

## Supporting Information

### Reactions of difluorocarbene with organozinc reagents

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**General Methods.** All reactions were performed in Schlenk flasks under an argon atmosphere. Acetonitrile was distilled from  $\text{CaH}_2$  and stored over MS 4A. DMF was distilled under vacuum from  $\text{P}_2\text{O}_5$  and stored over MS 4A. Tetrahydrofuran was either vacuum transferred from sodium/benzophenone (for small scale experiments) or distilled from  $\text{LiAlH}_4$  prior to use. Column chromatography was carried out employing silica gel (230-400 mesh). Precoated silica gel plates F-254 were used for thin-layer analytical chromatography visualizing with UV and/or acidic aq.  $\text{KMnO}_4$  solution. For NMR measurements,  $\text{CDCl}_3$  was distilled from  $\text{CaH}_2$ .

(Bromodifluoromethyl)trimethylsilane (**3**) was prepared according to literature procedure.<sup>1</sup>

**Commercial reagents:**

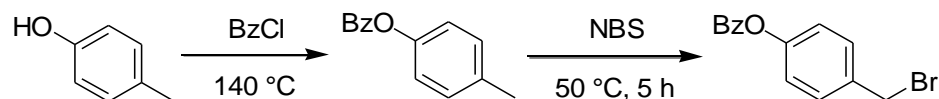
Benzyl bromide

1-Bromo-2-bromomethylbenzene

1-Bromo-4-bromomethylbenzene

1-Chloromethylnaphthalene

**4-(Bromomethyl)phenyl benzoate.**



*p*-Cresol (9.67 g, 89 mmol) was mixed with benzoyl chloride (10.4 mL, 89 mmol) at room temperature, and the mixture was heated with stirring at 140 °C for 1 hour. The mixture was cooled to room temperature, and the resulting solid was recrystallized from the mixture of hexane/EtOAc (2/1) to afford 17.47 g (92% yield) of *p*-tolyl benzoate.

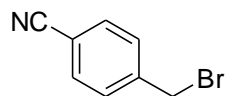
*p*-Tolyl benzoate (10.43 g, 49.1 mmol) was mixed with MeCN (50 mL) and NBS (9.19 g, 51.6 mmol). The mixture was heated to 50 °C, and dibenzoylperoxide (50 mg) was added. The reaction mixture was stirred at 50 °C for 5 hours under irradiation with fluorescent light bulb (20 W). The mixture was cooled to room temperature followed by addition of After cooling water (60 mL) and EtOAc (60 mL) were added. The upper layer was separated, dried with  $\text{Na}_2\text{SO}_4$ , and concentrated. The resulting solid was first recrystallized from MeCN and then from EtOAc (for complete separation of initial compound) to afford 8.59 g (60% yield) of 4-(bromomethyl)phenyl benzoate as a colorless powder.

Mp 111–112 °C.

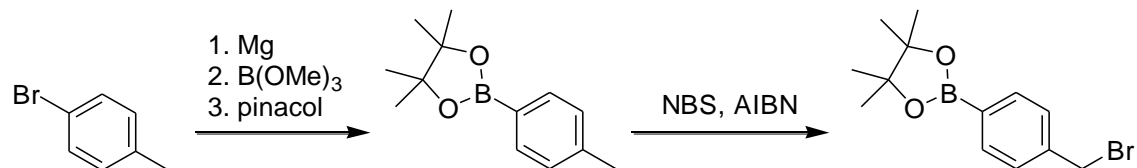
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 4.55 (s, 2H), 7.24 (d, 2H,  $J = 7.4$  Hz), 7.44–7.54 (m, 2H), 7.56 (d, 2H,  $J = 7.4$  Hz), 7.63–7.72 (m, 1H), 8.23 (d, 2H,  $J = 7.7$  Hz).  $^1\text{H}$  NMR spectra were identical to the reported data.<sup>2</sup>

<sup>1</sup> Kosobokov, M. D.; Dilman, A. D.; Levin, V. V.; Struchkova, M. I. *J. Org. Chem.* **2012**, 77, 5850–5855.

<sup>2</sup> Kitano, Y.; Manoda, T.; Miura, T.; Chiba, K.; Tada, M. *Synthesis* **2006**, 405–410.

**4-(Bromomethyl)benzonitrile.**

Synthesized according to literature procedure.<sup>3</sup>

**2-[4-(Bromomethyl)phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.**

1-Bromo-4-methylbenzene (8.55 g, 50 mmol) was gradually added to a stirred slurry of magnesium (1.34 g, 55 mmol) in THF (50 mL) to maintain gentle reflux. After the addition was complete, the mixture was refluxed for additional 1 hour. The resulting solution was transferred to a stirred solution of B(OMe)<sub>3</sub> (6.82 mL, 60 mmol) in Et<sub>2</sub>O (50 mL) cooled down to  $-95\text{ }^{\circ}\text{C}$  (acetone bath/liq. nitrogen bath). The temperature was allowed to rise to  $-50\text{ }^{\circ}\text{C}$  during 20 min, and the mixture was maintained at  $-50\text{ }^{\circ}\text{C}$  for 2 hours. Then, the cooling bath was removed, and the mixture was stirred for additional 2 hours at room temperature. The mixture was cooled with ice/water bath, and a solution of concentrated H<sub>2</sub>SO<sub>4</sub> (1.47 mL, 27.5 mmol) in water (30 mL) was added dropwise. After stirring for 10 min at room temperature, the organic layer was separated and aqueous layer was extracted with hexane (3×50 mL). The combined organic phase was filtered through Na<sub>2</sub>SO<sub>4</sub>, and concentrated. The residual solid substance was treated with pinacol (5.90 g, 50 mmol), and the mixture stirred for 20 minutes at  $60\text{ }^{\circ}\text{C}$  (water bath). The mixture transforms into two-phase emulsion. After cooling to room temperature, the upper layer was extracted with methyl *tert*-buthyl ether (50 mL, and 2×25 mL), the combined organic phase was filtered through Na<sub>2</sub>SO<sub>4</sub>, and concentrated. The residual solid was recrystallized from hexane to afford 9.05 g (83% yield) of pinacol ester of *p*-tolyl boronic acid.

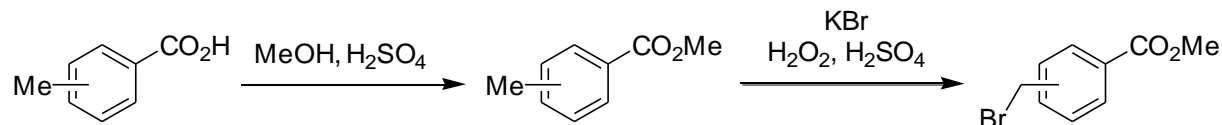
The product obtained in the previous step was mixed with NBS (8.2 g 46 mmol) and CCl<sub>4</sub> (48 mL). The mixture was heated to reflux under irradiation with fluorescent light bulb (20 W), and AIBN (20 mg) was added to refluxing mixture, then heating with irradiation was continued for 3 hours. The mixture was cooled to room temperature, water (50 mL) was added, and the flask was shaken. The lower phase was separated, filtered through Na<sub>2</sub>SO<sub>4</sub>, and concentrated. The residual solid was successively recrystallized from hexane and MeOH to afford 8.09 g (65%) of the product.

Colorless crystals. Mp  $85\text{--}86\text{ }^{\circ}\text{C}$ .

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$ : 1.37 (s, 12H), 4.48 (s, 2H), 7.22 (d, 2H,  $J = 7.6\text{ Hz}$ ), 7.39 (d, 2H,  $J = 8.1\text{ Hz}$ ), 7.78 (d, 2H,  $J = 8.1\text{ Hz}$ ). <sup>1</sup>H NMR spectrum was identical to the reported data.<sup>4</sup>

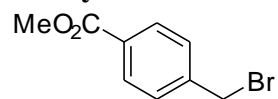
<sup>3</sup> Aliabadi, A.; Shamsa, F.; Ostad, S. N.; Emami, S.; Shafiee, A.; Davoodi, J.; Foroumadi, A. *Eur. J. Med. Chem.* **2010**, *45*, 5384–5389.

<sup>4</sup> White, J. R.; Price, G. J.; Schiffrers, S.; Raithby, P. R.; Plucinski, P. K.; Frost, C. G. *Tetrahedron Lett.* **2010**, *51*, 3913–3917.

**Methyl (bromomethyl)benzoates.**

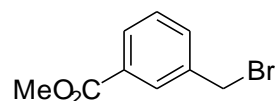
Concentrated sulfuric acid (6.1 mL, 112.5 mmol) was added dropwise to a suspension of *p*-, *m*- or *o*-toluic acid (10.21 g, 75 mmol) in MeOH (20 mL), and the mixture was refluxed for 3 hours. After cooling to room temperature, water (75 mL) and hexane (50 mL) were added. The upper layer was separated, dried with Na<sub>2</sub>SO<sub>4</sub>, and concentrated to afford crude material which was used in bromination step without additional purification.

A solution of KBr (5.89 g, 49.5 mmol) in 35% aqueous H<sub>2</sub>O<sub>2</sub> (5.5 mL, 56 mmol) and water (5.5 mL) was immersed in an ice/water bath followed by addition of chloroform (15 mL). Then, concentrated sulfuric acid (3.2 mL, 60 mmol) was added dropwise, the cooling bath was removed, and the crude methyl ester was added. The resulting mixture was refluxed under irradiation with fluorescent light bulb (20 W) until the color of elemental bromine disappeared (*ca.* 1.5 hours). The organic layer was separated, dried with Na<sub>2</sub>SO<sub>4</sub>, and concentrated. The residue was recrystallized from methanol.

**Methyl 4-bromomethylbenzoate.**

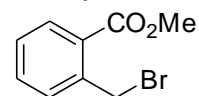
12.0 g (70% yield). Colorless crystals. Mp 52–53 °C.

<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>), δ: 3.91 (s, 3H), 4.49 (s, 2H), 7.45 (d, 2H, *J* = 8.3 Hz), 8.00 (d, 2H, *J* = 8.3 Hz). <sup>1</sup>H NMR spectrum was identical to the reported data.<sup>5</sup>

**Methyl 3-bromomethylbenzoate.**

12.2 g (71% yield). Colorless crystals. Mp 43–44 °C.

<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>), δ: 3.93 (s, 3H), 4.52 (s, 2H), 7.43 (t, 1H, *J* = 7.6 Hz), 7.60 (d, 1H, *J* = 7.8 Hz), 7.98 (d, 1H, *J* = 7.8 Hz), 8.08 (s, 1H). <sup>1</sup>H NMR spectrum was identical to the reported data.<sup>6</sup>

**Methyl 2-bromomethylbenzoate.**

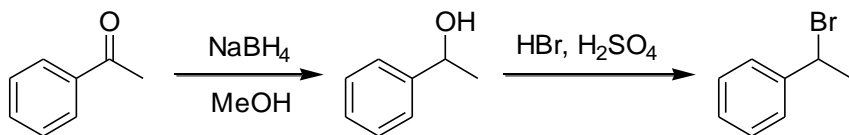
11.7 g (68% yield). Colorless crystals. Mp 32–33 °C.

<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>), δ: 3.94 (s, 3H), 4.97 (s, 2H), 7.30–7.55 (m, 3H), 7.97 (d, 1H, *J* = 7.8 Hz). <sup>1</sup>H NMR spectrum was identical to the reported data.<sup>7</sup>

<sup>5</sup> Pernia, G. J.; Kilburn, J. D.; Essex, J. W.; Mortishire-Smith, R. J.; Rowley, M. *J. Am. Chem. Soc.* **1996**, 118, 10220–10227.

<sup>6</sup> Dvornikovs, V.; Smithrud, D. B. *J. Org. Chem.* **2002**, 67, 2160–2167.

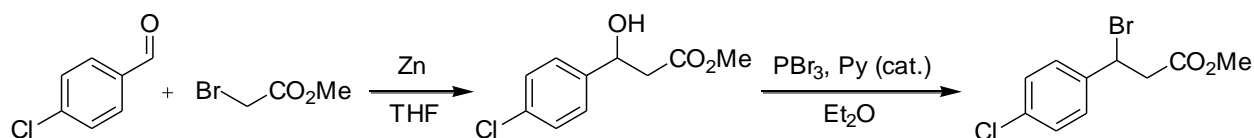
<sup>7</sup> Quagliato, D. A.; Andrae, P. M.; Matelan, E. M. *J. Org. Chem.* **2000**, 65, 5037–5042.

**(1-Bromoethyl)benzene**

Sodium borohydride (1.62 g, 42.8 mmol) was added in portions over 5 minutes to a stirred solution of acetophenone (10 mL, 85.6 mmol) in methanol (30 mL) which was immersed in an ice/water bath. The cooling bath was removed and the mixture was stirred for 2 hours. The reaction mixture was diluted with water (50 mL), and extracted with hexane (50 mL and 2×20 mL), the combined organic phase was concentrated under vacuum to give crude 1-phenylethanol. Hydrobromic acid (20.6 mL of 46% aqueous solution, 171.2 mmol) was added with stirring to the crude 1-phenylethanol followed by dropwise addition of concentrated sulfuric acid (6.88 mL, 128.4 mmol) (without external cooling), and the resulting heterogeneous mixture was vigorously stirred for 2 hours. The mixture was extracted with hexane (50 mL and 2×20 mL), the combined hexane solution was filtered through Na<sub>2</sub>SO<sub>4</sub>, concentrated, and the residue was distilled under vacuum to afford 12.67 g (80%) of (1-bromoethyl)benzene as a pale gray liquid.

Bp 90–92 °C/15 mm Hg.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>), δ: 2.09 (d, 3H, *J* = 6.8 Hz), 5.19 (q, 1H, *J* = 6.8 Hz), 7.25–7.40 (m, 3H), 7.41–7.48 (d, 2H, *J* = 7.0 Hz) <sup>1</sup>H NMR spectrum was identical to the reported data.<sup>8</sup>

**Methyl 3-bromo-3-(4-chlorophenyl)propanoate**

Chlorotrimethylsilane (127 μL, 1.0 mmol) was added to a suspension of zinc dust (3.92 g, 25.0 mmol) in THF (10 mL) and the mixture was briefly heated until boiling, the heating was discontinued, the mixture was stirred for 15 minutes and then cooled to 0 °C. The solution of *p*-chlorobenzaldehyde (2.82 g, 20.0 mmol) and methyl bromoacetate (3.21 g, 21.0 mmol) in THF (10 mL) was added dropwise at 0 °C with vigorous stirring. Then, the reaction mixture was allowed to warm to room temperature and stirred for 2 hours. Hydrochloric acid (50 mL of 2M aqueous solution) was added and the mixture was stirred for an additional 30 minutes. The product was extracted with a mixture of hexane/EtOAc (1/1, 3×10 mL), the combined organic phase was dried over MgSO<sub>4</sub>, and concentrated under vacuum. The residue was dissolved in Et<sub>2</sub>O (10 mL), and then pyridine (64 μL, 0.8 mmol) and phosphorus tribromide (0.76 mL, 8.0 mmol) were added. The reaction was refluxed for 2 hours, then cooled to 0 °C, and then iced water (10 mL) was slowly added at this temperature. The product was extracted with hexane (3×10 mL). The hexane phase was concentrated, and the residue was chromatographed on a short silica gel column eluting with hexane/EtOAc (15/1). After evaporation of the solvent, the residue was

<sup>8</sup> Denton, R. M.; An, J.; Adeniran, B.; Blake, A. J.; Lewis, W.; Poulton, A. M. *J. Org. Chem.* **2011**, 76, 6749–6767.

recrystallized from hexane to afford 2.94 g (53% based on *p*-chlorobenzaldehyde) of the product as colorless crystals.

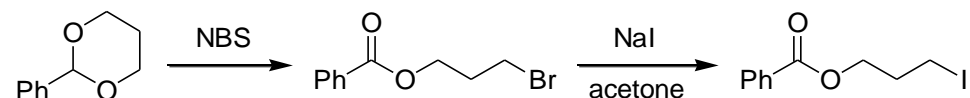
Mp 76–78 °C.  $R_f$  = 0.23 (hexanes/EtOAc, 15/1).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 3.17 (dd, 1 H,  $J$  = 16.3, 7.5 Hz), 3.29 (dd, 1H,  $J$  = 16.3, 7.5 Hz), 3.69 (s, 3H), 3.22 (dd, 1 H,  $J$  = 7.5, 7.5 Hz), 7.32 (d, 2 H,  $J$  = 8.8 Hz), 7.37 (d, 2 H,  $J$  = 8.8 Hz).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 44.6, 46.7, 52.2, 128.6, 128.9, 134.6, 139.4, 169.9.

Calcd for  $\text{C}_{10}\text{H}_{10}\text{BrClO}_2$  (277.54): C 43.28, H 3.63. Found: C 43.27, H 3.54.

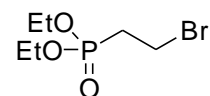
### 3-Iodopropylbenzoate.



The flask containing a stirred solution of 2-phenyl-1,3-dioxane<sup>9</sup> (8.04 g, 49 mmol) in benzene (25 mL) was immersed in a room temperature water bath, and NBS (9.61 g, 54 mmol) was gradually added. Then, the water bath was heated to 50 °C, and the mixture was stirred for 1 hour at 50 °C under irradiation with fluorescent light bulb (20 W). After cooling to room temperature, the mixture was diluted with water (30 mL) and hexane (20 mL), the upper layer was separated, dried with  $\text{Na}_2\text{SO}_4$ , and concentrated. The residue was filtered through short silica gel pad eluting with hexane/EtOAc (12/1), and the eluent was evaporated under vacuum to afford 3-bromopropylbenzoate as nonviscous oil. This product was added to a suspension of NaI (12.0 g, 80 mmol) in acetone (60 mL), and the mixture was refluxed for 12 hours. The solvent was evaporated under vacuum, the product was extracted with hexane (70 mL and 2×30 mL), and the combined hexane extract was concentrated. For the recrystallization, the residue was dissolved in small amount of hexane (*ca.* 25 mL) followed by cooling to −78 °C which led to the formation of crystals. The supernatant solution was decanted at −78 °C, and the residue was dried under vacuum at room temperature to give 3-iodopropyl benzoate as a pale yellow liquid. Yield 11.65 g (82%, based on 2-phenyl-1,3-dioxane).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 2.23–2.35 (m, 2H), 3.29 (t, 2H,  $J$  = 7.0 Hz), 4.39 (t, 2H,  $J$  = 6.1 Hz), 7.37–7.47 (m, 2H), 7.49–7.58 (m, 1H), 8.01 (d,  $J$  = 8.1 Hz).  $^1\text{H}$  NMR spectrum was identical to the reported data.<sup>10</sup>

### Diethyl (2-bromoethyl)phosphonate.



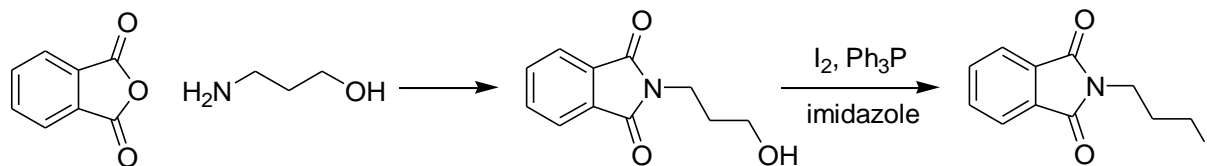
Synthesized according literature procedure.<sup>11</sup>

<sup>9</sup> Tokoroyama, T.; Kusaka, H. *Can. J. Chem.* **1996**, *74*, 2487–2502.

<sup>10</sup> Thompson, A. M.; Delaney, A. M.; Hamby, J. M.; Schroeder, M. C.; Spoon, T. A.; Crean, S. M.; Showalter, H. D. H.; Denny, W. A. *J. Med. Chem.* **2005**, *48*, 4628–4653.

<sup>11</sup> Cichowicz, N. R.; Nagorny, P. *Org. Lett.* **2012**, *14*, 1058–1061.

## 2-(3-Iodopropyl)isoindoline-1,3-dione



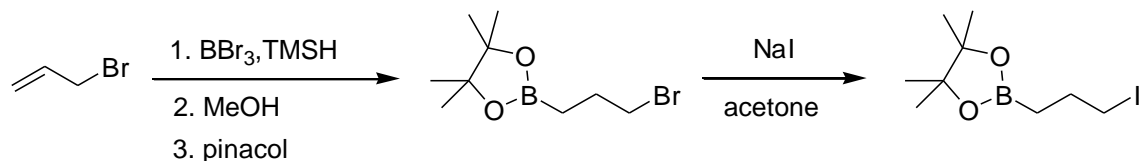
Phthalic anhydride (8.75 g, 59 mmol) and  $\text{NEt}_3$  (0.42 mL, 3 mmol) were added to a mixture of 3-aminopropanol (4.44 g, 59 mmol) and toluene (20 mL), and the reaction mixture was refluxed for 2.5 hours with Dean-Stark trap. Then, the Dean-Stark trap was removed, and the most part of toluene was evaporated at atmospheric pressure, and the residue was recrystallized from methanol to afford 9.49 g (78%) of white crystals of 3-phthalimidopropanol.

A solution of  $\text{PPh}_3$  (7.32 g, 28 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 mL) was immersed in an ice/water bath. To this solution, iodine (7.11 g, 28 mmol), imidazole (2.50 g, 36.8 mmol) and 3-phthalimidopropanol (4.31 g, 21 mmol) were successively added at 15-minute intervals. The cooling bath was removed, and the mixture was stirred for 4 hours. Then, water (20 mL) was added, and the mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (50 mL and  $2 \times 20$  mL). The combined organic phase was filtered through  $\text{Na}_2\text{SO}_4$ , and concentrated under vacuum to afford crystalline material containing the desired product and phosphine oxide. For the removal of phosphine oxide, the mixture was subjected to continuous extraction with hexane (using Soxhlet-type extractor). The resulting hexane solution was concentrated, and the product was purified by recrystallization from EtOH. Yield 4.85 g (73%).

Colorless crystals. Mp 89–90 °C.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 2.23 (quint, 2H,  $J = 6.9$  Hz), 3.16 (t, 2H,  $J = 7.0$  Hz), 3.75 (t, 2H,  $J = 6.8$  Hz), 7.66–7.76 (m, 2H), 7.79–7.87 (m, 2H).  $^1\text{H}$  NMR spectrum was identical to the reported data.<sup>12</sup>

<sup>12</sup> Zhou, J.; Fu, G. C. *J. Am. Chem. Soc.* **2003**, 125, 12527–12530.

**2-(3-Iodopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane**


A solution of  $\text{BBr}_3$  (7.52 g, 30.0 mmol) in hexanes (9 mL) was treated with  $\text{BH}_3\cdot\text{SMe}_2$  (86 mg, 0.9 mmol) and the mixture was cooled to  $-78^\circ\text{C}$ . Then, a solution of allyl bromide (3.63g, 30.0 mmol) and trimethylsilane (2.23 g, 30.0 mmol) in hexanes (9 mL) was added. The temperature was allowed to raise to  $0^\circ\text{C}$  during 2 hours. The solvent was evaporated under vacuum, the residue was cooled to  $-20^\circ\text{C}$  and treated with MeOH (120.0 mmol, 4.8 mL). The mixture was extracted with pentane ( $3\times 5$  mL), the combined pentane extract was concentrated at ambient pressure. The resulting yellow liquid was treated with pinacol (3.54 g, 30.0 mmol), and the mixture was heated to effect removal of methanol. The mixture was cooled to room temperature, and passed through short silica gel pad using hexane/EtOAc (15/1) as eluent. The eluent was evaporated under vacuum, the residue was added to a suspension of NaI (9.0 g, 60 mmol) in 30 ml of acetone, and the mixture was refluxed for 8 hours. The solvent was evaporated, and water (30 mL) was added. The mixture was extracted with hexane ( $3\times 20$  mL), the combined hexane phase was washed with aqueous solution of  $\text{Na}_2\text{S}_2\text{O}_3$  (0.5 M), and dried over  $\text{MgSO}_4$ . The solvent was evaporated under vacuum, and the residue was chromatographed through short silica gel column using hexane/EtOAc (15/1) as eluent affording 3.10 g (35%) of the product as a colorless liquid.

$R_f = 0.33$  (hexanes/EtOAc, 15/1).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 0.89 (t, 2H,  $J = 7.0$  Hz), 1.25 (s, 12H), 1.93 (quint, 2H,  $J = 7.4$  Hz), 3.22 (t, 2H,  $J = 7.2$  Hz).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 10.0, 24.9, 28.4, 83.2.

Calcd for  $\text{C}_9\text{H}_{18}\text{BIO}_2$  (295.95): C 36.52, H 6.13. Found: C 36.45, H 6.19.


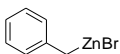

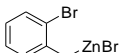
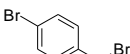
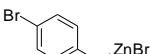
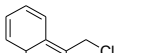
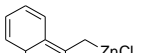
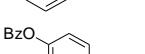
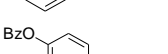
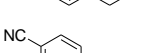
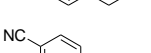
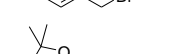
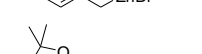
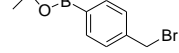
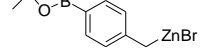


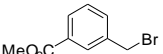
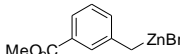
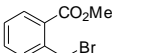
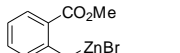
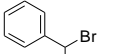
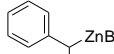
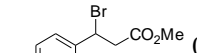
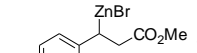


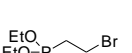
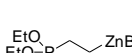
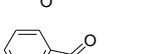
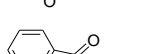
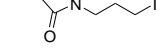
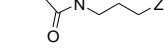
## General procedure for the preparation of organozinc reagents **2**.

To a stirred suspension of zinc dust (10.0 mmol, 654 mg) in THF (5 mL for **2a-e,g-p**, 10 mL for **2f**) a one drop of 1,2-dibromoethane was added. The mixture was heated to reflux, then two drops of Me<sub>3</sub>SiCl were added to a hot suspension, and the mixture was vigorously stirred for 15 minutes at 60 °C. In this period the formation of gas was observed and zinc dust appeared as a dark-grey fuzzy material (if this does not happen, an additional drop of Me<sub>3</sub>SiCl should be added). Then benzyl or alkyl halide (5.0 mmol) was slowly added at the temperature T<sub>1</sub> (shown in Table 1) not letting the reaction mixture to heat. The resulting mixture was stirred at the temperature T<sub>2</sub> for the appropriate time (shown in Table 1). The stirring was discontinued, and the unreacted zinc was allowed to settle down.

The concentration of organozinc reagent was determined by iodometric titration: a solution of organozinc reagent **2** was added dropwise to a stirred solution of iodine (51 mg, 0.2 mmol) in THF (1 mL) until decoloration. The volume of the solution needed for the titration was used to calculate the concentration of organozinc reagent.

**Table 1.** Preparation of organozinc reagents **2**.

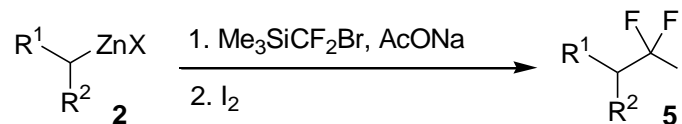
THF				
RX + Zn $\xrightarrow{\hspace{1.5cm}}$ RZnX				
mixing at T <sub>1</sub>				
2				
stirring at T <sub>2</sub> during the Time				
RX	T <sub>1</sub> , <sup>a</sup> °C	T <sub>2</sub> , <sup>b</sup> °C	Time, <sup>c</sup> h	RZnX
	rt	rt	4	 <b>2a</b>
	0	rt	2	 <b>2b</b>
	rt	rt	4	 <b>2c</b>
	rt	rt	4	 <b>2d</b>
	0	rt	16	 <b>2e</b>
	-25	rt	16	 <b>2f</b>
	0	rt	2	 <b>2g</b>
	0	rt	2	 <b>2h</b>

RX	T <sub>1</sub> , <sup>a</sup> °C	T <sub>2</sub> , <sup>b</sup> °C	Time, <sup>c</sup> h	RZnX
	0	rt	16	 <b>2i</b>
	0	rt	2	 <b>2j</b>
	rt	rt	4	 <b>2k</b>
	0	rt	4	 <b>2l</b>
	0	rt	16	 <b>2m</b>
	rt	50	9	 <b>2n</b>
	rt	rt	16	 <b>2o</b>
	rt	rt	16	 <b>2p</b>

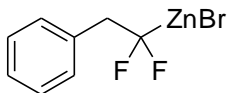
<sup>a</sup> Temperature at which addition of RX to Zn was carried out.

<sup>b</sup> Temperature for the formation of RZnX

<sup>c</sup> Time for the formation of RZnX

**General procedure** for iododifluoromethylation of organozinc reagents **2**.

A freshly titrated THF solution of **2** (1.5 mmol) was concentrated under vacuum until the solid or viscous residue was formed. The residue was dissolved in freshly distilled MeCN (1.5 mL). To the resulting solution was added sodium acetate (148 mg, 1.8 mmol for **2a-c,e-p**, or 172 mg, 2.1 mmol for **2d**) at room temperature, the reaction flask was immersed in a cold bath at  $-25\text{ }^{\circ}\text{C}$ , and the mixture was stirred for 10 minutes at  $-25\text{ }^{\circ}\text{C}$ . (Usually, after lowering the temperature the reaction mixture becomes homogeneous. In case of **2g**, the formation of a fine white precipitate may be observed, but this has no effect on the reaction.) In case of reagent **2n**, the resulting solution was diluted with DMF (232  $\mu\text{L}$ , 3.0 mmol). Then,  $\text{Me}_3\text{SiCF}_2\text{Br}$  (365 mg, 1.8 mmol for **2a-c,e-p**, or 426 mg, 2.1 mmol for **2d**) was added dropwise at  $-25\text{ }^{\circ}\text{C}$ , and the reaction mixture was stirred at this temperature for 18 h (21 h in case of **2d,n-p**). Iodine (401 mg, 1.58 mmol) was added at  $-25\text{ }^{\circ}\text{C}$  to the reaction mixture with vigorous stirring. After dissolution of iodine, the cooling bath was removed, the mixture was allowed to warm to room temperature and was stirred for additional 5 hours. The resulting reddish-brown mixture was quenched by addition of aqueous 0.5 M solution of  $\text{Na}_2\text{S}_2\text{O}_3$  until decoloration, diluted with water (10 mL), and extracted with hexane ( $3 \times 10\text{ mL}$ ) [or pentane ( $3 \times 10\text{ mL}$ ) in case of volatile **2a,b**]. The combined organic layer was filtered through  $\text{Na}_2\text{SO}_4$ , concentrated under vacuum (or under ambient pressure in case of **2a,b**). The residue was purified by column chromatography on silica gel.

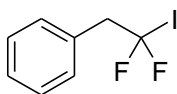
**(1,1-Difluoro-2-phenylethyl)zinc bromide (4a).**

The reaction of benzylzinc bromide (**2a**) with  $\text{Me}_3\text{SiCF}_2\text{Br}$  and  $\text{AcONa}$  was performed according to the general procedure using  $\text{CD}_3\text{CN}$  as solvent. Due to Schlenk equilibrium the reagent **4a** exists as a mixture of two organozinc species in a ratio of 5 : 1.

$^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ ),  $\delta$ : 3.07 (t, 2H,  $J = 24.5$  Hz, major), 2.88 (t, 0.4H,  $J = 24.5$  Hz, minor), 7.12–7.43 (m, 5H, Ph).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CD}_3\text{CN}$ ), selected signals of major isomer are given,  $\delta$ : 48.7 (t,  $J = 17.4$  Hz), 126.7, 128.4, 131.6, 137.2 (t,  $J = 9.1$ ).

$^{19}\text{F}$  NMR (282 MHz,  $\text{CD}_3\text{CN}$ ),  $\delta$ :  $-95.3$  (t,  $J = 24.5$  Hz, minor),  $-96.6$  (t,  $J = 24.5$  Hz, major).

**(2,2-Difluoro-2-iodoethyl)benzene (5a).**

342 mg (85%). Colorless oil.  $R_f = 0.33$  (pentane).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 3.69 (t, 2H,  $J = 15.4$  Hz), 7.29–7.44 (m, 5H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 54.3 (t,  $J = 20.3$  Hz), 101.4 (t,  $J = 314.3$  Hz), 128.3, 128.7, 130.8, 132.3 (t,  $J = 4.4$  Hz).

$^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ ),  $\delta$ :  $-37.8$  (t, 2F,  $J = 15.4$  Hz).

Calcd for  $\text{C}_8\text{H}_7\text{F}_2\text{I}$  (268.04): C 35.85, H 2.63. Found: C 35.74, H 2.64.

**1-Bromo-2-(2,2-difluoro-2-iodoethyl)benzene (5b).**

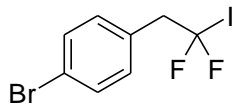
437 mg (84%). Colorless oil.  $R_f = 0.37$  (hexanes).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 4.00 (t, 2H,  $J = 15.8$  Hz), 7.24 (dd, 1H,  $J = 7.5, 7.3$  Hz), 7.34 (dd, 1H,  $J = 8.1, 7.5$  Hz), 7.44 (d, 1H,  $J = 7.3$  Hz), 7.65 (d, 1H,  $J = 8.1$  Hz).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 53.2 (t,  $J = 20.7$  Hz), 99.0 (t,  $J = 315.0$  Hz), 125.9, 127.6, 129.9, 132.2 (t,  $J = 2.9$  Hz), 132.4, 133.4.

$^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ ),  $\delta$ :  $-37.6$  (t, 2F,  $J = 15.8$  Hz).

Calcd for  $\text{C}_8\text{H}_6\text{BrF}_2\text{I}$  (346.94): C 27.70, H 1.74. Found: C 27.43, H 1.64.

**1-Bromo-4-(2,2-difluoro-2-iodoethyl)benzene (5c).**

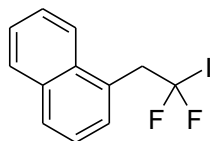
416 mg (80%). Colorless oil.  $R_f = 0.35$  (hexanes)

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 3.63 (t, 2H,  $J = 15.0$  Hz), 7.20 (d, 2H,  $J = 8.2$  Hz), 7.52 (d, 2H,  $J = 8.2$  Hz).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 53.6 (t,  $J = 20.7$  Hz), 100.5 (t,  $J = 314.1$  Hz), 122.7, 131.3 (t,  $J = 3.7$  Hz), 131.9, 132.4.

$^{19}\text{F}$  NMR (282,  $\text{CDCl}_3$ ),  $\delta$ :  $-38.5$  (t, 2F,  $J = 15.0$  Hz).

Calcd for  $\text{C}_8\text{H}_6\text{BrF}_2\text{I}$  (346.94): C 27.70, H 1.74. Found: C 27.74, H 1.88.

**1-(2,2-Difluoro-2-iodoethyl)naphthalene (5d).**

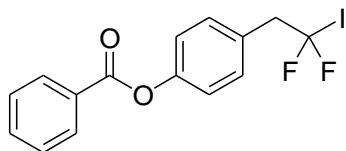
334 mg, 70%. Colorless oil.  $R_f = 0.21$  (hexanes).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 4.26 (t, 2H,  $J = 15.8$  Hz), 7.47–7.68 (m, 4H), 7.88–7.98 (m, 2H), 8.07 (d, 1H,  $J = 8.1$  Hz),

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 51.0 (t,  $J = 20.4$  Hz), 100.9 (t,  $J = 315.5$  Hz), 124.1 (t,  $J = 2.0$  Hz), 125.3, 126.0, 126.6, 128.6 (t,  $J = 2.6$  Hz), 128.9, 129.3, 130.1, 132.4, 134.1.

$^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$ :  $-36.4$  (t, 2F,  $J = 15.8$  Hz).

Calcd for  $\text{C}_{12}\text{H}_9\text{F}_2\text{I}$  (318.10): C 45.31, H 2.85. Found: C 45.28, H 2.71.

**4-(2,2-Difluoro-2-iodoethyl)phenyl benzoate (5e).**

495 mg (85%). Colorless crystals. Mp 89–91 °C.

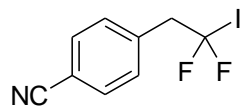
$R_f = 0.28$  (hexanes/EtOAc, 15/1).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 3.71 (t,  $J = 15.2$  Hz), 7.27 (d, 2H,  $J = 8.2$  Hz), 7.40 (d, 2H,  $J = 8.2$  Hz), 7.50–7.60 (m, 2H), 7.63–7.72 (m, 1H), 8.24 (d, 2H,  $J = 8.0$  Hz).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 53.6 (t,  $J = 20.4$  Hz), 101.0 (t,  $J = 314.1$  Hz), 122.0, 128.7, 129.5, 129.9 (t,  $J = 3.5$  Hz), 130.3, 131.9, 133.8, 151.2, 165.0.

$^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$ :  $-38.3$  (t, 2F,  $J = 15.2$  Hz).

Calcd for  $\text{C}_{15}\text{H}_{11}\text{F}_2\text{IO}_2$  (388.15): C 46.42, H 2.86. Found: C 46.41, H 2.77.

**4-(2,2-Difluoro-2-iodoethyl)benzonitrile (5f).**

308 mg (70%). Colorless crystals. Mp 54–55 °C (recrystallized from hexane at –78 °C).

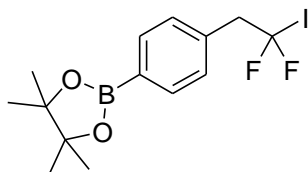
$R_f$  = 0.25 (hexanes/EtOAc, 8/1).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 3.74 (t, 2H,  $J$  = 14.9 Hz), 7.44 (d, 2H,  $J$  = 7.9 Hz), 7.68 (d, 2H,  $J$  = 7.9 Hz).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 54.0 (t,  $J$  = 21.0 Hz), 98.9 (t,  $J$  = 314.1 Hz), 112.5, 118.5, 131.5, 132.5, 137.4 (t,  $J$  = 3.7 Hz).

$^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$ : –38.7 (t,  $J$  = 14.9 Hz).

Calcd for  $\text{C}_9\text{H}_6\text{F}_2\text{IN}$  (293.05): C 36.89, H 2.06. Found: C 36.94, H 2.07.

**2-[4-(2,2-Difluoro-2-iodoethyl)phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5g).**

414 mg (70%).

Colorless crystals. Mp 56–57 °C (recrystallized twice from hexane at –78 °C).

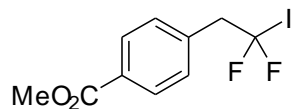
$R_f$  = 0.27 (hexanes/EtOAc, 15/1).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 1.37 (s, 12H), 3.69 (t, 2H,  $J$  = 15.2 Hz), 7.33 (d, 2H,  $J$  = 7.3 Hz), 7.83 (d, 2H,  $J$  = 8.1 Hz).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 29.6, 59.0 (t,  $J$  = 20.4 Hz), 88.6, 105.6 (t,  $J$  = 314.1 Hz), 134.7, 139.7, 139.9 (t,  $J$  = 3.7 Hz).

$^{19}\text{F}$  NMR (282,  $\text{CDCl}_3$ ),  $\delta$ : –37.8 (t, 2F,  $J$  = 15.2 Hz).

Calcd for  $\text{C}_{14}\text{H}_{18}\text{BF}_2\text{IO}_2$  (394.00): C 42.68, H 4.60. Found: C 42.74, H 4.65.

**Methyl 4-(2,2-difluoro-2-iodoethyl)benzoate (5h).**

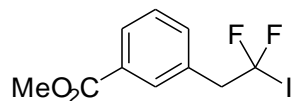
430 mg, 88%. Colorless crystals. Mp 42–43 °C  $R_f$  = 0.26 (hexanes/EtOAc, 12/1).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 3.73 (t, 2H,  $J$  = 15.0 Hz), 3.93 (s, 3H), 7.40 (d, 2H,  $J$  = 7.7 Hz), 8.05 (d, 2H,  $J$  = 7.7 Hz).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 52.2, 53.9 (t,  $J$  = 20.4 Hz), 99.9 (t,  $J$  = 314.4 Hz), 129.8, 130.1, 130.8, 137.1 (t,  $J$  = 3.7 Hz), 166.7.

