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1.0
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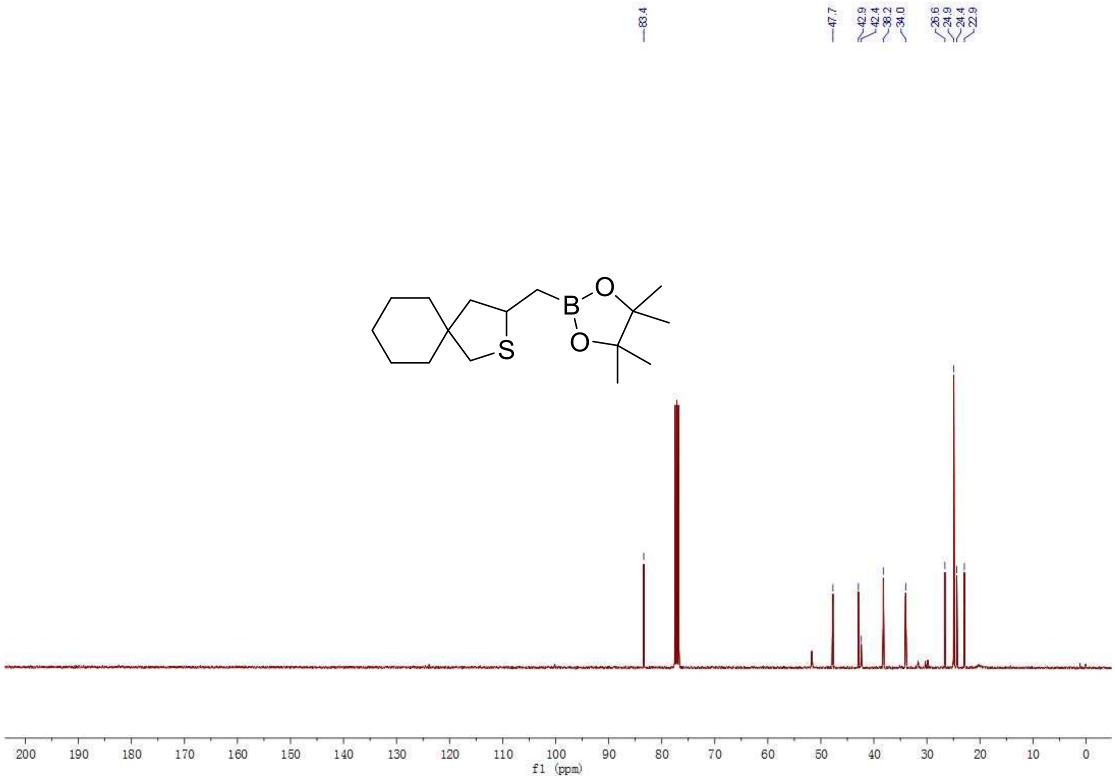
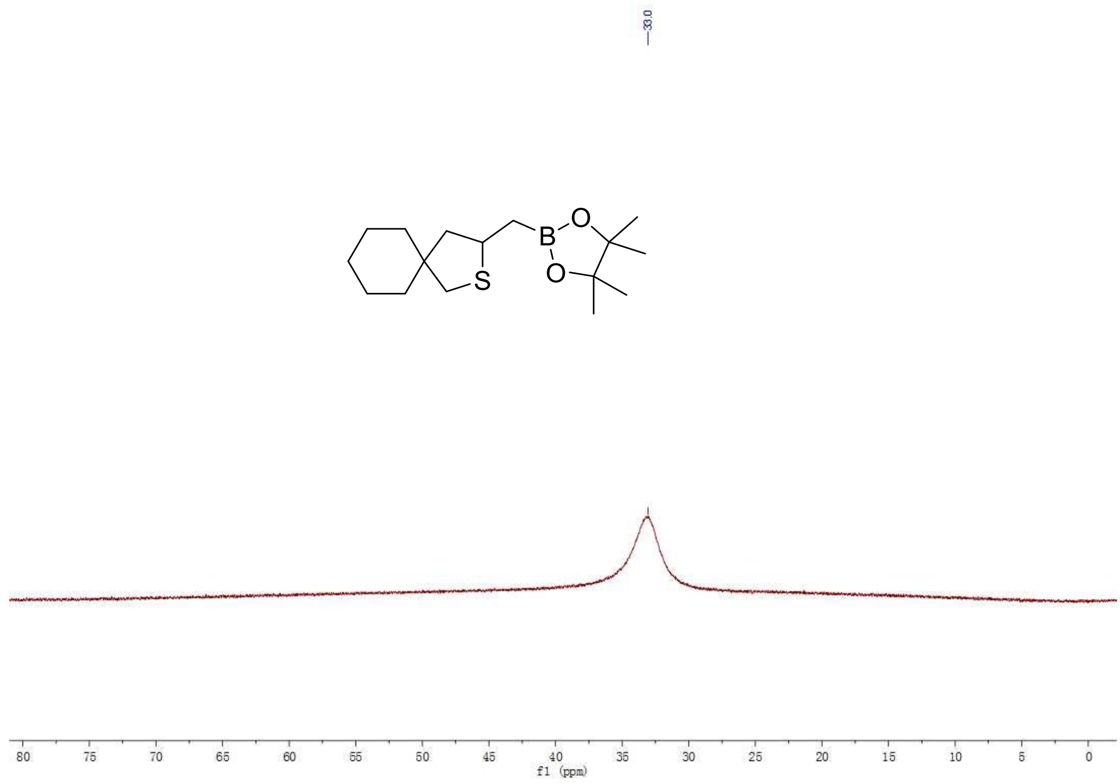
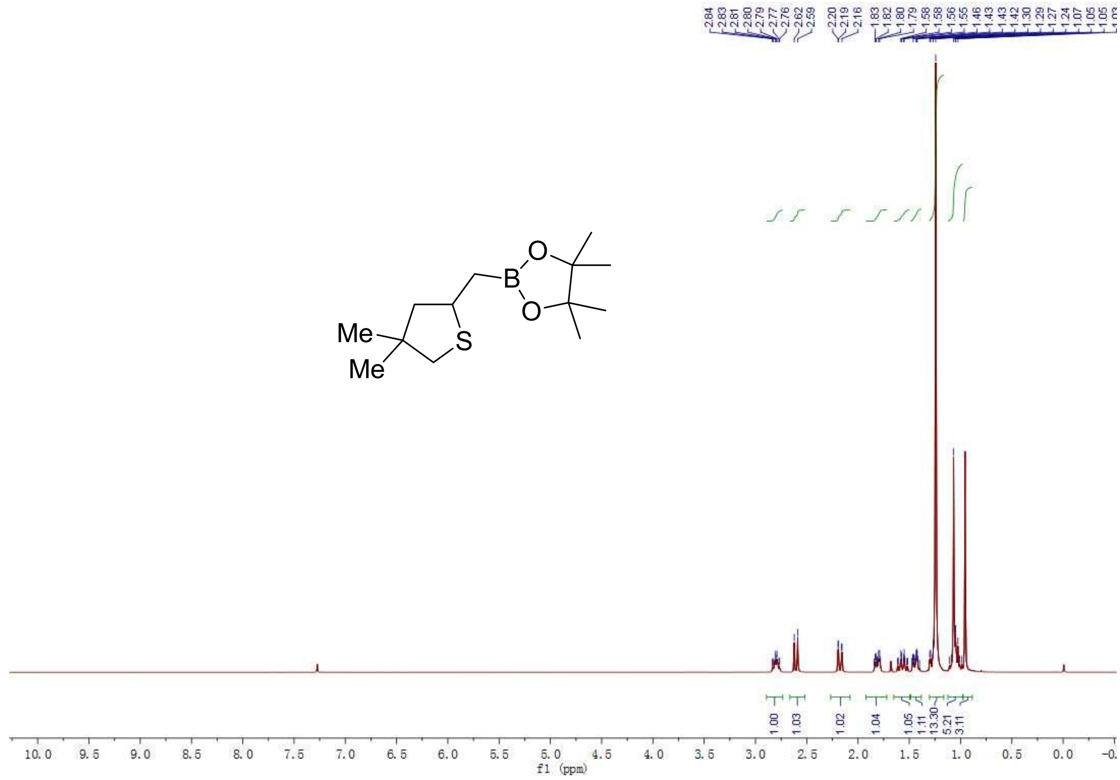
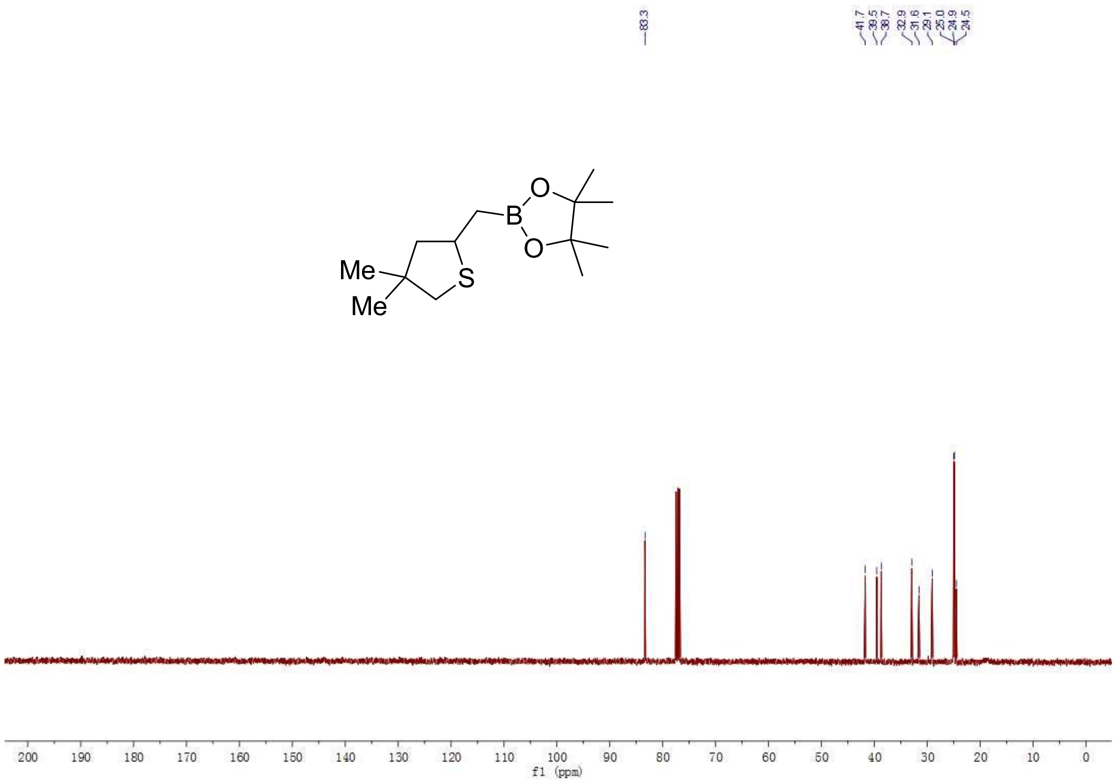
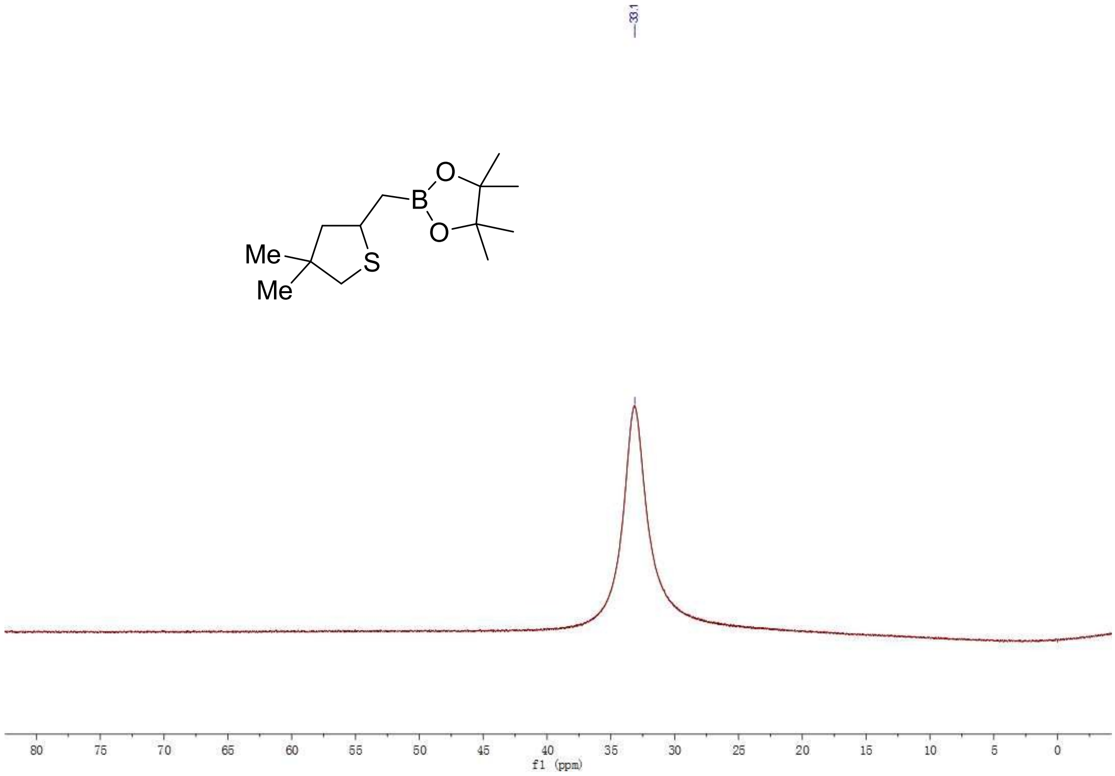
0.0
f1 (ppm)

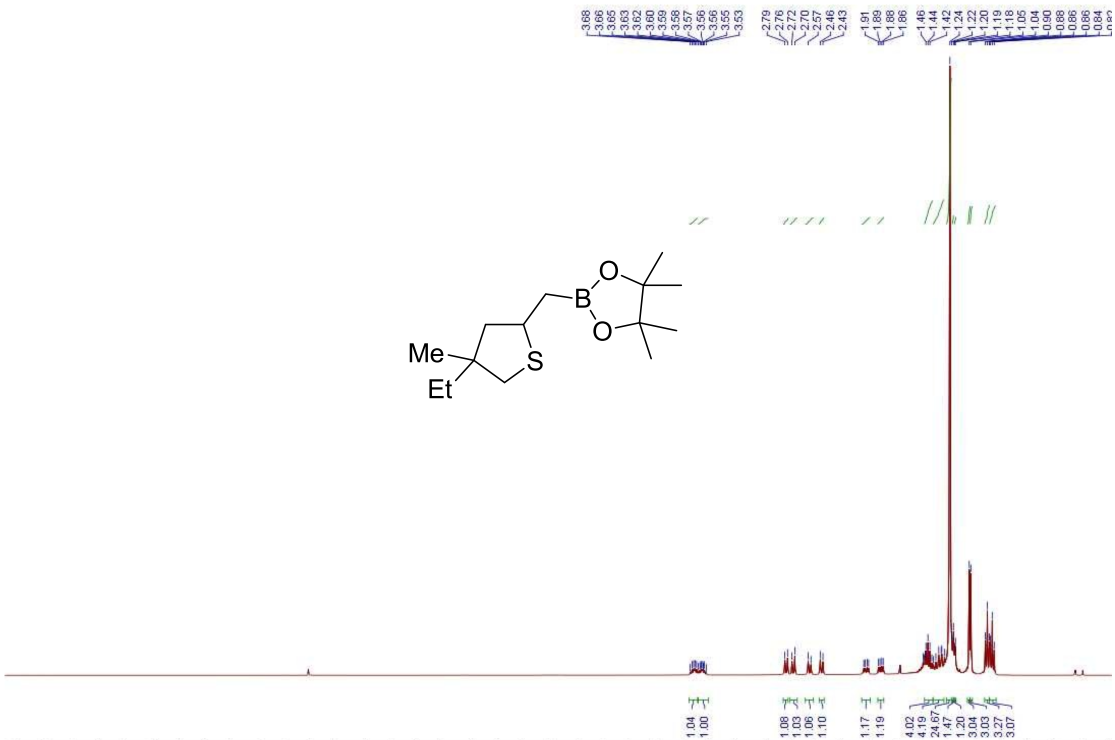

83.4
47.7
42.9
42.4
38.2
34.0
26.6
24.9
24.4
22.9
B
O
O
S
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

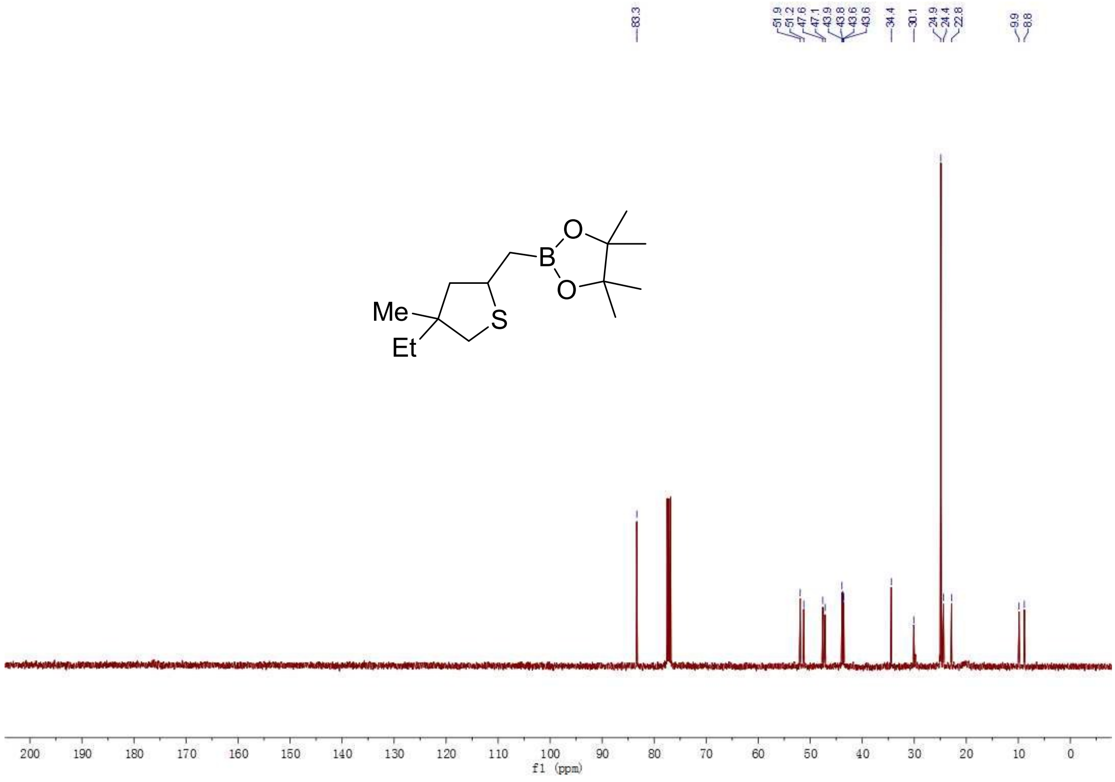

—33.0
B
O
O
S
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)

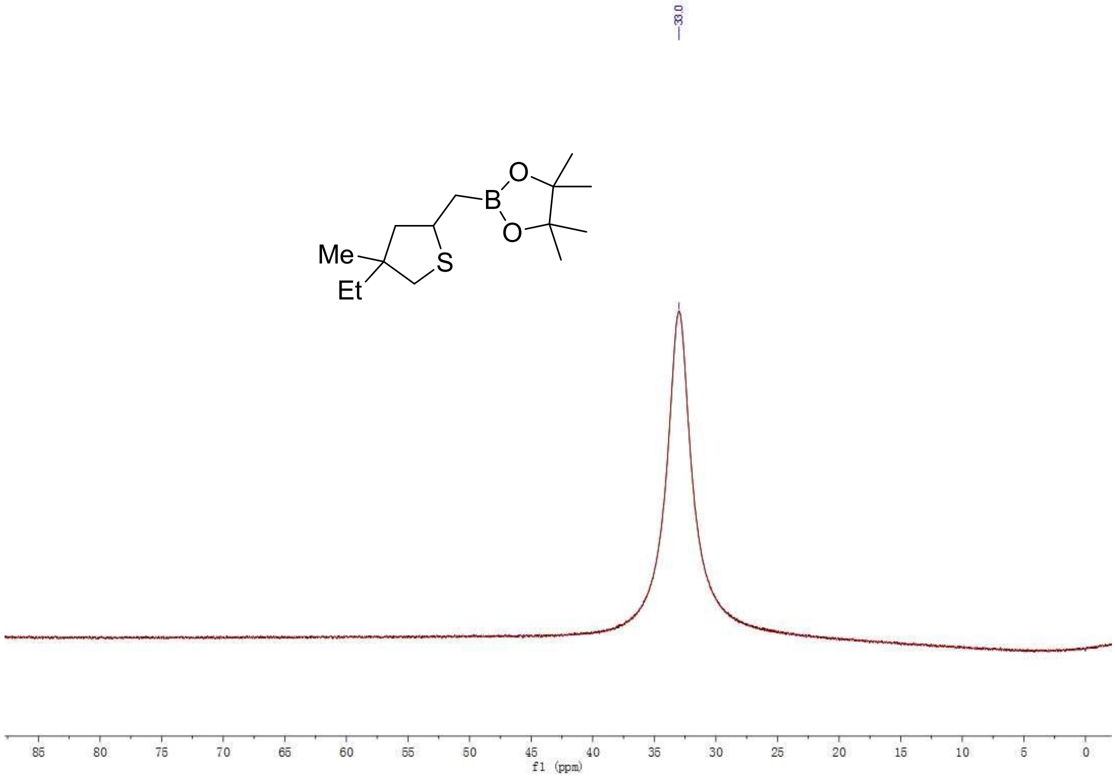

2.84
2.83
2.81
2.80
2.79
2.77
2.76
2.62
2.59
2.20
2.19
2.16
1.83
1.82
1.80
1.79
1.58
1.58
1.56
1.55
1.46
1.43
1.43
1.42
1.30
1.29
1.27
1.24
1.07
1.05
1.05
B
O
O
Me
Me
S
1.00
1.03
1.02
1.04
1.05
1.11
13.30
5.21
3.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

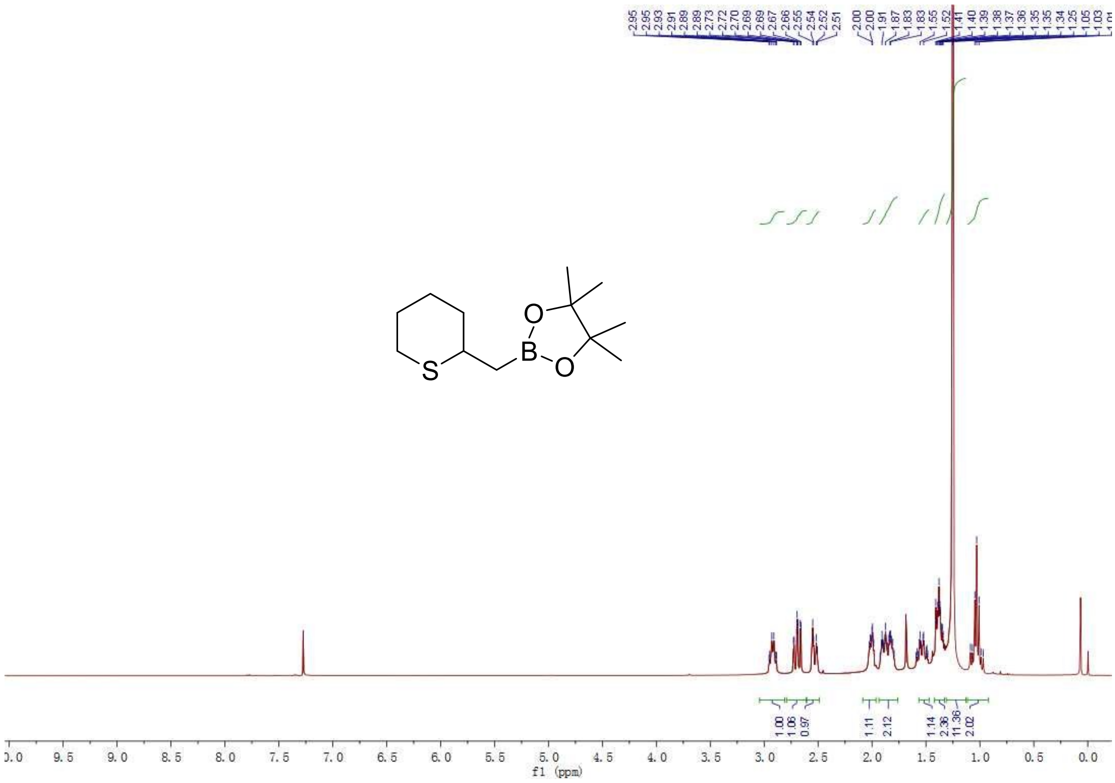

83.3
41.7
39.5
38.7
32.9
31.6
29.1
25.0
24.9
24.5
Me
Me
S
B
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

