

## Electronic Supplementary Information

# Synthesis of naphthalene-substituted aromatic esters via Rh(III)-catalyzed C-H bond naphthylation and cascade directing group transformation

Yue Cui,<sup>a</sup> Siyu Li,<sup>a</sup> Hesheng Wang,<sup>a</sup> Jing Zeng,<sup>a</sup> Yichen Wang,<sup>a</sup>  
Xiubin Bu,<sup>\*a</sup> Xiaobo Yang<sup>\*a,b</sup> and Zhen Zhao<sup>a</sup>

<sup>a</sup>Institute of Catalysis for Energy and Environment, College of Chemistry and Chemical Engineering, Shenyang Normal University, Shenyang 110034, P. R. China.

<sup>b</sup>Key Laboratory of Bioorganic Phosphorus Chemistry and Chemical Biology (Ministry of Education), Department of Chemistry, Tsinghua University, Beijing 100084, P. R. China.

E-mail: bxy1223@gmail.com; yangxb@synu.edu.cn; buxb@synu.edu.cn.

### Table of Contents

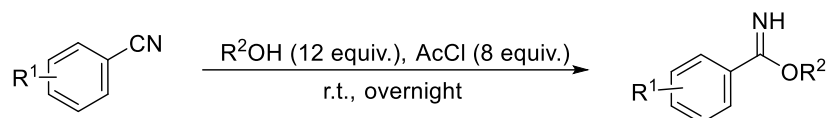
I. General remarks	S2
II. General procedure for the synthesis of starting materials	S2
III. General procedure for the synthesis of compounds <b>3</b>	S3
IV. Scale-up reaction and derivatization	S3
V. Mechanistic studies	S5
VI. Characterization data of compounds	S10
VII. References	S22
VIII. The <sup>1</sup> H and <sup>13</sup> C NMR spectra of compounds	S24

## I. General remarks

NMR spectra were recorded on Bruker 400 NMR, Bruker 500 NMR, Bruker 600 NMR in either  $\text{CDCl}_3$  or  $\text{DMSO}-d_6$ . Abbreviations for data quoted are s, singlet; brs, broad singlet; d, doublet; t, triplet; dd, doublet of doublets; m, multiplet or unresolved. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ( $\text{CDCl}_3$ :  $\delta_{\text{H}} = 7.26$  ppm,  $\delta_{\text{C}} = 77.16$  ppm;  $\text{DMSO}-d_6$ :  $\delta_{\text{H}} = 2.50$  ppm,  $\delta_{\text{C}} = 39.52$  ppm). High-resolution mass spectra were recorded on a Bruker solariX 7T mass spectrometer or Thermo LCQ Deca XP Max mass spectrometer. Silica gel 60 H (200-300 mesh) and preparative TLC (200 × 200 mm, 0.2-0.25 mm in thickness) manufactured by Qingdao Haiyang Chemical Group Co. (China) were used for general chromatography. All commercially available reagents and solvents were used as received unless otherwise specified.

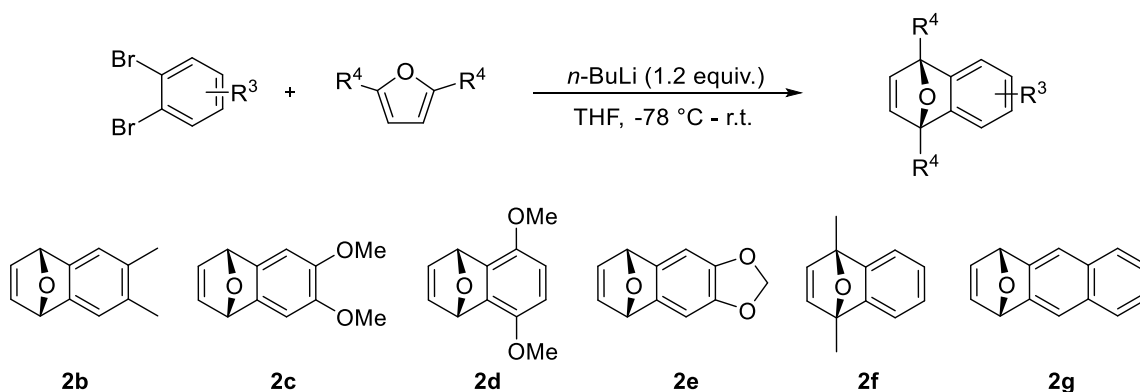
## II. General procedure for the synthesis of starting materials

### 1. General procedure for the synthesis of ethyl benzimidates<sup>1-4</sup>



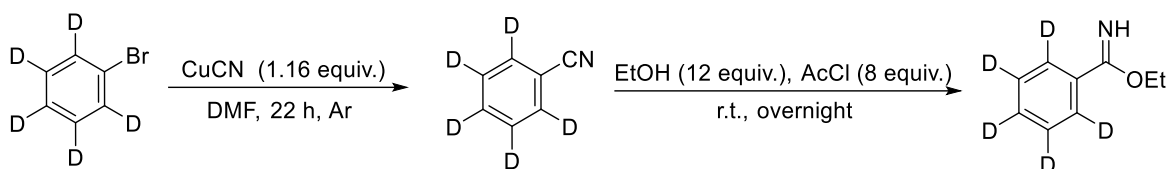
To a stirred solution of a nitrile (1 equiv.) and an alcohol (12 equiv.), AcCl was added (8 equiv.) dropwise at 0 °C. The Schlenk tube was stoppered tightly, and the stirring was continued at 25 °C. After the reaction was complete, the volatiles were removed under reduced pressure to isolate the benzimidate hydrochloride. Then slowly mixed benzimidate hydrochloride and saturated aqueous  $\text{NaHCO}_3$  solution in an ice bath until gas evolution had ceased. The product was extracted into EtOAc, and the organic solution was washed with  $\text{H}_2\text{O}$  and brine and concentrated under reduced pressure to obtain the benzimidates.

### 2. General procedure for the synthesis of oxa bicyclic alkenes<sup>5-7</sup>



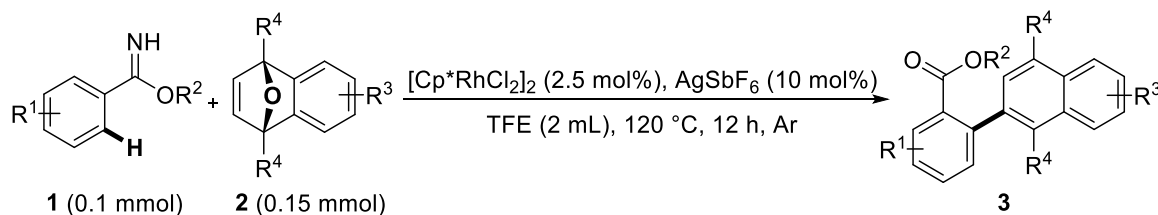
To a stirred solution of substituted 1,2-dibromobenzene (7.0 mmol) in anhydrous THF (15 mL) under Ar, freshly distilled furan (15 mL) was added. Then *n*-BuLi (2.5 M in hexane, 3.4 mL, 8.4 mmol, 1.2 equiv.) was added dropwise at -78 °C. The solution was stirred at -78 °C for 2.0 h. Then, distilled water (20 mL) was added to the reaction mixture, which was left to warm up to room temperature. Et<sub>2</sub>O was added to the reaction mixture, and the organic phase was separated. The aqueous solution was extracted with Et<sub>2</sub>O (20 mL × 3), and the combined organic solution was dried over MgSO<sub>4</sub>. The Et<sub>2</sub>O was then removed in vacuo, and the resulting mixture was purified by a flash silica gel column using a mixture of PE/EtOAc as eluent to give the desired pure product. Note that freshly prepared lithium diisopropylamide (LDA) was used rather than *n*-BuLi for compound **2d**, and anhydrous toluene was used as the solvent for compound **2f**.

### 3. General procedure for the synthesis of ethyl benzimidate-d<sub>5</sub><sup>8,9</sup>



A three-neck flask was charged with bromobenzene-d<sub>5</sub> (4.86 g, 30 mmol), CuCN (3.13 g, 35 mmol), and 4.5 mL of DMF. The mixture was heated to reflux for 22 h under argon. The reaction mixture was extracted with Et<sub>2</sub>O. The organic layer was washed with 6 M HCl and water, dried over MgSO<sub>4</sub>, and concentrated. Purification of the crude material by distillation and then by silica gel column chromatography (PE/EtOAc = 20/1) afforded benzonitrile-d<sub>5</sub> as a colorless oil (1.50 g, 46% yield).

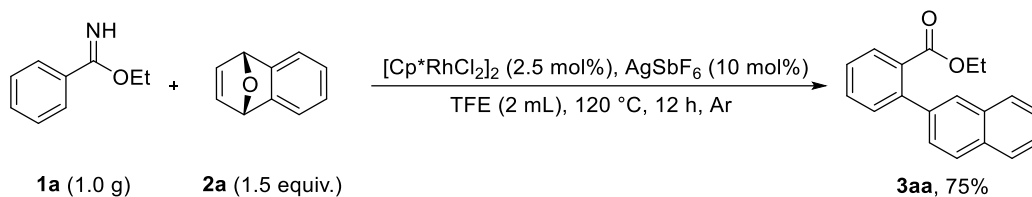
### III. General procedure for the synthesis of compounds **3**



A reaction tube with a magnetic stir bar was charged with **1** (0.10 mmol), **2** (0.15 mmol), [Cp\*RhCl<sub>2</sub>]<sub>2</sub> (0.0025 mmol), AgSbF<sub>6</sub> (0.01 mmol) was evacuated and purged with argon gas five times. Then, TFE (2 mL) was added to the system, and the mixture was stirred at 120 °C (oil bath) for 12 h and monitored by TLC. Upon completion, the solvent was removed under reduced pressure, and the residue was purified by silica gel flash chromatography (PE/EtOAc) to afford the desired product **3**.

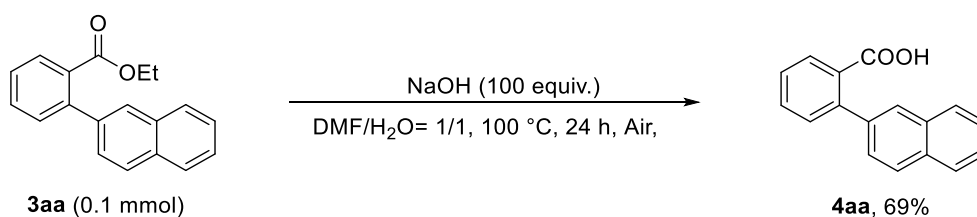
## IV. Scale-up reaction and derivatization

### 1. Scale-up reaction

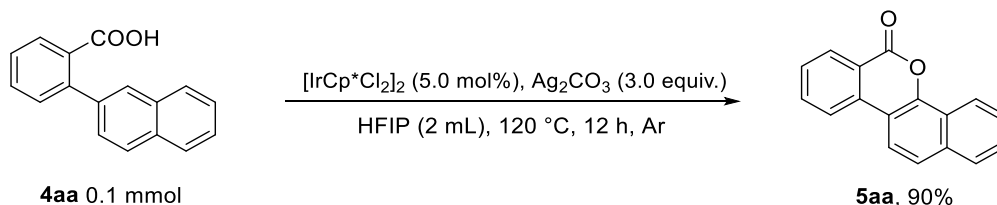


A reaction tube with a magnetic stir bar was charged with **1a** (6.71 mmol, 1.0 g), **2a** (10.07 mmol),  $[\text{Cp}^*\text{RhCl}_2]_2$  (0.168 mmol),  $\text{AgSbF}_6$  (0.671 mmol) was evacuated and purged with argon gas five times. Then, TFE (20 mL) was added to the system, and the mixture was stirred at 120 °C (oil bath) for 12 h and monitored by TLC. Upon completion, the solvent was removed under reduced pressure, and the residue was purified by silica gel flash chromatography (PE/EtOAc = 20/1) to afford the desired product **3aa** (1.39g, 75%).

### 2. Derivatization of **3aa**<sup>10-15</sup>

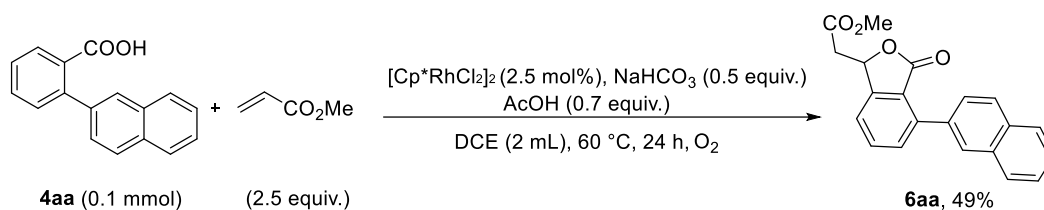


A reaction tube with a magnetic stir bar was charged with **3aa** (0.10 mmol), NaOH (100 equiv.) in (DMF/H<sub>2</sub>O=1/1) (4.0 mL), and the mixture was stirred for 24 h at 100 °C. The reaction solution was then cooled to room temperature. The reaction mixture was poured into water (3 × 20 mL) and extracted with EtOAc (3 × 20 mL). The combined water layer was washed with water (2 × 20 mL), saturated HCl (2 × 20 mL), extracted with EtOAc (3 × 20 mL), brine, and dried over anhydrous MgSO<sub>4</sub>. The solvent was removed under vacuum and got the desired product **4aa**. (17.0 mg, 69%).



A reaction tube with a magnetic stir bar was charged with **4aa** (0.10 mmol),  $[\text{IrCp}^*\text{Cl}_2]_2$  (3.99 mg, 0.005 mmol),  $\text{Ag}_2\text{CO}_3$  (82.70 mg, 0.30 mmol) and purged with argon gas five times. Then, HFIP (2 mL) was added to the system, and the mixture was stirred at 120 °C (oil bath) for 12 h and monitored by TLC. Upon completion, the solvent was removed under reduced pressure, and the residue was purified by silica

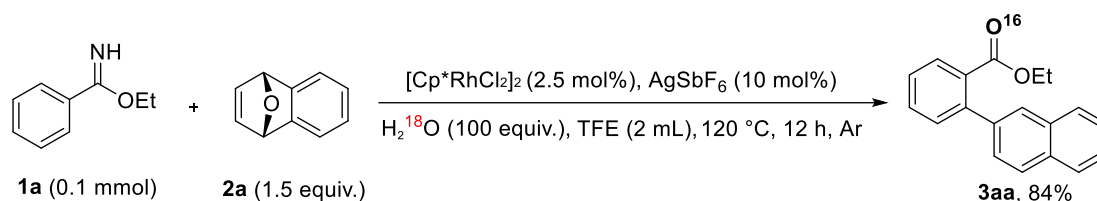
gel flash chromatography to afford the desired product **5aa** (22 mg, 90%).



A reaction tube with a magnetic stir bar was charged with **4aa** (0.10 mmol), methyl acrylate (21.60 mg, 0.25 mmol),  $[\text{Cp}^*\text{RhCl}_2]_2$  (0.0025 mmol),  $\text{NaHCO}_3$  (0.05 mmol), AcOH (0.07 mmol) and purged with  $\text{O}_2$  five times. Then, DCE (2 mL) was added to the system, and the mixture was stirred at 60 °C (oil bath) for 24 h and monitored by TLC. Upon completion, the solvent was removed under reduced pressure, and the residue was purified by silica gel flash chromatography to afford the desired product **6aa** (16 mg, 49%).

## V. Mechanistic studies

### 1. $^{18}\text{O}$ Labeling experiment with $\text{H}_2^{18}\text{O}$ and TFE



**1a** (0.10 mmol), **2a** (0.15 mmol, 1.5 equiv.),  $[\text{Cp}^*\text{RhCl}_2]_2$  (0.0025 mmol, 2.5 mol %),  $\text{AgSbF}_6$  (0.01 mmol, 10 mol %), TFE (2 mL) and  $\text{H}_2^{18}\text{O}$  (100 equiv., 98%  $^{18}\text{O}$  incorporation) were charged into a reaction tube. The reaction mixture was stirred for 12 h at 120 °C under Ar. Then the mixture was immediately cooled down to room temperature. Upon completion, solvents were removed under reduced pressure, and the residue was purified by silica gel flash chromatography (PE/EtOAc = 20/1) to afford **3aa** (84%). HR-MS (ESI)[ $\text{M}+\text{H}$ ] $^+$   $m/z$  calcd for  $\text{C}_{19}\text{H}_{17}\text{O}_2$  277.1229, found 277.1220.

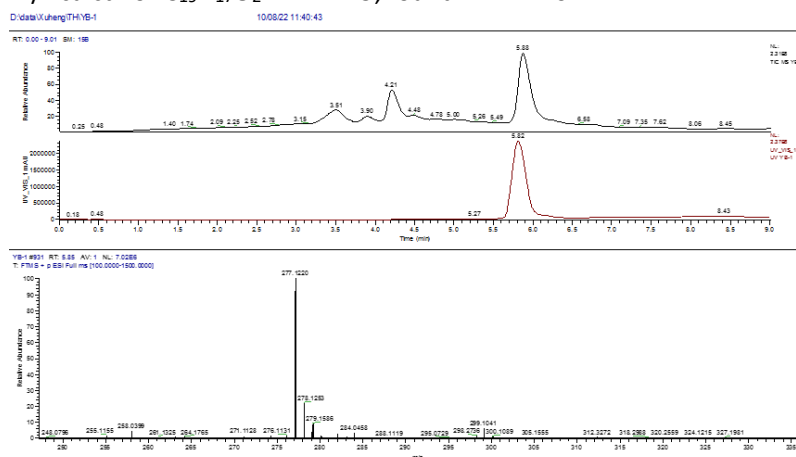
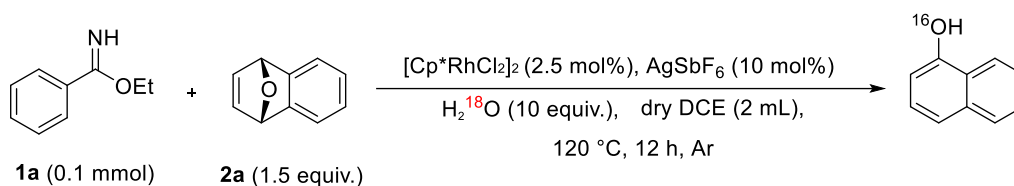
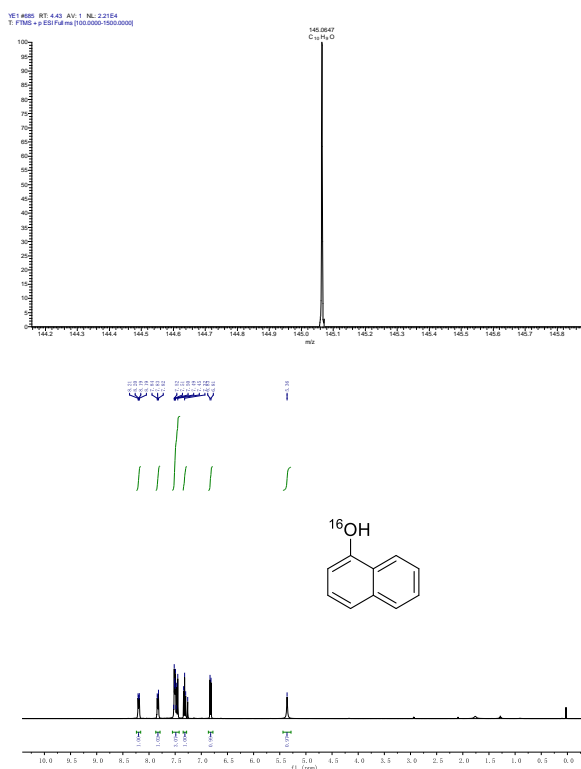


Figure S1. HR-MS for the product of the reaction with  $\text{H}_2^{18}\text{O}$ .

## 2. $^{18}\text{O}$ Labeling experiment with $\text{H}_2^{18}\text{O}$ and dry DCE

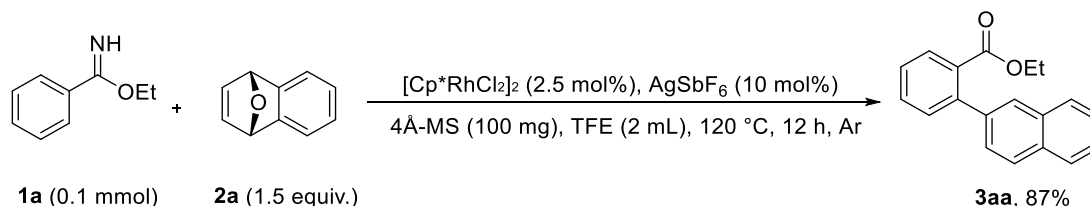


**1a** (0.10 mmol), **2a** (0.15 mmol, 1.5 equiv.),  $[\text{Cp}^*\text{RhCl}_2]_2$  (0.0025 mmol, 2.5 mol %),  $\text{AgSbF}_6$  (0.01 mmol, 10 mol %), dry DCE (2 mL) and  $\text{H}_2^{18}\text{O}$  (10 equiv., 98%  $^{18}\text{O}$  incorporation) were charged into a reaction tube. The reaction mixture was stirred for 12 h at 120 °C under Ar. Then the mixture was immediately cooled down to room temperature. Upon completion, solvents were removed under reduced pressure, and the residue was purified by silica gel flash chromatography (PE/EtOAc = 5/1) to afford naphthol. HR-MS (ESI)[ $\text{M}+\text{H}$ ] $^+$   $m/z$  calcd for  $\text{C}_{10}\text{H}_9\text{O}$  145.0647, found 145.0648.



**Figure S2.** The HR-MS and  $^1\text{H}$  NMR spectrum for the product of the reaction with dry DCE and  $\text{H}_2^{18}\text{O}$

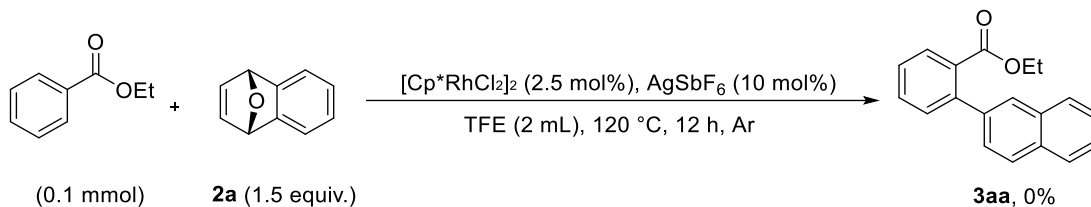
## 3. Reaction with dry molecular sieves



**1a** (0.10 mmol), **2a** (0.15 mmol, 1.5 equiv.),  $[\text{Cp}^*\text{RhCl}_2]_2$  (0.0025 mmol, 2.5 mol %),  $\text{AgSbF}_6$  (0.01 mmol, 10 mol %), TFE (2 mL) and dry molecular sieves (4Å) (100 mg) were charged into a reaction tube. The

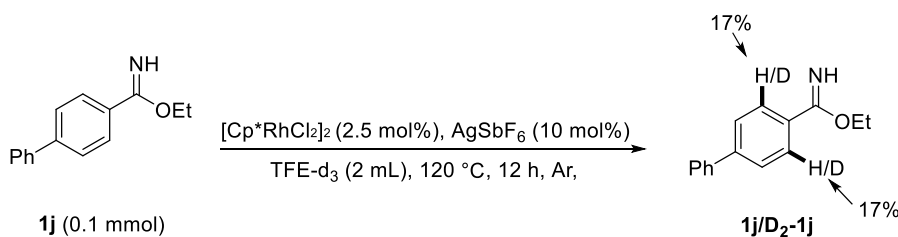
reaction mixture was stirred for 12 h at 120 °C under Ar. Then the mixture was immediately cooled down to room temperature. After the filtration, solvents were removed under reduced pressure, and the residue was purified by silica gel flash chromatography (PE/EtOAc = 20/1) to afford **3aa** (87 %).

#### 4. Reaction of ethyl benzoate and oxa bicyclic alkene **2a**



Ethyl benzoate (0.10 mmol), **2a** (0.15 mmol, 1.5 equiv.), [Cp\*RhCl<sub>2</sub>]<sub>2</sub> (0.0025 mmol, 2.5 mol %), AgSbF<sub>6</sub> (0.01 mmol, 10 mol %), TFE (2 mL) were charged into a reaction tube. The reaction mixture was stirred for 12 h at 120 °C under Ar. No desired naphthylated product **3aa** was observed by the reaction mixture's crude <sup>1</sup>H NMR and thin-layer chromatography (TLC).

#### 5. The H/D exchange experiment



**1j** (0.1 mmol), [Cp\*RhCl<sub>2</sub>]<sub>2</sub> (0.0025 mmol, 2.5 mol %), AgSbF<sub>6</sub> (0.01 mmol, 10 mol %), and TFE-d<sub>3</sub> (2 mL) were charged into a reaction tube. The reaction mixture was stirred for 12 h at 120 °C under Ar. Then the mixture after the filtration, solvents were removed under reduced pressure, and the residue was purified by silica gel flash chromatography (PE/EtOAc = 20/1) to afford **1j** and **D<sub>2</sub>-1j**. The deuterium incorporation was calculated using the <sup>1</sup>H-NMR spectrum of **1j** and **D<sub>2</sub>-1j**.

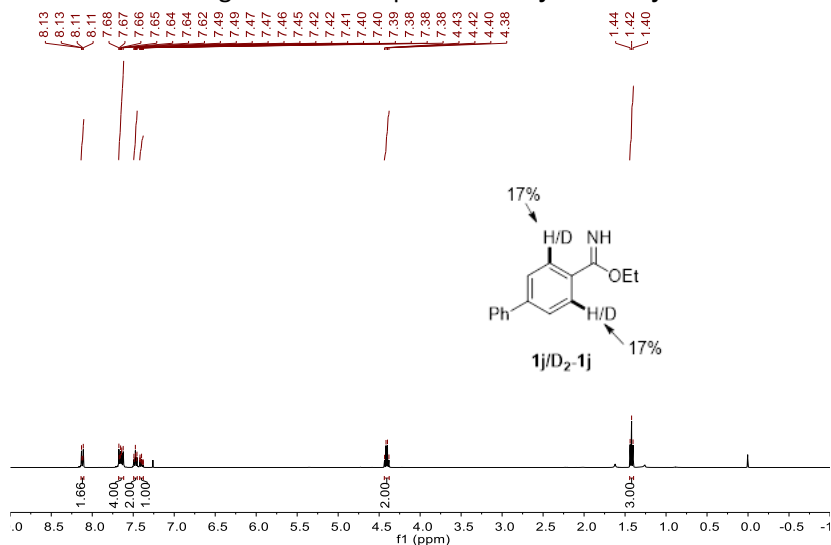
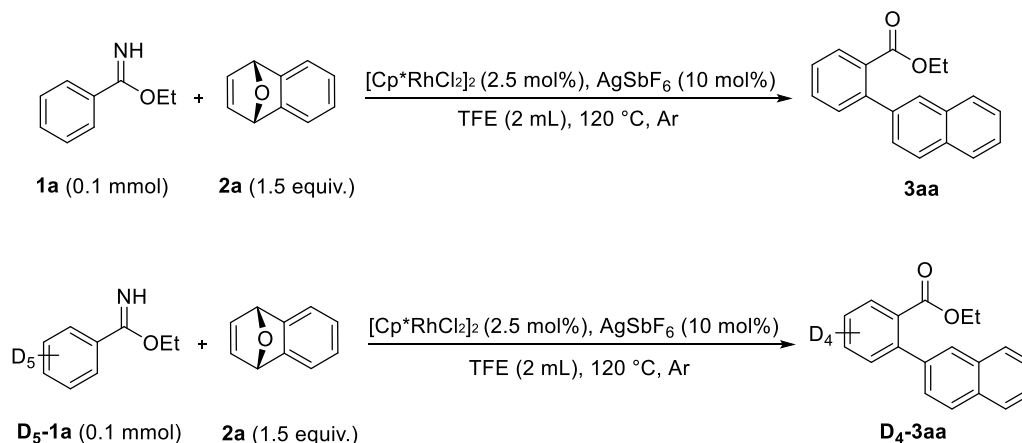


Figure S3. The <sup>1</sup>H NMR spectrum of **1j/D<sub>2</sub>-1j**.

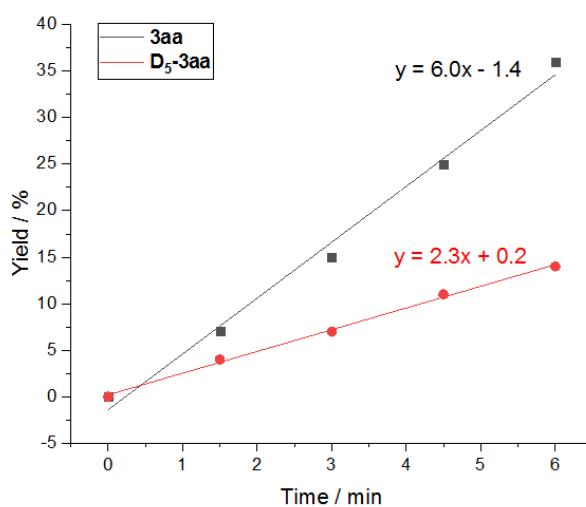
## 6. The measurement of kinetic isotope effect (KIE) value

(1) Two parallel reactions



**1a** (0.1 mmol) or **D<sub>5</sub>-1a** (0.1 mmol), **2a** (0.15 mmol, 1.5 equiv.),  $[\text{Cp}^*\text{RhCl}_2]_2$  (2.5 mol %),  $\text{AgSbF}_6$  (10 mol %), and TFE (2 mL) were added into a 25 mL Schlenk tube, and the tube was sealed. Then the reaction mixture was stirred at 120 °C under Ar for 1.5 min, 3 min, 4.5 min, or 6 min, respectively. After the corresponding reaction time, the mixture was immediately cooled down to room temperature with cold water. The corresponding yields of **3aa** or **D<sub>4</sub>-3aa** were calculated as follows:

	0 min	1.5 min	3.0 min	4.5 min	6 min
The yield of <b>3aa</b> (%)	0	7	15	25	36
The yield of <b>D<sub>4</sub>-3aa</b> (%)	0	4	7	11	14

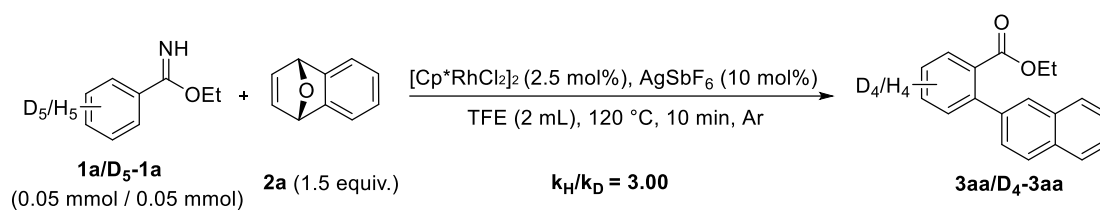


$$\text{KIE} = k_{\text{H}} / k_{\text{D}} = 6.00 / 2.30 = 2.61$$

**Figure S4.** The kinetic investigation of the above two parallel reactions.



(2) An intermolecular competition reaction



**1a** (0.05 mmol), **D<sub>5</sub>-1a** (0.05 mmol), **2a** (0.15 mmol, 1.5 equiv.), [Cp\*RhCl<sub>2</sub>]<sub>2</sub> (0.0025 mmol, 2.5 mol %), AgSbF<sub>6</sub> (0.01 mmol, 10 mol %), and TFE (2 mL) were evacuated and purged with argon gas five times. The reaction mixture was stirred for 10 minutes at 120 °C under Ar. Then the mixture was immediately cooled down to room temperature with water. After the filtration, solvents were removed under reduced pressure, and the residue was purified by silica gel flash chromatography (PE/EtOAc = 20/1) to afford **3aa** and **D<sub>4</sub>-3aa**. The ratio of the compounds was determined by <sup>1</sup>H NMR integration to give an intermolecular kinetic isotopic effect (KIE) value ( $k_H/k_D = 3.00$ ).

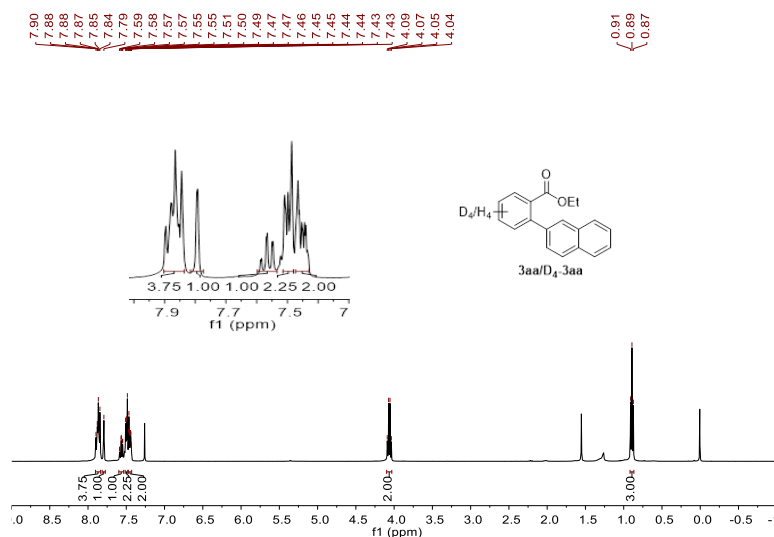
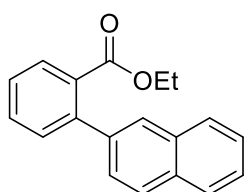


Figure S5. The <sup>1</sup>H NMR spectrum of **3aa/D<sub>4</sub>-3aa**.

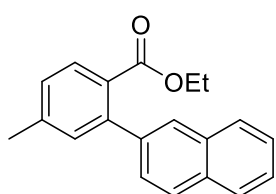
## VI. Characterization data of compounds

### ethyl 2-(naphthalen-2-yl) benzoate (**3aa**)<sup>16</sup>



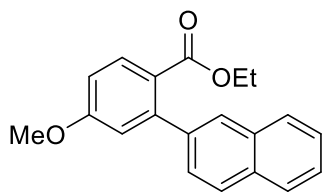
According to the general procedure (PE/EtOAc = 20/1), **3aa** was obtained in 87% yield (24 mg). Light yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.88 (m, 4H), 7.80 (s, 1H), 7.57 (m, 1H), 7.50 (m, 4H), 7.45 (m, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 0.90 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 168.9, 142.5, 139.2, 133.3, 132.6, 131.5, 131.4, 131.1, 130.0, 128.2, 127.8, 127.5, 127.4, 127.2, 127.0, 126.3, 126.1, 61.1, 13.8. HR-MS (ESI) [M+H]<sup>+</sup> *m/z* calcd for C<sub>19</sub>H<sub>17</sub>O<sub>2</sub> 277.1229, found 277.1224.

### ethyl 4-methyl-2-(naphthalen-2-yl) benzoate (**3ba**)



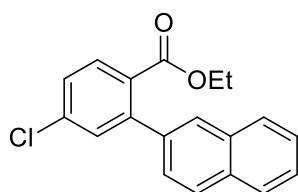
According to the general procedure (PE/EtOAc = 20/1), **3ba** was obtained in 87% yield (25 mg). Light yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.84 (m, 4H), 7.79 (s, 1H), 7.50 (m, 2H), 7.45 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.27 (m, 2H), 4.06 (q, *J* = 7.1 Hz, 2H), 2.46 (s, 3H), 0.90 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 168.7, 142.8, 141.9, 139.5, 133.4, 132.5, 131.9, 130.3, 128.5, 128.1, 128.1, 127.8, 127.4, 127.3, 126.9, 126.3, 126.0, 60.9, 21.6, 13.8. HR-MS (ESI) [M+H]<sup>+</sup> *m/z* calcd for C<sub>20</sub>H<sub>19</sub>O<sub>2</sub> 291.1385, found 291.1386.

### ethyl 4-methoxy-2-(naphthalen-2-yl) benzoate (**3ca**)



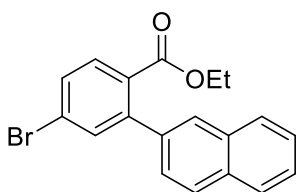
According to the general procedure (PE/EtOAc = 20/1), **3ca** was obtained in 59% yield (18 mg). Light yellow oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.95 (d, *J* = 8.5 Hz, 1H), 7.86 (m, 3H), 7.78 (s, 1H), 7.49 (m, 2H), 7.44 (dd, *J* = 8.4, 1.4 Hz, 2H), 6.96 (m, 2H), 4.04 (q, *J* = 7.1 Hz, 2H), 3.88 (s, 3H), 0.90 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 168.0, 161.9, 145.4, 139.6, 133.3, 132.6, 132.6, 128.2, 127.8, 127.3, 127.2, 126.8, 126.3, 126.0, 123.3, 116.6, 112.8, 60.7, 55.6, 13.8. HR-MS (ESI) [M+H]<sup>+</sup> *m/z* calcd for C<sub>20</sub>H<sub>19</sub>O<sub>3</sub> 307.1334, found 307.1333.

### ethyl 4-chloro-2-(naphthalen-2-yl) benzoate (**3da**)



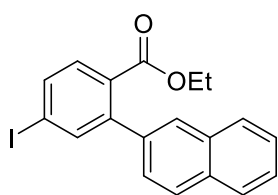
According to the general procedure (PE/EtOAc = 20/1), **3da** was obtained in 78% yield (24 mg). Light yellow oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.86 (m, 4H), 7.78 (s, 1H), 7.51 (m, 2H), 7.47 (d, *J* = 2.0 Hz, 1H), 7.42 (td, *J* = 8.2, 1.8 Hz, 2H), 4.06 (q, *J* = 7.1 Hz, 2H), 0.89 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.9, 144.4, 137.9, 137.4, 133.2, 132.7, 131.6, 131.1, 129.7, 128.2, 127.8, 127.6, 127.5, 127.1, 126.8, 126.5, 126.4, 61.3, 13.8. HR-MS (ESI) [M+H]<sup>+</sup> *m/z* calcd for C<sub>19</sub>H<sub>16</sub>ClO<sub>2</sub> 311.0839, found 311.0835.

### ethyl 4-bromo-2-(naphthalen-2-yl) benzoate (**3ea**)<sup>17</sup>



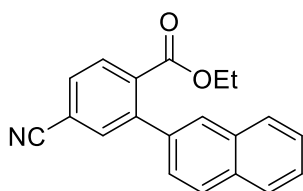
According to the general procedure (PE/EtOAc = 20/1), **3ea** was obtained in 77% yield (27 mg). Light yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.87 (m, 3H), 7.77 (m, 2H), 7.64 (d, *J* = 1.7 Hz, 1H), 7.59 (m, 1H), 7.52 (m, 2H), 7.40 (m, 1H), 4.06 (q, *J* = 7.1 Hz, 2H), 0.89 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 168.0, 144.5, 137.8, 134.0, 133.2, 132.7, 131.7, 130.5, 130.2, 128.2, 127.8, 127.7, 127.1, 126.9, 126.5, 126.4, 125.9, 61.3, 13.8. HR-MS (ESI) [M+H]<sup>+</sup> *m/z* calcd for C<sub>19</sub>H<sub>16</sub>BrO<sub>2</sub> 355.0334, found 355.0329.

### ethyl 4-iodo-2-(naphthalen-2-yl) benzoate (**3fa**)



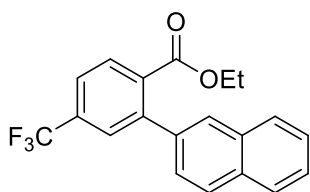
According to the general procedure (PE/EtOAc = 20/1), **3fa** was obtained in 53% yield (21 mg). Light yellow oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.86 (m, 4H), 7.80 (m, 1H), 7.77 (s, 1H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.51 (m, 2H), 7.40 (dd, *J* = 8.4, 1.6 Hz, 1H), 4.06 (q, *J* = 7.1 Hz, 2H), 0.89 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 168.1, 144.3, 139.9, 137.7, 136.5, 133.2, 132.7, 131.5, 130.9, 128.2, 127.8, 127.6, 127.1, 126.9, 126.5, 126.3, 98.3, 61.3, 13.8. HR-MS (ESI) [M+H]<sup>+</sup> *m/z* calcd for C<sub>19</sub>H<sub>16</sub>I<sub>2</sub>O<sub>2</sub> 403.0195, found 403.0186.

### ethyl 4-cyano-2-(naphthalen-2-yl) benzoate (**3ga**)



According to the general procedure (PE/EtOAc = 10/1), **3ga** was obtained in 67% yield (20 mg). Brown solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.93 (d, *J* = 8.0 Hz, 1H), 7.88 (m, 3H), 7.79 (s, 2H), 7.73 (m, 1H), 7.54 (m, 2H), 7.40 (m, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 0.90 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 167.5, 143.3, 136.7, 135.7, 134.5, 133.3, 132.9, 130.8, 130.5, 128.3, 128.1, 127.9, 127.4, 126.8, 126.8, 126.4, 118.1, 115.0, 61.8, 13.7. HR-MS (ESI) [M+H]<sup>+</sup> *m/z* calcd for C<sub>20</sub>H<sub>16</sub>NO<sub>2</sub> 302.1181, found 302.1183.

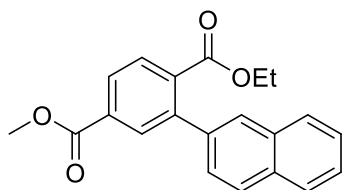
### ethyl 2-(naphthalen-2-yl)-4-(trifluoromethyl) benzoate (**3ha**)



According to the general procedure (PE/EtOAc = 20/1), **3ha** was obtained in 82% yield (28 mg). Light yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.16 (s, 1H), 7.88 (m, 3H), 7.81 (m, 2H), 7.61 (m, 1H), 7.53 (m, 2H), 7.43 (dd, *J* = 8.4, 1.5 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 0.93 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.6, 146.0, 137.7, 133.2, 132.8, 132.2, 131.7, 129.8 (q, *J* = 33.3 Hz), 128.2, 127.9, 127.9 (q, *J* = 4.0 Hz), 127.9, 127.8, 127.2, 127.1 (q, *J* = 3.0 Hz), 126.7, 126.6, 123.9 (q, *J* = 273.7 Hz), 61.6, 13.8. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) δ -62.90. HR-MS (ESI) [M+H]<sup>+</sup> *m/z* calcd for C<sub>20</sub>H<sub>16</sub>F<sub>3</sub>O<sub>2</sub> 345.1102, found

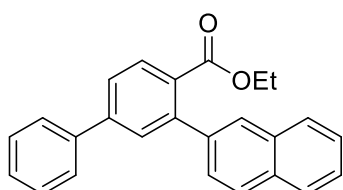
345.1101.

**1-ethyl 4-methyl 2-(naphthalen-2-yl) terephthalate (3ia)**



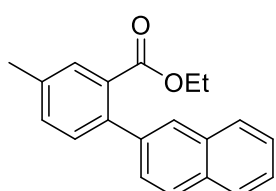
According to the general procedure (PE/EtOAc = 10/1), **3ia** was obtained in 51% yield (17 mg). Light yellow oil.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.17 (m, 1H), 8.10 (dd,  $J$  = 8.1, 1.6 Hz, 1H), 7.91 (m, 1H), 7.87 (m, 3H), 7.82 (s, 1H), 7.51 (m, 2H), 7.45 (dd,  $J$  = 8.4, 1.7 Hz, 1H), 4.08 (m, 2H), 3.96 (s, 3H), 0.91 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  168.3, 166.4, 142.5, 138.1, 135.6, 133.4, 132.8, 132.5, 132.1, 123.0, 128.3, 128.2, 127.8, 127.8, 127.3, 126.9, 126.5, 126.3, 61.5, 52.6, 13.8. HR-MS (ESI)  $[\text{M}+\text{H}]^+$   $m/z$  calcd for  $\text{C}_{21}\text{H}_{19}\text{O}_4$  335.1283, found 335.1285.

**ethyl 3-(naphthalen-2-yl)-[1,1'-biphenyl]-4-carboxylate (3ja)**



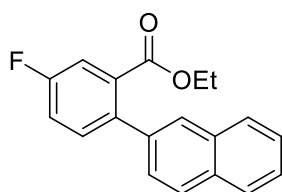
According to the general procedure (PE/EtOAc = 20/1), **3ja** was obtained in 63% yield (22 mg). Light yellow oil.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 (d,  $J$  = 8.0 Hz, 1H), 7.74 (m, 4H), 7.55 (m, 4H), 7.38 (m, 3H), 7.33 (t,  $J$  = 7.6 Hz, 2H), 7.26 (m, 1H), 3.96 (q,  $J$  = 7.1 Hz, 2H), 0.79 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  168.5, 144.2, 143.3, 140.0, 139.3, 133.4, 132.6, 130.8, 130.0, 129.9, 129.1, 128.2, 128.2, 127.8, 127.5, 127.4, 127.3, 127.1, 126.3, 126.1, 126.0, 61.0, 13.8. HR-MS (ESI)  $[\text{M}+\text{H}]^+$   $m/z$  calcd for  $\text{C}_{25}\text{H}_{21}\text{O}_2$  353.1542, found 353.1545.

**ethyl 5-methyl-2-(naphthalen-2-yl) benzoate (3ka)**



According to the general procedure (PE/EtOAc = 20/1), **3ka** was obtained in 80% yield (23 mg). Light yellow oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 (m, 3H), 7.78 (s, 1H), 7.70 (s, 1H), 7.50 (m, 2H), 7.44 (dd,  $J$  = 8.4, 1.6 Hz, 1H), 7.38 (m, 2H), 4.07 (q,  $J$  = 7.1 Hz, 2H), 2.46 (s, 3H), 0.90 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  169.1, 139.6, 139.1, 137.3, 133.4, 132.5, 132.1, 131.3, 131.0, 130.5, 128.1, 127.8, 127.4, 127.4, 127.0, 126.3, 125.9, 61.1, 21.1, 13.8. HR-MS (ESI)  $[\text{M}+\text{H}]^+$   $m/z$  calcd for  $\text{C}_{20}\text{H}_{19}\text{O}_2$  291.1385, found 291.1386.

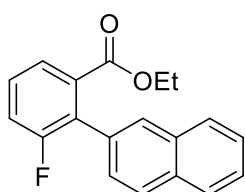
**ethyl 5-fluoro-2-(naphthalen-2-yl) benzoate (3la)**



According to the general procedure (PE/EtOAc = 20/1), **3la** was obtained in 21% yield (6 mg). Light yellow oil.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 (m, 3H), 7.75 (s, 1H), 7.60 (dd,  $J$  = 9.0, 2.7 Hz, 1H), 7.50 (m, 2H), 7.43 (m, 2H), 7.27 (m, 1H), 4.07 (q,  $J$  = 7.1 Hz, 2H), 0.91 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  167.5 (d,  $J$  = 2.5 Hz), 161.0 (d,  $J$  = 248.2 Hz), 138.7 (d,  $J$  = 3.8 Hz), 138.2, 133.3, 133.0 (d,  $J$  = 7.6 Hz),

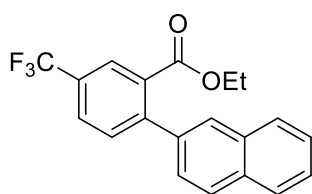
132.9 (d,  $J = 7.6$  Hz), 132.6, 128.1 127.8, 127.6, 127.2, 127.2, 126.5, 126.2, 118.4 (d,  $J = 21.4$  Hz), 116.9 (d,  $J = 23.9$  Hz), 61.4, 13.8.  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -114.61. HR-MS (ESI)  $[\text{M}+\text{H}]^+$   $m/z$  calcd for  $\text{C}_{19}\text{H}_{16}\text{FO}_2$  295.1134, found 295.1141.

