

## Supporting Information

### **Pairing Iron and Nickel Catalysis for Electrochemical Esterification of Aryl Halides with Carbazates**

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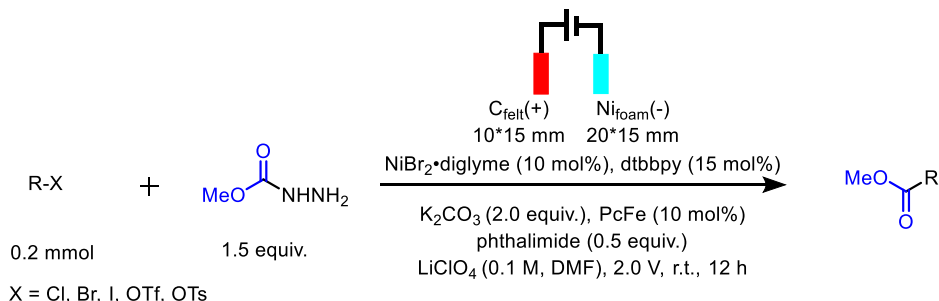
## Section 1. General Information

All reactions were performed in oven-dried two-neck glass tubes unless otherwise noted. The tubes were fitted with a rubber septum and a threaded Teflon cap with airtight electrical feed-throughs. The reactions were conducted under nitrogen atmosphere. Reactions required elevated temperature were performed in an oil bath. Flash chromatography was performed using silica gel 60 (230-400 mesh). Reagents obtained from commercial sources were used as supplied unless stated otherwise. Dimethylformamide (DMF) was dried over activated molecular sieves for 24 hours prior to use. Proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectra, carbon nuclear magnetic resonance ( $^{13}\text{C}$  NMR) spectra and fluorine nuclear magnetic resonance ( $^{19}\text{F}$  NMR) spectra were recorded on Bruker-Avance (400 MHz or 500 MHz) spectrometers. Chemical shifts for protons are reported in parts per million and are referenced to residual protium in the NMR solvent ( $\text{CHCl}_3 = \delta$  7.26). Chemical shifts for carbons are reported in parts per million and are referenced to tetramethylsilane ( $\text{TMS} = \delta$  0.00). Data are represented as follows: chemical shift, multiplicity (br. s = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz), integration. Infrared (IR) spectra were obtained using a Thermo Fisher Nicolet 6700 spectrometer. Cyclic voltammetry (CV) data were measured with Shanghai Chenhua CHI660E. The High-resolution mass spectral (HRMS) data were obtained on Thermo Fisher Scientific Exactive Orbitrap (APCI or ESI).

Electrolysis experiments were performed using HYELEC HY3001B potentiostat/galvanostat or a DC power supply. Carbon Felt was purchased from Shandong Guanzhi New Material Technology Co., Ltd. Nickel foam was purchased from MTI Corporation. The carbon felt was cut into  $1.0 \times 1.5 \times 0.4 \text{ cm}^3$  pieces and nickel foam was cut into  $2.0 \times 1.5 \text{ cm}^2$  pieces. The electrodes were connected to electrical feed-through on the Teflon cap of the electrochemical cell each via a piece of graphite (2B pencil lead, 2 mm in diameter).

## Section 2. General Procedure

### General procedure for electrochemical esterification (Method A):



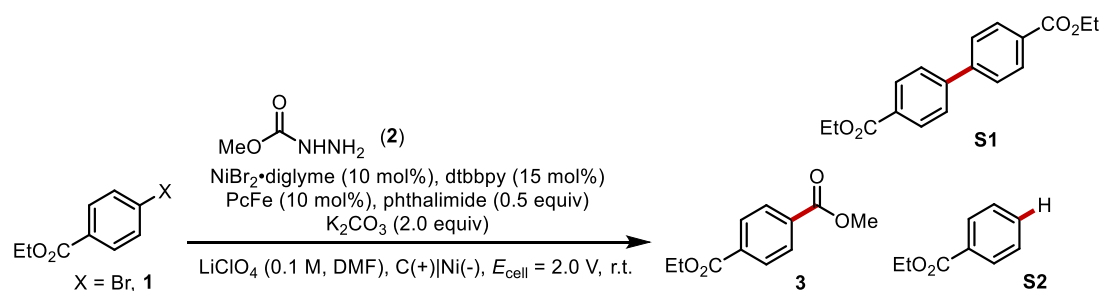
**Catalyst solutions preparation:** In a glove box, NiBr<sub>2</sub> diglyme (7.0 mg, 0.020 mmol, 10 mol%) and dtbbpy (8.0 mg, 0.030 mmol, 15 mol%) were dissolved in 1.0 mL DMF. The solution was stirred for 30 min prior to use.

**Reaction setup:** An oven-dried two-neck tube was equipped with a stir bar, a rubber septum, a threaded Teflon cap fitted with electrical feed-throughs, a carbon felt anode (1.0 × 1.5 × 0.4 cm<sup>3</sup>), and a nickel foam cathode (1.5 × 2.0 cm<sup>2</sup>).

The substrate of aryl bromide (0.20 mmol, 1.0 equiv.), methyl carbazate (0.30 mmol, 1.5 equiv.), PcFe (11.4 mg, 0.020 mmol, 0.1 equiv.), phthalimide (14.7 mg, 0.10 mmol, 0.5 equiv.), K<sub>2</sub>CO<sub>3</sub> (55 mg, 0.40 mmol, 2.0 equiv.), and LiClO<sub>4</sub> (42.6 mg, 0.40 mmol, 2.0 equiv.) were sequentially added into the oven-dried undivided tube. Under nitrogen atmosphere, catalyst solution [NiBr<sub>2</sub> diglyme (10 mol%), dtbbpy (15 mol%)] and DMF (3.0 mL) were added. The reaction mixture was then sparged with nitrogen for 5 minutes and maintained under nitrogen atmosphere with a balloon. The resulting suspension was pre-stirred for about 30 min. Then electrolysis was initiated at a constant cell potential of 2.0 V at room temperature. After the reaction, the tube cap was removed and electrodes were rinsed with EtOAc, which was combined with the crude mixture. The organic solution was further washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude material was purified by column chromatography or preparative thin layer chromatography (PTLC) to furnish the desired product.



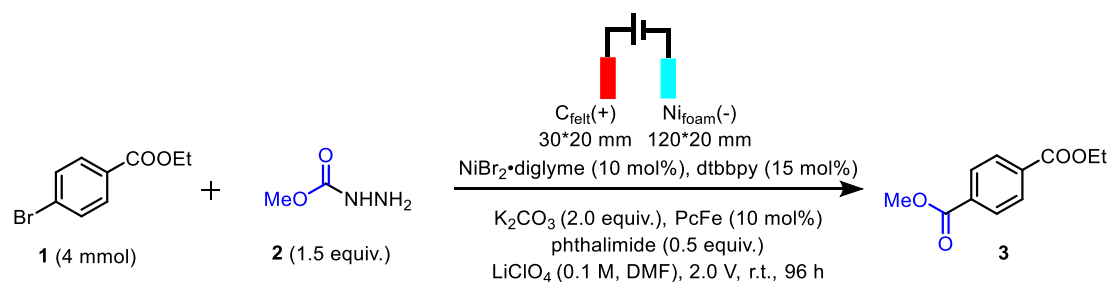
**Figure S1.** Components of the reaction setup (left). Assembled reaction vessel (right).

**Table S1.** Reaction discovery and optimization<sup>a</sup>

Entry	variation from above conditions	conv. (%) <sup>b</sup>	<b>3</b> (%) <sup>b</sup>	<b>S1</b> (%) <sup>b</sup>	<b>S2</b> (%) <sup>b</sup>
1	none	100	76 (74) <sup>c</sup>	trace	8
2	no PcFe, no phthalimide	100	14	31	16
3	no PcFe	100	19	16	20
4	no phthalimide	100	35	33	19
5	no K <sub>2</sub> CO <sub>3</sub>	35	8	trace	25
6	DIPEA instead of K <sub>2</sub> CO <sub>3</sub>	100	44	trace	36
7 <sup>d</sup>	TBABF <sub>4</sub> instead of LiClO <sub>4</sub>	100	53	trace	16
8 <sup>d</sup>	TBAPF <sub>6</sub> instead of LiClO <sub>4</sub>	100	58	trace	22
9	8.0 mA, 12 hours	100	52	8	25
10	X = Cl	100	55	trace	25
11	X = I	100	60	7	11
12	X = OTs	100	57	14	21

<sup>a</sup>Reaction conditions: **1** (0.2 mmol), **2** (0.3 mmol, 1.5 equiv), PcFe (10 mol %), NiBr<sub>2</sub>•diglyme (10 mol %), dtbbpy (15 mol %), K<sub>2</sub>CO<sub>3</sub> (2.0 equiv), phthalimide (0.5 equiv), carbon felt anode, nickel foam cathode, undivided cell, cell potential E<sub>cell</sub> = 2.0 V, 12 hours. <sup>b</sup>Conversion and yield determined by <sup>1</sup>H NMR spectroscopy. <sup>c</sup>Isolated yield. <sup>d</sup>with NiCl<sub>2</sub>•6H<sub>2</sub>O (20 mol %), dtbbpy (15 mol %)

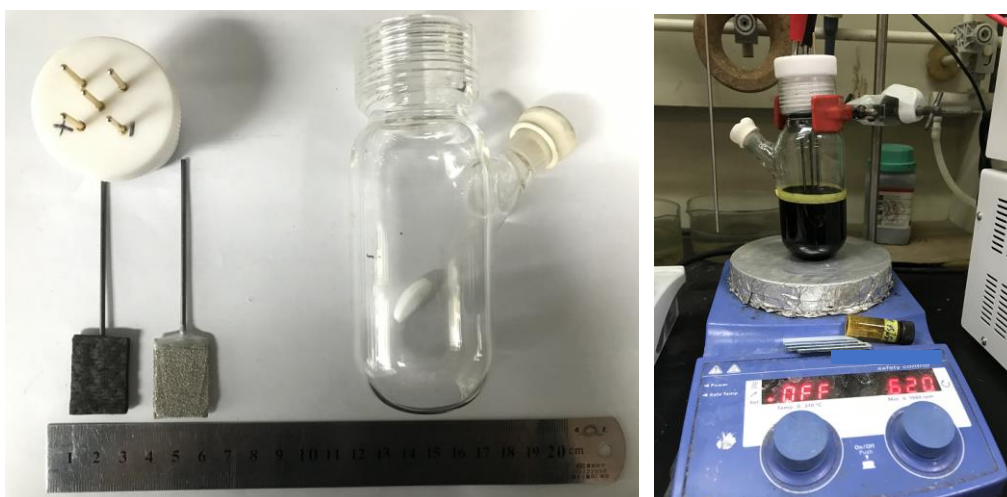
### General procedure for 4 mmol scale-up reaction:



**Catalyst solutions preparation:** In a glove box,  $\text{NiBr}_2 \cdot \text{diglyme}$  (140 mg, 0.40 mmol, 10 mol%) and  $\text{dtbbpy}$  (160 mg, 0.60 mmol, 15 mol%) were dissolved in 20 mL DMF. The solution was stirred for 30 min prior to use.

**Reaction setup:** An oven-dried two-neck tube was equipped with a stir bar, a rubber septum, a threaded Teflon cap fitted with electrical feedthroughs, a carbon felt anode ( $3.0 \times 2.0 \times 0.4 \text{ cm}^3$ ), and a nickel foam cathode ( $12 \times 2.0 \text{ cm}^2$ ).

Aryl bromide **1** (4.0 mmol, 1.0 equiv.), methyl carbazate (6.0 mmol, 1.5 equiv.),  $\text{PcFe}$  (228 mg, 0.40 mmol, 0.1 equiv.), phthalimide (294 mg, 2.0 mmol, 0.5 equiv.),  $\text{K}_2\text{CO}_3$  (1.1 g, 8.0 mmol, 2.0 equiv.), and  $\text{LiClO}_4$  (852 mg, 8.0 mmol, 2.0 equiv.) were sequentially added into the oven-dried undivided tube. Under nitrogen atmosphere, catalyst solution [ $\text{NiBr}_2 \cdot \text{diglyme}$  (10 mol%),  $\text{dtbbpy}$  (15 mol%)] and DMF (60 mL) were added. The reaction mixture was then sparged with nitrogen for 10 minutes and maintained under nitrogen atmosphere with a balloon. The resulting suspension was pre-stirred for about 30 min. Then electrolysis was initiated at a constant cell potential of 2.0 V at room temperature. After the reaction, the tube cap was removed and electrodes were rinsed with EtOAc, which was combined with the crude mixture. The organic solution was further washed with brine, dried over  $\text{Na}_2\text{SO}_4$  and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel (EtOAc/petroleum ether, 1:10) to afford 416.4 mg (50% yield) of product.



**Figure S2.** Components of the 4 mmol scale-up reaction setup (left); Typical reaction appearance for 4 mmol scale-up reaction (right).

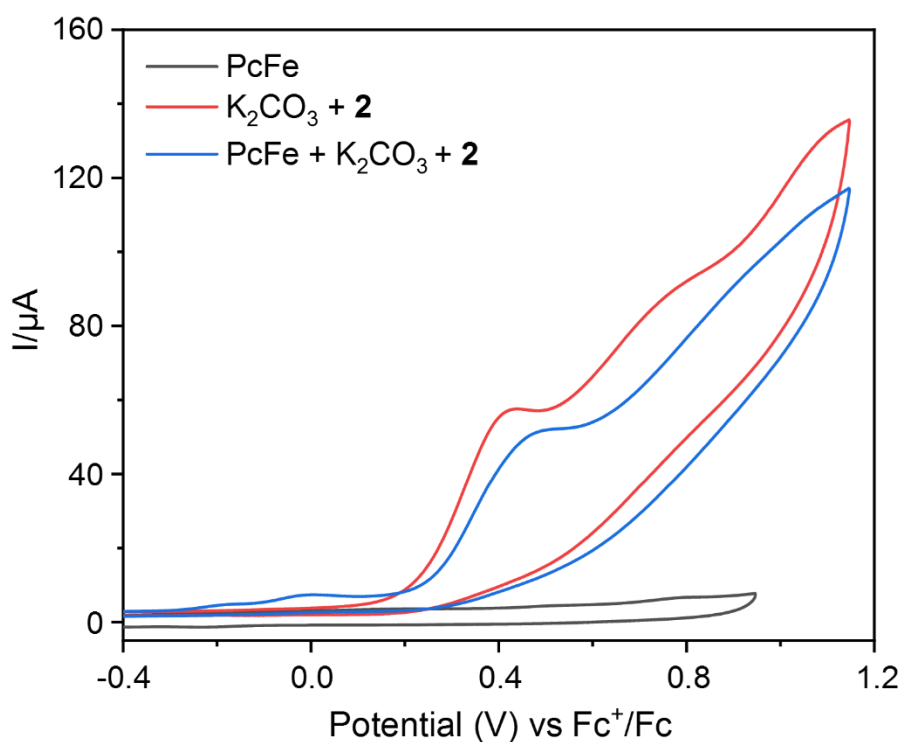
### Section 3. Cyclic Voltammetry Studies

All Cyclic Voltammetry (CV) studies were conducted under nitrogen atmosphere. Measurements were performed in DMF solution of  $\text{LiClO}_4$  (0.1 M) in a 10 mL glass vial. Scan rate is 100 mV/s unless specified.

**Working electrode:** The working electrode is a 3.0 mm diameter glassy carbon electrode. Polished with aluminum oxide and then sonicated in distilled water and acetone and air dried.

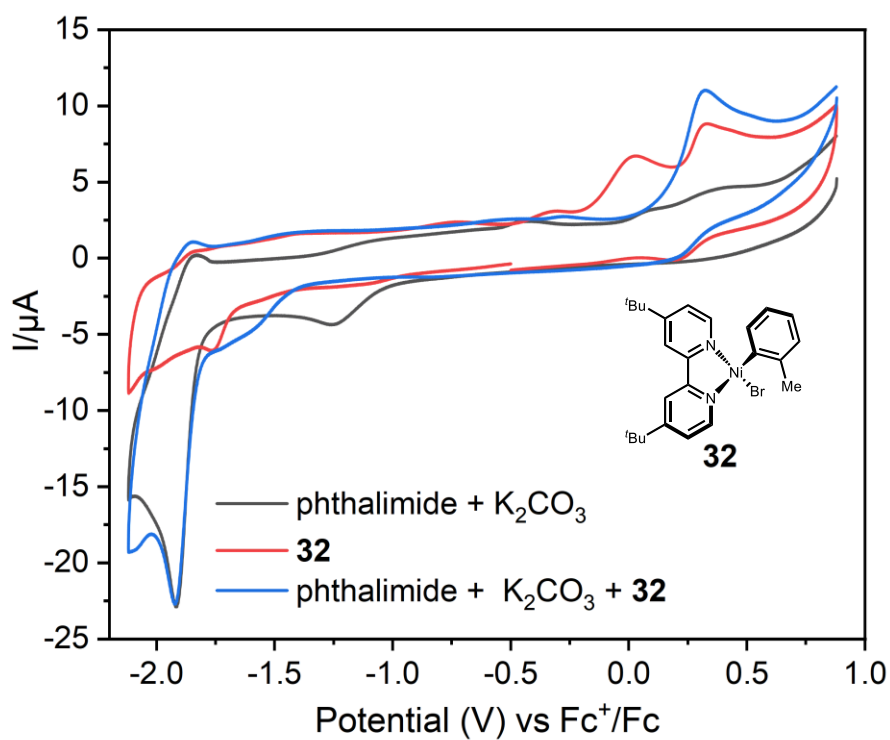
**Reference electrode:** The reference electrode is  $\text{Ag}/\text{AgNO}_3$  reference electrode ( $\text{AgNO}_3$ , 1 mM) in electrolyte solution.

**Counter electrode:** The counter electrode is a platinum wire.



**Figure S3.** Cyclic voltammetry of related compounds. Black: PcFe (0.33 mM); Red:  $\text{K}_2\text{CO}_3$  (6.6 mM) and **2** (5 mM); Blue: PcFe (0.33 mM),  $\text{K}_2\text{CO}_3$  (6.6 mM), and **2** (5 mM).

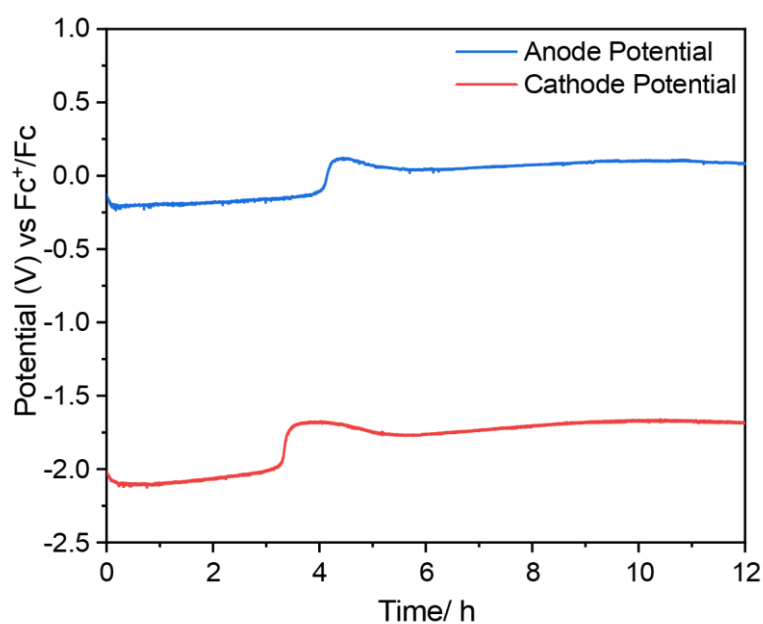




**Figure S4.** Cyclic voltammetry of related compounds. Black: phthalimide (1.67 mM) and  $K_2CO_3$  (6.6 mM); Red: **32** (0.33 mM); Blue: **32** (0.33 mM), phthalimide (1.67 mM) and  $K_2CO_3$  (6.6 mM).

## Section 4. Electrode potentials over the course of reaction

The reaction was set up following Method A with an extra Ag/AgNO<sub>3</sub> electrode as the reference electrode. The anodic and cathodic potentials were monitored by Shanghai Chenhua CHI660E electrochemical workstation. The reaction was terminated and worked up after 12 hours. <sup>1</sup>H NMR of the crude material with 1,1,2,2-tetrachloroethane (0.2 mmol) as the internal standard revealed a yield of 69%.



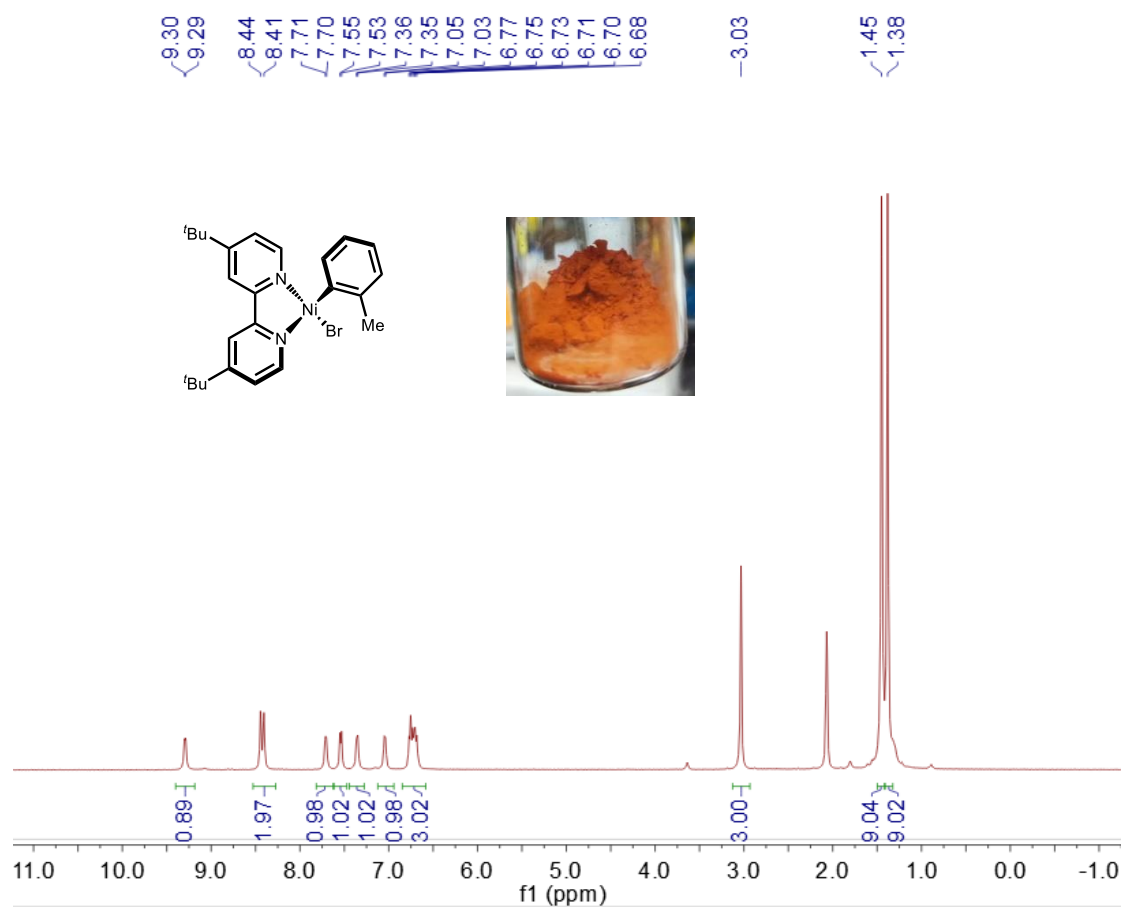
**Figure S5.** The change of anodic/cathodic potentials during the reaction.

## Section 5. Mechanistic studies

### 5.1 Synthesis of Complex [(dtbbpy)Ni(II)(2-tolyl)Br] (**32**)

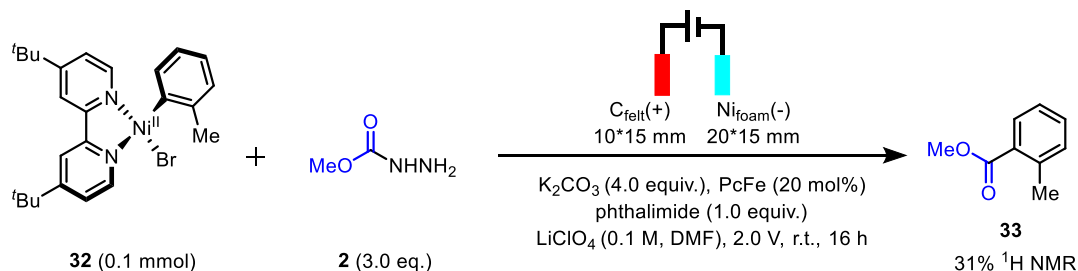
In an argon-filled glovebox, a 25 mL Schlenk tube was charged with Ni(COD)<sub>2</sub> (1.0 mmol, 275.0 mg), dtbbpy (1.0 mmol, 268.0 mg), and dry THF (10 mL). The reaction mixture was stirred overnight at room temperature, and the color of the solution turned into deep purple. 2-methyl phenyl bromide (10 mmol, 1700 mg) was added, and the reaction was left to stir for 3 h. Dry pentane (20 mL) was added to the deep red colored mixture and filtered. The resulting precipitate was washed with pentane (5 × 20 mL) to remove residual cyclooctadiene and phenyl bromide and dried under vacuum to give complex **32** as an orange powder (388 mg, 78% yield). Spectral data matched those previously reported.<sup>[1]</sup>

**<sup>1</sup>H NMR (400 MHz, Acetone-*d*<sub>6</sub>)**  $\delta$  9.29 (d, *J* = 5.8 Hz, 1H), 8.42 (d, *J* = 15.3 Hz, 2H), 7.71 (d, *J* = 5.8 Hz, 1H), 7.54 (d, *J* = 7.2 Hz, 1H), 7.36 (d, *J* = 6.2 Hz, 1H), 7.04 (d, *J* = 6.2 Hz, 1H), 6.87 – 6.58 (m, 3H), 3.03 (s, 3H), 1.45 (s, 9H), 1.38 (s, 9H).

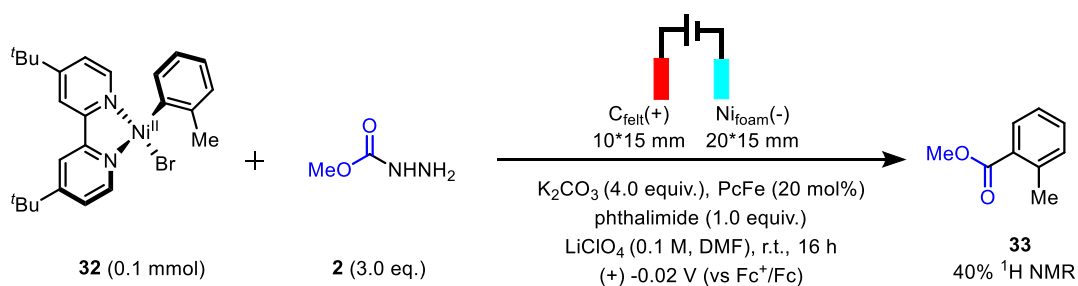


## 5.2 Studies of Reductive Elimination

### 5.2.1 Undivided Cell Reaction



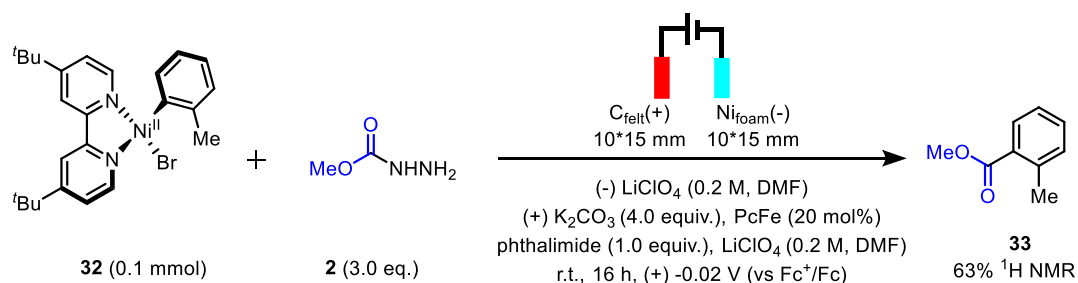
**Procedure:** In an argon-filled glove box, an oven-dried two-neck tube was charged with a stir bar. **32** (0.10 mmol, 1.0 equiv), methyl carbazate (0.30 mmol, 3.0 equiv.), PcFe (0.020 mmol, 0.2 equiv.), phthalimide (0.10 mmol, 1.0 equiv.), K<sub>2</sub>CO<sub>3</sub> (0.40 mmol, 4.0 equiv.), LiClO<sub>4</sub> (0.40 mmol, 4.0 equiv.) and DMF (4.0 mL) was sequentially added. The undivided cell was equipped with carbon felt (1.0 × 1.5 × 0.5 cm<sup>3</sup>) and Nickel foam (2.0 × 1.5 cm<sup>2</sup>) as anode and cathode respectively. Then the cell was brought out of glove box. The resulting mixture was pre-stirred for 30 minutes, and electrolysis was initiated at a constant cell potential of 2.0 V at room temperature for 16 hours. After the reaction, the mixture was diluted with brine. The aqueous layer was extracted with EtOAc and the combined organic layers were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure.



**Procedure:** In an argon-filled glove box, an oven-dried two-neck tube was charged with a stir bar. **32** (0.10 mmol, 1.0 equiv), methyl carbazate (0.30 mmol, 3.0 equiv.), PcFe (0.020 mmol, 0.2 equiv.), phthalimide (0.10 mmol, 1.0 equiv.), K<sub>2</sub>CO<sub>3</sub> (0.40 mmol, 4.0 equiv.), LiClO<sub>4</sub> (0.40 mmol, 4.0 equiv.) and DMF (4.0 mL) was sequentially added. The undivided cell was equipped with carbon felt (1.0 × 1.5 × 0.5 cm<sup>3</sup>), Nickel foam

( $2.0 \times 1.5 \text{ cm}^2$ ) and Ag/AgNO<sub>3</sub> electrode as anode, cathode and reference electrode respectively. Then the cell was brought out of glove box. The resulting mixture was pre-stirred for 30 minutes. The reaction mixture was electrolyzed at constant anodic potential of -0.02 V (vs Fc<sup>+</sup>/Fc) at room temperature for 16 hours. After the reaction, the mixture was diluted with brine. The aqueous layer was extracted with EtOAc and the combined organic layers were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure.

### 5.2.2 Divided Cell Reaction



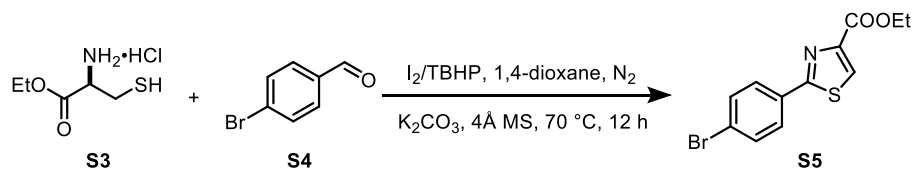
**Procedure:** In an argon-filled glove box, an oven-dried U-tube was charged with a stir bar at each side respectively. To the anodic chamber was added **32** (0.10 mmol, 1.0 equiv.), methyl carbazate (0.30 mmol, 3.0 equiv.), PcFe (0.020 mmol, 0.2 equiv.), phthalimide (0.10 mmol, 1.0 equiv.), K<sub>2</sub>CO<sub>3</sub> (0.40 mmol, 4.0 equiv.), LiClO<sub>4</sub> (0.80 mmol, 8.0 equiv.) and DMF (4.0 mL), while to the cathodic chamber was added LiClO<sub>4</sub> (0.80 mmol, 8.0 equiv.) and DMF (4.0 mL). The anodic chamber was equipped with carbon felt anode ( $1.0 \times 1.5 \times 0.5 \text{ cm}^3$ ) and Ag/AgNO<sub>3</sub> reference electrode. The cathodic chamber was equipped with Nickel foam ( $2.0 \times 1.5 \text{ cm}^2$ ) cathode. The cell was brought out of glove box. The resulting mixture was pre-stirred for 30 minutes. The reaction mixture was electrolyzed at constant anodic potential of -0.02 V (vs Fc<sup>+</sup>/Fc) at room temperature for 16 hours. After the reaction, the mixture was diluted with brine. The aqueous layer was extracted with EtOAc and the combined organic layers were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure.



**Figure S6.** Components of divided cell reaction setup.

## Section 6. Preparation of substrates

### Aryl bromide S5 for synthesizing compound 25:

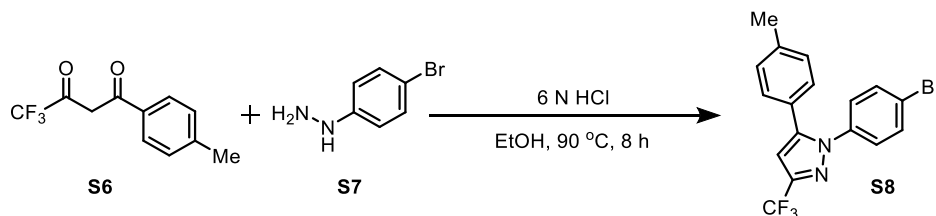


A Schlenk tube containing *L*-cysteine ethyl ester hydrochloride (CAS No.: 868-59-7, 12 mmol, 4.0 equiv.), 4-Bromobenzaldehyde (3.0 mmol, 1.0 equiv.),  $K_2CO_3$  (9.0 mmol, 3.0 equiv.),  $I_2$  (0.9 mmol, 0.3 equiv.), 4Å molecular sieve (3.8 g) was evacuated and refilled with nitrogen three times. 1,4-Dioxane (15 mL), and TBHP (70% in cyclohexane, 12 mmol, 4 equiv.) were then added slowly to the mixture at room temperature. The mixture was stirred at  $70\text{ }^\circ\text{C}$  for 12 hours. The resultant solution was quenched with aqueous saturated  $Na_2S_2O_3$  solution (50 mL) and extracted with EtOAc ( $3\times 50\text{ mL}$ ). The combined organic layers were washed with brine ( $3\times 50\text{ mL}$ ), dried over  $Na_2SO_4$ , filtered and concentrated under reduced pressure. The crude product was further purified by column chromatography on silica gel (EtOAc/petroleum ether = 1:20) to afford **S5** (200 mg, 22% yield) as a white solid. The spectroscopic data matched those reported in the literature.<sup>[2]</sup>

**$^1H$  NMR (500 MHz,  $CDCl_3$ )**  $\delta$  8.17 (s, 1H), 7.89 (d,  $J = 8.5\text{ Hz}$ , 2H), 7.59 (d,  $J = 8.6\text{ Hz}$ , 2H), 4.45 (q,  $J = 7.1\text{ Hz}$ , 2H), 1.43 (t,  $J = 7.1\text{ Hz}$ , 3H).

**$^{13}C$  NMR (126 MHz,  $CDCl_3$ )**  $\delta$  167.6, 161.3, 148.3, 132.2, 131.7, 128.4, 127.2, 125.1, 61.6, 14.4.

### Aryl bromide S8 for synthesizing compound 26:



To a 50 mL round-bottomed flask under nitrogen atmosphere was added **S6** (5.0 mmol, 1.0 equiv), **S7** (5.0 mmol, 1.0 equiv), ethanol (10 mL) and 6 N HCl (10 mmol). The reaction was heated to reflux ( $90\text{ }^\circ\text{C}$ ) and stirred for 8 h. After cooling to room



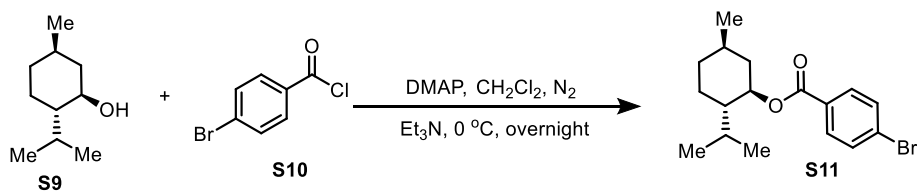
temperature, the reaction mixture was diluted with EtOAc (20 mL) and washed with 30 mL saturated K<sub>2</sub>CO<sub>3</sub> and 30 mL brine. Then the organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel (EtOAc/petroleum ether = 1:10) to afford **S8** (1.65 g, 87% yield) as a white solid. The spectroscopic data matched those reported in the literature.<sup>[3]</sup>

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.48 (d, *J* = 8.6 Hz, 2H), 7.20 (d, *J* = 8.7 Hz, 2H), 7.17 – 7.12 (m, 2H), 7.12 – 7.06 (m, 2H), 6.71 (s, 1H), 2.37 (s, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** 145.0, 143.6 (q, *J* = 38.5 Hz), 139.5, 138.4, 132.4, 129.7, 128.8, 127.0, 126.1, 122.3, 121.3 (q, *J* = 269.0 Hz) 105.8, 21.4.

**<sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>)**  $\delta$  -62.3.

#### Aryl bromide S11 for synthesizing compound 27:

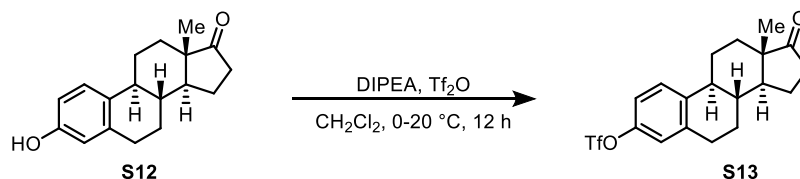


To a solution of *L*-Menthol (CAS NO.: 2216-51-5, 6.83 mmol, 1.5 equiv), 4-Bromobenzoyl chloride (1.0 equiv), DMAP (0.1 equiv), and pyridine (1.5 equiv) in DCM at 0 °C was added a solution of Et<sub>3</sub>N (1.6 equiv) in DCM (10 mL) dropwise. The reaction mixture was then stirred at room temperature for 18 hours. The reaction was quenched with saturated NH<sub>4</sub>Cl. The aqueous layer was washed with DCM, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel (EtOAc /petroleum ether= 1:20) to afford **S11** (1.2 g, 78% yield) as a colorless oil.

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  7.90 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 2H), 4.92 (td, *J* = 10.8, 4.5 Hz, 1H), 2.15 – 2.06 (m, 1H), 1.97 – 1.86 (m, 1H), 1.73 (d, 2H), 1.60 – 1.48 (m, 2H), 1.19 – 1.07 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 9H), 0.78 (d, *J* = 7.0 Hz, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**  $\delta$  165.4, 131.6, 131.1, 129.8, 127.8, 75.2, 47.3, 40.9, 34.3, 31.5, 26.6, 23.7, 22.0, 20.8, 16.5.