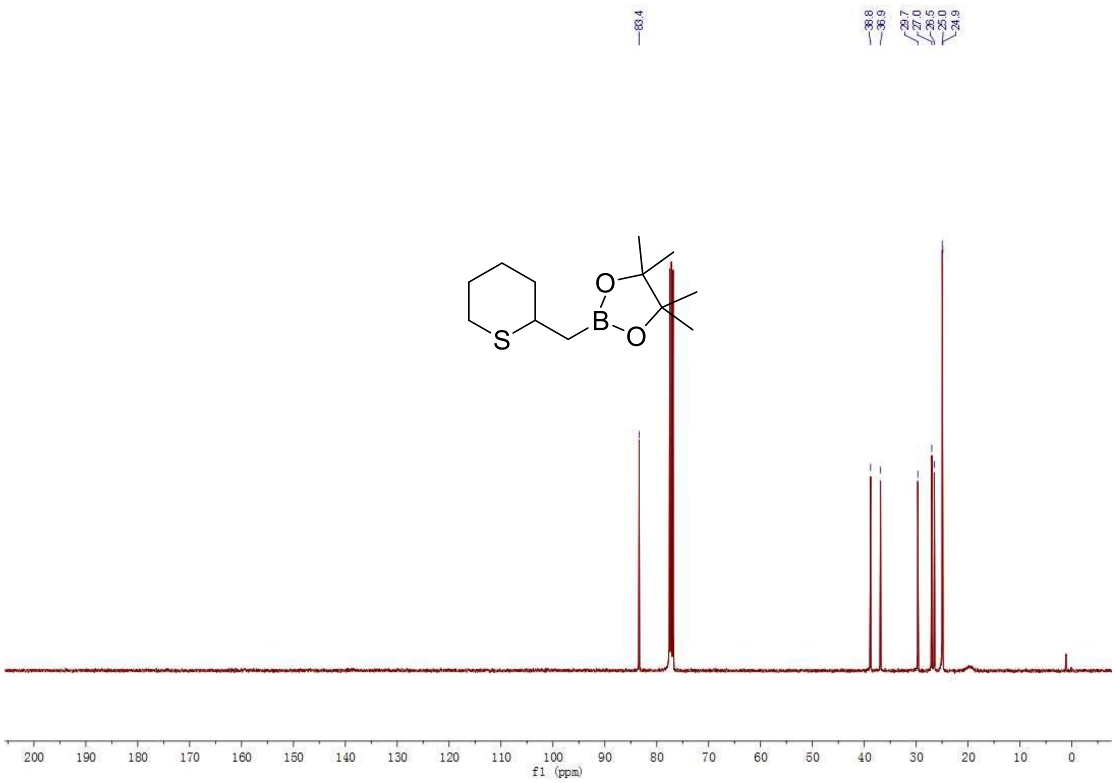

33.1
Me
Me
S
B
O
O
80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

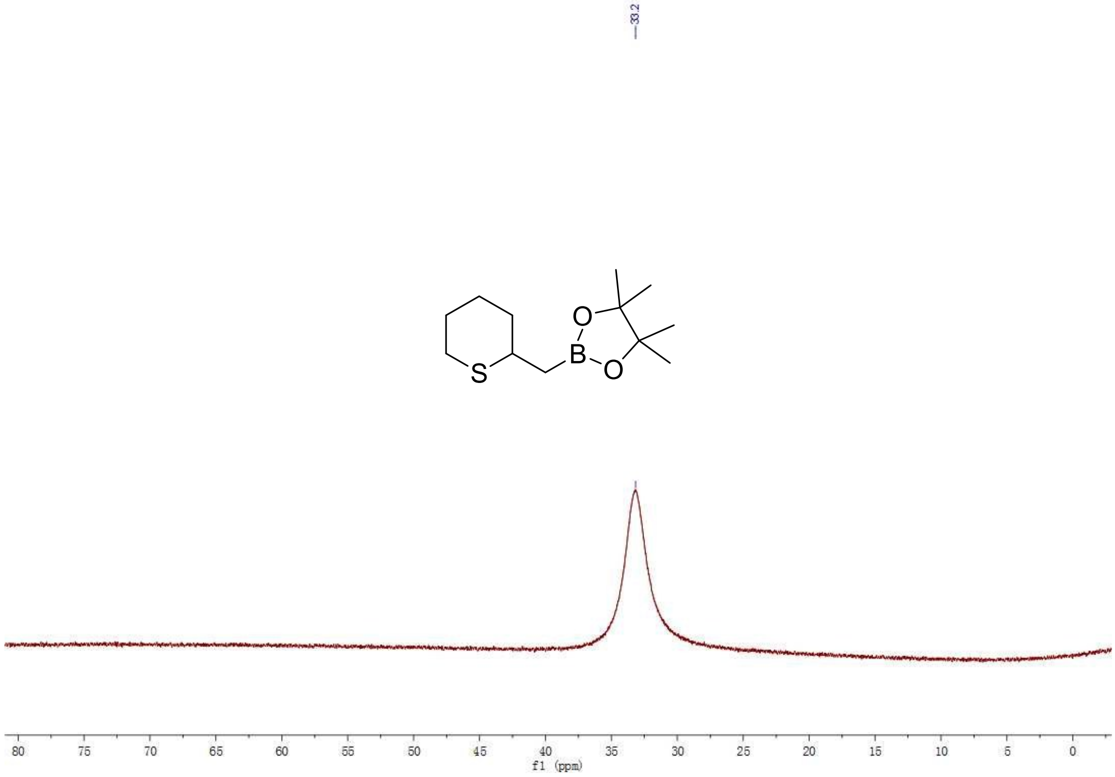

3.68
3.66
3.65
3.63
3.62
3.60
3.59
3.58
3.57
3.56
3.56
3.55
3.53
2.79
2.76
2.72
2.70
2.57
2.46
2.43
1.91
1.89
1.88
1.86
1.46
1.44
1.42
1.24
1.22
1.20
1.19
1.18
1.05
1.04
0.90
0.88
0.86
0.86
0.84
0.8
Me
Et
S
B
O
O
1.04
1.00
1.08
1.03
1.06
1.10
1.17
1.19
4.02
4.19
24.67
1.47
1.20
3.04
3.03
3.27
3.07
10.0
9.5
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)


83.3
51.9
51.2
47.6
47.1
43.9
43.8
43.6
43.6
34.4
30.1
24.9
24.4
22.8
9.9
8.8
Me
Et
S
B
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


33.0
Me
Et
S
B
O
O
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)


2.95
2.95
2.93
2.91
2.89
2.89
2.73
2.72
2.70
2.69
2.69
2.67
2.66
2.55
2.54
2.52
2.51
2.00
2.00
1.91
1.87
1.83
1.83
1.55
1.52
1.41
1.40
1.39
1.38
1.37
1.36
1.35
1.35
1.34
1.25
1.05
1.03
1.01
S
B
O
O
1.00
1.08
0.97
1.11
2.12
1.14
2.36
11.36
2.02
0.0
9.5
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)


83.4
38.8
36.9
29.7
27.0
26.5
25.0
24.9
S
B
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


33.2
S
B
O
O
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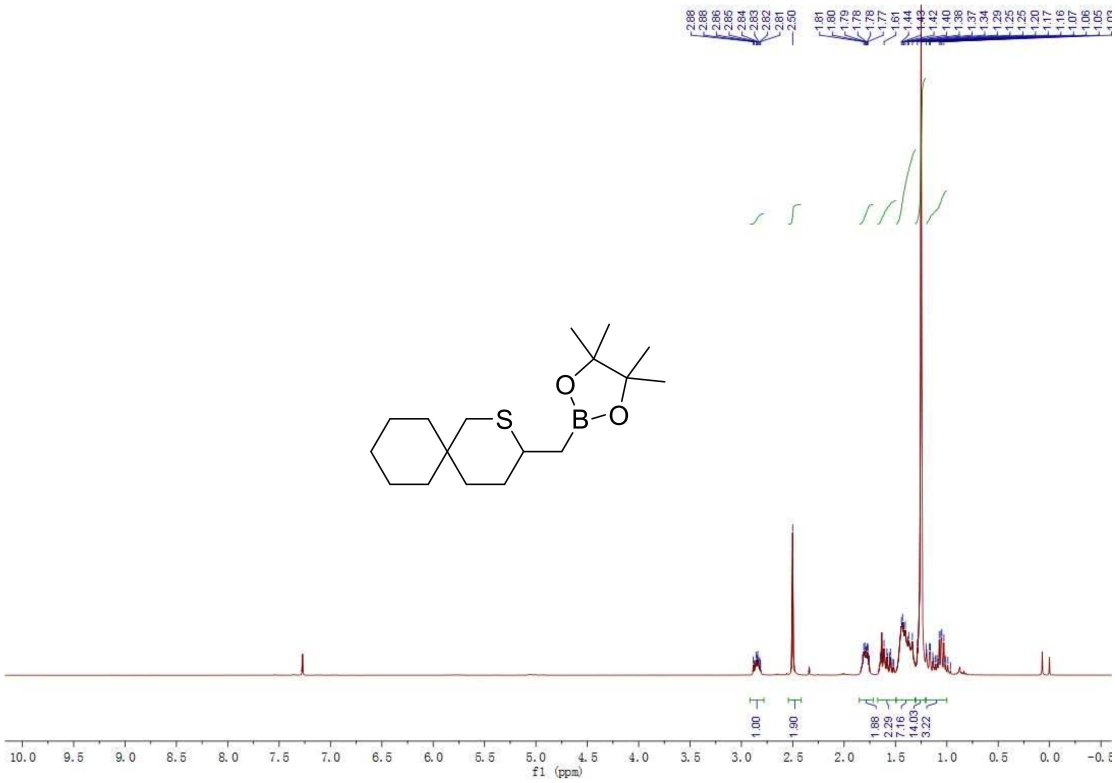
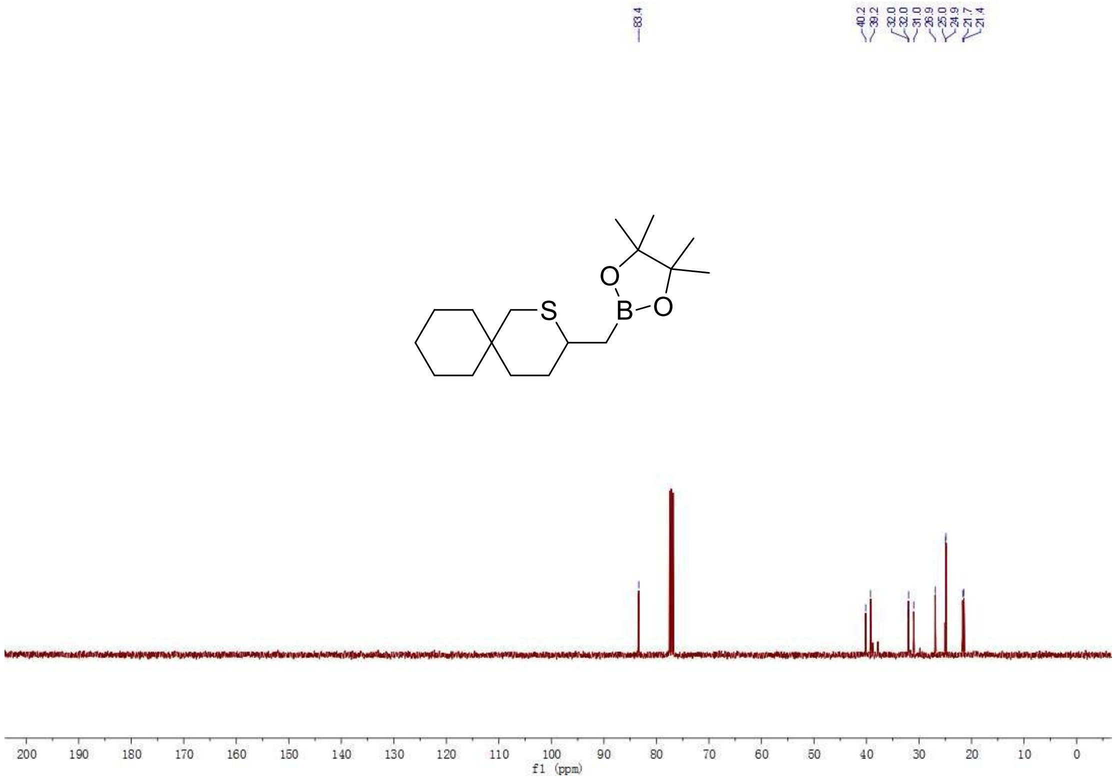
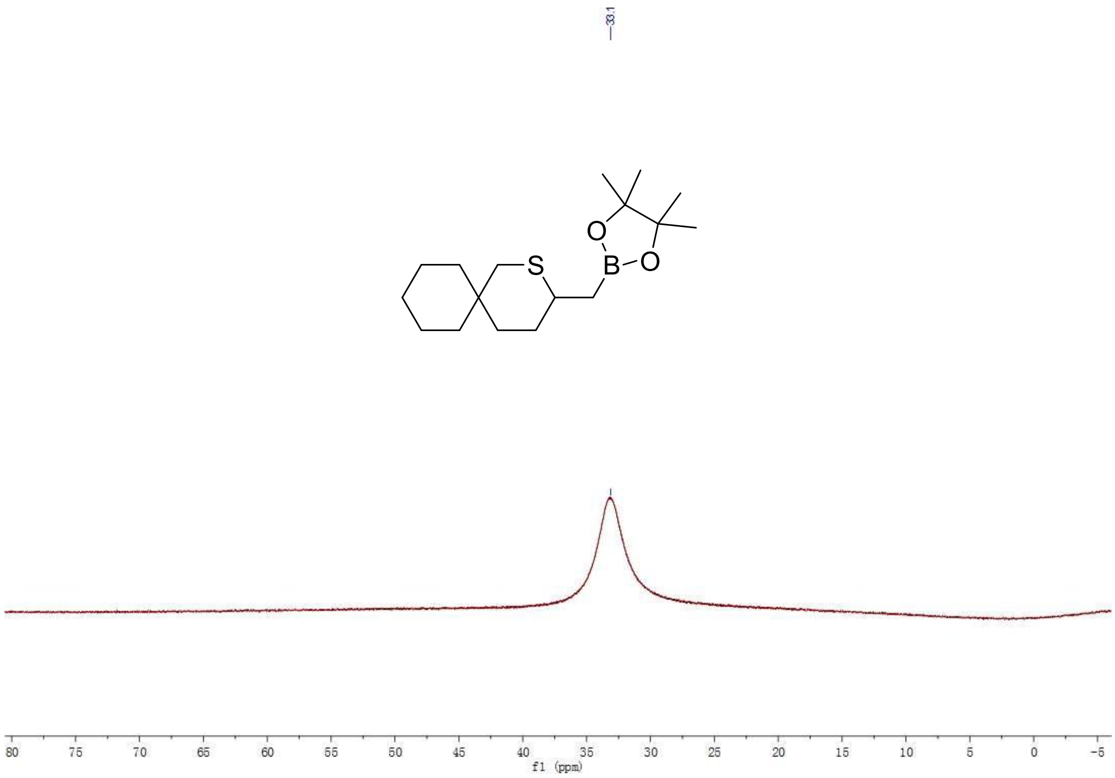
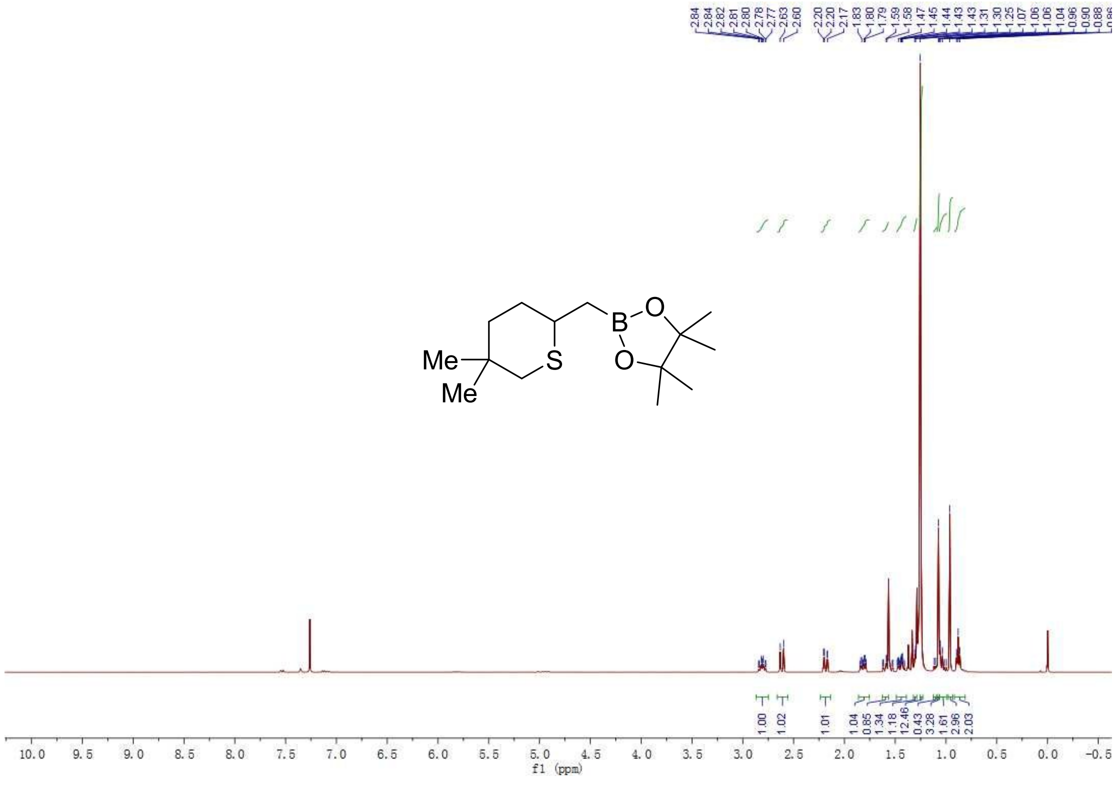
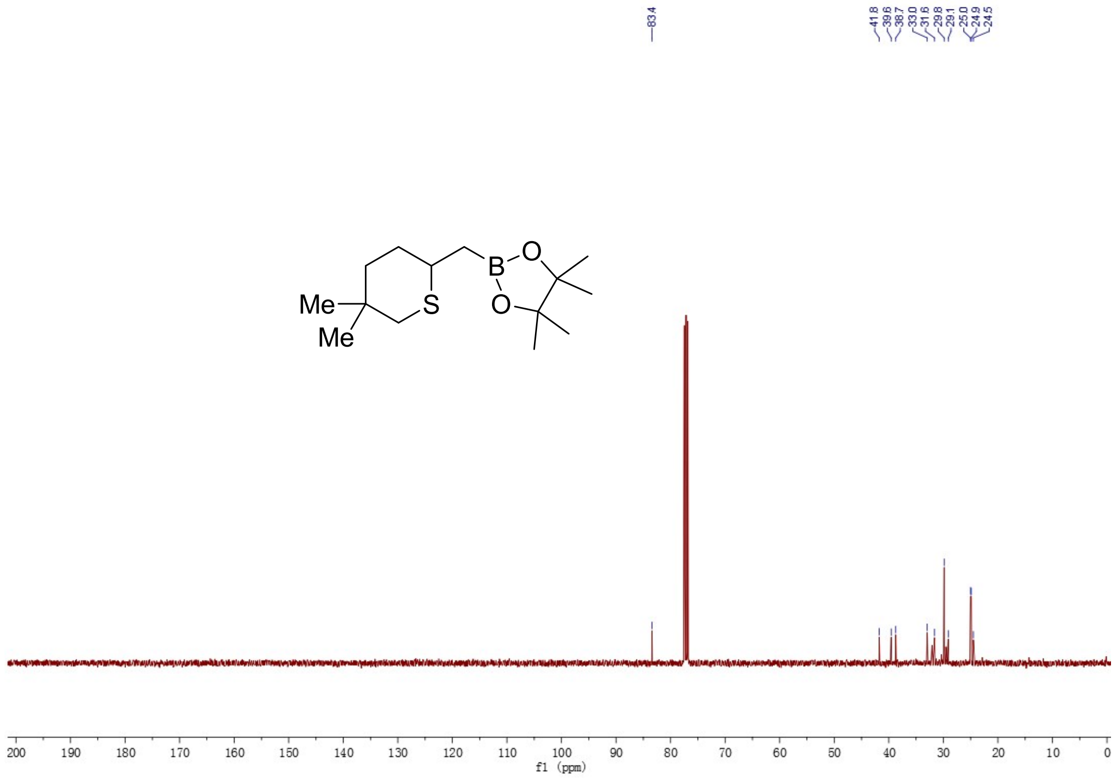
f1 (ppm)

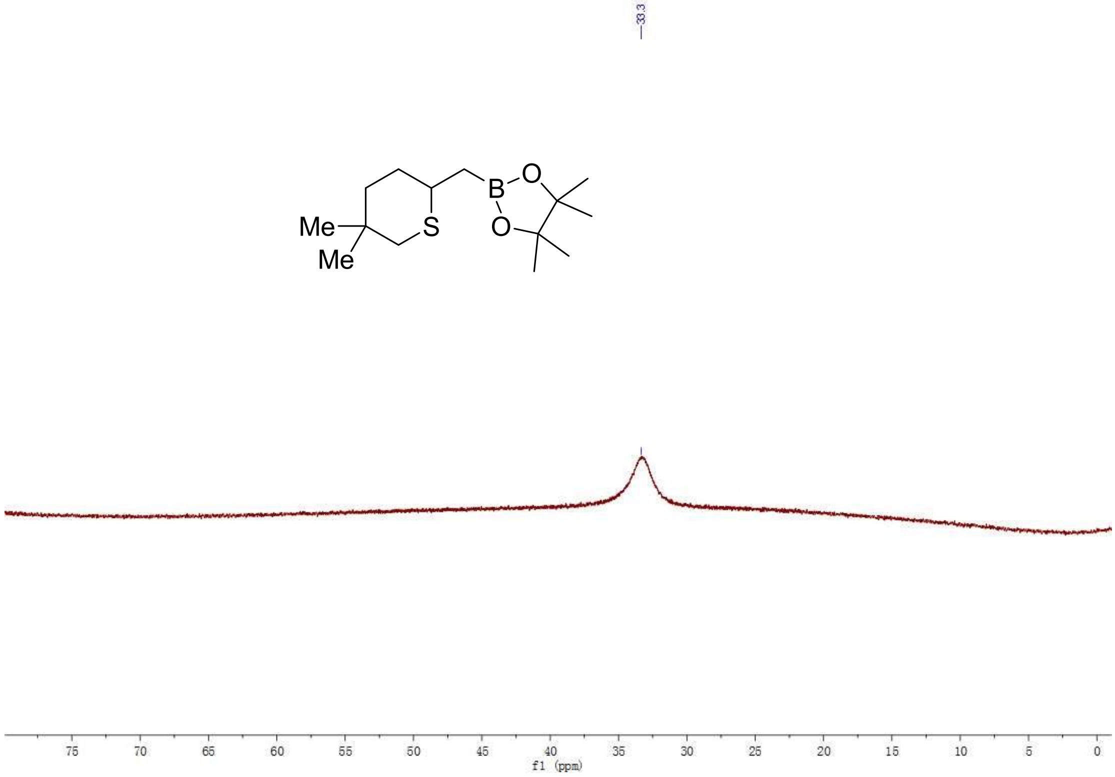

2.88
2.88
2.86
2.85
2.84
2.83
2.82
2.81
2.50
1.81
1.80
1.79
1.78
1.78
1.77
1.61
1.44
1.43
1.42
1.40
1.38
1.37
1.34
1.29
1.25
1.25
1.20
1.17
1.16
1.07
1.06
1.05
S
O
B
O
1.00
1.90
1.88
2.29
7.16
14.03
3.22
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

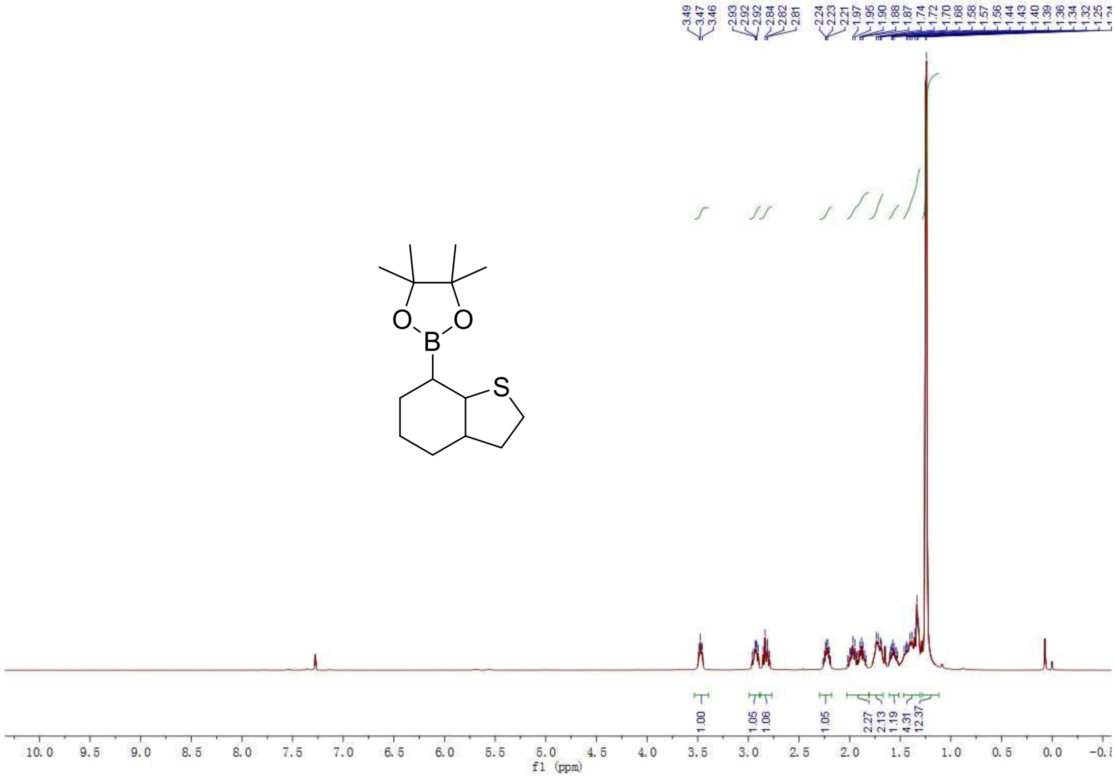

83.4
40.2
39.2
32.0
32.0
31.0
26.9
25.0
24.9
21.7
21.4
S
O
B
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

