Supplementary information

Synthesis of mono- and polyfunctional organosilicon derivatives of polyhedral carboranes for the preparation of hybrid polymer materials

E. O. Minyaylo, A. I. Kudryavtseva, V. Yu. Zubova, A.A. Anisimov, A.V. Zaitsev, V. A. Ol'shevskaya, A.S. Peregudov, A.M. Muzafarov

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Experimental

Karstedt catalyst (a xylene solution of a platinum (0) complex with 1,3-divinyl-1,1,3,3-tetramethyldisiloxane, Pt ~2%) was purchased from Aldrich.

1,1,3,3-Tetrametyldisiloxane was purchased from abcr GmbH.

Triethoxysilane was purchased from Acros Organics.

Dimethylchlorosilane was purchased from abcr GmbH.

Carboranyl precursors were synthesized according to the published technique [a, b].

1,1,3,3,5,5,7,7,9,9-Decamethylpentasiloxane was synthesized according to the published technique [c]

^{1}H, ^{11}B{H}, ^{13}C, and ^{29}Si NMR spectra were recorded on a Bruker Avance™ 500 spectrometer (Germany) (at 500.13, 160.46, 125.47, and 99.36 MHz for ^{1}H, ^{11}B{H}, ^{13}C, and ^{29}Si, respectively). The ^{1}H chemical shifts were measured relative to the signal of the solvents $CDCl_3$ and C_6D_6. The ^{29}Si chemical shifts were measured relative to TMS used as the external standard. The ^{11}B{H} chemical shifts were measured relative to $BF_3{\cdot}(C_2H_5)_2O$ used as the external standard.

IR spectra were obtained using an IR spectrometer with a Fourier transformer Bruker “Tensor 37”. The samples were prepared by pressing KBr pellets.

High-resolution mass spectra (HRMS) were measured using a Bruker micrOTOF II instrument with electrospray ionization (ESI).

Single-crystal X-ray diffraction experiment was carried out with a Bruker SMART APEX II diffractometer (graphite-monochromated Mo K_α radiation, λ = 0.71073 Å, ω-scan technique) [d].

Synthesis of carborane-containing functional derivatives

1. Synthesis of compound **6**

A test tube equipped with a magnetic stirrer was loaded with 1 g (5.4 mmol) of 9-allyl-*m*-carborane, 14.46 g (108 mmol) of 1,1,3,3-Tetrametyldisiloxane, and 5 µL of Karstedt catalyst. The stirring was continued for 1 hour. Excess of 1,1,3,3-Tetrametyldisiloxane was removed at a temperature of 80° C and a residual pressure of 1 mbar. The product mass after purge was 1.68 g, the yield was 97%.

^{1}H NMR (500.13 MHz, $CDCl_3$, ppm): δ 4.73-4.70 (m, 1H, -SiH); 2.88 (br s, 2H, -C_{carb}-H);); 3.00-1.80 (9H, B-H); 1.46-1.40 (m, 2H, -CH_2-); 0.95-0.92 (m, 2H, -BCH_2-); 0.66-0.63 (m, 2H, -$SiCH_2$-); 0.20-0.19 (d, *J* = 2.8 Hz, 6H, -$SiCH_3$); 0.09 (s, 6H, -$SiCH_3$).

^{13}C NMR (125.47 MHz, $CDCl_3$, ppm): δ 54.01, 23.94, 21.63, 19.93, 0.94, 0.22.

^{29}Si NMR (99.36 MHz, $CDCl_3$, ppm): δ 9.78, -7.06.

^{11}B{H} NMR (160.46 MHz, $CDCl_3$, ppm): δ 1.04, -6.53, -10.05, -13.28, -14.08, -17.71, -20.45.

IR (v/cm^{-1}): 2958.52, 2917.36, 2598.00, 2120.87, 1254.16, 1065.46, 1036.11, 908.82, 838.83.

Elemental analysis: Found %: C, 33.95; H, 9.51; B, 33.90; Si, 17.62; Calculated for $C_9H_{30}B_{10}OSi_2$ %: C, 33.93; H, 9.49; B, 33.93; O, 5.02; Si, 17.63

HRMS (ESI) *m/z* calcd. for $C_9H_{30}B_{10}OSi_2$ [(M+nNH4)$^+$]: 338.28, found 338.31; [(M+nNa)$^+$]: 343.28, found 343.27.

2. Synthesis of compound **7**

A test tube equipped with a magnetic stirrer was loaded with 0.5 g (2.7 mmol) of 9-allyl-*m*-carborane, 9.63 g (27 mmol) of 1,1,3,3,5,5,7,7,9,9-Decamethylpentasiloxane, and 8 µL of Karstedt catalyst. The stirring was continued for 1 hour. Excess of 1,1,3,3,5,5,7,7,9,9-Decamethylpentasiloxane was removed at a temperature of 80° C and a residual pressure of 1 mbar. The product mass after purge was 1.42 g, the yield was 97%.

^{1}H NMR (500.13 MHz, $CDCl_3$, ppm): δ 4.75-4.72 (dp, *J* = 5.5, 2.8 Hz, 1H, -SiH); 2.88 (br s, 2H, -C_{carb}-H); 3.00-1.80 (9H, B-H); 1.46-1.40 (m, 2H, -CH_2-); 0.95-0.92 (m, 2H, -BCH_2-); 0.66-0.63 (m, 2H, -$SiCH_2$-); 0.22-0.21 (d, *J* = 2.7 Hz, 6H, -$SiCH_3$); 0.11 (m, 18H, -$SiCH_3$); 0.08 (s, 6H, -$SiCH_3$).

^{13}C NMR (125.47 MHz, $CDCl_3$, ppm): δ 53.98, 23.97, 21.79, 19.90, 1.19, 1.07, 0.88, 0.71, 0.35.

^{29}Si NMR (99.36 MHz, $CDCl_3$, ppm): δ 7.40, -6.90, -19.84, -21.69, -21.93.

^{11}B{H} NMR (160.46 MHz, $CDCl_3$, ppm): δ 1.11, -6.54, -10.07, -13.31, -14.11, -17.74, -20.52.

IR (ν/cm^{-1}): 2961.50, 2917.36, 2598.84, 2127.51, 1258.92, 1085.41, 1036.11, 911.15, 800.16.

Elemental analysis: Found %: C, 33.21; H, 9.14; B, 19.97; Si, 25.87; Calculated for $C_{15}H_{49}B_{10}O_4Si_5$ %: C, 33.24; H, 9.11; B, 19.94; O, 11.81; Si, 25.90.

HRMS (ESI) *m/z* calcd. for $C_{15}H_{49}B_{10}O_4Si_5$ [(M-nH)]: 540.98, found 541.33; [(M+nNH4)$^+$]: 560.03, found 560.37; [(M+nNa)$^+$]: 564.98, found 565.32.

3. Synthesis of compound **8**

A test tube equipped with a magnetic stirrer was loaded with 0.1 g (0.54 mmol) of 9-allyl-*m*-carborane, 0.2 ml (1.1 mmol) of triethoxysilane, and 5 µL of Karstedt catalyst. The stirring was continued for 1 hour. Excess of triethoxysilane was removed at a temperature of 50° C and a residual pressure of 1 mbar. The product mass after purge was 0.18 g, the yield was 98%.

^{1}H NMR (500.13 MHz, C_6D_6, ppm): δ 3.86-3.82 (q, *J* = 7.0 Hz 6H, -OC_2H_5); 3.00-1.80 (9H, B-H); 2.01 (br s, 2H, -C_{carb}-H); 1.89-1.83 (dt, *J* = 16.5, 8.2 Hz, 2H, -BCH_2-); 1.25-1.22 (m, 2H, -CH_2-); 1.21-1.18 (t, *J* = 7.0 Hz,, 9H, -OC_2H_5); 0.94-0.91 (m, 2H, -$SiCH_2$-).

^{13}C NMR (125.47 MHz, C_6D_6, ppm): δ 58.08, 53.95, 24.00, 19.98, 18.31, 14.31.

^{29}Si NMR (99.36 MHz, C_6D_6, ppm): δ -45.55.

^{11}B{H} NMR (160.46 MHz, C_6D_6, ppm): δ 1.14, -6.52, -9.87. -13.28, -14.07, -17.92, -20.67.

IR (ν/cm^{-1}): 3047.97, 2974.56, 2925.47, 2886.21, 2596.49, 1390.22, 1340.55, 1167.20, 1102.64, 1076.55, 958.75, 784.36.

Elemental analysis: Found %: C, 37.88; H, 9.27; B, 31.05; Si, 8.03; Calculated for $C_{11}H_{32}B_{10}O_3Si$ %: C, 37.90; H, 9.25; B, 31.01; O, 13.77; Si, 8.06.

HRMS (ESI) *m/z* calcd. for $C_{11}H_{32}B_{10}O_3Si$ [(M+nH)$^+$]: 349.57, found 351.31; [(M+nNH4)$^+$]: 366.59, found 368.34; [(M+nNa)$^+$]: 371.55, found 373.29.

4. Synthesis of compound **13**

A test tube equipped with a magnetic stirrer was loaded with 0.1 g (0.33 mmol) of 1,2,9,12-tetraallyl-*o*-carborane, 0.49 ml (2.6 mmol) of triethoxysilane, and 5 µL of Karstedt catalyst. The stirring was continued for 1 hour. Excess of triethoxysilane was removed at a room temperature and a residual pressure of 1 mbar. The product mass after purge was 0.31 g, the yield was 97%.

^{1}H NMR (500.13 MHz, C_6D_6, ppm): δ 3.90-3.86 (q, *J* = 7.0 Hz, 12H, -OCH_2-); 3.79-3.74 (q, *J* = 7.0 Hz, 12H, -OCH_2-); 3.00-1.80 (9H, B-H); 1.96-1.91 (m, 4H, -CH_2-); 1.89-1.84 (m, 4H, -CH_2-); 1.64-1.55 (m, 4H, -CH_2-); 1.24-1.20 (m, 18H, -CH_3); 1.19-1.15 (m, 18H, -CH_3); 1.00-0.96 (t, 4H, -CH_2-); 0.47-0.44 (m, 4H, -CH_2-).

^{13}C NMR (125.47 MHz, C_6D_6, ppm): δ 72.85, 59.01, 58.19, 58.08, 39.80, 23.60, 23.54, 19.72, 18.35, 18.23, 14.57, 10.37.

^{29}Si NMR (99.36 MHz, C_6D_6, ppm): δ -45.36, -46.85.

^{11}B{H} NMR (160.46 MHz, C_6D_6, ppm): δ 17.13, 0.20, -6.48, -11.59, -16.78.

IR (ν/cm^{-1}): 2975.06, 2926.17, 2886.63, 2584.65, 1390.18, 1167.80, 1105.16, 1080.96, 957.89, 791.42.

Elemental analysis: Found %: C, 47.45; H, 9.67; B, 11.20; Si, 11.71; Calculated for $C_{38}H_{92}B_{10}O_{12}Si_4$ %: C, 47.47; H, 9.64; B, 11.24; O, 19.97; Si, 11.68.

HRMS (ESI) *m/z* calcd. for $C_{38}H_{92}B_{10}O_{12}Si_4$ [(M+nH)$^+$]: 962.66, found 963.67; [(M+nNH4)$^+$]: 980.66, found 980.69; [(M+nNa)$^+$]: 985.66, found 985.65; [(M+nK)$^+$]: 1001.66, found 1001.62.

5. Synthesis of compound **14**

A test tube equipped with a magnetic stirrer was loaded with 0.2 g (0.65 mmol) of 1,2,9,12-tetraallyl-*o*-carborane, 0.57 ml (5.2 mmol) of dimethylchlorosilane, and 5 µL of Karstedt catalyst. The stirring was continued for 1 hour. Excess of chlorosilane was removed at a temperature of 50° C a residual pressure of 2 mbar. The product mass after purge was 0.25 g, the yield was 98%.

^{1}H NMR (500.13 MHz, C_6D_6, ppm): δ 3.00-1.80 (9H, B-H); 1.83-1.75 (m, 8H, -CH_2-); 1.45-1.39 (m, 8H, -$SiCH_2$-); 1.18-1.15 (t, 4H, -BCH_2-); 0.96-0.93 (t, 4H, -$C_{carb}CH_2$-); 0.30 (s, 6H, -$SiCH_3$); 0.14 (s, 6H, -$SiCH_3$).

^{13}C NMR (125.47 MHz, C_6D_6, ppm): δ 72.77, 39.70, 23.61, 23.51, 22.39, 19.30, 18.15, 1.48, 1.05.

^{29}Si NMR (99.36 MHz, C_6D_6, ppm): δ 30.92, 30.49.

^{11}B{H} NMR (160.46 MHz, C_6D_6, ppm): δ 20.21, 0.27, -6.77, -11.66, -17.35.

IR (ν/cm^{-1}): 2956.67, 2922.02, 2888.80, 2587.31, 1254.48, 1072.40, 842.62, 799.86.

Elemental analysis: Found %: 38.70; H, 8.25; B, 15.85; Cl, 20.77; Si, 16.43; Calculated for $C_{22}H_{56}B_{10}Cl_4Si_4$ %: C, 38.69; H, 8.27; B, 15.83; Cl, 20.76; Si, 16.45.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{56}B_{10}Cl_4Si_4$ [(M+nH)$^+$]: 683.94, found 683.32; [(M+nNH4)$^+$]: 700.97, found 700.35; [(M+nNa)$^+$]: 705.92, found 705.30.

NMR characteristics of compounds 1, 2, 9, 10, 11

1. Compound **1** (9-allyl-*m*-carborane)

^{1}H NMR (500.13 MHz, $CDCl_3$, ppm): δ 5.88 (dd, *J* = 17.17 Hz, *J* = 9.54 Hz, 1H, CH_2=C**H**-); 4.86 (m, 2H, C**H$_2$**=CH-); 3.00-1.80 (9H, B-**H**); 2.91 (br. s., 2H, -C_{carb}-**H**); 1.81 (br. s., 2H, -C**H$_2$**-).

^{11}B{H} NMR (160.46 MHz, $CDCl_3$, ppm): δ 0.2; -6.4; -10.0; -13.2; -13.9; -17.6; -20.26.

^{13}C NMR (125.47 MHz, $CDCl_3$, ppm): δ 140.51; 111.84; 54.19; 21.99.

2. Compound **2** (1,2,9,12-tetraallyl-*o*-carborane)

^{1}H NMR (500.13 MHz, $CDCl_3$, ppm): δ 5.88 (m, 2H, CH_2=C**H**-CH_2-C_{carb}-); 5.65 (m, 2H, CH_2=C**H**-CH_2-B-); 5.03 (m, 4H, C**H$_2$**=CH-CH_2-C_{carb}-); 4.86 (m, 4H, C**H$_2$**=CH-CH_2-B-); 3.00-1.80 (8H, B-**H**); 2.62 (d, *J* = 7.32 Hz, 4H, -C**H$_2$**-C_{carb}-), 1.74 (d, *J* = 7.02 Hz, 4H, -C**H$_2$**-B-).

^{11}B{H} NMR (160.46 MHz, $CDCl_3$, ppm): δ -0.69; -6.74; -11.63; -17.26.

^{13}C NMR (125.47 MHz, $CDCl_3$, ppm): δ 140.20; 133.97; 118.03; 112.00; 71.77; 40.96; 21.18.

3. Compound **10** (9-allyl-*o*-carborane)

^{1}H NMR (500.13 MHz, $CDCl_3$, ppm): δ 5.78 (m, 1H, CH_2=C**H**-), 4.79 (m, 2H, C**H$_2$**=CH-), 3.53 (br. s., 1H, -C_{carb}-**H**); 3.46 (br. s., 1H, -C_{carb}-**H**); 3.00-1.80 (9H, B-**H**); 1.66 (br. s., 2H, -C**H$_2$**-).

^{11}B{H} NMR (160.46 MHz, $CDCl_3$, ppm): 7.77; -2.04; -8.87; -13.72; -14.31; -15.38.

^{13}C NMR (125.47 MHz, $CDCl_3$, ppm): 140.39; 111.87; 53.26; 48.40; 24.46.

4. Compound **9** (9-propenyl-*m*-carborane)

^{1}H NMR (500.13 MHz, $CDCl_3$, ppm): δ 5.94 (m, 1H, -C=C**H**-CH_3); 5.64 (d, ^{3}J (H,H)=17.3 Hz, 1H, B-C**H**=); 3.00-1.80 (9H, B-**H**); 2.91 (br s, 2H, -C_{carb}-**H**); 1.78 (dd, ^{3}J (H,H)= 6.2 Hz, ^{5}J (H,H)=1.6 Hz, 3H, -C**H$_3$**).

^{13}C NMR (125.47 MHz, $CDCl_3$, ppm): δ 137.25 (s, -CH=**C**H-CH_3); 127.50 (q, ^{1}J (^{13}C, ^{11}B) = 80 Hz, B-**C**H=C-); 53.82 (br s, -**C$_{carb}$**-H); 21.40 (s, -**C**H$_3$).

^{11}B{H} NMR (160.46 MHz, $CDCl_3$, ppm): δ -1.25; -6.65; -9.96; -13.29; -14.08; -17.68; -20.31.

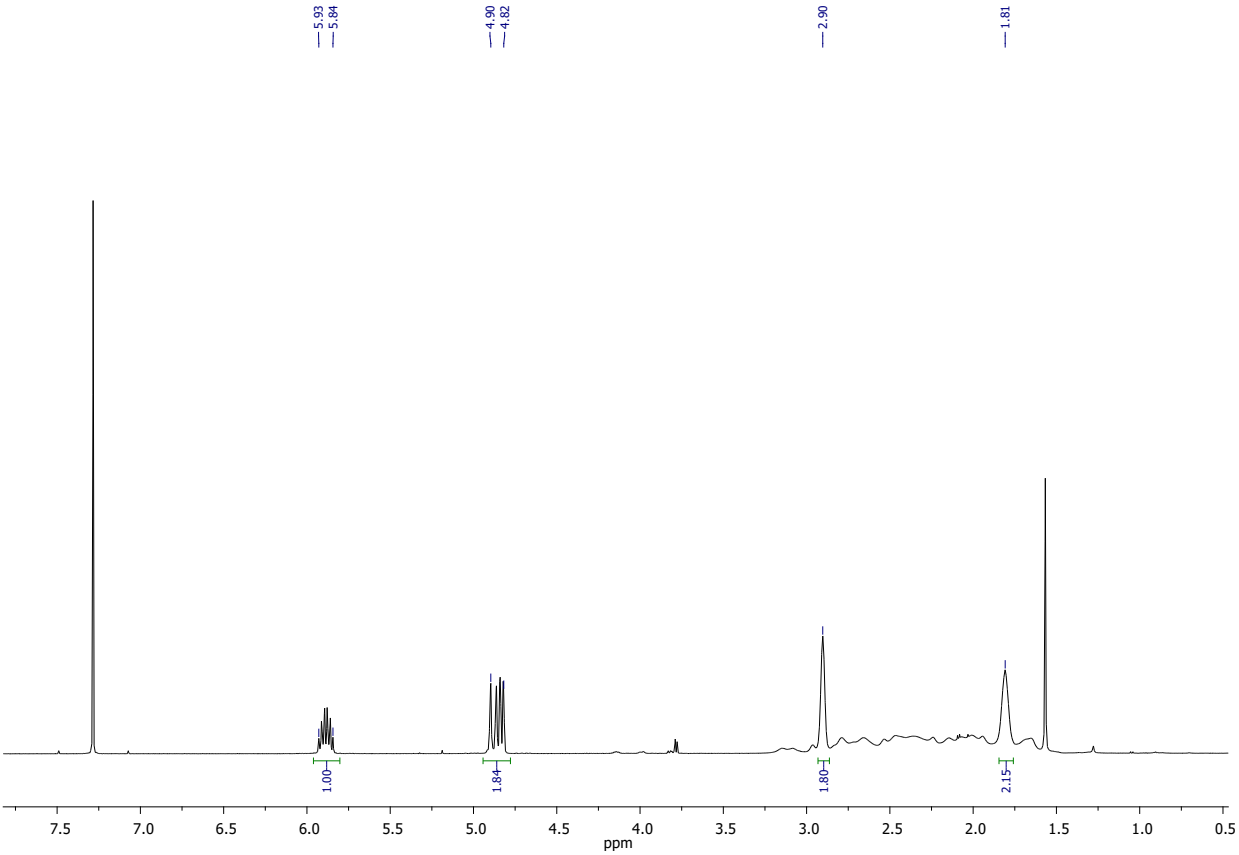
5. Compound **11** (9-propenyl-*o*-carborane)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.76 (m, 1H, -CH=C**H**-CH_3); 5.54 (d, ^{3}J (H,H)=17.2 Hz, 1H, B-C**H**=); 3.53 (s, 1H, -C_{carb}-**H**); 3.44 (s, 1H, -C_{carb}-**H**); 3.00-1.80 (9H, B-**H**); 1.72 (dd, ^{3}J (H,H)= 6.2 HZ, ^{5}J (H,H)=1.5 Hz, 3H, -C**H$_3$**).

