



## Supporting Information

### **Chiral Modification of the Tetrakis(pentafluorophenyl)borate Anion with Myrtanyl Groups**

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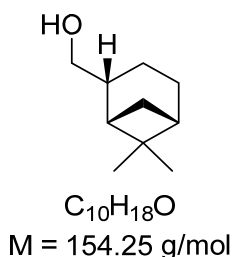
## 1 General Informations

All reactions were performed in dried glassware using an *MBraun* glove box ( $O_2 < 1$  ppm,  $H_2O < 1$  ppm) or conventional Schlenk techniques under a static pressure of argon (glove box) or nitrogen. All reactions under  $H_2$  or  $D_2$  pressure were carried out in glass vials (50 x 14 mm, *Schütt*), equipped with a magnetic stir bar and a rubber septum in autoclaves BR-100 or BR-300 (including the appropriate heating blocks, *Berghof*). The autoclave was purged with  $N_2$  (3 x 10 bar) before the vials were placed in the autoclave and the septum was pierced under a counter flow of  $N_2$ . The autoclave was purged with  $N_2$  (2 x 10 bar) and  $H_2$  or  $D_2$  (3 x 10 bar).  $H_2$  pressure was applied (pressure is given as initial pressure before heating). The heating block was preheated before the autoclave was placed inside. After the respective reaction time the autoclave was allowed to cool to r.t. and  $H_2$  was released. The autoclave was purged with  $N_2$  (3 x 10 bar) before the vials were taken out. Liquids and solutions were transferred with syringes. Solvents (benzene, 1,2- $Cl_2C_6H_4$ ,  $ClC_6H_5$ ,  $CH_2Cl_2$ , EtOH, THF,  $Et_2O$  and MeCN) were dried and purified following standard procedures. 1,2- $Cl_2C_6D_4$  (purchased from *Eurisotop*) was dried over  $CaH_2$ , distilled, and stored under argon. Technical grade solvents for extraction or chromatography (*tert*-butylmethyl ether, ethyl acetate, cyclohexane,  $CH_2Cl_2$ , *n*-pentane) were distilled prior to use.  $C_6D_6$  (purchased from *Eurisotop*) was stored over 4 Å molecular sieves or degassed and stored in a glove box over 4 Å molecular sieves.  $CD_2Cl_2$  (purchased from *Eurisotop*) was degassed and stored in a glove box over 4 Å molecular sieves.  $^1H$ ,  $^1H/^{13}C$  HSQC,  $^1H/^{13}C$  HMBC,  $^7Li$ ,  $^{11}B$ ,  $^{13}C$ ,  $^{19}F$ ,  $^{29}Si$ -DEPT and  $^1H/^{29}Si$ -HMQC NMR spectra were recorded in  $CDCl_3$ ,  $C_6D_6$  or  $CD_2Cl_2$  on Bruker AV400, Bruker AV500 and Bruker AV700 instruments. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard ( $C_6D_5H$   $\delta = 7.16$  ppm for  $^1H$  NMR,  $C_6D_6$   $\delta = 128.06$  ppm for  $^{13}C$  NMR,  $CHCl_3$ :  $\delta = 7.26$  ppm for  $^1H$  NMR,  $CDCl_3$ :  $\delta = 77.16$  ppm for  $^{13}C$  NMR and  $CHDCl_2$ :  $\delta = 5.32$  ppm for  $^1H$  NMR and  $CD_2Cl_2$ :  $\delta = 53.84$  ppm for  $^{13}C$  NMR). All other nuclei ( $^7Li$ ,  $^{11}B$ ,  $^{19}F$  and  $^{29}Si$ ) are referenced in compliance with the unified scale for NMR chemical shifts as recommended by the IUPAC stating the chemical shift relative to  $LiCl$ ,  $BF_3 \cdot Et_2O$ ,  $CCl_3F$  and  $Me_4Si$ .<sup>[S1]</sup> Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet,  $m_c$  = centrosymmetric multiplet), coupling constant (Hz), and integration. Analytical gas liquid chromatography (GLC) of reaction mixtures and pure substances was performed using a gas chromatograph 430-GC (*Varian Inc.*). The instrument was equipped with a FactorFour VF-WAXms capillary column (*Varian Inc.*, length: 30 m, inner diameter: 0.25 mm, film thickness of the stationary phase: 0.25  $\mu m$ ). The following temperature program was used for the analysis: carrier gas  $N_2$ ; injection temperature 270°C; detector temperature 270°C; flow rate 4.0 mL/min; temperature program: 40°C start temperature, 20°C/min heating rate to 250°C for 10 min, then 20°C/min heating rate to final temperature 260°C for 5 min. The data was

recorded with the program Galaxie 1.9.302.952 (*Varian Inc.*) High-resolution mass spectrometry (HRMS) was performed at the Analytical Facility of the Institut für Chemie, Technische Universität Berlin. Optical rotations were measured on a Perkin–Elmer 341 polarimeter with  $[\alpha]^{20}_{\text{D}}$  values reported in  $10^{-1}$  ( $^{\circ} \text{ cm}^2 \text{ g}^{-1}$ ); concentration  $c$  is in g/100 mL and  $\lambda = 589 \text{ nm}$  (Na-D-line). Analytical thin-layer chromatography (TLC) was performed on pre-coated aluminium sheets with silica gel 60 with fluorescent indicator from *Macherey-Nagel*. Flash column chromatography was performed on silica gel 60 (40–63  $\mu\text{m}$ , 230–400 mesh, ASTM) by *Grace* using the indicated solvents.

## 2 Experimental Details

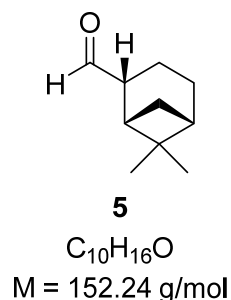
### 2.1 ((1*S*,2*R*,5*S*)-6,6-Dimethylbicyclo[3.1.1]heptan-2-yl)methanol



According to a literature-known procedure,<sup>[S2]</sup> a solution of (–)-β-pinene<sup>[S3]</sup> (6.0 g, 7.0 mL, 44 mmol, 1.0 equiv.) in THF (18 mL) was cooled to 0°C.  $\text{BH}_3\cdot\text{DMS}$  (90%, 4.6 mL, 44 mmol, 1.0 equiv.) was added dropwise over a period of 1 h, and the resulting solution stirred for 1 h at 0°C. Afterwards, EtOH (21 mL), aqueous NaOH (1.0M, 24 mL), and  $\text{H}_2\text{O}_2$  (30%, 11 mL) were added subsequently, and the resulting suspension was stirred for 30 min at room temperature before heating to 80°C for 2 h. The reaction mixture was extracted with *tert*-butylmethyl ether (3 x 100 mL). The combined organic phases were washed with  $\text{H}_2\text{O}$  (3 x 100 mL) and brine (100 mL) before drying over  $\text{MgSO}_4$ . After removal of all volatiles under reduced pressure, the residue was purified by flash column chromatography on silica gel using cyclohexane/*tert*-butylmethyl ether = 4/1 as eluent to afford myrtanol (5.0 g, 73%) as colorless oil.

**HRMS (APCI)** for  $\text{C}_{10}\text{H}_{17}\text{O}^+$   $[\text{M}-\text{H}]^+$ : calculated 153.1274, found 153.1277.  **$^1\text{H}$  NMR** (500 MHz,  $\text{CDCl}_3$ ):  $\delta/\text{ppm}$  = 0.94 (d,  $J$  = 9.5 Hz, 1H), 0.97 (s, 3H), 1.19 (s, 3H), 1.40–1.51 (m, 2H), 1.83–1.98 (m, 4H), 2.00 ( $m_c$ , 1H), 2.20–2.29 (m, 1H), 2.34–2.41 (m, 1H), 3.57 ( $m_c$ , 1H). The OH proton could not be detected.  **$^{13}\text{C}\{^1\text{H}\}$  NMR** (126 MHz,  $\text{CDCl}_3$ ):  $\delta/\text{ppm}$  = 18.9, 23.5, 26.1, 28.1, 33.3, 38.8, 41.6, 43.1, 44.6, 68.0.

### 2.2 (1*S*,2*R*,5*S*)-6,6-Dimethylbicyclo[3.1.1]heptane-2-carbaldehyde (5)

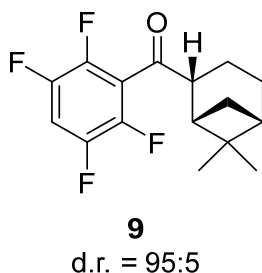


According to a literature-known procedure,<sup>[S2]</sup> a solution of oxalyl chloride (3.4 mL, 39 mmol, 1.5 equiv.) in  $\text{CH}_2\text{Cl}_2$  (100 mL) was cooled to –78°C. DMSO (5.0 mL, 70 mmol, 2.7 equiv.)

was added dropwise, and the resulting mixture was stirred for 5 min. Myrtanol (4.0 g, 26 mmol, 1.0 equiv.) in  $\text{CH}_2\text{Cl}_2$  (20 mL) and  $\text{Et}_3\text{N}$  (18 mL, 0.13 mol) were added subsequently, and the reaction mixture was stirred 5 min at  $-78^\circ\text{C}$ . Afterwards, the reaction was stirred for 1.5 h at room temperature and then quenched by the addition of  $\text{H}_2\text{O}$  (150 mL). The phases were separated, and the organic phase washed with  $\text{H}_2\text{O}$  (2 x 100 mL) and brine (100 mL) before drying over  $\text{MgSO}_4$ . After removal of all volatiles, the aldehyde **5** (4.4 g, quant.) was stored at  $-20^\circ\text{C}$  and used without further purification.

**HRMS (APCI)** for  $\text{C}_{10}\text{H}_{17}\text{O}^+$   $[\text{M}+\text{H}]^+$ : calculated 153.1274, found 153.1273.  **$^1\text{H}$  NMR** (500 MHz,  $\text{CDCl}_3$ ):  $\delta/\text{ppm}$  = 0.71 (s, 3H), 1.21 (s, 3H), 1.25 (d,  $J$  = 9.9 Hz, 1H), 1.82–1.97 (m, 4H), 2.22–2.31 (m, 1H), 2.36–2.43 (m, 1H), 2.51–2.57 (m, 1H), 2.70–2.77 (m, 1H), 9.76 (s, 1H).  **$^{13}\text{C}\{^1\text{H}\}$  NMR** (126 MHz,  $\text{CDCl}_3$ ):  $\delta/\text{ppm}$  = 13.4, 23.3, 24.8, 26.9, 29.5, 39.1, 40.8, 42.5, 52.9, 206.1.

### 2.3 ((1*S*,2*R*,5*S*)-6,6-Dimethylbicyclo[3.1.1]heptan-2-yl)(2,3,5,6-tetrafluorophenyl)methanone (**9**)



A solution of the alcohol **6** (1.7 g, 5.6 mmol, 1.0 equiv.) in  $\text{CH}_2\text{Cl}_2$  (60 mL) was cooled to  $0^\circ\text{C}$ . Dess–Martin periodinane (3.6 g, 8.4 mmol, 1.5 equiv.) was added in one portion and the resulting mixture stirred 4 h at room temperature. The reaction was quenched by the addition of  $\text{H}_2\text{O}$  (100 mL). The phases were separated, the organic phase washed with  $\text{H}_2\text{O}$  (5 x 100 mL) and dried over  $\text{MgSO}_4$ . After removal of all volatiles, the resulting white solid was removed by filtration through a pad of cotton to afford the ketone **9** (d.r. = 95:5, 1.4 g, 84%) as an orange brown oil without further purification. The diastereomeric ratio was determined by GLC analysis.

**HRMS (APCI)** for  $\text{C}_{16}\text{H}_{15}\text{F}_4\text{O}^+$   $[\text{M}-\text{H}]^+$ : calculated 299.1054, found 299.1051.

#### Major diastereomer [(1*S*,2*R*,5*S*)-**9**]:

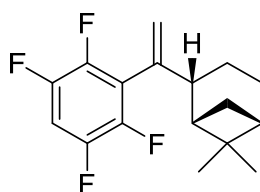
**$^1\text{H}$  NMR** (700 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta/\text{ppm}$  = 0.85 (d,  $J$  = 9.9 Hz, 1H), 0.88 (s, 3H), 1.06 (s, 3H), 1.55–1.65 (m, 2H), 1.67–1.71 (m, 1H), 1.76–1.83 (m, 1H), 2.12–2.19 (m, 1H), 2.25–2.31 (m, 1H), 2.34–2.39 (m, 1H), 3.13–3.20 ( $m_c$ , 1H), 6.08 ( $m_c$ , 1H).  **$^{13}\text{C}\{^1\text{H}\}$  NMR** (176 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta/\text{ppm}$

= 14.4, 22.7, 25.1, 27.1, 30.8, 39.0, 40.8, 43.0, 54.3, 107.2 (t,  $J$  = 23 Hz), 121.3 (t,  $J$  = 21 Hz), 142.9 (dm), 146.0 (dm), 196.9.  **$^{19}\text{F}$  NMR** (659 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta/\text{ppm}$  = -142.4 ( $m_c$ , 2F), -137.6 ( $m_c$ , 2F).

**Minor diastereomer [(1*S*,2*S*,5*S*)-9]:**

**$^1\text{H}$  NMR** (500 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta/\text{ppm}$  = 0.64 (s, 3H) 1.02 (s, 3H), 1.38–1.46 (m, 1H), 1.48 (d,  $J$  = 10.6 Hz, 1H), 1.59–1.70 (m, 3H), 2.02 ( $m_c$ , 1H), 2.21 ( $m_c$ , 1H), 2.26–2.37 (m, 1H), 3.31 ( $m_c$ , 1H), 6.06 ( $m_c$ , 1H).  **$^{13}\text{C}\{^1\text{H}\}$  NMR** (176 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta/\text{ppm}$  = 15.0, 20.2, 23.9, 24.2, 26.4, 39.4, 40.5, 42.6, 50.8, 107.2 (t,  $J$  = 23 Hz), 121.6 (t,  $J$  = 21 Hz), 143.2 (dm), 145.9 (dm), 196.8.

**2.4 (1*S*,2*R*,5*S*)-6,6-Dimethyl-2-(1-(2,3,5,6-tetrafluorophenyl)vinyl)bicyclo[3.1.1]heptane (10)**



**10**

d.r. = 96:4

Dimethyltitanocene (0.43M in THF, 5.9 mL, 2.5 mmol, 1.5 equiv.) was added to a solution of the ketone **9** (0.50 g, 1.7 mmol, 1.0 equiv.) in THF (10 mL), and the resulting mixture was heated to 65°C until full conversion as monitored by GLC analysis (18–48 h). The reaction was cooled to room temperature, quenched by the addition of  $\text{H}_2\text{O}$  (5.0 mL) and extracted with *tert*-butylmethyl ether (2 x 10 mL). The combined organic phases were dried over  $\text{MgSO}_4$ . After removal of all volatiles, the residue was purified by flash column chromatography on silica gel using *n*-pentane as eluent to afford the alkene **10** (d.r. = 96:4, 0.28 g, 57%) as a colorless liquid. The diastereomeric ratio was determined by GLC analysis.

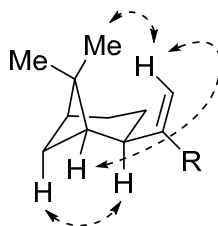
**HRMS (APCI)** for  $\text{C}_{17}\text{H}_{17}\text{F}_4$   $[\text{M}-\text{H}]^+$ : calculated 297.1261, found 297.1265.

**Major diastereomer [(1*S*,2*R*,5*S*)-10]:**

**$^1\text{H}$  NMR** (500 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta/\text{ppm}$  = 0.81 (d,  $J$  = 9.8 Hz, 1H), 1.00 (s, 3H), 1.15 (s, 3H), 1.48–1.70 (m, 3H), 1.75–1.88 (m, 2H), 2.18 ( $m_c$ , 1H), 2.27 ( $m_c$ , 1H), 3.07 ( $m_c$ , 1H), 4.95 (d,  $J$  = 2.0 Hz, 1H), 5.21 (d,  $J$  = 2.2 Hz, 1H), 6.24 ( $m_c$ , 1H).  **$^{13}\text{C}\{^1\text{H}\}$  NMR** (126 MHz,  $\text{CDCl}_3$ ):  $\delta/\text{ppm}$  = 19.6, 23.6, 26.2, 28.1, 33.5, 38.7, 41.6, 44.0, 44.6, 104.5 (t,  $J$  = 23 Hz), 117.2, 141.7. The *ortho*- and *meta*-carbon atom of the aromatic ring could not be detected.  **$^{19}\text{F}\{^1\text{H}\}$  NMR** (471



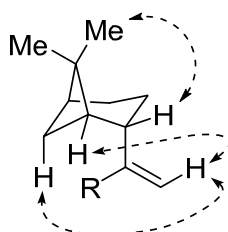
MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$ /ppm =  $-142.3$  (dd,  $J = 13$  Hz,  $J = 24$  Hz, 2F),  $-139.4$  (dd,  $J = 13$  Hz,  $J = 23$  Hz, 2F).



**Figure 1.** Proton correlation signals determined by nOe experiment; R = *p*-HC<sub>6</sub>F<sub>4</sub>.

Minor diastereomer [(1*S*,2*S*,5*S*)-10]:

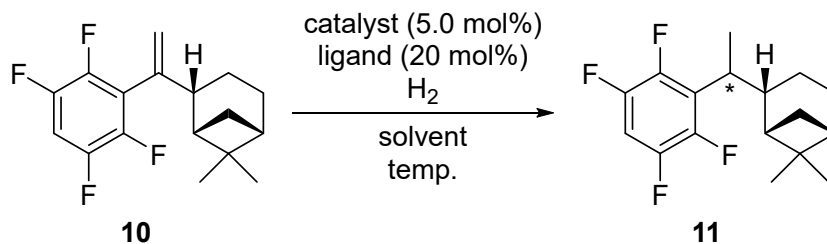
**<sup>1</sup>H NMR** (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$ /ppm = 0.70 (s, 3H), 1.11 (s, 3H), 1.38 (d,  $J = 9.4$  Hz, 1H), 1.41–1.47 (m, 1H), 1.52–1.69 (m, 3H), 1.71–1.76 (m, 1H), 1.99–2.08 (m, 2H), 2.96 (m<sub>c</sub>, 1H), 4.92 (br s, 1H), 5.23 (br s, 1H), 6.23 (m<sub>c</sub>, 1H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (126 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$ /ppm = 19.9, 20.8, 23.9, 24.5, 26.9, 39.6, 40.4, 40.6, 44.4, 104.5 (t,  $J = 23$  Hz), 116.8, 123.6 (t), 141.7. The *ortho*- and *meta*-carbon atom of the aromatic ring could not be detected. **<sup>19</sup>F{<sup>1</sup>H} NMR** (471 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$ /ppm =  $-142.3$  (dd,  $J = 13$  Hz,  $J = 24$  Hz, 2F),  $-139.4$  (dd,  $J = 13$  Hz,  $J = 23$  Hz, 2F).



**Figure 2.** Proton correlation signals determined by nOe experiment; R = *p*-HC<sub>6</sub>F<sub>4</sub>.

### 3 Investigation of Substrate-Controlled Hydrogenation of **10**

**Table 1.** Rhodium catalyzed substrate-controlled hydrogenation of **10**.<sup>[1]</sup>

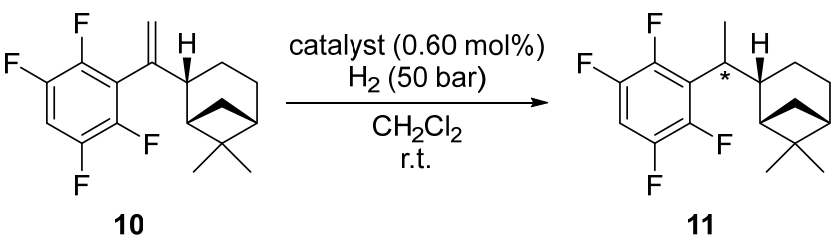
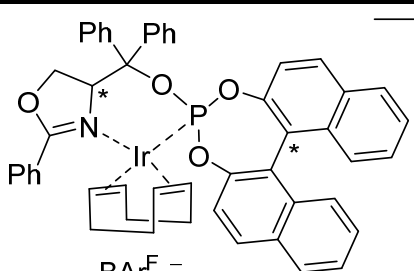
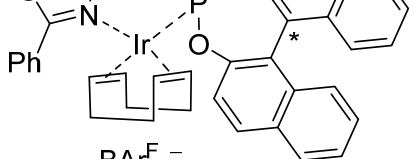
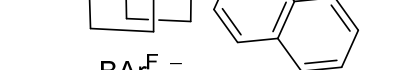

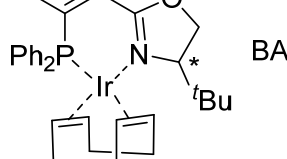



entry	catalyst	ligand	H <sub>2</sub> - pressure	solvent	temp.	conv. <sup>[2]</sup>	d.r. <sup>[3]</sup>
1	[Rh(cod)Cl] <sub>2</sub>	P(4- <i>t</i> BuC <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	25 bar	EtOH/ benzene	10 °C	85%	86:14
2	[Rh(cod)Cl] <sub>2</sub>	P(4-CF <sub>3</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	25 bar	EtOH/ benzene	10 °C	7%	–
3	[Rh(cod)Cl] <sub>2</sub>	P(4-MeOC <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	25 bar	EtOH/ benzene	10 °C	>99%	89:11
4	[Rh(cod)Cl] <sub>2</sub>	P(2-MeC <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	25 bar	EtOH/ benzene	10 °C	0	–
5	(Ph <sub>3</sub> P) <sub>3</sub> RhCl	–	25 bar	EtOH/ benzene	10 °C	20%	90:10
6	(Ph <sub>3</sub> P) <sub>3</sub> RhCl	–	25 bar	1,4-dioxane	10 °C	70%	85:15
7	(Ph <sub>3</sub> P) <sub>3</sub> RhCl	–	30 bar	benzene	30 °C	>99%	87:13
8	(Ph <sub>3</sub> P) <sub>3</sub> RhCl	–	25 bar	benzene	10 °C	>99%	88:12

[1] All reactions were performed in a 0.15 mmol scale respective to alkene **10**. [2] Conversion was determined by GLC analysis. [3] The d.r. was determined by <sup>1</sup>H NMR and GLC analysis.

## 4 Investigation of Catalyst-Controlled Hydrogenation of **10**

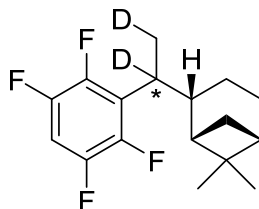
**Table 2.** Iridium catalyzed asymmetric hydrogenation of **10**.<sup>[1,S4]</sup>

			
entry	catalyst	conv. <sup>[2]</sup>	d.r. <sup>[3]</sup>
1		( <i>C</i> S, <i>S</i> <sub>a</sub> )	39% 63:37
2		( <i>C</i> S, <i>R</i> <sub>a</sub> )	0% –
3		( <i>C</i> R, <i>S</i> <sub>a</sub> )	0% –
4		( <i>C</i> R, <i>R</i> <sub>a</sub> )	0% –
5		( <i>S</i> )	65% 62:38
6		( <i>R</i> )	88% 64:36

[1] All reactions were performed in a 0.15 mmol scale respective to alkene **10**. [2] The conversion was determined by GLC analysis. [3] The d.r. was determined by <sup>1</sup>H NMR and GLC analysis.

## 5 Deuteration Experiments for the Investigation of Triphenylmethane Formation

### 5.1 (1*S*,2*S*,5*S*)-6,6-Dimethyl-2-(1-(2,3,5,6-tetrafluorophenyl)ethyl-1,2-*d*<sub>2</sub>)bicyclo-[3.1.1]heptane (11-*d*<sub>2</sub>)



**11-*d*<sub>2</sub>**

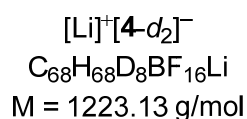
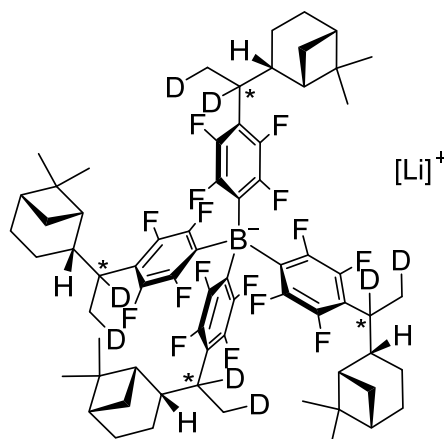
$C_{17}H_{18}D_2F_4$

$M = 302.35 \text{ g/mol}$

d.r. = 85:15

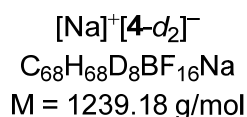
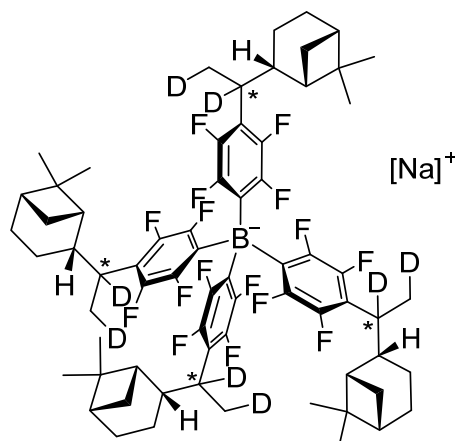
In a glass vial the alkene **10** (45 mg, 0.15 mmol, 1.0 equiv.) and  $(Ph_3P)_3RhCl$  (6.9 mg, 7.5  $\mu\text{mol}$ , 5.0 mol%) were placed under a nitrogen atmosphere and dissolved in degassed benzene (2.0 mL). The reaction vessel was transferred to an autoclave, pressurized with  $D_2$  (30 bar) and stirred for 18 h at 30°C (for further details, see section General Information). Afterwards the vial was removed from the autoclave and filtered through a plug of silica. Removal of all volatiles under reduced pressure gave the alkane **11-*d*<sub>2</sub>** (d.r. = 85:15, 45 mg, quant.) as a colorless liquid. The diastereomeric ratio was determined by GLC analysis.

**<sup>1</sup>H NMR** (500 MHz,  $C_6D_6$ ):  $\delta/\text{ppm} = 0.72$  (d,  $J = 9.7 \text{ Hz}$ , 1H), 1.01 (s, 3H), 1.03 (s, 3H), 1.11 (br s, 2H), 1.33–1.43 (m, 1H), 1.51 (mc, 1H), 1.68–1.90 (m, 4H), 2.17 (mc, 1H), 2.35–2.44 (m, 1H), 6.18 (mc, 1H). **<sup>2</sup>H NMR** (77 MHz,  $C_6D_6$ ):  $\delta/\text{ppm} = 0.98$ –1.15 (m), 3.05–3.22 (m). **<sup>13</sup>C{<sup>1</sup>H} NMR** (126 MHz,  $C_6D_6$ ):  $\delta/\text{ppm} = 17.0, 21.8, 22.9, 26.8, 28.3, 34.2, 36.8$  [Determined by  $^1H/^{13}C$  HMBC NMR (500/175 MHz,  $C_6D_6$ )], 38.6, 41.4, 44.9, 45.1, 103.6 (t,  $J = 22 \text{ Hz}$ ), 145.4 [Determined by  $^1H/^{13}C$  HMBC NMR (500/175 MHz,  $C_6D_6$ )], 147.2 [Determined by  $^1H/^{13}C$  HMBC NMR (500/175 MHz,  $C_6D_6$ )]. **<sup>19</sup>F NMR** (471 MHz,  $C_6D_6$ ):  $\delta/\text{ppm} = -144.7$ –[–140.8] (m, 2F), –139.6 (br s, 2F).

**5.2 Lithium tetrakis(4-(1-((1*S*,2*S*,5*S*)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl)ethyl-1,2-*d*<sub>2</sub>)-2,3,5,6-tetrafluorophenyl)borate ([Li]<sup>+</sup>[4-*d*<sub>2</sub>]<sup>-</sup>)**

To a solution of alkane **11-d<sub>2</sub>** (d.r. = 85:15, 0.35 g, 1.2 mmol, 5.0 equiv.) in Et<sub>2</sub>O (22 mL) was added dropwise *n*BuLi (2.7M in hexane, 0.42 mL, 1.1 mmol, 4.4 equiv.) at -78°C and the resulting mixture stirred for 3 h. Afterwards BCl<sub>3</sub> (1M in heptane, 0.23 mL, 0.23 mmol, 1.0 equiv.) was added dropwise and the solution was allowed to warm up to room temperature overnight slowly. The reaction was quenched by addition of H<sub>2</sub>O (20 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 x 10 mL). After removal of all volatiles the residue was purified by flash column chromatography on silica gel using subsequent CH<sub>2</sub>Cl<sub>2</sub> (200 mL) and acetone (500 mL) as eluent. The lithium borate [Li]<sup>+</sup>[4-*d*<sub>2</sub>]<sup>-</sup> was obtained as a white solid and directly used in the subsequent salt metathesis reaction.

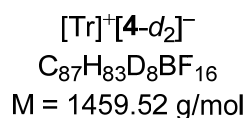
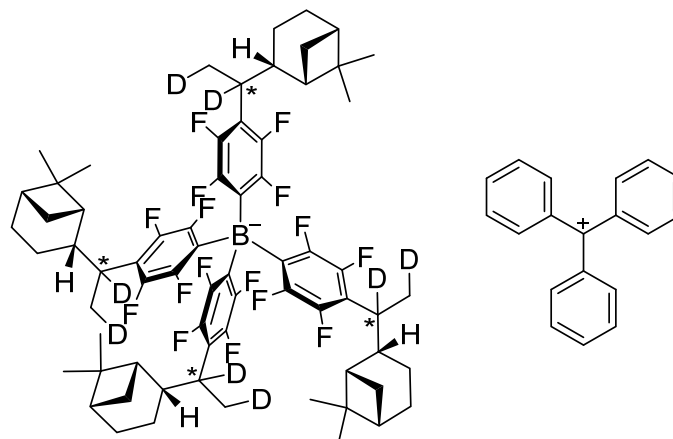
### 5.3 Sodium tetrakis(4-(1-((1*S*,2*S*,5*S*)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl)ethyl-1,2-*d*<sub>2</sub>)-2,3,5,6-tetrafluorophenyl)borate ([Na]<sup>+</sup>[4-*d*<sub>2</sub>]<sup>-</sup>)



To a solution of the lithium borate [Li]<sup>+</sup>[4-*d*<sub>2</sub>]<sup>-</sup> in CH<sub>2</sub>Cl<sub>2</sub> (5.0 mL) was added a saturated aqueous solution of NaCl (5.0 mL) and the two-phase mixture stirred overnight at room temperature rapidly. Afterwards the phases were separated, the organic phase was dried over Na<sub>2</sub>SO<sub>4</sub> and all volatiles removed under high vacuum (130°C/10<sup>-3</sup> mbar). The sodium borate [Na]<sup>+</sup>[4-*d*<sub>2</sub>]<sup>-</sup> (0.28 g, 94% over two steps) was obtained as a white solid.

**HRMS (APCI)** for C<sub>68</sub>H<sub>68</sub>D<sub>8</sub>BF<sub>16</sub><sup>-</sup> [M]<sup>-</sup>: calculated 1215.6292, found 1215.6276. **<sup>1</sup>H NMR** (500 MHz, C<sub>6</sub>D<sub>6</sub>): δ/ppm = 0.71–0.80 (br m, 4H), 1.01–1.12 (br m, 24H), 1.12–1.23 (br m, 8H), 1.42–1.53 (br m, 4H), 1.62–1.74 (br m, 4H), 1.74–1.96 (br m, 16H), 2.13–2.24 (br m, 4H), 2.42–2.54 (br m, 4H). **<sup>11</sup>B{<sup>1</sup>H} NMR** (160 MHz, C<sub>6</sub>D<sub>6</sub>): δ/ppm = –15.8. **<sup>13</sup>C{<sup>1</sup>H} NMR** (126 MHz, C<sub>6</sub>D<sub>6</sub>): δ/ppm = 17.6, 22.2, 23.0, 27.0, 28.3, 34.2, 36.8, 38.6, 41.5, 45.2, 45.4, 120.1 (t, *J* = 18 Hz). The *ortho*- and *meta* carbon atoms of the aromatic rings as well as the carbon atoms of the C–B bonds could not be detected. **<sup>19</sup>F NMR** (471 MHz, C<sub>6</sub>D<sub>6</sub>): δ/ppm = –150.8–[–143.5] (br m, 8F), –139.0–[–130.7] (br m, 8F).

#### 5.4 Triphenylmethylium tetrakis(4-(1-((1*S*,2*S*,5*S*)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl)ethyl-1,2-*d*<sub>2</sub>)-2,3,5,6-tetrafluorophenyl)borate ([Tr]<sup>+</sup>[4-*d*<sub>2</sub>]<sup>-</sup>)

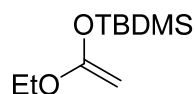


The borate [Na]<sup>+</sup>[4-*d*<sub>2</sub>]<sup>-</sup> (0.10 g, 80 μmol, 1.0 equiv.) and triphenylmethyl chloride (0.11 g, 0.40 mmol, 5.0 equiv.) were suspended in *n*-hexane (6.0 mL) and stirred 2.5 h at room temperature. The suspension was filtered under nitrogen and the remaining solid was washed with *n*-hexane (6 x 3.0 mL). The orange solid was redissolved in CH<sub>2</sub>Cl<sub>2</sub> (2.0 mL) and then dried under high vacuum (50°C/10<sup>-3</sup> mbar). The trityl salt [Tr]<sup>+</sup>[4-*d*<sub>2</sub>]<sup>-</sup> (86 mg, 0.058 mmol, 72%) was obtained as an orange solid with triphenylmethane (3.0 mg, 0.011 mmol, 14%) as byproduct. The amount of triphenylmethane was determined in <sup>1</sup>H NMR by integration of the baseline separated signals at δ 7.64 ppm and δ 7.13 ppm.

**HRMS (APCI)** for C<sub>68</sub>H<sub>68</sub>D<sub>8</sub>BF<sub>16</sub><sup>-</sup> [M]<sup>-</sup>: calculated 1215.6292, found 1215.6290. **HRMS (APCI)** for C<sub>19</sub>H<sub>15</sub><sup>+</sup> [M]<sup>+</sup>: calculated 243.1168, found 243.1167. **<sup>1</sup>H NMR** (700 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ/ppm = 0.74–0.80 (br m, 4H), 1.02 (br s, 24H), 1.19 (br s, 8H), 1.40–1.57 (br m, 4H), 1.57–1.67 (br m, 4H), 1.78–1.90 (br m, 8H), 1.93–2.08 (br m, 8H), 2.17–2.26 (br m, 4H), 2.29–2.40 (br m, 4H), 7.64 (dd, *J* = 8.5 Hz, *J* = 1.3 Hz, 6H), 7.84 (m<sub>c</sub>, 6H), 8.24 (tt, *J* = 7.5 Hz, *J* = 1.3 Hz, 3H). **<sup>2</sup>H NMR** (107 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ/ppm = 1.22 (br s), 3.12 (br s). **<sup>11</sup>B{<sup>1</sup>H} NMR** (161 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ/ppm = –16.5. **<sup>13</sup>C{<sup>1</sup>H} NMR** (176 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ/ppm = 17.7 (m<sub>c</sub>), 22.2, 22.9, 27.1, 28.3, 34.3, 36.1–36.7, 38.7, 41.6, 45.1, 45.4, 119.0 (t, *J* = 17 Hz), 131.0, 140.3, 143.0, 144.0, 211.1. The *ortho*- and *meta* carbon atoms of the aromatic rings as well as the carbon atoms of the C–B bonds could not be detected. **<sup>19</sup>F NMR** (471 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ/ppm = –151.3–[–145.6] (br m, 8F), –134.1 (br s, 8F).

## 6 Characterization Data of Mukaiyama Aldol Products

### 6.1 *tert*-Butyl((1-ethoxyvinyl)oxy)dimethylsilane (**18**)



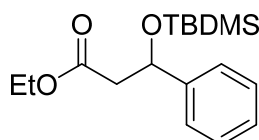
**18**

C<sub>10</sub>H<sub>22</sub>O<sub>2</sub>Si  
M = 202,37 g/mol

*n*BuLi (2.5M in hexane, 4.4 mL, 12 mmol, 1.1 equiv.) was added dropwise to a solution of freshly distilled *N,N*-diisopropylamine (1.7 mL, 12 mmol, 1.2 equiv.) in THF (20 mL) at 0 °C. The resulting solution was stirred for 20 min at 0 °C and then cooled to –78 °C. Ethyl acetate (1.0 mL, 10 mmol, 1.0 equiv.) was added dropwise over 10 min, and the mixture stirred for additional 30 min. DMPU (3 mL) was then added dropwise, followed by a solution of *tert*-butyldimethylsilyl chloride (1.8 g, 12 mmol, 1.2 equiv.) in THF (3.0 mL). The reaction mixture was stirred for 30 min at –78 °C and then allowed to warm to room temperature overnight. The volatiles were removed under reduced pressure, and the residue resolved in *n*-pentane (80 mL). The organic phase was washed successively with water (30 mL), saturated aqueous CuSO<sub>4</sub> solution (30 mL), saturated aqueous NaHCO<sub>3</sub> solution (30 mL), and brine (30 mL). After removal of volatiles under reduced pressure, the title compound was purified by distillation (bp 72 °C at 23 mbar) to give **18** (1.1 g, 54%) as colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ/ppm = 0.17 (s, 6H), 0.93 (s, 9H), 1.29 (t, <sup>3</sup>J = 7.0 Hz, 3H), 3.06 (d, *J* = 2.3 Hz, 1H), 3.22 (d, *J* = 2.3 Hz, 1H), 3.75 (q, *J* = 7.1 Hz, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>): δ/ppm = –4.4, 14.5, 18.3, 25.8, 60.6, 63.5, 161.4. <sup>29</sup>Si DEPT NMR (99 MHz, CDCl<sub>3</sub>): δ/ppm = 21.8.

### 6.2 Ethyl 3-((*tert*-butyldimethylsilyl)oxy)-3-phenylpropanoate (**20**)



**20**

C<sub>17</sub>H<sub>28</sub>O<sub>3</sub>Si  
M = 308,49 g/mol

In a glovebox, the trityl salt [<sup>Me</sup>Tr]<sup>+</sup>[**4**]<sup>–</sup> (41 mg, 0.021 mmol, 10 mol%) is placed in a medium-sized vial, dissolved in CH<sub>2</sub>Cl<sub>2</sub> (1 mL), transferred to a fume hood, and connected to a nitrogen–vacuum manifold. The trityl-cation solution was cooled to –78 °C, and a solution of



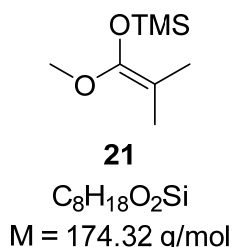
benzaldehyde (**19**, 21 mg, 0.20 mmol, 1.0 equiv.) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) was added. The mixture was stirred for 15 min, and a solution of 1-(*tert*-butyldimethylsilyloxy)-1-ethoxyethylen (**18**, 45 mg, 0.22 mmol, 1.1 equiv.) in CH<sub>2</sub>Cl<sub>2</sub> (0.7 mL) was then added dropwise over a period of 2 h. The reaction mixture was stirred for additional 4.5 h at –78°C and then quenched by the addition of aqueous saturated NaHCO<sub>3</sub> solution (30 mL). The aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 10 mL), the combined organic phases dried over MgSO<sub>4</sub>, and the solvent removed under reduced pressure. Purification of the residue by flash column chromatography on silica gel using cyclohexane/*tert*-butylmethyl ether = 50/1 as eluent afforded the silylether **20** (35 mg, 55%) as a yellow oil.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ/ppm = –0.18 (s, 3H), 0.02 (s, 3H), 0.85 (s, 9H), 1.25 (t, <sup>3</sup>*J* = 7.1 Hz, 3H), 2.54 (dd, *J* = 14.5, 4.2 Hz, 1H), 2.72 (dd, *J* = 14.6, 9.3 Hz, 1H), 4.13 (m, 2H), 5.15 (dd, *J* = 9.1, 4.1 Hz, 1H), 7.22–7.26 (m, 1H), 7.29–7.37 (m, 4H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (126 MHz, CDCl<sub>3</sub>): δ/ppm = –5.2, –4.6, 14.3, 18.2, 25.8, 46.6, 60.6, 72.4, 126.0 (2C), 127.6, 128.4 (2C), 144.3 171.4. **<sup>29</sup>Si DEPT NMR** (99 MHz, CDCl<sub>3</sub>): δ/ppm = 19.9.

The enantiomeric excess was determined by HPLC analysis on a chiral stationary phase of the corresponding alcohol (Daicel Chiralcel OD-H column, 20 °C, *n*-heptane/*i*-PrOH = 96/4, flow rate 0.50 mL/min, λ = 254 nm): *t*<sub>R</sub> = 29.8 min, *t*<sub>R</sub> = 45.5 min. Deprotection of **17** (20 mg, 0.065 mmol) in THF (1 mL) by the addition of aqueous HCl (1 M, 1 mL) gave the product as a yellow oil (11 mg) without further purification.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ/ppm = 1.27 (t, *J* = 7.1 Hz, 3H), 2.69–2.80 (m, 2H), 4.19 (q, *J* = 7.2 Hz, 2H), 5.14 (dd, *J* = 3.9 Hz, 8.9 Hz, 1H), 7.27–7.31 (m, 1H), 7.34–7.40 (m, 4H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (126 MHz, CDCl<sub>3</sub>): δ/ppm = 14.3, 43.5, 61.0, 70.5, 125.8 (2C), 128.0, 128.7 (2C), 142.6, 172.6.

### 6.3 *tert*-Butyl((1-ethoxyvinyl)oxy)dimethylsilan (**21**)

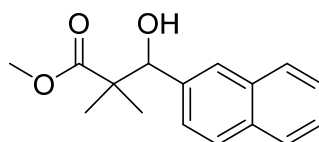


To a solution of *N,N*-diisopropylamine (4.8 mL, 34 mmol, 1.3 equiv.) in THF (20 mL) was added *n*BuLi (2.67M in hexane, 12 mL, 31 mmol, 1.2 equiv.) dropwise at 0°C and the mixture was stirred for 30 min. Methyl isobutyrate (3.0 mL, 26 mmol, 1.0 equiv.) was added and the solution stirred for an additional hour at 0°C before trimethylsilyl chloride (3.0 mL, 26 mmol,

1.0 equiv.) was added. After stirring for 1 h at 0°C the solution was filtered, all volatiles removed under reduced pressure and the residue taken up in Et<sub>2</sub>O (30 mL). The suspension was filtered again, the volatiles removed again under reduced pressure. Purification by distillation (bp. 42°C at 13 mbar) of the residue afforded the silylketene acetal **21** (2.0 g, 44%) as a colorless liquid.

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>): δ/ppm = 0.18 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>), 1.66 (s, 3H, 4-CH<sub>3</sub>-a), 1.73 (s, 3H, 4-CH<sub>3</sub>-b), 3.33 (s, 3H, H-1). <sup>1</sup>H/<sup>29</sup>Si-HMQC (500/99 MHz, 298K, optimized on *J* = 7.0 Hz): δ/ppm = 0.18/18.6.

#### 6.4 *rac*-Ethyl 3-hydroxy-2,2-dimethyl-3-phenylpropanoat (**23**)



**23**

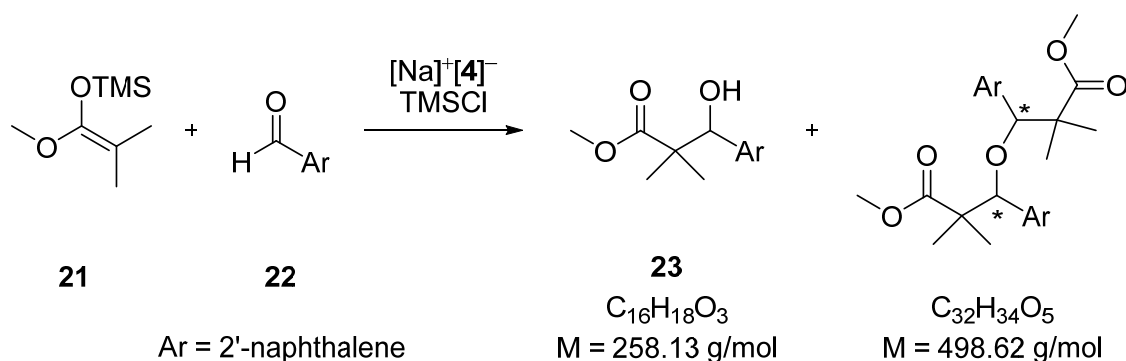
C<sub>16</sub>H<sub>18</sub>O<sub>3</sub>

M = 258.13 g/mol

*N,N*-Diisopropylamine (1.3 g, 13 mmol, 1.3 equiv.) was suspended in THF (44 mL) and cooled to –78°C. *n*BuLi (2.67M in hexane, 4.5 mL, 12 mmol, 1.2 equiv.) was added dropwise and the mixture stirred for 30 min at 0°C. The resulting solution was cooled to –78°C, methyl isobutyrate was added, and the mixture was stirred for 1 h before a solution of 2-naphthaldehyde (**22**, 1.9 g, 12 mmol, 1.2 equiv.) in THF (7 mL) was added dropwise. The mixture was warmed to room temperature and stirred for 1.5 h. The reaction was quenched by the addition of saturated aqueous solution of NH<sub>4</sub>Cl (10 mL) and extracted with *tert*-butylmethyl ether (2 x 15 mL). The combined organic phases were dried over MgSO<sub>4</sub>. After removal of all volatiles, the residue was purified by flash column chromatography on silica gel using cyclohexane/*tert*-butylmethyl ether = 5/1 as eluent to afford the title compound **23** (1.8 g, 70%) as colorless solid.

**HRMS (APCI)** for C<sub>16</sub>H<sub>17</sub>O<sub>2</sub><sup>+</sup> [M–OH]<sup>+</sup>: calculated 241.1229, found 241.1228. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ/ppm = 1.16 (s, 3H, 3-CH<sub>3</sub>), 1.20 (s, 3H, 3-CH<sub>3</sub>), 3.25 (d, <sup>3</sup>J<sub>H,H</sub> = 4.5 Hz, 1H, OH), 3.74 (s, 3H, H-1), 5.07 (d, <sup>3</sup>J<sub>H,H</sub> = 4.2 Hz, 1H, H-4), 7.41–7.52 (m, 3H, H-Ar), 7.74–7.87 (m, 4H, H-Ar). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>): δ/ppm = 19.3 (3-CH<sub>3</sub>), 23.3 (3-CH<sub>3</sub>), 48.1 (C-3), 52.3 (C-1), 78.9 (C-4), 125.8 (C-Ar), 126.1 (C-Ar), 126.2 (C-Ar), 126.8 (C-Ar), 127.4 (C-Ar), 127.7 (C-Ar), 128.2 (C-Ar), 133.0 (C-10')\*, 133.1 (C-6')\*, 137.6 (C-5), 178.4 (C-2).

### 6.5 Dimethyl 3,3'-oxybis(2,2-dimethyl-3-(naphthalen-2-yl)propanoate)



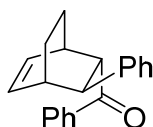
To a solution of sodium borate  $[\text{Na}]^+[\mathbf{4}]^-$  (24 mg, 0.020 mmol, 10 mol%) and 2-naphthaldehyde (**22**, 31 mg, 0.20 mmol, 1.0 equiv.) in toluene (2.0 mL) was added at  $-80^\circ\text{C}$  the silylketene acetal **21** (44 mg, 0.25 mmol, 1.25 equiv.) and trimethylsilyl chloride (0.05 mL). The reaction was stirred for 22 h at  $-80^\circ\text{C}$  (full conversion of aldehyde determined by GLC analysis) and then for 30 min at room temperature (full conversion of silyl ether to alcohol determined by GLC analysis). The reaction was quenched by the addition of saturated aqueous  $\text{NaHCO}_3$  solution (3.0 mL). The organic phase was dried over  $\text{Na}_2\text{SO}_4$ . During workup formation of the shown ether was determined by GLC. After removal of all volatiles the ether was observed exclusively.

**HRMS (APCI)** for  $\text{C}_{32}\text{H}_{35}\text{O}_5^+$   $[\text{M}+\text{H}]^+$ : calculated 499.2479, found 499.2484. Spectroscopic data of one diastereomer:  **$^1\text{H}$  NMR** (500 MHz,  $\text{CDCl}_3$ ):  $\delta/\text{ppm} = 0.98$  (s, 3H, 3- $\text{CH}_3$ ), 1.29 (s, 3H, 3- $\text{CH}_3$ ), 3.75 (s, 3H, H-1), 4.94 (s, 1H, H-4), 7.12 ( $m_c$ , 1H, H-12), 7.32–7.37 (m, 1H, H-8)\*, 7.37–7.42 (m, 2H, H-6, H-9\*), 7.46–7.52 (m, 2H, H-10\*, H-11), 7.70 (d,  $^3J_{\text{H,H}} = 8.2 \text{ Hz}$ , 1H, H-7).  **$^{13}\text{C}\{^1\text{H}\}$  NMR** (126 MHz,  $\text{CDCl}_3$ ):  $\delta/\text{ppm} = 19.6$  (3- $\text{CH}_3$ ), 22.9 (3- $\text{CH}_3$ ), 48.6 (C-3), 52.0 (C-1), 86.0 (C-4), 125.8 (C-8)\*, 125.9 (C-9)\*, 126.7 (C-10)\*, 126.9 (C-12), 127.5 (C-7), 128.0 (C-11), 128.2 (C-6), 132.6 (C-6'), 132.9 (C-10'), 136.1 (C-5), 177.2 (C-2).

The enantiomeric excess of **23** was determined by HPLC analysis of an aliquot of the reaction mixture, filtered over a plug of silica (Daicel Chiralcel OD-H column,  $20^\circ\text{C}$ , *n*-heptane/*i*-PrOH = 95/5, flow rate 1.00 mL/min,  $\lambda = 254 \text{ nm}$ ):  $t_R = 23.1 \text{ min}$ ,  $t_R = 26.7 \text{ min}$ .

## 7 Characterization Data of Diels–Alder Products

### 7.1 *endo*-Phenyl-(3-phenylbicyclo[2.2.2]oct-5-en-2-yl)methanone (**15**)



**15**

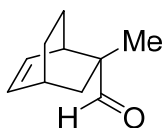
C<sub>21</sub>H<sub>20</sub>O

M = 288.39 g/mol

In a glovebox, the trityl salt [MeTr]<sup>+</sup>[4]<sup>−</sup> (23 mg, 13 μmol, 5.0 mol%) and chalcone (**13**, 52 mg, 0.25 mmol, 1.0 equiv.) were placed in a medium-sized vial and dissolved in benzene (0.80 mL). Cyclohexa-1,3-diene (**14**, 40 mg, 50 μL, 0.50 mmol, 2.0 equiv.) was added, and the mixture was maintained for 17 h at room temperature. The reaction was quenched by the addition of saturated aqueous NaHCO<sub>3</sub> solution (5.0 mL), the phases were separated, and the aqueous phase extracted with *tert*-butylmethyl ether (2 × 10 mL). The combined organic phases were dried over Na<sub>2</sub>SO<sub>4</sub>, and the volatiles removed under reduced pressure. Purification of the residue by flash column chromatography on silica gel using cyclohexane/*tert*-butylmethyl ether = 70/1 as eluent afforded the title compound **15** (58 mg, 80%).