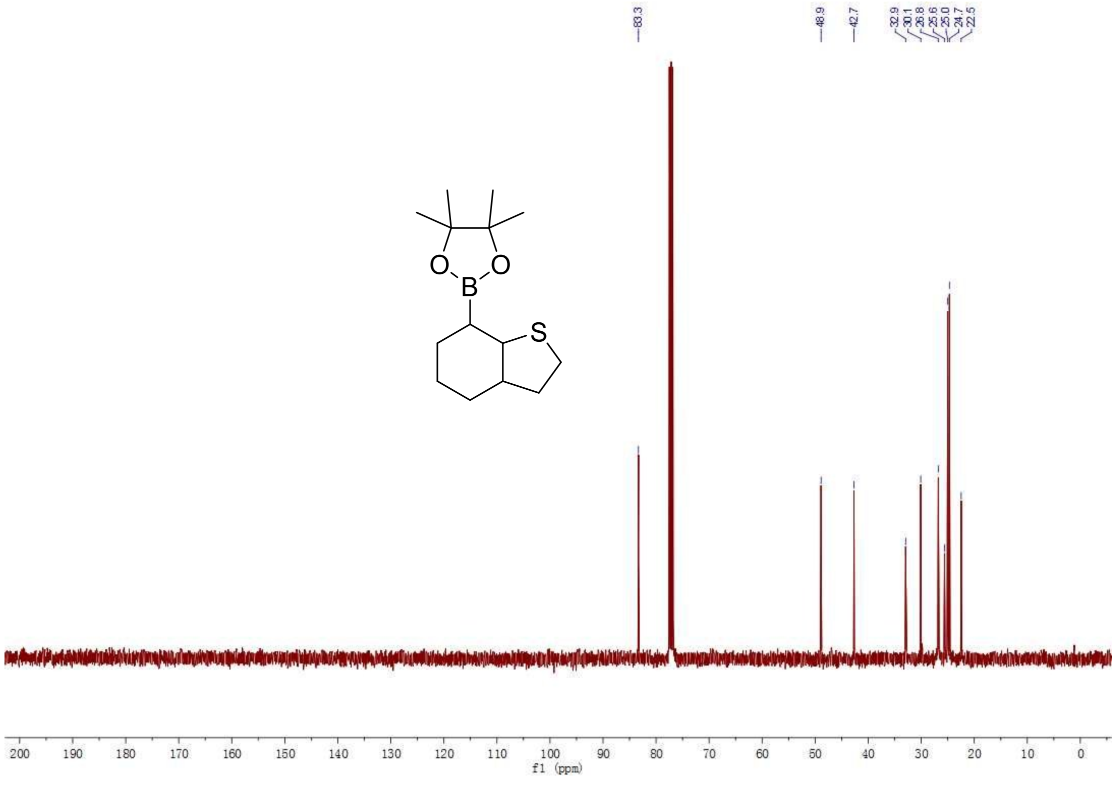

33.1
S
O
B
O
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
−5
f1 (ppm)

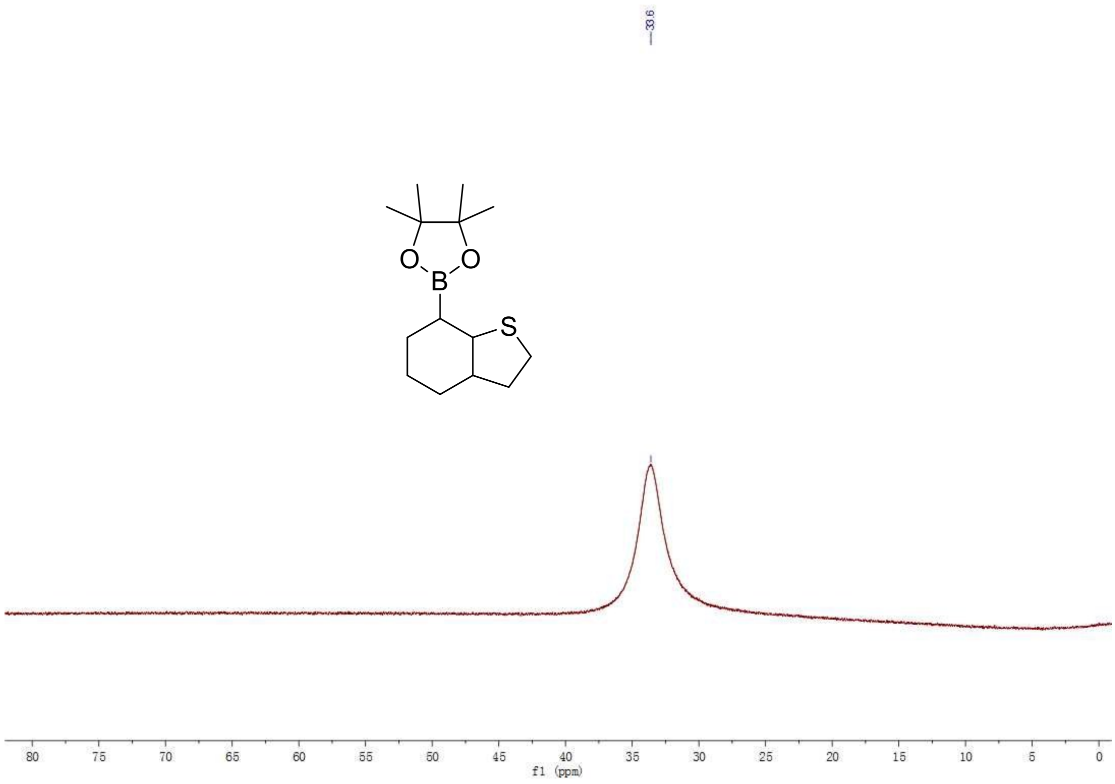

2.84
2.84
2.82
2.81
2.80
2.78
2.77
2.63
2.60
2.20
2.20
2.17
1.83
1.80
1.79
1.59
1.58
1.47
1.45
1.44
1.43
1.43
1.31
1.30
1.25
1.07
1.06
1.06
1.04
0.96
0.90
0.88
Me
Me
S
B
O
O
1.00
1.02
1.01
1.04
0.85
1.34
1.18
12.46
0.43
3.28
1.61
2.96
2.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


83.4
41.8
39.6
38.7
33.0
31.6
29.8
29.1
25.0
24.9
24.5
Me
Me
S
B
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

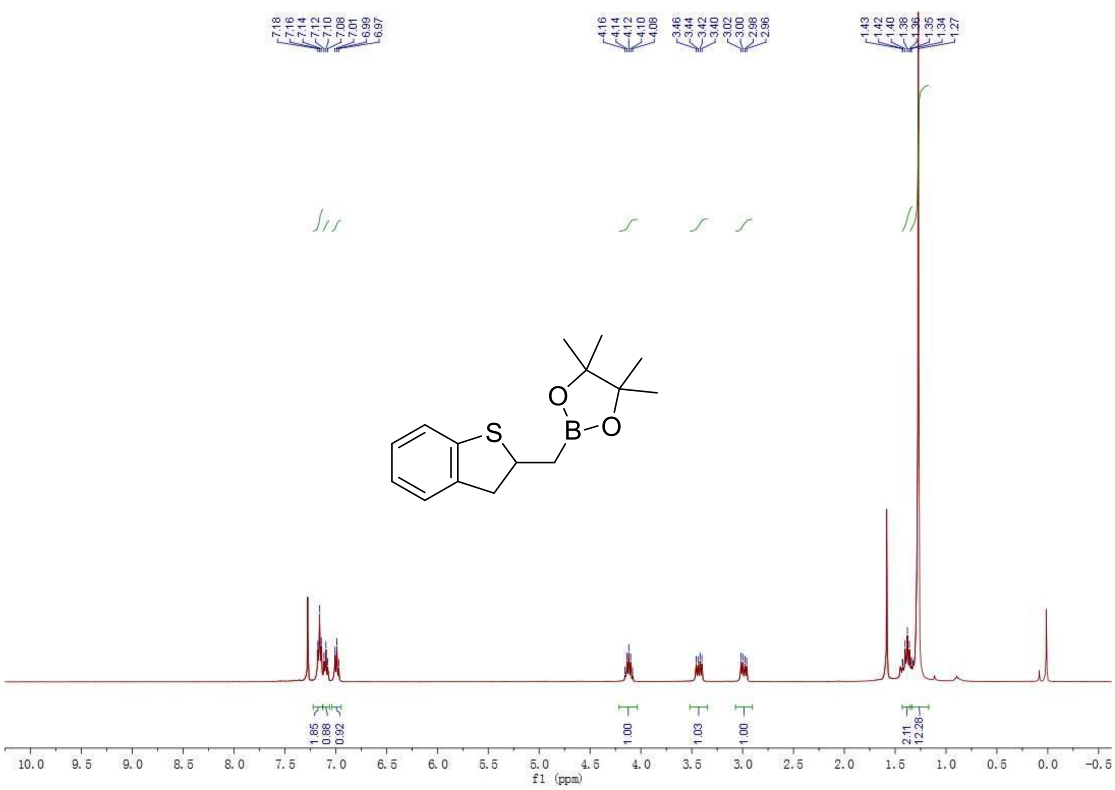

33.3
Me
Me
S
B
O
O
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)


3.49
3.47
3.46
2.93
2.92
2.92
2.84
2.82
2.81
2.24
2.23
2.21
1.97
1.95
1.90
1.88
1.87
1.74
1.72
1.70
1.68
1.58
1.57
1.56
1.44
1.43
1.40
1.39
1.36
1.34
1.32
1.25
O
B
O
S
1.00
1.05
1.06
1.05
2.27
2.13
1.19
4.31
12.37
10.0
9.5
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)

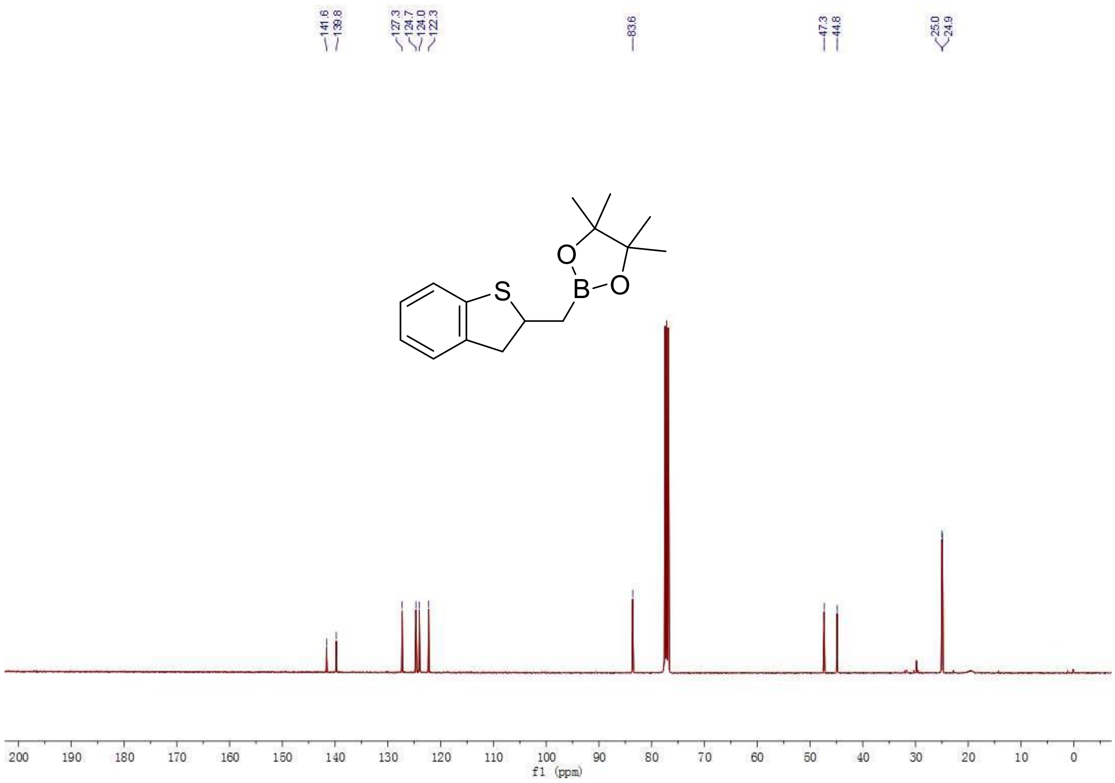

83.3
48.9
42.7
32.9
30.1
26.8
25.6
25.0
24.7
22.5
O
B
O
S
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

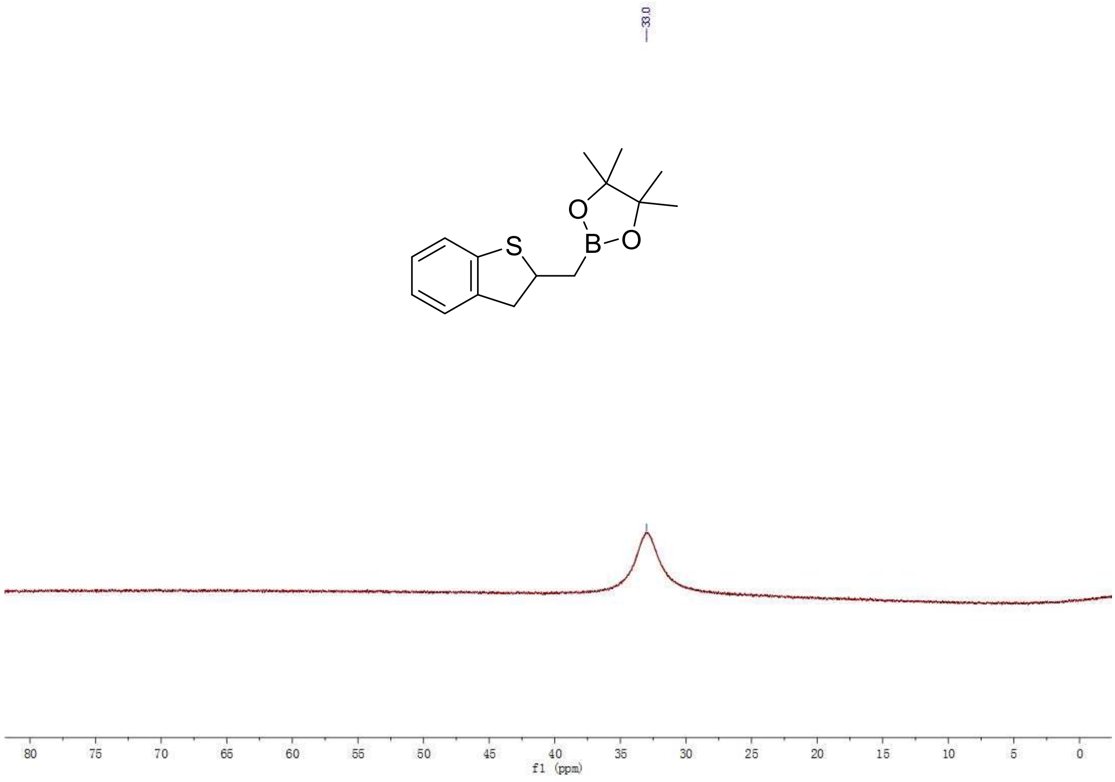


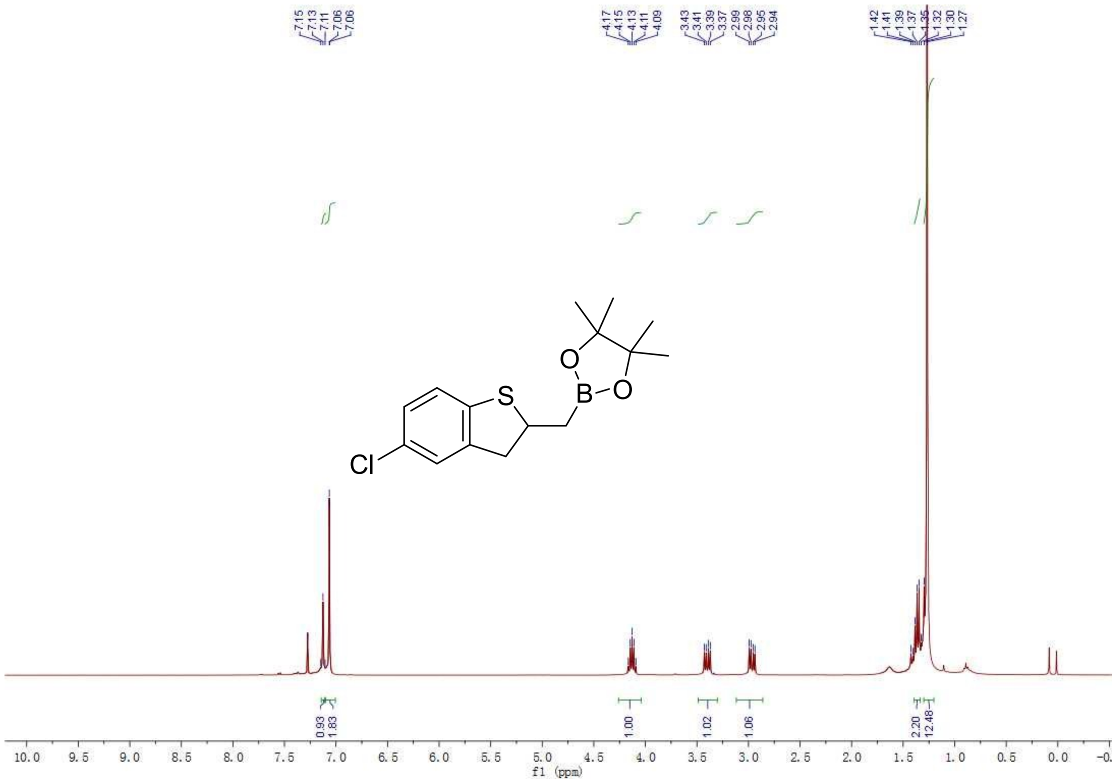
33.6
O
B
O
S
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)

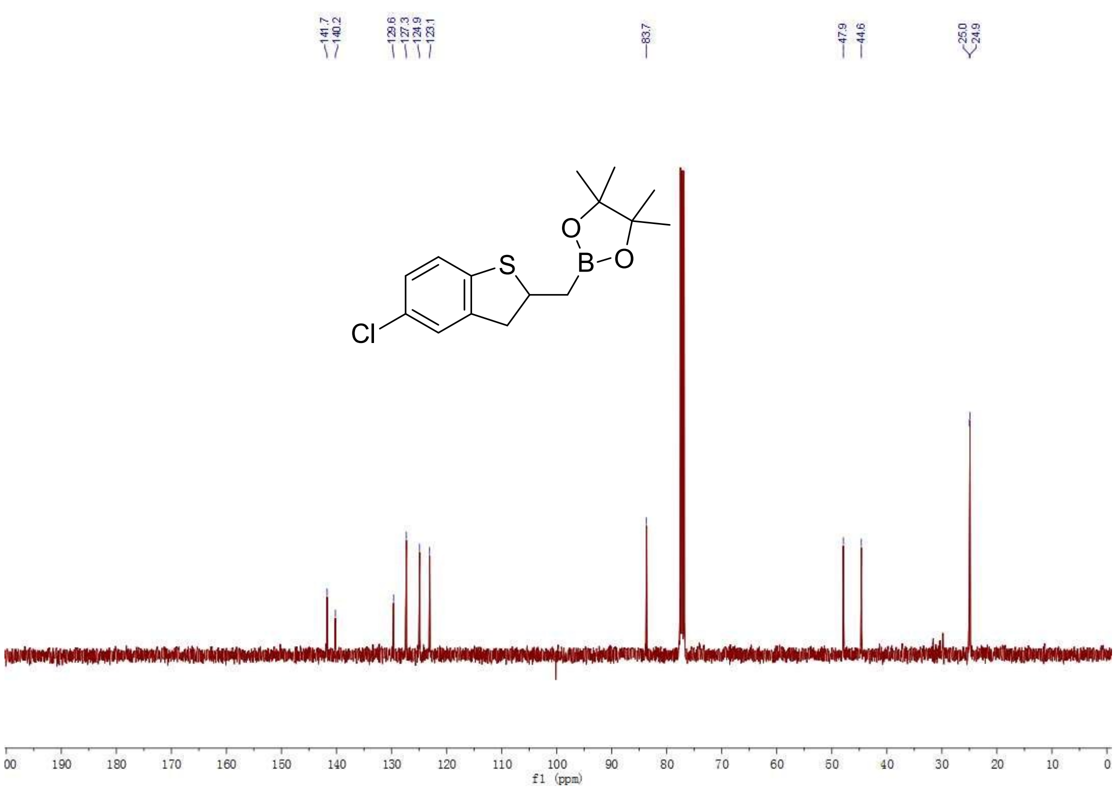


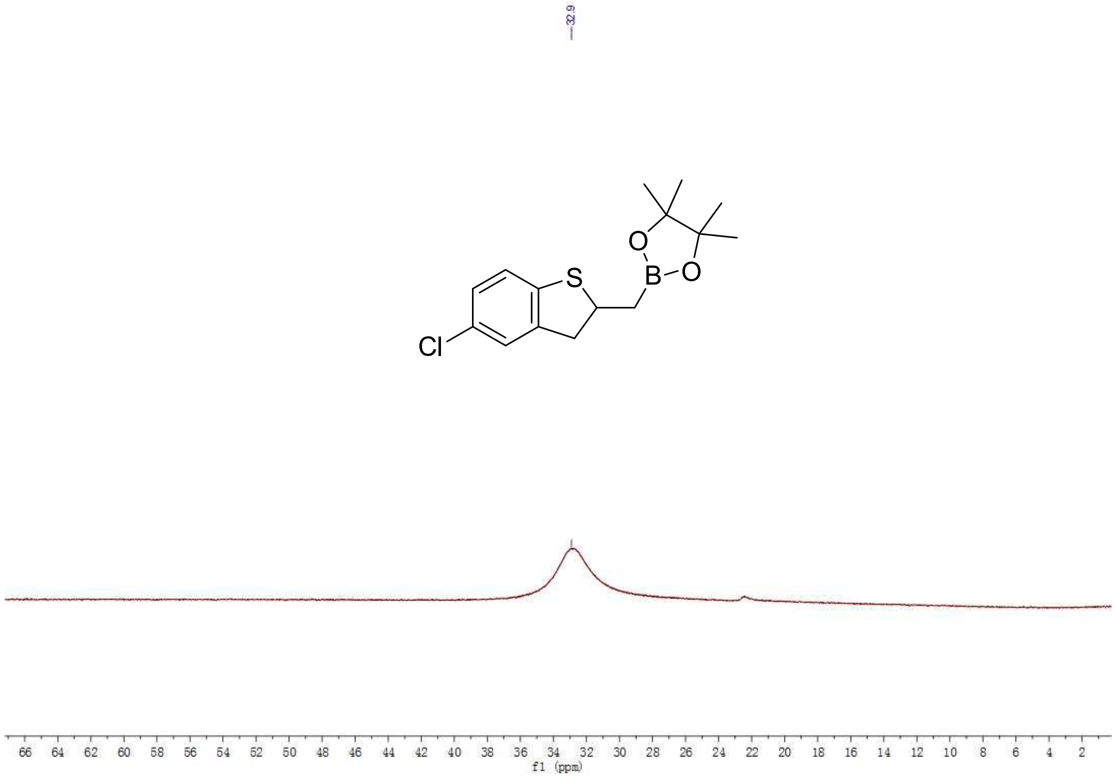
7.18
7.16
7.14
7.12
7.10
7.08
7.01
6.99
6.97
4.16
4.14
4.12
4.10
4.08
3.46
3.44
3.42
3.40
3.02
3.00
2.98
2.96
1.43
1.42
1.40
1.38
1.36
1.35
1.34
1.27
S
O
B
O
1.85
0.88
0.92
1.00
1.03
1.00
2.11
12.28
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