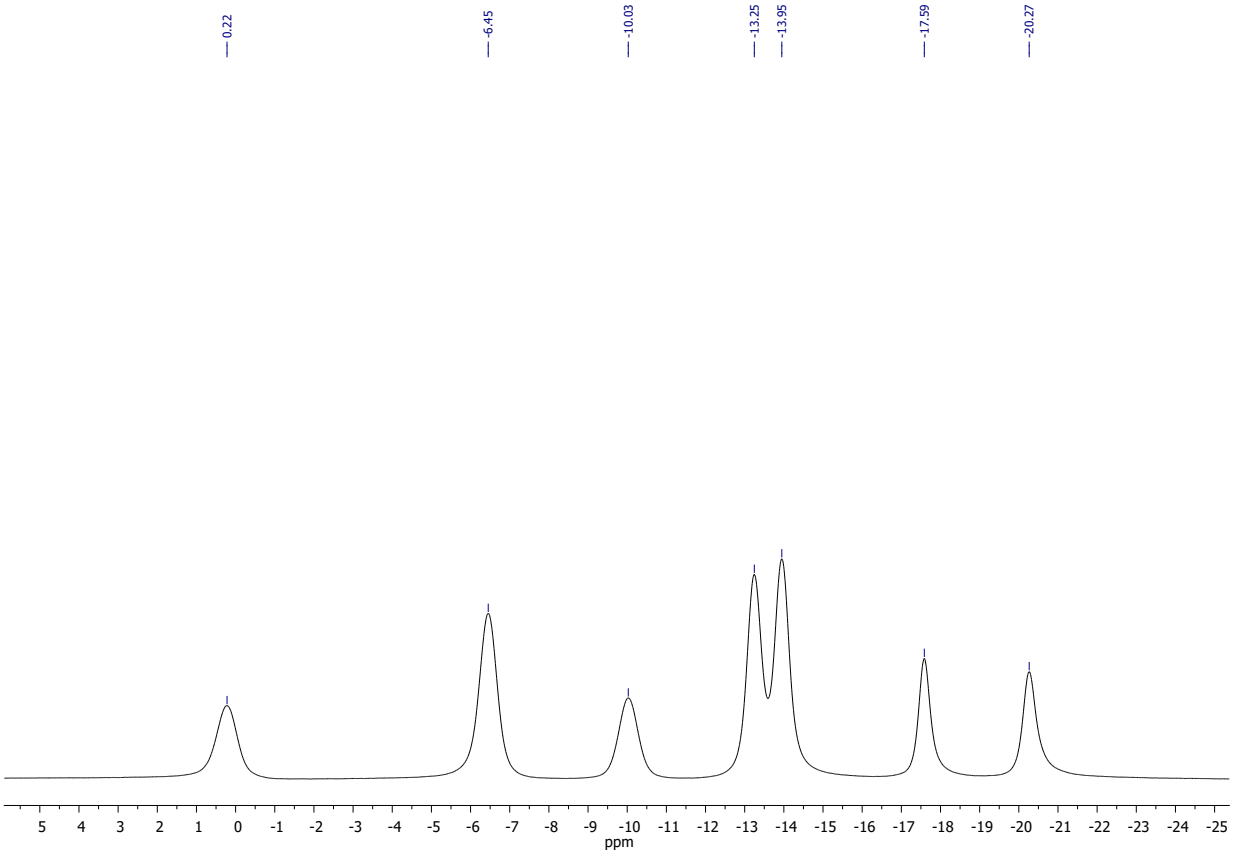
^{13}C NMR (125.47 MHz, $CDCl_3$, ppm): δ 136.38 (s, -CH=**C**H-CH_3); 129.96 (q, B-**C**H=C-); 52.91 (s, -**C$_{carb}$**-H); 48.07 (s, -**C$_{carb}$**-H); 21.32 (s, -**C**H$_3$).

^{11}B{H} NMR (160.46 MHz, $CDCl_3$, ppm): δ 6.17; 2.23; -8.88, -13.85; -14.48; -15.52.

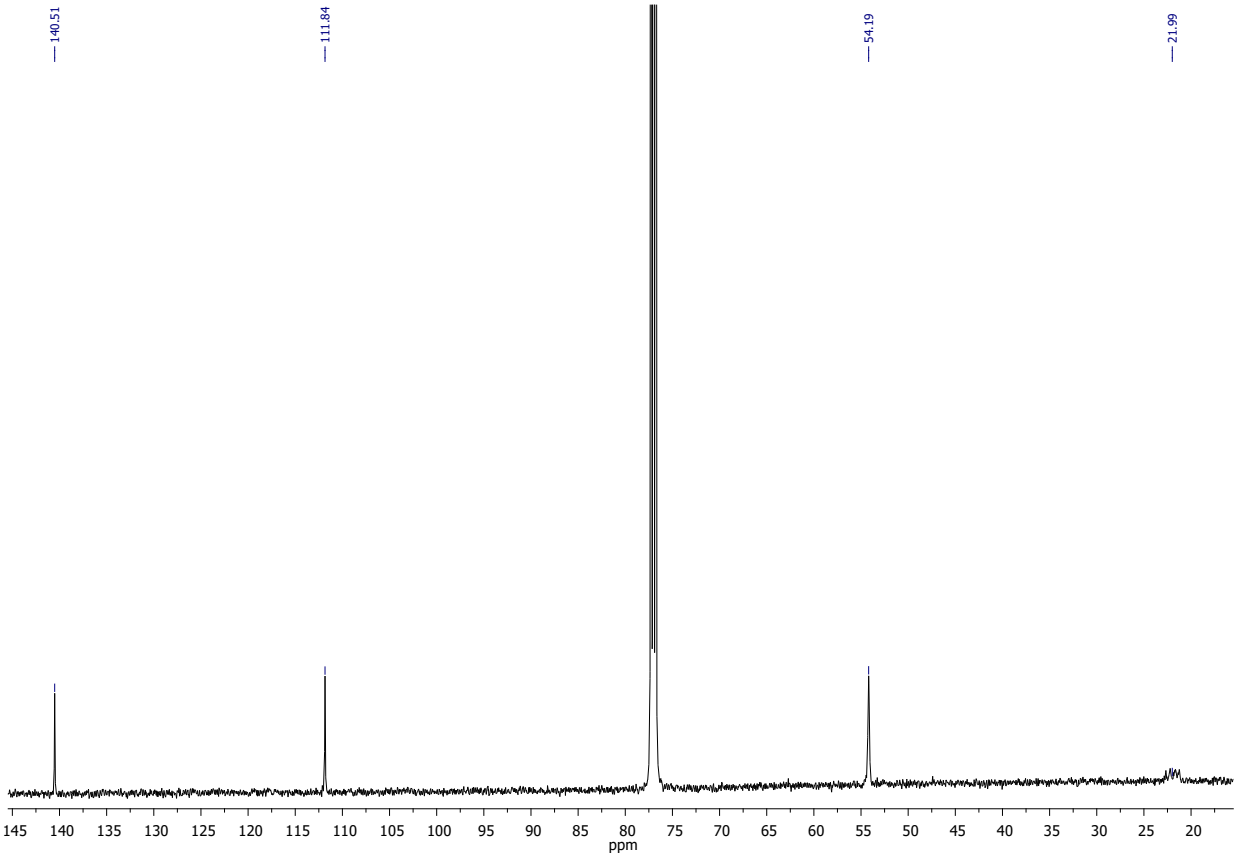
NMR spectra



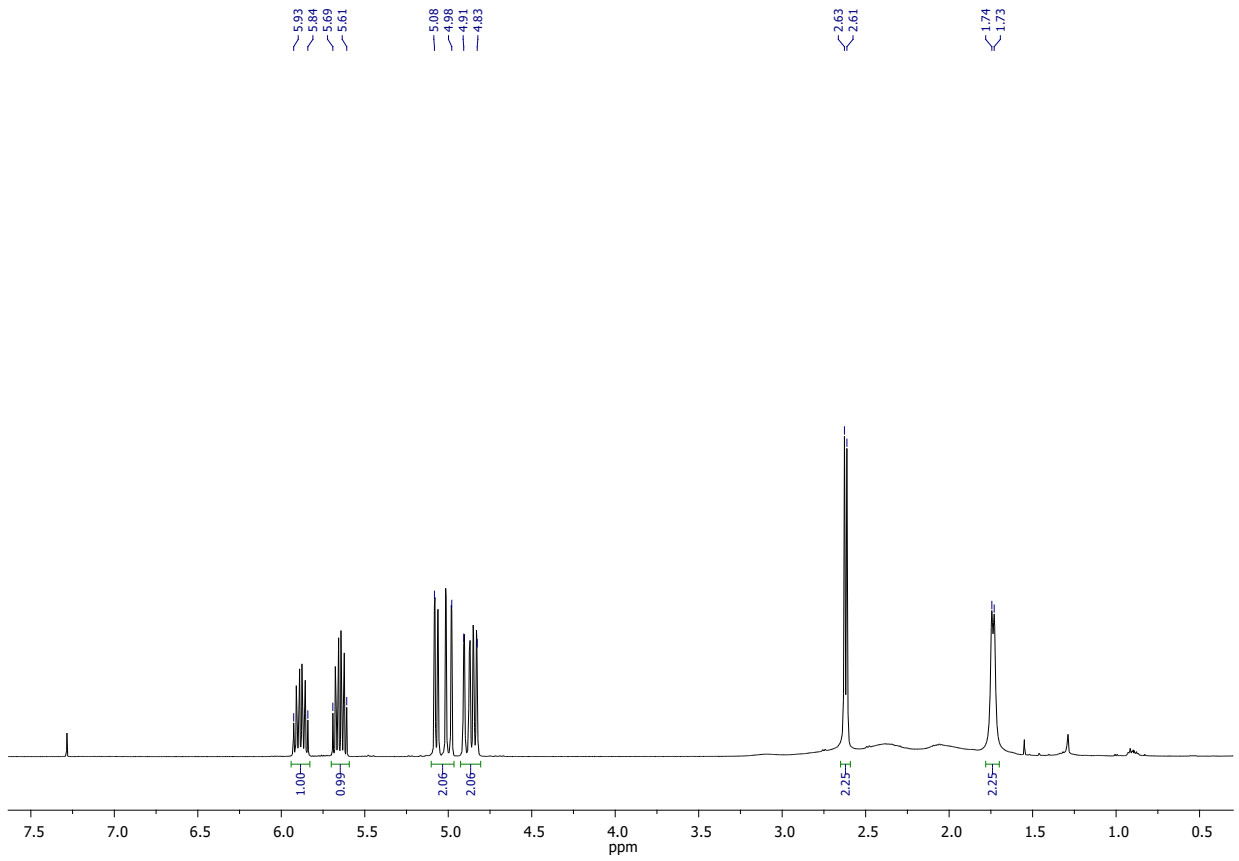
^{1}H NMR (500.13 MHz, $CDCl_3$) of **1**



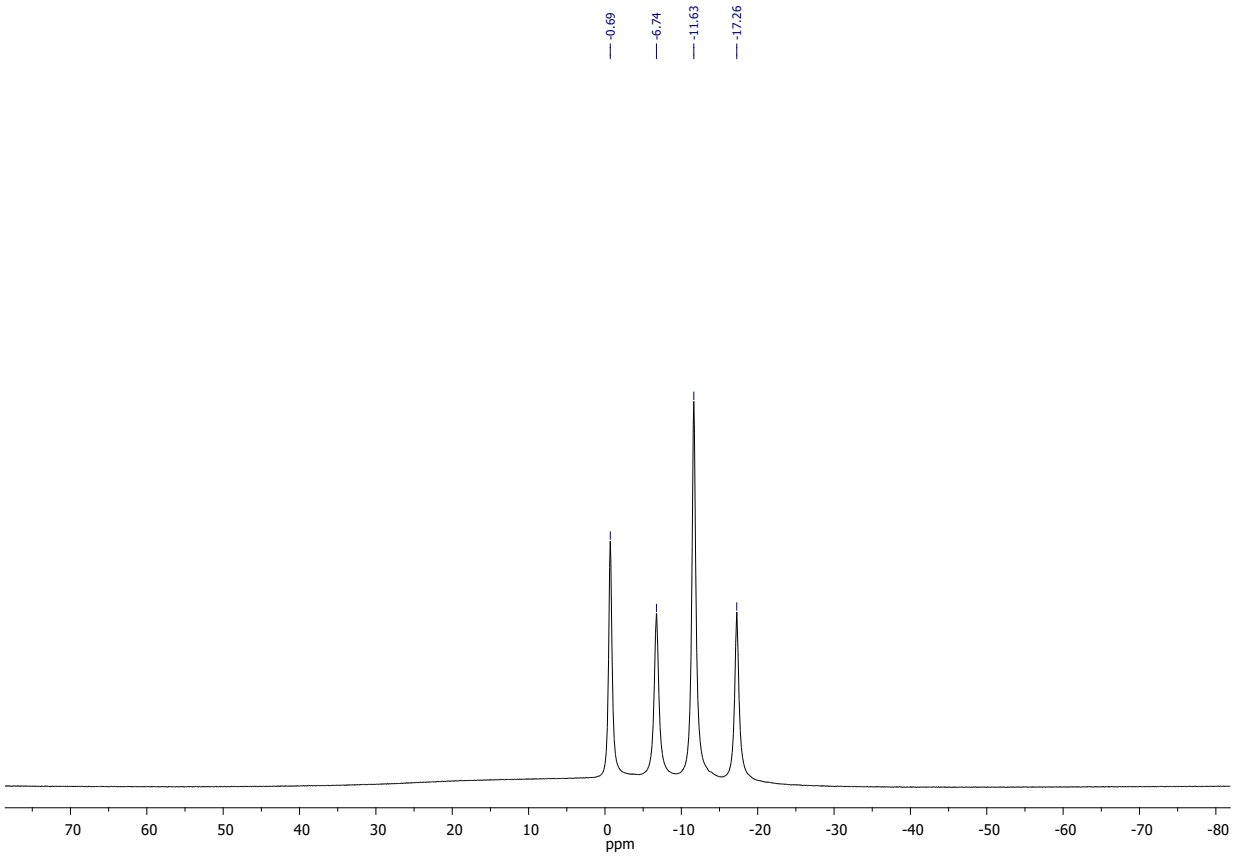
^{11}B{H} NMR (160.46 MHz, $CDCl_3$) of **1**



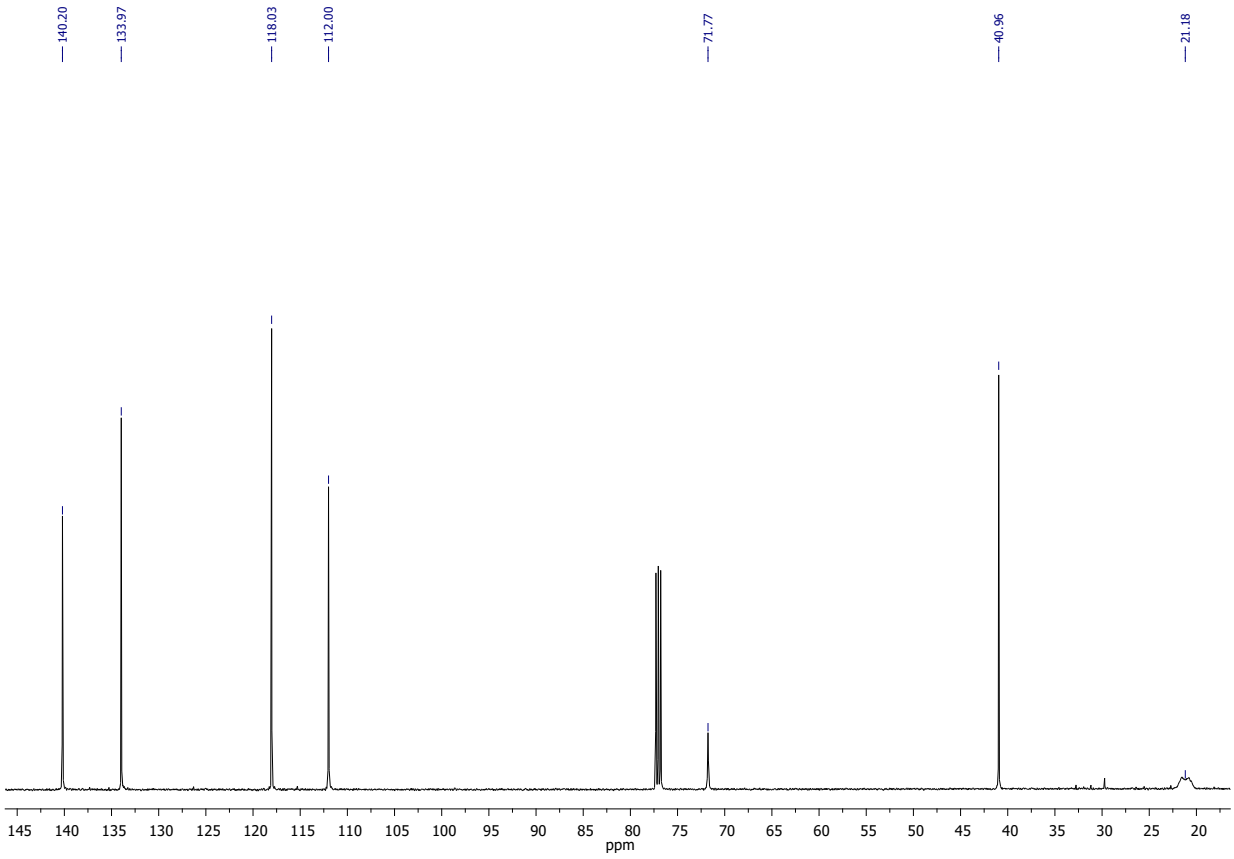
^{13}C NMR (125.47 MHz, $CDCl_3$) of **1**



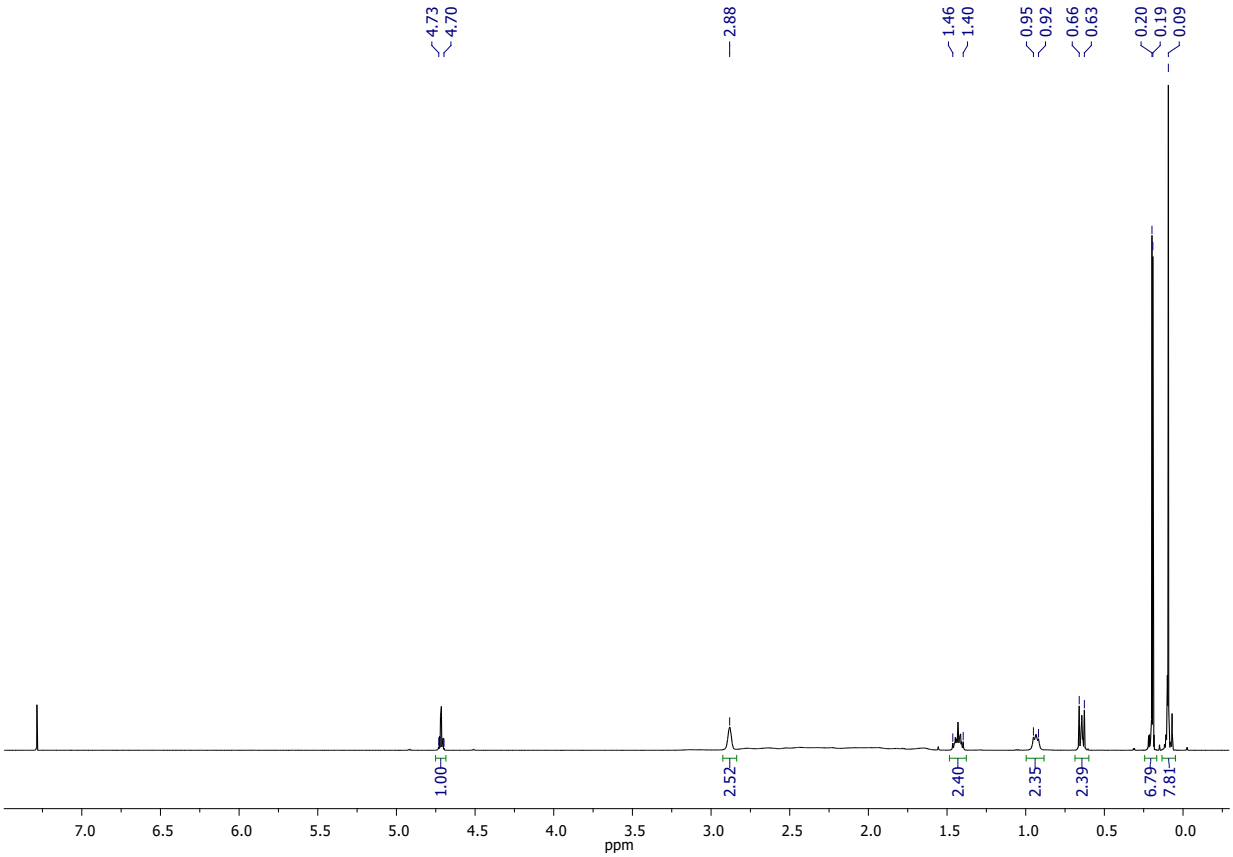
^{1}H NMR (500.13 MHz, $CDCl_3$) of **2**



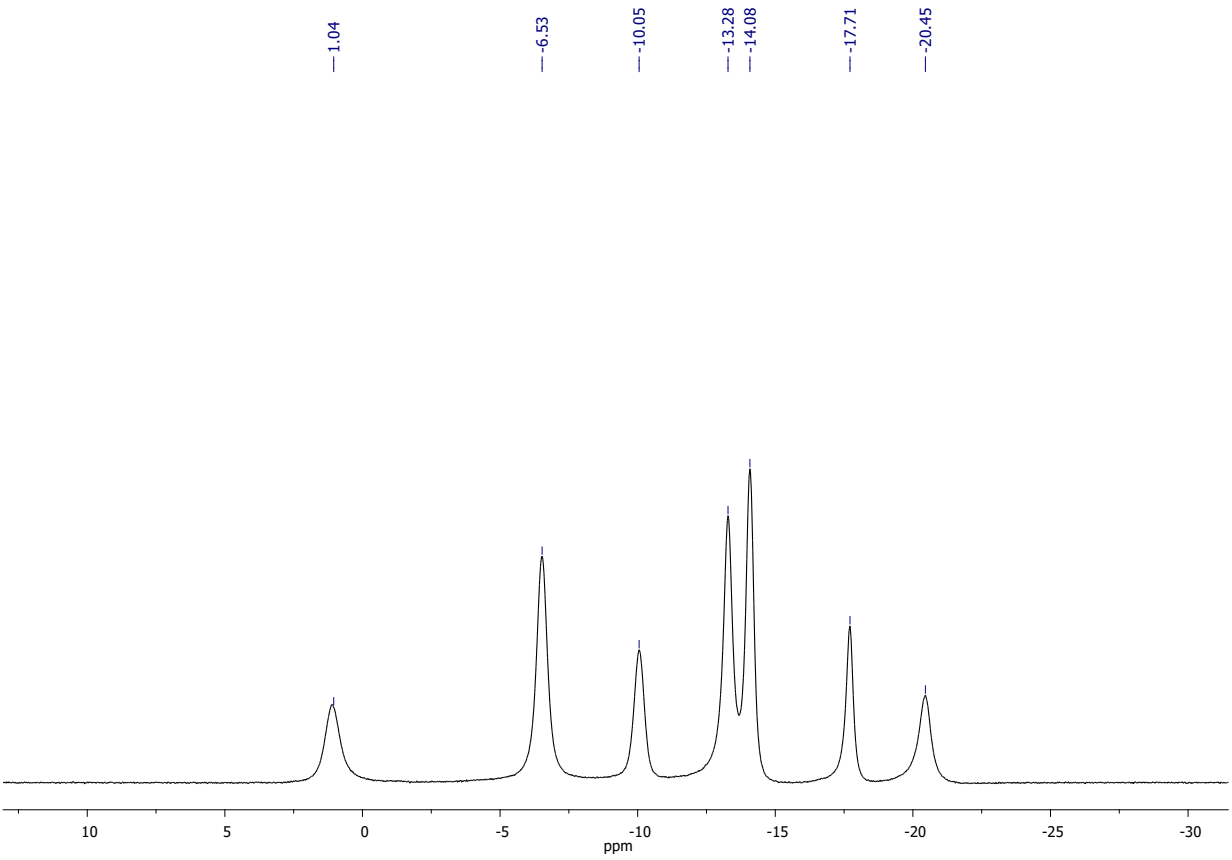
$^{11}B\{H\}$ NMR (160.46 MHz, $CDCl_3$) of **2**