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ/ppm = 1.08–1.17 (m, 1H), 1.49 (m<sub>c</sub> = 1H), 1.79–1.87 (m, 1H), 1.87–1.94 (m, 1H), 2.64–2.70 (m, 1H), 2.94–3.01 (m, 1H), 3.45–3.50 (m, 1H), 3.78–3.83 (m, 1H), 6.11 (m<sub>c</sub>, 1H), 6.56 (m<sub>c</sub>, 1H), 7.18–7.23 (m, 1H) 7.27–7.34 (m, 4H) 7.37–7.42 (m, 2H), 7.48–7.53 (m, 1H), 7.85–7.89 (m, 2H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (101 MHz, CDCl<sub>3</sub>): δ/ppm = 18.6, 26.6, 34.7, 36.6, 44.8, 51.1, 126.3, 128.3, 128.57 (3C), 128.62, 130.8, 132.8, 136.4, 136.5, 143.0, 200.9. **HPCL** (Daicel Chiralcel OD-H, 20 °C, *n*-heptane/*i*-PrOH = 97/3, flow rate 0.65 mL/min, λ = 254 nm): *t*<sub>R</sub> = 13.0 min, *t*<sub>R</sub> = 15.2 min.

### 7.2 *endo*-2-Methylbicyclo[2.2.2]oct-5-ene-2-carbaldehyde (**17**)



**17**

C<sub>10</sub>H<sub>14</sub>O

M = 150.22 g/mol

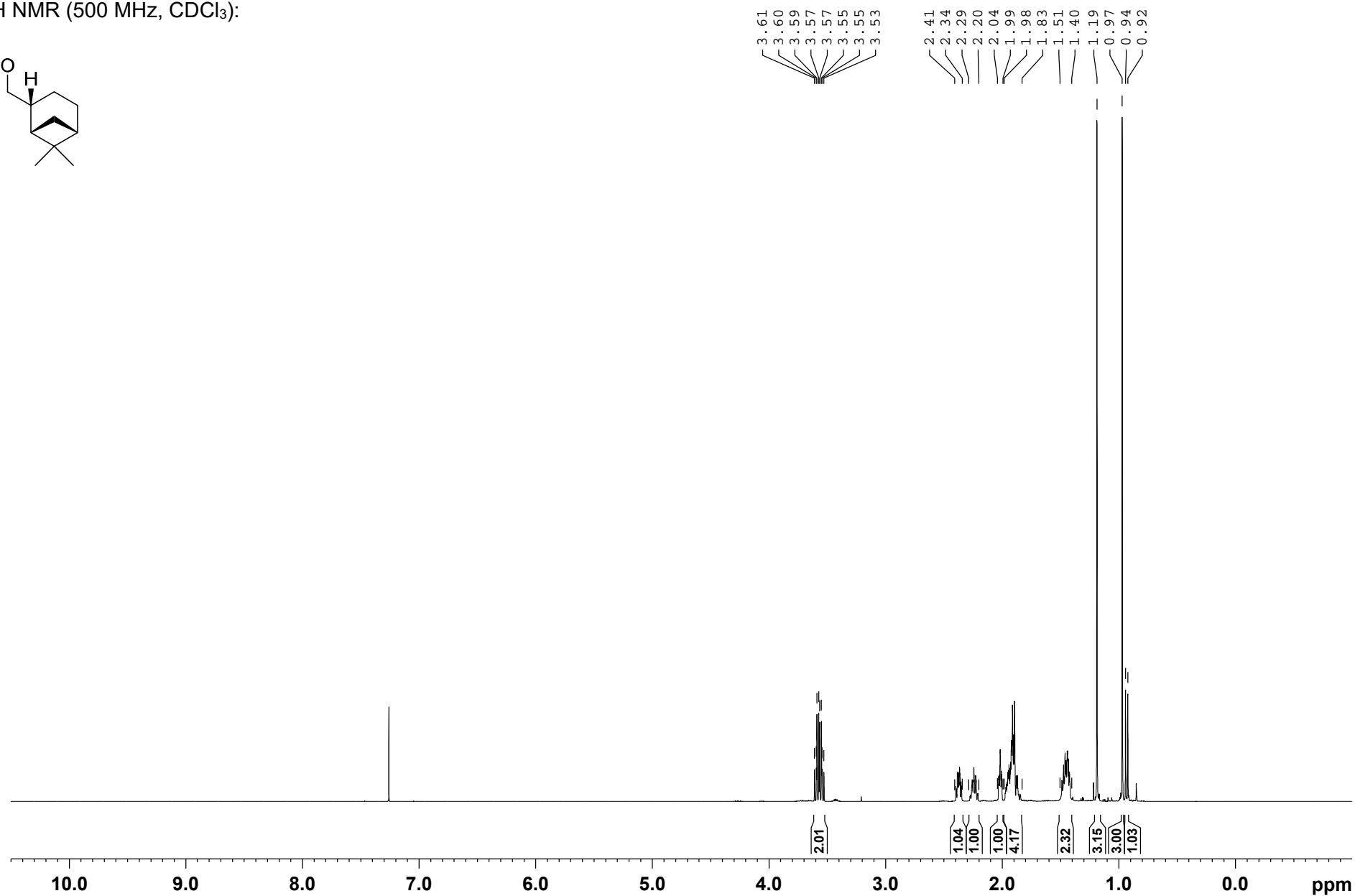
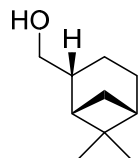
In a glovebox, the trityl salt [MeTr]<sup>+</sup>[4]<sup>−</sup> (13 mg, 7.0 μmol 5.0 mol%) is placed in a medium sized vial and dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (0.50 mL). Methacrolein (**16**, 9.8 mg, 0.14 mmol, 1.0

equiv.) and cyclohexa-1,3-diene (**14**, 14 mg, 0.14 mmol, 1.0 equiv.) were placed in a second medium sized vial. Both vials were transferred to a fume hood, connected to a nitrogen–vacuum manifold and cooled to  $-20\text{ }^{\circ}\text{C}$ . The trityl solution was transferred to the substrates and the mixture was stirred for 23 h at  $-20\text{ }^{\circ}\text{C}$ . Filtration over a plug of silica gave the product **17** (9.7 mg, 46%) as slightly yellow oil.

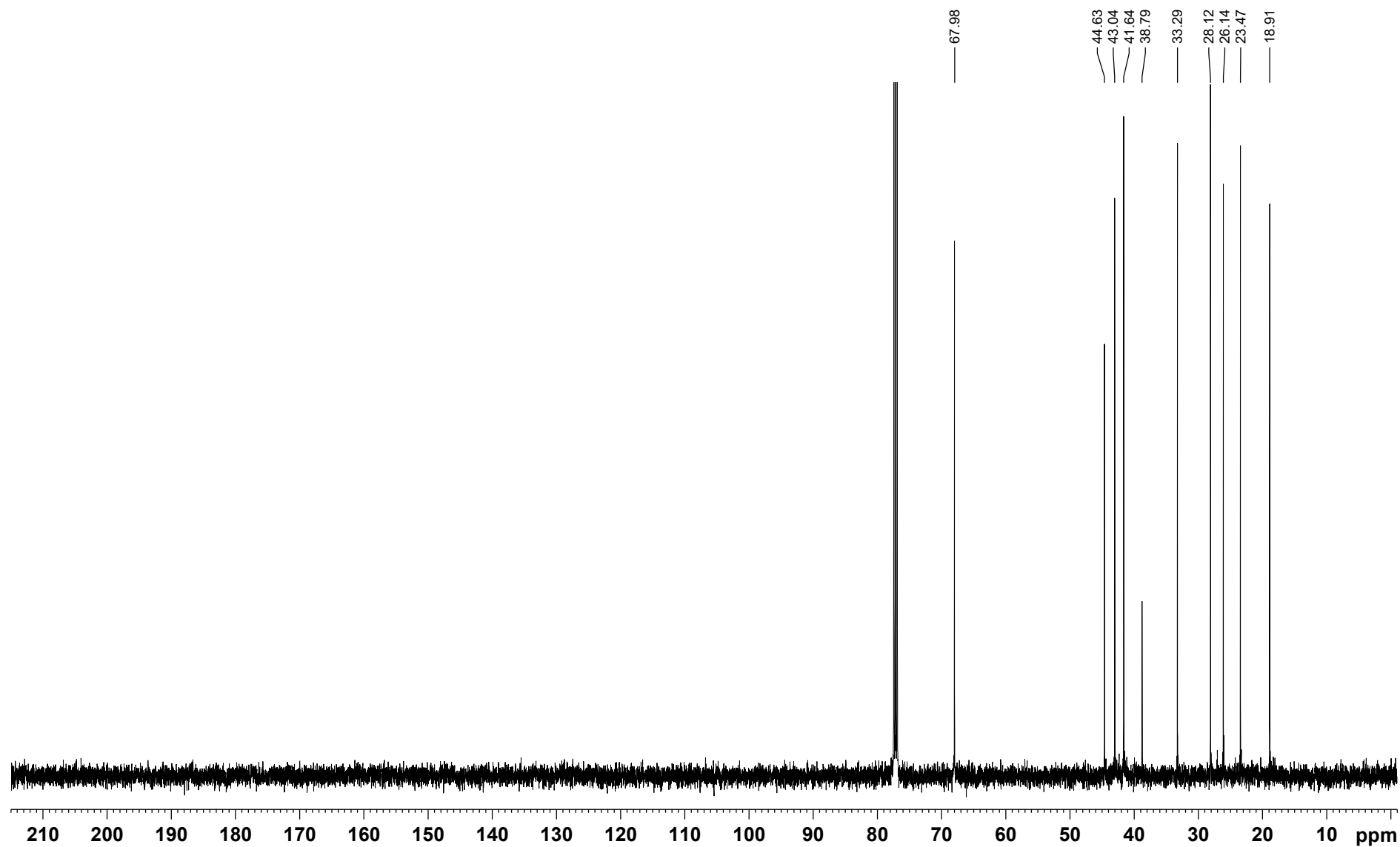
**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ ):  $\delta/\text{ppm}$  = 1.15 (s, 3H), 1.16–1.32 (m, 3H), 1.49–1.58 (m, 1H), 1.90 (dddd,  $J$  = 12.6 Hz,  $J$  = 9.5,  $J$  = 3.0,  $J$  = 2.5 Hz, 1H), 2.01 (ddd,  $J$  = 13 Hz,  $J$  = 9.6 Hz,  $J$  = 3.2 Hz, 1H), 2.48 ( $m_c$ , 1H), 2.60 ( $m_c$ , 1H), 6.25 ( $m_c$ , 2H), 9.32 (s, 1H).  **$^{13}\text{C}\{^1\text{H}\}$  NMR** (101 MHz,  $\text{CDCl}_3$ ):  $\delta/\text{ppm}$  = 20.3, 21.3, 25.2, 30.6, 35.6, 36.2, 50.1, 133.6, 135.2, 205.8.

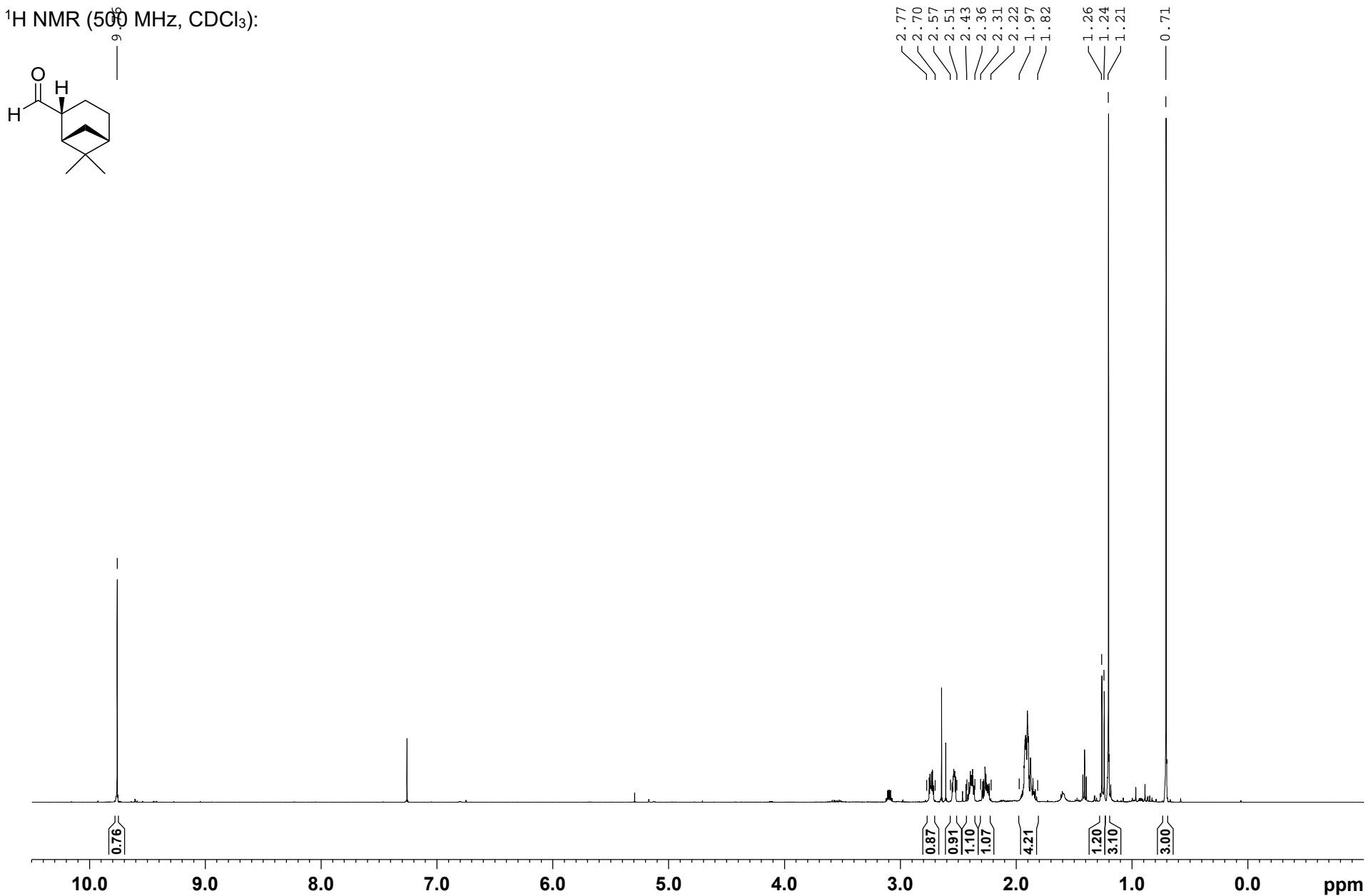
The enantiomeric excess was determined after reduction of **17** with  $\text{NaBH}_4$  to the corresponding alcohol, conversion to the (S)-MTPA ester derivate,<sup>[S5]</sup> and integration of the baseline-separated  $^1\text{H}$  NMR resonances (400 MHz,  $\text{CDCl}_3$ ):  $\delta/\text{ppm}$  = 3.99 (d,  $J$  = 10.4 Hz, 1H), (3.89, d,  $J$  = 10.4 Hz, 1H), 3.83 (d,  $J$  = 10.4 Hz, 1H), 3.72 (d,  $J$  = 10.4 Hz, 1H).

## 8 NMR Spectra of All Compounds

**((1S,2R,5S)-6,6-Dimethylbicyclo[3.1.1]heptan-2-yl)methanol**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):

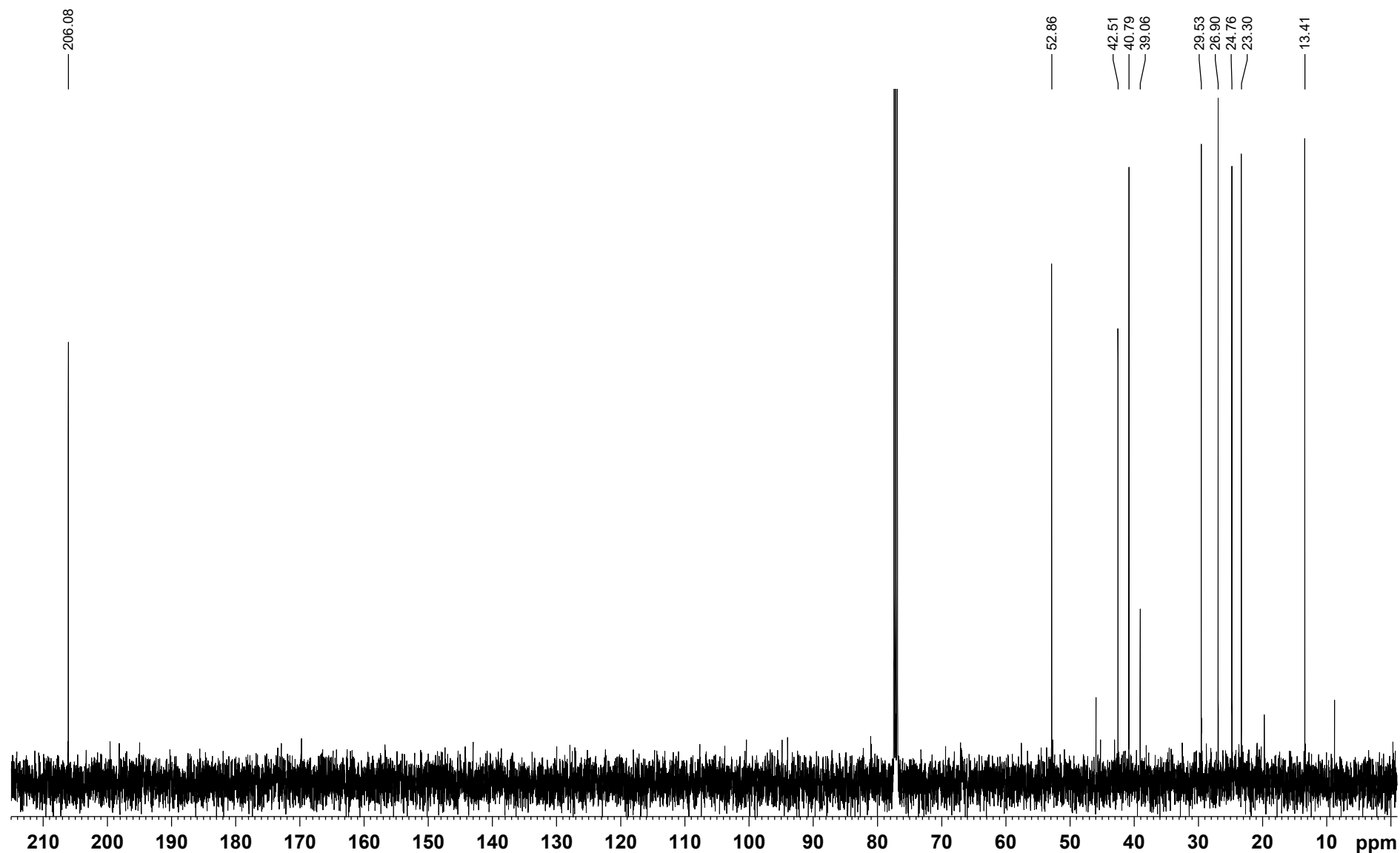
$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ ):

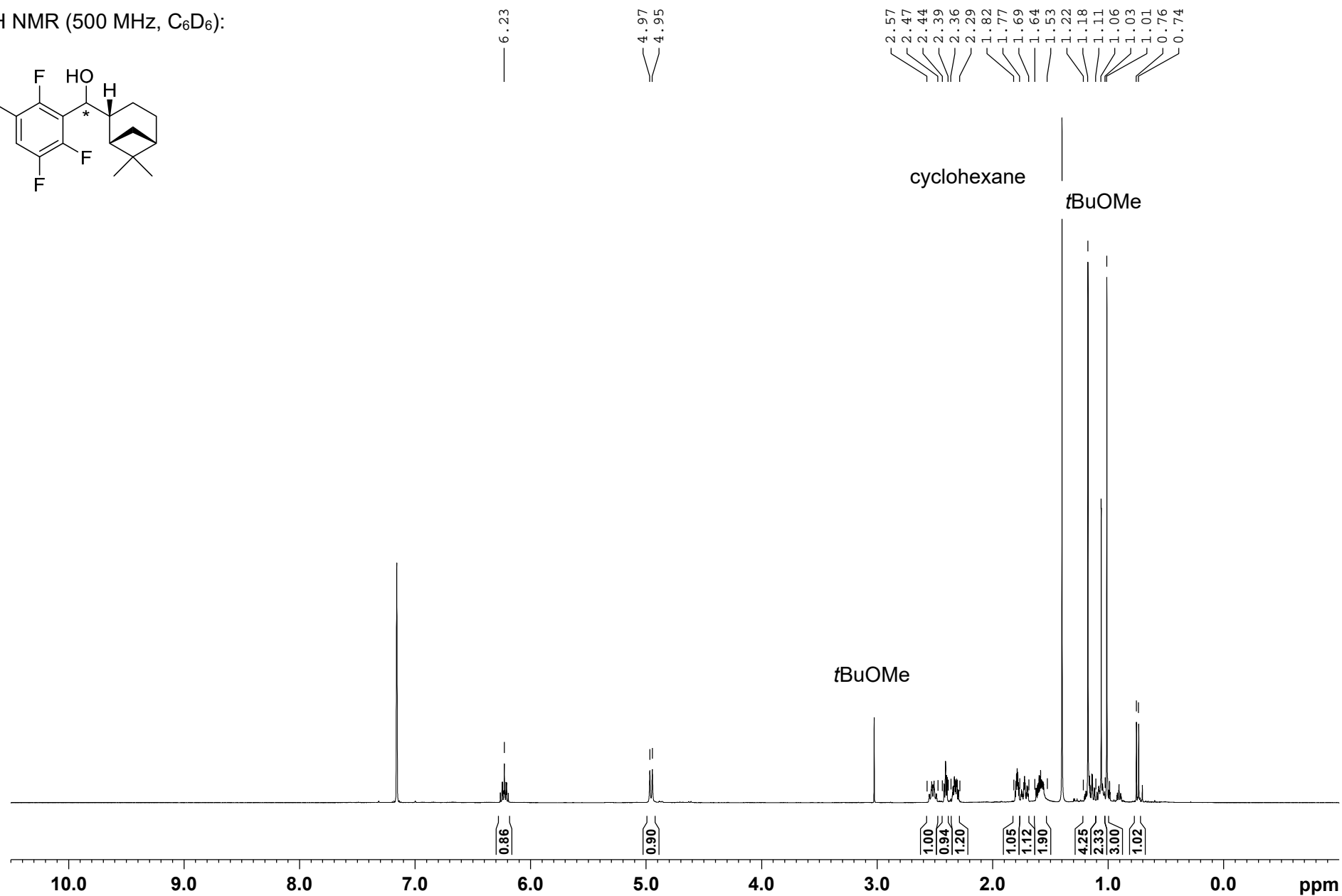
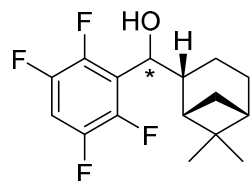


**(1S,2R,5S)-6,6-Dimethylbicyclo[3.1.1]heptane-2-carbaldehyde (5)**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):

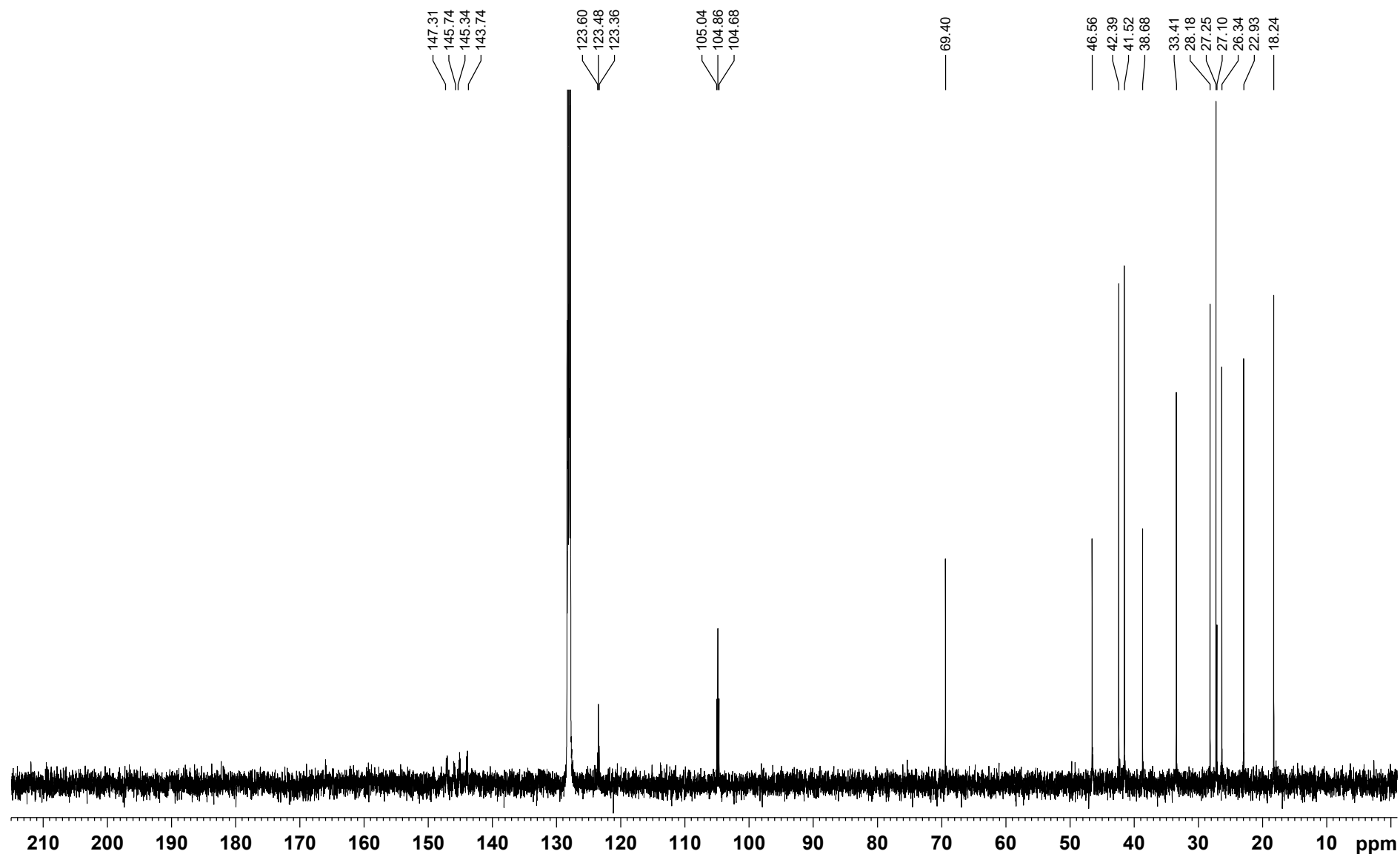


$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ ):

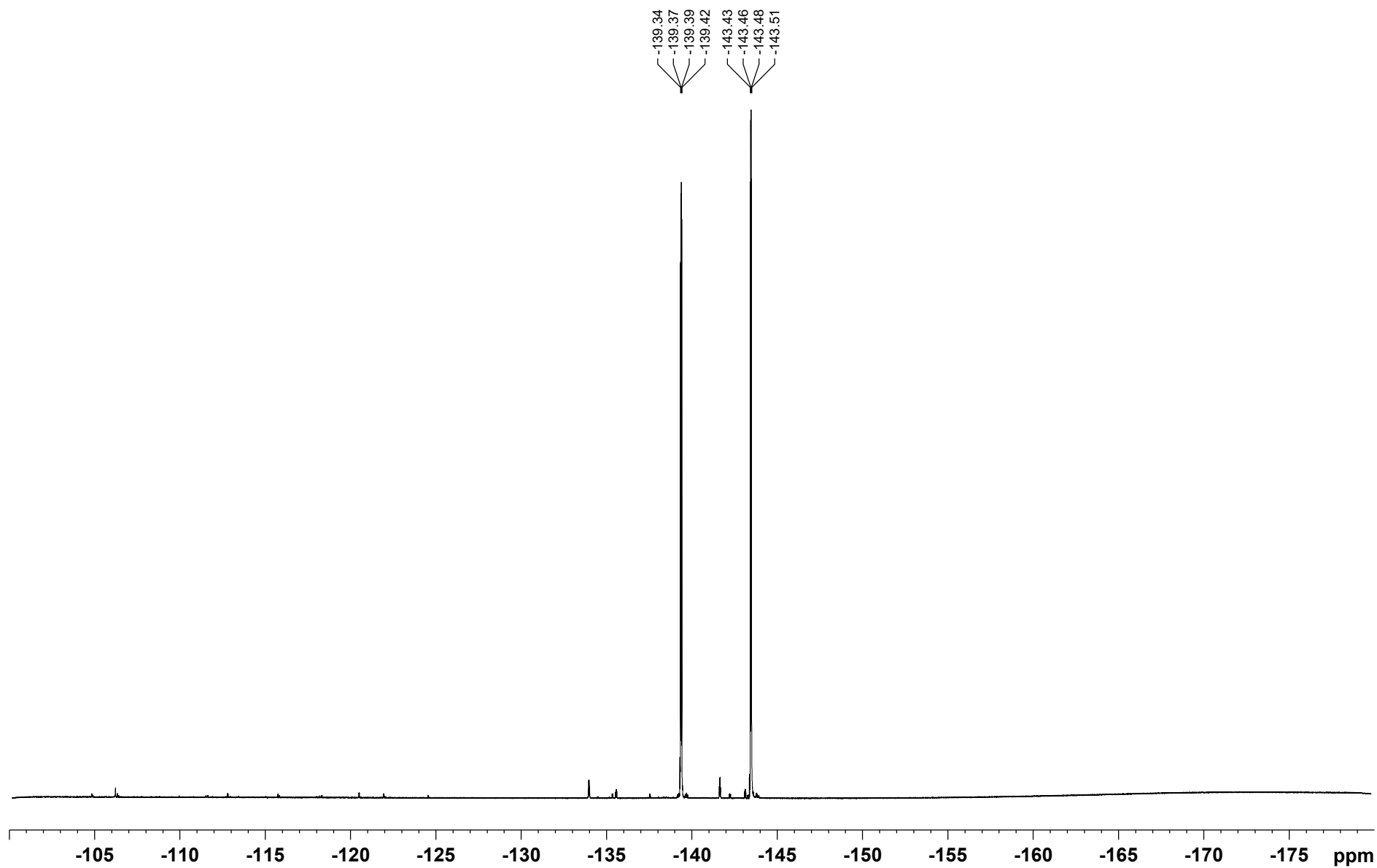


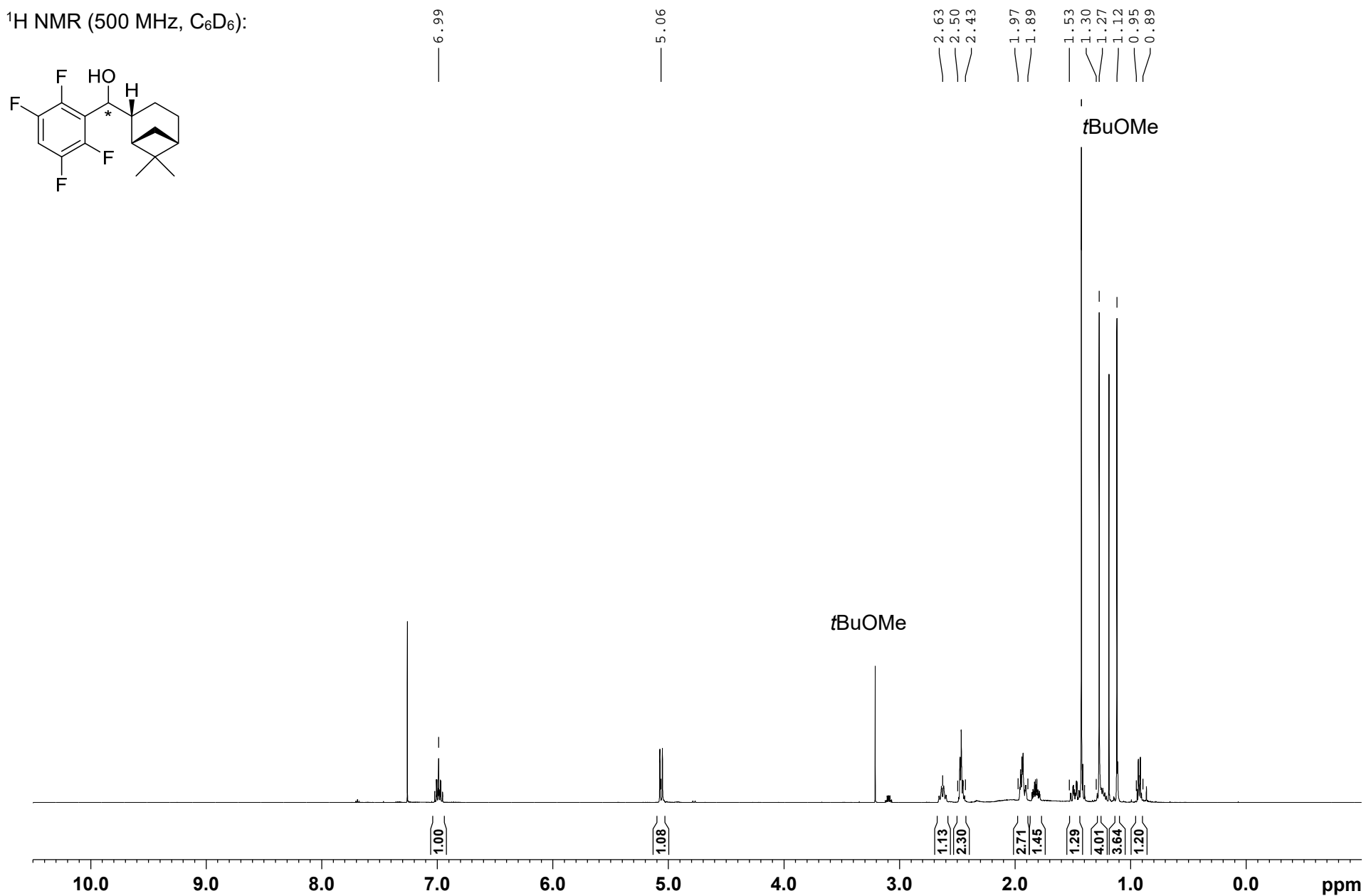
**((1*S*,2*R*,5*S*)-6,6-Dimethylbicyclo[3.1.1]heptan-2-yl)(2,3,5,6-tetrafluorophenyl)methanol (6, major diastereomer)**<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):

$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ ):

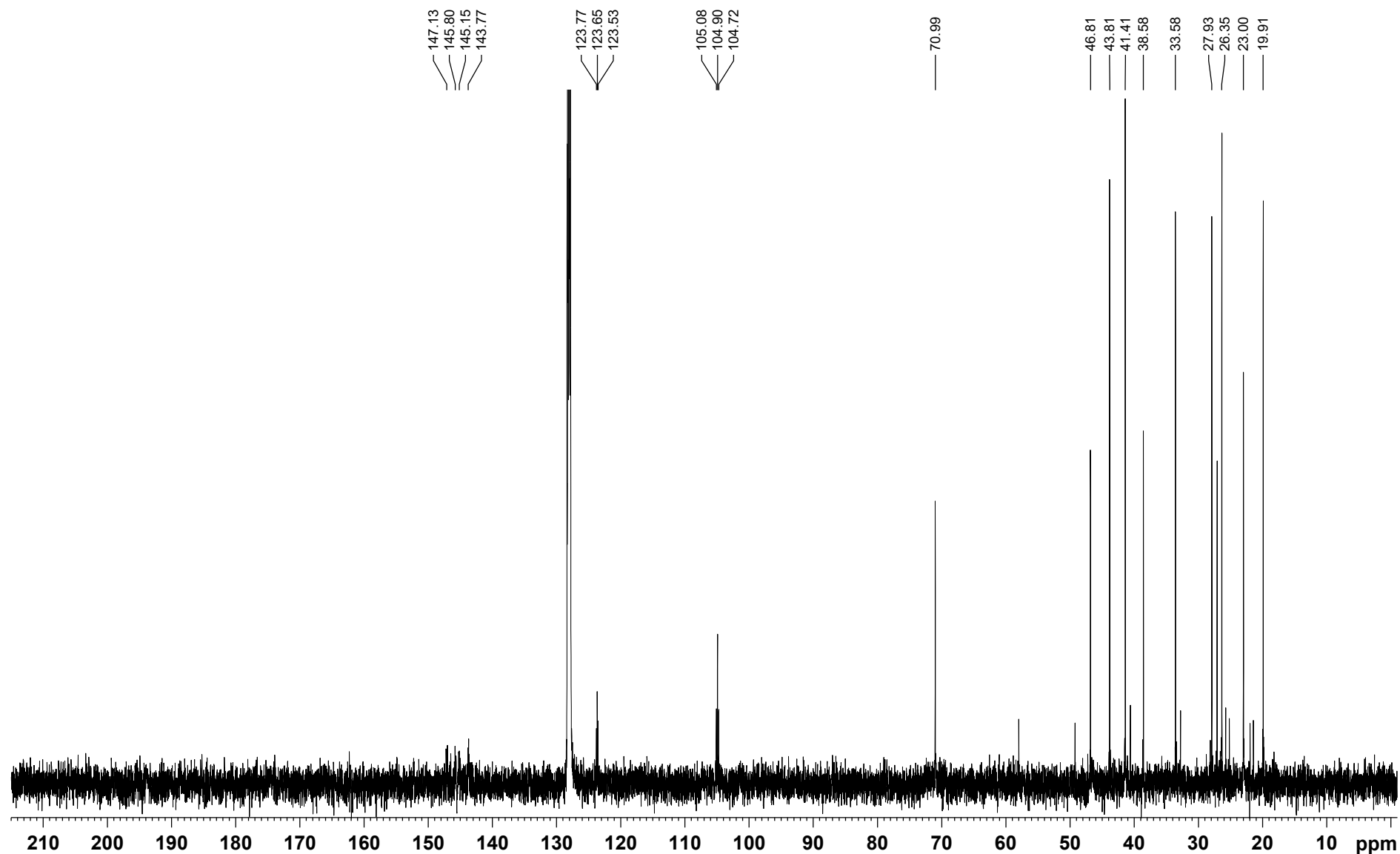


$^{19}\text{F}\{^1\text{H}\}$  NMR (471 MHz,  $\text{C}_6\text{D}_6$ ):

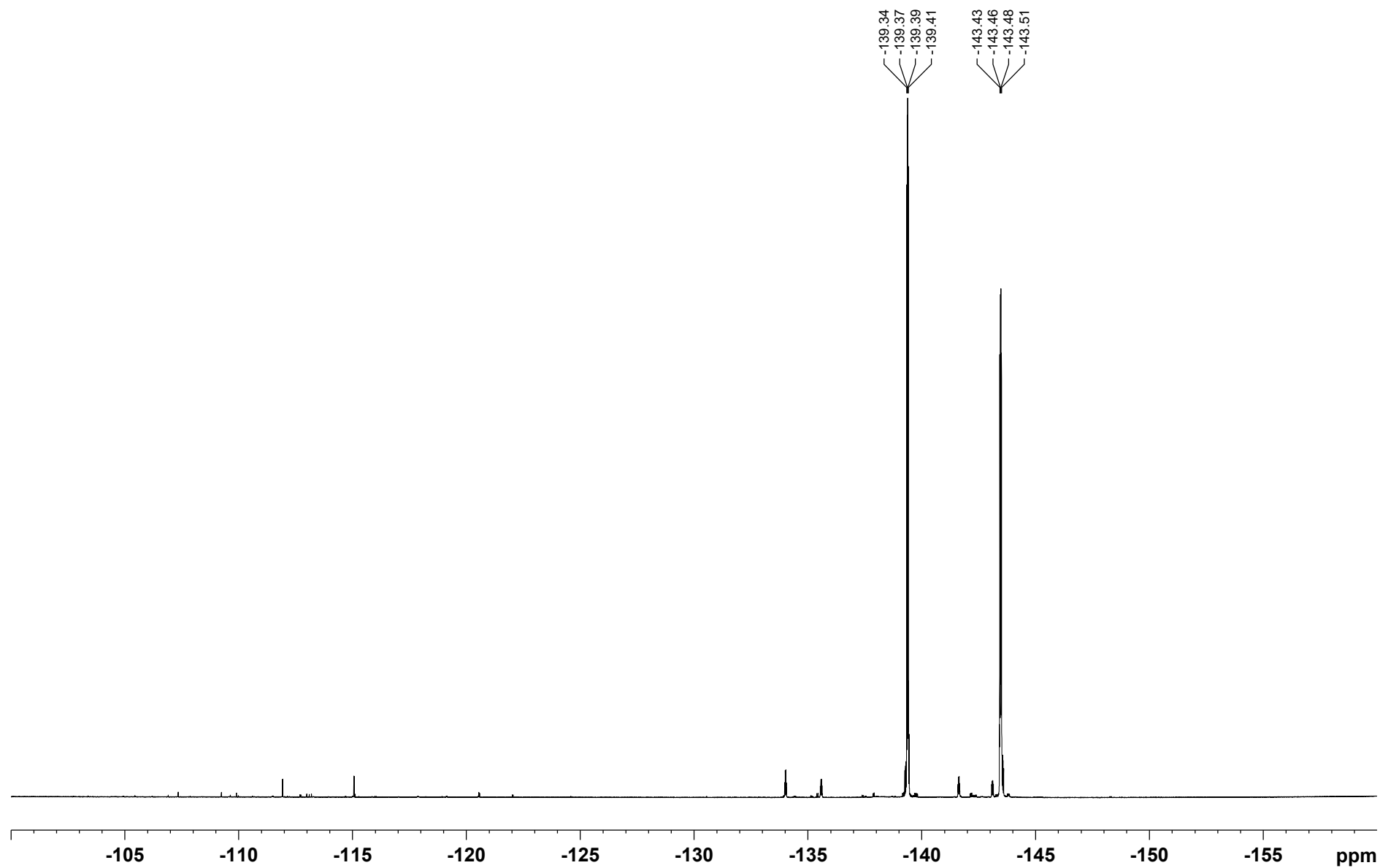


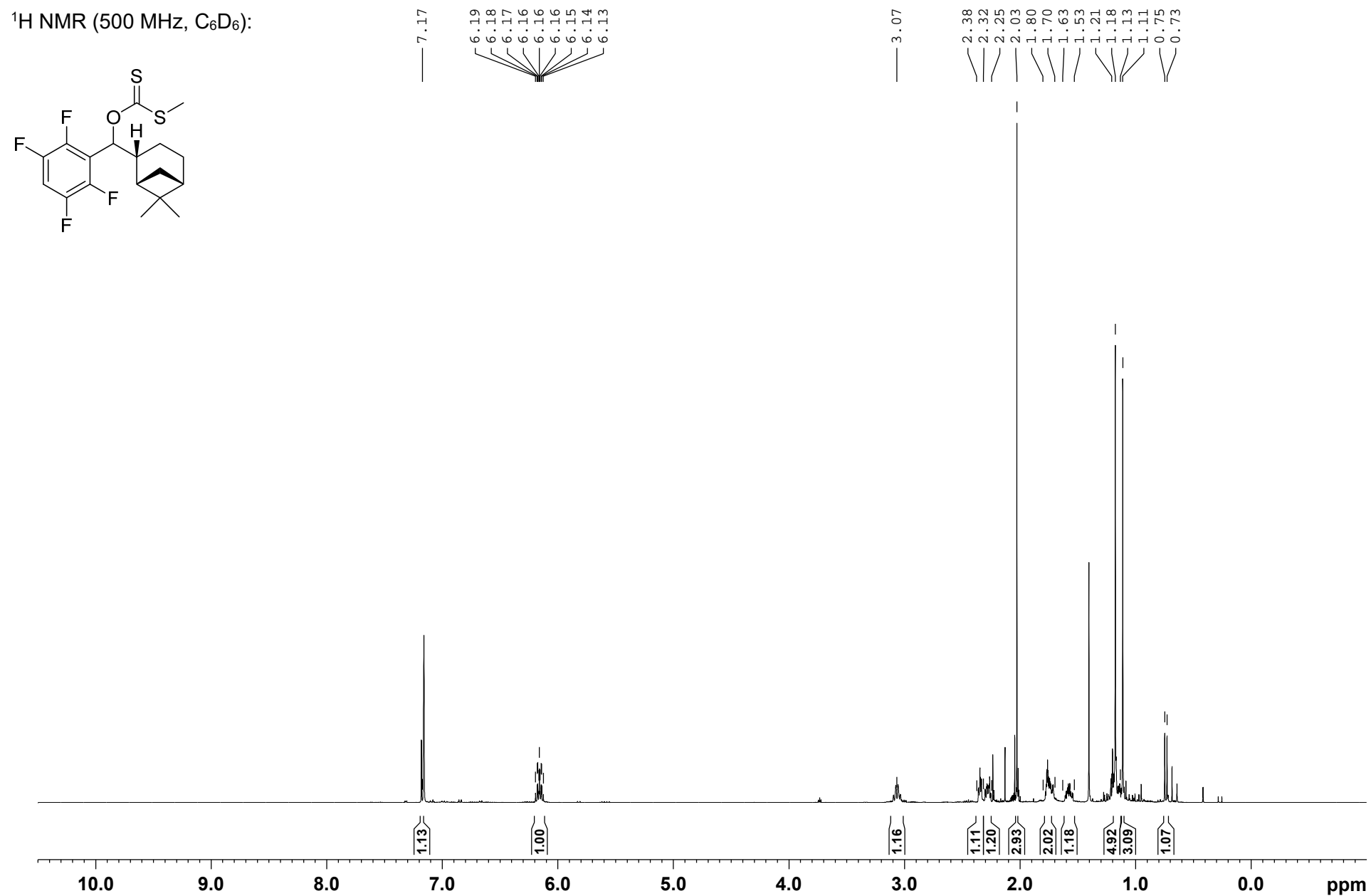
**((1*S*,2*R*,5*S*)-6,6-Dimethylbicyclo[3.1.1]heptan-2-yl)(2,3,5,6-tetrafluorophenyl)methanol (6, minor diastereomer)**<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):

$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ ):



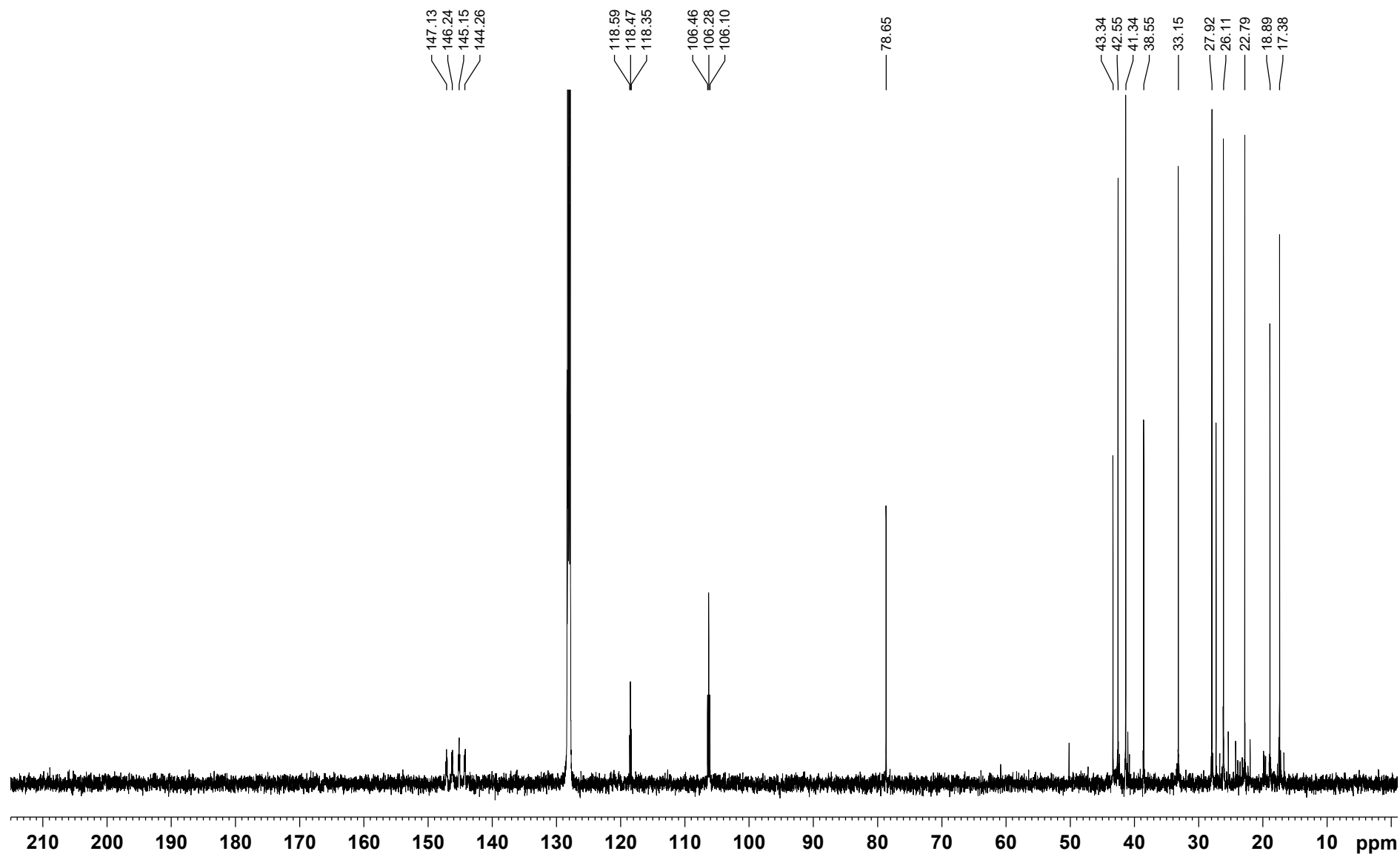
$^{19}\text{F}\{^1\text{H}\}$  NMR (471 MHz,  $\text{C}_6\text{D}_6$ ):



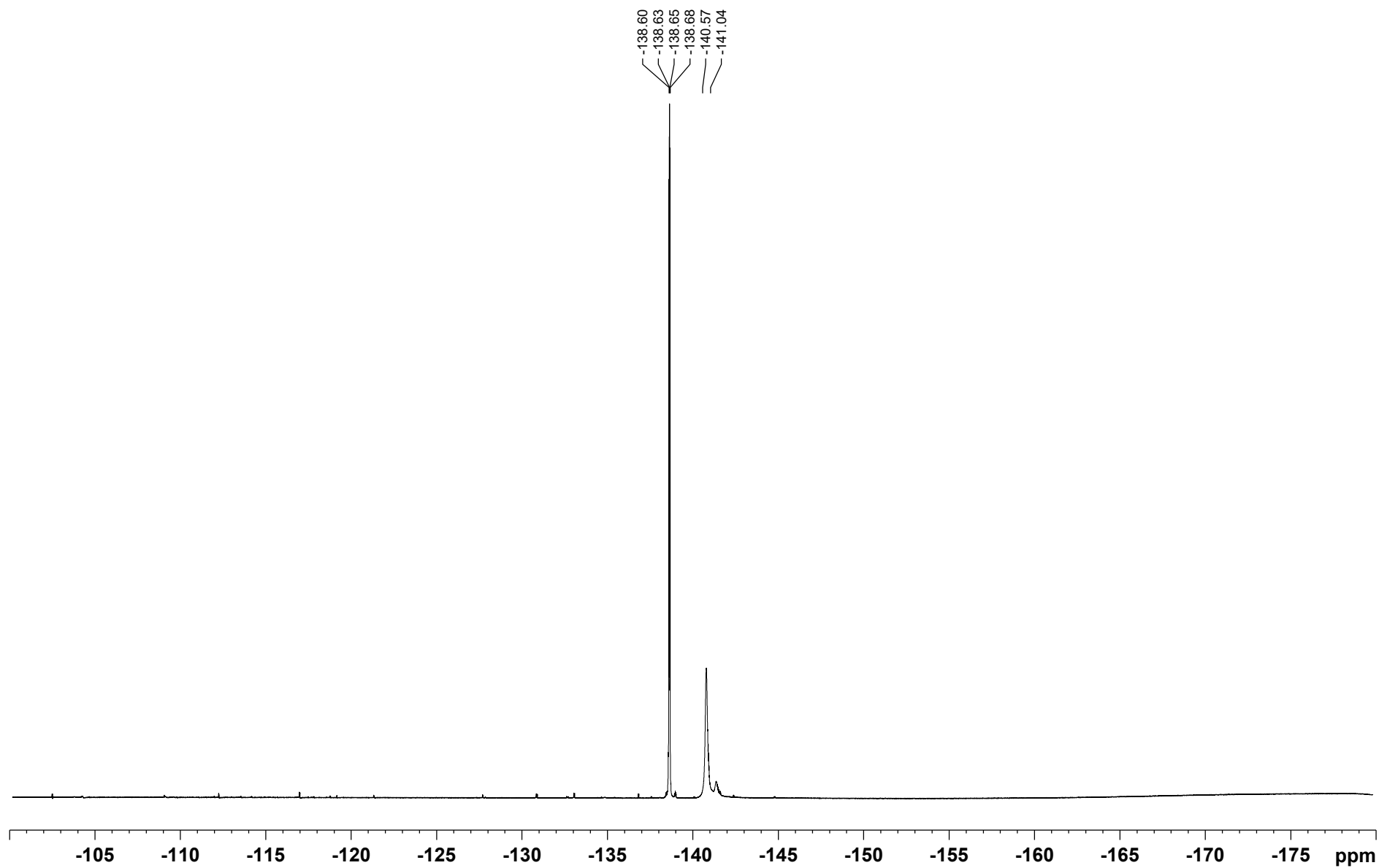
**O-(((1S,2R,5S)-6,6-Dimethylbicyclo[3.1.1]heptan-2-yl)(2,3,5,6-tetrafluorophenyl)-methyl) S-methyl carbonodithioate (7)**<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):