### Estrone derivative S13 for synthesizing compound 29:



To a solution of estrone (CAS No.: 53-16-7, 6 mmol, 1.0 equiv) in DCM (20 mL) under  $\text{N}_2$  was added DIPEA (9.0 mmol, 1.5 equiv). The solution was cooled to 0 °C and  $\text{Tf}_2\text{O}$  (7.2 mmol, 1.2 equiv) was added dropwise. Then the reaction was stirred at room temperature for 12 h. Water was added and the mixture was extracted with DCM. The combined organic layers were washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel (EtOAc /petroleum ether= 1:20) to afford **S13** (2.0 g, 83% yield) as a yellow solid. The spectroscopic data matched those reported in the literature.<sup>[4]</sup>

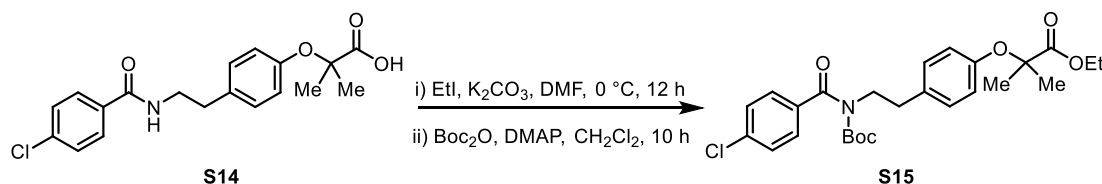
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.34 (d,  $J$  = 8.6 Hz, 1H), 7.04 (m, 1H), 6.99 (d,  $J$  = 2.7 Hz, 1H), 2.94 (m, 2H), 2.52 (m, 1H), 2.47 – 2.35 (m, 1H), 2.30 (m, 1H), 2.22 – 2.01 (m, 3H), 2.01 – 1.94 (m, 1H), 1.76 – 1.43 (m, 6H), 0.92 (s, 3H).

**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )**  $\delta$  147.6, 140.3, 139.3, 127.2, 121.2, 120.3, 118.3, 50.4, 47.9, 44.1, 37.8, 35.8, 31.5, 29.4, 26.1, 25.7, 21.6, 13.8.

**$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )**  $\delta$  –73.0.

**FT-IR (neat):** 2933, 1740, 1420, 1211, 1141, 920, 609  $\text{cm}^{-1}$ .

### Bezafibrate derivative S15 for synthesizing compound 31:



To a solution of bezafibrate (CAS No.: 41859-67-0, 3 mmol, 1.0 equiv) in DMF (18 mL) at 0 °C were added  $\text{K}_2\text{CO}_3$  (1.5 equiv) and EtI (1.2 equiv). The reaction was stirred at room temperature for 12 h. Water was added and the mixture was extracted with EtOAc. The combined organic layers were washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , and concentrated under reduced pressure. The crude material was purified by column

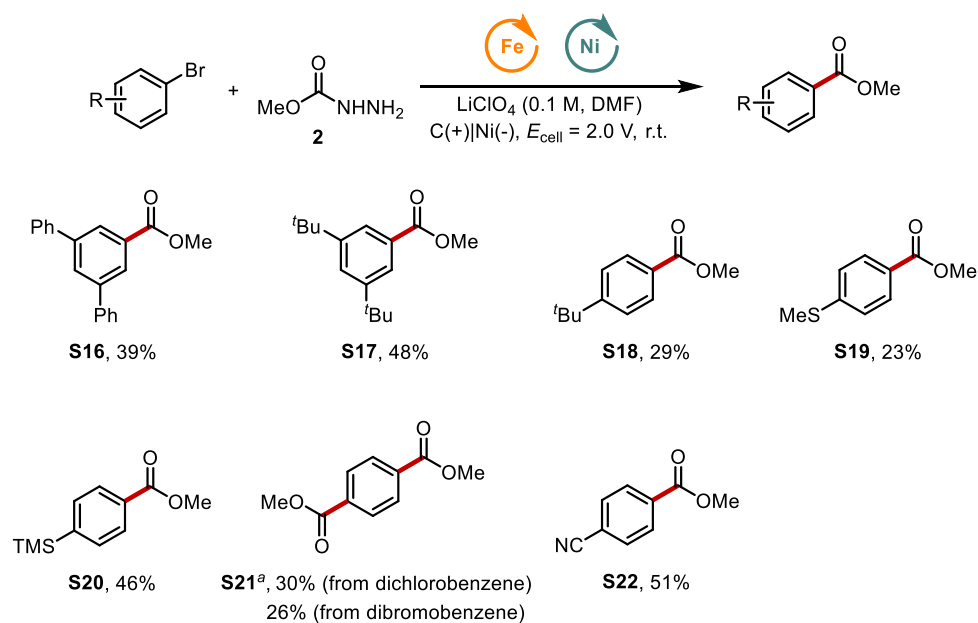
chromatography on silica gel to give the ethyl ester intermediate (1153 mg, 98%) as a white solid.

The synthetic substance mentioned above (875 mg, 2.25 mmol) was transferred into a dry 50 mL Schlenk tube with a stir bar. The flask was evacuated and back-filled with nitrogen. THF (20 mL) was added to dissolve and followed by addition of DMAP (0.1 equiv) and di-tert-butyl dicarbonate (1.1 equiv). The mixture was stirred at room temperature under argon for 10 hours. The solvent was removed under reduced pressure and the crude material was purified by chromatography on silica gel (EtOAc/petroleum ether = 1:2) to afford **S15** (349 mg, 32%) as a white solid.

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  7.33 (s, 4H), 7.13 (d,  $J$  = 8.6 Hz, 2H), 6.78 (d,  $J$  = 8.5 Hz, 2H), 4.22 (q,  $J$  = 7.1 Hz, 2H), 4.08 – 3.88 (m, 2H), 2.99 – 2.84 (m, 2H), 1.56 (s, 6H), 1.25 (t,  $J$  = 7.1 Hz, 3H), 1.19 (s, 9H).

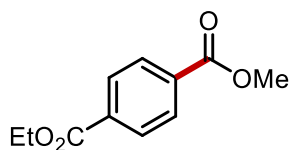
**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**  $\delta$  174.3, 172.1, 154., 153.1, 137.0, 136.2, 132.1, 129.7, 128.8, 128.2, 119.4, 83.3, 79.1, 61.4, 46.8, 34.0, 27.5, 25.3, 14.1.

## Section 7. Additional substrate scope



Reaction conditions were as follows: 0.2 mmol aryl bromides, **2** (1.5 equiv),  $\text{PcFe}$  (10 mol %),  $\text{NiBr}_2 \cdot \text{diglyme}$  (10 mol %),  $\text{dtbbpy}$  (15 mol %),  $\text{K}_2\text{CO}_3$  (2.0 equiv), phthalimide (0.5 equiv), under  $\text{N}_2$ . <sup>a</sup>With 3.0 equiv. of **2**, at  $40^\circ \text{C}$ .

## Section 8. Characterization of Products



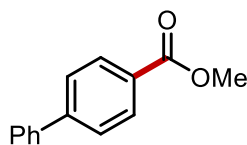
**Ethyl methyl terephthalate (3).** Followed Method A and purified using silica gel chromatography to give the product (30.8 mg, 74% yield) as yellow oil.

**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  8.09 (s, 4H), 4.40 (q,  $J = 7.1$  Hz, 2H), 3.94 (s, 3H), 1.40 (t,  $J = 7.1$  Hz, 3H).

**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  166.3, 165.8, 134.3, 133.8, 129.5, 61.4, 52.4, 14.3.

**TLC:**  $R_f = 0.4$  (silica, 1:10 EtOAc/Petroleum ether, UV).

Spectral data matched those previously reported.<sup>[5]</sup>



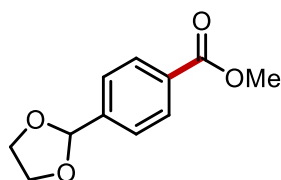
**Methyl [1,1'-biphenyl]-4-carboxylate (4).** Followed Method A and purified using silica gel chromatography to give the product (24.1 mg, 57% yield) as white solid.

**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  8.11 (d,  $J = 8.4$  Hz, 2H), 7.65 (m, 4H), 7.47 (app. t, 2H), 7.40 (app. t, 1H), 3.94 (s, 3H).

**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  167.0, 145.6, 140.0, 130.1, 128.9, 127.3, 127.1, 52.1.

**TLC:**  $R_f = 0.3$  (silica, 1:20 EtOAc/Petroleum ether, UV).

Spectral data matched those previously reported.<sup>[5]</sup>



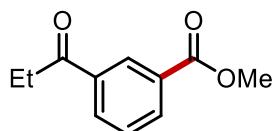
**Methyl 4-(1,3-dioxolan-2-yl) benzoate (5).** Followed Method A and purified using silica gel chromatography to give the product (14.2 mg, 34% yield) as colorless oil.

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**  $\delta$  8.05 (d,  $J$  = 8.5 Hz, 2H), 7.55 (d,  $J$  = 8.2 Hz, 2H), 5.86 (s, 1H), 4.23 – 3.99 (m, 4H), 3.92 (s, 3H).

**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )**  $\delta$  166.8, 142.8, 130.8, 129.7, 126.4, 103.0, 65.4, 52.2.

**TLC:**  $R_f$  = 0.4 (silica, 1:5 EtOAc/Petroleum ether, UV).

Spectral data matched those previously reported.<sup>[6]</sup>



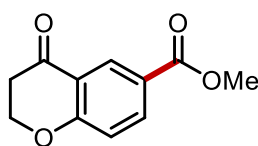
**1-(3-bromophenyl) propan-1-one (6).** Followed Method A and purified using silica gel chromatography to give the product (20.3 mg, 53% yield) as white solid.

**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  8.60 (s, 1H), 8.22 (d,  $J$  = 7.8 Hz, 1H), 8.16 (d,  $J$  = 7.8 Hz, 1H), 7.55 (t,  $J$  = 7.7 Hz, 1H), 3.95 (s, 3H), 3.05 (q,  $J$  = 7.2 Hz, 2H), 1.24 (t,  $J$  = 7.2 Hz, 3H).

**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  199.9, 166.4, 137.1, 133.7, 132.1, 130.7, 129.2, 128.8, 52.4, 32.0, 8.1.

**TLC:**  $R_f$  = 0.4 (silica, 1:10 EtOAc/Petroleum ether, UV).

Spectral data matched those previously reported.<sup>[7]</sup>



**Methyl 4-oxochromane-6-carboxylate (7).** Followed Method A and purified using silica gel chromatography to give the product (24.3 mg, 59% yield) as white solid.

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**  $\delta$  8.56 (d,  $J$  = 2.2 Hz, 1H), 8.11 (m, 1H), 7.00 (d,  $J$  = 8.7 Hz, 1H), 4.59 (t,  $J$  = 6.4 Hz, 2H), 3.89 (s, 3H), 2.84 (t,  $J$  = 6.4 Hz, 2H).

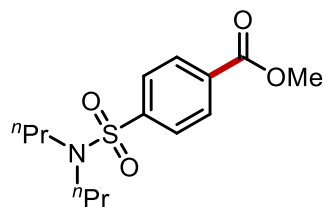
**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )**  $\delta$  190.7, 166.0, 164.9, 136.7, 129.6, 123.6, 120.8, 118.2, 67.2, 52.2, 37.5.

**HRMS (ESI):**  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{11}\text{H}_{11}\text{O}_4$   $m/z$  207.0652, found  $m/z$  207.0653.

**FT-IR (neat):** 1720, 1615, 1258  $\text{cm}^{-1}$ .

**TLC:**  $R_f$  = 0.45 (silica, 1:5 EtOAc/Petroleum ether, UV).

Spectral data matched those previously reported.<sup>[8]</sup>



**Methyl 4-(*N,N*-dipropyl sulfamoyl) benzoate (8).** Followed Method A and purified using silica gel chromatography to give the product (28.7 mg, 48% yield) as yellow oil.

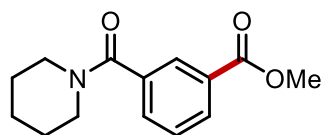
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  8.14 (d,  $J$  = 8.0 Hz, 2H), 7.86 (d,  $J$  = 8.1 Hz, 2H), 3.95 (s, 3H), 3.24 – 2.86 (m, 4H), 1.63 – 1.41 (m, 4H), 0.86 (t,  $J$  = 7.3 Hz, 6H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**  $\delta$  165.8, 144.3, 133.4, 130.2, 127.0, 52.6, 49.9, 21.9, 11.2.

**HRMS (ESI):**  $[M+H]^+$  calculated for C<sub>14</sub>H<sub>22</sub>O<sub>4</sub>NS  $m/z$  300.1264, found  $m/z$  300.1264.

**FT-IR (neat):** 2966, 2934, 1730, 1343, 1280, 1159, 1111, 1088, 993, 742, 603 cm<sup>-1</sup>.

**TLC:**  $R_f$  = 0.25 (silica, 1:10 EtOAc/Petroleum ether, UV).



**Methyl 3-(piperidine-1-carbonyl) benzoate (9).** Followed Method A and purified using silica gel chromatography to give the product (33.5 mg, 67% yield) as white solid.

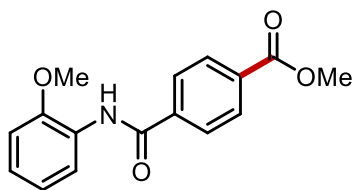
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  8.04 (m, 2H), 7.63 – 7.53 (m, 1H), 7.51 – 7.40 (m, 1H), 3.90 (s, 3H), 3.69 (s, 2H), 3.30 (s, 2H), 1.66 (s, 4H), 1.50 (s, 2H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  169.2, 166.4, 136.8, 131.3, 130.43, 130.35, 128.7, 127.9, 52.3, 48.8, 43.2, 24.5.

**HRMS (ESI):**  $[M+H]^+$  calculated for C<sub>14</sub>H<sub>18</sub>O<sub>3</sub>N  $m/z$  248.1281, found  $m/z$  248.1282.

**TLC:**  $R_f$  = 0.4 (silica, 1:2 EtOAc/Petroleum ether, UV).

Spectral data matched those previously reported.<sup>[9]</sup>



**Methyl 4-[(2-methoxyphenyl) carbamoyl] benzoate (10).** Followed Method A and purified using silica gel chromatography to give the product (38.7 mg, 68% yield) as yellow solid.

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  8.57 (s, 1H), 8.51 (d,  $J$  = 8.0 Hz, 1H), 8.15 (d,  $J$  = 8.3 Hz, 2H), 7.95 (d,  $J$  = 8.3 Hz, 2H), 7.10 (t,  $J$  = 7.7 Hz, 1H), 7.02 (t,  $J$  = 7.7 Hz, 1H), 6.93 (d,  $J$  = 7.7 Hz, 1H), 3.95 (s, 3H), 3.93 (s, 3H).

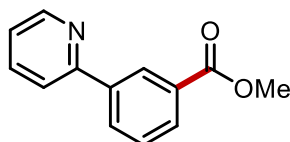
**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**  $\delta$  166.3, 164.3, 148.2, 139.2, 132.9, 130.0, 127.5, 127.1, 124.3, 121.2, 119.9, 110.0, 55.9, 52.5.

**HRMS (ESI):** [M+H]<sup>+</sup> calculated for C<sub>16</sub>H<sub>16</sub>O<sub>4</sub>N m/z 286.1074, found m/z 286.1074.

**FT-IR (neat):** 1724, 1677, 1528, 1461, 1434, 1282, 1253, 1110, cm<sup>-1</sup>.

**TLC:** R<sub>f</sub> = 0.35 (silica, 1:4 EtOAc/Petroleum ether, UV).

**Melting Point:** 121 – 124 °C



**Methyl 3-(pyridin-2-yl) benzoate (11).** Followed Method A and purified using silica gel chromatography to give the product (27.3 mg, 64% yield) as white solid.

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  8.71 (d,  $J$  = 4.8 Hz, 1H), 8.64 (s, 1H), 8.23 (d,  $J$  = 7.7 Hz, 1H), 8.09 (d,  $J$  = 7.5 Hz, 1H), 7.87 – 7.69 (m, 2H), 7.55 (t,  $J$  = 7.8 Hz, 1H), 7.31 – 7.19 (m, 1H), 3.95 (s, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**  $\delta$  167.0, 156.4, 149.8, 139.7, 136.9, 131.4, 130.7, 130.0, 128.9, 128.0, 122.6, 120.6, 52.2.

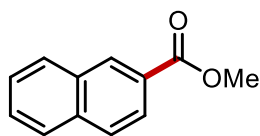
**HRMS (ESI):** [M+H]<sup>+</sup> calculated for C<sub>13</sub>H<sub>12</sub>O<sub>2</sub>N m/z 214.0863, found m/z 214.0864.

**FT-IR (neat):** 1722, 1461, 1251, 749 cm<sup>-1</sup>.

**TLC:** R<sub>f</sub> = 0.3 (silica, 1:5 EtOAc/Petroleum ether, UV).

Spectral data matched those previously reported.<sup>[10]</sup>





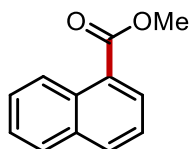
**Methyl 2-naphthoate (12).** Followed Method A and purified using silica gel chromatography to give the product (from Ar-Br 19.3 mg, 52% yield; from Ar-OTf 20.8 mg, 56% yield) as white solid.

**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  8.62 (s, 1H), 8.07 (d,  $J = 9.3$  Hz, 1H), 7.96 (d,  $J = 8.1$  Hz, 1H), 7.88 (d,  $J = 9.0$  Hz, 2H), 7.57 (m, 2H), 3.99 (s, 3H).

**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  167.3, 135.5, 132.5, 131.1, 129.4, 128.2, 128.1, 127.8, 127.4, 126.6, 125.2, 52.2.

**TLC:**  $R_f = 0.4$  (silica, 1:10 EtOAc/Petroleum ether, UV).

Spectral data matched those previously reported.<sup>[11]</sup>



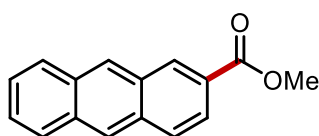
**Methyl 1-naphthoate (13).** Followed Method A and purified using silica gel chromatography to give the product (24.2 mg, 65% yield) as colorless oil.

**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  8.92 (d,  $J = 8.7$  Hz, 1H), 8.19 (dd,  $J = 7.3, 1.3$  Hz, 1H), 8.02 (d,  $J = 8.2$  Hz, 1H), 7.89 (d,  $J = 8.2$  Hz, 1H), 7.62 (ddd,  $J = 8.5, 6.9, 1.4$  Hz, 1H), 7.57 – 7.47 (m, 2H), 4.01 (s, 3H).

**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  168.0, 133.8, 133.4, 131.3, 130.2, 128.5, 127.7, 127.1, 126.2, 125.8, 124.5, 52.2.

**TLC:**  $R_f = 0.55$  (silica, 1:20 EtOAc/Petroleum ether, UV).

Spectral data matched those previously reported.<sup>[11]</sup>



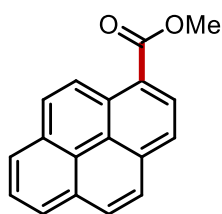
**Methyl anthracene-2-carboxylate (14).** Followed Method A and purified using silica gel chromatography to give the product (29.3 mg, 62% yield) as yellow solid.

**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  8.82 (s, 1H), 8.57 (s, 1H), 8.45 (s, 1H), 8.18 – 7.90 (m, 4H), 7.61 – 7.37 (m, 2H), 4.01 (s, 3H).

**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  167.3, 132.3, 128.7, 128.51, 128.47, 128.2, 126.6, 126.2, 125.9, 124.0, 52.3.

**TLC:**  $R_f$  = 0.5 (silica, 1:10 EtOAc/Petroleum ether, UV).

Spectral data matched those previously reported.<sup>[12]</sup>



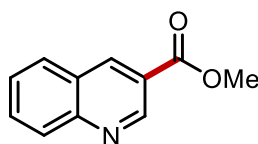
**Methyl pyrene-1-carboxylate (15).** Followed Method A and purified using silica gel chromatography to give the product (31.5 mg, 60% yield) as white solid.

**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  9.26 (d,  $J$  = 9.4 Hz, 1H), 8.61 (d,  $J$  = 9.0 Hz, 1H), 8.28 – 8.17 (m, 3H), 8.13 (m, 2H), 8.05 (m, 2H), 4.11 (s, 3H).

**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  168.4, 134.3, 131.1, 130.9, 130.3, 129.6, 129.4, 128.4, 127.1, 126.2, 126.1, 124.84, 124.76, 124.13, 124.06, 123.4, 52.3.

**TLC:**  $R_f$  = 0.45 (silica, 1:10 EtOAc/Petroleum ether, UV).

Spectral data matched those previously reported.<sup>[13]</sup>



**Methyl quinoline-3-carboxylate (16).** Followed Method A and purified using silica gel chromatography to give the product (15.0 mg, 40% yield) as white solid.

**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  9.44 (s, 1H), 8.85 (s, 1H), 8.16 (d,  $J$  = 8.5 Hz, 1H), 7.93 (d,  $J$  = 8.2 Hz, 1H), 7.88 – 7.81 (m, 1H), 7.66 – 7.60 (m, 1H), 4.01 (s, 3H).

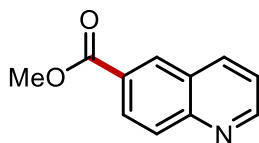
**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  165.8, 150.0, 149.8, 138.9, 131.9, 129.4, 129.1, 127.5, 126.8, 123.0, 52.5.

**HRMS (ESI):**  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{11}\text{H}_{10}\text{O}_2\text{N}$   $m/z$  188.0706, found  $m/z$  188.0707.

**FT-IR (neat):** 1717, 1293, 791  $\text{cm}^{-1}$ .

**TLC:**  $R_f$  = 0.15 (silica, 1:10 EtOAc/Petroleum ether, UV).

Spectral data matched those previously reported.<sup>[14]</sup>



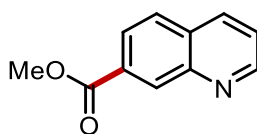
**Methyl quinoline-6-carboxylate (17).** Followed Method A and purified using silica gel chromatography to give the product (19.9 mg, 53% yield) as white solid.

**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  9.00 (s, 1H), 8.59 (s, 1H), 8.34 – 8.21 (m, 2H), 8.15 (d,  $J$  = 8.9 Hz, 1H), 7.47 (m, 1H), 3.99 (s, 3H).

**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  166.6, 152.4, 150.0, 137.4, 131.0, 129.8, 129.0, 128.2, 127.4, 121.9, 52.5.

**TLC:**  $R_f$  = 0.3 (silica, 1:10 EtOAc/Petroleum ether, UV).

Spectral data matched those previously reported.<sup>[15]</sup>



**Methyl quinoline-7-carboxylate (18).** Followed Method A and purified using silica gel chromatography to give the product (16.1 mg, 43% yield) as white solid.

**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  9.01 (m, 1H), 8.90 – 8.76 (m, 1H), 8.28 – 8.06 (m, 2H), 7.88 (d,  $J$  = 8.5 Hz, 1H), 7.50 (m, 1H), 4.01 (s, 3H).

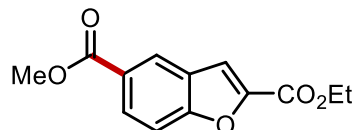
**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  166.8, 151.4, 147.6, 135.8, 132.2, 131.0, 130.7, 128.1, 126.1, 122.8, 52.5.

**HRMS (ESI):**  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{11}\text{H}_{10}\text{O}_2\text{N}$   $m/z$  188.0706, found  $m/z$  188.0707.

**FT-IR (neat):** 1750, 1726, 1291  $\text{cm}^{-1}$ .

**TLC:**  $R_f$  = 0.2 (silica, 1:4 EtOAc/Petroleum ether, UV).

**Melting Point:** sublimed over 220 °C



**2-ethyl 5-methyl benzofuran-2,5-dicarboxylate (19).** Followed Method A and purified using silica gel chromatography to give the product (27.5 mg, 44% yield) as yellow solid.

**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  8.42 (d,  $J$  = 1.8 Hz, 1H), 8.15 (m, 1H), 7.61 (d,  $J$  = 8.8 Hz, 1H), 7.59 – 7.53 (m, 1H), 4.45 (d,  $J$  = 7.1 Hz, 2H), 3.95 (s, 3H), 1.43 (t,  $J$  = 7.1 Hz, 3H).

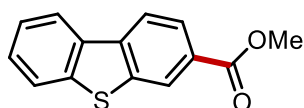
**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  166.7, 159.2, 158.0, 147.1, 128.9, 127.0, 126.3, 125.4, 114.0, 112.3, 61.8, 52.3, 14.3.

**HRMS (ESI):**  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{13}\text{H}_{13}\text{O}_5$   $m/z$  249.0758, found  $m/z$  249.0757.

**FT-IR (neat):** 2924, 1722, 1291, 1165, 1015  $\text{cm}^{-1}$ .

**TLC:**  $R_f$  = 0.35 (silica, 1:10 EtOAc/Petroleum ether, UV).

Spectral data matched those previously reported.<sup>[16]</sup>



**Methyl dibenzo[b,d] thiophene-3-carboxylate (20).** Followed Method A and purified using silica gel chromatography to give the product (24.2 mg, 50 % yield) as white solid.

**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  8.56 (s, 1H), 8.25 – 8.15 (m, 2H), 8.12 (d,  $J$  = 8.2 Hz, 1H), 7.88 (d,  $J$  = 7.6 Hz, 1H), 7.54 – 7.43 (m, 2H), 3.98 (s, 3H).

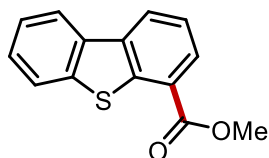
**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  166.9, 141.0, 139.2, 139.1, 134.6, 128.3, 127.8, 125.4, 124.69, 124.66, 123.0, 122.4, 121.3, 52.3.

**HRMS (ESI):**  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{14}\text{H}_{11}\text{O}_2\text{S}$   $m/z$  243.0474, found  $m/z$  243.0476.

**FT-IR (neat):** 1715, 1289, 1255, 1231, 1112, 751  $\text{cm}^{-1}$ .

**TLC:**  $R_f$  = 0.55 (silica, 1:10 EtOAc/Petroleum ether, UV).

Spectral data matched those previously reported.<sup>[17]</sup>



**Methyl dibenzo[*b,d*]thiophene-4-carboxylate (21).** Followed Method A and purified using silica gel chromatography to give the product (23.7 mg, 49% yield) as white solid.

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  8.35 (d,  $J$  = 7.8 Hz, 1H), 8.22 (d,  $J$  = 7.4 Hz, 1H), 8.17 (d,  $J$  = 7.8 Hz, 1H), 7.92 (d,  $J$  = 7.3 Hz, 1H), 7.66 – 7.39 (m, 3H), 4.05 (s, 3H).

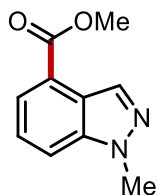
**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**  $\delta$  166.7, 141.1, 141.0, 137.0, 134.3, 128.8, 127.2, 125.8, 124.5, 124.21, 124.15, 122.6, 121.4, 52.4.

**HRMS (ESI):**  $[M+H]^+$  calculated for C<sub>14</sub>H<sub>11</sub>O<sub>2</sub>S  $m/z$  243.0474, found  $m/z$  243.0481.

**FT-IR (neat):** 1715, 1289, 1231, 752 cm<sup>-1</sup>.

**TLC:**  $R_f$  = 0.55 (silica, 1:10 EtOAc/Petroleum ether, UV).

**Melting Point:** 93 – 97 °C



**Methyl 1-methyl-1H-indazole-4-carboxylate (22).** Followed Method A and purified using silica gel chromatography to give the product (19.4 mg, 51% yield) as white solid.

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  8.47 (s, 1H), 7.93 (d,  $J$  = 7.2 Hz, 1H), 7.62 (d,  $J$  = 8.4 Hz, 1H), 7.51 – 7.41 (m, 1H), 4.12 (s, 3H), 4.02 (s, 3H).

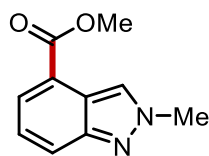
**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**  $\delta$  166.8, 140.3, 133.7, 125.5, 124.1, 122.9, 122.4, 113.9, 52.1, 35.7.

**HRMS (ESI):**  $[M+H]^+$  calculated for C<sub>10</sub>H<sub>11</sub>O<sub>2</sub>N<sub>2</sub>  $m/z$  191.0815, found  $m/z$  191.0815.

**FT-IR (neat):** 1717, 1283, 1197, 1129, 753 cm<sup>-1</sup>.

**TLC:**  $R_f$  = 0.5 (silica, 1:2 EtOAc/Petroleum ether, UV).

**Melting Point:** 87 – 88 °C



**Methyl 2-methyl-2H-indazole-4-carboxylate (23).** Followed Method A and purified using silica gel chromatography to give the product (22.8 mg, 60% yield) as colorless oil.

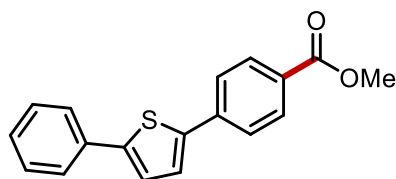
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  8.41 (s, 1H), 7.92 (t,  $J$  = 7.6 Hz, 2H), 7.34 (m, 1H), 4.26 (s, 3H), 3.98 (s, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**  $\delta$  166.8, 149.3, 126.2, 125.5, 125.0, 123.1, 122.2, 120.3, 52.0, 40.5.

**HRMS (ESI):**  $[M+H]^+$  calculated for C<sub>10</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub>  $m/z$  191.0815, found  $m/z$  191.0813.

**FT-IR (neat):** 2921, 1713, 1274, 1201, 1140, 757 cm<sup>-1</sup>.

**TLC:**  $R_f$  = 0.25 (silica, 1:2 EtOAc/Petroleum ether, UV).



**Methyl 4-(5-phenylthiophen-2-yl) benzoate (24).** Followed Method A and purified using silica gel chromatography to give the product (26.5 mg, 45% yield) as white solid.

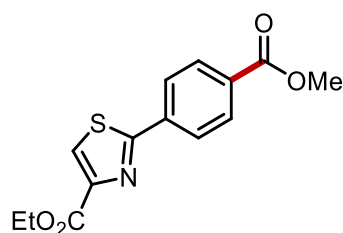
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** 8.05 (d,  $J$  = 8.3 Hz, 2H), 7.69 (d,  $J$  = 8.2 Hz, 2H), 7.67 – 7.59 (m, 2H), 7.47 – 7.37 (m, 3H), 7.35 – 7.28 (m, 2H), 3.94 (s, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**  $\delta$  166.7, 145.2, 142.1, 138.5, 134.0, 130.3, 129.0, 128.7, 127.9, 125.8, 125.5, 125.2, 124.3, 52.2.

**FT-IR (neat):** 2921, 1714, 1453, 1284, 1114, 761, 692 cm<sup>-1</sup>.

**TLC:**  $R_f$  = 0.4 (silica, 1:10 EtOAc/Petroleum ether, UV).

Spectral data matched those previously reported.<sup>[18]</sup>



**Ethyl 2-(4-(methoxycarbonyl) phenyl) thiazole-4-carboxylate (25).** Followed Method A and purified using silica gel chromatography to give the product (27.3 mg, 47% yield) as white solid.

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  8.28 – 8.20 (m, 1H), 8.19 – 8.02 (m, 4H), 4.57 – 4.35 (m, 2H), 3.95 (s, 3H), 1.53 – 1.33 (m, 3H).

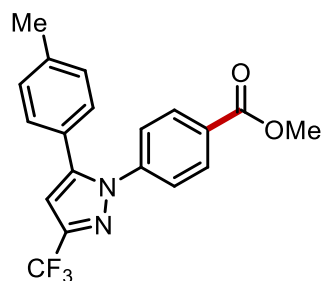
**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**  $\delta$  167.5, 166.4, 161.3, 148.5, 136.5, 131.9, 130.3, 127.8, 126.9, 61.7, 52.4, 14.4.

**HRMS (ESI):** [M+H]<sup>+</sup> calculated for C<sub>14</sub>H<sub>14</sub>O<sub>4</sub>NS m/z 292.0638, found m/z 292.0636.

**FT-IR (neat):** 1722, 1283, 1218, 1100, 771 cm<sup>-1</sup>.

**TLC:** R<sub>f</sub> = 0.5 (silica, 1:4 EtOAc/Petroleum ether, UV).

The spectroscopic data matched those reported in the literature.<sup>[19]</sup>



**Methyl 4-[5-(*p*-tolyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl] benzoate (26).** Followed Method A and purified using silica gel chromatography to give the product (44.6 mg, 62% yield) as yellow oil.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  8.03 (d, *J* = 8.7 Hz, 2H), 7.40 (d, *J* = 8.7 Hz, 2H), 7.21 – 7.04 (m, 4H), 6.73 (s, 1H), 3.92 (s, 3H), 2.36 (s, 3H).

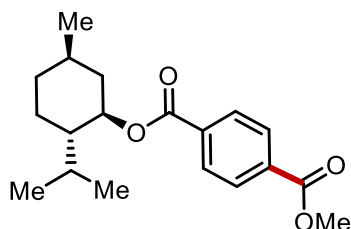
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  166.1, 145.1, 143.8 (q, *J* = 39 Hz), 142.8, 139.5, 130.5, 129.7, 129.6, 128.7, 126.0, 125.0, 121.2 (q, *J* = 269 Hz), 106.01 (q, *J* = 2 Hz), 52.3, 21.3.

**<sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>)**  $\delta$  -62.4.

**HRMS (ESI):**  $[M+H]^+$  calculated for  $C_{19}H_{16}O_2N_2F_3$   $m/z$  361.1158, found  $m/z$  361.1156.

**FT-IR (neat):** 1725, 1279, 1236  $cm^{-1}$ .

**TLC:  $R_f$**  = 0.3 (silica, 1:20 EtOAc/Petroleum ether, UV).



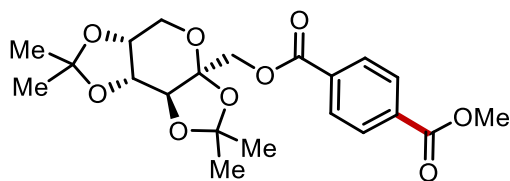
**(1R, 2S, 5R)-2-isopropyl-5-methylcyclohexyl methyl terephthalate (27).** Followed Method A and purified using silica gel chromatography to give the product (28 mg, 44% yield) as light-yellow oil.

**$^1H$  NMR (400 MHz,  $CDCl_3$ )**  $\delta$  8.09 (s, 4H), 5.04 – 4.84 (m, 1H), 3.94 (s, 3H), 2.12 (d,  $J$  = 10.4, 5.9 Hz, 1H), 2.02 – 1.88 (m, 1H), 1.80 – 1.67 (m, 2H), 1.62 – 1.49 (m, 2H), 1.20 – 1.03 (m, 2H), 1.00 – 0.87 (m, 7H), 0.79 (d,  $J$  = 6.9 Hz, 3H).

**$^{13}C$  NMR (101 MHz,  $CDCl_3$ )**  $\delta$  166.4, 165.3, 134.7, 133.7, 129.5, 75.4, 52.4, 47.2, 40.9, 34.3, 31.5, 26.5, 23.6, 22.0, 20.8, 16.5.

**TLC:  $R_f$**  = 0.6 (silica, 1:10 EtOAc/Petroleum ether, UV).

The spectroscopic data matched those reported in the literature.<sup>[20]</sup>



**Methyl [((3aS,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-3aH-bis ([1,3] dioxolo) [4,5-b:4',5'-d] pyran-3a-yl) methyl] terephthalate (28).** Followed Method A and purified using silica gel chromatography to give the product (57.4 mg, 68% yield) as yellow oil.

**$^1H$  NMR (500 MHz,  $CDCl_3$ )**  $\delta$  8.13 (d,  $J$  = 8.2 Hz, 2H), 8.09 (d,  $J$  = 8.2 Hz, 2H), 4.70 (d,  $J$  = 11.7 Hz, 1H), 4.64 (m, 1H), 4.45 (d,  $J$  = 2.7 Hz, 1H), 4.34 (d,  $J$  = 11.8 Hz, 1H),



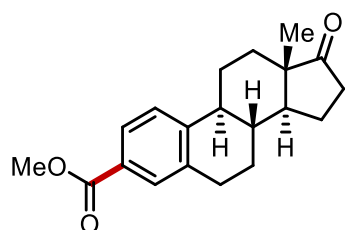
4.25 (d,  $J = 7.9$  Hz, 1H), 3.96 (s, 1H), 3.94 (s, 3H), 3.80 (d,  $J = 13.0$  Hz, 1H), 1.54 (s, 3H), 1.45 (s, 3H), 1.34 (d,  $J = 5.3$  Hz, 6H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  166.2, 165.2, 134.1, 133.7, 129.7, 129.6, 109.2, 108.9, 101.6, 70.8, 70.6, 70.1, 65.8, 61.4, 52.5, 26.5, 25.9, 25.5, 24.0.

HRMS (ESI):  $[\text{M}+\text{Na}]^+$  calculated for  $\text{C}_{21}\text{H}_{26}\text{O}_9\text{Na}$   $m/z$  445.1469, found  $m/z$  445.1465.

FT-IR (neat): 2991, 1726, 1275, 1253, 1114, 1072, 731  $\text{cm}^{-1}$ .

TLC:  $R_f = 0.4$  (silica, 1:5 EtOAc/Petroleum ether, UV).



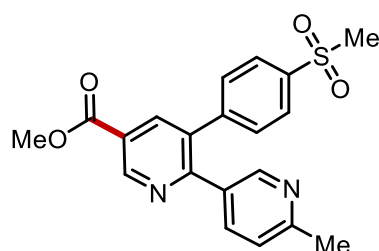
**Methyl (8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[*a*]phenanthrene-3-carboxylate (29).** Followed Method A using triflate **S11** and purified using silica gel chromatography to give the product (28.7 mg, 46% yield) as yellow solid.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 – 7.78 (m, 2H), 7.35 (d,  $J = 8.1, 3.0$  Hz, 1H), 3.90 (s, 3H), 2.98 – 2.95 (m, 2H), 2.56 – 2.48 (m, 1H), 2.31 (d,  $J = 11.2$  Hz, 1H), 2.16 – 2.11 (m, 1H), 2.11 – 2.01 (m, 1H), 2.01 – 1.97 (m, 3H), 1.64 – 1.50 (m, 6H), 0.92 (d,  $J = 3.1$  Hz, 3H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  220.3, 167.2, 145.1, 136.7, 130.2, 127.6, 126.9, 125.4, 52.0, 50.5, 47.9, 44.7, 37.8, 35.8, 31.6, 29.2, 26.3, 25.6, 21.6, 13.8.

TLC:  $R_f = 0.45$  (silica, 1:4 EtOAc/Petroleum ether, UV).

The spectroscopic data matched those reported in the literature.<sup>[13]</sup>



**Methyl 6'-methyl-3-(4-(methyl sulfonyl) phenyl)-[2,3'-bipyridine]-5-carboxylate (30).** Followed Method A and purified using silica gel chromatography to give the product (29 mg, 38% yield) as white solid.

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  9.31 (d,  $J$  = 2.0 Hz, 1H), 8.45 (d,  $J$  = 2.4 Hz, 1H), 8.32 (d,  $J$  = 2.1 Hz, 1H), 7.91 (d,  $J$  = 8.0 Hz, 2H), 7.63 (m, 1H), 7.43 (d,  $J$  = 8.0 Hz, 2H), 7.11 (d,  $J$  = 8.1 Hz, 1H), 4.00 (s, 3H), 3.09 (s, 3H), 2.55 (s, 3H).

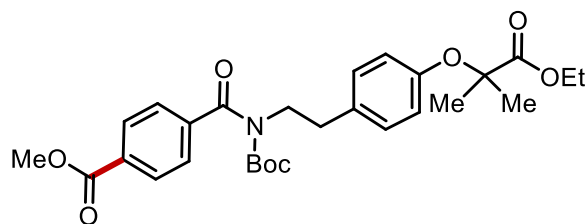
**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**  $\delta$  165.2, 159.1, 157.8, 150.4, 150.0, 144.3, 140.1, 139.7, 137.5, 134.1, 131.4, 130.4, 128.0, 124.8, 122.9, 52.7, 44.5, 24.3.

