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The ESI for *Org. Biomol. Chem.*, 2019, **17**, 1531–1534, originally published on 23<sup>rd</sup> January 2019, was updated on 21<sup>st</sup> March 2019. The catalyst was given incorrectly as Ru(bpy)<sub>2</sub>Cl<sub>2</sub> and has been changed to Ru(bpy)<sub>3</sub>Cl<sub>2</sub>·6H<sub>2</sub>O.

## Supporting Information

### For

## Radical alkylation of isocyanides with amino acid-/peptide-derived Katritzky salts via photoredox catalysis

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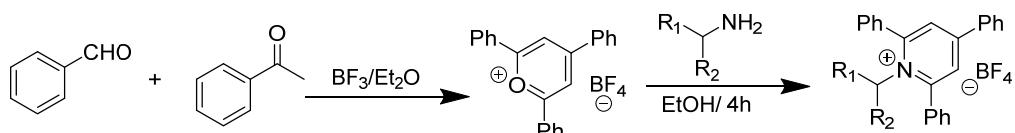
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## 1. General remarks

<sup>1</sup>H NMR spectra were recorded on 400 or 600 MHz (100 or 150 MHz for <sup>13</sup>C NMR, 376 or 564 MHz for <sup>19</sup>F NMR) agilent NMR spectrometer with CDCl<sub>3</sub> as the solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts were reported in parts per million (ppm,  $\delta$  scale) downfield from TMS at 0.00 ppm and referenced to the CDCl<sub>3</sub> at 7.26 ppm (for <sup>1</sup>H NMR) or 77.16 ppm (for <sup>13</sup>C NMR). <sup>19</sup>F NMR chemical shifts were determined relative to CFCl<sub>3</sub> at  $\delta$  0.00 ppm. Mass spectroscopy data of the products were collected on a GCT PremierTM (CI) and Agilent Technologies 1290 Infinity (ESI). Mass Spectrometer Infrared (FT-IR) spectra were recorded on a Varian 1000FT-IR,  $\nu_{\text{max}}$  in cm<sup>-1</sup>. Melting points were measured using SGW, X-4B and values are uncorrected. All commercially available reagents and solvents were used as received unless otherwise specified. The substrates were readily prepared according to known methods. (*Angew. Chem. Int. Ed.* **2017**, 56, 12336; *Org. Lett.* **2013**, 15, 5520; *Org. Chem. Front.* **2017**, 4, 2049).

## 2. Synthesis of pyridinium salts



Synthesis of triphenylpyrylium tetrafluoroborate: Benzaldehyde (1 equiv) and acetophenone (2 equiv) were placed in a closed two-necked flask equipped with a magnetic stirrer, then boron trifluoride etherate (2.5 equiv) was added dropwise under argon treatment. The mixture was reacted at 100 °C for two hours and cooled to ambient temperature. Methyl *tert*-butyl ether was added to the reaction mixture and the resulting suspension stirred at ambient temperature. The solid was collected by filtration and washed with methyl *tert*-butyl ether. Recrystallization by acetone and methyl *tert*-butyl ether to get pure light yellow solid.

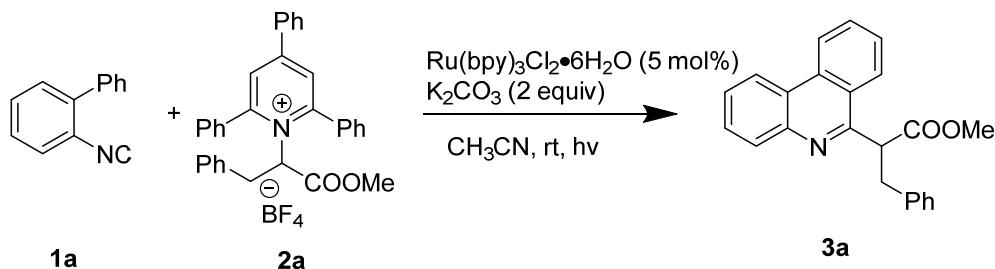
A closed flask equipped with a magnetic stirrer bar was charged with triphenylpyrylium tetrafluoroborate (1.0 equiv) and the corresponding primary amine (1.2 equiv). Ethanol (1.0 M) was added to the reaction vessel and the tube sealed. No precautions to protect the reaction mixture from air and moisture were taken. The reaction mixture was heated to 90 °C for 4 h and then cooled to ambient temperature. Methyl *tert*-butyl ether was added to the reaction mixture and the resulting suspension

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stirred at room temperature. The solid was collected by filtration and washed with methyl *tert*-butyl ether. After the operations required the solids were dried under reduced pressure to obtain the analytically pure pyridinium salts.

Amine hydrochlorides as starting materials: In case amine hydrochlorides were used as feedstocks for the pyridinium salts, the amine hydrochloride (1.2 equiv) was added to a clean and closed flask. Ethanol (1.0 M) and triethyl amine (1.2 equiv) were added. The resulting suspension was stirred for 30 min at ambient temperature. Triphenylpyrylium tetrafluoroborate (1.0 equiv) was added, the tube sealed and stirred for 4 h at 90 °C. Methyl *tert*-butyl ether was added to the reaction mixture and the resulting suspension stirred at room temperature for at least 1 h to complete the precipitation process. The solid was collected by filtration and washed with methyl *tert*-butyl ether. After the operations required the solids were dried under reduced pressure to obtain the analytically pure pyridinium salts. To remove water-soluble impurities, the collected solids were washed with water before washing with methyl *tert*-butyl ether.

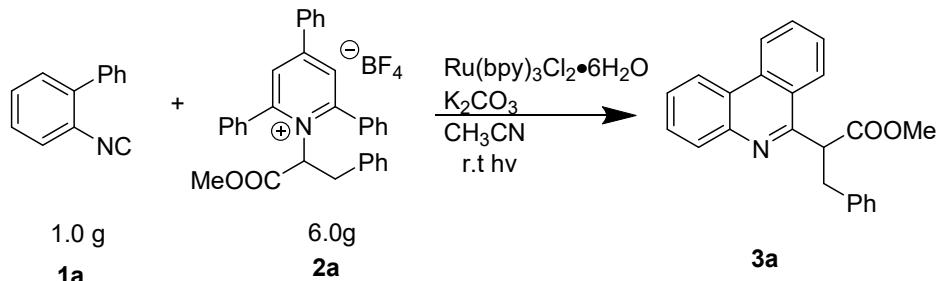
### 3. Typical experimental procedure



To a solution of **1a** (27 mg, 0.15 mmol), **2a** (167.2 mg, 0.3 mmol), Ru(bpy)<sub>3</sub>Cl<sub>2</sub>·6H<sub>2</sub>O (5.6 mg, 0.0075 mmol) in CH<sub>3</sub>CN (2 ml) was added K<sub>2</sub>CO<sub>3</sub> (41.5 mg, 0.3 mmol) at room temperature under N<sub>2</sub> atmosphere. The resulting mixture was stirred for 12 hours upon 22W blue LEDs irradiation. The solvent was then removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 100:1 to 30:1) to give **3a** as a yellow solid (48 mg, 94% yield).

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## 4. Gram-scale Reactions

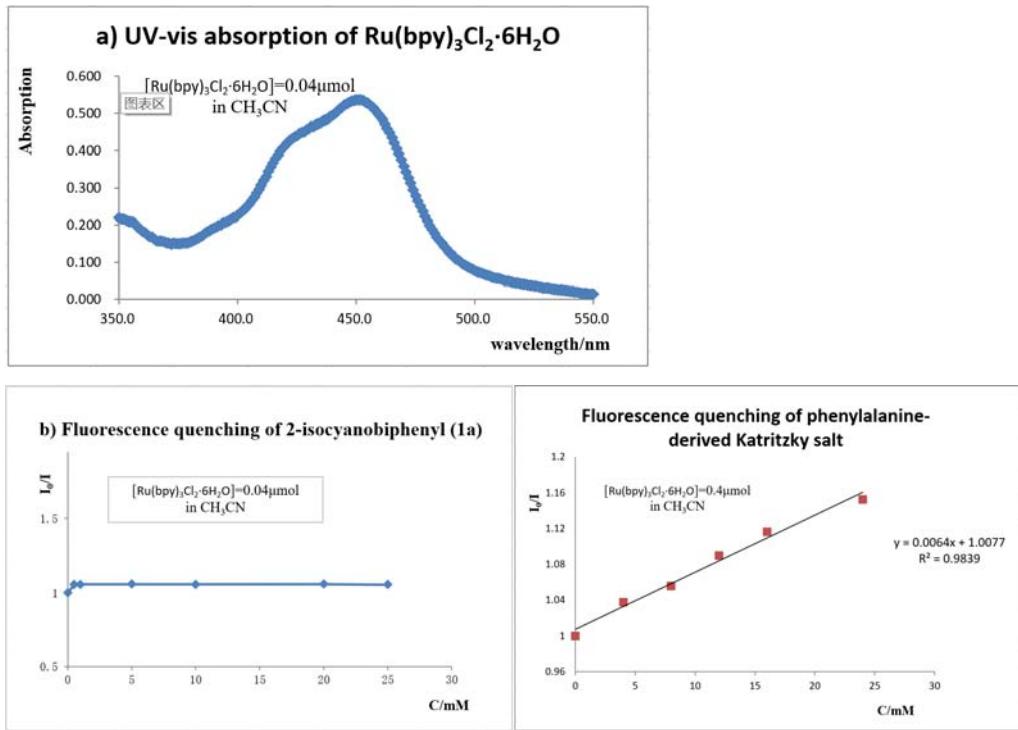


To a solution of **1a** (1.0 g, 5.6 mmol), **2a** (6.0 g, 11.2 mmol),  $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$  (209 mg, 0.28 mmol) in  $\text{CH}_3\text{CN}$  (35 ml) was added  $\text{K}_2\text{CO}_3$  (1.55 g, 11.2 mmol) at room temperature under  $\text{N}_2$  atmosphere. The resulting mixture was stirred for 12 hours upon 22W blue LEDs irradiation. The solvent was then removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 100:1 to 30:1) to give **3a** as a yellow solid (1.73 g, 90% yield).

## 5. Mechanistic studies

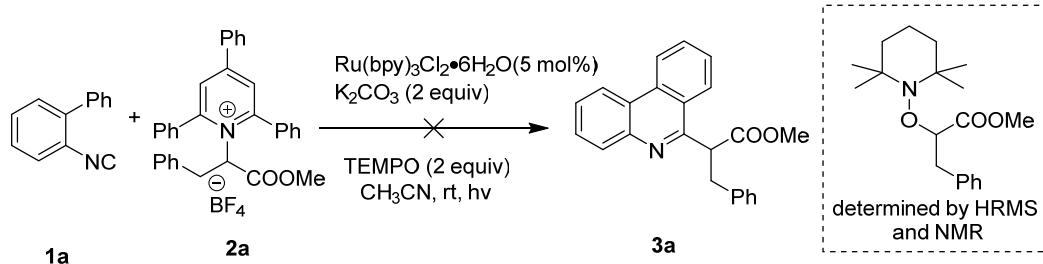
### 5.1 Fluorescence quenching experiment

Emission intensities were recorded using LS55 Luminescence Spectrometer for all experiments. Acetonitrile was degassed with argon for at least 30 minutes by ultrasonic treatment. All  $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$  solutions were excited at 450 nm and the emission intensity was collected at 580-630 nm. In a typical experiment, the  $\text{CH}_3\text{CN}$  solution of  $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$  (0.04  $\mu\text{M}$ ) was added the appropriate amount of quencher in a screw-top 1.0cm quartz cuvette. After degassing with argon for 10 min, the emission spectra of the samples were collected. The results showed that pyridinium salt **2a** quenched the photoexcited  $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$  effectively but isocyanobiphenyl **1a** did not.



**Figure S1.** a) UV-vis absorption spectrum of  $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ . b)  $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$  emission quenched by 2-isocyanobiphenyl **1a**. c)  $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$  emission quenched by Katritzky salt **2a**.

## 5.2 TEMPO-radical trapping experiment



When 2.0 equiv of TEMPO was added to the reaction of **1a** with **2a** under the standard conditions, no desired product (**3a**) was detected by TLC. A TEMPO-trapped product was determined by HRMS and NMR.

**Methyl 3-phenyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propanoate:** colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 (t,  $J = 7.0$  Hz, 2H), 7.27 (d,  $J = 6.8$  Hz, 1H), 7.25 – 7.19 (m, 2H), 4.52 (dd,  $J = 10.0, 5.4$  Hz, 1H), 3.57 (s, 3H), 3.32 (dd,  $J = 13.1, 5.2$  Hz, 1H), 3.11 – 3.01 (m, 1H), 1.57 – 1.45 (m, 4H), 1.42 – 1.32 (m, 2H), 1.30 (s, 3H), 1.19 (s, 6H), 1.09 (s, 3H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  172.9, 135.8, 129.2, 128.2, 126.5, 86.4, 60.4, 59.3, 50.9, 40.1, 40.0, 38.4, 33.4, 32.7, 20.1, 19.9, 16.9; HRMS (CI) calcd  $\text{C}_{19}\text{H}_{30}\text{NO}_3$  [ $\text{M} + \text{H}$ ] $^+$ : 320.2226, found: 320.2234.

**Multiple Mass Analysis: 3 mass(es) processed - displaying only valid results**

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 Element prediction: Off

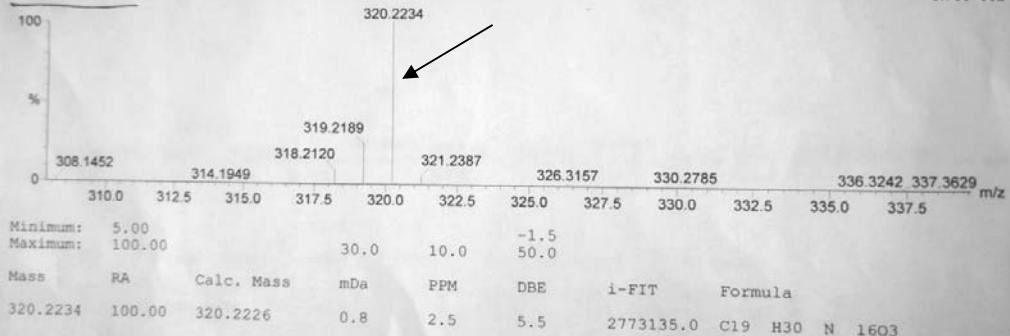
Monoisotopic Mass, Odd and Even Electron Ions  
 18 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-19 H: 0-30 N: 0-1 16O: 0-3

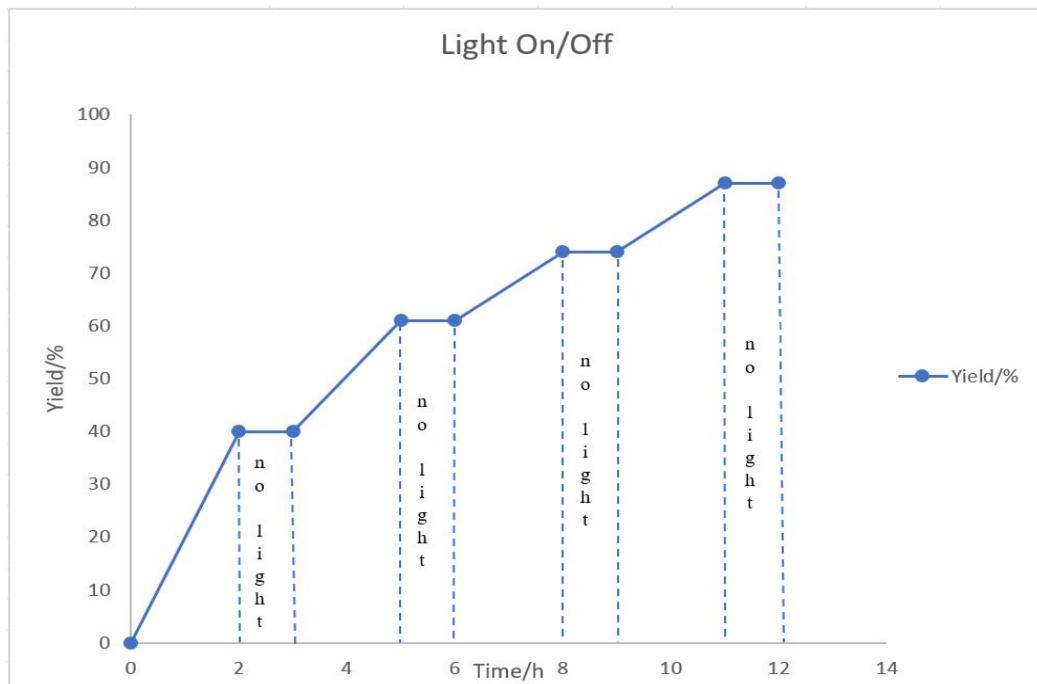
DEFAULT

SD46-115 134 (2.233) Cr (134.140-(88.96+63.73))

TOF MS Cl+  
5.78e+002

**Figure S2.** HRMS trace of the TEMPO trapping experiment.

### 5.3 Light on/off experiment

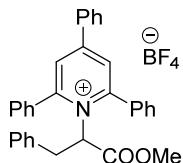


**Figure S3.** Profile of the reaction with the light on/off over time. Yield was determined by <sup>1</sup>H NMR.

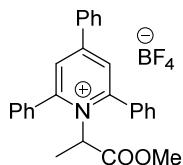
## 6 References for known products

Entry	References	Compounds
1	<i>Angew. Chem. Int. Ed.</i> <b>2017</b> , 56, 12336–12339.	<b>2a, 2b, 2d, 2f, 2h</b>

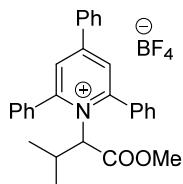
## 7 Characterization of the substrates and products



**(1-Methoxy-1-oxo-3-phenylpropan-2-yl)-2,4,6-triphenylpyridin-1-iutmtrafluoro borate (2a):**  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 (s, 2H), 7.86 – 7.69 (m, 4H), 7.60 (t,  $J$  = 7.2 Hz, 2H), 7.57 – 7.40 (m, 9H), 7.14 – 7.05 (m, 3H), 6.77 (d,  $J$  = 7.3 Hz, 2H), 5.64 (dd,  $J$  = 7.5, 3.7 Hz, 1H), 3.69 (s, 3H), 3.49 – 3.42 (m, 1H), 2.93 (dd,  $J$  = 14.4, 8.0 Hz, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  168.0, 157.1, 157.0, 136.4, 133.8, 132.5, 132.4, 131.7, 129.8, 129.6, 129.2, 129.1, 128.72, 128.66, 128.0, 127.3, 70.3, 53.9, 37.8;  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -152.80 (d,  $J$  = 4.5 Hz), -152.86 (d,  $J$  = 3.5 Hz).