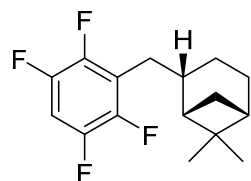


$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ ):



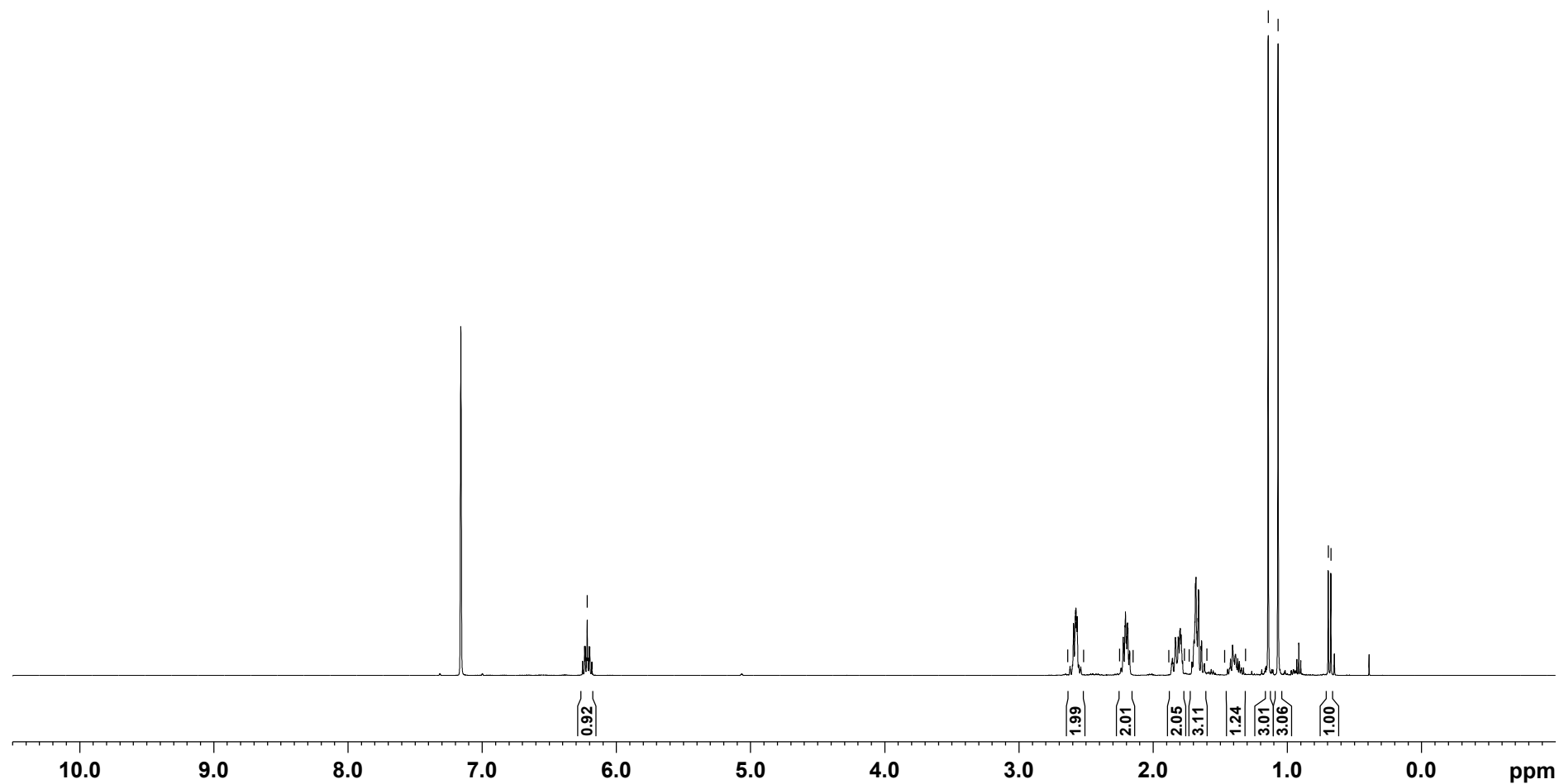
$^{19}\text{F}\{^1\text{H}\}$  NMR (471 MHz,  $\text{C}_6\text{D}_6$ ):



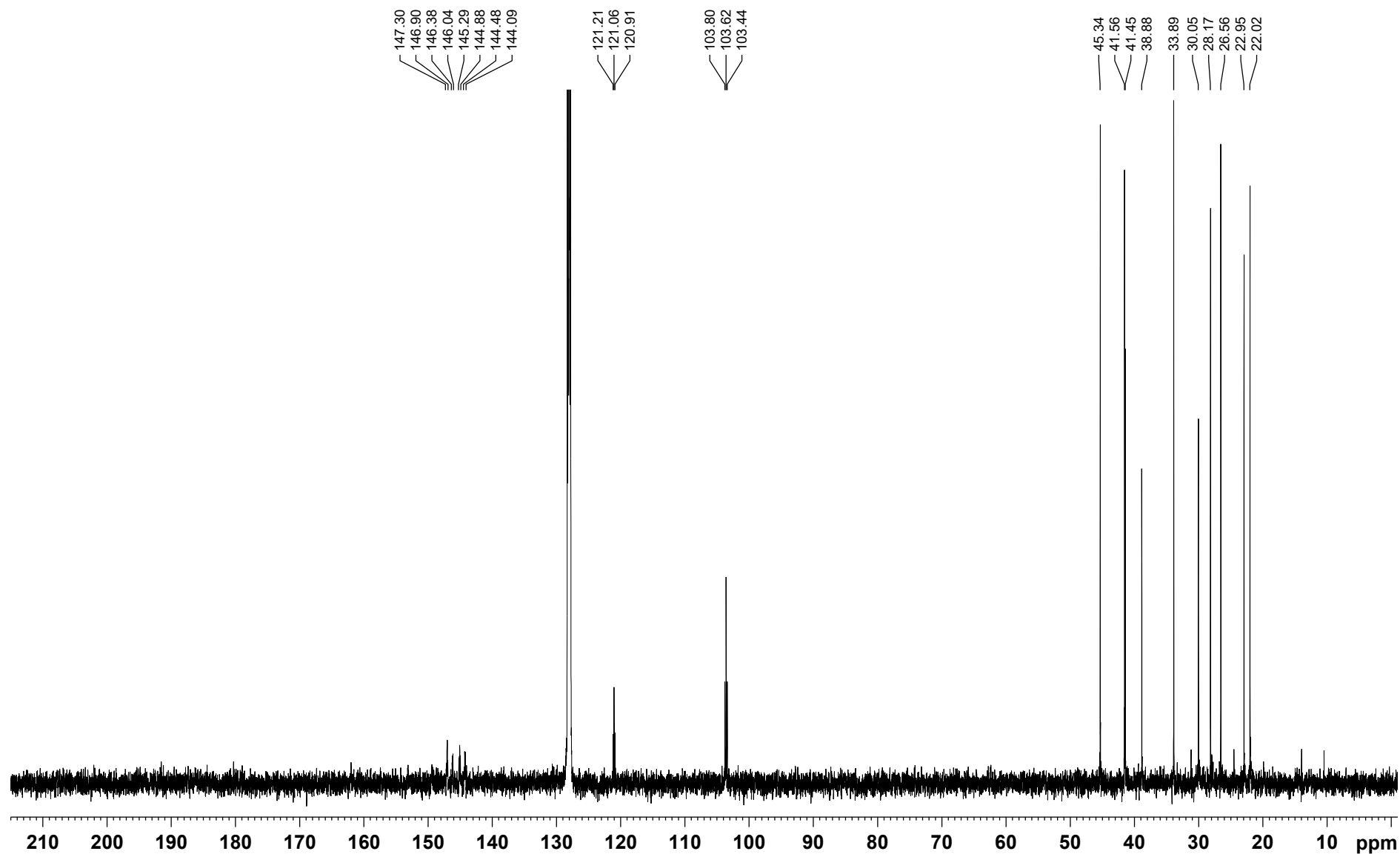
**(1S,2S,5S)-6,6-Dimethyl-2-(2,3,5,6-tetrafluorobenzyl)bicyclo[3.1.1]heptane (8)**<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):

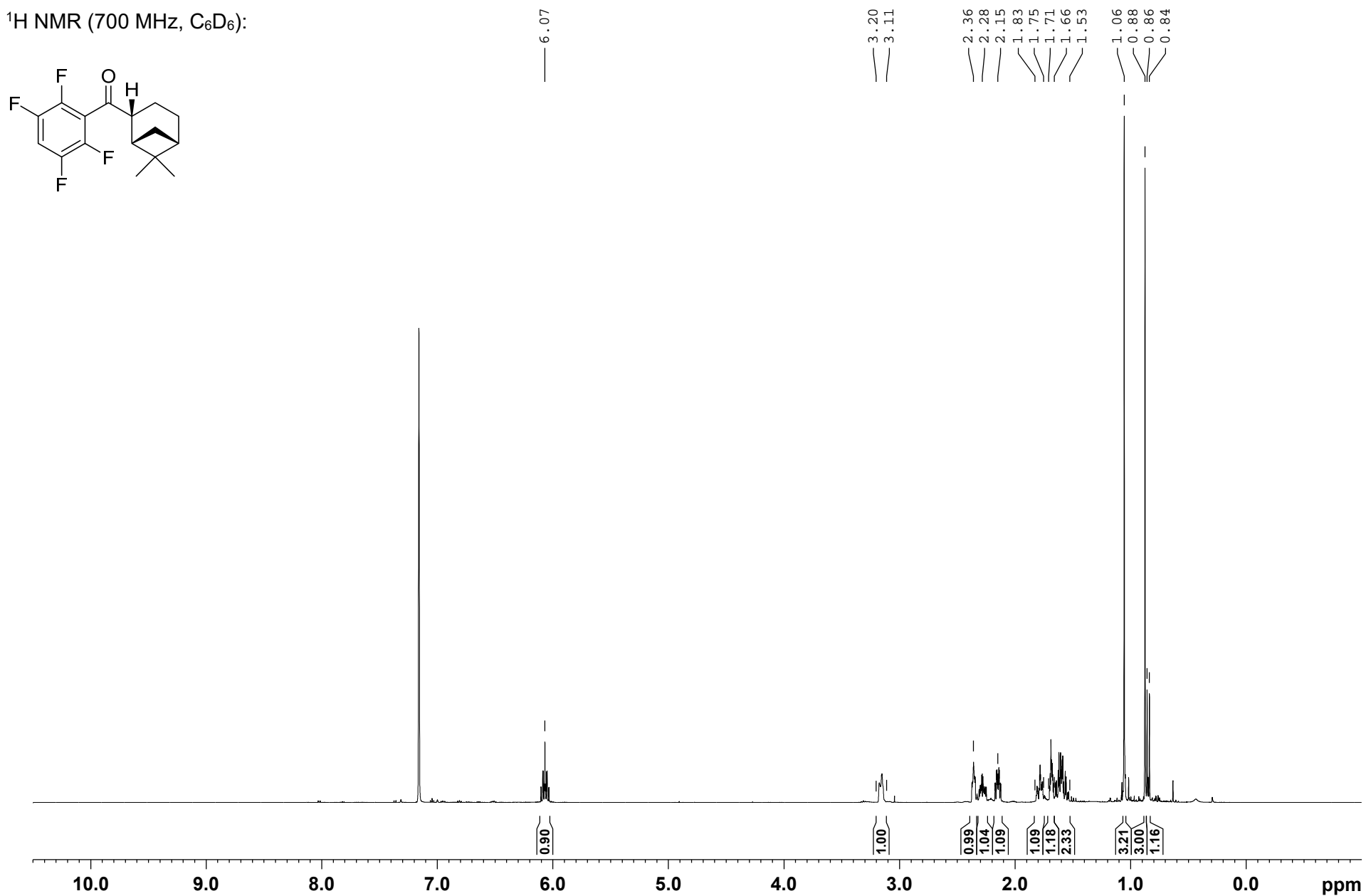
— 6.22

2.64  
2.52  
2.25  
2.15  
1.88  
1.77  
1.73  
1.60  
1.47  
1.31  
1.14  
1.07  
0.70  
0.68

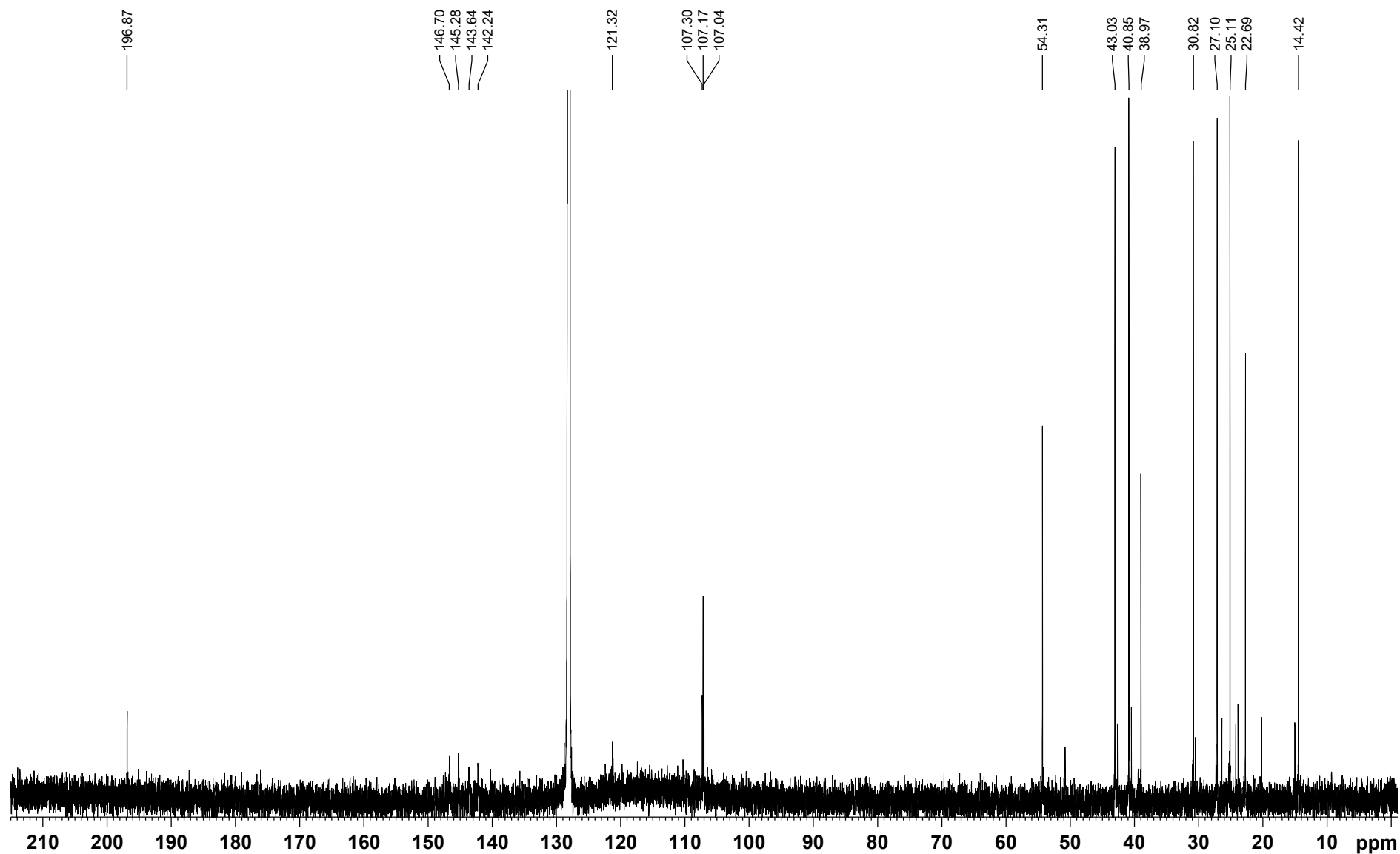


$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ ):

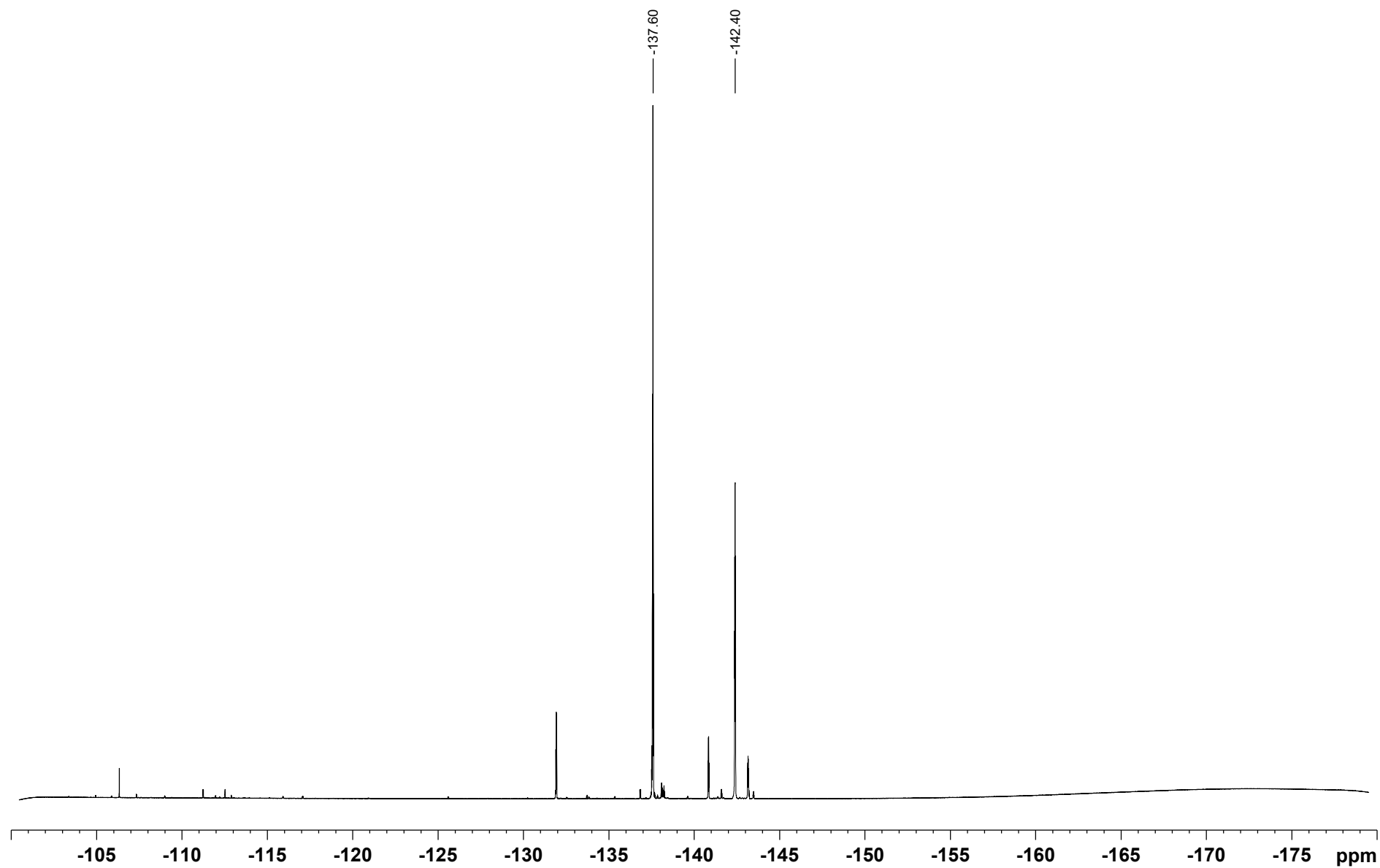


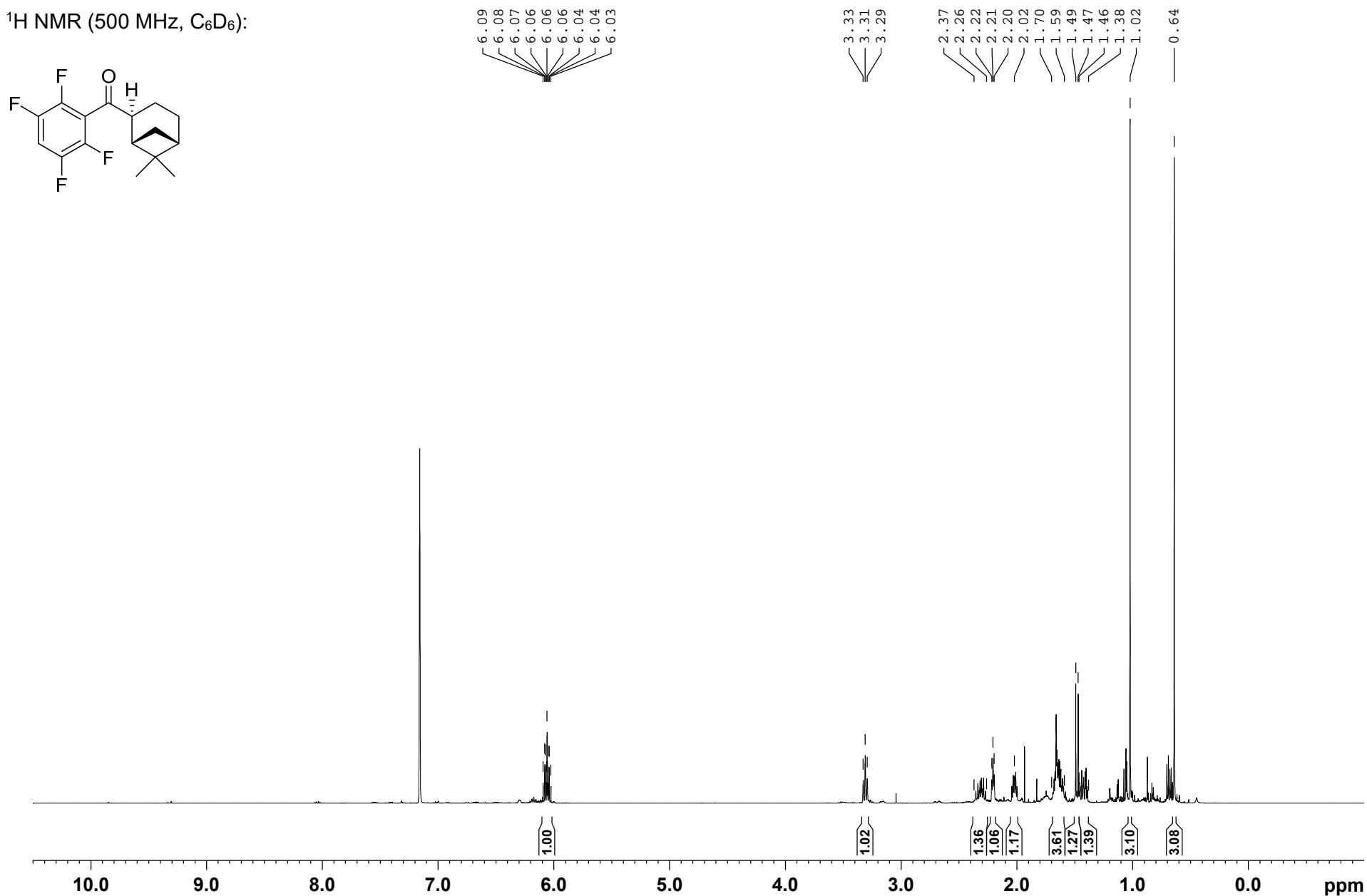
**((1S,2R,5S)-6,6-Dimethylbicyclo[3.1.1]heptan-2-yl)(2,3,5,6-tetrafluorophenyl)methanone (9, major diastereomer)**<sup>1</sup>H NMR (700 MHz, C<sub>6</sub>D<sub>6</sub>):

$^{13}\text{C}\{^1\text{H}\}$  NMR (176 MHz,  $\text{C}_6\text{D}_6$ ):



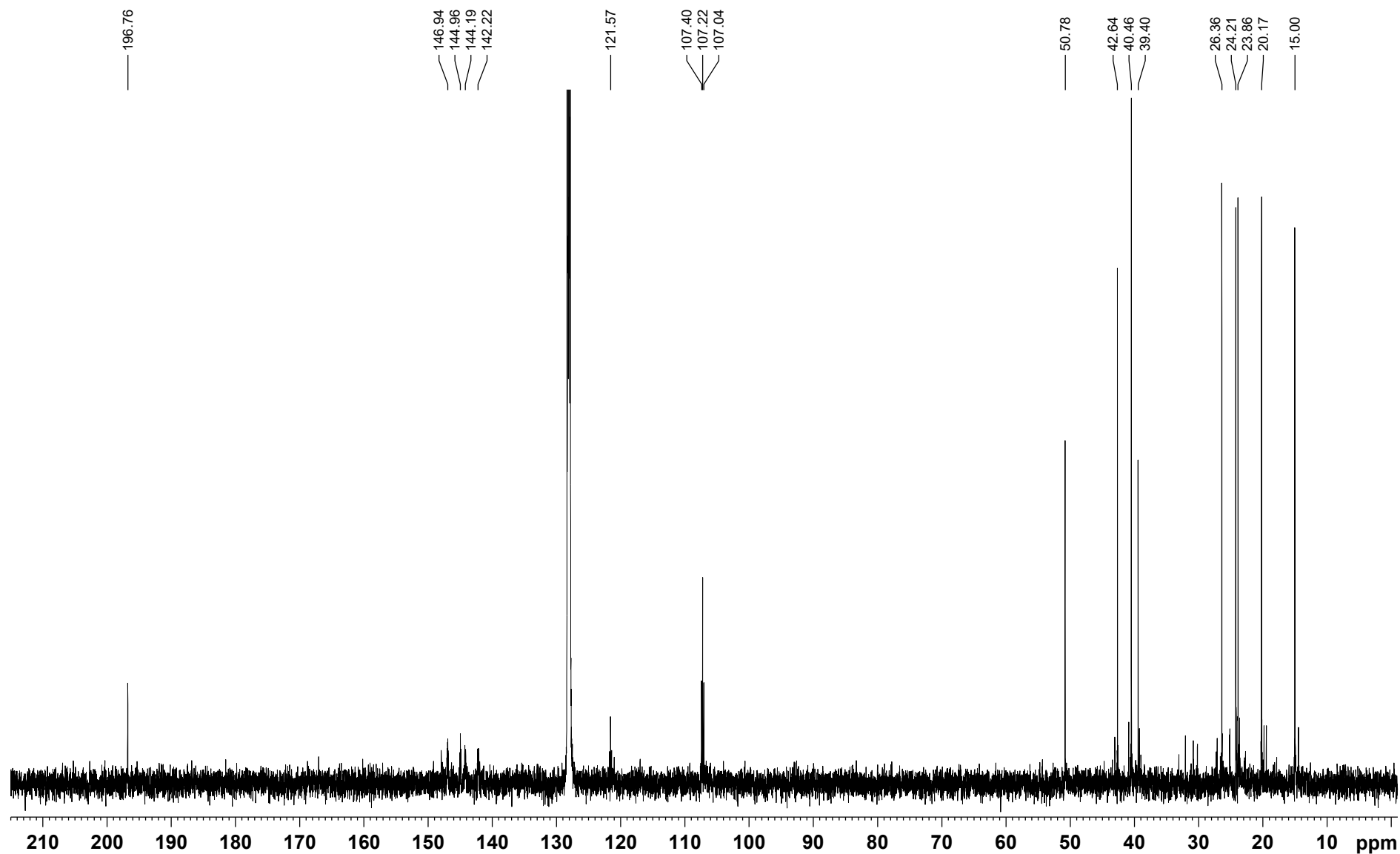
$^{19}\text{F}\{^1\text{H}\}$  NMR (659 MHz,  $\text{C}_6\text{D}_6$ ):

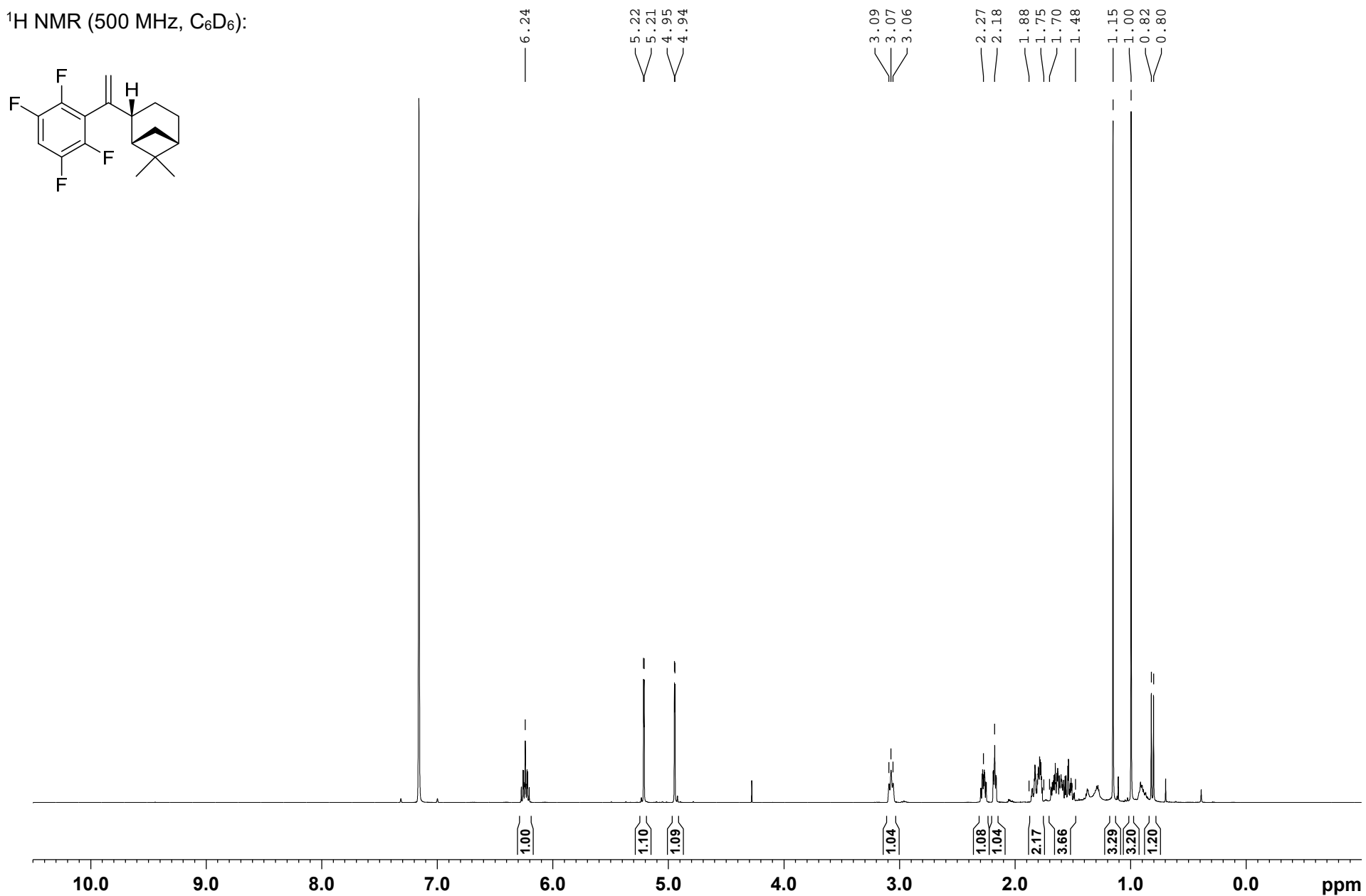


**((1S,2S,5S)-6,6-Dimethylbicyclo[3.1.1]heptan-2-yl)(2,3,5,6-tetrafluorophenyl)methanone (9, minor diastereomer)**<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):

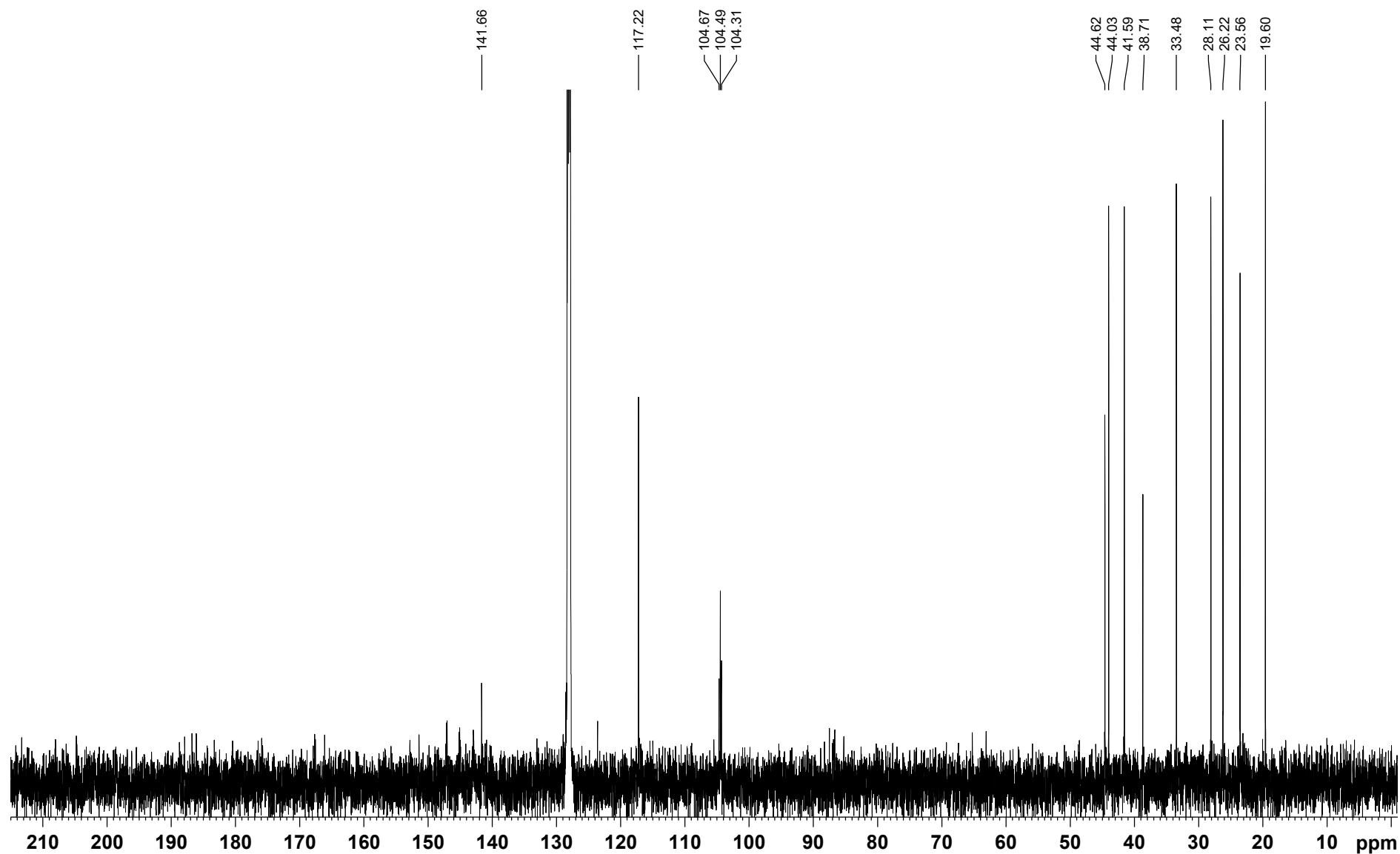


$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ ):

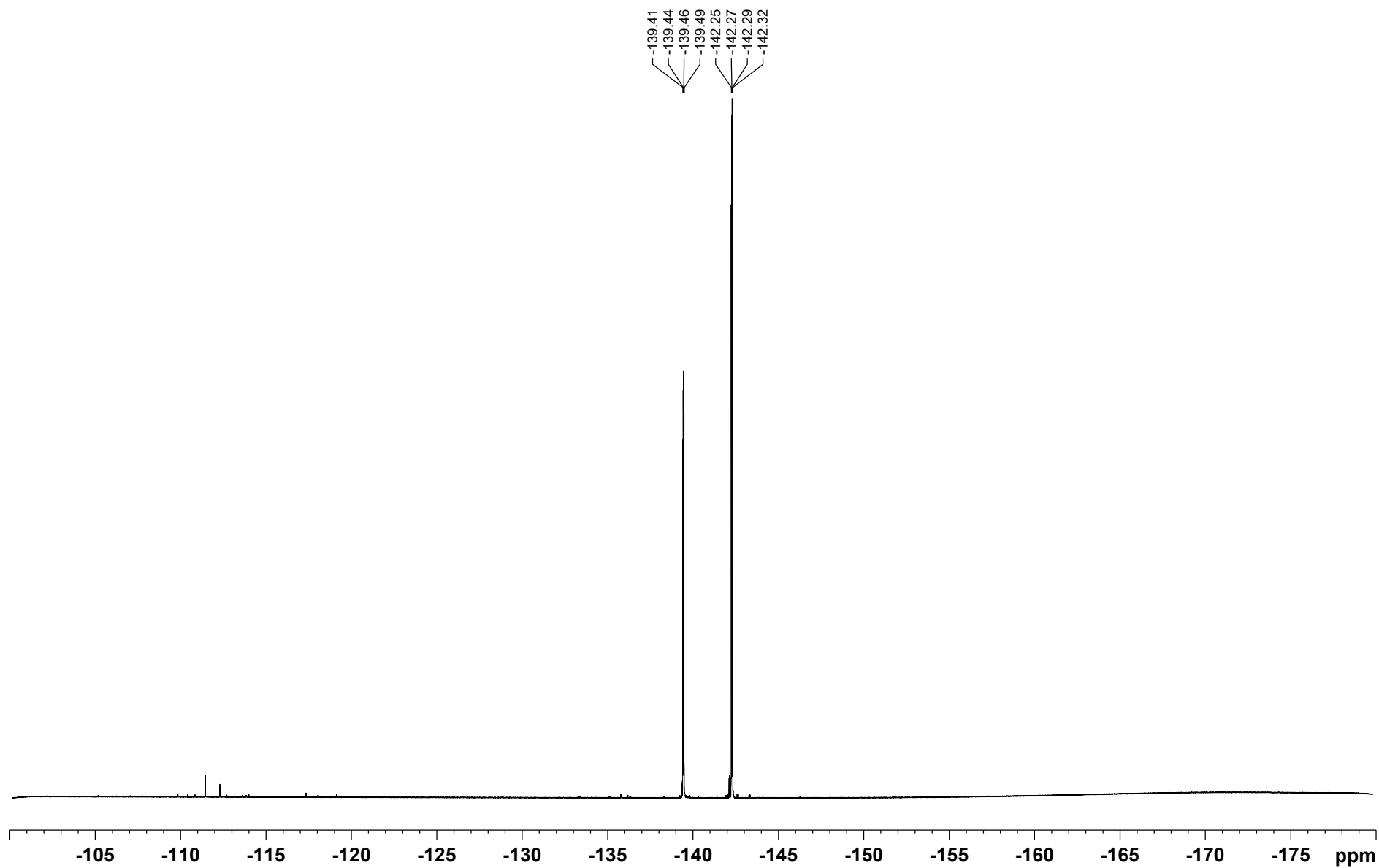


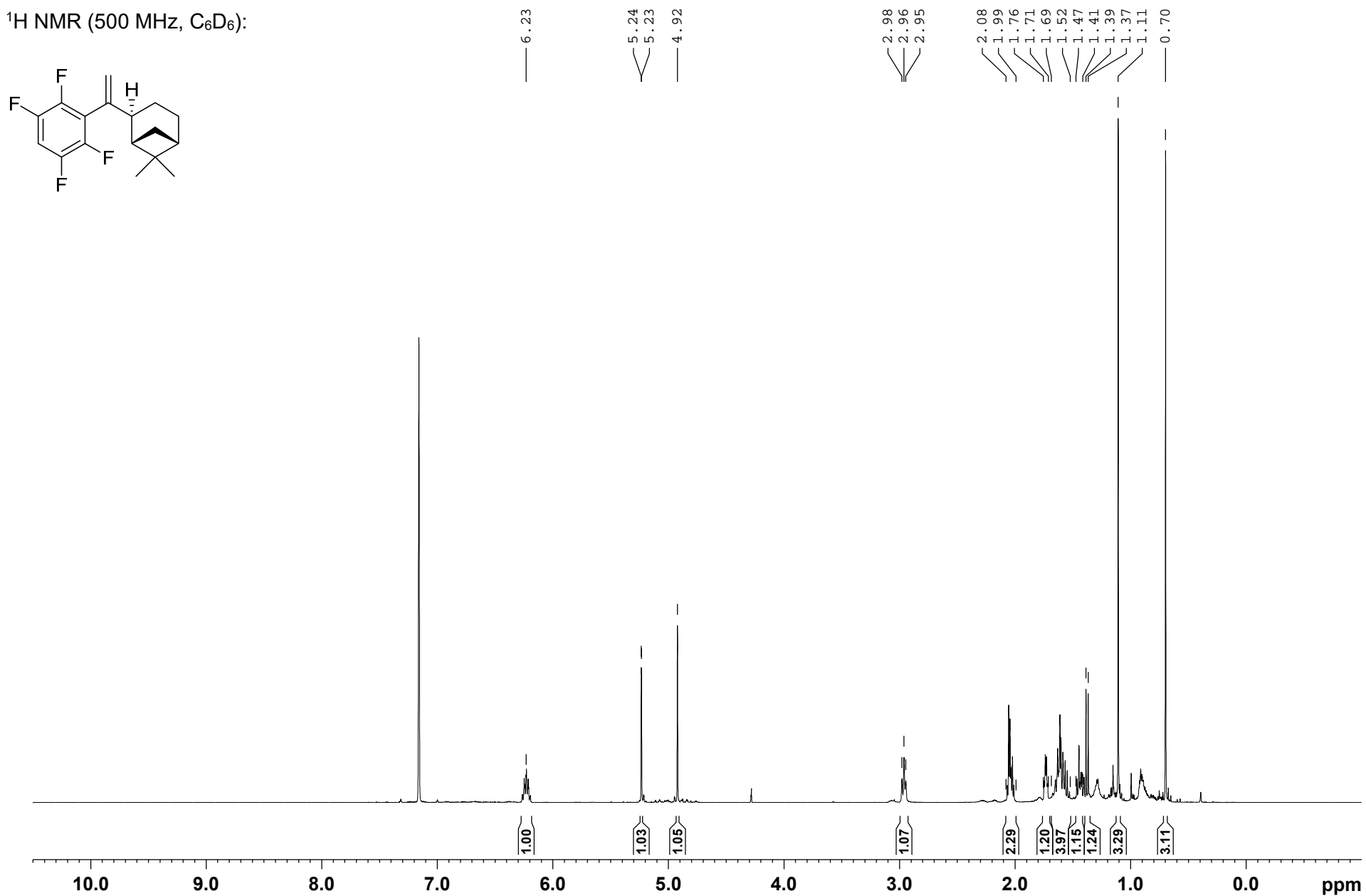
**(1*S*,2*R*,5*S*)-6,6-Dimethyl-2-(1-(2,3,5,6-tetrafluorophenyl)vinyl)bicyclo[3.1.1]heptane (10, major diastereomer)**<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):

$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ ):

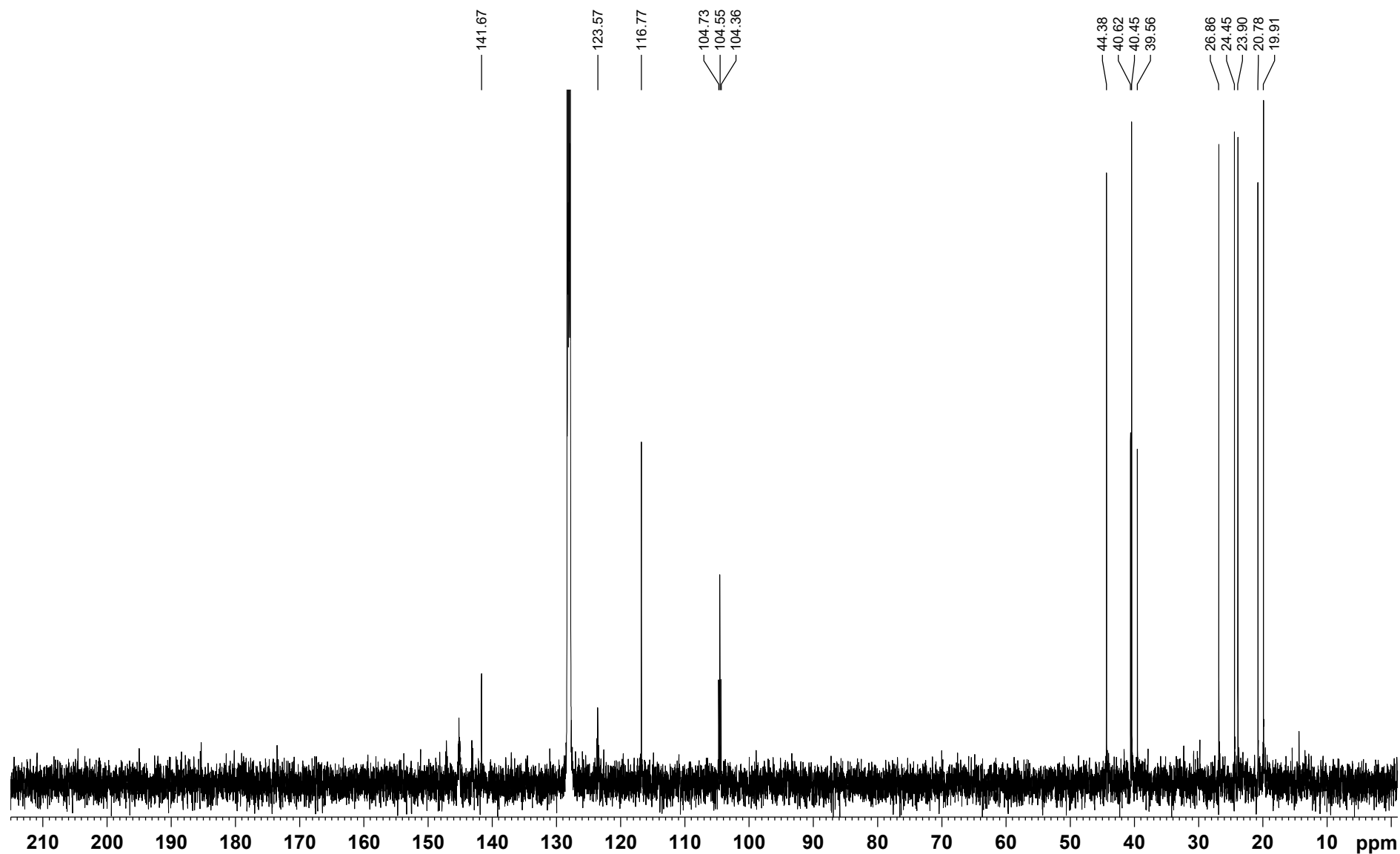


$^{19}\text{F}\{^1\text{H}\}$  NMR (659 MHz,  $\text{C}_6\text{D}_6$ ):