**HRMS (ESI):** [M+H]<sup>+</sup> calculated for C<sub>20</sub>H<sub>19</sub>O<sub>4</sub>N<sub>2</sub>S m/z 383.1060, found m/z 383.1060.

**FT-IR (neat):** 1724, 1312, 1253, 1151 cm<sup>-1</sup>.

**TLC:** R<sub>f</sub> = 0.25 (silica, 1:2 Acetone/Petroleum ether, 3rd, UV).

**Melting Point:** 168 – 172 °C



**Methyl 4- [(tert-butoxy carbonyl) (4-((1-ethoxy-2-methyl-1-oxopropan-2-yl) oxy) phenethyl) carbamoyl] benzoate (31).** Followed Method A and purified using silica gel chromatography to give the product (38mg, 37% yield) as white solid.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  8.03 (d,  $J$  = 8.0 Hz, 2H), 7.43 (d,  $J$  = 7.9 Hz, 2H), 7.14 (d,  $J$  = 8.1 Hz, 2H), 6.78 (d,  $J$  = 8.1 Hz, 2H), 4.22 (q,  $J$  = 7.1 Hz, 2H), 4.02 (t,  $J$  = 8.7, 6.6 Hz, 2H), 3.93 (s, 3H), 2.94 (t,  $J$  = 7.6 Hz, 2H), 1.56 (s, 6H), 1.24 (t,  $J$  = 6.8 Hz, 3H), 1.13 (s, 9H).

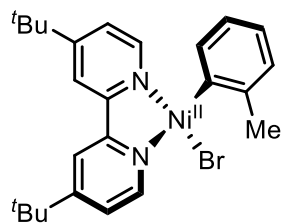
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  174.3, 172.2, 166.3, 154.1, 152.9, 142.1, 132.0, 131.8, 129.8, 129.3, 127.1, 119.4, 83.5, 79.1, 61.4, 52.4, 46.7, 34.0, 27.4, 25.4, 25.3, 14.1.

**HRMS (ESI):** [M+H]<sup>+</sup> calculated for C<sub>28</sub>H<sub>36</sub>O<sub>8</sub>N m/z 514.2435, found m/z 514.2438.

**FT-IR (neat):** 3202, 1773, 1751, 1730, 1674, 1278, 1141, 713 cm<sup>-1</sup>.

**TLC:** R<sub>f</sub> = 0.5 (silica, 1:4 EtOAc/Petroleum ether, UV).

**Melting Point:** 92 – 95 °C

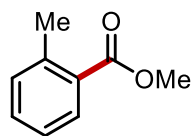


**[(dtbbpy)Ni(II)(2-tolyl)Br] (32).**

Followed those previously reported<sup>[1]</sup> and give the product (388 mg, 78% yield) as orange powder.

**<sup>1</sup>H NMR (400 MHz, Acetone-*d*<sub>6</sub>)**  $\delta$  9.29 (d, *J* = 5.8 Hz, 1H), 8.42 (d, *J* = 15.3 Hz, 2H), 7.71 (d, *J* = 5.8 Hz, 1H), 7.54 (d, *J* = 7.2 Hz, 1H), 7.36 (d, *J* = 6.2 Hz, 1H), 7.04 (d, *J* = 6.2 Hz, 1H), 6.87 – 6.58 (m, 3H), 3.03 (s, 3H), 1.45 (s, 9H), 1.38 (s, 9H).

Spectral data matched those previously reported.<sup>[1]</sup>

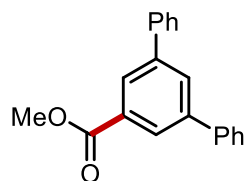


**Methyl 2-methylbenzoate (33).** Purified using silica gel chromatography (EtOAc/Petroleum ether) to give the product (from the procedure using divided cell, 9.0 mg, 60% yield) as yellow oil.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.91 (m, 1H), 7.39 (td, *J* = 7.5, 1.5 Hz, 1H), 7.28 – 7.19 (m, 2H), 3.89 (s, 3H), 2.60 (s, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  168.07, 140.16, 131.93, 131.66, 130.55, 129.58, 125.67, 51.78, 21.69.

Spectral data matched those previously reported.<sup>[21]</sup>



**Methyl [1,1':3',1''-terphenyl]-5'-carboxylate (S16).** Followed Method A and purified using silica gel chromatography to give the product (20 mg, 33% yield) as

white solid.

**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  8.25 (d,  $J = 1.8$  Hz, 2H), 7.99 (t,  $J = 1.8$  Hz, 1H), 7.71 – 7.64 (m, 4H), 7.47 (t,  $J = 7.7$  Hz, 4H), 7.42 – 7.35 (m, 2H), 3.97 (s, 3H).

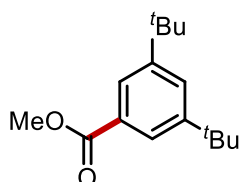
**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  167.0, 142.1, 140.2, 131.3, 130.3, 128.9, 127.9, 127.3, 127.1, 52.2.

**HRMS (APCI):**  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{20}\text{H}_{17}\text{O}_2$   $m/z$  289.1223, found  $m/z$  289.1229.

**TLC:**  $R_f = 0.4$  (silica, 1:20 Ethyl Acetate/Petroleum ether, UV).

Spectral data matched those previously reported.<sup>[22]</sup>

**Melting Point:** 86 – 89 °C



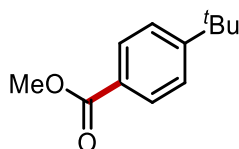
**Methyl 3,5-di-tert-butylbenzoate (S17).** Followed Method A and purified using silica gel chromatography to give the product (23.8 mg, 48% yield) as white solid.

**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.90 (d,  $J = 2.0$  Hz, 2H), 7.63 (s, 1H), 3.92 (s, 3H), 1.35 (s, 18H).

**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  167.8, 151.0, 129.5, 127.1, 123.8, 52.0, 35.0, 31.4.

**TLC:**  $R_f = 0.5$  (silica, 1:20 Ethyl Acetate/Petroleum ether, UV).

Spectral data matched those previously reported.<sup>[23]</sup>



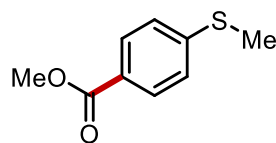
**Methyl 4-(tert-butyl) benzoate (S18).** Followed Method A and purified using silica gel chromatography to give the product (11.2 mg, 29% yield) as yellow oil.

**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.97 (d,  $J = 8.4$  Hz, 2H), 7.45 (d,  $J = 8.4$  Hz, 2H), 3.90 (s, 3H), 1.34 (s, 9H).

**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  167.2, 156.5, 129.4, 127.4, 125.3, 52.0, 35.1, 31.1.

**TLC:**  $R_f = 0.6$  (silica, 1:20 Ethyl Acetate/Petroleum ether, UV).

Spectral data matched those previously reported.<sup>[11]</sup>



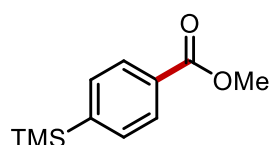
**Methyl 4-(methylthio) benzoate (S19).** Followed Method A and purified using silica gel chromatography to give the product (8.4 mg, 23% yield) as white solid.

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  7.93 (d,  $J$  = 8.5 Hz, 2H), 7.25 (d,  $J$  = 8.5 Hz, 2H), 3.90 (s, 3H), 2.51 (s, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**  $\delta$  166.9, 145.4, 129.9, 126.3, 124.9, 52.0, 14.8

**TLC:**  $R_f$  = 0.6 (silica, 1:20 Ethyl Acetate/Petroleum ether, UV).

Spectral data matched those previously reported.<sup>[24]</sup>



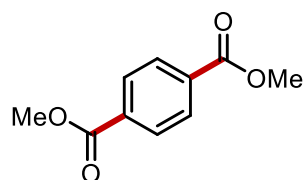
**Methyl 4-(trimethylsilyl) benzoate (S20).** Followed Method A and purified using silica gel chromatography to give the product (19.2 mg, 46% yield) as white solid.

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  8.13 – 7.82 (m, 2H), 7.70 – 7.44 (m, 2H), 3.92 (s, 3H), 0.29 (s, 9H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**  $\delta$  167.29, 146.86, 133.28, 130.26, 128.47, 52.08, – 1.32.

**TLC:**  $R_f$  = 0.5 (silica, 1:10 Ethyl Acetate/Petroleum ether, UV).

Spectral data matched those previously reported.<sup>[13]</sup>

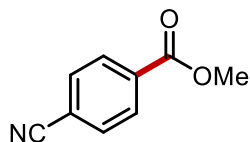


**Dimethyl terephthalate (S21).** Followed Method A, at 40 °C, and purified using silica gel chromatography to give the product (10 mg, 26% from dibromobenzene; 11.6 mg, 30% from dichlorobenzene) as yellow solid.

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**  $\delta$  8.09 (s, 4H), 3.94 (s, 6H).

**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )**  $\delta$  166.3, 133.9, 129.6, 52.4.

Spectral data matched those previously reported.<sup>[11]</sup>



**Methyl 4-cyanobenzoate (S22).** Followed Method A and purified using silica gel chromatography to give the product (16.4 mg, 51%) as yellow solid.

**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  8.13 (d,  $J = 8.4$  Hz, 2H), 7.74 (d,  $J = 8.4$  Hz, 2H), 3.96 (s, 3H).

**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  165.4, 134.0, 132.2, 130.1, 117.9, 116.5, 52.7.

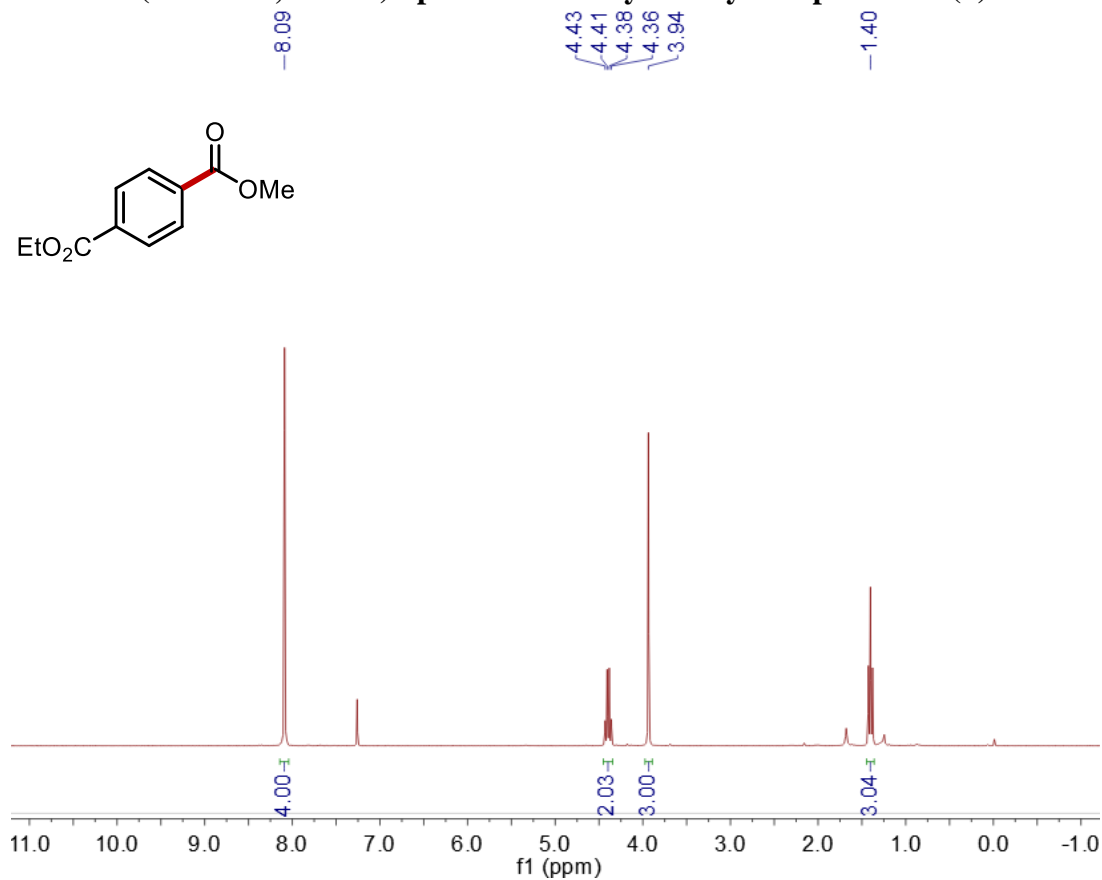
Spectral data matched those previously reported.<sup>[25]</sup>

## Section 9. References

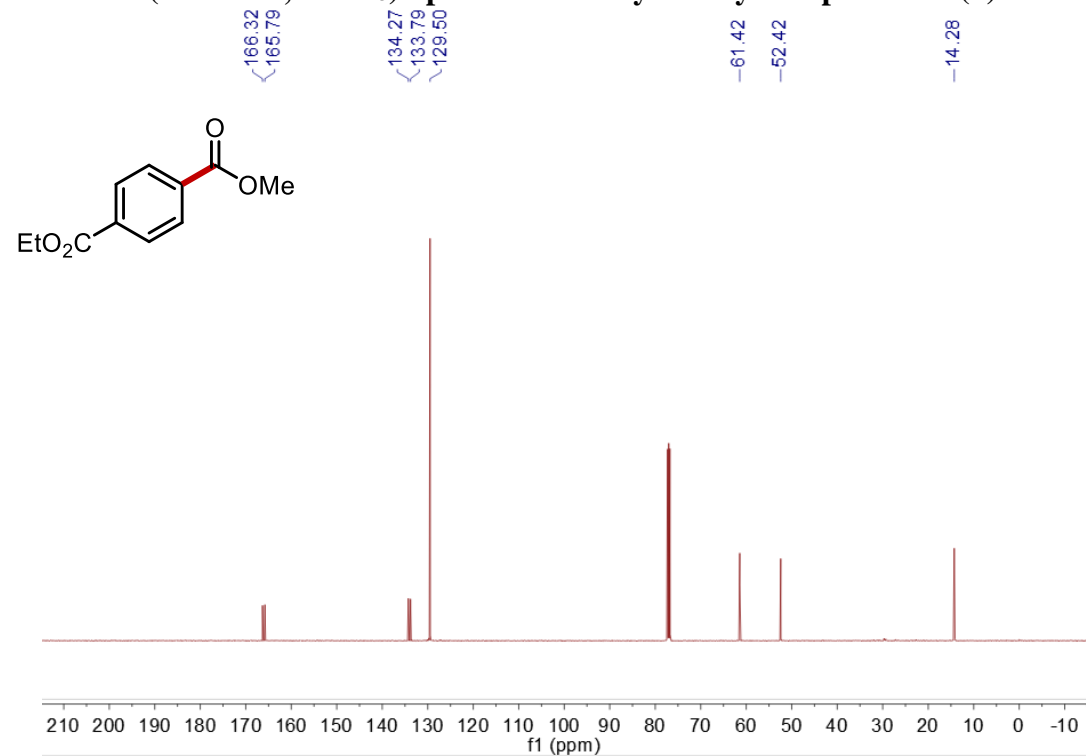
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## Section 10. NMR Spectra Data for Materials and Products

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) Spectrum of Ethyl methyl terephthalate (3).

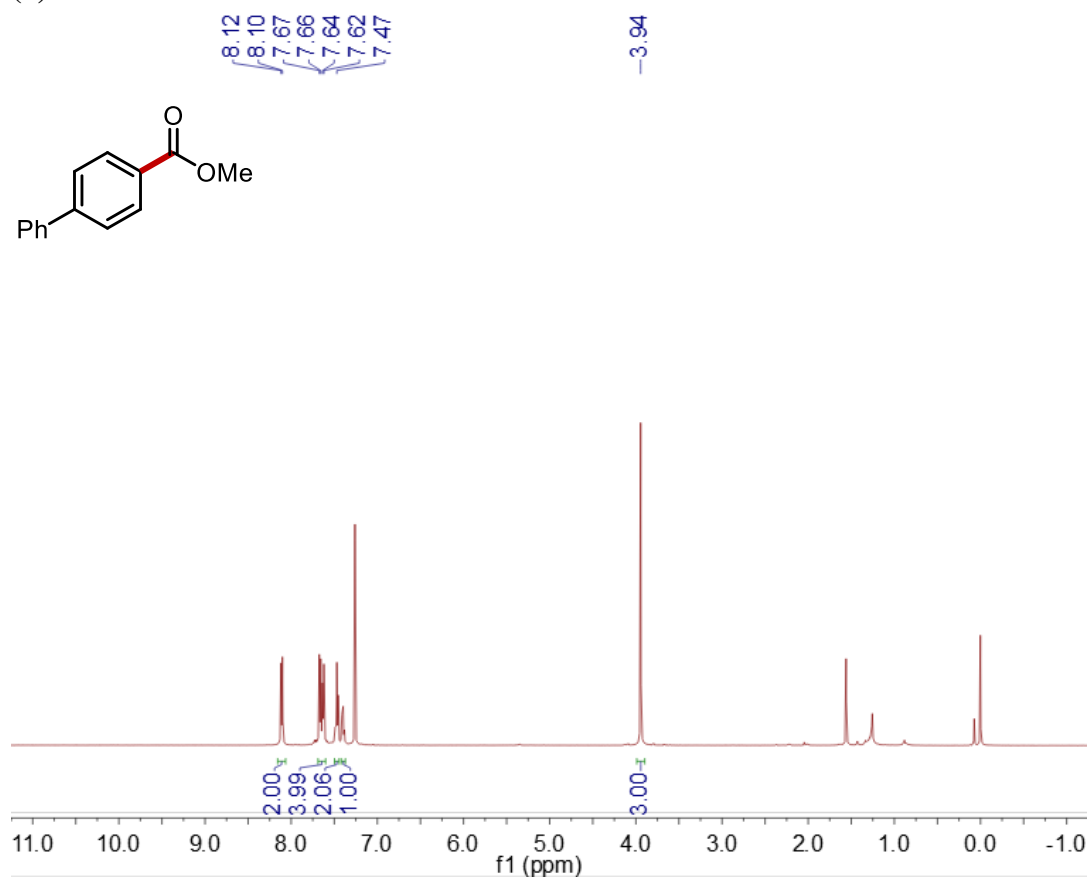


$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) Spectrum of Ethyl methyl terephthalate (3).

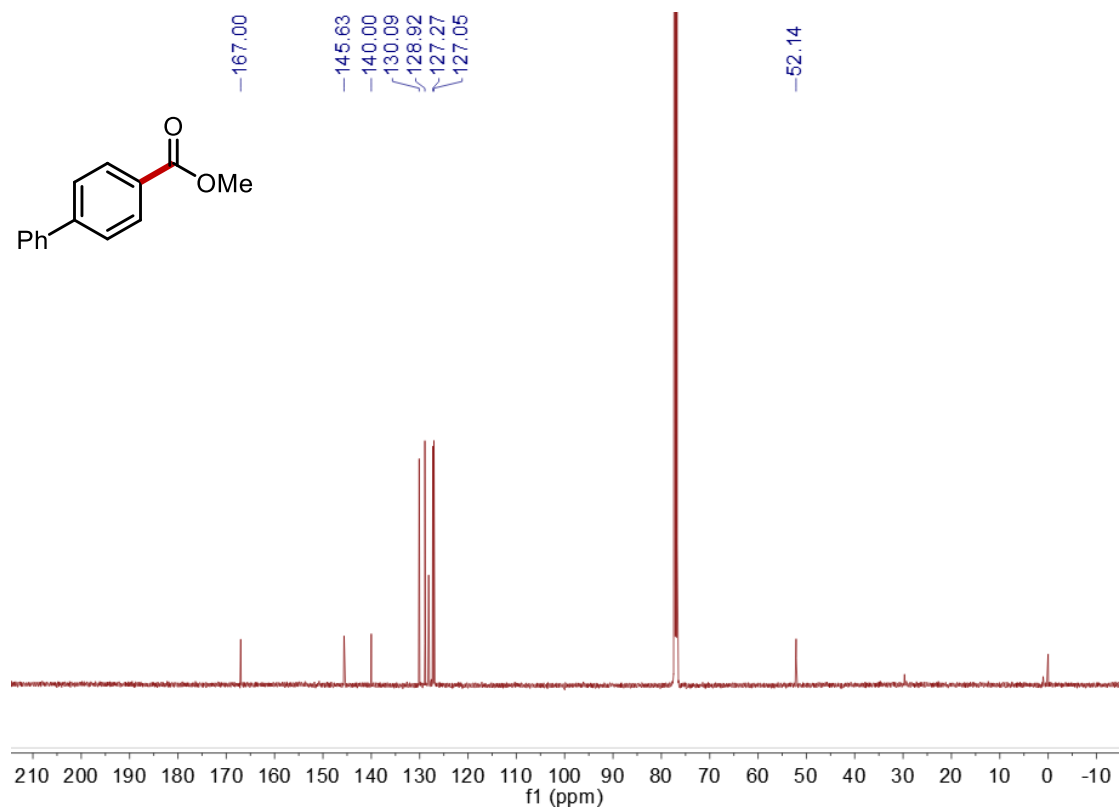




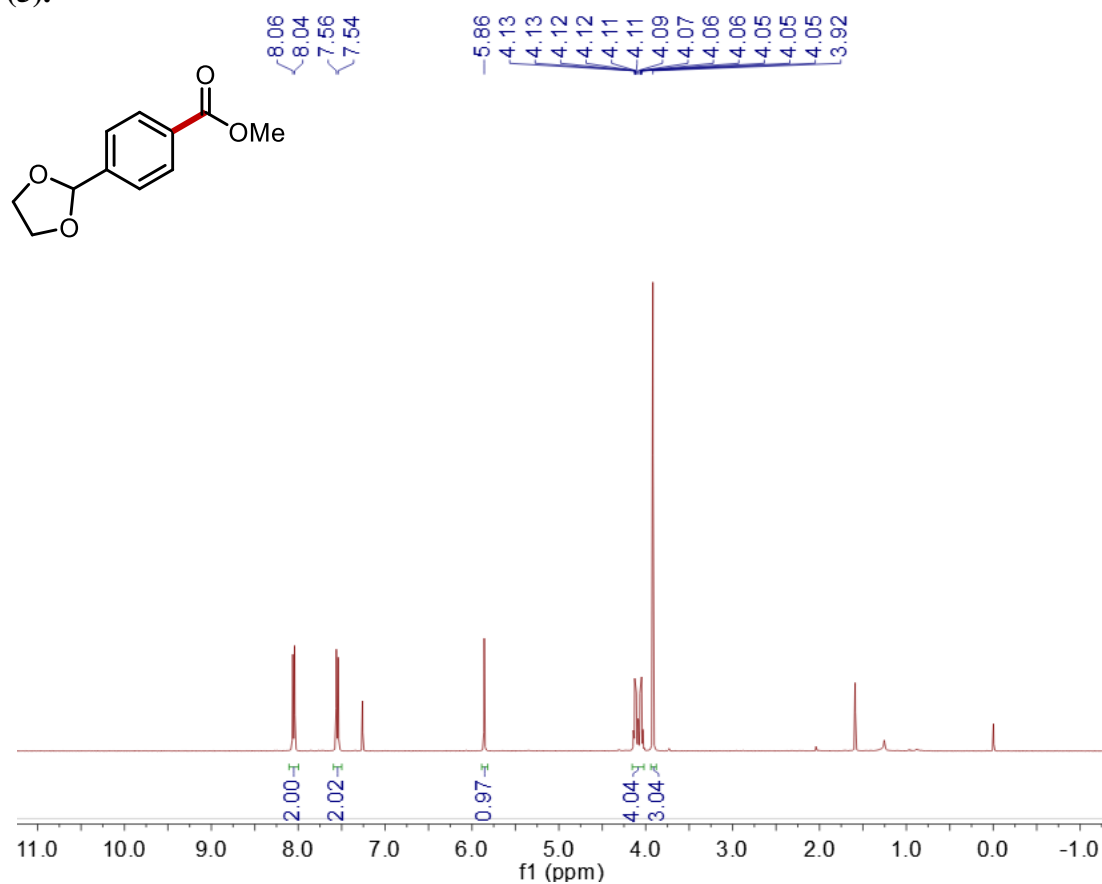
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum of Methyl [1,1'-biphenyl]-4-carboxylate (4).**



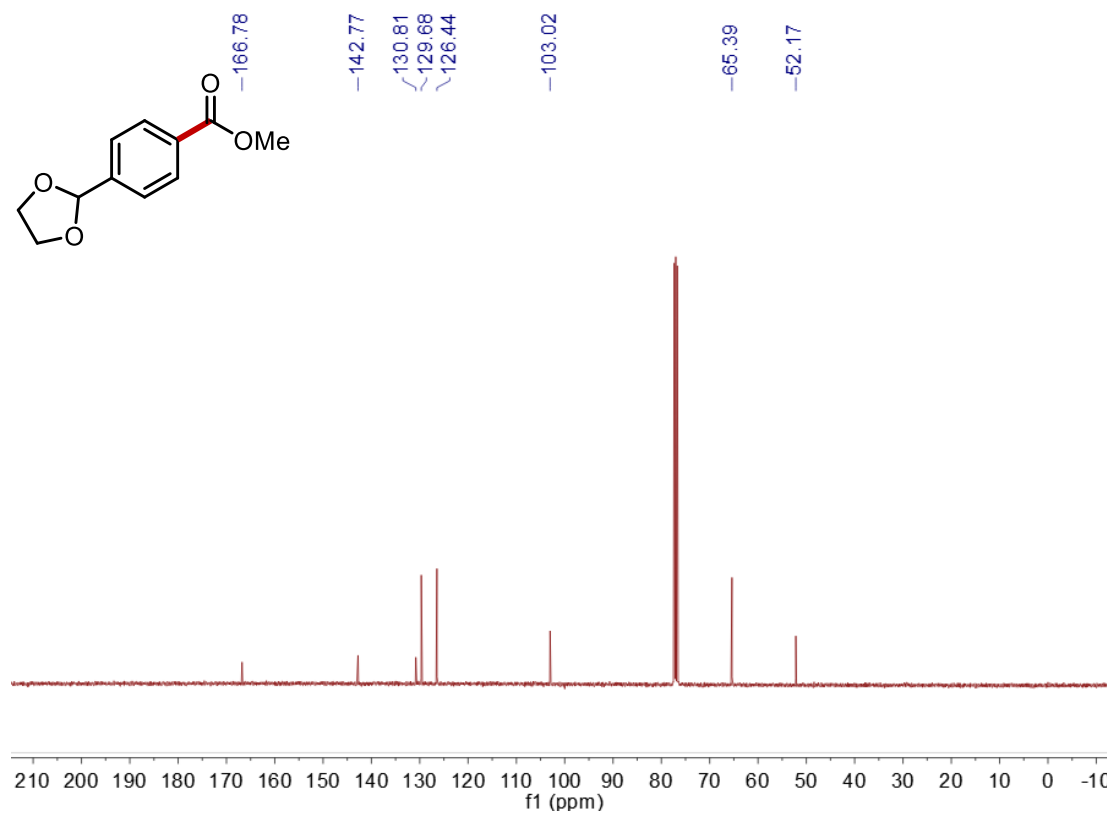
**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) Spectrum of Methyl [1,1'-biphenyl]-4-carboxylate (4).**



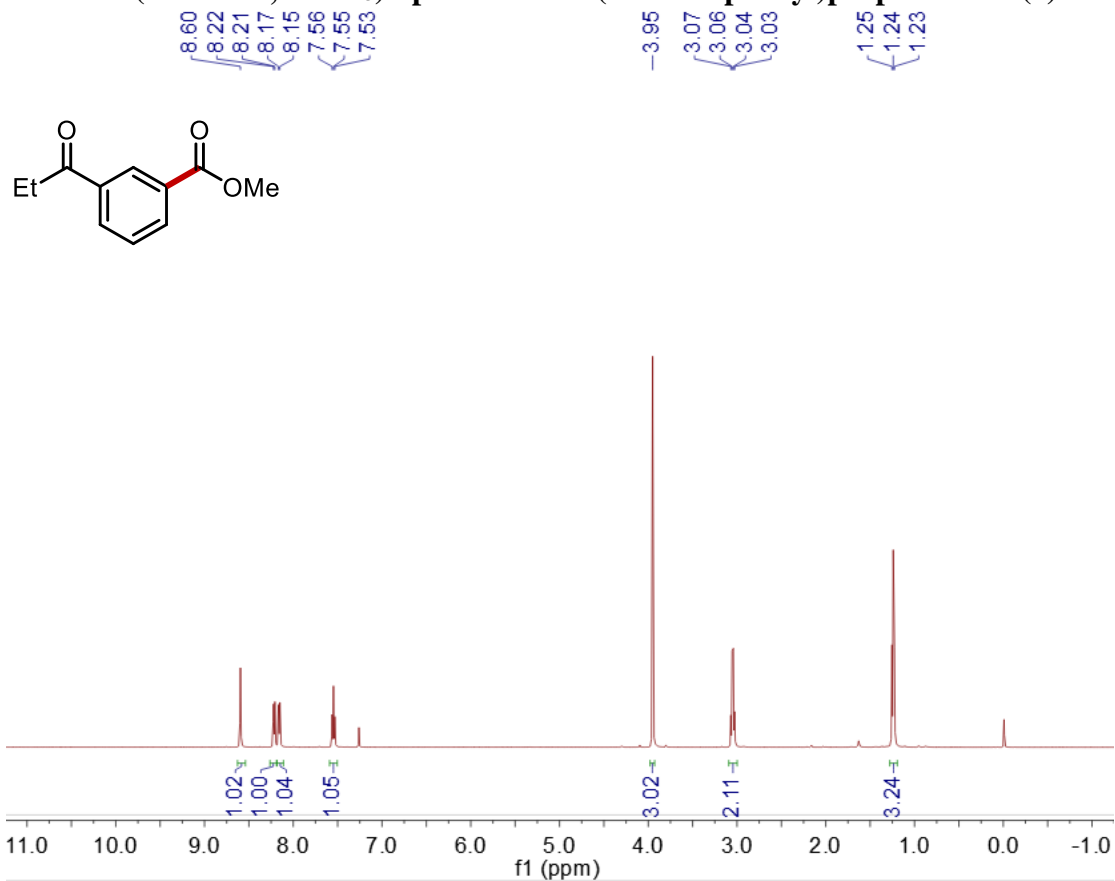
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) Spectrum of Methyl 4-(1,3-dioxolan-2-yl) benzoate (5).**



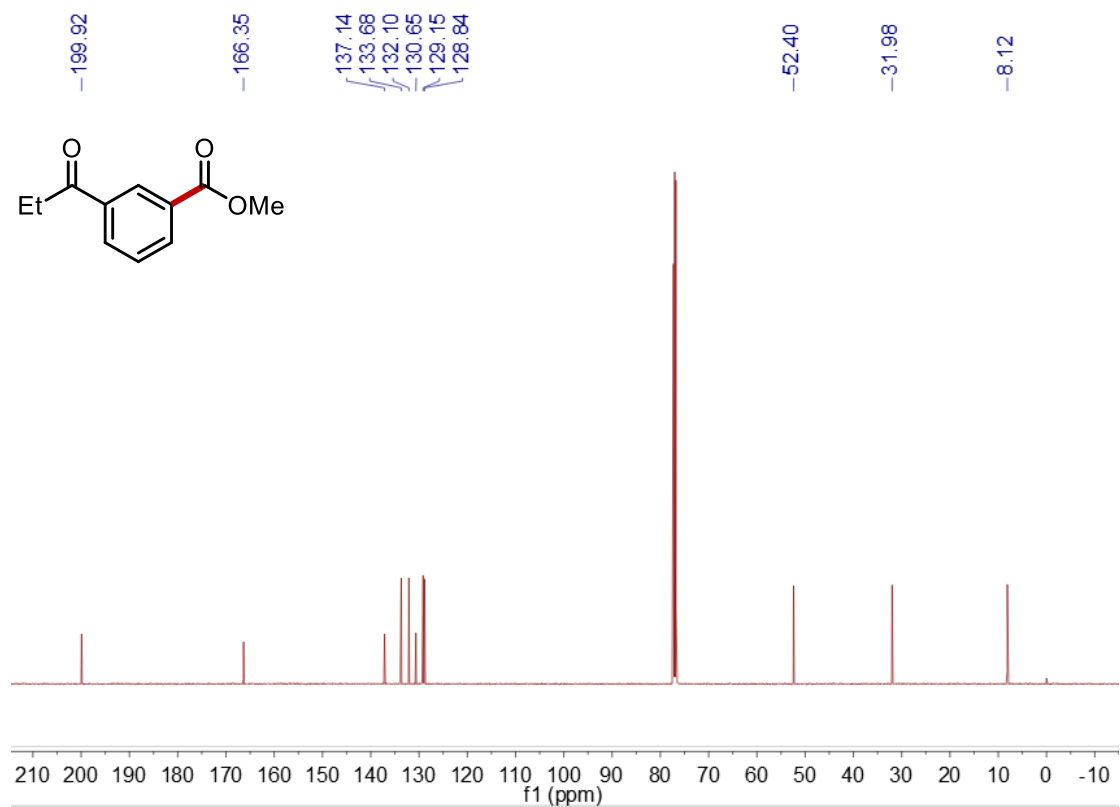
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) Spectrum of Methyl 4-(1,3-dioxolan-2-yl) benzoate (5).**



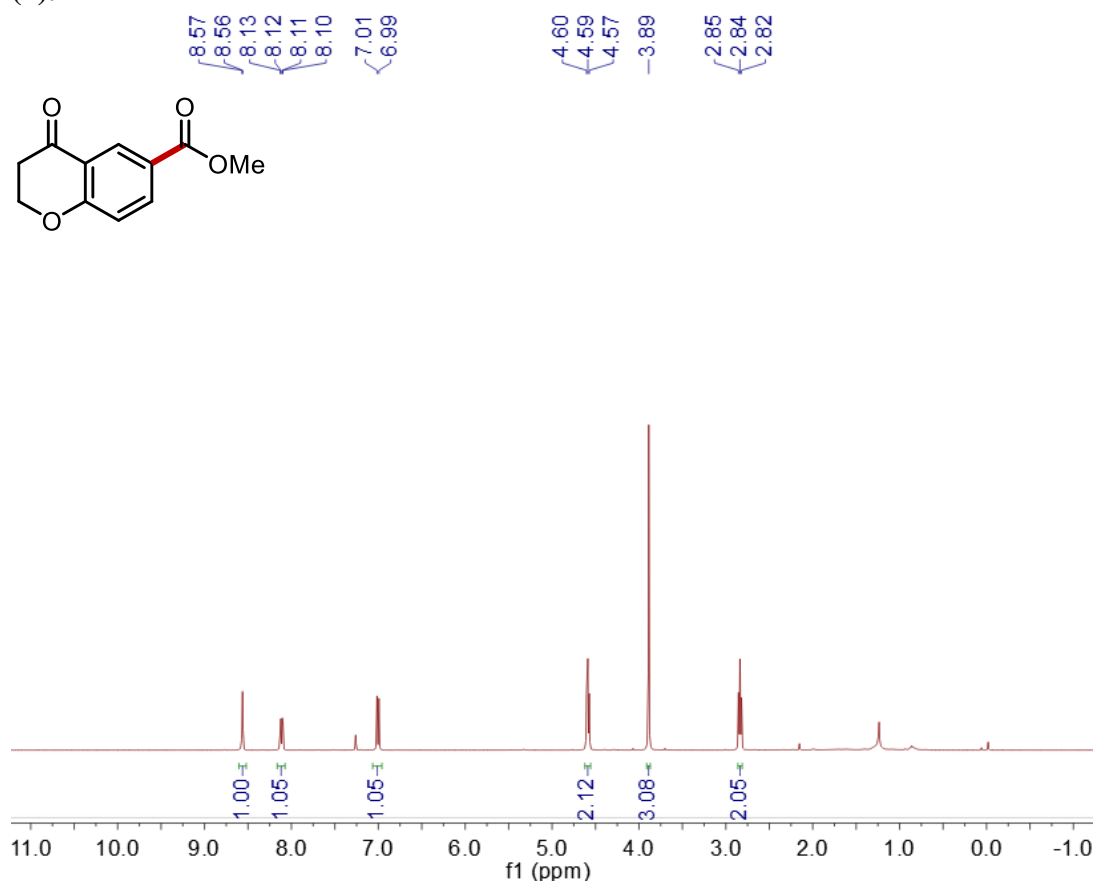
**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) Spectrum of 1-(3-bromophenyl)propan-1-one (6).**



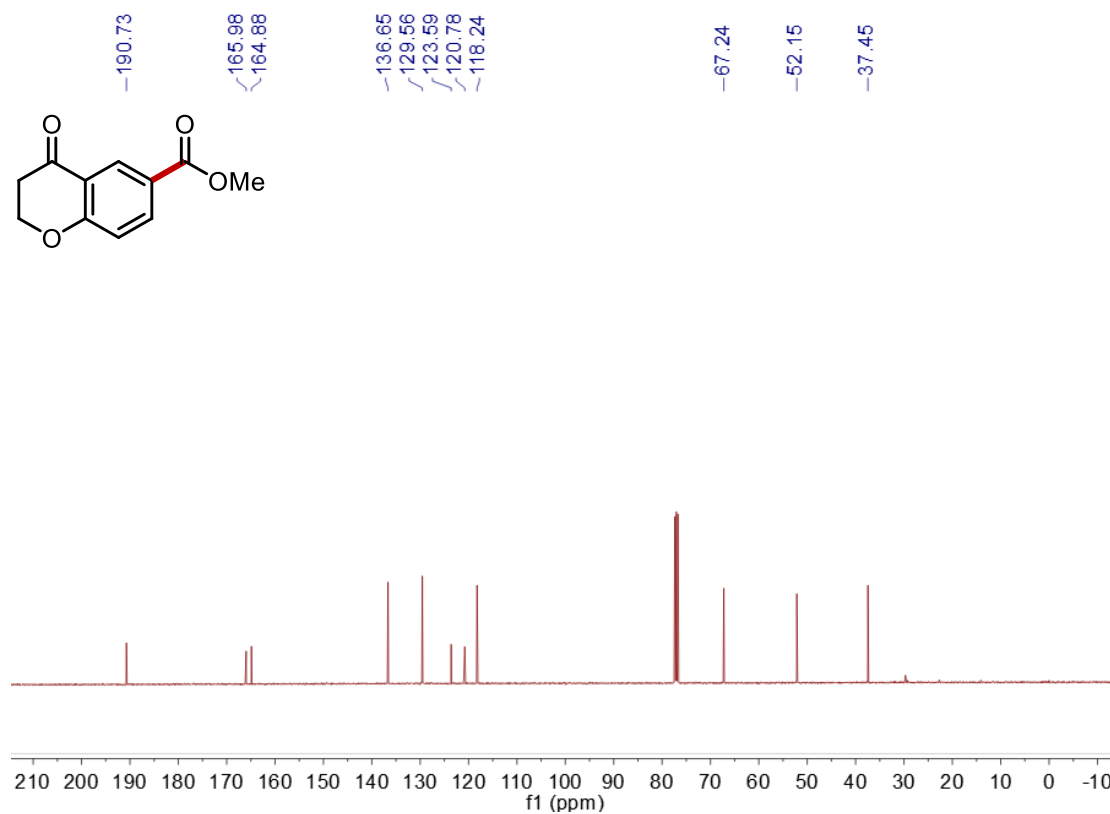
**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) Spectrum of 1-(3-bromophenyl)propan-1-one (6).**



