

## Supporting Information

### Iodine-DMSO Promoted Divergent Reactivities of Acetylenes.

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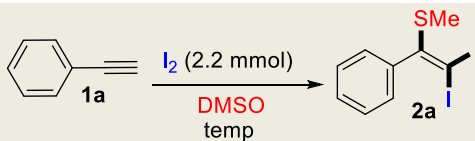
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## 1. General information

All chemicals were obtained from Sigma-Aldrich, Alfa Aesar and S. D. Fine chemicals and used as received. The progress of the reactions was monitored by thin-layer chromatography (TLC) on precoated silica-gel plates using Merck Silica Gel 60 F<sub>254</sub>, Cat. No. 1.05554.0007 and visualized by short-wave ultraviolet light as well as by treatment with I<sub>2</sub>. Column chromatography was performed by hand using silica-gel (100–200 mesh, Silicycle). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker-Avance DPX FT-NMR 500 and 400 MHz instruments. Chemical data for protons are reported in parts per million (ppm) downfield from tetramethylsilane and are referenced to the residual proton in the NMR solvent (CDCl<sub>3</sub>: 7.26 ppm). Carbon nuclear magnetic resonance spectra (<sup>13</sup>C NMR solvent CDCl<sub>3</sub>: 77.0 ppm) were recorded at 125 MHz or 100 MHz: chemical data for carbons are reported in parts per million (ppm, δ scale) down field from tetramethylsilane and are referenced to the carbon resonance of the solvent. ESI-MS and HRMS spectra were recorded on Agilent 1100 LC-Q-TOF and HRMS-6540-UHD machines respectively. IR spectra were recorded on Perkin-Elmer IR spectrophotometer with absorption band given in cm<sup>-1</sup>. Melting points of compounds were recorded with BUCHI (B-545) instrument.

## 2) Optimization tables:

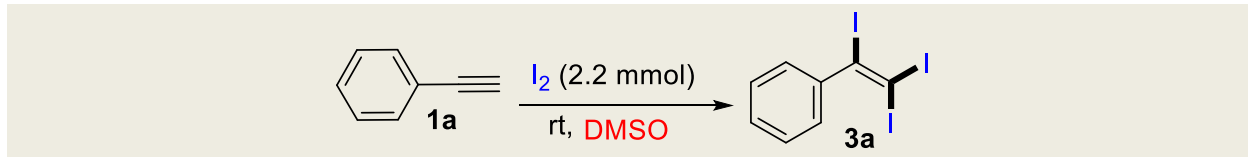
### Optimization table for (2,2-diiodo-1-phenylvinyl)(methyl)sulfane 2a:



entry	Reactant (mmol)	I <sub>2</sub> (mmol)	temp °C	%yield
1	1.0	1.0	rt	17
2	1.0	1.0	60	27
3	1.0	1.0	80	33
4	1.2	1.0	80	36
5	1.0	1.5	80	53
6	1.0	2.0	80	67
<b>7</b>	<b>1.0</b>	<b>2.2</b>	<b>80</b>	<b>79</b>
8	1.0	2.5	80	79

Reaction conditions: phenylacetylene **1a** (1.0 mmol), I<sub>2</sub> (2.2 mmol) in 3 mL of DMSO at 80 °C for 2 h,

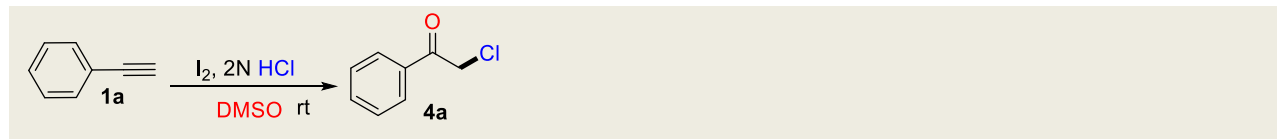
**Optimization table for (1,2,2-triiodovinyl)benzene 3a:**



entry	1 (mmol)	$I_2$ (mmol)	temp °C	%yield <b>3a</b>
1	1.0	1.0	rt	61
2	1.2	1.0	-	62
3	1.0	1.2	-	67
4	1.0	1.5	-	71
5	1.0	2.1	-	77
<b>6</b>	<b>1.0</b>	<b>2.2</b>	-	<b>81</b>
7	1.0	2.5	-	81

Reaction conditions: phenylacetylene **1a** (1.0 mmol),  $I_2$  (2.2 mmol) in 3 mL of DMSO at rt for 4 h

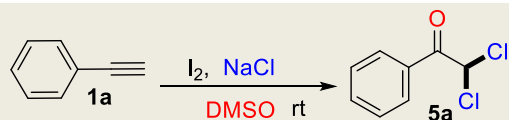
**Optimization table for 2-chloro-1-phenylethan-1-one 4a:**



entry	1 (mmol)	$I_2$ (mmol)	reagent	temp °C	%yield
1	1.0	1.0	HCl (2N,0.5ml)	rt	40
2	1.0	1.5	HCl (2N,0.5ml)	rt	46
3	1.0	2.0	HCl (2N,0.5ml)	rt	63
<b>4</b>	<b>1.0</b>	<b>2.2</b>	<b>HCl (2N,0.5ml)</b>	<b>rt</b>	<b>72</b>
5	1.0	2.5	HCl (2N,0.5ml)	rt	73
6	1.0	2.2	HCl (3N,0.5ml)	rt	68

Reaction condition: phenylacetylene **1a** (1.0 mmol),  $I_2$  (2.2 mmol), 2N HCl (0.5 mL) in 3 mL of DMSO at rt for 16 h

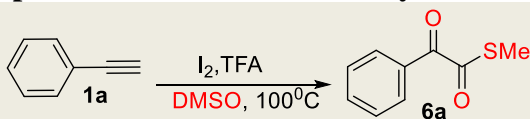
**Optimization table for 2,2-dichloro-1-phenylethan-1-one 5a:**



entry	1 (mmol)	$I_2$ (mmol)	reagent	Temp °C	%yield
1	1.0	1.0	HCl (2N)	rt	16
2	1.0	1.0	NaCl(1.0 mmol)	rt	34
3	1.0	1.5	NaCl(1.0 mmol)	rt	46
4	1.0	2.0	NaCl(1.0 mmol)	rt	53
5	1.0	2.2	NaCl(1.0 mmol)	rt	57
<b>6</b>	<b>1.0</b>	<b>2.2</b>	<b>NaCl(2.0mmol)</b>	<b>rt</b>	<b>78</b>
7	1.0	2.5	NaCl(2.0 mmol)	rt	78
8	1.0	2.5	kCl(2.0 mmol)	rt	23

Reaction conditions: phenylacetylene **1a** (1.0 mmol),  $I_2$  (2.2 mmol), NaCl (2.0 mmol) in 3 mL of DMSO at rt for 4 h.

**Optimization table for S-methyl 2-oxo-2-phenylethanethioate 6a:**



entry	1 (mmol)	$I_2$ (mmol)	reagent	Temp °C	%yield
1	1.0	1.0	TFA	rt	10
2	1.0	1.0	TFA	50	13
3	1.0	1.0	TFA	80	17
4	1.0	1.5	TFA	100	23
5	1.0	2	TFA	100	57
<b>6</b>	<b>1.0</b>	<b>2.2</b>	<b>TFA</b>	<b>100</b>	<b>69</b>
7	1.0	2.5	TFA	100	69
8	1.0	2.2	AcOH	100	27

Reaction condition: phenylacetylene **1a** (1.0 mmol),  $I_2$  (2.2 mmol), TFA (1.0 mmol) in 3 mL of DMSO at 100 °C for 4 h.

### 3. General procedure

#### a) For the synthesis of 2a-2k:

A reaction vessel was charged with arylacetylene **1** (1.0 mmol) and Iodine (2.2 mmol) in 3 mL of DMSO solvent. The reaction mixture was stirred at 80 °C for 2h. After completion of the reaction, confirmed by thin layer chromatography, the reaction mixture was extracted with ethyl acetate and ice chilled water, quenched with saturated solution of Na<sub>2</sub>SO<sub>3</sub> and dried with Na<sub>2</sub>SO<sub>4</sub> followed by removal of solvent under reduced pressure to afford crude product, which was purified by column chromatography on silica gel (100-200#) using hexane as an eluent. It afforded the corresponding products **2a-2k** in good yields (69-79%).

#### b) For the synthesis of 3a-3k:

A reaction vessel was charged with arylacetylene **1** (1.0 mmol), I<sub>2</sub> (2.2 mmol) and liquid ammonia (0.746 mmol) in 3 mL of DMSO solvent. The reaction mixture was stirred at room temperature for 4 h. After completion of the reaction, confirmed by thin layer chromatography, the reaction mixture was extracted with ethyl acetate and ice chilled water, quenched with saturated solution of Na<sub>2</sub>SO<sub>3</sub> and dried with Na<sub>2</sub>SO<sub>4</sub>, followed by removal of solvent under reduced pressure. The crude mixture was purified by column chromatography on silica gel (100-200#) using hexane as an eluent. It afforded the corresponding products **3a-3k** in good yields (67-83%).

#### c) For the synthesis of 4a-4k:

A reaction vessel was charged with arylacetylene **1** (1.0 mmol), I<sub>2</sub> (2.2 mmol) and HCl (2N, 0.5 ml) in 3 mL of DMSO solvent. The reaction mixture was stirred at room temperature for 16 h. After completion of the reaction, confirmed by thin layer chromatography, the reaction mixture was extracted with ethyl acetate and ice chilled water, quenched with saturated solution of Na<sub>2</sub>SO<sub>3</sub> and dried with Na<sub>2</sub>SO<sub>4</sub>, followed by removal of solvent under reduced pressure. The crude mixture was purified by column chromatography on silica gel (100-200#) using hexane and ethyl acetate (9.8:0.2) as an eluent. It afforded the corresponding products **4a-4k** in good yields (67-79%).

#### d) For the synthesis of 5a-5k:

A reaction vessel was charged with arylacetylene **1** (1 mmol), I<sub>2</sub> (2.2 mmol) and NaCl (2 mmol) in 2 mL of DMSO solvent. The reaction mixture was stirred at room temperature for 4 h. After completion of the reaction, confirmed by thin layer chromatography, the reaction mixture was

extracted with ethyl acetate and ice chilled water, quenched with saturated solution of Na<sub>2</sub>SO<sub>3</sub> and dried with Na<sub>2</sub>SO<sub>4</sub>, followed by removal of solvent under reduced pressure. The crude mixture was purified by column chromatography on silica gel (100-200#) using hexane and ethyl acetate (9.8:0.2) as an eluent. It afforded the corresponding products **5a-5k** in good yields (66-83%).

**(e) For the synthesis of 6a-6f:**

A reaction vessel was charged with arylacetylene **1** (1 mmol), I<sub>2</sub> (2.2 mmol) and TFA (1.0 mmol) in 3 mL of DMSO solvent. The reaction mixture was stirred at 100 °C for 4h. After completion of the reaction, confirmed by thin layer chromatography, the reaction mixture was extracted with ethyl acetate and ice chilled water, quenched with saturated solution of Na<sub>2</sub>SO<sub>3</sub> and dried with Na<sub>2</sub>SO<sub>4</sub>, followed by removal of solvent under reduced pressure. The crude mixture was purified by column chromatography on silica gel (100-200#) using hexane and ethyl acetate (9.9:0.1) as an eluent. It afforded the corresponding product **6a-6f** in good (64-72%).

**Gram Scale Reaction.**

We have also conducted the same reaction in gram scale by using arylacetylenes **1** (9.8 mmol), I<sub>2</sub> (21.6 mmol) and TFA (9.8 mmol) in 30 mL of DMSO solvent. The reaction mixture was stirred at 100 °C for 8h and isolated the desired product **6a** in 57% yield.

**(f) For the synthesis of A<sup>[1]</sup>:** TO a reaction mixture of phenylacetylene **1a** (0.3 mmol) and TIBA (0.36 mmol), PIDA (0.3 mmol) was added in portions over a period of 20 min in CH<sub>3</sub>CN (3 mL), and the reaction mixture was stirred at room temperature for 24 h. The reaction progress was monitored by TLC. Upon completion, the reaction mixture was quenched with saturated aqueous solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, washed with brine, extracted with ethyl acetate, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration, the solvent was removed under reduced pressure to afford the crude product, which was purified by column chromatography using hexane.

**4. Procedures of control experiments:**

**Control experiment with iodoethynylbenzene A:**

**Procedure for experiment 1:** A reaction vessel was charged with iodoethynylbenzene **A** (1.0 mmol) and I<sub>2</sub> (2.2 mmol) in 3 mL of DMSO solvent and stirred 80 °C for 2h. After completion of the reaction, confirmed by thin layer chromatography, the reaction mixture was extracted with ethyl acetate and ice chilled water, quenched with saturated solution of Na<sub>2</sub>SO<sub>3</sub> and dried with Na<sub>2</sub>SO<sub>4</sub>, followed by removal of solvent under reduced pressure. The crude mixture was purified by column

chromatography on silica gel (100-200#) using hexane as an eluent. It afforded the corresponding product **2a** in good (83%).

**Procedure for experiment 2:** A reaction vessel was charged with iodoethynylbenzene **A** (1mmol) and I<sub>2</sub> (2.2 mmol) in 3mL of DMSO solvent and stirred at rt for 4h. After completion of the reaction, confirmed by thin layer chromatography, the reaction mixture was extracted with ethyl acetate and ice chilled water, quenched with saturated solution of Na<sub>2</sub>SO<sub>3</sub> and dried with Na<sub>2</sub>SO<sub>4</sub>, followed by removal of solvent under reduced pressure. The crude mixture was purified by column chromatography on silica gel (100-200#) using hexane as an eluent. It afforded the corresponding product **3a** in good (86%).

**Procedure for experiment 3:** A reaction vessel was charged with iodoethynylbenzene **A** (1mmol), I<sub>2</sub> (2.2 mmol) and HCl (2N, 0.5ml) in 3 mL of DMSO solvent and stirred at rt for 16 h. After completion of the reaction, confirmed by thin layer chromatography, the reaction mixture was extracted with ethyl acetate and ice chilled water, quenched with saturated solution of Na<sub>2</sub>SO<sub>3</sub> and dried with Na<sub>2</sub>SO<sub>4</sub>, followed by removal of solvent under reduced pressure. The crude mixture was purified by column chromatography on silica gel (100-200#) using hexane and ethyl acetate (9.8:0.2) as an eluent. It afforded the corresponding product **4a** in good (77%).

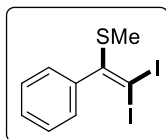
**Procedure for experiment 4:** A reaction vessel was charged with iodoethynylbenzene **A** (1mmol), I<sub>2</sub> (2.2 mmol) and NaCl (2.0 mmol) in 3mL of DMSO solvent and stirred at rt for 4h. After completion of the reaction, confirmed by thin layer chromatography, the reaction mixture was extracted with ethyl acetate and ice chilled water, quenched with saturated solution of Na<sub>2</sub>SO<sub>3</sub> and dried with Na<sub>2</sub>SO<sub>4</sub>, followed by removal of solvent under reduced pressure. The crude mixture was purified by column chromatography on silica gel (100-200#) using hexane and ethyl acetate (9.8:0.2) as an eluent. It afforded the corresponding product **5a** in good (81%).

**Procedure for experiment 5:** A reaction vessel was charged with iodoethynylbenzene **A** (1.0 mmol), I<sub>2</sub> (2.2 mmol) and TFA (1.0 mmol) in 3mL of DMSO solvent and stirred at 100°C for 4 h. After completion of the reaction, confirmed by thin layer chromatography, the reaction mixture was extracted with ethyl acetate and ice chilled water, quenched with saturated solution of Na<sub>2</sub>SO<sub>3</sub> and dried with Na<sub>2</sub>SO<sub>4</sub>, followed by removal of solvent under reduced pressure. The crude mixture was purified by column chromatography on silica gel (100-200#) using hexane and ethyl acetate (9.9:0.1) as an eluent. It afforded the corresponding product **6a** in good (74%).

**Procedure for experiment 6:** A reaction vessel was charged with phenylacetylene **1a** (1.0 mmol), I<sub>2</sub> (1 mmol) and TFA (1 mmol) in 3 mL of DMSO solvent and stirred at 100 °C for 4 h. It was found that both E & Z isomers of **8** were formed, with collective yield of 71%.

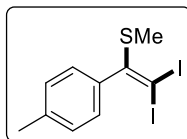
## 6. Characterization data for compounds

### 2a. (2,2-diiodo-1-phenylvinyl)(methyl)sulfane



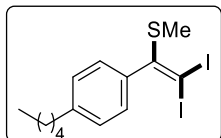
Yellow solid (311 mg, 79% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.47 – 7.34 (m, 3H), 7.21 – 7.12 (m, 2H), 1.91 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.13, 141.00, 128.78, 128.55, 128.52, 19.32, 6.90. IR (CHCl<sub>3</sub>, cm<sup>-1</sup>) ν; 3410, 2920, 2850, 1649, 1422, 1019, 771. HRMS (TOF) m/z [M + H]<sup>+</sup> Calcd for C<sub>9</sub>H<sub>9</sub>I<sub>2</sub>S 402.8509 found 402.8513.

### 2b. (2,2-diiodo-1-(p-tolyl)vinyl)(methyl)sulfane



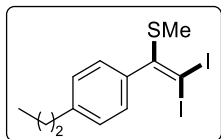
Yellow solid (279 mg, 78% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.22 (d, *J* = 7.9 Hz, 2H), 7.06 (d, *J* = 8.1 Hz, 2H), 2.38 (s, 3H), 1.91 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.30, 138.53, 137.98, 129.48, 128.39, 21.42, 19.45, 6.87. IR (CHCl<sub>3</sub>, cm<sup>-1</sup>) ν; 3386, 2919, 2850, 1659, 1649, 1218, 771. HRMS (TOF) m/z [M + H]<sup>+</sup> Calcd for C<sub>10</sub>H<sub>11</sub>I<sub>2</sub>S 416.8665 found 416.8661.

### 2c. (2,2-diiodo-1-(4-pentylphenyl)vinyl)(methyl)sulfane



Yellow semi solid (184 mg, 74% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.22 (d, *J* = 8.1 Hz, 2H), 7.07 (d, *J* = 8.1 Hz, 2H), 2.68 – 2.58 (m, 2H), 1.91 (s, 3H), 1.68 – 1.59 (m, 2H), 1.38 – 1.30 (m, 4H), 0.90 (t, *J* = 6.9 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.37, 143.56, 138.14, 128.72, 128.35, 35.76, 31.53, 30.81, 22.50, 19.42, 14.02, 6.76. IR (CHCl<sub>3</sub>, cm<sup>-1</sup>) ν; 3378, 2923, 2853, 1606, 1430, 1020, 728, 771. HRMS (TOF) m/z [M + H]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>19</sub>I<sub>2</sub>S 472.9291 found 472.9297.

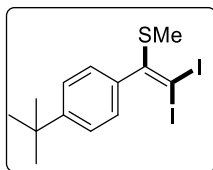
### 2d. (2,2-diiodo-1-(4-propylphenyl)vinyl)(methyl)sulfane



Yellow liquid (241 mg, 81% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.22 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.1 Hz, 2H), 2.60 (dd, *J* = 15.5, 7.8 Hz, 2H), 1.91 (s, 3H), 1.66 (dt, *J* = 14.3, 7.2 Hz, 2H), 0.99 – 0.89 (m, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 143.25 (s), 138.15 (s), 128.82 (s), 128.36 (s), 128.29 (s), 37.81 (s), 24.24 (s), 19.46 (s), 13.79 (s), 6.80 (s). IR (CHCl<sub>3</sub>, cm<sup>-1</sup>) ν; 3328, 2919, 2809, 1598, 1448, 1067, 1260, 765. HRMS (TOF) m/z [M + Na]<sup>+</sup> Calcd for C<sub>12</sub>H<sub>14</sub>I<sub>2</sub>NaS 466.8798 found 466.8805.

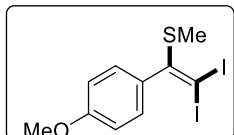
### 2e. (1-(4-(tert-butyl)phenyl)-2,2-diiodovinyl)(methyl)sulfane





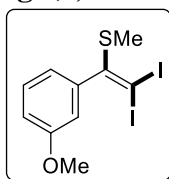
Yellow oil (229 mg, 79% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 – 7.38 (m, 2H), 7.09 (d,  $J = 8.4$  Hz, 2H), 1.90 (s, 3H), 1.34 (s, 9H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.34, 151.70, 137.88, 128.15, 125.58, 34.77, 31.29, 19.41, 6.85. IR ( $\text{CHCl}_3$ ,  $\text{cm}^{-1}$ )  $\nu$ , 3401, 3323, 2834, 1577, 1390, 1050, 788, 709. HRMS (TOF)  $m/z$   $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{13}\text{H}_{17}\text{I}_2\text{S}$  458.9135 found 458.9127.

**2f. (2,2-diiodo-1-(4-methoxyphenyl)vinyl)(methyl)sulfane**



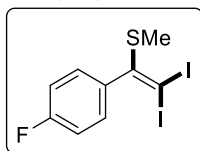
Yellow semi solid (268 mg, 82% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.13 – 7.04 (m, 2H), 6.96 – 6.87 (m, 2H), 3.84 (s, 3H), 1.92 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.59, 152.11, 133.16, 130.00, 114.12, 55.31, 19.53, 7.33. IR ( $\text{CHCl}_3$ ,  $\text{cm}^{-1}$ )  $\nu$ , 3407, 3361, 2927, 2855, 1594, 1427, 1046, 692. HRMS (TOF)  $m/z$   $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{10}\text{H}_{11}\text{I}_2\text{OS}$  432.8614 found 432.8612.

**2g. (2,2-diiodo-1-(3-methoxyphenyl)vinyl)(methyl)sulfane**



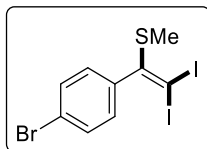
Yellow oil (255 mg, 78% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (t,  $J = 7.9$  Hz, 1H), 6.92 – 6.87 (m, 1H), 6.74 (d,  $J = 7.6$  Hz, 1H), 6.71 – 6.68 (m, 1H), 3.82 (s, 3H), 1.93 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.83, 151.87, 142.12, 129.83, 120.90, 114.39, 113.85, 55.46, 19.36, 7.13. IR ( $\text{CHCl}_3$ ,  $\text{cm}^{-1}$ )  $\nu$ , 3377, 3061, 2919, 2831, 1594, 1433, 1011, 732. HRMS (TOF)  $m/z$   $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{10}\text{H}_{11}\text{I}_2\text{OS}$  432.8614 found 432.8618.

**2h. (1-(4-fluorophenyl)-2,2-diiodovinyl)(methyl)sulfane**



Yellow liquid (255 mg, 73% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.21 – 7.04 (m, 4H), 1.92 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.47 (d,  $J = 249.2$  Hz), 151.08 (s), 136.86 (d,  $J = 3.5$  Hz), 130.44 (d,  $J = 8.3$  Hz), 115.95 (d,  $J = 21.8$  Hz), 19.39 (s), 8.18 (s). IR ( $\text{CHCl}_3$ ,  $\text{cm}^{-1}$ )  $\nu$ , 3584, 3386, 2919, 2849, 1600, 1496, 1223, 1155, 839, 811.

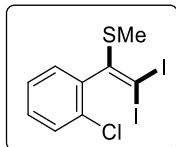
**2i. (1-(4-bromophenyl)-2,2-diiodovinyl)(methyl)sulfane**



Brown solid (190 mg, 71% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59 (d,  $J = 8.4$  Hz, 2H), 7.09 (d,  $J = 8.4$  Hz, 2H), 1.95 (s, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  150.84 (s), 139.73 (s), 132.11 (s), 130.16

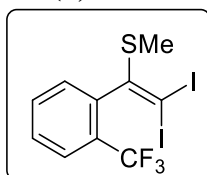
(s), 122.80 (s), 19.36 (s), 8.14 (s).IR (CHCl<sub>3</sub>, cm<sup>-1</sup>)  $\nu$ , 3386, 2920, 2850, 1649, 1584, 1478, 1313, 1011, 825, 768, HRMS(TOF) m/z [M + H]<sup>+</sup> Calcd for C<sub>9</sub>H<sub>8</sub>BrI<sub>2</sub>S480.7614 found 480.7609

**2j. (1-(2-chlorophenyl)-2,2-diiodovinyl)(methyl)sulfane**



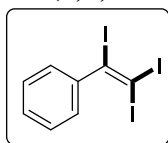
Yellow oil (233 mg, 73% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.49 – 7.42 (m, 1H), 7.36 – 7.32 (m, 2H), 7.18 – 7.12 (m, 1H), 1.96 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  149.25 (s), 139.93 (s), 132.40 (s), 130.05 (s), 130.01 (s), 127.35 (s), 18.49 (s), 8.17 (s).IR (CHCl<sub>3</sub>, cm<sup>-1</sup>)  $\nu$ , 3377, 2920, 2849, 1463, 1427, 1060, 748, 772, 665. HRMS (TOF) m/z [M + H]<sup>+</sup> Calcd for C<sub>9</sub>H<sub>8</sub>ClI<sub>2</sub>S436.8119 found 436.8114.

**2k. (2,2-diiodo-1-(2-(trifluoromethyl)phenyl)vinyl)(methyl)sulfane**



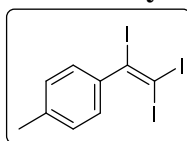
Yellow solid (190 mg, 69% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.77 (d, *J* = 7.9 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 1H), 7.23 (d, *J* = 7.7 Hz, 1H), 1.95 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  148.71 (s), 139.35 (s), 132.46 (s), 129.85 (d, *J* = 183.4 Hz), 128.02 (s), 127.78 (s), 127.13 (dd, *J* = 9.5, 4.8 Hz), 123.30 (d, *J* = 274.6 Hz), 18.99 (s), 6.65 (s).IR (CHCl<sub>3</sub>, cm<sup>-1</sup>)  $\nu$ , 3385, 2925, 2850, 1443, 1313, 1172, 1130, 1035, 767. HRMS (TOF) m/z [M + H]<sup>+</sup> Calcd for C<sub>10</sub>H<sub>8</sub>F<sub>3</sub>I<sub>2</sub>S470.8383 found 470.8381.

**3a. (1,2,2-triiodovinyl)benzene<sup>[1]</sup>**



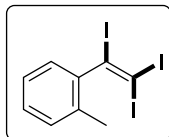
Pale Yellow solid (382 mg, 81% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.44 – 7.32 (m, 3H), 7.32 – 7.27 (m, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  147.71, 128.75, 128.62, 127.42, 112.47, 22.50.

**3b. 1-methyl-4-(1,2,2-triiodovinyl)benzene<sup>[1]</sup>**



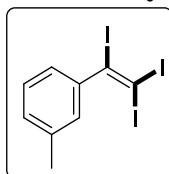
Pale yellow solid (354 mg, 83% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.19 (s, 4H), 2.37 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  144.96, 138.87, 129.26, 127.38, 112.86, 21.97, 21.77.

**3c. 1-methyl-2-(1,2,2-triiodovinyl)benzene**



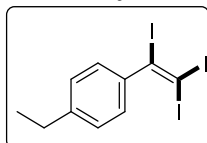
Yellow solid (346 mg, 81% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30 – 7.20 (m, 2H), 7.16 – 7.10 (m, 2H), 2.24 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  146.83 (s), 133.91 (s), 130.84 (s), 129.06 (s), 126.95 (s), 126.45 (s), 113.07 (s), 23.90 (s), 19.71 (s).

**3d. 1-methyl-3-(1,2,2-triiodovinyl)benzene**



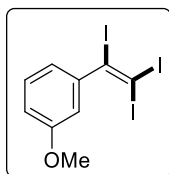
Pale yellow solid (333 mg, 78% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28 (dd,  $J = 10.1, 4.8$  Hz, 1H), 7.16 (d,  $J = 7.6$  Hz, 1H), 7.09 (d,  $J = 9.9$  Hz, 2H), 2.39 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  147.58 (s), 138.41 (s), 129.56 (s), 128.47 (s), 127.91 (s), 124.46 (s), 112.78 (s), 22.35 (s), 21.45 (s).

**3e. 1-ethyl-4-(1,2,2-triiodovinyl)benzene**



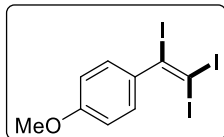
Yellow semi solid (290 mg, 74% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.22 (s, 4H), 2.68 (q,  $J = 7.6$  Hz, 2H), 1.28 (t,  $J = 7.6$  Hz, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  145.06 (s), 145.03 (s), 128.05 (s), 127.43 (s), 113.01 (s), 28.73 (s), 22.34 (s), 15.17 (s).

**3f. 1-methoxy-3-(1,2,2-triiodovinyl)benzene**



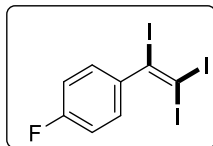
Pale yellow solid (317 mg, 82% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29 (d,  $J = 8.0$  Hz, 1H), 6.93 – 6.83 (m, 2H), 6.82 – 6.78 (m, 1H), 3.85 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.40, 148.80, 129.65, 119.79, 114.70, 112.81, 112.14, 55.43, 22.31.

**3g. 1-methoxy-4-(1,2,2-triiodovinyl)benzene<sup>[1]</sup>**



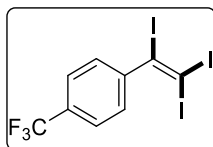
Black solid (325 mg, 84% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25 (d,  $J = 8.7$  Hz, 2H), 6.89 (d,  $J = 8.7$  Hz, 2H), 3.85 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.68 (s), 140.24 (s), 129.08 (s), 113.89 (s), 112.84 (s), 55.33 (s), 22.31 (s).

**3h. 1-fluoro-4-(1,2,2-triiodovinyl)benzene**



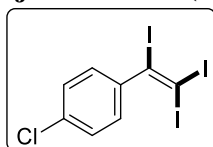
Pale yellow solid (287 mg, 69% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 – 7.24 (m, 2H), 7.08 (m,  $J = 8.8, 5.9, 2.5$  Hz, 2H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  162.37 (d,  $J = 250.0$  Hz), 143.80 (d,  $J = 3.5$  Hz), 129.51 (d,  $J = 8.5$  Hz), 115.75 (d,  $J = 22.0$  Hz), 111.24 (s), 23.61 (s).

**3i. 1-(trifluoromethyl)-4-(1,2,2-triiodovinyl)benzene**



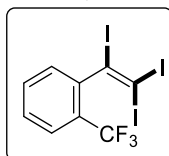
Red solid (229 mg, 71% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 (d,  $J = 8.1$  Hz, 2H), 7.41 (d,  $J = 8.1$  Hz, 2H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  150.94 (s), 130.73 (s), 127.89 (s), 125.74 (dd,  $J = 7.5, 3.8$  Hz), 123.75 (d,  $J = 272.5$  Hz), 110.07 (s), 23.56 (s).

**3j. 1-chloro-4-(1,2,2-triiodovinyl)benzene**



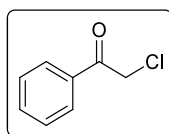
Yellow solid (273 mg, 72% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 – 7.34 (m, 2H), 7.27 – 7.20 (m, 2H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.11, 134.71, 128.94, 128.91, 110.89, 23.42.

**3k. 1-(trifluoromethyl)-2-(1,2,2-triiodovinyl)benzene**



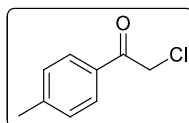
Brown solid (216 mg, 67% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 (d,  $J = 7.9$  Hz, 1H), 7.63 (t,  $J = 7.5$  Hz, 1H), 7.51 (t,  $J = 7.7$  Hz, 1H), 7.32 – 7.26 (m, 1H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  145.71 (d,  $J = 1.6$  Hz), 132.49 (s), 130.44 (s), 129.80 (s), 129.05 (d,  $J = 2.4$  Hz), 127.06 (q,  $J = 4.9$  Hz), 126.22 (d,  $J = 31.1$  Hz), 123.40 (d,  $J = 274.4$  Hz), 25.96 (s).

**4a. 2-chloro-1-phenylethanone<sup>[3]</sup>**



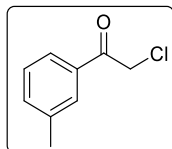
Light yellow oil (109 mg, 72%);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (dd,  $J = 8.2, 1.0$  Hz, 2H), 7.65 (dd,  $J = 10.5, 4.3$  Hz, 1H), 7.52 (t,  $J = 7.7$  Hz, 2H), 4.74 (s, 2H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  191.12 (s), 134.31 (s), 134.01 (s), 128.92 (s), 128.55 (s), 45.96 (s).

**4b. 2-chloro-1-(p-tolyl)ethanone<sup>[4]</sup>**



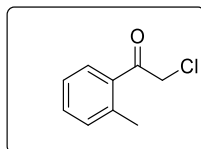
White solid (114 mg, 79% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.14 – 8.05 (m, 2H), 7.70 – 7.62 (m, 2H), 7.53 (dd,  $J = 11.0, 4.6$  Hz, 2H), 6.69 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  190.74 (s), 145.10 (s), 131.74 (s), 129.61 (s), 128.65 (s), 46.04 (s), 21.79 (s).

**4c. 2-chloro-1-(*m*-tolyl)ethanone**<sup>[5]</sup>



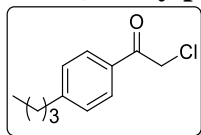
Yellow liquid (112 mg, 77% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 – 7.74 (m, 2H), 7.42 (m,  $J = 15.1, 7.6$  Hz, 2H), 4.73 (s, 2H), 2.45 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  191.27 (s), 138.87 (s), 134.85 (s), 134.26 (s), 129.00 (s), 128.78 (s), 125.71 (s), 46.23 (s), 21.38 (s).

**4d. 2-chloro-1-(*o*-tolyl)ethan-1-one**<sup>[5]</sup>



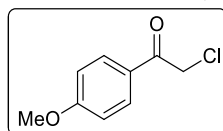
Colourless liquid (109 mg, 75% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 (d,  $J = 7.5$  Hz, 1H), 7.47 (t,  $J = 7.5$  Hz, 1H), 7.32 (t,  $J = 7.4$  Hz, 2H), 4.67 (s, 2H), 2.56 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  194.22 (s), 139.53 (s), 134.51 (s), 132.41 (s), 132.41 (s), 128.70 (s), 125.87 (s), 47.97 (s), 21.42 (s).

**4e. 1-(4-butylphenyl)-2-chloroethan-1-one**



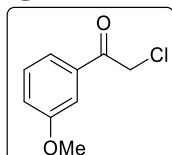
Colourless liquid (104 mg, 78% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (d,  $J = 8.3$  Hz, 2H), 7.33 (d,  $J = 8.3$  Hz, 2H), 4.72 (s, 2H), 2.77 – 2.68 (m, 2H), 1.66 (dd,  $J = 15.3, 7.5$  Hz, 2H), 1.45 – 1.33 (m, 2H), 0.96 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  190.76 (s), 149.96 (s), 132.02 (s), 128.95 (s), 128.70 (s), 45.84 (s), 35.76 (s), 33.12 (s), 22.30 (s), 13.84 (s).

**4f. 2-chloro-1-(4-methoxyphenyl)ethanone**<sup>[3]</sup>



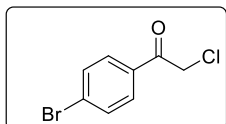
Yellow solid (106 mg, 76% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 – 7.93 (m, 2H), 7.03 – 6.93 (m, 2H), 4.67 (s, 2H), 3.91 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  189.69 (s), 164.18 (s), 130.96 (s), 127.18 (s), 114.11 (s), 55.60 (s), 45.74 (s).

**4g. 2-chloro-1-(3-methoxyphenyl)ethanone**<sup>[6]</sup>



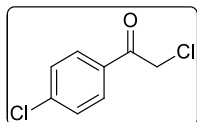
white solid (103 mg, 74% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59 – 7.50 (m, 2H), 7.43 (t,  $J = 7.9$  Hz, 1H), 7.19 (dd,  $J = 8.2, 2.5$  Hz, 1H), 4.74 (s, 2H), 3.90 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  190.94 (s), 160.01 (s), 135.53 (s), 129.91 (s), 121.00 (s), 120.56 (s), 112.76 (s), 55.55 (s), 46.18 (s).

**4h. 1-(4-bromophenyl)-2-chloroethan-1-one**<sup>[3]</sup>



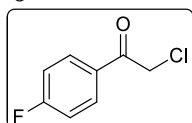
White solid (92mg, 71% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 – 7.80 (m, 2H), 7.73 – 7.60 (m, 2H), 4.68 (s, 2H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  190.28 (s), 132.90 (s), 132.30 (s), 130.07 (s), 129.40 (s), 45.62 (s).

**4i. 2-chloro-1-(4-chlorophenyl)ethanone**<sup>[5]</sup>



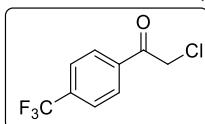
White solid (95 mg, 69% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 – 7.87 (m, 2H), 7.56 – 7.45 (m, 2H), 4.68 (s, 2H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  190.07 (s), 140.63 (s), 132.49 (s), 130.01 (s), 129.30 (s), 45.65 (s).

**4j. 2-chloro-1-(4-fluorophenyl)ethanone**<sup>[5]</sup>



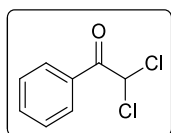
White solid (96 mg, 67% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 – 7.96 (m, 2H), 7.26 – 7.13 (m, 2H), 4.69 (s, 2H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  189.68 (s), 166.23 (d,  $J = 256.6$  Hz), 131.37 (d,  $J = 9.5$  Hz), 130.70 (d,  $J = 3.0$  Hz), 116.15 (d,  $J = 22.1$  Hz), 45.50 (s).

**4k. 2-chloro-1-(4-(trifluoromethyl)phenyl)ethan-1-one**<sup>[5]</sup>



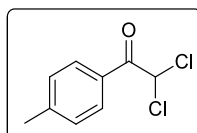
White solid (91 mg, 70% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.11 (d,  $J = 8.3$  Hz, 2H), 7.80 (d,  $J = 8.3$  Hz, 2H), 4.74 (s, 2H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  190.36 (s), 136.82 (s), 135.25 (q,  $J = 33.0$  Hz), 129.00 (s), 126.01 (q,  $J = 3.7$  Hz), 123.38 (d,  $J = 272.8$  Hz), 45.75 (s).

**5a. dichloro-1-phenylethanone**<sup>[7]</sup>



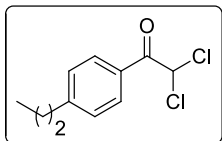
Yellow oil (143 mg, 78% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.12 (dd,  $J = 8.4, 1.1$  Hz, 2H), 7.68 (t,  $J = 7.4$  Hz, 1H), 7.55 (t,  $J = 7.8$  Hz, 2H), 6.71 (s, 1H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  185.92, 134.58, 131.34, 129.76, 128.94, 67.79.