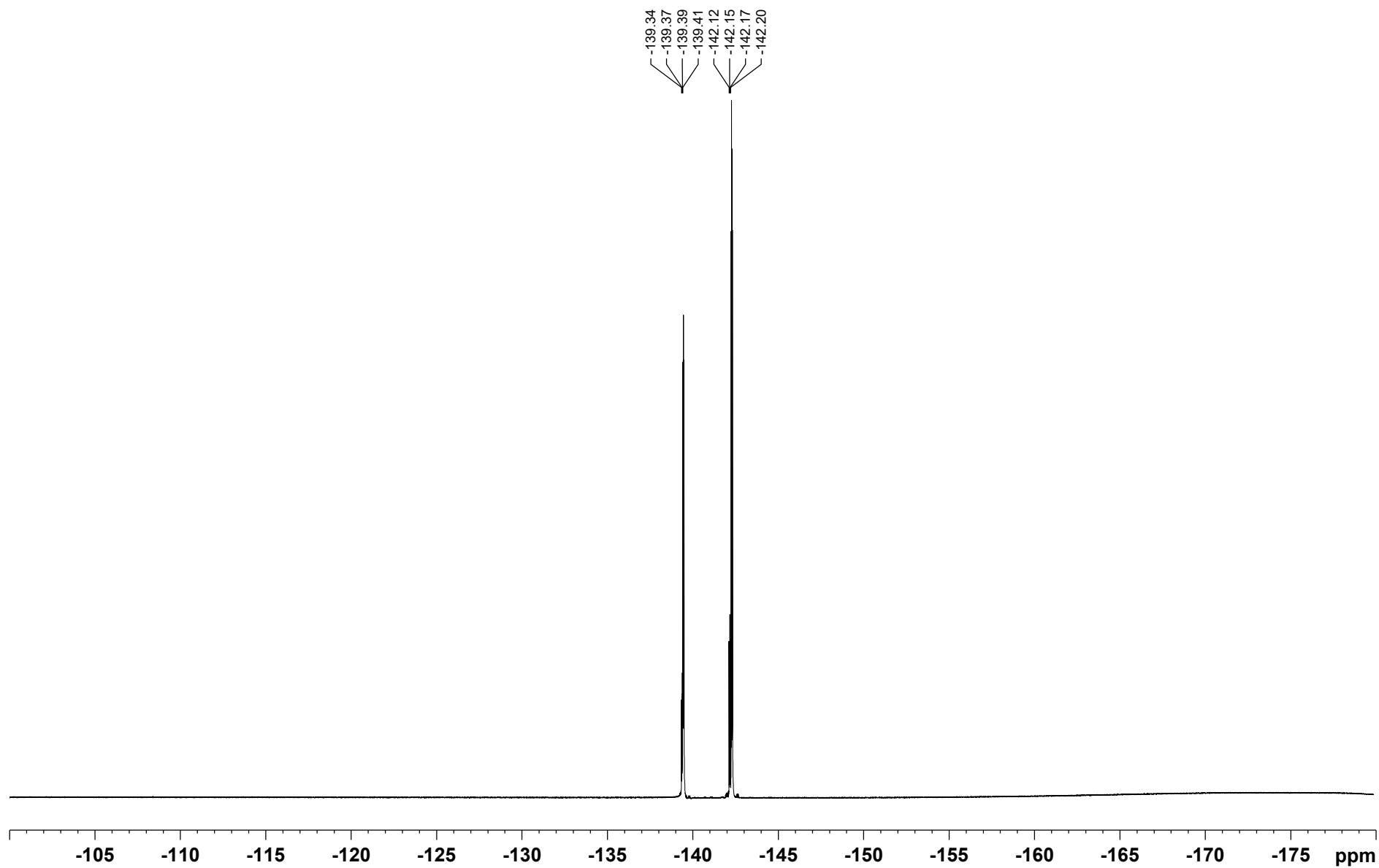


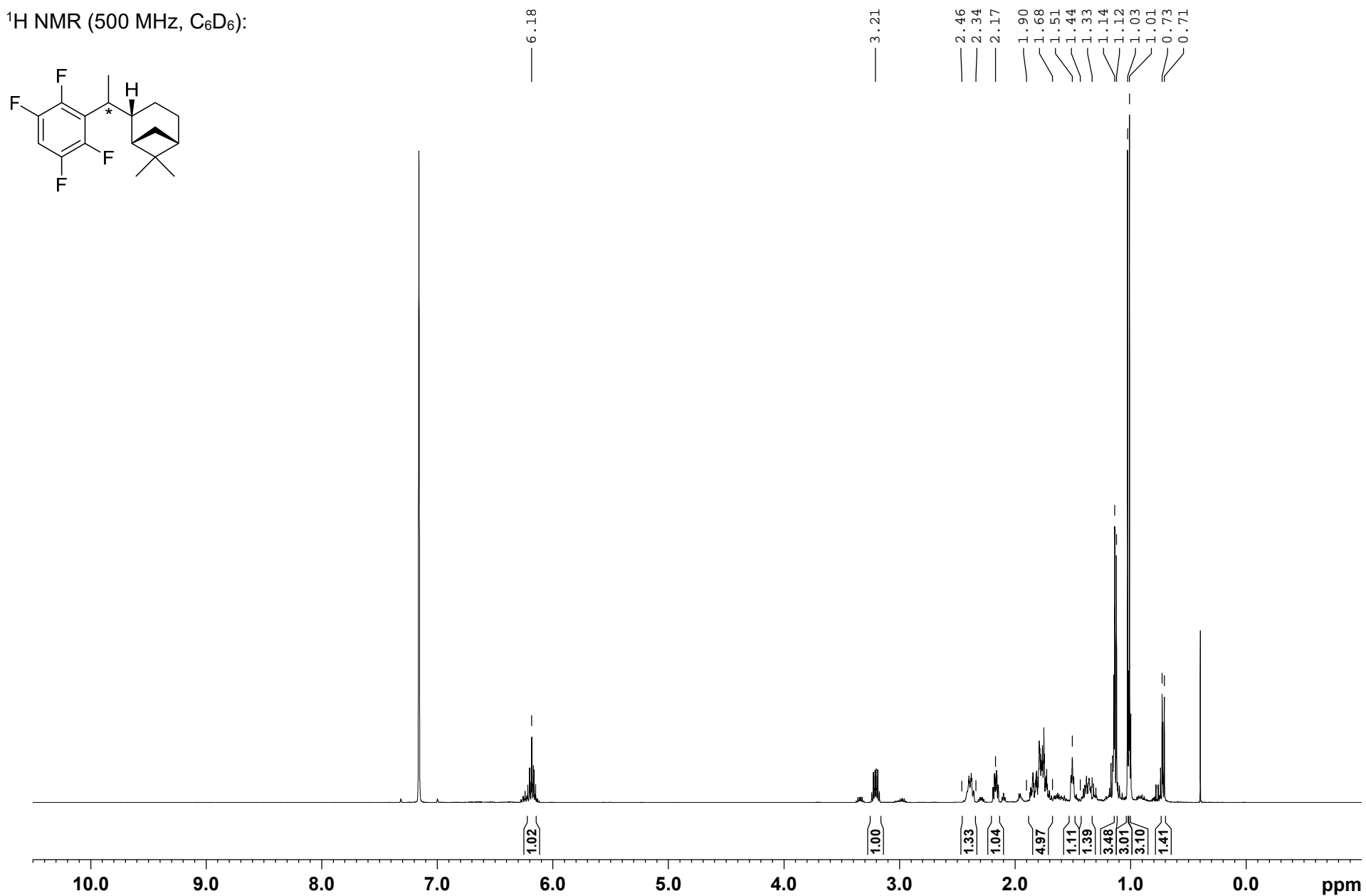
**(1S,2S,5S)-6,6-Dimethyl-2-(1-(2,3,5,6-tetrafluorophenyl)vinyl)bicyclo[3.1.1]heptane (10, minor diastereomer)**<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):

$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ ):



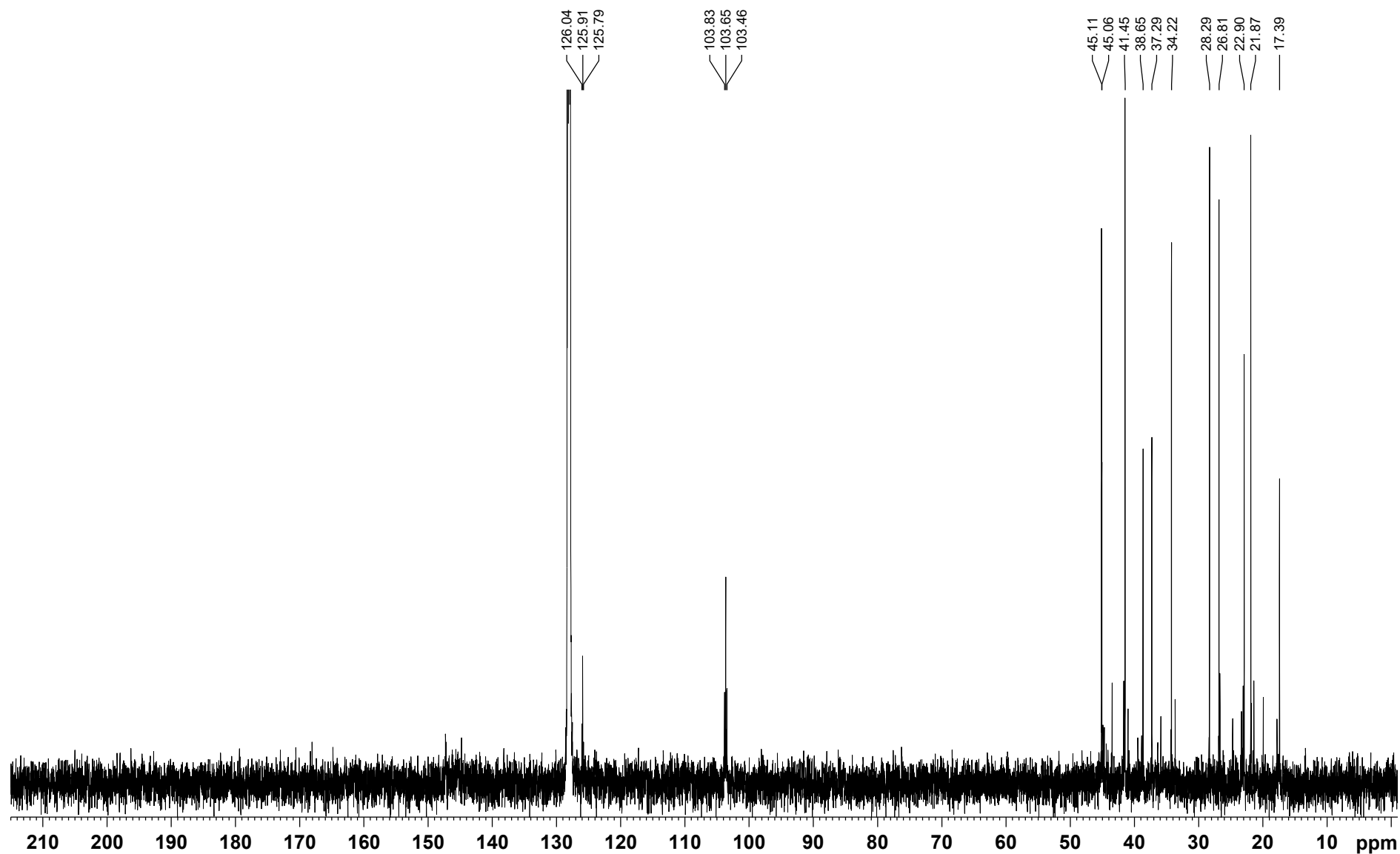
$^{19}\text{F}\{^1\text{H}\}$  NMR (659 MHz,  $\text{C}_6\text{D}_6$ ):



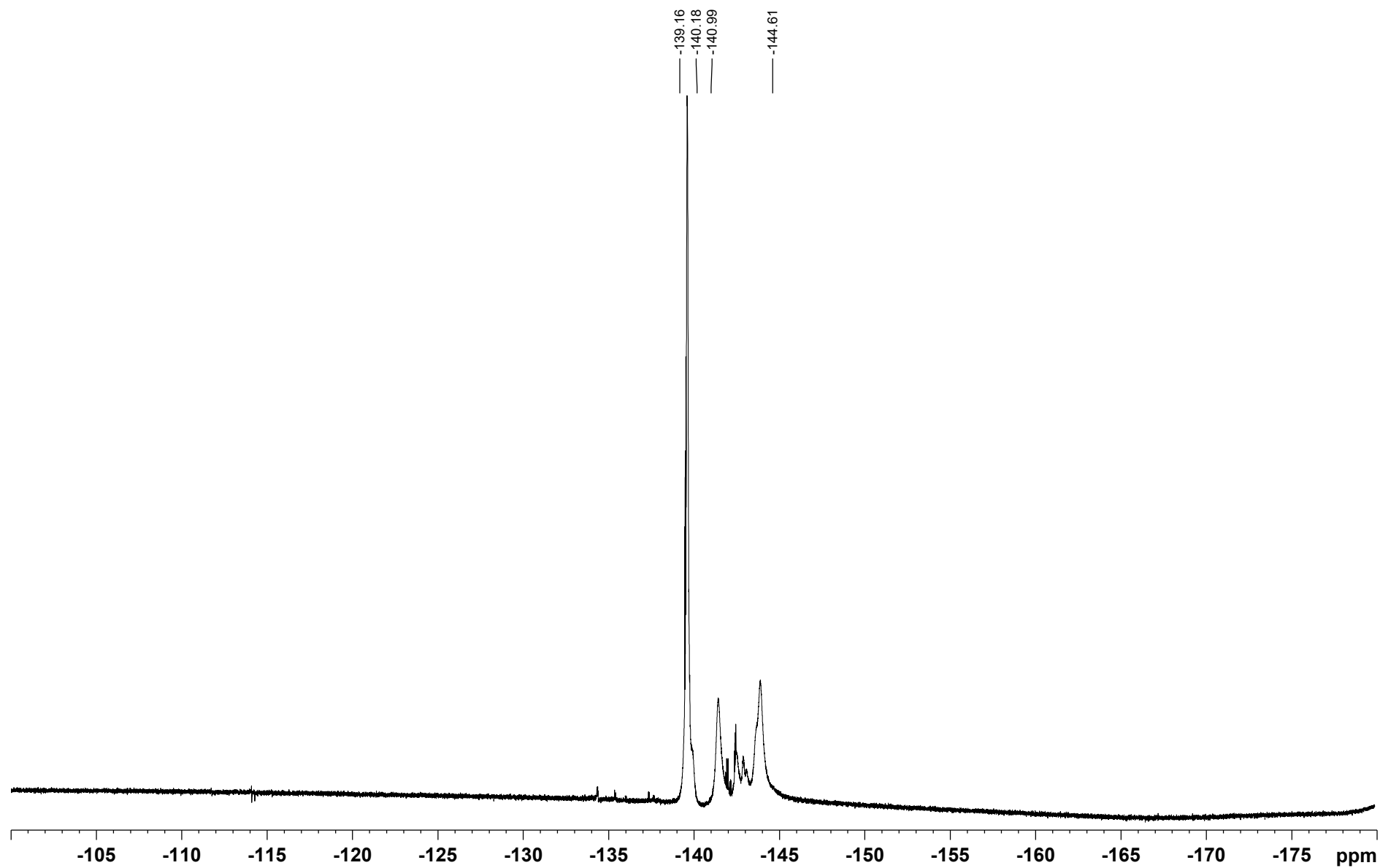
**(1S,2S,5S)-6,6-Dimethyl-2-(1-(2,3,5,6-tetrafluorophenyl)ethyl)bicyclo[3.1.1]heptane (11)**<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):

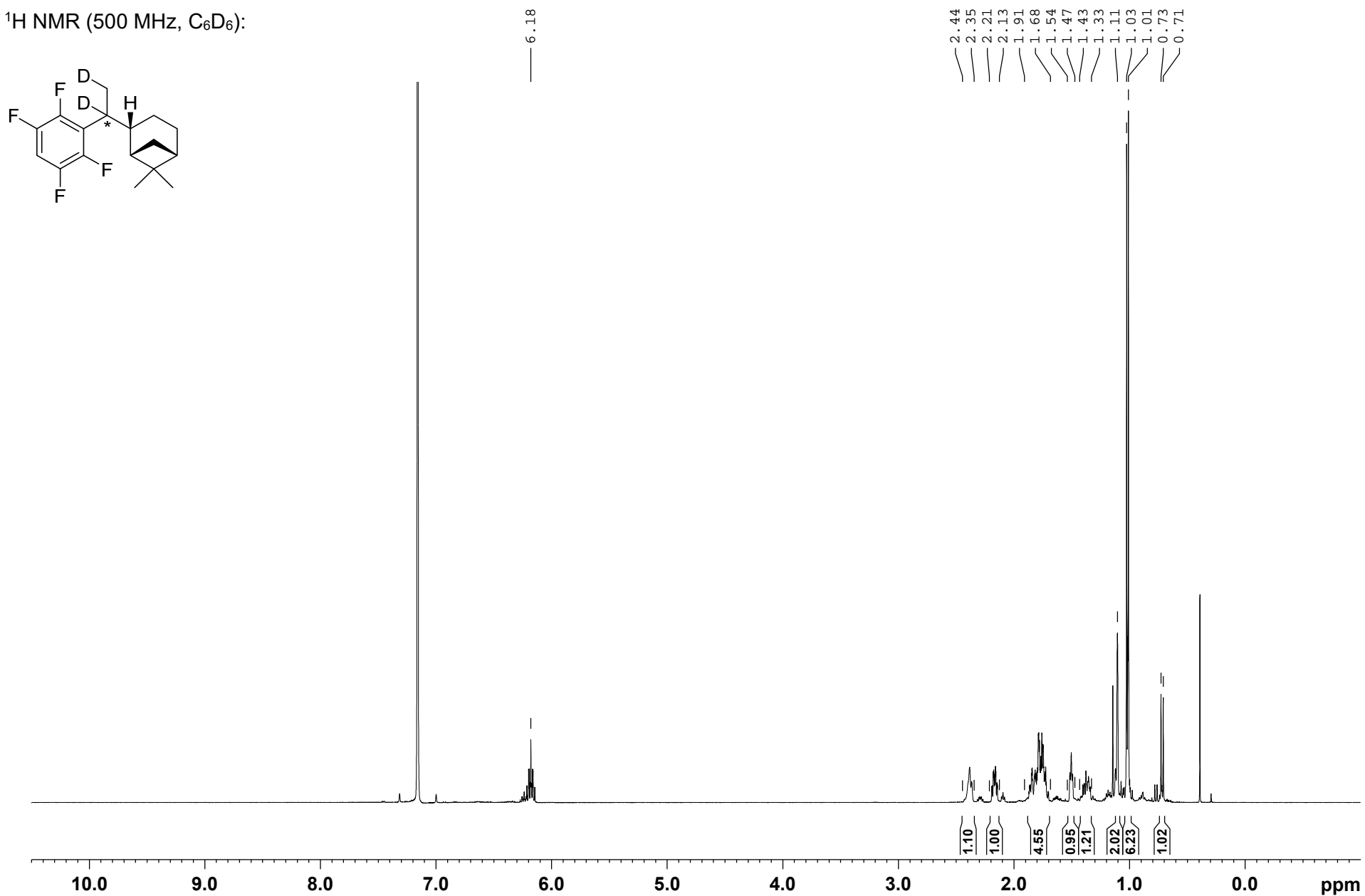


$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ ):

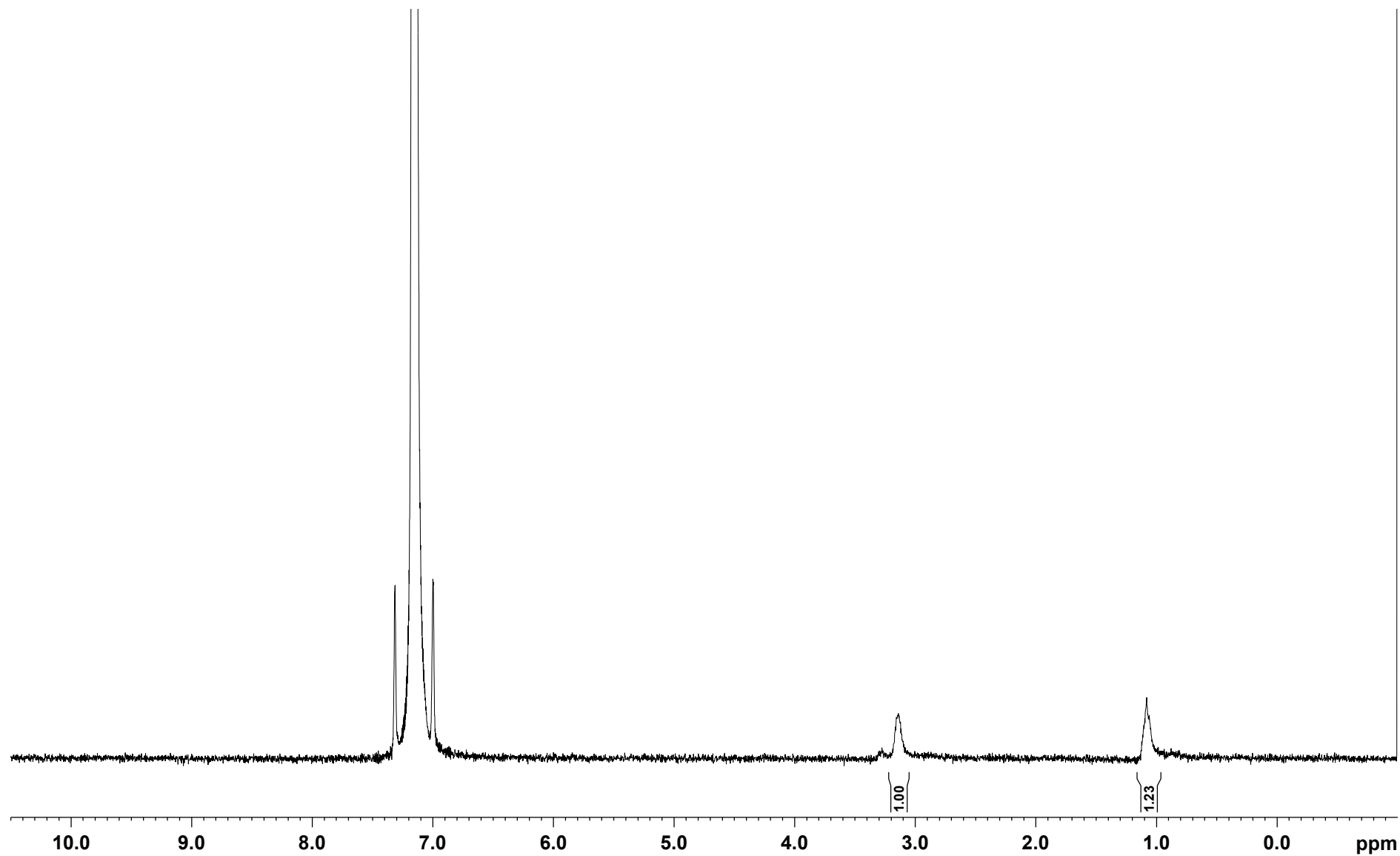


$^{19}\text{F}\{^1\text{H}\}$  NMR (471 MHz,  $\text{C}_6\text{D}_6$ ):

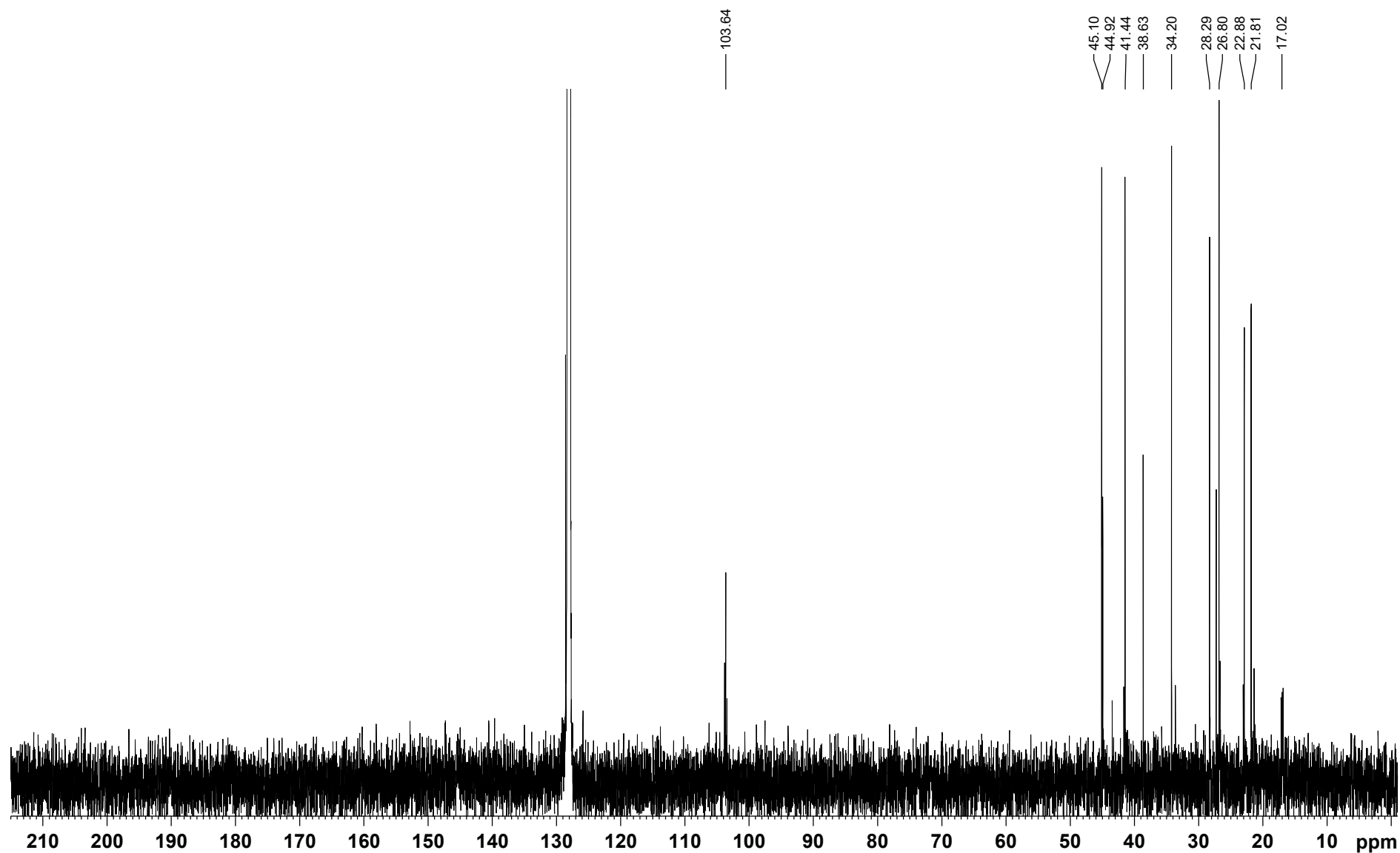


**(1S,2S,5S)-6,6-Dimethyl-2-(1-(2,3,5,6-tetrafluorophenyl)ethyl-1,2-*d*<sub>2</sub>)bicyclo-[3.1.1]heptane (11-*d*<sub>2</sub>)**<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):

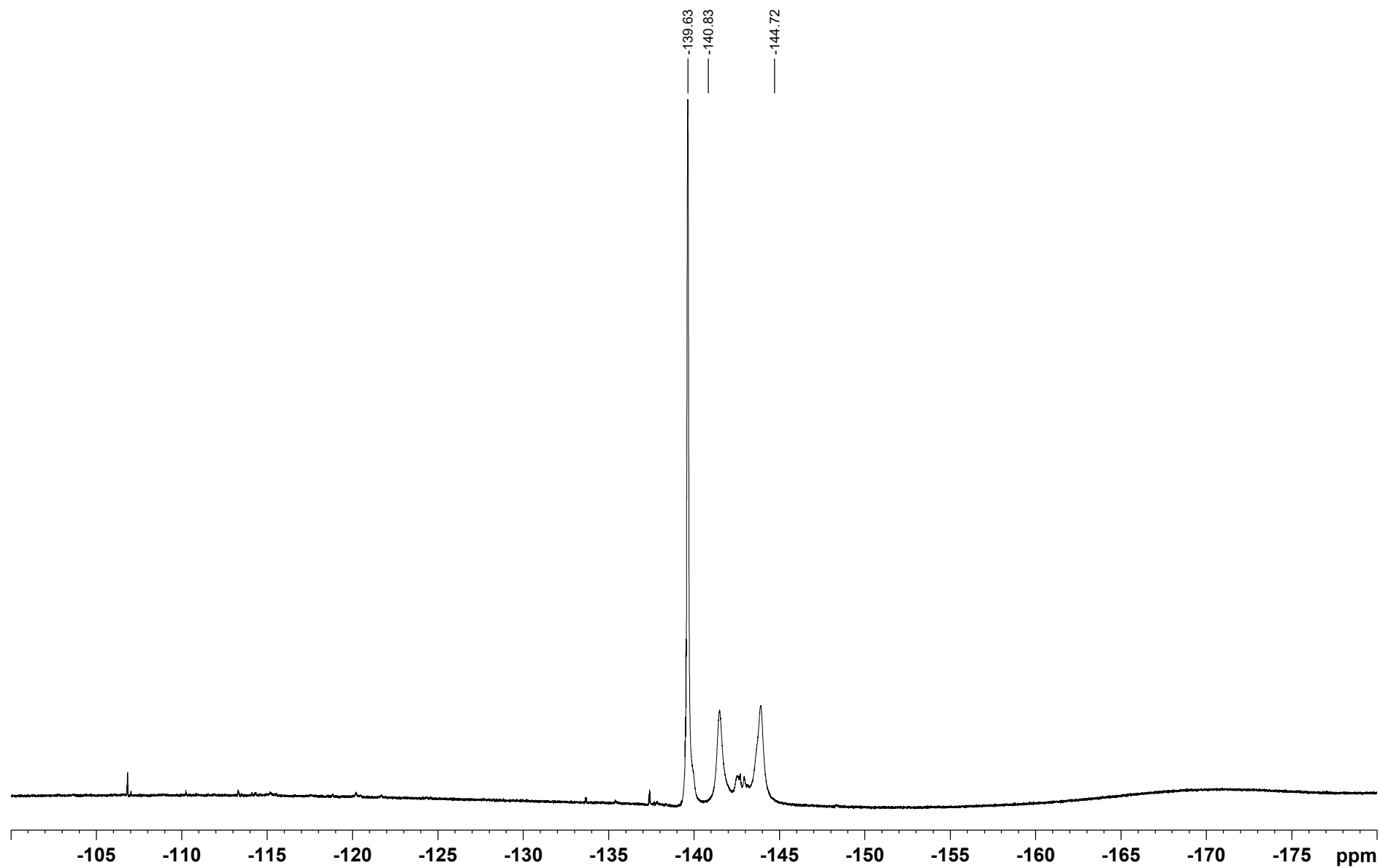
$^2\text{H}$  NMR (77 MHz,  $\text{C}_6\text{D}_6$ ):

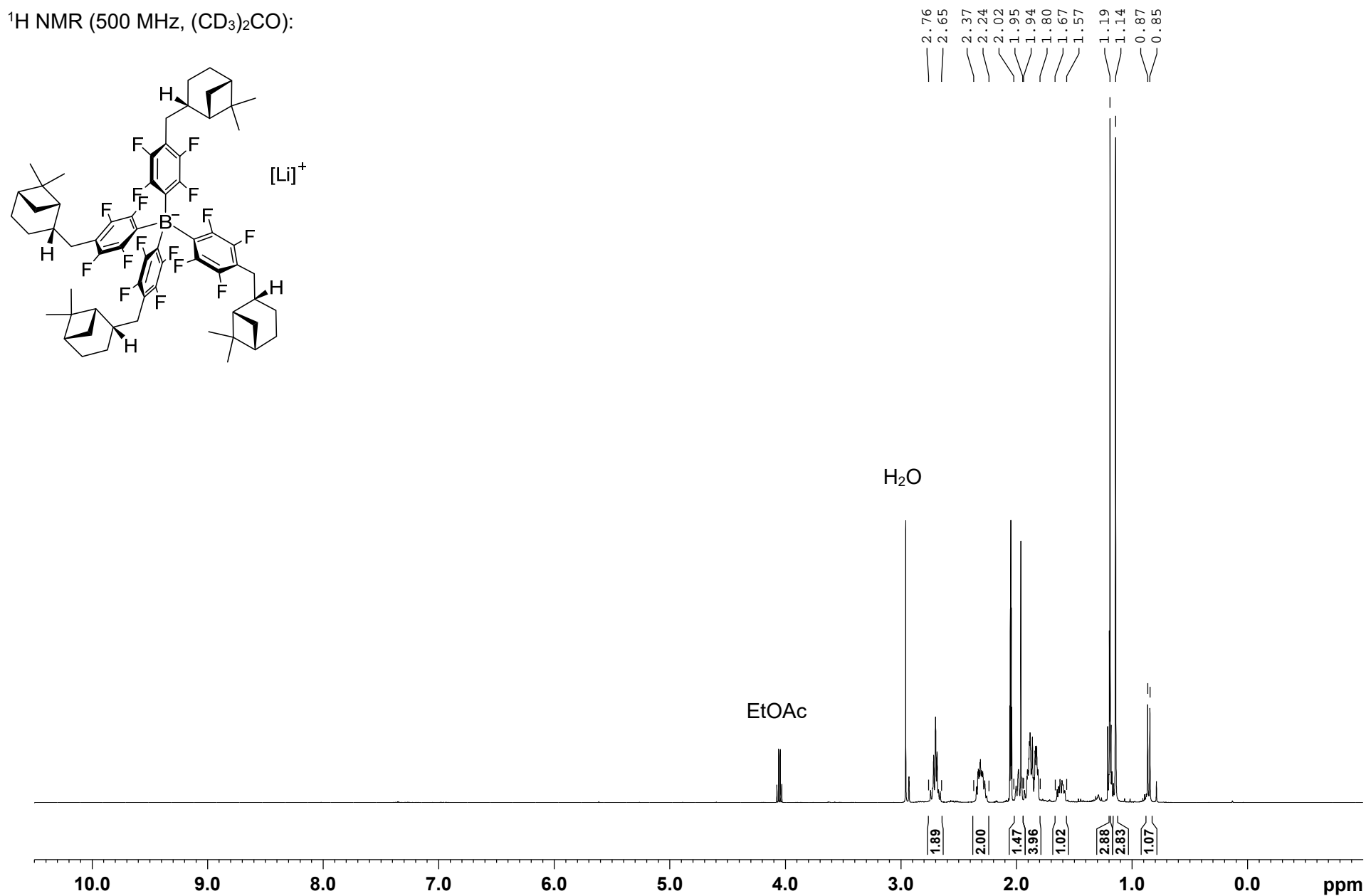


$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ ):

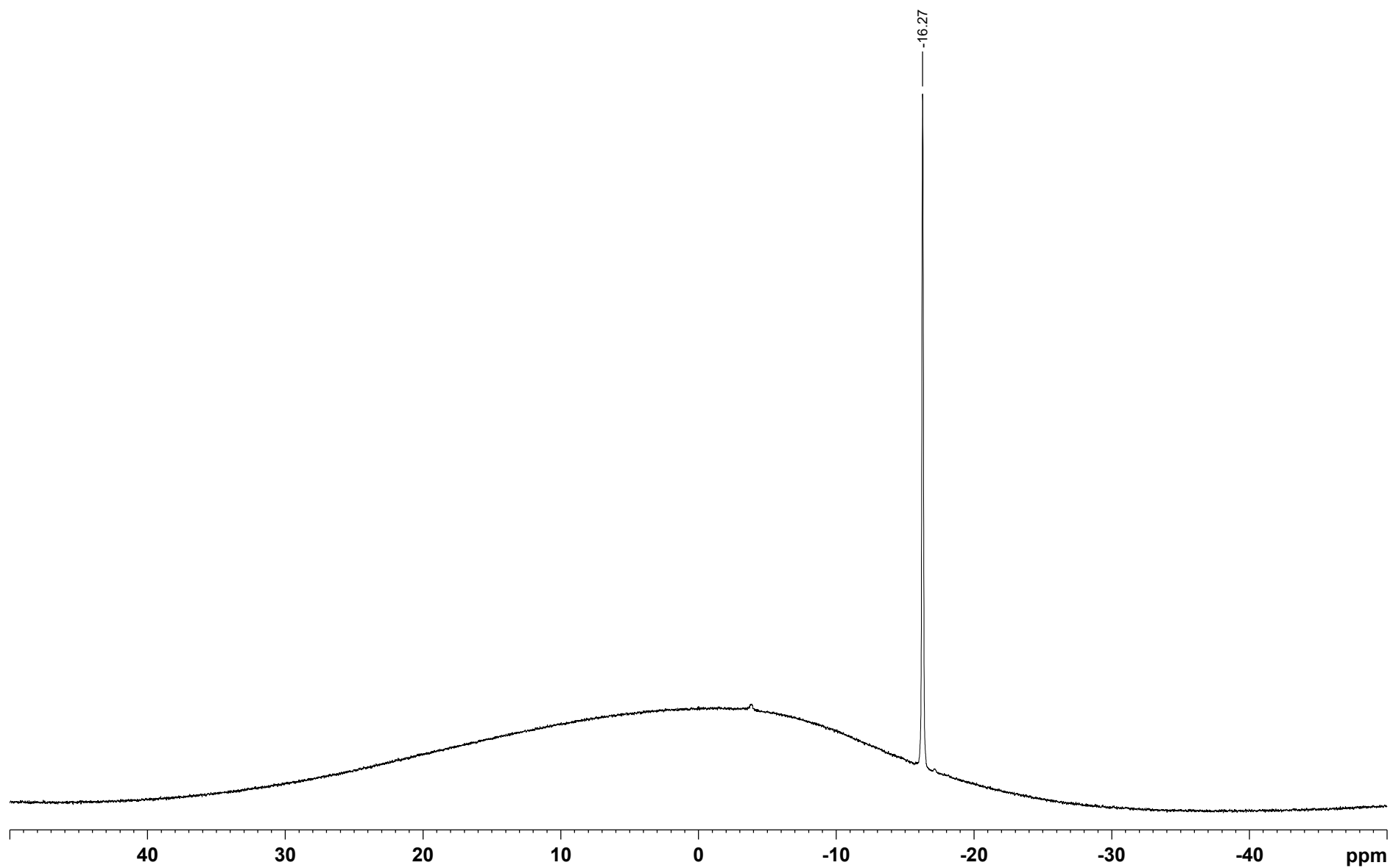


$^{19}\text{F}\{^1\text{H}\}$  NMR (471 MHz,  $\text{C}_6\text{D}_6$ ):



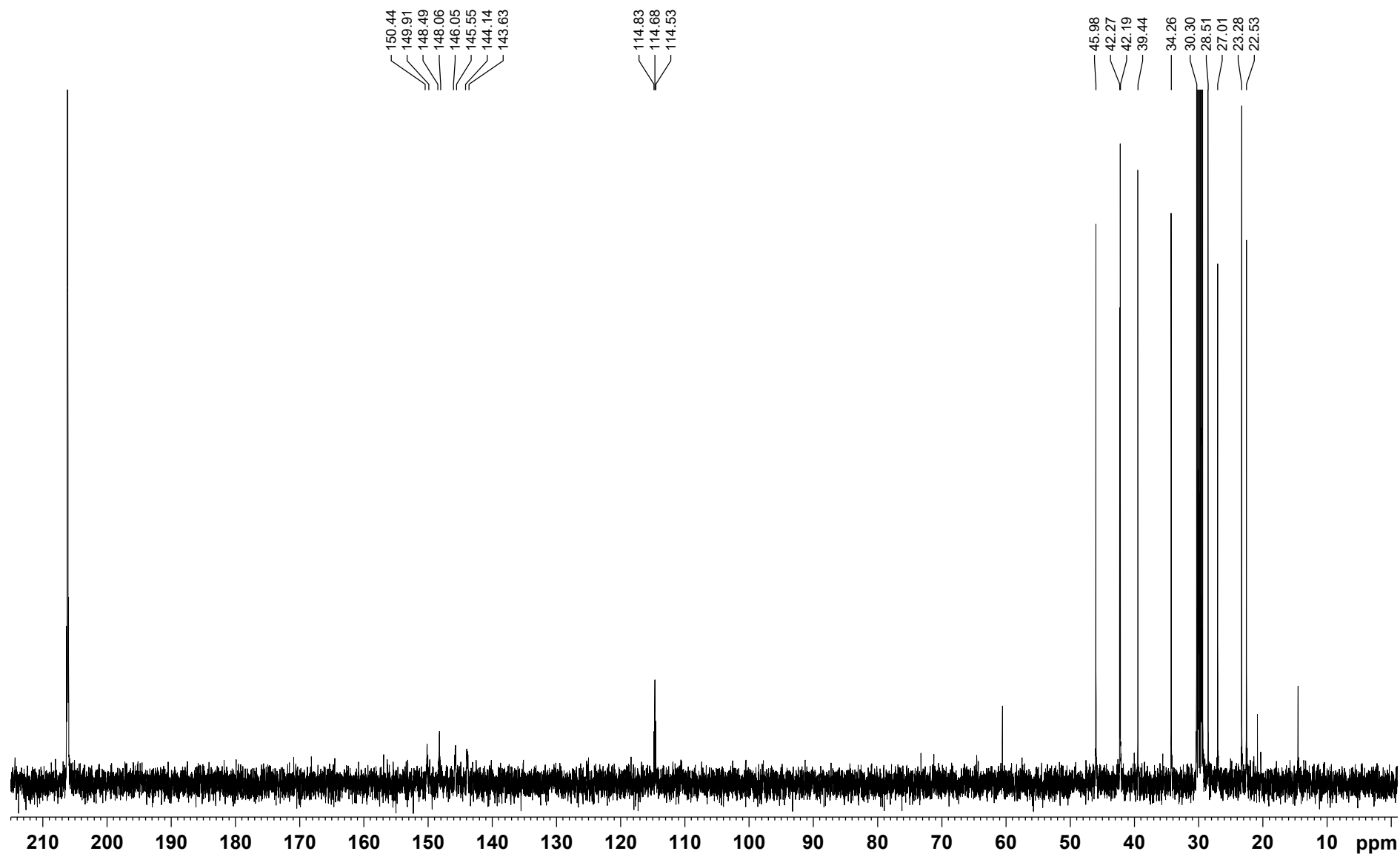
**Lithium tetrakis(4-(((1S,2S,5S)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl)methyl)-2,3,5,6-tetrafluorophenyl)borate [Li]<sup>+</sup>[3]<sup>-</sup>**<sup>1</sup>H NMR (500 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):

$^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $(\text{CD}_3)_2\text{CO}$ )

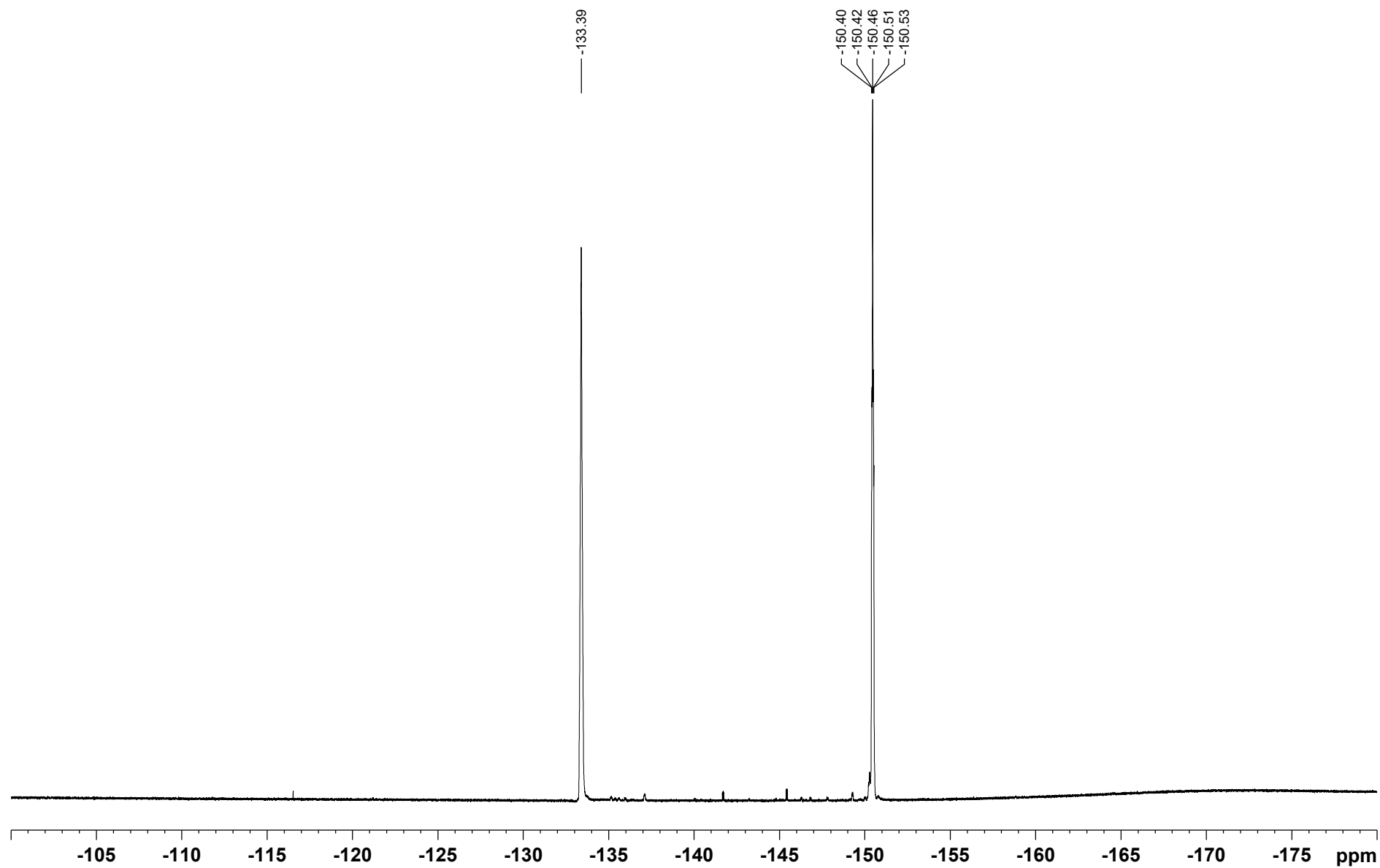


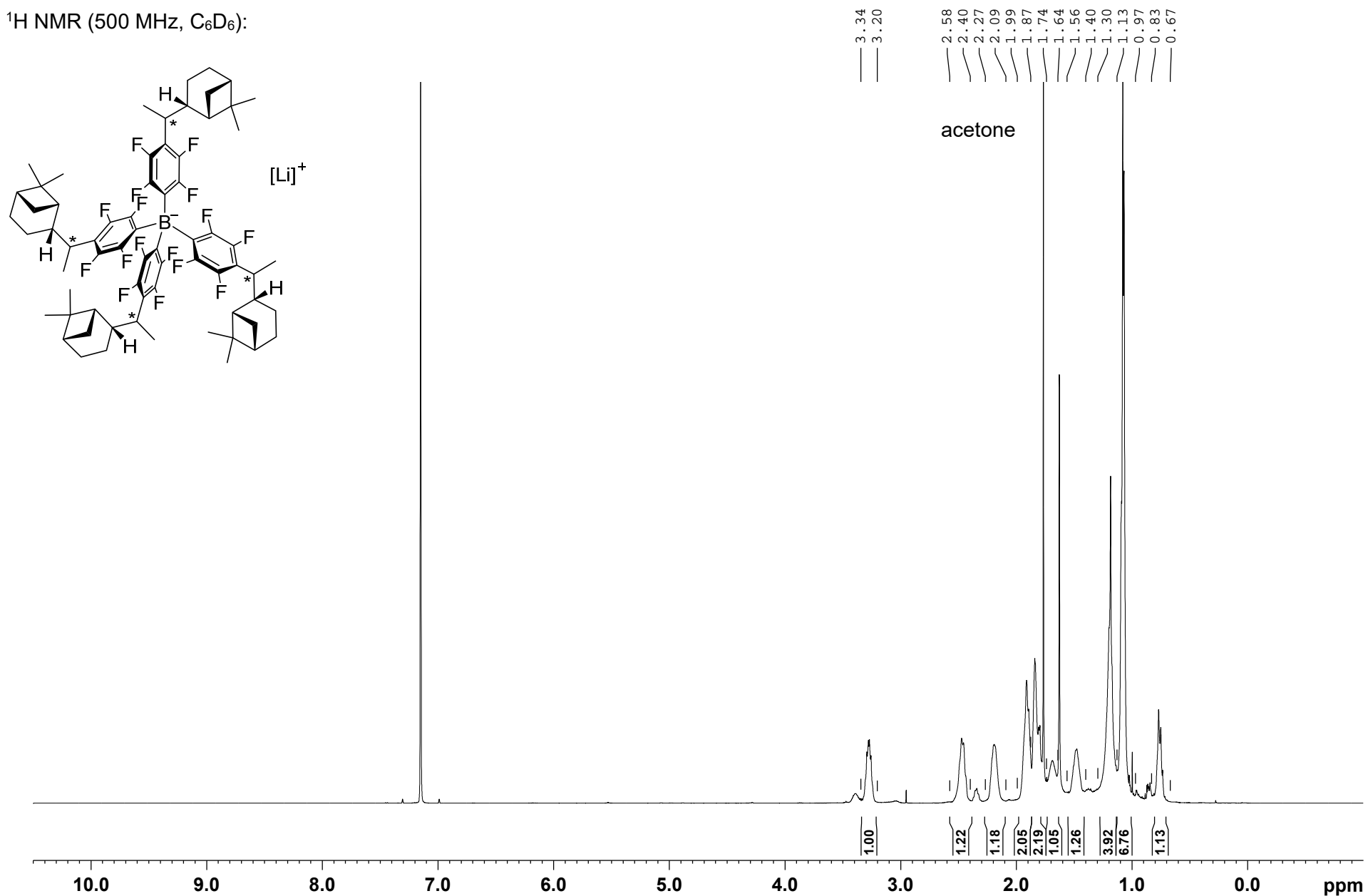


$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $(\text{CD}_3)_2\text{CO}$ ):

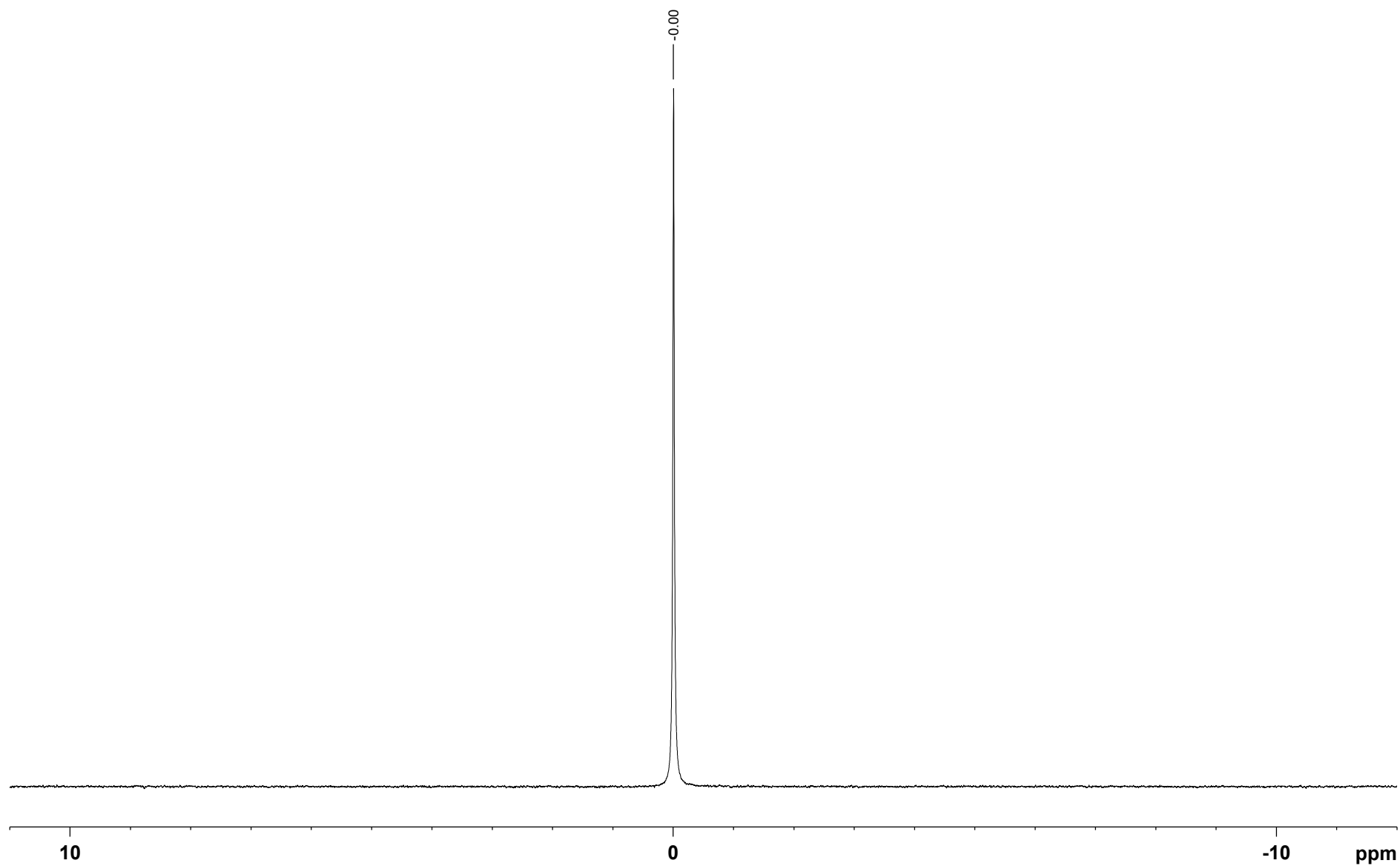


$^{19}\text{F}\{^1\text{H}\}$  NMR (471 MHz,  $(\text{CD}_3)_2\text{CO}$ ):