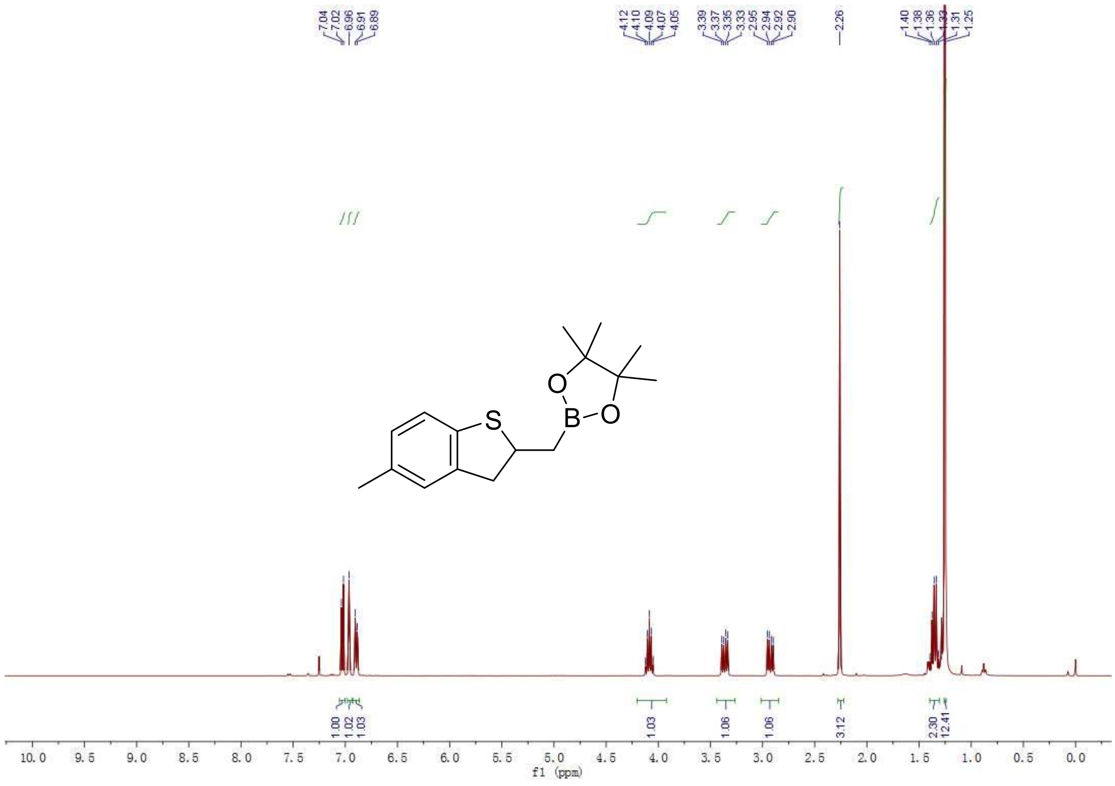

141.6
139.8
127.3
124.7
124.0
122.3
83.6
47.3
44.8
25.0
24.9
S
B
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

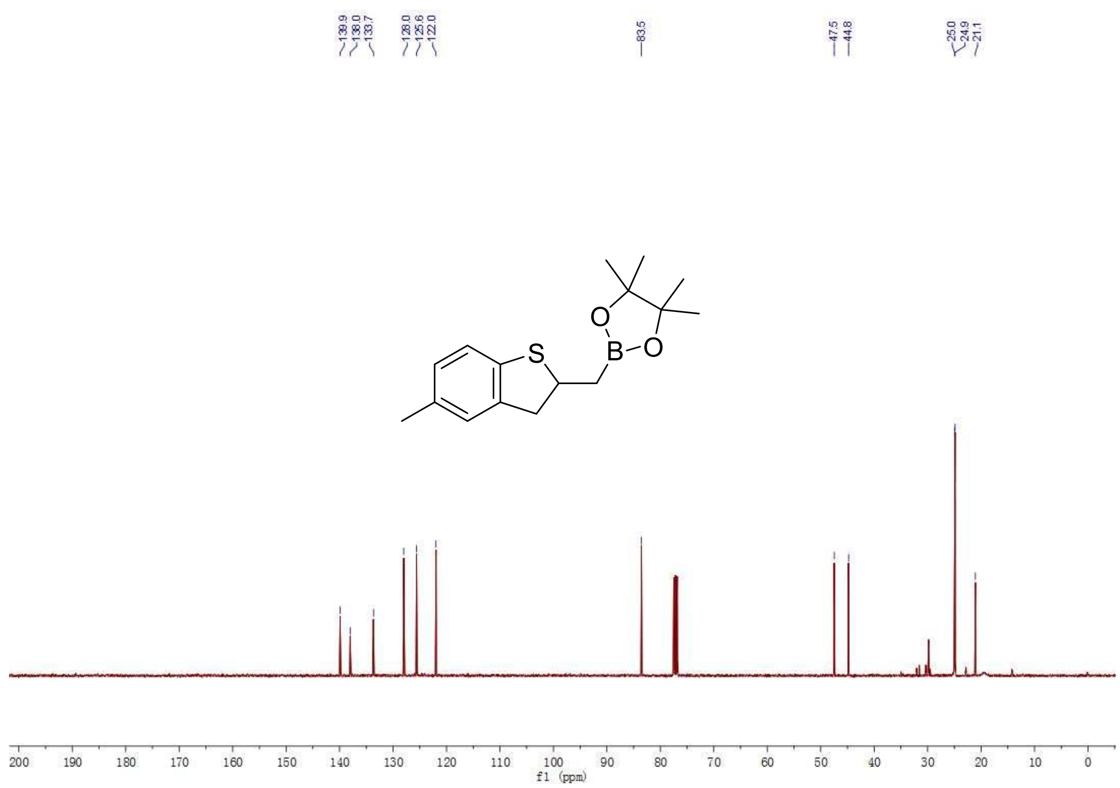

33.0
S
B
O
O
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)

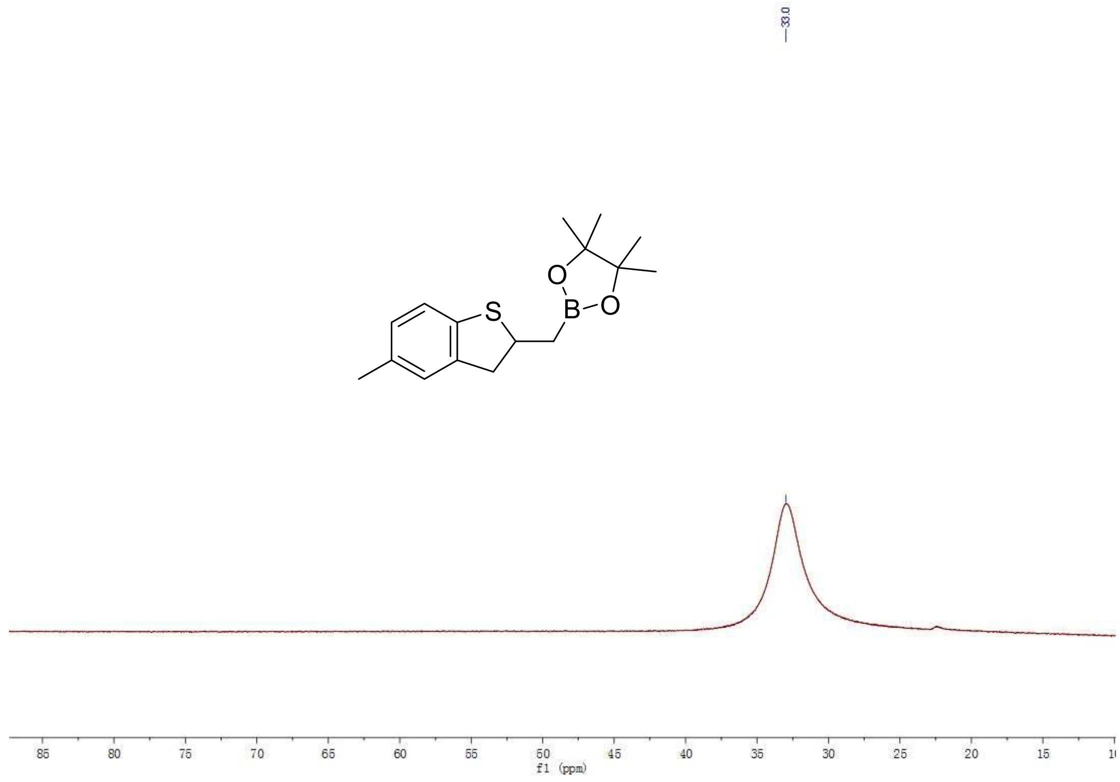

7.15
7.13
7.11
7.06
7.06
4.17
4.15
4.13
4.11
4.09
3.43
3.41
3.39
3.37
2.99
2.98
2.95
2.94
1.42
1.41
1.39
1.37
1.35
1.32
1.30
1.27
S
O
B
O
Cl
0.93
1.83
1.00
1.02
1.06
2.20
12.48
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

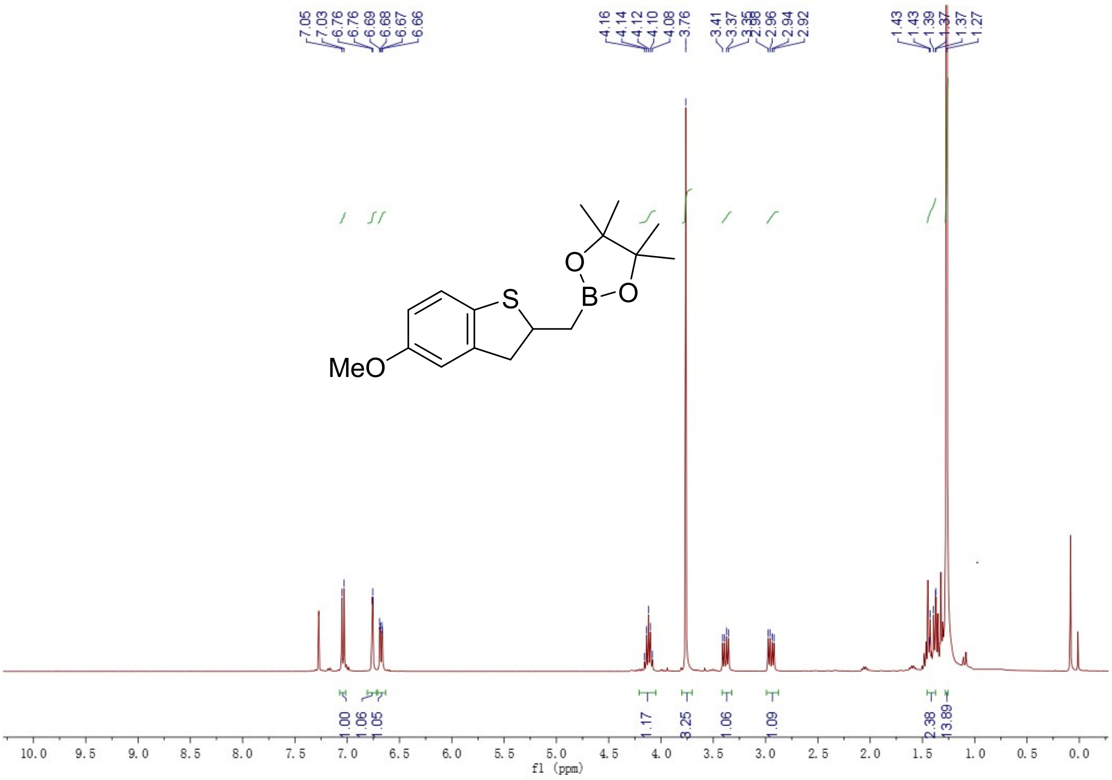

141.7
140.2
129.6
127.3
124.9
123.1
83.7
47.9
44.6
25.0
24.9
S
O
B
O
Cl
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


32.9
S
O
B
O
Cl
66 64 62 60 58 56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2
f1 (ppm)


7.04
7.02
6.96
6.91
6.89
4.12
4.10
4.09
4.07
4.05
3.39
3.37
3.35
3.33
2.95
2.94
2.92
2.90
2.26
1.40
1.38
1.36
1.32
1.31
1.25
S
O
B
O
1.00
1.02
1.03
1.03
1.06
1.06
3.12
2.30
12.41
10.0 9.5 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)


139.9
138.0
133.7
128.0
125.6
122.0
83.5
47.5
44.8
25.0
24.9
21.1
S
O
B
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


33.0
S
O
B
O
85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
f1 (ppm)


7.05
7.03
6.76
6.76
6.69
6.68
6.67
6.66
4.16
4.14
4.12
4.10
4.08
3.76
3.41
3.37
3.35
2.98
2.96
2.94
2.92
1.43
1.43
1.39
1.37
1.37
1.27
S
O
B
O
MeO
1.00
1.06
1.05
1.17
3.25
1.06
1.09
2.38
13.89
10.0
9.5
9.0
8.5
8.0
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7.0
6.5
6.0
5.5
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1.0
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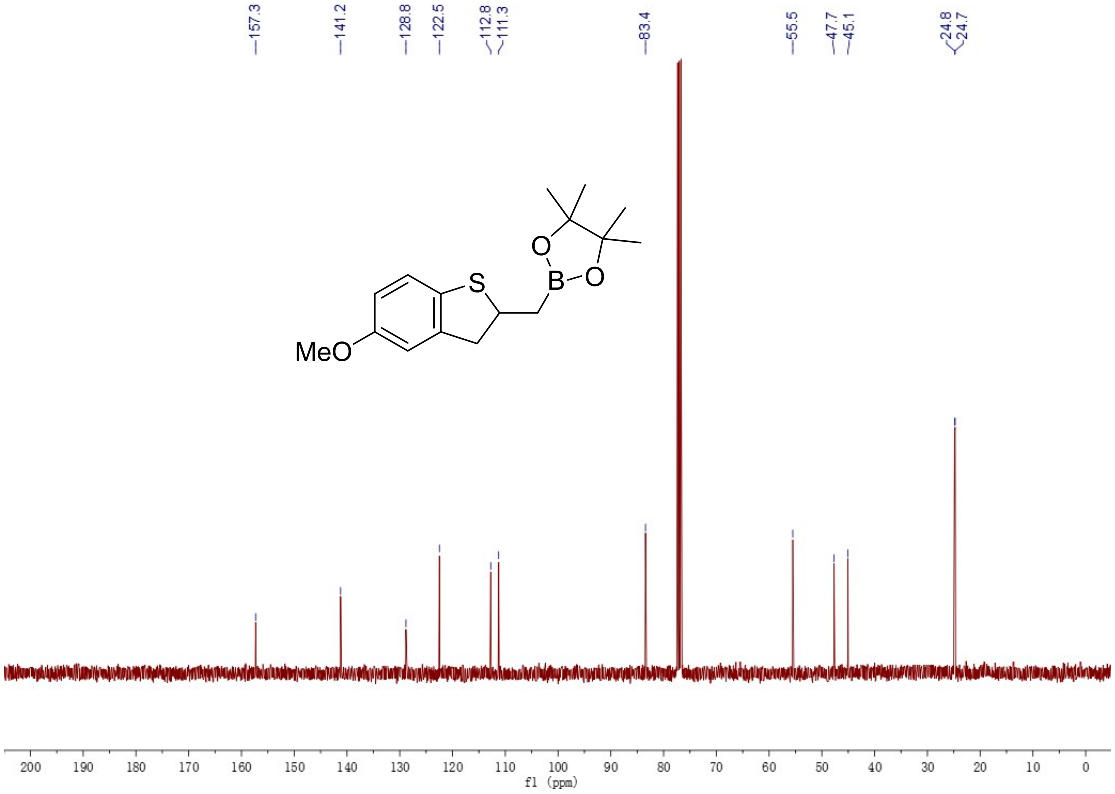
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111.3
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55.5
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24.8
24.7
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O
B
O
MeO
200
190
180
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130
120
110
100
90
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50
40
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10
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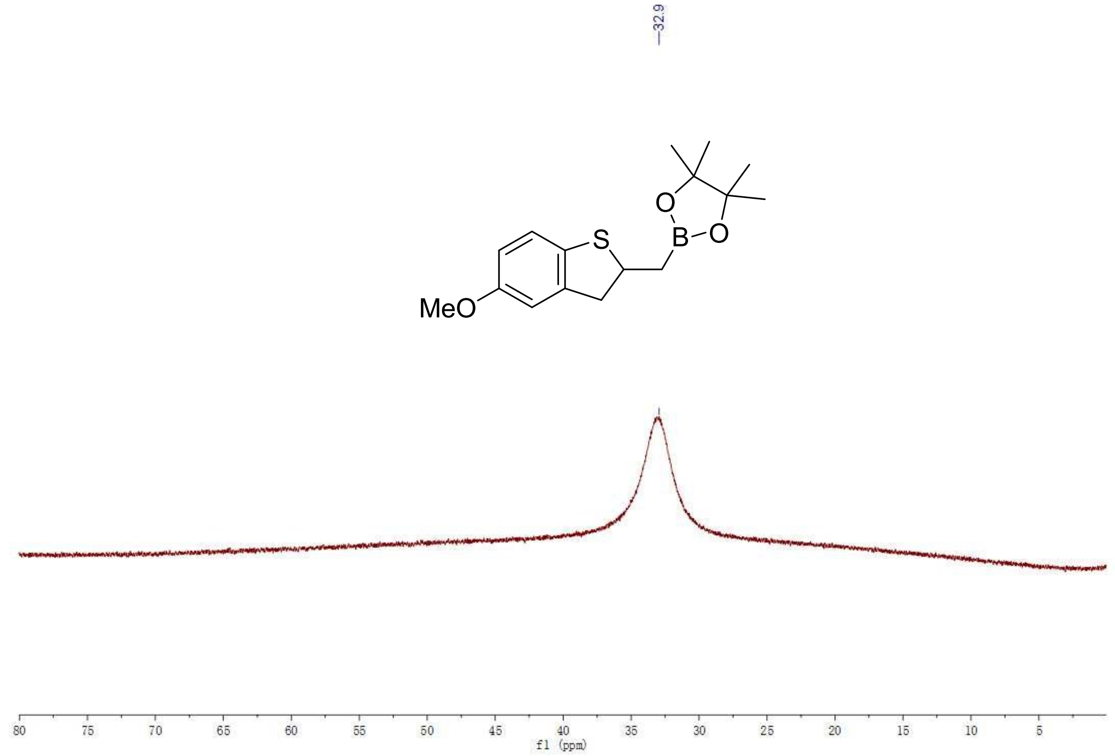
f1 (ppm)



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O
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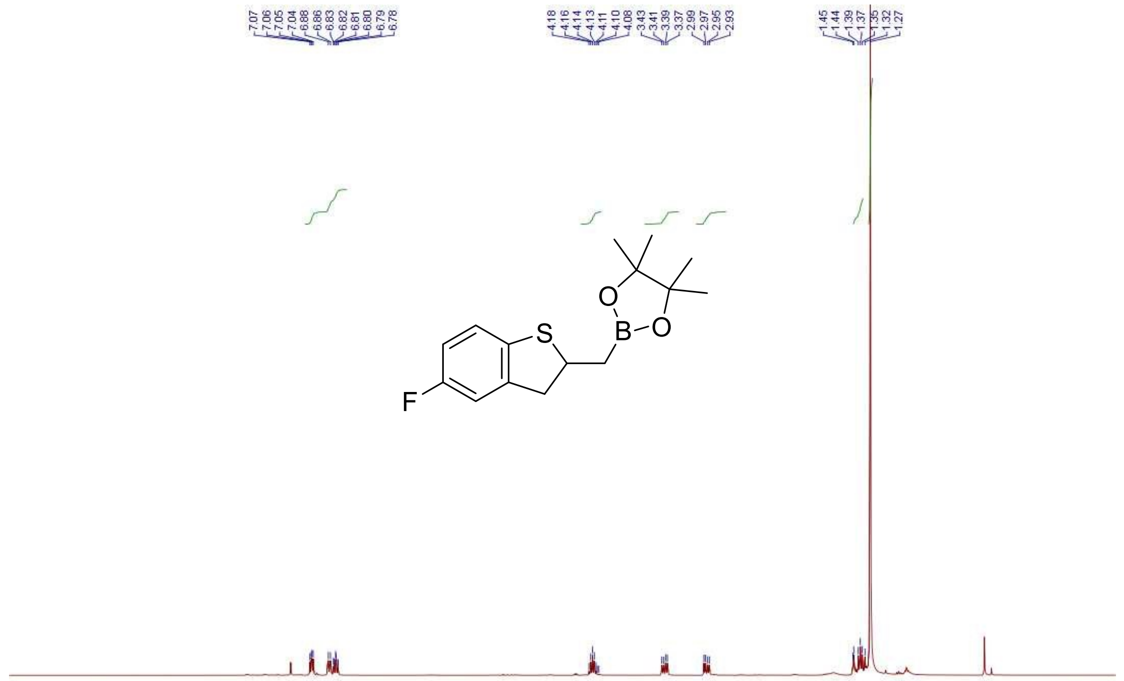
f1 (ppm)