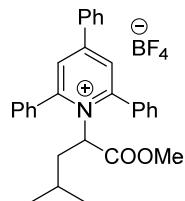


**(1-Methoxy-1-oxopropan-2-yl)-2,4,6-triphenylpyridin-1-iutmtrafluoroborate (2b):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 (s, 2H), 7.81 – 7.70 (m, 4H), 7.65 – 7.50 (m, 9H), 7.47 (t,  $J$  = 7.2 Hz, 2H), 5.52 (q,  $J$  = 7.0 Hz, 1H), 3.66 (s, 3H), 1.46 (d,  $J$  = 6.8 Hz, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  168.9, 157.0, 156.8, 134.0, 132.7, 132.3, 131.5, 129.7, 129.3, 129.2, 129.1, 128.5, 127.9, 64.6, 53.8, 17.3;  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -153.17 (s), -153.22 (s).

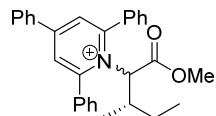


**(1-Methoxy-3-methyl-1-oxobutan-2-yl)-2,4,6-triphenylpyridin-1-iutmtrafluoroborate (2c):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (s, 2H), 7.87 (d,  $J$  = 7.2 Hz, 2H), 7.75 – 7.54 (m, 9H), 7.53 – 7.46 (m, 4H), 5.14 (d,  $J$  = 10.2 Hz, 1H), 3.74 (s, 3H), 2.12 – 2.01 (m, 1H), 0.73 (d,  $J$  = 6.3 Hz, 3H), 0.71 (d,  $J$  = 7.2 Hz, 3H);  $^{13}\text{C}$  NMR (150 MHz,

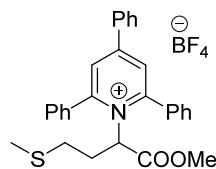
$\text{CDCl}_3$ )  $\delta$  167.0, 157.2, 157.1, 133.1, 133.0, 132.0, 130.0, 129.6, 129.5, 129.0, 128.8, 127.9, 73.7, 53.9, 30.1, 22.4, 19.3;  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -153.22 (s), -153.28 (s); HRMS (ESI) calcd  $\text{C}_{29}\text{H}_{28}\text{NO}_2[\text{M}-\text{BF}_4]^+$ : 422.2115, found: 422.2114.



**(1-Methoxy-4-methyl-1-oxopentan-2-yl)-2,4,6-triphenylpyridin-1-iumtetrafluoroborate (2d):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89 (s, 2H), 7.80 (d,  $J = 7.3$  Hz, 2H), 7.70 (br, 2H), 7.62 – 7.52 (m, 7H), 7.51 – 7.45 (m, 2H), 5.46 (dd,  $J = 7.8, 2.8$  Hz, 1H), 3.74 (s, 3H), 1.76 – 1.64 (m, 1H), 1.62 – 1.50 (m, 1H), 1.35 – 1.24 (m, 1H), 0.56 (d,  $J = 6.5$  Hz, 3H), 0.41 (d,  $J = 6.4$  Hz, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  168.7, 156.8, 156.7, 133.7, 132.5, 132.3, 131.6, 129.6, 129.4, 129.1, 128.5, 127.9, 67.4, 53.9, 40.4, 26.1, 22.3, 20.7.  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -153.01 (s), -153.07 (s).

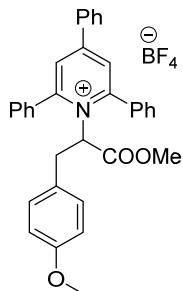


**(1-Methoxy-3-methyl-1-oxopentan-2-yl)-2,4,6-triphenylpyridin-1-iumtetrafluoroborate (2e):** Two isomers, *d.r.*: 1.1:1;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 (s, 2H), 7.93 – 7.87 (m, 2H), 7.68 (s, 1H), 7.65 – 7.58 (m, 7H), 7.56 – 7.46 (m, 5H), 5.32 (d,  $J = 10.2$  Hz, 0.5H)/5.18 (d,  $J = 10.2$  Hz, 0.6H), 3.77 (s, 1.6H)/ 3.74 (s, 1.3H), 2.02 – 1.93 (m, 0.6H)/ 1.75 – 1.66 (m, 0.9H), 1.41 – 1.34 (m, 0.6H)/ 1.01 – 0.91 (m, 0.9H), 1.30 – 1.18 (m, 1.6H)/ 0.50 – 0.43 (m, 1.3H), 0.84 (t, 2.3H)/ 0.70 (t,  $J = 7.6$  Hz, 3H), 0.82 – 0.75 (m, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  167.0, 166.8, 157.10, 157.06, 133.1, 133.0, 131.9, 129.9, 129.8, 129.7, 129.4, 129.2 128.9, 128.8, 128.6, 127.8, 73.5, 71.3, 53.93, 53.87, 36.0, 35.6, 27.8, 25.4, 18.5, 15.2, 11.1, 9.5;  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -153.28 (s), -153.34 (s); HRMS (ESI) calcd  $\text{C}_{30}\text{H}_{30}\text{NO}_2[\text{M}-\text{BF}_4]^+$ : 436.2271, found: 436.2270.

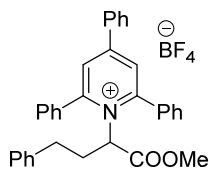


**(1-Methoxy-4-(methylthio)-1-oxobutan-2-yl)-2,4,6-triphenylpyridin-1-iumtetrafluoroborate (2f):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 (s, 2H), 7.74 (dd,  $J = 31.7, 8.1$  Hz, 4H), 7.63 – 7.50 (m, 7H), 7.46 (t,  $J = 7.3$  Hz, 2H), 5.92 (dd,  $J = 7.7$  Hz, 1H), 3.73 (s, 3H), 2.37 – 2.16 (m, 3H), 1.95 – 1.85 (m, 1H), 1.84 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,

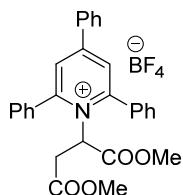
$\text{CDCl}_3$ )  $\delta$  168.4, 156.9, 133.8, 132.5, 132.2, 131.5, 129.6, 129.1, 128.5, 66.7, 53.9, 31.4, 30.8, 14.7;  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -152.74 (s), -152.79 (s).



**1-(1-Methoxy-3-(4-methoxyphenyl)-1-oxopropan-2-yl)-2,4,6-triphenylpyridin-1-i um tetrafluoroborate (2g):**  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (s, 2H), 7.84 – 7.68 (m, 4H), 7.59 (t,  $J$  = 7.4 Hz, 2H), 7.56 – 7.50 (m, 5H), 7.50 – 7.36 (m, 4H), 6.67 (d,  $J$  = 8.2 Hz, 2H), 6.60 (d,  $J$  = 7.8 Hz, 2H), 5.58 (dd,  $J$  = 7.1, 4.9 Hz, 1H), 3.68 (d,  $J$  = 9.9 Hz, 6H), 3.31 (dd,  $J$  = 14.5, 4.3 Hz, 1H), 2.89 (dd,  $J$  = 14.6, 7.7 Hz, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  167.8, 158.7, 156.9, 133.6, 132.5, 132.2, 131.6, 130.1, 129.7, 129.5, 129.2, 128.6, 128.0, 127.8, 114.0, 70.4, 55.3, 53.8, 36.9;  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -152.75 – -152.79 (m), -152.80 – -152.85 (m); HRMS (ESI) calcd  $\text{C}_{34}\text{H}_{30}\text{NO}_3[\text{M}-\text{BF}_4]^+$ : 500.2220, found: 500.2217.

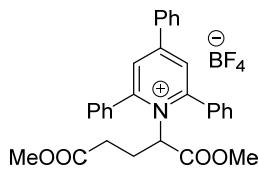


**1-(1-Methoxy-1-oxo-4-phenylbutan-2-yl)-2,4,6-triphenylpyridin-1-i umtetrafluoroborate (2h):**  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (s, 2H), 7.84 – 7.65 (m, 4H), 7.59 – 7.43 (m, 11H), 7.16 – 7.09 (m, 3H), 6.92 (d,  $J$  = 6.5 Hz, 2H), 5.37 (dd,  $J$  = 8.5, 2.1 Hz, 1H), 3.71 (s, 3H), 2.48 – 2.36 (m, 3H), 2.03 – 1.96 (m, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  168.7, 157.1, 156.9, 138.7, 134.0, 132.6, 132.4, 131.5, 129.8, 129.2, 128.71, 128.65, 128.56, 128.1, 126.6, 68.1, 53.8, 33.5, 33.2;  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -152.86 (s), -152.92 (s).

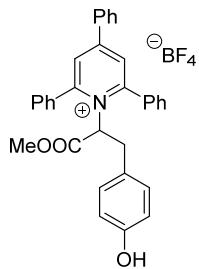


**1-(1,4-Dimethoxy-1,4-dioxobutan-2-yl)-2,4,6-triphenylpyridin-1-i umtetrafluoroborate (2i):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 (s, 3H), 7.79 (t,  $J$  = 11.8 Hz, 3H), 7.73 – 7.37 (m, 11H), 6.22 (d,  $J$  = 9.4 Hz, 1H), 3.63 (s, 3H), 3.53 (s, 3H), 3.38 (dd,  $J$  = 17.4 Hz, 1H), 2.55 (dd,  $J$  = 17.4, 9.7 Hz, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  169.6, 167.74, 167.70, 157.4, 133.9, 132.5, 131.7, 129.8, 129.4, 128.6, 64.1, 54.1, 52.6, 36.0;

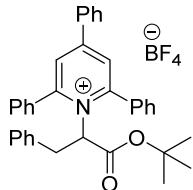
<sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -152.78 (d, *J* = 4.1 Hz), -152.83 (s); HRMS (ESI) calcd C<sub>29</sub>H<sub>26</sub>NO<sub>4</sub>[M-BF<sub>4</sub>]<sup>+</sup>: 452.1856, found: 452.1853.



**1-(1,5-Dimethoxy-1,5-dioxopentan-2-yl)-2,4,6-triphenylpyridin-1-i umtetrafluoroborate (2j):** <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.93 (s, 2H), 7.83 (d, *J* = 7.7 Hz, 2H), 7.80 – 7.52 (m, 11H), 7.49 (t, *J* = 7.5 Hz, 2H), 5.60 (t, *J* = 6.2 Hz, 1H), 3.71 (s, 3H), 3.46 (s, 3H), 2.26 (tt, *J* = 13.5, 6.9 Hz, 1H), 2.21 – 2.14 (m, 2H), 2.06 (tt, *J* = 14.6, 7.3 Hz, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 172.1, 168.2, 157.2, 133.7, 132.5, 132.4, 131.7, 129.8, 129.4, 128.6, 128.1, 67.6, 54.0, 51.8, 30.8, 27.0; <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -153.06 (s), -153.11 (s); HRMS (ESI) calcd C<sub>30</sub>H<sub>28</sub>NO<sub>4</sub>[M-BF<sub>4</sub>]<sup>+</sup>: 466.2013, found: 466.2012.

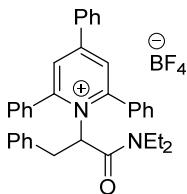


**1-(3-(4-hydroxyphenyl)-1-methoxy-1-oxopropan-2-yl)-2,4,6-triphenylpyridin-1-i um tetrafluoroborate(2k):** <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.92 (s, 2H), 7.86 – 7.83 (m, 2H), 7.79 – 7.46 (m, 13H), 6.62 (d, *J* = 8.5 Hz, 2H), 6.44 (d, *J* = 8.4 Hz, 2H), 5.60 (t, *J* = 6.7 Hz, 1H), 3.70 (s, 3H), 3.15 (dd, *J* = 14.8, 7.1 Hz, 1H), 2.89 (dd, *J* = 14.8, 6.4 Hz, 1H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 168.2, 157.1, 156.3, 132.9, 132.2, 131.9, 130.0, 129.8, 129.4, 128.7, 116.3, 70.9, 53.9, 36.7; <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -151.85 (s), -151.90 (s); HRMS (ESI) calcd C<sub>33</sub>H<sub>28</sub>NO<sub>3</sub>[M-BF<sub>4</sub>]<sup>+</sup>: 486.2064, found: 486.2062.

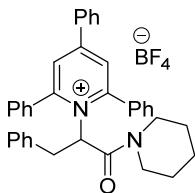


**(1-(tert-Butoxy)-1-oxo-3-phenylpropan-2-yl)-2,4,6-triphenylpyridin-1-i umtetrafluoroborate (2l):** <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.95 (d, *J* = 2.9 Hz, 2H), 7.88 – 7.78 (m, 3H), 7.79 – 7.44 (m, 12H), 7.07 (dd, *J* = 9.3, 5.7 Hz, 3H), 6.83 – 6.76 (m, 2H), 5.55 (dd, *J* = 8.3, 2.8 Hz, 1H), 3.45 – 3.39 (m, 1H), 2.48 – 2.41 (m, 1H), 1.35 (s, 9H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 167.84, 167.80, 156.8, 146.0, 137.3, 137.2, 134.0, 133.0, 132.4, 131.5, 129.8, 128.9, 128.6, 128.5, 127.0, 85.6, 72.0, 37.8, 27.8; <sup>19</sup>F NMR

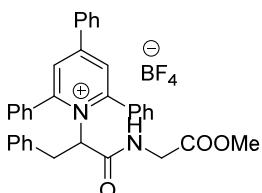
NMR (564 MHz, CDCl<sub>3</sub>) δ -152.65 (s), -152.70 (s); HRMS (ESI) calcd C<sub>36</sub>H<sub>34</sub>NO<sub>2</sub> [M-BF<sub>4</sub>]<sup>+</sup>: 512.2584, found: 512.2586.



**1-(1-(Diethylamino)-1-oxo-3-phenylpropan-2-yl)-2,4,6-triphenylpyridin-1-iumtetrafluoroborate (2m):** <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.04 (br, 2H), 7.85 (s, 2H), 7.76 (d, *J* = 7.7 Hz, 2H), 7.74 – 7.49 (m, 9H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.16 – 7.07 (m, 3H), 6.87 (d, *J* = 7.5 Hz, 2H), 5.96 (dd, *J* = 9.5, 3.4 Hz, 1H), 3.53 (dd, *J* = 14.3, 3.2 Hz, 1H), 3.23 – 3.04 (m, 2H), 2.96 – 2.85 (m, 1H), 2.26 – 2.10 (m, 2H), 0.98 (t, *J* = 6.2 Hz, 3H), 0.37 (t, *J* = 6.3 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 165.2, 157.7, 155.8, 145.8, 135.8, 133.9, 133.6, 132.4, 131.2, 129.9, 129.7, 129.0, 128.93, 128.87, 128.5, 128.4, 127.4, 70.9, 41.3, 40.6, 39.1, 12.8, 12.2; <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -152.75 (s), -152.80 (s); HRMS (ESI) calcd C<sub>36</sub>H<sub>35</sub>N<sub>2</sub>O [M-BF<sub>4</sub>]<sup>+</sup>: 511.2744, found: 511.2743.

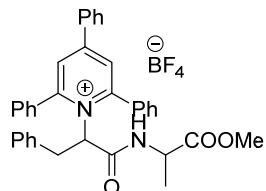


**1-(1-Oxo-3-phenyl-1-(piperidin-1-yl)propan-2-yl)-2,4,6-triphenylpyridin-1-iumtetrafluoroborate (2n):** <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.27 (br, 2H), 7.83 (s, 2H), 7.77 (d, *J* = 7.8 Hz, 2H), 7.65 – 7.43 (m, 11H), 7.14 (t, *J* = 7.4 Hz, 2H), 7.10 (t, *J* = 7.2 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 2H), 6.18 (dd, *J* = 10.5, 3.1 Hz, 1H), 3.79 – 3.68 (m, 1H), 3.61 (dd, *J* = 13.5, 2.7 Hz, 1H), 2.86 – 2.73 (m, 1H), 2.47 (dd, *J* = 13.0, 11.1 Hz, 1H), 1.98 – 1.88 (m, 1H), 1.62 – 1.51 (m, 1H), 1.47 – 1.38 (m, 1H), 1.34 – 1.08 (m, 3H), 0.67 – 0.53 (m, 1H), 0.28 – 0.13 (m, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 165.9, 157.8, 155.4, 135.7, 134.6, 133.8, 132.3, 131.0, 129.9, 129.7, 129.5, 129.0, 128.4, 128.3, 127.6, 71.2, 46.1, 43.8, 39.6, 24.9, 24.5, 23.5; <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -152.70 (s), -152.75 (s); HRMS (ESI) calcd C<sub>37</sub>H<sub>35</sub>N<sub>2</sub>O [M-BF<sub>4</sub>]<sup>+</sup>: 523.2744, found: 523.2739.

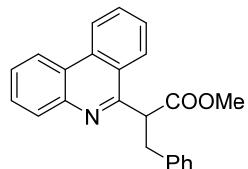


**1-(1-((2-methoxy-2-oxoethyl)amino)-1-oxo-3-phenylpropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2o):** <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.89 (s, 2H), 7.79 (d, *J* = 7.7 Hz, 2H), 7.64 (br, 2H), 7.61 – 7.36 (m, 11H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 2H), 6.69 (d, *J* = 7.5 Hz, 2H), 5.74 (t, *J* = 7.0 Hz, 1H), 4.01 – 3.88

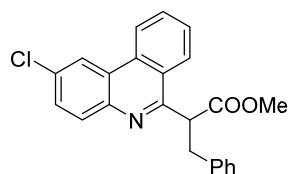
(m, 2H), 3.70 (s, 3H), 3.26 – 3.15 (m, 2H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  169.3, 167.0, 157.9, 156.6, 135.6, 133.7, 132.63, 132.56, 131.6, 129.9, 129.7, 129.3, 129.2, 128.8, 128.5, 128.0, 127.8, 71.4, 52.4, 41.9, 36.6;  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -152.45 (s), -152.50 (s); HRMS (ESI) calcd  $\text{C}_{35}\text{H}_{31}\text{N}_2\text{O}_3$  [M-BF<sub>4</sub>]<sup>+</sup>: 527.2329, found: 527.2330.