**5b. 2,2-dichloro-1-(p-tolyl)ethanone**<sup>[7]</sup>



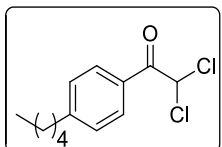
Colourless oil (144 mg, 83% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (d,  $J = 8.3$  Hz, 2H), 7.31 (d,  $J = 8.2$  Hz, 2H), 6.68 (s, 1H), 2.44 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  185.59, 145.86, 129.86, 129.66, 128.81, 67.87, 21.84.

**5c. 2,2-dichloro-1-(4-propylphenyl)ethanone**



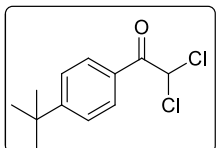
Yellow solid (126 mg, 79% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 (d,  $J = 8.3$  Hz, 2H), 7.32 (d,  $J = 8.3$  Hz, 2H), 6.67 (s, 1H), 2.81 – 2.60 (m, 2H), 1.80 – 1.62 (m, 2H), 0.96 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  185.62, 150.50, 129.91, 129.06, 128.99, 67.84, 38.16, 24.08, 13.76.

**5d. 2,2-dichloro-1-(4-pentylphenyl)ethanone**<sup>[9]</sup>



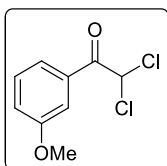
Yellow solid (144mg, 76 yield);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 (d,  $J = 8.3$  Hz, 2H), 7.32 (d,  $J = 8.3$  Hz, 2H), 6.68 (s, 1H), 2.73 – 2.62 (m, 2H), 1.70 – 1.59 (m, 2H), 1.34 (dd,  $J = 7.2, 3.7$  Hz, 4H), 0.90 (t,  $J = 6.9$  Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  185.61, 150.78, 129.91, 129.02, 128.96, 67.83, 36.11, 31.43, 30.62, 22.47, 13.95.

**5e. 1-(4-(tert-butyl)phenyl)-2,2-dichloroethanone**



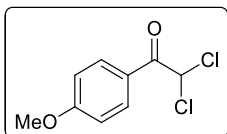
Yellow solid (125 mg, 81% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 (d,  $J = 8.6$  Hz, 2H), 7.53 (d,  $J = 8.6$  Hz, 2H), 6.68 (s, 1H), 1.36 (s, 9H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  185.81 (s), 160.02 (s), 132.69 (s), 129.87 (s), 122.06 (s), 121.14 (s), 114.11 (s), 67.74 (s), 55.57 (s).

**5f. 2,2-dichloro-1-(3-methoxyphenyl)ethanone**<sup>[8]</sup>



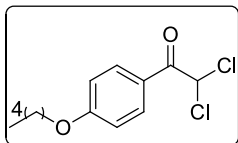
Yellow solid (123 mg, 75% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69 – 7.62 (m, 1H), 7.62 – 7.55 (m, 1H), 7.42 (t,  $J = 8.0$  Hz, 1H), 7.24 – 7.16 (m, 1H), 6.68 (s, 1H), 3.88 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  185.81, 160.02, 132.69, 129.87, 122.06, 121.14, 114.11, 77.34, 77.02, 76.70, 67.74, 55.57.

**5g. 2,2-dichloro-1-(4-methoxyphenyl)ethanone**<sup>[7]</sup>



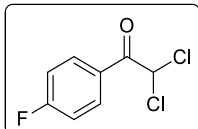
Yellow liquid (127 mg, 77% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 (d,  $J = 8.9$  Hz, 2H), 6.97 (d,  $J = 8.9$  Hz, 2H), 6.65 (s, 1H), 3.89 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  184.62, 164.68, 132.25, 123.98, 114.24, 67.91, 55.65.

**5h. 2,2-dichloro-1-(4-(pentyloxy)phenyl)ethanone**



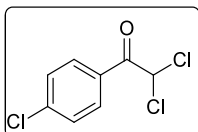
Yellow solid (105 mg, 72% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.08 (d,  $J = 9.0$  Hz, 2H), 6.99 (d,  $J = 9.0$  Hz, 2H), 6.67 (s, 1H), 4.07 (t,  $J = 6.5$  Hz, 2H), 1.90 – 1.79 (m, 2H), 1.59 – 1.39 (m, 4H), 0.97 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  184.60, 164.31, 132.27, 123.61, 114.64, 68.51, 67.89, 28.72, 28.10, 22.43, 14.03.

**5i. 2,2-dichloro-1-(4-fluorophenyl)ethanone**<sup>[7]</sup>



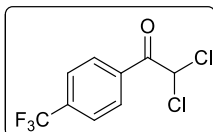
Yellow liquid (118mg, 69% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.14 (m,  $J = 8.2, 5.2, 2.6$  Hz, 2H), 7.24 – 7.16 (m, 2H), 6.61 (s, 1H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  184.58 (s), 166.46 (d,  $J = 258.1$  Hz), 132.73 (d,  $J = 9.6$  Hz), 127.59 (d,  $J = 3.0$  Hz), 116.23 (d,  $J = 22.2$  Hz), 67.84 (s).

**5j. 2,2-dichloro-1-(4-chlorophenyl)ethanone**<sup>[7]</sup>



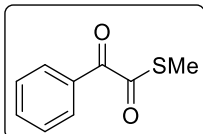
Yellow liquid (115 mg, 71% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.13 – 8.03 (m, 2H), 7.58 – 7.49 (m, 2H), 6.62 (s, 1H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  184.95 (s), 141.25 (s), 131.25 (s), 129.48 (s), 129.31 (s), 67.78 (s).

**5k. 2,2-dichloro-1-(4-(trifluoromethyl)phenyl)ethanone**<sup>[7b]</sup>



Colourless liquid (99 mg, 66% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.26 (d,  $J = 8.2$  Hz, 2H), 7.82 (d,  $J = 8.3$  Hz, 2H), 6.65 (s, 1H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  185.13 (s), 135.62 (q,  $J = 33.0$  Hz), 133.99 (s), 130.27 (s), 125.93 (q,  $J = 3.6$  Hz), 123.28 (d,  $J = 273.0$  Hz), 67.79 (s).

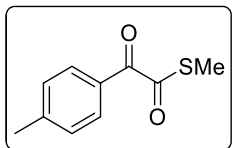
**6a. S-methyl 2-oxo-2-phenylethanethioate**



Yellow oil (122 mg, 69% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.22 – 8.12 (m, 2H), 7.68 (t,  $J = 7.4$  Hz, 1H), 7.53 (t,  $J = 7.8$  Hz, 2H), 2.49 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  193.26 (s), 186.10 (s), 134.84 (s), 131.69 (s), 130.79 (s), 128.83 (s), 11.45 (s). IR ( $\text{CHCl}_3$ ,  $\text{cm}^{-1}$ )  $\nu$ : 3357, 2920, 2850, 1674, 1595, 1449, 1266, 1068, 826. HRMS (TOF)  $m/z$   $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_9\text{H}_9\text{O}_2\text{S}$  181.0318 found 181.0324.

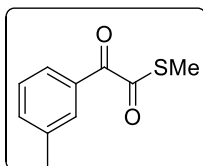
**6b. S-methyl 2-oxo-2-(p-tolyl)ethanethioate**





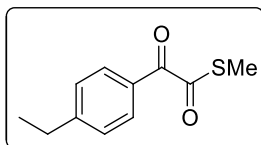
Yellow oil (119 mg, 71% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.08 (d,  $J = 8.3$  Hz, 2H), 7.33 (d,  $J = 8.1$  Hz, 2H), 2.48 (s, 3H), 2.47 (s, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  193.55 (s), 185.71 (s), 146.30 (s), 130.97 (s), 129.63 (s), 129.03 (s), 21.97 (s), 11.52 (s). IR ( $\text{CHCl}_3, \text{cm}^{-1}$ )  $\nu$ ; 3329, 2920, 2849, 1680, 1604, 1410, 1313, 1270, 1073, 774, 845. HRMS (TOF)  $m/z$   $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{10}\text{H}_{10}\text{NaO}_2\text{S}$  217.0294 found 217.0288.

#### 6c. S-methyl 2-oxo-2-(m-tolyl)ethanethioate



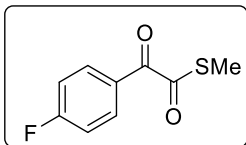
Yellow oil (120 mg, 72% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (d,  $J = 7.1$  Hz, 1H), 7.50 (d,  $J = 7.3$  Hz, 1H), 7.41 (dd,  $J = 11.2, 4.9$  Hz, 2H), 2.49 (s, 3H), 2.45 (s, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  193.44 (s), 186.44 (s), 138.78 (s), 135.78 (s), 131.56 (s), 131.11 (s), 128.75 (s), 128.11 (s), 21.34 (s), 11.52 (s). IR ( $\text{CHCl}_3, \text{cm}^{-1}$ )  $\nu$ ; 3330, 2924, 2851, 1677, 1584, 1453, 1276, 1083, 900. HRMS (TOF)  $m/z$   $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{10}\text{H}_{10}\text{NaO}_2\text{S}$  217.0294 found 217.0291.

#### 6d. S-methyl 2-(4-ethylphenyl)-2-oxoethanethioate



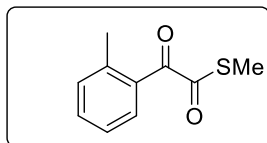
Yellow oil (112 mg, 70% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.10 (d,  $J = 8.4$  Hz, 2H), 7.35 (d,  $J = 8.4$  Hz, 2H), 2.76 (q,  $J = 7.6$  Hz, 2H), 2.48 (s, 3H), 1.29 (t,  $J = 7.6$  Hz, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  193.55 (s), 185.75 (s), 152.37 (s), 131.09 (s), 129.23 (s), 128.46 (s), 29.19 (s), 15.07 (s), 11.51 (s). IR ( $\text{CHCl}_3, \text{cm}^{-1}$ )  $\nu$ ; 3328, 2968, 2930, 1680, 1604, 1416, 1312, 1269, 1184, 1074, 829. HRMS (TOF)  $m/z$   $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{11}\text{H}_{12}\text{NaO}_2\text{S}$  231.0450 found 231.0454.

#### 6e. S-methyl 2-(4-fluorophenyl)-2-oxoethanethioate



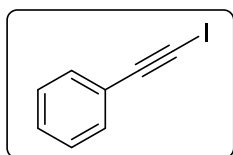
Yellow oil (110 mg, 67% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.30 – 8.21 (m, 2H), 7.25 – 7.16 (m, 2H), 2.49 (s, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  193.18 (s), 184.19 (s), 166.90 (d,  $J = 258.6$  Hz), 133.80 (d,  $J = 9.7$  Hz), 128.06 (d,  $J = 2.8$  Hz), 116.23 (d,  $J = 22.0$  Hz), 11.58 (s). IR ( $\text{CHCl}_3, \text{cm}^{-1}$ )  $\nu$ ; 3393, 2926, 2851, 1680, 1596, 1505, 1443, 1239, 845. HRMS (TOF)  $m/z$   $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_9\text{H}_8\text{FO}_2\text{S}$  199.0224 found 199.0223.

#### 6f. S-methyl 2-oxo-2-(o-tolyl)ethanethioate



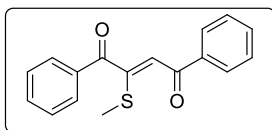
Yellow oil (107 mg, 64% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (d,  $J = 7.7$  Hz, 1H), 7.51 (t,  $J = 7.5$  Hz, 1H), 7.33 (t,  $J = 8.3$  Hz, 2H), 2.58 (s, 3H), 2.49 (s, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  193.83 (s), 189.02 (s), 141.14 (s), 133.41 (s), 132.16 (s), 130.89 (s), 125.65 (s), 21.31 (s), 11.58 (s). IR ( $\text{CHCl}_3, \text{cm}^{-1}$ ); 3331, 2851, 2927, 1681, 1455, 1249, 1060, 844. HRMS (TOF)  $m/z$   $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{10}\text{H}_{10}\text{NaO}_2\text{S}$  217.0294 found 217.0297.

#### A. (iodoethynyl)benzene<sup>[1]</sup>



Yellow oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 – 7.47 (m, 1H), 7.40 – 7.33 (m, 2H).

#### 8. (Z)-2-(methylthio)-1,4-diphenylbut-2-ene-1,4-dione<sup>[2]</sup>



$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.13 – 8.07 (m, 1H), 8.01 – 7.94 (m, 1H), 7.70 (t,  $J = 7.4$  Hz, 1H), 7.56 (t,  $J = 7.8$  Hz, 2H), 7.47 (t,  $J = 7.5$  Hz, 1H), 7.12 (s, 1H), 2.19 (s, 2H), 1.62.

#### References:

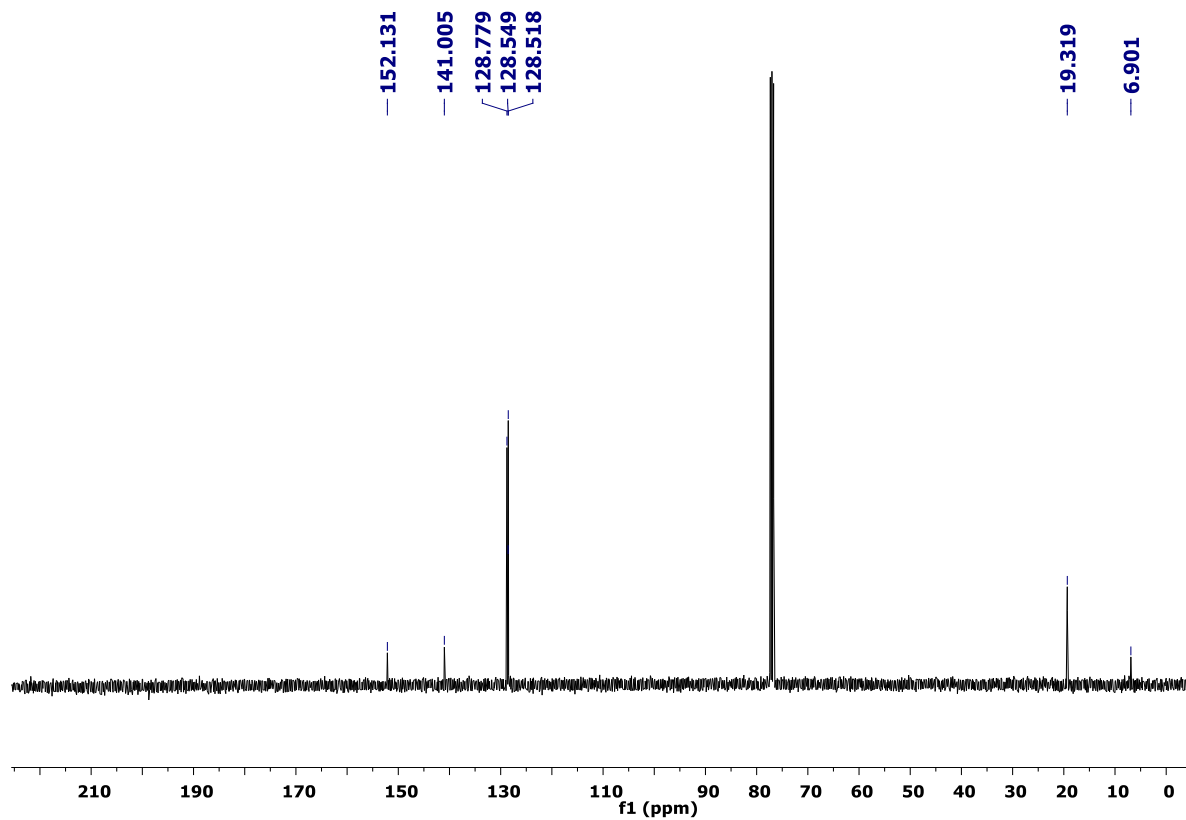
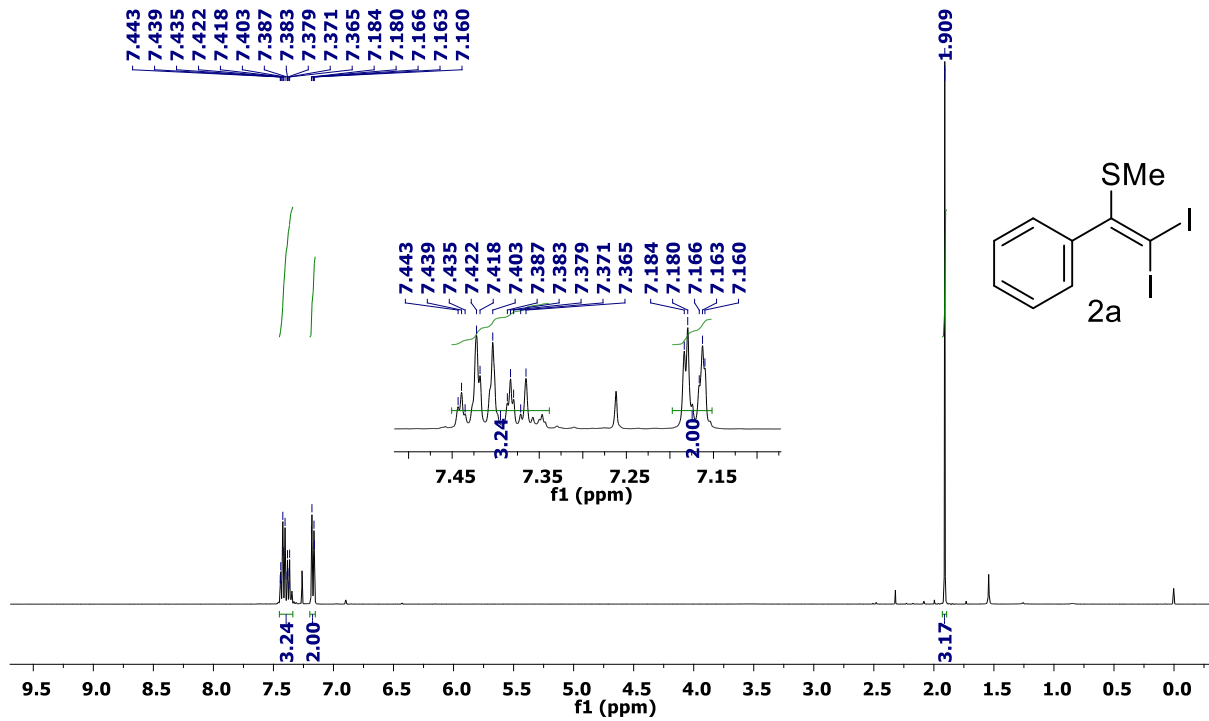
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9515-9519

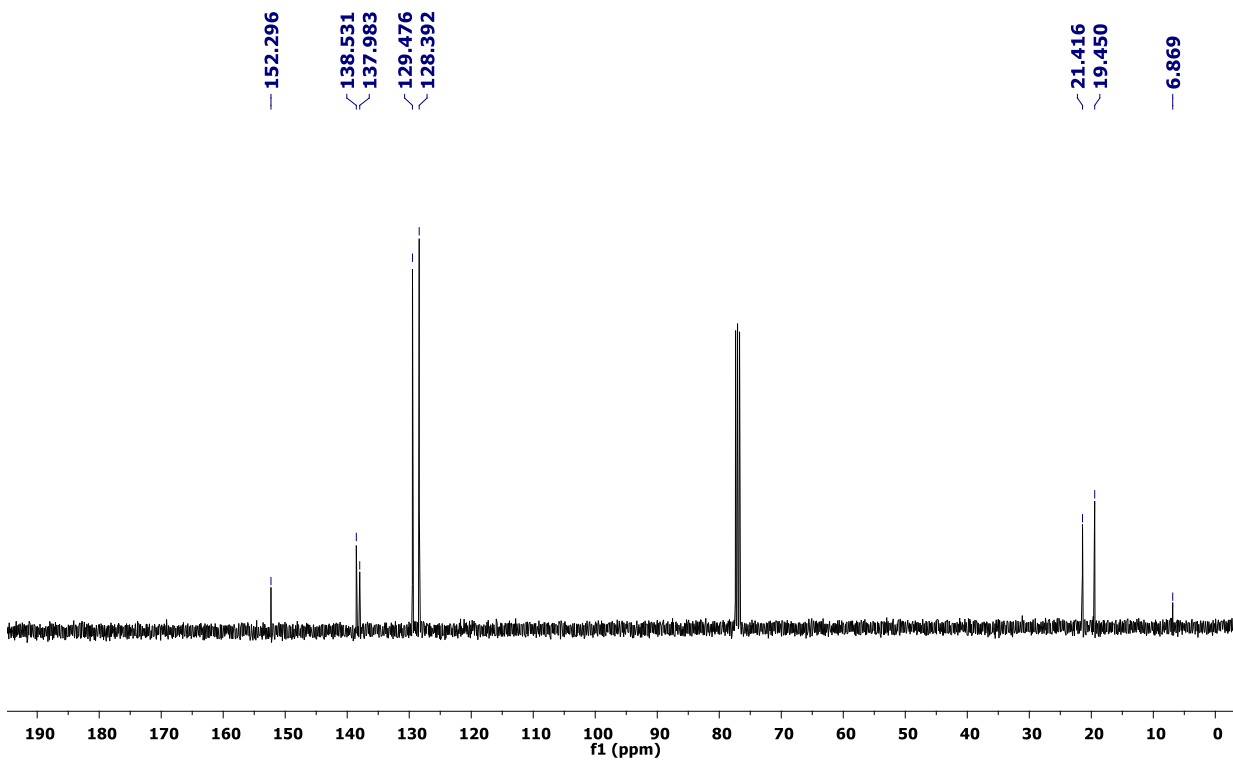
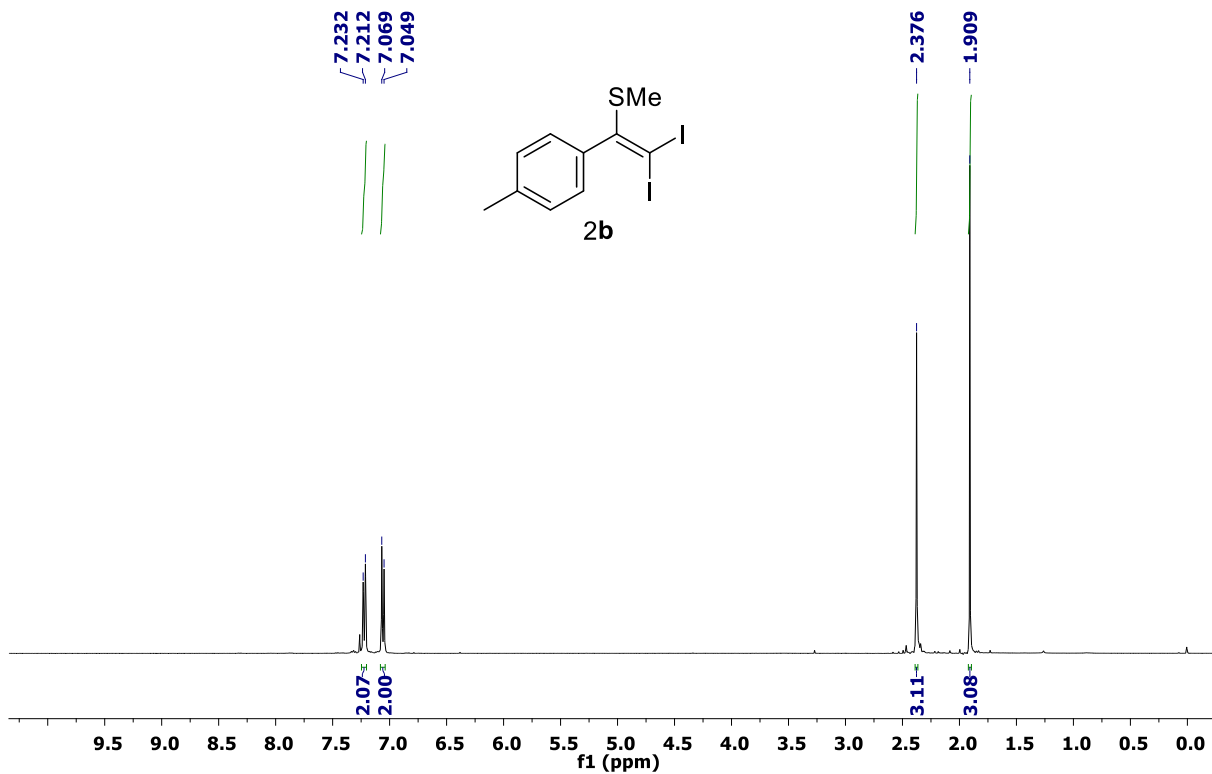
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Letters*,2013,**54**,3993-3996.

**<sup>1</sup>H and <sup>13</sup>C NMR spectra of all compounds.**

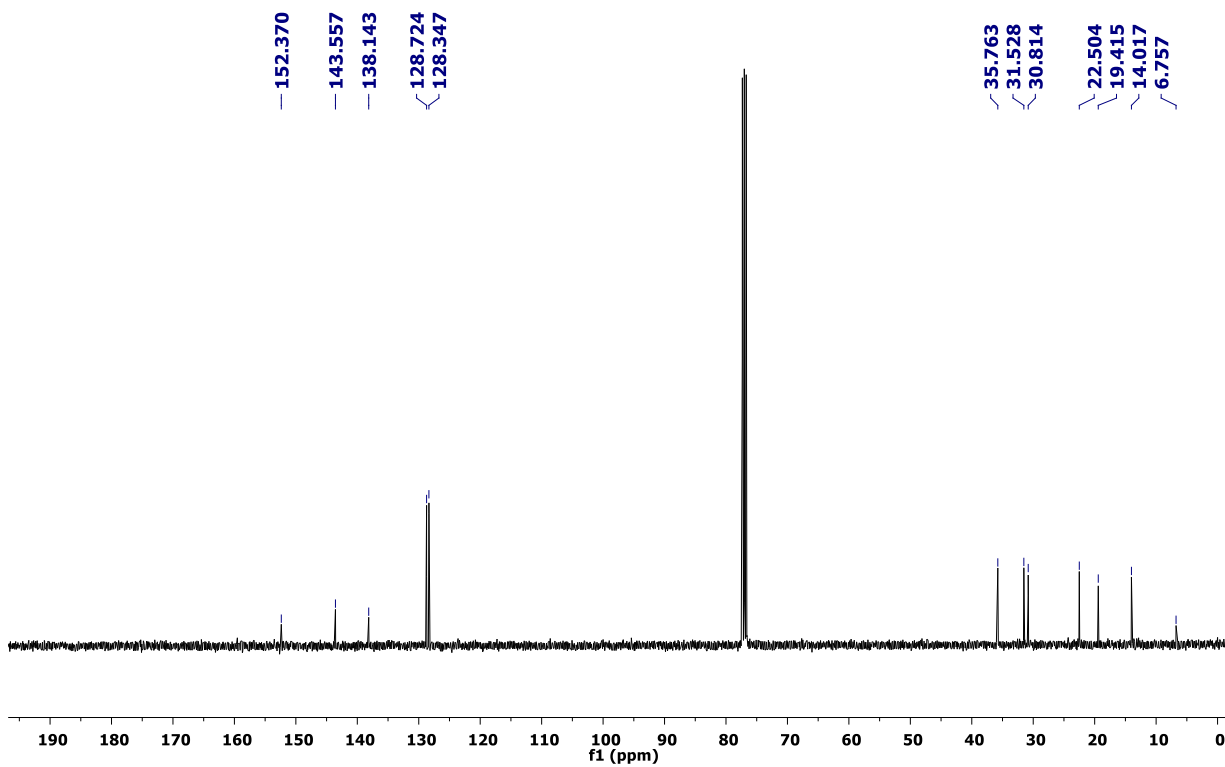
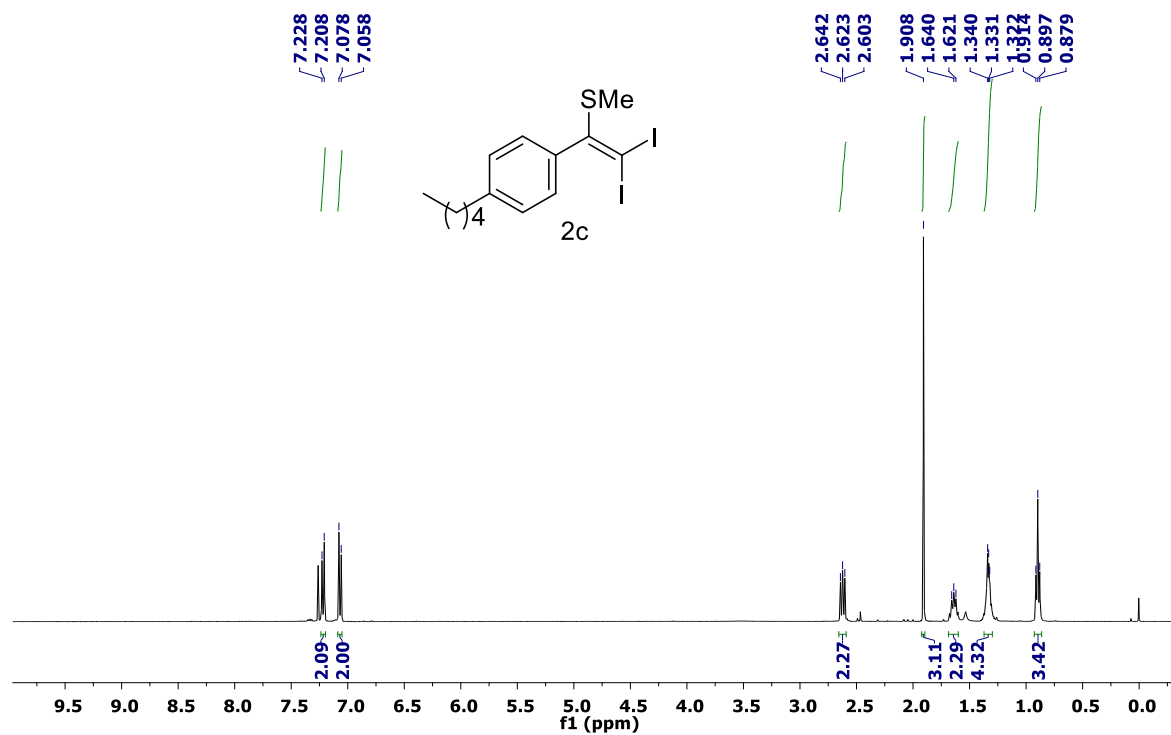
**<sup>1</sup>H and <sup>13</sup>C NMR spectra of 2a (CDCl<sub>3</sub>)**



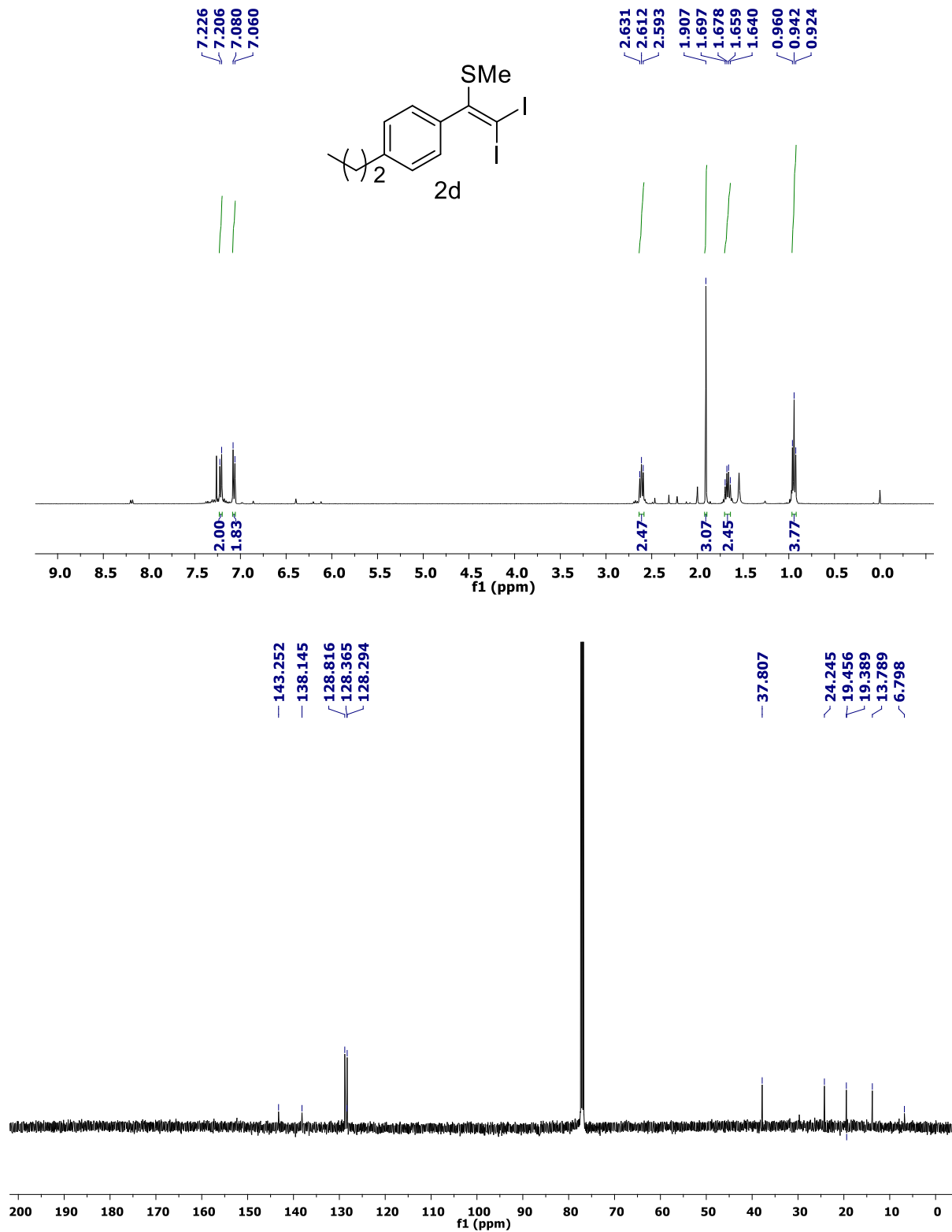
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 2b ( $\text{CDCl}_3$ )



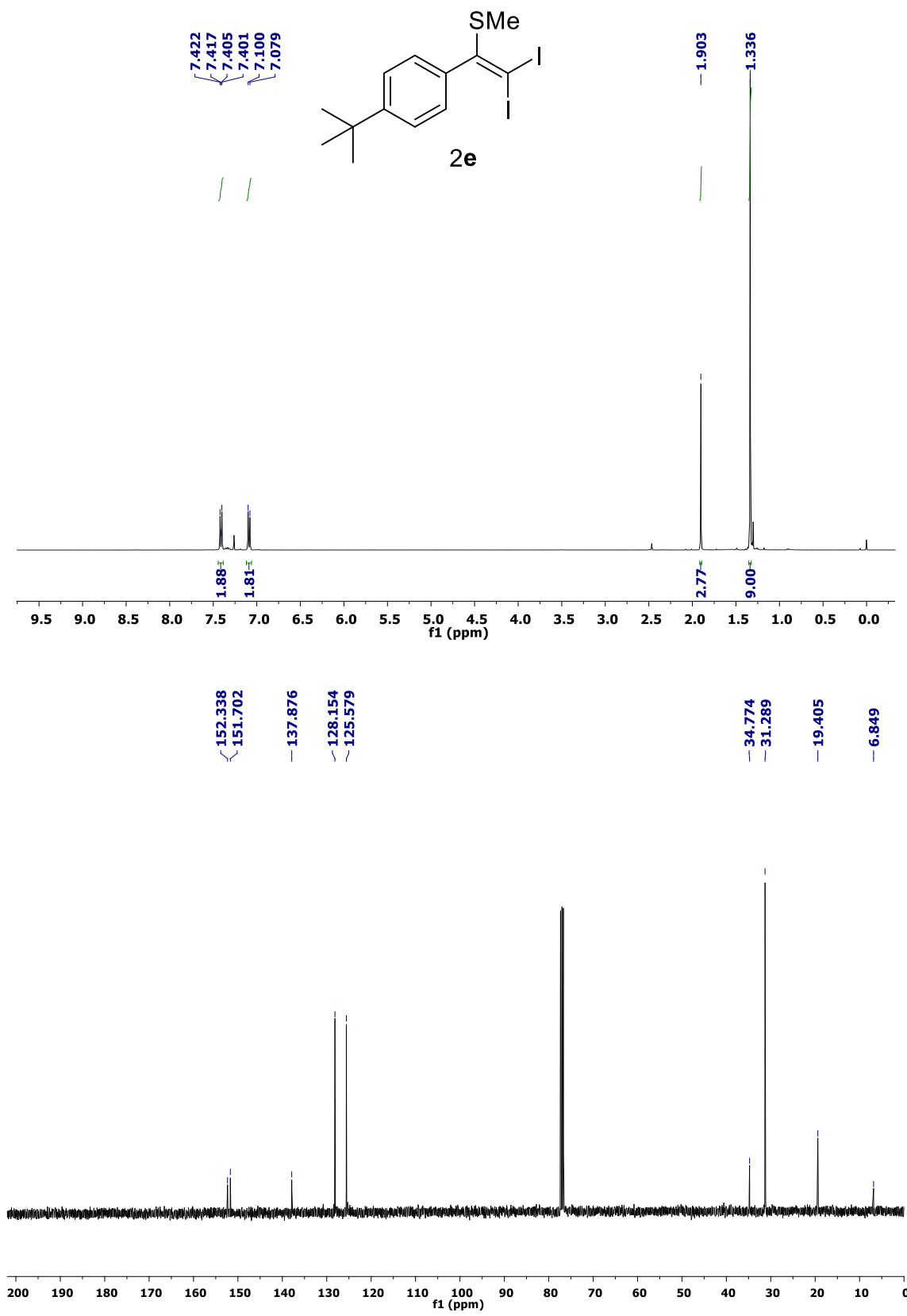
<sup>1</sup>H and <sup>13</sup>C NMR spectra of 2c (CDCl<sub>3</sub>)



$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 2d ( $\text{CDCl}_3$ )

