# **Supporting Information**

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#### **Part 1. General Information**

Unless otherwise noted, materials obtained from commercial suppliers were used directly without further purification. Proton nuclear magnetic resonance ( $^{1}$ H NMR) spectra were recorded on Bruker 600 MHz spectrometer and Bruker 400 MHz spectrometer. Chemical shifts were recorded in parts per million (ppm,  $\delta$ ) relative to tetramethylsilane ( $\delta = 0.00$ ) or chloroform ( $\delta = 7.26$ , singlet).  $^{1}$ H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), dd (doublet of doublets), m (multiplets), and etc. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). Carbon nuclear magnetic resonance ( $^{13}$ C NMR) spectra were recorded on a Bruker 600 MHz (150 MHz) spectrometer and Bruker 400 MHz (100 MHz) spectrometer. High-resolution mass spectrometry (HRMS) analysis was carried out using a MS instrument with ESI source.

# Part 2. General procedure for the synthesis of products

#### Method A

To an oven-dried Schlenk tube equipped with a magnetic stirrer, were added **1a** (56.4 mg, 0.2 mmol), *fac*-Ir(ppy)<sub>3</sub> (2.4 mg, 0.004 mmol, 0.02 equiv.) and Na<sub>2</sub>HPO<sub>4</sub> (56 mg, 0.4 mmol, 2.0 eq.). To this mixture were added 2 mL dioxane, CF<sub>2</sub>HSO<sub>2</sub>Cl (60 mg, 0.4 mmol, 2.0 eq.) under a blanket of nitrogen. The vial was sealed, and stirred under visible light at room temperature for overnight. After 16 hours, the dioxane was removed in vacuo, and the residue purified by column chromatography on silica gel. This gave product **2a** as colorless liquid (43.0 mg, 82% yield).

#### Method B

To an oven-dried Schlenk tube equipped with a magnetic stirrer, were added **3a** (73.4 mg, 0.2 mmol), *fac*-Ir(ppy)<sub>3</sub> (2.4 mg, 0.004 mmol, 0.02 equiv.) and Na<sub>2</sub>HPO<sub>4</sub> (56 mg, 0.4 mmol, 2.0 eq.). To this mixture were added 2 mL CH<sub>3</sub>CN, CF<sub>2</sub>HSO<sub>2</sub>Cl (60 mg, 0.4 mmol, 2.0 eq.) under a blanket of nitrogen. The vial was sealed, and stirred under blue light at room temperature for overnight. After 16 hours, the CH<sub>3</sub>CN was removed in vacuo, and the residue purified by column chromatography on silica gel. This gave product **4a** as colorless liquid (59.3 mg, 86% yield).

#### Part 3. Mechanistic Studies

#### **Quantum Yield Measurements**

BESTLLON® LED lamps (\(\lambda\) max = 456 nm) was used with 100% intensity for measurement of quantum yield. According to the procedure of Hong \(^1\) the photon flux of the LED was determined by standard ferrioxalate actinometry. A 0.15 M solution of ferrioxalate was prepared by dissolving potassium ferrioxalate hydrate (0.737 g) in H2SO4 (10 mL of a 0.05 M solution). A buffered solution of 1,10-phenanthroline was prepared by dissolving 1,10-phenanthroline (5.0 mg) and sodium acetate (1.13 g) in H2SO4 (5.0 mL of a 0.5 M solution). Both solutions were stored in the dark. To determine the photon flux of the LED, the ferrioxalate solution (2.0 mL) was placed in a cuvette and irradiated for 90 seconds. After irradiation, the phenanthroline solution (0.35 mL) was added to the cuvette and the mixture was allowed to stir in the dark for 1 h to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the solution was measured at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm was measured. Conversion was calculated using eq 1.

	Non-irrad	Irrad
$A_{510}$	0.527	1.114

$$mol \ of \ Fe^{2+} = \frac{V\Delta_{510nm}}{l \cdot \varepsilon} = \frac{0.00235L \times 0.587}{1 \ cm \times 11100 \frac{L}{mol} cm} = 1.24 \times 10^{-7} mol$$
 (1)

V is the total volume (0.00235 L) of the solution after addition of phenanthroline,  $\Delta A$  is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, 1 is the path length (1.00 cm), and  $\epsilon$  is the molar absorptivity of the ferrioxalate actinometer at 510 nm (11,100 Lmol<sup>-1</sup> cm <sup>-1</sup>). The photon flux can be calculated using eq 2.

Photon flux = 
$$\frac{mol \ of \ Fe^{2+}}{\emptyset \cdot t \cdot f}$$
 =  $\frac{1.24 \times 10^{-7} mol}{0.84 \times 90s \times 0.908}$  =  $1.80 \times 10^{-9} einsein/s$ 

(2)

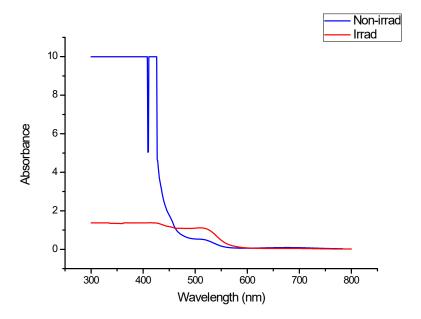


Figure 1 Absorption spectra of irradiation experiment and non-irradiation experiment

Where  $\Phi$  is the quantum yield for the ferrioxalate actinometer (0.84 at  $\lambda$  = 456 nm) is the irradiation time (90 s), and f is the fraction of light absorbed at 456 nm by the ferrioxalate actinometer. This value is calculated using eq 2 where  $A_{456}$  nm is the absorbance of the ferrioxalate solution at 456 nm. An absorption spectrum gave an  $A_{456nm}$  value of 1.037, indicating that the fraction of absorbed light (f) is 0.908. The photon flux was thus calculated to be  $1.80 \times 10^{-9}$  einsteins s<sup>-1</sup>.

$$f_{Fe} = 1 - 10^{-A_{456nm}} = 1 - 10^{-1.037} = 0.908$$
 (3)

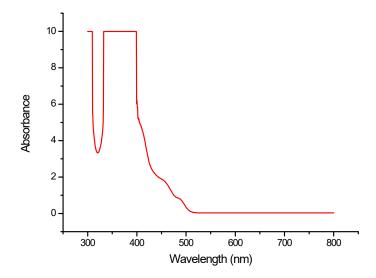


Figure 2 Absorption spectra of 0.001 M solution of fac-Ir(ppy)<sub>3</sub> in dioxane

Figure 3 Determination of the reaction quantum yield

The reaction mixture was stirred and irradiated by BESTLLON® LED lamps ( $\lambda$ max = 456 nm) for 7200 s. The yield of product was determined by <sup>1</sup>H NMR analysis using dibromomethane as an internal standard. The yield of **2a** was determined to be 40% ( $0.08 \times 10^{-3}$  mol of **2a**). The reaction quantum yield ( $\Phi$ ) was determined using eq 5 where the photon flux is  $1.80 \times 10^{-9}$  einsteins s<sup>-1</sup> (determined by actinometry as described above), t is the reaction time (2 h) and f is the fraction of incident light absorbed by the catalyst, determined using eq 4. An absorption spectrum of the catalyst (0.001 M) gave an absorbance value of 1.777 at 456 nm, indicating that the fraction of light absorbed by the photocatalyst (f) is 0.980.

$$f_{Ir} = 1 - 10^{-A_{456nm}} = 1 - 10^{-1.777} = 0.980_{(4)}$$

$$\emptyset = \frac{mol\ of\ product}{flux \cdot t \cdot f} = \frac{0.08 \times 10^{-3}mol}{1.80 \times 10^{-9}einsein/s \times 7200s \times 0.9800} = 6.29_{(5)}$$

The reaction quantum yield  $(\Phi)$  was calculated to be 6.29.

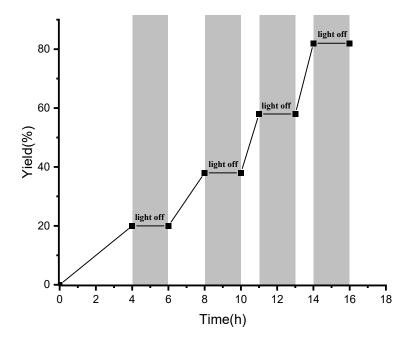


Figure 4. Light on/off experiments of the model reaction delivering, detected by <sup>1</sup>H NMR.

# Part 3. Characterizations of products

#### 4,4-difluoro-1,2-diphenylbutan-1-one (2a)

Prepared according to general method A and isolated in 82% yield after chromoatography as colorless liquid (43.0 mg)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.97 – 7.92 (m, 2H), 7.49 (t, J = 7.4 Hz, 1H), 7.39 (t, J = 7.6 Hz, 2H), 7.35 – 7.28 (m, 5H), 5.73 (tt, J = 56.8, 4.8 Hz, 1H), 4.80 (t, J = 7.3 Hz, 1H), 2.85 – 2.68 (m, 1H), 2.43 – 2.26 (m, 1H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 197.93, 137.91, 135.93, 133.41, 129.54, 128.99, 128.76, 128.22, 127.85, 116.30 (t, J = 238.7 Hz), 47.84 (t, J = 5.5 Hz), 38.06 (t, J = 21.7 Hz).

<sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>)  $\delta$  -115.64 – -117.91 (m).

HRMS (ESI) for  $C_{16}H_{15}F_2O^+$  [M+H]<sup>+</sup> m/z: calcd 261.1085, found 261.1109.

#### 4,4-difluoro-1,2-di-p-tolylbutan-1-one (2b)

Prepared according to general method A and isolated in 62% yield after chromoatography as colorless liquid (35.7 mg)

1H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.88 (d, J = 8.2 Hz, 2H), 7.20 (d, J = 8.2 Hz, 4H), 7.13 (d, J = 8.0 Hz, 2H), 5.75 (tt, J = 56.9, 4.9 Hz, 1H), 4.76 (t, J = 7.4 Hz, 1H), 2.86 – 2.63 (m, 1H), 2.45 – 2.24 (m, 7H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  197.63, 144.21, 137.48, 135.08, 133.45, 130.17, 129.42, 129.11, 128.04, 116.46 (t, J = 238.6 Hz), 47.33 (t, J = 5.5 Hz), 38.05 (t, J = 21.6 Hz), 21.73, 21.14.

<sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>)  $\delta$  -115.62 – -117.93 (m).

HRMS (ESI) for  $C_{18}H_{19}F_2O^+$  [M+H]<sup>+</sup> m/z: calcd 289.1398, found 289.1407.

#### 4,4-difluoro-1,2-bis(4-methoxyphenyl)butan-1-one (2c)

Prepared according to general method A and isolated in 71% yield after chromoatography as colorless liquid (45.4mg)

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.96 (d, J = 8.9 Hz, 2H), 7.23 (d, J = 8.7 Hz, 2H), 6.88 – 6.81 (m, 4H), 5.74 (tt, J = 56.9, 4.8 Hz, 1H), 4.72 (t, J = 7.4 Hz, 1H), 3.84 (s, 3H), 3.78 (s, 3H), 2.78 – 2.65 (m, 1H), 2.78 – 2.65 (m, 1H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 196.58, 163.65, 159.08, 131.30, 130.26, 129.21, 128.89, 116.53 (t, J = 238.5 Hz), 114.86, 113.92, 55.58, 55.37, 46.64 (t, J = 5.5 Hz), 38.12 (t, J = 21.4 Hz).

<sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>)  $\delta$  -115.63 – -117.98 (m).