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4.16
4.14
4.13
4.11
4.10
4.08
3.43
3.41
3.39
3.37
2.99
2.97
2.95
2.93
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1.37
1.35
1.32
1.27
F
S
O
B
O
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1.07
1.08
2.26
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6.0
5.5
5.0
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4.0
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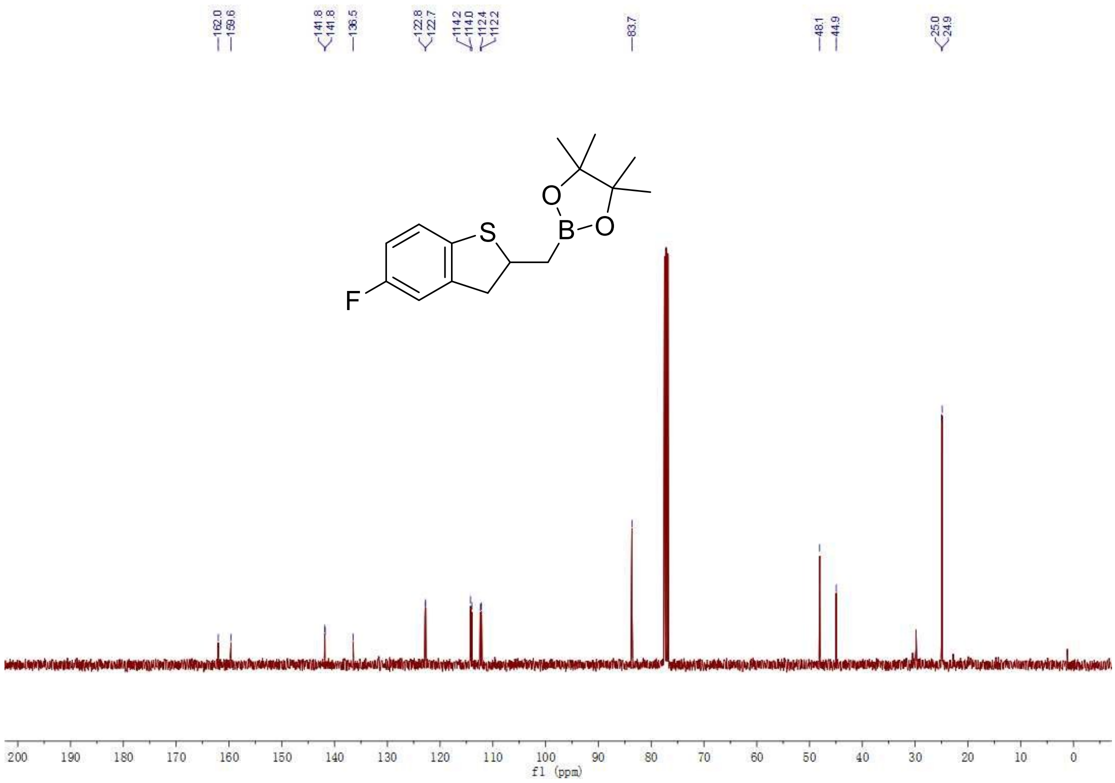
f1 (ppm)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44.9
25.0
24.9
O
S
B
O
F
200
190
180
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130
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100
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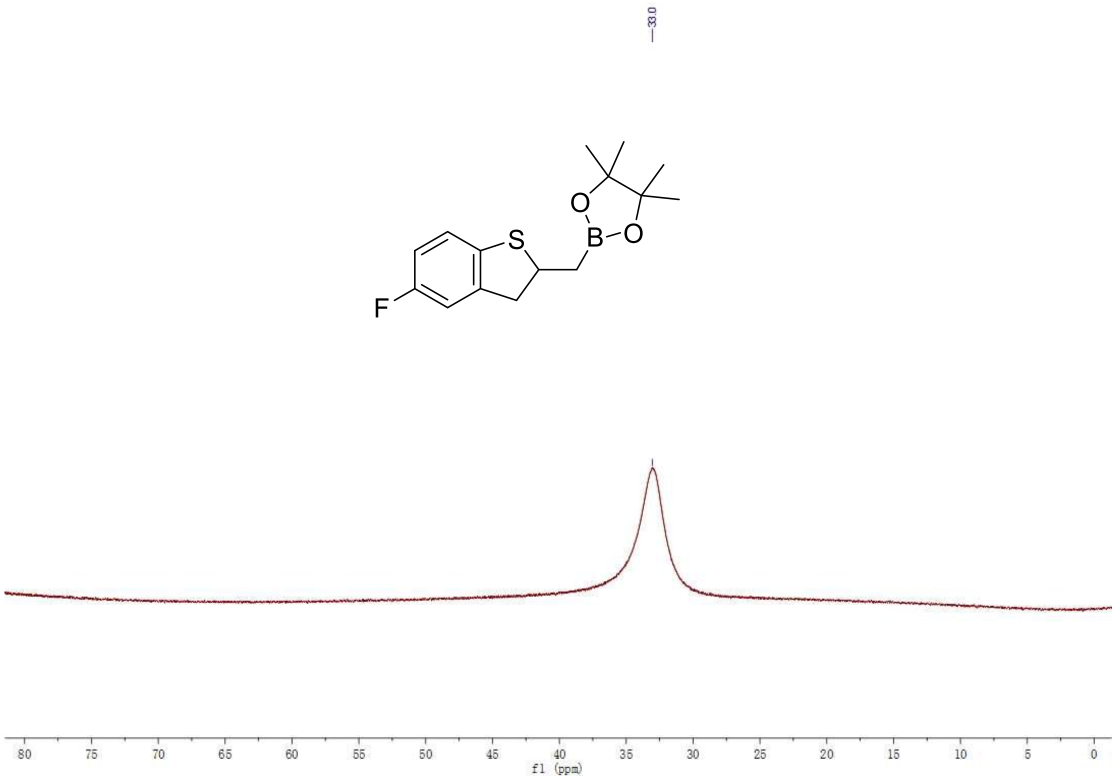
f1 (ppm)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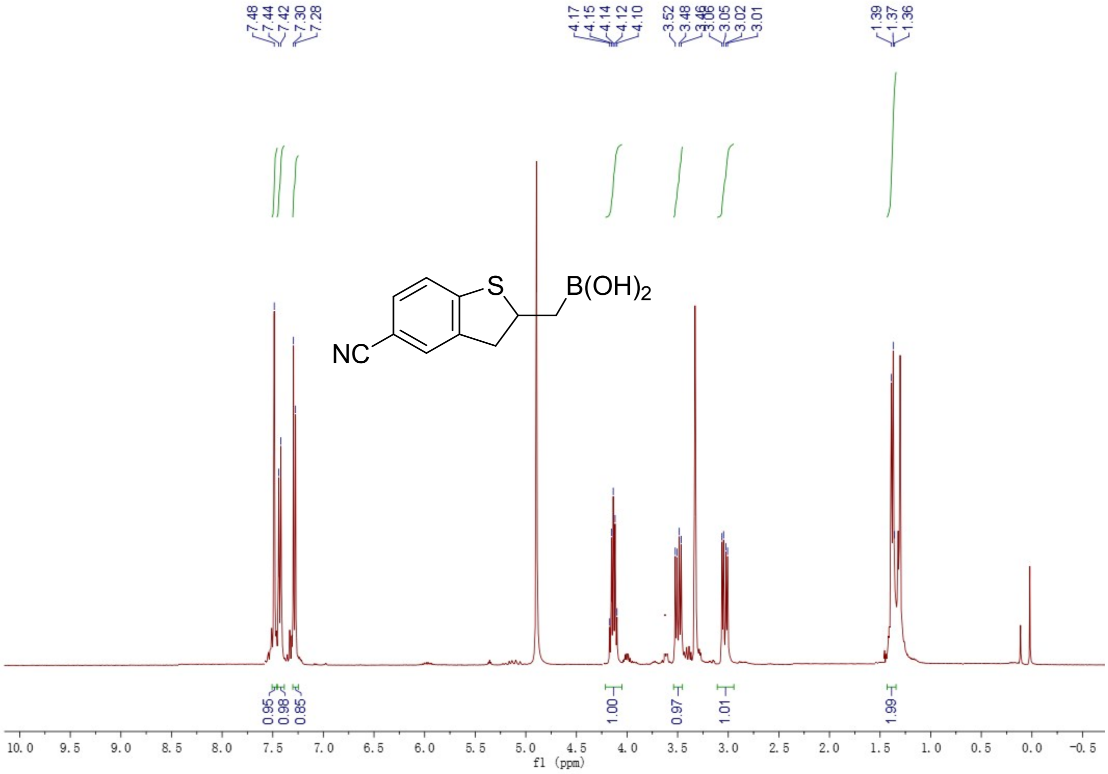
f1 (ppm)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4.10
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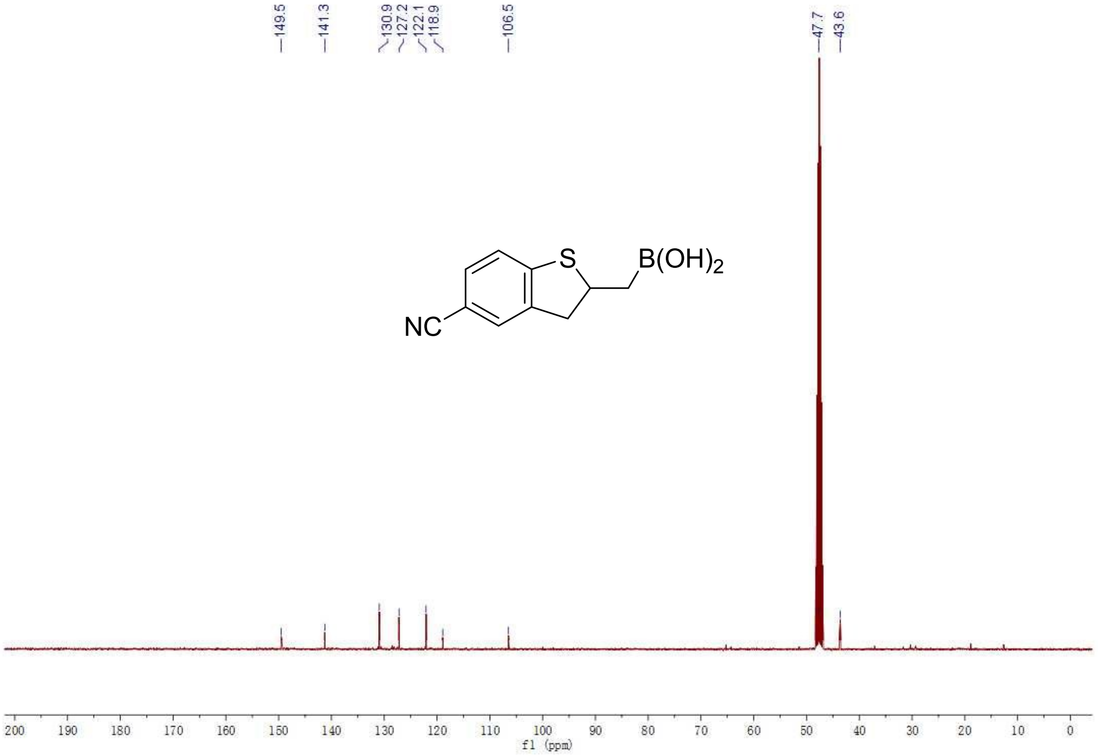
3.46
3.06
3.05
3.02
3.01
1.39
1.37
1.36
S
B(OH)2
NC
0.95
0.98
0.85
1.00
0.97
1.01
1.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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122.1
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S
B(OH)2
NC
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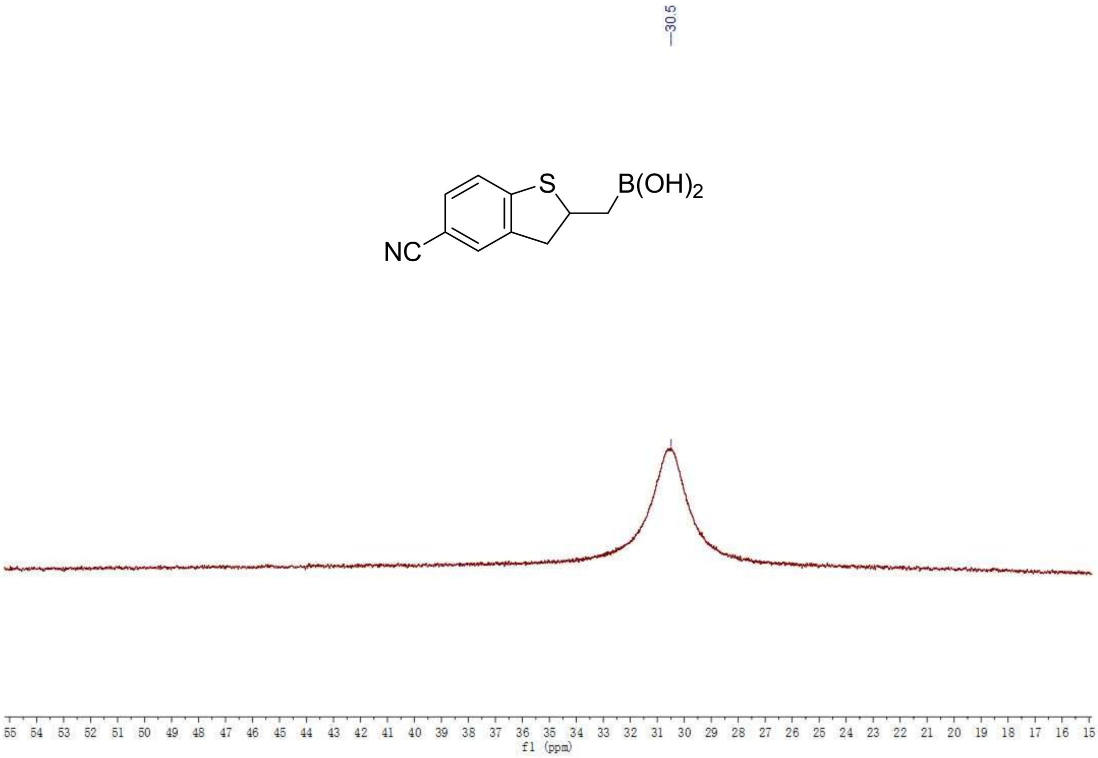
f1 (ppm)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B(OH)2
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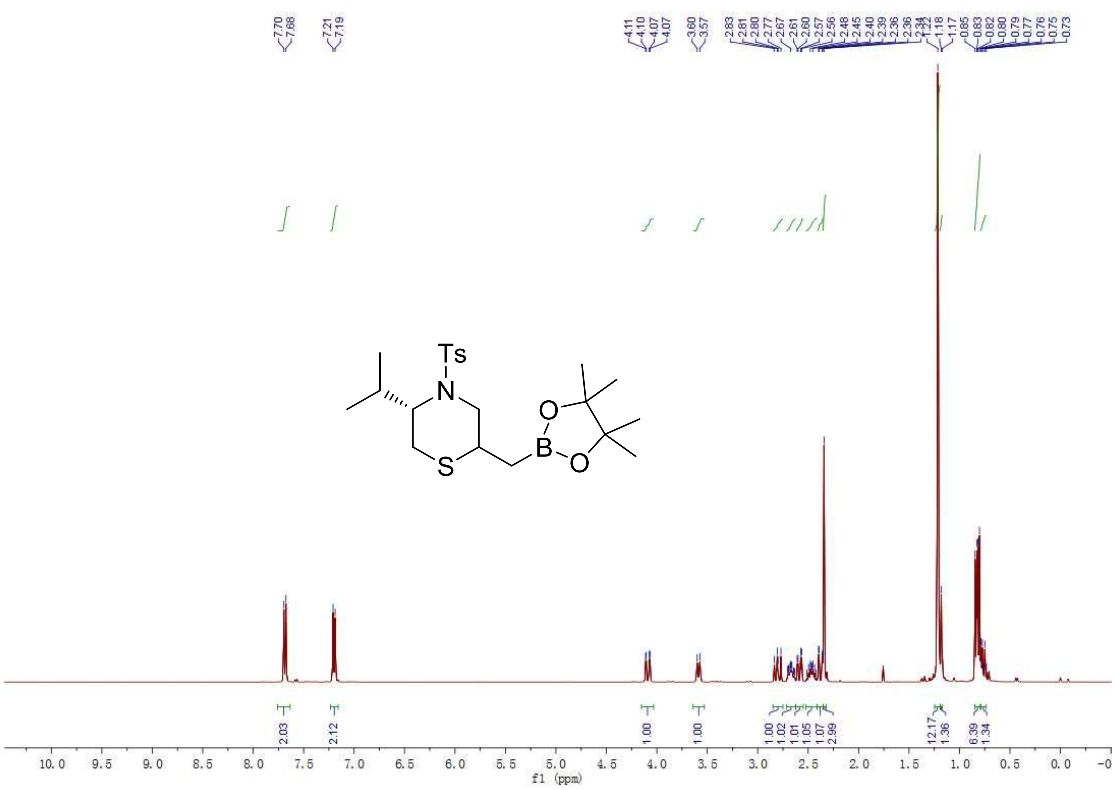
f1 (ppm)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4.11 4.10 4.07 4.07 3.60 3.57
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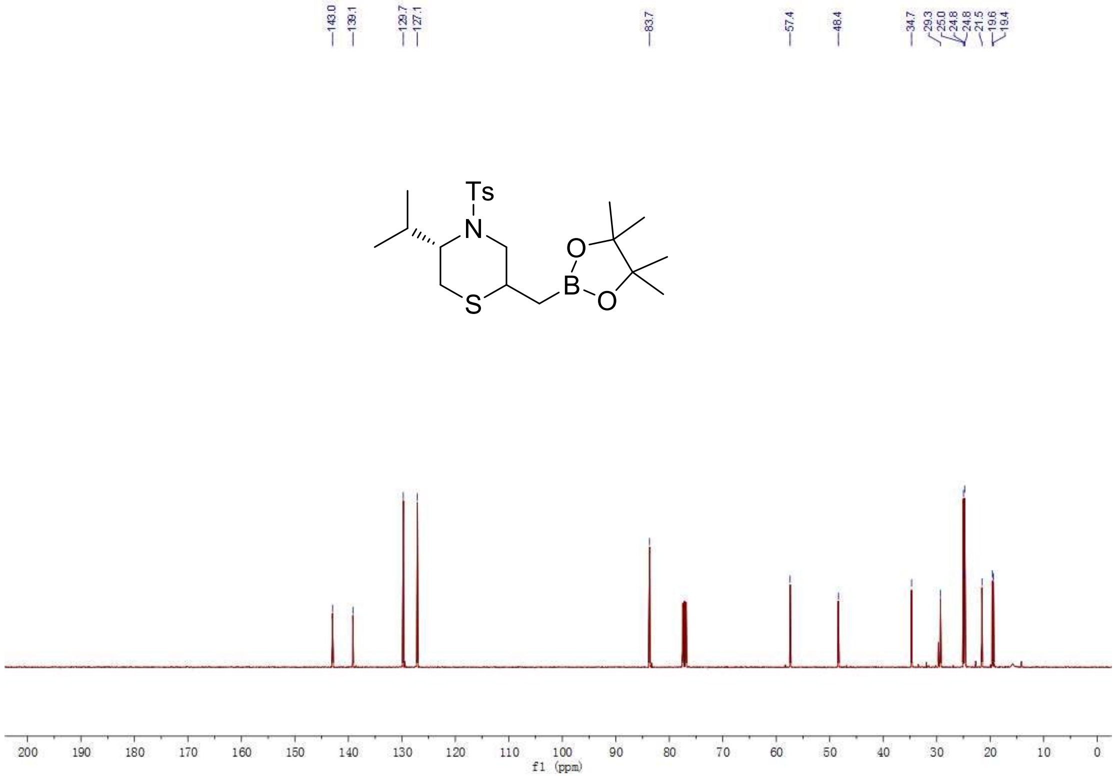
1.22 1.18 1.17 0.85 0.83 0.82 0.80 0.79 0.77 0.76 0.75 0.73
Ts
N
S
O
B
O
2.03 2.12 1.00 1.00 1.00 1.02 1.01 1.05 1.07 2.99 12.17 1.36 6.39 1.34
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)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19.4
Ts
N
S
B
O
O
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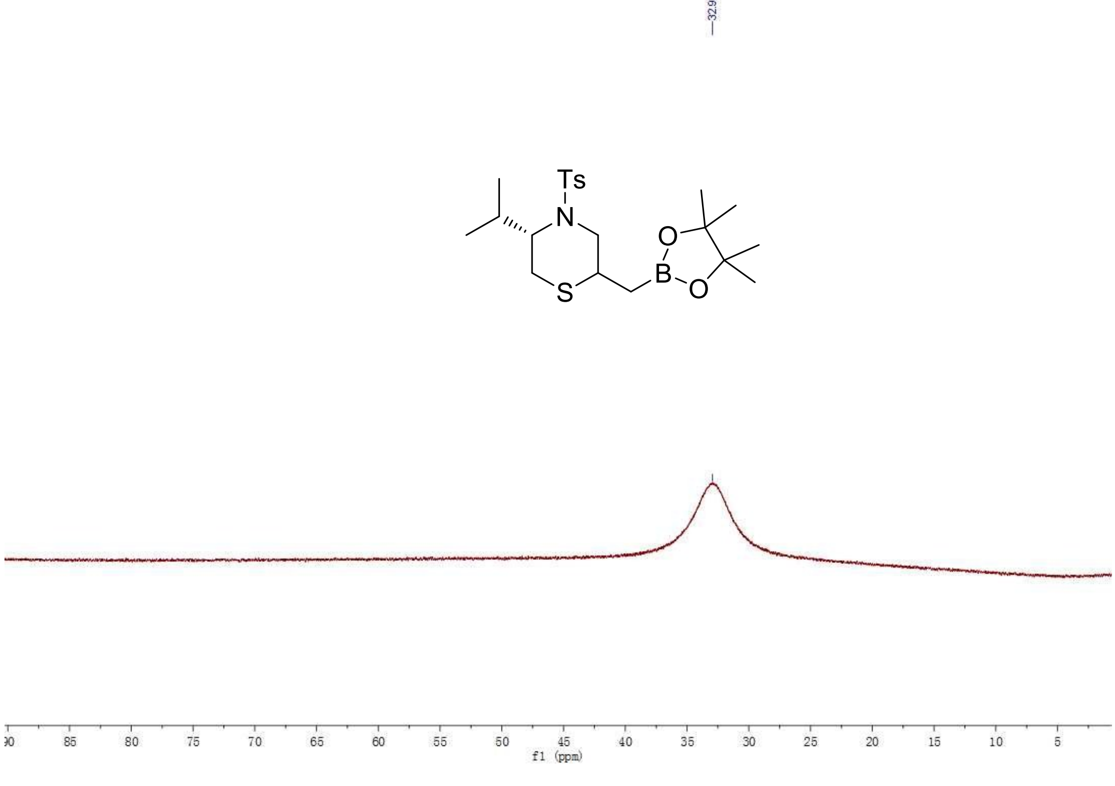
f1 (ppm)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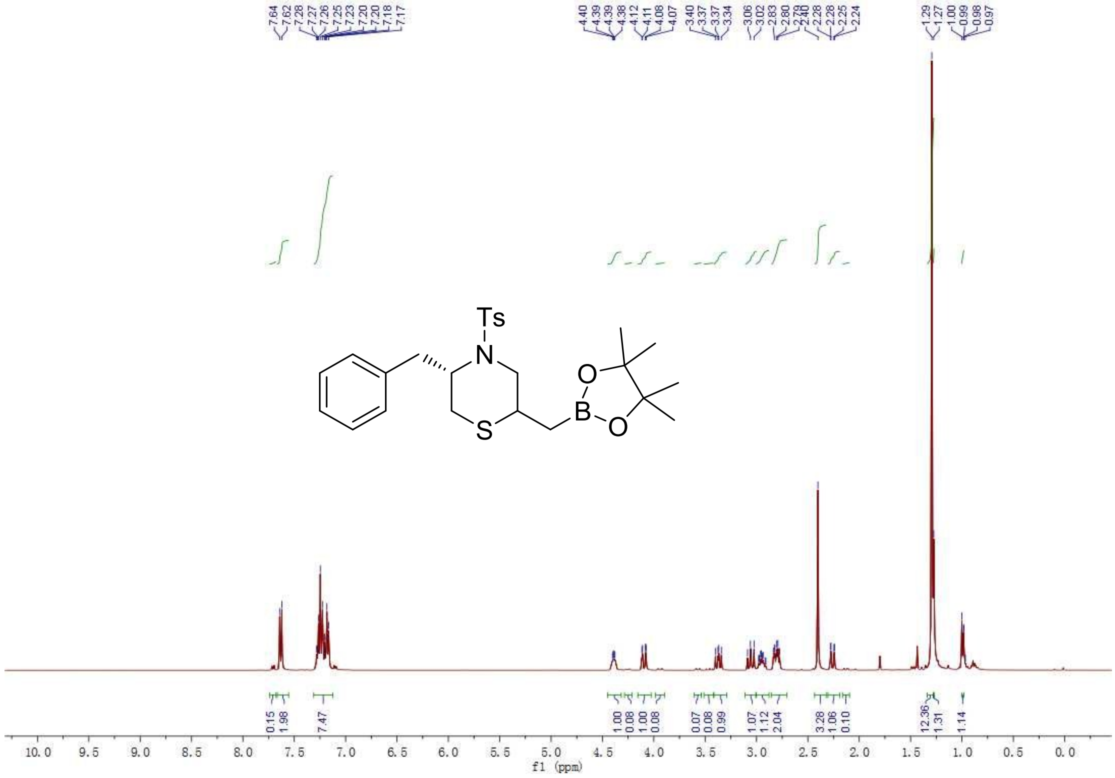
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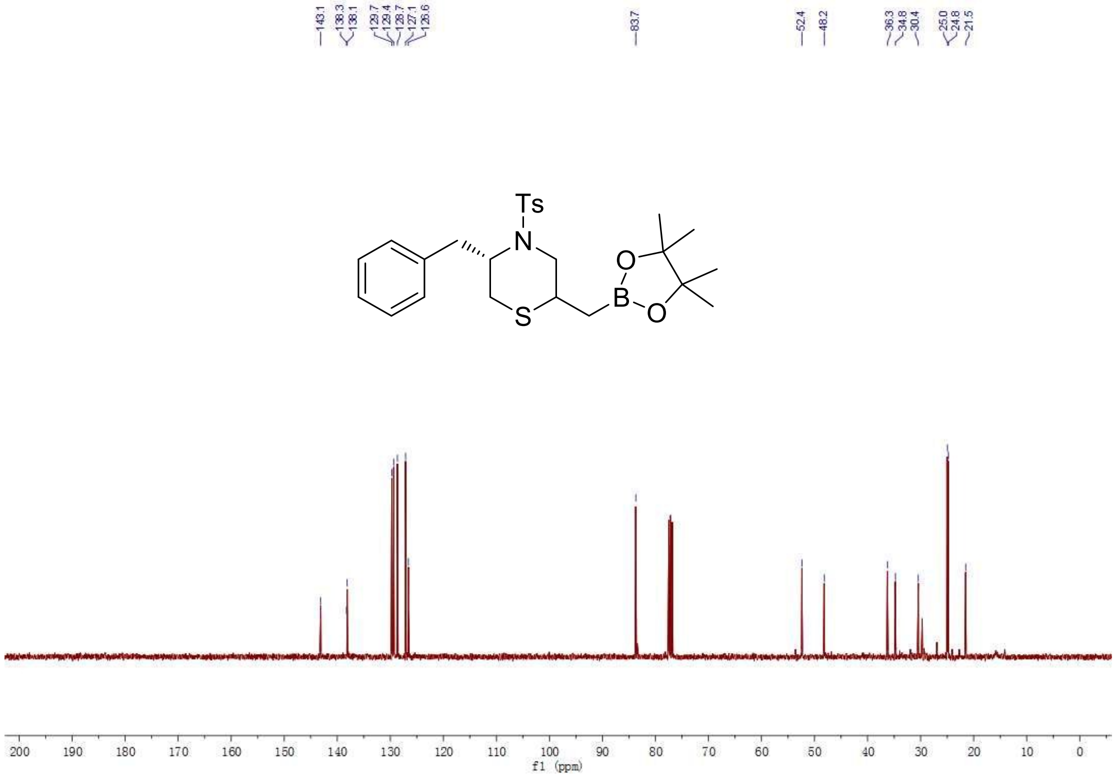
4.39
4.38
4.12
4.11
4.08
4.07
3.40
3.37
3.37
3.34
3.06
3.02
2.83
2.80
2.79
2.40
2.28
2.28
2.25
2.24
1.29
1.27
1.00
0.99
0.98
0.97
Ts
N
S
O
B
O
0.15
1.98
7.47
1.00
0.08
1.00
0.08
0.07
0.08
0.99
1.07
1.12
2.04
3.28
1.06
0.10
12.36
1.31
1.14
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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129.4
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127.1
126.6
83.7
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34.8
30.4
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24.8
21.5
Ts
N
S
O
B
O
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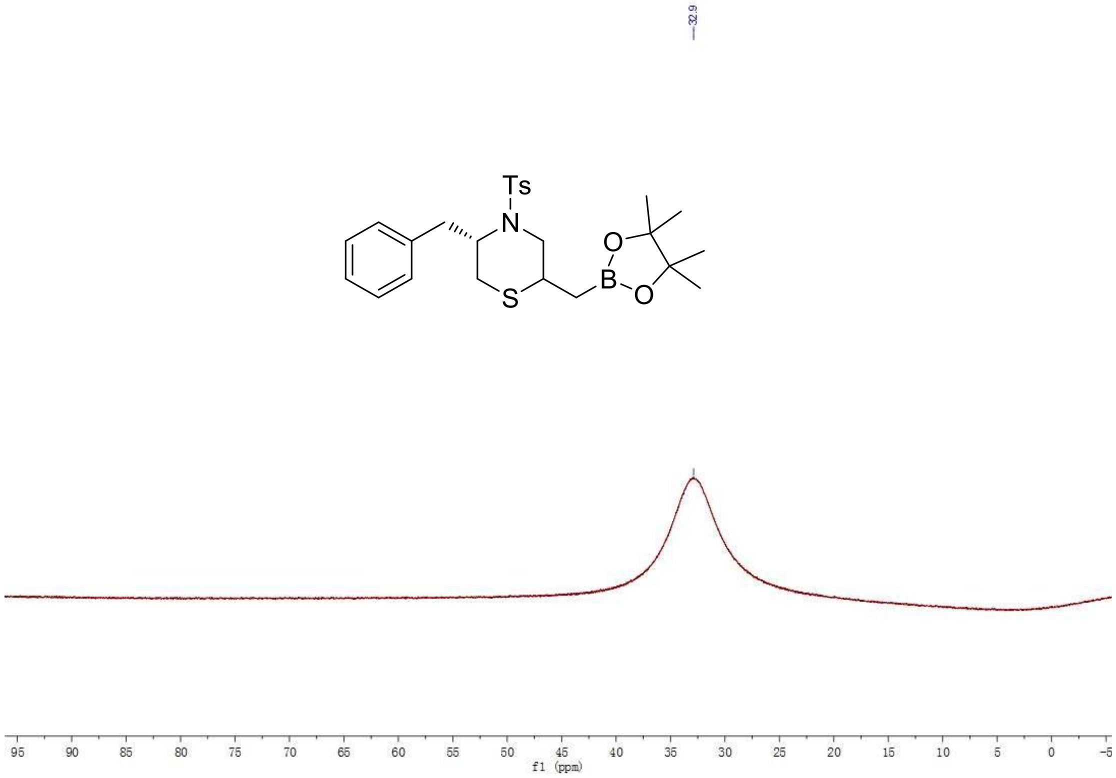
f1 (ppm)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15
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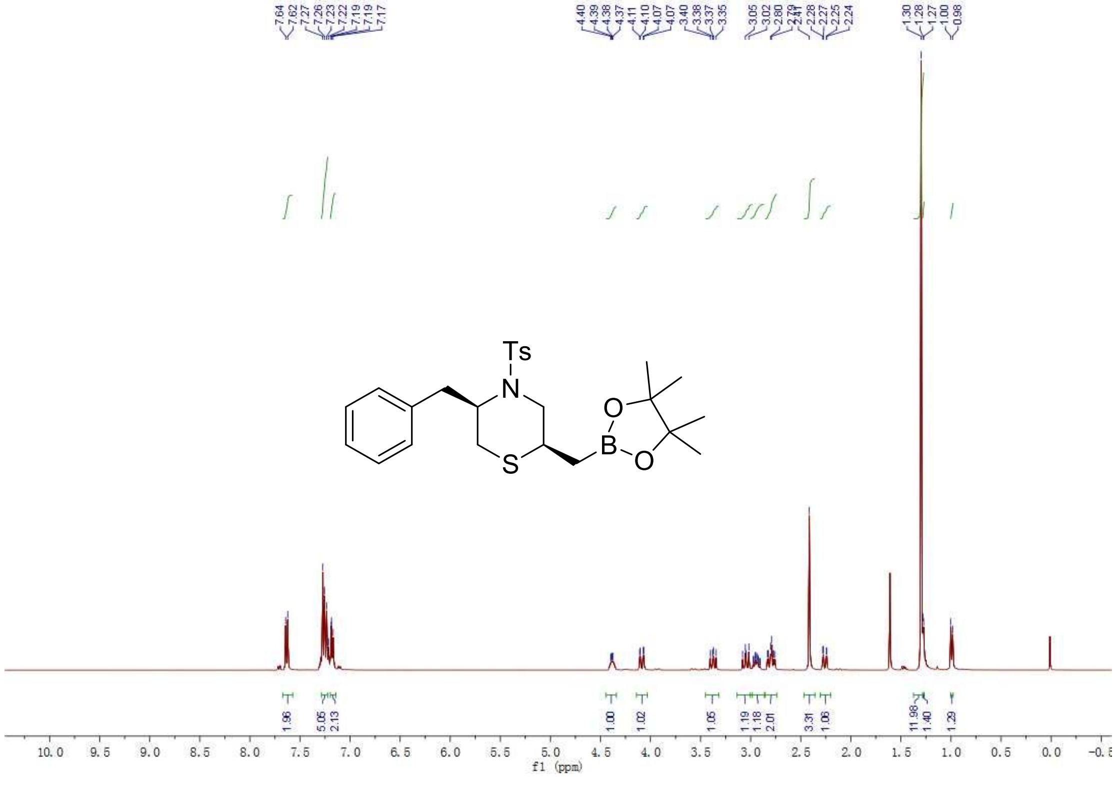
f1 (ppm)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4.37
4.11
4.10
4.07
4.07
3.40
3.38
3.37
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3.05
3.02
2.80
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2.28
2.27
2.25
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1.28
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1.00
0.98
Ts
N
S
O
B
O
1.96
5.05
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1.02
1.05
1.19
1.18
2.01
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1.08
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9.0
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7.0
6.5
6.0
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5.0
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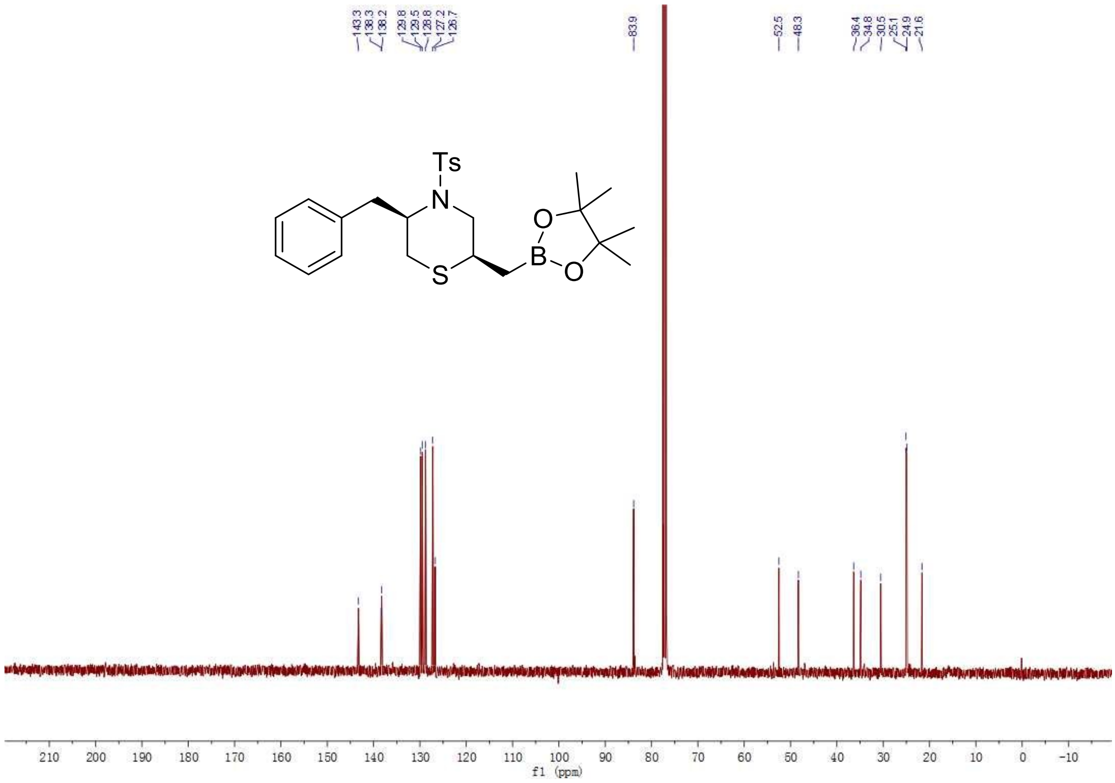