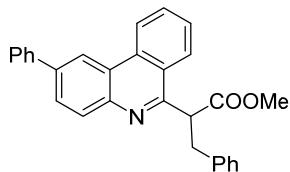
**1-(1-((1-methoxy-1-oxopropan-2-yl)amino)-1-oxo-3-phenylpropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2p):** Two isomers, *d.r.*: 1.3:1;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (s, 2H), 7.83 (d,  $J$  = 8.2 Hz, 2H), 7.77 – 7.71 (m, 3H), 7.65 – 7.51 (m, 10H), 7.19 – 7.13 (m, 3H), 6.77 – 6.72 (m, 2H), 5.79 (dd,  $J$  = 9.0, 4.3 Hz, 0.64H)/5.74 (dd,  $J$  = 8.1, 5.6 Hz, 0.5H), 4.35 – 4.25 (m, 1H), 3.74 (s, 1.3H)/3.63 (s, 1.7H), 3.65 (dd,  $J$  = 14.9, 4.3 Hz, 0.81H)/3.48 (dd,  $J$  = 15.0, 5.6 Hz, 0.64H), 2.85 (dd,  $J$  = 14.9, 8.2 Hz, 0.57H)/2.59 (dd,  $J$  = 14.9, 9.1 Hz, 0.75H), 1.33 (d,  $J$  = 7.1 Hz, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  172.3, 171.9, 167.7, 166.8, 157.4, 157.0, 156.8, 136.0, 136.0, 134.2, 133.2, 133.0, 132.4, 131.5, 129.8, 129.6, 129.5, 129.3, 129.2, 128.7, 128.6, 128.6, 128.6, 128.2, 128.0, 127.9, 71.7, 71.4, 52.70, 52.65, 49.4, 37.3, 37.2, 29.9, 17.7, 17.2;  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -152.21 (s), -152.26 (s); HRMS (ESI) calcd  $\text{C}_{36}\text{H}_{33}\text{N}_2\text{O}_3$  [M-BF<sub>4</sub>]<sup>+</sup>: 541.2486, found: 541.2484.



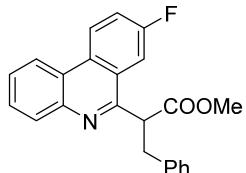
**Methyl 2-(phenanthridin-6-yl)-3-phenylpropanoate (3a):** Yellow solid; m.p. 126-127 °C; 94% yield (48 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.63 (d,  $J$  = 8.2 Hz, 1H), 8.53 (d,  $J$  = 8.1 Hz, 1H), 8.30 – 8.21 (m, 2H), 7.81 (t,  $J$  = 7.5 Hz, 1H), 7.74 (t,  $J$  = 7.4 Hz, 1H), 7.70 – 7.61 (m, 2H), 7.33 (d,  $J$  = 7.2 Hz, 2H), 7.24 (t,  $J$  = 7.2 Hz, 2H), 7.17 (t,  $J$  = 7.0 Hz, 1H), 5.03 (t,  $J$  = 6.1 Hz, 1H), 3.79 (dd,  $J$  = 13.8, 8.1 Hz, 1H), 3.68 – 3.58 (m, 4H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  172.7, 157.4, 143.5, 139.8, 133.3, 130.5, 129.2, 128.7, 128.4, 127.6, 127.1, 126.4, 125.6, 125.2, 123.8, 122.7, 121.9, 52.36, 52.32, 37.2; FT-IR (thin film, KBr):  $\nu$  (cm<sup>-1</sup>) 2918, 1745, 1722, 1161, 751; HRMS (CI) calcd  $\text{C}_{23}\text{H}_{20}\text{NO}_2$  [M + H]<sup>+</sup>: 342.1494, found: 342.1489.



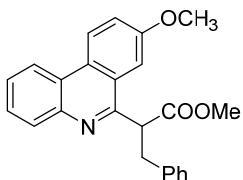
**Methyl 2-(2-chlorophenanthridin-6-yl)-3-phenylpropanoate (3b):** Yellowish solid; m.p. 115–116 °C; 88% yield (49 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.51 (d, *J* = 8.3 Hz, 1H), 8.47 (s, 1H), 8.25 (d, *J* = 8.3 Hz, 1H), 8.15 (d, *J* = 8.7 Hz, 1H), 7.81 (t, *J* = 7.6 Hz, 1H), 7.71 – 7.65 (m, 2H), 7.29 (d, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 4.99 (t, *J* = 7.3 Hz, 1H), 3.75 (dd, *J* = 14.0, 8.0 Hz, 1H), 3.66 (s, 3H), 3.60 (dd, *J* = 14.0, 6.6 Hz, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 172.6, 157.7, 142.0, 139.6, 133.0, 132.3, 131.9, 130.8, 129.3, 129.2, 128.5, 128.3, 126.5, 125.7, 125.4, 124.9, 122.7, 121.7, 52.4, 52.3, 37.1; FT-IR (thin film, KBr):  $\nu$  (cm<sup>-1</sup>) 1733, 1537, 1150, 766, 695; HRMS (CI) calcd C<sub>23</sub>H<sub>19</sub><sup>35</sup>ClNO<sub>2</sub> [M + H]<sup>+</sup>: 376.1104, found: 376.1098.



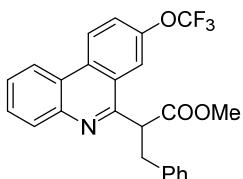
**Methyl 3-phenyl-2-(2-phenylphenanthridin-6-yl)propanoate (3c):** Yellow solid; m.p. 147–148 °C; 70% (42 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.76 – 8.66 (m, 2H), 8.31 – 8.21 (m, 2H), 7.96 (d, *J* = 8.3 Hz, 1H), 7.85 – 7.73 (m, 3H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 1H), 7.30 (d, *J* = 7.3 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 2H), 7.14 (t, *J* = 7.1 Hz, 1H), 5.00 (t, *J* = 7.2 Hz, 1H), 3.77 (dd, *J* = 13.9, 8.0 Hz, 1H), 3.64 (s, 3H), 3.62 – 3.57 (m, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 172.7, 157.4, 143.0, 141.1, 140.0, 139.8, 133.4, 130.9, 130.5, 129.2, 129.1, 128.53, 128.47, 128.2, 127.74, 127.69, 126.4, 125.7, 125.4, 124.0, 122.7, 120.3, 52.40, 52.37, 37.2; FT-IR (thin film, KBr):  $\nu$  (cm<sup>-1</sup>) 1730, 1251, 1212, 1149, 760; HRMS (CI) calcd C<sub>29</sub>H<sub>24</sub>NO<sub>2</sub> [M + H]<sup>+</sup>: 418.1807, found: 418.1806.



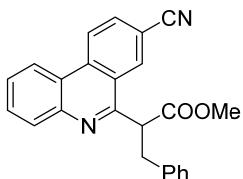
**Methyl 2-(8-fluorophenanthridin-6-yl)-3-phenylpropanoate (3d):** White solid; m.p. 121–122 °C; 85% (46 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.54 (dd, *J* = 8.9, 5.4 Hz, 1H), 8.40 (d, *J* = 8.1 Hz, 1H), 8.21 (d, *J* = 8.1 Hz, 1H), 7.84 (d, *J* = 9.4 Hz, 1H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 8.4 Hz, 1H), 7.26 (d, *J* = 9.4 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 2H), 7.13 (t, *J* = 7.3 Hz, 1H), 4.85 (t, *J* = 7.3 Hz, 1H), 3.74 (dd, *J* = 13.9, 7.7 Hz, 1H), 3.66 – 3.57 (m, 4H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 172.4, 161.5 (d, *J* = 248.5 Hz), 156.4 (d, *J*<sub>C-F</sub> = 3.8 Hz), 143.2, 139.5, 130.6, 129.9, 129.2, 128.6, 128.5, 127.5, 126.6 (d, *J*<sub>C-F</sub> = 7.6 Hz), 125.2 (d, *J*<sub>C-F</sub> = 8.5 Hz), 123.4, 121.7, 119.6 (d, *J*<sub>C-F</sub> = 23.8 Hz), 110.3 (d, *J* = 22.0 Hz), 52.42, 52.35, 37.0; <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -111.40 – -111.47 (m, 1F); FT-IR (thin film, KBr):  $\nu$  (cm<sup>-1</sup>) 2923, 2227, 1739, 1209, 757; HRMS (CI) calcd C<sub>23</sub>H<sub>19</sub>FNO<sub>2</sub> [M + H]<sup>+</sup>: 360.1400, found: 360.1396.



**Methyl 2-(8-methoxyphenanthridin-6-yl)-3-phenylpropanoate (3e):** Yellowish solid; m.p. 124–125 °C; 76% (42mg); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.48 (d, *J* = 9.0 Hz, 1H), 8.40 (d, *J* = 8.1 Hz, 1H), 8.17 (d, *J* = 8.1 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.51 (d, *J* = 2.1 Hz, 1H), 7.39 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.27 (d, *J* = 7.3 Hz, 2H), 7.19 (t, *J* = 16.6, 9.0 Hz, 2H), 7.13 (t, *J* = 7.3 Hz, 1H), 4.86 (t, *J* = 7.2 Hz, 1H), 3.88 (s, 3H), 3.75 (dd, *J* = 14.0, 8.0 Hz, 1H), 3.62 (s, 3H), 3.57 (dd, *J* = 14.0, 6.4 Hz, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 172.8, 158.8, 156.5, 142.8, 139.9, 130.4, 129.2, 128.5, 127.7, 127.6, 127.1, 126.5, 126.4, 124.3, 124.0, 121.5, 121.1, 105.8, 55.6, 52.9, 52.3, 37.1; FT-IR (thin film, KBr): ν (cm<sup>-1</sup>) 2950, 1718, 1221, 1162, 703; HRMS (CI) calcd C<sub>24</sub>H<sub>22</sub>NO<sub>3</sub> [M + H]<sup>+</sup>: 372.1600, found: 372.1613.



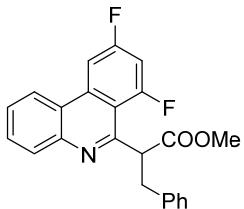
**Methyl 3-phenyl-2-(8-(trifluoromethoxy)phenanthridin-6-yl)propanoate (3f):** Yellowish solid; m.p. 98–99 °C; 67% (43 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.67 (d, *J* = 9.0 Hz, 1H), 8.50 (d, *J* = 8.0 Hz, 1H), 8.24 (d, *J* = 8.0 Hz, 1H), 8.06 (s, 1H), 7.77 (t, *J* = 7.4 Hz, 1H), 7.68 (t, *J* = 8.8 Hz, 2H), 7.27 (d, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 2H), 7.14 (t, *J* = 6.8 Hz, 1H), 4.88 (t, *J* = 7.2 Hz, 1H), 3.75 (dd, 1H), 3.68 – 3.55 (m, 4H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, overlapping peaks) δ 172.4, 156.6, 148.0, 143.7, 139.4, 131.8, 130.7, 129.2, 128.5, 127.7, 126.6, 126.1, 125.0, 124.0, 123.1, 122.0, 122.0, 120.7 (q, *J* = 258.3 Hz), 117.0, 52.5, 37.1; <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -57.77 (s, 3F). FT-IR (thin film, KBr): ν (cm<sup>-1</sup>) 3030, 1727, 1191, 1153, 760; HRMS (CI) calcd C<sub>24</sub>H<sub>19</sub>F<sub>3</sub>NO<sub>3</sub> [M + H]<sup>+</sup>: 426.1317, found: 426.1308.



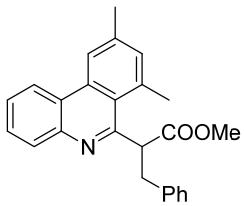
**Methyl 2-(8-cyanophenanthridin-6-yl)-3-phenylpropanoate (3g):** Yellow solid; m.p. 166–167 °C; 65% (36 mg); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.68 (d, *J* = 8.5 Hz, 1H), 8.52 (d, *J* = 8.2 Hz, 1H), 8.47 (s, 1H), 8.27 (d, *J* = 8.1 Hz, 1H), 7.95 (d, *J* = 8.5 Hz, 1H), 7.85 (t, *J* = 7.6 Hz, 1H), 7.73 (t, *J* = 7.5 Hz, 1H), 7.24 – 7.16 (m, 4H), 7.13 (t, *J* = 6.9 Hz, 1H), 4.92 (t, *J* = 7.3 Hz, 1H), 3.75 (dd, *J* = 13.9, 6.9 Hz, 1H), 3.67 (s, 3H), 3.62 (dd, *J* = 13.9, 7.7 Hz, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 172.1, 156.7, 144.5,

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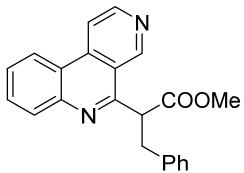
139.1, 135.8, 131.6, 131.2, 130.8, 130.6, 129.2, 128.6, 128.0, 126.7, 124.9, 123.9, 122.5, 118.6, 111.0, 52.6, 51.9, 37.2; FT-IR (thin film, KBr):  $\nu$  (cm<sup>-1</sup>) 2923, 1727, 1144, 760, 697; HRMS (CI) calcd C<sub>24</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub> [M + H]<sup>+</sup>: 367.1447, found: 367.1438.



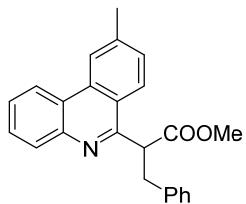
**Methyl 2-(7,9-difluorophenanthridin-6-yl)-3-phenylpropanoate (3h):** Light green solid; m.p. 95-96 °C; 88% (49 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.35 (d, *J* = 7.9 Hz, 1H), 8.16 (d, *J* = 7.8 Hz, 1H), 8.07 (d, *J* = 9.5 Hz, 1H), 7.78 (t, *J* = 7.1 Hz, 1H), 7.66 (t, *J* = 7.1 Hz, 1H), 7.35 (d, *J* = 6.5 Hz, 2H), 7.22 (t, *J* = 6.7 Hz, 2H), 7.19 – 7.09 (m, 2H), 5.13 (t, *J* = 6.0 Hz, 1H), 3.70 (s, 3H), 3.57 (d, *J* = 6.0 Hz, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  172.8, 163.1 (dd, *J* = 253.0, 14.1 Hz), 161.0 (dd, *J* = 256.7, 13.1 Hz), 154.7 (d, *J* = 6.4 Hz), 143.5, 139.9, 137.4 (dd, *J* = 10.5, 4.7 Hz), 130.6, 130.1, 129.5, 128.3, 127.7, 126.3, 122.4, 122.0 (t, *J* = 3.6 Hz), 112.5 (d, *J* = 11.7 Hz), 104.4 (dd, *J* = 21.9, 3.9 Hz), 104.1 (t, *J* = 28.1 Hz), 55.7, 52.2, 37.3; <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>)  $\delta$  -103.02 (t, *J* = 11.8 Hz), -104.28 (dd, *J* = 20.3, 9.3 Hz); FT-IR (thin film, KBr):  $\nu$  (cm<sup>-1</sup>) 2917, 1745, 1150, 754, 700; HRMS (CI) calcd C<sub>23</sub>H<sub>18</sub>F<sub>2</sub>NO<sub>2</sub> [M + H]<sup>+</sup>: 378.1306, found: 378.1302.



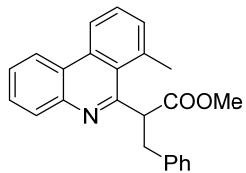
**Methyl 2-(7,9-dimethylphenanthridin-6-yl)-3-phenylpropanoate (3i):** Yellow solid; m.p. 123-125 °C; 64% (36 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.52 (d, *J* = 8.1 Hz, 1H), 8.35 (s, 1H), 8.14 (d, *J* = 7.9 Hz, 1H), 7.70 (t, *J* = 7.3 Hz, 1H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.28 (s, 1H), 7.24 – 7.07 (m, 5H), 5.40 (t, *J* = 6.8 Hz, 1H), 3.74 – 3.60 (m, 4H), 3.51 (dd, *J* = 14.1, 6.3 Hz, 1H), 2.94 (s, 3H), 2.55 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  173.1, 158.3, 143.0, 139.9, 135.2, 135.1, 134.0, 129.9, 129.1, 128.4, 128.3, 126.7, 126.2, 123.7, 123.6, 122.3, 121.0, 53.9, 52.2, 38.5, 26.1, 21.9; FT-IR (thin film, KBr):  $\nu$  (cm<sup>-1</sup>) 1738, 1715, 1171, 757, 703; HRMS (CI) calcd C<sub>25</sub>H<sub>24</sub>NO<sub>2</sub> [M + H]<sup>+</sup>: 370.1807, found: 370.1793.



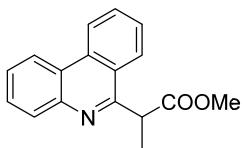
**Methyl 2-(benzo[c][2,7]naphthyridin-5-yl)-3-phenylpropanoate (3j):** Yellowish solid; m.p. 160–161 °C; 91% (47 mg); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 9.59 (s, 1H), 8.88 (d, *J* = 5.6 Hz, 1H), 8.49 (d, *J* = 8.1 Hz, 1H), 8.34 (d, *J* = 5.6 Hz, 1H), 8.25 (d, *J* = 8.2 Hz, 1H), 7.84 (t, *J* = 7.6 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 7.5 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 2H), 7.12 (t, *J* = 7.3 Hz, 1H), 5.07 (t, *J* = 7.3 Hz, 1H), 3.76 (dd, *J* = 13.9, 7.4 Hz, 1H), 3.68 – 3.61 (m, 4H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 172.1, 157.2, 149.6, 149.4, 148.4, 144.9, 139.2, 138.1, 131.0, 130.6, 129.2, 128.5, 127.7, 126.6, 122.5, 121.7, 120.3, 115.7, 52.5, 51.6, 37.1; FT-IR (thin film, KBr):  $\nu$  (cm<sup>-1</sup>) 2920, 1730, 1144, 769, 700; HRMS (CI) calcd C<sub>22</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub> [M + H]<sup>+</sup>: 343.1447, found: 343.1444.