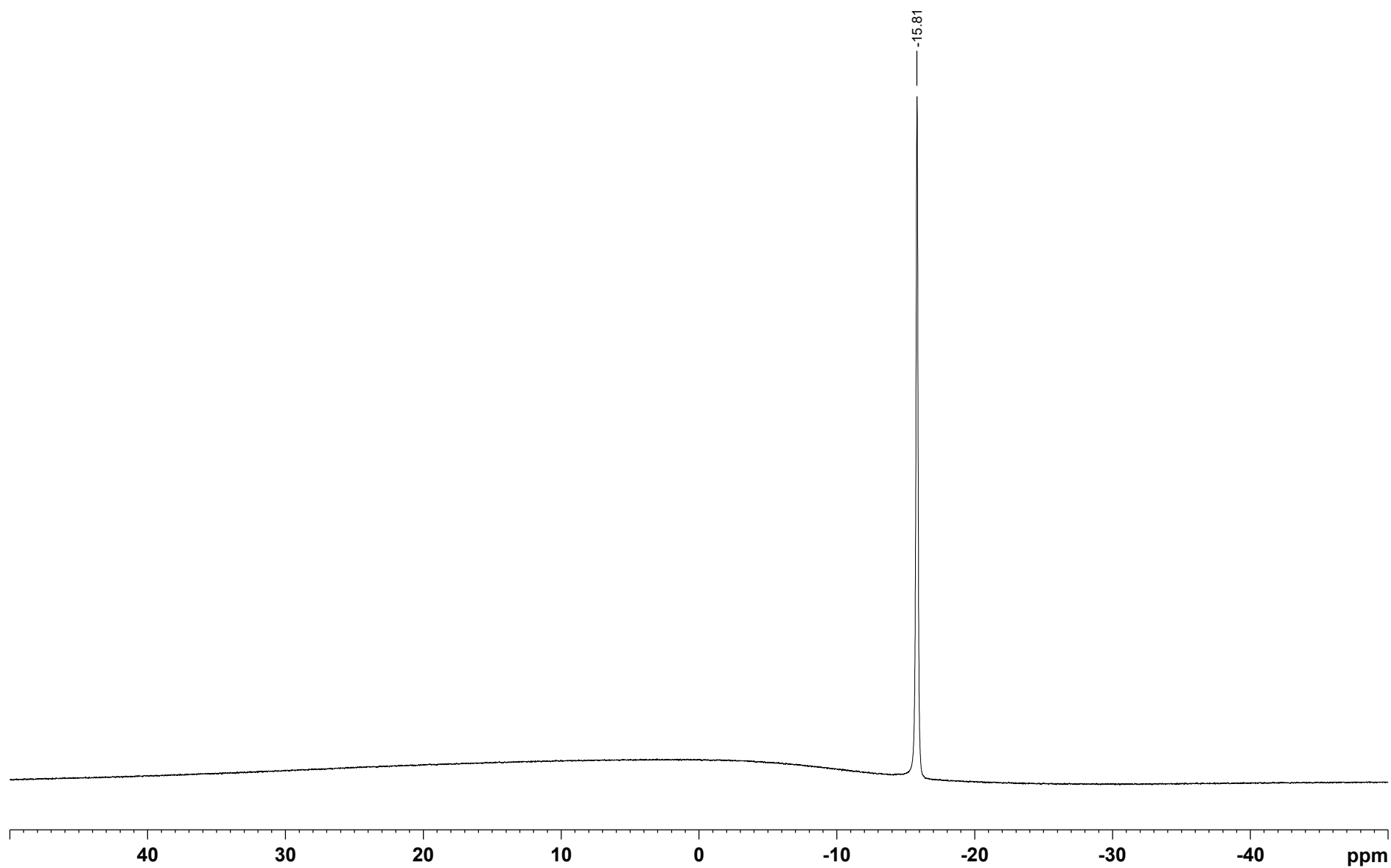


**Lithium tetrakis(4-(1-((1*S*,2*S*,5*S*)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl)ethyl)-2,3,5,6-tetrafluorophenyl)borate [Li]<sup>+</sup>[4]<sup>-</sup>**<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):

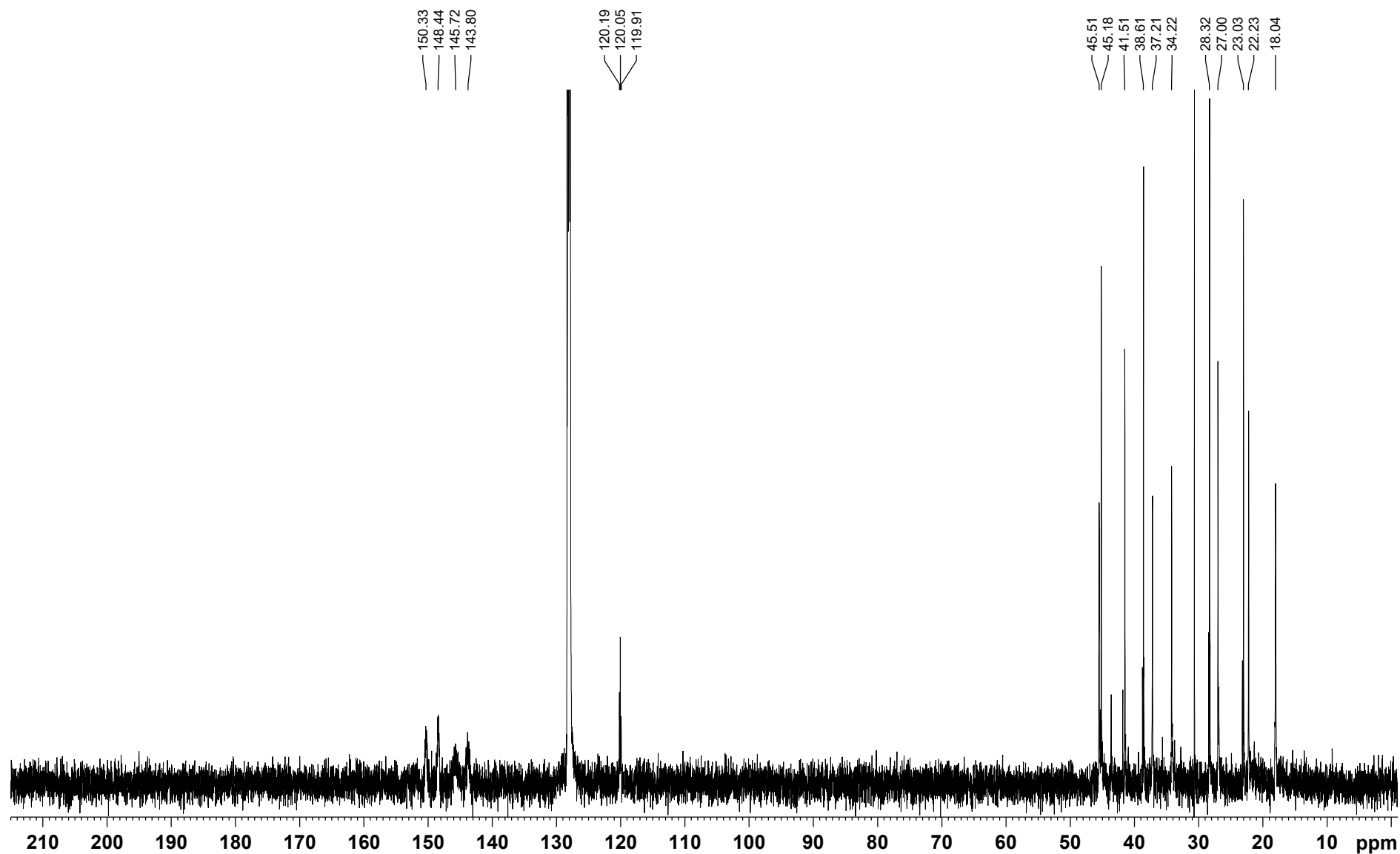
$^7\text{Li}$  NMR (194 MHz,  $\text{C}_6\text{D}_6$ )



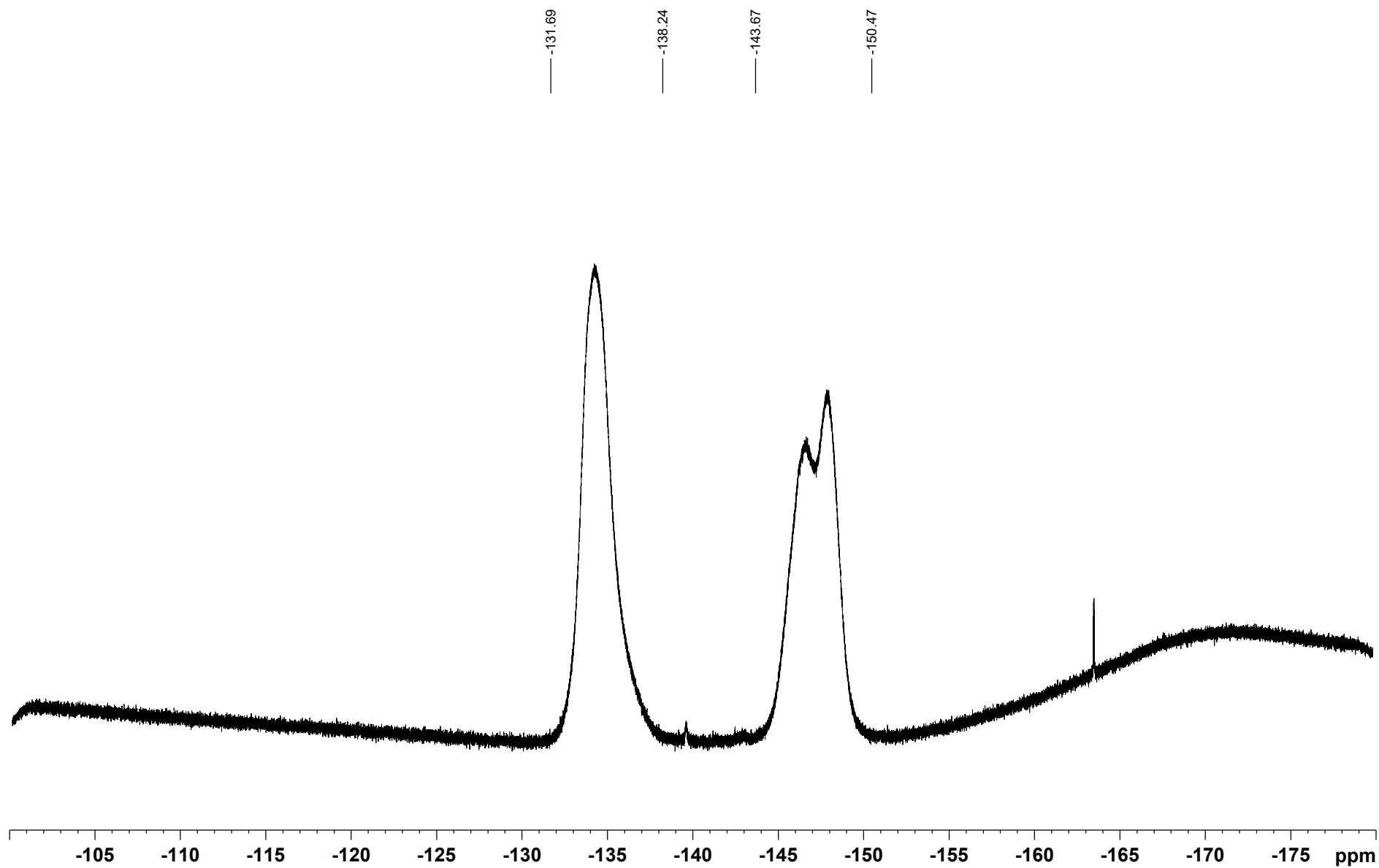
$^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{C}_6\text{D}_6$ ):

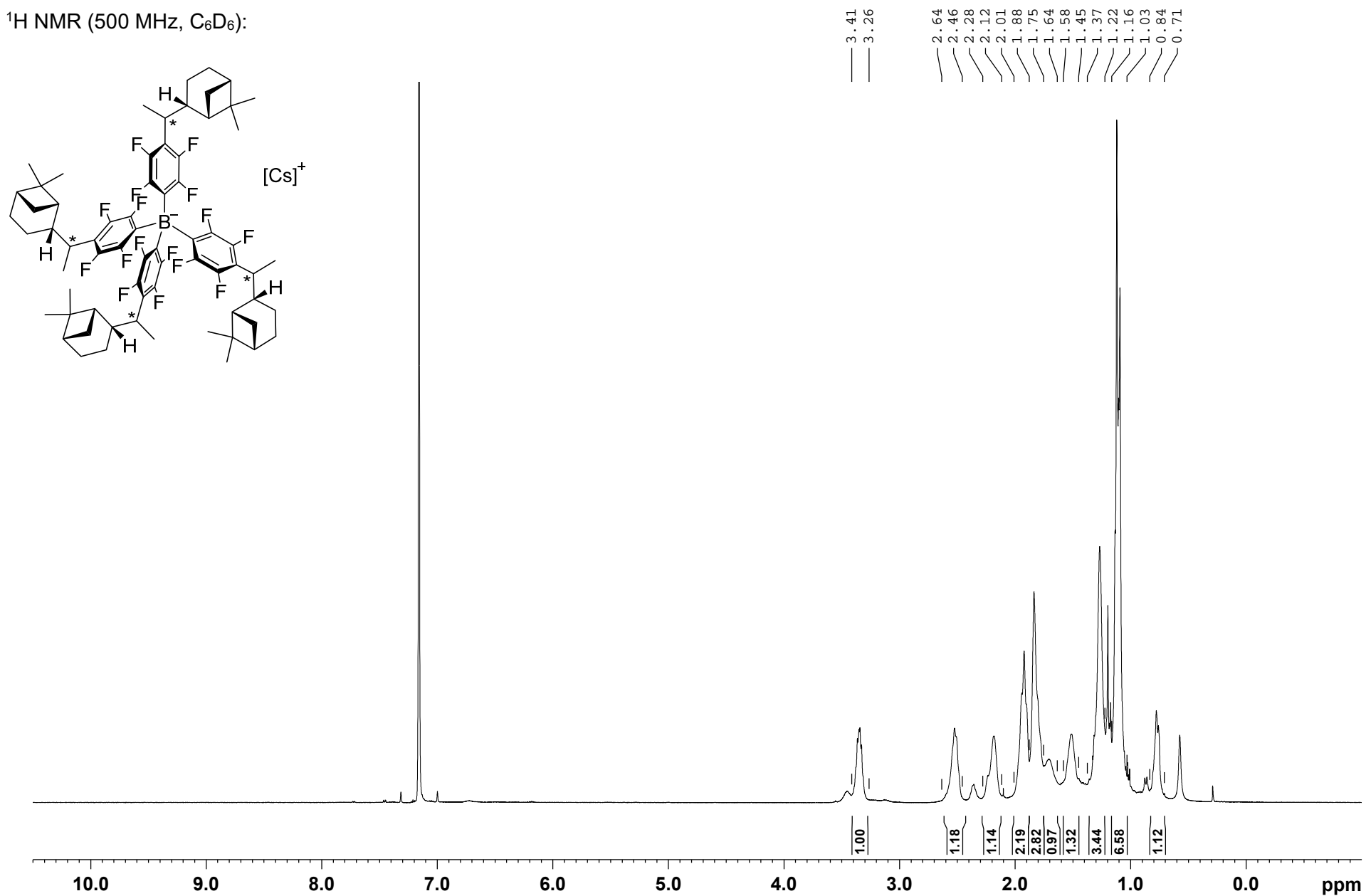


$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ ):



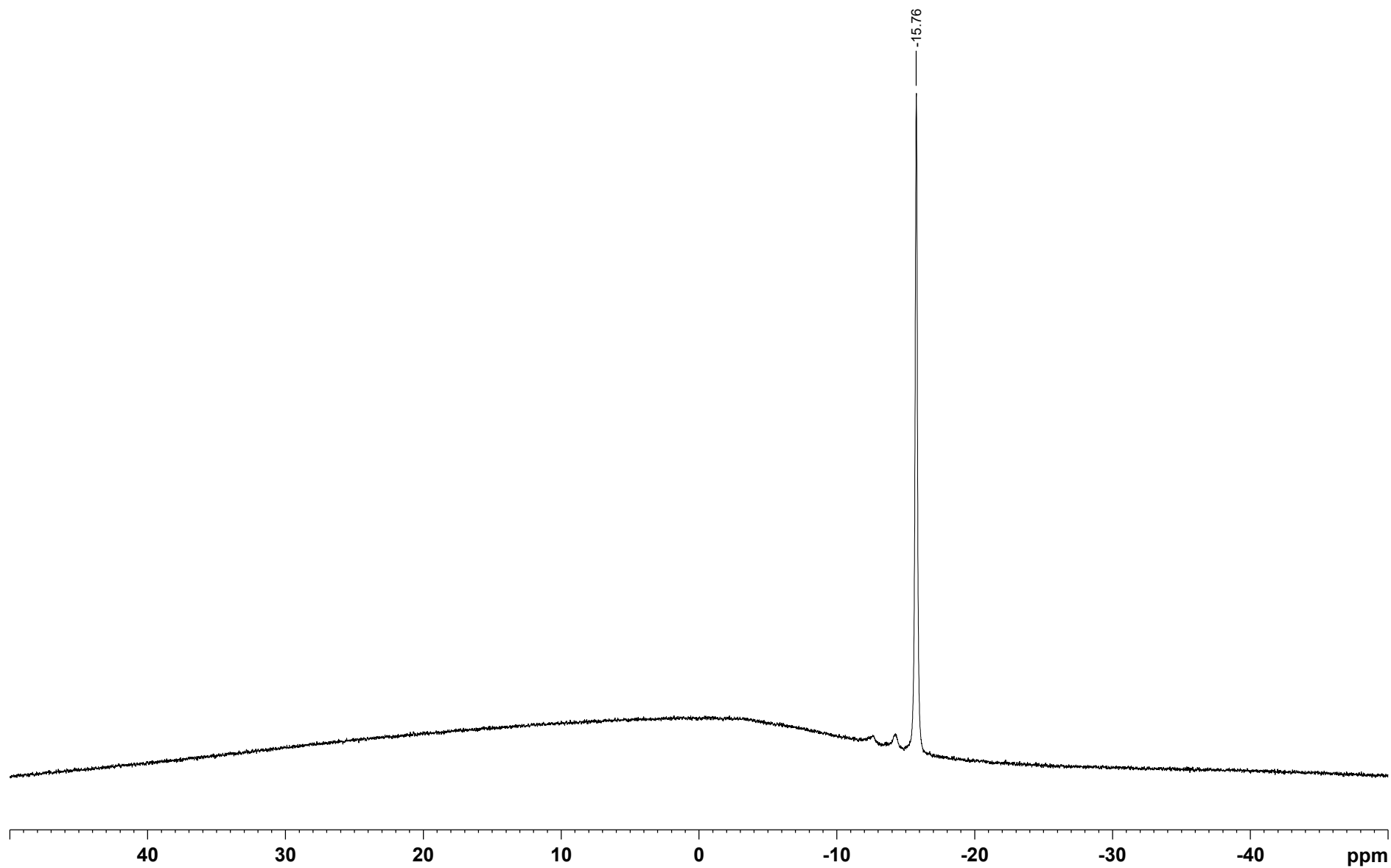
$^{19}\text{F}$  NMR (471 MHz,  $\text{C}_6\text{D}_6$ ):



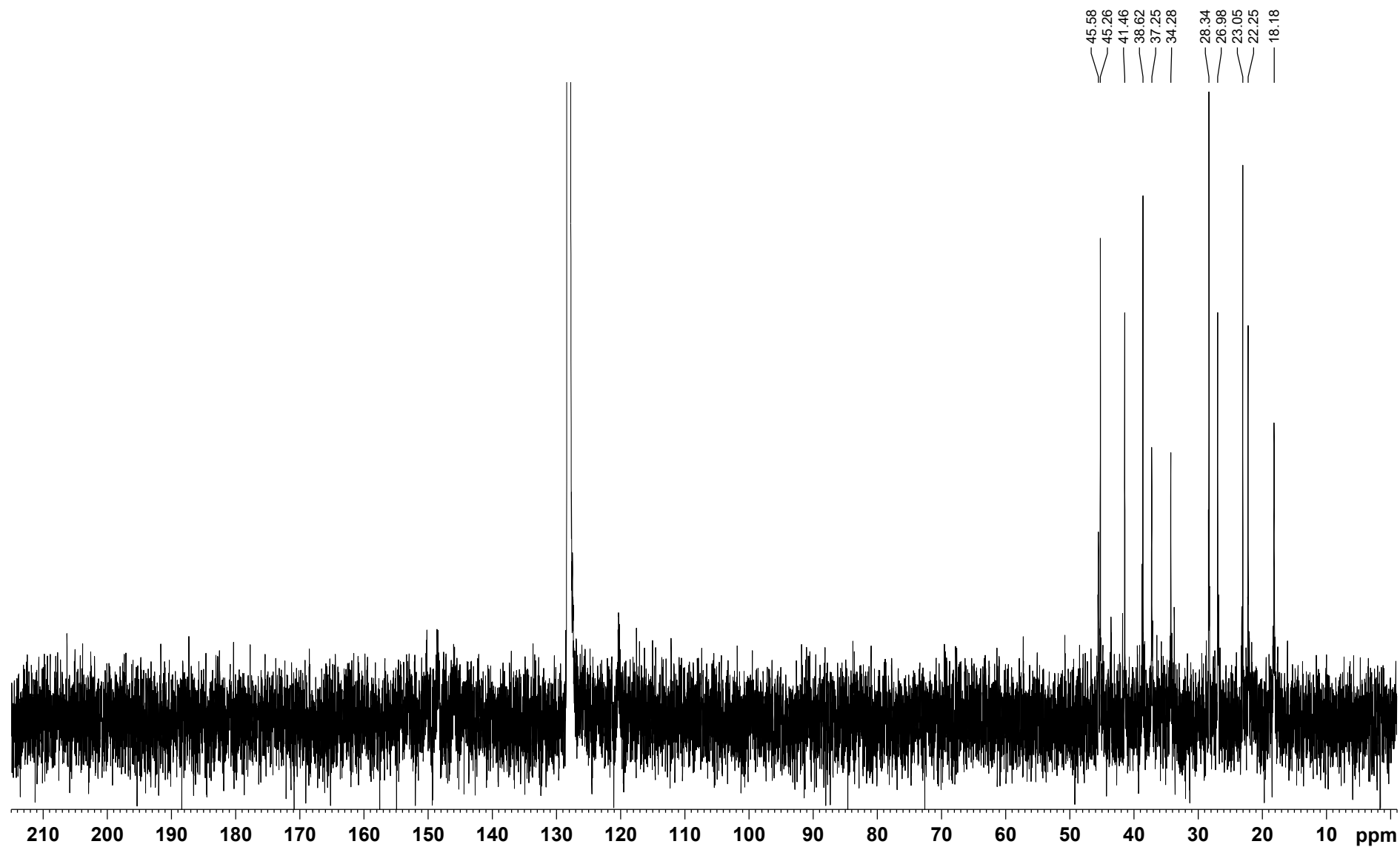
**Cesium tetrakis(4-(1-((1*S*,2*S*,5*S*)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl)ethyl)-2,3,5,6-tetrafluorophenyl)borate [Cs]<sup>+</sup>[4]<sup>-</sup>**<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):



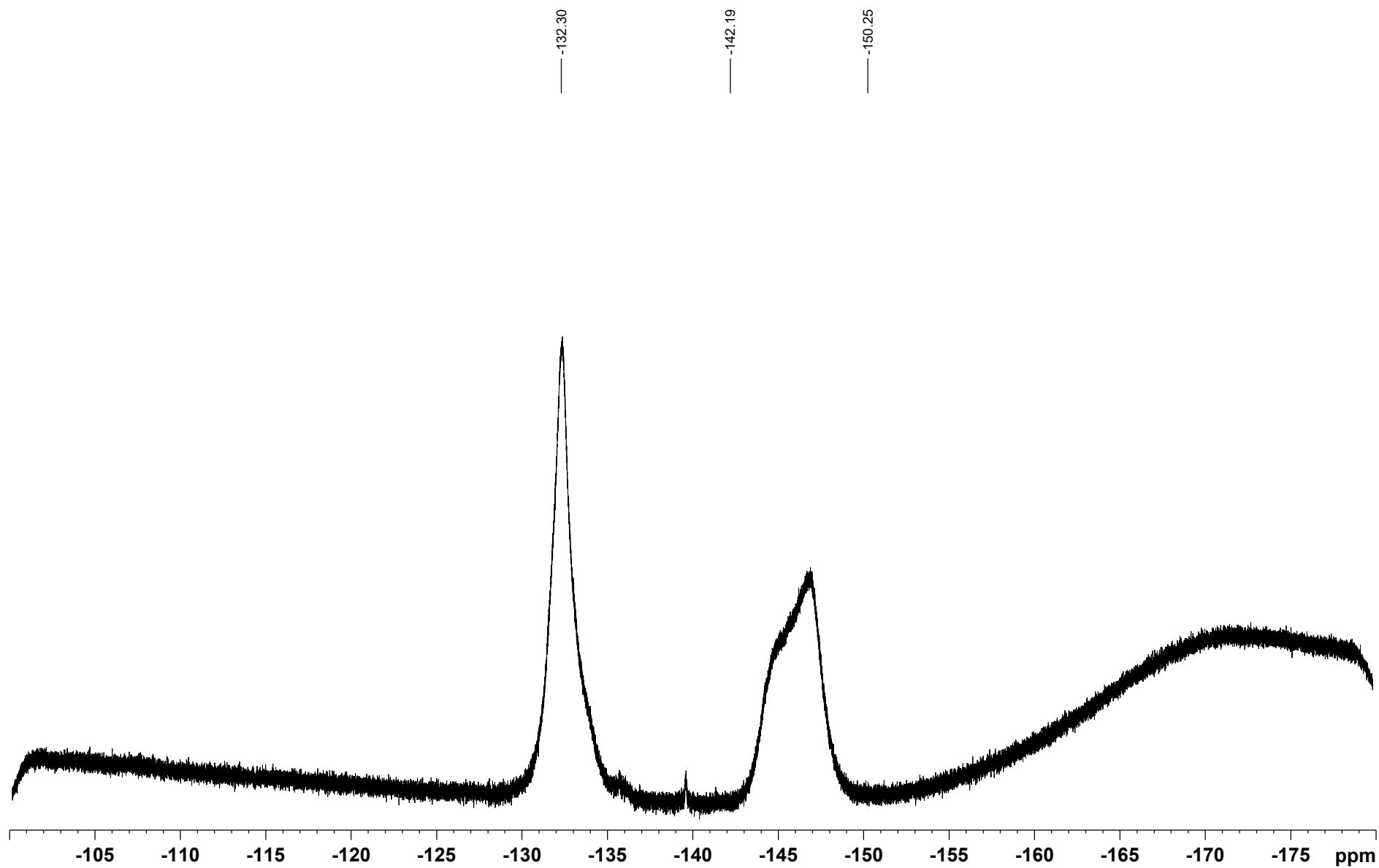
$^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{C}_6\text{D}_6$ ):

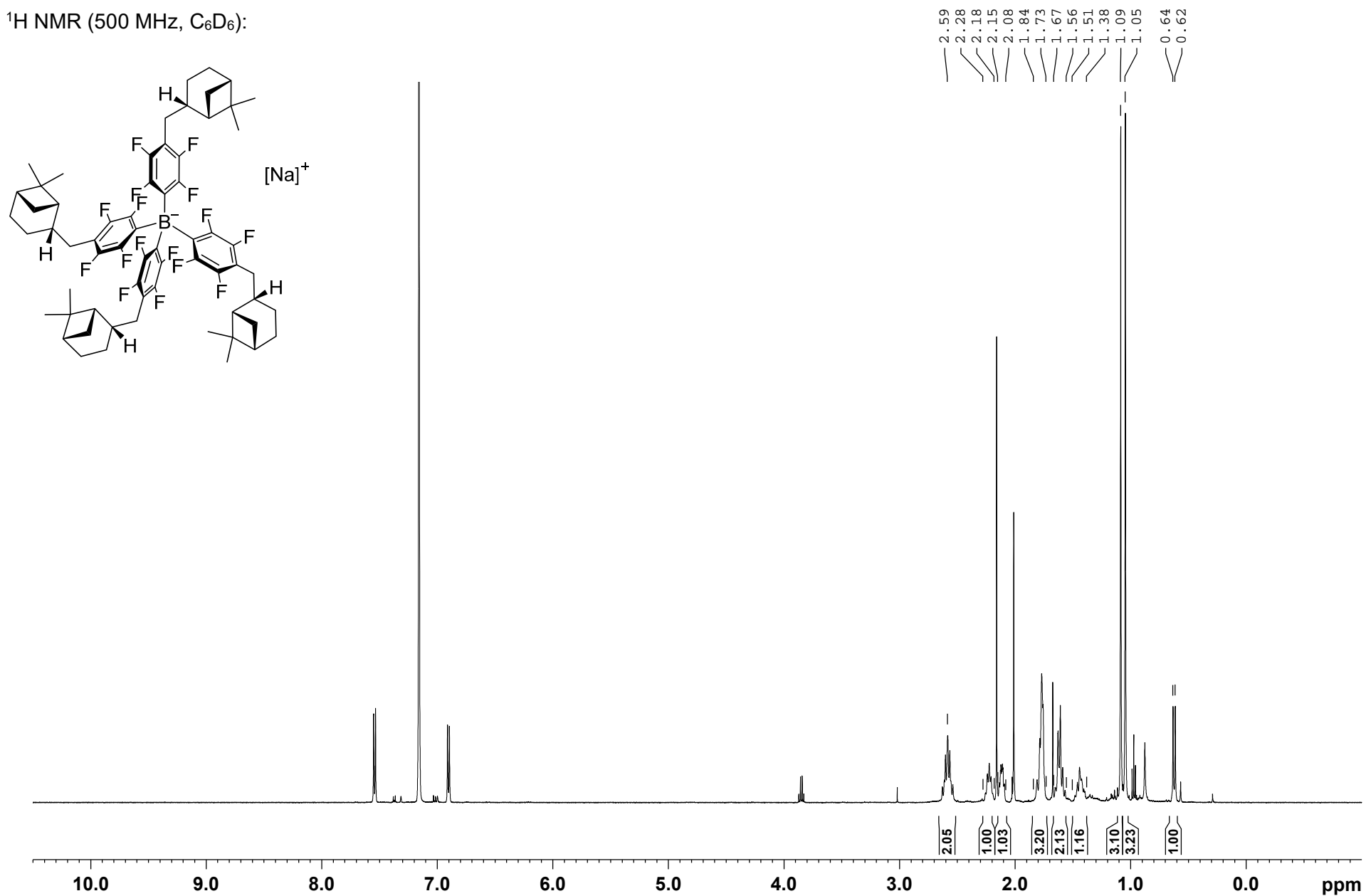


$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ ):

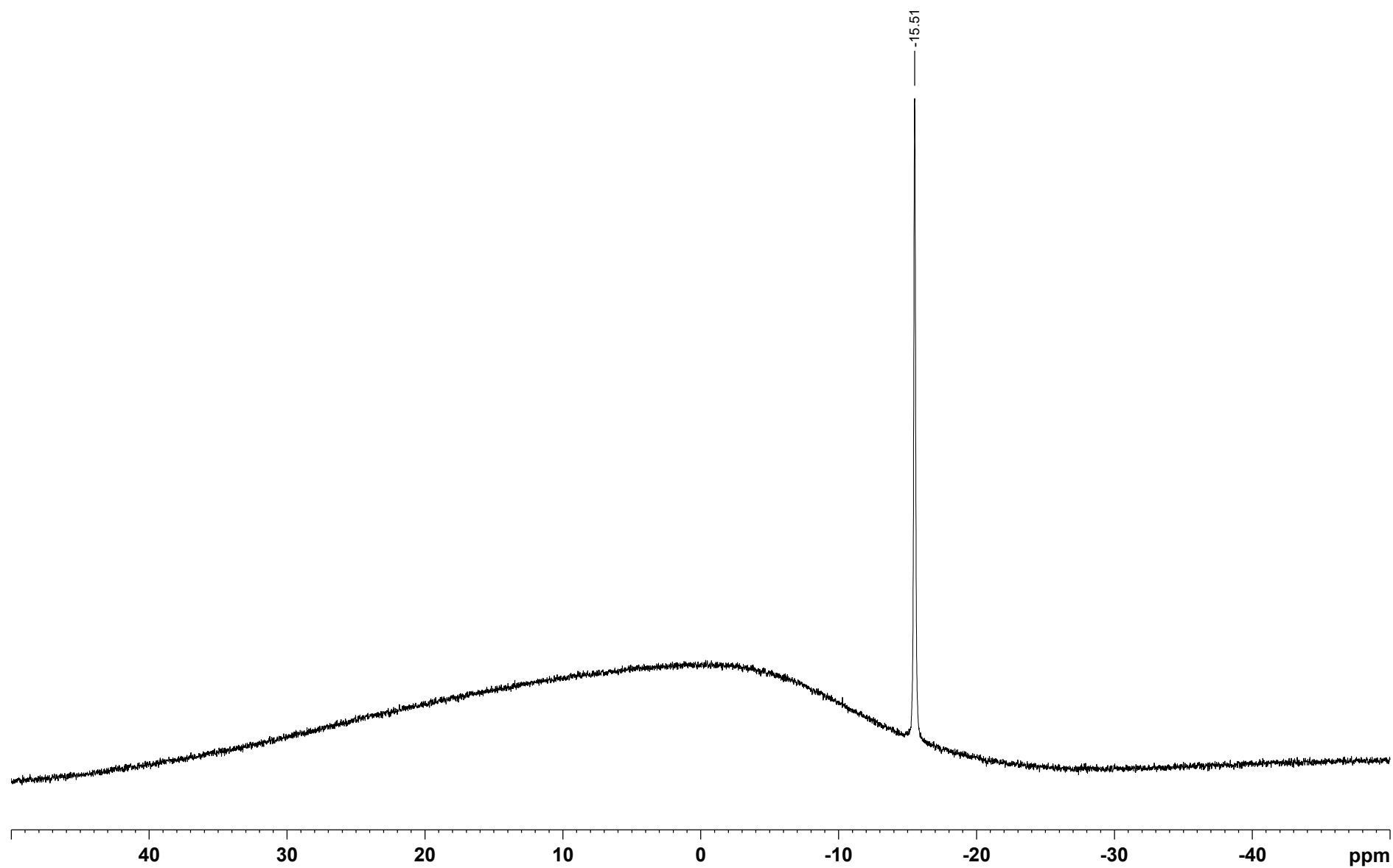


$^{19}\text{F}$  NMR (471 MHz,  $\text{C}_6\text{D}_6$ ):

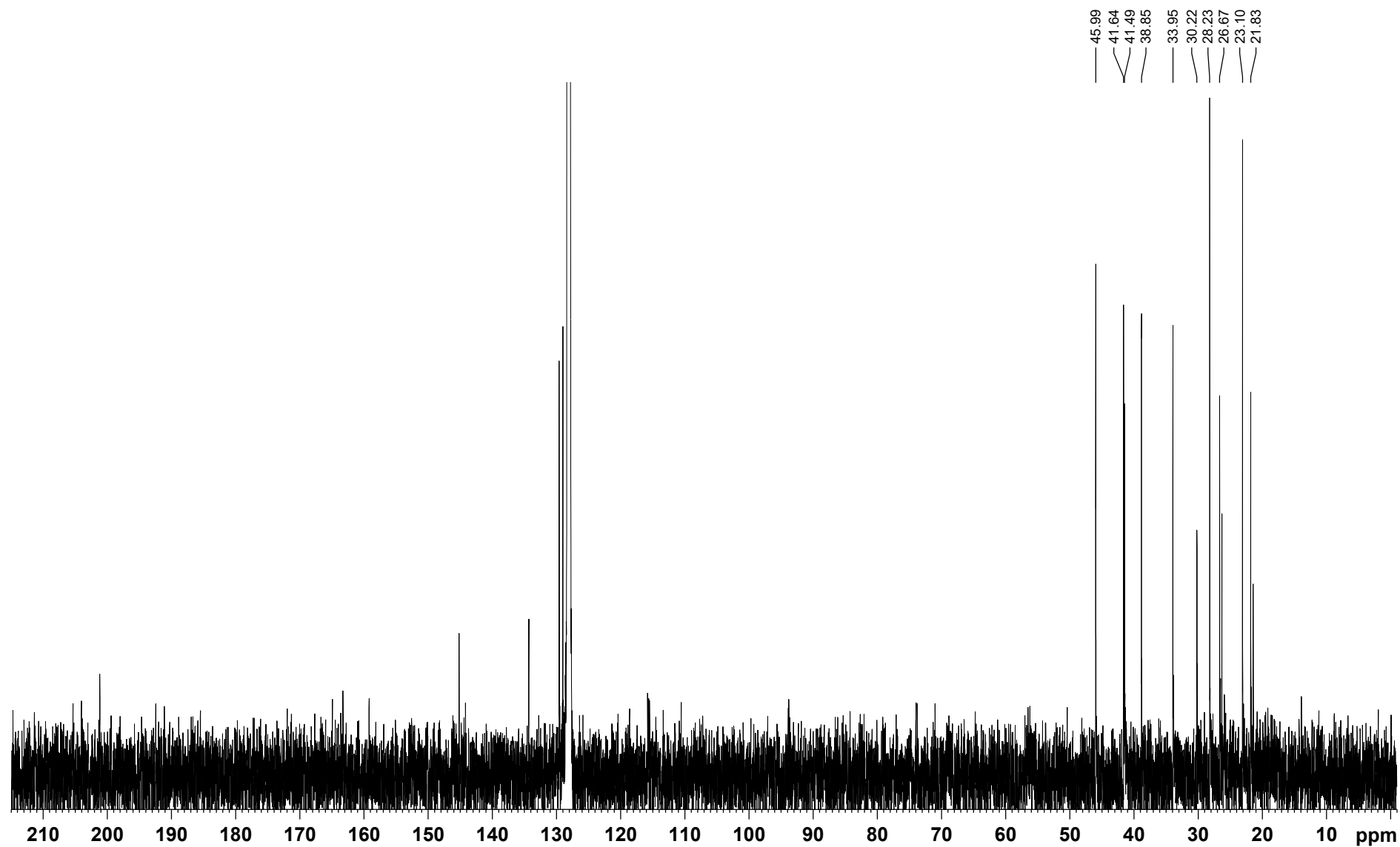


**Sodium tetrakis(4-(((1S,2S,5S)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl)methyl)-2,3,5,6-tetrafluorophenyl)borate [Na]<sup>+</sup>[3]<sup>-</sup>**<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):

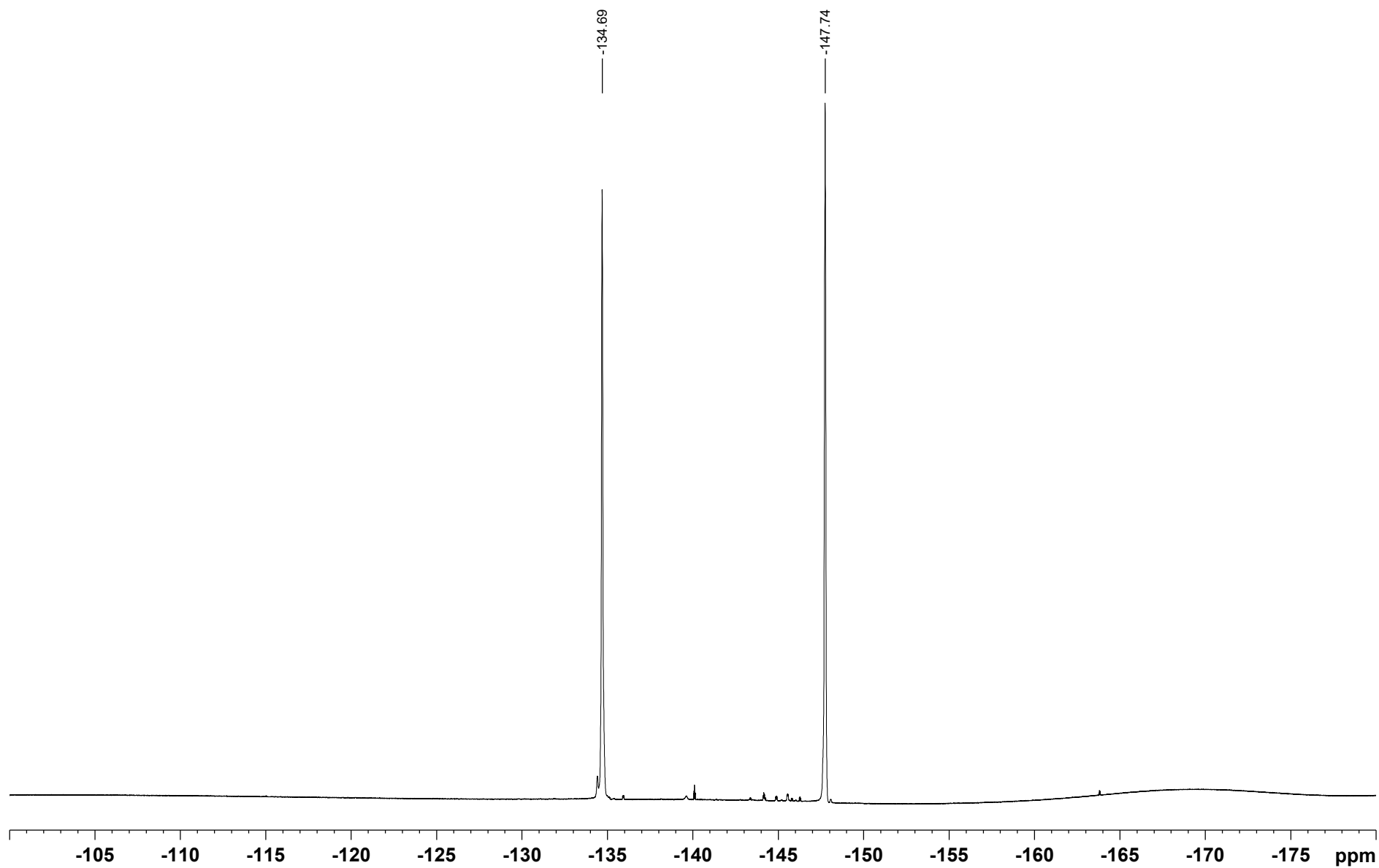
$^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{C}_6\text{D}_6$ ):

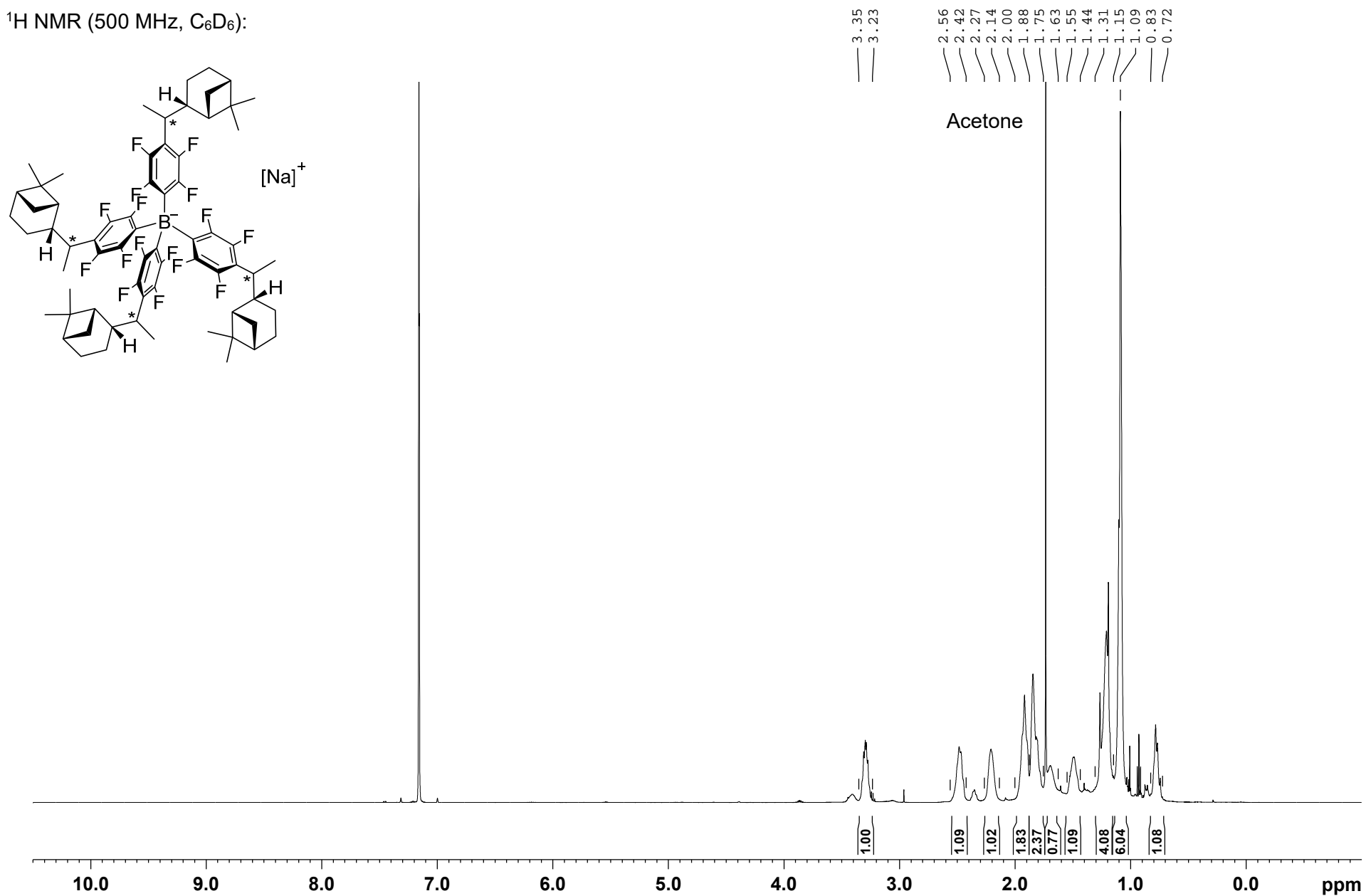


$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ ):



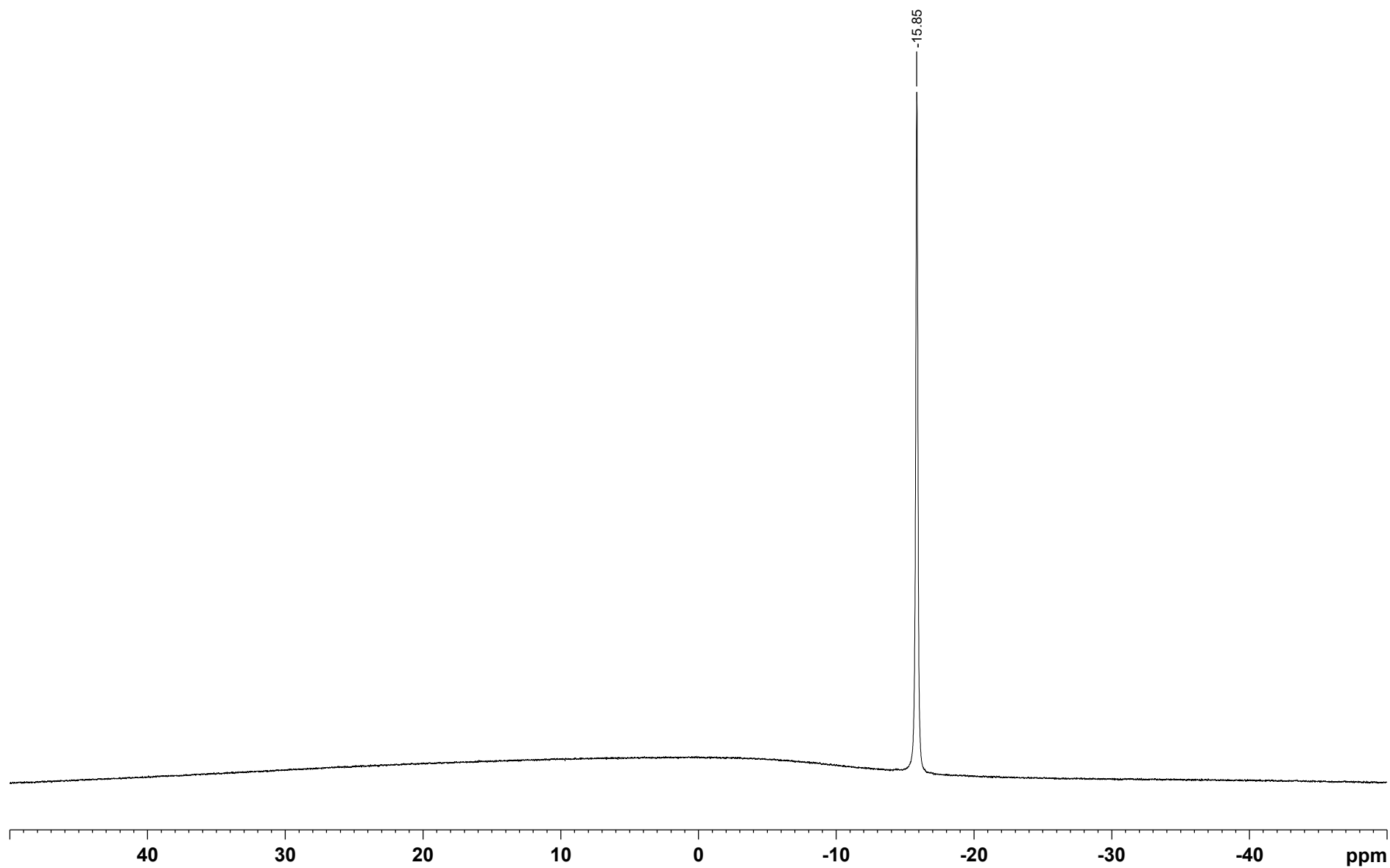
$^{19}\text{F}\{^1\text{H}\}$  NMR (471 MHz,  $\text{C}_6\text{D}_6$ ):



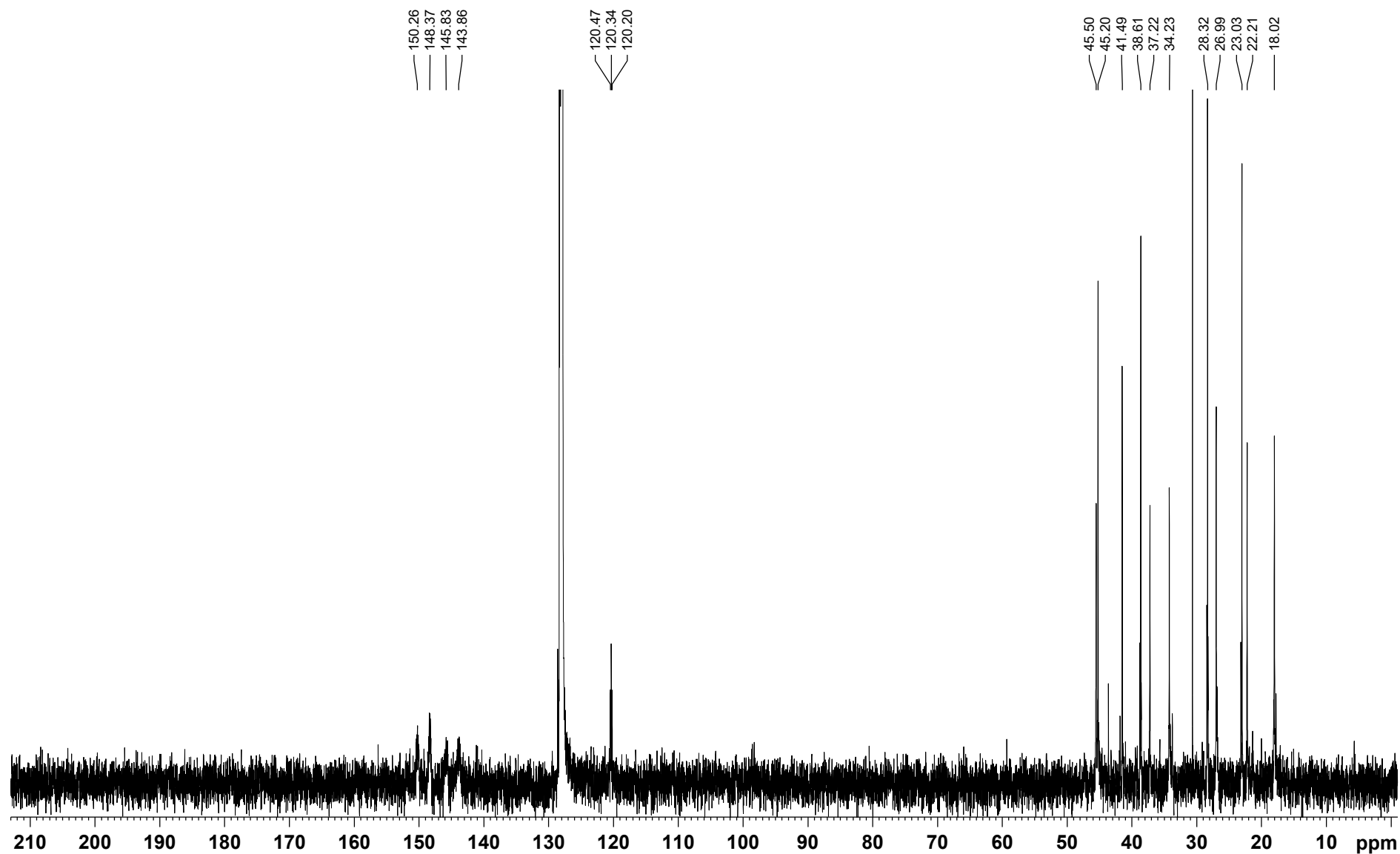
**Sodium tetrakis(4-(1-((1S,2S,5S)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl)ethyl)-2,3,5,6-tetrafluorophenyl)borate [Na]<sup>+</sup>[4]<sup>-</sup>**<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):



