

# **Supporting Information**

## **Engaging $\alpha$ -Fluorocarboxylic Acids Directly in Decarboxylative C–C Bond Formation**

Hongyu Wang,<sup>1,†</sup> Chen-fei Liu,<sup>1,†</sup> Zhihui Song,<sup>2,‡</sup> Mingbin Yuan,<sup>2,‡</sup> Yee Ann Ho,<sup>1</sup> Osvaldo Gutierrez<sup>2,\*</sup> and Ming Joo Koh<sup>1,\*</sup>

<sup>1</sup>Department of Chemistry, National University of Singapore, 12 Science Drive 2, Republic of Singapore, 117549

<sup>2</sup>Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland, 20742, United States

<sup>†</sup>These authors contributed equally.

<sup>‡</sup>These authors contributed equally.

Correspondence: chmkmj@nus.edu.sg

Correspondence: ogs@umd.edu

## Content

1. General information .....	3
2. General procedures for the preparation of $\alpha$ -fluoro acids .....	3
3. Characterization of $\alpha$ -fluoroacids .....	4
4. Cyclic voltammogram of 2-fluoro-2-phenylacetic acid .....	11
5. Experimental procedures for decarboxylative cross-coupling .....	12
Table S1. Optimization of the photoredox catalysts. ....	13
Table S2. Optimization of the metal catalysts. ....	14
Table S3. Optimization of the bases. ....	14
Scheme S1. Screening of aryl electrophiles. ....	15
Scheme S2. Extended substrate scope under the optimized conditions. ....	15
Scheme S3. Investigations on the SET mechanism of cross-coupling. ....	15
6. Reaction set-up .....	15
7. Characterization of cross-coupling products.....	16
8. Synthesis of mitochondrial complex 1 inhibitor (2).....	36
9. Synthesis of 4-(4-fluoropiperidin-4-yl)benzonitrile (17) .....	37
10. Characterization of additional cross-coupling products.....	38
11. Spectroscopic data ( $^1\text{H}$ , $^{13}\text{C}$ and $^{19}\text{F}$ NMR spectra) .....	42
12. DFT calculations.....	120
13. References .....	249

## 1. General information

All commercial reagents were used without additional purification, unless otherwise stated. Anhydrous solvent was purchased from commercial sources and transferred under an argon atmosphere. Solvents (acetonitrile, CH<sub>2</sub>Cl<sub>2</sub>, diethyl ether, DMSO, tetrahydrofuran and toluene) were purified under a positive pressure of dry nitrogen gas by a modified Innovative Technologies purification system. N,N-Dimethylacetamide (anhydrous), N,N-dimethylformamide (anhydrous) and 1,4-dioxane (anhydrous) were used as received. All purification procedures of products were carried out with reagent grade solvents. NMR spectra were recorded on Bruker 400 MHz and Bruker DPX 500 MHz spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance resulting from incomplete deuterium incorporation as the internal standard (CDCl<sub>3</sub>: δ 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), and coupling constants (Hz). <sup>13</sup>C NMR spectra were recorded on Bruker 400 MHz and Bruker DPX 500 MHz spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl<sub>3</sub>: δ 77.16 ppm). <sup>19</sup>F NMR spectra were recorded on Bruker 400 MHz spectrometer with complete proton decoupling or proton coupling. High-resolution mass spectrometric data were obtained using Agilent 7200 Q-TOF and Bruker MicroTOF-Q<sup>II</sup>. GC-MS analysis was performed on Shimadzu GCMS-QP2020 gas chromatography coupled to a Shimadzu QP2010 mass selective detector. Column chromatography purification conditions are reported in the experimental section below. Diastereomeric ratios of products were determined by GC (GC-QP2030) and <sup>1</sup>H NMR analyses.

## 2. General procedures for the preparation of α-fluoro acids

### General procedure 1 (GP 1):

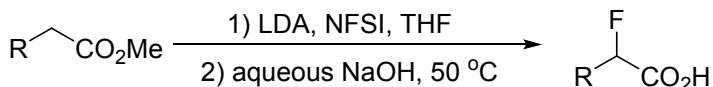


Modified procedure for the preparation of 2-aryl-2-fluoroacetic acid according to the reported literature.<sup>1</sup> To a solution of 2-arylacetic acid (1.0 equiv.) and TBSCl (2.3 equiv.) in THF was added dropwise LiHMDS (2.2 equiv.) under argon at 0 °C. The resulting mixture was warmed up to room temperature and allowed to stir until the completion of the reaction (determined by TLC analysis). The solvent was removed *in vacuo*, then the mixture was diluted by hexane and filtered. After that, the solution was concentrated to obtain the crude product, which was used directly in the next step.

To a solution of Selectfluor® (2.2 equiv.) in CH<sub>3</sub>CN was slowly added a solution of the above product in CH<sub>3</sub>CN at 0 °C. The resulting mixture was warmed up to room temperature and allowed to stir until the completion of the reaction (determined

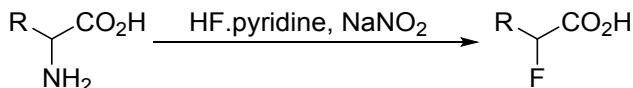
by TLC analysis). After that, the mixture was acidified to pH = 4.0 by 1 N HCl and extracted using Et<sub>2</sub>O for two times. The organic layer was collected and neutralized by 0.5 N NaOH to pH = 10. Then the mixture was extracted with 0.5 N NaOH for two times. The collected aqueous layers were acidified by 3.0 N HCl, and extracted with Et<sub>2</sub>O for two times. The combined organic layers were dried by Na<sub>2</sub>SO<sub>4</sub>, concentrated and purified by flash column chromatography.

### General procedure 2 (GP 2):



Modified procedure for the preparation of 2-aryl-2-fluoroacetic acid according to the reported literature.<sup>2</sup> To a solution of the ester (1.0 equiv.) in THF was added dropwise LDA (2.0 M in THF, 1.2 equiv.) under argon at -78 °C, and the mixture was allowed to stir for 30 min. Then a solution of NFSI (1.5 equiv.) in THF was slowly added to the reaction system under Ar. The resulting mixture was warmed up to room temperature and allowed to stir until the completion of the reaction (determined by TLC analysis). The mixture was concentrated *in vacuo*, diluted by hexane and filtered through a pad of silica gel. After that, the mixture was concentrated and 0.5 N NaOH was added. After ester hydrolysis was completed, the mixture was acidified by 1 N HCl. The mixture was extracted with E<sub>2</sub>O for three times, and the combined organic layers were dried by Na<sub>2</sub>SO and concentrated. The crude product was purified by flash column chromatography.

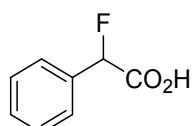
### General procedure 3 (GP 3):



Modified procedure for the preparation of  $\alpha$ -fluoro acid according to the reported literature.<sup>3</sup> Sodium nitrite was first dried in an oven at 120 °C for 48 h. The amino acid (1.0 equiv.) was first dissolved in hydrogen fluoride-pyridine, then sodium nitrite (3.0 equiv.) was added to the solution at -10 °C. The mixture was warmed up to room temperature and allowed to stir for 3 h. The reaction was quenched with water and the resulting mixture was adjusted to pH = 4.0. After extracting with CH<sub>2</sub>Cl<sub>2</sub> for three times, the combined organic layers were dried and concentrated *in vacuo*. The crude product was purified by flash column chromatography.

## 3. Characterization of $\alpha$ -fluoroacids

### 2-fluoro-2-phenylacetic acid



The title compound was commercially available and could be synthesized by the

procedure GP1 using 2-phenylacetic acid (6.8g, 50 mmol), LiHMDS (120 mL, 120 mmol), TBSCl (15.0g, 0.1 mmol) and Selectfluor® (21.24g, 60 mmol). The desired compound was isolated as a white solid.

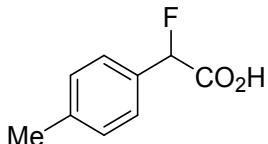
White solid; 95% yield (7.3 g).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 9.01 (br, 1H), 7.49-7.47 (m, 2H), 7.44-7.26 (m, 3H), 5.88-5.76 (d, *J* = 48 Hz, 1H).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -180.83.

The physical data were identical in all respects to those previously reported.<sup>1</sup>

### 2-fluoro-2-(p-tolyl)acetic acid



The title compound was synthesized by the procedure GP1 using 2-(4-chlorophenyl)acetic acid (1.5g, 10 mmol), LiHMDS (24 mL, 24 mmol), TBSCl (3.0g, 20 mmol) and Selectfluor® (3.54g, 10 mmol). The desired compound was isolated as a white solid

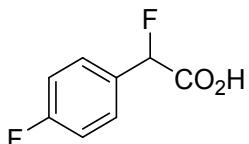
White solid; 77% yield (1.29 g).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 13.51 (br, 1H), 7.38-7.25 (m, 4H), 5.95-5.83 (d, *J* = 48 Hz, 1H), 2.35 (s, 3H).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -178.32.

The physical data were identical in all respects to those previously reported.<sup>4</sup>

### 2-fluoro-2-(4-fluorophenyl)acetic acid



The title compound was synthesized by the procedure GP1 using 2-(4-fluorophenyl)acetic acid (1.54g, 10 mmol), LiHMDS (24 mL, 24 mmol), TBSCl (3.0g, 20 mmol) and Selectfluor® (3.54g, 10 mmol). The desired compound was isolated as a white solid.

White solid; 80% yield ((1.37 g).

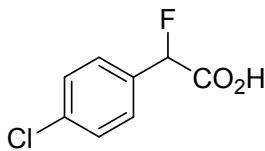
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.49-7.45 (dd, *J* = 8 Hz, *J* = 4 Hz, 2H), 7.13-7.09 (dd, *J* = 8 Hz, *J* = 4 Hz, 2H), 5.86-5.74 (d, *J* = 48 Hz, 1H), 4.87 (br, 1H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 172.73-172.45 (d, *J*<sub>C-F</sub> = 28 Hz), 164.87-164.85 (d, *J*<sub>C-F</sub> = 2 Hz), 128.84-128.78 (d, *J*<sub>C-F</sub> = 6 Hz), 128.76-128.70 (d, *J*<sub>C-F</sub> = 6 Hz), 116.15-115.93 (d, *J*<sub>C-F</sub> = 22 Hz), 89.12-87.26 (d, *J*<sub>C-F</sub> = 186 Hz).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -110.74, -179.08.

**HRMS (ESI) m/z** calcd for C<sub>8</sub>H<sub>6</sub>F<sub>2</sub>NaO<sub>2</sub> [(M+Na)<sup>+</sup>]: 195.0234, found: 195.0243.

### 2-(4-chlorophenyl)-2-fluoroacetic acid



The title compound was synthesized by the procedure GP1 using 2-(4-chlorophenyl)acetic acid (1.7g, 10 mmol), LiHMDS (24 mL, 24 mmol), TBSCl (3.0g, 20 mmol) and Selectfluor® (3.54g, 10 mmol). The desired compound was isolated as a white solid.

White solid; 86% yield (1.61 g).

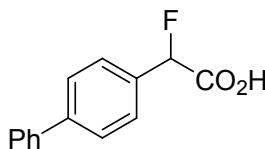
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 9.09 (s, 1H), 7.44-7.41 (d, *J* = 8 Hz, 2H), 7.40-7.38 (d, *J* = 8 Hz, 2H), 5.95 (d, *J* = 48 Hz, 1H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 173.81-173.53 (d, *J*<sub>C-F</sub> = 28 Hz), 136.12-136.10 (d, *J*<sub>C-F</sub> = 2 Hz), 131.98-131.77 (d, *J*<sub>C-F</sub> = 21 Hz), 129.21, 128.00-127.95 (d, *J*<sub>C-F</sub> = 6 Hz), 89.02-87.15 (d, *J*<sub>C-F</sub> = 186 Hz).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -181.78.

**HRMS (ESI) m/z** calcd for C<sub>8</sub>H<sub>6</sub>ClFNaO<sub>2</sub> [(M+Na)<sup>+</sup>]: 210.9938, found: 210.9931.

### 2-([1,1'-biphenyl]-4-yl)-2-fluoroacetic acid



The title compound was synthesized by the procedure GP1 using 2-([1,1'-biphenyl]-4-yl)acetic acid (2.12g, 10 mmol), LiHMDS (24 mL, 24 mmol), TBSCl (3.0g, 20 mmol) and Selectfluor® (3.54g, 10 mmol). The desired compound was isolated as a white solid.

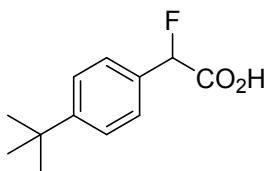
White solid; 90% yield (2.1 g).

**<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)** δ 13.56 (br, 1H), 7.74-7.72 (d, *J* = 8 Hz, 2H), 7.69-7.67 (d, *J* = 8 Hz, 2H), 7.54-7.52 (d, *J* = 8 Hz, 2H), 7.50-7.46 (t, *J* = 8 Hz, 2H), 7.41-7.37 (t, *J* = 8 Hz, 2H), 6.10-5.98 (d, *J* = 48 Hz, 1H).

**<sup>19</sup>F NMR (376 MHz, DMSO-d<sub>6</sub>)** δ -175.62.

The physical data were identical in all respects to those previously reported.<sup>4</sup>

### 2-(4-(tert-butyl)phenyl)-2-fluoroacetic acid



The title compound was synthesized by the procedure GP1 using 2-(4-(tert-butyl)phenyl)acetic acid (1.92g, 10 mmol), LiHMDS (24 mL, 24 mmol), TBSCl (3.0g, 20 mmol) and Selectfluor® (3.54g, 10 mmol). The desired compound (1.53g, 73% yield) was isolated as a white solid.

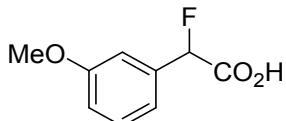
White solid; 73% yield (1.53 g).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.45-7.43 (d, *J* = 8 Hz, 2H), 7.42-7.40 (d, *J* = 8 Hz, 2H), 5.97 (br, 1H), 5.85-5.73 (d, *J* = 48 Hz, 1H), 1.32 (s, 9H).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -178.95.

The physical data were identical in all respects to those previously reported.<sup>4</sup>

### 2-fluoro-2-(3-methoxyphenyl)acetic acid



The title compound was synthesized by the procedure GP1 using 2-(3-methoxyphenyl)acetic acid (1.66g, 10 mmol), LiHMDS (24 mL, 24 mmol), TBSCl (3.0g, 20 mmol) and Selectfluor® (3.54g, 10 mmol). The desired compound was isolated as a white solid.

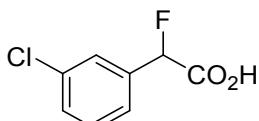
White solid; 86% yield (1.6 g).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 9.58 (s, 1H), 7.35-7.31 (t, *J* = 8 Hz, 1H), 7.07-7.05 (d, *J* = 8 Hz, 1H), 7.02 (s, 1H), 6.97-6.95 (d, *J* = 8 Hz, 1H), 5.85-5.73 (d, *J* = 48 Hz, 1H), 3.82 (s, 3H).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -181.23.

The physical data were identical in all respects to those previously reported.<sup>1</sup>

### 2-(3-chlorophenyl)-2-fluoroacetic acid



The title compound was synthesized by the procedure GP1 using 2-(3-chlorophenyl)acetic acid (1.7g, 10 mmol), LiHMDS (24 mL, 24 mmol), TBSCl (3.0g, 20 mmol) and Selectfluor® (3.54g, 10 mmol). The desired compound was isolated as a white solid.

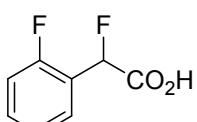
White solid; 76% yield (1.43 g).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.49 (s, 1H), 7.41 (br, 1H), 7.40-7.35 (m, 3H), 5.86-5.74 (d, *J* = 48 Hz, 1H).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -183.00.

The physical data were identical in all respects to those previously reported.<sup>5</sup>

### 2-fluoro-2-(2-fluorophenyl)acetic acid



The title compound was synthesized by the procedure GP1 using 2-(2-fluorophenyl)acetic acid (1.54g, 10 mmol), LiHMDS (24 mL, 24 mmol), TBSCl (3.0g, 20 mmol) and Selectfluor® (3.54g, 10 mmol). The desired compound was

isolated as a white solid.

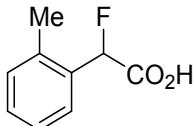
White solid; 75% yield (1.29 g).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.47-7.44 (t, *J* = 8 Hz, 1H), 7.42-7.37 (m, 1H), 7.22 (br, 1H), 7.20-7.16 (m, 1H), 7.13-7.08 (dt, *J* = 20 Hz, *J* = 8 Hz, 1H), 6.13-6.01 (d, *J* = 48 Hz, 1H).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -117.21, -180.68.

The physical data were identical in all respects to those previously reported.<sup>1</sup>

### 2-fluoro-2-(o-tolyl)acetic acid



The title compound was synthesized by the procedure GP1 using 2-fluoro-2-(o-tolyl)acetic acid (1.50 g, 10 mmol), LiHMDS (24 mL, 24 mmol), TBSCl (3.0g, 20 mmol) and Selectfluor® (3.54g, 10 mmol). The desired compound was isolated as a white solid.

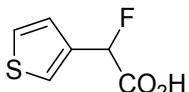
White solid; 70% yield (1.17 g).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.62 (br, 1H), 7.28-7.17 (m, 4H), 5.48 (d, *J* = 48 Hz, 1H), 2.27 (s, 3H).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -178.9.

The physical data were identical in all respects to those previously reported.<sup>1</sup>

### 2-fluoro-2-(thiophen-3-yl)acetic acid



The title compound was synthesized by the procedure GP1 using 2-(thiophen-3-yl)acetic acid (1.42g, 10 mmol), LiHMDS (24 mL, 24 mmol), TBSCl (3.0g, 20 mmol) and Selectfluor® (3.54g, 6 mmol). The desired compound was isolated as an off-white solid.

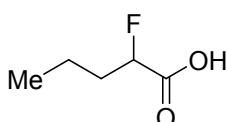
Off-white solid; 80% yield (1.28 g).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.72 (br, 1H), 7.52-7.50 (m, 1H), 7.39-7.37 (m, 1H), 7.20-7.19 (d, *J* = 4 Hz, 1H), 5.99-5.87 (d, *J* = 48 Hz, 1H).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -177.06.

The physical data were identical in all respects to those previously reported.<sup>1</sup>

### 2-fluoropentanoic acid



The title compound was synthesized by the procedure GP1 using pentanoic acid (1.02 g, 10 mmol), LiHMDS (24 mL, 24 mmol), TBSCl (3.0g, 20 mmol) and Selectfluor®

(3.54g, 6 mmol). The desired compound was isolated as a yellowish oil.

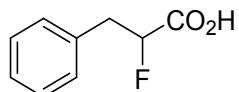
Yellowish oil; 47% yield (0.56 g).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.25 (br, 1H), 4.93-4.81 (dt, *J* = 47 Hz, *J* = 4 Hz, 1H), 1.77-1.61 (m, 2H), 1.41-1.24 (m, 2H), 0.95-0.91 (t, *J* = 8 Hz, 3H).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -192.21.

The physical data were identical in all respects to those previously reported.<sup>6</sup>

### 2-fluoro-3-phenylpropanoic acid



The title compound was synthesized by the procedure GP2 using methyl 3-phenylpropanoate (1.64 g, 10 mmol), LDA (6 mL, 12 mmol, 2.0 M in THF) and NFSI (4.73 g, 15 mmol). The desired compound was isolated as a colorless oil.

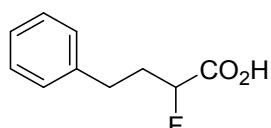
Colorless oil; 66% yield (1.11 g).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.35-7.32 (m, 2H), 7.30-7.26 (m, 3H), 5.57 (br, 1H), 5.22-5.10 (dt, *J* = 48 Hz, *J* = 4 Hz, 1H), 3.34-3.14 (m, 2H).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -190.18.

The physical data were identical in all respects to those previously reported.<sup>7</sup>

### 2-fluoro-4-phenylbutanoic acid



The title compound was synthesized by the procedure GP2 using methyl 4-phenylbutanoate (1.78 g, 10 mmol), LDA (6 mL, 12 mmol, 2.0 M in THF) and NFSI (4.73 g, 15 mmol). The desired compound was isolated as a colorless oil.

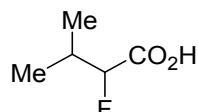
Colorless oil; 51% yield (0.92 g)

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.26 (br, 1H), 7.34-7.29 (m, 2H), 7.28-7.22 (m, 3H), 4.97-4.80 (dt, *J* = 48 Hz, *J* = 6 Hz, 1H), 2.93-2.80 (m, 2H), 2.34-2.22 (m, 2H).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -192.13.

The physical data were identical in all respects to those previously reported.<sup>8</sup>

### 2-fluoro-3-methylbutanoic acid



The title compound was synthesized by the procedure GP3 using valine (1.17 g, 10 mmol) and NaNO<sub>2</sub> (2.07 g, 30 mmol). The desired compound was isolated as a colorless oil.

Colorless oil, 46% yield (0.55 g)

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.55 (br, 1H), 4.77-4.65 (dd, *J* = 42 Hz, *J* = 4 Hz, 1H), 2.28-2.18 (m, 1H), 0.96 (d, *J* = 6 Hz, 6H).

**$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$**  -191.34.

The physical data were identical in all respects to those previously reported.<sup>9</sup>

### 1-fluorocyclohexane-1-carboxylic acid



The title compound was synthesized by the procedure GP1 using cyclohexanecarboxylic acid (1.28g, 10 mmol), LiHMDS (24 mL, 24 mmol), TBSCl (3.0g, 20 mmol) and Selectfluor® (3.54g, 6 mmol). The desired compound was isolated as a white solid.

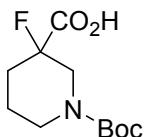
White solid; 82% yield (1.05 g).

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$**  10.72 (br, 1H), 2.02-1.96 (m, 2H), 1.92-1.78 (m, 2H), 1.76-1.57 (m, 5H), 1.37-1.27 (m, 1H).

**$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$**  -165.44.

The physical data were identical in all respects to those previously reported.<sup>10</sup>

### 1-(*tert*-butoxycarbonyl)-3-fluoropiperidine-3-carboxylic acid



The title compound was commercially available and could be synthesized by the procedure GP1 using 1-(*tert*-butoxycarbonyl)piperidine-3-carboxylic acid (2.29g, 10 mmol), LiHMDS (24 mL, 24 mmol), TBSCl (3.0g, 20 mmol) and Selectfluor® (3.54g, 6 mmol). The desired compound was isolated as a white solid.

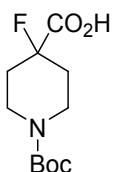
White solid; 57% yield (1.40 g).

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$**  8.21 (br, 1H), 4.23-4.10 (br, 2H), 3.34-3.28 (br, 1H), 2.86 (br, 1H), 2.16-2.03 (m, 1H), 2.01-1.91 (m, 1H), 1.84-1.78 (m, 1H), 1.67-1.61 (m, 1H), 1.45 (s, 9H).

**$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$**  -168.31.

The physical data were identical in all respects to those previously reported.<sup>11</sup>

### 1-(*tert*-butoxycarbonyl)-4-fluoropiperidine-4-carboxylic acid



The title compound was commercially available and could be synthesized by the procedure GP1 using 1-(*tert*-butoxycarbonyl)-4-fluoropiperidine-4-carboxylic acid (2.29g, 10 mmol), LiHMDS (24 mL, 24 mmol), TBSCl (3.0g, 20 mmol) and Selectfluor® (3.54g, 6 mmol). The desired compound was isolated as a white solid.

White solid; 60% yield (1.50 g).

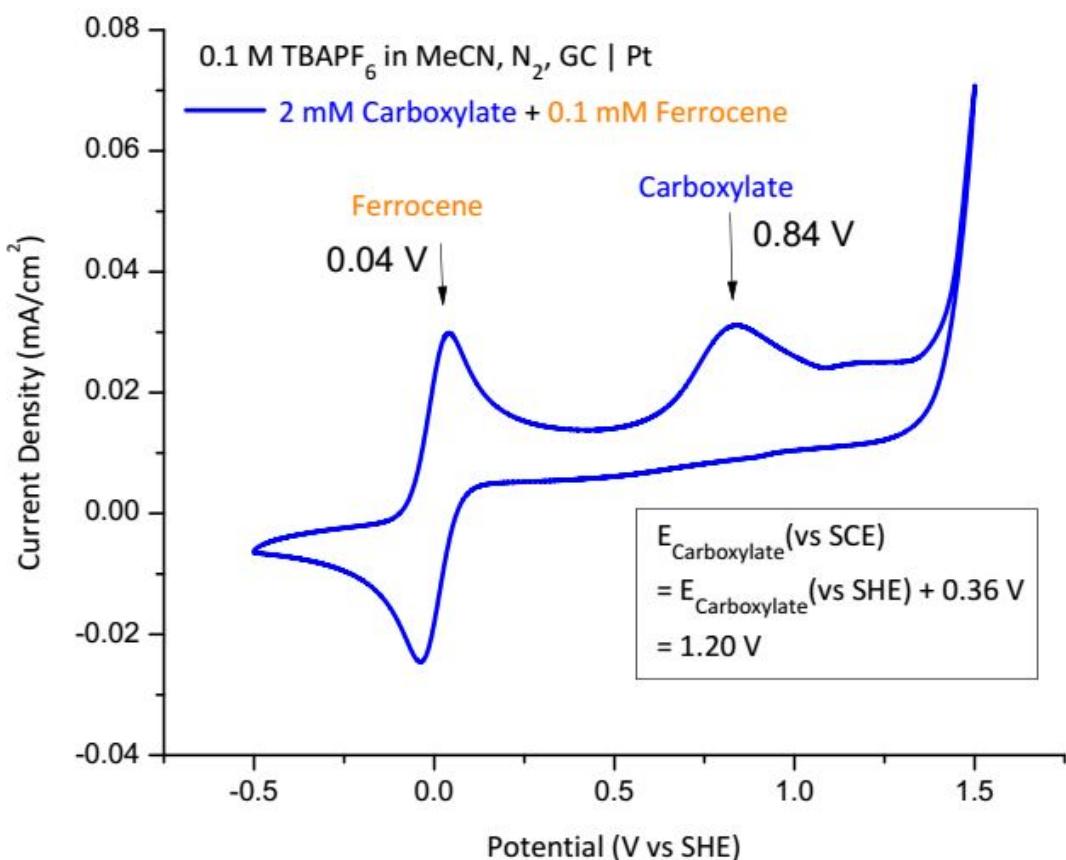
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.25 (br, 1H), 4.04 (br, 2H), 3.14-3.09 (br, 2H), 2.14-2.05 (m, 1H), 2.03-1.93 (m, 3H), 1.47 (s, 9H).

**$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )**  $\delta$  -168.36.

The physical data were identical in all respects to those previously reported.<sup>12</sup>

#### 4. Cyclic voltammogram of 2-fluoro-2-phenylacetic acid

The electrochemical measurements was performed according to the reported method.<sup>13</sup> The electrochemical measurements were carried out by a computer controlled electrochemical analyzer. Electrochemical measurements (cyclic voltammetry) were performed in a three-electrode cell (volume 10 mL; acetonitrile as solvent,  $\text{nBu}_4\text{N}^+\text{ClO}_4^-$  0.1 M as the supporting electrolyte, 2 mM concentration of the tested compound) with glassy carbon (diameter 3 mm) as the working electrode, Pt wire as the auxiliary electrode, and Ag/AgCl (3 M NaCl) as the reference electrode. The scan speed was 100 mV s<sup>-1</sup>. The potential ranges investigated for oxidations were 0 to +2.0 V vs Ag/AgCl (3 M NaCl). In contrast, for reduction processes the range 0 to -2.0 V vs Ag/AgCl (3 M NaCl) has been explored. The potentials measured were then referred to SCE by applying the equation  $E_{\text{Carboxylate}}(\text{vs SCE}) = E_{\text{Carboxylate}}(\text{vs SHE}) + 0.36 \text{ V}$ .



## **5. Experimental procedures for decarboxylative cross-coupling**

### **General Procedure 4 (GP 4) in glovebox:**

In a N<sub>2</sub>-filled glovebox, NiBr<sub>2</sub>·DME (0.6 mg, 2 mol%), 4,4'-dimethoxy-2,2'-bipyridine (0.4 mg, 2 mol%), and anhydrous dimethylacetamide (DMA, 1.0 mL) were added into a 2.5 mL vial with a stir bar. Then the corresponding α-fluoro acid (0.2 mmol), the electrophile (0.1 mmol), KOTf (1.0 equiv.) and Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)(PF<sub>6</sub>) (1.1 mg, 1 mol%) were added into the mixture. After that, 1,1,3,3-tetramethylguanidine (TMG, 2.0 equiv.) was added. The vial was sealed with a teflon-lined septum cap, transferred out of the glovebox, and the reaction mixture was allowed to stir vigorously under blue LED irradiation. The reaction time was 36 h unless otherwise noted. When the reaction was completed, the mixture was transferred to a 50 mL separatory funnel, diluted with ethyl acetate, and washed with deionized water (twice). The organic phase was concentrated *in vacuo* and purified by chromatography.

### **General Procedure 5 (GP 5) in glovebox:**

In a N<sub>2</sub>-filled glovebox, NiBr<sub>2</sub>·DME (0.6 mg, 2 mol%), 4,4'-dimethoxy-2,2'-bipyridine (0.4 mg, 2 mol%), and anhydrous dimethylacetamide (DMA, 1.0 mL) were added into a 2.5 mL vial with a stir bar. Then the corresponding α-fluoro acid (0.2 mmol), the electrophile (0.1 mmol), and Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)(PF<sub>6</sub>) (1.1 mg, 1 mol%) were added into the mixture. After that, 1,1,3,3-tetramethylguanidine (TMG, 2.0 equiv.) was added. The vial was sealed with a teflon-lined septum cap, transferred out of the glovebox, and the reaction mixture was allowed to stir vigorously under blue LED irradiation. The reaction time was 36 h unless otherwise noted. When the reaction was completed, the mixture was transferred to a 50 mL separatory funnel, diluted with ethyl acetate, and washed with deionized water (twice). The organic phase was concentrated *in vacuo* and purified by chromatography.

### **General Procedure 6 (GP 6) in glovebox:**

In a N<sub>2</sub>-filled glovebox, NiBr<sub>2</sub>·DME (2.2 mg, 10 mol%), 4,4'-dimethoxy-2,2'-bipyridine (2.6 mg, 12 mol%), and anhydrous dimethylacetamide (DMA, 1.0 mL) were added into a 2.5 mL vial with a stir bar. Then the corresponding α-fluoro acid (0.2 mmol), the electrophile (0.1 mmol), and Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)(PF<sub>6</sub>) (1.1 mg, 1 mol%) were added into the mixture. After that, 1,1,3,3-tetramethylguanidine (TMG, 2.0 equiv.) was added. The vial was sealed with a teflon-lined septum cap, transferred out of the glovebox, and the reaction mixture was allowed to stir vigorously under blue LED irradiation. The reaction time was 36 h unless otherwise noted. When the reaction was completed, the mixture was transferred to a 50 mL separatory funnel, diluted with ethyl acetate, and washed with deionized water (twice). The organic phase was concentrated *in vacuo* and purified by chromatography.

### **General Procedure 7 (GP 7) in glovebox:**

In a  $\text{N}_2$ -filled glovebox,  $\text{NiCl}_2\cdot\text{DME}$  (3.3 mg, 15 mol%), 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.4 mg, 20 mol%), and anhydrous dimethylacetamide (DMA, 1.0 mL) were added into a 2.5 mL vial with a stir bar. Then the corresponding  $\alpha$ -fluoro acid (0.2 mmol), the electrophile (0.1 mmol), and  $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})(\text{PF}_6)$  (1.1 mg, 1 mol%) were added into the mixture. After that, 1,1,3,3-tetramethylguanidine (TMG, 2.0 equiv.) was added. The vial was sealed with a teflon-lined septum cap, transferred out of the glovebox, and the reaction mixture was allowed to stir vigorously under blue LED irradiation. The reaction time was 36 h unless otherwise noted. When the reaction was completed, the mixture was transferred to a 50 mL separatory funnel, diluted with ethyl acetate, and washed with deionized water (twice). The organic phase was concentrated *in vacuo* and purified by chromatography.

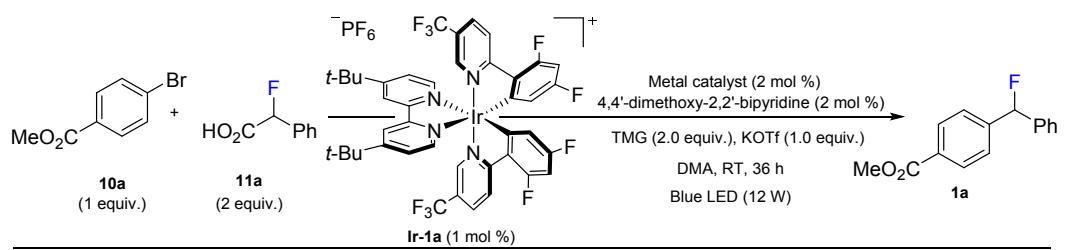
**Table S1. Optimization of the photoredox catalysts.<sup>a</sup>**

The reaction scheme shows the conversion of compound **10a** (1 equiv.) and **11a** (2 equiv.) in the presence of Photoredox catalyst (1 mol%),  $\text{NiBr}_2\cdot\text{DME}$  (2 mol %), 4,4'-dimethoxy-2,2'-bipyridine (2 mol %), TMG (2.0 equiv.),  $\text{KOTf}$  (1.0 equiv.), DMA, at room temperature (RT) under Blue LED (12 W) irradiation to yield product **1a**.

		Photoredox catalyst (1 mol%)				
		$\text{NiBr}_2\cdot\text{DME}$ (2 mol %)				
		4,4'-dimethoxy-2,2'-bipyridine (2 mol %)				
		TMG (2.0 equiv.), $\text{KOTf}$ (1.0 equiv.)				
		DMA, RT, 36 h				
		Blue LED (12 W)				
<b>10a</b> (1 equiv.)	<b>11a</b> (2 equiv.)	<b>1a</b>				
<b>Photocatalyst:</b>						
2CzIPN + 1.36 V - 1.51 V trace	4CzIPN + 1.35 V - 1.21 V 50% yield	4CzTPN + 1.41 V - 1.02 V no reaction	4DPAPIPN + 1.10 V - 1.52 V 15% yield	5CzBN + 1.41 V - 1.52 V trace	A:  B: 	
+ 1.30 V - 1.07 V no reaction	+ 1.32 V - 1.37 V 72% yield	+ 1.21 V - 1.37 V 86% yield				

<sup>a</sup>All reactions were carried out with **10a** (0.10 mmol) and **11a** (0.20 mmol) using photoredox catalyst (1 mol%) and  $\text{NiBr}_2\cdot\text{DME}$  (2 mol%) according to the General Procedure 4 (GP 4). The yields were isolated yields.

**Table S2. Optimization of the metal catalysts.<sup>a</sup>**

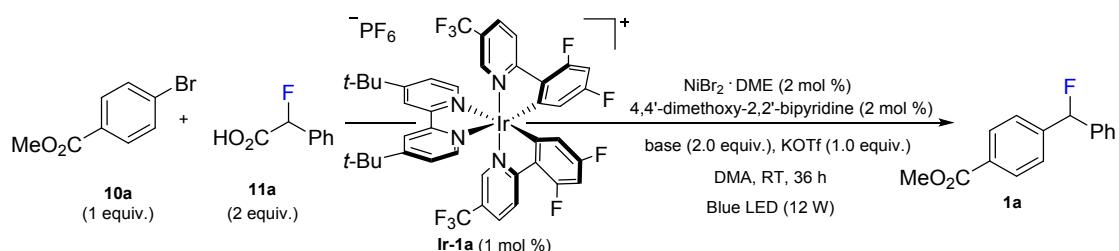


**Metal catalysts:**

Ni(TMHD) <sub>2</sub>	Ni(acac) <sub>2</sub>	Ni(cod) <sub>2</sub>	Ni(OTf) <sub>2</sub>	NiBr <sub>2</sub> · DME	NiCl <sub>2</sub> · DME	NiBr <sub>2</sub> · diglyme
trace	trace	75% yield	trace	86% yield	70% yield	78% yield

<sup>a</sup>All reactions were carried out with **10a** (0.10 mmol) and **11a** (0.20 mmol) using  $[\text{Ir}\{\text{dFCF}_3\text{ppy}\}_2(\text{bpy})]\text{PF}_6$  (1 mol%) and metal catalyst (2 mol%) according to the General Procedure 4 (GP 4). The yields were isolated yields.

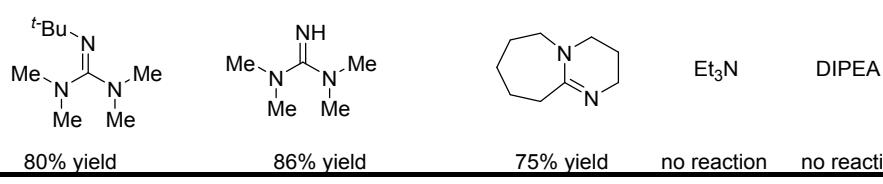
**Table S3. Optimization of the bases.<sup>a</sup>**



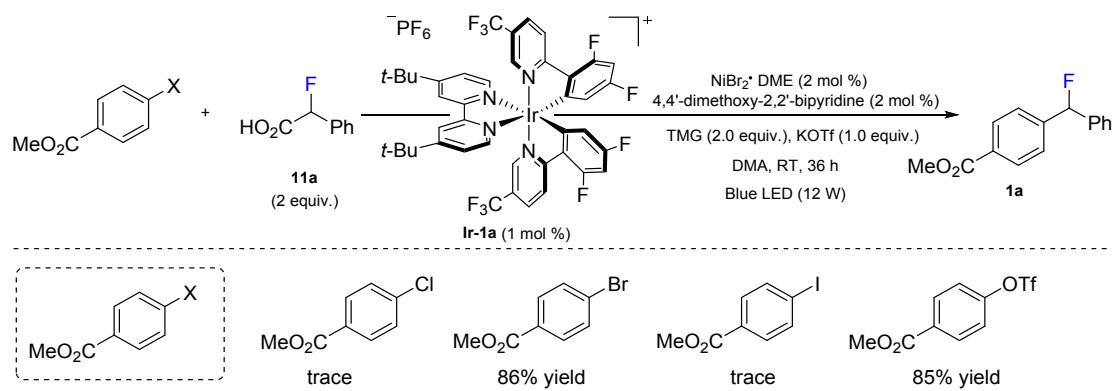
**Inorganic bases:**

Na <sub>2</sub> CO <sub>3</sub>	K <sub>2</sub> CO <sub>3</sub>	Cs <sub>2</sub> CO <sub>3</sub>	K <sub>3</sub> PO <sub>4</sub>	t-BuOK	MeOK	LiOH	NaOH	KOH
trace	55% yield	50% yield	trace	trace	trace	trace	trace	trace

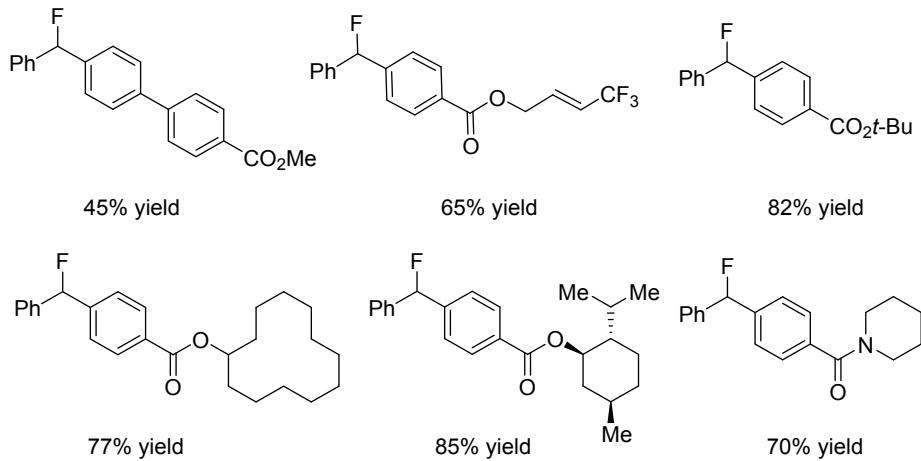
**Organic bases:**



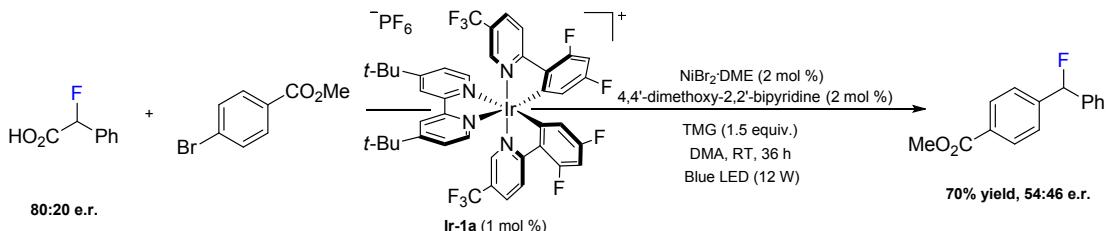
<sup>a</sup>All reactions were carried out with **10a** (0.10 mmol) and **11a** (0.20 mmol) using  $[\text{Ir}\{\text{dFCF}_3\text{ppy}\}_2(\text{bpy})]\text{PF}_6$  (1 mol%) and NiBr<sub>2</sub> · DME (2 mol%) according to the General Procedure 4 (GP 4). The yields were isolated yields.



**Scheme S1. Screening of aryl electrophiles.**



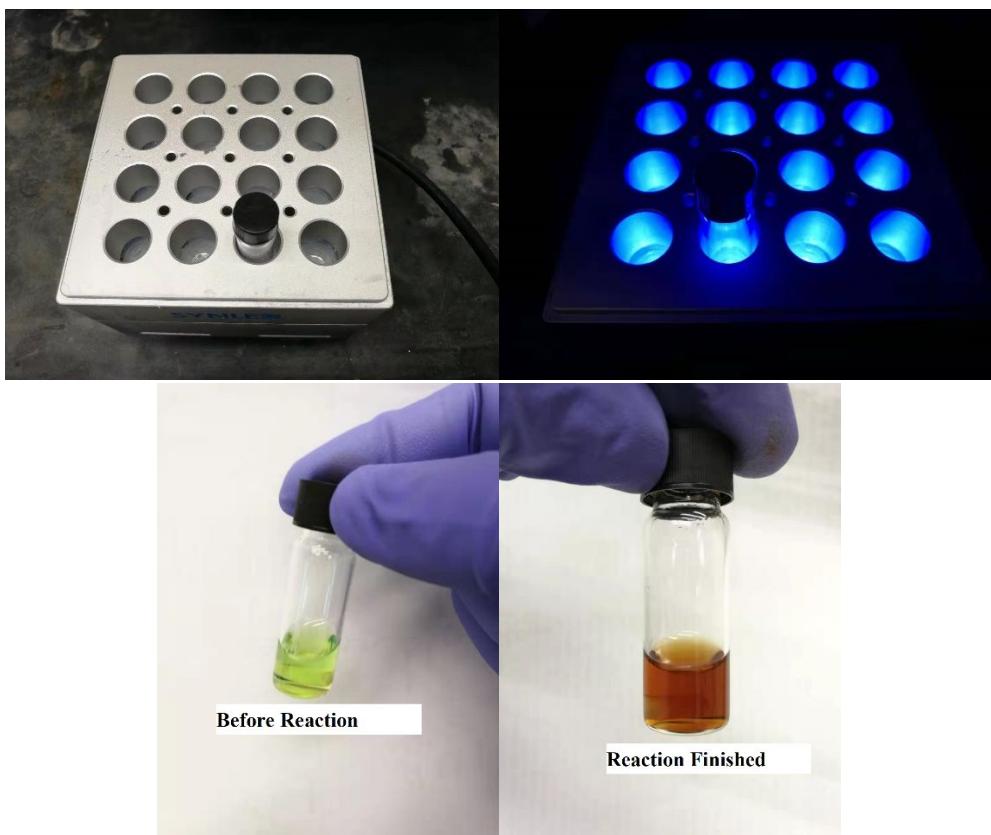
**Scheme S2.** Extended substrate scope under the optimized conditions.



**Scheme S3. Investigations on the SET mechanism of cross-coupling.**

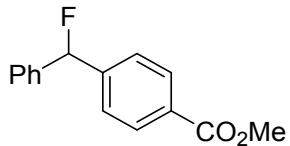
## 6. Reaction set-up

The photoredox reactor was purchased from Shenzhen Bamboo Bio-tech Co. LTD. INPUT: AC100-240 V 50/60 Hz; OUTPUT: 12 W; Wavelength (blue LED): 460-470 nm.



## 7. Characterization of cross-coupling products

### methyl 4-(fluoro(phenyl)methyl)benzoate (1a)



The title compound was synthesized according to the General Procedure 4, using methyl 4-bromobenzoate (21 mg, 0.1 mmol) and 2-fluoro-2-phenylacetic acid (31 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane. Colorless oil; 86% yield (21 mg).

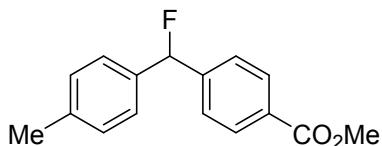
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.082-8.066 (d, *J* = 8 Hz, 2H), 7.463-7.447 (d, *J* = 8 Hz, 2H), 7.412-7.349 (m, 5H), 6.578-6.484 (d, *J* = 47 Hz, 1H), 3.946 (s, 1H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 166.70, 144.81-144.63 (d, *J*<sub>C-F</sub> = 22 Hz), 139.19-139.03 (d, *J*<sub>C-F</sub> = 20 Hz), 130.10, 129.81, 128.85, 128.68, 126.83-126.79 (d, *J*<sub>C-F</sub> = 5 Hz), 126.20-126.15 (d, *J*<sub>C-F</sub> = 6 Hz), 94.67-93.28 (d, *J*<sub>C-F</sub> = 173 Hz), 52.17.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -168.59.

**HRMS (EI) m/z** calcd for C<sub>15</sub>H<sub>13</sub>FO<sub>2</sub>: 244.0900, found: 244.0884.

### methyl 4-(fluoro(p-tolyl)methyl)benzoate (1b)



The title compound was synthesized according to the General Procedure 4, using methyl 4-bromobenzoate (21 mg, 0.1 mmol) and 2-fluoro-2-(*p*-tolyl)acetic acid (34 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

Colorless oil; 64% yield (17 mg).

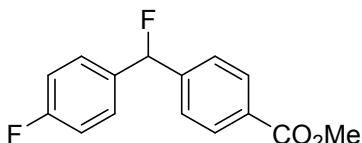
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.074-8.057 (d, *J* = 8 Hz, 2H), 7.455-7.437 (d, *J* = 8 Hz, 2H), 7.248-7.201 (m, 4H), 6.547-6.452 (d, *J* = 47 Hz, 1H), 3.944 (s, 3H), 2.381 (s, 3H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 166.74, 144.94, 138.84, 136.19, 129.97, 129.76, 129.35, 126.98-126.94 (d, *J*<sub>C-F</sub> = 6 Hz), 126.08-126.03 (d, *J*<sub>C-F</sub> = 6 Hz), 94.63-93.25 (d, *J*<sub>C-F</sub> = 173 Hz), 52.16, 21.19.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -169.16.

**HRMS (EI) m/z** calcd for C<sub>16</sub>H<sub>15</sub>FO<sub>2</sub>: 258.1056, found: 258.1049.

### methyl 4-(fluoro(4-fluorophenyl)methyl)benzoate (1c)



The title compound was synthesized according to the General Procedure 4, using methyl 4-bromobenzoate (21 mg, 0.1 mmol) and 2-fluoro-2-(4-fluorophenyl)acetic acid (34 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

Colorless oil; 76% yield (20 mg).

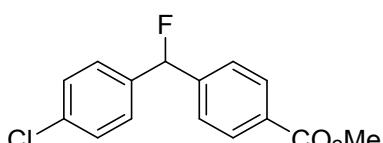
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.059-8.043 (d, *J* = 8 Hz, 2H), 7.411-7.395 (d, *J* = 8 Hz, 2H), 7.314-7.286 (m, 2H), 7.083-7.048 (t, *J* = 8 Hz, 2H), 6.534-6.439 (d, *J* = 47 Hz, 1H), 3.920 (s, 3H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 166.64, 144.52-144.33 (d, *J*<sub>C-F</sub> = 22 Hz), 135.07-134.93 (d, *J*<sub>C-F</sub> = 17 Hz), 130.24, 129.86, 128.95, 126.09, 115.78, 94.02-92.64 (d, *J*<sub>C-F</sub> = 173 Hz), 52.22

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -116.36, -174.00.

**HRMS (EI) m/z** calcd for C<sub>15</sub>H<sub>12</sub>F<sub>2</sub>O<sub>2</sub>: 262.0805, found: 265.0801.

### methyl 4-((4-chlorophenyl)fluoromethyl)benzoate (1d)



The title compound was synthesized according to the General Procedure 4, using methyl 4-bromobenzoate (21 mg, 0.1 mmol) and 2-(4-chlorophenyl)-2-fluoroacetic acid (37 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

Colorless oil; 73% yield (20 mg).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.059-8.042 (d, *J* = 8 Hz, 2H), 7.406-7.391 (d, *J* = 8

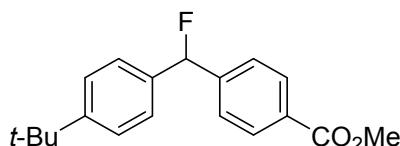
Hz, 2H), 7.363-7.347 (d,  $J$  = 8 Hz, 2H), 7.268-7.260 (d,  $J$  = 4 Hz, 2H), 7.260-7.252 (d,  $J$  = 4 Hz, 2H), 6.519-6.424 (d,  $J$  = 47 Hz, 1H), 3.921 (s, 3H).

**$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )**  $\delta$  166.58, 144.22-144.04 (d,  $J_{\text{C}-\text{F}}$  = 22 Hz), 137.71-137.53 (d,  $J_{\text{C}-\text{F}}$  = 22 Hz), 134.85, 130.37, 129.91, 128.92, 128.19-128.14 (d,  $J_{\text{C}-\text{F}}$  = 6 Hz), 126.19-126.14 (d,  $J_{\text{C}-\text{F}}$  = 6 Hz), 93.96-92.57 (d,  $J_{\text{C}-\text{F}}$  = 174 Hz), 52.22.

**$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )**  $\delta$  -169.65.

**HRMS (EI) m/z** calcd for  $\text{C}_{15}\text{H}_{12}\text{ClFO}_2$ : 278.0510, found: 278.0501.

#### methyl 4-((4-(tert-butyl)phenyl)fluoromethyl)benzoate (1e)



The title compound was synthesized according to the General Procedure 4, using methyl 4-bromobenzoate (21 mg, 0.1 mmol) and 2-([1,1'-biphenyl]-4-yl)-2-fluoroacetic acid (42 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

White solid; 76% yield (22 mg).

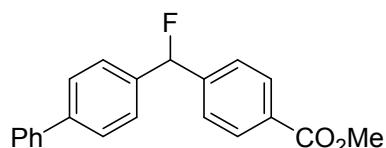
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**  $\delta$  8.05-8.03 (d,  $J$  = 8 Hz, 2H), 7.44-7.42 (d,  $J$  = 8 Hz, 2H), 7.40-7.38 (d,  $J$  = 8 Hz, 2H), 7.26-7.24 (d,  $J$  = 8 Hz, 2H), 6.54-6.42 (d,  $J$  = 48 Hz, 1H), 3.91 (s, 3H), 1.31 (s, 9H).

**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )**  $\delta$  166.75, 152.03-152.00 (d,  $J_{\text{C}-\text{F}}$  = 3 Hz), 145.03-144.81 (d,  $J_{\text{C}-\text{F}}$  = 102 Hz), 136.19-135.98 (d,  $J_{\text{C}-\text{F}}$  = 21 Hz), 129.97, 129.76, 126.77-126.72 (d,  $J_{\text{C}-\text{F}}$  = 5 Hz), 126.11-126.04 (d,  $J_{\text{C}-\text{F}}$  = 7 Hz), 125.62, 94.78-93.06 (d,  $J_{\text{C}-\text{F}}$  = 172 Hz), 52.17, 34.66, 31.27.

**$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )**  $\delta$  -167.36.

**HRMS (EI) m/z** calcd for  $\text{C}_{19}\text{H}_{21}\text{FO}_2$ : 300.1526, found: 300.1521.

#### methyl 4-([1,1'-biphenyl]-4-ylfluoromethyl)benzoate (1f)



The title compound was synthesized according to the General Procedure 4, using methyl 4-bromobenzoate (21 mg, 0.1 mmol) and 2-([1,1'-biphenyl]-4-yl)-2-fluoroacetic acid (46 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

White solid; 72% yield (23 mg).

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**  $\delta$  8.08-8.06 (d,  $J$  = 8 Hz, 2H), 7.62-7.60 (d,  $J$  = 8 Hz, 2H), 7.59-7.57 (d,  $J$  = 8 Hz, 2H), 7.48-7.46 (d,  $J$  = 8 Hz, 2H), 7.46-7.34 (m, 5H), 6.62-6.50 (d,  $J$  = 48 Hz, 1H), 3.93 (s, 3H).

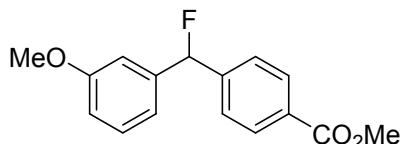
**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )**  $\delta$  166.71, 144.78-144.56 (d,  $J_{\text{C}-\text{F}}$  = 22 Hz), 141.86-141.84 (d,  $J_{\text{C}-\text{F}}$  = 2 Hz), 140.44, 138.15-137.94 (d,  $J_{\text{C}-\text{F}}$  = 21 Hz), 130.17, 129.88, 128.86, 127.64, 127.45, 127.36, 127.30-127.17 (d,  $J_{\text{C}-\text{F}}$  = 13 Hz),

126.23-126.16 (d,  $J_{C-F} = 7$  Hz), 94.70-92.97 (d,  $J_{C-F} = 173$  Hz), 52.21.

**$^{19}F$  NMR (376 MHz, CDCl<sub>3</sub>)**  $\delta$  -168.19.

**HRMS (EI) m/z** calcd for C<sub>21</sub>H<sub>17</sub>FO<sub>2</sub>: 320.1213, found: 320.1210.

### **methyl 4-(fluoro(3-methoxyphenyl)methyl)benzoate (1g)**



The title compound was synthesized according to the General Procedure 4, using methyl 4-bromobenzoate (21 mg, 0.1 mmol) and 2-fluoro-2-(3-methoxyphenyl)acetic acid (36 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

Colorless oil; 65% yield (17 mg).

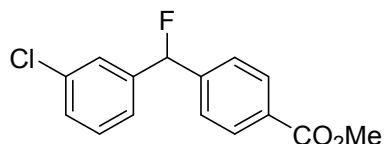
**$^1H$  NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  8.049-8.033 (d,  $J = 8$  Hz, 2H), 7.435-7.419 (d,  $J = 8$  Hz, 2H), 7.290-7.260 (t,  $J = 8$  Hz, 1H), 6.906-6.877 (m, 3H), 6.512-6.418 (d,  $J = 47$  Hz, 1H), 3.916 (s, 3H), 3.790 (s, 3H).

**$^{13}C$  NMR (125 MHz, CDCl<sub>3</sub>)**  $\delta$  166.70, 159.86, 144.68-144.51 (d,  $J_{C-F} = 21$  Hz), 140.70, 130.14, 129.81-129.76 (d,  $J_{C-F} = 6$  Hz), 126.34, 126.22-126.17 (d,  $J_{C-F} = 6$  Hz), 119.05-119.00 (d,  $J_{C-F} = 6$  Hz), 114.25, 112, 94.52-93.13 (d,  $J_{C-F} = 174$  Hz), 55.28, 52.17.

**$^{19}F$  NMR (376 MHz, CDCl<sub>3</sub>)**  $\delta$  -169.26.

**HRMS (EI) m/z** calcd for C<sub>16</sub>H<sub>15</sub>FO<sub>3</sub>: 274.1005, found: 274.1000.

### **methyl 4-((3-chlorophenyl)fluoromethyl)benzoate (1h)**



The title compound was synthesized according to the General Procedure 4, using methyl 4-bromobenzoate (21 mg, 0.1 mmol) and 2-(3-chlorophenyl)-2-fluoroacetic acid (37 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

Colorless oil; 73% yield (20 mg).

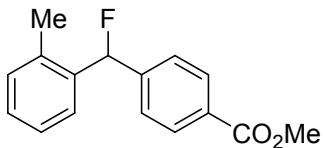
**$^1H$  NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  8.093-8.077 (d,  $J = 8$  Hz, 2H), 7.447-7.431 (d,  $J = 8$  Hz, 2H), 7.351-7.339 (br, 3H), 7.239-7.225 (m, 1H), 6.533-6.440 (d,  $J = 47$  Hz, 1H), 3.948 (s, 3H).

**$^{13}C$  NMR (125 MHz, CDCl<sub>3</sub>)**  $\delta$  166.59, 143.95-143.78 (d,  $J_{C-F} = 22$  Hz), 141.17-141.00 (d,  $J_{C-F} = 22$  Hz), 134.72, 130.44, 130.00, 129.96, 128.98, 126.80-126.75 (d,  $J_{C-F} = 6$  Hz), 126.27-126.22 (d,  $J_{C-F} = 6$  Hz), 124.79-124.74 (d,  $J_{C-F} = 6$  Hz), 93.88-92.48 (d,  $J_{C-F} = 175$  Hz), 52.25.

**$^{19}F$  NMR (376 MHz, CDCl<sub>3</sub>)**  $\delta$  -169.71

**HRMS (EI) m/z** calcd for C<sub>15</sub>H<sub>12</sub>ClFO<sub>2</sub>: 278.0510, found: 278.0503.

**methyl 4-(fluoro(o-tolyl)methyl)benzoate (1i)**



The title compound was synthesized according to the General Procedure 4, using methyl 4-bromobenzoate (21 mg, 0.1 mmol) and 2-fluoro-2-(o-tolyl)acetic acid (34 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

Colorless oil; 47% yield (12 mg).

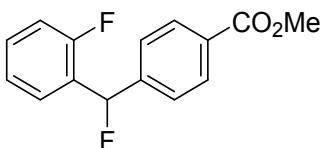
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.04-8.02 (d, *J* = 8 Hz, 2H), 7.39-7.37 (d, *J* = 8 Hz, 2H), 7.30-7.28 (d, *J* = 8 Hz, 2H), 7.25-7.19 (t, *J* = 8 Hz, 2H), 6.73-6.61 (d, *J* = 48 Hz, 1H), 3.91 (s, 3H), 2.27 (s, 3H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 166.72, 145.04-144.86 (d, *J*<sub>C-F</sub> = 22 Hz), 138.80, 136.25-136.07 (d, *J*<sub>C-F</sub> = 22 Hz), 129.95, 129.73, 129.33, 126.96-126.92 (d, *J*<sub>C-F</sub> = 6 Hz), 126.64, 126.25, 126.06-126.01 (d, *J*<sub>C-F</sub> = 6 Hz), 94.60-93.23 (d, *J*<sub>C-F</sub> = 173 Hz), 52.13, 21.17.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -169.50.

**HRMS (EI) m/z** calcd for C<sub>16</sub>H<sub>15</sub>FO<sub>2</sub>: 258.1056, found: 258.1042.

**methyl 4-(fluoro(2-fluorophenyl)methyl)benzoate (1j)**



The title compound was synthesized according to the General Procedure 4, using methyl 4-bromobenzoate (21 mg, 0.1 mmol) and 2-fluoro-2-(2-fluorophenyl)acetic acid (34 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

Colorless oil; 40% yield (10 mg).

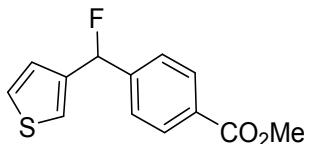
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.05-8.03 (d, *J* = 8 Hz, 2H), 7.46-7.44 (d, *J* = 8 Hz, 2H), 7.39-7.32 (m, 2H), 7.19-7.16 (m, 1H), 7.10-7.06 (m, 1H), 6.86-6.77 (d, *J* = 46 Hz, 1H), 3.91 (s, 3H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 166.66, 143.92-143.69 (d, *J*<sub>C-F</sub> = 28 Hz), 130.67-130.64 (d, *J*<sub>C-F</sub> = 2 Hz), 130.59-130.56 (d, *J*<sub>C-F</sub> = 2 Hz), 130.24-130.21 (d, *J*<sub>C-F</sub> = 2 Hz), 127.88-127.84 (d, *J*<sub>C-F</sub> = 4 Hz), 127.81-127.78 (d, *J*<sub>C-F</sub> = 4 Hz), 125.96-125.89 (d, *J*<sub>C-F</sub> = 6 Hz), 124.54-124.50 (d, *J*<sub>C-F</sub> = 6 Hz), 115.79-115.58 (d, *J*<sub>C-F</sub> = 26 Hz), 88.93-87.19 (d, *J*<sub>C-F</sub> = 217 Hz), 52.20.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -117.94, -175.58.

**HRMS (EI) m/z** calcd for C<sub>15</sub>H<sub>12</sub>F<sub>2</sub>O<sub>2</sub>: 262.0805, found: 262.0803.

**methyl 4-(fluoro(thiophen-3-yl)methyl)benzoate (1k)**



The title compound was synthesized according to the General Procedure 4, using methyl 4-bromobenzoate (21 mg, 0.1 mmol) and 2-fluoro-2-(thiophen-3-yl)acetic acid (32 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

Yellow oil; 60% yield (15 mg).

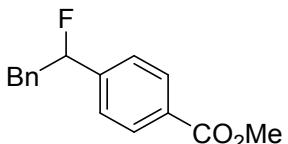
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.07-8.05 (d, *J* = 8 Hz, 2H), 7.46-7.44 (d, *J* = 8 Hz, 2H), 7.33-7.32 (br, 1H), 7.223 (s, 1H), 7.01-7.00 (d, *J* = 5 Hz, 1H), 6.60-6.51 (d, *J* = 47 Hz, 1H), 3.92 (s, 3H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 166.69, 144.35-144.17 (d, *J*<sub>C-F</sub> = 18 Hz), 140.48-140.30 (d, *J*<sub>C-F</sub> = 18 Hz), 131.74, 131.14, 129.84, 126.83, 126.24-126.22 (d, *J*<sub>C-F</sub> = 2 Hz), 126.07-126.02 (d, *J*<sub>C-F</sub> = 5 Hz), 124.21-124.15 (d, *J*<sub>C-F</sub> = 6 Hz), 90.83-89.46 (d, *J*<sub>C-F</sub> = 171 Hz), 52.22.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -163.99-164.12 (d, *J*<sub>F-H</sub> = 48 Hz).

**HRMS (EI) m/z** calcd for C<sub>13</sub>H<sub>11</sub>FO<sub>2</sub>S: 250.0464, found: 250.0461.

### methyl 4-(1-fluoro-2-phenylethyl)benzoate (1l)



The title compound was synthesized according to the General Procedure 6, using methyl 4-bromobenzoate (21 mg, 0.1 mmol) and 2-fluoro-3-phenylpropanoic acid (34 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

Colorless oil; 46% yield (11 mg).

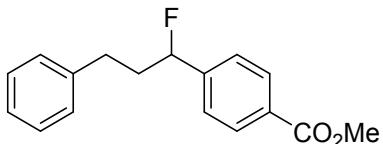
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.024-8.008 (d, *J* = 8 Hz, 2H), 7.332-7.315 (d, *J* = 8 Hz, 2H), 7.293-7.235 (m, 3H), 7.138-7.124 (d, *J* = 7 Hz, 2H), 5.739-5.620 (dt, *J* = 47 Hz, *J* = 5 Hz, 1H), 3.921 (s, 3H), 3.293-3.213 (m, 1H), 3.165-3.073 (m, 1H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 166.83, 144.78-144.51 (d, *J*<sub>C-F</sub> = 27 Hz), 135.98, 129.69, 129.57, 128.46, 126.90, 125.51, 125.45, 94.97-93.49 (d, *J*<sub>C-F</sub> = 148 Hz), 52.13, 43.93, 43.72.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -174.30.

**HRMS (ESI) m/z** calcd for C<sub>16</sub>H<sub>15</sub>FNaO<sub>2</sub> [(M+Na)<sup>+</sup>]: 281.0954, found: 281.0947.

### methyl 4-(1-fluoro-3-phenylpropyl)benzoate (1m)



The title compound was synthesized according to the General Procedure 6, using

methyl methyl 4-bromobenzoate (21 mg, 0.1 mmol) and 2-fluoro-4-phenylbutanoic acid (36 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

Colorless oil; 43% yield (16 mg).

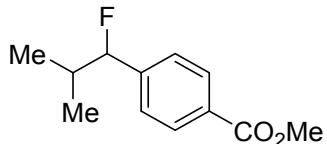
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.08-8.06 (d, *J* = 8 Hz, 2H), 7.41-7.39 (d, *J* = 8 Hz, 2H), 7.33-7.30 (m, 2H), 7.25-7.21 (m, 3H), 5.58-5.43 (dq, *J* = 47 Hz, *J* = 4 Hz, 1H), 3.76 (s, 3H), 2.85-2.74 (m, 2H), 2.33-2.06 (m, 2H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 166.75, 145.38-145.18 (d, *J*<sub>C-F</sub> = 20 Hz), 140.86, 130.05, 130.03, 129.85, 128.59, 128.50, 126.22, 125.34, 125.27, 93.81-92.09 (d, *J*<sub>C-F</sub> = 172 Hz), 52.18, 39.02, 38.79, 31.19, 31.15.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -180.11.

**HRMS (EI)** m/z calcd for C<sub>17</sub>H<sub>17</sub>FO<sub>2</sub>: 272.1213, found: 272.1207.

#### **methyl 4-(1-fluoro-2-methylpropyl)benzoate (1n)**



The title compound was synthesized according to the General Procedure 6, using methyl 4-bromobenzoate (21 mg, 0.1 mmol) and 2-fluoro-3-methylbutanoic acid (24 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

Colorless oil; 40% yield (8 mg).

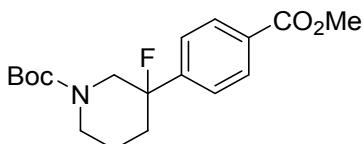
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.04-8.02 (d, *J* = 8 Hz, 2H), 7.36-7.34 (d, *J* = 8 Hz, 2H), 5.25-5.14 (dd, *J* = 47 Hz, *J* = 6 Hz, 1H), 3.92 (s, 3H), 2.14-2.04 (m, 1H), 0.98-0.97 (d, *J* = 6 Hz, 3H), 0.90-0.88 (d, *J* = 6 Hz, 3H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 166.84, 144.55-144.34 (d, *J*<sub>C-F</sub> = 25 Hz), 129.86, 129.51, 125.95, 125.88, 99.32-97.57 (d, *J*<sub>C-F</sub> = 217 Hz), 52.14, 34.47-34.24 (d, *J*<sub>C-F</sub> = 28 Hz), 18.29, 17.10.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -174.65.

**HRMS (EI)** m/z calcd for C<sub>12</sub>H<sub>15</sub>FO<sub>2</sub>: 210.1056, found: 210.1050.

#### **tert-butyl 3-fluoro-3-(4-(methoxycarbonyl)phenyl)piperidine-1-carboxylate (1o)**



The title compound was synthesized according to the General Procedure 7, using methyl 4-bromobenzoate (21 mg, 0.1 mmol) and 1-(tert-butoxycarbonyl)-3-fluoropiperidine-3-carboxylic acid (50 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

Colorless oil; 47% yield (16 mg).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.06-8.04 (d, *J* = 8 Hz, 2H), 7.49-7.47 (d, *J* = 8 Hz, 2H), 4.40-4.10 (m, 2H), 3.92 (s, 3H), 3.22-3.03 (m, 1H), 2.95-2.77 (m, 1H), 2.05-1.89

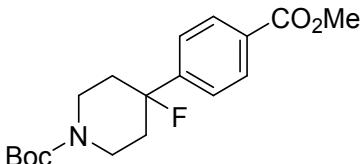
(m, 2H), 1.68-1.62 (m, 2H), 1.46 (s, 9H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 166.67, 155.10, 129.86, 129.79, 124.37-124.29 (d, J<sub>C-F</sub> = 8 Hz), 93.93-92.12 (d, J<sub>C-F</sub> = 180 Hz), 80.00, 65.93, 52.20, 44.58, 42.77, 35.07, 34.82, 28.39, 20.68.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -162.08.

**HRMS (ESI) m/z** calcd for C<sub>18</sub>H<sub>24</sub>FNNaO<sub>4</sub> [M+Na]<sup>+</sup>: 360.1587, found: 360.1579.

#### **tert-butyl 4-fluoro-4-(4-(methoxycarbonyl)phenyl)piperidine-1-carboxylate (1p)**



The title compound was synthesized according to the General Procedure 7, using methyl 4-bromobenzoate (21 mg, 0.1 mmol) and 1-(tert-butoxycarbonyl)-4-fluoropiperidine-4-carboxylic acid (50 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

White solid; 51% yield (17 mg).

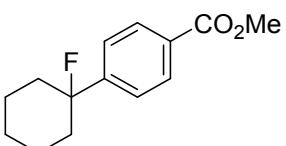
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.05-8.03 (d, J = 8 Hz, 2H), 7.44-7.42 (d, J = 8 Hz, 2H), 4.15-4.12 (br, 2H), 3.92 (s, 3H), 3.21-3.13 (m, 2H), 2.04-1.92 (m, 4H), 1.49 (s, 9H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 166.70, 154.83-154.75 (d, J<sub>C-F</sub> = 6 Hz), 148.97-148.76 (d, J<sub>C-F</sub> = 21 Hz), 129.91, 126.85, 126.85, 123.99, 123.90, 95.15-93.40 (d, J<sub>C-F</sub> = 174 Hz), 79.87, 52.18, 39.64, 36.51, 36.28, 28.45.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -163.81.

**HRMS (ESI) m/z** calcd for C<sub>18</sub>H<sub>24</sub>FNNaO<sub>4</sub> [M+Na]<sup>+</sup>: 360.1587, found: 360.1581.

#### **methyl 4-(1-fluorocyclohexyl)benzoate (1q)**



The title compound was synthesized according to the General Procedure 7, using methyl 4-bromobenzoate (21 mg, 0.1 mmol) and 1-fluorocyclohexane-1-carboxylic acid (30 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

Colorless oil; 53% yield (12 mg).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.02-8.01 (d, J = 8 Hz, 2H), 7.45-7.43 (d, J = 8 Hz, 2H), 3.91 (s, 3H), 2.01-1.97 (m, 2H), 1.83-1.68 (m, 7H), 1.34-1.27 (m, 1H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 166.89, 151.01-150.79 (d, J<sub>C-F</sub> = 27 Hz), 129.64, 124.03, 123.94, 96.85-95.11 (d, J<sub>C-F</sub> = 217 Hz), 52.10, 37.10-36.87 (d, J<sub>C-F</sub> = 29 Hz), 24.85, 21.80.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -160.02.

**HRMS (EI) m/z** calcd for C<sub>14</sub>H<sub>17</sub>FO<sub>2</sub>: 236.1213, found: 236.1210.

### **1-(fluoro(phenyl)methyl)-2-methylbenzene (1r)**



The title compound was synthesized according to the General Procedure 6, using 1-iodo-2-methylbenzene (22mg, 0.1 mmol) and 2-fluoro-2-phenylacetic acid (31 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. The title compound must be purified by EtOAc/Hexane quickly, which is easily decomposed.

Colorless oil; 65% yield (13 mg).

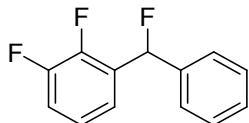
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.42-7.21 (m, 8H), 7.19-7.16 (m, 1H), 6.76-6.67 (d, *J* = 47 Hz, 1H), 2.32 (s, 3H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 141.78-141.44 (d, *J*<sub>C-F</sub> = 42 Hz), 139.93-139.54 (d, *J*<sub>C-F</sub> = 42 Hz), 135.69, 130.53, 128.33, 128.24, 127.64, 127.42, 126.22, 126.15, 93.21-91.85 (d, *J*<sub>C-F</sub> = 170 Hz), 19.36.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -166.87.

**HRMS (EI) m/z** calcd for C<sub>14</sub>H<sub>13</sub>F: 200.1001, found: 200.1005.

### **1,2-difluoro-3-(fluoro(phenyl)methyl)benzene (1s)**



The title compound was synthesized according to the General Procedure 6, using 1-bromo-2,3-difluorobenzene (19 mg, 0.1 mmol) and 2-fluoro-2-phenylacetic acid (31 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

Colorless oil; 62% yield (13 mg).

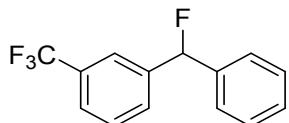
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.40-7.33 (m, 5H), 7.24-7.19 (m, 1H), 7.17-7.11 (m, 2H), 6.82-7.71 (d, *J* = 46 Hz, 1H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 151.72-151.60 (d, *J*<sub>C-F</sub> = 12 Hz), 149.25-149.12 (d, *J*<sub>C-F</sub> = 12 Hz), 138.42-138.20 (d, *J*<sub>C-F</sub> = 22 Hz), 129.93-129.59 (dd, *J*<sub>C-F</sub> = 20 Hz, *J*<sub>C-F</sub> = 10 Hz), 128.84, 128.66, 126.27-126.21 (d, *J*<sub>C-F</sub> = 6 Hz), 124.44-124.32 (dd, *J*<sub>C-F</sub> = 12 Hz, *J*<sub>C-F</sub> = 6 Hz), 122.31-122.18, 117.40-117.23 (d, *J*<sub>C-F</sub> = 16 Hz), 89.19-87.40 (dt, *J*<sub>C-F</sub> = 173 Hz, *J*<sub>C-F</sub> = 3 Hz).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -138.05, -142.83, -172.98.

**HRMS (EI) m/z** calcd for C<sub>13</sub>H<sub>9</sub>F<sub>3</sub>: 222.0656, found: 222.0651.

### **1-(fluoro(phenyl)methyl)-3-(trifluoromethyl)benzene (1t)**



The title compound was synthesized according to the General Procedure 6, using 1-iodo-3-(trifluoromethyl)benzene (27 mg, 0.1 mmol) and 2-fluoro-2-phenylacetic acid (31 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

Colorless oil; 57% yield (14 mg).

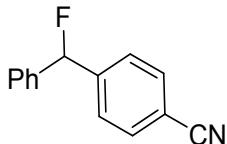
**<sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>-C<sub>6</sub>D<sub>5</sub>)** δ 7.58 (s, 1H), 7.24-7.23 (d, *J* = 7 Hz, 1H), 7.14-7.13 (d, *J* = 7 Hz, 1H), 7.05-7.01 (m, 5H), 6.90-6.87 (t, *J* = 8 Hz, 1H), 6.07-5.97 (d, *J* = 47 Hz, 1H).

**<sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>-C<sub>6</sub>D<sub>5</sub>)** δ 141.72-141.54 (d, *J*<sub>C-F</sub> = 22 Hz), 139.52-139.36 (d, *J*<sub>C-F</sub> = 22 Hz), 129.84-129.80 (d, *J*<sub>C-F</sub> = 5 Hz), 129.15, 129.03, 128.76, 128.65, 128.12, 127.74, 127.64, 126.83, 126.78, 125.28, 124.90, 131.43-130.68 (q, *J* = 32 Hz, CF<sub>3</sub>), 127.64-121.41 (q, *J* = 270 Hz, CF<sub>3</sub>), 123.58-123.28 (q, *J* = 3 Hz, CF<sub>3</sub>), 94.39-93.00 (d, *J*<sub>C-F</sub> = 174 Hz).

**<sup>19</sup>F NMR (376 MHz, CD<sub>3</sub>-C<sub>6</sub>D<sub>5</sub>)** δ -62.17, -167.83.

**HRMS (EI) m/z** calcd for C<sub>14</sub>H<sub>10</sub>F<sub>4</sub>: 254.0719, found: 254.0711.

#### 4-(fluoro(phenyl)methyl)benzonitrile (**1u**)



The title compound was synthesized according to the General Procedure 4, using 4-bromobenzonitrile (18 mg, 0.1 mmol) and 2-fluoro-2-phenylacetic acid (31 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

Colorless oil; 71% yield (15 mg).

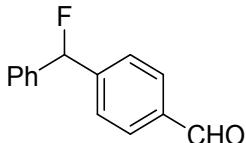
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.67-7.66 (d, *J* = 8 Hz, 2H), 7.47-7.45 (d, *J* = 8 Hz, 2H), 7.41-7.37 (m, 3H), 7.31-7.30 (d, *J* = 7 Hz, 2H), 6.53-6.44 (d, *J* = 47 Hz, 1H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 145.08-144.90 (d, *J*<sub>C-F</sub> = 22 Hz), 138.53-138.36 (d, *J*<sub>C-F</sub> = 21 Hz), 132.36, 129.19, 128.86, 126.88, 126.76, 118.50, 112.23, 94.26-92.87 (d, *J*<sub>C-F</sub> = 174 Hz).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -169.30--169.42 (d, *J*<sub>F-H</sub> = 45 Hz).

**HRMS (EI) m/z** calcd for C<sub>14</sub>H<sub>10</sub>FN: 211.0797, found: 211.0789.

#### 4-(fluoro(phenyl)methyl)benzaldehyde (**1v**)



The title compound was synthesized according to the General Procedure 4, using 4-bromobenzaldehyde (18 mg, 0.1 mmol) and 2-fluoro-2-phenylacetic acid (31 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

Colorless oil; 62% yield (13 mg).

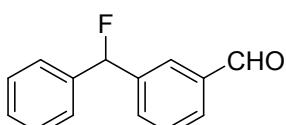
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 10.026 (s, 1H), 7.906-7.889 (d, *J* = 8.5 Hz, 2H), 7.539-7.522 (d, *J* = 8.5 Hz, 2H), 7.410-7.331 (m, 5H), 6.569-6.475 (d, *J* = 47 Hz, 1H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 191.77, 146.49-146.29 (d, J<sub>C-F</sub> = 25 Hz), 138.76, 136.20, 129.93, 129.02-129.00 (d, J<sub>C-F</sub> = 2 Hz), 128.78, 126.88-126.83 (d, J<sub>C-F</sub> = 6 Hz), 126.74-126.68 (d, J<sub>C-F</sub> = 6 Hz), 94.58-93.19 (d, J<sub>C-F</sub> = 173 Hz).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -168.94--169.06 (d, J<sub>F-H</sub> = 48 Hz).

**HRMS (EI) m/z** calcd for C<sub>14</sub>H<sub>11</sub>FO: 214.0794, found: 214.0790.

### 3-(fluoro(phenyl)methyl)benzaldehyde (**1w**)



The title compound was synthesized according to the General Procedure 4, using 3-bromobenzaldehyde (18 mg, 0.1 mmol) and 2-fluoro-2-phenylacetic acid (31 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane. Colorless oil; 60% yield (12 mg).

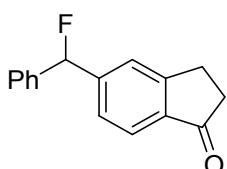
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 10.01 (s, 1H), 7.87-7.85 (d, J = 8 Hz, 2H), 7.64-7.62 (d, J = 8 Hz, 2H), 7.57-7.53 (t, J = 8 Hz, 2H), 7.40-7.33 (m, 5H), 6.59-6.48 (d, J = 47 Hz).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 191.93, 141.32-141.09 (d, J<sub>C-F</sub> = 22 Hz), 139.13-138.92 (d, J<sub>C-F</sub> = 22 Hz), 136.61, 132.28-132.22 (d, J<sub>C-F</sub> = 6 Hz), 129.66, 129.32, 128.91, 128.89, 128.76, 127.55, 127.48, 126.71, 126.65, 94.67-92.94 (d, J<sub>C-F</sub> = 173 Hz).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -167.91

**HRMS (ESI) m/z** calcd for C<sub>14</sub>H<sub>11</sub>FO [(M+Na)<sup>+</sup>]: 237.0692, found: 237.0688.

### 5-(fluoro(phenyl)methyl)-2,3-dihydro-1H-inden-1-one (**1x**)



The title compound was synthesized according to the General Procedure 4, using 5-bromo-2,3-dihydro-1H-inden-1-one (21 mg, 0.1 mmol) and 2-fluoro-2-phenylacetic acid (31 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

Colorless oil; 79% yield (19 mg).

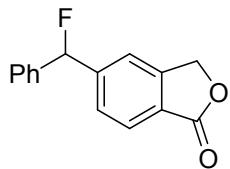
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.761-7.744 (d, J = 8 Hz, 1H), 7.498 (s, 1H), 7.395-7.336 (m, 6H), 6.565-6.472 (d, J = 47 Hz, 1H), 3.156-3.132 (t, J = 6.5 Hz, 2H), 2.720-2.696 (t, J = 6.5 Hz, 2H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 206.40, 155.51, 146.81-146.63 (d, J<sub>C-F</sub> = 22 Hz), 139.14-138.97 (d, J<sub>C-F</sub> = 22 Hz), 137.05, 128.92, 128.74, 126.79-126.74 (d, J<sub>C-F</sub> = 6 Hz), 125.55-125.50 (d, J<sub>C-F</sub> = 6 Hz), 124.19-124.13 (d, J<sub>C-F</sub> = 6 Hz), 123.91, 94.81-93.42 (d, J<sub>C-F</sub> = 173 Hz), 36.42, 25.84.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -168.51.

**HRMS (EI) m/z** calcd for C<sub>16</sub>H<sub>13</sub>FO: 240.0950, found: 240.0944.

**5-(fluoro(phenyl)methyl)isobenzofuran-1(3H)-one (1y)**



The title compound was synthesized according to the General Procedure 4, using 5-bromo(isobenzofuran-1(3H)-one (21 mg, 0.1 mmol) and 2-fluoro-2-phenylacetic acid (31 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

Colorless oil; 77% yield (18 mg).

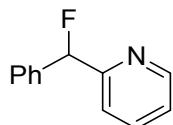
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.917-7.900 (d, *J* = 8.5 Hz, 1H), 7.512 (br, 2H), 7.415-7.372 (m, 3H), 7.343-7.327 (d, *J* = 8 Hz, 2H), 6.609-6.515 (d, *J* = 47 Hz, 1H), 5.323 (s, 2H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 170.56, 147.02, 146.69-146.51 (d, *J*<sub>C-F</sub> = 21 Hz), 138.74-138.57 (d, *J*<sub>C-F</sub> = 21 Hz), 129.18-129.16 (d, *J*<sub>C-F</sub> = 2 Hz), 128.87, 127.28-127.23 (d, *J*<sub>C-F</sub> = 6 Hz), 126.83-126.79 (d, *J*<sub>C-F</sub> = 5 Hz), 125.94, 119.68-119.63 (d, *J*<sub>C-F</sub> = 6 Hz), 94.56-93.16 (d, *J*<sub>C-F</sub> = 175 Hz), 69.61.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -168.38--168.51 (d, *J*<sub>F-H</sub> = 48 Hz).