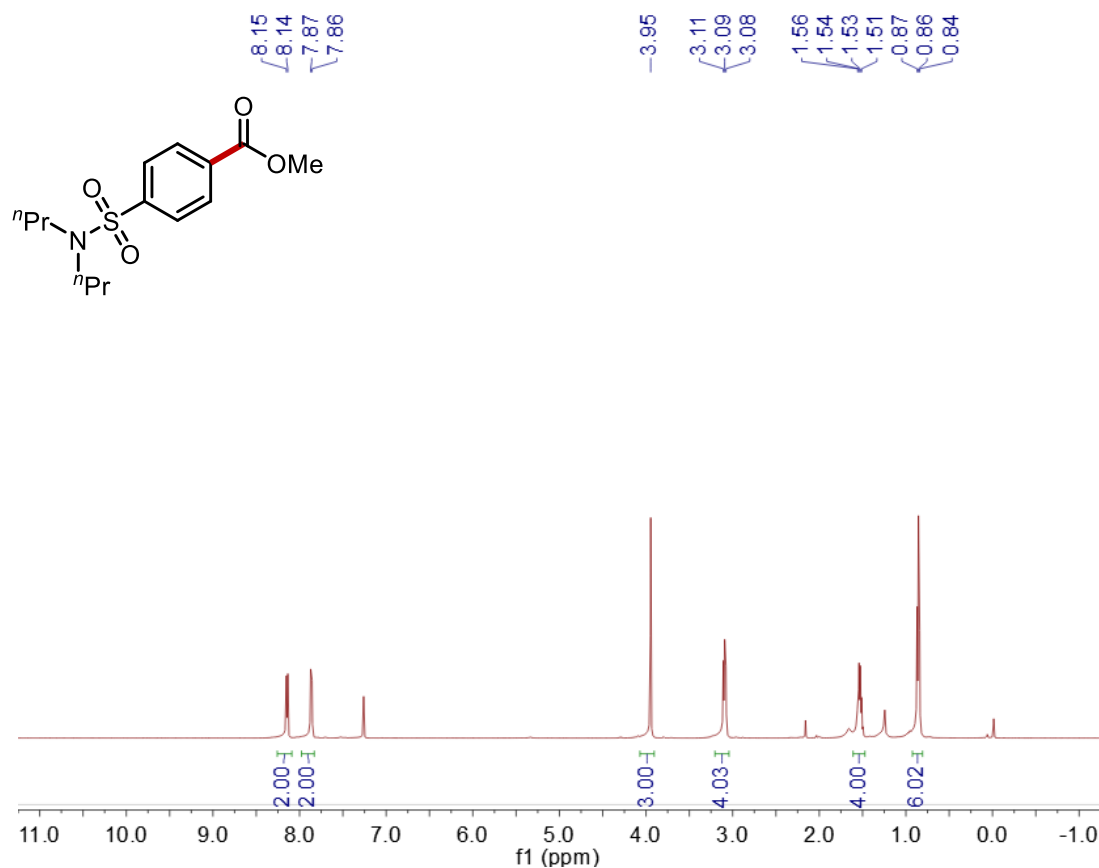
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) Spectrum of Methyl 4-oxochromane-6-carboxylate (7).**



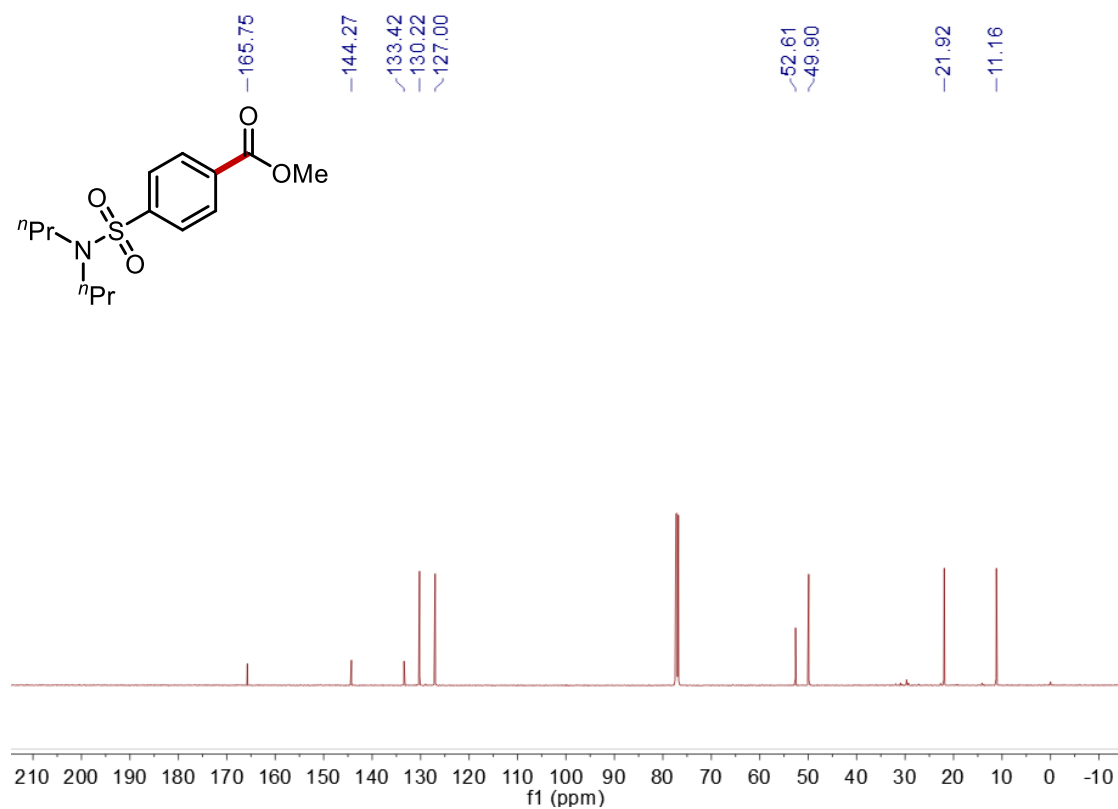
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) Spectrum of Methyl 4-oxochromane-6-carboxylate (7).**



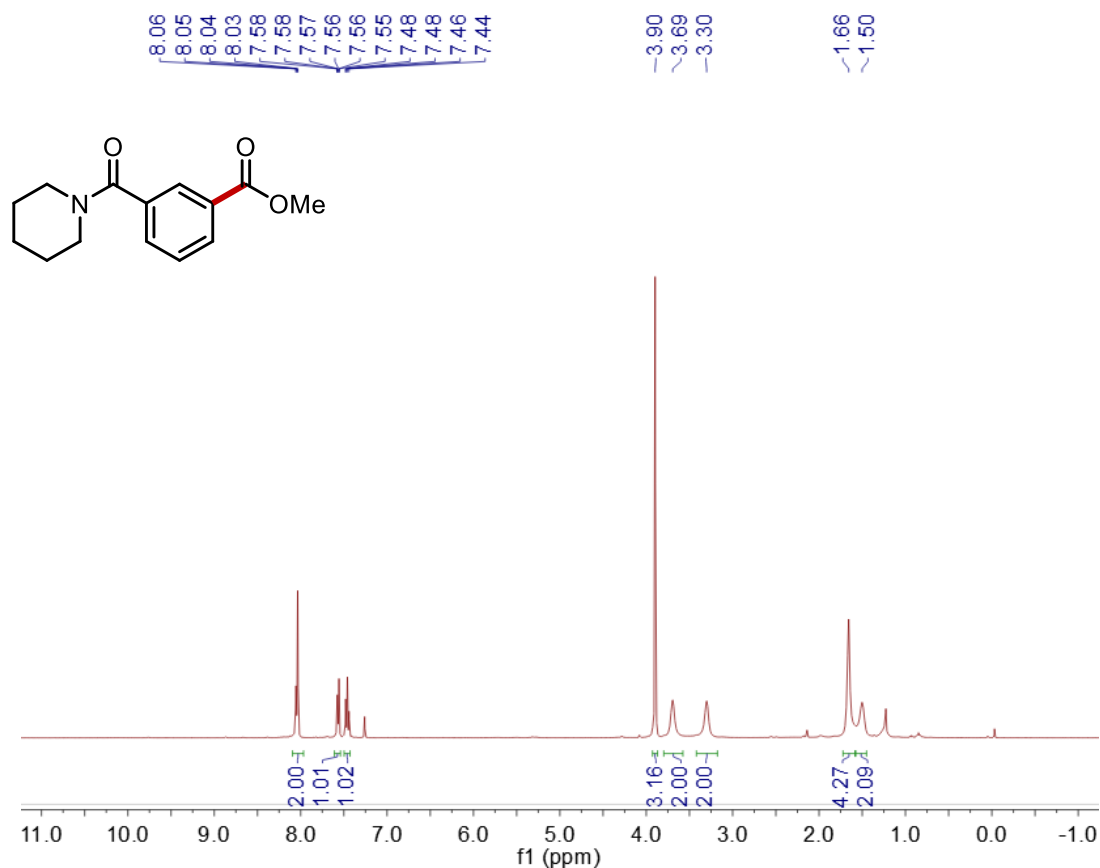
**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) Spectrum of Methyl 4-(*N,N*-dipropyl sulfamoyl) benzoate (8).**



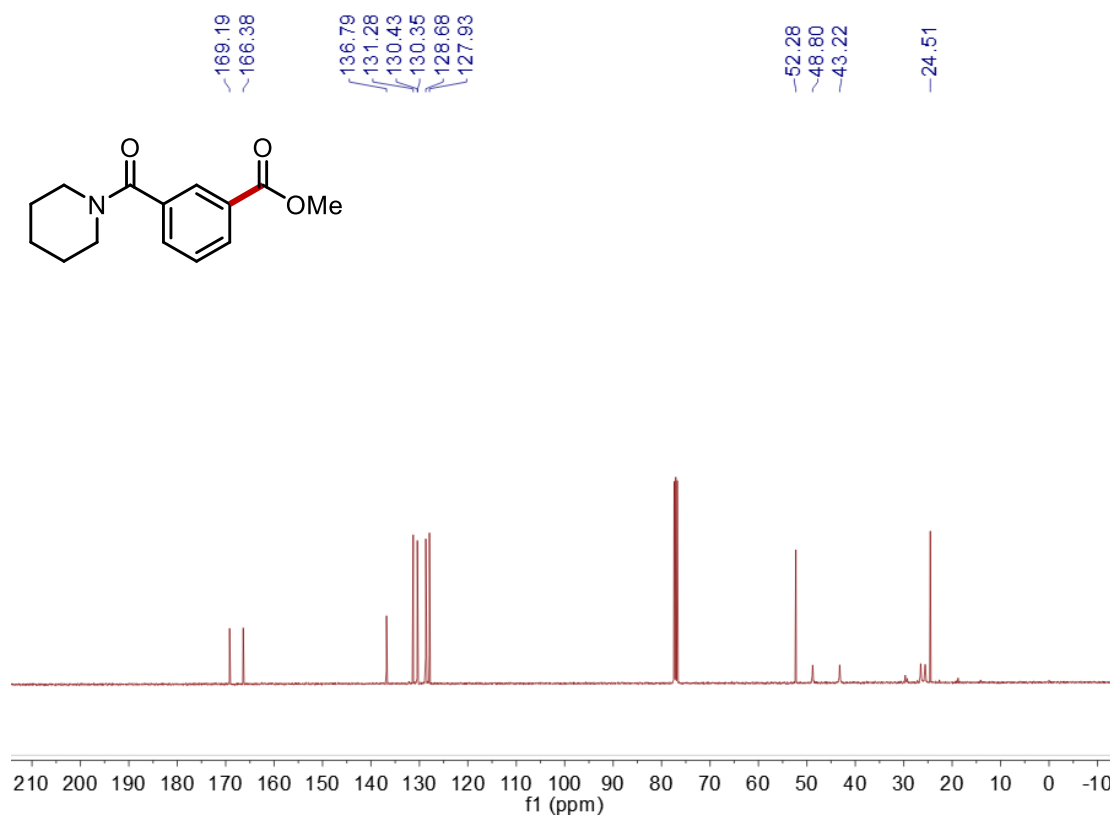
**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) Spectrum of Methyl 4-(*N,N*-dipropyl sulfamoyl) benzoate (8).**



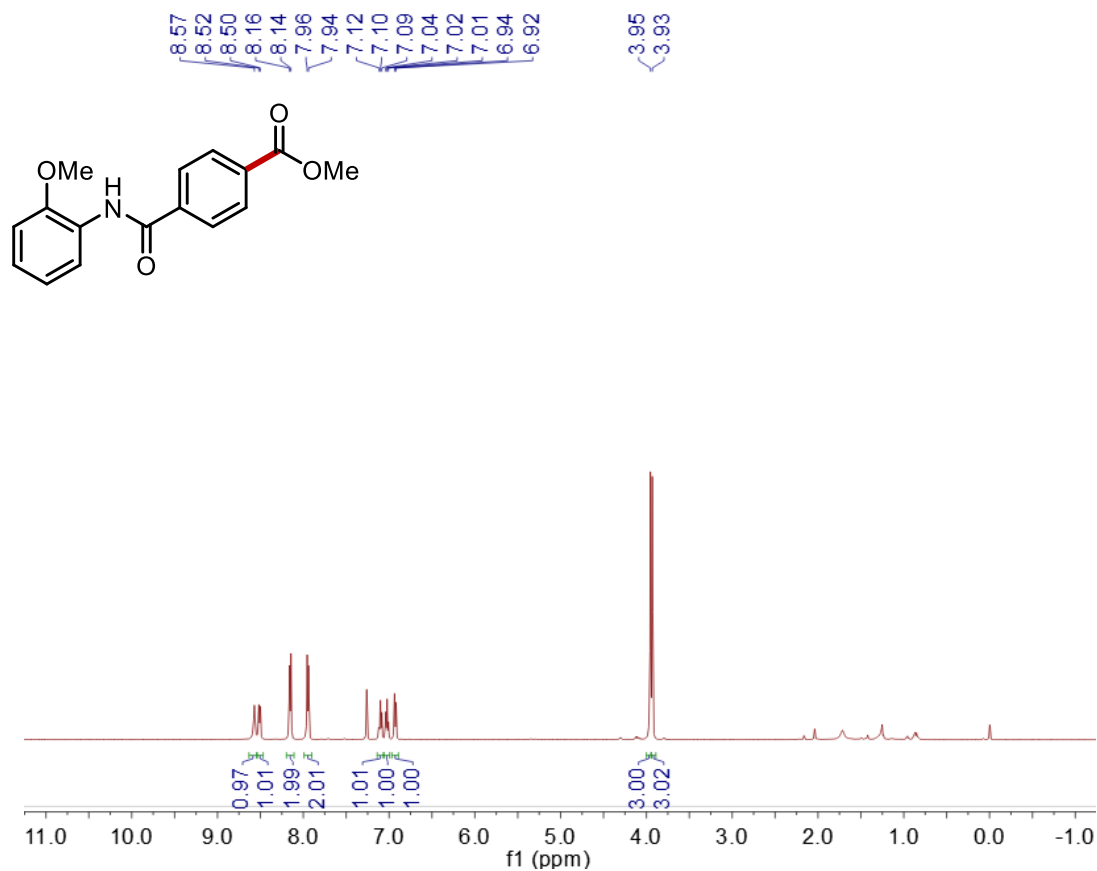
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) Spectrum of Methyl 3-(piperidine-1-carbonyl)benzoate (9).**



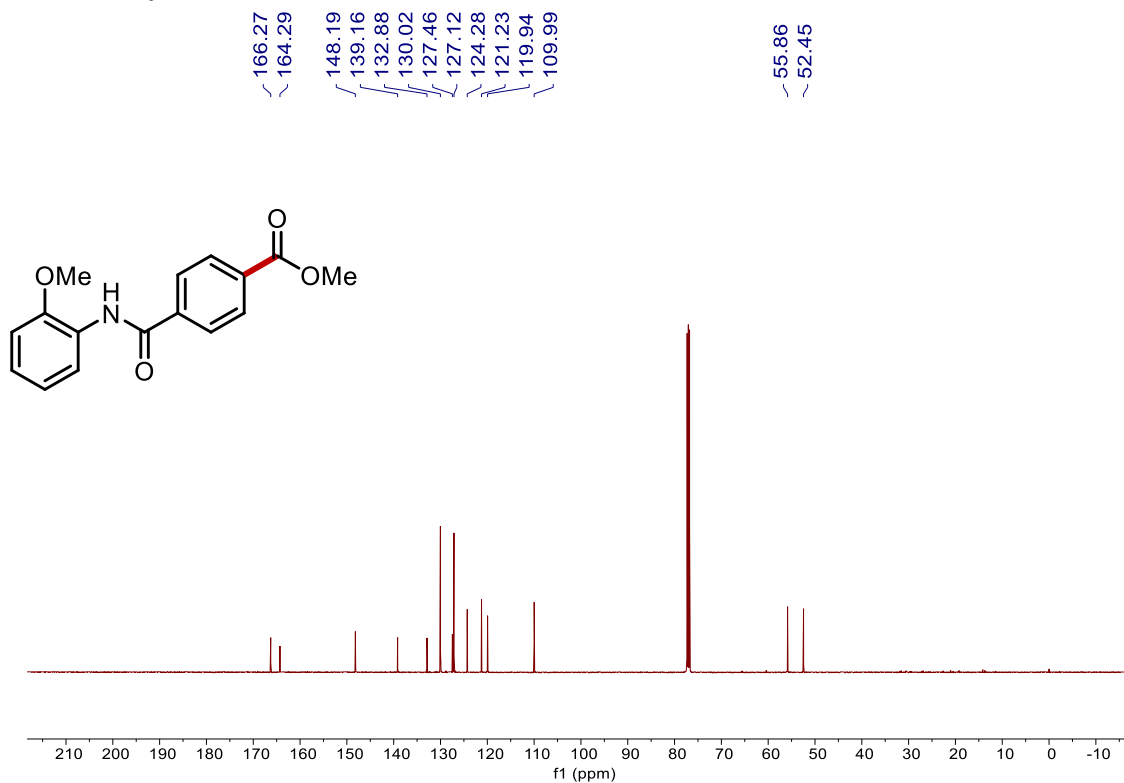
**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) Spectrum of Methyl 3-(piperidine-1-carbonyl)benzoate (9).**



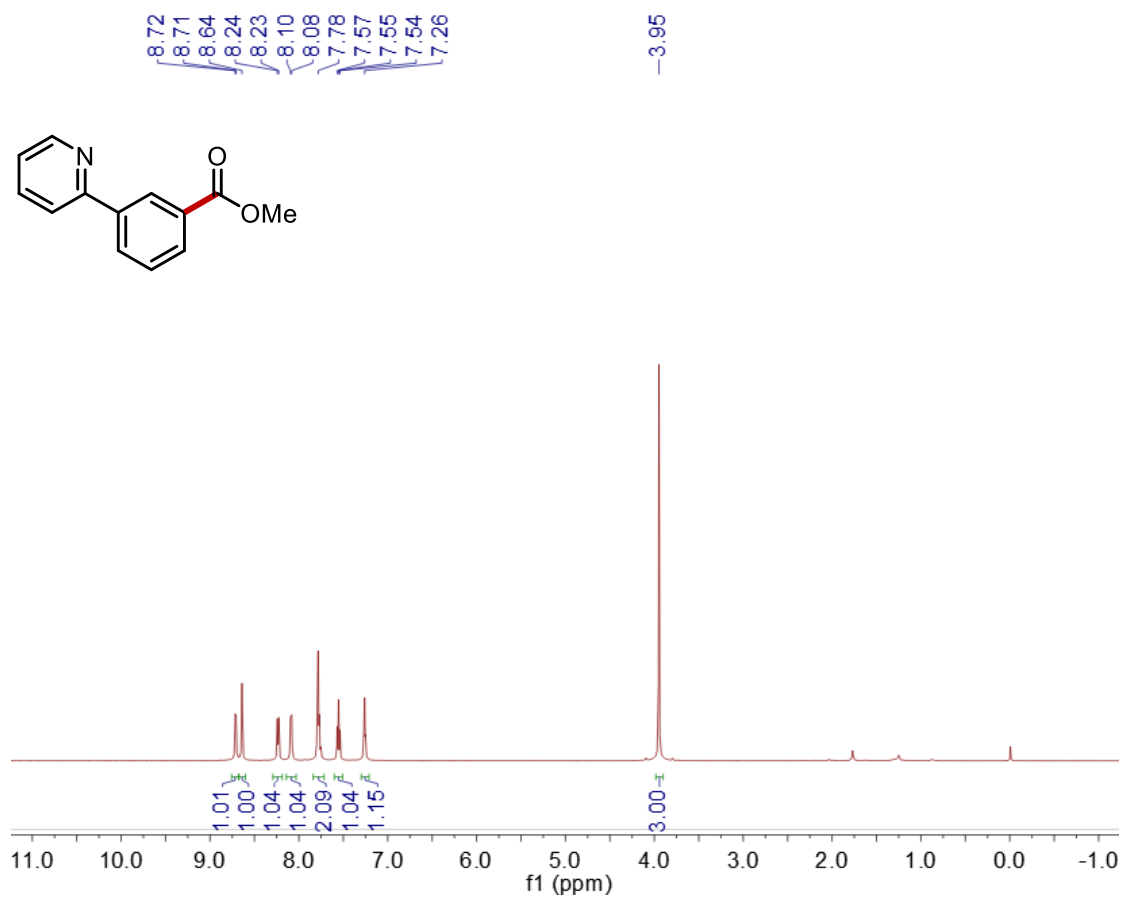
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum of Methyl 4-[(2-methoxyphenyl) carbamoyl] benzoate (10).**



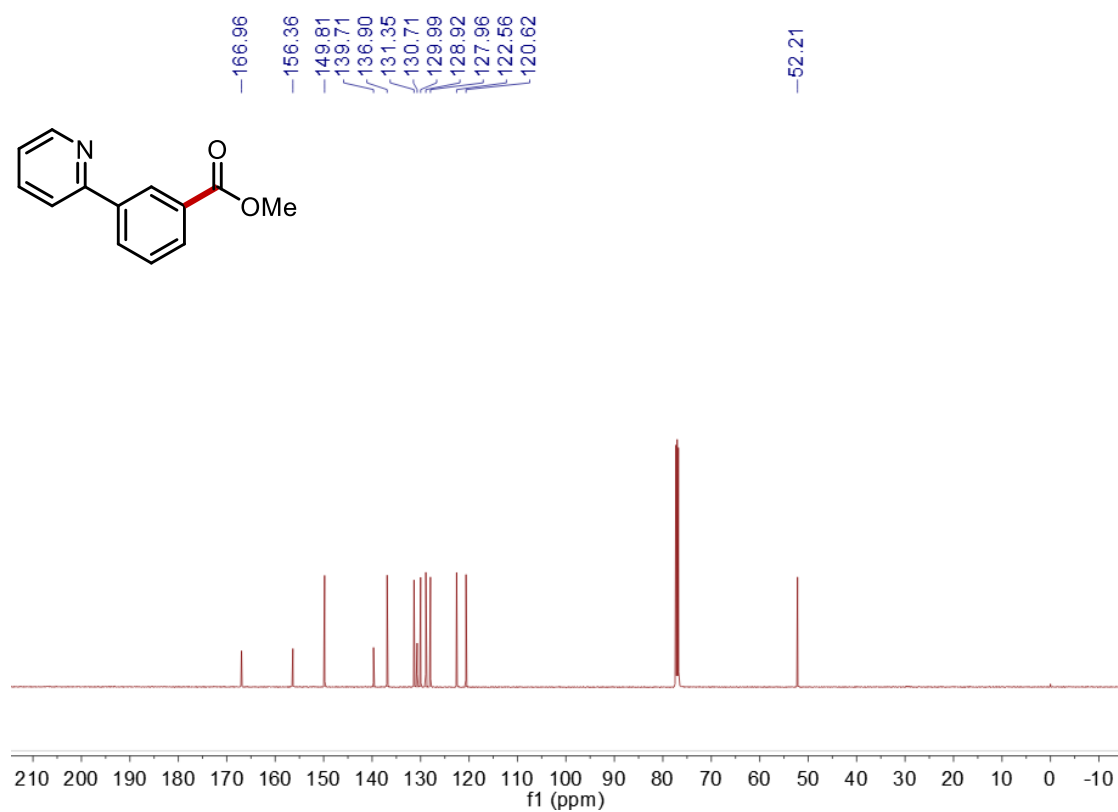
**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) Spectrum of Methyl 4-[(2-methoxyphenyl) carbamoyl] benzoate (10).**



**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum of Methyl 3-(pyridin-2-yl) benzoate (11).**

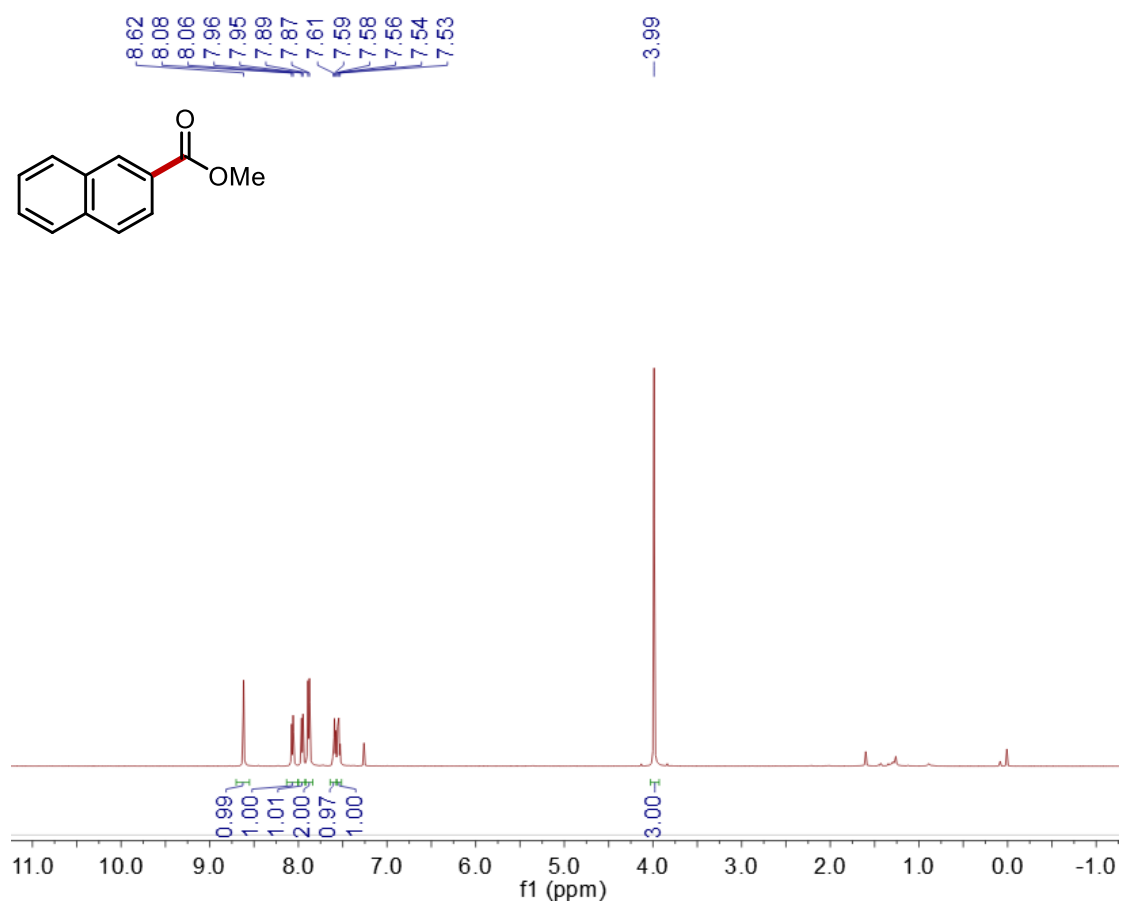


**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) Spectrum of Methyl 3-(pyridin-2-yl) benzoate (11).**

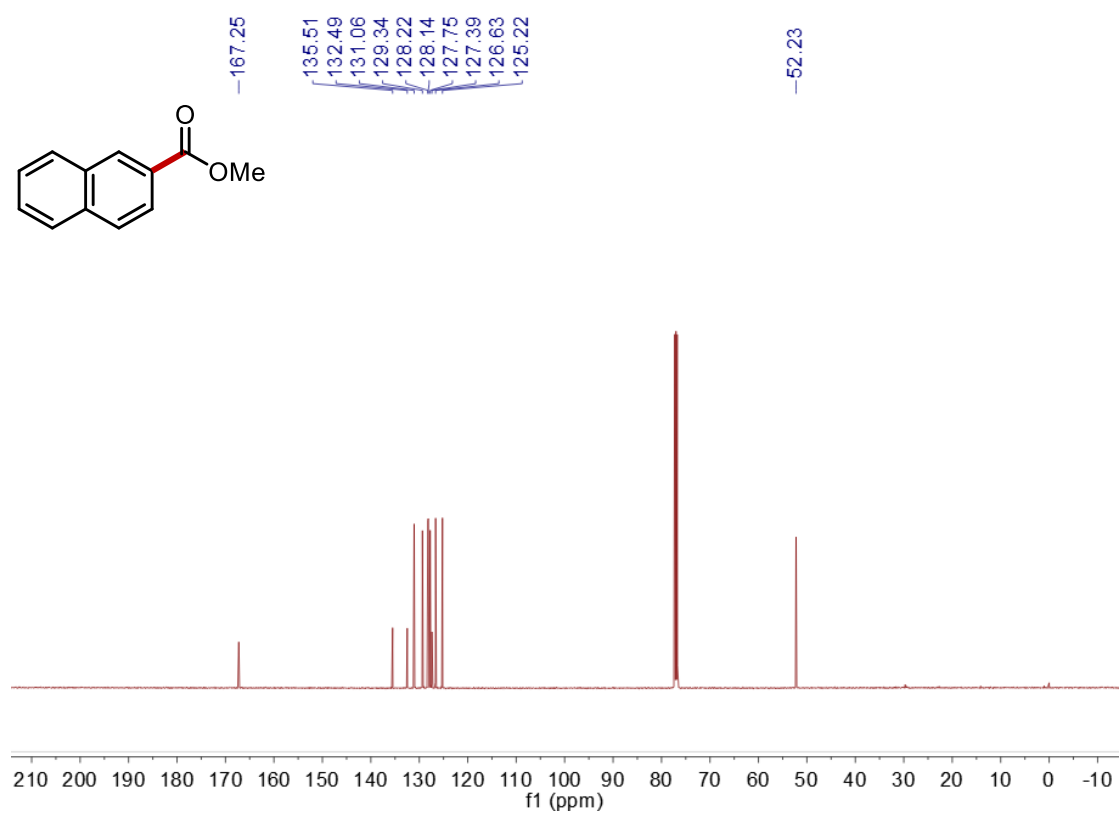




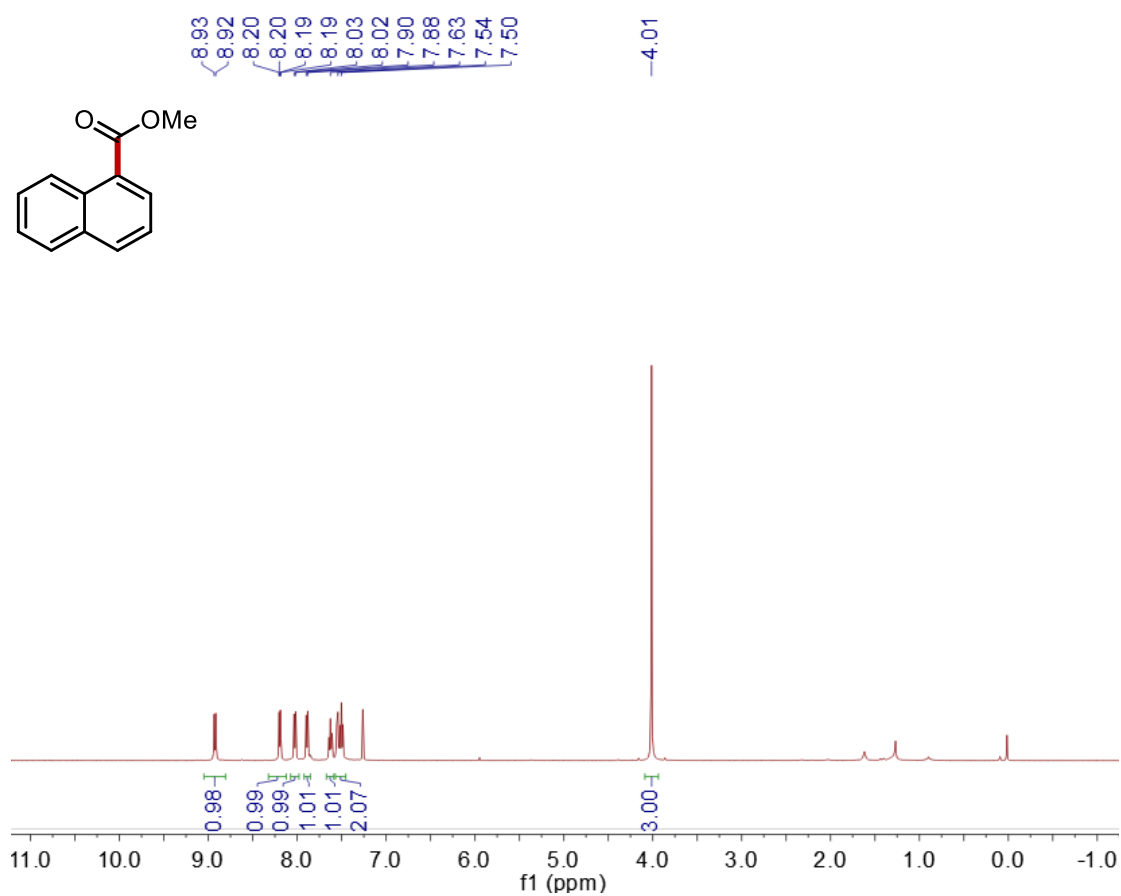
**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) Spectrum of Methyl 2-naphthoate (12).**



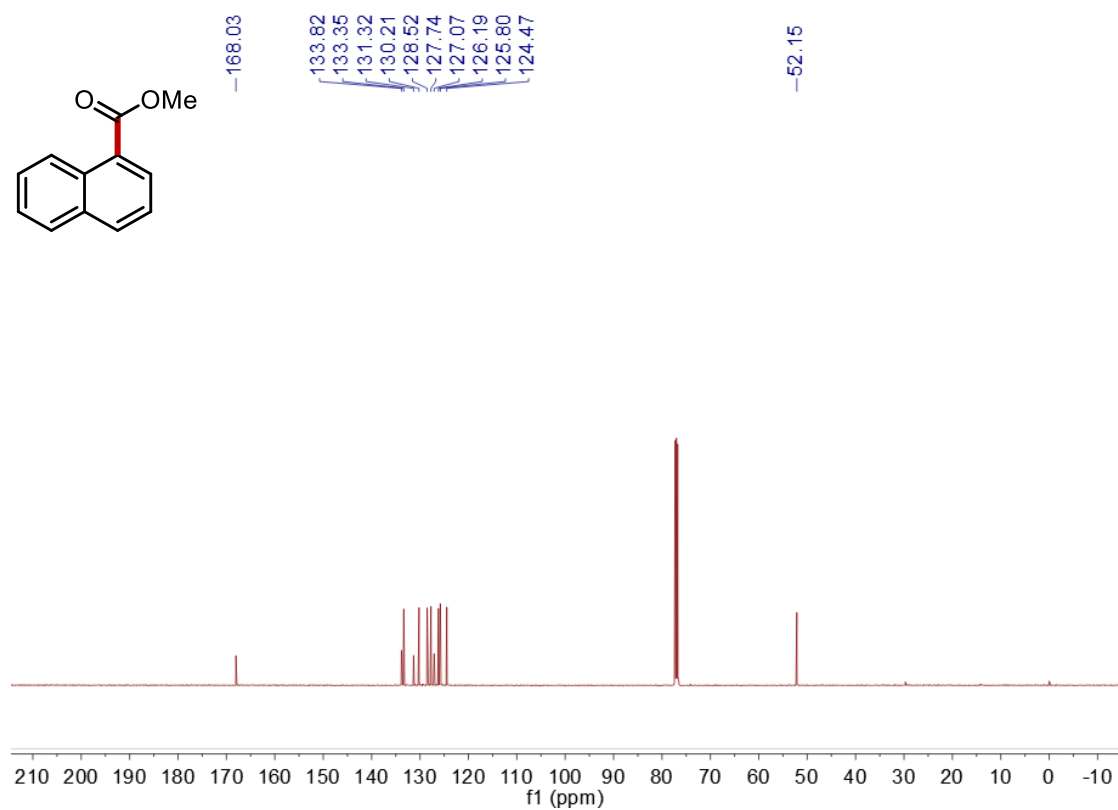
**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) Spectrum of Methyl 2-naphthoate (12).**



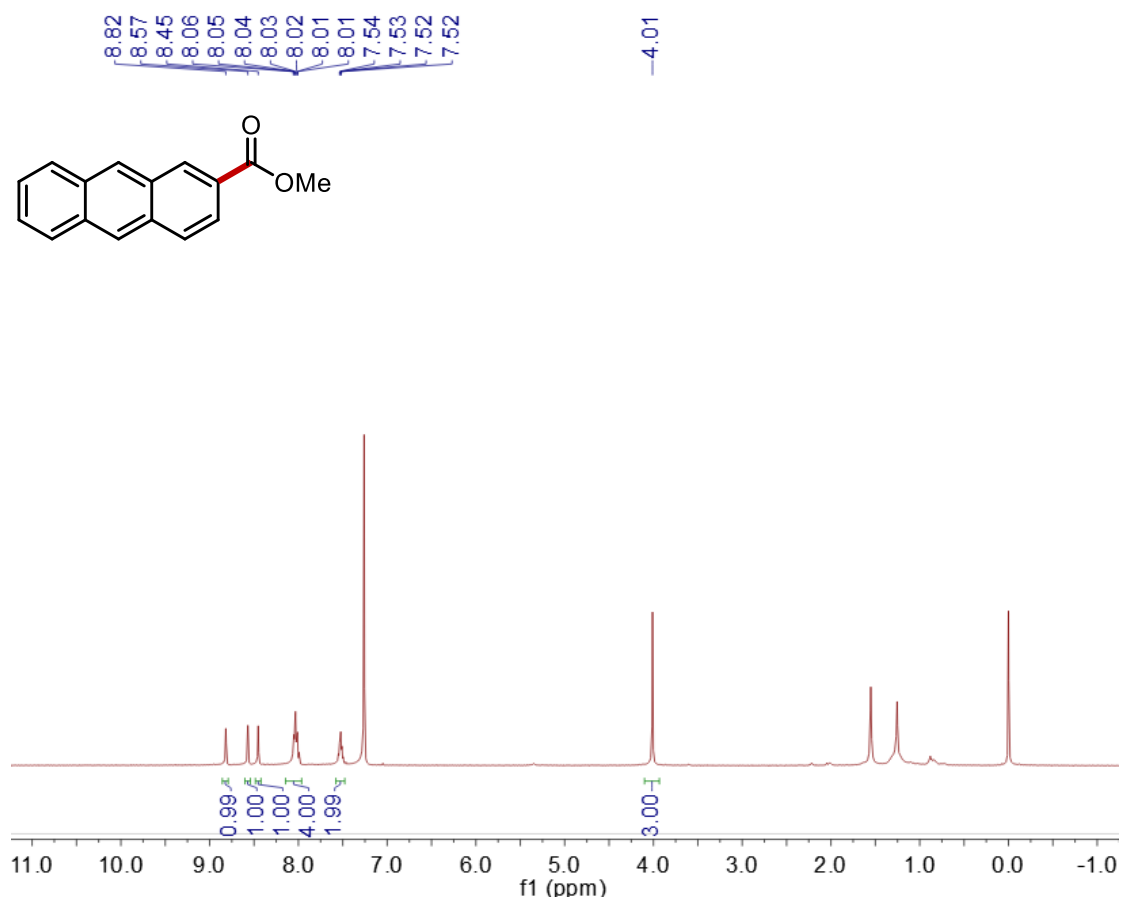
**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) Spectrum of Methyl 1-naphthoate (13).**