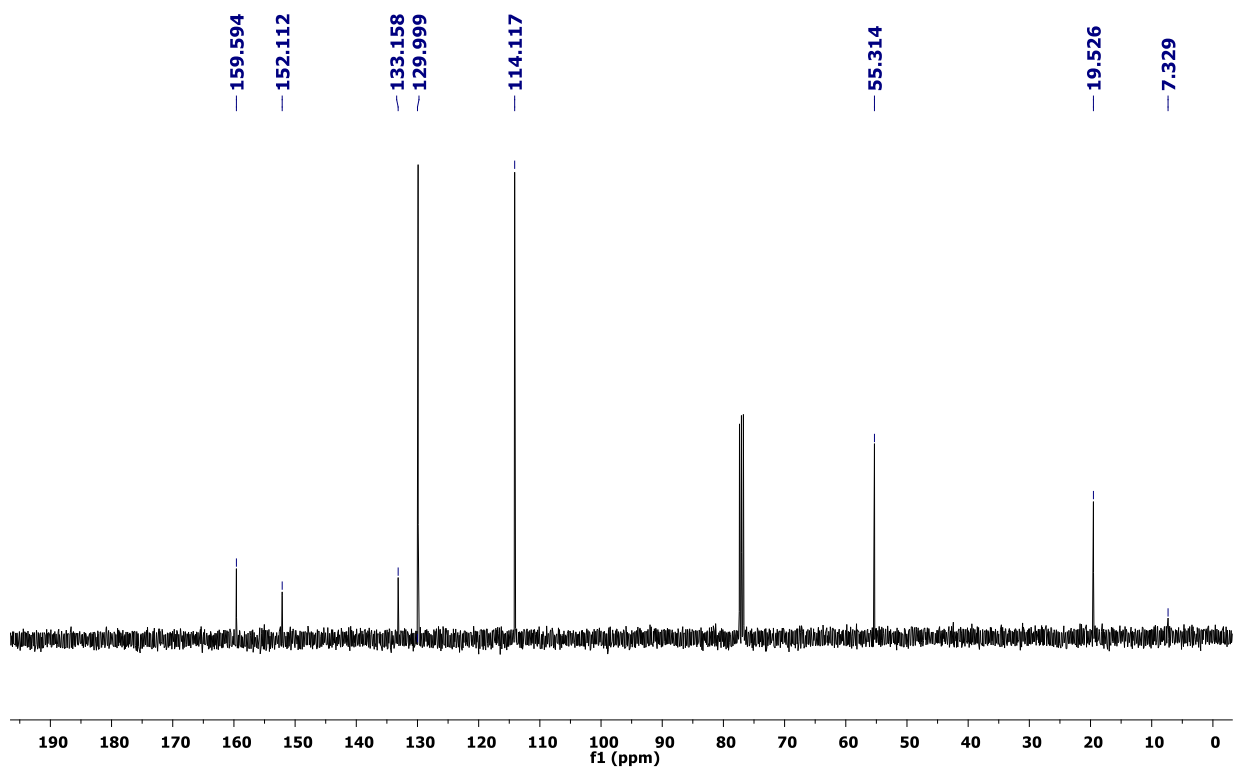
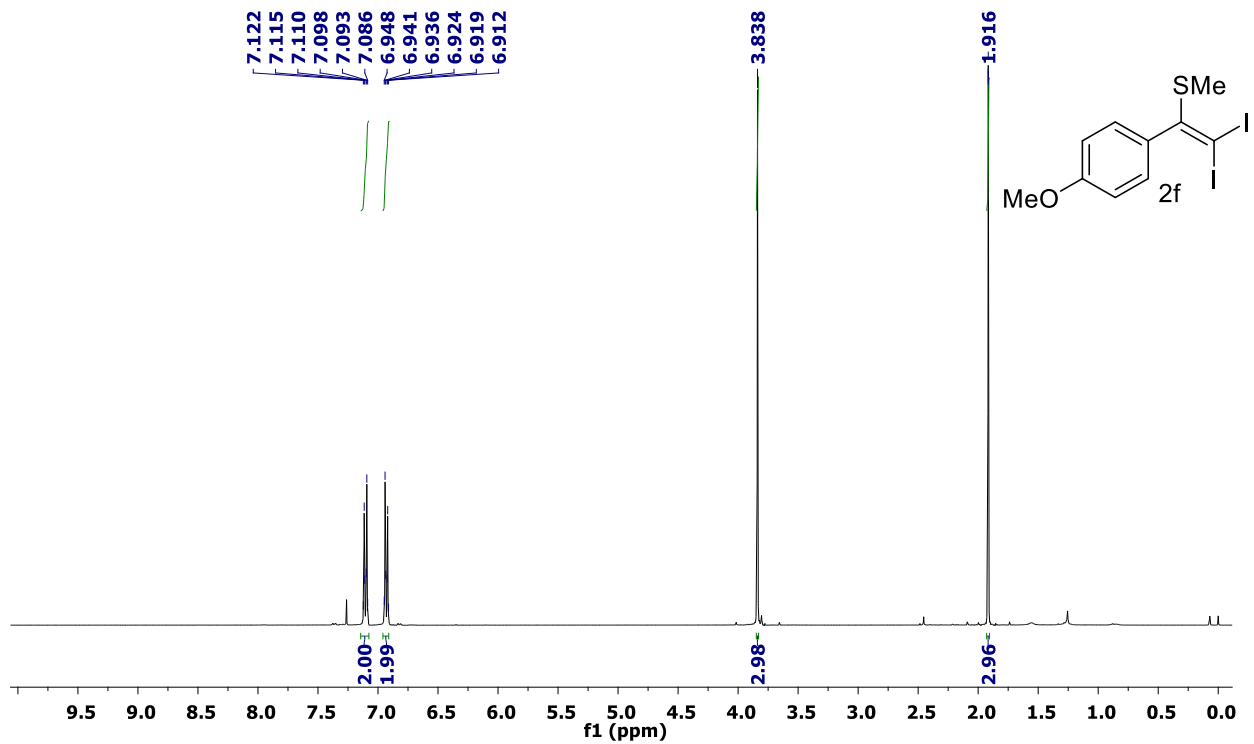


$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 2e ( $\text{CDCl}_3$ )

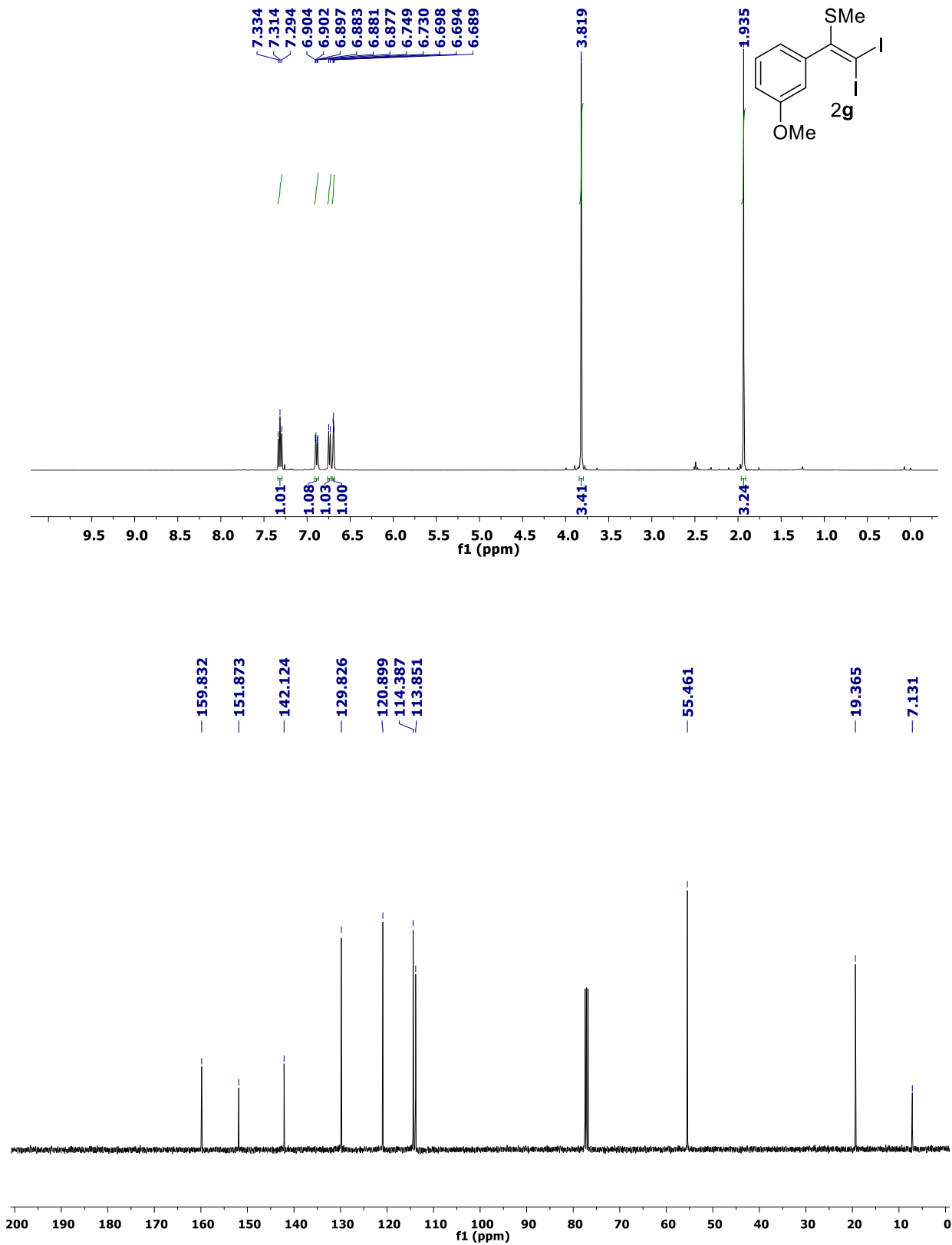




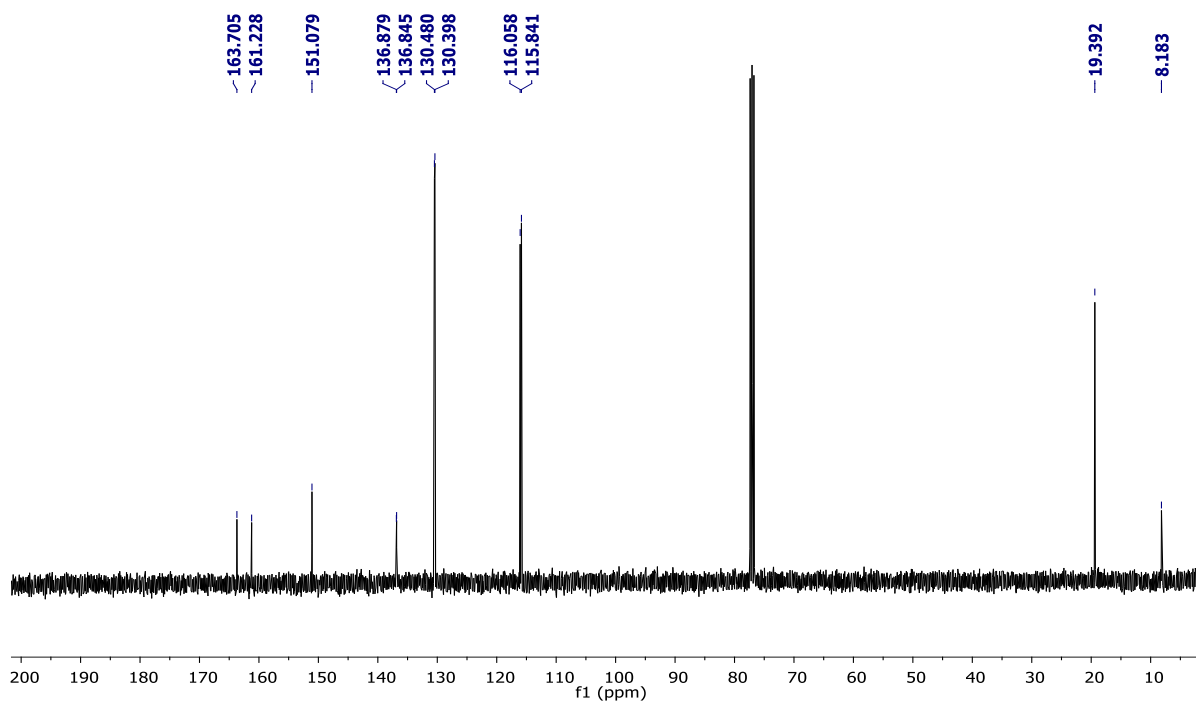
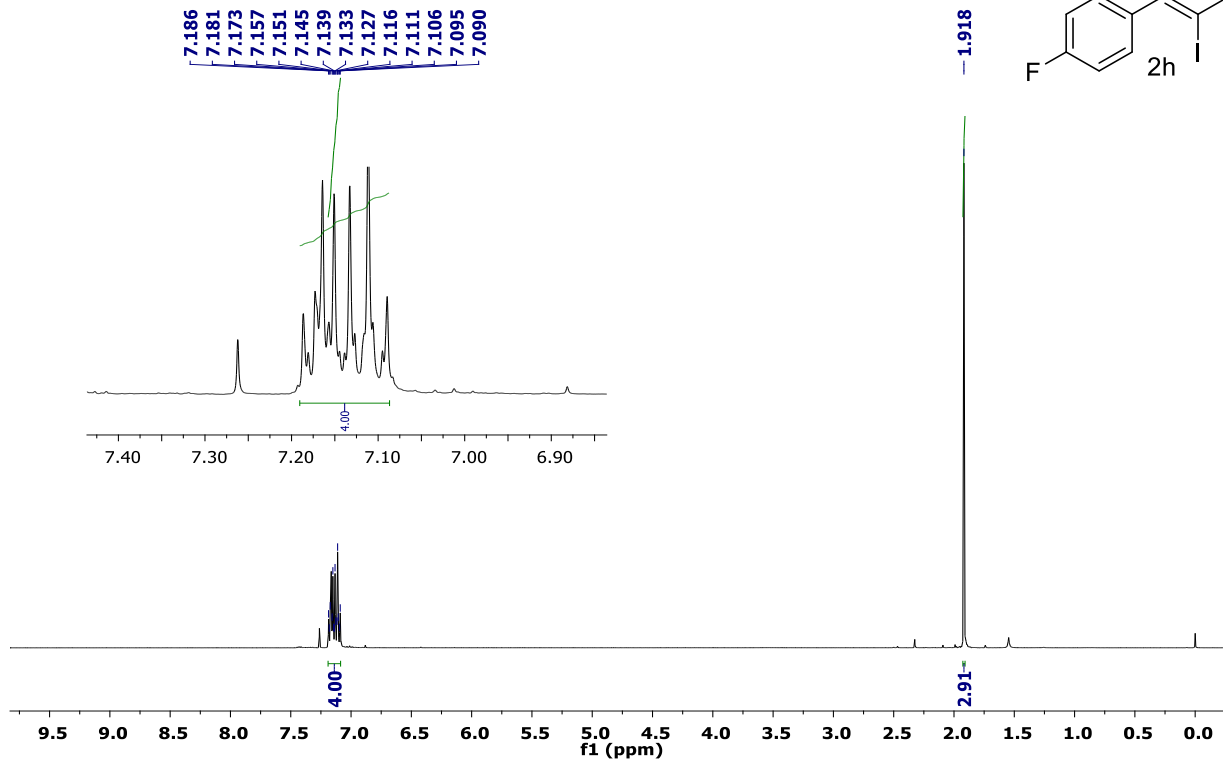
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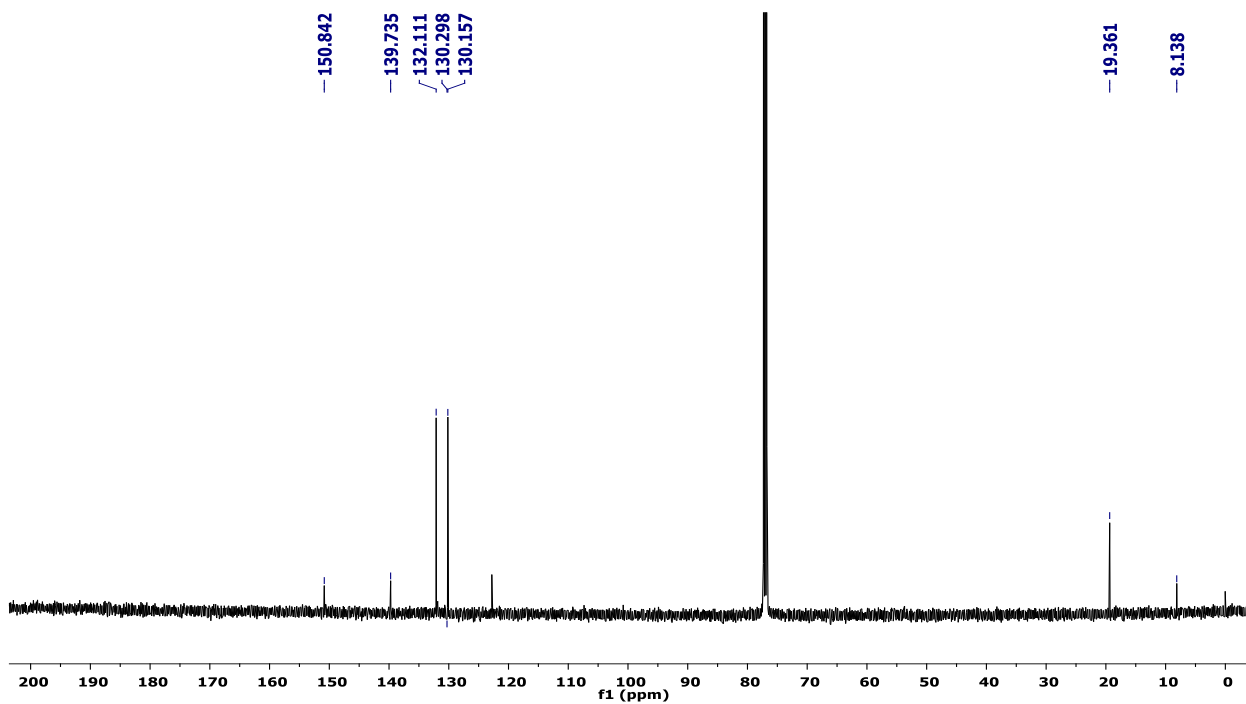
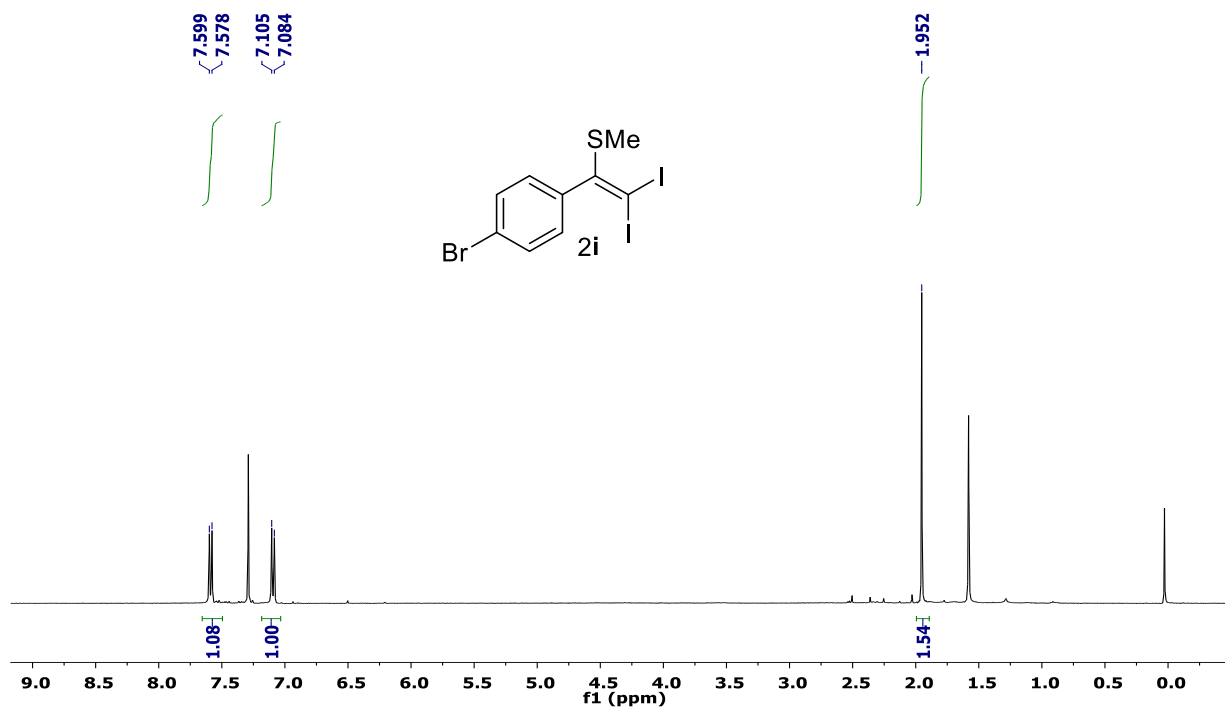
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 2g ( $\text{CDCl}_3$ )



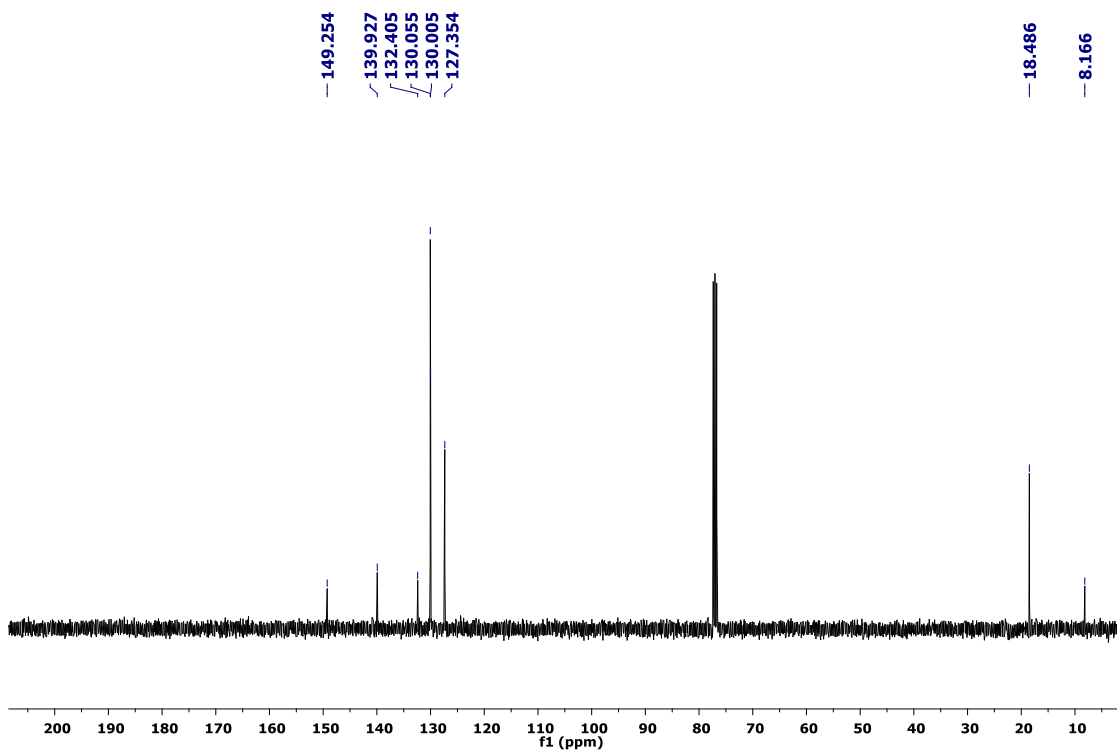
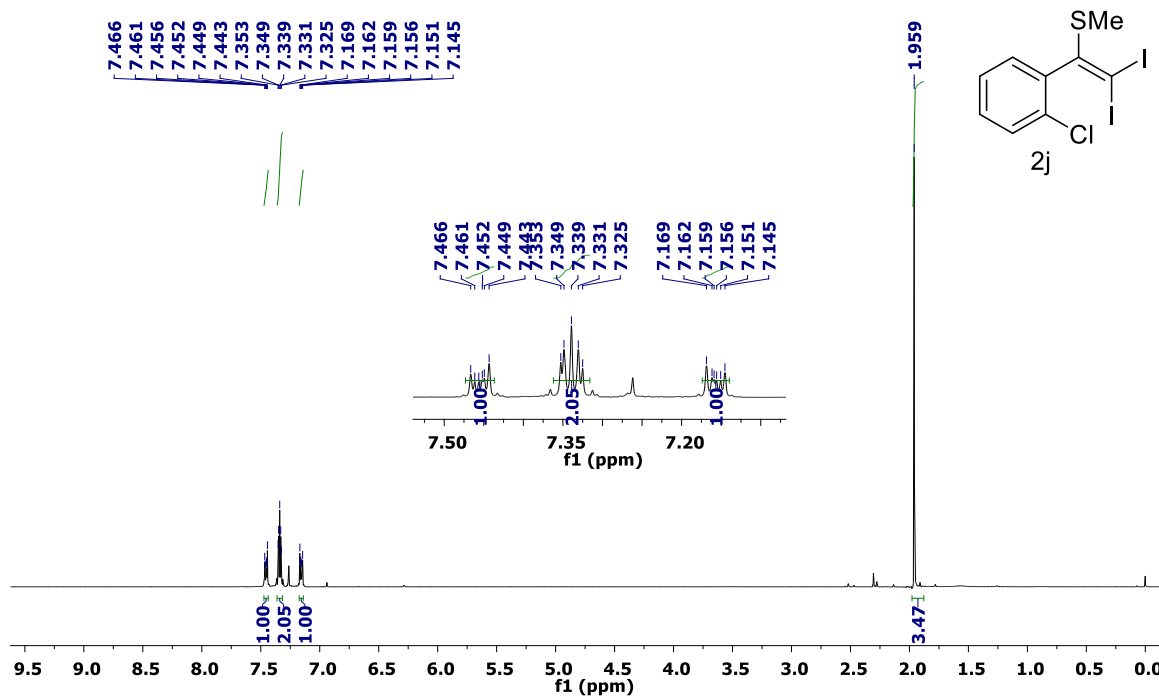
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 2h ( $\text{CDCl}_3$ )



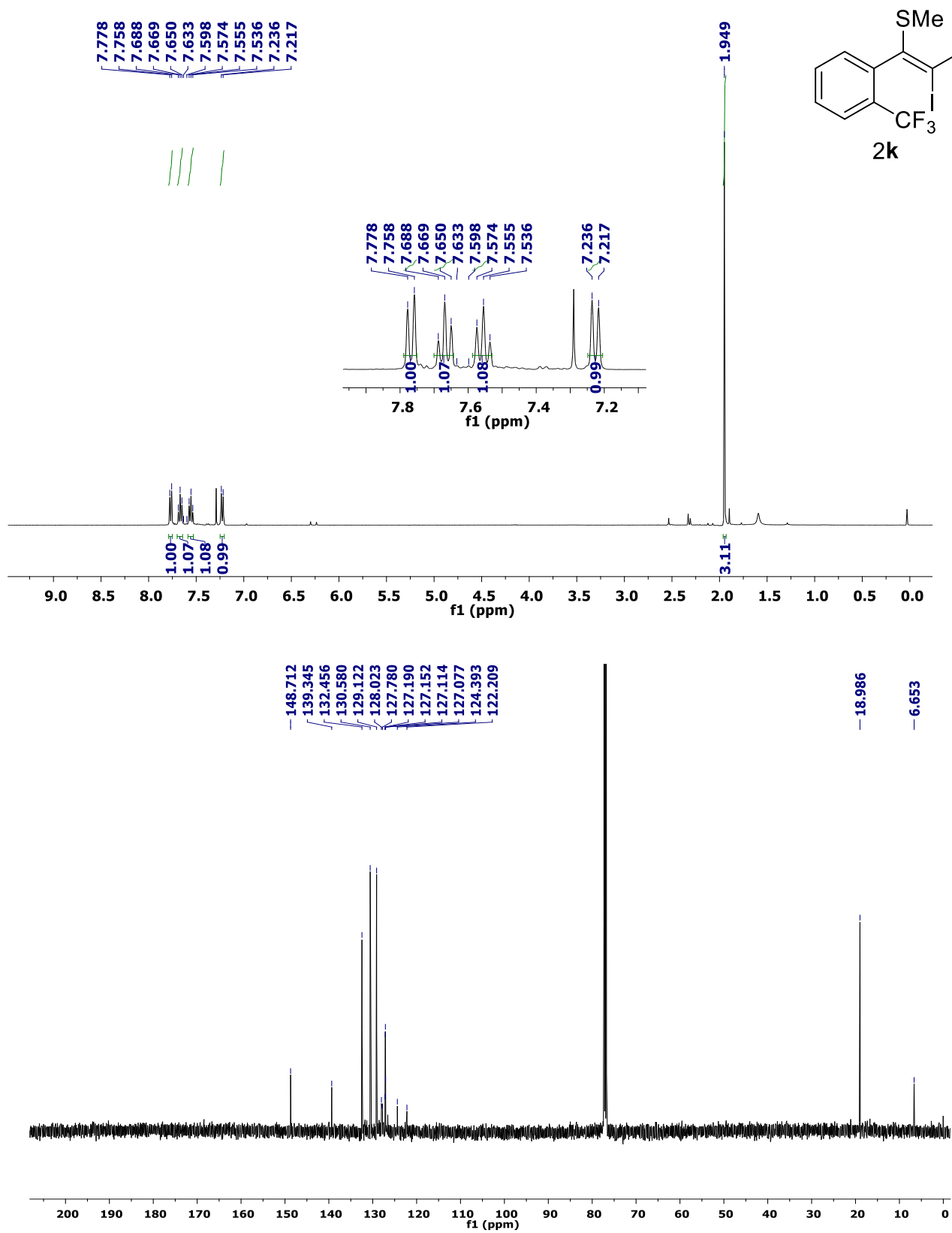
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 2i (CDCl<sub>3</sub>)



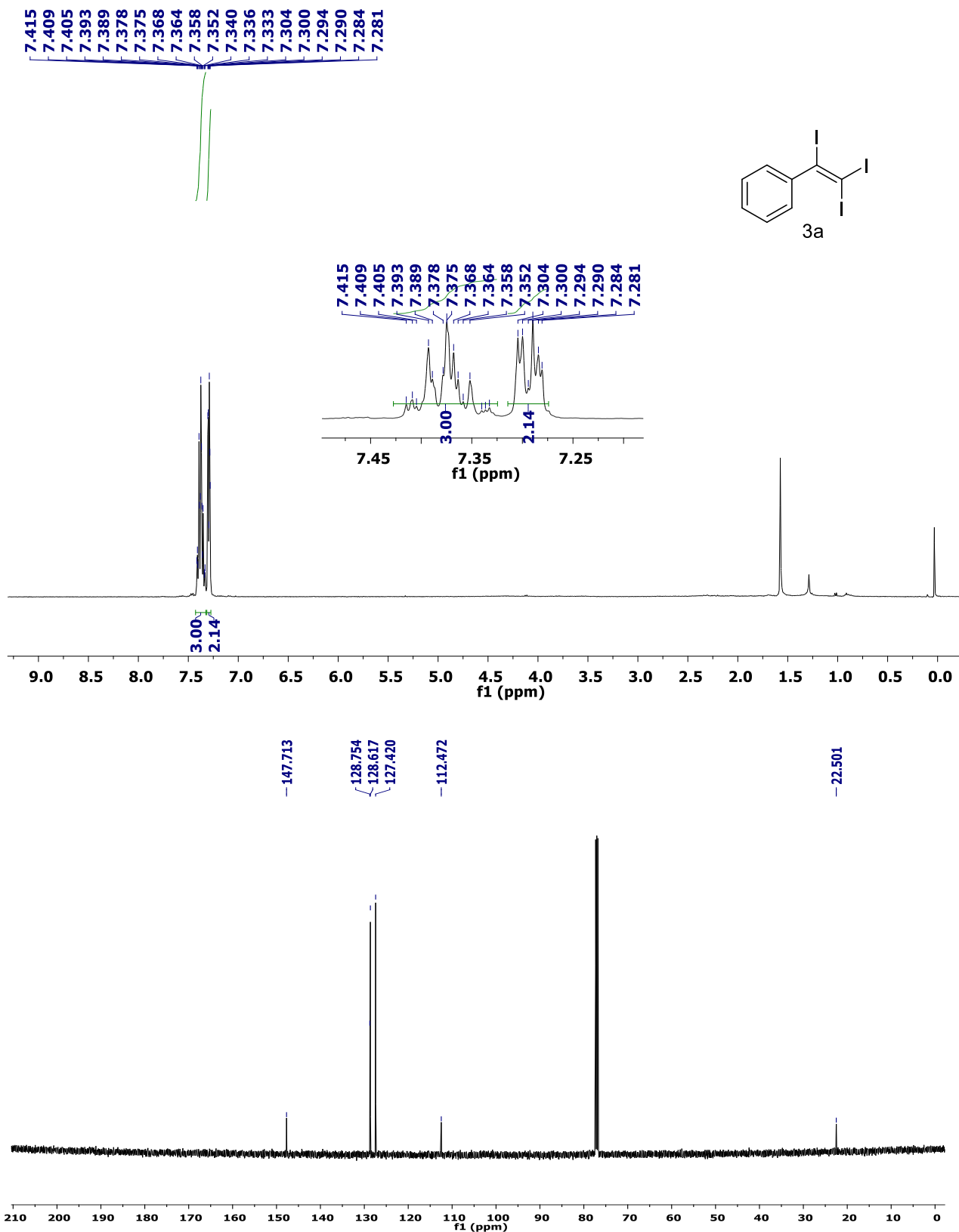
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 2j ( $\text{CDCl}_3$ )



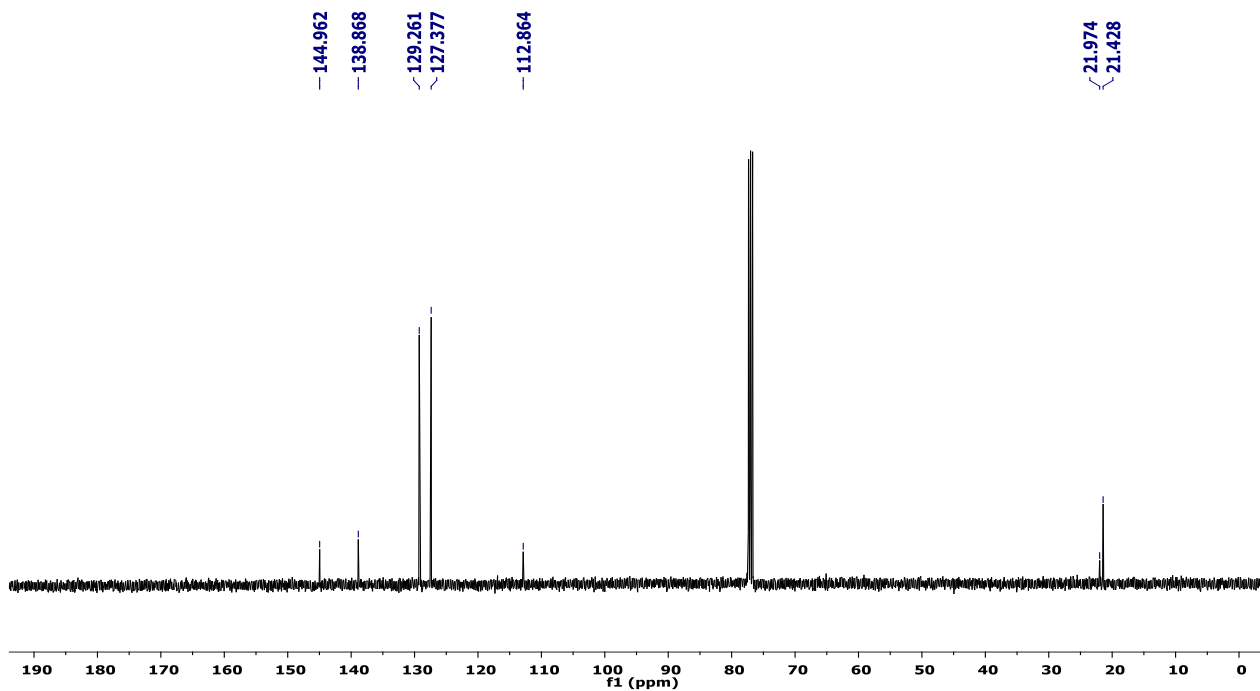
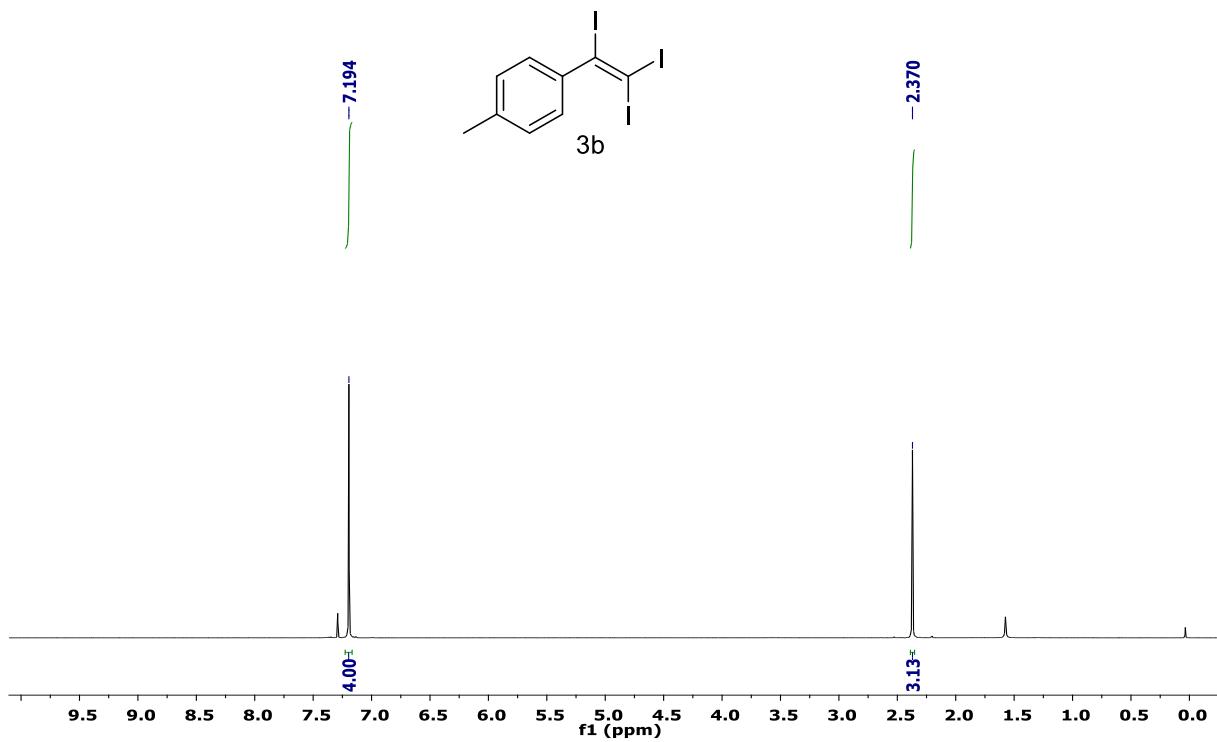
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 2k ( $\text{CDCl}_3$ )