**HRMS (ESI) m/z** calcd for C<sub>15</sub>H<sub>11</sub>FO<sub>2</sub> [(M+Na)<sup>+</sup>]: 265.0641, found: 265.0644.

**2-(fluoro(phenyl)methyl)pyridine (1z)**



The title compound was synthesized according to the General Procedure 5, using 2-bromopyridine (16 mg, 0.1 mmol) and 2-fluoro-2-phenylacetic acid (31 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

Colorless oil; 55% yield (10 mg).

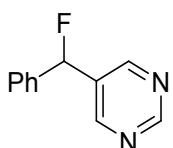
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.583-8.574 (d, *J* = 4.5 Hz, 1H), 7.772-7.738 (dt, *J* = 7.5 Hz, *J* = 2 Hz, 1H), 7.564-7.547 (d, *J* = 8.5 Hz, 1H), 7.433-7.416 (br, 2H), 7.386-7.327 (m, 3H), 7.246-7.221 (m, 1H), 6.575-6.482 (d, *J* = 46.5 Hz, 1H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 149.18, 137.04, 128.69, 128.68, 128.59, 126.67, 126.61, 123.06, 120.11, 120.07, 95.43-94.04 (d, *J*<sub>C-F</sub> = 173 Hz).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -174.77--174.89 (d, *J*<sub>F-H</sub> = 45 Hz).

**HRMS (ESI) m/z** calcd for C<sub>12</sub>H<sub>11</sub>FN [(M+H)<sup>+</sup>]: 188.0876, found: 188.0868.

**5-(fluoro(phenyl)methyl)pyrimidine (1aa)**



The title compound was synthesized according to the General Procedure 5, using 5-bromopyrimidine (16 mg, 0.1 mmol) and 2-fluoro-2-phenylacetic acid (31 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

Colorless oil; 55% yield (10 mg).

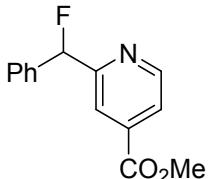
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 9.237 (s, 1H), 8.743 (s, 2H), 7.484-7.438 (m, 3H), 7.385-7.370 (m, 2H), 6.601-6.508 (d, *J* = 47 Hz, 1H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 158.66, 155.18-155.13 (d, *J*<sub>C-F</sub> = 6 Hz), 129.48, 129.07, 126.61-126.56 (d, *J*<sub>C-F</sub> = 6 Hz), 91.57-90.18 (d, *J*<sub>C-F</sub> = 173 Hz).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -171.56.

**HRMS (EI) m/z** calcd for C<sub>11</sub>H<sub>9</sub>FN<sub>2</sub>: 188.0750, found: 188.0745.

#### **methyl 2-(fluoro(phenyl)methyl)isonicotinate (1ab)**



The title compound was synthesized according to the General Procedure 4, using methyl 2-bromoisonicotinate (22 mg, 0.1 mmol) and 2-fluoro-2-phenylacetic acid (31 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

Colorless oil; 54% yield (13 mg).

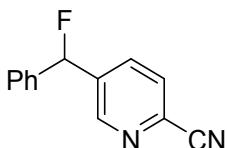
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.725-8.715 (d, *J* = 5 Hz, 1H), 8.120 (s, 1H), 7.795-7.781 (dd, *J* = 5 Hz, *J* = 2 Hz, 1H), 7.438-7.421 (br, 2H), 7.390-7.334 (m, 3H), 6.625-6.531 (d, *J* = 47 Hz, 1H), 3.967 (s, 3H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 168.39, 160.64-160.42 (d, *J*<sub>C-F</sub> = 27 Hz), 150.07, 138.49, 128.87, 128.68, 126.63, 126.58, 122.29, 119.25, 95.14-93.75 (d, *J*<sub>C-F</sub> = 174 Hz), 52.81.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -175.73.

**HRMS (ESI) m/z** calcd for C<sub>14</sub>H<sub>12</sub>FNO<sub>2</sub> [(M+Na)<sup>+</sup>]: 268.0750, found: 268.0933.

#### **5-(fluoro(phenyl)methyl)picolinonitrile (1ac)**



The title compound was synthesized according to the General Procedure 4, using 5-bromopicolinonitrile (18 mg, 0.1 mmol) and 2-fluoro-2-phenylacetic acid (31 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

Colorless oil; 51% yield (12 mg).

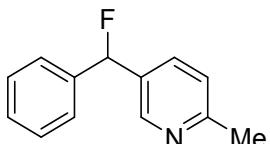
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.700 (s, 1H), 7.816-7.800 (d, *J* = 8 Hz, 1H), 7.721-7.706 (d, *J* = 8 Hz, 1H), 7.429-7.418 (br, 3H), 7.327-7.312 (br, 2H), 6.597-6.504 (d, *J* = 47 Hz, 1H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 149.15-149.09 (d, *J<sub>C-F</sub>* = 7 Hz), 139.39-139.21 (d, *J<sub>C-F</sub>* = 22 Hz), 137.47-137.31 (d, *J<sub>C-F</sub>* = 20 Hz), 134.63-134.58 (d, *J<sub>C-F</sub>* = 6 Hz), 129.65, 129.63, 129.12, 128.19, 126.81, 126.76, 116.94, 92.59-91.18 (d, *J<sub>C-F</sub>* = 175 Hz).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -171.36--171.49 (d, *J<sub>F-H</sub>* = 48 Hz).

**HRMS (EI) m/z** calcd for C<sub>13</sub>H<sub>9</sub>FN<sub>2</sub>: 212.0750, found: 212.0743.

### 5-(fluoro(phenyl)methyl)-2-methylpyridine (1ad)



The title compound was synthesized according to the General Procedure 5, using 5-bromo-2-methylpyridine (17 mg, 0.1 mmol) and 2-fluoro-2-phenylacetic acid (31 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

Colorless oil; 58% yield (11 mg).

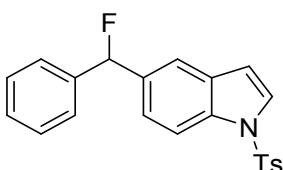
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.49 (s, 1H), 7.58-7.56 (d, *J* = 8 Hz, 1H), 7.41-7.31 (m, 5H), 7.20-7.18 (d, *J* = 8 Hz, 1H), 6.54-6.43 (d, *J* = 47 Hz, 1H), 2.60-2.59 (d, *J* = 1 Hz, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 158.48, 146.97-146.90 (d, *J<sub>C-F</sub>* = 7 Hz), 138.85-138.63 (d, *J<sub>C-F</sub>* = 2Hz), 135.35-135.30 (d, *J<sub>C-F</sub>* = 5 Hz), 132.98-132.77 (d, *J<sub>C-F</sub>* = 21 Hz), 128.86-128.84 (d, *J<sub>C-F</sub>* = 2 Hz), 128.74, 126.45-126.39 (d, *J<sub>C-F</sub>* = 6 Hz), 123.43, 93.27-91.55 (d, *J<sub>C-F</sub>* = 172 Hz), 23.85.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -168.38.

**HRMS (EI) m/z** calcd for C<sub>13</sub>H<sub>12</sub>FN: 201.0954, found: 201.0947.

### 5-(fluoro(phenyl)methyl)-1-tosyl-1H-indole (1ae)



The title compound was synthesized according to the General Procedure 5, using 5-bromo-1-tosyl-1H-indole (35 mg, 0.1 mmol) and 2-fluoro-2-phenylacetic acid (31 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

Colorless oil; 62% yield (23 mg).

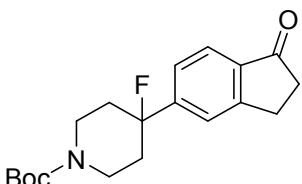
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.97-7.95 (d, *J* = 8 Hz, 1H), 7.76-7.74 (d, *J* = 8 Hz, 2H), 7.58-7.57 (d, *J* = 4 Hz, 1H), 7.50 (br, 1H), 7.37-7.27 (m, 6H), 7.23-7.21 (d, *J* = 8 Hz, 2H), 6.63-6.62 (dd, *J* = 4 Hz, *J* = 0.8 Hz, 1H), 6.59-6.47 (d, *J* = 47 Hz, 1H), 2.34 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 145.09-144.97 (d, *J*<sub>C-F</sub> = 12 Hz), 139.11, 135.29, 130.75, 129.96, 128.47, 127.60, 126.86, 126.49, 123.53, 119.85, 119.35, 113.59, 109.01, 95.47-93.75 (d, *J*<sub>C-F</sub> = 171 Hz), 21.56.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -164.01.

**HRMS (EI) m/z** calcd for C<sub>22</sub>H<sub>18</sub>FNO<sub>2</sub>S: 379.1042, found: 379.1037.

**tert-butyl 4-fluoro-4-(1-oxo-2,3-dihydro-1H-inden-5-yl)piperidine-1-carboxylate (1af)**



The title compound was synthesized according to the General Procedure 7, using 5-bromo-2,3-dihydro-1H-inden-1-one (21 mg, 0.1 mmol) and 1-(tert-butoxycarbonyl)-4-fluoropiperidine-4-carboxylic acid (50 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

Colorless oil; 57% yield (19 mg).

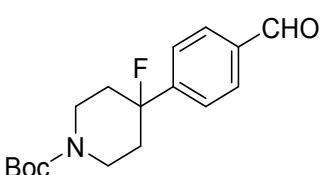
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.76-7.74 (d, *J* = 8 Hz, 1H), 7.50 (s, 1H), 7.36-7.34 (d, *J* = 8 Hz, 1H), 4.16-4.12 (m, 2H), 3.16-3.13 (m, 4H), 2.72-2.69 (m, 2H), 2.09-2.01 (m, 1H), 1.97-1.93 (m, 3H), 1.49 (s, 9H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 206.41, 155.56, 154.73, 151.00-150.79 (d, *J*<sub>C-F</sub> = 21 Hz), 136.61, 123.93, 123.91, 123.40, 123.32, 122.16, 122.06, 95.36-93.60 (d, *J*<sub>C-F</sub> = 176 Hz), 79.92, 39.62, 36.62, 36.45, 36.39, 28.46, 25.92.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -163.21.

**HRMS (ESI) m/z** calcd for C<sub>19</sub>H<sub>24</sub>FNaNO<sub>3</sub> [(M+Na)<sup>+</sup>]: 356.1638, found: 356.1634.

**tert-butyl 4-fluoro-4-(4-formylphenyl)piperidine-1-carboxylate (1ag)**



The title compound was synthesized according to the General Procedure 7, using 4-bromobenzaldehyde (18 mg, 0.1 mmol) and 1-(tert-butoxycarbonyl)-4-fluoropiperidine-4-carboxylic acid (50 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

Colorless oil; 54% yield (16 mg).

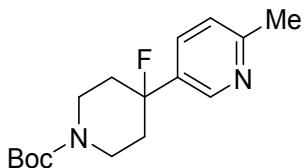
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 10.00 (s, 1H), 7.96-7.94 (d, *J* = 8 Hz, 2H), 7.31-7.29 (d, *J* = 8 Hz, 2H), 4.11-4.08 (br, 2H), 3.22-3.15 (m, 2H), 2.23-2.09 (m, 4H), 1.48 (s, 9H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 190.87, 168.88-168.63 (d, *J*<sub>C-F</sub> = 25 Hz), 162.24, 154.69, 122.05, 116.01, 93.00-91.13 (d, *J*<sub>C-F</sub> = 187 Hz), 80.53, 38.88, 32.21, 31.99, 28.41.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -167.99.

**HRMS (ESI) m/z** calcd for C<sub>17</sub>H<sub>23</sub>FNO<sub>3</sub> [(M+H)<sup>+</sup>]: 308.1662, found: 308.1656.

**tert-butyl 4-fluoro-4-(6-methylpyridin-3-yl)piperidine-1-carboxylate (1ah)**



The title compound was synthesized according to the General Procedure 7, using 5-bromo-2,3-dihydro-1H-inden-1-one (21 mg, 0.1 mmol) and 1-(tert-butoxycarbonyl)-4-fluoropiperidine-4-carboxylic acid (50 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

Colorless oil; 43% yield (16 mg).

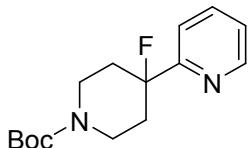
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.53 (s, 1H), 7.73-7.71 (d, J = 8 Hz, 1H), 7.28-7.26 (d, J = 8 Hz, 1H), 4.14-4.11 (m, 2H), 3.16 (br, 2H), 2.65 (s, 3H), 2.01-1.89 (m, 4H), 1.47 (s, 9H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 156.98, 154.67, 143.31-143.22 (d, J<sub>C-F</sub> = 10 Hz), 137.69-137.47 (d, J<sub>C-F</sub> = 22 Hz), 134.22-134.14 (d, J<sub>C-F</sub> = 8 Hz), 123.94, 93.96-92.22 (d, J<sub>C-F</sub> = 173 Hz), 80.02, 39.42, 36.47, 36.25, 28.43, 22.99.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -163.64.

**HRMS (ESI) m/z** calcd for C<sub>16</sub>H<sub>24</sub>FN<sub>2</sub>O<sub>2</sub> [(M+H)<sup>+</sup>]: 295.1822, found: 295.1814.

**tert-butyl 4-fluoro-4-(pyridin-2-yl)piperidine-1-carboxylate (1ai)**



The title compound was synthesized according to the General Procedure 7, using 2-bromopyridine (16 mg, 0.1 mmol) and 1-(tert-butoxycarbonyl)-4-fluoropiperidine-4-carboxylic acid (50 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

Colorless oil; 51% yield (14 mg).

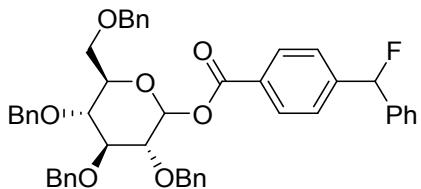
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.56-8.55 (d, J = 3 Hz, 1H), 7.76-7.72 (dt, J = 5 Hz, J = 1 Hz, 1H), 7.57-7.56 (d, J = 8 Hz, 1H), 7.23-7.21 (dd, J = 8 Hz, J = 5 Hz, 1H), 4.16-4.10 (m, 2H), 3.16 (br, 2H), 2.34-2.22 (m, 2H), 1.89-1.84 (m, 2H), 1.47 (s, 9H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 154.65, 148.61, 137.18-137.10 (d, J<sub>C-F</sub> = 8 Hz), 122.69, 118.73, 118.64, 96.44-94.72 (d, J<sub>C-F</sub> = 173 Hz), 79.62, 39.78, 35.10, 34.88, 28.48.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -167.04.

**HRMS (ESI) m/z** calcd for C<sub>15</sub>H<sub>21</sub>FNaN<sub>2</sub>O<sub>2</sub> [(M+Na)<sup>+</sup>]: 303.1485, found: 303.1483.

**(3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl 4-(fluoro(phenyl)methyl)benzoate (1aj)**



The title compound was synthesized according to the General Procedure 4, using (*3R,4S,5R,6R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl 4-bromobenzoate (72 mg, 0.1 mmol) and 2-fluoro-2-phenylacetic acid (31 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

White solid; 47% yield (36 mg).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.064-8.048 (d, *J* = 8 Hz, 2H), 7.443-7.428 (d, *J* = 8 Hz, 2H), 7.400-7.263 (m, 20H), 7.210-7.153 (m, 7H), 6.565-6.471 (d, *J* = 47 Hz, 1H), 5.891-5.877 (d, *J* = 7 Hz, 1H), 4.925-4.904 (d, *J* = 10.5 Hz, 1H), 4.863-4.828 (m, 2H), 4.794-4.784 (m, 2H), 4.629-4.605 (d, *J* = 10.5 Hz, 1H), 4.576-4.554 (d, *J* = 10.5 Hz, 1H), 4.495-4.471 (d, *J* = 12 Hz, 1H), 3.829-3.673 (m, 6H).

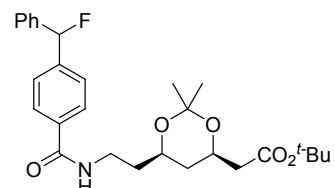
**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 164.52, 138.41, 138.06, 137.90, 137.81, 130.29, 128.94, 128.73, 128.44, 128.38, 128.01, 127.98, 127.93, 127.81, 127.72, 127.71, 127.66, 126.91, 126.87, 126.82, 126.26, 126.21, 126.15, 94.74, 94.63-93.23 (d, JC-F = 174 Hz), 84.92, 80.92, 75.69, 75.65, 75.03, 68.14, 67.54.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -168.77--168.82 (d, *J*<sub>F-H</sub> = 18 Hz).

**HRMS (ESI) m/z** calcd for C<sub>48</sub>H<sub>45</sub>FO<sub>7</sub> [(M+Na)<sup>+</sup>]: 775.3047, found: 775.3038.

### *tert*-butyl

#### **2-((4*R*,6*R*)-6-(2-(4-(fluoro(phenyl)methyl)benzamido)ethyl)-2,2-dimethyl-1,3-dioxan-4-yl)acetate (1ak)**



The title compound was synthesized according to the General Procedure 4, using *tert*-butyl 2-((4*R*,6*R*)-6-(2-(4-bromobenzamido)ethyl)-2,2-dimethyl-1,3-dioxan-4-yl)acetate (91 mg, 0.1 mmol) and 2-fluoro-2-phenylacetic acid (31 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

Colorless oil; 84% yield (40 mg).

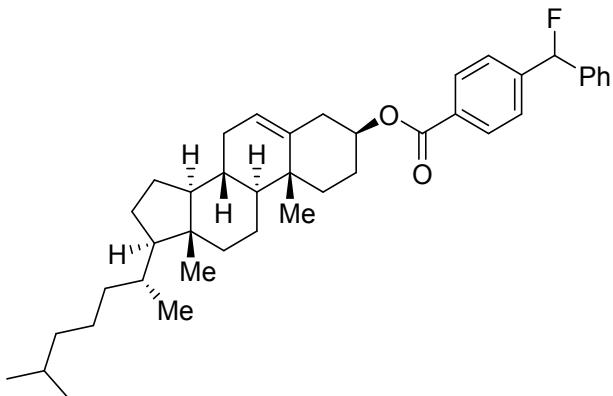
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.76-7.75 (d, *J* = 8 Hz, 2H), 7.40-7.39 (d, *J* = 8 Hz, 2H), 7.37-7.31 (m, 4H), 7.110 (br, 1H), 6.53-6.44 (d, *J* = 47 Hz, 1H), 4.31-4.26 (m, 1H), 4.14-4.08 (m, 1H), 3.78-3.71 (m, 1H), 3.45-3.39 (m, 1H), 2.45-2.41 (dd, *J* = 15 Hz, *J* = 7 Hz, 1H), 2.33-2.29 (dd, *J* = 15 Hz, *J* = 7 Hz, 1H), 1.87-1.81 (m, 1H), 1.76-1.68 (m, 1H), 1.59-1.56 (m, 2H), 1.47 (s, 3H), 1.44 (s, 9H), 1.41 (s, 3H).

**<sup>13</sup>C NMR (MHz, CDCl<sub>3</sub>)** δ 170.12, 166.45, 128.78, 128.76, 128.64, 127.01, 126.76, 126.45, 126.38, 98.89, 94.86-93.13 (d, *J* = 173 Hz), 80.81, 71.16, 66.18, 42.56, 38.04, 36.04, 34.68, 30.28, 28.11, 19.84.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -167.98.

**HRMS (ESI) m/z** calcd for C<sub>28</sub>H<sub>36</sub>FNO<sub>5</sub> [(M+Na)<sup>+</sup>]: 508.2475, found: 508.2468.

**(3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-(fluoro(phenyl)methyl)benzoate (1al)**



The title compound was synthesized according to the General Procedure 4, using (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-bromobenzoate (57 mg, 0.1 mmol) and 2-fluoro-2-phenylacetic acid (31 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane. White solid; 60% yield (36 mg).

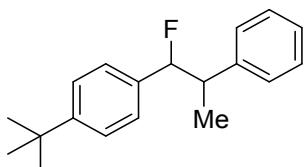
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.07-8.05 (d, *J* = 8 Hz, 2H), 7.43-7.41 (d, *J* = 8 Hz, 2H), 7.38-7.32 (m, 5H), 6.56-6.44 (d, *J* = 47 Hz), 5.44-5.40 (dd, *J* = 12 Hz, *J* = 4 Hz, 2H), 4.92-4.84 (m, 1H), 4.49-4.29 (m, 1H), 2.48-2.44 (br, 3H), 2.05-1.99 (m, 3H), 1.91-1.86 (m, 2H), 1.65-1.49 (m, 3H), 1.38-1.36 (br, 3H), 1.16-1.14 (m, 2H), 1.08 (s, 3H), 1.04 (s, 3H), 0.96-0.93 (m, 5H), 0.90-0.88 (d, *J* = 8 Hz, 8H), 0.71-0.70 (d, *J* = 4 Hz, 6H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 165.54, 144.66-144.44 (d, *J*<sub>C-F</sub> = 22 Hz), 139.62, 139.33, 130.80, 129.79, 128.80, 128.67, 126.85-126.79 (d, *J*<sub>C-F</sub> = 6 Hz), 126.12-126.06 (d, *J*<sub>C-F</sub> = 6 Hz), 123.05-122.87 (d, *J*<sub>C-F</sub> = 18 Hz), 94.85-93.11 (d, *J*<sub>C-F</sub> = 173 Hz), 74.74, 56.76, 56.22, 50.10, 42.36, 39.79, 39.58, 38.25, 37.08, 36.68, 36.25, 35.84, 31.98, 28.92, 28.75, 28.28, 27.92, 24.33, 23.91, 22.88, 22.62, 21.16, 19.34, 18.78, 11.91.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -167.68.

**HRMS (EI) m/z** calcd for C<sub>41</sub>H<sub>55</sub>FO<sub>2</sub>: 598.4186, found: 598.4178.

**1-(tert-butyl)-4-(1-fluoro-2-phenylpropyl)benzene (1am)**



The title compound was synthesized according to the General Procedure 5, using

1-(1-chloroethyl)-2-methylbenzene (15 mg, 0.1 mmol) and 2-(4-(*tert*-butyl)phenyl)-2-fluoroacetic acid (54 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

Colorless oil; 60% yield (16 mg) in 1:2 d.r.

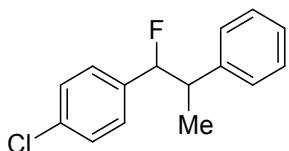
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.30-7.28 (d, J = 8 Hz, 2H), 7.25-7.19 (m, 3H), 7.16-7.14 (d, J = 8 Hz, 2H), 7.10-7.08 (d, J = 8 Hz, 2H), 5.56-5.43 (dd, J = 47 Hz, J = 6 Hz, 1H), 3.24-3.16 (m, 1H), 1.39-1.37 (dd, J = 7 Hz, J = 1 Hz, 3H), 1.29 (s, 9H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 150.88, 142.68, 135.96, 128.26, 128.10, 126.62, 125.65, 125.58, 124.91, 98.68-96.92 (d, J = 177 Hz), 46.42, 34.53, 31.31, 15.68.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -182.77

**HRMS (EI)** m/z calcd for C<sub>19</sub>H<sub>23</sub>F: 270.1784, found: 270.1779.

### 1-chloro-4-(1-fluoro-2-phenylpropyl)benzene (1an)



The title compound was synthesized according to the General Procedure 5, using 1-(1-chloroethyl)-2-methylbenzene (15 mg, 0.1 mmol) and 2-(4-chlorophenyl)-2-fluoroacetic acid (37 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

Colorless oil; 52% yield (13 mg) in 1:1.5 d.r.

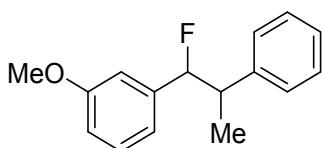
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.24-7.20 (m, 5H), 7.08-7.06 (d, J = 8 Hz, 2H), 7.03-7.01 (d, J = 8 Hz, 2H), 5.50-5.37 (dd, J = 46 Hz, J = 7 Hz, 1H), 3.20-3.12 (m, 1H), 1.40-1.39 (dd, J = 7 Hz, J = 1 Hz, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 141.64, 137.38, 128.38, 128.18, 128.12, 127.39, 126.88, 98.28-96.50 (d, J<sub>C-F</sub> = 178 Hz), 46.64, 16.05.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -180.85.

**HRMS (EI)** m/z calcd for C<sub>15</sub>H<sub>14</sub>ClF: 248.0768, found: 248.0760.

### 1-(1-fluoro-2-phenylpropyl)-3-methoxybenzene (1ao)



The title compound was synthesized according to the General Procedure 5, using methyl (1-chloroethyl)benzene (14 mg, 0.1 mmol) and 2-fluoro-2-(3-methoxyphenyl)acetic acid (36 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

Colorless oil; 50% yield (13 mg) in 1:1.5 d.r.

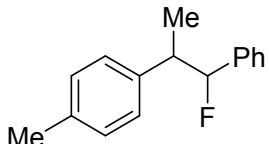
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.321-7.292 (t, J = 7 Hz, 1H), 7.260-7.162 (m, 4H), 7.135-7.121 (d, J = 7 Hz, 1H), 6.858-6.776 (m, 1H), 6.724-6.712 (br, 1H), 6.650 (s, 1H), 5.523-5.380 (dd, J = 17 Hz, J = 6 Hz, 1H), 3.750 (s, 3H), 3.237-3.176 (m, 1H), 1.397-1.204 (d, J = 7 Hz, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 159.44, 142.28, 141.94, 140.49, 129.17, 128.30, 128.19, 126.77, 118.83, 118.27, 114.09, 111.75, 111.36, 98.91-96.87 (d, *J* = 175 Hz), 55.21, 46.55, 46.16, 17.29.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -174.57, -182.63 (diastereomers).

**HRMS (ESI) m/z** calcd for C<sub>16</sub>H<sub>17</sub>FO [(M+Na)<sup>+</sup>]: 267.1161, found: 267.1165.

### 1-(1-fluoro-2-phenylpropyl)-4-methylbenzene (1ap)



The title compound was synthesized according to the General Procedure 5, using 1-(1-chloroethyl)-4-methylbenzene (15 mg, 0.1 mmol) and 2-fluoro-2-phenylacetic acid (31 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

Colorless oil; 50% yield (11 mg) in 1:1 d.r.

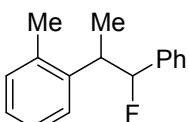
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.34-7.32 (d, *J* = 8 Hz, 2H), 7.27-7.24 (d, *J* = 8 Hz, 2H), 7.15-7.12 (m, 3H), 7.06-6.99 (d, *J* = 8 Hz, 2H), 5.54-5.35 (dd, *J* = 47 Hz, *J* = 6 Hz, 1H), 3.25-3.13 (m, 1H), 2.33-2.29 (s, 3H), 1.38-1.36 and 1.17-1.15 (d, *J* = 8 Hz, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 139.26, 136.28, 129.00, 128.34, 128.15, 127.97, 127.90, 126.50, 99.15-97.17 (d, *J*<sub>C-F</sub> = 174 Hz), 46.16, 21.06, 17.34.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -173.50 and -182.19 (diastereomers).

**HRMS (EI) m/z** calcd for C<sub>16</sub>H<sub>17</sub>F: 228.1314, found: 228.1307.

### 1-(1-fluoro-2-phenylpropyl)-2-methylbenzene (1aq)



The title compound was synthesized according to the General Procedure 5, using 1-(1-chloroethyl)-2-methylbenzene (15 mg, 0.1 mmol) and 2-fluoro-2-phenylacetic acid (31 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

Colorless oil; 55% yield (13 mg) in 1:2 d.r.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.47-7.46 (br, 1H), 7.41-7.38 (m, 4H), 7.34-7.32 (m, 1H), 7.21-7.18 (m, 1H), 7.15-7.13 (m, 1H), 7.09-7.02 (m, 1H), 6.19-6.10 (q, *J* = 12 Hz, *J* = 6 Hz, 1H), 5.85-5.72 (d, *J* = 48 Hz, 1H), 2.35 and 2.26 (s, 3H), 1.54-1.52 and 1.45-1.44 (d, *J* = 6 Hz, 3H).

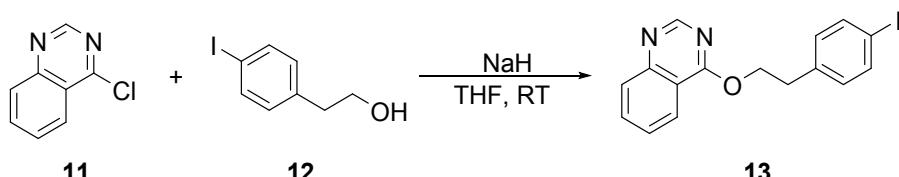
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 139.00-138.93 (d, *J*<sub>C-F</sub> = 7 Hz), 134.85-134.68 (d, *J*<sub>C-F</sub> = 17 Hz), 130.54, 130.35, 129.63, 128.76, 128.00, 126.93, 127.78, 126.93-126.87 (d, *J*<sub>C-F</sub> = 7 Hz), 126.66-126.60 (d, *J*<sub>C-F</sub> = 7 Hz), 126.34, 126.17, 125.38, 124.91, 90.36-88.51 (d, *J*<sub>C-F</sub> = 184 Hz), 71.07, 21.23, 18.99.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -179.29 and -180.14 (diastereomers).

**HRMS (EI) m/z** calcd for C<sub>16</sub>H<sub>17</sub>F: 228.1314, found: 228.1306.

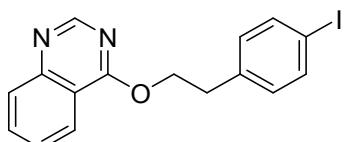
## **8. Synthesis of mitochondrial complex 1 inhibitor (2)**

### a. Synthesis of 4-(4-iodophenethoxy)quinazoline (13)



To a dried round-bottom flask was added NaH (2.0 equiv.), and the flask was purged with nitrogen three times. After that, dried THF was added into the flask under N<sub>2</sub>. 2-(4-Iodophenyl)ethan-1-ol (**12**) in THF was slowly added at 0 °C. After the mixture was allowed to stir for 1 h, 4-chloroquinazoline in THF was slowly added. The mixture was then allowed to stir overnight at room temperature. When the reaction was completed, aqueous NH<sub>4</sub>Cl was added to quench the reaction. The mixture was extracted with ethyl acetate for three times. The combined organic layers were dried with Na<sub>2</sub>SO<sub>4</sub>, concentrated and purified by flash column chromatography.

#### 4-(4-iodophenethoxy)quinazoline (13)



The title compound was synthesized according to the above method, using 2-(4-iodophenyl)ethan-1-ol (248 mg, 1 mmol) and 4-chloroquinazoline (164 mg, 1 mmol). The title compound must be purified by EtOAc/Hexane.

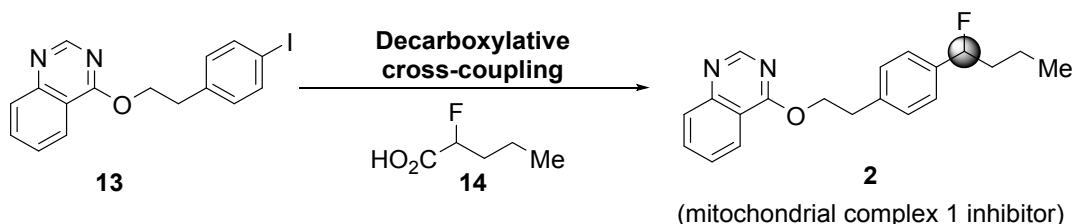
White solid; 92% yield (346 mg).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.80 (s, 1H), 8.11-8.09 (dd, J = 8 Hz, J = 1 Hz, 1H), 7.98-7.96 (d, J = 8 Hz, 1H), 7.86-7.82 (dt, J = 8 Hz, J = 1 Hz, 1H), 7.59-7.55 (dt, J = 8 Hz, J = 1 Hz, 1H), 7.45-7.43 (d, J = 8 Hz, 2H), 7.21-7.19 (d, J = 8 Hz, 2H), 4.79-4.76 (t, J = 6 Hz, 2H), 3.18-3.14 (t, J = 6 Hz, 2H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 166.72, 154.11, 150.41, 136.93, 133.87, 131.68, 130.75, 127.39, 127.34, 123.44, 120.58, 116.54, 67.33, 34.63.

**HRMS (ESI) m/z** calcd for C<sub>16</sub>H<sub>14</sub>IN<sub>2</sub>O [(M+H)<sup>+</sup>]: 377.0151, found: 377.0160.

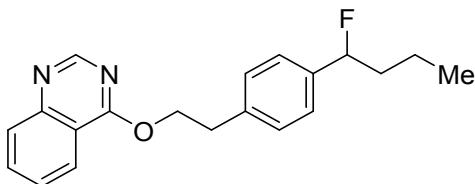
### b. Decarboxylative cross-coupling to access (2)



In a N<sub>2</sub>-filled glovebox, NiBr<sub>2</sub>·DME (4.4 mg, 20 mol%), 4,4'-dimethoxy-2,2'-bipyridine (4.7 mg, 22 mol%), and anhydrous dimethylacetamide

(DMA, 1.0 mL) were added into a 2.5 mL vial with a stir bar. Then 2-fluoropentanoic acid (0.2 mmol), 4-(4-iodophenethoxy)quinazoline (0.1 mmol), and Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)(PF<sub>6</sub>) (1.1 mg, 1 mol%) were added into the mixture. After that, 1,1,3,3-tetramethylguanidine (TMG, 2.0 equiv.) was added. The vial was sealed with a teflon-lined septum cap, transferred out of the glovebox, and the reaction mixture was allowed to stir vigorously under blue LED irradiation for 36 h. When the reaction was completed, the mixture was transferred to a 50 mL separatory funnel, diluted with ethyl acetate, and washed with deionized water (twice). The organic phase was concentrated *in vacuo* and purified by flash column chromatography.

#### 4-(4-(1-fluorobutyl)phenethoxy)quinazoline (2)



White solid, 52% yield (17 mg).

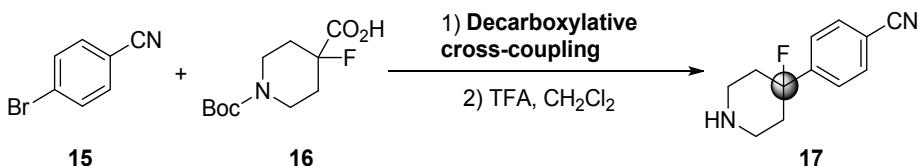
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.34-8.31 (dd, *J* = 8 Hz, *J* = 1 Hz, 1H), 7.77-7.73 (dt, *J* = 8 Hz, *J* = 1 Hz, 1H), 7.75 (s, 1H), 7.69-7.67 (d, *J* = 8 Hz, 1H), 7.53-7.49 (dt, *J* = 8 Hz, *J* = 1 Hz, 1H), 7.25-7.23 (d, *J* = 8 Hz, 2H), 7.18-7.16 (d, *J* = 8 Hz, 2H), 5.46-5.31 (dq, *J* = 47 Hz, *J* = 4 Hz, 1H), 4.23-4.19 (dt, *J* = 8 Hz, *J* = 2 Hz, 2H), 3.11-3.08 (t, *J* = 8 Hz, 2H), 1.99-1.86 (m, 1H), 1.81-1.66 (m, 1H), 1.51-1.34 (m, 2H), 0.96-0.92 (t, *J* = 8 Hz, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 160.95, 147.72, 146.52, 139.59, 137.35, 134.33, 128.94, 127.38, 126.71, 126.17, 122.00, 115.05, 94.99-93.29 (d, *J*<sub>C-F</sub> = 169 Hz), 48.79, 39.32, 39.08, 34.85, 18.39, 13.81.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -174.39.

**HRMS (ESI) m/z** calcd for C<sub>20</sub>H<sub>21</sub>FN<sub>2</sub>NaO [(M+Na)<sup>+</sup>]: 347.1536, found: 347.1531.

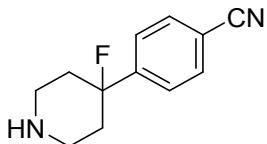
#### 9. Synthesis of 4-(4-fluoropiperidin-4-yl)benzonitrile (17)



In a N<sub>2</sub>-filled glovebox, NiCl<sub>2</sub>·DME (3.3 mg, 15 mol%), 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.4 mg, 20 mol%), and anhydrous dimethylacetamide (DMA, 1.0 mL) were added into a 2.5 mL vial with a stir bar. Then 1-(*tert*-butoxycarbonyl)-4-fluoropiperidine-4-carboxylic acid (0.2 mmol), 4-bromobenzonitrile (0.1 mmol), and Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)(PF<sub>6</sub>) (1.1 mg, 1 mol%) were added into the mixture. After that, 1,1,3,3-tetramethylguanidine (TMG, 2.0 equiv.) was added. The vial was sealed with a teflon-lined septum cap, transferred out of the glovebox, and the reaction mixture was allowed to stir vigorously under blue LED irradiation for 36 h. When the reaction was completed, the mixture was

transferred to a 50 mL separatory funnel, diluted with ethyl acetate, and washed with deionized water (twice). The organic phase was concentrated *in vacuo* and purified by chromatography. After that, the product was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (1mL), then TFA (10 equiv.) was added into the mixture. When the reaction was completed (determined by TLC analysis), the mixture was neutralized with NaHCO<sub>3</sub> and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was dried with Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. The product was purified by flash column chromatography.

#### **4-(4-fluoropiperidin-4-yl)benzonitrile (17)**



White solid; 60% yield (12 mg).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.68-7.66 (d, *J* = 8 Hz, 2H), 7.51-7.49 (d, *J* = 8 Hz, 2H), 3.13-3.11 (br, 4H), 2.83 (br, 1H), 2.18-1.92 (m, 4H).

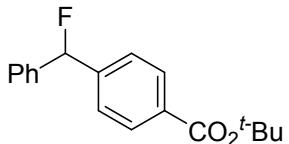
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 149.51-149.29 (d, *J*<sub>C-F</sub> = 22 Hz), 132.40, 124.83-124.72 (d, *J*<sub>C-F</sub> = 10 Hz), 118.56, 111.68, 94.87-93.11 (d, *J*<sub>C-F</sub> = 176 Hz), 41.75, 36.63, 36.41.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -161.87.

**HRMS (ESI) m/z** calcd for C<sub>12</sub>H<sub>14</sub>FN<sub>2</sub> [(M+H)<sup>+</sup>]: 205.1141, found: 205.1135.

#### **10. Characterization of additional cross-coupling products**

##### ***tert*-butyl 4-(fluoro(phenyl)methyl)benzoate**



The title compound was synthesized according to the General Procedure 4, using methyl *tert*-butyl 4-bromobenzoate (25 mg, 0.1 mmol) and 2-fluoro-2-phenylacetic acid (31 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

Colorless oil; 82% yield (23 mg).

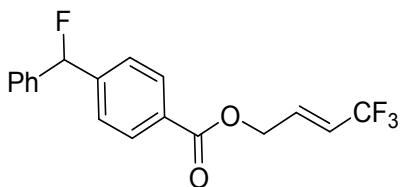
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.01-7.99 (d, *J* = 8 Hz, 2H), 7.41-7.39 (d, *J* = 8 Hz, 2H), 7.37-7.31 (m, 5H), 6.55-6.45 (d, *J* = 47 Hz, 1H), 1.59 (s, 9H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 165.37, 144.27-144.10 (d, *J*<sub>C-F</sub> = 22 Hz), 139.35-139.19 (d, *J*<sub>C-F</sub> = 21 Hz), 131.98, 129.64, 128.79, 128.65, 126.82-126.77 (d, *J*<sub>C-F</sub> = 6 Hz), 126.05-125.99 (d, *J*<sub>C-F</sub> = 7 Hz), 94.72-93.33 (d, *J*<sub>C-F</sub> = 173 Hz), 81.19, 28.18.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -168.41--168.54 (d, *J*<sub>F-H</sub> = 48 Hz).

**HRMS (EI) m/z** calcd for C<sub>18</sub>H<sub>19</sub>FO<sub>2</sub>: 286.1369, found: 286.1369.

##### **(E)-4,4,4-trifluorobut-2-en-1-yl 4-(fluoro(phenyl)methyl)benzoate**



The title compound was synthesized according to the General Procedure 4, using (*E*)-4,4,4-trifluorobut-2-en-1-yl 4-bromobenzoate (31 mg, 0.1 mmol) and 2-fluoro-2-phenylacetic acid (31 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

Colorless oil; 65% yield (22 mg).

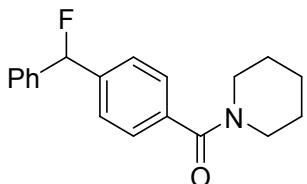
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.09-8.07 (d, *J* = 8 Hz, 2H), 7.47-7.45 (d, *J* = 8 Hz, 2H), 7.41-7.33 (m, 5H), 6.56-6.47 (d, *J* = 47 Hz, 1H), 6.56-6.52 (m, 1H), 6.00-5.93 (m, 1H), 4.96-4.94 (m, 2H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 165.34, 145.48-145.30 (d, *J<sub>C-F</sub>* = 22 Hz), 139.06-138.90 (d, *J<sub>C-F</sub>* = 20 Hz), 134.10-133.94 (q, *J<sub>C-F</sub>* = 13 Hz, *J<sub>C-F</sub>* = 6 Hz), 129.96, 129.26, 128.95, 128.73, 126.85-126.80 (d, *J<sub>C-F</sub>* = 6 Hz), 126.33-126.28 (d, *J<sub>C-F</sub>* = 6 Hz), 123.71 (q, *J<sub>C-F</sub>* = 267 Hz), 120.45-119.62 (q, *J<sub>C-F</sub>* = 68 Hz, *J<sub>C-F</sub>* = 34 Hz), 94.60-93.21 (d, *J<sub>C-F</sub>* = 173 Hz), 62.24.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -64.51 (-CF<sub>3</sub>), -168.81--168.93 (d, *J<sub>F-H</sub>* = 45 Hz).

**HRMS (EI) m/z** calcd for C<sub>18</sub>H<sub>14</sub>F<sub>4</sub>O<sub>2</sub>: 338.0930, found: 338.0927.

#### (4-(fluoro(phenyl)methyl)phenyl)(piperidin-1-yl)methanone



The title compound was synthesized according to the General Procedure 4, using (4-bromophenyl)(piperidin-1-yl)methanone (27 mg, 0.1 mmol) and 2-fluoro-2-phenylacetic acid (31 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

Colorless oil; 70% yield (21 mg).

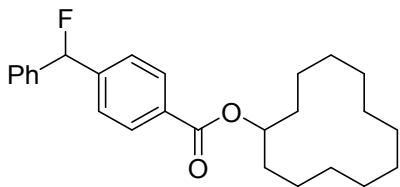
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.432-7.288 (m, 9H), 6.551-6.456 (d, *J* = 47 Hz, 1H), 3.730 (br, 2H), 3.357 (br, 2H), 1.700 (br, 6H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 169.84, 141.15-140.98 (d, *J<sub>C-F</sub>* = 22 Hz), 139.43-139.26 (d, *J<sub>C-F</sub>* = 22 Hz), 136.57, 128.673, 128.58, 128.55, 127.72, 127.04, 126.71, 126.67, 126.58, 126.53, 94.79-93.41 (d, *J<sub>C-F</sub>* = 173 Hz), 48.75, 43.16, 26.57, 25.61, 24.59.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -167.44--167.56 (d, *J<sub>F-H</sub>* = 45 Hz).

**HRMS (ESI) m/z** calcd for C<sub>19</sub>H<sub>20</sub>FNO [(M+Na)<sup>+</sup>]: 320.1427, found: 320.1423.

#### cyclododecyl 4-(fluoro(phenyl)methyl)benzoate



The title compound was synthesized according to the General Procedure 4, using cyclododecyl 4-bromobenzoate (37 mg, 0.1 mmol) and 2-fluoro-2-phenylacetic acid (31 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

Colorless oil; 77% yield (30 mg).

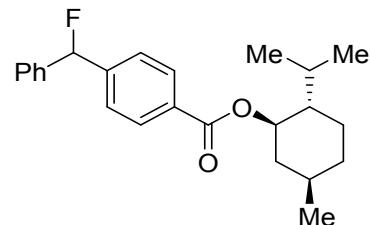
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.049-8.033 (d, *J* = 8 Hz, 2H), 7.424-7.408 (d, *J* = 8 Hz, 2H), 7.395-7.318 (m, 5H), 6.550-6.456 (d, *J* = 47 Hz, 1H), 5.279-5.233 (m, 1H), 1.859-1.792 (m, 3H), 1.672-1.601 (m, 4H), 1.482-1.364 (m, 15H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 165.85, 144.56-144.38 (d, *J*<sub>C-F</sub> = 22 Hz), 139.29-139.12 (d, *J*<sub>C-F</sub> = 22 Hz), 130.91, 129.75, 128.81, 128.67, 126.82-126.77 (d, *J*<sub>C-F</sub> = 6 Hz), 126.12-126.07 (d, *J*<sub>C-F</sub> = 6 Hz), 94.70-93.31 (d, *J*<sub>C-F</sub> = 173 Hz), 73.14, 29.14, 24.20, 23.99, 23.37, 23.18, 20.90.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -168.51--168.64 (d, *J*<sub>F-H</sub> = 48 Hz).

**HRMS (EI) m/z** calcd for C<sub>26</sub>H<sub>33</sub>FO<sub>2</sub>: 396.2465, found: 396.2459.

#### (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 4-(fluoro(phenyl)methyl)benzoate



The title compound was synthesized according to the General Procedure 4, using (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 4-bromobenzoate (34 mg, 0.1 mmol) and 2-fluoro-2-phenylacetic acid (31 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

Colorless oil; 85% yield (31 mg).

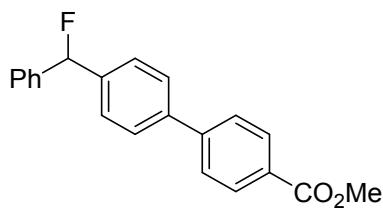
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.064-8.048 (d, *J* = 8 Hz, 2H), 7.437-7.421 (d, *J* = 8 Hz, 2H), 7.413-7.317 (m, 5H), 6.555-6.461 (d, *J* = 47 Hz, 1H), 4.963-4.911 (m, 1H), 2.134-2.110 (d, *J* = 12 Hz, 1H), 1.973-1.923 (m, 1H), 1.744-1.720 (d, *J* = 11 Hz, 2H), 1.584-1.528 (br, 2H), 1.172-0.938 (m, 2H), 0.923-0.908 (m, 6H), 0.800-0.786 (d, *J* = 7 Hz, 3H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 165.69, 144.45, 139.29, 129.79, 129.64, 128.68, 126.82, 126.77, 126.12, 94.70-93.31 (d, *J*<sub>C-F</sub> = 174 Hz), 47.28, 40.97, 34.32, 31.46, 28.18, 26.52, 23.64, 22.05, 20.77.

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -168.61--168.73 (d, *J*<sub>F-H</sub> = 47 Hz).

**HRMS (EI) m/z** calcd for C<sub>24</sub>H<sub>29</sub>FO<sub>2</sub>: 368.2152, found: 368.2148.

#### methyl 4'-(fluoro(phenyl)methyl)-[1,1'-biphenyl]-4-carboxylate



The title compound was synthesized according to the General Procedure 4, using methyl 4'-bromo-[1,1'-biphenyl]-4-carboxylate (29 mg, 0.1 mmol) and 2-fluoro-2-phenylacetic acid (31 mg, 0.2 mmol). Reaction was conducted at 25 °C for 36 h. Purified by EtOAc/Hexane.

White solid; 45% yield (14 mg).

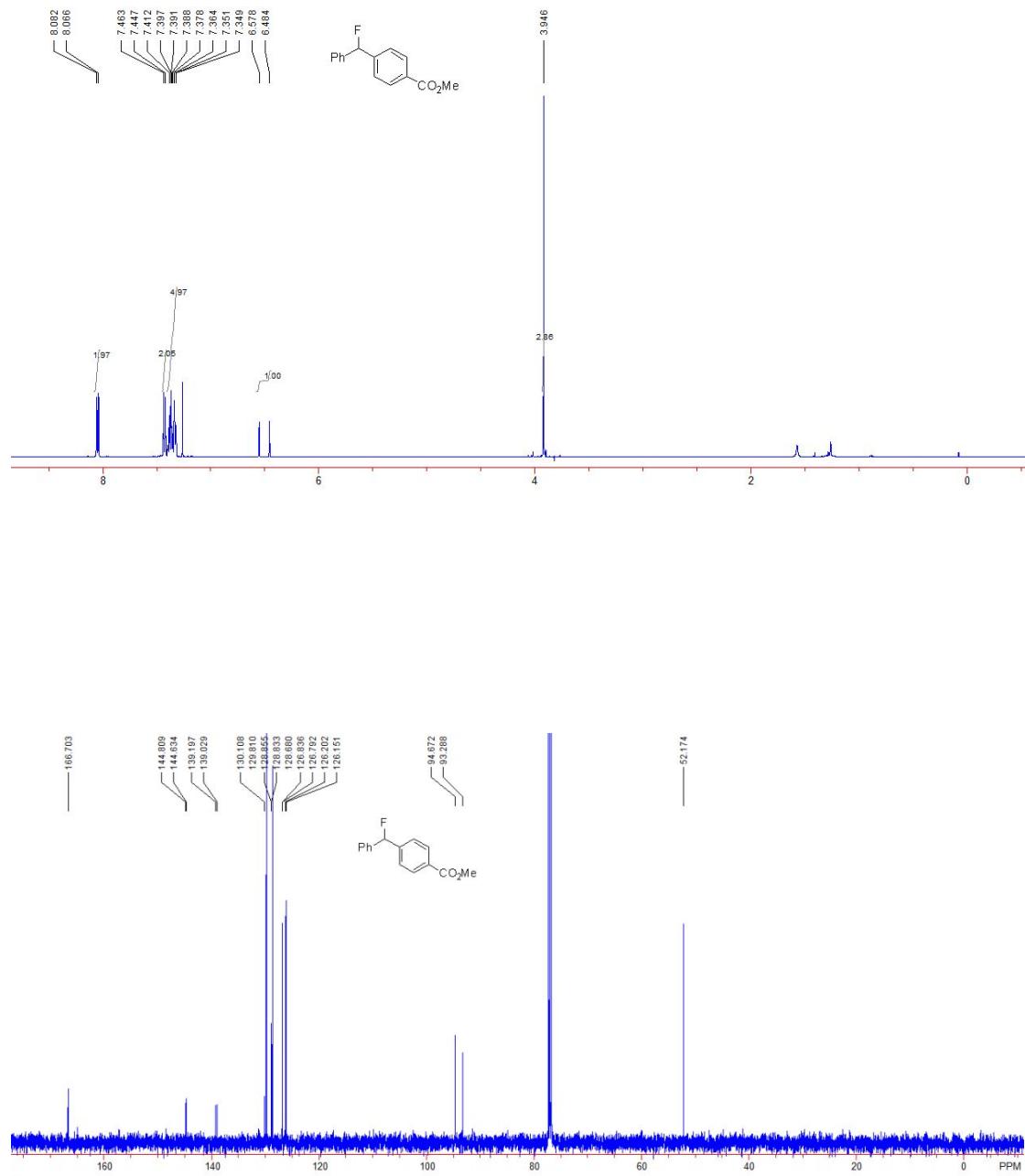
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.116-8.100 (d, *J* = 8 Hz, 2H), 7.661-7.624 (m, 4H), 7.458-7.442 (d, *J* = 8 Hz, 2H), 7.404-7.373 (m, 5H), 6.579-6.485 (d, *J* = 47 Hz, 1H), 3.944 (s, 3H);

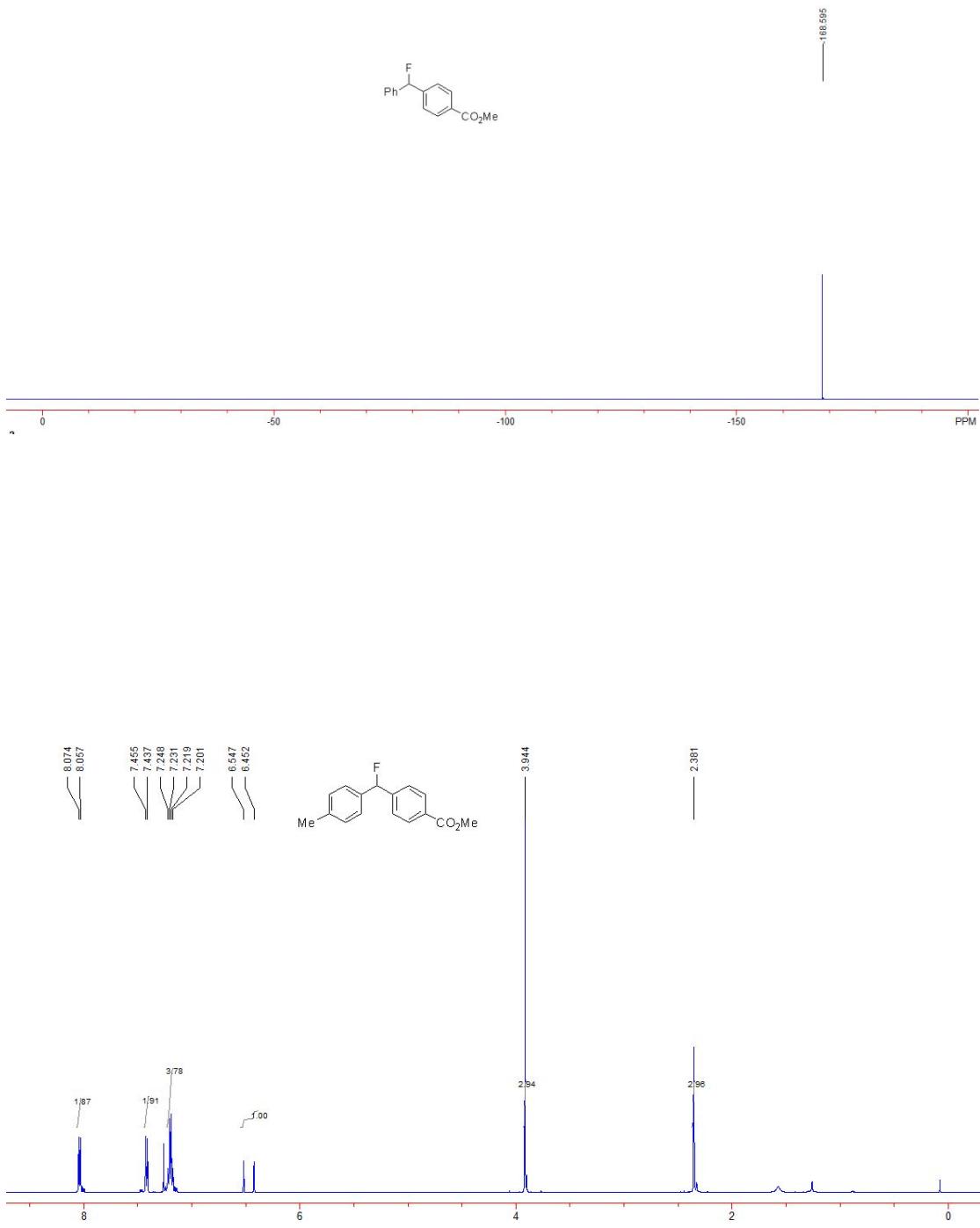
**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 166.95, 144.99, 140.11, 139.91, 139.73, 139.71, 130.16, 129.15, 128.60, 127.41, 127.16-127.12 (d, *J*<sub>C-F</sub> = 6 Hz), 127.06, 126.65-126.60 (d, *J*<sub>C-F</sub> = 6 Hz), 94.89-93.52 (d, *J*<sub>C-F</sub> = 171 Hz), 52.16.

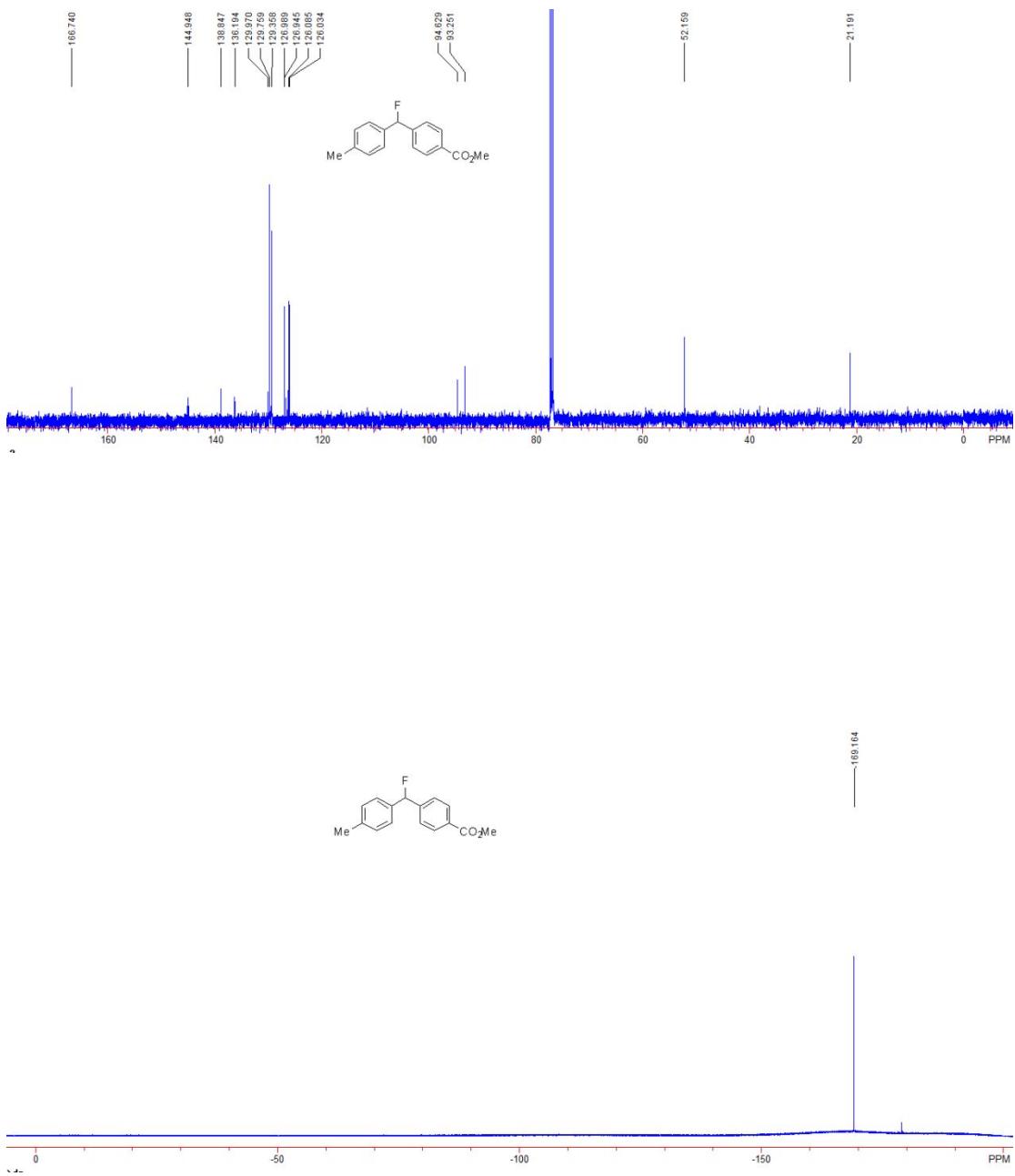
**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -166.90--167.03 (d, *J*<sub>F-H</sub> = 48 Hz).

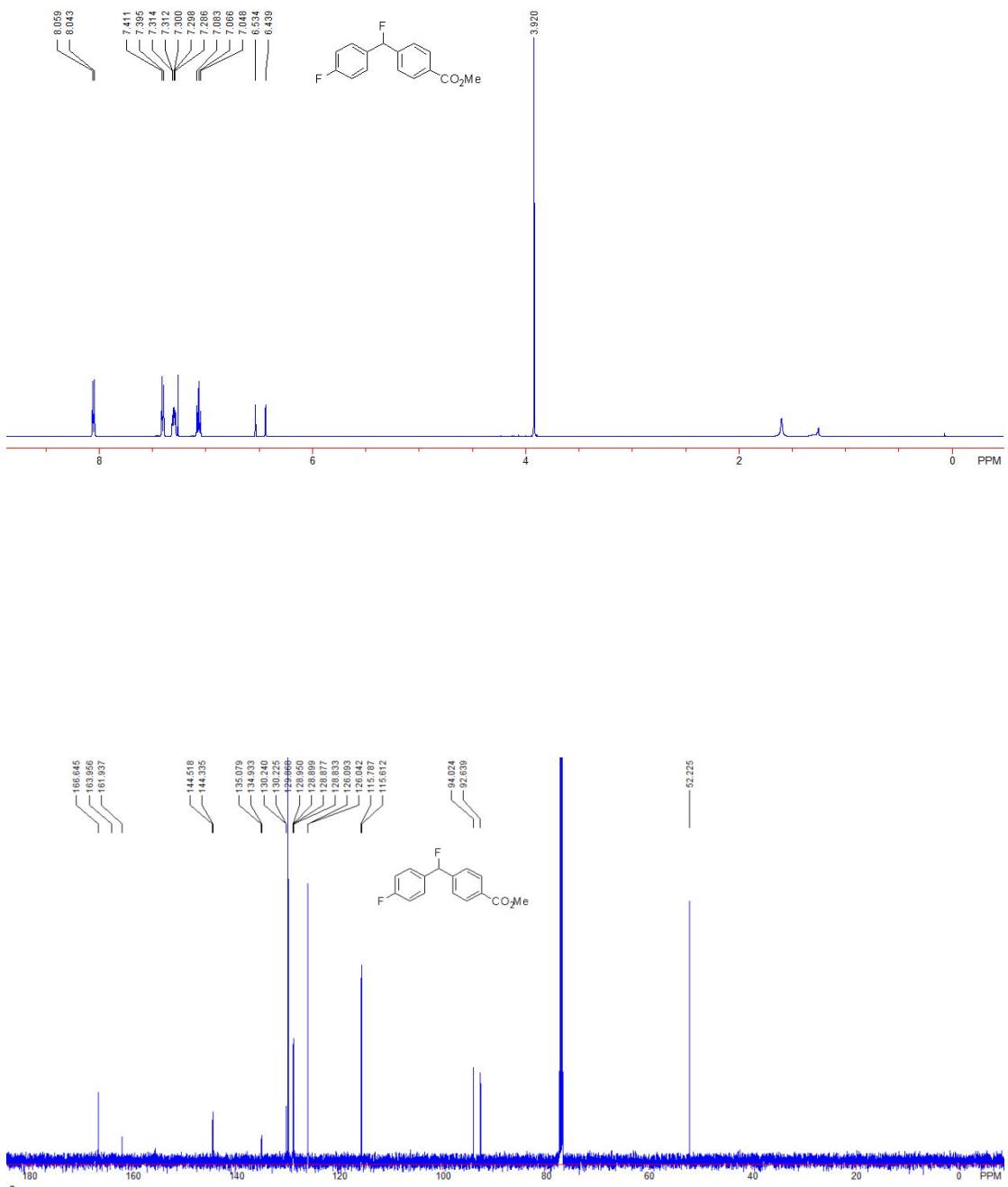
**HRMS (EI) m/z** calcd for C<sub>21</sub>H<sub>17</sub>FO<sub>2</sub>: 320.1213, found: 320.1207.

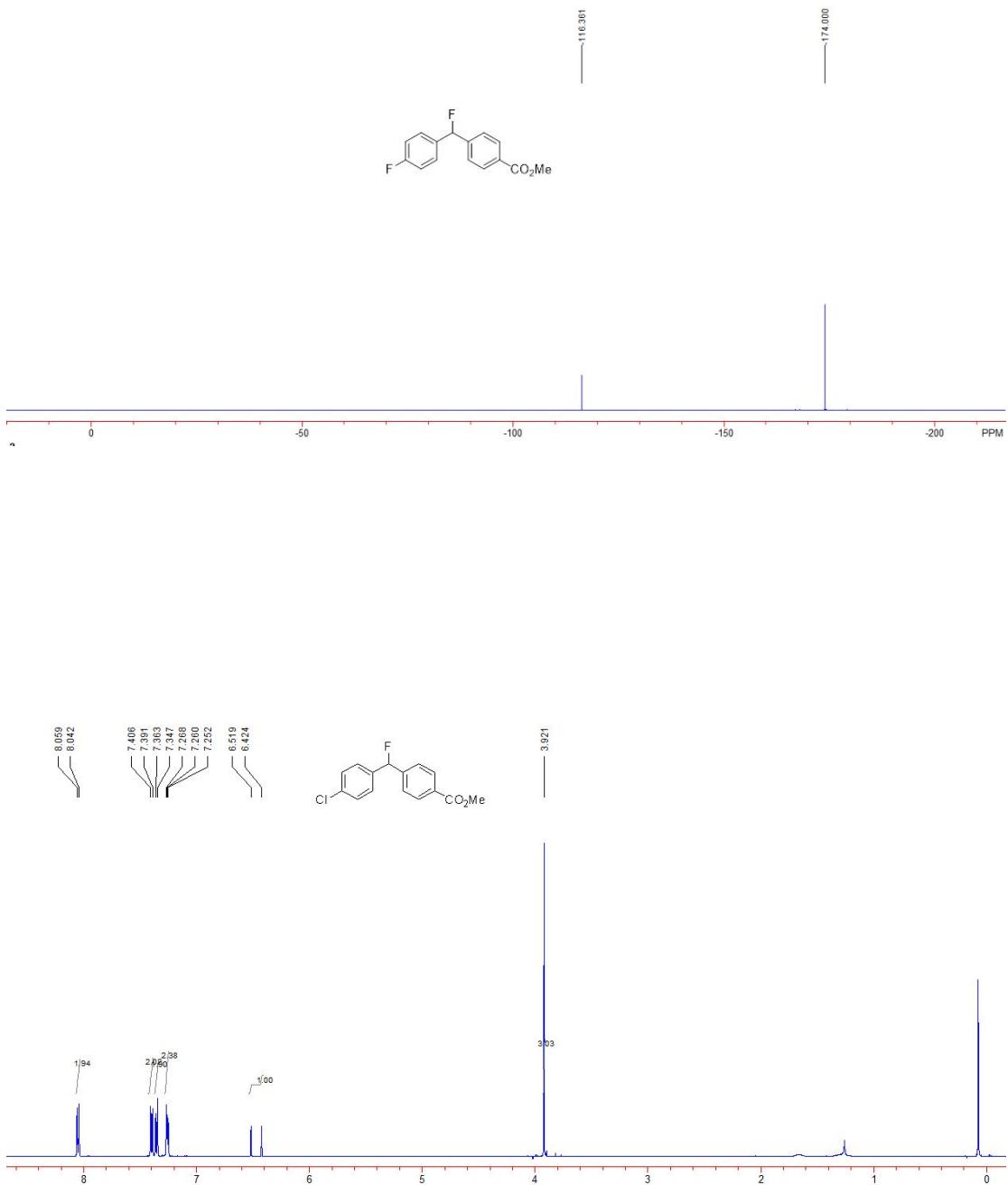
## 11. Spectroscopic data (<sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR spectra)

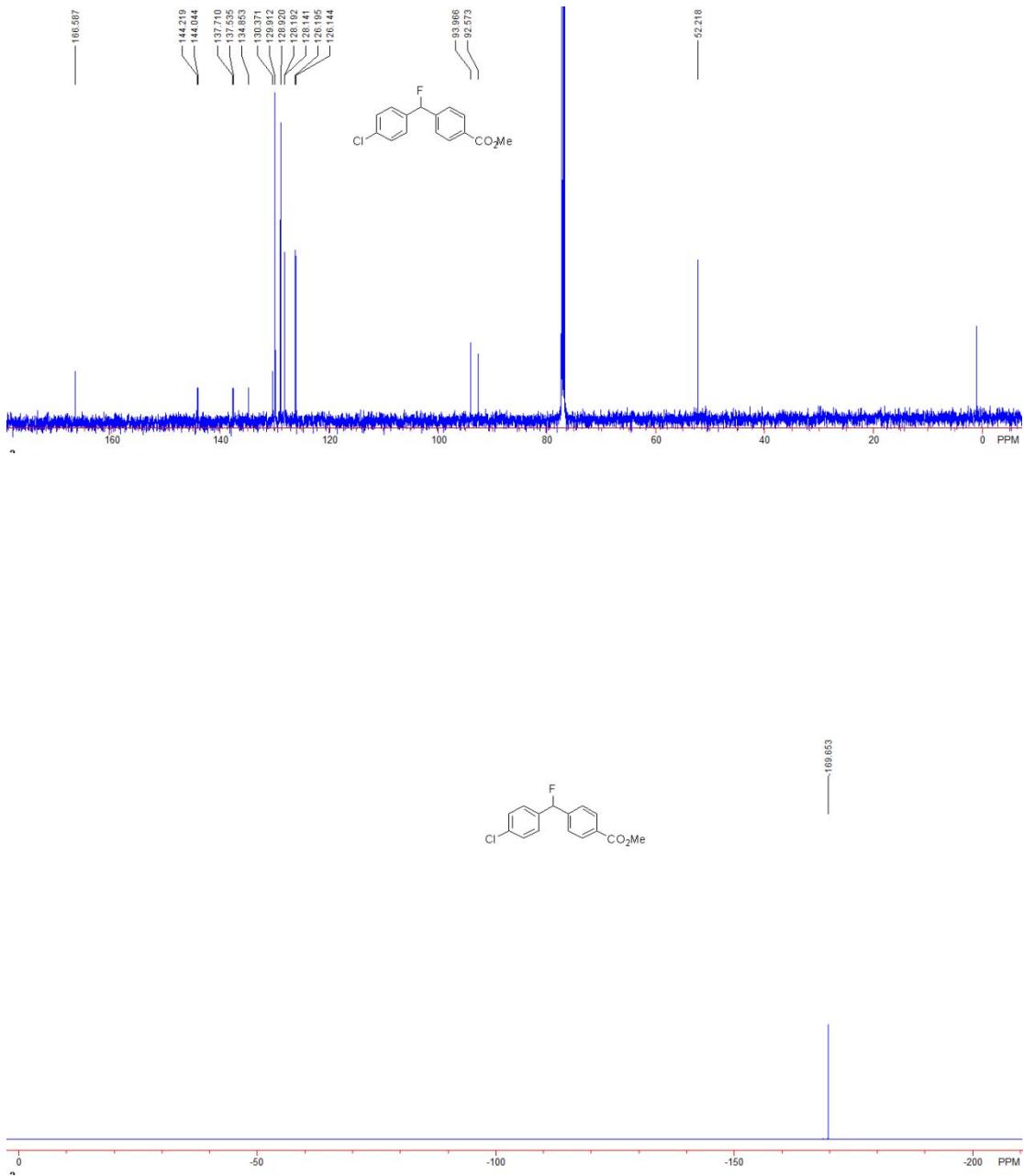


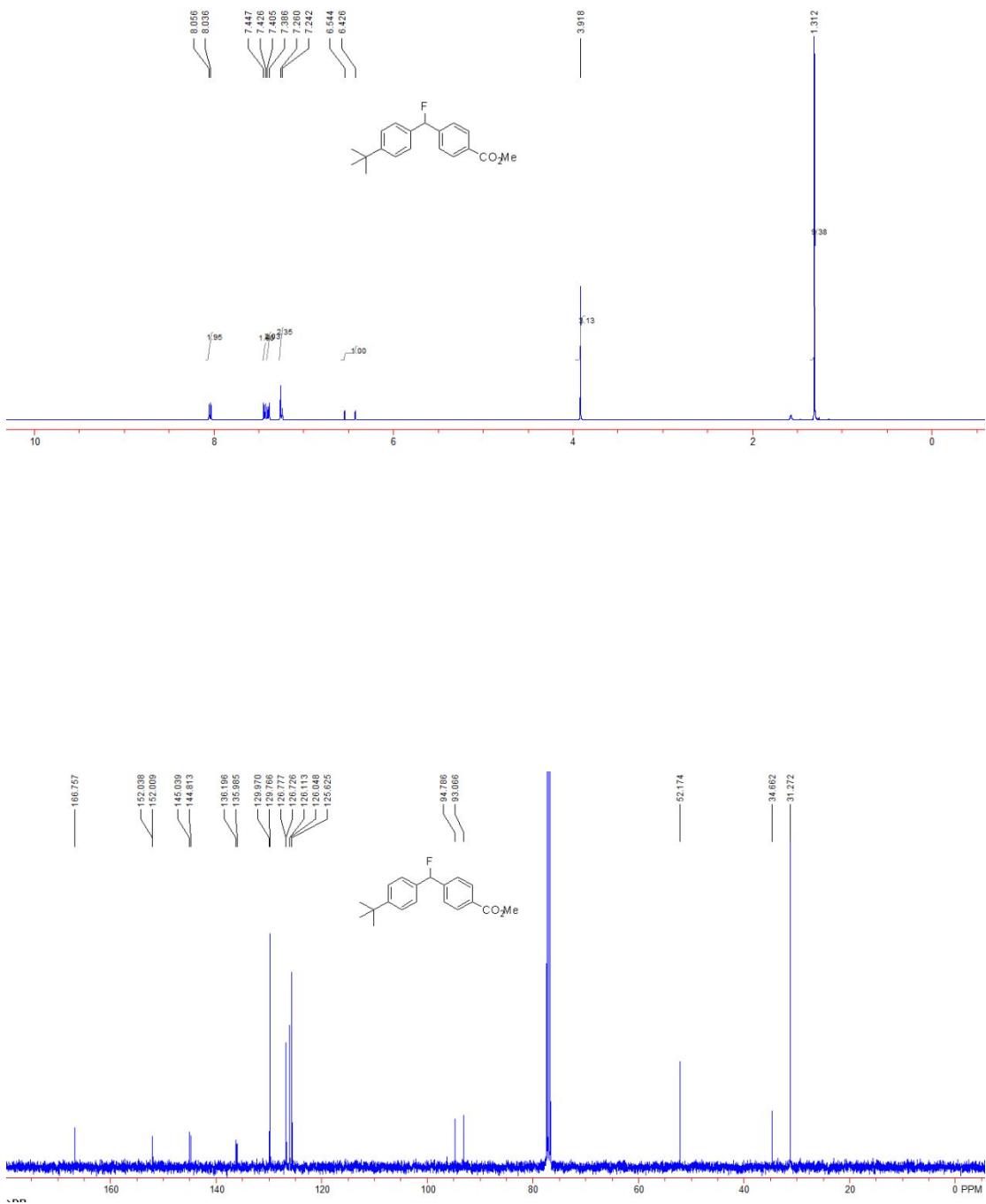


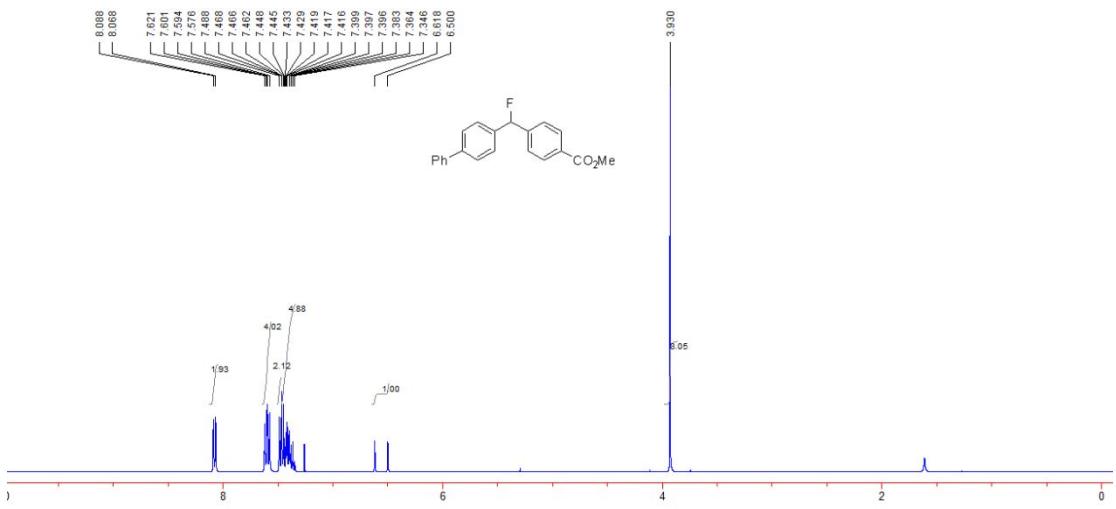
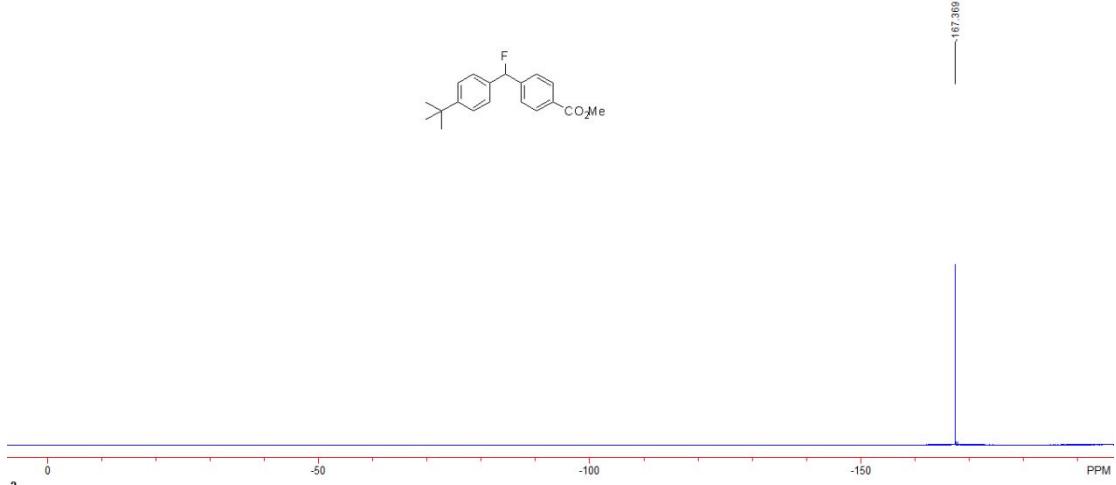


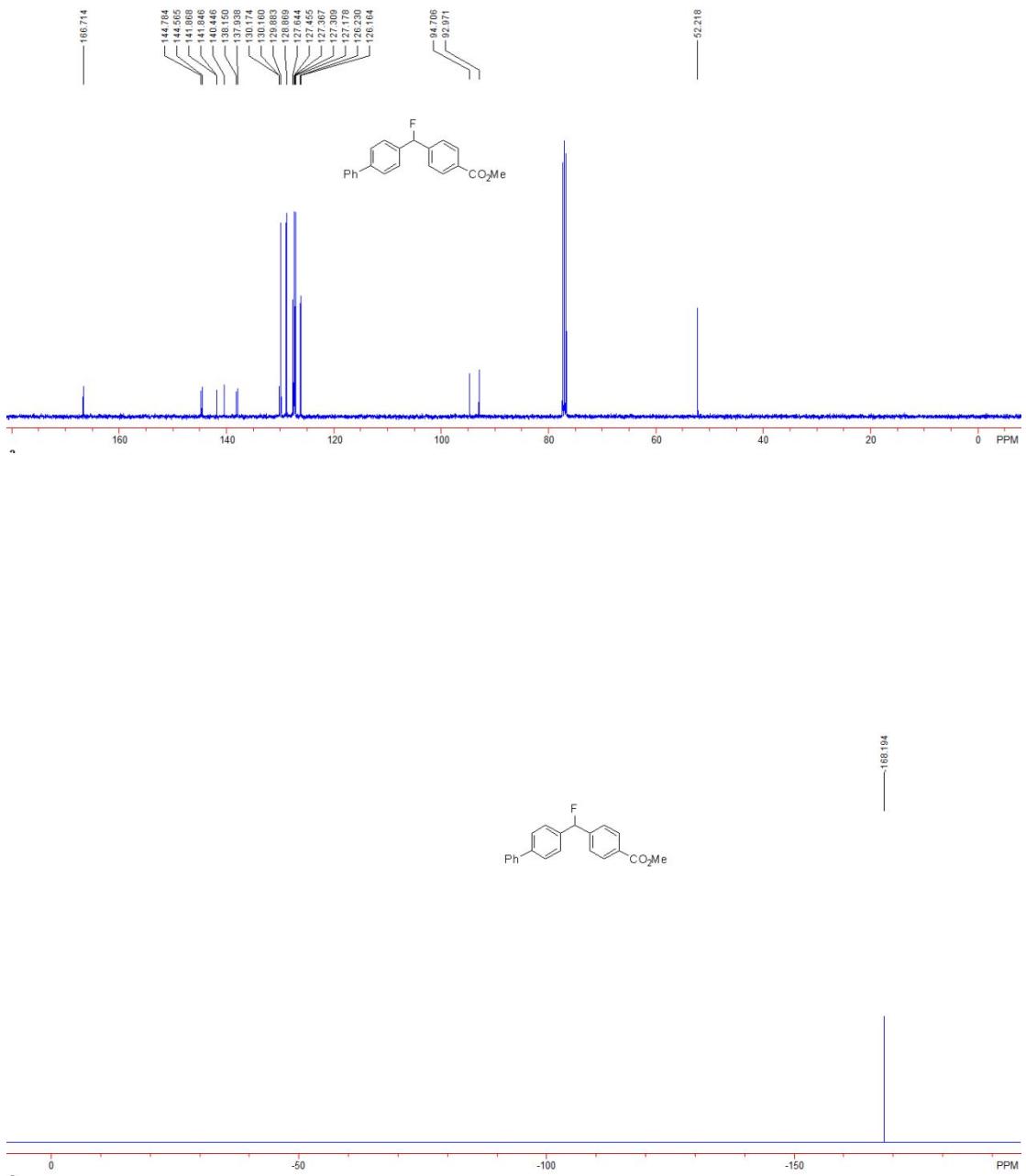


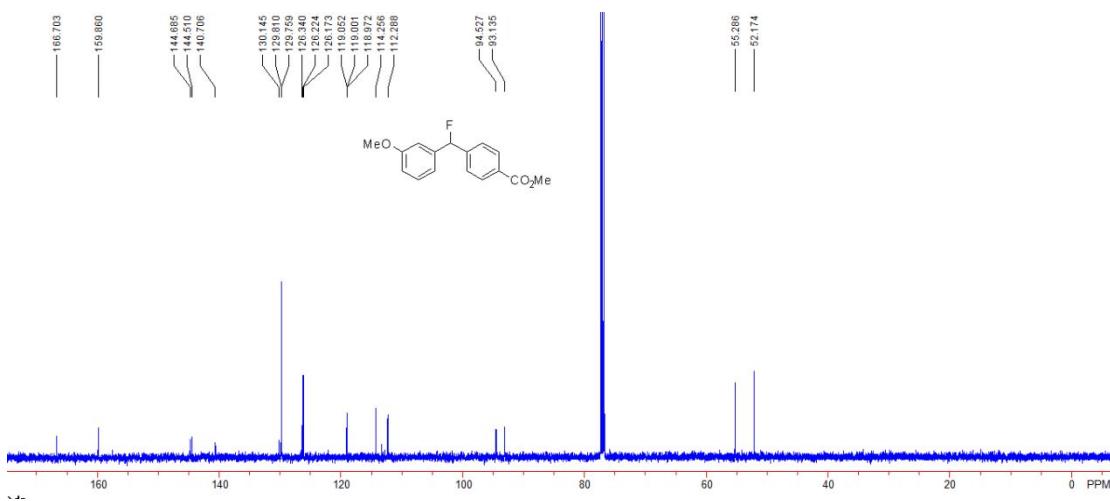
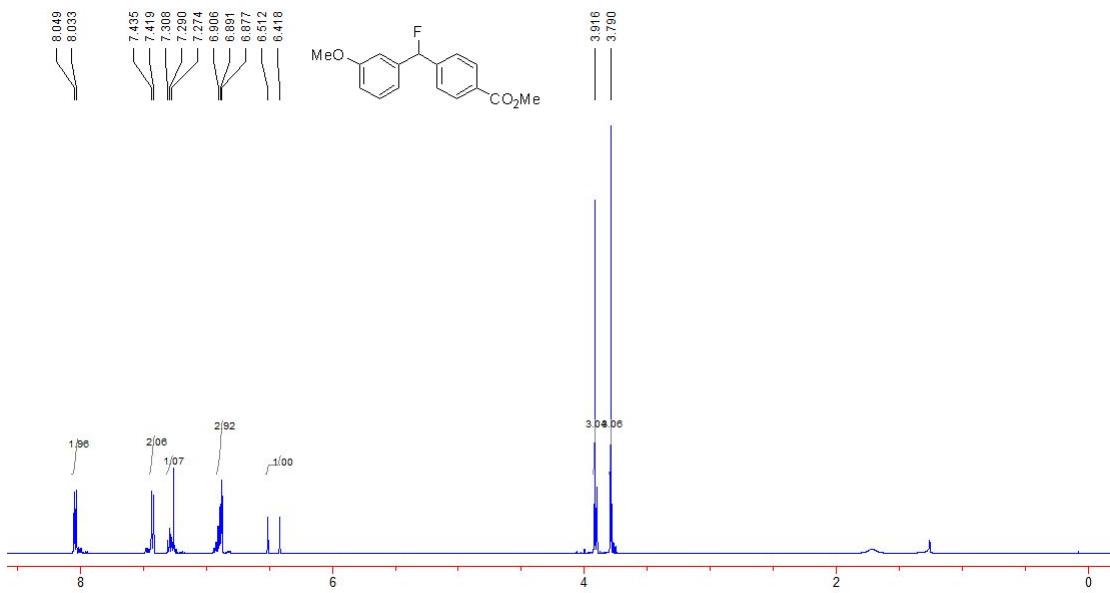