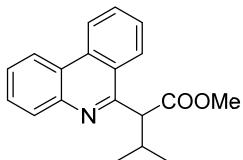
**Methyl 2-(9-methylphenanthridin-6-yl)-3-phenylpropanoate (3k):** Yellowish solid; m.p. 88–90 °C; 44% (19 mg); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.54 (d, *J* = 8.1 Hz, 1H), 8.43 (s, 1H), 8.20 (d, *J* = 8.1 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.72 (t, *J* = 7.5 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.29 (d, *J* = 10.8 Hz, 2H), 7.22 (t, *J* = 13.9, 6.4 Hz, 2H), 7.15 (t, *J* = 7.3 Hz, 1H), 4.96 (t, *J* = 7.2 Hz, 1H), 3.75 (dd, *J* = 14.0, 8.1 Hz, 1H), 3.64 (s, 3H), 3.58 (dd, *J* = 14.0, 6.4 Hz, 1H), 2.64 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 172.8, 157.3, 140.9, 139.9, 133.5, 130.5, 129.3, 129.2, 129.1, 128.6, 128.5, 126.9, 126.4, 125.5, 123.7, 123.4, 122.4, 122.0, 52.5, 52.4, 37.2, 22.3; FT-IR (thin film, KBr):  $\nu$  (cm<sup>-1</sup>) 2923, 1742, 1191, 1159, 697; HRMS (CI) calcd C<sub>24</sub>H<sub>22</sub>NO<sub>2</sub> [M + H]<sup>+</sup>: 356.1651, found: 356.1649.



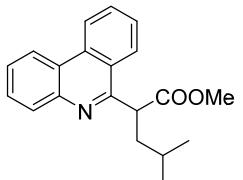
**Methyl 2-(7-methylphenanthridin-6-yl)-3-phenylpropanoate (3k'): Yellow oil; 40% (17 mg);** <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.56 (d, *J* = 8.3 Hz, 1H), 8.53 (d, *J* = 8.3 Hz, 1H), 8.17 (d, *J* = 8.1 Hz, 1H), 7.72 (t, *J* = 7.5 Hz, 1H), 7.67 – 7.60 (m, 2H), 7.44 (d, *J* = 8.7 Hz, 1H), 7.21 – 7.13 (m, 4H), 7.11 (t, *J* = 6.8 Hz, 1H), 5.43 (t, *J* = 7.1 Hz, 1H), 3.69 (s, 3H), 3.68 – 3.64 (m, 1H), 3.51 (dd, *J* = 14.2, 6.6 Hz, 1H), 2.97 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 173.0, 158.4, 142.8, 139.7, 135.3, 135.0, 132.2, 129.9, 129.8, 129.1, 128.6, 128.3, 127.0, 126.2, 125.5, 123.9, 122.3, 121.3, 53.9, 52.3, 38.5, 26.2; FT-IR (thin film, KBr):  $\nu$  (cm<sup>-1</sup>) 2917, 1721, 1173, 748, 698; HRMS (CI) calcd C<sub>24</sub>H<sub>22</sub>NO<sub>2</sub> [M + H]<sup>+</sup>: 356.1651, found: 356.1646.



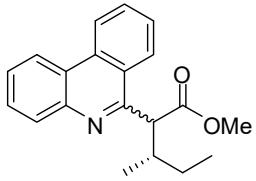
**Methyl 2-(phenanthridin-6-yl)propanoate (4a):** White solid; m.p. 85-86 °C; 83% (33 mg); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.65 (d, *J* = 8.3 Hz, 1H), 8.53 (d, *J* = 9.7 Hz, 1H), 8.21 (d, *J* = 8.2 Hz, 1H), 8.16 (d, *J* = 8.1 Hz, 1H), 7.83 (t, *J* = 7.6 Hz, 1H), 7.70 (dt, *J* = 14.9, 7.5 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 4.77 (q, *J* = 7.1 Hz, 1H), 3.70 (s, 3H), 1.80 (d, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 174.3, 159.4, 143.6, 133.4, 130.5, 130.3, 128.7, 127.6, 127.0, 125.6, 124.8, 123.8, 122.8, 121.9, 52.3, 45.6, 16.6; FT-IR (thin film, KBr): ν (cm<sup>-1</sup>) 2950, 1724, 1221, 754, 727; HRMS (CI) calcd C<sub>17</sub>H<sub>16</sub>NO<sub>2</sub> [M + H]<sup>+</sup>: 266.1181, found: 266.1182.



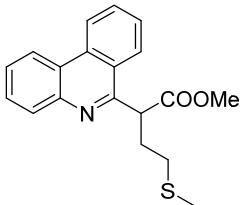
**Methyl 3-methyl-2-(phenanthridin-6-yl)butanoate (4b):** Yellowish solid; m.p. 86-88 °C; 68% (30 mg); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.67 (d, *J* = 8.3 Hz, 1H), 8.56 (d, *J* = 8.1 Hz, 1H), 8.41 (d, *J* = 8.3 Hz, 1H), 8.21 (d, *J* = 8.1 Hz, 1H), 7.84 (t, *J* = 7.6 Hz, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.64 (t, *J* = 17.6, 9.8 Hz, 1H), 4.39 (d, *J* = 10.0 Hz, 1H), 3.63 (s, 3H), 3.16 – 3.06 (m, 1H), 1.23 (d, *J* = 6.6 Hz, 3H), 0.83 (d, *J* = 6.7 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 172.9, 157.4, 143.8, 133.3, 130.5, 130.4, 128.7, 127.6, 127.0, 125.9, 123.7, 122.7, 122.0, 58.1, 52.1, 30.1, 21.6, 21.0; FT-IR (thin film, KBr): ν (cm<sup>-1</sup>) 2917, 1733, 1149, 757, 721; HRMS (CI) calcd C<sub>19</sub>H<sub>20</sub>NO<sub>2</sub> [M + H]<sup>+</sup>: 294.1494, found: 294.1499.



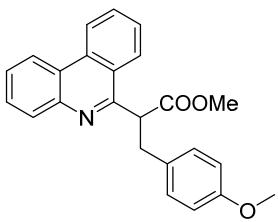
**Methyl 4-methyl-2-(phenanthridin-6-yl)pentanoate (4c):** Yellow solid; m.p. 89-90 °C; 75% (35 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.67 (d, *J* = 8.2 Hz, 1H), 8.55 (d, *J* = 8.1 Hz, 1H), 8.28 (d, *J* = 8.2 Hz, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 7.84 (t, *J* = 7.5 Hz, 1H), 7.72 (t, *J* = 6.5 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 4.77 (t, *J* = 7.2 Hz, 1H), 3.68 (s, 3H), 2.38 – 2.28 (m, 1H), 2.17 – 2.07 (m, 1H), 1.76 – 1.66 (m, 1H), 1.01 (d, *J* = 7.3 Hz, 3H), 0.99 (d, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 173.6, 158.5, 143.7, 133.4, 130.5, 128.7, 127.6, 127.0, 125.6, 125.1, 123.8, 122.8, 121.9, 52.3, 49.2, 40.2, 26.6, 22.8, 22.7; FT-IR (thin film, KBr): ν (cm<sup>-1</sup>) 2938, 1718, 1162, 751, 724; HRMS (CI) calcd C<sub>20</sub>H<sub>22</sub>NO<sub>2</sub> [M + H]<sup>+</sup>: 308.1651, found: 308.1646.



**Methyl 3-methyl-2-(phenanthridin-6-yl)pentanoate (4d):** Yellowish oil; 74% (34 mg); Two isomers, *d.r.*: 1.3:1;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.67 (d,  $J = 8.3$  Hz, 1H), 8.56 (d,  $J = 8.1$  Hz, 1H), 8.41 (t,  $J = 7.5$  Hz, 1H), 8.22 (d,  $J = 8.1$  Hz, 1H), 7.84 (t,  $J = 7.6$  Hz, 1H), 7.74 (d,  $J = 7.5$  Hz, 1H), 7.71 (d,  $J = 8.2$  Hz, 1H), 7.65 (t,  $J = 7.5$  Hz, 1H), 4.52 (d,  $J = 10.0$  Hz, 0.44H)/4.50 (d,  $J = 10.2$  Hz, 0.56H), 3.63 (s, 3H), 2.98 – 2.87 (m, 1H), 1.86 – 1.08 (m, 2H), 1.20 (d,  $J = 6.6$  Hz, 1.3H)/0.79 (d,  $J = 6.7$  Hz, 1.7H), 1.06 (t,  $J = 7.4$  Hz, 1.7H)/0.84 (t,  $J = 7.4$  Hz, 1.3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  172.9, 172.8, 157.4, 157.2, 143.8, 133.24, 133.22, 130.59, 130.53, 130.46, 128.7, 127.62, 127.59, 127.0, 125.99, 125.95, 125.8, 123.7, 122.7, 121.9, 56.8, 56.5, 52.12, 52.10, 36.1, 36.0, 28.1, 27.3, 17.4, 16.8, 11.5, 11.4; FT-IR (thin film, KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 2965, 1730, 1165, 754, 721; HRMS (CI) calcd  $\text{C}_{20}\text{H}_{22}\text{NO}_2$  [M + H] $^+$ : 308.1651, found: 308.1651.

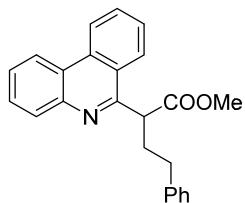


**Methyl 4-(methylthio)-2-(phenanthridin-6-yl)butanoate (4e):** Yellow oil; 84% (42 mg);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.68 (d,  $J = 8.3$  Hz, 1H), 8.56 (d,  $J = 8.1$  Hz, 1H), 8.34 (d,  $J = 8.3$  Hz, 1H), 8.15 (d,  $J = 8.1$  Hz, 1H), 7.86 (t,  $J = 7.6$  Hz, 1H), 7.76 – 7.69 (m, 2H), 7.66 (t,  $J = 7.5$  Hz, 1H), 4.96 (t,  $J = 6.5$  Hz, 1H), 3.68 (s, 3H), 2.69 – 2.64 (m, 2H), 2.64 – 2.54 (m, 2H), 2.13 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  173.1, 157.8, 143.6, 133.4, 130.6, 130.4, 128.8, 127.8, 127.1, 125.7, 125.2, 123.9, 122.8, 122.0, 52.4, 48.8, 32.6, 30.4, 15.5; FT-IR (thin film, KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 2923, 1748, 1724, 1127, 760; HRMS (CI) calcd  $\text{C}_{19}\text{H}_{20}\text{NO}_2\text{S}$  [M + H] $^+$ : 326.1215, found: 326.1211.

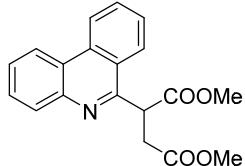


**Methyl 3-(4-methoxyphenyl)-2-(phenanthridin-6-yl)propanoate (4f):** Yellowish oil; 97% (60 mg);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.65 (d,  $J = 6.7$  Hz, 1H), 8.55 (d,  $J = 8.1$  Hz, 1H), 8.25 (d,  $J = 8.2$  Hz, 1H), 8.21 (d,  $J = 6.7$  Hz, 1H), 7.83 (t,  $J = 7.6$  Hz, 1H), 7.75 (t, 1H), 7.70 – 7.64 (m, 2H), 7.22 (d,  $J = 8.5$  Hz, 2H), 6.76 (d,  $J = 8.5$  Hz, 2H), 4.94 (t,  $J = 7.7$ , 6.8 Hz, 1H), 3.74 (s, 3H), 3.69 (dd,  $J = 14.1$ , 8.1 Hz, 1H), 3.64 (s,

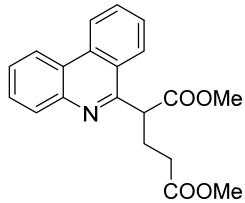
3H), 3.53 (dd,  $J$  = 14.1, 6.4 Hz, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  172.8, 158.2, 157.5, 143.6, 133.3, 131.9, 130.5, 130.2, 128.8, 127.6, 127.1, 125.7, 125.3, 123.9, 122.7, 122.0, 113.9, 55.3, 52.7, 52.4, 36.3; FT-IR (thin film, KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 1730, 1510, 1245, 754, 721; HRMS (CI) calcd  $\text{C}_{24}\text{H}_{22}\text{NO}_3$  [ $\text{M} + \text{H}]^+$ : 372.1600, found: 372.1593.



**Methyl 2-(phenanthridin-6-yl)-4-phenylbutanoate (4g):** Yellow solid; m.p. 90–91 °C; 92% (48 mg);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.66 (d,  $J$  = 8.2 Hz, 1H), 8.56 (d,  $J$  = 8.0 Hz, 1H), 8.18 (d, 1H), 8.04 (d,  $J$  = 8.2 Hz, 1H), 7.83 (t, 1H), 7.73 (t, 1H), 7.68 – 7.62 (m, 2H), 7.32 – 7.26 (m, 2H), 7.23 – 7.18 (m, 3H), 4.66 (t,  $J$  = 6.7 Hz, 1H), 3.69 (s, 3H), 2.84 – 2.70 (m, 3H), 2.63 – 2.55 (m, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  173.3, 158.0, 143.7, 141.6, 133.4, 130.5, 130.4, 128.8, 128.7, 128.5, 127.6, 127.1, 126.1, 125.7, 125.2, 123.8, 122.8, 122.0, 52.4, 49.9, 34.1, 32.9; FT-IR (thin film, KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 1730, 1435, 1153, 760, 727; HRMS (CI) calcd  $\text{C}_{24}\text{H}_{22}\text{NO}_2$  [ $\text{M} + \text{H}]^+$ : 356.1651, found: 356.1649.

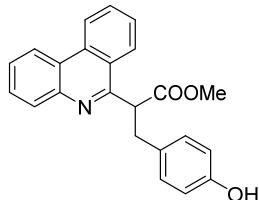


**Dimethyl 2-(phenanthridin-6-yl)succinate (4h):** Yellowish oil; 98% (48 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.66 (d,  $J$  = 8.2 Hz, 1H), 8.55 (d,  $J$  = 8.0 Hz, 1H), 8.35 (d,  $J$  = 8.2 Hz, 1H), 8.13 (d,  $J$  = 8.0 Hz, 1H), 7.86 (t,  $J$  = 7.5 Hz, 1H), 7.74 (d,  $J$  = 8.2 Hz, 1H), 7.70 (d,  $J$  = 8.2 Hz, 1H), 7.65 (t,  $J$  = 7.4 Hz, 1H), 5.27 (t, 1H), 3.70 (s, 3H), 3.68 (s, 3H), 3.49 (dd,  $J$  = 17.1, 8.1 Hz, 1H), 3.28 (dd,  $J$  = 17.1, 6.2 Hz, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  172.7, 172.4, 156.7, 143.4, 133.4, 130.7, 130.4, 128.7, 127.7, 127.2, 125.8, 125.0, 123.9, 122.7, 122.0, 52.7, 52.1, 45.9, 35.5; FT-IR (thin film, KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 2953, 1727, 1153, 757, 727; HRMS (CI) calcd  $\text{C}_{19}\text{H}_{18}\text{NO}_4$  [ $\text{M} + \text{H}]^+$ : 324.1236, found: 324.1226.

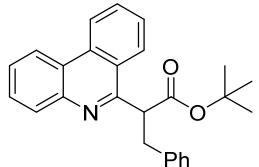


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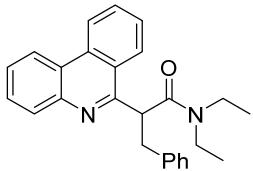
**Dimethyl 2-(phenanthridin-6-yl)pentanedioate (4i):** Yellow oil; 88% (44 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.66 (d, *J* = 8.2 Hz, 1H), 8.55 (d, *J* = 8.0 Hz, 1H), 8.35 (d, *J* = 8.2 Hz, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 7.86 (t, *J* = 19.9, 12.5 Hz, 1H), 7.77 – 7.69 (m, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 4.83 (t, *J* = 6.8 Hz, 1H), 3.69 (s, 3H), 3.66 (s, 3H), 2.71 – 2.58 (m, 2H), 2.57 – 2.45 (m, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 173.8, 173.0, 157.8, 143.5, 133.3, 130.6, 130.4, 128.7, 127.7, 127.1, 125.7, 125.1, 123.8, 122.7, 122.0, 52.4, 51.7, 49.4, 31.8, 26.3; FT-IR (thin film, KBr): ν (cm<sup>-1</sup>) 2923, 2848, 1724, 1156, 697; HRMS (CI) calcd C<sub>20</sub>H<sub>20</sub>NO<sub>4</sub> [M + H]<sup>+</sup>: 338.1392, found: 338.1388.



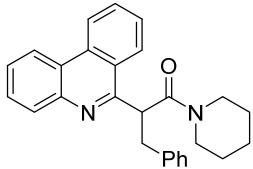
**Methyl 3-(4-hydroxyphenyl)-2-(phenanthridin-6-yl)propanoate (4j):** Yellow oil; 68% (36.1 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.66 (d, *J* = 8.3 Hz, 1H), 8.58 – 8.54 (m, 1H), 8.25 (d, *J* = 8.2 Hz, 1H), 8.19 (d, *J* = 8.1, 1.0 Hz, 1H), 7.87 – 7.81 (m, 1H), 7.75 – 7.63 (m, 3H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.60 (d, *J* = 8.5 Hz, 2H), 4.92 (t, *J* = 7.3 Hz, 1H), 3.69 (dd, *J* = 14.1, 7.7 Hz, 1H), 3.62 (s, 3H), 3.49 (dd, *J* = 14.1, 6.9 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 173.1, 157.7, 154.5, 143.3, 133.5, 131.2, 130.7, 130.3, 130.2, 128.9, 127.7, 127.2, 125.8, 125.2, 123.9, 122.8, 122.1, 115.5, 53.3, 52.5, 36.4; HRMS (CI) calcd C<sub>23</sub>H<sub>20</sub>NO<sub>3</sub> [M+H]<sup>+</sup>: 358.1443, found: 358.1435.



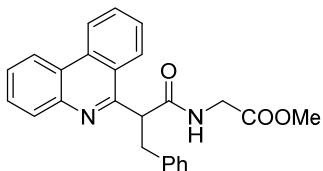
**tert-Butyl 2-(phenanthridin-6-yl)-3-phenylpropanoate (4k):** White solid; m.p. 147–148 °C; 94% (54 mg); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.62 (d, *J* = 8.3 Hz, 1H), 8.53 (d, *J* = 8.1 Hz, 1H), 8.25 (d, *J* = 8.3 Hz, 1H), 8.20 (d, *J* = 8.1 Hz, 1H), 7.79 (t, *J* = 13.6, 6.2 Hz, 1H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.66 – 7.61 (m, 2H), 7.31 (d, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.5 Hz, 2H), 7.14 (t, *J* = 7.3 Hz, 1H), 4.89 – 4.84 (m, 1H), 3.71 (dd, *J* = 14.1, 8.3 Hz, 1H), 3.54 (dd, *J* = 14.1, 6.2 Hz, 1H), 1.31 (s, 9H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 171.5, 158.1, 143.7, 140.2, 133.3, 130.5, 130.3, 129.3, 128.6, 128.4, 127.3, 126.9, 126.3, 125.8, 125.3, 123.8, 122.6, 122.0, 81.3, 53.2, 37.1, 28.1; FT-IR (thin film, KBr): ν (cm<sup>-1</sup>) 2971, 1635, 757, 724, 695; HRMS (CI) calcd C<sub>26</sub>H<sub>26</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 384.1964, found: 384.1970.