# $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of 3a ( $\text{CDCl}_3$ )

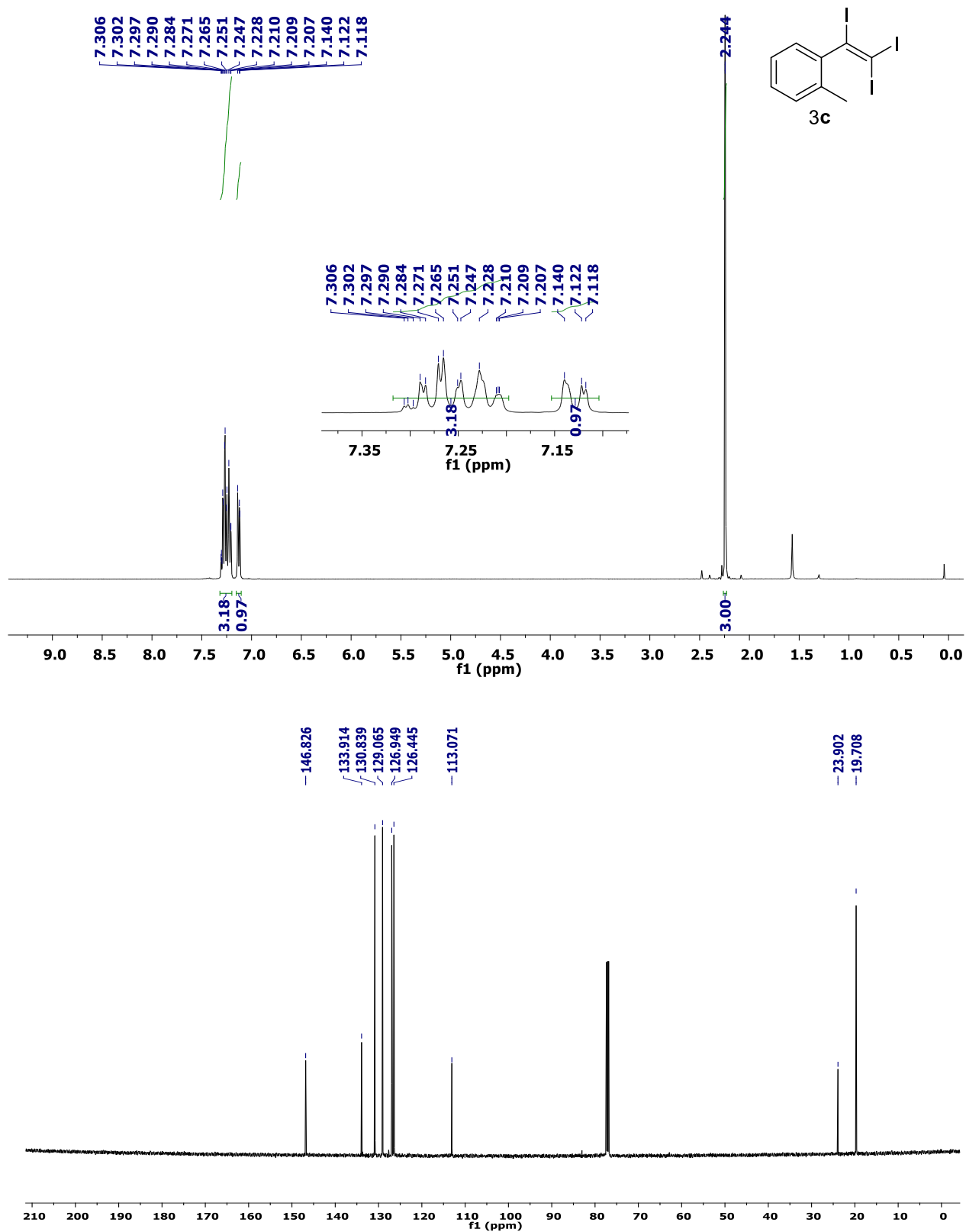


$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 3b ( $\text{CDCl}_3$ )

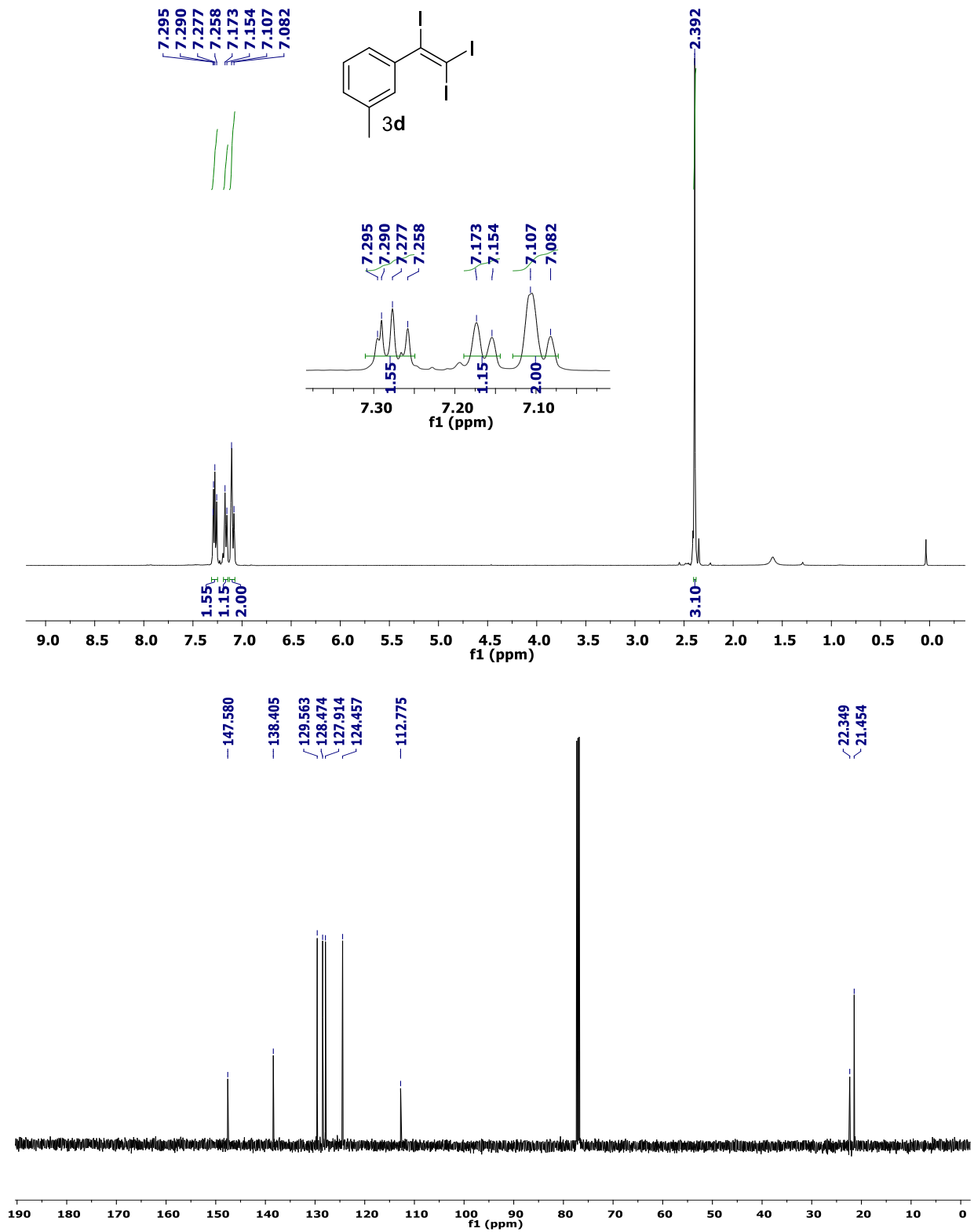




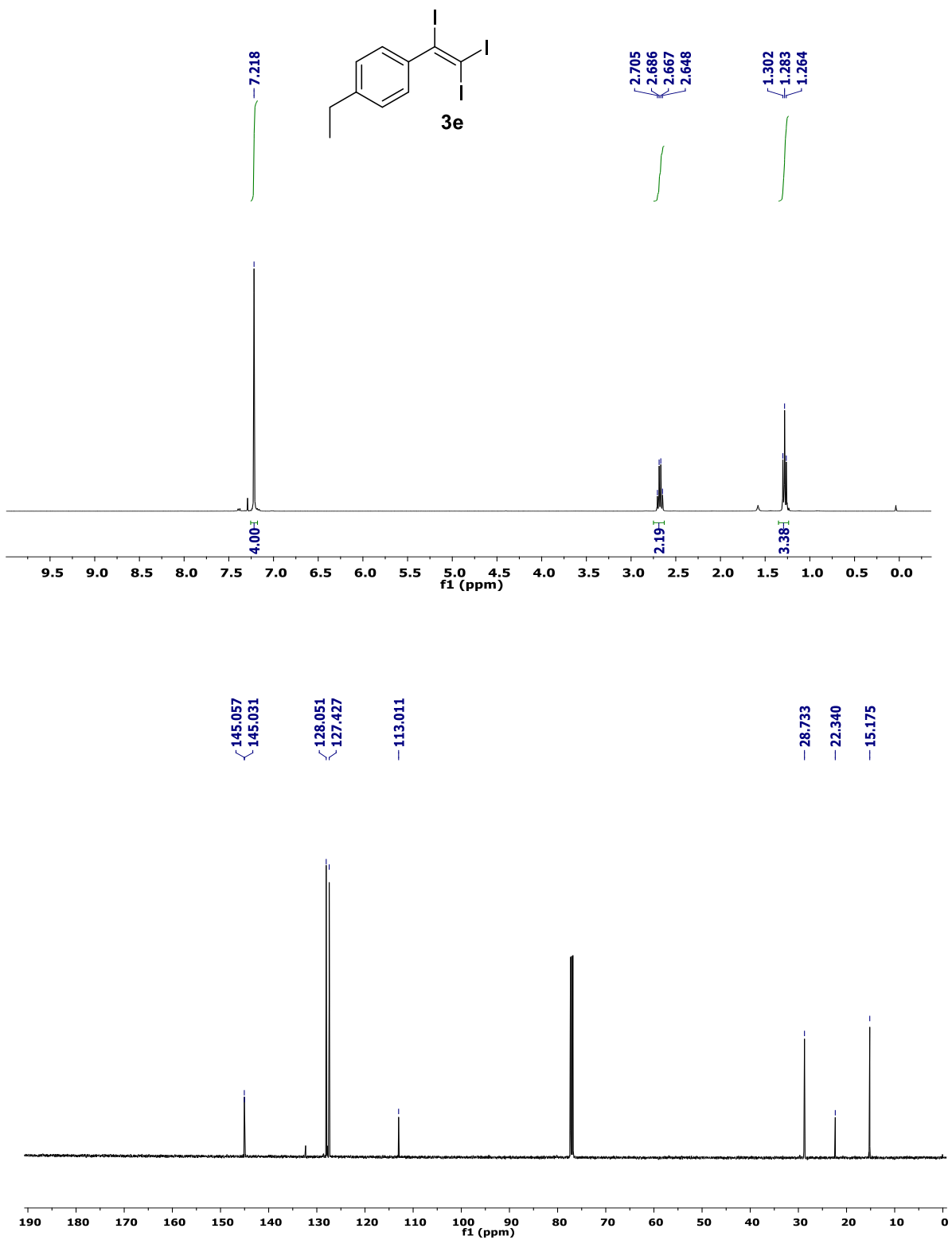
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 3c ( $\text{CDCl}_3$ )



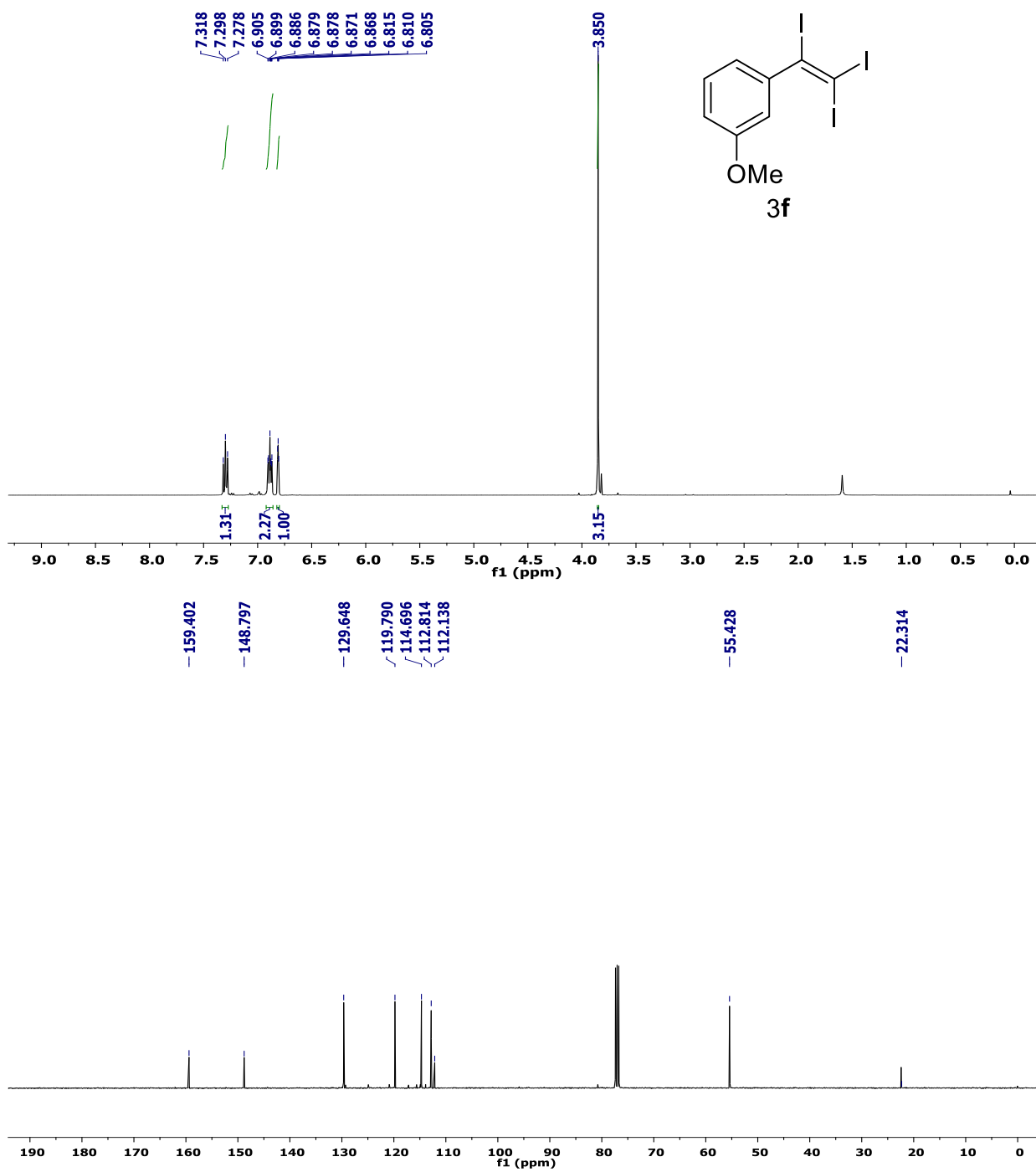
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 3d ( $\text{CDCl}_3$ )



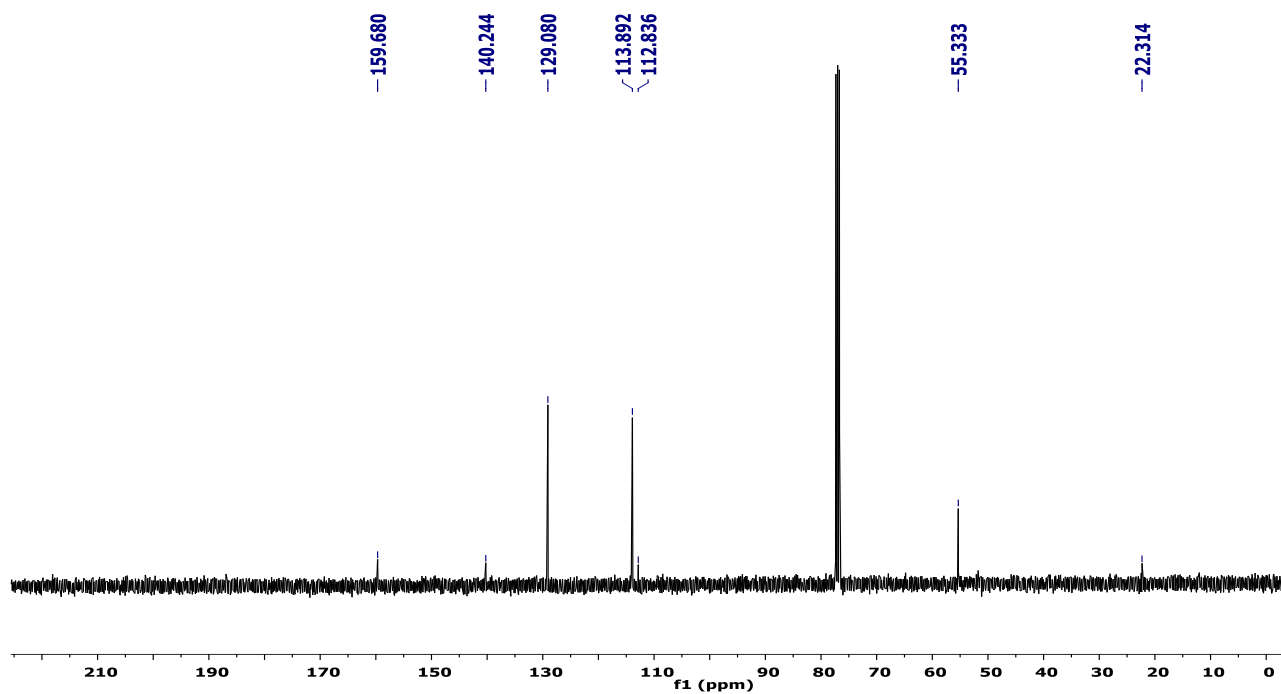
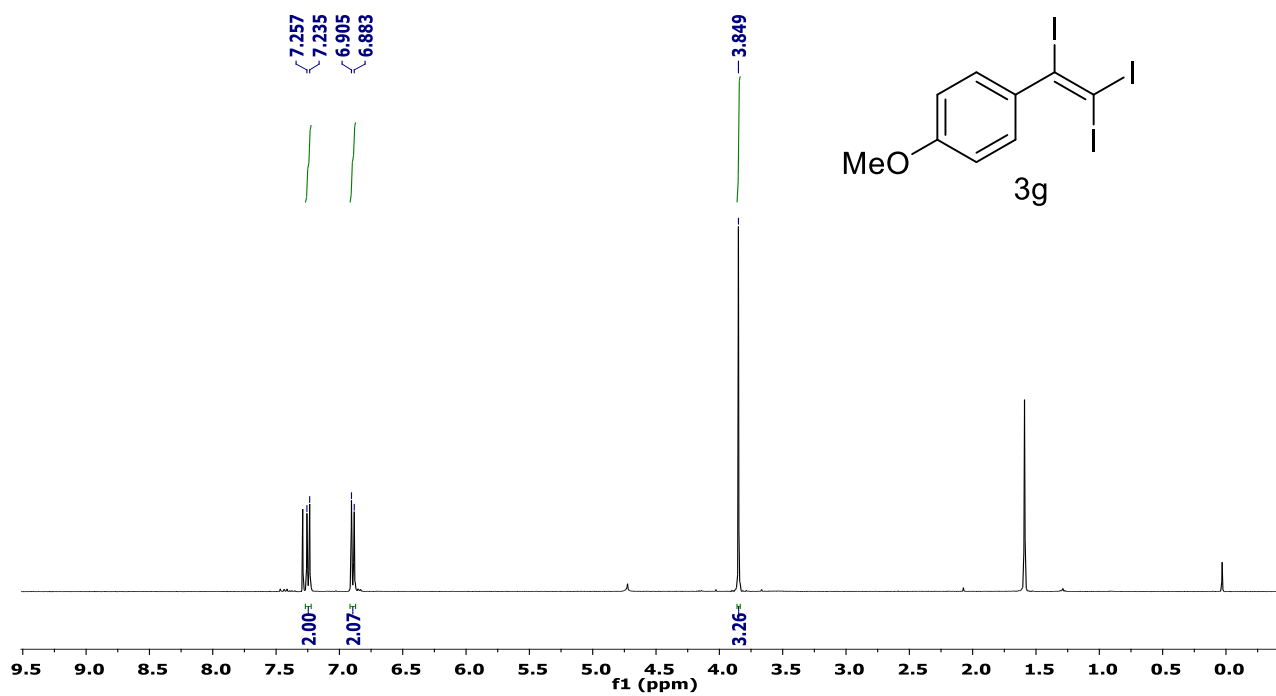
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 3e ( $\text{CDCl}_3$ )



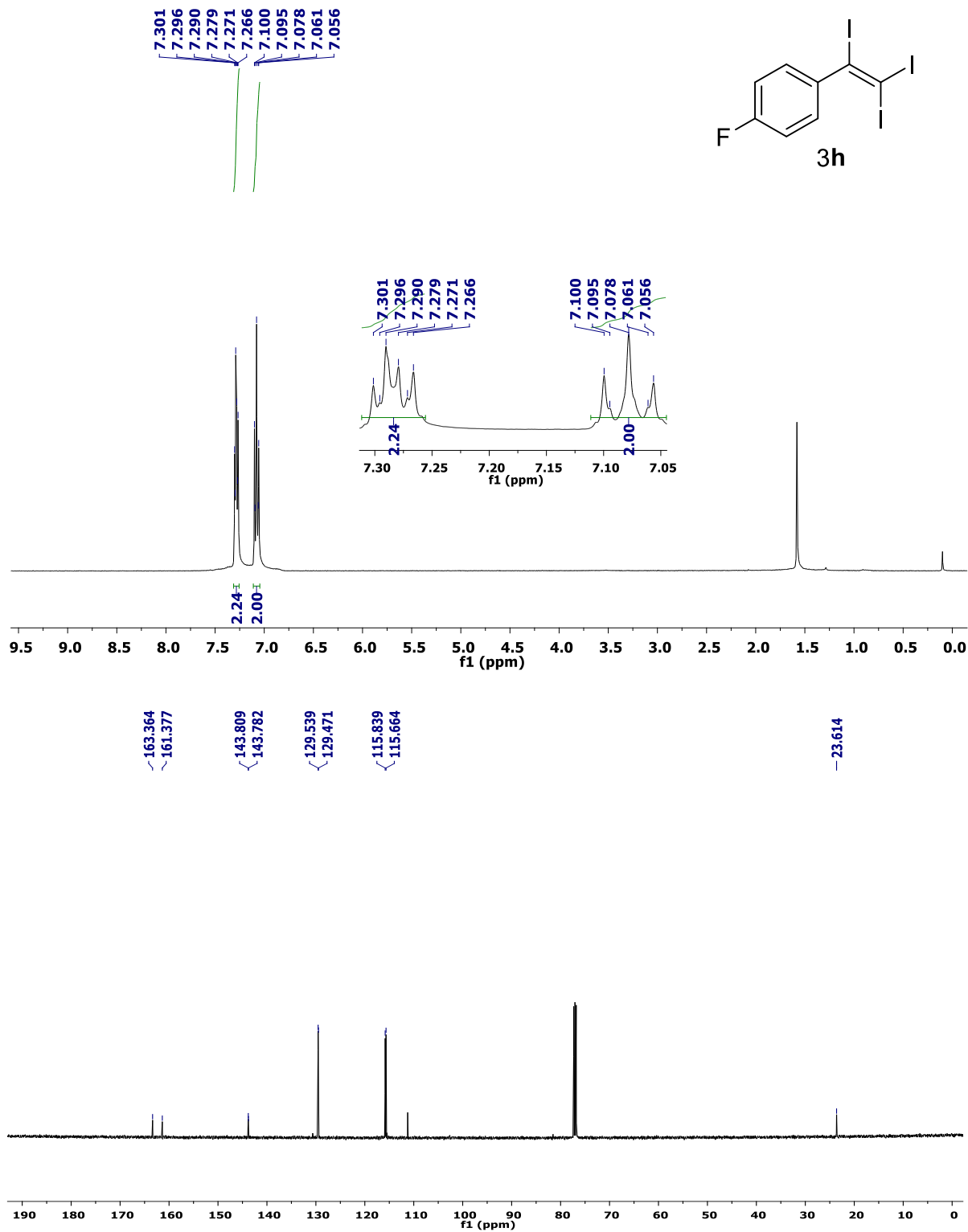
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 3f ( $\text{CDCl}_3$ )



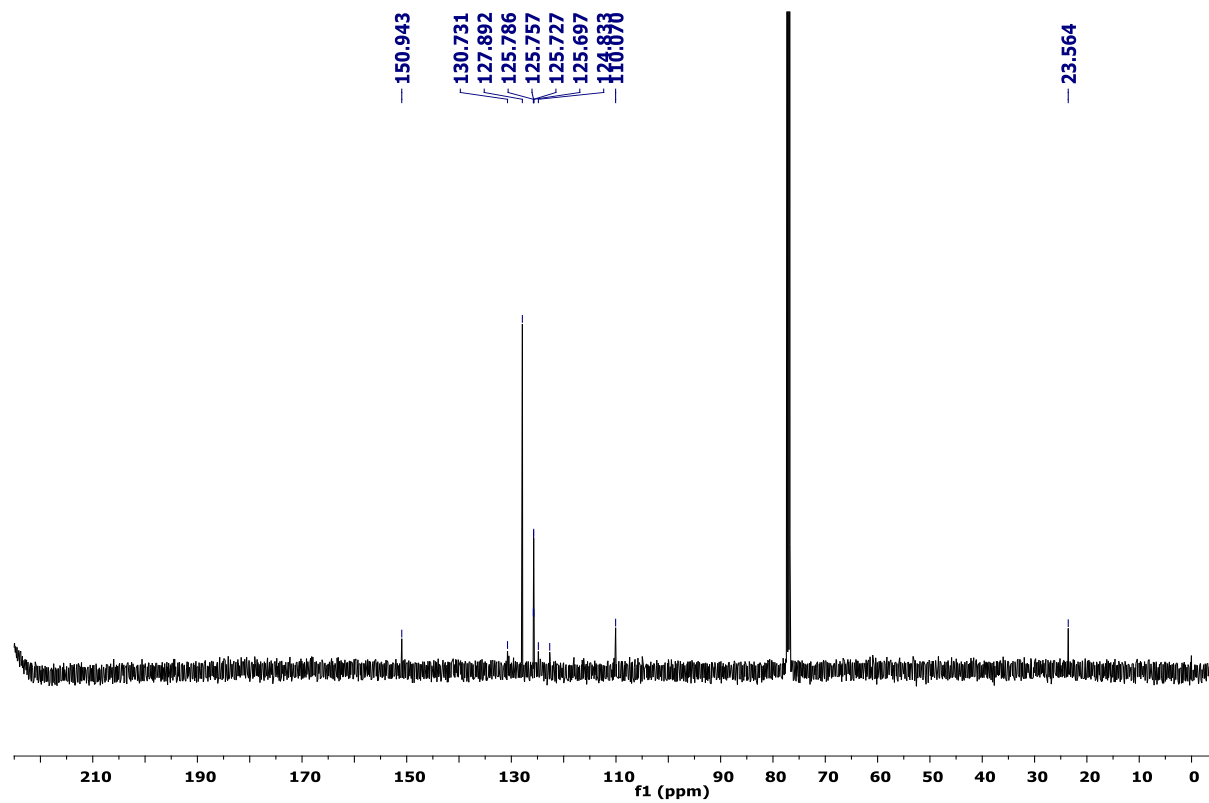
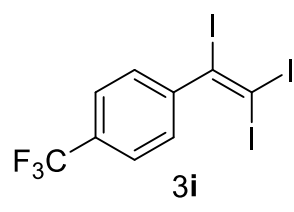
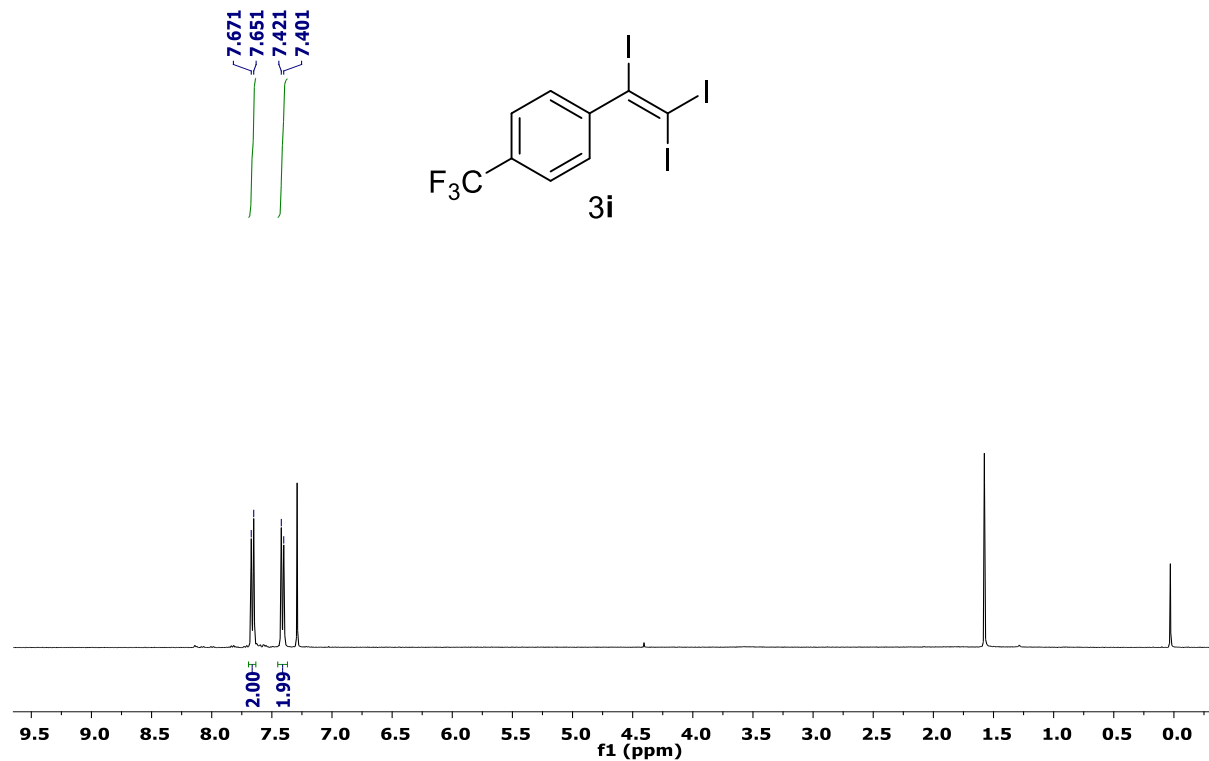
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 3g ( $\text{CDCl}_3$ )



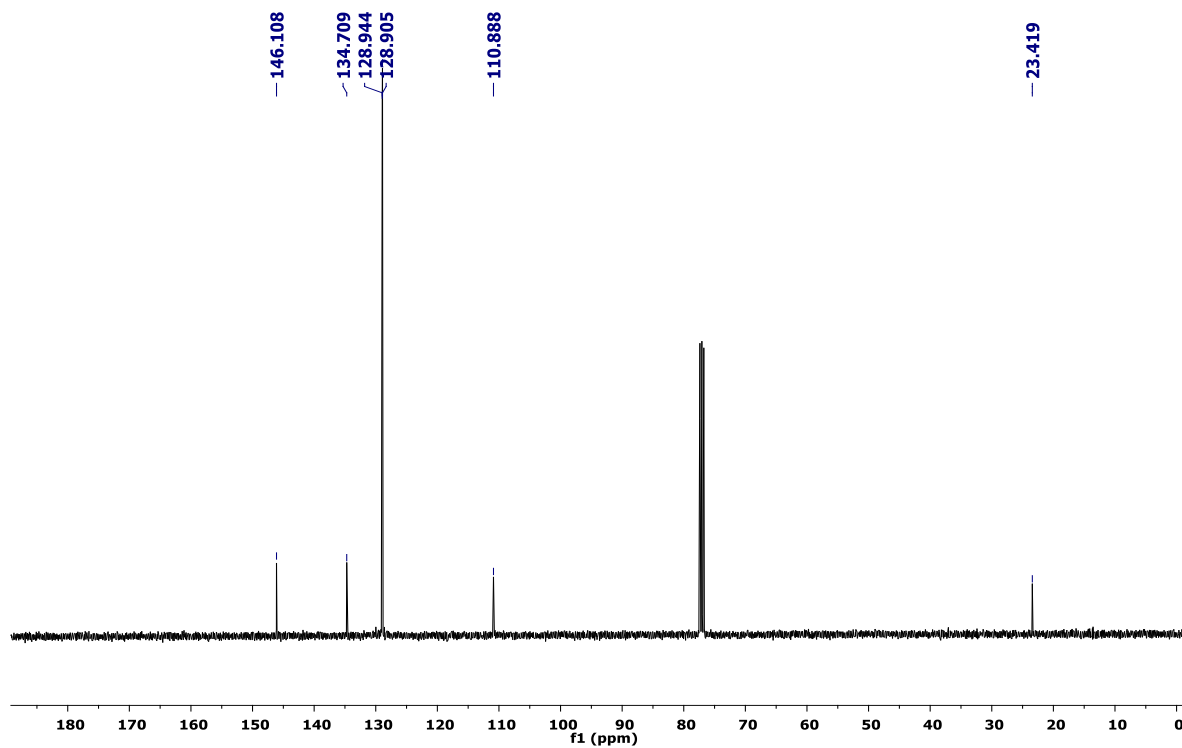
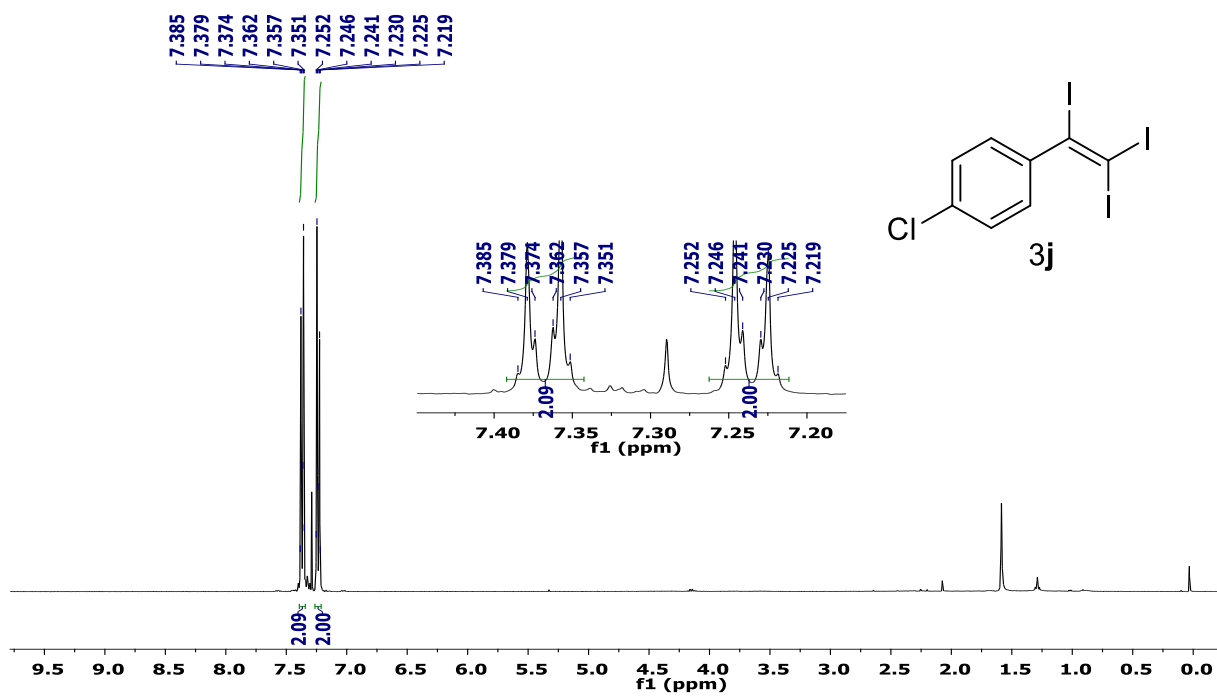
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 3h ( $\text{CDCl}_3$ )



$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 3i ( $\text{CDCl}_3$ )

