

## Selective alkyl ether cleavage by cationic bis(phosphine)iridium complexes.

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### Supporting Information

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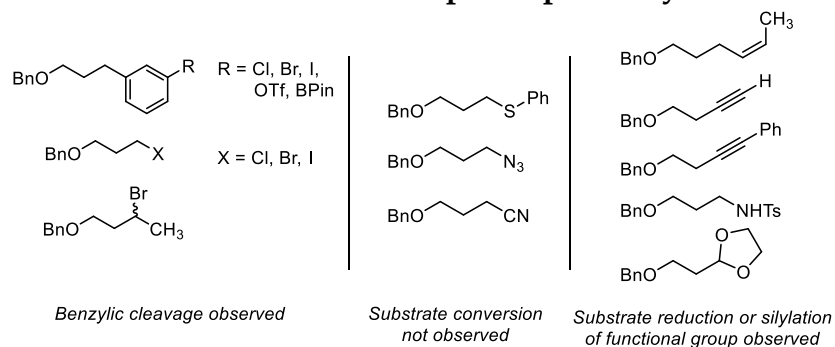
#### I. General Information

**General Considerations.** Syntheses and manipulations were conducted in air unless otherwise specified. Tetrahydrofuran, toluene, dichloromethane, pentane, and diethyl ether were degassed with argon and dried over activated alumina using a solvent purification system. All reagents and building blocks including 3-benzyloxy-propanol were procured from commercial vendors. Complex **2**<sup>1</sup>,  $\text{BAr}^{\text{F}_3}$ ,<sup>2</sup> and  $[\text{CPh}_3]\text{BAr}^{\text{F}_4}$ <sup>3-4</sup> were prepared using reported procedures.

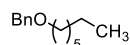
**Spectroscopy.** <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectra were recorded on Bruker NMR spectrometers at ambient temperature unless otherwise noted. <sup>1</sup>H and <sup>13</sup>C chemical shifts are referenced to residual solvent signals; <sup>31</sup>P chemical shifts are referenced to an external H<sub>3</sub>PO<sub>4</sub> standard.

**Mass Spectrometry.** High resolution mass spectrometry was conducted by the Center for Innovative Technology at Vanderbilt University. Acetonitrile solutions of purified products were diluted into a carrier solvent of 20:80 H<sub>2</sub>O:MeCN containing 0.1% formic acid analyzed in either positive or negative ion mode by APCI or ESI.

## II. Functional Group Compatibility

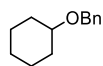


## III. Synthesis and Characterization



**6a**

**Benzyl heptyl ether:** This compound was prepared using a reported method<sup>5</sup>



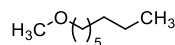
**6b**

**Benzyl cyclohexyl ether:** This compound was prepared using a reported method<sup>5</sup>



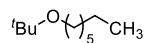
**6c**

**Benzyl tert-butyl ether:** This compound was prepared using a reported method<sup>6</sup>



**6d**

**Methyl octyl ether:** This compound was prepared using a reported method<sup>7</sup>

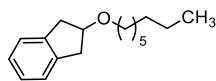


**6e**

**Tert-butyl heptyl ether:** A 50 mL round bottom flask was charged with a stir bar and fitted with a reflux condenser and  $\text{Mg}(\text{ClO}_4)_2$  (0.310 g, 1.09 mmol, 0.1 equiv.) and heptanol (1.6 mL, 10.9 mmol, 1.0 equiv.) were combined in 16 mL dichloromethane. This solution was treated with di-tert-butyl dicarbonate (5.47 g, 25.1 mmol, 2.3 equiv.) and was refluxed while the reaction progress was monitored by TLC. Upon completion, the sample was diluted with 40 mL of water and extracted with three 30 mL portions of dichloromethane. The combined organic layers were then dried with  $\text{Na}_2\text{SO}_4$ , filtered

and concentrated on a rotary evaporator. The crude oil was then purified by silica gel chromatography (5 % EtOAc/hexanes) to give the product as a colorless oil. Yield: 0.6725 g (36%). Spectroscopic data for this product has been previously reported.<sup>8</sup>

<sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>) δ: 3.37 (t, J = 6.5 Hz, 2H), 1.70 (p, J = 6.1 Hz, 2H), 1.46-1.50 (m, 2H), 1.36 (bs, 6H), 1.24 (s, 9H), 0.96-0.98 (m, 3H)



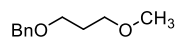
**6f**

**2-(octyloxy)-2,3-dihydro-1H-indene:** A flame-dried Schlenk flask was charged with NaH (90%, 0.546 g, 22.8 mmol, 2.2 equiv.) and THF (43.5 mL) in the glove box and fitted with a rubber stopper. The vessel was then brought outside of the box and attached to an oil bubbler. 1-indanol (2.78 g, 20.17 mmol, 2.0 equiv.) was added slowly using a syringe. The resulting mixture was allowed to stir at room temperature for 30 minutes after which 1-bromooctane (1.8 mL, 10.4 mmol, 1.0 equiv.) was added dropwise. The reaction mixture was then refluxed for 6 hours at which point the reaction was quenched with saturated NH<sub>4</sub>Cl and the layers separated. The aqueous layer was extracted with three 50 mL portions of ethyl acetate. The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The resulting oil was then purified by silica gel chromatography (10% EtOAc/hexanes) to give the product as a colorless oil. Yield: 1.15 g (45%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.12-7.22 (m, 4H), 4.33 (p, J = 6.5 Hz, 1H), 3.48 (t, J = 6.8 Hz, 2H), 2.94-3.20 (ddd, J = 16.5, 8.2, 6.8 Hz, 4H), 1.59 (p, J = 7.0 Hz, 2H), 1.28-1.36 (m, 10H), 0.89 (t, J = 7.3 Hz, 3H)

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 141.15, 126.59, 124.83, 80.43, 69.49, 39.51, 31.98, 30.11, 29.61, 29.42, 26.40, 22.81, 14.25

HRMS (APCI/Q-TOF) m/z [M+H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>26</sub>OH<sup>+</sup>: 247.2062, found: 247.2054

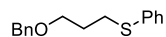


**6g**

**((3-methoxypropoxy)methyl)benzene:** A flame-dried Schlenk flask was charged with NaH (90%, 0.330 g, 13.8 mmol, 1.2 equiv.) and THF (11.5 mL) in the glove box and fitted with a rubber stopper. The vessel was then brought outside of the box and attached to an oil bubbler. 3-benzyloxy-propanol (1.9 mL, 11.46 mmol, 1.0 equiv.) was added slowly using a syringe. The resulting mixture was allowed to stir at room temperature for 30 minutes after which iodomethane (2.1 mL, 34.4 mmol, 3.0 equiv.) was added dropwise. The reaction progress was monitored by TLC. Upon completion, the reaction was quenched with saturated NH<sub>4</sub>Cl and the layers separated. The aqueous layer was extracted with three 50 mL portions of ethyl acetate. The combined organic layers were

dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated on a rotary evaporator to give the product as a yellow oil. Yield: 1.65 g (80%). The compound has been previously reported.<sup>9</sup>

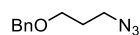
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.26-7.37 (m, 5H), 4.52 (s, 2H), 3.57 (t, J = 5.4 Hz, 2H), 3.50 (t, J = 5.9 Hz, 2H), 3.34 (s, 3H), 1.90 (p, J = 6.3 Hz, 2H)



**6h**

**(3-(benzyloxy)propyl)(phenyl)sufane:** Triethylamine (6.4 mL, 45.9 mmol, 4.0 equiv.) was added to a solution of 3-benzyloxy-1-propanol (1.9 mL, 11.5 mmol, 1.0 equiv.) in 88 mL THF. Methanesulfonyl chloride (2.6 mL, 22.9 mmol, 2.0 equiv.) was then added and the solution was allowed to stir overnight at room temperature. The reaction was then quenched with 25 mL saturated NH<sub>4</sub>Cl. The layers were separated and the aqueous layer was extracted twice with ether. The combined organic layers were then dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to give an orange oil. This oil was taken up in 1.8 mL DMF and was treated with thiophenol (1.8 mL, 17.2 mmol, 1.5 equiv.) and K<sub>2</sub>CO<sub>3</sub> (2.38 g, 17.2 mmol, 1.5 equiv.). The resulting suspension was stirred at room temperature for 2 hours, after which the reaction was quenched with a 5% aqueous KOH solution and then extracted with three 20 mL portions of dichloromethane. The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under vacuum. The resulting residue was purified by silica gel chromatography (2%-10% EtOAc/hexanes) to give the product as an oil. Yield: 0.3375 g (11%). Spectroscopic data for this product has been previously reported.<sup>10</sup>

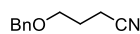
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.20-7.38 (m, 10H), 4.52 (s, 2H), 3.62 (t, J = 6.0 Hz, 2H), 3.08 (t, J = 7.1 Hz, 2H), 1.98 (p, J = 6.6 Hz, 2H)



**6i**

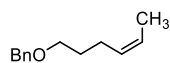
**((3-azidopropoxy)methyl)benzene:** Triethylamine (3.4 mL, 24.1 mmol, 4.0 equiv.) was added to a solution of 3-benzyloxy-1-propanol (0.95 mL, 6.0 mmol, 1.0 equiv.) in 46 mL THF. Methanesulfonyl chloride (0.95 mL, 12.0 mmol, 2.0 equiv.) was then added and the solution was allowed to stir overnight at room temperature. The reaction was then quenched with 25 mL saturated NH<sub>4</sub>Cl. The layers were separated and the aqueous layer was extracted twice with ether. The combined organic layers were then dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to give an orange oil. This oil was taken up in 40 mL DMF and was treated with NaN<sub>3</sub> (2.0 g, 30.1 mmol, 5.0 equiv.) and then heated to 60 °C for five hours. The crude reaction mixture was then treated with brine and extracted with diethyl ether. The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under vacuum. This crude residue was purified by silica gel chromatography (10% EtOAc/hexanes) to give the product as a colorless oil. Yield: 0.424 g (37%). Spectroscopic data for this product has been previously reported.<sup>11</sup>

$^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.18-7.32 (m, 5H), 4.30 (s, 2H), 3.23 (t,  $J = 6.1$  Hz, 2H), 2.99 (t,  $J = 6.5$  Hz, 2H), 1.54 (p,  $J = 6.2$  Hz, 2H)



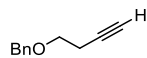
**6j**

**4-(benzyloxy)butanenitrile:** This compound was prepared using a reported method.<sup>12</sup>



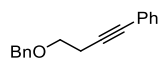
**6k**

**(Z)-((hex-4-en-1-yloxy)methyl)benzene:** This compound was prepared using a reported method.<sup>13</sup>



**6l**

**((but-3-yn-1-yloxy)methyl)benzene:** This compound was prepared using a reported method.<sup>14</sup>



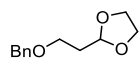
**6m**

**(4-(benzyloxy)but-1-yn-1-yl)benzene:** This compound was prepared using a reported method.<sup>15</sup>



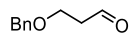
**6n**

**N-(3-benzyloxy)propyl)-4-methylbenzenesulfonamide:** This compound was prepared using a reported method.<sup>16</sup>



**6o**

**2-(2-(benzyloxy)ethyl)-1,3-dioxolane:** This compound was prepared using a reported method.<sup>17</sup>

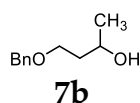


**7a**

**3-(benzyloxy)propanal:** DMSO (8.5 mL, 120.3 mmol, 10 equiv.), triethylamine (6.7 mL, 48.1 mmol, 4 equiv.), and  $\text{SO}_3$ ·pyridine (5.7g, 36.1 mmol, 3.0 equiv.) were added sequentially to a solution of 3-benzyloxy-1-propanol (1.9 mL, 12.0 mmol, 1.0 equiv.) in

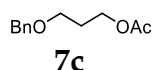
60 mL dichloromethane at 0 °C and the resulting mixture was stirred for 1.5 hours. The crude reaction mixture was then quenched with NaHCO<sub>3</sub> and the layers separated. The organic layer was washed three times with saturated aqueous NH<sub>4</sub>Cl, two times with water, and three times with brine followed by drying over Na<sub>2</sub>SO<sub>4</sub>. The resulting solution was filtered concentrated under vacuum to give a yellow oil. This crude residue was purified by silica gel chromatography (25% EtOAc/hexanes) to give the product as an oil. Yield: 1.34 g (68%). The crude aldehyde used without further purification. Spectroscopic data for this product has been previously reported.<sup>18</sup>

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.78 (d, J = 1.6 Hz, 1H), 7.24-7.35 (m, 5H), 4.51 (s, 2H), 3.80 (t, J = 6.4 Hz, 2H), 2.68 (t, J = 6.0 Hz, 2H)



**4-(benzyloxy)butan-2-ol:** A solution of 3-(benzyloxy)propanal (0.960 g, 5.85 mmol, 1.0 equiv.) in 12 mL THF was cooled to 0 °C and treated with a 3M solution of MeMgBr in THF (2.1 mL, 6.43 mmol, 1.1 equiv.) dropwise. The cold bath was removed after stirring for 10 minutes and the reaction was allowed to come to room temperature. After 2 hours the reaction mixture was quenched with saturated aqueous NH<sub>4</sub>Cl, diluted with 50 mL of water, and extracted with diethyl ether. The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under vacuum to give the product as an oil. Yield: 1.03g (98%). Spectroscopic data for this product has been previously reported.<sup>19</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.26-7.34 (m, 5H), 4.52 (s, 2H), 3.98-4.03 (m, 1H), 3.61-3.74 (m, 2H), 2.87 (s, 1H), 1.68-1.80 (m, 2H), 1.19 (d, J= 6.3 Hz, 3H)

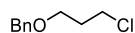


**3-(benzyloxy)propyl acetate.** A 25 mL flame-dried Schlenk flask was charged with 3-benzyloxy-1-propanol (0.48 mL, 3.00 mmol, 1.0 equiv.), pyridine (0.32 mL, 3.90 mmol, 1.3 equiv.), and 6 mL of dichloromethane. The flask was then cooled to 0 °C and acetic anhydride (0.37 mL, 3.90, 1.3 equiv.) was added dropwise. The cooling bath was removed and the reaction was allowed to come to room temperature. The reaction progress was monitored by TLC. Upon completion the solution was poured into 20 mL of 1M aqueous HCl and extracted with three 20 mL portions of Et<sub>2</sub>O. The combined organic extracts were then washed with saturated NaHCO<sub>3</sub> and dried over Na<sub>2</sub>SO<sub>4</sub>. Removal of the solvent on a rotary evaporator gave the product as a yellow oil. Yield: 0.4941 g (79%).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.29-7.37 (m, 5H), 4.51 (s, 2H), 4.20 (t, J = 6.9 Hz, 2H), 3.56 (t, J = 6.3 Hz, 2H), 2.03 (s, 3H), 1.95 (p, J = 6.7 Hz, 2H)

$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  171.19, 138.42, 128.48, 127.72, 127.71, 73.10, 66.74, 61.81, 29.13, 21.05

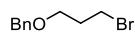
HRMS (APCI/Q-TOF)  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{12}\text{H}_{16}\text{O}_3\text{H}^+$ : 209.1178, found: 209.1177



**7d**

**((3-chloropropoxy)methyl)benzene:** A solution of 3-benzyloxy-1-propanol (0.95 mL, 6.0 mmol, 1.0 equiv.) in 20 mL diisopropyl ether was treated with triethylamine (0.13 mL, 0.90 mmol, 0.15 equiv.) and was then cooled to  $-10\text{ }^\circ\text{C}$  with a salt-ice bath. Separately, a solution of 0.5 mL of  $\text{SOCl}_2$  (7.06 mmol, 1.18 equiv.) in 20 mL of diisopropyl ether was prepared. A 10 mL portion of the  $\text{SOCl}_2$  solution was added dropwise to the reaction mixture at  $-10\text{ }^\circ\text{C}$ . The resulting solution was allowed to stir for 10 minutes, after which point the cooling bath was removed and the second portion of the  $\text{SOCl}_2$  solution was added. The reaction mixture was then heated to  $75\text{ }^\circ\text{C}$  and stirred overnight. After cooling, the crude reaction mixture was treated with saturated aqueous  $\text{NaHCO}_3$  and layers separated. The aqueous layer was extracted with three 50 mL portions of dichloromethane. The combined organic layers were dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated on a rotary evaporator to give the product as a yellow oil. Yield: 0.6792 g (61%). The compound has been previously reported.<sup>20</sup>

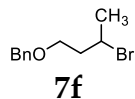
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.22-7.28 (m, 5H), 4.44 (s, 2H), 3.60 (t,  $J = 6.6\text{ Hz}$ , 2H), 3.54 (t,  $J = 6.0\text{ Hz}$ , 2H), 1.98 (p,  $J = 6.1\text{ Hz}$ , 2H)



**7e**

**((3-bromopropoxy)methyl)benzene:** A solution of  $\text{PPh}_3$  (3.15 g, 12.0 mmol, 1.0 equiv.) in 34 mL of dichloromethane in the dark was treated with  $\text{Br}_2$  (0.6 mL, 12.0 mmol, 1.0 equiv.) dropwise over 20 minutes. After an additional 15 minutes, a solution of 3-benzyloxy-1-propanol (1.9 mL, 12.03 mmol, 1.0 equiv.) and imidazole (0.982 g, 14.4 mmol, 1.2 equiv.) in 24 mL of DCM was added dropwise over 15 minutes. The reaction mixture was then stirred at room temperature for 2.5 hours. Upon completion, the mixture was treated with excess solid  $\text{Na}_2\text{SO}_3$  and the resulting suspension concentrated under vacuum. The resulting residue was extracted with pentane, filtered, and concentrated to give a crude oil which was purified by silica gel chromatography (25% EtOAc/hexanes) to give the product as a colorless oil. Yield: 0.8104 g (58%). The compound has been previously reported.<sup>21</sup>

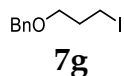
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 7.24-7.35 (m, 5H), 4.51 (s, 2H), 3.59 (t,  $J = 5.5\text{ Hz}$ , 2H), 3.52 (t,  $J = 7.1\text{ Hz}$ , 2H), 2.13 (p,  $J = 6.1\text{ Hz}$ , 2H)



**((3-bromobutoxy)methyl)benzene:** A solution of PPh<sub>3</sub> (1.50 g, 5.70 mmol, 1.0 equiv.) in 16 mL of DCM in the dark was treated with Br<sub>2</sub> (0.3 mL, 5.70 mmol, 1.0 equiv.) dropwise over 20 minutes. After an additional 15 minutes, a solution of 4-(benzyloxy)butan-2-ol (1.03 g, 5.70 mmol, 1.0 equiv.) and imidazole (0.466 g, 6.84 mmol, 1.2 equiv.) in 11 mL of DCM was added dropwise over 15 minutes. The reaction mixture was then stirred at room temperature for 2.5 hours. Upon completion, the mixture was treated with excess solid Na<sub>2</sub>SO<sub>3</sub> and the resulting suspension concentrated under vacuum. The resulting residue was extracted with pentane, filtered, and concentrated to give a crude oil which was purified by silica gel chromatography (25% EtOAc/hexanes) to give the product as a yellow oil. Yield: 0.883 g (64%).

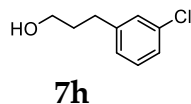
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.27-7.39 (m, 5H), 4.54 (d, J = 2.2 Hz, 2H), 4.37 (sextet, J = 6.6 Hz, 1H), 3.65 (t, J = 5.6 Hz, 2H), 2.04-2.13 (m, 2H), 1.76 (d, J = 6.7 Hz, 3H)

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 138.40, 128.53, 127.80, 127.78, 73.32, 68.28, 48.43, 41.22, 26.75

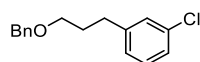


**((3-iodopropoxy)methyl)benzene:** A solution of PPh<sub>3</sub> (3.15 g, 12.03 mmol, 1.0 equiv.) in 34 mL of dichloromethane in the dark was treated with I<sub>2</sub> (3.05 g, 12.03 mmol, 1.0 equiv.) and stirred for 15 minutes. A solution of 3-benzyloxy-1-propanol (1.9 mL, 12.03 mmol, 1.0 equiv.) and imidazole (0.982 g, 14.4 mmol, 1.2 equiv.) in 24 mL of DCM was added over dropwise over 15 minutes. The resulting mixture was stirred at room temperature for 2.5 hours. Upon completion, the mixture was treated with excess solid Na<sub>2</sub>SO<sub>3</sub> and the resulting suspension concentrated under vacuum. The resulting residue was extracted with pentane, filtered, and concentrated to give a crude oil which was purified by silica gel chromatography (25% EtOAc/hexanes) to give the product as a clear oil. Yield: 2.78 g (84%). The compound has been previously reported.<sup>22</sup>

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.24-7.36, (m, 5H), 4.51 (s, 2H), 3.53 (t, J = 5.8 Hz, 2H), 3.30 (t, J = 6.6 Hz, 2H), 2.08 (p, J = 6.1 Hz, 2H)



**3-(3-chlorophenyl)propan-1-ol:** This compound was prepared using a reported method.<sup>23</sup>



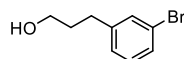


**1-(3-(benzyloxy)propyl)3-chlorobenzene:** A flame-dried Schlenk flask was charged with NaH (90%, 0.066 g, 2.76 mmol, 1.3 equiv.) and 2.1 mL THF in an inert atmosphere glove box. The vessel was then brought outside of the box and attached to an oil bubbler. 3-(3-chlorophenyl)propan-1-ol (0.362 g, 2.12 mmol, 1.0 equiv.) was added dropwise. The reaction mixture was allowed to stir at room temperature for 30 minutes before the addition of benzyl bromide (0.33 mL, 2.76 mmol, 1.3 equiv.). Upon completion, the reaction mixture was quenched with saturated aqueous NH<sub>4</sub>Cl and the layers separated. The aqueous layer was extracted with three 50 mL portions of ethyl acetate. The combined organic layers were washed with 20 mL of 1M NaOH and 20 mL water, then dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under vacuum to give the product as a colorless oil. Yield: 0.4985 g (90%).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.06-7.38 (m, 9H), 4.52 (s, 2H), 3.49 (t, J = 6.3 Hz, 2H), 2.72 (t, J = 8.0 Hz, 2H), 1.94 (p, J = 7.4 Hz, 2H)

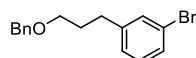
<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 144.18, 138.63, 134.20, 129.68, 128.77, 128.53, 127.82, 127.73, 126.83, 126.10, 73.10, 69.30, 32.21, 31.25

HRMS (APCI/Q-TOF) m/z [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>17</sub>ClO<sup>+</sup>: 261.1046, found: 261.1036



8a

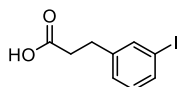
**3-(3-bromophenyl)propan-1-ol:** This compound was prepared using a reported method.<sup>24</sup>



8b

**1-(3-(benzyloxy)propyl)3-bromobenzene:** A flame-dried Schlenk flask was charged with NaH (90%, 0.060 g, 1.93 mmol, 1.3 equiv.) and 3 mL THF in an inert atmosphere glove box. The vessel was then brought outside of the box and attached to an oil bubbler. 3-(3-bromophenyl)propan-1-ol (0.363 g, 1.48 mmol, 1.0 equiv.) was added dropwise. The resulting mixture was stirred for 30 minutes at room temperature before the addition of benzyl bromide (0.23 mL, 1.92 mmol, 1.3 equiv.). Upon completion, the reaction mixture was quenched with saturated aqueous NH<sub>4</sub>Cl and the layers separated. The aqueous layer was extracted with three 50 mL portions of ethyl acetate. The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under vacuum. The resulting oil was then purified by silica gel chromatography (5% EtOAc/hexanes) to give the product as a colorless oil. Yield: 0.4084 g (91%). This compound has been previously reported.<sup>25</sup>

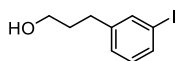
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32-7.38 (m, 7H), 7.11-7.17 (m, 2H), 4.52 (s, 2H), 3.49 (t,  $J$  = 6.2 Hz), 2.71 (t,  $J$  = 8.1 Hz, 2H), 1.94 (p,  $J$  = 6.1 Hz, 2H)



**9a**

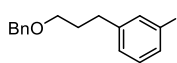
**3-(3-iodophenyl)propanoic acid:** A flame-dried Schlenk flask was charged with formic acid (0.25 mL, 6.46 mmol, 3.0 equiv.) and triethylamine (0.36 mL, 2.59 mmol, 1.2 equiv.) under nitrogen. After 15 min, 2 mL DMF was added followed by 3-iodobenzaldehyde (0.500 g, 2.15 mmol, 1.0 equiv.) and Meldrum's acid (0.311 g, 2.16 mmol, 1.0 equiv.). The resulting mixture was heated to 100 °C and stirred overnight. Upon completion, the solution was poured into 15 mL ice water and extracted two 15 mL portions of dichloromethane. The combined organic layers were shaken with a 10% aqueous NaOH solution and the layers were separated. The aqueous layer was acidified with concentrated aqueous HCl and extracted with EtOAc. The organic extract was washed with water, brine, dried over  $\text{Na}_2\text{SO}_4$  and concentrated under vacuum to give the product as an off-white solid. Yield: 0.5664 g (95%). Spectroscopic data for this product has been previously reported.<sup>26</sup>

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55-7.58 (m, 2H), 7.17-7.19 (d,  $J$  = 7.6 Hz, 1H), 7.03 (t,  $J$  = 7.6 Hz, 1H), 2.90 (t,  $J$  = 7.8 Hz, 2H), 2.67 (t,  $J$  = 7.7 Hz, 2H)



**9b**

**3-(3-iodophenyl)propan-1-ol:** This compound was prepared using a reported method.<sup>27</sup>



**9c**

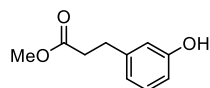
**1-(3-(benzyloxy)propyl)3-iodobenzene:** A flame-dried Schlenk flask was charged with NaH (90%, 0.053 g, 2.22 mmol, 1.3 equiv.) and 1.7 mL THF in an inert atmosphere glove box. The vessel was then brought outside of the box and attached to an oil bubbler. 3-(3-iodophenyl)propan-1-ol (0.448 g, 1.71 mmol, 1.0 equiv.) was added dropwise. The reaction mixture was allowed to stir at room temperature for 30 minutes before the addition of benzyl bromide (0.26 mL, 2.22 mmol, 1.3 equiv.). Upon completion, the reaction mixture was quenched with saturated aqueous  $\text{NH}_4\text{Cl}$  and the layers separated. The aqueous layer was extracted with three 50 mL portions of ethyl acetate. The combined organic layers were washed with 20 mL of 1M NaOH and 20 mL water,

then dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under vacuum to give the product as a colorless oil. Yield: 0.1027 g (90%)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.51-7.57 (m, 2H), 7.31-7.41 (m, 5H), 7.13-7.18 (m, 1H), 7.01 (t, J = 7.7 Hz, 1H), 4.51 (s, 2H), 3.48 (t, J = 6.2 Hz, 2H), 2.67 (t, J = 7.9 Hz, 2H), 1.90 (p, J = 6.7 Hz, 2H)

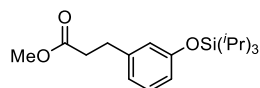
<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 144.62, 138.63, 137.68, 135.01, 130.20, 128.55, 127.94, 127.82, 127.74, 94.62, 73.11, 69.31, 32.10, 31.30

HRMS (APCI/Q-TOF) m/z [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>17</sub>IOH<sup>+</sup>: 351.0246, found: 351.0232



**10a**

**Methyl 3-(3-hydroxyphenyl)propanoate:** This compound was prepared using a reported method.<sup>28</sup>



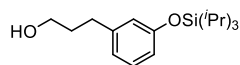
**10b**

**Methyl 3-(3-((triisopropylsilyl)oxy)phenyl)propanoate:** A flame-dried Schlenk flask was charged with 6 mL DMF, methyl 3-(3-hydroxyphenyl)propanoate (2.12 g, 11.8 mmol, 1.0 equiv.), and imidazole (2.41 g, 35.4 mmol, 3.0 equiv.) under nitrogen. The mixture was stirred for 10 min at room temperature followed by the dropwise addition of triisopropylchlorosilane (3.8 mL, 17.7 mmol, 1.5 equiv.). After stirring overnight the reaction mixture was quenched with H<sub>2</sub>O and extracted with diethyl ether. The combined organic layers were washed with water and brine and dried over Na<sub>2</sub>SO<sub>4</sub> then concentrated under vacuum. The resulting crude residue was purified using silica gel chromatography to give the product as a pale yellow oil. Yield: 2.98 g (75%)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.12 (t, J = 8.4 Hz, 1H), 6.75 (d, J = 7.5 Hz, 1H), 6.72 (s, 2H), 3.67 (s, 3H), 2.89 (t, J = 8.2 Hz, 2H), 2.61 (t, J = 8.2 Hz, 2H), 1.24 (sextet, J = 7.7 Hz, 3H), 1.10 (d, J = 7.7 Hz, 18H)

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>) δ 173.46, 156.28, 142.10, 129.46, 121.08, 119.98, 117.90, 51.72, 35.79, 30.98, 18.05, 12.81

HRMS (APCI/Q-TOF) m/z [M+H]<sup>+</sup> calcd for C<sub>19</sub>H<sub>32</sub>O<sub>3</sub>SiH<sup>+</sup>: 337.2199, found: 337.2194



**10c**

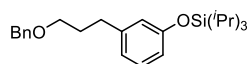
**3-(3-((triisopropylsilyl)oxy)phenyl)propan-1-ol:** A solution of LiAlH<sub>4</sub> (0.402 g, 10.6 mmol, 1.2 equiv.) in 9 mL dry THF was prepared and cooled to 0 °C. A solution of

methyl 3-(3-((triisopropylsilyl)oxy)phenyl)propanoate (2.98 g, 8.85 mmol, 1.0 equiv.) in 9 mL THF was then added dropwise. The bath was removed and the mixture was allowed to come to room temperature where it was stirred for 3 hours. At this point the vessel was cooled back to 0 °C and treated with 10 mL of ether followed by the dropwise addition of 0.6 mL of water, 0.6 mL of a 15% aqueous NaOH solution and 1.8 mL of water. The reaction mixture was then warmed to room temperature and stirred for 15 minutes. Anhydrous Na<sub>2</sub>SO<sub>4</sub> was then added with vigorous stirring for an additional 15 minutes. The material was filtered and the filtrate layers were separated. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuum to give the product as a yellow oil. Yield: 2.27 g (56%).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.12 (t, J = 7.9 Hz, 1H), 6.71-6.78 (m, J = 7.5 Hz, 3H), 3.66 (s, 2H), 2.65 (t, J = 7.9 Hz, 2H), 1.87 (p, J = 7.4 Hz, 2H), 1.25 (sextet, J = 8.0 Hz, 3H), 1.10 (d, J = 7.2 Hz, 18H)

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>) δ 156.23, 143.41, 129.31, 121.28, 120.16, 117.49, 62.43, 34.26, 32.12, 18.06, 12.82

HRMS (APCI/Q-TOF) m/z [M+H]<sup>+</sup> calcd for C<sub>18</sub>H<sub>32</sub>O<sub>2</sub>SiH<sup>+</sup>: 309.2250, found: 309.2262



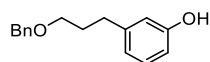
**10d**

**(3-(3-(benzyloxy)propyl)phenoxy)triisopropylsilane:** A flame-dried Schlenk flask was charged with NaH (90%, 0.229 g, 9.55 mmol, 1.3 equiv.) and 7.3 mL THF in an inert atmosphere glove box. The vessel was then brought outside of the box and attached to an oil bubbler. A solution of 3-(3-((triisopropylsilyl)oxy)phenyl)propan-1-ol (2.27 g, 7.35 mmol, 1.0 equiv.) in 7 mL THF was added dropwise. The reaction mixture was allowed to stir at room temperature for 30 minutes before the addition of benzyl bromide (1.1 mL, 9.6 mmol, 1.1 equiv.). Upon completion, the reaction mixture was quenched with saturated aqueous NH<sub>4</sub>Cl and the layers separated. The aqueous layer was extracted with three 50 mL portions of ethyl acetate. The combined organic layers were washed with 20 mL of 1M NaOH and 20 mL water, then dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under vacuum. The resulting oil was then purified by silica gel chromatography (1% to 2% EtOAc/hexanes) to give the product as a colorless oil. Yield: 2.01 (69%).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.24-7.35 (m, 5H), 7.08-7.12 (m, 1H), 6.69-6.75 (m, 3H), 4.49 (s, 2H), 3.48 (t, J = 6.4 Hz, 2H), 2.65 (t, J = 7.5 Hz, 2H), 1.91 (p, J = 7.1 Hz, 2H), 1.24 (sextet, J = 7.6 Hz, 3H), 1.09 (d, J = 7.1 Hz, 18H)

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>) δ 156.17, 143.60, 138.74, 129.22, 128.51, 127.78, 127.66, 121.38, 120.23, 117.41, 73.09, 69.71, 32.41, 31.41, 18.08, 12.83

HRMS (APCI/Q-TOF) m/z [M+H]<sup>+</sup> calcd for C<sub>25</sub>H<sub>38</sub>O<sub>2</sub>SiH<sup>+</sup>: 399.2719, found: 399.2730



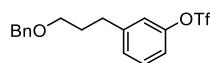
**10e**

**3-(3-(benzyloxy)propyl)phenol:** (3-(3-(benzyloxy)propyl)phenoxy)triisopropylsilane (1.66 g, 4.16 mmol, 1.0 equiv.) was taken up in 21 mL THF and treated with tetra-n-butylammonium fluoride (1.71 g, 5.41 mmol, 1.3 equiv.) at 0 °C. After stirring overnight at room temperature 20 mL ethyl acetate was added. The solution was extracted with three 20 mL portions of water and three 15 mL portions of brine. The organic phase was then dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under vacuum. The residue was then purified by silica gel chromatography to give the product as an oil. Yield: 0.7405 g (74%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.37 (d, J = 4.4 Hz, 4H), 7.28-7.34 (m, 1H), 7.14 (t, J = 7.8 Hz, 1H), 6.75 (d, 7.5 Hz, 1H), 6.61-6.66 (m, 2H), 5.08 (bs, 1H), 4.53 (s, 2H), 3.51 (t, J = 6.3 Hz, 2H), 2.67 (t, J = 7.8 Hz, 2H), 1.90-1.97 (m, 2H)

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 155.72, 143.97, 138.55, 129.61, 128.54, 127.95, 127.74, 121.02, 115.54, 112.85, 73.05, 69.52, 32.30, 31.23

HRMS (APCI-/Q-TOF) m/z [M-H]<sup>-</sup> calcd for C<sub>16</sub>H<sub>17</sub>O<sub>2</sub><sup>-</sup>: 241.1229, found: 241.1219



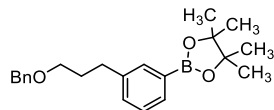
**10f**

**3-(3-(benzyloxy)propyl)phenyl trifluoromethanesulfonate:** A flame dried Schlenk flask was charged with 3-(3-(benzyloxy)propyl)phenol (0.200 g, 0.83 mmol, 1.0 equiv.), 4.1 mL dichloromethane, 2,6-lutidine (0.15 mL, 1.24 mmol, 1.5 equiv.) and DMAP (0.020 g, 0.17 mmol, 0.2 equiv.). The resulting solution was cooled to 0 °C and triflic anhydride (0.21 mL, 1.24 mmol, 1.5 equiv.) was added dropwise. The mixture was then allowed to come to room temperature and the reaction was stirred for 3.5 hours. The reaction mixture was quenched with saturated aqueous NH<sub>4</sub>Cl and then extracted with two 30 mL portions of dichloromethane. The combined organic layers were then washed sequentially with 30 mL water, 30 mL saturated aqueous NaHCO<sub>3</sub>, and 30 mL water. The organic layer was then dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under vacuum. The resulting residue was then purified by silica gel chromatography (10% EtOAc/hexanes) to give the product as a colorless oil. Yield: 0.2061 g (67%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.10-7.39 (m, 9H), 4.52 (s, 2H), 3.49 (t, J = 5.9 Hz, 2H), 2.79 (t, J = 8.0 Hz, 2H), 1.91-1.98 (m, 2H)

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 149.80, 145.24, 138.54, 130.15, 128.71, 128.56, 127.85, 127.79, 121.43, 118.91 (q, <sup>1</sup>J<sub>C-F</sub> = 320.9 Hz), 118.74, 73.17, 69.05, 32.23, 31.18

HRMS (APCI-/Q-TOF) m/z [M-H]<sup>-</sup> calcd for C<sub>17</sub>H<sub>16</sub>F<sub>3</sub>O<sub>4</sub>S<sup>-</sup>: 373.0721, found: 373.0705



**11**

**2-(3-((3-(benzyloxy)propoxy)methyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane:**

A flame-dried Schlenk flask under N<sub>2</sub> was charged with 1-(3-(benzyloxy)propyl)-3-bromobenzene (0.200 g, 0.65 mmol, 1.0 equiv.) and 2.2 mL THF and the resulting solution was cooled to -78 °C. A solution of 2.5M <sup>n</sup>BuLi in hexanes (0.3 mL, 0.72 mmol, 1.1 equiv.) was then added and the solution was allowed to stir for one hour. A solution of B<sub>2</sub>Pin<sub>2</sub> (0.219 g, 0.87 mmol, 1.2 equiv.) in 2.2 mL THF was then added, at which point the solution was allowed to warm to room temperature overnight. Upon completion the reaction mixture was quenched with 1M aqueous HCl and the phases separated. The aqueous layer was extracted with three 25 mL portions of diethyl ether and the combined organic extracts were then dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under vacuum. The resulting residue was purified by silica gel chromatography (5% to 10% EtOAc/hexanes) to give the product as a colorless oil. Yield: 0.1518 g (66%)

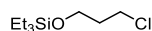
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.64-7.67 (m, 2H), 7.35 (d, J = 4.5 Hz, 4H), 7.29 (d, J = 5 Hz, 3H), 4.51 (s, 2H), 3.49 (t, J = 6.3 Hz, 2H), 2.73 (t, J = 8.0 Hz, 2H), 1.96 (p, J = 7.5 Hz, 2H), 1.35 (s, 12H)

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 141.38, 138.76, 134.98, 132.38, 131.63, 128.49, 127.89, 127.81, 127.64, 83.86, 73.04, 69.75, 32.44, 31.56, 25.01 (Note: A <sup>13</sup>C resonance for the aromatic boron-attached carbon is not observed.)