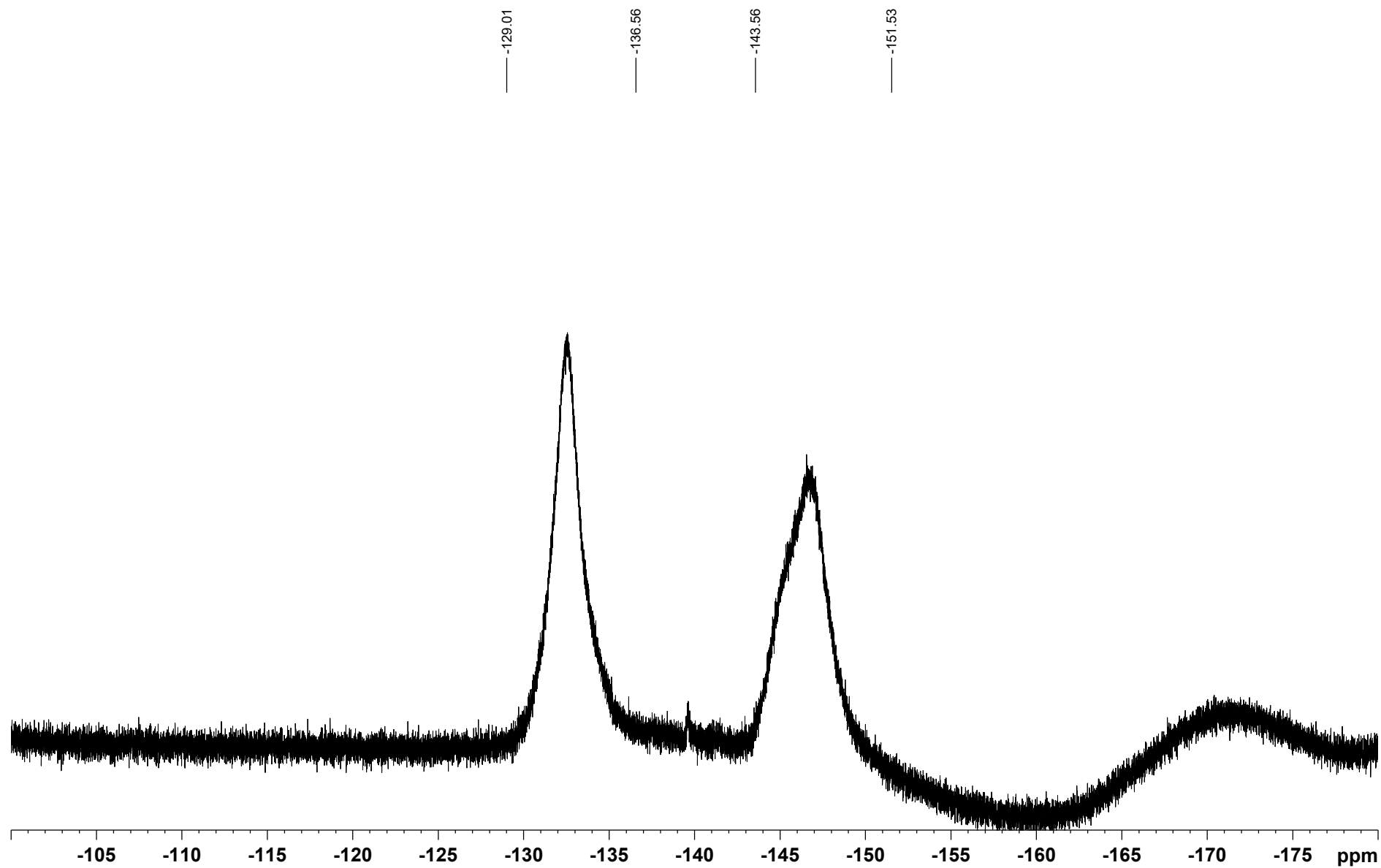
$^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{C}_6\text{D}_6$ ):

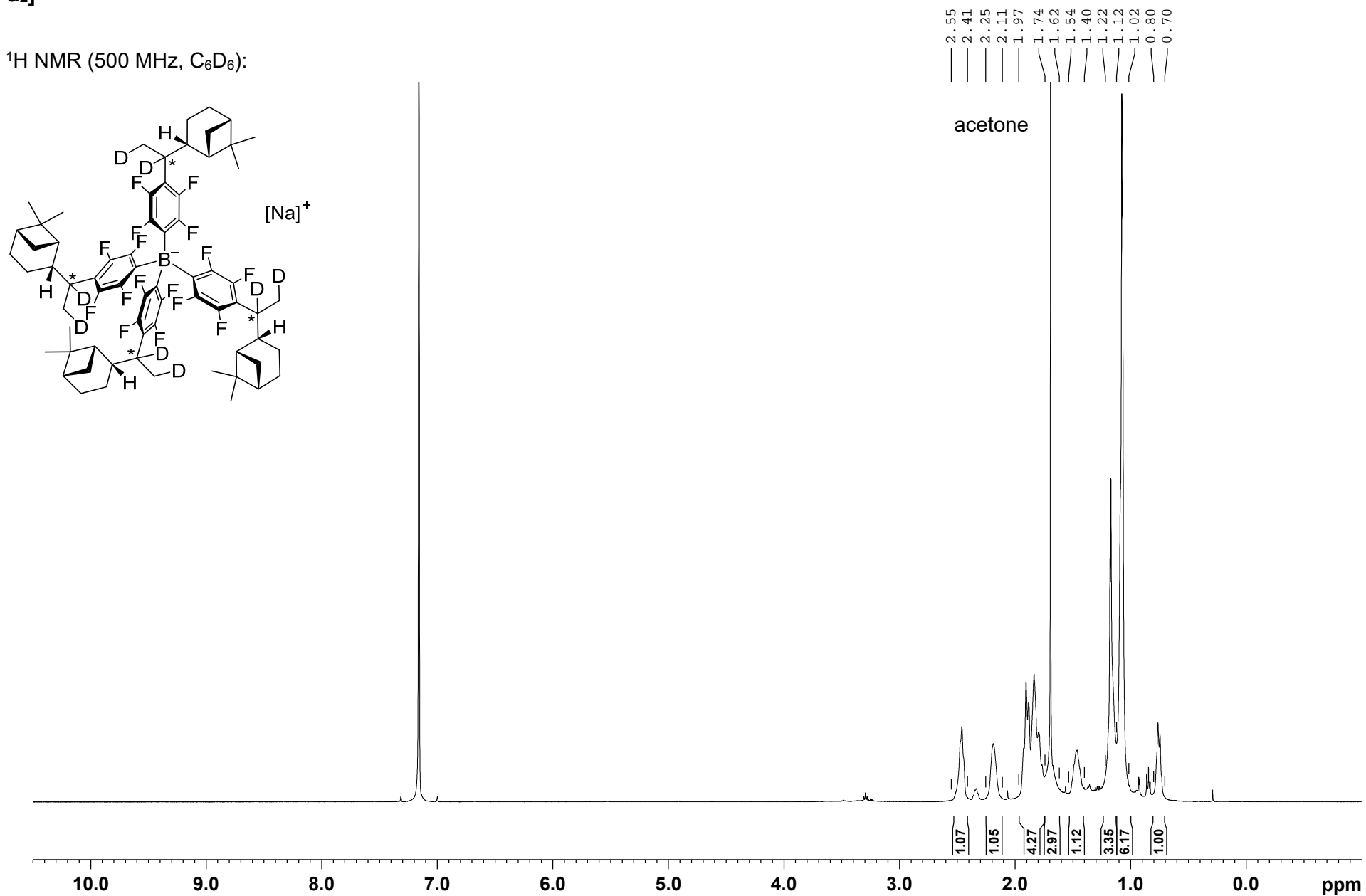


$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ ):

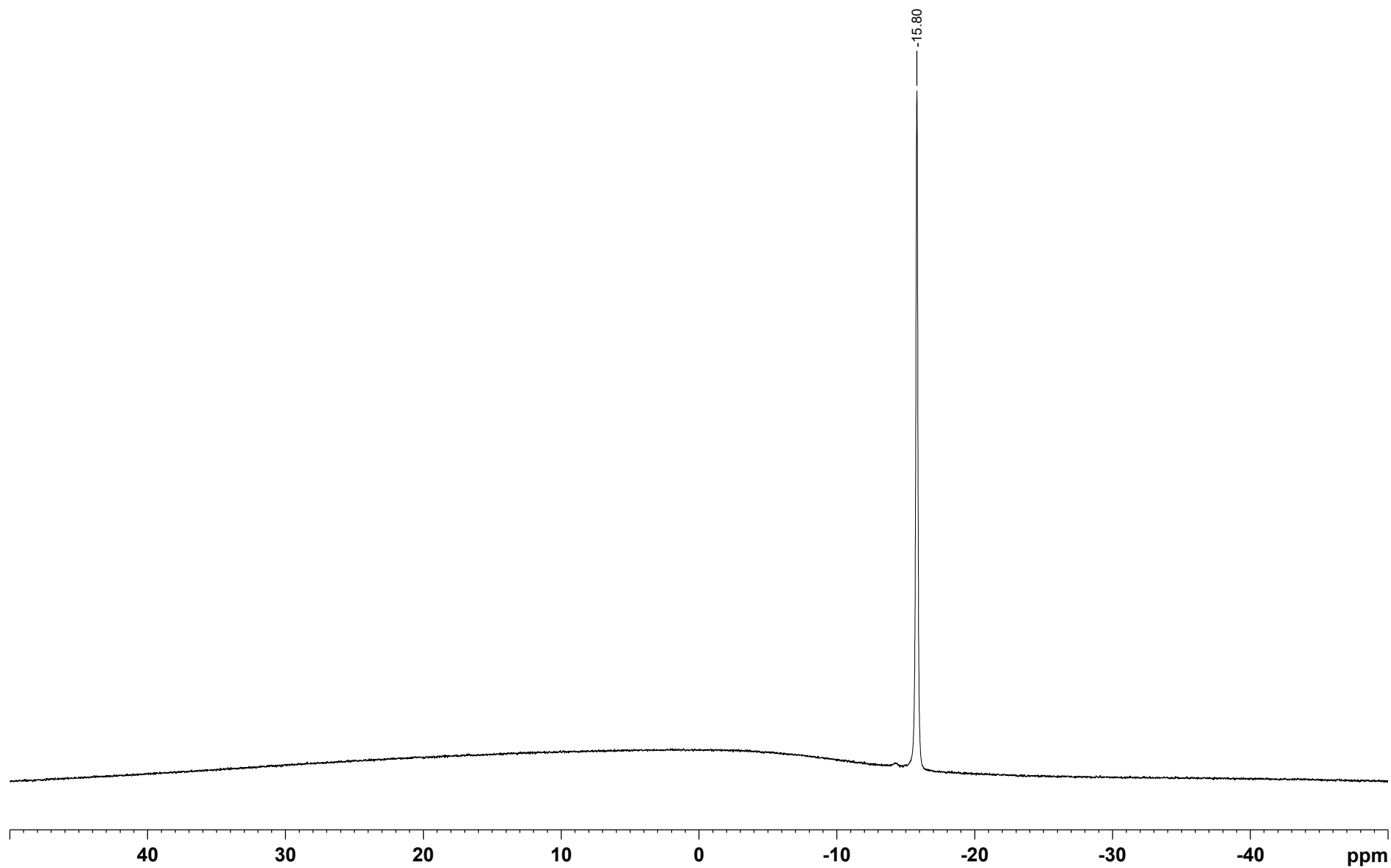


$^{19}\text{F}$  NMR (471 MHz,  $\text{C}_6\text{D}_6$ ):

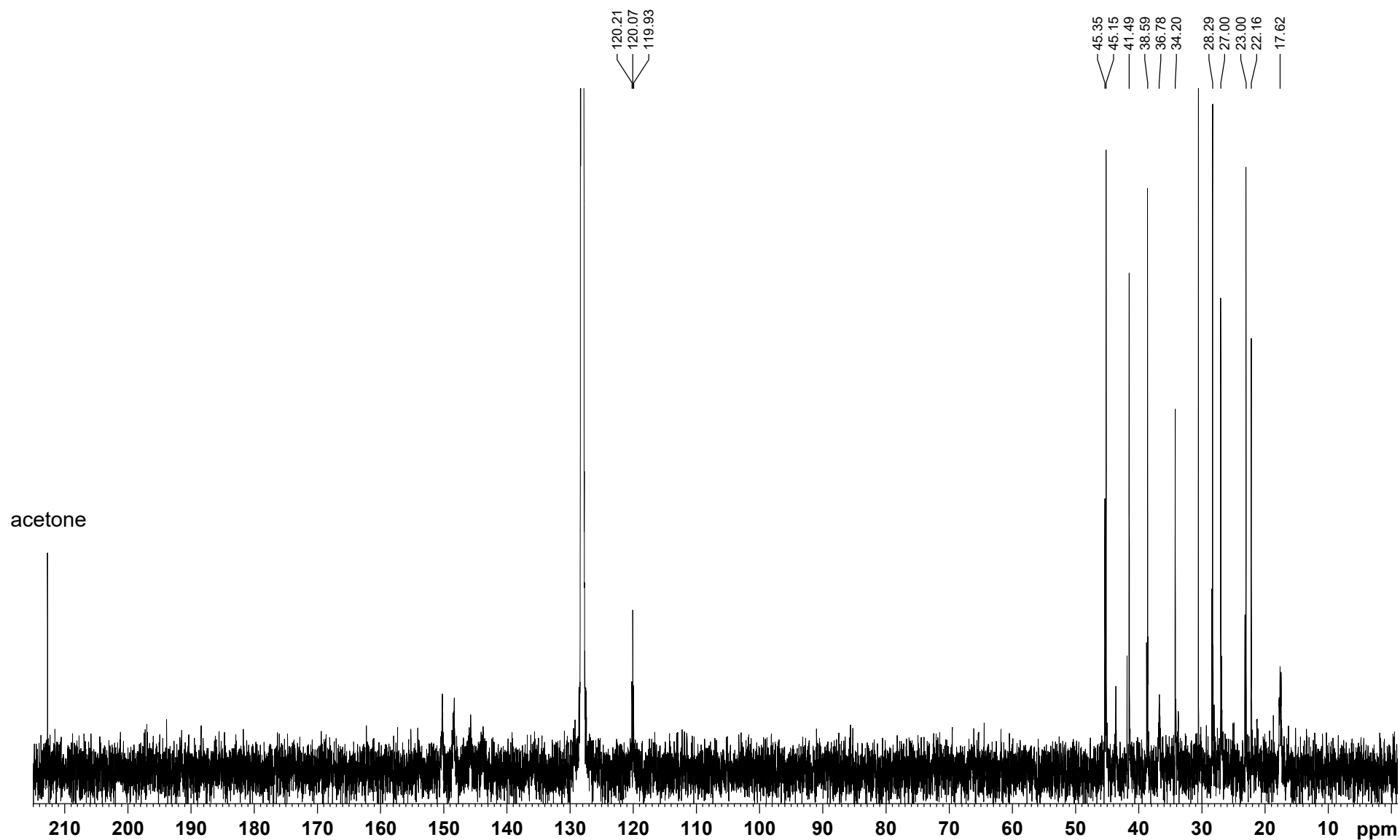


**Sodium tetrakis(4-(1-((1*S*,2*S*,5*S*)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl)ethyl-1,2-*d*<sub>2</sub>)-2,3,5,6-tetrafluorophenyl)borate [Na]<sup>+</sup>[4-*d*<sub>2</sub>]<sup>-</sup>**<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):

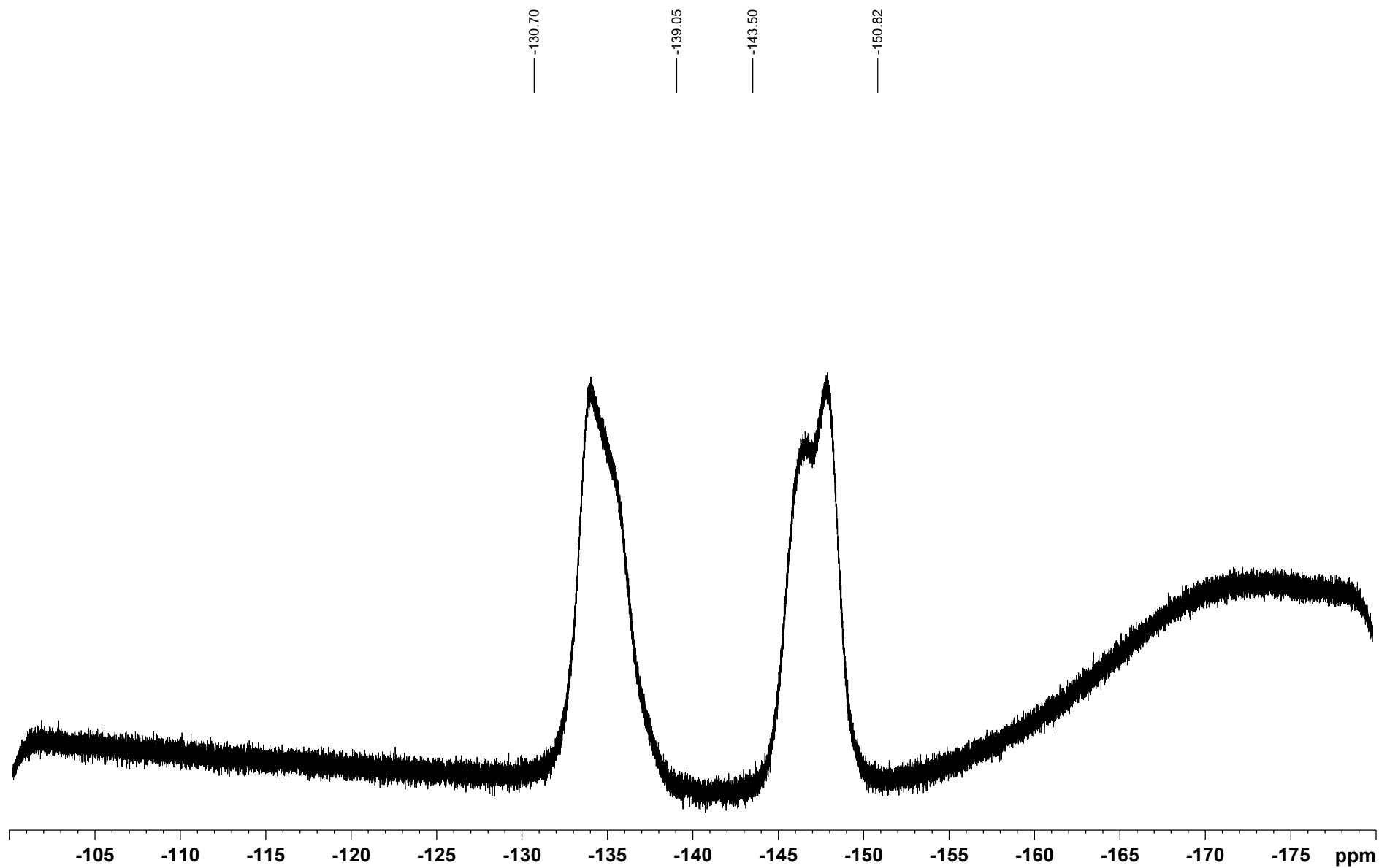
$^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{C}_6\text{D}_6$ ):



$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ ):

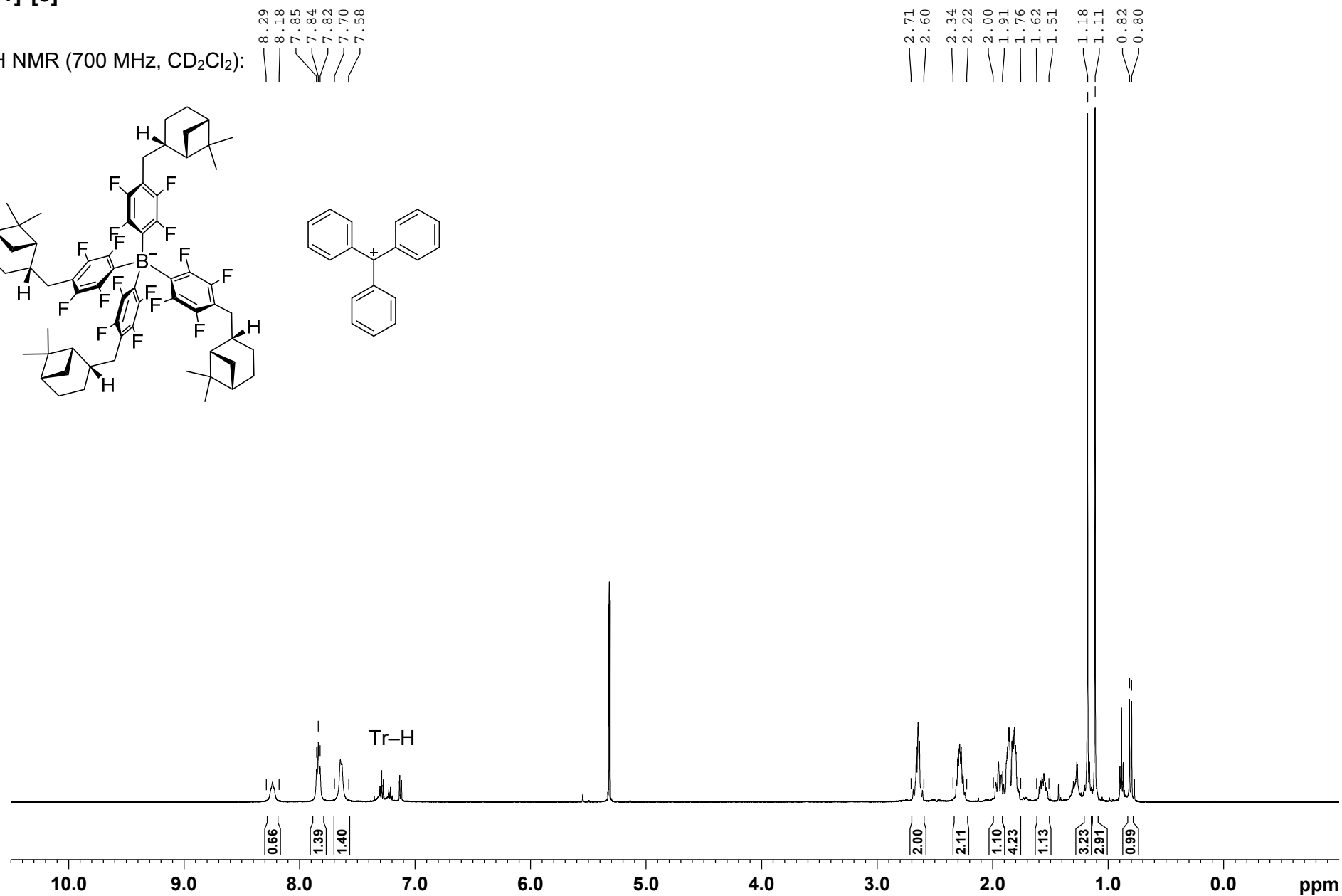
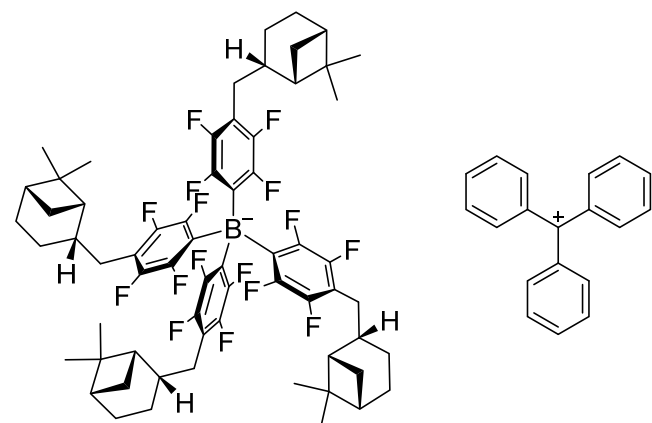


$^{19}\text{F}$  NMR (471 MHz,  $\text{C}_6\text{D}_6$ ):



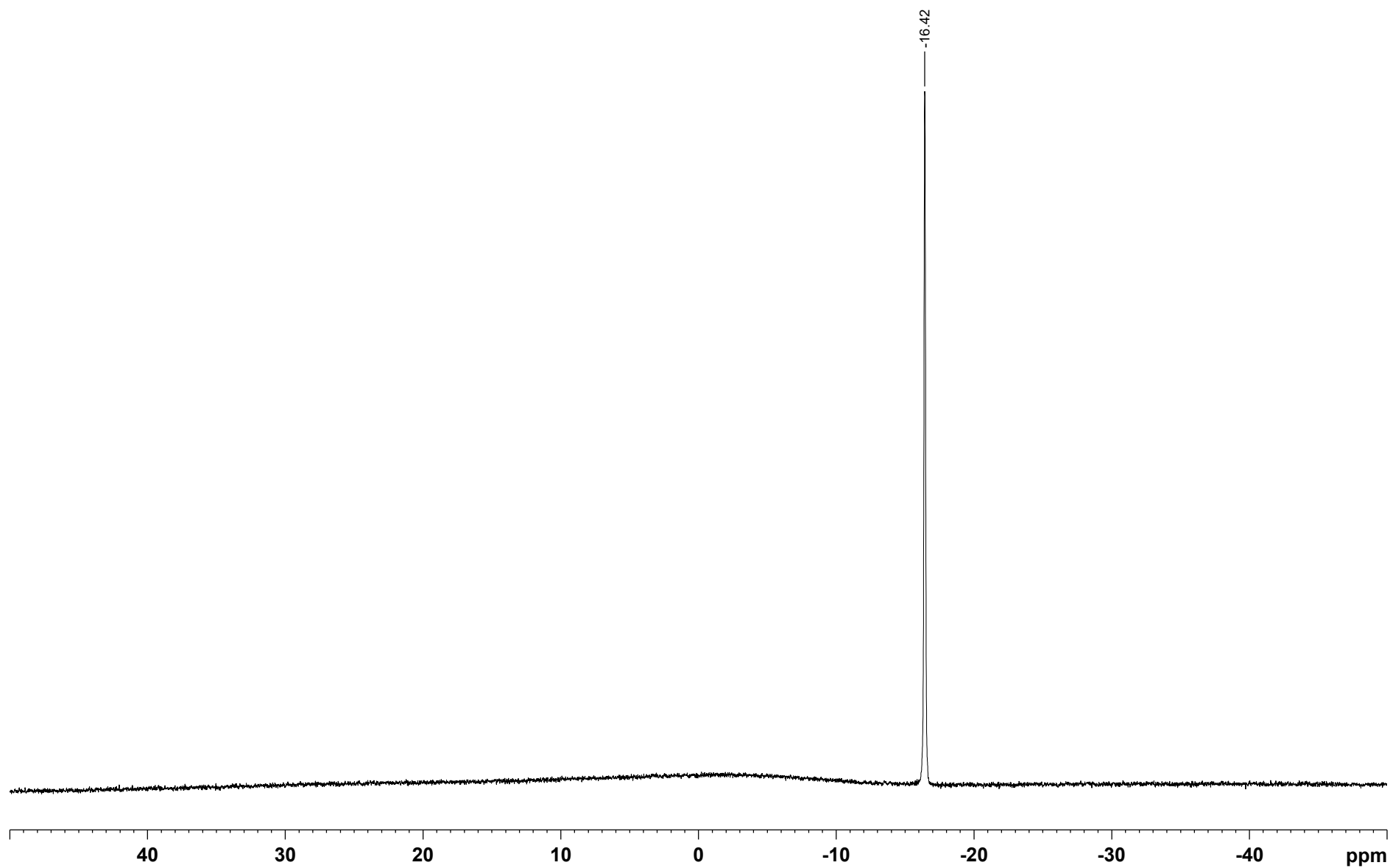
**Triphenylmethylium tetrakis(4-(((1*S*,2*S*,5*S*)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl)methyl)-2,3,5,6-tetrafluorophenyl)borate**  
**[Tr]<sup>+</sup>[3]<sup>-</sup>**

<sup>1</sup>H NMR (700 MHz, CD<sub>2</sub>Cl<sub>2</sub>):

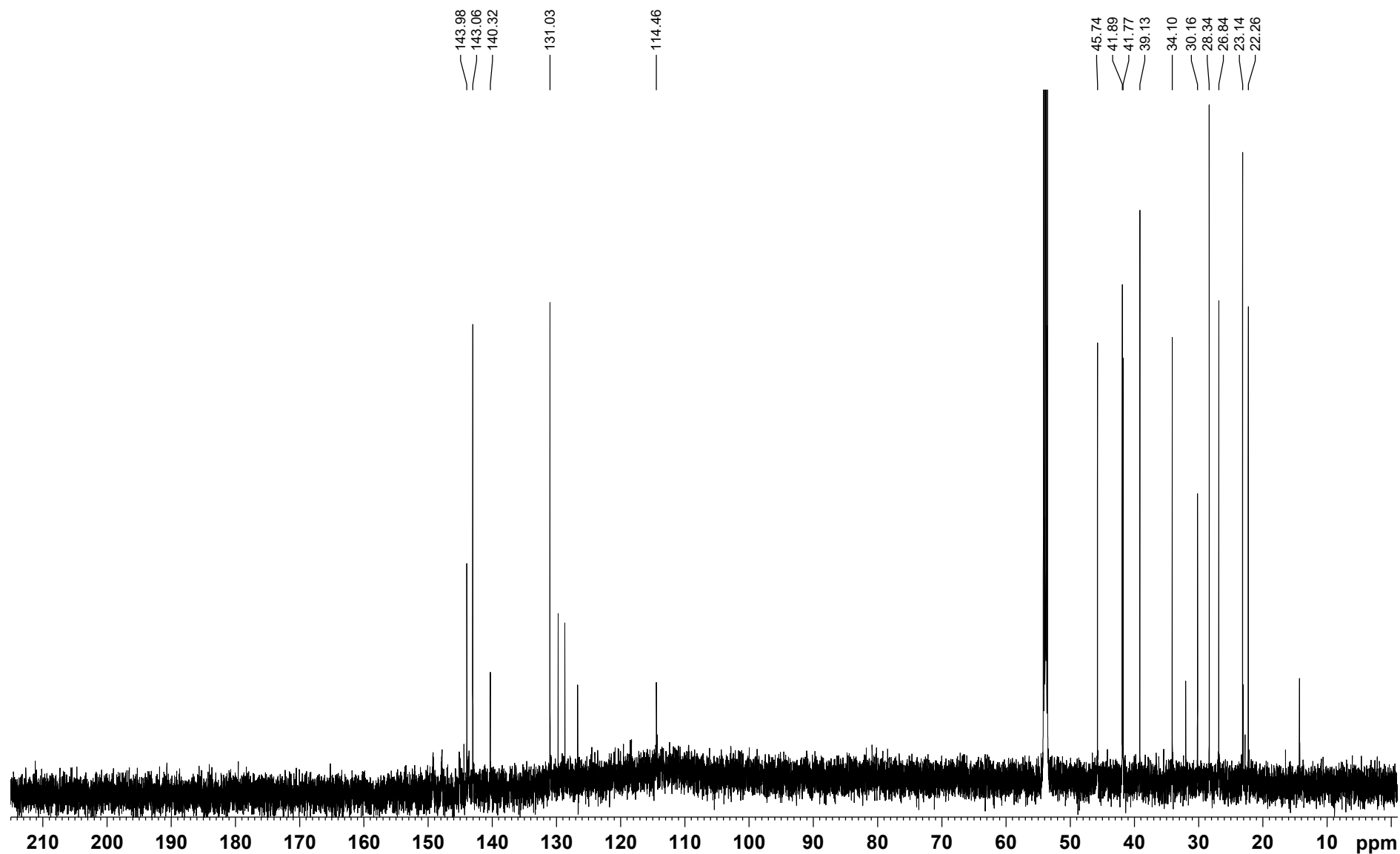




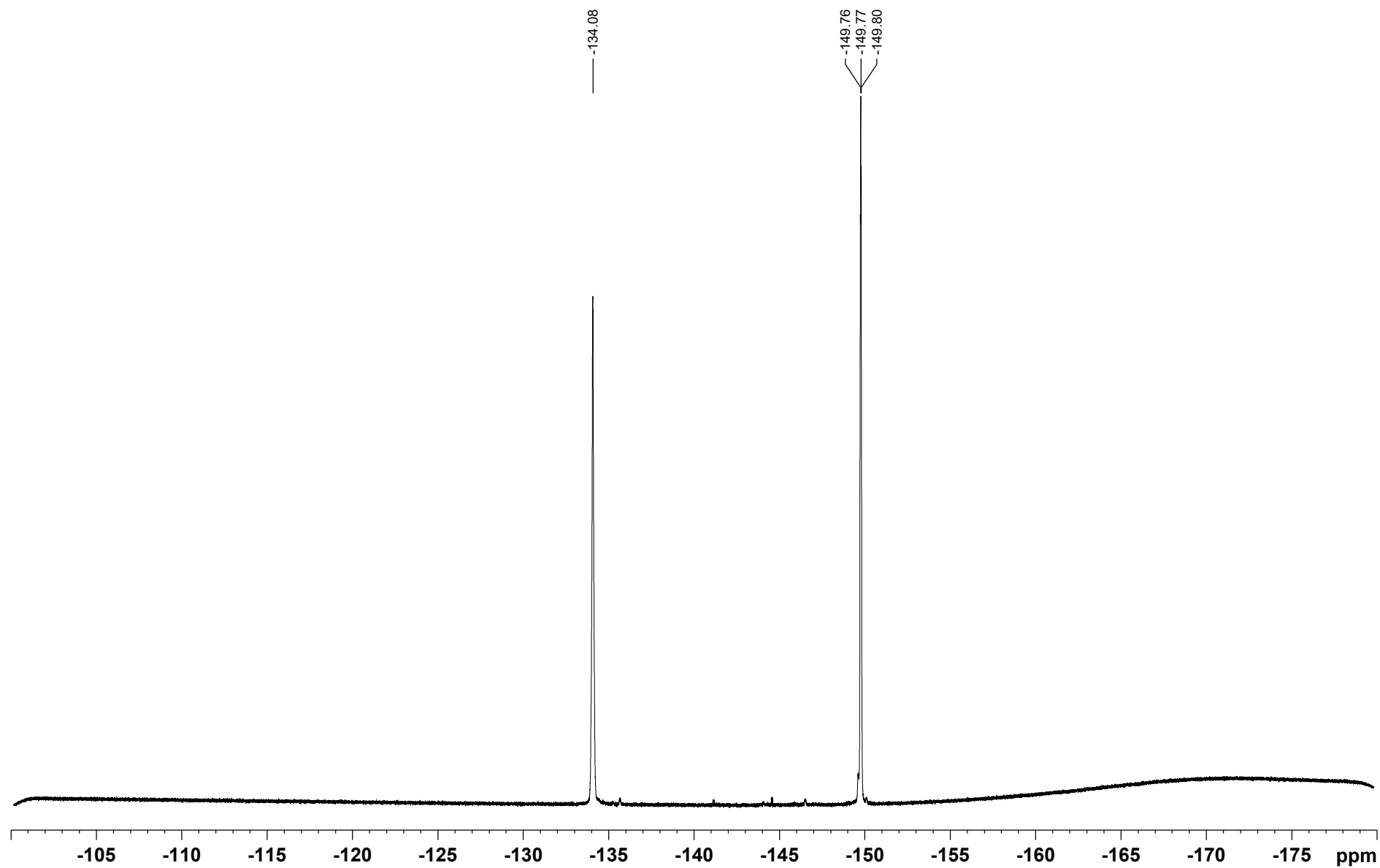
$^{11}\text{B}\{^1\text{H}\}$  NMR (161 MHz,  $\text{CD}_2\text{Cl}_2$ ):

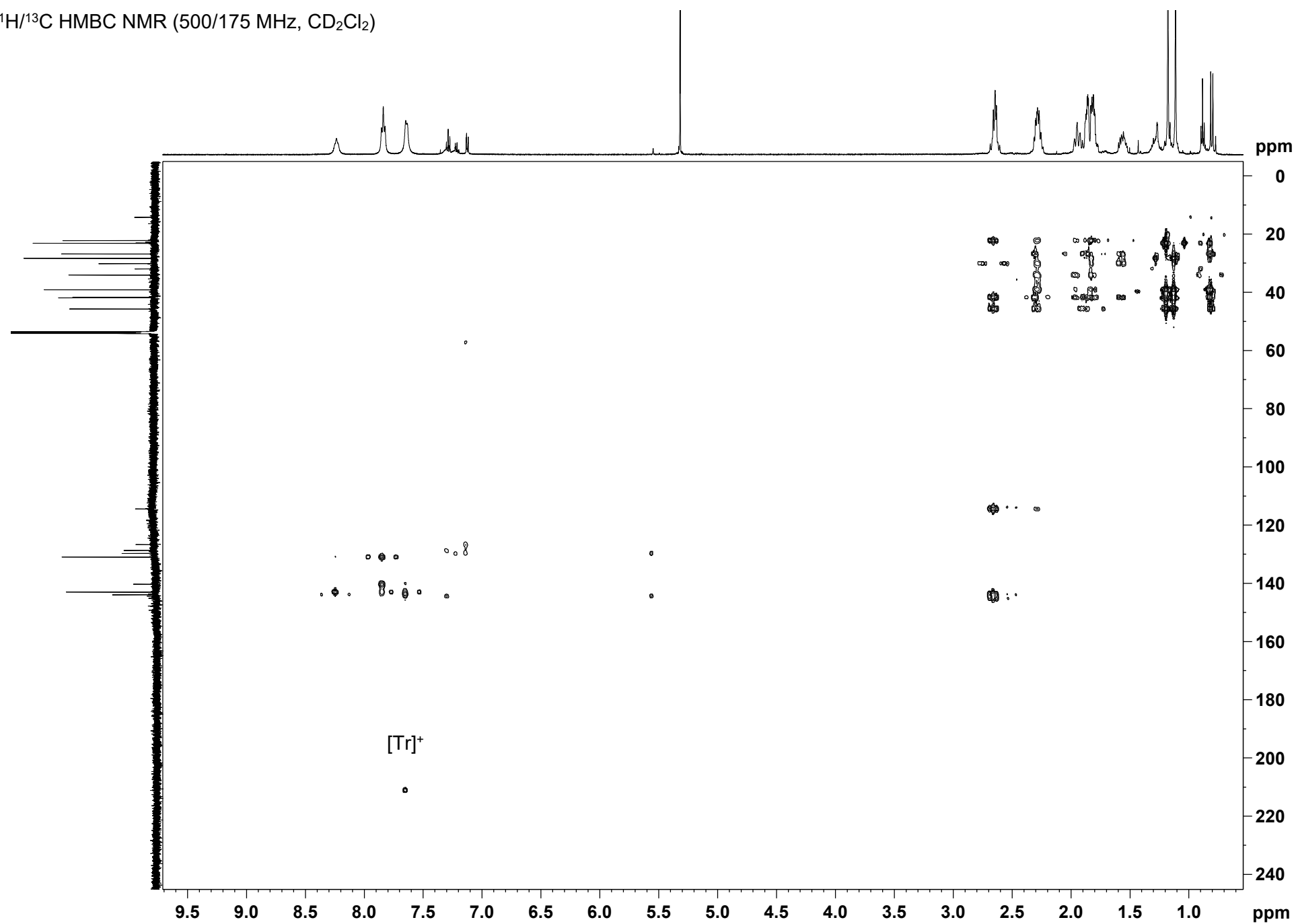


$^{13}\text{C}\{^1\text{H}\}$  NMR (176 MHz,  $\text{CD}_2\text{Cl}_2$ ):

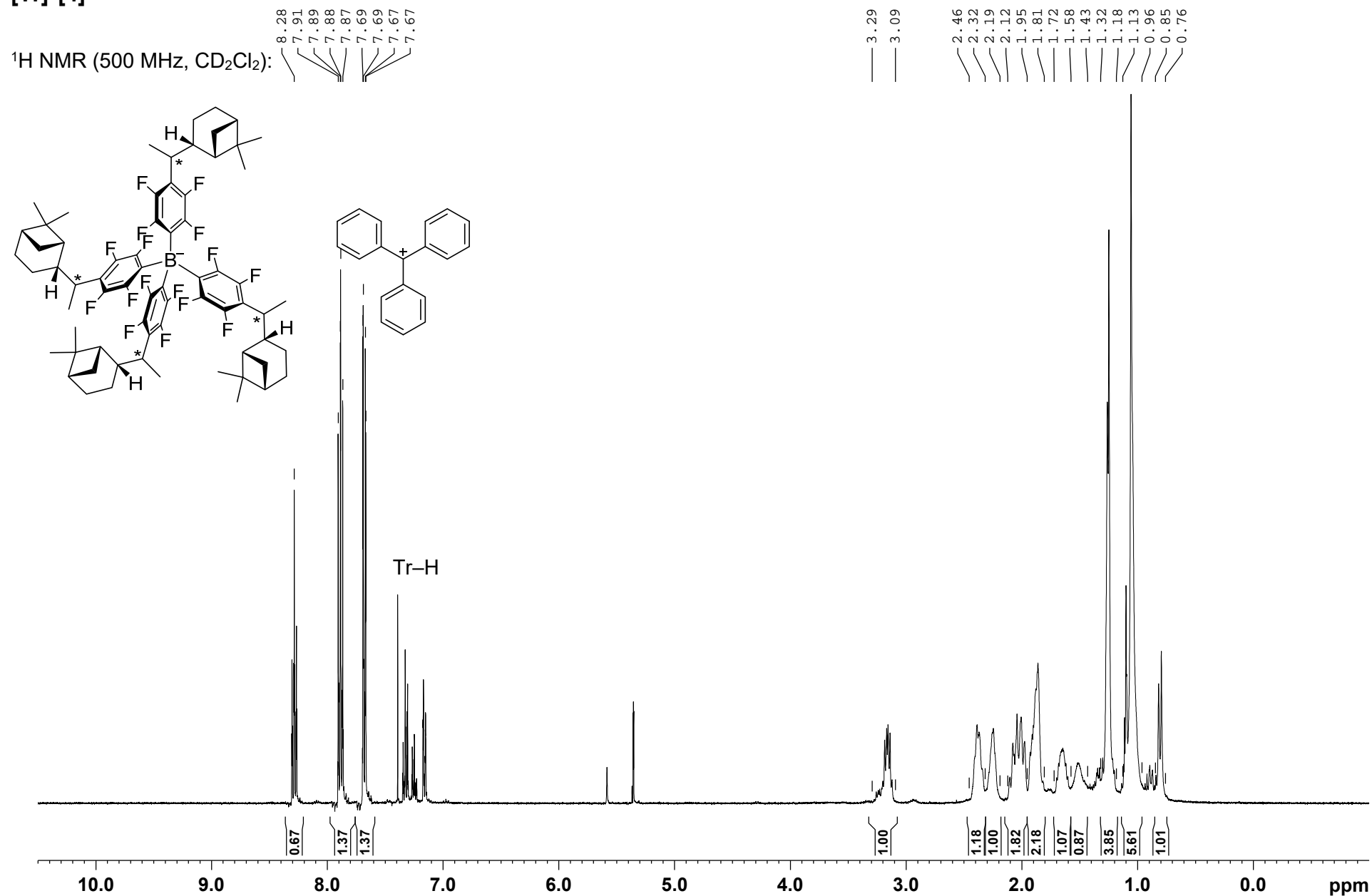


$^{19}\text{F}\{^1\text{H}\}$  NMR (471 MHz,  $\text{CD}_2\text{Cl}_2$ ):

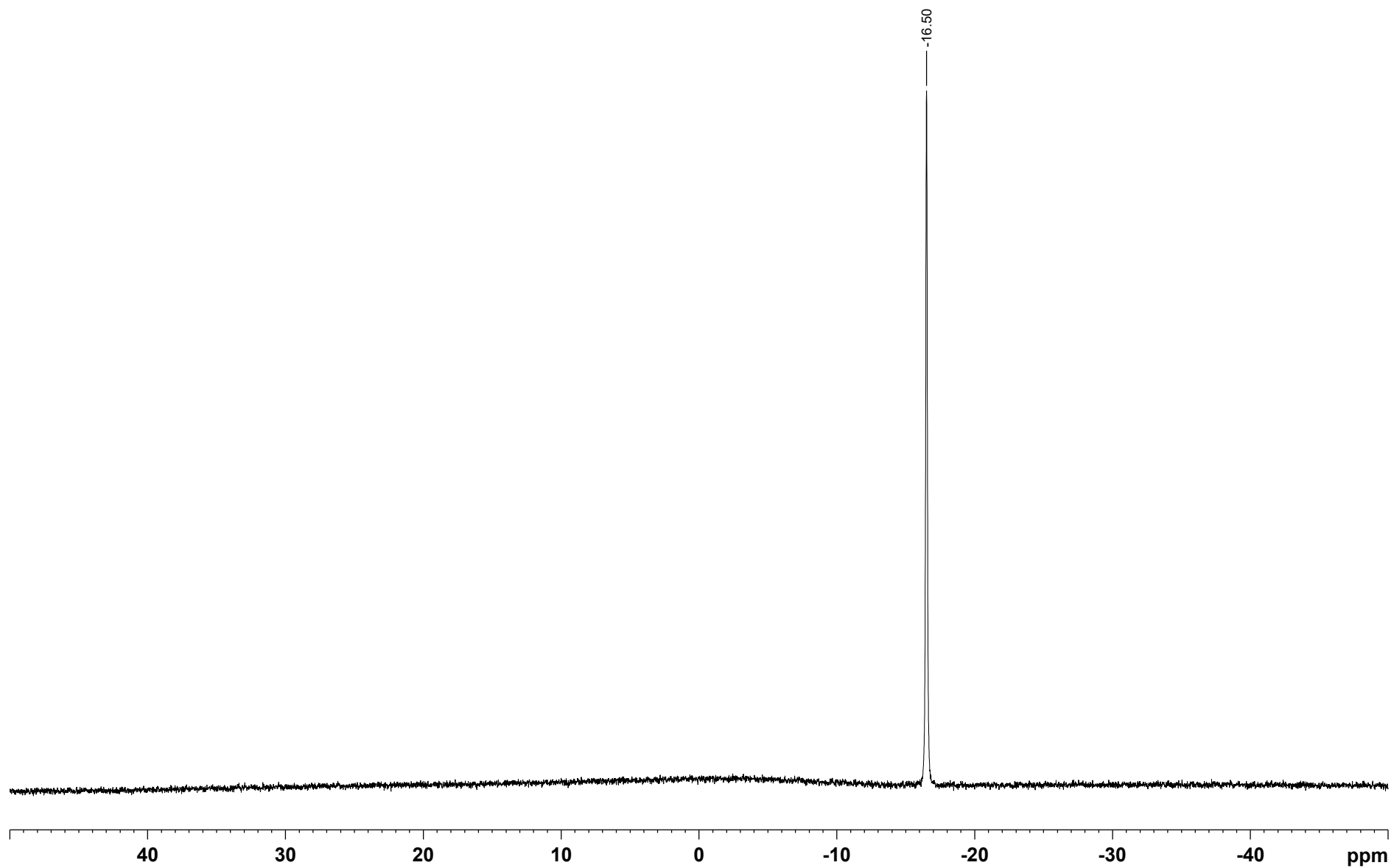


$^1\text{H}/^{13}\text{C}$  HMBC NMR (500/175 MHz,  $\text{CD}_2\text{Cl}_2$ )

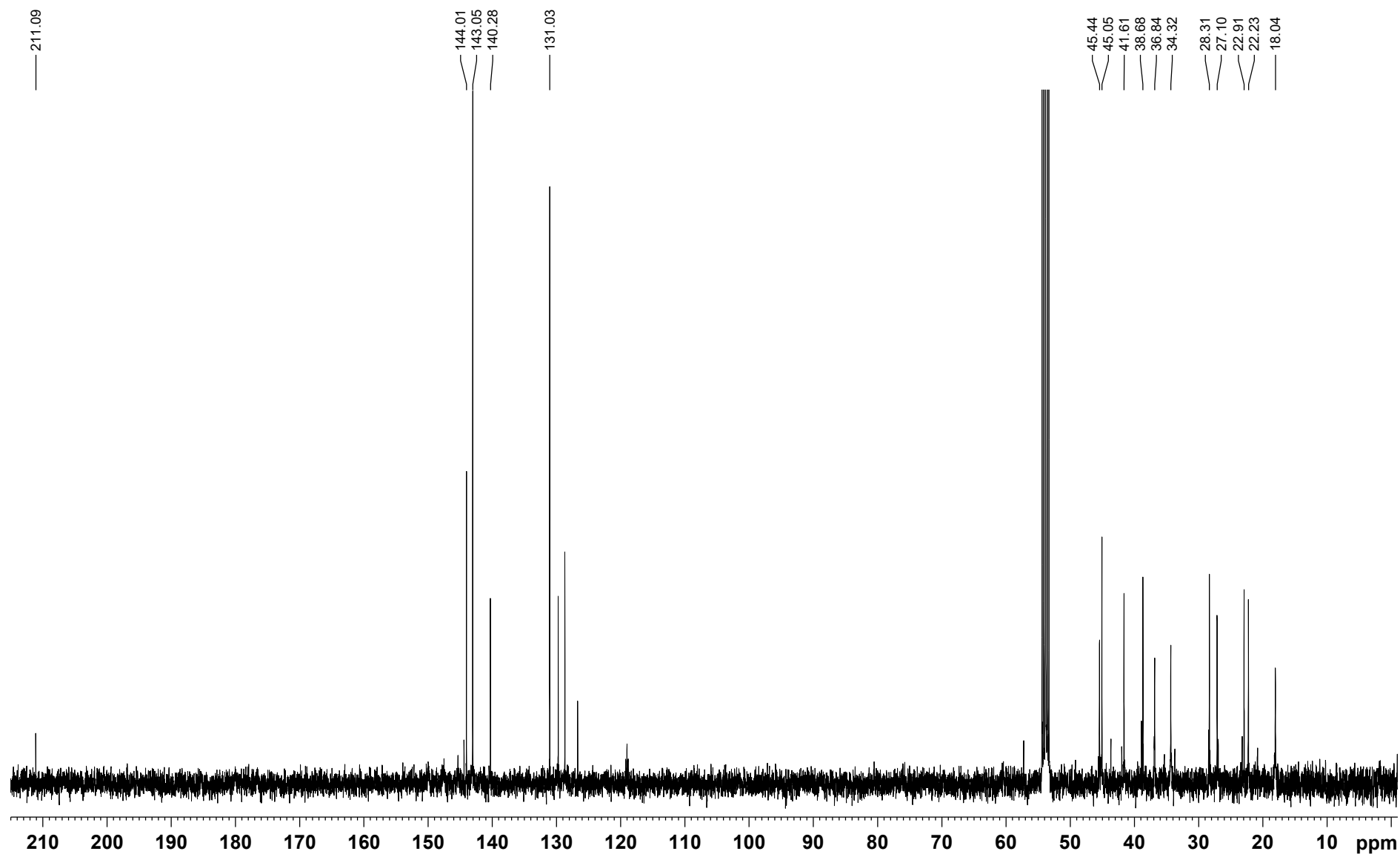
**Triphenylmethylium tetrakis(4-(1-((1*S*,2*S*,5*S*)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl)ethyl)-2,3,5,6-tetrafluorophenyl)borate**  
**[Tr]<sup>+</sup>[4]<sup>-</sup>**