$^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$ : –38.2 (t,  $J$  = 15.0 Hz).

Calcd for  $\text{C}_{10}\text{H}_9\text{F}_2\text{IO}_2$  (326.08): C 36.83, H 2.78. Found: C 36.87, H 2.87.

**Methyl 3-(2-bromo-2,2-difluoroethyl)benzoate (5i).**

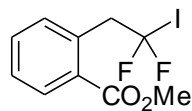
416 mg (85%). Colorless oil.  $R_f$  = 0.12 (hexanes/EtOAc, 15/1).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 3.72 (t, 2H,  $J$  = 15.0 Hz), 3.93 (s, 3H), 7.40–7.55 (m, 2H), 8.00 (s, 1H, Ar), 8.06 (d, 1H,  $J$  = 7.4).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 52.3, 53.9 (t,  $J$  = 20.7 Hz), 100.5 (t,  $J$  = 314.1 Hz), 128.8, 129.5, 130.7, 131.9, 132.7 (t,  $J$  = 3.7 Hz), 135.1, 166.6.

$^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$ : -38.5 (t,  $J$  = 15.0 Hz).

Calcd for  $\text{C}_{10}\text{H}_9\text{F}_2\text{IO}_2$  (326.08): C 36.83, H 2.78. Found: C 36.67, H 2.81.

**Methyl 2-(2-bromo-2,2-difluoroethyl)benzoate (5j).**

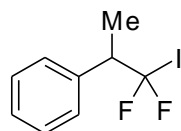
279 mg (57%). Yellow oil.  $R_f$  = 0.34 (hexanes/EtOAc, 15/1).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 3.93 (s, 3H), 4.37 (t, 2H,  $J$  = 15.8 Hz), 7.38–7.58 (m, 3H), 7.93–8.00 (m, 1H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 50.7 (t,  $J$  = 20.2 Hz), 52.3, 100.1 (t,  $J$  = 315.0 Hz), 128.3, 131.0, 131.3, 132.0, 133.0 (t,  $J$  = 3.2 Hz), 133.1, 167.8.

$^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ ),  $\delta$ : -37.7 (t,  $J$  = 15.8 Hz)

Calcd for  $\text{C}_{10}\text{H}_9\text{F}_2\text{IO}_2$  (326.08): C 36.83, H 2.78. Found: C 36.77, H 2.81.

**(1,1-Difluoro-1-iodopropan-2-yl)benzene (5k).**

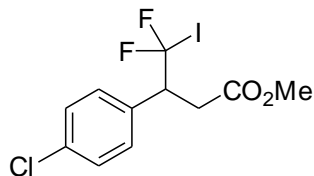
455 mg (93%). Colorless oil.  $R_f$  = 0.33 (pentanes).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 1.56 (d, 3H,  $J$  = 7.1 Hz), 3.31–3.50 (m, 1H), 7.34–7.44 (m, 5H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 16.8 (t,  $J$  = 3.5 Hz), 55.3 (t,  $J$  = 18.4 Hz), 108.3 (t,  $J$  = 317.6 Hz), 128.2, 128.5, 129.2, 137.8 (t,  $J$  = 2.6 Hz).

$^{19}\text{F}$  NMR (282,  $\text{CDCl}_3$ ),  $\delta$ : -41.2 (dd, 1F,  $J$  = 171.7, 12.7), -41.8 (dd, 1F,  $J$  = 171.7, 12.7).

Calcd for  $\text{C}_9\text{H}_9\text{F}_2\text{I}$  (282.07): C 38.32, H 3.22. Found: C 38.60, H 3.28.

**Methyl 3-(4-chlorophenyl)-4,4-difluoro-4-iodobutanoate (5l).**

410 mg (73%).  $R_f$  = 0.29 (hexanes/EtOAc, 15/1). Clear colorless oil.

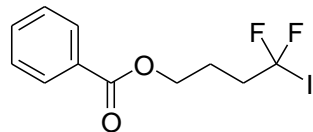
The material after chromatography contained traces of by-products which were removed as follows. The oil was dissolved in small amount of hot hexane followed by cooling to  $-78\text{ }^{\circ}\text{C}$  which led to the formation of crystals. The supernatant solution was decanted at  $-78\text{ }^{\circ}\text{C}$ , and the residue was dried under vacuum at room temperature affording product **5l**.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 2.88 (dd, 1H,  $J$  = 16.1, 10.3 Hz), 3.13 (dd, 1H,  $J$  = 16.1, 4.2 Hz), 3.61 (s, 3H), 3.84–4.01 (m, 1H), 7.28 (d, 2H,  $J$  = 8.8 Hz), 7.36 (d, 2H,  $J$  = 8.8 Hz).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 35.5 (t,  $J$  = 2.9 Hz), 52.2, 56.6 (t,  $J$  = 19.3 Hz), 104.6 (t,  $J$  = 317.3 Hz), 128.9, 130.8, 133.9 (t,  $J$  = 2.6 Hz), 134.8, 170.0.

$^{19}\text{F}$  NMR (282,  $\text{CDCl}_3$ ),  $\delta$ :  $-44.1$  (dd, 1F,  $J$  = 177.0, 14.8 Hz),  $-41.7$  (dd, 1F,  $J$  = 177.0, 14.8 Hz).

Calcd for  $\text{C}_{11}\text{H}_{10}\text{ClF}_2\text{IO}_2$  (374.55): C 35.27, H 2.69. Found: C 35.18, H 2.64.

**4,4-Difluoro-4-iodobutyl benzoate (5m).**

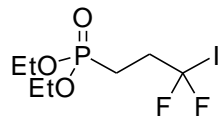
418 mg (82%). Colorless oil.  $R_f$  = 0.27 (hexanes/EtOAc, 15/1).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 2.01–2.17 (m, 2H), 2.42–2.66 (m, 2H), 4.41 (t, 2H,  $J$  = 6.2 Hz), 7.41–7.53 (m, 2H), 7.59 (t, 1H,  $J$  = 7.2 Hz), 8.06 (d, 2H,  $J$  = 7.2 Hz).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 25.0 (t,  $J$  = 3.7 Hz), 45.2 (t,  $J$  = 20.2 Hz), 62.9, 101.2 (t,  $J$  = 313.0 Hz), 128.5, 129.7, 130.0, 133.2, 166.4.

$^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$ :  $-37.0$  (t,  $J$  = 14.8 Hz).

Calcd for  $\text{C}_{11}\text{H}_{11}\text{F}_2\text{IO}_2$  (340.11): C 38.85, H 3.26. Found: C 38.91, H 3.21.

**Diethyl (3,3-difluoro-3-iodopropyl)phosphonate (5n).**

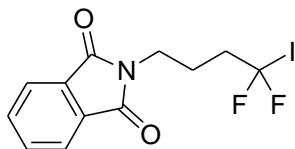
328 mg, (64%). Pale yellow oil.  $R_f$  = 0.16 (hexanes/EtOAc, 1/1).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 1.34 (t, 6H,  $J$  = 7.0 Hz), 1.90–2.06 (m, 2H), 2.51–2.71 (m, 2H), 4.06–4.22 (m, 4H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 16.4 (d,  $J$  = 5.8 Hz), 22.0 (dt,  $J$  = 145.1, 3.5 Hz), 42.2 (td,  $J$  = 21.9, 2.9 Hz), 62.1 (d,  $J$  = 6.3 Hz), 100.3 (td,  $J$  = 313.2, 26.5 Hz).

$^{19}\text{F}$  NMR (282,  $\text{CDCl}_3$ ),  $\delta$ : –39.3 (t, 2F,  $J$  = 13.8 Hz).

Calcd for  $\text{C}_7\text{H}_{14}\text{F}_2\text{IO}_3\text{P}$  (342.06): C 24.58, H 4.13. Found: C 24.49, H 4.34.

**2-(4,4-Difluoro-4-iodobutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5o).**

252 mg (46%).

Colorless crystals. Mp 59–60 °C (recrystallized from hexane/EtOAc, 12/1, at –25 °C).

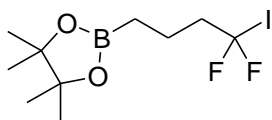
$R_f$  = 0.16 (hexanes/EtOAc, 8/1).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 1.99 (tt, 2H,  $J$  = 7.7, 7.5 Hz), 2.32–2.52 (m, 2H), 3.78 (t, 2H,  $J$  = 7.7 Hz), 7.71–7.79 (m, 2H), 7.71–7.79 (m, 2H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 24.7 (t,  $J$  = 3.5 Hz), 36.3, 45.8 (t,  $J$  = 20.2 Hz), 100.9 (t,  $J$  = 313.2 Hz), 123.4, 132.0, 134.2, 168.2.

$^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$ : –36.0 (t,  $J$  = 14.8 Hz).

Calcd for  $\text{C}_{12}\text{H}_{10}\text{F}_2\text{INO}_2$  (364.11): C 39.47, H 2.76, N 3.84. Found: C 39.44, H 2.74, N 3.76.

**2-(4,4-Difluoro-4-iodobutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5p).**

166 mg (32%). Colorless oil.  $R_f$  = 0.32 (hexanes/EtOAc, 12/1)

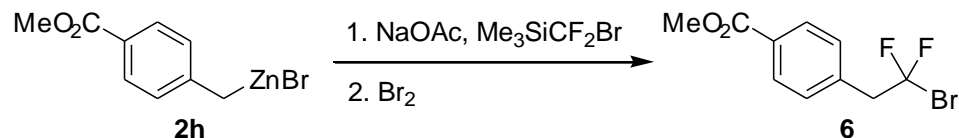
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 0.87 (t, 2H,  $J$  = 8.1), 1.26 (s, 9H), 1.62–1.77 (m, 2H), 2.23–2.43 (m, 2H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 10.0 (br s), 19.9 (t,  $J$  = 3.5 Hz), 24.8, 50.3 (t,  $J$  = 19.0 Hz), 83.2, 102.5 (t,  $J$  = 313.5 Hz).

$^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$ : –35.9 (t,  $J$  = 14.8 Hz).

Calcd for  $\text{C}_{10}\text{H}_{18}\text{BF}_2\text{IO}_2$  (345.96): C 34.72, H 5.24. Found: C 34.71, H 5.09.



**Methyl 4-(2-bromo-2,2-difluoroethyl)benzoate (6).**

The reaction of reagent **2h** with  $\text{Me}_3\text{SiCF}_2\text{Br}$  was performed according to the general procedure. The resulting mixture containing the fluorinated zinc reagent was treated with bromine (81  $\mu\text{L}$ , 1.58 mmol) at  $-25^\circ\text{C}$ . The mixture was stirred for 5 minutes at  $-25^\circ\text{C}$ , then allowed to warm to room temperature, and stirred for additional 5 min. The resulting orange solution was quenched by addition of aqueous 0.5M solution of  $\text{Na}_2\text{S}_2\text{O}_3$  until decoloration, diluted with water (10 mL), and extracted with hexane ( $3 \times 10$  mL). The combined organic layer was filtered through  $\text{Na}_2\text{SO}_4$ , concentrated under vacuum, and the residue was purified by chromatography on silica gel (hexane/EtOAc, 15/1 eluent), affording 360 mg (86%) of compound **6**.

Colorless crystals. Mp  $25\text{--}26^\circ\text{C}$  (recrystallized from hexane/EtOAc, 12/1).

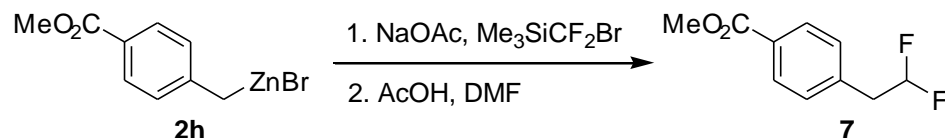
$R_f = 0.22$  (hexanes/EtOAc, 15/1).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 3.73 (t, 2H,  $J = 14.7$  Hz), 3.94 (s, 3H), 7.41 (d, 2H,  $J = 7.7$  Hz), 8.05 (d, 2H,  $J = 7.7$  Hz).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 50.2 (t,  $J = 23.0$  Hz), 52.2, 120.9 (t,  $J = 306.0$  Hz), 129.9, 130.2, 130.7, 136.3 (t,  $J = 3.2$  Hz), 166.7.

$^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$ :  $-45.4$  (t, 2F,  $J = 14.7$  Hz).

Calcd for  $\text{C}_{10}\text{H}_9\text{BrF}_2\text{O}_2$  (200.18): C 43.04, H 3.25. Found: C 43.09, H 3.27.

**Methyl 4-(2,2-difluoroethyl)benzoate (7).**

The reaction of reagent **2h** with  $\text{Me}_3\text{SiCF}_2\text{Br}$  was performed according to the general procedure. The resulting mixture containing the fluorinated zinc reagent was treated with DMF (232  $\mu\text{L}$ , 3.0 mmol) and AcOH (107  $\mu\text{L}$ , 1.88 mmol) at  $-25^\circ\text{C}$ , the cooling bath was removed, and the mixture was stirred for 30 min at room temperature. The resulting solution was diluted with water (10 mL), and extracted with pentane ( $3 \times 10$  mL). The combined organic layer was filtered through  $\text{Na}_2\text{SO}_4$ , and concentrated at atmospheric pressure. The residue was purified by chromatography on silica gel (pentane/EtOAc, 8/1) affording 255 mg (85%) of compound **7**.

255 mg (85%). Colorless crystals. Mp  $57\text{--}58^\circ\text{C}$  (recrystallized from hexane).

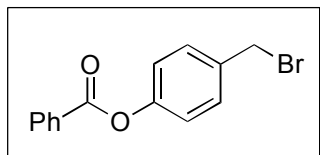
$R_f = 0.25$  (hexanes/EtOAc, 8/1).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 3.21 (td, 2H,  $J = 16.9, 4.4$  Hz), 3.93 (s, 3H), 5.96 (tt, 1H,  $J = 57.0, 4.4$  Hz), 7.34 (d, 2H,  $J = 7.7$  Hz), 8.02 (d, 2H,  $J = 7.7$  Hz).

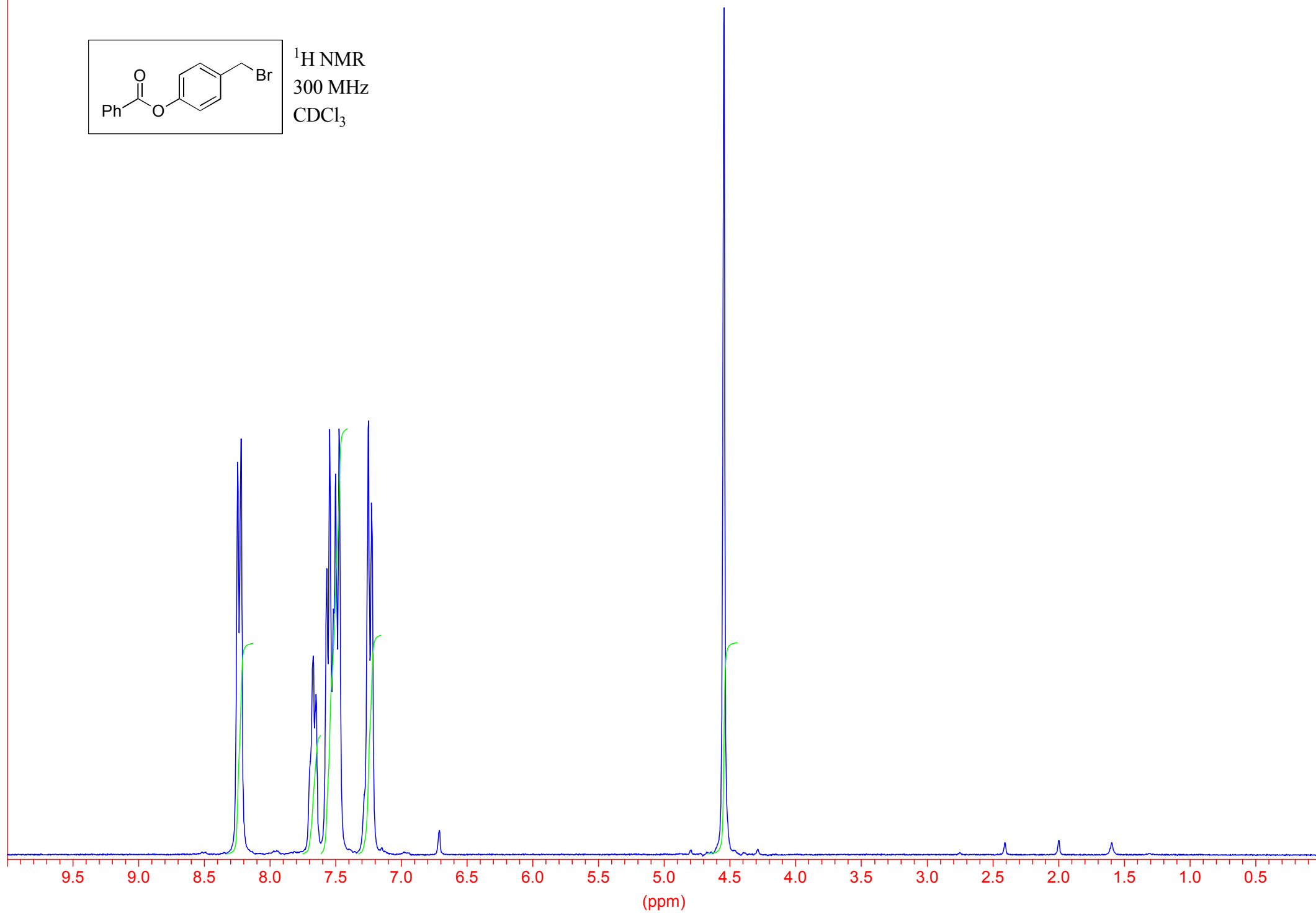
$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 40.7 (t,  $J = 22.2$  Hz), 52.1, 116.0 (t,  $J = 241.6$  Hz), 129.5, 129.8, 129.9, 137.5 (t,  $J = 5.8$  Hz), 166.7.

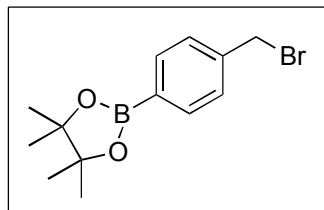
$^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$ :  $-115.7$  (dt, 2F,  $J = 57.0, 16.9$  Hz).

Calcd for  $\text{C}_{10}\text{H}_{10}\text{F}_2\text{O}_2$  (200.18): C 60.00, H 5.04. Found: C 60.01, H 5.06.

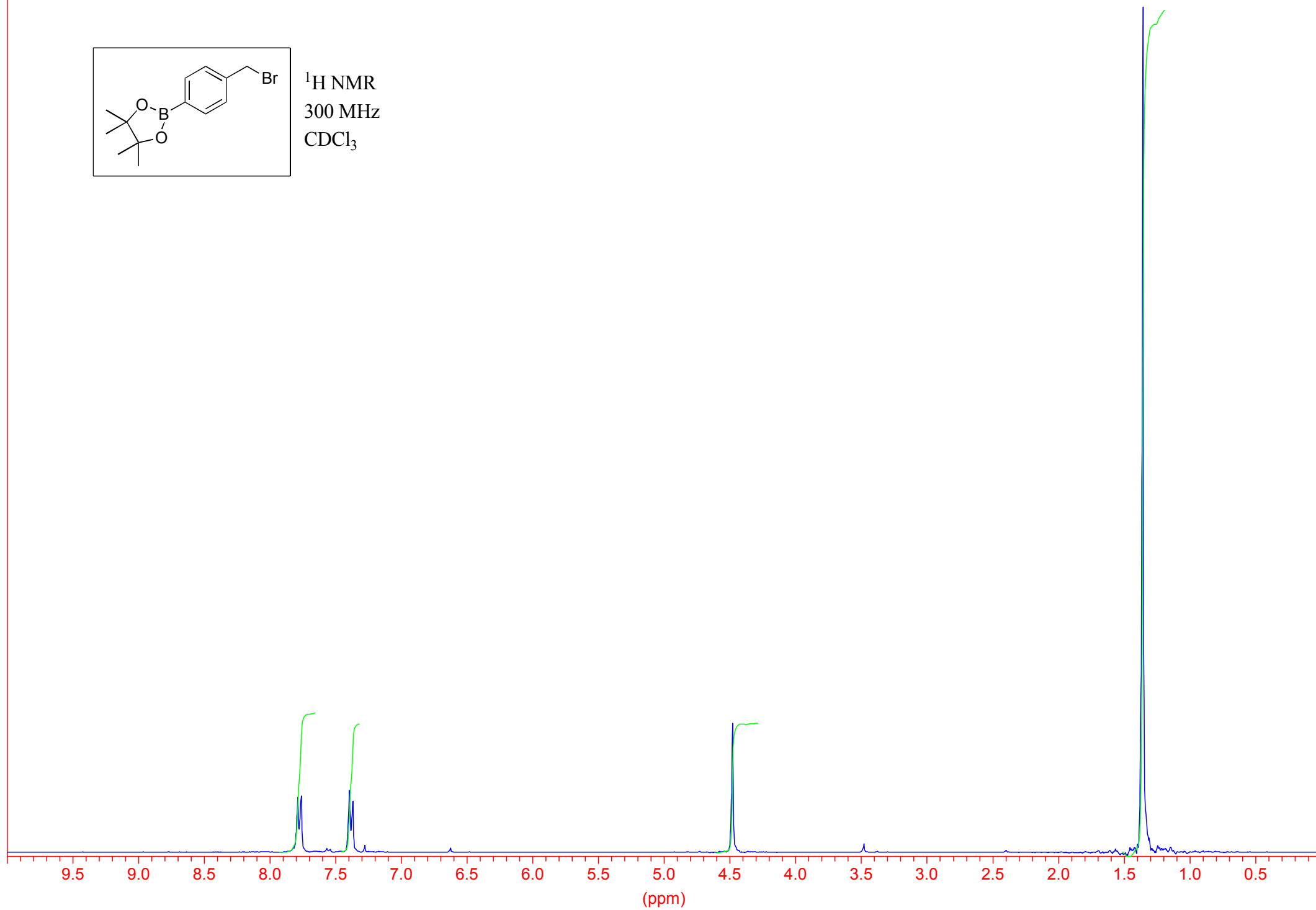


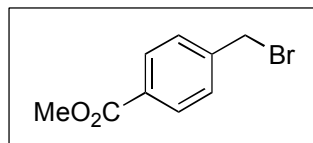
$^1\text{H}$  NMR  
300 MHz  
 $\text{CDCl}_3$



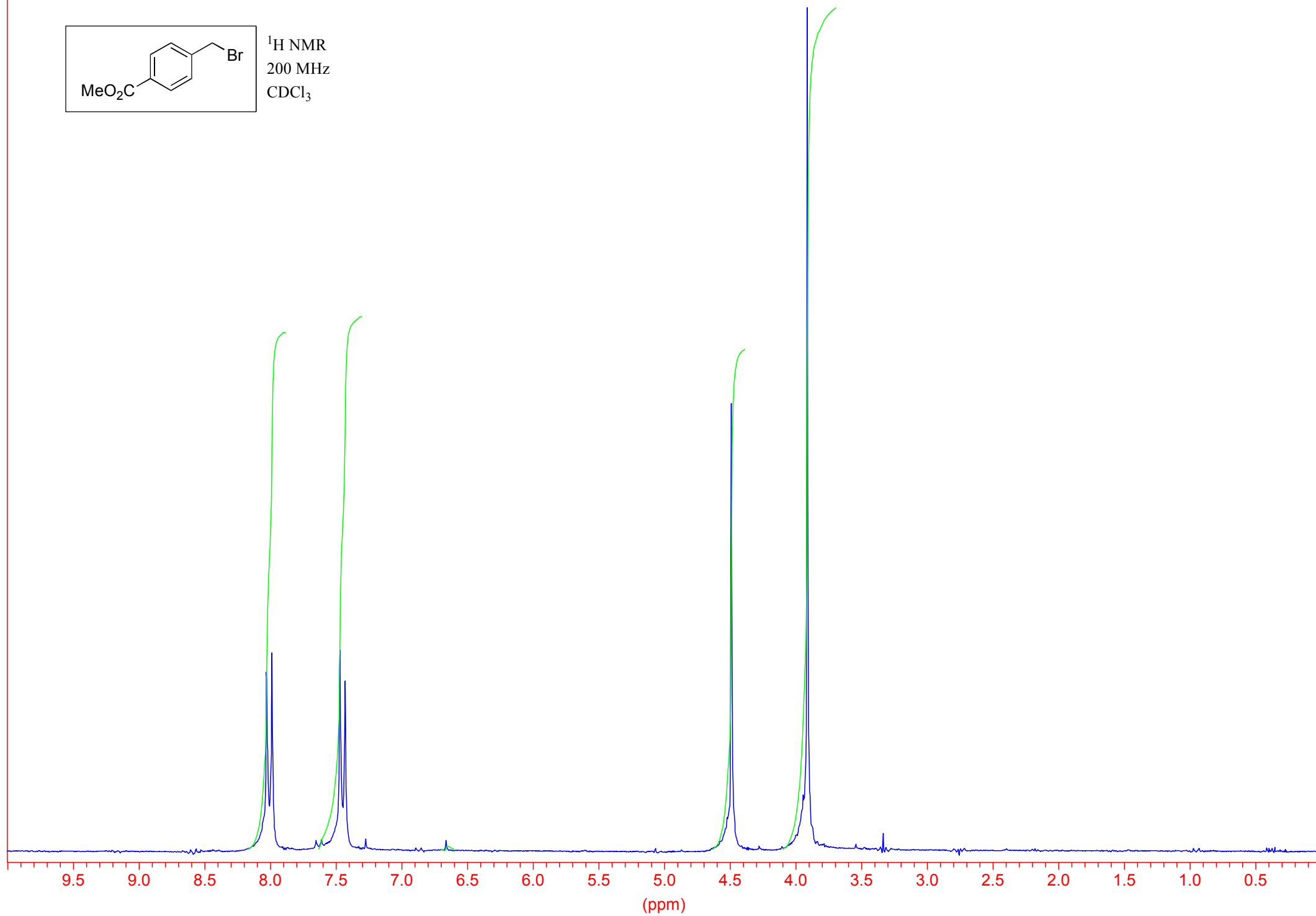


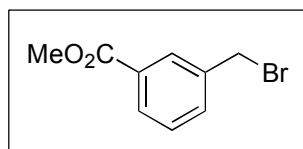
$^1\text{H}$  NMR  
300 MHz  
 $\text{CDCl}_3$



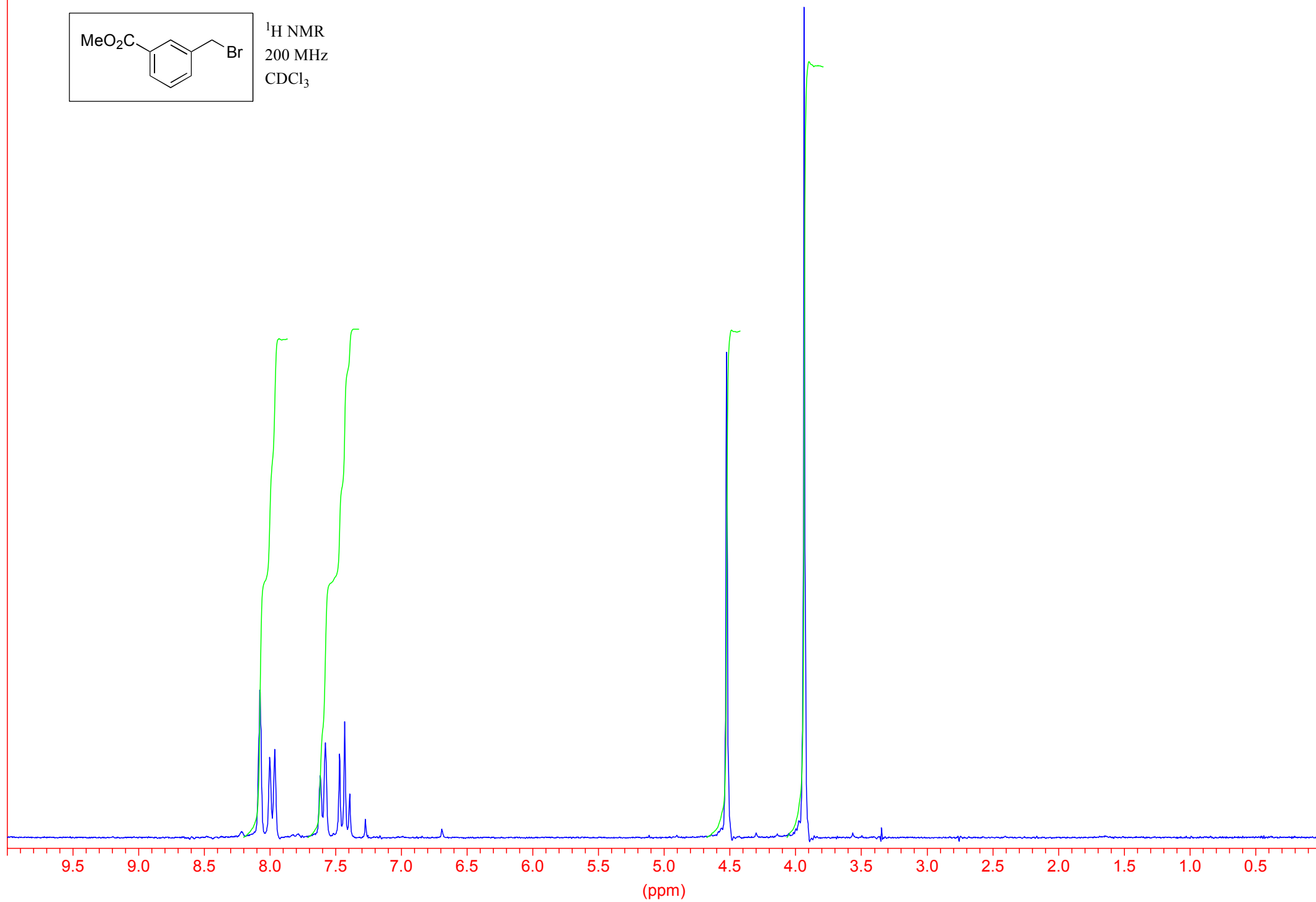


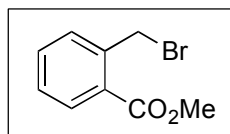
$^1\text{H}$  NMR  
200 MHz  
 $\text{CDCl}_3$



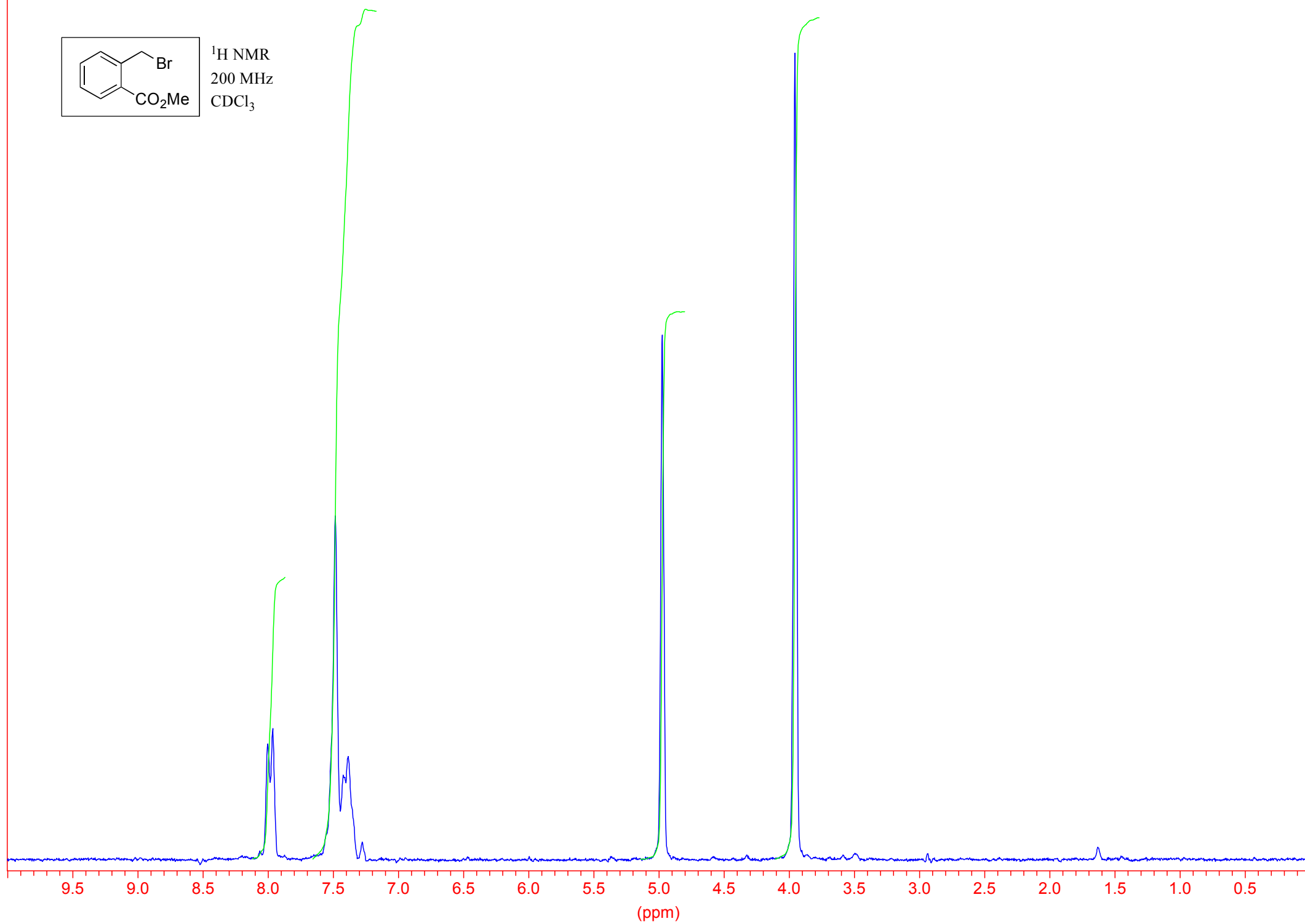


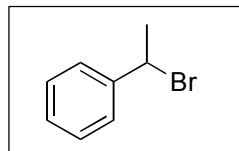
$^1\text{H}$  NMR  
200 MHz  
 $\text{CDCl}_3$



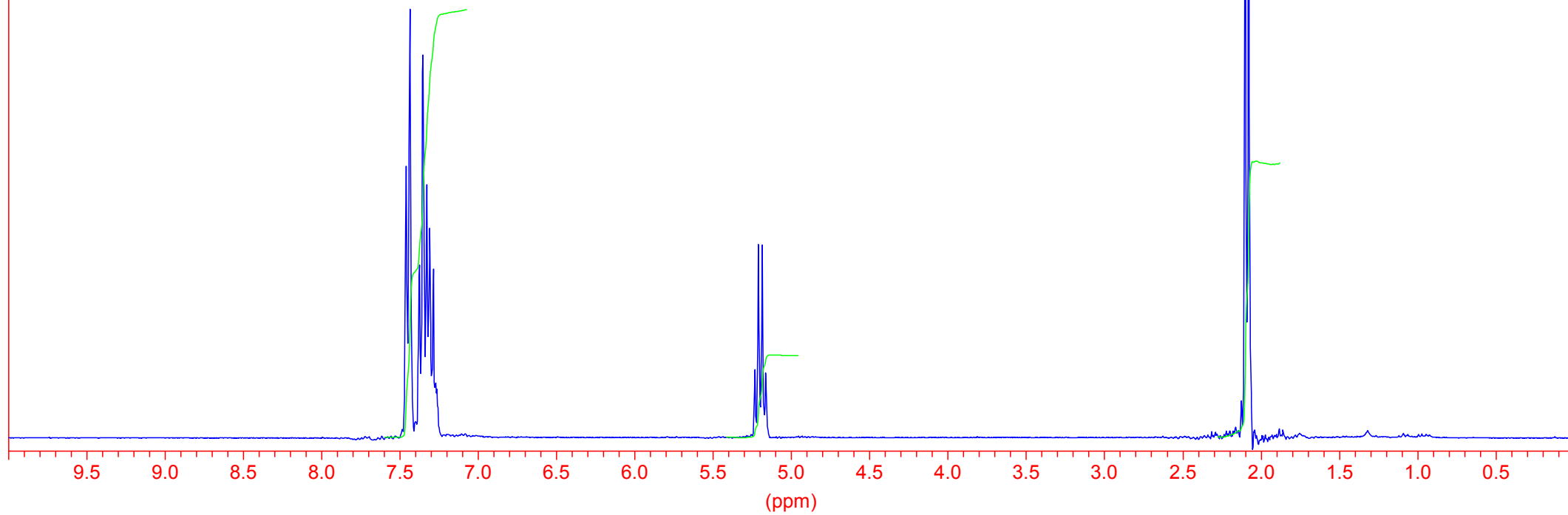


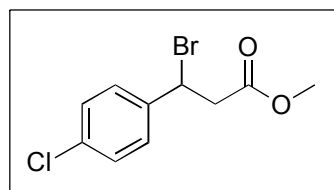
$^1\text{H}$  NMR  
200 MHz  
 $\text{CDCl}_3$