HRMS (APCI/Q-TOF) m/z [M+H]<sup>+</sup> calcd for C<sub>22</sub>H<sub>29</sub>BO<sub>3</sub>H<sup>+</sup>: 353.2288, found: 353.2274

**General procedure for ether silylation:**

In an inert-atmosphere glove box a 20 mL scintillation vial was charged with a stir bar, the solid precatalyst [H<sub>2</sub>Ir(PPh<sub>3</sub>)<sub>2</sub>(THF)<sub>2</sub>]BAR<sup>F</sup><sub>4</sub> (0.03 equiv.), and dry, degassed toluene (1 mL per 0.30 mmol of ether substrate). The HSiEt<sub>3</sub> (2.2 equiv.) was then added followed by the substrate ether (1.0 equiv.). The vial was fitted with a cap and removed from the glove box. The reaction mixture was stirred at room temperature for 2 hours and the resulting products purified by silica gel chromatography.



**12a**

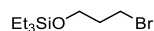
**(3-chloropropoxy)triethylsilane:** This compound was prepared according to the general procedure. [H<sub>2</sub>Ir(PPh<sub>3</sub>)<sub>2</sub>(THF)<sub>2</sub>]BAR<sup>F</sup><sub>4</sub> (0.028 g, 0.016 mmol, 0.03 equiv.), and 1.8 mL toluene were combined in a vial which was treated with HSiEt<sub>3</sub> (0.19 mL, 1.19 mmol, 2.2 equiv.) followed by ((3-chloropropoxy)methyl)benzene (0.100 g, 0.54 mmol, 1.0 equiv.). The crude reaction mixture was purified by silica gel chromatography (1%

EtOAc/hexanes to 2% EtOAc/hexanes) to give the product as a colorless oil. Yield: 0.0799 g (71%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.75 (t,  $J = 6.0$ , 2H), 3.65 (t,  $J = 6.4$  Hz, 2H), 1.96 (p,  $J = 5.9$  Hz, 2H), 0.96 (t,  $J = 8.0$  Hz, 9H), 0.60 (q,  $J = 7.9$  Hz, 6H)

$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  59.25, 41.89, 35.62, 6.84, 4.47

HRMS (APCI/Q-TOF)  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_9\text{H}_{21}\text{ClOSiH}^+$ : 209.1128, found: 209.1131

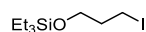


**12b**

**(3-bromopropoxy)triethylsilane:** This compound was prepared according to the general procedure.  $[\text{H}_2\text{Ir}(\text{PPh}_3)_2(\text{THF})_2]\text{BAr}^{\text{F}_4}$  (0.0226 g, 0.013 mmol, 0.03 equiv.), and 1.5 mL toluene were combined in a vial which was treated with  $\text{HSiEt}_3$  (0.16 mL, 0.96 mmol, 2.2 equiv.) followed by ((3-bromopropoxy)methyl)benzene (0.100 g, 0.44 mmol, 1.0 equiv.). The crude reaction mixture was purified by silica gel chromatography (1% EtOAc/hexanes to 2% EtOAc/hexanes) to give the product as a colorless oil. Yield: 0.074 g (67%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  3.74 (t,  $J = 5.5$ , 2H), 3.52 (t,  $J = 6.4$  Hz, 2H), 2.04 (p,  $J = 5.8$  Hz, 2H), 0.96 (t,  $J = 8.1$  Hz, 9H), 0.61 (q,  $J = 8.1$  Hz, 6H)

$^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  60.26, 35.73, 30.77, 6.87, 4.46



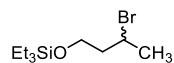
**12c**

**(3-iodopropoxy)triethylsilane:** This compound was prepared according to the general procedure.  $[\text{H}_2\text{Ir}(\text{PPh}_3)_2(\text{THF})_2]\text{BAr}^{\text{F}_4}$  (0.0190 g, 0.011 mmol, 0.03 equiv.), and 1.2 mL toluene were combined in a vial which was treated with  $\text{HSiEt}_3$  (0.13 mL, 0.80 mmol, 2.2 equiv.) followed by ((3-iodopropoxy)methyl)benzene (0.100 g, 0.36 mmol, 1.0 equiv.). The crude reaction mixture was purified by silica gel chromatography (1% EtOAc/hexanes to 2% EtOAc/hexanes) to give the product as a colorless oil. Yield: 0.0656 g (60%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.67 (t,  $J = 5.6$ , 2H), 3.28 (t,  $J = 6.6$  Hz, 2H), 2.00 (p,  $J = 6.0$  Hz, 2H), 0.96 (t,  $J = 8.4$  Hz, 9H), 0.61 (q,  $J = 7.8$  Hz, 6H)

$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  62.25, 36.40, 6.92, 4.52, 3.73

HRMS (APCI/Q-TOF)  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_9\text{H}_{21}\text{IOSiH}^+$ : 301.0485, found: 301.0475



**12d**

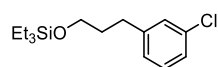
**(3-bromobutoxy)triethylsilane:** This compound was prepared according to the general procedure.  $[\text{H}_2\text{Ir}(\text{PPh}_3)_2(\text{THF})_2]\text{BAr}^{\text{F}_4}$  (0.0213 g, 0.012 mmol, 0.03 equiv.), and 1.4 mL

toluene were combined in a vial which was treated with HSiEt<sub>3</sub> (0.15 mL, 0.90 mmol, 2.2 equiv.) followed by ((3-bromobutoxy)methyl)benzene (0.100 g, 0.41 mmol, 1.0 equiv.). The crude reaction mixture was purified by silica gel chromatography (1% EtOAc/hexanes to 2% EtOAc/hexanes) to give the product as a colorless oil. Yield: 0.051 g (46%).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 4.32 (sext, J = 6.8 Hz, 1H), 3.75 (t, J = 5.6, 2H), 1.98 (q, J = 6.1 Hz, 2H), 1.74 (d, J = 6.6 Hz, 3H), 0.96 (t, J = 7.71 Hz, 9H), 0.61 (q, J = 7.8 Hz, 6H)

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>) δ 60.80, 48.46, 43.03, 26.83, 6.91, 4.51

HRMS (ESI/Q-TOF) m/z [M-H]<sup>-</sup> calcd for C<sub>10</sub>H<sub>22</sub>BrOSiH<sup>-</sup>: 265.0623, found: 265.0630



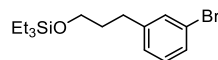
**12e**

**(3-(3-bromophenyl)propoxy)triethylsilane:** This compound was prepared according to the general procedure. [H<sub>2</sub>Ir(PPh<sub>3</sub>)<sub>2</sub>(THF)<sub>2</sub>]BAR<sup>F</sup><sub>4</sub> (0.020 g, 0.012 mmol, 0.03 equiv.), and 1.3 mL toluene were combined in a vial which was treated with HSiEt<sub>3</sub> (0.14 mL, 0.84 mmol, 2.2 equiv.) followed by 1-(3-(benzyloxy)propyl)-3-chlorobenzene (0.100 g, 0.38 mmol, 1.0 equiv.). The crude reaction mixture was purified by silica gel chromatography (1% EtOAc/hexanes to 2% EtOAc/hexanes) to give the product as a colorless oil. Yield: 0.0836 g (76%).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.14-7.20 (m, 3H), 7.06 (d, J = 7.7 Hz, 1H), 3.62 (t, J = 6.3, 2H), 2.66 (t, J = 7.6 Hz, 2H), 1.82 (p, J = 7.5 Hz, 2H), 0.96 (t, J = 7.9 Hz, 9H), 0.60 (q, J = 7.9 Hz, 6H)

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>) δ 144.43, 134.16, 129.63, 128.74, 126.78, 126.00, 61.94, 34.28, 31.96, 6.93, 4.57

HRMS (APCI/Q-TOF) m/z [M-H]<sup>-</sup> calcd for C<sub>15</sub>H<sub>24</sub>ClOSi<sup>-</sup>: 283.1285, found: 283.1298



**12f**

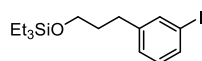
**(3-(3-bromophenyl)propoxy)triethylsilane:** This compound was prepared according to the general procedure. [H<sub>2</sub>Ir(PPh<sub>3</sub>)<sub>2</sub>(THF)<sub>2</sub>]BAR<sup>F</sup><sub>4</sub> (0.017 g, 0.010 mmol, 0.04 equiv.), and 1.1 mL toluene were combined in a vial which was treated with HSiEt<sub>3</sub> (0.12 mL, 0.72 mmol, 2.7 equiv.) followed by 1-(3-(benzyloxy)propyl)-3-bromobenzene (0.081 g, 0.27 mmol, 1.0 equiv.). The crude reaction mixture was purified by silica gel chromatography (1% EtOAc/hexanes to 2% EtOAc/hexanes) to give the product as a colorless oil. Yield: 0.0672 g (77%).



$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34 (s, 1H), 7.31 (d,  $J$  = 6.24 Hz, 1H), 7.10-7.14 (m, 2H), 3.62 (t,  $J$  = 5.8, 2H), 2.65 (t,  $J$  = 8.0 Hz, 2H), 1.82 (p,  $J$  = 6.9 Hz, 2H), 0.96 (t,  $J$  = 7.7 Hz, 9H), 0.60 (q,  $J$  = 7.7 Hz, 6H)

$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  144.75, 131.68, 129.95, 128.93, 127.25, 122.49, 61.91, 34.29, 31.94, 6.93, 4.58

HRMS (APCI/Q-TOF)  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{15}\text{H}_{24}\text{BrOSiH}^+$ : 329.0936, found: 329.0948



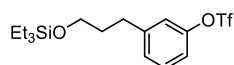
**12g**

**(3-(3-iodophenyl)propoxy)triethylsilane:** This compound was prepared according to the general procedure.  $[\text{H}_2\text{Ir}(\text{PPh}_3)_2(\text{THF})_2]\text{BAr}^{\text{F}_4}$  (0.0142 g, 0.0082 mmol, 0.03 equiv.), and 0.95 mL toluene were combined in a vial which was treated with  $\text{HSiEt}_3$  (0.10 mL, 0.62 mmol, 2.2 equiv.) followed by 1-(3-(benzyloxy)propyl)-3-iodobenzene (0.100 g, 0.28 mmol, 1.0 equiv.). The crude reaction mixture was purified by silica gel chromatography (1% EtOAc/hexanes to 2% EtOAc/hexanes) to give the product as a colorless oil. Yield: 0.1051 g (98%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (s, 1H), 7.50 (d,  $J$  = 7.5 Hz, 1H), 7.14 (d,  $J$  = 7.7 Hz, 2H), 6.99 (t,  $J$  = 8.1 Hz, 1H), 3.61 (t,  $J$  = 6.3, 2H), 2.62 (t,  $J$  = 7.8 Hz, 2H), 1.81 (p,  $J$  = 6.6 Hz, 2H), 0.96 (t,  $J$  = 8.1 Hz, 9H), 0.60 (q,  $J$  = 7.9 Hz, 6H)

$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  144.85, 137.65, 134.91, 130.14, 127.88, 94.55, 61.89, 34.28, 31.82, 6.94, 4.58

HRMS (APCI/Q-TOF)  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{15}\text{H}_{24}\text{IOSiH}^+$ : 377.0798, found: 377.0785



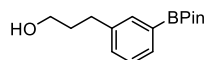
**12h**

**(3-(3-(triethylsilyloxy)propyl)phenyl) triflate:** This compound was prepared according to the general procedure.  $[\text{H}_2\text{Ir}(\text{PPh}_3)_2(\text{THF})_2]\text{BAr}^{\text{F}_4}$  (0.0138 g, 0.0080 mmol, 0.03 equiv.), and 0.90 mL toluene were combined in a vial which was treated with  $\text{HSiEt}_3$  (0.95 mL, 0.59 mmol, 2.2 equiv.) followed by 3-(3-(benzyloxy)propyl)phenyl triflate (0.100 g, 0.27 mmol, 1.0 equiv.). The crude reaction mixture was purified by silica gel chromatography (1% EtOAc/hexanes to 2% EtOAc/hexanes) to give the product as a colorless oil. Yield: 0.101 g (95%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33 (t,  $J$  = 7.7, 1H), 7.21 (d,  $J$  = 7.7 Hz, 1H), 7.08-7.10 (m, 2H), 3.63 (t,  $J$  = 6.2, 2H), 2.74 (t,  $J$  = 7.7 Hz, 2H), 1.84 (p,  $J$  = 6.9 Hz, 2H), 0.97 (t,  $J$  = 7.6 Hz, 9H), 0.60 (q,  $J$  = 8.1 Hz, 6H)

$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  149.81, 145.52, 130.08, 128.67, 121.37, 118.91 (q,  $^1J_{\text{C-F}}$  = 320.9 Hz), 118.64, 61.71, 34.14, 31.97, 6.88, 4.54

HRMS (APCI/Q-TOF)  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{16}\text{H}_{25}\text{F}_3\text{O}_4\text{SSiH}^+$ : 399.1273, found: 399.1268



**12i**

**3-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propan-1-ol:** This compound was prepared according to the general procedure.  $[\text{H}_2\text{Ir}(\text{PPh}_3)_2(\text{THF})_2]\text{BAR}^{\text{F}_4}$  (0.0147, 0.0085 mmol, 0.03 equiv.), and 1.0 mL toluene were combined in a vial which was treated with  $\text{HSiEt}_3$  (1.0 mL, 0.62 mmol, 2.2 equiv.) followed by 2-(3-(3-(benzyloxy)propyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.100 g, 0.28 mmol, 1.0 equiv.).

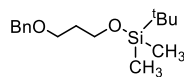
Upon completion after 2 hours, the solution was concentrated on a rotatory evaporator and the resulting residue was dissolved in 1.4 mL of THF. The mixture was cooled to 0 °C and tetra-*n*-butylammonium fluoride (0.200 g, 0.63 mmol, 2.2 equiv.) was added. This solution was allowed to come to room temperature and was stirred for 30 minutes before being diluted with 2 mL of EtOAc and extracted with water and brine. The organic layer was separated, dried over  $\text{Na}_2\text{SO}_4$ , and concentrated on a rotary evaporator. This residue was purified by silica gel chromatography (25% EtOAc/hexanes) to give the product as a colorless oil. Yield: 0.0299 g (40%).

*Note:* NMR Analysis suggests benzyl cleavage proceeds in high yield (>90%) however we have not been able to purify the resulting triethylsilyl ether. We suspect the low yields of the free alcohol obtained results from challenges in the selective desilylation of the product of benzylic ether cleavage.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 (s, 2H), 7.29 (d,  $J = 4.0$  Hz, 2H), 3.66 (t,  $J = 6.3$ , 2H), 2.71 (t,  $J = 7.3$  Hz, 2H), 1.90 (p,  $J = 7.4$  Hz, 2H), 1.34 (s, 12H)

$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  141.20, 134.88, 132.50, 131.57, 127.97, 83.90, 62.47, 34.45, 32.10, 25.00. (*Note:* A  $^{13}\text{C}$  resonance for the aromatic boron-attached carbon is not observed.)

HRMS (APCI/Q-TOF)  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{15}\text{H}_{23}\text{BrO}_3\text{H}^+$ : 263.1818, found: 263.1831



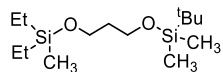
**12j**

**3-(benzyloxy)propoxy)(tert-butyl)dimethylsilane (eqn. 1):**

In an inert atmosphere glovebox a 20 mL scintillation vial was charged with  $[\text{H}_2\text{Ir}(\text{PPh}_3)_2(\text{THF})_2]\text{BAR}^{\text{F}_4}$  (0.0312 g, 0.018 mmol, 0.03 equiv.) and 2 mL toluene followed by tert-butyl(dimethyl)silane (0.11 mL, 0.662 mmol, 1.1 equiv.) and 3-benzyloxy-1-propanol (95  $\mu\text{L}$ , 0.602 mmol, 1.0 equiv.). The resulting solution was stirred for 15 before being filtered through a short filter pad of silica using diethyl ether. The filtrate was then concentrated by rotatory evaporation and the resulting residue was purified by silica gel chromatography (5% EtOAc/hexanes) to give the product as a yellow oil.

Yield: 0.1533 g (91%). Spectroscopic data for this product has been previously reported.<sup>29</sup>

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.26-7.34 (m, 5H), 4.50 (s, 2H), 3.72 (t, J = 6.3 Hz, 2H), 3.57 (t, J = 6.3 Hz, 2H), 1.83 (t, J = 6.3, 2H), 0.89 (s, 9H), 0.05 (s, 6H)



**12k**

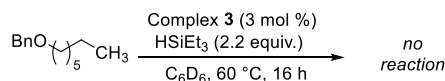
### 9,9-diethyl-2,2,3,3-tetramethyl-4,8-dioxa-3,9-disilaundecane (eqn. 1):

This compound was prepared according to a variation to the general procedure. In an inert atmosphere glovebox a 20 mL scintillation vial was charged with [H<sub>2</sub>Ir(PPh<sub>3</sub>)<sub>2</sub>(THF)<sub>2</sub>]BAr<sup>F</sup><sub>4</sub> (0.0312 mg, 0.018 mmol, 0.03 equiv.) and 2 mL toluene followed by tert-butyl(dimethyl)silane (0.11 mL, 0.662 mmol, 1.1 equiv.) and 3-benzyloxy-1-propanol (95 μL, 0.602 mmol, 1.0 equiv.). The resulting solution was stirred 15 minutes, at which point ethyl(dimethyl)silane (0.20 mL, 1.05 mmol, 2.2 equiv.) was added. The reaction mixture stirred for two hours and was purified by silica gel chromatography (1% EtOAc/hexanes) to give the product as a colorless oil. Yield: 0.1365 g (78%).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 3.67-3.71 (m, 4H), 1.73 (t, J = 6.4 Hz, 2H), 0.95 (t, J = 7.9 Hz, 6H), 0.90 (s, 9H), 0.56-0.61 (m, 4H), 0.05 (2s, 9H)

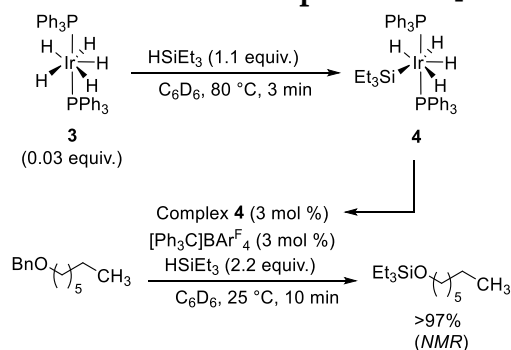
<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>) δ 59.83, 59.50, 36.05, 26.07, 18.45, 6.89, 6.37, -4.88, -5.22  
HRMS (APCI/Q-TOF) m/z [M+H]<sup>+</sup> calcd for C<sub>14</sub>H<sub>34</sub>O<sub>2</sub>Si<sub>2</sub>H<sup>+</sup>: 291.2175, found: 291.2174

### Catalytic ether silylation conducted with (PPh<sub>3</sub>)<sub>2</sub>IrH<sub>5</sub> (3) as the precatalyst (eqn. 3):



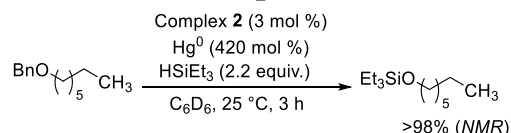
In an inert-atmosphere glove box a septum-capped NMR tube was charged with (PPh<sub>3</sub>)<sub>2</sub>IrH<sub>5</sub> (3) (0.0032 g, 0.0045 mmol, 0.03 equiv.) followed by 0.5 mL of C<sub>6</sub>D<sub>6</sub>. Triethylsilane (53 μL, 0.33 mmol, 2.2 equiv.) was then added and the NMR tube was inverted to ensure appropriate mixing. Benzyl heptyl ether (37 μL, 0.15 mmol, 1.0 equiv.) was then added and the NMR tube was inverted once more. The reaction was monitored by <sup>1</sup>H NMR. As no change was observed at 25 °C, the sample was heated to 40 °C for 2 hours and then to 60 °C for 16 hours. No substrate reduction was observed. Analysis by <sup>31</sup>P{<sup>1</sup>H} NMR at various points show complete consumption of 3 and formation of complex 4.

### Catalytic ether silylation conducted with complex 4 and [CPh<sub>3</sub>]BAr<sup>F</sup><sub>4</sub> (eqn. 4):



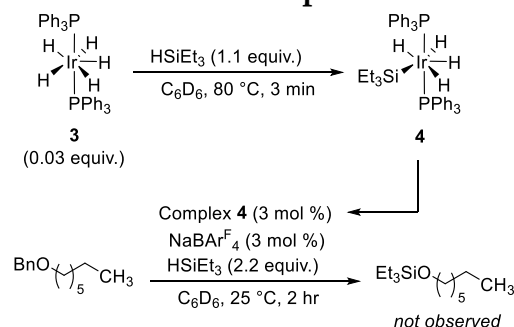
In an inert-atmosphere glove box a septum-capped NMR tube was charged with (PPh<sub>3</sub>)<sub>2</sub>IrH<sub>5</sub> (**3**) (0.0032 g, 0.0045 mmol, 0.03 equiv.) followed by 0.25 mL of C<sub>6</sub>D<sub>6</sub>. Triethylsilane (26.2 μL, 0.17 mmol, 1.1 equiv.) was then added and the NMR tube was heated to 80 °C for three minutes with periodic agitation of the reaction vessel. Analysis of this sample by <sup>31</sup>P{<sup>1</sup>H} and <sup>1</sup>H NMR show complete consumption of **3** and formation of complex **4**. The NMR tube was then brought back into the glovebox and the solution was frozen solid using a cold well. In a separate vial a solution of [CPh<sub>3</sub>]BAr<sup>F</sup><sub>4</sub> (0.0053 g, 0.0048 mmol, 0.032 equiv.) in 0.25 mL of C<sub>6</sub>D<sub>6</sub> was prepared. Triethylsilane (26.2 μL, 0.17 mmol, 1.1 equiv.) was then added followed by benzyl heptyl ether (37 μL, 0.15 mmol, 1.0 equiv.). The resulting solution was transferred into the NMR tube and layered onto the frozen iridium solution in the cold well. The sample was allowed to freeze solid. The sealed NMR tube was then brought out of the box and thawed immediately before analysis by NMR. Quantitative conversion of benzyl heptyl ether to triethyl(hexyloxy)silane was observed within 10 minutes.

### Catalytic ether silylation conducted in the presence of excess mercury (eqn. 6).



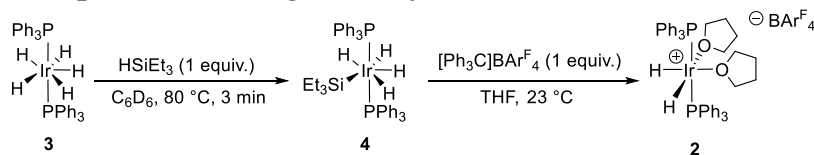
To a 4 mL vial containing a stir bar was added Hg<sup>0</sup> (0.033 g, 0.17 mmol, 4.20 equiv.) followed by [H<sub>2</sub>Ir(PPh<sub>3</sub>)<sub>2</sub>(THF)<sub>2</sub>]BAr<sup>F</sup><sub>4</sub> (0.0020 g, 0.0012 mmol, 0.03 equiv.) as a solution in C<sub>6</sub>D<sub>6</sub>. The solution was then diluted to 0.5 mL of C<sub>6</sub>D<sub>6</sub>. Triethylsilane (13.7 μL, 0.085 mmol, 2.2 equiv.) was then added and the solution was stirred briefly to ensure appropriate mixing. Benzyl heptyl ether (8.9 μL, 0.039 mmol, 1.0 equiv.) was then added and the solution was allowed to stir vigorously for two hours, ensuring maximal contact between the liquid mercury and the reaction solvent. The solution was then transferred to an NMR tube and 10 μL of pyridine was added as an internal standard. The NMR yield was determined to be >98%.

### Catalytic ether silylation conducted with complex **4** and NaBAR<sup>F</sup><sub>4</sub>:



In an inert-atmosphere glove box a septum-capped NMR tube was charged with (PPh<sub>3</sub>)<sub>2</sub>IrH<sub>5</sub> (**3**) (0.0032 g, 0.0045 mmol, 0.03 equiv.) followed by 0.25 mL of C<sub>6</sub>D<sub>6</sub>. Triethylsilane (26.2 μL, 0.17 mmol, 1.1 equiv.) was then added and the NMR tube was heated to 80 °C for three minutes with periodic agitation of the reaction vessel. Analysis of this sample by <sup>31</sup>P{<sup>1</sup>H} and <sup>1</sup>H NMR show complete consumption of **3** and formation of complex **4**. The NMR tube was then brought back into the glovebox and the solution was frozen solid using a cold well. In a separate vial a solution of NaBAR<sup>F</sup><sub>4</sub> (0.0043 g, 0.0048 mmol, 0.032 equiv.) in 0.25 mL of C<sub>6</sub>D<sub>6</sub> was prepared. Triethylsilane (26.2 μL, 0.17 mmol, 1.1 equiv.) was then added followed by benzyl heptyl ether (37 μL, 0.15 mmol, 1.0 equiv.). The resulting solution was transferred into the NMR tube and layered onto the frozen iridium solution in the cold well. The sample was allowed to freeze solid. The sealed NMR tube was then brought out of the box and thawed immediately before analysis by NMR. No reaction was observed over 30 minutes at room temperature.

### Observation of complex **2** resulting from hydride abstraction from **4**:



In an inert-atmosphere glove box a septum-capped NMR tube was charged with (PPh<sub>3</sub>)<sub>2</sub>IrH<sub>5</sub> (**3**) (0.0100 g, 0.0139 mmol, 1.0 equiv.) followed by 0.5 mL of C<sub>6</sub>D<sub>6</sub> and triethylsilane (22.5 μL, 0.139 mmol, 10 equiv.). The suspension was then heated to 80 °C until a clear solution formed (~ 3 minutes). The mixture was brought back into the glove box and the solution was concentrated under vacuum. The resulting solid was dissolved in 0.5 mL of THF and was treated with [Ph<sub>3</sub>C]BAR<sup>F</sup><sub>4</sub> (0.0153 g, 0.0139 mmol, 1.0 equiv.). Analysis by <sup>31</sup>P{<sup>1</sup>H} NMR gave a single signal at 30.4 ppm which we have assigned as complex **2** by comparison to the authentic material in THF.