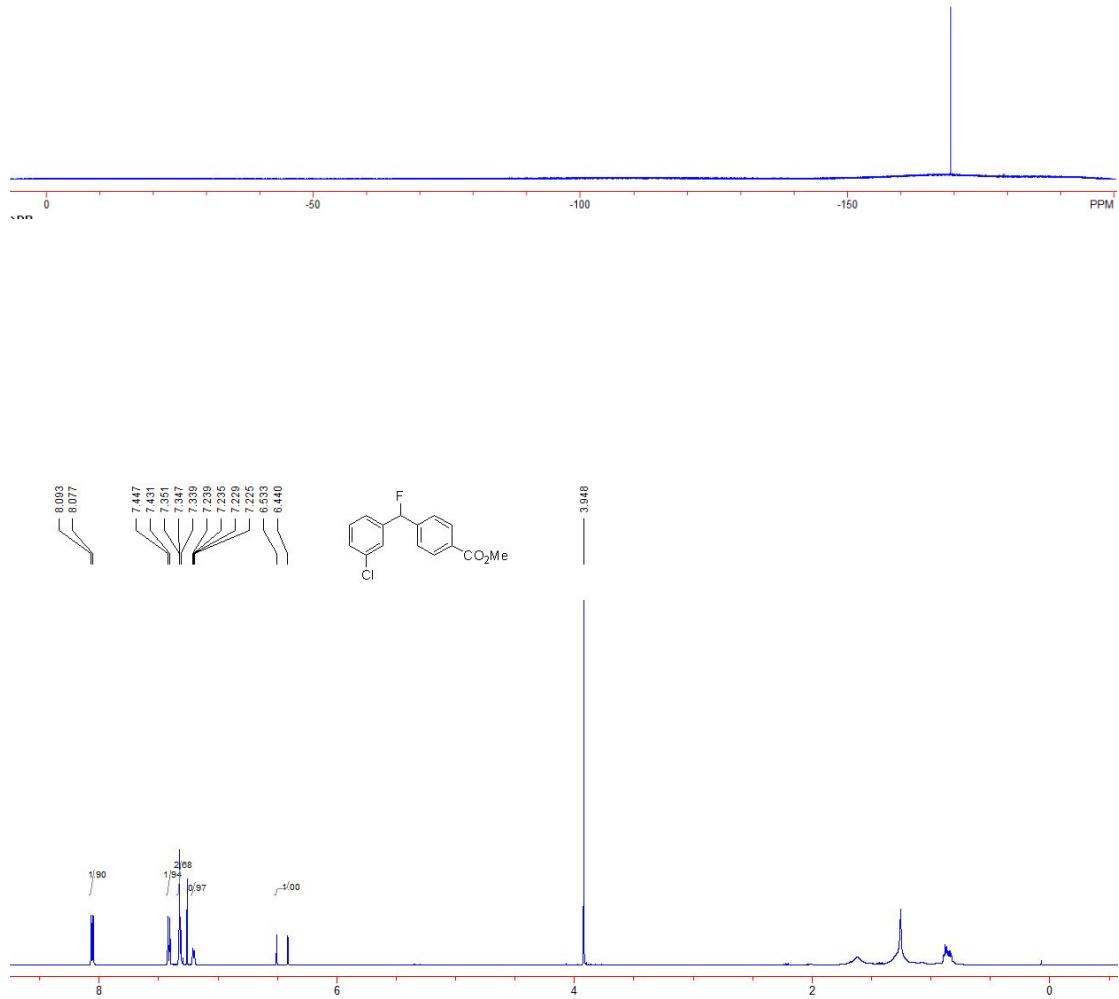
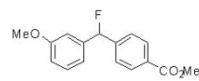


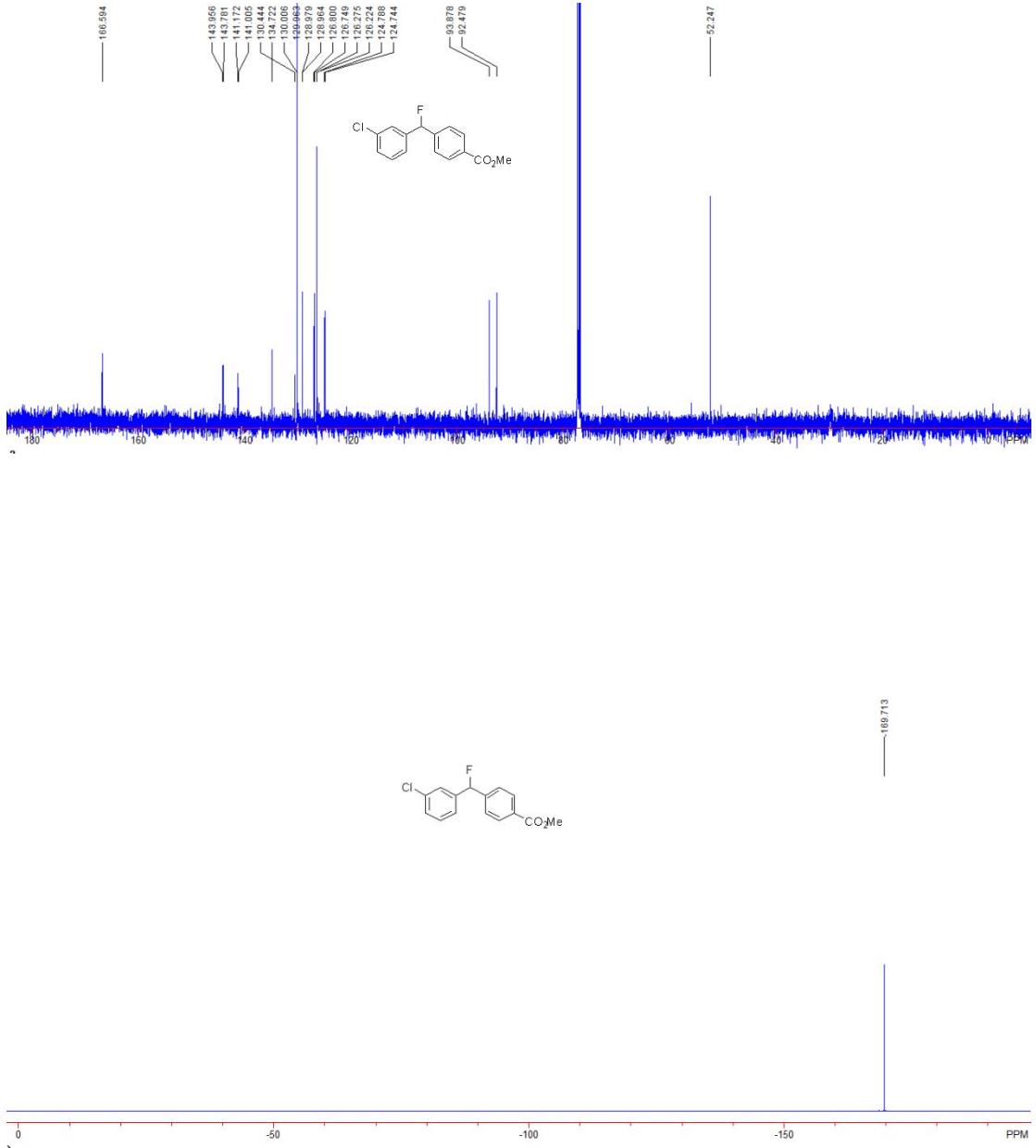


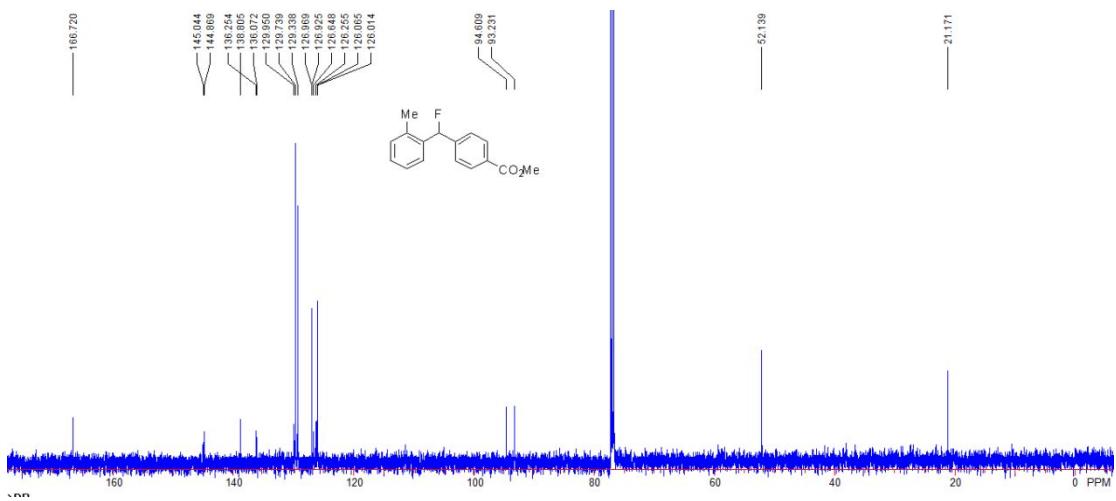
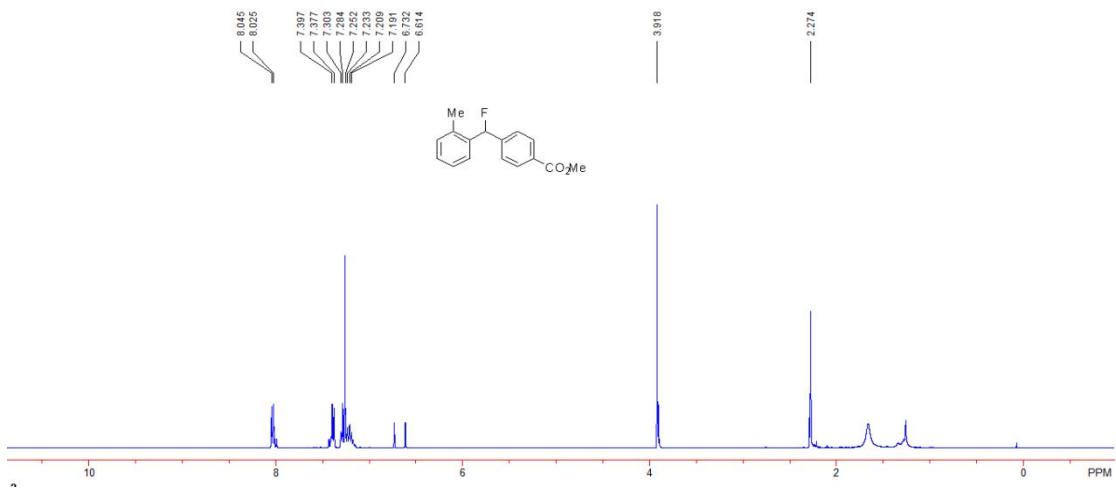


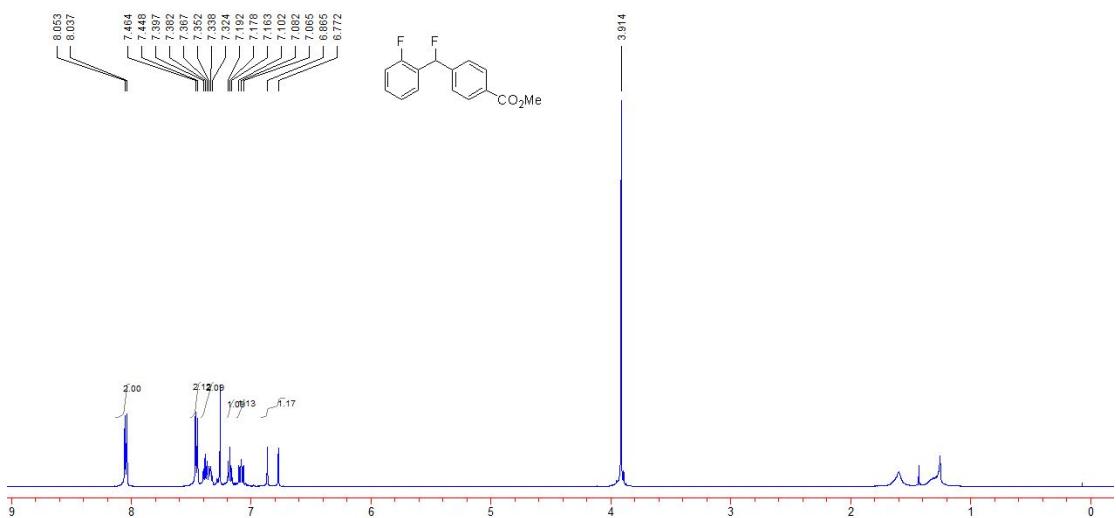
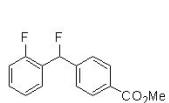
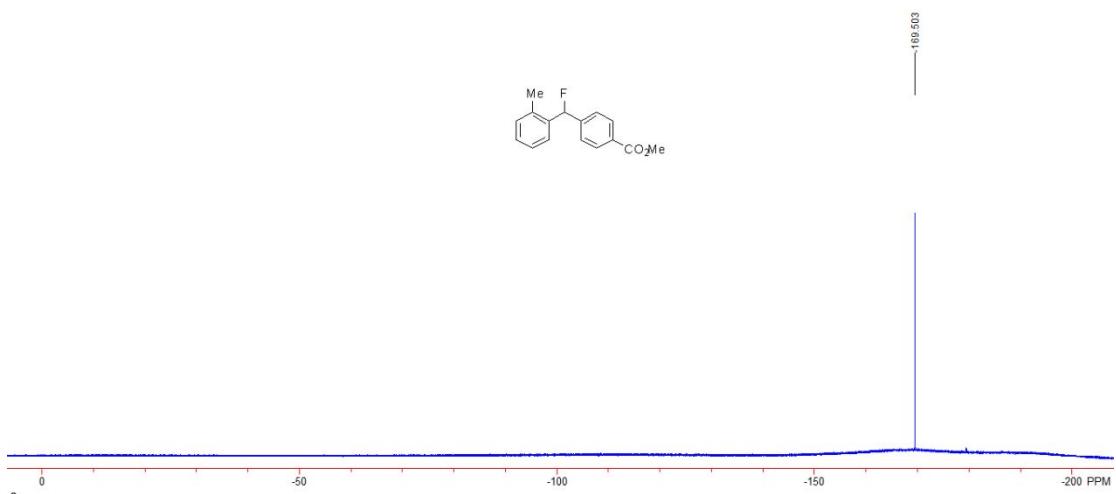
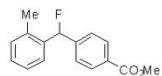


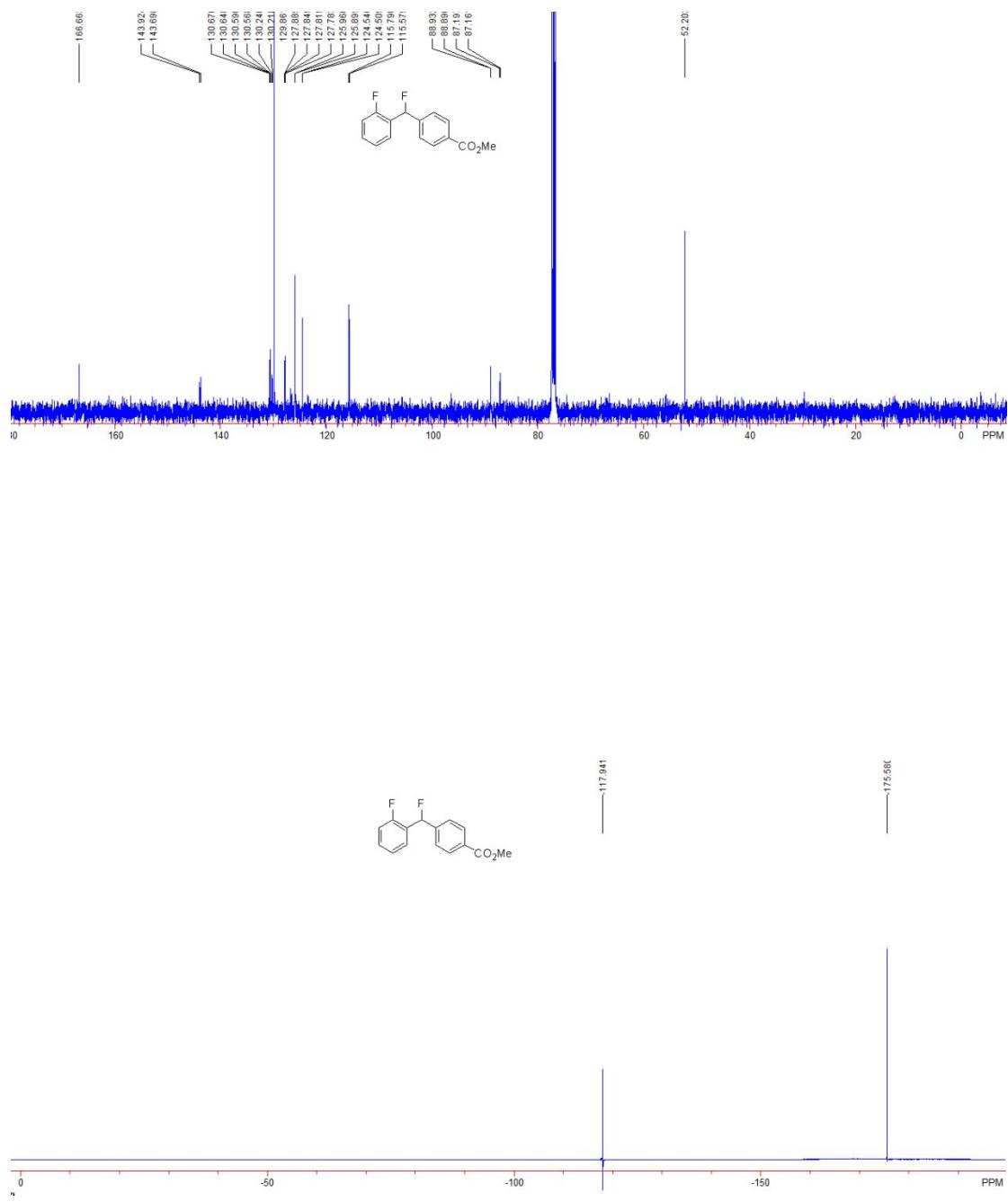


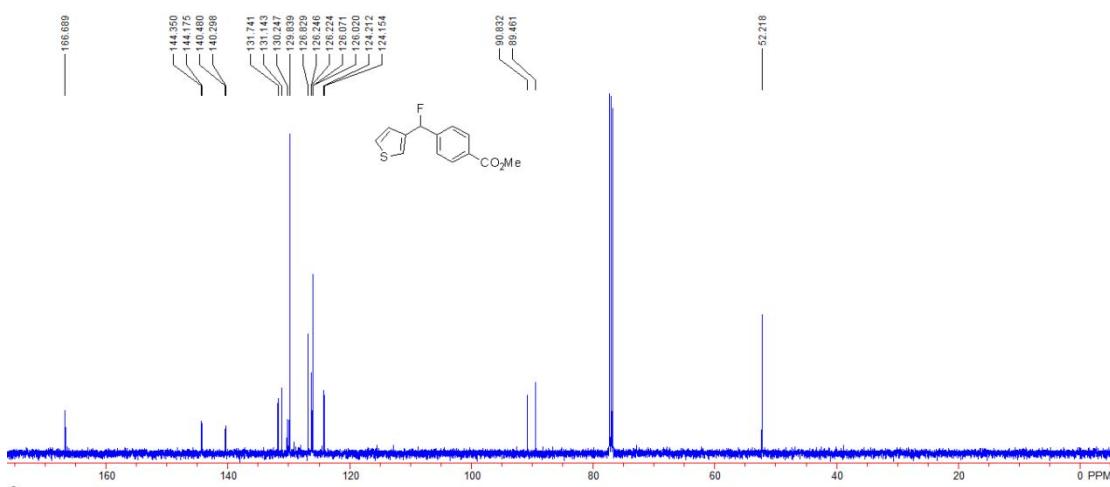
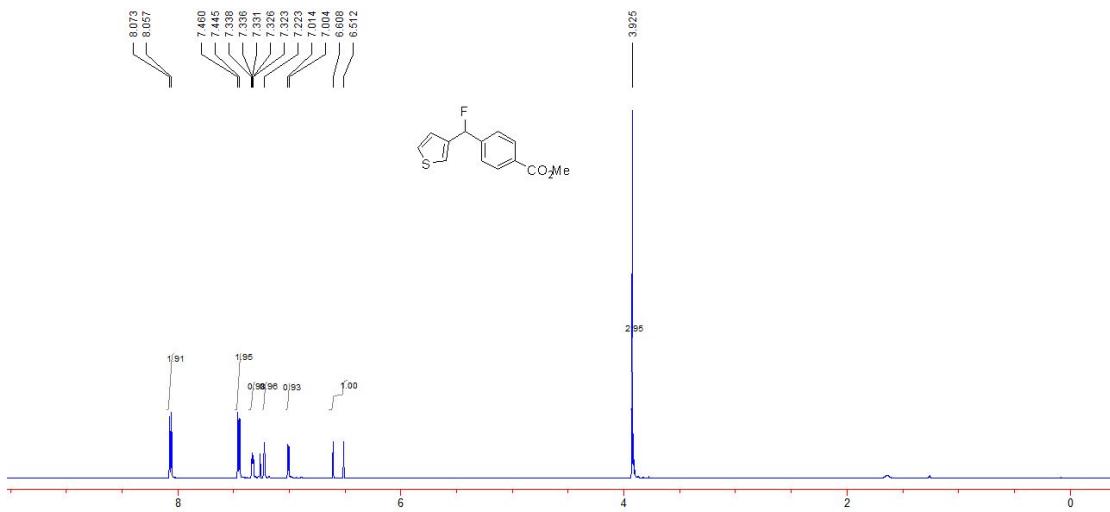


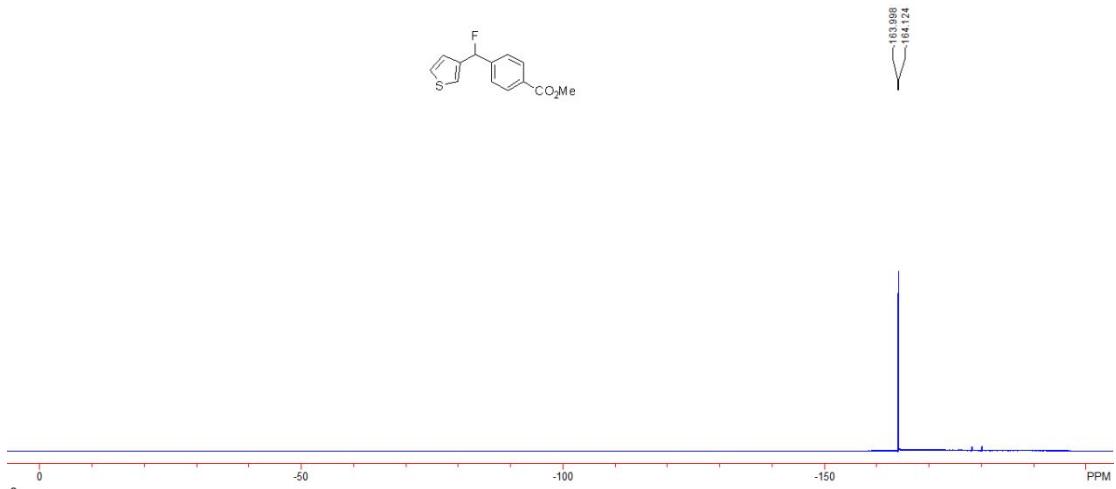


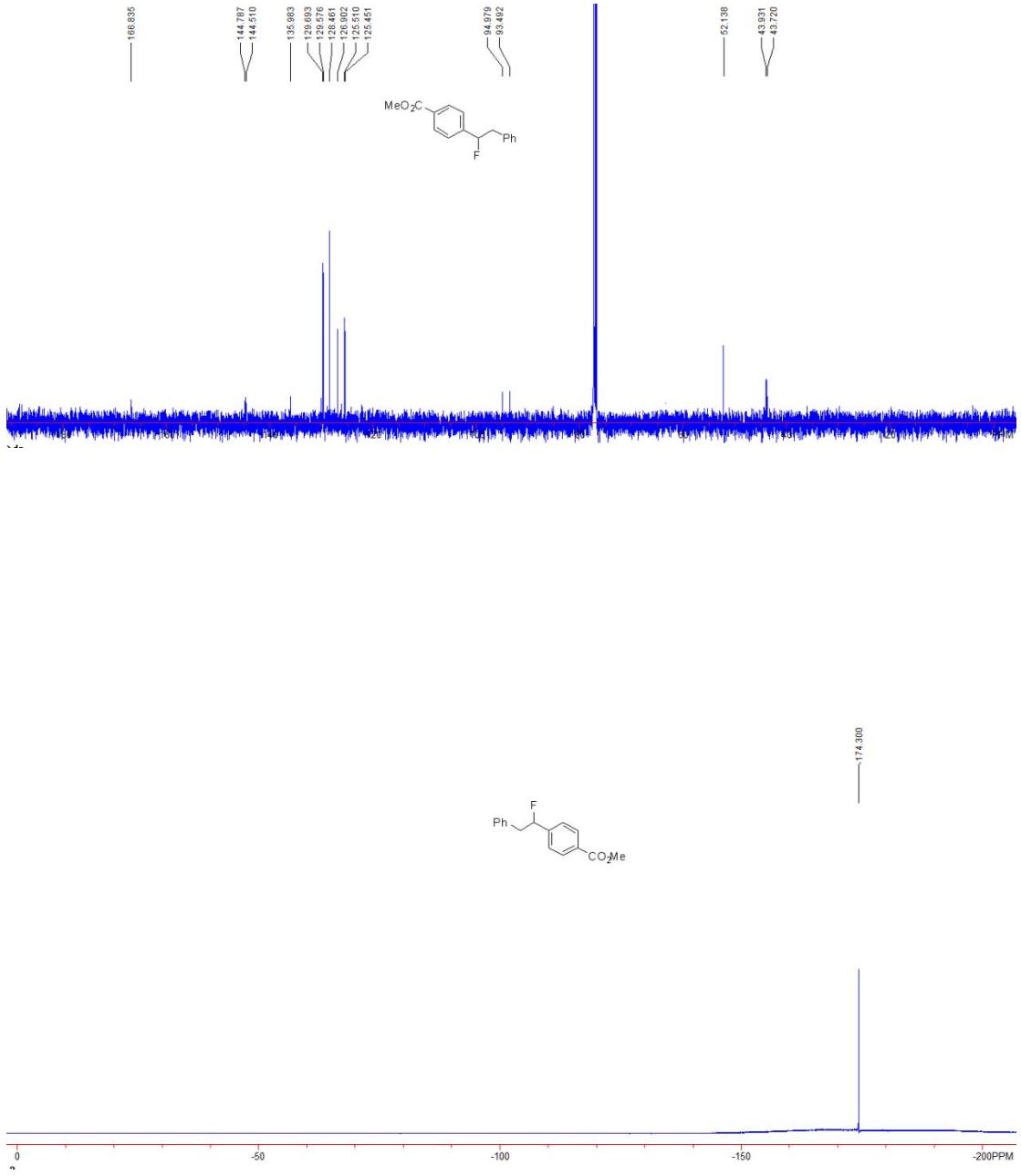


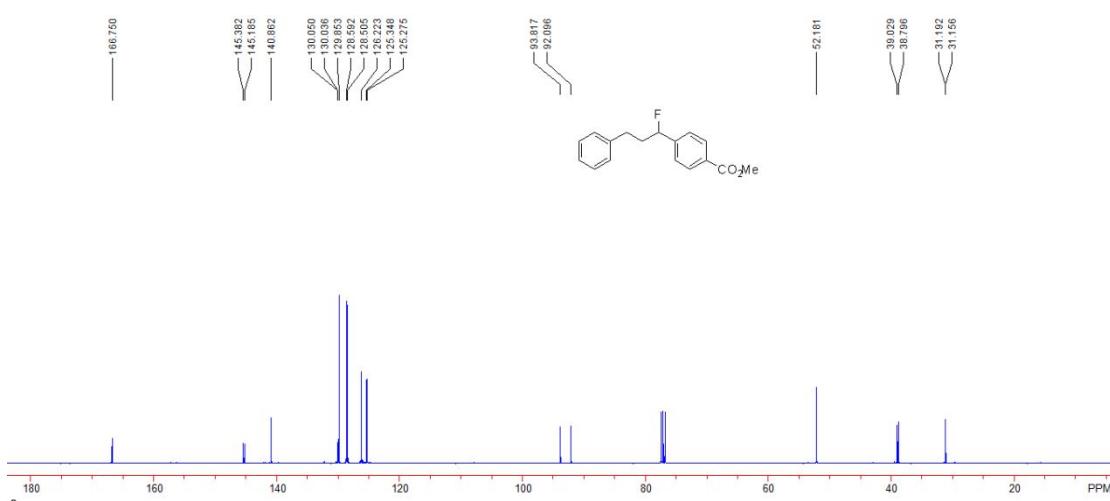
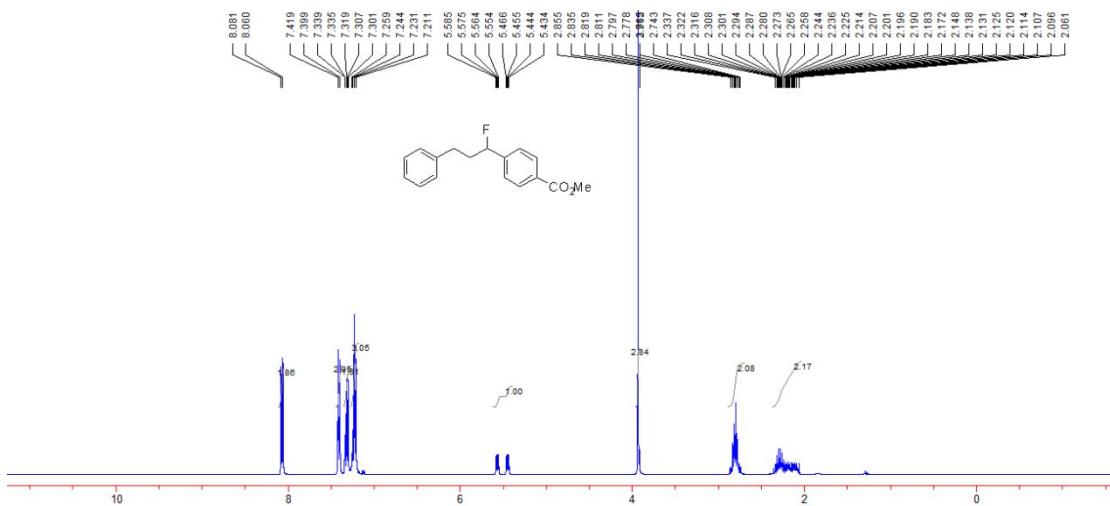


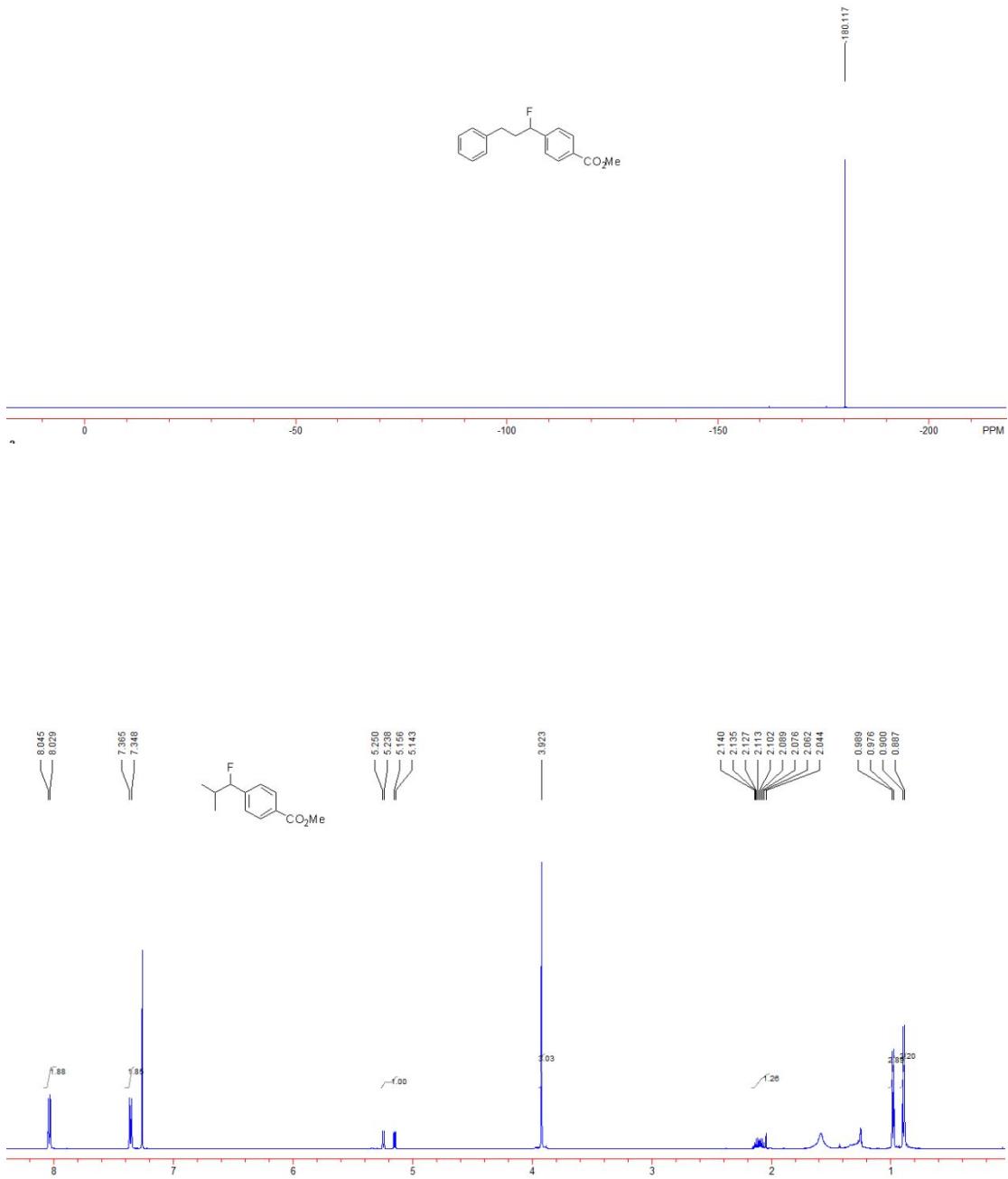


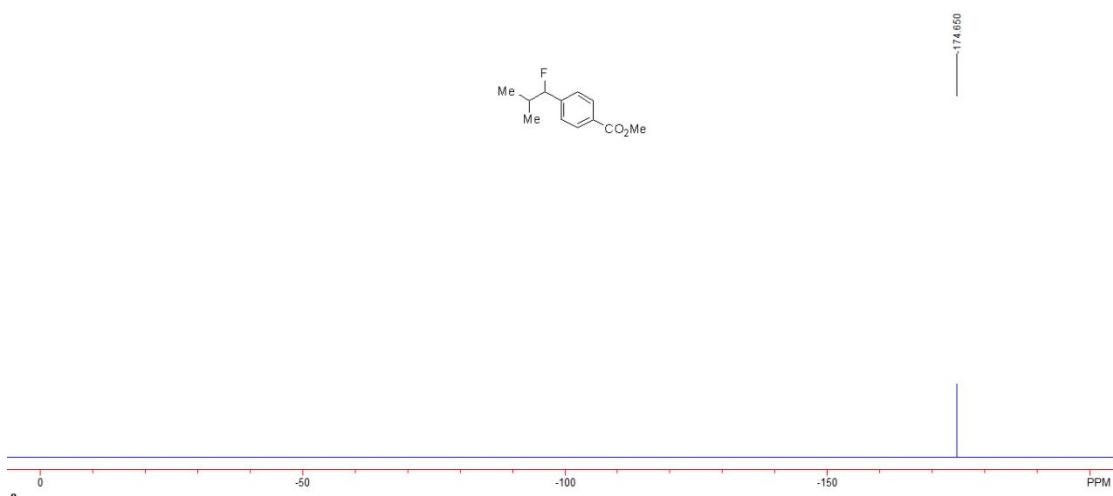
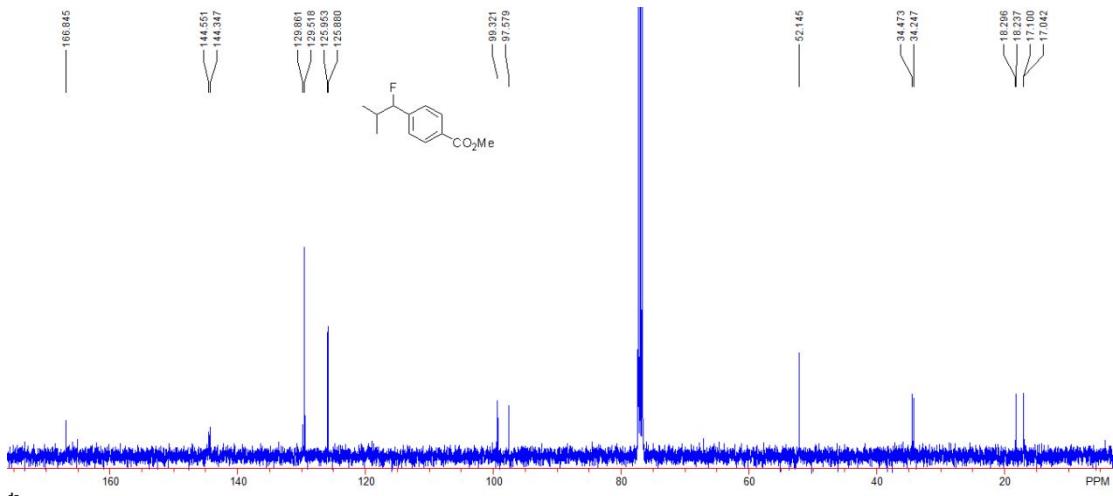


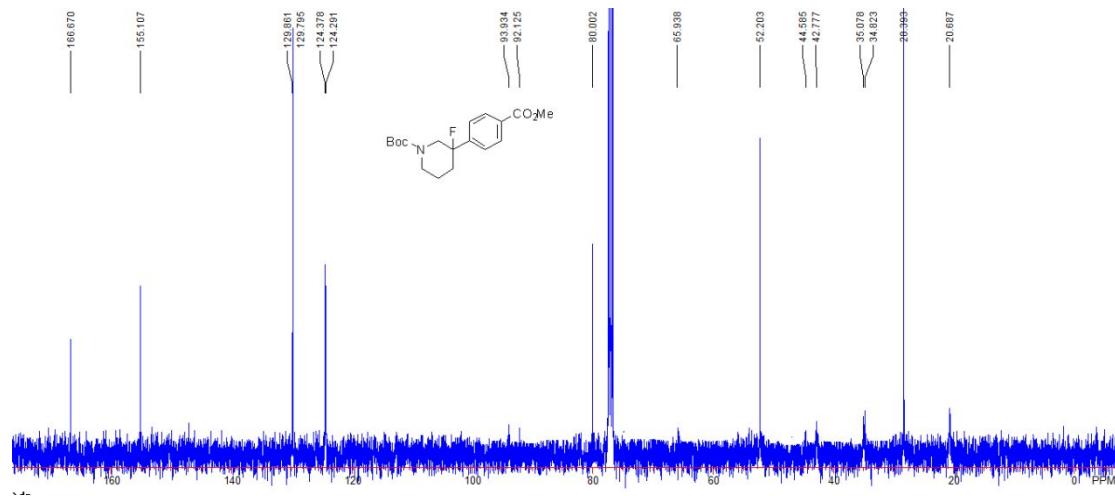
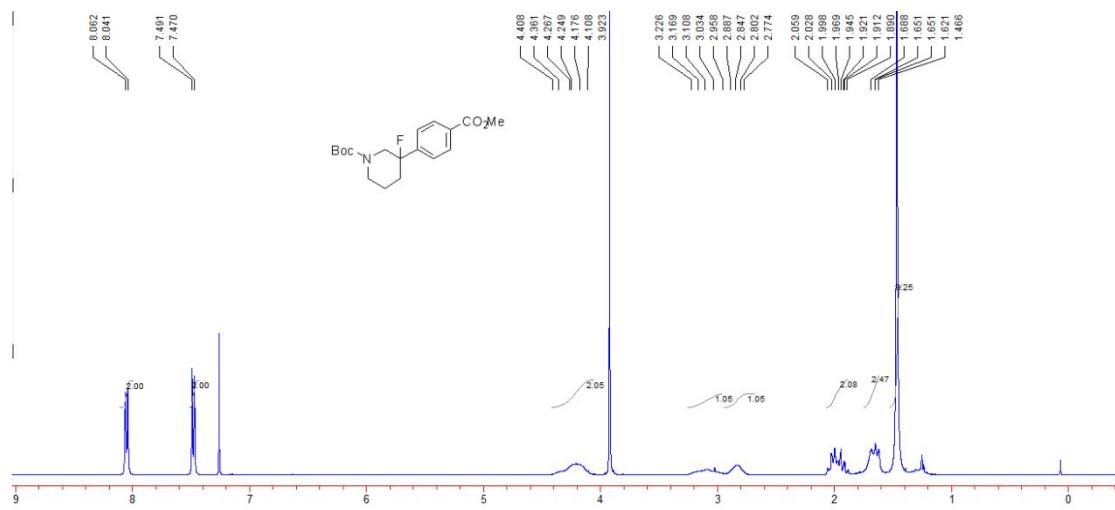


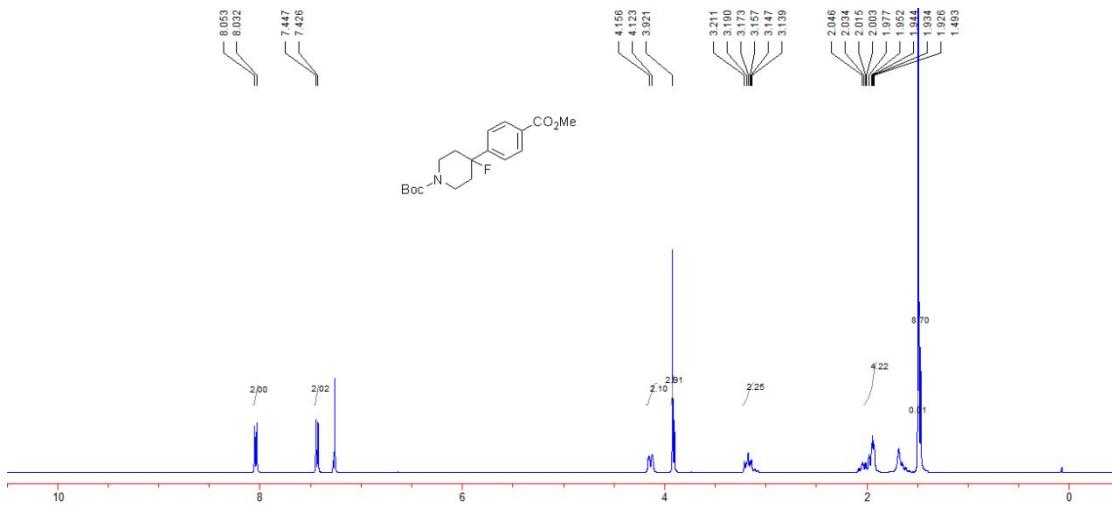
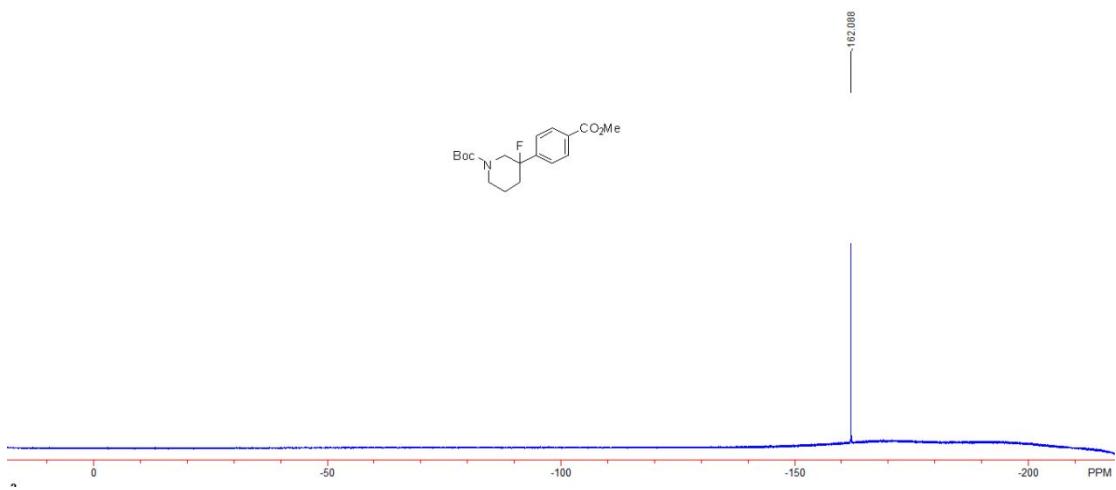


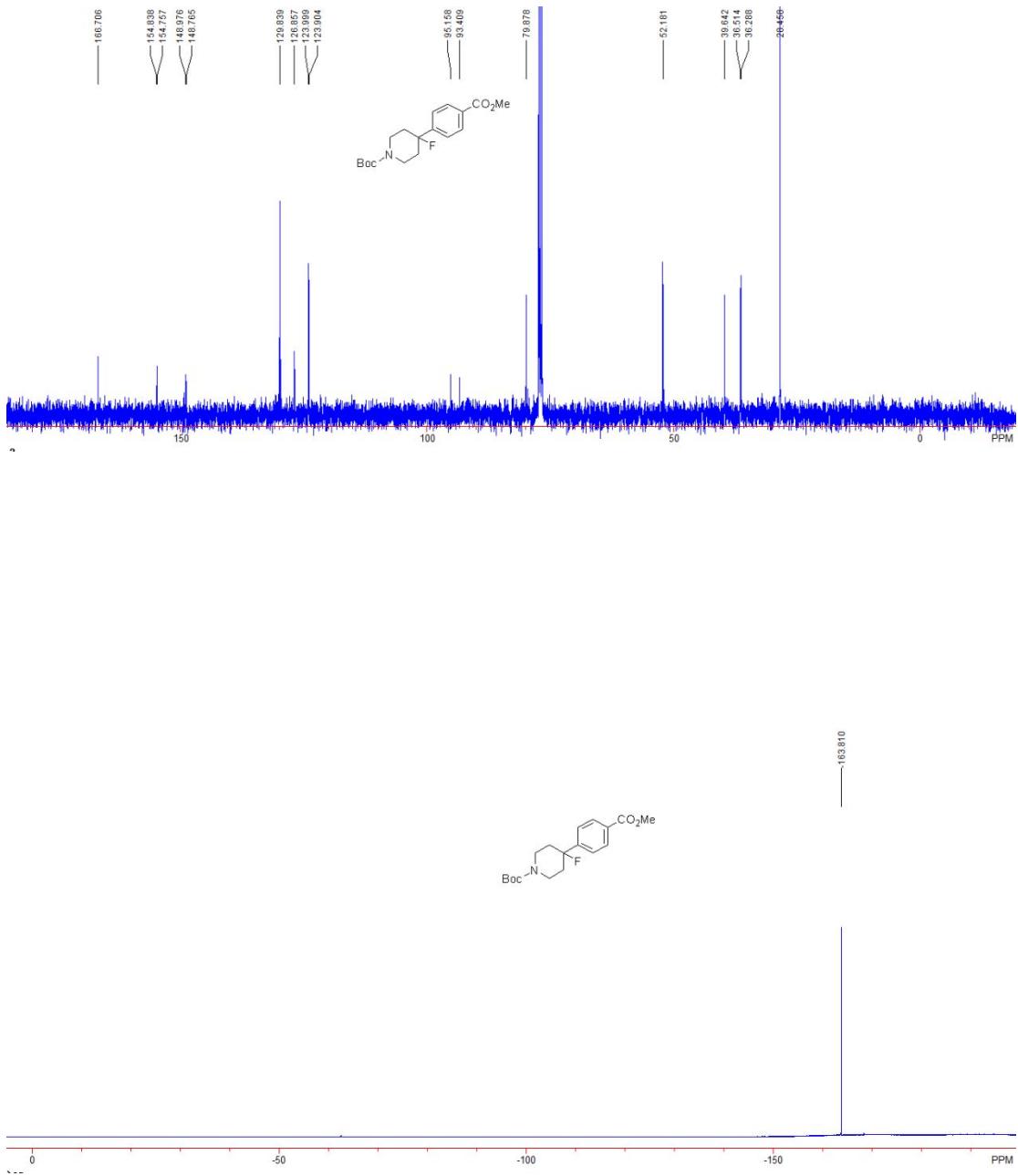


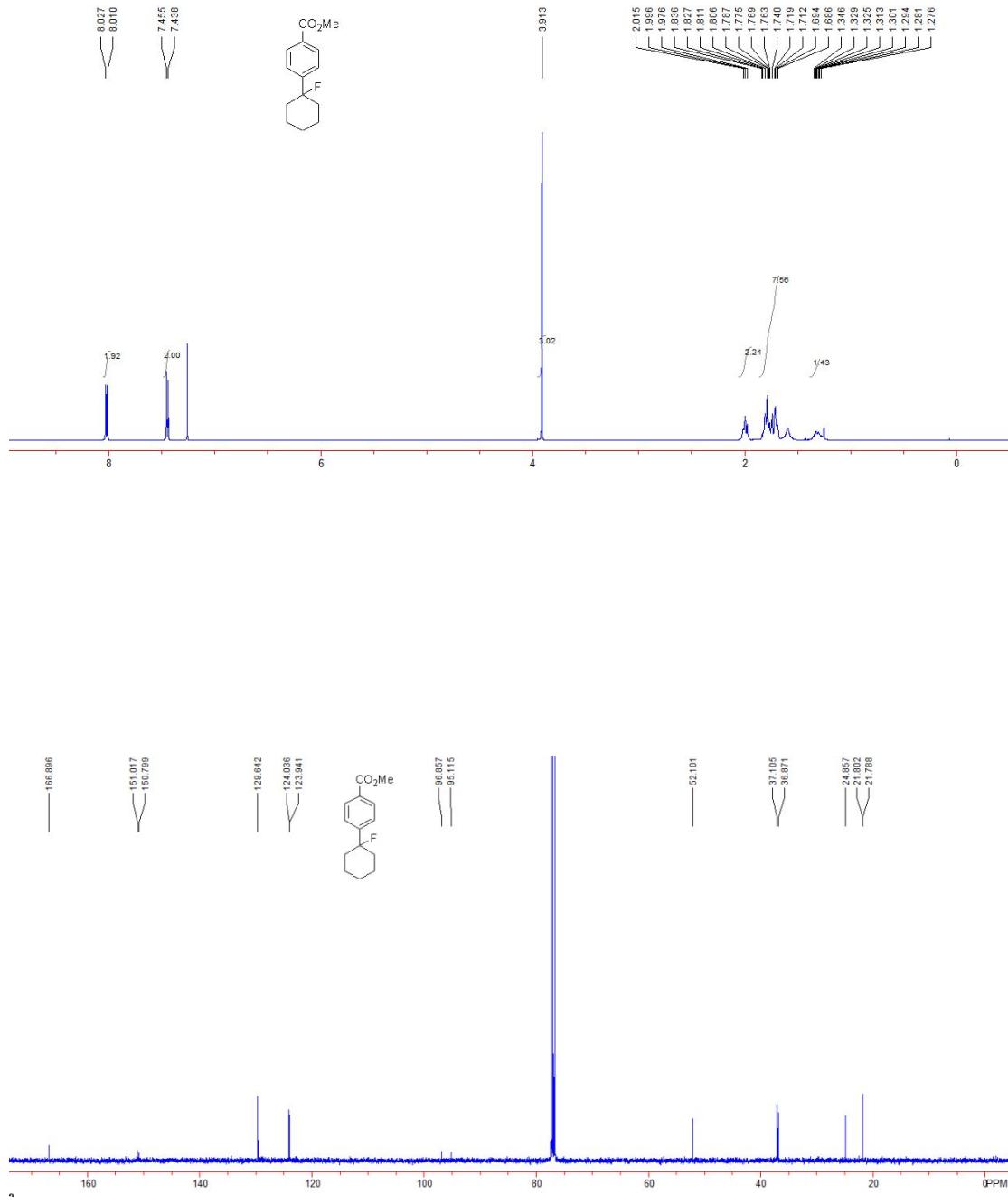


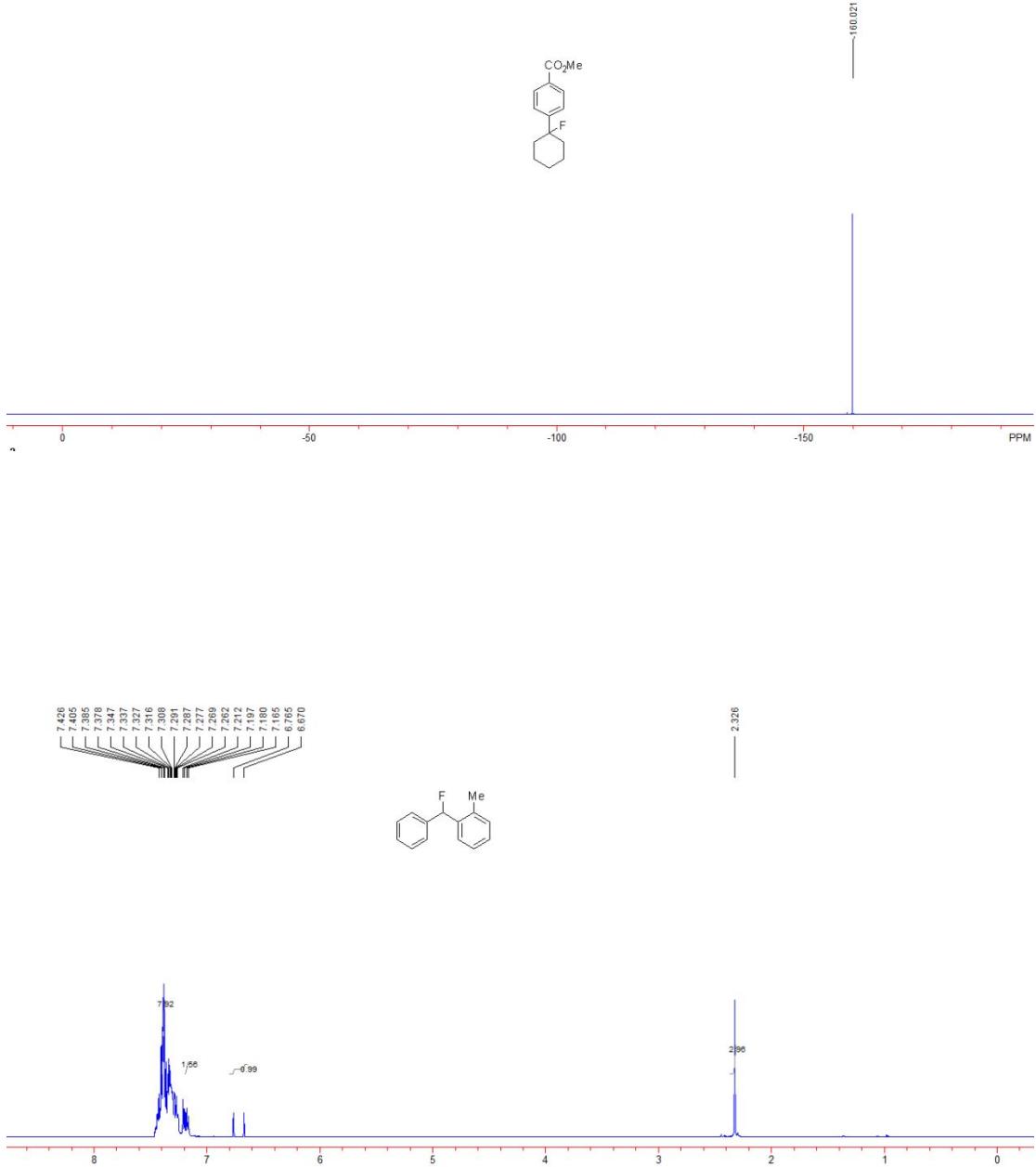


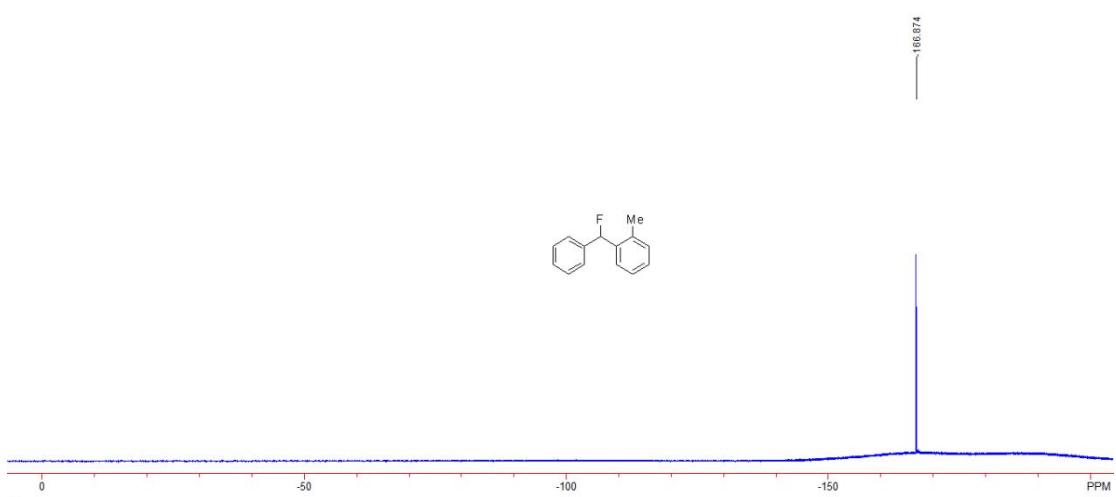
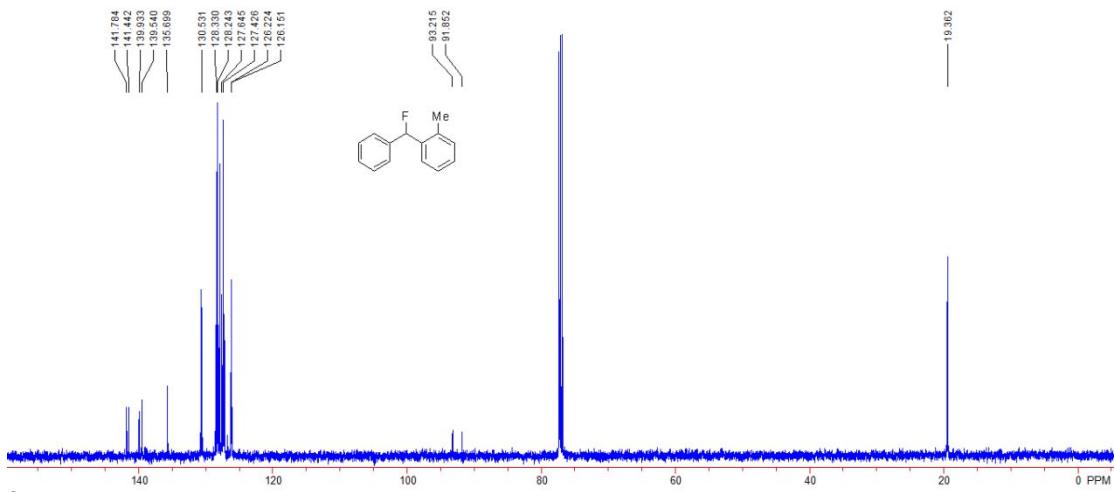


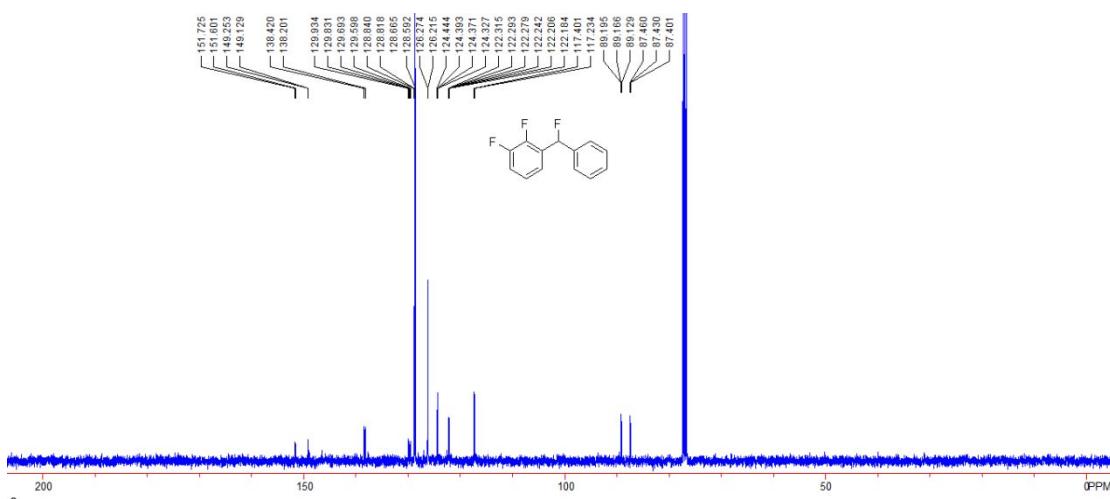
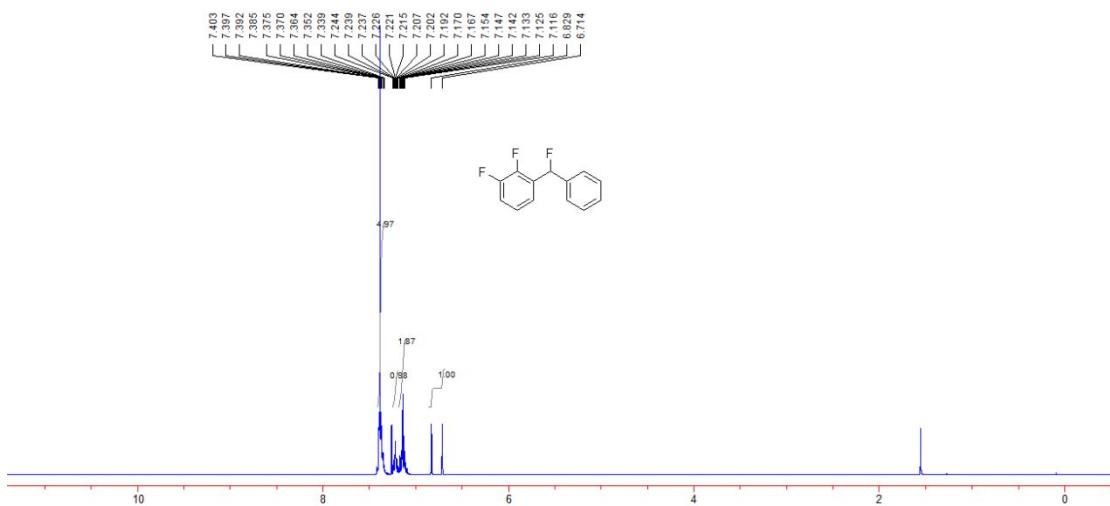


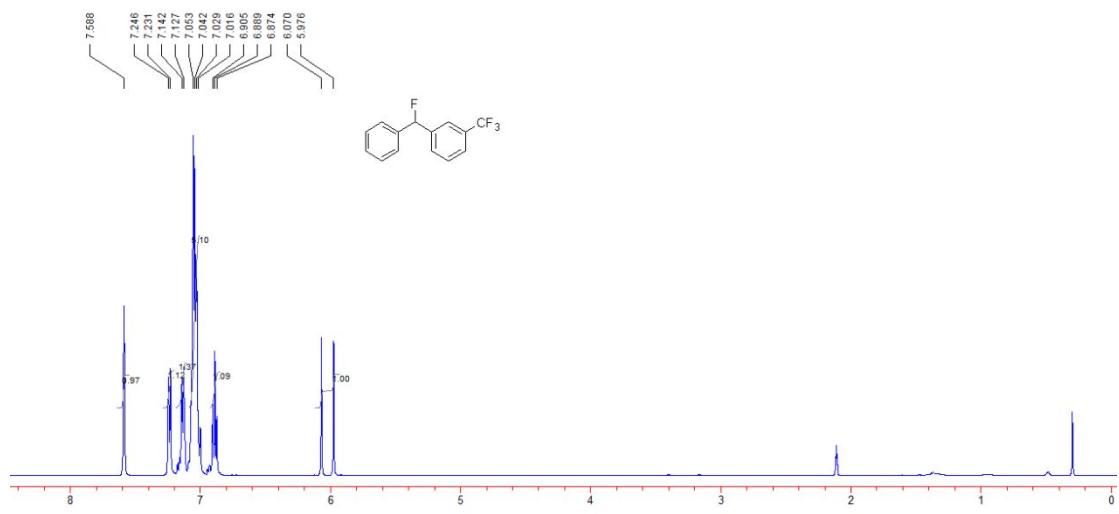
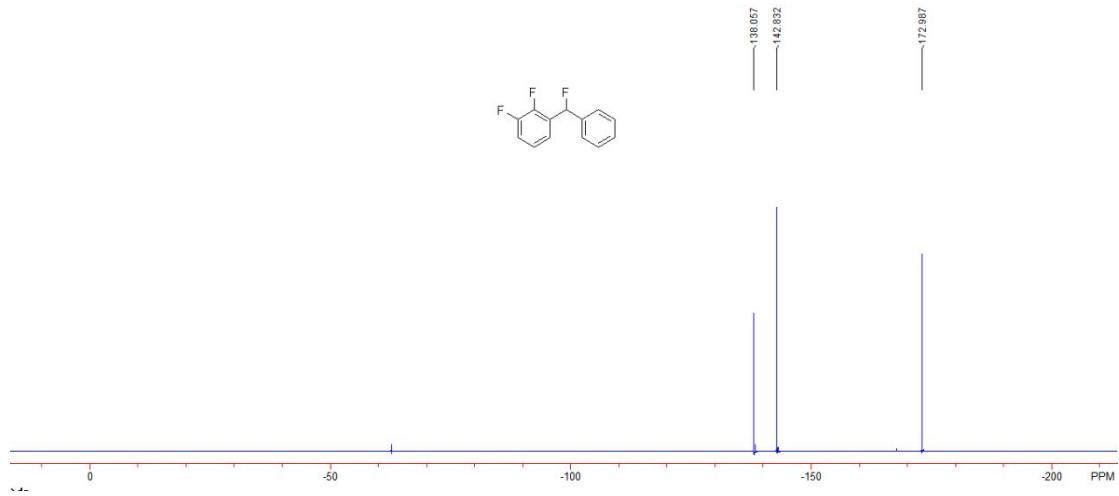


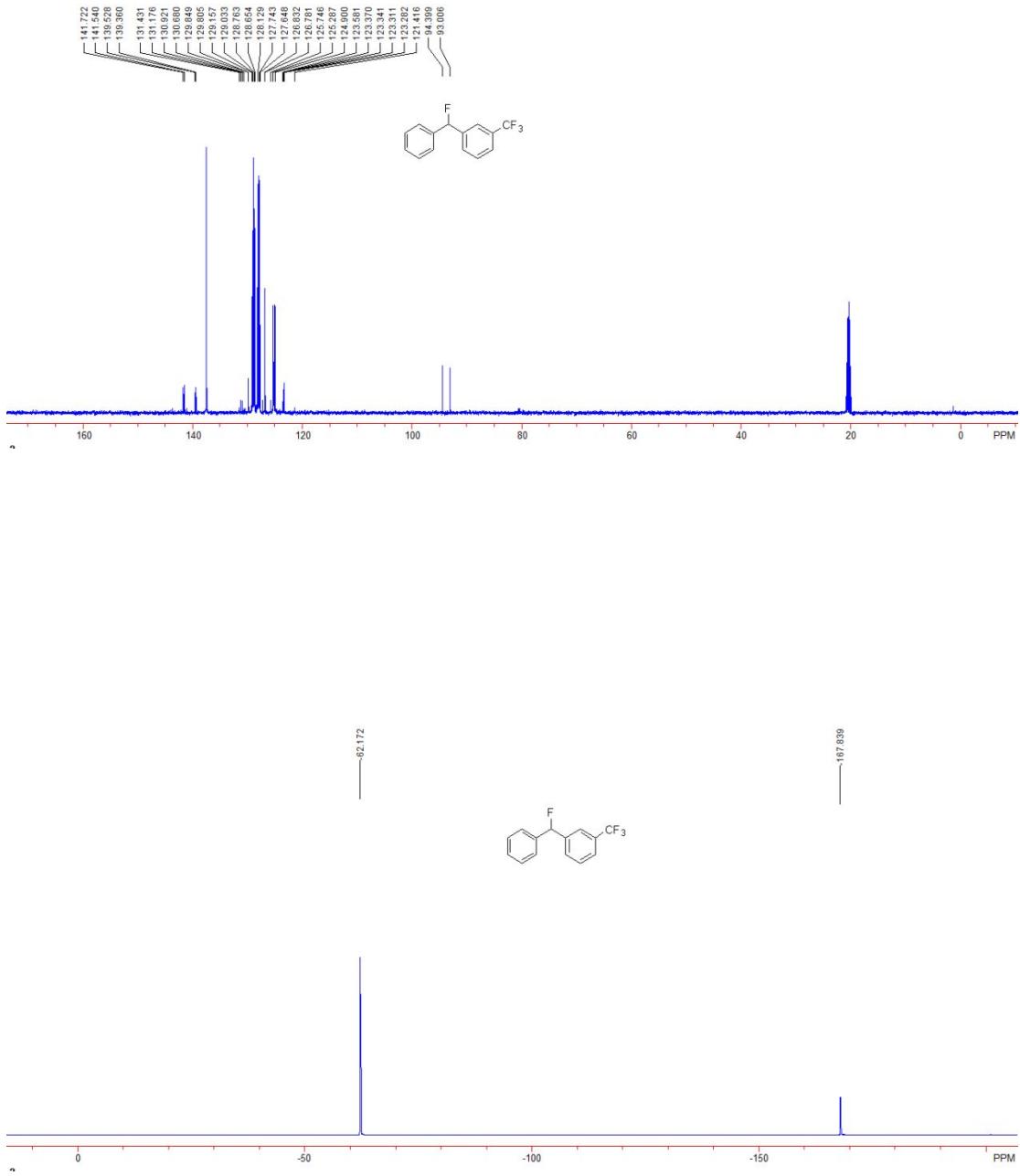


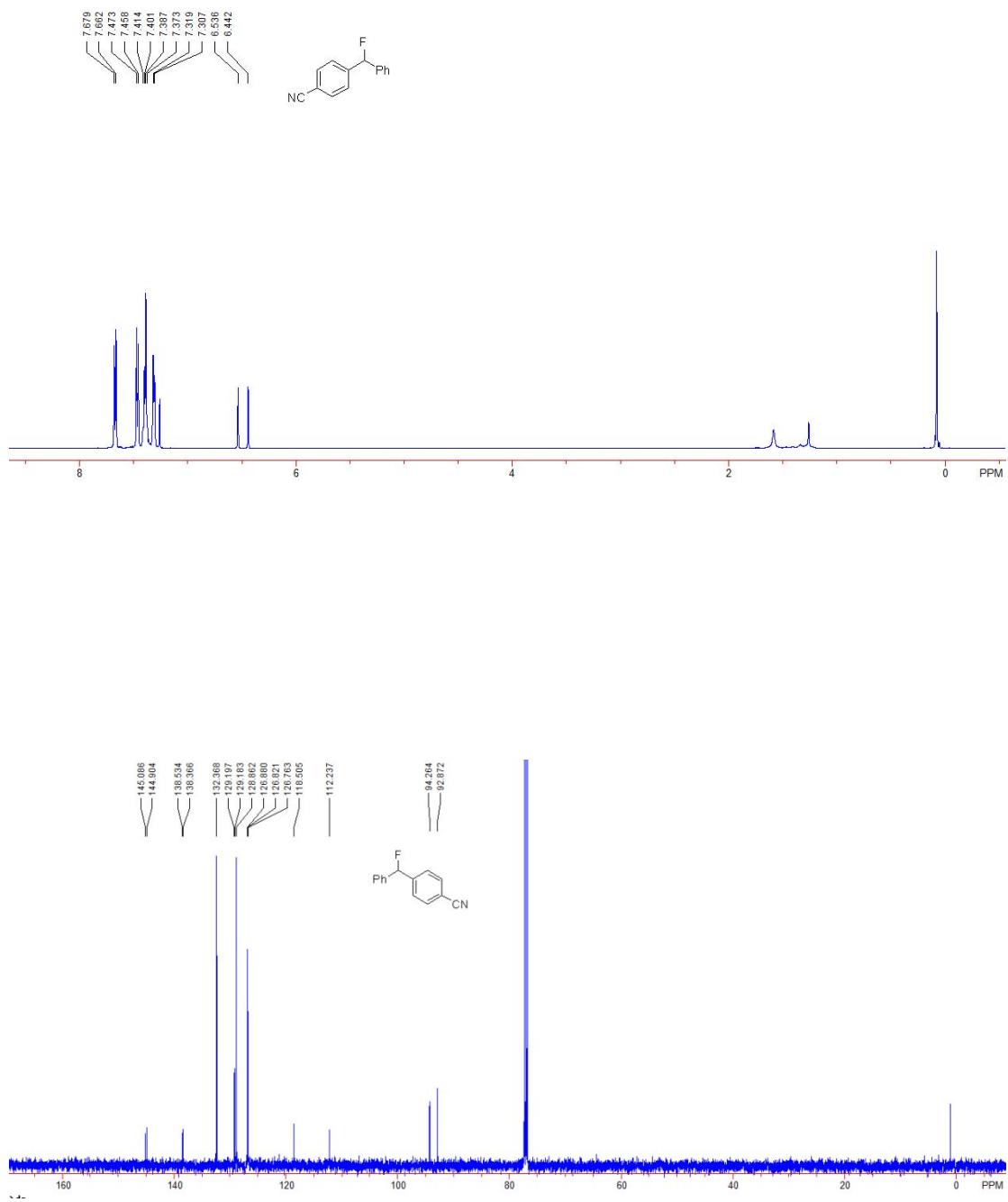


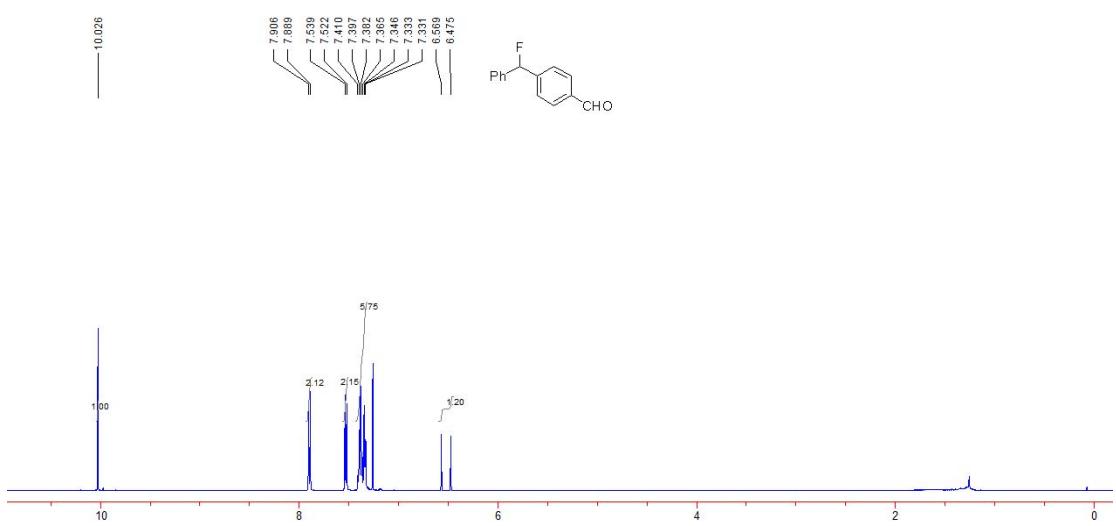
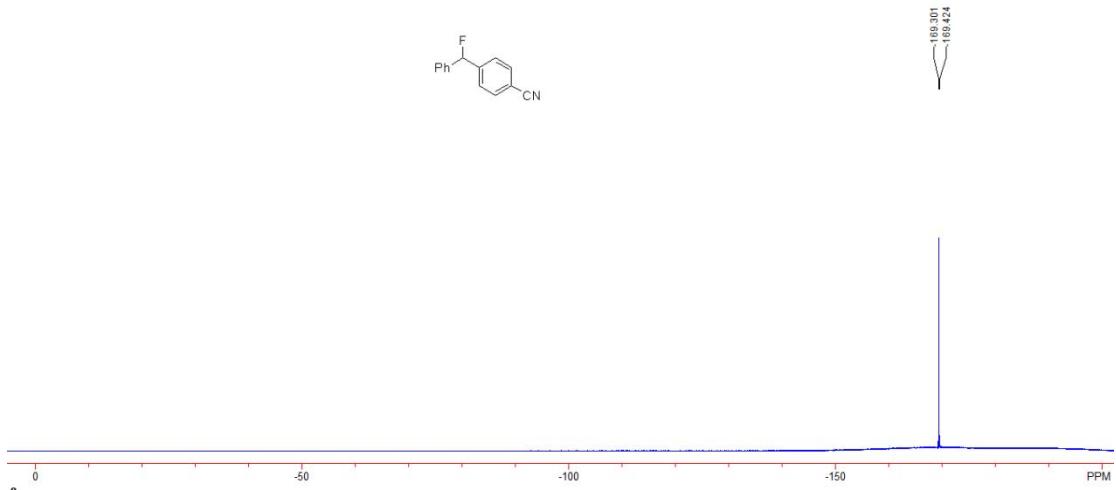


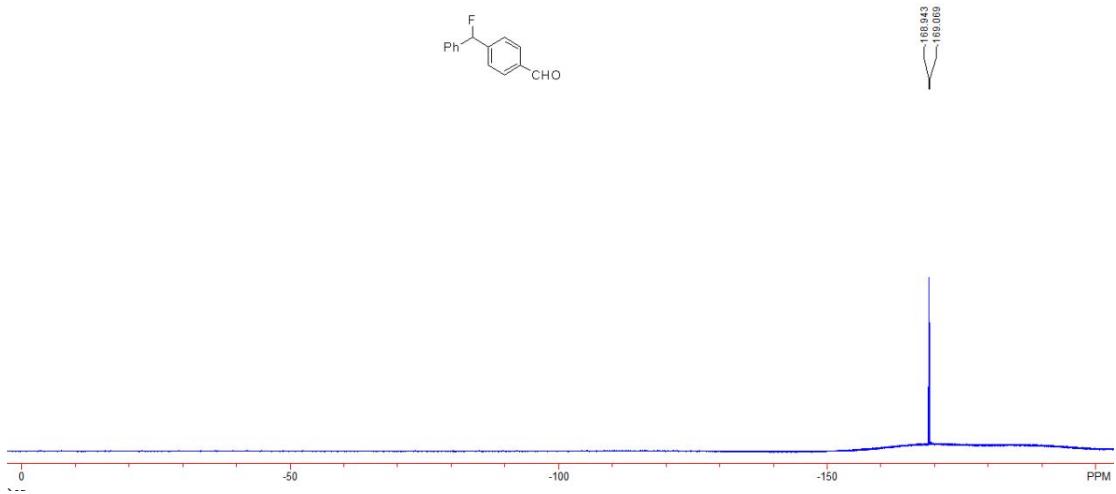
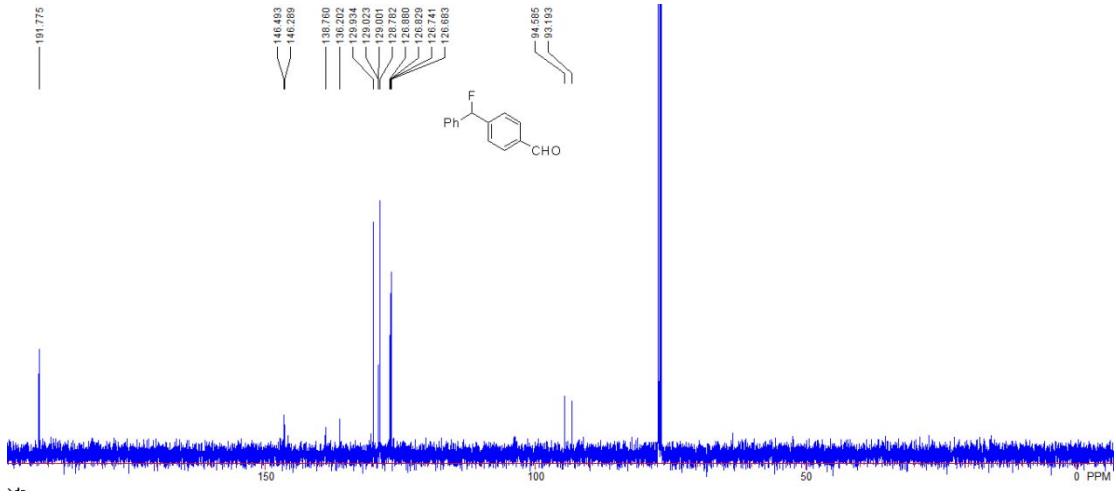