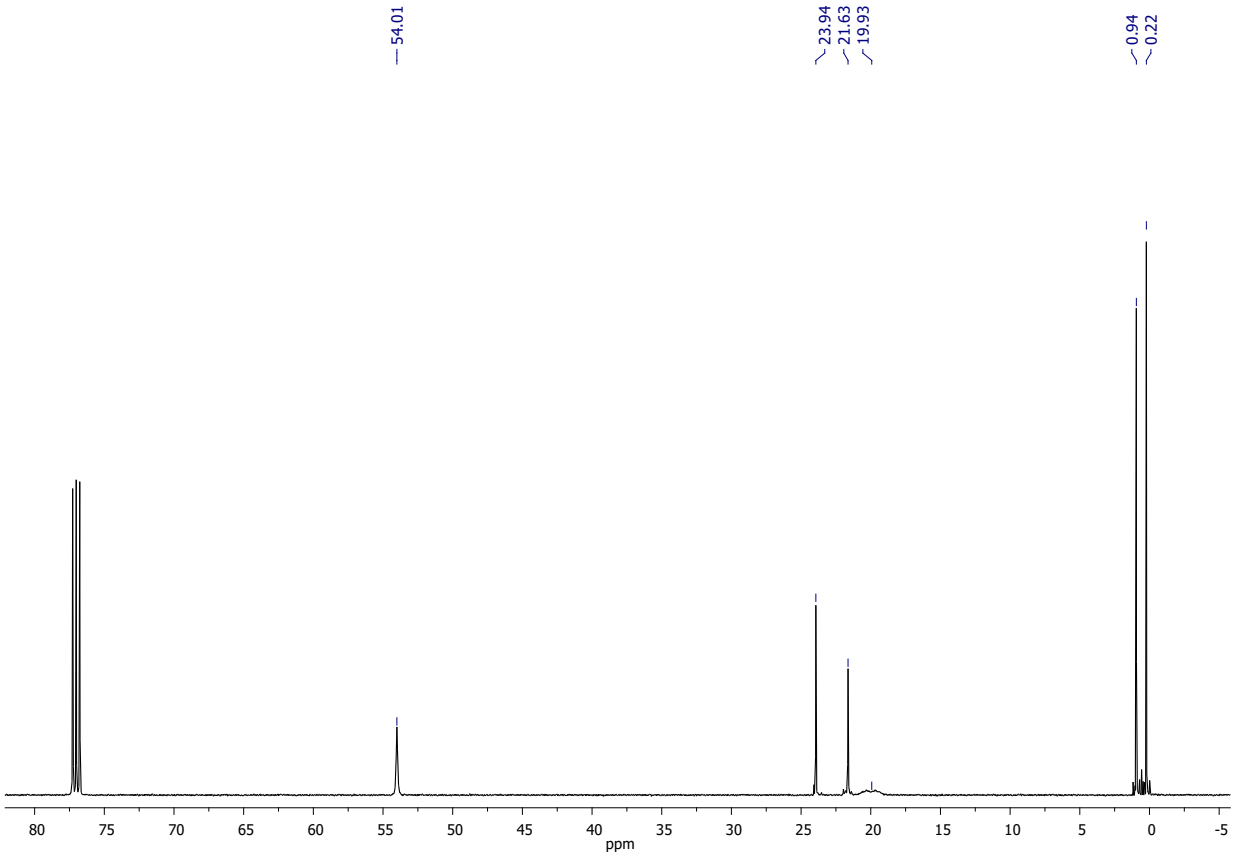
^{13}C NMR (125.47 MHz, $CDCl_3$) of **2**



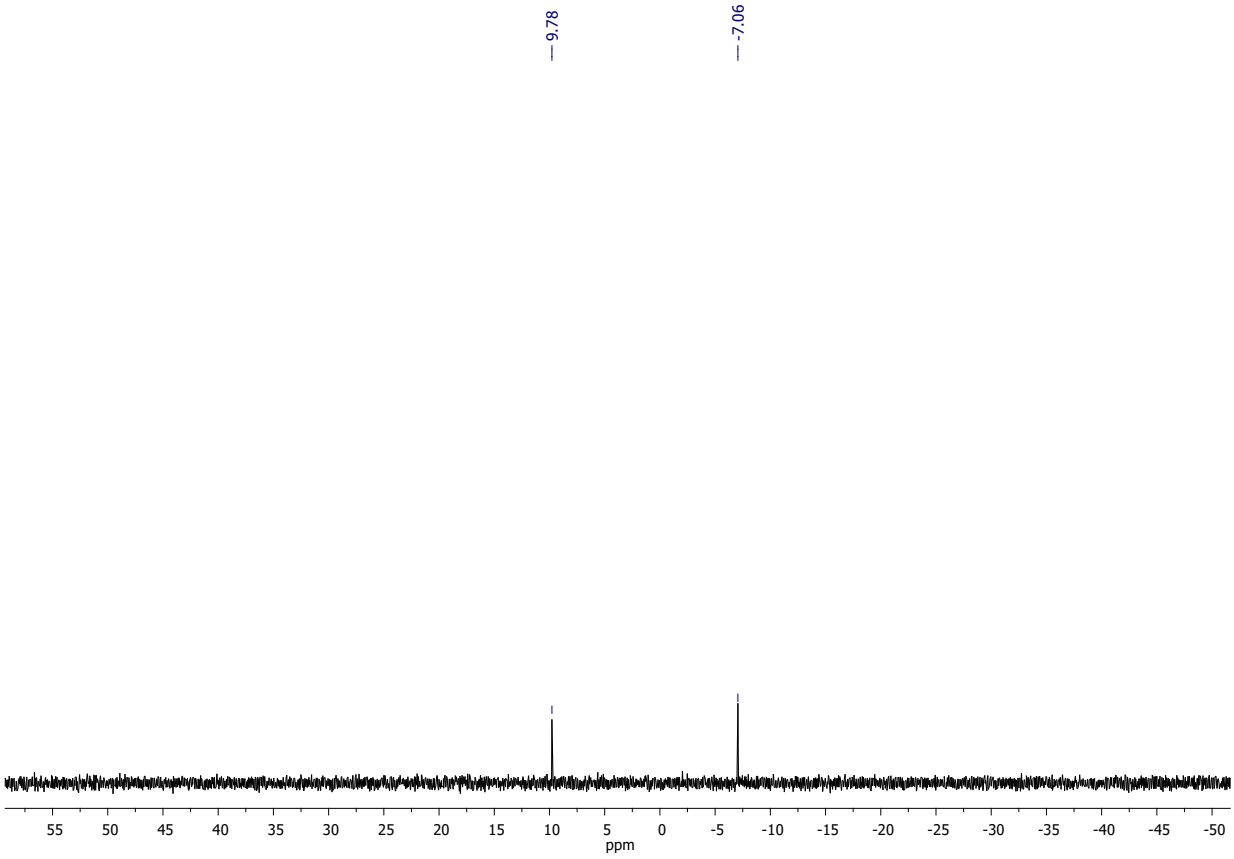
^{1}H NMR (500.13 MHz, $CDCl_3$) of **6**



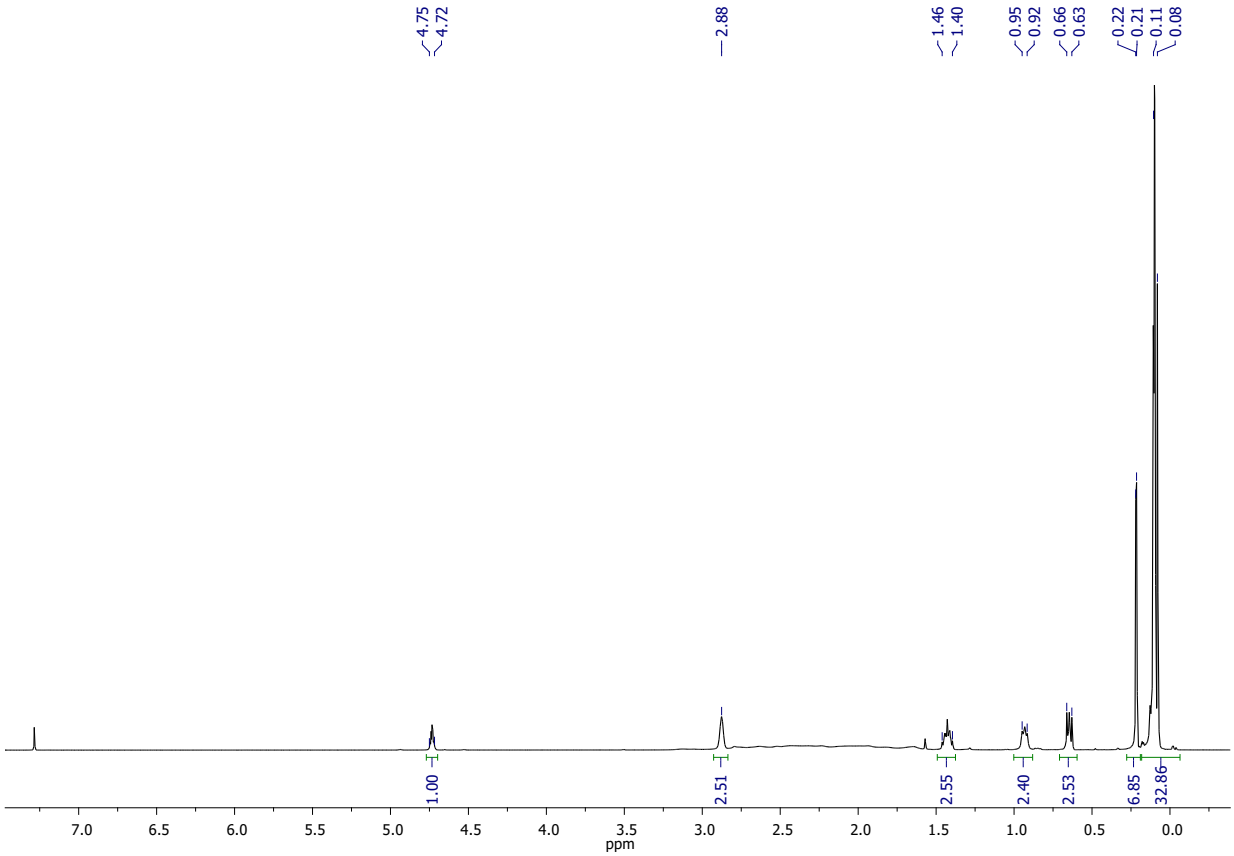
^{11}B{H} NMR (160.46 MHz, $CDCl_3$) of **6**



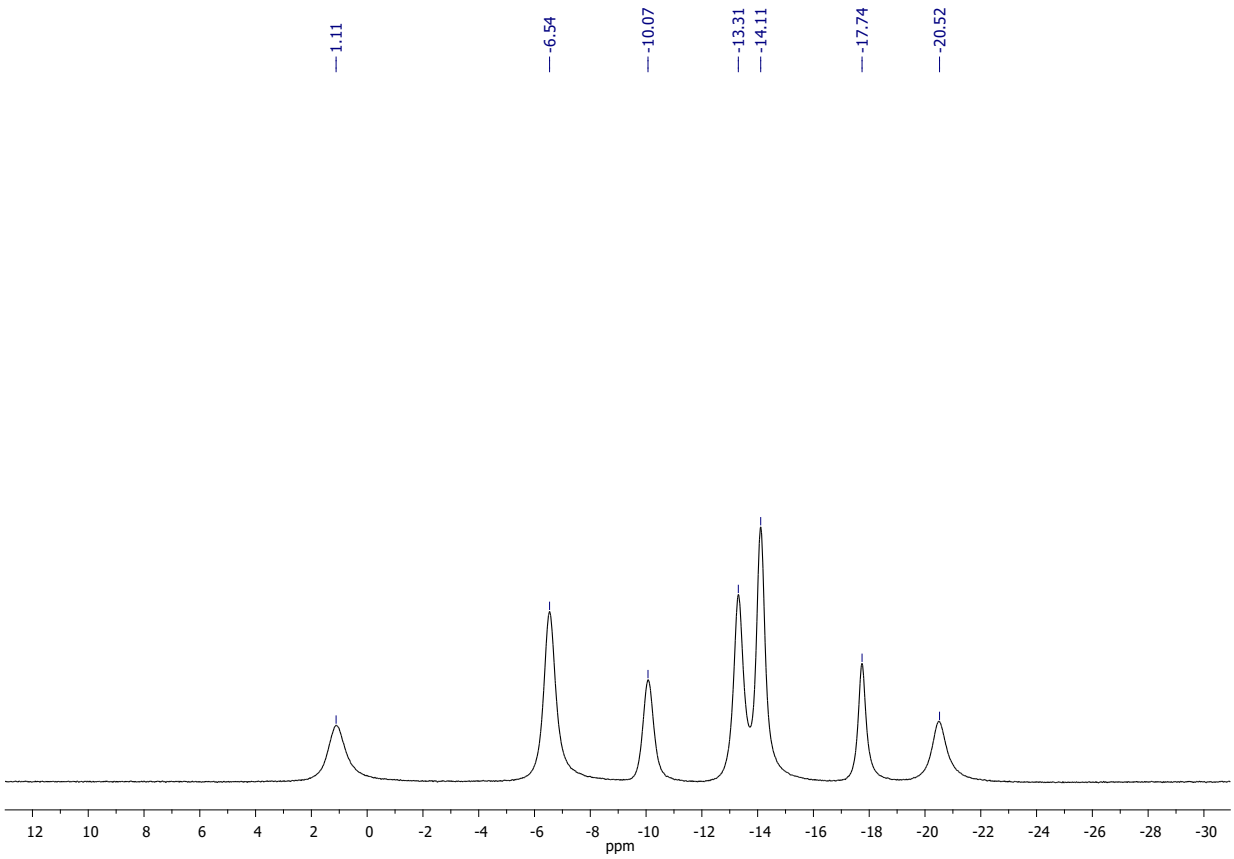
^{13}C NMR (125.47 MHz, $CDCl_3$) of **6**



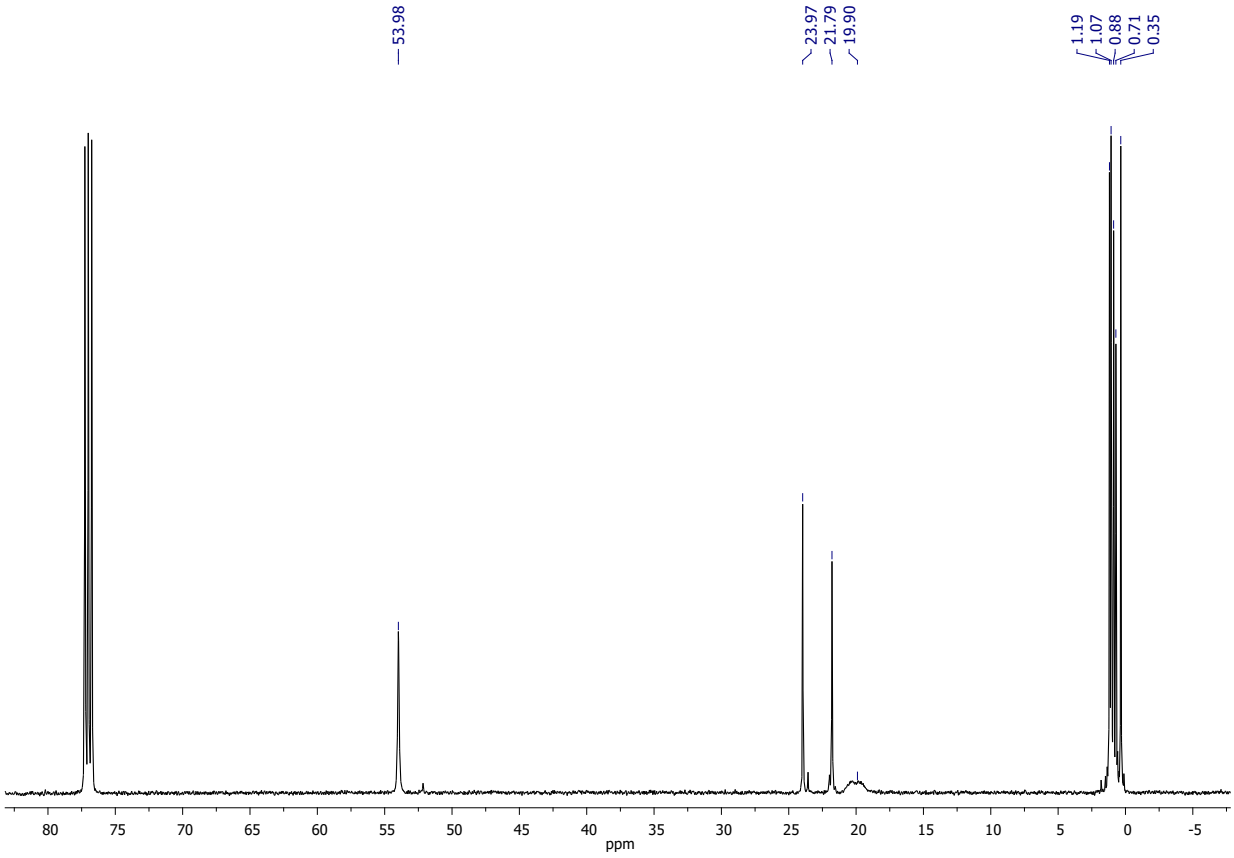
^{29}Si NMR (99.36 MHz, $CDCl_3$) of **6**



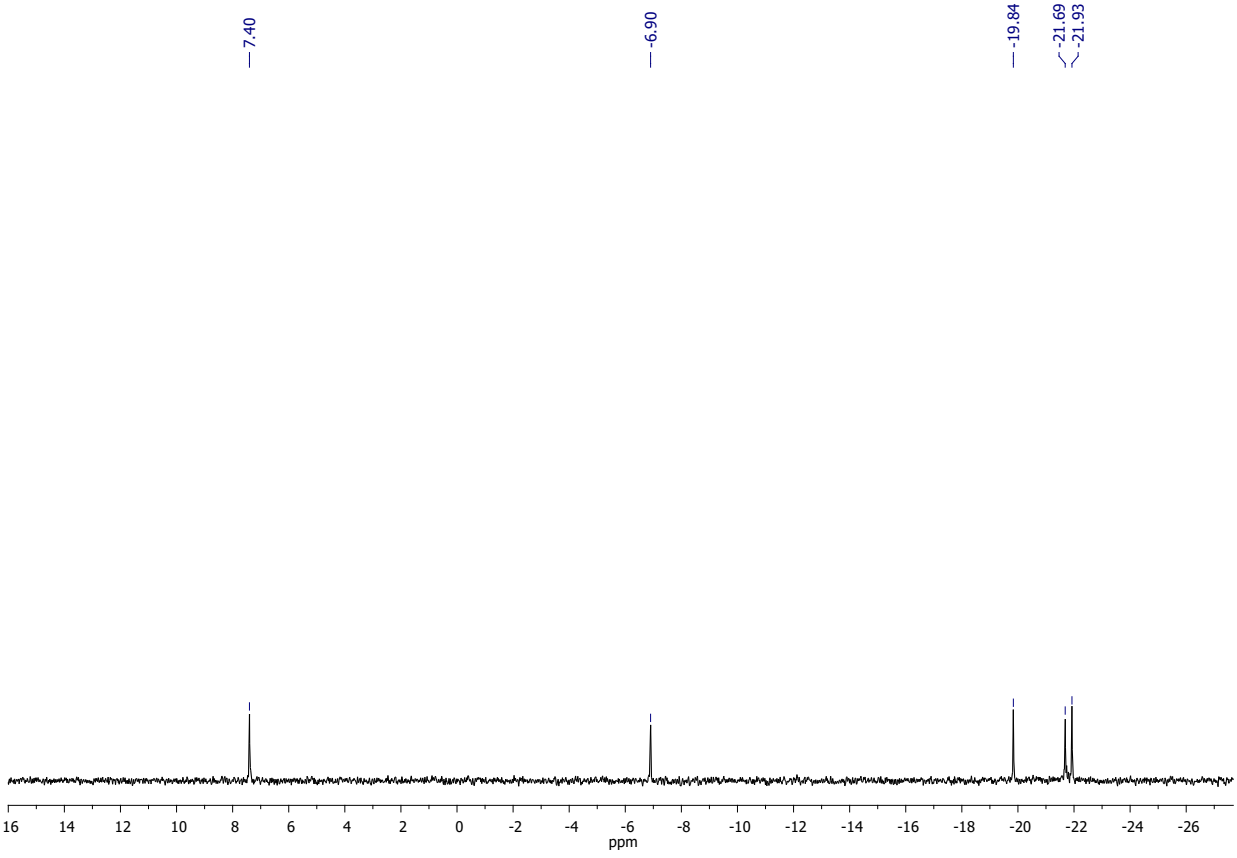
^{1}H NMR (500.13 MHz, $CDCl_3$) of **7**