## IV. NMR Spectra

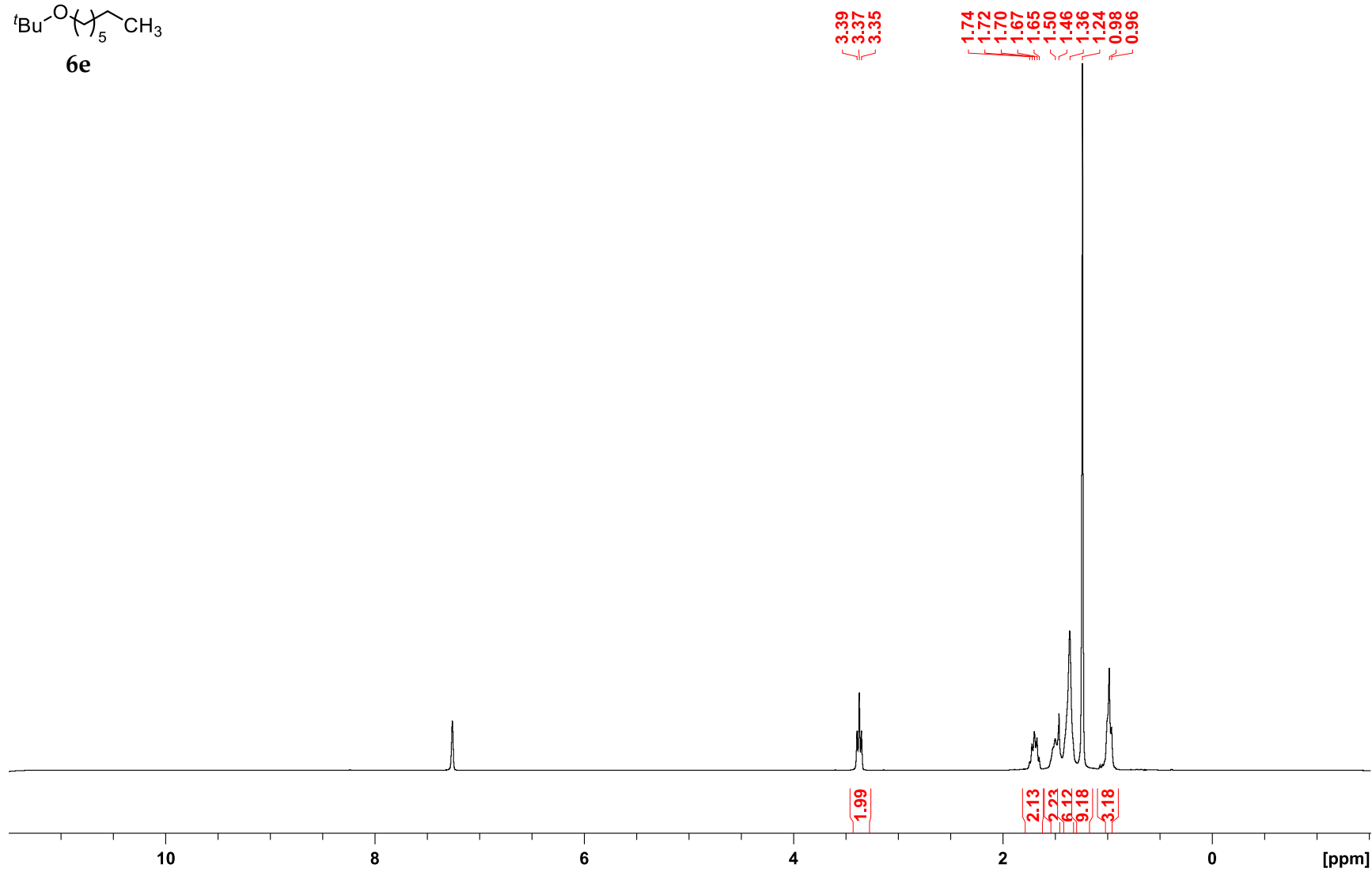
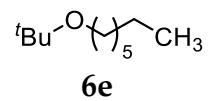
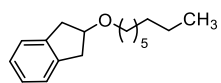


Figure S1.  $^1\text{H}$  NMR Spectrum of **6e**



6f

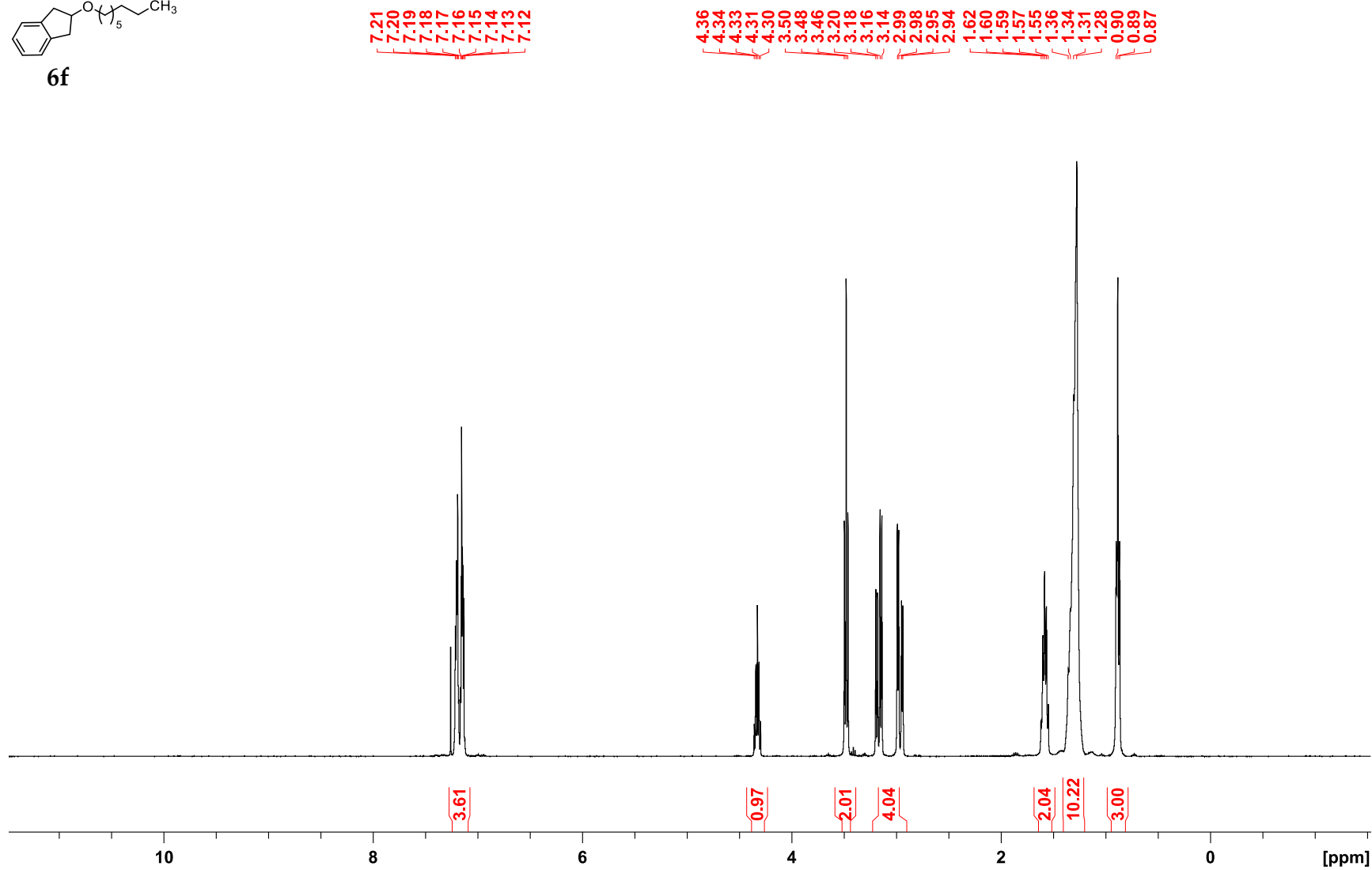


Figure S2. <sup>1</sup>H NMR Spectrum of 6f

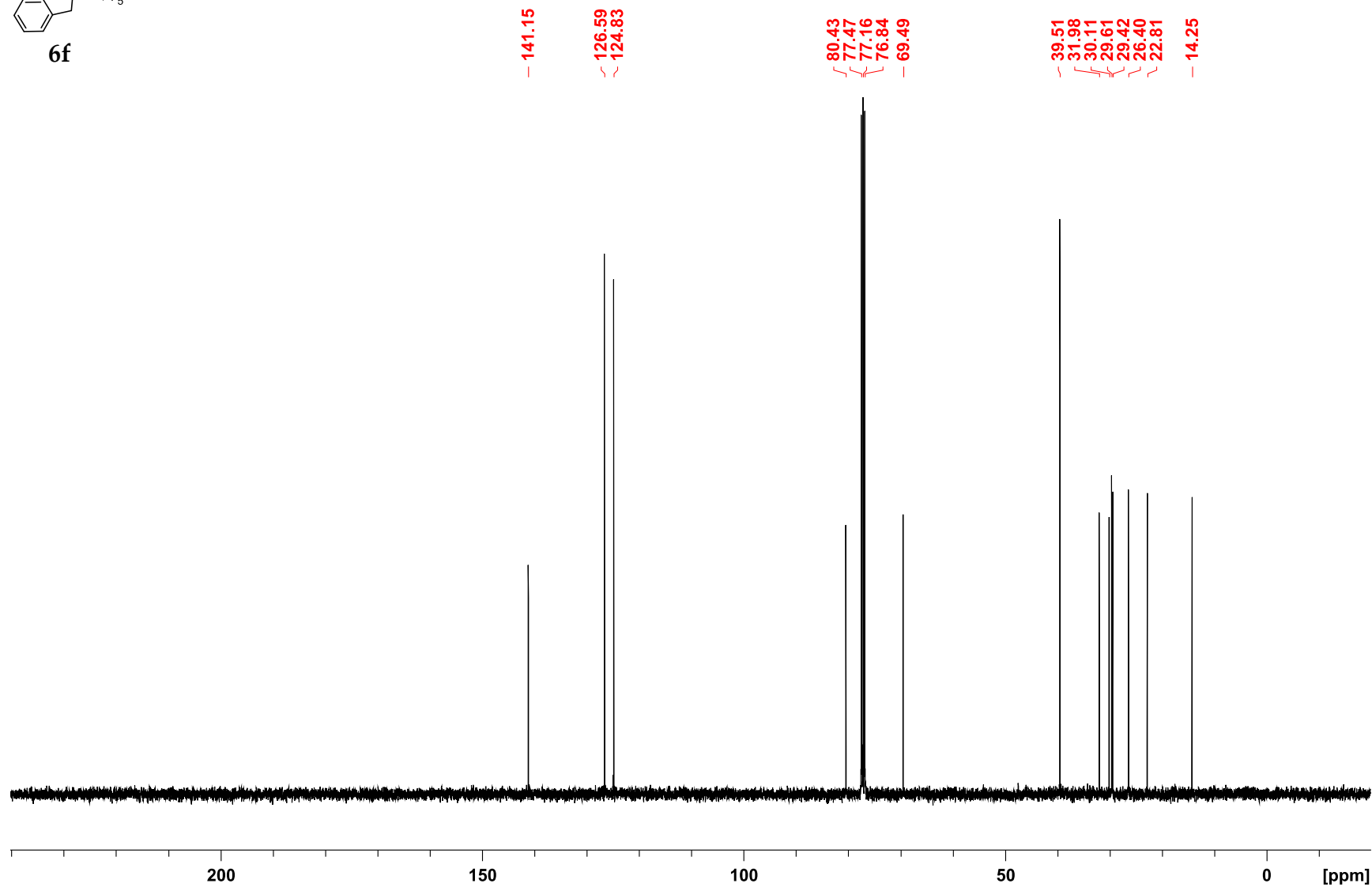
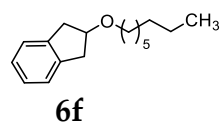


Figure S3.  $^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of **6f**



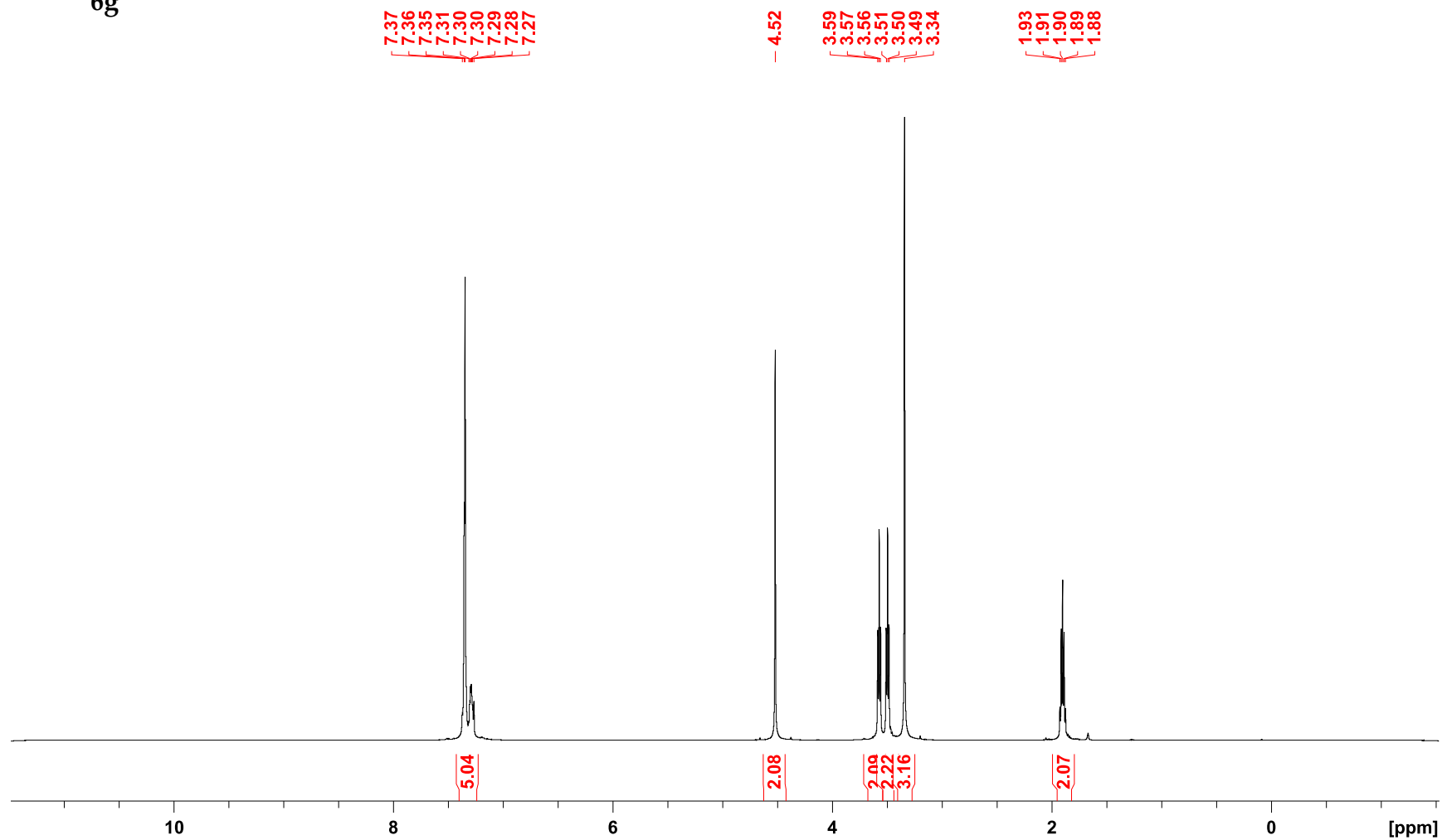
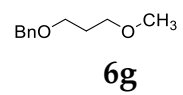


Figure S4. <sup>1</sup>H NMR Spectrum of **6g**

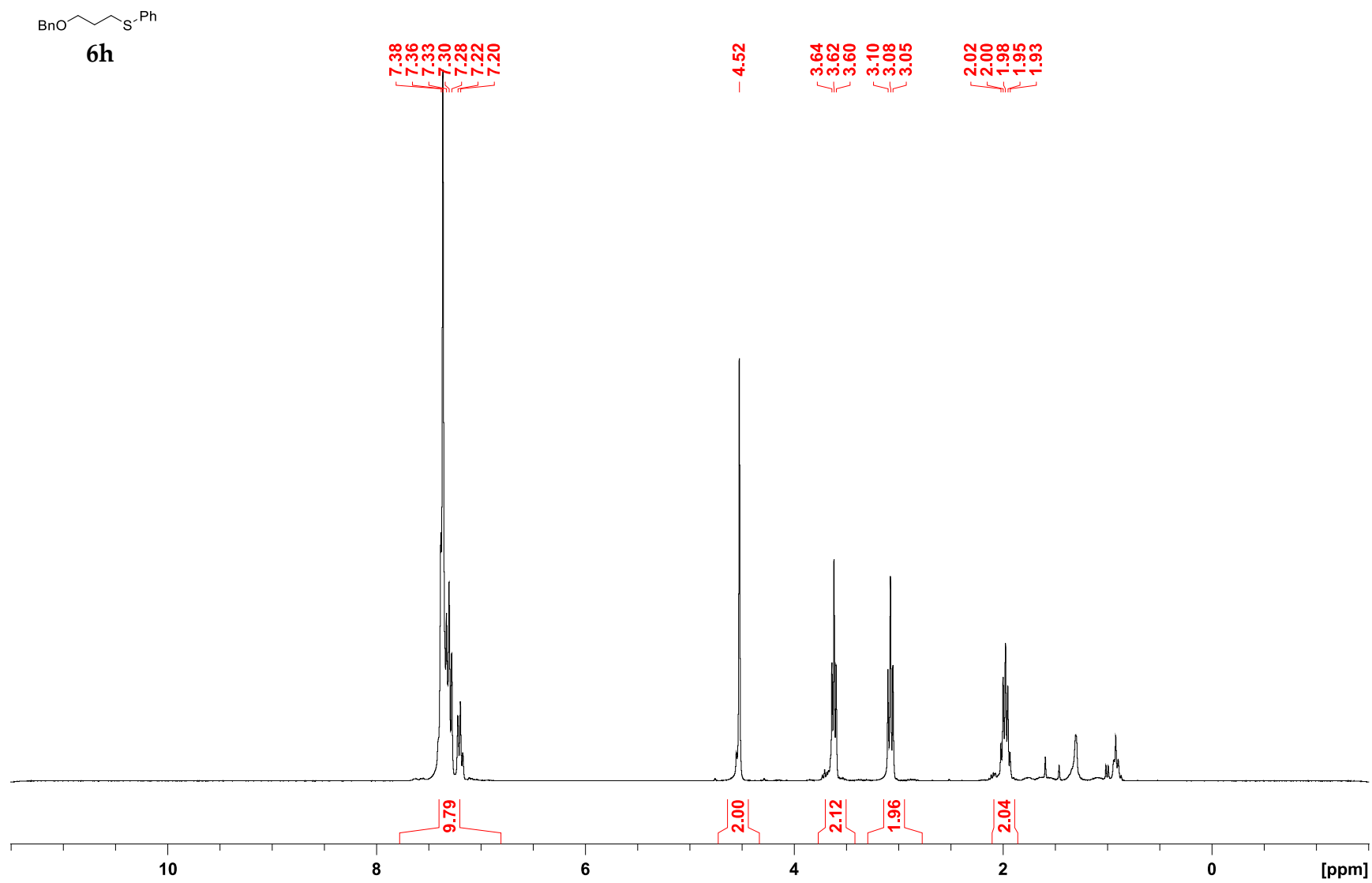


Figure S5.  $^1\text{H}$  NMR Spectrum of **6h**

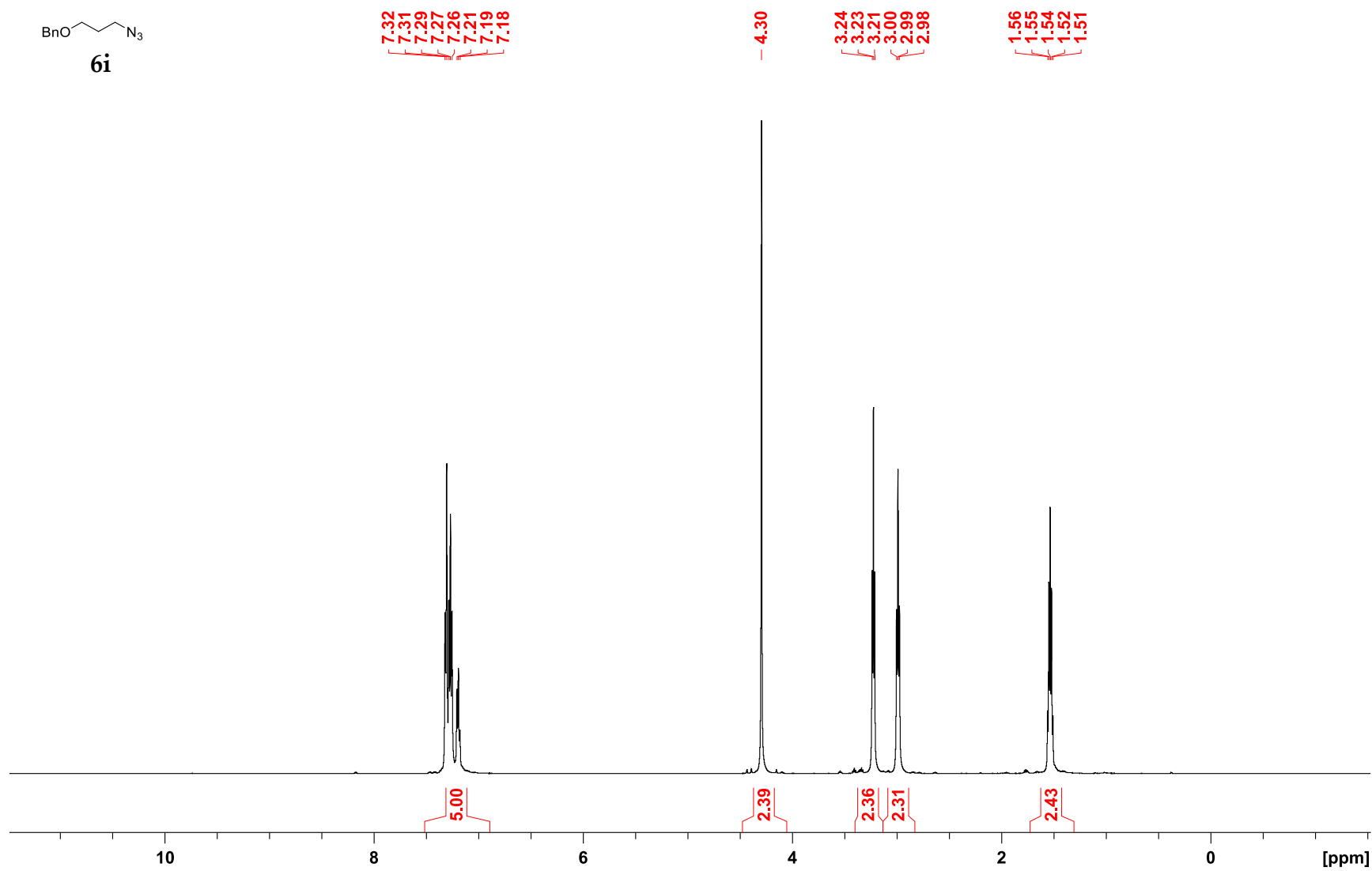
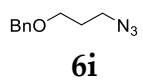


Figure S6.  $^1\text{H}$  NMR Spectrum of **6i**

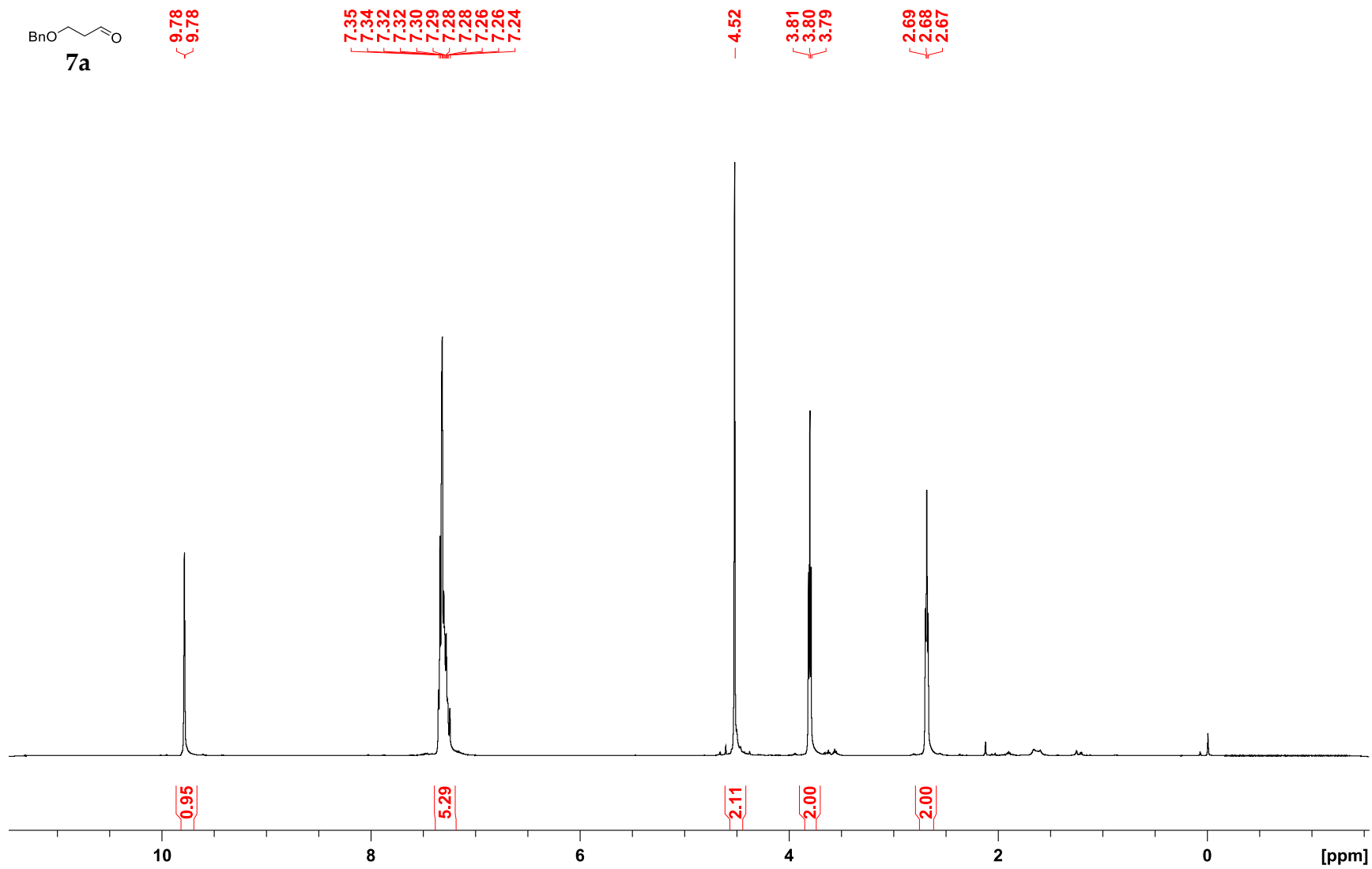


Figure S7.  $^1\text{H}$  NMR Spectrum of **7a**

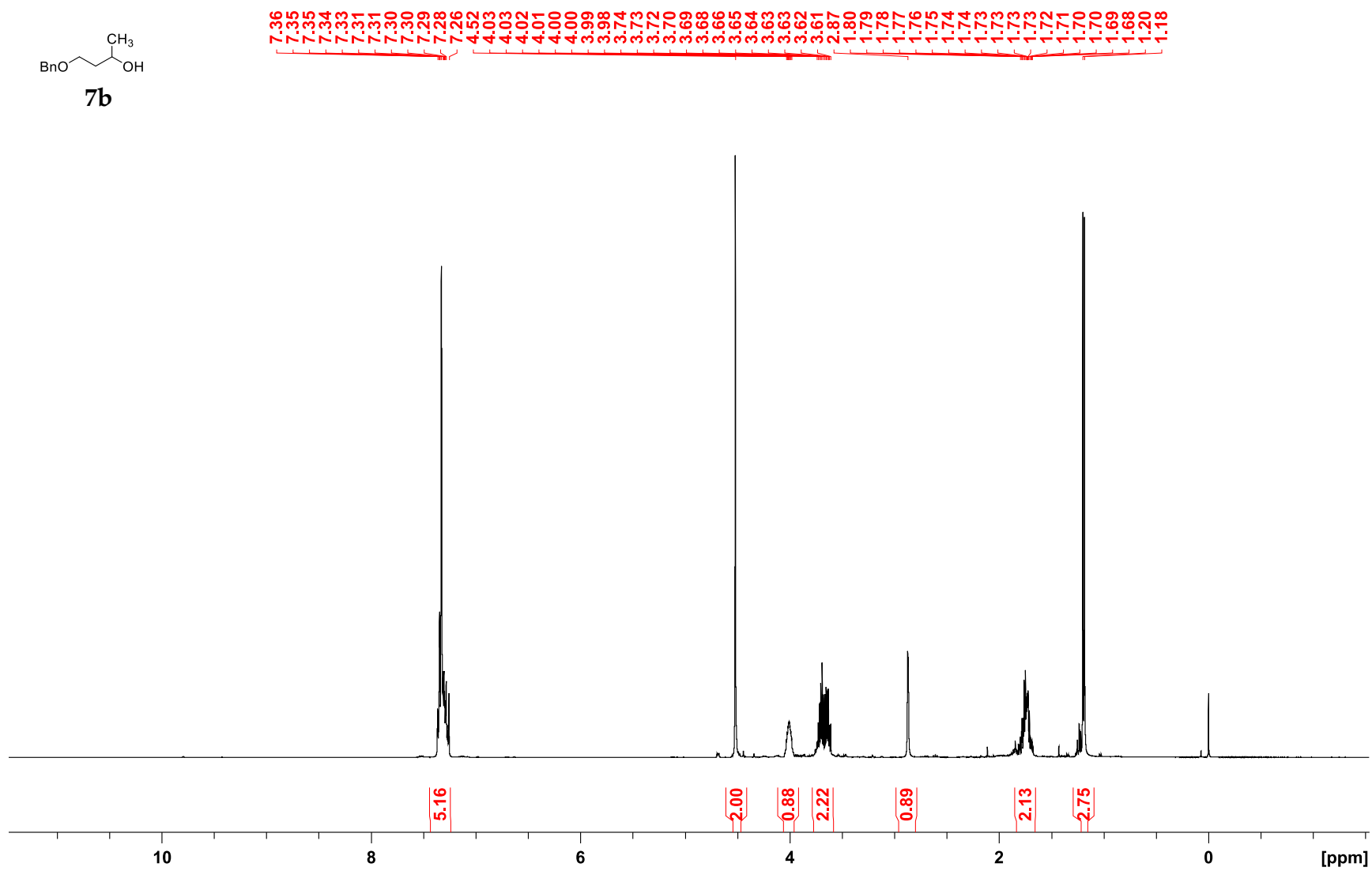
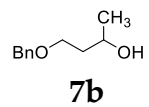


Figure S8. <sup>1</sup>H NMR Spectrum of **7b**

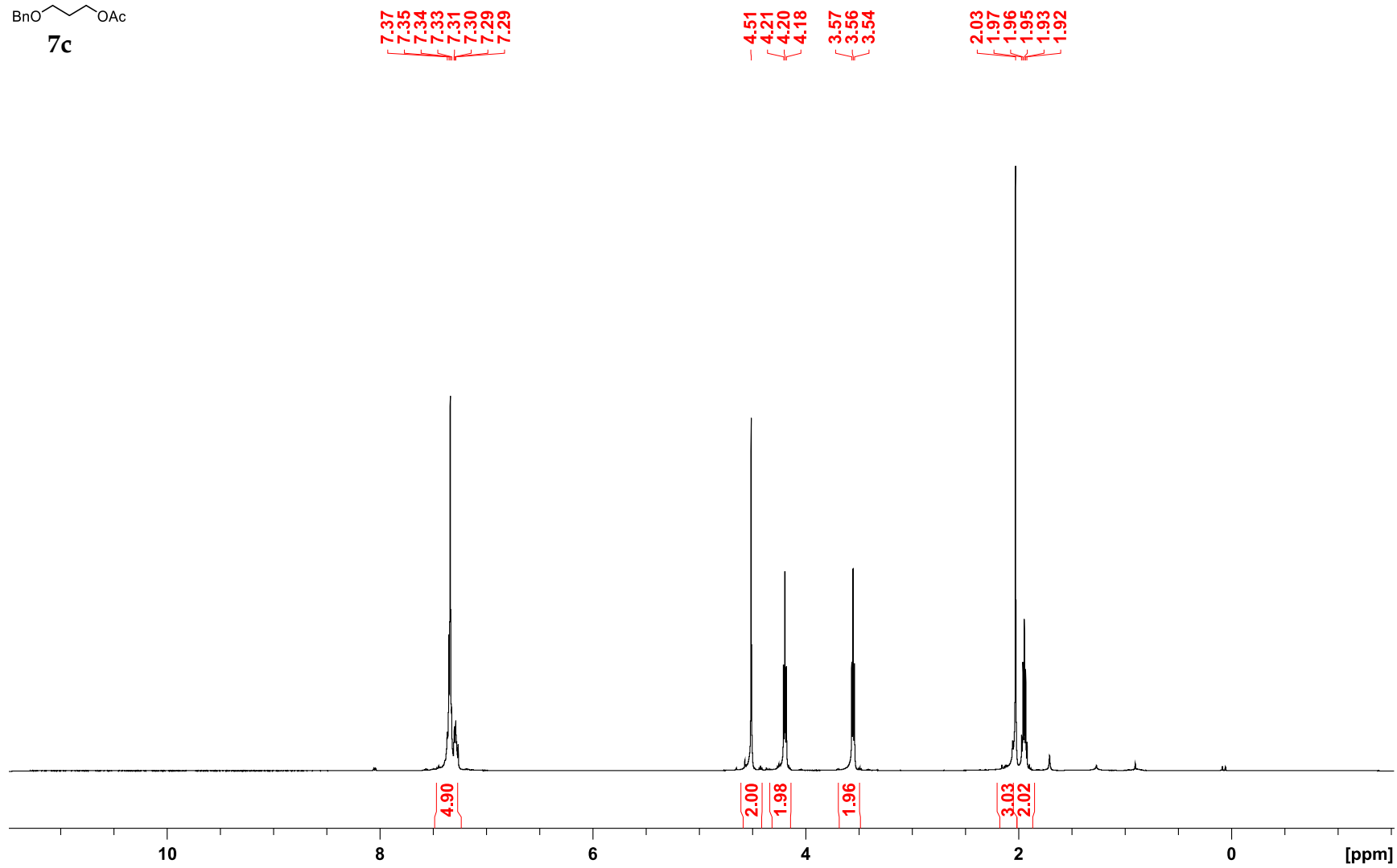
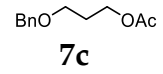


Figure S9. <sup>1</sup>H NMR Spectrum of 7c

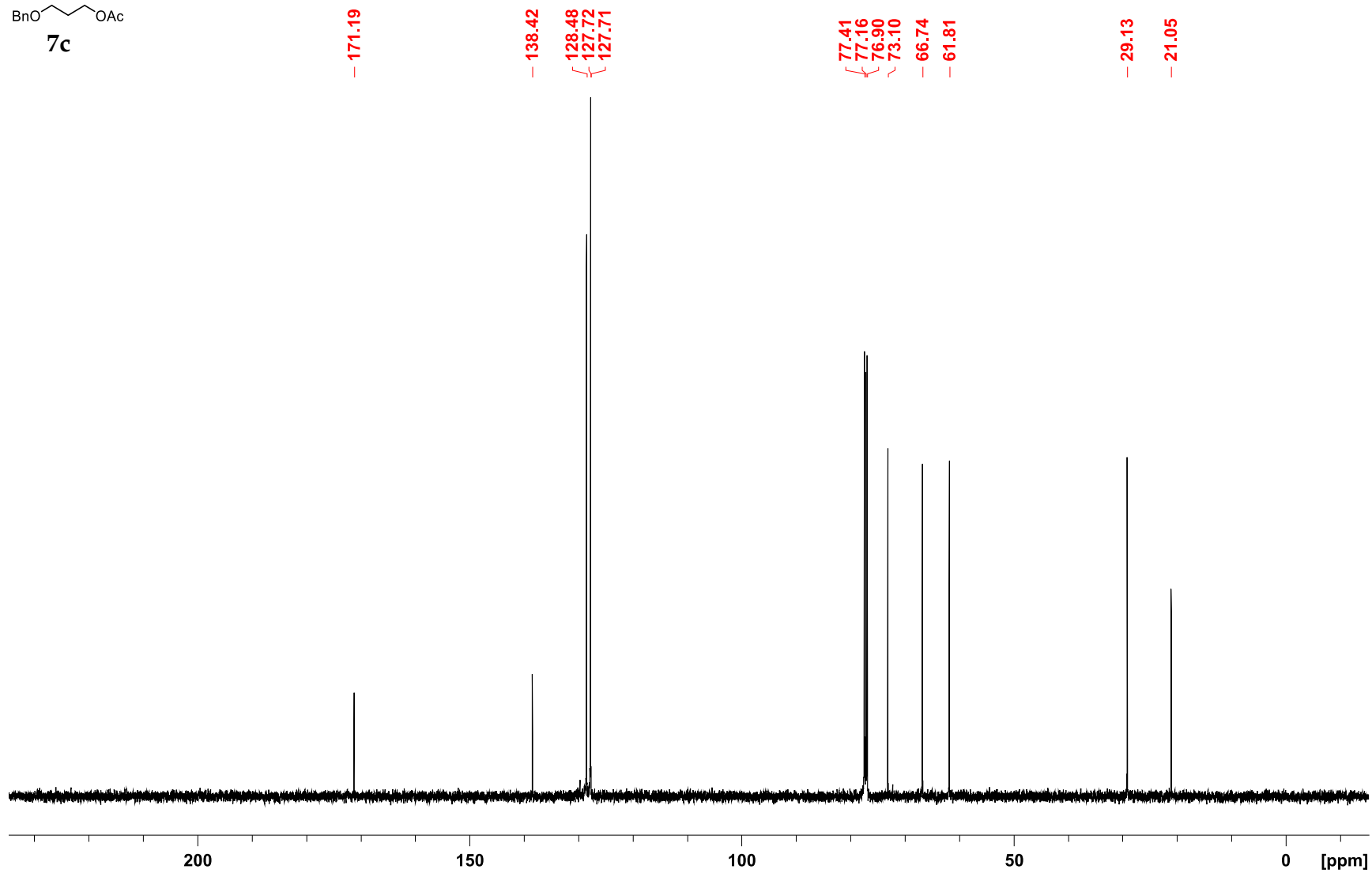
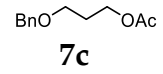
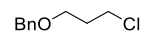