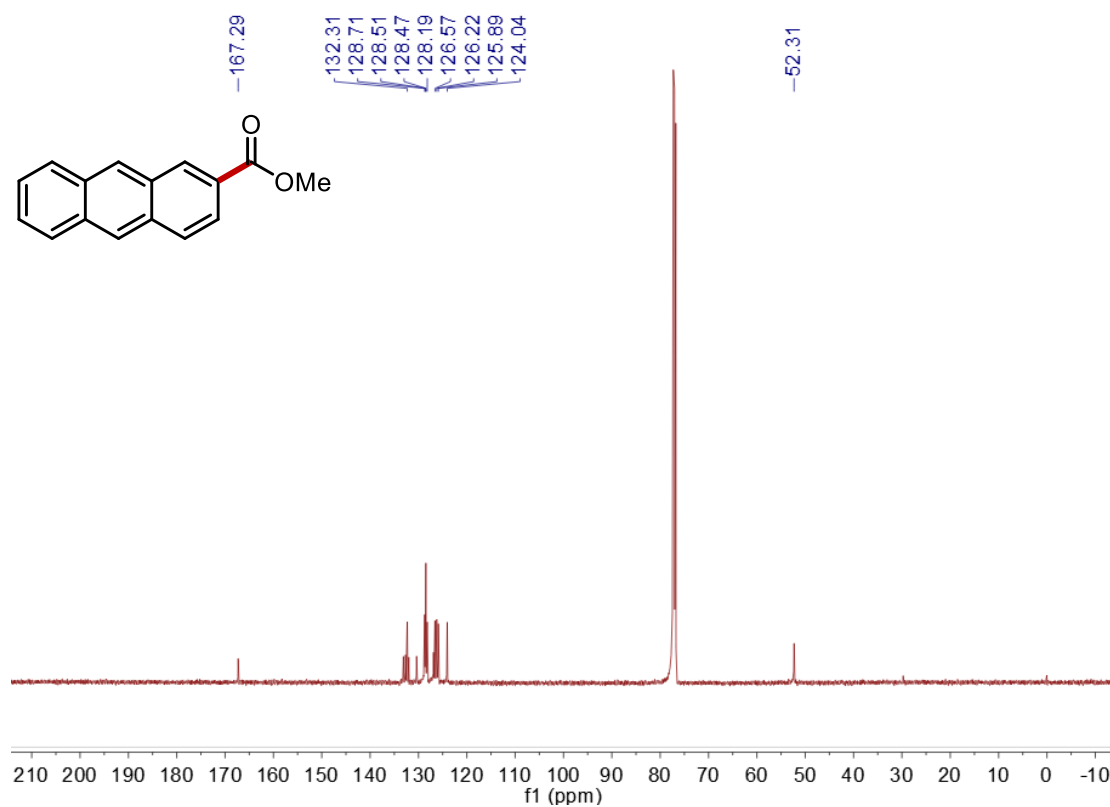
**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) Spectrum of Methyl 1-naphthoate (13).**



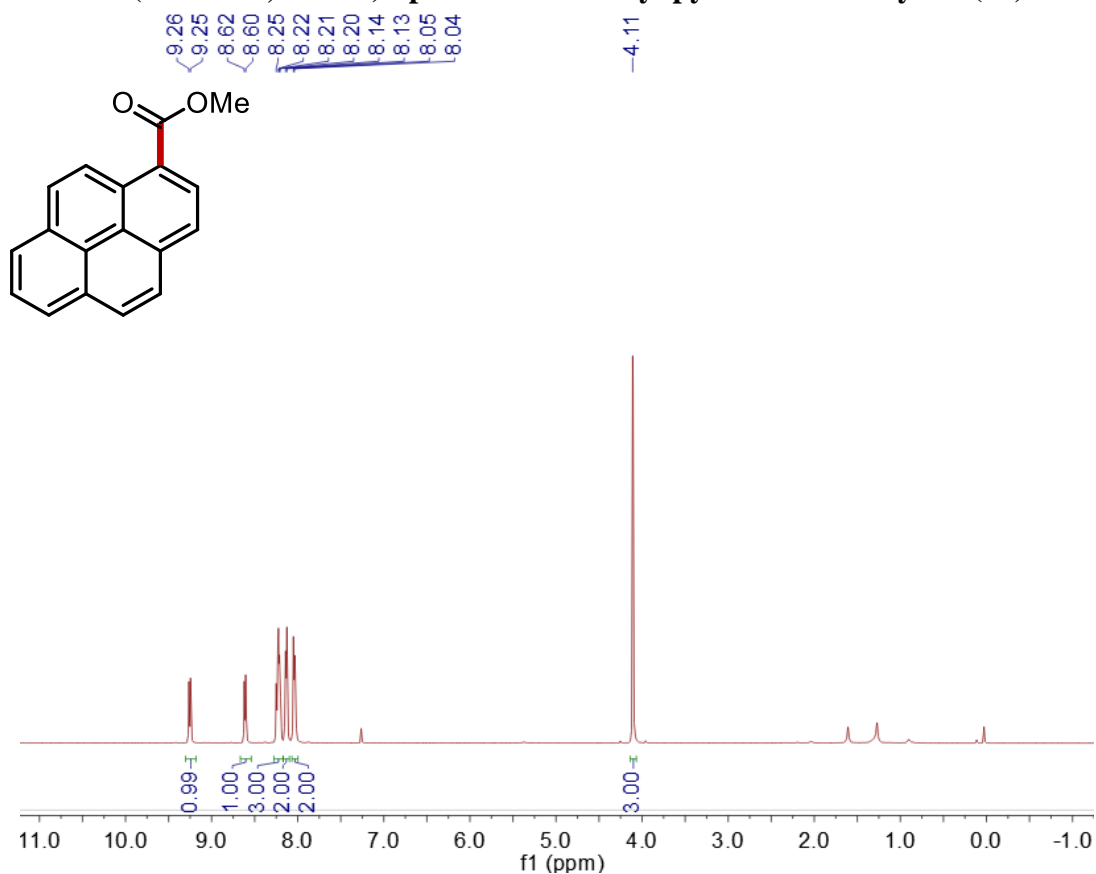
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum of Methyl anthracene-2-carboxylate (14).**



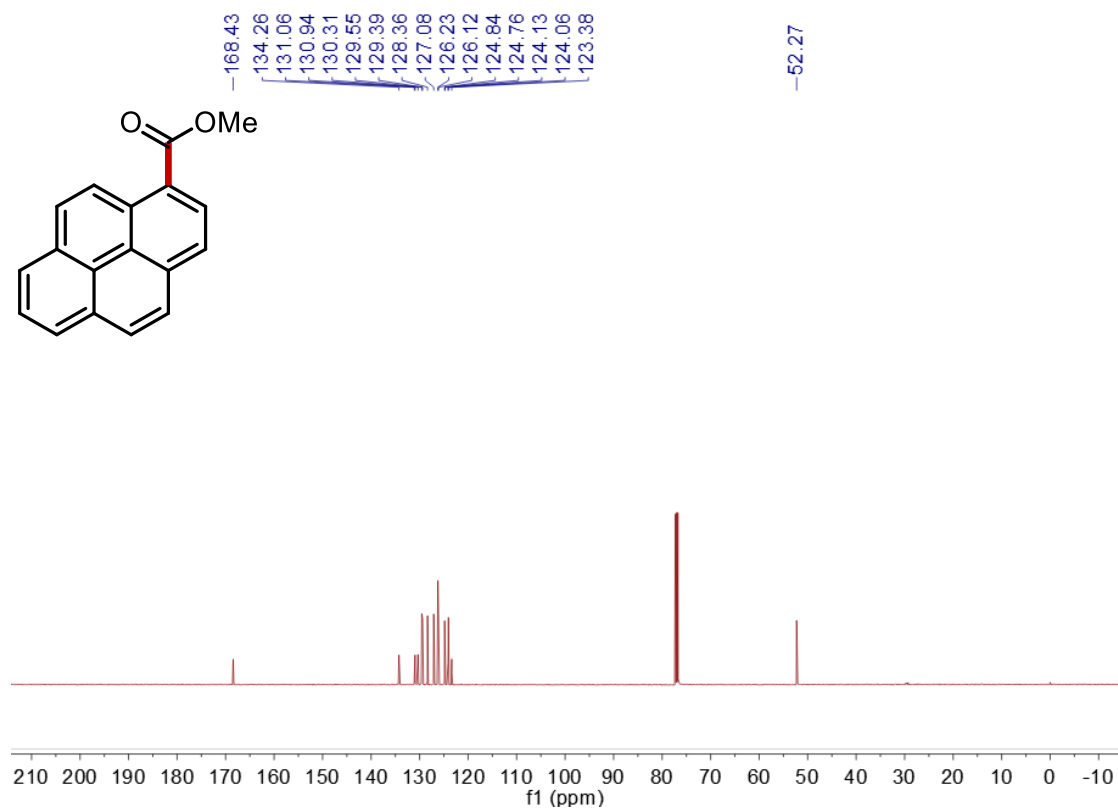
**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) Spectrum of Methyl anthracene-2-carboxylate (14).**



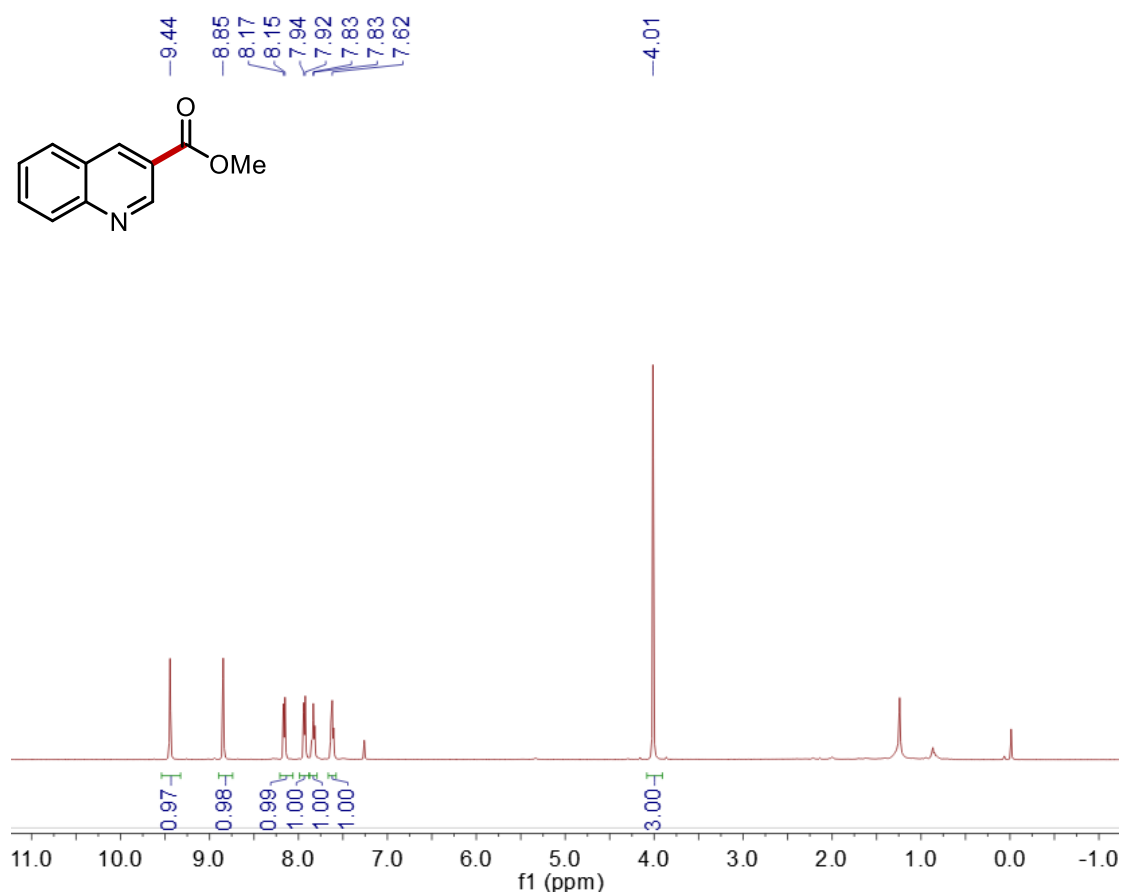
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum of Methyl pyrene-1-carboxylate (15).**



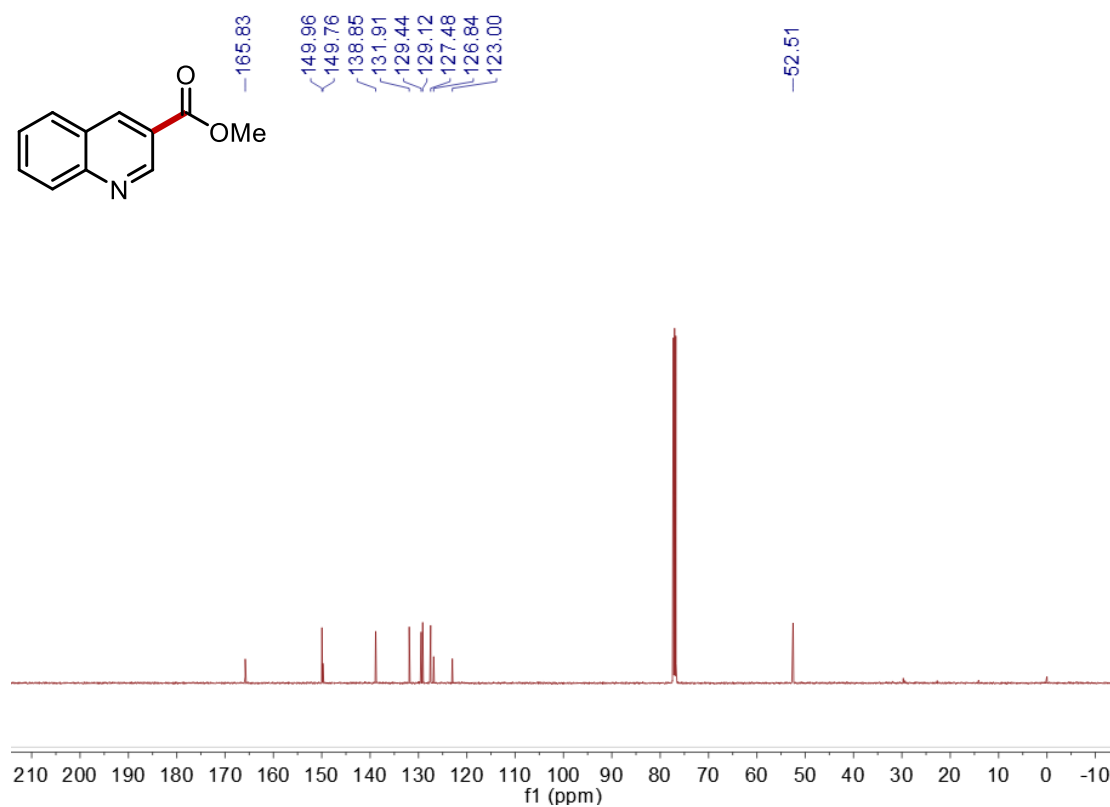
**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) Spectrum of Methyl pyrene-1-carboxylate (15).**



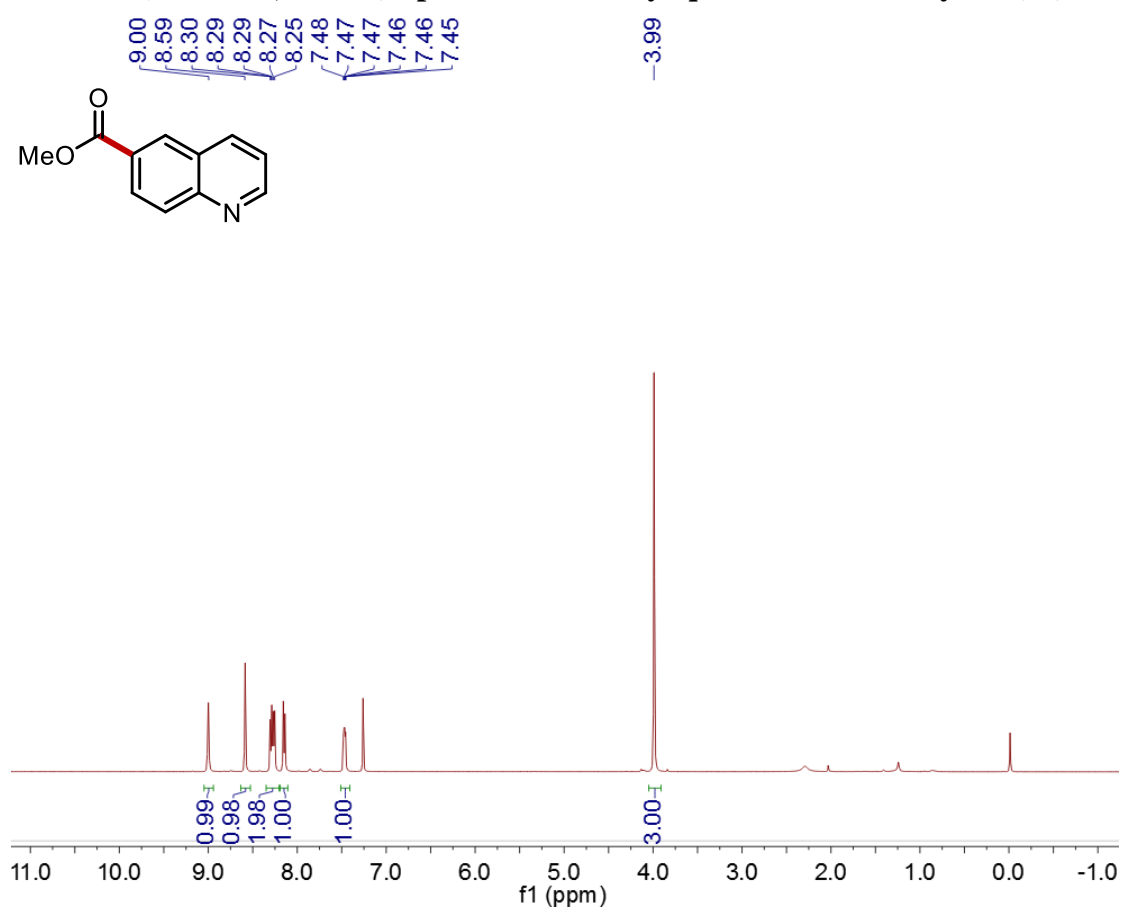
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum of Methyl quinoline-3-carboxylate (16).**



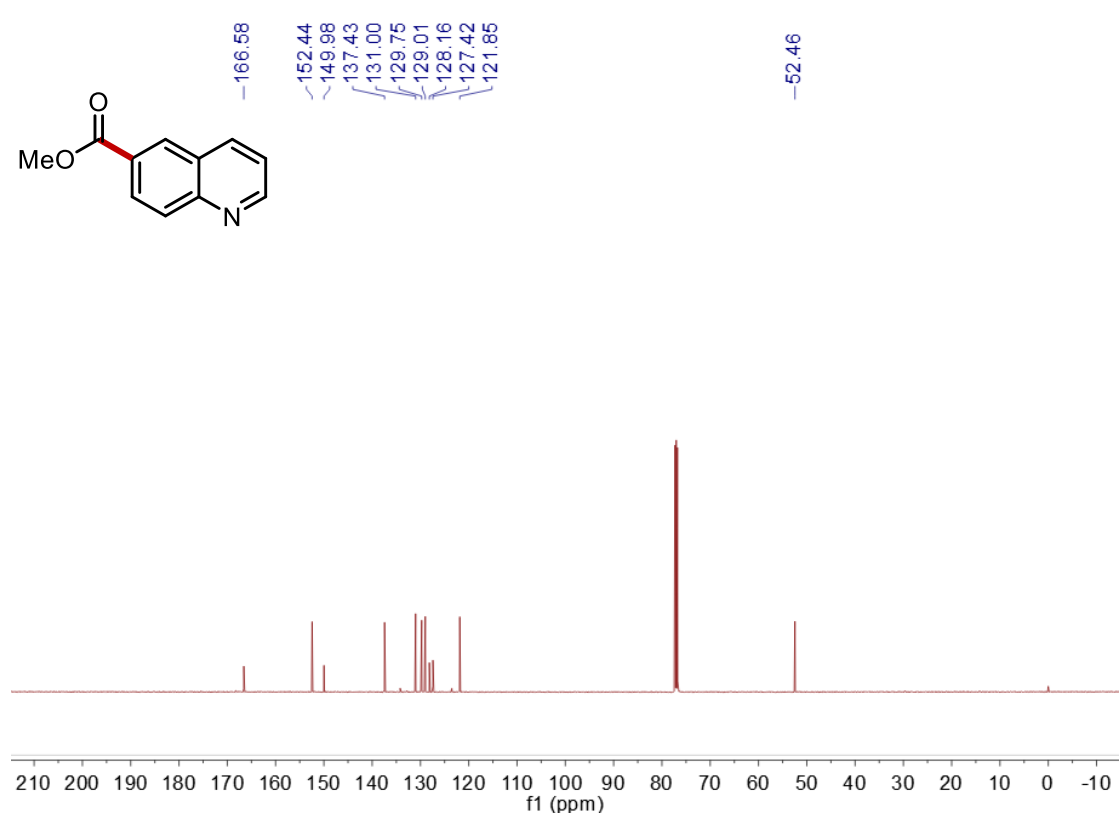
**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) Spectrum of Methyl quinoline-3-carboxylate (16).**



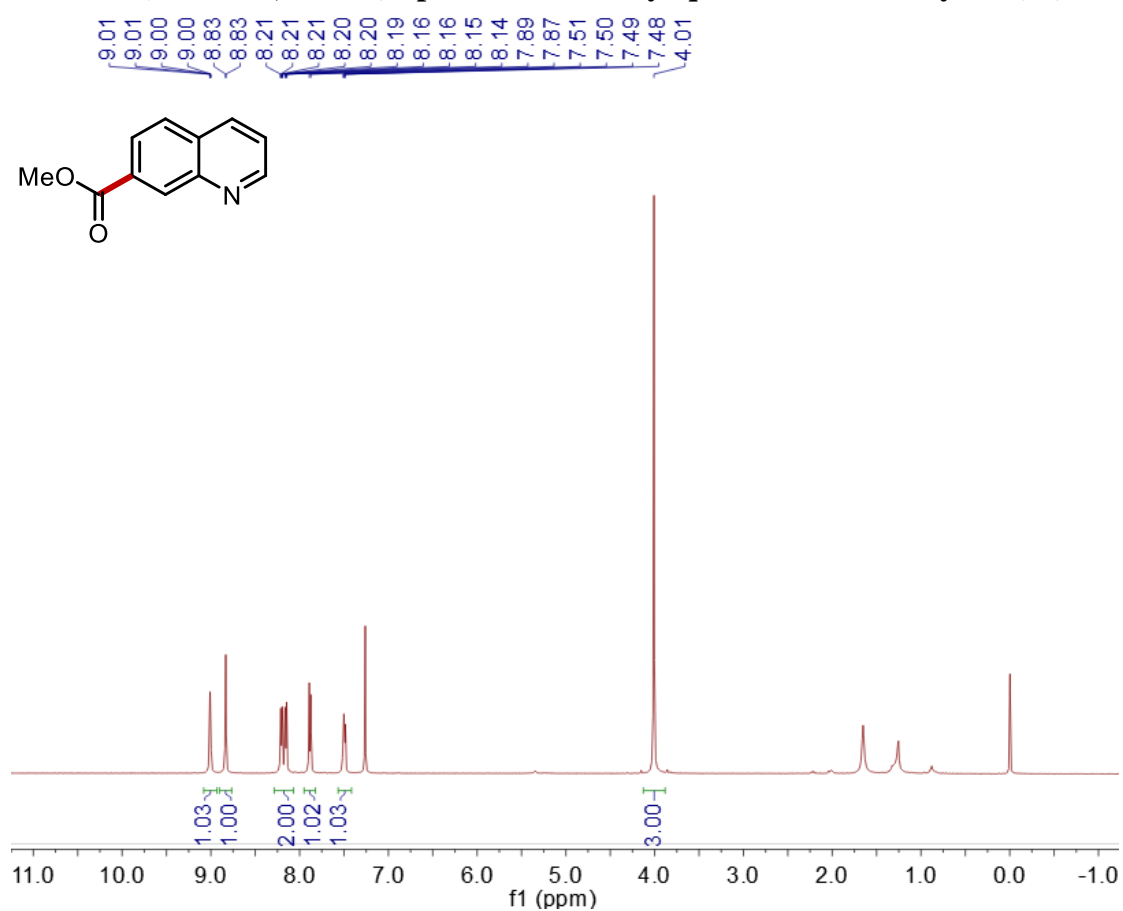
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum of Methyl quinoline-6-carboxylate (17).**



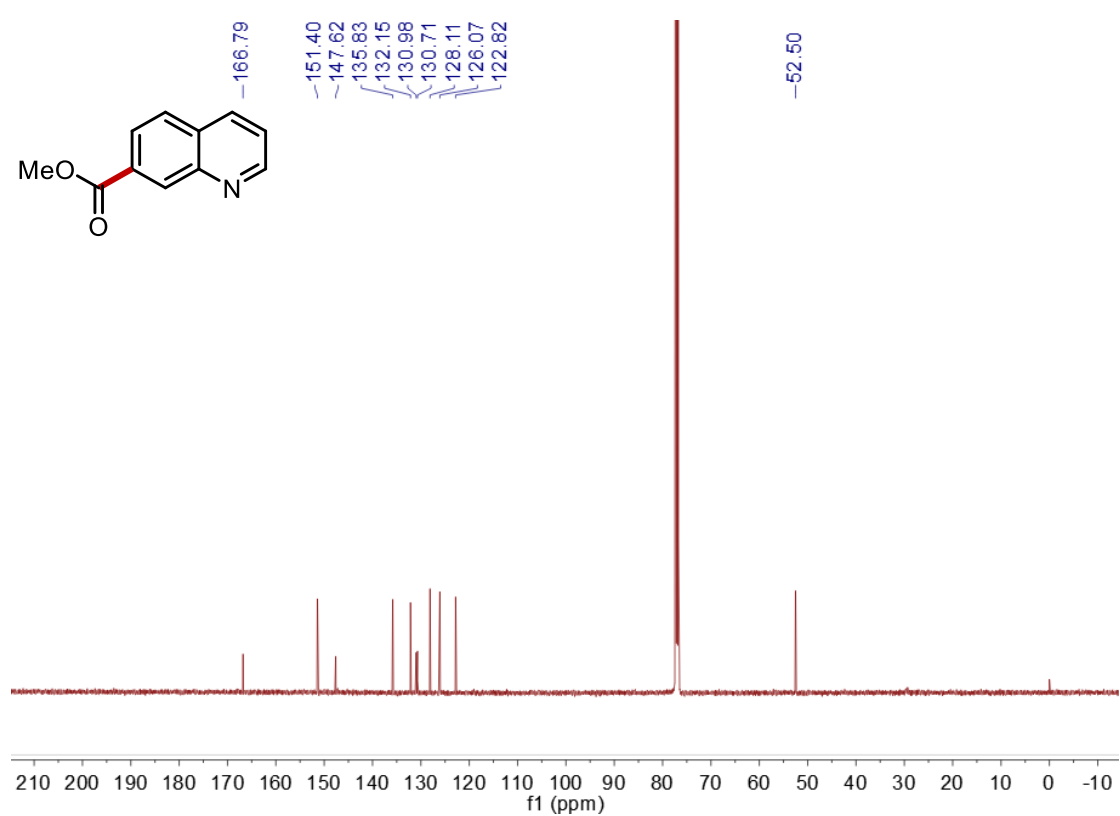
**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) Spectrum of Methyl quinoline-6-carboxylate (17).**



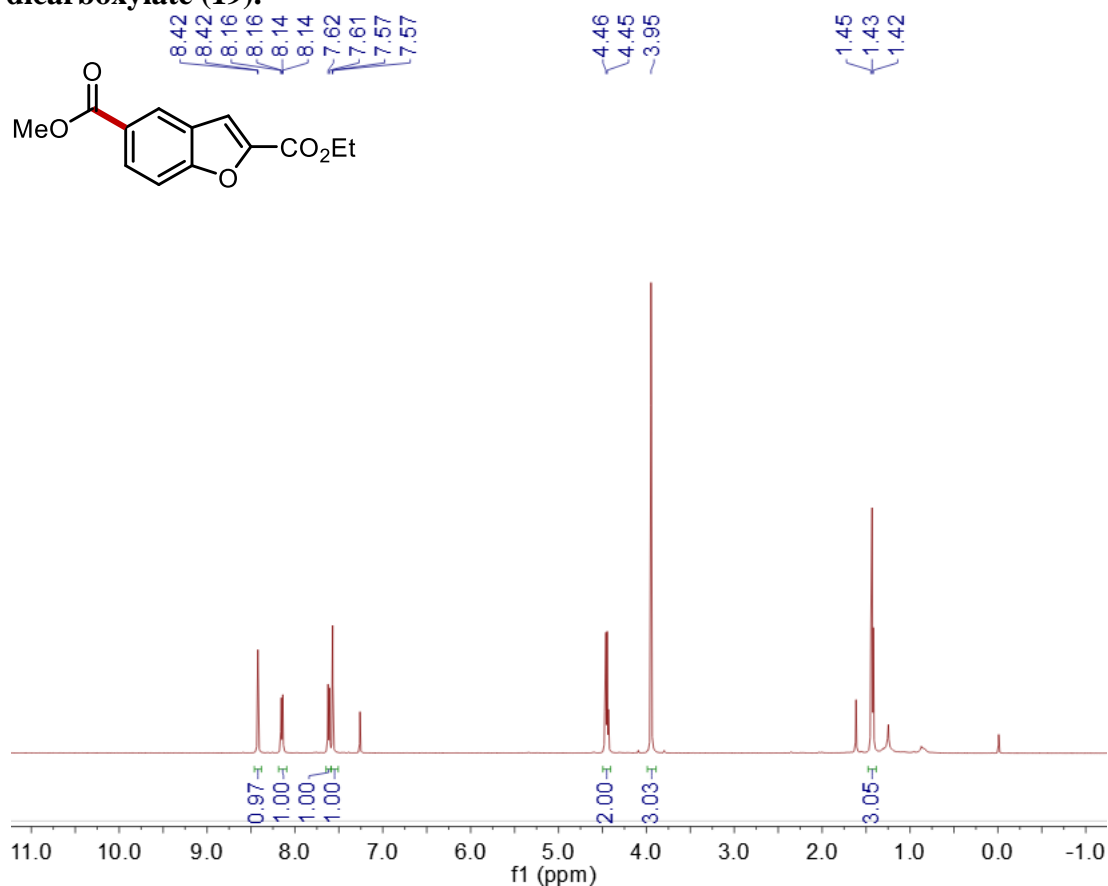
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum of Methyl quinoline-7-carboxylate (18).**



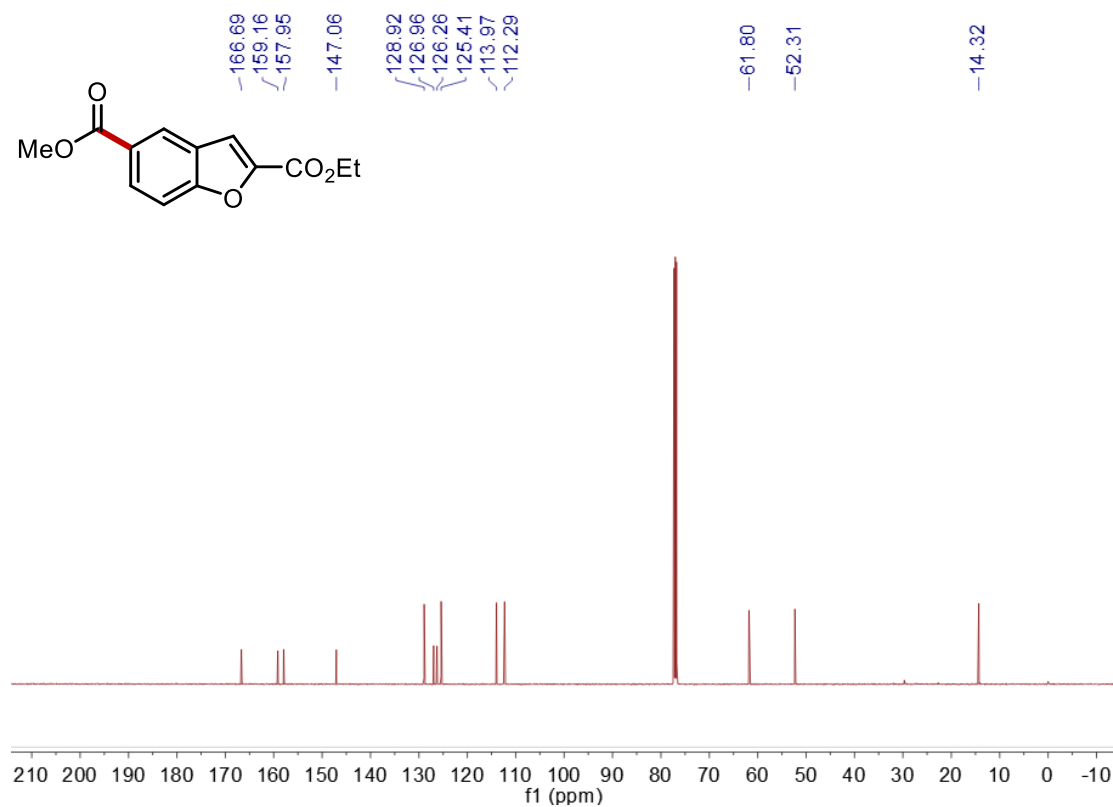
**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) Spectrum of Methyl quinoline-7-carboxylate (18).**



**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) Spectrum of 2-ethyl 5-methyl benzofuran-2,5-dicarboxylate (19).**

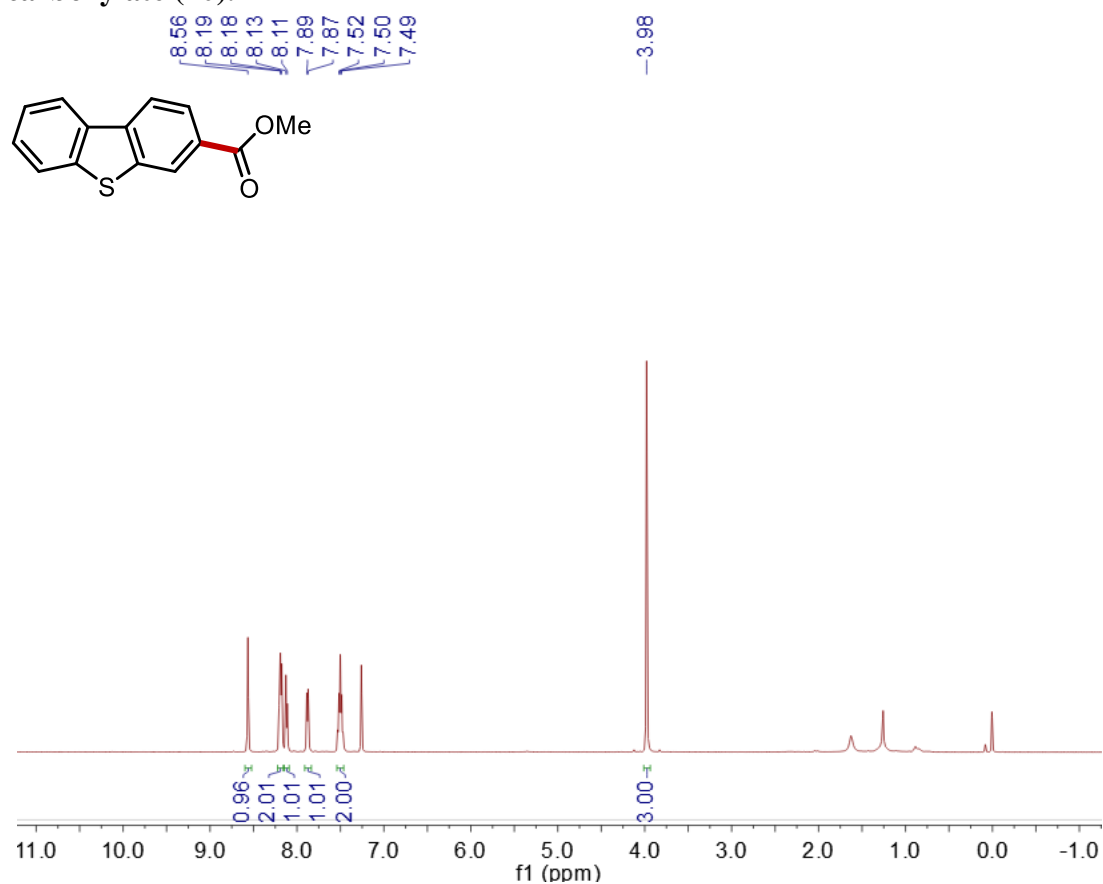


**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) Spectrum of 2-ethyl 5-methyl benzofuran-2,5-dicarboxylate (19).**