#### ethyl 3-fluoro-2-(naphthalen-2-yl) benzoate (**3la'**)



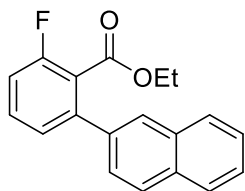
According to the general procedure (PE/EtOAc = 20/1), **3la'** was obtained in 62% yield (18 mg). Light yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (m, 2H), 7.86 (m, 1H), 7.79 (s, 1H), 7.71 (d,  $J = 7.7$  Hz, 1H), 7.52 (m, 2H), 7.44 (m, 2H), 7.33 (t,  $J = 8.7$  Hz, 1H), 4.01 (q,  $J = 7.1$  Hz, 2H), 0.82 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  167.5 (d,  $J = 3.8$  Hz), 160.0 (d,  $J = 246.9$  Hz), 134.1 (d,  $J = 2.5$  Hz), 133.2, 132.8, 131.8, 129.9 (d,  $J = 18.9$  Hz), 129.0, 128.9, 128.4, 128.2, 127.8, 127.9, 127.5, 126.3, 125.5 (d,  $J = 3.8$  Hz), 118.9 (d,  $J = 23.9$  Hz), 61.2, 13.6.  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -114.20. HR-MS (ESI)  $[\text{M}+\text{H}]^+$   $m/z$  calcd for  $\text{C}_{19}\text{H}_{16}\text{FO}_2$  295.1134, found 295.1131.

#### ethyl 2-(naphthalen-2-yl)-5-(trifluoromethyl) benzoate (**3ma**)



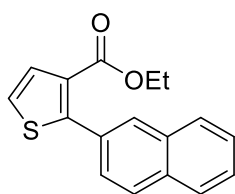
According to the general procedure (PE/EtOAc = 20/1), **3ma** was obtained in 79% yield (27 mg). Light yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (d,  $J = 8.1$  Hz, 1H), 7.89 (m, 3H), 7.82 (m, 1H), 7.76 (s, 1H), 7.71 (m, 1H), 7.53 (m, 2H), 7.45 (dd,  $J = 8.4, 1.8$  Hz, 1H), 4.09 (q,  $J = 7.1$  Hz, 2H), 0.91 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  167.6, 146.0, 137.8, 133.3, 132.9, 132.2, 131.7, 129.8 (q,  $J = 32.8$  Hz), 128.3, 127.9, 127.9, 127.9 (q,  $J = 3.8$  Hz), 127.9, 127.3, 127.1 (q,  $J = 3.8$  Hz), 126.7, 126.6, 123.9 (q,  $J = 272.2$  Hz), 61.6, 13.8.  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.55. HR-MS (ESI)  $[\text{M}+\text{H}]^+$   $m/z$  calcd for  $\text{C}_{20}\text{H}_{16}\text{F}_3\text{O}_2$  345.1102, found 345.1097.

#### ethyl 2-fluoro-6-(naphthalen-2-yl) benzoate (**3na**)



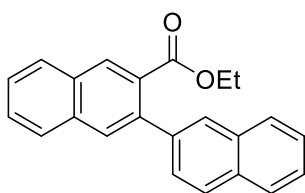
According to the general procedure (PE/EtOAc = 20/1), **3na** was obtained in 58% yield (17 mg). Light yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 (m, 4H), 7.51 (m, 3H), 7.47 (m, 1H), 7.30 (d,  $J = 7.7$  Hz, 1H), 7.16 (t,  $J = 8.8$  Hz, 1H), 4.13 (q,  $J = 7.1$  Hz, 2H), 0.97 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  165.8, 159.9 (d,  $J = 252.0$  Hz), 142.6 (d,  $J = 2.5$  Hz), 137.0, 133.1, 132.9, 131.3, 131.2, 128.3, 128.2, 127.8, 127.5, 126.6, 126.5 (d,  $J = 3.8$  Hz), 125.9 (d,  $J = 2.5$  Hz), 122.2 (d,  $J = 16.4$  Hz), 114.9 (d,  $J = 21.4$  Hz), 61.7, 13.9.  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -115.38. HR-MS (ESI)  $[\text{M}+\text{H}]^+$   $m/z$  calcd for  $\text{C}_{19}\text{H}_{16}\text{FO}_2$  295.1134, found 295.1127.

### ethyl 4-(naphthalen-2-yl) thiophene-3-carboxylate (3oa)



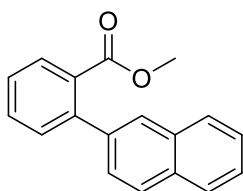
According to the general procedure (PE/EtOAc = 20/1), **3oa** was obtained in 64% yield (18 mg). Light yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (s, 1H), 7.87 (m, 3H), 7.63 (dd,  $J$  = 8.5, 1.5 Hz, 1H), 7.59 (d,  $J$  = 5.4 Hz, 1H), 7.52 (m, 2H), 7.29 (d,  $J$  = 5.4 Hz, 1H), 4.22 (q,  $J$  = 7.1 Hz, 2H), 1.17 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  163.5, 150.8, 133.2, 133.0, 131.1, 130.3, 128.9, 128.6, 128.3, 128.1, 127.8, 127.4, 126.7, 126.5, 124.3, 60.6, 14.2. HR-MS (ESI)  $[\text{M}+\text{H}]^+$   $m/z$  calcd for  $\text{C}_{17}\text{H}_{15}\text{O}_2\text{S}$  283.0793, found 283.0787.

### ethyl [2,2'-binaphthalene]-3-carboxylate (3pa)



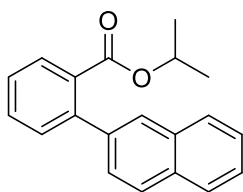
According to the general procedure (PE/EtOAc = 20/1), **3pa** was obtained in 74% yield (24 mg). Light yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.46 (s, 1H), 7.98 (d,  $J$  = 8.2 Hz, 1H), 7.93 (s, 1H), 7.90 (m, 5H), 7.60 (m, 2H), 7.53 (m, 3H), 4.13 (q,  $J$  = 7.1 Hz, 2H), 0.95 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  168.8, 139.4, 138.9, 134.5, 133.5, 132.6, 131.8, 131.2, 130.2, 129.7, 128.8, 128.4, 128.2, 130.0, 127.8, 127.5, 127.5, 127.1, 126.9, 126.4, 126.0, 61.2, 13.9. HR-MS (ESI)  $[\text{M}+\text{H}]^+$   $m/z$  calcd for  $\text{C}_{23}\text{H}_{19}\text{O}_2$  327.1385, found 327.1386.

### methyl 2-(naphthalen-2-yl) benzoate (3qa)



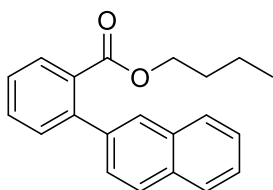
According to the general procedure (PE/EtOAc = 20/1), **3qa** was obtained in 73% yield (19 mg). Light yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89 (m, 4H), 7.82 (s, 1H), 7.58 (m, 1H), 7.49 (m, 5H), 3.62 (d,  $J$  = 2.5 Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  169.3, 142.6, 139.1, 133.4, 132.6, 131.5, 131.2, 131.1, 130.1, 128.2, 127.8, 127.5, 127.4, 127.1, 127.0, 126.3, 126.1, 52.1. HR-MS (ESI)  $[\text{M}+\text{Na}]^+$   $m/z$  calcd for  $\text{C}_{18}\text{H}_{14}\text{NaO}_2$  285.0892, found 285.0890.

### isopropyl 2-(naphthalen-2-yl) benzoate (3ra)



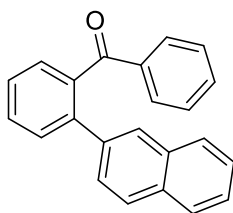
According to the general procedure (PE/EtOAc = 20/1), **3ra** was obtained in 52% yield (15 mg). Light yellow oil.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 (m, 4H), 7.78 (s, 1H), 7.55 (m, 1H), 7.50 (m, 2H), 7.45 (m, 3H), 4.96 (p,  $J$  = 6.2 Hz, 1H), 0.93 (d,  $J$  = 6.3 Hz, 6H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  168.5, 142.3, 139.2, 133.3, 132.6, 132.1, 131.2, 131.0, 129.8, 128.1, 127.8, 127.6, 127.4, 127.3, 127.2, 126.3, 126.0, 68.7, 21.5. HR-MS (ESI)  $[\text{M}+\text{H}]^+$   $m/z$  calcd for  $\text{C}_{20}\text{H}_{19}\text{O}_2$  291.1385, found 291.1386.

### butyl 2-(naphthalen-2-yl) benzoate (3sa)



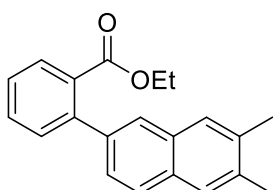
According to the general procedure (PE/EtOAc = 20/1), **3sa** was obtained in 60% yield (18 mg). Light yellow oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 (m, 4H), 7.79 (s, 1H), 7.57 (m, 1H), 7.47 (m, 5H), 4.01 (m, 2H), 1.21 (m, 2H), 0.88 (m, 2H), 0.57 (m, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  169.1, 142.5, 139.3, 133.4, 132.7, 131.7, 131.3, 131.1, 130.0, 128.2, 127.8, 127.6, 127.4, 127.2, 127.0, 126.3, 126.1, 65.1, 30.4, 19.0, 13.5. HR-MS (ESI)  $[\text{M}+\text{Na}]^+$   $m/z$  calcd for  $\text{C}_{21}\text{H}_{20}\text{NaO}_2$  327.1361, found 327.1358.

### (2-(naphthalen-2-yl)phenyl)(phenyl)methanone (3ta)



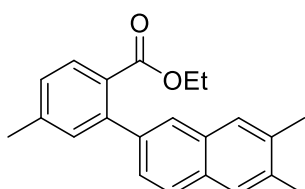
According to the general procedure (PE/EtOAc = 20/1), **3ta** was obtained in 72% yield (22 mg). Brown solid.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 (m, 3H), 7.68 (m, 3H), 7.60 (m, 3H), 7.51 (m, 1H), 7.43 (m, 3H), 7.34 (m, 1H), 7.22 (m, 2H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  198.9, 141.2, 139.3, 137.8, 137.5, 133.2, 132.9, 132.4, 130.5, 129.9, 130.0, 128.3, 128.2, 128.2, 128.1, 127.6, 127.2, 127.1, 126.3, 126.1. HR-MS (ESI)  $[\text{M}+\text{H}]^+$   $m/z$  calcd for  $\text{C}_{23}\text{H}_{17}\text{O}$  309.1279, found 309.1271.

### ethyl 2-(6,7-dimethylnaphthalen-2-yl) benzoate (3ab)



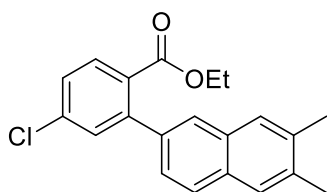
According to the general procedure (PE/EtOAc = 20/1), **3ab** was obtained in 86% yield (26 mg). Light yellow oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 (d,  $J$  = 7.7 Hz, 1H), 7.74 (d,  $J$  = 8.4 Hz, 1H), 7.69 (s, 1H), 7.61 (d,  $J$  = 7.9 Hz, 2H), 7.56 (m, 1H), 7.45 (m, 2H), 7.36 (dd,  $J$  = 8.4, 1.5 Hz, 1H), 4.06 (q,  $J$  = 7.1 Hz, 2H), 2.45 (d,  $J$  = 2.5 Hz, 6H), 0.88 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  169.2, 142.7, 138.2, 136.0, 135.8, 132.3, 131.6, 131.5, 131.2, 131.0, 129.9, 127.6, 127.3, 127.2, 126.5, 126.3, 126.1, 61.1, 20.4, 13.8. HR-MS (ESI)  $[\text{M}+\text{H}]^+$   $m/z$  calcd for  $\text{C}_{21}\text{H}_{21}\text{O}_2$  305.1542, found 305.1528.

### ethyl 2-(6,7-dimethylnaphthalen-2-yl)-4-methylbenzoate (3bb)



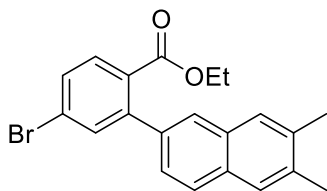
According to the general procedure (PE/EtOAc = 20/1), **3bb** was obtained in 85% yield (27 mg). Light yellow oil.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (d,  $J$  = 7.9 Hz, 1H), 7.71 (d,  $J$  = 8.4 Hz, 1H), 7.65 (s, 1H), 7.59 (d,  $J$  = 9.9 Hz, 2H), 7.33 (dd,  $J$  = 8.4, 1.6 Hz, 1H), 7.25 (d,  $J$  = 5.1 Hz, 1H), 7.23 (d,  $J$  = 8.0 Hz, 1H), 4.03 (q,  $J$  = 7.1 Hz, 2H), 2.44 (s, 3H), 2.43 (s, 3H), 2.43 (s, 3H), 0.87 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  169.0, 143.0, 141.7, 138.6, 135.9, 135.7, 132.3, 131.9, 131.5, 130.2, 128.7, 127.9, 127.7, 127.3, 126.5, 126.4, 126.0, 60.8, 21.6, 20.3, 13.8. HR-MS (ESI)  $[\text{M}+\text{H}]^+$   $m/z$  calcd for  $\text{C}_{22}\text{H}_{23}\text{O}_2$  319.1698, found 319.1699.

### ethyl 4-chloro-2-(6,7-dimethylnaphthalen-2-yl) benzoate (**3db**)



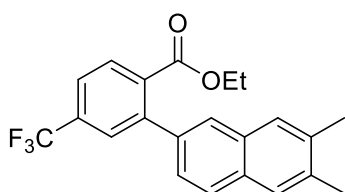
According to the general procedure (PE/EtOAc = 20/1), **3db** was obtained in 77% yield (26 mg). White solid.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 (d,  $J = 8.3$  Hz, 1H), 7.73 (d,  $J = 8.4$  Hz, 1H), 7.65 (s, 1H), 7.61 (d,  $J = 10.9$  Hz, 2H), 7.47 (d,  $J = 2.0$  Hz, 1H), 7.40 (dd,  $J = 8.3, 2.1$  Hz, 1H), 7.31 (dd,  $J = 8.4, 1.5$  Hz, 1H), 4.05 (q,  $J = 7.1$  Hz, 2H), 2.45 (s, 3H), 2.44 (s, 3H), 0.88 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  168.1, 144.7, 137.3, 137.0, 136.2, 136.2, 132.2, 131.7, 131.5, 131.1, 130.0, 127.7, 127.3, 126.7, 126.2, 126.0, 61.2, 20.3, 13.8. HR-MS (ESI)  $[\text{M}+\text{H}]^+$   $m/z$  calcd for  $\text{C}_{21}\text{H}_{20}\text{ClO}_2$  339.1152, found 339.1158.

### ethyl 4-bromo-2-(6,7-dimethylnaphthalen-2-yl) benzoate (**3eb**)



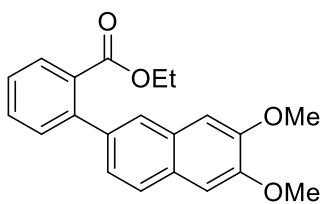
According to the general procedure (PE/EtOAc = 20/1), **3eb** was obtained in 76% yield (29 mg). Light yellow solid.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73 (dd,  $J = 8.3, 1.7$  Hz, 2H), 7.63 (m, 4H), 7.56 (dd,  $J = 8.3, 2.0$  Hz, 1H), 7.30 (dd,  $J = 8.4, 1.7$  Hz, 1H), 4.04 (q,  $J = 7.1$  Hz, 2H), 2.45 (s, 3H), 2.44 (s, 3H), 0.87 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  168.3, 144.7, 136.9, 136.3, 136.2, 134.0, 132.2, 131.7, 131.5, 130.4, 130.3, 127.7, 127.3, 126.7, 126.2, 126.0, 125.7, 61.3, 20.4, 13.8. HR-MS (ESI)  $[\text{M}+\text{H}]^+$   $m/z$  calcd for  $\text{C}_{21}\text{H}_{20}\text{BrO}_2$  383.0647, found 383.0641.

### ethyl 2-(6,7-dimethylnaphthalen-2-yl)-4-(trifluoromethyl) benzoate (**3hb**)



According to the general procedure (PE/EtOAc = 20/1), **3hb** was obtained in 62% yield (23 mg). Light yellow solid.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 (d,  $J = 8.1$  Hz, 1H), 7.76 (m, 2H), 7.68 (m, 2H), 7.62 (d,  $J = 7.8$  Hz, 2H), 7.34 (dd,  $J = 8.4, 1.6$  Hz, 1H), 4.07 (q,  $J = 7.1$  Hz, 2H), 2.46 (s, 3H), 2.45 (s, 3H), 0.89 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  168.1, 143.1, 136.5, 136.3, 136.2, 135.0, 132.8 (d,  $J = 32.8$  Hz), 132.1, 131.7, 130.1, 127.7 (q,  $J = 3.8$  Hz), 127.6, 127.2, 126.8, 126.2, 125.7, 123.8 (q,  $J = 3.8$  Hz), 123.7 (q,  $J = 273.4$  Hz), 61.4, 20.2, 20.2, 13.6.  $^{19}\text{F NMR}$  (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.92. HR-MS (ESI)  $[\text{M}+\text{H}]^+$   $m/z$  calcd for  $\text{C}_{22}\text{H}_{20}\text{F}_3\text{O}_2$  373.1415, found 373.1426.

### ethyl 2-(6,7-dimethoxynaphthalen-2-yl) benzoate (**3ac**)

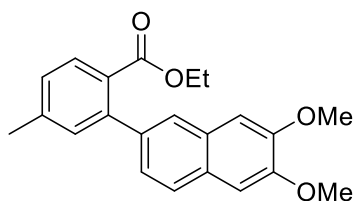


According to the general procedure (PE/EtOAc = 5/1), **3ac** was obtained in 81% yield (27 mg). White solid.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 (m, 1H), 7.70 (d,  $J = 8.3$  Hz, 1H), 7.64 (m, 1H), 7.54 (td,  $J = 7.6, 1.3$  Hz, 1H), 7.44 (m, 2H), 7.30 (dd,  $J = 8.3, 1.7$  Hz, 1H), 7.14 (d,  $J = 9.0$  Hz, 2H), 4.07



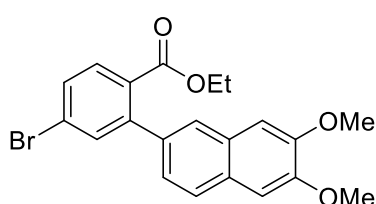
(m, 2H), 4.02 (s, 3H), 4.00 (s, 3H), 0.89 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  169.2, 149.9, 149.7, 142.6, 137.5, 131.7, 131.2, 130.9, 129.8, 129.1, 128.3, 127.1, 126.0, 125.7, 125.4, 106.5, 106.2, 61.0, 56.0, 13.8. HR-MS (ESI)  $[\text{M}+\text{H}]^+$   $m/z$  calcd for  $\text{C}_{21}\text{H}_{21}\text{O}_4$  337.1440, found 337.1439.

#### ethyl 2-(6,7-dimethoxynaphthalen-2-yl)-4-methylbenzoate (**3bc**)



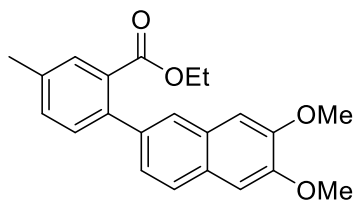
According to the general procedure (PE/EtOAc = 5/1), **3bc** was obtained in 78% yield (27 mg). White solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78 (d,  $J = 7.9$  Hz, 1H), 7.68 (d,  $J = 8.3$  Hz, 1H), 7.63 (s, 1H), 7.29 (dd,  $J = 8.3, 1.7$  Hz, 1H), 7.23 (d,  $J = 7.9$  Hz, 1H), 7.15 (s, 1H), 7.13 (s, 1H), 4.05 (m, 2H), 4.01 (s, 3H), 4.00 (s, 3H), 2.43 (s, 3H), 0.89 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  169.0, 149.9, 149.7, 142.9, 141.6, 137.8, 131.8, 130.1, 129.1, 128.6, 128.3, 127.8, 125.8, 125.6, 125.6, 106.6, 106.3, 60.8, 56.0, 56.0, 21.6, 13.8. HR-MS (ESI)  $[\text{M}+\text{H}]^+$   $m/z$  calcd for  $\text{C}_{22}\text{H}_{23}\text{O}_4$  351.1596, found 351.1599.

#### ethyl 4-bromo-2-(6,7-dimethoxynaphthalen-2-yl) benzoate (**3ec**)



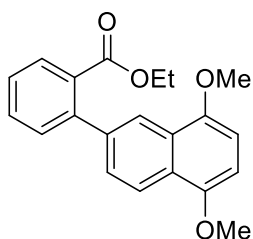
According to the general procedure (PE/EtOAc = 5/1), **3ec** was obtained in 76% yield (32 mg). White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72 (m, 2H), 7.64 (s, 2H), 7.56 (d,  $J = 8.2$  Hz, 1H), 7.27 (d,  $J = 7.5$  Hz, 1H), 7.15 (d,  $J = 7.2$  Hz, 2H), 4.08 (m, 2H), 4.03 (s, 3H), 4.02 (s, 3H), 0.90 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  168.3, 150.0, 149.9, 144.7, 136.1, 133.9, 131.5, 130.4, 130.2, 129.0, 128.6, 126.1, 125.7, 125.7, 125.1, 106.6, 106.2, 61.2, 56.0, 13.8. HR-MS (ESI)  $[\text{M}+\text{H}]^+$   $m/z$  calcd for  $\text{C}_{21}\text{H}_{20}\text{BrO}_4$  415.0545, found 415.0549.

#### ethyl 2-(6,7-dimethoxynaphthalen-2-yl)-5-methylbenzoate (**3kc**)



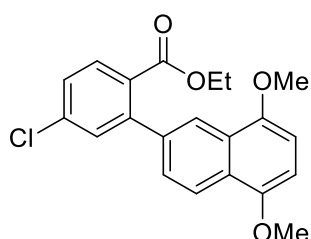
According to the general procedure (PE/EtOAc = 5/1), **3kc** was obtained in 78% yield (27 mg). White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67 (s, 1H), 7.64 (d,  $J = 11.7$  Hz, 2H), 7.35 (s, 2H), 7.29 (d,  $J = 8.3$  Hz, 1H), 7.13 (d,  $J = 8.8$  Hz, 2H), 4.07 (m, 2H), 4.01 (s, 3H), 4.00 (s, 3H), 2.44 (s, 3H), 0.89 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  169.4, 149.8, 149.6, 139.8, 137.4, 137.0, 131.9, 131.4, 130.8, 130.3, 129.1, 128.2, 125.9, 125.9, 125.6, 125.5, 106.5, 106.2, 61.0, 56.0, 21.0, 13.8. HR-MS (ESI)  $[\text{M}+\text{H}]^+$   $m/z$  calcd for  $\text{C}_{22}\text{H}_{23}\text{O}_4$  351.1596, found 351.1603.

### ethyl 2-(5,8-dimethoxynaphthalen-2-yl) benzoate (3ad)



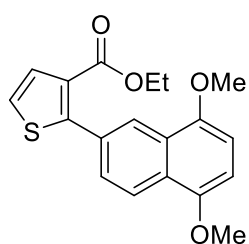
According to the general procedure (PE/EtOAc = 10/1), **3ad** was obtained in 75% yield (25 mg). Light yellow oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.23 (m, 1H), 8.18 (m, 1H), 7.87 (dd,  $J = 7.7, 1.1$  Hz, 1H), 7.55 (m, 1H), 7.49 (m, 2H), 7.44 (m, 1H), 6.72 (s, 2H), 4.07 (q,  $J = 7.1$  Hz, 2H), 3.98 (s, 3H), 3.94 (s, 3H), 0.92 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  169.0, 149.8, 149.6, 142.8, 139.1, 131.5, 131.3, 131.2, 129.9, 127.3, 127.0, 126.3, 125.4, 121.5, 121.3, 103.6, 103.4, 61.1, 55.9, 55.8, 13.8. HR-MS (ESI)  $[\text{M}+\text{H}]^+$   $m/z$  calcd for  $\text{C}_{21}\text{H}_{21}\text{O}_4$  337.1440, found 337.1427.

### ethyl 4-chloro-2-(5,8-dimethoxynaphthalen-2-yl) benzoate (3dd)



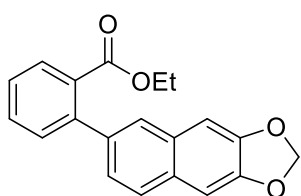
According to the general procedure (PE/EtOAc = 10/1), **3dd** was obtained in 63% yield (23 mg). Light yellow solid.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.21 (dd,  $J = 8.6, 0.6$  Hz, 1H), 8.16 (dd,  $J = 1.9, 0.6$  Hz, 1H), 7.83 (d,  $J = 8.3$  Hz, 1H), 7.49 (d,  $J = 2.0$  Hz, 1H), 7.41 (m, 2H), 6.73 (s, 2H), 4.05 (q,  $J = 7.1$  Hz, 2H), 3.98 (s, 3H), 3.95 (s, 3H), 0.91 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  168.0, 149.8, 149.5, 144.7, 137.8, 137.3, 131.5, 131.2, 129.8, 127.4, 126.7, 126.2, 125.6, 121.7, 121.3, 103.8, 103.7, 61.3, 55.9, 55.8, 13.8. HR-MS (ESI)  $[\text{M}+\text{H}]^+$   $m/z$  calcd for  $\text{C}_{21}\text{H}_{20}\text{ClO}_4$  371.1050, found 371.1049.

### ethyl 4-(5,8-dimethoxynaphthalen-2-yl) thiophene-3-carboxylate (3od)



According to the general procedure (PE/EtOAc = 10/1), **3od** was obtained in 71% yield (24 mg). Light yellow oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.37-8.30 (m, 1H), 8.21 (m, 1H), 7.62 (dd,  $J = 8.7, 1.8$  Hz, 1H), 7.56 (d,  $J = 5.4$  Hz, 1H), 7.27 (d,  $J = 5.3$  Hz, 1H), 6.73 (d,  $J = 1.3$  Hz, 2H), 4.18 (q,  $J = 7.1$  Hz, 2H), 3.97 (s, 3H), 3.95 (s, 3H), 1.13 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.7, 151.1, 149.8, 149.6, 131.1, 130.2, 128.7, 127.9, 126.0, 125.9, 124.3, 123.1, 121.5, 104.2, 103.8, 60.7, 55.9, 55.8, 14.1. HR-MS (ESI)  $[\text{M}+\text{H}]^+$   $m/z$  calcd for  $\text{C}_{19}\text{H}_{19}\text{O}_4\text{S}$  343.1004, found 343.1002.

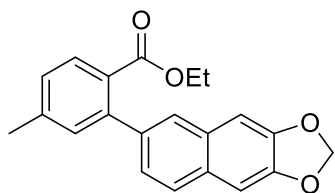
### ethyl 2-(naphtho[2,3-*d*][1,3]dioxol-6-yl)benzoate (3ae)



According to the general procedure (PE/EtOAc = 10/1), **3ae** was obtained in 82% yield (26 mg). Light yellow oil.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (d,  $J = 7.6$  Hz, 1H), 7.67 (d,  $J = 8.3$  Hz, 1H), 7.61 (s, 1H), 7.54 (t,  $J = 7.5$  Hz, 1H), 7.43 (m, 2H), 7.29 (dd,  $J = 8.3, 1.6$  Hz, 1H), 7.13 (d,  $J = 11.3$  Hz, 2H), 6.04 (s, 2H), 4.07 (q,  $J = 7.1$  Hz, 2H), 0.92 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  169.1, 148.0, 147.9,

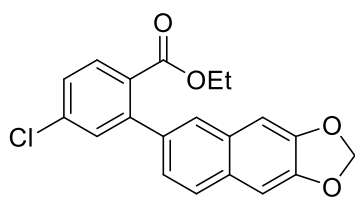
142.5, 137.7, 131.7, 131.2, 131.0, 130.4, 129.9, 129.7, 127.2, 126.7, 126.4, 125.6, 104.2, 103.9, 101.2, 61.1, 13.8. HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>20</sub>H<sub>17</sub>O<sub>4</sub> 321.1127, found 321.1121.

#### ethyl 4-methyl-2-(naphtho[2,3-*d*][1,3]dioxol-6-yl)benzoate (**3be**)



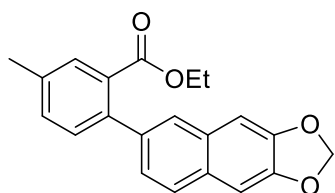
According to the general procedure (PE/EtOAc = 10/1), **3be** was obtained in 78% yield (26 mg). Light yellow oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.79 (d, *J* = 7.9 Hz, 1H), 7.65 (d, *J* = 8.3 Hz, 1H), 7.59 (s, 1H), 7.29 (m, 1H), 7.24 (m, 2H), 7.13 (d, *J* = 10.7 Hz, 2H), 6.04 (s, 2H), 4.06 (q, *J* = 7.1 Hz, 2H), 2.44 (s, 3H), 0.92 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 168.9, 148.0, 147.8, 142.8, 141.7, 138.0, 131.8, 130.4, 130.2, 129.6, 128.6, 127.9, 126.5, 126.3, 125.7, 104.1, 103.9, 101.1, 60.8, 21.6, 13.8. HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>21</sub>H<sub>19</sub>O<sub>4</sub> 335.1283, found 335.1277.

#### ethyl 4-chloro-2-(naphtho[2,3-*d*][1,3]dioxol-6-yl)benzoate (**3de**)



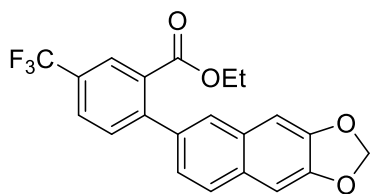
According to the general procedure (PE/EtOAc = 10/1), **3de** was obtained in 63% yield (22 mg). White solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.80 (d, *J* = 8.3 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 1.7 Hz, 1H), 7.45 (d, *J* = 2.1 Hz, 1H), 7.39 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.25 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.13 (d, *J* = 11.6 Hz, 2H), 6.05 (s, 2H), 4.06 (q, *J* = 7.1 Hz, 2H), 0.92 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 168.0, 148.2, 148.1, 144.4, 137.3, 136.5, 131.5, 131.0, 130.4, 129.9, 129.9, 127.3, 126.8, 126.4, 125.3, 104.2, 103.9, 101.3, 61.2, 13.8. HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>20</sub>H<sub>16</sub>ClO<sub>4</sub> 355.0737, found 355.0731.

#### ethyl 5-methyl-2-(naphtho[2,3-*d*][1,3]dioxol-6-yl)benzoate (**3ke**)



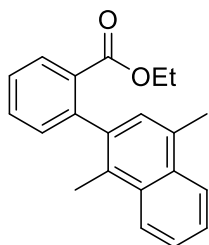
According to the general procedure (PE/EtOAc = 10/1), **3ke** was obtained in 69% yield (23 mg). Light yellow oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.66-7.63 (m, 2H), 7.59 (s, 1H), 7.34 (s, 2H), 7.27 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.12 (d, *J* = 11.2 Hz, 2H), 6.04 (s, 2H), 4.06 (q, *J* = 7.1 Hz, 2H), 2.44 (s, 3H), 0.91 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 169.3, 148.0, 147.8, 139.7, 137.7, 137.1, 132.0, 131.4, 130.9, 130.4, 130.4, 129.6, 126.6, 126.4, 125.8, 104.1, 103.9, 101.2, 61.0, 21.1, 13.9. HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>21</sub>H<sub>19</sub>O<sub>4</sub> 335.1283, found 335.1281.

### ethyl 2-(naphtho[2,3-*d*][1,3]dioxol-6-yl)-5-(trifluoromethyl)benzoate (**3me**)



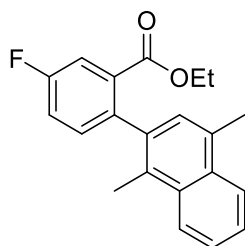
According to the general procedure (PE/EtOAc = 10/1), **3me** was obtained in 60% yield (23 mg). Light yellow oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.11 (s, 1H), 7.79 (m, 1H), 7.69 (d,  $J = 8.4$  Hz, 1H), 7.59 (m, 2H), 7.27 (m, 1H), 7.14 (d,  $J = 10.0$  Hz, 2H), 6.06 (s, 2H), 4.11 (q,  $J = 7.1$  Hz, 2H), 0.95 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.8, 148.3, 148.2, 146.0, 136.2, 132.3, 131.6, 130.4, 130.1, 129.6 (d,  $J = 33.3$  Hz), 127.7 (q,  $J = 3.0$  Hz), 127.0 (q,  $J = 3.0$  Hz), 126.9, 126.5, 125.1, 123.9 (q,  $J = 272.7$  Hz), 104.2, 103.9, 101.3, 61.6, 13.8.  $^{19}\text{F NMR}$  (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.58. HR-MS (ESI)  $[\text{M}+\text{H}]^+$   $m/z$  calcd for  $\text{C}_{21}\text{H}_{16}\text{F}_3\text{O}_4$  389.1001, found 389.0993.

### ethyl 2-(1,4-dimethylnaphthalen-2-yl) benzoate (**3af**)



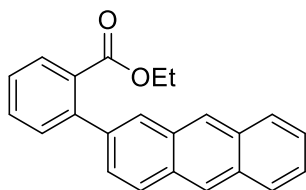
According to the general procedure (PE/EtOAc = 20/1), **3af** was obtained in 40% yield (12 mg). Light yellow oil.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.08 (m, 1H), 8.04 (m, 1H), 7.99 (m, 1H), 7.55 (m, 3H), 7.46 (m, 1H), 7.30 (m, 1H), 7.13 (s, 1H), 3.98 (q,  $J = 7.1$  Hz, 2H), 2.68 (s, 3H), 2.40 (s, 3H), 0.78 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  168.0, 143.5, 138.3, 132.9, 132.1, 131.4, 131.4, 131.4, 131.2, 130.0, 128.9, 128.4, 127.2, 125.8, 125.2, 125.0, 124.7, 60.8, 19.4, 16.1, 13.6. HR-MS (ESI)  $[\text{M}+\text{H}]^+$   $m/z$  calcd for  $\text{C}_{21}\text{H}_{21}\text{O}_2$  305.1542, found 305.1532.

### ethyl 2-(1,4-dimethylnaphthalen-2-yl)-5-fluorobenzoate (**3lf**)



According to the general procedure (PE/EtOAc = 20/1), **3lf** was obtained in 38% yield (12 mg). Light yellow oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.17 (m, 2H), 7.78 (d,  $J = 7.7$  Hz, 1H), 7.58-7.53 (m, 2H), 7.45 (m, 1H), 7.32 (t,  $J = 8.5$  Hz, 1H), 7.09 (s, 1H), 3.95 (q,  $J = 7.0$  Hz, 2H), 2.67 (s, 3H), 2.43 (s, 3H), 0.74 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  167.0 (d,  $J = 2.5$  Hz), 160.0 (d,  $J = 244.4$  Hz), 133.8 (d,  $J = 2.5$  Hz), 132.8, 132.5, 131.6, 130.7 (d,  $J = 3.8$  Hz), 130.5 (d,  $J = 8.8$  Hz), 128.9 (d,  $J = 8.8$  Hz), 128.2, 125.8, 125.7 (d,  $J = 3.8$  Hz), 125.5, 125.1, 124.8, 119.0, 118.9, 61.1, 19.4, 16.1, 13.5.  $^{19}\text{F NMR}$  (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -112.34. HR-MS (ESI)  $[\text{M}+\text{H}]^+$   $m/z$  calcd for  $\text{C}_{21}\text{H}_{20}\text{FO}_2$  323.1447, found 323.1440.

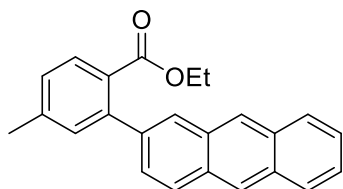
### ethyl 2-(anthracen-2-yl) benzoate (**3ag**)



According to the general procedure (PE/EtOAc = 20/1), **3ag** was obtained in 80% yield (26 mg). Light yellow solid.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.45 (d,  $J = 7.1$  Hz, 2H), 8.03 (m, 3H), 7.96 (m, 2H), 7.59 (m, 1H), 7.54 (m, 1H), 7.47 (m, 4H), 4.09 (q,  $J = 7.1$  Hz, 2H), 0.88 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C NMR}$  (101

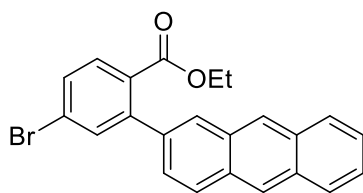
MHz, CDCl<sub>3</sub>) δ 168.9, 142.5, 138.7, 132.1, 131.9, 131.6, 131.5, 131.0, 130.8, 130.1, 128.3, 128.3, 127.7, 127.5, 127.3, 126.9, 126.6, 126.2, 125.6, 125.5, 61.1, 13.8. HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>23</sub>H<sub>19</sub>O<sub>2</sub> 327.1385, found 327.1381.

#### ethyl 2-(anthracen-2-yl)-4-methylbenzoate (**3bg**)



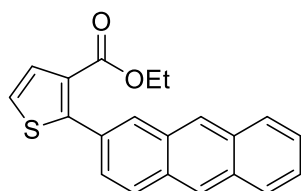
According to the general procedure (PE/EtOAc = 20/1), **3bg** was obtained in 77% yield (26 mg). Light yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.41 (d, *J* = 6.7 Hz, 2H), 7.98 (m, 3H), 7.91 (s, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.45 (m, 2H), 7.40 (dd, *J* = 8.7, 1.5 Hz, 1H), 7.30 (s, 1H), 7.25 (m, 1H), 4.03 (q, *J* = 7.1 Hz, 2H), 2.44 (s, 3H), 0.84 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 168.7, 142.8, 142.0, 139.1, 132.1, 131.9, 131.6, 130.8, 130.5, 128.4, 128.3, 128.3, 128.2, 127.5, 126.7, 126.5, 126.1, 125.5, 125.5, 60.9, 21.6, 13.8. HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>24</sub>H<sub>21</sub>O<sub>2</sub> 341.1542, found 341.1541.

#### ethyl 2-(anthracen-2-yl)-4-bromobenzoate (**3eg**)



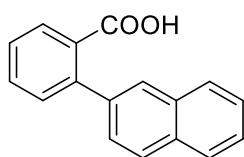
According to the general procedure (PE/EtOAc = 20/1), **3eg** was obtained in 62% yield (25 mg). Light yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.44 (d, *J* = 6.5 Hz, 2H), 8.02 (m, 3H), 7.93 (s, 1H), 7.80 (m, 1H), 7.70 (d, *J* = 1.9 Hz, 1H), 7.61 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.49 (m, 2H), 7.39 (dd, *J* = 8.7, 1.6 Hz, 1H), 4.06 (q, *J* = 7.1 Hz, 2H), 0.86 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 168.0, 144.5, 137.4, 134.0, 132.2, 132.1, 131.8, 131.4, 130.9, 130.6, 130.2, 128.3, 127.9, 127.1, 126.8, 126.7, 126.3, 126.0, 125.7, 61.3, 13.7. HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>23</sub>H<sub>18</sub>BrO<sub>2</sub> 405.0490, found 405.0488.

#### ethyl 4-(anthracen-2-yl) thiophene-3-carboxylate (**3og**)



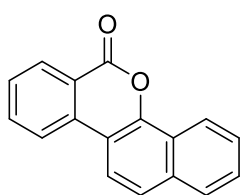
According to the general procedure (PE/EtOAc = 20/1), **3og** was obtained in 76% yield (25 mg). Light yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.44 (d, *J* = 4.0 Hz, 2H), 8.13 (s, 1H), 8.01 (m, 3H), 7.60 (m, 2H), 7.49 (m, 2H), 7.30 (d, *J* = 5.4 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 1.17 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.5, 150.9, 132.3, 132.1, 131.2, 131.1, 130.7, 130.4, 129.0, 128.7, 128.3, 128.3, 127.8, 127.6, 127.0, 126.2, 125.8, 125.7, 124.4, 60.7, 14.2. HR-MS (ESI) [M+H]<sup>+</sup> m/z calcd for C<sub>21</sub>H<sub>17</sub>O<sub>2</sub>S 333.0949, found 333.0948.

### 2-(naphthalen-2-yl) benzoic acid (**4aa**)<sup>17</sup>



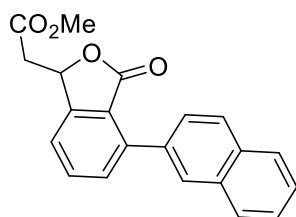
According to the general procedure (PE/(EtOAc/EtOH/AcOH=3/1/0.08) = 7/3), **4aa** was obtained in 69% yield (17 mg). White solid. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.94 (m, 3H), 7.87 (s, 1H), 7.80 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.62 (td, *J* = 7.6, 1.3 Hz, 1H), 7.51 (m, 5H). <sup>13</sup>C NMR (101 MHz, DMSO) δ 169.6, 141.2, 138.7, 132.9, 132.3, 132.1, 131.1, 130.9, 129.4, 128.0, 127.5, 127.5, 127.3, 127.2, 126.7, 126.3, 126.1. HR-MS (ESI) [M+H]<sup>+</sup> *m/z* calcd for C<sub>17</sub>H<sub>13</sub>O<sub>2</sub> 249.0916, found 249.0906.

### 6*H*-dibenzo[*c,h*]chromen-6-one (**5aa**)<sup>12</sup>



According to the general procedure (PE/EtOAc = 20/1), **5aa** was obtained in 90% yield (22 mg). White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.57 (m, 1H), 8.45 (m, 1H), 8.16 (d, *J* = 8.1 Hz, 1H), 8.03 (d, *J* = 8.8 Hz, 1H), 7.85 (m, 2H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.63 (dd, *J* = 6.9, 1.5 Hz, 1H), 7.61-7.55 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 161.3, 147.4, 135.5, 135.1, 134.4, 130.8, 128.7, 128.0, 127.8, 127.2, 124.6, 124.0, 122.4, 122.1, 121.3, 119.3, 113.1. HR-MS (ESI) [M+H]<sup>+</sup> *m/z* calcd for C<sub>17</sub>H<sub>11</sub>O<sub>2</sub> 247.0759, found 247.0754.

### methyl 2-(4-(naphthalen-2-yl)-3-oxo-1,3-dihydroisobenzofuran-1-yl) acetate (**6aa**)<sup>15</sup>



According to the general procedure (PE/EtOAc = 2/1), **6aa** was obtained in 49% yield (16 mg). Light yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.00 (m, 1H), 7.90 (m, 3H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.67 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.51 (m, 2H), 7.48 (d, *J* = 7.6 Hz, 1H), 5.91 (t, *J* = 6.6 Hz, 1H), 3.79 (s, 3H), 2.96 (d, *J* = 6.6 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 169.9, 168.7, 150.1, 142.9, 134.2, 133.9, 133.2, 133.1, 131.7, 128.7, 128.4, 127.8, 127.5, 127.4, 126.5, 126.3, 122.1, 120.8, 75.7, 52.3, 39.7. HR-MS (ESI) [M+H]<sup>+</sup> *m/z* calcd for C<sub>21</sub>H<sub>17</sub>O<sub>4</sub> 333.1127, found 333.1133.

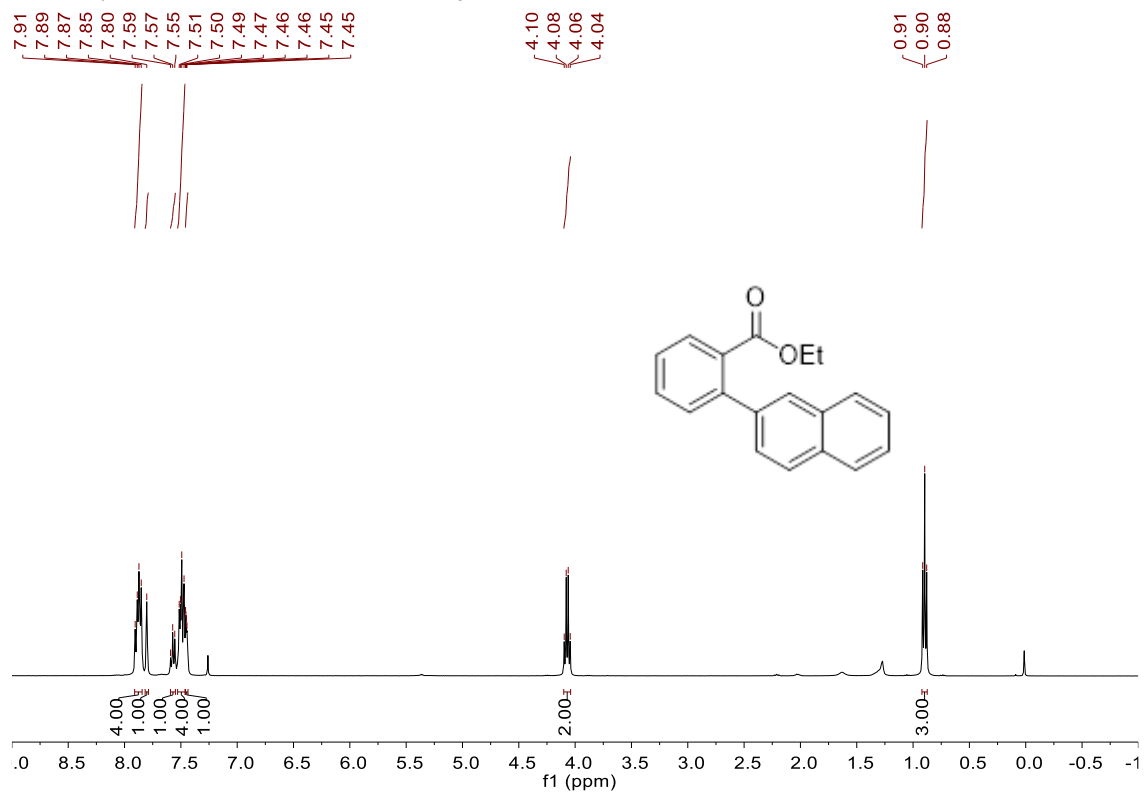
## VII. References

1. A. Thomas, An efficient, stereocontrolled and versatile synthetic route to bicyclic partially saturated privileged scaffolds. *Chem. Commun.*, 2020, **56**, 6818-6821.
2. B. Jiang, S. Wu, J. Zeng and X. Yang, Controllable Rh (III)-Catalyzed C–H Arylation and Dealcoholization: Access to Biphenyl-2-carbonitriles and Biphenyl-2-carbimides. *Org. Lett.*, 2018, **20**, 6573-6577.
3. E. A. Wappes, K. M. Nakafuku and D. A. Nagib, Directed β C–H amination of alcohols via radical relay chaperones. *J. Am. Chem. Soc.*, 2017, **139**, 10204-10207.
4. P. Gandeepan, P. Rajamalli, C. H. Cheng, Diastereoselective [3+2] Annulation of Aromatic/Vinylic Amides with Bicyclic Alkenes through Cobalt-Catalyzed C-H Activation and Intramolecular Nucleophilic Addition. *Angew. Chem. Int. Ed.*, 2016, **128**, 4380-4383.