Figure S10.  $^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of **7c**



**7d**

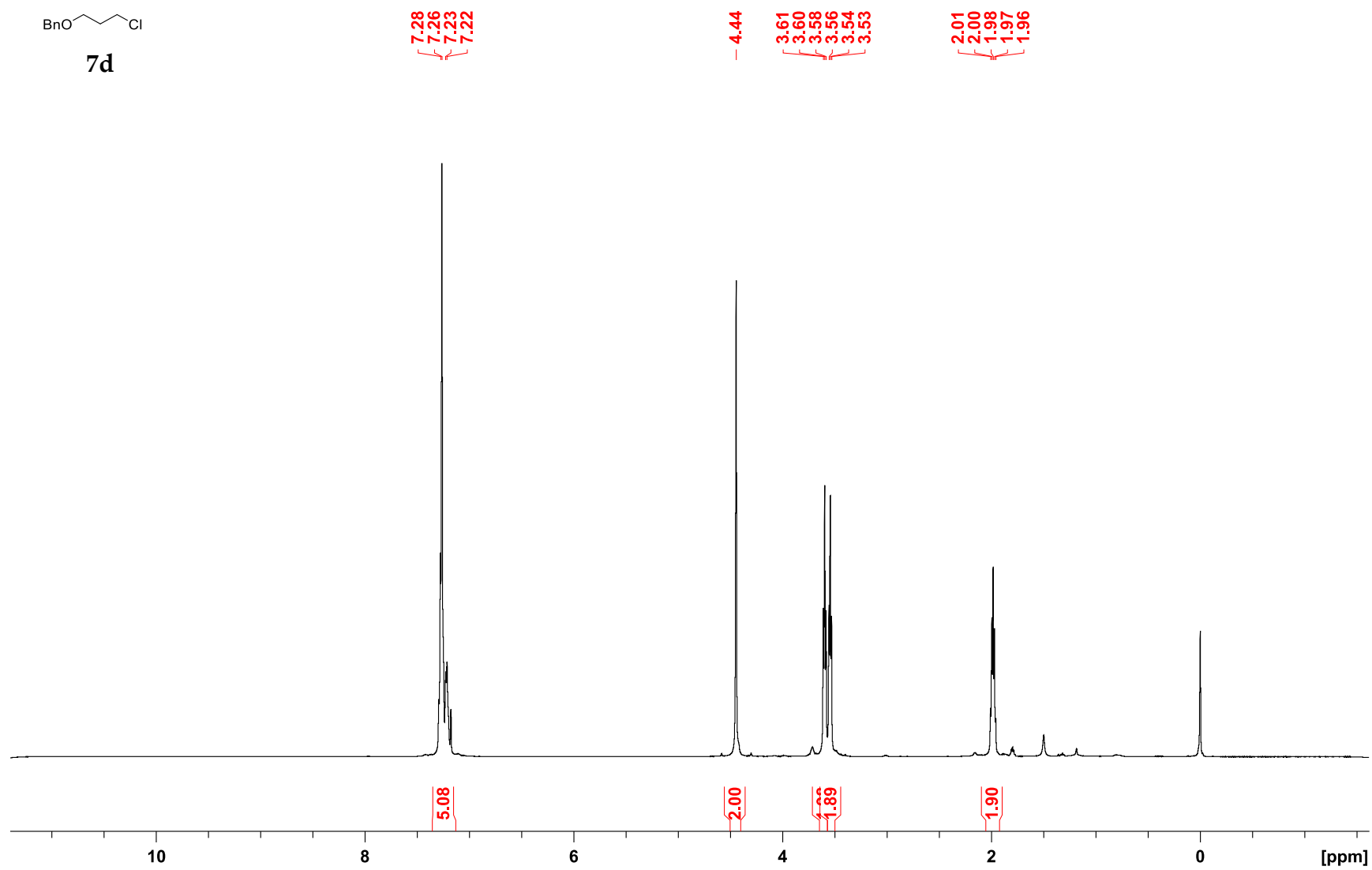


Figure S11.  $^1\text{H}$  NMR Spectrum of **7d**



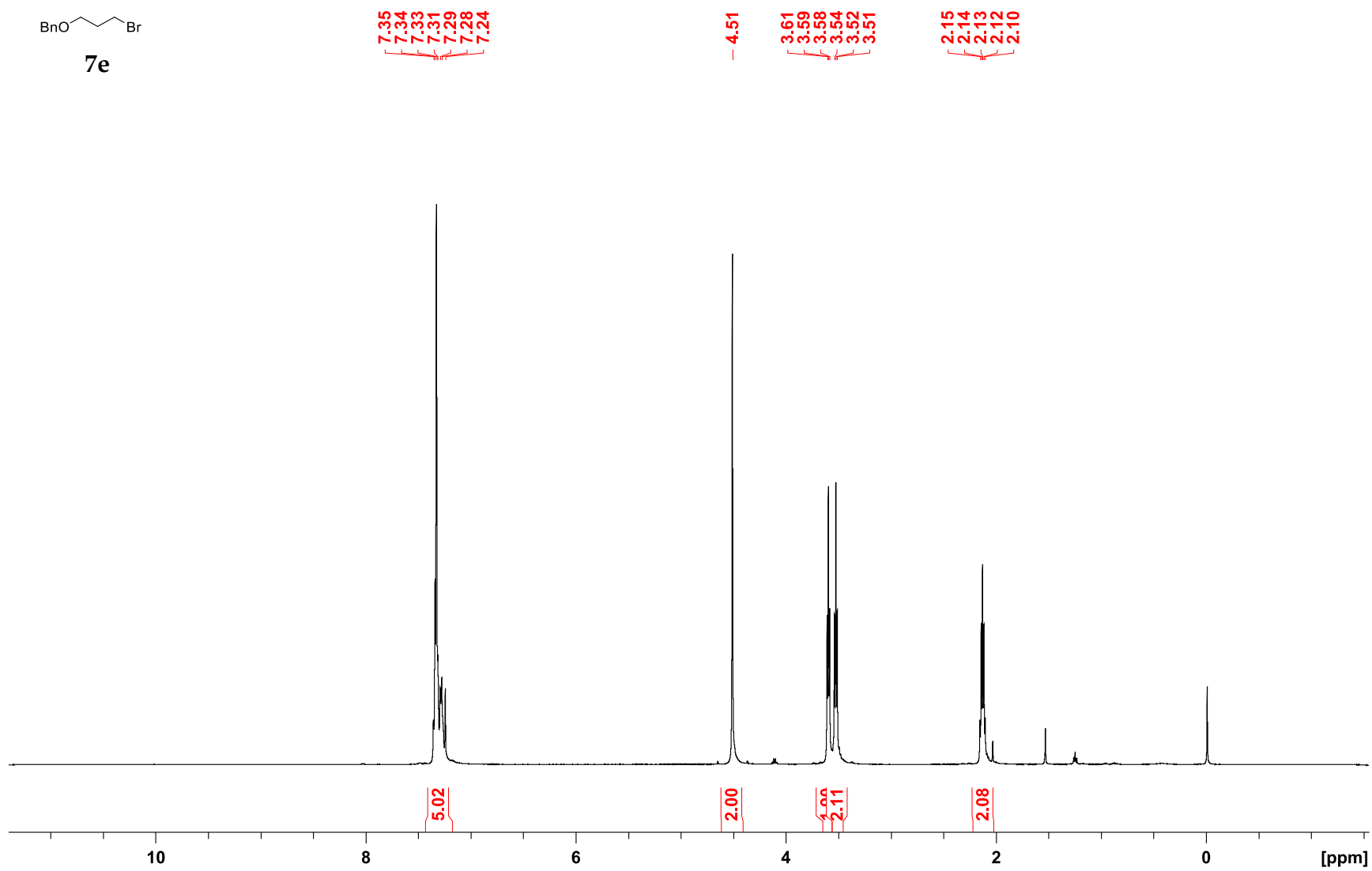
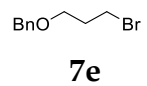


Figure S12.  $^1\text{H}$  NMR Spectrum of **7e**

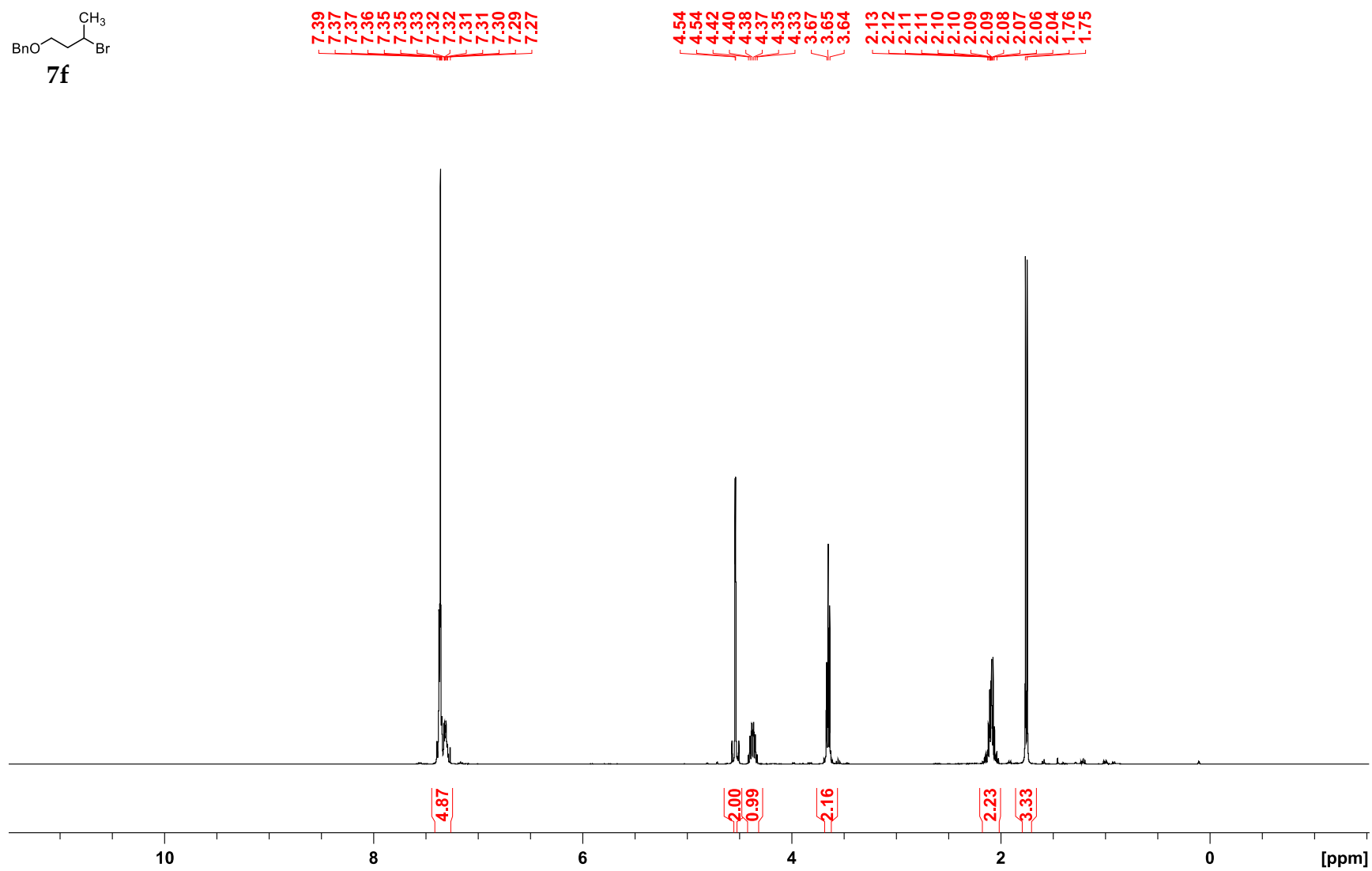
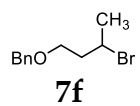


Figure S13. <sup>1</sup>H NMR Spectrum of 7f

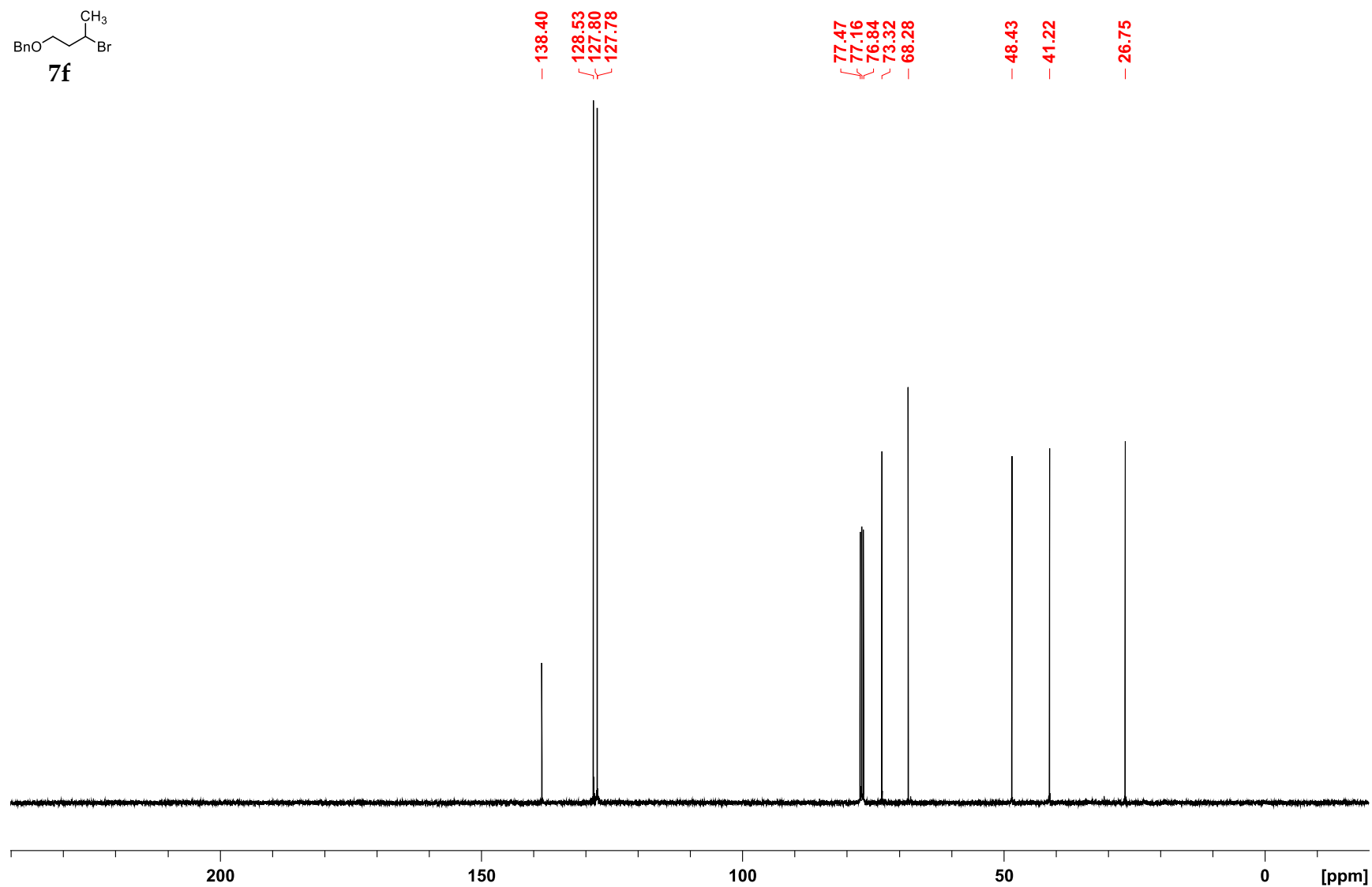
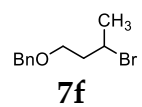


Figure S14.  $^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of **7f**

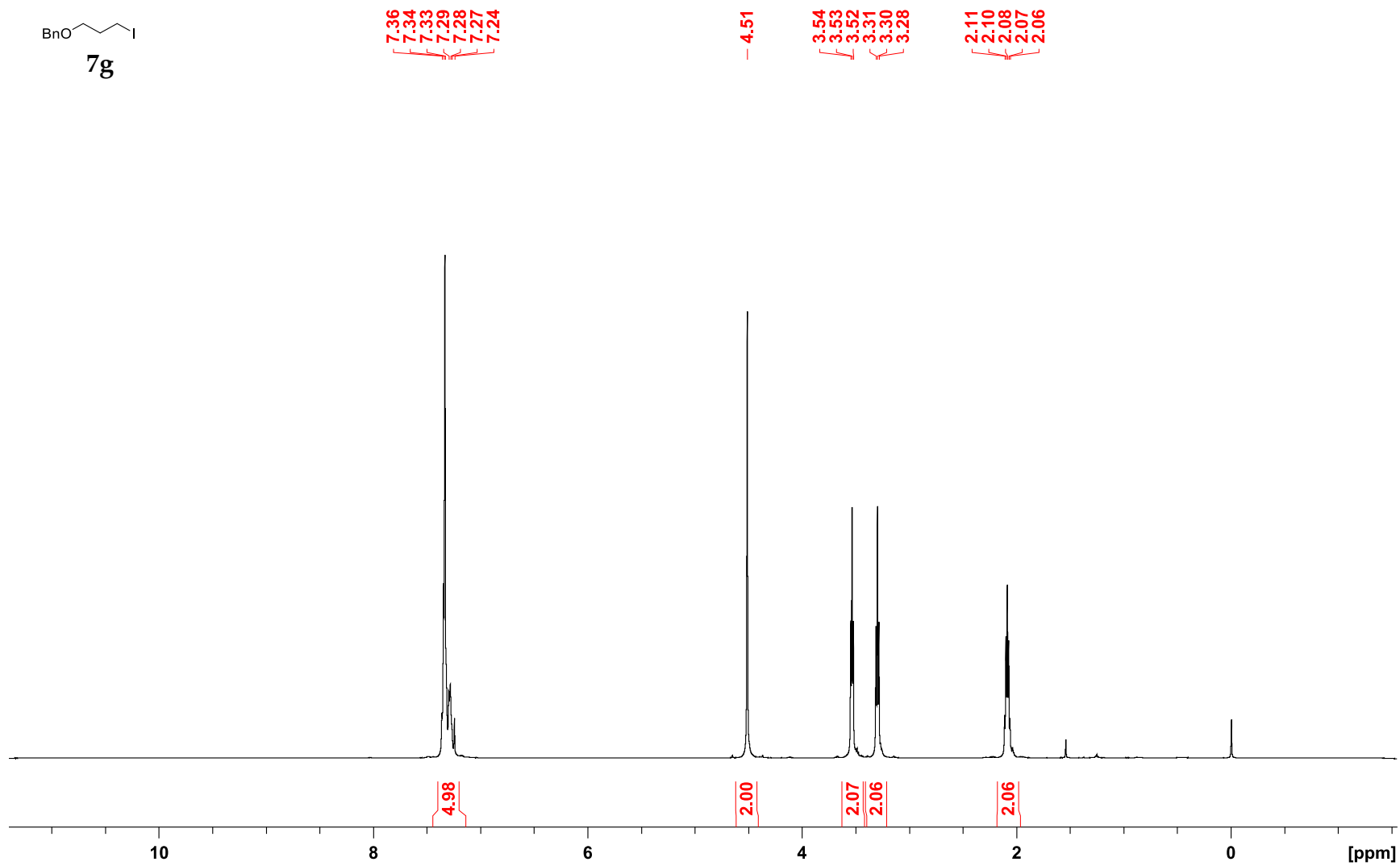
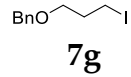
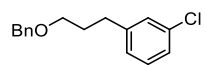


Figure S15. <sup>1</sup>H NMR Spectrum of 7g



7i

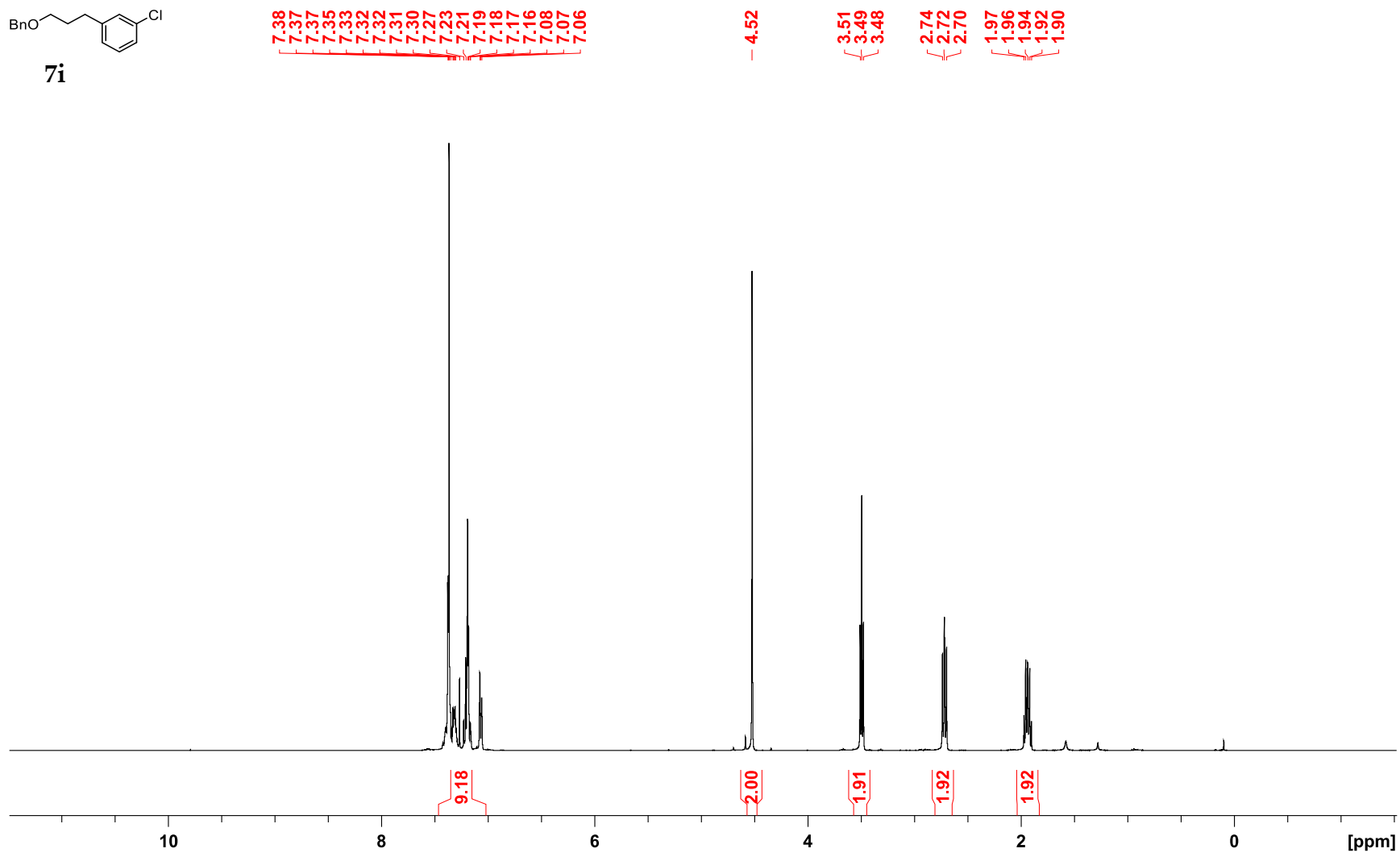
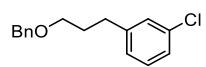


Figure S16. <sup>1</sup>H NMR Spectrum of 7i



7i

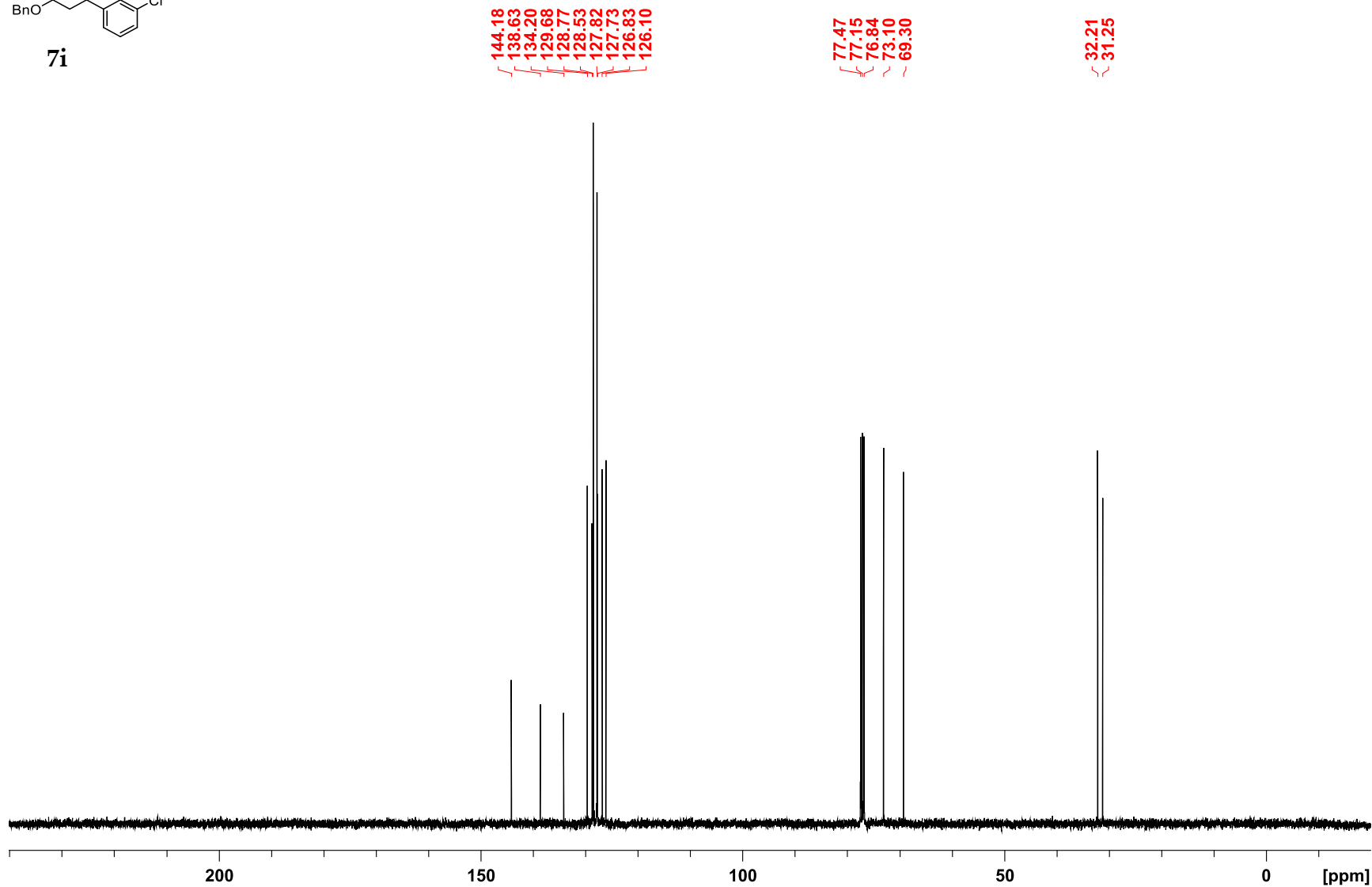


Figure S17.  $^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of 7i

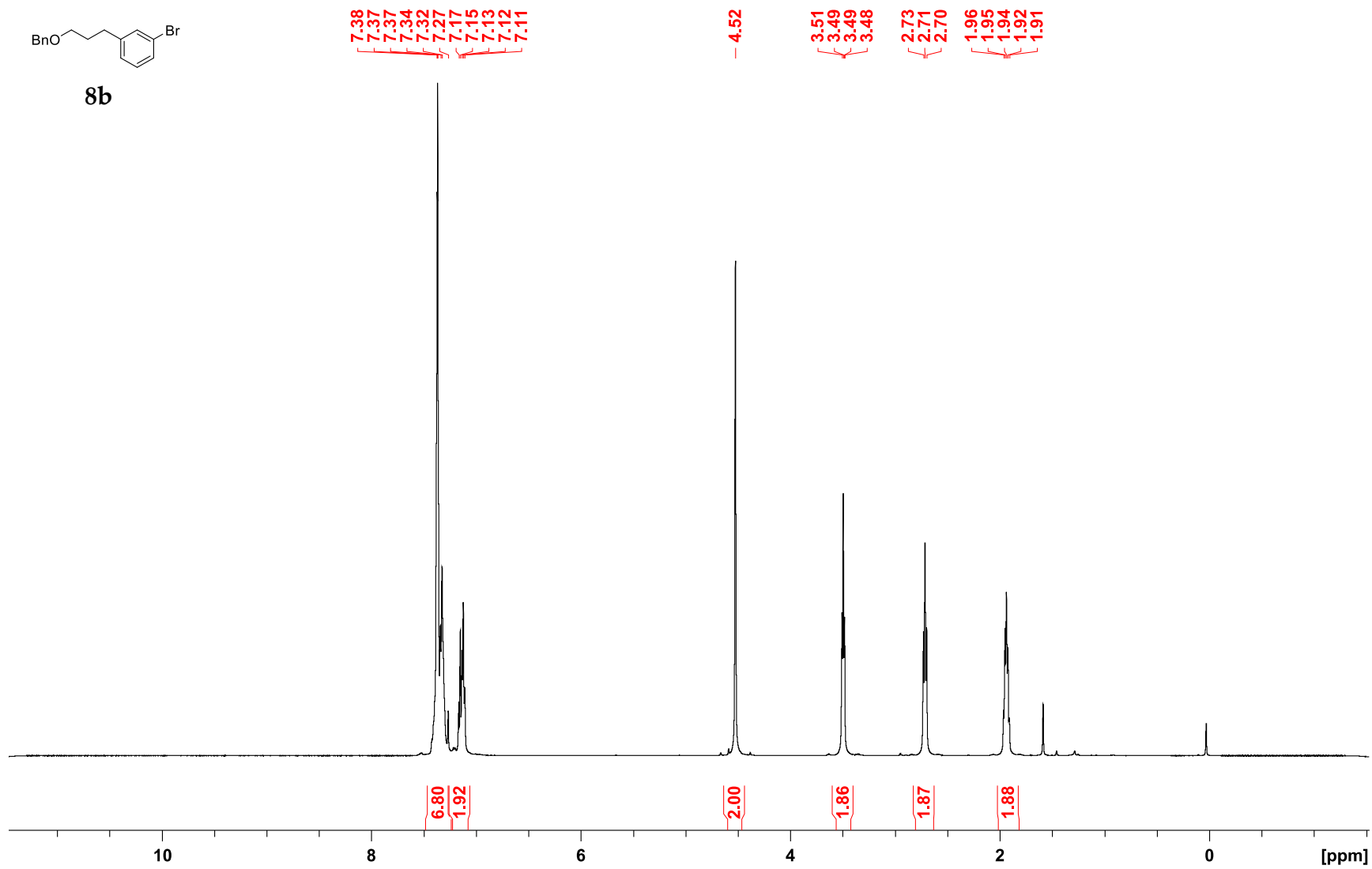


Figure S18.  $^1\text{H}$  NMR Spectrum of **8b**

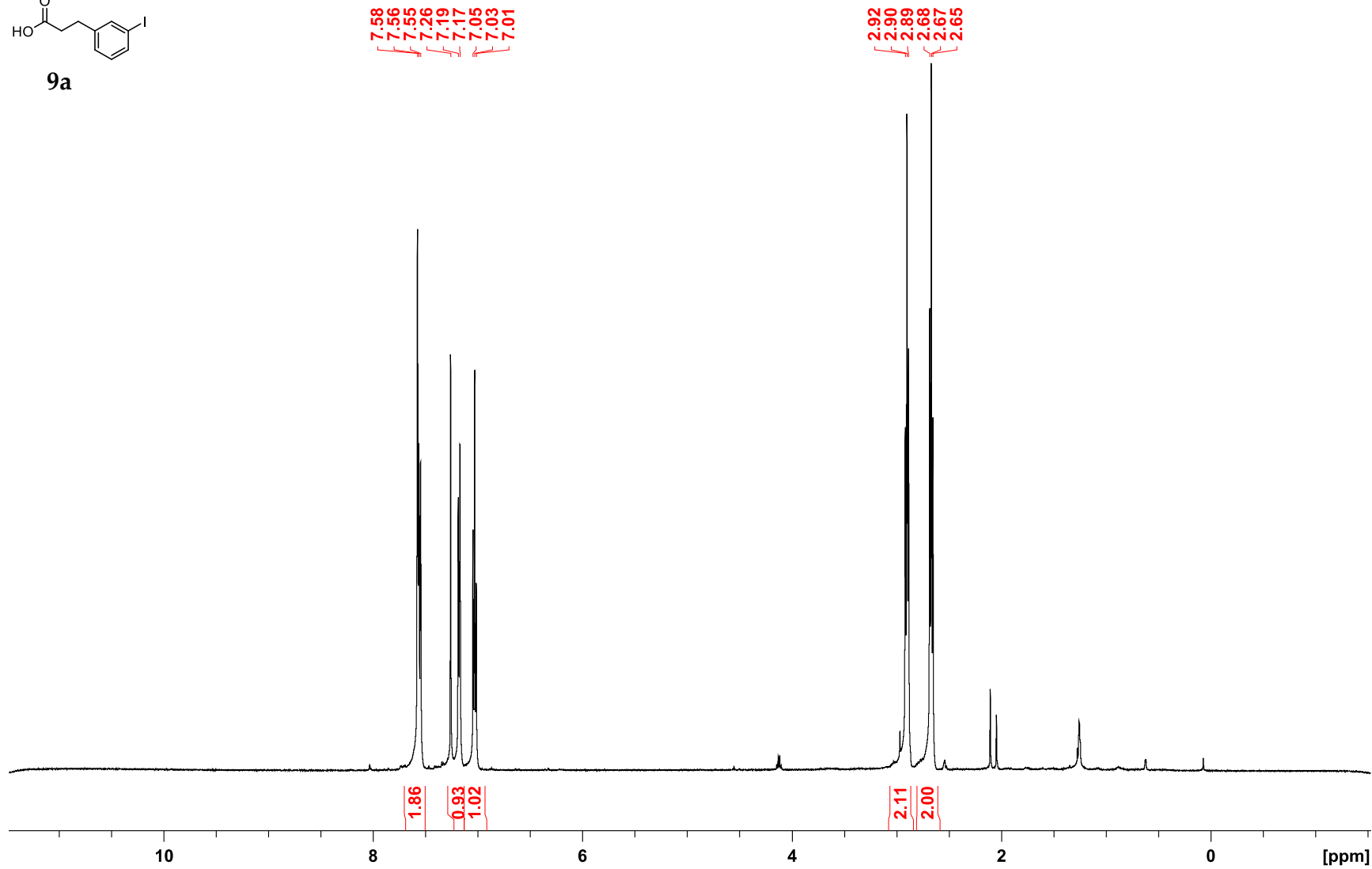
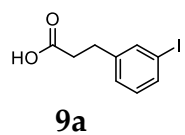