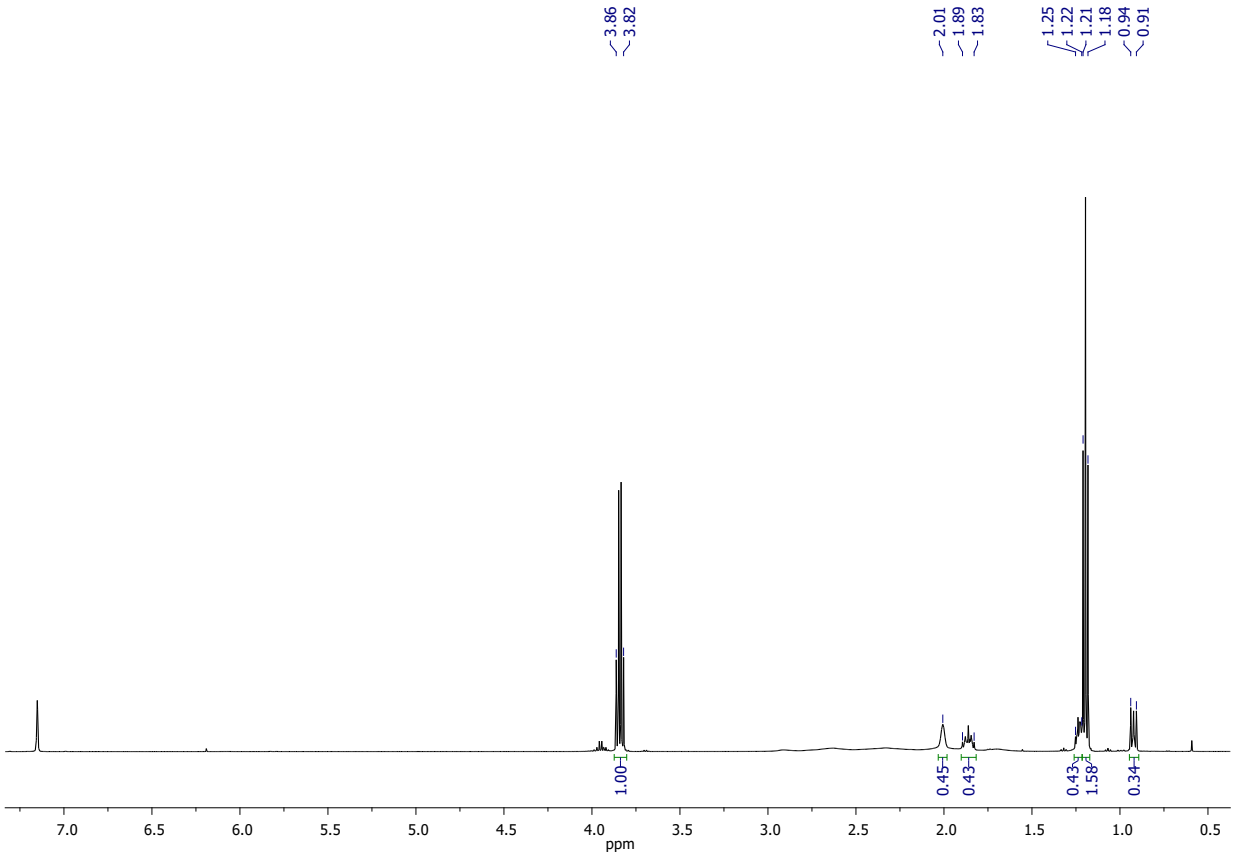
^{11}B{H} NMR (160.46 MHz, $CDCl_3$) of **7**



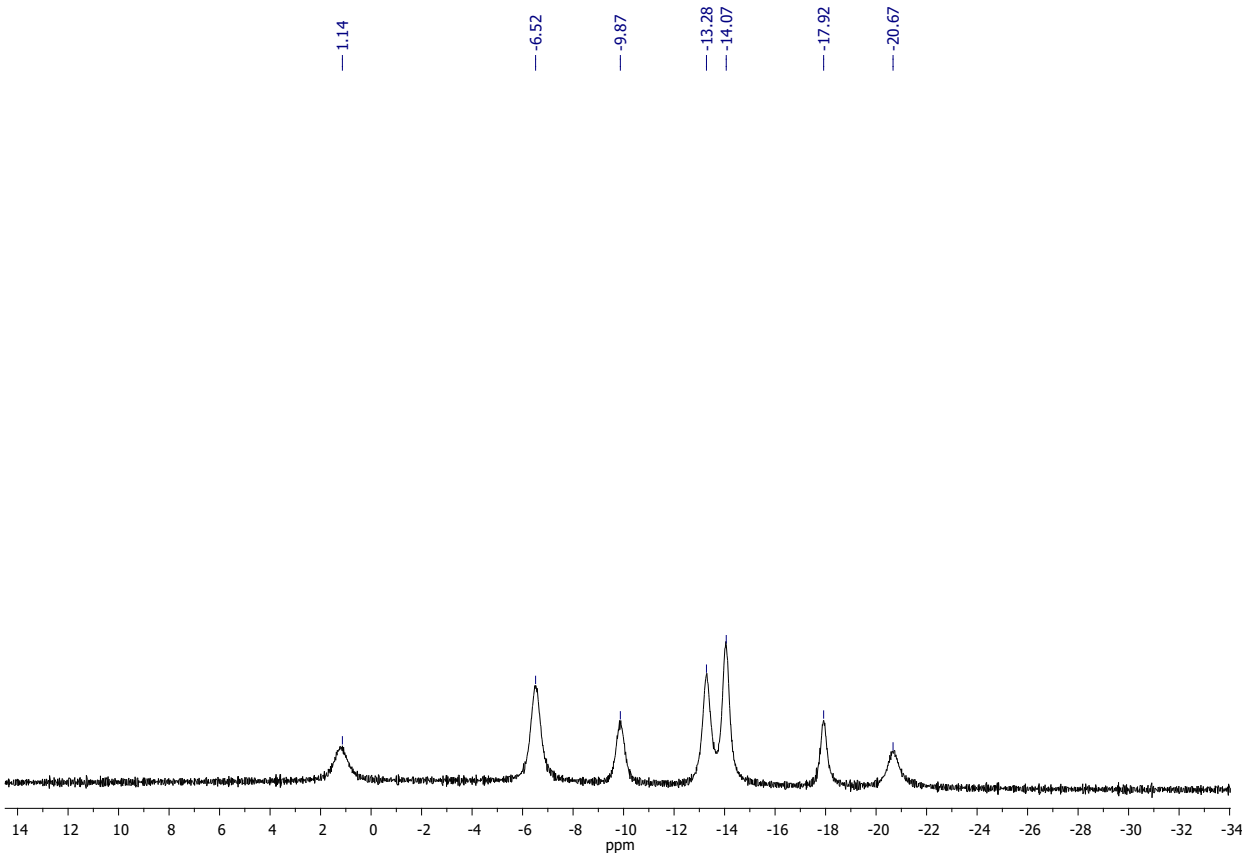
^{13}C NMR (125.47 MHz, $CDCl_3$) of **7**



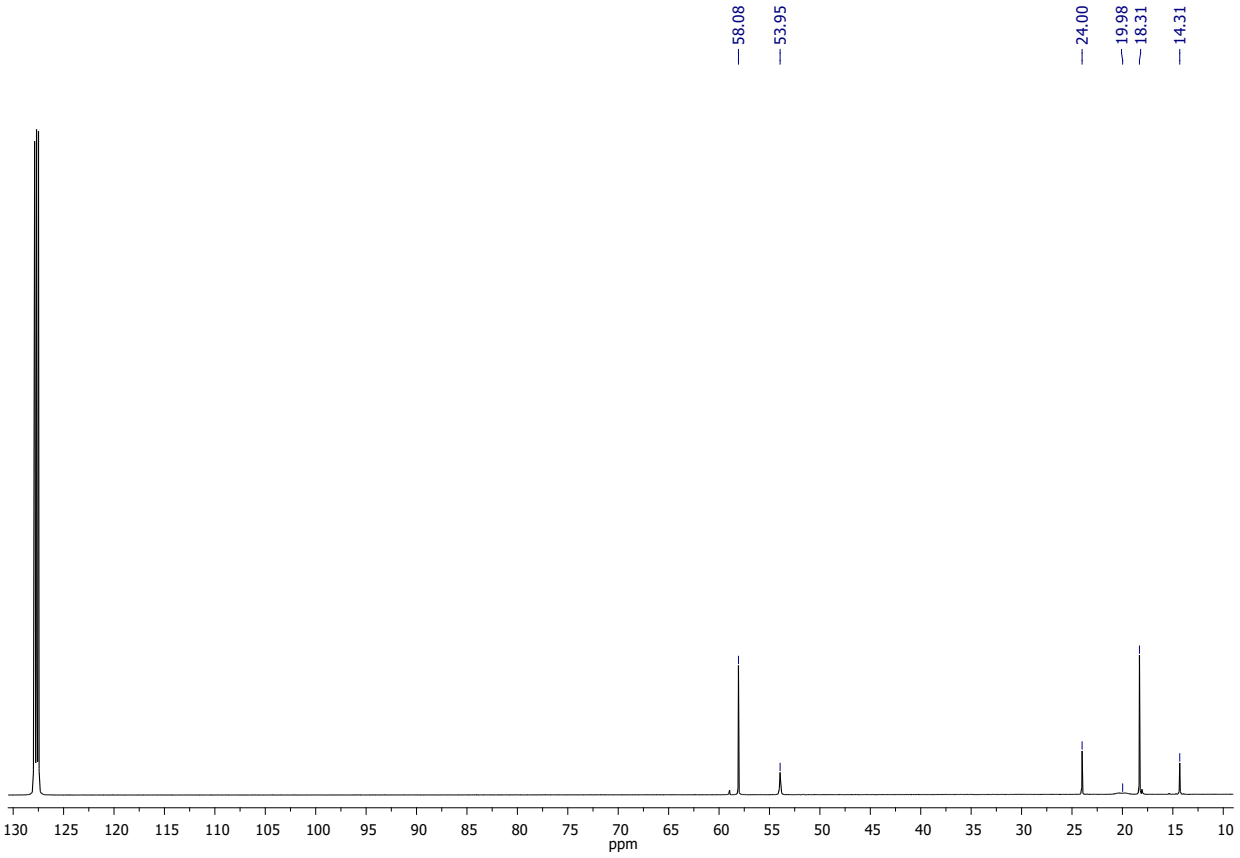
^{29}Si NMR (99.36 MHz, $CDCl_3$) of **7**



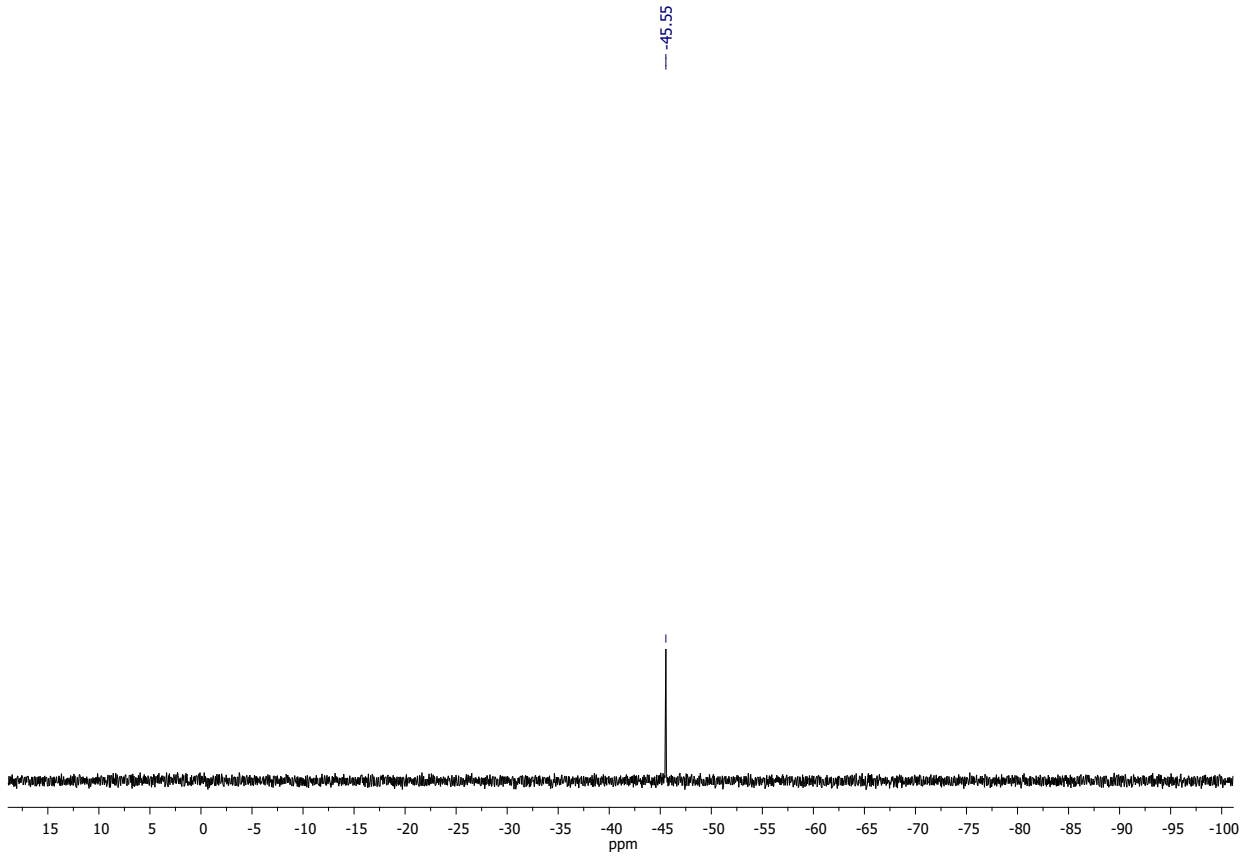
^{1}H NMR (500.13 MHz, C_6D_6) of **8**



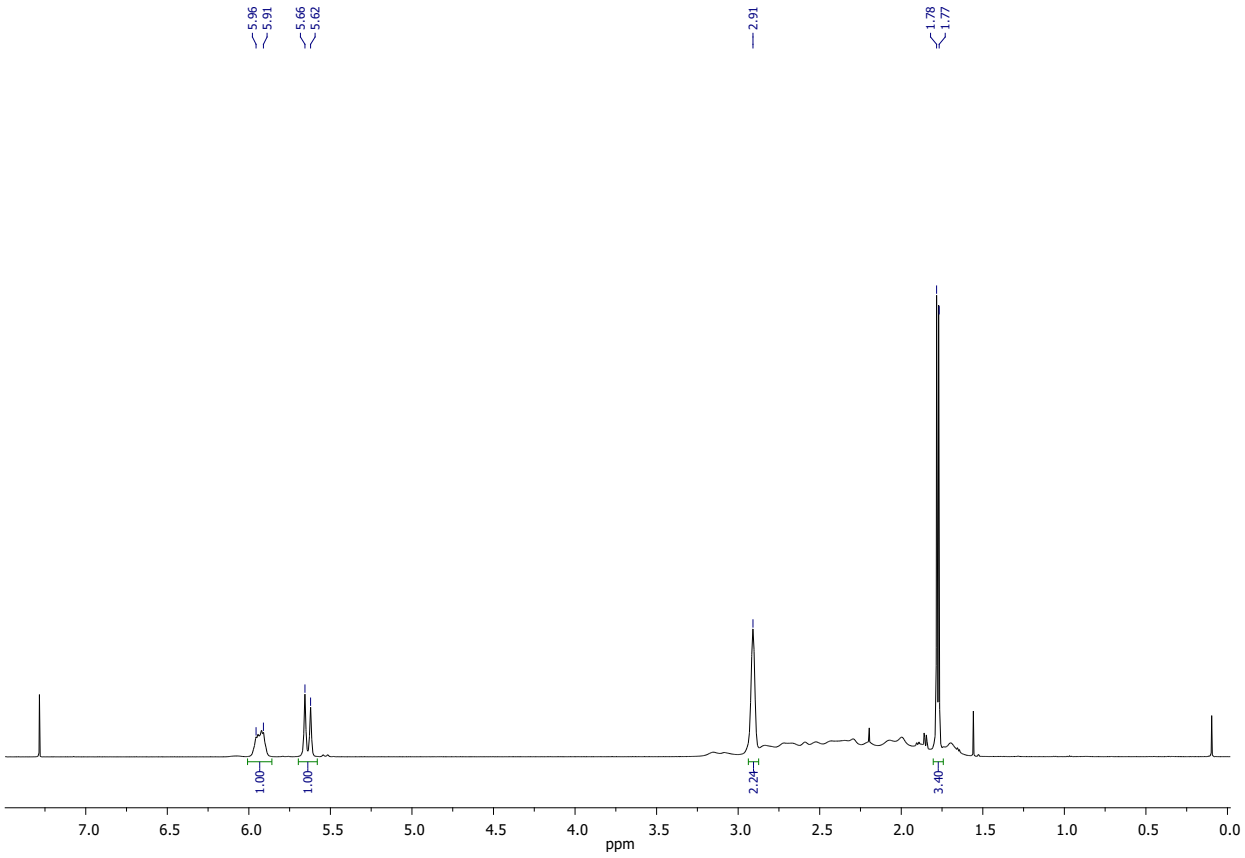
^{11}B{H} NMR (160.46 MHz, C_6D_6) of **8**



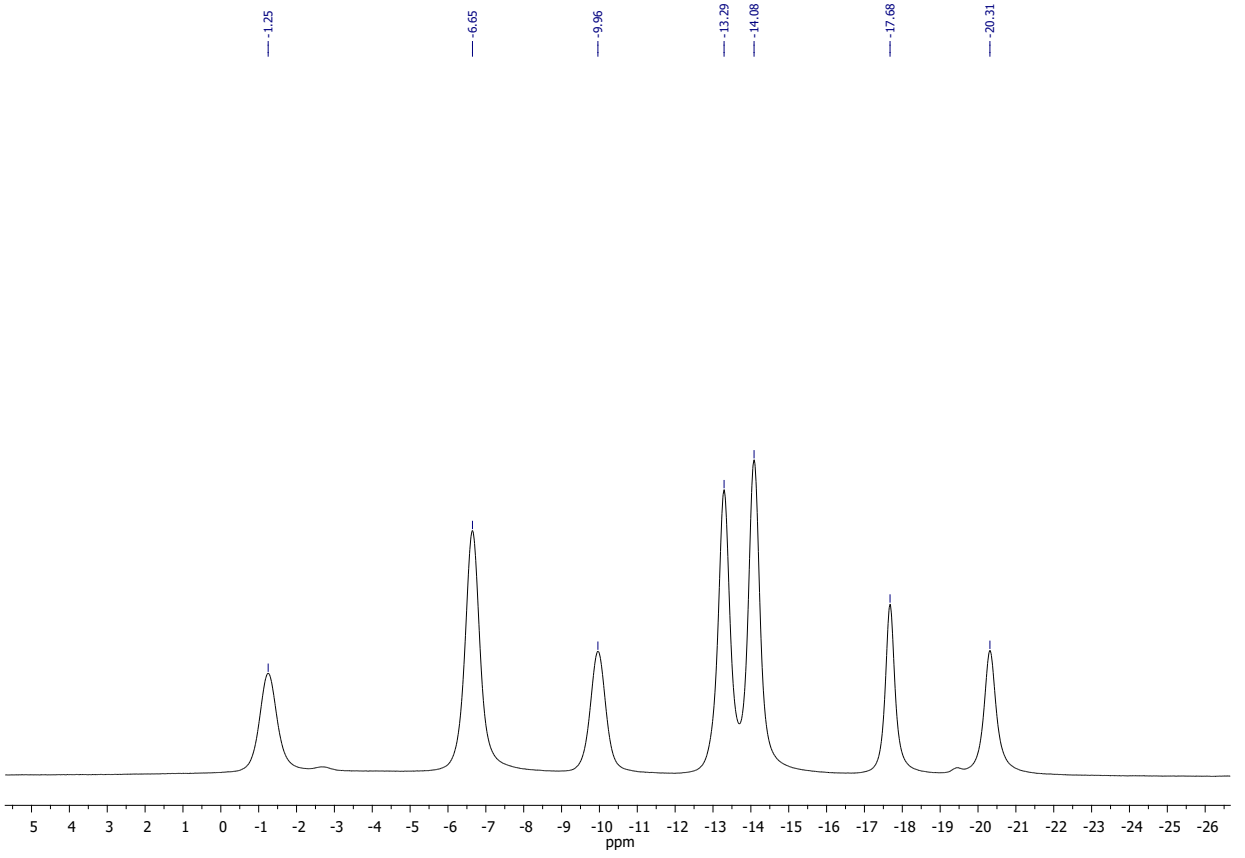
^{13}C NMR (125.47 MHz, C_6D_6) of **8**