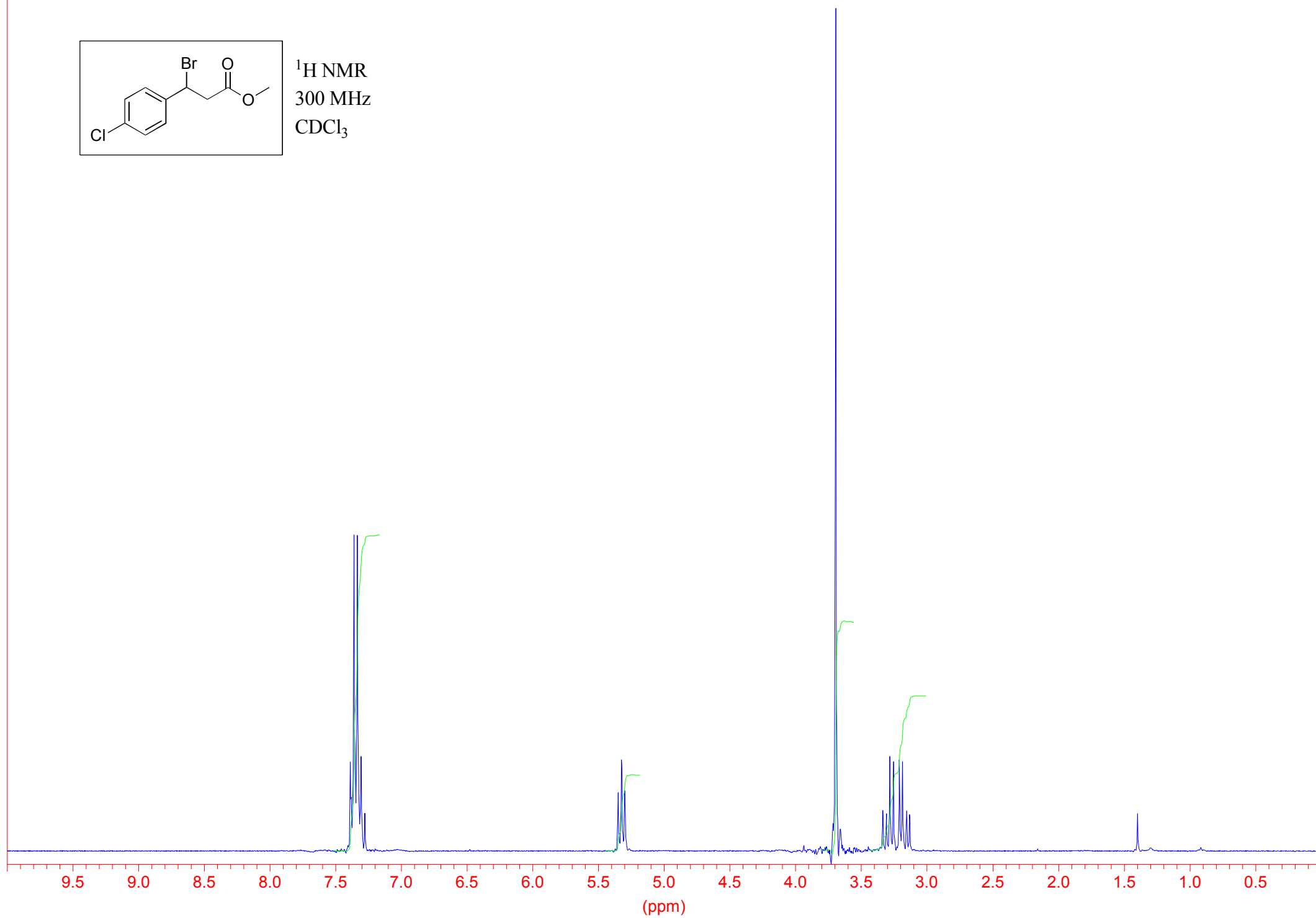


$^1\text{H}$  NMR  
300 MHz  
 $\text{CDCl}_3$

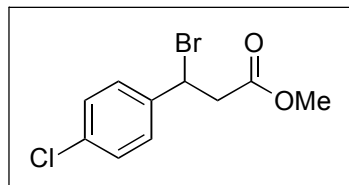




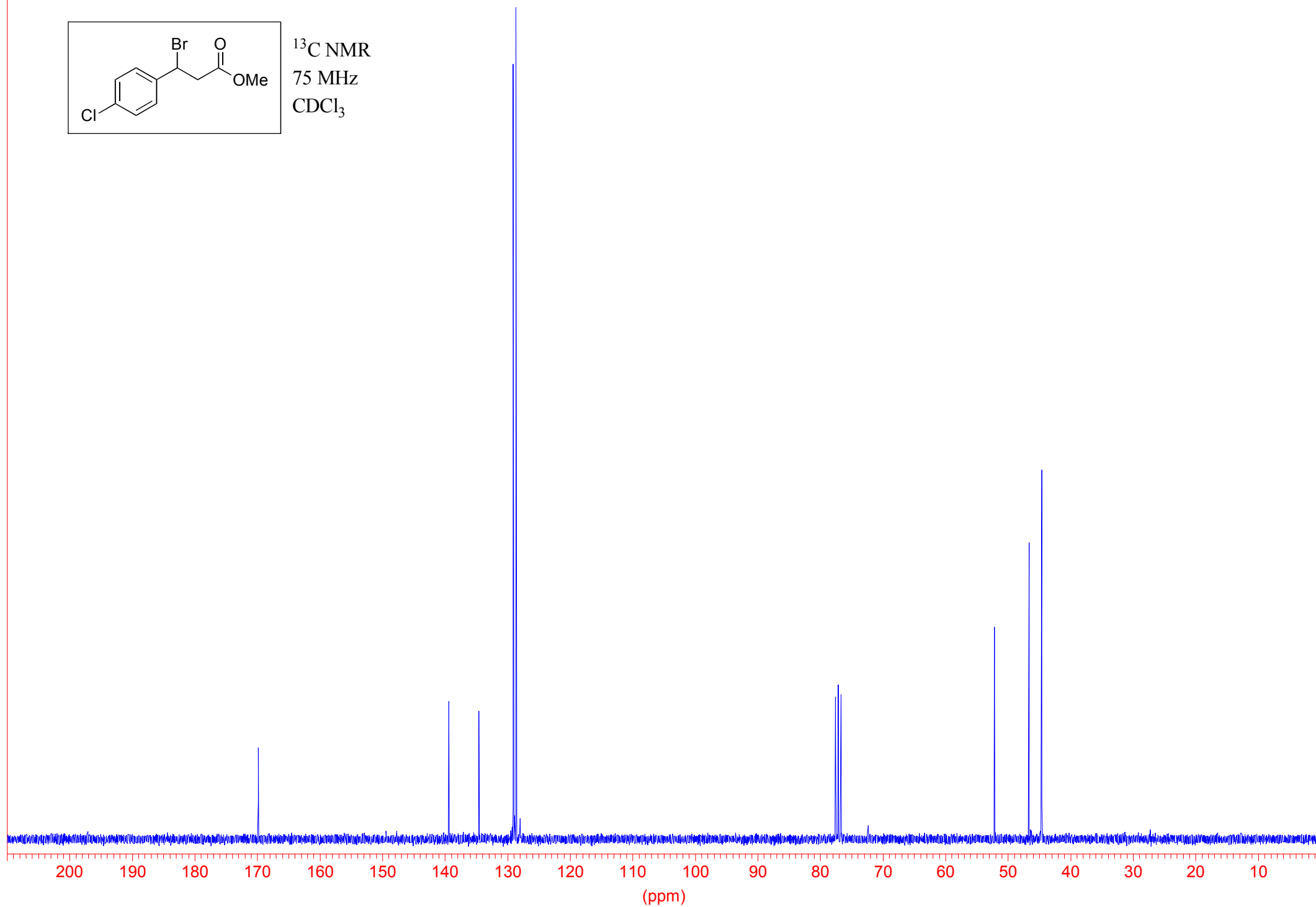
$^1\text{H}$  NMR  
300 MHz  
 $\text{CDCl}_3$

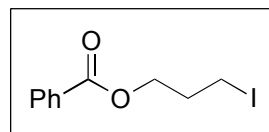




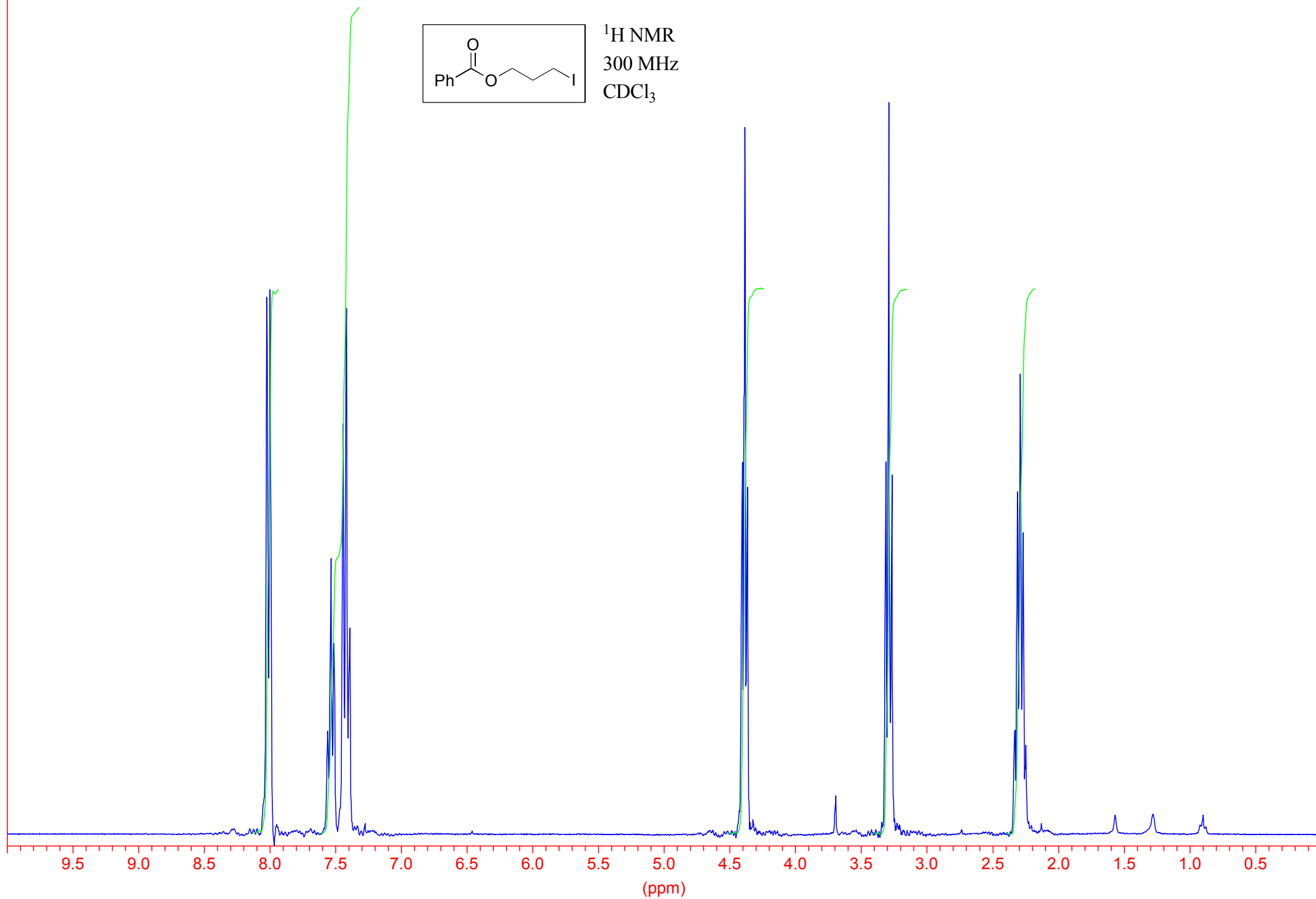


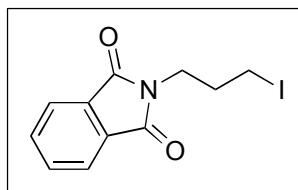
$^{13}\text{C}$  NMR  
75 MHz  
 $\text{CDCl}_3$



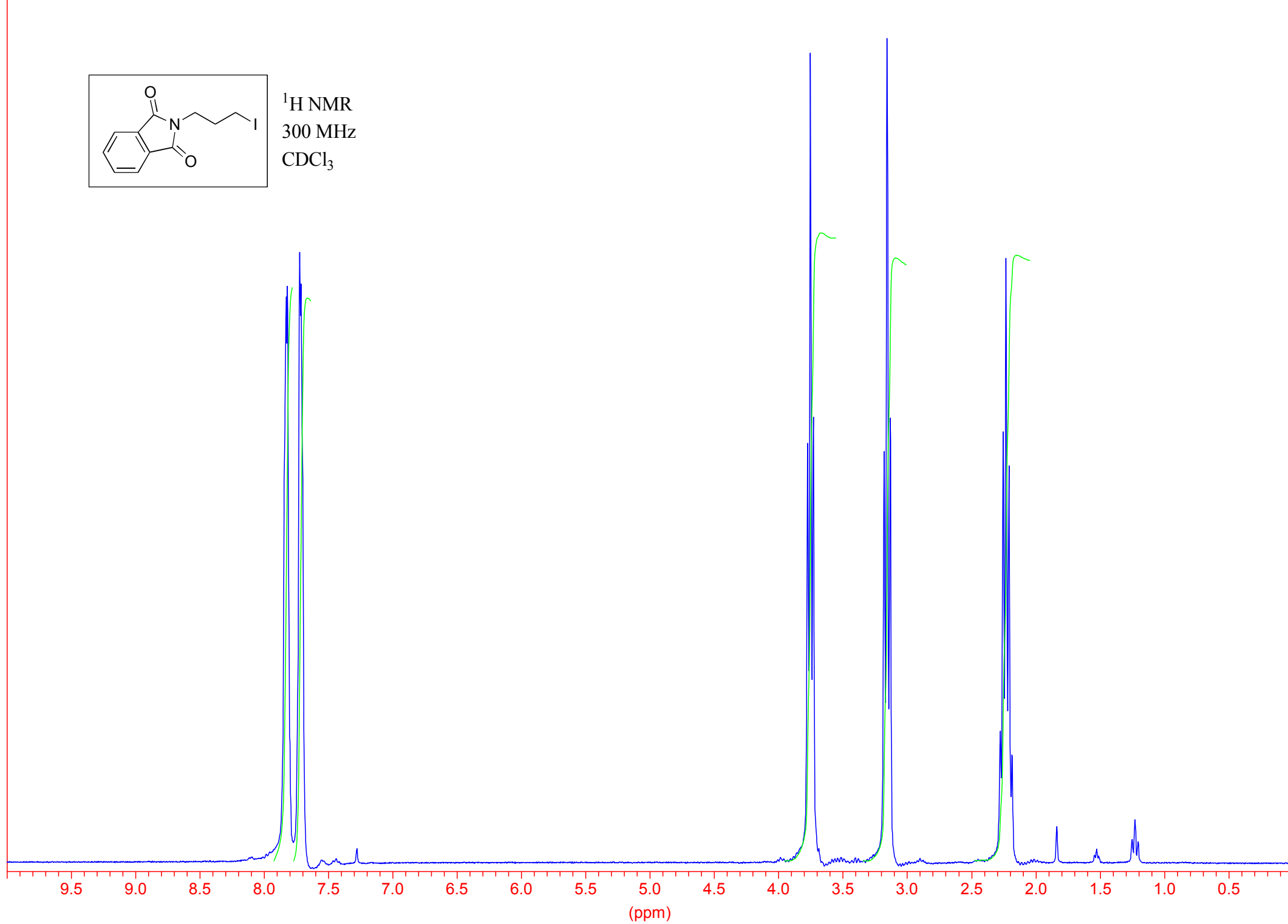


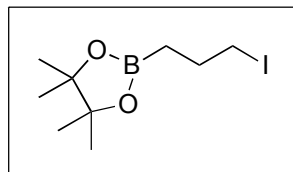
$^1\text{H}$  NMR  
300 MHz  
 $\text{CDCl}_3$



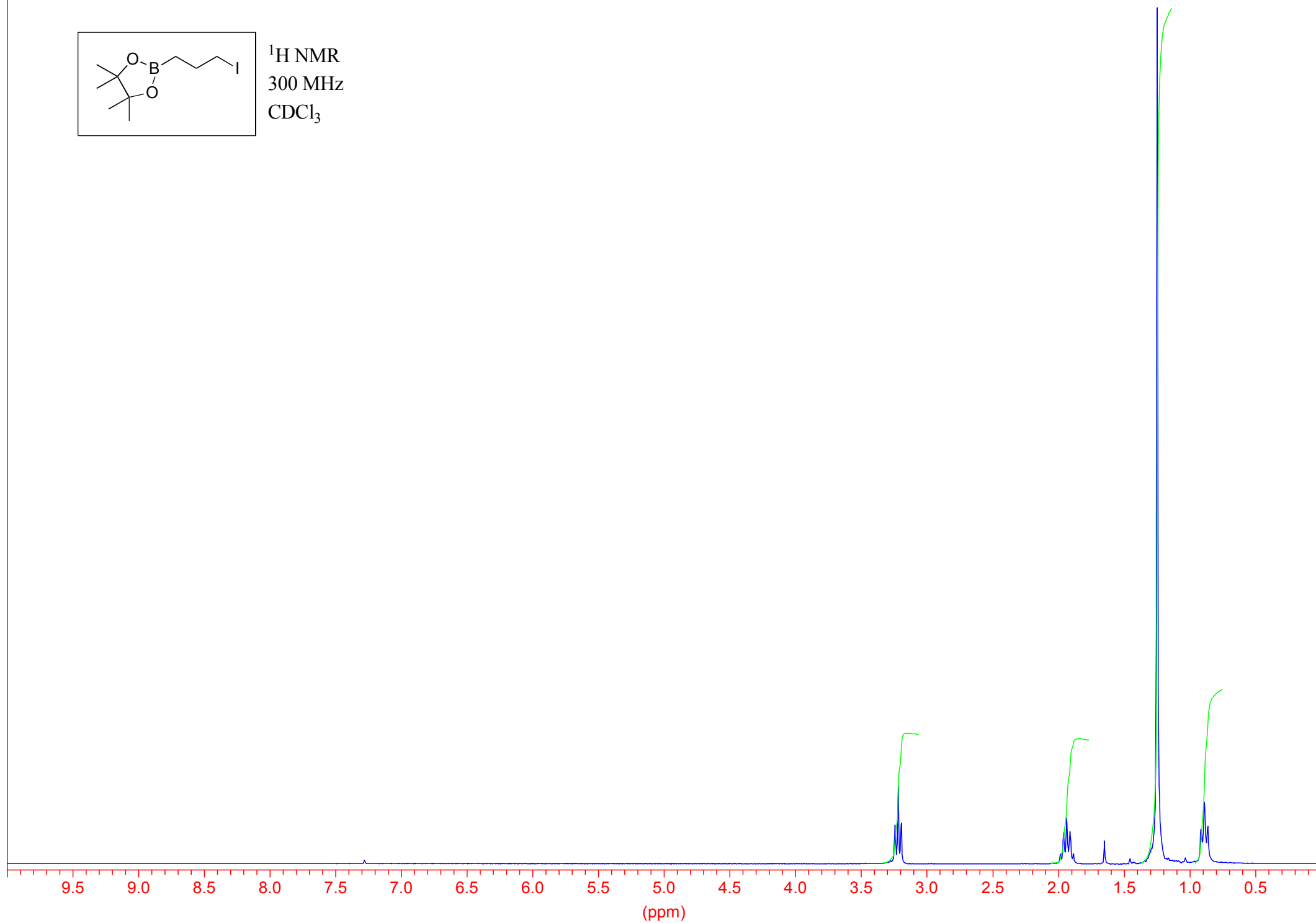


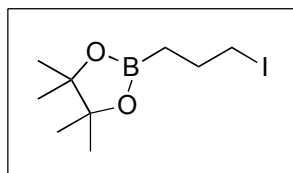
$^1\text{H}$  NMR  
300 MHz  
 $\text{CDCl}_3$



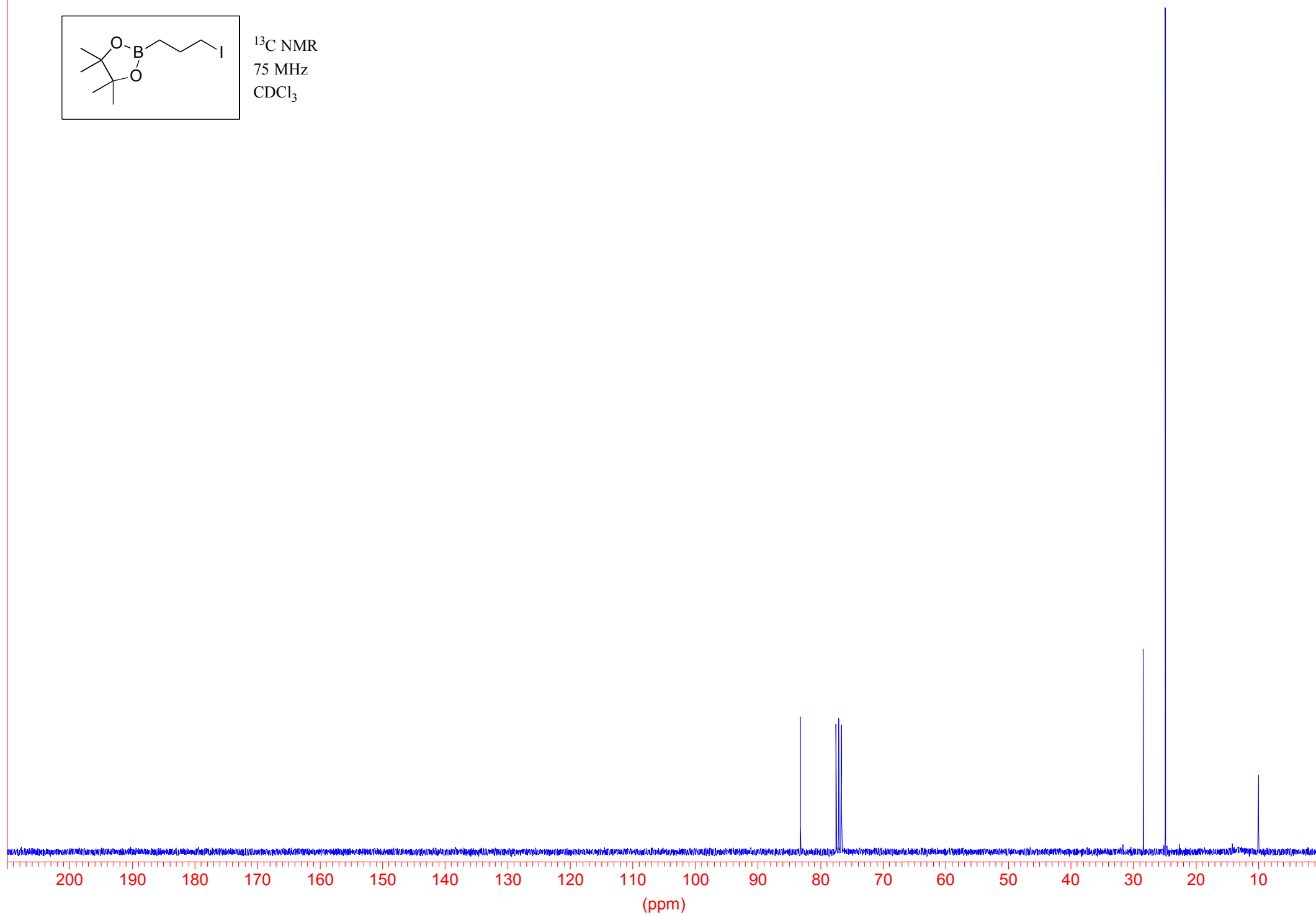


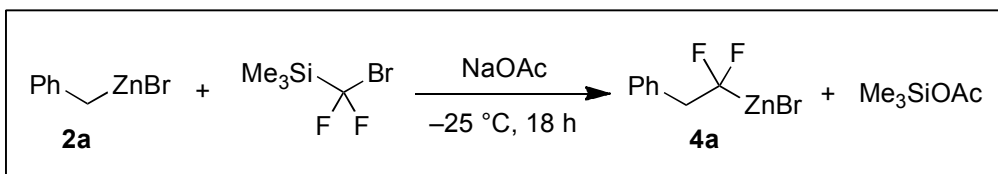
$^1\text{H}$  NMR  
300 MHz  
 $\text{CDCl}_3$



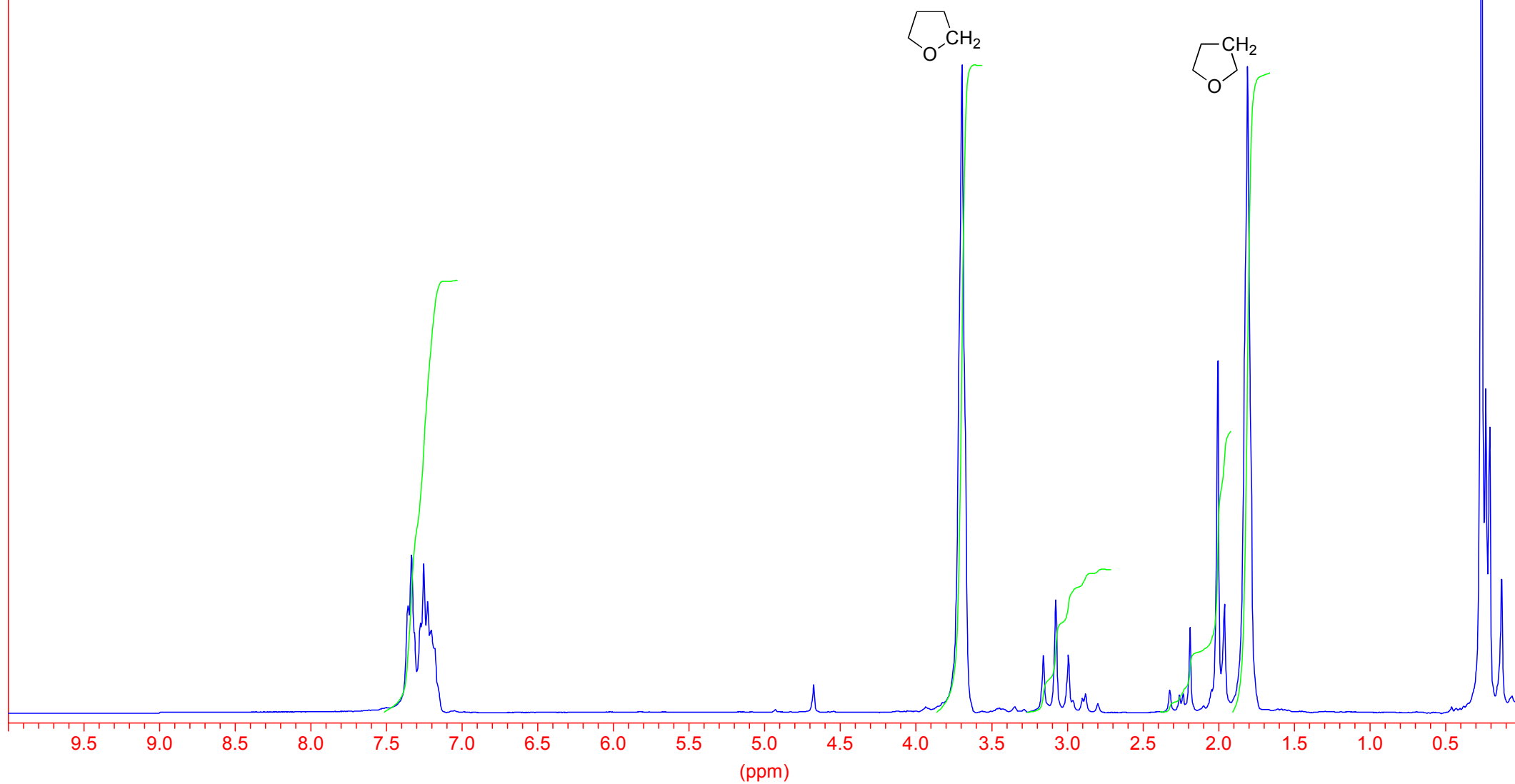


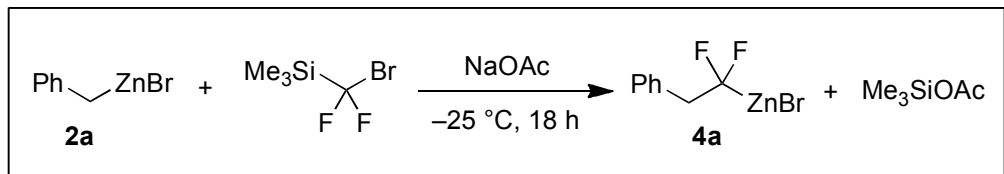
$^{13}\text{C}$  NMR  
75 MHz  
 $\text{CDCl}_3$



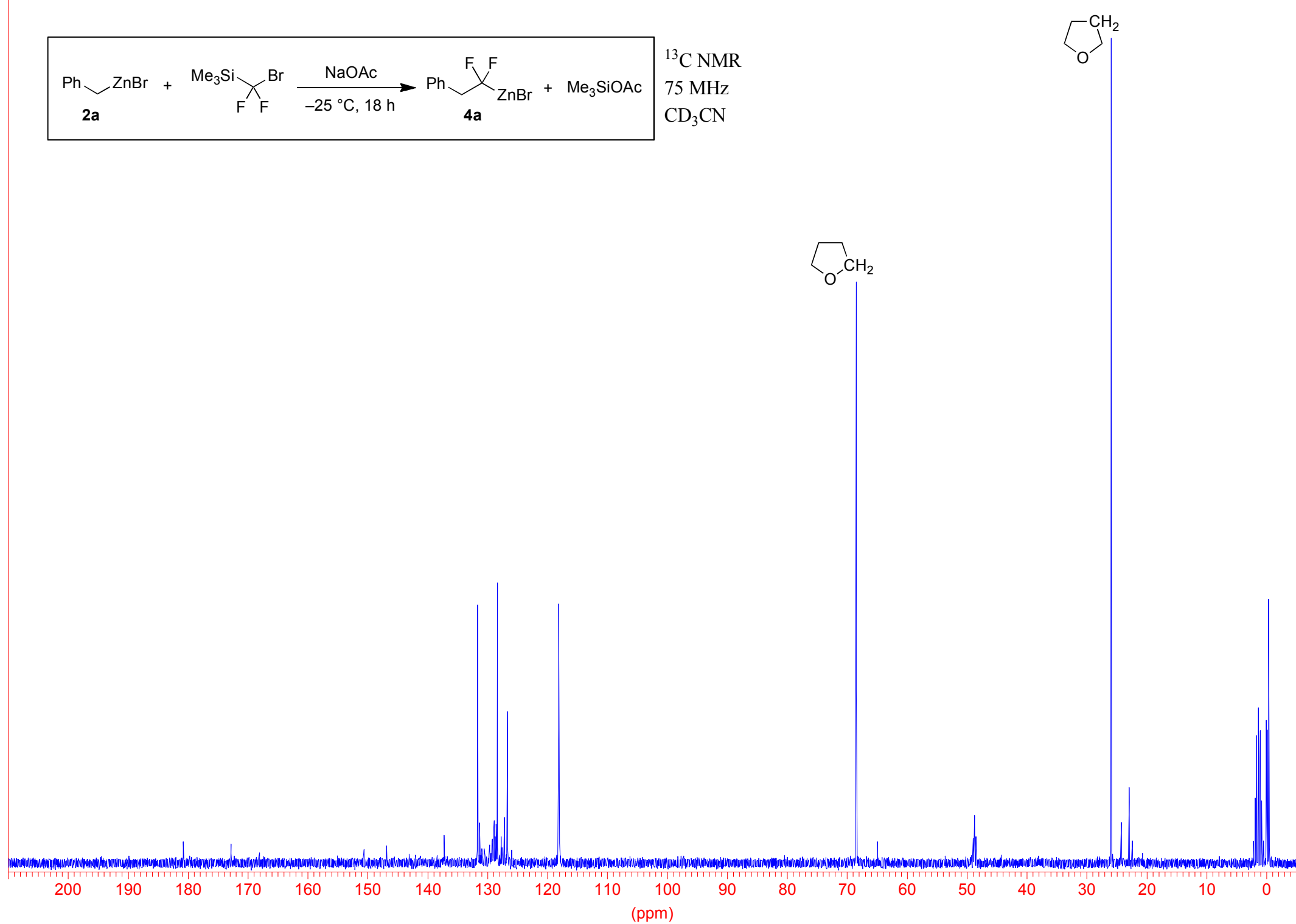


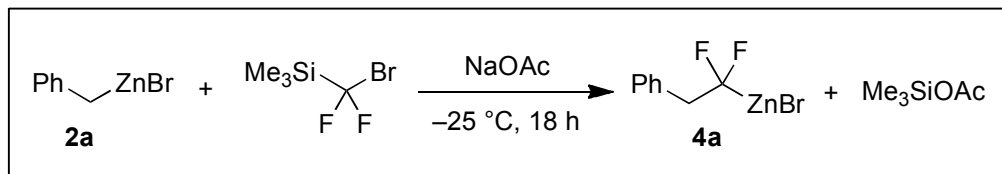
$^1\text{H}$  NMR  
300 MHz  
 $\text{CD}_3\text{CN}$



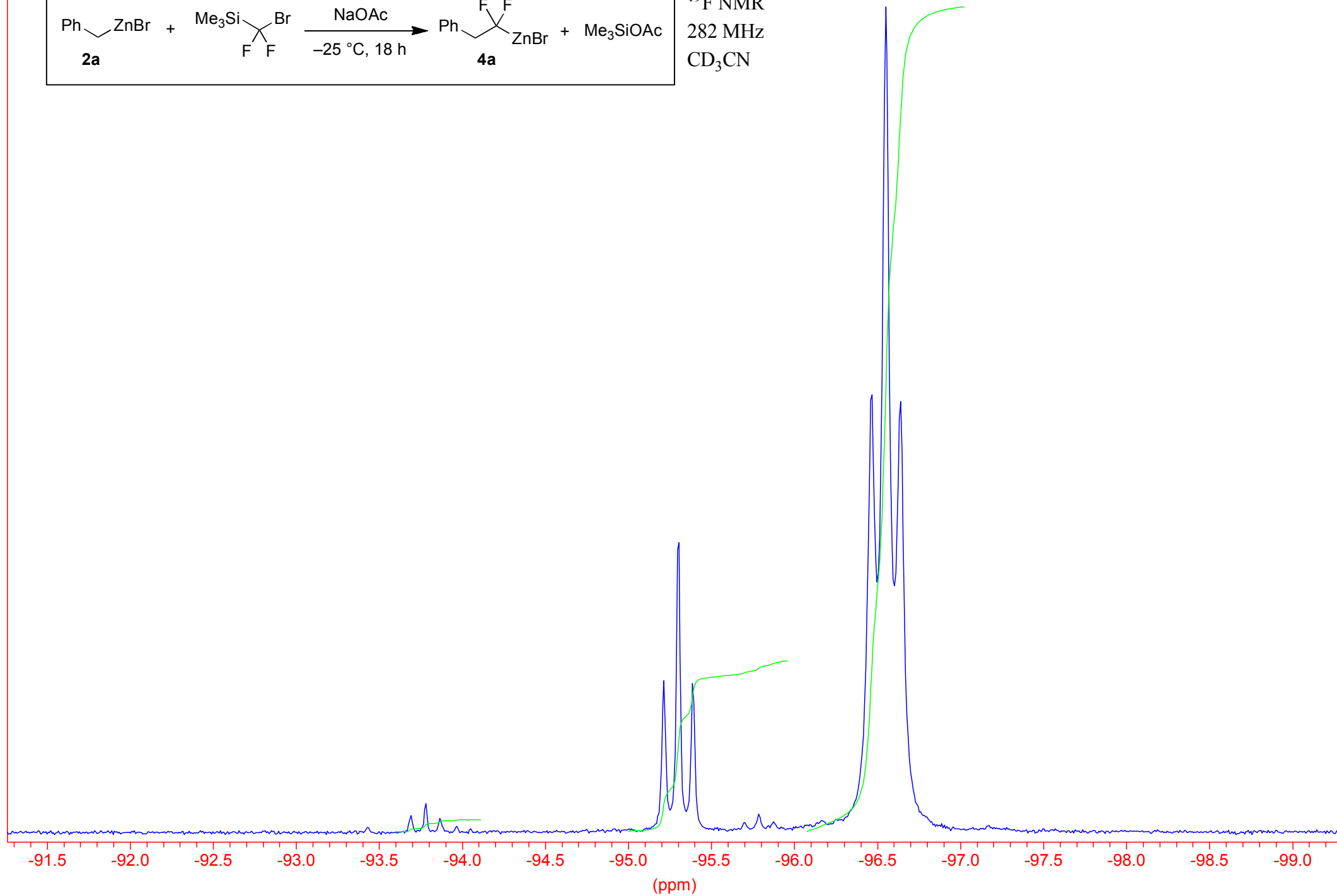


<sup>13</sup>C NMR  
75 MHz  
CD<sub>3</sub>CN

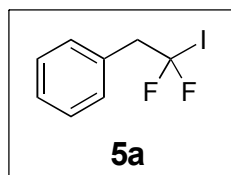




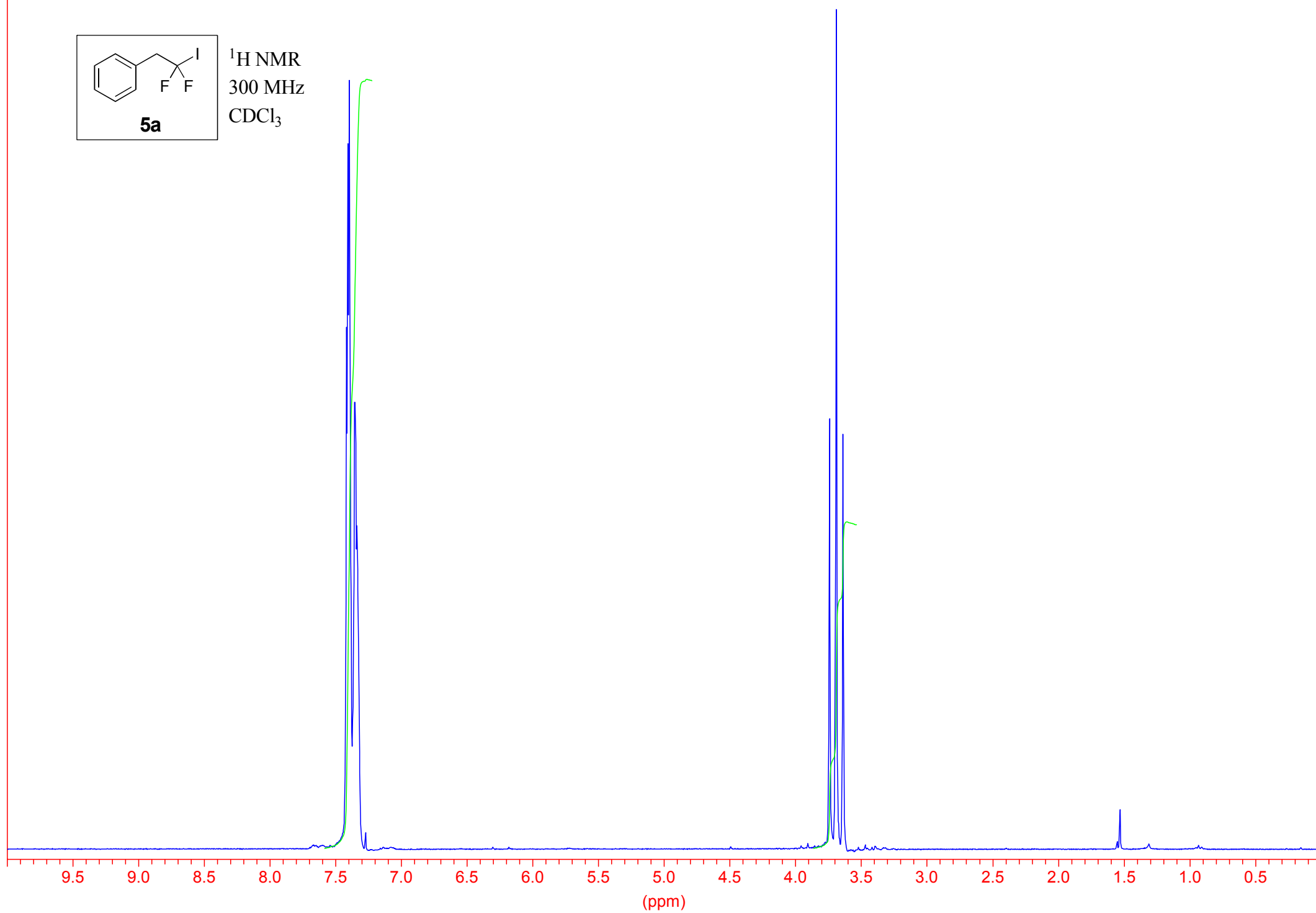
$^{19}\text{F}$  NMR  
282 MHz  
 $\text{CD}_3\text{CN}$