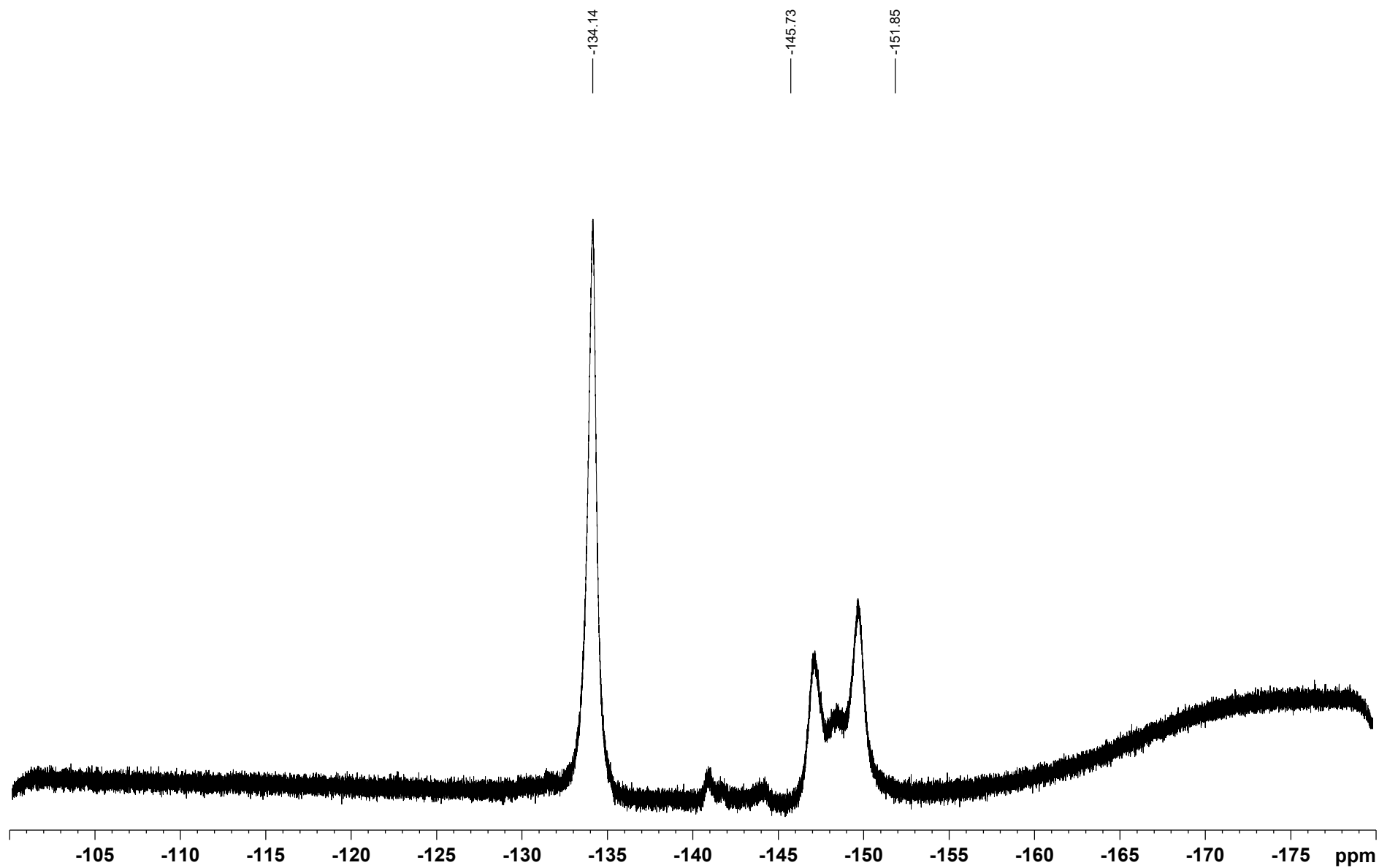
$^{11}\text{B}\{^1\text{H}\}$  NMR (161 MHz,  $\text{CD}_2\text{Cl}_2$ ):



$^{13}\text{C}\{^1\text{H}\}$  NMR (176 MHz,  $\text{CD}_2\text{Cl}_2$ ):



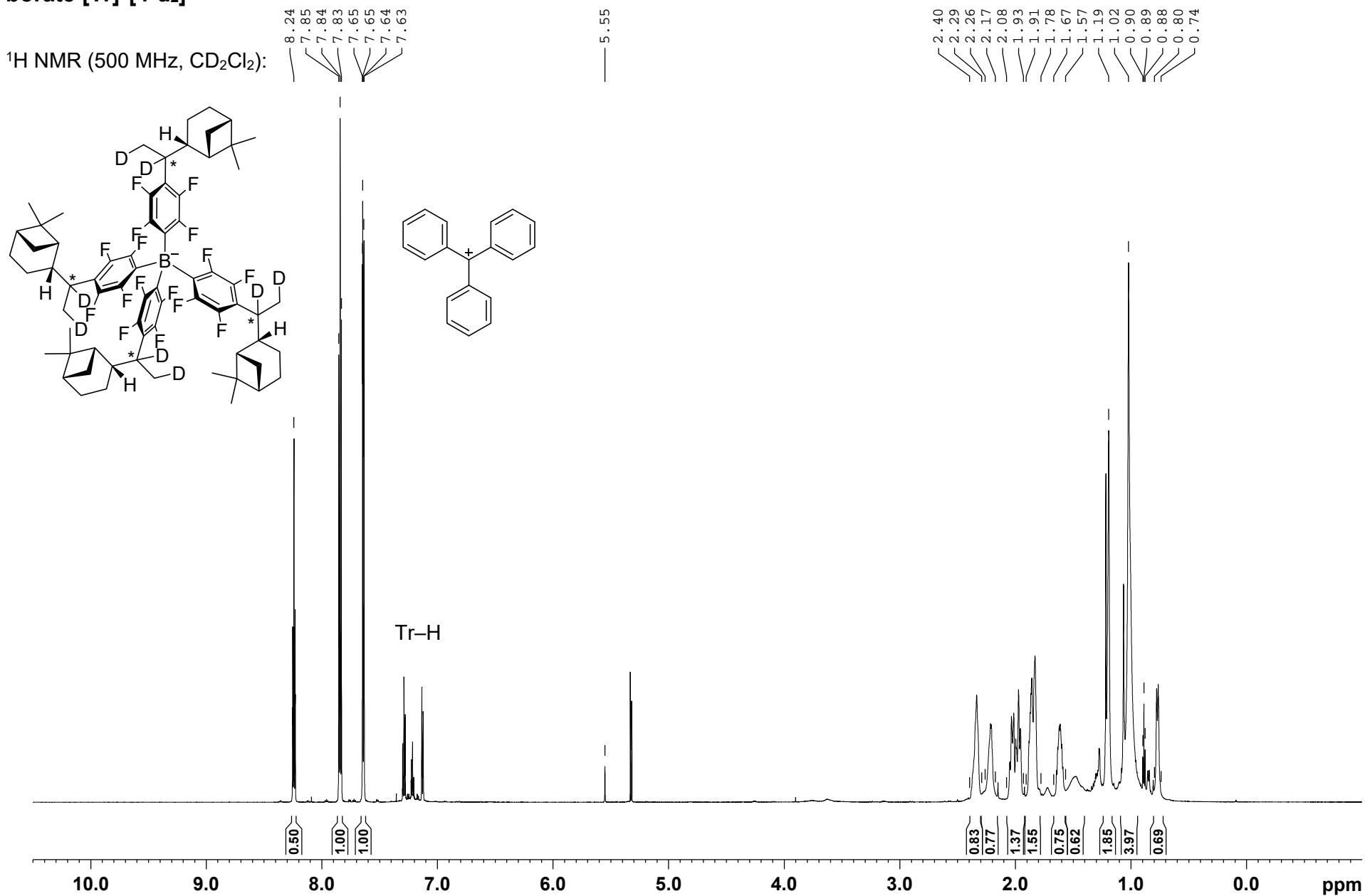
$^{19}\text{F}$  NMR (471 MHz,  $\text{CD}_2\text{Cl}_2$ ):



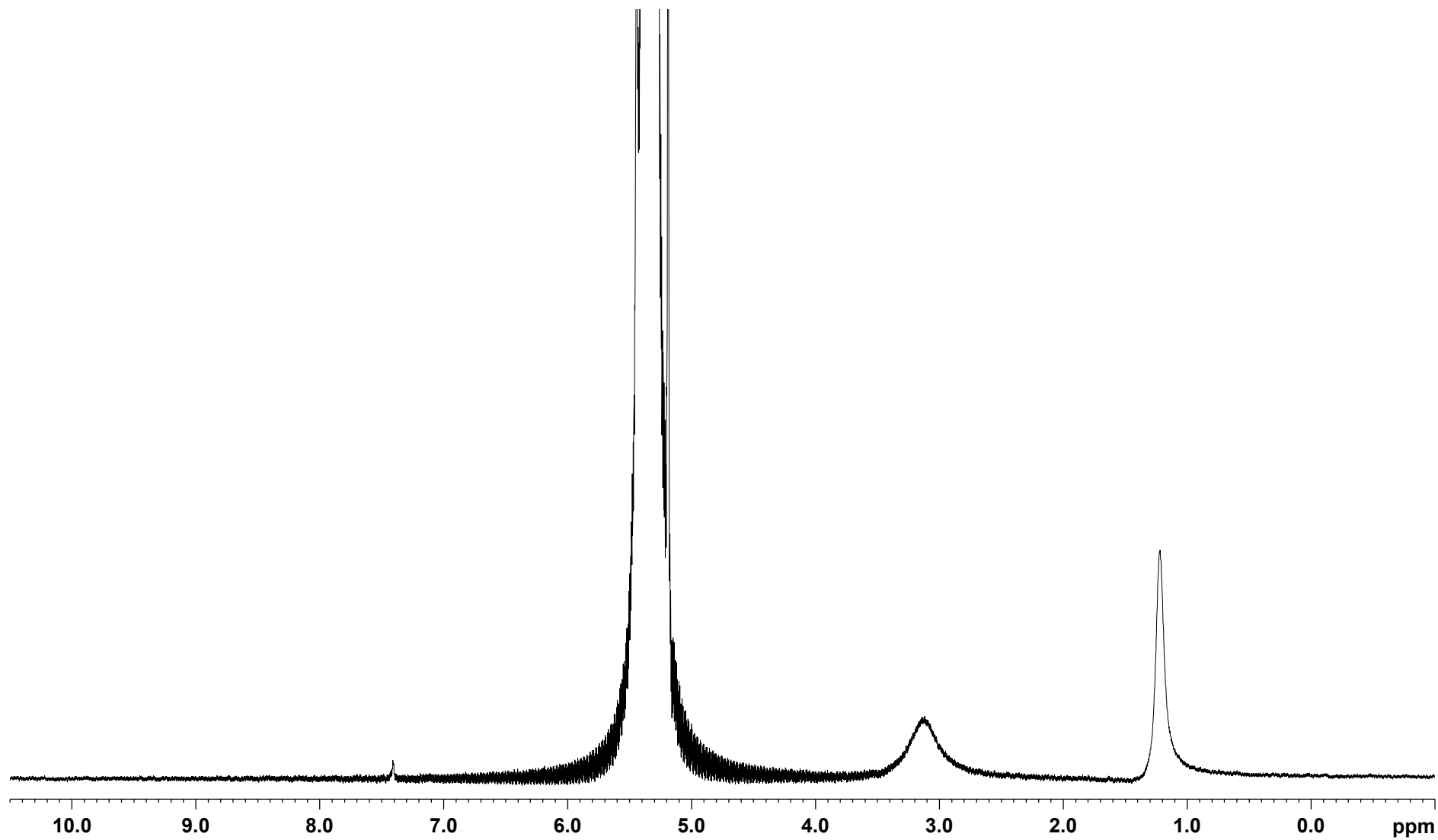


**Triphenylmethylium tetrakis(4-(1-((1*S*,2*S*,5*S*)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl)ethyl-1,2-*d*<sub>2</sub>)-2,3,5,6-tetrafluorophenyl)-borate [Tr]<sup>+</sup>[4-*d*<sub>2</sub>]<sup>-</sup>**

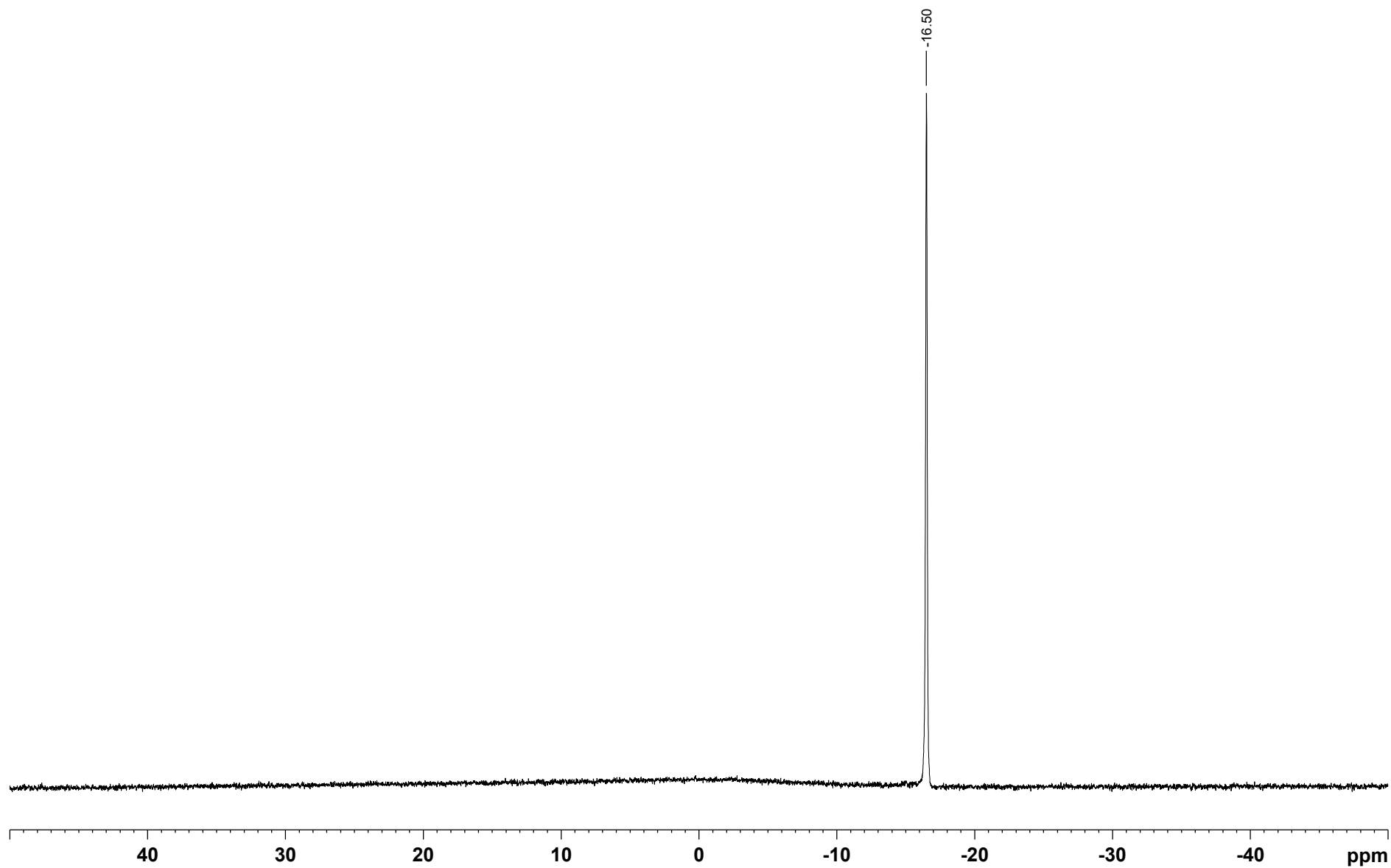
<sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>):



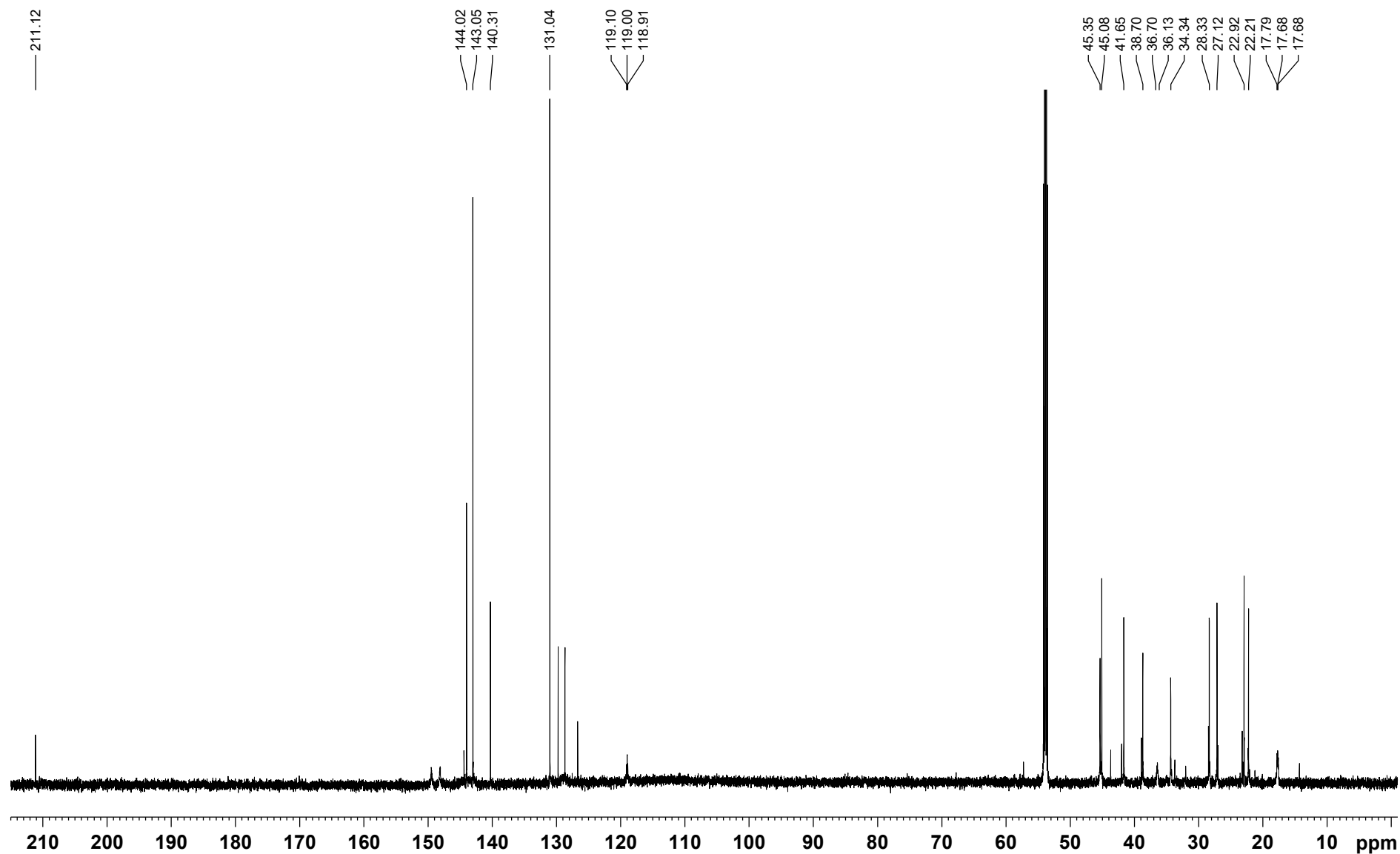
$^2\text{H}$  NMR (107 MHz,  $\text{CD}_2\text{Cl}_2$ )



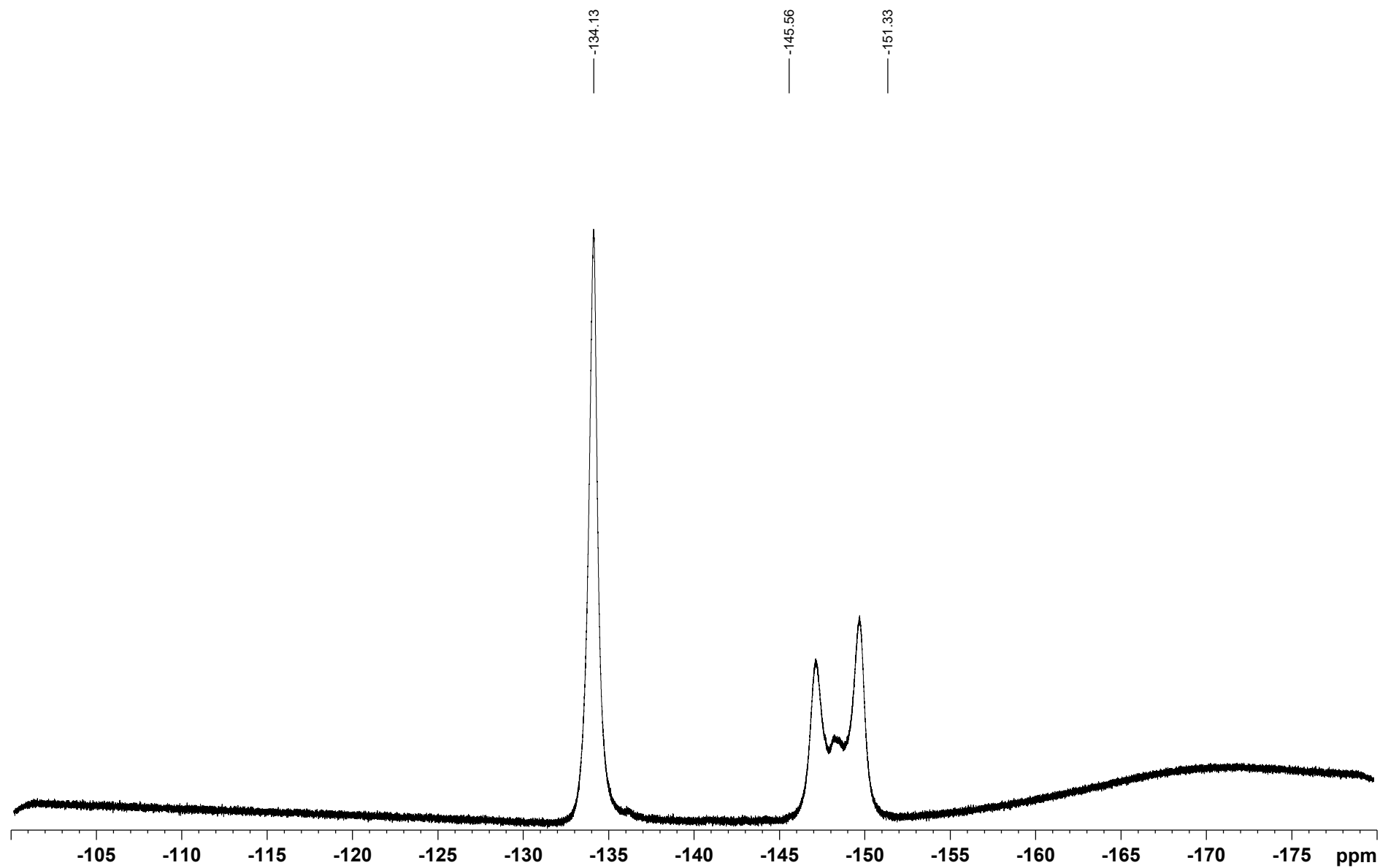
$^{11}\text{B}\{^1\text{H}\}$  NMR (161 MHz,  $\text{CD}_2\text{Cl}_2$ ):



$^{13}\text{C}\{^1\text{H}\}$  NMR (176 MHz,  $\text{CD}_2\text{Cl}_2$ ):

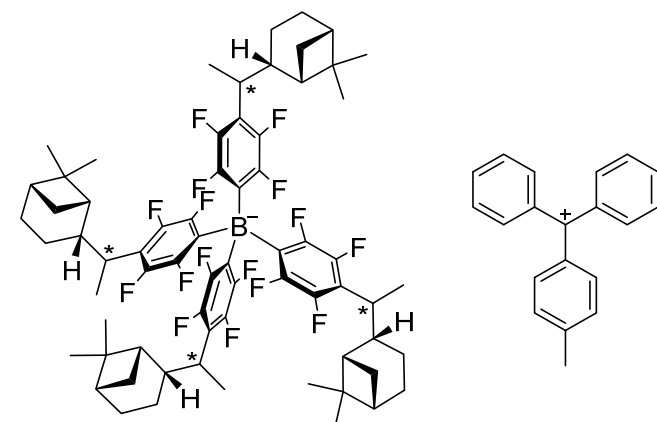


$^{19}\text{F}$  NMR (471 MHz,  $\text{CD}_2\text{Cl}_2$ ):

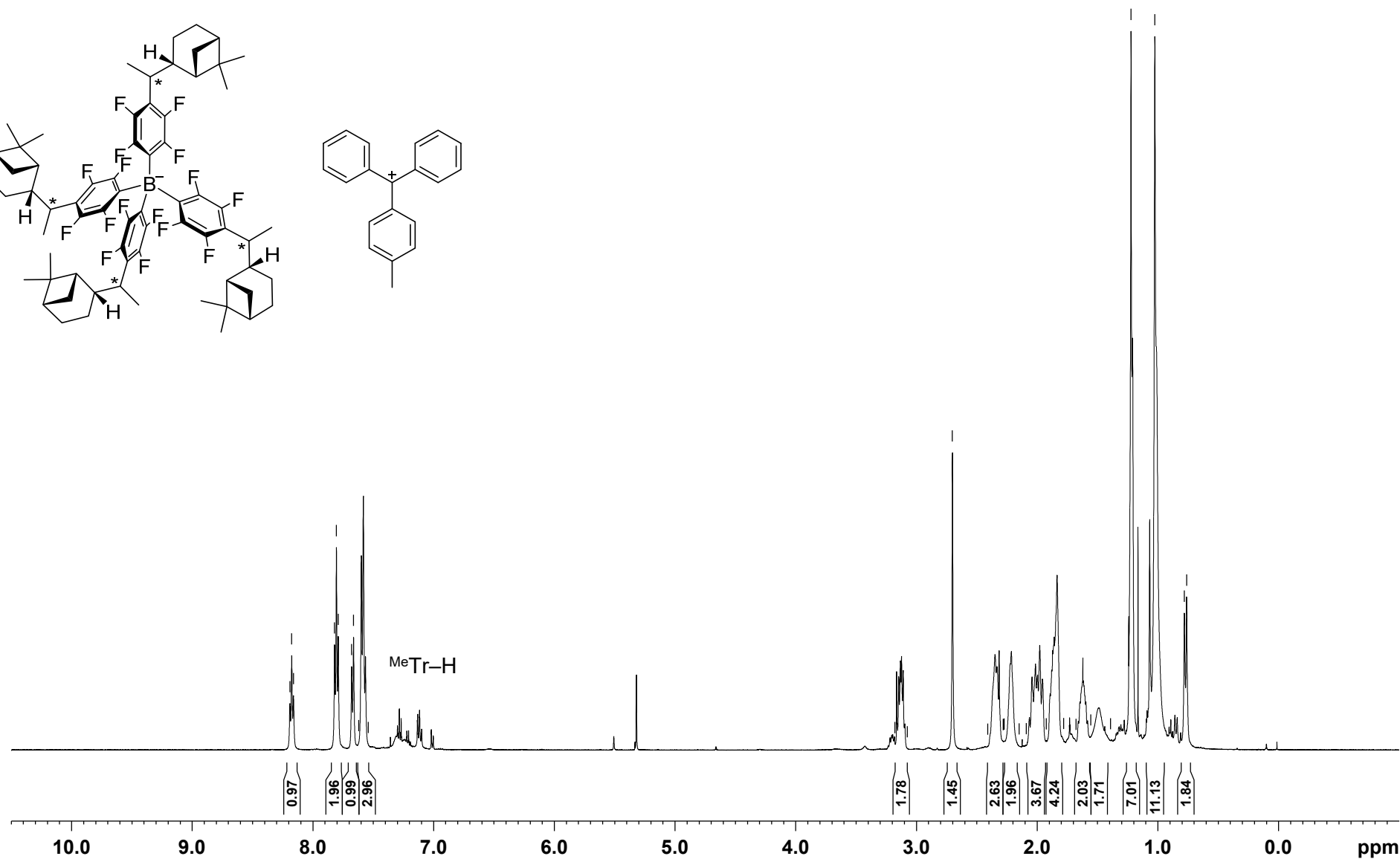


**Diphenyl(4-tolyl)methylium tetrakis(4-(1-((1S,2S,5S)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl)ethyl)-2,3,5,6-tetrafluorophenyl)-borate [MeTr]<sup>+</sup>[4]<sup>-</sup>**

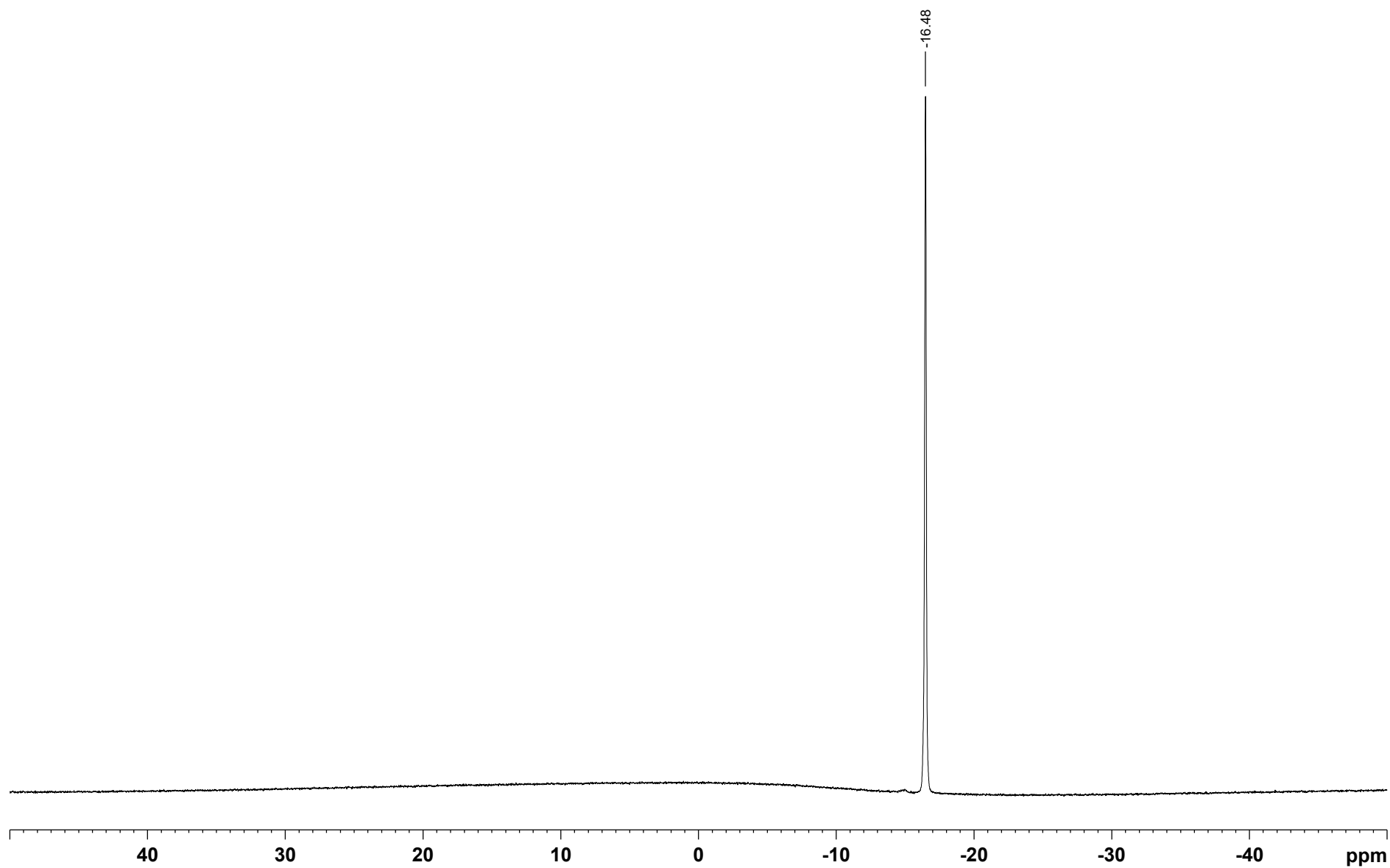
<sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>):



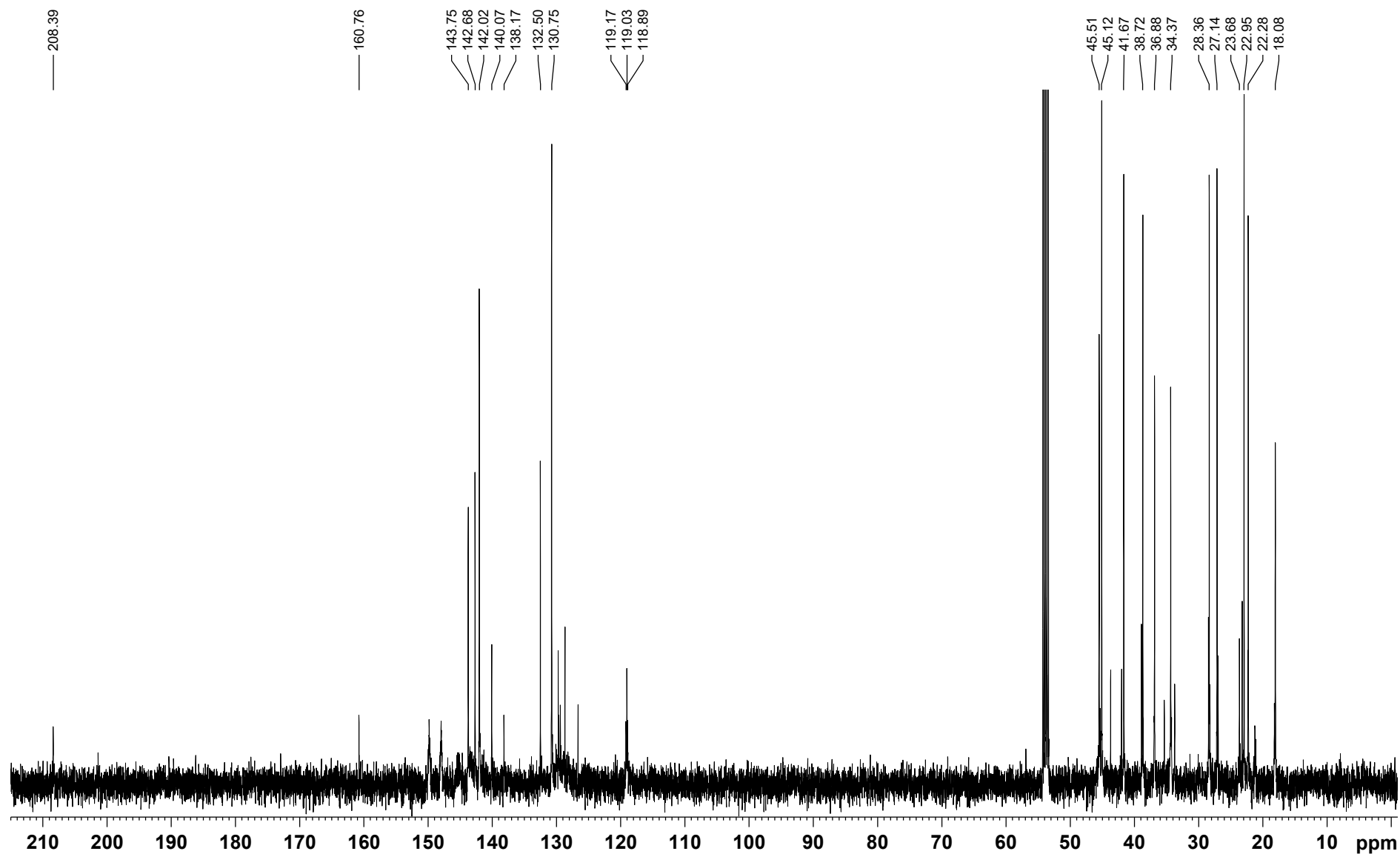
8.19  
8.18  
8.16  
7.82  
7.81  
7.79  
7.68  
7.66  
7.62  
7.54  
3.18  
3.08  
2.70  
2.41  
2.28  
2.27  
2.15  
2.09  
1.92  
1.78  
1.68  
1.56  
1.39  
1.22  
1.03  
0.78  
0.76



$^{11}\text{B}\{^1\text{H}\}$  NMR (161 MHz,  $\text{CD}_2\text{Cl}_2$ ):

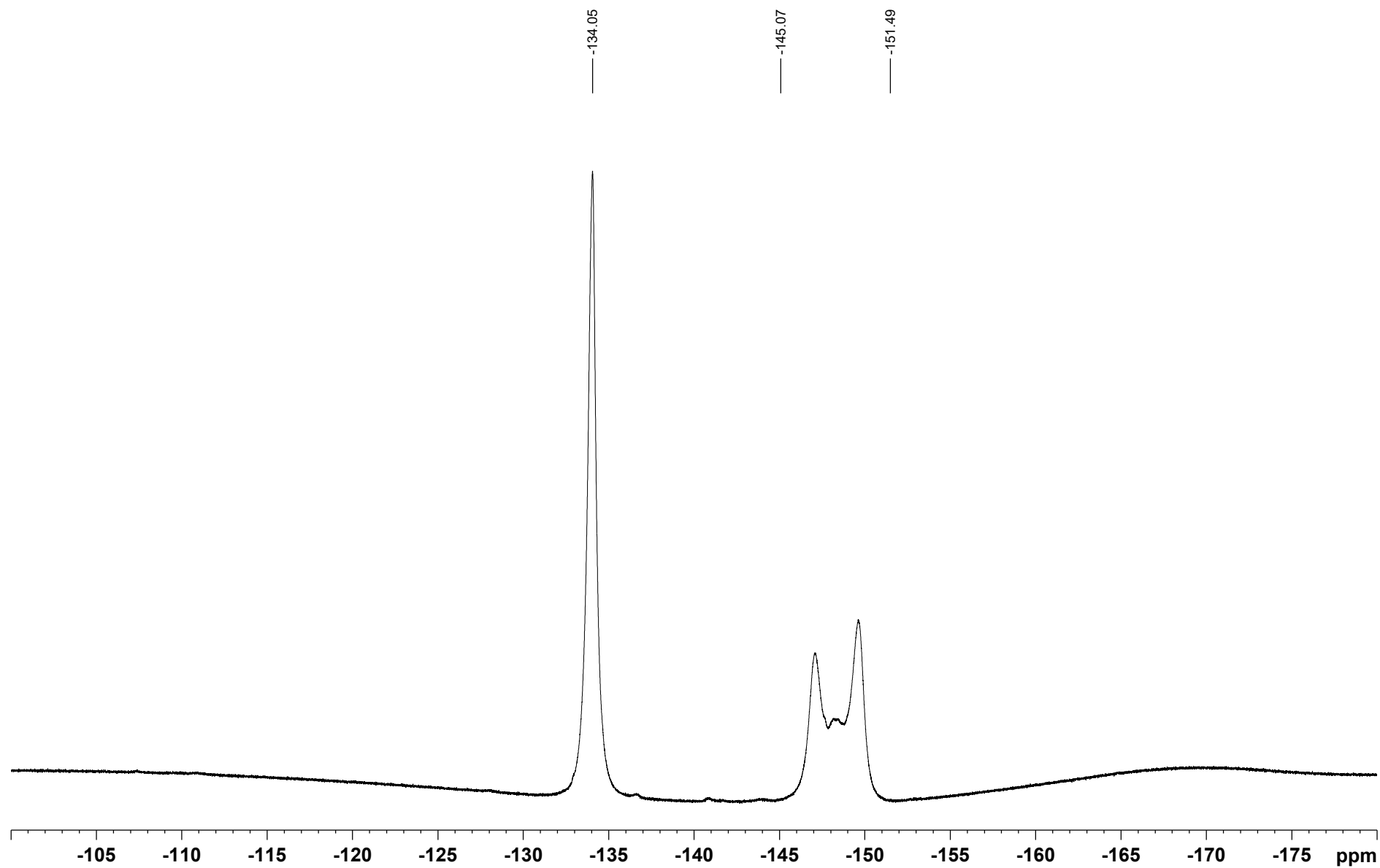


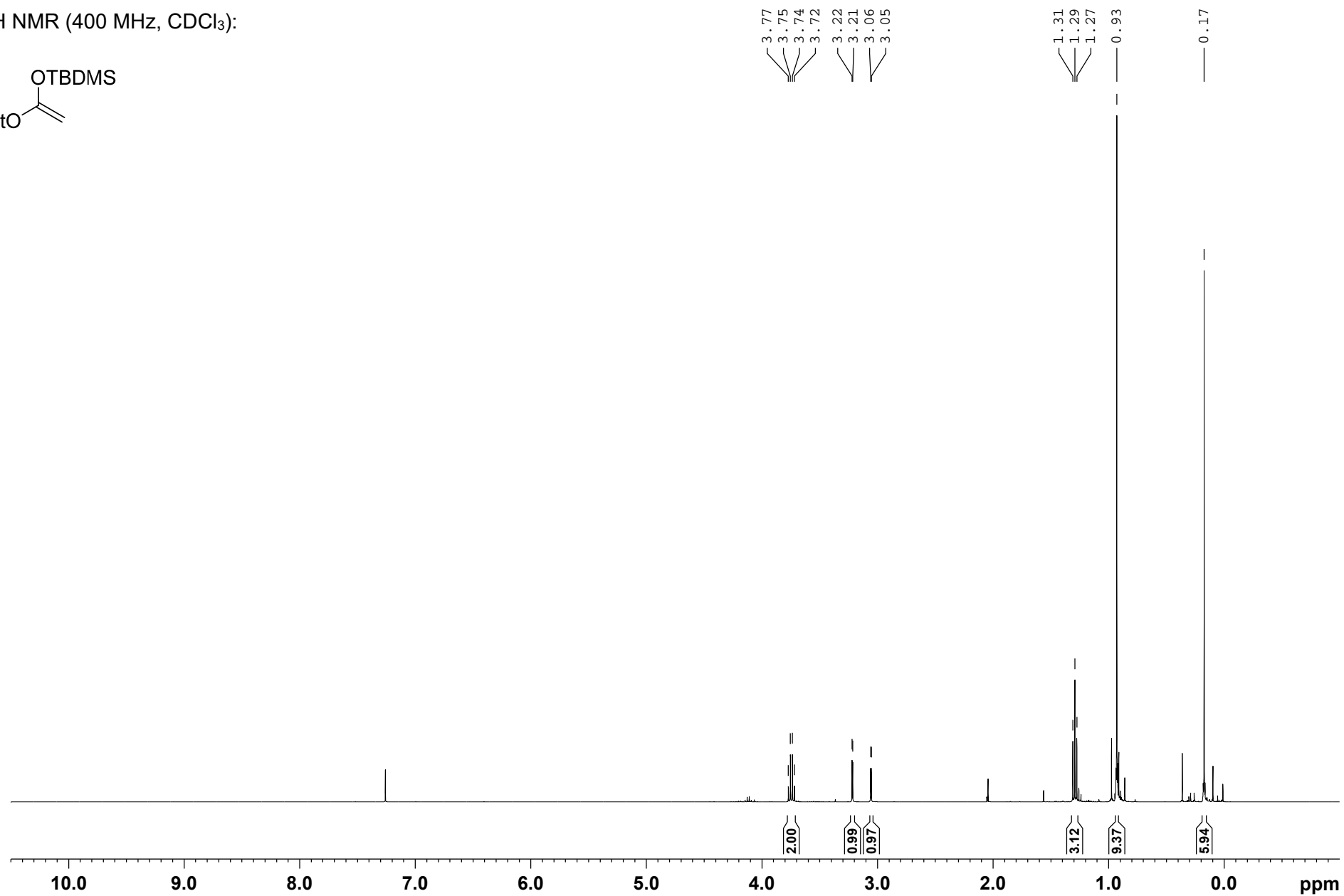
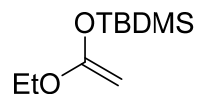
$^{13}\text{C}\{^1\text{H}\}$  NMR (176 MHz,  $\text{CD}_2\text{Cl}_2$ ):

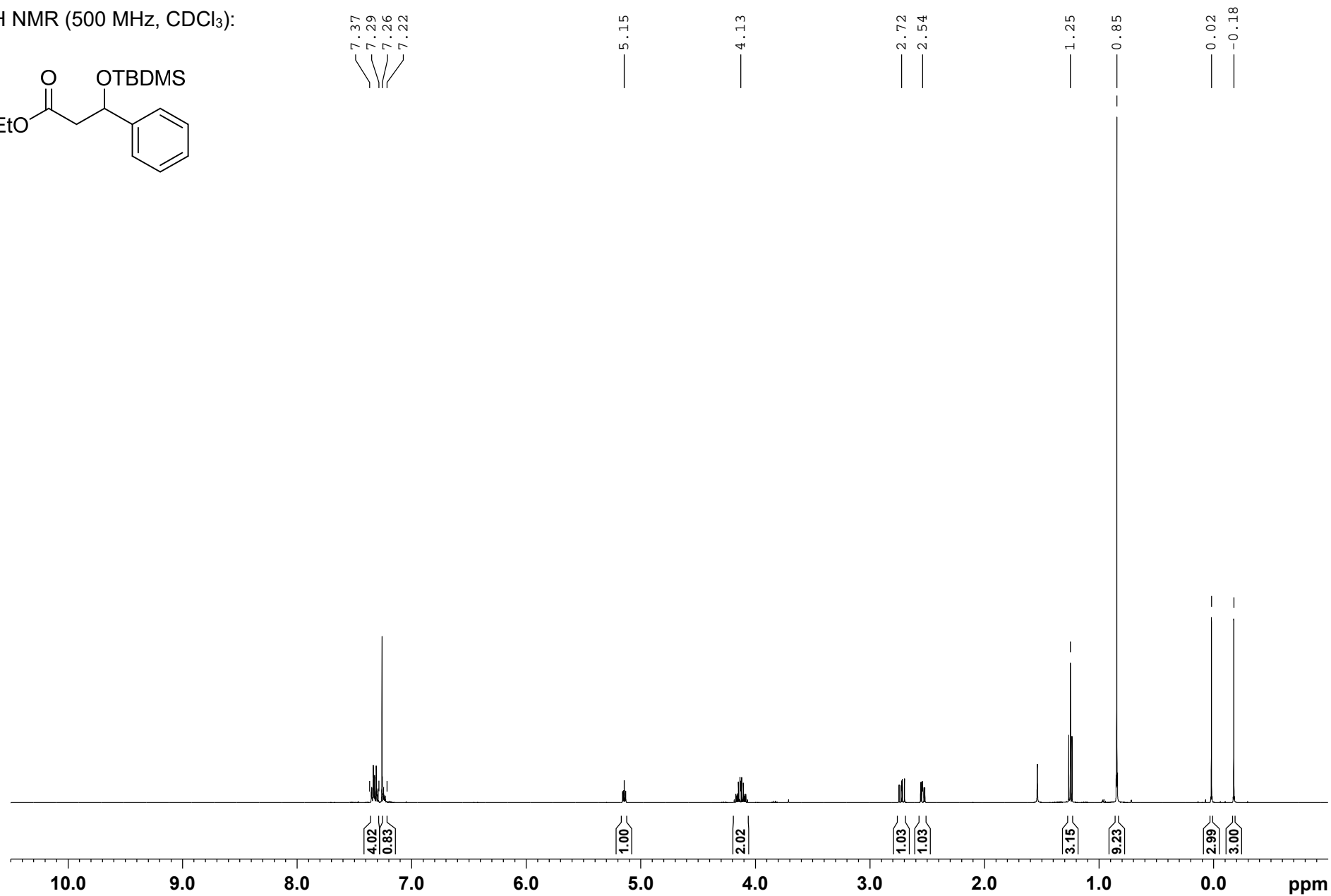
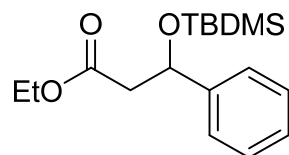




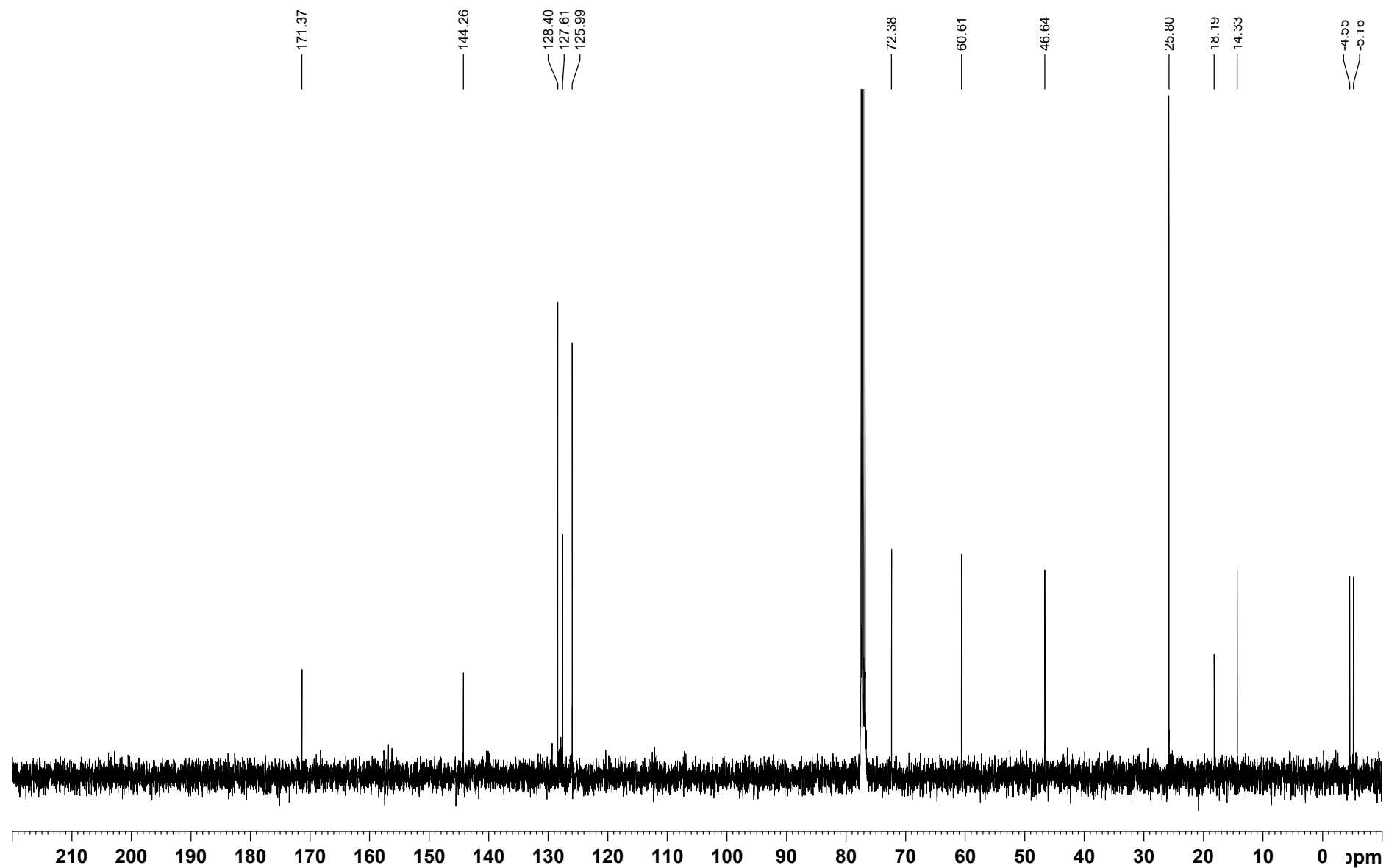
$^{19}\text{F}$  NMR (471 MHz,  $\text{CD}_2\text{Cl}_2$ ):