f1 (ppm)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30.5
25.1
24.9
21.6
Ts
N
S
B
O
O
210
200
190
180
170
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100
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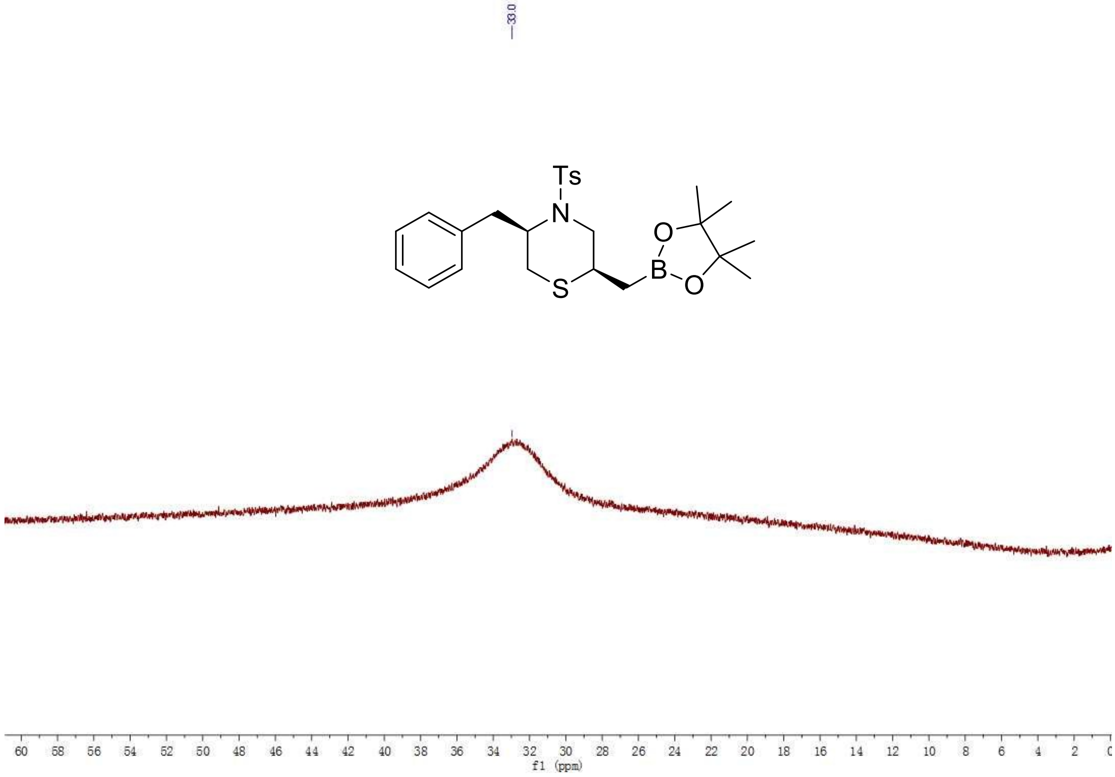
f1 (ppm)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B
O
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60
58
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52
50
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46
44
42
40
38
36
34
32
30
28
26
24
22
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18
16
14
12
10
8
6
4
2
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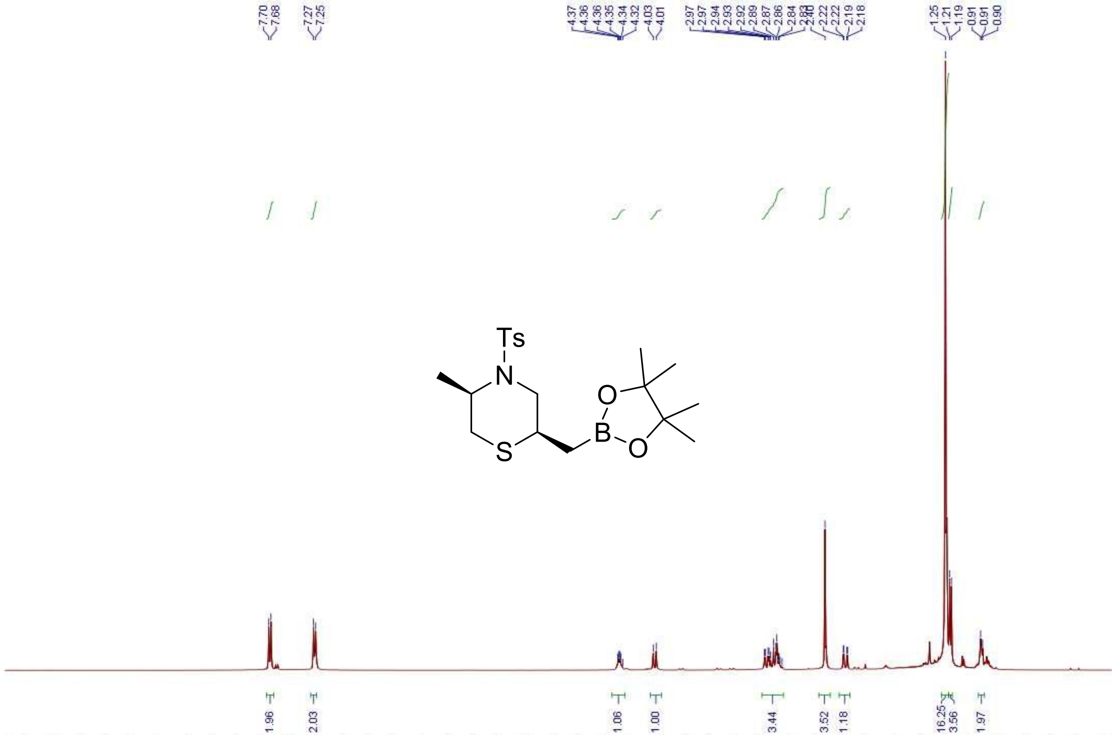
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4.34
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4.01
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2.97
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2.93
2.92
2.89
2.87
2.86
2.84
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2.40
2.22
2.22
2.19
2.18
1.25
1.21
1.19
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0.91
0.90
Ts
N
S
B
O
O
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1.18
16.25
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1.97
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9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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2.5
2.0
1.5
1.0
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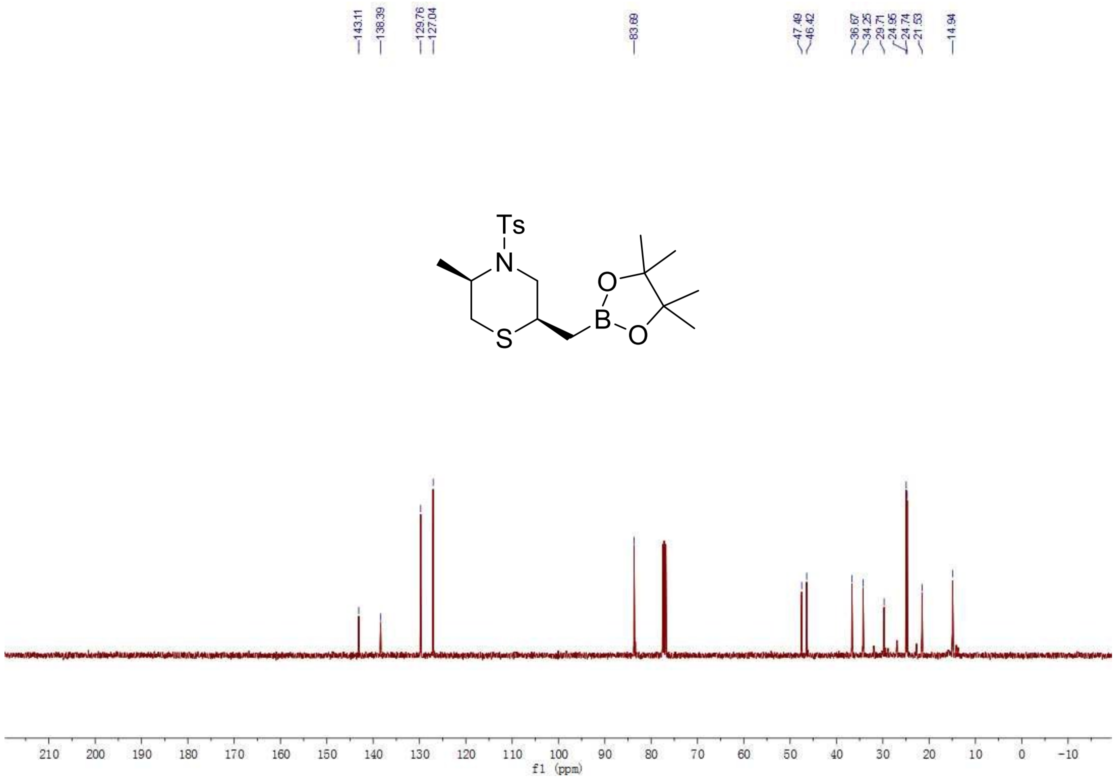
f1 (ppm)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S
B
O
O
210
200
190
180
170
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110
100
90
80
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30
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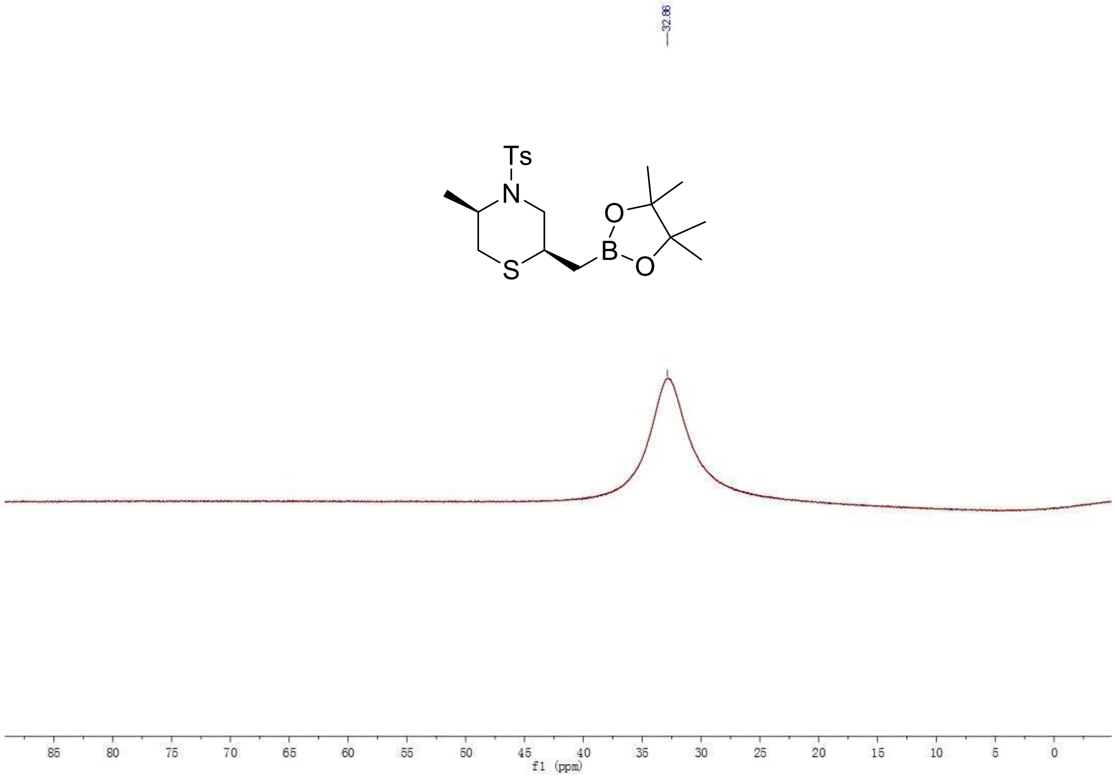
f1 (ppm)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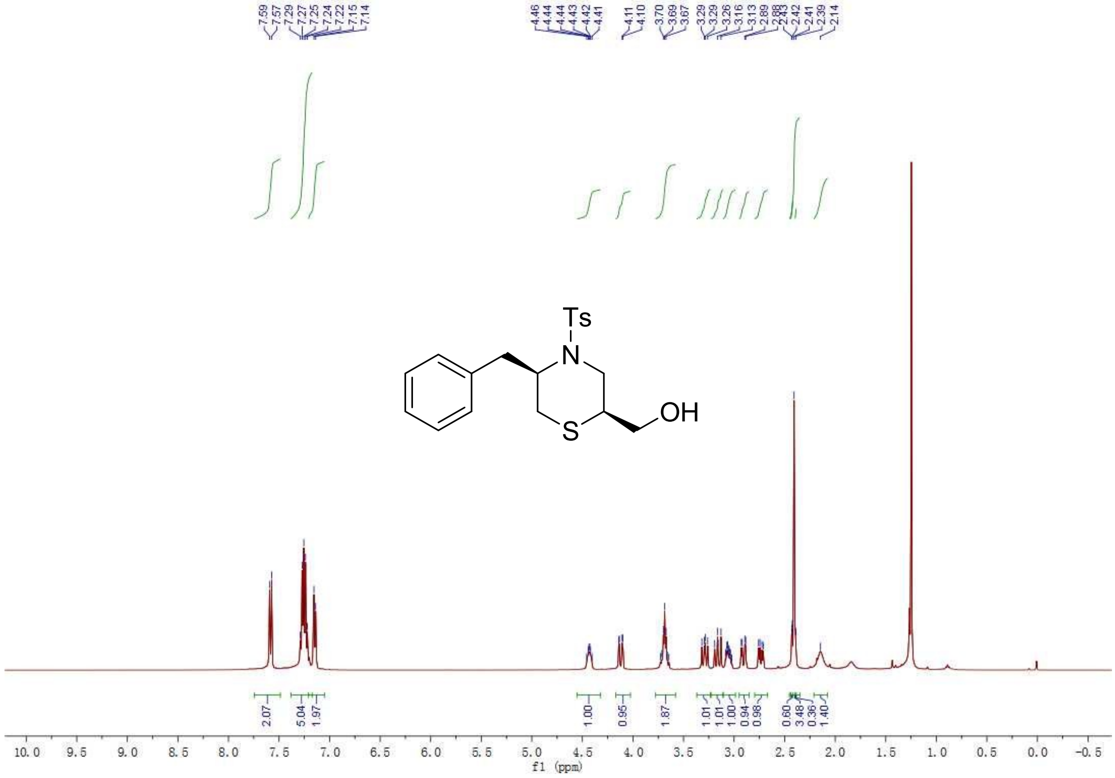
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4.42
4.41
4.11
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3.29
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Ts
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S
OH
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1.01
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1.40
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5.0
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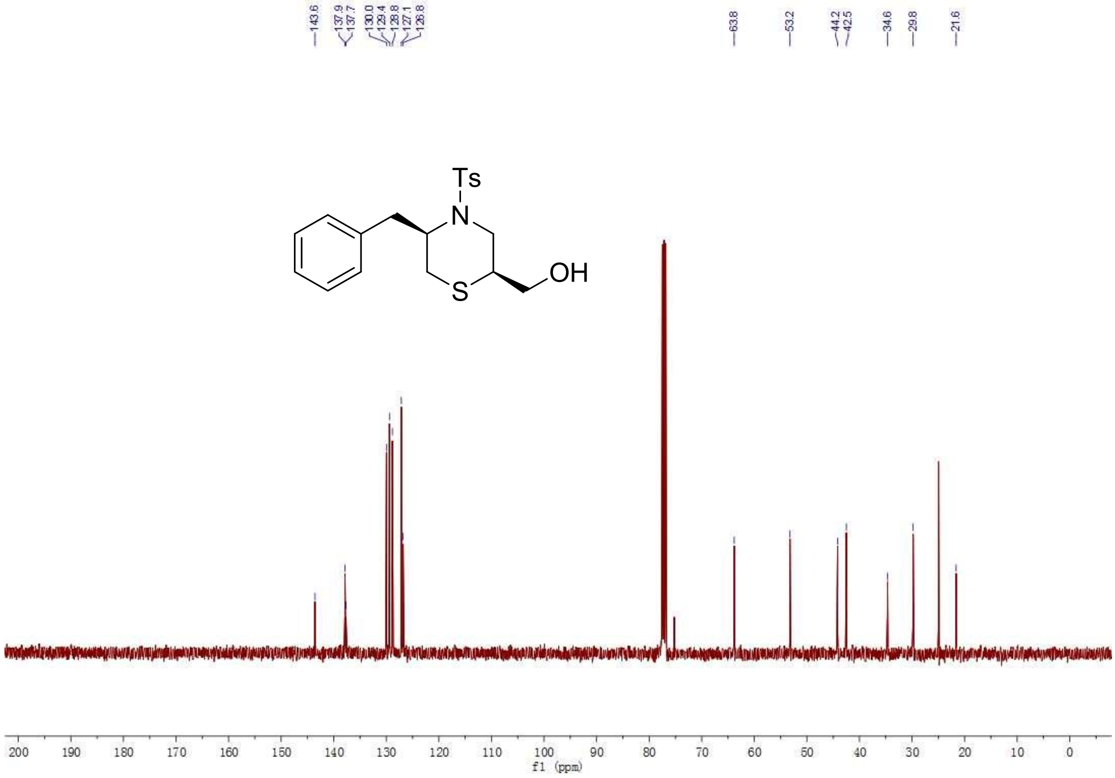
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44.2
42.5
34.6
29.8
21.6
Ts
N
S
OH
200
190
180
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160
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130
120
110
100
90
80
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50
40
30
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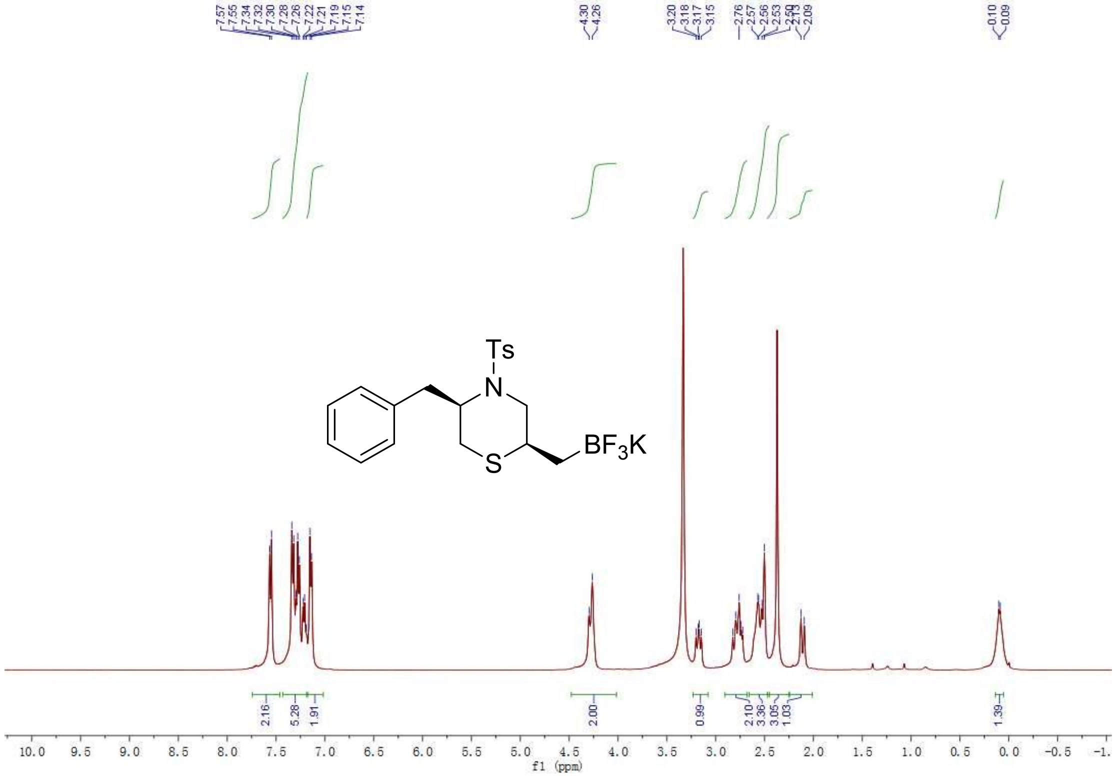
f1 (ppm)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3.20
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3.17
3.15
2.76
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2.50
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S
BF3K
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2.00
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3.36
3.05
1.03
1.39
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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2.0
1.5
1.0
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0.0
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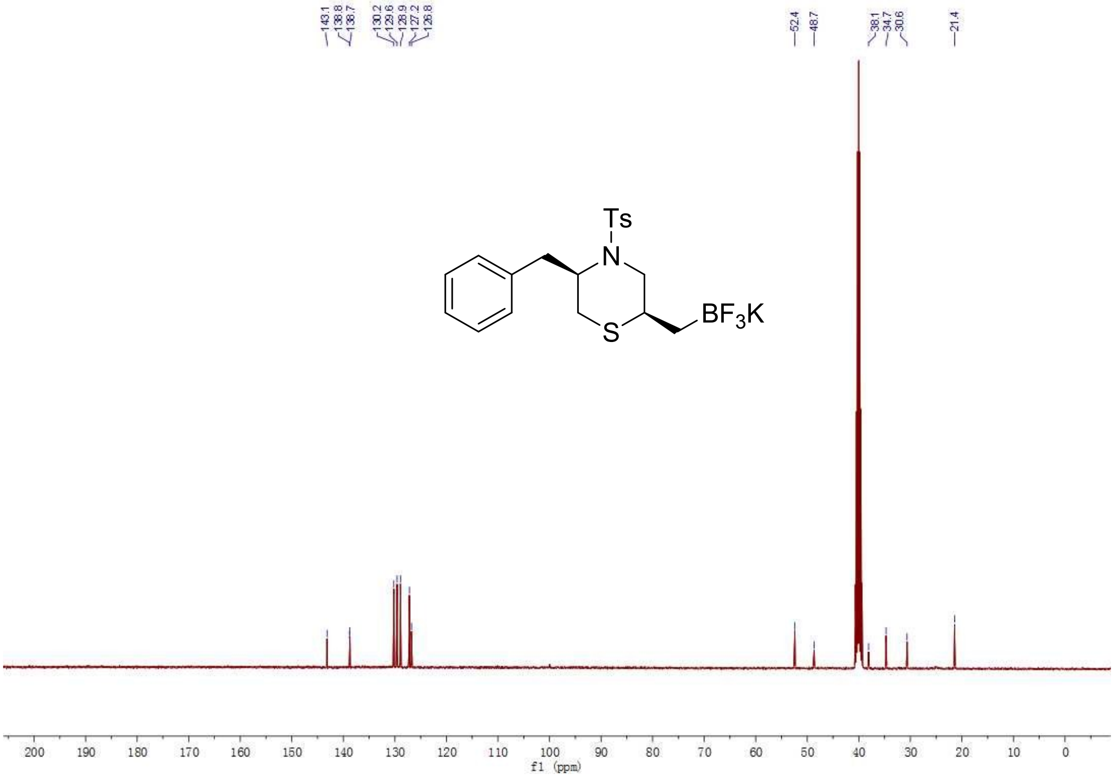
-1.
f1 (ppm)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130.2
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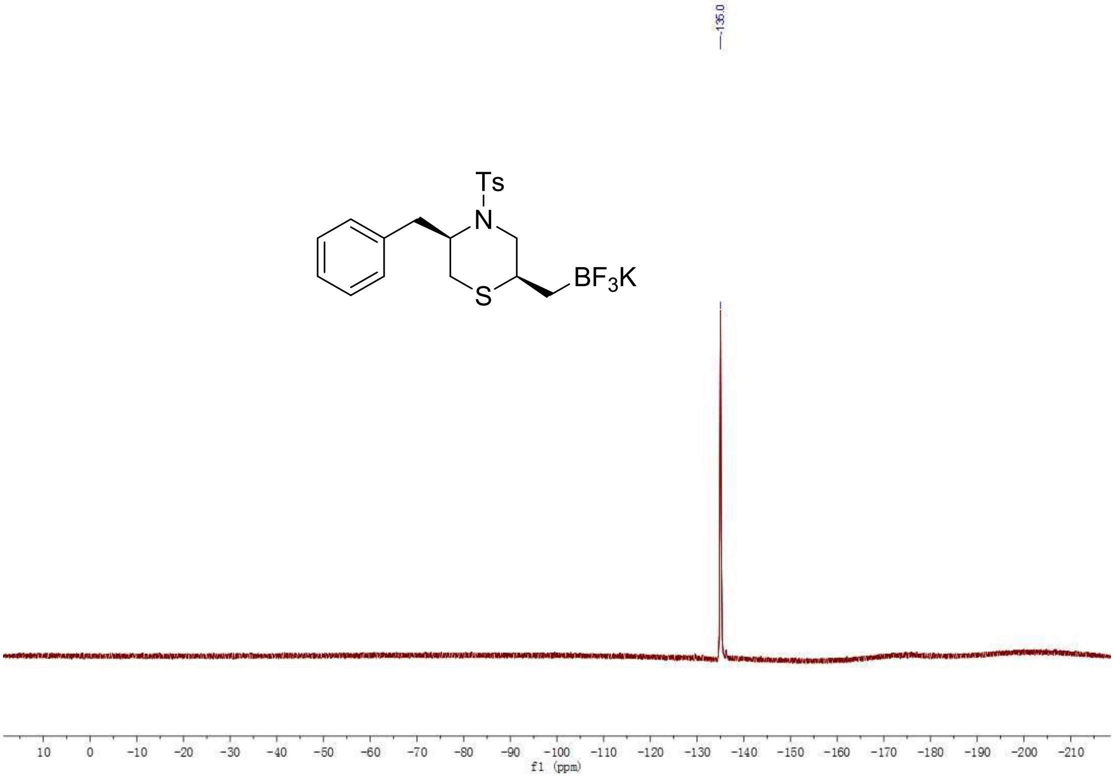
128.9
127.2
126.8
52.4
48.7
38.1
34.7
30.6
21.4
Ts
N
S
BF$_3$K
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-135.0
Ts
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S
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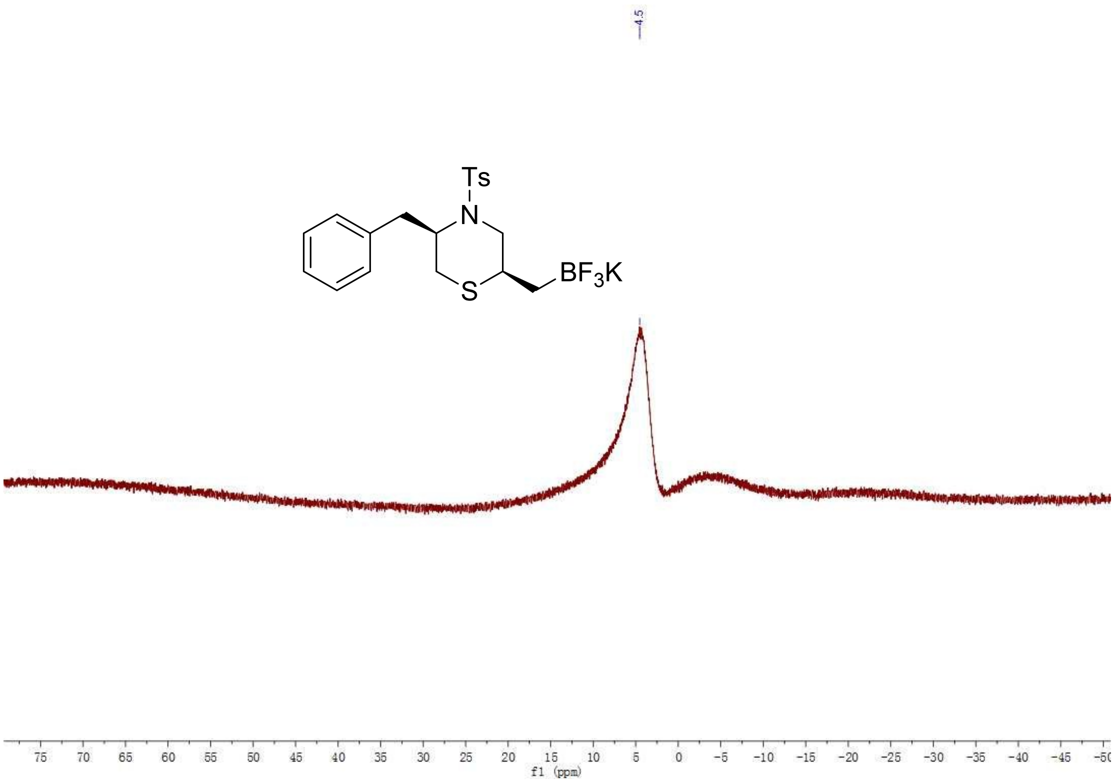
f1 (ppm)