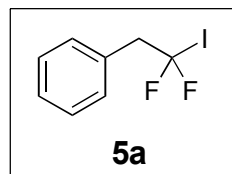




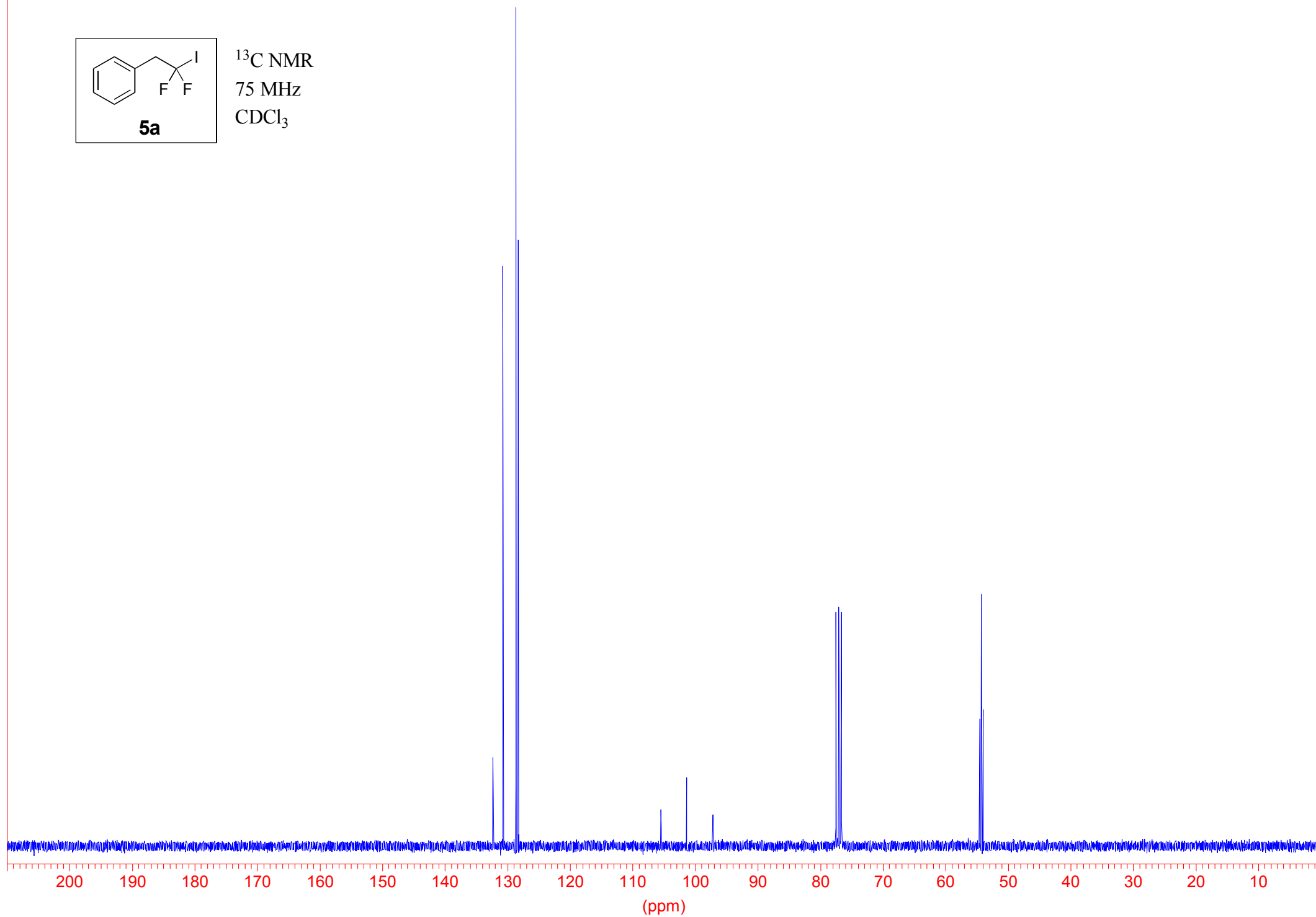


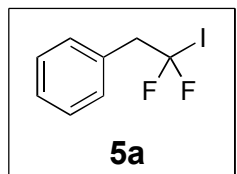
$^1\text{H}$  NMR  
300 MHz  
 $\text{CDCl}_3$



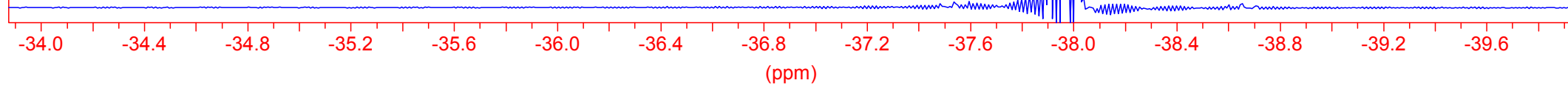


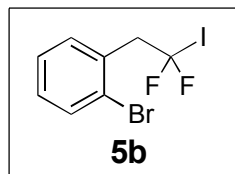
$^{13}\text{C}$  NMR  
75 MHz  
 $\text{CDCl}_3$



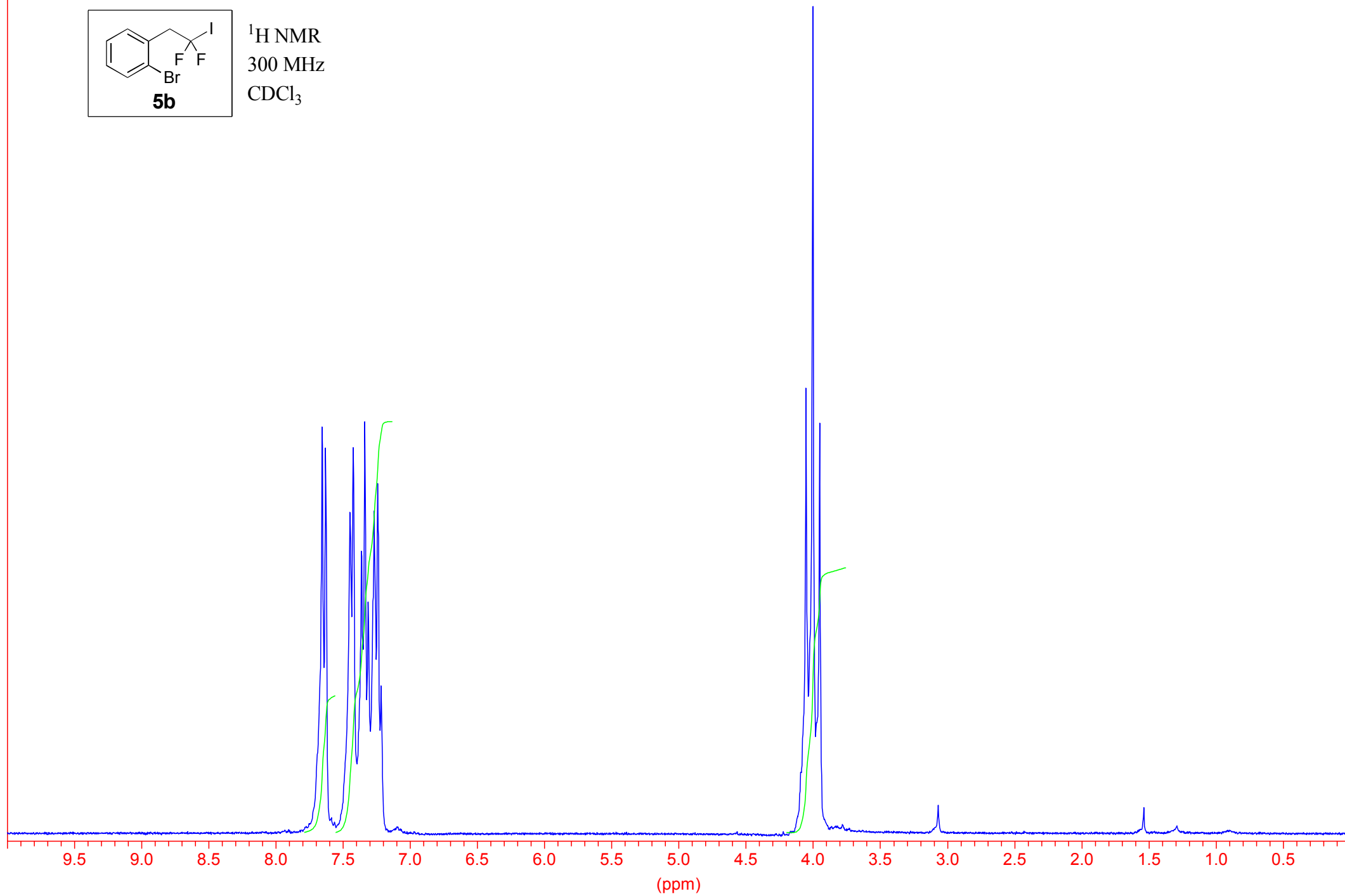


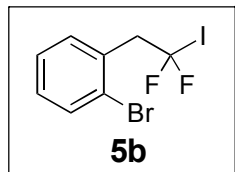
$^{19}\text{F}$  NMR  
282 MHz  
 $\text{CDCl}_3$



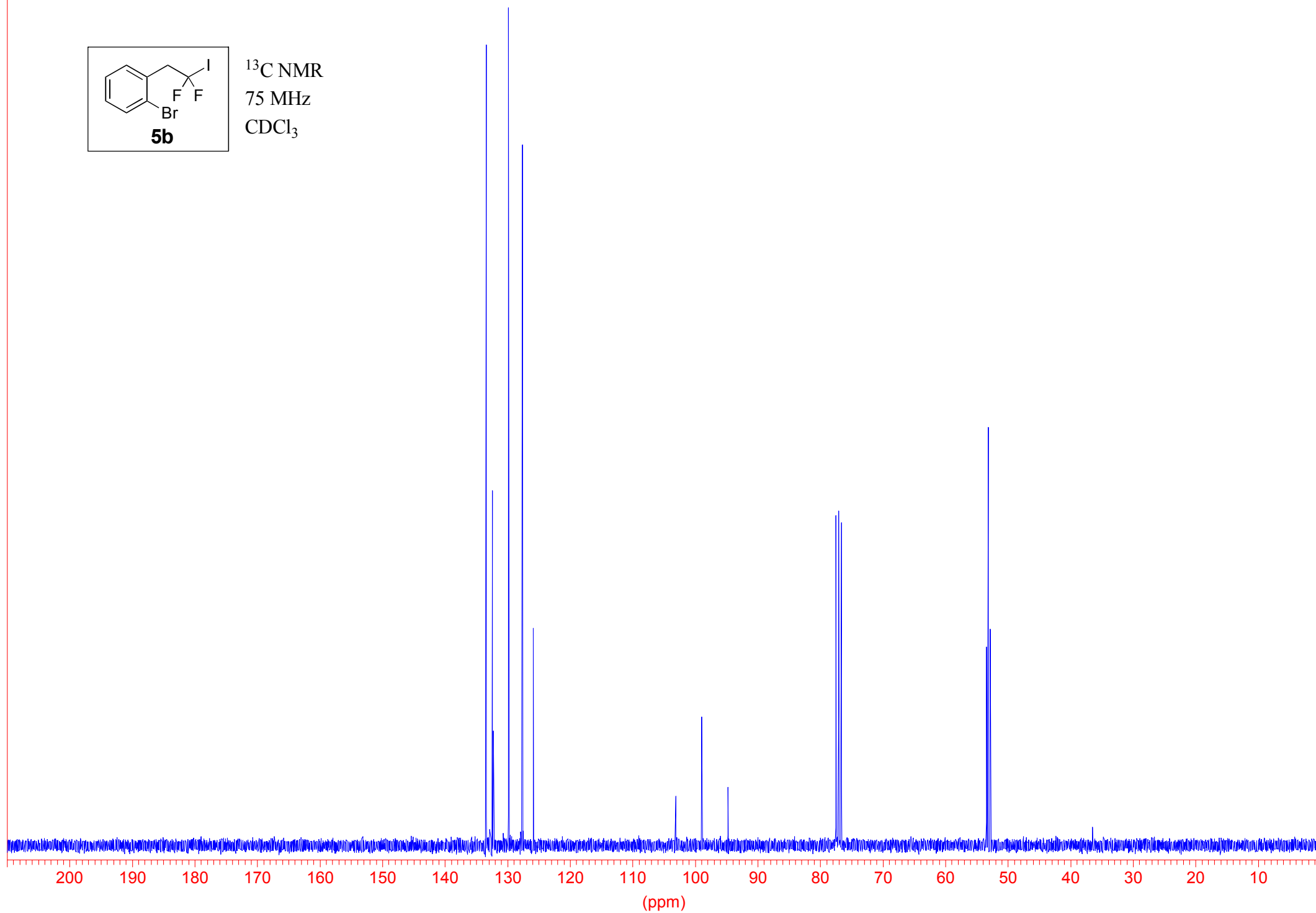


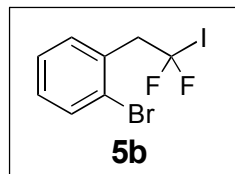
$^1\text{H}$  NMR  
300 MHz  
 $\text{CDCl}_3$



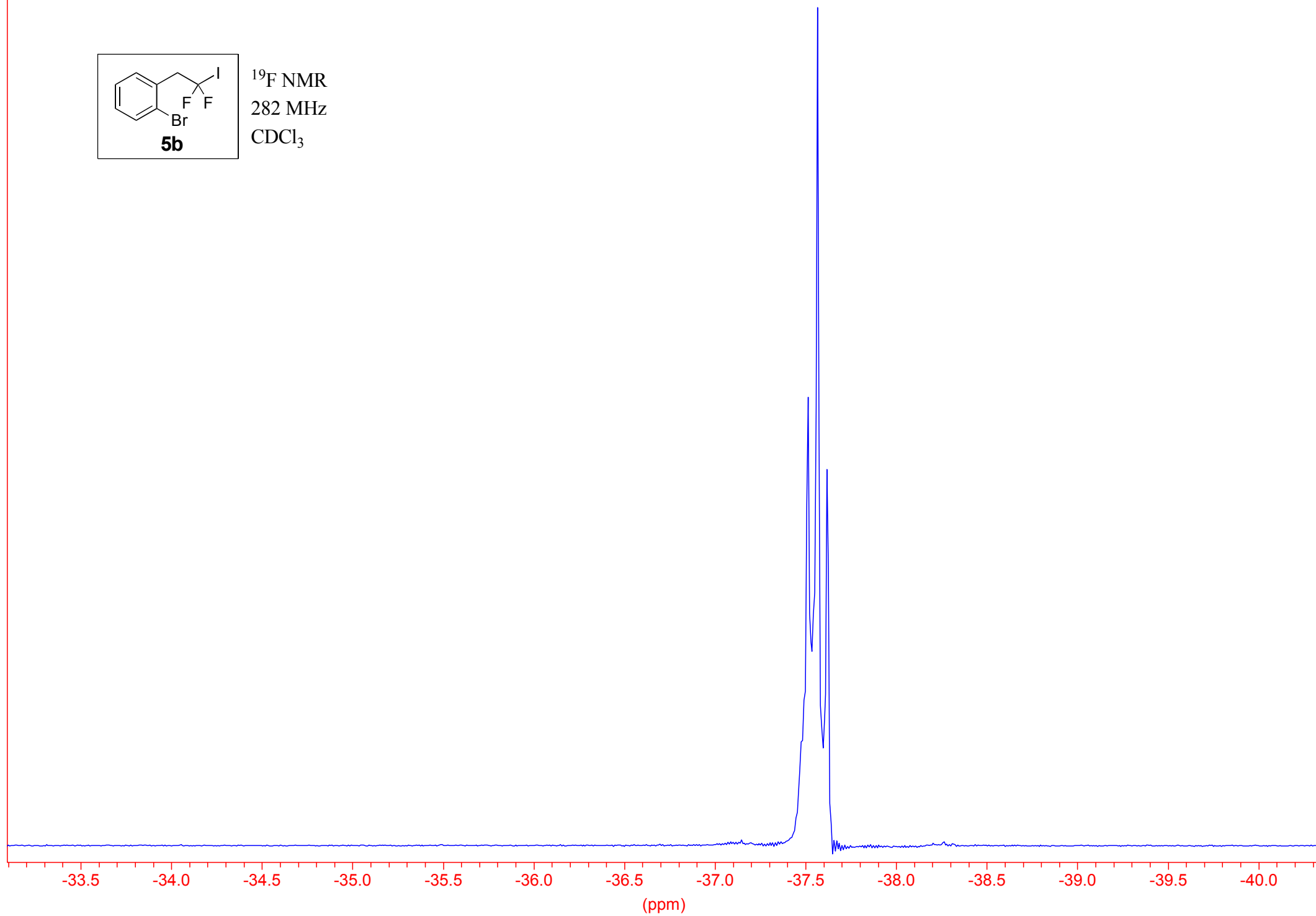


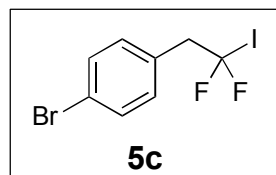
$^{13}\text{C}$  NMR  
75 MHz  
 $\text{CDCl}_3$



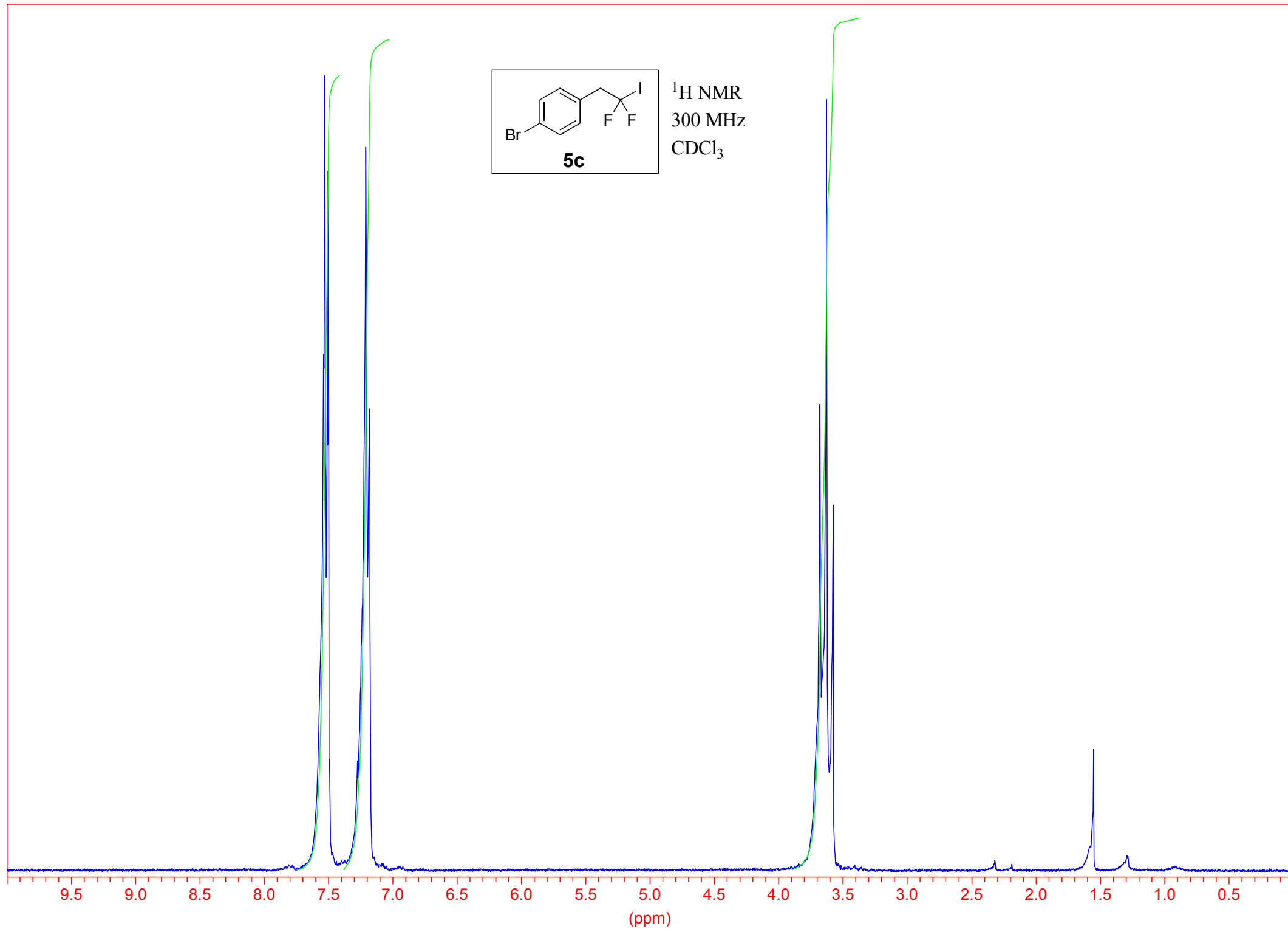


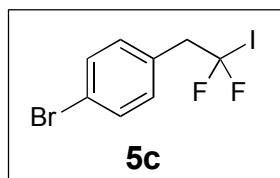
$^{19}\text{F}$  NMR  
282 MHz  
 $\text{CDCl}_3$



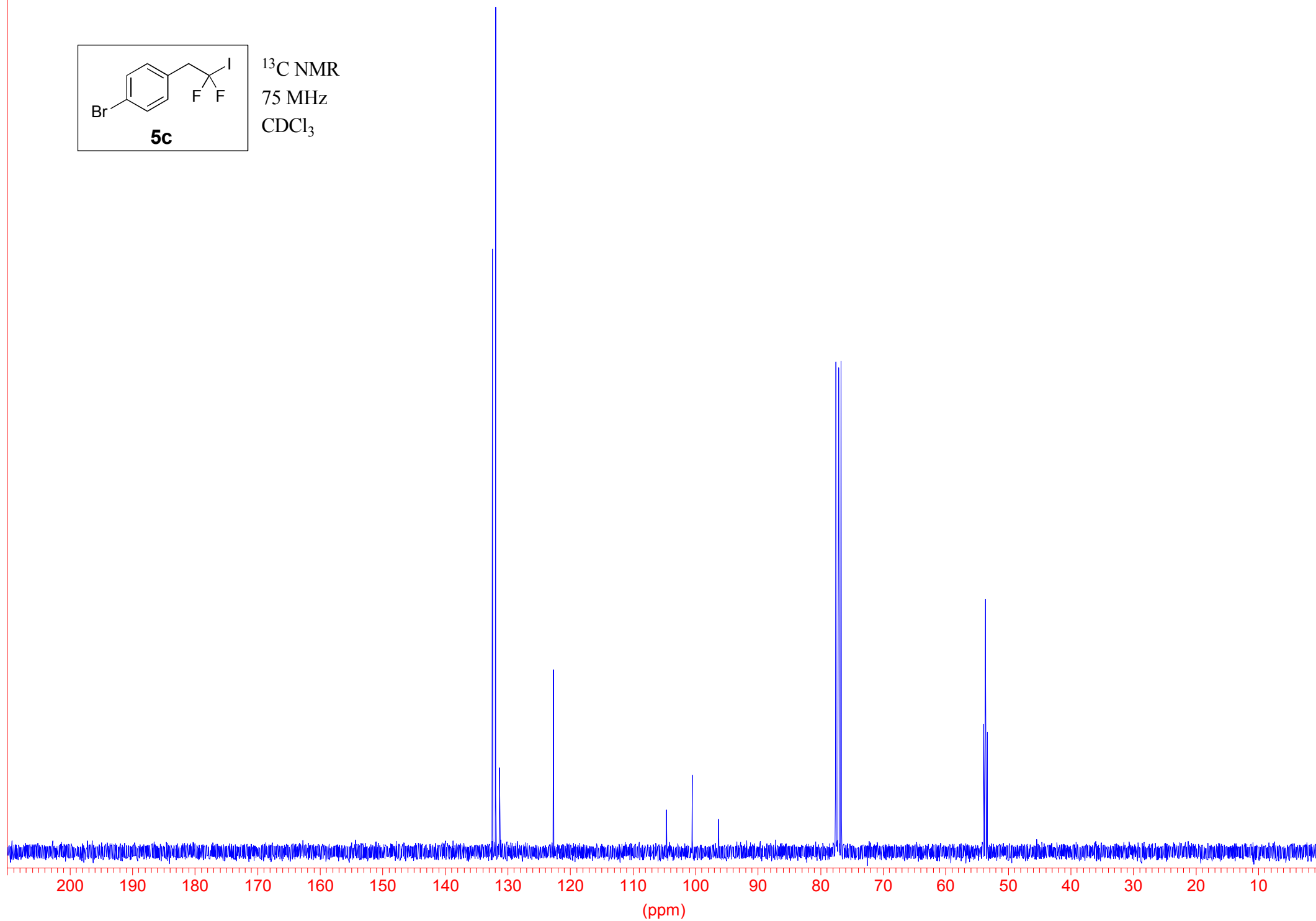


$^1\text{H}$  NMR  
300 MHz  
 $\text{CDCl}_3$

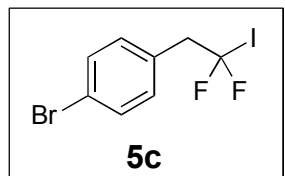




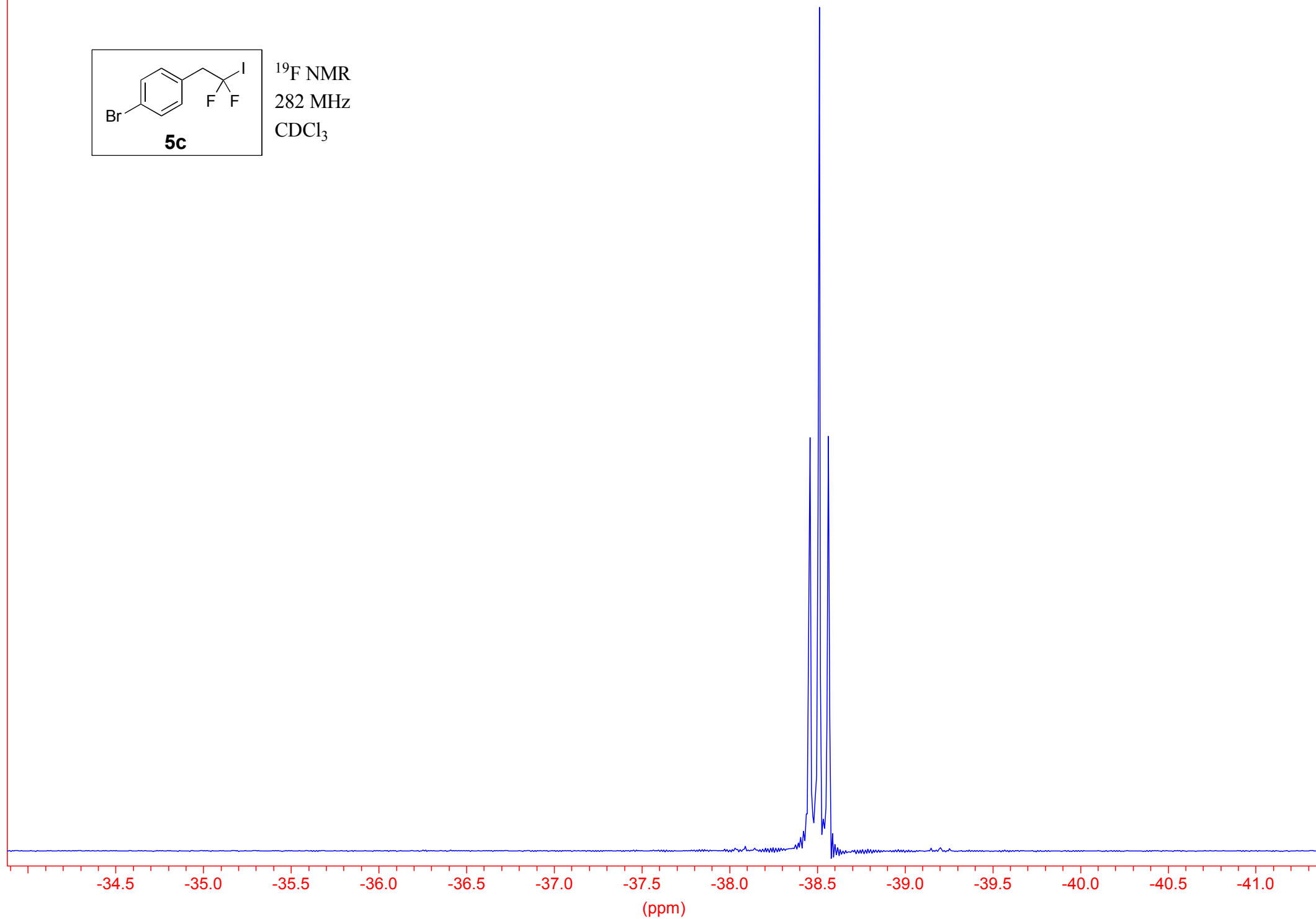
$^{13}\text{C}$  NMR  
75 MHz  
 $\text{CDCl}_3$

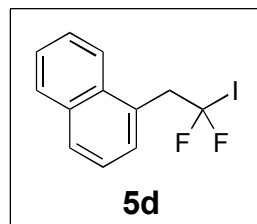




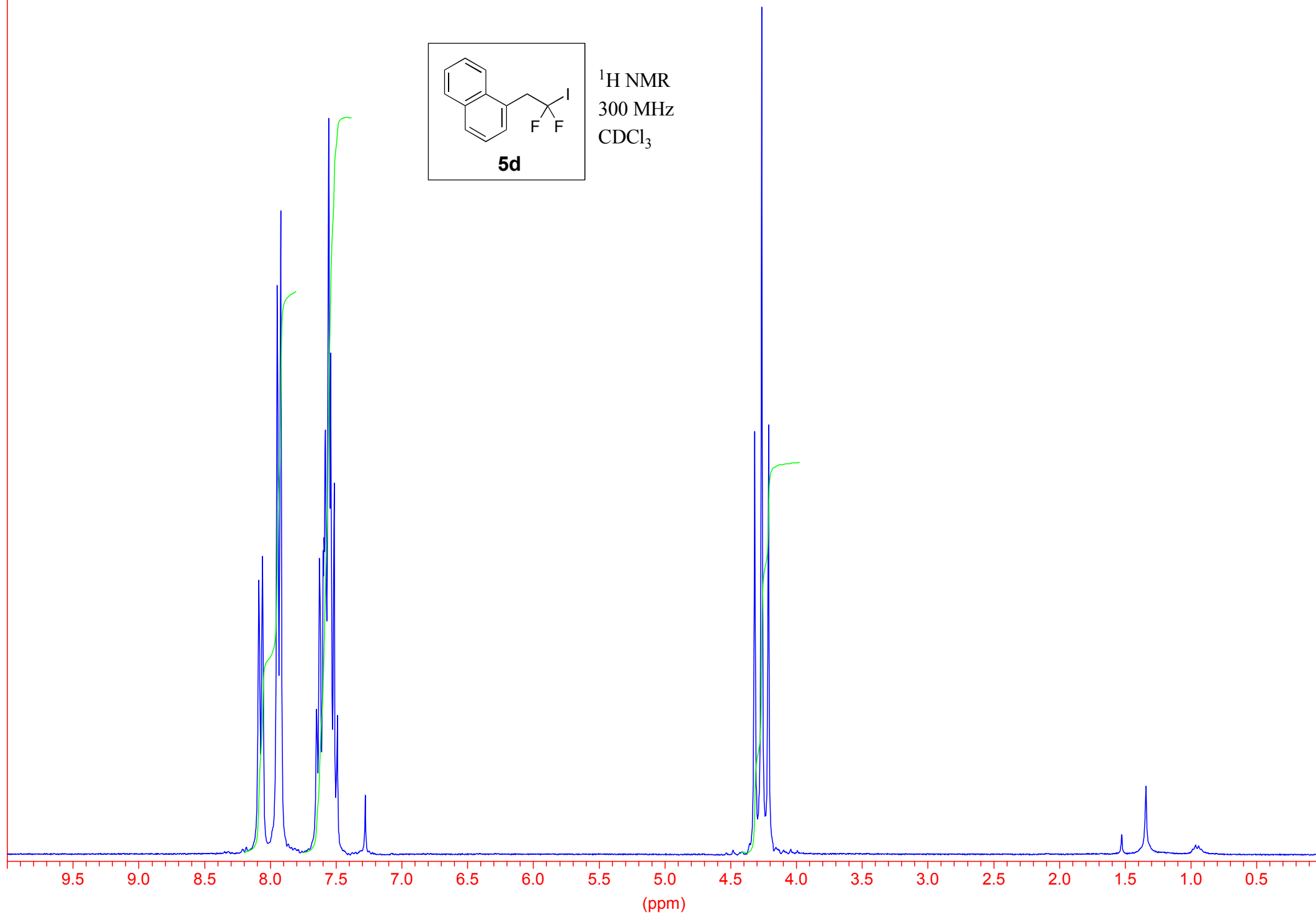


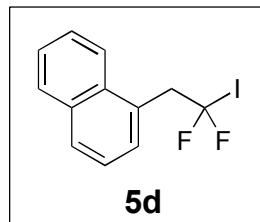
$^{19}\text{F}$  NMR  
282 MHz  
 $\text{CDCl}_3$



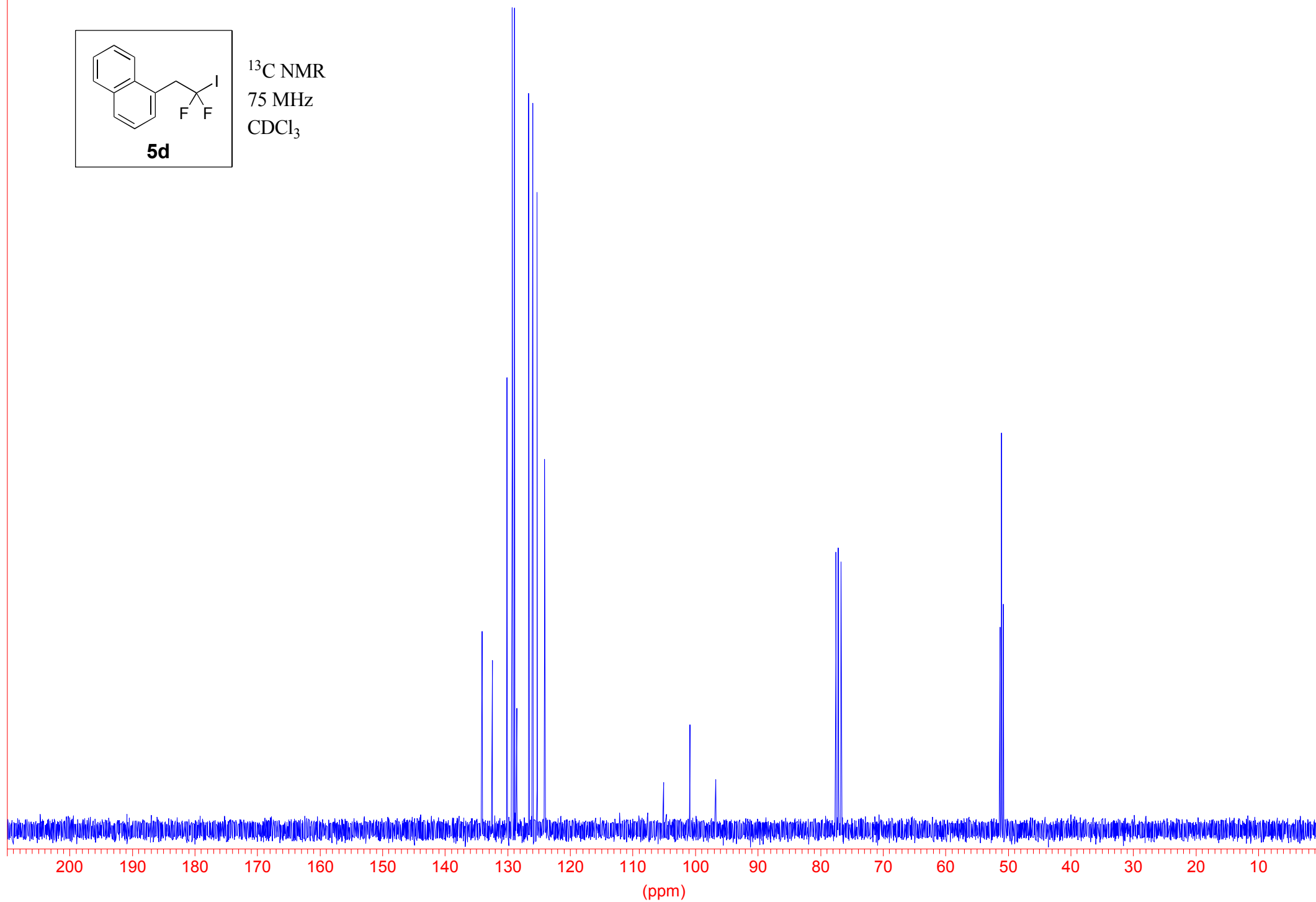


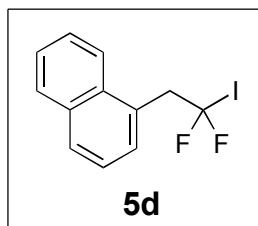
$^1\text{H}$  NMR  
300 MHz  
 $\text{CDCl}_3$



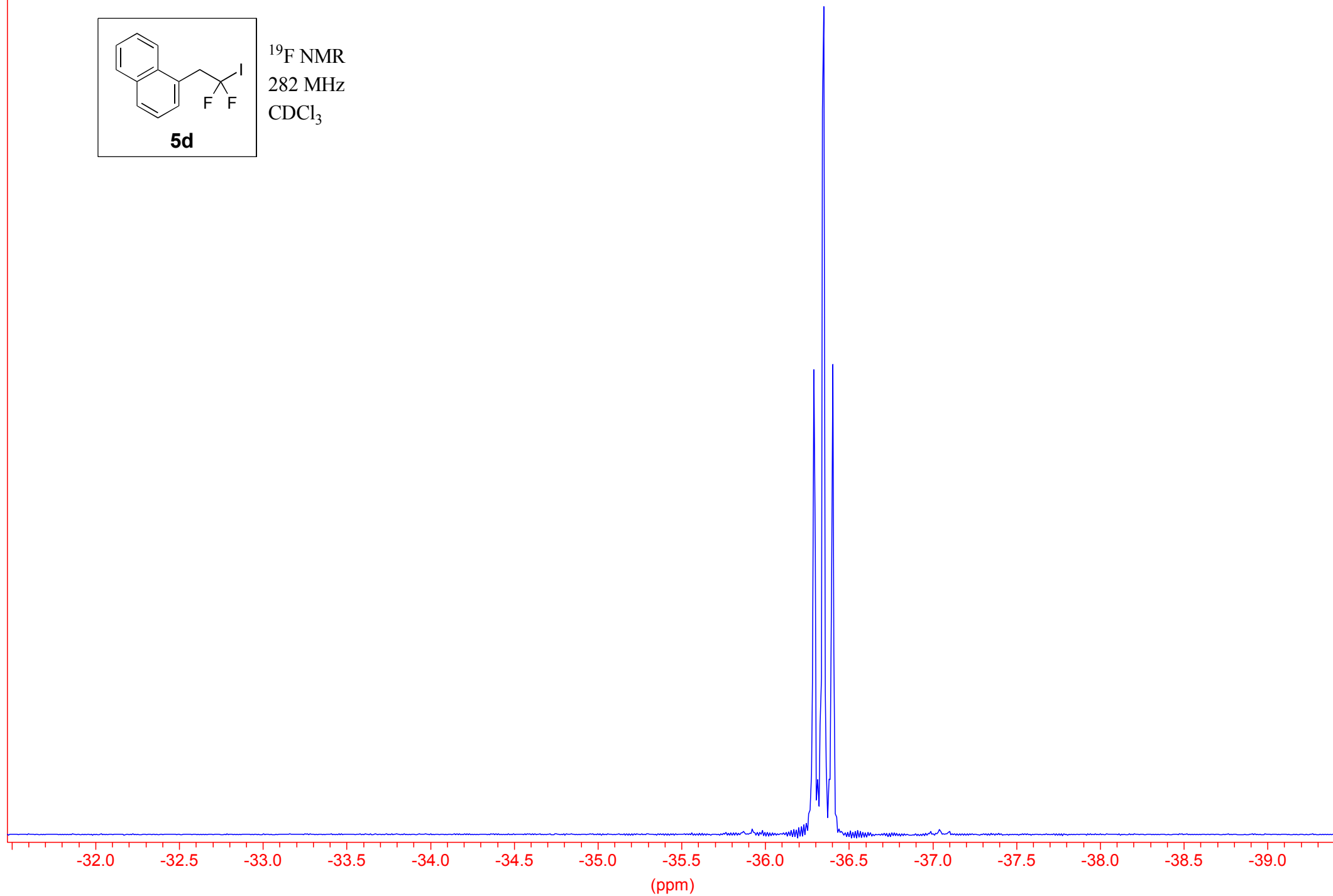


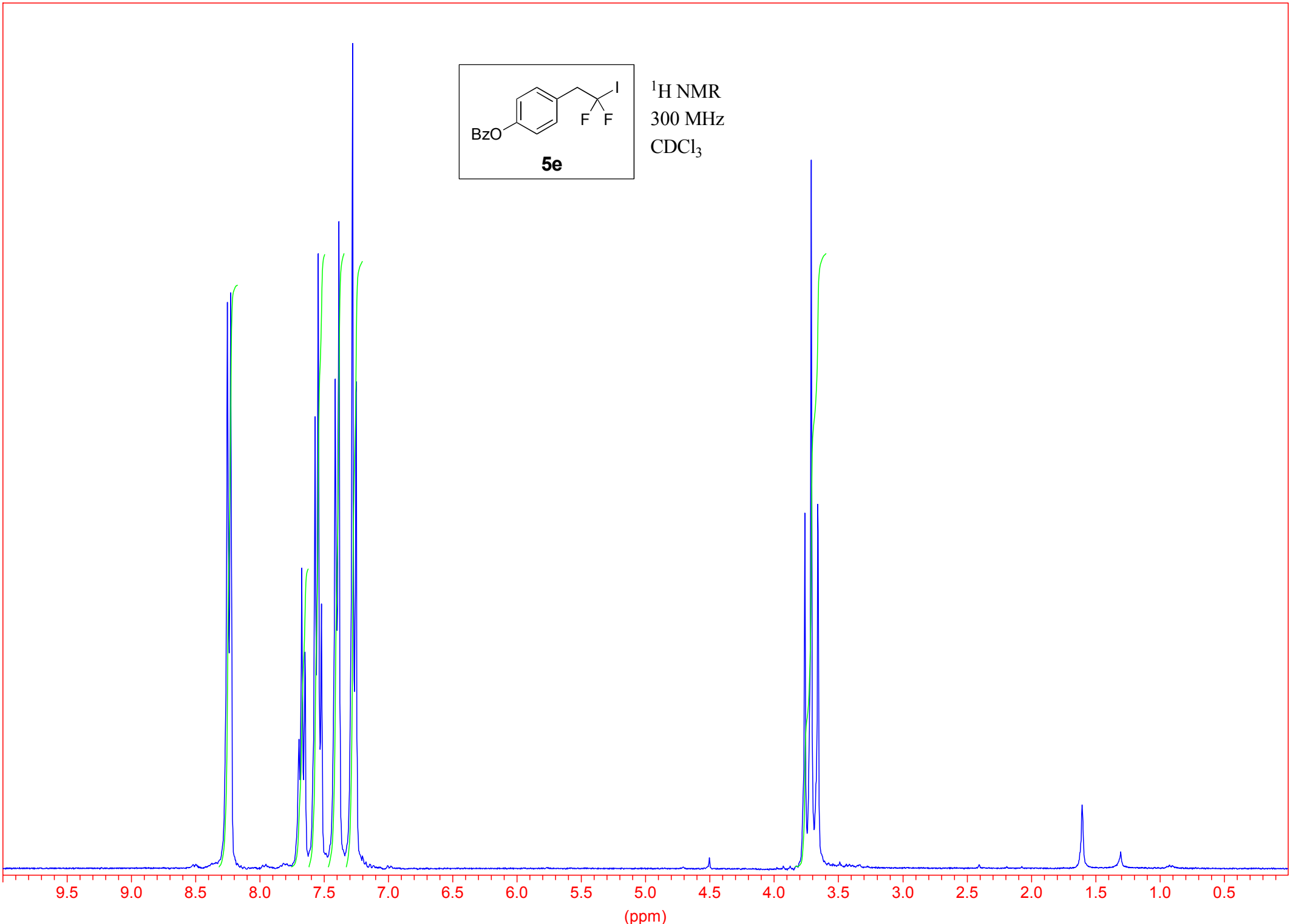
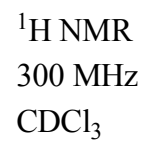
$^{13}\text{C}$  NMR  
75 MHz  
 $\text{CDCl}_3$