**N,N-Diethyl-2-(phenanthridin-6-yl)-3-phenylpropanamide (4l):** Yellow oil; 95% (57 mg);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.66 (d,  $J = 8.3$  Hz, 1H), 8.55 (d,  $J = 8.1$  Hz, 1H), 8.40 (d,  $J = 8.2$  Hz, 1H), 8.17 (d,  $J = 8.0$  Hz, 1H), 7.82 (t,  $J = 7.6$  Hz, 1H), 7.71 (t,  $J = 7.5$  Hz, 1H), 7.69 – 7.62 (m, 2H), 7.29 (d,  $J = 7.5$  Hz, 2H), 7.21 (t,  $J = 7.4$  Hz, 2H), 7.14 (t,  $J = 7.3$  Hz, 1H), 4.97 – 4.93 (m, 1H), 3.89 (dd,  $J = 13.9, 8.2$  Hz, 1H), 3.62 (dq,  $J = 13.8, 6.9$  Hz, 1H), 3.35 (dd,  $J = 14.0, 5.4$  Hz, 1H), 3.25 – 3.13 (m, 2H), 3.07 (dq,  $J = 14.2, 6.9$  Hz, 1H), 1.11 (t,  $J = 7.0$  Hz, 3H), 0.69 (t,  $J = 7.0$  Hz, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  170.4, 159.1, 143.6, 140.7, 133.4, 130.5, 130.4, 129.2, 128.7, 128.3, 127.5, 127.0, 126.2, 125.7, 124.8, 123.6, 122.8, 121.9, 52.8, 41.6, 40.5, 38.2, 13.9, 12.7; FT-IR (thin film, KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 2938, 1629, 1218, 760, 695; HRMS (CI) calcd  $\text{C}_{26}\text{H}_{27}\text{N}_2\text{O} [\text{M} + \text{H}]^+$ : 383.2123, found: 383.2140.



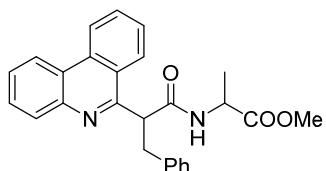
**2-(Phenanthridin-6-yl)-3-phenyl-1-(piperidin-1-yl)propan-1-one (4m):** Light yellow solid; m.p. 116–117 °C; 98% (58 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.53 (d,  $J = 8.2$  Hz, 1H), 8.41 (d,  $J = 8.0$  Hz, 1H), 8.19 (d,  $J = 8.2$  Hz, 1H), 8.04 (d,  $J = 7.9$  Hz, 1H), 7.69 (t,  $J = 7.5$  Hz, 1H), 7.59 (t,  $J = 7.4$  Hz, 1H), 7.54 – 7.46 (m, 2H), 7.17 – 7.11 (m, 2H), 7.08 (t,  $J = 7.2$  Hz, 2H), 7.04 – 6.98 (m, 1H), 4.86 (t,  $J = 6.6$  Hz, 1H), 3.74 (dd,  $J = 13.8, 8.0$  Hz, 1H), 3.69 – 3.59 (m, 1H), 3.34 – 3.20 (m, 2H), 3.18 – 2.98 (m, 2H), 1.40 – 1.20 (m, 4H), 0.96 – 0.81 (m, 1H), 0.70 – 0.57 (m, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  169.8, 159.0, 143.6, 140.7, 133.4, 130.5, 130.4, 129.4, 128.7, 128.4, 127.6, 127.0, 126.2, 125.6, 124.8, 123.6, 122.8, 121.9, 52.4, 46.7, 43.6, 38.1, 25.8, 25.6, 24.5; FT-IR (thin film, KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 2935, 1632, 1221, 763, 698; HRMS (CI) calcd  $\text{C}_{27}\text{H}_{27}\text{N}_2\text{O} [\text{M} + \text{H}]^+$ : 395.2123, found: 395.2140.



**Methyl (2-(phenanthridin-6-yl)-3-phenylpropanoyl)glycinate (4n):** Yellow oil; 72% (39 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.61 (d,  $J = 8.3$  Hz, 1H), 8.56 (d,  $J = 8.1$  Hz, 1H), 8.48 (br, 1H), 8.27 (d,  $J = 8.0$  Hz, 1H), 8.16 (d,  $J = 8.2$  Hz, 1H), 7.79 (t,  $J = 7.5$  Hz, 2H), 7.69 (t,  $J = 7.5$  Hz, 1H), 7.58 (t,  $J = 7.6$  Hz, 1H), 7.16 – 6.98 (m, 5H), 4.98 (t,  $J = 8.3, 6.1$  Hz, 1H), 4.13 (dd,  $J = 18.5, 5.2$  Hz, 1H), 3.96 (dd,  $J = 18.5, 4.7$

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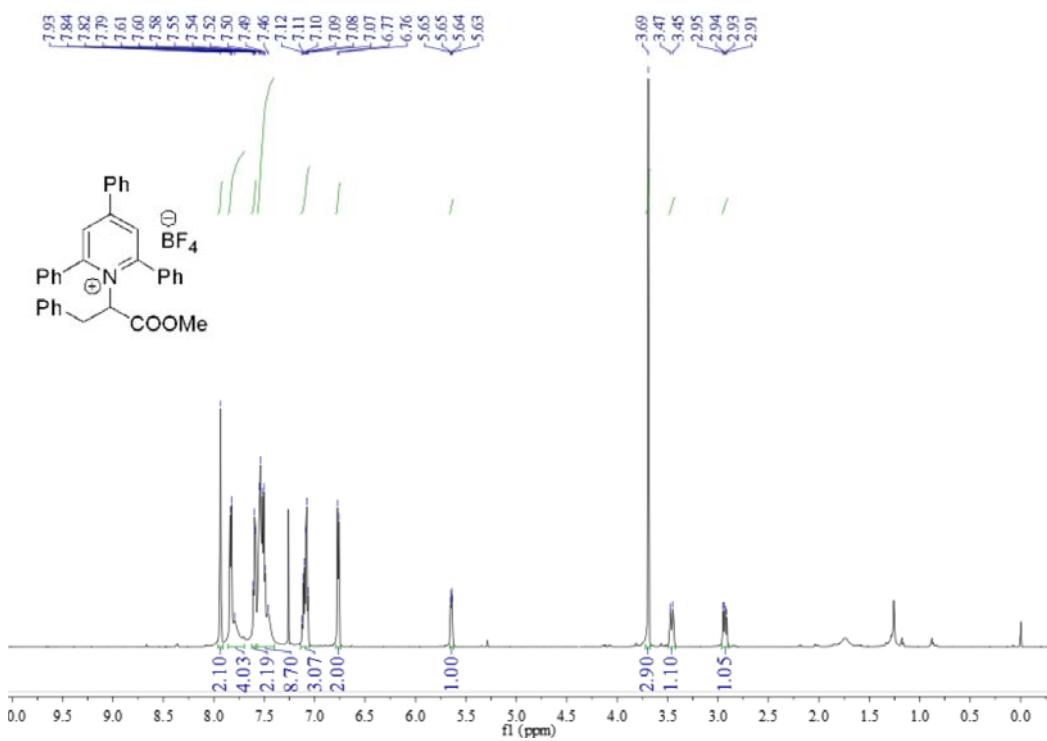
Hz, 1H), 3.76 – 3.67 (m, 4H), 3.63 (dd,  $J$  = 13.3, 5.7 Hz, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  172.1, 170.4, 158.7, 142.9, 139.0, 133.1, 130.9, 129.9, 129.1, 129.0, 128.3, 127.7, 127.3, 126.4, 125.8, 125.6, 123.8, 122.5, 122.2, 52.5, 52.4, 41.7, 41.3; FT-IR (thin film, KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 2923, 1754, 1206, 751, 692; HRMS (ESI) calcd  $\text{C}_{25}\text{H}_{23}\text{N}_2\text{O}_3$  [M + H] $^+$ : 399.1709, found: 399.1703.



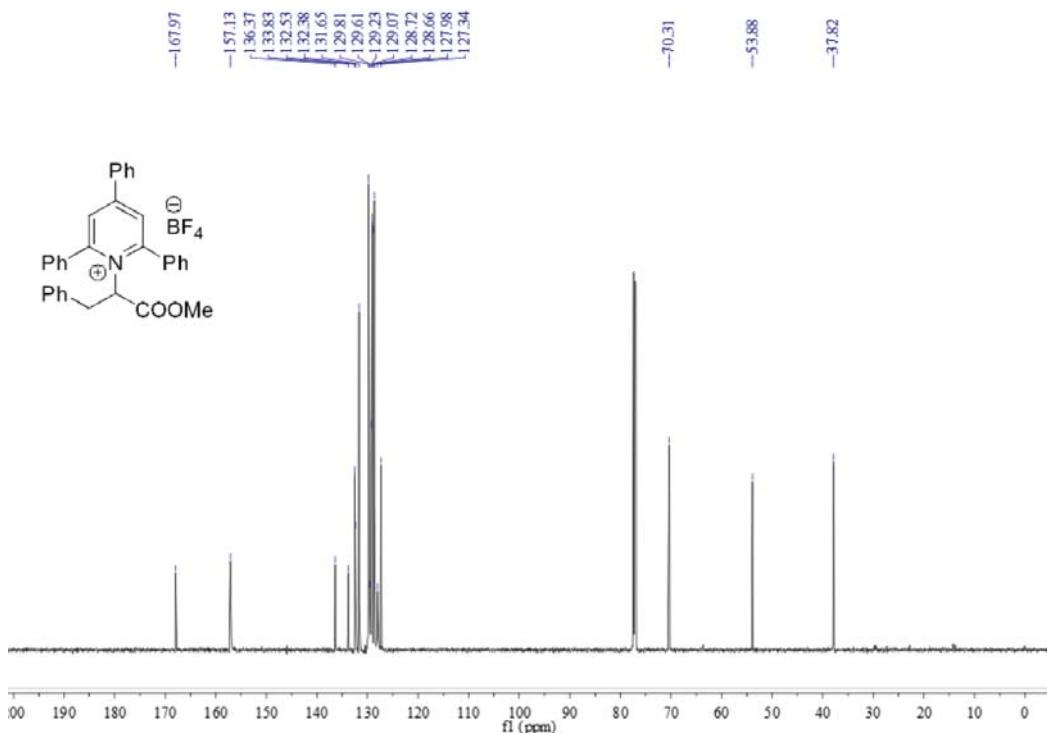
**Methyl (2-(phenanthridin-6-yl)-3-phenylpropanoyl)alaninate (4o):** Yellow solid; m.p. 163–165 °C; 80% (49 mg); Two isomers, *d.r.*: 1.2:1;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.75 (d,  $J$  = 5.9 Hz, 0.55H)/8.47 (d,  $J$  = 6.6 Hz, 0.45H), 8.64 – 8.58 (m, 1H), 8.56 (d,  $J$  = 8.1 Hz, 1H), 8.26 (t,  $J$  = 8.5 Hz, 1H), 8.22 – 8.12 (m, 1H), 7.79 (t,  $J$  = 7.0 Hz, 2H), 7.69 (t,  $J$  = 7.5 Hz, 1H), 7.58 (dd,  $J$  = 14.4, 7.1 Hz, 1H), 7.15 – 6.96 (m, 5H), 4.93 (dd,  $J$  = 14.7, 7.9 Hz, 1H), 4.62 – 4.52 (m, 1H), 3.78 (s, 1.4H)/ 3.57 (s, 1.7H), 3.74 – 3.59 (m, 2H), 1.46 (d,  $J$  = 7.1 Hz, 1.7H)/ 1.28 (d,  $J$  = 7.3 Hz, 1.3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  173.6, 173.3, 171.39, 171.37, 158.8, 158.7, 142.9, 139.1, 138.8, 133.1, 133.0, 130.8, 129.8, 129.21, 129.17, 129.0, 128.3, 127.7, 127.3, 127.2, 126.5, 126.4, 125.7, 125.6, 125.5, 123.7, 122.53, 122.48, 122.2, 122.1, 52.6, 52.5, 52.3, 48.44, 48.38, 41.5, 41.3, 18.7, 18.4; FT-IR (thin film, KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 1715, 1364, 1141, 754, 698; HRMS (CI) calcd  $\text{C}_{26}\text{H}_{25}\text{N}_2\text{O}_3$  [M + H] $^+$ : 413.1865, found: 413.1872.