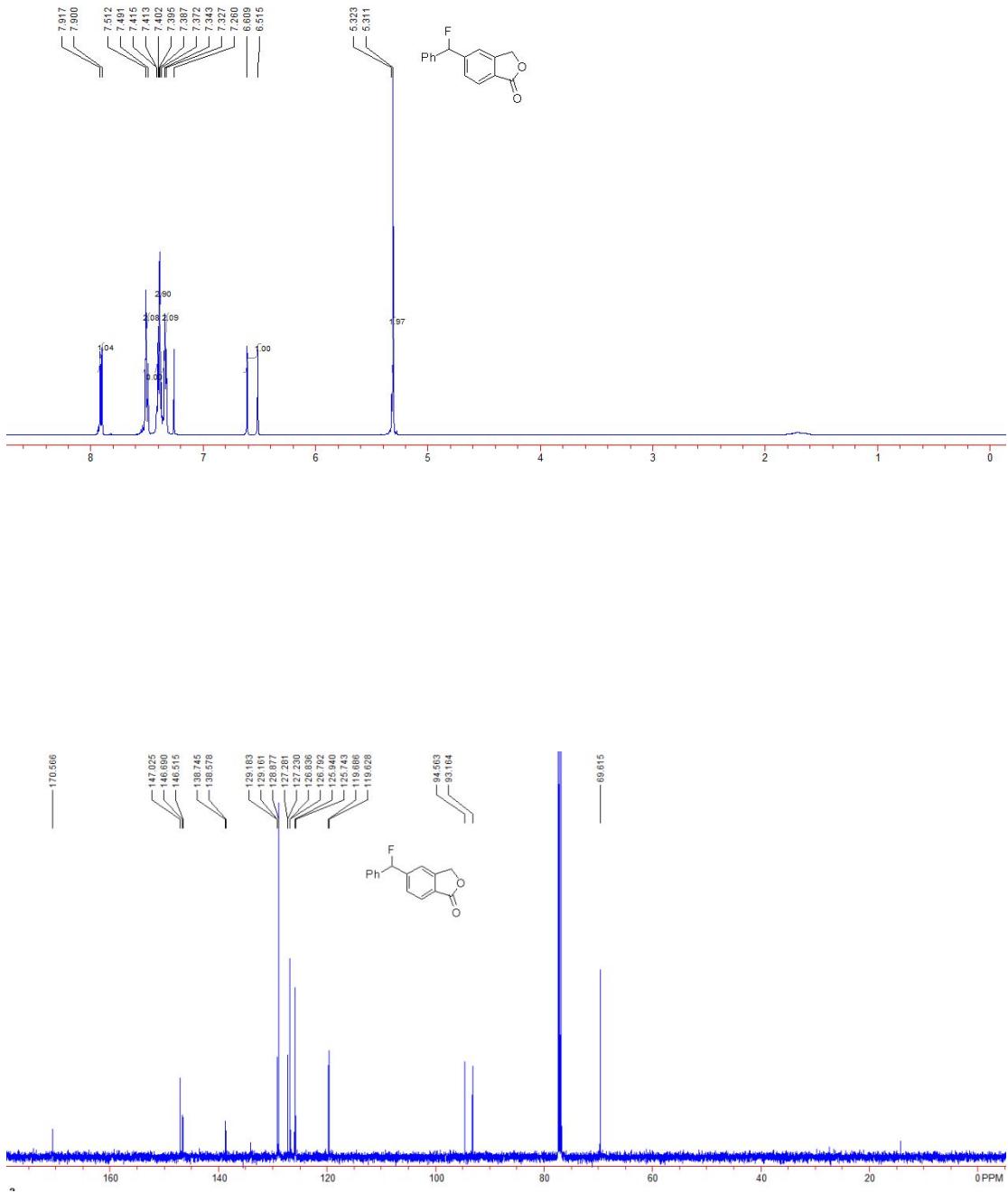


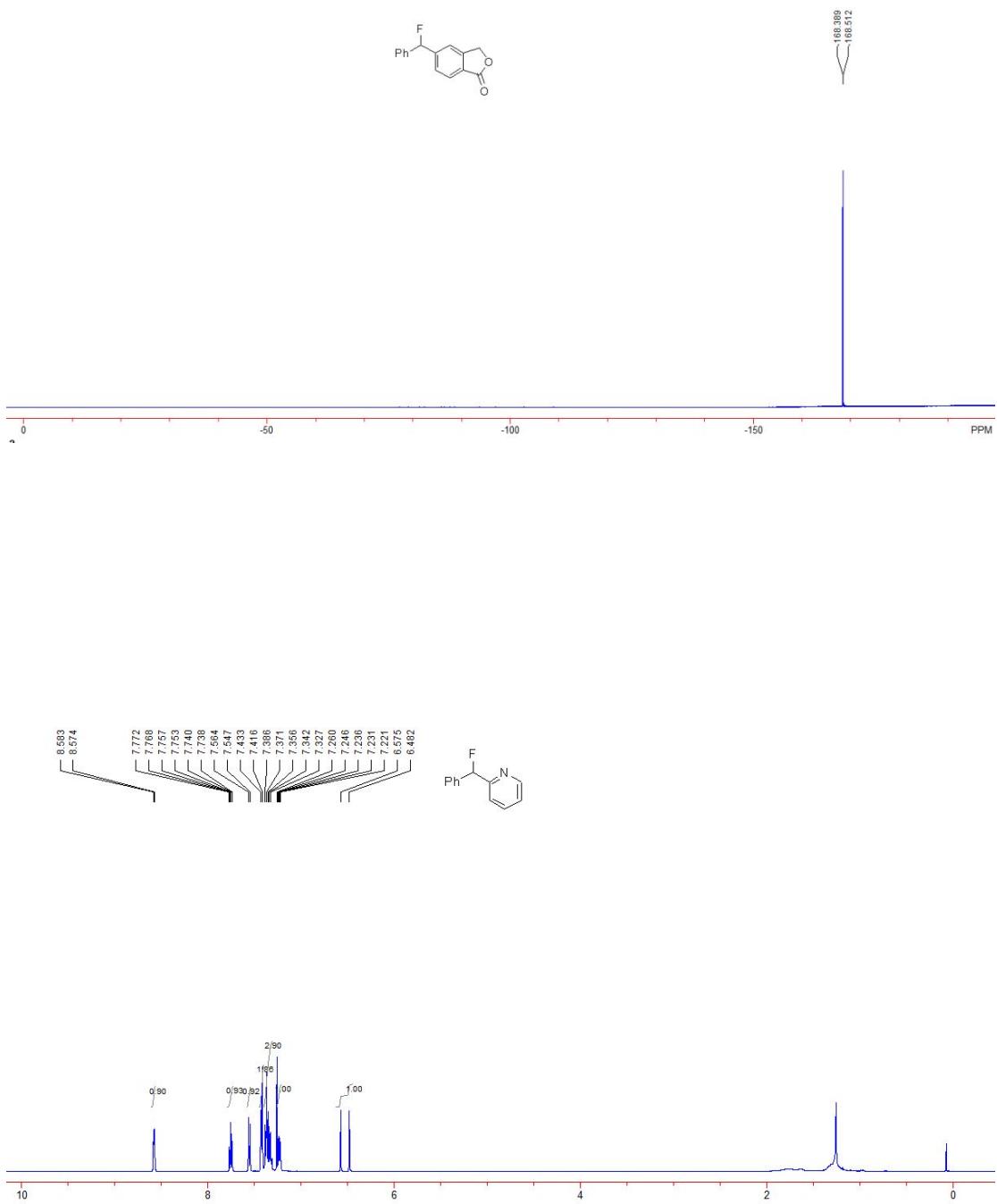
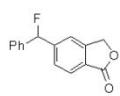


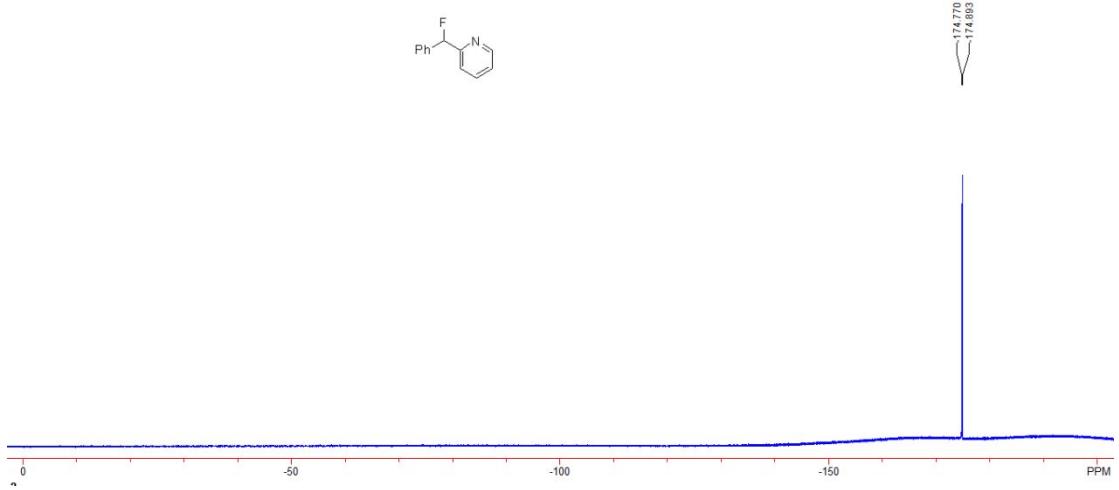
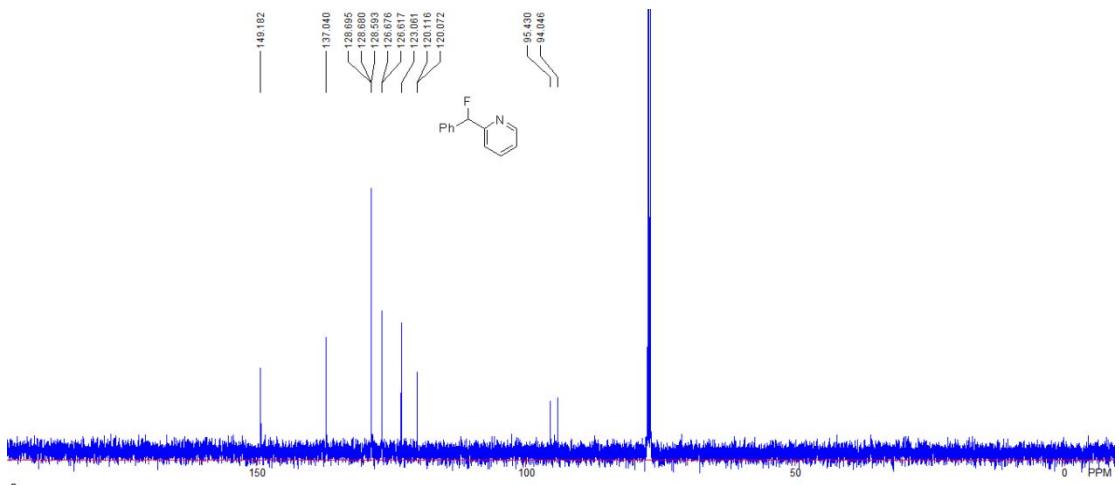


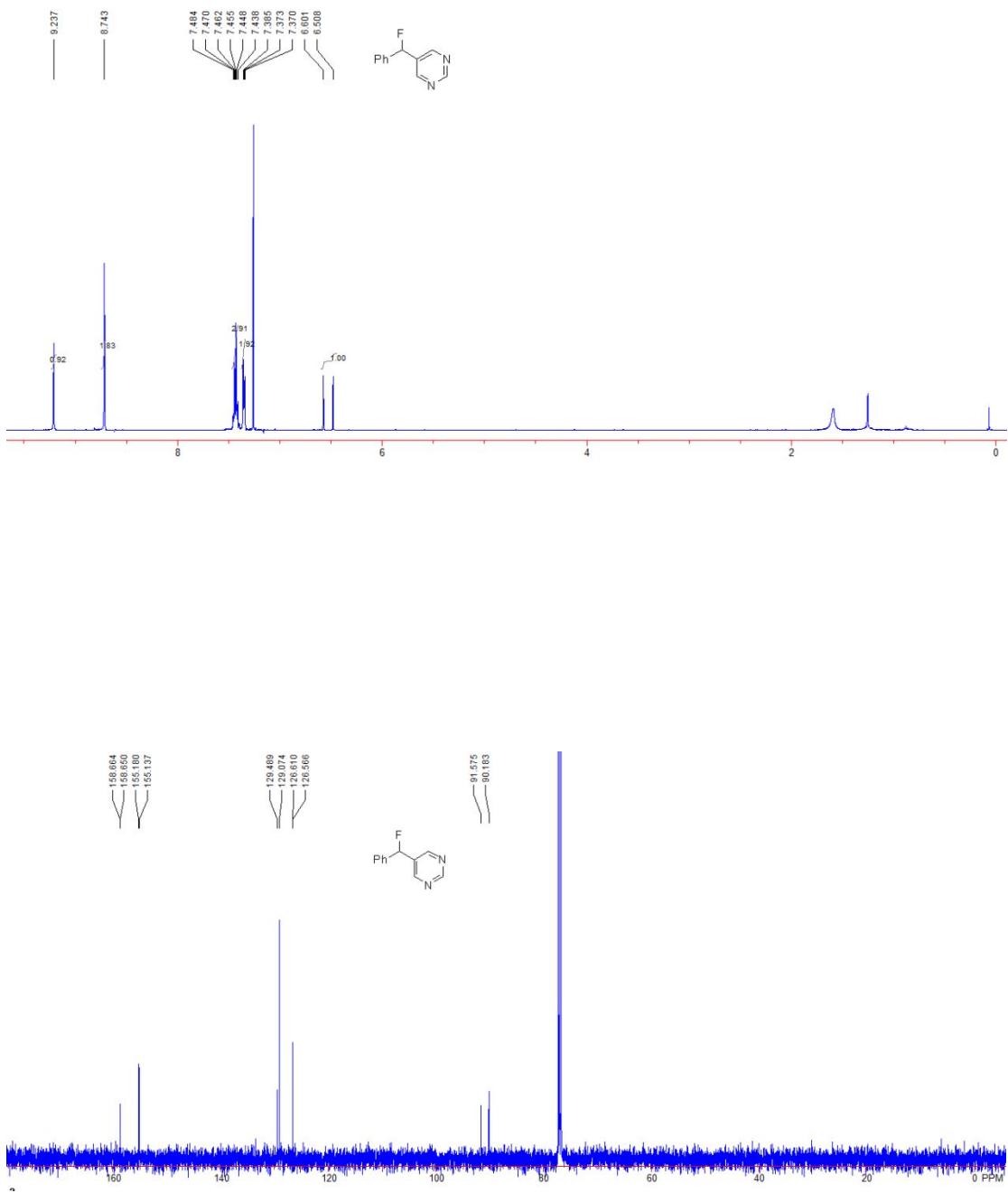


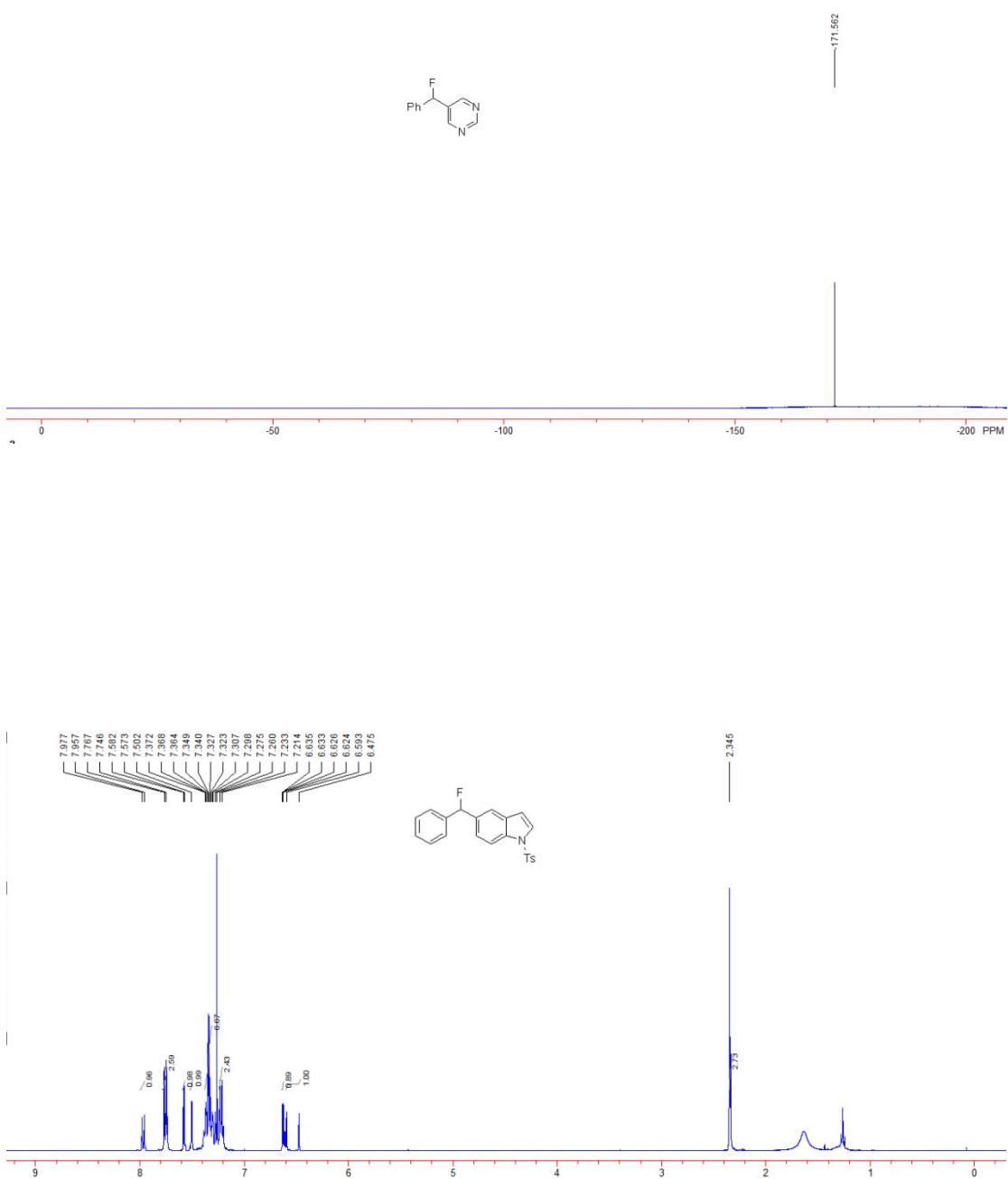


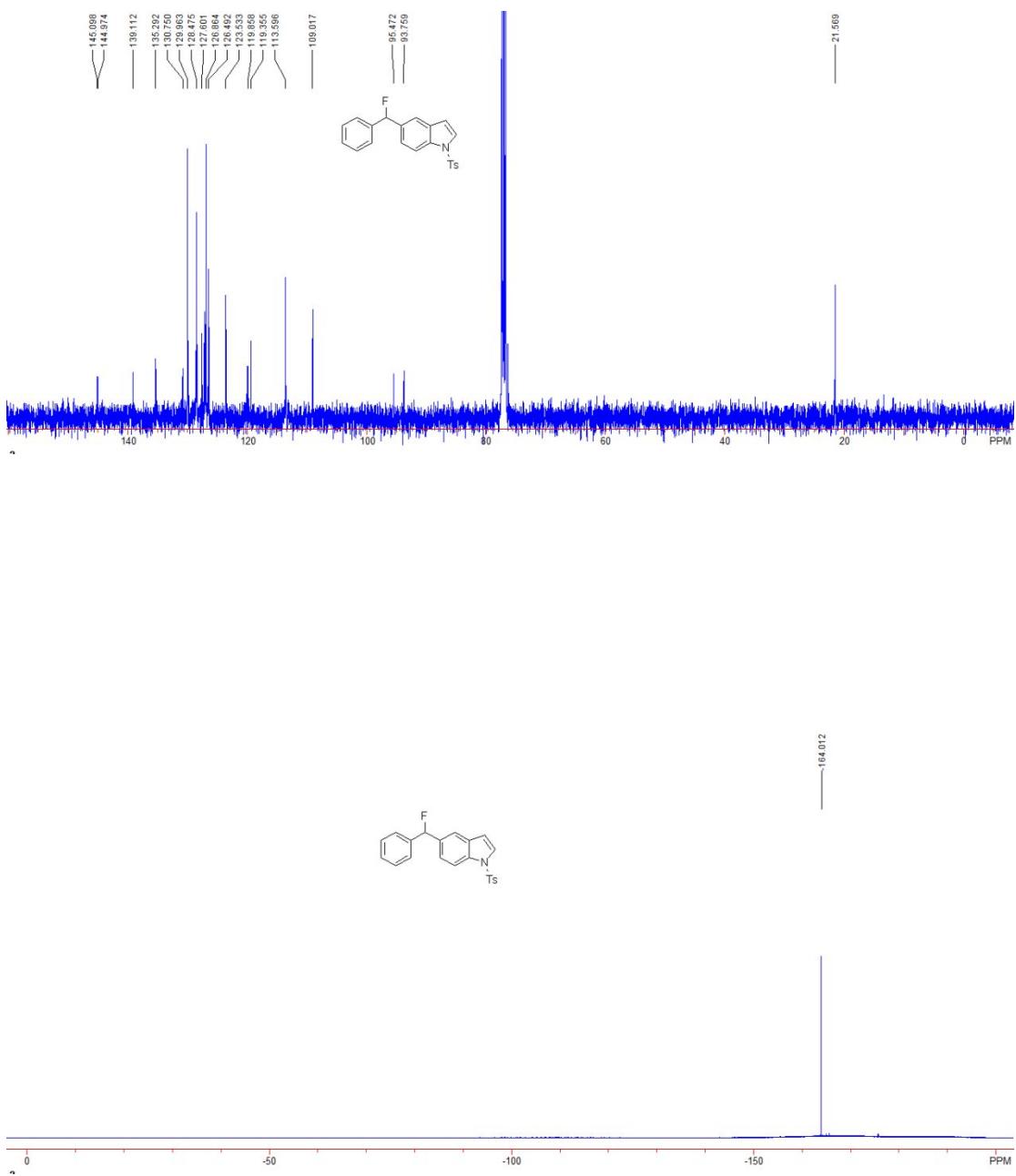


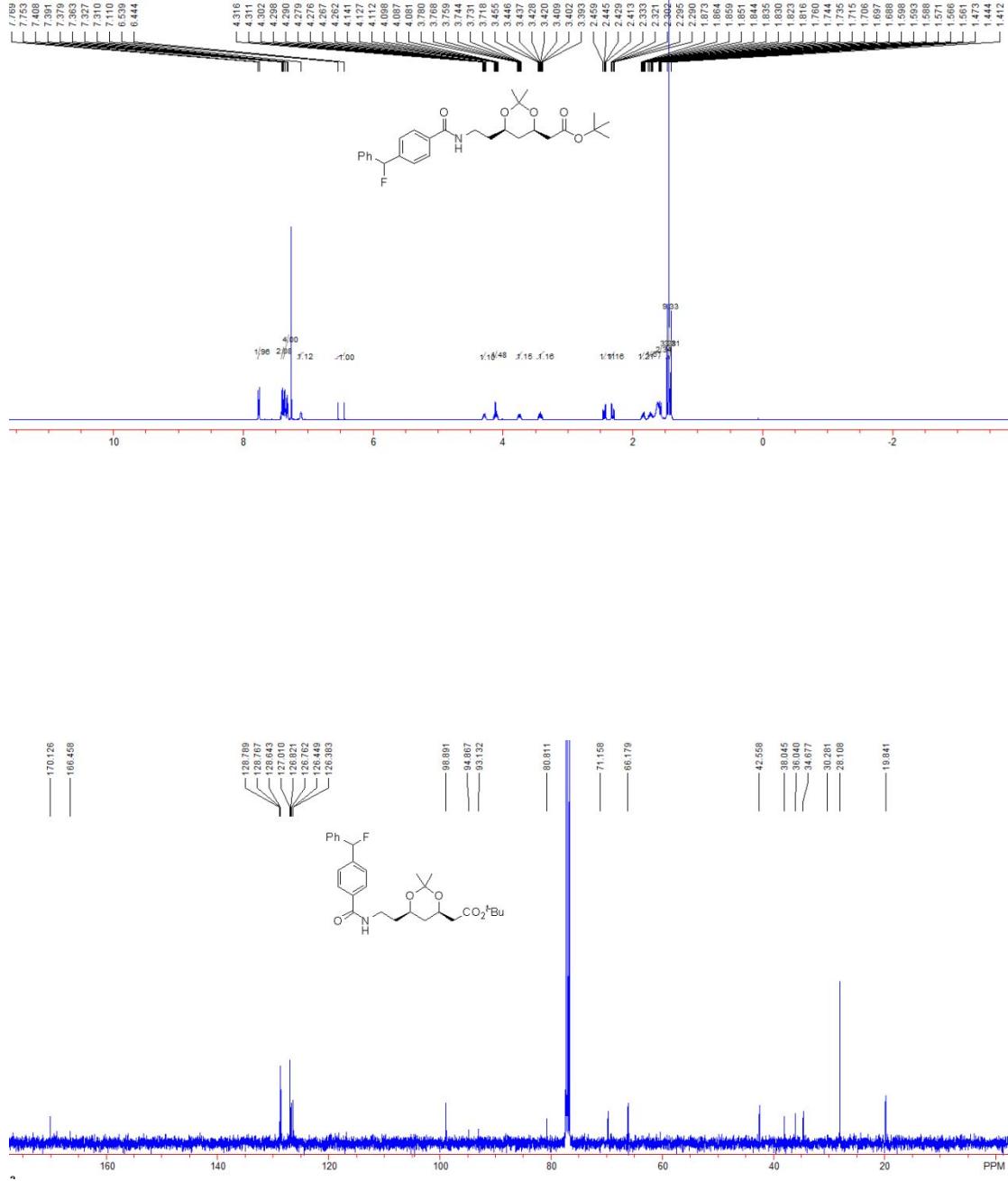


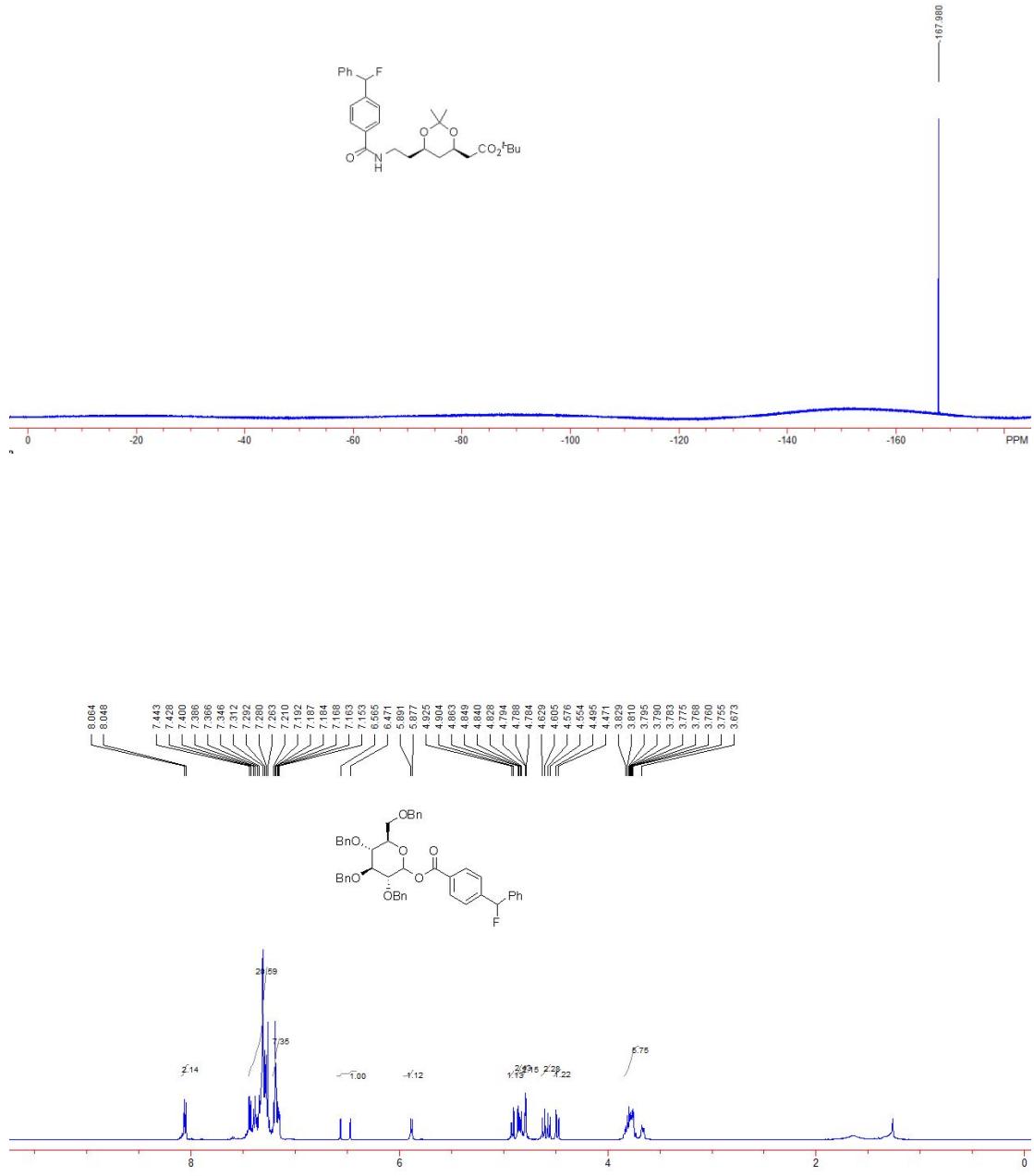


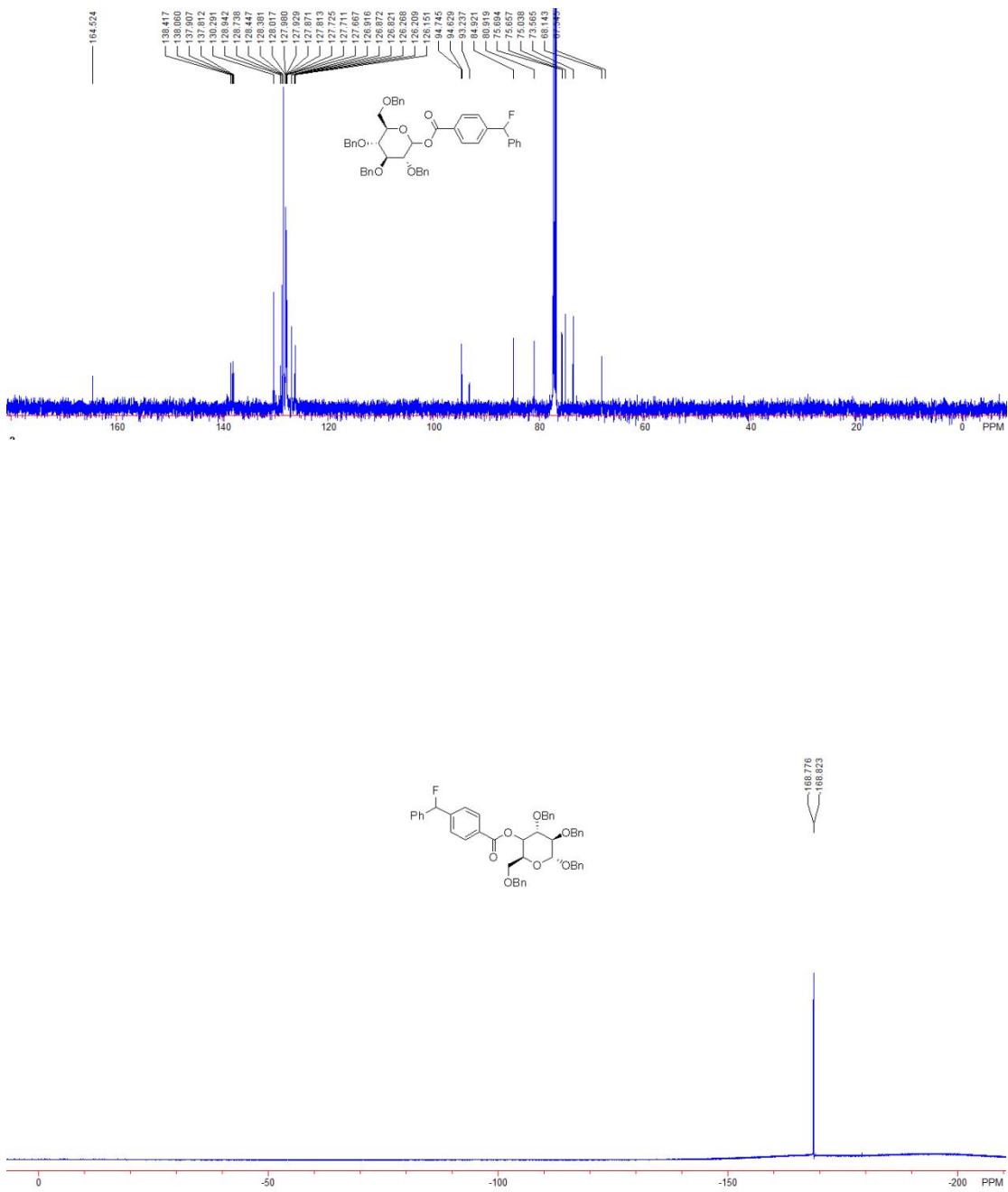


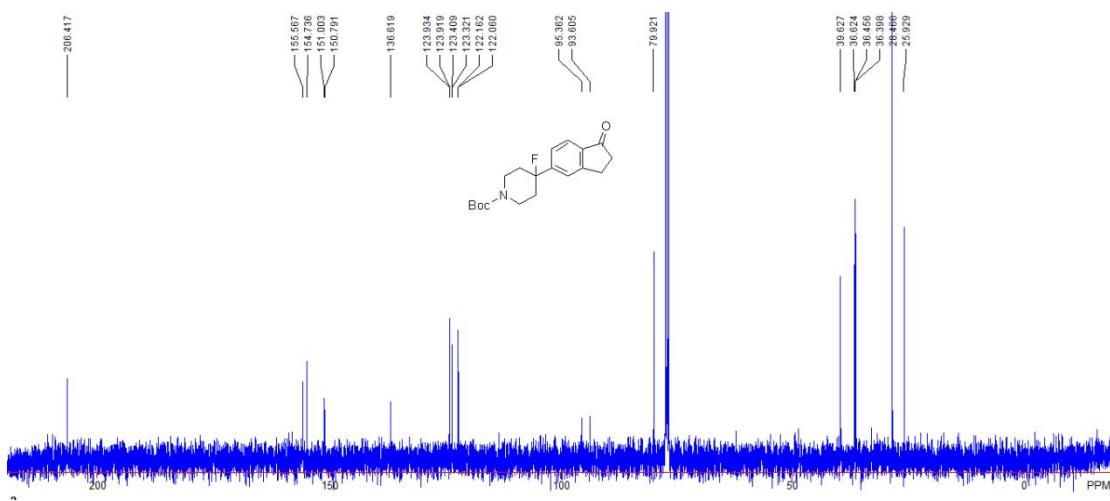
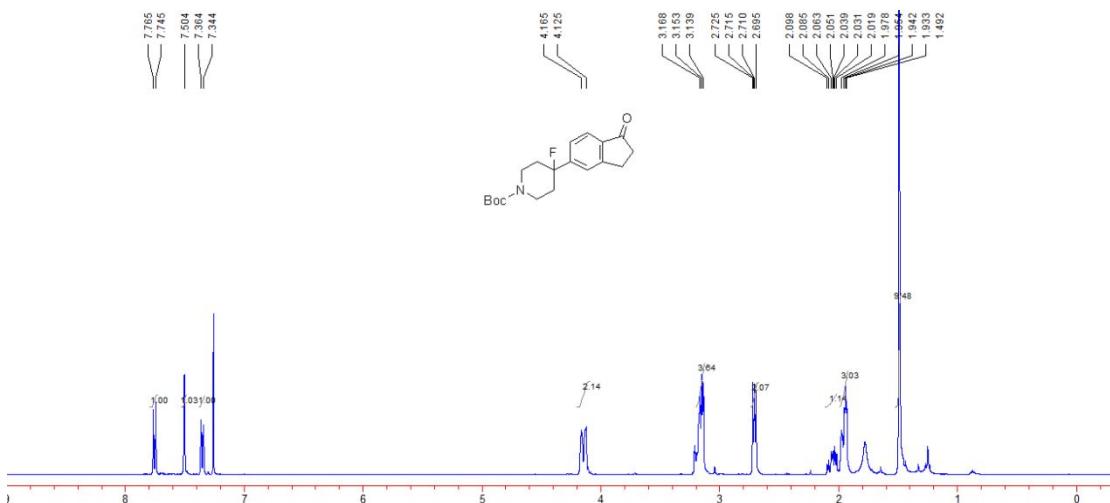


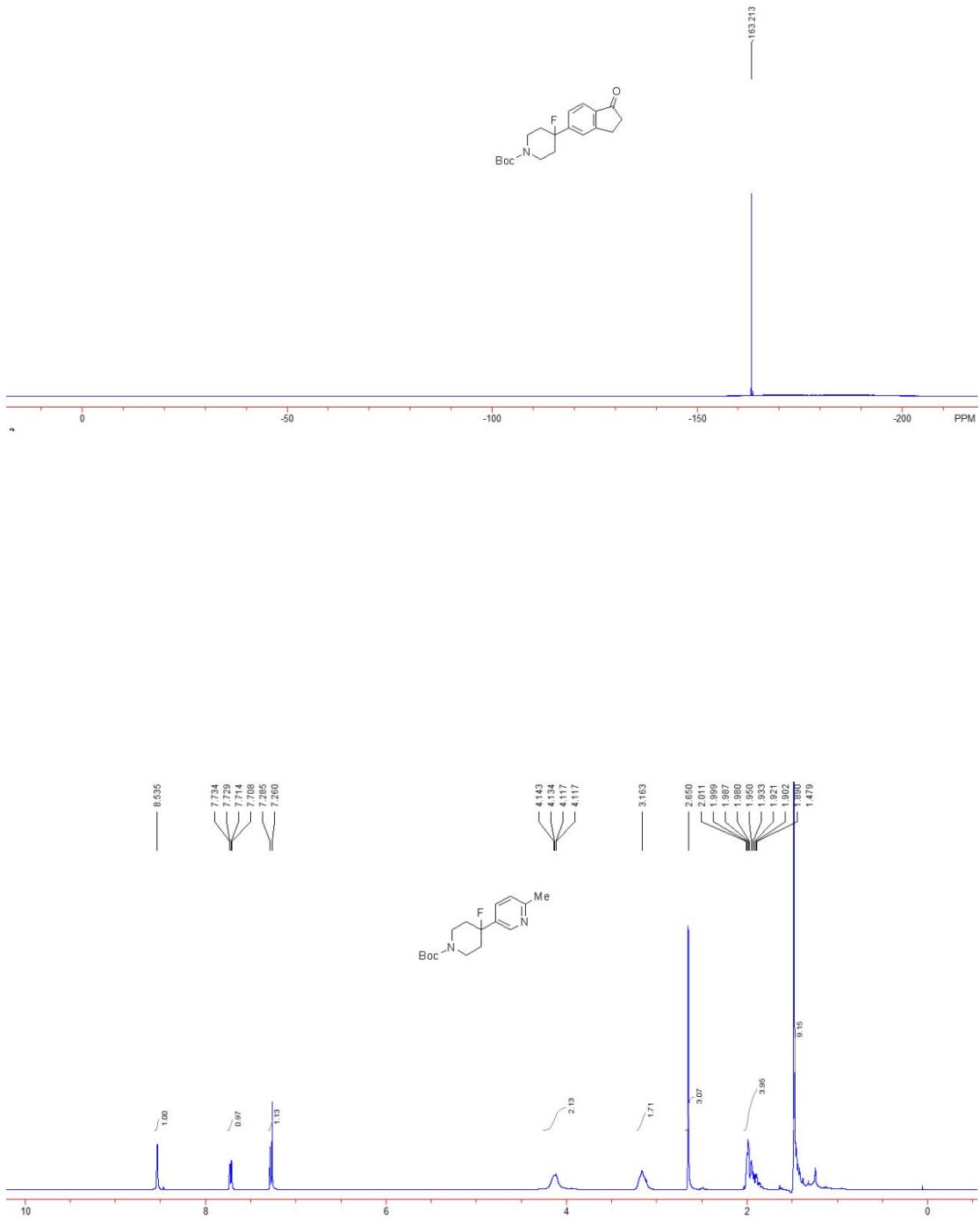


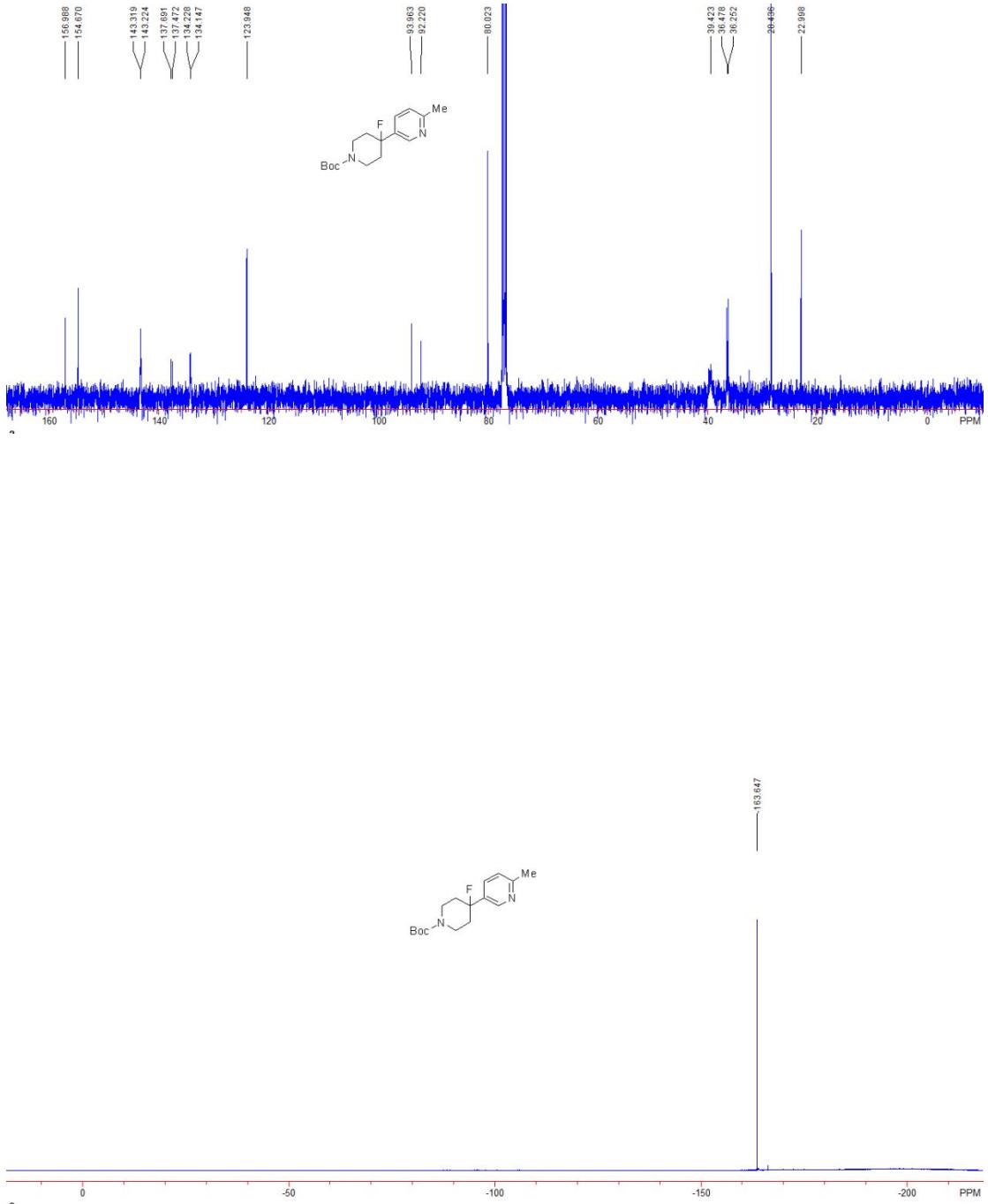


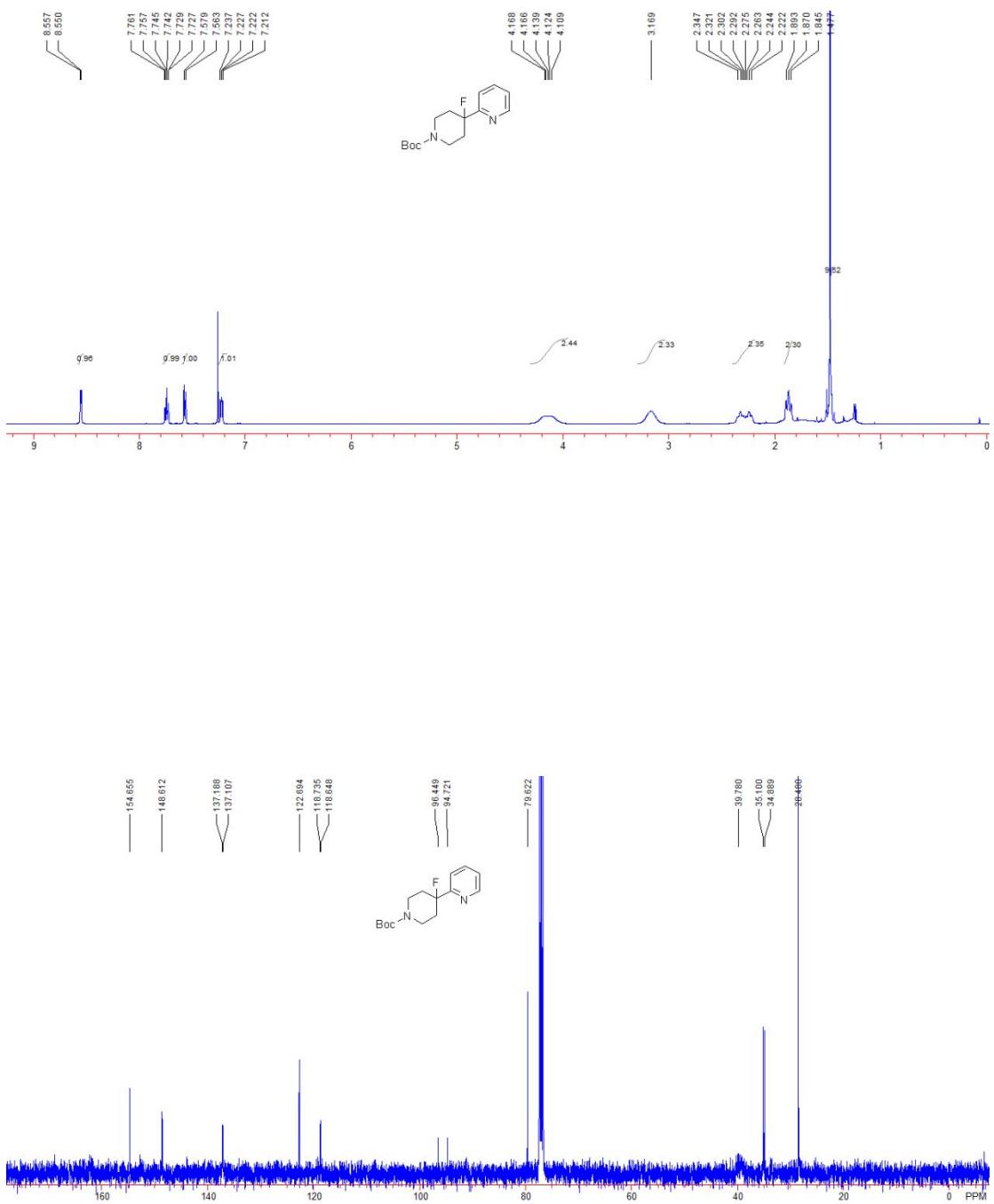


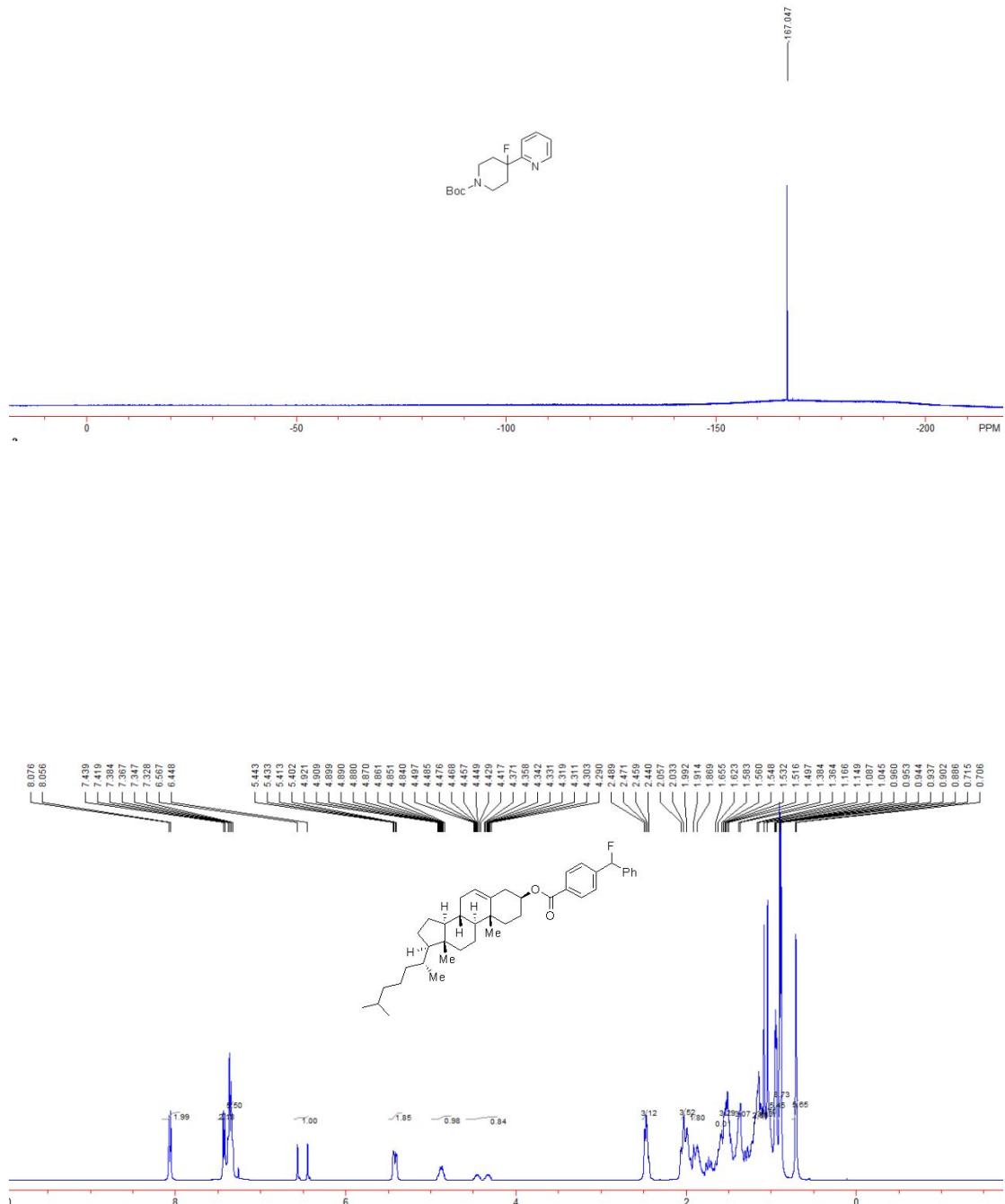


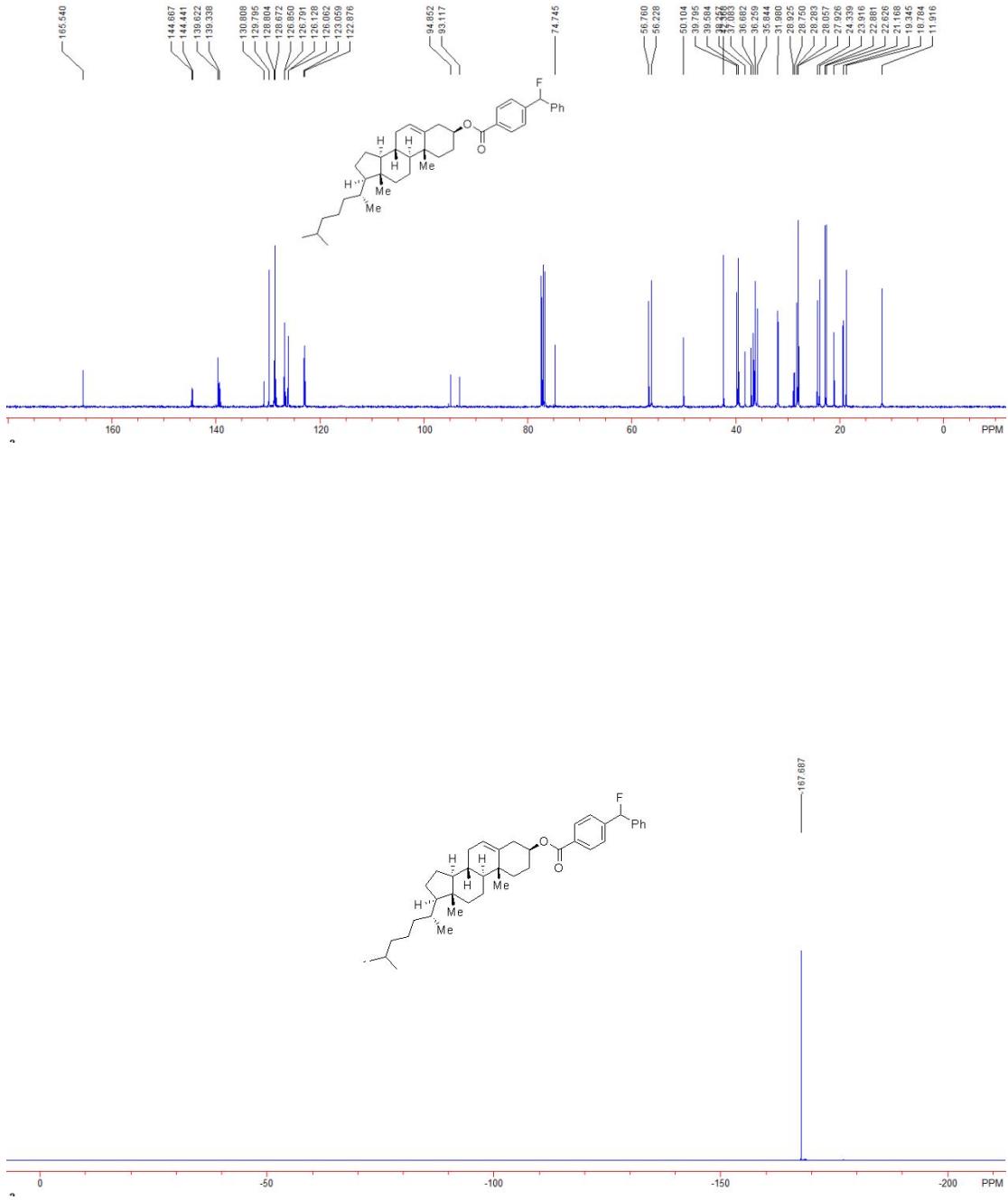


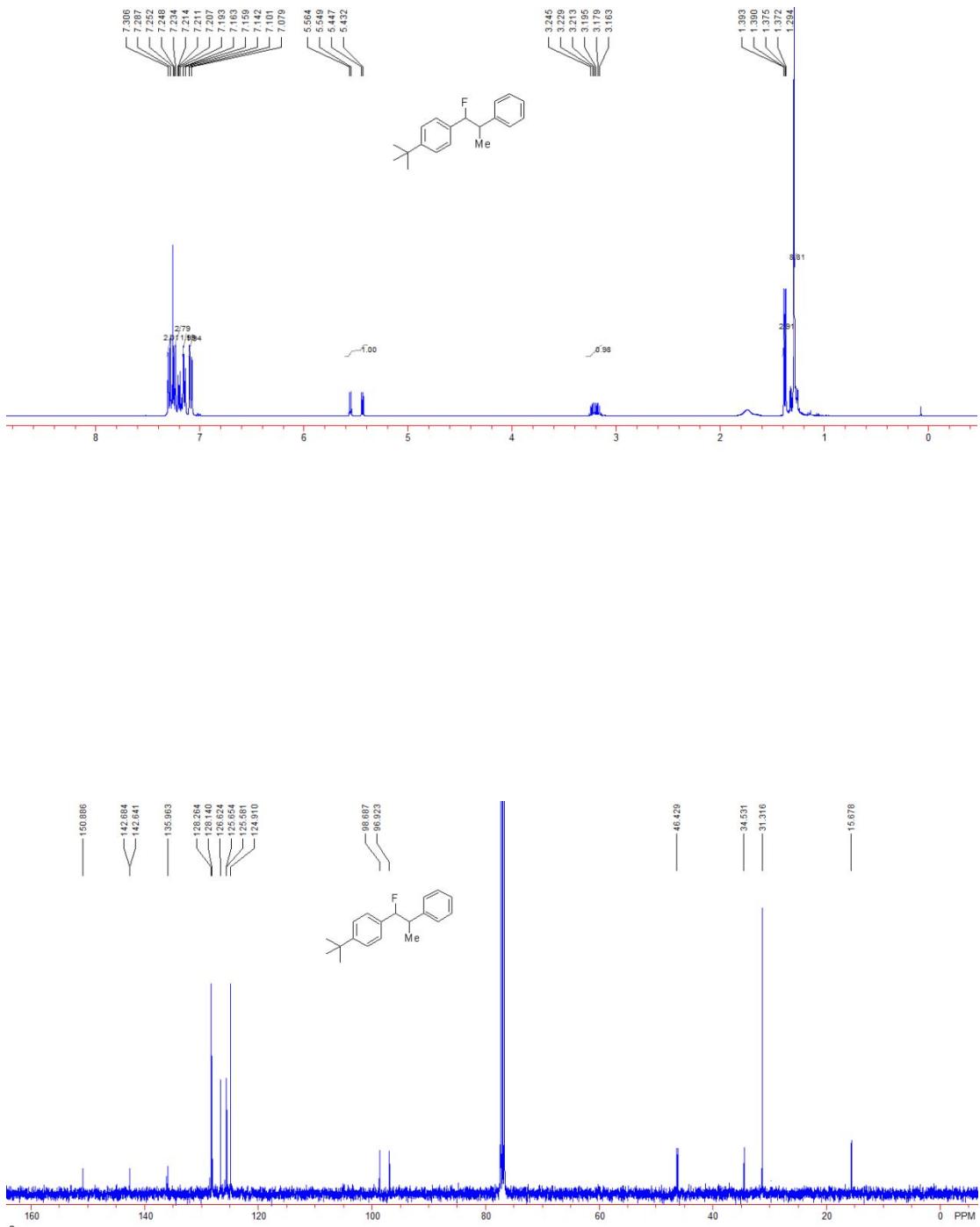


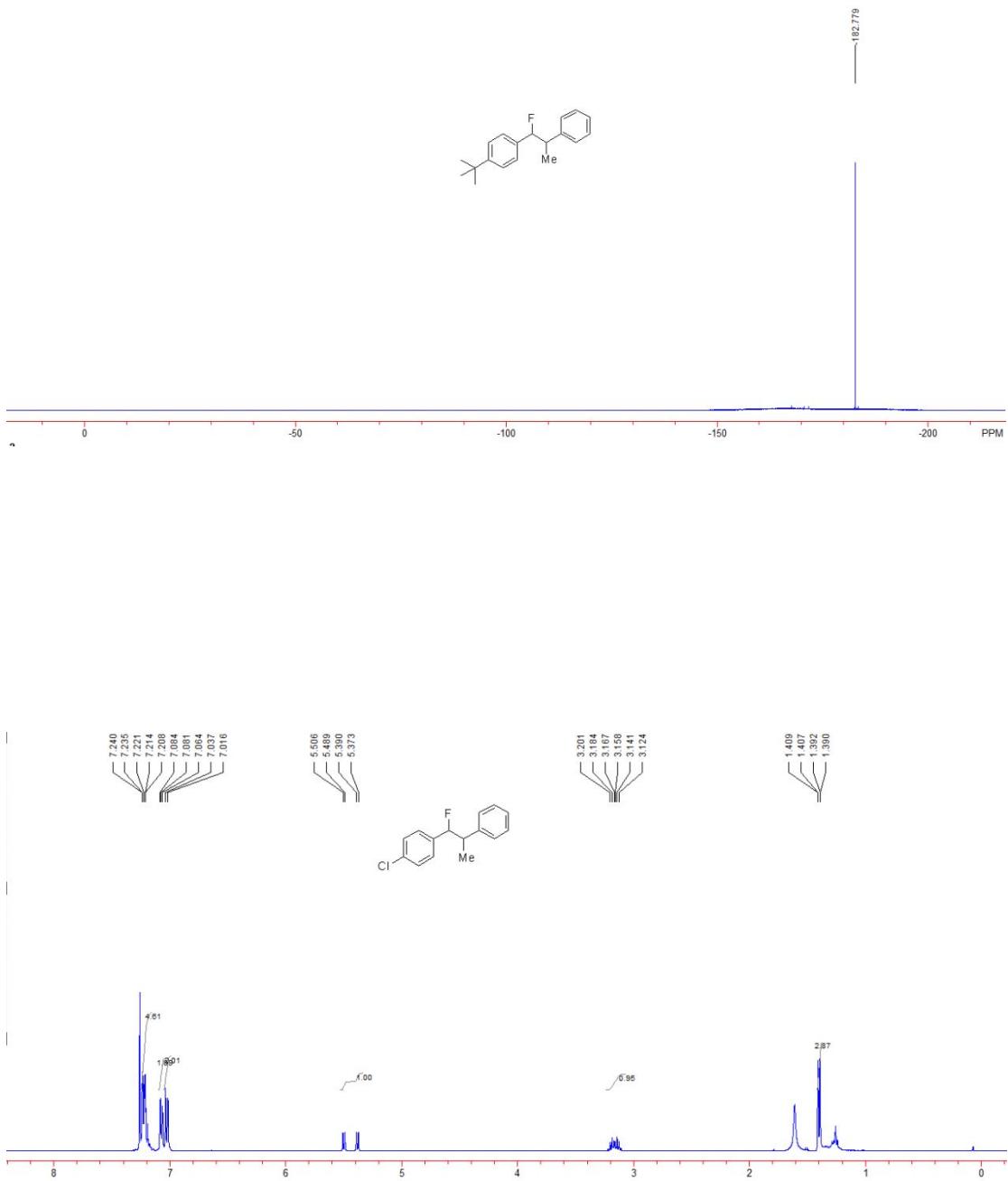


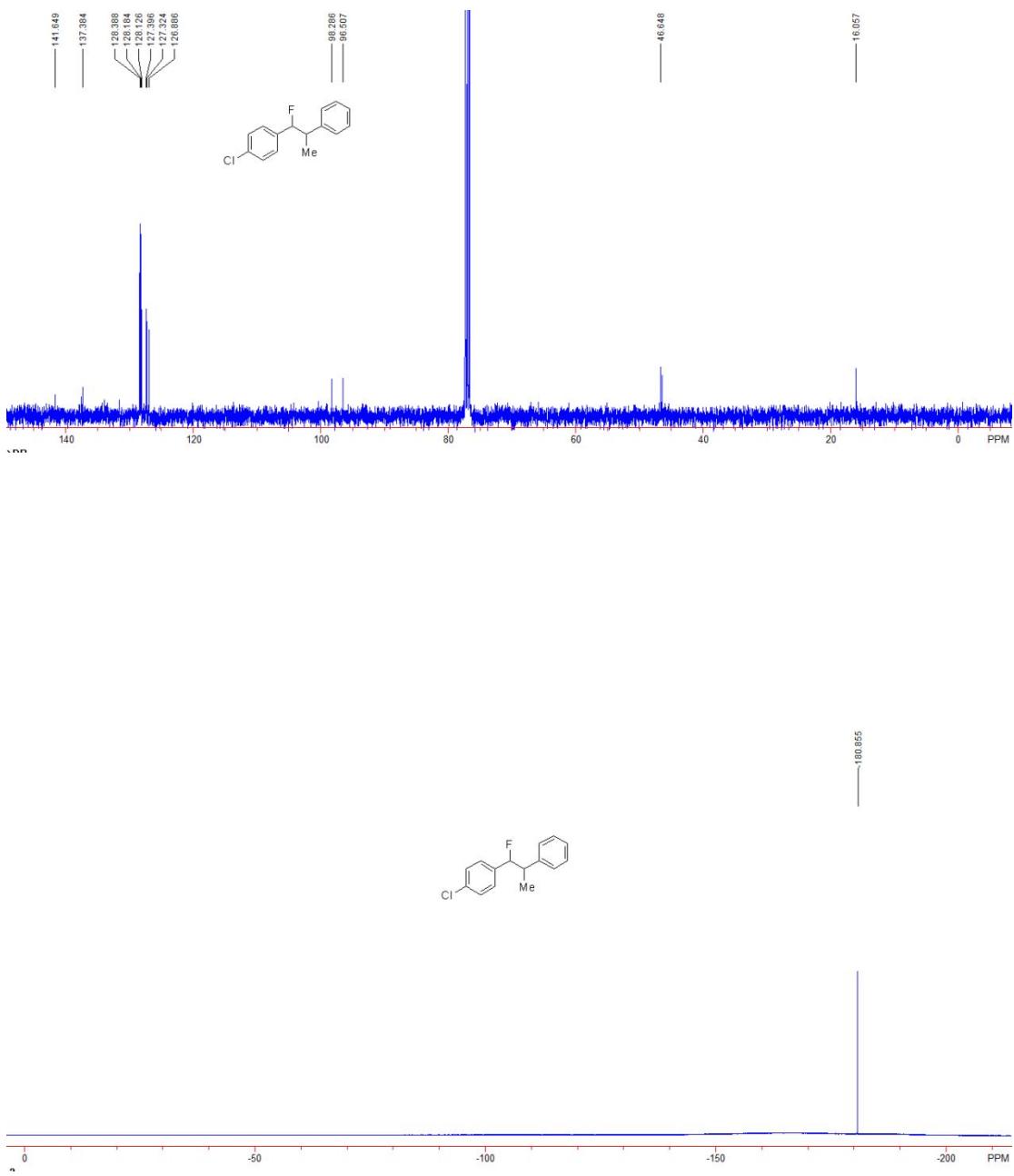


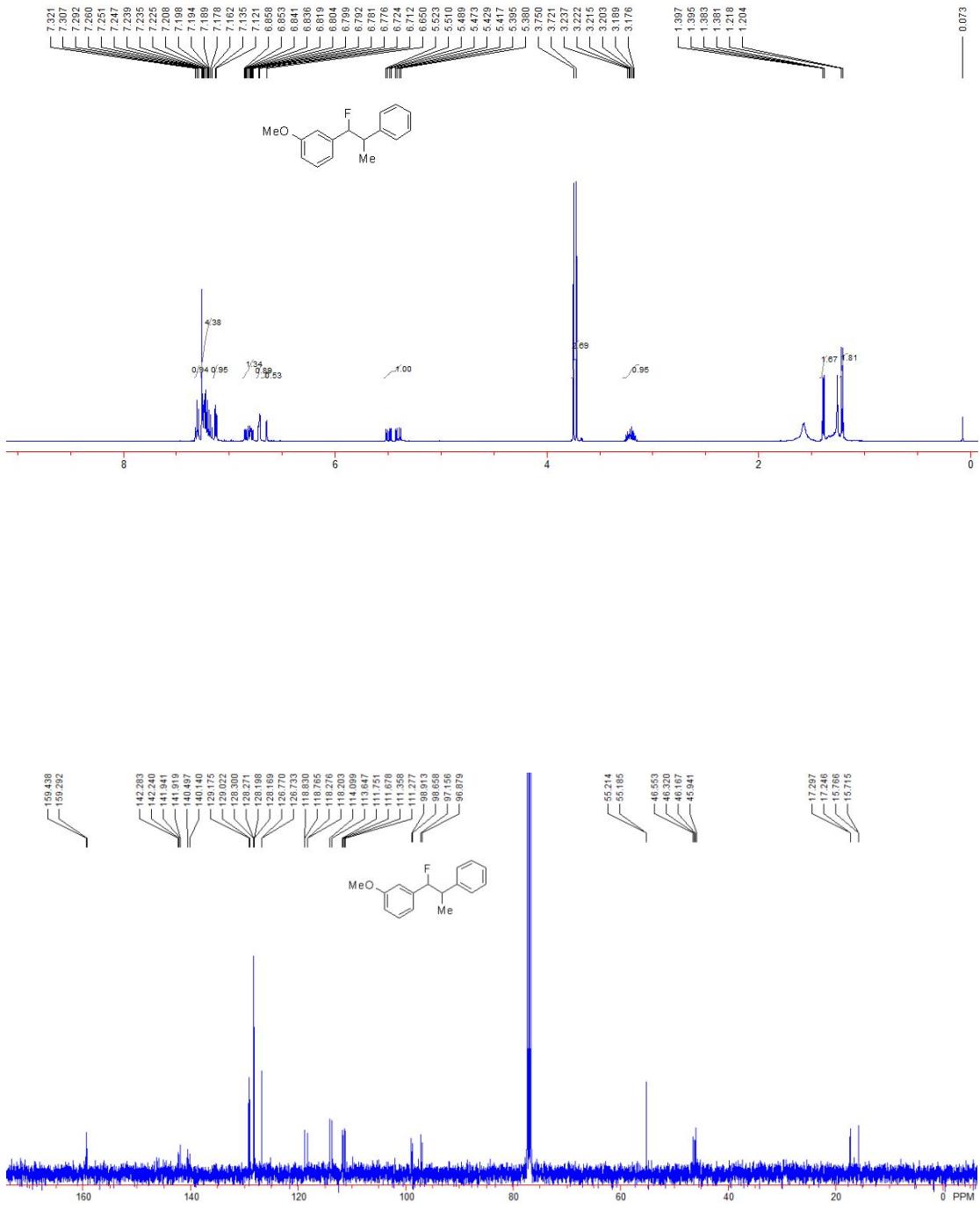


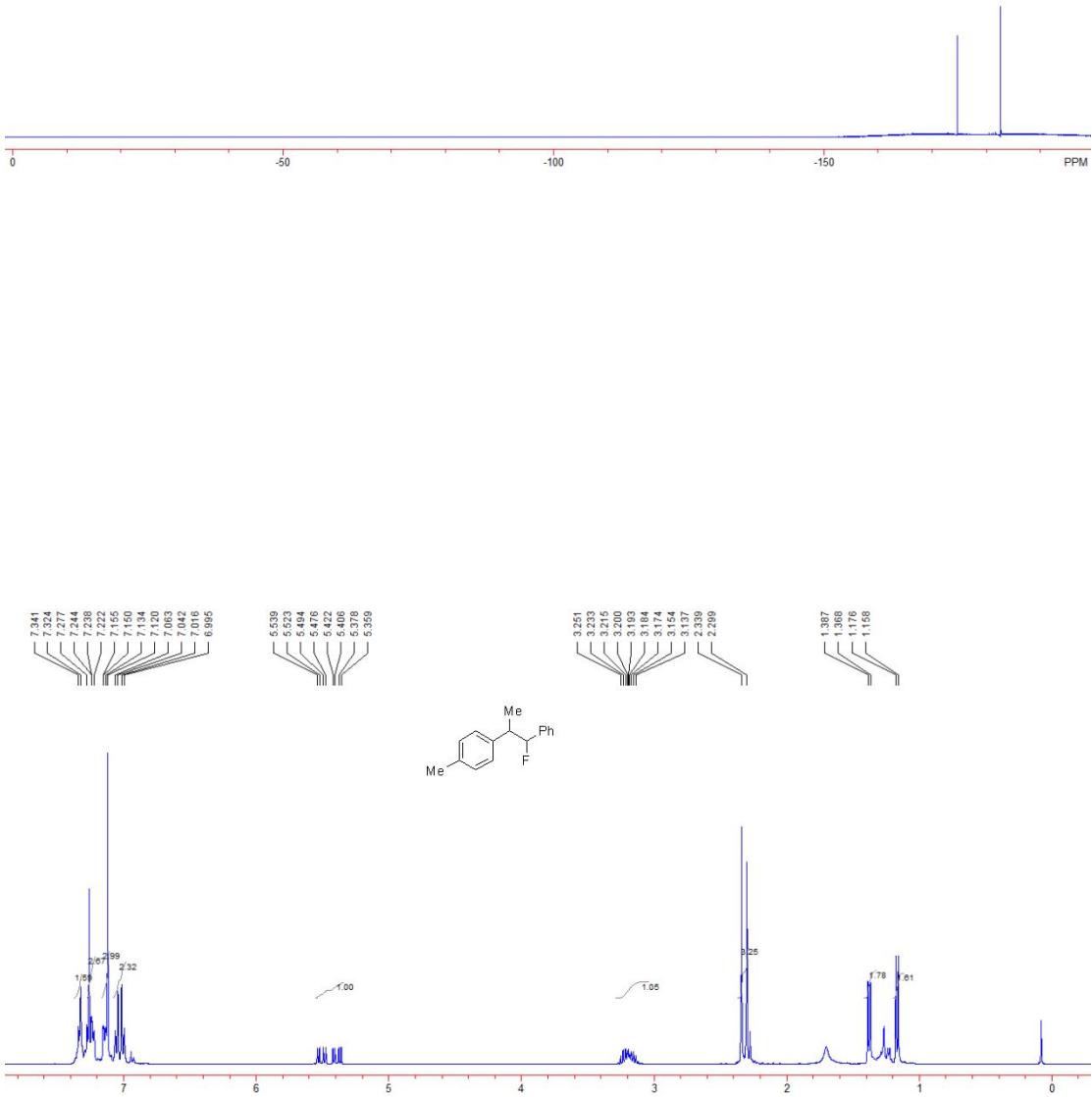
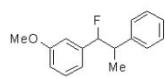


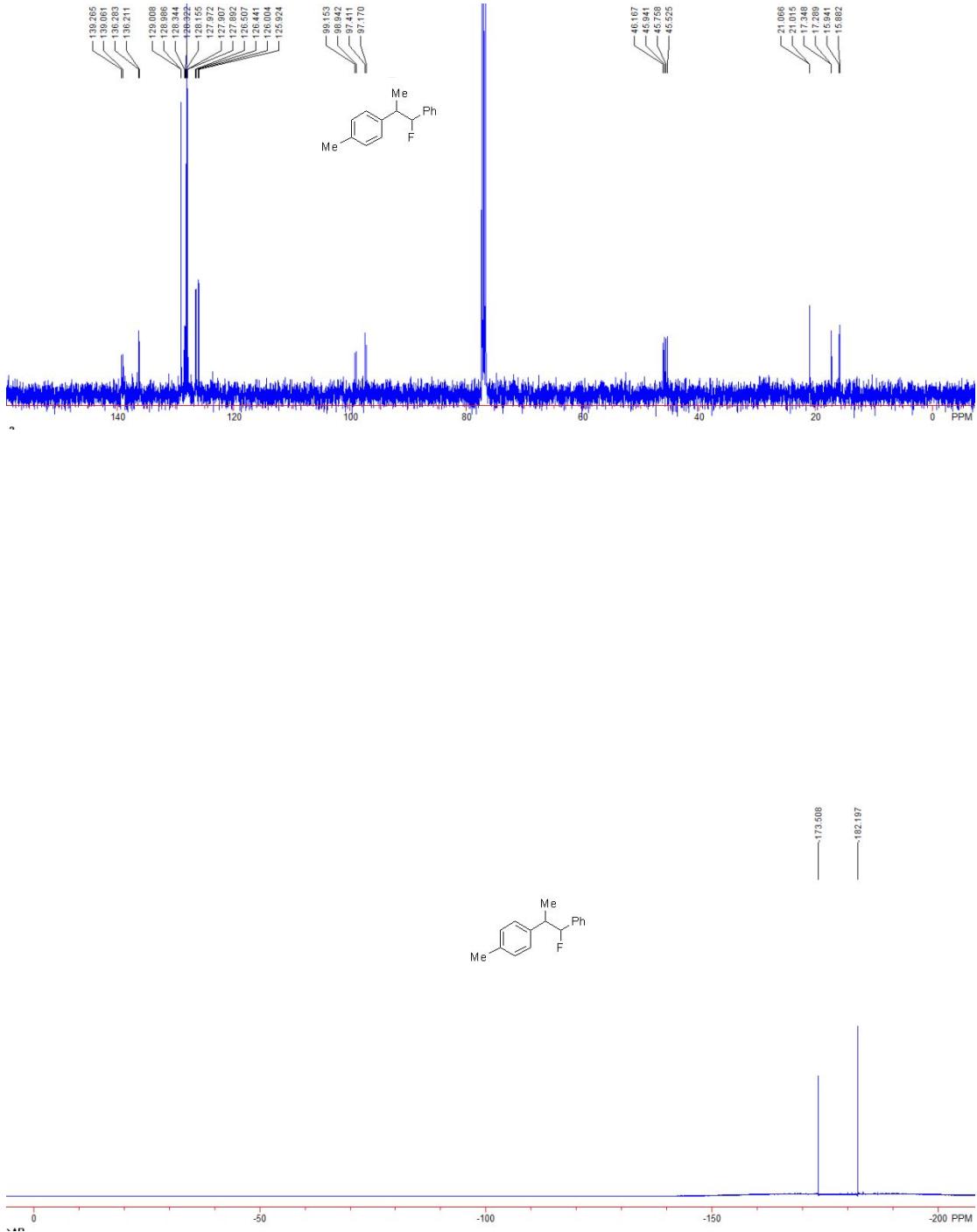


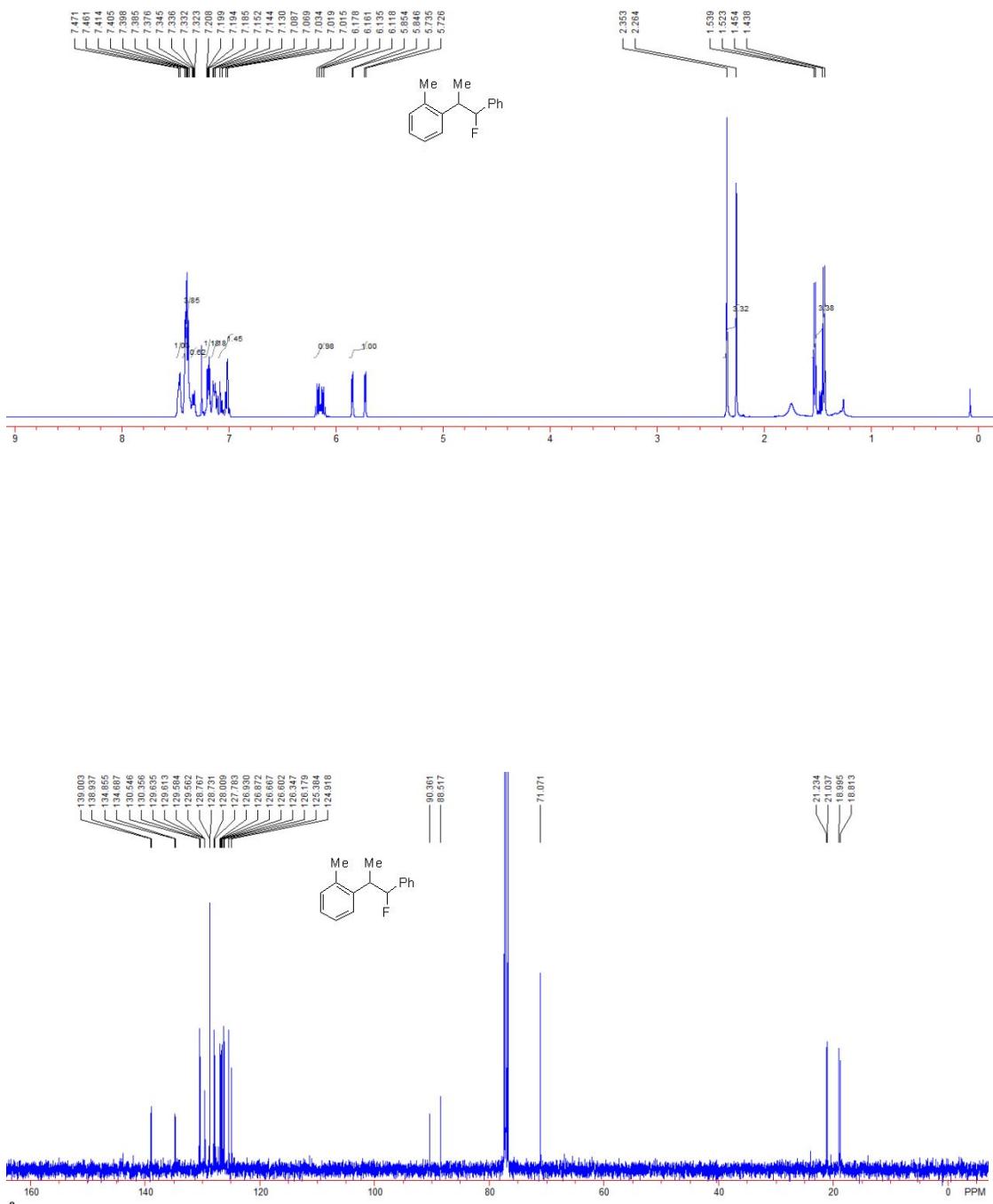


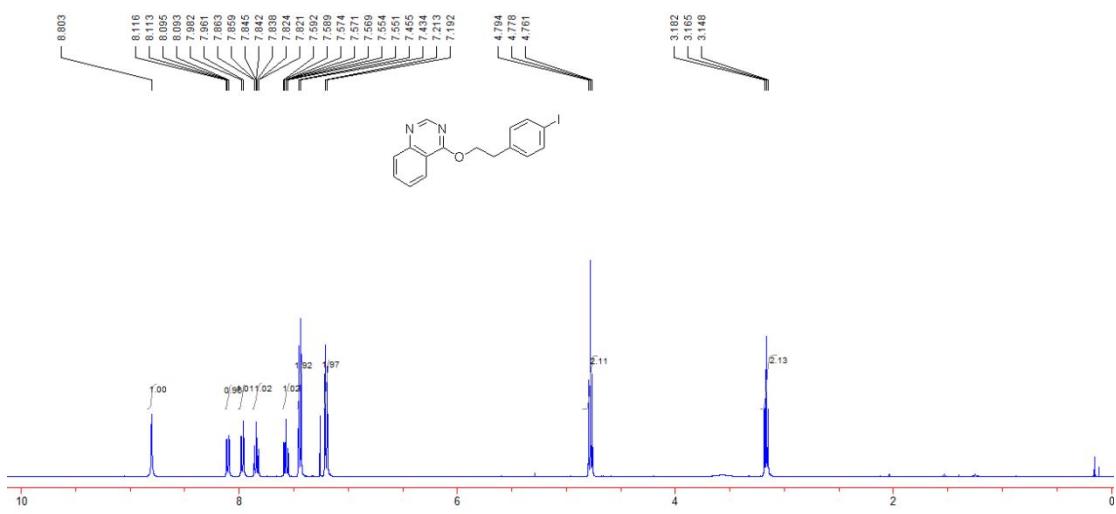
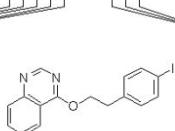
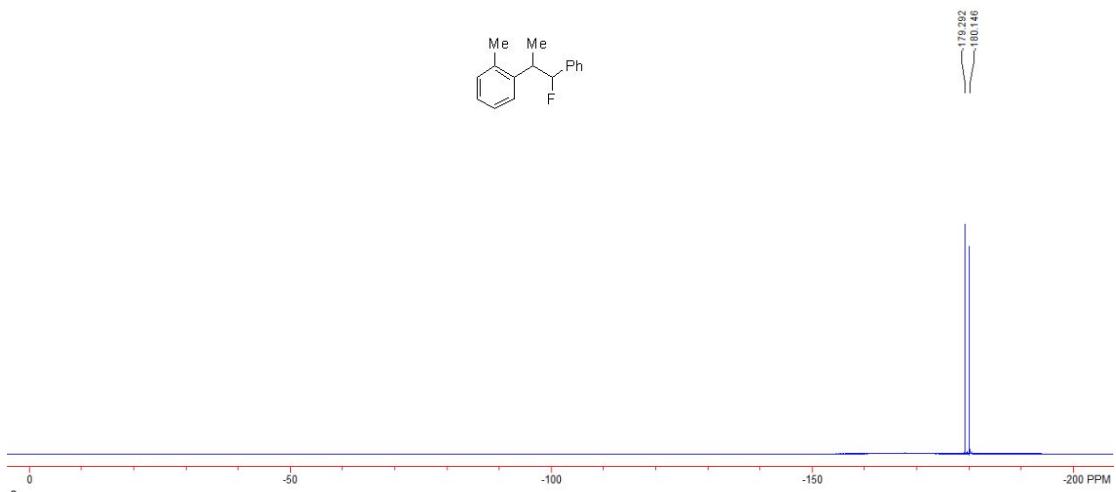
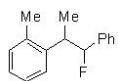