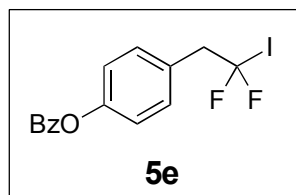




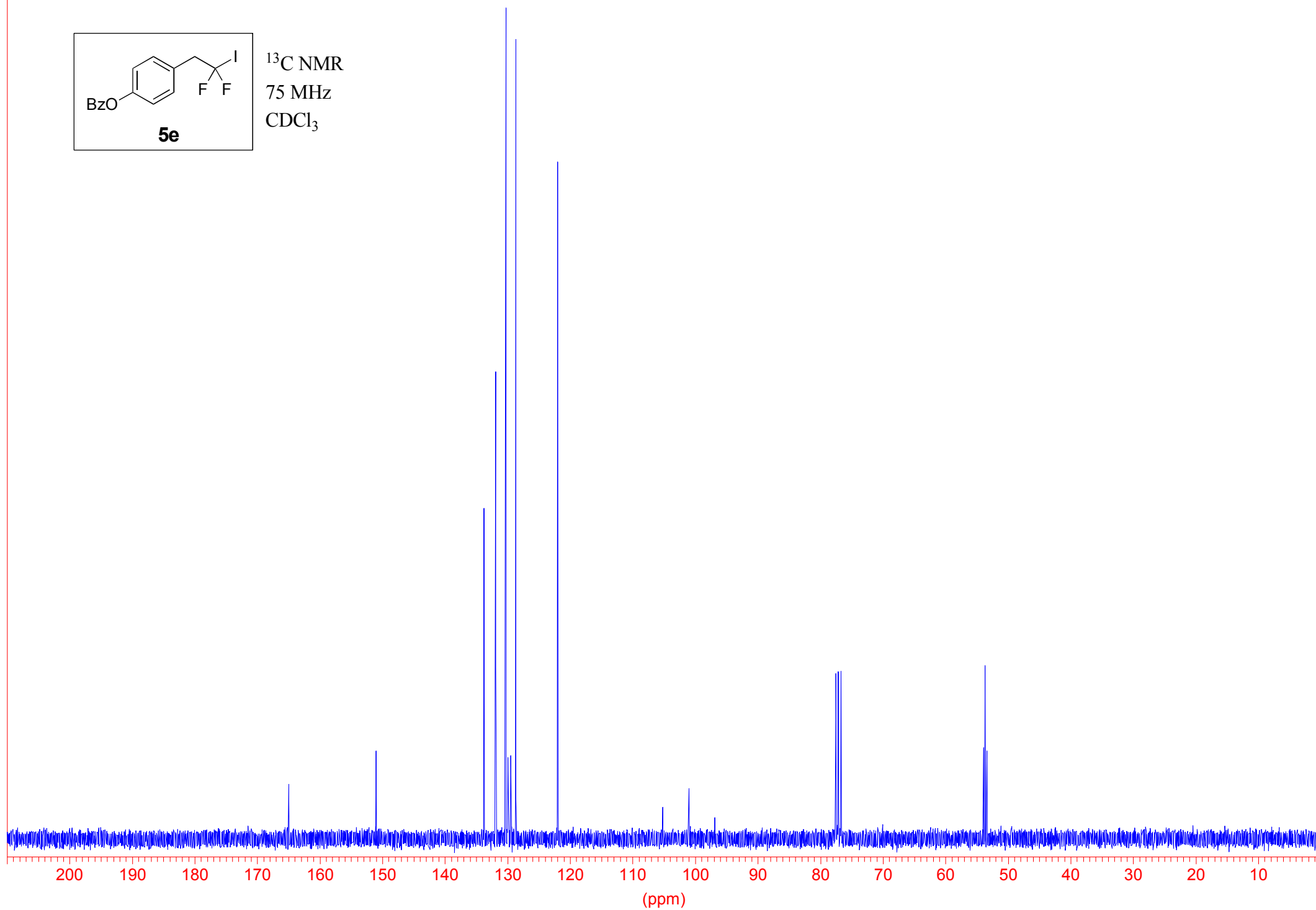
$^{19}\text{F}$  NMR  
282 MHz  
 $\text{CDCl}_3$

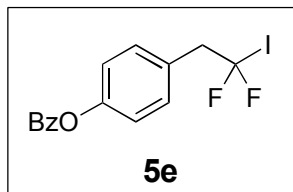




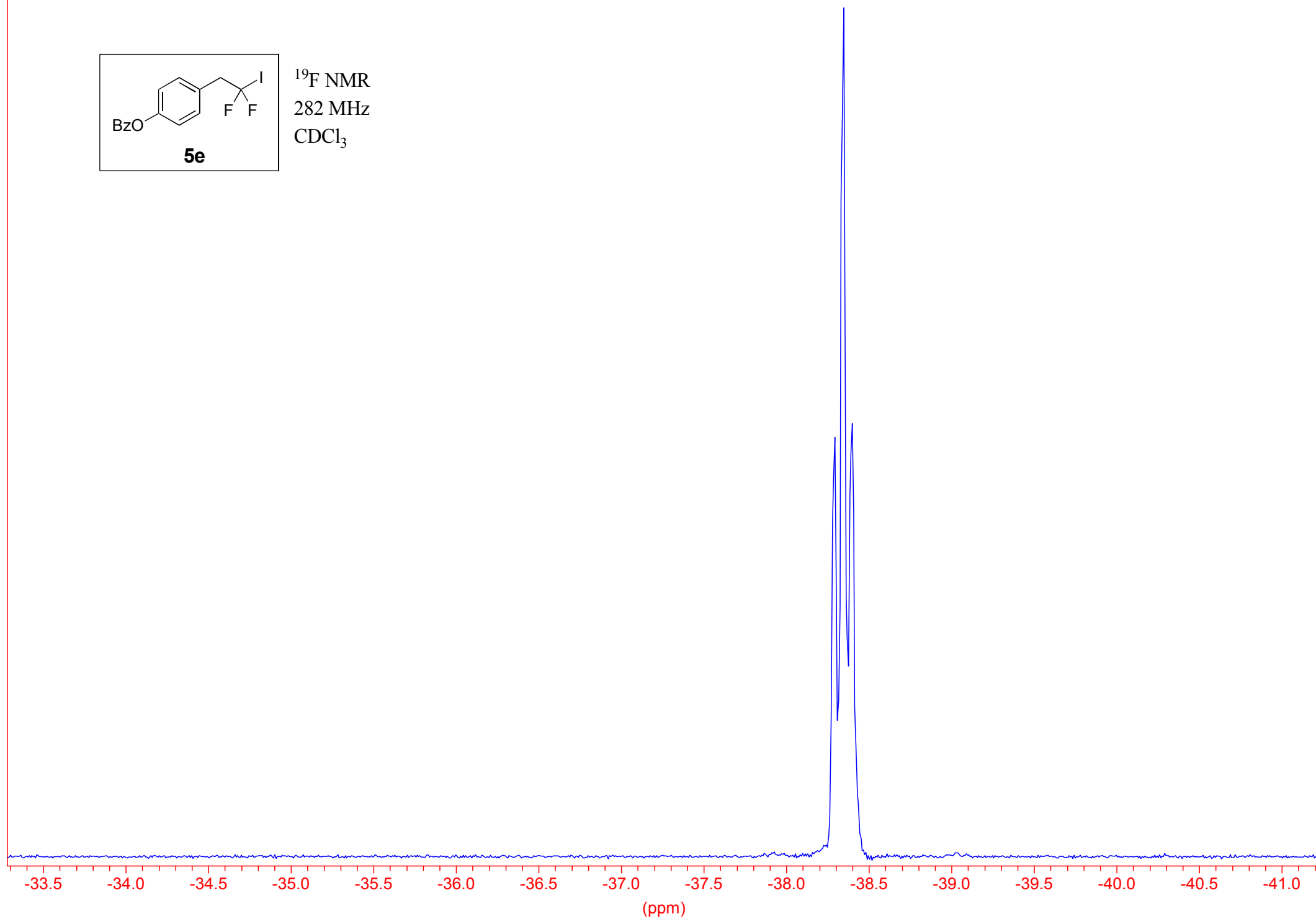


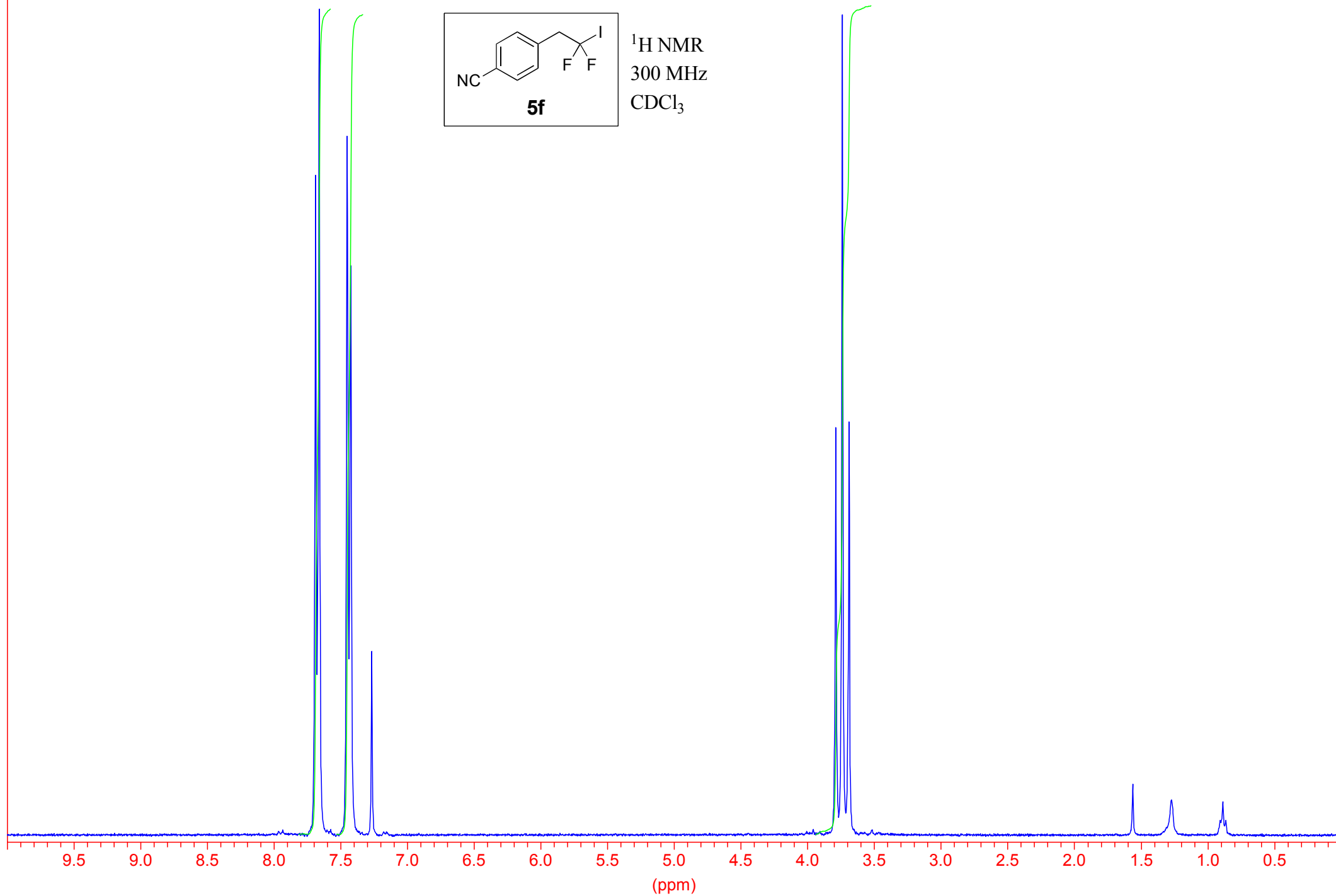
$^{13}\text{C}$  NMR  
75 MHz  
 $\text{CDCl}_3$



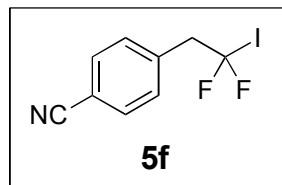


$^{19}\text{F}$  NMR  
282 MHz  
 $\text{CDCl}_3$

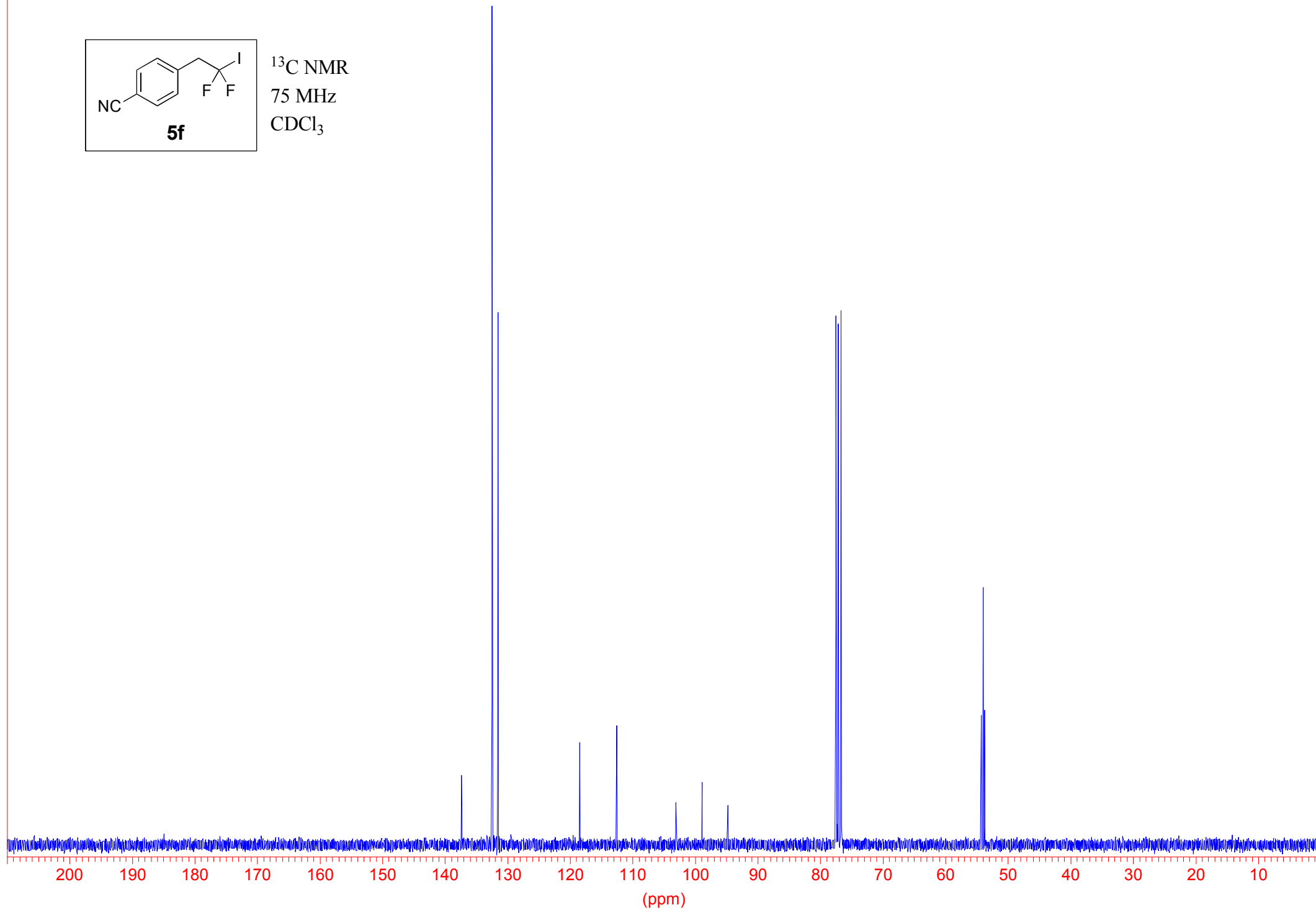


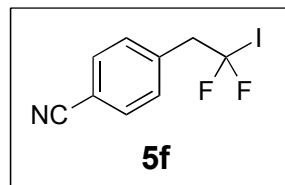




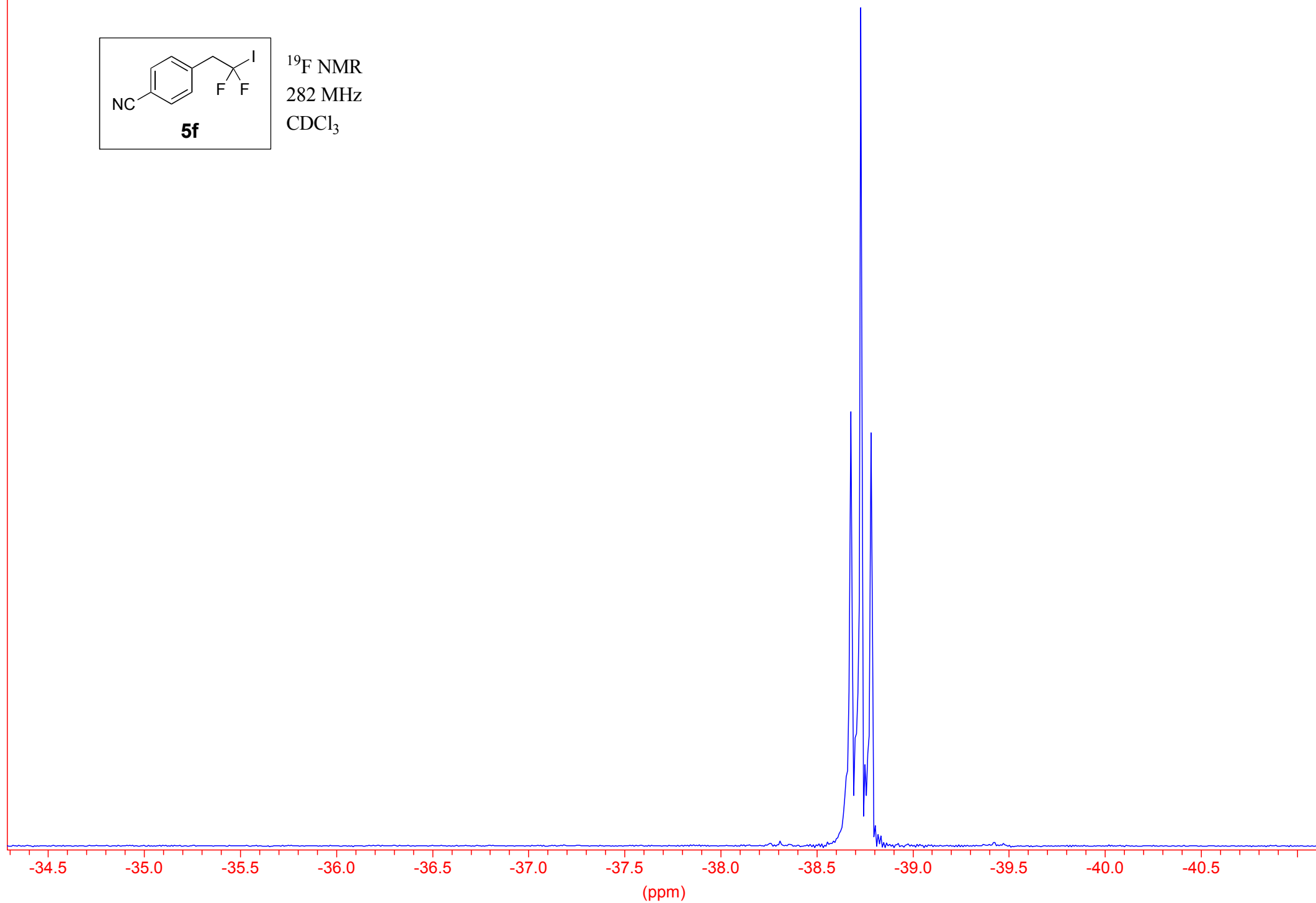


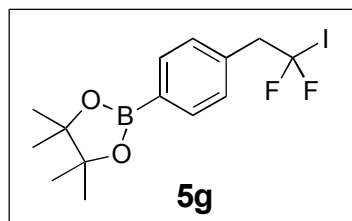
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75 MHz  
 $\text{CDCl}_3$



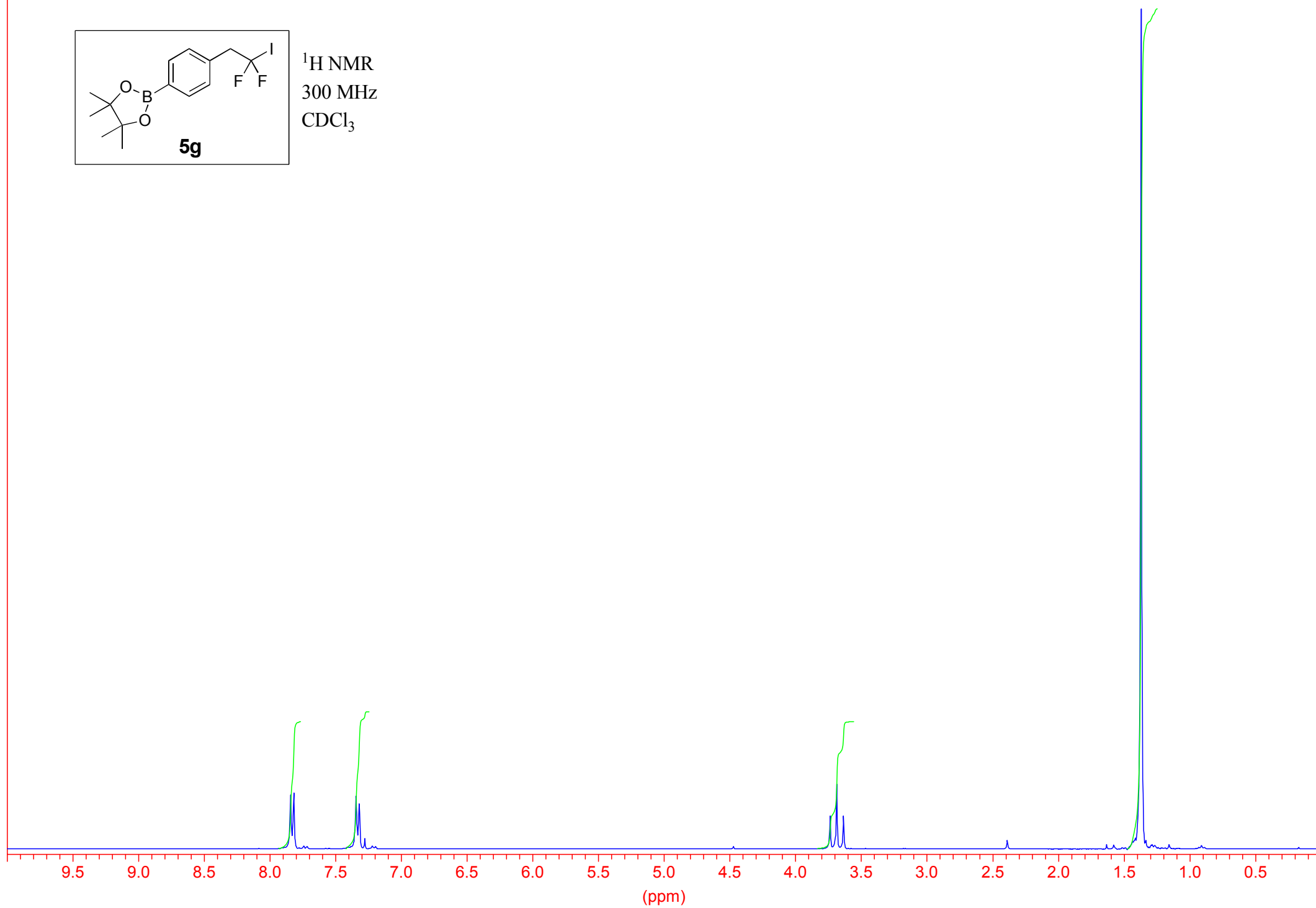


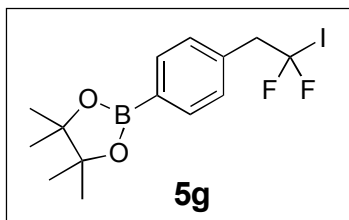
$^{19}\text{F}$  NMR  
282 MHz  
 $\text{CDCl}_3$



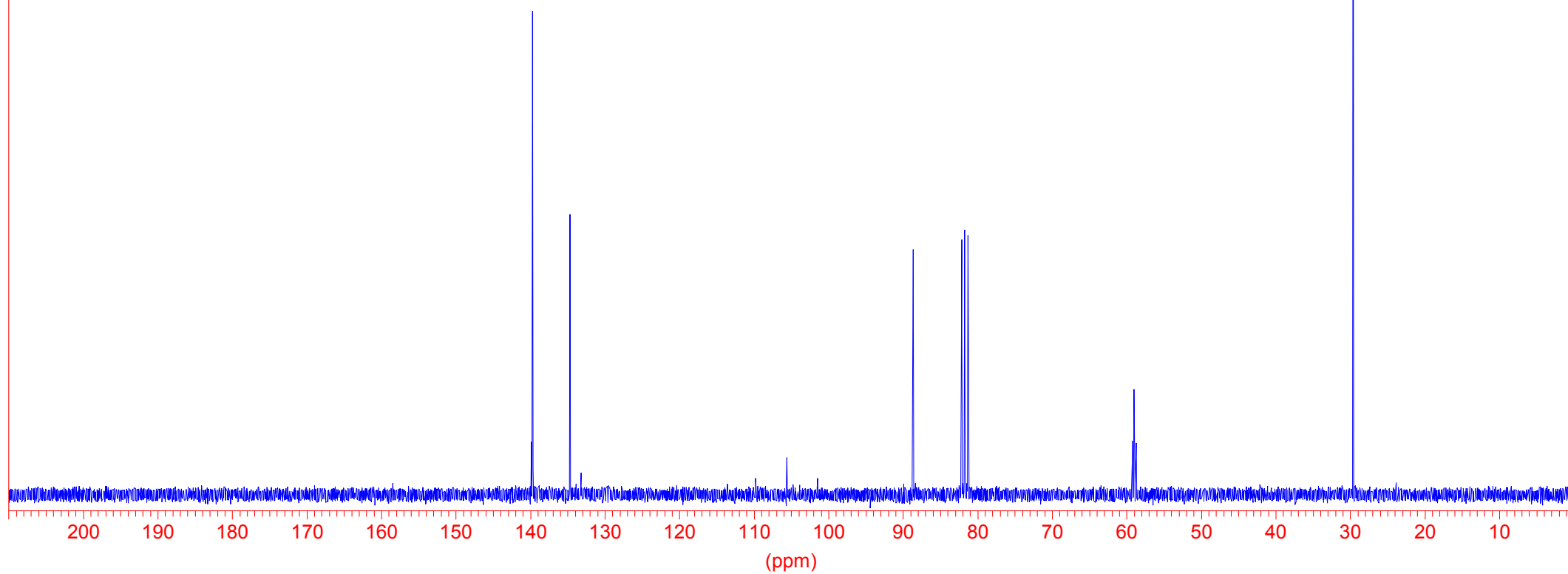


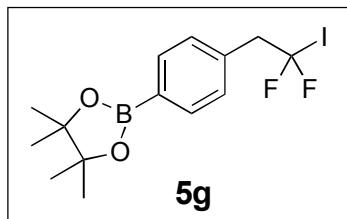
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300 MHz  
 $\text{CDCl}_3$



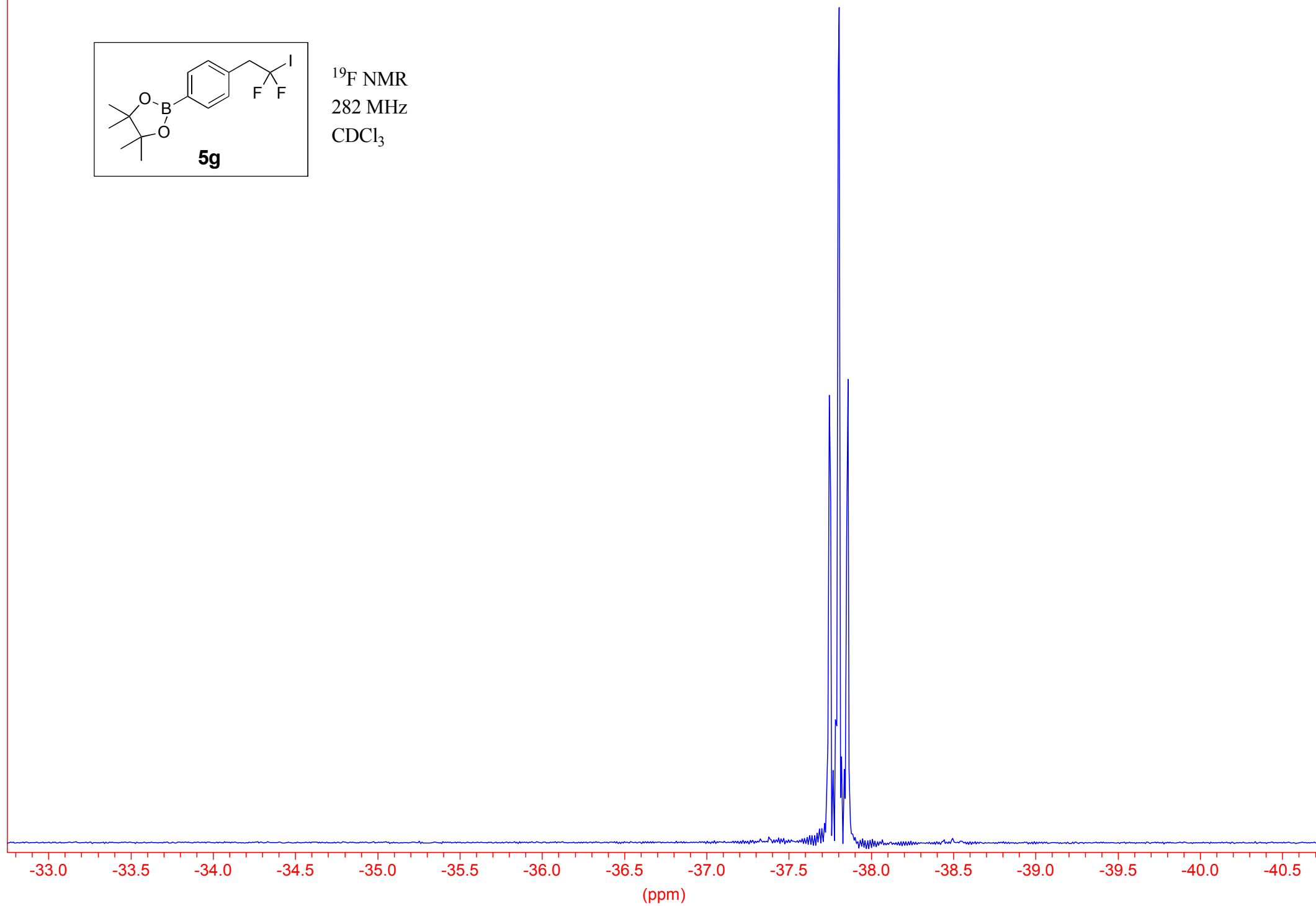


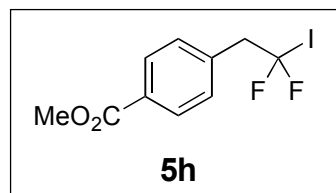
<sup>13</sup>C NMR  
75 MHz  
CDCl<sub>3</sub>



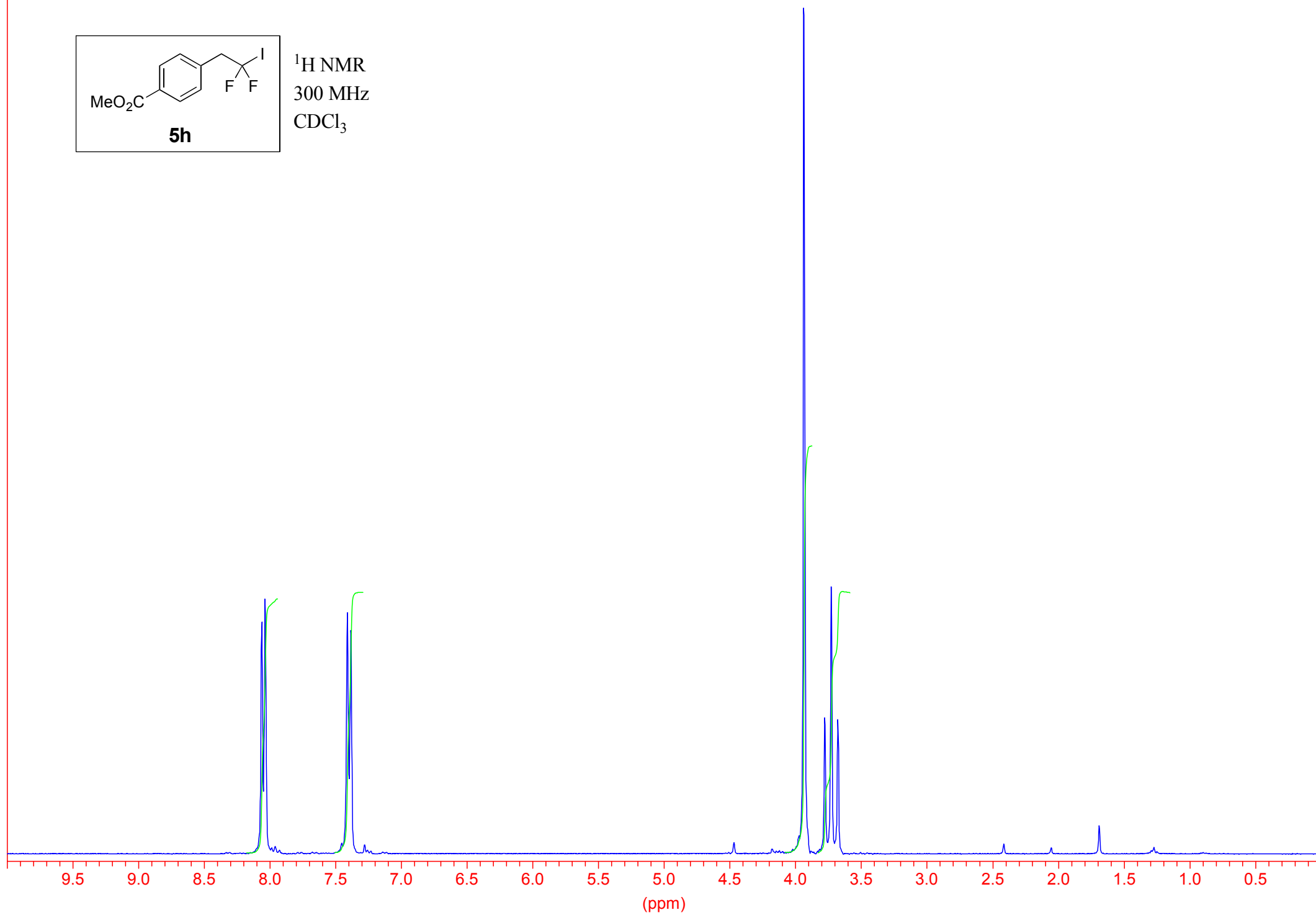


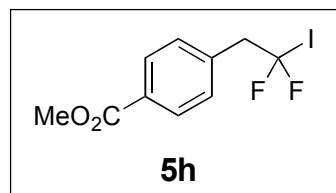
<sup>19</sup>F NMR  
282 MHz  
CDCl<sub>3</sub>