## 8 NMR Spectra for the substrates and products

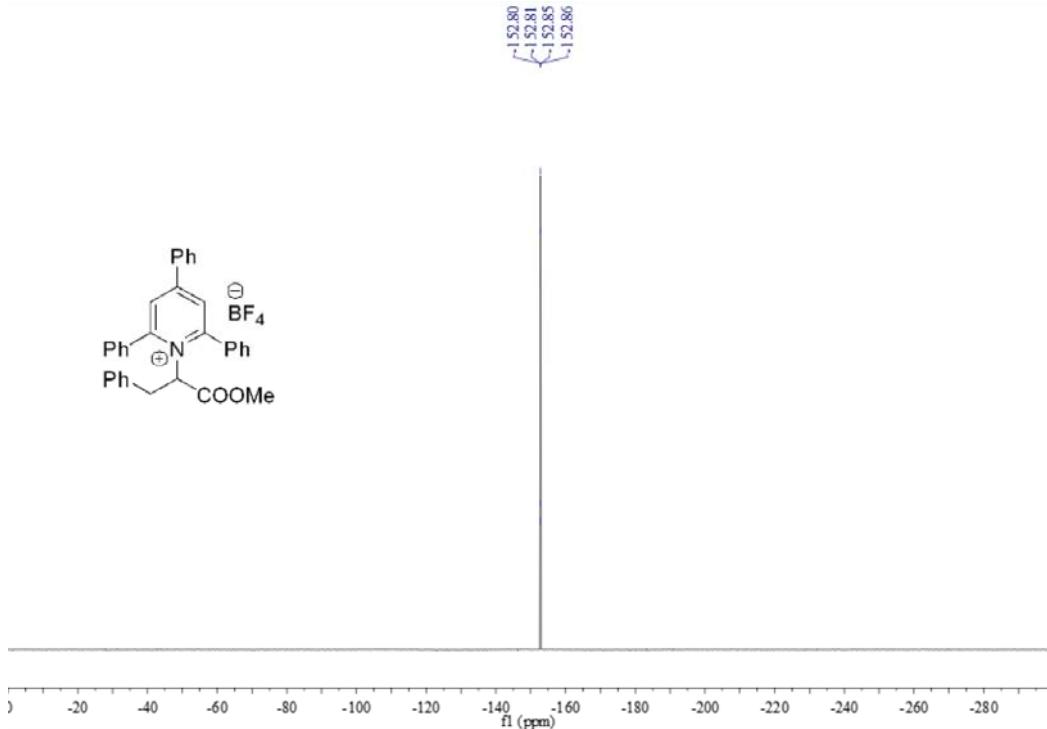
<sup>1</sup>H NMR of **2a**



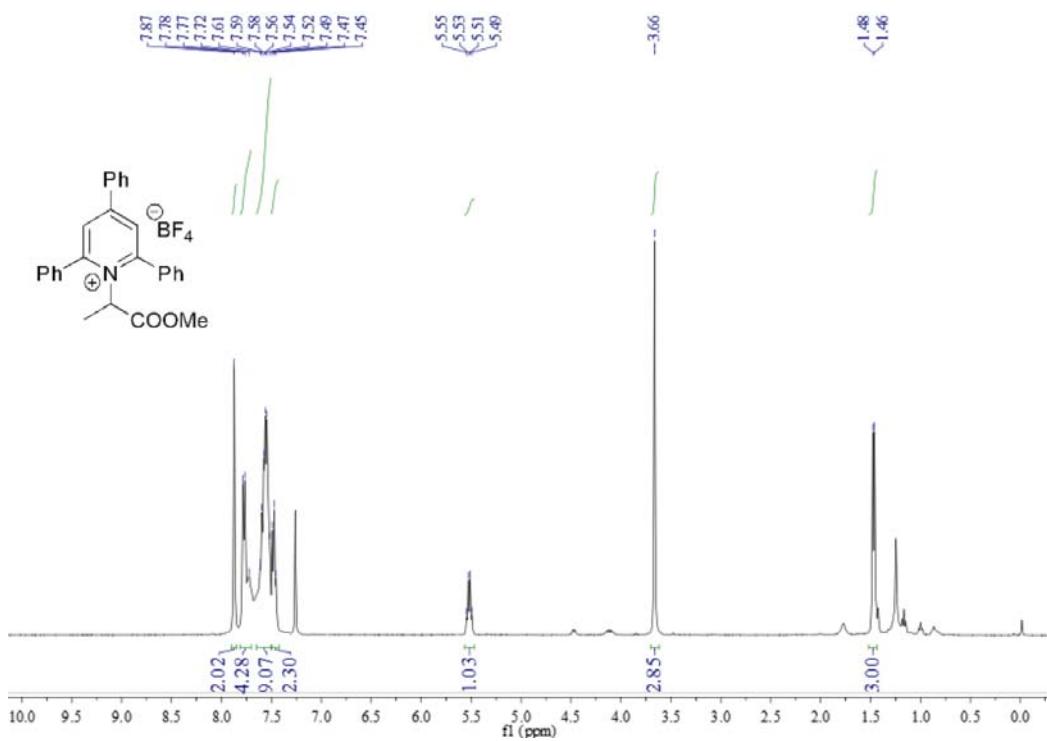
<sup>13</sup>C NMR of **2a**



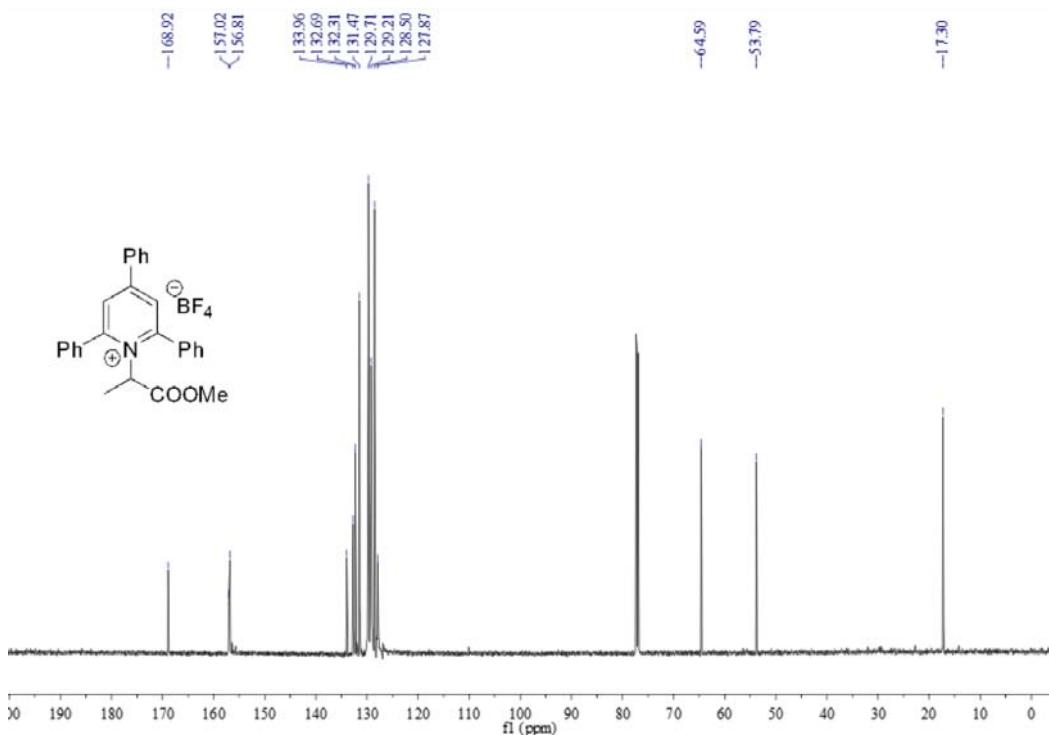
<sup>19</sup>F NMR of **2a**



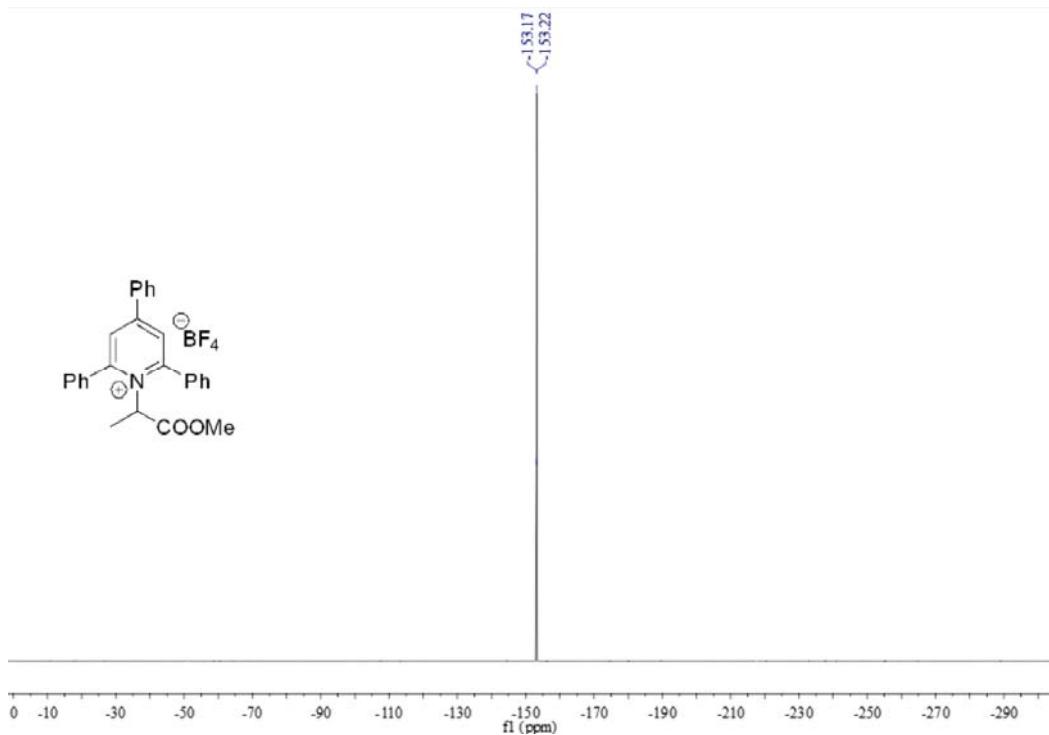
### $^1\text{H}$ NMR of 2b



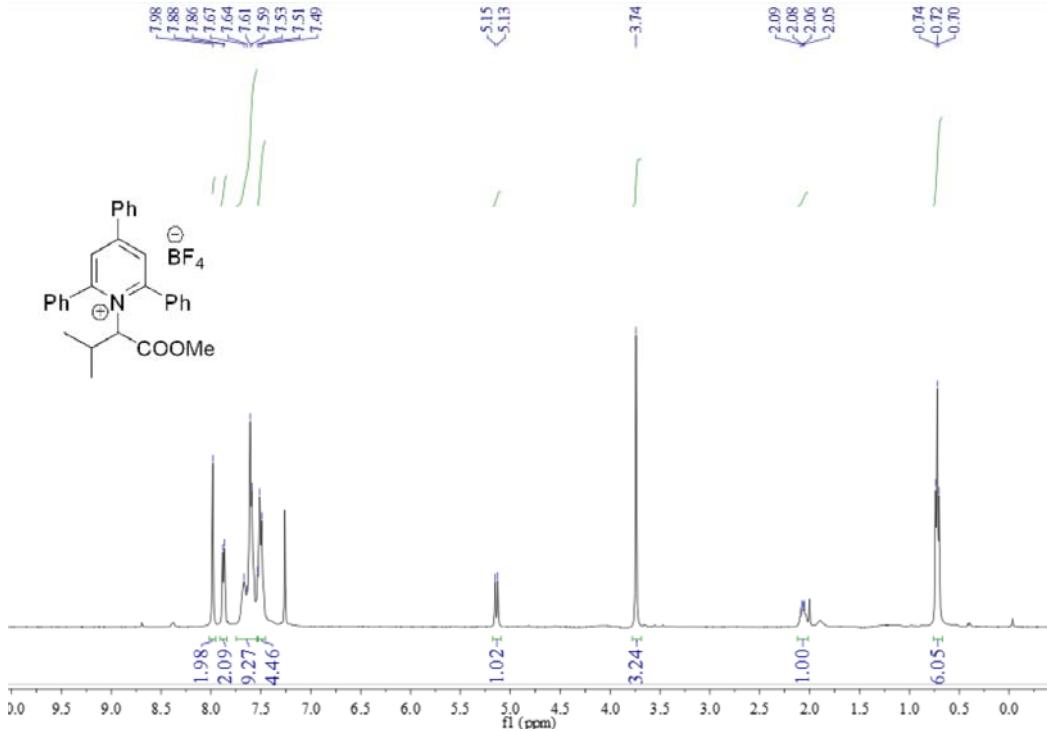
### $^{13}\text{C}$ NMR of 2b



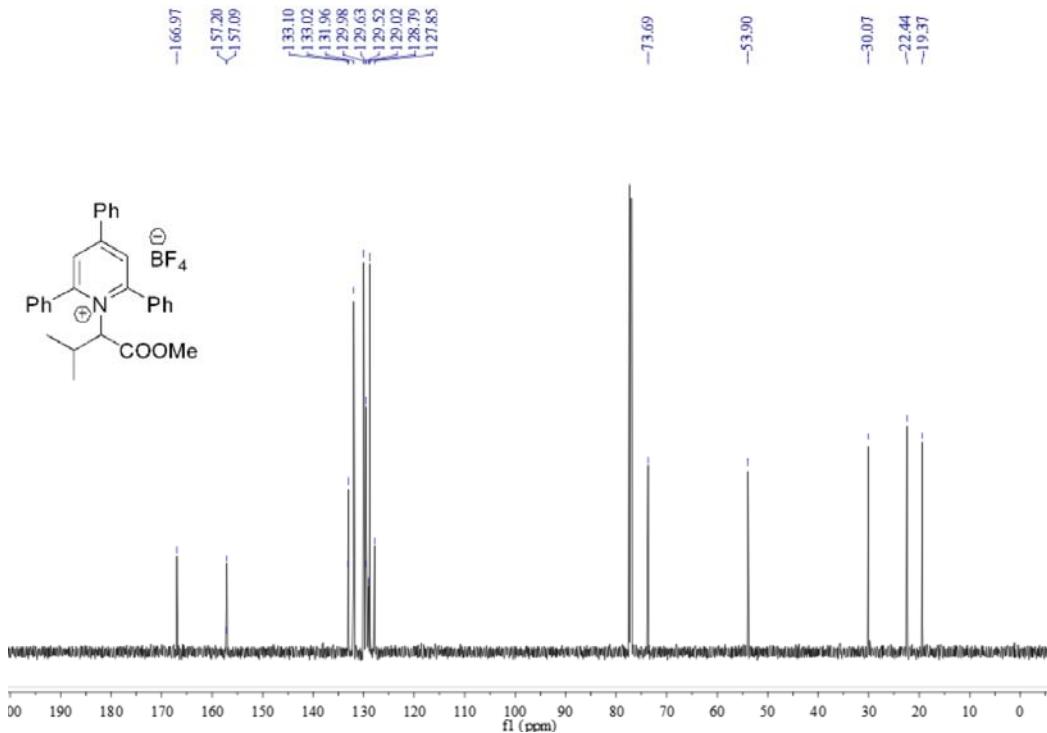
<sup>13</sup>C NMR of **2b**



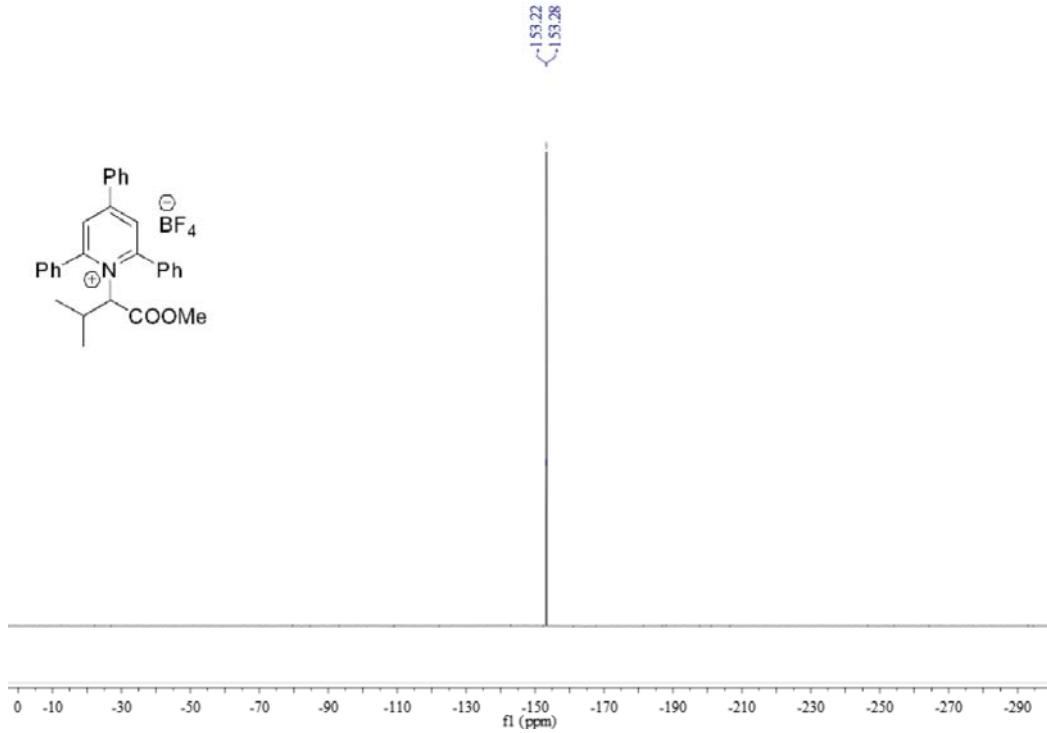
<sup>1</sup>H NMR of **2c**



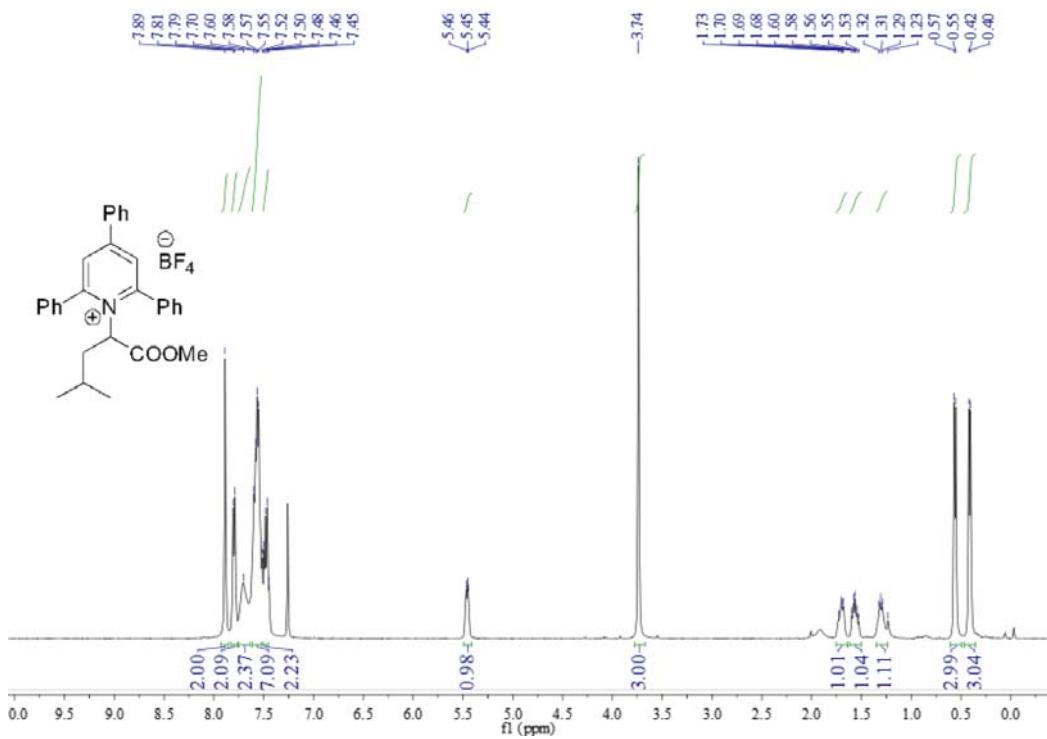