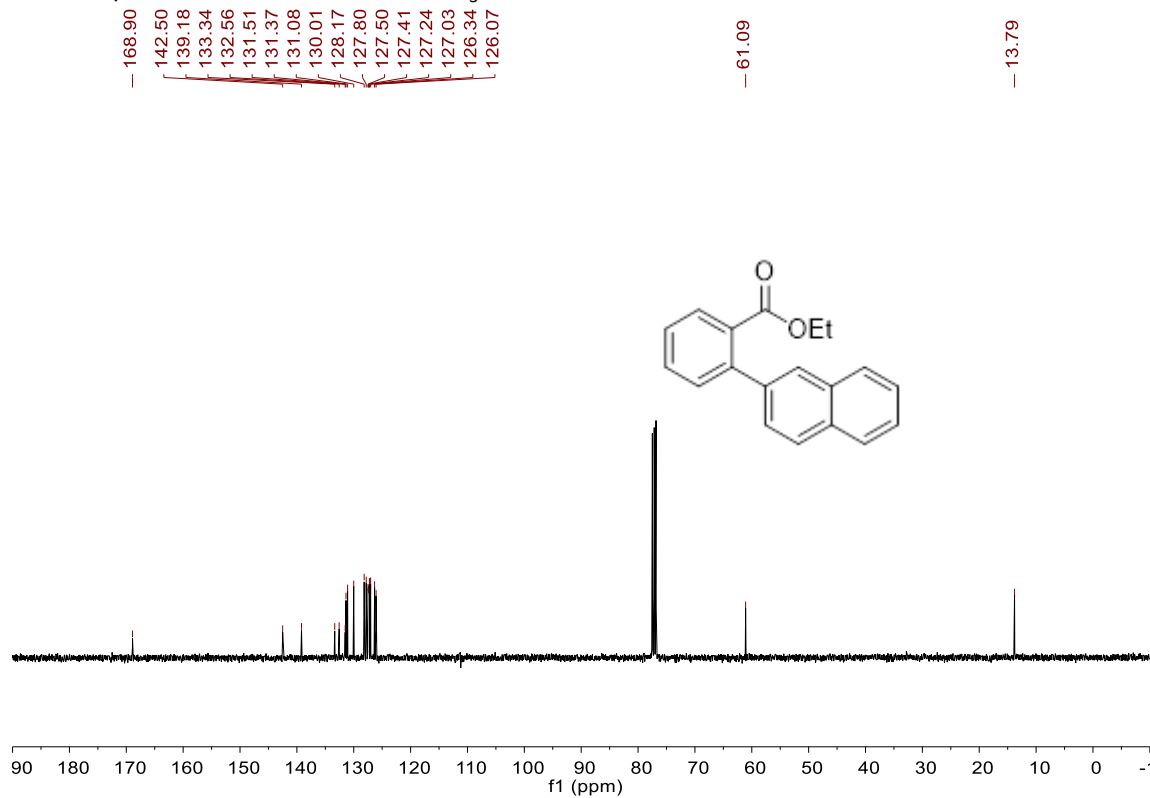
5. S. Qiu, S. Zhai, H. Wang, X. Chen and H. Zhai, One-pot synthesis of benzo [*b*] fluorenones via a cobalt-catalyzed MHP-directed [3+2] annulation/ring-opening/ dehydration sequence. *Chem. Commun.*, 2019, **55**, 4206-4209.
6. M. Lautens, K. Fagnou and D. Yang, Rhodium-catalyzed asymmetric ring opening reactions of oxabicyclic alkenes: Application of halide effects in the development of a general process. *J. Am. Chem. Soc.*, 2003, **125**, 14884-14892.
7. Z. Jin, Y. C. Teo, N. G. Zulaybar, M. D. Smith and Y. Xia, Streamlined synthesis of polycyclic conjugated hydrocarbons containing cyclobutadienoids via C–H activated annulation and aromatization. *J. Am. Chem. Soc.*, 2017, **139**, 1806-1809.
8. Y. Koseki, K. Kitazawa, M. Miyake, T. Kochi and F. Kakiuchi, Ruthenium-catalyzed ortho C–H arylation of aromatic nitriles with arylboronates and observation of partial para arylation. *J. Org. Chem.*, 2017, **82**, 6503-6510.
9. H. Wang, M. M. Lorion and L. Ackermann, Domino C–H/N–H allylations of imidates by cobalt catalysis. *ACS Catal.*, 2017, **7**, 3430-3433.
10. H. Gu, B. Yu, P. F. Zhang, and W. M. Xu, Organic Preparations and Procedures International: The New Journal for Organic Synthesis. *Org. Prep. Proced. Int.*, 2009, **41**, 162-164.
11. J. M. Khurana, A. Sehgal, An Efficient and Convenient Procedure for Ester Hydrolysis. *Org. Prep. Proced. Int.*, 1994, **26**, 580-583.
12. G. Tan, Q. You, J. Lan and J. You, Iridium-Catalyzed Annulation Reactions of Thiophenes with Carboxylic Acids: Direct Evidence for a Heck-type Pathway. *Angew. Chem. Int. Ed.* 2018, **57**, 6309-6313.
13. N. P. Ramirez, I. Bosque and J. C. Gonzalez-Gomez, Photocatalytic dehydrogenative lactonization of 2-arylbenzoic acids. *Org. Lett.*, 2015, **17**, 4550-4553.
14. M. Chao, F. Wang, L. Xu, Y. Ju, Z. Chen, B. Wang, P. Gong, J. You, M. Jin and D. Shen, Cerium Ammonium Nitrate-Mediated Access to Biaryl Lactones: Substrate Scopes and Mechanism Studies. *J. Org. Chem.*, 2021, **86**, 13371-13380.
15. Q. Jiang, C. Zhu, H. Zhao and W. Su, Rh(III)-Catalyzed C–H Olefination of Benzoic Acids under Mild Conditions using Oxygen as the Sole Oxidant. *Chem-Asian J.*, 2016, **11**, 356-359.
16. C. Wang, S. Rakshit and F. Glorius, Palladium-catalyzed intermolecular decarboxylative coupling of 2-phenylbenzoic acids with alkynes via C–H and C–C bond activation. *J. Am. Chem. Soc.*, 2010, **132**, 14006-14008.
17. M. Kawamura, Y. Mizuki, H. Ito, T. Hayama, T. Haketa, Anthracene derivative, organic electroluminescent (EL) element having it and electric device having it. WO2015033559A1, 2015.

## VIII. The $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of compounds

$^1\text{H}$  NMR spectrum of **3aa**, 400 MHz,  $\text{CDCl}_3$

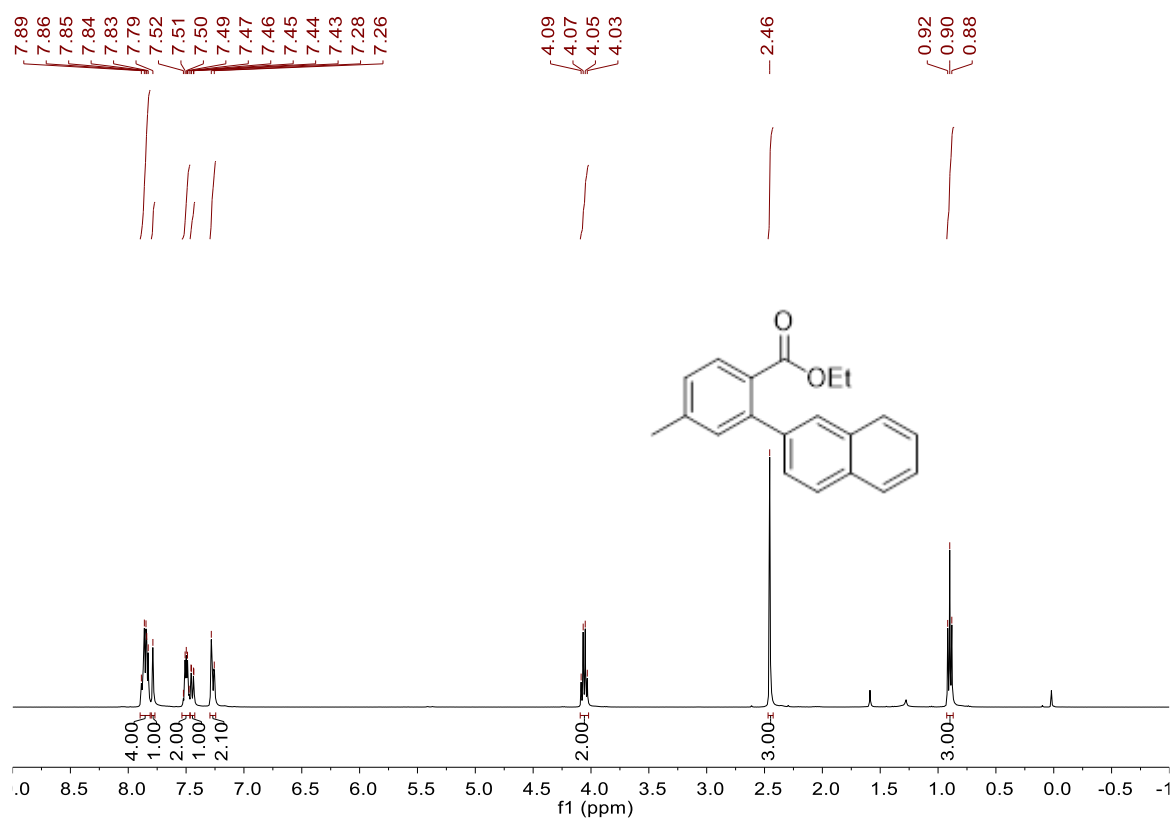


$^{13}\text{C}$  NMR spectrum of **3aa**, 101 MHz,  $\text{CDCl}_3$

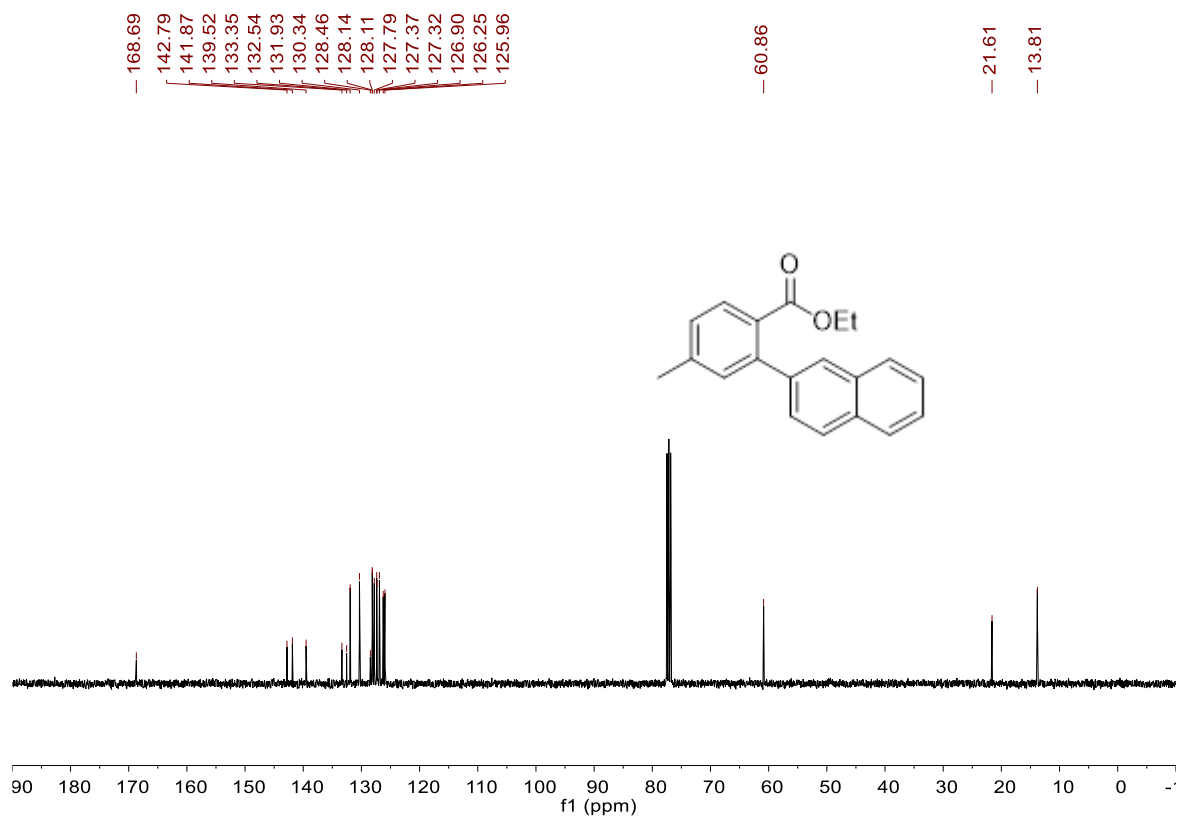




<sup>1</sup>H NMR spectrum of **3ba**, 400 MHz, CDCl<sub>3</sub>

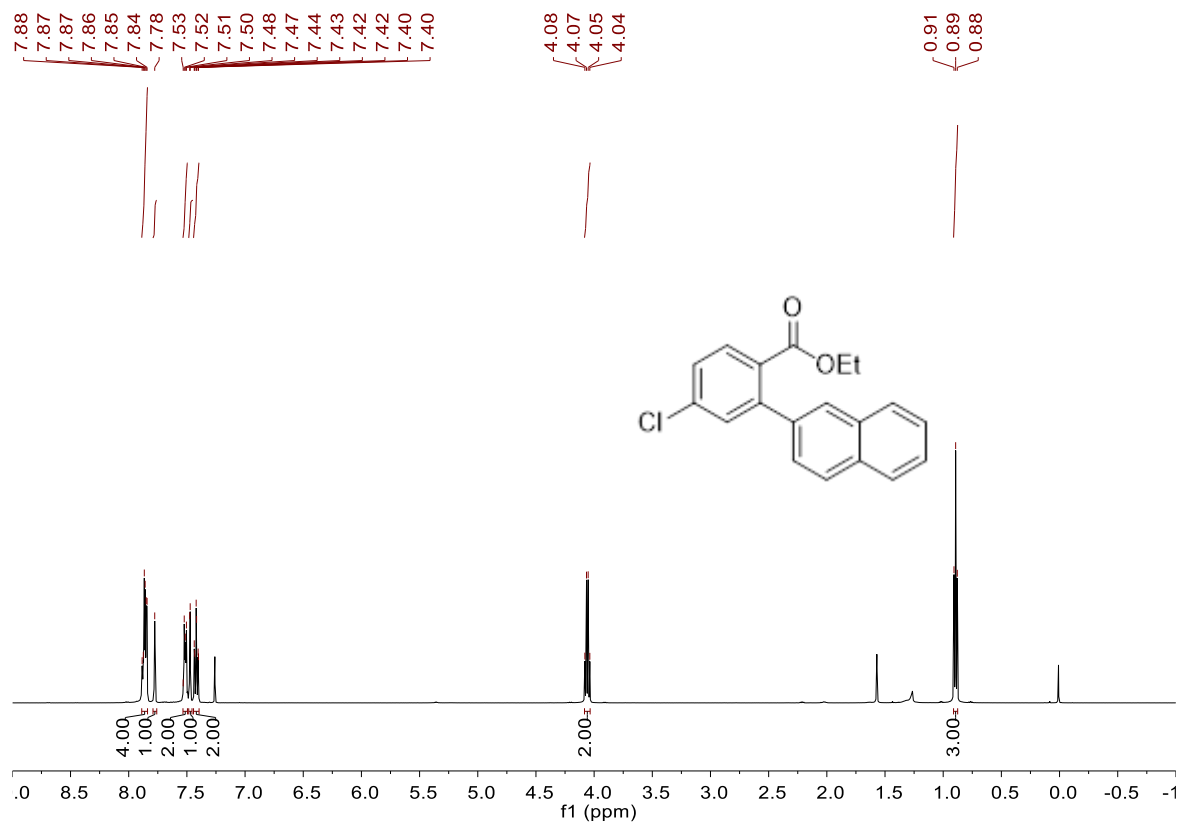


<sup>13</sup>C NMR spectrum of **3ba**, 101 MHz, CDCl<sub>3</sub>

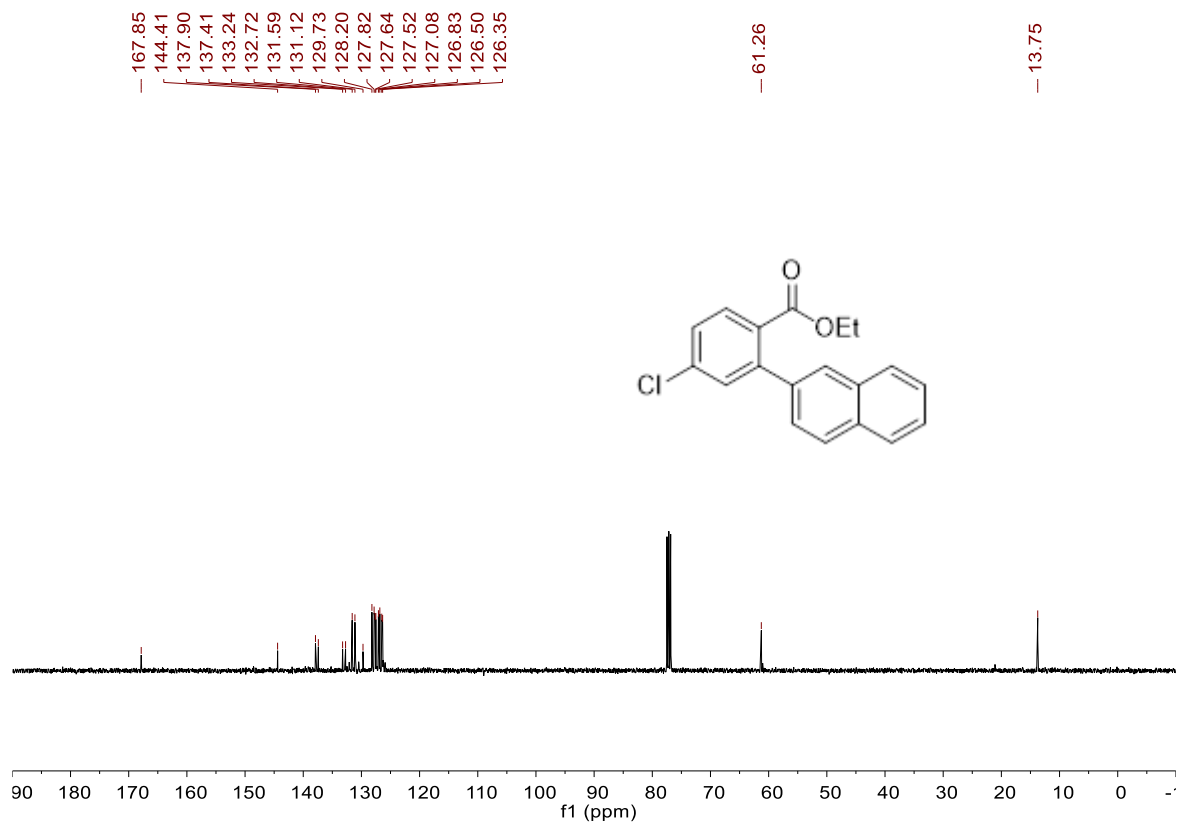




<sup>1</sup>H NMR spectrum of **3da**, 500 MHz, CDCl<sub>3</sub>

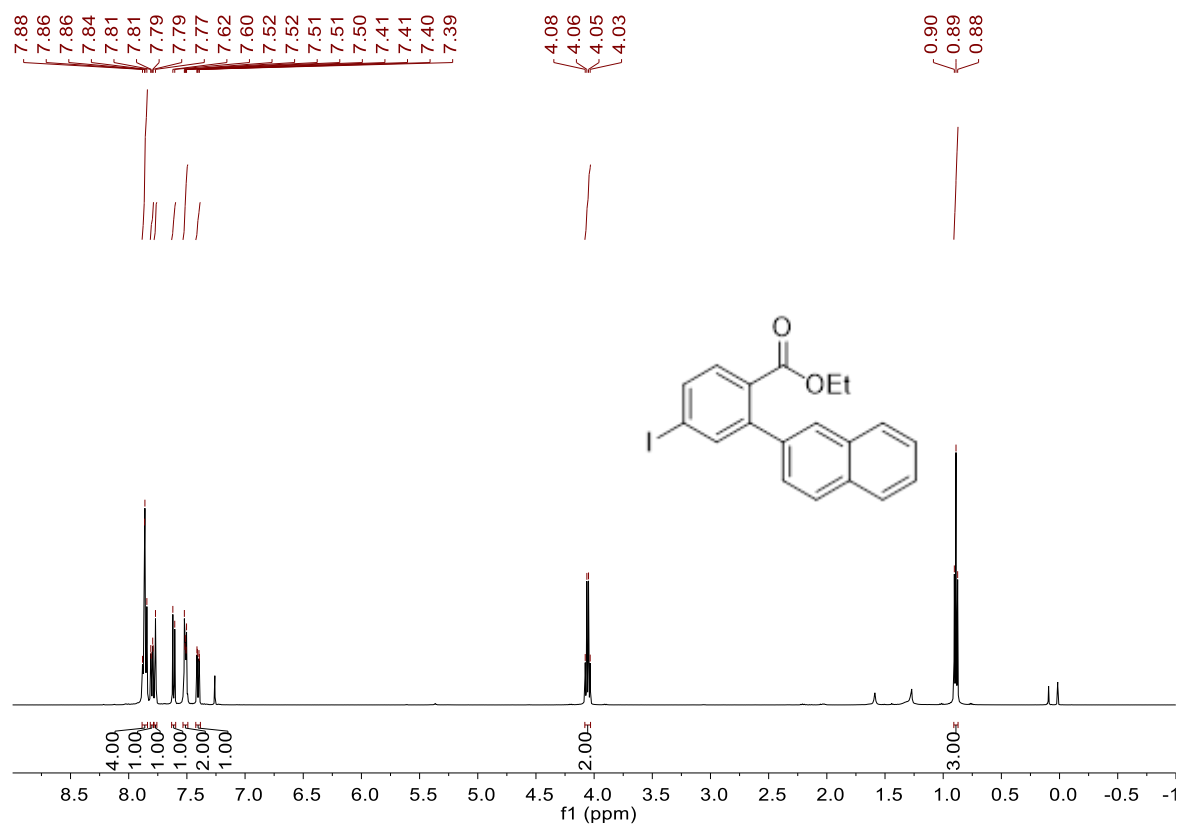


<sup>13</sup>C NMR spectrum of **3da**, 101 MHz, CDCl<sub>3</sub>

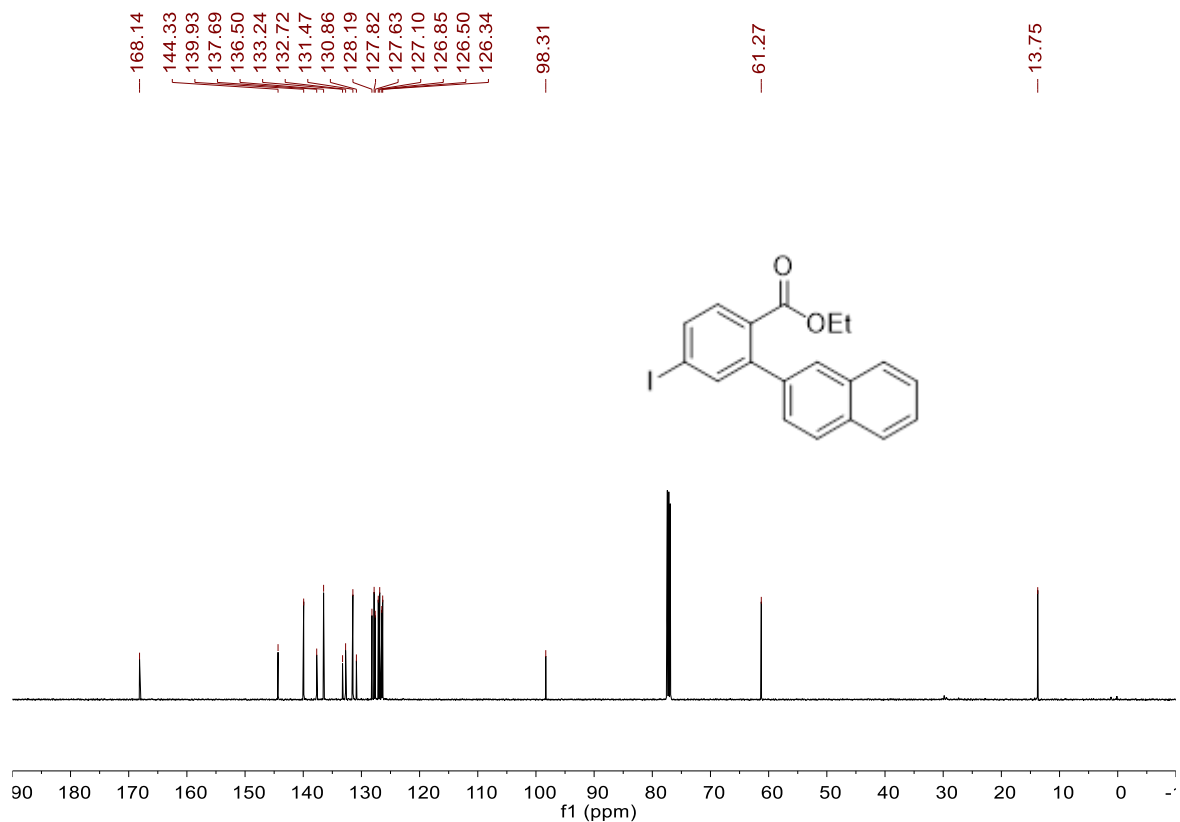




<sup>1</sup>H NMR spectrum of **3fa**, 500 MHz, CDCl<sub>3</sub>

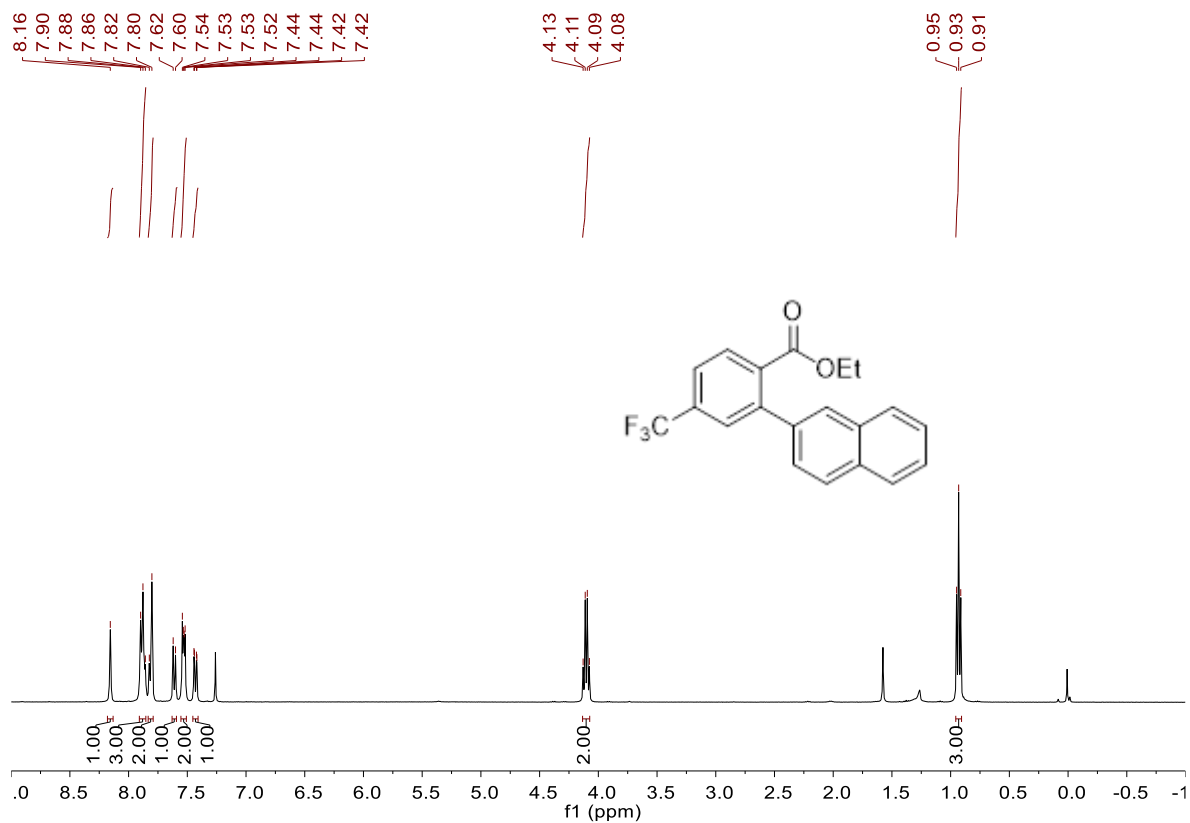


<sup>13</sup>C NMR spectrum of **3fa**, 126 MHz, CDCl<sub>3</sub>

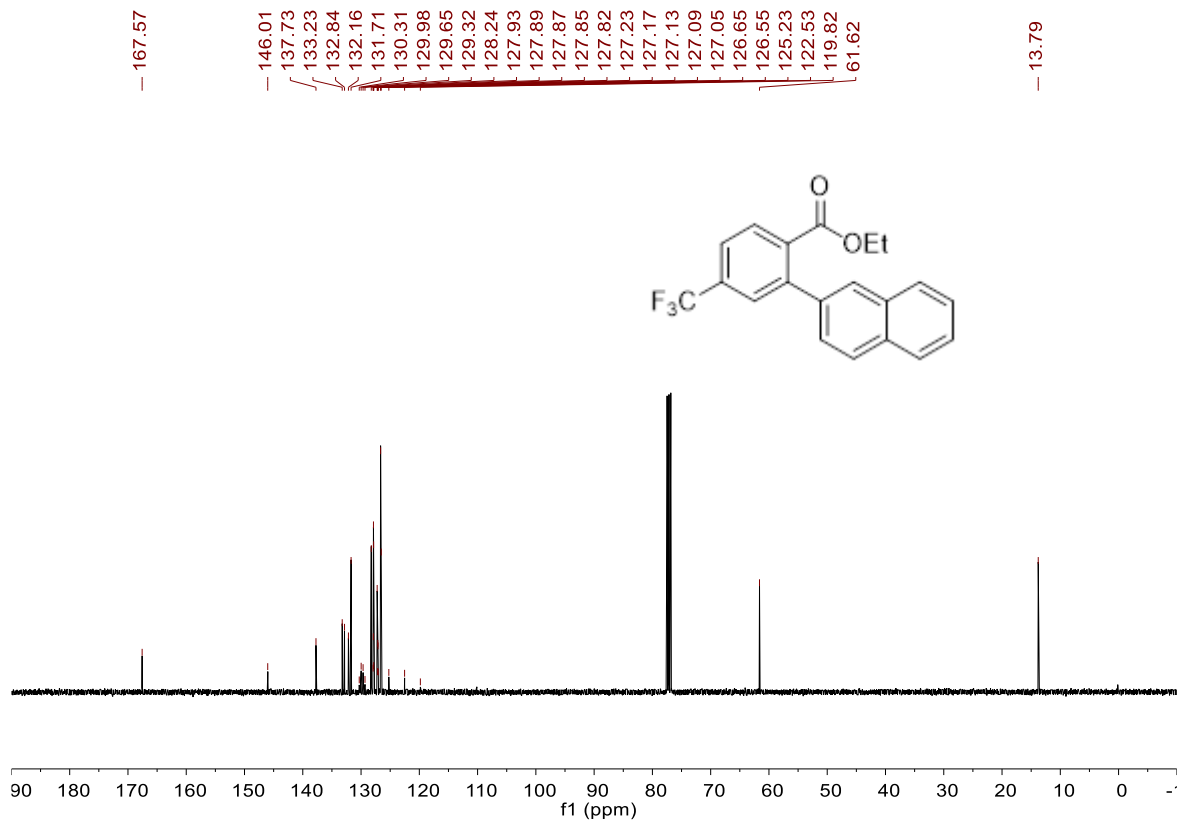




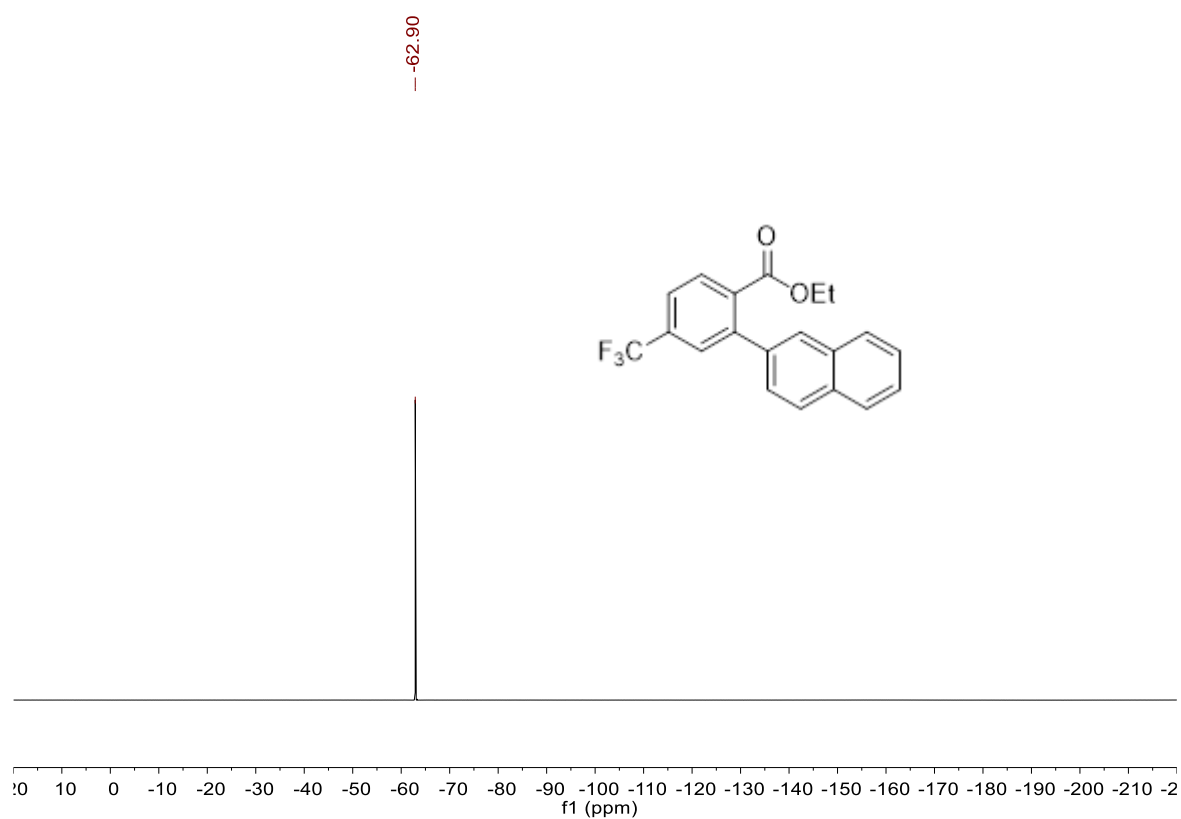
<sup>1</sup>H NMR spectrum of **3ha**, 400 MHz, CDCl<sub>3</sub>



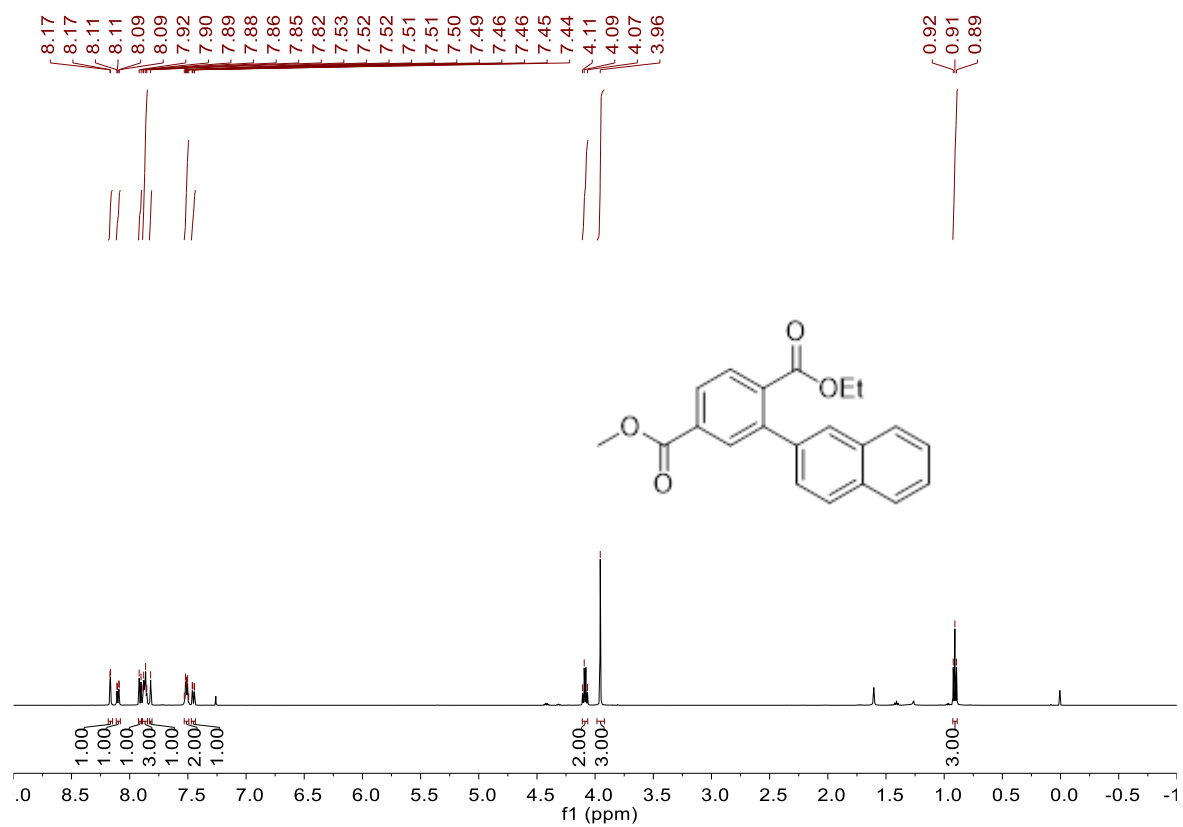
<sup>13</sup>C NMR spectrum of **3ha**, 101 MHz, CDCl<sub>3</sub>