9. X-ray crystal Structure and data of *cis*-9a

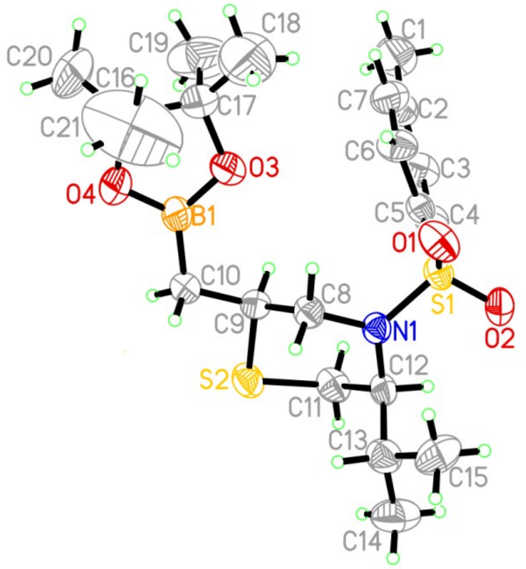


Figure S3. X-ray crystallography structure of 2,5-*cis*-**9a**.

Table S1. Crystal data and structure refinement for 2,5-*cis*-**9a**.

Empirical formula	C21 H34 B N O4 S2

Formula weight	439.42	
Temperature	293(2) K	
Wavelength	0.71073 A	
Crystal system, space group	Triclinic, P1	
Unit cell dimensions	a = 6.4466(13) A	alpha = 73.16(3) deg.
	b = 13.706(3) A	beta = 87.55(3) deg.
	c = 14.920(3) A	gamma = 89.48(3) deg.
Volume	1260.5(4) A^3	
Z, Calculated density	2, 1.158 Mg/m^3	
Absorption coefficient	0.235 mm^-1	
F(000)	472	
Crystal size	0.20 x 0.15 x 0.10 mm	
Theta range for data collection	2.39 to 28.56 deg.	
Limiting indices	-8<=h<=8, -18<=k<=18, -16<=l<=20	
Reflections collected / unique	12871 / 9599 [R(int) = 0.0572]	
Completeness to theta = 28.56	97.3 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9599 / 3 / 523	
Goodness-of-fit on F^2	0.891	
Final R indices [I>2sigma(I)]	R1 = 0.0763, wR2 = 0.2019	
R indices (all data)	R1 = 0.1566, wR2 = 0.2755	
Absolute structure parameter	0.03(12)	
Largest diff. peak and hole	0.479 and -0.355 e.A^-3	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 2,5-*cis*-**9a**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
S(1)	4098(2)	7363(1)	951(1)	63(1)
S(3)	3706(2)	3320(1)	7872(1)	61(1)
S(2)	7602(3)	5385(2)	3456(2)	83(1)
S(4)	385(3)	3053(2)	5267(1)	81(1)
N(2)	3020(8)	3503(4)	6815(4)	59(1)
O(5)	3028(8)	4171(4)	8165(4)	76(1)
O(1)	1907(7)	7144(5)	908(4)	85(2)
O(2)	4765(9)	8403(4)	684(4)	79(1)
O(6)	5845(7)	3063(5)	7917(4)	84(2)
N(1)	4795(8)	6849(4)	2012(4)	60(1)
C(5)	5449(9)	6756(5)	222(5)	58(2)
C(12)	6372(10)	7328(5)	2439(5)	63(2)
C(33)	1462(10)	4272(5)	6389(5)	61(2)
C(29)	3873(11)	2842(6)	6269(5)	66(2)
C(26)	2330(10)	2261(5)	8591(4)	57(2)
C(8)	4008(10)	5829(6)	2527(5)	64(2)
C(27)	248(10)	2362(6)	8837(5)	67(2)
C(34)	2406(12)	5169(6)	5615(5)	69(2)
C(28)	-732(11)	1530(7)	9460(6)	82(2)
C(30)	2220(13)	2212(6)	5999(5)	75(2)
O(3)	2941(14)	3901(5)	1838(5)	123(3)
C(25)	3310(13)	1346(7)	8936(6)	83(2)
C(9)	5665(12)	5048(6)	2749(5)	69(2)
C(3)	8520(12)	6572(7)	-663(6)	84(2)
C(4)	7495(10)	7005(6)	-37(5)	71(2)
C(10)	4789(15)	3995(6)	3290(6)	82(2)
C(31)	3178(17)	1499(6)	5455(6)	92(3)
C(23)	217(14)	629(7)	9845(6)	81(2)
C(6)	4465(12)	6056(7)	-121(6)	87(2)
C(32)	-353(11)	3761(7)	6066(7)	80(2)
O(8)	4831(15)	451(6)	6944(5)	129(3)
C(24)	2267(19)	542(7)	9560(8)	105(3)
C(35)	4340(14)	5582(7)	5949(7)	97(3)

B(1)	3553(17)	3470(8)	2703(7)	80(2)
O(7)	5290(17)	-132(6)	5725(5)	144(3)
O(4)	2918(16)	2492(5)	3012(6)	133(3)
C(11)	8254(12)	6630(7)	2655(6)	81(2)
C(36)	911(16)	6005(7)	5292(8)	104(3)
C(13)	5505(14)	7703(7)	3241(6)	86(2)
C(7)	5497(17)	5660(8)	-746(7)	99(3)
C(2)	7514(16)	5908(7)	-1037(6)	89(3)
C(14)	7160(20)	8257(11)	3615(10)	133(4)
B(2)	4426(18)	624(7)	6042(7)	83(3)
C(22)	-920(20)	-257(10)	10553(10)	137(4)
C(37)	5970(20)	-481(9)	7255(9)	133(5)
C(17)	1870(20)	3153(9)	1504(9)	116(4)
C(15)	3562(16)	8361(9)	2947(9)	112(3)
C(41)	7650(40)	-301(17)	7820(20)	258(15)
C(21)	-800(30)	2560(30)	2680(20)	350(20)
C(1)	8620(20)	5486(11)	-1778(9)	143(5)
C(20)	2120(60)	1265(12)	2289(18)	320(20)
C(42)	4340(40)	-1238(15)	7967(15)	231(12)
C(16)	1630(30)	2255(10)	2337(10)	140(5)
C(19)	3590(30)	2824(18)	811(14)	209(10)
C(18)	340(30)	3597(16)	856(17)	224(11)
C(38)	6390(20)	-804(10)	6434(9)	134(5)
C(40)	8540(40)	-710(40)	6120(20)	380(30)
C(39)	6060(80)	-1833(15)	6428(19)	350(30)

Table 3. Selected bond lengths [A] and angles [deg] for 2,5-*cis*-**9a**.

Symmetry transformations used to generate equivalent atoms:

Table S4. Bond lengths [A] and angles [deg] for 2,5-*cis*-**9a**.

S(1)-O(2)	1.429(6)
S(1)-O(1)	1.455(5)
S(1)-N(1)	1.616(6)
S(1)-C(5)	1.751(7)
S(3)-O(5)	1.419(6)
S(3)-O(6)	1.420(5)
S(3)-N(2)	1.605(5)
S(3)-C(26)	1.756(7)
S(2)-C(9)	1.814(8)
S(2)-C(11)	1.817(9)
S(4)-C(32)	1.790(9)
S(4)-C(30)	1.811(7)
N(2)-C(29)	1.472(9)
N(2)-C(33)	1.474(8)
N(1)-C(8)	1.469(9)
N(1)-C(12)	1.477(9)
C(5)-C(4)	1.376(10)
C(5)-C(6)	1.381(10)
C(12)-C(13)	1.516(11)
C(12)-C(11)	1.525(10)
C(12)-H(12A)	0.9800
C(33)-C(34)	1.531(10)
C(33)-C(32)	1.533(10)
C(33)-H(33A)	0.9800
C(29)-C(30)	1.516(11)
C(29)-H(29A)	0.9700
C(29)-H(29B)	0.9700
C(26)-C(25)	1.370(10)
C(26)-C(27)	1.392(9)
C(8)-C(9)	1.484(10)
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(27)-C(28)	1.383(11)
C(27)-H(27A)	0.9300
C(34)-C(36)	1.475(11)
C(34)-C(35)	1.533(11)
C(34)-H(34A)	0.9800
C(28)-C(23)	1.355(12)
C(28)-H(28A)	0.9300
C(30)-C(31)	1.550(12)
C(30)-H(30A)	0.9800

O(3)-B(1)	1.329(11)
O(3)-C(17)	1.454(12)
C(25)-C(24)	1.378(13)
C(25)-H(25A)	0.9300
C(9)-C(10)	1.534(12)
C(9)-H(9A)	0.9800
C(3)-C(2)	1.378(13)
C(3)-C(4)	1.386(11)
C(3)-H(3A)	0.9300
C(4)-H(4A)	0.9300
C(10)-B(1)	1.535(13)
C(10)-H(10A)	0.9700
C(10)-H(10B)	0.9700
C(31)-B(2)	1.511(12)
C(31)-H(31A)	0.9700
C(31)-H(31B)	0.9700
C(23)-C(24)	1.385(14)
C(23)-C(22)	1.528(14)
C(6)-C(7)	1.357(13)
C(6)-H(6A)	0.9300
C(32)-H(32A)	0.9700
C(32)-H(32B)	0.9700
O(8)-B(2)	1.334(12)
O(8)-C(37)	1.435(11)
C(24)-H(24A)	0.9300
C(35)-H(35A)	0.9600
C(35)-H(35B)	0.9600
C(35)-H(35C)	0.9600
B(1)-O(4)	1.347(12)
O(7)-B(2)	1.364(12)
O(7)-C(38)	1.400(14)
O(4)-C(16)	1.442(13)
C(11)-H(11A)	0.9700
C(11)-H(11B)	0.9700
C(36)-H(36A)	0.9600
C(36)-H(36B)	0.9600
C(36)-H(36C)	0.9600
C(13)-C(14)	1.528(13)
C(13)-C(15)	1.540(13)
C(13)-H(13A)	0.9800
C(7)-C(2)	1.367(14)
C(7)-H(7A)	0.9300
C(2)-C(1)	1.536(14)
C(14)-H(14A)	0.9600

C(14)-H(14B)	0.9600
C(14)-H(14C)	0.9600
C(22)-H(22A)	0.9600
C(22)-H(22B)	0.9600
C(22)-H(22C)	0.9600
C(37)-C(38)	1.433(17)
C(37)-C(41)	1.465(19)
C(37)-C(42)	1.61(3)
C(17)-C(18)	1.417(18)
C(17)-C(16)	1.477(19)
C(17)-C(19)	1.63(2)
C(15)-H(15A)	0.9600
C(15)-H(15B)	0.9600
C(15)-H(15C)	0.9600
C(41)-H(41A)	0.9600
C(41)-H(41B)	0.9600
C(41)-H(41C)	0.9600
C(21)-C(16)	1.71(3)
C(21)-H(21A)	0.9600
C(21)-H(21B)	0.9600
C(21)-H(21C)	0.9600
C(1)-H(1A)	0.9600
C(1)-H(1B)	0.9600
C(1)-H(1C)	0.9600
C(20)-C(16)	1.41(2)
C(20)-H(20A)	0.9600
C(20)-H(20B)	0.9600
C(20)-H(20C)	0.9600
C(42)-H(42A)	0.9600
C(42)-H(42B)	0.9600
C(42)-H(42C)	0.9600
C(19)-H(19A)	0.9600
C(19)-H(19B)	0.9600
C(19)-H(19C)	0.9600
C(18)-H(18A)	0.9600
C(18)-H(18B)	0.9600
C(18)-H(18C)	0.9600
C(38)-C(39)	1.43(3)
C(38)-C(40)	1.44(3)
C(40)-H(40A)	0.9600
C(40)-H(40B)	0.9600
C(40)-H(40C)	0.9600
C(39)-H(39A)	0.9600
C(39)-H(39B)	0.9600

C(39)-H(39C)	0.9600

O(2)-S(1)-O(1)	118.7(3)
O(2)-S(1)-N(1)	107.1(3)
O(1)-S(1)-N(1)	108.3(3)
O(2)-S(1)-C(5)	107.6(4)
O(1)-S(1)-C(5)	106.6(3)
N(1)-S(1)-C(5)	108.0(3)
O(5)-S(3)-O(6)	118.7(3)
O(5)-S(3)-N(2)	107.7(3)
O(6)-S(3)-N(2)	108.6(3)
O(5)-S(3)-C(26)	106.3(3)
O(6)-S(3)-C(26)	107.1(3)
N(2)-S(3)-C(26)	108.2(3)
C(9)-S(2)-C(11)	96.8(4)
C(32)-S(4)-C(30)	97.4(4)
C(29)-N(2)-C(33)	118.6(5)
C(29)-N(2)-S(3)	119.2(4)
C(33)-N(2)-S(3)	122.1(4)
C(8)-N(1)-C(12)	119.0(5)
C(8)-N(1)-S(1)	119.1(4)
C(12)-N(1)-S(1)	121.6(5)
C(4)-C(5)-C(6)	119.7(7)
C(4)-C(5)-S(1)	119.5(5)
C(6)-C(5)-S(1)	120.7(6)
N(1)-C(12)-C(13)	113.4(6)
N(1)-C(12)-C(11)	109.2(6)
C(13)-C(12)-C(11)	115.7(6)
N(1)-C(12)-H(12A)	105.9
C(13)-C(12)-H(12A)	105.9
C(11)-C(12)-H(12A)	105.9
N(2)-C(33)-C(34)	112.6(5)
N(2)-C(33)-C(32)	110.0(6)
C(34)-C(33)-C(32)	113.3(6)
N(2)-C(33)-H(33A)	106.9
C(34)-C(33)-H(33A)	106.9
C(32)-C(33)-H(33A)	106.9
N(2)-C(29)-C(30)	112.8(6)
N(2)-C(29)-H(29A)	109.0
C(30)-C(29)-H(29A)	109.0
N(2)-C(29)-H(29B)	109.0
C(30)-C(29)-H(29B)	109.0
H(29A)-C(29)-H(29B)	107.8
C(25)-C(26)-C(27)	119.8(7)