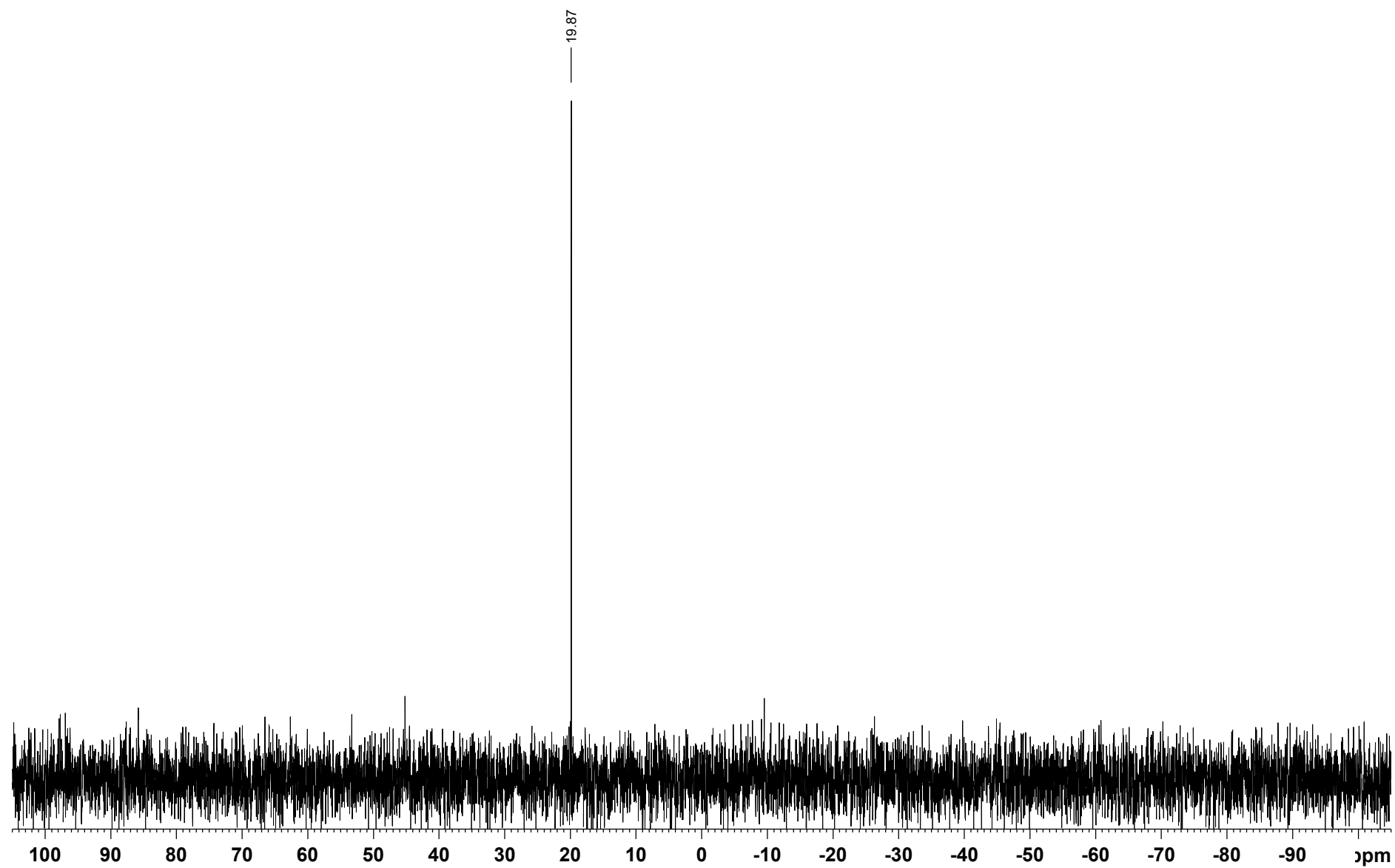
***tert*-Butyl((1-ethoxyvinyl)oxy)dimethylsilane (18)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):

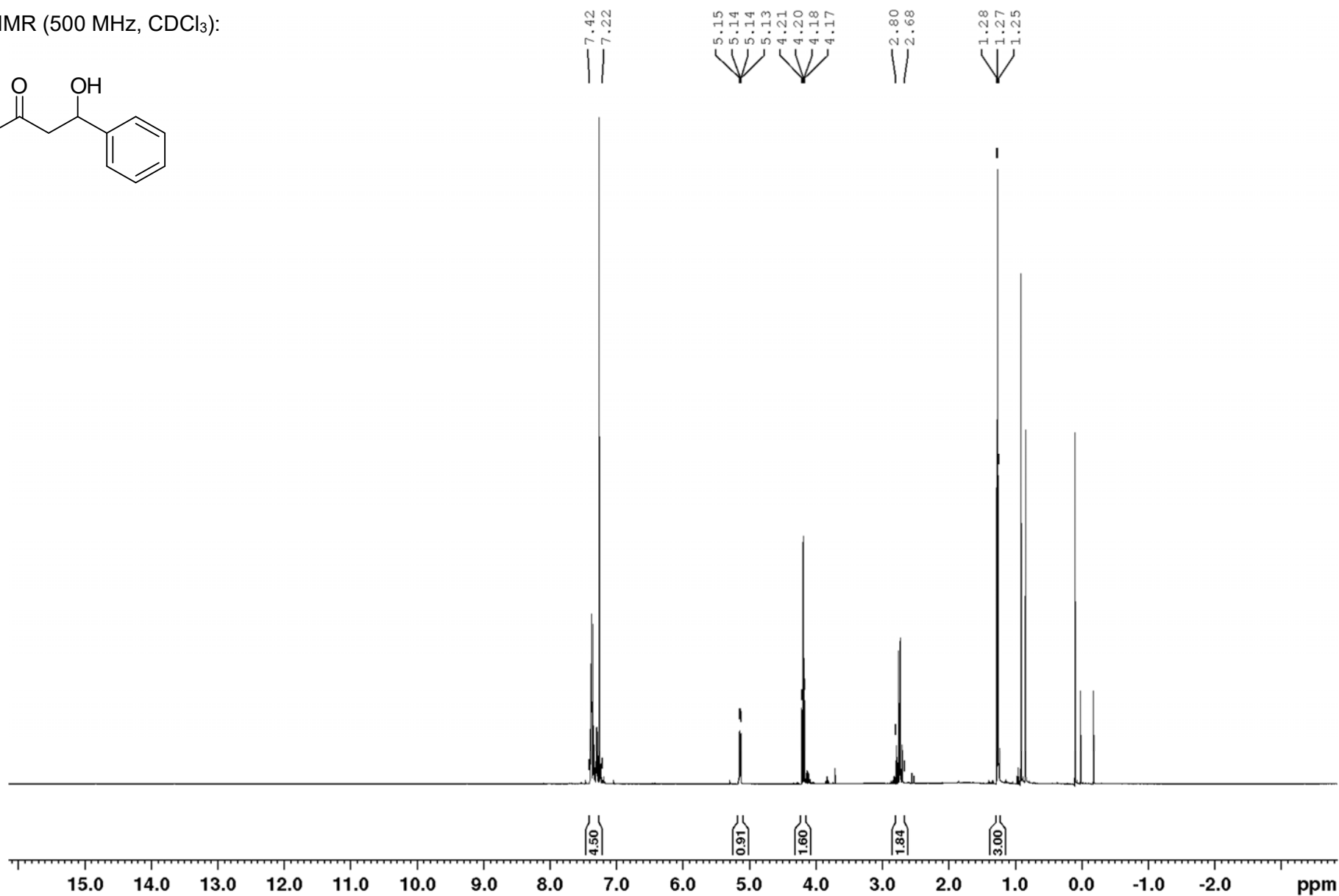
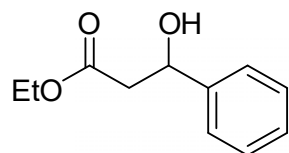
**Ethyl 3-((*tert*-butyldimethylsilyl)oxy)-3-phenylpropanoate (20)**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):

$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):

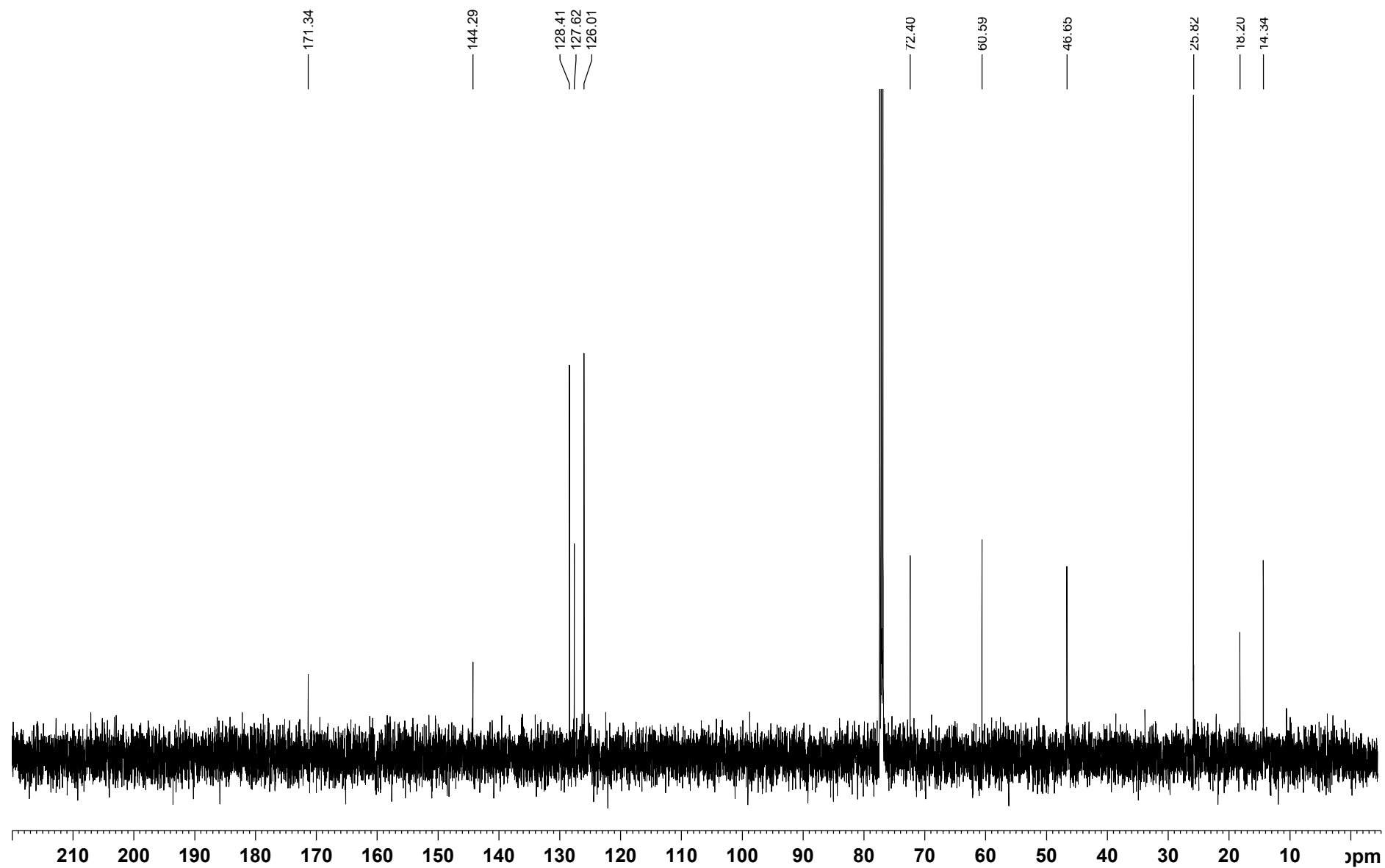


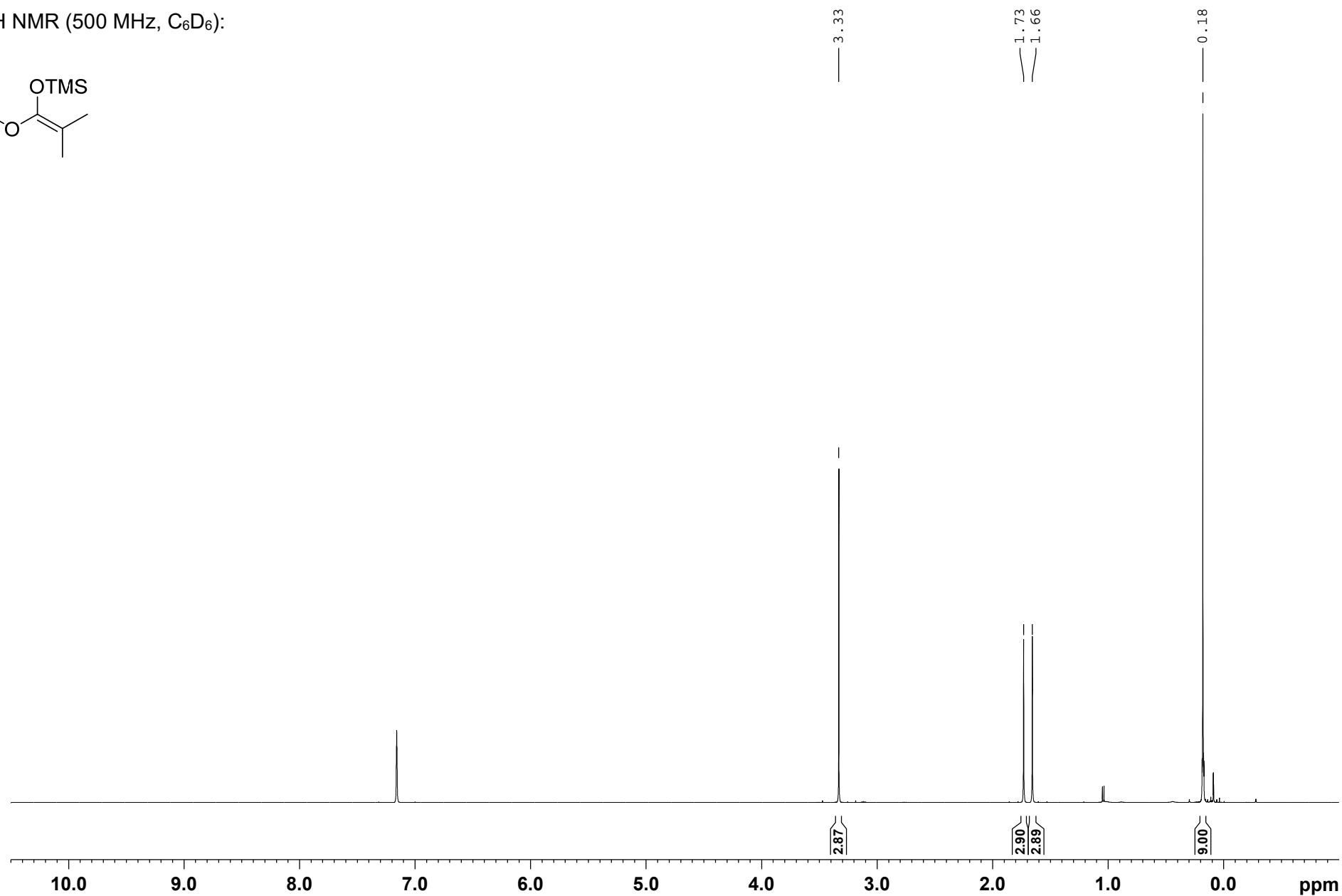
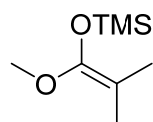
$^{29}\text{Si}$  DEPT NMR (99 MHz,  $\text{CDCl}_3$ ):



**Ethyl 3-hydroxy-3-phenylpropanoate**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):

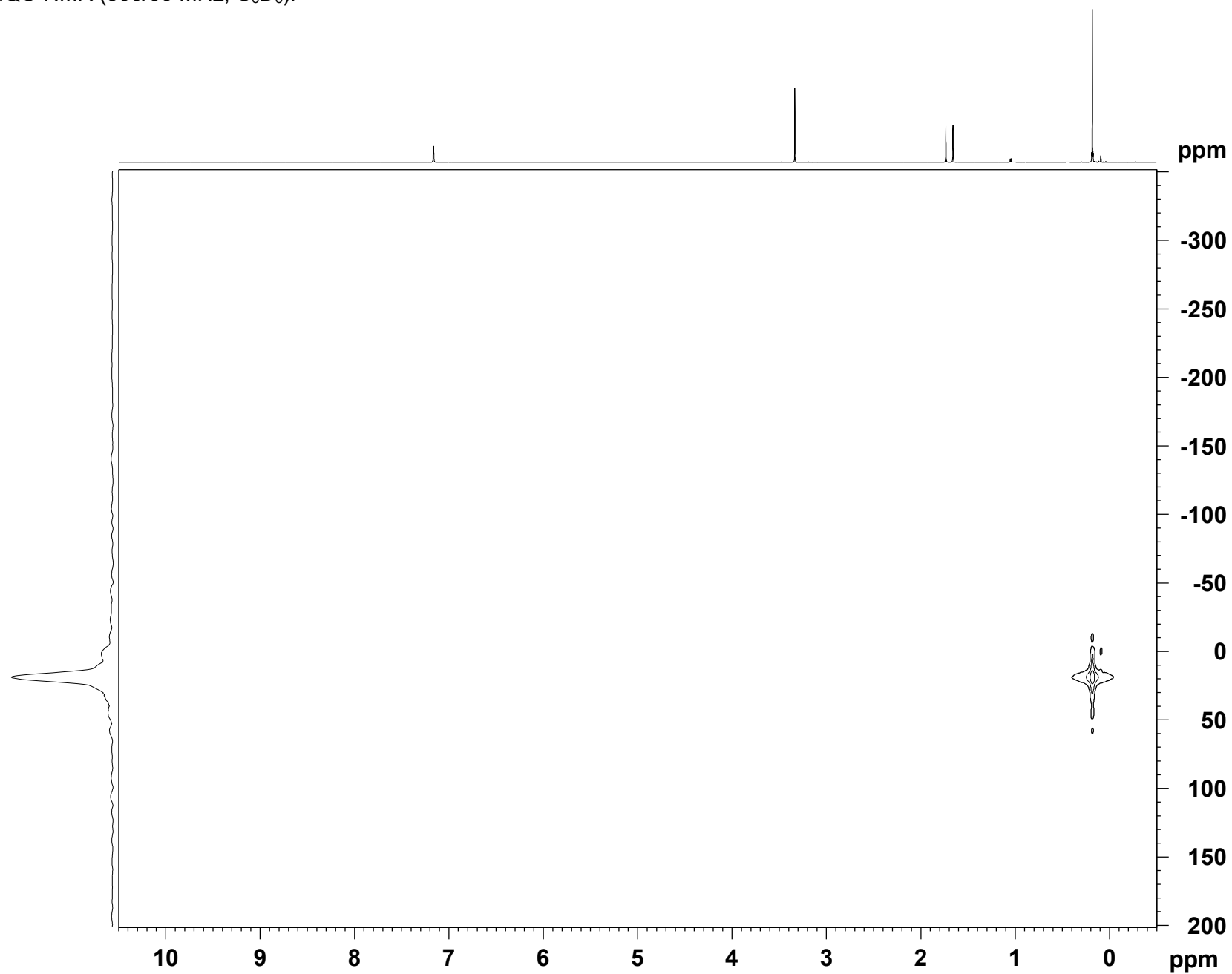
$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ ):

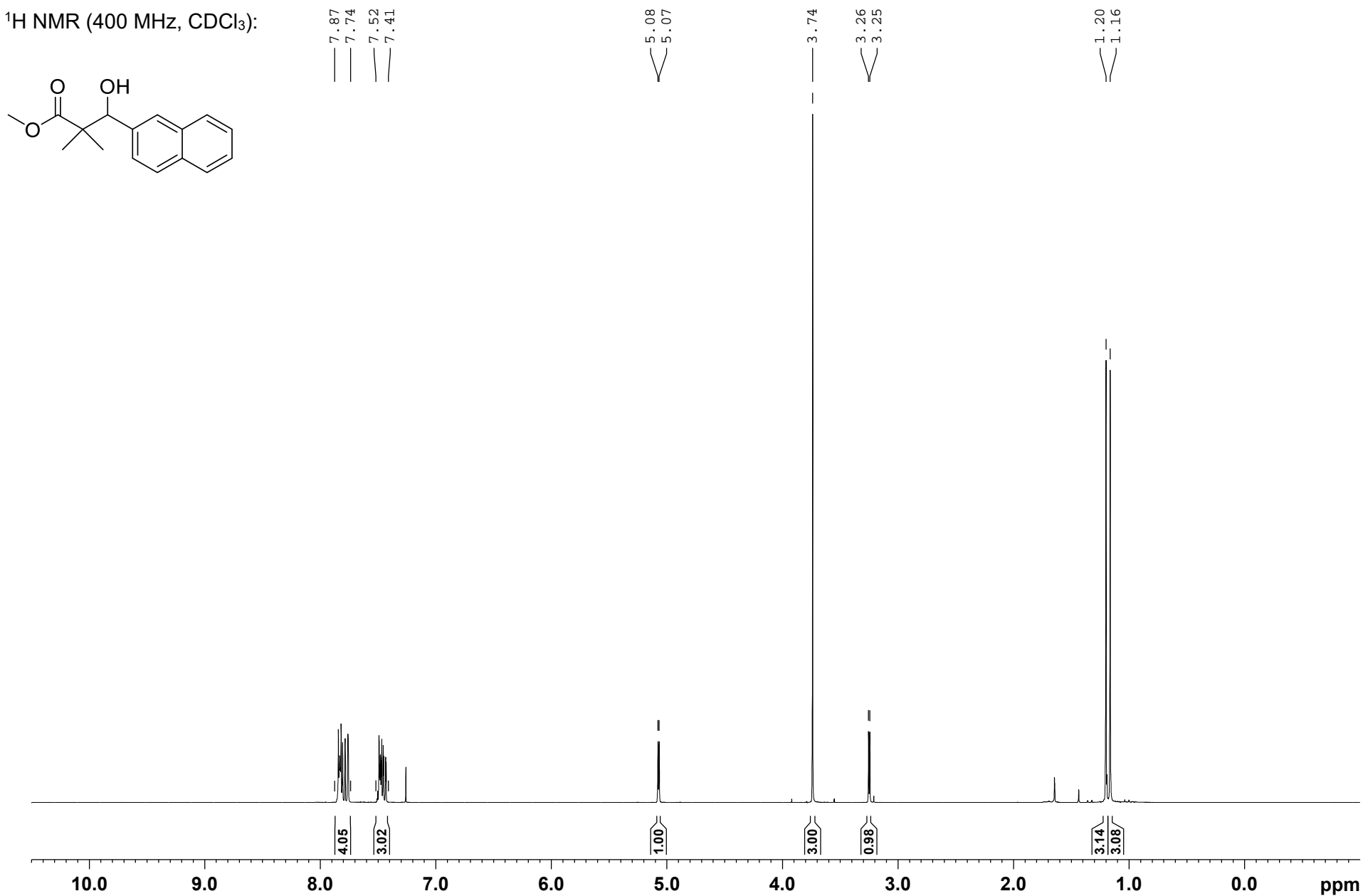


***tert*-Butyl((1-ethoxyvinyl)oxy)dimethylsilan (21)**<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):

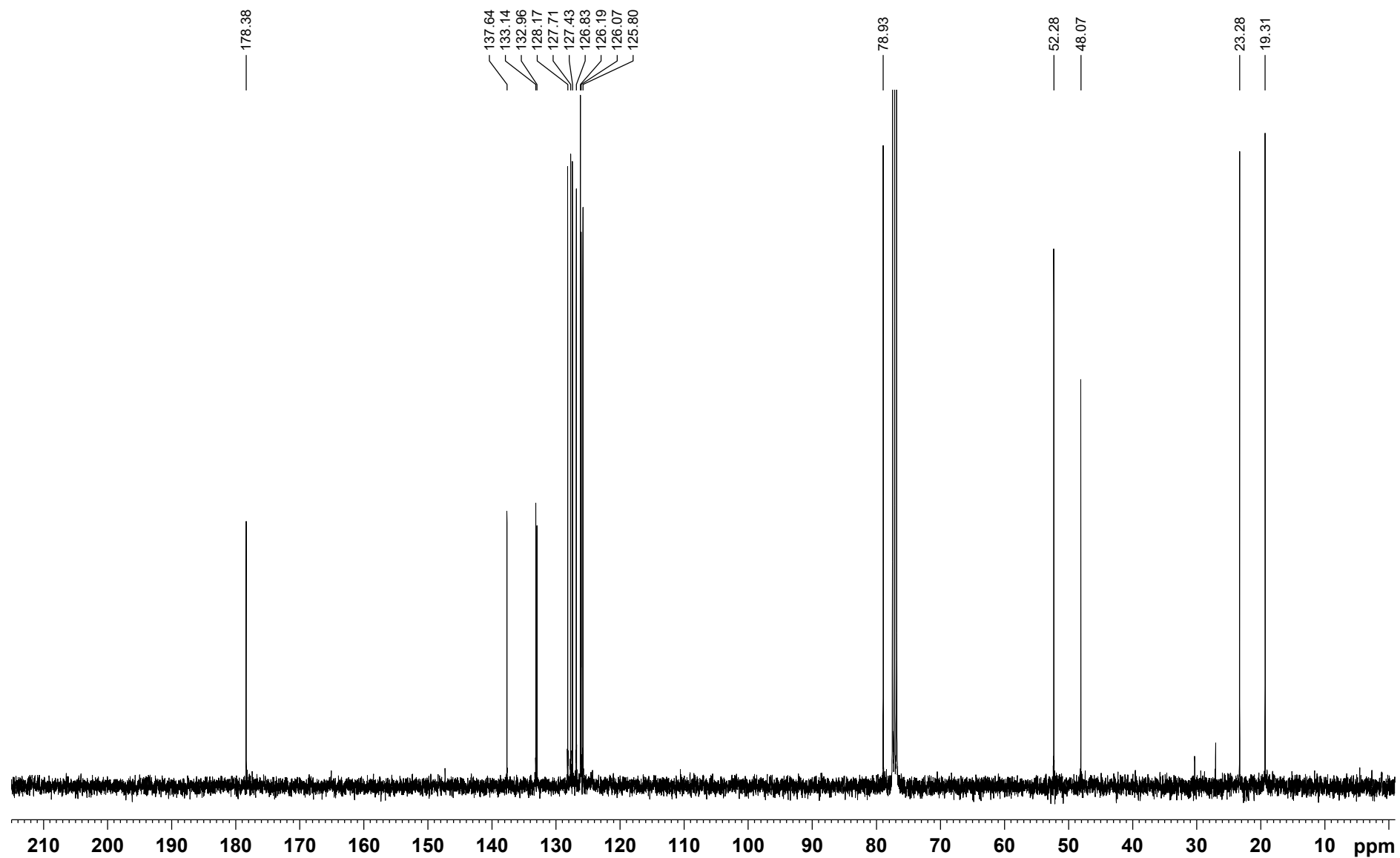


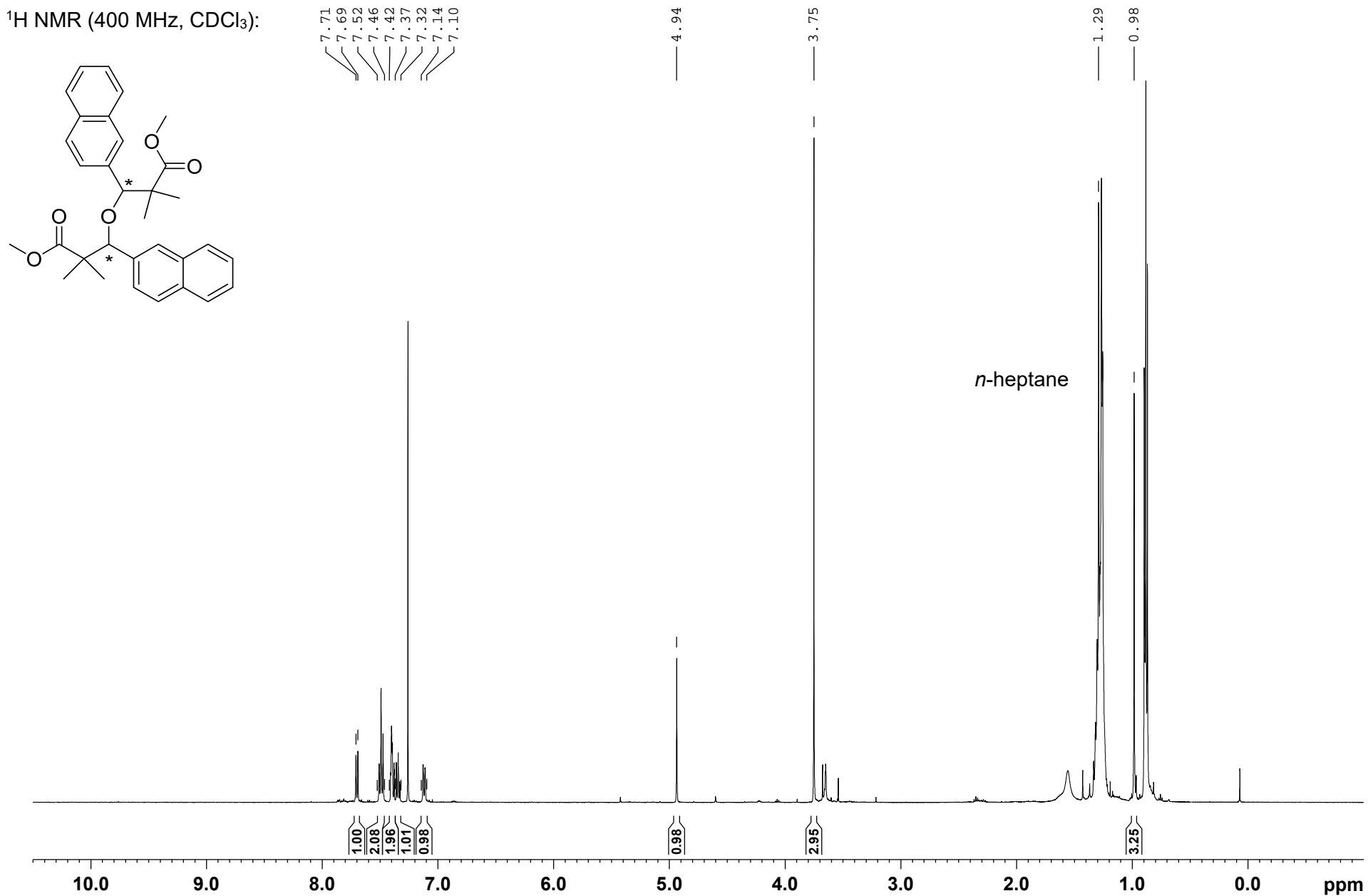
$^1\text{H}/^{29}\text{Si}$ -HMQC-NMR (500/99 MHz,  $\text{C}_6\text{D}_6$ ):



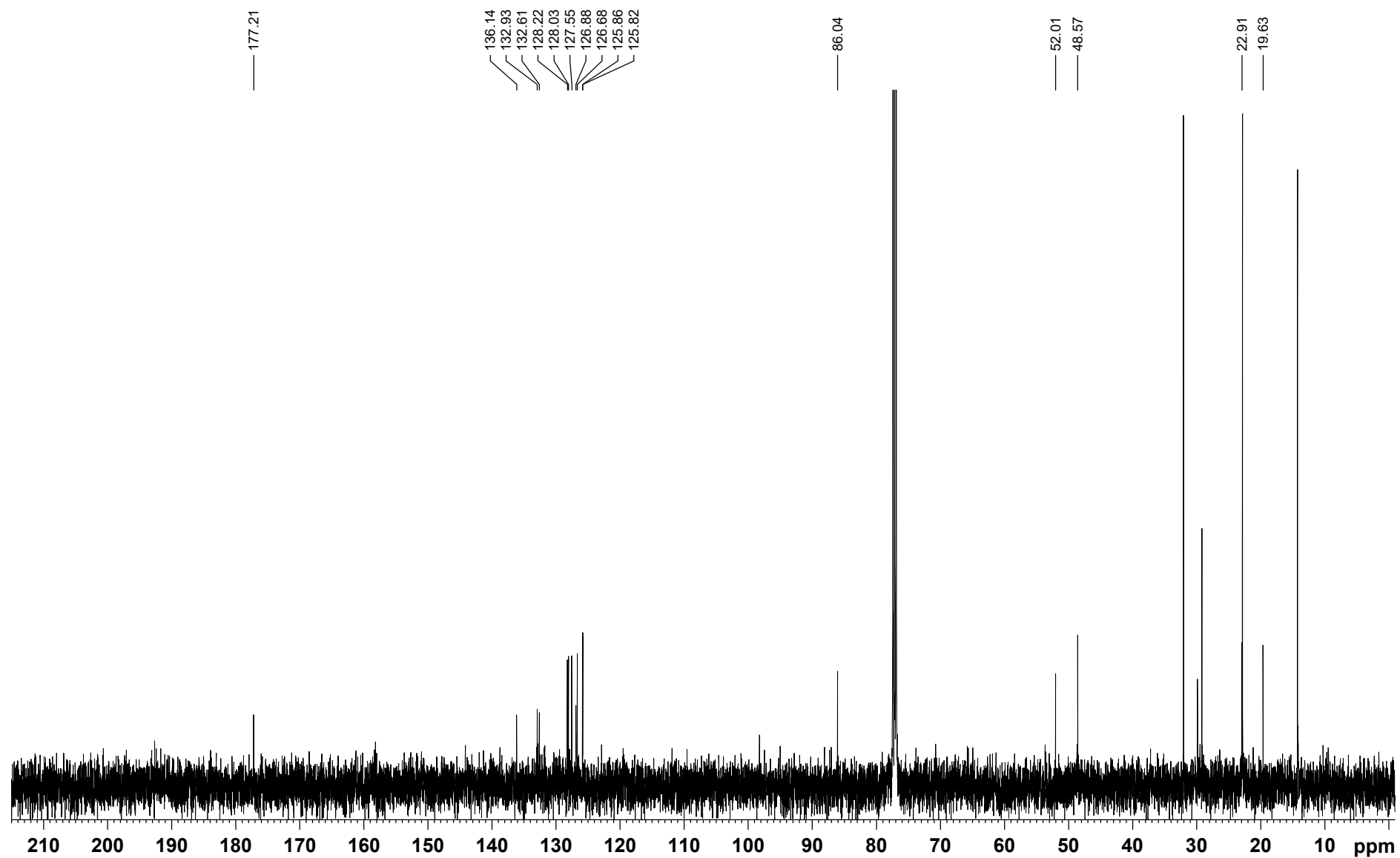
**rac-Ethyl 3-hydroxy-2,2-dimethyl-3-phenylpropanoat (23)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):

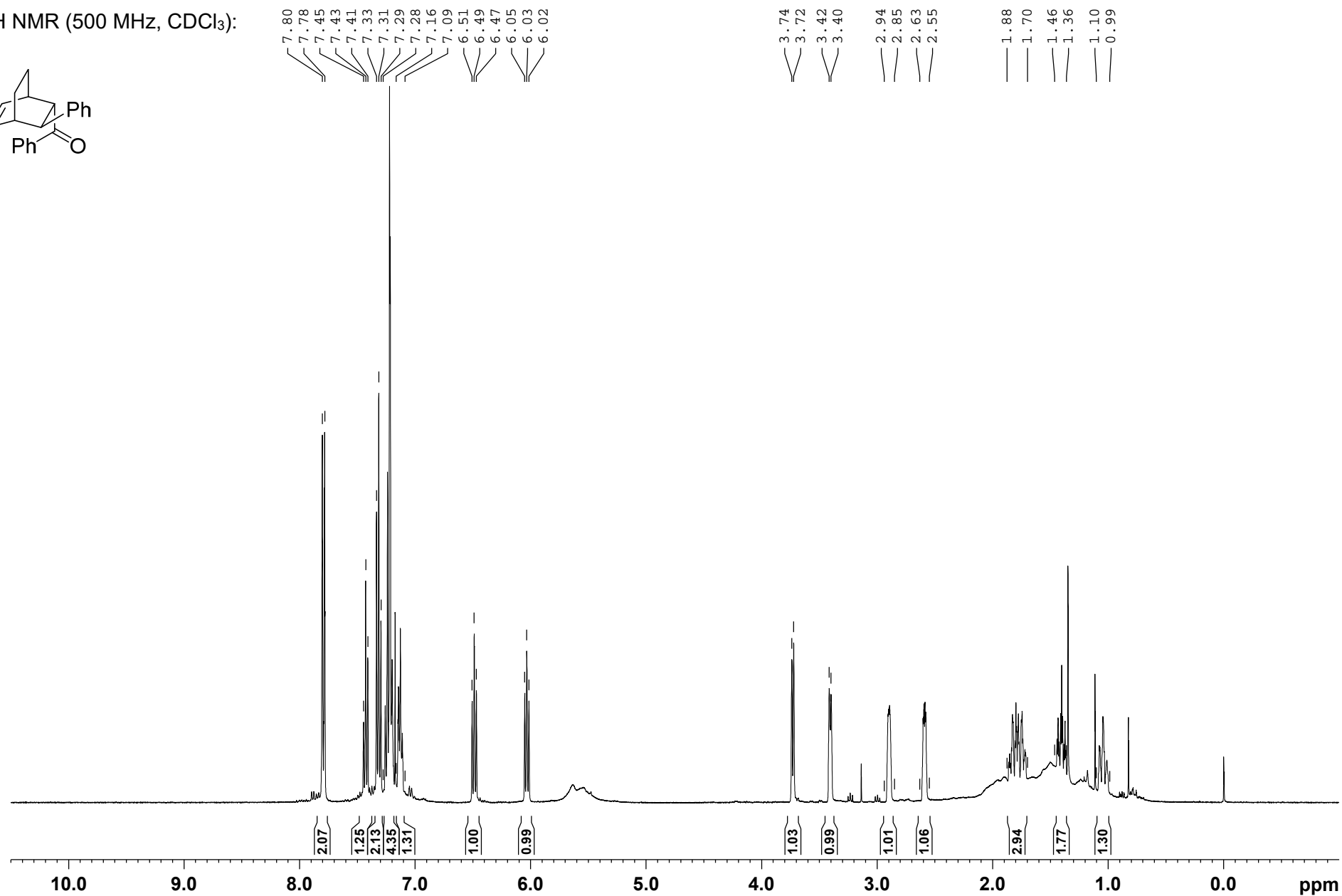
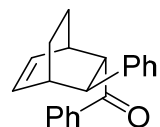
$^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz,  $\text{CDCl}_3$ ):



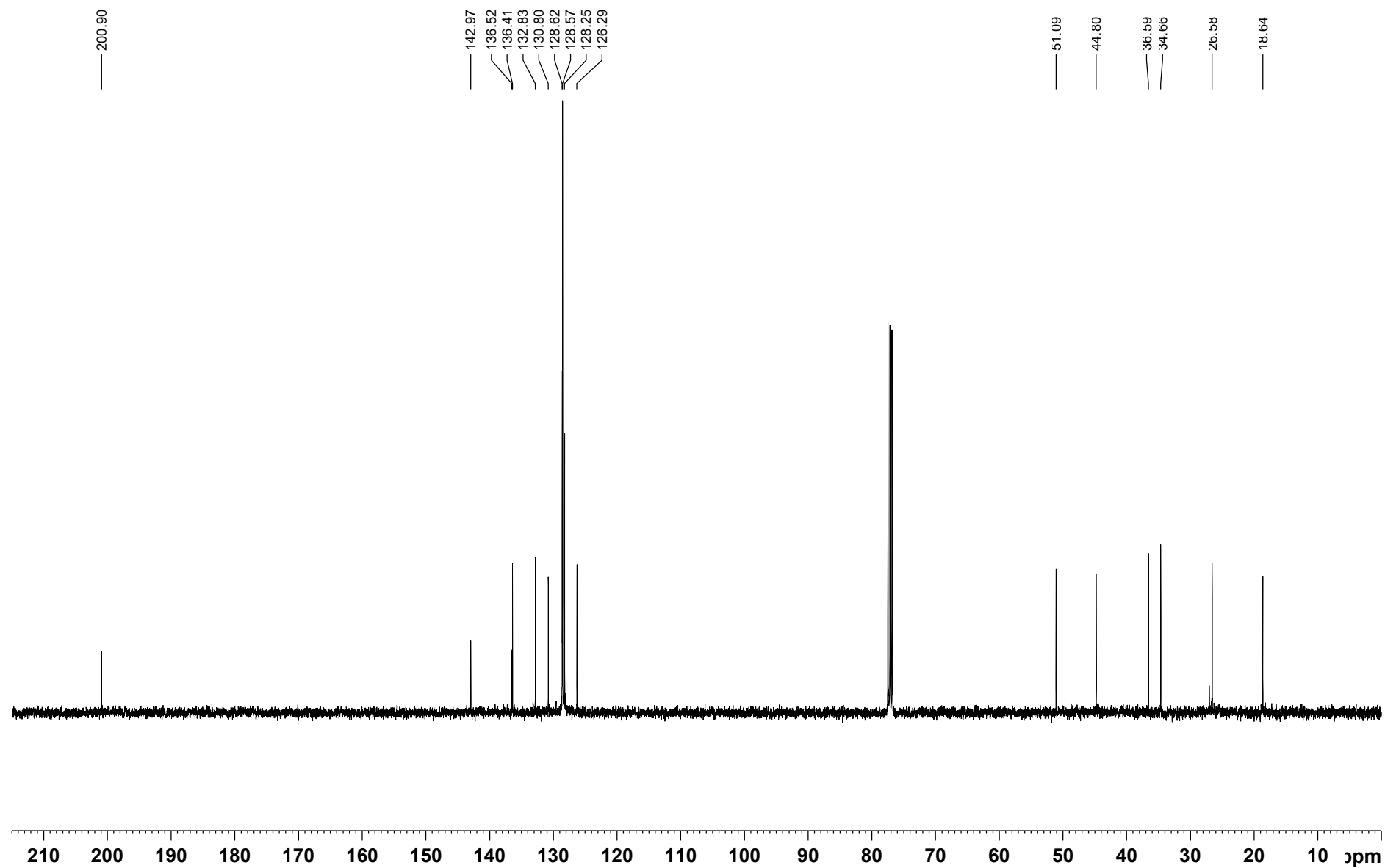
**Dimethyl 3,3'-oxybis(2,2-dimethyl-3-(naphthalen-2-yl)propanoate)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):

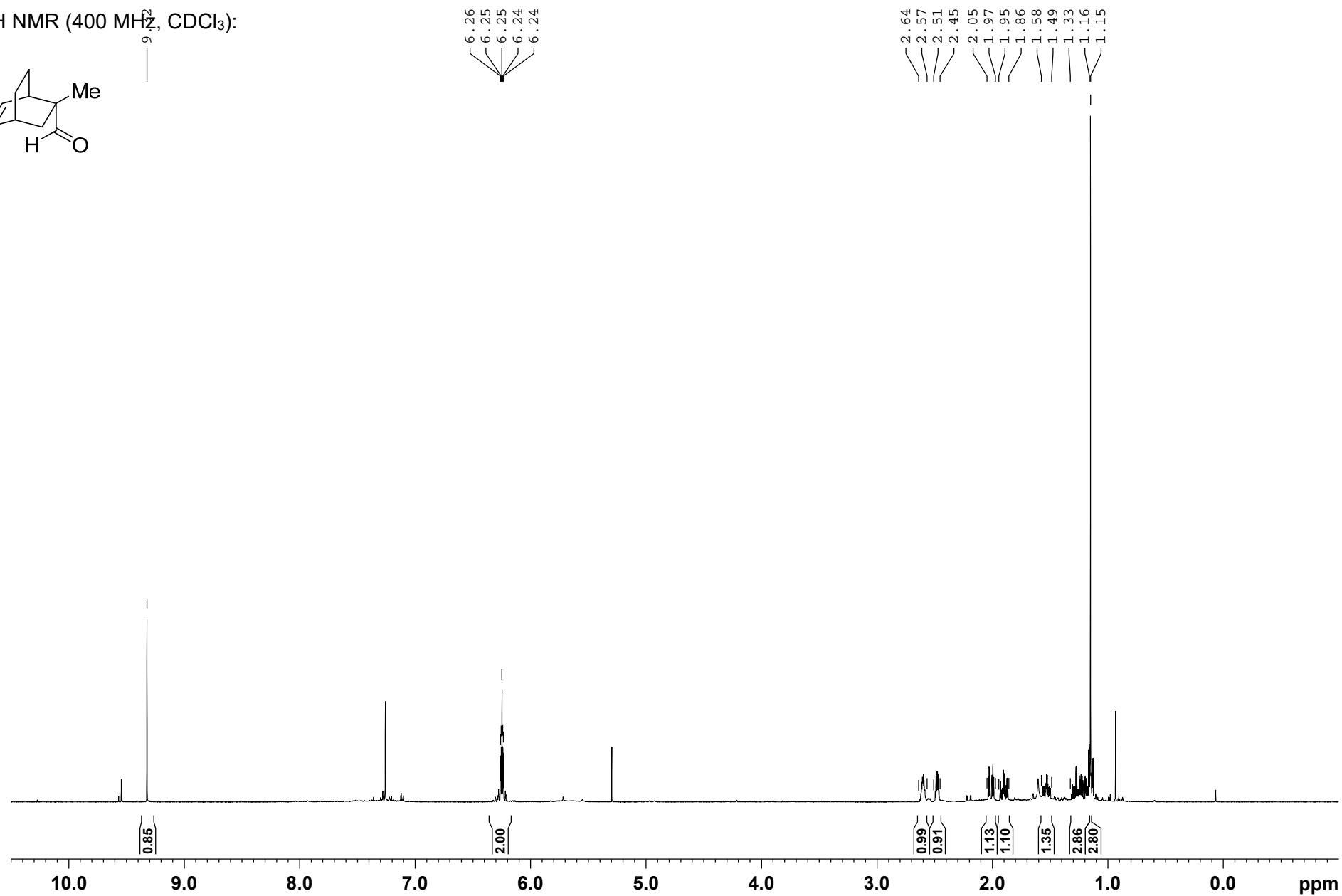
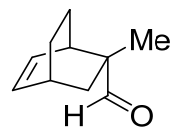
$^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz,  $\text{CDCl}_3$ ):



**endo-Phenyl-(3-phenylbicyclo[2.2.2]oct-5-en-2-yl)methanone (15)**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):

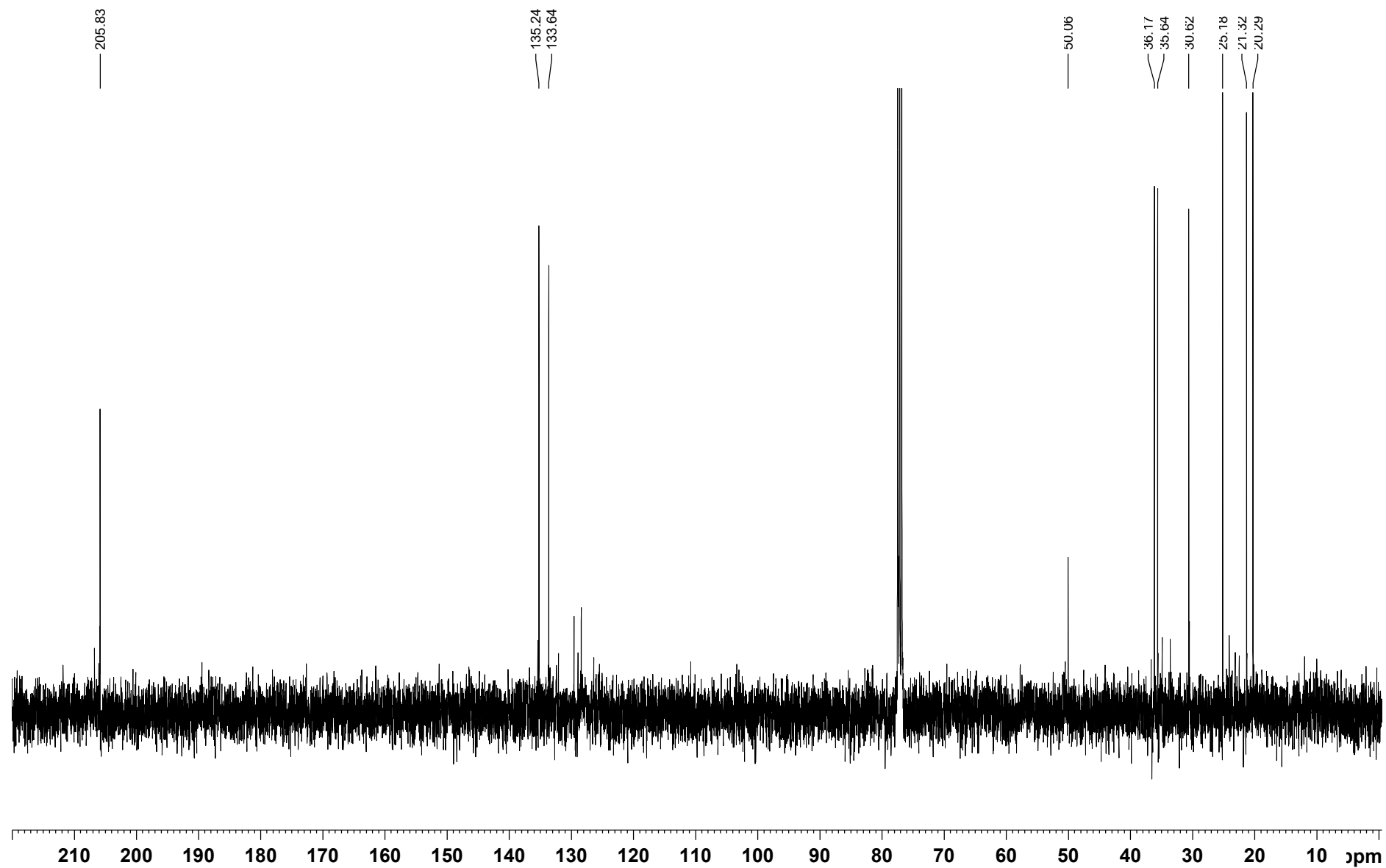
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):



**endo-2-Methylbicyclo[2.2.2]oct-5-ene-2-carbaldehyde (17)**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):



$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):



## 9 References

- [S1] R. Harris, E. D. Becker, R. Goodfellow, P. Granger, *Pure Appl. Chem.* **2001**, *73*, 1795–1818.
- [S2] For the synthesis of myrtanol, see: a) M. F. Sainz, J. A. Souto, D. Regentova, M. K. G. Johansson, S. T. Timhagen, D. J. Irvine, P. Buijsen, C. E. Koning, R. A. Stockman, S. M. Howdle, *Polym. Chem.* **2016**, *7*, 2882–2887; for the oxidation of myrtanol to myrtanal (**5**), see: b) P. E. Peterson, G. Grant, *J. Org. Chem.* **1991**, *56*, 16–20.
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