$^{19}\text{F}$  NMR spectrum of **3ha**, 471 MHz,  $\text{CDCl}_3$

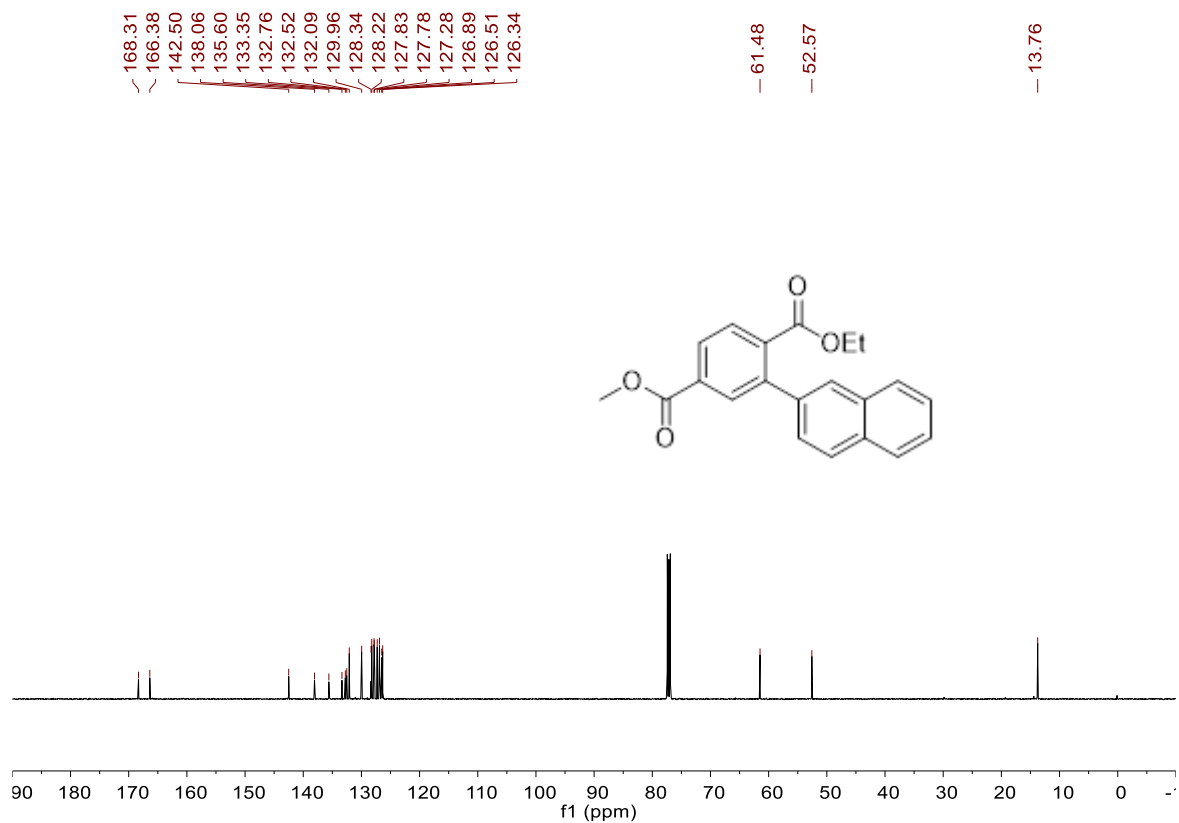


$^1\text{H}$  NMR spectrum of **3ia**, 500 MHz,  $\text{CDCl}_3$

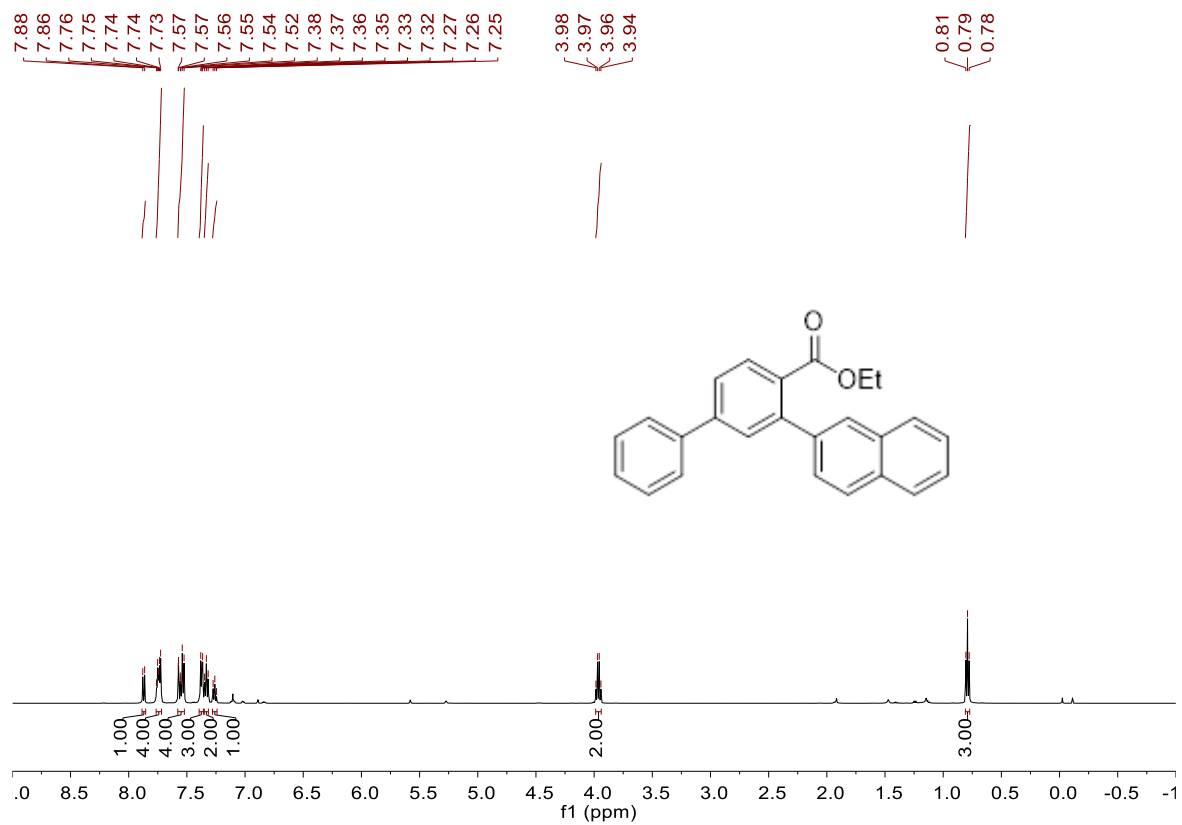




<sup>13</sup>C NMR spectrum of **3ia**, 126 MHz, CDCl<sub>3</sub>

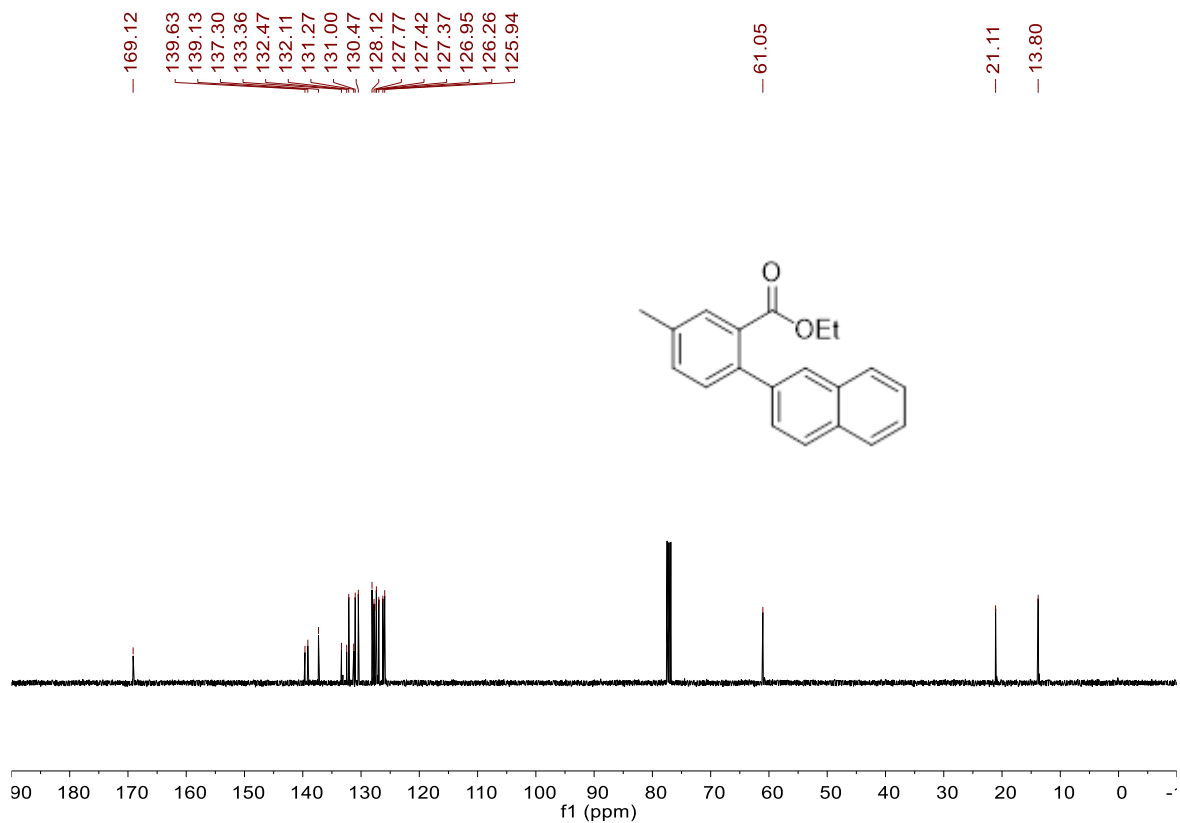


<sup>1</sup>H NMR spectrum of **3ja**, 500 MHz, CDCl<sub>3</sub>

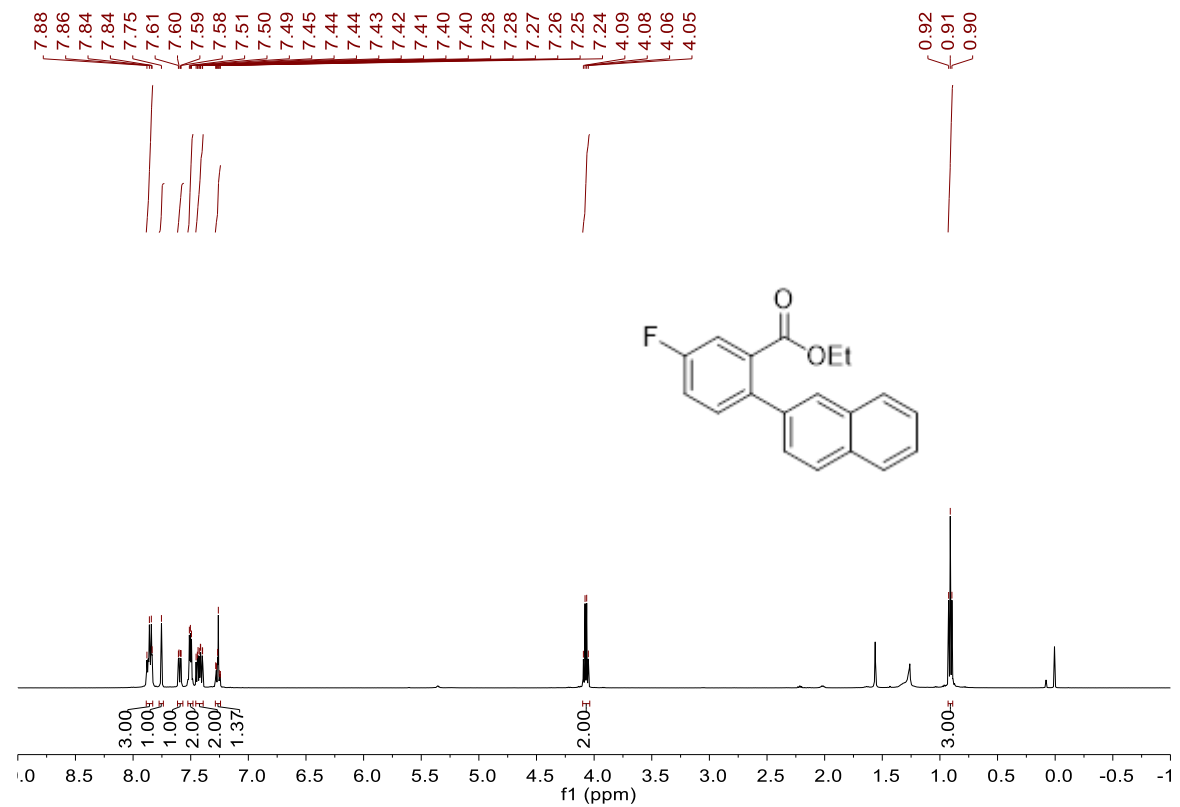




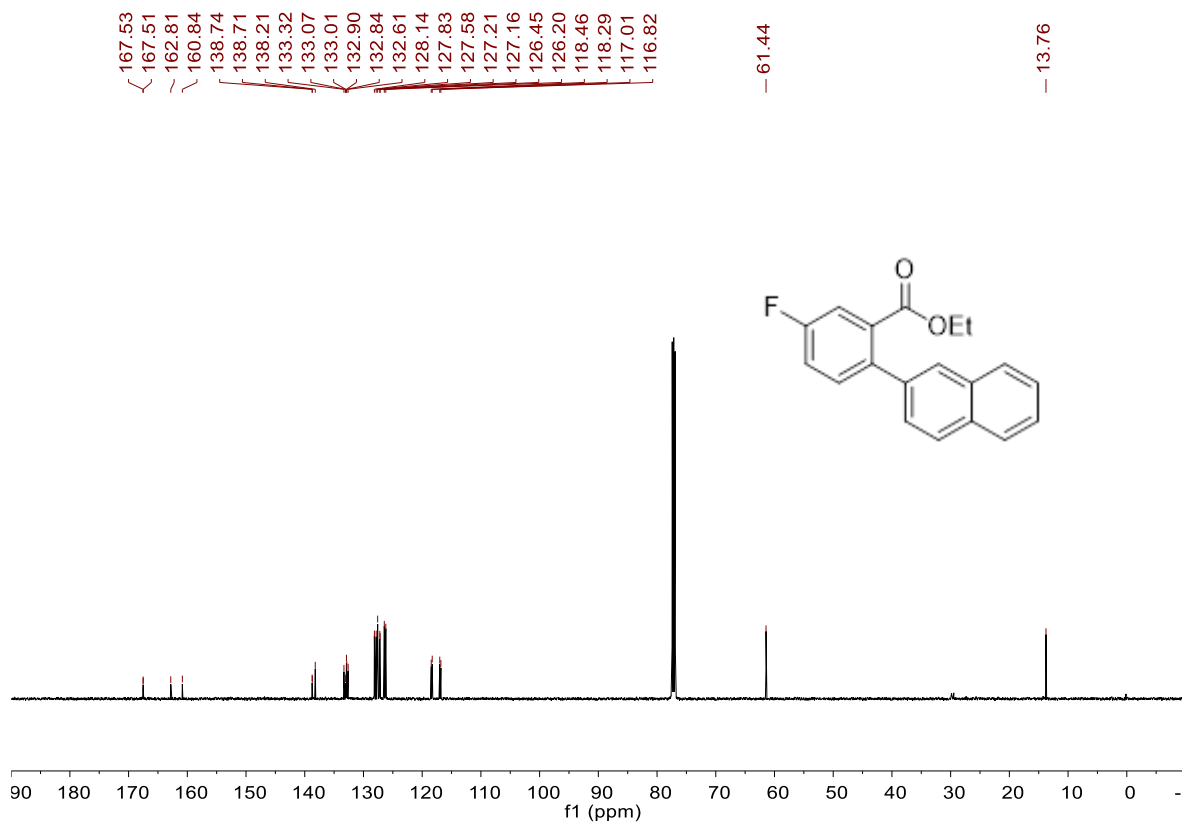
<sup>13</sup>C NMR spectrum of **3ka**, 101 MHz, CDCl<sub>3</sub>



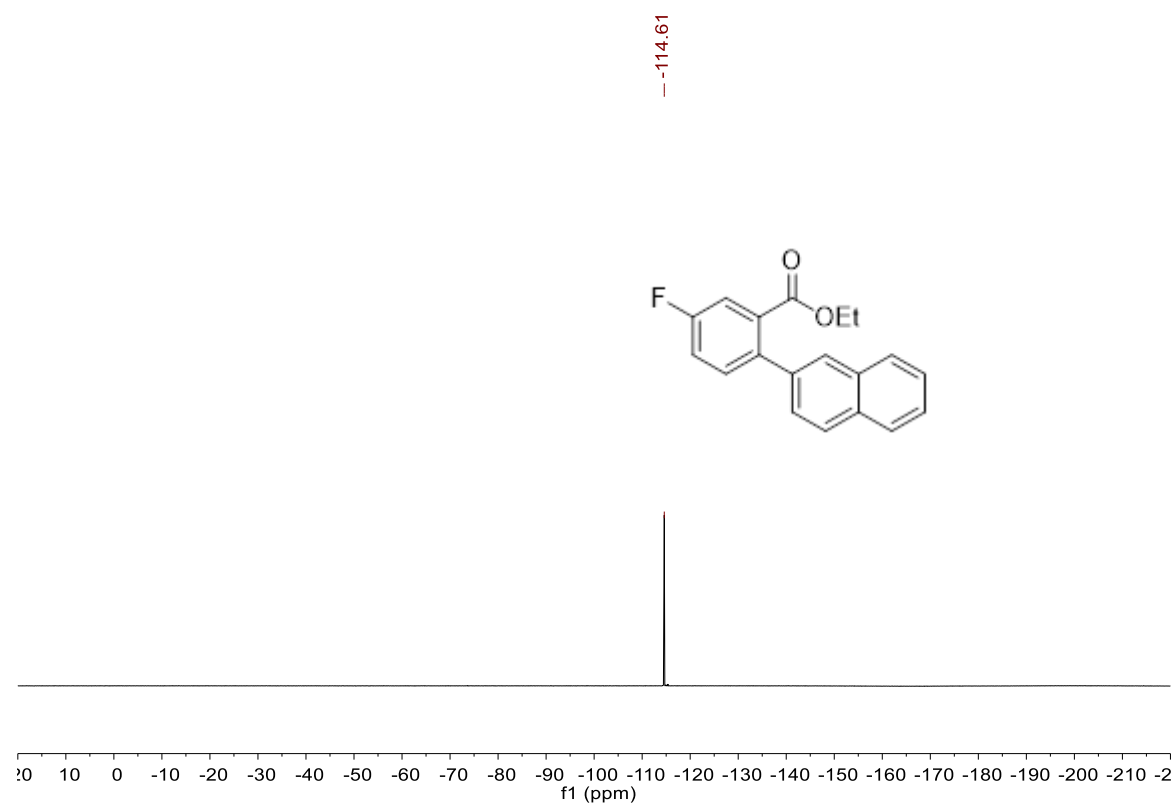
<sup>1</sup>H NMR spectrum of **3la**, 500 MHz, CDCl<sub>3</sub>



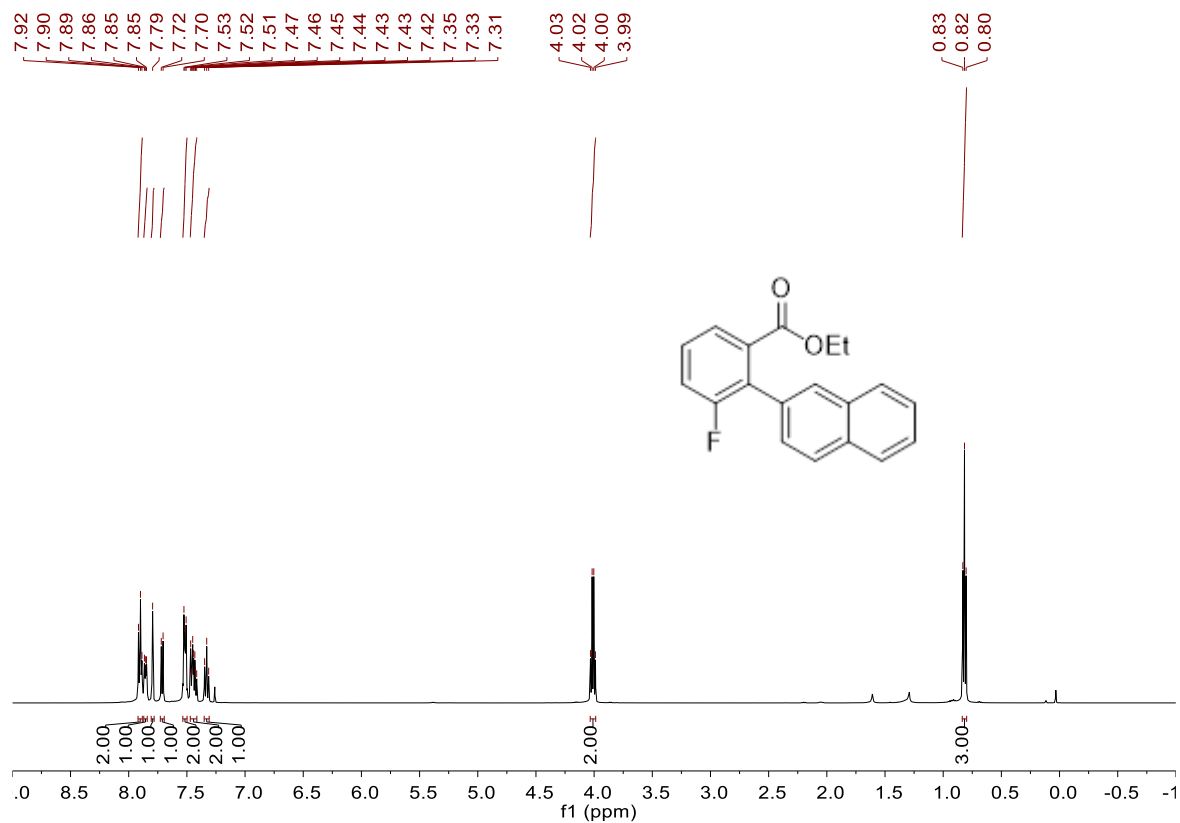
<sup>13</sup>C NMR spectrum of **3la**, 126 MHz, CDCl<sub>3</sub>



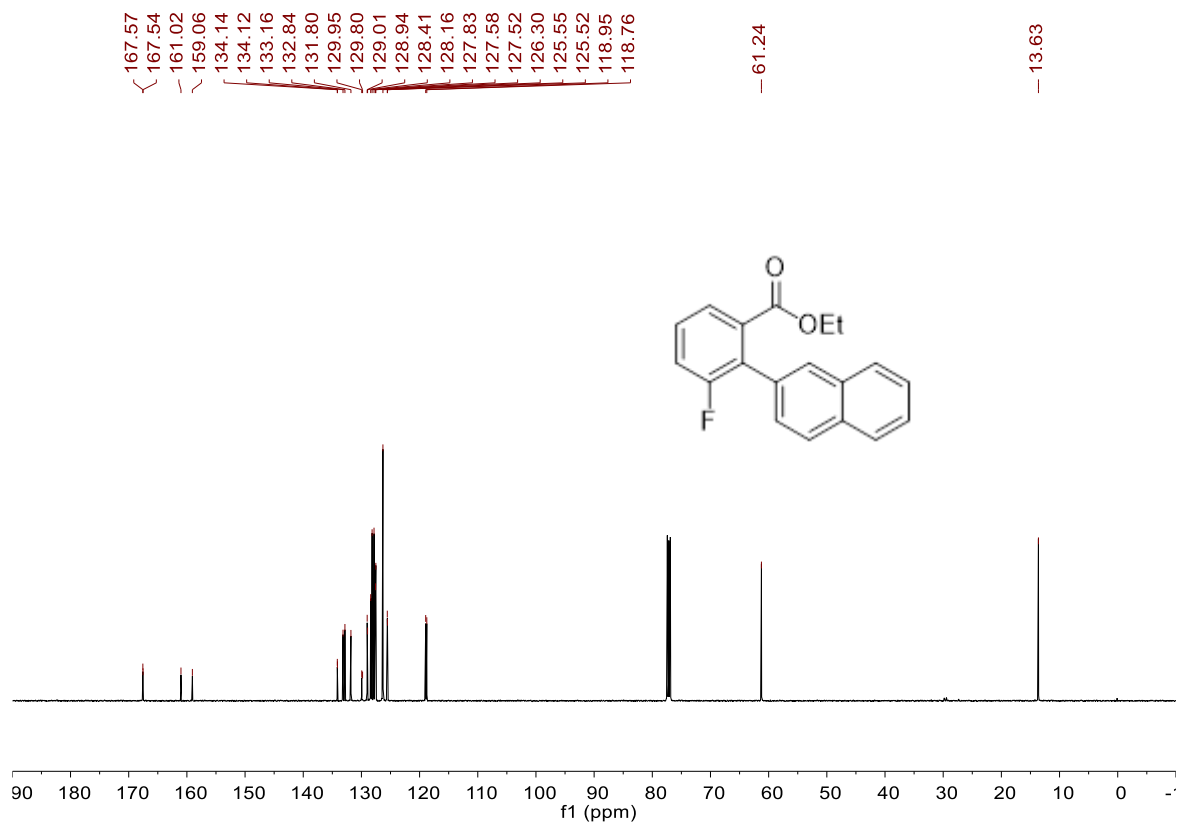
<sup>19</sup>F NMR spectrum of **3la**, 471 MHz, CDCl<sub>3</sub>



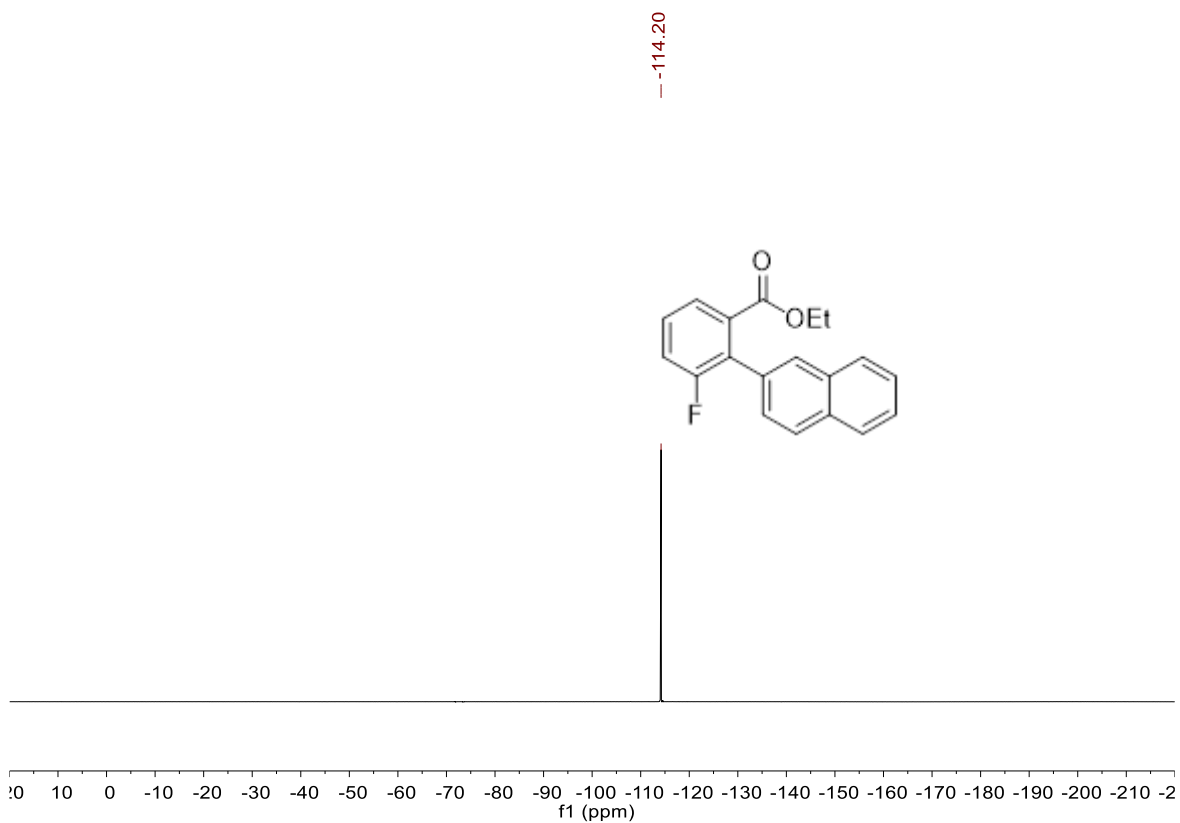
<sup>1</sup>H NMR spectrum of **3la'**, 500 MHz, CDCl<sub>3</sub>



<sup>13</sup>C NMR spectrum of **3la'**, 126 MHz, CDCl<sub>3</sub>



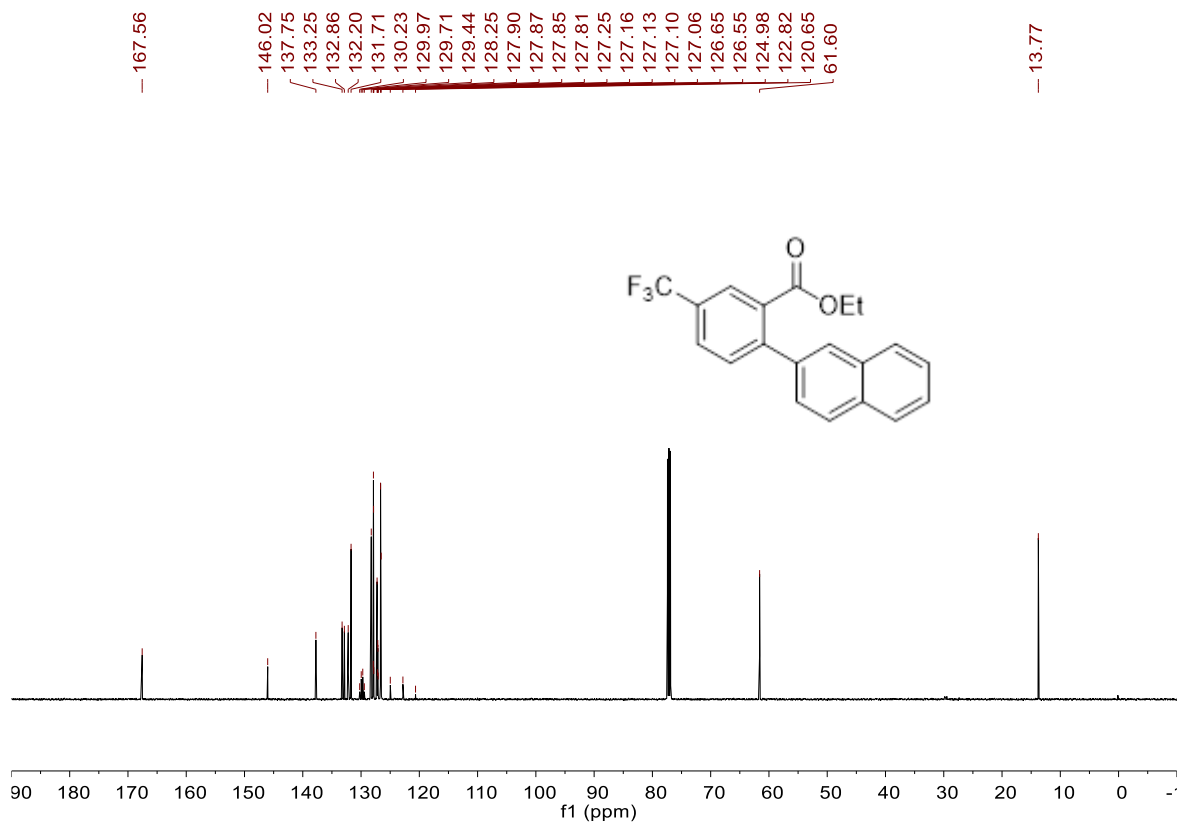
$^{19}\text{F}$  NMR spectrum of **3la'**, 471 MHz,  $\text{CDCl}_3$



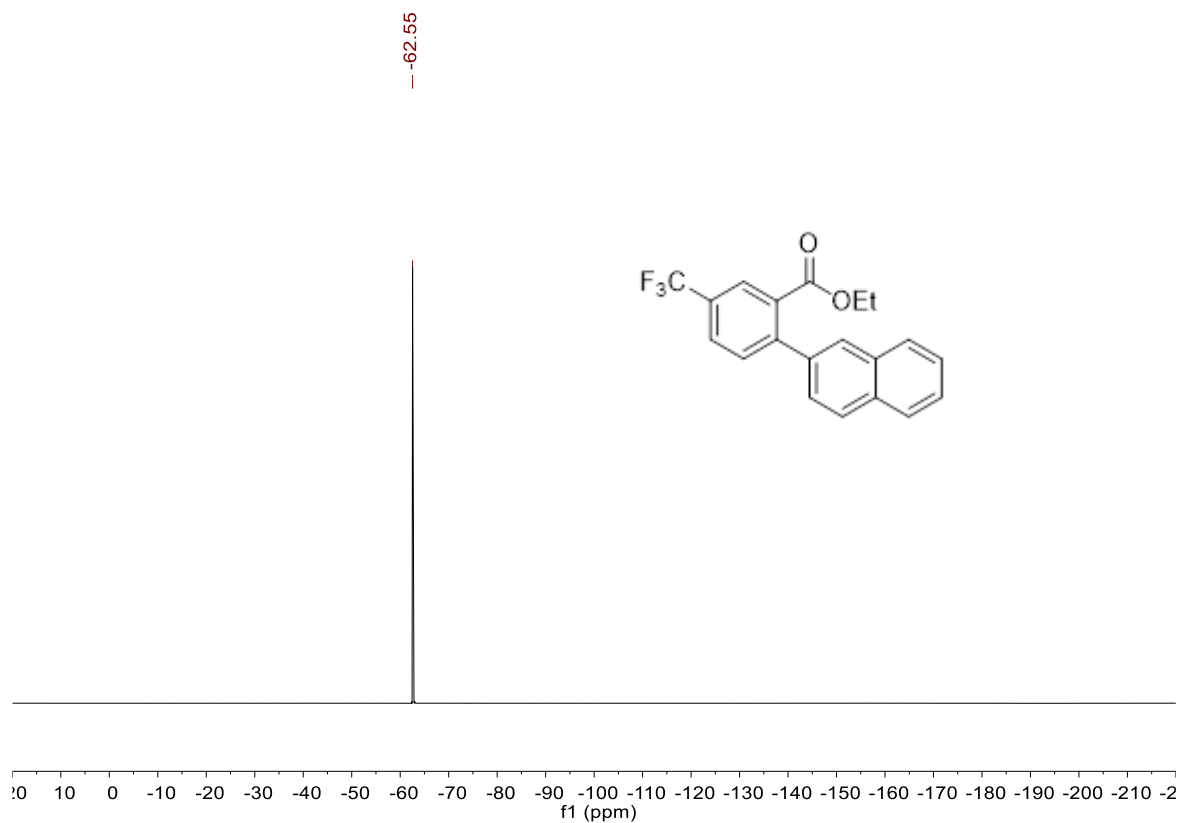
$^1\text{H}$  NMR spectrum of **3ma**, 400 MHz,  $\text{CDCl}_3$



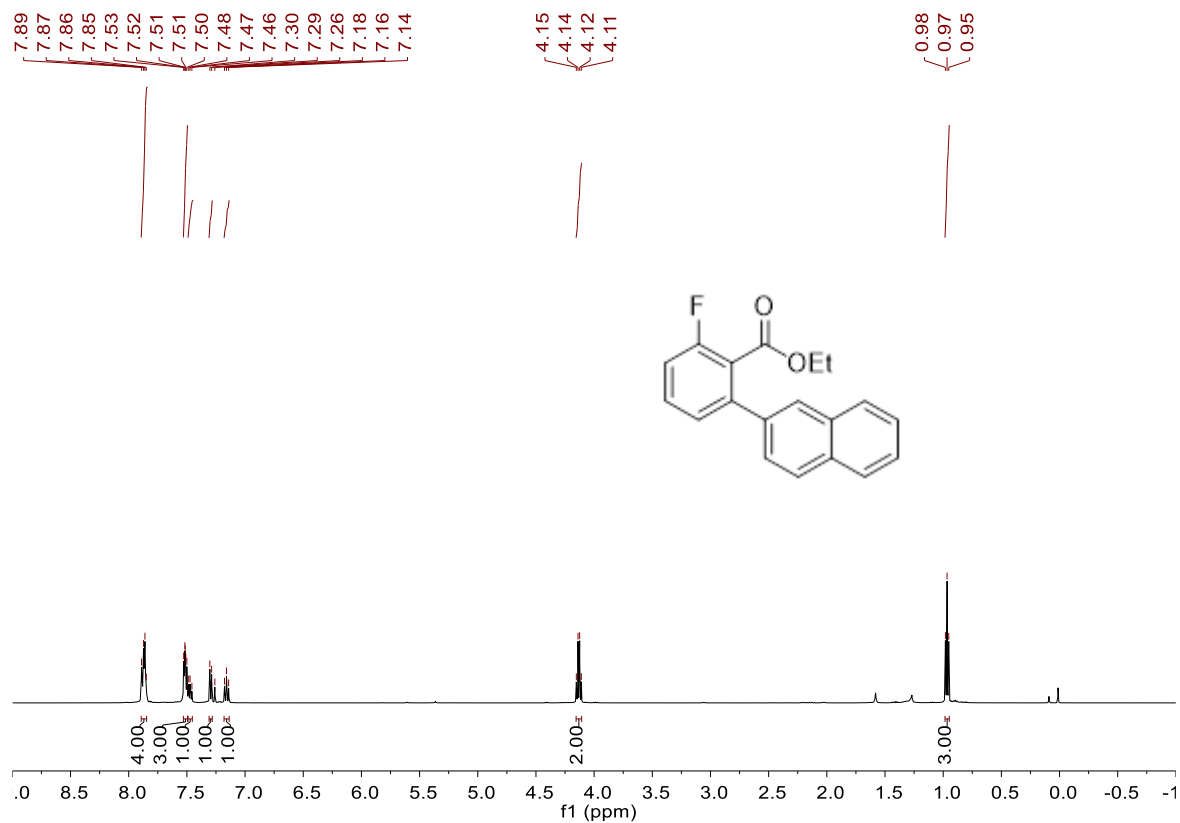
<sup>13</sup>C NMR spectrum of **3ma**, 126 MHz, CDCl<sub>3</sub>



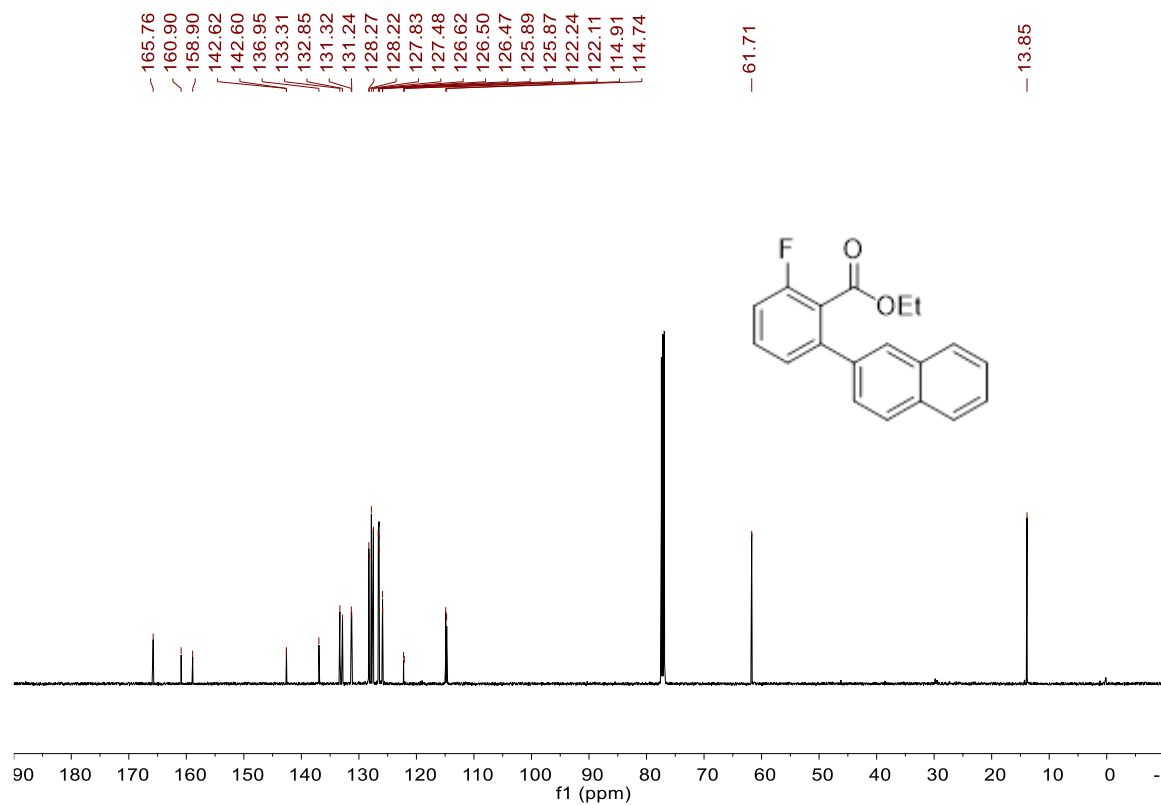
<sup>19</sup>F NMR spectrum of **3ma**, 471 MHz, CDCl<sub>3</sub>



<sup>1</sup>H NMR spectrum of **3na**, 500 MHz, CDCl<sub>3</sub>

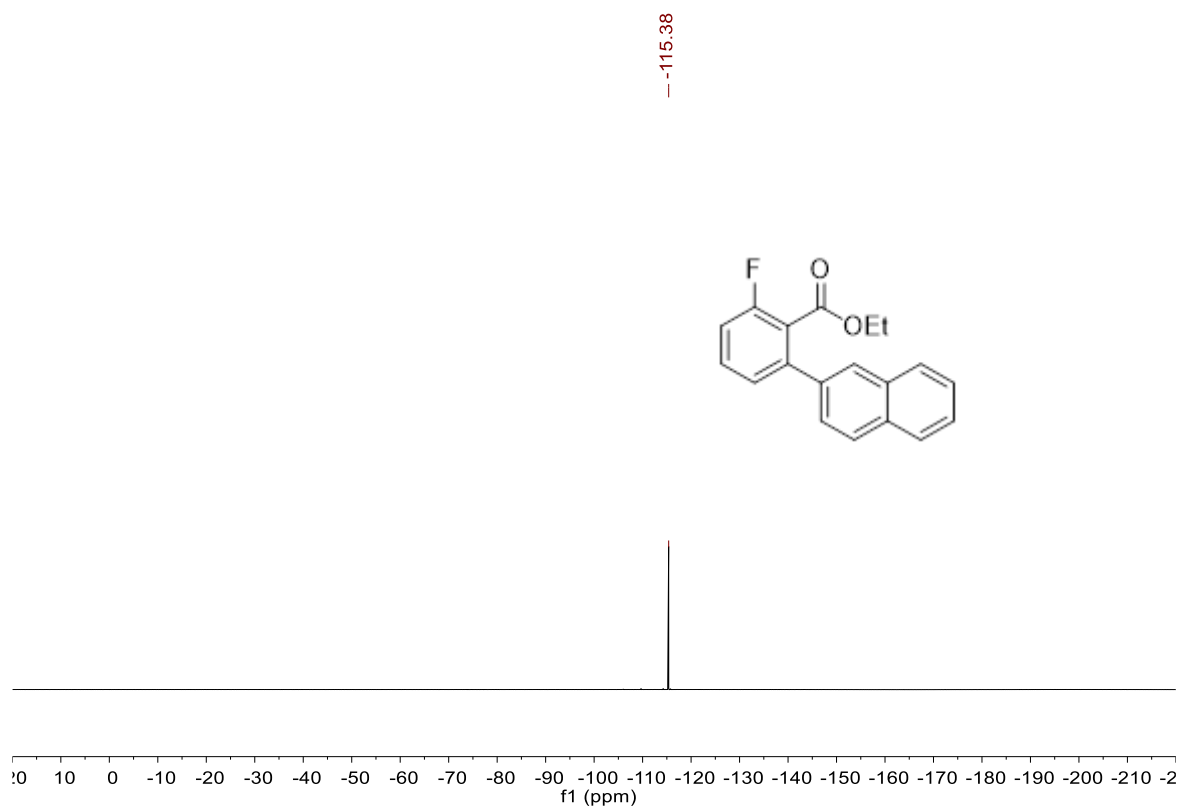


<sup>13</sup>C NMR spectrum of **3na**, 126 MHz, CDCl<sub>3</sub>





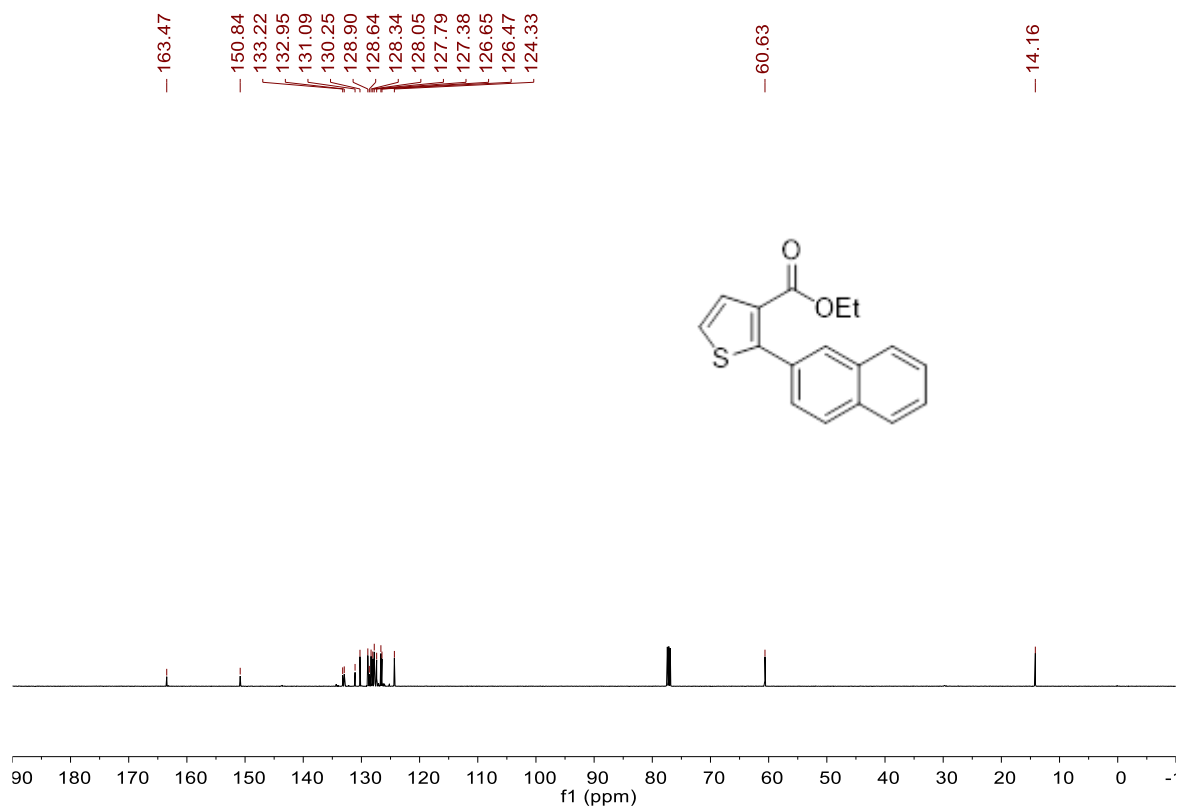
$^{19}\text{F}$  NMR spectrum of **3na**, 471 MHz,  $\text{CDCl}_3$



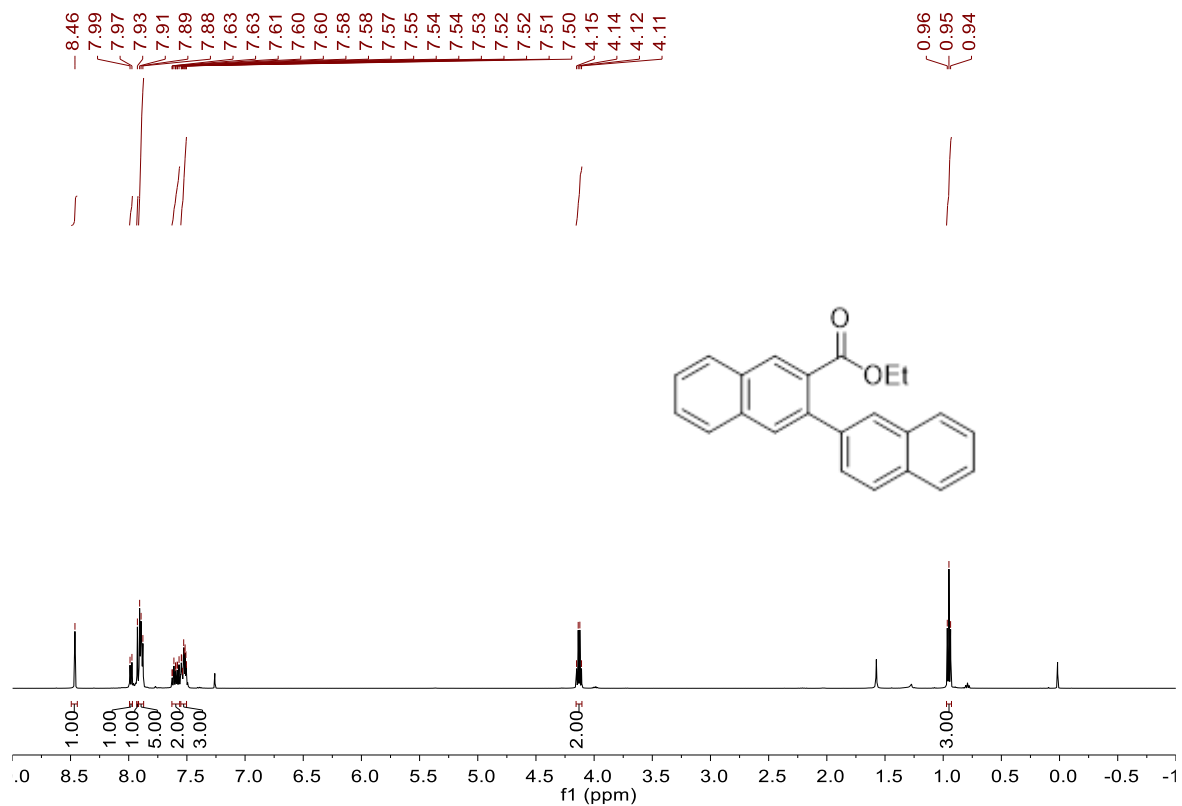
$^1\text{H}$  NMR spectrum of **3oa**, 500 MHz,  $\text{CDCl}_3$



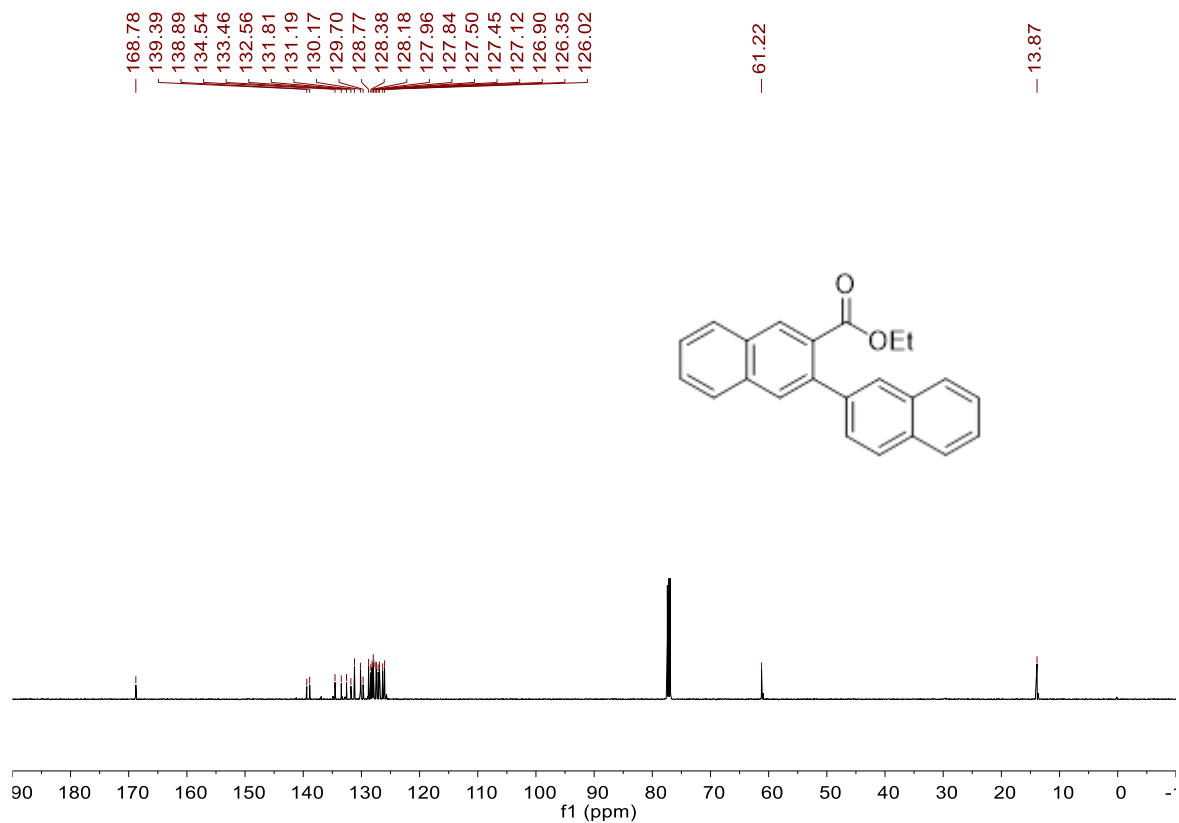
$^{13}\text{C}$  NMR spectrum of **30a**, 126 MHz,  $\text{CDCl}_3$