HRMS (ESI) for  $C_{18}H_{19}F_2O_3^+$  [M+H]<sup>+</sup> m/z: calcd 321.1297, found 321.1271.

#### 4,4-difluoro-1,2-bis(4-fluorophenyl)butan-1-one (2d)

Prepared according to general method A and isolated in 67% yield after chromoatography as colorless liquid (39.6 mg)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.99 – 7.91 (m, 2H), 7.30 – 7.21 (m, 2H), 7.10 – 6.97 (m, 4H), 5.74 (tt, J = 56.7, 4.7 Hz, 1H), 4.75 (t, J = 7.4 Hz, 1H), 2.84 – 2.66 (m, 1H), 2.41 – 2.21 (m, 1H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 196.25, δ 165.93 (d, J = 256.0 Hz), 162.37 (d, J = 247.4 Hz), 133.54 (d, J = 3.4 Hz), 132.15 (d, J = 2.7 Hz), 131.63 (d, J = 9.4 Hz), 129.77 (d, J = 8.1 Hz), 116.62 (d, J = 21.6 Hz), 116.06 (t, J = 239.0 Hz) 116.03 (d, J = 22.0 Hz), 46.88 (t, J = 5.4 Hz), 38.07 (t, J = 21.6 Hz).

<sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>) δ -104.20, -114.02, -115.70 – -118.01(m).

HRMS (ESI) for  $C_{16}H_{13}F_4O^+$  [M+H]<sup>+</sup> m/z: calcd 297.0897, found 297.0901

#### 1,2-bis(4-chlorophenyl)-4,4-difluorobutan-1-one (2e)

Prepared according to general method A and isolated in 71% yield after chromoatography as colorless liquid (46.6 mg)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.85 (d, J = 8.6 Hz, 2H), 7.37 (d, J = 8.6 Hz, 2H), 7.30 (d, J = 8.5 Hz, 2H), 7.21 (d, J = 8.5 Hz, 2H), 5.74 (tt, J = 56.6, 4.6 Hz, 1H), 4.73 (t, J = 7.3 Hz, 1H), 2.85 – 2.67 (m, 1H), 2.40 – 2.21 (m, 1H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  196.40, 140.16, 136.11, 134.08, 133.97, 130.32, 129.85, 129.48, 129.21, 115.93 (t, J = 239.1 Hz), 47.07 (t, J = 5.5 Hz), 37.86 (t, J = 21.7 Hz).

<sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>)  $\delta$ -115.65 – -117.96. (m).

HRMS (ESI) for  $C_{16}H_{13}Cl_2F_2O^+$  [M+H]<sup>+</sup> m/z: calcd 329.0306, found 329.0312.

#### 4,4-difluoro-1,2-di(pyridin-2-yl)butan-1-one (2f)

Prepared according to general method A and isolated in 76% yield after chromoatography as colorless liquid (39.8 mg)

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.59 (d, J = 4.2 Hz, 1H), 8.47 (d, J = 4.0 Hz, 1H), 8.04 (d, J = 7.8 Hz, 1H), 7.77 (td, J = 7.7, 1.1 Hz, 1H), 7.59 (td, J = 7.7, 1.3 Hz, 1H), 7.48 (d, J = 7.8 Hz, 1H), 7.38 (dd, J = 6.4, 5.0 Hz, 1H), 7.08 (dd, J = 6.5, 5.2 Hz, 1H), 5.85 (tt, J = 56.8, 4.6 Hz, 1H), 5.71 (t, J = 7.3 Hz, 1H), 2.90 – 2.74 (m, 1H), 2.64 – 2.49 (m, 1H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 198.18, 157.90, 152.44, 149.81, 148.95, 137.02, 136.88, 127.27, 124.72, 123.08, 122.10, 116.52 (t, J = 238.9 Hz), 48.01 (t, J = 5.3 Hz), 35.78 (t, J = 21.8 Hz).

<sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>)  $\delta$  -115.09 – -116.71(m).

HRMS (ESI) for  $C_{14}H_{13}F_2N_2O^+$  [M+H]<sup>+</sup> m/z: calcd 263.0990, found 263.0994.

#### 1,2-bis(2,4-dimethoxyphenyl)-4,4-difluorobutan-1-one (2g)

Prepared according to general method A and isolated in 78% yield after chromoatography as colorless liquid (59.2 mg)

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.65 (d, J = 8.7 Hz, 1H), 6.94 (d, J = 8.6 Hz, 1H), 6.42 (dd, J = 8.7, 2.3 Hz, 1H), 6.36 – 6.32 (m, 2H), 6.27 (d, J = 2.2 Hz, 1H), 5.81 (tt, J = 57.4, 5.0 Hz, 1H), 4.98 (t, J = 7.2 Hz, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 3.74 (s, 3H), 3.73 (s, 3H), 2.76 – 2.62 (m, 1H), 2.19 – 2.04 (m, 1H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 199.83, 164.04, 160.03, 159.99, 157.84, 132.82, 129.81, 120.94, 120.01, 117.18 (t, J = 238.2 Hz), 104.98, 104.29, 98.69, 98.17, 55.53, 55.38, 55.31, 45.42 (t, J = 5.5 Hz), 36.62 (t, J = 21.3 Hz).

<sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>)  $\delta$  -114.28 – -117.42(m).

HRMS (ESI) for  $C_{20}H_{23}F_2O_5^+$  [M+H]<sup>+</sup> m/z: calcd 381.1508, found 381.1518.

#### 4,4-difluoro-1,2-bis(3-(trifluoromethyl)phenyl)butan-1-one (2h)

Prepared according to general method A and isolated in 76% yield after chromoatography as colorless liquid (61.7 mg)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.20 (s, 1H), 8.10 (d, J = 7.9 Hz, 1H), 7.78 (d, J = 7.8 Hz, 1H), 7.62 – 7.43 (m, 5H), 5.79 (tt, J = 56.4, 4.5 Hz, 1H), 4.90 (t, 1H), 2.96 – 2.78 (m, 1H), 2.45 – 2.28 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 196.10, 138.34, 136.03, 131.97, 131.55, 132.14 (q, J = 33.8 Hz), 131.67 (q, J = 33.1 Hz), 130.29, 130.18 (q, J = 3.5 Hz), 129.68, 125.82 (q, J = 3.9 Hz), 125.18 (q, J = 3.7 Hz), 124.94 (q, J = 3.8 Hz), 122.42, 122.23, 115.65 (t, J = 239.4 Hz), 47.42 (t, J = 5.2 Hz), 37.91 (t, J = 21.8 Hz).

<sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>)  $\delta$  -62.76, -63.02, -115.47 – -118.04(m).

HRMS (ESI) for  $C_{18}H_{13}F_8O^+$  [M+H]<sup>+</sup> m/z: calcd 397.0833, found 397.0845

#### 1-(2,4-dimethoxyphenyl)-4,4-difluoro-2-phenylbutan-1-one (2i)

Prepared according to general method A and isolated in 63% yield after chromoatography as colorless liquid (40.0 mg)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.70 (d, J = 8.7 Hz, 1H), 7.29 – 7.16 (m, 5H), 6.45 (dd, J = 8.7, 2.3 Hz, 1H), 6.35 (d, J = 2.2 Hz, 1H), 5.72 (tt, J = 57.0, 4.9 Hz, 1H), 4.94 (t, J = 7.5 Hz, 1H), 3.83 (s, 3H), 3.79 (s, 3H), 2.83 – 2.65 (m, 1H), 2.34 – 2.16 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 198.70, 164.67, 160.31, 138.58, 133.47, 128.84, 128.56, 127.30, 120.43, 116.72 (t, J = 238.5 Hz), 105.43, 98.43, 55.62, 55.42, 51.24 (t, J = 5.5 Hz), 38.18 (t, J = 21.5 Hz).

<sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>)  $\delta$  -115.18 – -117.73 (m).

HRMS (ESI) for  $C_{18}H_{19}F_2O_3^+$  [M+H]<sup>+</sup> m/z: calcd 321.1297, found 321.1286.

#### 1-(4-chlorophenyl)-4,4-difluoro-2-(4-methoxyphenyl)butan-1-one (2j)

Prepared according to general method A and isolated in 65% yield after chromoatography as colorless liquid (42.1 mg)

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.93 (d, J = 8.9 Hz, 2H), 7.33 – 7.29 (m, 2H), 7.28 – 7.25 (m, 2H), 6.92 – 6.86 (m, 2H), 5.76 (tt, J = 56.7, 4.8 Hz, 1H), 4.76 (t, J = 7.4 Hz, 1H), 3.85 (s, 3H), 2.82 – 2.70 (m, 1H), 2.38 – 2.25 (m, 1H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 196.01, 163.90, 136.91, 133.73, 131.30, 129.66, 129.48, 128.61, 116.17 (t, J = 239.0 Hz), 114.06, 55.63, 46.67 (t, J = 5.4 Hz), 38.02 (t, J = 21.6 Hz).

<sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>)  $\delta$  -115.47 – -117.97 (m).

HRMS (ESI) for  $C_{17}H_{16}ClF_2O_2^+$  [M+H]<sup>+</sup> m/z: calcd 325.0801, found 325.0785.

#### 4,4-difluoro-2-methyl-1,2-diphenylbutan-1-one (2k)

Prepared according to general method A and isolated in 78% yield after chromoatography as colorless liquid (42.8 mg)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.48 – 7.30 (m, 8H), 7.25-7.21 (m, 2H), 5.62 (tdd, J = 56.4, 5.3, 4.1 Hz, 1H), 2.74 – 2.38 (m, 2H), 1.76 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  202.06, 141.73, 135.72, 132.06, 129.67, 129.45, 128.12, 127.72, 126.13, 116.67 (t, J = 238.3 Hz), 52.09 (dd, J = 5.7, 4.1 Hz), 44.92 (t, J = 21.5 Hz), 22.76.

<sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>)  $\delta$  -109.75 – -112.62 (m).

HRMS (ESI) for  $C_{17}H_{17}F_2O^+$  [M+H]<sup>+</sup> m/z: calcd 275.1253, found 275.1233.

## 2-(2,2-difluoroethyl)-2-phenylcyclopentan-1-one (2l)



Prepared according to general method B and isolated in 83% yield after chromoatography as colorless liquid (37.2 mg)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.45 – 7.33 (m, 4H), 7.32 – 7.27 (m, 1H), 5.41 (tdd, J = 56.2, 7.2, 2.5 Hz, 1H), 2.93 – 2.82 (m, 1H), 2.69 – 2.50 (m, 1H), 2.39 – 2.15 (m, 2H), 2.13 – 1.91 (m, 3H), 1.89 – 1.72 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 217.31, 136.44, 129.26, 127.82, 126.86, 116.51 (t, J = 238.7 Hz), 53.74 (t, J = 5.3 Hz), 42.69 (t, J = 21.5 Hz), 36.05, 33.85, 18.53.

<sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ -113.82 (d, J = 4.0 Hz).

HRMS (ESI) for  $C_{13}H_{15}F_2O^+$  [M+H]<sup>+</sup> m/z: calcd 225.1085, found 225.1071.

#### 4-(benzo[d]thiazol-2-yl)-6,6-difluoro-1-phenylhexan-1-one (4a)

Prepared according to general method B and isolated in 86% yield after chromoatography as colorless liquid (59.3 mg)

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.00 (d, J = 8.1 Hz, 1H), 7.87 (m, 3H), 7.53 (t, J = 7.4 Hz, 1H), 7.51 – 7.47 (m, 1H), 7.44 – 7.37 (m, 3H), 5.89 (tdd, J = 56.5, 6.0, 3.5 Hz, 1H), 3.61 – 3.53 (m, 1H), 3.07 – 2.95 (m, 2H), 2.65 – 2.52 (m, 1H), 2.42 – 2.27 (m, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 198.95, 172.90, 153.18, 136.70, 134.78, 133.34, 128.72, 128.11, 126.36, 125.37, 123.11, 121.87, 115.96 (t, J = 239.6 Hz), 39.85 (t, J = 21.7 Hz), 38.62 (dd, J = 7.0, 3.9 Hz), 35.61, 30.22.

<sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>)  $\delta$  -114.69 – -117.12 (m).

HRMS (ESI) for  $C_{19}H_{18}F_2OS^+$  [M+H]<sup>+</sup> m/z: calcd 346.1072, found 346.1079.

## 4-(benzo[d]thiazol-2-yl)-1-(4-chlorophenyl)-6,6-difluorohexan-1-one (4b)

Prepared according to general method B and isolated in 88% yield after chromoatography as colorless liquid (66.7 mg)

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.99 (d, J = 8.2 Hz, 1H), 7.87 (d, J = 7.9 Hz, 1H), 7.83 - 7.79 (m, 2H), 7.52 - 7.47 (m, 1H), 7.42 - 7.36 (m, 3H), 5.89 (tdd, J = 56.5, 6.0, 3.5 Hz, 1H), 3.59 - 3.52 (m, 1H), 3.03 - 2.91 (m, 2H), 2.64 - 2.52 (m, 1H), 2.41 - 2.27 (m, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 197.72, 172.74, 153.19, 139.79, 135.02, 134.77, 129.54, 129.04, 126.41, 125.43, 123.12, 121.88, 115.91 (t, J = 239.6 Hz), 39.87 (t, J = 21.7 Hz), 38.56 (dd, J = 7.0, 4.2 Hz), 35.59, 30.13.

<sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>)  $\delta$  -114.70 – -117.14(m).

HRMS (ESI) for  $C_{19}H_{17}C1F_2OS^+$  [M+H]<sup>+</sup> m/z: calcd 380.0682, found 380.0663.

#### 4-(benzo[d]thiazol-2-yl)-6,6-difluoro-1-(4-fluorophenyl)hexan-1-one (4c)

Prepared according to general method B and isolated in 91% yield after chromoatography as colorless liquid (66.0 mg)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.99 (d, J = 7.9 Hz, 1H), 7.93 – 7.83 (m, 3H), 7.53 – 7.46 (m, 1H), 7.44 – 7.37 (m, 1H), 7.11 – 7.04 (m, 2H), 5.89 (tdd, J = 56.5, 6.0, 3.5 Hz, 1H), 3.61 – 3.51 (m, 1H), 3.06 – 2.89 (m, 2H), 2.68 – 2.48 (m, 1H), 2.45 – 2.25 (m, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 197.18, 172.69, 165.77 (d, J = 255.0 Hz), 153.02, 134.63, 133.03 (d, J = 2.9 Hz), 130.62 (d, J = 9.3 Hz), 126.27, 125.29, 122.97, 121.74, 115.79 (t, J = 239.5 Hz), 115.68 (d, J = 21.9 Hz), 39.73 (t, J = 21.8 Hz), 38.45 (dd, J = 6.8, 4.2 Hz), 35.39, 30.05.

<sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>)  $\delta$  -104.95, -114.52 – -117.29 (m).

HRMS (ESI) for  $C_{19}H_{17}F_3OS^+$  [M+H]<sup>+</sup> m/z: calcd 364.0977, found 364.0960.

#### 4-(benzo[d]thiazol-2-yl)-6,6-difluoro-1-(m-tolyl)hexan-1-one (4d)

Prepared according to general method B and isolated in 56% yield after chromoatography as colorless liquid (40.0 mg)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.00 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 7.6 Hz, 1H), 7.66 (d, J = 8.4 Hz, 2H), 7.52 – 7.46 (m, 1H), 7.43 – 7.37 (m, 1H), 7.36 – 7.27 (m, 2H), 5.89 (tdd, J = 56.5, 6.0, 3.5 Hz, 1H), 3.63 – 3.50 (m, 1H), 3.07 – 2.92 (m, 2H), 2.67 – 2.49 (m, 1H), 2.44 – 2.27 (m, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 199.19, 172.97, 153.17, 138.52, 136.74, 134.79, 134.09, 128.62, 128.59, 126.35, 125.36, 125.33, 123.10, 121.87, 115.97 (t, J = 239.5 Hz), 39.84 (t, J = 21.8 Hz), 38.63 (dd, J = 7.0, 4.2 Hz), 35.65, 30.29, 21.45.

<sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>)  $\delta$  -114.51 – -117.27 (m).

HRMS (ESI) for  $C_{20}H_{20}F_2OS^+$  [M+H]<sup>+</sup> m/z: calcd 360.1228, found 360.1221.

#### 4-(benzo[d]thiazol-2-yl)-6,6-difluoro-1-(p-tolyl)hexan-1-one (4e)

Prepared according to general method B and isolated in 83% yield after chromoatography as colorless liquid (59.6 mg)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.00 (d, J = 8.1 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 8.1 Hz, 2H), 7.49 (t, J = 7.7 Hz, 1H), 7.39 (t, J = 7.9 Hz, 1H), 7.21 (d, J = 7.9 Hz, 2H), 5.89 (tdd, J = 56.6, 5.7, 3.6 Hz, 1H), 3.64 – 3.49 (m, 1H), 3.07 – 2.91 (m, 2H), 2.69 – 2.46 (m, 1H), 2.44 – 2.24 (m, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 198.61, 172.98, 153.21, 144.14, 134.81, 134.28, 129.39, 128.23, 126.34, 125.35, 123.11, 121.86, 115.98 (t, J = 239.4 Hz), 39.84 (t, J = 21.7 Hz), 38.66 (dd, J = 7.0, 4.3 Hz), 35.49, 30.32, 21.76.

<sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>)  $\delta$  -114.50 – -117.24 (m).

HRMS (ESI) for  $C_{20}H_{20}F_2OS^+$  [M+H]<sup>+</sup> m/z: calcd 360.1228, found 360.1219.

#### 4-(benzo[d]thiazol-2-yl)-6,6-difluoro-1-(4-methoxyphenyl)hexan-1-one (4f)

Prepared according to general method B and isolated in 67% yield after chromoatography as colorless liquid (50.2 mg)

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.00 (d, J = 8.1 Hz, 1H), 7.89 – 7.83 (m, 3H), 7.52 – 7.45 (m, 1H), 7.41 – 7.37 (m, 1H), 6.91 – 6.86 (m, 2H), 5.89 (tdd, J = 56.5, 6.0, 3.6 Hz, 1H), 3.85 (d, J = 3.3 Hz, 3H), 3.59 – 3.52 (m, 1H), 3.01 – 2.89 (m, 2H), 2.64 – 2.51 (m, 1H), 2.43 – 2.26 (m, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 197.50, 173.03, 163.68, 153.23, 134.83, 130.41, 129.87, 126.34, 125.34, 123.12, 121.87, 116.00 (t, J = 239.4 Hz), 113.85, 55.60, 39.87 (t, J = 21.6 Hz), 38.72 (dd, J = 6.7, 4.1 Hz), 35.26,

30.45.

<sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>)  $\delta$  -114.69 – -117.09 (m).

HRMS (ESI) for  $C_{20}H_{20}F_2O_2S^+$  [M+H]<sup>+</sup> m/z: calcd 376.1177, found 376.1166.

# 4-(benzo[d]thiazol-2-yl)-6,6-difluoro-1-(4-(trifluoromethyl)phenyl)hexan-1-one (4g)

Prepared according to general method B and isolated in 70% yield after chromoatography as colorless liquid (57.8 mg)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.01 – 7.92 (m, 3H), 7.89 (d, J = 7.9 Hz, 1H), 7.70 (d, J = 8.1 Hz, 2H), 7.52 (t, J = 7.7 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H), 5.91 (tdd, J = 9.2, 5.7, 3.5 Hz, 1H), 3.65 – 3.54 (m, 1H), 3.14 – 2.98 (m, 2H), 2.71 – 2.51 (m, 1H), 2.48 – 2.29 (m, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 197.86, 172.49, 153.06, 134.63, 134.49 (q, J = 32.6 Hz), 128.33, 126.33, 125.69 (q, J = 3.6 Hz), 125.35, 123.54 (q, J = 272.6 Hz), 123.01, 121.77, 115.76 (t, J = 239.5 Hz), 39.74 (t, J = 21.8 Hz), 38.44 (dd, J = 6.9, 4.1 Hz), 35.80, 29.88.

<sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>)  $\delta$  -63.15, -114.51 – -117.30 (m).

HRMS (ESI) for  $C_{20}H_{17}F_5NOS^+$  [M+H]<sup>+</sup> m/z: calcd 414.0946, found 414.0938.

#### 4-(benzo[d]thiazol-2-yl)-6,6-difluoro-1-(naphthalen-2-yl)hexan-1-one (4h)

Prepared according to general method B and isolated in 50% yield after chromoatography as colorless liquid (39.5 mg)

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.36 (s, 1H), 8.01 (d, J = 8.1 Hz, 1H), 7.96 (dd, J = 8.6, 1.3 Hz, 1H), 7.91 – 7.82 (m, 4H), 7.58 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.7 Hz, 1H), 7.40 (t, J = 7.6 Hz, 1H), 5.92 (tdd, J = 56.4, 5.9, 3.5 Hz, 1H),

3.66 - 3.57 (m, 1H), 3.22 - 3.09 (m, 2H), 2.68 - 2.55 (m, 1H), 2.47 - 2.34 (m, 3H).  $^{13}$ C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  198.92, 172.97, 153.22, 135.75, 134.83, 134.04, 132.56, 129.84, 129.69, 128.64, 128.61, 127.89, 126.91, 126.38, 125.40, 123.84, 123.13, 121.90, 115.98 (t, J = 239.5 Hz), 39.90 (t, J = 21.7 Hz), 38.70 (dd, J = 6.8, 4.2 Hz), 35.68, 30.44.

<sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>)  $\delta$  -114.66 – -117.08 (m).

HRMS (ESI) for  $C_{23}H_{20}F_2OS^+$  [M+H]<sup>+</sup> m/z: calcd 396.1228, found 396.1220.

#### 4-(benzo[d]thiazol-2-yl)-6,6-difluoro-1-(thiophen-2-yl)hexan-1-one (4i)

Prepared according to general method B and isolated in 85% yield after chromoatography as colorless liquid (59.7 mg)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.02 (d, J = 8.1 Hz, 1H), 7.90 (d, J = 8.0, 0.5 Hz, 1H), 7.67 – 7.60 (m, 2H), 7.54 – 7.48 (m, 1H), 7.45 – 7.39 (m, 1H), 7.10 – 7.05 (m, 1H), 5.91 (tdd, J = 56.5, 6.0, 3.5 Hz, 1H), 3.63 – 3.53 (m, 1H), 3.03 – 2.93 (m, 2H), 2.69 – 2.51 (m, 1H), 2.46 – 2.29 (m, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 191.87, 172.73, 153.20, 143.98, 134.80, 133.88, 132.09, 128.21, 126.37, 125.39, 123.12, 121.87, 115.93 (t, J = 239.6 Hz), 39.78 (t, J = 21.8 Hz), 38.60 (dd, J = 6.9, 4.1 Hz), 36.29, 30.41.

<sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>)  $\delta$  -114.67 – -117.08 (m).