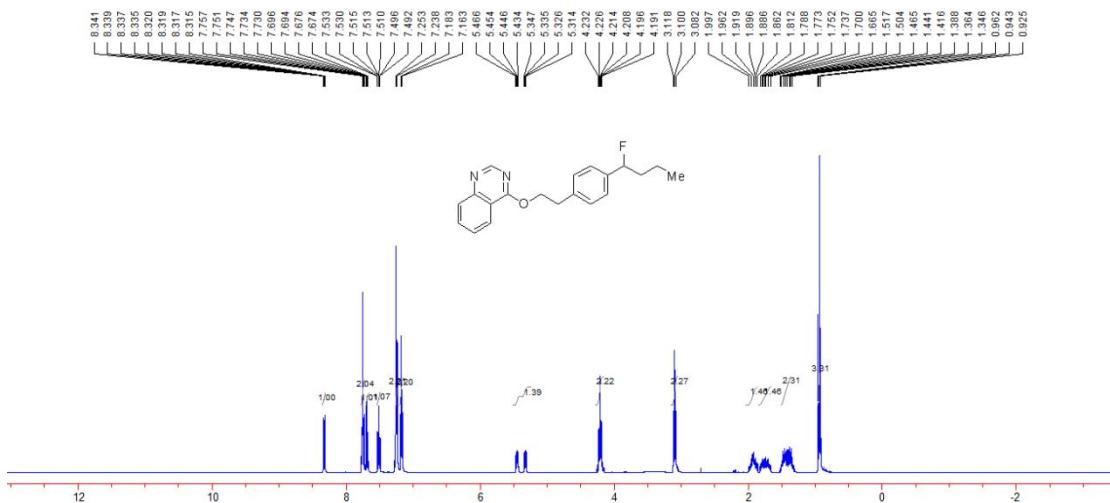
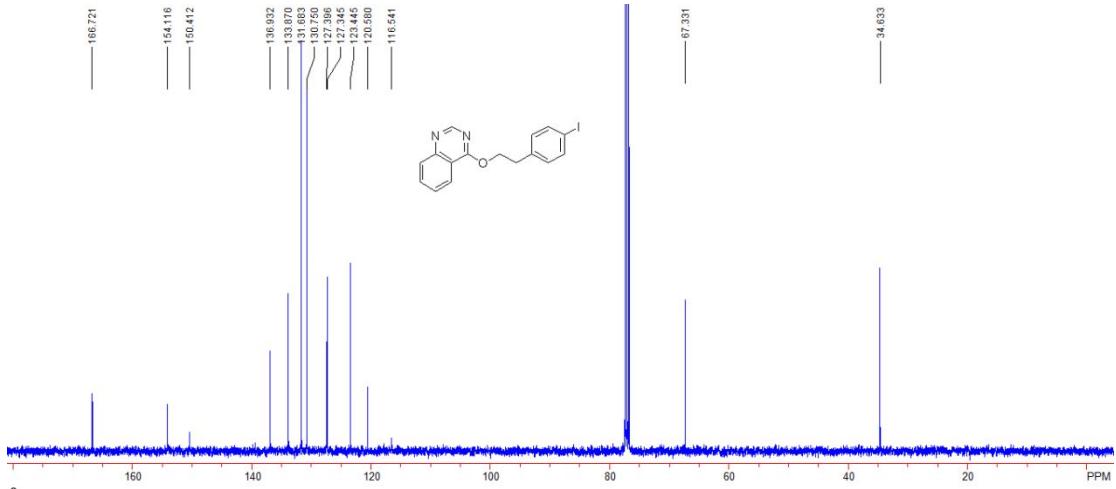


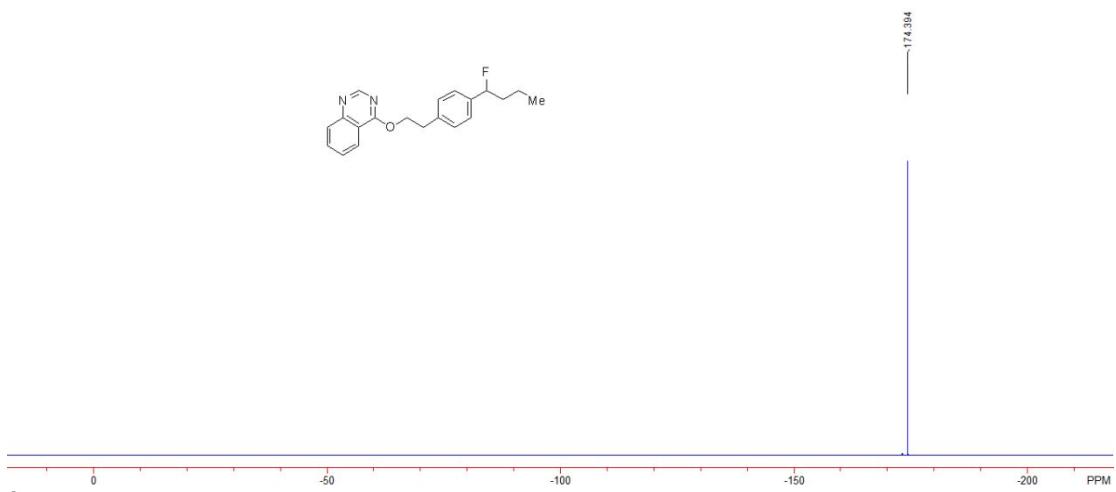
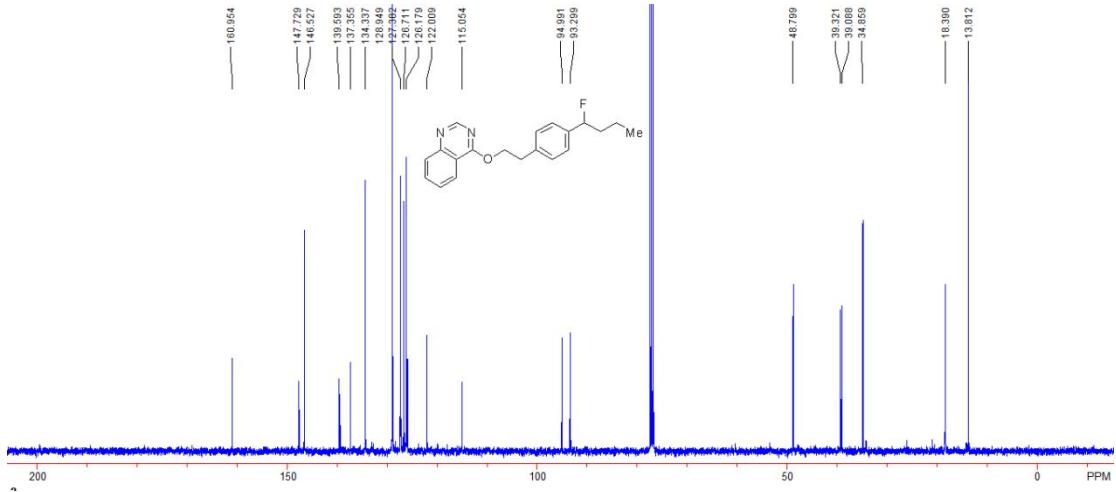


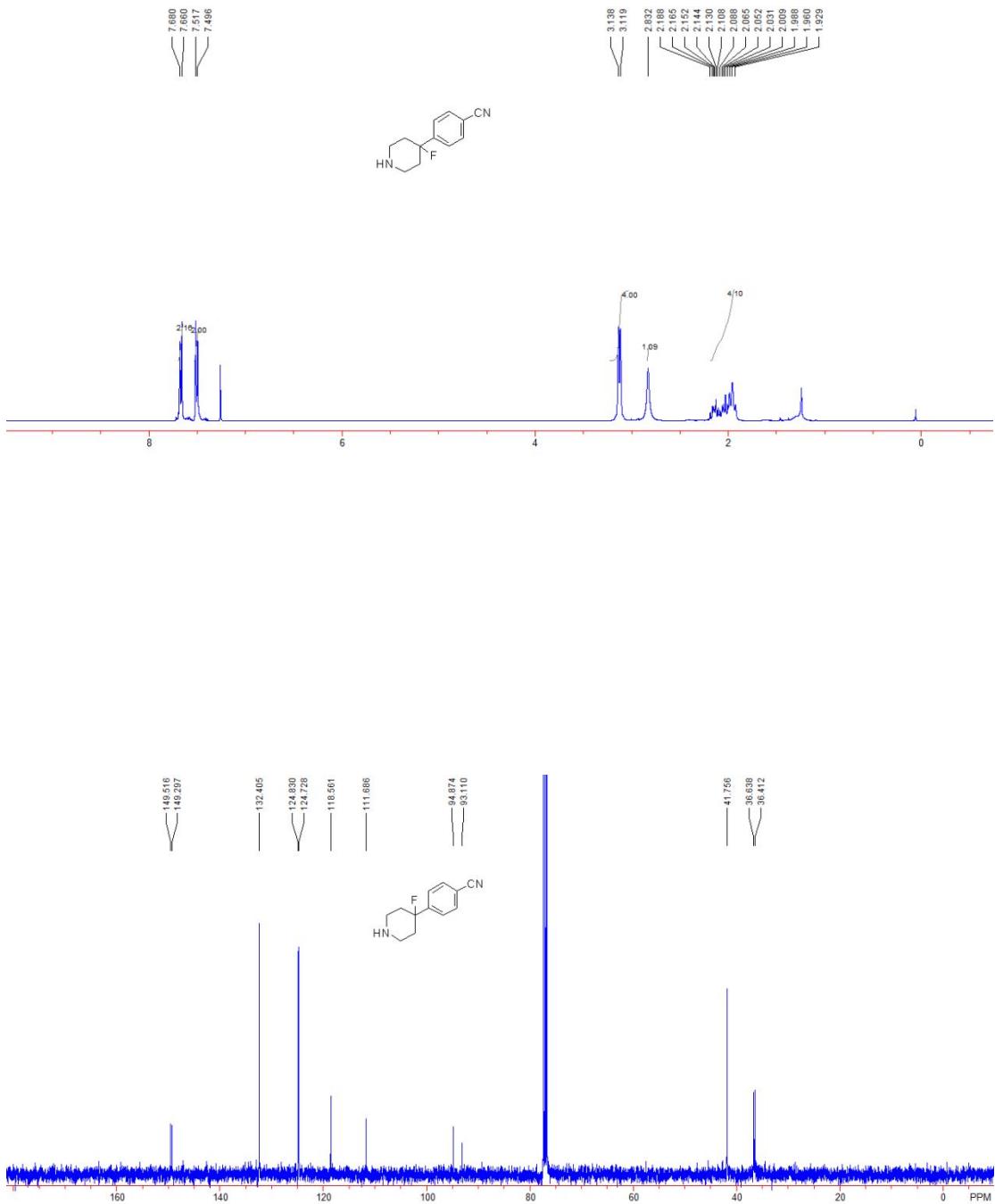


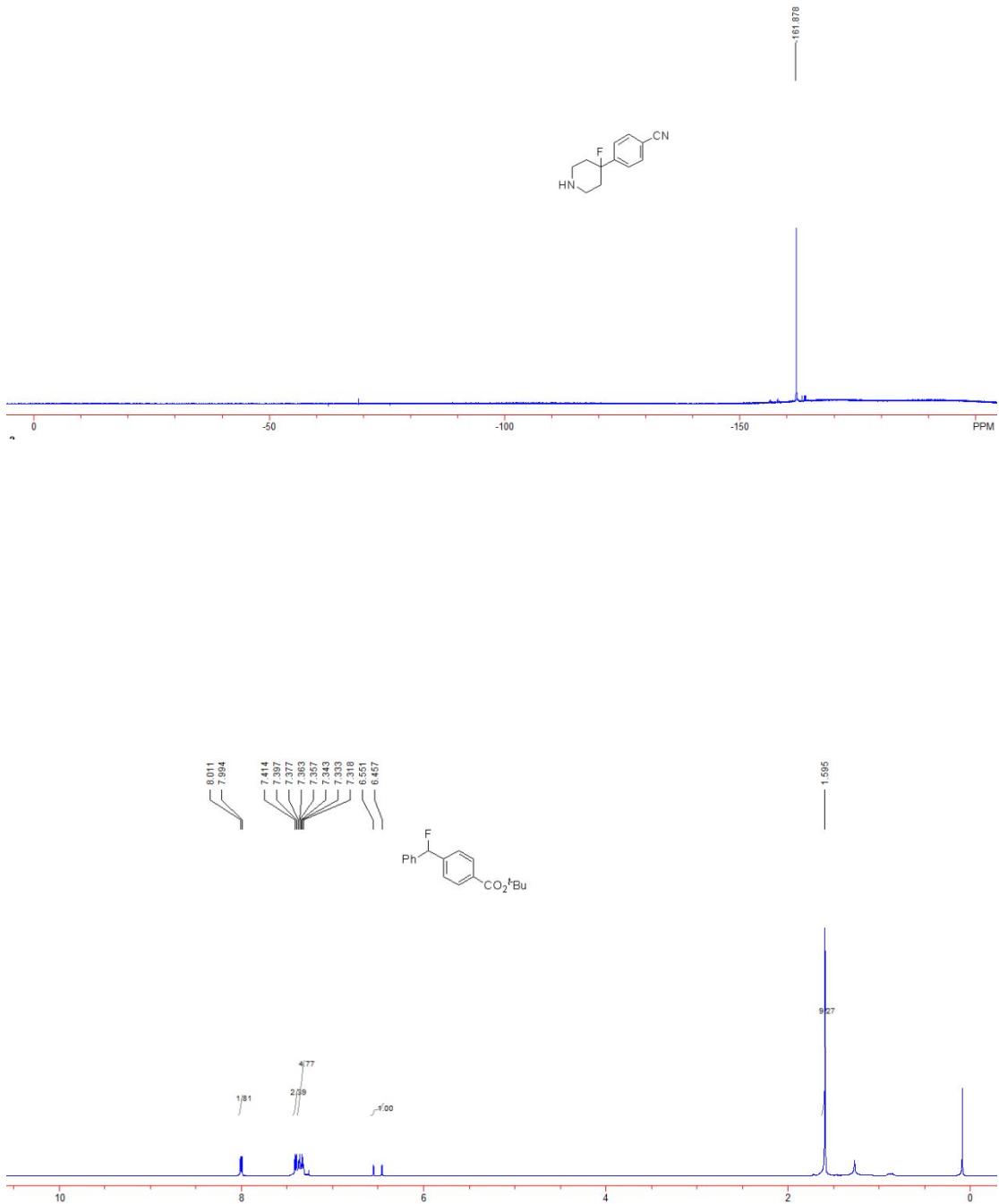


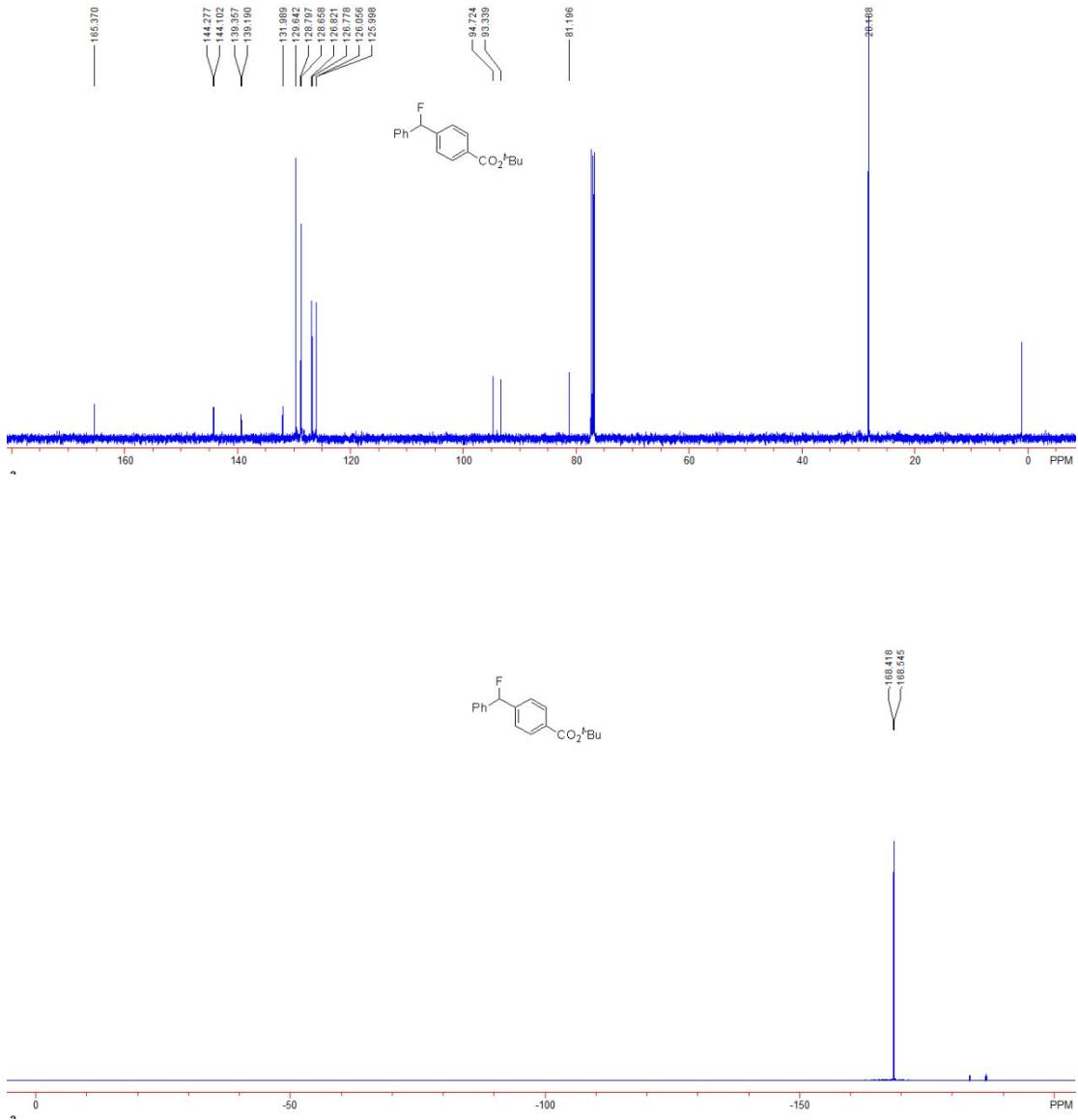


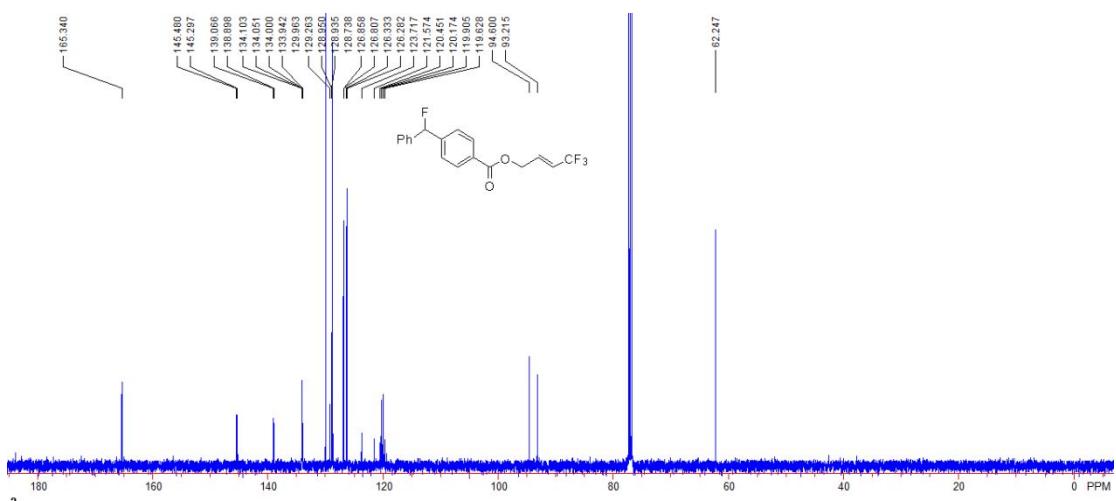
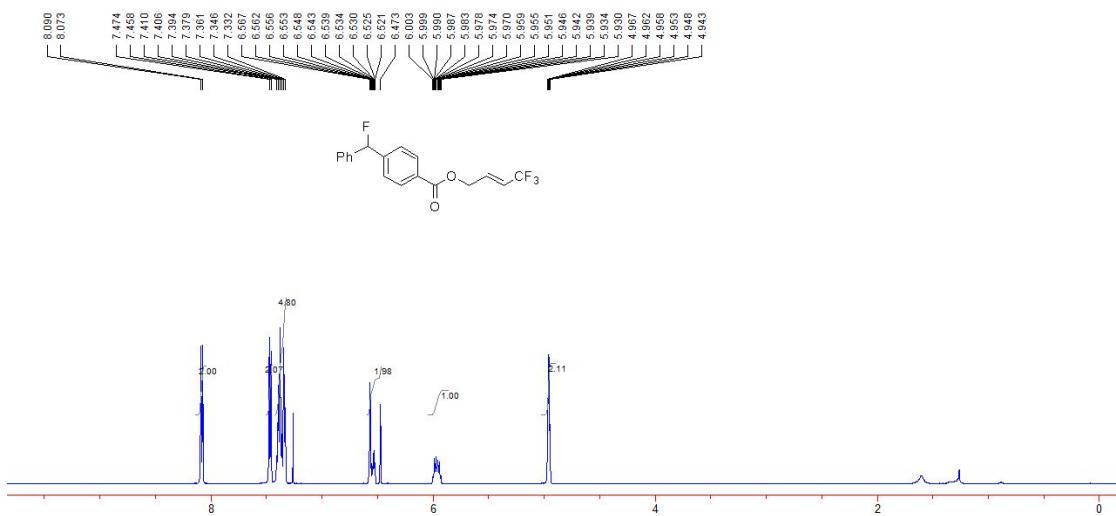


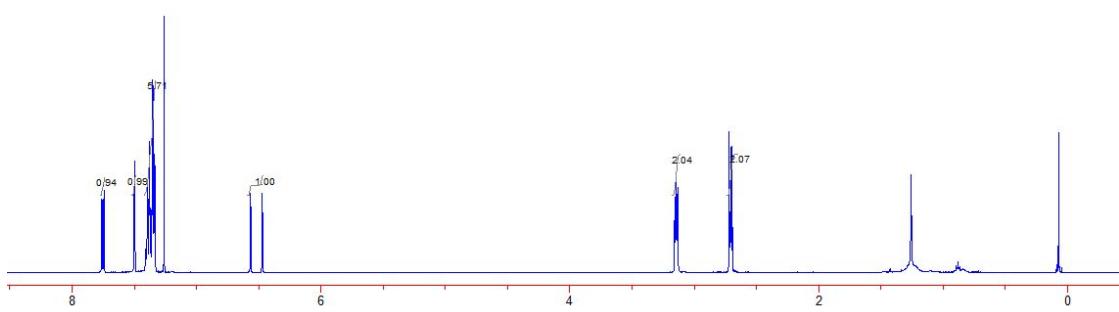
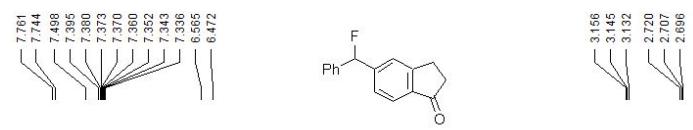
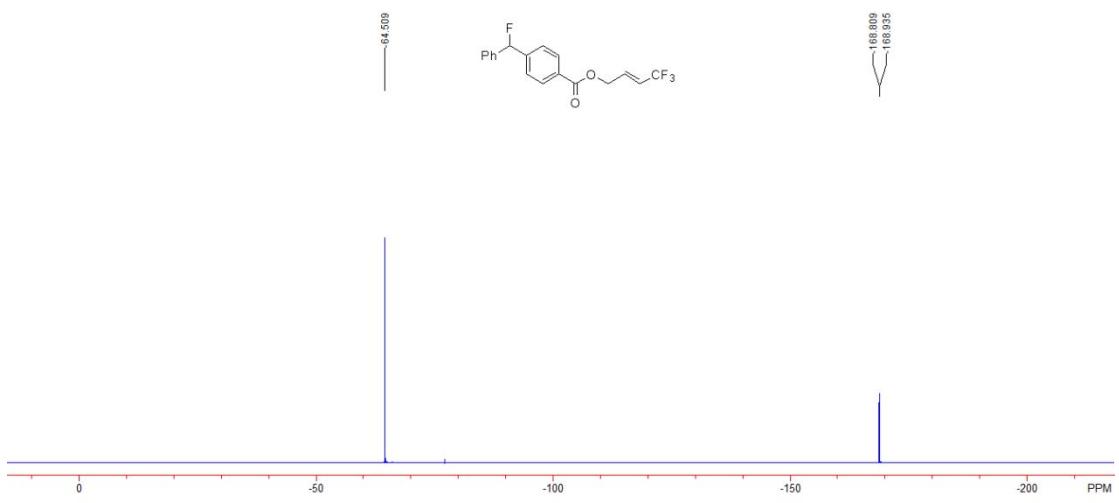


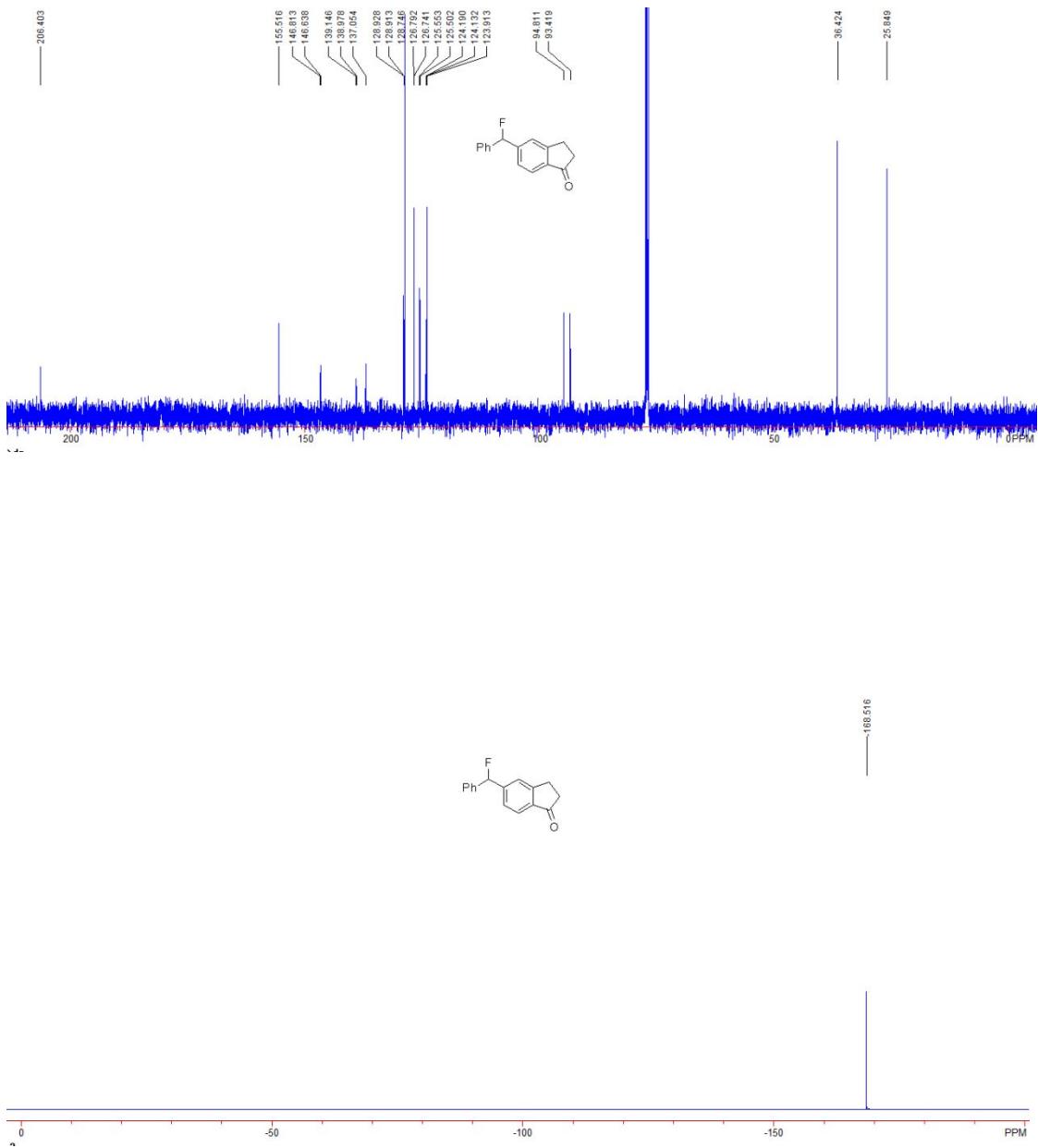


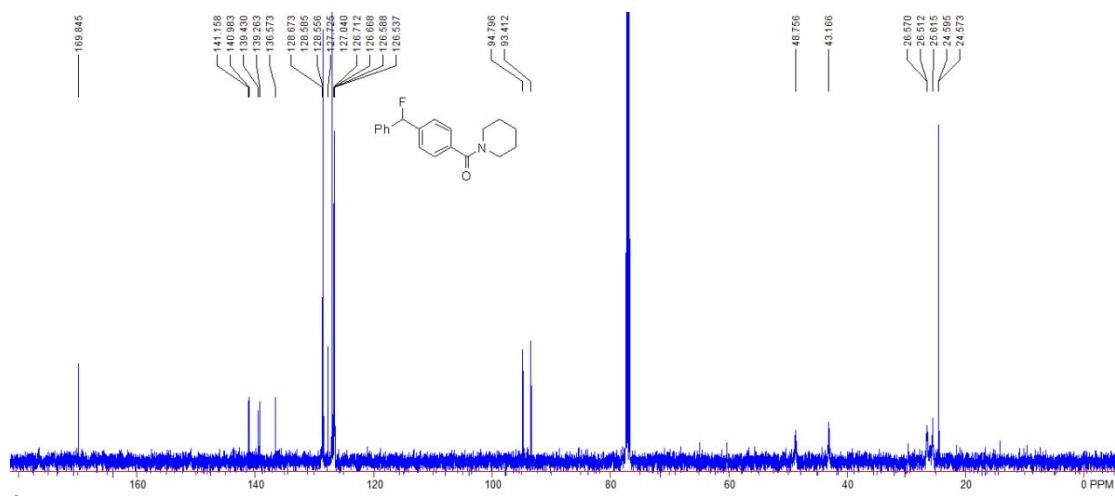
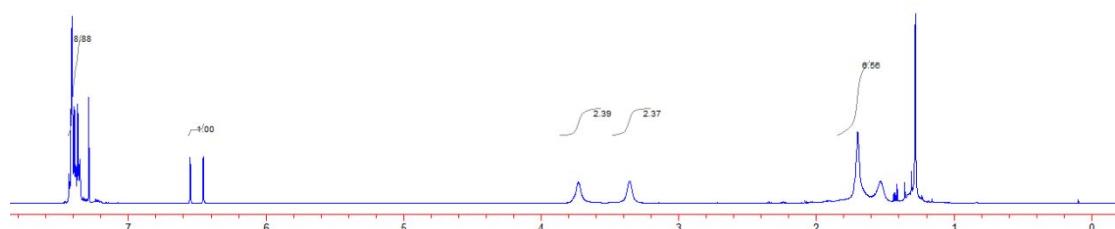
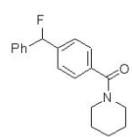
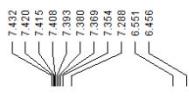


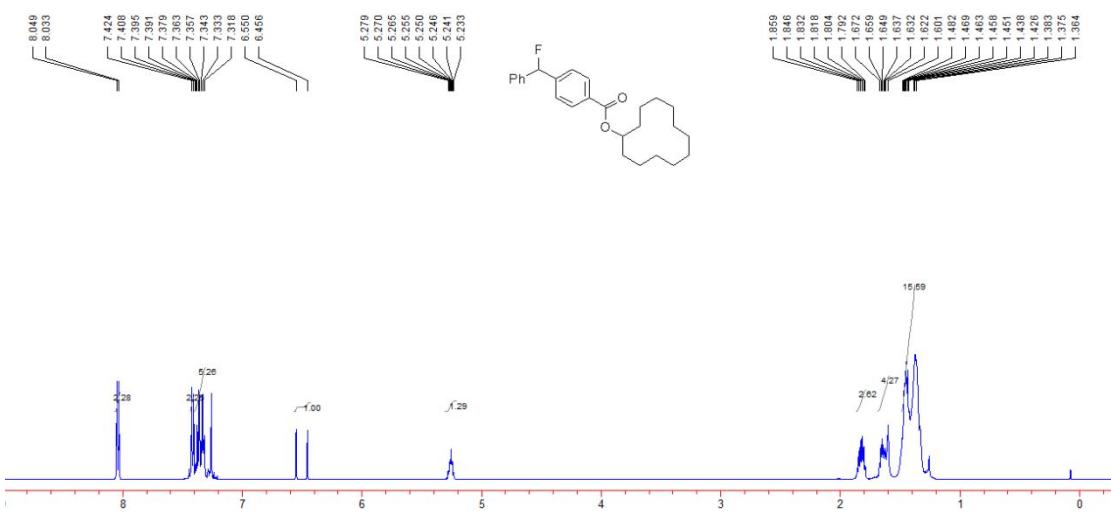
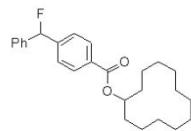
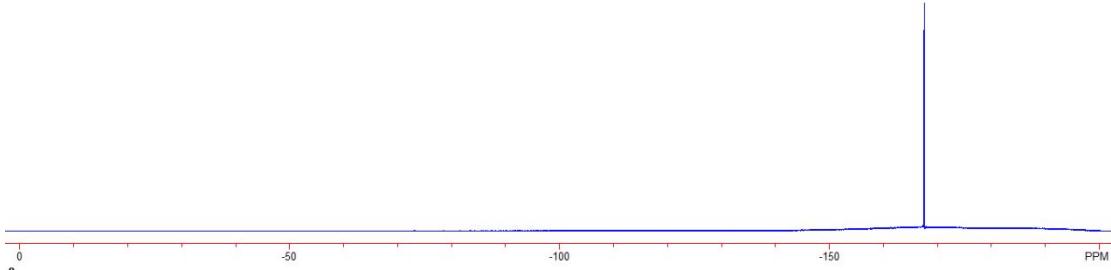
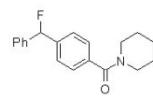


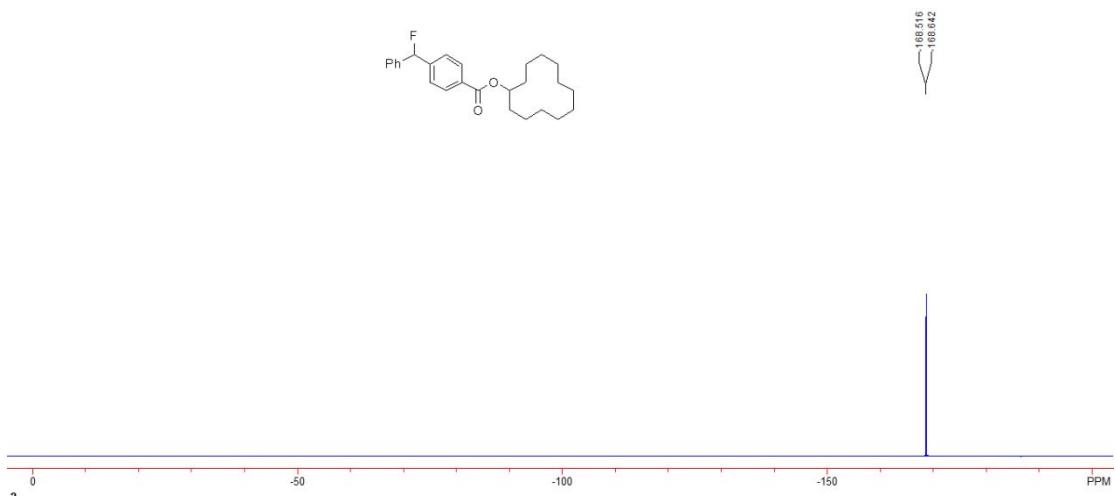
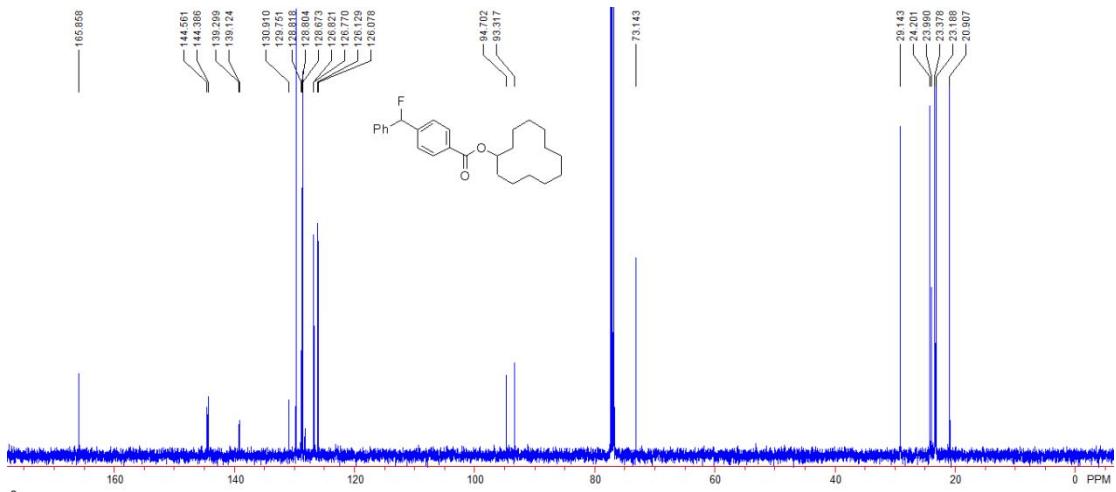


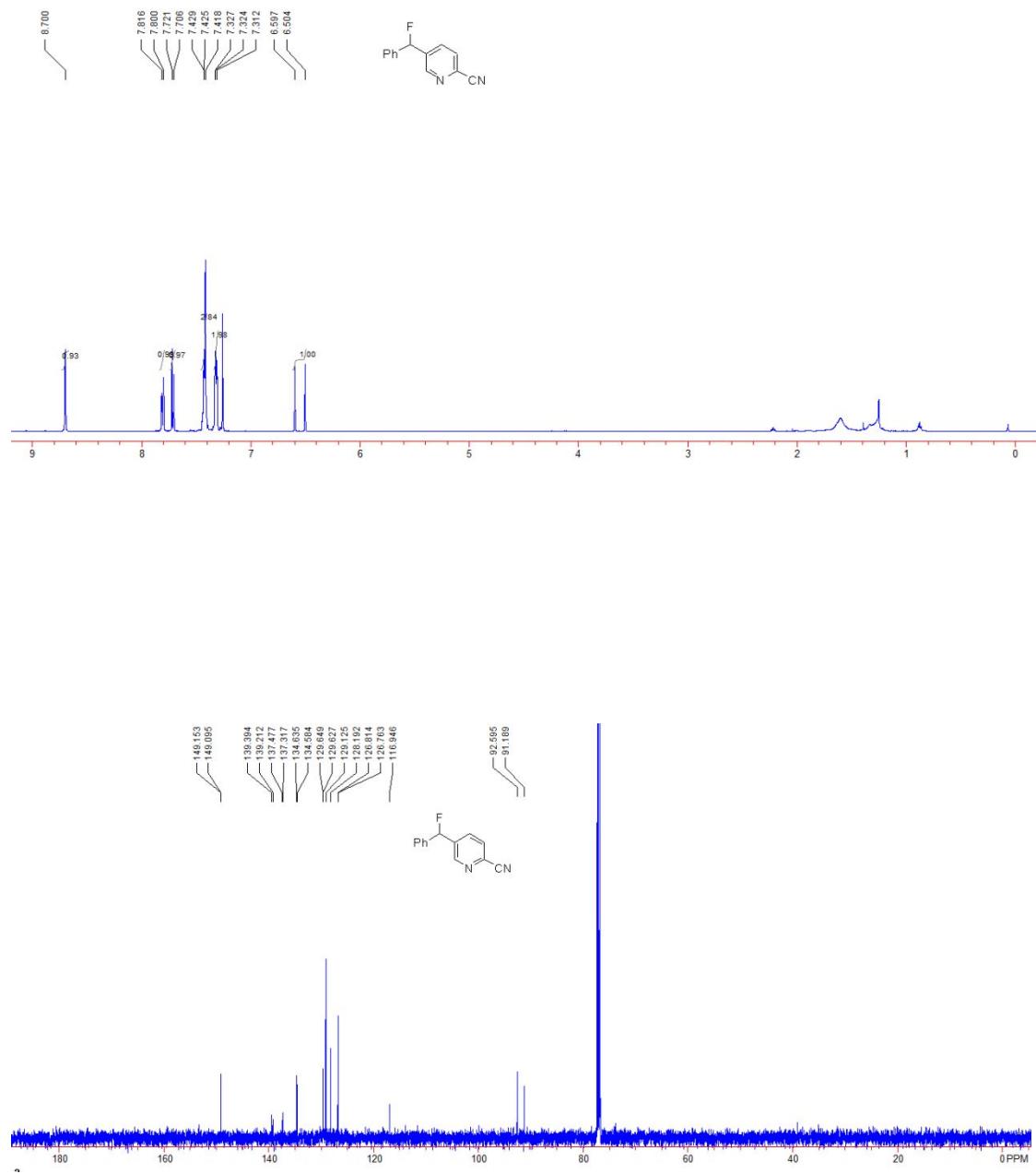


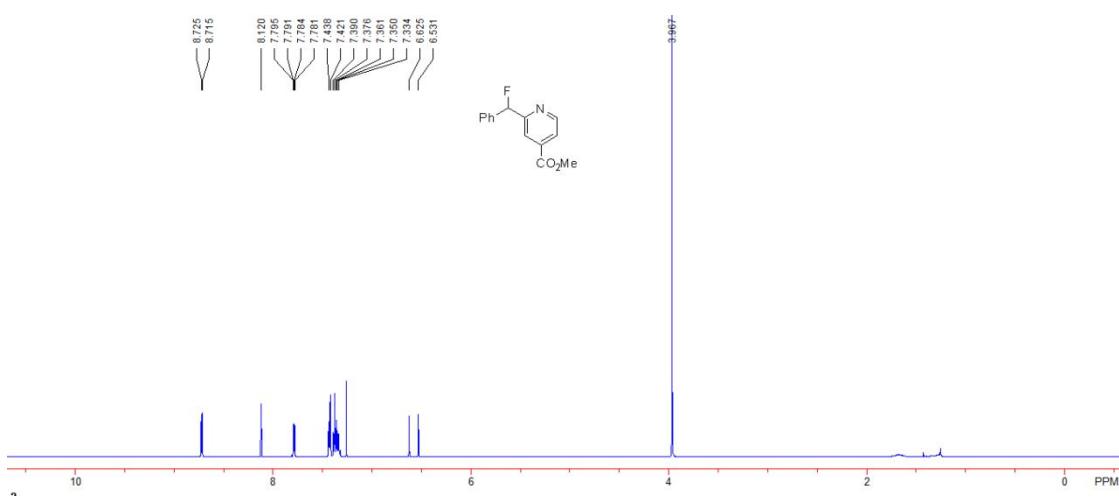
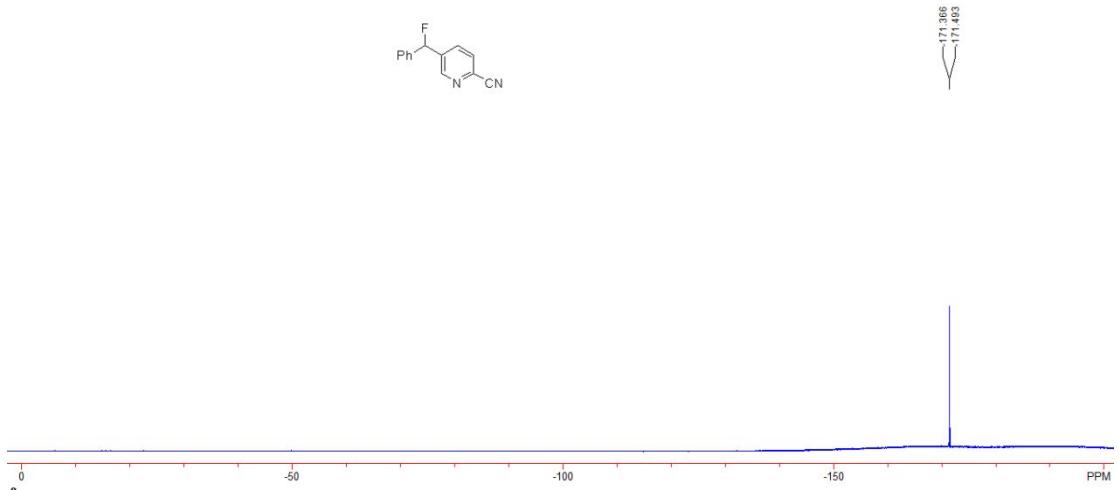


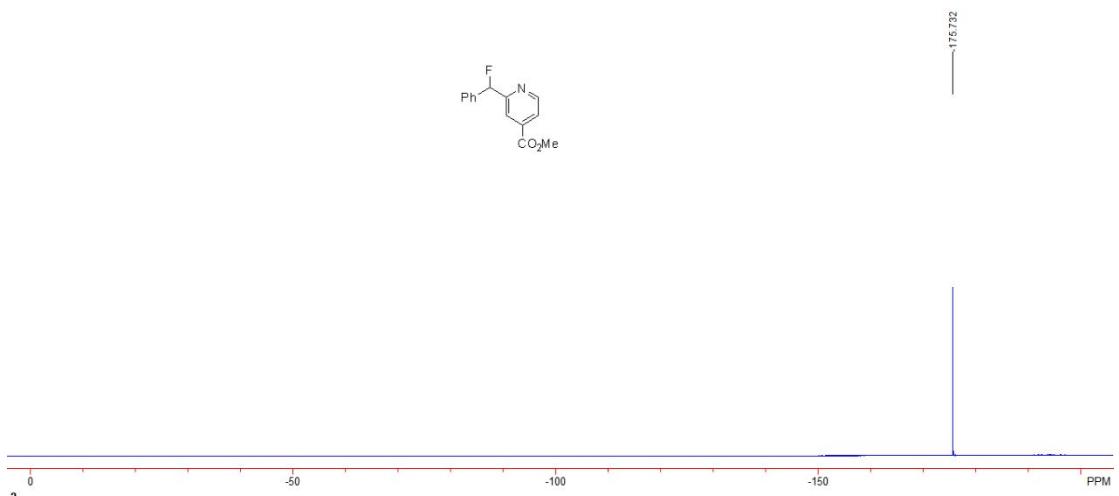
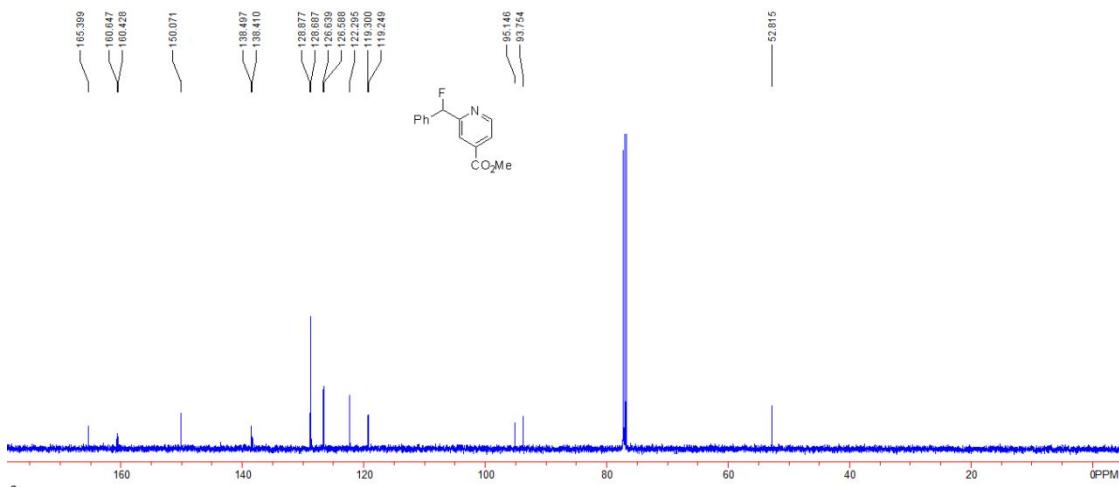


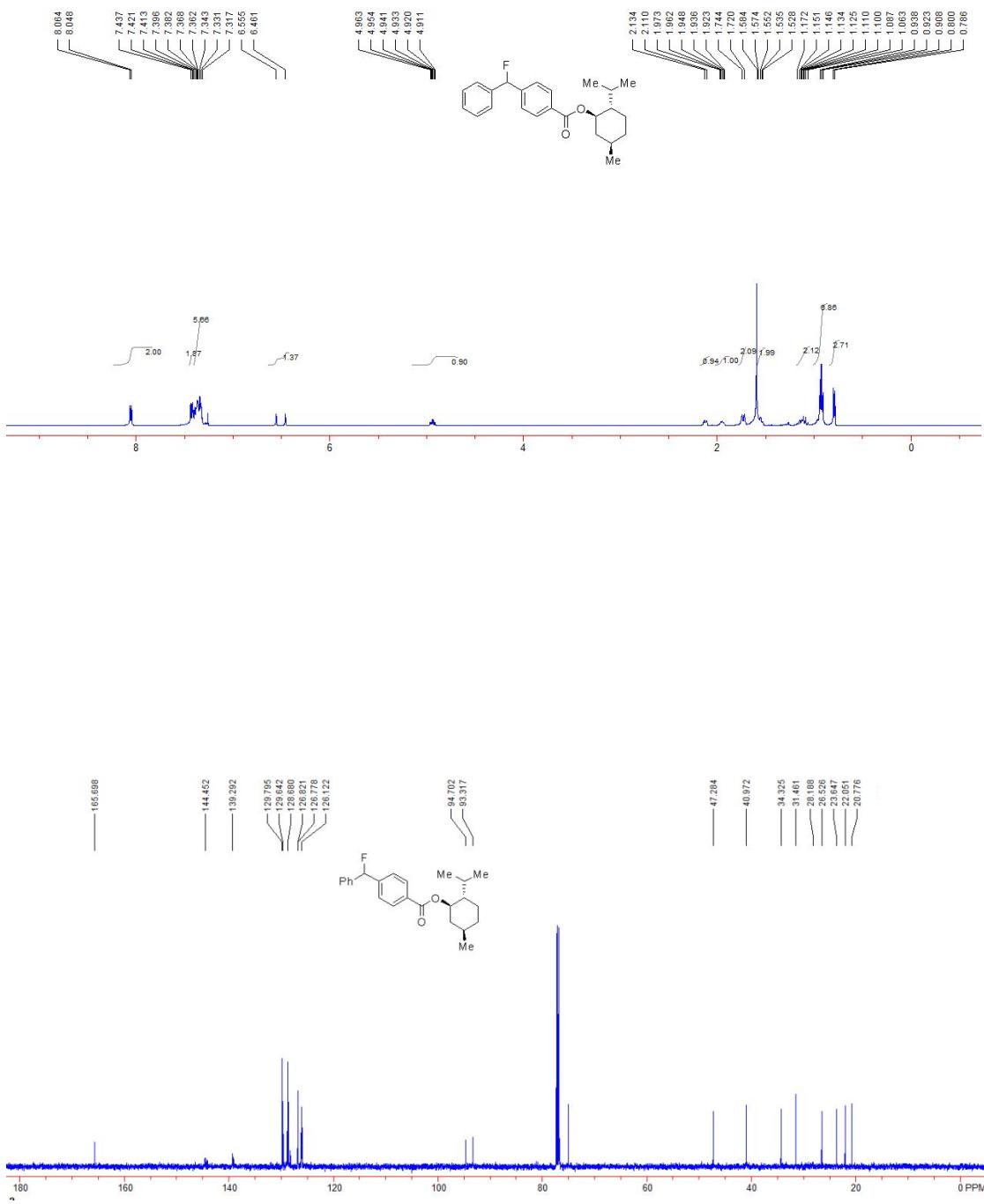


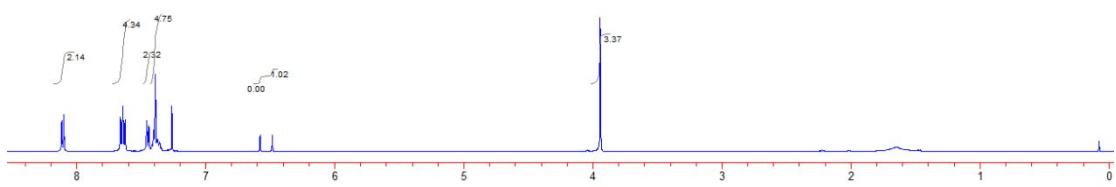
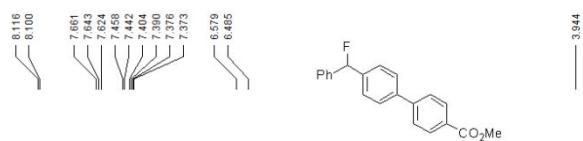
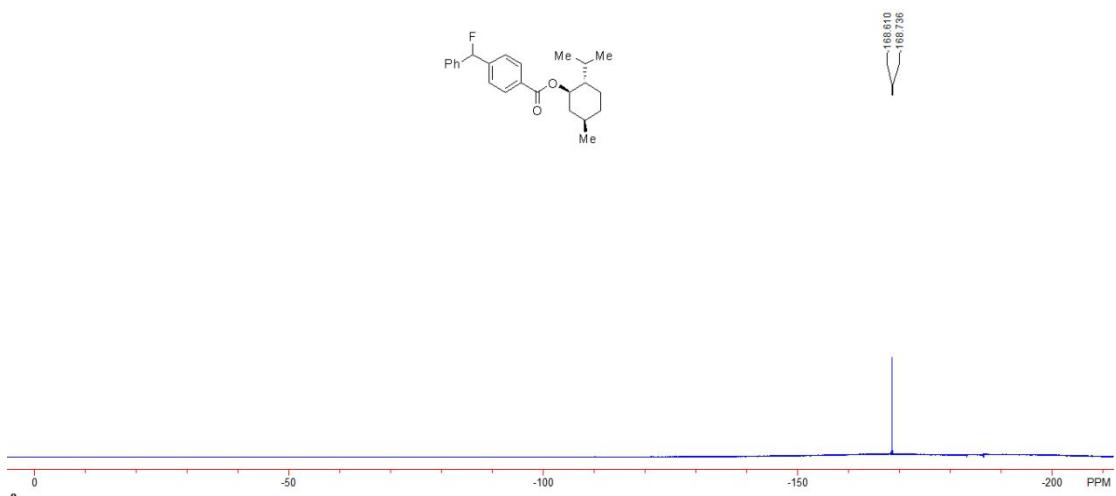


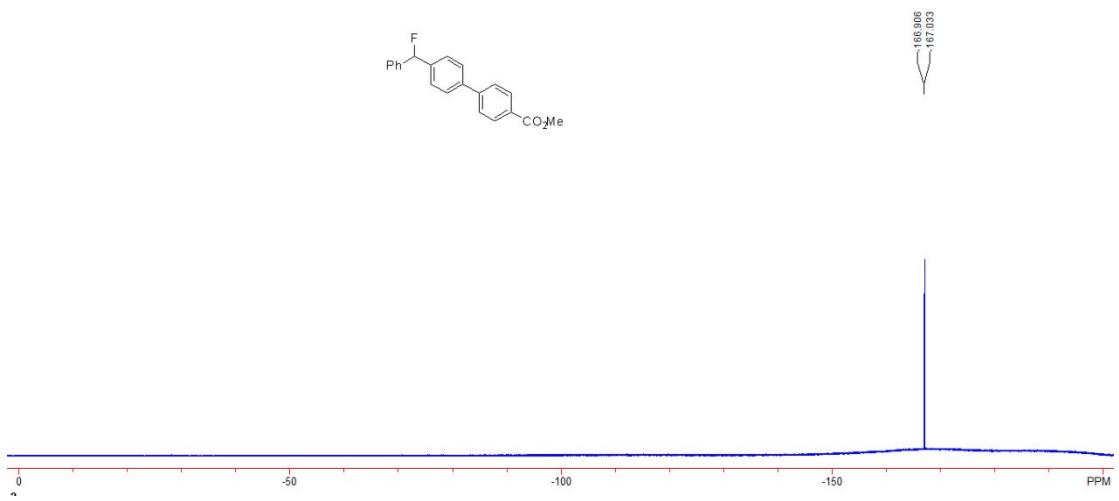
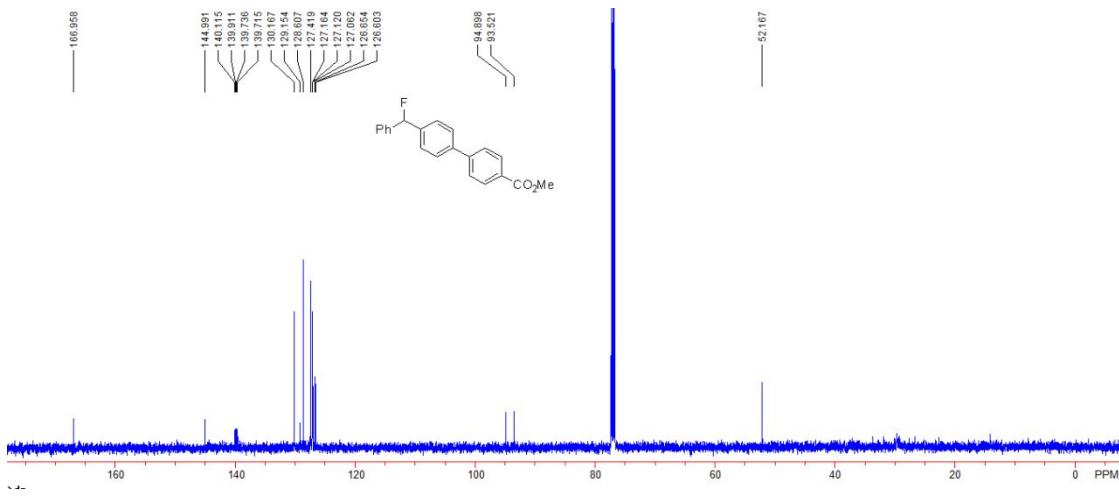


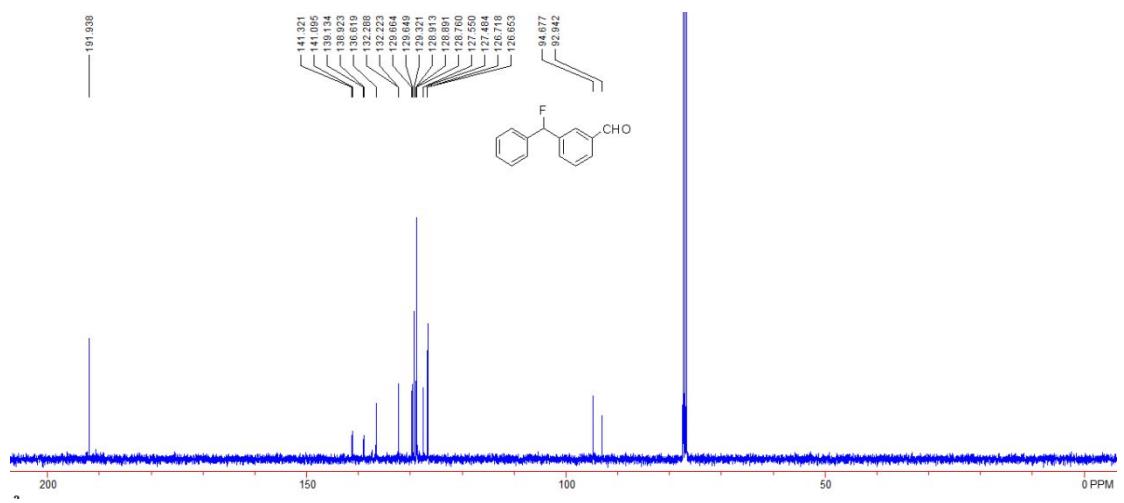
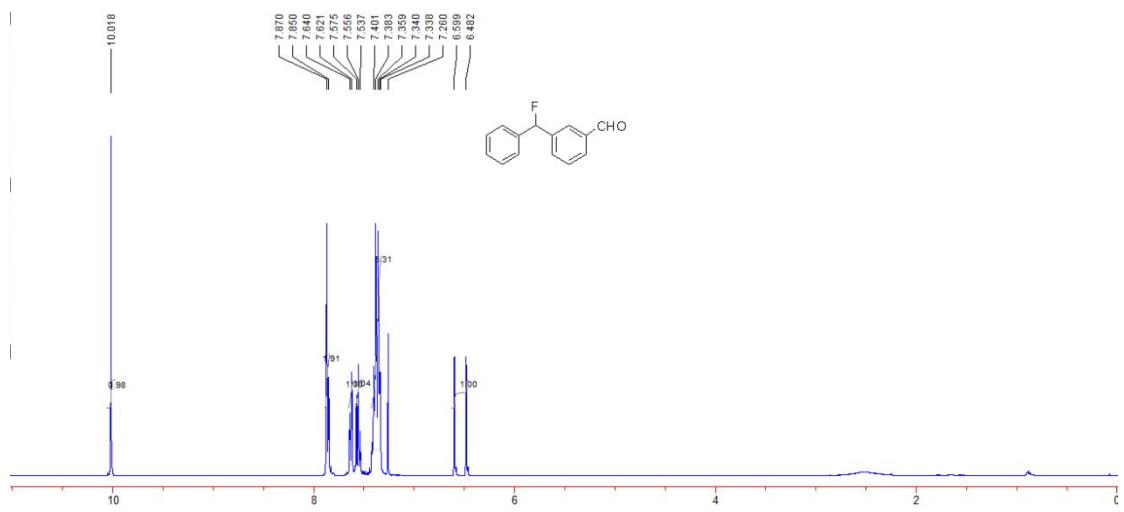


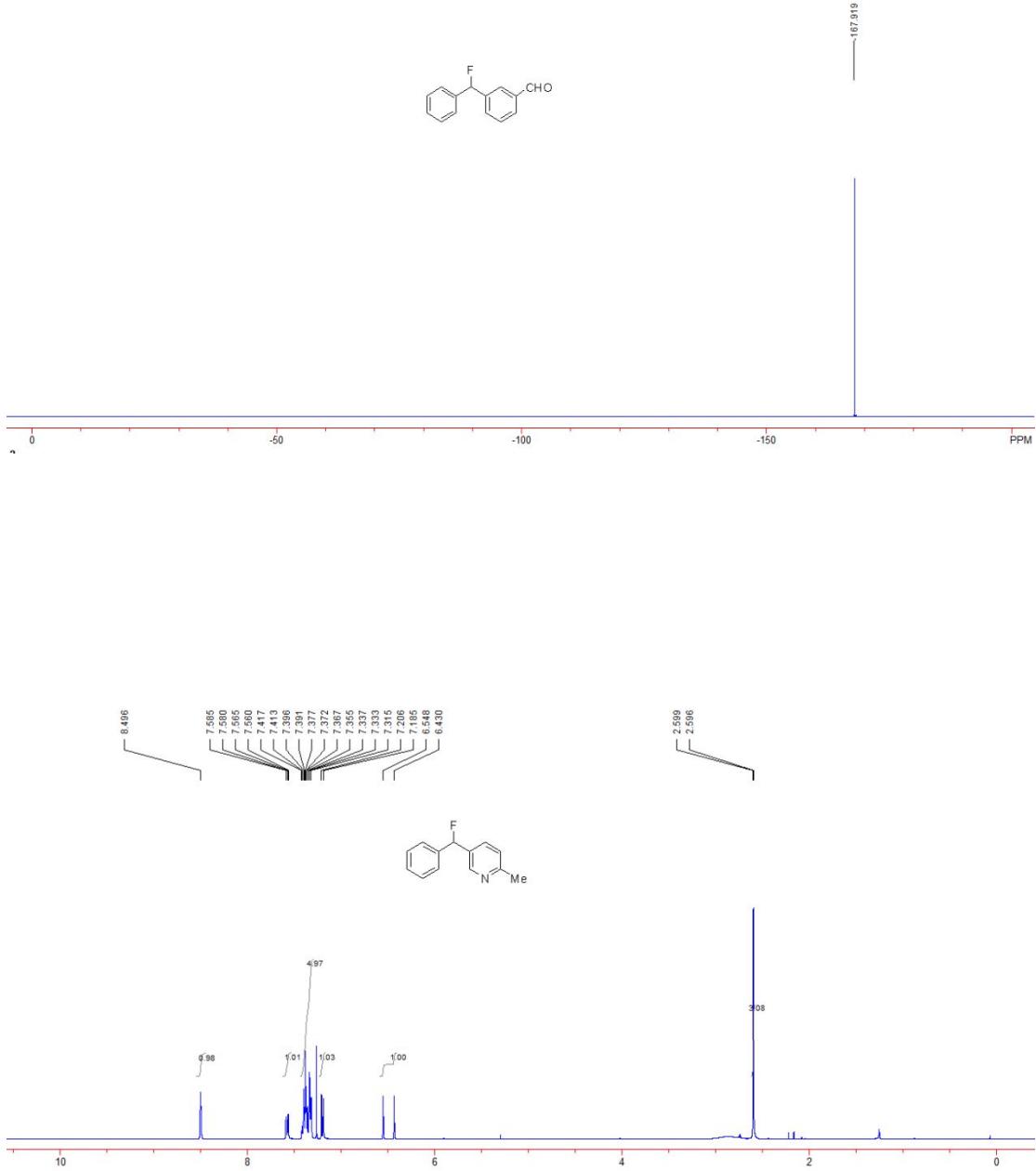


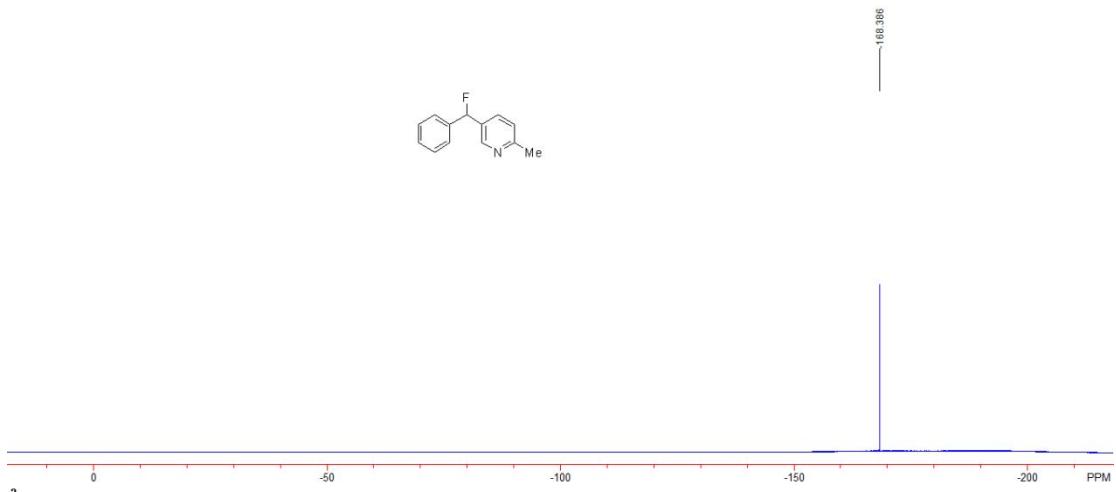
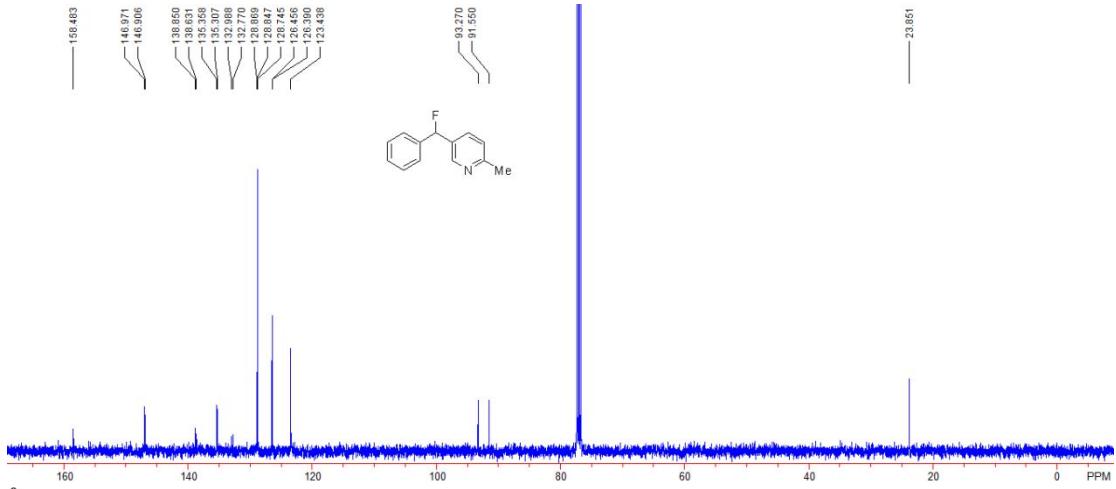


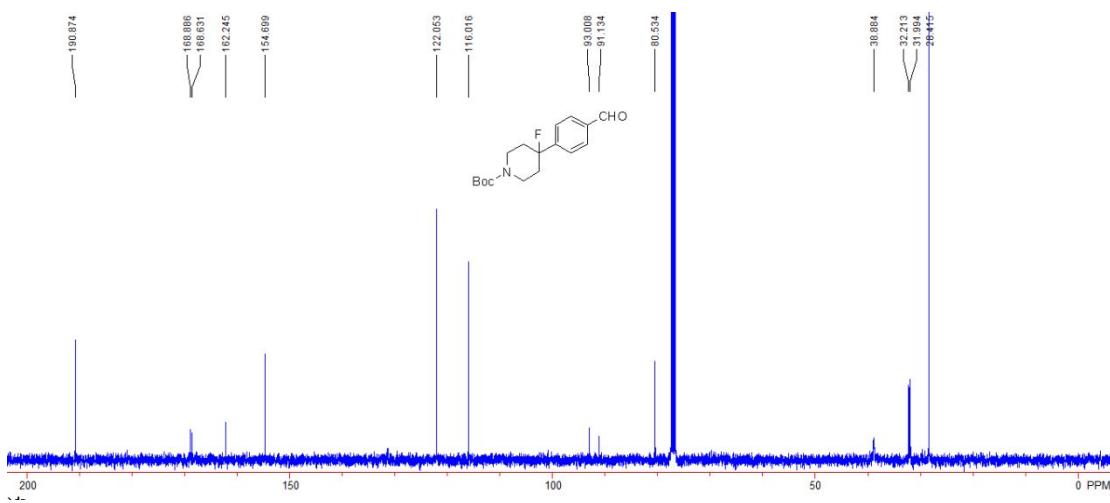
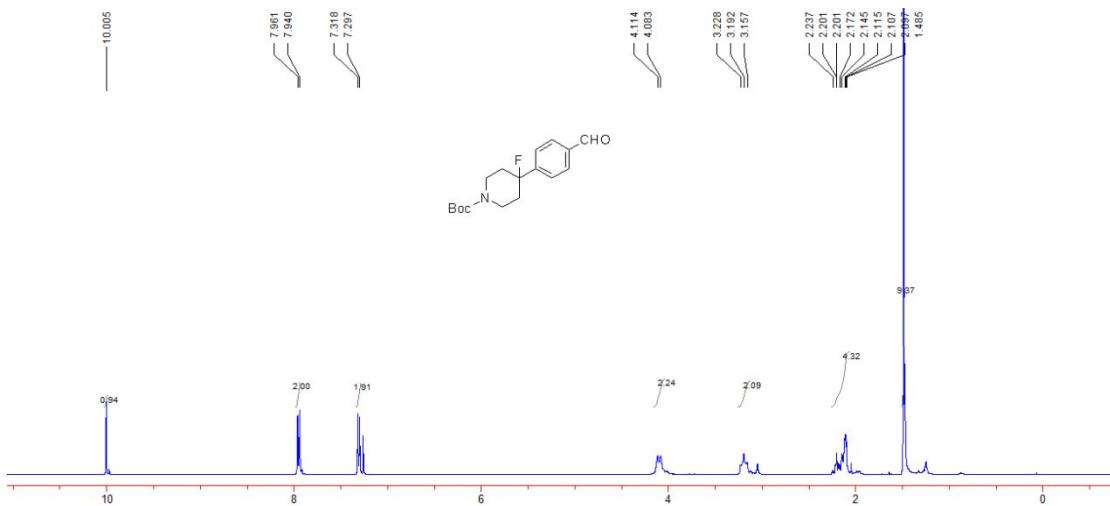


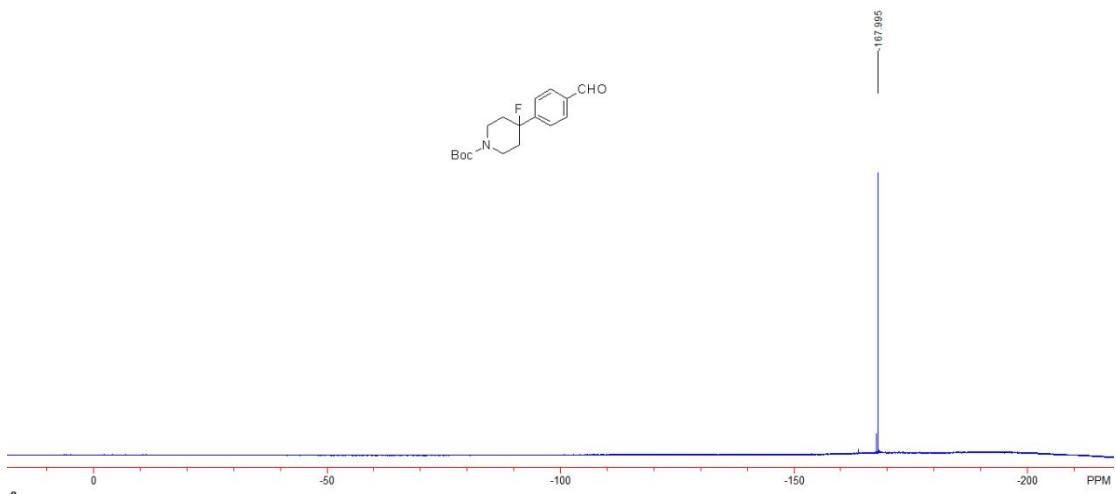










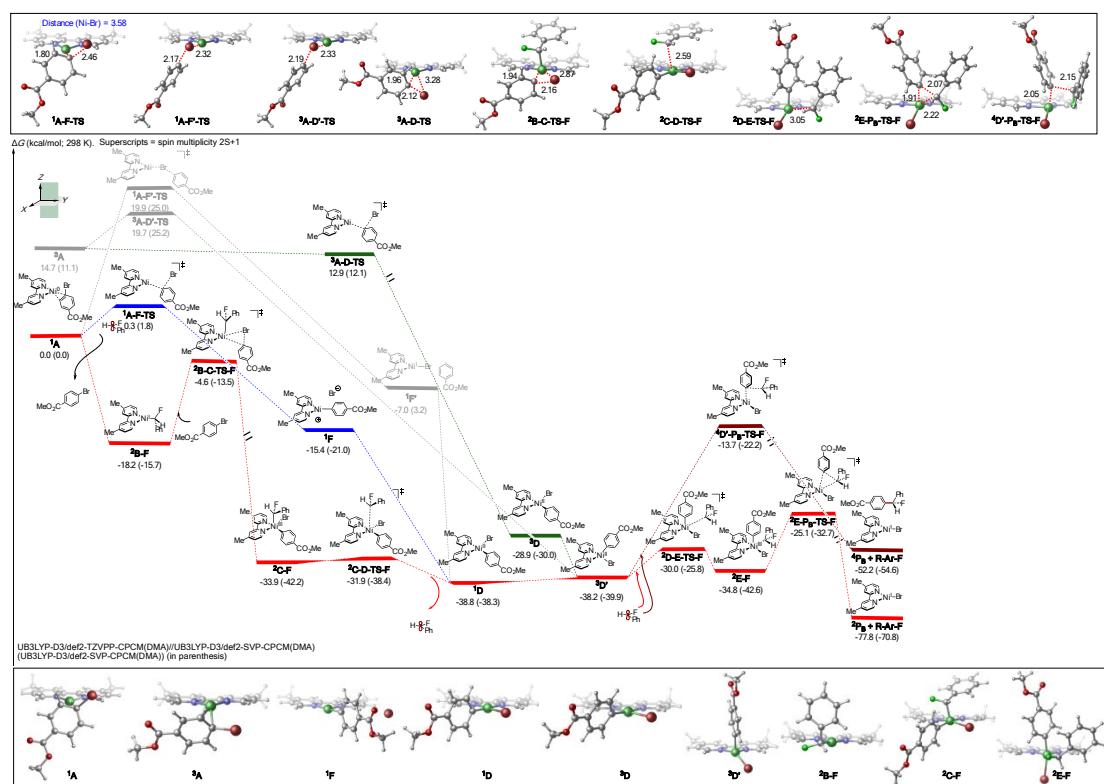


## 12. DFT calculations

### A. Computational Details

All geometry optimizations of intermediates and transition states were achieved using spin-unrestricted UB3LYP<sup>14</sup>-D3<sup>15</sup>/def2-SVP<sup>16</sup> method, in DMA solvent using the CPCM solvent model<sup>17</sup> with “opt=noeigen” and “guess=mix” keywords as implemented in Gaussian09<sup>18</sup>. Frequency calculations were also conducted at the same level of theory to obtain vibrational frequencies to determine the identity of stationary points as intermediates (no imaginary frequencies) or transition states (only one imaginary frequency), as well as obtaining the thermal corrections to enthalpy ( $H_{\text{correction}}$ ) and free energy ( $G_{\text{correction}}$ ) at the temperature of 298 K. Energies were refined by computing single point energies in implicit solvent with UB3LYP-D3/def2-TZVPP<sup>16</sup> method using larger basis set compared to optimization method. 4,4'-(*t*-Bu)<sub>2</sub>-bpy ligand was truncated as 4,4'-(Me)<sub>2</sub>-bpy due to computational cost. All structural figures were generated with CYLview.<sup>19</sup> Distances in structural figures are shown in Å and energies are in kcal/mol.

### B. Complete Energetic Diagrams

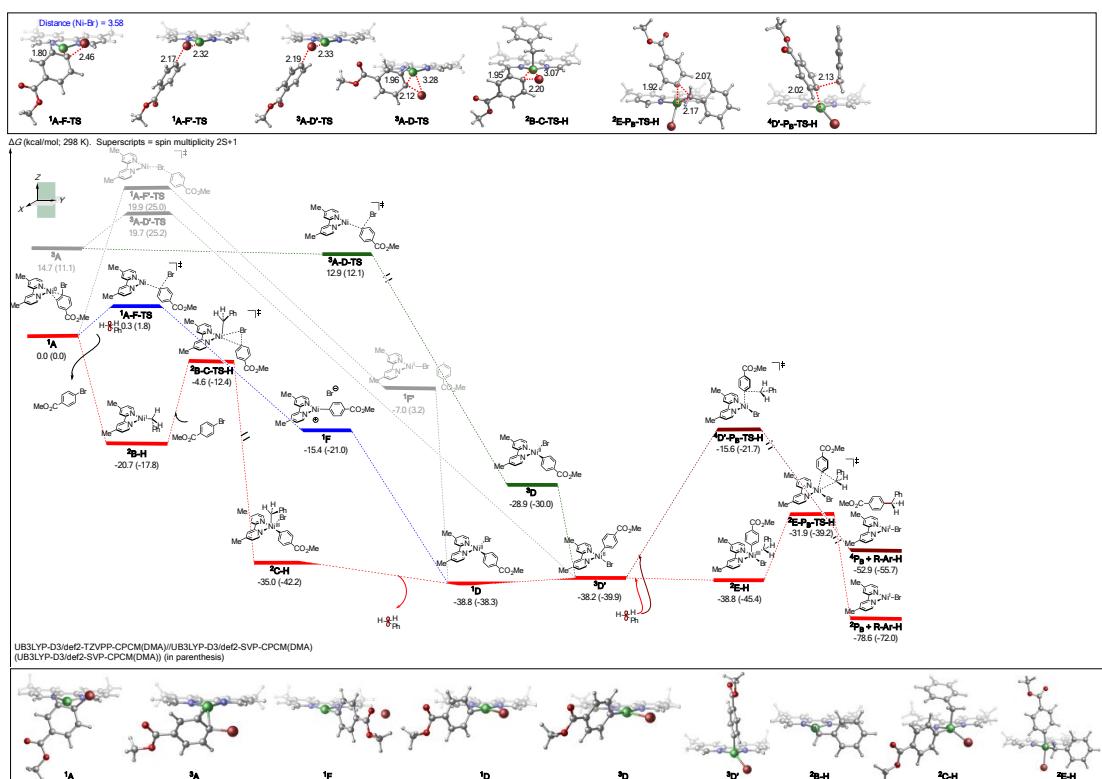


**Figure S1.** Calculated energetics of the Ni-catalyzed cross-coupling between fluorinated benzyl radical and aryl bromide using 4,4'-(Me)<sub>2</sub>-bpy as ligand. Free energies (kcal/mol) were computed at the UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA), and UB3LYP-D3/def2-SVP-CPCM(DMA) (in parenthesis) levels of theory.