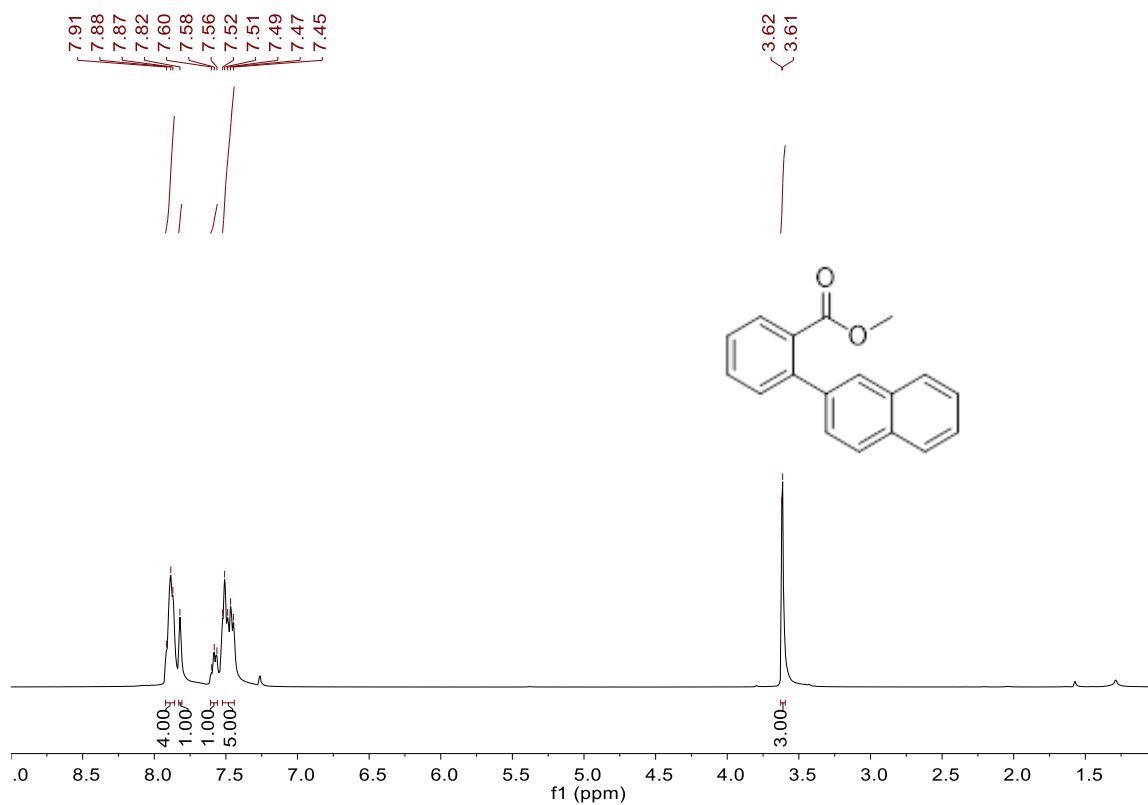
$^1\text{H}$  NMR spectrum of **3pa**, 500 MHz,  $\text{CDCl}_3$



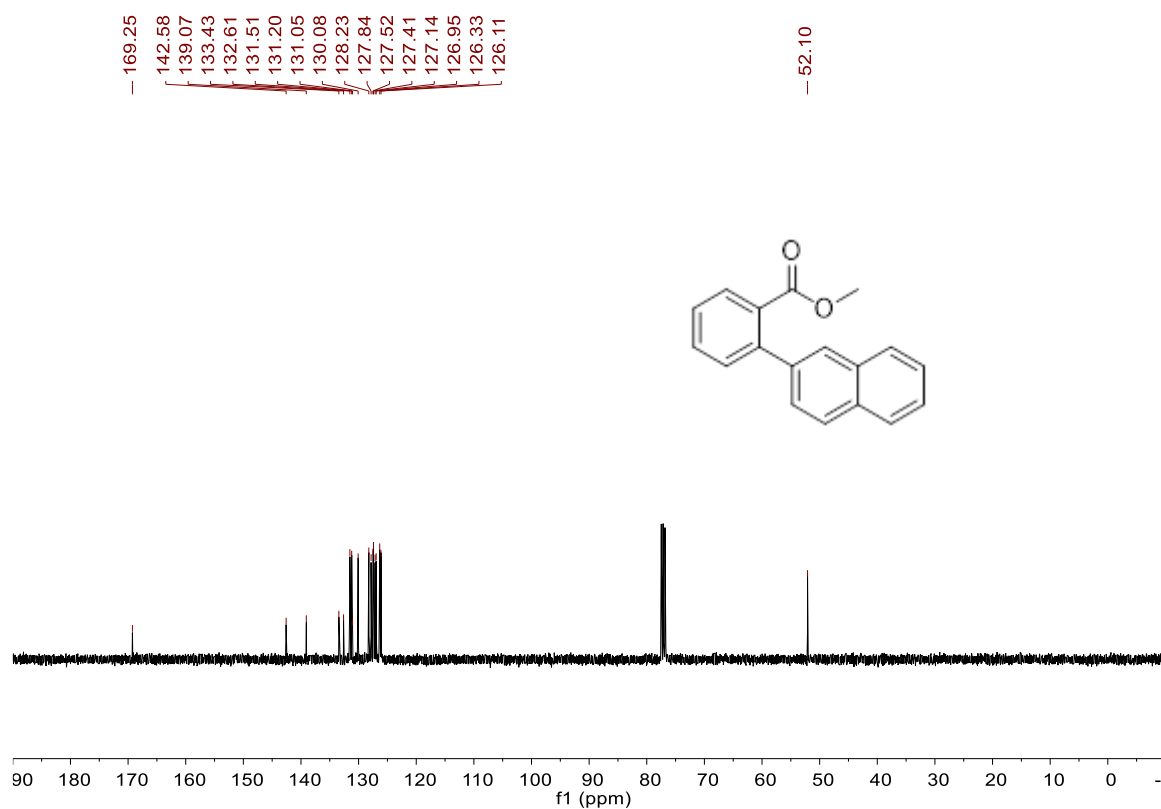
<sup>13</sup>C NMR spectrum of **3pa**, 126 MHz, CDCl<sub>3</sub>



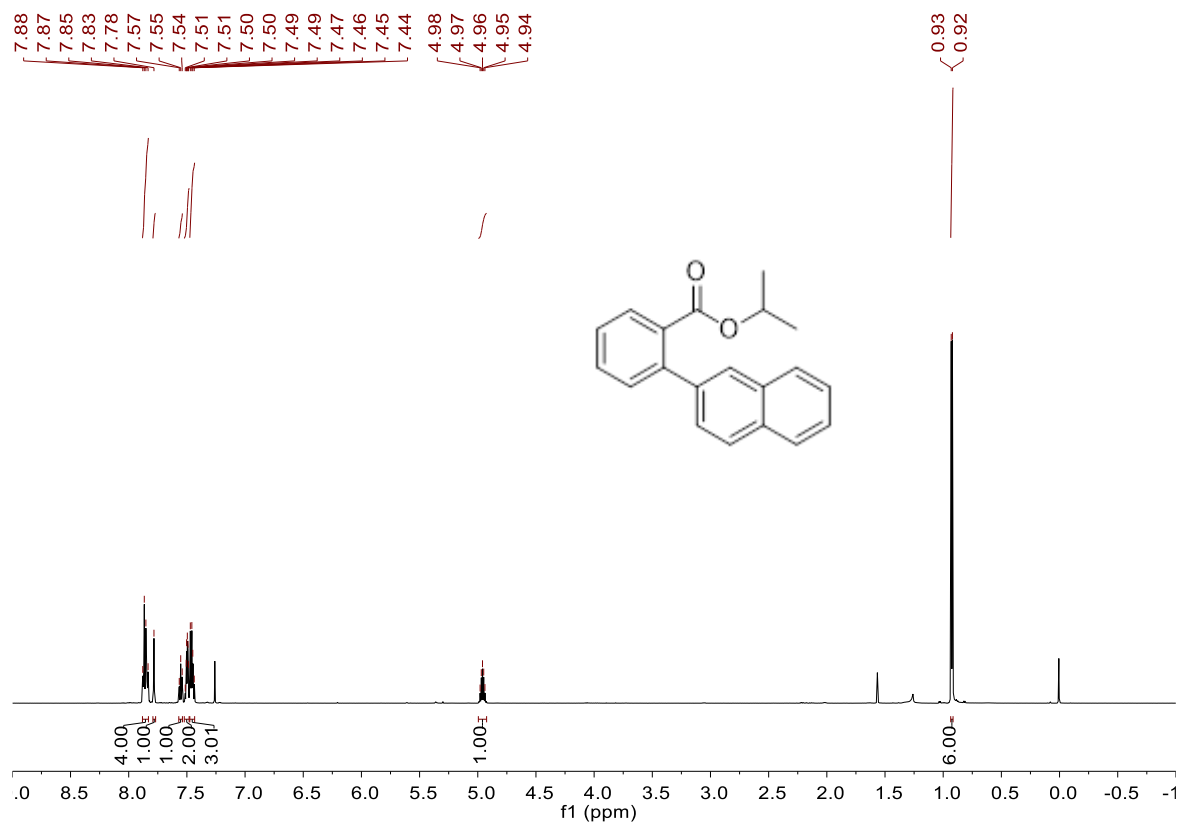
<sup>1</sup>H NMR spectrum of **3qa**, 400 MHz, CDCl<sub>3</sub>



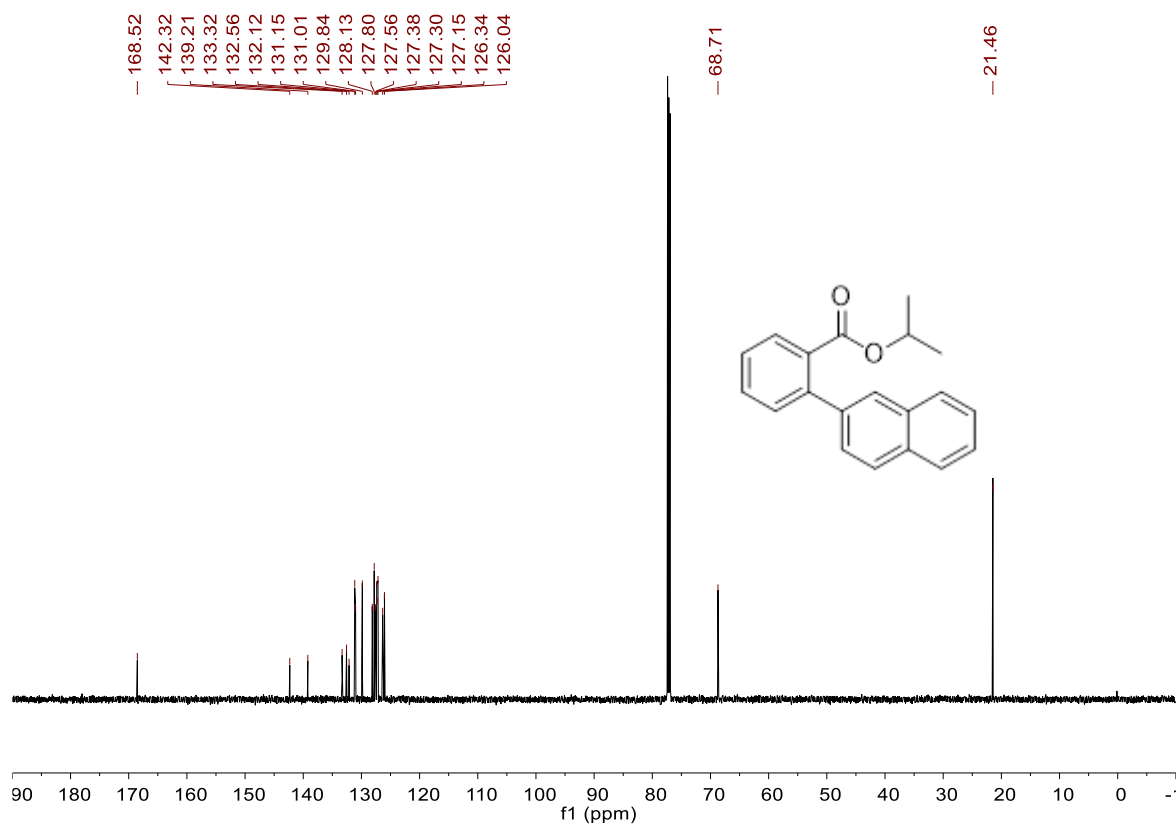
<sup>13</sup>C NMR spectrum of **3qa**, 101 MHz, CDCl<sub>3</sub>



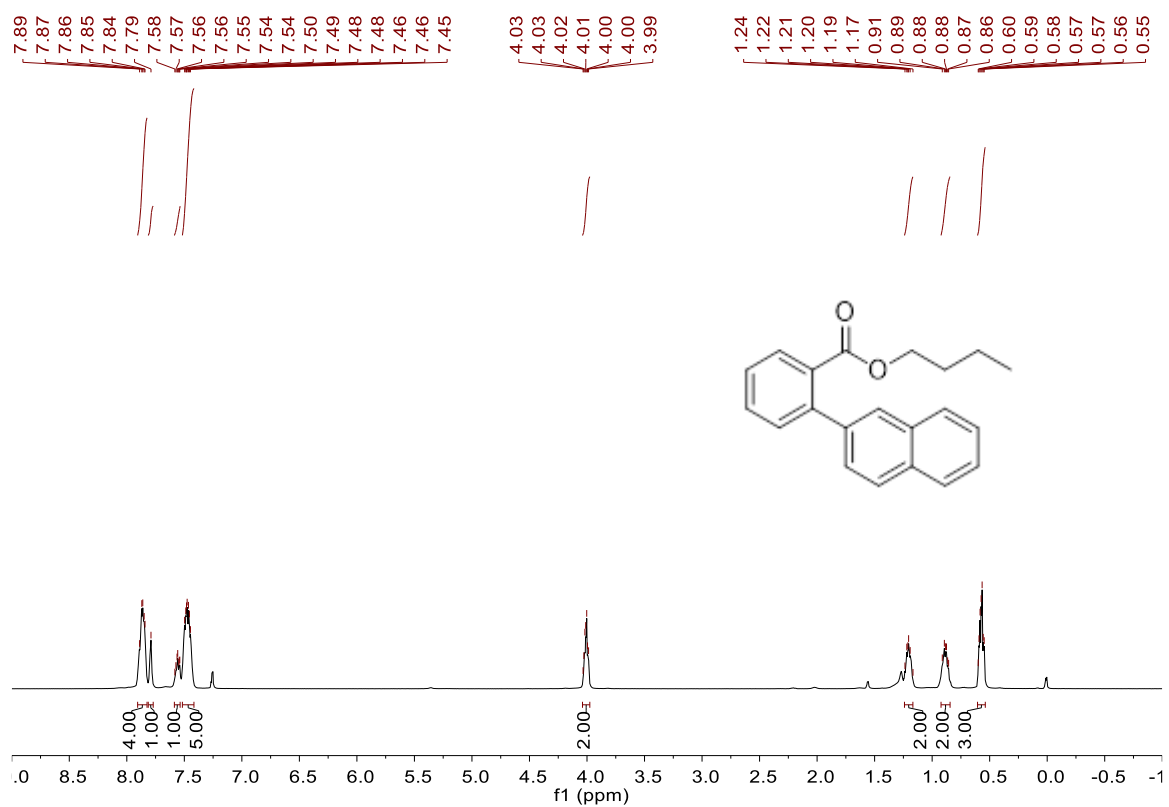
<sup>1</sup>H NMR spectrum of **3ra**, 600 MHz, CDCl<sub>3</sub>



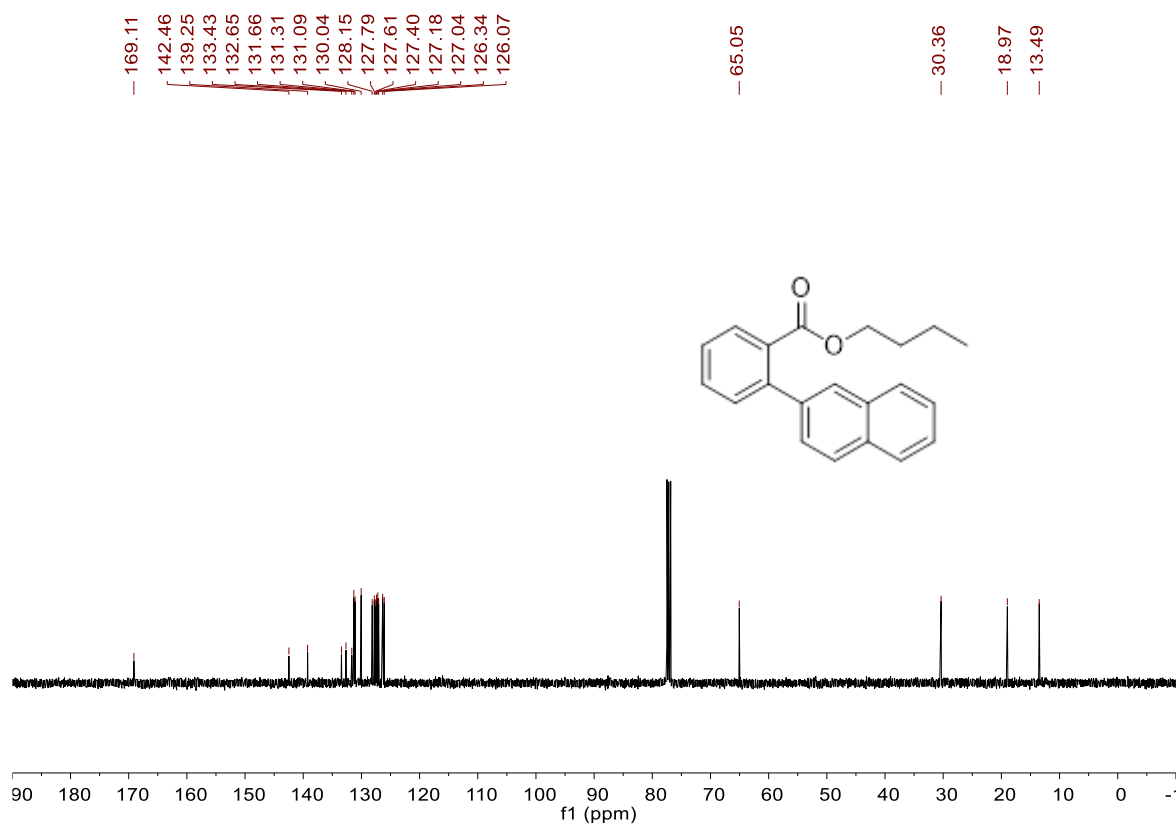
<sup>13</sup>C NMR spectrum of **3ra**, 151 MHz, CDCl<sub>3</sub>



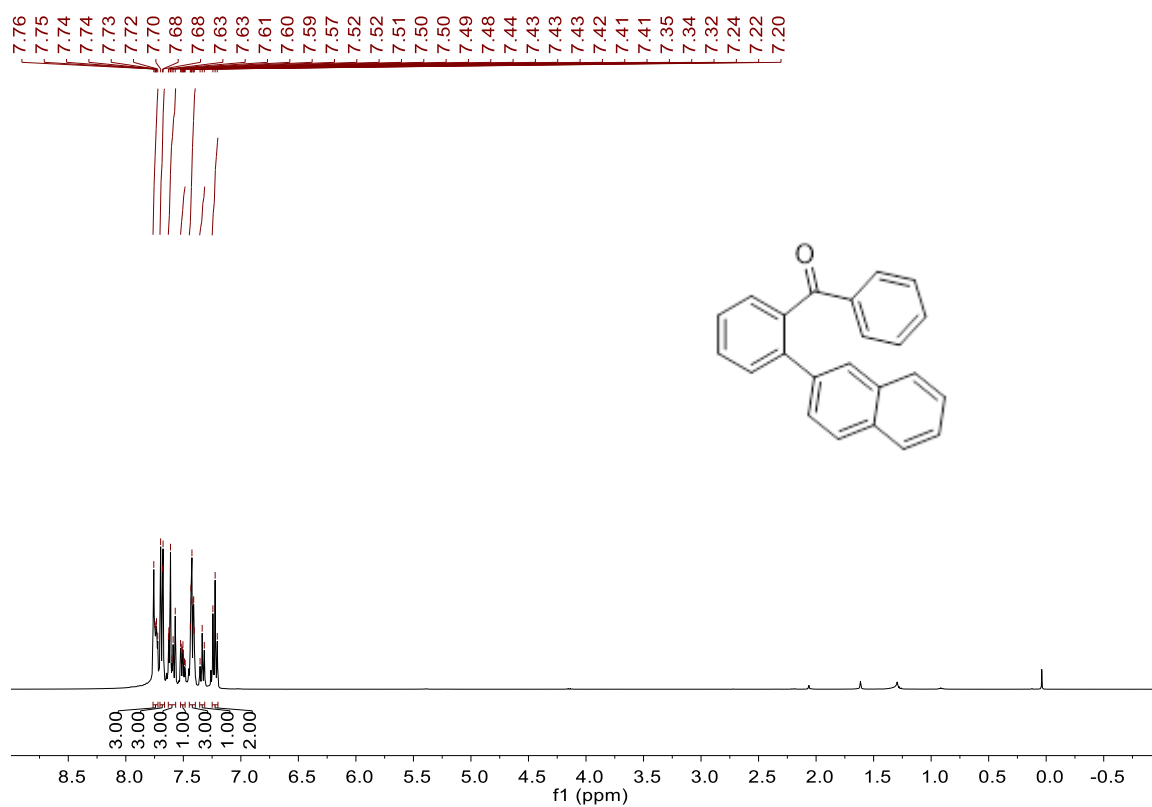
<sup>1</sup>H NMR spectrum of **3sa**, 400 MHz, CDCl<sub>3</sub>



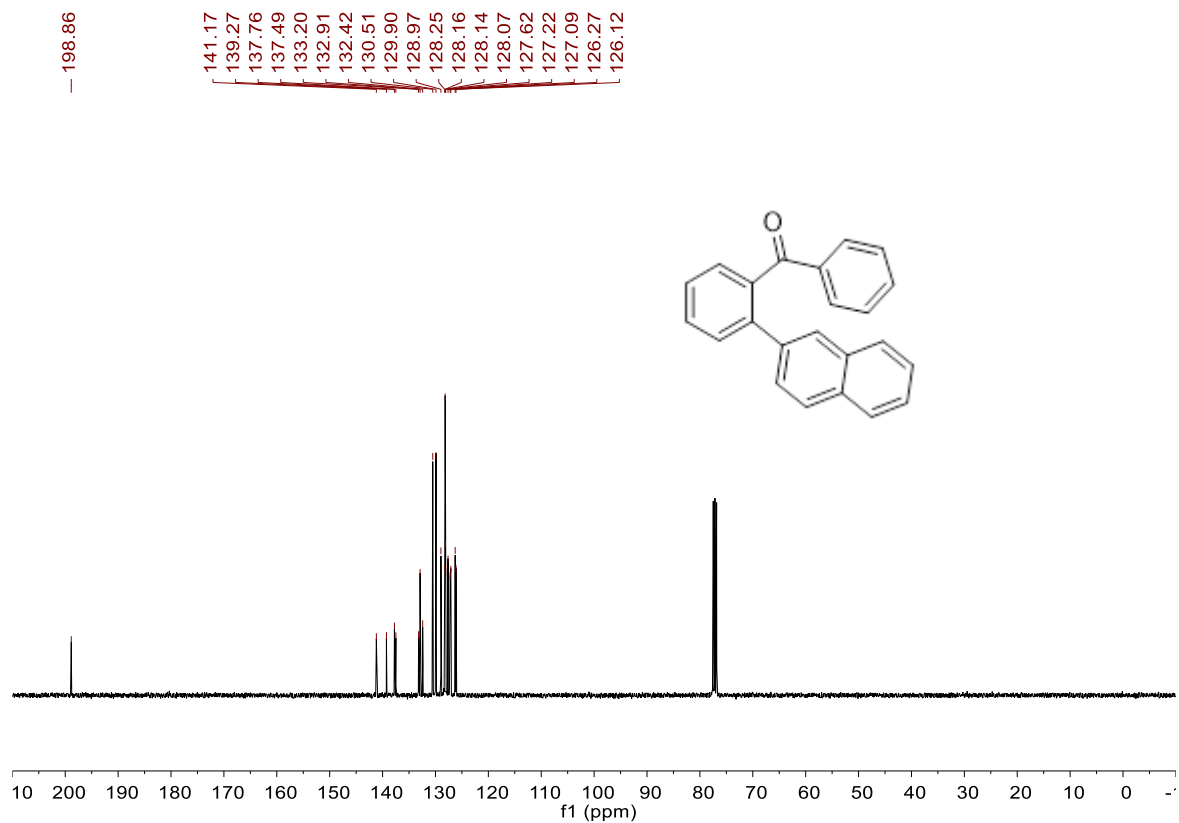
<sup>13</sup>C NMR spectrum of **3sa**, 101 MHz, CDCl<sub>3</sub>



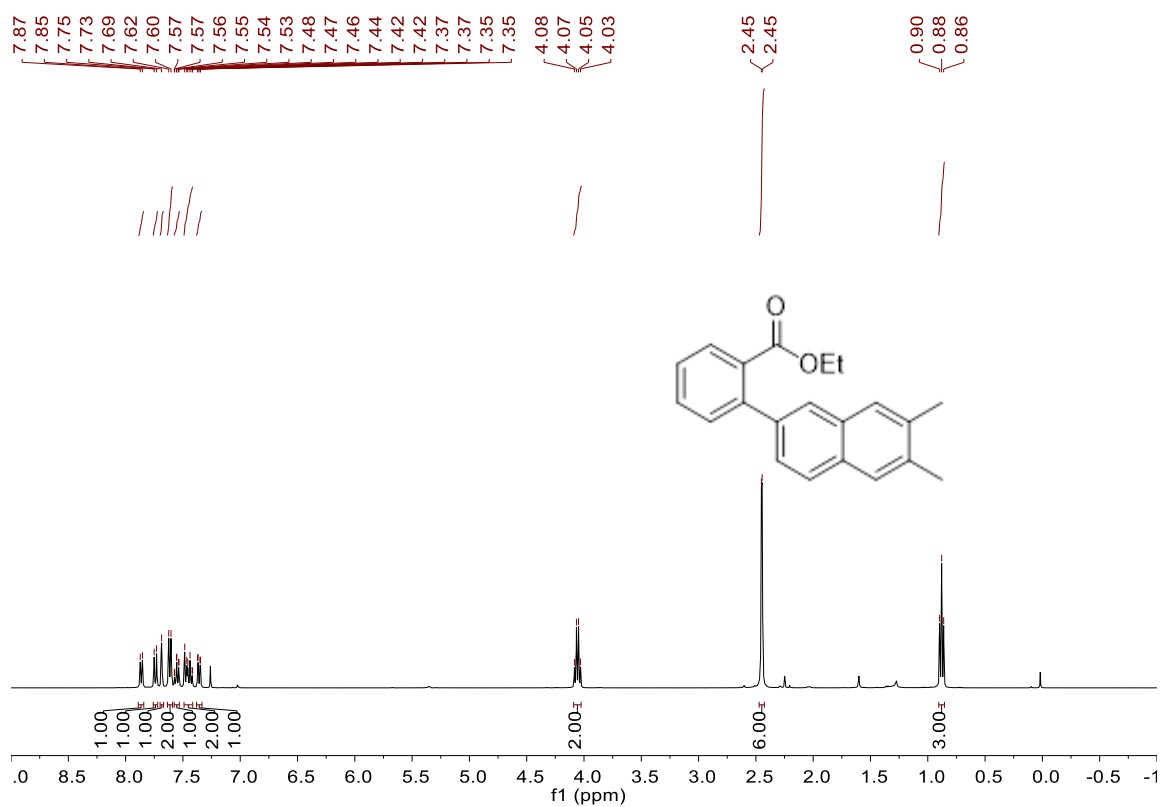
<sup>1</sup>H NMR spectrum of **3ta**, 400 MHz, CDCl<sub>3</sub>



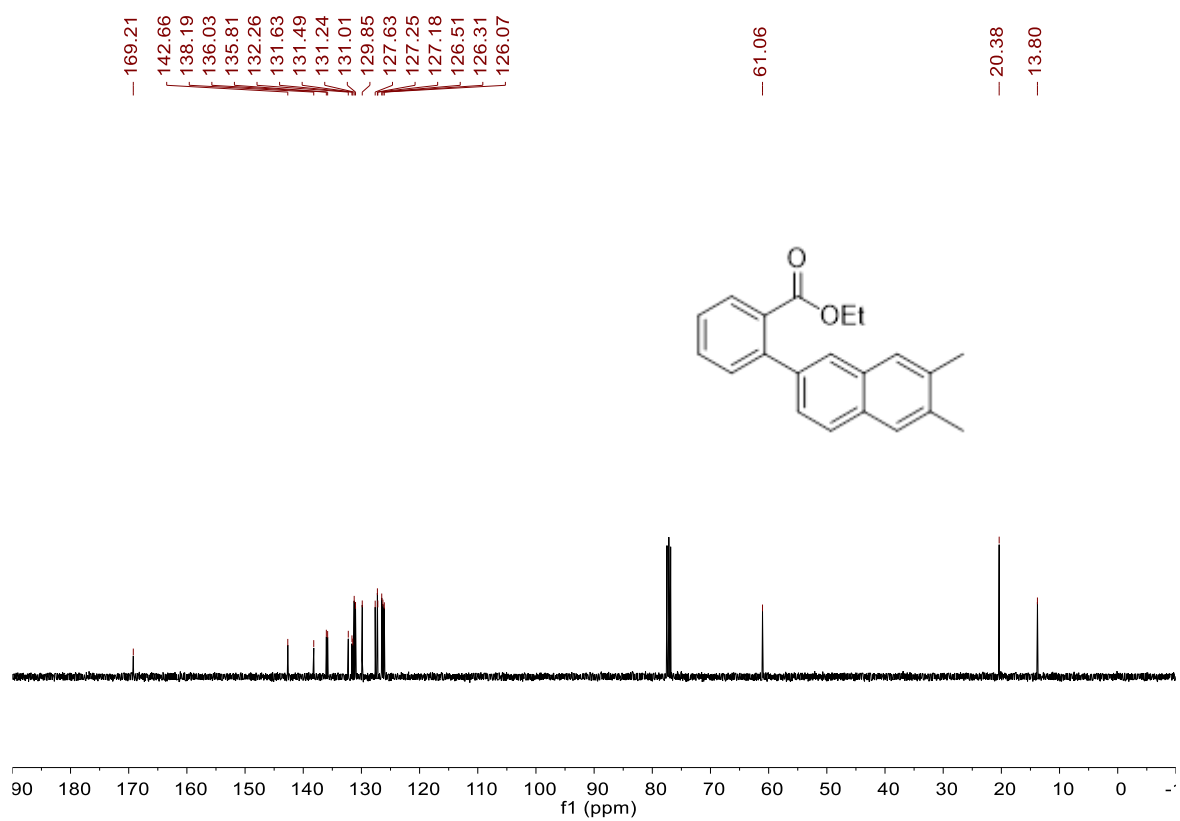
$^{13}\text{C}$  NMR spectrum of **3ta**, 101 MHz,  $\text{CDCl}_3$



$^1\text{H}$  NMR spectrum of **3ab**, 400 MHz,  $\text{CDCl}_3$



<sup>13</sup>C NMR spectrum of **3ab**, 101 MHz, CDCl<sub>3</sub>

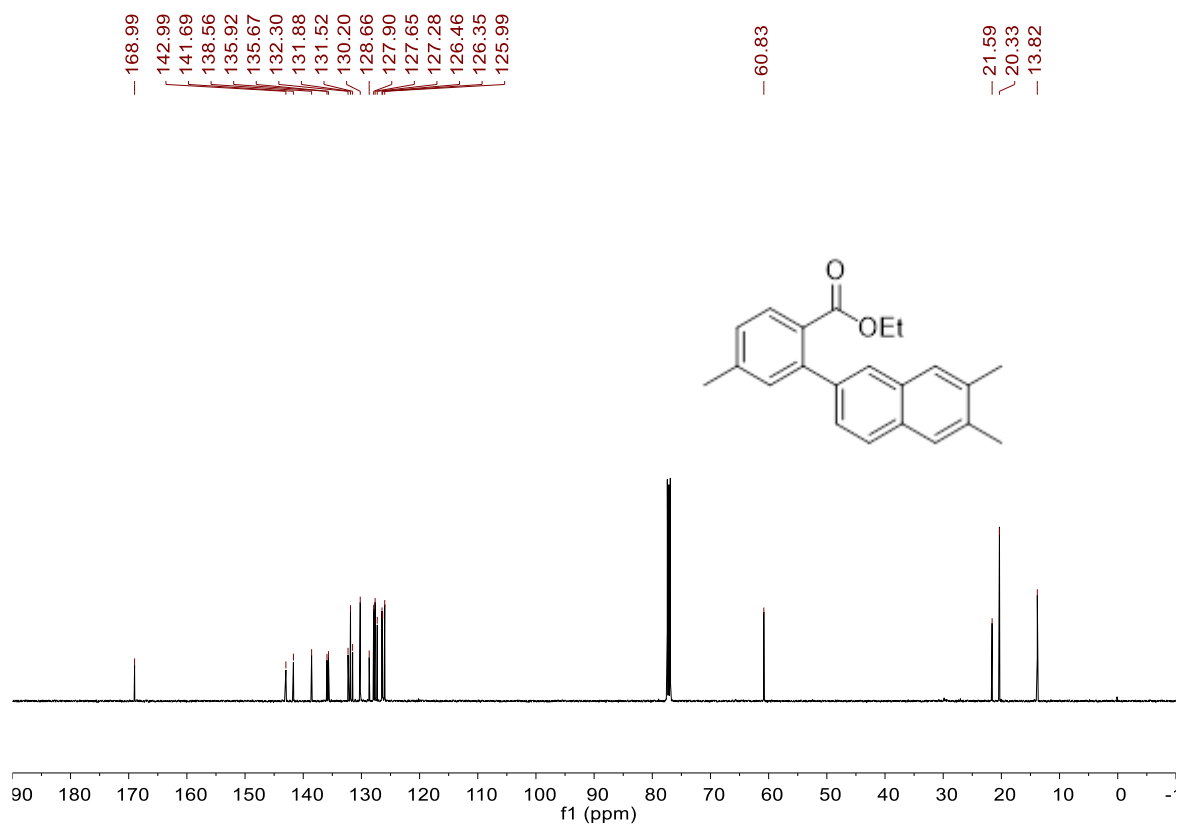


<sup>1</sup>H NMR spectrum of **3bb**, 500 MHz, CDCl<sub>3</sub>

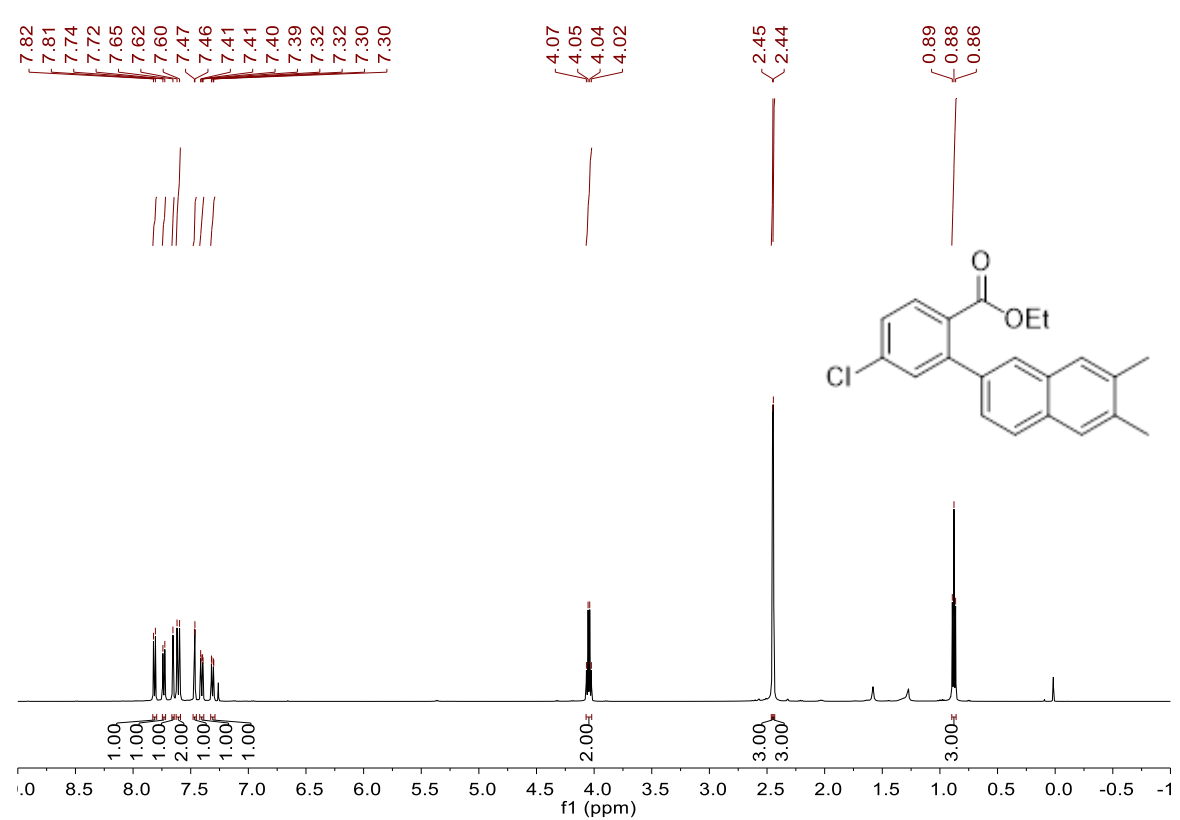




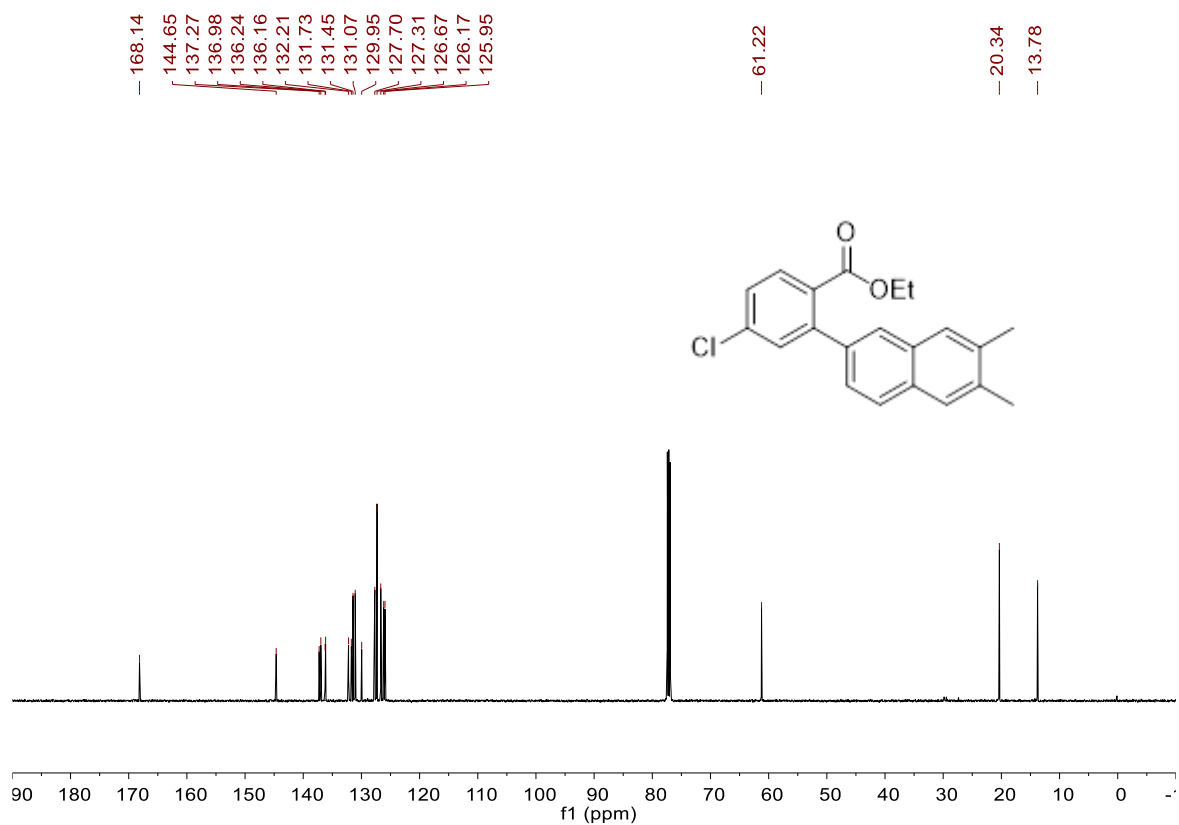
$^{13}\text{C}$  NMR spectrum of **3bb**, 126 MHz,  $\text{CDCl}_3$



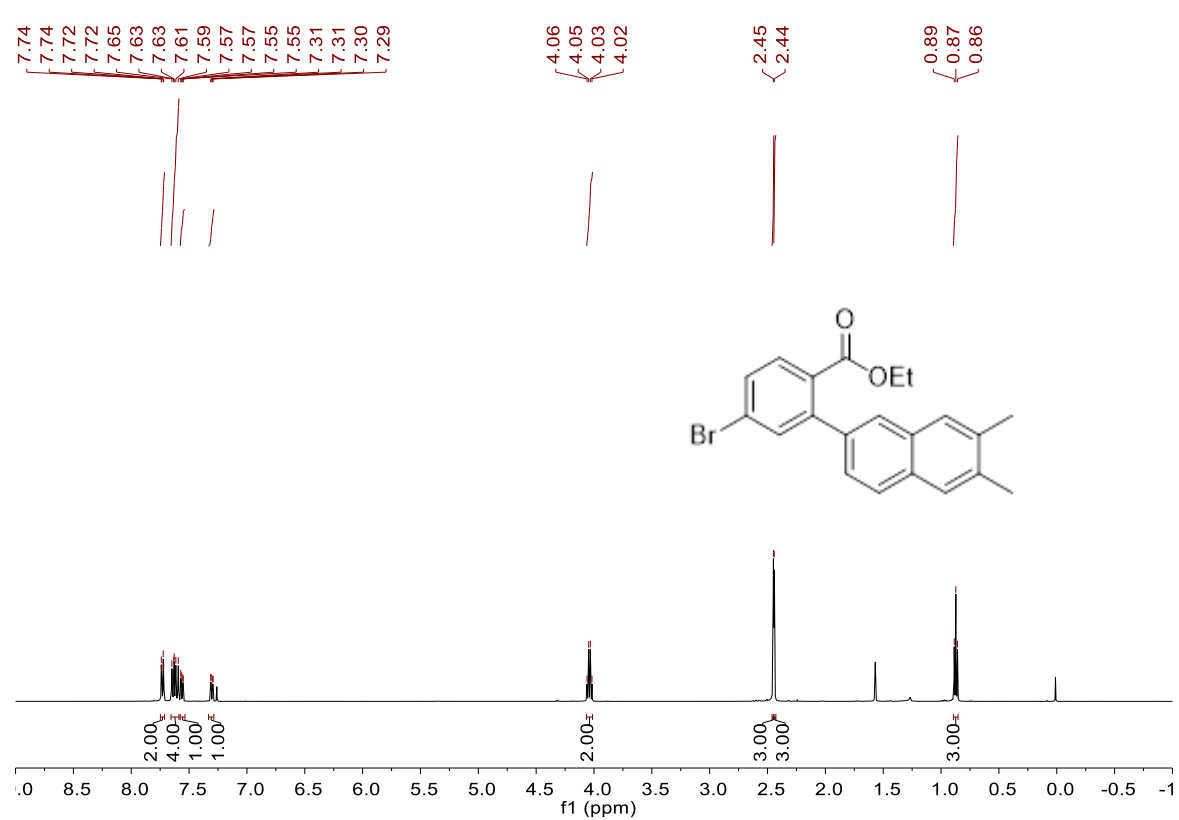
$^1\text{H}$  NMR spectrum of **3db**, 500 MHz,  $\text{CDCl}_3$



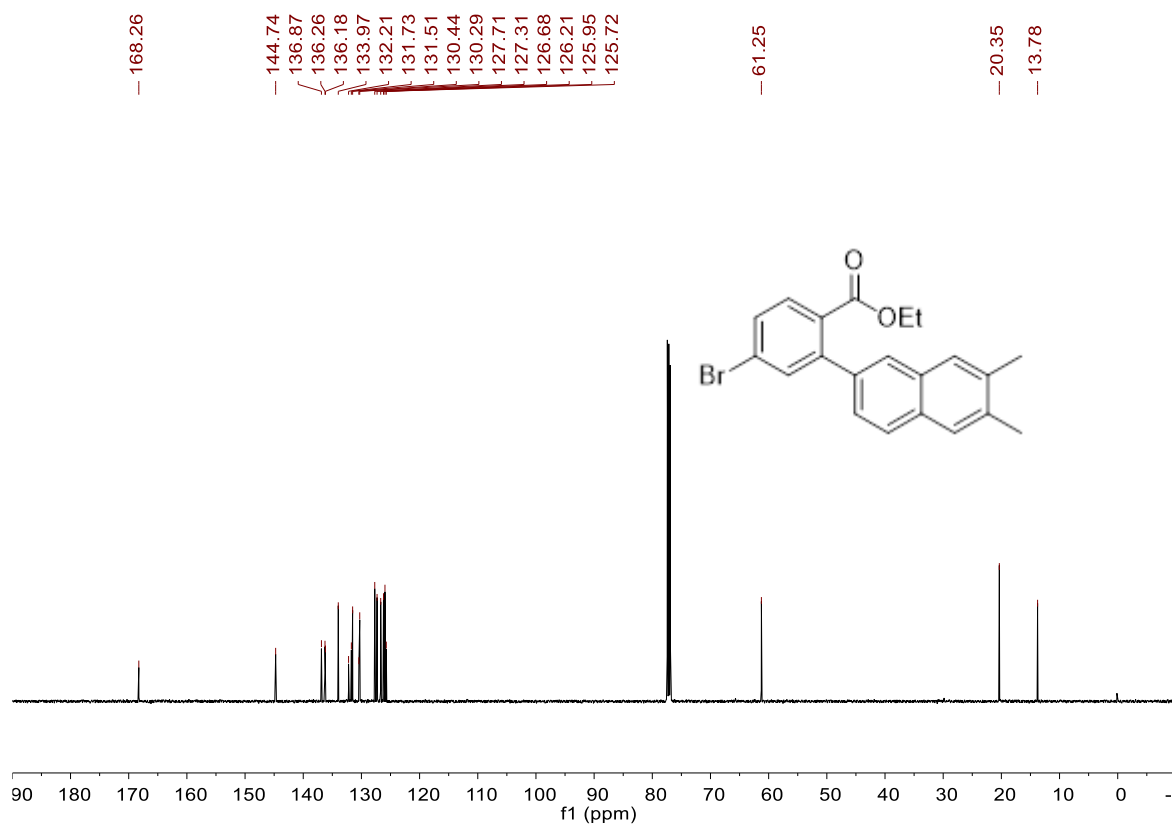
<sup>13</sup>C NMR spectrum of **3db**, 126 MHz, CDCl<sub>3</sub>