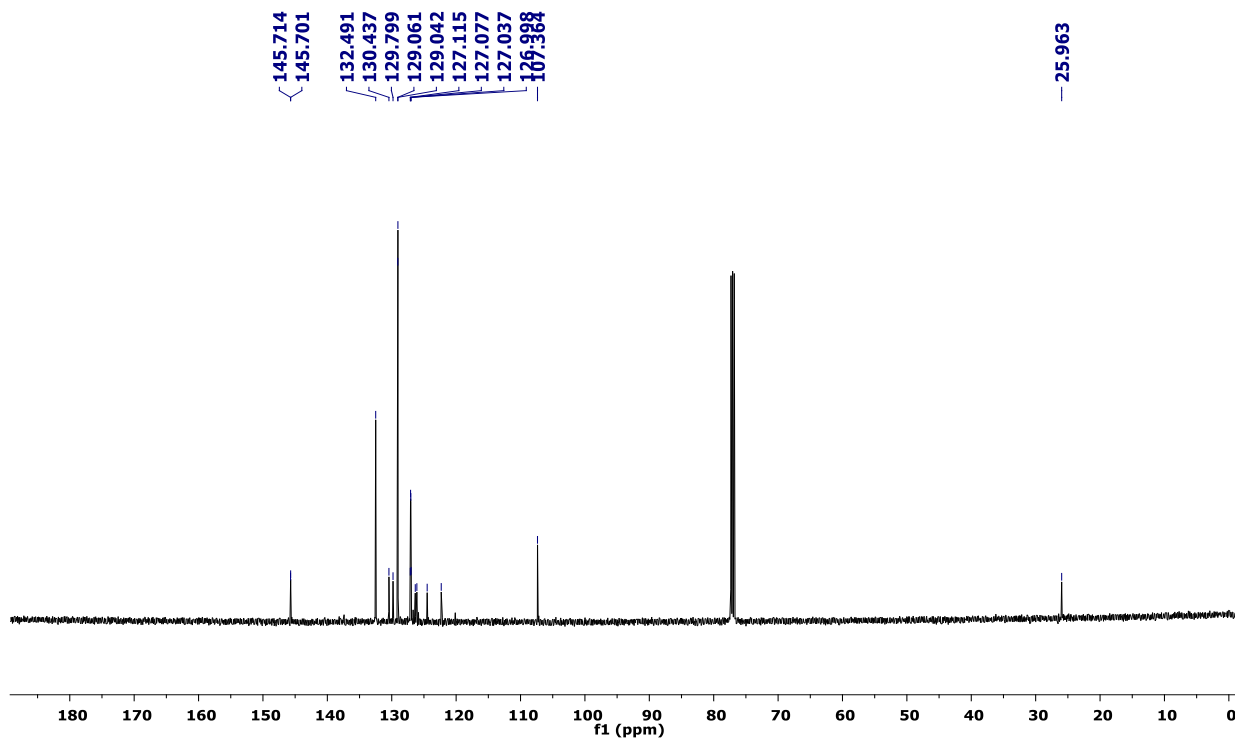
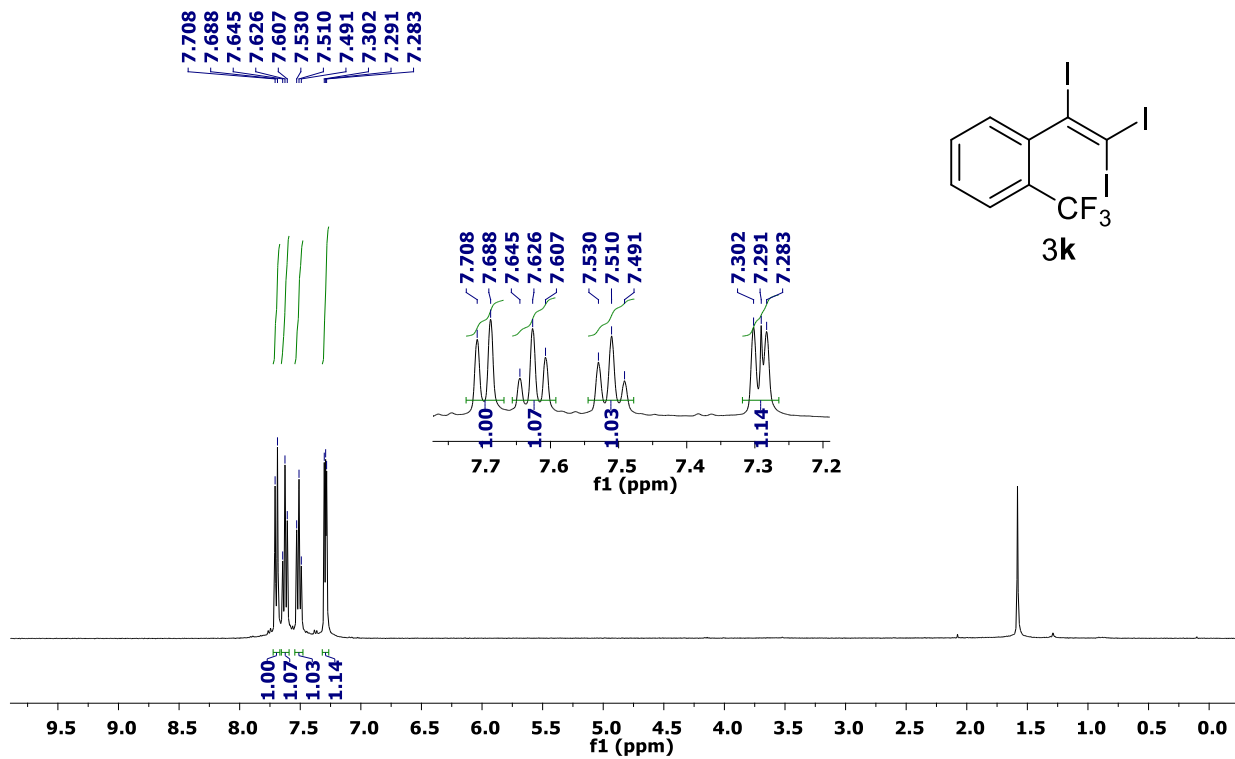


$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **3j** ( $\text{CDCl}_3$ )

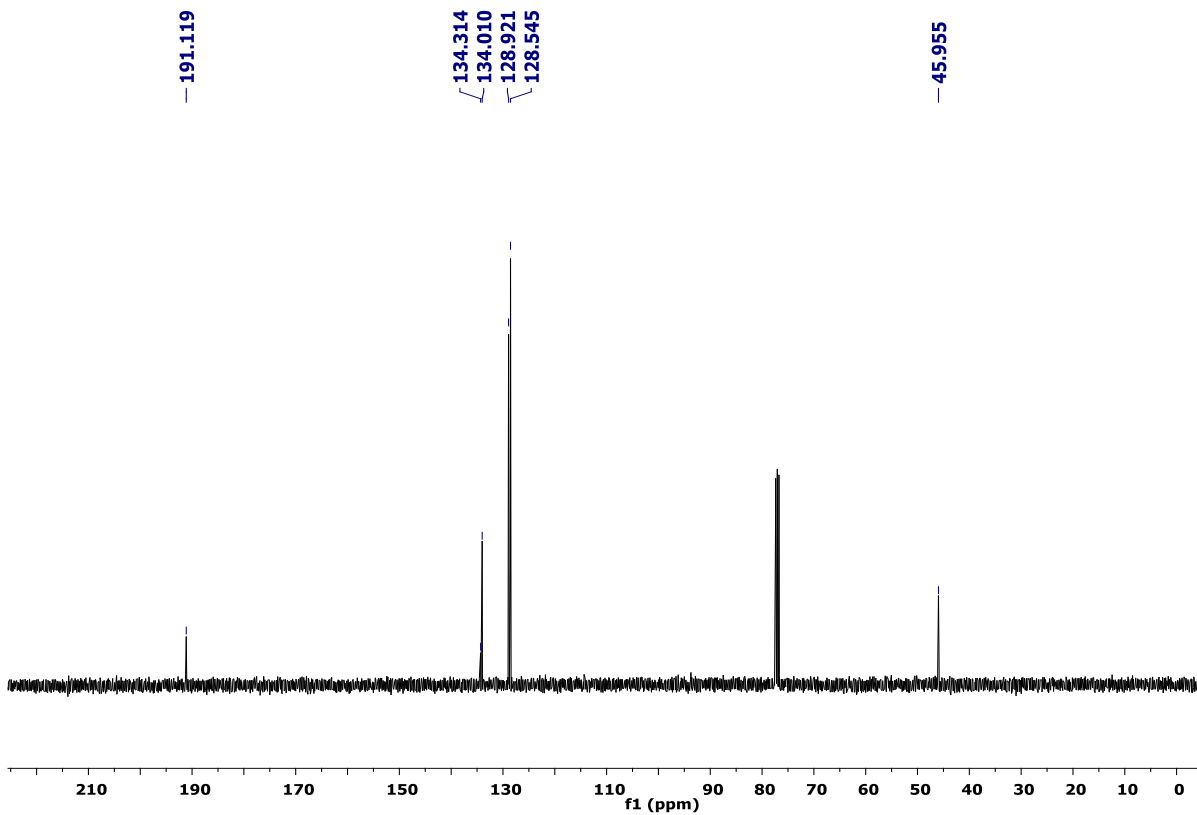
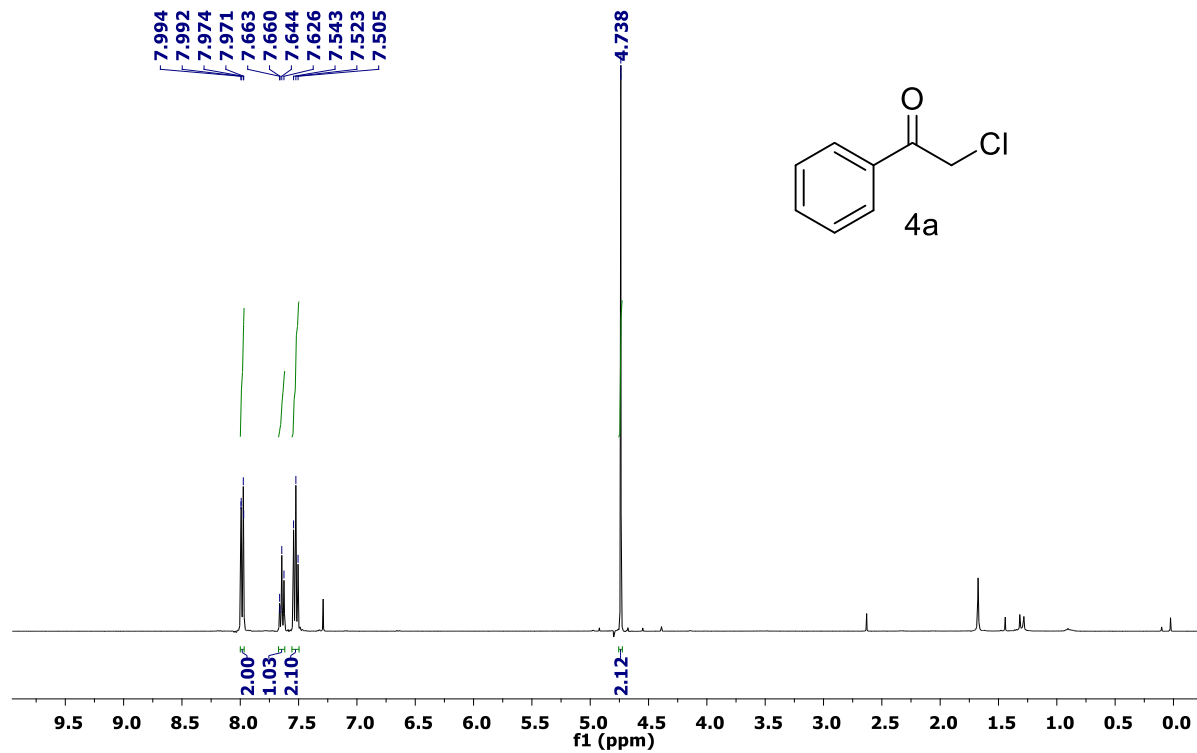




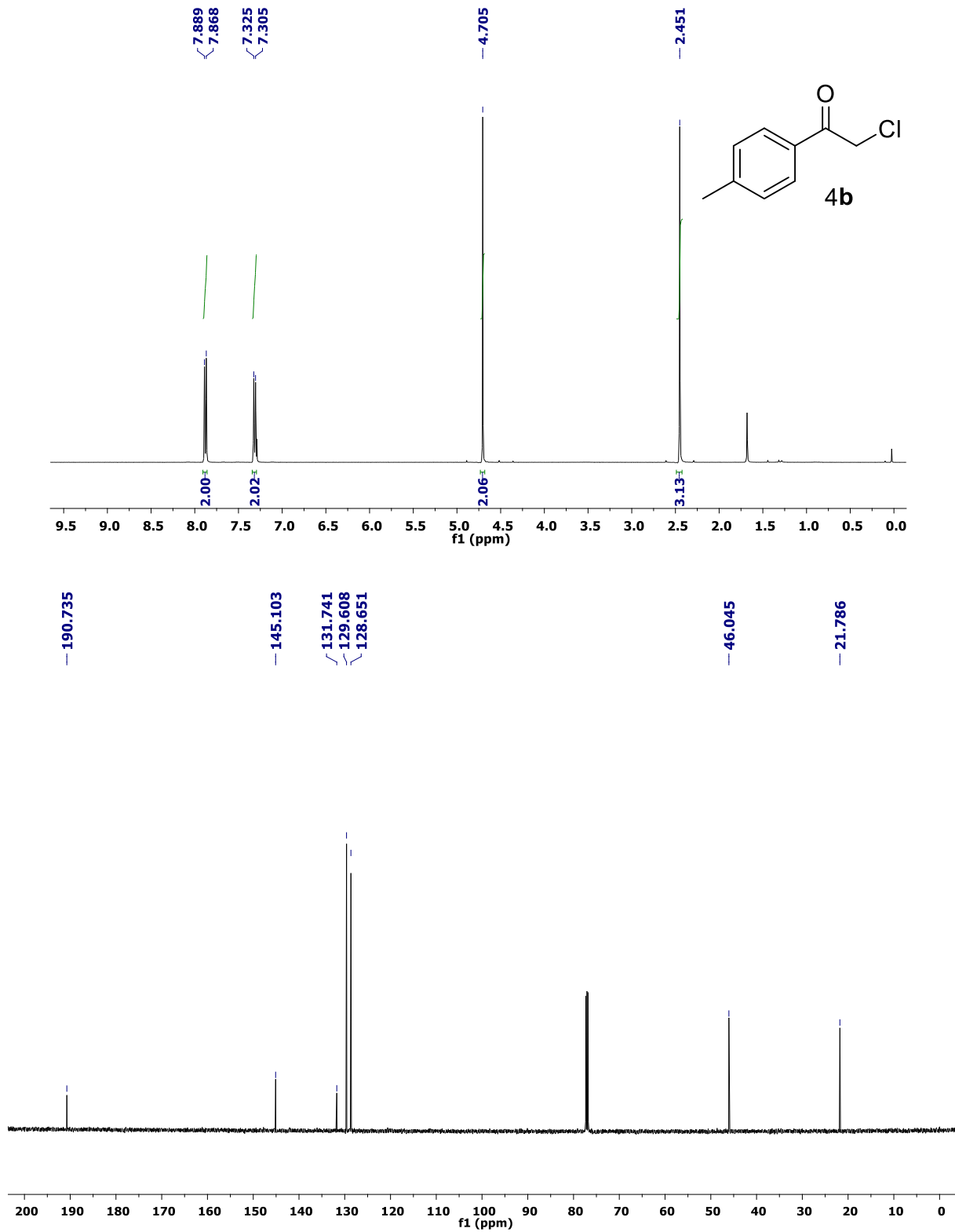
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 3k ( $\text{CDCl}_3$ )



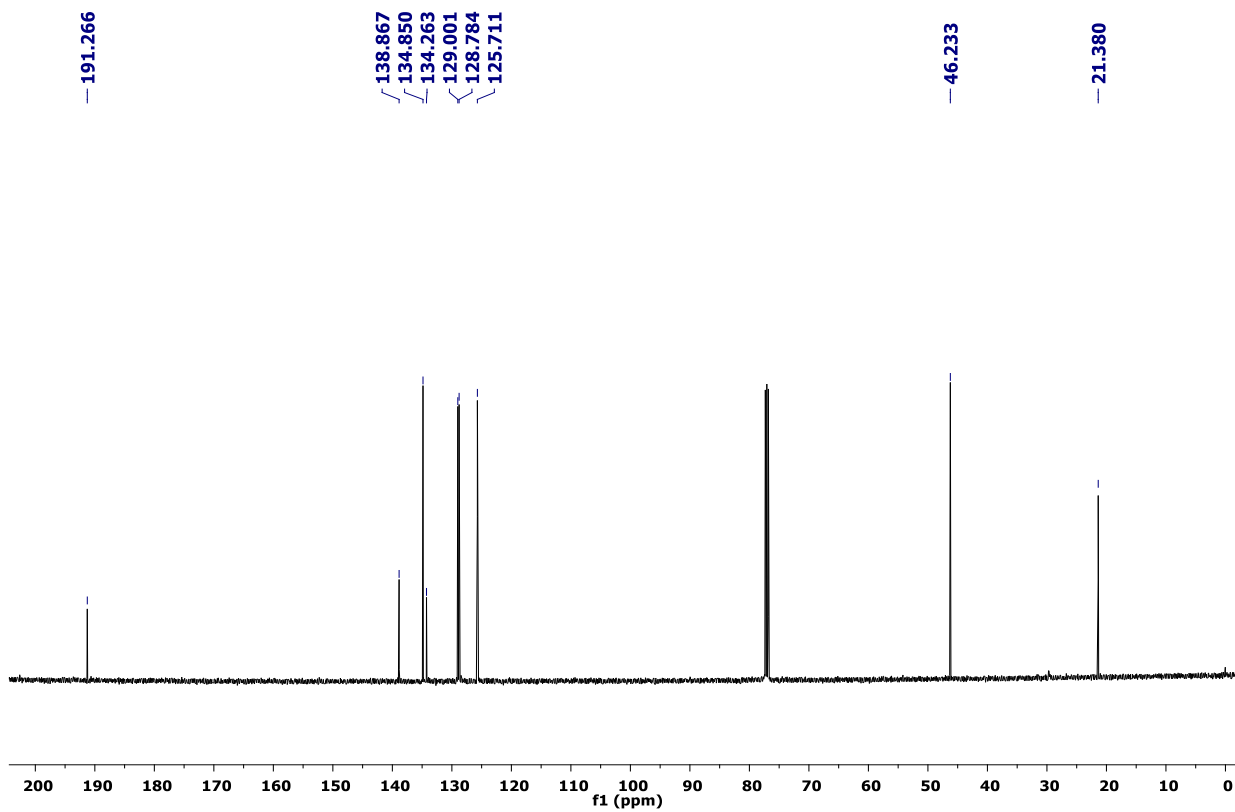
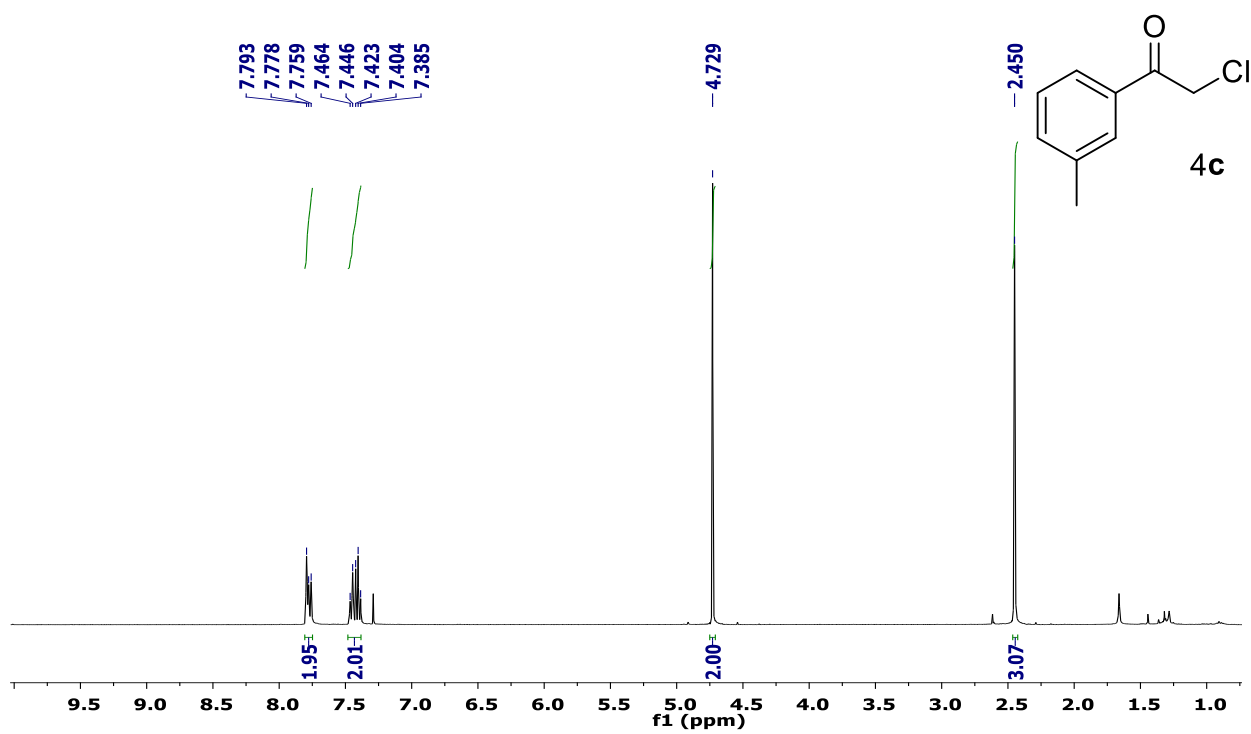
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 4a ( $\text{CDCl}_3$ )



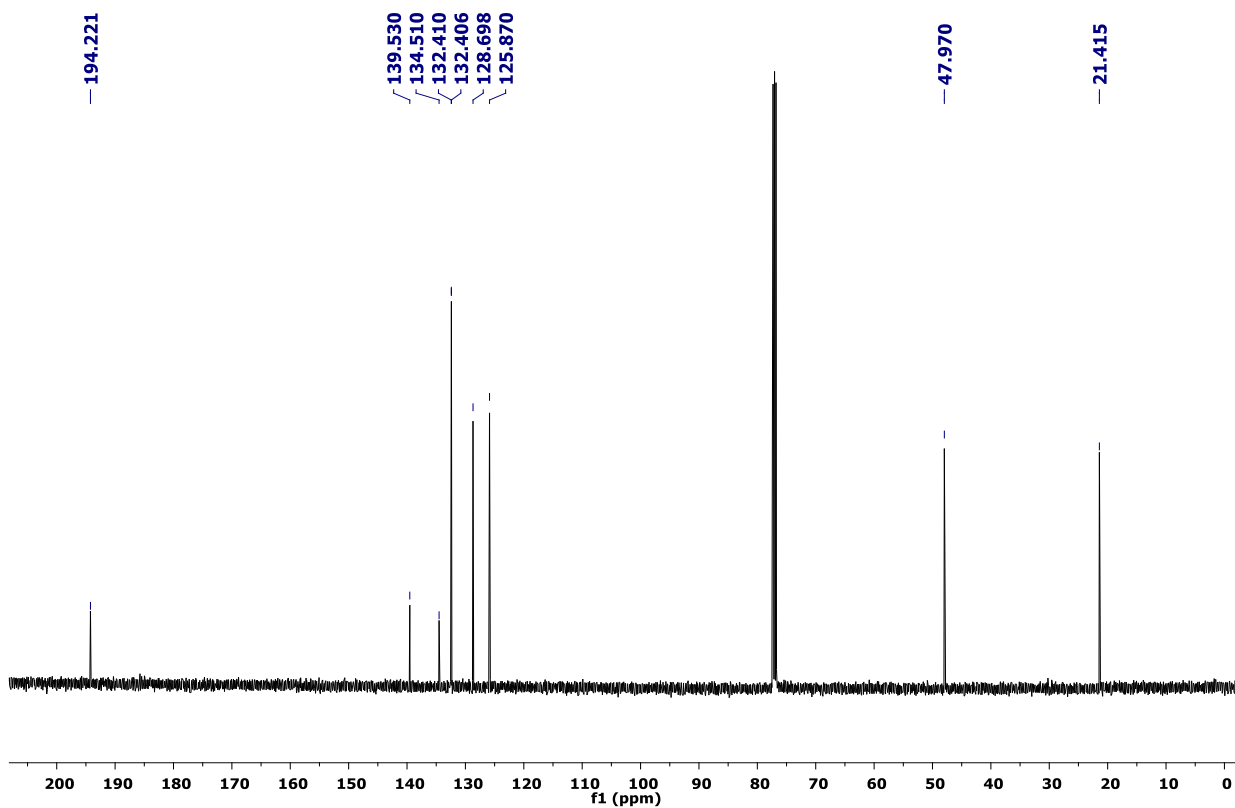
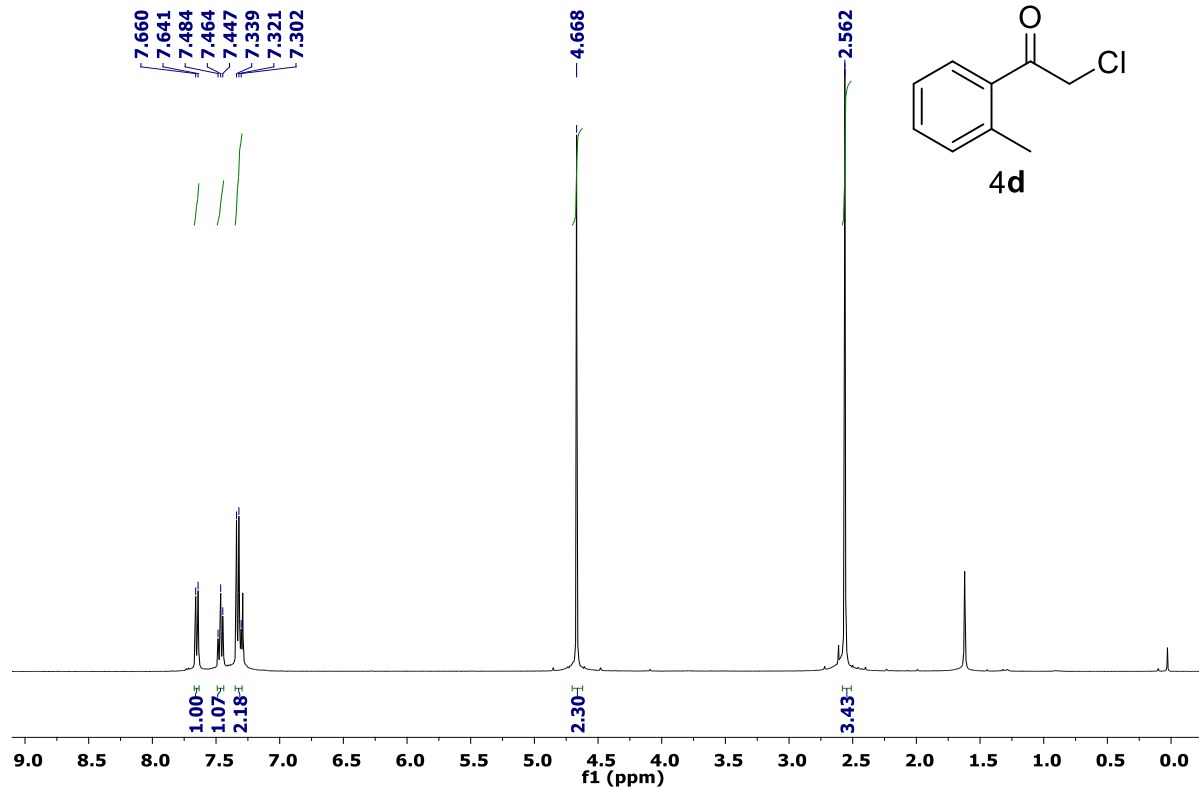
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 4b ( $\text{CDCl}_3$ )



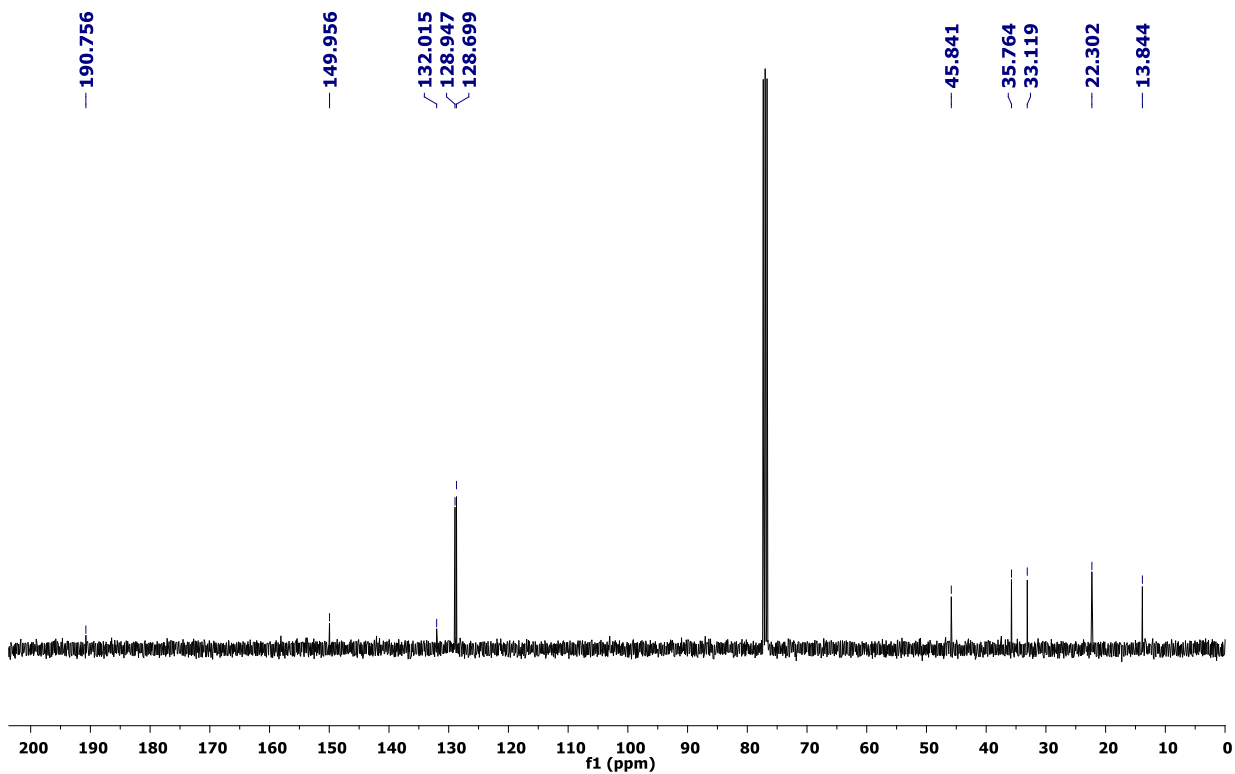
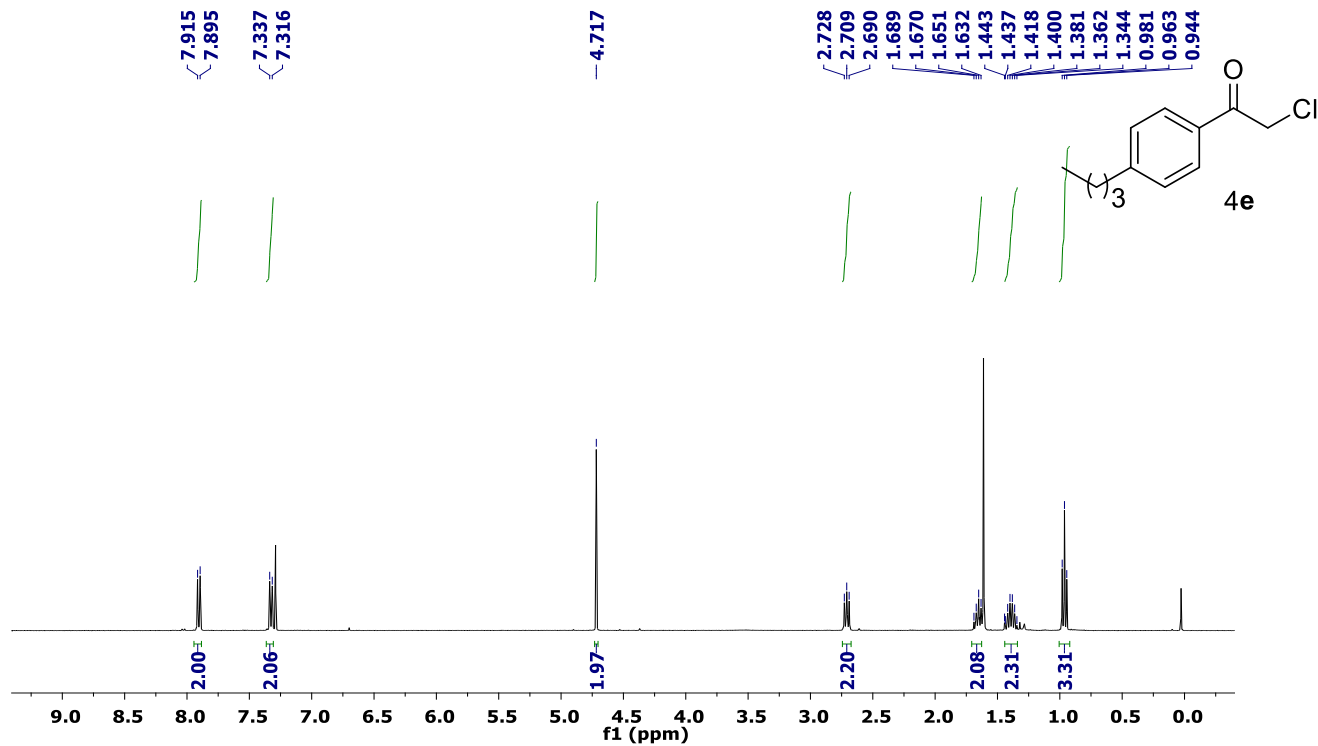
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 4c ( $\text{CDCl}_3$ )



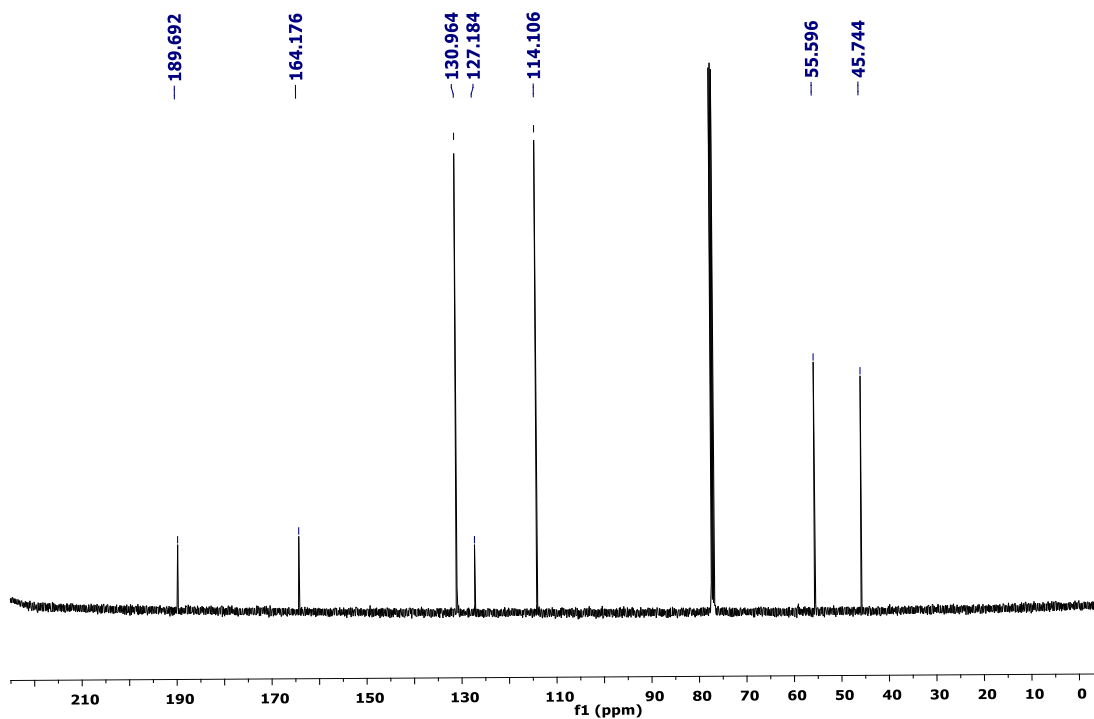
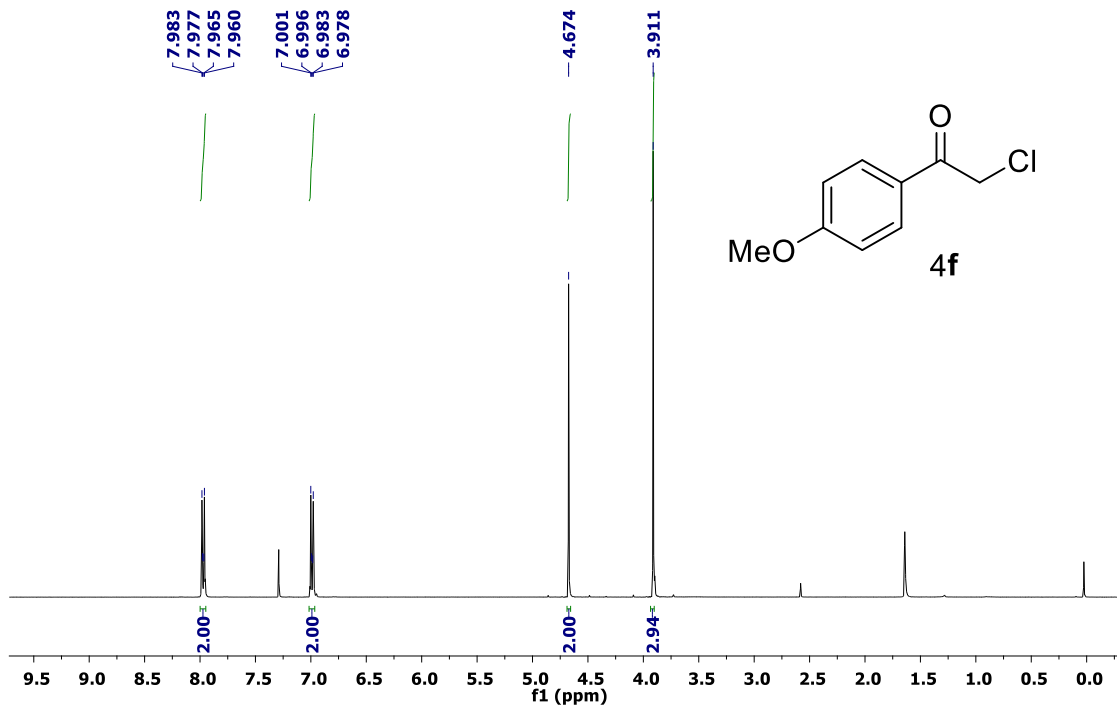
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 4d ( $\text{CDCl}_3$ )