<sup>1</sup>H NMR of **2c**



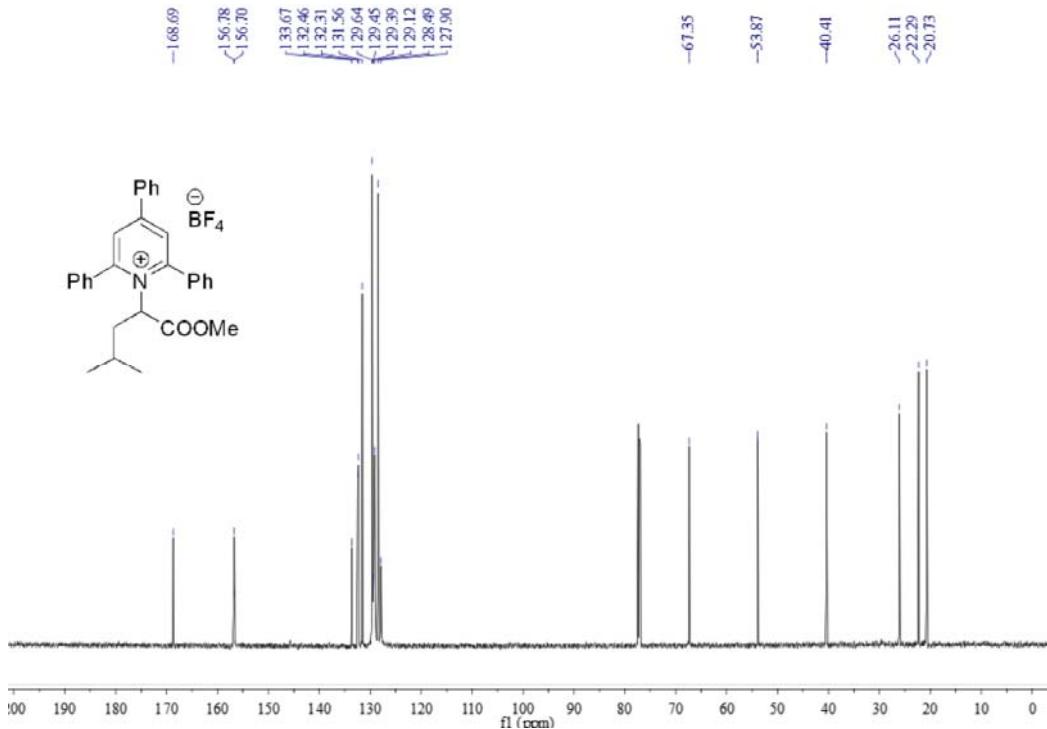
<sup>13</sup>C NMR of **2c**



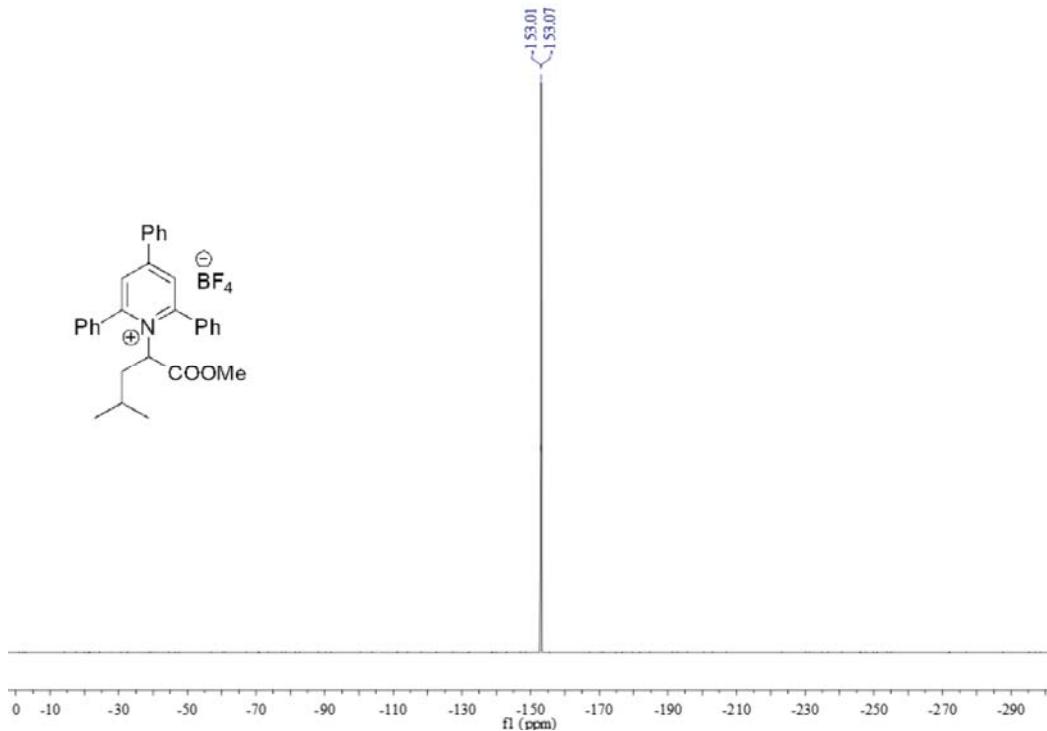
### <sup>1</sup>H NMR of 2d



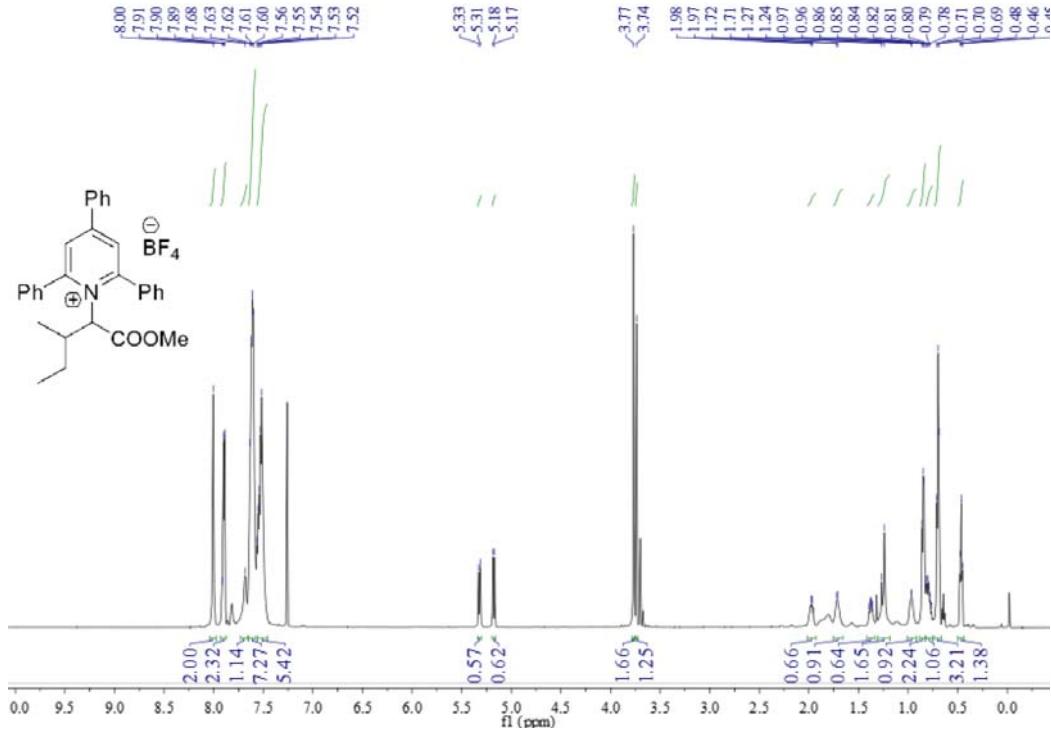
### <sup>13</sup>C NMR of 2d



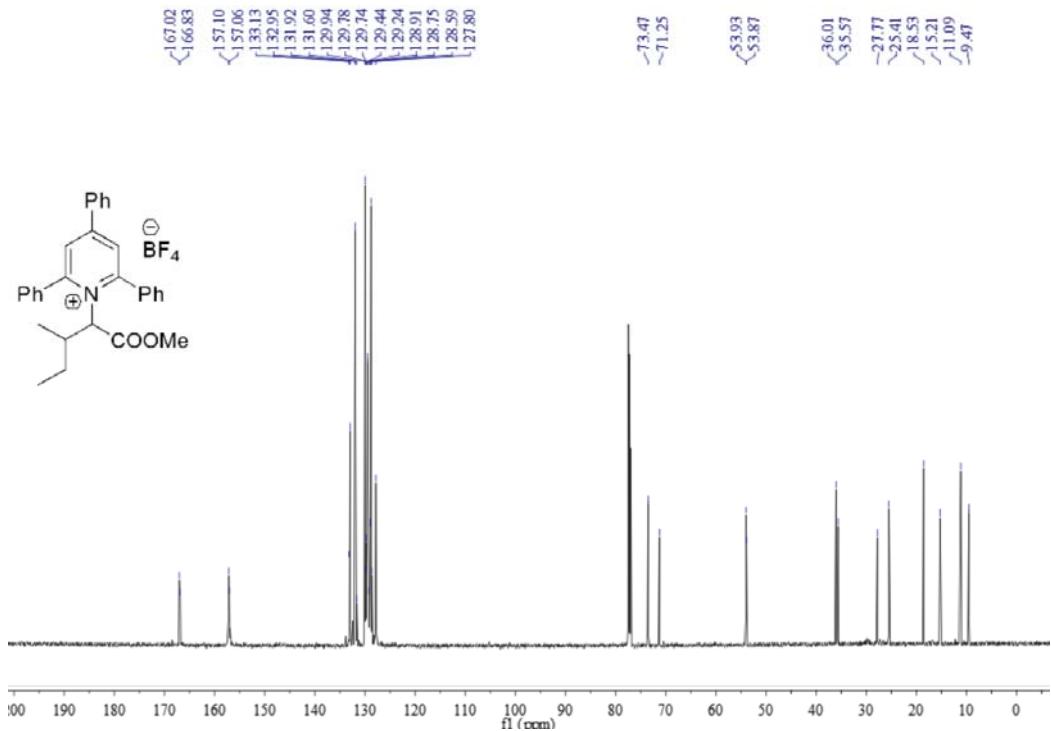
<sup>1</sup>H NMR of **2d**



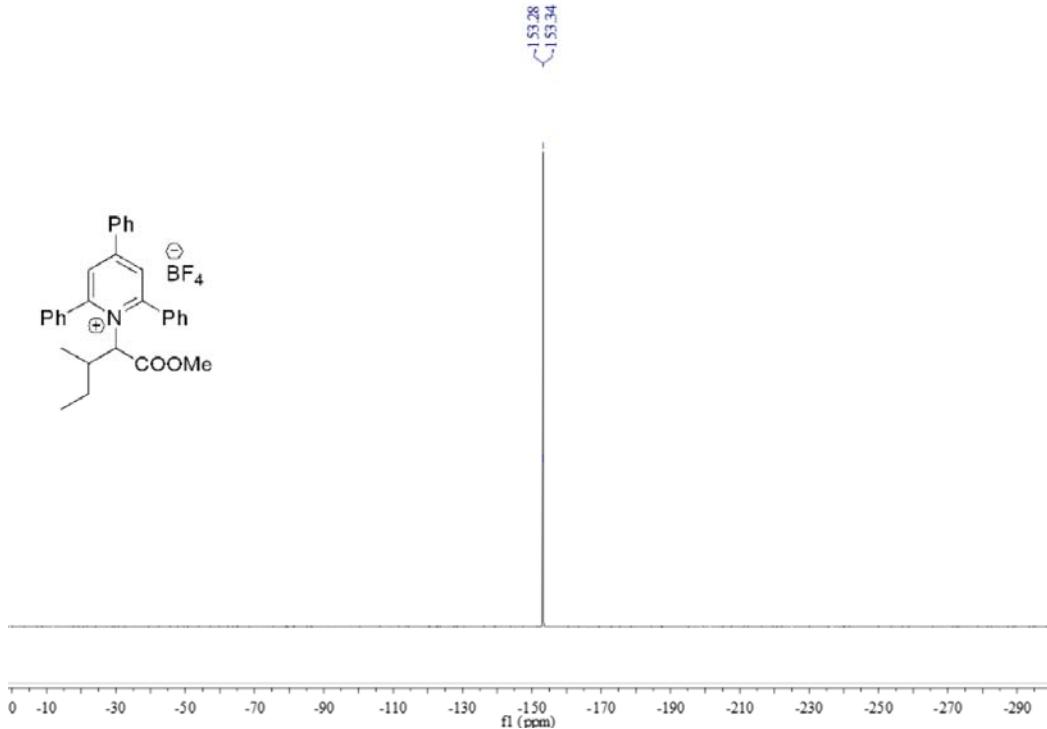
<sup>1</sup>H NMR of **2e**



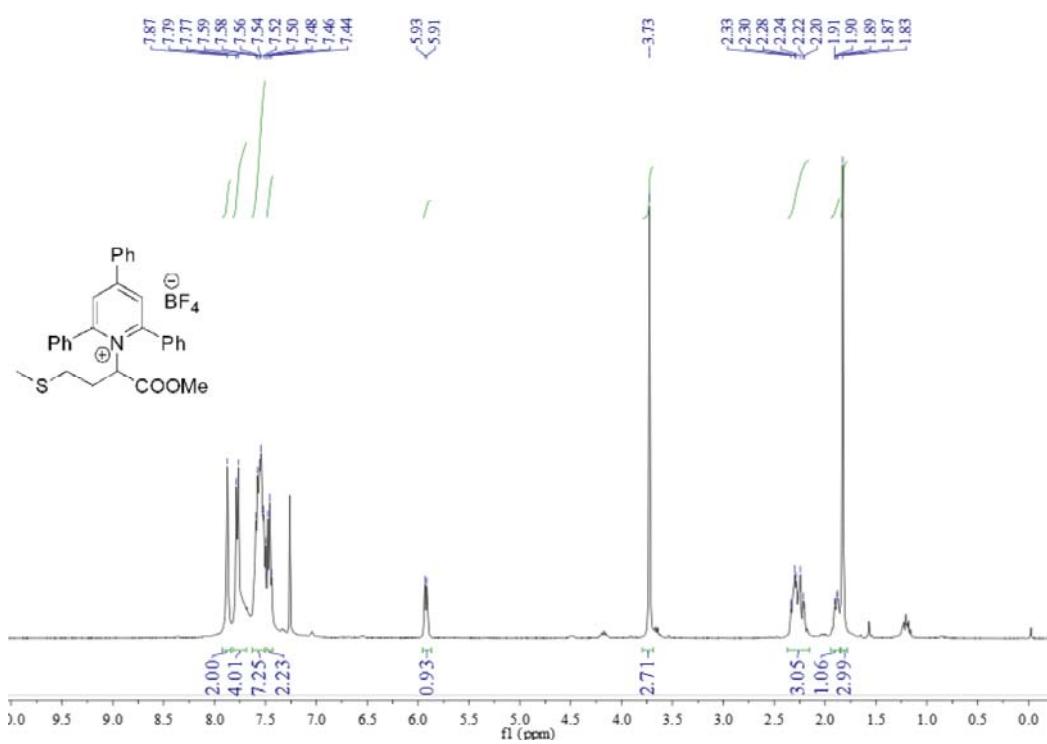
<sup>13</sup>C NMR of **2e**



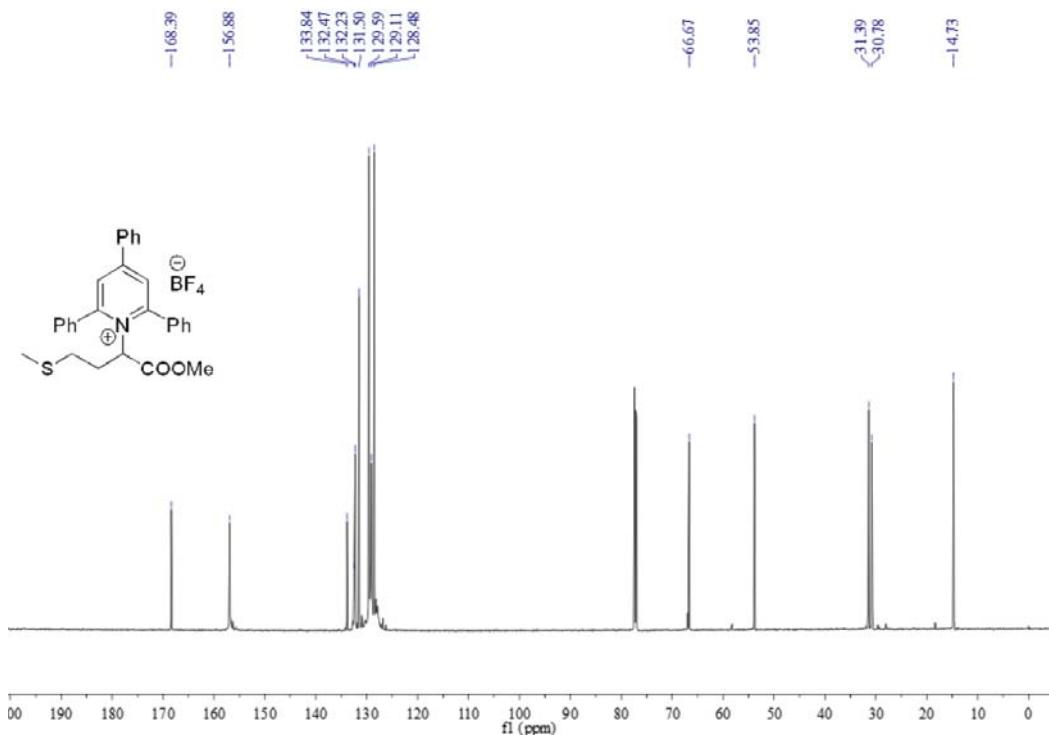
<sup>19</sup>F NMR of **2e**



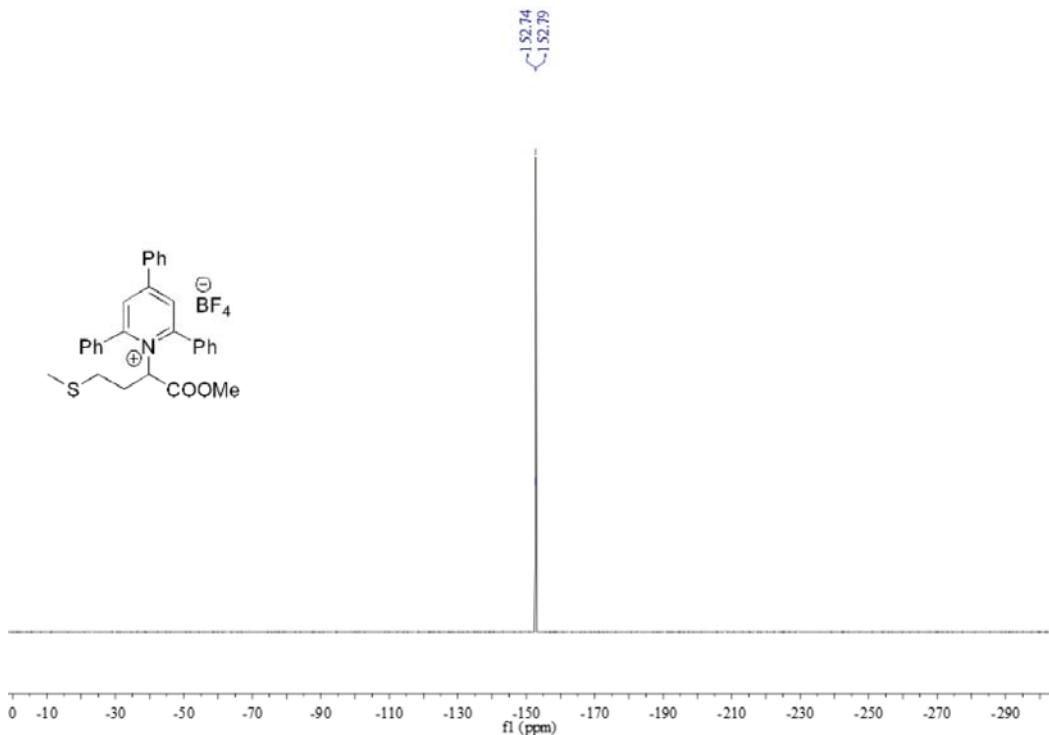
$^1\text{H}$  NMR of **2f**