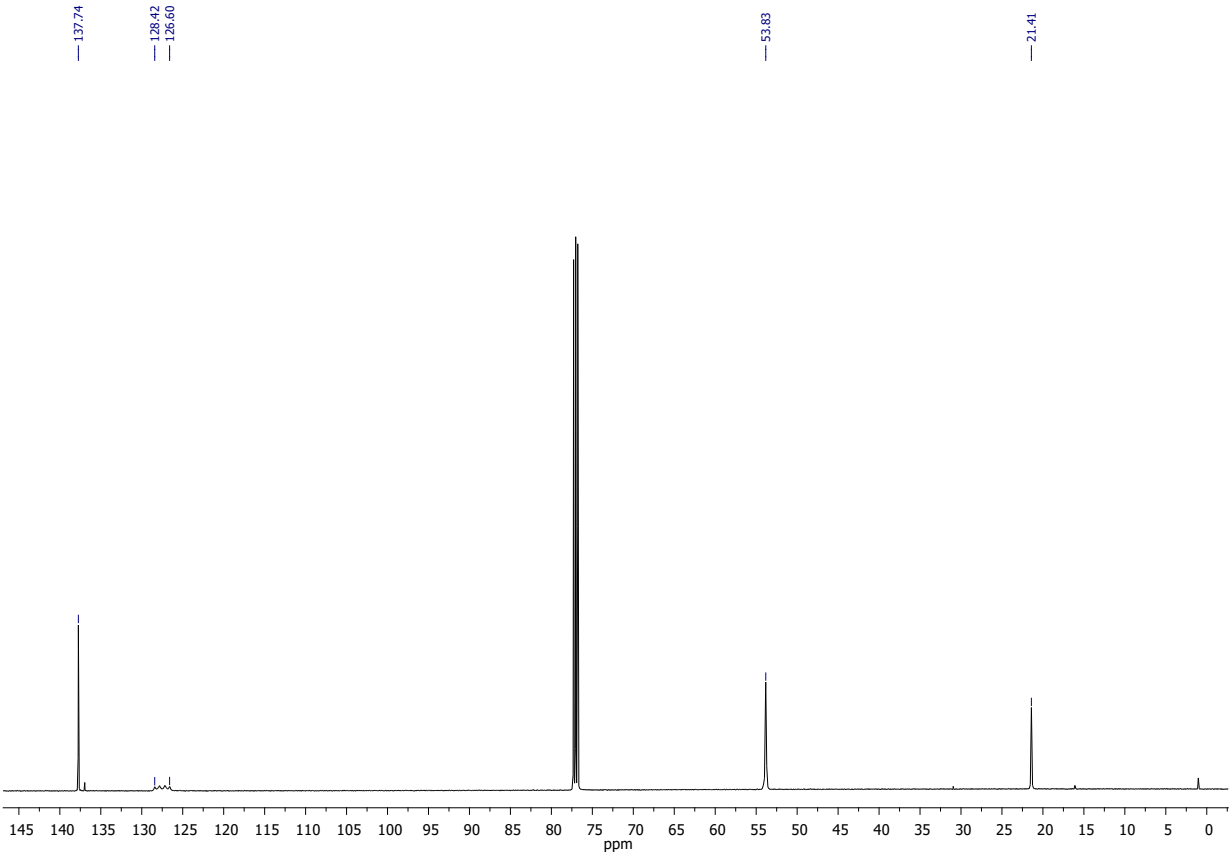
^{29}Si NMR (99.36 MHz, C_6D_6) of **8**



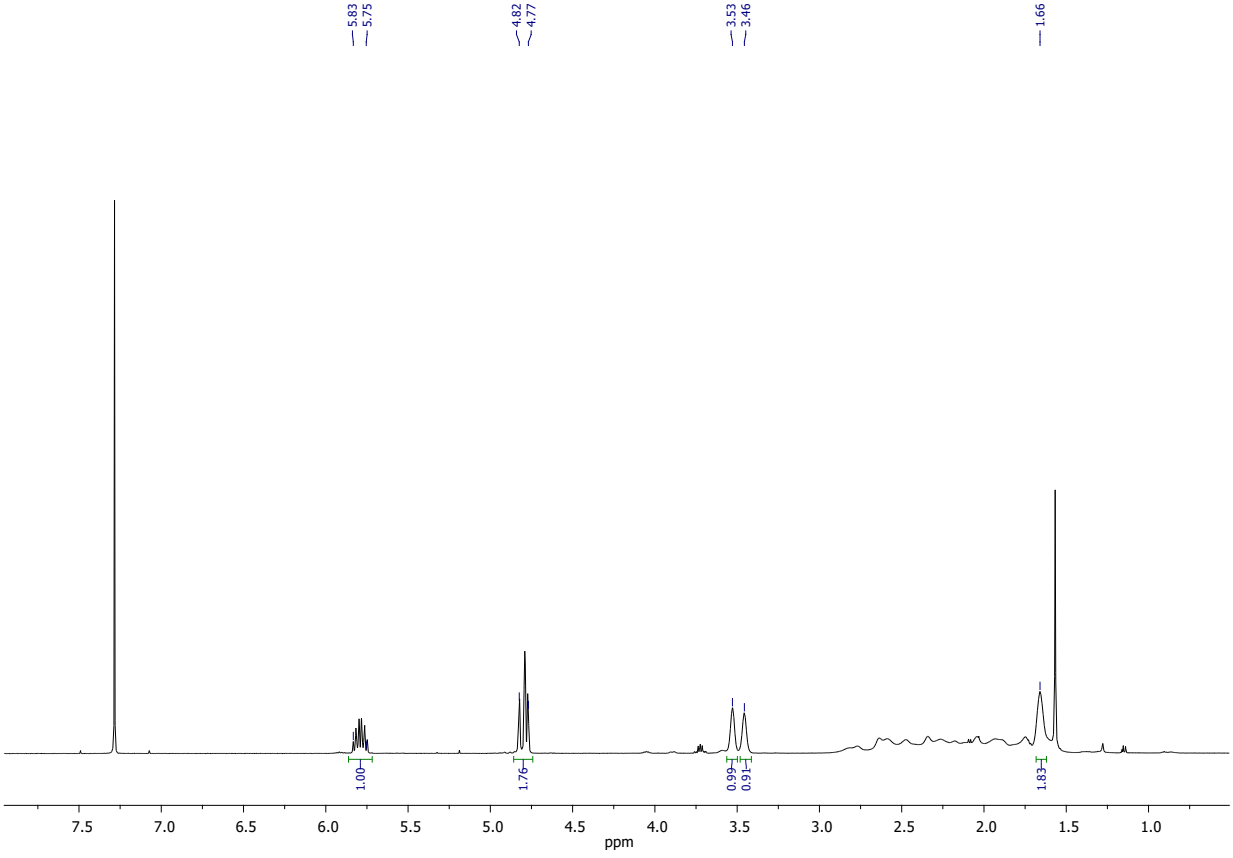
^{1}H NMR (500.13 MHz, $CDCl_3$) of **9**



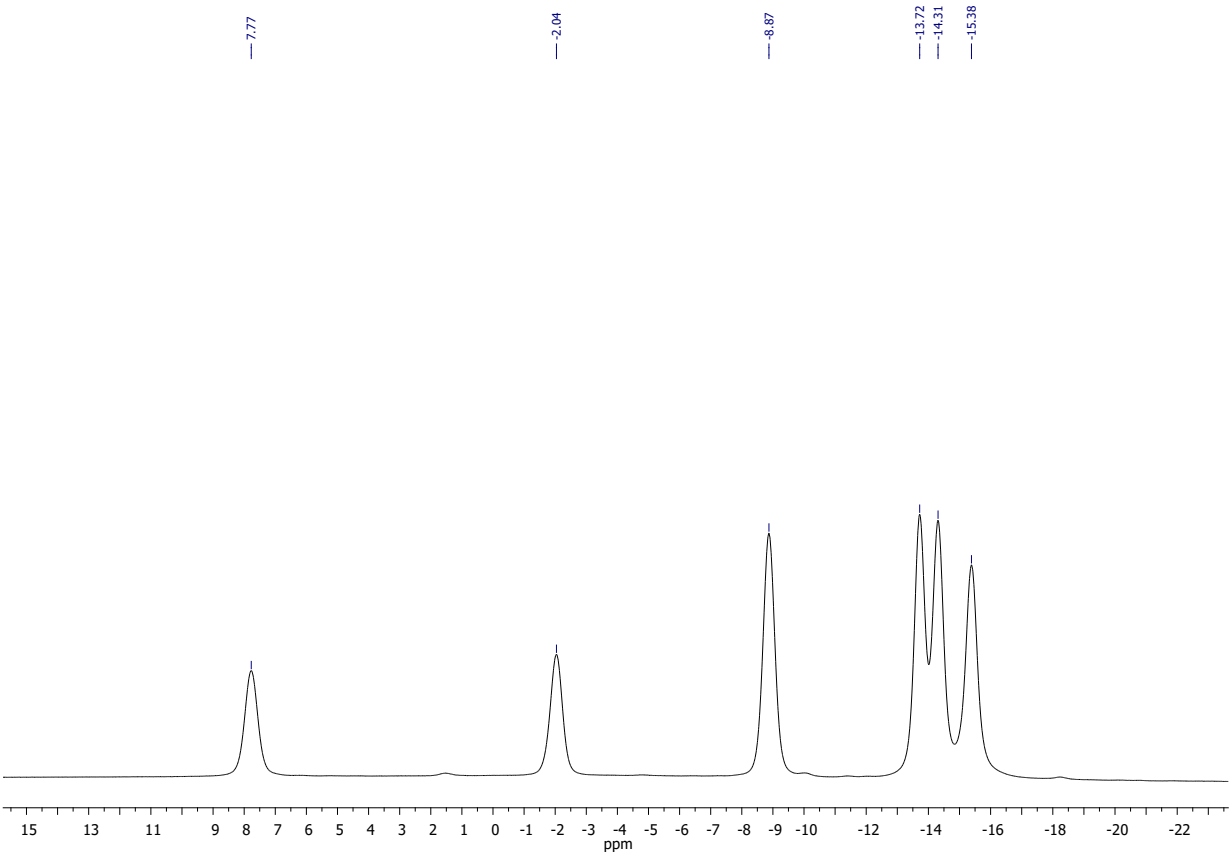
^{11}B{H} NMR (160.46 MHz, $CDCl_3$) of **9**



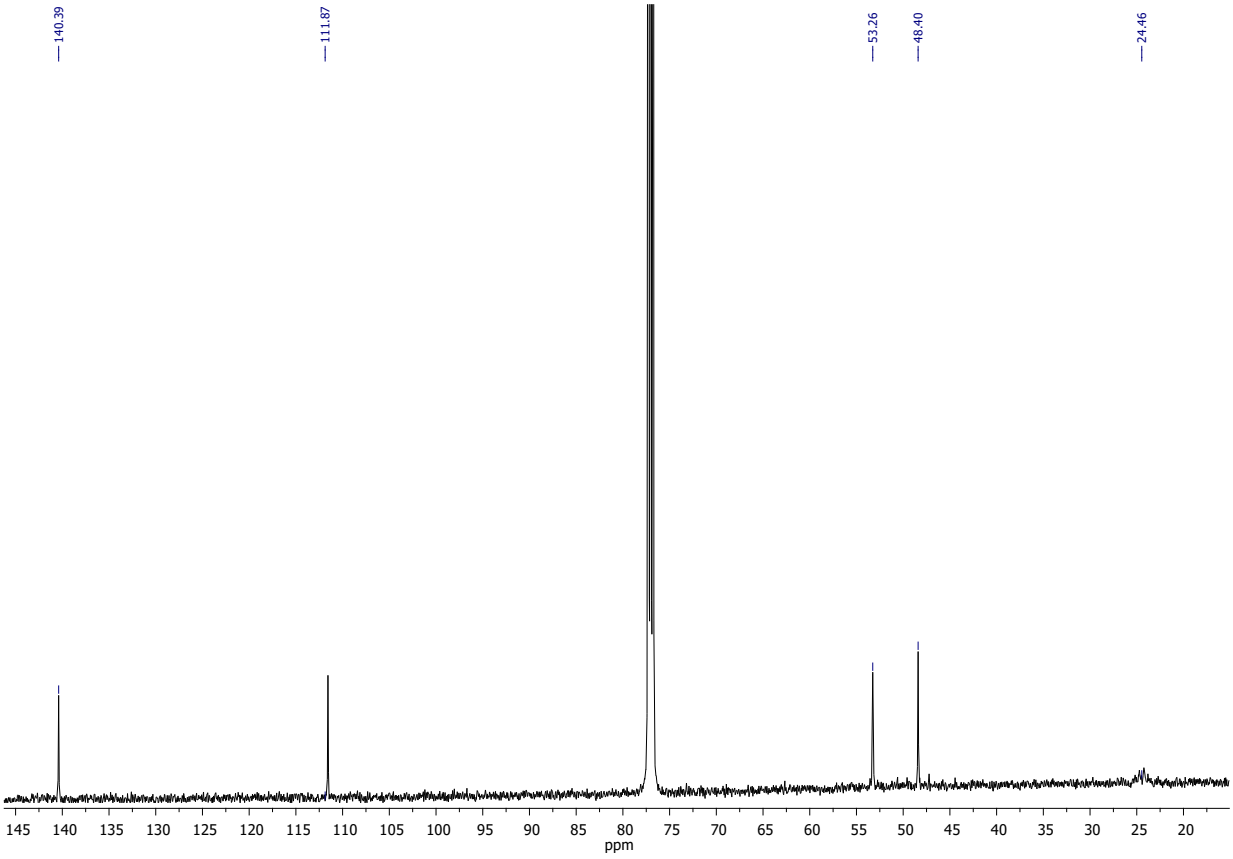
^{13}C NMR (125.47 MHz, $CDCl_3$) of **9**



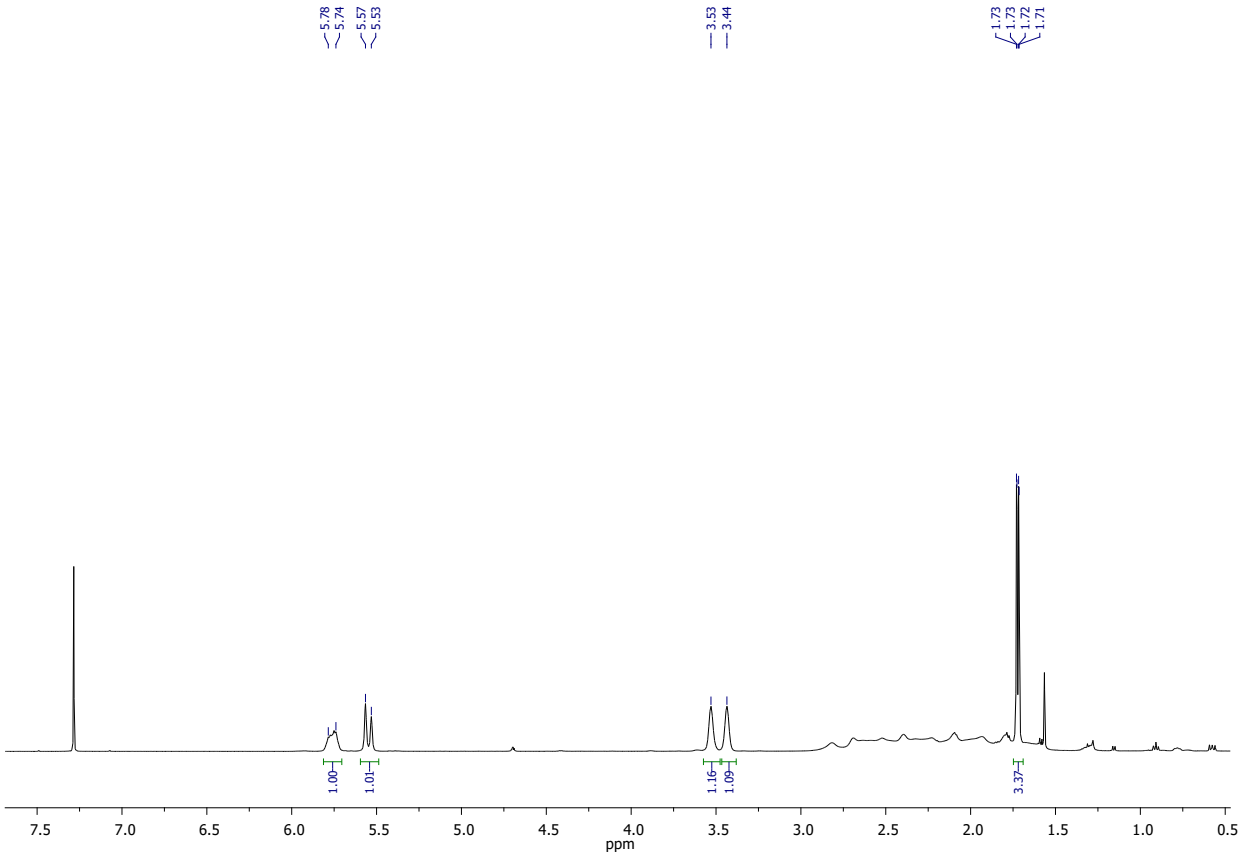
^{1}H NMR (500.13 MHz, $CDCl_3$) of **10**



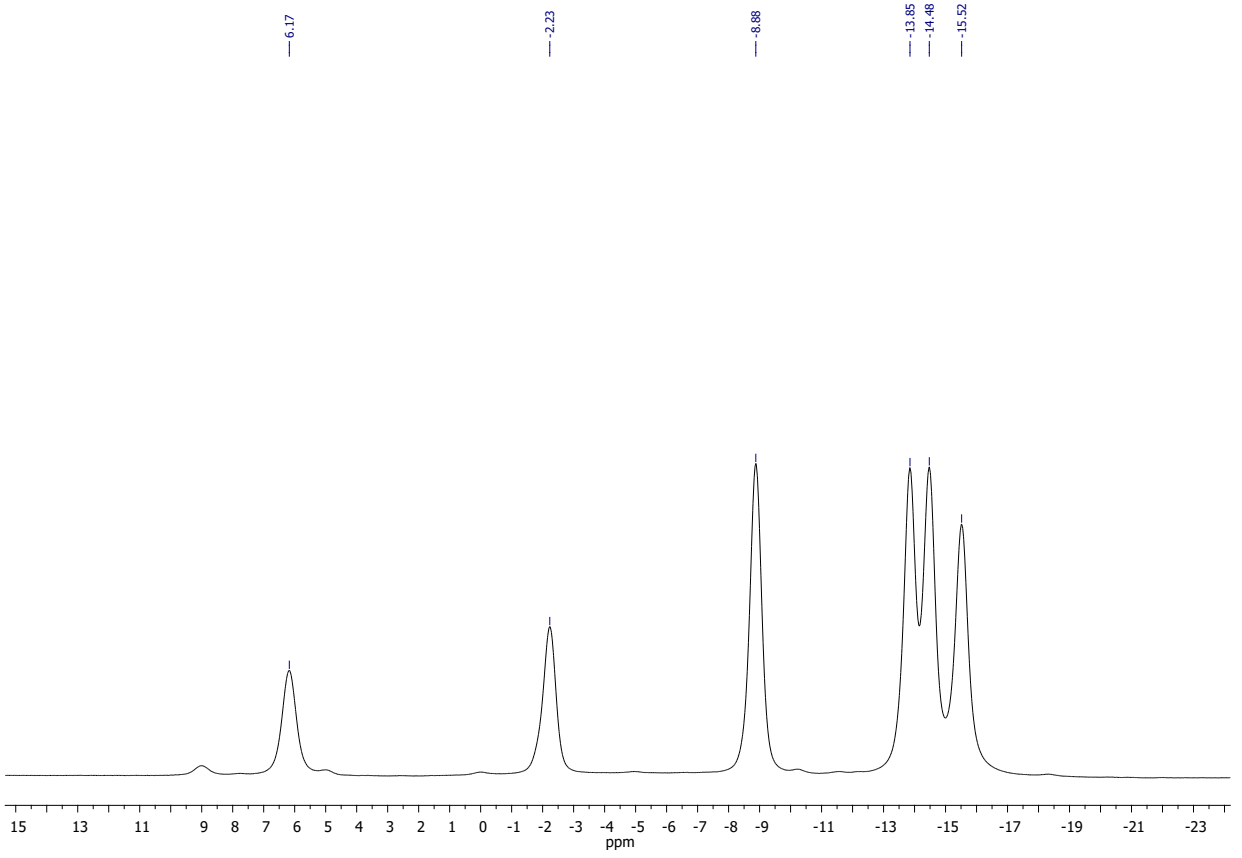
$^{11}B\{H\}$ NMR (160.46 MHz, $CDCl_3$) of **10**



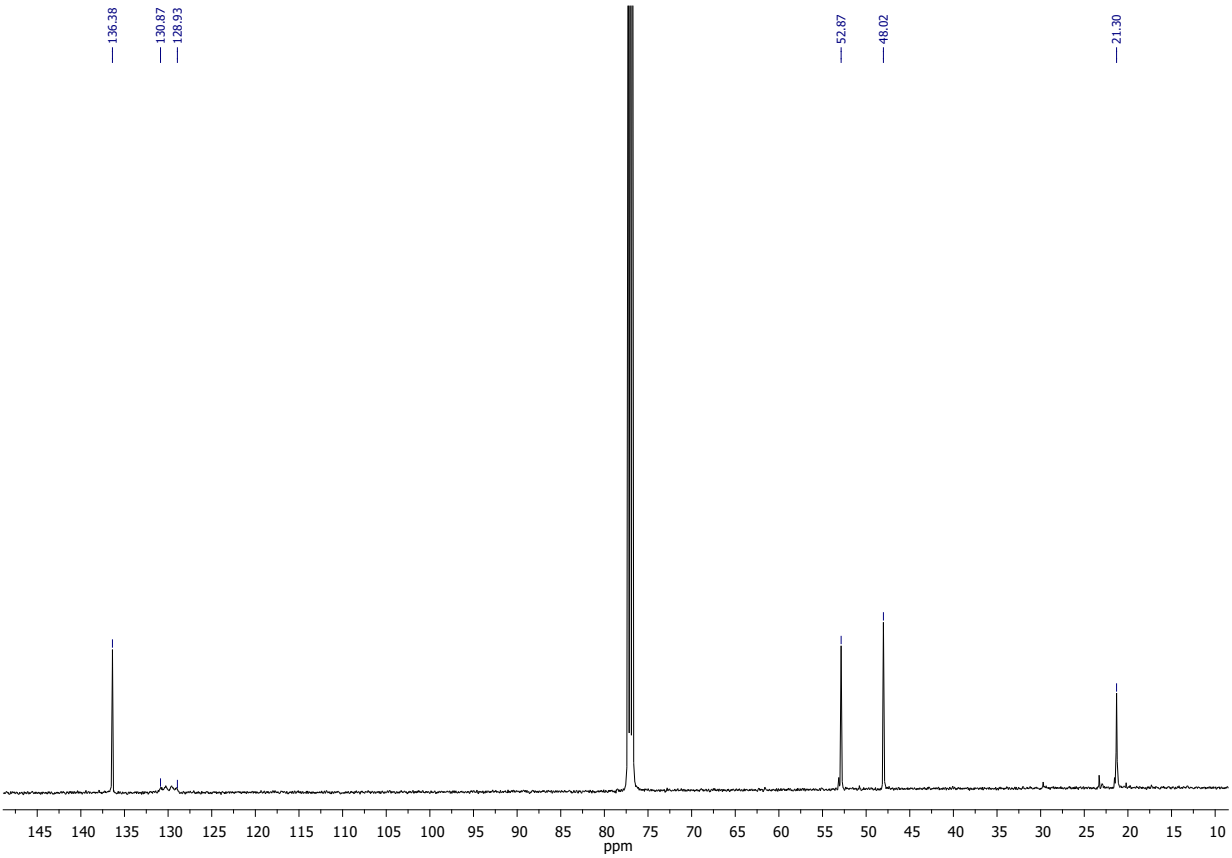
^{13}C NMR (125.47 MHz, $CDCl_3$) of **10**