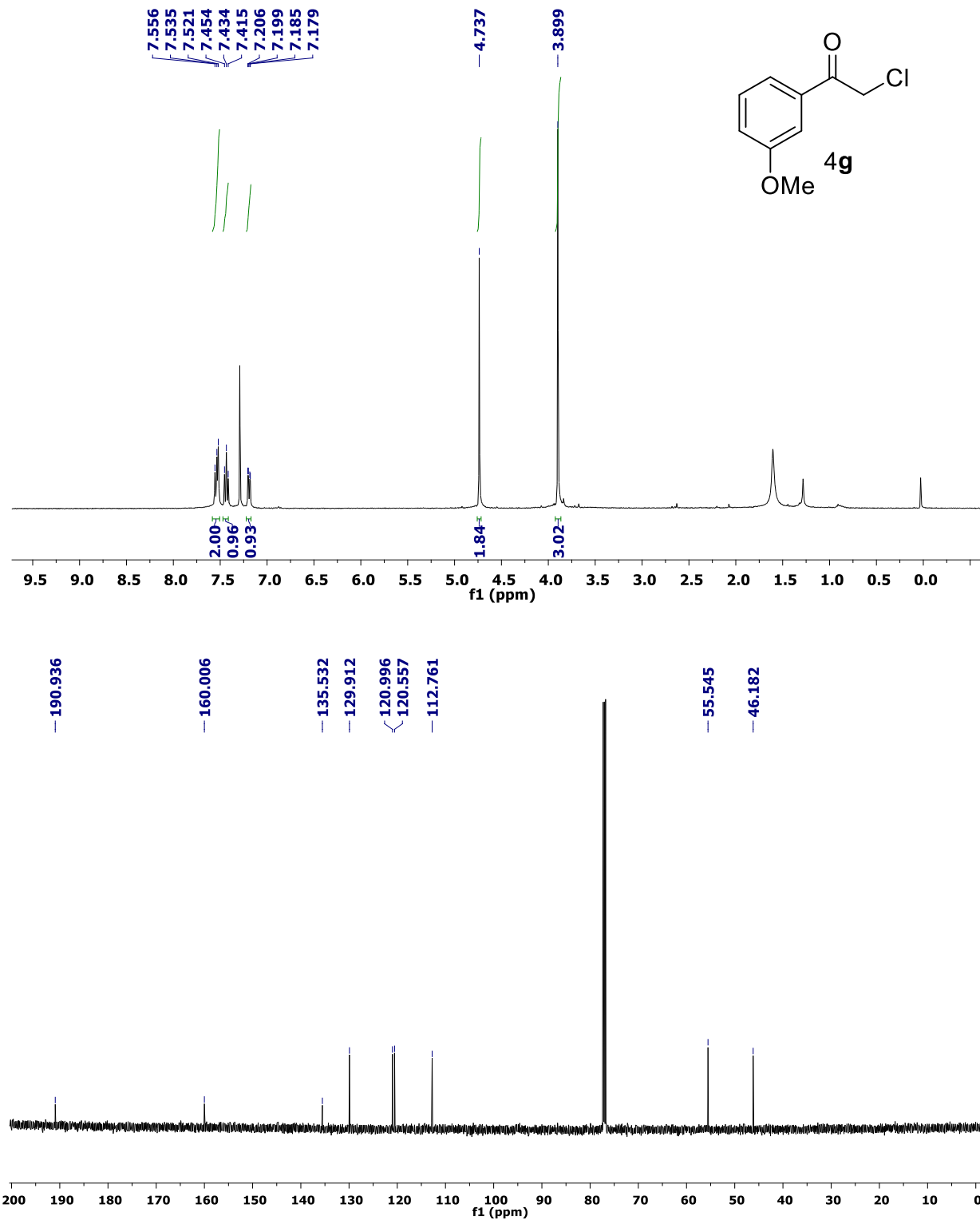
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 4e ( $\text{CDCl}_3$ )



$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 4f ( $\text{CDCl}_3$ )

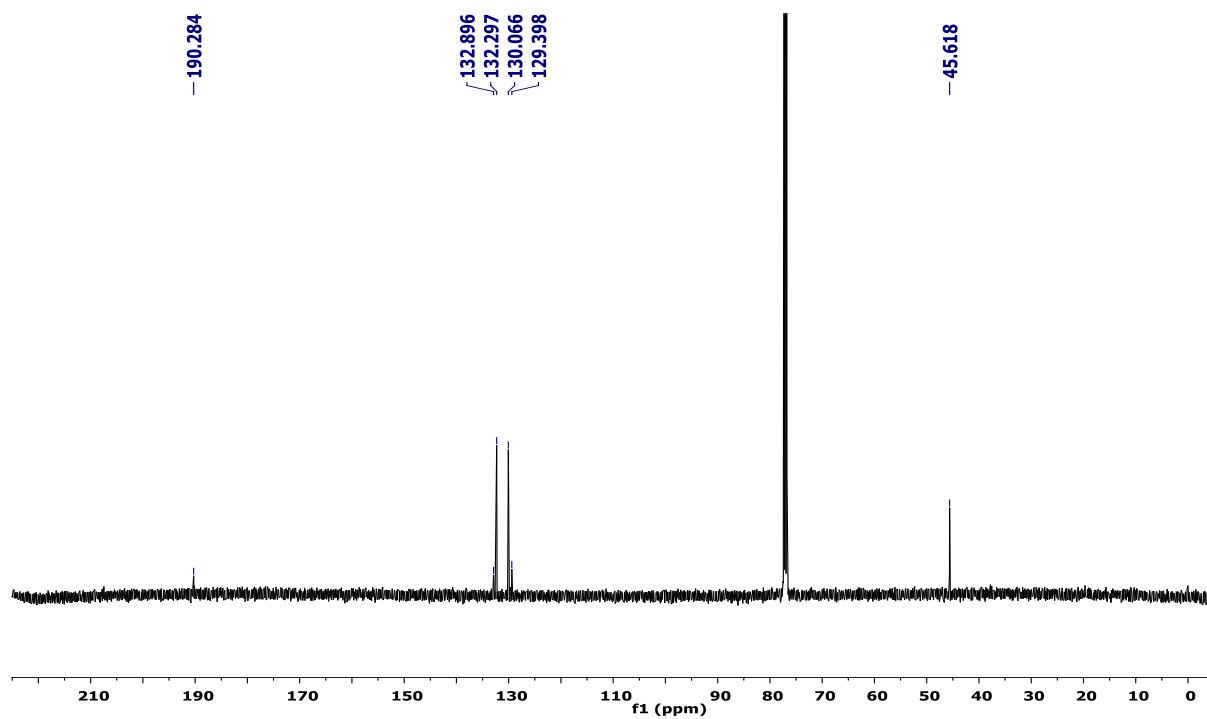
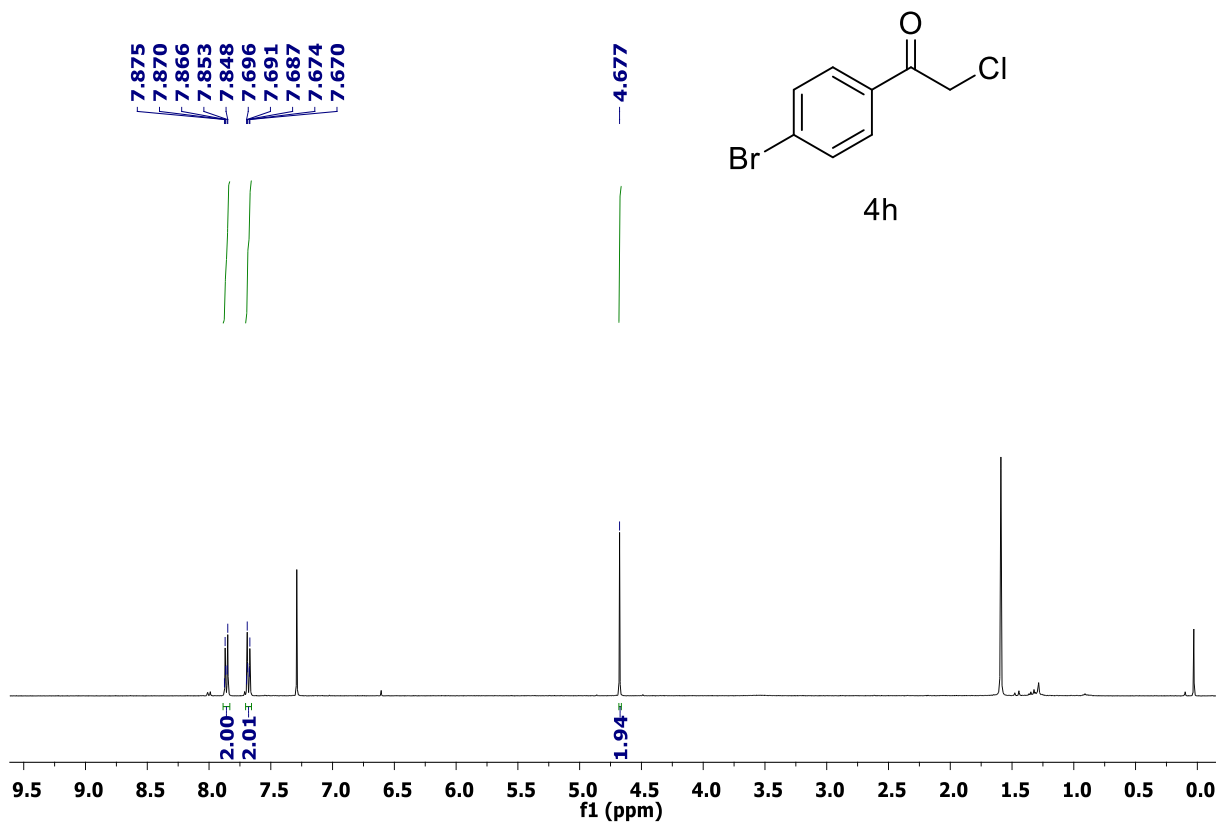


$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 4g ( $\text{CDCl}_3$ )

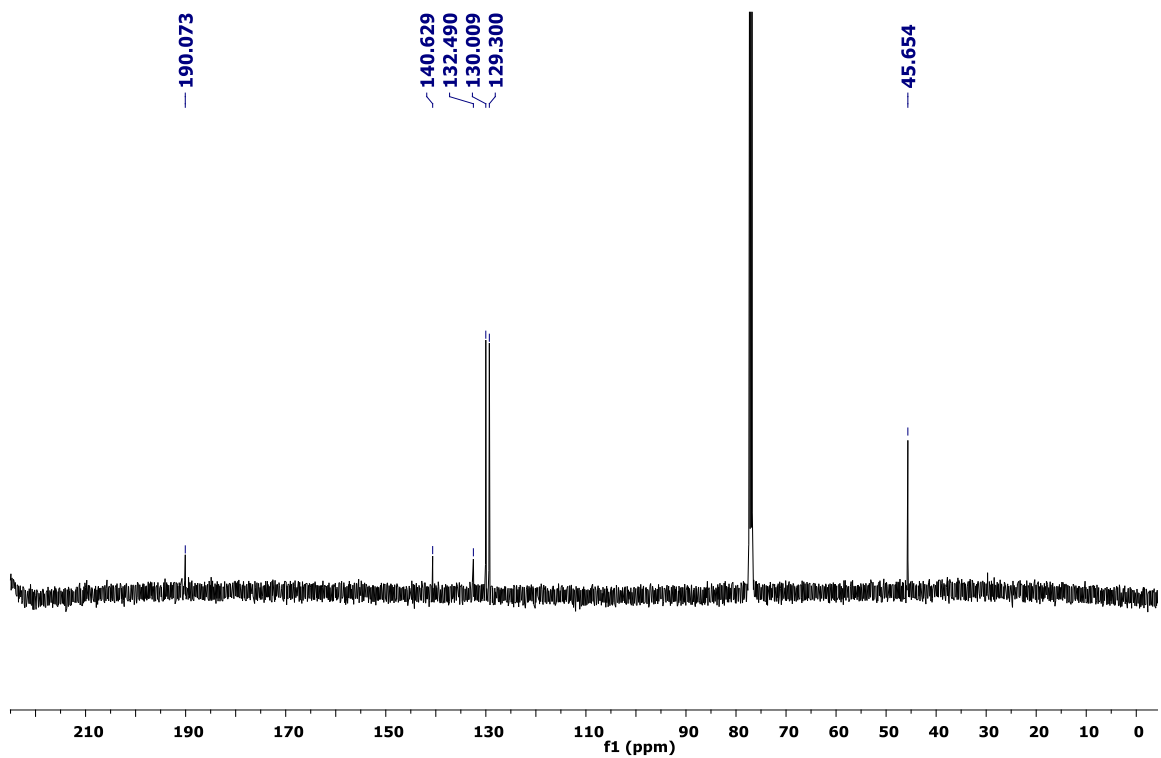
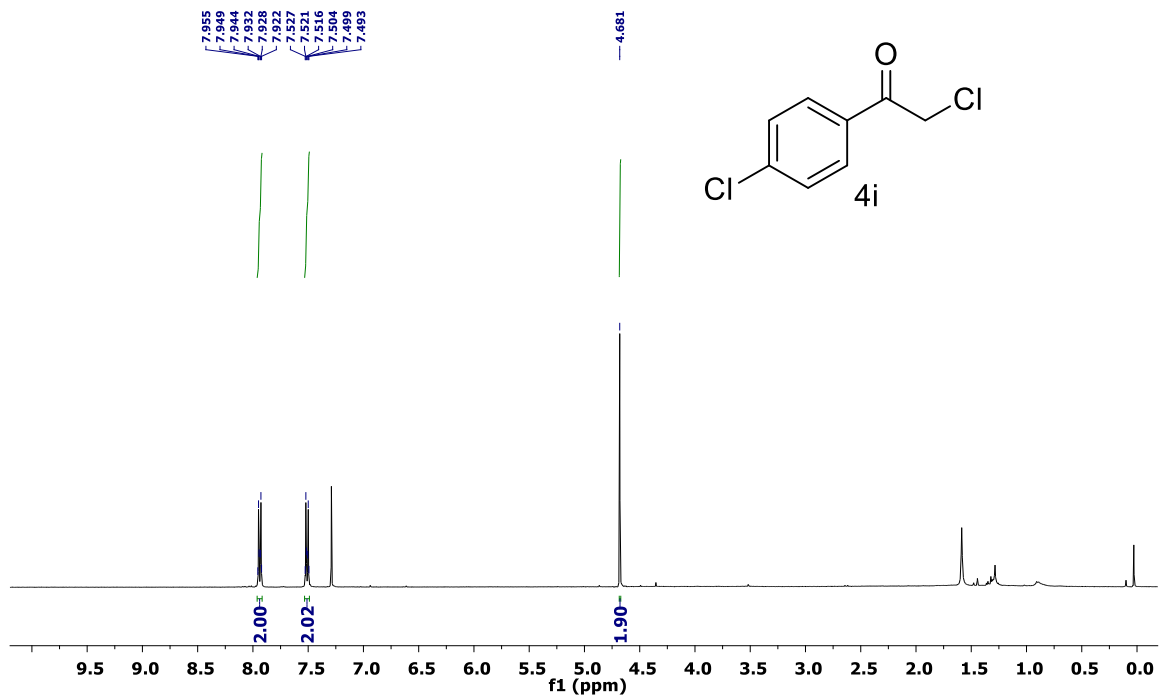




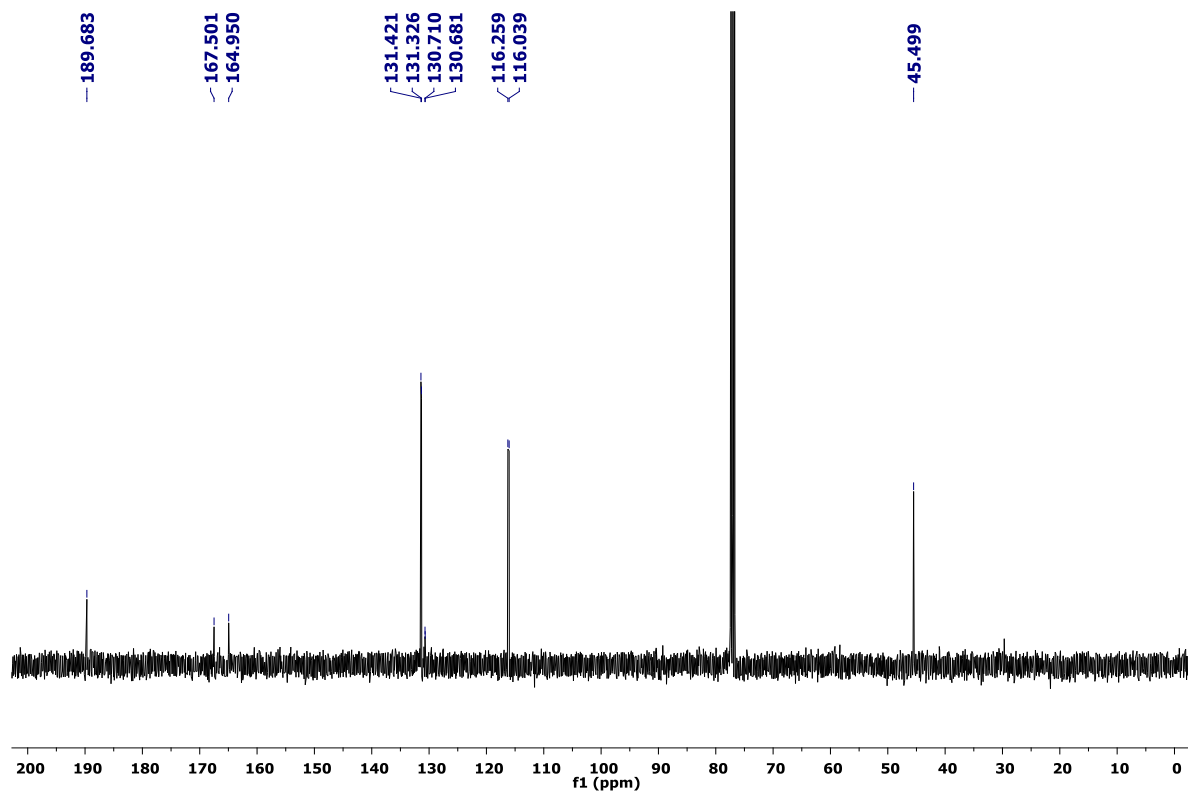
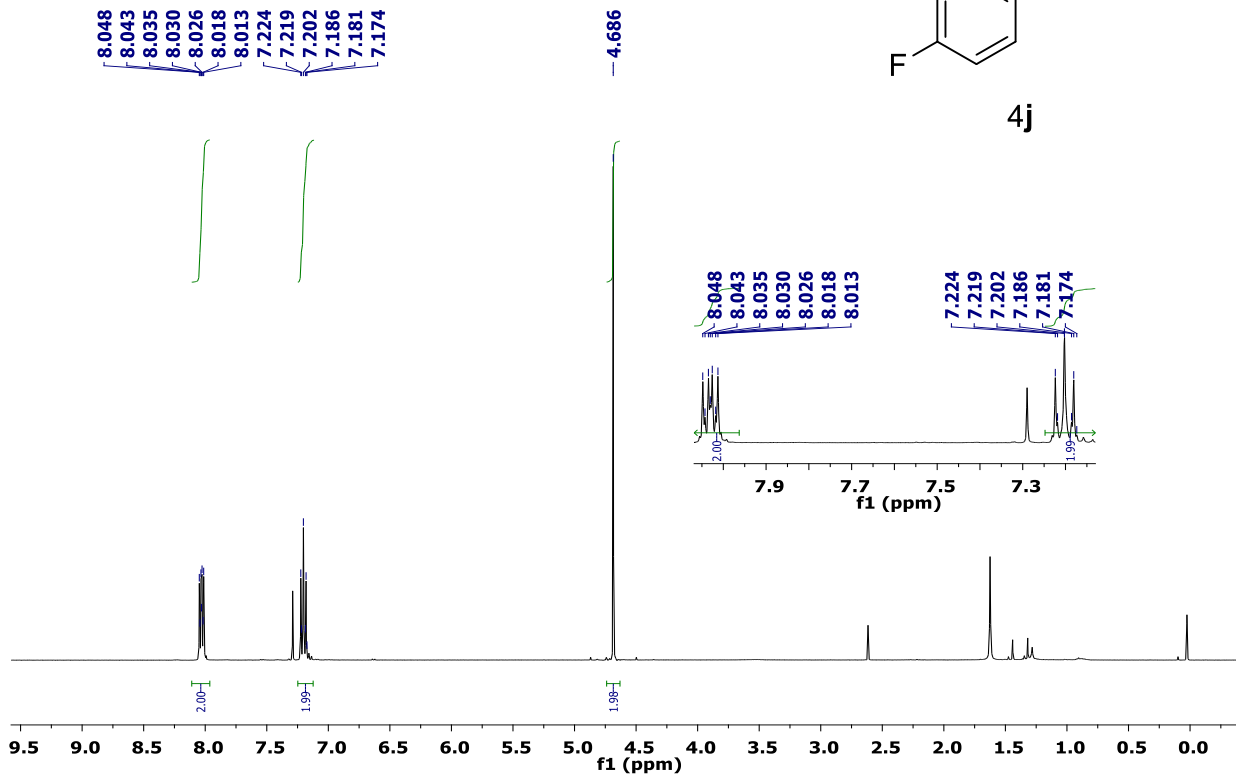
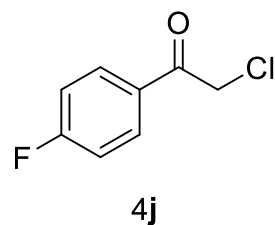
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 4h ( $\text{CDCl}_3$ )



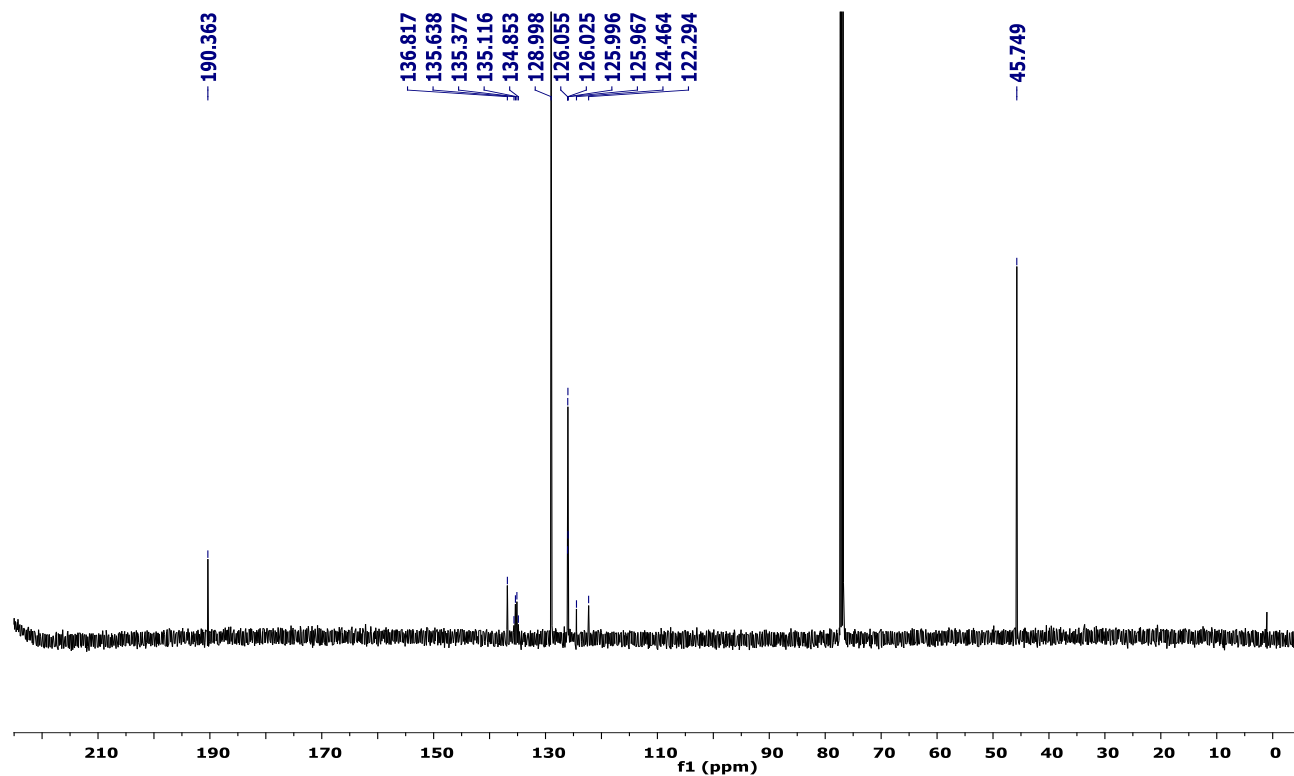
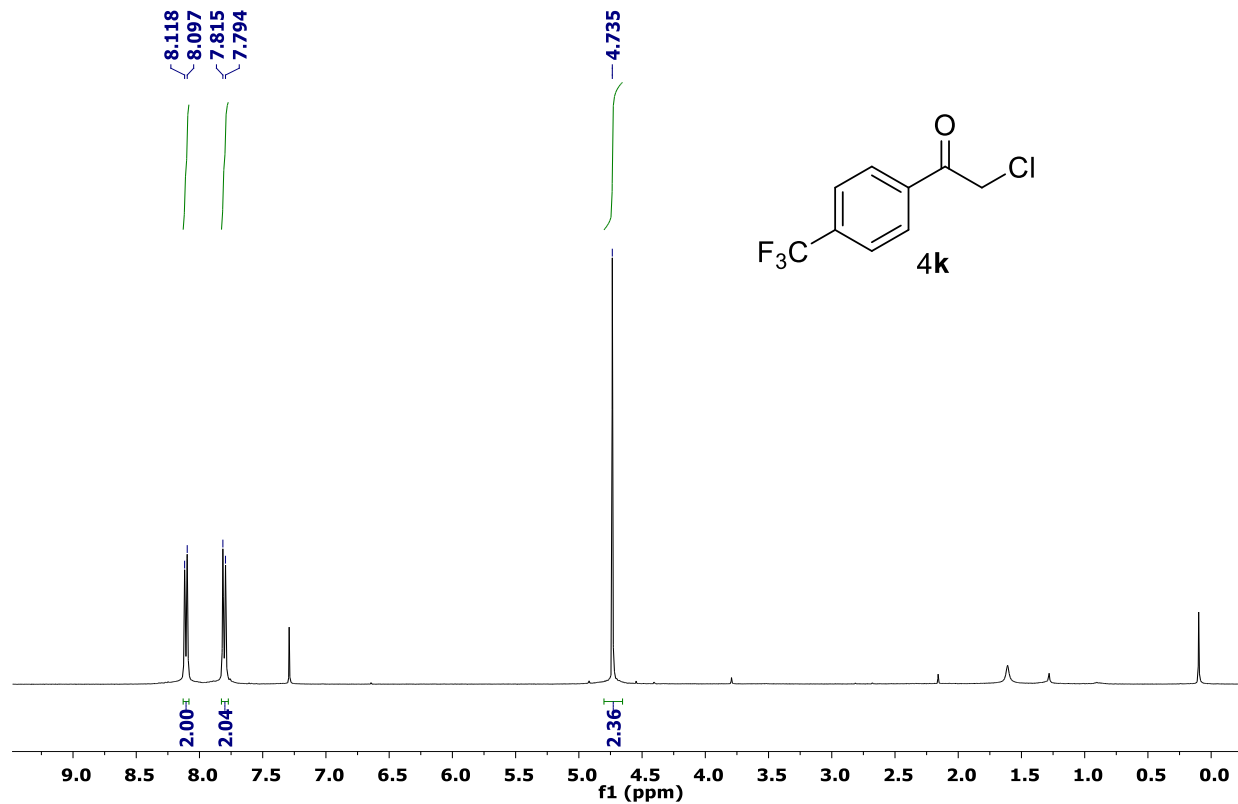
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 4i (CDCl<sub>3</sub>)



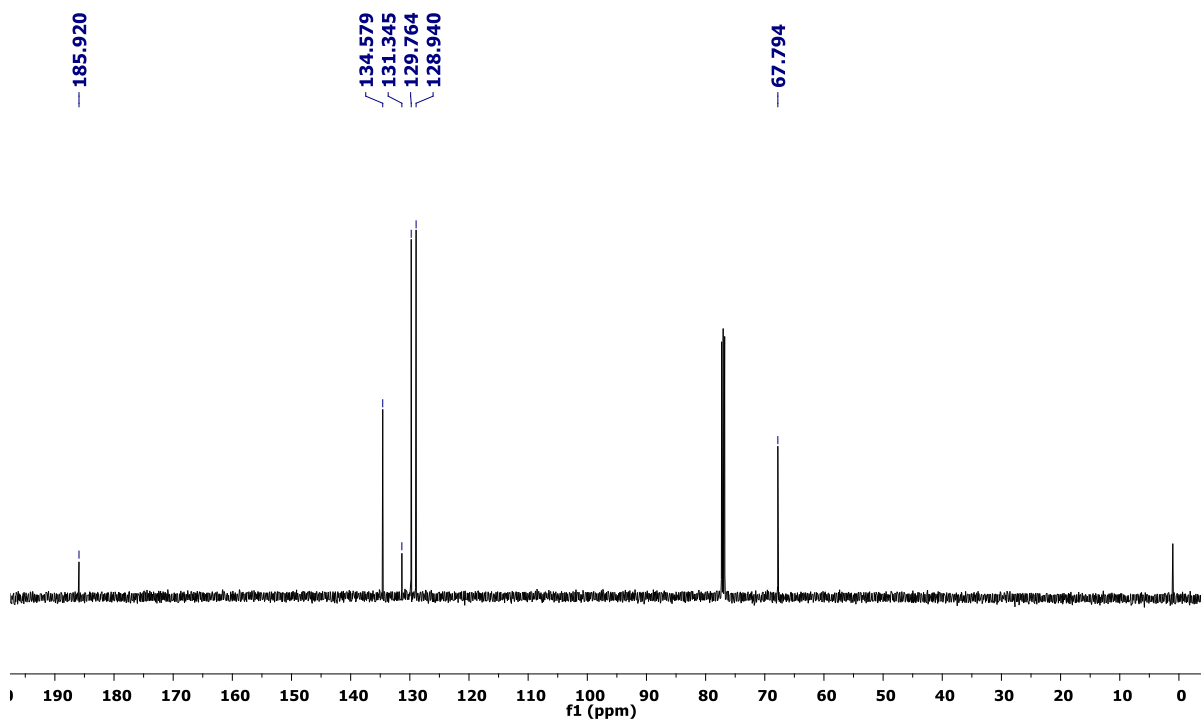
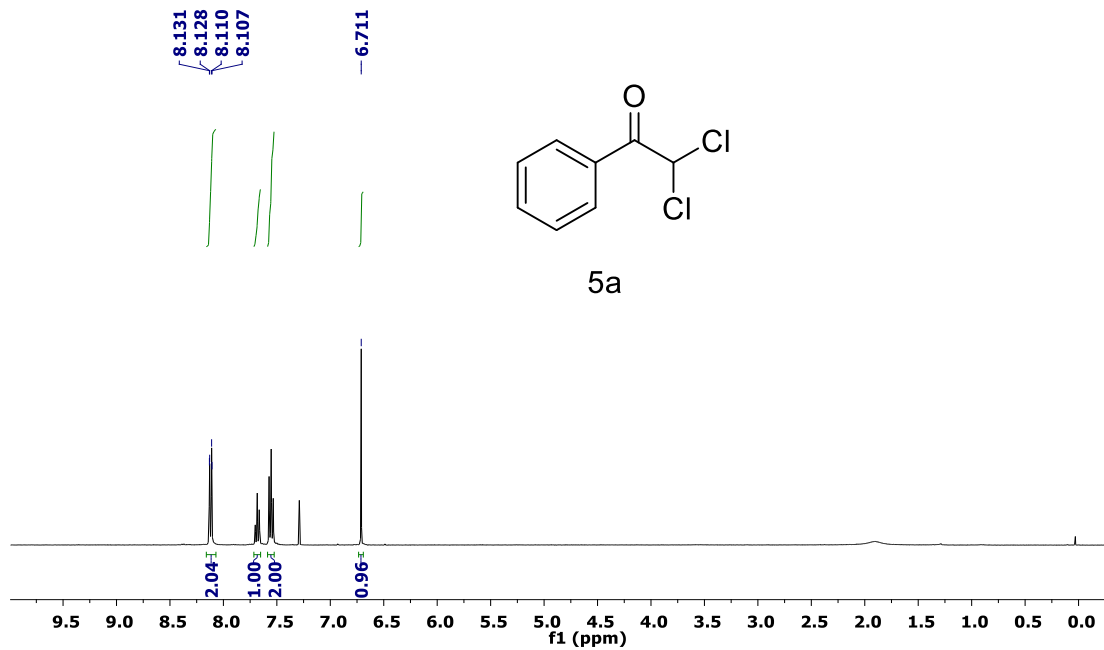
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 4j ( $\text{CDCl}_3$ )



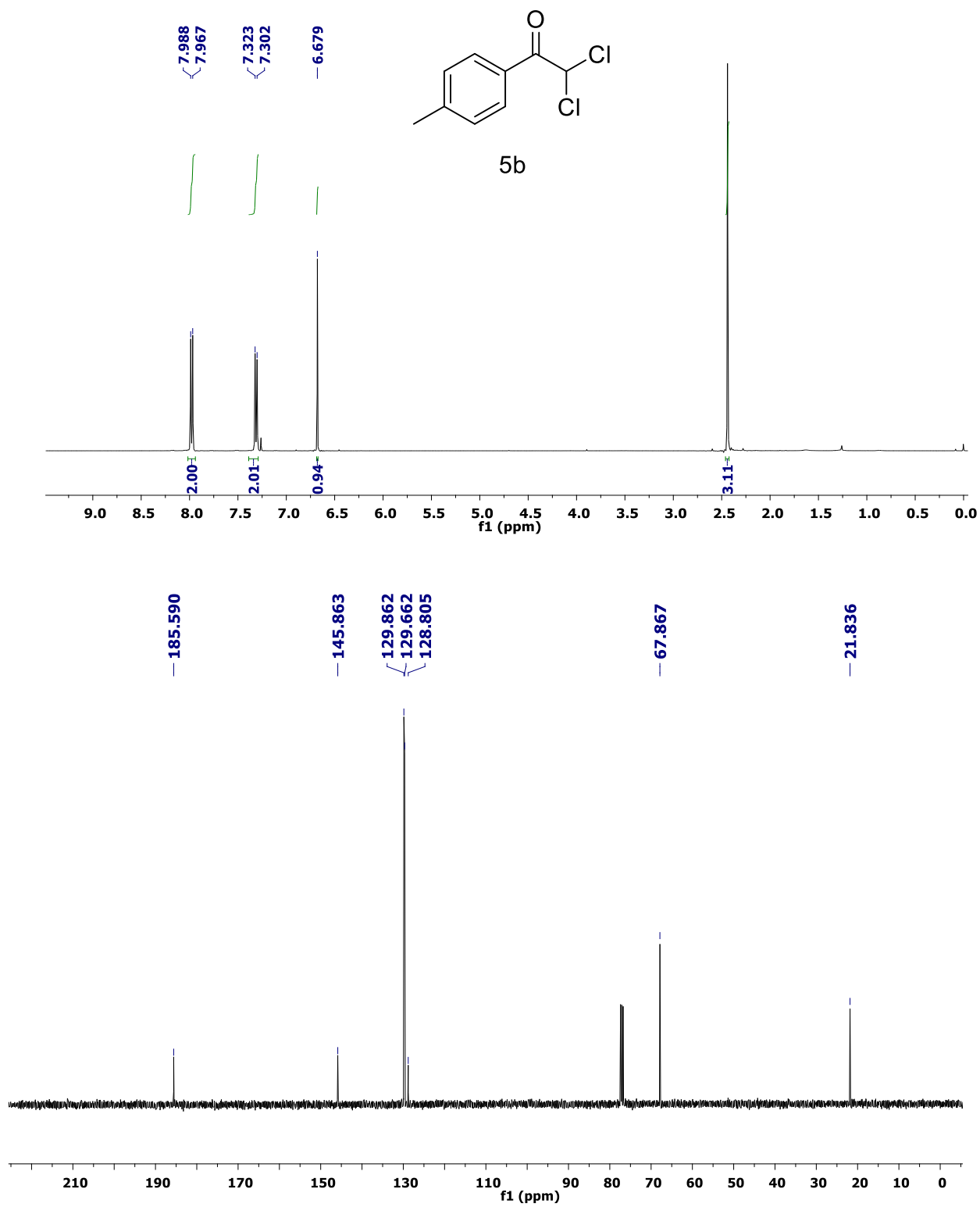
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 4k ( $\text{CDCl}_3$ )



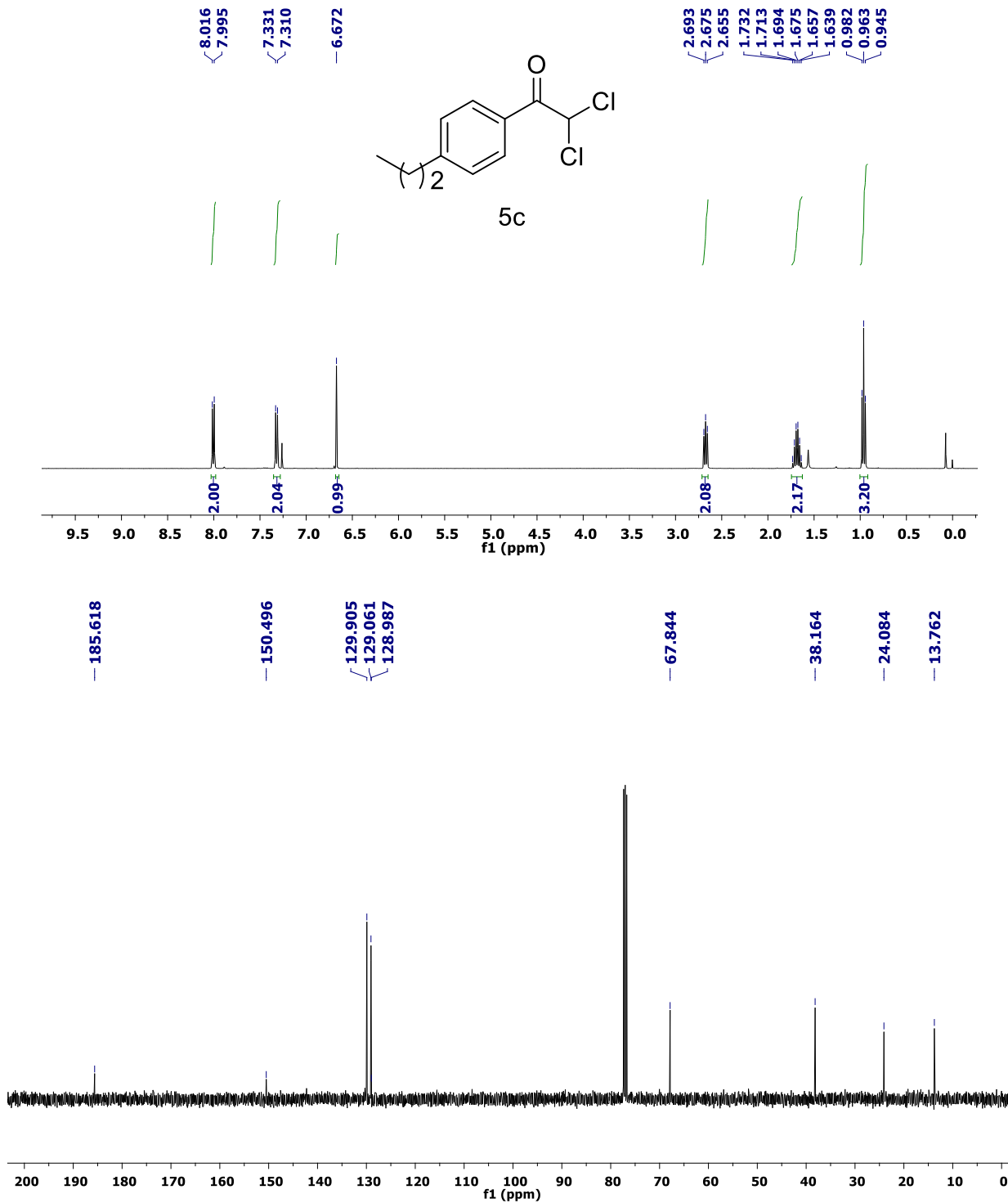
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 5a ( $\text{CDCl}_3$ )