HRMS (ESI) for  $C_{16}H_{17}F_2NOS_2^+$  [M+H]<sup>+</sup> m/z: calcd 352.0636, found 352.0629.

#### 1-(adamantan-1-yl)-4-(benzo[d]thiazol-2-yl)-6,6-difluorohexan-1-one (4j)

Prepared according to general method B and isolated in 41% yield after chromoatography as colorless liquid (33.0 mg)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.02 (d, J = 8.1 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.52 (dt, J = 8.2, 2.7 Hz, 1H), 7.41 (dt, J = 20.2, 6.5 Hz, 1H), 5.88 (tdd, J = 56.5, 6.0, 3.5 Hz, 1H), 3.50 – 3.38 (m, 1H), 2.66 – 2.43 (m, 3H), 2.37 – 2.21 (m, 1H), 2.20 – 2.08 (m, 2H), 2.02 (s, 3H), 1.74 – 1.60 (m, 12H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 214.60, 173.17, 153.18, 134.79, 126.32, 125.31, 123.08, 121.87, 116.00 (t, J = 239.4 Hz), 46.45, 39.84 (t, J = 21.7 Hz), 38.57 (dd, J = 7.0, 4.1 Hz), 38.37, 36.62, 33.08, 29.88, 28.02.

<sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>)  $\delta$  -114.47 – -117.22(m).

HRMS (ESI) for  $C_{23}H_{28}F_2NOS^+$  [M+H]<sup>+</sup> m/z: calcd 404.1854, found 404.1844.

#### 6,6-difluoro-1-phenyl-4-(thiazol-2-yl)hexan-1-one (4k)

Prepared according to general method B and isolated in 89% yield after chromoatography as colorless liquid (52.5 mg)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.88 (d, J = 7.3 Hz, 2H), 7.74 (d, J = 3.3 Hz, 1H), 7.54 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.7 Hz, 2H), 7.25 (s, 1H), 5.80 (tdd, J = 56.5, 6.0, 3.5 Hz, 1H), 3.55 – 3.45 (m, 1H), 3.05 – 2.83 (m, 2H), 2.57 – 2.39 (m, 1H), 2.37 – 2.17 (m, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 199.07, 172.07, 142.81, 136.77, 133.32, 128.74, 128.09, 118.71, 116.05 (t, J = 239.2 Hz), 40.09(t, J = 21.5 Hz), 37.59 (dd, J = 7.1, 4.3 Hz), 35.57, 30.51.

<sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ - 114.67 – -117.37 (m).

HRMS (ESI) for  $C_{15}H_{16}F_2NOS^+$  [M+H]<sup>+</sup> m/z: calcd 296.0915, found 296.0916.

#### 6,6-difluoro-1-phenyl-4-(pyridin-2-yl)hexan-1-one (4l)

Prepared according to general method B and isolated in 61% yield after chromoatography as colorless liquid (35.3 mg)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.59 (d, J = 4.4 Hz, 1H), 7.84 (d, J = 7.4 Hz, 2H), 7.62 (td, J = 7.6, 1.7 Hz, 1H), 7.53 (t, J = 7.4 Hz, 1H), 7.41 (t, J = 7.7 Hz, 2H), 7.19 – 7.13 (m, 2H). 5.62 (tdd, J = 56.8, 6.2, 3.5 Hz, 1H), 3.20 – 3.04 (m, 1H), 2.89 – 2.74 (m, 2H), 2.59 – 2.38 (m, 1H), 2.32 – 2.11 (m, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 199.62, 161.94, 149.91, 136.87, 136.85, 133.18, 128.68, 128.09, 123.56, 122.16, 116.60 (t, J = 238.9 Hz), 41.18 (dd, J = 7.0, 3.6 Hz), 39.46 (t, J = 20.9 Hz), 35.92, 29.98.

<sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>)  $\delta$  -114.45 – -117.25 (m).

HRMS (ESI) for  $C_{17}H_{18}F_2NO^+$  [M+H]<sup>+</sup> m/z: calcd 290.1351, found 290.1365.

#### 6,6-difluoro-1-phenyl-4-(thiophen-2-yl)hexan-1-one (4m)

Prepared according to general method B and isolated in 34% yield after chromoatography as colorless liquid (19.9 mg)

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.89 – 7.84 (m, 2H), 7.57 – 7.51 (m, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.21 (d, J = 5.1 Hz, 1H), 6.97 – 6.92 (m, 1H), 6.87 – 6.84 (m, 1H), 5.64 (tdd, J = 56.8, 6.8, 3.2 Hz, 1H), 3.32 – 3.22 (m, 1H), 3.01 – 2.78 (m, 2H), 2.34 – 2.09 (m, 3H), 2.05 – 1.92 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 199.50, 146.19, 136.91, 133.24, 128.71, 128.09, 127.06, 125.17, 124.20, 116.41 (t, J = 238.9 Hz), 42.37 (t, J = 21.3 Hz), 36.03, 35.50 (dd, J = 8.1, 3.6 Hz), 32.03.

<sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>)  $\delta$  -115.51 – -118.28(m).

HRMS (ESI) for  $C_{16}H_{17}F_2OS_2^+$  [M+H]<sup>+</sup> m/z: calcd 295.0963, found 295.0959

#### 2-(2,2-difluoroethyl)-5-oxo-5-phenylpentanenitrile (4n)

Prepared according to general method B and isolated in 96% yield after chromoatography as colorless liquid (45.5 mg)

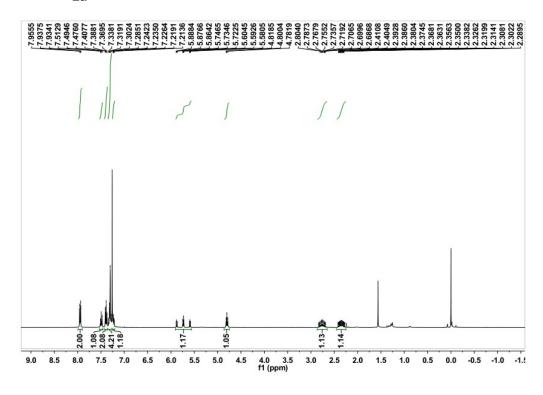
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.97 (dd, J = 8.2, 1.0 Hz, 2H), 7.64 – 7.56 (m, 1H), 7.49 (t, J = 7.8 Hz, 2H), 6.04 (tdd, J = 55.6, 5.3, 3.6 Hz, 1H), 3.32 – 3.19 (m, 2H),

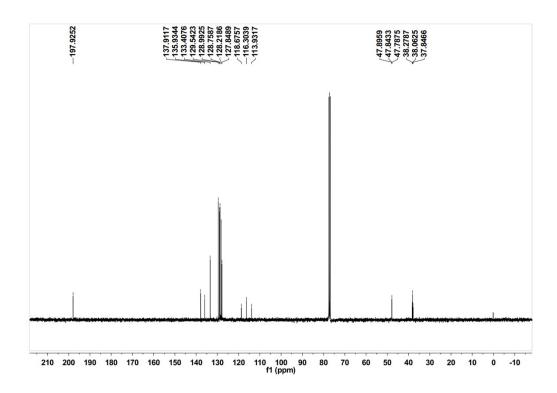
3.07 - 2.98 (m, 1H), 2.35 - 2.11 (m, 3H), 2.08 - 1.98 (m, 1H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  197.92, 136.36, 133.74, 128.90, 128.12, 120.25, 114.83 (t, J = 240.6 Hz),  $\delta$  36.82 (t, J = 22.7 Hz), 35.31, 26.50, 25.25 (dd, J = 6.5, 4.9 Hz).

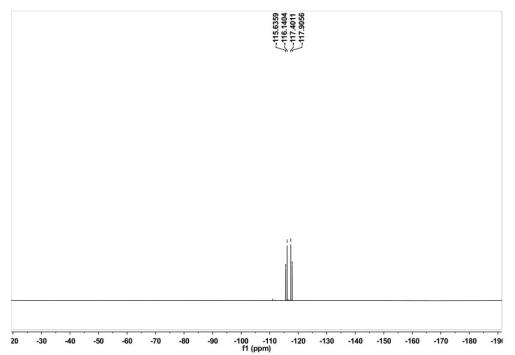
 $^{19}F$  NMR (565 MHz, CDCl3)  $\delta$  -115.91 - -117.33(m).

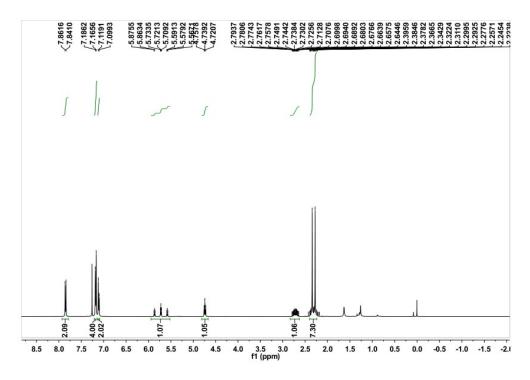
HRMS (ESI) for  $C_{13}H_{14}F_2NO^+$  [M+H]<sup>+</sup> m/z: calcd 238.1038, found 238.1028.

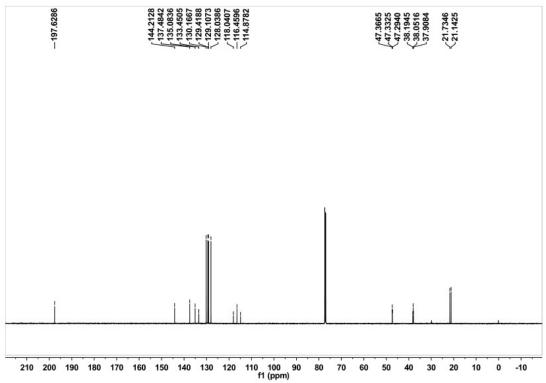
# Part 4. <sup>1</sup>H NMR, <sup>13</sup>C NMR and <sup>19</sup>F NMR Spectra