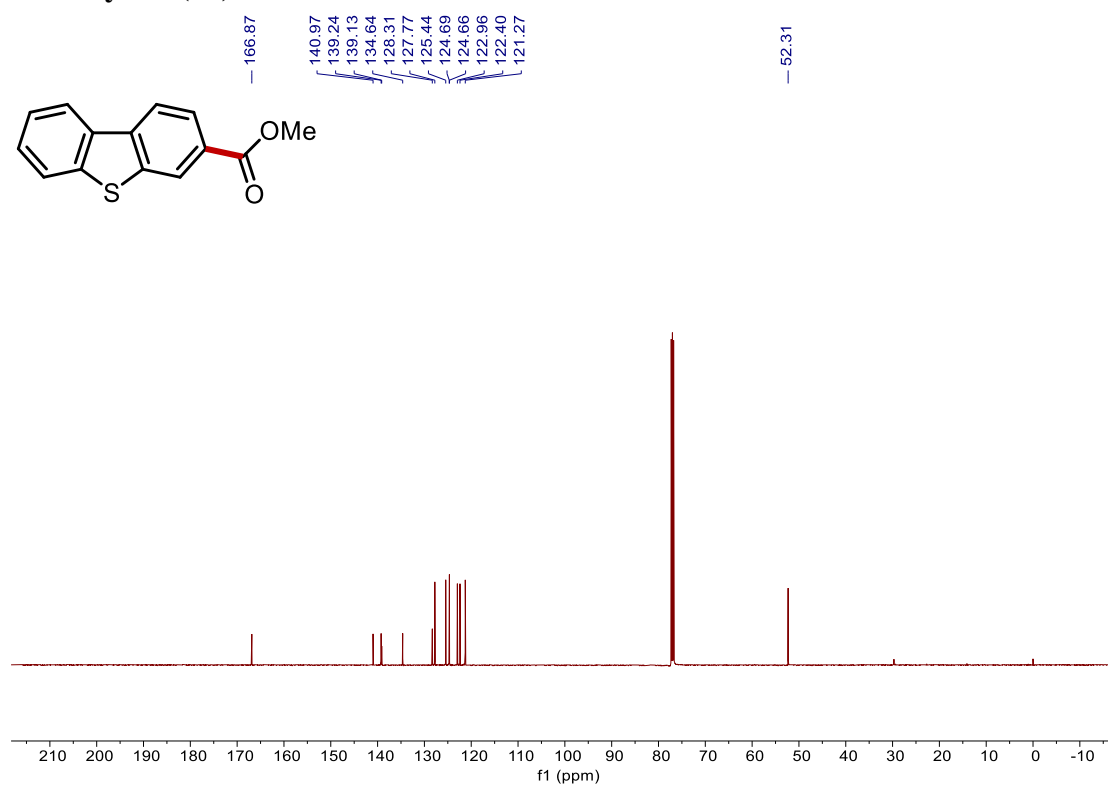




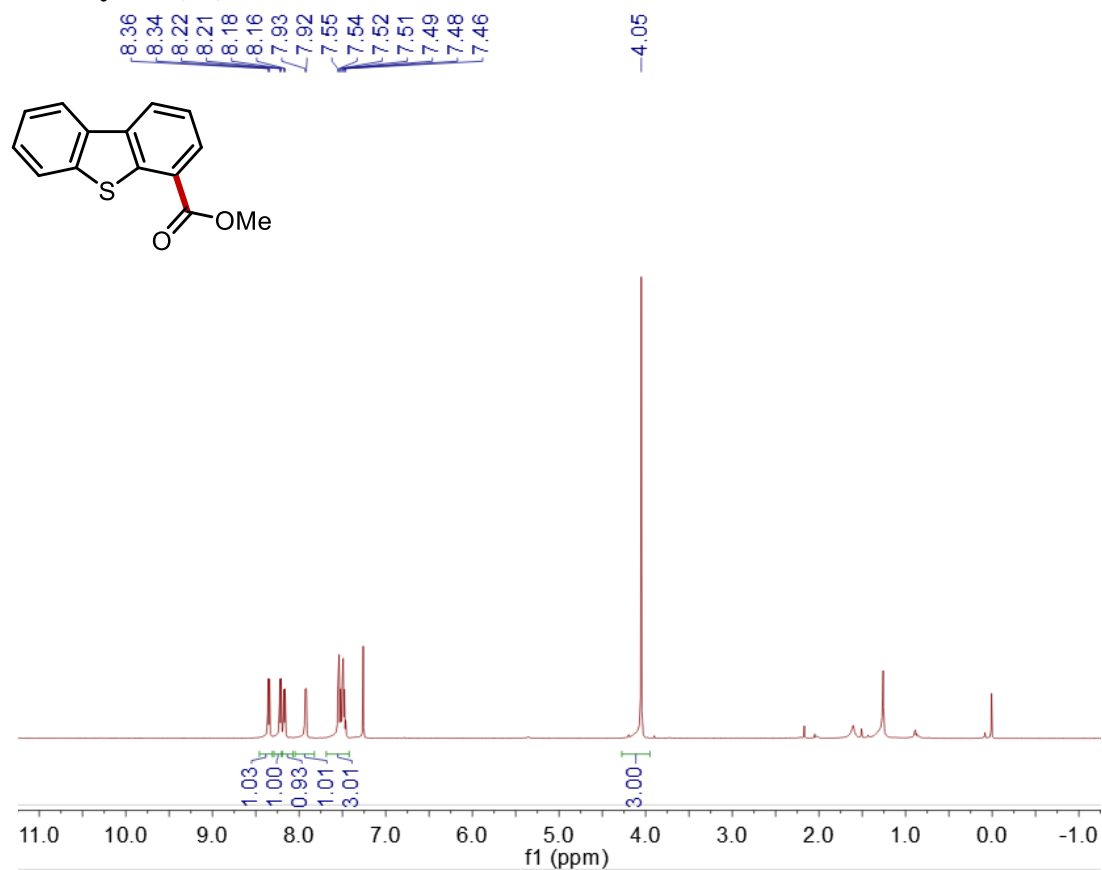
**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) Spectrum of Methyl dibenzo[b,d]thiophene-3-carboxylate (20).**



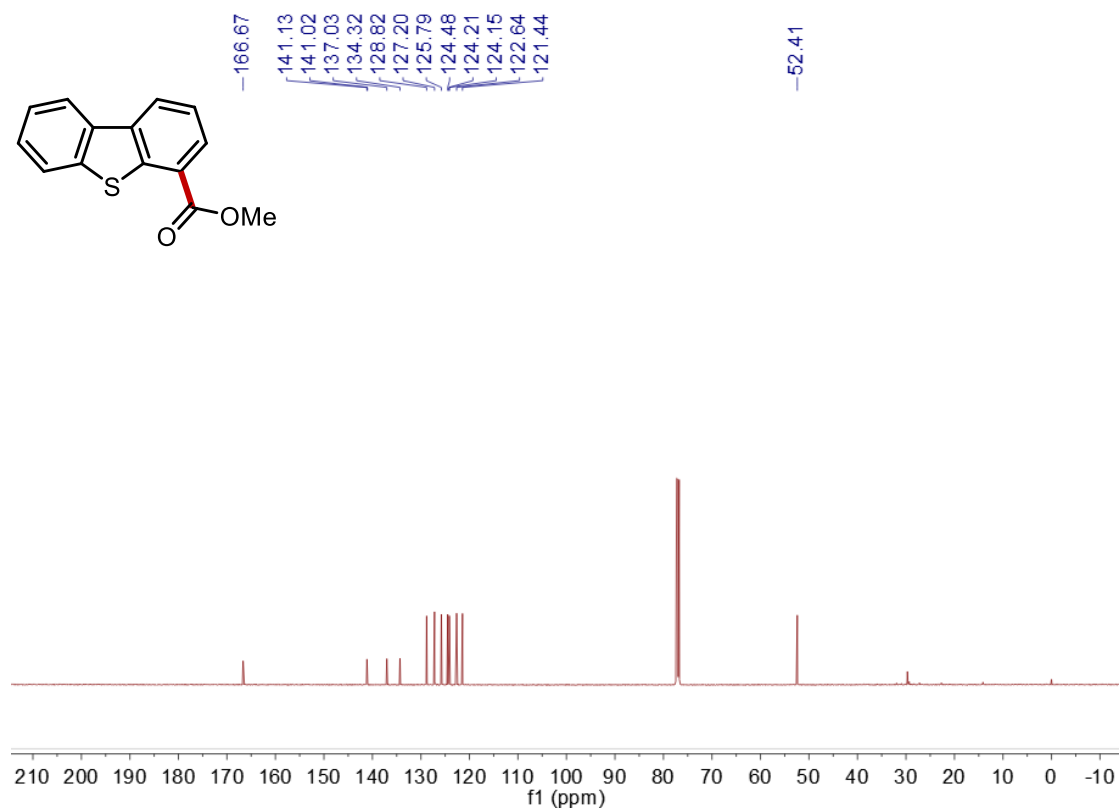
**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) Spectrum of Methyl dibenzo[b,d]thiophene-3-carboxylate (20).**



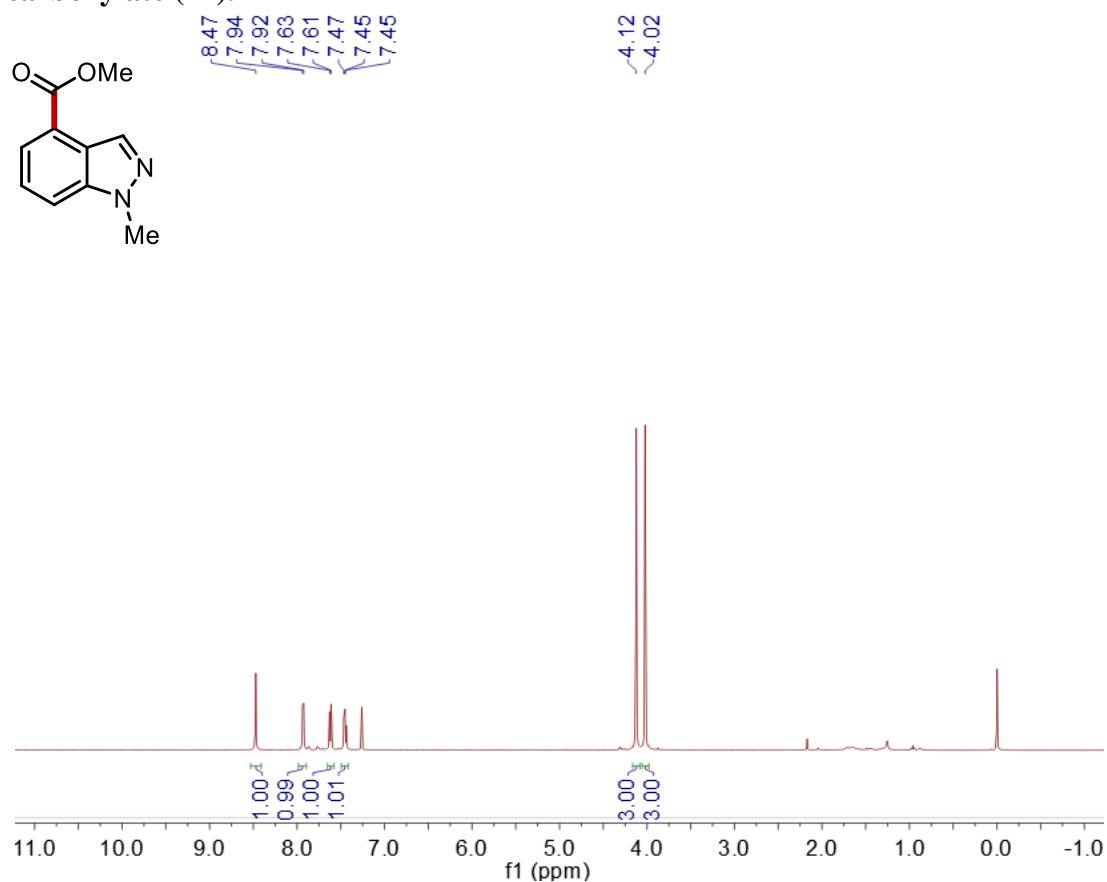
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum of Methyl dibenzo[b,d]thiophene-4-carboxylate (21).**



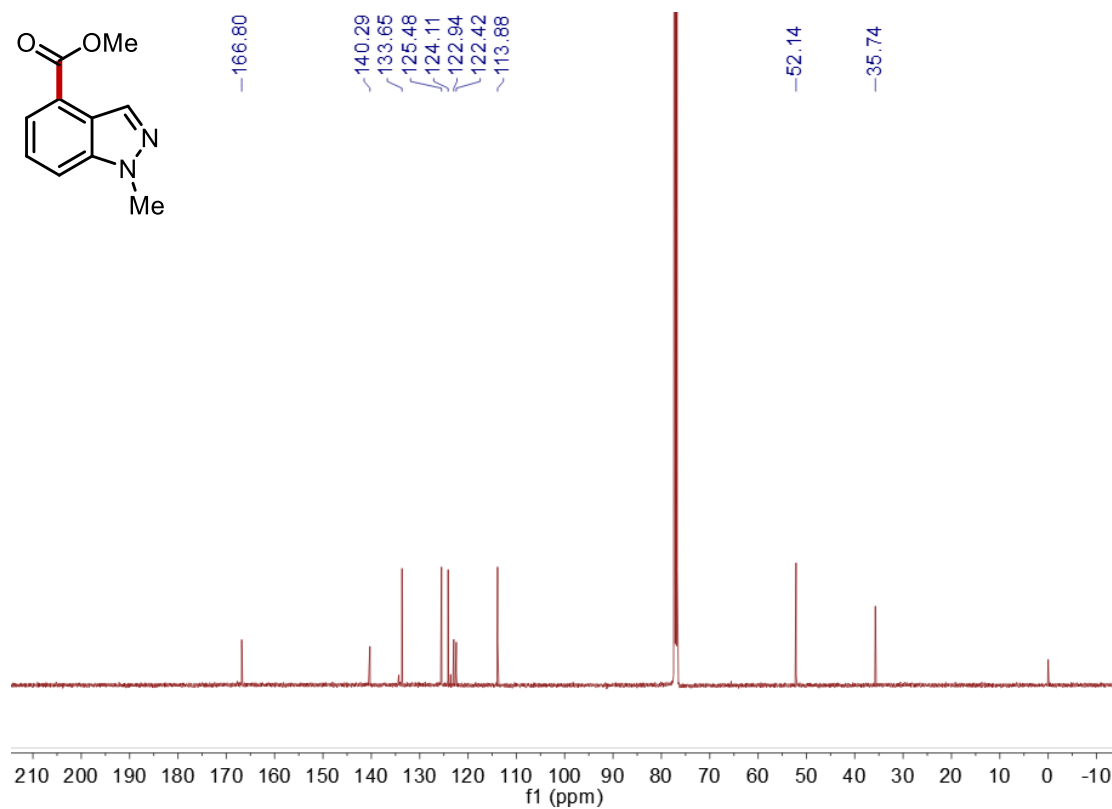
**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) Spectrum of Methyl dibenzo[b,d]thiophene-4-carboxylate (21).**



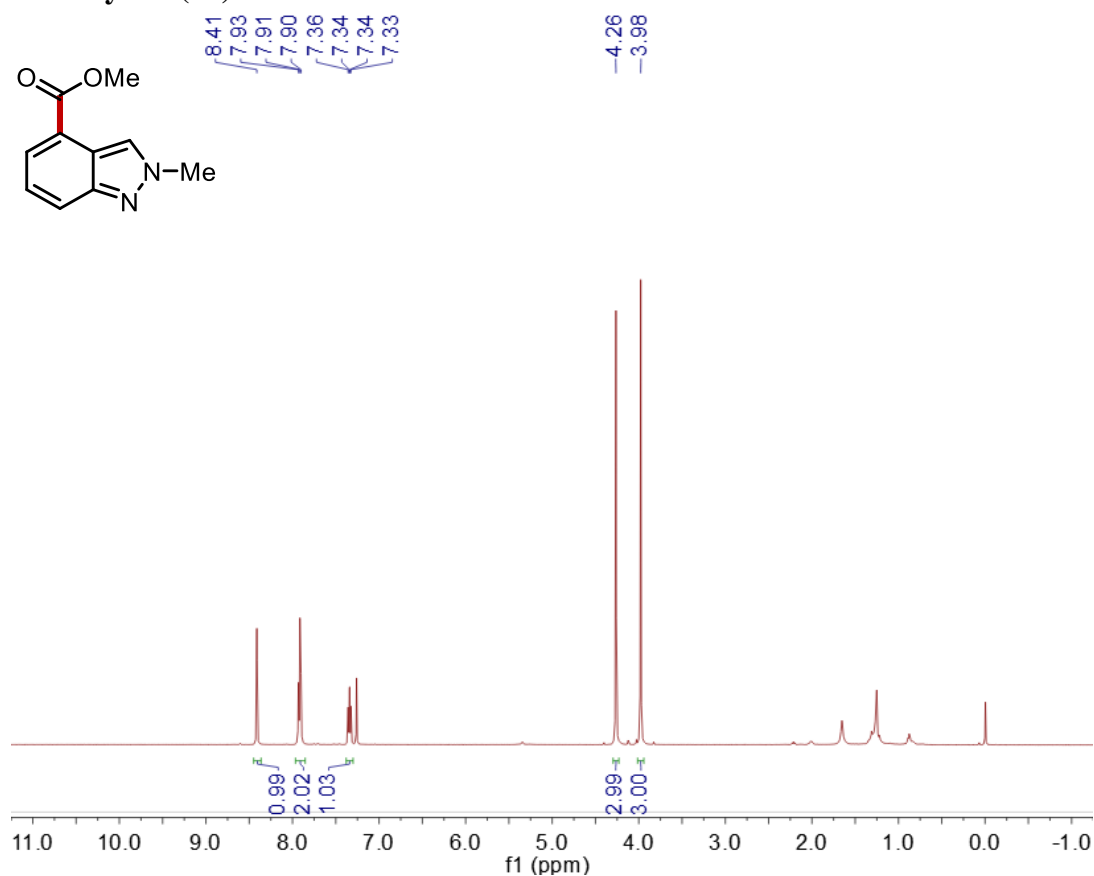
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum of Methyl 1-methyl-1H-indazole-4-carboxylate (22).**



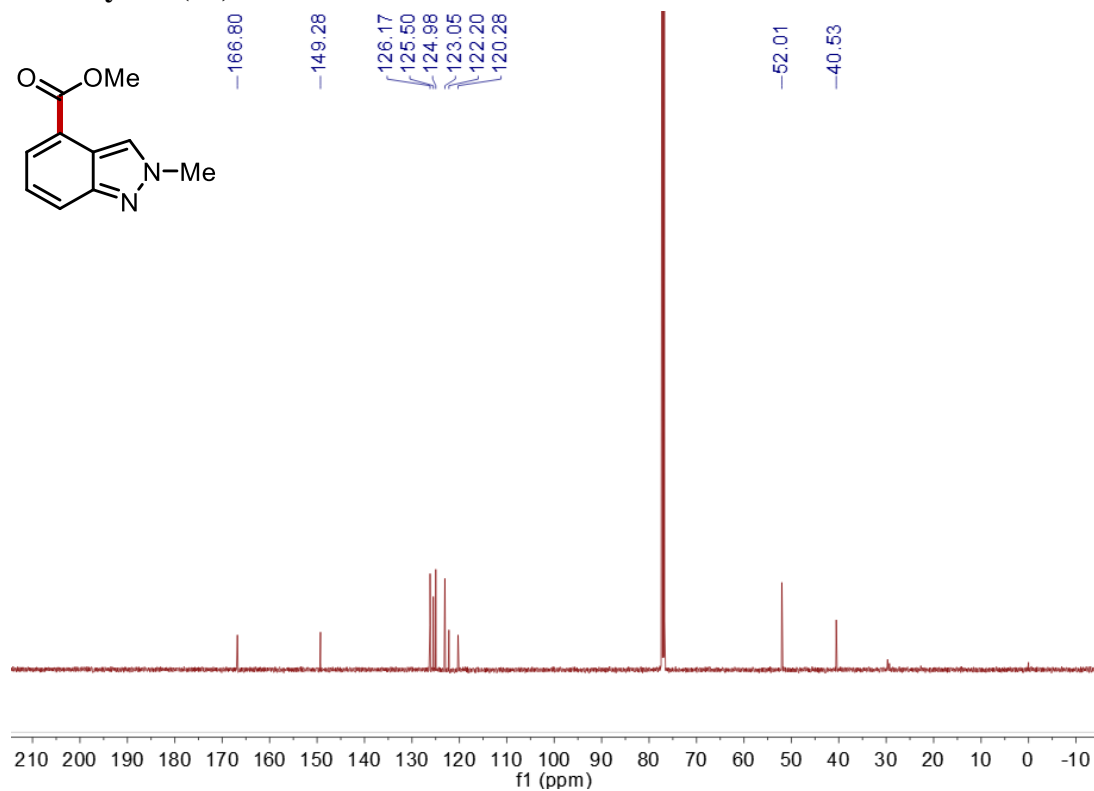
**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) Spectrum of Methyl 1-methyl-1H-indazole-4-carboxylate (22).**



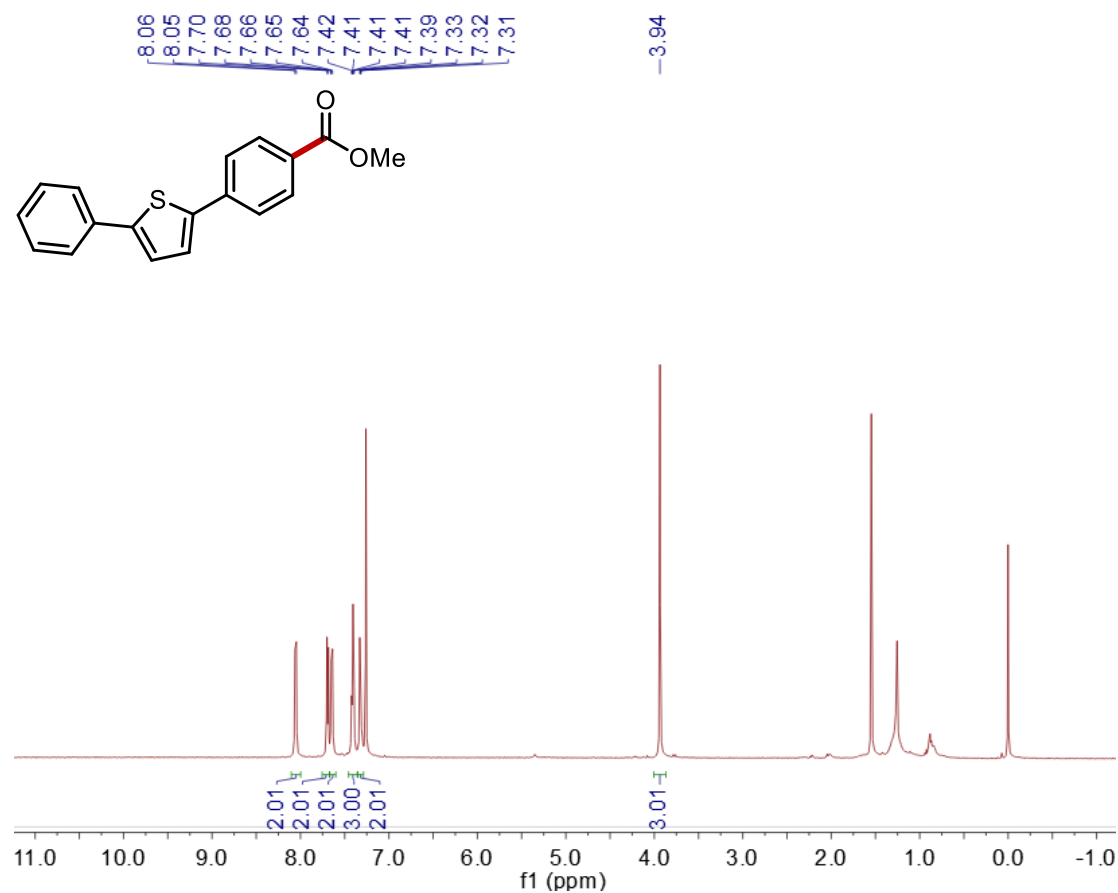
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum of Methyl 2-methyl-2H-indazole-4-carboxylate (23).**



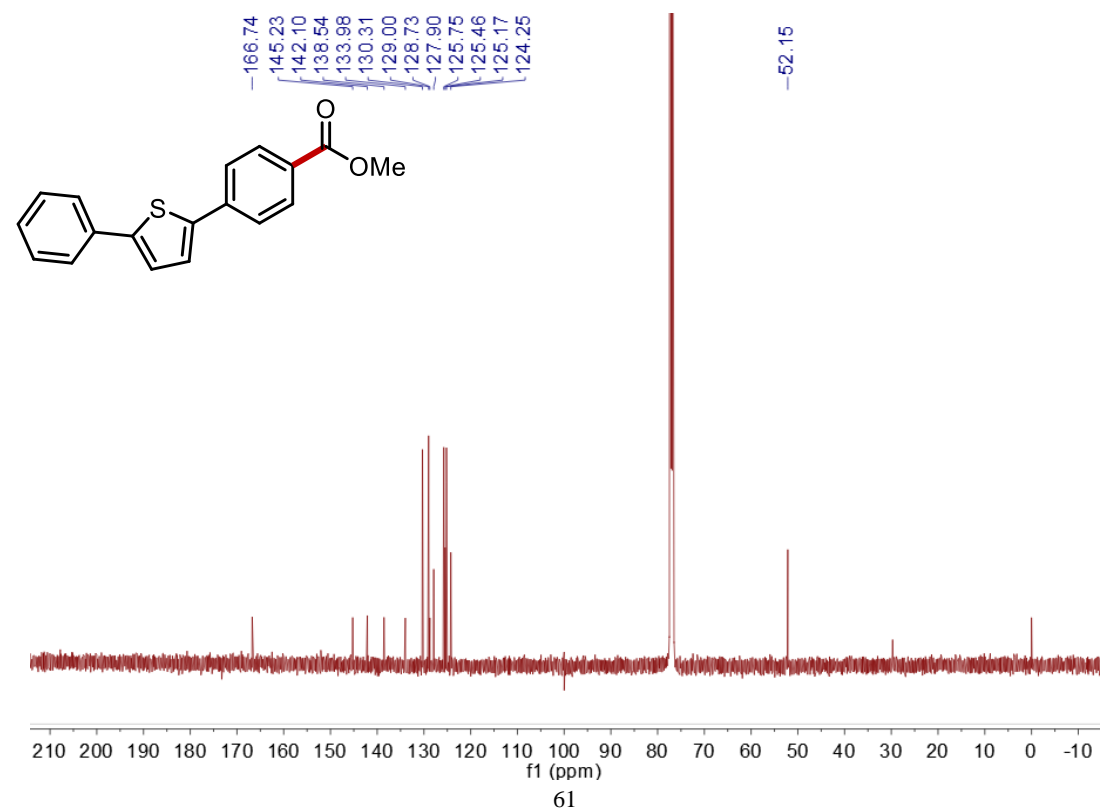
**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) Spectrum of Methyl 2-methyl-2H-indazole-4-carboxylate (23).**



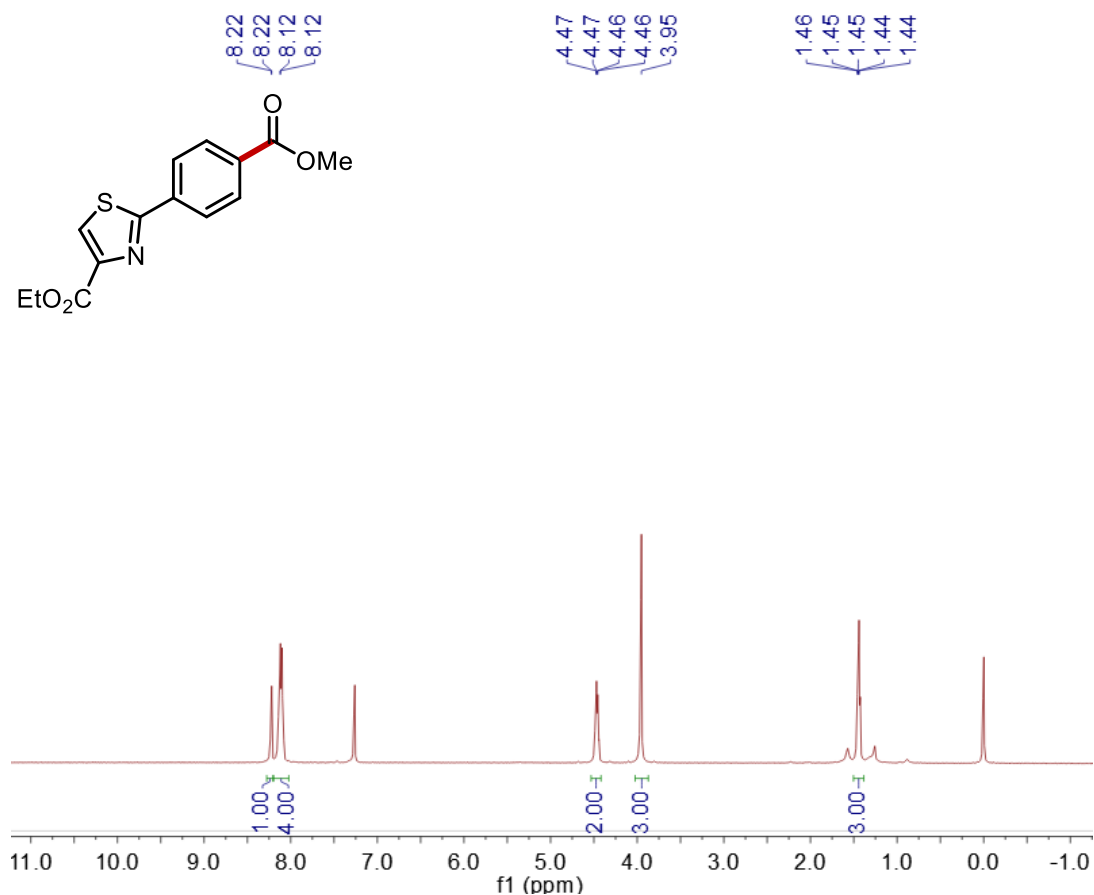
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum of Methyl 4-(5-phenylthiophen-2-yl)benzoate (24).**



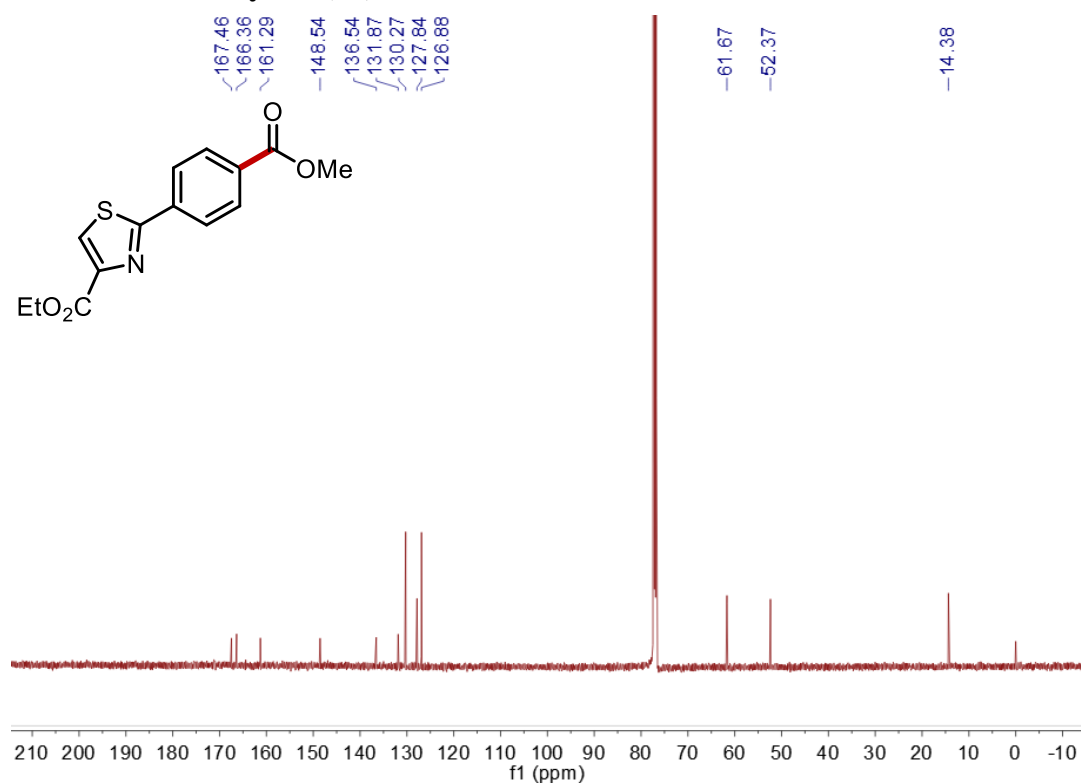
**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) Spectrum of Methyl 4-(5-phenylthiophen-2-yl)benzoate (24).**



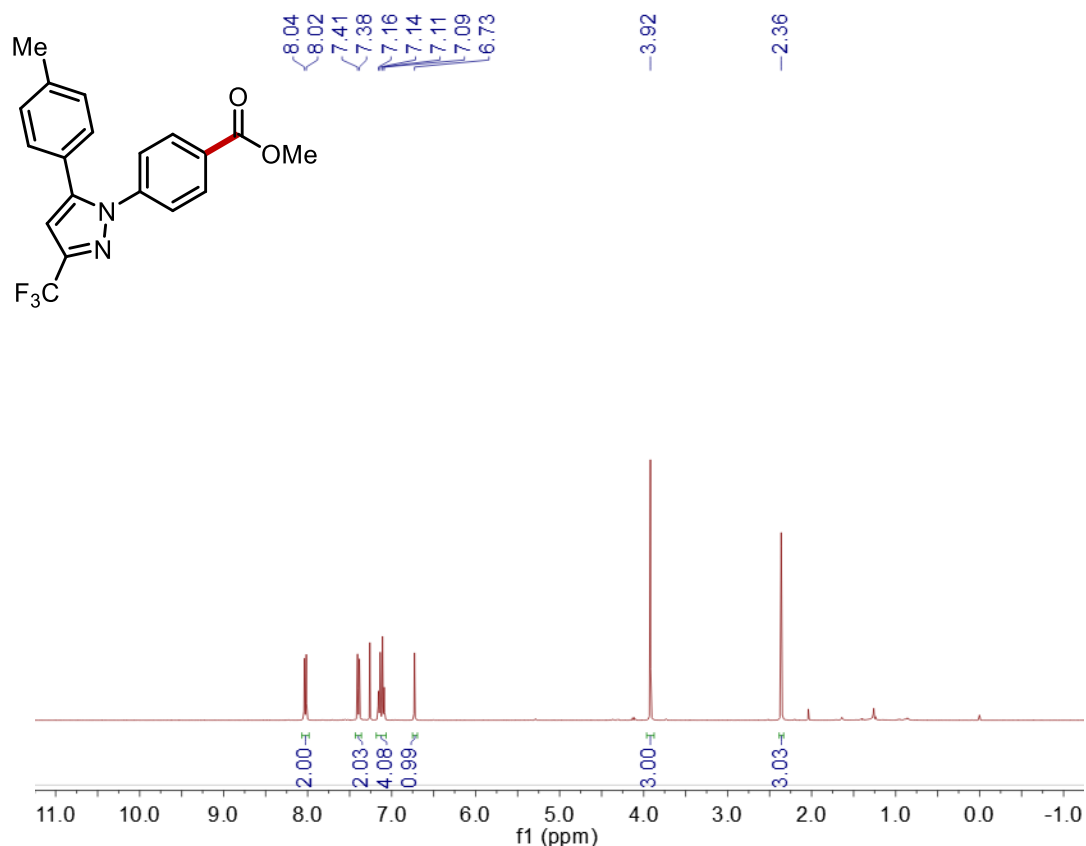
**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) Spectrum of Ethyl 2-(4-(methoxycarbonyl) phenyl) thiazole-4-carboxylate (25).**



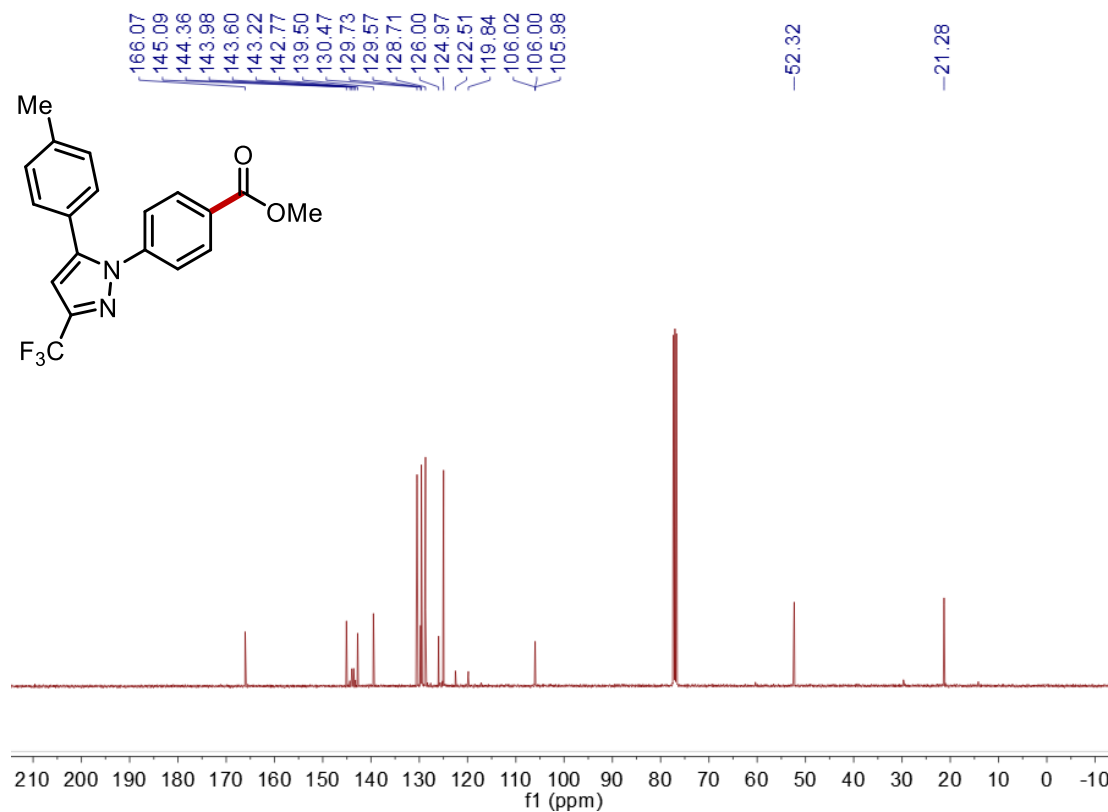
**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) Spectrum of Ethyl 2-(4-(methoxycarbonyl) phenyl) thiazole-4-carboxylate (25).**



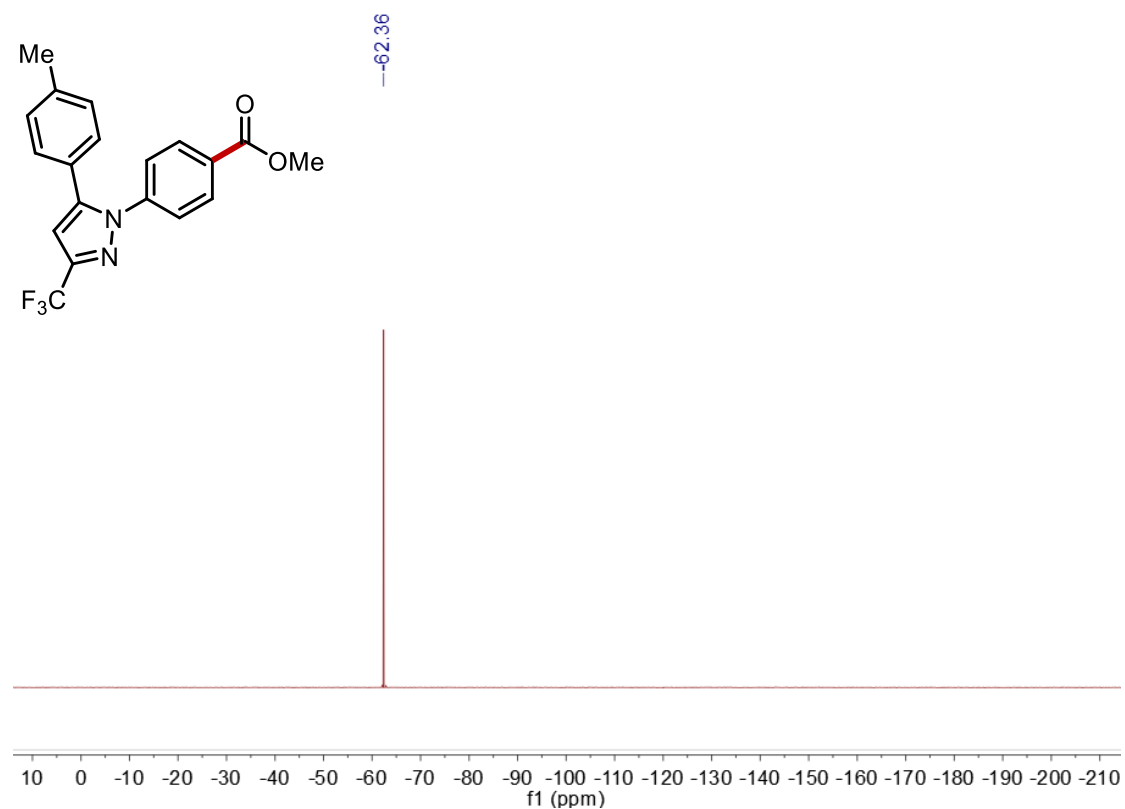
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) Spectrum of Methyl 4-(5-(p-tolyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl) benzoate (26).**