<sup>1</sup>H NMR spectrum of **3eb**, 500 MHz, CDCl<sub>3</sub>



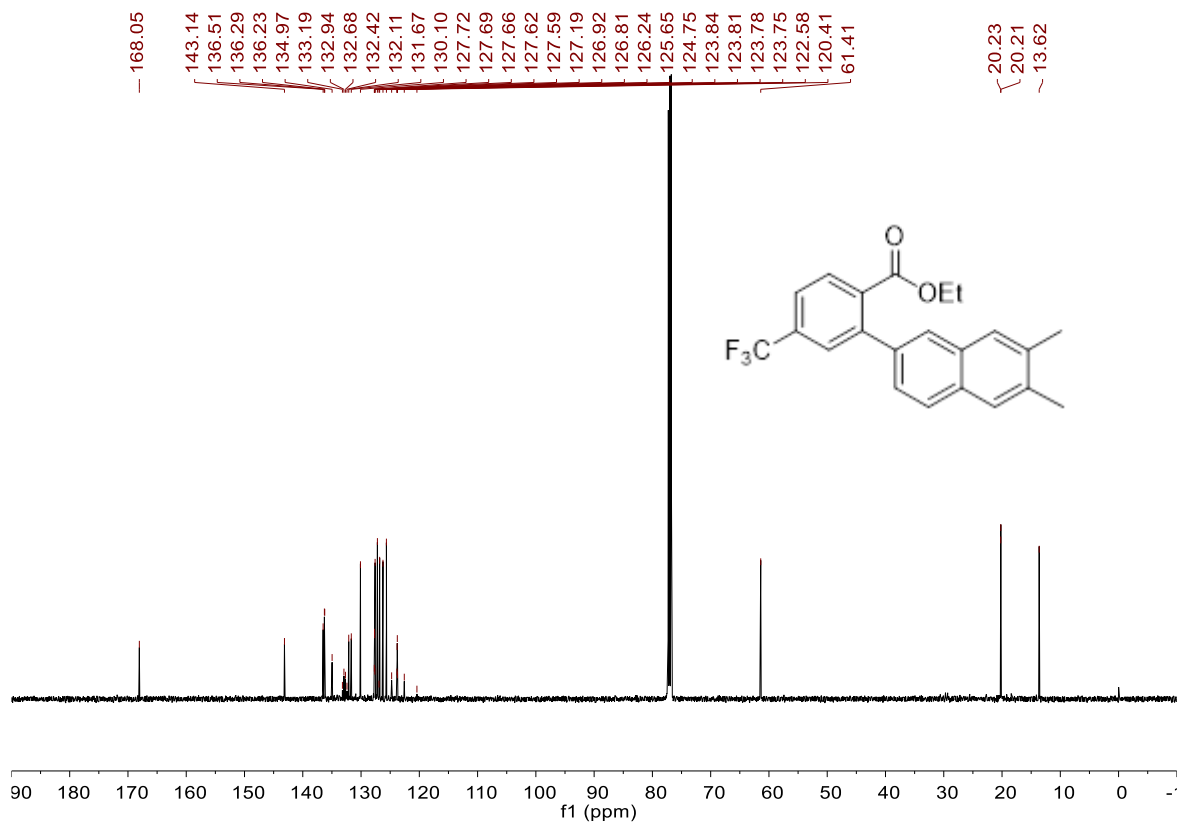
<sup>13</sup>C NMR spectrum of **3eb**, 126 MHz, CDCl<sub>3</sub>



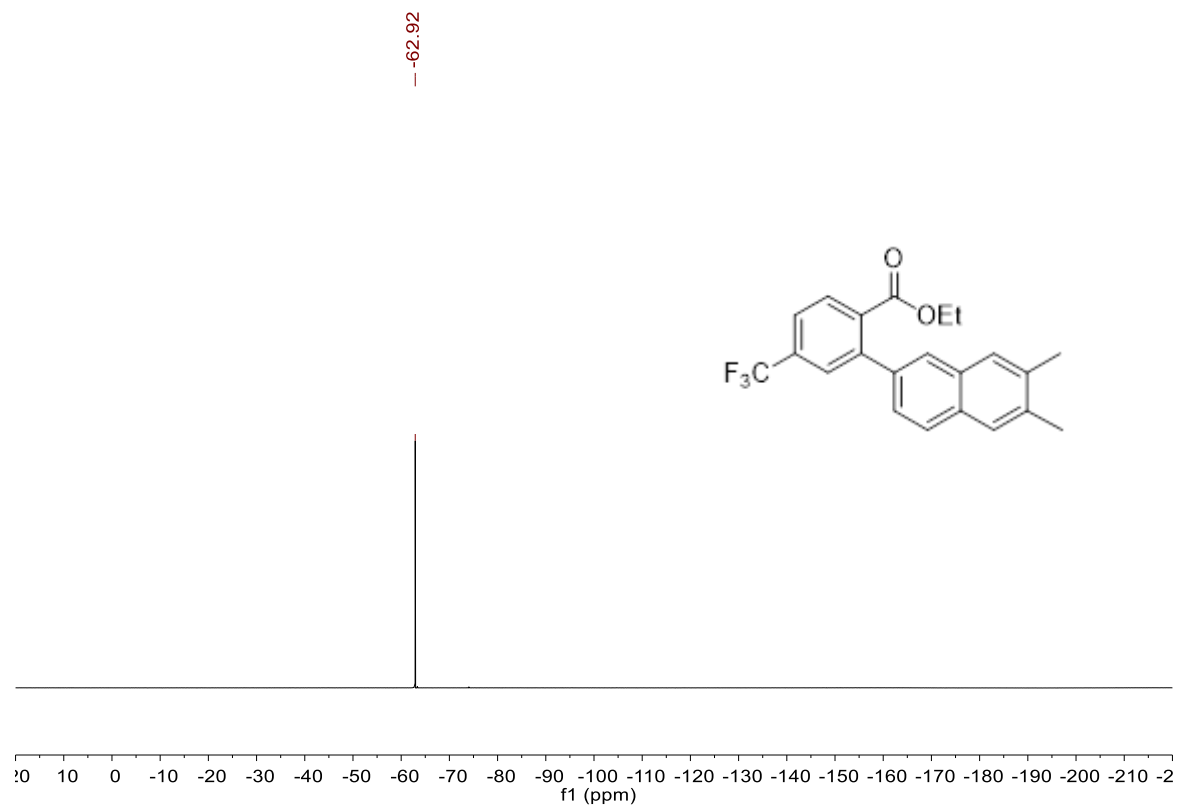
<sup>1</sup>H NMR spectrum of **3hb**, 500 MHz, CDCl<sub>3</sub>



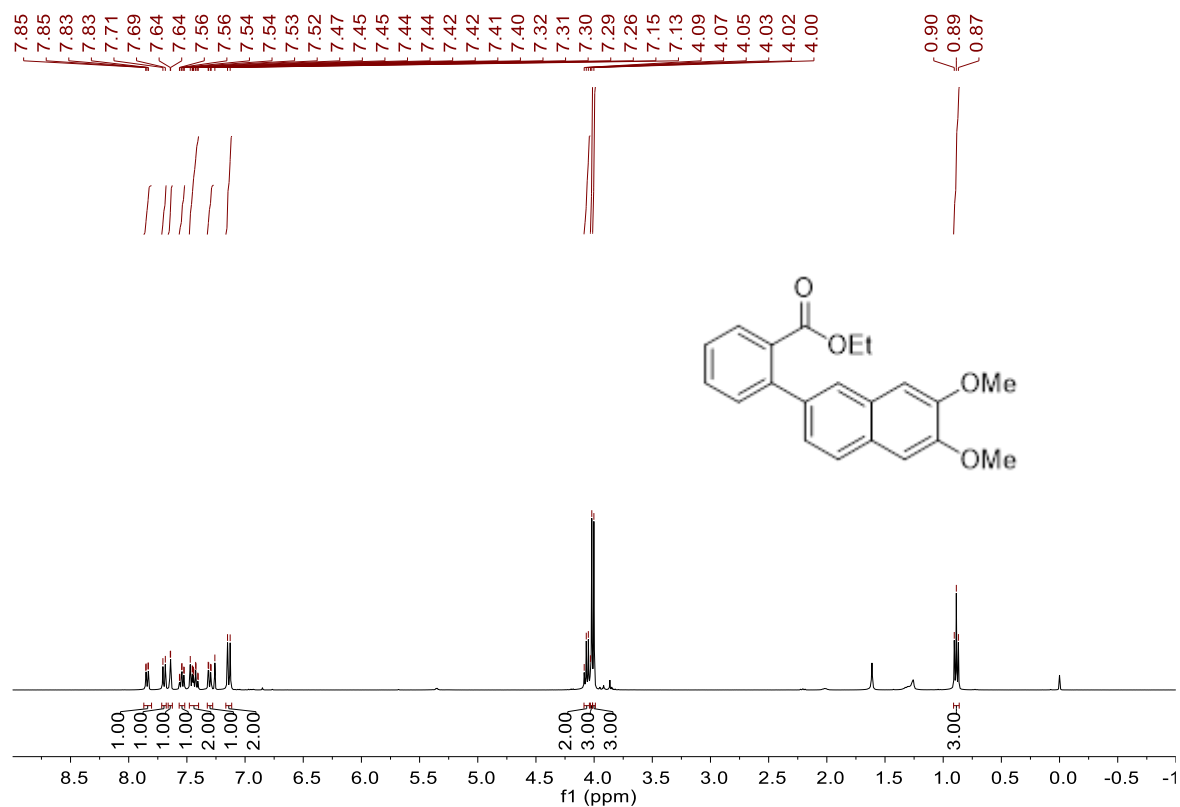
<sup>13</sup>C NMR spectrum of **3hb**, 126 MHz, CDCl<sub>3</sub>



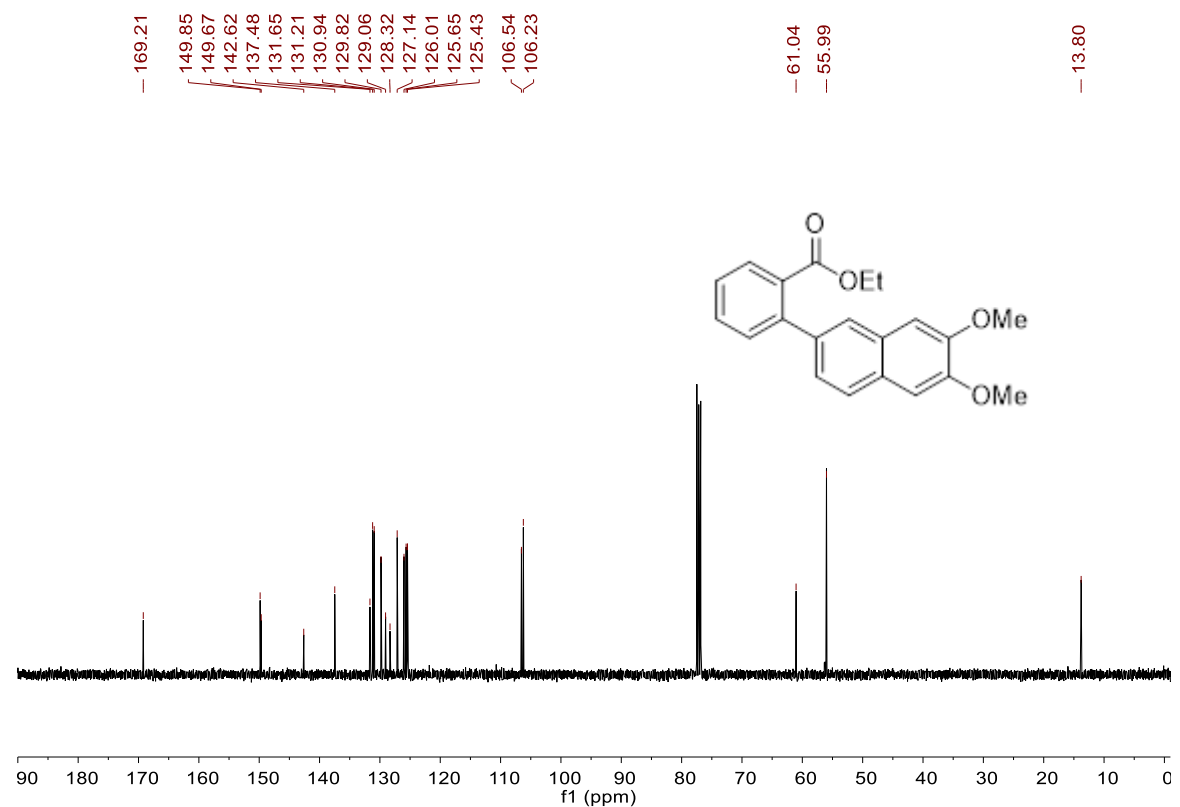
<sup>19</sup>F NMR spectrum of **3hb**, 471 MHz, CDCl<sub>3</sub>



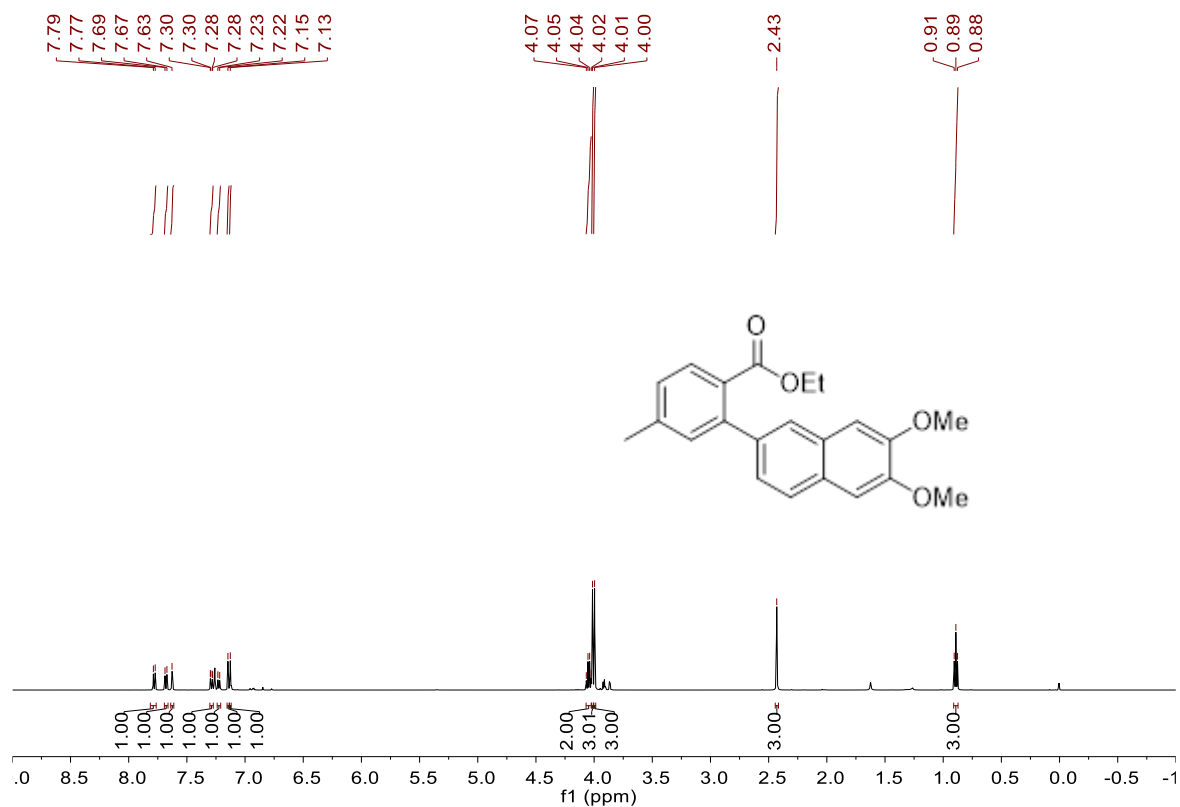
<sup>1</sup>H NMR spectrum of **3ac**, 400 MHz, CDCl<sub>3</sub>



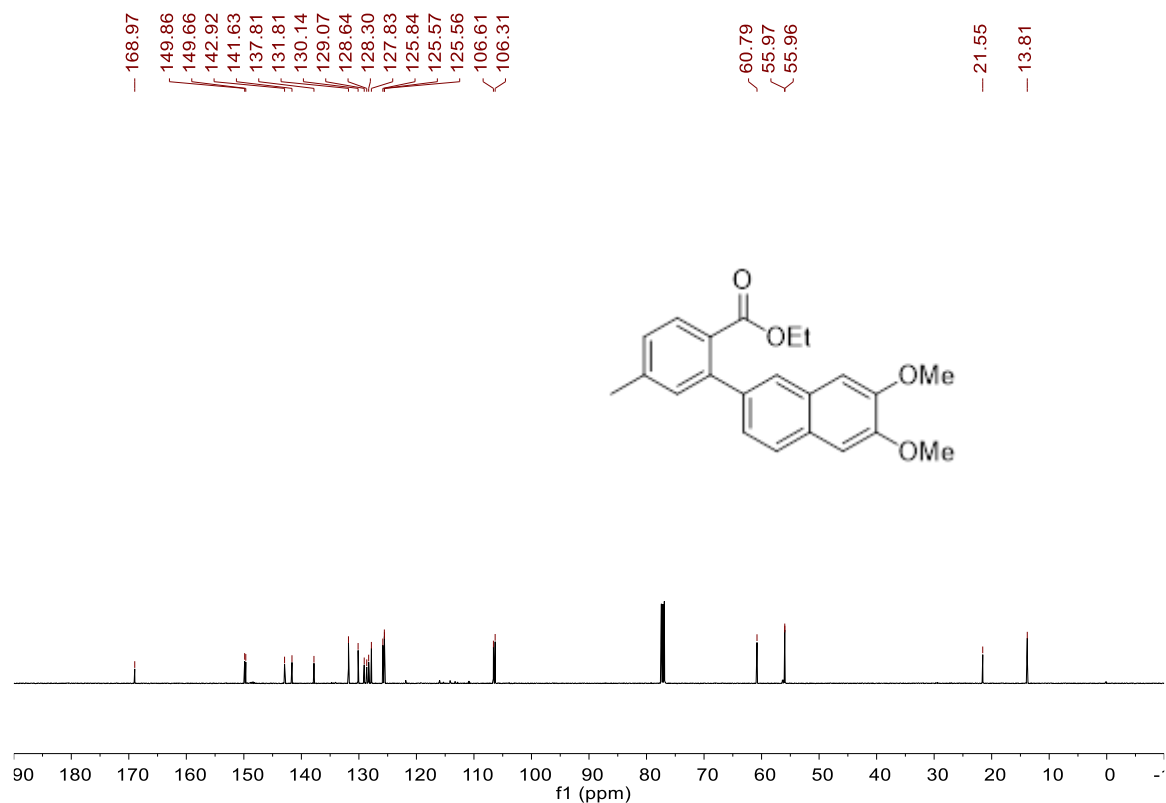
<sup>13</sup>C NMR spectrum of **3ac**, 101 MHz, CDCl<sub>3</sub>



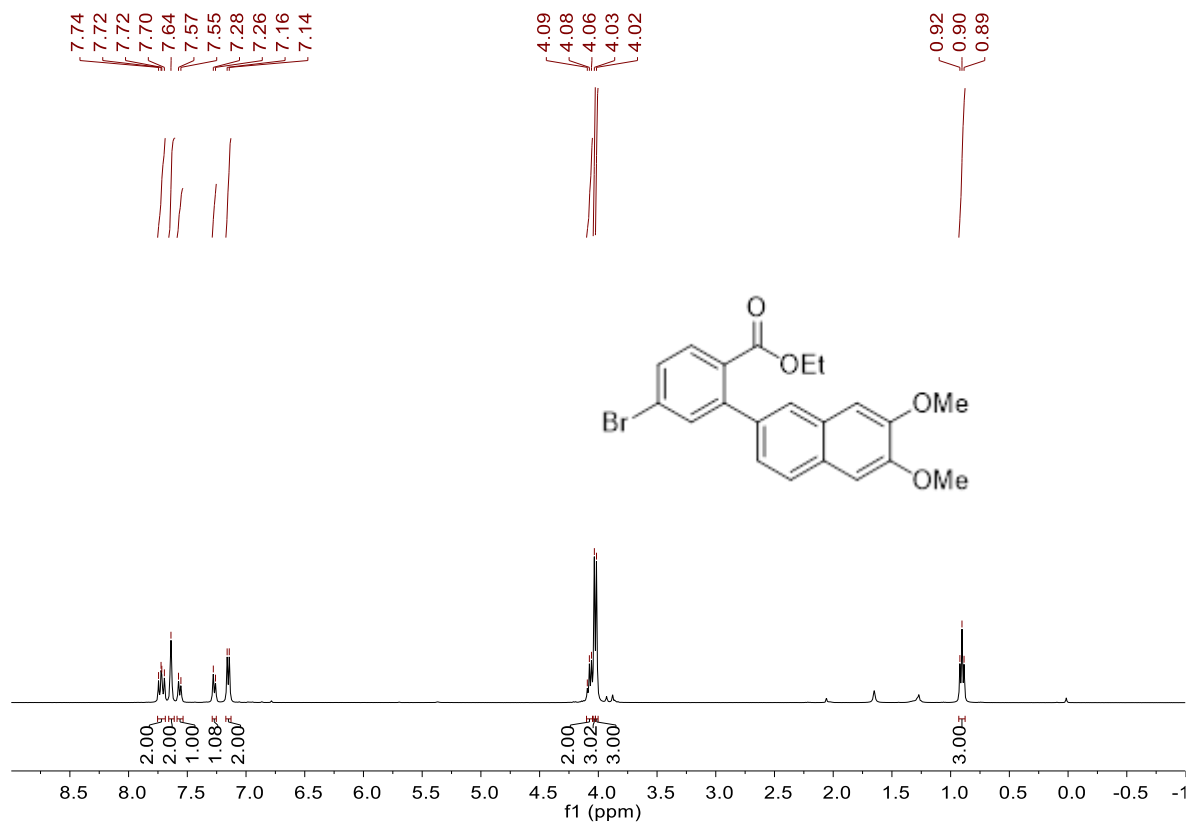
<sup>1</sup>H NMR spectrum of **3bc**, 500 MHz, CDCl<sub>3</sub>



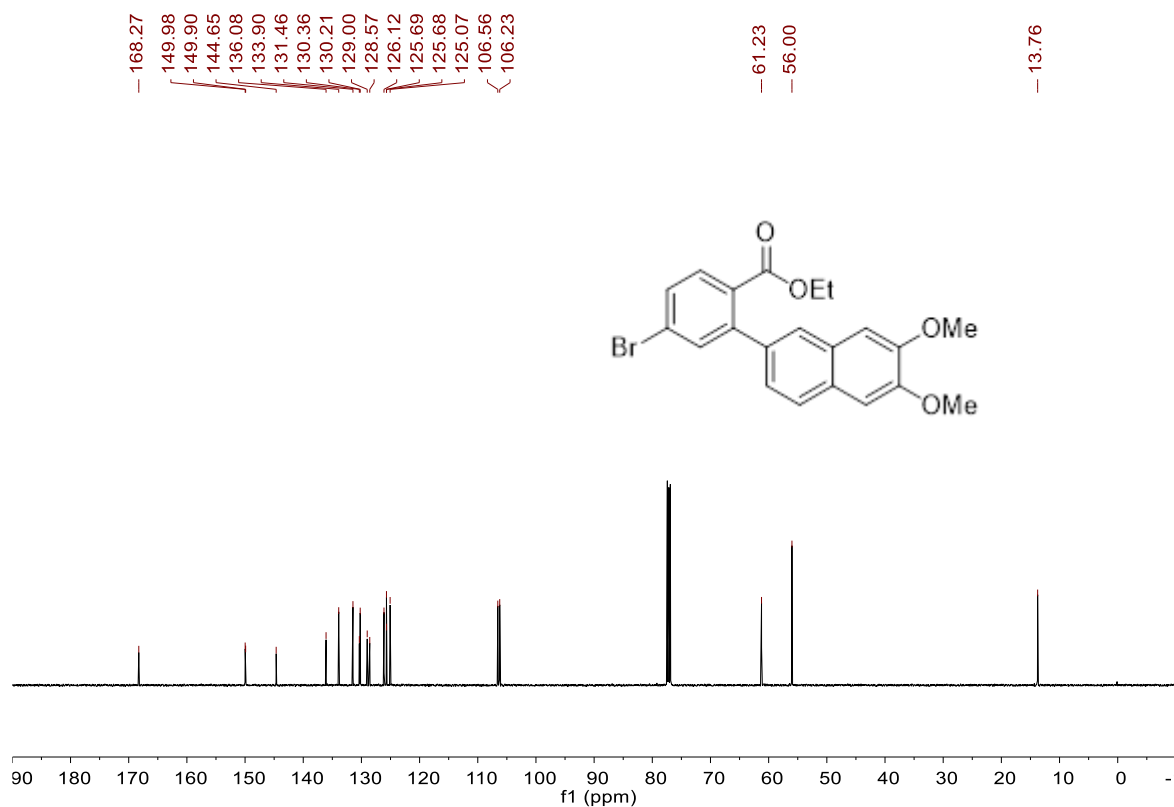
<sup>13</sup>C NMR spectrum of **3bc**, 126 MHz, CDCl<sub>3</sub>



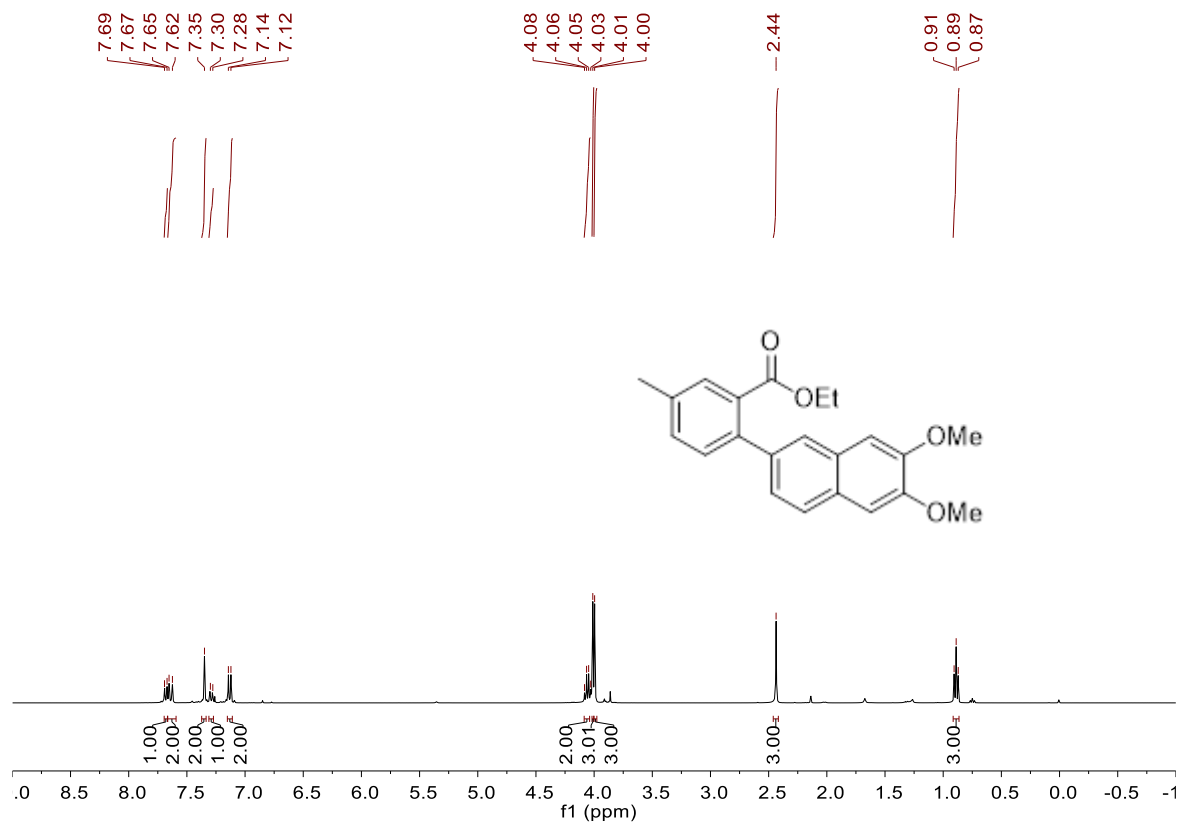
<sup>1</sup>H NMR spectrum of **3ec**, 400 MHz, CDCl<sub>3</sub>



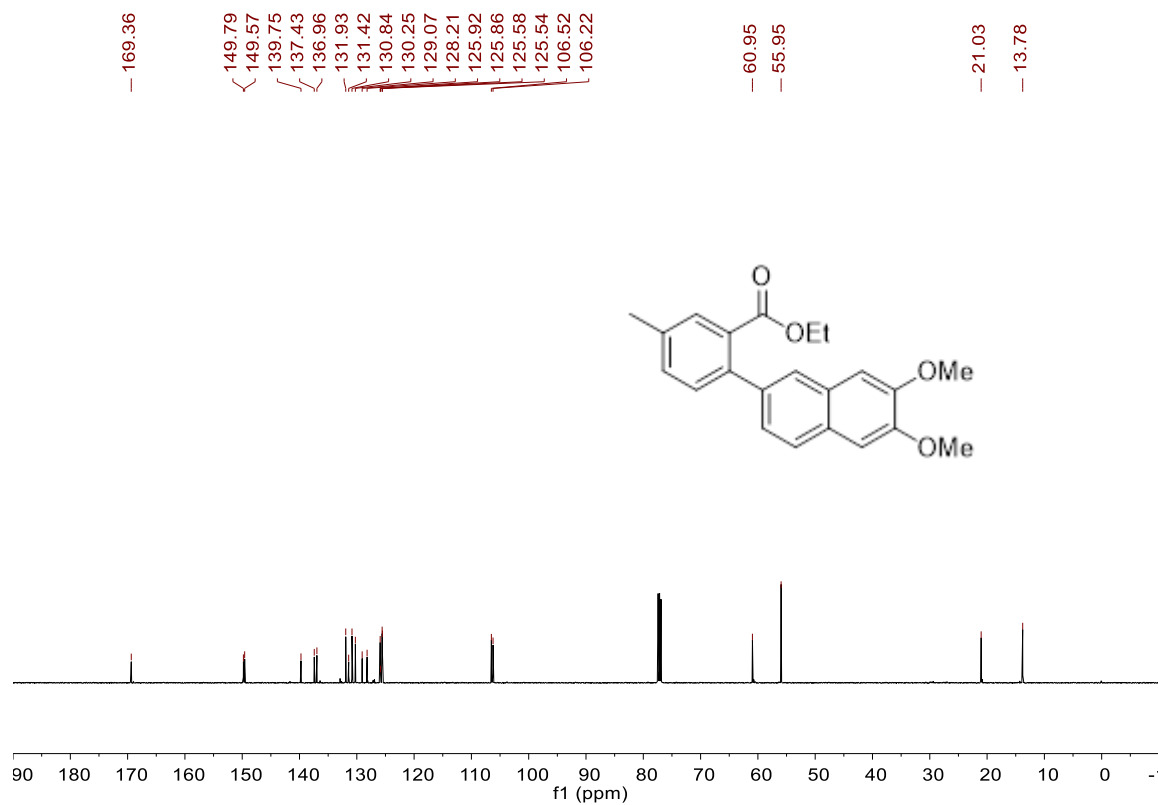
<sup>13</sup>C NMR spectrum of **3ec**, 126 MHz, CDCl<sub>3</sub>



<sup>1</sup>H NMR spectrum of **3kc**, 400 MHz, CDCl<sub>3</sub>

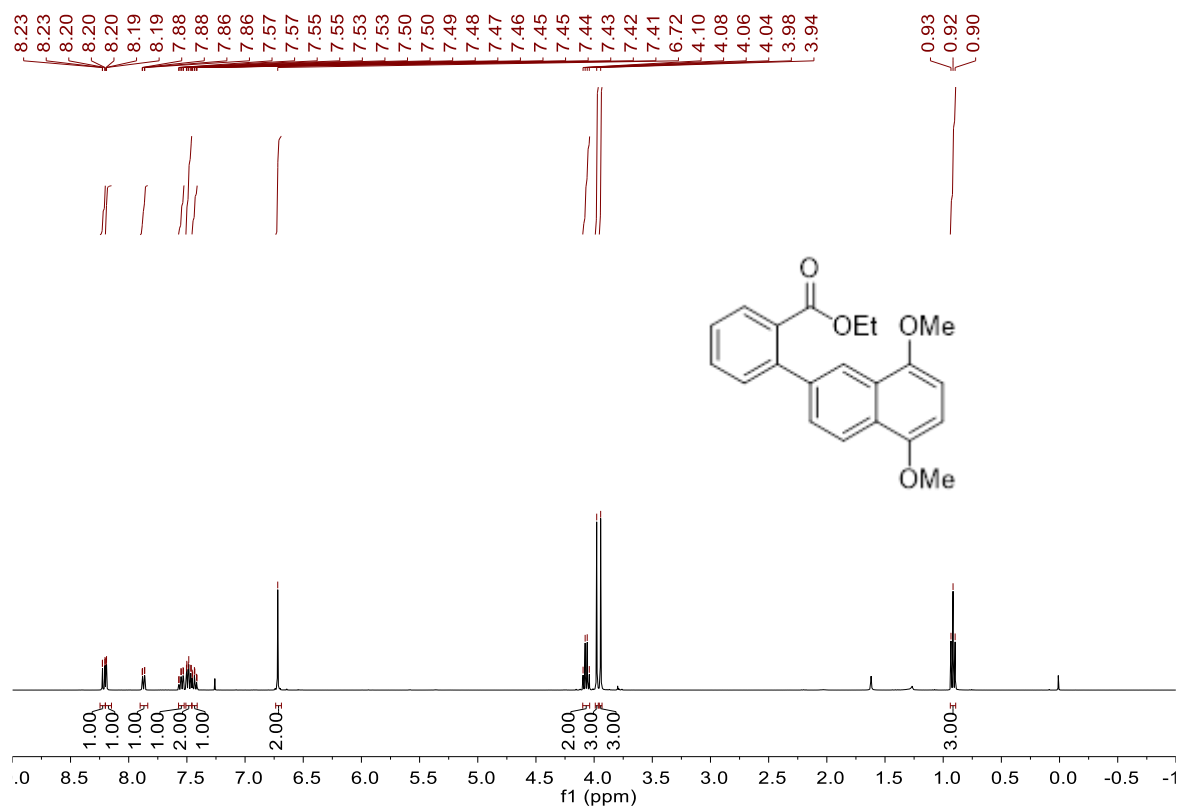


<sup>13</sup>C NMR spectrum of **3kc**, 126 MHz, CDCl<sub>3</sub>

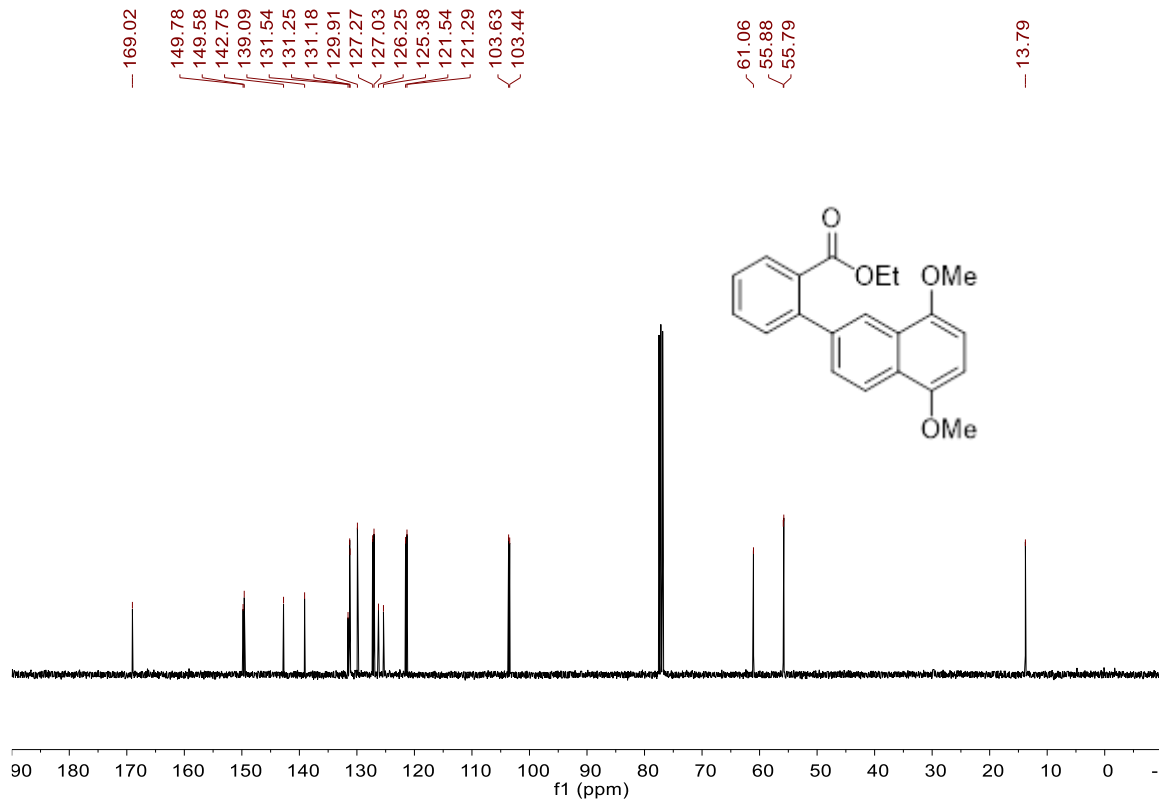




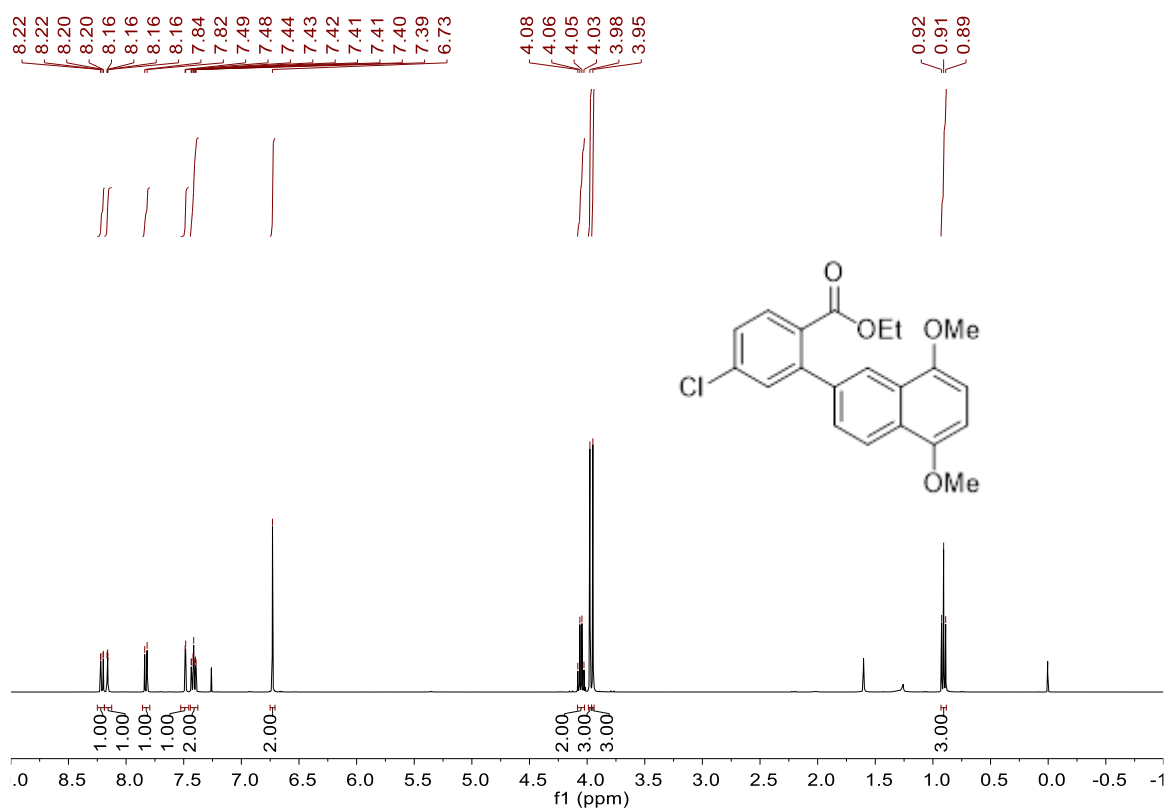
<sup>1</sup>H NMR spectrum of **3ad**, 400 MHz, CDCl<sub>3</sub>



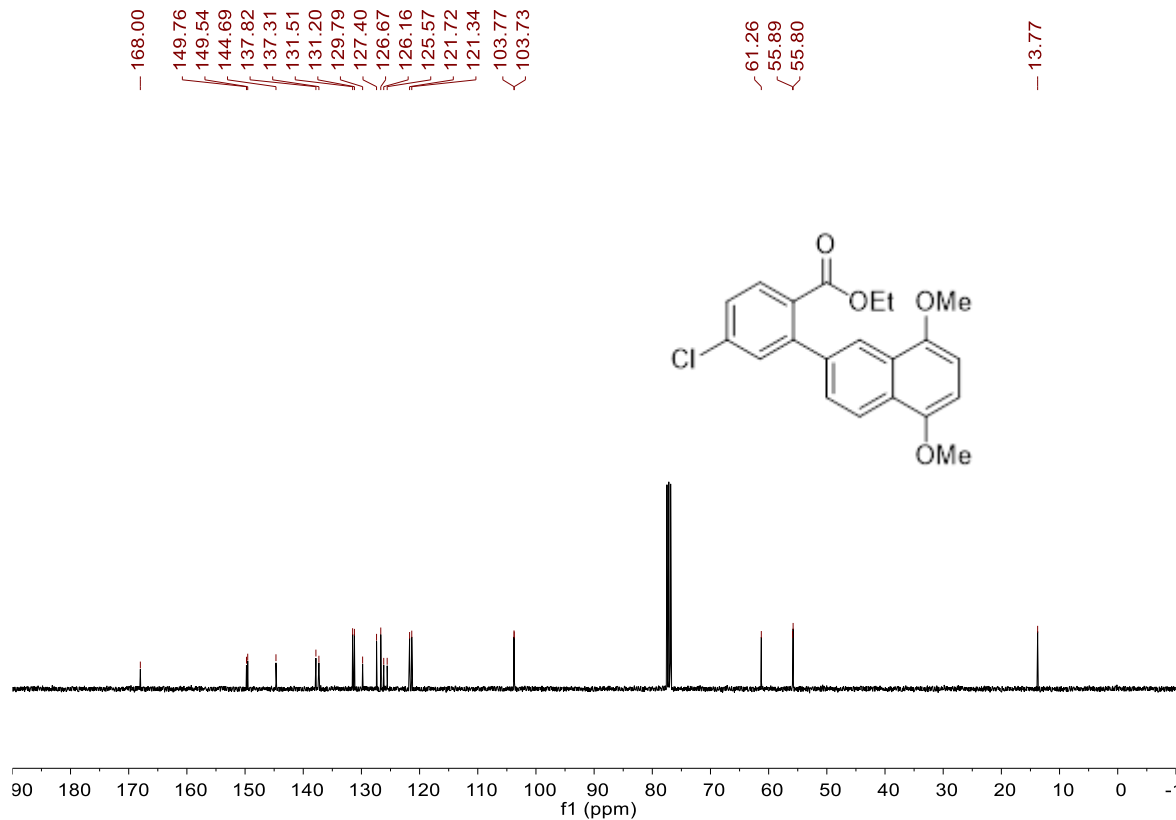
<sup>13</sup>C NMR spectrum of **3ad**, 101 MHz, CDCl<sub>3</sub>



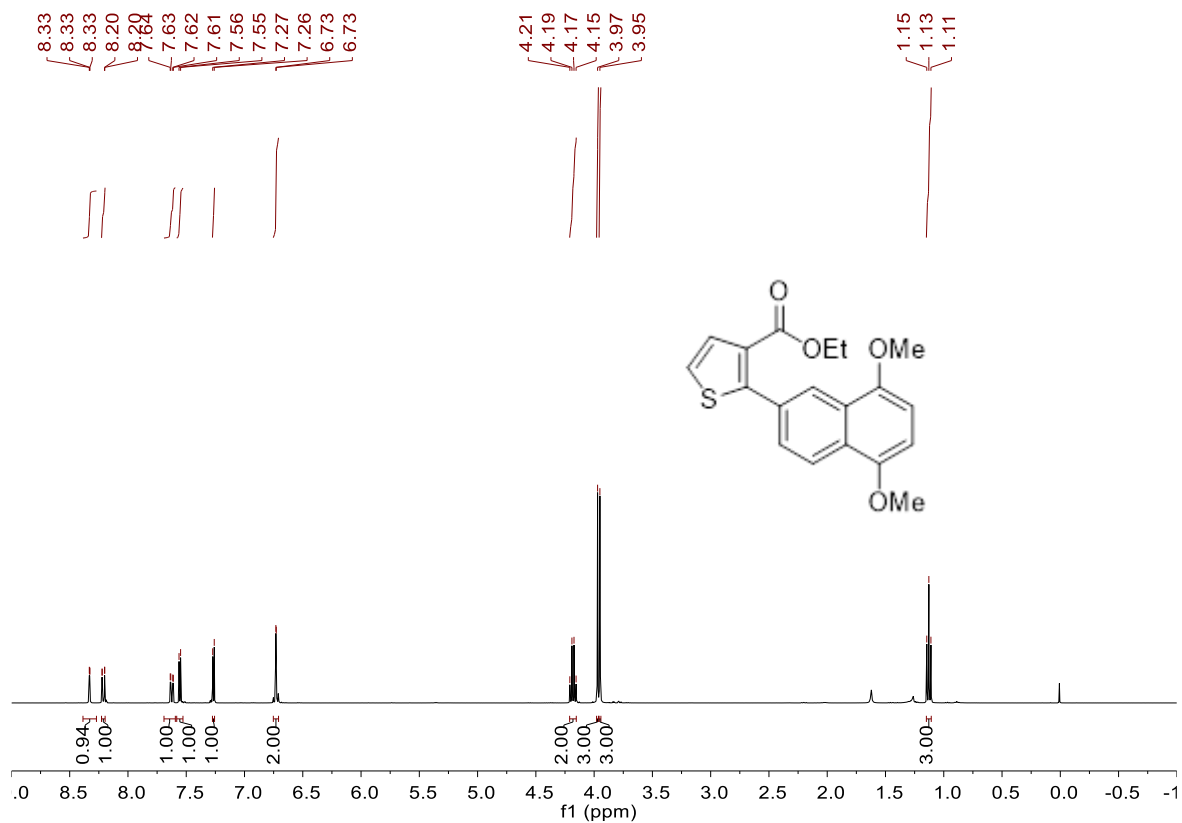
$^1\text{H}$  NMR spectrum of **3dd**, 400 MHz,  $\text{CDCl}_3$