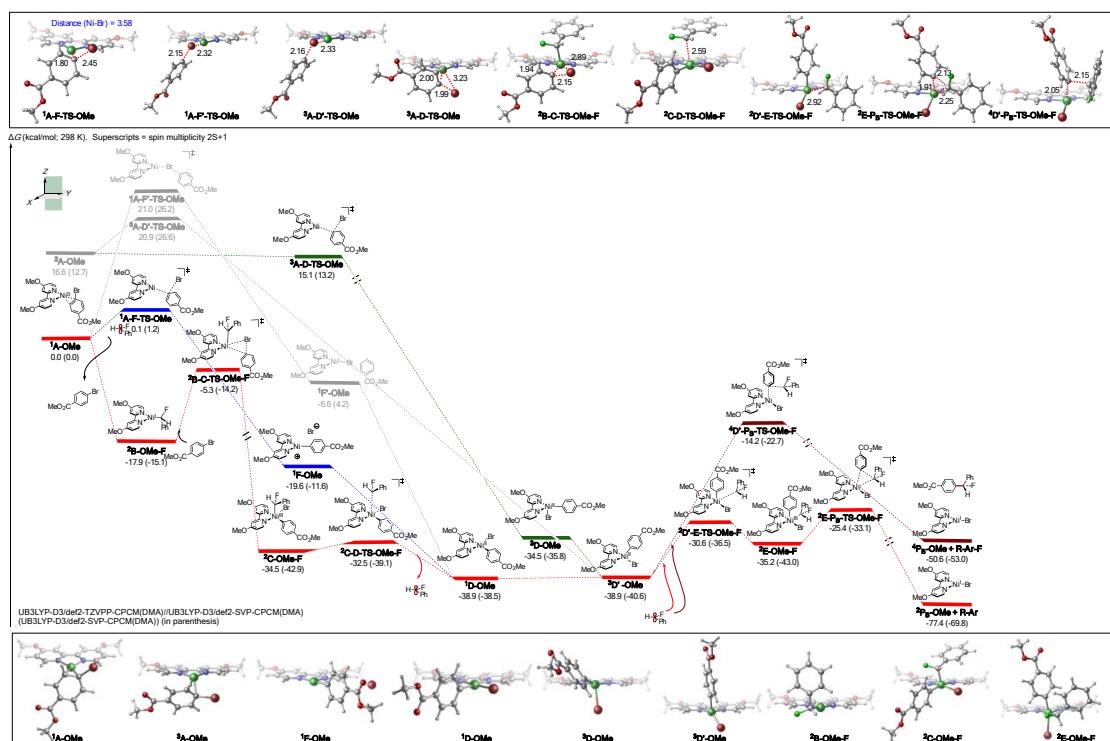
The lowest energy pathway is Ni(0)/Ni(I)/Ni(III) pathway as discussed in the main text: starting from singlet Ni(0) species **1A**, benzyl radical is favored to add to Ni(0) to form Ni(I)-benzyl intermediate (**2B**), which can then undergo oxidative addition (via **2B-C-TS-F**) to form the corresponding Ni(III) intermediate **2C**. This Ni(III) intermediate **2C** needs to undergo radical dissociation (via **2C-D-TS**) to form the square planar Ni(II) intermediate **1D**. However, for unsubstituted benzyl radical, this radical dissociation is barrierless. Then, this square planar Ni(II) intermediate **1D** undergoes isomerization-intersystem crossing to form the tetrahedral Ni(II) intermediate **3D'**, followed by radical addition from equatorial position to generate Ni(III) intermediate **2E** (via **2D-E-TS**) with C(sp<sup>2</sup>) moiety along the z-axis that is poised to undergo inner-sphere reductive elimination (via **2E-P<sub>B</sub>-TS**) leading to the desired cross-coupled product and Ni(I).

We also considered Ni(0)/Ni(II)/Ni(III) pathway. As shown in **Figure S1**, Ni(0) complex **1A** can undergo facile oxidative addition via **1A-F-TS** to form Ni(II) cation **1F** and bromide anion. Then the bromide anion binds back to the Ni complex to form square planar Ni(II) intermediate **1D**, which can then undergo isomerization-intersystem crossing, radical addition and inner-sphere reductive elimination to form desired product as seen in the latter part of Ni(0)/Ni(I)/Ni(III) pathway. Alternatively, triplet tetrahedral **3D'** can be formed from oxidative addition (via **3A-D-TS**) starting from triplet Ni(0) complex **3A** to generate triplet square planar Ni(II) complex **3D** followed by isomerization. We also located singlet and triplet transition states for halogen abstraction (**1A-F'-TS** and **3A-D'-TS**) that can lead to **1D** and **3D'**, respectively. However, calculations predict a high barrier for both transition states (~20 kcal/mol) thus the halogen abstraction pathways can be ruled out. Moreover, we considered the possibility of quartet outer-sphere C(sp<sup>2</sup>)-C(sp<sup>3</sup>) formation pathway (via **4D'-P<sub>B</sub>-TS**) but they were found with much higher barrier than the doublet inner-sphere pathway.

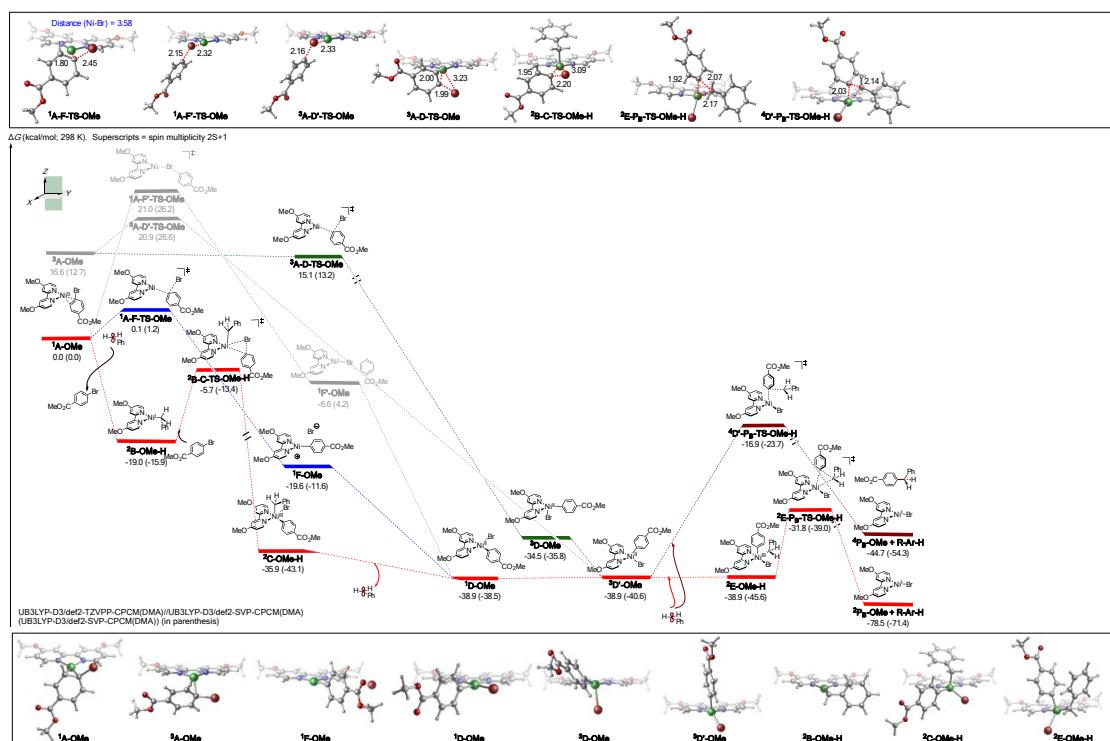
Taken together, since Ni(0)/Ni(II)/Ni(III) pathway is higher in energy level, Ni(0)/Ni(I)/Ni(III) pathway is more favorable in the presence of benzyl radical. The observed trends are consistent for both fluoro-substituted (Figure S1, 4,4'-dimethoxy bpy ligand system see Figure S3) and unsubstituted benzyl radical (Figure S2, 4,4'-dimethoxy bpy ligand system see Figure S4).



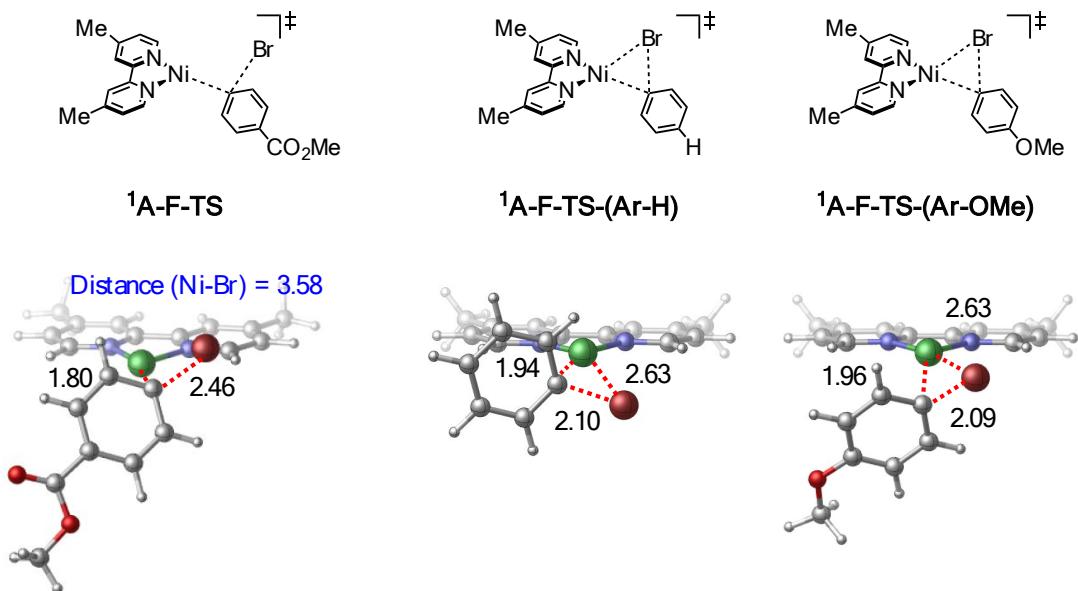
**Figure S2.** Calculated energetics of the Ni-catalyzed cross-coupling between unsubstituted benzyl radical and aryl bromide using 4,4'-(Me)<sub>2</sub>-bpy as ligand. Free energies (kcal/mol) were computed at the UB3LYP-D3/def2-TZVPP-CPCM(DMA)/UB3LYP-D3/def2-SVP-CPCM(DMA), and UB3LYP-D3/def2-SVP-CPCM(DMA) (in parenthesis) levels of theory.



**Figure S3.** Calculated energetics of the Ni-catalyzed cross-coupling between fluorinated benzyl radical and aryl bromide using 4,4'-(OMe)<sub>2</sub>-bpy as ligand. Free energies (kcal/mol) were computed at the UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA), and UB3LYP-D3/def2-SVP-CPCM(DMA) (in parenthesis) levels of theory.

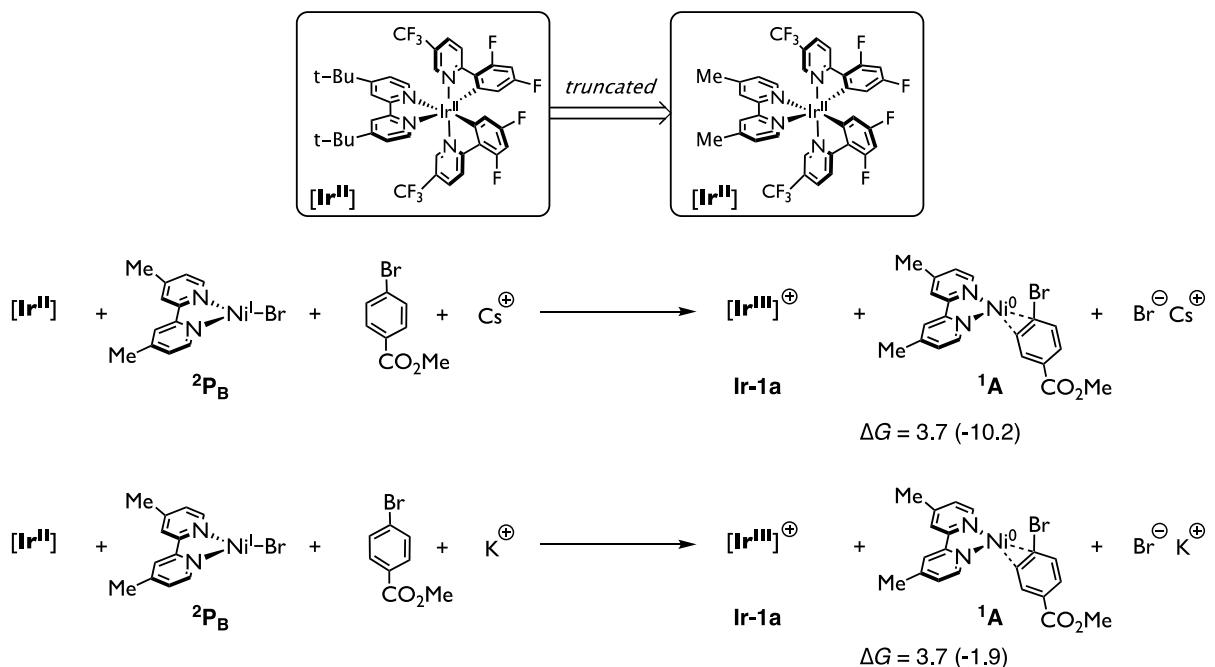


**Figure S4.** Calculated energetics of the Ni-catalyzed cross-coupling between unsubstituted benzyl radical and aryl bromide using 4,4'-(OMe)<sub>2</sub>-bpy as ligand. Free energies (kcal/mol) were computed at the UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA), and UB3LYP-D3/def2-SVP-CPCM(DMA) (in parenthesis) levels of theory.



**Figure S5.** Explored oxidative addition transition states from Ni(0) with different substituents on para- position of aryl bromide using 4,4'-(Me)<sub>2</sub>-bpy as ligand. Optimizations were done at UB3LYP-D3/def2-SVP-CPCM(DMA) level of theory.

We tried to locate the transition state of concerted 2e-oxidative addition from Ni(0) to Ni(II) with *p*-CO<sub>2</sub>Me-ArBr but all attempts failed, instead a nucleophilic substitution transition state from Ni(0) was found (**<sup>1</sup>A-F-TS**), leading to the generation of [Ni(II)(Ar)]<sup>+</sup>Br<sup>-</sup> species as confirmed by intrinsic reaction coordinate (IRC) calculation, where Br was stabilized by aryl ring (see Figure S1 for structures). Contrarily, the concerted oxidative addition transition states were obtained with phenyl bromide (**<sup>1</sup>A-F-TS-(Ar-H)**) and 4-methoxy-aryl bromide (**<sup>1</sup>A-F-TS-(Ar-OMe)**), with much shorter Ni-Br distance compared to **<sup>1</sup>A-F-TS**. Taken together, we attribute such difference in oxidative addition pathway to the electronic character of aryl ring. Specifically, nucleophilic substitution pathway is favorable for electron-deficient aryl bromide, while concerted 2e-oxidative addition is favorable for electron-neutral and electron-rich aryl bromide.



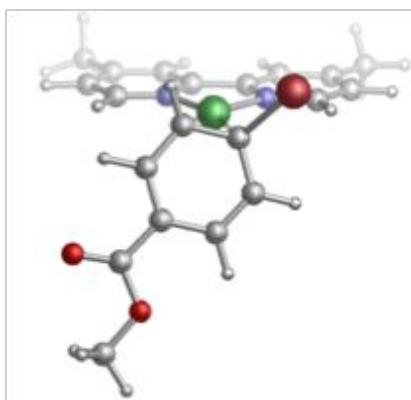
**Figure S6.** Calculated energetics of regeneration of Ni(0) catalyst **1A** from Ni(I) **2P<sub>B</sub>** by reduction of the reduced form of photocatalyst **Ir-1a**. Thermodynamic data were calculated using different counterions Cs<sup>+</sup> and K<sup>+</sup> for comparison. Free energies (kcal/mol) were computed at the UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA), and UB3LYP-D3/def2-SVP-CPCM(DMA) (in parenthesis) levels of theory.

After cross-coupling product and bromo Ni(I) species **2P<sub>B</sub>** were formed, catalytic cycle can be closed by single electron transfer (SET) between the reduced form of photocatalyst Ir(II) and bromo Ni(I) to regenerate photocatalyst **Ir-1a** and starting Ni(0) catalyst **1A** in the presence of aryl bromide and counterion in solution. As shown in Figure S6, this step is slightly uphill in energy by 3.7 kcal/mol (same for both counterions), and the counterion in solution (Cs<sup>+</sup> or K<sup>+</sup>, depending on the base used in catalytic system) have a minor effect on the energetics of this step. Although this step is slightly endergonic, the low barrier of oxidative addition and the barrierless radical addition of benzyl radical on Ni(0) species **1A** (as shown in Figure 1) can move the reaction forward and finish the nickel and photoredox catalytic cycles based on the energy span model proposed by Kozuch and Shaik.<sup>20</sup>

### C. Coordinates and Energies

**Figure S1**

<sup>1</sup>A



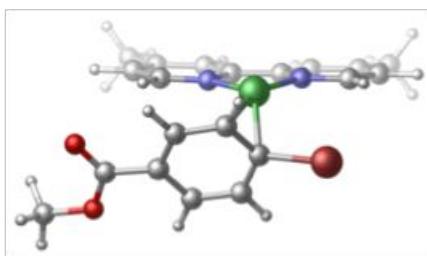
UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction=	0.346862 (Hartree/Particle)		
Thermal correction to Energy=	0.372667		
Thermal correction to Enthalpy=	0.373611		
Thermal correction to Gibbs Free Energy=	0.286466		
Sum of electronic and zero-point Energies=	-5114.604540		
Sum of electronic and thermal Energies=	-5114.578735		
Sum of electronic and thermal Enthalpies=	-5114.577791		
Sum of electronic and thermal Free Energies=	-5114.664937		
C	-2.67825000	-0.01313400	-0.82116700
C	-2.48473000	1.23743700	-1.57705100
C	-3.04079200	2.44993500	-1.01046200
C	-3.65884400	2.44884300	0.21215800
C	-3.85929900	1.22544300	0.94631100
C	-3.39843000	0.03409200	0.40667100
Br	-2.73154900	1.15670000	-3.62318600
H	-2.93349700	3.38370000	-1.56903100
H	-2.63404800	-0.97968000	-1.33827400
H	-3.61539800	-0.89586400	0.93973300
H	-4.01587500	3.38622600	0.64134600
C	1.76420200	0.40151800	0.05108800
C	0.31789700	-1.01338800	1.19396100
C	1.35332700	-1.50947900	1.98327900
C	2.65804200	-1.02976400	1.79616600
C	2.84653400	-0.05096400	0.80743100
C	1.85209200	1.43413900	-1.01255400
C	0.63231700	2.63568400	-2.58548600
C	1.77304700	3.30949800	-3.01894300
C	3.01120500	3.03520000	-2.42173400
C	3.03080000	2.07117500	-1.40050600

H	-0.71058100	-1.36003400	1.31544400
H	1.13821600	-2.26555700	2.74089400
H	3.84433300	0.35512100	0.63731400
H	-0.34564700	2.81453800	-3.03802700
H	1.69028800	4.04431200	-3.82219100
H	3.97533200	1.82392200	-0.91433600
N	0.51325100	-0.08512600	0.24905800
N	0.66439300	1.72379400	-1.60538400
Ni	-0.84533100	0.72932000	-0.90056200
C	4.27401500	3.73742500	-2.83824200
H	5.06419700	3.00980900	-3.08265100
H	4.11130000	4.38440400	-3.71127900
H	4.65622600	4.36122600	-2.01329500
C	3.81780500	-1.55162900	2.59824300
H	4.37757900	-2.29904600	2.01025000
H	4.52233000	-0.74558400	2.85292400
H	3.48326600	-2.03797400	3.52545300
C	-4.55193900	1.18653500	2.24737700
O	-4.75363600	0.18517500	2.91428100
O	-4.96165500	2.40902400	2.65838900
C	-5.63955500	2.46607600	3.91239200
H	-4.99441800	2.10188300	4.72727300
H	-5.89471800	3.52024900	4.07770700
H	-6.55503600	1.85425600	3.89482500

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)  
HF=-5116.618886

<sup>3</sup>A



UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction= 0.345561 (Hartree/Particle)

Thermal correction to Energy= 0.371305

Thermal correction to Enthalpy= 0.372249

Thermal correction to Gibbs Free Energy= 0.285631

Sum of electronic and zero-point Energies= -5114.587274

Sum of electronic and thermal Energies= -5114.561531

Sum of electronic and thermal Enthalpies= -5114.560586

Sum of electronic and thermal Free Energies= -5114.647204

C	-2.85357300	-0.49941000	1.79519100
---	-------------	-------------	------------

C	-2.38570800	-1.12341200	0.58929700
---	-------------	-------------	------------

C	-2.58616000	-0.46871000	-0.66815200
---	-------------	-------------	-------------

C	-3.11403600	0.80226900	-0.70307700
---	-------------	------------	-------------

C	-3.51175300	1.46325900	0.49539700
---	-------------	------------	------------

C	-3.39540800	0.79965300	1.71496900
---	-------------	------------	------------

Br	-2.23432100	-3.06959300	0.55993400
----	-------------	-------------	------------

H	-2.29090700	-0.97779000	-1.58672200
---	-------------	-------------	-------------

H	-2.94790900	-1.07291900	2.72095000
---	-------------	-------------	------------

H	-3.73872600	1.29753300	2.62376100
---	-------------	------------	------------

H	-3.22371100	1.31852500	-1.65711400
---	-------------	------------	-------------

C	1.79063500	0.02166700	0.29776700
---	------------	------------	------------

C	1.43802100	-2.27338000	0.70082500
---	------------	-------------	------------

C	2.63059200	-2.62873900	0.09934100
---	------------	-------------	------------

C	3.46360900	-1.60189000	-0.44330500
---	------------	-------------	-------------

C	3.02510200	-0.29442500	-0.33679600
---	------------	-------------	-------------

C	1.26223100	1.34693100	0.46625600
---	------------	------------	------------

C	-0.50758500	2.64129400	1.31700600
---	-------------	------------	------------

C	0.11051800	3.83021500	0.97520800
---	------------	------------	------------

C	1.38100100	3.78664900	0.32331300
---	------------	------------	------------

C	1.93706400	2.54284300	0.08803400
---	------------	------------	------------

H	0.76641100	-3.03085400	1.11526300
---	------------	-------------	------------

H	2.92397100	-3.67880900	0.04108200
---	------------	-------------	------------

H	3.63386600	0.50983600	-0.75390700
---	------------	------------	-------------

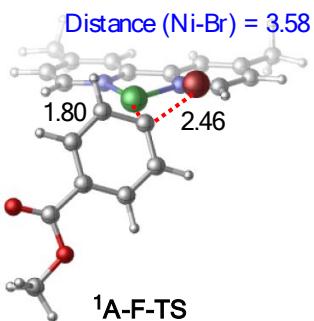
H	-1.47896900	2.64939800	1.81443200
---	-------------	------------	------------

H	-0.37399900	4.78189400	1.20240700
---	-------------	------------	------------

H	2.91580800	2.47521300	-0.39020300
N	1.01525200	-1.00077000	0.82025600
N	0.01386800	1.42525300	1.06628700
Ni	-0.73071600	-0.38378500	1.46304300
C	2.07037100	5.06399900	-0.07214300
H	3.04136800	4.87634900	-0.55361700
H	1.44536200	5.64597300	-0.77141900
H	2.23932300	5.70896600	0.80730100
C	4.76438100	-1.96060900	-1.10920300
H	5.29683000	-1.07160300	-1.47799300
H	5.42977900	-2.49554100	-0.40977700
H	4.59573800	-2.64014200	-1.96245700
C	-4.00292400	2.86110900	0.50377600
O	-4.22089400	3.50876600	1.51140200
O	-4.16004000	3.36444100	-0.73229900
C	-4.58639000	4.72690100	-0.82091100
H	-3.86062800	5.39359700	-0.33071100
H	-4.65205800	4.95833900	-1.89066000
H	-5.56791500	4.86084300	-0.34142100

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)  
HF=-5116.5946122

**<sup>1</sup>A-F-TS**



UB3LYP-D3/def2-SVP-CPCM(DMA)

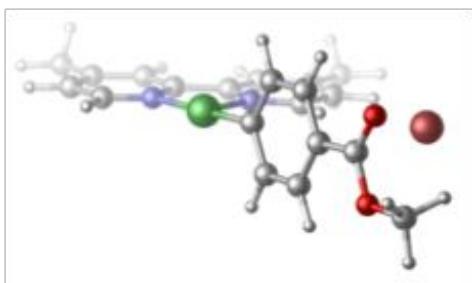
Zero-point correction=	0.347064 (Hartree/Particle)		
Thermal correction to Energy=	0.372296		
Thermal correction to Enthalpy=	0.373240		
Thermal correction to Gibbs Free Energy=	0.287214		
Sum of electronic and zero-point Energies=	-5114.602298		
Sum of electronic and thermal Energies=	-5114.577066		
Sum of electronic and thermal Enthalpies=	-5114.576122		
Sum of electronic and thermal Free Energies=	-5114.662148		
C	-2.69843100	0.14536100	-0.50663600
C	-2.34946700	1.41220600	-1.10480800
C	-2.93709300	2.60421500	-0.58453500
C	-3.76594200	2.54793700	0.51545200
C	-4.11326800	1.29888800	1.11657900
C	-3.59439000	0.12050600	0.58934200
Br	-2.72642500	1.48863000	-3.53495200
H	-2.68905500	3.56547600	-1.04079000
H	-2.50711700	-0.79867700	-1.02984100
H	-3.91767200	-0.83286900	1.01462600
H	-4.16020000	3.46926100	0.94748300
C	1.96929500	0.38566800	0.06918700
C	0.57838200	-0.96814100	1.34943800
C	1.66209300	-1.49786900	2.04809400
C	2.95984000	-1.06409100	1.74370200
C	3.09630700	-0.09967400	0.73127600
C	1.99558500	1.39615900	-1.01744300
C	0.67672000	2.59401200	-2.51740400
C	1.79559100	3.22781900	-3.05559200
C	3.07125700	2.93480200	-2.55487800
C	3.15230100	1.99446000	-1.51451100
H	-0.44666600	-1.27922400	1.56292600
H	1.48874900	-2.24410900	2.82556600
H	4.08965300	0.26508700	0.46772000

H	-0.33233200	2.77579800	-2.89595100
H	1.66512500	3.94718800	-3.86631200
H	4.12669500	1.73568300	-1.09871200
N	0.72497500	-0.05306000	0.38475500
N	0.77155700	1.70448800	-1.52087100
Ni	-0.71013500	0.81544700	-0.65808700
C	4.31385900	3.57515100	-3.10760300
H	4.91808300	2.82842700	-3.64938500
H	4.07618000	4.39238900	-3.80235500
H	4.94470100	3.97179300	-2.29675900
C	4.17006200	-1.59939600	2.45666200
H	4.84232400	-2.10509900	1.74446800
H	4.74574200	-0.77835100	2.91321000
H	3.89666700	-2.31527900	3.24377100
C	-5.02934200	1.20649100	2.27718600
O	-5.36078300	0.17145400	2.82609600
O	-5.47722500	2.41121400	2.68514700
C	-6.36549000	2.41821300	3.80387500
H	-5.88086500	1.98527900	4.69261200
H	-6.62075100	3.46902500	3.98729400
H	-7.27612700	1.83934700	3.58556700

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)

HF=-5116.6191322

**<sup>1</sup>F**



UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction= 0.348696 (Hartree/Particle)

Thermal correction to Energy= 0.374834

Thermal correction to Enthalpy= 0.375778

Thermal correction to Gibbs Free Energy= 0.286344

Sum of electronic and zero-point Energies= -5114.618610

Sum of electronic and thermal Energies= -5114.592472

Sum of electronic and thermal Enthalpies= -5114.591528

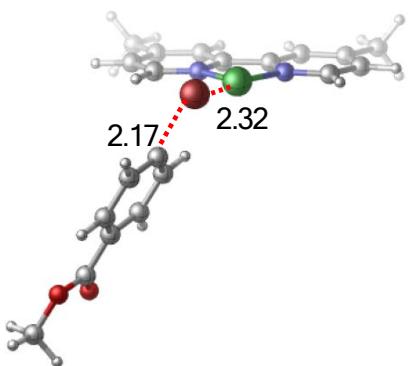
Sum of electronic and thermal Free Energies= -5114.680962

C	-2.74510400	0.21999500	0.21534400
C	-1.79543400	0.88669700	1.01071500
C	-2.22414800	1.95791300	1.81483200
C	-3.56510200	2.34886700	1.83712500
C	-4.50739300	1.67109800	1.04426500
C	-4.08710900	0.60271200	0.23364200
Br	-2.85150600	4.10111100	-2.13297800
H	-1.50077300	2.50545100	2.42693700
H	-2.43252700	-0.60228900	-0.43548900
H	-4.82700600	0.08885700	-0.38401100
H	-3.88722300	3.18429100	2.46081000
C	2.62388500	-0.00031500	0.37189000
C	2.21141100	-1.35331000	2.21991000
C	3.52494200	-1.81831500	2.22618200
C	4.42801700	-1.35384200	1.25875900
C	3.95013100	-0.42454000	0.31917100
C	1.99733400	0.97345100	-0.54573400
C	0.02769000	2.10418800	-1.07315100
C	0.65016600	2.77218200	-2.12479100
C	1.99928200	2.53479500	-2.40702400
C	2.66716400	1.61084200	-1.58544400
H	1.47896000	-1.69322700	2.95645500
H	3.83700800	-2.53927500	2.98361500
H	4.62197300	-0.03935400	-0.44844900
H	-1.02412800	2.29708200	-0.86320400
H	0.04141400	3.47311700	-2.70037200

H	3.72040900	1.39172400	-1.76311600
N	1.77670300	-0.46970400	1.31618500
N	0.67694000	1.22154100	-0.29638300
Ni	-0.04164800	0.25414700	1.14900200
C	2.72180600	3.23263800	-3.52323800
H	3.23806900	2.50471400	-4.16880400
H	2.03586700	3.82943700	-4.13945200
H	3.49498700	3.90429900	-3.11469200
C	5.85557500	-1.82016700	1.21128200
H	6.06908500	-2.30394700	0.24442600
H	6.54332000	-0.96388600	1.30034100
H	6.07917000	-2.53384000	2.01569600
C	-5.94455700	2.06045000	1.00728100
O	-6.79261100	1.50193900	0.33966600
O	-6.21996100	3.11272500	1.79630600
C	-7.57729000	3.56228100	1.81568300
H	-8.24825400	2.76413000	2.16823900
H	-7.60793100	4.41499700	2.50442700
H	-7.89913300	3.87387300	0.81025700

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)  
HF=-5116.6455269

**<sup>1</sup>A-F'-TS**



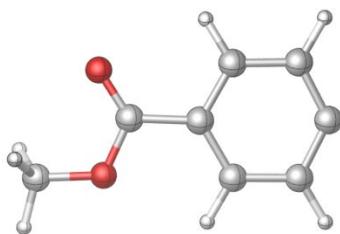
UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction=	0.344632 (Hartree/Particle)		
Thermal correction to Energy=	0.370422		
Thermal correction to Enthalpy=	0.371366		
Thermal correction to Gibbs Free Energy=	0.284212		
Sum of electronic and zero-point Energies=	-5114.564725		
Sum of electronic and thermal Energies=	-5114.538935		
Sum of electronic and thermal Enthalpies=	-5114.537990		
Sum of electronic and thermal Free Energies=	-5114.625145		
Ni	-3.25104500	1.75471800	-0.76136000
C	-6.31606800	2.76816700	0.69602600
C	-7.50976900	3.45588200	0.86603000
C	-5.82352000	1.85256700	1.61455200
C	-8.24849200	3.21400900	2.03026100
H	-7.86771500	4.16775900	0.11723500
C	-6.56700800	1.61700300	2.77320700
H	-4.88005400	1.33059100	1.42189900
C	-7.78011600	2.29532900	2.98648100
H	-9.19001100	3.73852200	2.20090500
H	-6.21952900	0.90674100	3.52674700
Br	-5.15122300	3.03112900	-1.11799100
N	-1.43300400	1.17011500	-0.53415100
C	1.12931700	0.01721500	-0.23138100
C	-0.32275800	1.93757600	-0.49261500
C	-1.29546500	-0.19800700	-0.41181300
C	-0.01092800	-0.77307500	-0.26907800
C	0.95211800	1.42588200	-0.34288700
N	-3.66831300	-0.16952600	-0.58270600
C	-3.89389900	-2.96997800	-0.37193000
C	-4.87034300	-0.77071500	-0.62522600
C	-2.54007900	-0.94199900	-0.44139900
C	-2.65228500	-2.34948200	-0.33586500

C	-5.04001600	-2.14050700	-0.52387800
H	-0.49104200	3.01384600	-0.59030100
H	0.08511300	-1.85697400	-0.18427600
H	1.81007200	2.10104600	-0.31567400
H	-5.72625500	-0.09935700	-0.74281200
H	-1.75195200	-2.95606700	-0.22386200
H	-6.04253200	-2.57186400	-0.56058800
C	-4.04706400	-4.46228700	-0.25624200
H	-4.66965400	-4.72560400	0.61577100
H	-4.55736900	-4.87439400	-1.14332100
H	-3.07632400	-4.96812500	-0.15113000
C	2.50723900	-0.56655700	-0.07738000
H	3.00183000	-0.17326100	0.82724700
H	2.48212700	-1.66368100	-0.00558900
H	3.14926200	-0.29164800	-0.93166700
C	-8.53220400	2.00551500	4.24276500
O	-8.16521700	1.22176200	5.09460700
O	-9.67097100	2.70803400	4.33959500
C	-10.45835200	2.49780100	5.51610000
H	-9.88935300	2.76910600	6.41828400
H	-11.33865600	3.14331300	5.41414300
H	-10.76535800	1.44400200	5.59576900

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)  
HF=-5116.5848436

**$^1F'$  (**Ni(I)-Br + Ar $\bullet$** )**



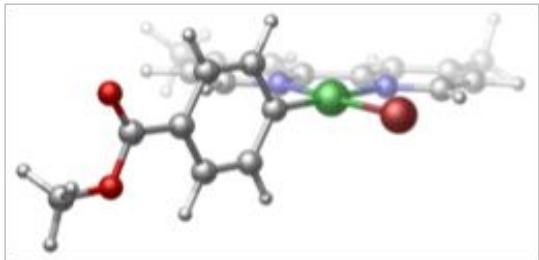
UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction=	0.130183 (Hartree/Particle)		
Thermal correction to Energy=	0.138924		
Thermal correction to Enthalpy=	0.139868		
Thermal correction to Gibbs Free Energy=	0.095198		
Sum of electronic and zero-point Energies=	-458.993935		
Sum of electronic and thermal Energies=	-458.985193		
Sum of electronic and thermal Enthalpies=	-458.984249		
Sum of electronic and thermal Free Energies=	-459.028919		
C	-2.46127700	0.25626500	2.02644000
C	-2.33883400	-0.73702400	1.07425600
C	-2.90783100	-0.73400500	-0.18401700
C	-3.68192000	0.38782300	-0.52034000
C	-3.84648200	1.43529000	0.40411400
C	-3.23875900	1.36796800	1.67052500
H	-2.77385100	-1.55350200	-0.89528100
H	-1.98534000	0.19650200	3.00892500
H	-3.38232000	2.19426800	2.37020400
H	-4.15842600	0.45023800	-1.49996300
C	-4.66069100	2.64691900	0.08731500
O	-4.83251800	3.57404500	0.85190500
O	-5.19015600	2.60782500	-1.14387200
C	-5.98859100	3.72928700	-1.53630900
H	-5.39568500	4.65606300	-1.51136200
H	-6.32627500	3.52124600	-2.55836200
H	-6.85293800	3.84452400	-0.86499100

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)

HF=-459.6405115

**1D**



UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction= 0.349108 (Hartree/Particle)

Thermal correction to Energy= 0.374861

Thermal correction to Enthalpy= 0.375806

Thermal correction to Gibbs Free Energy= 0.287717

Sum of electronic and zero-point Energies= -5114.664630

Sum of electronic and thermal Energies= -5114.638877

Sum of electronic and thermal Enthalpies= -5114.637933

Sum of electronic and thermal Free Energies= -5114.726021

Ni	-5.43961300	-0.37969800	0.47184900
----	-------------	-------------	------------

C	-5.93084000	0.86052500	1.80114100
---	-------------	------------	------------

C	-6.08725700	2.22575100	1.49001200
---	-------------	------------	------------

C	-6.10284200	0.47465500	3.14544200
---	-------------	------------	------------

C	-6.38137700	3.17120800	2.47398200
---	-------------	------------	------------

H	-5.96934900	2.56035400	0.45489800
---	-------------	------------	------------

C	-6.39524400	1.41001300	4.13783400
---	-------------	------------	------------

H	-6.00018300	-0.57879200	3.42254200
---	-------------	-------------	------------

C	-6.53632700	2.77167000	3.81418700
---	-------------	------------	------------

H	-6.49214800	4.22496800	2.21143700
---	-------------	------------	------------

H	-6.51958800	1.10301800	5.17908400
---	-------------	------------	------------

Br	-7.74349200	-0.78684300	0.12852600
----	-------------	-------------	------------

N	-3.52502200	-0.08638700	0.72077200
---	-------------	-------------	------------

C	-0.71641700	0.17220000	0.88568700
---	-------------	------------	------------

C	-2.95011700	0.73092900	1.62159500
---	-------------	------------	------------

C	-2.71268400	-0.79385200	-0.10928800
---	-------------	-------------	-------------

C	-1.32168000	-0.67951100	-0.04620000
---	-------------	-------------	-------------

C	-1.57354800	0.88493500	1.73609700
---	-------------	------------	------------

N	-4.76389200	-1.65778900	-0.94871800
---	-------------	-------------	-------------

C	-3.51628300	-3.31460500	-2.85097100
---	-------------	-------------	-------------

C	-5.48875700	-2.43498300	-1.76492600
---	-------------	-------------	-------------

C	-3.41537200	-1.68344300	-1.05687300
---	-------------	-------------	-------------

C	-2.76976200	-2.49514300	-1.99367700
---	-------------	-------------	-------------

C	-4.91179800	-3.26811800	-2.71896200
---	-------------	-------------	-------------

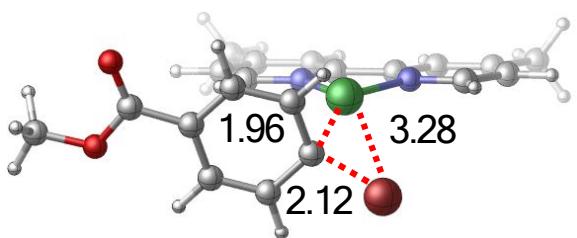
H	-3.62776300	1.27827900	2.27384300
---	-------------	------------	------------

H	-0.69819900	-1.26078600	-0.72500000
---	-------------	-------------	-------------

H	-1.17629600	1.56296600	2.49395700
H	-6.57101900	-2.37163000	-1.63537400
H	-1.68216300	-2.49531600	-2.06419000
H	-5.55475900	-3.87672800	-3.35799900
C	-2.85010700	-4.22263600	-3.84612000
H	-2.73561400	-5.23176400	-3.41437100
H	-3.45402900	-4.32527700	-4.75967400
H	-1.84787900	-3.86200300	-4.11841200
C	0.77534000	0.33307900	0.95792700
H	1.11428500	0.42151100	2.00094800
H	1.29964200	-0.50743200	0.48181800
H	1.07880400	1.25783200	0.43802500
C	-6.84387000	3.73061600	4.90546500
O	-6.98952600	3.42757300	6.07470000
O	-6.94933400	5.00173800	4.47285000
C	-7.24501100	5.99112500	5.46054200
H	-6.46225100	6.01886600	6.23416300
H	-7.28766400	6.95072900	4.93119900
H	-8.21046300	5.78311900	5.94703600

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)  
HF=-5116.6819407

<sup>3</sup>A-D-TS



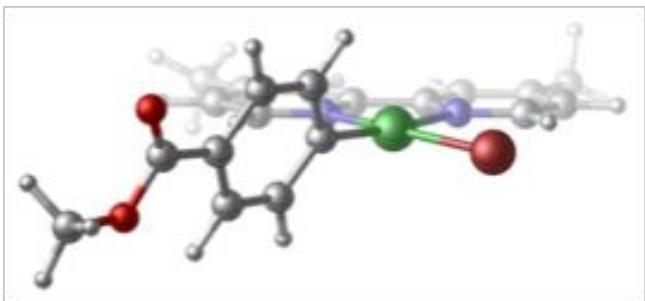
UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction=	0.344621 (Hartree/Particle)	
Thermal correction to Energy=	0.370344	
Thermal correction to Enthalpy=	0.371288	
Thermal correction to Gibbs Free Energy=	0.283476	
Sum of electronic and zero-point Energies=	-5114.584512	
Sum of electronic and thermal Energies=	-5114.558789	
Sum of electronic and thermal Enthalpies=	-5114.557845	
Sum of electronic and thermal Free Energies=	-5114.645657	
C	-2.82015300	-0.40965200
C	-2.47235300	-0.69667000
C	-2.96151200	0.20148400
C	-3.62308400	1.35467100
C	-3.89515400	1.68050500
C	-3.49582800	0.77144700
Br	-2.64362200	-2.74394000
H	-2.75905700	-0.02552300
H	-2.66638200	-1.16571500
H	-3.72748400	1.00054500
H	-3.93286100	2.05437900
C	2.10133100	-0.11722200
C	1.61329100	-2.35329700
C	2.92585300	-2.73787500
C	3.88314900	-1.76672600
C	3.44260500	-0.44710800
C	1.54381200	1.24284500
C	-0.39175300	2.52686300
C	0.29505300	3.69638400
C	1.67985600	3.64336200
C	2.29338000	2.38968500
H	0.84275000	-3.07959500
H	3.20866900	-3.78701700
H	4.14909800	0.33091100
H	-1.46370600	2.53154000
H	-0.24222700	4.64688500

H	3.36342500	2.30618300	-0.37394200
N	1.20099400	-1.07636800	0.56788100
N	0.20682600	1.32422000	0.36560700
Ni	-0.66292600	-0.44419100	0.67090800
C	2.44919900	4.89363200	-0.56091400
H	3.51486400	4.68661500	-0.73262300
H	2.03965600	5.37640900	-1.46357600
H	2.36509000	5.62680100	0.25816200
C	5.31309500	-2.15527000	-0.17196400
H	5.93049800	-1.28840500	-0.44663600
H	5.75347800	-2.62568200	0.72272800
H	5.37549200	-2.89742900	-0.98498200
C	-4.56762900	2.91899100	1.06120500
O	-4.82311100	3.24464500	2.21187200
O	-4.89049600	3.71089600	0.00742000
C	-5.54322200	4.94030200	0.31386400
H	-4.91177600	5.57556400	0.95503400
H	-5.72683800	5.44058600	-0.64534400
H	-6.49732100	4.76337100	0.83504200

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)  
HF=-5116.5953426

**<sup>3</sup>D**



UB3LYP-D3/def2-SVP-CPCM(DMA)

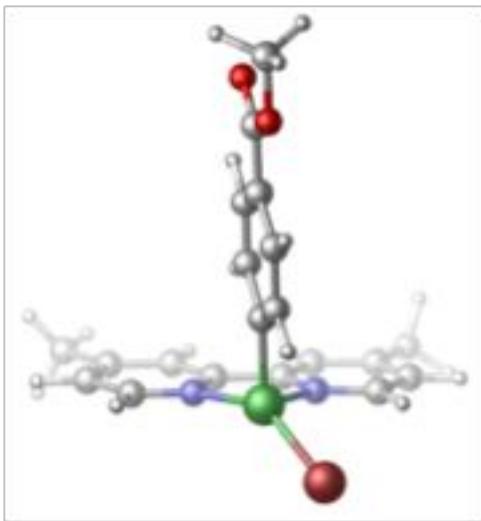
Zero-point correction=		0.347566 (Hartree/Particle)
Thermal correction to Energy=		0.374053
Thermal correction to Enthalpy=		0.374997
Thermal correction to Gibbs Free Energy=		0.283679
Sum of electronic and zero-point Energies=		-5114.648934
Sum of electronic and thermal Energies=		-5114.622446
Sum of electronic and thermal Enthalpies=		-5114.621502
Sum of electronic and thermal Free Energies=		-5114.712820
C	-2.88403200	0.77861900
C	-2.20528900	0.73039400
C	-2.81998700	1.41214600
C	-4.02648300	2.10371900
C	-4.67066500	2.14418600
C	-4.08246300	1.47257100
Br	-1.71227600	-2.54693200
H	-2.33744300	1.41165700
H	-2.46356500	0.24993000
H	-4.58631100	1.50453200
H	-4.47477700	2.61886300
C	2.47961600	-0.29900900
C	1.72118600	-2.47791000
C	3.00908600	-2.99239100
C	4.08893100	-2.11691500
C	3.79664000	-0.74598900
C	2.10878500	1.14140000
C	0.37447500	2.67205600
C	1.24758500	3.75075100
C	2.62360300	3.51306700
C	3.04381300	2.17558000
H	0.85263900	-3.12800900
H	3.16232300	-4.07302600
H	4.60808100	-0.03250200
H	-0.70170600	2.81995500

H	0.85307700	4.76862000	-0.00640300
H	4.10695000	1.95231400	-0.23907100
N	1.45597600	-1.16622500	0.14307700
N	0.79056500	1.40078200	0.08229800
Ni	-0.50440500	-0.29373300	0.29970300
C	3.60666600	4.63928700	-0.30681300
H	4.59844400	4.36694000	0.08224000
H	3.72650400	4.88601500	-1.37575300
H	3.25895600	5.54916300	0.20351700
C	5.50210100	-2.61436600	-0.25385400
H	5.98295200	-2.62136600	0.73940600
H	5.53575300	-3.64115000	-0.64529100
H	6.10400500	-1.96308600	-0.90455900
C	-5.94854500	2.86789600	1.05922400
O	-6.53829200	2.92988600	2.12171100
O	-6.41089500	3.46833100	-0.05499900
C	-7.63838200	4.18873400	0.06931000
H	-7.54444500	4.99979000	0.80786400
H	-7.85295400	4.60424700	-0.92279300
H	-8.45482300	3.52121300	0.38539700

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)

HF=-5116.6621788

**<sup>3</sup>D'**



UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction= 0.347800 (Hartree/Particle)

Thermal correction to Energy= 0.374182

Thermal correction to Enthalpy= 0.375126

Thermal correction to Gibbs Free Energy= 0.283695

Sum of electronic and zero-point Energies= -5114.664385

Sum of electronic and thermal Energies= -5114.638003

Sum of electronic and thermal Enthalpies= -5114.637059

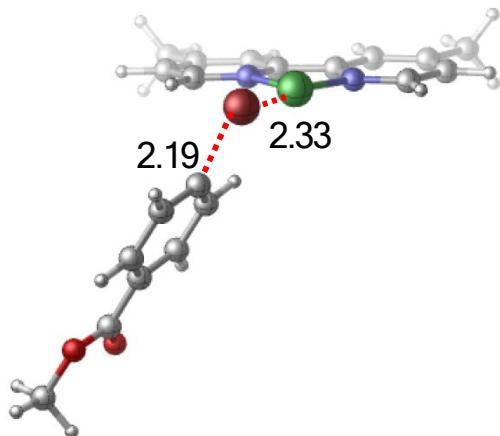
Sum of electronic and thermal Free Energies= -5114.728490

Ni	-4.41876100	1.54473900	-1.02818200
C	-5.33727500	1.80248000	0.71254700
C	-6.41086100	2.70730300	0.84879600
C	-4.95879700	1.09351500	1.87201500
C	-7.06502700	2.90989100	2.06722900
H	-6.74686500	3.26699200	-0.03036500
C	-5.60277100	1.27521000	3.09663400
H	-4.13145800	0.37686400	1.82164400
C	-6.66370500	2.19200700	3.20818700
H	-7.88997700	3.62126000	2.14309200
H	-5.29581800	0.71749200	3.98501100
Br	-5.77357100	2.34380200	-2.88366500
N	-2.51063300	1.18299800	-0.35158700
C	-0.04569300	0.43452500	0.74541100
C	-1.66037400	2.11059900	0.10335500
C	-2.17863700	-0.12327200	-0.27076000
C	-0.95371400	-0.52310400	0.27483900
C	-0.42488100	1.78435100	0.65166800
N	-4.33452800	-0.47755100	-1.24256200
C	-4.09882500	-3.26390700	-1.29464700

C	-5.32852300	-1.23027900	-1.72522100
C	-3.20880200	-1.06460500	-0.78316300
C	-3.06528900	-2.45537000	-0.80029400
C	-5.25280500	-2.61902600	-1.76922100
H	-1.99468400	3.14826200	0.02635600
H	-0.69972200	-1.58108500	0.34005800
H	0.23629200	2.57733400	1.00667000
H	-6.20142700	-0.68323900	-2.09030800
H	-2.15067300	-2.91949100	-0.43110600
H	-6.08832300	-3.19389100	-2.17333500
C	-3.98738900	-4.76297000	-1.29131700
H	-4.49135600	-5.20305100	-2.16441000
H	-2.93870700	-5.09247800	-1.27963900
H	-4.47643700	-5.17233500	-0.39071800
C	1.28645500	0.04404700	1.32147600
H	1.44767100	0.52994900	2.29651100
H	1.37455400	-1.04351600	1.45038600
H	2.10014600	0.37944800	0.65712000
C	-7.31421500	2.36407400	4.53331000
O	-7.00528400	1.75757200	5.54161100
O	-8.30195700	3.27923100	4.51865500
C	-8.97788500	3.51111500	5.75602800
H	-8.27550000	3.86718100	6.52540600
H	-9.73621800	4.27703600	5.55312900
H	-9.45742100	2.58932400	6.11976000

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)  
HF=-5116.677036

<sup>3</sup>A-D'-TS



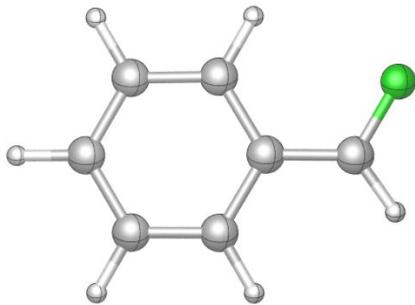
UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction=	0.344403 (Hartree/Particle)		
Thermal correction to Energy=	0.370288		
Thermal correction to Enthalpy=	0.371232		
Thermal correction to Gibbs Free Energy=	0.282596		
Sum of electronic and zero-point Energies=	-5114.562962		
Sum of electronic and thermal Energies=	-5114.537077		
Sum of electronic and thermal Enthalpies=	-5114.536133		
Sum of electronic and thermal Free Energies=	-5114.624769		
Ni	-3.19634700	1.79227300	-0.86467000
C	-6.25751600	2.81218200	0.60726200
C	-7.47633300	3.45741500	0.76484900
C	-5.75497800	1.89356800	1.51706900
C	-8.22761800	3.17368400	1.91152500
H	-7.84365500	4.17021700	0.02125800
C	-6.50987800	1.61770200	2.65943000
H	-4.79490000	1.40042200	1.33037400
C	-7.74742500	2.25453500	2.86184400
H	-9.18738300	3.66691800	2.07414300
H	-6.15277800	0.90760000	3.40872200
Br	-5.10456300	3.07445200	-1.23449500
N	-1.40086000	1.18878300	-0.52897700
C	1.13320000	0.00105200	-0.14781700
C	-0.27807300	1.93586300	-0.50237400
C	-1.29072500	-0.17391000	-0.36171000
C	-0.02299400	-0.76907800	-0.17656500
C	0.98554500	1.40479400	-0.31485600
N	-3.64933100	-0.11806800	-0.66511500
C	-3.95456100	-2.88257800	-0.21494500
C	-4.86279200	-0.69534300	-0.71075000

C	-2.55183100	-0.89662500	-0.39451100
C	-2.70109900	-2.28389100	-0.16688500
C	-5.06899800	-2.04829900	-0.50071400
H	-0.42409300	3.01096700	-0.63914000
H	0.05049500	-1.85153900	-0.05866200
H	1.85569200	2.06450400	-0.29737600
H	-5.69531700	-0.01912900	-0.92619900
H	-1.82369500	-2.89285900	0.05763800
H	-6.07827100	-2.46189300	-0.55450100
C	-4.14837000	-4.35459700	0.02882900
H	-4.62486600	-4.83684500	-0.84145200
H	-3.19579300	-4.86665100	0.22772600
H	-4.81764800	-4.52471100	0.88924700
C	2.49611800	-0.60476800	0.04864700
H	2.98559900	-0.18664800	0.94468400
H	2.44654900	-1.69740800	0.16239000
H	3.15510200	-0.37636900	-0.80618700
C	-8.51212100	1.92024700	4.09863000
O	-8.13612700	1.13451900	4.94498300
O	-9.67501800	2.58427500	4.18548800
C	-10.47712200	2.32808100	5.34254100
H	-9.93254900	2.59590700	6.26067800
H	-11.37323700	2.95097600	5.23737000
H	-10.75630500	1.26480300	5.39507700

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)  
HF=-5116.583607

### Fluoro-substituted benzyl radical



UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction= 0.107464 (Hartree/Particle)

Thermal correction to Energy= 0.113942

Thermal correction to Enthalpy= 0.114886

Thermal correction to Gibbs Free Energy= 0.076183

Sum of electronic and zero-point Energies= -369.784861

Sum of electronic and thermal Energies= -369.778383

Sum of electronic and thermal Enthalpies= -369.777439

Sum of electronic and thermal Free Energies= -369.816143

C 2.24760400 -0.07600700 0.88498100

C 2.62463300 0.81876700 1.90090900

C 2.70149400 0.41119100 3.26714200

C 2.94244700 2.17347500 1.57915500

C 3.07726600 1.31888900 4.25012400

H 2.46106600 -0.62142800 3.52660300

C 3.31557900 3.06469800 2.57687000

H 2.88947800 2.50312900 0.53811000

C 3.38680000 2.64913100 3.91858300

H 3.13163100 0.99241600 5.29212300

H 3.55563000 4.09840400 2.31451200

H 3.68079500 3.35597400 4.69793400

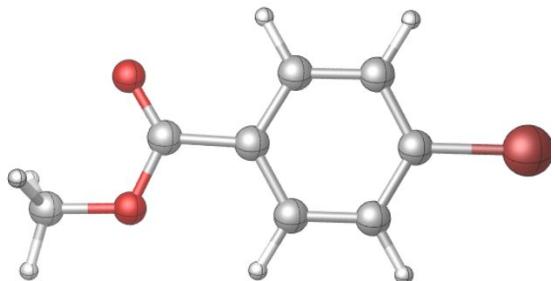
H 2.16579000 0.15974300 -0.17821000

F 1.94961200 -1.34698600 1.19159000

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)

HF=-370.3106978

### 4-CO<sub>2</sub>Me-aryl bromide



UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction=	0.133176 (Hartree/Particle)		
Thermal correction to Energy=	0.143404		
Thermal correction to Enthalpy=	0.144348		
Thermal correction to Gibbs Free Energy=	0.095501		
Sum of electronic and zero-point Energies=	-3032.950270		
Sum of electronic and thermal Energies=	-3032.940042		
Sum of electronic and thermal Enthalpies=	-3032.939098		
Sum of electronic and thermal Free Energies=	-3032.987945		
C	-2.57275500	0.19996600	2.05087800
C	-2.44957300	-0.85234700	1.13602800
C	-3.04002200	-0.78700600	-0.13096500
C	-3.76459400	0.35159000	-0.48557700
C	-3.89915700	1.41806400	0.41792900
C	-3.29933200	1.33185600	1.68410600
Br	-1.45643600	-2.40609800	1.62589400
H	-2.93481200	-1.61588900	-0.83239400
H	-2.10710000	0.13470900	3.03533000
H	-3.40960200	2.16573100	2.37963500
H	-4.22894100	0.41365300	-1.47024400
C	-4.66302300	2.65652100	0.08303400
O	-4.80064800	3.59747500	0.83730500
O	-5.18655200	2.62227300	-1.15000500
C	-5.93743600	3.76947700	-1.56251500
H	-5.30692900	4.67128700	-1.54875200
H	-6.27951900	3.55993900	-2.58273900
H	-6.79858100	3.92952600	-0.89636500

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)

HF=-3033.9127241

**<sup>2</sup>B-F**



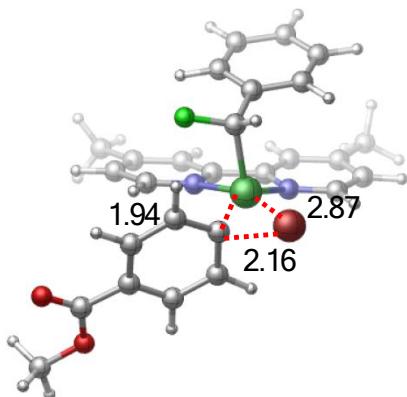
UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction=	0.323031 (Hartree/Particle)		
Thermal correction to Energy=	0.344846		
Thermal correction to Enthalpy=	0.345790		
Thermal correction to Gibbs Free Energy=	0.266940		
Sum of electronic and zero-point Energies=	-2451.462073		
Sum of electronic and thermal Energies=	-2451.440258		
Sum of electronic and thermal Enthalpies=	-2451.439314		
Sum of electronic and thermal Free Energies=	-2451.518164		
Ni	0.33737100	-0.72781000	0.54094600
N	1.55594100	0.87681700	0.51357100
C	3.44654600	2.94510200	0.32551700
C	1.37875500	2.02691000	1.18023800
C	2.65526000	0.72695300	-0.26033700
C	3.61347400	1.74211200	-0.37176100
C	2.29125000	3.07522100	1.11657700
N	1.68453800	-1.40687800	-0.70315800
C	3.76351300	-2.22073100	-2.42092900
C	1.66626700	-2.61860500	-1.28711600
C	2.73133200	-0.57957100	-0.95585200
C	3.77416100	-0.96233100	-1.80729000
C	2.66969400	-3.05954600	-2.14034600
H	0.46179200	2.08414200	1.77050500
H	4.49343200	1.60272100	-1.00082800
H	2.10259700	3.99167200	1.68027100
H	0.80457800	-3.24772500	-1.05134100
H	4.60318900	-0.27953900	-1.99680000
H	2.59993200	-4.05367800	-2.58711300
C	-1.13237600	-0.43121900	1.83532500
C	4.87143900	-2.67155900	-3.33249200
H	5.42178800	-3.51442400	-2.88196500
H	4.46688000	-3.03040200	-4.29239800
H	5.58859300	-1.86386000	-3.53562400

C	4.45307100	4.05949300	0.23724500
H	5.29146000	3.80317800	-0.42548900
H	3.97994500	4.98039600	-0.14082700
H	4.85860400	4.29503100	1.23476600
C	-0.57345500	-1.06226700	3.05446100
C	-0.45201800	-2.47212300	3.12595300
C	-0.08894200	-0.31254600	4.14745400
C	0.13571700	-3.09469700	4.22384800
H	-0.81106800	-3.07350600	2.28397000
C	0.50729800	-0.94125800	5.24683900
H	-0.18333600	0.77453800	4.11922200
C	0.62878800	-2.33368700	5.29774600
H	0.21536500	-4.18581500	4.24653000
H	0.87867200	-0.33200600	6.07690800
H	1.09591300	-2.82215000	6.15673300
F	-1.44784200	0.94591400	2.10141800
H	-2.09769000	-0.90582200	1.57140200

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)  
HF=-2453.0456197

**<sup>2</sup>B-C-TS-F**



UB3LYP-D3/def2-SVP-CPCM(DMA)

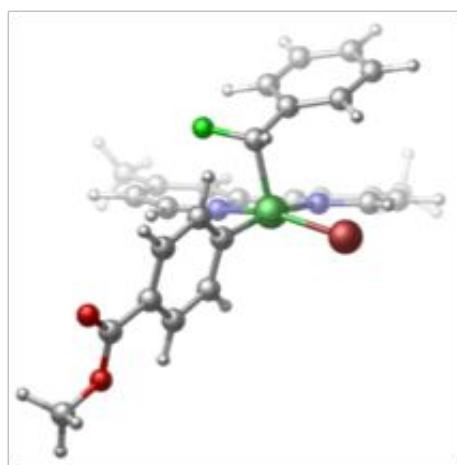
Zero-point correction=	0.456777 (Hartree/Particle)		
Thermal correction to Energy=	0.489739		
Thermal correction to Enthalpy=	0.490683		
Thermal correction to Gibbs Free Energy=	0.388358		
Sum of electronic and zero-point Energies=	-5484.434145		
Sum of electronic and thermal Energies=	-5484.401183		
Sum of electronic and thermal Enthalpies=	-5484.400239		
Sum of electronic and thermal Free Energies=	-5484.502564		
Ni	-0.61722100	-0.10687300	-0.37425200
C	-2.21184700	0.85671500	-0.92521200
C	-2.03857200	3.58043400	-1.64607000
C	-2.87929500	1.84609500	-0.14275500
C	-1.60330800	1.24160200	-2.16200200
C	-1.47759700	2.59507200	-2.47525900
C	-2.76230100	3.17474300	-0.48996600
H	-3.40155000	1.54768600	0.76623500
H	-1.25453300	0.48575100	-2.86963100
H	-0.96005300	2.89102400	-3.38909100
H	-3.20748800	3.94817800	0.13973200
N	0.89206000	1.24211200	-0.01087200
C	3.08762800	2.79793200	0.76238100
C	0.71472000	2.49432900	0.42576600
C	2.13536200	0.72186000	-0.05711500
C	3.25079500	1.48090100	0.31731200
C	1.77643800	3.30207600	0.81782600
N	1.03072300	-1.22259300	-0.91307700
C	3.35478500	-2.78947700	-0.92397000
C	0.99576800	-2.49253200	-1.33304100
C	2.20637300	-0.69164300	-0.50742700
C	3.37787300	-1.45431800	-0.49978500

C	2.12519700	-3.30408700	-1.36407700
H	-0.31856400	2.83938900	0.47046000
H	4.25114300	1.05077300	0.26785500
H	1.58286000	4.31875300	1.16612200
H	0.01740100	-2.86832900	-1.64388300
H	4.31346200	-1.02043000	-0.14681200
H	2.04277600	-4.33415800	-1.71613900
Br	-3.22685200	-1.03612600	-1.12164300
C	-1.07778800	-0.36117900	1.57360500
C	4.58896400	-3.64561600	-0.86463600
H	4.65853000	-4.12752800	0.12598800
H	4.56321000	-4.44482100	-1.61946400
H	5.50273600	-3.04988100	-1.00522600
C	4.25986000	3.64674100	1.17092500
H	5.20721300	3.09304200	1.11132000
H	4.33638100	4.53577900	0.52372500
H	4.13270500	4.01185800	2.20276700
C	0.08791600	-1.03765100	2.17440300
C	0.27736000	-2.42515100	1.98309600
C	1.09914700	-0.32000900	2.84590000
C	1.43897000	-3.05886000	2.41841900
H	-0.49038600	-2.99771000	1.45416200
C	2.26094200	-0.95996800	3.28691000
H	0.96748800	0.75204500	3.00070900
C	2.44464800	-2.32996100	3.07185300
H	1.56764500	-4.13062200	2.24349800
H	3.03536800	-0.37827600	3.79523900
H	3.35818200	-2.82716200	3.40738200
F	-1.30477800	0.88955000	2.18391500
H	-2.00962100	-0.94592000	1.65161800
C	-1.91958500	5.02252900	-1.93007700
O	-2.39729800	5.91015000	-1.24407600
O	-1.20400500	5.28354100	-3.04583200
C	-1.03145400	6.65887800	-3.38665600
H	-0.50364500	7.19980400	-2.58577900
H	-0.43588900	6.67535400	-4.30773300
H	-2.00314500	7.14834400	-3.55605500

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)

HF=-5486.962612

**<sup>2</sup>C-F**



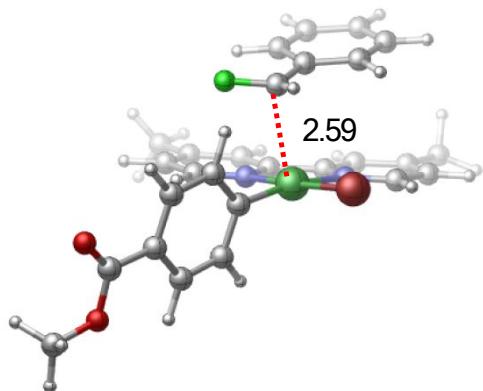
UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction=	0.459647	(Hartree/Particle)	
Thermal correction to Energy=	0.493097		
Thermal correction to Enthalpy=	0.494041		
Thermal correction to Gibbs Free Energy=	0.389334		
Sum of electronic and zero-point Energies=	-5484.478088		
Sum of electronic and thermal Energies=	-5484.444638		
Sum of electronic and thermal Enthalpies=	-5484.443693		
Sum of electronic and thermal Free Energies=	-5484.548401		
Ni	-0.10292600	0.21293300	-0.44422900
C	-1.20729500	1.73581000	-0.78614000
C	-2.49591300	4.02073400	-1.83453900
C	-2.31807600	2.28666400	-0.13643800
C	-0.75077200	2.34124600	-1.97031400
C	-1.38389300	3.46992400	-2.49438400
C	-2.95463300	3.41661600	-0.65222700
H	-2.70111500	1.84863500	0.78678600
H	0.12111000	1.94068200	-2.49898900
H	-1.01538400	3.93101300	-3.41211600
H	-3.81933800	3.84818100	-0.14314600
N	1.65411100	1.34343300	-0.04525000
C	3.98154900	2.52831200	0.98467700
C	1.65981600	2.62889900	0.32929700
C	2.78215600	0.61847200	0.08633800
C	3.95724900	1.18337500	0.59699600
C	2.79016100	3.25723600	0.83954200
N	1.40963900	-1.24545200	-0.53781500
C	3.59082200	-3.00909800	-0.74682900
C	1.22609300	-2.53222200	-0.85612200
C	2.66723600	-0.80655500	-0.30702000

C	3.76929500	-1.65973200	-0.41339300
C	2.27577800	-3.43934300	-0.96920800
H	0.71596200	3.16411600	0.22117600
H	4.85356600	0.57480900	0.71445800
H	2.73858000	4.30841000	1.13030800
H	0.18989300	-2.82971900	-1.02740100
H	4.77586100	-1.27782600	-0.24365400
H	2.06219100	-4.47751500	-1.23105000
Br	-1.87520200	-1.25534800	-1.52483300
C	-0.72129900	0.22226300	1.44476900
C	4.75514900	-3.95559700	-0.82750200
H	4.90789000	-4.44256600	0.15108900
H	4.57584600	-4.75125800	-1.56525100
H	5.68688200	-3.43152200	-1.08489300
C	5.22221800	3.17265000	1.53650000
H	6.03235200	2.44492200	1.68276100
H	5.58171100	3.95739700	0.85054500
H	5.00995800	3.66236500	2.50003400
C	-0.01225400	-0.90379100	2.08376500
C	-0.50261300	-2.21541600	1.92943100
C	1.19123200	-0.70051000	2.78460700
C	0.20692800	-3.29835000	2.44607200
H	-1.42261400	-2.37427100	1.36163200
C	1.89829900	-1.78816000	3.29984000
H	1.56923400	0.31530900	2.90905400
C	1.41377400	-3.09091600	3.12825500
H	-0.17703600	-4.31278100	2.31132100
H	2.83692700	-1.62032900	3.83430100
H	1.97289800	-3.94152300	3.52584500
F	-0.43556500	1.42256700	2.07088400
H	-1.81012700	0.08685000	1.38884400
C	-3.20744000	5.22677200	-2.33675600
O	-4.17254500	5.73313500	-1.79838600
O	-2.66930300	5.71612500	-3.46783800
C	-3.28982900	6.87885400	-4.02237300
H	-3.25921400	7.71615400	-3.30846000
H	-2.71989500	7.12970900	-4.92502000
H	-4.34043300	6.67568800	-4.28054200

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)  
HF=-5487.0103156

<sup>2</sup>C-D-TS-F



UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction= 0.457952 (Hartree/Particle)

Thermal correction to Energy= 0.491122

Thermal correction to Enthalpy= 0.492066

Thermal correction to Gibbs Free Energy= 0.387758

Sum of electronic and zero-point Energies= -5484.472147

Sum of electronic and thermal Energies= -5484.438977

Sum of electronic and thermal Enthalpies= -5484.438033

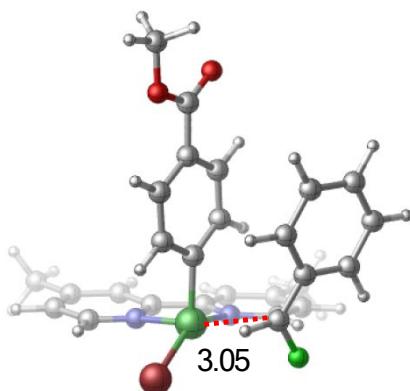
Sum of electronic and thermal Free Energies= -5484.542342

Ni	-0.13232800	0.19703500	-0.80201500
C	-1.16083300	1.75275600	-1.12995600
C	-2.49209400	4.14843100	-1.87787900
C	-2.18585500	2.29358500	-0.33278700
C	-0.83165200	2.43388800	-2.31944200
C	-1.48099100	3.61158600	-2.69404700
C	-2.83572500	3.47429500	-0.69274800
H	-2.48001600	1.79747500	0.59327800
H	-0.03938600	2.04646600	-2.96794400
H	-1.20533500	4.12297900	-3.61810400
H	-3.62410900	3.89192100	-0.06194400
N	1.44278700	1.19768200	-0.21037400
C	3.75470700	2.35317000	0.91476500
C	1.46524600	2.49255200	0.15135800
C	2.55527400	0.44974400	-0.00002400
C	3.71533700	1.00425900	0.54848200
C	2.58360400	3.09910200	0.70790900
N	1.19382900	-1.32571900	-0.80758900
C	3.24065500	-3.24410700	-0.61541600
C	0.98179700	-2.59526300	-1.17352100
C	2.42406200	-0.97379500	-0.36572800
C	3.45642500	-1.90656000	-0.25689000
C	1.96827400	-3.57490300	-1.09867000

H	0.54748400	3.05314300	-0.01385200
H	4.59168700	0.37764300	0.71021400
H	2.53616200	4.15512400	0.98077000
H	-0.02718900	-2.82389700	-1.52106600
H	4.43471500	-1.60220800	0.11406100
H	1.73352600	-4.59576200	-1.40610700
Br	-2.02342400	-1.09961700	-1.44510400
C	-0.66055200	0.06789300	1.72678700
C	4.32041500	-4.27445200	-0.44442400
H	4.14513500	-5.15619100	-1.07683400
H	5.31299400	-3.85955500	-0.67476200
H	4.34326900	-4.61317600	0.60578800
C	4.98585200	2.98213200	1.50271300
H	4.74073500	3.52869300	2.42684300
H	5.75916200	2.23513200	1.72924400
H	5.41162900	3.71635900	0.79867800
C	0.29722300	-0.84546200	2.24409500
C	0.13832800	-2.24132300	2.02326600
C	1.46152900	-0.39624800	2.92244000
C	1.10661700	-3.13805800	2.45527100
H	-0.73907800	-2.59464500	1.47596600
C	2.42203500	-1.30767800	3.35278500
H	1.59846700	0.67309800	3.09053600
C	2.25778800	-2.68094700	3.12089500
H	0.97659300	-4.20614000	2.26380200
H	3.31634200	-0.94472300	3.86614200
H	3.01989500	-3.39088900	3.45062600
F	-0.55839000	1.36128700	2.11251800
H	-1.66714600	-0.21991200	1.41964200
C	-3.21296300	5.40232100	-2.21715000
O	-4.09122000	5.90216500	-1.54015100
O	-2.79420300	5.95025800	-3.37361100
C	-3.43509000	7.16197600	-3.77758500
H	-3.28720500	7.95269900	-3.02598900
H	-2.97136000	7.45259000	-4.72801800
H	-4.51628300	7.00665600	-3.91463400

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)  
HF=-5487.0055842

<sup>2</sup>D-E-TS-F



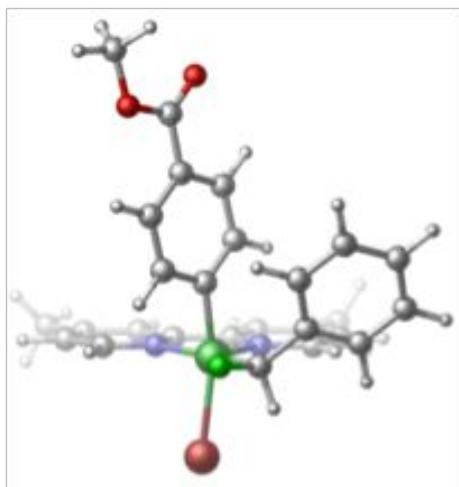
UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction=	0.456500 (Hartree/Particle)	
Thermal correction to Energy=	0.490448	
Thermal correction to Enthalpy=	0.491392	
Thermal correction to Gibbs Free Energy=	0.383500	
Sum of electronic and zero-point Energies=	-5484.449157	
Sum of electronic and thermal Energies=	-5484.415209	
Sum of electronic and thermal Enthalpies=	-5484.414265	
Sum of electronic and thermal Free Energies=	-5484.522157	
C	-2.84984300	1.56273800
C	-3.51369000	2.79353300
C	-2.78583400	3.98749000
C	-1.38539100	3.88614200
C	-0.78872400	2.63171800
C	-3.54484600	0.25019400
C	-4.93132100	0.10263700
C	-5.49691700	-1.17770500
C	-4.62159000	-2.27529700
C	-3.25321000	-2.05298500
H	-4.60274500	2.83100600
H	-0.76048700	4.77830700
H	0.29445300	2.51313800
H	-5.57856400	0.97838600
H	-5.00354800	-3.29715100
H	-2.53165400	-2.87292100
N	-1.50061300	1.50050900
N	-2.73337500	-0.82371700
Br	0.35573400	-2.30585300
Ni	-0.71088000	-0.36319100
C	-0.52296000	-0.36603200
C	-0.79837200	0.74350200
C	-0.19544300	-1.57805300
		1.28823100
		2.11050800
		1.92843400

C	-0.71736600	0.66113700	3.49967300
H	-1.05827600	1.70582300	1.66337800
C	-0.11041500	-1.67491300	3.31928700
H	0.01846200	-2.46121500	1.32000000
H	-0.91198400	1.53563900	4.12471200
H	0.16116900	-2.62129600	3.79100600
C	-0.36423100	-0.54837400	4.12128100
C	-3.46546600	5.32699300	-1.02685900
H	-3.14304300	5.89251900	-1.91567900
H	-4.55970200	5.23128900	-1.04973800
H	-3.18733600	5.92864600	-0.14603700
C	-6.98027500	-1.38029200	-0.42670800
H	-7.20691300	-1.94836700	0.48998900
H	-7.52325200	-0.42586700	-0.38779800
H	-7.36981100	-1.96913000	-1.27290100
C	2.17473000	0.49847800	-0.16102600
C	2.43335400	1.21217100	1.02786400
C	2.58516900	0.50497000	2.25421800
C	2.52508700	2.63285600	1.04915900
C	2.79832700	1.19149700	3.44168400
H	2.49805200	-0.58279200	2.25710600
C	2.73948700	3.30495000	2.24842600
H	2.42713800	3.18945000	0.11530100
C	2.87507100	2.59462000	3.45200700
H	2.89484000	0.63308700	4.37610400
H	2.80321700	4.39632000	2.25040500
H	3.03770500	3.12970300	4.39058500
C	-0.25039400	-0.57462900	5.60151100
O	0.11651300	-1.77923900	6.07920200
O	-0.45397000	0.37855100	6.32974500
C	0.25848900	-1.88887500	7.49682000
H	1.02537900	-1.19210400	7.86894500
H	-0.69251000	-1.66635000	8.00492400
H	0.56008700	-2.92428800	7.69634300
F	2.11471900	1.17652000	-1.32698200
H	2.15959300	-0.58417100	-0.28010900

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)  
HF=-5486.9982117

**<sup>2</sup>E-F**



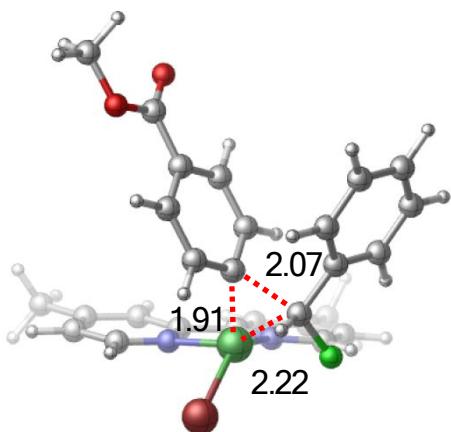
UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction=	0.459736	(Hartree/Particle)	
Thermal correction to Energy=	0.493231		
Thermal correction to Enthalpy=	0.494175		
Thermal correction to Gibbs Free Energy=	0.388107		
Sum of electronic and zero-point Energies=	-5484.477382		
Sum of electronic and thermal Energies=	-5484.443887		
Sum of electronic and thermal Enthalpies=	-5484.442943		
Sum of electronic and thermal Free Energies=	-5484.549011		
C	-2.58122000	1.70236600	-0.70348400
C	-3.31158200	2.89123900	-0.78657700
C	-2.66273100	4.10390800	-1.05920200
C	-1.27652500	4.05330100	-1.26471000
C	-0.61215800	2.83495000	-1.15782200
C	-3.20024300	0.37386100	-0.47868500
C	-4.57217000	0.17589500	-0.28413500
C	-5.07861200	-1.11589500	-0.09603900
C	-4.15636100	-2.17508600	-0.11373700
C	-2.80630500	-1.90665300	-0.30759200
H	-4.39285000	2.88244800	-0.65044300
H	-0.71070100	4.95414000	-1.50975700
H	0.45837400	2.75801400	-1.32770800
H	-5.25454100	1.02544100	-0.27650600
H	-4.48599400	-3.20619600	0.02853100
H	-2.05619000	-2.69924800	-0.32677600
N	-1.23759400	1.69064900	-0.86040300
N	-2.34122200	-0.66494900	-0.48996900
Br	0.31566000	-2.20394600	-1.81020700
Ni	-0.34191200	-0.16849300	-0.46252400
C	-0.41291600	-0.37780100	1.43730900

C	-0.87810900	0.63379900	2.28568300
C	-0.10566800	-1.63858600	1.96474500
C	-1.02331400	0.39196800	3.65159500
H	-1.11463100	1.62252200	1.88526200
C	-0.24098800	-1.88313900	3.33388400
H	0.25476500	-2.42977900	1.30166400
H	-1.38153700	1.17513800	4.32329600
H	0.01078800	-2.86181600	3.74559000
C	-0.69800700	-0.86560700	4.18961100
C	-3.42034200	5.40021000	-1.11433200
H	-2.96204900	6.10239800	-1.82578000
H	-4.47252100	5.24340700	-1.39208200
H	-3.40696400	5.88202400	-0.12157200
C	-6.54587300	-1.36932500	0.10839600
H	-6.71314400	-1.97397900	1.01370500
H	-7.11514200	-0.43404200	0.19957900
H	-6.95525300	-1.94204300	-0.74011200
C	1.57176800	0.36238000	-0.23539900
C	2.09404800	1.31685400	0.78585600
C	2.33123700	0.88053900	2.10516400
C	2.42397300	2.64445500	0.45961800
C	2.83253400	1.75319600	3.07008700
H	2.11328600	-0.15277800	2.37742600
C	2.92310600	3.52116800	1.42876500
H	2.32022100	2.99044700	-0.56846800
C	3.12067600	3.08439200	2.74116900
H	3.00109300	1.39080300	4.08748900
H	3.16826700	4.54911800	1.14903800
H	3.50928600	3.76894200	3.49931300
C	-0.85179100	-1.06649200	5.65634300
O	-0.50379700	-2.30312800	6.05246600
O	-1.24584900	-0.21705400	6.43137000
C	-0.61620700	-2.58512100	7.44982000
H	0.02462000	-1.90989500	8.03723500
H	-1.65639400	-2.46671300	7.78985800
H	-0.29115400	-3.62430200	7.57990100
F	1.77327800	0.88061400	-1.52137000
H	2.07440700	-0.61381000	-0.17978000

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)  
HF=-5487.010454

**<sup>2</sup>E-P<sub>B</sub>-TS-F**



UB3LYP-D3/def2-SVP-CPCM(DMA)

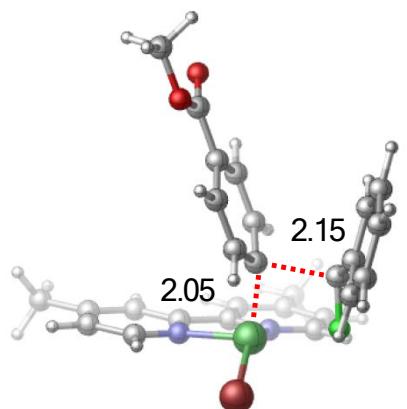
Zero-point correction=	0.458894 (Hartree/Particle)		
Thermal correction to Energy=	0.491911		
Thermal correction to Enthalpy=	0.492855		
Thermal correction to Gibbs Free Energy=	0.388753		
Sum of electronic and zero-point Energies=	-5484.463048		
Sum of electronic and thermal Energies=	-5484.430031		
Sum of electronic and thermal Enthalpies=	-5484.429087		
Sum of electronic and thermal Free Energies=	-5484.533189		
C	-2.40359200	1.76222800	-0.05268900
C	-3.13967300	2.95115400	-0.00269400
C	-2.48608800	4.19013800	-0.01290400
C	-1.08495000	4.17212800	-0.09271100
C	-0.41661500	2.95282600	-0.13556600
C	-3.02953000	0.41477800	-0.07948000
C	-4.40454900	0.18653700	0.05394000
C	-4.90807900	-1.11978900	0.00795400
C	-3.98281500	-2.16080000	-0.17801300
C	-2.63016500	-1.86122600	-0.29912400
H	-4.22851600	2.92100800	0.03383800
H	-0.51264400	5.10141300	-0.12272800
H	0.67006100	2.90394100	-0.20339700
H	-5.09049700	1.02067800	0.20152300
H	-4.31361400	-3.20046600	-0.22458400
H	-1.87298300	-2.63543400	-0.44582000
N	-1.05249100	1.77389100	-0.10092300
N	-2.16860700	-0.60696100	-0.25180100
Br	0.72638200	-1.83884500	-1.65825200
Ni	-0.18885800	-0.12902500	-0.08652400
C	0.03443700	-0.52292200	1.76464100
C	-0.56838200	0.30511200	2.73471700