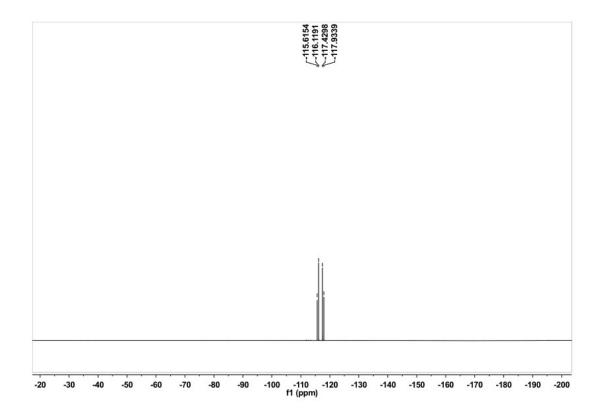


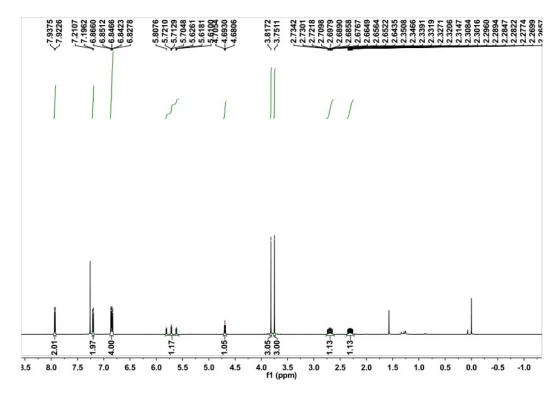


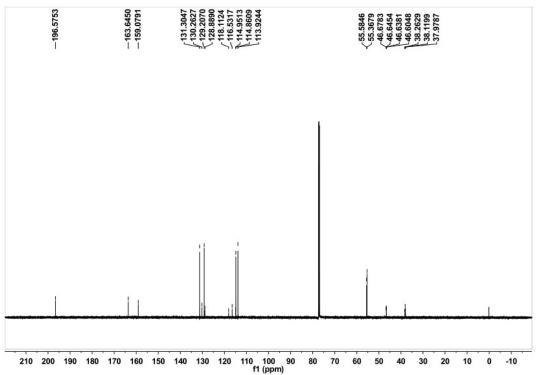


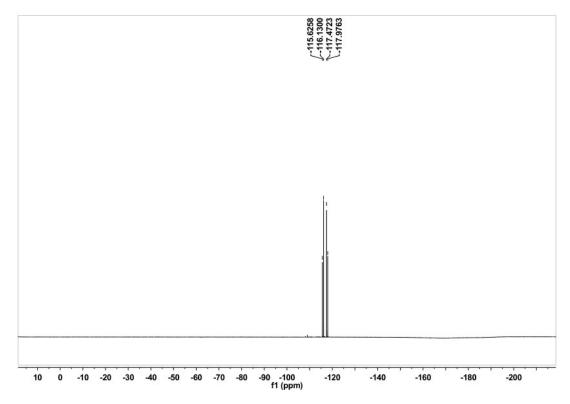












2d

8.5 8.0

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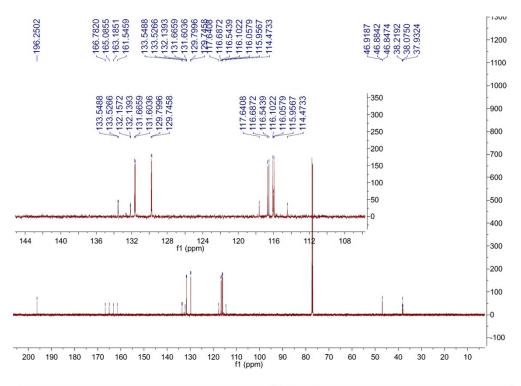
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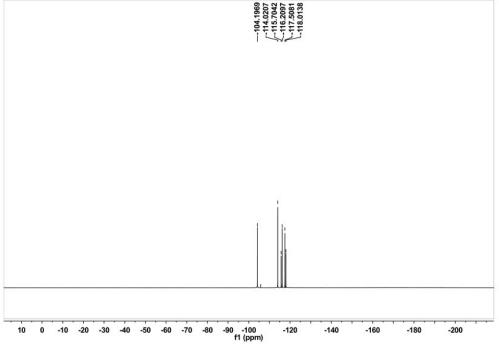
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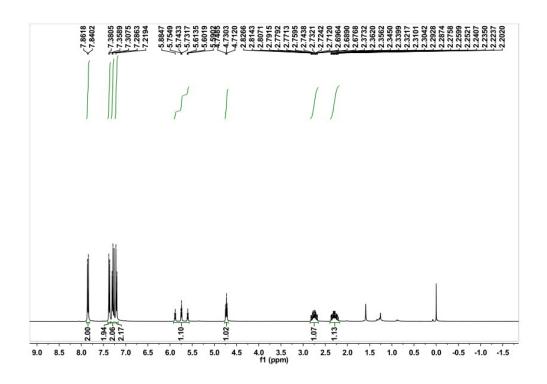
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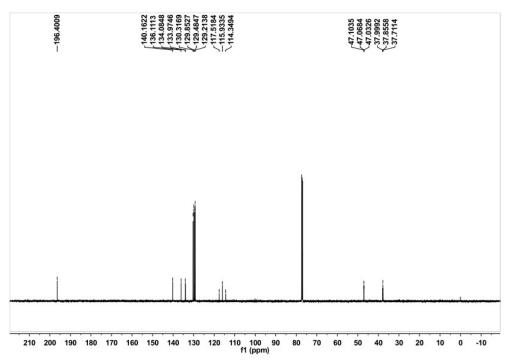
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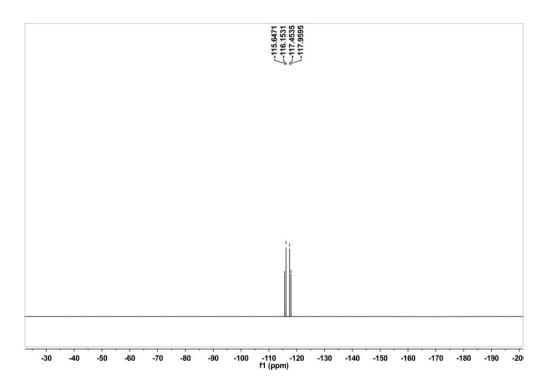
4.5 4.0 f1 (ppm)

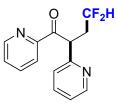




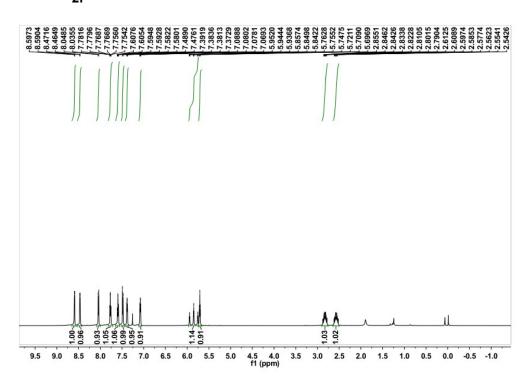


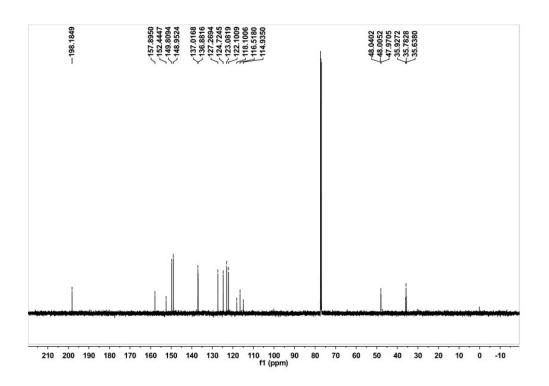


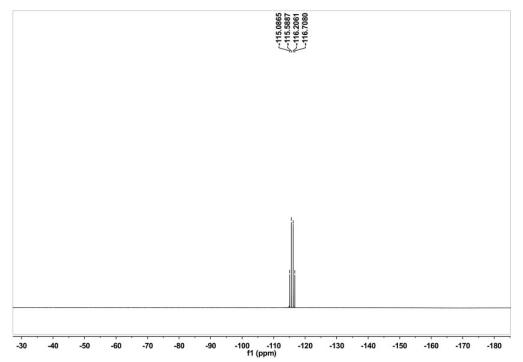


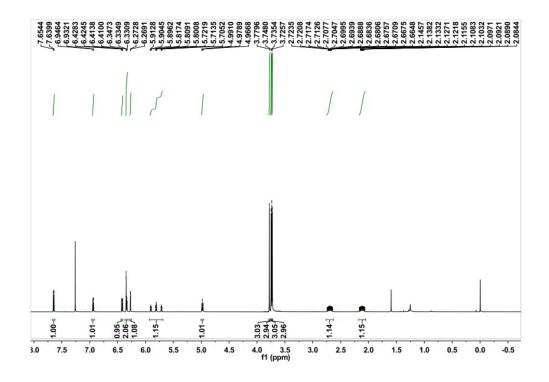


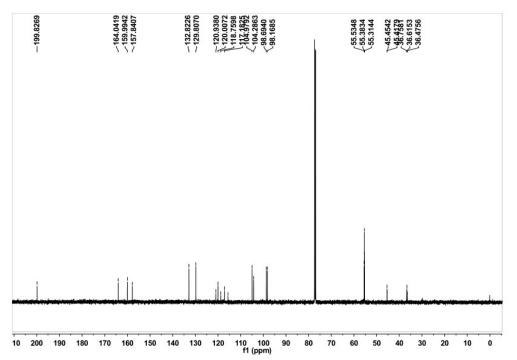
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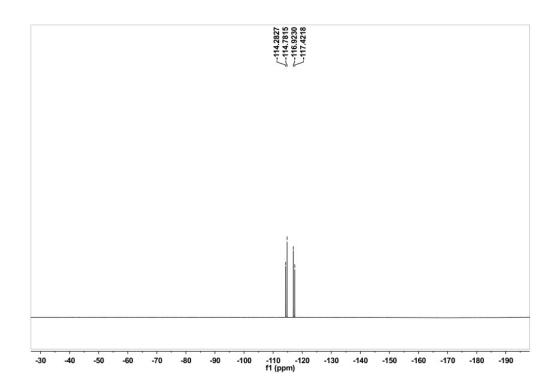