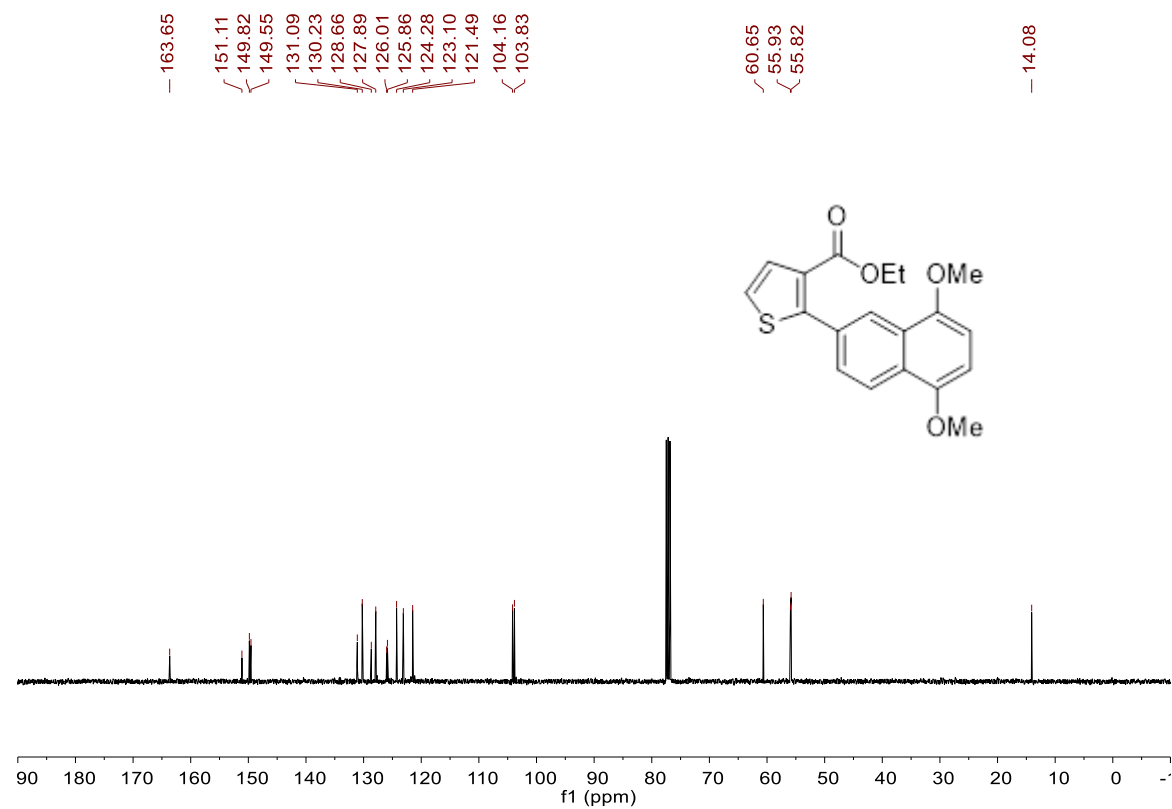
$^{13}\text{C}$  NMR spectrum of **3dd**, 101 MHz,  $\text{CDCl}_3$



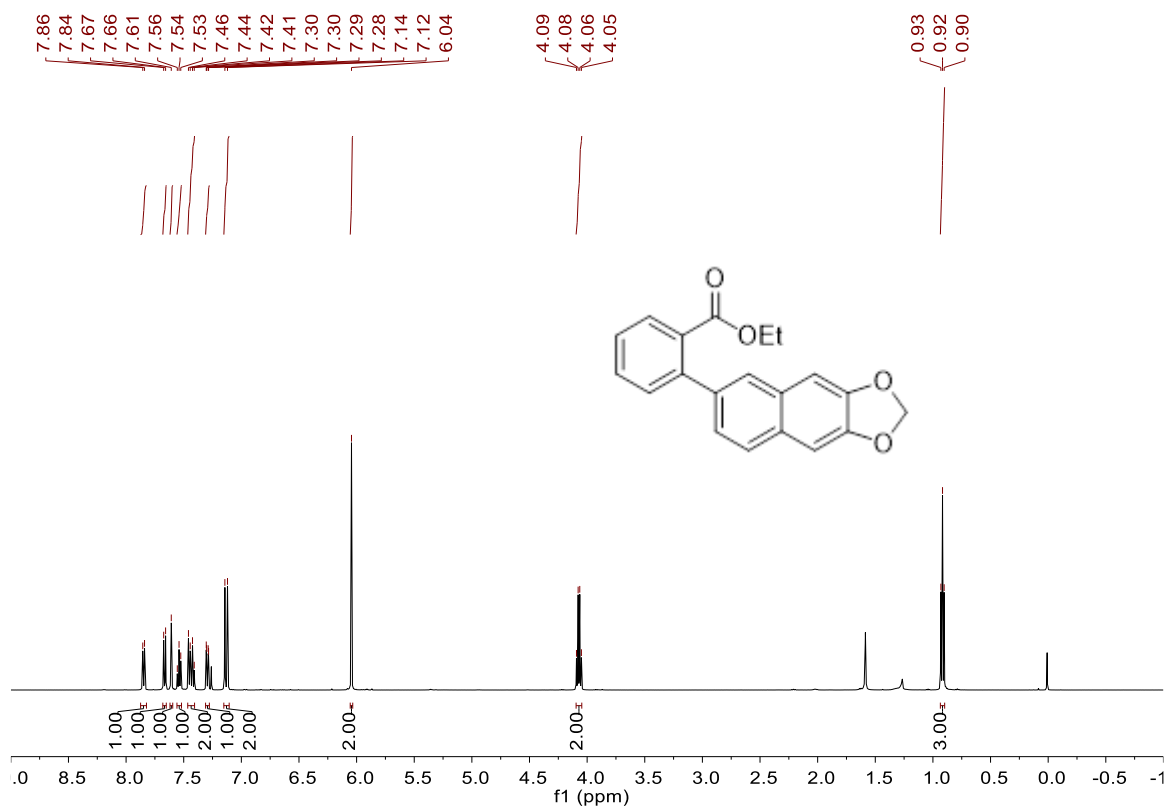
<sup>1</sup>H NMR spectrum of **3od**, 400 MHz, CDCl<sub>3</sub>



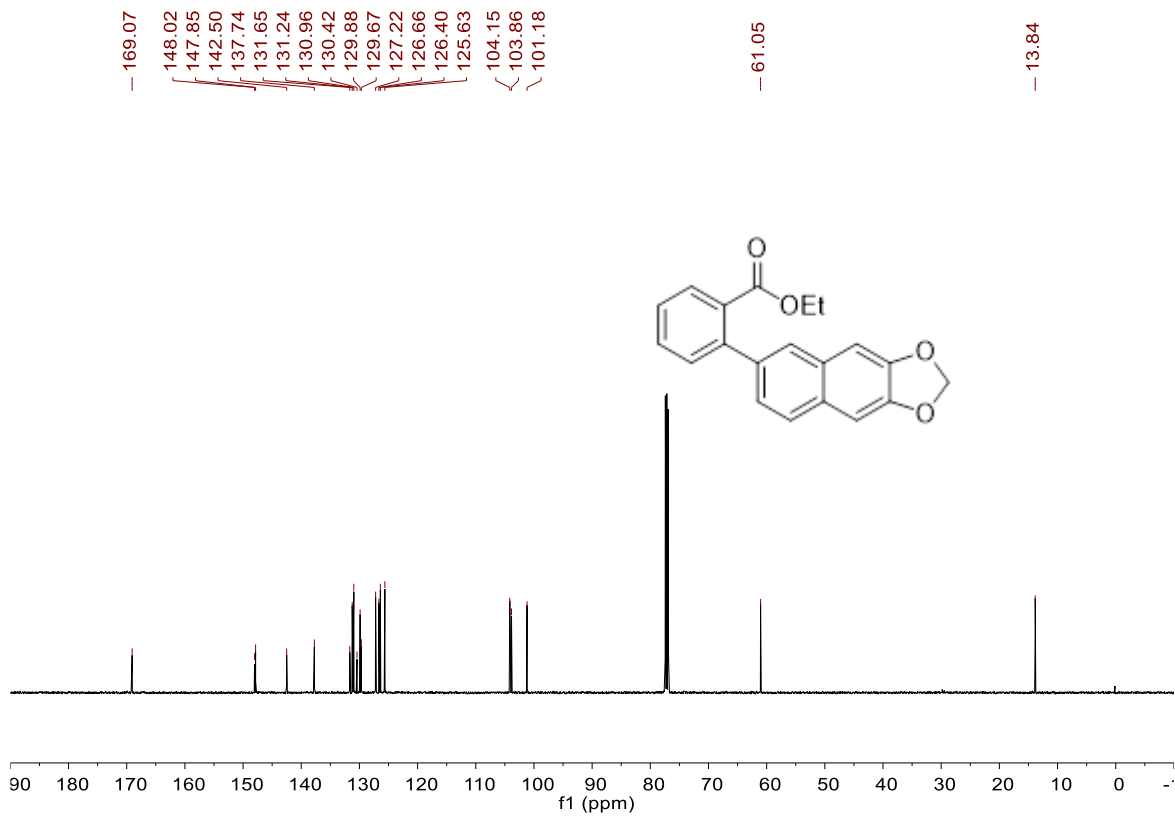
<sup>13</sup>C NMR spectrum of **3od**, 101 MHz, CDCl<sub>3</sub>



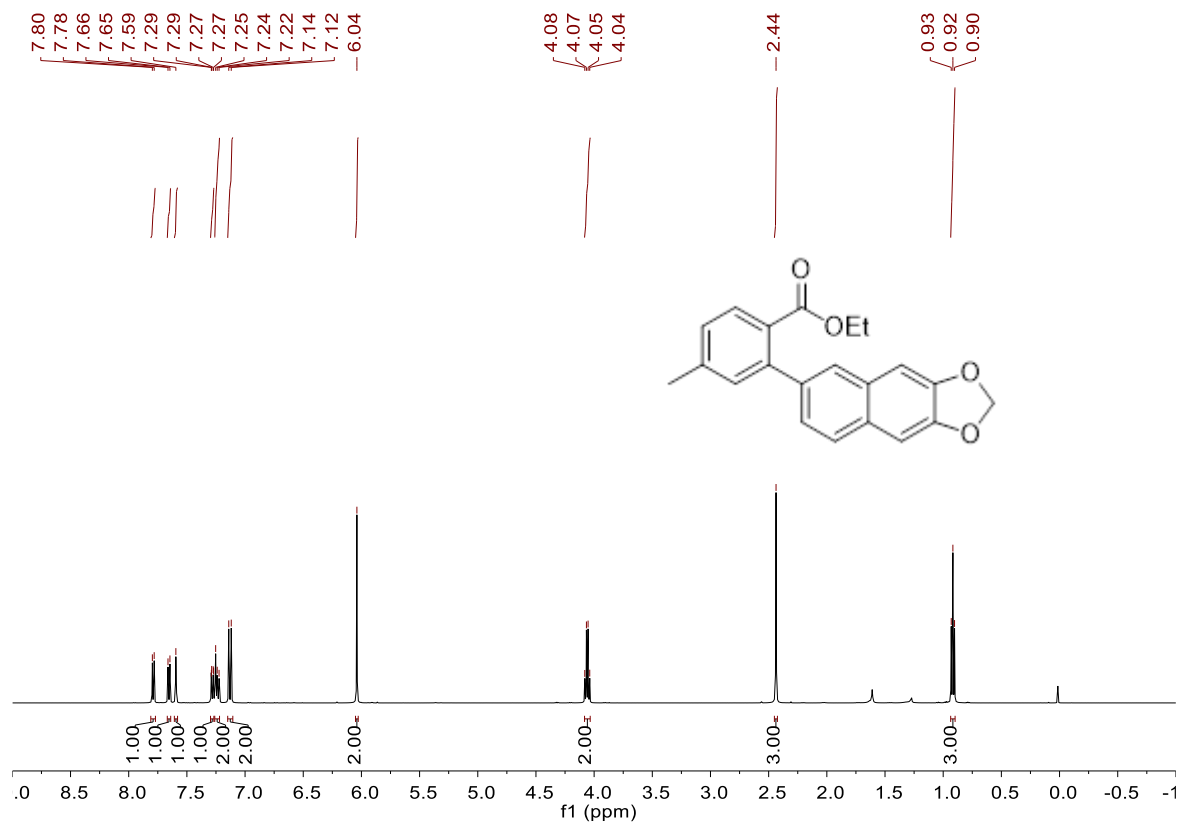
<sup>1</sup>H NMR spectrum of **3ae**, 500 MHz, CDCl<sub>3</sub>



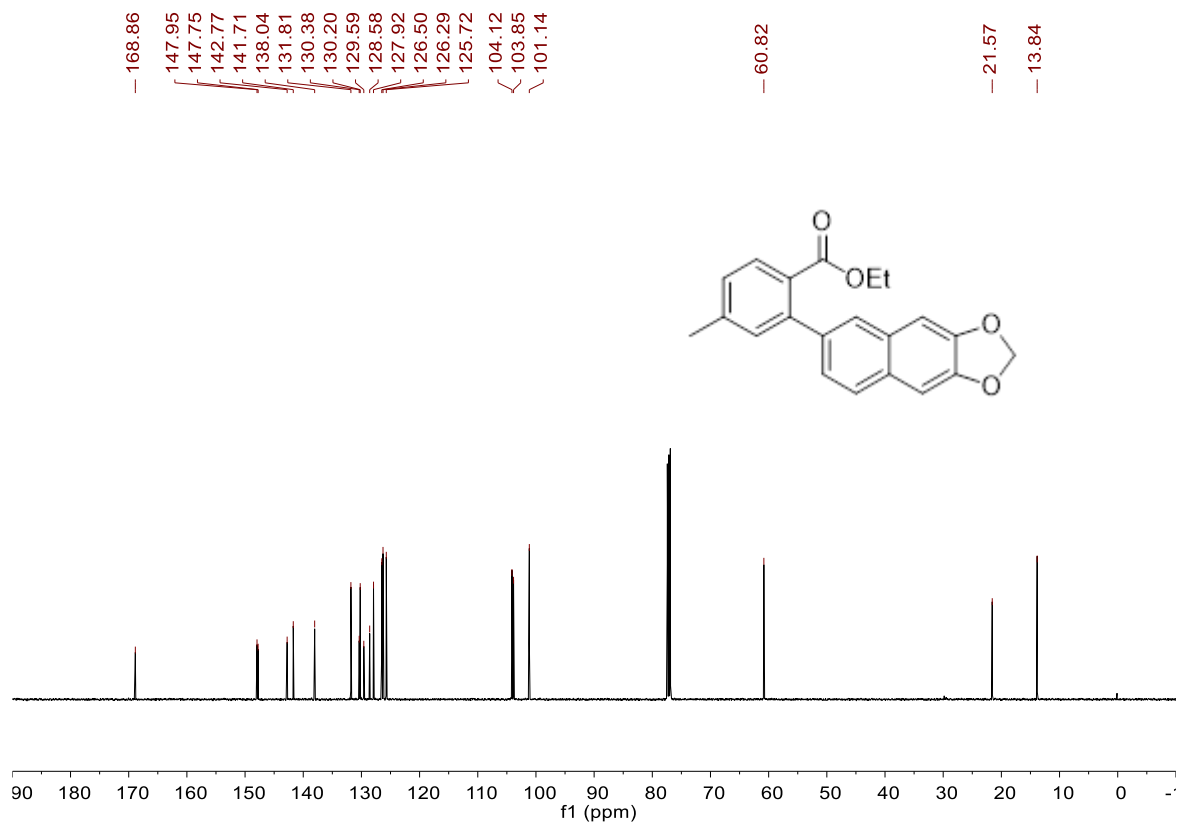
<sup>13</sup>C NMR spectrum of **3ae**, 126 MHz, CDCl<sub>3</sub>



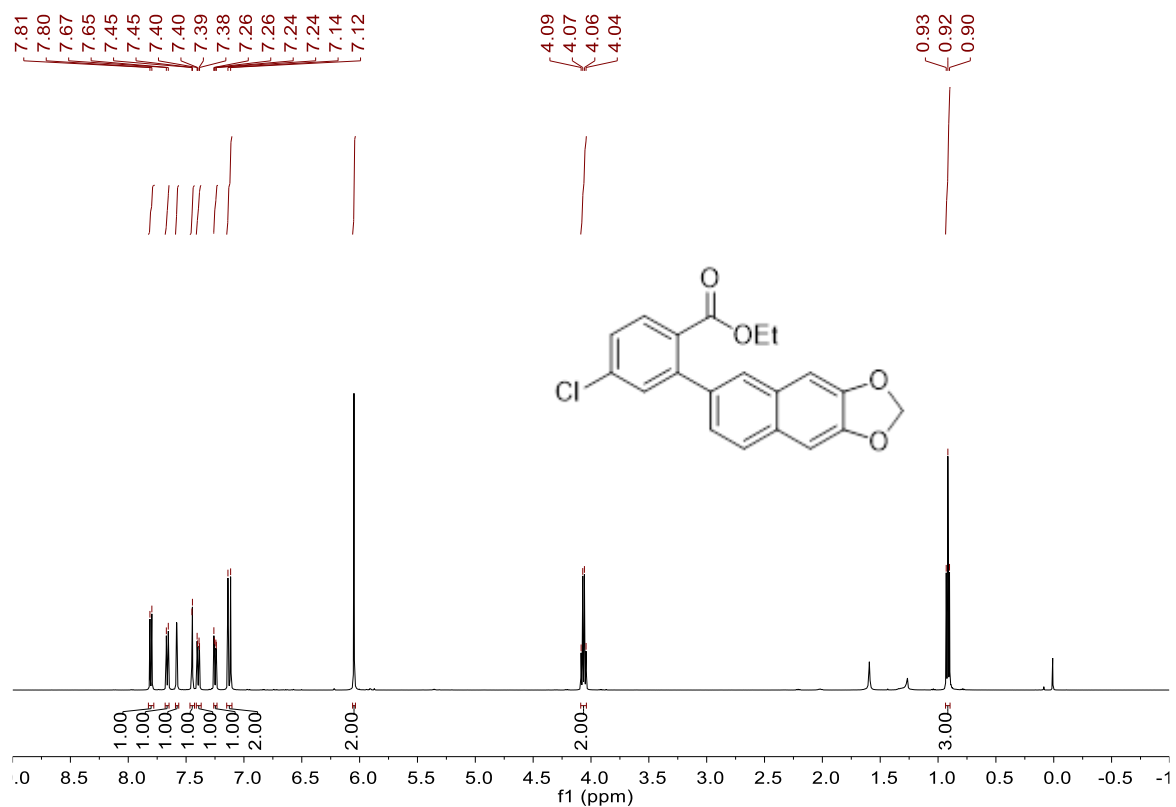
<sup>1</sup>H NMR spectrum of **3be**, 500 MHz, CDCl<sub>3</sub>



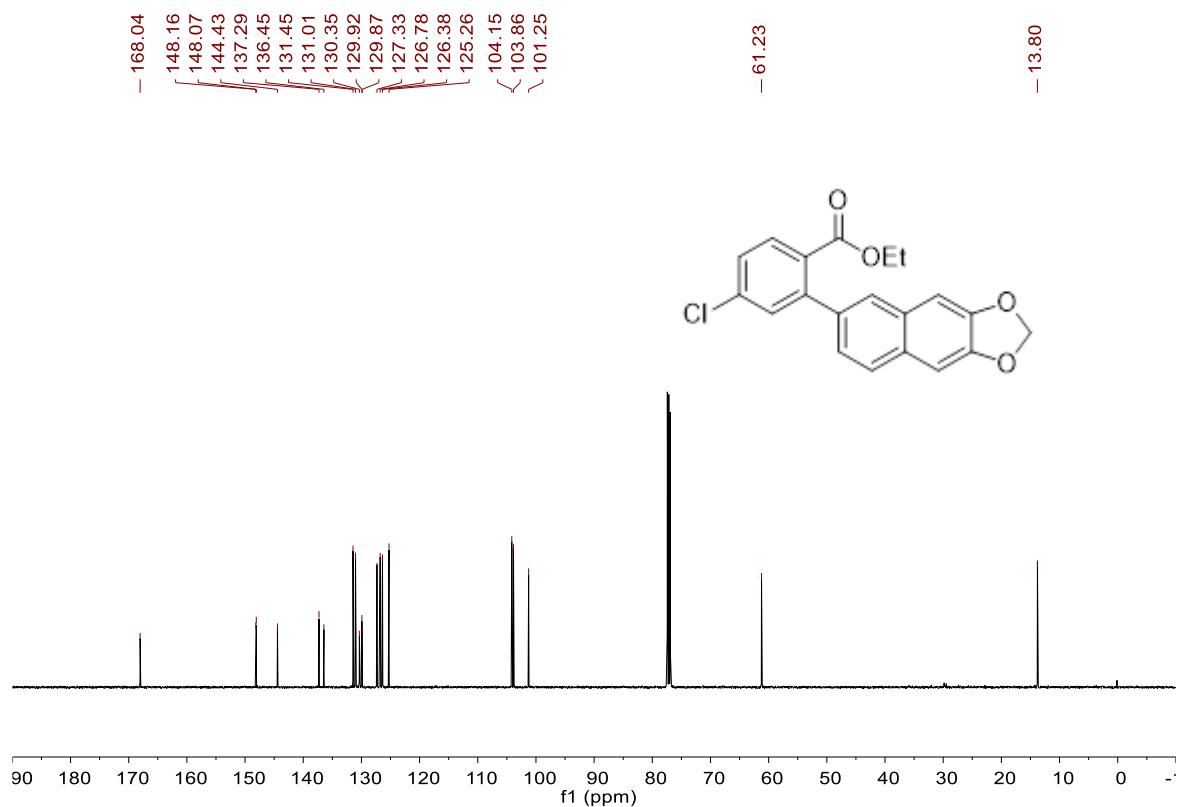
<sup>13</sup>C NMR spectrum of **3be**, 126 MHz, CDCl<sub>3</sub>



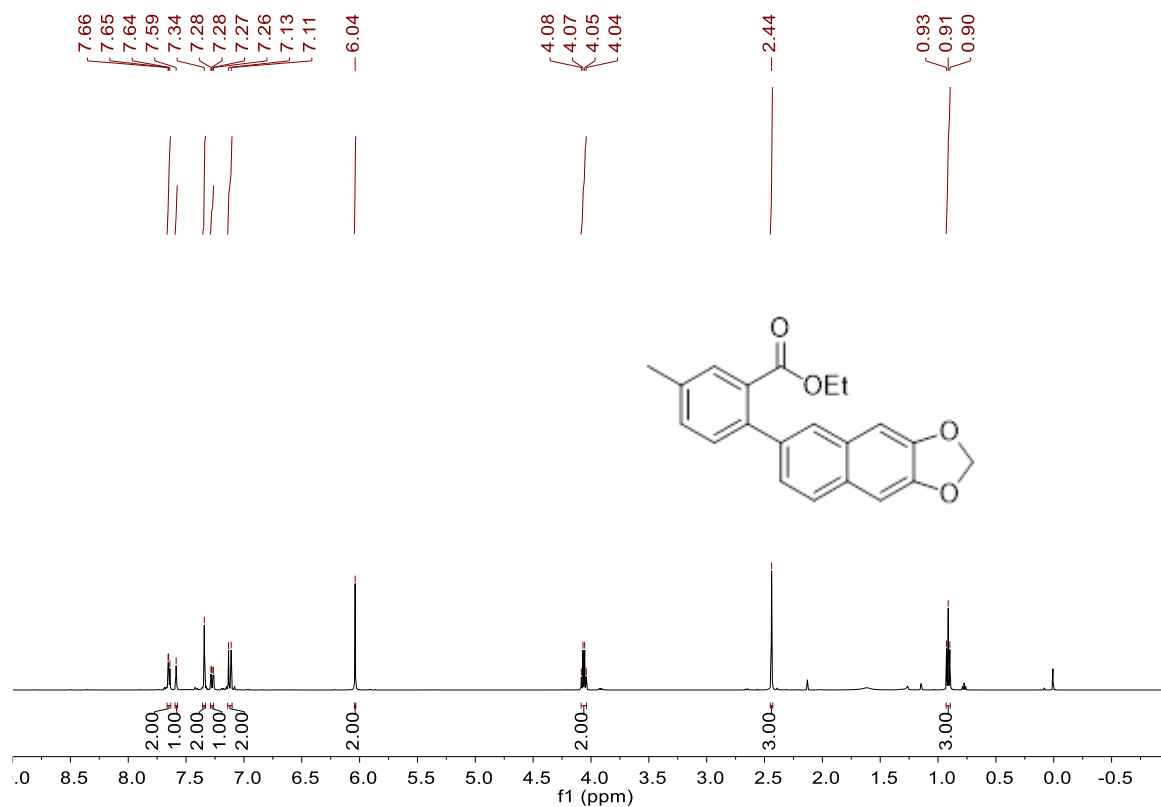
<sup>1</sup>H NMR spectrum of **3de**, 500 MHz, CDCl<sub>3</sub>



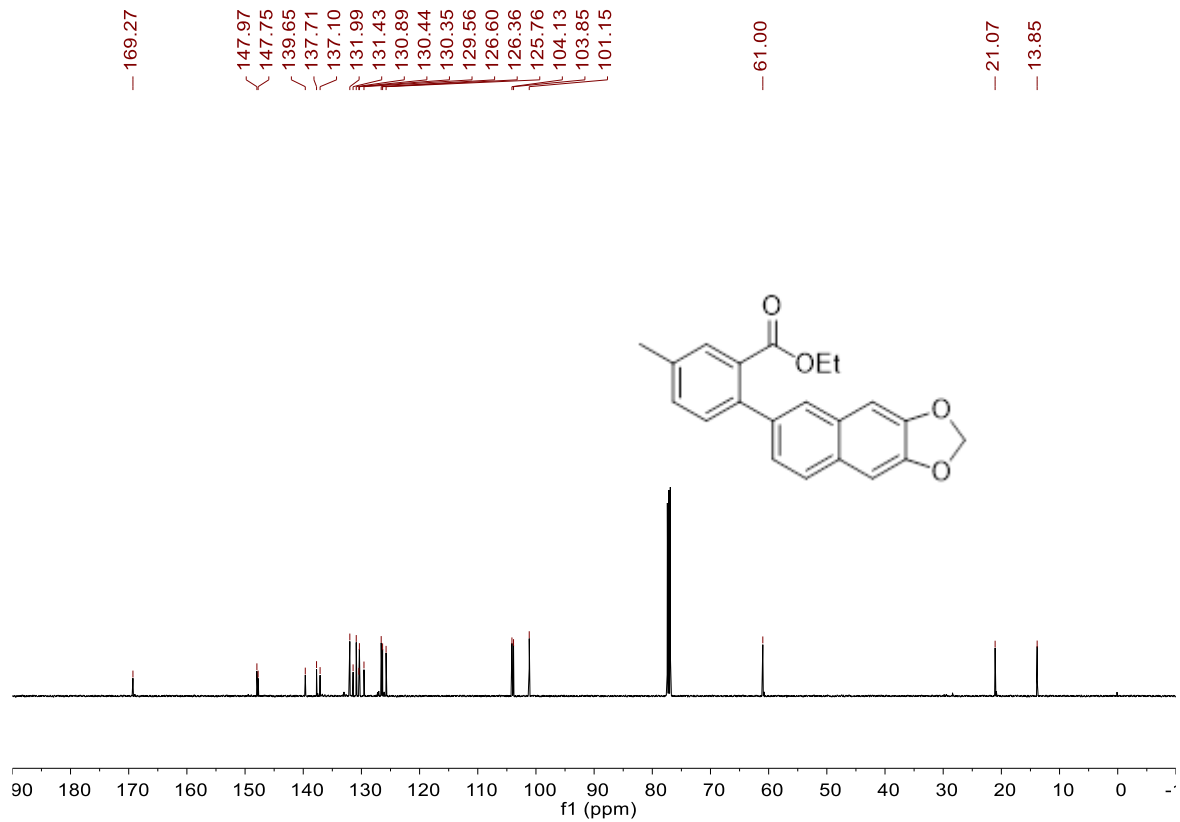
<sup>13</sup>C NMR spectrum of **3de**, 126 MHz, CDCl<sub>3</sub>



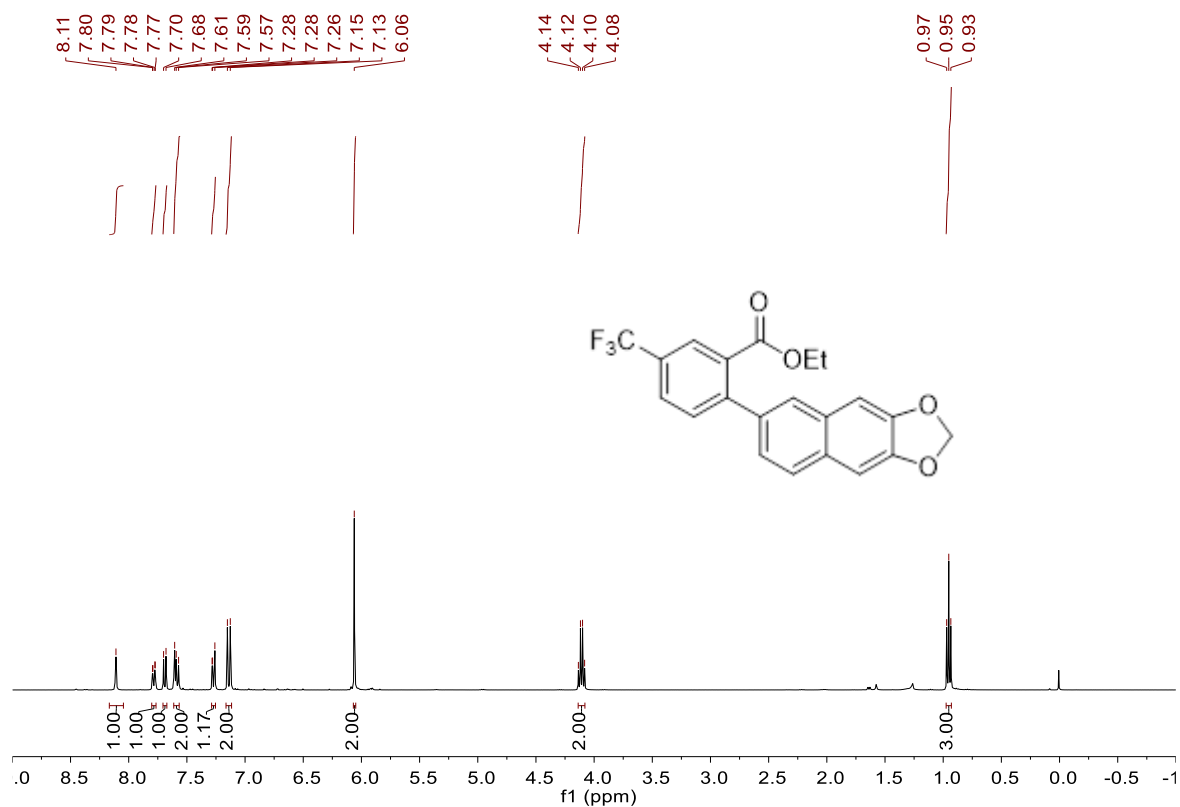
<sup>1</sup>H NMR spectrum of **3ke**, 500 MHz, CDCl<sub>3</sub>



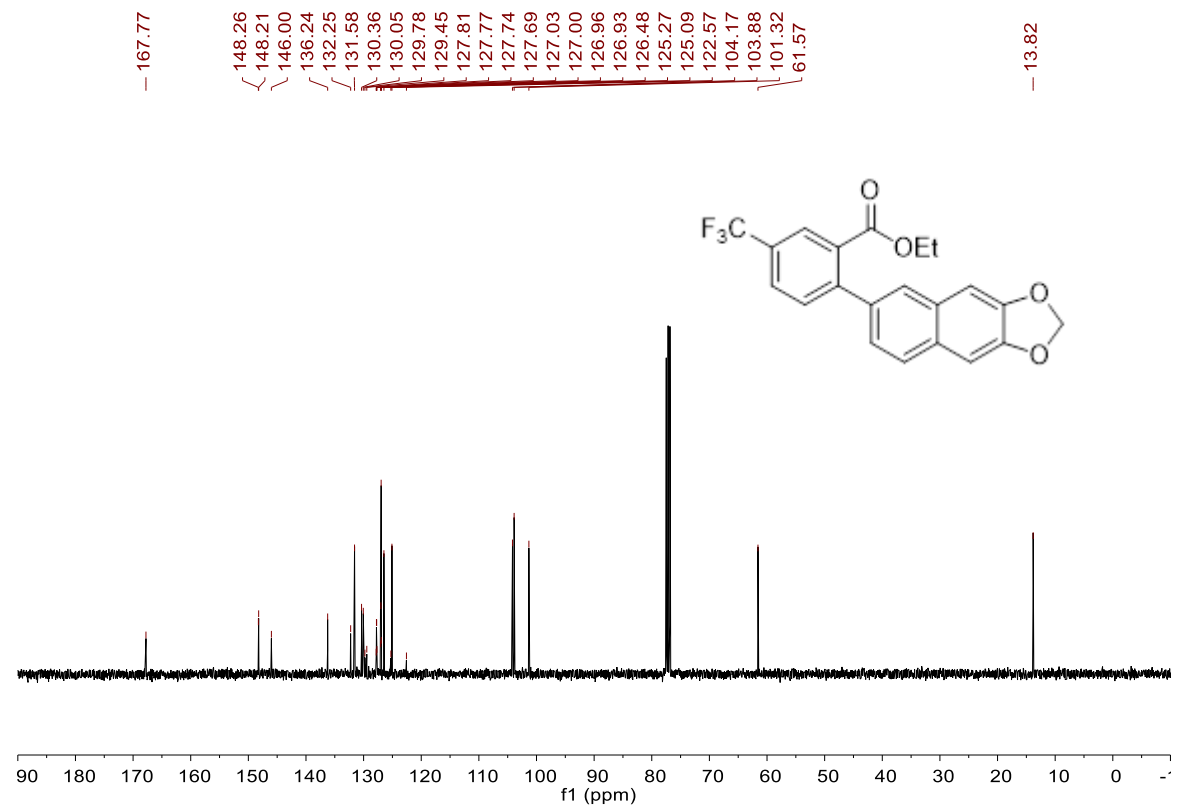
<sup>13</sup>C NMR spectrum of **3ke**, 126 MHz, CDCl<sub>3</sub>



<sup>1</sup>H NMR spectrum of **3me**, 400 MHz, CDCl<sub>3</sub>

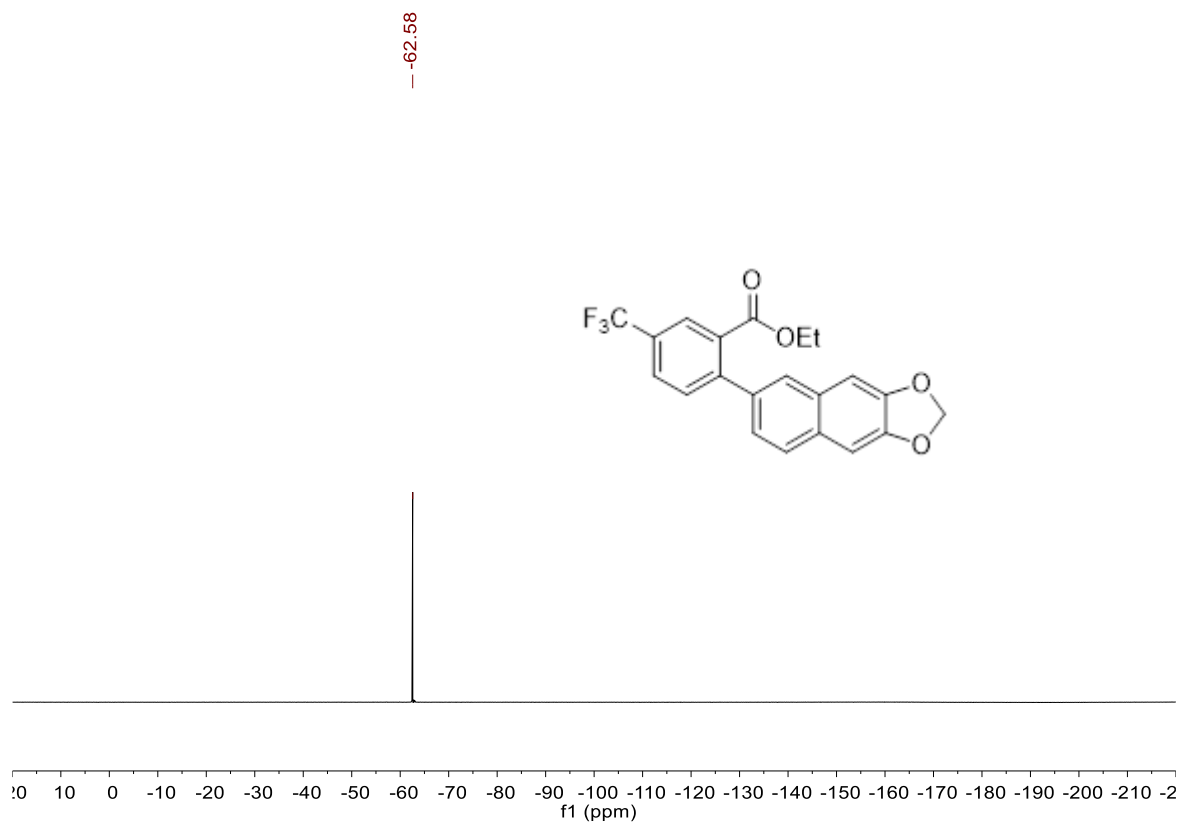


<sup>13</sup>C NMR spectrum of **3me**, 101 MHz, CDCl<sub>3</sub>

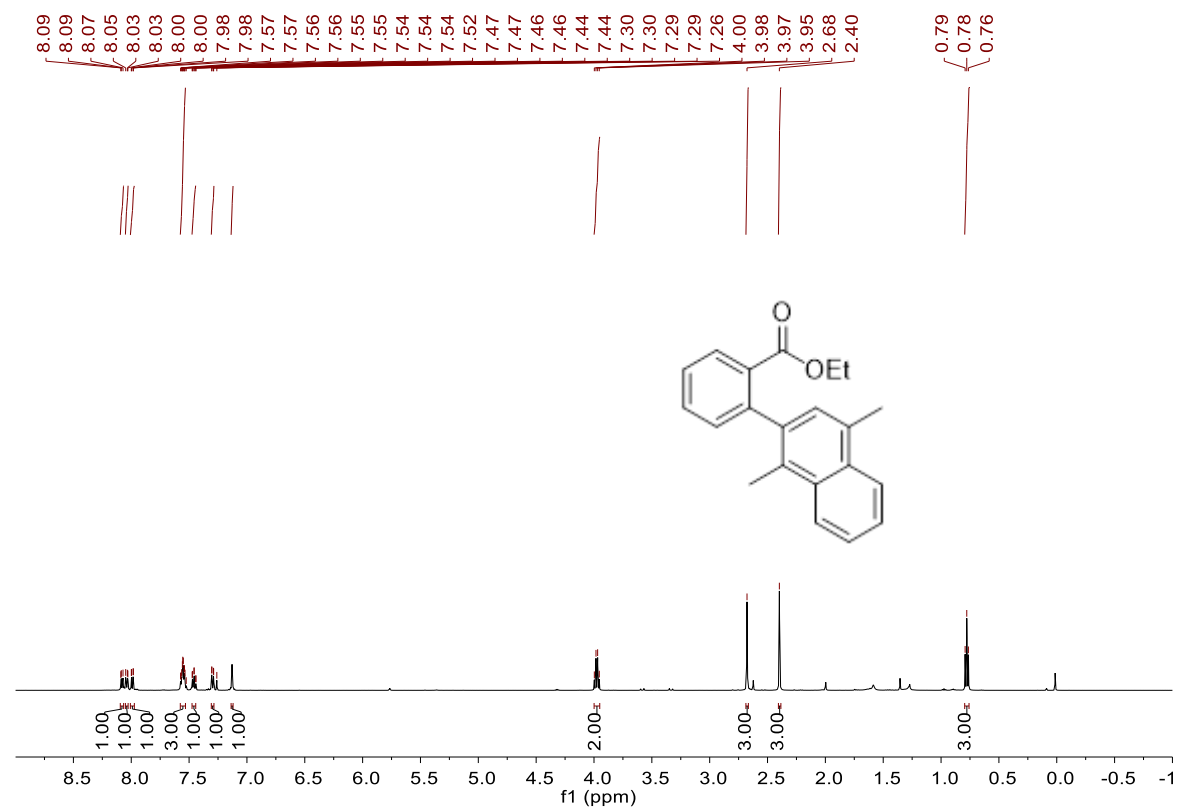




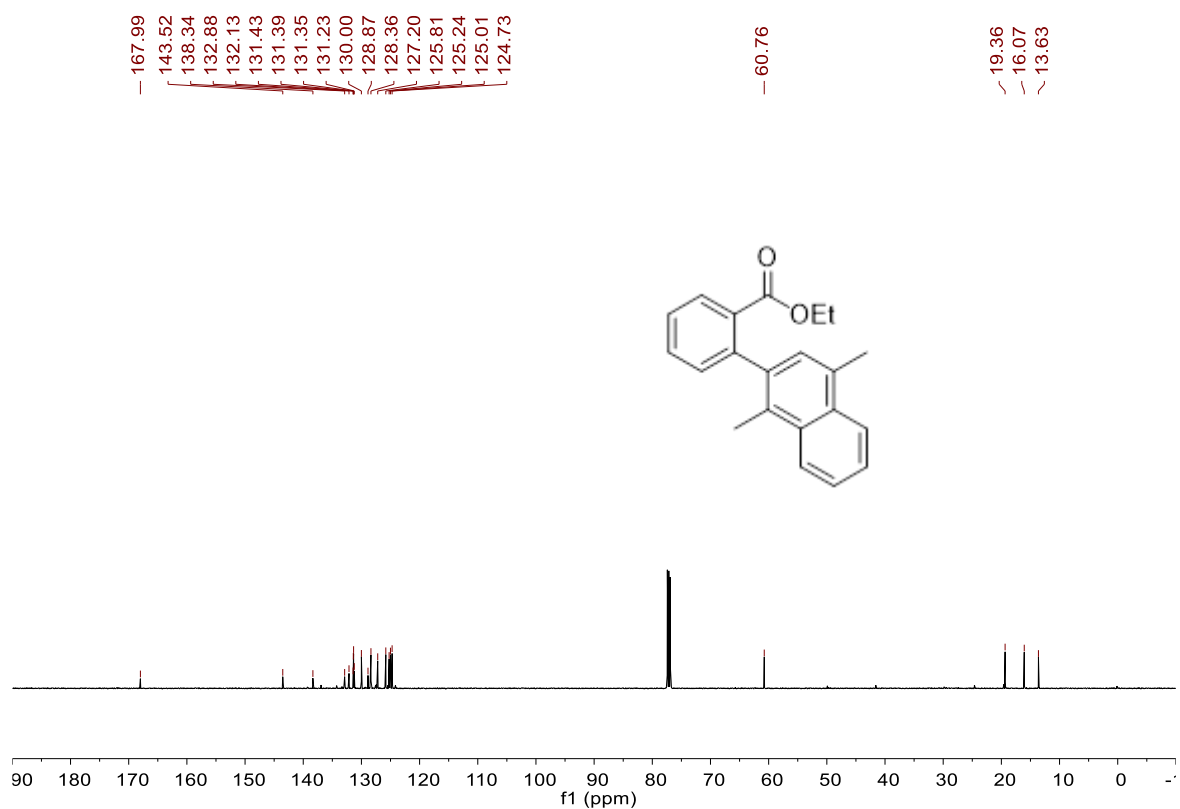
$^{19}\text{F}$  NMR spectrum of **3me**, 471 MHz,  $\text{CDCl}_3$



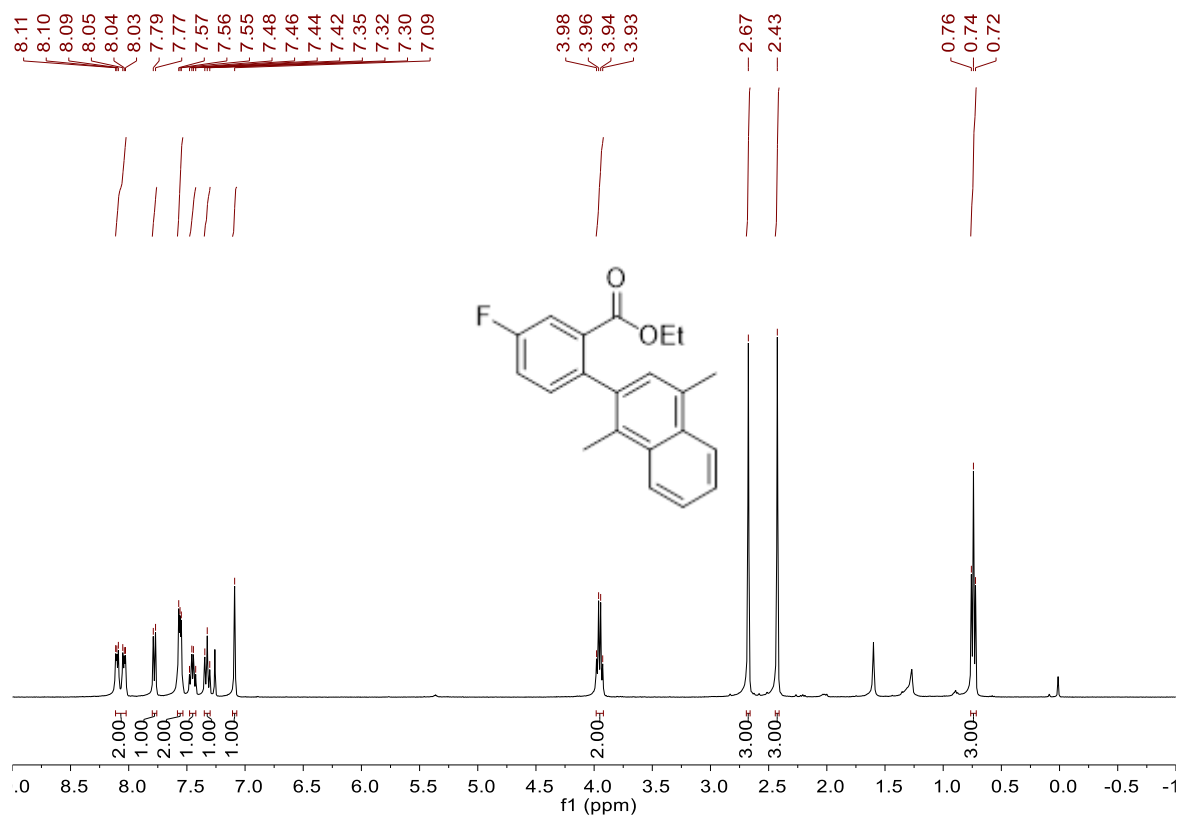
$^1\text{H}$  NMR spectrum of **3af**, 500 MHz,  $\text{CDCl}_3$