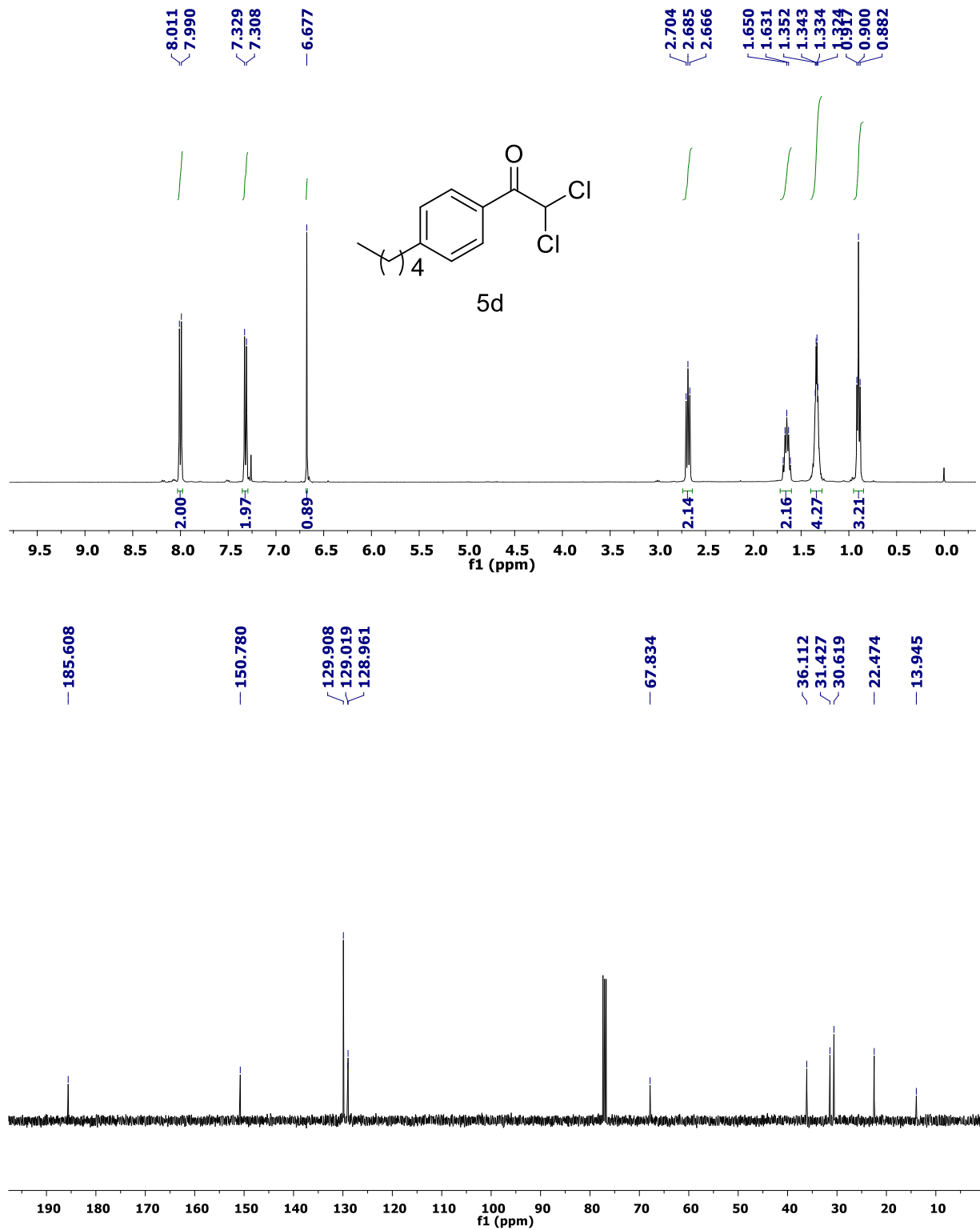
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 5b ( $\text{CDCl}_3$ )



$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 5c ( $\text{CDCl}_3$ )

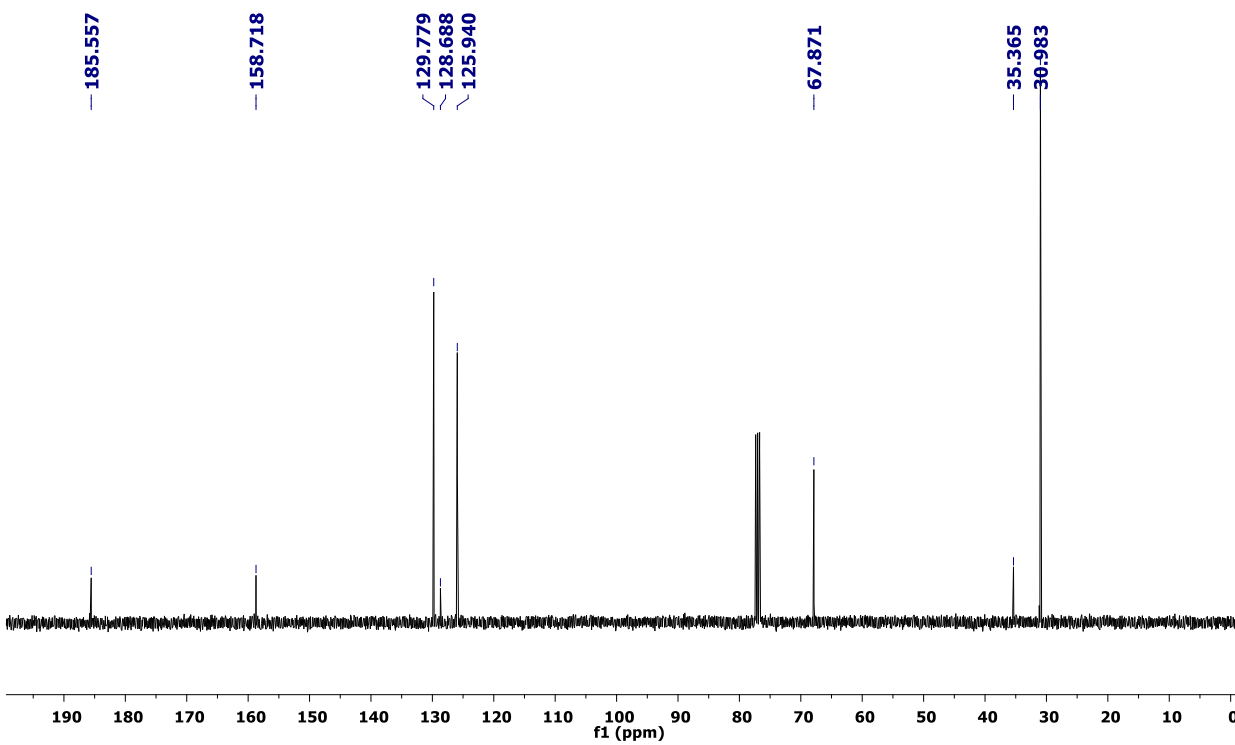
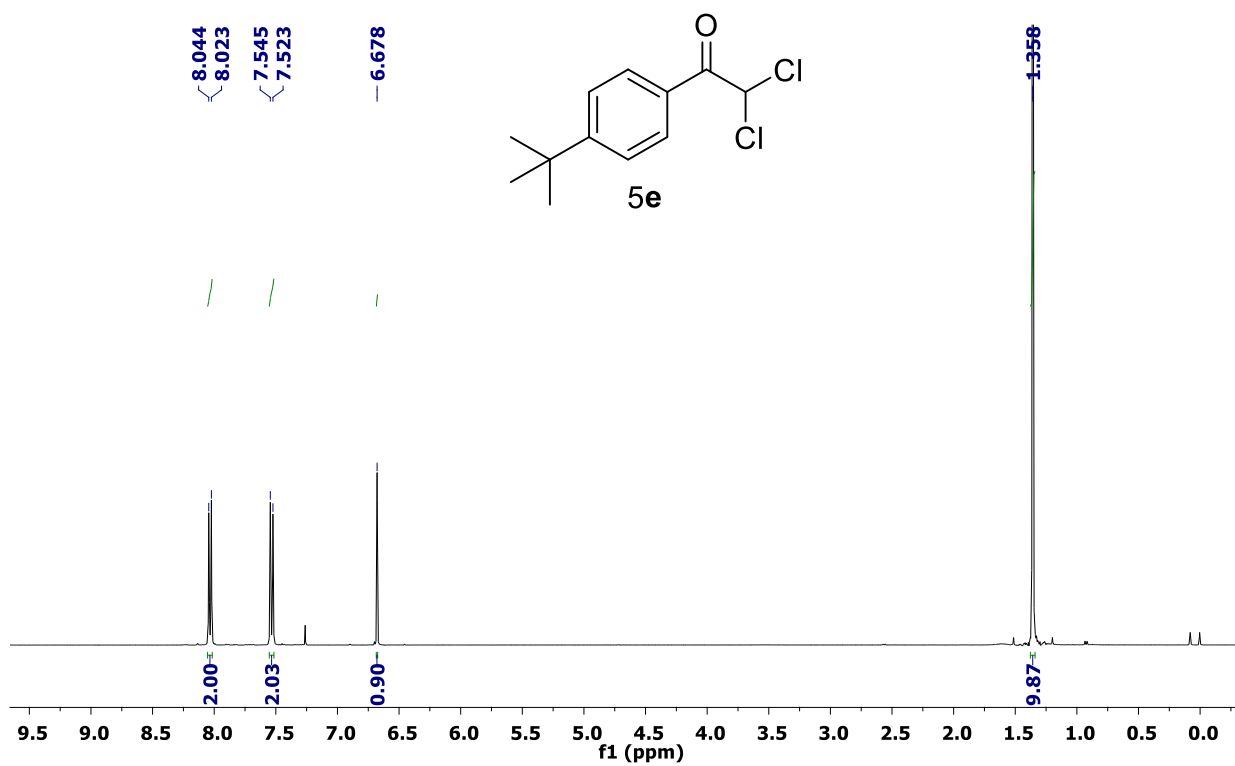


$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 5d ( $\text{CDCl}_3$ )

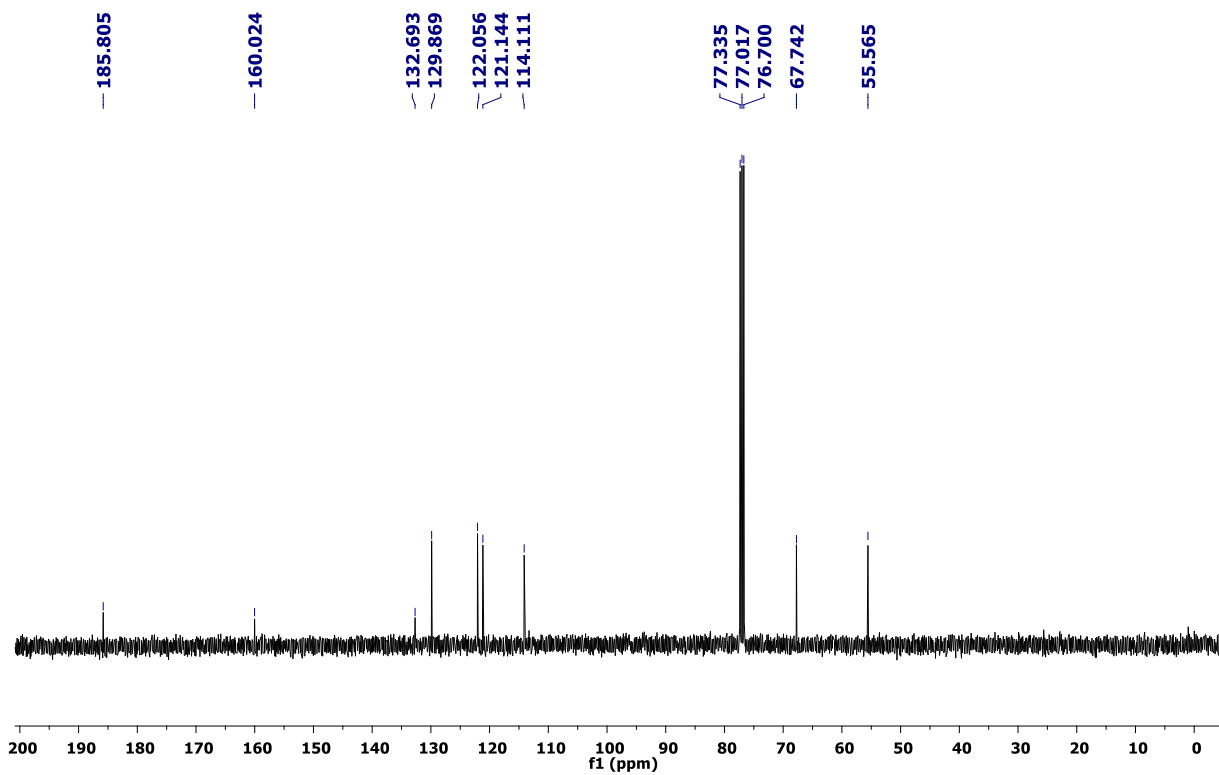
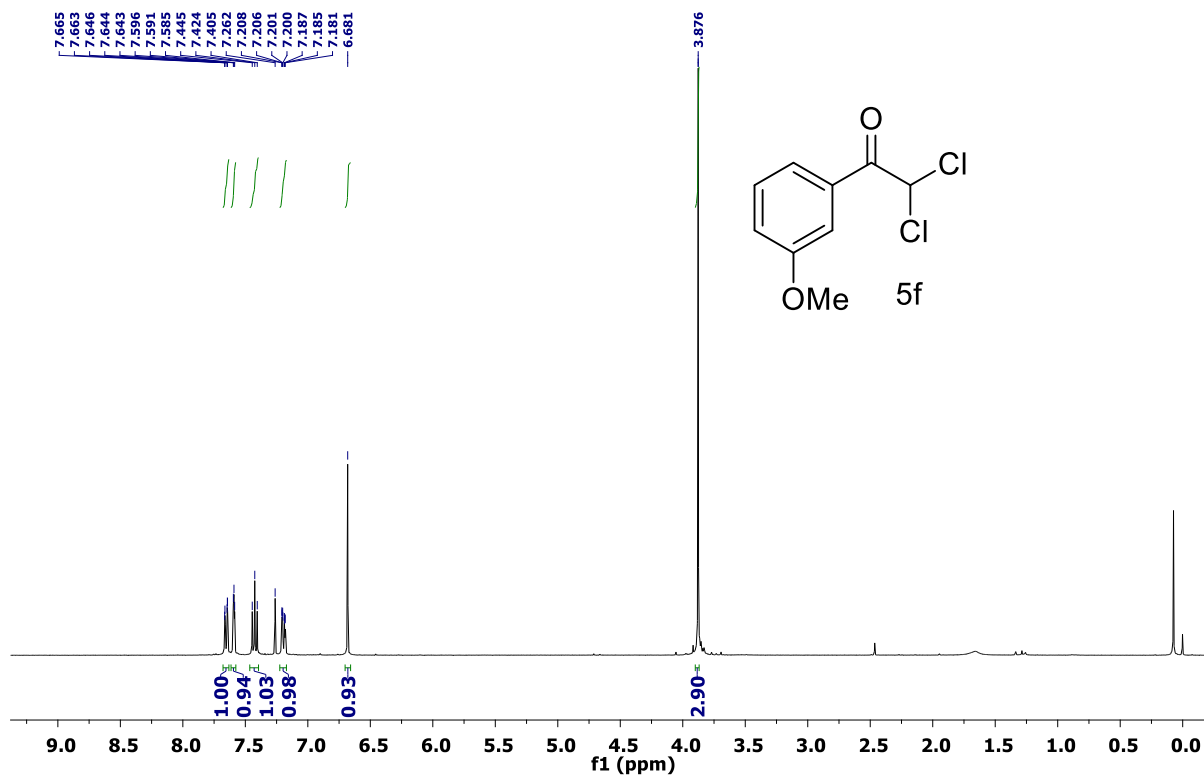




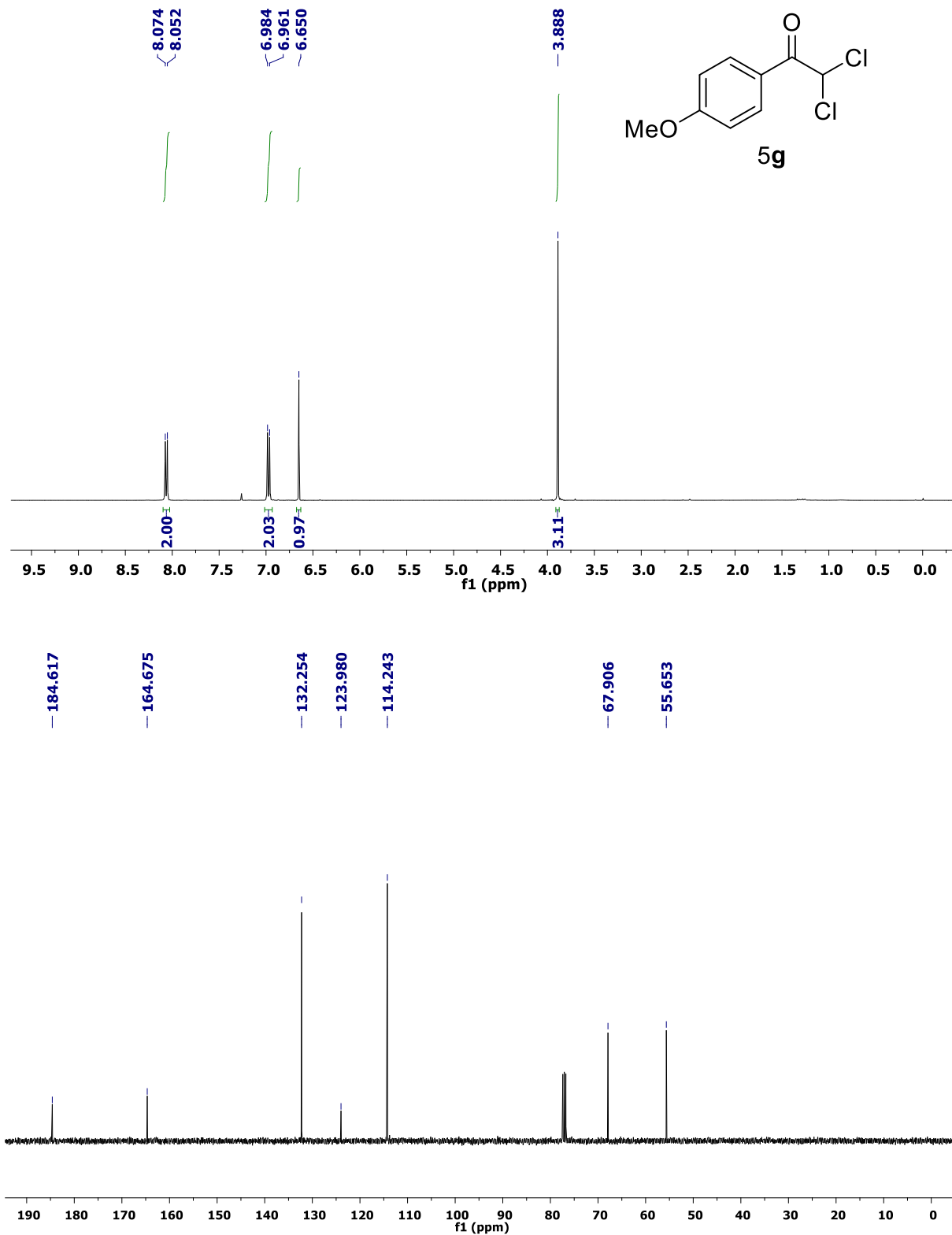
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 5e ( $\text{CDCl}_3$ )



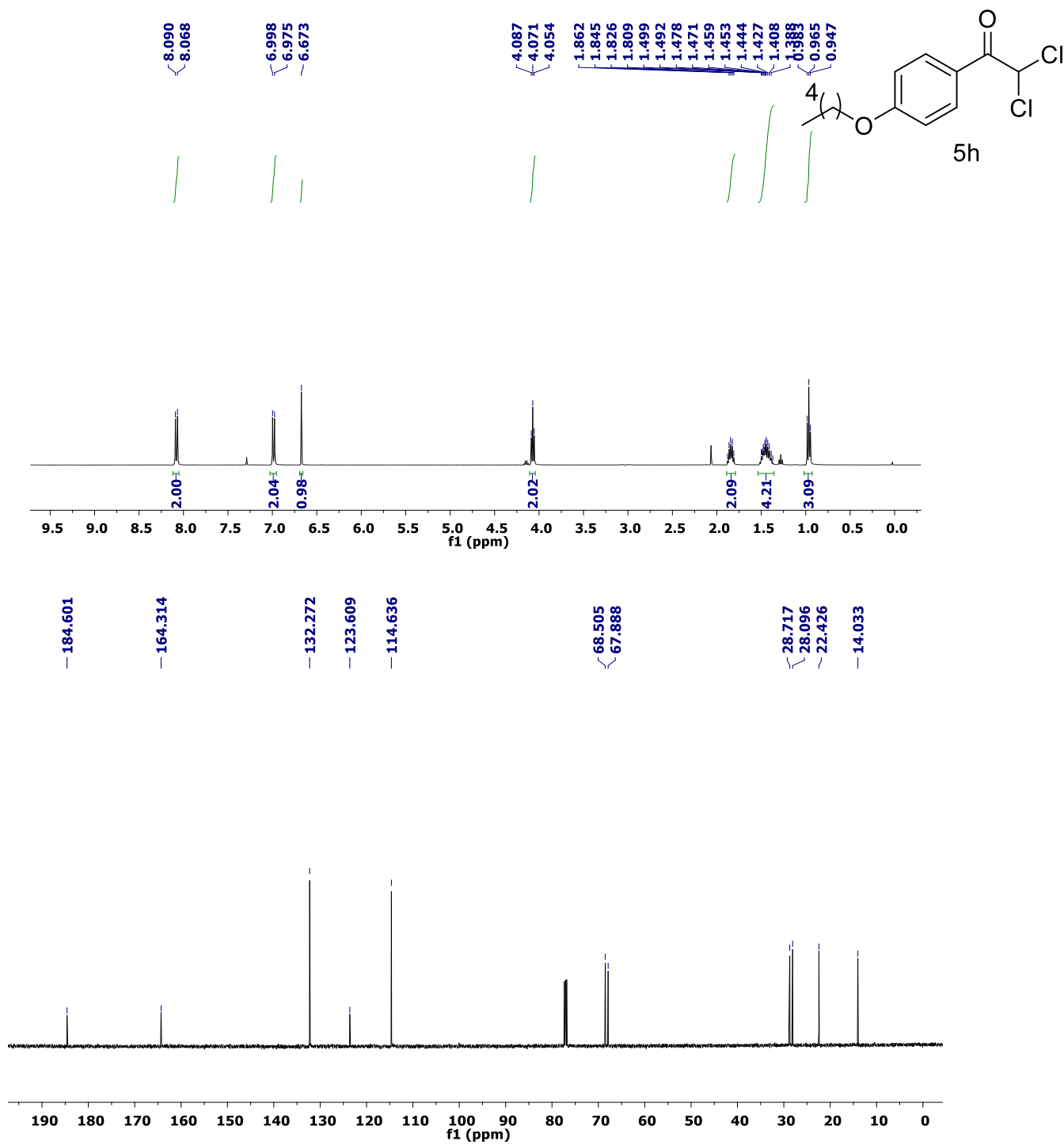
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 5f ( $\text{CDCl}_3$ )



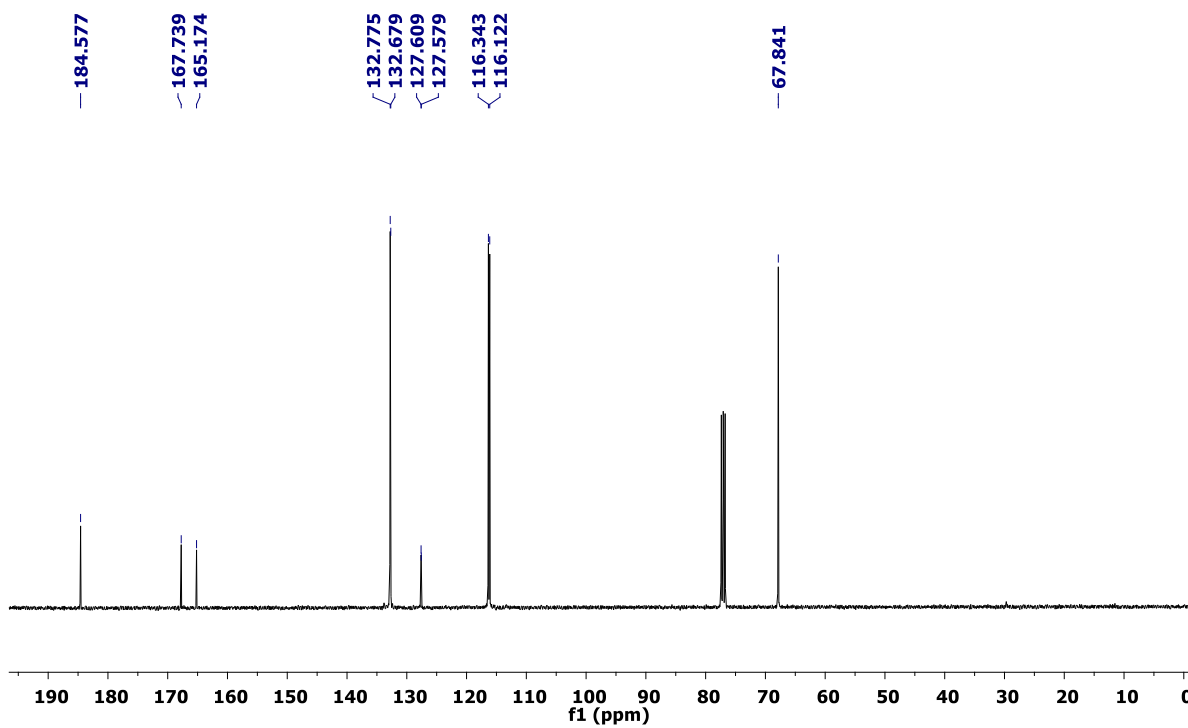
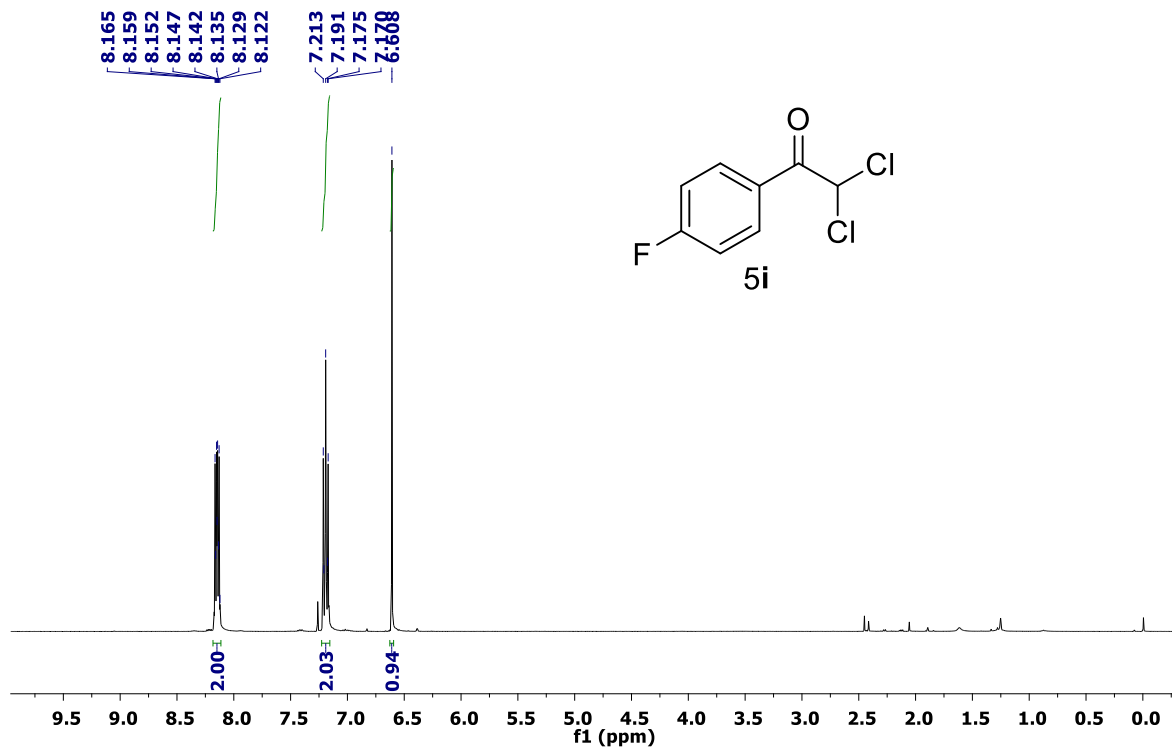
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 5g ( $\text{CDCl}_3$ )



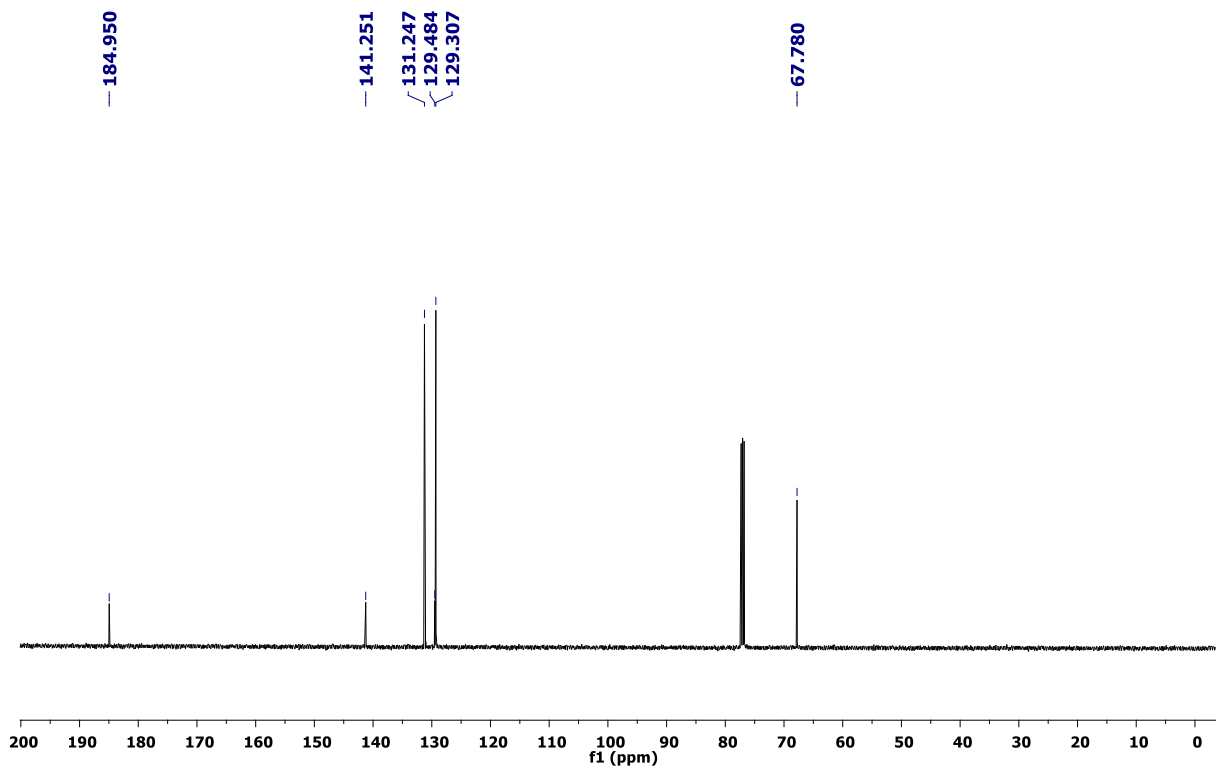
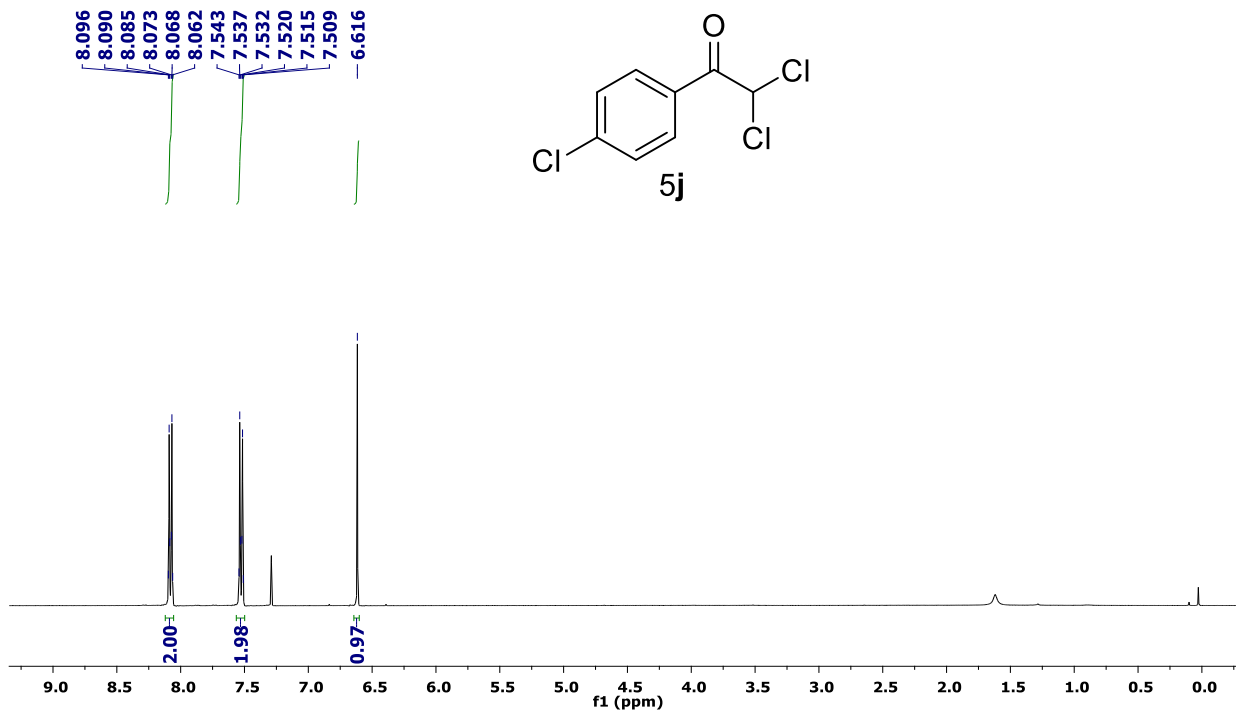
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 5h ( $\text{CDCl}_3$ )



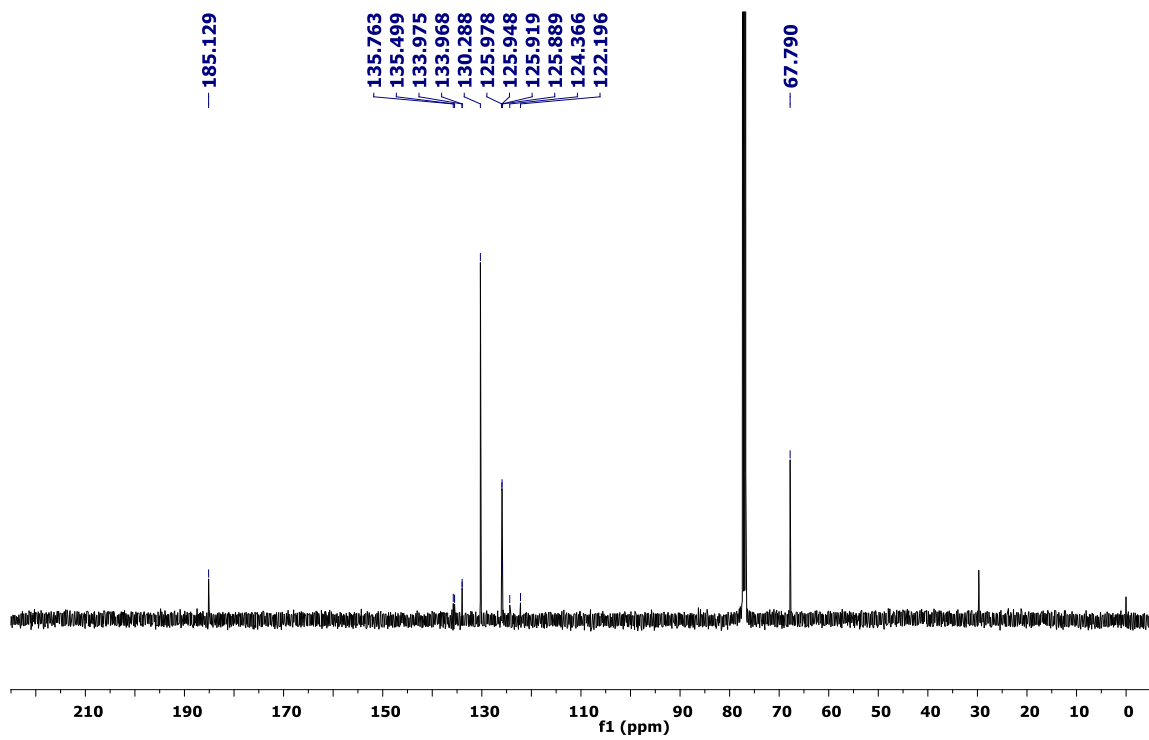
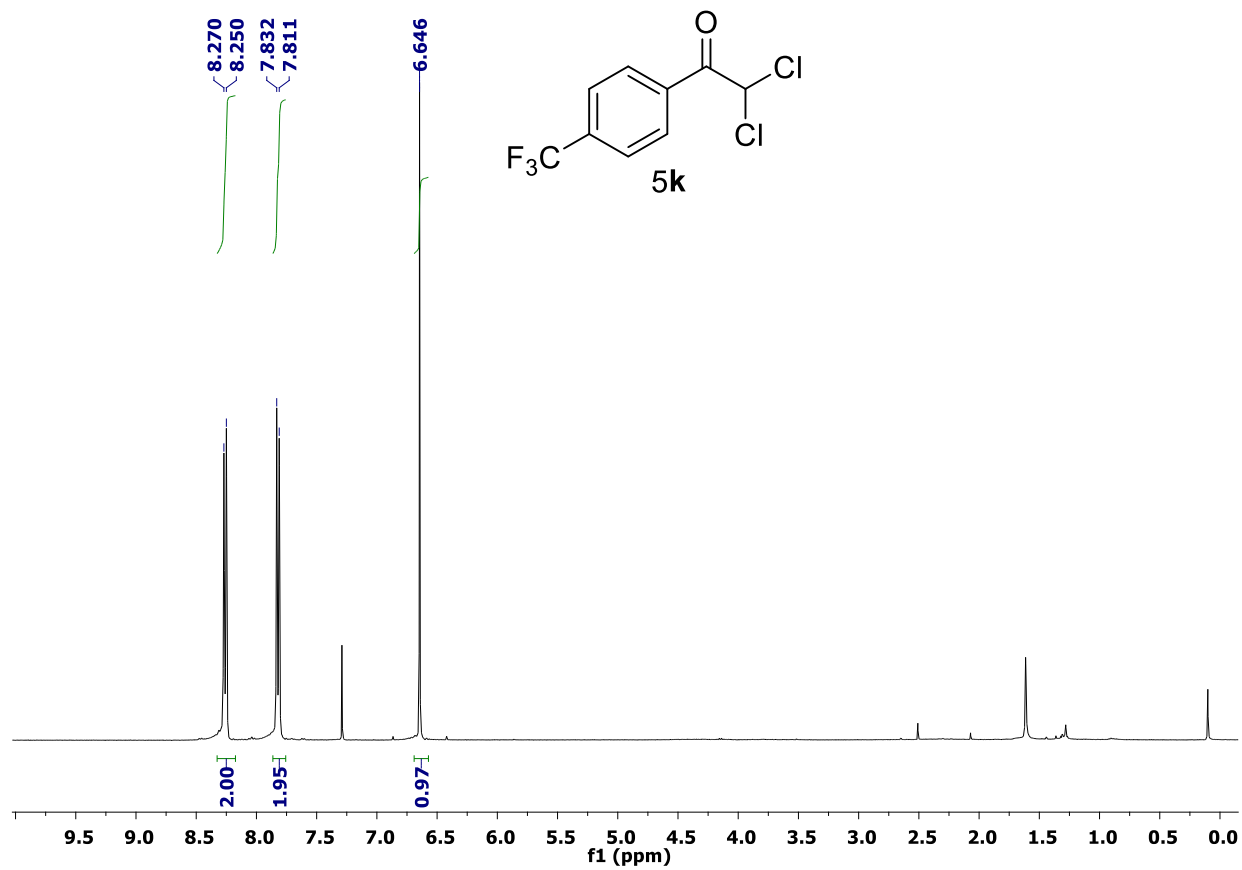
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 5i ( $\text{CDCl}_3$ )