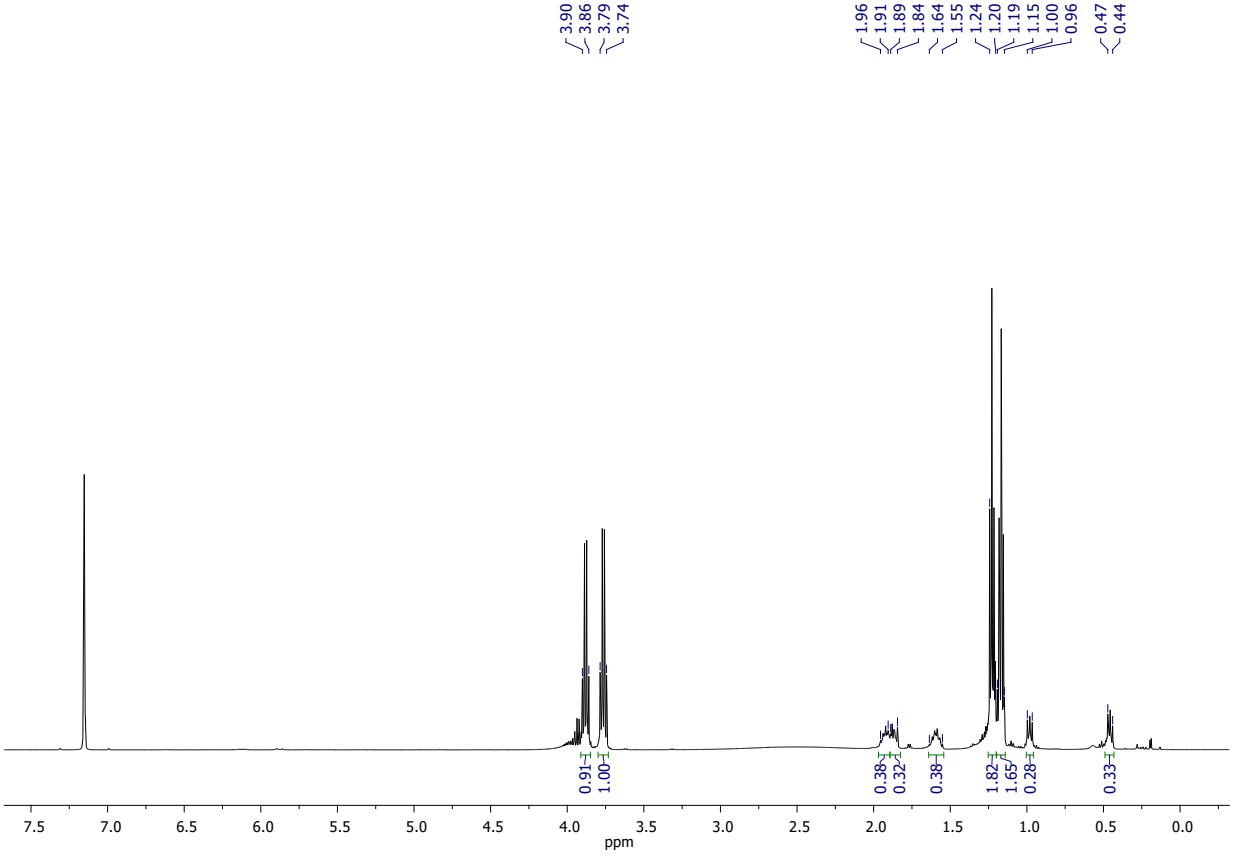
^{1}H NMR (500.13 MHz, $CDCl_3$) of **11**



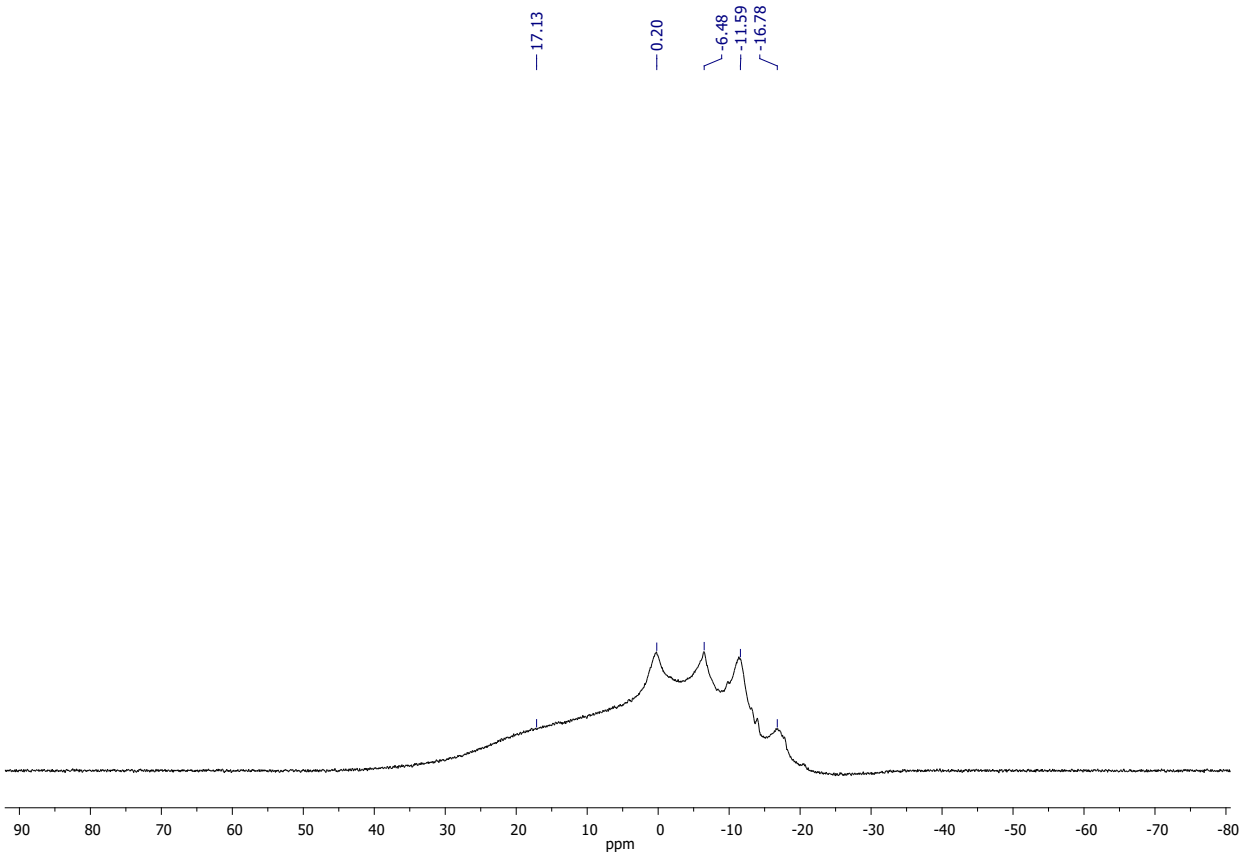
^{11}B{H} NMR (160.46 MHz, $CDCl_3$) of **11**



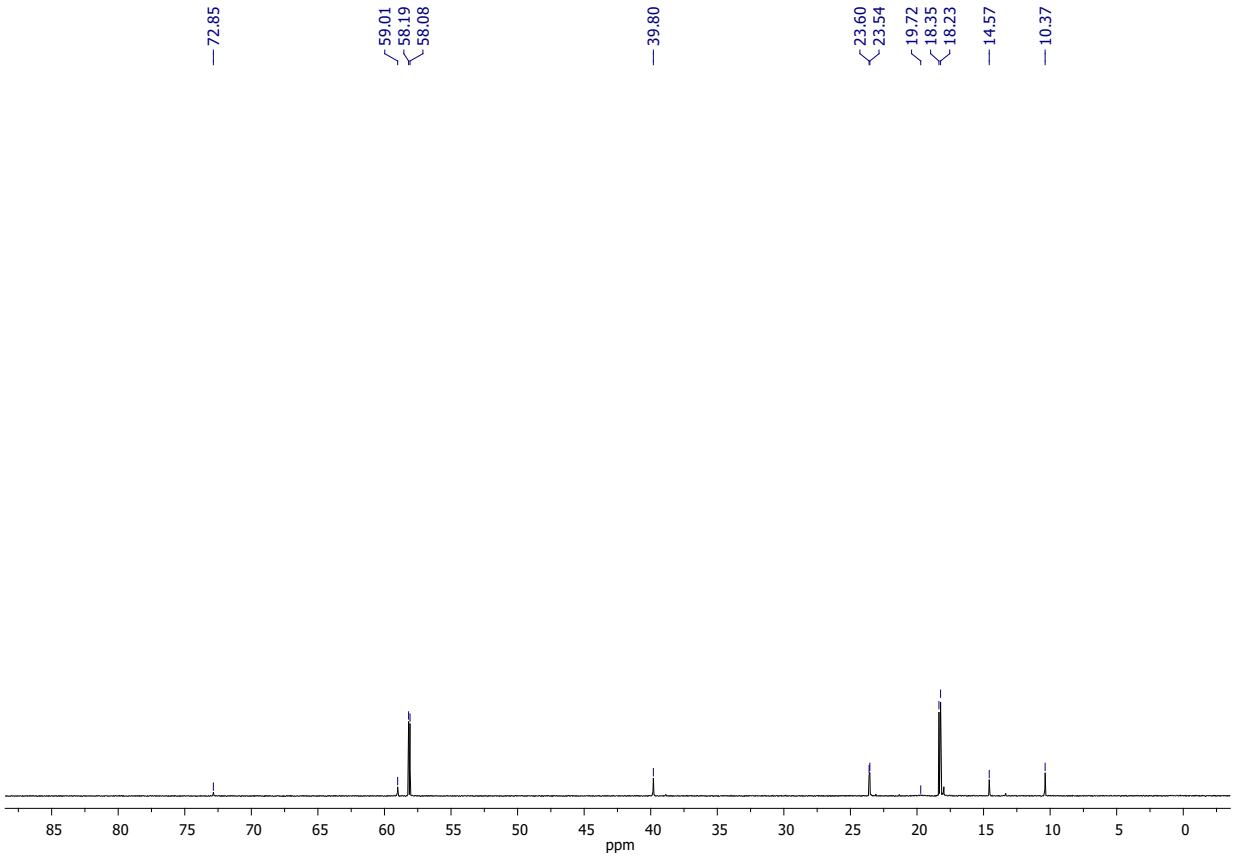
^{13}C NMR (125.47 MHz, $CDCl_3$) of **11**



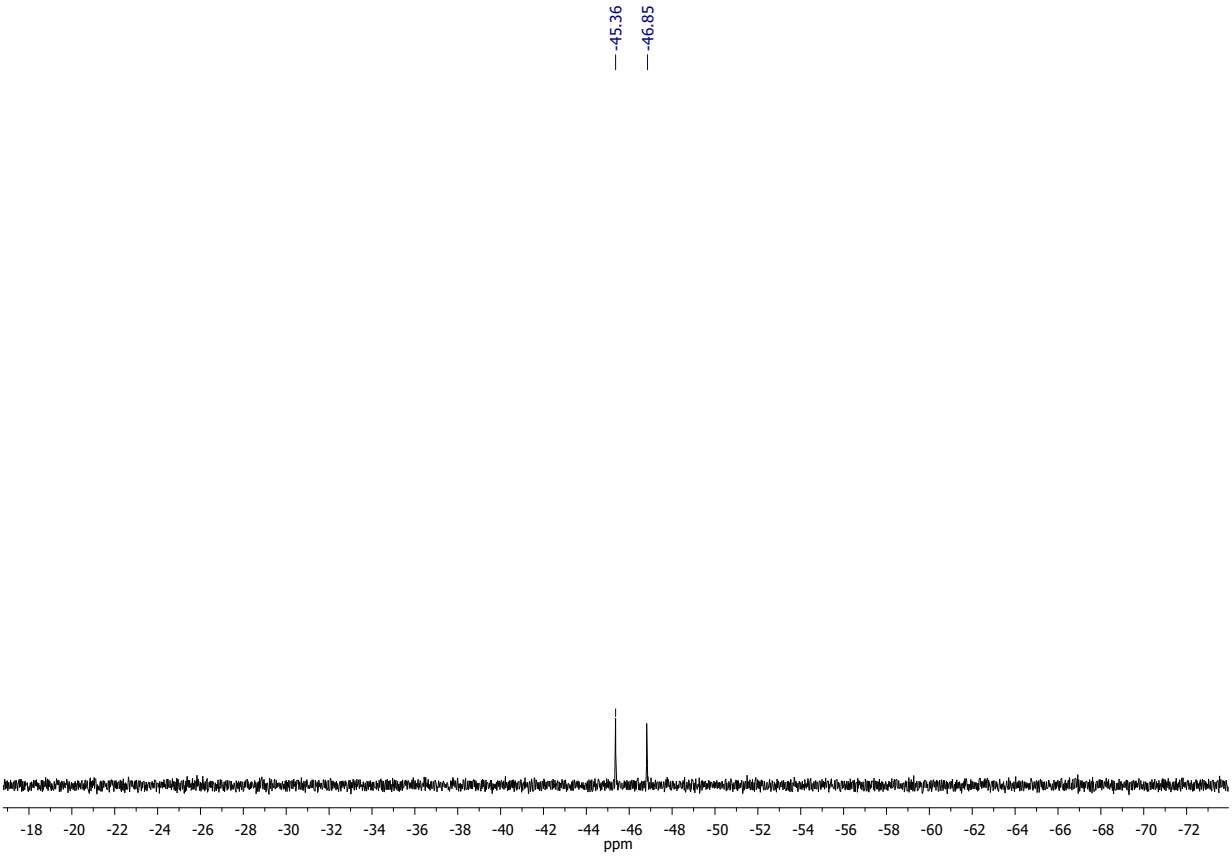
^{1}H NMR (500.13 MHz, C_6D_6) of **13**



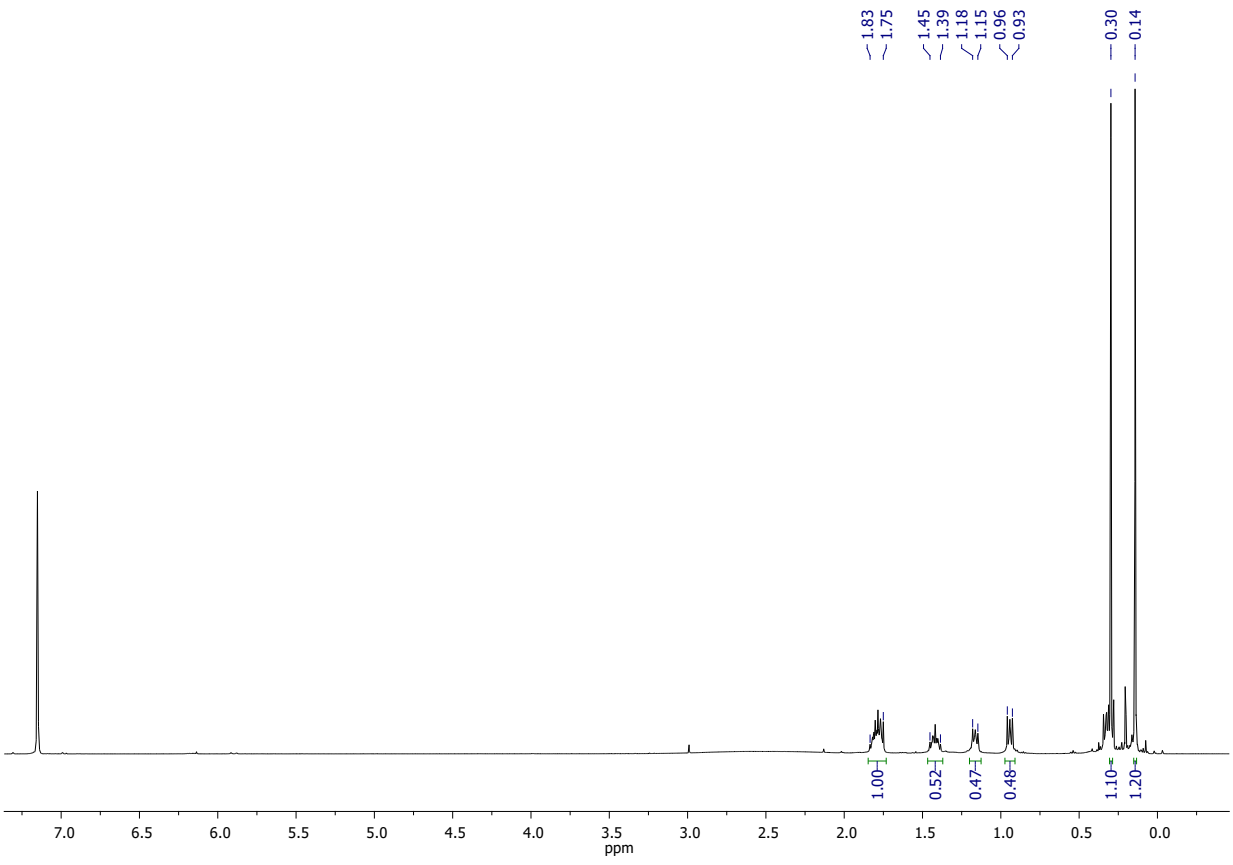
$^{11}B\{H\}$ NMR (160.46 MHz, C_6D_6) of **13**



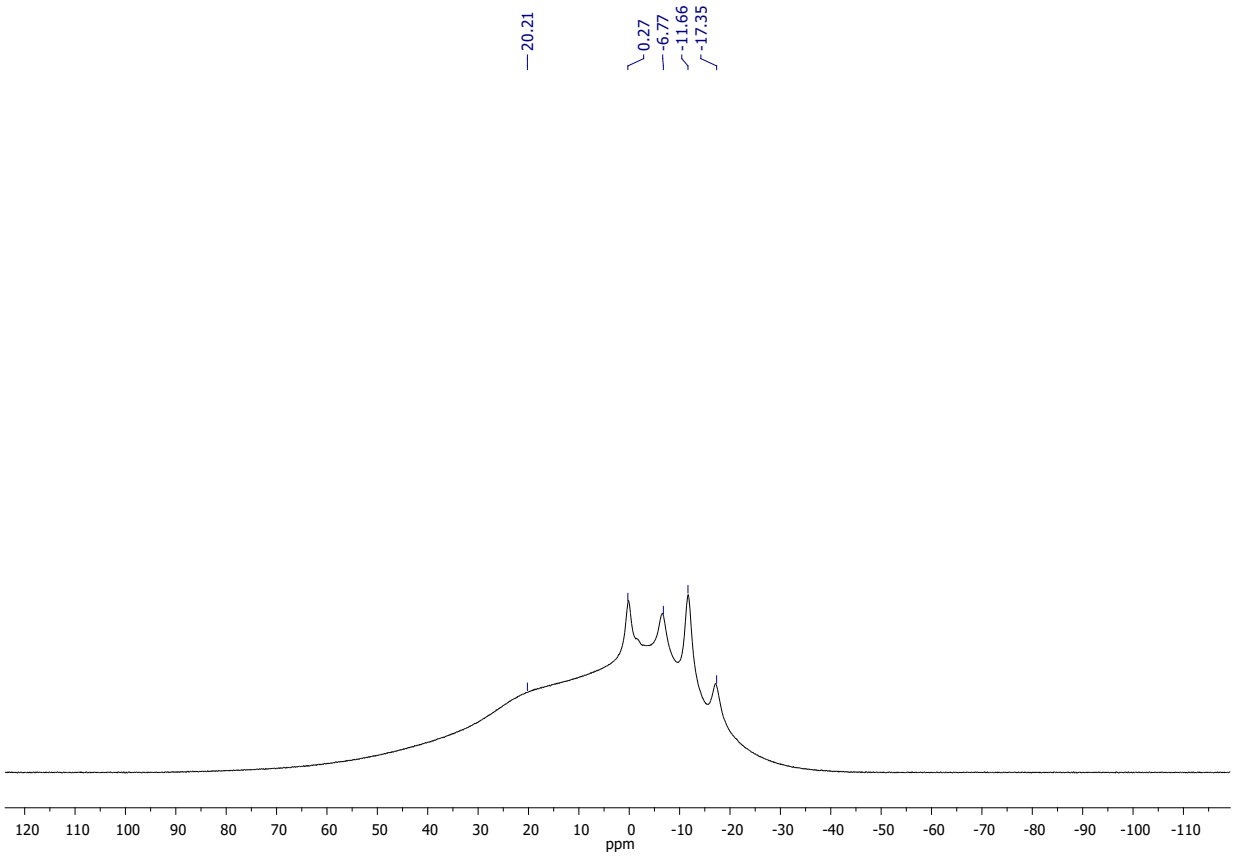
^{13}C NMR (125.47 MHz, C_6D_6) of **13**