C	0.20567300	-1.89130100	2.05152800
C	-1.03325400	-0.23228900	3.92739800
H	-0.66708500	1.37552900	2.54756700
C	-0.25663000	-2.42929100	3.25205700
H	0.68497800	-2.53625000	1.31161600
H	-1.51894600	0.40305000	4.67098600
H	-0.13447400	-3.49415900	3.45583500
C	-0.88512500	-1.60687000	4.20322200
C	-3.24509600	5.48471100	0.06771800
H	-3.12864600	5.92781200	1.07126000
H	-2.85359000	6.21677900	-0.65505300
H	-4.31888700	5.34169500	-0.11716200
C	-6.37652700	-1.40811700	0.15328900
H	-6.75366500	-1.94454400	-0.73237400
H	-6.55660600	-2.06021900	1.02331400
H	-6.96484400	-0.48891300	0.28029800
C	1.77980300	0.17520900	0.90186600
C	2.34604500	0.73859600	2.16131100
C	2.90636800	-0.11932400	3.12359000
C	2.30910200	2.11784500	2.42212300
C	3.39968800	0.38781600	4.32674700
H	2.94123000	-1.19407400	2.93016600
C	2.80727300	2.62523100	3.62542700
H	1.88383200	2.79748500	1.68351600
C	3.34974600	1.76341100	4.58453000
H	3.82992300	-0.29326200	5.06541900
H	2.76937500	3.70109300	3.81450500
H	3.73597800	2.16100900	5.52636000
C	-1.39732400	-2.12696800	5.49584600
O	-1.19459200	-3.44906800	5.64448900
O	-1.94593300	-1.45001100	6.34471800
C	-1.65903800	-4.03583800	6.86229600
H	-1.16334400	-3.57713500	7.73158900
H	-2.74687700	-3.90557900	6.96960000
H	-1.40981600	-5.10219100	6.80374400
F	1.97849900	1.10579600	-0.13922000
H	2.25167500	-0.76691700	0.59775200

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)

HF=-5486.9956648

**<sup>4</sup>D'-P<sub>B</sub>-TS-F**



UB3LYP-D3/def2-SVP-CPCM(DMA)

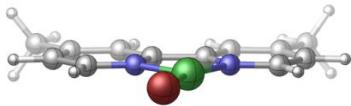
Zero-point correction=	0.456681 (Hartree/Particle)	
Thermal correction to Energy=	0.490218	
Thermal correction to Enthalpy=	0.491162	
Thermal correction to Gibbs Free Energy=	0.384409	
Sum of electronic and zero-point Energies=	-5484.444177	
Sum of electronic and thermal Energies=	-5484.410640	
Sum of electronic and thermal Enthalpies=	-5484.409696	
Sum of electronic and thermal Free Energies=	-5484.516449	
C -1.20696300 2.32446400 -1.60440700		
C -0.87788000 3.64443700 -1.93292500		
C 0.31031500 3.92729200 -2.61794200		
C 1.13620900 2.83986100 -2.95073100		
C 0.75298300 1.55355500 -2.58931100		
C -2.44437500 1.93748600 -0.87977300		
C -3.40662200 2.84711700 -0.42684000		
C -4.54108200 2.38960000 0.25627800		
C -4.65919600 1.00355700 0.45800900		
C -3.66571100 0.15517700 -0.01809000		
H -1.54493900 4.46101800 -1.65714100		
H 2.07492900 2.99339700 -3.48657600		
H 1.37403800 0.68533200 -2.81781700		
H -3.27858300 3.91566300 -0.59893800		
H -5.51993000 0.58695900 0.98502100		
H -3.71330600 -0.92885400 0.11151300		
N -0.38803100 1.30060200 -1.93391000		
N -2.59073700 0.61288200 -0.66954100		
Br -1.91783900 -2.72657700 -1.56846000		
Ni -0.96137300 -0.51469100 -1.16141700		
C -0.01426600 -0.40641000 0.65707900		
C 0.39853200 0.84570500 1.21762600		

C	-0.39383100	-1.40563500	1.61233400
C	0.49622900	1.05630600	2.58371400
H	0.66922800	1.66546000	0.54360400
C	-0.30296700	-1.20644200	2.97980700
H	-0.75306100	-2.36864400	1.23917600
H	0.82253500	2.02053800	2.98121000
H	-0.59698800	-1.99647600	3.67364800
C	0.15328100	0.03095100	3.49532200
C	0.69757500	5.33204500	-2.98561400
H	0.81836200	5.42457200	-4.07704800
H	-0.05129500	6.06436200	-2.65412400
H	1.66740100	5.59420600	-2.53276600
C	-5.60109100	3.33498800	0.74849900
H	-5.30103400	4.38526200	0.62944500
H	-6.53910000	3.17900900	0.19018000
H	-5.82553300	3.15001600	1.81072400
C	1.74433100	-1.09644200	-0.36869600
C	2.23629900	-2.25799900	0.32452500
C	1.77025200	-3.55443600	0.00533600
C	3.11225200	-2.09648300	1.42285800
C	2.19039400	-4.65366200	0.75222600
H	1.06187900	-3.67551900	-0.81666100
C	3.51853800	-3.20175000	2.16806100
H	3.46512000	-1.09596800	1.68711800
C	3.06556800	-4.48710100	1.83557300
H	1.82721700	-5.65218000	0.49426800
H	4.19727200	-3.06377100	3.01383900
H	3.38922100	-5.35205500	2.41969000
H	2.31253300	-0.16421300	-0.35599800
F	1.23515500	-1.34082600	-1.63139500
C	0.27186200	0.29908100	4.94191400
O	-0.08957400	-0.75591200	5.70509600
O	0.65387600	1.34932900	5.43019700
C	-0.00324200	-0.58020600	7.11874900
H	1.03025700	-0.35567600	7.42565800
H	-0.65257100	0.24344600	7.45437000
H	-0.33205300	-1.52570400	7.56748000

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)

HF=-5486.9731981

**<sup>2</sup>P<sub>B</sub>**



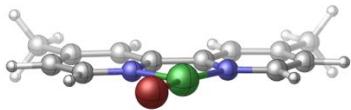
UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction=	0.214680 (Hartree/Particle)	
Thermal correction to Energy=	0.230880	
Thermal correction to Enthalpy=	0.231824	
Thermal correction to Gibbs Free Energy=	0.166140	
Sum of electronic and zero-point Energies=	-4655.582428	
Sum of electronic and thermal Energies=	-4655.566229	
Sum of electronic and thermal Enthalpies=	-4655.565284	
Sum of electronic and thermal Free Energies=	-4655.630968	
C -2.43007900	1.26871400	0.10445200
C -2.93075100	2.53326500	0.43295100
C -2.21616600	3.68903100	0.09610200
C -0.99403200	3.51076500	-0.57801100
C -0.55261100	2.22816400	-0.87622900
C -3.10999500	-0.00864600	0.42051800
C -4.33738700	-0.11938400	1.08504000
C -4.89067100	-1.38152800	1.33497800
C -4.16501400	-2.50317300	0.89316400
C -2.95200100	-2.32042200	0.23918500
H -3.88394700	2.62388500	0.95521600
H -0.38786700	4.37096700	-0.87041400
H 0.39165600	2.05926700	-1.39915500
H -4.86830800	0.77555700	1.41141400
H -4.54472200	-3.51370600	1.05922000
H -2.35456900	-3.16250000	-0.12079700
N -1.24576800	1.12230100	-0.54728700
N -2.43405000	-1.10596500	0.00715500
Br 0.55028100	-2.53170600	-1.66471300
Ni -0.72240500	-0.71159000	-0.90655100
C -2.71904800	5.06420200	0.43891300
H -2.79150000	5.69012700	-0.46530700
H -3.70750700	5.03035800	0.91813900
H -2.02032100	5.57208400	1.12415400
C -6.20744900	-1.54457600	2.04347000
H -6.09194300	-2.18063300	2.93595200
H -6.62681600	-0.57835800	2.35693700
H -6.93976900	-2.04373300	1.38782600

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)

HF=-4656.964463

**<sup>4</sup>P<sub>B</sub>**

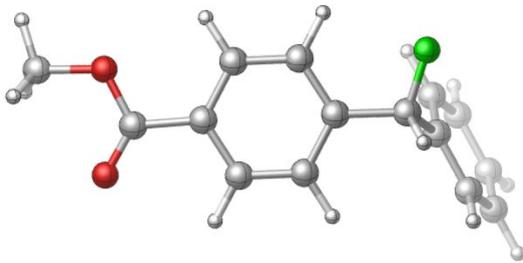


UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction=		0.213368 (Hartree/Particle)
Thermal correction to Energy=		0.229223
Thermal correction to Enthalpy=		0.230167
Thermal correction to Gibbs Free Energy=		0.166952
Sum of electronic and zero-point Energies=		-4655.558652
Sum of electronic and thermal Energies=		-4655.542797
Sum of electronic and thermal Enthalpies=		-4655.541853
Sum of electronic and thermal Free Energies=		-4655.605068
C	-2.45870300	1.18519800
C	-2.92439200	2.49793500
C	-2.19030300	3.61436000
C	-0.94226700	3.41272800
C	-0.53017700	2.12327000
C	-3.13532900	-0.03536100
C	-4.38997400	-0.14314700
C	-4.96039500	-1.37494000
C	-4.24863600	-2.54581100
C	-3.03845900	-2.39619000
H	-3.87953400	2.62157600
H	-0.32380800	4.26073600
H	0.41163400	1.91771500
H	-4.90935700	0.76645300
H	-4.65261300	-3.54316300
H	-2.46591300	-3.26493700
N	-1.24735700	1.03695000
N	-2.48303300	-1.19523500
Br	1.18598300	-1.20249300
Ni	-0.80044200	-0.85449900
C	-2.66415300	5.01123400
H	-2.75858800	5.59742800
H	-3.63831800	5.01663100
H	-1.93783100	5.54666900
C	-6.28702600	-1.51604500
H	-6.18493500	-2.11049300
H	-6.72056900	-0.54031500
H	-7.00826300	-2.05348100

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)

HF=-4656.9245214

**R-Ar-F**

UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction= 0.244915 (Hartree/Particle)

Thermal correction to Energy= 0.260485

Thermal correction to Enthalpy= 0.261429

Thermal correction to Gibbs Free Energy= 0.199006

Sum of electronic and zero-point Energies= -828.917077

Sum of electronic and thermal Energies= -828.901507

Sum of electronic and thermal Enthalpies= -828.900563

Sum of electronic and thermal Free Energies= -828.962986

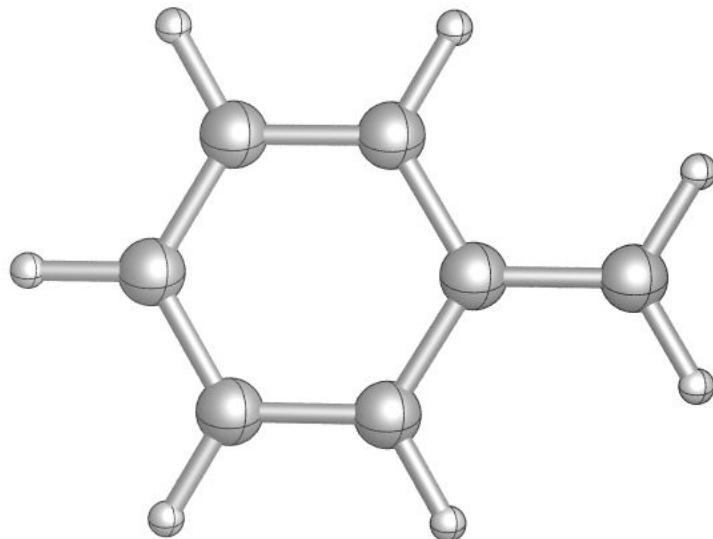
C	0.51796500	-0.19354600	1.42218900
C	-0.71988900	0.46694700	1.48618400
C	0.68099200	-1.41501300	2.08757300
C	-1.77435000	-0.08430600	2.20782200
H	-0.85365800	1.42159600	0.97099000
C	-0.37483400	-1.96822200	2.81529000
H	1.63861400	-1.93322300	2.03134000
H	-2.73944800	0.42254400	2.26195700
H	-0.24294900	-2.91788900	3.33488800
C	-1.61032400	-1.30714200	2.88137100
C	1.66237800	0.43565100	0.64708400
C	2.14796300	1.72311400	1.28193000
C	2.84197700	1.67475800	2.50114800
C	1.90048000	2.96174000	0.67836800
C	3.28331400	2.85283300	3.10618800
H	3.03642200	0.70792300	2.97187400
C	2.33305300	4.14435000	1.29063100
H	1.36945800	3.00517000	-0.27647400
C	3.02600000	4.09165600	2.50349800
H	3.82713500	2.80747200	4.05313800
H	2.13406300	5.10709200	0.81330900
H	3.36837300	5.01378000	2.97982400
H	1.33252800	0.63445900	-0.38663100
F	2.72551400	-0.46676200	0.57570300
C	-2.76932800	-1.85394600	3.64543500
O	-2.48926200	-3.01980800	4.24729200

O	-3.85387000	-1.31331400	3.72382000
C	-3.54218400	-3.62071100	5.00778800
H	-3.85942200	-2.95587700	5.82549400
H	-4.41199700	-3.83336300	4.36796800
H	-3.13238700	-4.55302700	5.41390600

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)

HF=-830.0916249

**Figure S2**  
**Benzyl radical**



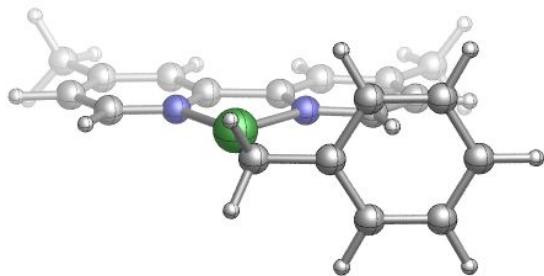
UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction=	0.114617 (Hartree/Particle)	
Thermal correction to Energy=	0.120263	
Thermal correction to Enthalpy=	0.121207	
Thermal correction to Gibbs Free Energy=	0.084958	
Sum of electronic and zero-point Energies=	-270.617865	
Sum of electronic and thermal Energies=	-270.612219	
Sum of electronic and thermal Enthalpies=	-270.611275	
Sum of electronic and thermal Free Energies=	-270.647524	
C	-6.29929000	5.26531800
C	-7.02582100	5.40676600
C	-6.55819200	6.24577300
C	-8.23779700	4.67984000
C	-7.25570500	6.34368800
H	-5.63029100	6.80632900
C	-8.92170600	4.78360200
H	-8.59439200	4.01083400
C	-8.44006100	5.61337200
H	-6.87582700	6.98895800
H	-9.83921900	4.20874400
H	-8.98105500	5.68839100
H	-6.67401800	4.64186800
H	-5.35158400	5.78629800

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)

HF=-271.0295758.

**<sup>2</sup>B-H**



UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction= 0.330279 (Hartree/Particle)

Thermal correction to Energy= 0.351373

Thermal correction to Enthalpy= 0.352317

Thermal correction to Gibbs Free Energy= 0.273755

Sum of electronic and zero-point Energies= -2352.296436

Sum of electronic and thermal Energies= -2352.275342

Sum of electronic and thermal Enthalpies= -2352.274397

Sum of electronic and thermal Free Energies= -2352.352959

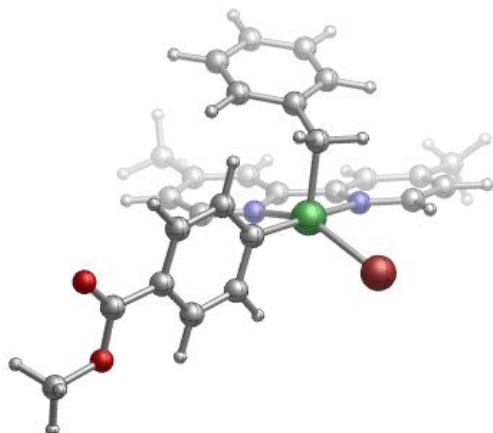
Ni	0.70977000	-1.69414500	1.10067900
N	1.95240600	-0.09239200	1.09120300
C	3.78700200	2.02857000	0.82489400
C	2.02979100	0.87380800	2.02080600
C	2.77744800	-0.02677900	0.01864900
C	3.69821800	1.01626900	-0.13804300
C	2.92100000	1.93805700	1.92804700
N	1.66488800	-2.04170700	-0.58291400
C	3.11862300	-2.37704400	-2.97134400
C	1.43885300	-3.09424500	-1.38837100
C	2.61169000	-1.14052400	-0.94280700
C	3.34724400	-1.28555900	-2.12505600
C	2.13242300	-3.29877500	-2.57439500
H	1.34789200	0.78068600	2.86692800
H	4.35155100	1.04560900	-1.01083700
H	2.93842200	2.69431900	2.71591700
H	0.66714100	-3.79111100	-1.05192300
H	4.10383700	-0.54722300	-2.39277700
H	1.90679500	-4.17342200	-3.18839700
C	-0.65801800	-2.13107200	2.52313900
H	-0.43727100	-3.11266700	2.98040900
H	-1.66929900	-2.17109000	2.07907000
C	-0.53256200	-1.03350300	3.49774900
C	0.37857500	-1.09386100	4.58496400
C	-1.26517100	0.17565800	3.36654500
C	0.56791600	-0.01683800	5.45223500

H	0.96627600	-2.00701800	4.72439500
C	-1.07634000	1.25274300	4.23362200
H	-1.97840600	0.26762500	2.54100700
C	-0.15154500	1.17545000	5.28531200
H	1.29070900	-0.10632500	6.26943800
H	-1.65626800	2.16923000	4.08538400
H	0.00091700	2.02105000	5.96058500
C	3.88033100	-2.56240900	-4.25481600
H	3.20273200	-2.47877900	-5.12086400
H	4.67704100	-1.81402700	-4.36972300
H	4.33376400	-3.56563200	-4.29943700
C	4.76111600	3.16706300	0.69419600
H	5.37144600	3.08150900	-0.21574000
H	4.22800700	4.13143100	0.66508500
H	5.43669900	3.20160800	1.56434600

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)

HF=-2353.76652664

<sup>2</sup>C-H



UB3LYP-D3/def2-SVP-CPCM(DMA)

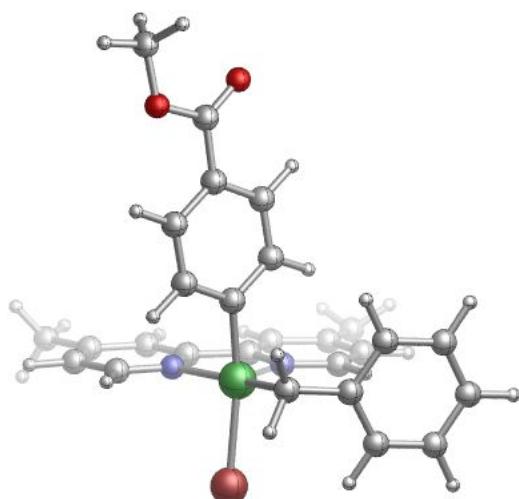
Zero-point correction=	0.467679 (Hartree/Particle)		
Thermal correction to Energy=	0.500085		
Thermal correction to Enthalpy=	0.501030		
Thermal correction to Gibbs Free Energy=	0.399072		
Sum of electronic and zero-point Energies=	-5385.311065		
Sum of electronic and thermal Energies=	-5385.278658		
Sum of electronic and thermal Enthalpies=	-5385.277714		
Sum of electronic and thermal Free Energies=	-5385.379672		
Ni	-0.35646800	-0.11983600	-0.94100700
C	-1.49286300	1.43243600	-0.91190400
C	-2.74636200	3.94590600	-1.31810400
C	-2.37546200	1.96094800	0.03959200
C	-1.25725000	2.18740300	-2.08000600
C	-1.86625500	3.42530400	-2.28428000
C	-2.99457900	3.19904400	-0.15757400
H	-2.59719200	1.42176200	0.96189700
H	-0.58184700	1.81045300	-2.85487900
H	-1.66507200	3.99282700	-3.19433000
H	-3.67670700	3.60347900	0.59365000
N	1.39257000	0.99562700	-0.45663300
C	3.67855200	2.06459000	0.77856300
C	1.44972100	2.28844700	-0.11880400
C	2.46597200	0.21154800	-0.21488700
C	3.61227100	0.71603500	0.40419800
C	2.56467800	2.86249200	0.48559000
N	1.07825400	-1.57229500	-1.01477900
C	3.14296100	-3.47235000	-0.91061900
C	0.84918600	-2.85135100	-1.34095600
C	2.31683500	-1.20711700	-0.61622600
C	3.36433000	-2.13256300	-0.56991000

C	1.84058500	-3.82544000	-1.29681600
H	0.55952200	2.88213200	-0.32968600
H	4.45460900	0.05928300	0.61974200
H	2.55143700	3.92388400	0.74053100
H	-0.17153500	-3.08110700	-1.65273900
H	4.36051800	-1.81569000	-0.26261800
H	1.59500100	-4.85502500	-1.56439600
Br	-1.83307200	-1.22030900	-2.68144700
C	-1.01763200	-0.83371700	0.82039700
H	-1.18917200	-1.88537000	0.55174700
H	-1.96825600	-0.34657200	1.05227200
C	0.01595400	-0.65300300	1.85686700
C	0.92242600	-1.68727500	2.17430300
C	0.18008200	0.58528000	2.51661200
C	1.95379100	-1.49091500	3.09498600
H	0.81955800	-2.65544800	1.67730500
C	1.21387100	0.78610000	3.43023400
H	-0.49843500	1.40725600	2.27612000
C	2.11142100	-0.25024100	3.72244700
H	2.64538200	-2.30846500	3.31516900
H	1.32861300	1.76026000	3.91288600
H	2.92604100	-0.08998400	4.43313100
C	-3.42634900	5.25961700	-1.47692700
O	-4.19305500	5.74252400	-0.66661000
O	-3.10513100	5.87675500	-2.62758500
C	-3.71420900	7.14839200	-2.86512700
H	-3.44550700	7.86441800	-2.07346100
H	-3.33407000	7.49436000	-3.83380700
H	-4.81061600	7.05634200	-2.89817400
C	4.87569000	2.60789800	1.50558300
H	4.77932500	2.39398300	2.58412400
H	5.80638200	2.13380400	1.16052700
H	4.96270200	3.69731300	1.38781000
C	4.25402900	-4.48375500	-0.88679400
H	4.64172400	-4.63953600	-1.90804200
H	5.09195700	-4.15380000	-0.25653900
H	3.89541300	-5.45849900	-0.52374900

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)

HF=-5387.73190027

<sup>2</sup>E-H



UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction= 0.467738 (Hartree/Particle)

Thermal correction to Energy= 0.500206

Thermal correction to Enthalpy= 0.501150

Thermal correction to Gibbs Free Energy= 0.398608

Sum of electronic and zero-point Energies= -5385.315732

Sum of electronic and thermal Energies= -5385.283264

Sum of electronic and thermal Enthalpies= -5385.282320

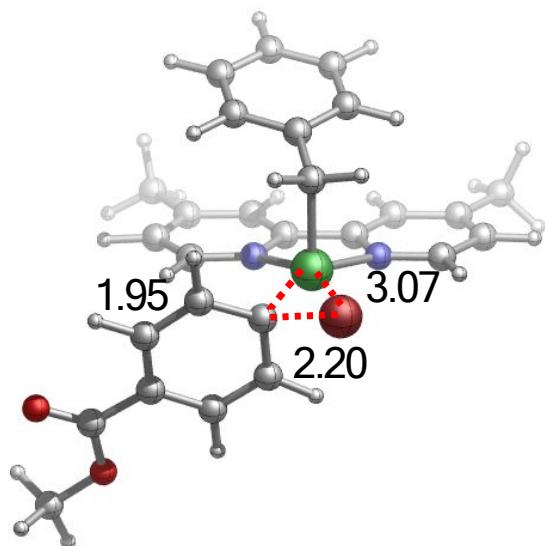
Sum of electronic and thermal Free Energies= -5385.384862

C	-2.45678600	1.66224700	-0.11155900
C	-3.29297300	2.78433100	-0.09811600
C	-2.75602400	4.06687300	0.07008700
C	-1.36500400	4.15692800	0.22315000
C	-0.59355000	2.99830100	0.20201000
C	-2.96030700	0.27956200	-0.30243600
C	-4.30887700	-0.04626700	-0.49799600
C	-4.69161800	-1.37891400	-0.69086300
C	-3.67477700	-2.34913200	-0.68129100
C	-2.35758000	-1.95432500	-0.47954200
H	-4.36989600	2.66703500	-0.21703100
H	-0.87545500	5.12280900	0.36248100
H	0.48621000	3.04831800	0.32399400
H	-5.06849500	0.73500700	-0.50360500
H	-3.90694400	-3.40553500	-0.82990000
H	-1.54168500	-2.68077900	-0.47011100
N	-1.11956600	1.77826900	0.04098000
N	-2.01491700	-0.67601200	-0.29235300
Br	0.28142800	-0.06945000	-2.44862200
Ni	-0.08272200	-0.07170800	0.01916500

C	-0.24773300	-0.45889800	1.89642600
C	-0.45327900	0.53399800	2.86535800
C	-0.27399100	-1.80482900	2.29839500
C	-0.69933200	0.19109700	4.19612300
H	-0.41709500	1.58929900	2.58960700
C	-0.52127400	-2.15639700	3.62651300
H	-0.09540200	-2.59869400	1.56704600
H	-0.86352500	0.96545500	4.94889500
H	-0.54451500	-3.20652000	3.92249100
C	-0.74036400	-1.15650900	4.59092900
C	1.90150400	0.00227600	0.44749500
C	2.37719400	1.39883400	0.53192300
C	2.48803300	2.05060600	1.77928500
C	2.69443900	2.13931000	-0.62808600
C	2.87822100	3.38970300	1.86326100
H	2.25009400	1.49572400	2.68985600
C	3.09015100	3.47551900	-0.54355200
H	2.59023800	1.65640000	-1.60235200
C	3.17765200	4.11237200	0.70190000
H	2.94825600	3.87316900	2.84148100
H	3.32545200	4.02922900	-1.45667400
H	3.47971900	5.16070700	0.76623400
H	2.28068000	-0.52858000	-0.43540000
H	2.12887300	-0.56483800	1.35659900
C	-1.01271400	-1.46798700	6.01941900
O	-1.20679100	-0.63487100	6.88341200
O	-1.02612900	-2.78898000	6.27222400
C	-1.28368100	-3.18087800	7.62276900
H	-1.25210100	-4.27696200	7.63549000
H	-0.52027900	-2.77074600	8.30149800
H	-2.27254800	-2.82561200	7.95104600
C	-6.12716600	-1.76699300	-0.91149200
H	-6.43264000	-2.54712200	-0.19631000
H	-6.80511800	-0.90889300	-0.80526100
H	-6.25810100	-2.18880300	-1.92160900
C	-3.62524000	5.29302200	0.06063800
H	-4.67707800	5.04885800	0.26621300
H	-3.27884500	6.03093500	0.79961200
H	-3.57958500	5.77805400	-0.9293420

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)  
HF=-5387.73744736

<sup>2</sup>B-C-TS-H



UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction= 0.464538 (Hartree/Particle)

Thermal correction to Energy= 0.496614

Thermal correction to Enthalpy= 0.497558

Thermal correction to Gibbs Free Energy= 0.396984

Sum of electronic and zero-point Energies= -5385.264622

Sum of electronic and thermal Energies= -5385.232546

Sum of electronic and thermal Enthalpies= -5385.231602

Sum of electronic and thermal Free Energies= -5385.332176

Ni	-0.69276100	-0.23082600	-0.51656000
----	-------------	-------------	-------------

C	-2.26499500	0.87743600	-0.84995500
---	-------------	------------	-------------

C	-1.97160200	3.60885700	-1.56881900
---	-------------	------------	-------------

C	-2.75826500	1.91305700	0.00661600
---	-------------	------------	------------

C	-1.74071200	1.24924400	-2.13175000
---	-------------	------------	-------------

C	-1.55796000	2.59627200	-2.44951100
---	-------------	------------	-------------

C	-2.59530000	3.23477600	-0.34325800
---	-------------	------------	-------------

H	-3.22317100	1.64410700	0.95719700
---	-------------	------------	------------

H	-1.53308900	0.48826300	-2.88877900
---	-------------	------------	-------------

H	-1.11793200	2.86700300	-3.41080300
---	-------------	------------	-------------

H	-2.92281200	4.02732200	0.33336500
---	-------------	------------	------------

N	0.90753100	1.02350200	-0.14624500
---	------------	------------	-------------

C	3.19052800	2.37391700	0.76649600
---	------------	------------	------------

C	0.82803300	2.28835900	0.27749800
---	------------	------------	------------

C	2.10736900	0.40096600	-0.14261000
---	------------	------------	-------------

C	3.25916600	1.05112800	0.30962700
---	------------	------------	------------

C	1.93566200	2.99908700	0.73144400
---	------------	------------	------------

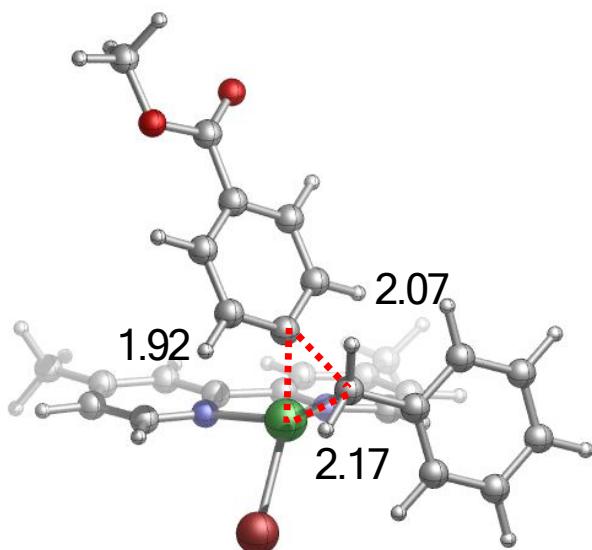
N	0.87590100	-1.46094800	-0.99598200
---	------------	-------------	-------------

C	3.11332700	-3.14201800	-1.14020300
---	------------	-------------	-------------

C	0.75211900	-2.72618800	-1.42049100
C	2.08963100	-1.00139600	-0.62717500
C	3.22375200	-1.82039600	-0.69557000
C	1.83352100	-3.59374100	-1.51042800
H	-0.16466900	2.73799800	0.25967900
H	4.21639800	0.53015800	0.31926400
H	1.81304100	4.03079700	1.06682600
H	-0.25828500	-3.04506400	-1.68984800
H	4.19731500	-1.43626300	-0.39163700
H	1.68204200	-4.61482300	-1.86610900
Br	-3.65922100	-0.81020100	-1.05388200
C	-1.15470900	-0.90909000	1.34478200
H	-1.49609800	-1.93795000	1.14697200
H	-1.98740700	-0.29966900	1.72123300
C	0.04489500	-0.84148400	2.19135500
C	0.99621500	-1.88785800	2.22439700
C	0.34984100	0.32283200	2.93757400
C	2.18673800	-1.77267300	2.94518900
H	0.79807200	-2.79922800	1.65289500
C	1.54073100	0.44249100	3.65274800
H	-0.36095400	1.15419900	2.92626900
C	2.47387200	-0.60431500	3.66125200
H	2.90238500	-2.59999300	2.93922600
H	1.74895700	1.36346400	4.20511100
H	3.40947200	-0.50924400	4.21816100
C	-1.79806700	5.04167400	-1.86122100
O	-2.15012000	5.95146500	-1.12889700
O	-1.18784700	5.27011700	-3.04575300
C	-0.97673000	6.63609000	-3.40102200
H	-0.47556900	6.62665100	-4.37684000
H	-1.93288400	7.17764700	-3.47285800
H	-0.34424100	7.14416400	-2.65637000
C	4.40442500	3.07334200	1.31164000
H	4.48554200	2.88420000	2.39604500
H	5.32900000	2.70541300	0.84328500
H	4.34106500	4.16211500	1.17042200
C	4.30357700	-4.05843700	-1.20232600
H	5.24647800	-3.51628400	-1.04536500
H	4.22362000	-4.83820200	-0.42641100
H	4.35032400	-4.57555400	-2.17343200

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)  
HF=-5387.68140959

<sup>2</sup>E-P<sub>B</sub>-TS-H



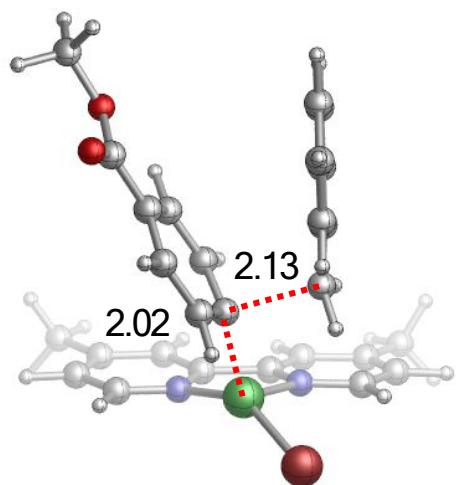
UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction=		0.466837 (Hartree/Particle)
Thermal correction to Energy=		0.498964
Thermal correction to Enthalpy=		0.499909
Thermal correction to Gibbs Free Energy=		0.396710
Sum of electronic and zero-point Energies=		-5385.304741
Sum of electronic and thermal Energies=		-5385.272613
Sum of electronic and thermal Enthalpies=		-5385.271669
Sum of electronic and thermal Free Energies=		-5385.374868
C	-2.33724800	1.67095700
C	-3.20553300	2.75365600
C	-2.70500400	4.05861400
C	-1.31591700	4.21429100
C	-0.51031400	3.09291100
C	-2.80974500	0.26994900
C	-4.15446400	-0.11766300
C	-4.50729700	-1.46168000
C	-3.46820700	-2.37520800
C	-2.15567200	-1.91934700
H	-4.28016800	2.58777900
H	-0.85486200	5.20302700
H	0.56865800	3.19623300
H	-4.93439100	0.62068700
H	-3.68070500	-3.43522600
H	-1.31645400	-2.59095300
N	-0.99832600	1.84574000
N	-1.83846700	-0.63296100
Br	0.88885100	-0.94508400
		-2.24715900

Ni	0.08450500	0.04205500	-0.07010200
C	0.20298500	-0.31369700	1.81062000
C	-0.23667500	0.63121400	2.76004200
C	0.11917600	-1.68513400	2.14038100
C	-0.79409600	0.21698900	3.96565900
H	-0.15635200	1.69738600	2.54207300
C	-0.44590700	-2.09966600	3.34193500
H	0.49446600	-2.43159800	1.43428400
H	-1.15326600	0.95124400	4.69017300
H	-0.52700400	-3.16379600	3.56944800
C	-0.91496000	-1.15156500	4.27265800
C	2.01446000	0.11994200	0.91192500
C	2.42754800	1.51844100	0.63236800
C	2.53007700	2.45335700	1.68306000
C	2.72981600	1.95297200	-0.67604100
C	2.89896100	3.77830400	1.43404800
H	2.31680000	2.13334100	2.70582500
C	3.10993600	3.27367800	-0.92152700
H	2.63893400	1.24187900	-1.50015000
C	3.18832700	4.19682100	0.13020900
H	2.96459700	4.48719600	2.26355200
H	3.34010200	3.58865500	-1.94277300
H	3.47671900	5.23252500	-0.06530300
H	2.36590400	-0.61062200	0.17321100
H	2.35226200	-0.19469300	1.90064200
C	-1.52651300	-1.53569700	5.56714300
O	-1.93911200	-0.74999000	6.39997000
O	-1.58722600	-2.87009700	5.74181100
C	-2.16625300	-3.33007800	6.96444000
H	-2.12847100	-4.42560000	6.92918300
H	-1.59840700	-2.95856900	7.83130600
H	-3.20904700	-2.98940200	7.05680600
C	-5.93733700	-1.91996600	-0.10890600
H	-6.07069400	-2.62245100	0.73006900
H	-6.63021500	-1.07875900	0.03114500
H	-6.22135400	-2.45933000	-1.02663300
C	-3.60826800	5.24481900	0.51521000
H	-4.64926900	4.94311900	0.69587500
H	-3.26783400	5.86136900	1.36211200
H	-3.58561100	5.88869300	-0.37956400

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)  
HF=-5387.72466391

**<sup>4</sup>D'-P<sub>B</sub>-TS-H**



UB3LYP-D3/def2-SVP-CPCM(DMA)

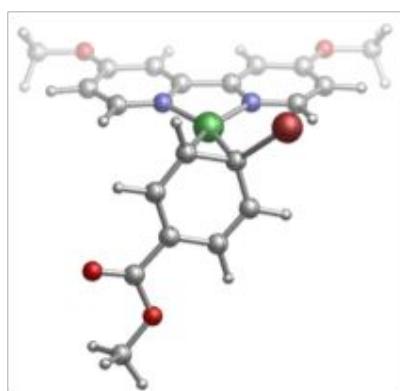
Zero-point correction=	0.464258 (Hartree/Particle)		
Thermal correction to Energy=	0.496861		
Thermal correction to Enthalpy=	0.497806		
Thermal correction to Gibbs Free Energy=	0.393139		
Sum of electronic and zero-point Energies=	-5385.275965		
Sum of electronic and thermal Energies=	-5385.243361		
Sum of electronic and thermal Enthalpies=	-5385.242417		
Sum of electronic and thermal Free Energies=	-5385.347083		
Ni	1.14937000	1.53744700	-0.27007000
C	2.11738000	0.16244000	0.85039200
C	3.61420600	-2.22169300	1.40463500
C	3.53852600	0.08823800	0.64751200
C	1.48180600	-1.07620700	1.20594000
C	2.19832500	-2.21755300	1.50770500
C	4.26456600	-1.05064000	0.93976000
H	4.06169000	0.98705300	0.30442700
H	0.39014900	-1.10060000	1.29617200
H	1.68490600	-3.12956100	1.81831000
H	5.35022300	-1.07373300	0.81709600
N	-0.68356800	1.85488600	0.55447800
C	-3.25432800	2.04278800	1.64236900
C	-0.96755400	2.79787200	1.46172900
C	-1.64807600	0.99981900	0.15123300
C	-2.94040500	1.07156600	0.68257400
C	-2.23036400	2.92511600	2.02842900
N	0.03968900	0.18240200	-1.33071200
C	-1.53415900	-1.91318500	-2.31477900
C	0.53147100	-0.66486400	-2.24273600
C	-1.22073300	0.01654000	-0.87653900

C	-2.02749600	-1.02351200	-1.35179000
C	-0.21687400	-1.71407100	-2.76324600
H	-0.14335800	3.46541800	1.72418200
H	-3.71180500	0.37865400	0.34686600
H	-2.41640700	3.70938800	2.76474600
H	1.56484400	-0.49060000	-2.55253400
H	-3.04022400	-1.15259600	-0.96985300
H	0.22528100	-2.37618600	-3.51024700
Br	2.32064600	3.66550100	-0.22226700
C	1.98227200	1.22934300	2.68716800
H	0.89321900	1.21595800	2.75776600
H	2.40463900	2.16284000	2.31039000
C	2.71944300	0.49643000	3.68894800
C	4.10907800	0.70556500	3.87673800
C	2.09745000	-0.51674200	4.46133800
C	4.83409500	-0.05118600	4.79573400
H	4.61243100	1.47298600	3.28283400
C	2.82469400	-1.27248500	5.37929500
H	1.02930600	-0.70466300	4.32403200
C	4.19872600	-1.04848800	5.55022800
H	5.90480900	0.13052500	4.92390700
H	2.32151400	-2.04728600	5.96447700
H	4.76884900	-1.64369400	6.26818000
C	4.43510600	-3.38705800	1.76797700
O	5.65276000	-3.44150400	1.69170400
O	3.70145400	-4.43165800	2.22055900
C	4.42615000	-5.59697700	2.60834800
H	3.67964200	-6.32752700	2.94428800
H	5.00043300	-6.00638800	1.76240400
H	5.12782300	-5.37125300	3.42678200
C	-4.62751600	2.14294800	2.24494600
H	-5.34111600	1.46647900	1.75476300
H	-4.59102600	1.88846900	3.31719800
H	-5.01020800	3.17314700	2.17273400
C	-2.36638400	-3.04623200	-2.84625900
H	-3.38028800	-3.04445200	-2.42314800
H	-2.44395400	-2.98625100	-3.94372700
H	-1.89245500	-4.01313400	-2.61101500

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)  
HF=-5387.69496314

**Figure S3**

**<sup>1</sup>A-OMe**



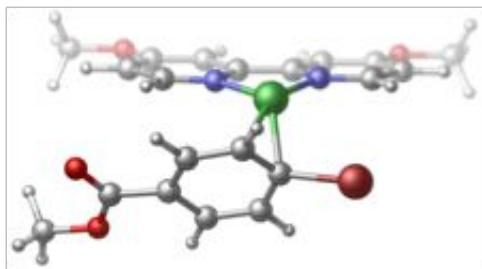
UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction=		0.357686 (Hartree/Particle)
Thermal correction to Energy=		0.384893
Thermal correction to Enthalpy=		0.385837
Thermal correction to Gibbs Free Energy=		0.296780
Sum of electronic and zero-point Energies=		-5264.901889
Sum of electronic and thermal Energies=		-5264.874682
Sum of electronic and thermal Enthalpies=		-5264.873738
Sum of electronic and thermal Free Energies=		-5264.962795
C	2.2499543	-0.9653313
C	1.7807733	-2.1260333
C	2.4197883	-2.3719993
C	3.3729583	-1.5227733
C	3.8432923	-0.3971233
C	3.3007123	-0.1645913
Br	1.4323193	-3.8866773
H	2.1044253	-3.2420533
H	2.0995203	-0.9357233
H	3.7123413	0.6516997
H	3.7936073	-1.6985413
C	-1.7582647	0.8139747
C	0.0098413	2.0408177
C	-0.7117317	3.2312747
C	-2.0299387	3.1911597
C	-2.5507667	1.9515467
C	-2.2006657	-0.5431913
C	-1.5610797	-2.7692583
C	-2.7996907	-3.1481273
C	-3.7807537	-2.1565383
C	-3.4623667	-0.8317863
H	1.0380243	2.0261147
		-1.7539000

H	-0.2422657	4.1532237	-1.6780330
H	-3.5706057	1.9192387	-0.0514110
H	-0.7737937	-3.5082773	-0.0965370
H	-2.9759367	-4.1933973	0.8290890
H	-4.2217497	-0.0617993	0.5316940
N	-0.4855797	0.8618807	-0.9922130
N	-1.2558427	-1.5087923	-0.2628090
Ni	0.4390083	-0.8675973	-0.9606360
O	-5.0112337	-2.3662523	1.2370090
O	-2.8452497	4.2459037	-0.7486470
C	-2.3885567	5.5331857	-1.1563690
H	-2.1262897	5.5423027	-2.2271660
H	-3.2226777	6.2231927	-0.9808020
H	-1.5177167	5.8541947	-0.5614170
C	-5.4043947	-3.6825323	1.6164830
H	-6.4376327	-3.6018363	1.9751470
H	-5.3688757	-4.3725993	0.7573430
H	-4.7658717	-4.0712883	2.4268290
C	4.8945513	0.5118457	0.5168050
O	5.3307323	1.4819537	-0.0807950
O	5.3555663	0.1656017	1.7414900
C	6.3762193	0.9941057	2.2955870
H	6.6195833	0.5693387	3.2774440
H	7.2716763	1.0001207	1.6545920
H	6.0246353	2.0314457	2.4097020

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)  
HF=-5267.1058385

<sup>3</sup>A-OMe



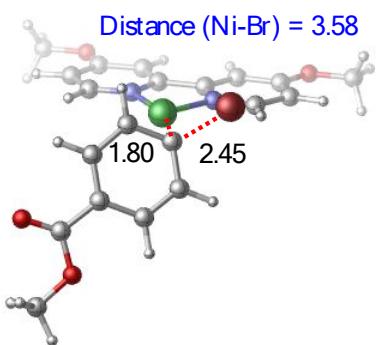
UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction=	0.355652 (Hartree/Particle)		
Thermal correction to Energy=	0.383193		
Thermal correction to Enthalpy=	0.384137		
Thermal correction to Gibbs Free Energy=	0.293638		
Sum of electronic and zero-point Energies=	-5264.880489		
Sum of electronic and thermal Energies=	-5264.852948		
Sum of electronic and thermal Enthalpies=	-5264.852004		
Sum of electronic and thermal Free Energies=	-5264.942503		
C	-2.94990400	-0.44815100	1.93399100
C	-2.42900200	-1.15835400	0.79890500
C	-2.56116000	-0.59222200	-0.51007500
C	-3.05110000	0.68566500	-0.65598500
C	-3.48630600	1.43739400	0.47470200
C	-3.45943600	0.85033000	1.73928900
Br	-2.29164800	-3.10341300	0.91956400
H	-2.23427400	-1.16963400	-1.37593500
H	-3.09565400	-0.95501700	2.89111700
H	-3.83710000	1.41524300	2.59369000
H	-3.09820100	1.13907200	-1.64643500
C	1.65215500	-0.00457100	0.35946800
C	1.36545200	-2.27801300	0.89845700
C	2.52097100	-2.66599900	0.23439000
C	3.28183700	-1.64647000	-0.40930100
C	2.84281100	-0.33250700	-0.34548500
C	1.11914100	1.31816400	0.49987000
C	-0.60725700	2.62738000	1.40784700
C	-0.05041000	3.81998100	0.96306200
C	1.16784800	3.74103200	0.22857500
C	1.74572400	2.49915900	0.01139800
H	0.73792900	-3.02606000	1.39168600
H	2.80829700	-3.71516700	0.21868800
H	3.42512400	0.43533800	-0.85465300
H	-1.54081100	2.65097500	1.97238200
H	-0.55180700	4.76054300	1.18087100

H	2.68883800	2.45199700	-0.53272500
N	0.93210000	-1.01471700	0.98630100
N	-0.08623900	1.41476000	1.18606300
Ni	-0.79835700	-0.38650400	1.67428800
C	-3.90947700	2.85205300	0.37180800
O	-4.17452900	3.56395500	1.32381200
O	-3.93648600	3.29749300	-0.89671100
C	-4.26941100	4.67546900	-1.08452600
H	-3.53988900	5.32343800	-0.57476500
H	-4.24249500	4.85261700	-2.16630200
H	-5.27244000	4.89367000	-0.68771100
O	1.81638900	4.81872600	-0.27072200
O	4.42345400	-1.88074000	-1.09860300
C	1.27165300	6.11404900	-0.07399300
H	1.20251700	6.36929200	0.99749400
H	1.95748900	6.81689900	-0.56481500
H	0.27163100	6.21006500	-0.53088400
C	4.91160500	-3.20770200	-1.21326700
H	5.83115800	-3.14934800	-1.81024400
H	5.15153600	-3.64192700	-0.22735100
H	4.19054000	-3.86514600	-1.72909700

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)  
HF=-5267.0763011

**<sup>1</sup>A-F-TS-OMe**

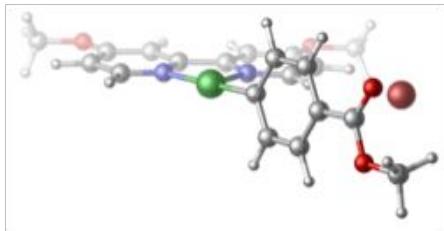


UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction=	0.357871 (Hartree/Particle)		
Thermal correction to Energy=	0.384534		
Thermal correction to Enthalpy=	0.385478		
Thermal correction to Gibbs Free Energy=	0.297199		
Sum of electronic and zero-point Energies=	-5264.900195		
Sum of electronic and thermal Energies=	-5264.873532		
Sum of electronic and thermal Enthalpies=	-5264.872588		
Sum of electronic and thermal Free Energies=	-5264.960866		
C	-2.77557700	0.14469100	-0.62258500
C	-2.40291900	1.42187200	-1.18746300
C	-2.91578200	2.61298900	-0.58862900
C	-3.68862500	2.54298000	0.55030300
C	-4.05837500	1.28404500	1.11755200
C	-3.61794000	0.10982400	0.51523000
Br	-2.87504700	1.61579900	-3.58102800
H	-2.65185600	3.58242500	-1.01795300
H	-2.65269400	-0.78236200	-1.19416500
H	-3.96024000	-0.84721200	0.91694300
H	-4.02039300	3.46016600	1.03983800
C	1.90740900	0.20623500	-0.16130200
C	0.50196800	-1.10172800	1.14649300
C	1.57098400	-1.68576200	1.82069200
C	2.87410800	-1.28783900	1.47178400
C	3.03154100	-0.32050300	0.45954900
C	1.94596100	1.22494300	-1.24140100
C	0.64059900	2.49159300	-2.69289600
C	1.75951100	3.08585100	-3.27046600
C	3.03175300	2.72112800	-2.79613300
C	3.11217600	1.76748900	-1.76225200
H	-0.52730500	-1.37698900	1.38728000
H	1.37390000	-2.42687400	2.59318000
H	4.04008700	-0.00970800	0.19003300

H	-0.36927800	2.72323600	-3.04169600
H	1.62161300	3.80971200	-4.07176900
H	4.09666000	1.47749800	-1.39732600
N	0.65242300	-0.18550100	0.18355200
N	0.71972600	1.59167600	-1.70448600
Ni	-0.77558400	0.75372600	-0.80901600
C	-4.91265300	1.17907000	2.32267800
O	-5.26070300	0.13594500	2.84575600
O	-5.28178100	2.38263600	2.80704500
C	-6.10537300	2.37685900	3.97401500
H	-5.59208600	1.88452200	4.81446900
H	-6.30303400	3.42819500	4.21629900
H	-7.05164200	1.84713100	3.78414300
O	3.99487400	-1.75473400	2.02741800
O	4.19101300	3.20476600	-3.25048600
C	3.91736900	-2.73601500	3.05955400
H	4.95177000	-2.95670400	3.34894100
H	3.36717200	-2.35079700	3.93355400
H	3.43443500	-3.65791700	2.69639800
C	4.19097700	4.17107400	-4.29931500
H	3.65773800	5.08699000	-3.99627600
H	5.24332800	4.41012000	-4.49408400
H	3.73278600	3.76365000	-5.21536700

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)  
HF=-5267.1064595

**<sup>1</sup>F-OMe**

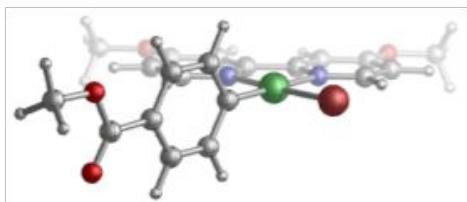
UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction=	0.359582 (Hartree/Particle)		
Thermal correction to Energy=	0.387147		
Thermal correction to Enthalpy=	0.388092		
Thermal correction to Gibbs Free Energy=	0.296249		
Sum of electronic and zero-point Energies=	-5264.917913		
Sum of electronic and thermal Energies=	-5264.890347		
Sum of electronic and thermal Enthalpies=	-5264.889403		
Sum of electronic and thermal Free Energies=	-5264.981246		
C	-2.78692100	0.31168900	0.05360900
C	-1.81275300	0.88229300	0.89351600
C	-2.19105800	1.94630800	1.73247400
C	-3.50407500	2.42300100	1.74493400
C	-4.47063000	1.83979300	0.90757000
C	-4.10176400	0.77932100	0.06205700
Br	-2.62666900	4.21319000	-2.24266500
H	-1.44819400	2.42126700	2.38097000
H	-2.51355700	-0.50197800	-0.62508500
H	-4.85963600	0.33902400	-0.58968400
H	-3.78533100	3.25203800	2.39634200
C	2.54040300	-0.27179300	0.23165300
C	2.06567600	-1.59077500	2.08765900
C	3.33483800	-2.16057000	2.08141300
C	4.24364700	-1.75113900	1.08714600
C	3.82619200	-0.78462000	0.14947200
C	1.96857100	0.74150000	-0.68087300
C	0.07470300	2.00429000	-1.18078200
C	0.71041100	2.63752400	-2.24096300
C	2.03999000	2.29559100	-2.53247200
C	2.66834200	1.32698900	-1.72344200
H	1.32612900	-1.87891200	2.83902200
H	3.59116500	-2.90205100	2.83577300
H	4.52786200	-0.46814500	-0.62097100
H	-0.95762100	2.27114700	-0.95578400
H	0.12814400	3.37570300	-2.79329700
H	3.70233700	1.05808500	-1.93503300

N	1.67515100	-0.67573000	1.19439500
N	0.66881200	1.07520400	-0.41265700
Ni	-0.09599000	0.15467300	1.03659700
C	-5.87989400	2.31938100	0.86402000
O	-6.74710300	1.84727400	0.15551000
O	-6.10671900	3.34702600	1.69988300
C	-7.43511800	3.87568800	1.72076800
H	-8.15840100	3.10288800	2.02283600
H	-7.42795800	4.69394100	2.45075100
H	-7.71975800	4.25475700	0.72736800
O	5.48792700	-2.20792900	0.95170800
O	2.76873200	2.81634200	-3.51843900
C	5.98609500	-3.19629400	1.85335200
H	7.01473400	-3.40521100	1.53662200
H	5.99054500	-2.82128100	2.88956000
H	5.38982300	-4.12131200	1.79573000
C	2.18821000	3.80203900	-4.37374400
H	1.89074500	4.69586000	-3.80210800
H	2.96537300	4.07212400	-5.09835500
H	1.31258600	3.39698300	-4.90605400

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)

HF=-5267.1366107

**<sup>1</sup>D-OMe**

UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction= 0.360031 (Hartree/Particle)

Thermal correction to Energy= 0.387146

Thermal correction to Enthalpy= 0.388091

Thermal correction to Gibbs Free Energy= 0.298627

Sum of electronic and zero-point Energies= -5264.962792

Sum of electronic and thermal Energies= -5264.935677

Sum of electronic and thermal Enthalpies= -5264.934733

Sum of electronic and thermal Free Energies= -5265.024196

Ni -5.32106700 -0.56546600 0.88149500

C -5.98541600 0.96857100 1.74838900

C -6.30580200 2.13066600 1.01826500

C -6.13351500 1.01948700 3.14919300

C -6.73522900 3.29825300 1.65112600

H -6.21063500 2.12563400 -0.07184300

C -6.56084600 2.18032300 3.79363400

H -5.90520800 0.13322900 3.74888700

C -6.86585700 3.33583900 3.05166300

H -6.97187300 4.18866500 1.06562400

H -6.66676400 2.21230100 4.88072200

Br -7.55373600 -1.33532100 0.72068500

N -3.46358900 0.02956100 0.97219400

C -0.72704200 0.68579600 0.94916500

C -3.00945900 1.16803300 1.52234500

C -2.54990600 -0.80838700 0.40299800

C -1.19420300 -0.51001300 0.37545800

C -1.67062200 1.54186900 1.54040700

N -4.46600800 -2.15022000 -0.04563500

C -2.99104000 -4.18172600 -1.29431500

C -5.06686800 -3.24356200 -0.53095400

C -3.11866600 -2.04706100 -0.17063100

C -2.35702800 -3.03396000 -0.78414100

C -4.38622700 -4.28233600 -1.15928900

H -3.76023800 1.81561400 1.97143900

H -0.47018200 -1.18136200 -0.08313400

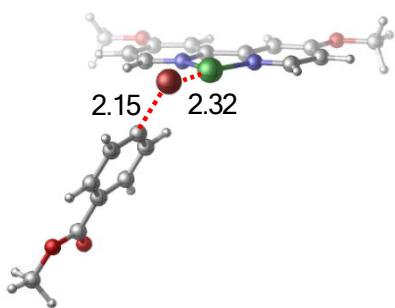
H -1.39340100 2.48418900 2.00956800

H -6.15099600 -3.27753200 -0.40487900

H	-1.27597200	-2.95194900	-0.88459700
H	-4.94780100	-5.13935200	-1.52730300
C	-7.31504200	4.54842600	3.78135600
O	-7.43988900	4.62538200	4.98914500
O	-7.57980900	5.58506000	2.96294100
C	-8.02026100	6.79448700	3.58323900
H	-7.25967300	7.17685700	4.28136200
H	-8.18415300	7.51397300	2.77183600
H	-8.95582300	6.63137100	4.14012300
O	-2.20349200	-5.09270100	-1.87145700
O	0.58643800	0.91019400	0.88407900
C	-2.77737500	-6.28060300	-2.41349000
H	-3.49458700	-6.04481600	-3.21661300
H	-1.94407300	-6.86031800	-2.82825700
H	-3.28079500	-6.87212400	-1.63135400
C	1.12705600	2.10696200	1.44199900
H	2.20775400	2.06677400	1.26092600
H	0.70622200	2.99918800	0.95034000
H	0.93935400	2.15954100	2.52679500

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)  
HF=-5267.1696621

**<sup>1</sup>A-F'-TS-OMe**



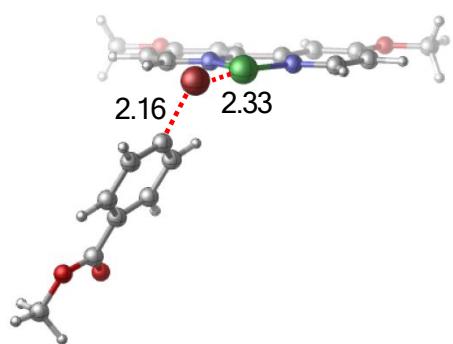
UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction=		0.354823 (Hartree/Particle)
Thermal correction to Energy=		0.382370
Thermal correction to Enthalpy=		0.383314
Thermal correction to Gibbs Free Energy=		0.291951
Sum of electronic and zero-point Energies=		-5264.857895
Sum of electronic and thermal Energies=		-5264.830348
Sum of electronic and thermal Enthalpies=		-5264.829404
Sum of electronic and thermal Free Energies=		-5264.920767
Ni	-3.29052000	1.75698400
C	-6.37200800	2.78130600
C	-7.57656300	3.45907000
C	-5.87849900	1.90704100
C	-8.32537600	3.25026000
H	-7.93477000	4.13813700
C	-6.63181100	1.70523100
H	-4.92698500	1.39007200
C	-7.85616900	2.37412400
H	-9.27570800	3.76779100
H	-6.28326500	1.02849600
Br	-5.21038000	2.99495500
N	-1.45560200	1.21886400
C	1.12016200	0.13740200
C	-0.36398100	2.00204000
C	-1.29159300	-0.14436600
C	0.00285200	-0.69015300
C	0.93307300	1.53711200
N	-3.66789600	-0.16595000
C	-3.83735800	-2.94310600
C	-4.85070600	-0.79231900
C	-2.51787700	-0.91008400
C	-2.59779700	-2.31019200
C	-5.01038500	-2.16117700
H	-0.55051900	3.07014600

H	0.15155900	-1.76187700	0.01676500
H	1.76208400	2.24180900	-0.32215800
H	-5.72372300	-0.14873500	-0.55745000
H	-1.70288800	-2.91735700	0.07151600
H	-6.00909900	-2.59316200	-0.25272900
C	-8.61937100	2.12049300	4.26421600
O	-8.25151500	1.37460200	5.14895200
O	-9.76905400	2.80926900	4.32104100
C	-10.56837700	2.63083000	5.49485000
H	-10.01331200	2.93930100	6.39374100
H	-11.45441000	3.26233200	5.36018200
H	-10.86470700	1.57692900	5.60708300
O	-3.84021700	-4.28203200	0.11953000
O	2.32642100	-0.45411100	0.01620500
C	-5.07449000	-4.98349700	0.13059900
H	-5.60929900	-4.88042000	-0.82910600
H	-4.82808000	-6.04100000	0.29120300
H	-5.73107500	-4.63900300	0.94792800
C	3.50133100	0.34229700	0.00686900
H	4.34428200	-0.34764300	0.14219000
H	3.62411300	0.87594300	-0.95130300
H	3.50246100	1.07658300	0.83074800

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)  
HF=-5267.0673323

<sup>3</sup>A-D'-TS-OMe



UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction= 0.354623 (Hartree/Particle)

Thermal correction to Energy= 0.382196

Thermal correction to Enthalpy= 0.383141

Thermal correction to Gibbs Free Energy= 0.290851

Sum of electronic and zero-point Energies= -5264.856455

Sum of electronic and thermal Energies= -5264.828882

Sum of electronic and thermal Enthalpies= -5264.827938

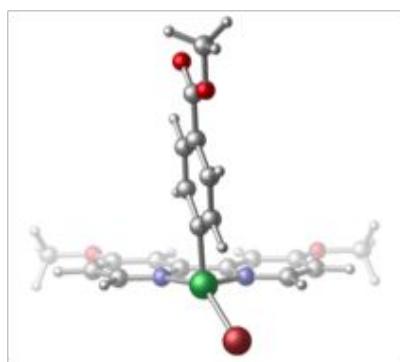
Sum of electronic and thermal Free Energies= -5264.920228

Ni	-3.14978300	1.92574500	-0.78733500
C	-6.24554500	2.86447600	0.64520200
C	-7.46880900	3.50262100	0.80253500
C	-5.77014900	1.89922400	1.52163500
C	-8.25198600	3.16188200	1.91145800
H	-7.81450800	4.25369900	0.08692400
C	-6.55599700	1.56826600	2.62742000
H	-4.80612500	1.41359900	1.33669000
C	-7.79892000	2.19528500	2.82732500
H	-9.21569300	3.64813600	2.07167300
H	-6.21883200	0.82188300	3.35016400
Br	-5.06511500	3.20961000	-1.13254500
N	-1.35758000	1.30357700	-0.44238800
C	1.15219200	0.10295500	-0.04568000
C	-0.24147500	2.04148500	-0.33164200
C	-1.25260500	-0.07253700	-0.35192300
C	0.00609900	-0.67914800	-0.16060300
C	1.02656400	1.51521700	-0.12991300
N	-3.60480300	0.00401800	-0.71223000
C	-3.91037200	-2.77314800	-0.48169000
C	-4.80677800	-0.57140300	-0.83436700
C	-2.50611600	-0.79101300	-0.46794000
C	-2.65238400	-2.18956000	-0.34865300
C	-5.03109500	-1.93848000	-0.73516600

H	-0.38041000	3.12344200	-0.40942200
H	0.10819800	-1.76277100	-0.10157700
H	1.87915800	2.18606200	-0.04354900
H	-5.63867400	0.11387300	-1.02286600
H	-1.79825600	-2.83580400	-0.14639400
H	-6.04002800	-2.32922500	-0.85212900
C	-8.59758900	1.79930000	4.02367200
O	-8.24364600	0.97272200	4.84013800
O	-9.76404200	2.45699500	4.11040800
C	-10.59797600	2.14182100	5.22982200
H	-10.07940700	2.36147000	6.17537600
H	-11.49140200	2.76973900	5.13196200
H	-10.87746600	1.07735200	5.21937800
O	-3.97757600	-4.11579800	-0.35423200
O	2.32203000	-0.54640300	0.13808100
C	-5.23322100	-4.76776100	-0.47374100
H	-5.04036800	-5.83894200	-0.33197500
H	-5.94435300	-4.42493800	0.29728700
H	-5.67934800	-4.61155000	-1.47088000
C	3.52342800	0.20009900	0.26163400
H	4.32975800	-0.53162000	0.39998300
H	3.72814600	0.79405000	-0.64563900
H	3.49525300	0.87385300	1.13511600

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)  
HF=-5267.0663634

**<sup>3</sup>D'-OMe**



UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction= 0.358594 (Hartree/Particle)

Thermal correction to Energy= 0.386406

Thermal correction to Enthalpy= 0.387350

Thermal correction to Gibbs Free Energy= 0.293420

Sum of electronic and zero-point Energies= -5264.962311

Sum of electronic and thermal Energies= -5264.934499

Sum of electronic and thermal Enthalpies= -5264.933555

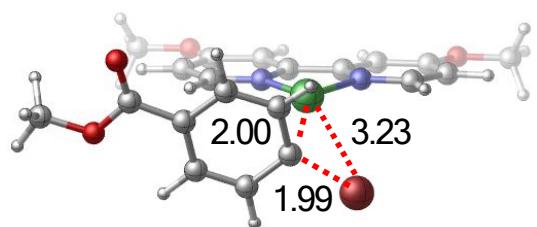
Sum of electronic and thermal Free Energies= -5265.027485

Ni	-4.41702900	1.54701300	-1.09190000
C	-5.28010800	1.87449500	0.66698000
C	-6.31755700	2.81799200	0.82120100
C	-4.89748400	1.16479600	1.82502900
C	-6.93478500	3.05415800	2.05279000
H	-6.65573900	3.38074900	-0.05527200
C	-5.50482300	1.37940500	3.06291100
H	-4.09666400	0.41952800	1.76165400
C	-6.53166400	2.33234200	3.19076400
H	-7.73280600	3.79426100	2.14135200
H	-5.19607400	0.81918300	3.94915000
Br	-5.82433200	2.32861800	-2.91966300
N	-2.49555600	1.16151900	-0.46443100
C	-0.01697500	0.38508800	0.55712100
C	-1.60802600	2.07299100	-0.05726500
C	-2.18425000	-0.15410300	-0.36706300
C	-0.95915600	-0.57364600	0.13786000
C	-0.35635900	1.74679000	0.45598600
N	-4.37863600	-0.47910300	-1.26831800
C	-4.20808600	-3.26064400	-1.25737200
C	-5.39904600	-1.22442400	-1.70078900
C	-3.25078000	-1.08440400	-0.82613000
C	-3.13330300	-2.46921100	-0.80819900
C	-5.37082100	-2.61547100	-1.71813300

H	-1.91834300	3.11756200	-0.14211400
H	-0.69817200	-1.62747900	0.22334000
H	0.31927100	2.54220900	0.76528900
H	-6.27279100	-0.66988900	-2.05258700
H	-2.23362600	-2.97044700	-0.45437500
H	-6.23733300	-3.16449500	-2.08235500
C	-7.14672700	2.53485900	4.52821700
O	-6.83226500	1.92913600	5.53536500
O	-8.10967800	3.47642300	4.52676800
C	-8.75229400	3.73627200	5.77622200
H	-8.02440300	4.07946000	6.52752400
H	-9.49421600	4.52056800	5.58305500
H	-9.24827600	2.83058200	6.15799500
O	-4.03270500	-4.58347200	-1.20919000
O	1.14042100	-0.08465800	1.02816800
C	-5.07932900	-5.45243600	-1.63791100
H	-4.70359100	-6.47339100	-1.50041000
H	-5.98714500	-5.31161500	-1.02878600
H	-5.31963800	-5.29129900	-2.70152000
C	2.14785600	0.82493300	1.46696100
H	2.99164600	0.20833200	1.79889300
H	2.47550700	1.48151300	0.64448000
H	1.78968000	1.43885900	2.30941200

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)  
HF=-5267.1644081

<sup>3</sup>A-D-TS-OMe



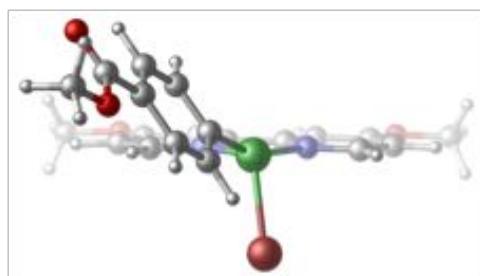
UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction=	0.354575 (Hartree/Particle)	
Thermal correction to Energy=	0.381621	
Thermal correction to Enthalpy=	0.382566	
Thermal correction to Gibbs Free Energy=	0.293221	
Sum of electronic and zero-point Energies=	-5264.880406	
Sum of electronic and thermal Energies=	-5264.853360	
Sum of electronic and thermal Enthalpies=	-5264.852415	
Sum of electronic and thermal Free Energies=	-5264.941760	
C	-2.87817900	-0.60942800
C	-2.59234600	-0.86447200
C	-3.07318000	0.07831600
C	-3.66985300	1.24941300
C	-3.87676700	1.54953200
C	-3.48563400	0.59952300
Br	-2.52645800	-2.76612800
H	-2.92860100	-0.13874300
H	-2.75468500	-1.40269000
H	-3.67631300	0.80718800
H	-3.98248400	1.97778200
C	1.95439600	-0.07954600
C	1.44151600	-2.30983700
C	2.74632600	-2.72820600
C	3.70679000	-1.75347600
C	3.29420900	-0.42788800
C	1.41082200	1.26806000
C	-0.52067000	2.57361500
C	0.16456300	3.74245000
C	1.55895500	3.65647600
C	2.17289100	2.40541700
H	0.66508700	-3.02865800
H	2.99871600	-3.77949200
H	4.03128700	0.31629400
H	-1.59604800	2.59977200
H	-0.38023000	4.68383500
		-0.11834000

H	3.24688100	2.34039000	-0.39626400
N	1.03672300	-1.03440900	0.57154900
N	0.05562700	1.36369200	0.30070700
Ni	-0.81276500	-0.39116800	0.67664500
C	-4.46459300	2.81049900	1.15640100
O	-4.69198000	3.10239200	2.32207300
O	-4.73153700	3.66755600	0.13853800
C	-5.29973700	4.92415600	0.49937900
H	-4.63007300	5.48277300	1.17214900
H	-5.44099000	5.47983800	-0.43615200
H	-6.26770000	4.78989400	1.00756600
O	2.34872900	4.70439200	-0.61256700
O	5.00573800	-2.01680400	-0.12566300
C	1.78059700	6.00396300	-0.70801300
H	1.33387500	6.32117900	0.24952000
H	2.60421500	6.68277100	-0.96281100
H	1.01375600	6.05256100	-1.49957000
C	5.48507900	-3.34964500	-0.00606300
H	6.55527300	-3.31498700	-0.24602200
H	5.35727000	-3.73502400	1.01966800
H	4.97781000	-4.02682900	-0.71406500

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)  
HF=-5267.0781924

<sup>3</sup>D-OMe



UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction= 0.358968 (Hartree/Particle)

Thermal correction to Energy= 0.386611

Thermal correction to Enthalpy= 0.387555

Thermal correction to Gibbs Free Energy= 0.295766

Sum of electronic and zero-point Energies= -5264.956685

Sum of electronic and thermal Energies= -5264.929042

Sum of electronic and thermal Enthalpies= -5264.928098

Sum of electronic and thermal Free Energies= -5265.019887

C	-2.31420000	1.80187700	1.19856800
---	-------------	------------	------------

C	-2.24832700	0.90079800	0.11091800
---	-------------	------------	------------

C	-3.46500600	0.64065200	-0.55667800
---	-------------	------------	-------------

C	-4.67123900	1.22995300	-0.17207300
---	-------------	------------	-------------

C	-4.70383200	2.12353000	0.91453900
---	-------------	------------	------------

C	-3.50868100	2.40420000	1.59922600
---	-------------	------------	------------

Br	-0.75846300	-0.45798800	-2.79711500
----	-------------	-------------	-------------

H	-3.45903900	-0.03820600	-1.41549200
---	-------------	-------------	-------------

H	-1.39931400	2.04738200	1.75007600
---	-------------	------------	------------

H	-3.53642000	3.10053400	2.44112400
---	-------------	------------	------------

H	-5.59460100	1.00851800	-0.71128500
---	-------------	------------	-------------

C	2.37372100	-0.20992700	-0.04552600
---	------------	-------------	-------------

C	1.37160900	-2.30211500	-0.06047200
---	------------	-------------	-------------

C	2.58815200	-2.96013000	0.09383000
---	------------	-------------	------------

C	3.75506100	-2.17966400	0.18444300
---	------------	-------------	------------

C	3.63252700	-0.77879500	0.10814200
---	------------	-------------	------------

C	2.14003300	1.25606100	-0.15599600
---	------------	------------	-------------

C	0.53880600	2.91058900	-0.45643400
---	------------	------------	-------------

C	1.48865400	3.92748600	-0.42617500
---	------------	------------	-------------

C	2.83647000	3.56904500	-0.24298300
---	------------	------------	-------------

C	3.15515200	2.20359500	-0.10792800
---	------------	------------	-------------

H	0.44091300	-2.86859100	-0.14696400
---	------------	-------------	-------------

H	2.60803600	-4.04753000	0.13787900
---	------------	-------------	------------

H	4.53776300	-0.17647800	0.16883800
---	------------	-------------	------------

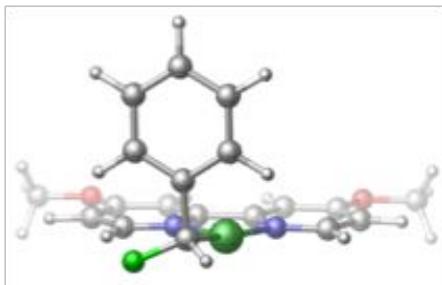
H	-0.52182000	3.13654500	-0.58807600
---	-------------	------------	-------------

H	1.16904700	4.96162000	-0.54153500
---	------------	------------	-------------

H	4.19965400	1.92750500	0.02890800
N	1.25771800	-0.97286200	-0.12105800
N	0.84520200	1.61761000	-0.32370400
Ni	-0.51503300	0.07695100	-0.38817000
C	-5.95340000	2.79059400	1.36549500
O	-6.02630700	3.57280500	2.29426000
O	-7.02737200	2.44209900	0.63185500
C	-8.27307500	3.04147400	0.99339000
H	-8.22009800	4.13773000	0.90719200
H	-9.01958100	2.64336600	0.29544300
H	-8.54638400	2.78447400	2.02838900
O	3.85822700	4.42593500	-0.18641000
O	4.99083200	-2.66181700	0.33420800
C	3.61652200	5.82581200	-0.31628100
H	2.95793600	6.19139000	0.48838000
H	4.59552900	6.31300500	-0.23525000
H	3.16980000	6.06267100	-1.29570800
C	5.19614300	-4.07142000	0.41151500
H	6.27638100	-4.21596700	0.53214900
H	4.67019000	-4.50285000	1.27880600
H	4.86042200	-4.57276300	-0.51093100

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)  
HF=-5267.1597268

**<sup>2</sup>B-OMe-F**



UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction= 0.334032 (Hartree/Particle)

Thermal correction to Energy= 0.357219

Thermal correction to Enthalpy= 0.358164

Thermal correction to Gibbs Free Energy= 0.277392

Sum of electronic and zero-point Energies= -2601.758466

Sum of electronic and thermal Energies= -2601.735279

Sum of electronic and thermal Enthalpies= -2601.734335

Sum of electronic and thermal Free Energies= -2601.815106

Ni	0.11567600	-0.76530100	0.38443300
----	------------	-------------	------------

N	1.29267400	0.87660700	0.31818700
---	------------	------------	------------

C	3.15442000	2.95539500	0.13044700
---	------------	------------	------------

C	1.11542600	2.01894900	0.99074500
---	------------	------------	------------

C	2.38716200	0.74552000	-0.47143100
---	------------	------------	-------------

C	3.33386200	1.75852100	-0.58733700
---	------------	------------	-------------

C	2.00973800	3.08647600	0.93699000
---	------------	------------	------------

N	1.42777700	-1.39766900	-0.93157800
---	------------	-------------	-------------

C	3.48781900	-2.16129800	-2.67693800
---	------------	-------------	-------------

C	1.41966200	-2.59512900	-1.53591400
---	------------	-------------	-------------

C	2.46617600	-0.55421300	-1.18559800
---	------------	-------------	-------------

C	3.50087500	-0.90435900	-2.04604500
---	------------	-------------	-------------

C	2.41233300	-3.02756500	-2.41056100
---	------------	-------------	-------------

H	0.20559500	2.06670600	1.59295200
---	------------	------------	------------

H	4.21619900	1.65886200	-1.21854800
---	------------	------------	-------------

H	1.80295200	3.98678600	1.51336400
---	------------	------------	------------

H	0.56975600	-3.24092800	-1.30283300
---	------------	-------------	-------------

H	4.33250400	-0.23072100	-2.24971900
---	------------	-------------	-------------

H	2.33295300	-4.01539900	-2.86126100
---	------------	-------------	-------------

C	-1.23661000	-0.52411300	1.80538300
---	-------------	-------------	------------

C	-0.50476200	-1.01280400	2.99827600
---	-------------	-------------	------------

C	-0.24306000	-2.39743100	3.14730600
---	-------------	-------------	------------

C	0.00930100	-0.14601400	3.98609100
---	------------	-------------	------------

C	0.50538100	-2.88378800	4.21554800
---	------------	-------------	------------

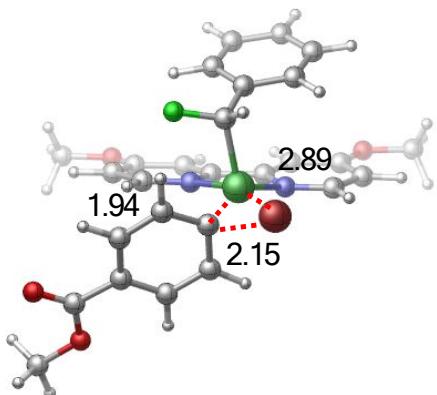
H	-0.62236600	-3.08798500	2.38666400
---	-------------	-------------	------------

C	0.76873300	-0.63720700	5.05479500
---	------------	-------------	------------

H	-0.19295300	0.92303200	3.90080600
C	1.02744700	-2.00562700	5.18124100
H	0.69050200	-3.95905300	4.29933900
H	1.15935300	0.06179700	5.80112700
H	1.62148800	-2.38681600	6.01582500
F	-1.65195800	0.83817400	2.01790100
H	-2.17589700	-1.09707400	1.67661300
O	4.10355200	3.88956100	-0.01902700
O	4.51573500	-2.43445700	-3.49180500
C	4.56619700	-3.69015900	-4.16172800
H	5.48664100	-3.68301400	-4.75816900
H	4.60423900	-4.52575100	-3.44314200
H	3.69957300	-3.82147100	-4.83082300
C	3.99031400	5.12427800	0.68139800
H	3.97969100	4.96553800	1.77255200
H	4.87446900	5.71366700	0.40936800
H	3.08125100	5.67217400	0.38251800

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)  
HF=-2603.5323409

**<sup>2</sup>B-C-TS-OMe-F**



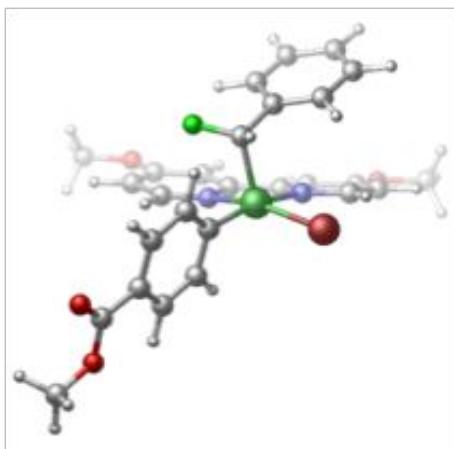
UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction=	0.467584	(Hartree/Particle)	
Thermal correction to Energy=	0.502026		
Thermal correction to Enthalpy=	0.502971		
Thermal correction to Gibbs Free Energy=	0.397618		
Sum of electronic and zero-point Energies=	-5634.731618		
Sum of electronic and thermal Energies=	-5634.697175		
Sum of electronic and thermal Enthalpies=	-5634.696231		
Sum of electronic and thermal Free Energies=	-5634.801583		
Ni	-0.66915800	-0.10312900	-0.38472100
C	-2.27815800	0.84646300	-0.91293200
C	-2.09226100	3.57069700	-1.63491100
C	-2.92771400	1.84201600	-0.12152700
C	-1.68792600	1.22809100	-2.16102200
C	-1.55581700	2.58046800	-2.47498400
C	-2.80331800	3.16954300	-0.46881000
H	-3.43895500	1.54735400	0.79490900
H	-1.35717100	0.46973200	-2.87446000
H	-1.05058800	2.87265600	-3.39694000
H	-3.23154900	3.94620400	0.16870700
N	0.83621100	1.26195200	-0.04838300
C	3.02863700	2.85015700	0.62293000
C	0.66282400	2.50509600	0.40589900
C	2.09025800	0.76612000	-0.15910700
C	3.20550900	1.53333700	0.16099000
C	1.71819900	3.34423800	0.75371000
N	0.97858000	-1.19268500	-0.98328700
C	3.31804400	-2.71286800	-1.10574500
C	0.95256700	-2.46057100	-1.40531700
C	2.16526200	-0.64430600	-0.62402200
C	3.34680800	-1.37522500	-0.67247400
C	2.08439800	-3.26469500	-1.49486500

H	-0.37217500	2.83308900	0.50714700
H	4.21999200	1.14817000	0.06979100
H	1.50583600	4.34887800	1.11500500
H	-0.03015800	-2.85601600	-1.67526700
H	4.30150800	-0.95144100	-0.36489000
H	1.98717100	-4.29051100	-1.84558500
Br	-3.30923100	-1.03506800	-1.08944600
C	-1.10093700	-0.36917000	1.56539200
C	0.08783500	-1.03095900	2.13644500
C	0.29724700	-2.41290200	1.92634100
C	1.09987600	-0.30324100	2.79573700
C	1.47869000	-3.03080400	2.32999500
H	-0.47142800	-2.99323100	1.40721100
C	2.28130100	-0.92756100	3.20588900
H	0.95244300	0.76435900	2.96617900
C	2.48481900	-2.29154000	2.97097500
H	1.62204000	-4.09825300	2.14039200
H	3.05539600	-0.33823300	3.70594800
H	3.41379500	-2.77596900	3.28190000
F	-1.33180400	0.87659100	2.18565100
H	-2.02270000	-0.96703900	1.66217100
C	-1.95903100	5.01123300	-1.91538800
O	-2.41441200	5.90321000	-1.21933800
O	-1.25592300	5.26789500	-3.04082400
C	-1.06928000	6.64225100	-3.37714800
H	-0.52115200	7.17150200	-2.58206600
H	-0.48810500	6.65545400	-4.30747100
H	-2.03627100	7.14675800	-3.52859800
O	4.14143300	3.53654800	0.91008700
O	4.48635200	-3.36437100	-1.10947000
C	4.03877700	4.87495700	1.38772200
H	3.48899900	4.91682800	2.34251800
H	5.06664900	5.22370200	1.54511700
H	3.54163100	5.52551400	0.64930300
C	4.52923500	-4.73120800	-1.51033100
H	5.57658300	-5.04390800	-1.42083500
H	3.90340300	-5.35828800	-0.85387100
H	4.20072200	-4.85157800	-2.55582500