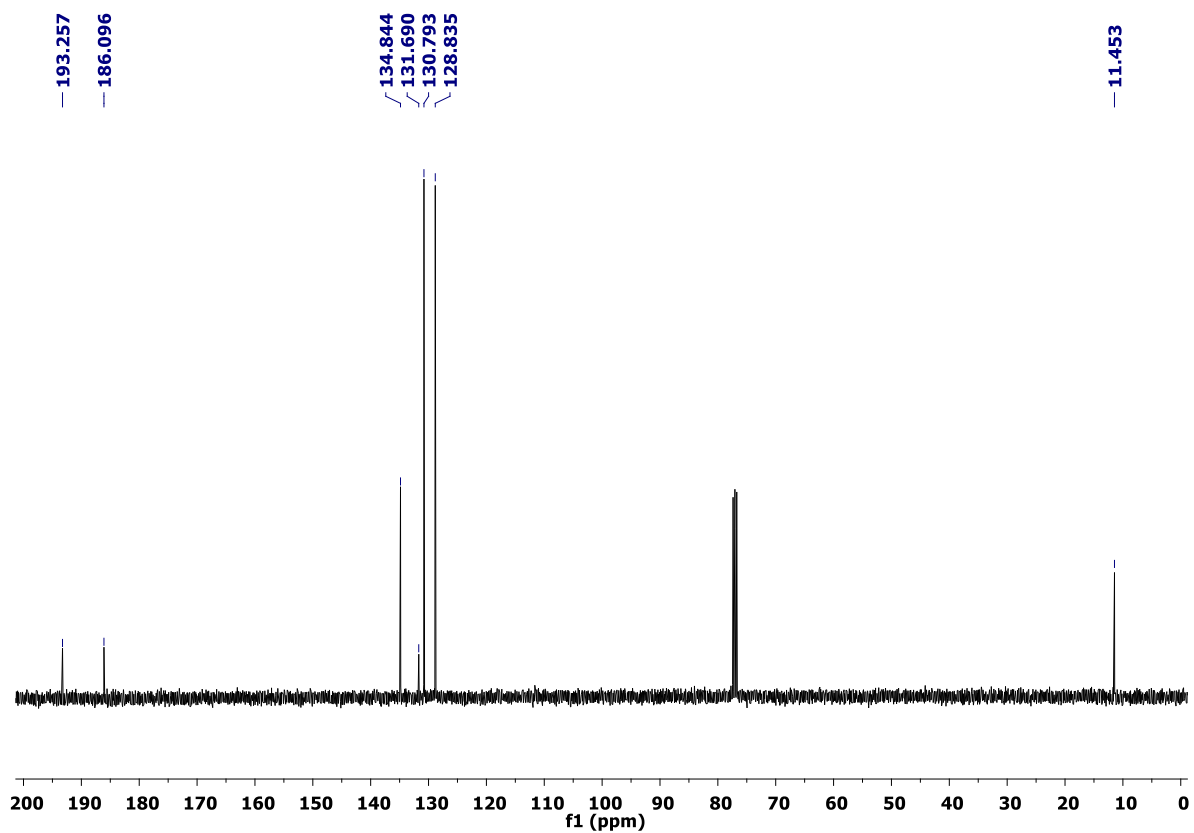
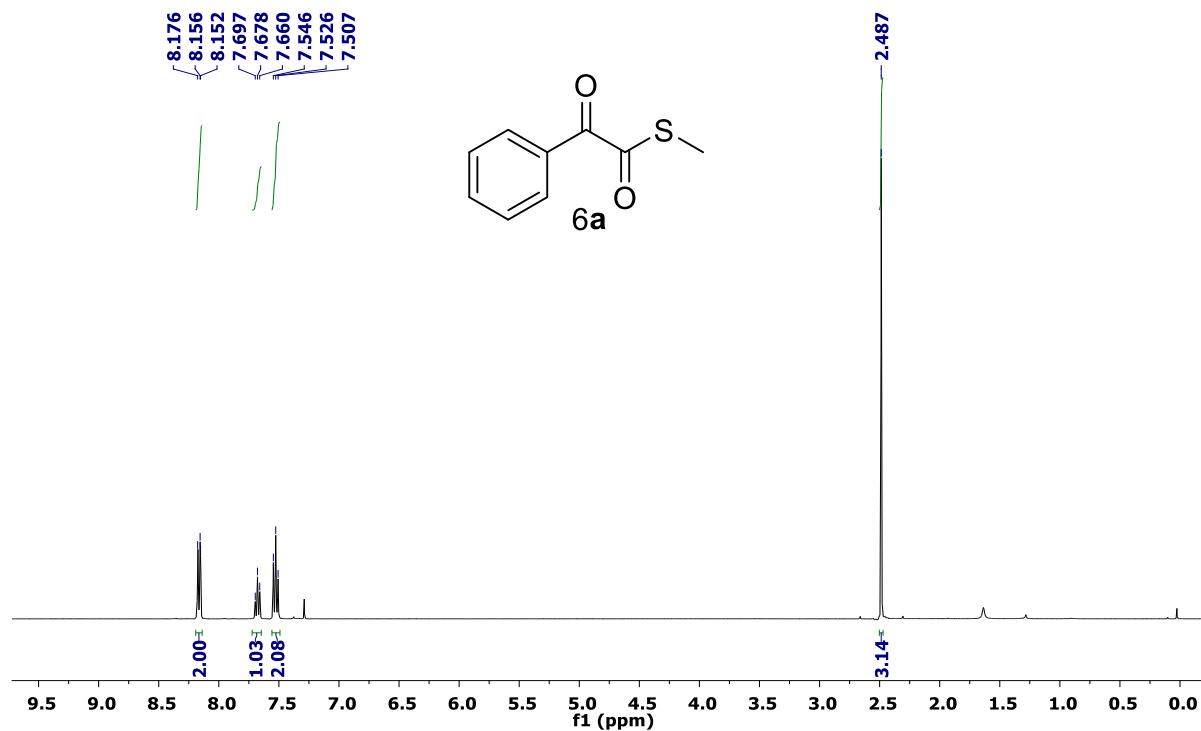
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 5j ( $\text{CDCl}_3$ )



$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 5k ( $\text{CDCl}_3$ )

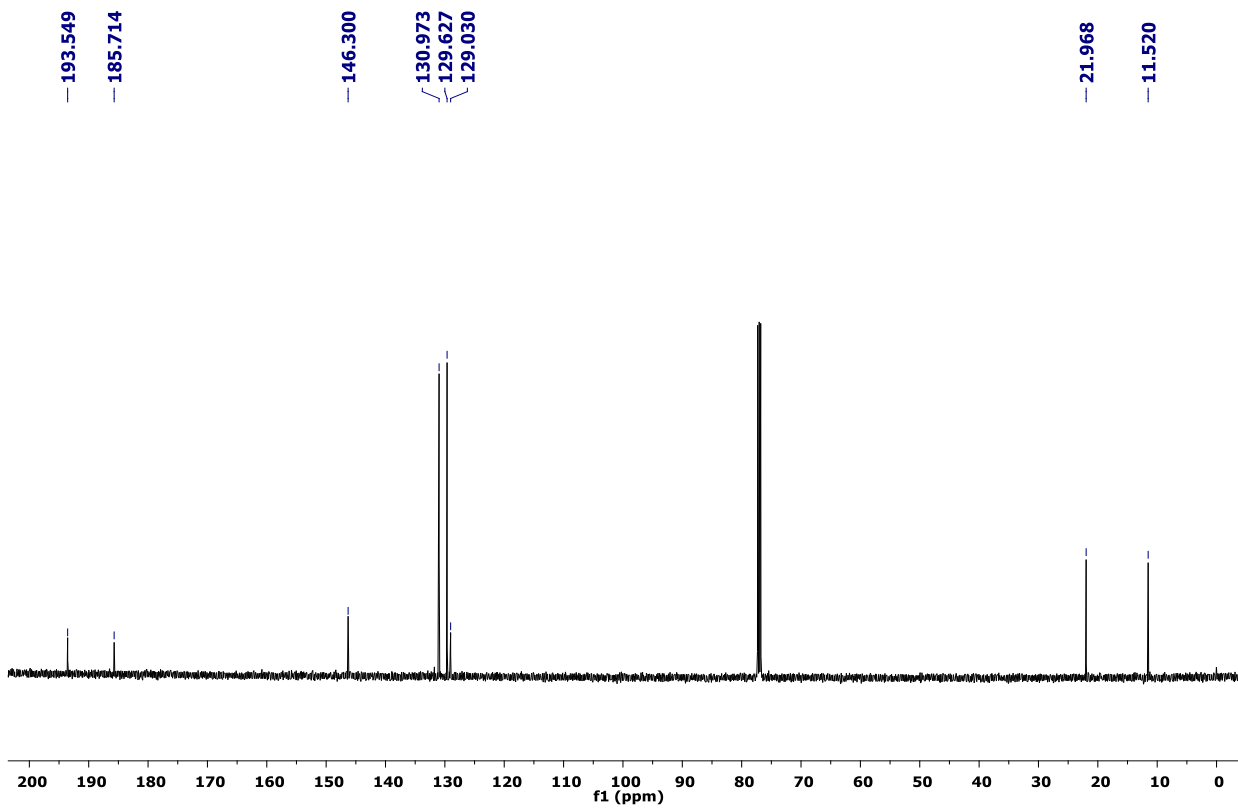
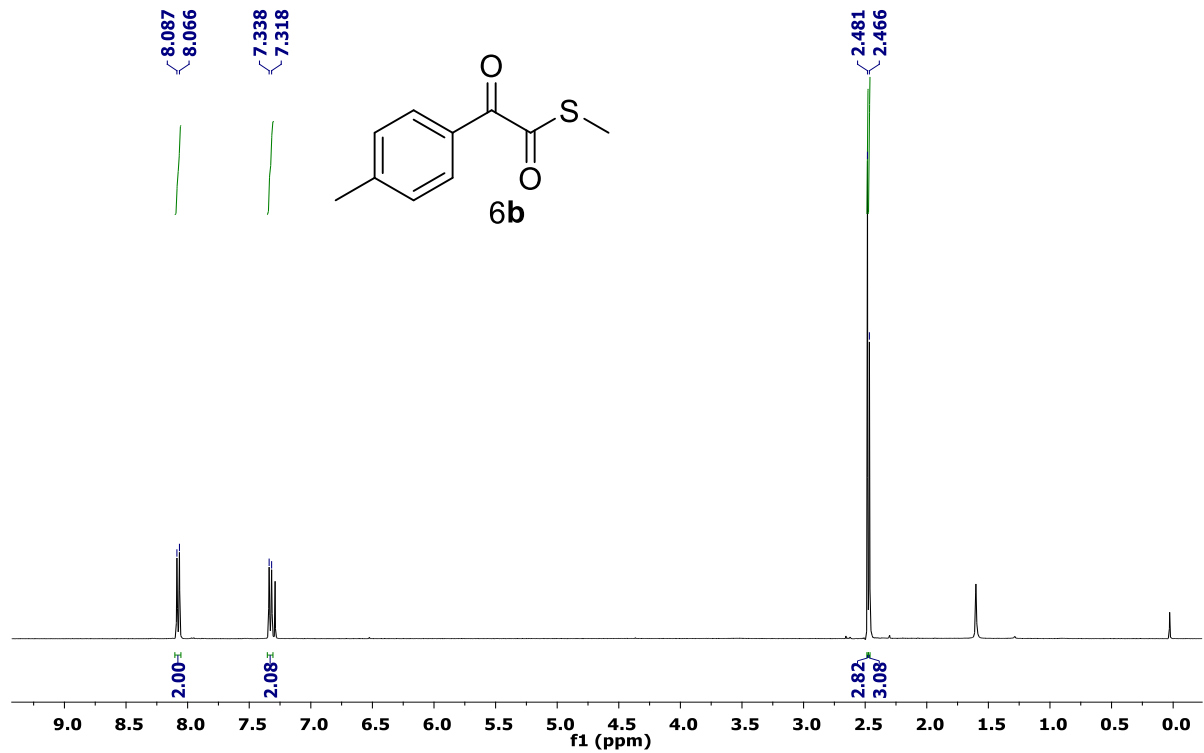


<sup>1</sup>H and <sup>13</sup>C NMR spectra of 6a (CDCl<sub>3</sub>)

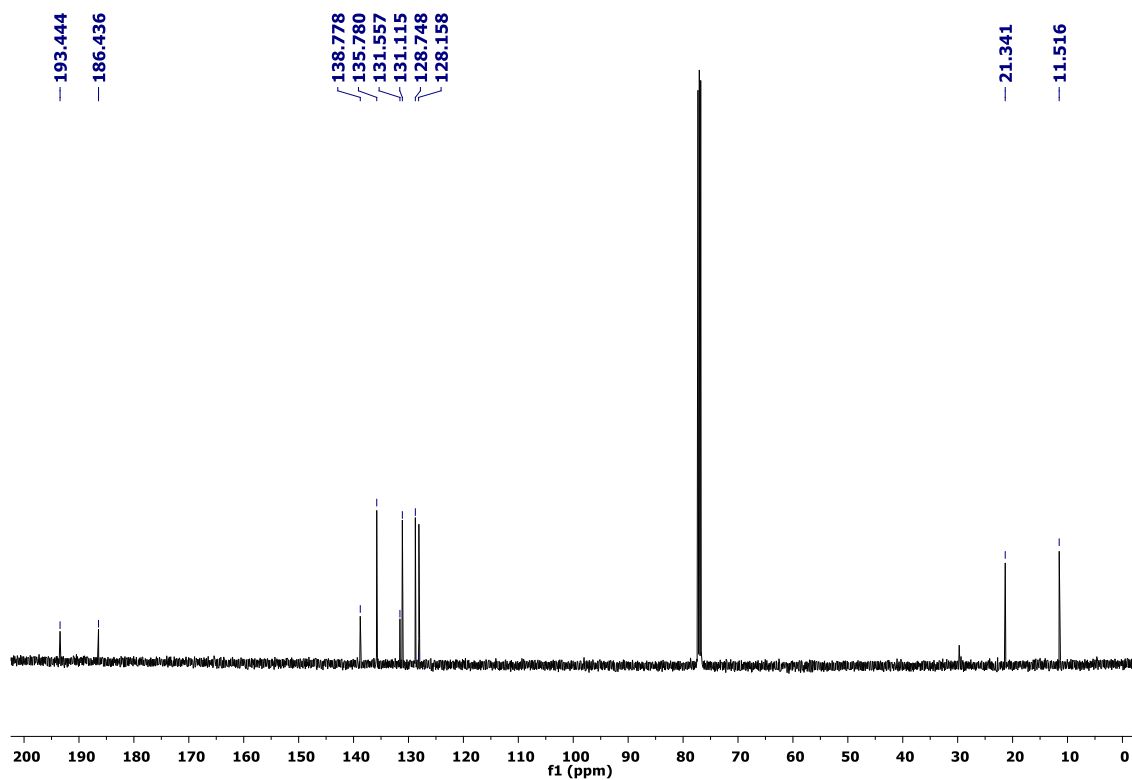
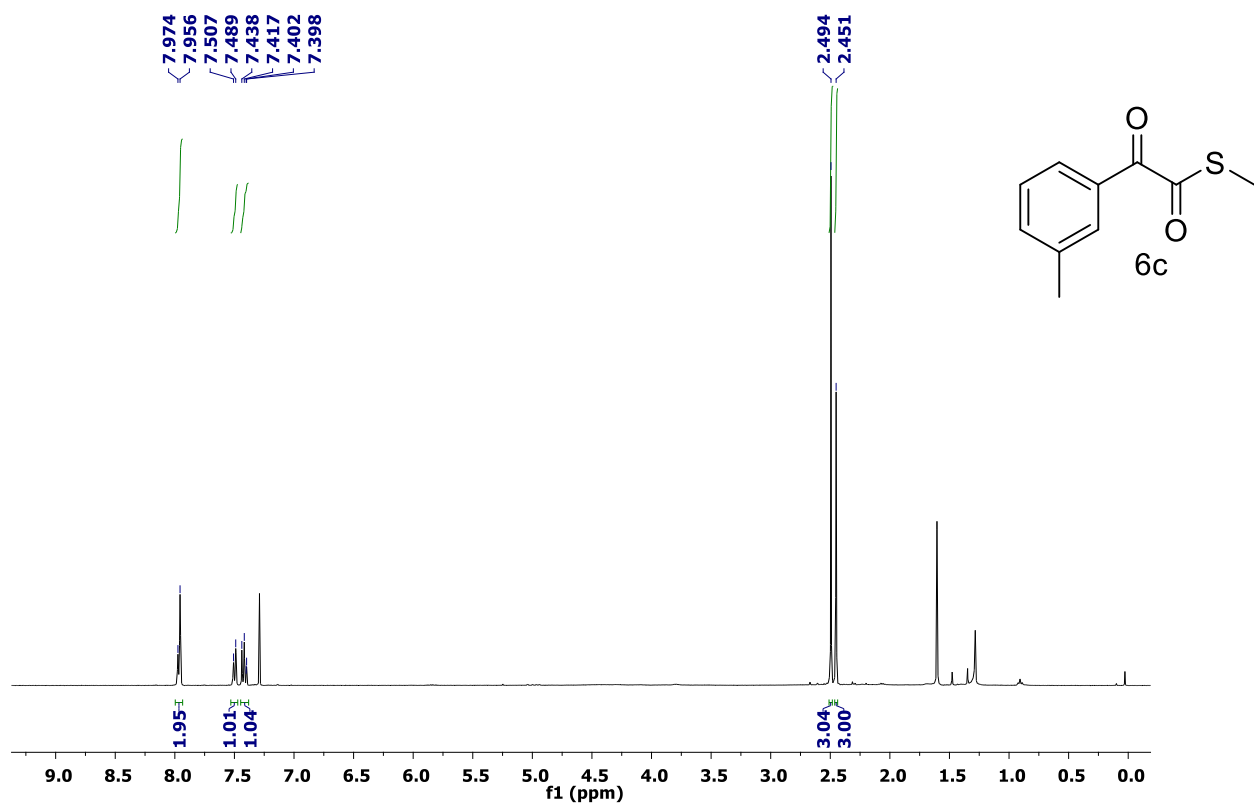




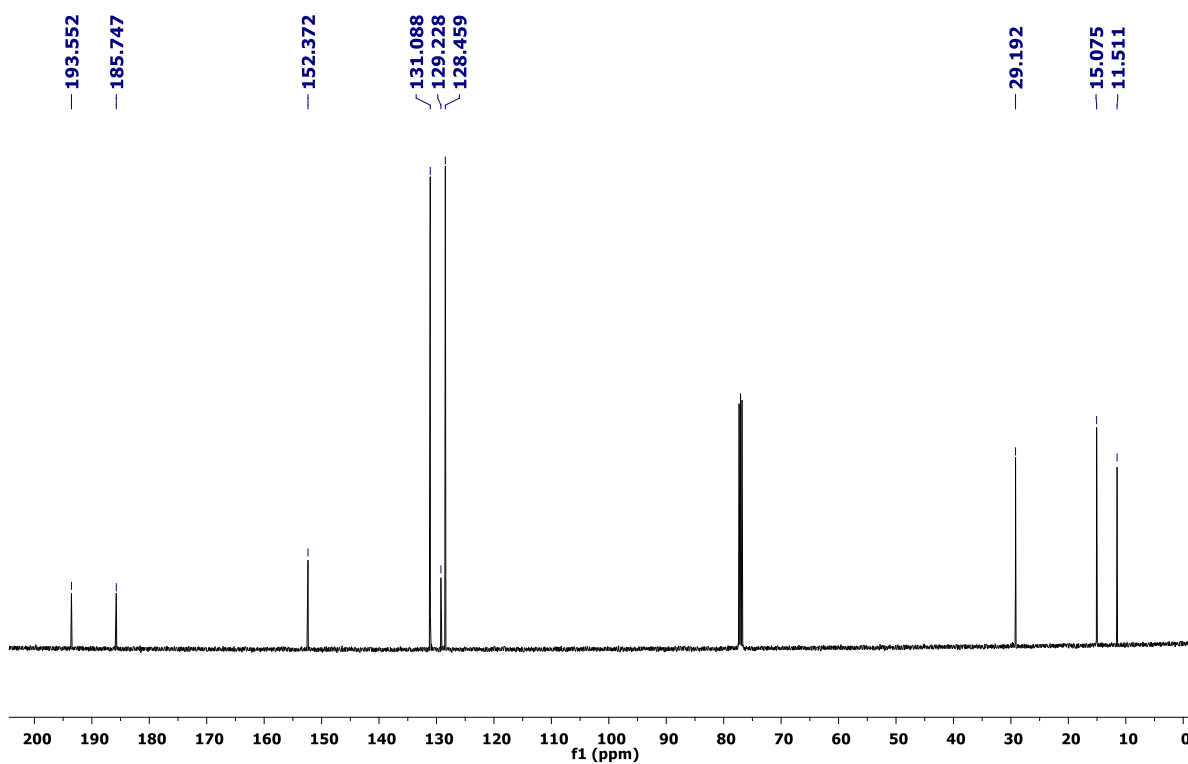
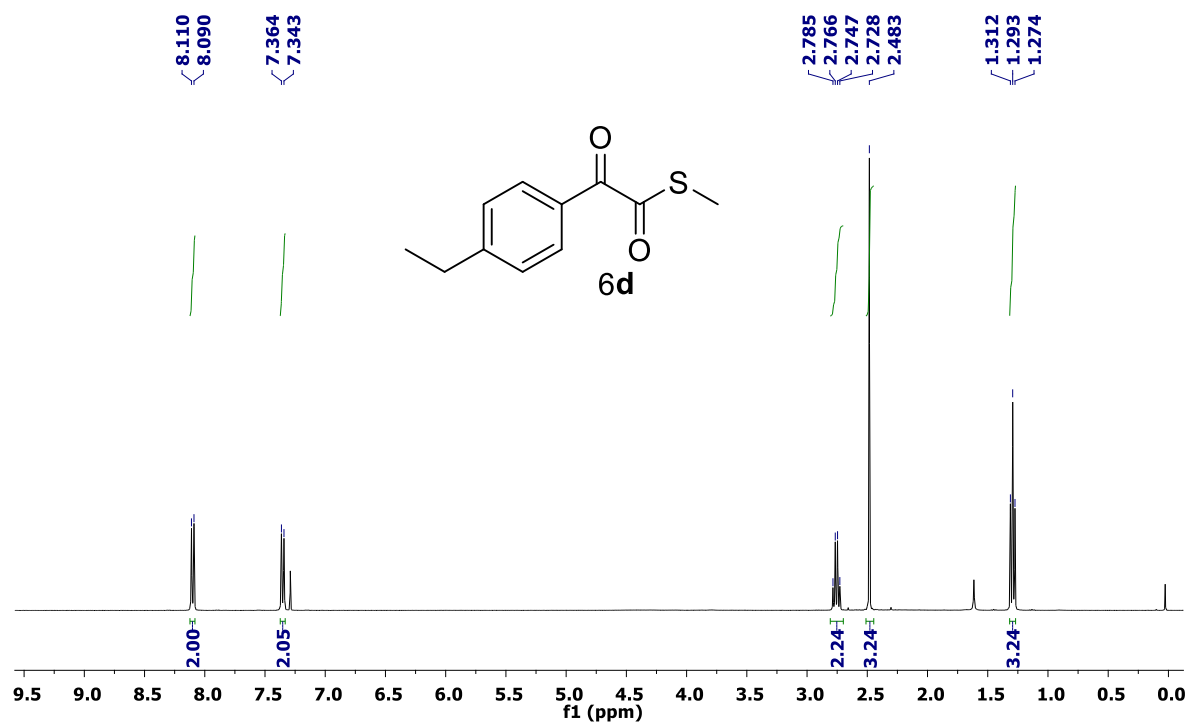
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 6b ( $\text{CDCl}_3$ )



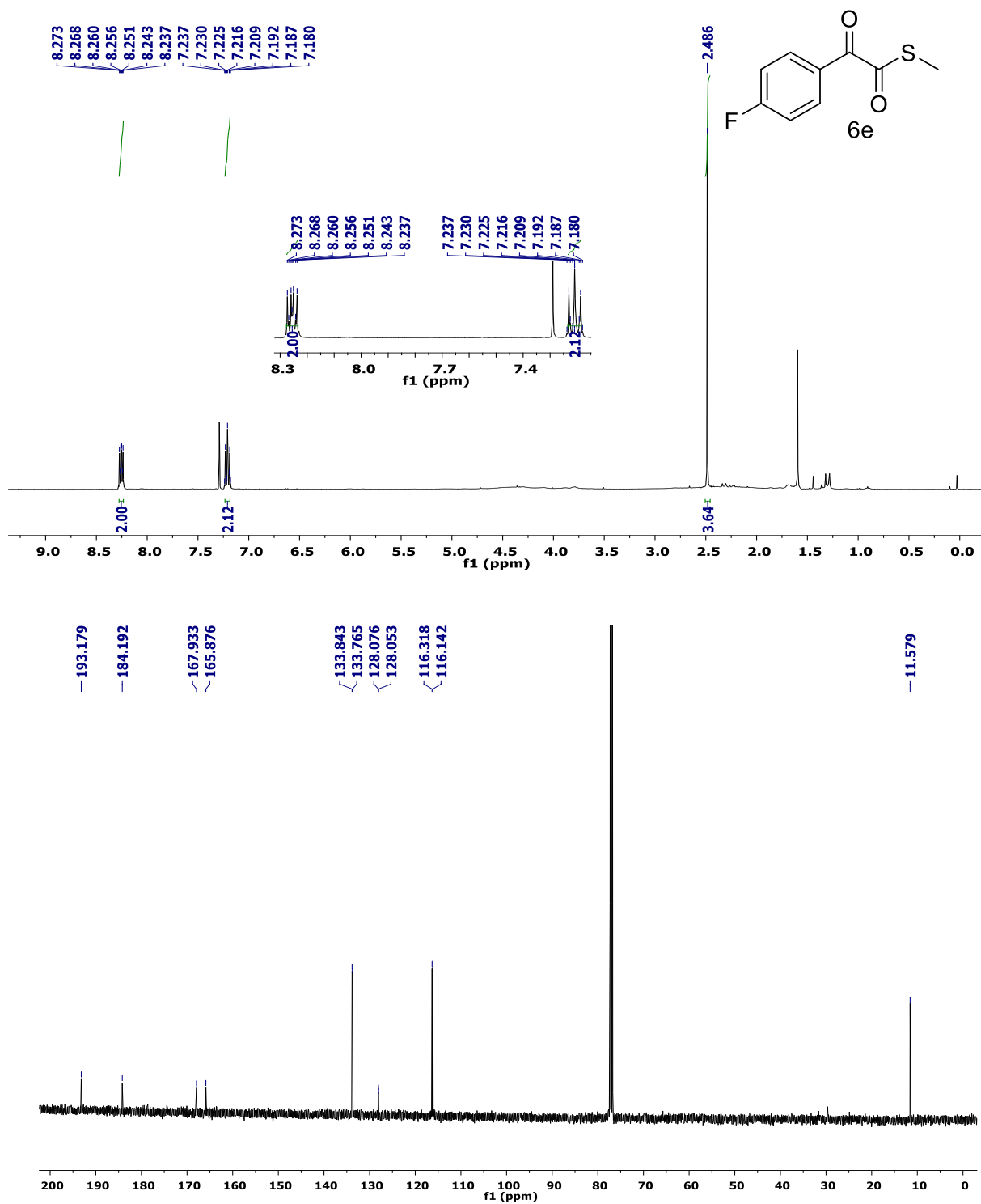
<sup>1</sup>H and <sup>13</sup>C NMR spectra of 6c (CDCl<sub>3</sub>)



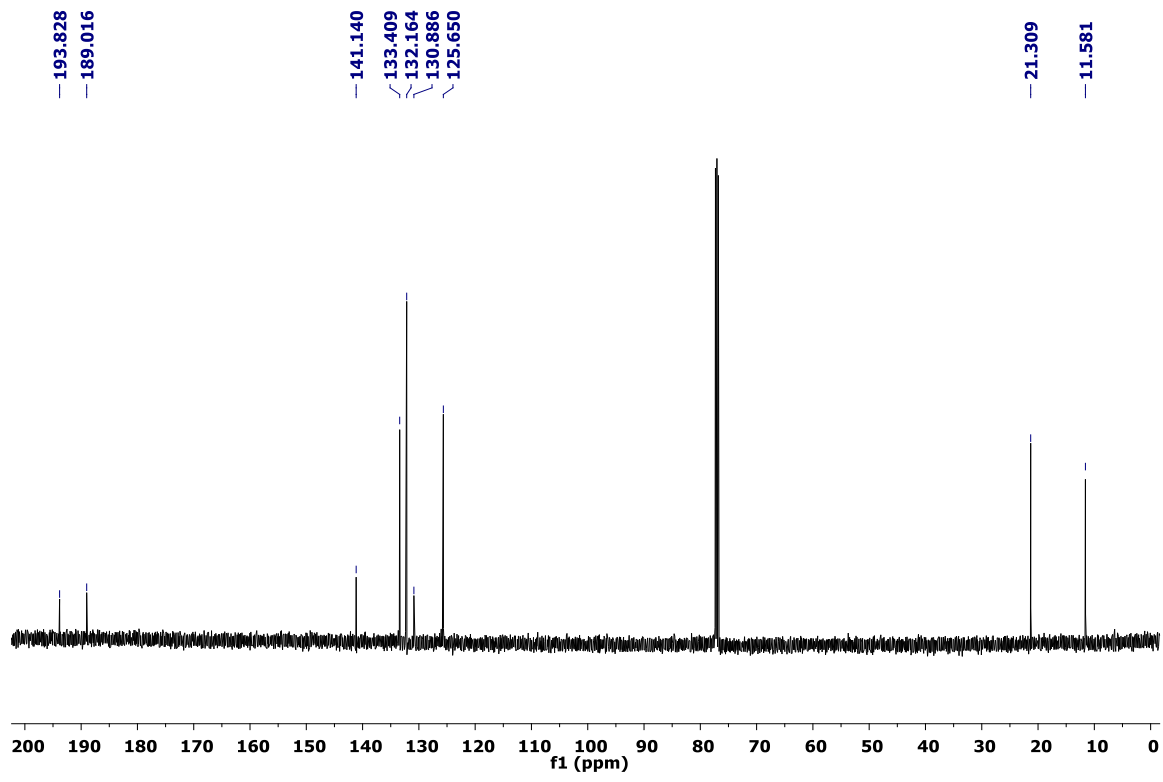
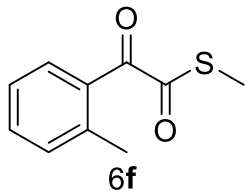
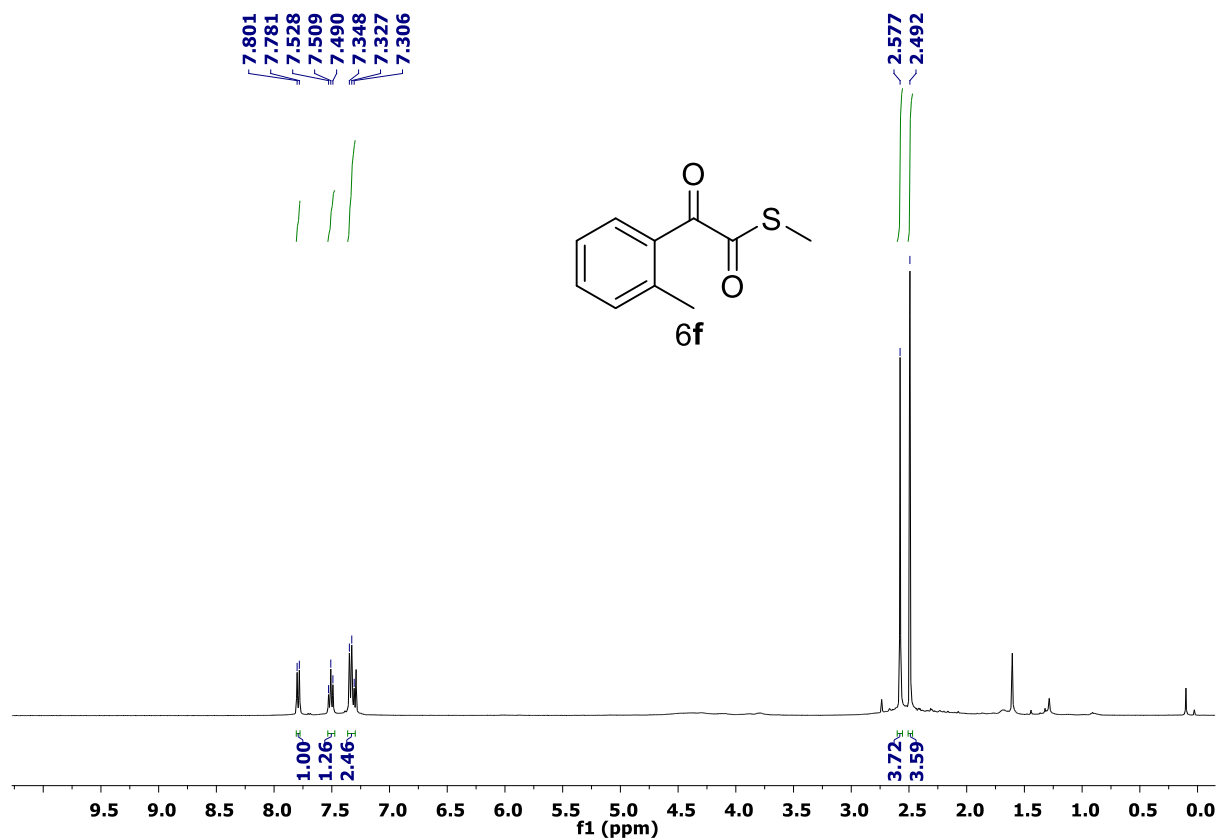
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 6d ( $\text{CDCl}_3$ )



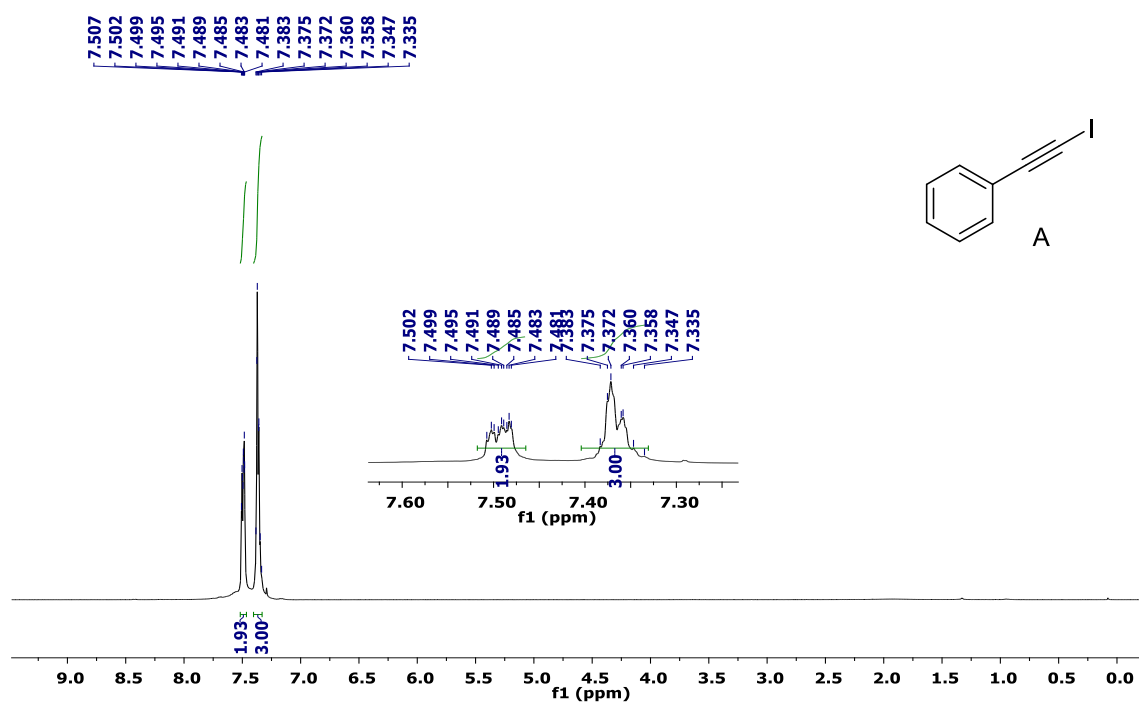
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 6e ( $\text{CDCl}_3$ )



$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 6f ( $\text{CDCl}_3$ )



<sup>1</sup>H NMR spectra of A (CDCl<sub>3</sub>)



<sup>1</sup>H NMR spectra of 8 (CDCl<sub>3</sub>)