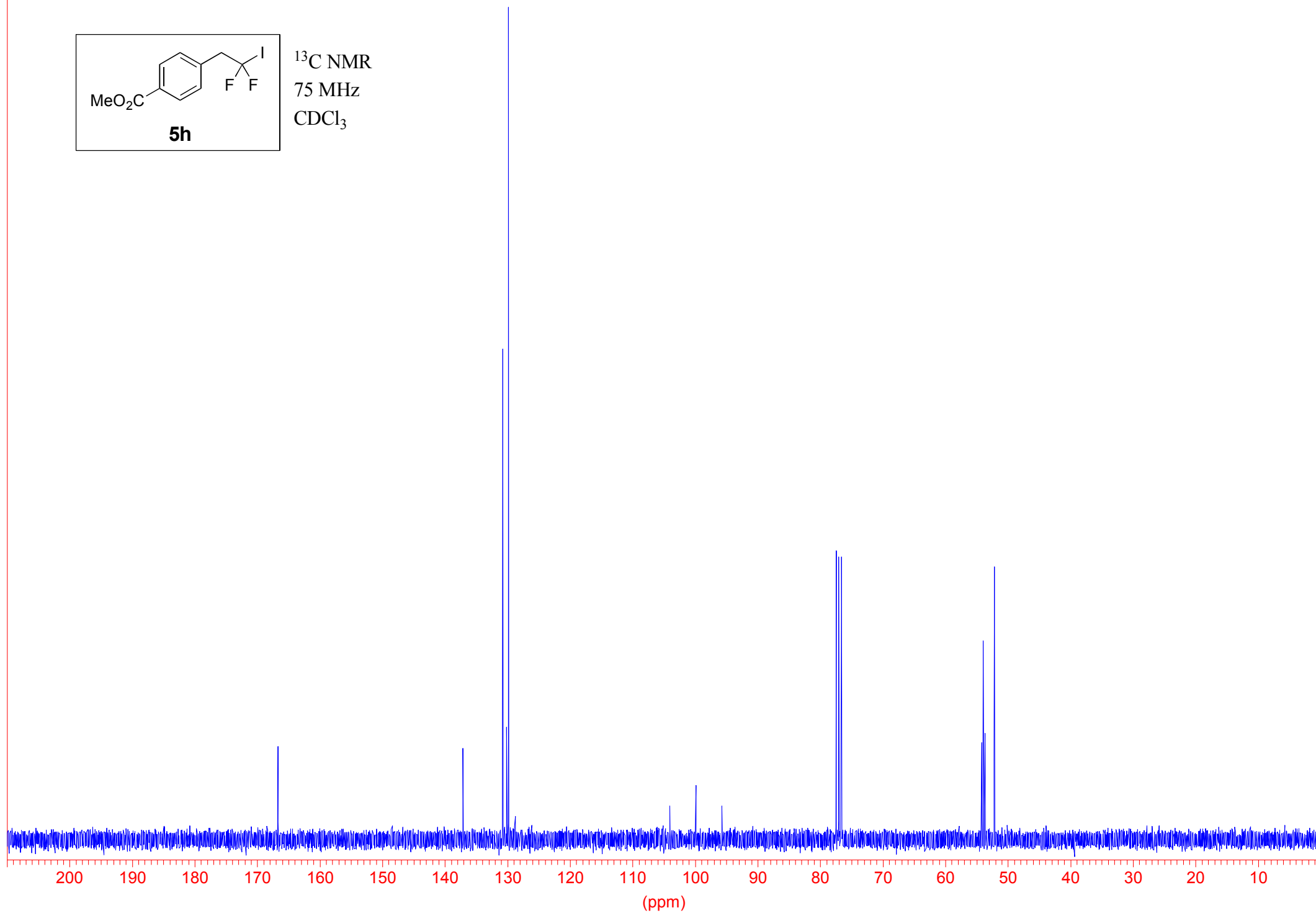


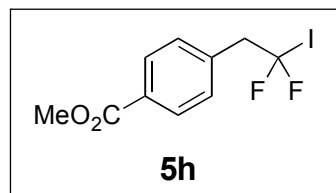
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300 MHz  
 $\text{CDCl}_3$



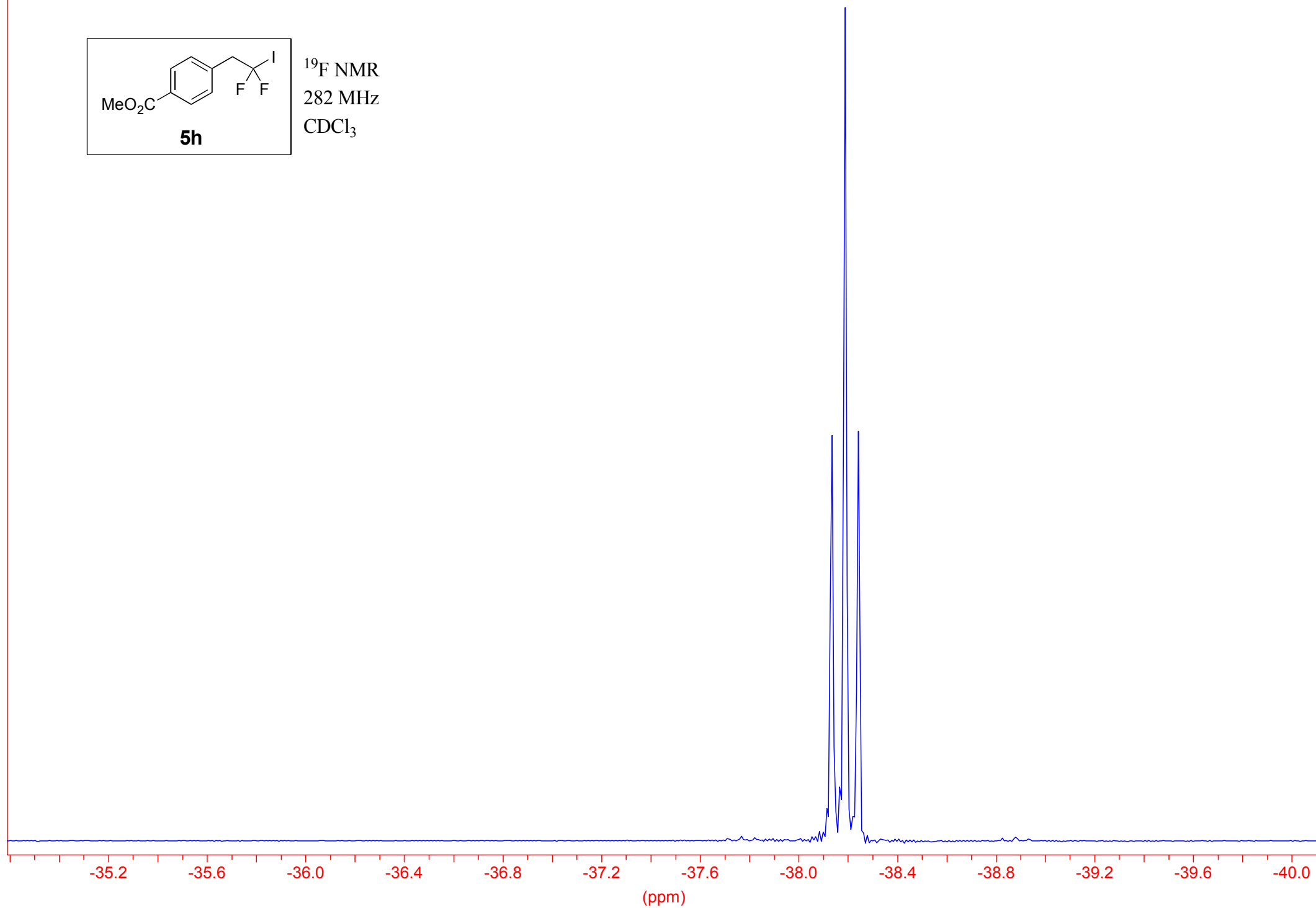


$^{13}\text{C}$  NMR  
75 MHz  
 $\text{CDCl}_3$

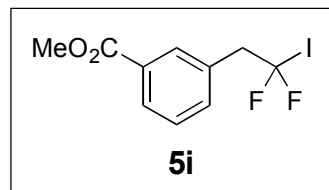




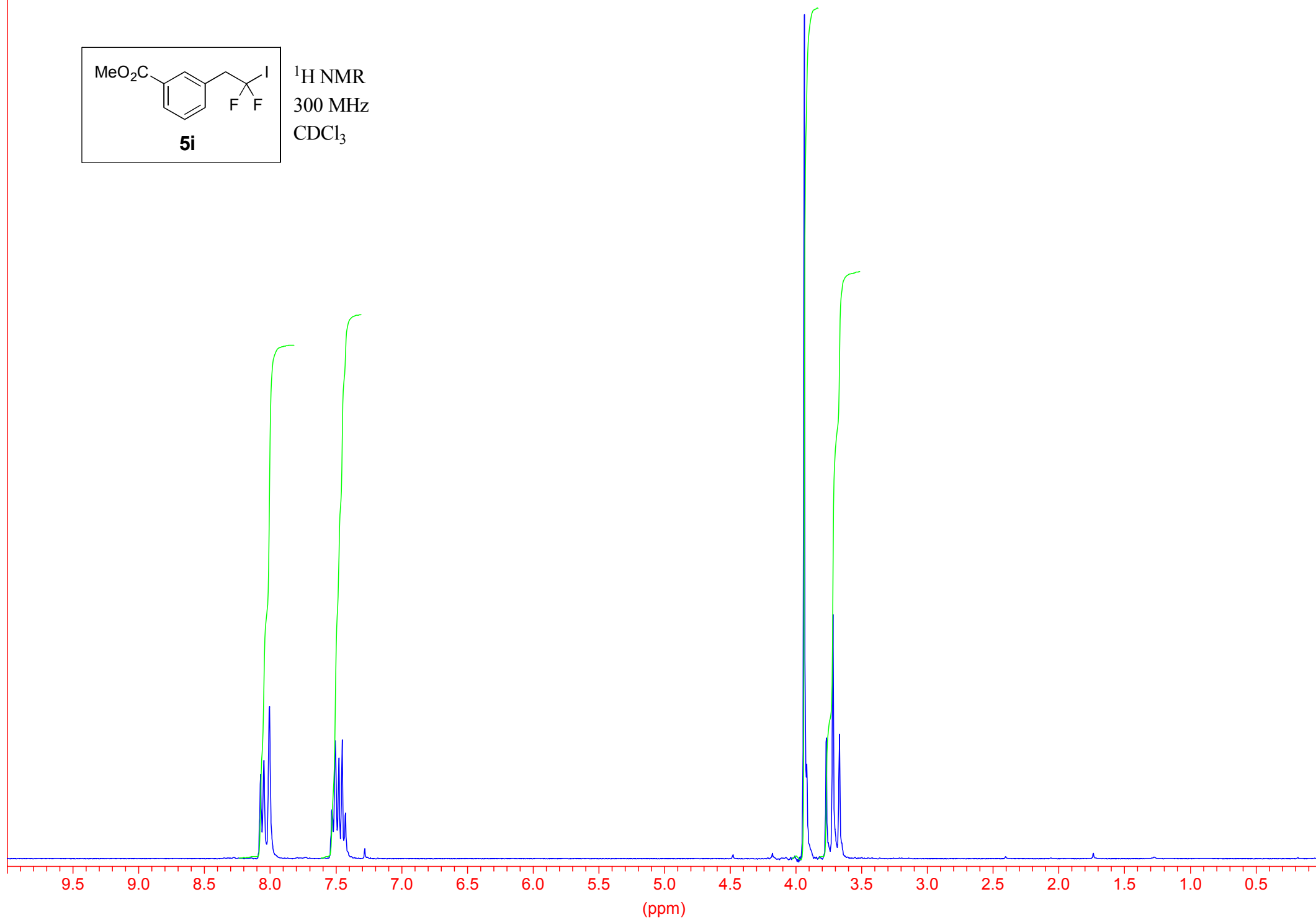
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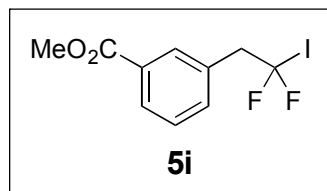




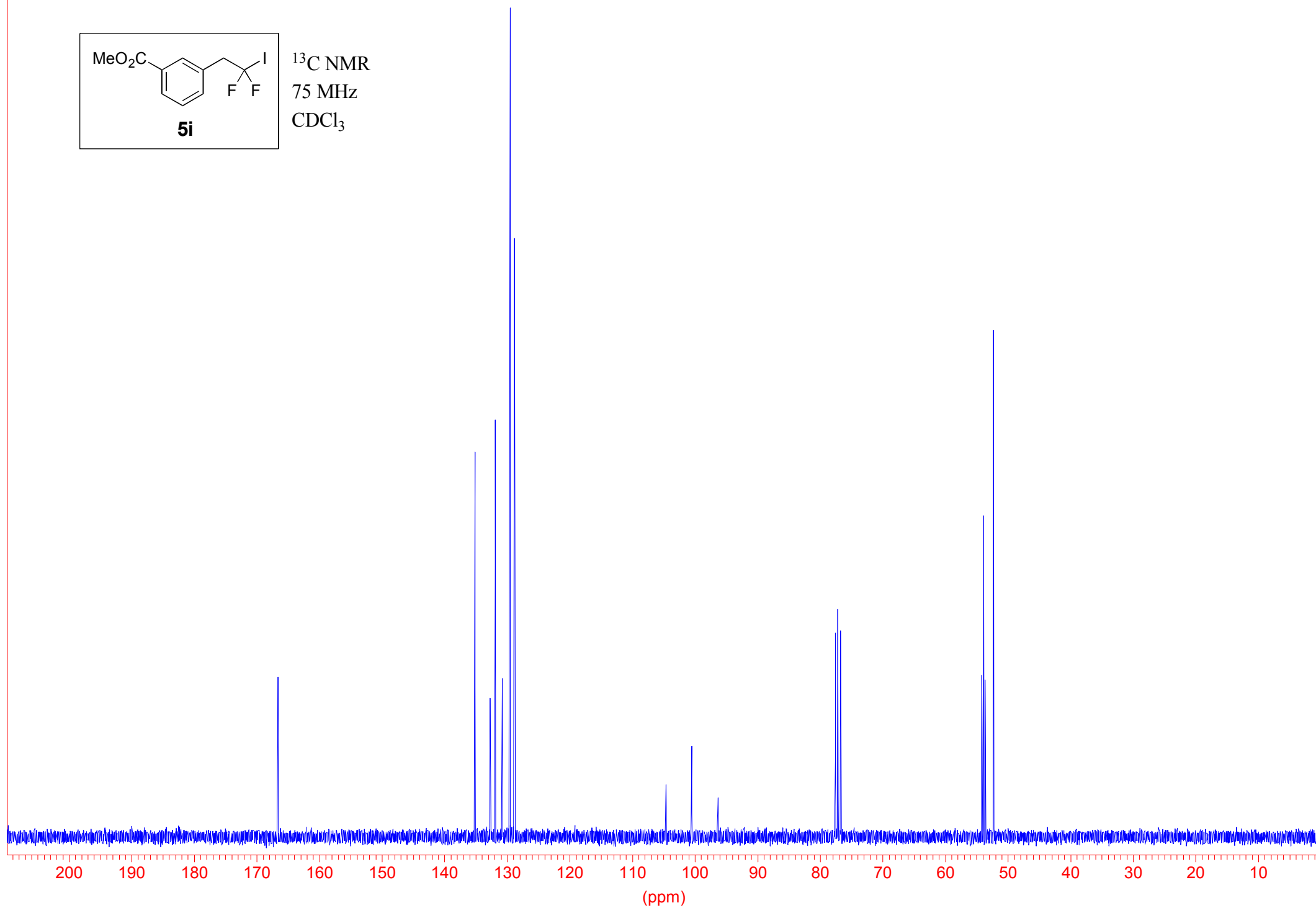


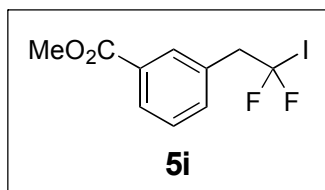
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300 MHz  
 $\text{CDCl}_3$



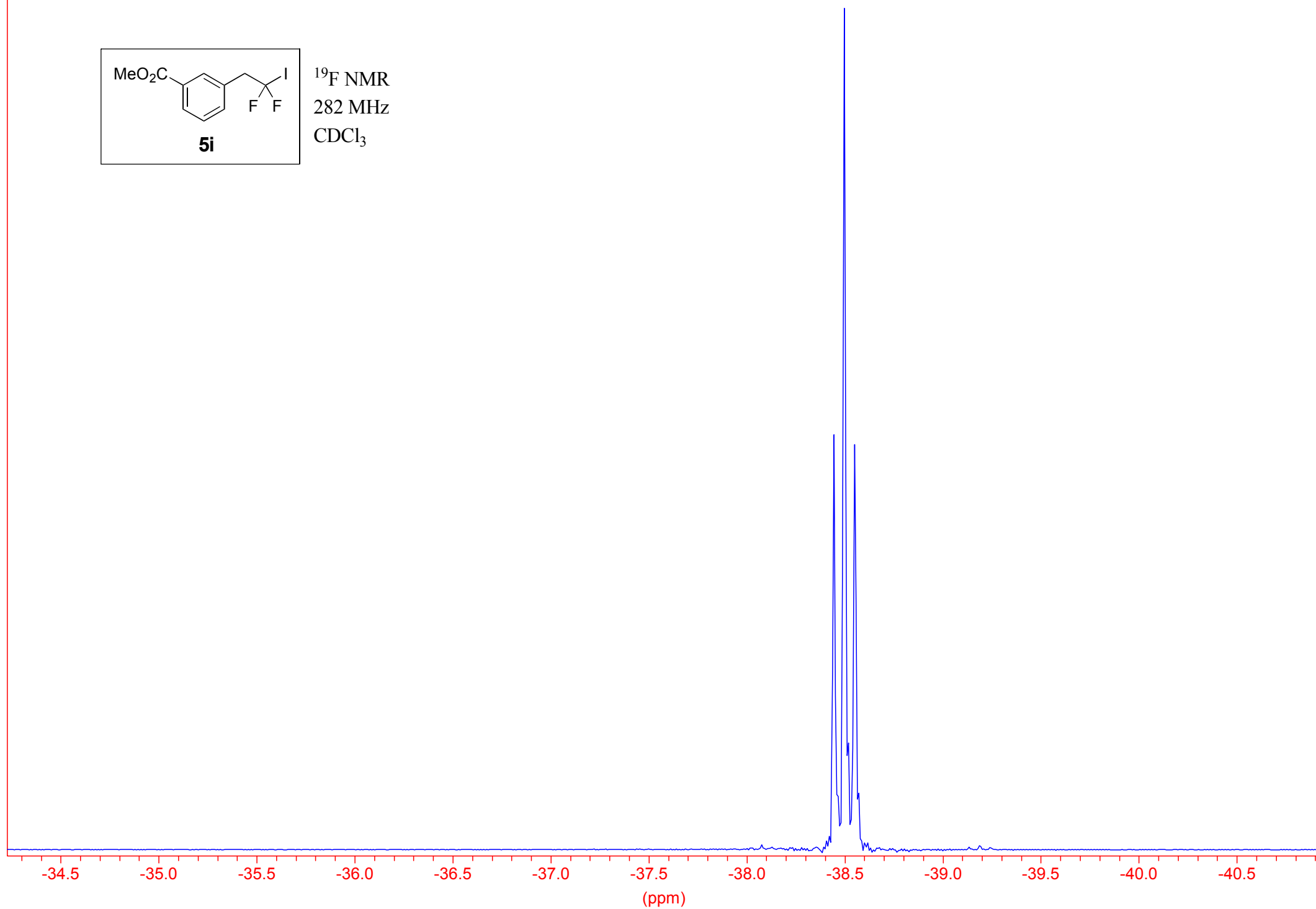


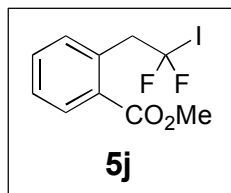
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75 MHz  
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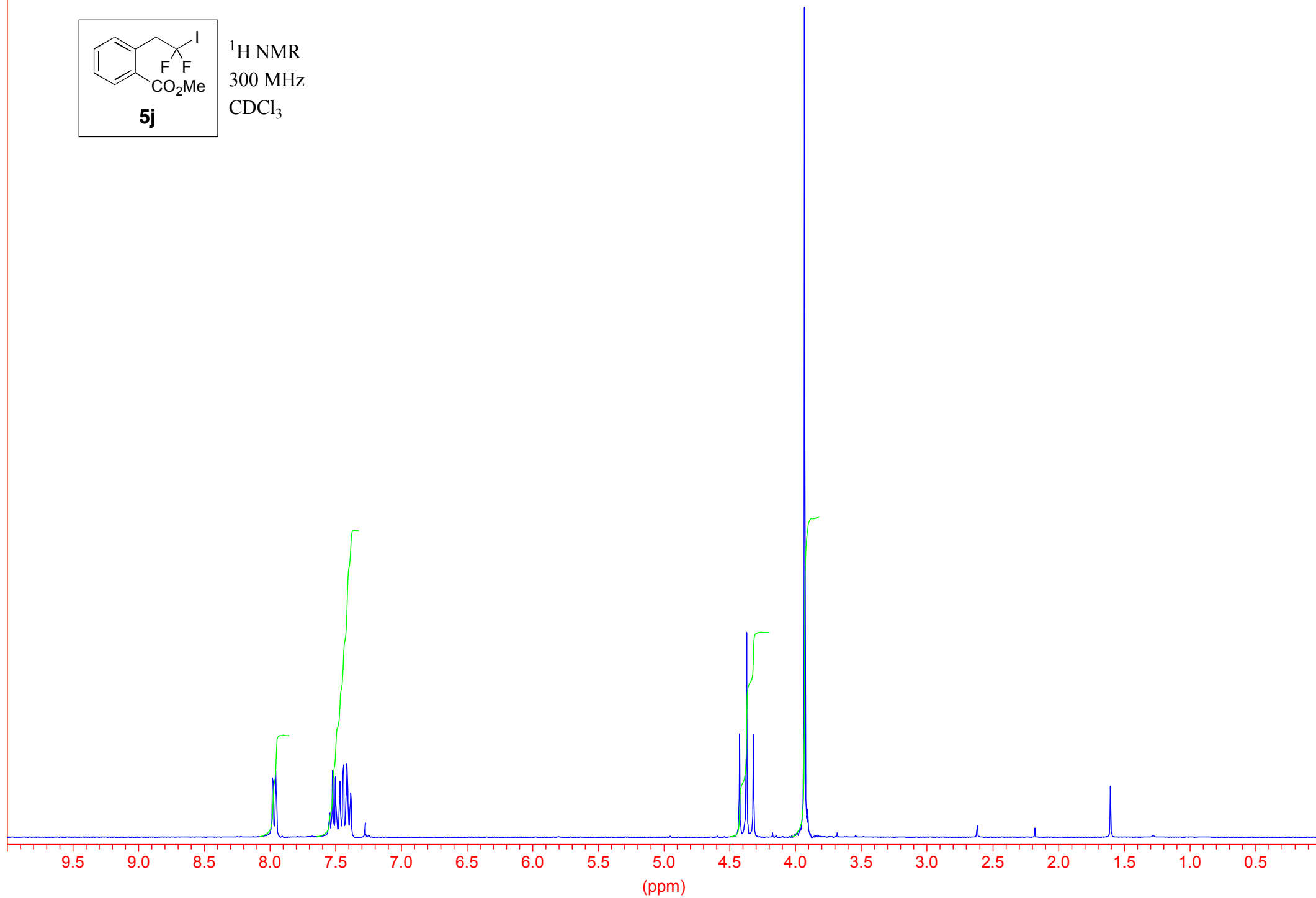


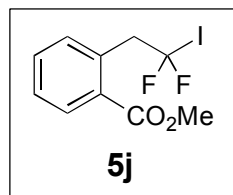
$^{19}\text{F}$  NMR  
282 MHz  
 $\text{CDCl}_3$



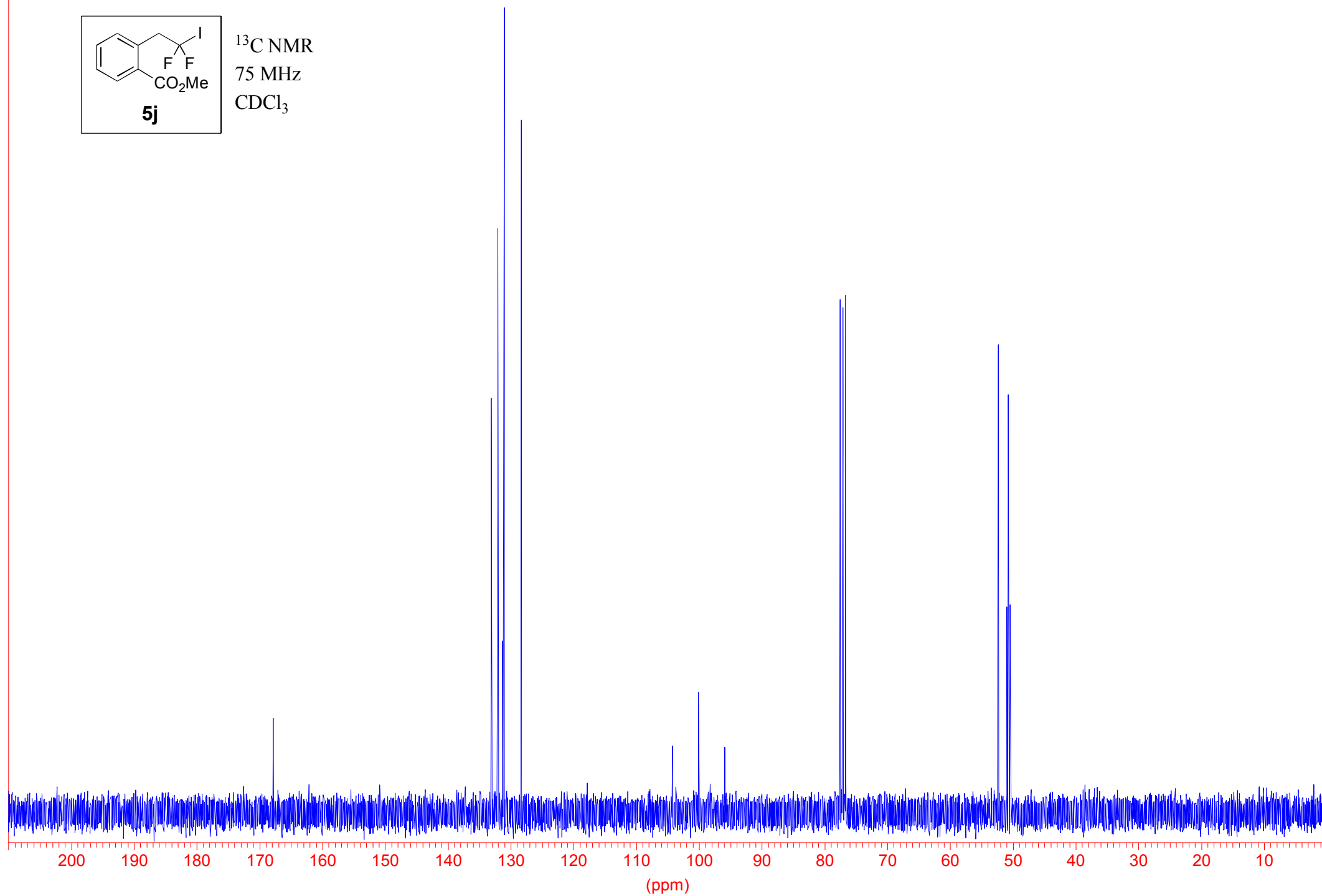


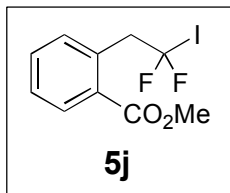
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300 MHz  
 $\text{CDCl}_3$



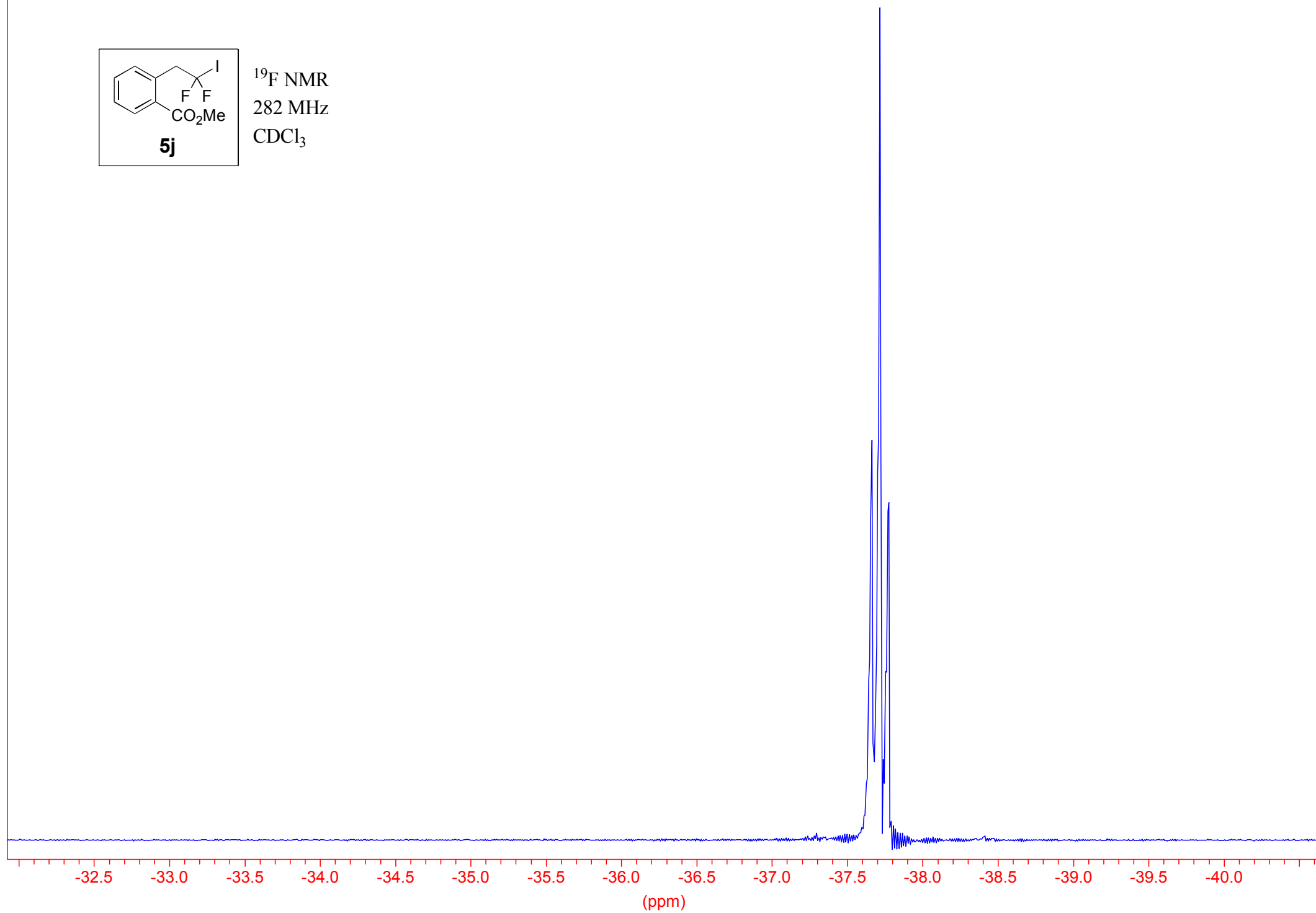


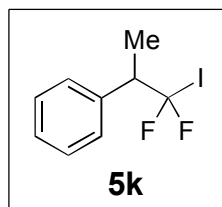
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75 MHz  
 $\text{CDCl}_3$



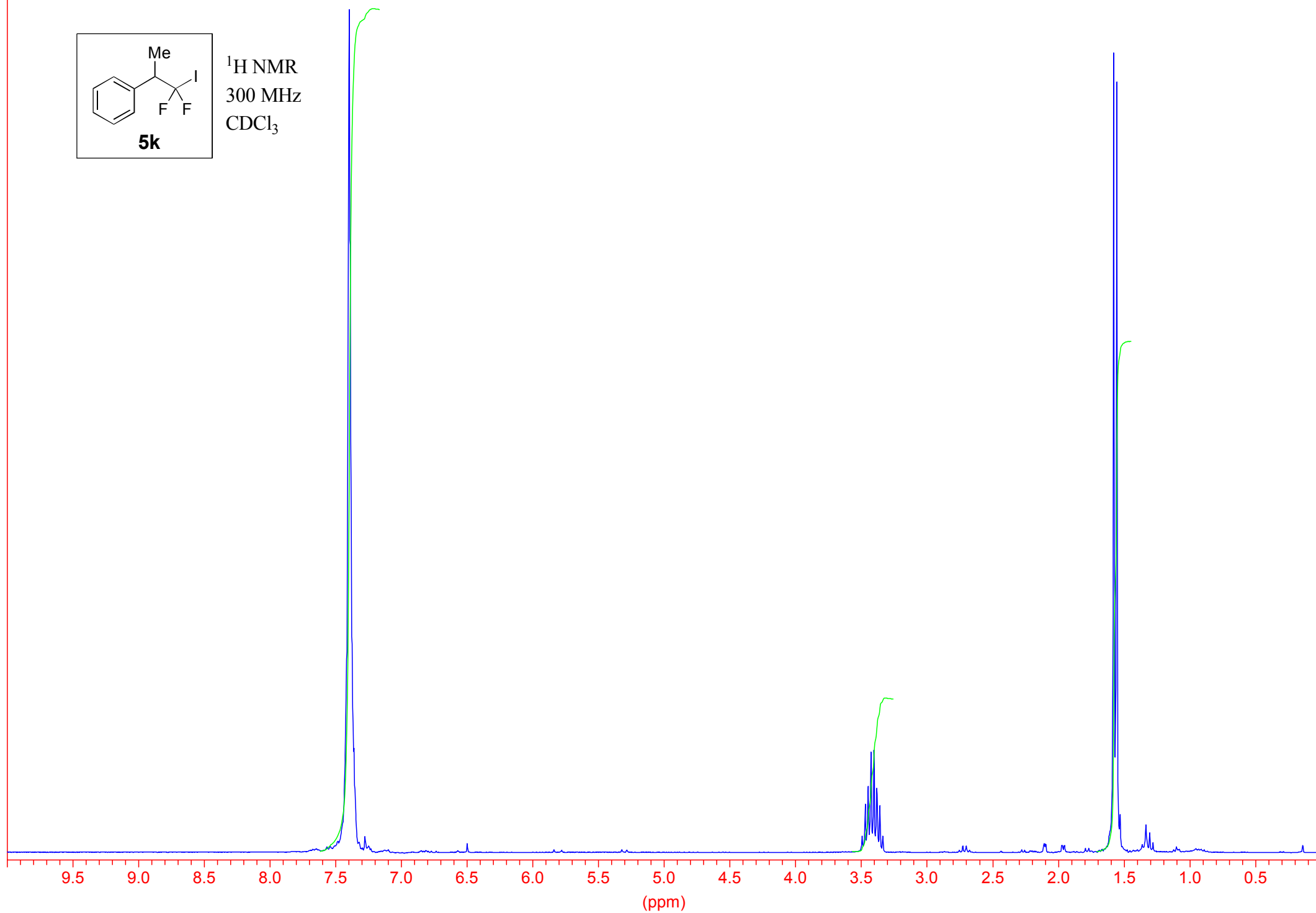


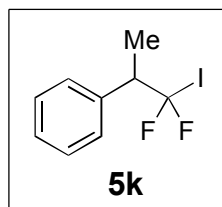
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282 MHz  
 $\text{CDCl}_3$



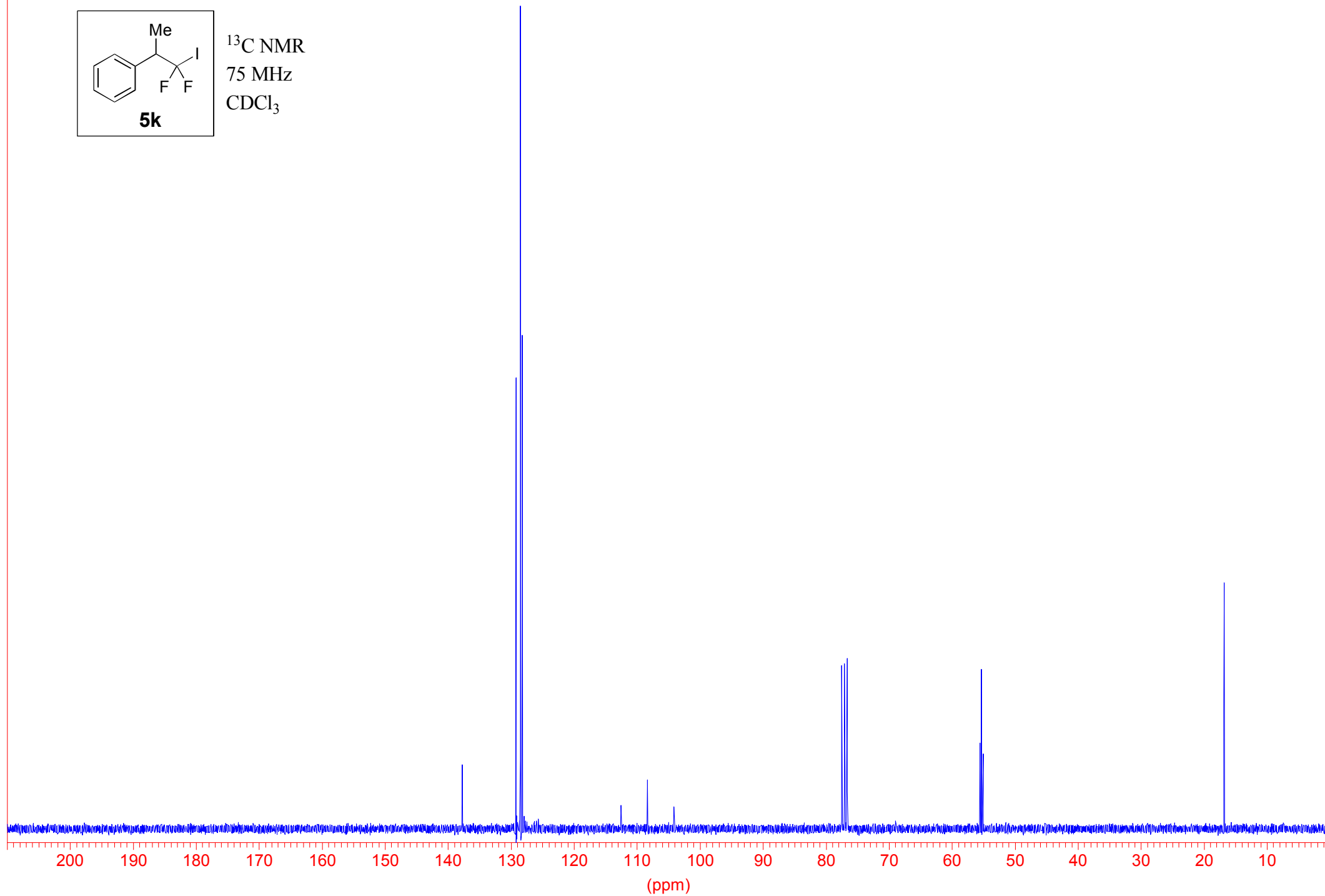


$^1\text{H}$  NMR  
300 MHz  
 $\text{CDCl}_3$

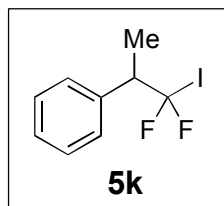




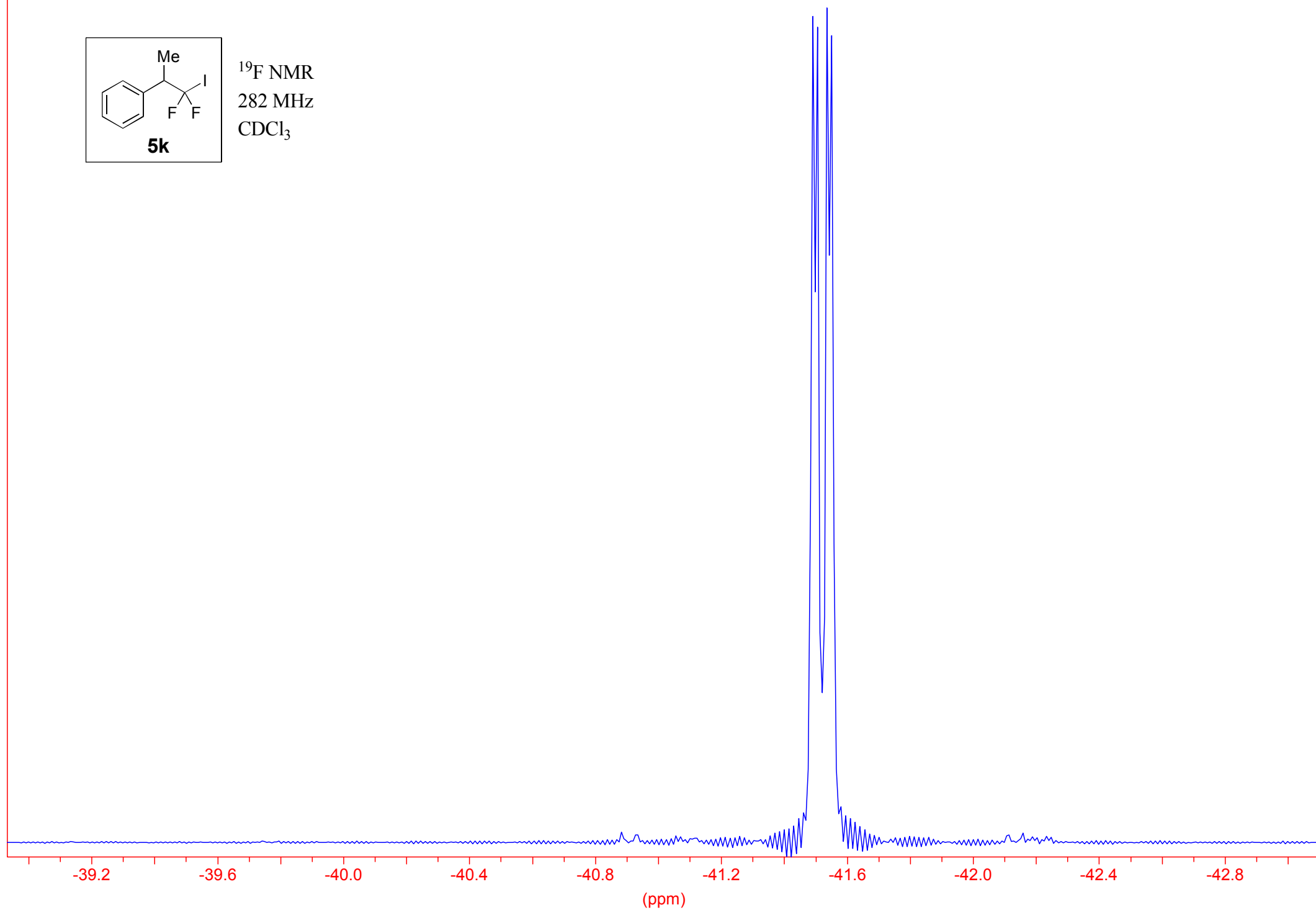
$^{13}\text{C}$  NMR  
75 MHz  
 $\text{CDCl}_3$