C(25)-C(26)-S(3)	120.4(6)
C(27)-C(26)-S(3)	119.8(5)
N(1)-C(8)-C(9)	113.1(6)
N(1)-C(8)-H(8A)	109.0
C(9)-C(8)-H(8A)	109.0
N(1)-C(8)-H(8B)	109.0
C(9)-C(8)-H(8B)	109.0
H(8A)-C(8)-H(8B)	107.8
C(28)-C(27)-C(26)	117.8(6)
C(28)-C(27)-H(27A)	121.1
C(26)-C(27)-H(27A)	121.1
C(36)-C(34)-C(33)	112.2(7)
C(36)-C(34)-C(35)	109.2(7)
C(33)-C(34)-C(35)	110.9(6)
C(36)-C(34)-H(34A)	108.1
C(33)-C(34)-H(34A)	108.1
C(35)-C(34)-H(34A)	108.1
C(23)-C(28)-C(27)	123.8(7)
C(23)-C(28)-H(28A)	118.1
C(27)-C(28)-H(28A)	118.1
C(29)-C(30)-C(31)	111.5(7)
C(29)-C(30)-S(4)	109.4(5)
C(31)-C(30)-S(4)	108.7(5)
C(29)-C(30)-H(30A)	109.0
C(31)-C(30)-H(30A)	109.0
S(4)-C(30)-H(30A)	109.0
B(1)-O(3)-C(17)	109.8(8)
C(26)-C(25)-C(24)	120.1(8)
C(26)-C(25)-H(25A)	120.0
C(24)-C(25)-H(25A)	120.0
C(8)-C(9)-C(10)	111.7(7)
C(8)-C(9)-S(2)	111.0(5)
C(10)-C(9)-S(2)	107.9(5)
C(8)-C(9)-H(9A)	108.8
C(10)-C(9)-H(9A)	108.8
S(2)-C(9)-H(9A)	108.8
C(2)-C(3)-C(4)	121.0(8)
C(2)-C(3)-H(3A)	119.5
C(4)-C(3)-H(3A)	119.5
C(5)-C(4)-C(3)	119.4(7)
C(5)-C(4)-H(4A)	120.3
C(3)-C(4)-H(4A)	120.3
C(9)-C(10)-B(1)	114.8(7)
C(9)-C(10)-H(10A)	108.6

B(1)-C(10)-H(10A)	108.6
C(9)-C(10)-H(10B)	108.6
B(1)-C(10)-H(10B)	108.6
H(10A)-C(10)-H(10B)	107.6
B(2)-C(31)-C(30)	114.5(7)
B(2)-C(31)-H(31A)	108.6
C(30)-C(31)-H(31A)	108.6
B(2)-C(31)-H(31B)	108.6
C(30)-C(31)-H(31B)	108.6
H(31A)-C(31)-H(31B)	107.6
C(28)-C(23)-C(24)	116.9(8)
C(28)-C(23)-C(22)	121.7(9)
C(24)-C(23)-C(22)	121.4(9)
C(7)-C(6)-C(5)	119.5(8)
C(7)-C(6)-H(6A)	120.2
C(5)-C(6)-H(6A)	120.2
C(33)-C(32)-S(4)	114.3(5)
C(33)-C(32)-H(32A)	108.7
S(4)-C(32)-H(32A)	108.7
C(33)-C(32)-H(32B)	108.7
S(4)-C(32)-H(32B)	108.7
H(32A)-C(32)-H(32B)	107.6
B(2)-O(8)-C(37)	109.4(8)
C(25)-C(24)-C(23)	121.5(8)
C(25)-C(24)-H(24A)	119.3
C(23)-C(24)-H(24A)	119.3
C(34)-C(35)-H(35A)	109.5
C(34)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35B)	109.5
C(34)-C(35)-H(35C)	109.5
H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5
O(3)-B(1)-O(4)	110.5(8)
O(3)-B(1)-C(10)	125.9(8)
O(4)-B(1)-C(10)	123.6(8)
B(2)-O(7)-C(38)	110.2(8)
B(1)-O(4)-C(16)	110.3(9)
C(12)-C(11)-S(2)	112.4(6)
C(12)-C(11)-H(11A)	109.1
S(2)-C(11)-H(11A)	109.1
C(12)-C(11)-H(11B)	109.1
S(2)-C(11)-H(11B)	109.1
H(11A)-C(11)-H(11B)	107.8
C(34)-C(36)-H(36A)	109.5

C(34)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	109.5
C(34)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5
C(12)-C(13)-C(14)	111.6(8)
C(12)-C(13)-C(15)	110.7(7)
C(14)-C(13)-C(15)	112.3(9)
C(12)-C(13)-H(13A)	107.4
C(14)-C(13)-H(13A)	107.4
C(15)-C(13)-H(13A)	107.4
C(6)-C(7)-C(2)	122.4(9)
C(6)-C(7)-H(7A)	118.8
C(2)-C(7)-H(7A)	118.8
C(7)-C(2)-C(3)	117.9(8)
C(7)-C(2)-C(1)	121.4(10)
C(3)-C(2)-C(1)	120.7(11)
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
O(8)-B(2)-O(7)	109.0(8)
O(8)-B(2)-C(31)	126.5(8)
O(7)-B(2)-C(31)	124.5(8)
C(23)-C(22)-H(22A)	109.5
C(23)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(23)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(38)-C(37)-O(8)	105.5(9)
C(38)-C(37)-C(41)	121.6(16)
O(8)-C(37)-C(41)	107.5(11)
C(38)-C(37)-C(42)	110.9(15)
O(8)-C(37)-C(42)	103.2(12)
C(41)-C(37)-C(42)	106.6(18)
C(18)-C(17)-O(3)	112.7(11)
C(18)-C(17)-C(16)	127.3(15)
O(3)-C(17)-C(16)	104.4(8)
C(18)-C(17)-C(19)	100.3(16)
O(3)-C(17)-C(19)	104.2(11)
C(16)-C(17)-C(19)	105.4(13)

C(13)-C(15)-H(15A)	109.5
C(13)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(13)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(37)-C(41)-H(41A)	109.5
C(37)-C(41)-H(41B)	109.5
H(41A)-C(41)-H(41B)	109.5
C(37)-C(41)-H(41C)	109.5
H(41A)-C(41)-H(41C)	109.5
H(41B)-C(41)-H(41C)	109.5
C(16)-C(21)-H(21A)	109.5
C(16)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(16)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(2)-C(1)-H(1A)	109.5
C(2)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
C(2)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
C(16)-C(20)-H(20A)	109.5
C(16)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(16)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(37)-C(42)-H(42A)	109.5
C(37)-C(42)-H(42B)	109.5
H(42A)-C(42)-H(42B)	109.5
C(37)-C(42)-H(42C)	109.5
H(42A)-C(42)-H(42C)	109.5
H(42B)-C(42)-H(42C)	109.5
C(20)-C(16)-O(4)	108.6(15)
C(20)-C(16)-C(17)	121.3(17)
O(4)-C(16)-C(17)	103.8(10)
C(20)-C(16)-C(21)	122(2)
O(4)-C(16)-C(21)	102.5(15)
C(17)-C(16)-C(21)	96.2(17)
C(17)-C(19)-H(19A)	109.5
C(17)-C(19)-H(19B)	109.5

H(19A)-C(19)-H(19B)	109.5
C(17)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(17)-C(18)-H(18A)	109.5
C(17)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(17)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
O(7)-C(38)-C(39)	110.1(16)
O(7)-C(38)-C(37)	105.5(9)
C(39)-C(38)-C(37)	122.0(19)
O(7)-C(38)-C(40)	106.4(19)
C(39)-C(38)-C(40)	99(2)
C(37)-C(38)-C(40)	113.3(19)
C(38)-C(40)-H(40A)	109.5
C(38)-C(40)-H(40B)	109.5
H(40A)-C(40)-H(40B)	109.5
C(38)-C(40)-H(40C)	109.5
H(40A)-C(40)-H(40C)	109.5
H(40B)-C(40)-H(40C)	109.5
C(38)-C(39)-H(39A)	109.5
C(38)-C(39)-H(39B)	109.5
H(39A)-C(39)-H(39B)	109.5
C(38)-C(39)-H(39C)	109.5
H(39A)-C(39)-H(39C)	109.5
H(39B)-C(39)-H(39C)	109.5

Symmetry transformations used to generate equivalent atoms:

TableS 5. Anisotropic displacement parameters (A^2 x 10^3) for 2,5-*cis*-**9a**.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
S(1)	54(1)	68(1)	61(1)	-10(1)	-9(1)	5(1)
S(3)	56(1)	67(1)	58(1)	-14(1)	-8(1)	-4(1)
S(2)	86(1)	84(1)	74(1)	-9(1)	-24(1)	-1(1)
S(4)	82(1)	87(2)	74(1)	-20(1)	-21(1)	-1(1)
N(2)	54(3)	62(3)	57(3)	-13(3)	-6(2)	11(2)
O(5)	95(4)	68(3)	65(3)	-18(3)	-6(3)	-13(3)
O(1)	42(2)	125(5)	79(3)	-16(3)	-11(2)	5(3)
O(2)	91(3)	59(3)	76(3)	-3(3)	-3(3)	5(3)
O(6)	49(2)	127(5)	71(3)	-20(3)	-9(2)	0(3)
N(1)	60(3)	56(4)	57(3)	-9(3)	-1(2)	-8(3)
C(5)	53(3)	63(4)	55(4)	-12(3)	-11(3)	4(3)
C(12)	67(4)	57(4)	55(4)	-4(3)	-2(3)	-4(3)
C(33)	60(3)	67(5)	51(3)	-10(3)	2(3)	5(3)
C(29)	71(4)	65(4)	61(4)	-14(3)	-12(3)	7(3)
C(26)	58(3)	58(4)	52(4)	-12(3)	-10(3)	3(3)
C(8)	60(4)	67(5)	62(4)	-13(4)	-2(3)	-8(3)
C(27)	54(3)	67(5)	77(5)	-14(4)	-6(3)	9(3)
C(34)	87(5)	60(4)	55(4)	-10(3)	-2(3)	-5(4)
C(28)	49(3)	101(7)	86(5)	-11(5)	-4(3)	-7(4)
C(30)	98(5)	64(5)	55(4)	-2(4)	-12(4)	4(4)
O(3)	196(8)	92(5)	77(4)	-11(4)	-43(4)	-38(5)
C(25)	85(5)	73(6)	85(6)	-16(5)	9(4)	22(4)
C(9)	86(5)	63(5)	59(4)	-19(4)	0(3)	1(4)
C(3)	60(4)	108(7)	89(5)	-35(5)	-14(4)	28(4)
C(4)	52(3)	91(6)	72(4)	-29(4)	-10(3)	2(3)
C(10)	116(6)	68(5)	61(4)	-18(4)	-13(4)	2(5)
C(31)	145(8)	61(5)	71(5)	-16(4)	-25(5)	13(5)
C(23)	93(6)	78(6)	68(5)	-13(4)	1(4)	-20(5)
C(6)	71(4)	111(7)	85(6)	-37(5)	-1(4)	-21(5)
C(32)	53(4)	95(6)	87(5)	-20(5)	1(3)	-4(4)
O(8)	191(8)	106(5)	96(5)	-35(4)	-25(5)	63(5)
C(24)	140(9)	60(5)	98(7)	4(5)	-8(6)	5(6)
C(35)	83(5)	87(6)	105(7)	1(5)	-14(5)	-17(5)
B(1)	105(7)	69(6)	57(5)	-7(5)	15(4)	-18(5)

O(7)	234(9)	120(6)	90(5)	-43(5)	-50(6)	69(6)
O(4)	213(8)	71(4)	106(6)	-4(4)	-43(5)	-45(5)
C(11)	64(4)	96(6)	76(5)	-14(5)	-9(4)	-12(4)
C(36)	110(7)	82(6)	102(7)	9(5)	-32(6)	7(5)
C(13)	92(5)	91(6)	73(5)	-20(5)	-1(4)	-12(5)
C(7)	118(8)	93(7)	94(7)	-41(6)	-4(6)	-8(6)
C(2)	110(7)	85(6)	74(5)	-24(5)	-9(5)	28(5)
C(14)	135(9)	161(11)	134(10)	-87(9)	-33(8)	0(8)
B(2)	122(8)	61(6)	68(6)	-23(5)	-5(5)	5(5)
C(22)	173(12)	104(9)	118(10)	-9(7)	22(8)	-61(8)
C(37)	196(13)	103(8)	106(8)	-30(7)	-66(9)	72(9)
C(17)	162(10)	90(7)	98(7)	-27(6)	-35(7)	-26(7)
C(15)	101(7)	107(8)	148(10)	-71(7)	3(6)	14(6)
C(41)	260(20)	220(20)	370(30)	-180(20)	-210(30)	134(19)
C(21)	104(12)	660(70)	300(40)	-190(40)	21(16)	-10(20)
C(1)	196(13)	140(10)	108(9)	-62(8)	-7(8)	72(10)
C(20)	710(70)	70(9)	200(20)	-50(11)	-90(30)	8(19)
C(42)	290(30)	178(16)	156(16)	52(13)	85(16)	94(17)
C(16)	198(14)	115(10)	123(10)	-55(9)	-43(10)	-24(9)
C(19)	250(20)	270(20)	147(14)	-114(16)	75(14)	-120(18)
C(18)	220(20)	194(17)	270(30)	-76(18)	-150(20)	44(15)
C(38)	173(12)	128(10)	107(9)	-44(8)	-20(8)	55(9)
C(40)	160(19)	760(90)	230(30)	-180(40)	-1(19)	180(30)
C(39)	770(80)	104(12)	190(20)	-77(14)	-130(40)	130(30)

Table S6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 2,5-*cis*-**9a**.

	x	y	z	U(eq)
H(12A)	6849	7938	1948	75
H(33A)	904	4549	6885	73
H(29A)	4890	2387	6635	80
H(29B)	4583	3261	5705	80
H(8A)	2991	5623	2156	77
H(8B)	3311	5861	3107	77
H(27A)	-460	2968	8590	81
H(34A)	2828	4922	5081	83
H(28A)	-2124	1593	9626	98
H(30A)	1485	1797	6569	90
H(25A)	4680	1268	8749	100
H(9A)	6341	5004	2161	83
H(3A)	9908	6732	-832	101
H(4A)	8183	7460	205	85
H(10A)	3895	4068	3807	98
H(10B)	5933	3557	3556	98
H(31A)	2067	1222	5183	111
H(31B)	4070	1901	4943	111
H(6A)	3104	5858	75	104
H(32A)	-1336	4282	5769	96
H(32B)	-1057	3305	6614	96
H(24A)	2954	-73	9795	126
H(35A)	4916	6137	5451	146
H(35B)	5352	5049	6124	146
H(35C)	3964	5817	6480	146
H(11A)	9296	6949	2928	97
H(11B)	8848	6543	2075	97
H(36A)	-293	5752	5073	157
H(36B)	1546	6537	4791	157
H(36C)	506	6270	5803	157
H(13A)	5069	7101	3751	103
H(7A)	4807	5203	-984	118
H(14A)	8323	7815	3801	200
H(14B)	6584	8445	4146	200
H(14C)	7599	8859	3134	200
H(22A)	-2312	-53	10669	206

H(22B)	-204	-444	11128	206
H(22C)	-965	-829	10306	206
H(15A)	2565	7983	2721	168
H(15B)	3944	8970	2460	168
H(15C)	2965	8542	3478	168
H(41A)	8661	152	7423	386
H(41B)	8300	-937	8126	386
H(41C)	7091	1	8284	386
H(21A)	-835	3258	2672	520
H(21B)	-1142	2133	3305	520
H(21C)	-1798	2442	2261	520
H(1A)	7692	5040	-1962	215
H(1B)	9827	5113	-1520	215
H(1C)	9024	6040	-2316	215
H(20A)	3575	1231	2135	480
H(20B)	1330	1112	1815	480
H(20C)	1792	779	2885	480
H(42A)	3239	-1398	7622	347
H(42B)	3783	-914	8414	347
H(42C)	5039	-1854	8291	347
H(19A)	3824	3382	254	314
H(19B)	3088	2245	644	314
H(19C)	4867	2651	1127	314
H(18A)	-804	3826	1177	336
H(18B)	-148	3099	574	336
H(18C)	928	4166	378	336
H(40A)	8728	-936	5572	569
H(40B)	9379	-1111	6608	569
H(40C)	8960	-4	5971	569
H(39A)	6469	-1902	5823	518
H(39B)	4614	-2003	6559	518
H(39C)	6869	-2285	6897	518

Table S7. Selected torsion angles [deg] for 2,5-*cis*-**9a**.

Symmetry transformations used to generate equivalent atoms:

Table S8. Torsion angles [deg] for 2,5-*cis*-**9a**.

O(5)-S(3)-N(2)-C(29)	168.0(5)
O(6)-S(3)-N(2)-C(29)	38.4(6)
C(26)-S(3)-N(2)-C(29)	-77.5(6)
O(5)-S(3)-N(2)-C(33)	-15.7(6)
O(6)-S(3)-N(2)-C(33)	-145.4(5)
C(26)-S(3)-N(2)-C(33)	98.7(6)
O(2)-S(1)-N(1)-C(8)	169.8(5)
O(1)-S(1)-N(1)-C(8)	40.6(6)
C(5)-S(1)-N(1)-C(8)	-74.5(6)
O(2)-S(1)-N(1)-C(12)	-16.9(6)
O(1)-S(1)-N(1)-C(12)	-146.1(5)
C(5)-S(1)-N(1)-C(12)	98.8(5)
O(2)-S(1)-C(5)-C(4)	37.6(6)
O(1)-S(1)-C(5)-C(4)	166.0(6)
N(1)-S(1)-C(5)-C(4)	-77.8(6)
O(2)-S(1)-C(5)-C(6)	-140.2(6)
O(1)-S(1)-C(5)-C(6)	-11.8(7)
N(1)-S(1)-C(5)-C(6)	104.4(6)
C(8)-N(1)-C(12)-C(13)	-73.6(8)
S(1)-N(1)-C(12)-C(13)	113.1(7)
C(8)-N(1)-C(12)-C(11)	57.1(8)
S(1)-N(1)-C(12)-C(11)	-116.2(6)
C(29)-N(2)-C(33)-C(34)	-72.7(8)
S(3)-N(2)-C(33)-C(34)	111.0(6)
C(29)-N(2)-C(33)-C(32)	54.6(8)
S(3)-N(2)-C(33)-C(32)	-121.7(6)
C(33)-N(2)-C(29)-C(30)	-59.8(8)
S(3)-N(2)-C(29)-C(30)	116.6(6)
O(5)-S(3)-C(26)-C(25)	-138.8(6)
O(6)-S(3)-C(26)-C(25)	-11.0(7)
N(2)-S(3)-C(26)-C(25)	105.9(6)
O(5)-S(3)-C(26)-C(27)	39.2(6)
O(6)-S(3)-C(26)-C(27)	166.9(5)
N(2)-S(3)-C(26)-C(27)	-76.2(6)
C(12)-N(1)-C(8)-C(9)	-58.7(8)
S(1)-N(1)-C(8)-C(9)	114.8(6)
C(25)-C(26)-C(27)-C(28)	2.7(10)
S(3)-C(26)-C(27)-C(28)	-175.2(6)
N(2)-C(33)-C(34)-C(36)	-171.3(7)
C(32)-C(33)-C(34)-C(36)	63.1(9)
N(2)-C(33)-C(34)-C(35)	-48.9(8)

C(32)-C(33)-C(34)-C(35)	-174.5(7)
C(26)-C(27)-C(28)-C(23)	0.1(12)
N(2)-C(29)-C(30)-C(31)	-178.1(6)
N(2)-C(29)-C(30)-S(4)	61.6(7)
C(32)-S(4)-C(30)-C(29)	-56.8(6)
C(32)-S(4)-C(30)-C(31)	-178.8(7)
C(27)-C(26)-C(25)-C(24)	-3.1(12)
S(3)-C(26)-C(25)-C(24)	174.8(7)
N(1)-C(8)-C(9)-C(10)	179.7(6)
N(1)-C(8)-C(9)-S(2)	59.3(7)
C(11)-S(2)-C(9)-C(8)	-56.2(6)
C(11)-S(2)-C(9)-C(10)	-178.9(6)
C(6)-C(5)-C(4)-C(3)	2.0(11)
S(1)-C(5)-C(4)-C(3)	-175.9(6)
C(2)-C(3)-C(4)-C(5)	0.9(12)
C(8)-C(9)-C(10)-B(1)	72.7(9)
S(2)-C(9)-C(10)-B(1)	-165.1(7)
C(29)-C(30)-C(31)-B(2)	70.4(10)
S(4)-C(30)-C(31)-B(2)	-168.9(8)
C(27)-C(28)-C(23)-C(24)	-2.4(14)
C(27)-C(28)-C(23)-C(22)	178.2(9)
C(4)-C(5)-C(6)-C(7)	-3.2(12)
S(1)-C(5)-C(6)-C(7)	174.6(7)
N(2)-C(33)-C(32)-S(4)	-56.5(7)
C(34)-C(33)-C(32)-S(4)	70.5(8)
C(30)-S(4)-C(32)-C(33)	56.5(7)
C(26)-C(25)-C(24)-C(23)	0.8(15)
C(28)-C(23)-C(24)-C(25)	1.9(15)
C(22)-C(23)-C(24)-C(25)	-178.6(9)
C(17)-O(3)-B(1)-O(4)	-2.5(14)
C(17)-O(3)-B(1)-C(10)	178.2(10)
C(9)-C(10)-B(1)-O(3)	-10.6(14)
C(9)-C(10)-B(1)-O(4)	170.2(9)
O(3)-B(1)-O(4)-C(16)	-4.9(14)
C(10)-B(1)-O(4)-C(16)	174.4(11)
N(1)-C(12)-C(11)-S(2)	-59.5(7)
C(13)-C(12)-C(11)-S(2)	69.9(8)
C(9)-S(2)-C(11)-C(12)	57.8(6)
N(1)-C(12)-C(13)-C(14)	-176.0(8)
C(11)-C(12)-C(13)-C(14)	56.6(11)
N(1)-C(12)-C(13)-C(15)	-50.3(10)
C(11)-C(12)-C(13)-C(15)	-177.6(8)
C(5)-C(6)-C(7)-C(2)	1.7(15)
C(6)-C(7)-C(2)-C(3)	1.1(15)

C(6)-C(7)-C(2)-C(1)	-177.2(10)
C(4)-C(3)-C(2)-C(7)	-2.4(13)
C(4)-C(3)-C(2)-C(1)	176.0(8)
C(37)-O(8)-B(2)-O(7)	-1.6(14)
C(37)-O(8)-B(2)-C(31)	177.2(13)
C(38)-O(7)-B(2)-O(8)	-2.9(15)
C(38)-O(7)-B(2)-C(31)	178.2(12)
C(30)-C(31)-B(2)-O(8)	-3.2(16)
C(30)-C(31)-B(2)-O(7)	175.5(10)
B(2)-O(8)-C(37)-C(38)	5.3(16)
B(2)-O(8)-C(37)-C(41)	136.4(17)
B(2)-O(8)-C(37)-C(42)	-111.2(14)
B(1)-O(3)-C(17)-C(18)	150.3(16)
B(1)-O(3)-C(17)-C(16)	8.6(15)
B(1)-O(3)-C(17)-C(19)	-101.8(14)
B(1)-O(4)-C(16)-C(20)	140.3(19)
B(1)-O(4)-C(16)-C(17)	9.9(16)
B(1)-O(4)-C(16)-C(21)	-89.7(18)
C(18)-C(17)-C(16)-C(20)	93(3)
O(3)-C(17)-C(16)-C(20)	-133(2)
C(19)-C(17)-C(16)-C(20)	-24(2)
C(18)-C(17)-C(16)-O(4)	-144.9(16)
O(3)-C(17)-C(16)-O(4)	-10.7(15)
C(19)-C(17)-C(16)-O(4)	98.7(12)
C(18)-C(17)-C(16)-C(21)	-40(2)
O(3)-C(17)-C(16)-C(21)	93.8(15)
C(19)-C(17)-C(16)-C(21)	-156.7(15)
B(2)-O(7)-C(38)-C(39)	140(2)
B(2)-O(7)-C(38)-C(37)	6.1(17)
B(2)-O(7)-C(38)-C(40)	-115(2)
O(8)-C(37)-C(38)-O(7)	-6.7(17)
C(41)-C(37)-C(38)-O(7)	-129.2(17)
C(42)-C(37)-C(38)-O(7)	104.4(13)
O(8)-C(37)-C(38)-C(39)	-133(2)
C(41)-C(37)-C(38)-C(39)	104(3)
C(42)-C(37)-C(38)-C(39)	-22(3)
O(8)-C(37)-C(38)-C(40)	109(2)
C(41)-C(37)-C(38)-C(40)	-13(3)
C(42)-C(37)-C(38)-C(40)	-140(2)

Symmetry transformations used to generate equivalent atoms:

Table S9. Hydrogen bonds for 2,5-*cis*-**9a** [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)