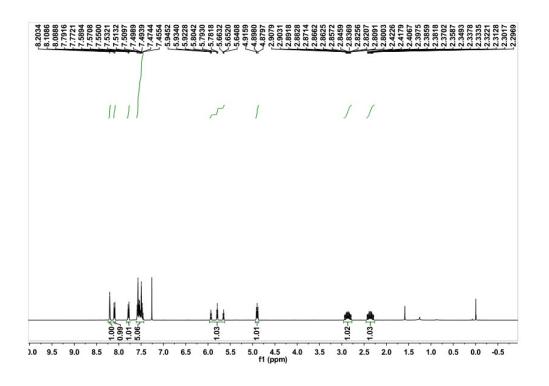


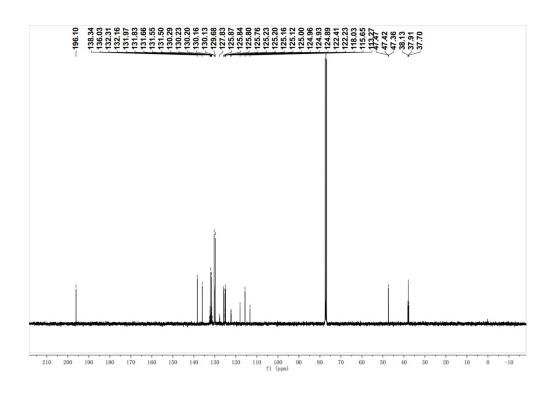


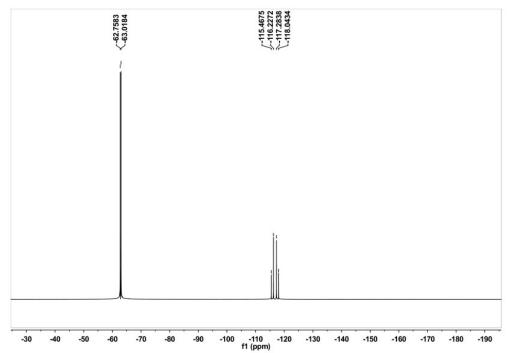




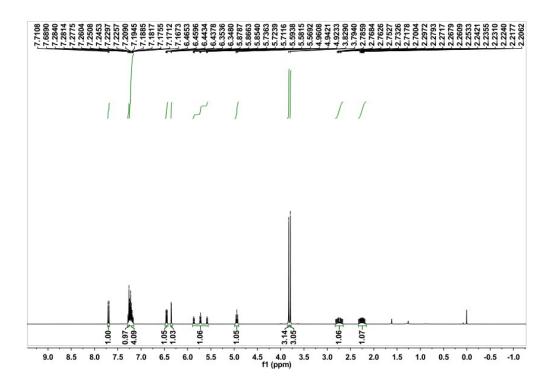


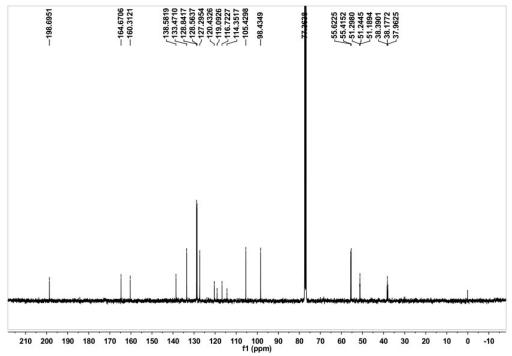


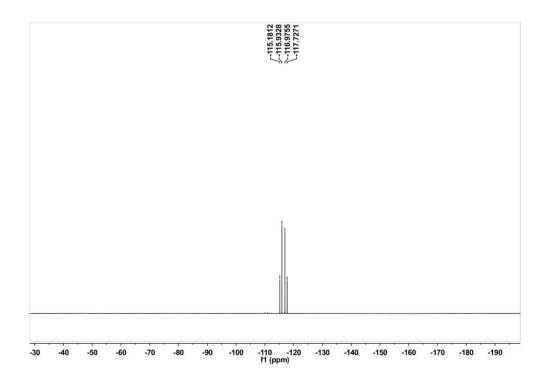


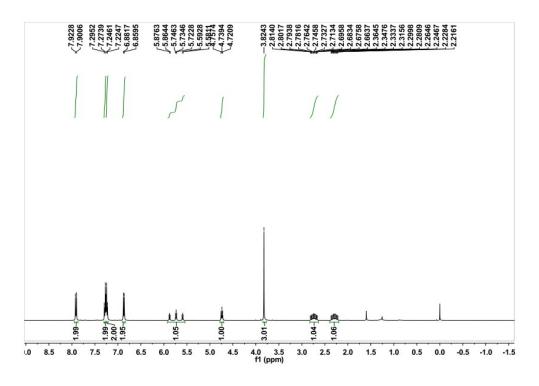


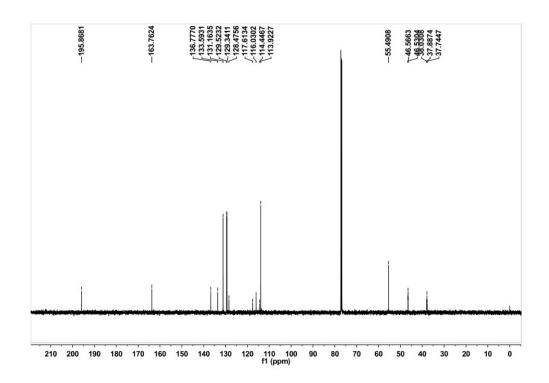
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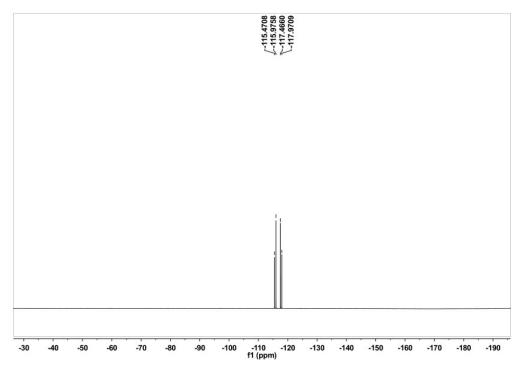