**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) Spectrum of Methyl 4-(5-(p-tolyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl) benzoate (26).**

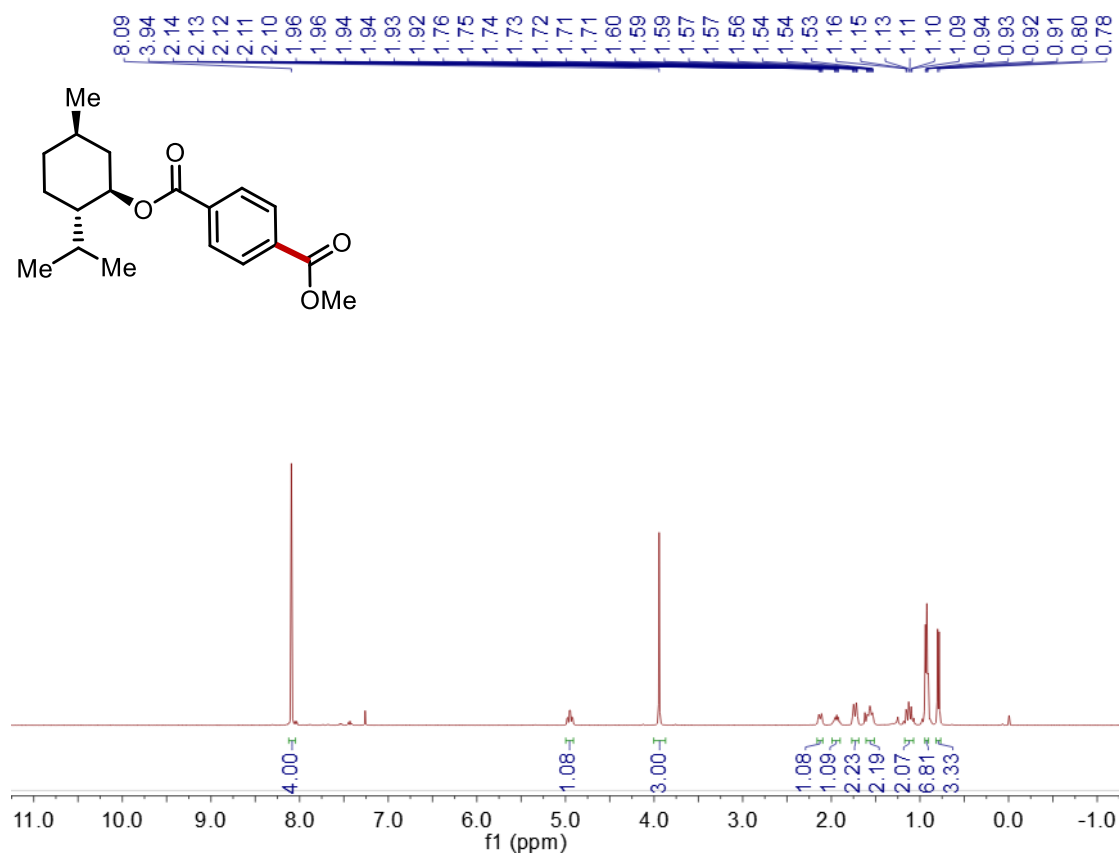


**$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ) Spectrum of Methyl 4-(5-(p-tolyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl) benzoate (26).**

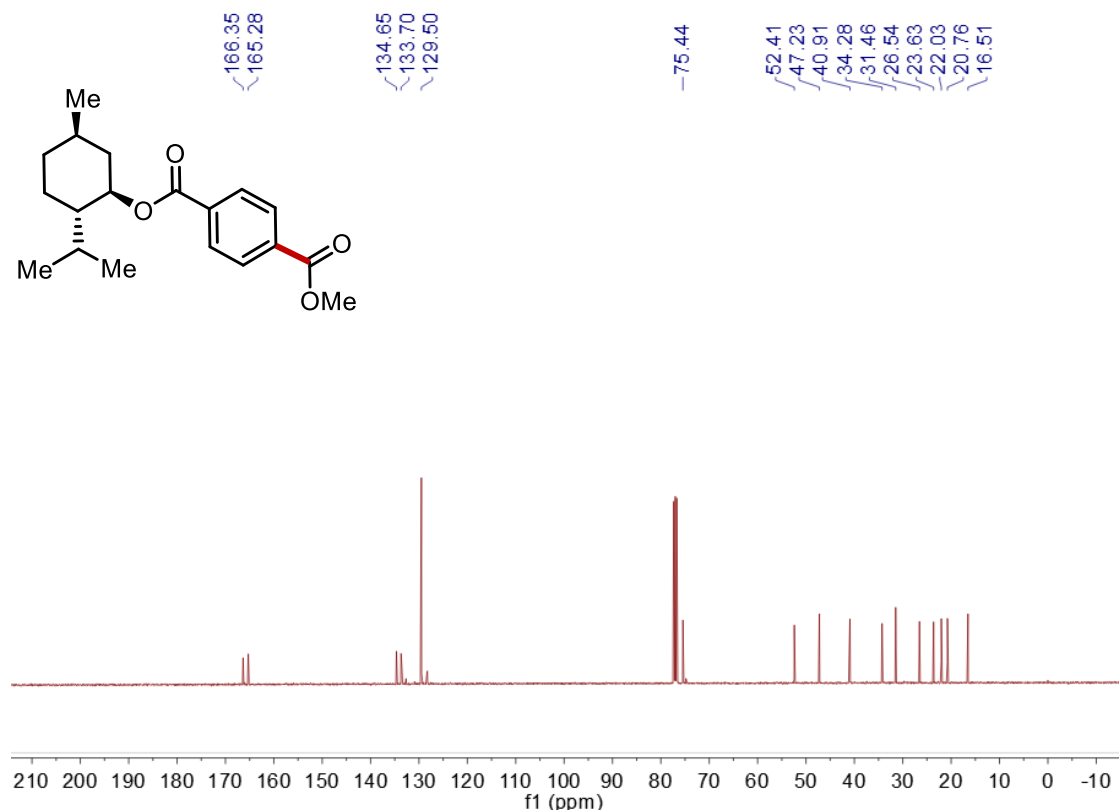




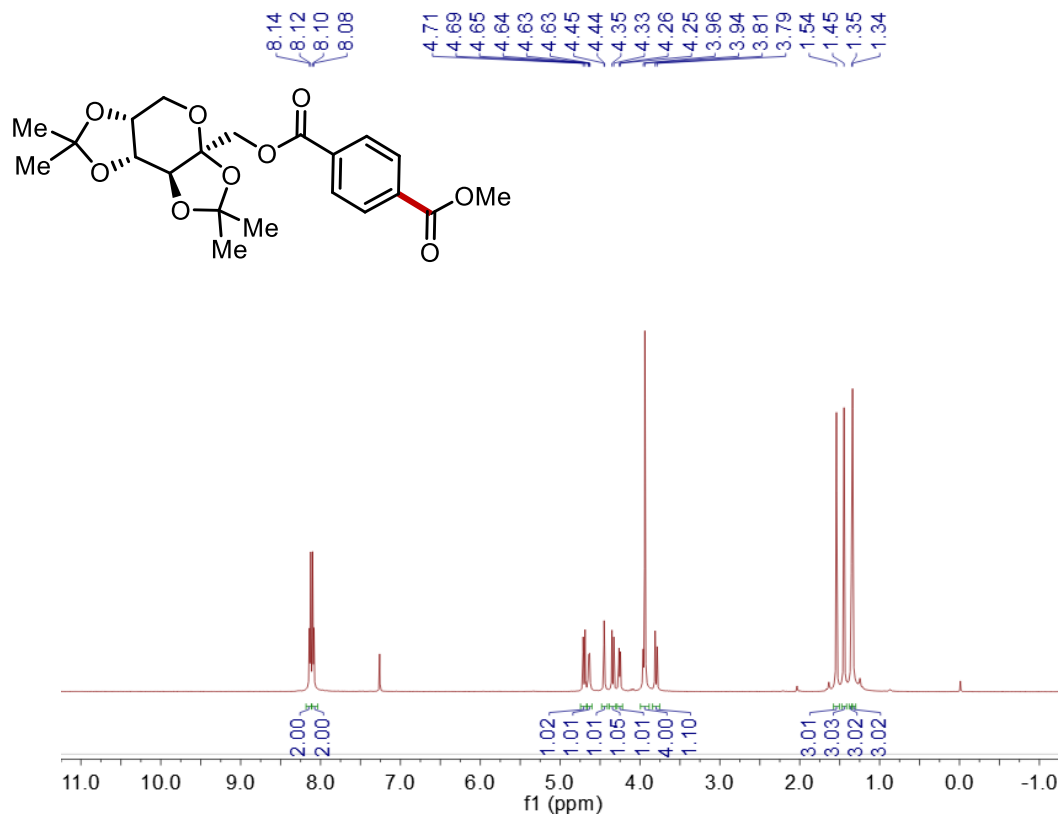
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) Spectrum of (1R,2S,5R)-2-isopropyl-5-methylcyclohexyl methyl terephthalate (27).**



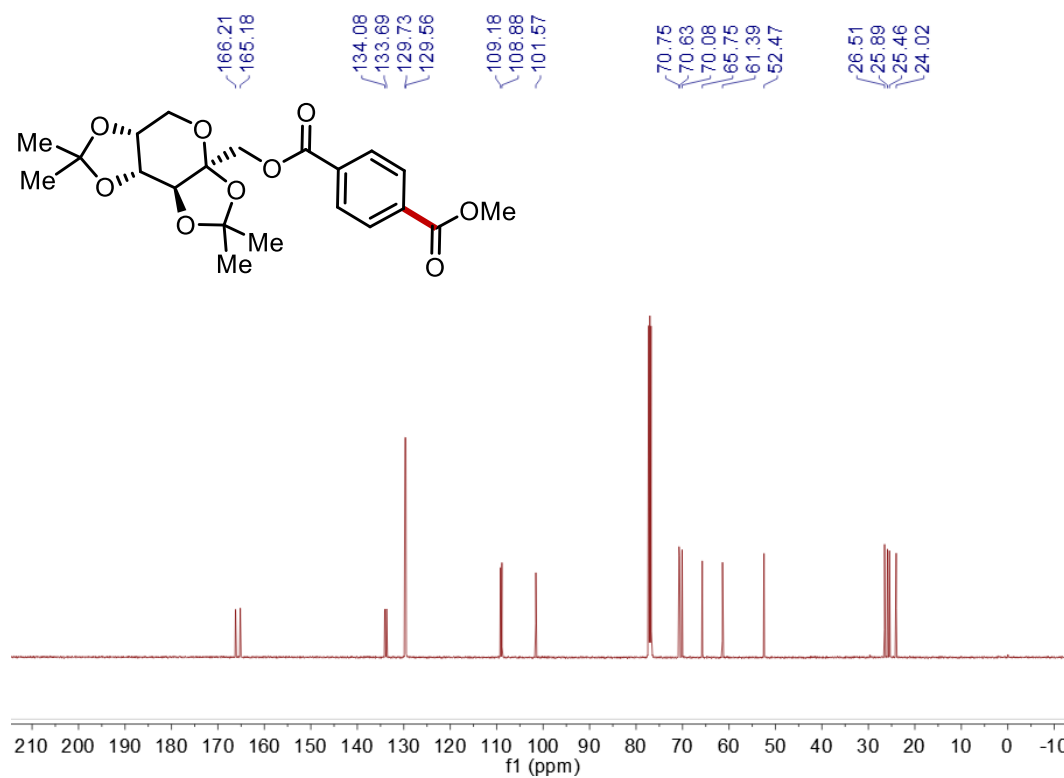
**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) Spectrum of (1R,2S,5R)-2-isopropyl-5-methylcyclohexyl methyl terephthalate (27).**



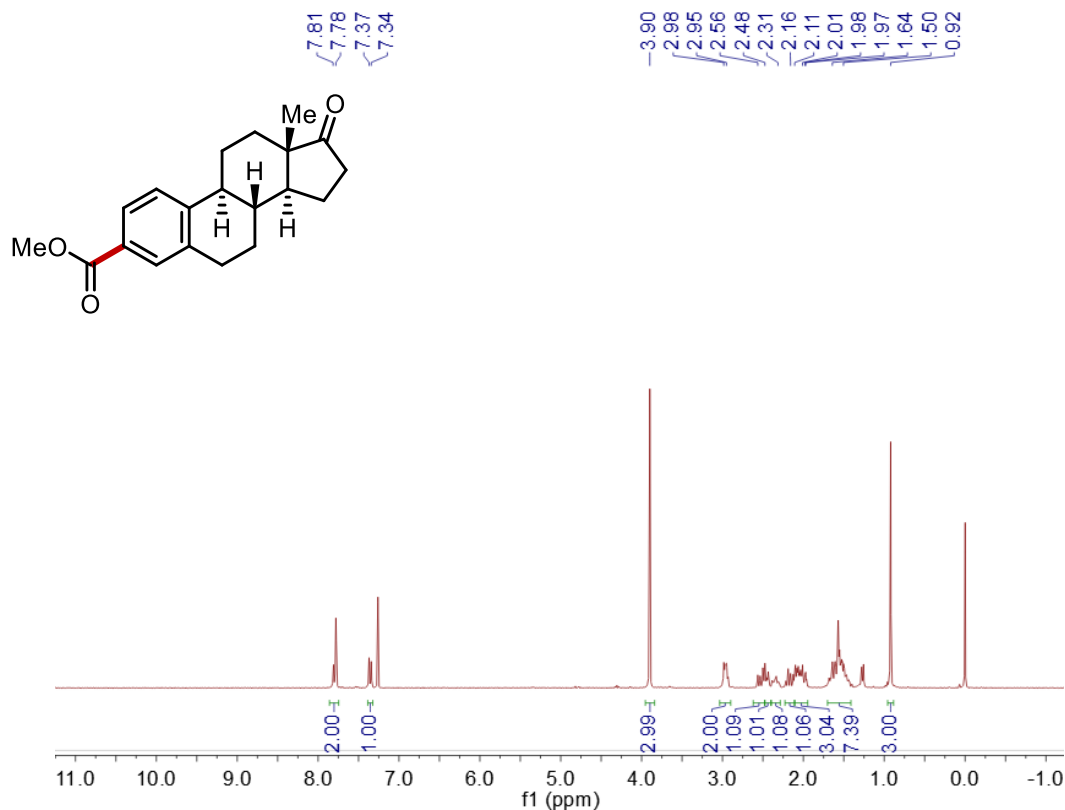
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum of Methyl [((3aS,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-3aH-bis ([1,3] dioxolo) [4,5-b:4',5'-d] pyran-3a-yl) methyl] terephthalate (28).**



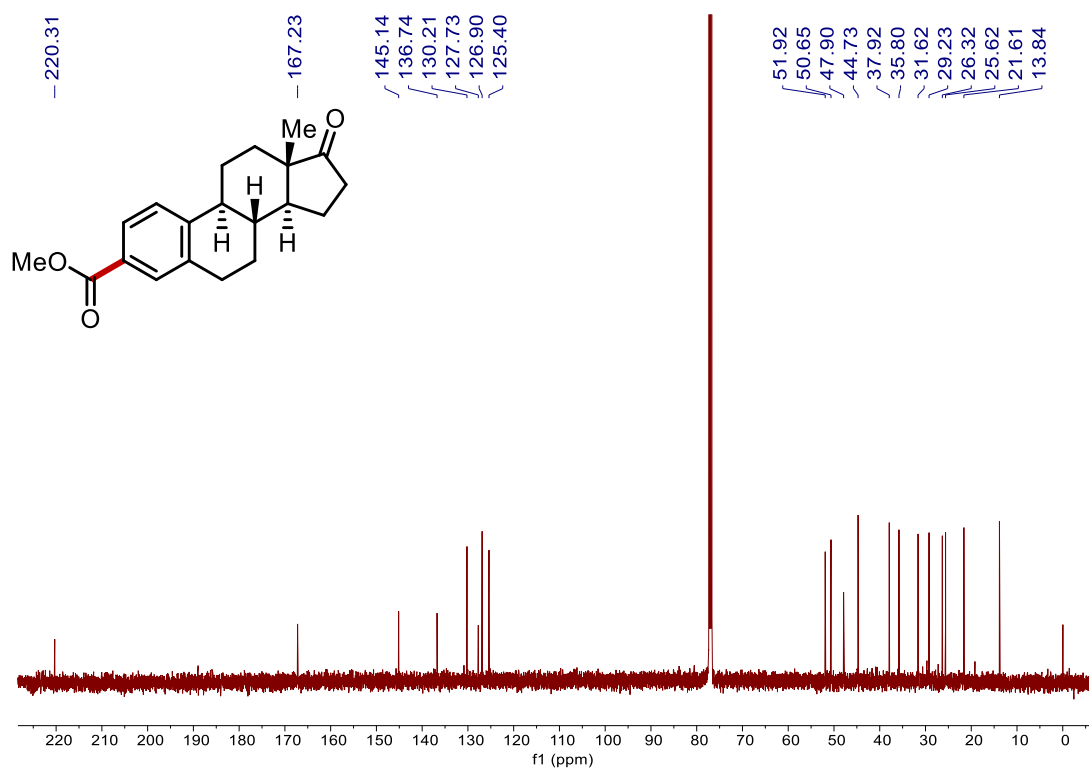
**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) Spectrum of Methyl [((3aS,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-3aH-bis ([1,3] dioxolo) [4,5-b:4',5'-d] pyran-3a-yl) methyl] terephthalate (28).**



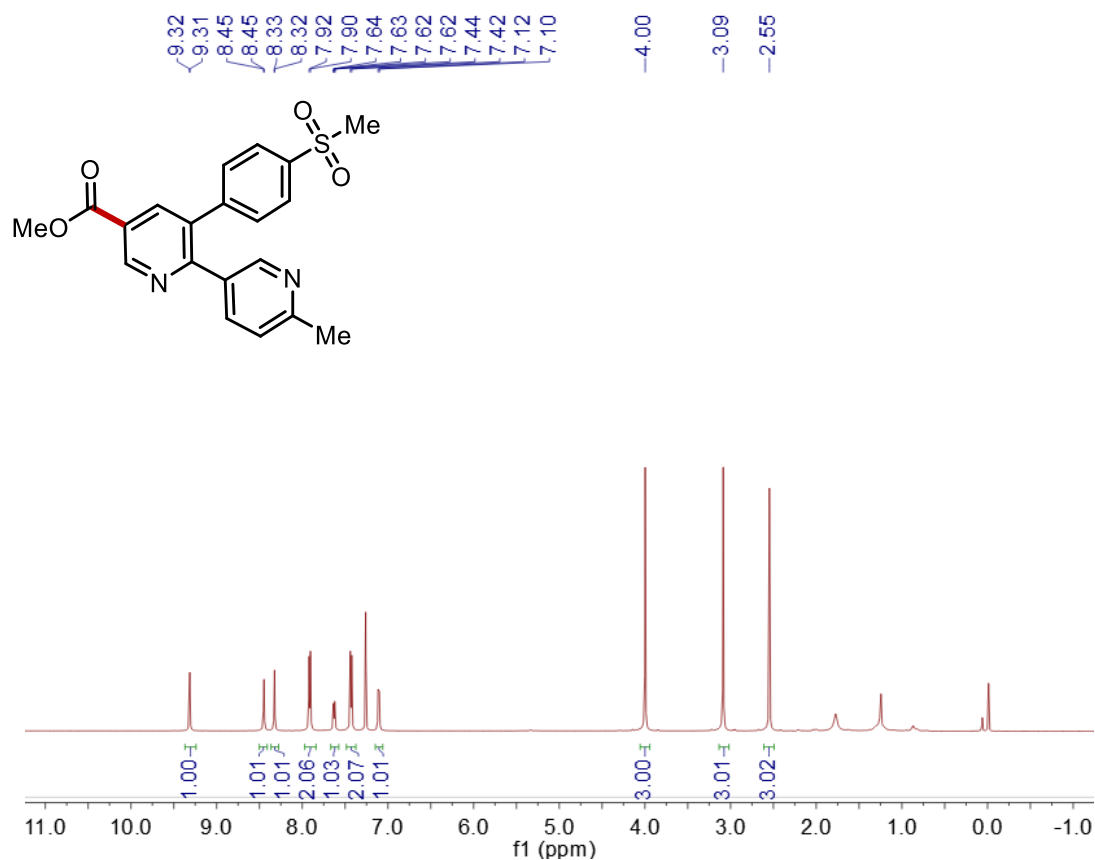
**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) Spectrum of Methyl (8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthrene-3-carboxylate (29).**



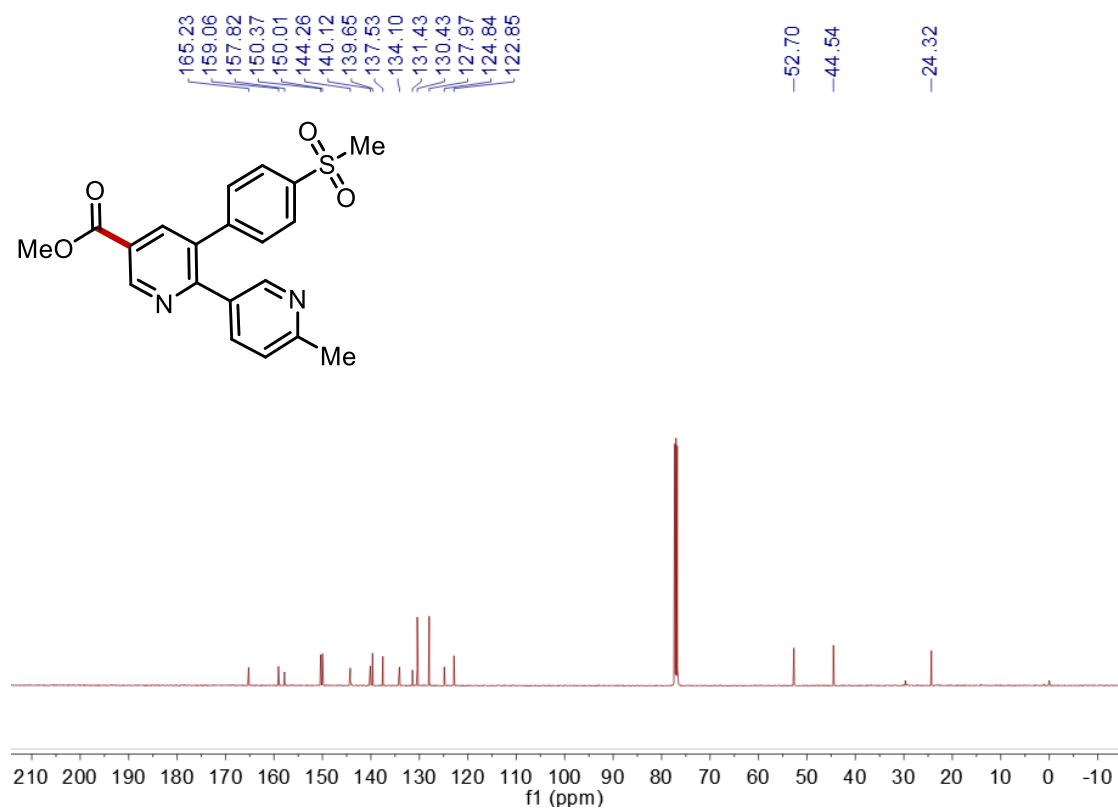
**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) Spectrum of Methyl (8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthrene-3-carboxylate (29).**



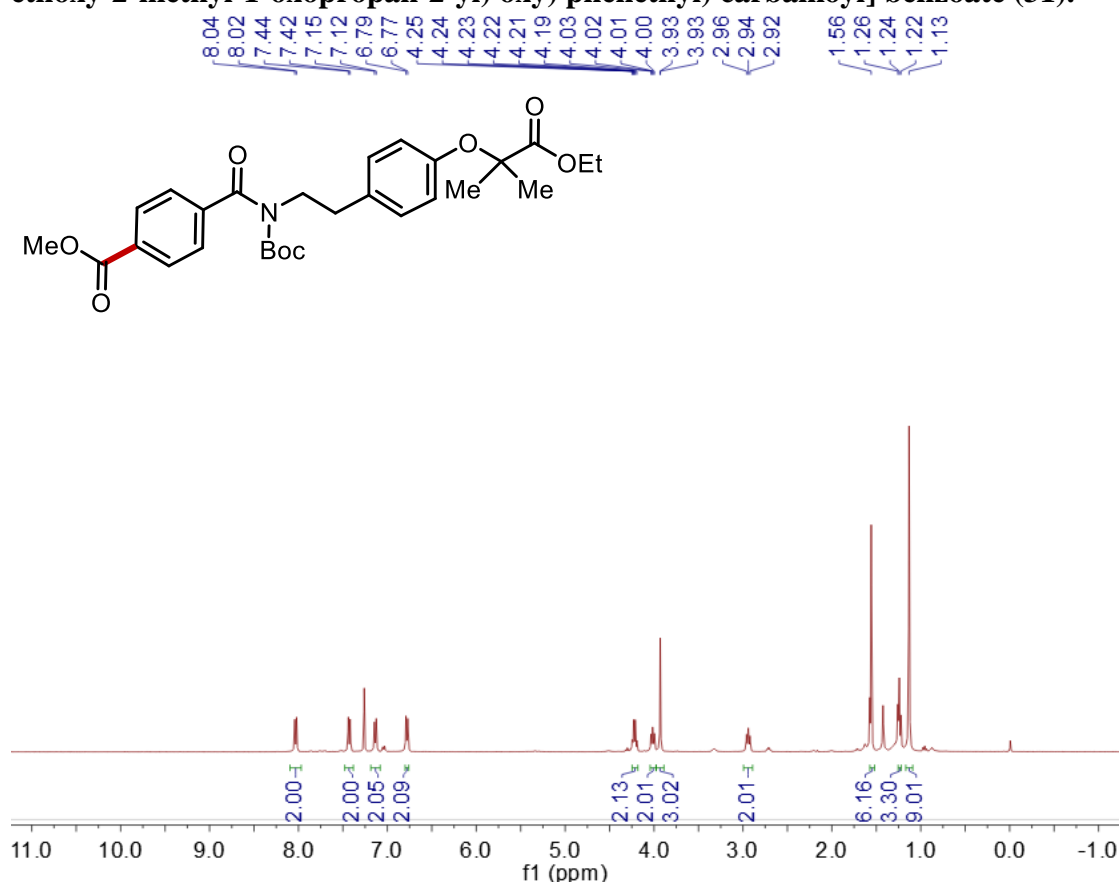
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum of (Methyl 6'-methyl-3-(4-(methylsulfonyl) phenyl)-[2,3'-bipyridine]-5-carboxylate (30).**



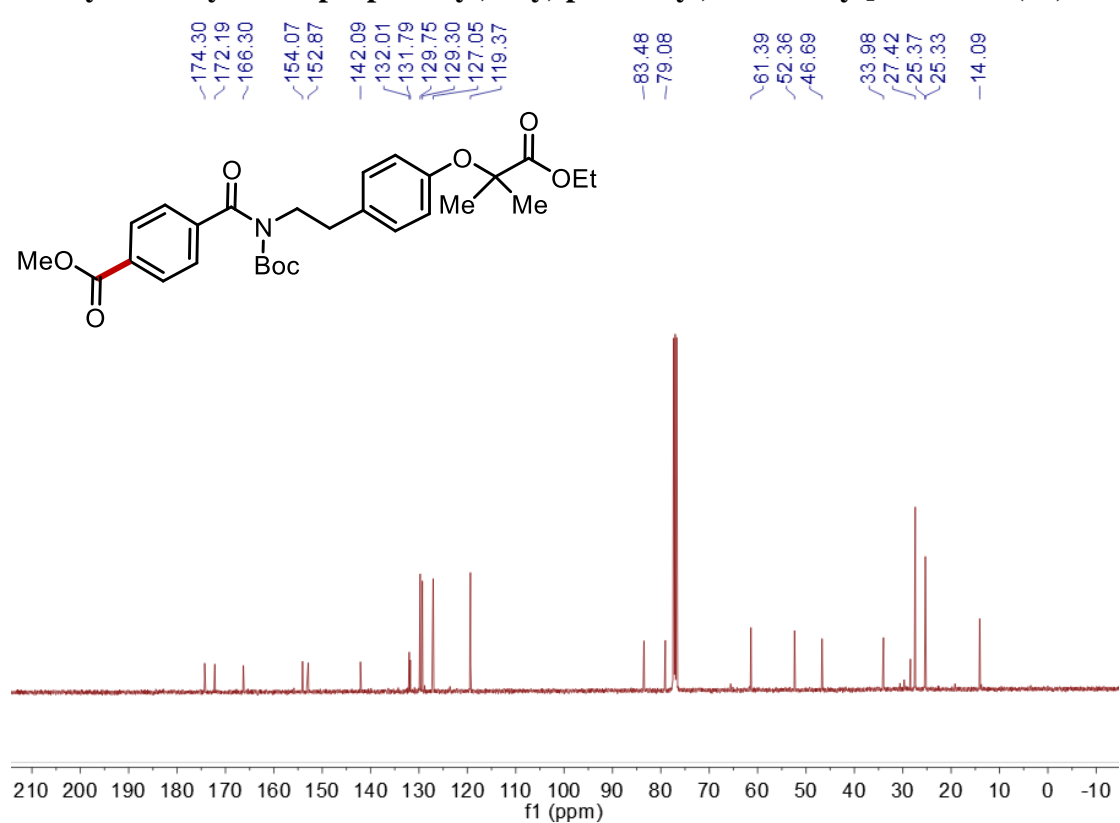
**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) Spectrum of (Methyl 6'-methyl-3-(4-(methylsulfonyl) phenyl)-[2,3'-bipyridine]-5-carboxylate (30).**



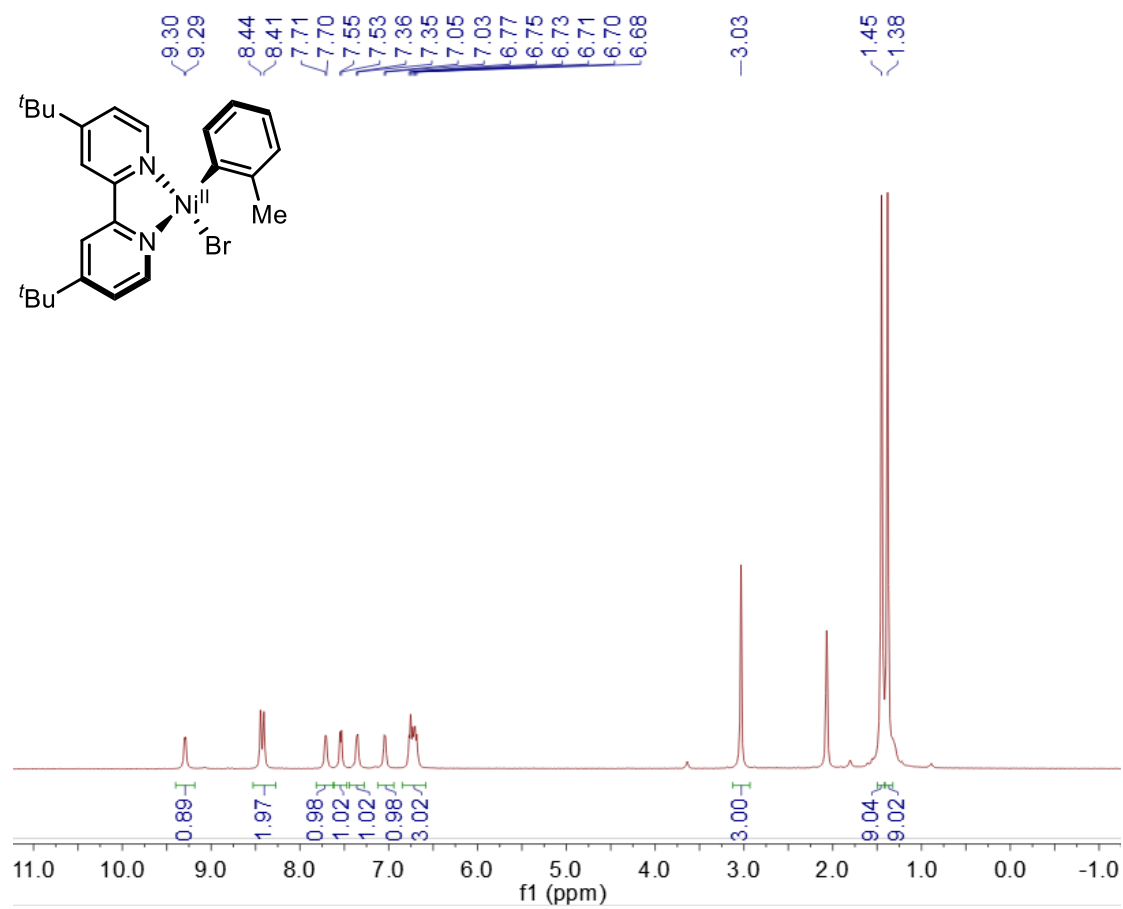
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) Spectrum of Methyl 4-[(tert-butoxycarbonyl) (4-((1-ethoxy-2-methyl-1-oxopropan-2-yl) oxy) phenethyl) carbamoyl] benzoate (31).**



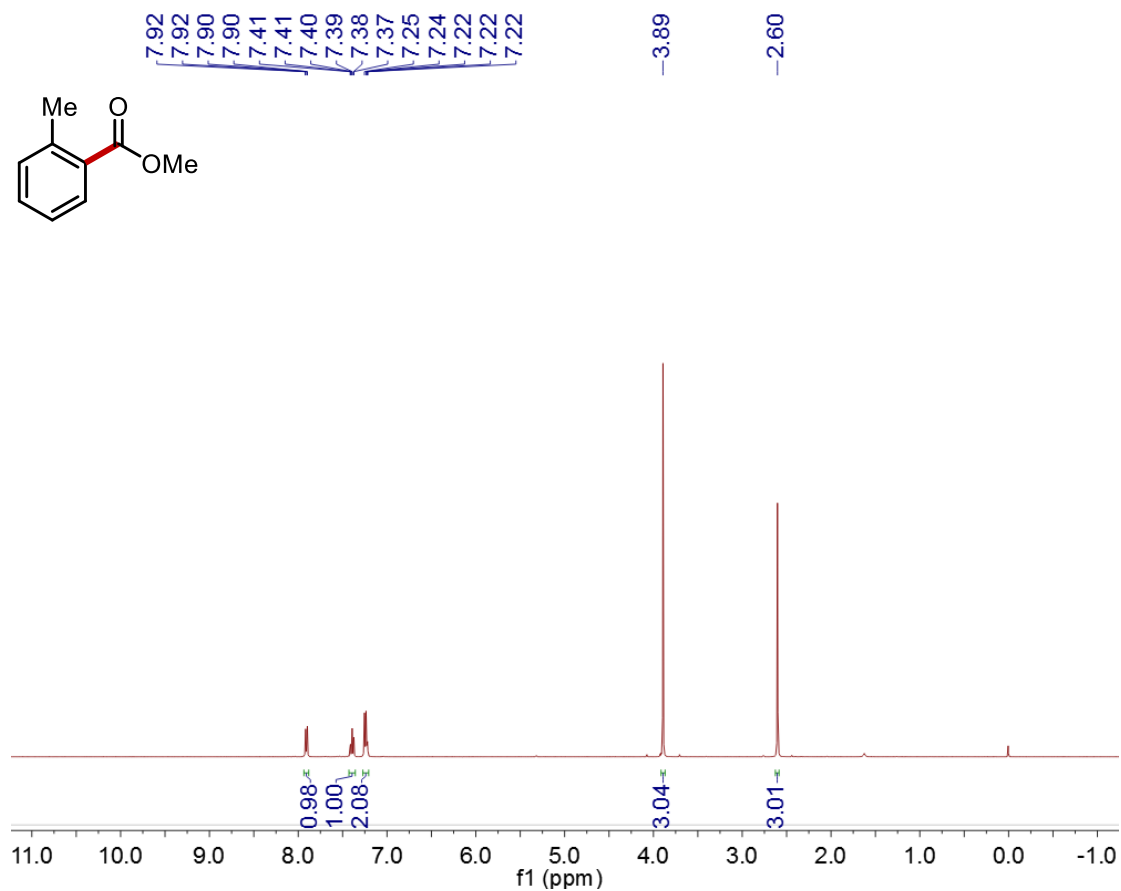
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) Spectrum of Methyl 4-[(tert-butoxycarbonyl) (4-((1-ethoxy-2-methyl-1-oxopropan-2-yl) oxy) phenethyl) carbamoyl] benzoate (31).**



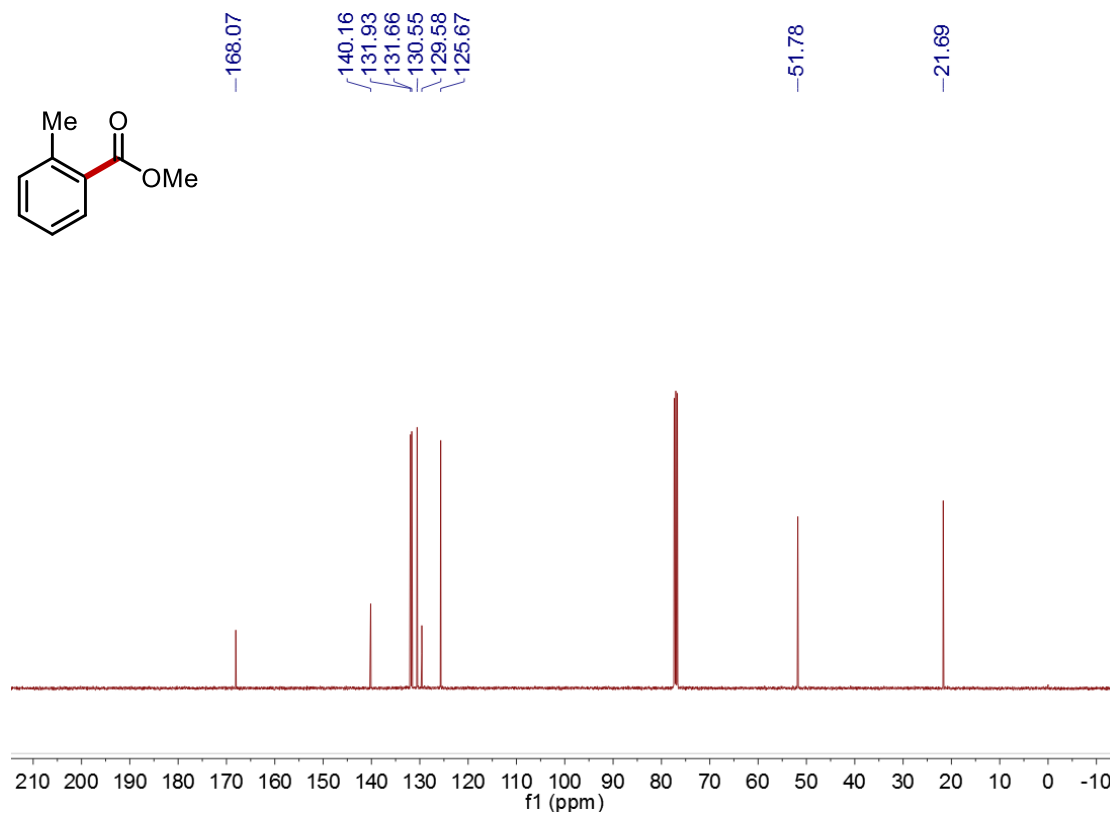
**$^1\text{H}$  NMR (400 MHz, Acetone- $d_6$ ) Spectrum of [(dtbbpy)Ni(II)(2-tolyl)Br] (32).**