Figure S19. <sup>1</sup>H NMR Spectrum of 9a



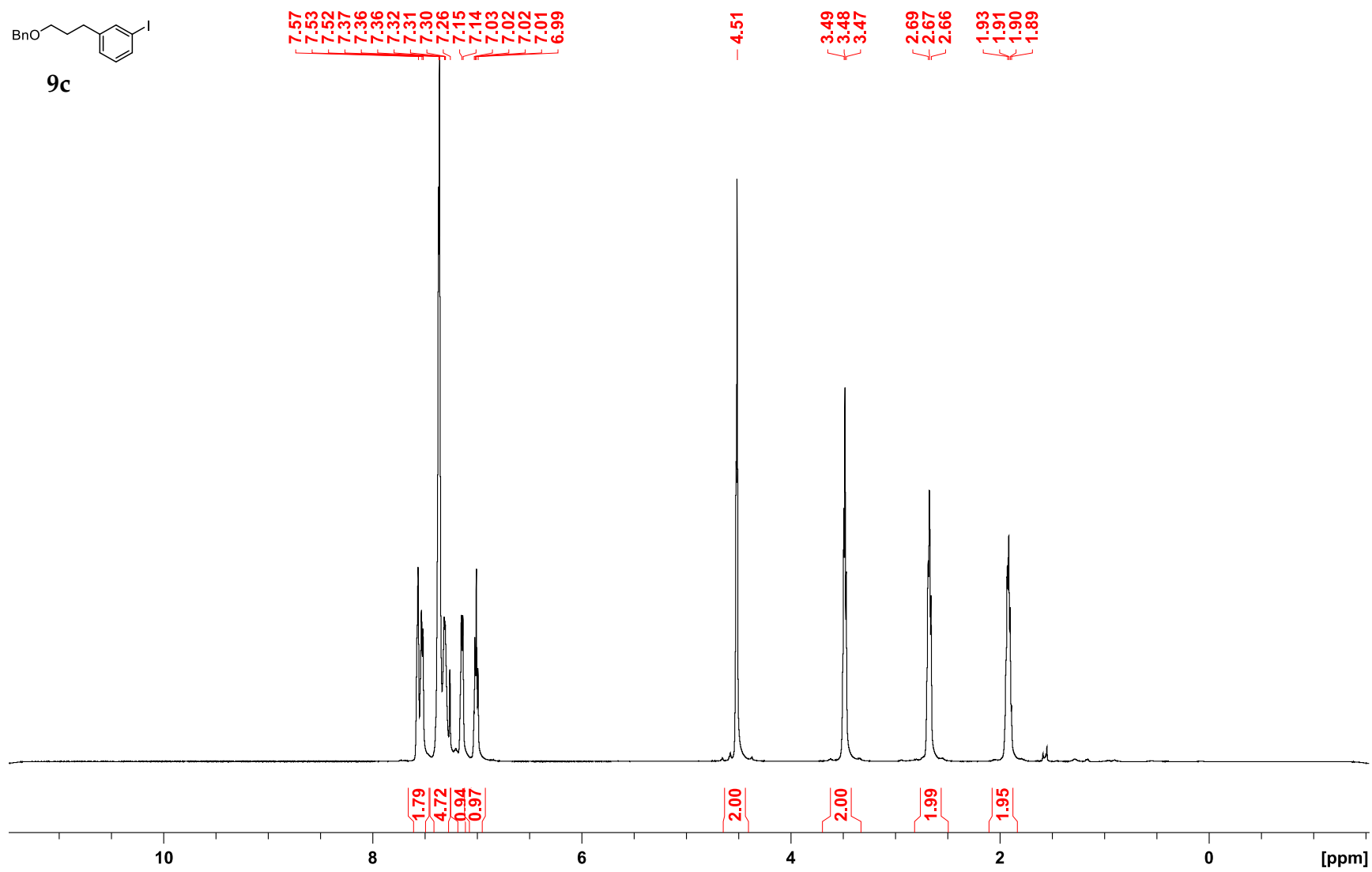
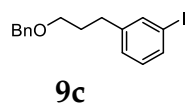


Figure S20. <sup>1</sup>H NMR Spectrum of 9c

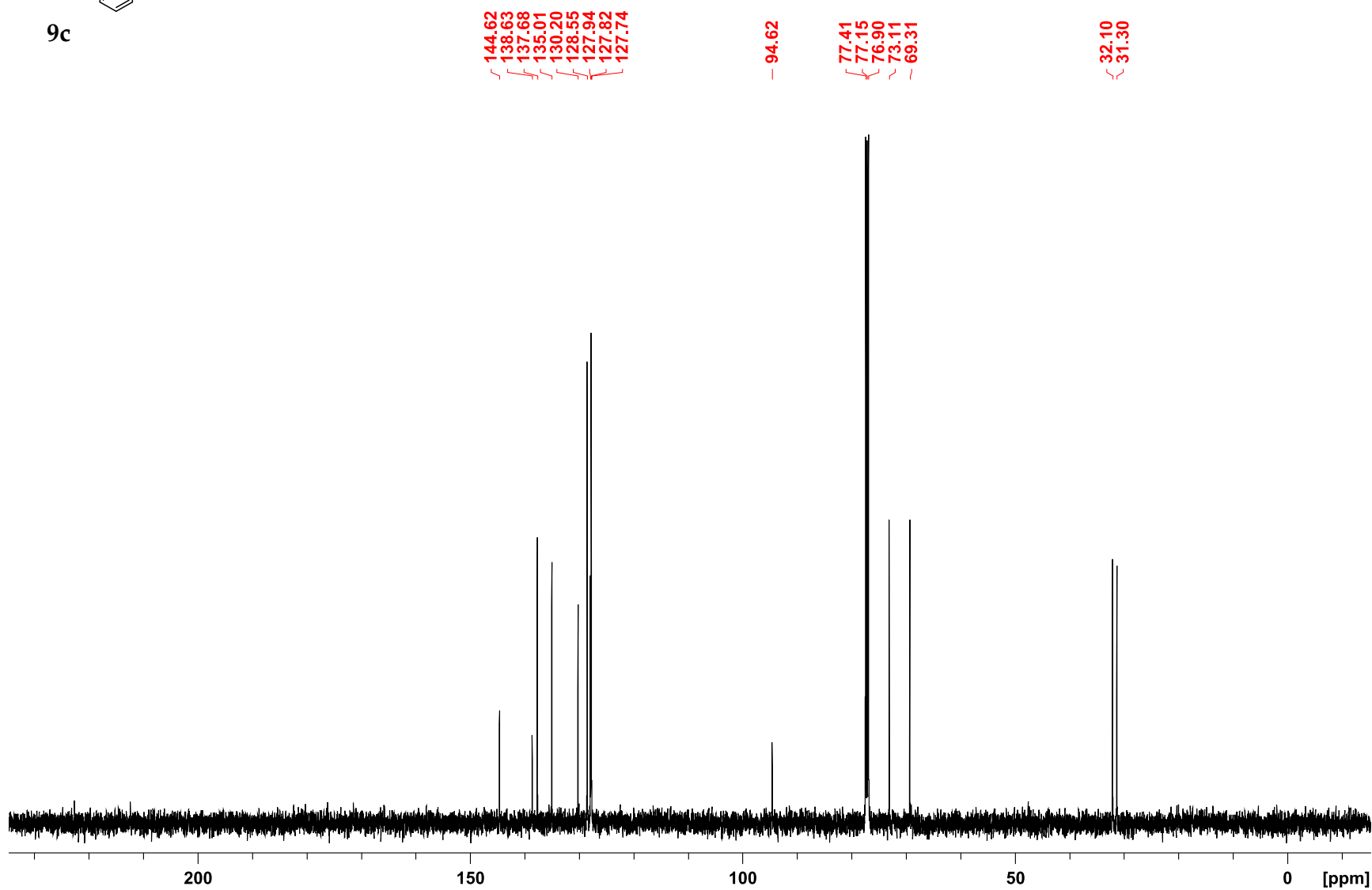
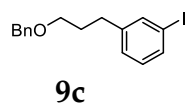


Figure S21.  $^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of **9c**

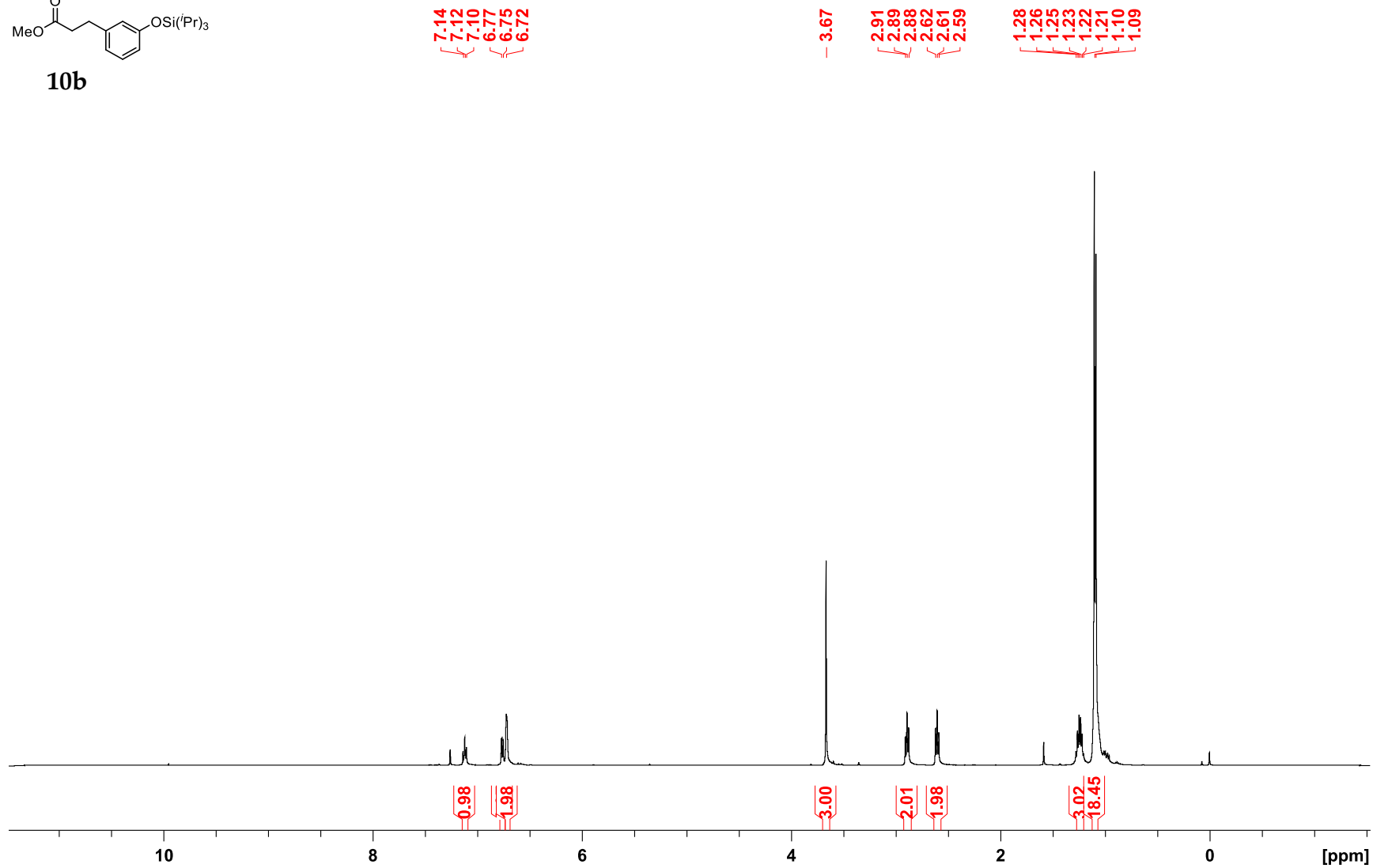
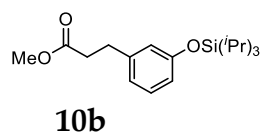


Figure S22. <sup>1</sup>H NMR Spectrum of **10b**

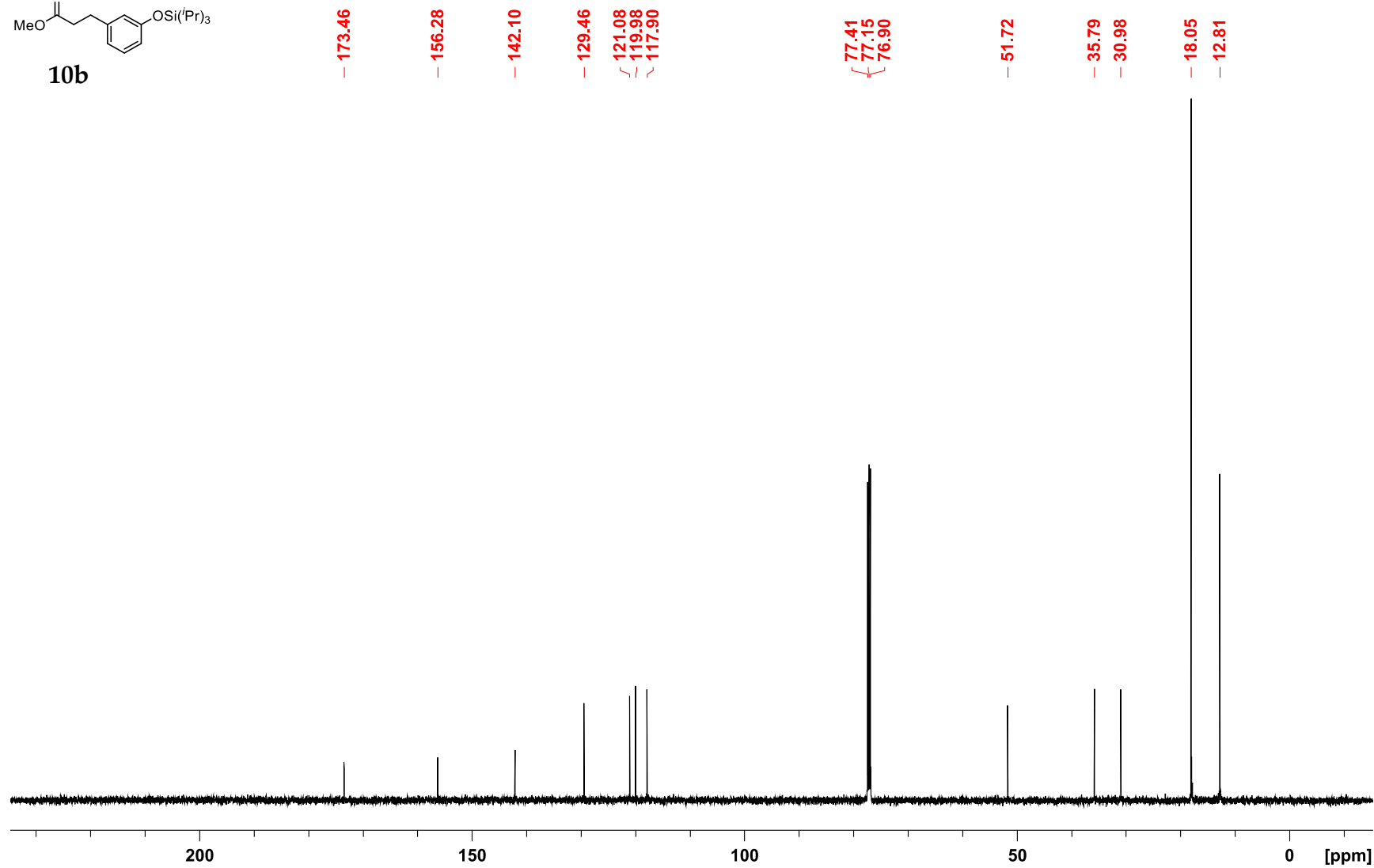
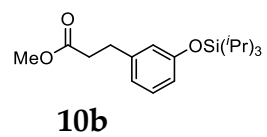


Figure S23.  $^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of **10b**

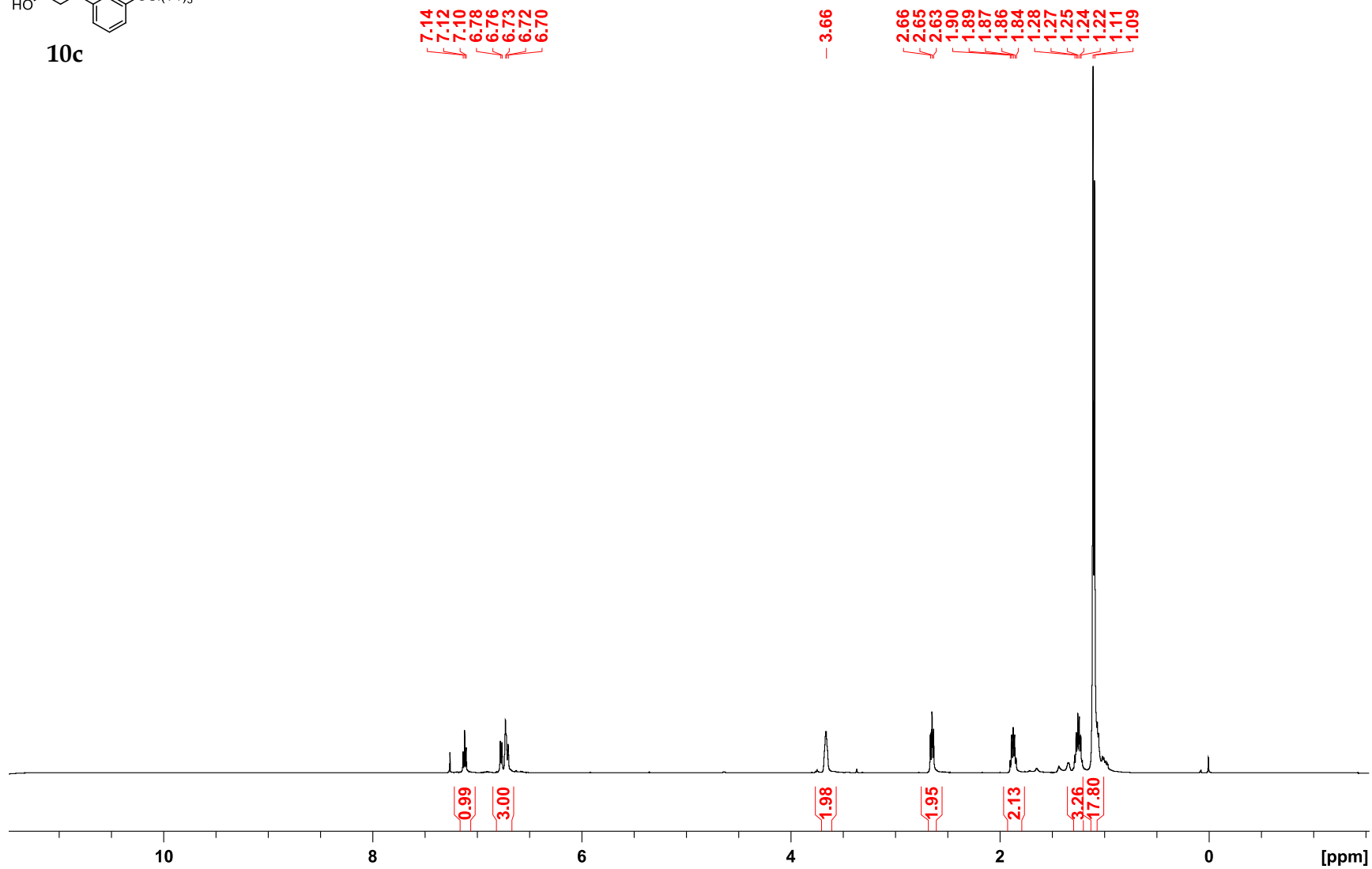
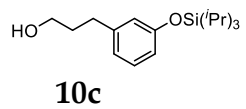


Figure S24. <sup>1</sup>H NMR Spectrum of **10c**

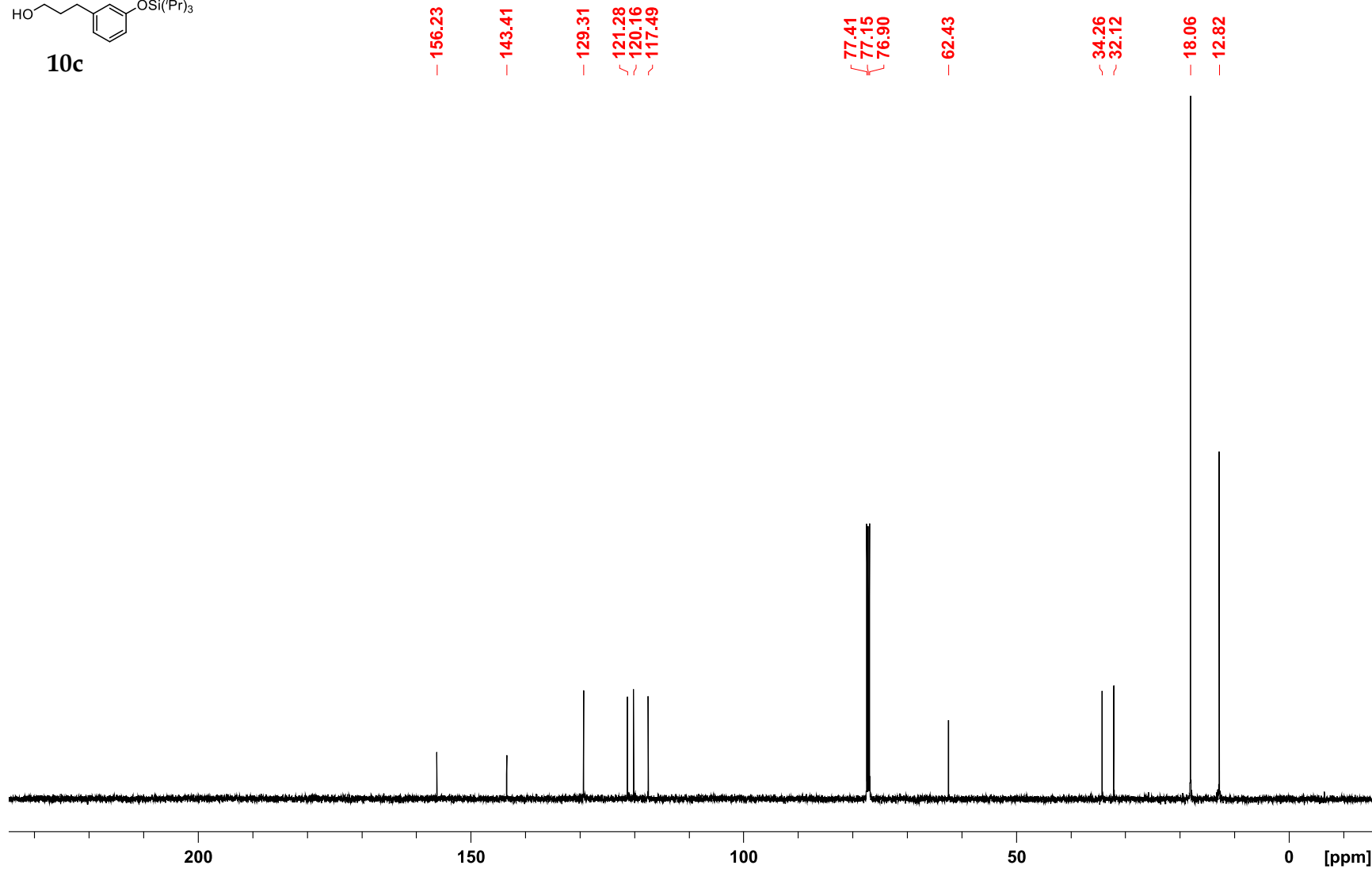
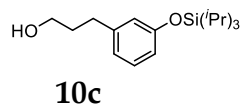


Figure S25.  $^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of **10c**

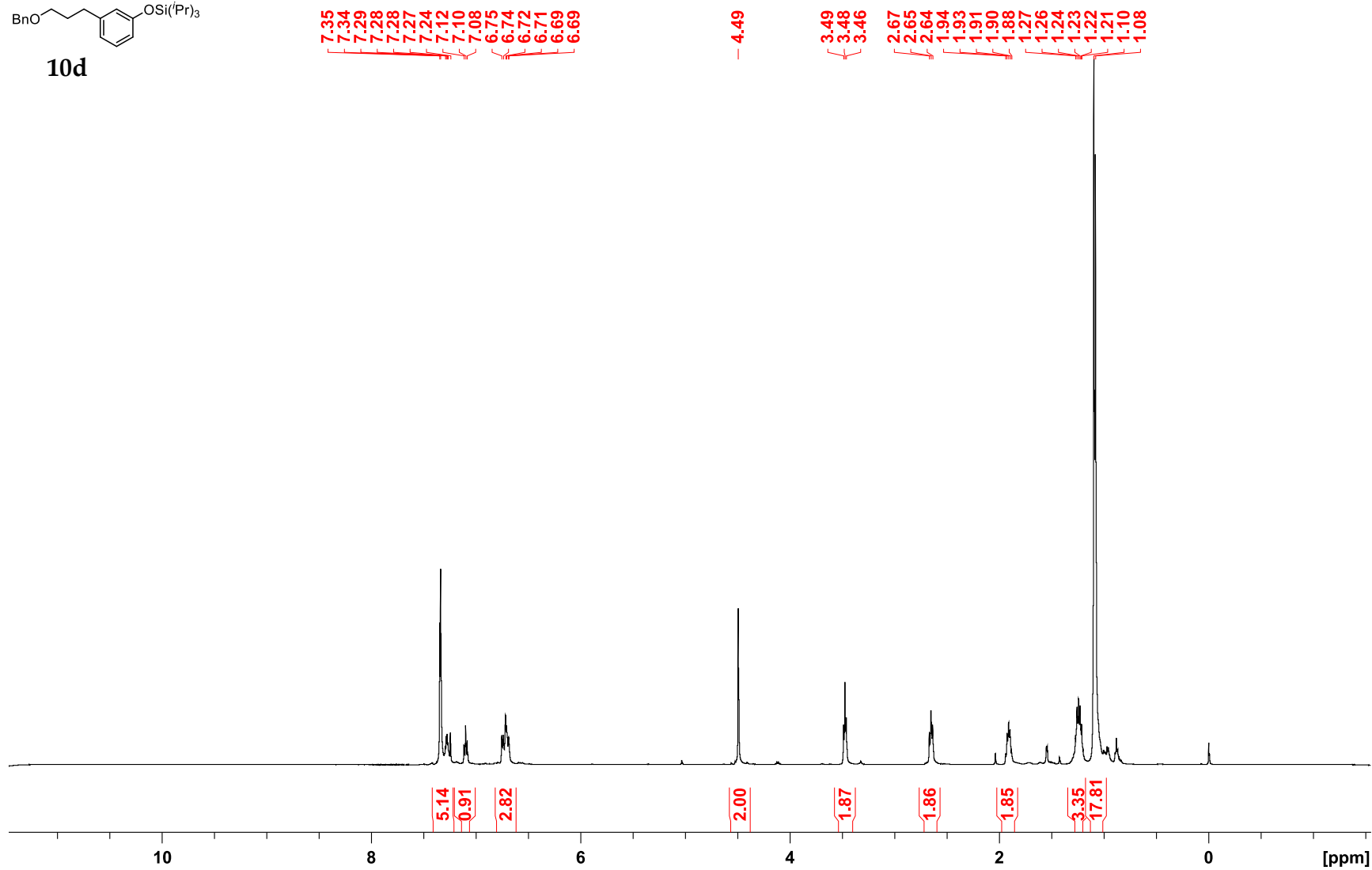
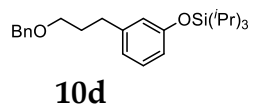


Figure S26. <sup>1</sup>H NMR Spectrum of 10d

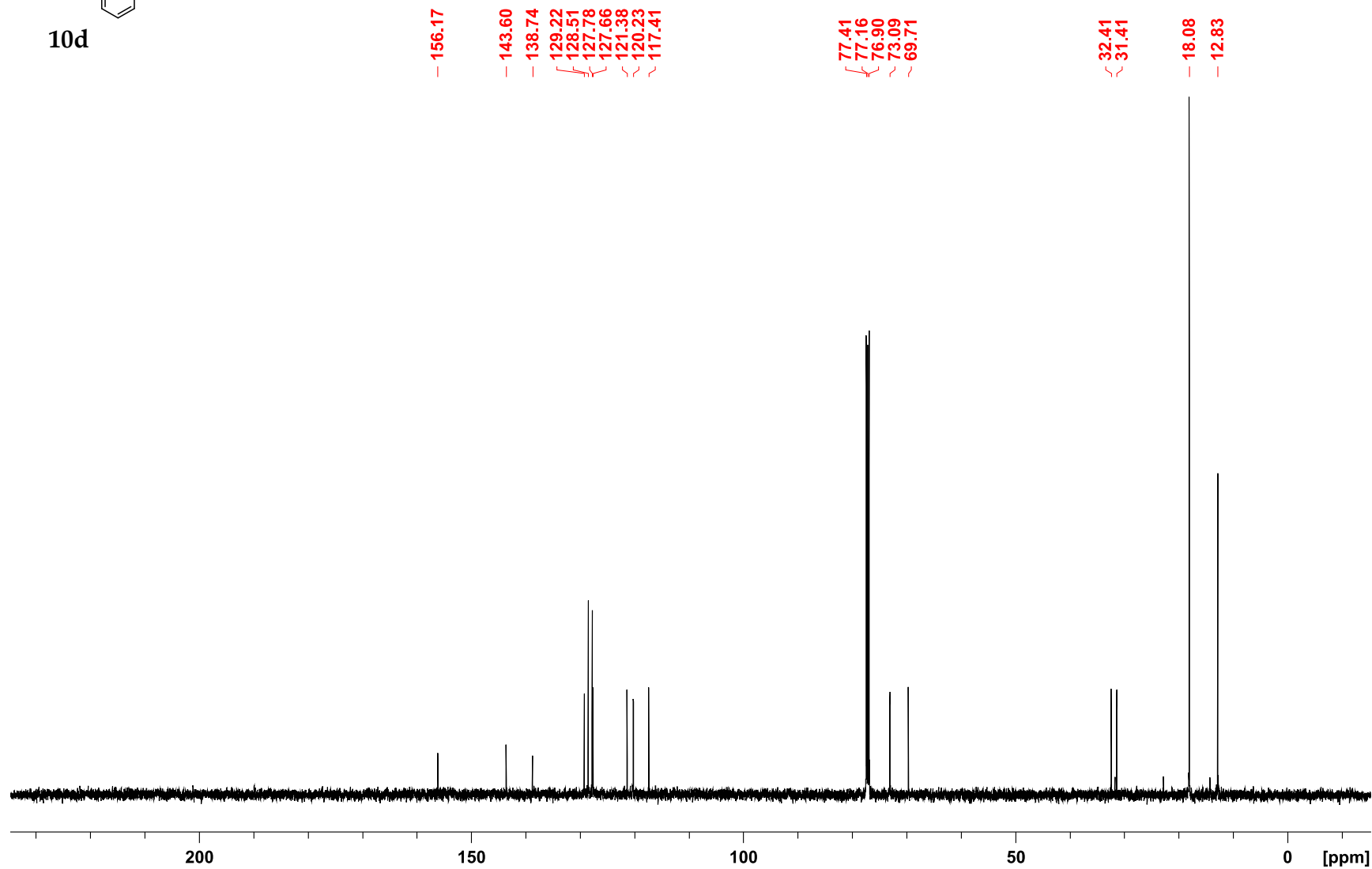
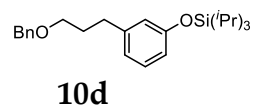