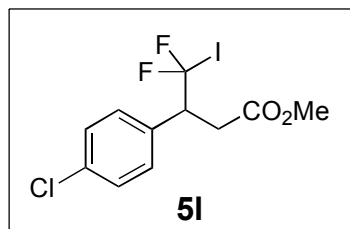




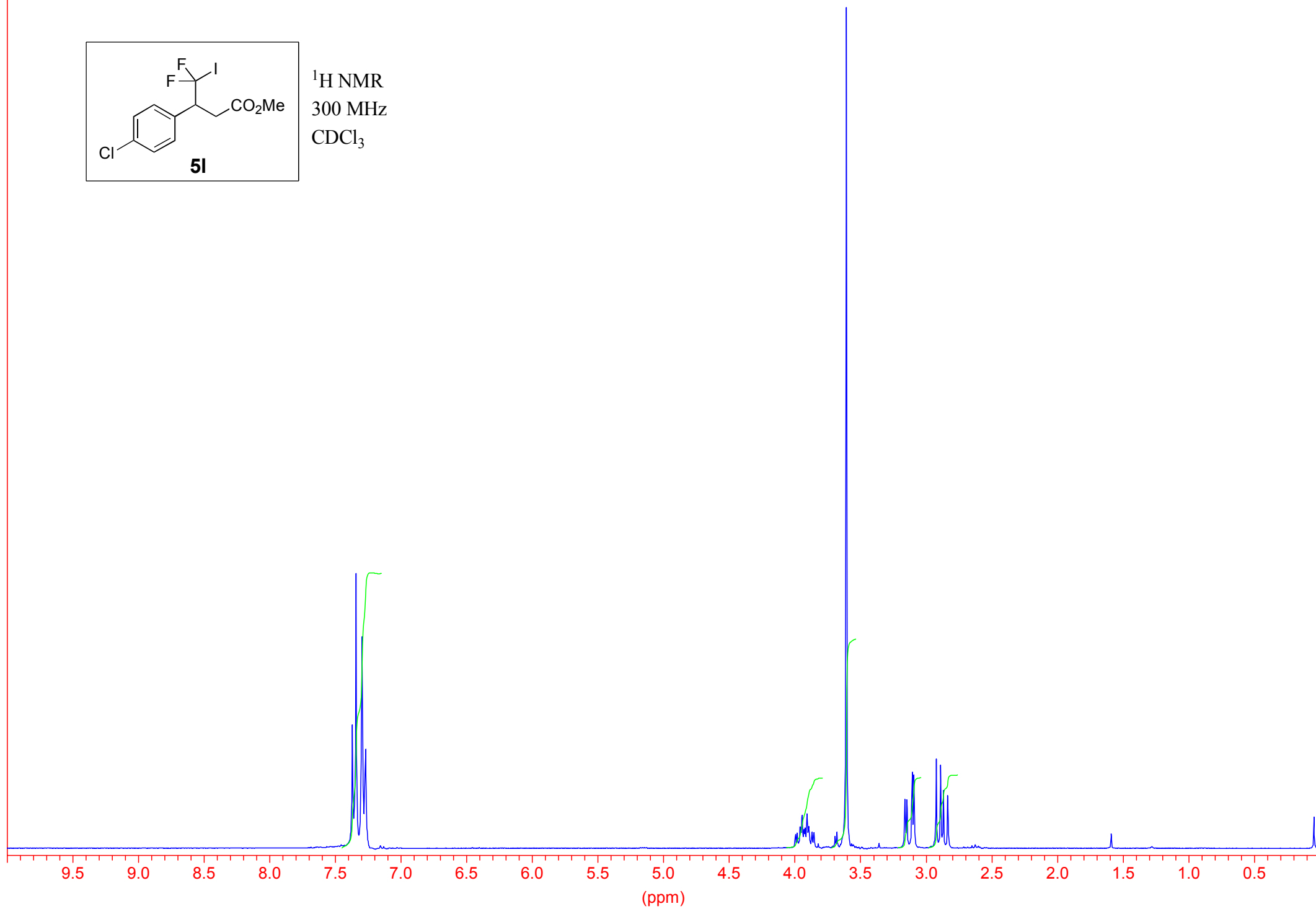


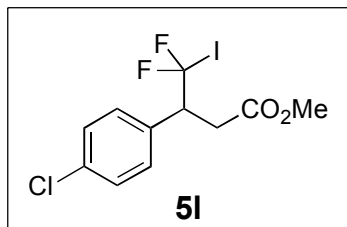
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282 MHz  
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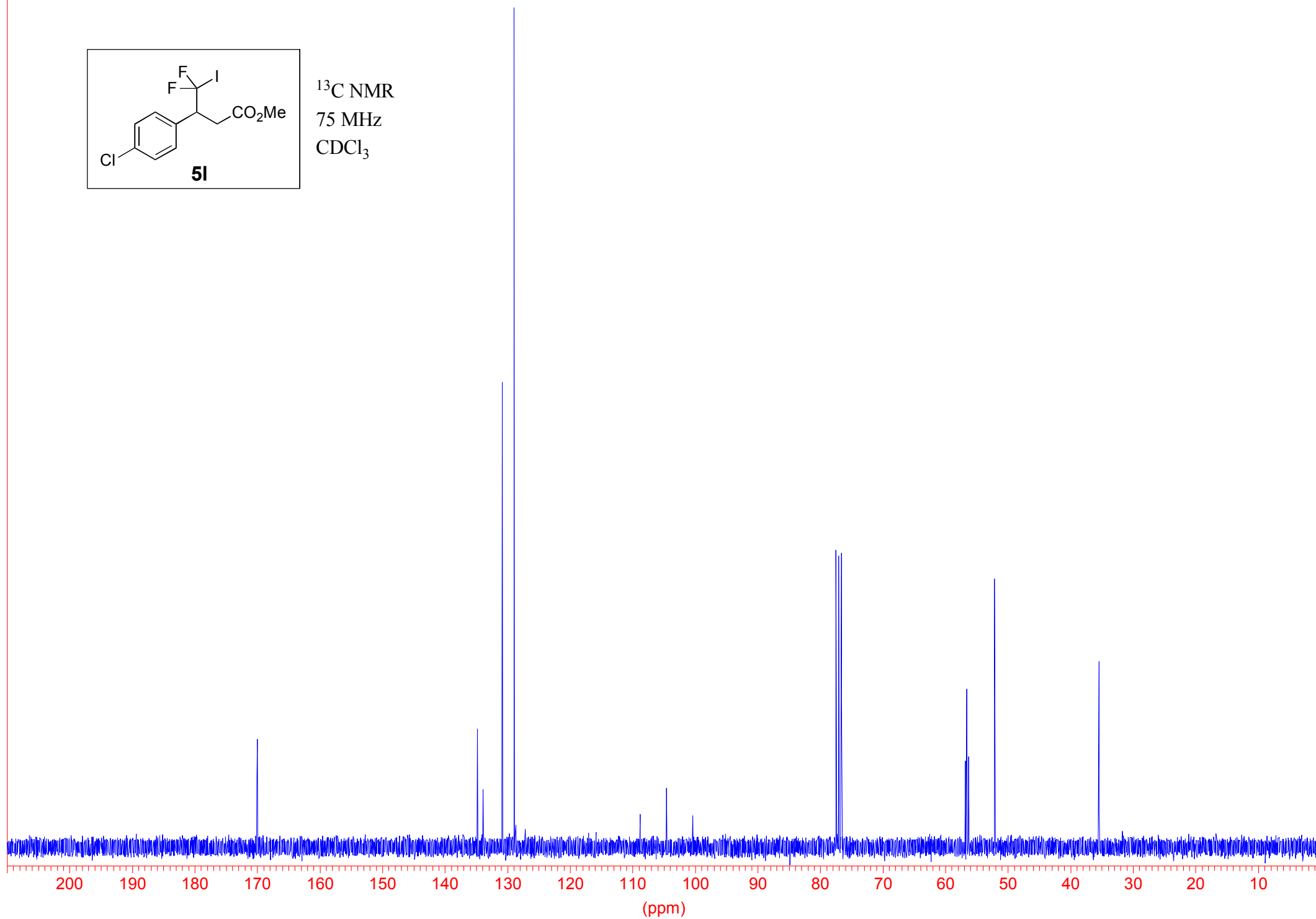


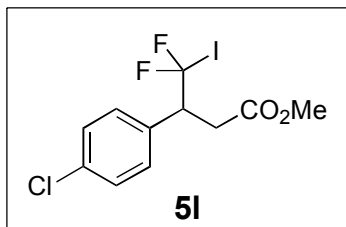
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300 MHz  
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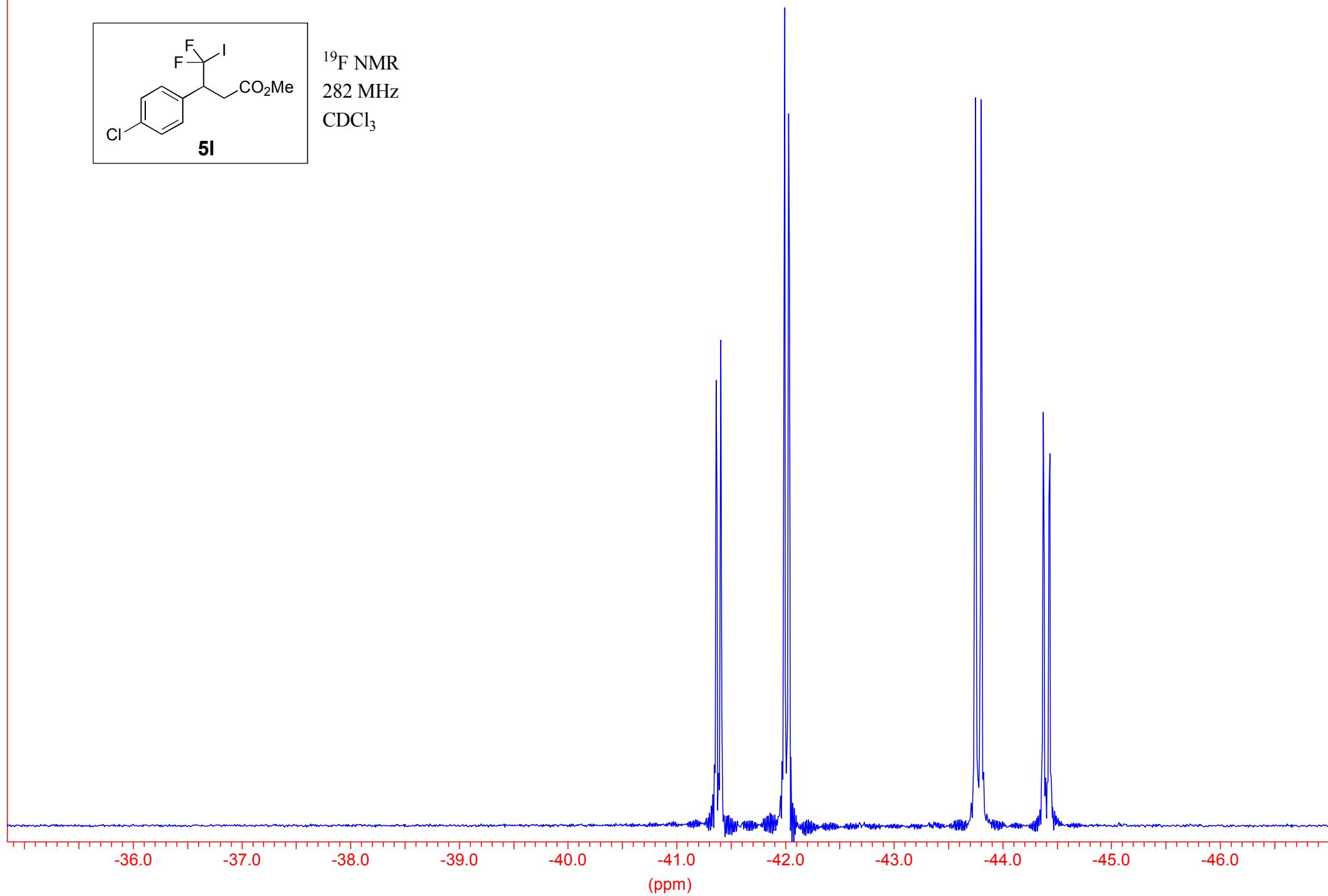


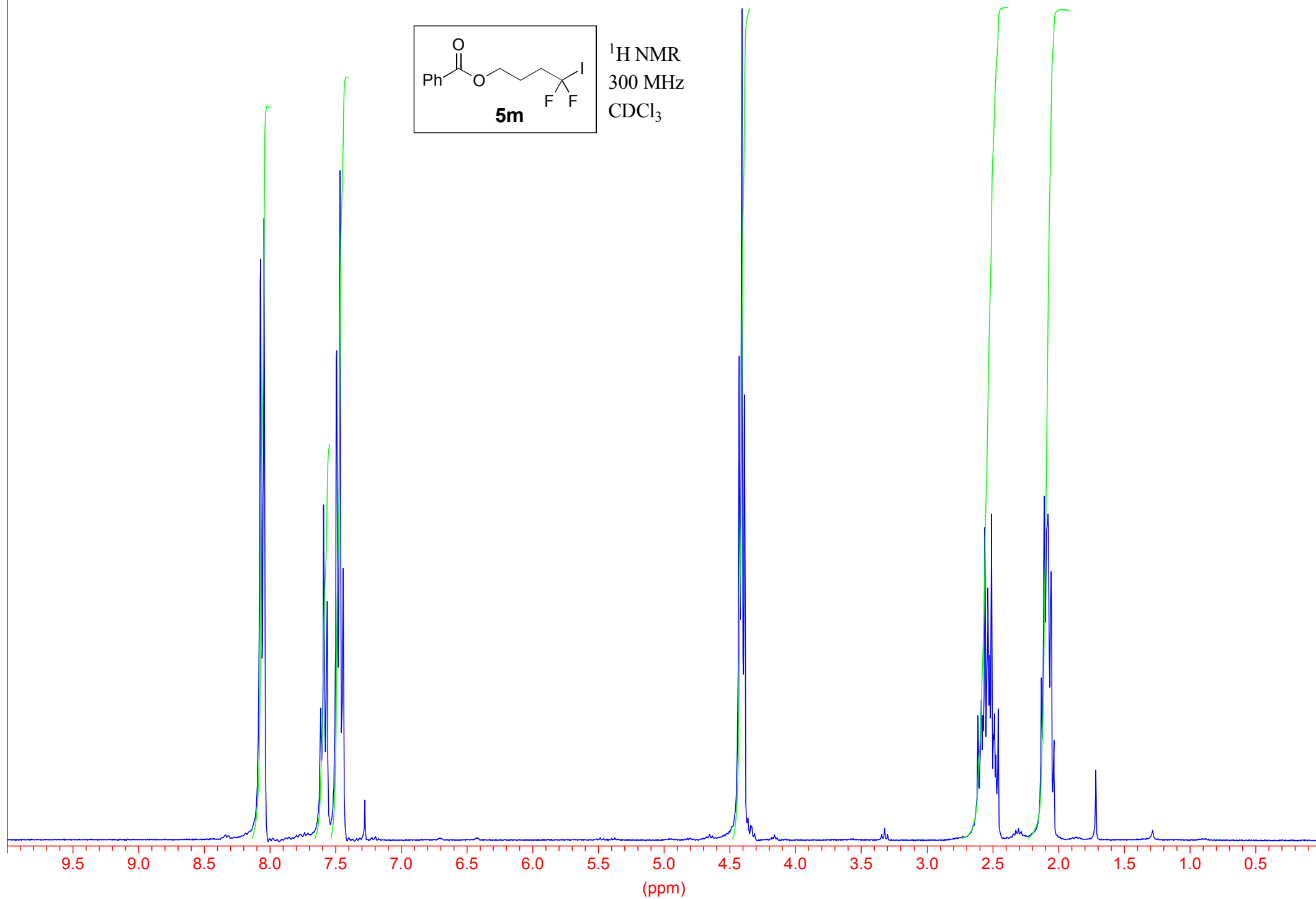
<sup>13</sup>C NMR  
75 MHz  
CDCl<sub>3</sub>

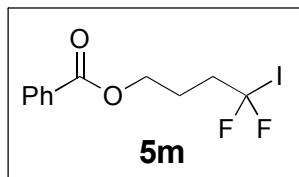




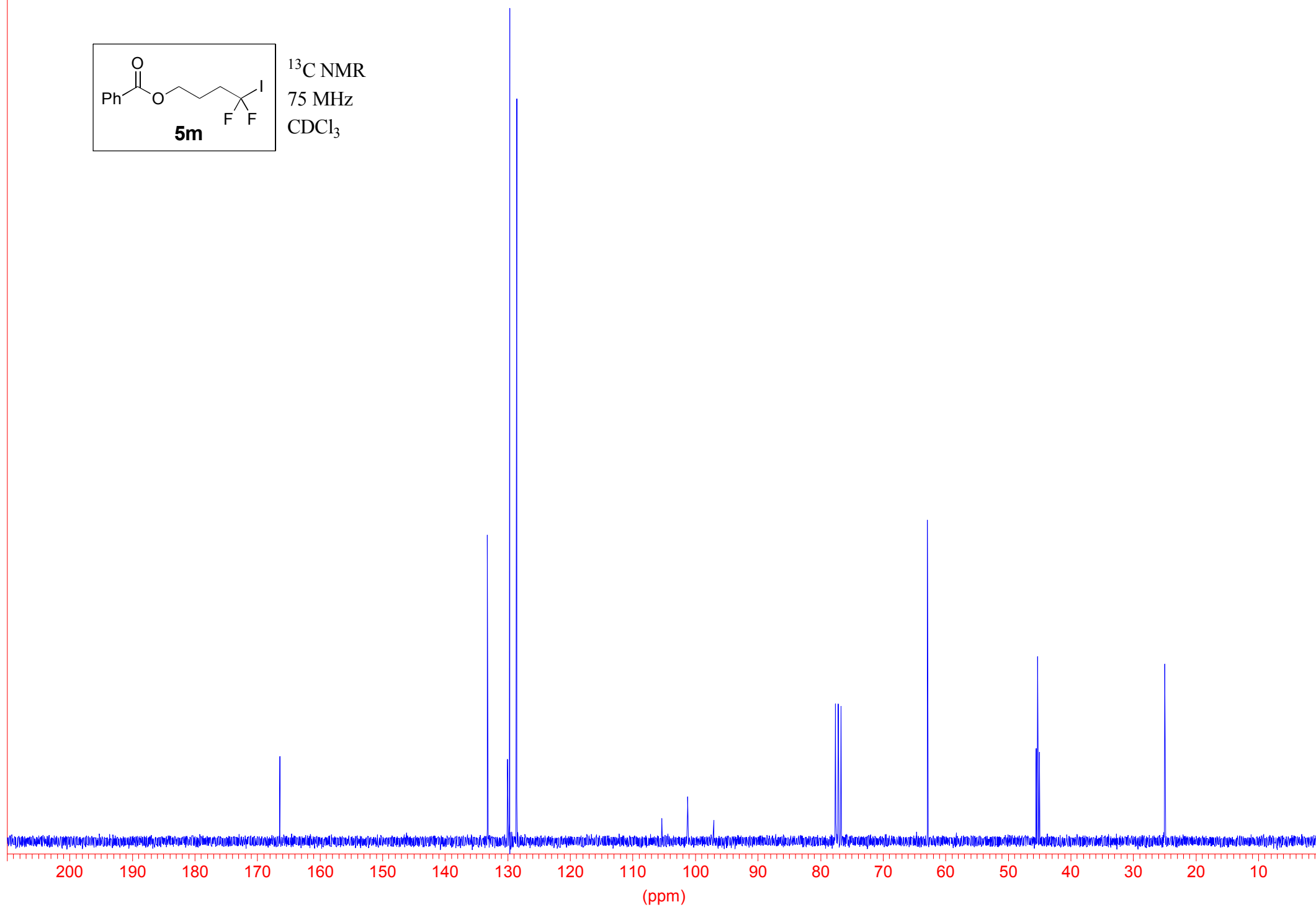
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282 MHz  
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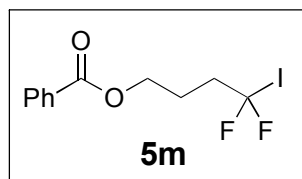




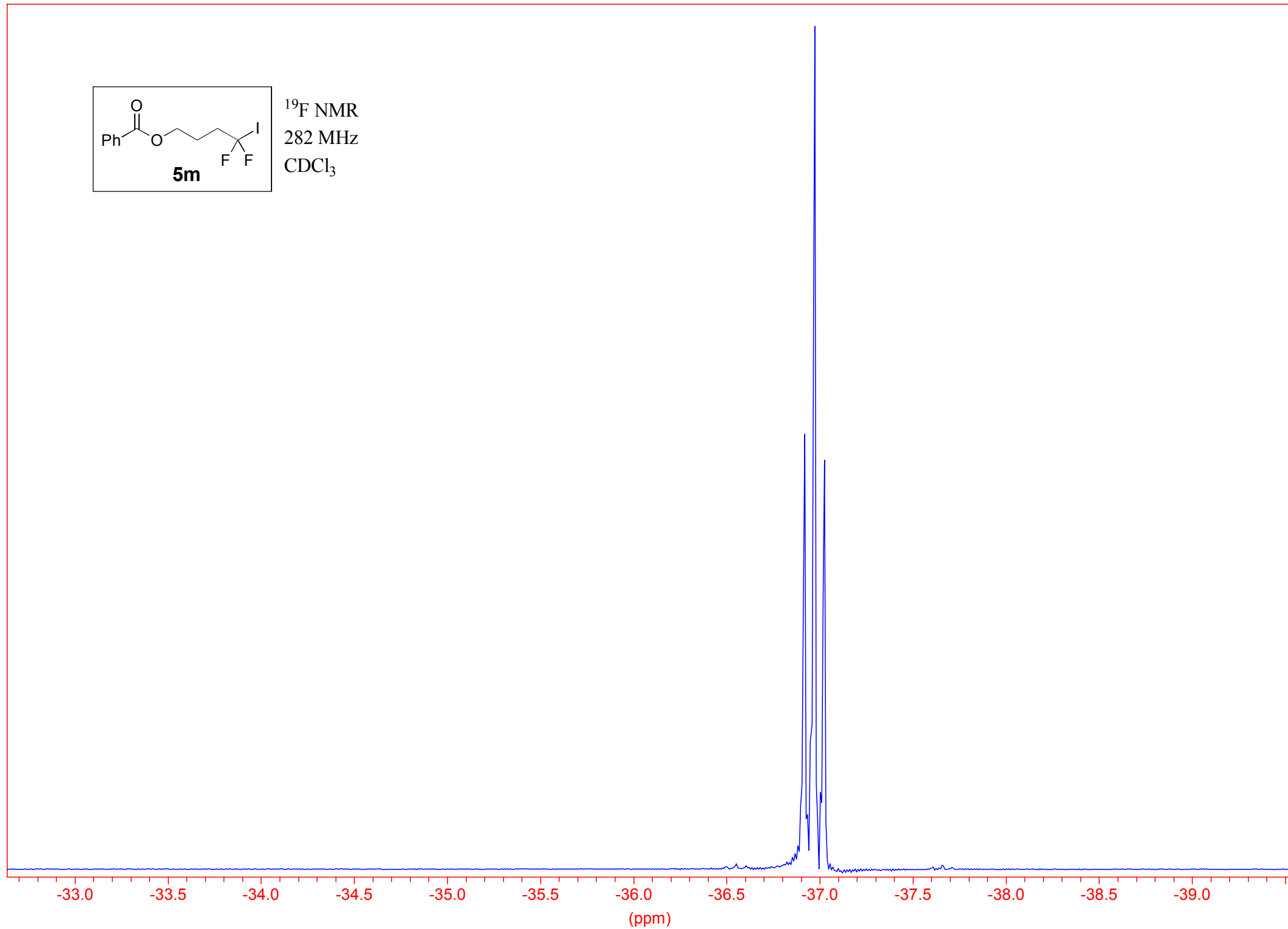


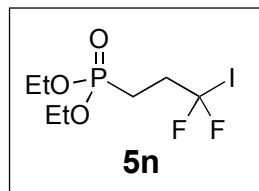
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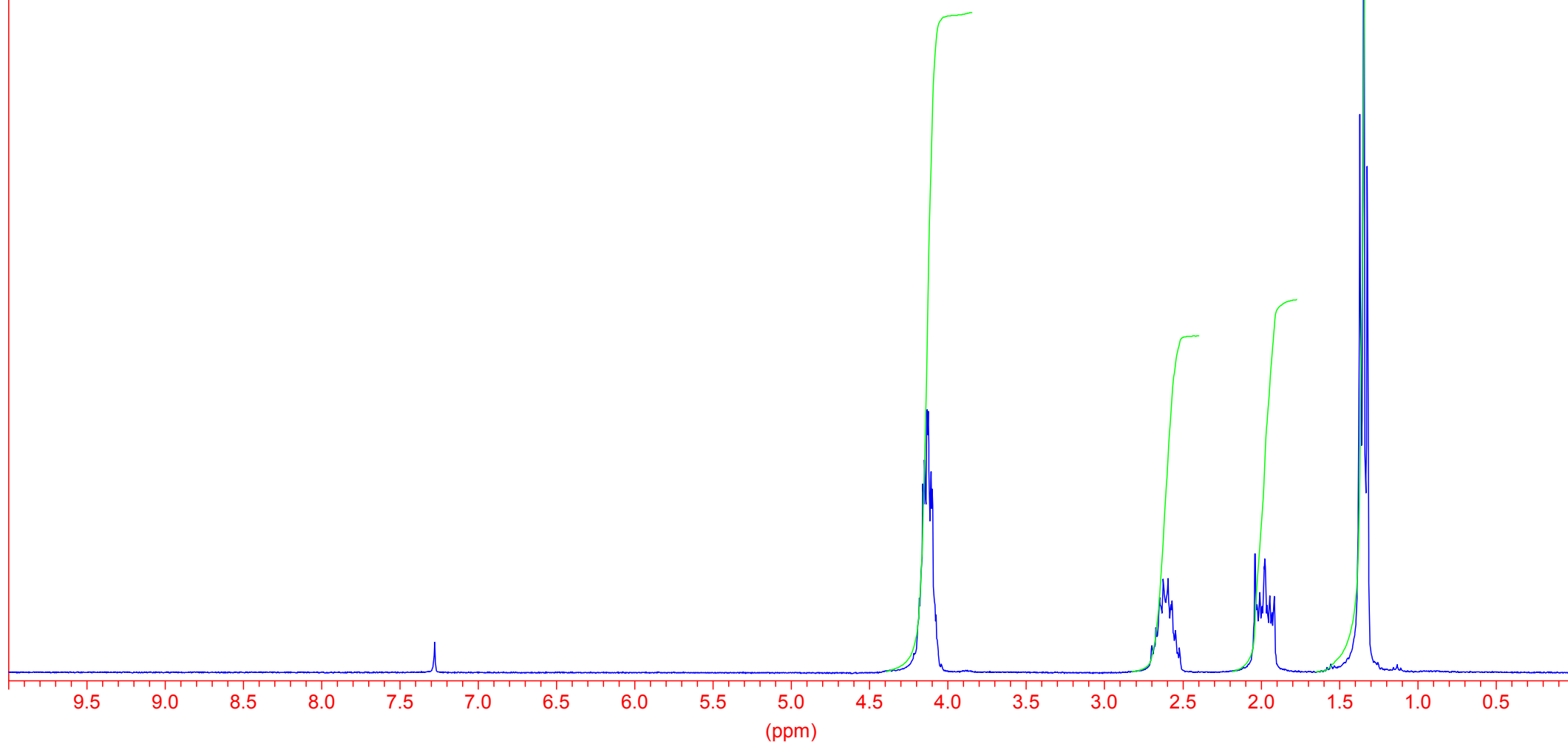


$^{19}\text{F}$  NMR  
282 MHz  
 $\text{CDCl}_3$

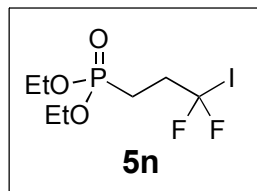




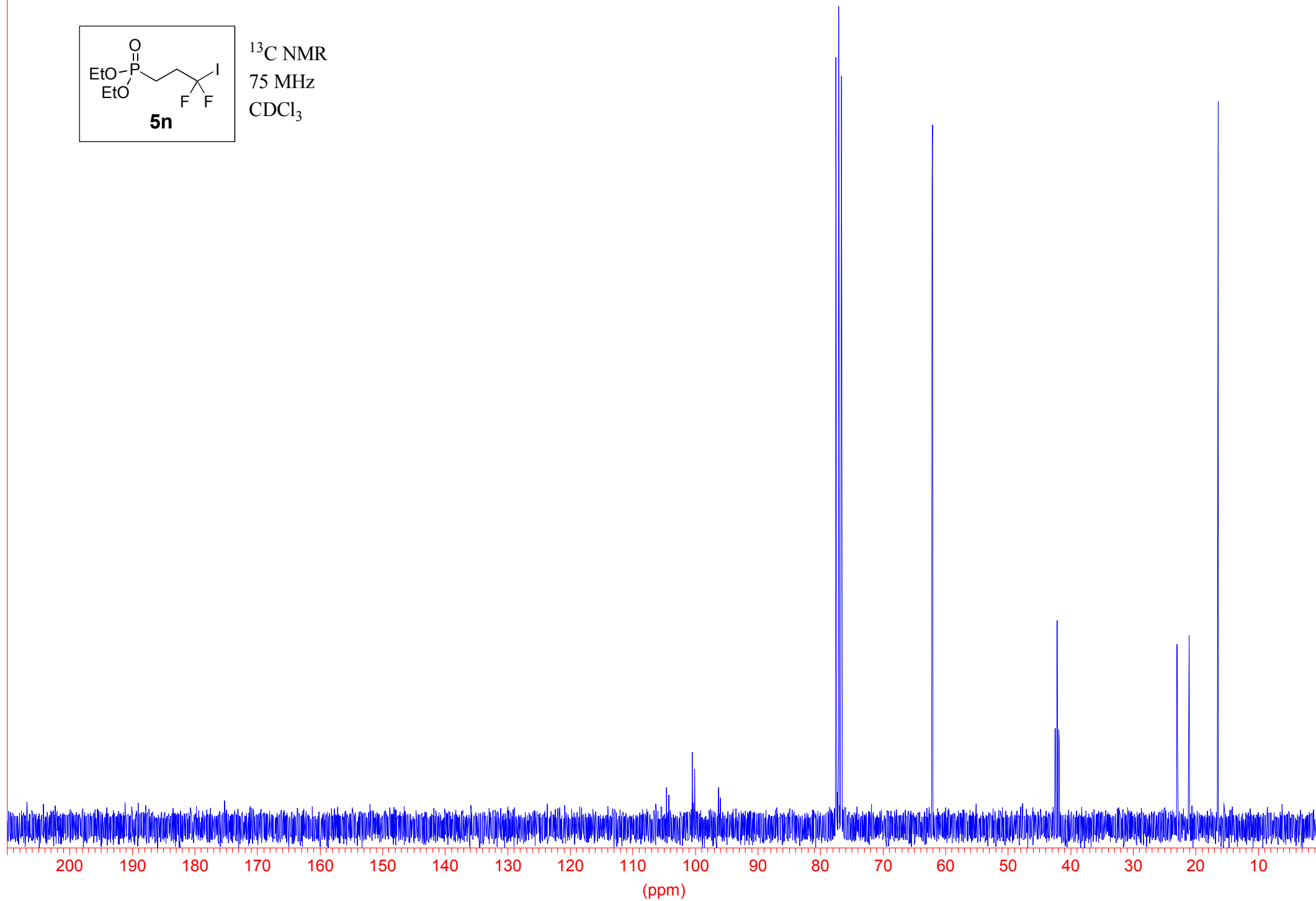
$^1\text{H}$  NMR  
300 MHz  
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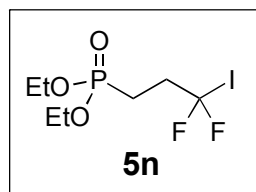




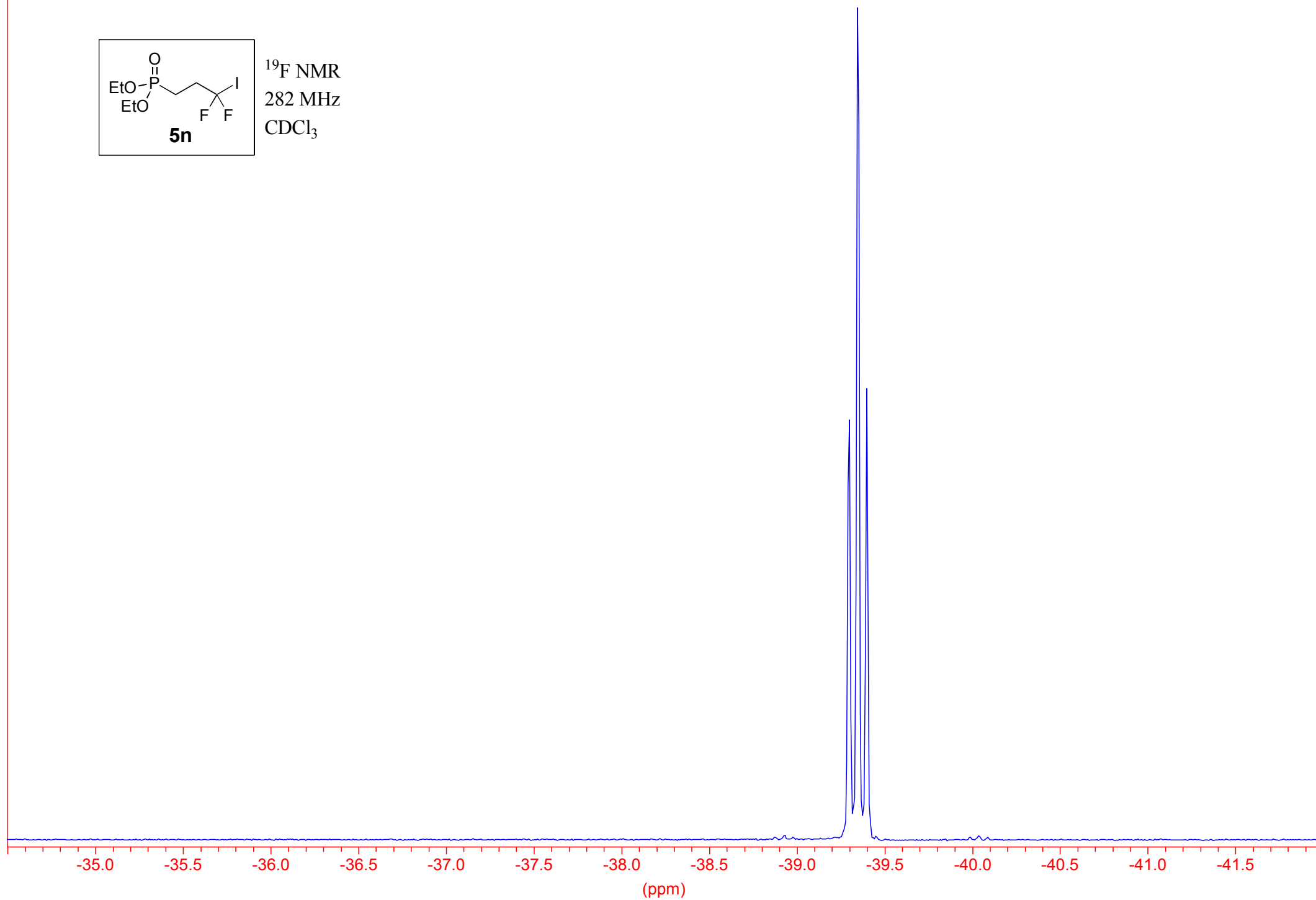


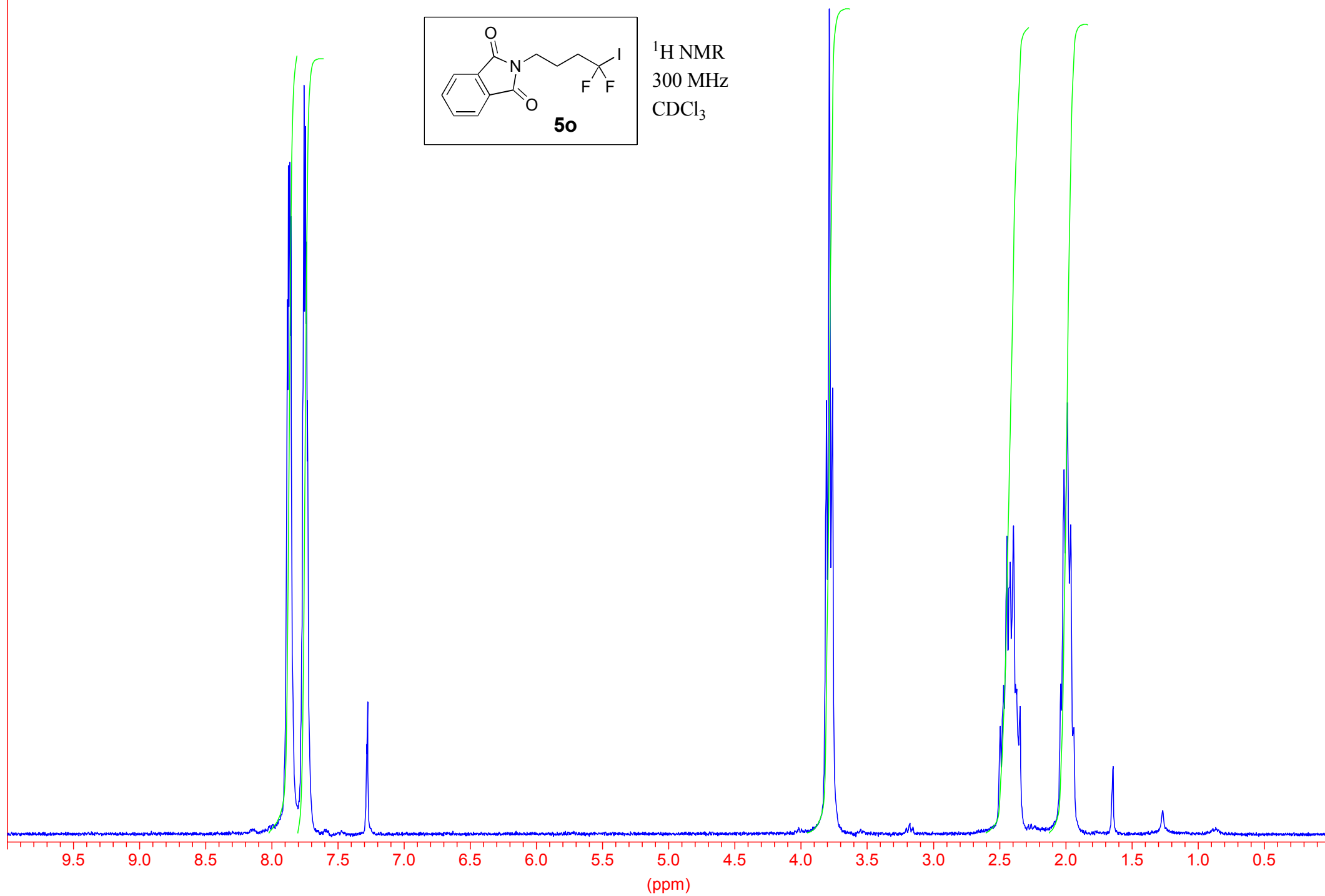
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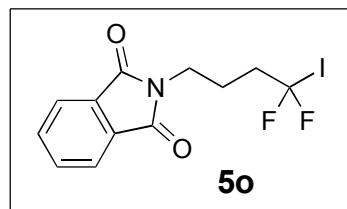