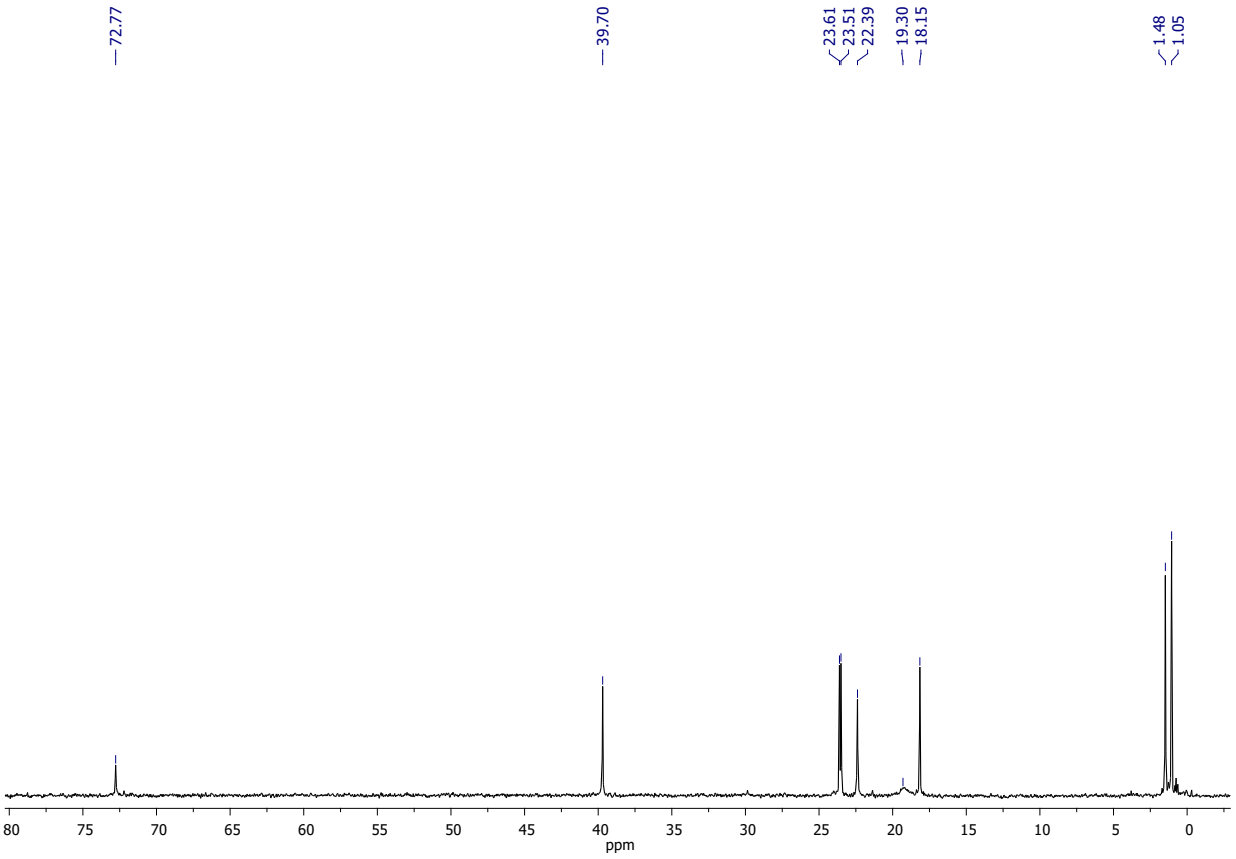
^{29}Si NMR (99.36 MHz, C_6D_6) of **13**



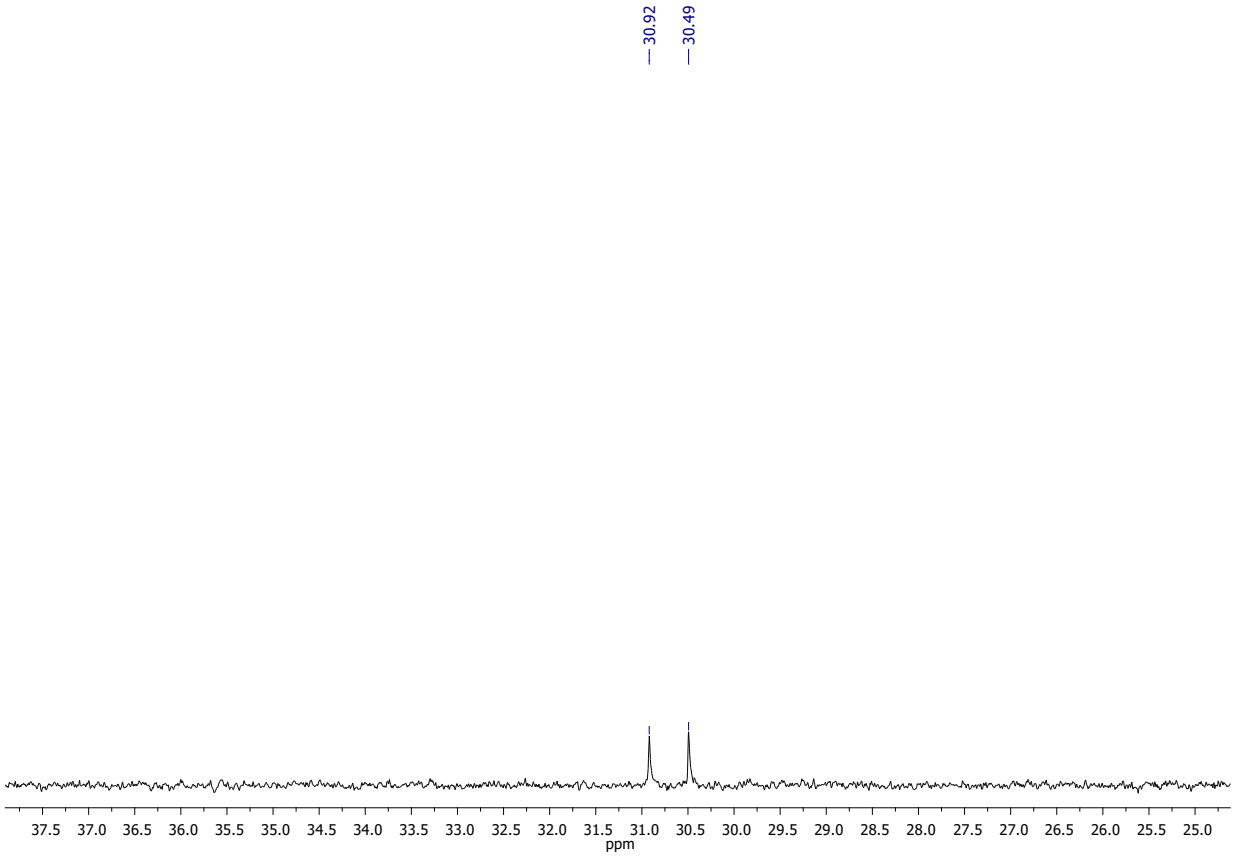
^{1}H NMR (500.13 MHz, C_6D_6) of **14**