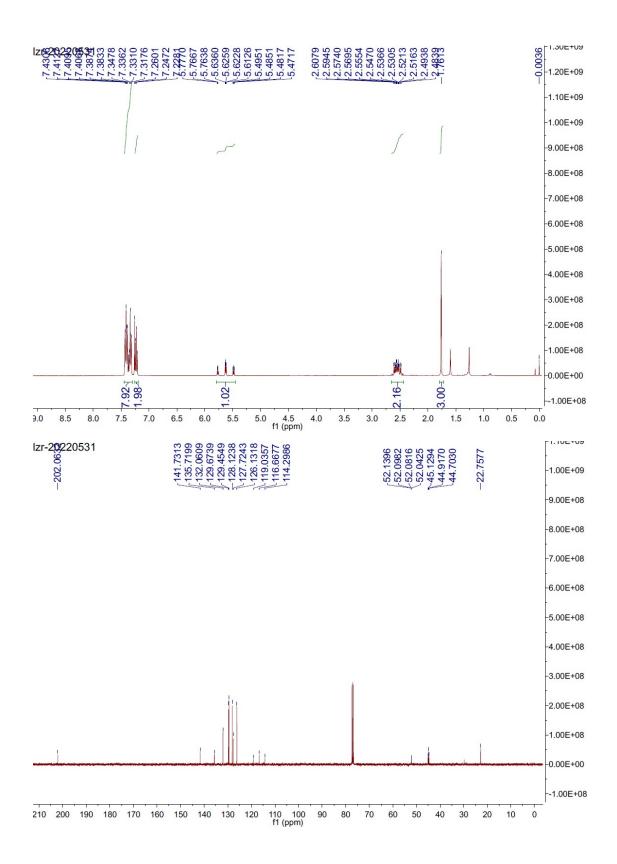


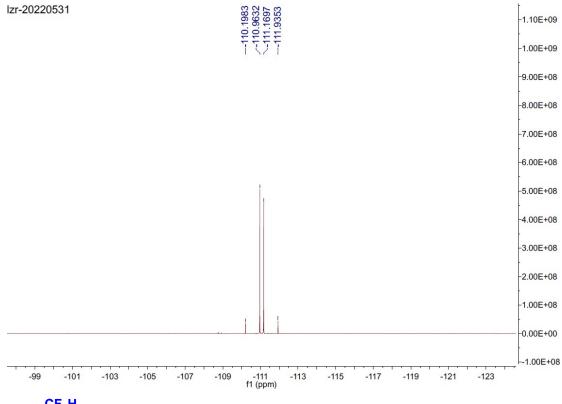




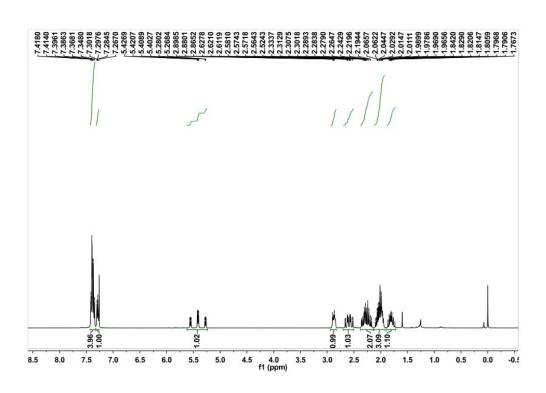


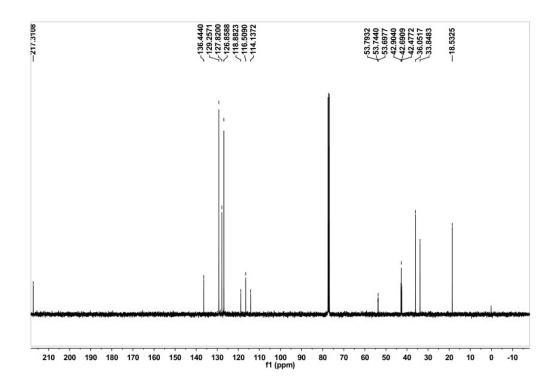


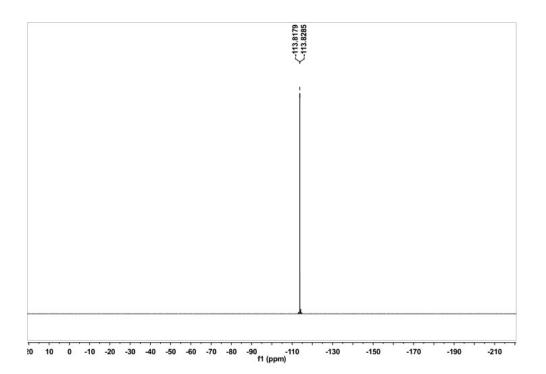


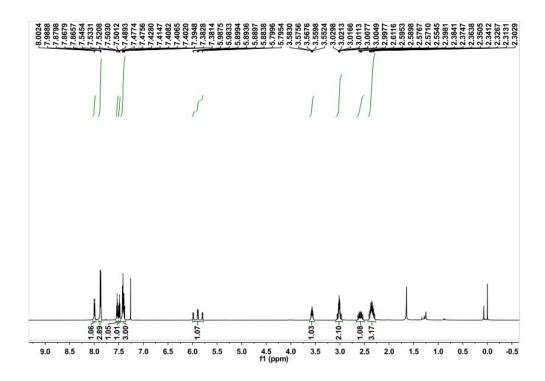


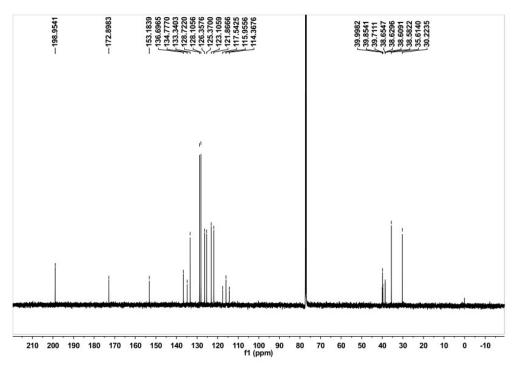


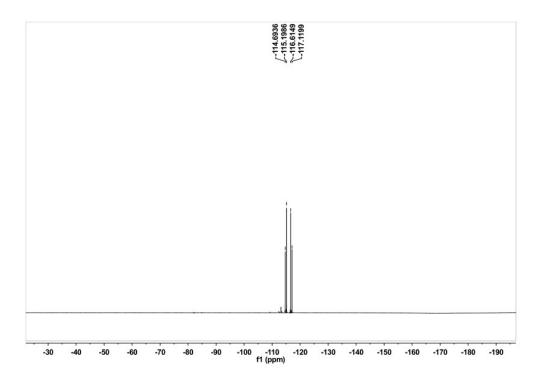


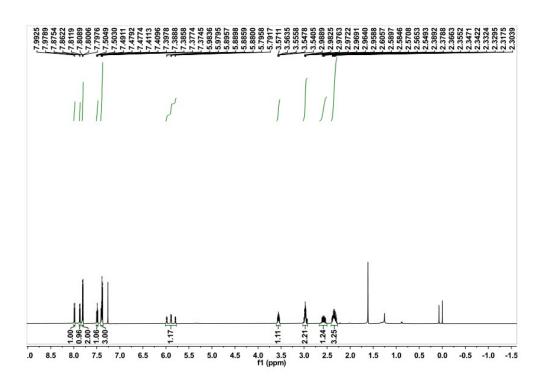


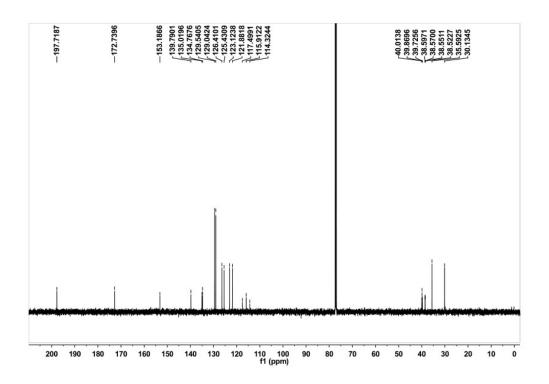


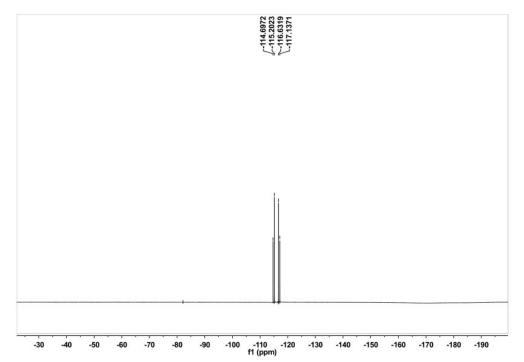




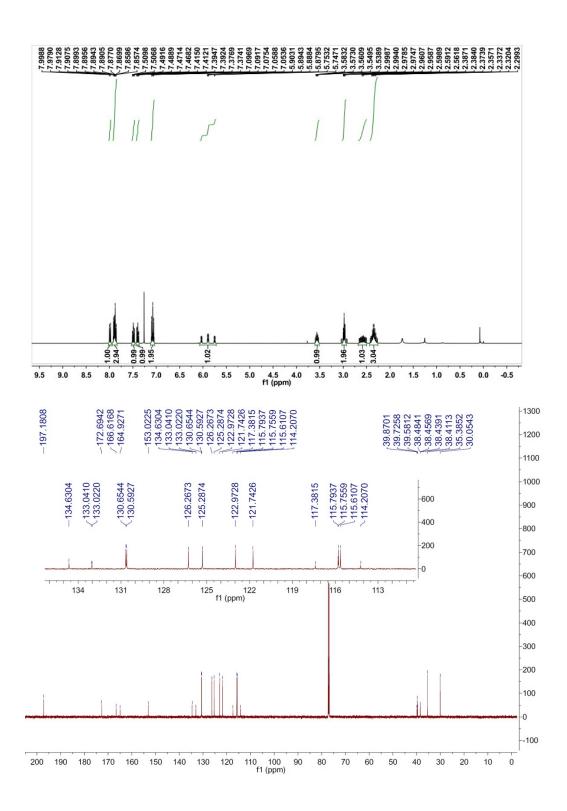


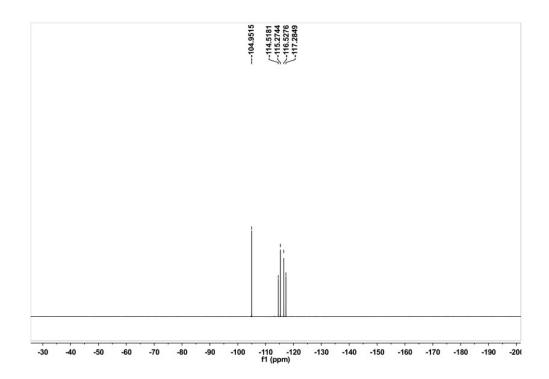


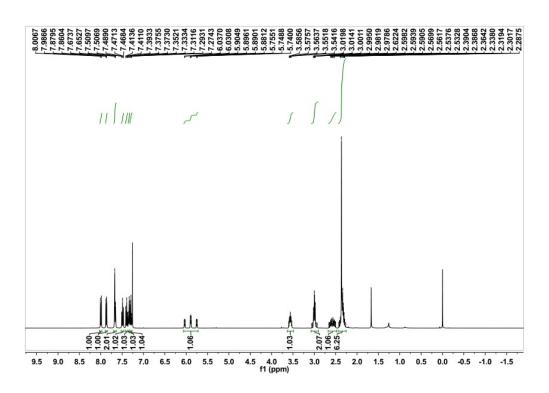


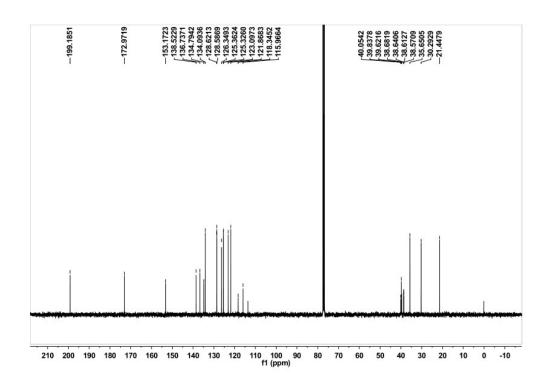


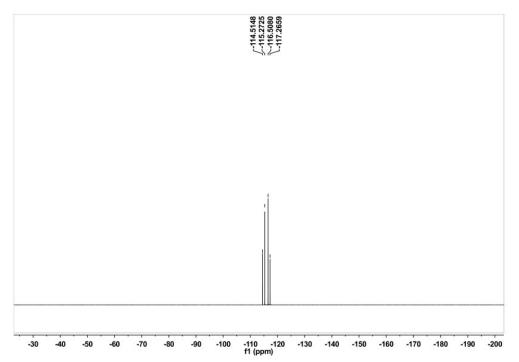
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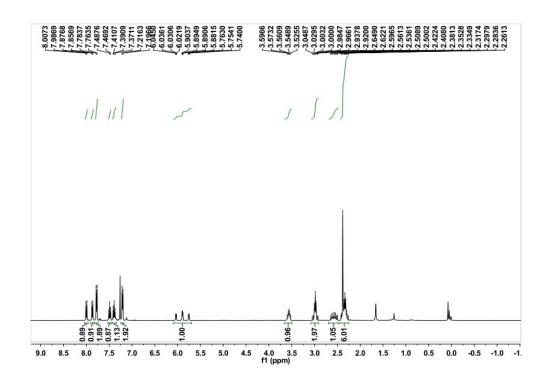