Figure S27.  $^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of **10d**



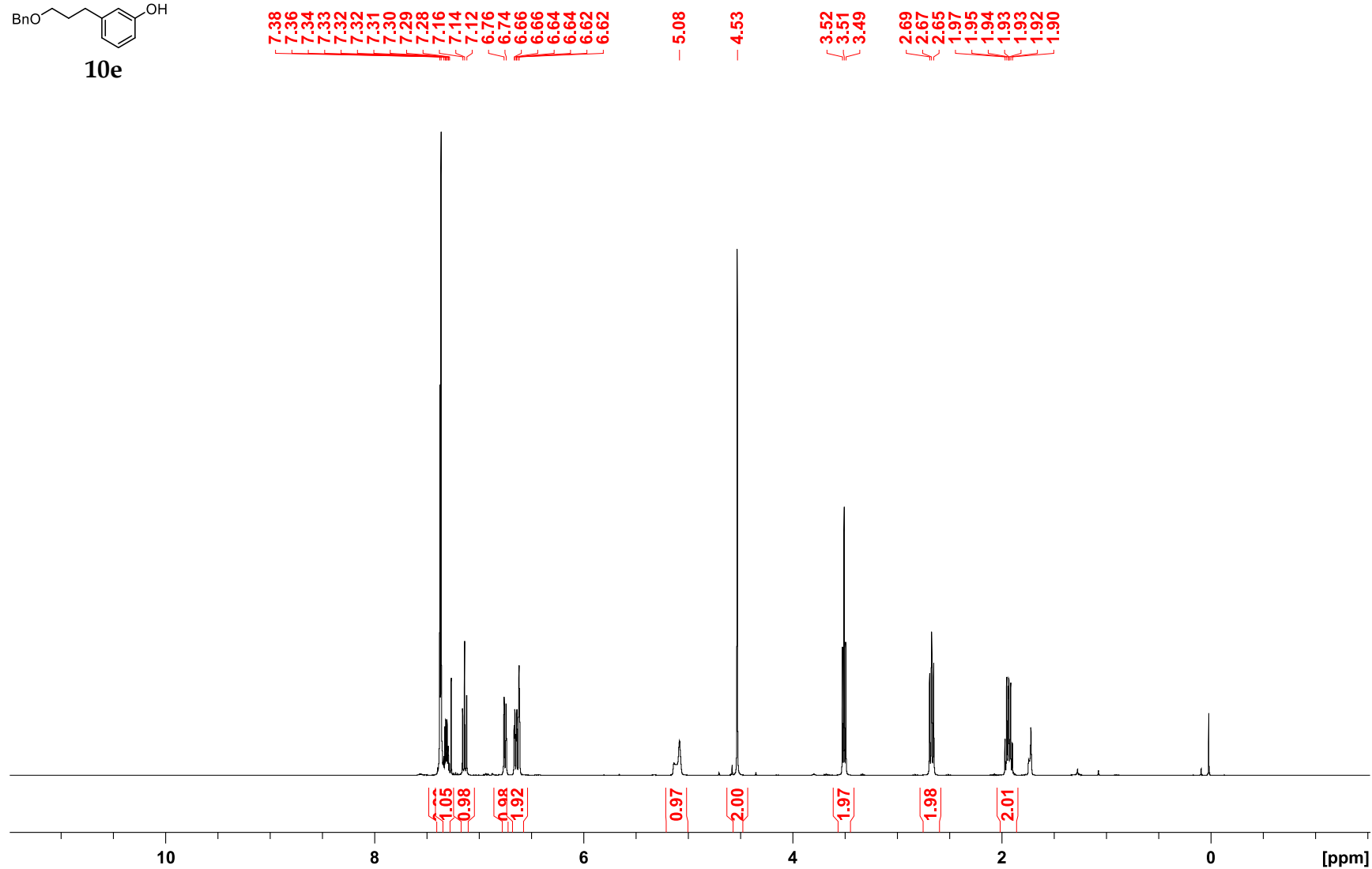
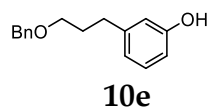


Figure S28. <sup>1</sup>H NMR Spectrum of 10e

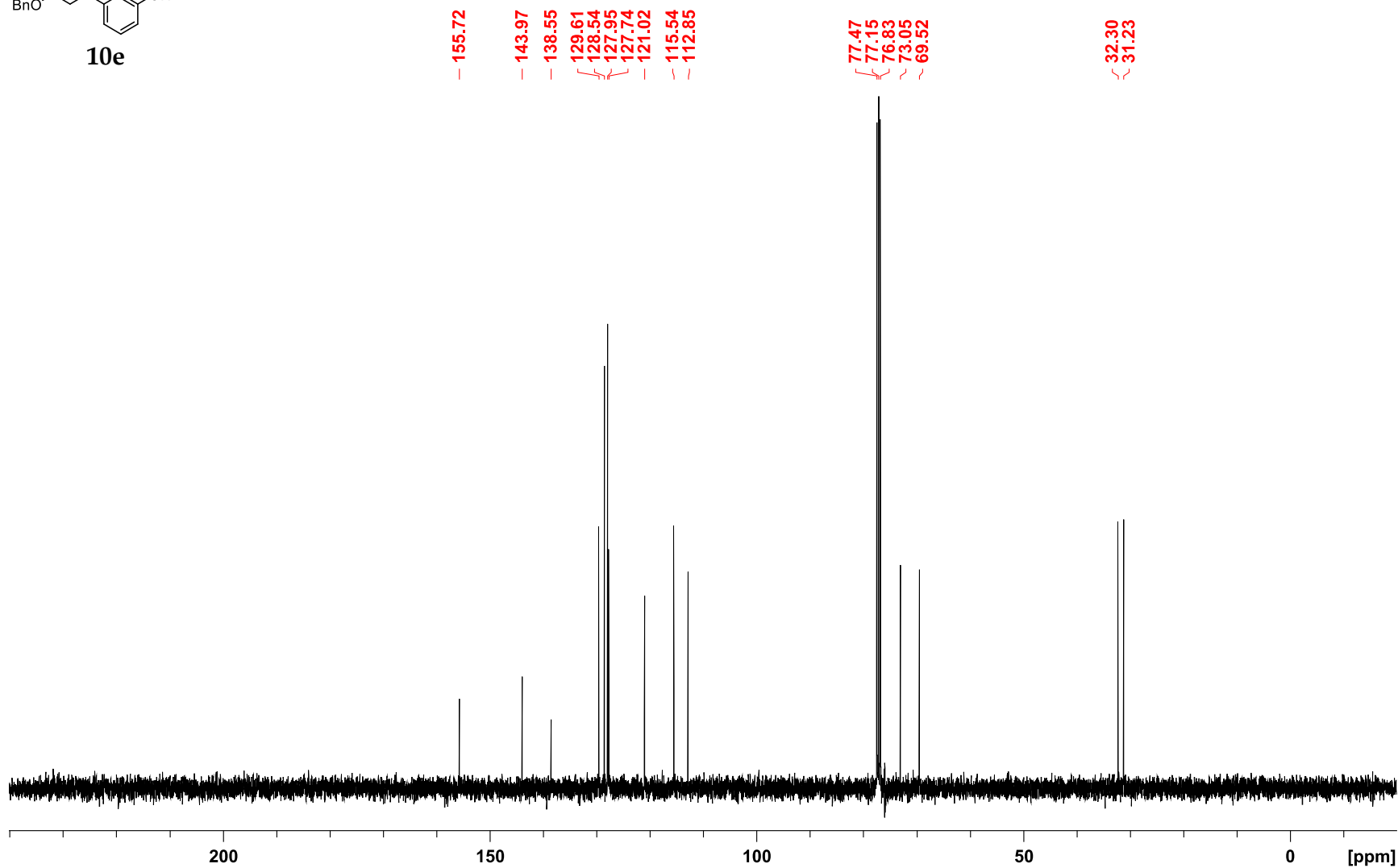
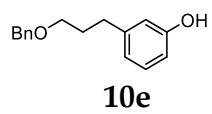


Figure S29.  $^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of **10e**

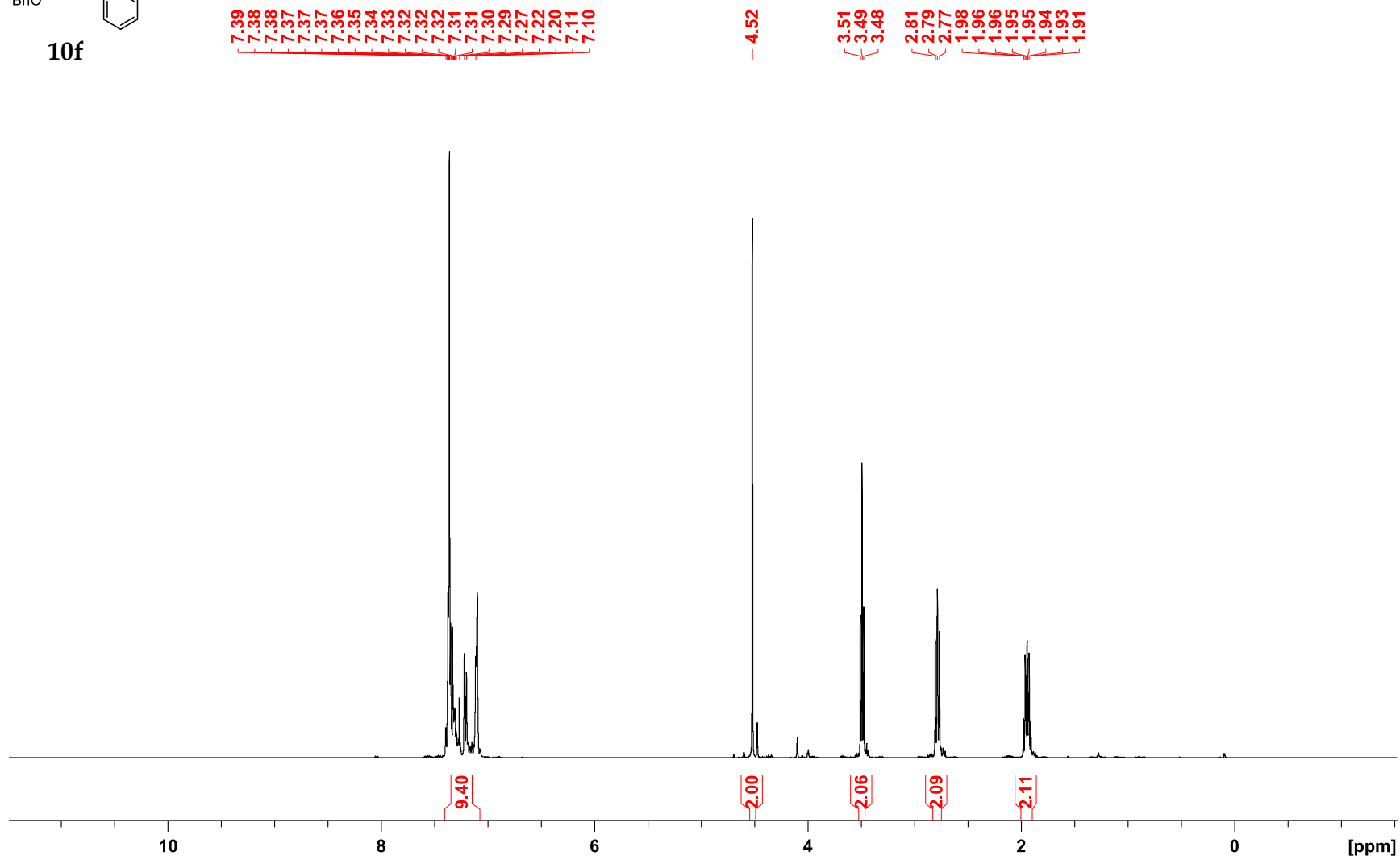
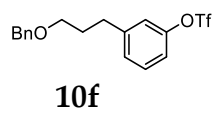


Figure S30. <sup>1</sup>H NMR Spectrum of **10f**

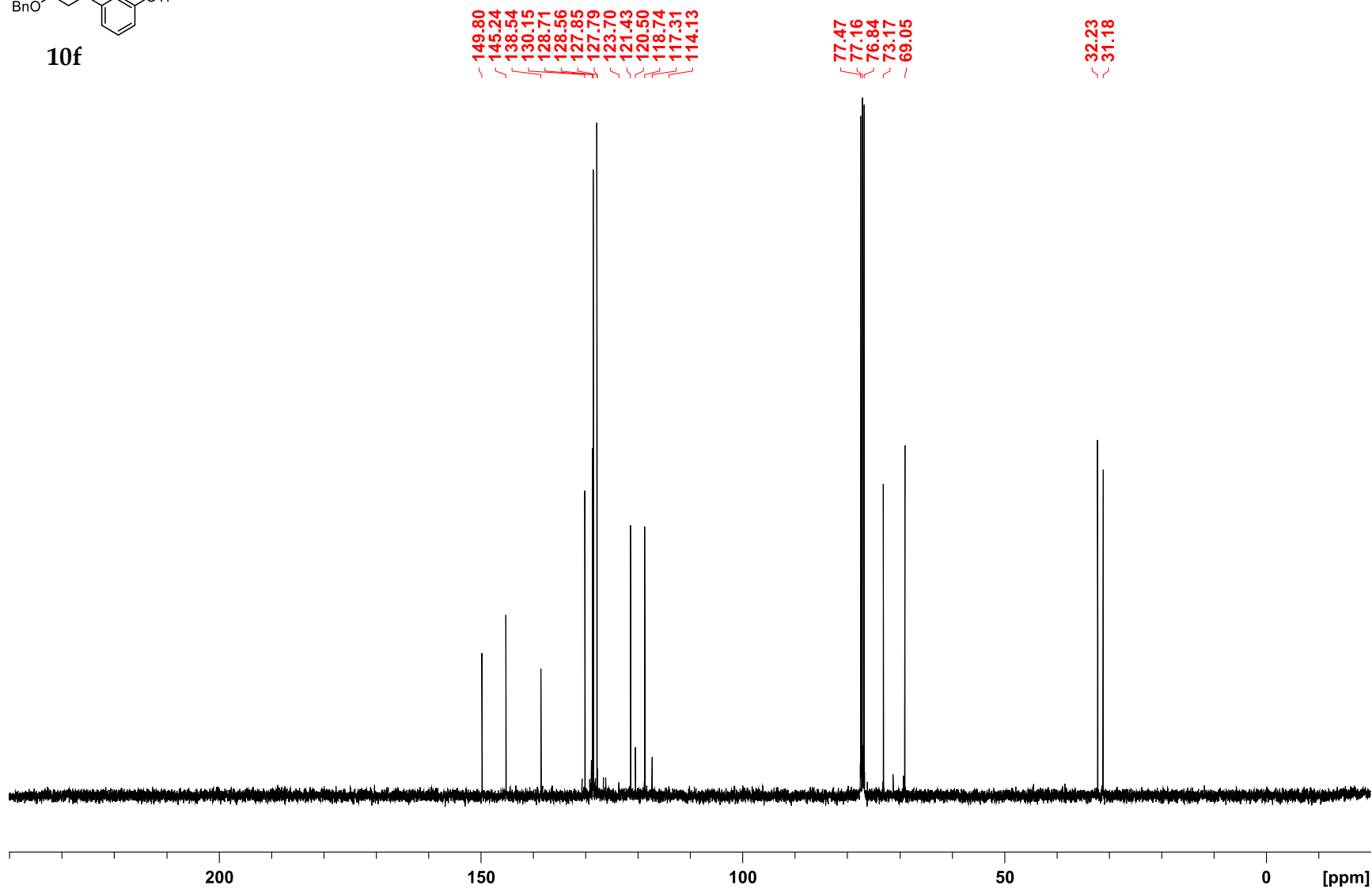
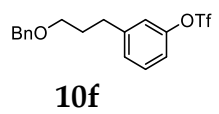
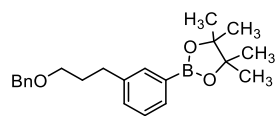


Figure S31.  $^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of **10f**



11

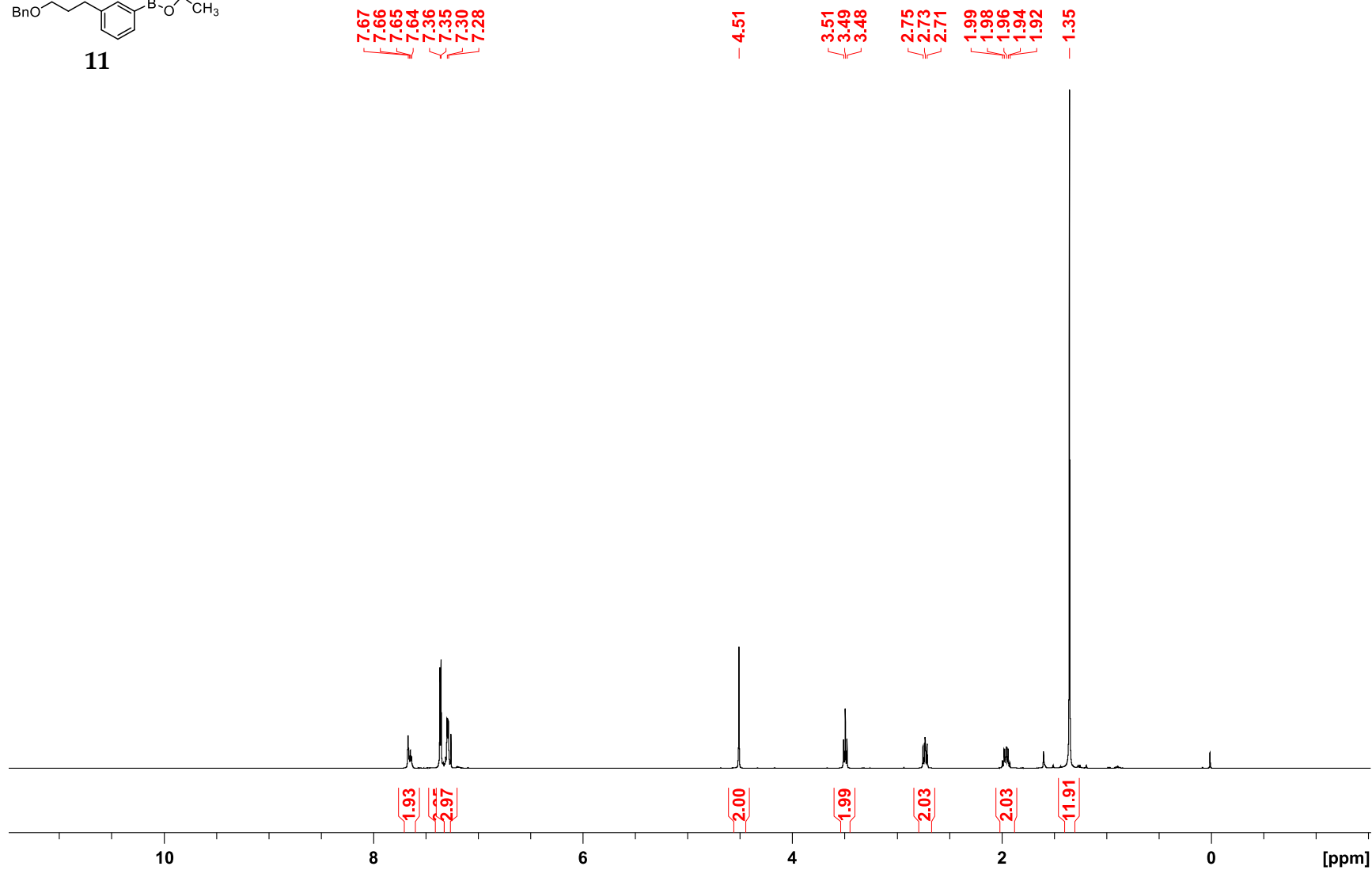
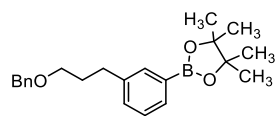


Figure S32. <sup>1</sup>H NMR Spectrum of 11



**11**

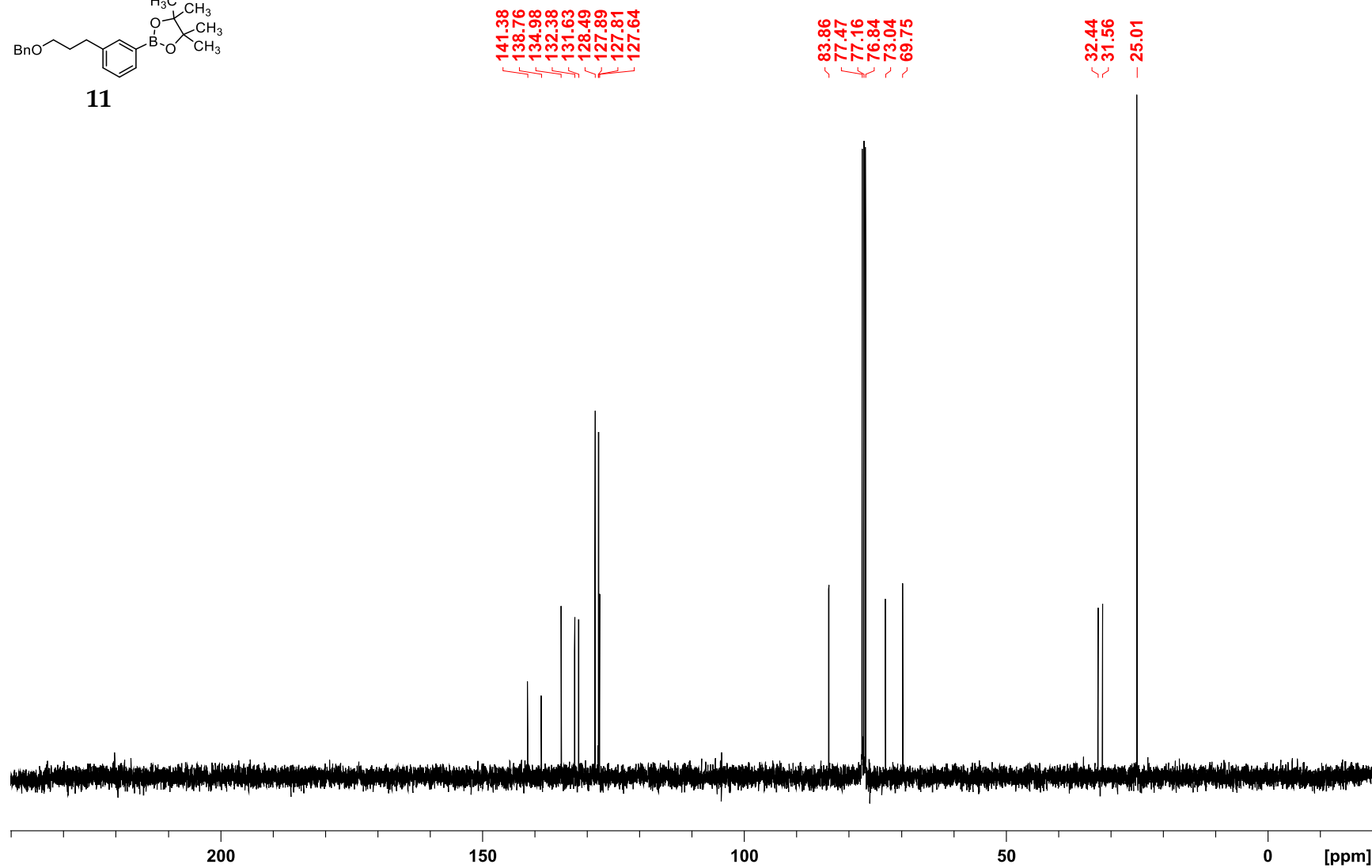
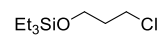


Figure S33. <sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of 11



**12a**

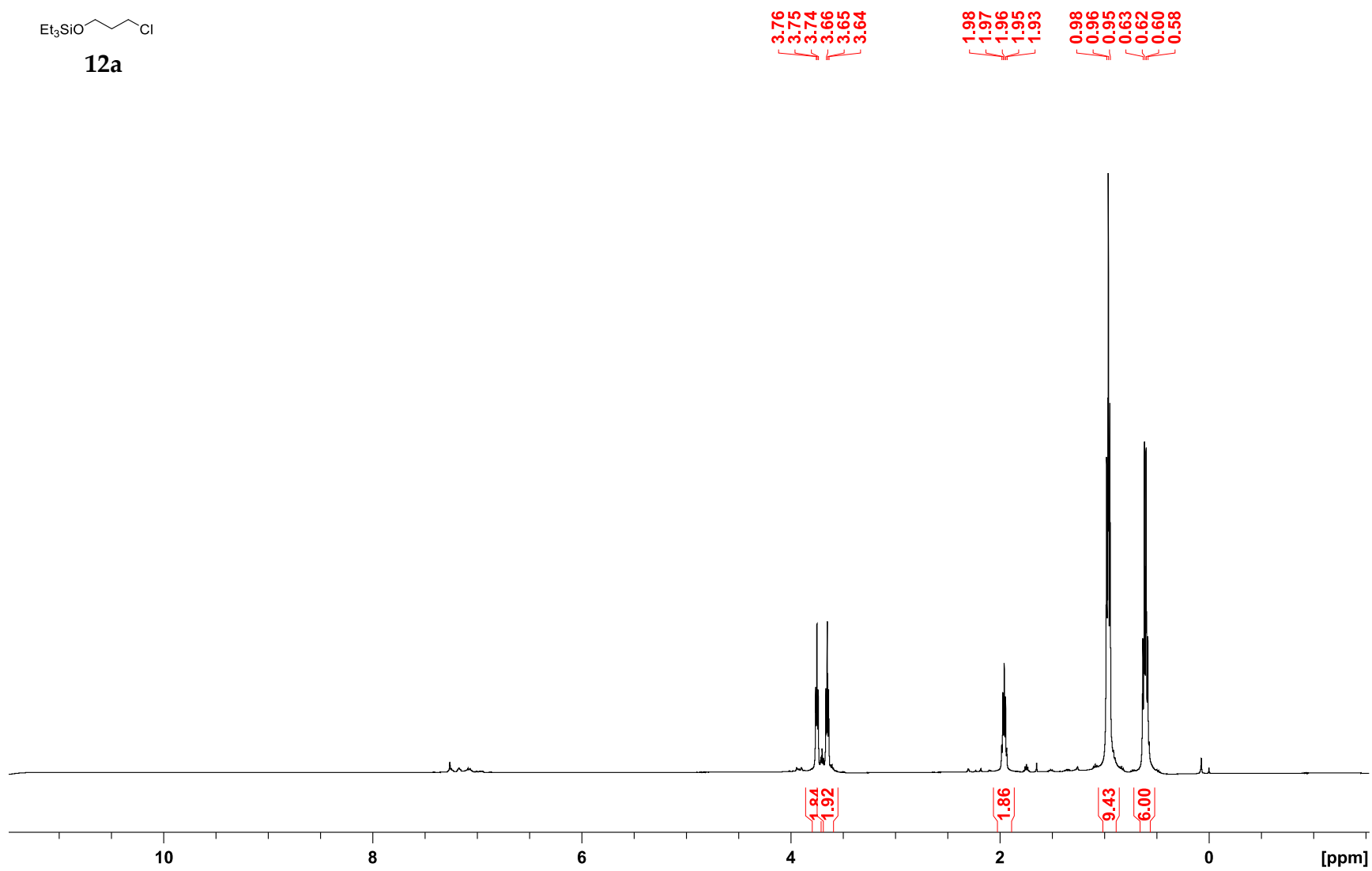


Figure S34. <sup>1</sup>H NMR Spectrum of 12a

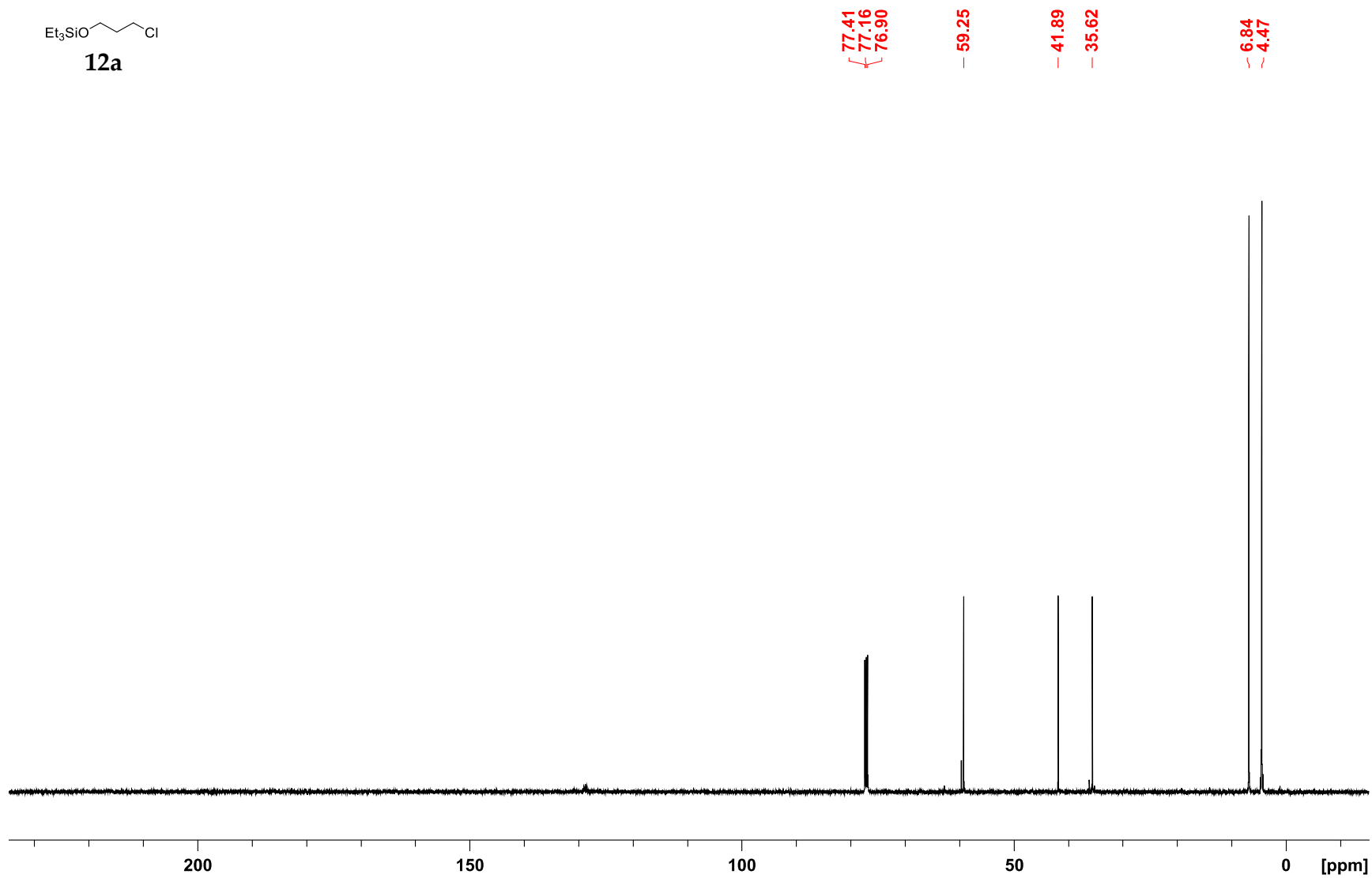
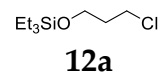


Figure S35. <sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of **12a**



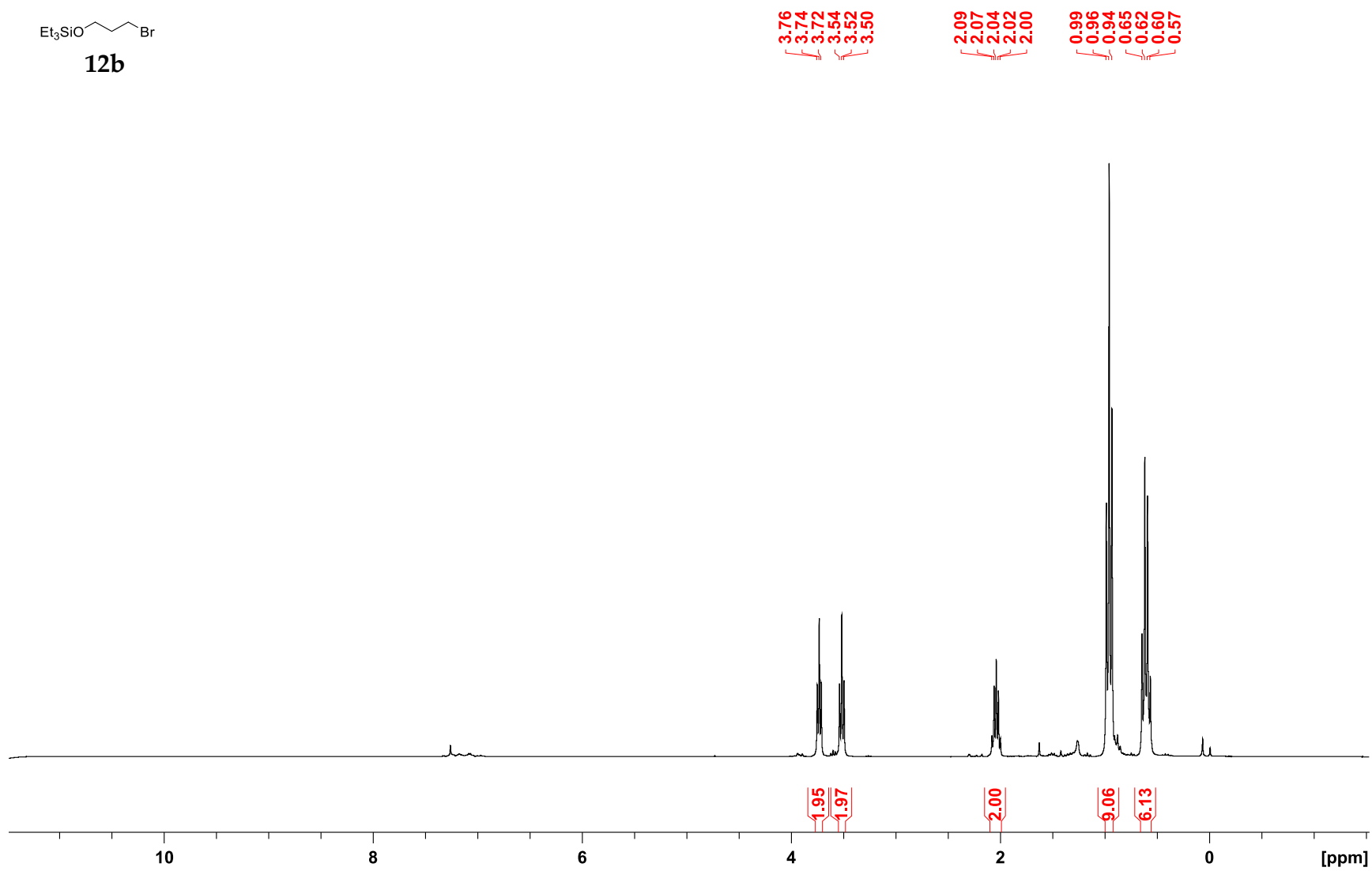
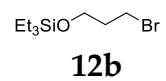
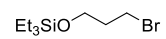