$^{11}B\{H\}$ NMR (160.46 MHz, C_6D_6) of **14**

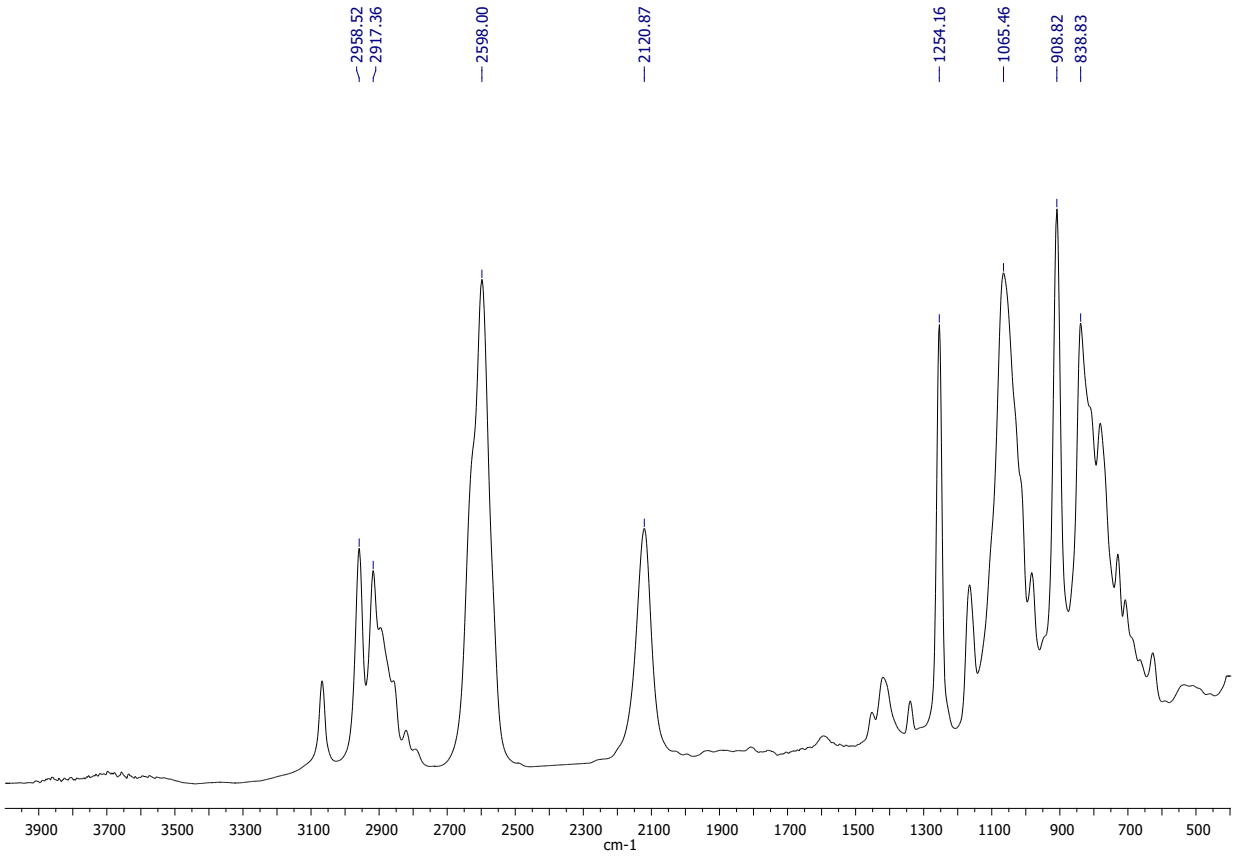


^{13}C NMR (125.47 MHz, C_6D_6) of **14**

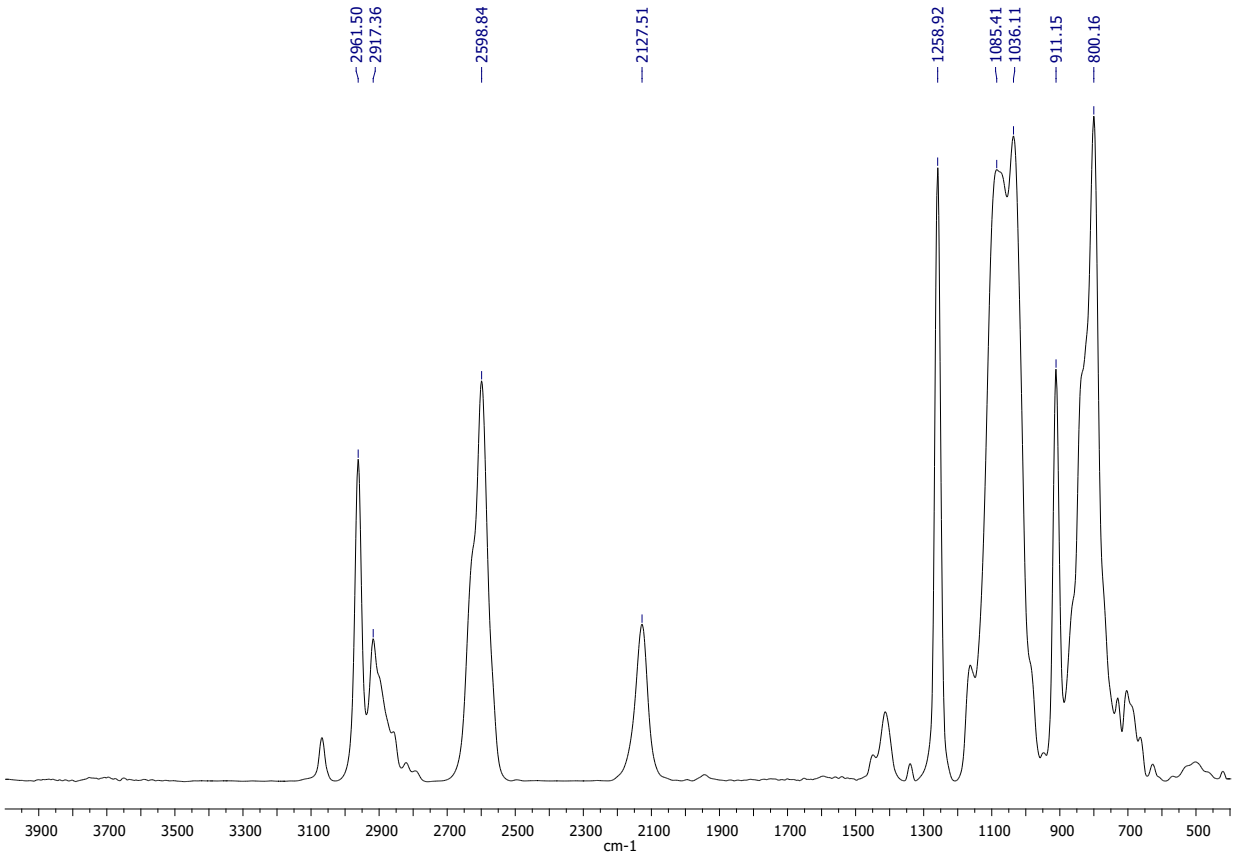


^{29}Si NMR (99.36 MHz, C_6D_6) of **14**

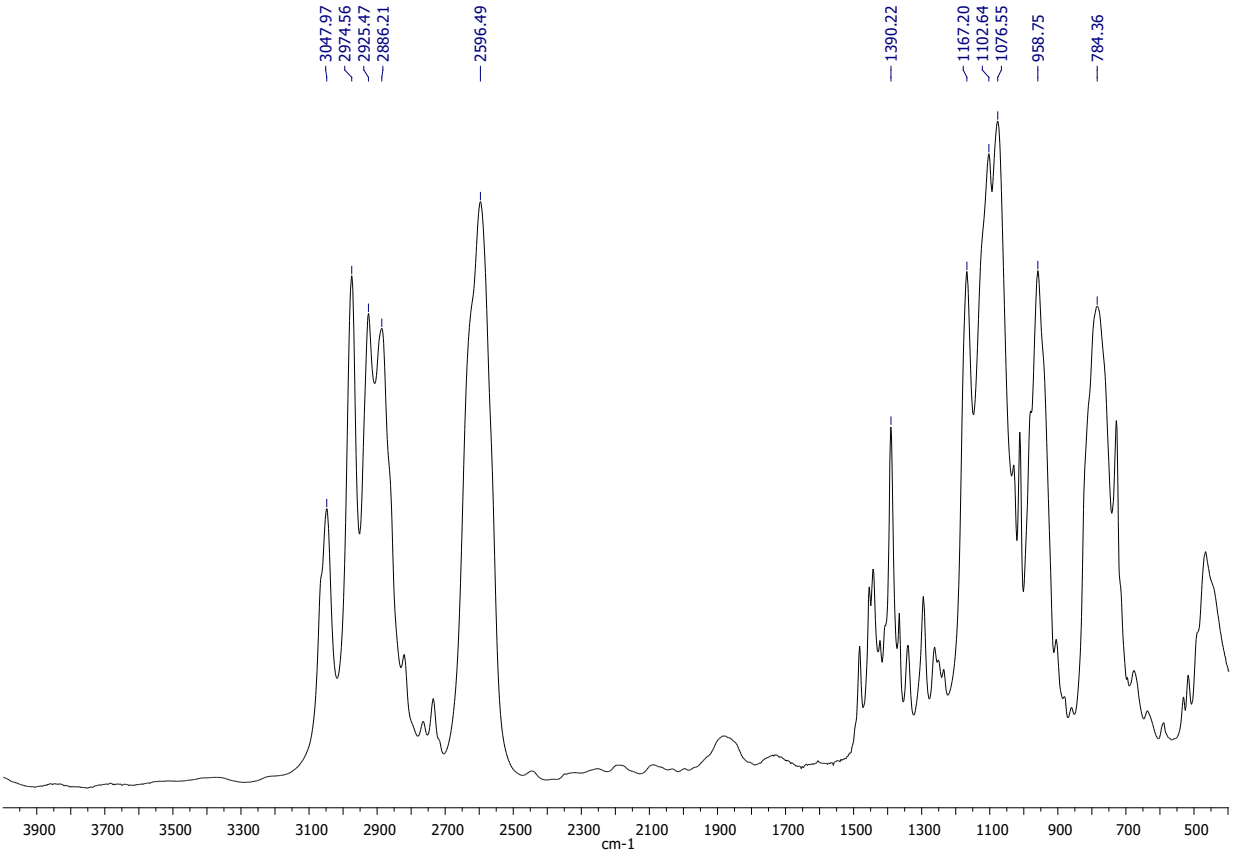
IR spectra



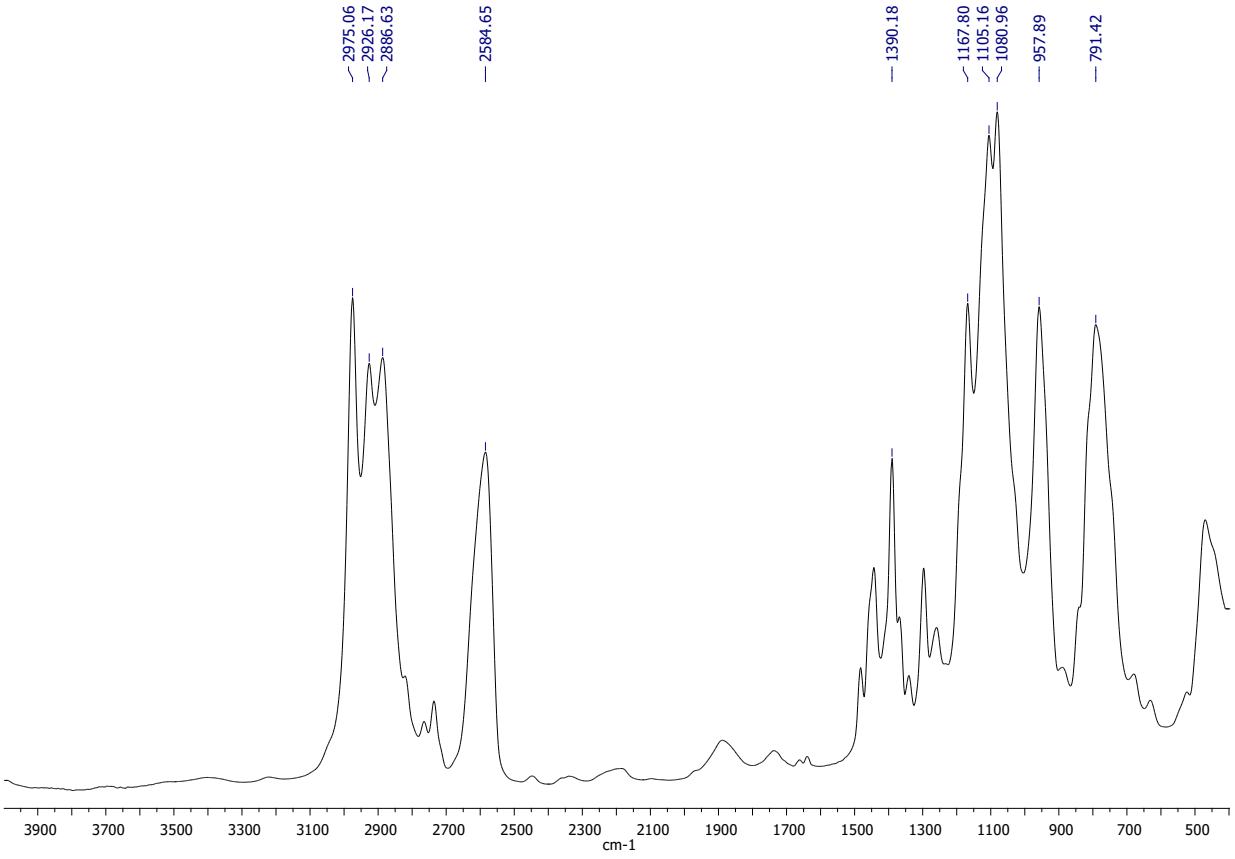
IR (cm^{-1}) of **6**



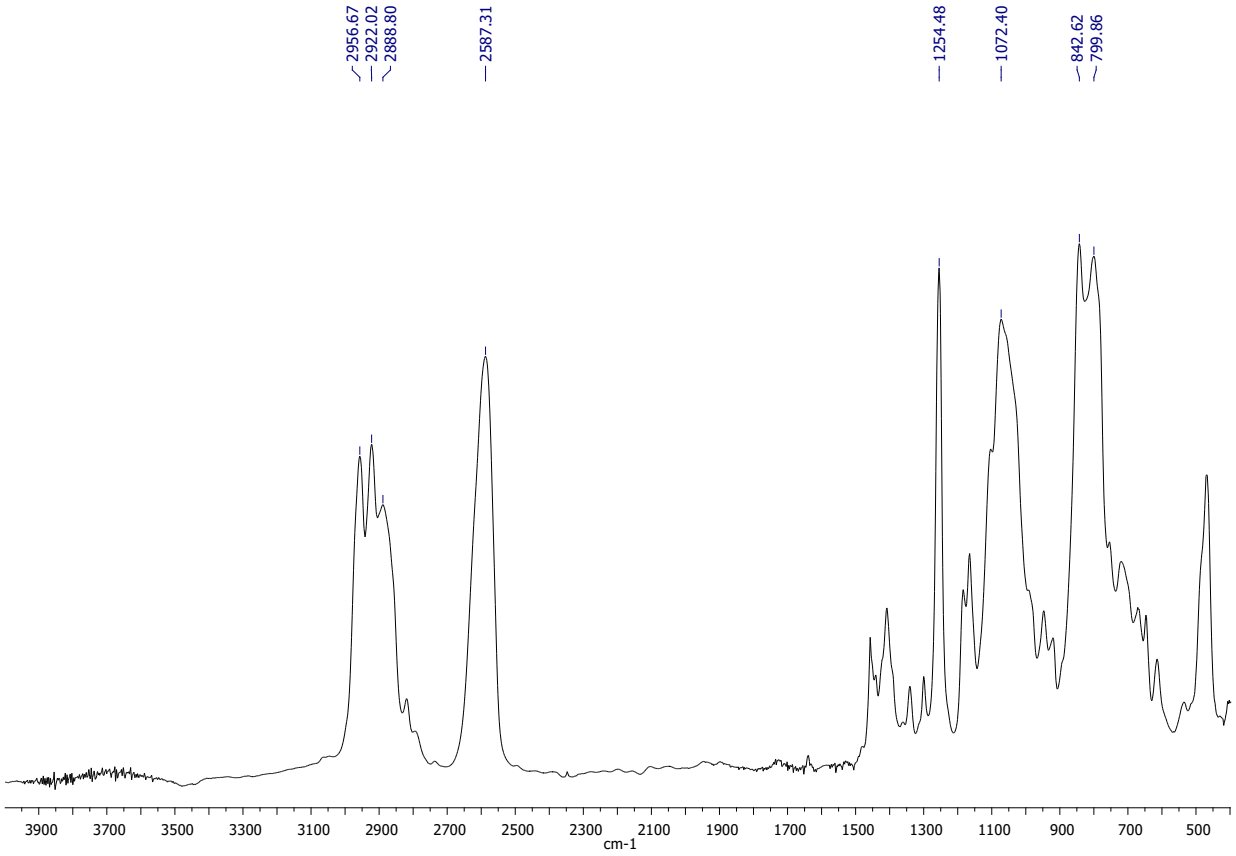
IR (cm^{-1}) of **7**



IR (cm^{-1}) of **8**



IR (cm^{-1}) of **13**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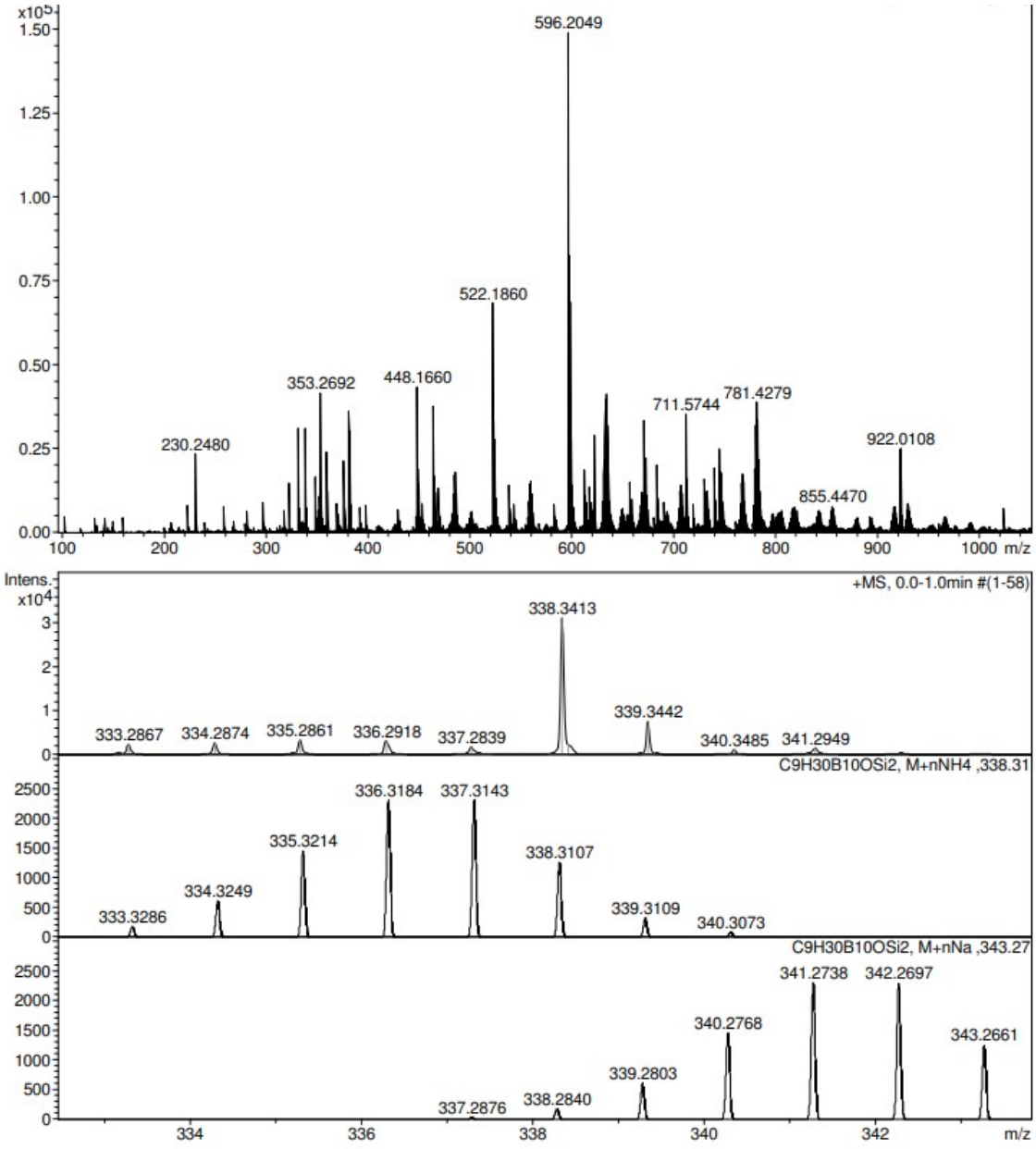
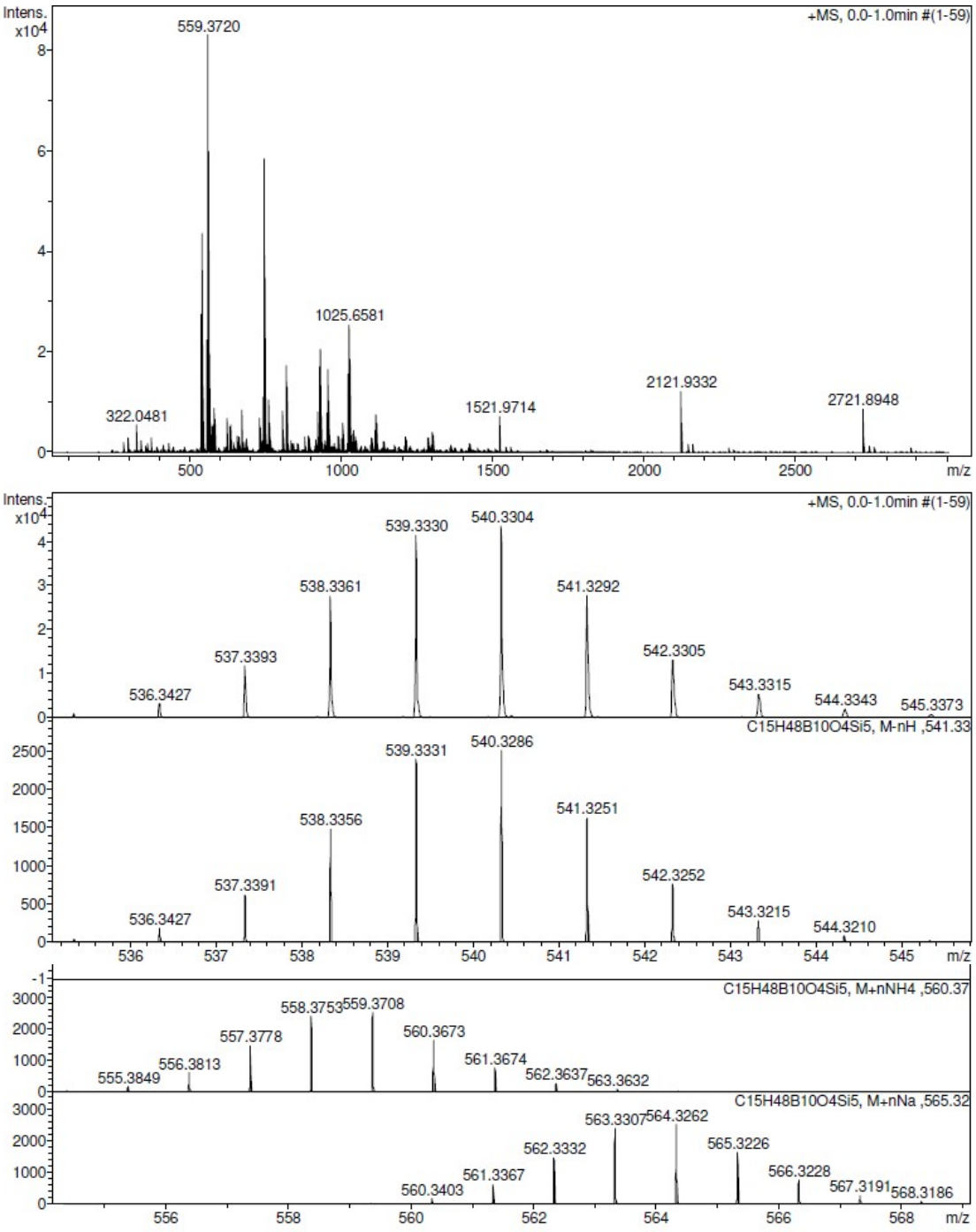
2922.02
2888.80
2587.31
1254.48
1072.40
842.62
799.86
3900
3700
3500
3300
3100
2900
2700
2500
2300
2100
1900
1700
1500
1300
1100
900
700
500
cm-1

IR (cm^{-1}) of **14**

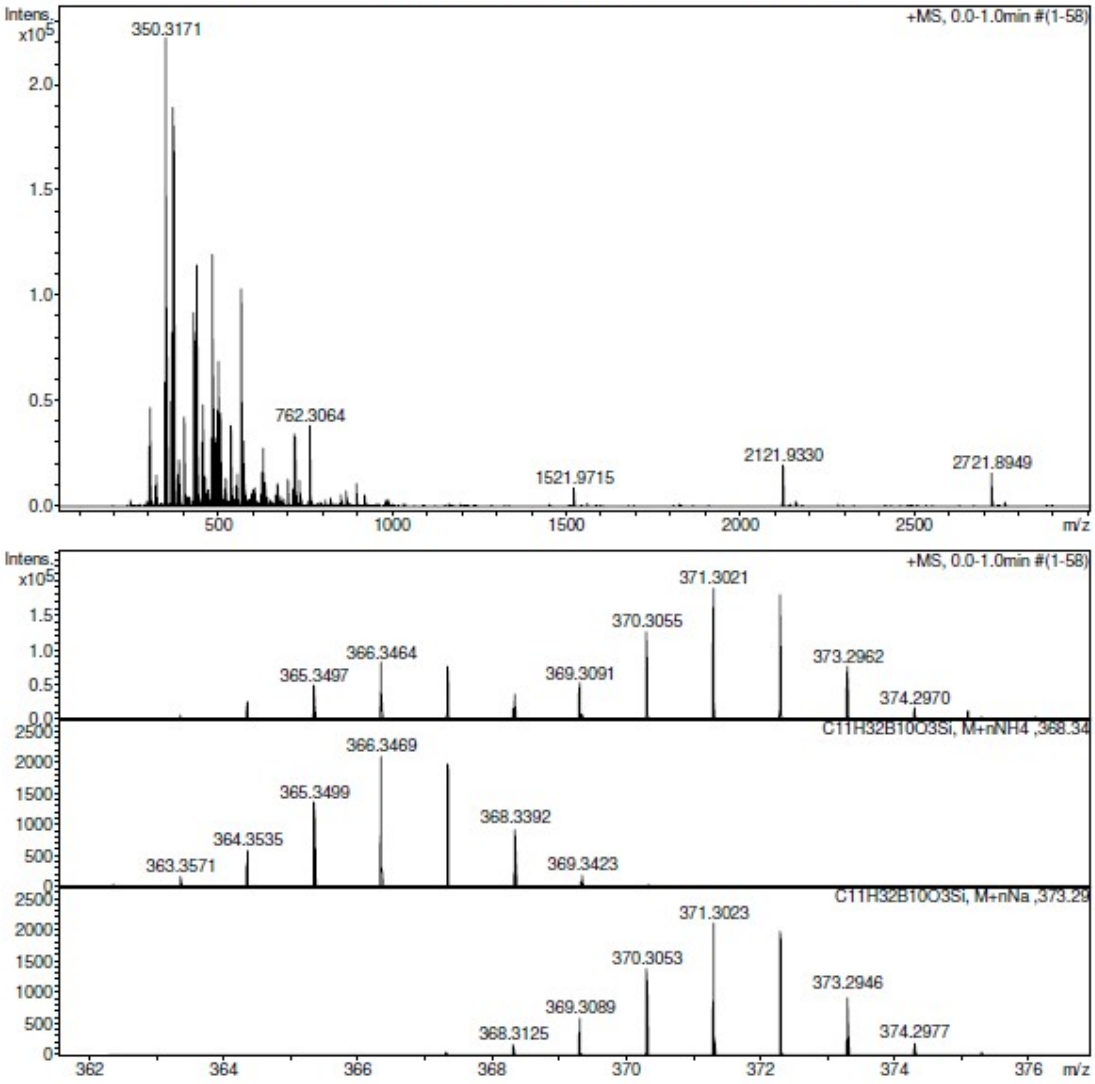
Mass spectra



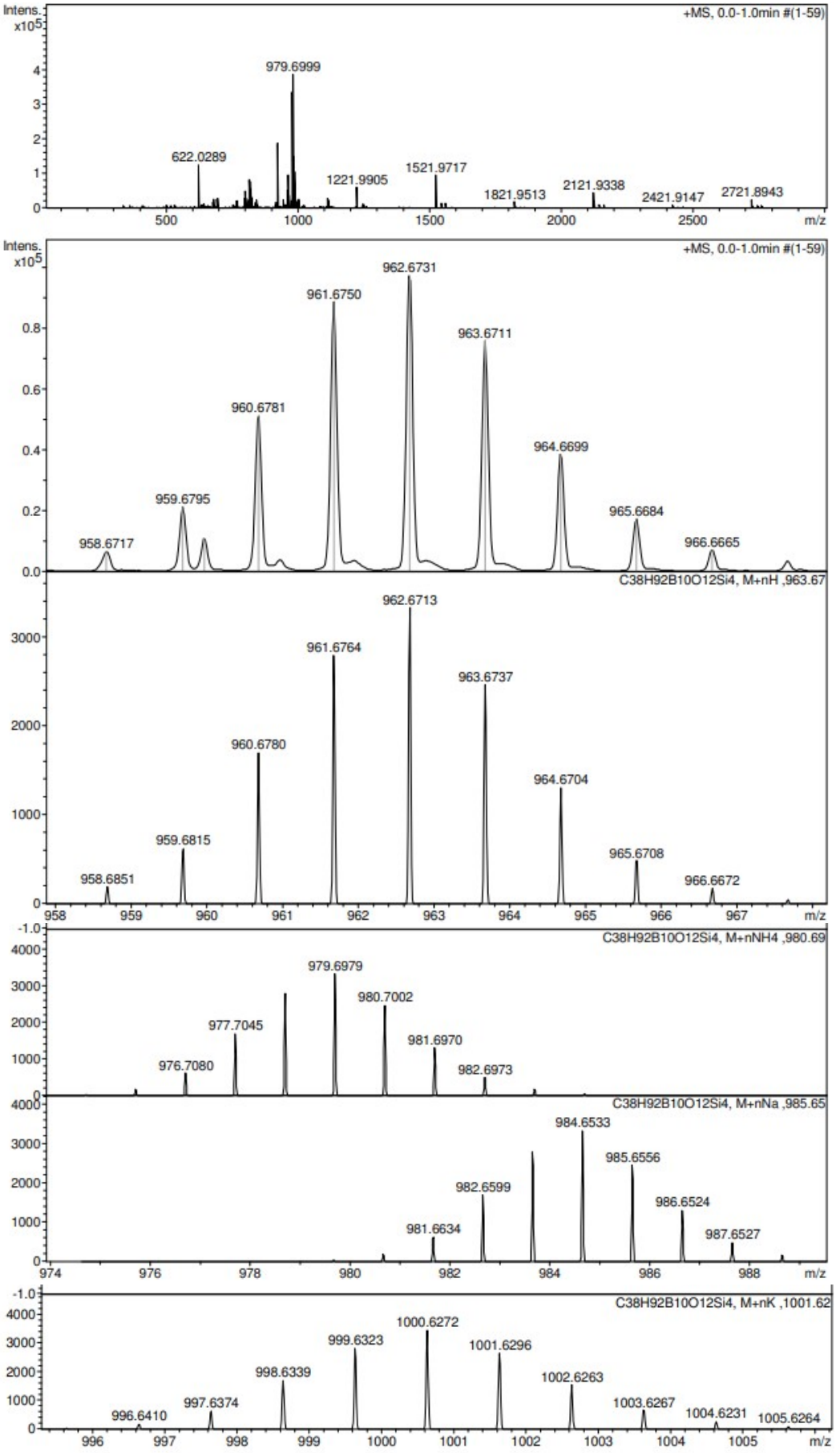
Mass spectra of **6**



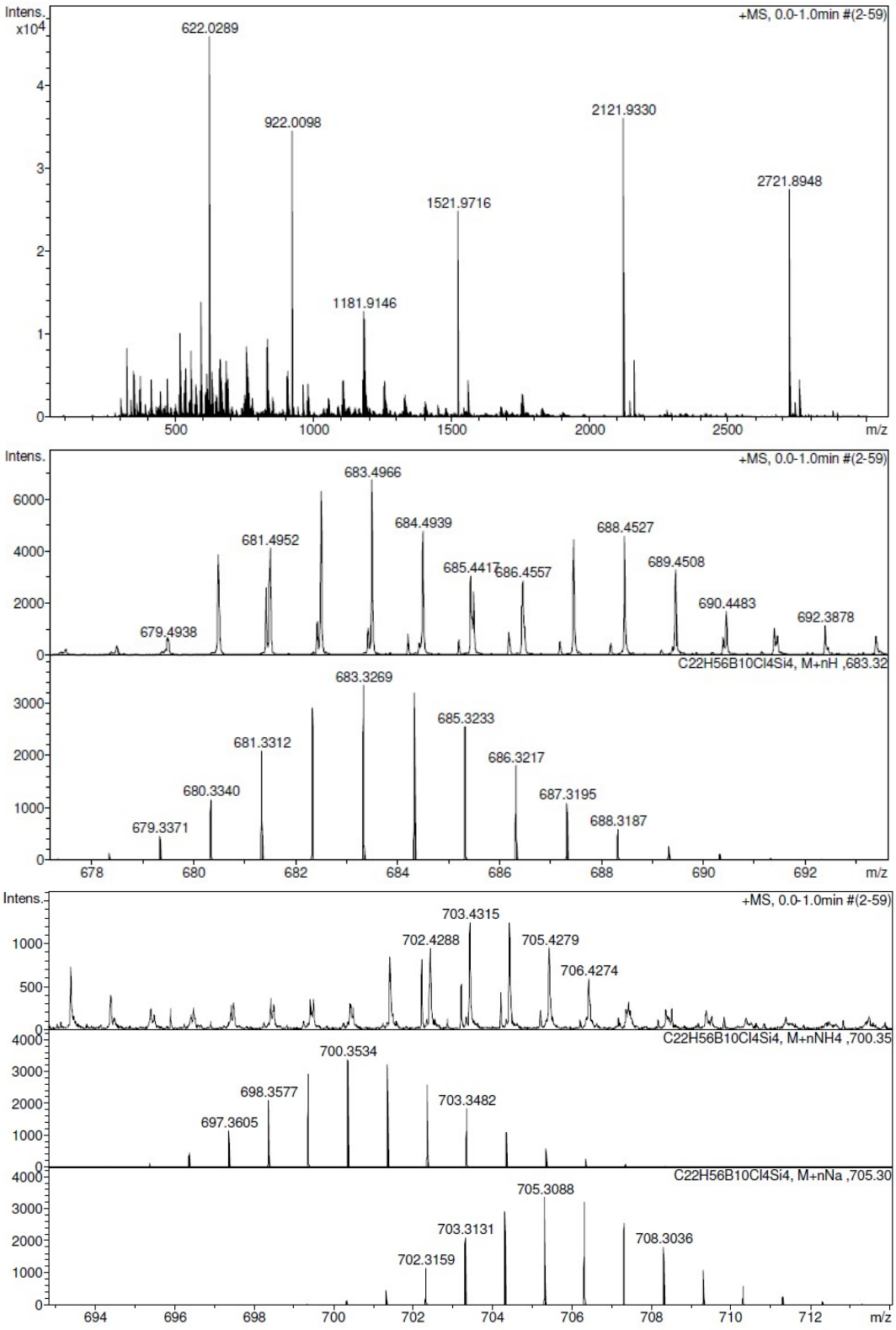
Mass spectra of **7**



Mass spectra of **8**



Mass spectra of **13**



Mass spectra of **14**

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b. Teixidor F., Pepiol A., Viñas C. *Chem. Eur. J*. **2015**. 21, 10650 – 10653

c. Talalaeva, E.V., Kalinina, A.A., Vasilenko, N.G., Demchenko, N.V., Cherkaev, G.V., Goloveshkin, A.S., Muzafarov, A.M. *J. Organomet. Chem.* **2020**. 906,

d. G.M. Sheldrick, Crystal structure refinement with SHELXL, *Acta Cryst.* **C71** (2015) 3-8.