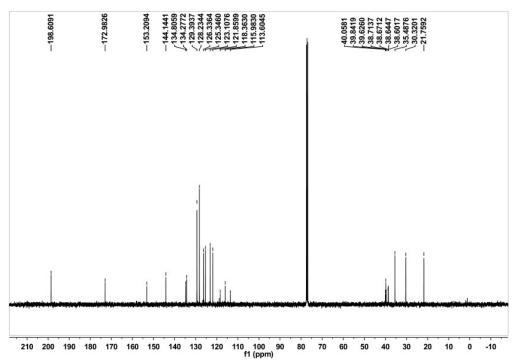


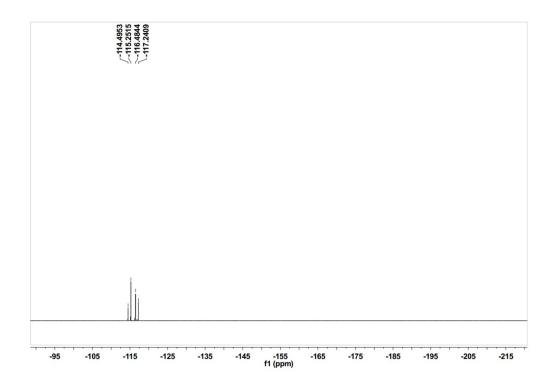


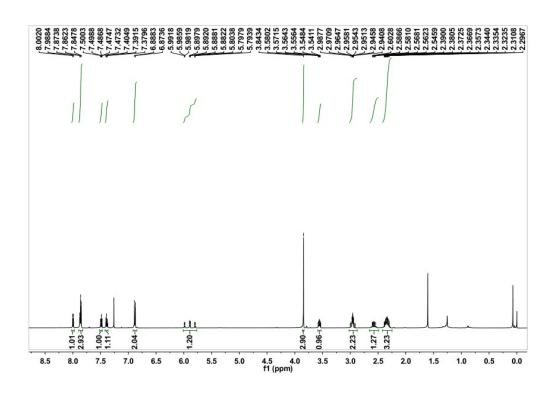


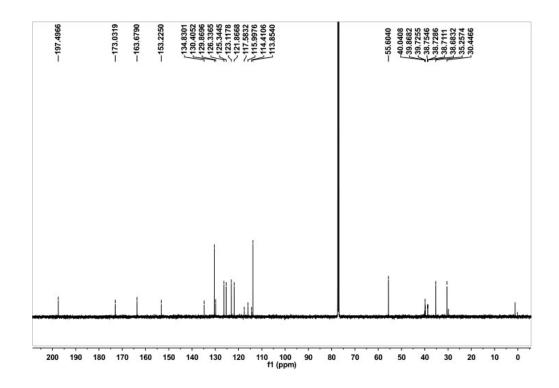


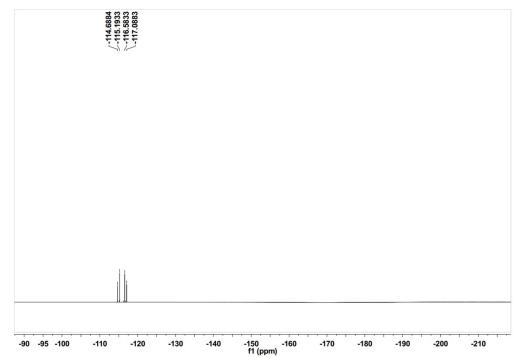


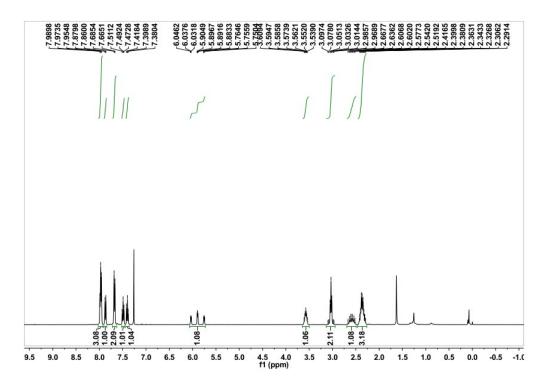


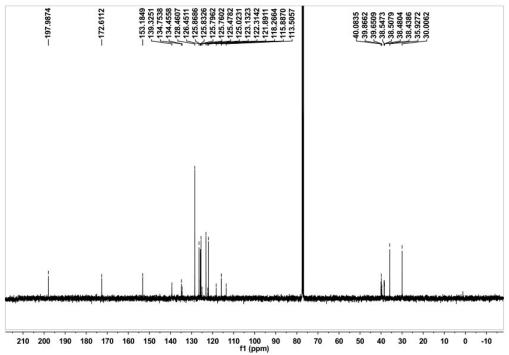


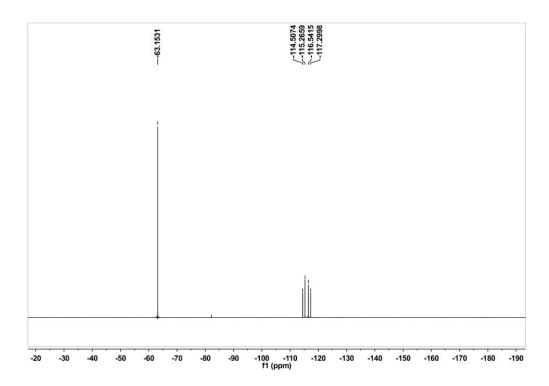


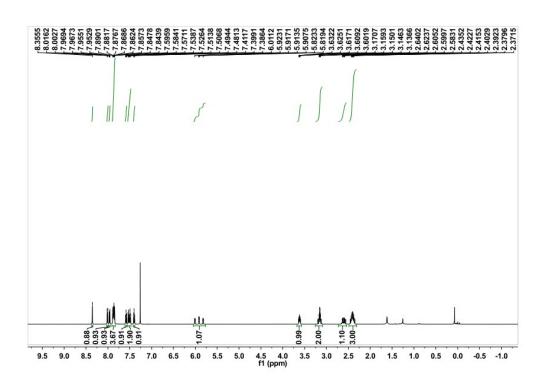


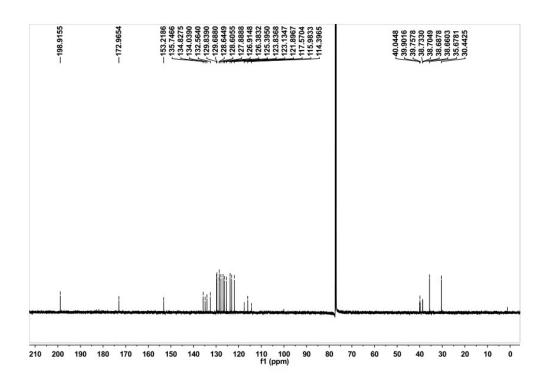


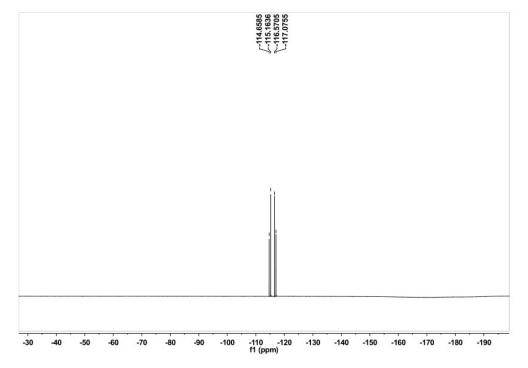




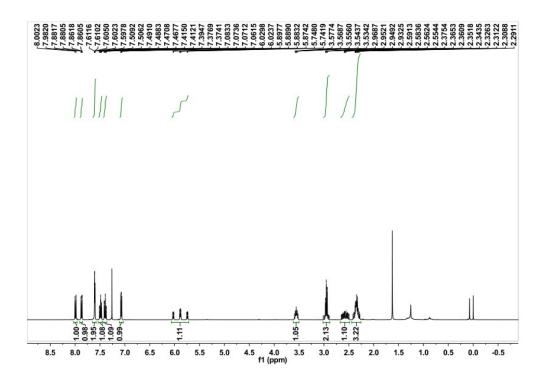


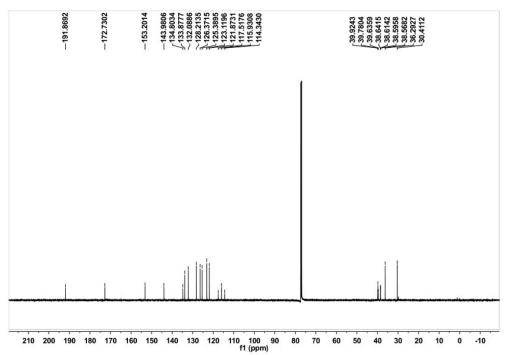


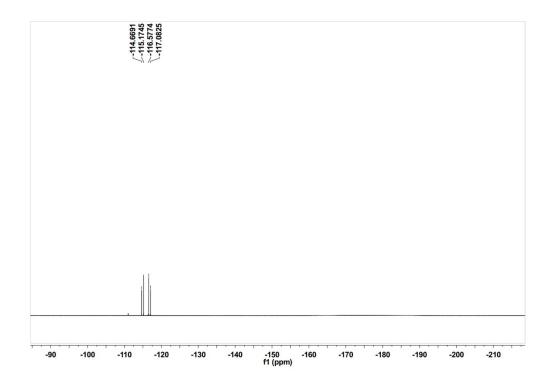


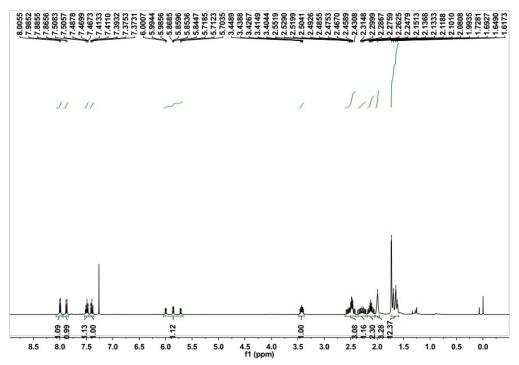


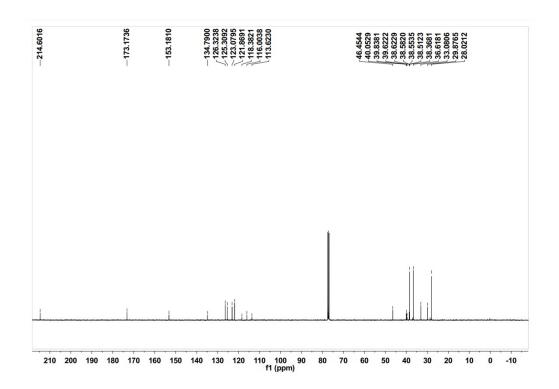
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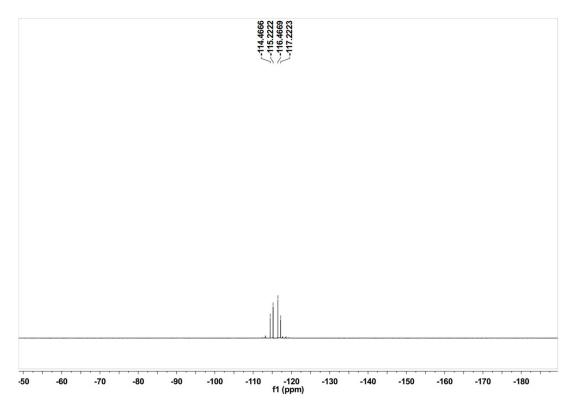




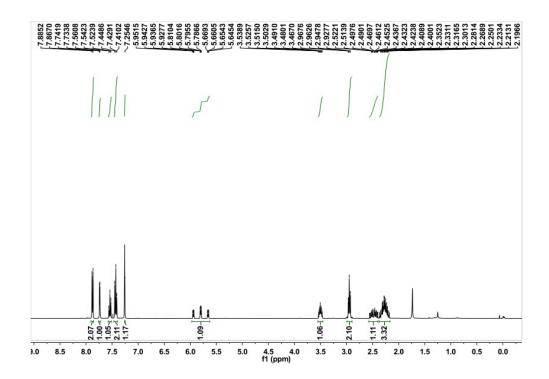


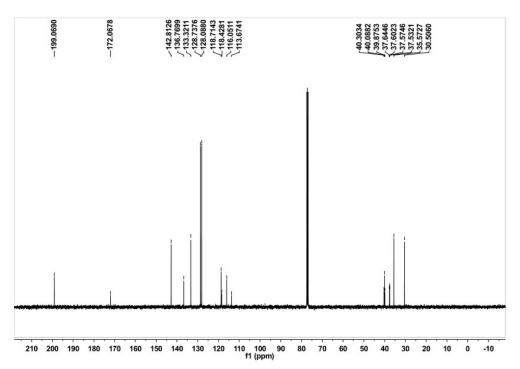


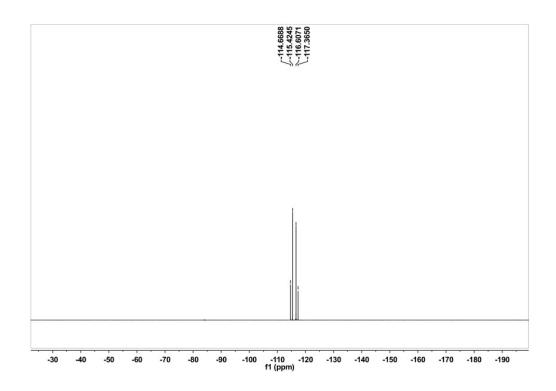


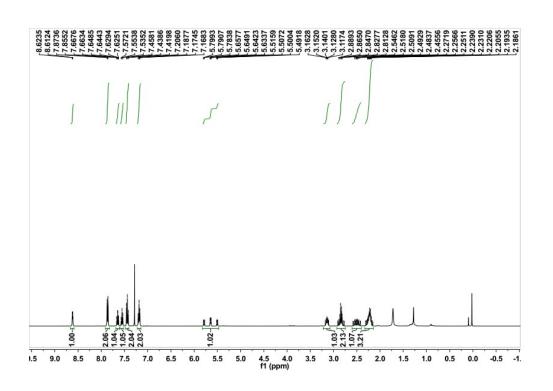


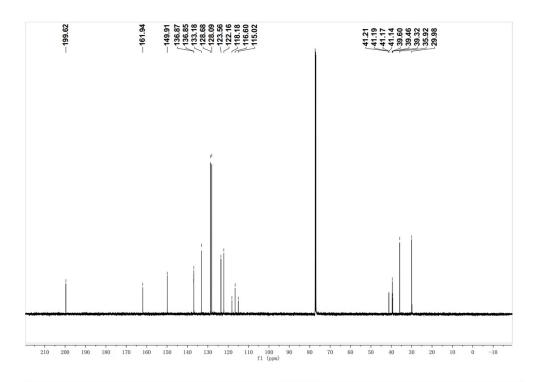
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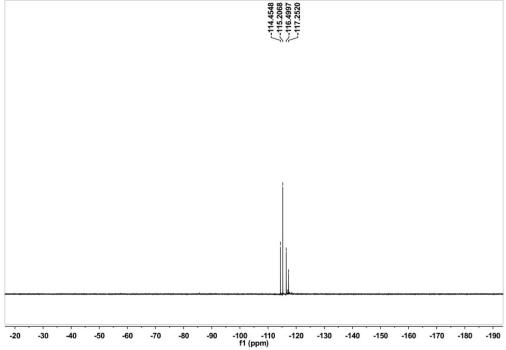


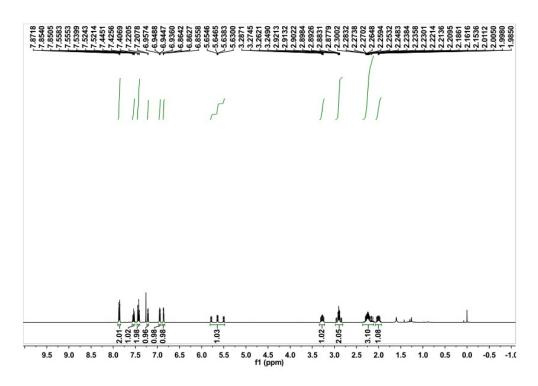


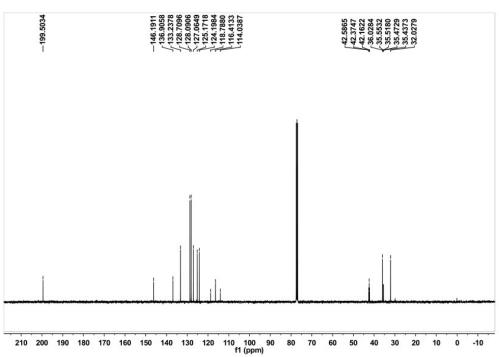


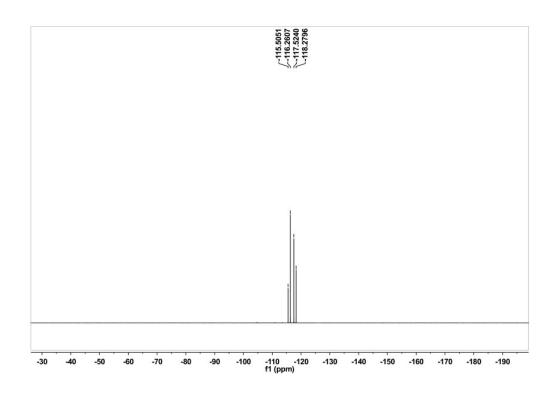












4n