Figure S36. <sup>1</sup>H NMR Spectrum of **12b**



**12b**

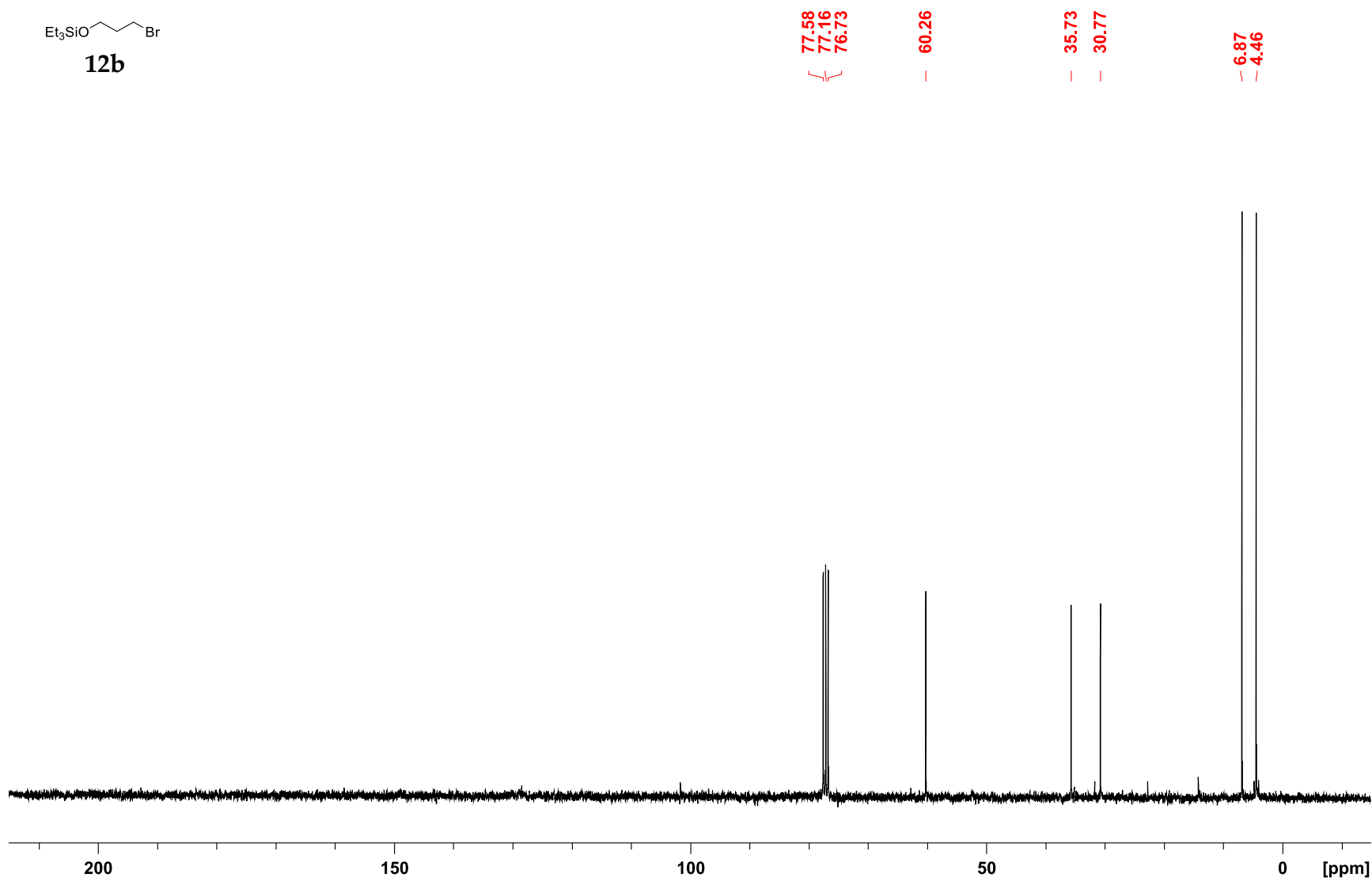
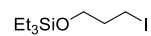


Figure S37. <sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of **12b**



**12c**

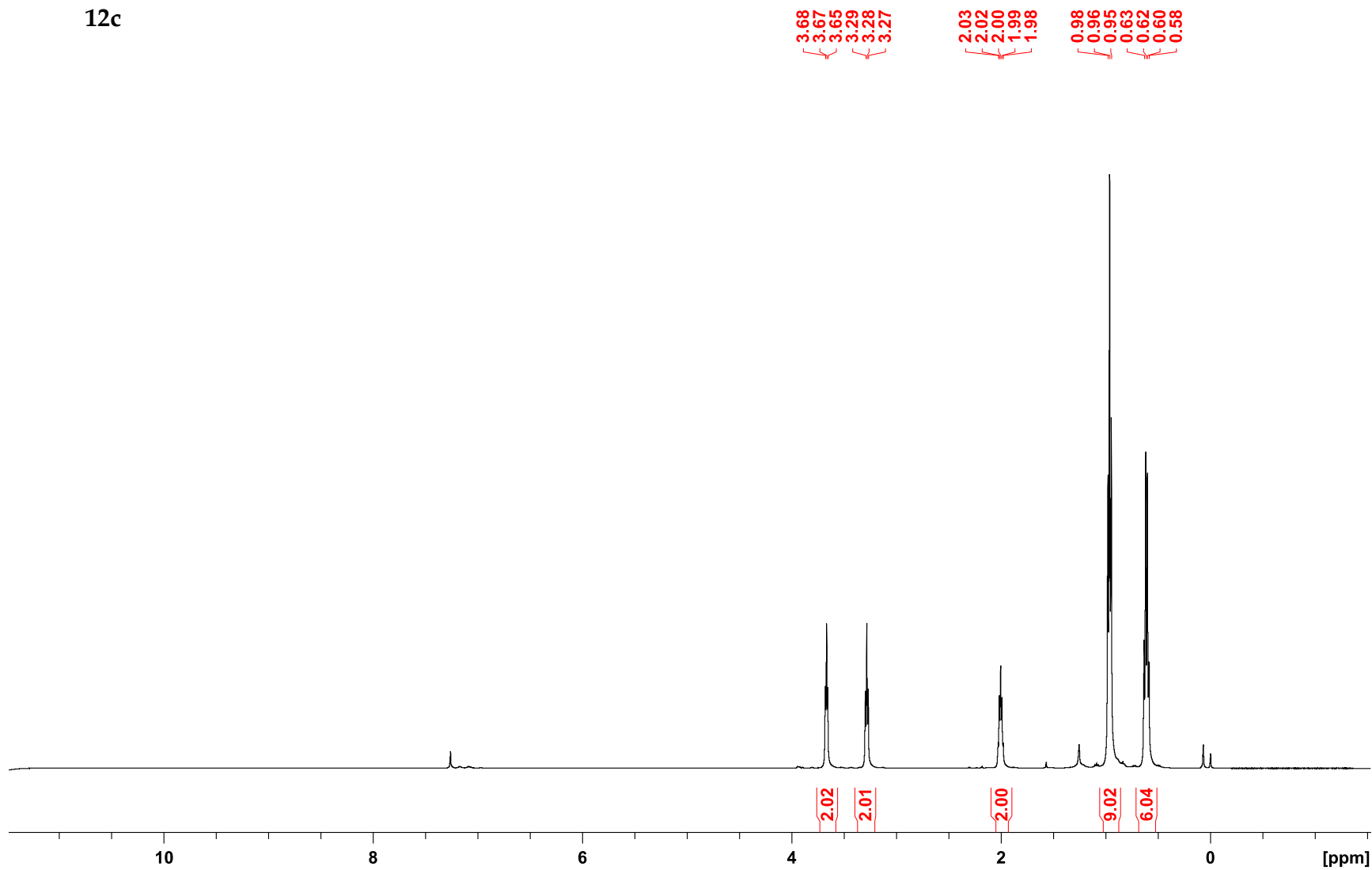


Figure S38. <sup>1</sup>H NMR Spectrum of 12c

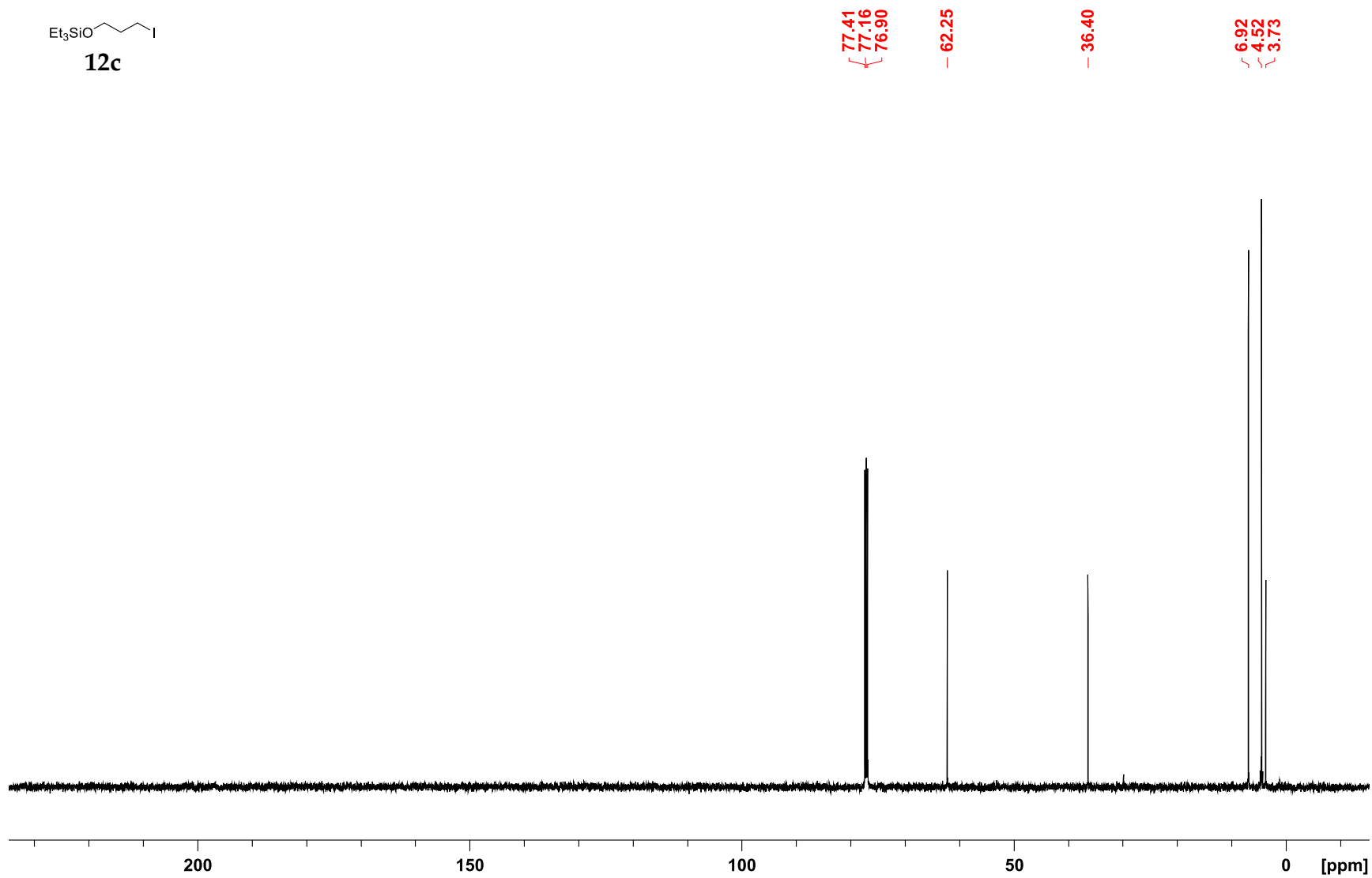
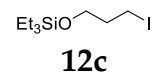


Figure S39. <sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of **12c**

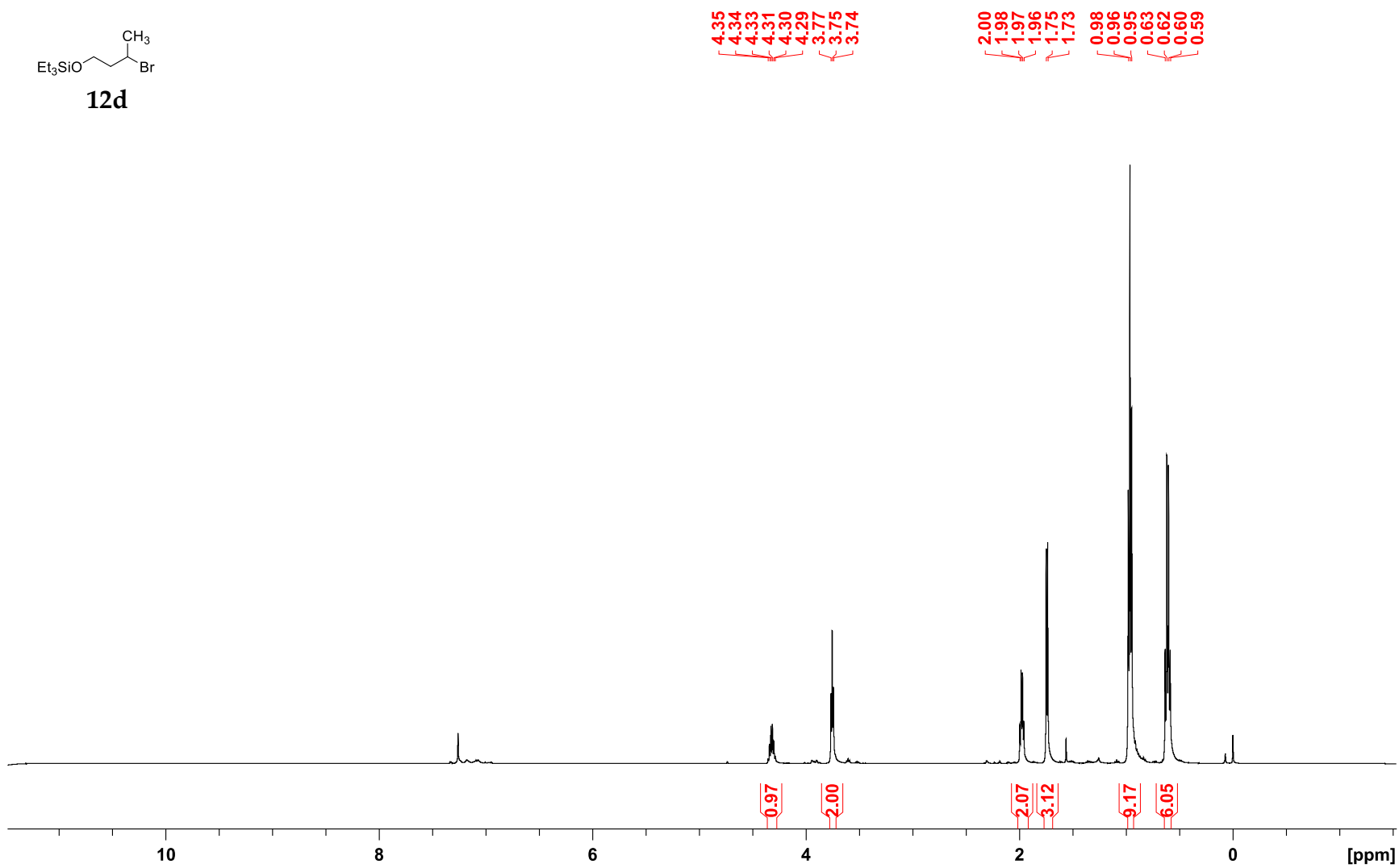
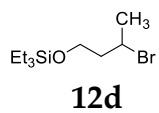


Figure S40. <sup>1</sup>H NMR Spectrum of **12d**

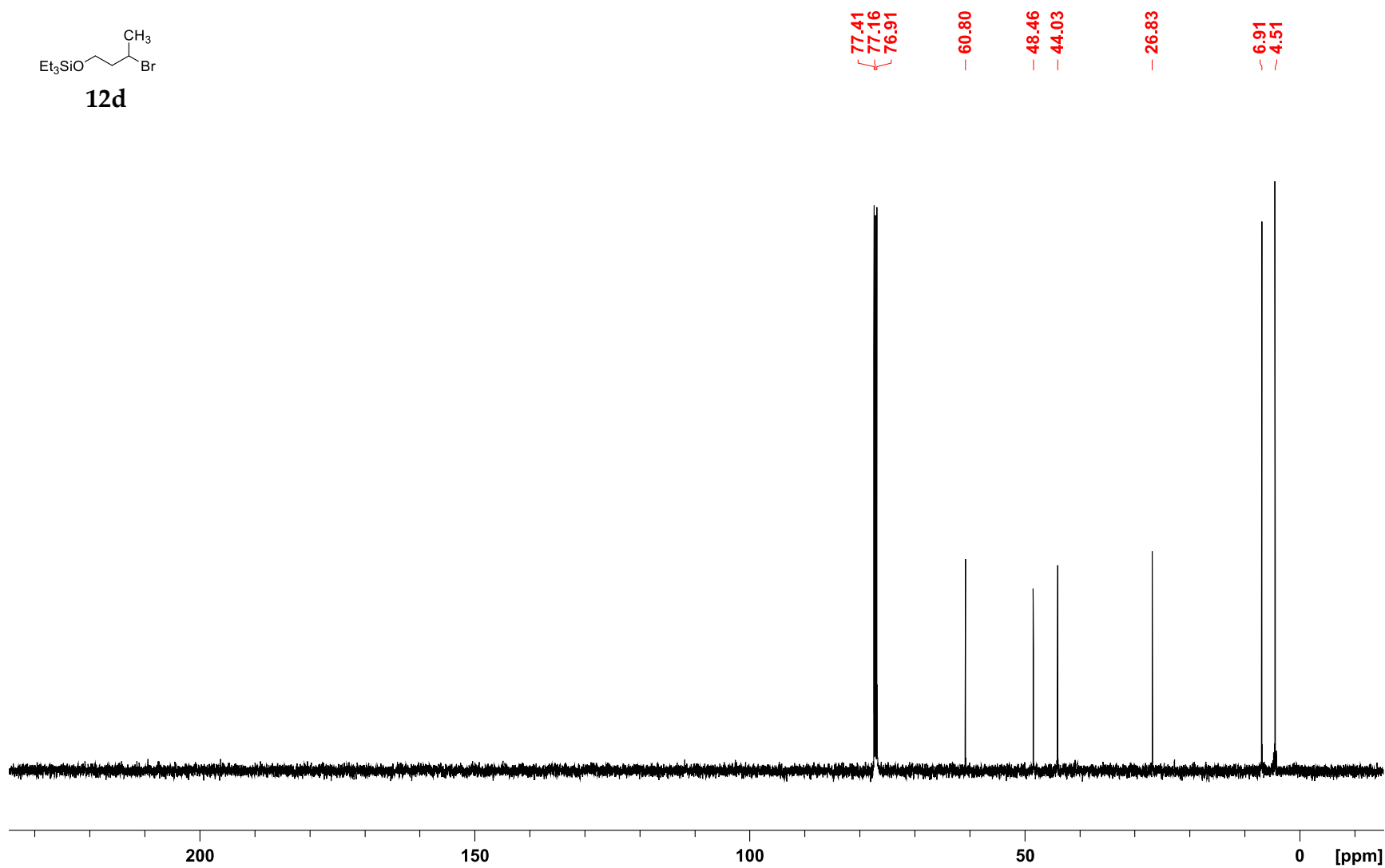
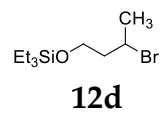


Figure S41.  $^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of **12d**

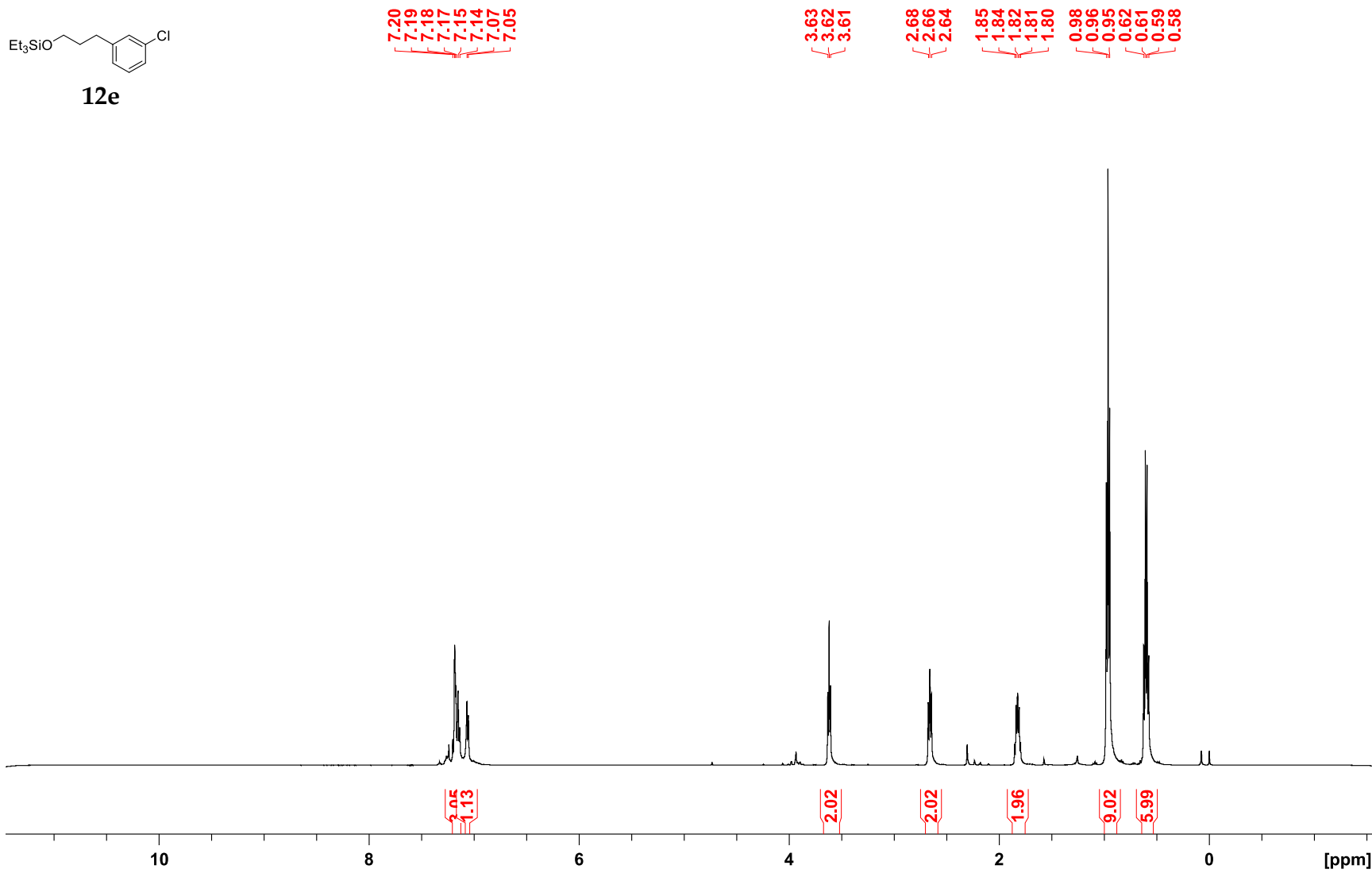


Figure S42.  $^1\text{H}$  NMR Spectrum of **12e**

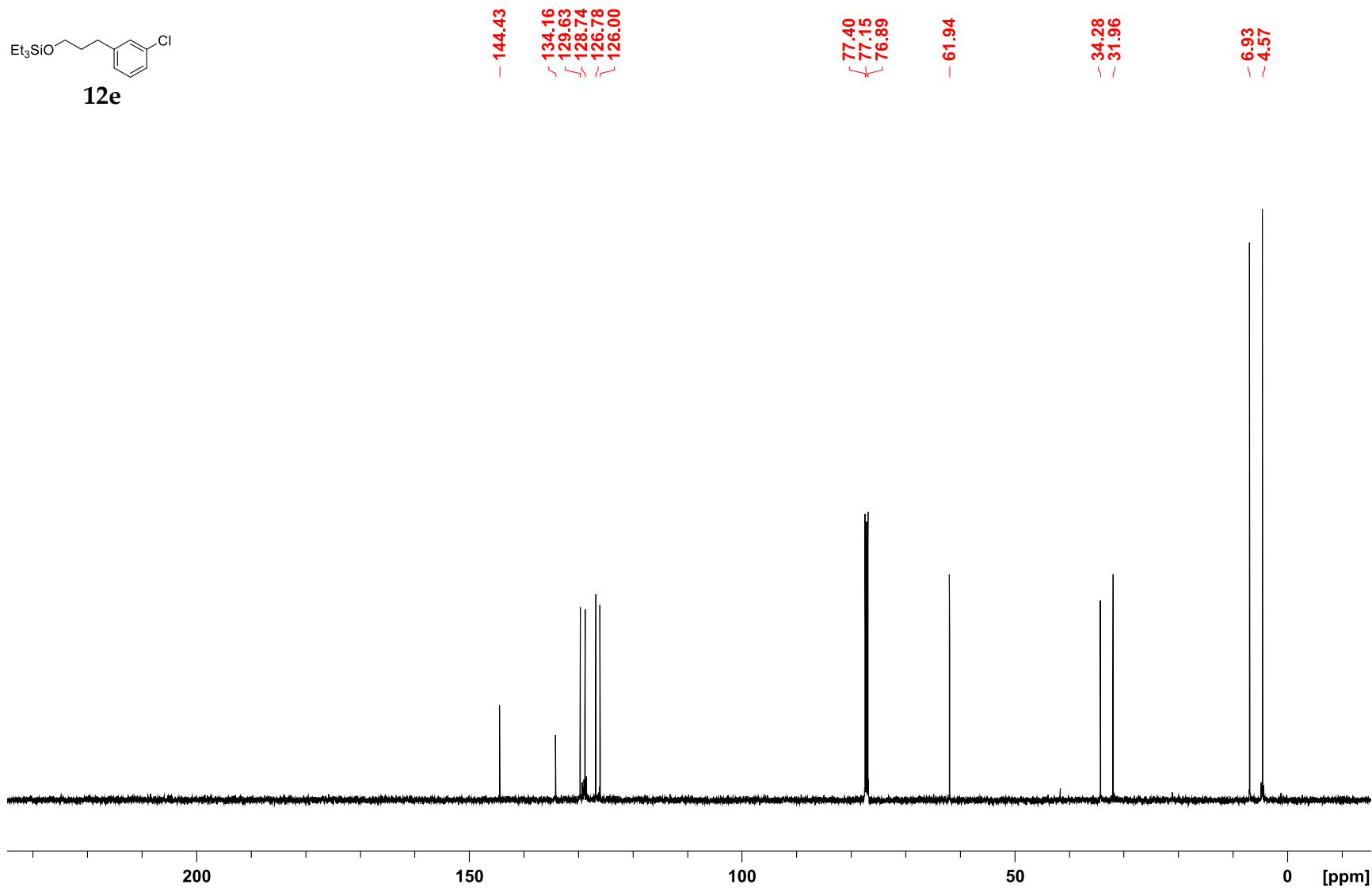


Figure S43.  $^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of **12e**



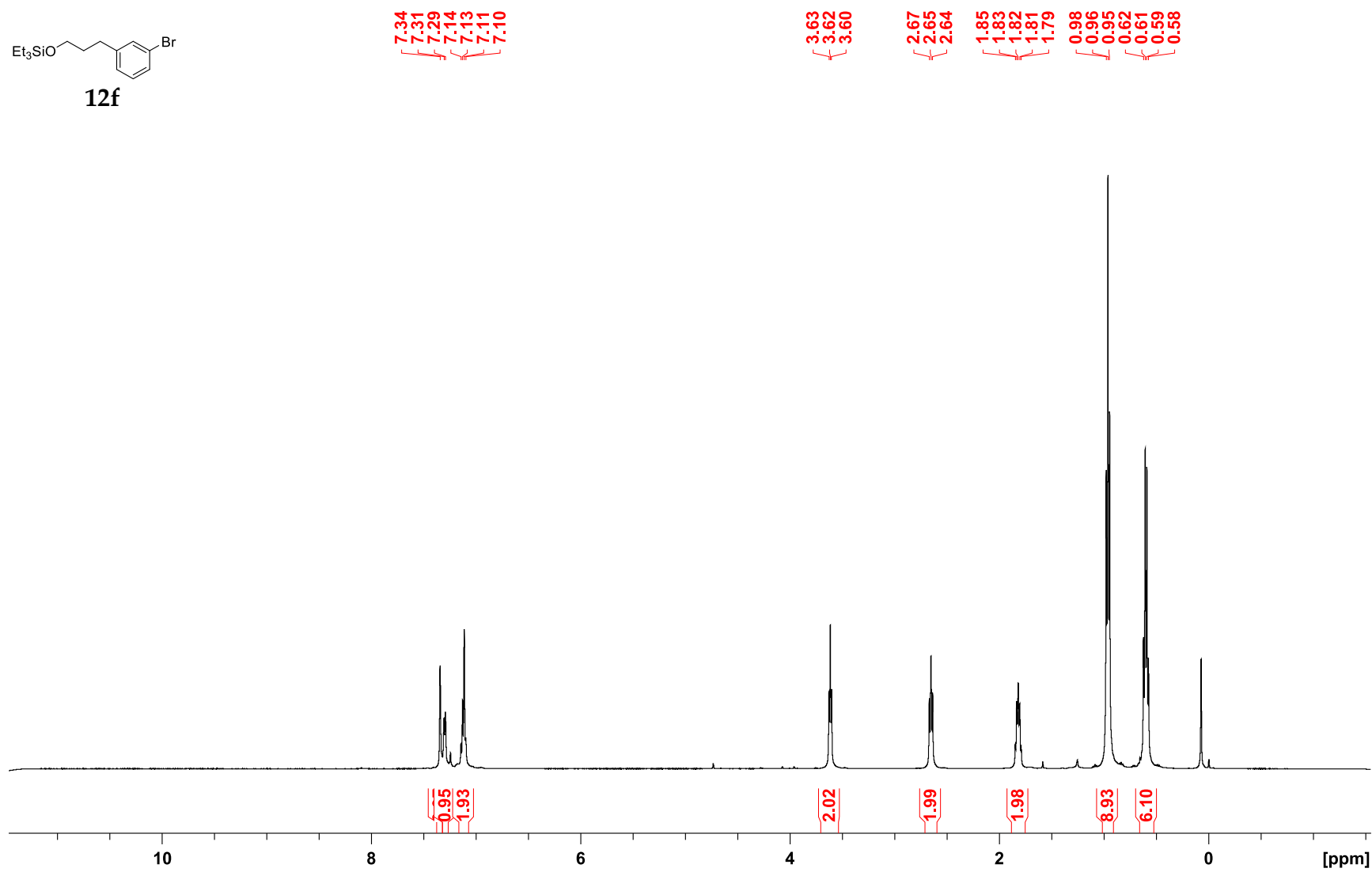
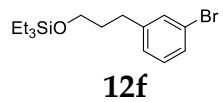