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)  
HF=-5637.449614

<sup>2</sup>C-OMe-F



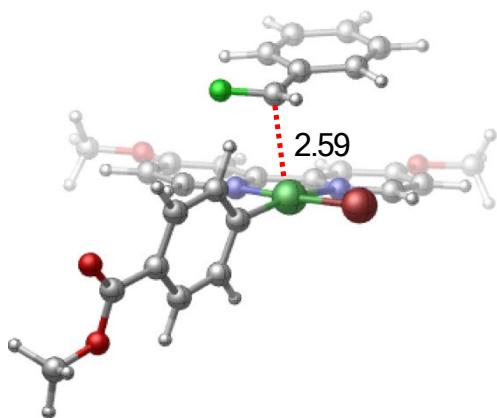
UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction=	0.470547 (Hartree/Particle)		
Thermal correction to Energy=	0.505391		
Thermal correction to Enthalpy=	0.506335		
Thermal correction to Gibbs Free Energy=	0.399697		
Sum of electronic and zero-point Energies=	-5634.776434		
Sum of electronic and thermal Energies=	-5634.741590		
Sum of electronic and thermal Enthalpies=	-5634.740646		
Sum of electronic and thermal Free Energies=	-5634.847284		
Ni	-0.20301000	0.21523900	-0.38668200
C	-1.29302000	1.75148800	-0.71649500
C	-2.57471600	4.04669400	-1.75344500
C	-2.37756000	2.32659300	-0.04338500
C	-0.85895400	2.33949700	-1.91801700
C	-1.48859000	3.47266700	-2.43642000
C	-3.01064100	3.46114400	-0.55333700
H	-2.74214800	1.90409600	0.89442100
H	-0.00717000	1.92106100	-2.46525300
H	-1.13743500	3.91931600	-3.36801100
H	-3.85488000	3.91073100	-0.02579100
N	1.57634000	1.32276200	-0.04232100
C	3.94660400	2.49042900	0.87564000
C	1.61624400	2.60986800	0.31562500
C	2.70497000	0.58475800	0.05887300
C	3.90132900	1.13300400	0.50928300
C	2.76511500	3.24600900	0.77564400
N	1.28139400	-1.26343200	-0.50605900
C	3.41652900	-3.06418500	-0.73145900
C	1.07320900	-2.55187400	-0.79691000
C	2.55584700	-0.84505800	-0.30869800
C	3.63762100	-1.71035000	-0.42019800

C	2.09224500	-3.49129400	-0.92181100
H	0.67709800	3.15867800	0.23649000
H	4.80920600	0.53993500	0.60691900
H	2.71968600	4.29871600	1.04893700
H	0.02886100	-2.83625900	-0.93911200
H	4.66250400	-1.37340400	-0.27415600
H	1.83820900	-4.52307700	-1.15820100
Br	-2.01539500	-1.23559500	-1.43134200
C	-0.78346900	0.24456700	1.51237300
C	-0.07947500	-0.88712800	2.14753700
C	-0.59393200	-2.19188900	2.01607600
C	1.14075400	-0.69691300	2.82234400
C	0.10672500	-3.28101800	2.53210100
H	-1.52653000	-2.34112800	1.46634300
C	1.83859600	-1.79063300	3.33756900
H	1.53851500	0.31359400	2.92712000
C	1.32871900	-3.08660700	3.19066400
H	-0.29644300	-4.29026200	2.41551900
H	2.78985400	-1.63284300	3.85245700
H	1.88043000	-3.94216700	3.58801600
F	-0.46642400	1.44544500	2.12311900
H	-1.87531600	0.12540600	1.48142200
C	-3.28154400	5.25792900	-2.24941300
O	-4.22358900	5.78521700	-1.69057900
O	-2.76791100	5.72627000	-3.40070200
C	-3.38652100	6.89161700	-3.95170700
H	-3.32208000	7.73720100	-3.24989700
H	-2.83959300	7.12229700	-4.87376700
H	-4.44725100	6.70185100	-4.17646500
O	5.12346200	2.95492200	1.30390300
O	4.49901700	-3.84206000	-0.81955300
C	5.23964900	4.31684700	1.71054600
H	6.28279800	4.45541800	2.01904400
H	5.01040800	5.00192800	0.87803700
H	4.57433600	4.53568300	2.56177600
C	4.34848500	-5.22787200	-1.11978000
H	5.36095500	-5.64886000	-1.13546900
H	3.75146600	-5.73959700	-0.34717900
H	3.87690100	-5.37292400	-2.10549100

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)  
HF=-5637.4982052

<sup>2</sup>C-D-TS-OMe-F



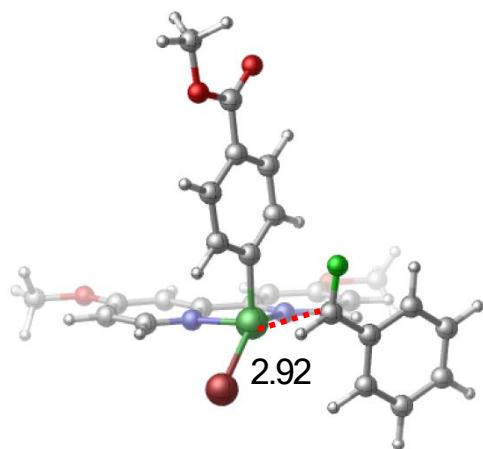
UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction=	0.468742 (Hartree/Particle)		
Thermal correction to Energy=	0.503390		
Thermal correction to Enthalpy=	0.504334		
Thermal correction to Gibbs Free Energy=	0.397634		
Sum of electronic and zero-point Energies=	-5634.770076		
Sum of electronic and thermal Energies=	-5634.735428		
Sum of electronic and thermal Enthalpies=	-5634.734484		
Sum of electronic and thermal Free Energies=	-5634.841184		
Ni	-0.18627300	0.18963900	-0.79427500
C	-1.20811600	1.75002300	-1.12477500
C	-2.52573900	4.15528700	-1.87061500
C	-2.26218400	2.27174300	-0.35259300
C	-0.84337300	2.45647700	-2.28915500
C	-1.48571200	3.63827300	-2.66290800
C	-2.90522900	3.45666900	-0.71072500
H	-2.58550600	1.75570100	0.55268800
H	-0.02736900	2.08554800	-2.91761600
H	-1.18204300	4.16853300	-3.56735800
H	-3.71620300	3.85867500	-0.09863800
N	1.38141800	1.18637200	-0.16951400
C	3.67708600	2.33488100	0.96775800
C	1.40072600	2.47250500	0.21244600
C	2.50150200	0.43970900	0.03494400
C	3.65499900	0.98312200	0.58446100
C	2.50802000	3.09200000	0.77994400
N	1.14167300	-1.33301400	-0.79089500
C	3.18220800	-3.24300700	-0.59970800
C	0.93619000	-2.60333100	-1.15568500
C	2.37348200	-0.98259100	-0.34289500
C	3.40659600	-1.90381900	-0.23447900

C	1.91205800	-3.59256700	-1.08613300
H	0.48112200	3.03310100	0.05642400
H	4.54704600	0.38188200	0.75042300
H	2.43835300	4.14102600	1.06191600
H	-0.07127900	-2.83532700	-1.50592900
H	4.39081500	-1.62593600	0.13813500
H	1.66282000	-4.60598400	-1.39540500
Br	-2.06465300	-1.10734400	-1.48453400
C	-0.76910800	0.04574300	1.72798400
C	0.18853200	-0.86212500	2.25358600
C	0.04609300	-2.25802700	2.02141300
C	1.33791900	-0.40718000	2.95334900
C	1.01601500	-3.14869700	2.46240100
H	-0.81929700	-2.61574000	1.45809300
C	2.30005600	-1.31256000	3.39247100
H	1.46187800	0.66219400	3.13118200
C	2.15251000	-2.68567300	3.14881000
H	0.89884000	-4.21661600	2.26163300
H	3.18276300	-0.94486200	3.92233400
H	2.91654900	-3.39056800	3.48463400
F	-0.68154800	1.33904600	2.11801000
H	-1.76688400	-0.24746200	1.39828500
C	-3.24006200	5.41285000	-2.20943300
O	-4.14346600	5.89592200	-1.55358300
O	-2.78382300	5.98576800	-3.33951600
C	-3.41541700	7.20315000	-3.74082200
H	-3.29686200	7.97897800	-2.96877000
H	-2.92050100	7.51464300	-4.66865300
H	-4.49060800	7.04696800	-3.91820300
O	4.81587800	2.79102200	1.49451100
O	4.21049700	-4.08322900	-0.45096100
C	4.90108700	4.14917500	1.92160900
H	5.91682500	4.28322200	2.31242200
H	4.73839200	4.84170300	1.07971400
H	4.17087600	4.36092000	2.71969200
C	4.04738000	-5.46012800	-0.78259900
H	5.00957200	-5.94184800	-0.57116200
H	3.26143800	-5.92648800	-0.16610300
H	3.80172400	-5.58669500	-1.84973700

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)  
HF=-5637.4930147

**<sup>2</sup>D'-E-TS-OMe-F**



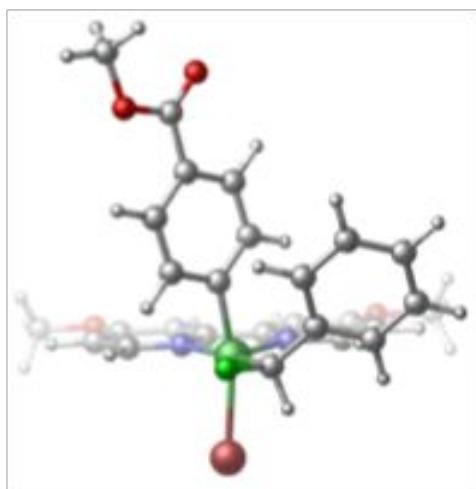
UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction=	0.467728	(Hartree/Particle)
Thermal correction to Energy=	0.502901	
Thermal correction to Enthalpy=	0.503845	
Thermal correction to Gibbs Free Energy=	0.394738	
Sum of electronic and zero-point Energies=	-5634.764159	
Sum of electronic and thermal Energies=	-5634.728986	
Sum of electronic and thermal Enthalpies=	-5634.728042	
Sum of electronic and thermal Free Energies=	-5634.837149	
C	-2.48588800	1.57359900
C	-3.14992600	2.78411000
C	-2.40795200	3.96336800
C	-1.00489100	3.87304400
C	-0.42622500	2.61887700
C	-3.18431200	0.27983800
C	-4.56572800	0.15201200
C	-5.13082300	-1.11945600
C	-4.26855100	-2.22422200
C	-2.89849400	-2.00168400
H	-4.23638200	2.85507300
H	-0.36383900	4.74087700
H	0.65742100	2.50534800
H	-5.23455000	1.00650400
H	-4.63547800	-3.23486400
H	-2.18158700	-2.82150600
N	-1.13214600	1.49803700
N	-2.36869700	-0.79382200
Br	0.71338000	-2.21335400
Ni	-0.40274000	-0.43706500
C	-0.46630000	-0.79182200
		1.80952600

C	-0.81899700	0.17738900	2.77009100
C	-0.20496900	-2.09250800	2.28712200
C	-0.87323600	-0.11847100	4.13137200
H	-1.03363000	1.20279600	2.45447800
C	-0.25485500	-2.40885400	3.64668200
H	0.06964000	-2.87417300	1.57106600
H	-1.12525200	0.65057600	4.86540600
H	-0.03067400	-3.42095000	3.98966200
C	-0.58297600	-1.41613600	4.58713500
C	2.38981500	0.32003100	0.61177100
C	2.50626000	0.71516200	1.96383500
C	2.56780200	-0.27902700	2.97956200
C	2.53273800	2.08362600	2.34975600
C	2.62586800	0.08433200	4.31791600
H	2.53820700	-1.33250100	2.69767800
C	2.59251200	2.43114300	3.69599900
H	2.50507300	2.85849700	1.58163600
C	2.63566400	1.43934900	4.68835300
H	2.65314800	-0.69222100	5.08592900
H	2.60659900	3.48660600	3.98018600
H	2.67452000	1.71980600	5.74360200
C	-0.61065100	-1.67343300	6.04860500
O	-0.28464700	-2.94183600	6.36613700
O	-0.88732700	-0.84415400	6.89516900
C	-0.27869900	-3.27154900	7.75612400
H	0.44752000	-2.65080600	8.30331300
H	-1.27420000	-3.11815500	8.20062700
H	0.00462700	-4.32919000	7.82015700
F	2.46555700	1.26445800	-0.35022500
H	2.45335400	-0.69956200	0.23069900
O	-6.46375000	-1.17325800	-0.82587200
O	-3.10795600	5.08956000	0.29229800
C	-7.11049300	-2.42626300	-1.03848100
H	-8.18652800	-2.21544100	-1.05401600
H	-6.81102000	-2.87011100	-2.00197600
H	-6.88794400	-3.13253900	-0.22195700
C	-2.42339300	6.32302600	0.50371800
H	-3.20047900	7.08998900	0.60501600
H	-1.81968200	6.28927400	1.42532800
H	-1.77514100	6.56977000	-0.35293500

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)  
HF=-5637.4871274

**<sup>2</sup>E-OMe-F**



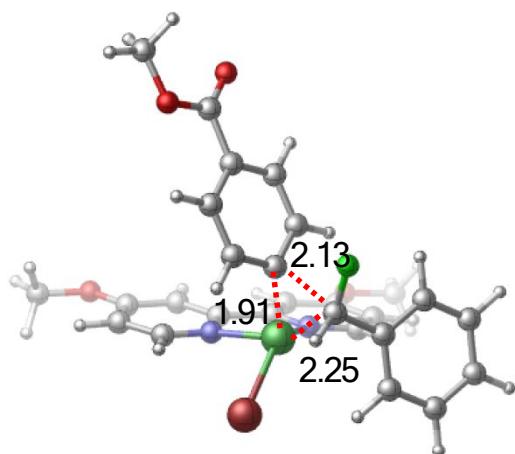
UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction=	0.470594	(Hartree/Particle)
Thermal correction to Energy=	0.505507	
Thermal correction to Enthalpy=	0.506451	
Thermal correction to Gibbs Free Energy=	0.399011	
Sum of electronic and zero-point Energies=	-5634.775890	
Sum of electronic and thermal Energies=	-5634.740978	
Sum of electronic and thermal Enthalpies=	-5634.740034	
Sum of electronic and thermal Free Energies=	-5634.847473	
C	-2.25408700	1.72272000
C	-2.98538900	2.90208700
C	-2.31489300	4.13941900
C	-0.91456800	4.13245400
C	-0.26636100	2.90223300
C	-2.88712300	0.38167700
C	-4.26005000	0.17348000
C	-4.76904400	-1.13454000
C	-3.85945800	-2.19259900
C	-2.50266300	-1.89016400
H	-4.07275300	2.90429500
H	-0.32615900	5.04678900
H	0.81553100	2.85363200
H	-4.96399100	0.99358200
H	-4.17938800	-3.22899100
H	-1.75477200	-2.67407500
N	-0.89817400	1.72472100
N	-2.02452100	-0.64710000
Br	0.72989900	-1.83270200
Ni	-0.04320300	-0.20075300
C	-0.30673000	-0.71567500
		1.83918400

C	-0.77363900	0.17068600	2.81637500
C	-0.12700700	-2.06759200	2.15629700
C	-1.05342100	-0.28901200	4.10252900
H	-0.89645200	1.23052100	2.58208500
C	-0.39985500	-2.53241200	3.44536000
H	0.23995800	-2.76052200	1.39348700
H	-1.41424500	0.39386100	4.87476200
H	-0.25133300	-3.58439400	3.69430500
C	-0.86379500	-1.64344000	4.43061300
C	1.83853600	0.22271400	0.54489200
C	2.22177800	0.75097400	1.88253400
C	2.58551700	-0.15642900	2.89590800
C	2.22152700	2.12244900	2.18433500
C	2.90205500	0.28949500	4.17837300
H	2.60037400	-1.22592500	2.67568200
C	2.54256200	2.57139500	3.46962700
H	1.97437500	2.84946900	1.41226900
C	2.87566400	1.65856400	4.47493500
H	3.17298500	-0.43416200	4.95150500
H	2.53316900	3.64331600	3.68396200
H	3.12199600	2.01004600	5.48003400
C	-1.16112700	-2.07983200	5.82145400
O	-0.93216600	-3.39042800	6.01786100
O	-1.56704600	-1.34760000	6.70298700
C	-1.19102400	-3.89715600	7.32947200
H	-0.56502000	-3.38598200	8.07679000
H	-2.24829800	-3.75602700	7.60140900
H	-0.94751400	-4.96595300	7.29892300
F	2.16614100	1.14030900	-0.46332700
H	2.35246300	-0.72177300	0.31851400
O	-6.09547100	-1.26572300	-0.08194200
O	-3.07598600	5.23210200	0.08252900
C	-6.68467200	-2.56163000	-0.17032700
H	-7.76709100	-2.41133300	-0.07960300
H	-6.46122700	-3.03526000	-1.14023000
H	-6.33608600	-3.21326400	0.64749200
C	-2.46623300	6.52180600	0.06261400
H	-3.28424200	7.24710900	0.14707700
H	-1.77578700	6.64751000	0.91250600
H	-1.92376700	6.69017600	-0.88195800

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)  
HF=-5637.4986182

**<sup>2</sup>E-P<sub>B</sub>-TS-OMe-F**



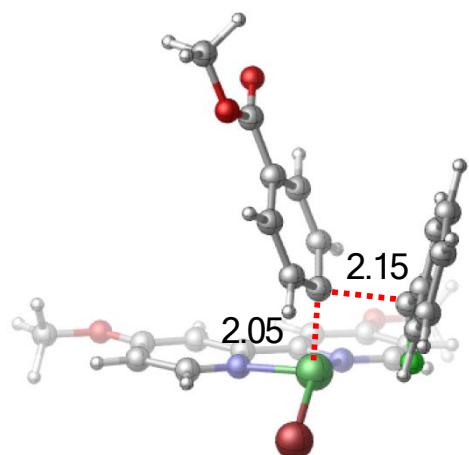
UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction=	0.469849 (Hartree/Particle)		
Thermal correction to Energy=	0.504240		
Thermal correction to Enthalpy=	0.505184		
Thermal correction to Gibbs Free Energy=	0.399082		
Sum of electronic and zero-point Energies=	-5634.760924		
Sum of electronic and thermal Energies=	-5634.726533		
Sum of electronic and thermal Enthalpies=	-5634.725589		
Sum of electronic and thermal Free Energies=	-5634.831691		
C	-2.34773300	1.71044000	-0.09761000
C	-3.08347300	2.88950500	-0.06503300
C	-2.41603900	4.12820600	-0.08814700
C	-1.01237600	4.12475700	-0.16096200
C	-0.35996600	2.89537300	-0.18618800
C	-2.97678000	0.36274000	-0.10831900
C	-4.34501700	0.14816300	0.02006900
C	-4.84472700	-1.16733900	-0.01141600
C	-3.93331600	-2.22586100	-0.17647300
C	-2.58142300	-1.91480700	-0.29335700
H	-4.17184000	2.89012900	-0.03145400
H	-0.42534700	5.04071200	-0.19791700
H	0.72735100	2.84829000	-0.24687800
H	-5.05140300	0.96648500	0.15159000
H	-4.24839600	-3.26734400	-0.21137700
H	-1.82853000	-2.69623000	-0.42408300
N	-0.99161500	1.71693200	-0.14120600
N	-2.11246500	-0.66543200	-0.26250100
Br	0.79229900	-1.94210000	-1.60805600
Ni	-0.13373300	-0.18949800	-0.08383500
C	0.08397500	-0.55264700	1.77317400

C	-0.52729700	0.29042800	2.72548600
C	0.25795800	-1.91524600	2.08690400
C	-0.99636200	-0.22650400	3.92541900
H	-0.62885200	1.35684000	2.51821100
C	-0.20876900	-2.43260600	3.29453900
H	0.74276300	-2.57214800	1.36128300
H	-1.48797700	0.42084900	4.65464900
H	-0.08420600	-3.49319400	3.51837000
C	-0.84497000	-1.59529000	4.22767200
C	1.83028900	0.13445500	0.91338300
C	2.38906400	0.71917700	2.16647200
C	2.95225900	-0.12104200	3.14253800
C	2.34076000	2.10162400	2.40825900
C	3.43755000	0.40644300	4.34031600
H	2.99586400	-1.19809100	2.96411900
C	2.83080500	2.62938100	3.60604500
H	1.91255700	2.76780300	1.65915000
C	3.37645400	1.78501200	4.57884100
H	3.87028800	-0.26105500	5.08985300
H	2.78398600	3.70742700	3.78016700
H	3.75640100	2.19853700	5.51636400
C	-1.36142300	-2.09338200	5.52678300
O	-1.15346900	-3.41182200	5.70112000
O	-1.91744800	-1.40357800	6.36053700
C	-1.62107200	-3.97790500	6.92731300
H	-1.13135700	-3.50130000	7.79037500
H	-2.70994000	-3.85039900	7.02742200
H	-1.36716500	-5.04411800	6.88967200
F	2.03266400	1.04992600	-0.14115700
H	2.30672300	-0.81058500	0.62578900
O	-6.16777200	-1.30508500	0.12134000
O	-3.18285200	5.22065800	-0.04789100
C	-6.74685800	-2.60767500	0.10808200
H	-7.82686900	-2.46316800	0.23199000
H	-6.55442000	-3.12010700	-0.84885300
H	-6.36290200	-3.22260400	0.93858100
C	-2.57584400	6.51105400	-0.07211700
H	-3.39766700	7.23580100	-0.02946900
H	-1.91491500	6.65583100	0.79808500
H	-2.00172200	6.66333200	-1.00070200

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)  
HF=-5637.483112

**<sup>4</sup>D'-P<sub>B</sub>-TS-OMe-F**



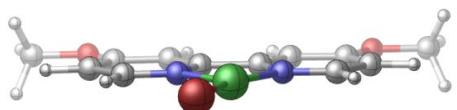
UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction=	0.467574 (Hartree/Particle)		
Thermal correction to Energy=	0.502529		
Thermal correction to Enthalpy=	0.503473		
Thermal correction to Gibbs Free Energy=	0.394510		
Sum of electronic and zero-point Energies=	-5634.742082		
Sum of electronic and thermal Energies=	-5634.707127		
Sum of electronic and thermal Enthalpies=	-5634.706183		
Sum of electronic and thermal Free Energies=	-5634.815146		
C	-1.22341600	2.26539900	-1.61514700
C	-0.91514900	3.57164900	-1.97586400
C	0.27656800	3.83697900	-2.67666500
C	1.12195700	2.75714100	-2.99082500
C	0.73601400	1.48318200	-2.58647900
C	-2.45667000	1.88872900	-0.87426300
C	-3.41531700	2.80234400	-0.45167800
C	-4.54800900	2.34350000	0.24789200
C	-4.67115200	0.96364500	0.49519000
C	-3.66239900	0.12264000	0.03543400
H	-1.56919800	4.40787500	-1.73340400
H	2.05793200	2.88557800	-3.53137500
H	1.36572400	0.61662500	-2.79728500
H	-3.32189100	3.87051600	-0.64151800
H	-5.51988800	0.53980800	1.02902700
H	-3.70647900	-0.95760600	0.19528300
N	-0.39663200	1.23373700	-1.92059100
N	-2.59103900	0.56437900	-0.62799000
Br	-1.93414500	-2.78559900	-1.49156300
Ni	-0.96403200	-0.56965900	-1.10748500
C	0.01041900	-0.46185900	0.69473000

C	0.42739400	0.79576200	1.24121100
C	-0.34852800	-1.45638900	1.66351700
C	0.54784700	1.01552500	2.60385700
H	0.68150500	1.61225000	0.55667400
C	-0.23468200	-1.24847800	3.02784600
H	-0.71019000	-2.42313000	1.30239400
H	0.87584400	1.98386700	2.98996800
H	-0.51389500	-2.03505700	3.73172700
C	0.22525400	-0.00580500	3.52788700
C	1.75126500	-1.15204200	-0.35336700
C	2.25460500	-2.31394400	0.33155400
C	1.77858200	-3.60953100	0.02361700
C	3.15251000	-2.15373600	1.41220300
C	2.21052300	-4.70905700	0.76331500
H	1.05259400	-3.72931100	-0.78309200
C	3.57041700	-3.25925100	2.15068000
H	3.51308300	-1.15384700	1.66838700
C	3.10761600	-4.54381200	1.82884100
H	1.83926200	-5.70683300	0.51403800
H	4.26615000	-3.12205800	2.98269900
H	3.44048200	-5.40897500	2.40745600
H	2.32217200	-0.22130800	-0.35154600
F	1.22374800	-1.39804400	-1.60915500
C	0.36672600	0.27226200	4.97011100
O	0.02535200	-0.78019800	5.74647500
O	0.74998800	1.32810300	5.44557200
C	0.13363400	-0.59392900	7.15714600
H	1.17012600	-0.35872900	7.44548700
H	-0.51688300	0.22667900	7.49798700
H	-0.17987300	-1.53889500	7.61783900
O	-5.42971400	3.27268600	0.62595900
O	0.51161100	5.11267700	-2.99041300
C	-6.60382500	2.88660100	1.33765100
H	-7.16189300	3.81082900	1.52956300
H	-7.22547300	2.20180600	0.73795500
H	-6.34834800	2.40785300	2.29715900
C	1.70323200	5.46084300	-3.69331800
H	1.67060800	6.54849500	-3.82849200
H	2.60005200	5.19075300	-3.11224000
H	1.74060100	4.97030700	-4.67963200

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)  
HF=-5637.4606384

**<sup>2</sup>P<sub>B</sub>-OMe**

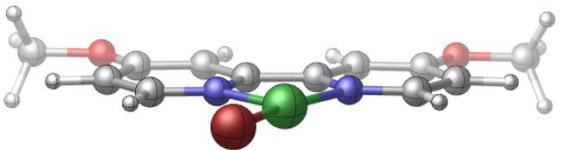


UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction=	0.225730 (Hartree/Particle)	
Thermal correction to Energy=	0.243268	
Thermal correction to Enthalpy=	0.244213	
Thermal correction to Gibbs Free Energy=	0.176980	
Sum of electronic and zero-point Energies=	-4805.878509	
Sum of electronic and thermal Energies=	-4805.860971	
Sum of electronic and thermal Enthalpies=	-4805.860026	
Sum of electronic and thermal Free Energies=	-4805.927259	
C -2.36363400	1.23675600	0.04393900
C -2.87193900	2.49392600	0.34950600
C -2.19914400	3.64515700	-0.09776600
C -1.02198200	3.47739000	-0.84930100
C -0.58463300	2.18186400	-1.10923900
C -2.99349500	-0.03822100	0.46899600
C -4.16510300	-0.12733200	1.21309300
C -4.66844000	-1.39491700	1.56017900
C -3.96136100	-2.53556100	1.13700500
C -2.79793700	-2.34907300	0.39474600
H -3.78410600	2.61851100	0.93215200
H -0.44766400	4.32045000	-1.23001400
H 0.32531400	2.01109900	-1.68922400
H -4.71177000	0.75665800	1.53987400
H -4.29232800	-3.54648100	1.36928800
H -2.21159400	-3.20158200	0.04118100
N -1.22175000	1.08032300	-0.68340500
N -2.31934000	-1.14487000	0.06503100
Br 0.59745300	-2.58118800	-1.74449800
Ni -0.67954100	-0.76597800	-0.98394800
O -2.74218500	4.82428900	0.23418600
O -5.79944800	-1.41258600	2.27766700
C -6.36844700	-2.66004500	2.66365200
H -7.27433000	-2.42047000	3.23382400
H -6.64153200	-3.26475200	1.78288100
H -5.67703200	-3.23441700	3.30240200
C -2.10933100	6.03074100	-0.18060200
H -2.72686500	6.85016600	0.20713500
H -1.09173300	6.11273700	0.23648600
H -2.06106400	6.10005700	-1.28010500

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)  
HF=-4807.4512253

**<sup>4</sup>P<sub>B</sub>-OMe**



UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction= 0.223458 (Hartree/Particle)

Thermal correction to Energy= 0.241238

Thermal correction to Enthalpy= 0.242182

Thermal correction to Gibbs Free Energy= 0.174205

Sum of electronic and zero-point Energies= -4805.851191

Sum of electronic and thermal Energies= -4805.833410

Sum of electronic and thermal Enthalpies= -4805.832466

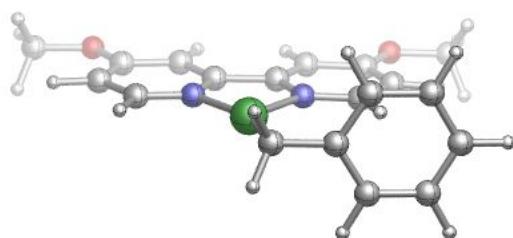
Sum of electronic and thermal Free Energies= -4805.900443

C	-2.38407200	1.23079700	0.06126000
C	-2.88170600	2.53141900	0.35527500
C	-2.20547500	3.65783900	-0.08469100
C	-0.99879700	3.50368800	-0.83553000
C	-0.56399500	2.21212500	-1.08662000
C	-2.99338400	0.00169800	0.45131500
C	-4.18505000	-0.13109100	1.21838100
C	-4.67007200	-1.38774100	1.54610400
C	-3.96859600	-2.55087700	1.10151400
C	-2.81727400	-2.35586500	0.35479400
H	-3.80156400	2.66341000	0.92491500
H	-0.42433200	4.34879900	-1.20812600
H	0.35417800	2.04171200	-1.65738200
H	-4.72939900	0.74666500	1.56664400
H	-4.30151100	-3.56163700	1.32652100
H	-2.23563300	-3.20655100	-0.01330800
N	-1.20330500	1.11057900	-0.67026000
N	-2.33425100	-1.14993100	0.03256800
Br	0.48430100	-2.75227400	-1.62164300
Ni	-0.68408300	-0.76922400	-0.98426600
O	-2.74209400	4.85849900	0.23054800
O	-5.80224800	-1.43439400	2.28449800
C	-6.33609400	-2.69030200	2.67463500
H	-7.23453500	-2.47378700	3.26715200
H	-6.62131900	-3.30223000	1.80178000
H	-5.62485700	-3.26012000	3.29693100
C	-2.10442100	6.04999800	-0.20321100
H	-2.71893900	6.88144400	0.16583400
H	-1.08693900	6.14402500	0.21341900

H -2.04949600 6.10597800 -1.30392800  
UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)  
HF=-4807.4057811

**Figure S4**

**$^2\text{B}-\text{OMe-H}$**



UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction= 0.341408 (Hartree/Particle)

Thermal correction to Energy= 0.363768

Thermal correction to Enthalpy= 0.364712

Thermal correction to Gibbs Free Energy= 0.286977

Sum of electronic and zero-point Energies= -2502.592742

Sum of electronic and thermal Energies= -2502.570382

Sum of electronic and thermal Enthalpies= -2502.569438

Sum of electronic and thermal Free Energies= -2502.647174

Ni 0.72939300 -1.70503100 1.12483400

N 1.95975400 -0.09015800 1.10093700

C 3.75910100 2.04336800 0.81204500

C 2.04189400 0.87732100 2.02402300

C 2.77340800 -0.01387400 0.01573600

C 3.67639100 1.02959700 -0.15925300

C 2.91565600 1.95918000 1.93320000

N 1.68227000 -2.05158700 -0.57046300

C 3.10194600 -2.36024700 -2.96893300

C 1.46801600 -3.10310400 -1.37362100

C 2.61074600 -1.13251600 -0.94502900

C 3.33074100 -1.25597900 -2.12868200

C 2.14203300 -3.30973000 -2.57386700

H 1.37367000 0.78160100 2.88077500

H 4.32897900 1.08976500 -1.02958900

H 2.92189900 2.70480800 2.72666200

H 0.71313300 -3.81531700 -1.03127800

H 4.07368900 -0.51869600 -2.43085600

H 1.91190600 -4.19038200 -3.17124900

C -0.64257400 -2.15888800 2.53392900

H -0.42180800 -3.13855000 2.99513900

H -1.65495500 -2.19745700 2.09255100

C -0.50868300 -1.05615200 3.50032300

C 0.40733200 -1.11216000 4.58451800

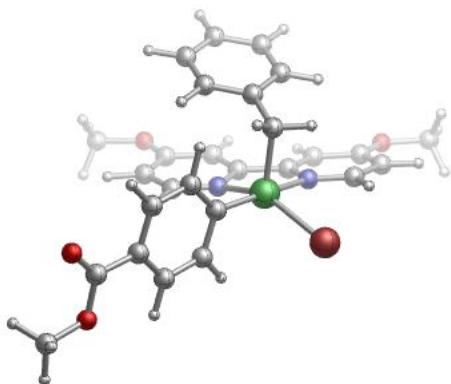
C -1.23958400 0.15454200 3.36690300

C 0.60295500 -0.03093800 5.44488600

H	0.99372600	-2.02579200	4.72628200
C	-1.04424500	1.23567600	4.22725100
H	-1.95653300	0.24377400	2.54430100
C	-0.11455700	1.16240100	5.27514500
H	1.32937400	-0.11776100	6.25920000
H	-1.62298200	2.15257500	4.07670300
H	0.04298400	2.01127500	5.94510100
O	4.64866400	3.01957100	0.58555700
O	3.82764600	-2.41902200	-4.09411500
C	4.78479100	4.07717700	1.52947700
H	5.56026900	4.74421800	1.13347600
H	3.84226700	4.63874800	1.63960100
H	5.10047800	3.69590300	2.51486800
C	3.64795100	-3.51182400	-4.98926900
H	2.61458400	-3.54977600	-5.37255000
H	4.33804100	-3.34112700	-5.82458100
H	3.89372100	-4.47108100	-4.50394800

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)  
HF=-2504.25322426

<sup>2</sup>C-OMe-H



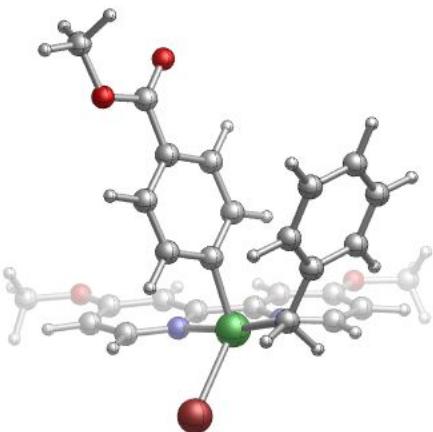
UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction=	0.478597 (Hartree/Particle)		
Thermal correction to Energy=	0.512428		
Thermal correction to Enthalpy=	0.513372		
Thermal correction to Gibbs Free Energy=	0.409231		
Sum of electronic and zero-point Energies=	-5535.609225		
Sum of electronic and thermal Energies=	-5535.575394		
Sum of electronic and thermal Enthalpies=	-5535.574450		
Sum of electronic and thermal Free Energies=	-5535.678591		
Ni	-0.34935100	-0.12516300	-0.92480100
C	-1.48596500	1.42718500	-0.90097100
C	-2.73746200	3.94155200	-1.31331700
C	-2.37076400	1.95800800	0.04753600
C	-1.24752200	2.18114600	-2.06933900
C	-1.85536800	3.41908400	-2.27673500
C	-2.98875000	3.19619300	-0.15242600
H	-2.59526800	1.41991100	0.96986800
H	-0.57058200	1.80287300	-2.84223500
H	-1.65174100	3.98535500	-3.18704200
H	-3.67247600	3.60192400	0.59666900
N	1.39786500	0.98989400	-0.44157300
C	3.68984100	2.06782200	0.75112700
C	1.45787500	2.28095000	-0.10055000
C	2.48106600	0.20996000	-0.21066000
C	3.63292000	0.71201600	0.38286300
C	2.57056100	2.87465300	0.48692700
N	1.08535600	-1.57520600	-1.00182100
C	3.13905800	-3.47200000	-0.89484300
C	0.86007400	-2.85394200	-1.32429800
C	2.32983200	-1.21189900	-0.60414800
C	3.37377400	-2.12785200	-0.55407100
C	1.83964900	-3.84055200	-1.28537500

H	0.56253500	2.87252800	-0.29558900
H	4.49434600	0.08187000	0.59658000
H	2.53882300	3.93318100	0.73868200
H	-0.15984200	-3.08604200	-1.63759000
H	4.37866000	-1.83950800	-0.25059800
H	1.57792100	-4.86111500	-1.55893900
Br	-1.82289600	-1.23214500	-2.67621600
C	-1.02732100	-0.84240900	0.82547200
H	-1.19554900	-1.89430600	0.55574400
H	-1.97988700	-0.35733800	1.05412900
C	0.00332600	-0.65973000	1.86473600
C	0.91052100	-1.69237800	2.18458200
C	0.16490100	0.57930800	2.52366900
C	1.93936900	-1.49433100	3.10780600
H	0.81025100	-2.66081700	1.68758500
C	1.19653800	0.78207700	3.43930400
H	-0.51348100	1.40055600	2.28055100
C	2.09411000	-0.25327200	3.73491600
H	2.63133000	-2.31100700	3.33016000
H	1.30885200	1.75682700	3.92146400
H	2.90699400	-0.09173400	4.44729400
O	4.81764600	2.48123400	1.33550700
O	4.18384400	-4.29935700	-0.81764900
C	4.93469300	3.83749100	1.75969800
H	5.92970700	3.93194300	2.21088800
H	4.85290000	4.53037800	0.90634700
H	4.16695500	4.08581100	2.51078200
C	4.01919100	-5.67805200	-1.14407900
H	3.69840800	-5.80314800	-2.19119900
H	5.00236500	-6.14372200	-1.00638900
H	3.28875900	-6.16057900	-0.47437600
C	-3.41634400	5.25530500	-1.47535600
O	-4.18416200	5.74010100	-0.66715600
O	-3.09296800	5.87052200	-2.62654700
C	-3.70100600	7.14207100	-2.86697500
H	-3.43227500	7.85952200	-2.07663800
H	-3.32007200	7.48584500	-3.83611300
H	-4.79743700	7.05079600	-2.90045200

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)  
HF=-5538.21965160

**<sup>2</sup>E-OMe-H**



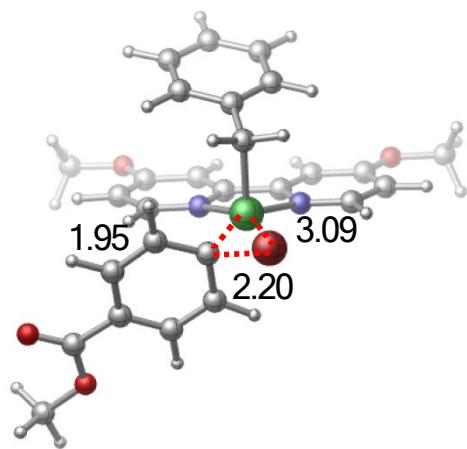
UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction=	0.477752 (Hartree/Particle)	
Thermal correction to Energy=	0.511846	
Thermal correction to Enthalpy=	0.512791	
Thermal correction to Gibbs Free Energy=	0.407277	
Sum of electronic and zero-point Energies=	-5535.608660	
Sum of electronic and thermal Energies=	-5535.574566	
Sum of electronic and thermal Enthalpies=	-5535.573622	
Sum of electronic and thermal Free Energies=	-5535.679135	
C	-2.18204600	1.61445300
C	-2.88146400	2.79749600
C	-2.17686900	4.00864800
C	-0.77535800	3.97706400
C	-0.16273600	2.74292700
C	-2.84579300	0.30404600
C	-4.22415800	0.12378700
C	-4.76153900	-1.15331500
C	-3.87452500	-2.20847800
C	-2.51031000	-1.93540400
H	-3.96862600	2.82438400
H	-0.16164200	4.87369000
H	0.92252600	2.68607500
H	-4.91130300	0.94227700
H	-4.21721700	-3.22074000
H	-1.77969800	-2.71840900
N	-0.82680000	1.58776300
N	-2.00508800	-0.72301500
Br	0.70032600	-1.68172300
Ni	-0.01377600	-0.35497100
C	-0.27273300	-1.02982300
C	-0.72136300	-0.24686700

C	-0.12483200	-2.41277300	1.99111800
C	-1.01755900	-0.83902900	4.11877000
H	-0.82290200	0.83460300	2.77498100
C	-0.41449200	-3.01104900	3.21937300
H	0.22787100	-3.02834900	1.15805100
H	-1.36681700	-0.23694800	4.96053500
H	-0.29185200	-4.08741800	3.35048300
C	-0.86197700	-2.22573400	4.29652400
C	1.88436500	-0.01436800	0.63230300
H	2.38393600	-0.90592600	0.23404900
O	-6.09188400	-1.25979600	-0.19757700
O	-2.90817500	5.10503300	0.73625600
C	-6.70917300	-2.52404000	-0.43107800
H	-7.78883100	-2.35924000	-0.33273400
H	-6.48661000	-2.89416700	-1.44520300
H	-6.38352800	-3.26889600	0.31334100
C	-2.26223900	6.36902400	0.87960000
H	-1.71048500	6.63883800	-0.03555900
H	-3.05976100	7.10117500	1.05341300
H	-1.57278100	6.36670900	1.73948800
C	-1.17528900	-2.80525000	5.62943600
O	-1.56551800	-2.16559000	6.58710600
O	-0.98007700	-4.13548200	5.68018000
C	2.30175000	0.26277700	2.02739500
C	2.23375200	1.54897900	2.59825100
C	2.77151000	-0.78628900	2.84662700
C	2.60007500	1.77503500	3.92827000
H	1.88776800	2.39045800	1.99657100
C	3.13778100	-0.56616200	4.17429300
H	2.83013800	-1.79471600	2.42945000
C	3.04958200	0.71842400	4.72721600
H	2.53464600	2.78506400	4.34209600
H	3.49283000	-1.40142000	4.78422800
H	3.33389100	0.89353400	5.76796800
H	2.06444700	0.83814600	-0.04384500
C	-1.25337400	-4.77630600	6.92835800
H	-2.30642800	-4.63706200	7.21746600
H	-1.03939100	-5.84159400	6.77975200
H	-0.61361500	-4.36807900	7.72583100

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)  
HF=-5538.21811379

**<sup>2</sup>B-C-TS-OMe-H**



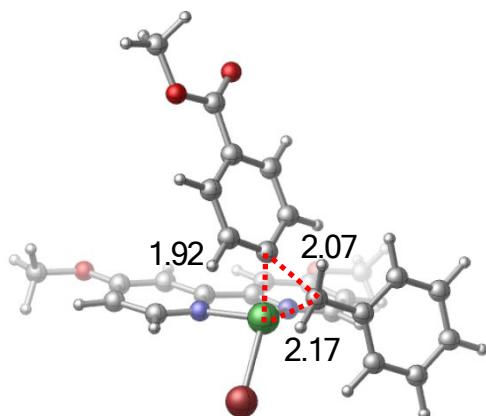
UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction=	0.475167 (Hartree/Particle)		
Thermal correction to Energy=	0.508773		
Thermal correction to Enthalpy=	0.509717		
Thermal correction to Gibbs Free Energy=	0.406192		
Sum of electronic and zero-point Energies=	-5535.562279		
Sum of electronic and thermal Energies=	-5535.528673		
Sum of electronic and thermal Enthalpies=	-5535.527729		
Sum of electronic and thermal Free Energies=	-5535.631254		
Ni	-0.70413900	-0.23769200	-0.48213000
C	-2.26944300	0.86768300	-0.84647100
C	-1.93077500	3.59204000	-1.57820300
C	-2.76178800	1.91612300	-0.00383700
C	-1.72444100	1.22576100	-2.12480900
C	-1.52049900	2.56825200	-2.44788100
C	-2.57678600	3.23314800	-0.35931500
H	-3.24235200	1.65900200	0.94227800
H	-1.51648700	0.45738700	-2.87423900
H	-1.06417900	2.82744600	-3.40481300
H	-2.90263000	4.03385800	0.30849100
N	0.89074200	1.02522200	-0.09669800
C	3.16416300	2.39519300	0.77810900
C	0.80776000	2.28299600	0.34278000
C	2.10209800	0.41872900	-0.11863300
C	3.25192900	1.07222100	0.30968600
C	1.90471600	3.01782000	0.78472900
N	0.87770700	-1.45261300	-0.97258300
C	3.12448000	-3.10047100	-1.15438600
C	0.77002100	-2.71385600	-1.40338500
C	2.09536300	-0.98172100	-0.61379300

C	3.23465800	-1.77539400	-0.69808600
C	1.85197800	-3.58070300	-1.51755800
H	-0.19013900	2.72163000	0.35069700
H	4.22722300	0.58837200	0.30613400
H	1.75745200	4.03932600	1.13062400
H	-0.23791200	-3.04791500	-1.66358700
H	4.21741500	-1.40874300	-0.40603200
H	1.69045500	-4.59518800	-1.87737000
Br	-3.68573400	-0.79806500	-1.05630000
C	-1.19794300	-0.92387700	1.36482100
H	-1.54878000	-1.94833500	1.16032300
H	-2.02616200	-0.30824600	1.74157400
C	0.00114300	-0.87213500	2.21317300
C	0.94474000	-1.92575600	2.23794600
C	0.31503400	0.28403400	2.96820400
C	2.13640000	-1.82465100	2.95873100
H	0.73988500	-2.83124200	1.65947000
C	1.50740600	0.38987600	3.68321500
H	-0.38959800	1.12072900	2.96373700
C	2.43273700	-0.66376200	3.68338400
H	2.84591100	-2.65721200	2.94646500
H	1.72211300	1.30504500	4.24275500
H	3.36954600	-0.57980100	4.24007000
O	4.30627300	2.96064500	1.18685700
O	4.25574700	-3.81196600	-1.20325400
C	4.28959800	4.29209600	1.69364100
H	5.32498600	4.52879300	1.96725900
H	3.94202500	5.00681100	0.92942900
H	3.64877500	4.37006000	2.58750700
C	4.22033100	-5.16558700	-1.64842100
H	3.85882300	-5.23458800	-2.68759200
H	5.25318200	-5.53084500	-1.59847400
H	3.58276400	-5.78374500	-0.99505300
C	-1.73096900	5.01978400	-1.87471500
O	-2.07866600	5.93936400	-1.15212900
O	-1.10004500	5.23320300	-3.05179300
C	-0.86149800	6.59379800	-3.40929200
H	-0.34669500	6.57224400	-4.37783100
H	-1.80731300	7.15102400	-3.49701400
H	-0.23133000	7.09471600	-2.65778900

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)  
HF=-5538.16840406

**<sup>2</sup>E-P<sub>B</sub>-TS-OMe-H**



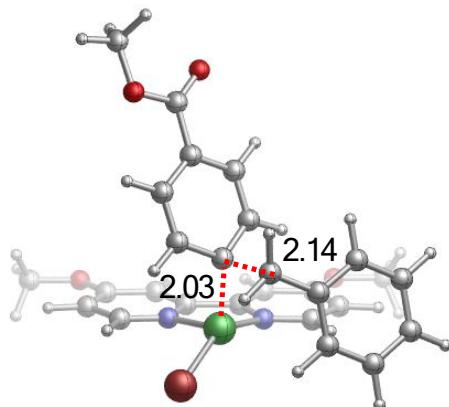
UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction=	0.477004 (Hartree/Particle)		
Thermal correction to Energy=	0.510715		
Thermal correction to Enthalpy=	0.511659		
Thermal correction to Gibbs Free Energy=	0.406502		
Sum of electronic and zero-point Energies=	-5535.602034		
Sum of electronic and thermal Energies=	-5535.568323		
Sum of electronic and thermal Enthalpies=	-5535.567379		
Sum of electronic and thermal Free Energies=	-5535.672536		
C	-2.19939100	1.65598400	0.18880100
C	-2.88459200	2.85549300	0.34292700
C	-2.16575500	4.06249100	0.42994100
C	-0.76386500	4.00975600	0.33379200
C	-0.16602800	2.76096900	0.19152800
C	-2.88161900	0.34494100	0.02516000
C	-4.25579000	0.16872000	0.14653700
C	-4.80835500	-1.11088000	-0.05064200
C	-3.94204200	-2.17206900	-0.36999000
C	-2.57976800	-1.90087700	-0.46423300
H	-3.97190900	2.89758400	0.38417800
H	-0.13970200	4.90092800	0.36783600
H	0.92041100	2.68738500	0.10979600
H	-4.92675100	0.98982300	0.39495300
H	-4.29881100	-3.18670800	-0.53852600
H	-1.85960800	-2.68632300	-0.70677800
N	-0.84404400	1.61045800	0.14083000
N	-2.06037300	-0.68608700	-0.27514600
Br	0.77161000	-1.85864800	-1.82531100
Ni	-0.05834800	-0.32727400	-0.00237900
C	0.03686300	-1.06627600	1.74963100
C	-0.57290400	-0.36900800	2.81078300

C	0.17744500	-2.46303500	1.84738400
C	-1.06612800	-1.05368200	3.91509000
H	-0.65394700	0.71893500	2.76656900
C	-0.30829700	-3.15024500	2.95930400
H	0.65808500	-3.00827400	1.03206700
H	-1.55689100	-0.51616000	4.72940200
H	-0.20237300	-4.23455300	3.02067700
C	-0.93886700	-2.45382000	4.00627000
C	1.81807600	-0.21194000	0.97543200
H	2.31502500	-1.12546300	0.63368200
O	-6.13422500	-1.21423800	0.08450200
O	-2.88506600	5.17604600	0.58438300
C	-6.76609400	-2.47903500	-0.09781900
H	-7.83770400	-2.31139600	0.06404600
H	-6.60643100	-2.86074700	-1.11964500
H	-6.39746500	-3.21757300	0.63287300
C	-2.22465200	6.43727500	0.67328100
H	-1.66096500	6.65606900	-0.24828100
H	-3.01432100	7.18676500	0.80390100
H	-1.54316200	6.46821100	1.53901700
C	-1.47346100	-3.13529000	5.21105500
O	-2.03033300	-2.57323200	6.13536300
O	-1.28093100	-4.46786900	5.18740800
C	2.32182400	0.25135300	2.29487600
C	2.19084900	1.58599600	2.72078700
C	2.92828700	-0.66385400	3.17870400
C	2.64041500	1.99053600	3.98103300
H	1.72429300	2.31947400	2.06246400
C	3.38010500	-0.26320700	4.43702700
H	3.02992800	-1.70834900	2.87230800
C	3.23628300	1.06822800	4.84779700
H	2.52438400	3.03398600	4.28613100
H	3.84654000	-0.99409400	5.10317200
H	3.58769200	1.38329400	5.83356600
H	1.93482600	0.57187200	0.20541900
C	-1.76698200	-5.20546200	6.31073000
H	-1.51763900	-6.25616200	6.11929000
H	-1.28663000	-4.86474900	7.24079000
H	-2.85649900	-5.08726800	6.41537800

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)  
HF=-5538.21143499

**<sup>4</sup>D'-P<sub>B</sub>-TS-OMe-H**

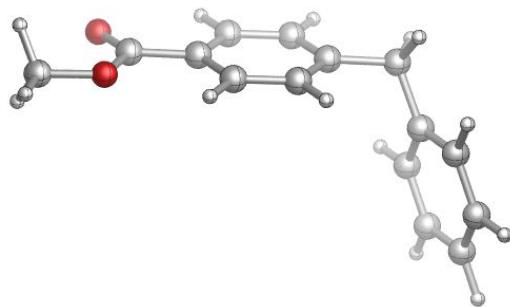


UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction=	0.475378 (Hartree/Particle)		
Thermal correction to Energy=	0.509374		
Thermal correction to Enthalpy=	0.510318		
Thermal correction to Gibbs Free Energy=	0.404432		
Sum of electronic and zero-point Energies=	-5535.576654		
Sum of electronic and thermal Energies=	-5535.542657		
Sum of electronic and thermal Enthalpies=	-5535.541713		
Sum of electronic and thermal Free Energies=	-5535.647599		
C	-2.32893700	1.67786600	-0.04709200
C	-3.12871200	2.79226300	0.17669300
C	-2.52860200	4.05381800	0.35279100
C	-1.12581300	4.14069200	0.29544500
C	-0.40421500	2.97271900	0.06981100
C	-2.86537900	0.30357100	-0.23235800
C	-4.21980900	-0.00821000	-0.23027600
C	-4.62236300	-1.34620500	-0.40669300
C	-3.63018600	-2.32891200	-0.58054200
C	-2.29869000	-1.92545700	-0.56928800
H	-4.21446000	2.72367500	0.22627600
H	-0.58993400	5.07881900	0.42687700
H	0.68595400	2.99284600	0.03529400
H	-4.98876100	0.75143100	-0.09744000
H	-3.86883400	-3.38135300	-0.72283600
H	-1.48683600	-2.64420000	-0.70510600
N	-0.97755700	1.77718400	-0.10213600
N	-1.92348000	-0.65449500	-0.40269600
Br	1.33770600	-1.62677500	-1.42798100
Ni	-0.00597500	-0.02515900	-0.16663900
C	0.21428000	-0.36172800	1.82080000
C	-0.34430500	0.54643000	2.78479600

C	0.17368400	-1.74792700	2.20143600
C	-0.80290600	0.13079100	4.02187900
H	-0.38382300	1.61281000	2.54477300
C	-0.28456300	-2.17564700	3.43533600
H	0.54097600	-2.48850700	1.48319100
H	-1.21208100	0.84705200	4.73892400
H	-0.29349800	-3.23870500	3.68492500
C	-0.77651600	-1.23970500	4.38009900
C	2.31702400	0.01835600	1.96579900
C	2.62272600	1.37295500	1.55739300
C	2.46715100	2.46275400	2.45153200
C	3.03657500	1.66538000	0.23163000
C	2.71809400	3.77157200	2.04323800
H	2.13832300	2.26369500	3.47482100
C	3.29282600	2.97634800	-0.17081700
H	3.13444700	0.84148700	-0.48066100
C	3.13581500	4.03970300	0.73046600
H	2.58771900	4.59428600	2.75154800
H	3.61241400	3.17444400	-1.19748700
H	3.33262200	5.06652000	0.41298200
H	2.63197900	-0.78623700	1.29799200
H	2.37286400	-0.20825800	3.03248200
O	-5.93754200	-1.57799800	-0.39559600
O	-3.35393500	5.08134300	0.56706800
C	-6.42262200	-2.90800700	-0.56892400
H	-7.51619700	-2.84250300	-0.52195300
H	-6.12239300	-3.31640900	-1.54779000
H	-6.06101000	-3.57091700	0.23407800
C	-2.81939000	6.38956400	0.76045000
H	-2.25568500	6.72396400	-0.12575500
H	-3.68038100	7.05082500	0.91501200
H	-2.16673800	6.42526000	1.64804600
C	-1.29057000	-1.63445000	5.70362500
O	-1.74408300	-0.86725700	6.53754100
O	-1.21453200	-2.96687700	5.92528100
C	-1.69886100	-3.43148800	7.18415900
H	-1.55614800	-4.51926600	7.18734900
H	-1.13942700	-2.97475400	8.01555400
H	-2.76610800	-3.19049800	7.31020800

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)  
HF=-5538.18455588

**Ar-H**

UB3LYP-D3/def2-SVP-CPCM(DMA)

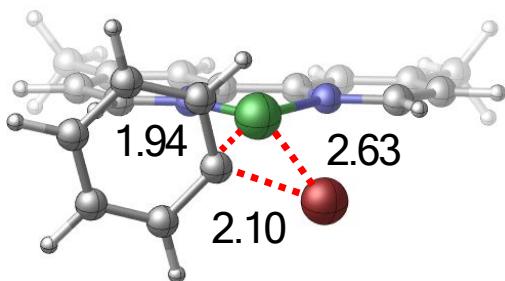
Zero-point correction=	0.252675 (Hartree/Particle)		
Thermal correction to Energy=	0.267437		
Thermal correction to Enthalpy=	0.268381		
Thermal correction to Gibbs Free Energy=	0.207777		
Sum of electronic and zero-point Energies=	-729.751307		
Sum of electronic and thermal Energies=	-729.736544		
Sum of electronic and thermal Enthalpies=	-729.735600		
Sum of electronic and thermal Free Energies=	-729.796204		
C	2.46756200	-0.14078600	1.70220000
C	1.57475300	-2.51340500	0.46016800
C	3.35565800	-0.94513800	0.97133500
C	1.12405600	-0.54431300	1.80265000
C	0.67783700	-1.71318900	1.19058300
C	2.91658100	-2.11812100	0.35623600
H	4.40388900	-0.64810100	0.88271500
H	0.42199600	0.06776200	2.37517900
H	-0.36703900	-2.01427300	1.27470800
H	3.60810700	-2.74343000	-0.21167800
C	2.93821100	1.12556200	2.39292900
H	2.33233400	1.97618900	2.04168900
H	3.97966800	1.33196900	2.10041700
C	2.84170400	1.03359200	3.90579600
C	3.68335200	0.16006300	4.61557300
C	1.90173900	1.78867700	4.62226300
C	3.58884100	0.04614600	6.00467300
H	4.41761200	-0.43926000	4.06935400
C	1.80319200	1.67668900	6.01474000
H	1.23985600	2.47426500	4.08549800
C	2.64601400	0.80491900	6.71028000
H	4.25337300	-0.63690800	6.54042100
H	1.06477700	2.27422600	6.55586500
H	2.57099000	0.71640800	7.79709700

C	1.15505300	-3.77626500	-0.21194100
O	1.89801100	-4.49272000	-0.85247100
O	-0.14747400	-4.04991000	-0.03561900
C	-0.64034000	-5.24761600	-0.64365500
H	-0.11126900	-6.12947700	-0.25153900
H	-1.70631300	-5.30201400	-0.39288200
H	-0.50714100	-5.21340700	-1.73562300

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)

HF=-730.811488813

**Figure S5**  
<sup>1</sup>A-F-TS-(Ar-H)

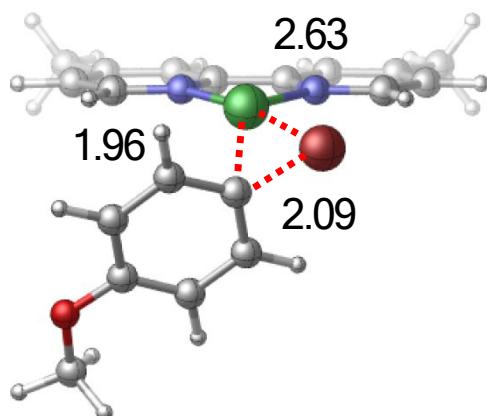


UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction=	0.301821 (Hartree/Particle)		
Thermal correction to Energy=	0.322788		
Thermal correction to Enthalpy=	0.323732		
Thermal correction to Gibbs Free Energy=	0.249618		
Sum of electronic and zero-point Energies=	-4886.900033		
Sum of electronic and thermal Energies=	-4886.879066		
Sum of electronic and thermal Enthalpies=	-4886.878122		
Sum of electronic and thermal Free Energies=	-4886.952236		
C	-2.72287000	-0.06657000	1.35517600
C	-2.47691800	-0.38917700	-0.00404100
C	-3.02493500	0.39090700	-1.05158900
C	-3.71221800	1.55038000	-0.72749000
C	-3.90801500	1.92766000	0.62145600
C	-3.41819300	1.12563900	1.64664600
Br	-2.11155500	-2.42275300	-0.38250300
H	-2.86724200	0.09585200	-2.09031800
H	-2.48329200	-0.76684500	2.15891600
H	-3.60231000	1.39117500	2.69085500
H	-4.46260300	2.83909000	0.85462100
H	-4.10122100	2.18336000	-1.52936900
C	2.19690000	-0.18557800	0.13965900
C	1.61400800	-2.43638000	0.50055400
C	2.92189100	-2.85911900	0.37088800
C	3.94193700	-1.89444500	0.10420500
C	3.55514900	-0.56975800	-0.01054900
C	1.69851900	1.16398200	0.04084700
C	-0.22055300	2.51634200	0.09466600
C	0.51379500	3.67389700	-0.09319000
C	1.92981300	3.58089100	-0.22695600
C	2.49980500	2.31974200	-0.15235500
H	0.80477500	-3.14739700	0.69342700
H	3.16707000	-3.91844200	0.47225300

H	4.30673700	0.19199400	-0.22641900
H	-1.30692400	2.54866000	0.20081000
H	0.00794300	4.64047300	-0.14050100
H	3.58302100	2.21410300	-0.23667300
N	1.23522000	-1.14543200	0.39998300
N	0.32820900	1.28968600	0.14889000
Ni	-0.59274300	-0.44417800	0.45116900
C	2.75362100	4.82271800	-0.43553000
H	3.82712400	4.59628600	-0.51258900
H	2.44511100	5.34766700	-1.35589000
H	2.60972900	5.53462200	0.39518500
C	5.37352100	-2.33098300	-0.04894300
H	6.04332800	-1.48112900	-0.24628400
H	5.72788800	-2.84466500	0.86139200
H	5.47977500	-3.05258600	-0.87734300

<sup>1</sup>A-F-TS-(Ar-OMe)

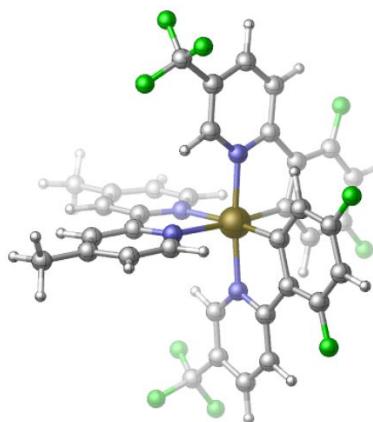


UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction=	0.334564 (Hartree/Particle)		
Thermal correction to Energy=	0.358013		
Thermal correction to Enthalpy=	0.358957		
Thermal correction to Gibbs Free Energy=	0.279115		
Sum of electronic and zero-point Energies=	-5001.311434		
Sum of electronic and thermal Energies=	-5001.287985		
Sum of electronic and thermal Enthalpies=	-5001.287041		
Sum of electronic and thermal Free Energies=	-5001.366883		
C	-2.92562400	0.46141300	1.90411000
C	-2.34023700	-0.50453600	1.05305100
C	-2.48704200	-0.40748700	-0.34550800
C	-3.07503100	0.72657900	-0.89513300
C	-3.58327000	1.74509200	-0.05574400
C	-3.51315500	1.59445100	1.33817500
Br	-2.03883600	-2.39048000	1.90522900
H	-2.08289100	-1.19034200	-0.98863600
H	-2.90375200	0.33397600	2.98782000
H	-3.93783500	2.37656600	1.97085600
H	-3.13120100	0.81444900	-1.97995900
C	1.97427400	-0.02784500	0.28049500
C	1.42508200	-2.30870300	0.47668400
C	2.54550400	-2.70796700	-0.22954800
C	3.44387000	-1.71020900	-0.71897700
C	3.14052400	-0.38707100	-0.45436100
C	1.58683400	1.31781000	0.60234400
C	-0.01956400	2.67762500	1.66098500
C	0.64553700	3.84211800	1.32259500
C	1.86219600	3.74933800	0.57721500
C	2.30852000	2.48782000	0.22858800
H	0.71068700	-3.04350600	0.86006300

H	2.73253200	-3.76877400	-0.40851600
H	3.80696000	0.39728400	-0.81818000
H	-0.95950200	2.70843900	2.22027500
H	0.24040600	4.81189700	1.61853100
H	3.23025100	2.38666700	-0.34743300
N	1.12502600	-1.02408500	0.73843700
N	0.41594800	1.44717800	1.33483300
Ni	-0.48713500	-0.28437200	1.63649500
C	2.60735300	4.99925000	0.19408600
H	3.52096100	4.77583200	-0.37644300
H	1.97289100	5.66388900	-0.41757700
H	2.89328400	5.57737800	1.08978600
C	4.66839500	-2.11449600	-1.49460200
H	5.26112200	-1.24388700	-1.81196000
H	5.31762500	-2.77215600	-0.89104800
H	4.39142800	-2.68955200	-2.39511300
O	-4.16717800	2.88096500	-0.50629000
C	-4.27933800	3.10300200	-1.90206000
H	-4.76983500	4.07750500	-2.02339200
H	-3.28946100	3.13552600	-2.39008600
H	-4.89510400	2.32753000	-2.39048400

**Figure S6**  
**Ir-1a [Ir(III)]**



UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction=	0.513899 (Hartree/Particle)		
Thermal correction to Energy=	0.557348		
Thermal correction to Enthalpy=	0.558293		
Thermal correction to Gibbs Free Energy=	0.431809		
Sum of electronic and zero-point Energies=	-2704.606353		
Sum of electronic and thermal Energies=	-2704.562904		
Sum of electronic and thermal Enthalpies=	-2704.561959		
Sum of electronic and thermal Free Energies=	-2704.688443		
Ir	-0.40726200	0.78075900	0.01528500
C	2.45813100	1.39740700	0.81554100
C	2.39926200	0.72261100	-1.41410900
C	3.85020400	1.52271600	0.75467500
C	1.66960500	1.68373100	2.04119600
C	3.77858600	0.83265100	-1.53482600
H	1.78071100	0.40443900	-2.25514200
C	4.54163900	1.24254400	-0.43015300
H	4.40974000	1.83520100	1.63535000
C	2.24076900	2.16591500	3.22409100
H	4.25388500	0.59538800	-2.48830100
C	-0.44061600	1.69337600	3.03017600
C	1.44693000	2.41800300	4.34945500
H	3.31206100	2.35528200	3.27634200
C	0.07021500	2.16877900	4.23083400
H	-1.50624700	1.49190500	2.90711100
H	-0.60635500	2.34546600	5.06896000
C	-0.27455500	-2.04851300	-0.77304500
C	0.30366200	-1.76335000	1.49351900
C	-0.06039300	-3.43460000	-0.65180400
C	-0.70162700	-1.32803500	-1.97102800

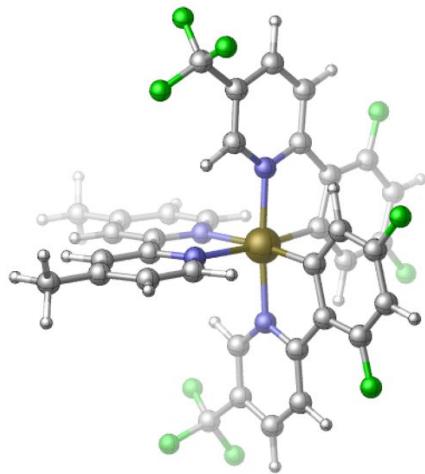
C	0.52117000	-3.12446000	1.66108700
H	0.43800500	-1.06644900	2.31936400
C	0.33732700	-3.97427200	0.56329800
H	-0.20787200	-4.07792900	-1.51393500
C	-0.86243900	0.08414600	-1.82266700
C	-0.95509400	-1.90558300	-3.22952400
H	0.50763500	-5.04832600	0.65783500
C	-1.26899400	0.84552600	-2.92652500
C	-1.35453800	-1.15743500	-4.32808400
C	-1.50375900	0.21759800	-4.14665100
H	-1.40902100	1.92501600	-2.86208900
H	-1.54195300	-1.63251400	-5.29046300
C	-2.37125200	0.73727200	0.47744600
C	-3.03238400	1.99722900	0.34650700
C	-3.09684100	-0.37097900	0.93459100
C	-4.39535800	2.08062700	0.68865900
C	-2.20568900	3.10228400	-0.13573100
C	-4.44326400	-0.22662400	1.25780700
H	-2.63888900	-1.35389800	1.04863100
C	-5.11952700	0.98809700	1.14497900
C	-2.61971000	4.42730600	-0.36858500
H	-6.17350700	1.08385700	1.40365900
C	-0.02498900	3.66433300	-0.83010700
C	-1.71370900	5.36792200	-0.83763000
H	-3.65208900	4.70814400	-0.18336100
C	-0.38849200	4.98229200	-1.07354500
H	-2.03555800	6.39365300	-1.02657400
N	1.75019600	0.99906300	-0.27072100
N	0.33598000	1.45258100	1.96046000
N	-0.07881900	-1.24252000	0.31778100
N	-0.90175500	2.75558000	-0.37649800
C	0.90944500	-3.67530800	3.00744700
F	-0.13884800	-4.25380800	3.62422600
F	1.37441400	-2.71734200	3.82706300
F	1.86269200	-4.61646600	2.89328900
F	-0.81192500	-3.23008800	-3.41276200
F	-1.89071800	0.95657900	-5.19545600
F	-5.05385600	3.24851500	0.58516200
F	-5.12585900	-1.29336900	1.69575200
H	0.99224500	3.31959600	-1.00990900
C	0.63336000	5.98187200	-1.54632600
F	0.12504500	6.78905400	-2.49370300
F	1.72246100	5.38364300	-2.05758100
F	1.04972300	6.77442900	-0.53995000

C	2.03332400	2.93038800	5.63389900
H	1.87313500	2.20016300	6.44385900
H	3.11156300	3.12098900	5.54583600
H	1.53393200	3.86333400	5.94013900
C	6.03377900	1.38450300	-0.52690500
H	6.29012500	2.24117500	-1.17232700
H	6.49461000	1.54646200	0.45711300
H	6.48169100	0.49006300	-0.98682200

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)

HF=-2708.0793233

### Reduced form of Ir-1a [Ir(II)]



UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction=	0.510364 (Hartree/Particle)		
Thermal correction to Energy=	0.553872		
Thermal correction to Enthalpy=	0.554816		
Thermal correction to Gibbs Free Energy=	0.428642		
Sum of electronic and zero-point Energies=	-2704.717838		
Sum of electronic and thermal Energies=	-2704.674329		
Sum of electronic and thermal Enthalpies=	-2704.673385		
Sum of electronic and thermal Free Energies=	-2704.799559		
Ir	-0.41664000	0.76711300	0.00893100
C	2.41518900	1.42944300	0.81471200
C	2.37454000	0.74949300	-1.44923800
C	3.82591100	1.63032300	0.70085900
C	1.66206100	1.65340900	2.00984100
C	3.73872000	0.92365000	-1.59748900
H	1.76084700	0.40247500	-2.28457200
C	4.49874100	1.38802100	-0.47962200
H	4.38440400	1.98411800	1.56853700
C	2.22456500	2.09744700	3.24672200
H	4.21607900	0.71000400	-2.55538100
C	-0.46462200	1.61549800	3.04202000
C	1.44301200	2.29773600	4.36671000
H	3.29776200	2.28323300	3.30652100
C	0.04012800	2.04780900	4.25511600
H	-1.53155500	1.41120000	2.91987500
H	-0.62852700	2.19175000	5.10556300
C	-0.28302600	-2.07024000	-0.74337700
C	0.29904700	-1.74371400	1.51713700
C	-0.06364900	-3.45407800	-0.59851800
C	-0.70825400	-1.36979500	-1.95432200

C	0.52534800	-3.10109500	1.70609600
H	0.43435400	-1.02505200	2.32450000
C	0.33957400	-3.97163400	0.62424000
H	-0.20952600	-4.11221700	-1.44980700
C	-0.86464800	0.04674400	-1.82717500
C	-0.96389000	-1.96884900	-3.20194100
H	0.51476900	-5.04316600	0.73708700
C	-1.27259600	0.78668200	-2.94784800
C	-1.36292000	-1.24033000	-4.31390600
C	-1.50980200	0.13884700	-4.15556900
H	-1.40903900	1.86829000	-2.90001600
H	-1.55217400	-1.73193400	-5.26759800
C	-2.38732600	0.75803600	0.46807300
C	-3.02658600	2.03028300	0.32870100
C	-3.14341100	-0.33364800	0.92268500
C	-4.38985600	2.14166700	0.66039600
C	-2.17494900	3.11735100	-0.15189300
C	-4.48784800	-0.16236900	1.23536900
H	-2.70345000	-1.32480300	1.04305400
C	-5.13995900	1.06586300	1.11483900
C	-2.55890400	4.45226300	-0.38538900
H	-6.19364200	1.18345500	1.36562500
C	0.02307400	3.63408200	-0.82776700
C	-1.62958000	5.37480000	-0.84401300
H	-3.58631000	4.75490000	-0.20641200
C	-0.31001300	4.96125300	-1.06756300
H	-1.92748400	6.40797400	-1.03207100
N	1.71158800	0.99286300	-0.30311600
N	0.29401200	1.41146600	1.94896700
N	-0.09290600	-1.24572300	0.33489800
N	-0.87799900	2.74227000	-0.38891900
C	0.92547900	-3.62620000	3.05768000
F	-0.11474700	-4.20075900	3.69429200
F	1.39174500	-2.65335900	3.85944200
F	1.88304800	-4.56592200	2.95508200
F	-0.82396200	-3.29898200	-3.36363900
F	-1.89727600	0.85922600	-5.22016000
F	-5.02697800	3.32342000	0.54867300
F	-5.19794600	-1.21462700	1.67221500
H	1.03346900	3.26190000	-0.99273700
C	0.73742500	5.94171000	-1.51929500
F	0.26348400	6.75985400	-2.47684600
F	1.82722600	5.32678000	-2.00977500
F	1.14905100	6.72926500	-0.50547200

C	2.02079400	2.76345600	5.67552000
H	1.82068400	2.02987700	6.47540800
H	3.10791300	2.91902300	5.61482000
H	1.55295300	3.71044500	5.99528700
C	5.98262200	1.59656800	-0.61475000
H	6.20454200	2.33303300	-1.40620700
H	6.43665600	1.95060500	0.32236500
H	6.48467600	0.65911900	-0.90987300

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)

HF= -2708.190034

## Cs<sup>+</sup>

UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction= 0.000000 (Hartree/Particle)

Thermal correction to Energy= 0.001416

Thermal correction to Enthalpy= 0.002360

Thermal correction to Gibbs Free Energy= -0.016914

Sum of electronic and zero-point Energies= -20.095015

Sum of electronic and thermal Energies= -20.093599

Sum of electronic and thermal Enthalpies= -20.092655

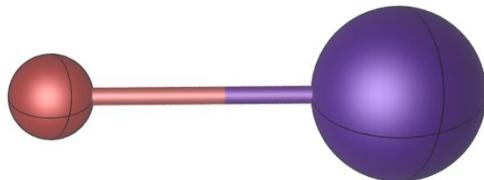
Sum of electronic and thermal Free Energies= -20.111929

Cs 13.06467800 6.05312700 -0.55883900

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)

HF= -20.1066031

## CsBr



UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction= 0.000168 (Hartree/Particle)

Thermal correction to Energy= 0.003315

Thermal correction to Enthalpy= 0.004259

Thermal correction to Gibbs Free Energy= -0.026975

Sum of electronic and zero-point Energies= -2594.166090

Sum of electronic and thermal Energies= -2594.162943

Sum of electronic and thermal Enthalpies= -2594.161999

Sum of electronic and thermal Free Energies= -2594.193233

Cs 13.06467800 6.05312700 -0.55883900

Br 9.72989000 6.06865800 -1.70166200

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)

HF= -2594.4876913

## **K<sup>+</sup>**

UB3LYP-D3/def2-SVP-CPCM(DMA)

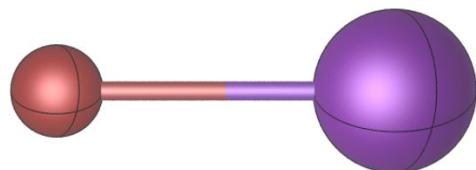
Zero-point correction=	0.000000	(Hartree/Particle)
Thermal correction to Energy=	0.001416	
Thermal correction to Enthalpy=	0.002360	
Thermal correction to Gibbs Free Energy=	-0.015176	
Sum of electronic and zero-point Energies=	-599.805913	
Sum of electronic and thermal Energies=	-599.804496	
Sum of electronic and thermal Enthalpies=	-599.803552	
Sum of electronic and thermal Free Energies=	-599.821089	

K            0.67977525    1.81953727    -2.01383638

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)

HF= -599.8834585

## **KBr**



UB3LYP-D3/def2-SVP-CPCM(DMA)

Zero-point correction=	0.000253	(Hartree/Particle)
Thermal correction to Energy=	0.003327	
Thermal correction to Enthalpy=	0.004271	
Thermal correction to Gibbs Free Energy=	-0.024954	
Sum of electronic and zero-point Energies=	-3173.864013	
Sum of electronic and thermal Energies=	-3173.860938	
Sum of electronic and thermal Enthalpies=	-3173.859994	
Sum of electronic and thermal Free Energies=	-3173.889219	

K            -0.24084300    1.80647700    -1.00469500

Br            -3.41823300    1.80647700    -1.00469500

UB3LYP-D3/def2-TZVPP-CPCM(DMA)//UB3LYP-D3/def2-SVP-CPCM(DMA)

HF= -3174.2647611

### 13. References

1. Zhang, F. and Song, J. Z. (2006). A novel general method for preparation of  $\alpha$ -fluoro- $\alpha$ -arylcarboxylic acid. Direct fluorination of silylketene acetals with selectfluor. *Tetrahedron Lett.* 47, 7641-7644.
2. Tanasova, M., Yang, Q., Olmsted, C. C., Vasileiou, C., Li, X., Anyika, M. and Borhan, B. (2009). An unusual conformation of  $\alpha$ -haloamides due to cooperative binding with zinced porphyrins. *Eur. J. Org. Chem.* 2009, 4242-4253.
3. Laurent, S. A.-L., Boissier, J., Coslédan, F., Gornitzka, H., Robert, A. and Meunier, B. (2008). Synthesis of “Trioxaquantel”® dericatives as potential new antischistosomal drugs. *Eur. J. Org. Chem.* 5, 895-913.
4. Sap, J. B. I., Wilson, T. C., Kee, C. W., Straathof, N. J. W., Ende, C. W. a., Mukherjee, P., Zhang, L., Genicot, C. and Gouverneur, V. (2019). Synthesis of  $^{18}\text{F}$ -difluoromethylarennes using aryl boronic acids, ethyl bromofluoroacetate and  $[^{18}\text{F}]$  fluoride. *Chem. Sci.* 10, 3237-3241.
5. Middleton, W., J. and Bingham, E. M. (1980).  $\alpha$ -Fluorination of carbonyl compounds with trifluoromethyl hypofluorite. *J. Am. Chem. Soc.* 102, 4845-4846.
6. Hoffmann, M., Chen, X., Hirano, M., Arimitsu, K., Kimura, H., Higuchi, T. and Decker, M. (2018).  $^{18}\text{F}$ -labeled derivatives of irbesartan for angiotensin II receptor PET imaging. *ChemMedChem* 13, 2546-2557.
7. Buckingham, F., Kirjavainen, A. K., Forsback, S., Krzyczmonik, A., Keller, T., Newington, I. M., Glaser, M., Luthra, S. K., Solin, O., Gouverneur, V. (2015). Organomediated enantioselective  $^{18}\text{F}$  fluorination for PET applications. *Angew. Chem. Int. Ed.* 54, 13366-13369.
8. Dong, X., Yang, W., Hu, W., Sun, J. (2015). N-heterocyclic carbene catalyzed enantioselective  $\alpha$ -fluorination of aliphatic aldehydes and  $\alpha$ -chloro aldehydes: synthesis of  $\alpha$ -fluoro esters, amides, and thioesters. *Angew. Chem. Int. Ed.* 54, 660-663.
9. Tanasova, M., Yang, Q., Olmsted, C. C., Vasileiou, C., Li, X., Anyika, M., Borhan, B. (2009). An unusual conformation of  $\alpha$ -haloamides due to cooperative binding with zinced porphyrins. *Eur. J. Org. Chem.* 2009, 4242-4253.
10. Amanetullah, A. O., Chaabouni, M. M. and Baklouti, A. (1996). Synthesis of 2-fluoro- acids, esters, and amides from  $\tilde{\text{A}}$ -dicyanoepoxides. *Synth. Commun.* 26, 1155-1161.
11. Hutchings, K. M., Lisabeth, E. M., Rajeswaran, W., Wilson, M. W., Sorenson, R. J., (2017). Campbell, P. L., Ruth, R. H., Amin, A., Tsou, P. S., Leipprandt, J. R., Olson, S. R., Wen, B., Zhao, T., Sun, D., Khanna, D., Fox, D. A., Neubig, R. R., Larsen, S. D. Pharmacokinetic optimization of CCG-203971: novel inhibitors of the Rho/MRTF/SRF transcriptional pathway as potential antifibrotic therapeutics for systemic scleroderma. *Bioorg. Med. Chem. Lett.* 27, 1744-1749.
12. Bender, A. M., Cho, H. P., Nance, K. D., Lingenfelter, K. S., Luscombe, V. B., Gentry, P. R., Voigtritter, K., Berizzi, A. E., Sexton, P. M., Langmead, C. J., Christopoulos, A., Locuson, C. W., Bridges, T. M., Chang, S., O'Neill, J. C., Zhan, X., Niswender, C. M., Jones, C. K., Conn, P. J., Lindsley, C. W. (2018). Discovery and optimization of potent and CNS penetrant M5-preferring positive allosteric

- modulators derived from a novel, chiral N-(indanyl)piperidine amide scaffold. *ACS Chem. Neurosci.* 9, 1572-1581.
13. Capaldo, L., Buzzetti, L., Merli, D., Fagnoni, M. and Ravelli, D. (2016). Smooth photocatalyzed benzylation of electrophilic olefins by decarboxylation of arylacetic acids. *J. Org. Chem.* 81, 7102-7109.
14. (a) Lee, C.; Yang, W.; Parr, R. G. (1988). Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B.* 37, 785-789. (b) Becke, A. D. (1993). Density-Functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* 98, 5648-5652.
15. (a) Grimme, S. (2004). Accurate description of van der Waals complexes by density functional theory including empirical corrections. *J. Comput. Chem.* 25, 1463-1473. (b) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. (2010). A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* 132, 154104. (c) Grimme, S. (2011). Density functional theory with London dispersion corrections. *WIREs Comput. Mol. Sci.* 1, 211-228. (d) Ehrlich, S.; Moellmann, J.; Grimme, S. (2012). Dispersion-Corrected Density Functional Theory for Aromatic Interactions in Complex Systems. *Acc. Chem. Res.* 46, 916-926.
16. (a) Weigend, F.; Ahlrichs, R. (2005). Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* 7, 3297-3305. (b) Weigend, F. (2006). Accurate Coulomb-fitting basis sets for H to Rn. *Phys. Chem. Chem. Phys.* 8, 1057-1065.
17. (a) Klamt, A.; Schüürmann, G. (1993). COSMO: a new approach to dielectric screening in solvents with explicit expressions for the screening energy and its gradient. *J. Chem. Soc. Perkin Trans. 2.* 0, 799-805. (b) Tomasi, J.; Persico, M. (1994). Molecular Interactions in Solution: An Overview of Methods Based on Continuous Distributions of the Solvent. *Chem. Rev.* 94, 2027-2094. (c) Andzelm, J.; Kölmel, C.; Klamt, A. (1995). Incorporation of solvent effects into density functional calculations of molecular energies and geometries. *J. Chem. Phys.* 103, 9312-9320. (d) Barone, V.; Cossi, M. Quantum Calculation of Molecular Energies and Energy Gradients in Solution by a Conductor Solvent Model. (1998). *J. Phys. Chem. A.* 102, 1995-2001. (e) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. (2003). Energies, structures, and electronic properties of molecules in solution with the C-PCM solvation model. *J. Comput. Chem.* 24, 669-681.
18. Frisch, M. J. T., G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A.; Peralta, Jr., J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.;

- Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. (2009). Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford CT.
19. CYLview, 1.0b; Legault, C. Y., Université de Sherbrooke, 2009 (<http://www.cylview.org>).
20. (a) Kozuch, S.; Shaik, S. (2011). How to Conceptualize Catalytic Cycles? The Energetic Span Model. *Acc. Chem. Res.* *44*, 101-110. (b) Kozuch, S.; Shaik, S. (2006). A Combined Kinetic-Quantum Mechanical Model for Assessment of Catalytic Cycles: Application to Cross-Coupling and Heck Reactions. *J. Am. Chem. Soc.* *128*, 3355-3365. (c) Kozuch, S.; Shaik, S. (2008). Kinetic-Quantum Chemical Model for Catalytic Cycles: The Haber-Bosch Process and the Effect of Reagent Concentration. *J. Phys. Chem. A.* *112*, 6032-6041.