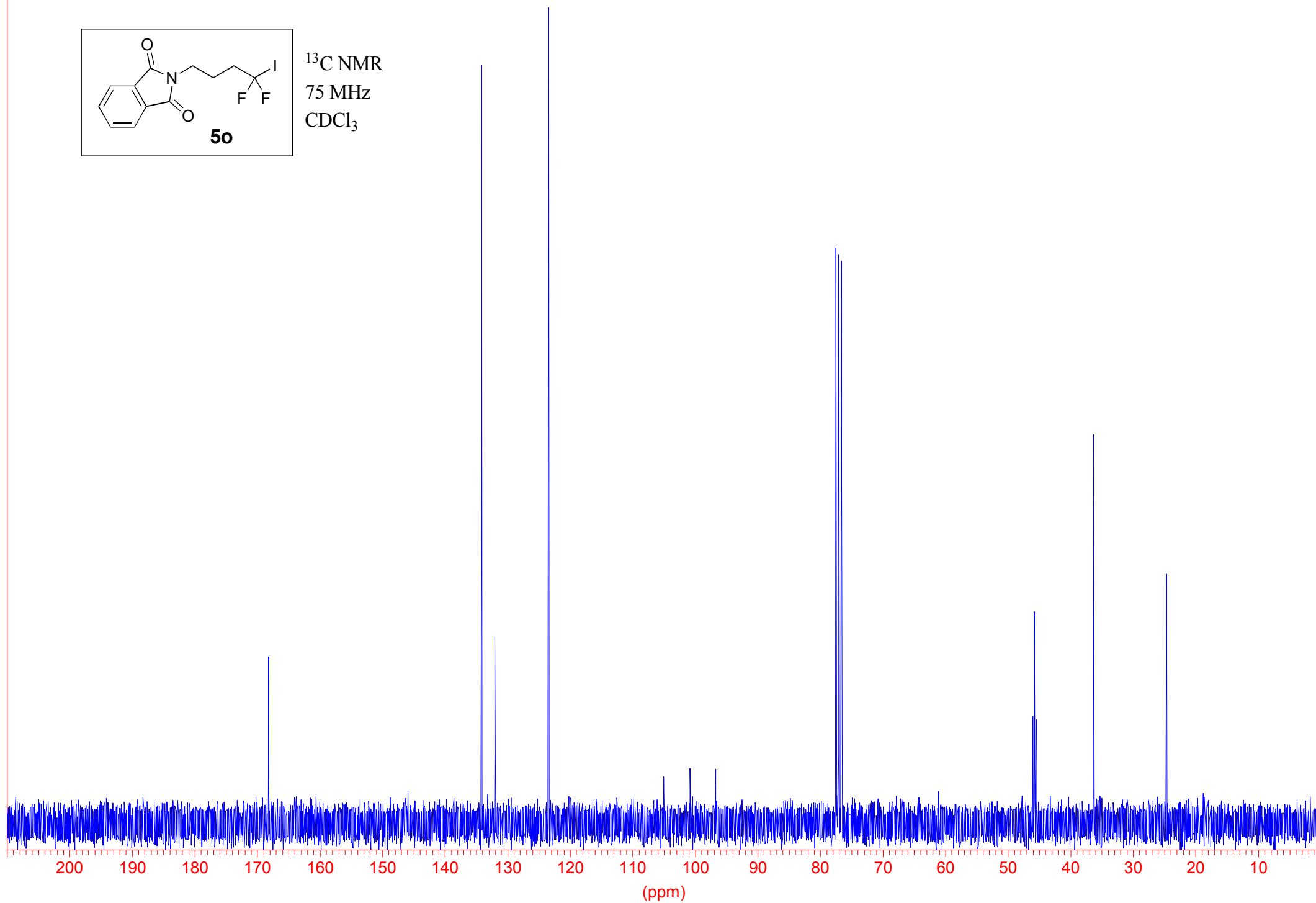
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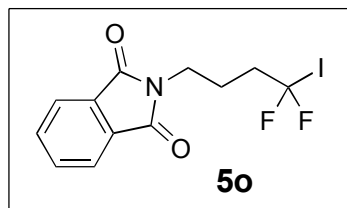




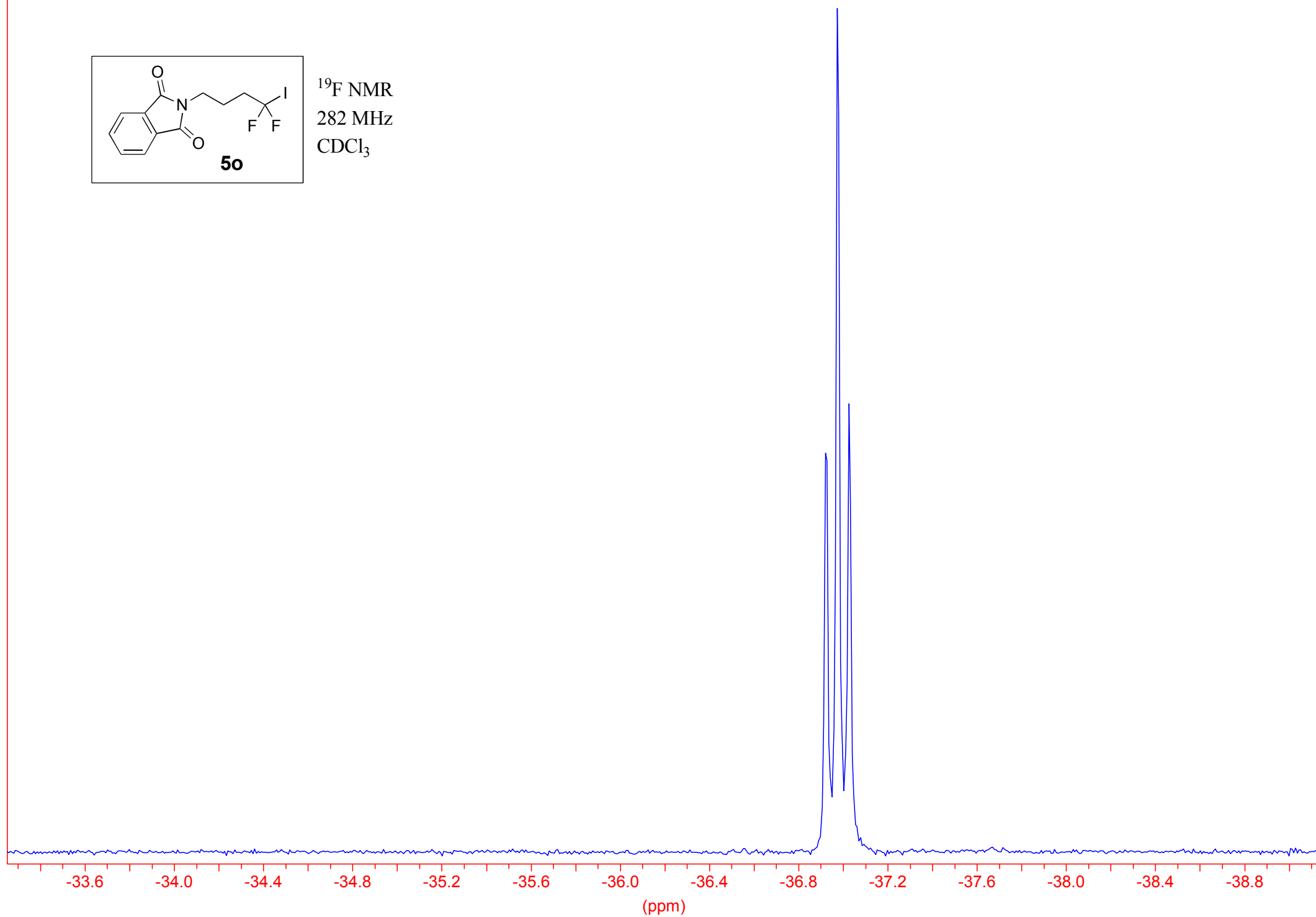


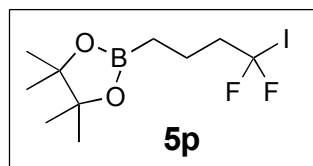
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 $\text{CDCl}_3$



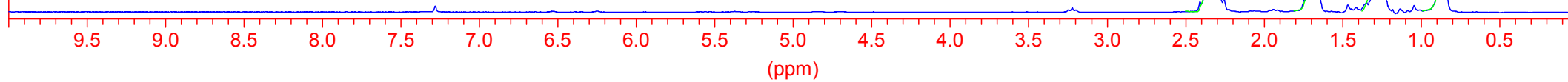


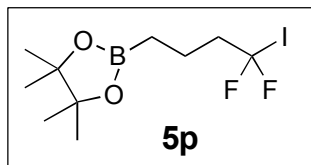
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282 MHz  
 $\text{CDCl}_3$



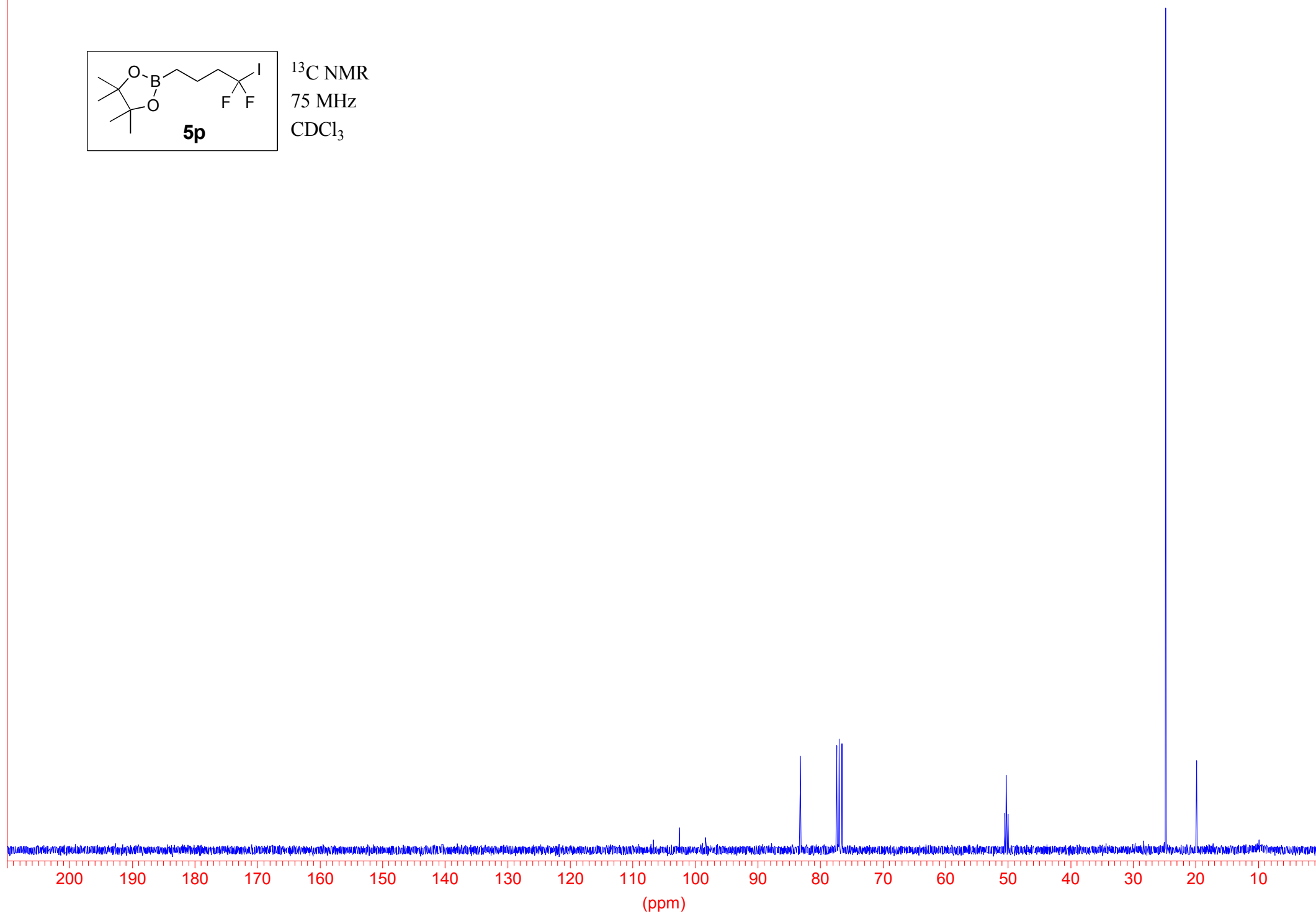


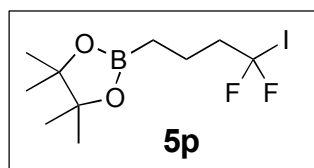
$^1\text{H}$  NMR  
300 MHz  
 $\text{CDCl}_3$



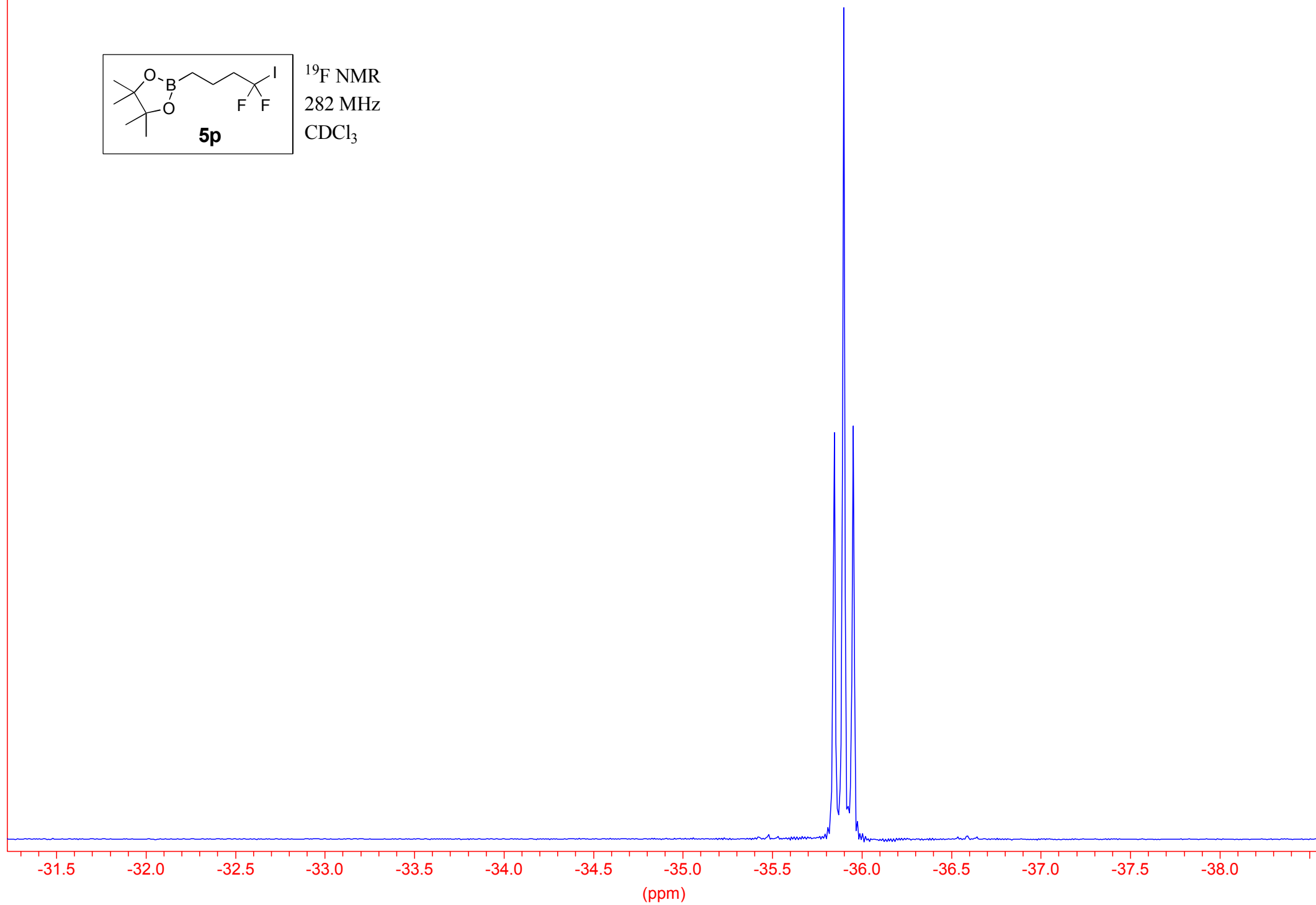


$^{13}\text{C}$  NMR  
75 MHz  
 $\text{CDCl}_3$

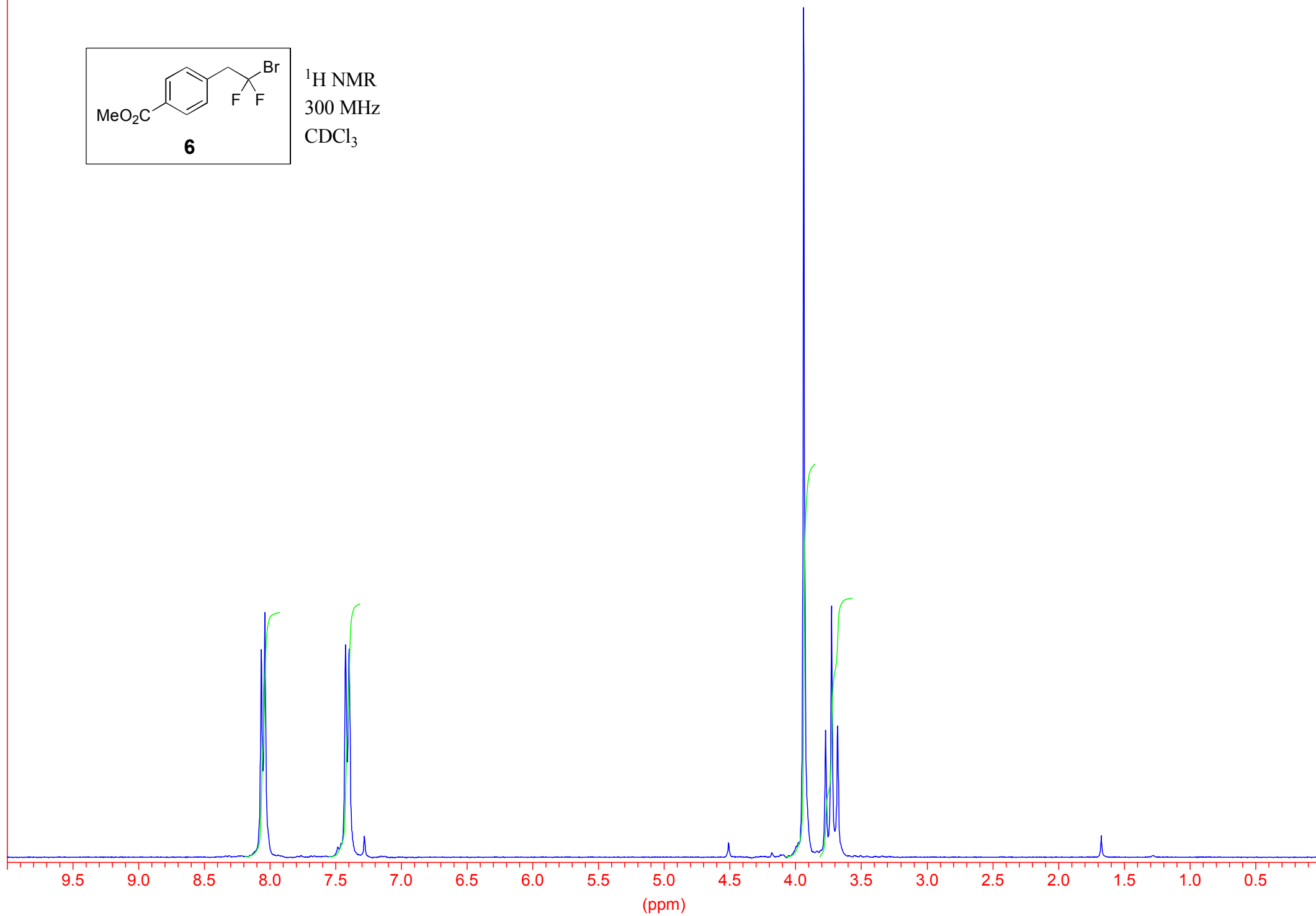
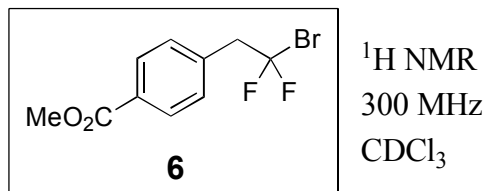


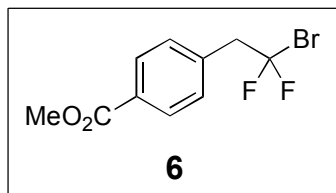


$^{19}\text{F}$  NMR  
282 MHz  
 $\text{CDCl}_3$

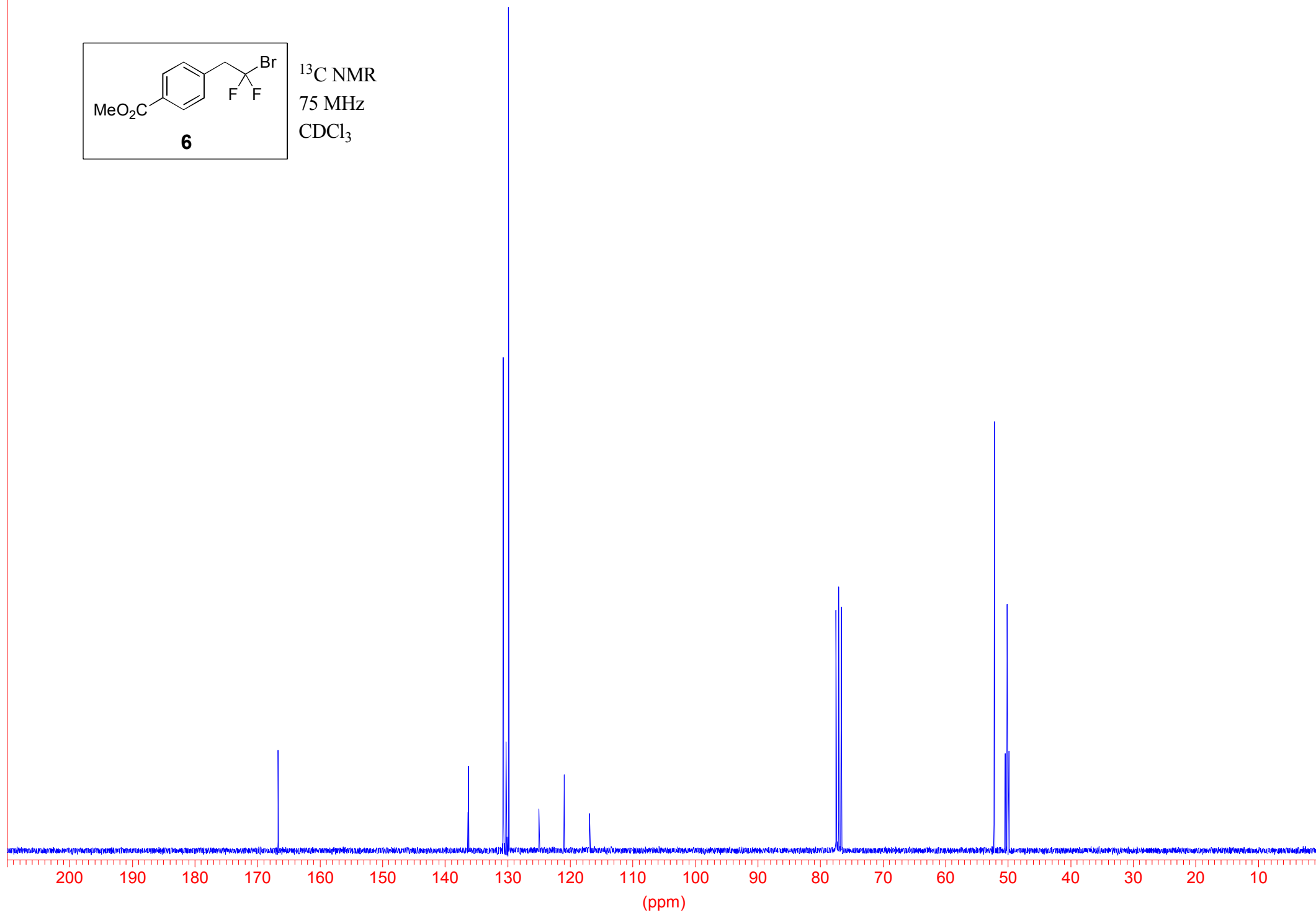


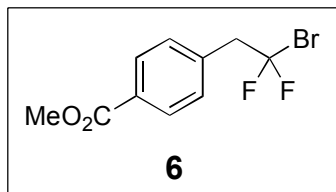




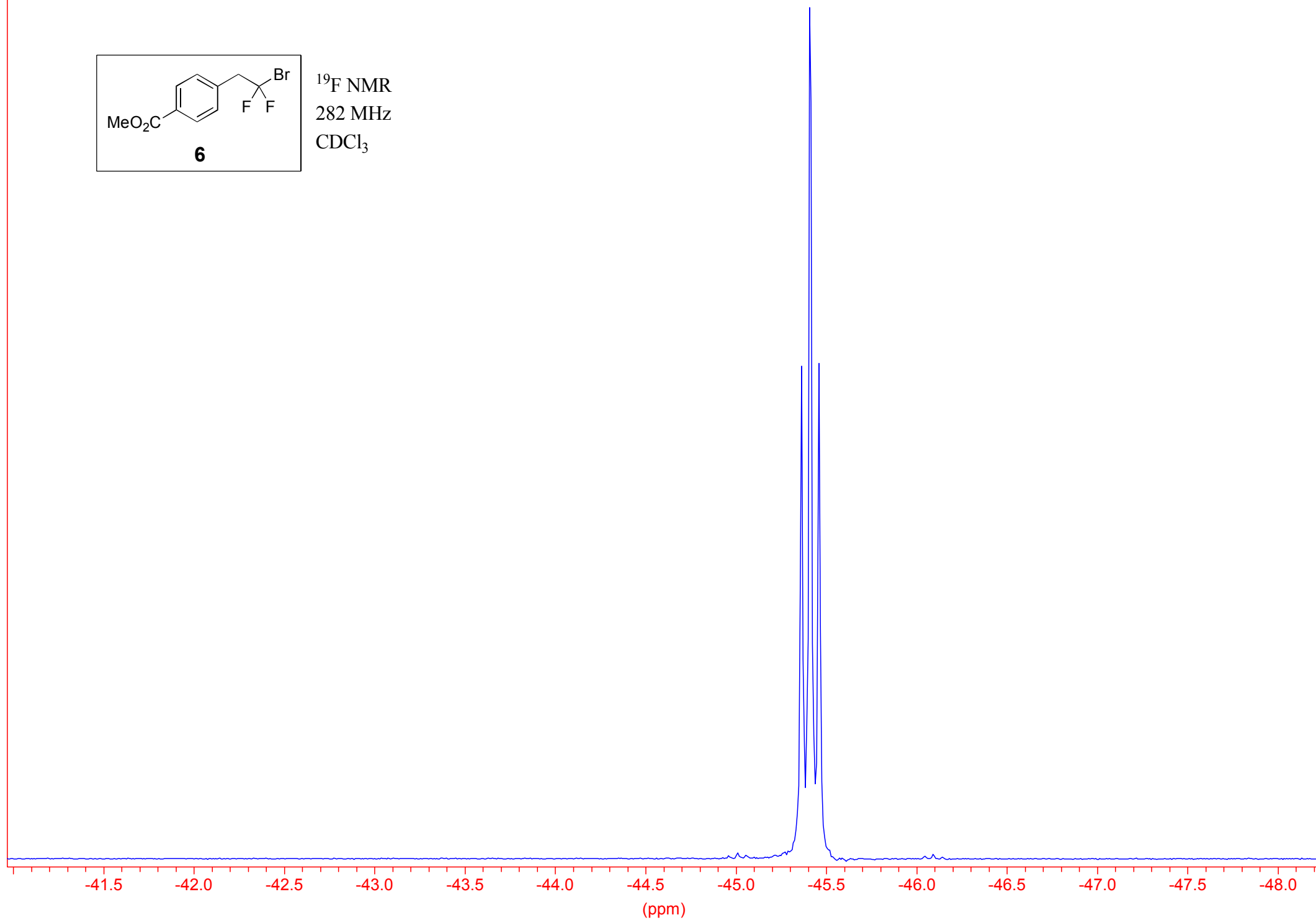


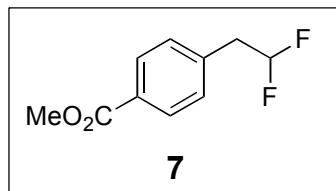
$^{13}\text{C}$  NMR  
75 MHz  
 $\text{CDCl}_3$



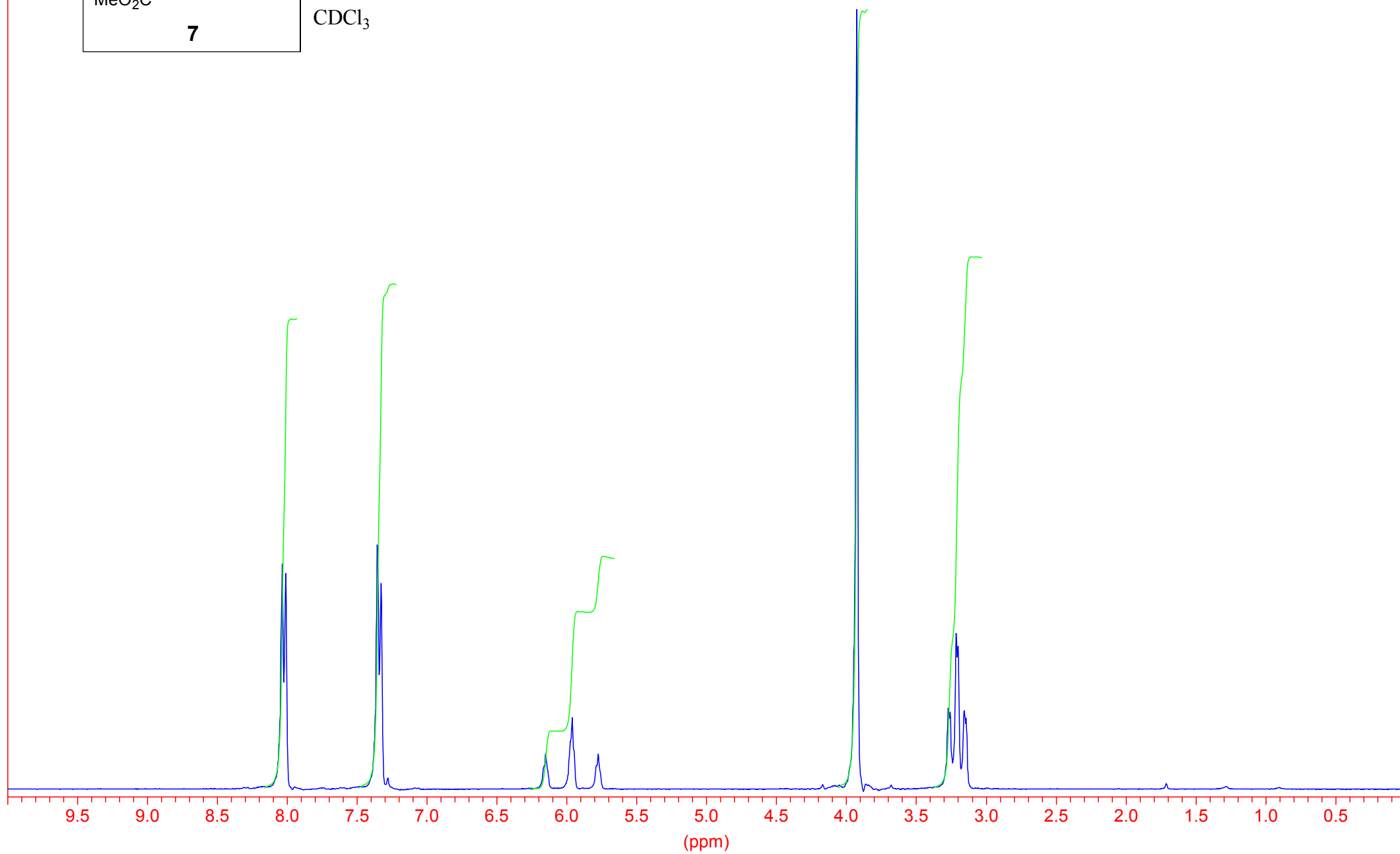


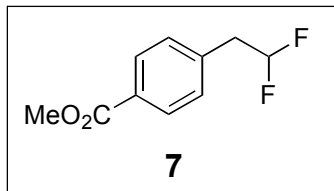
$^{19}\text{F}$  NMR  
282 MHz  
 $\text{CDCl}_3$



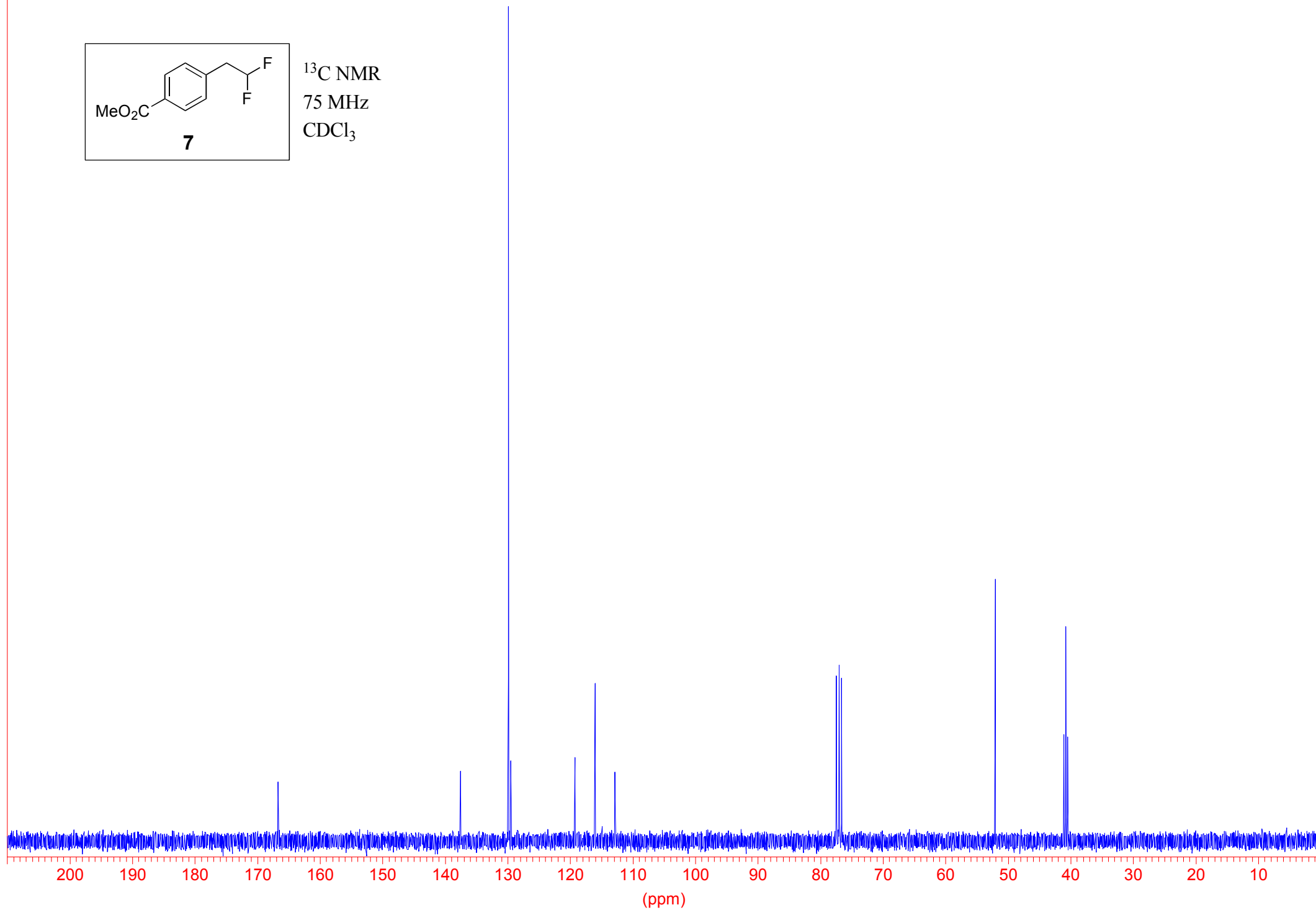


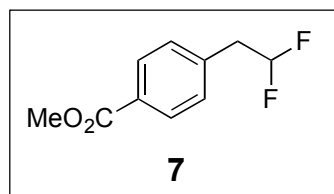
$^1\text{H}$  NMR  
300 MHz  
 $\text{CDCl}_3$





$^{13}\text{C}$  NMR  
75 MHz  
 $\text{CDCl}_3$





$^{19}\text{F}$  NMR  
282 MHz  
 $\text{CDCl}_3$