Figure S44. <sup>1</sup>H NMR Spectrum of **12f**

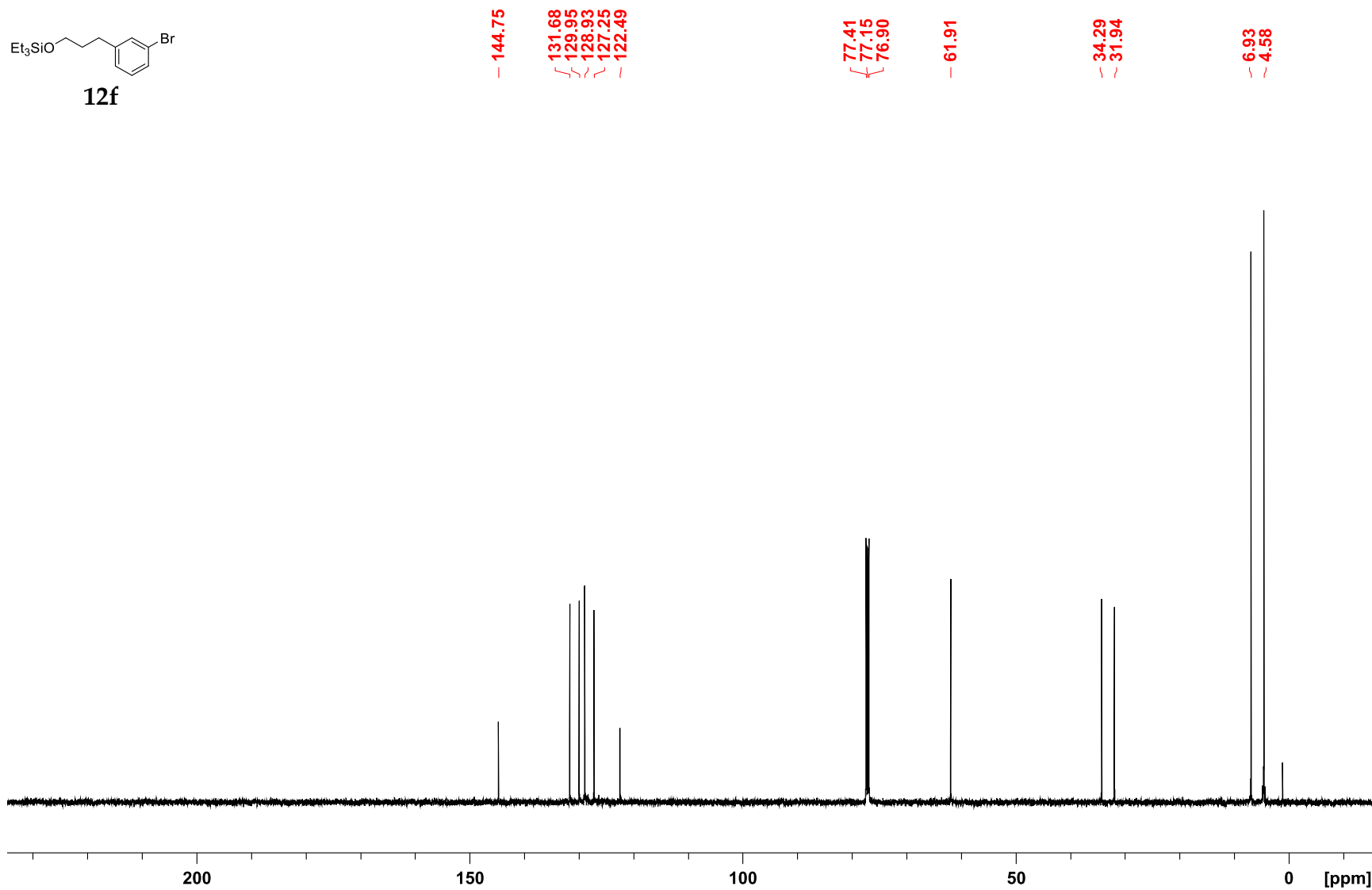


Figure S45.  $^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of **12f**

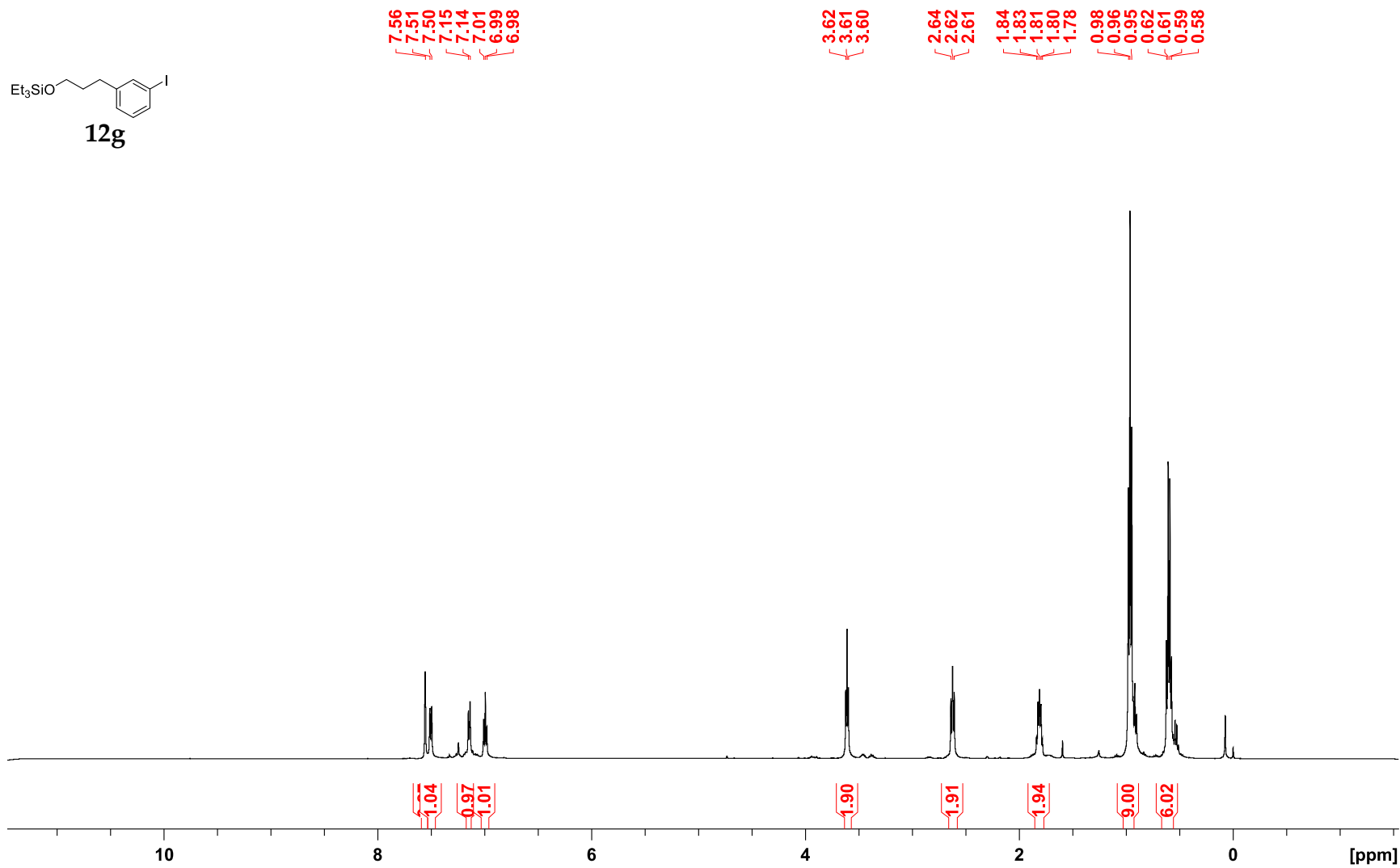


Figure S46.  $^1\text{H}$  NMR Spectrum of **12g**

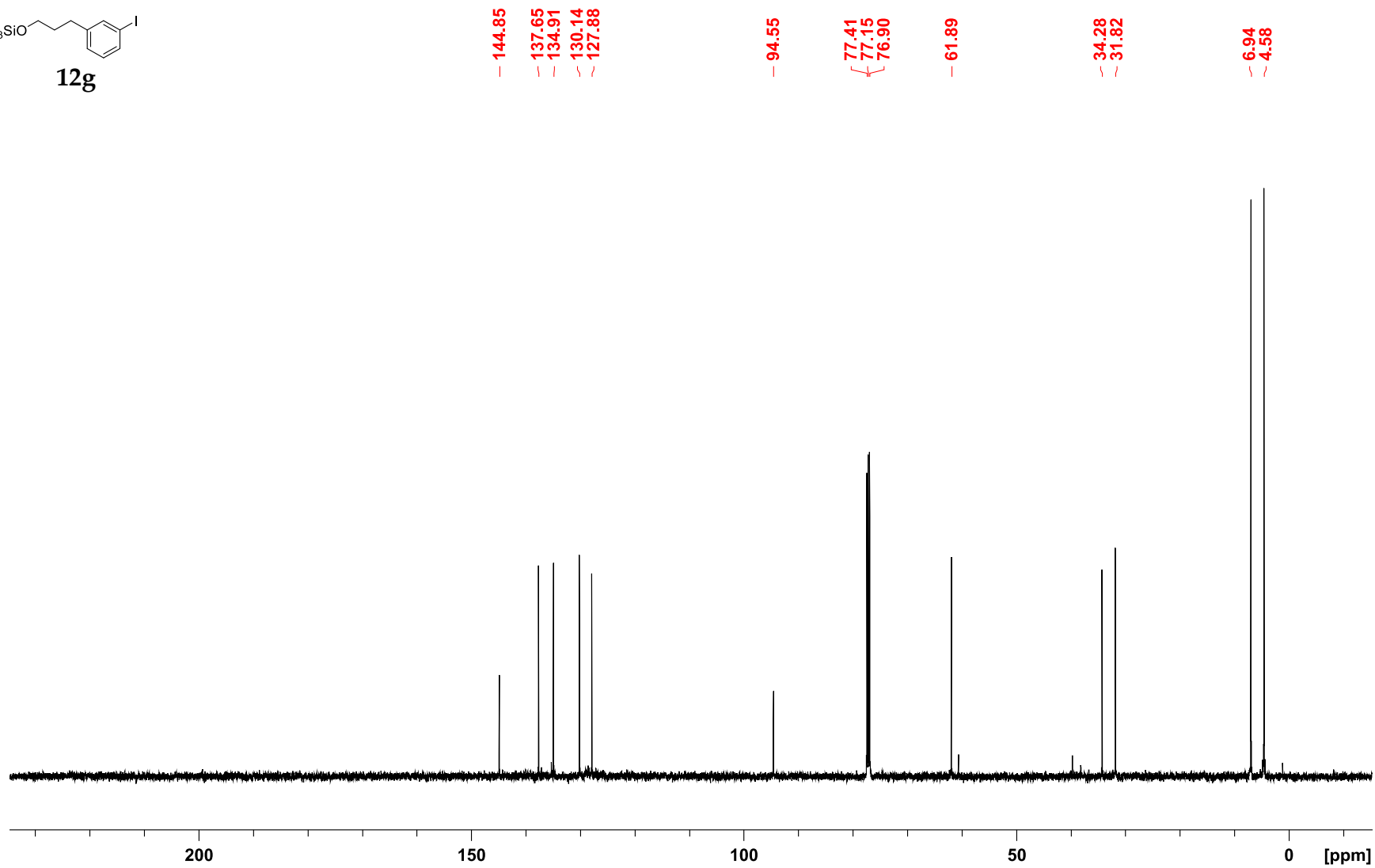
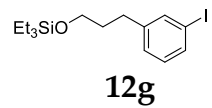


Figure S47.  $^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of **12g**

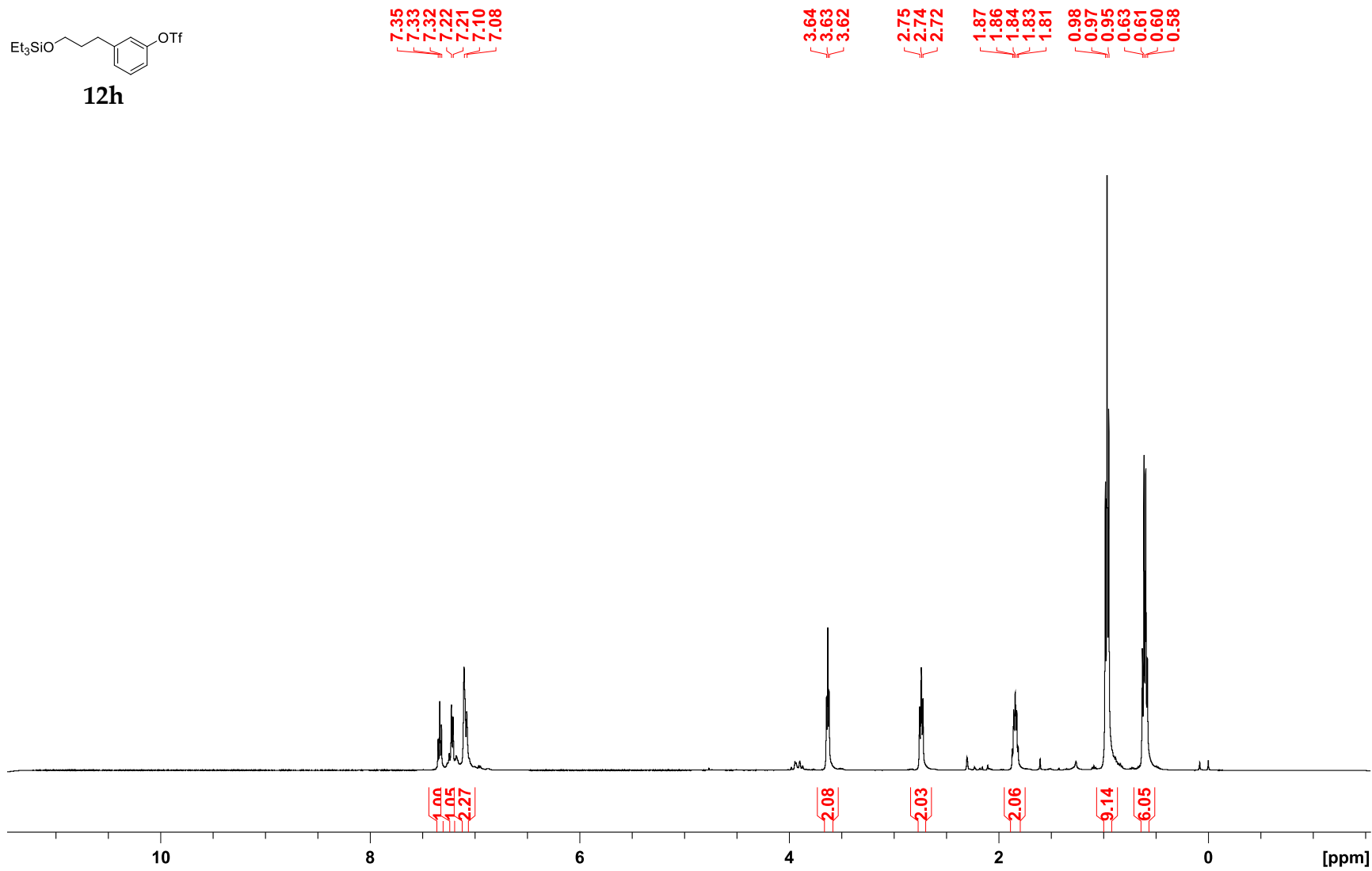
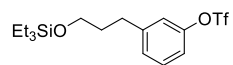


Figure S48.  $^1\text{H}$  NMR Spectrum of **12h**



**12h**

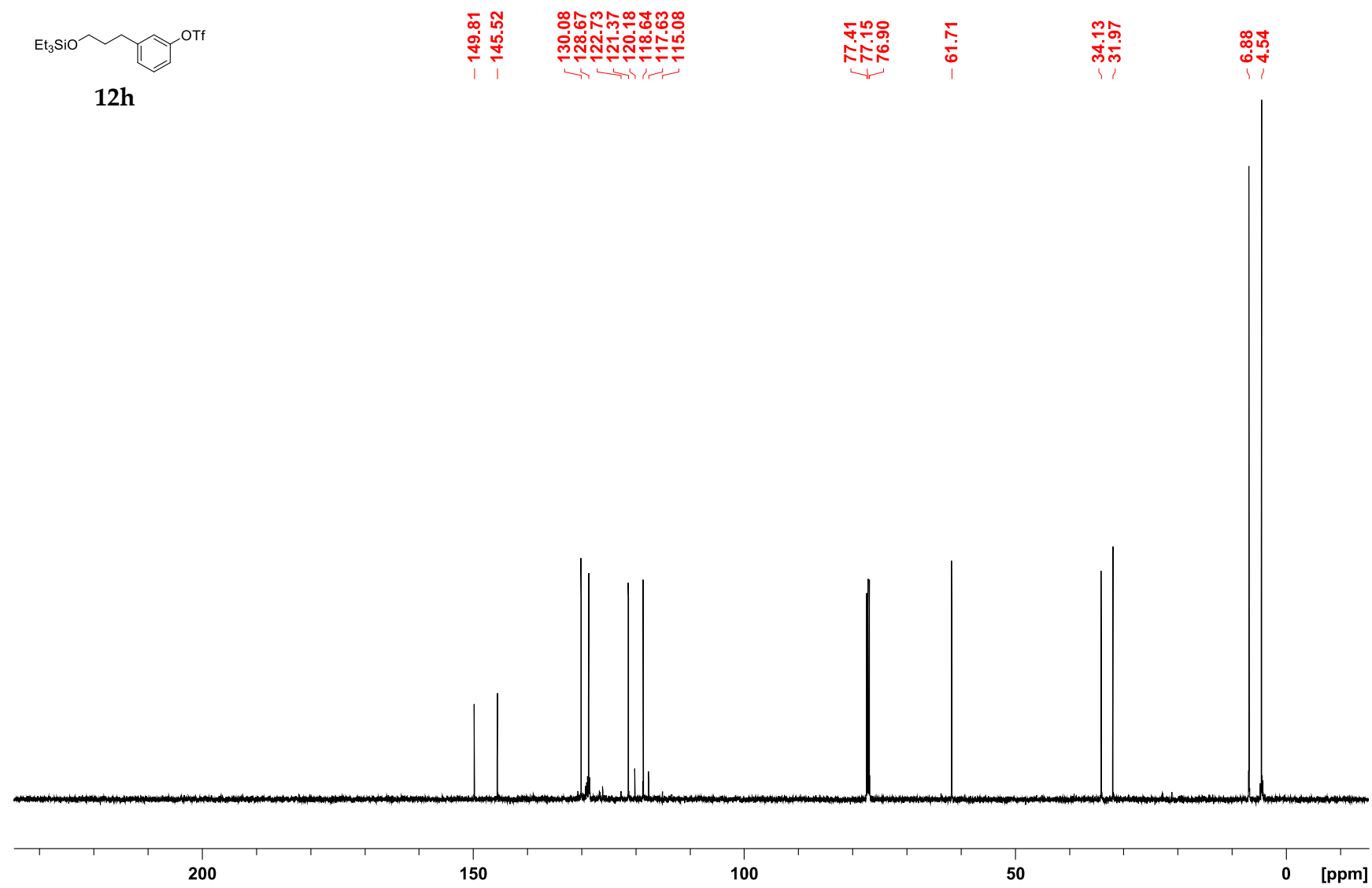
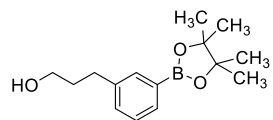
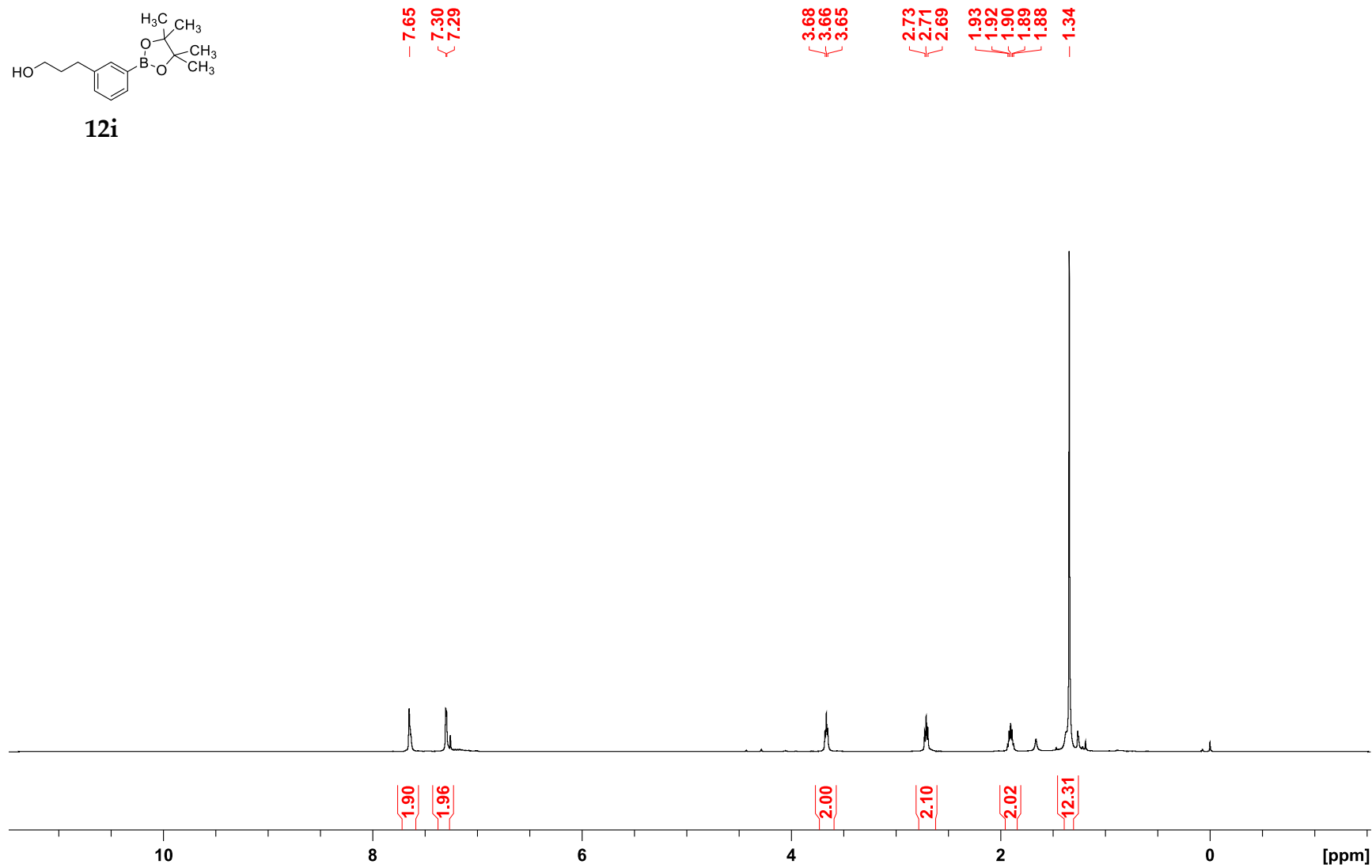
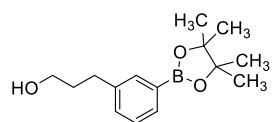


Figure S49.  $^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of **12h**



**12i**





**12i**

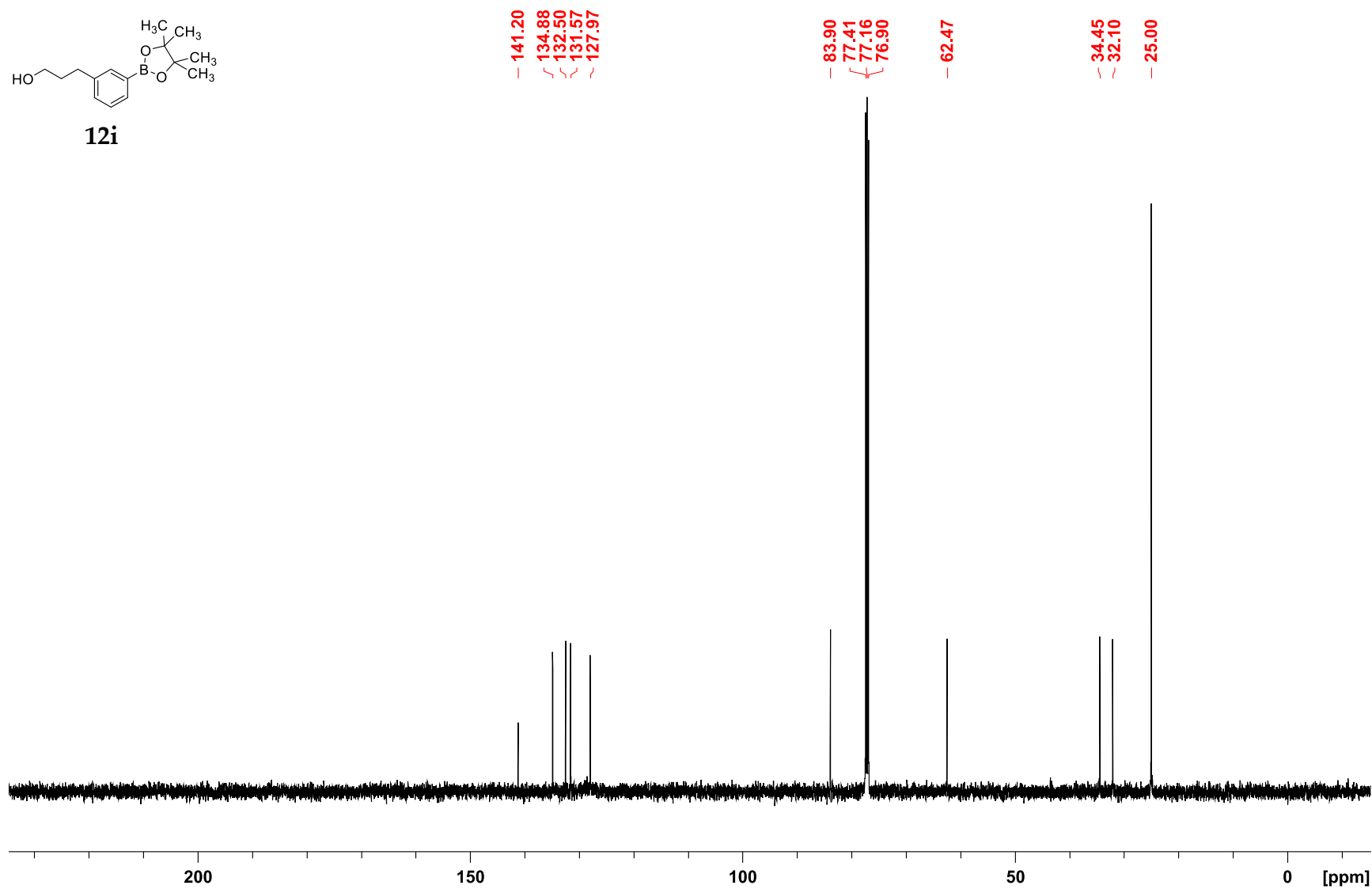
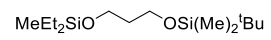


Figure S51.  $^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of **12i**





**12k**

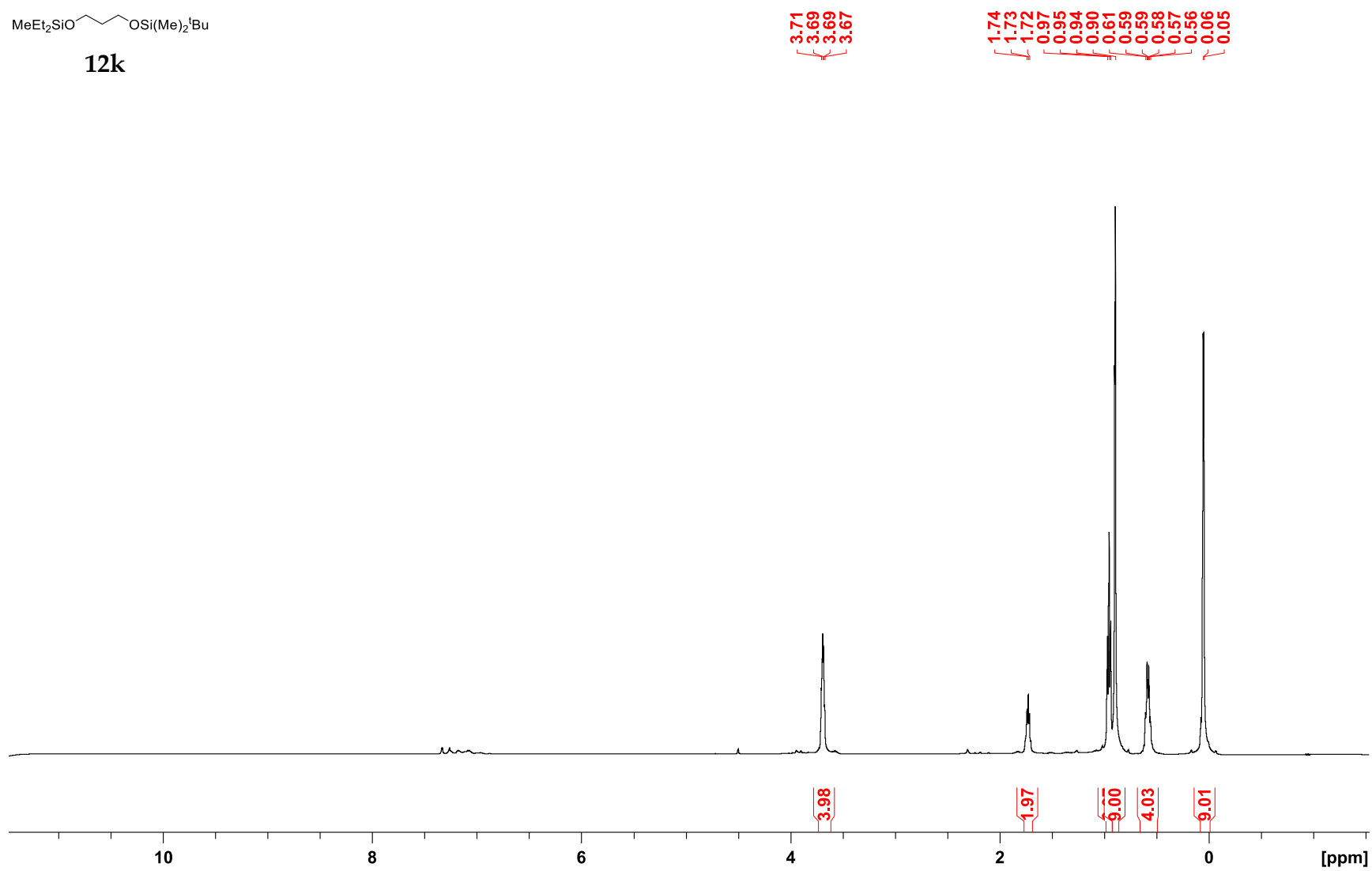
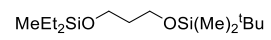


Figure S52. <sup>1</sup>H NMR Spectrum of **12k**



**12k**

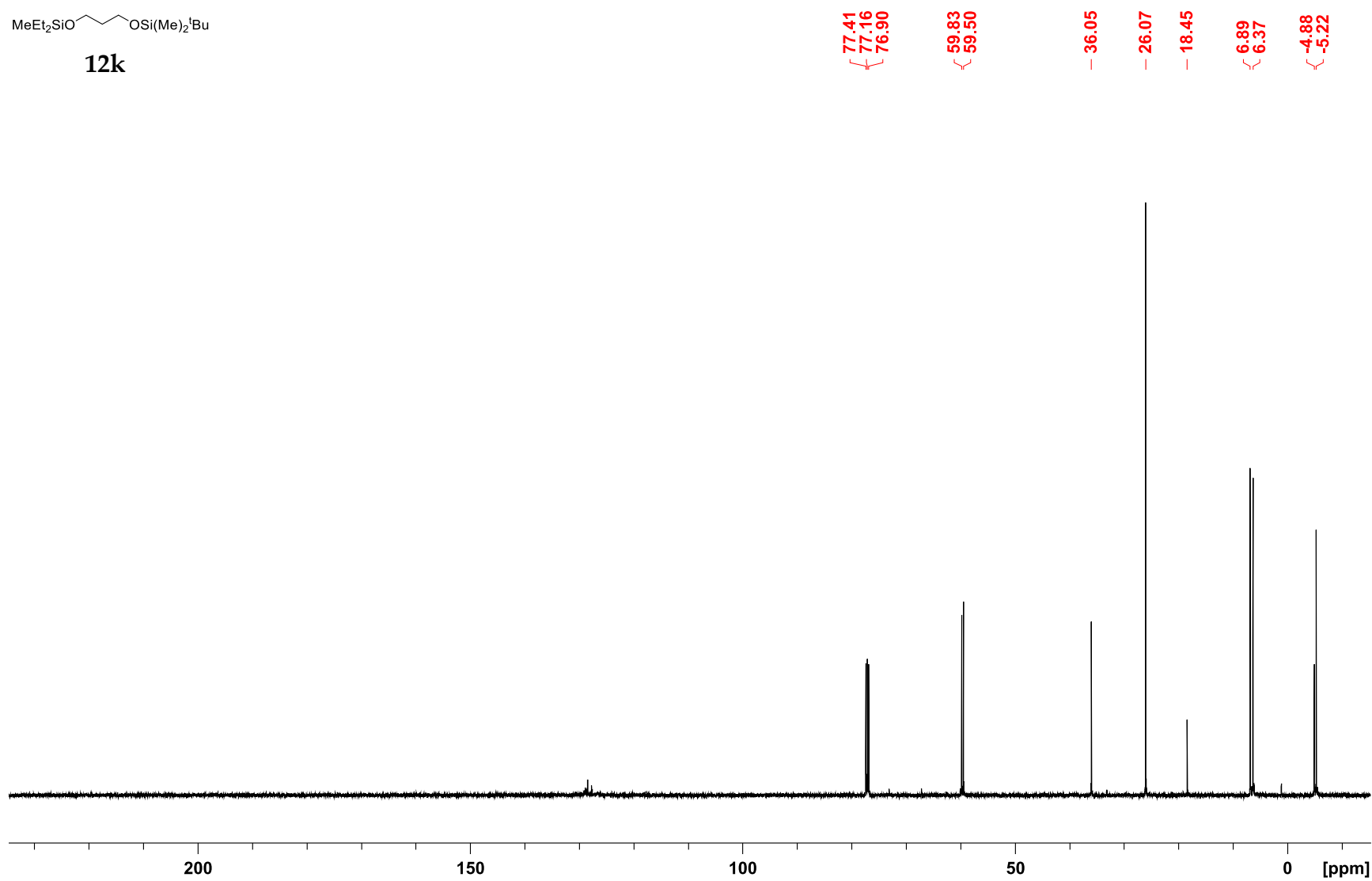


Figure S53. <sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of **12k**

## V. References

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