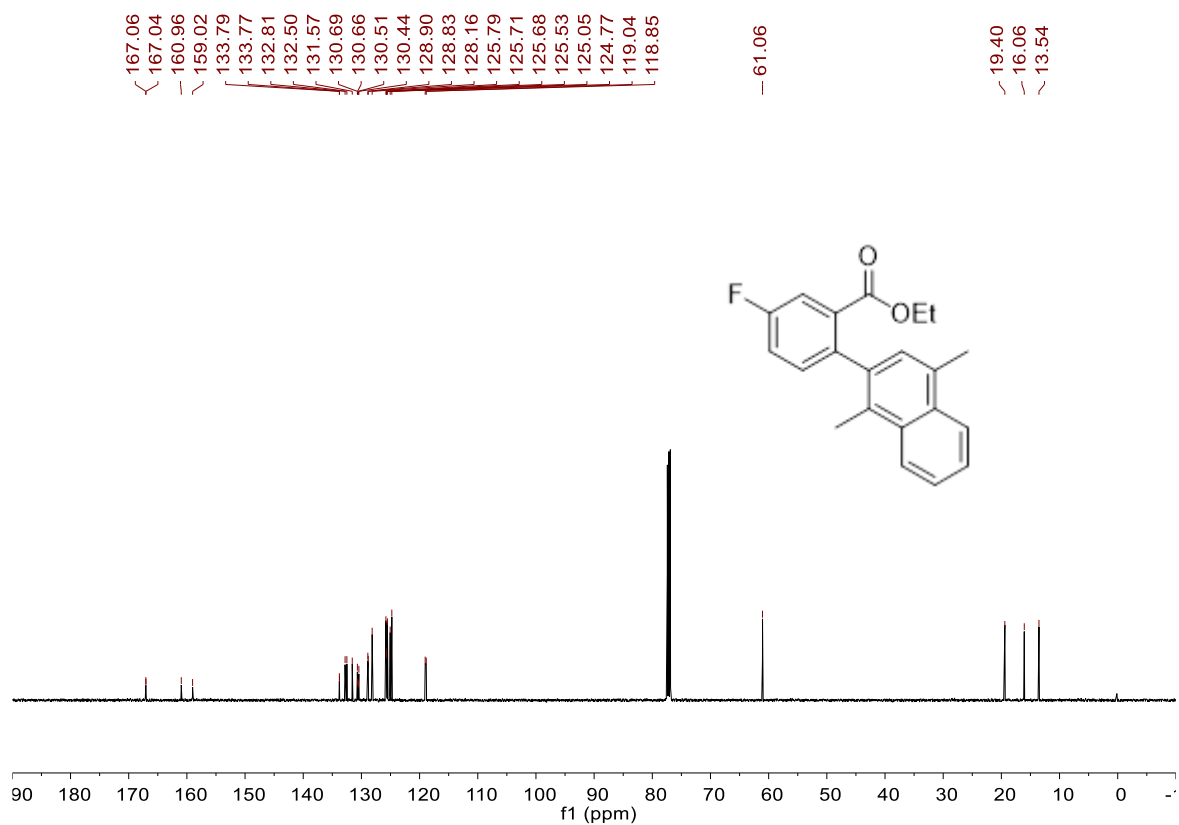
<sup>13</sup>C NMR spectrum of **3af**, 126 MHz, CDCl<sub>3</sub>



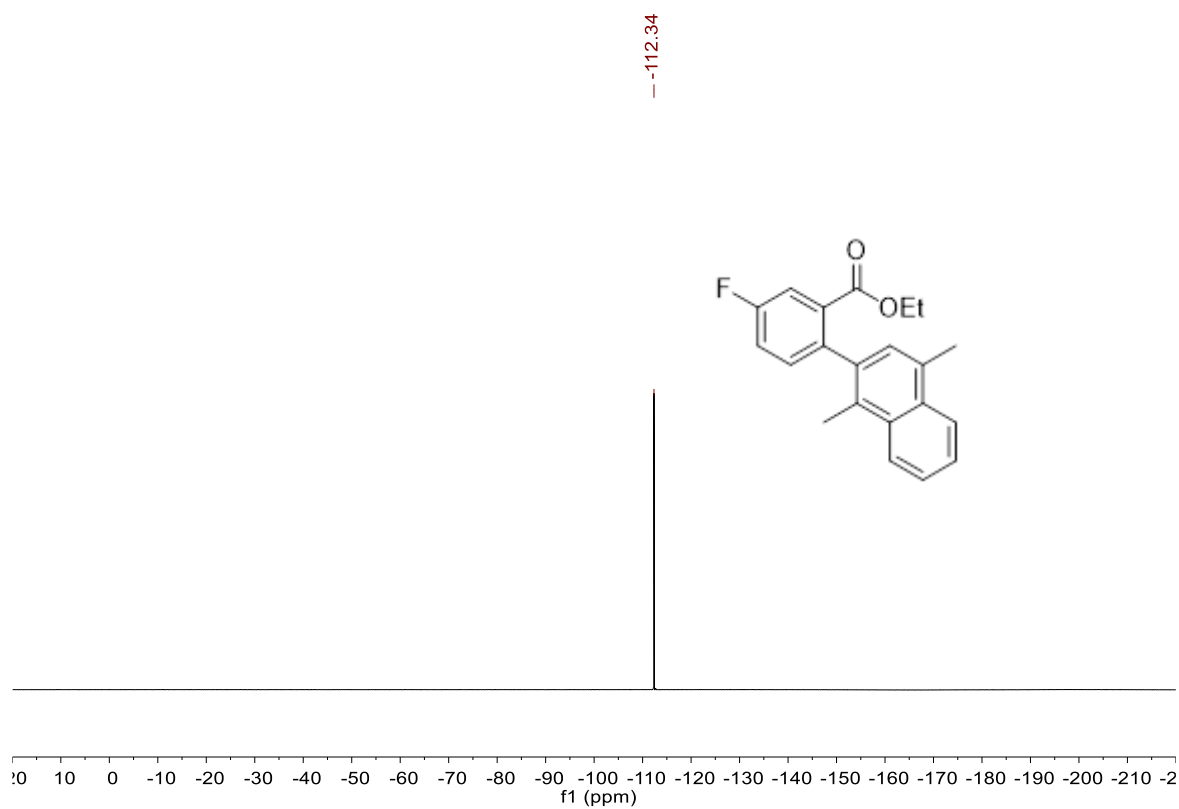
<sup>1</sup>H NMR spectrum of **3lf**, 400 MHz, CDCl<sub>3</sub>



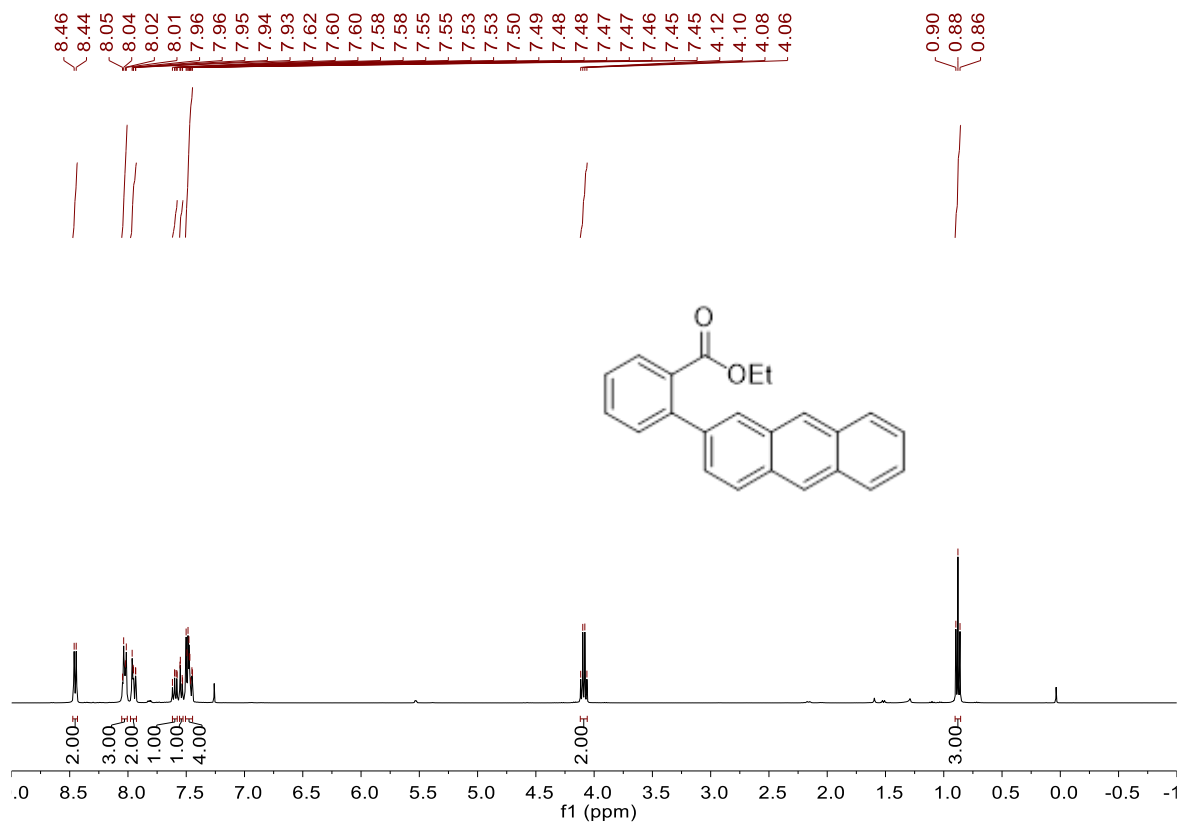
<sup>13</sup>C NMR spectrum of **3lf**, 126 MHz, CDCl<sub>3</sub>



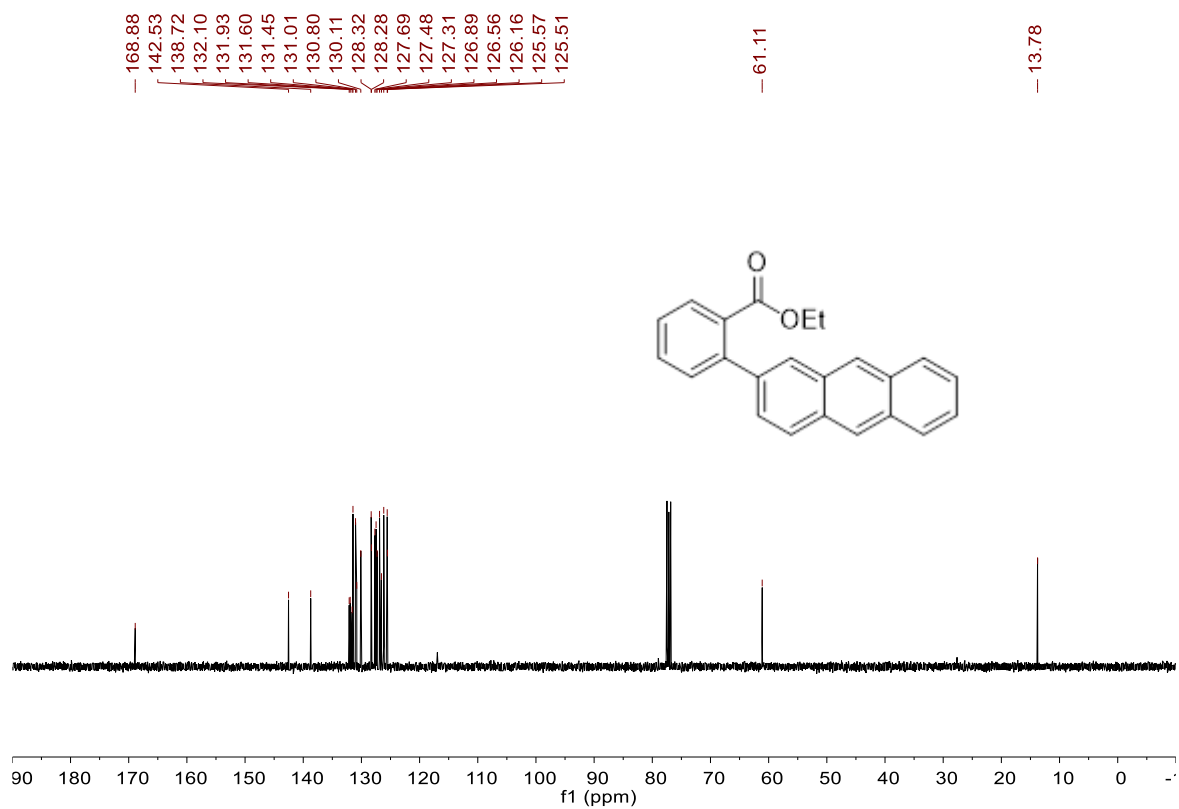
<sup>19</sup>F NMR spectrum of **3lf**, 471 MHz, CDCl<sub>3</sub>



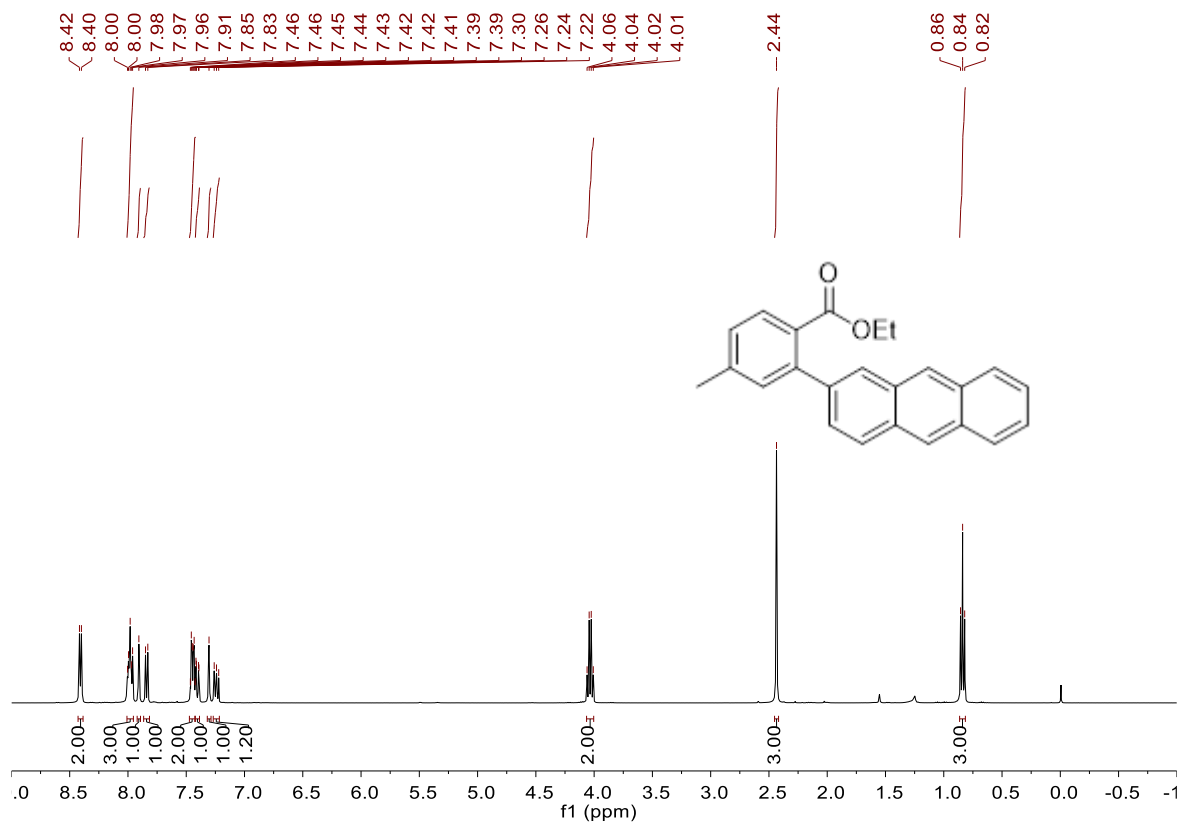
<sup>1</sup>H NMR spectrum of **3ag**, 400 MHz, CDCl<sub>3</sub>



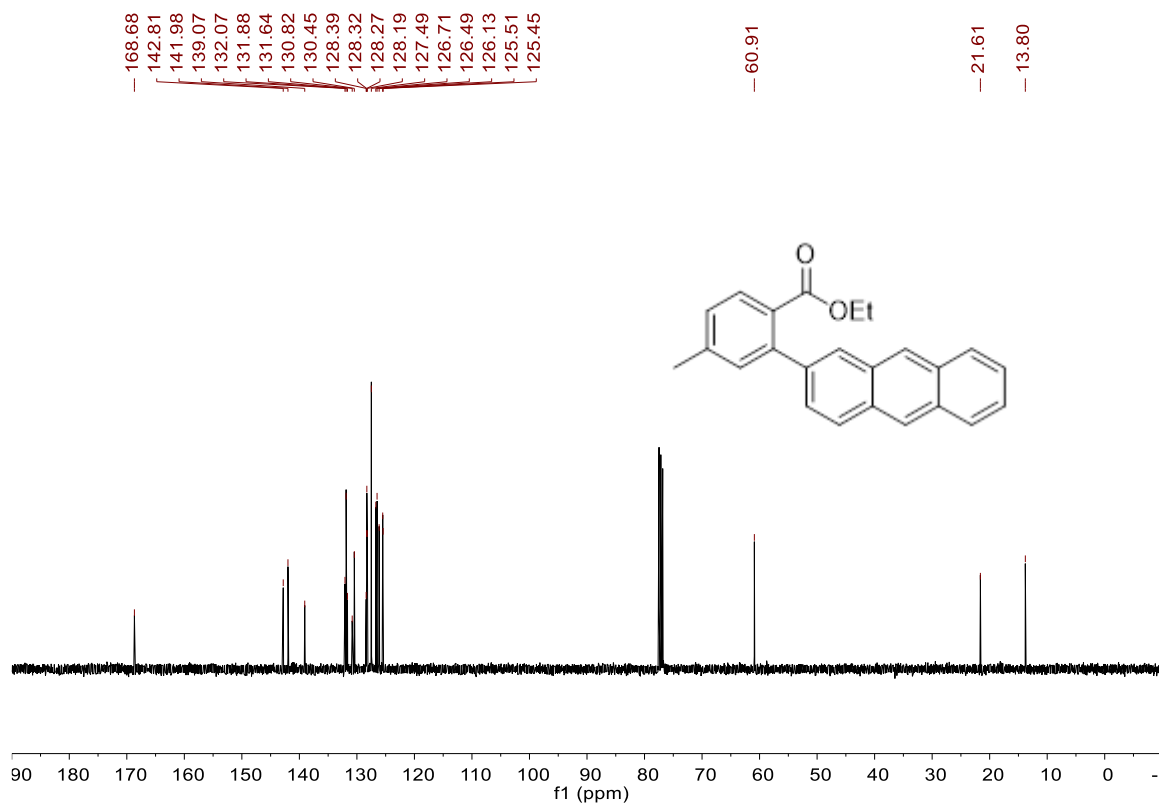
<sup>13</sup>C NMR spectrum of **3ag**, 101 MHz, CDCl<sub>3</sub>



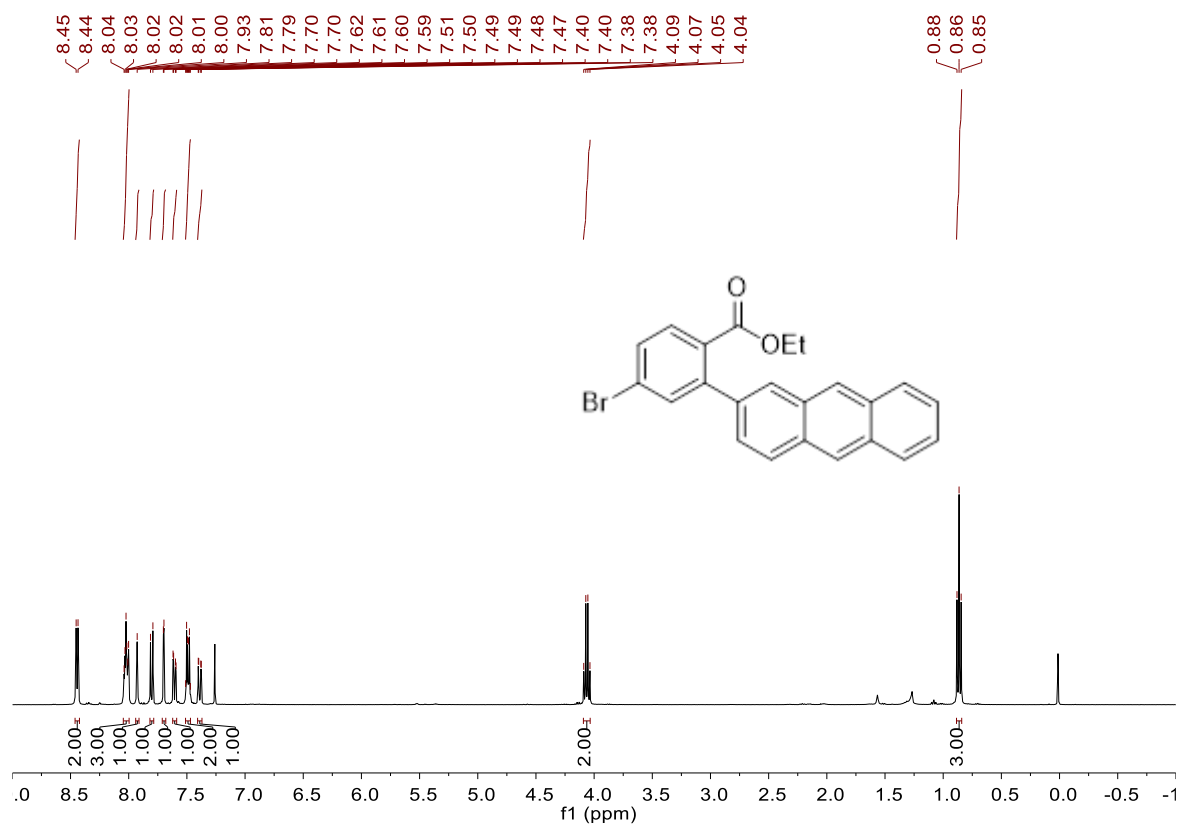
<sup>1</sup>H NMR spectrum of **3bg**, 400 MHz, CDCl<sub>3</sub>



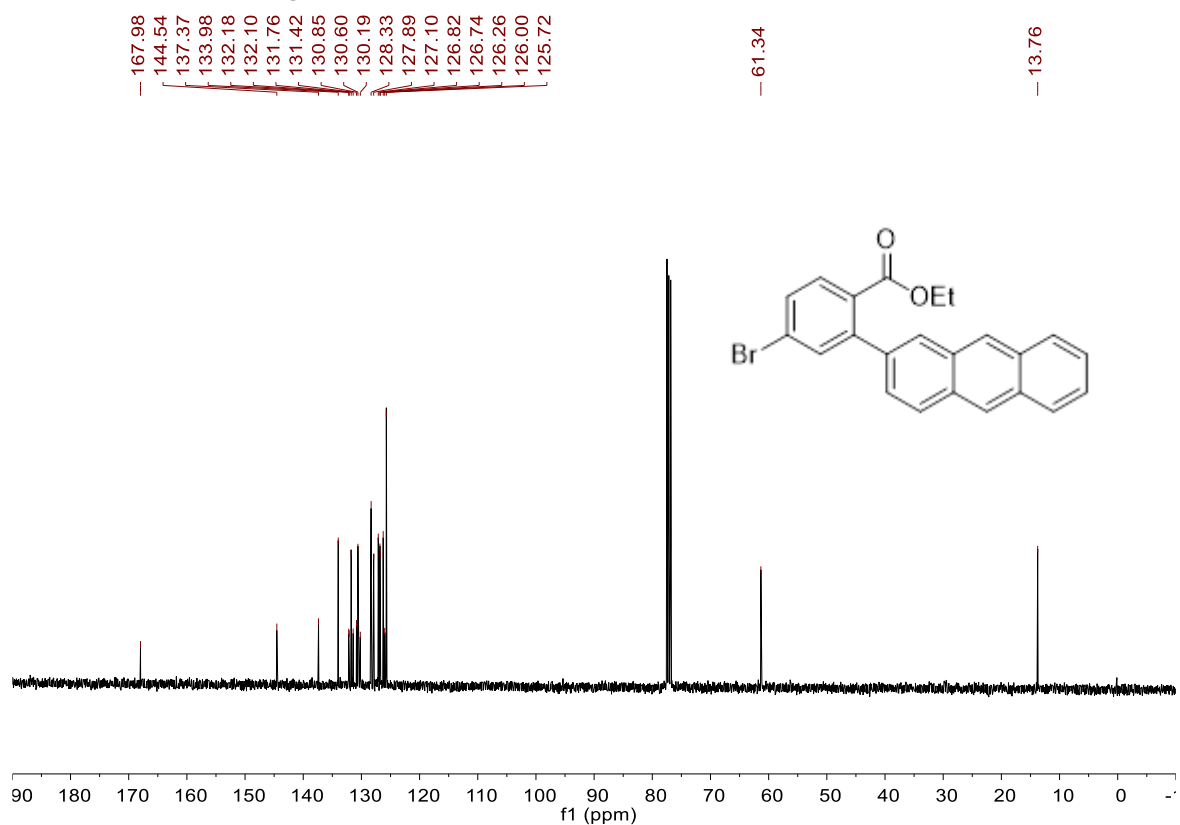
<sup>13</sup>C NMR spectrum of **3bg**, 101 MHz, CDCl<sub>3</sub>



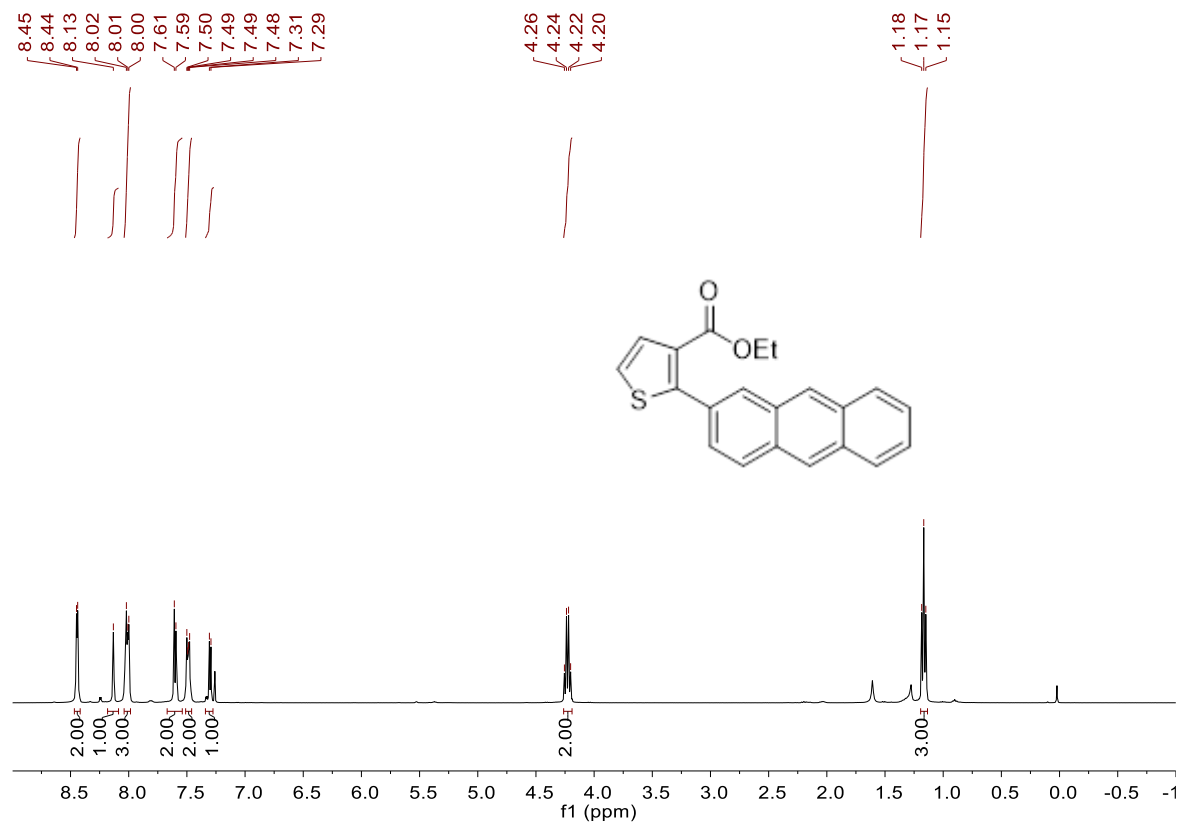
<sup>1</sup>H NMR spectrum of **3eg**, 400 MHz, CDCl<sub>3</sub>



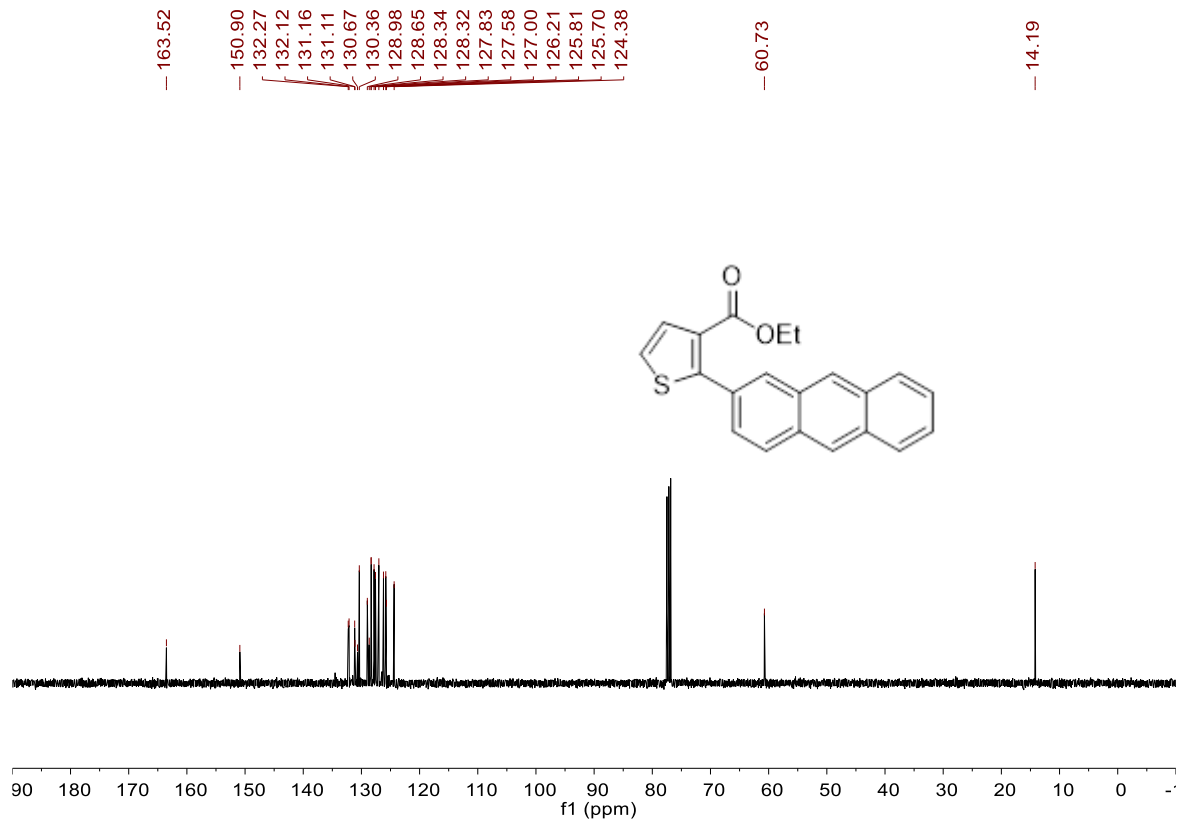
<sup>13</sup>C NMR spectrum of **3eg**, 101 MHz, CDCl<sub>3</sub>



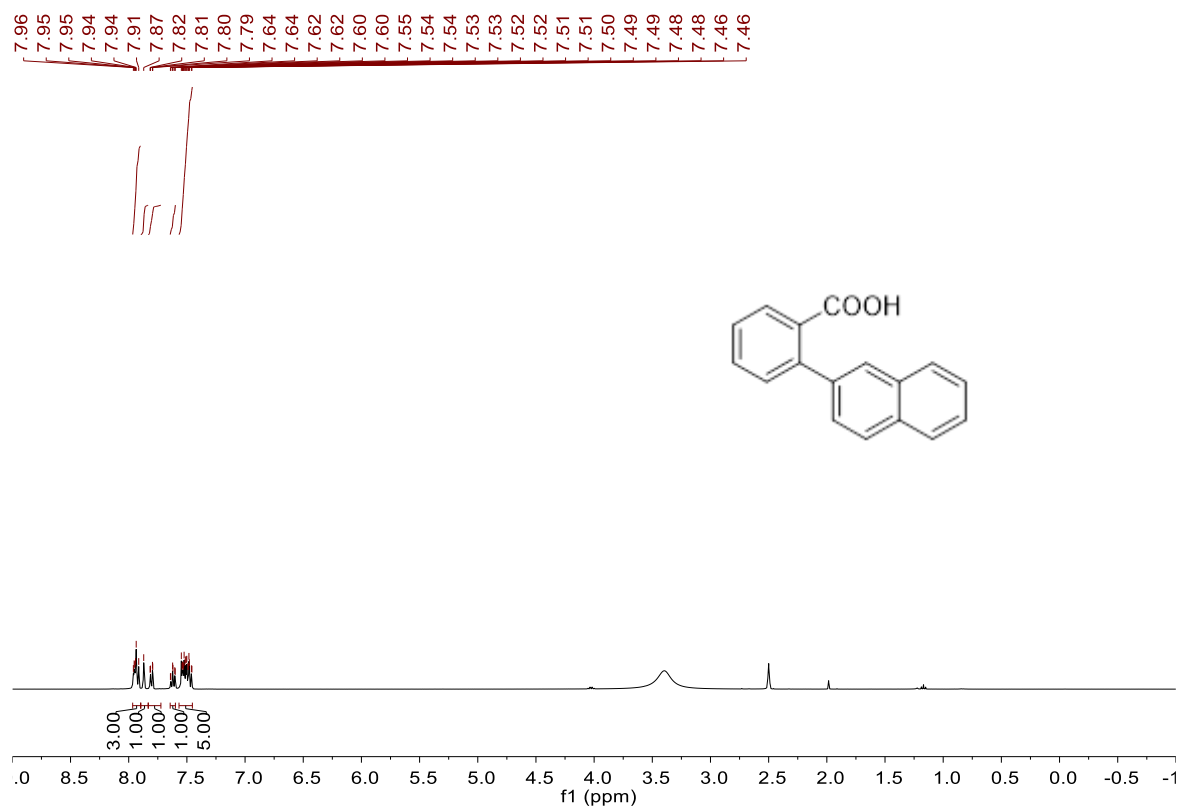
<sup>1</sup>H NMR spectrum of **3og**, 400 MHz, CDCl<sub>3</sub>



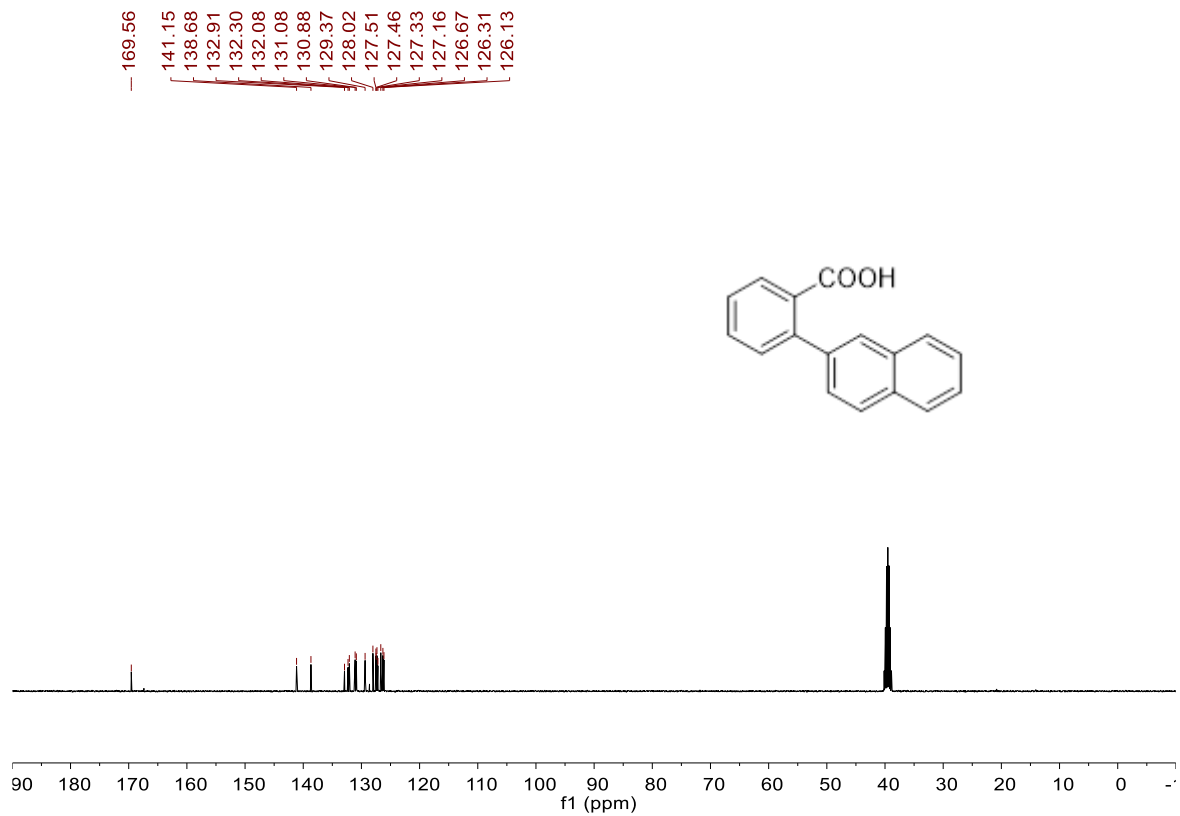
<sup>13</sup>C NMR spectrum of **3og**, 101 MHz, CDCl<sub>3</sub>



<sup>1</sup>H NMR spectrum of **4aa**, 400 MHz, DMSO-*d*<sub>6</sub>

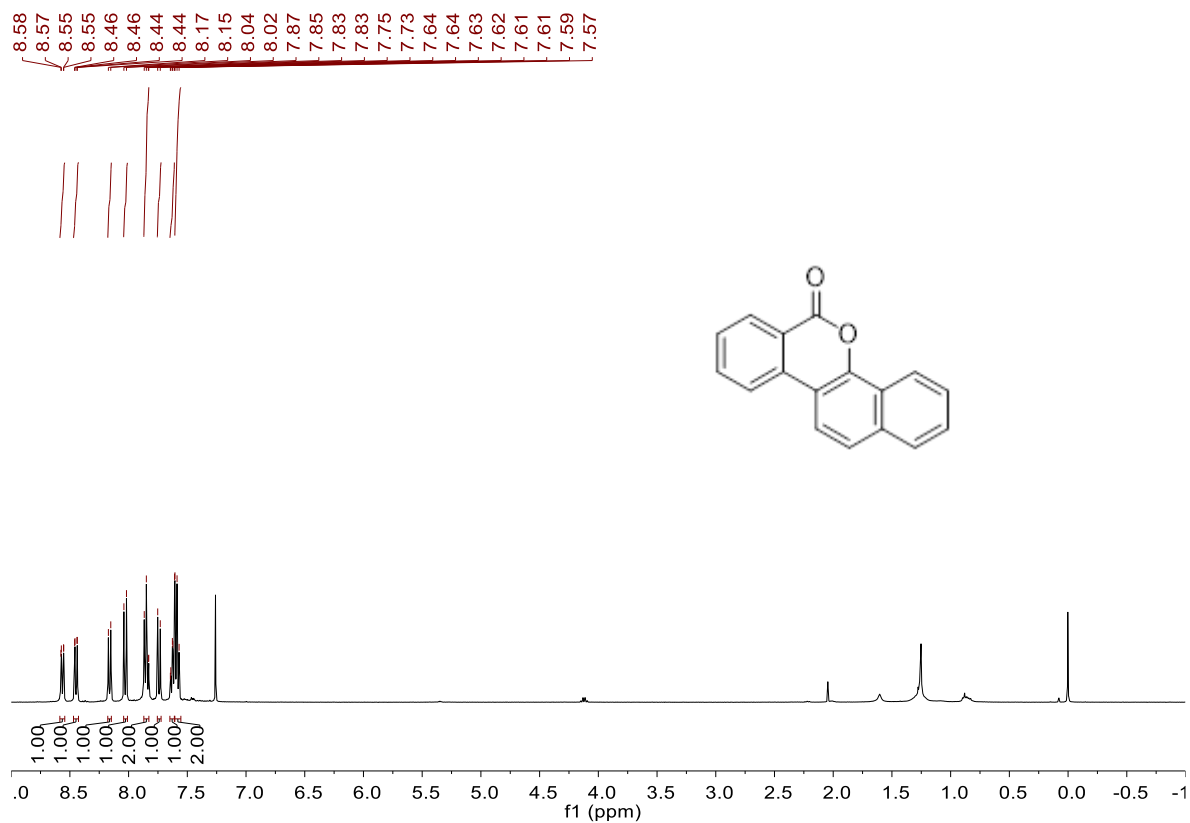


<sup>13</sup>C NMR spectrum of **4aa**, 101 MHz, DMSO-*d*<sub>6</sub>

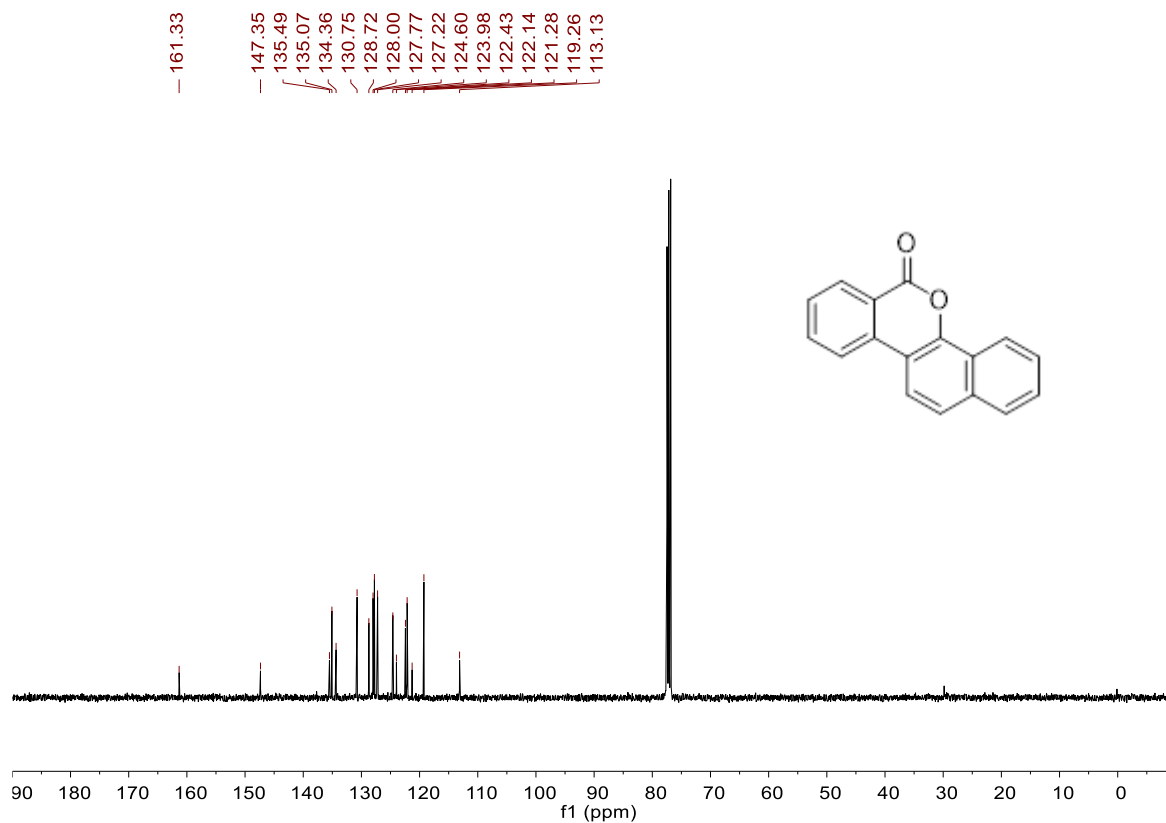




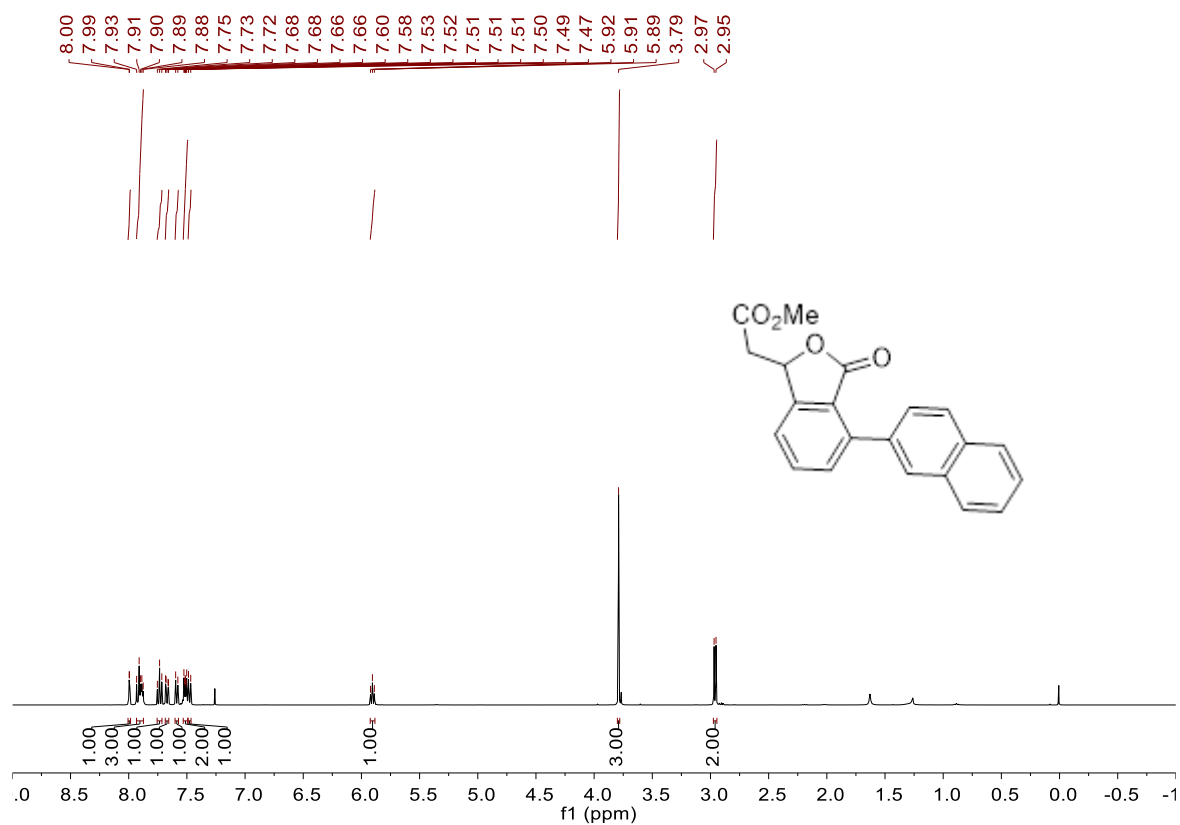
<sup>1</sup>H NMR spectrum of **5aa**, 400 MHz, CDCl<sub>3</sub>



<sup>13</sup>C NMR spectrum of **5aa**, 101 MHz, CDCl<sub>3</sub>



<sup>1</sup>H NMR spectrum of **6aa**, 400 MHz, CDCl<sub>3</sub>



<sup>13</sup>C NMR spectrum of **6aa**, 101 MHz, CDCl<sub>3</sub>