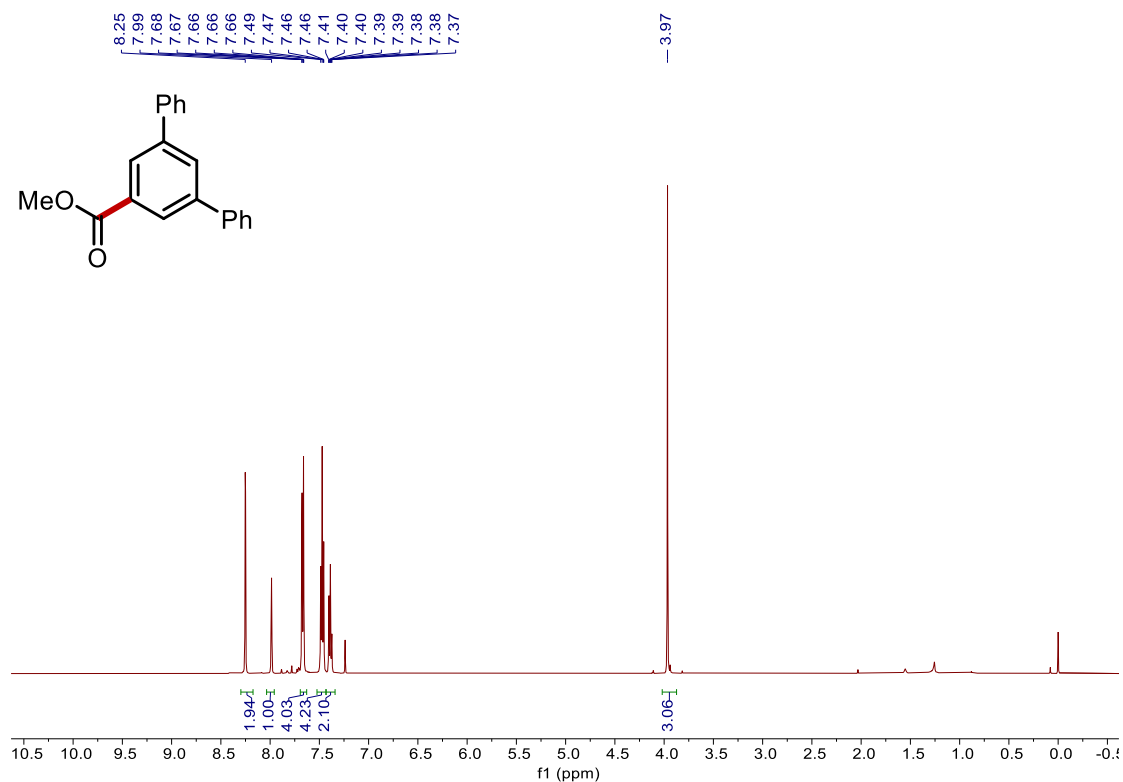
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) Spectrum of Methyl 2-methylbenzoate (33).**



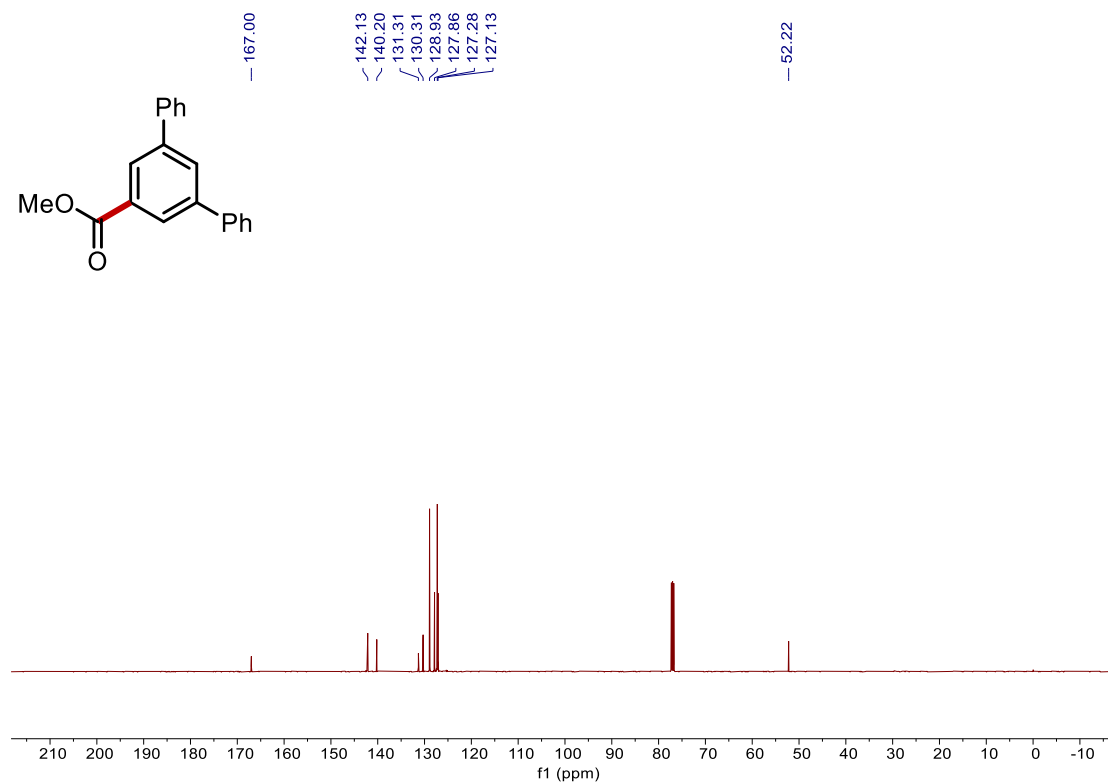
**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) Spectrum of Methyl 2-methylbenzoate (33).**



**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) Spectrum of methyl [1,1':3',1''-terphenyl]-5'-carboxylate (S16).**

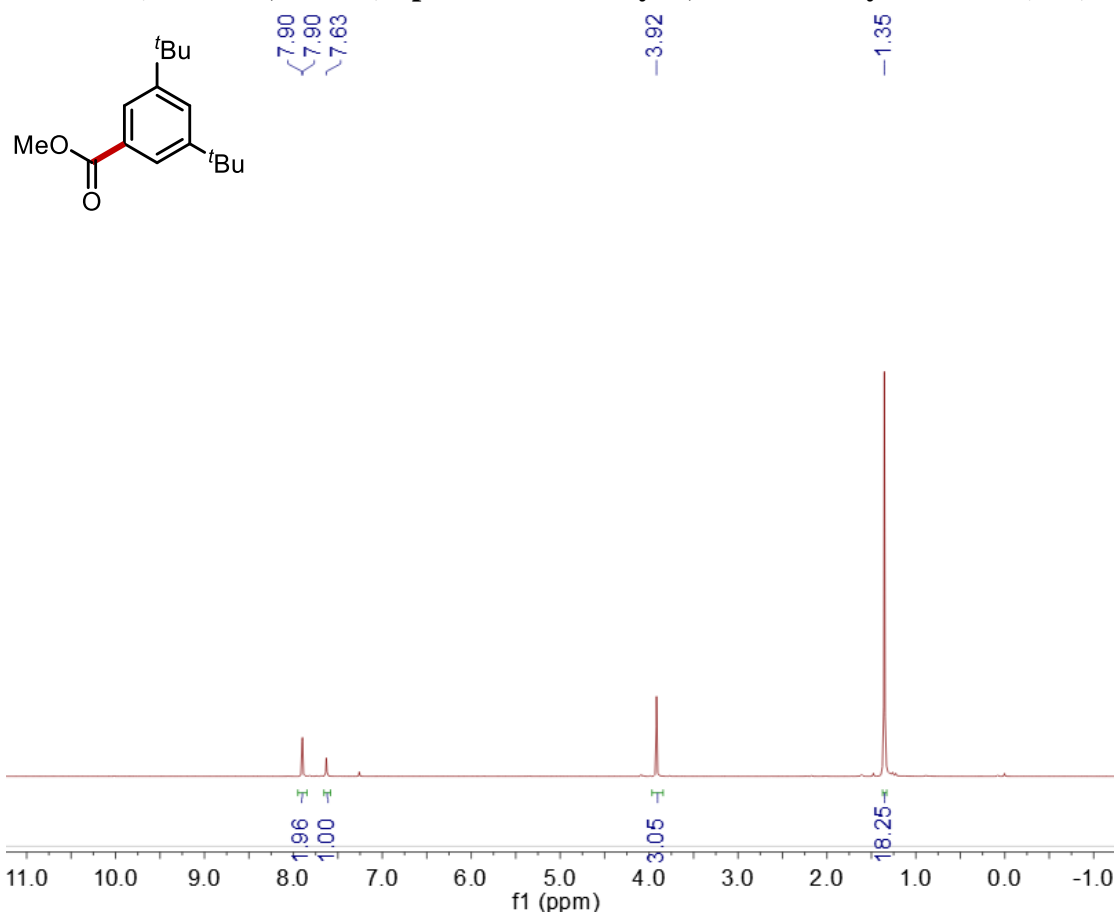


**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) Spectrum of methyl [1,1':3',1''-terphenyl]-5'-carboxylate (S16).**

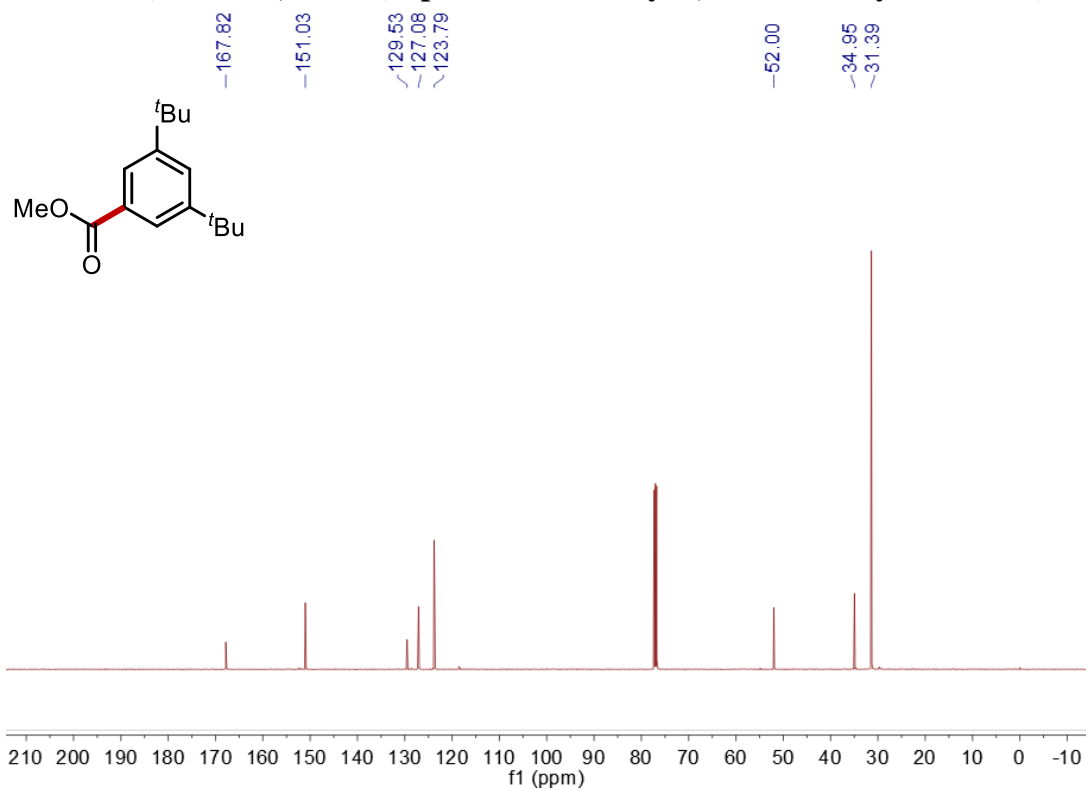




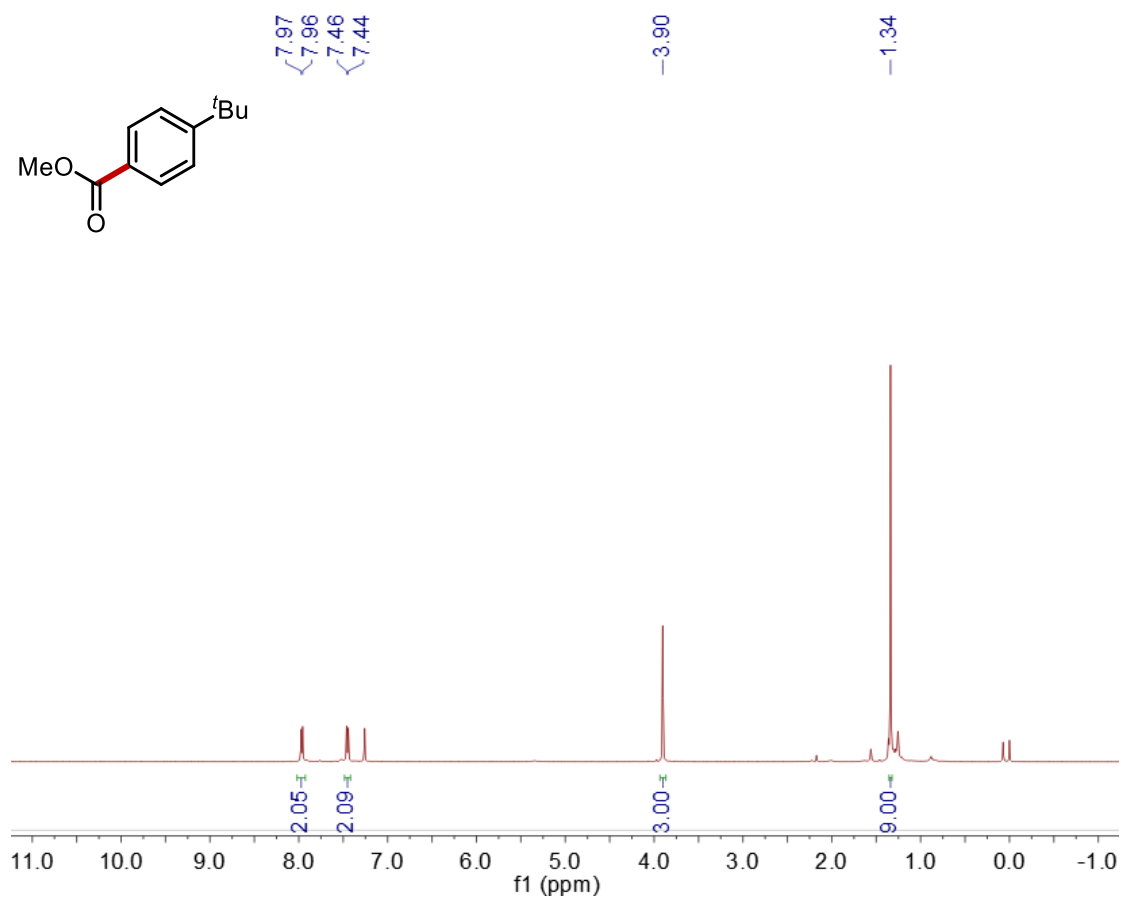
**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) Spectrum of methyl 3,5-di-tert-butylbenzoate (S17)**



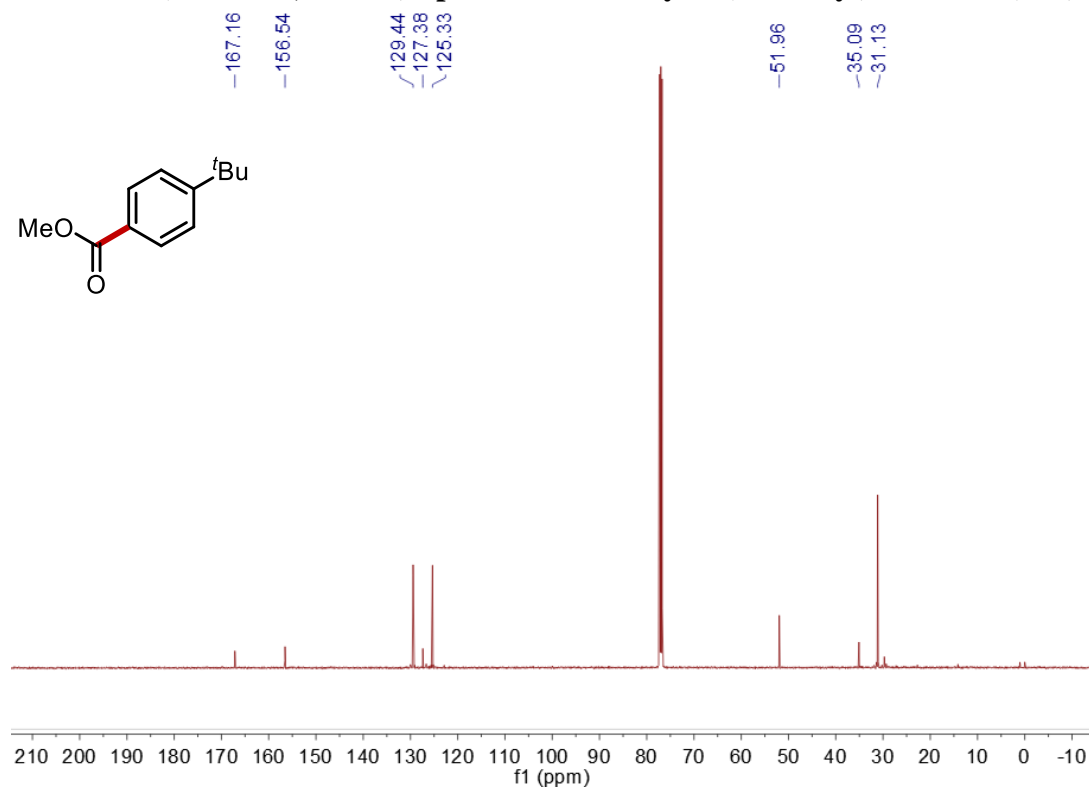
**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) Spectrum of methyl 3,5-di-tert-butylbenzoate (S17)**



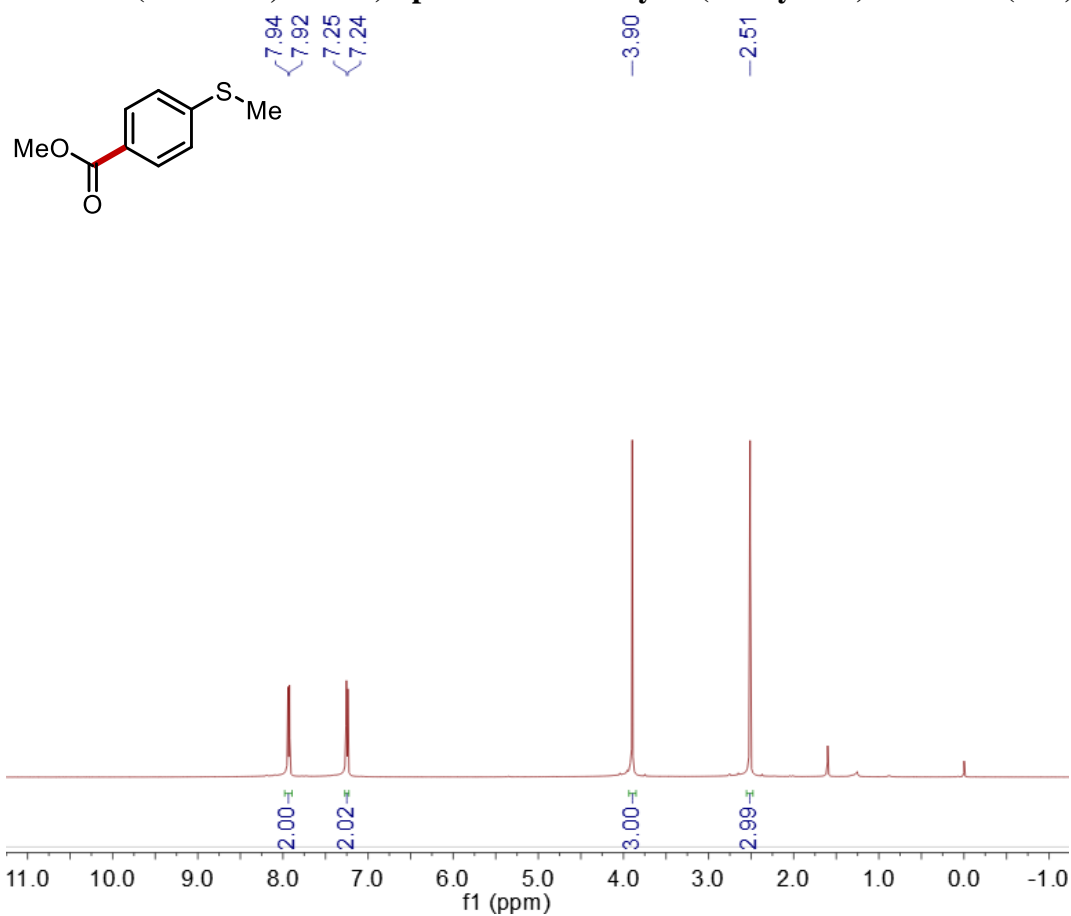
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum of methyl 4-(*tert*-butyl) benzoate (S18).**



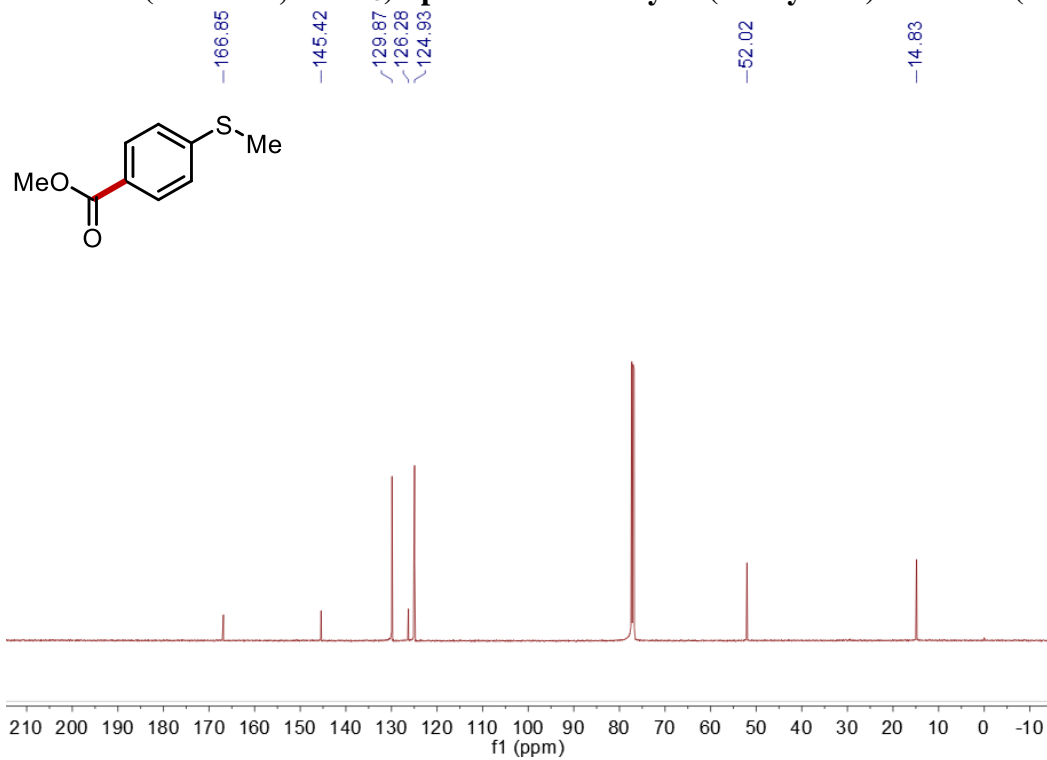
**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) Spectrum of methyl 4-(*tert*-butyl) benzoate (S18).**



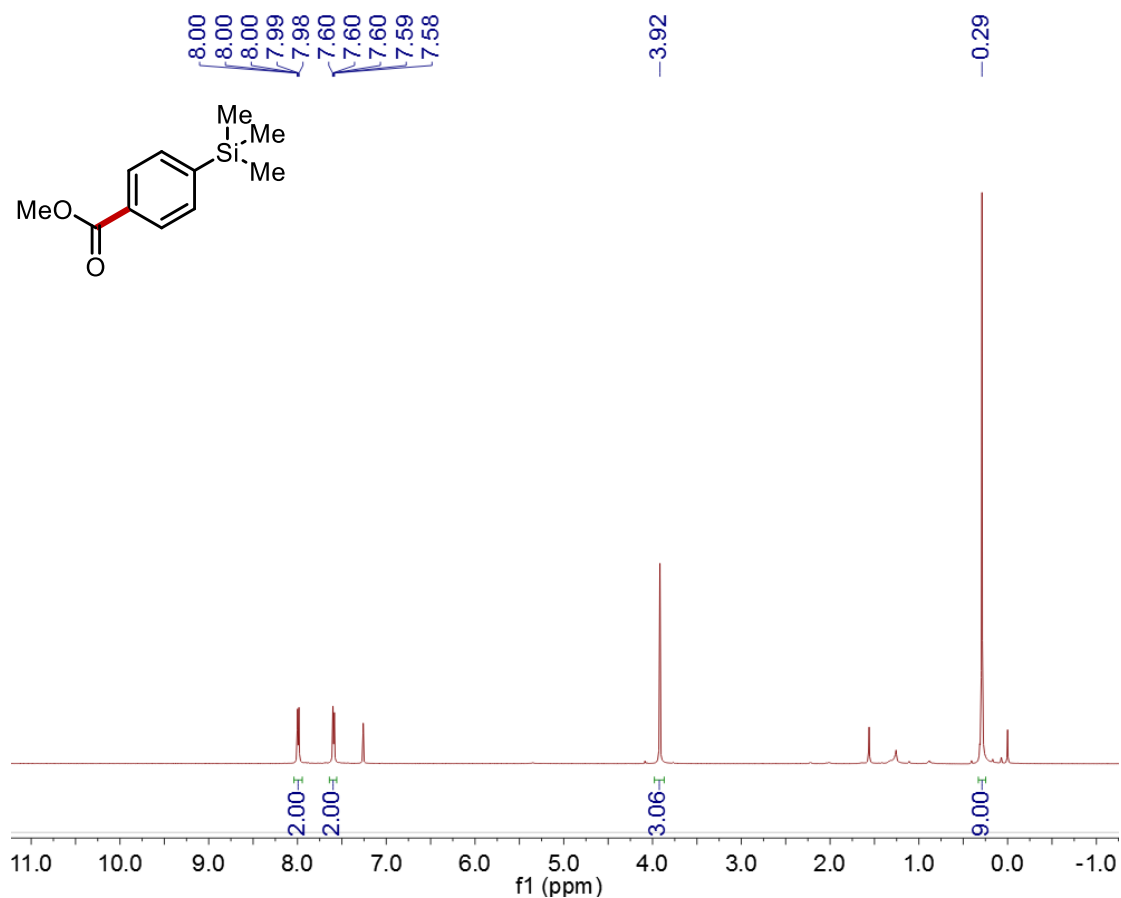
**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) Spectrum of methyl 4-(methylthio) benzoate (S19).**



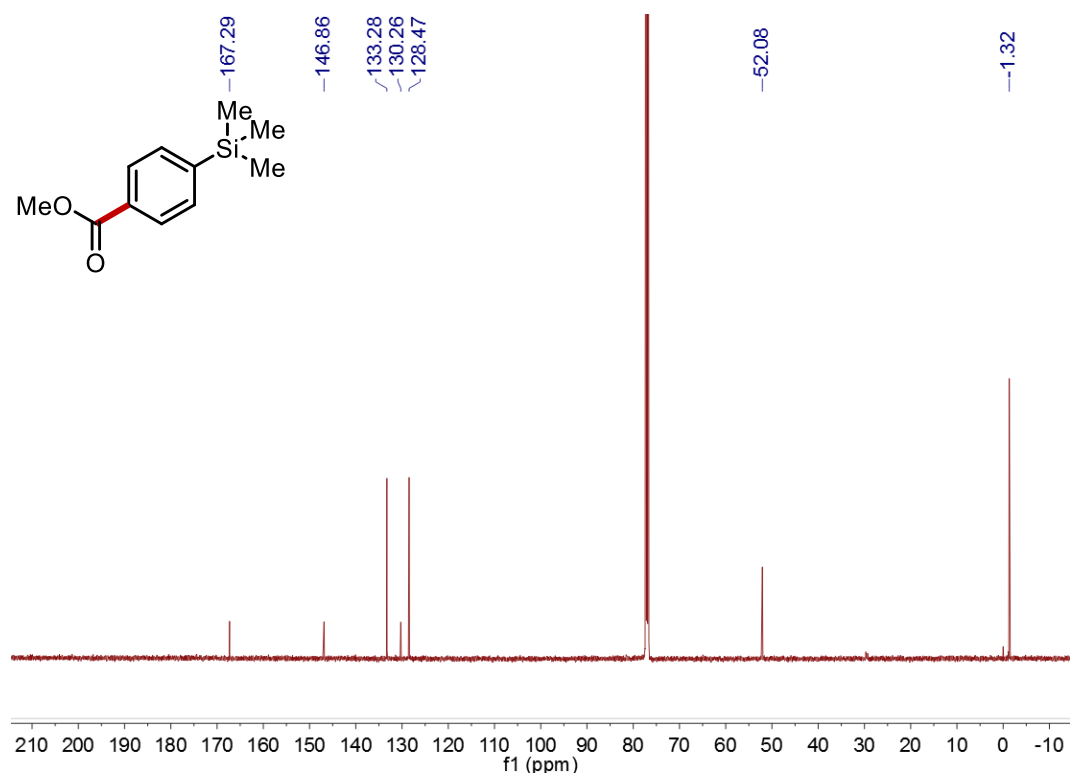
**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) Spectrum of methyl 4-(methylthio) benzoate (S19).**



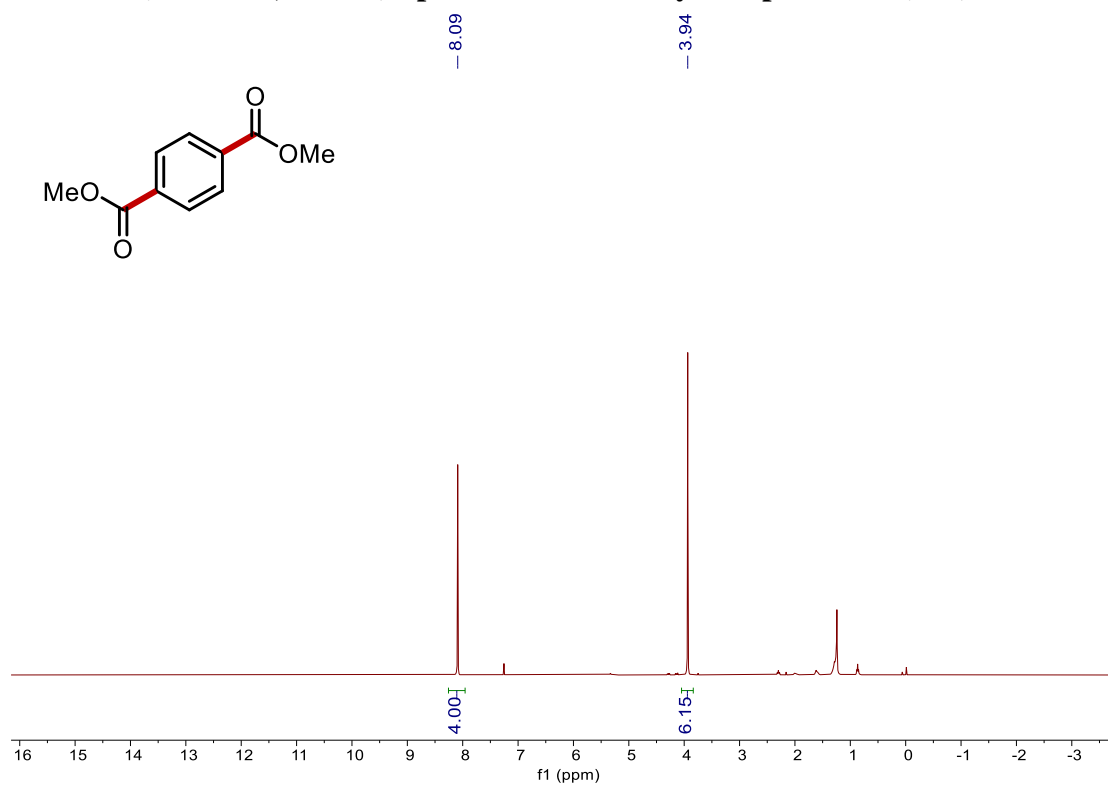
**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) Spectrum of methyl 4-(trimethylsilyl) benzoate (S20).**



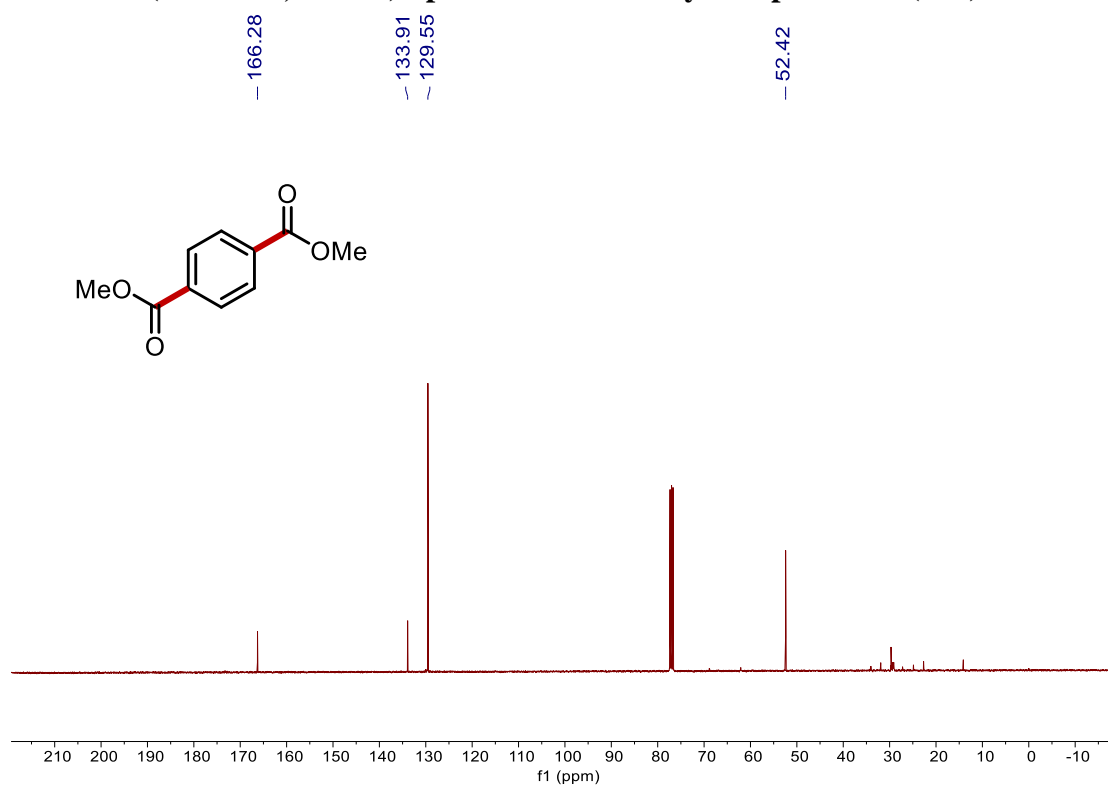
**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) Spectrum of methyl 4-(trimethylsilyl) benzoate (S20).**



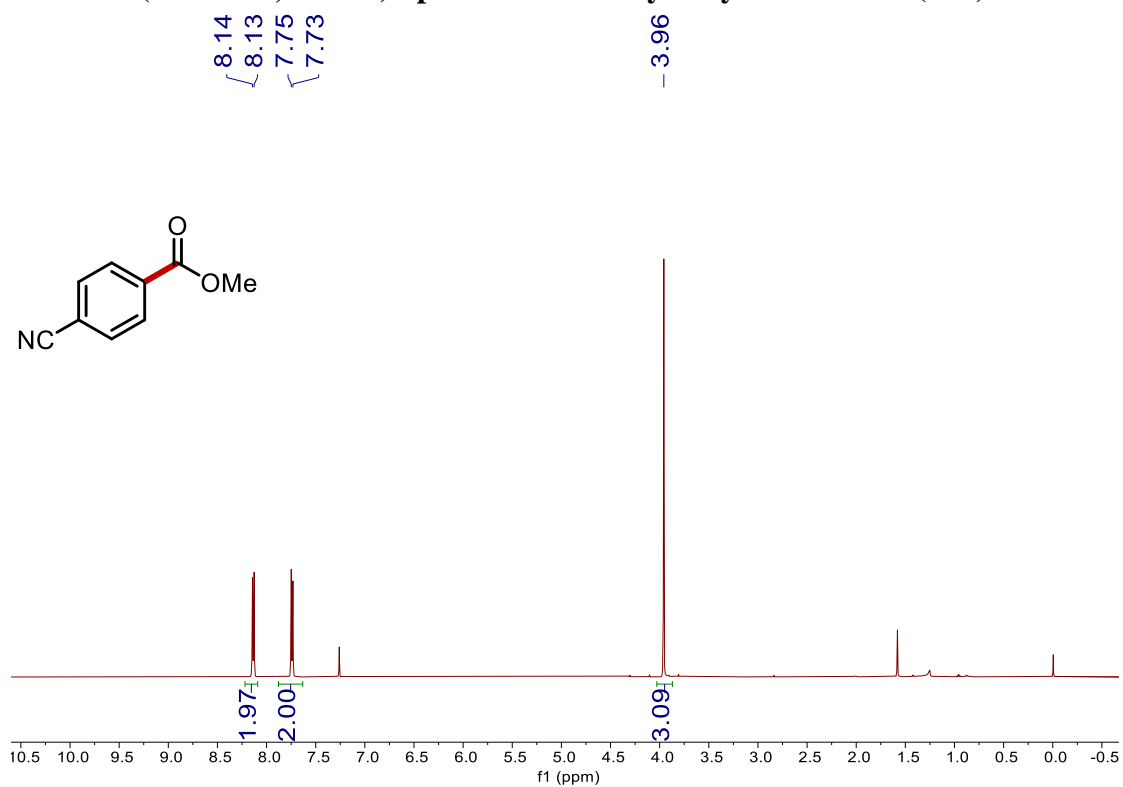
**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) Spectrum of Dimethyl terephthalate (S21).**



**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) Spectrum of Dimethyl terephthalate (S21).**



**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) Spectrum of Methyl 4-cyanobenzoate (S22).**



**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) Spectrum of Methyl 4-cyanobenzoate (S22).**