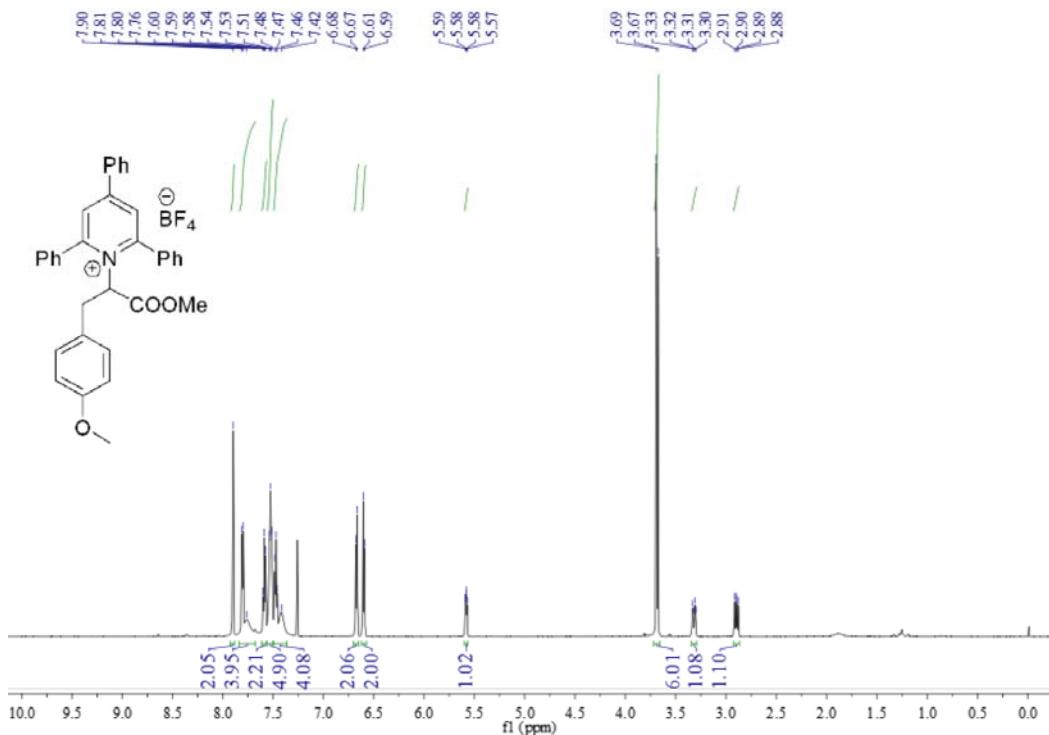
$^{13}\text{C}$  NMR of **2f**



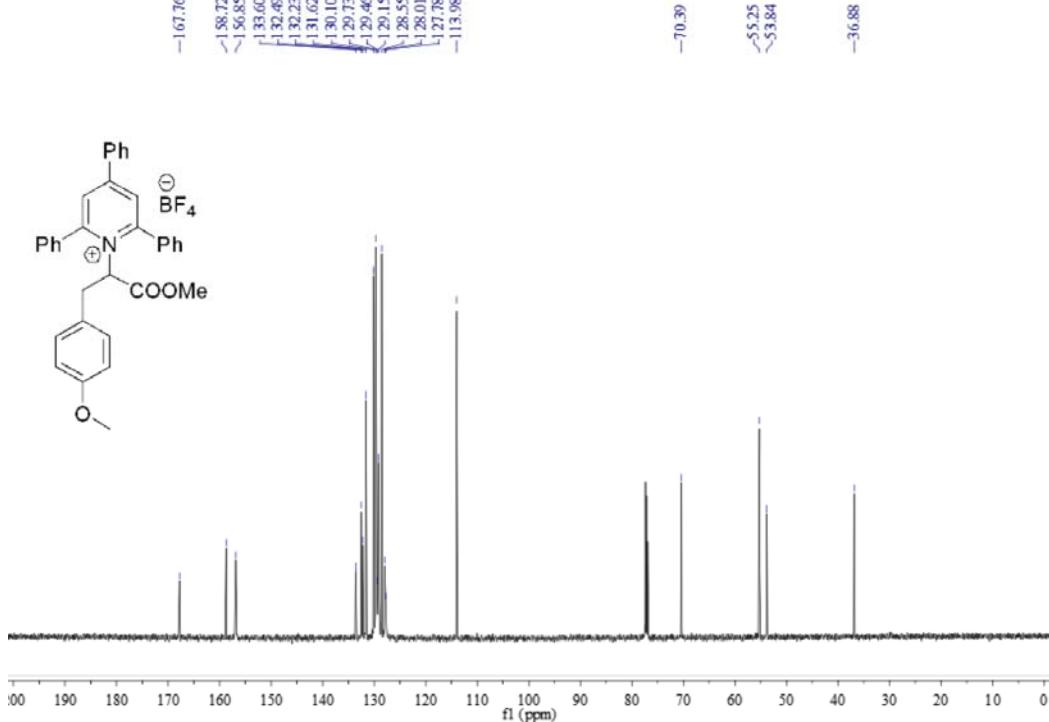
<sup>19</sup>F NMR of **2f**



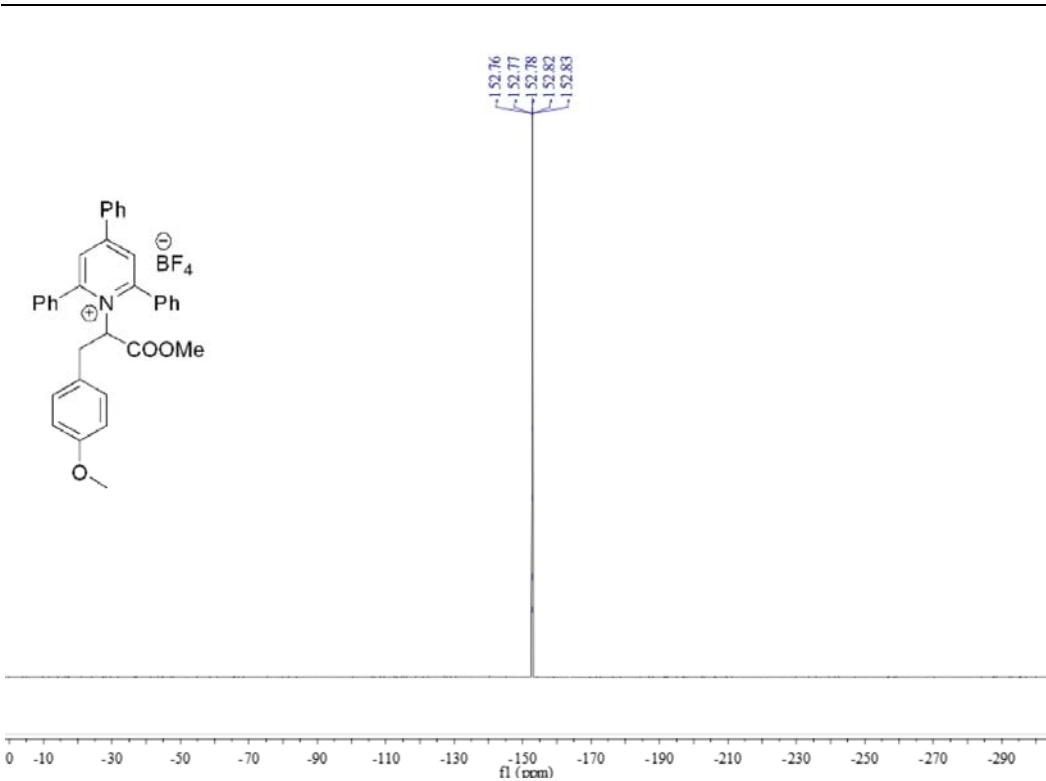
<sup>1</sup>H NMR of **2g**



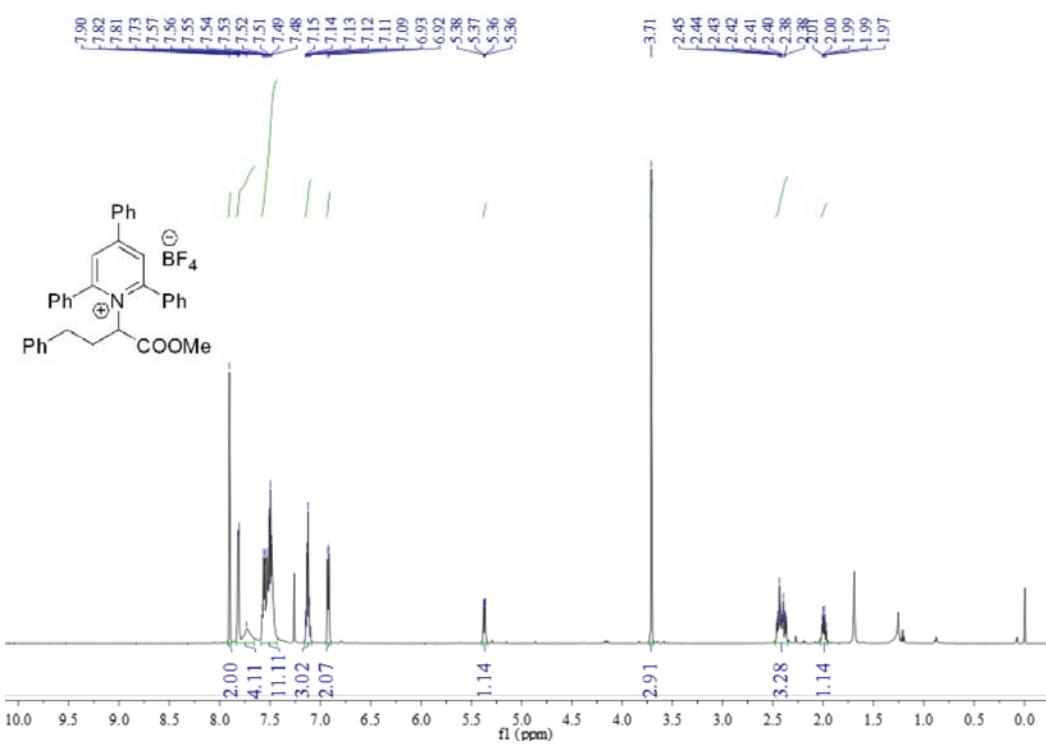
<sup>1</sup>H NMR of **2g**



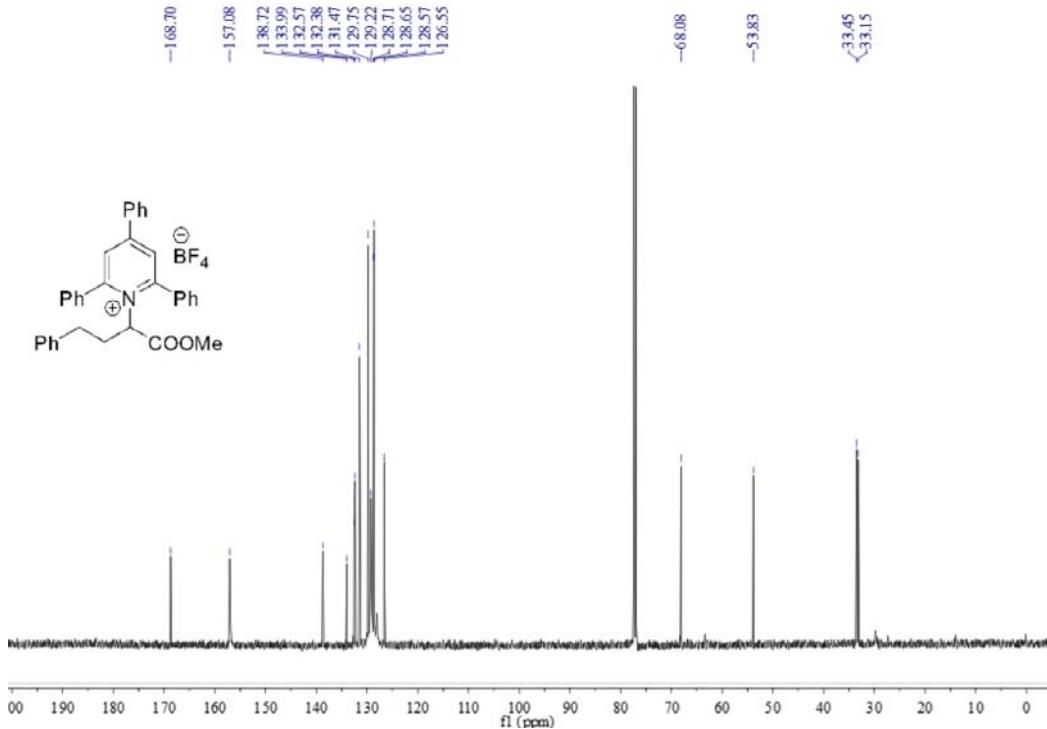
<sup>13</sup>C NMR of **2g**



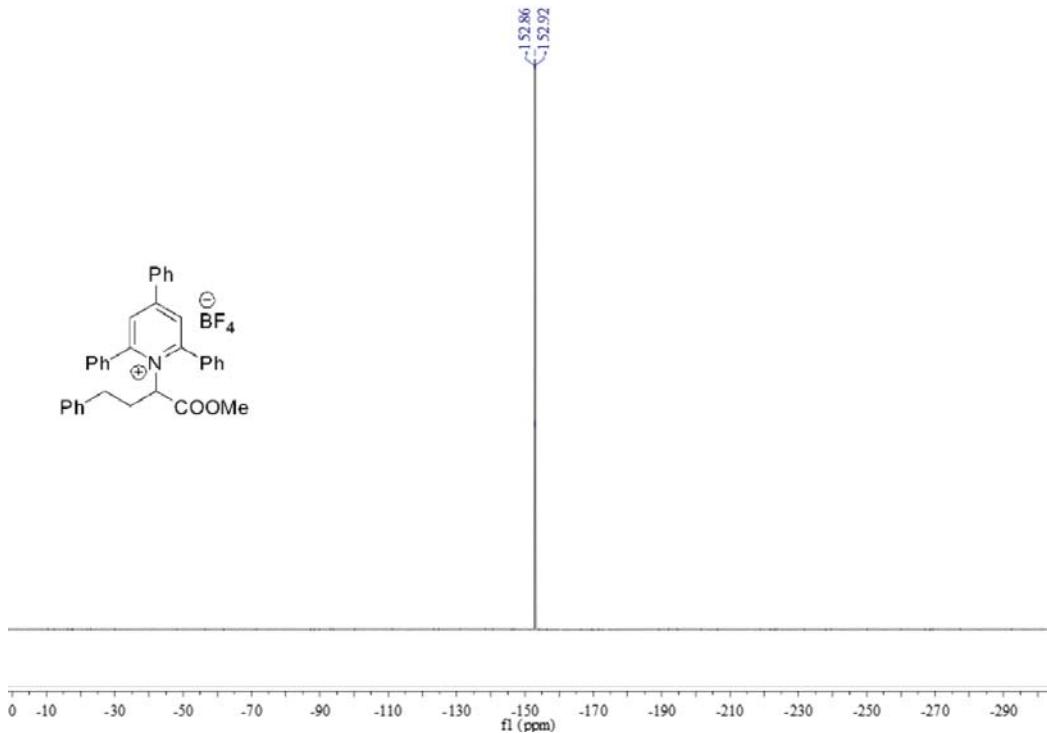
$^1\text{H}$  NMR of **2h**



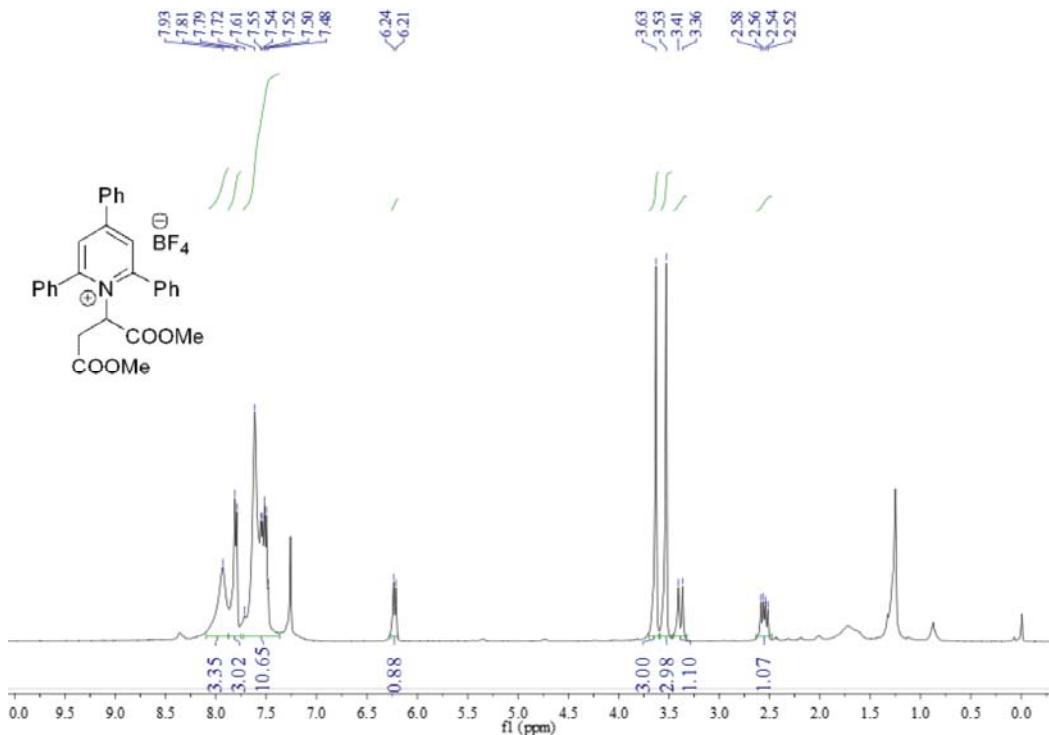
$^{13}\text{C}$  NMR of **2h**



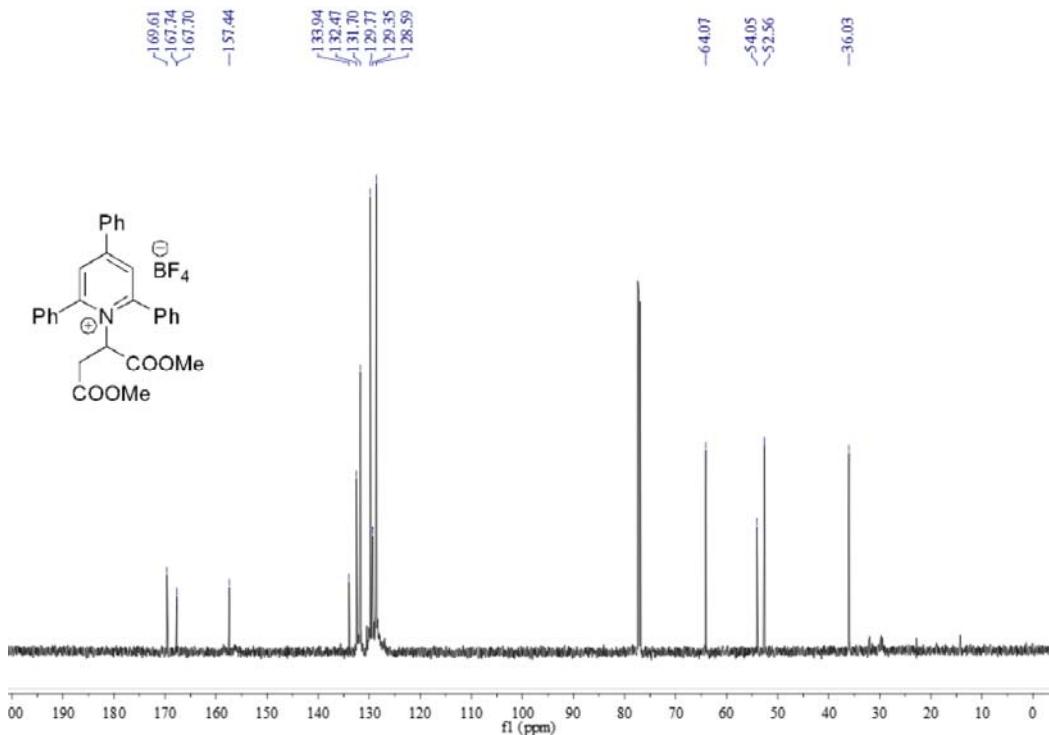
<sup>19</sup>F NMR of **2h**



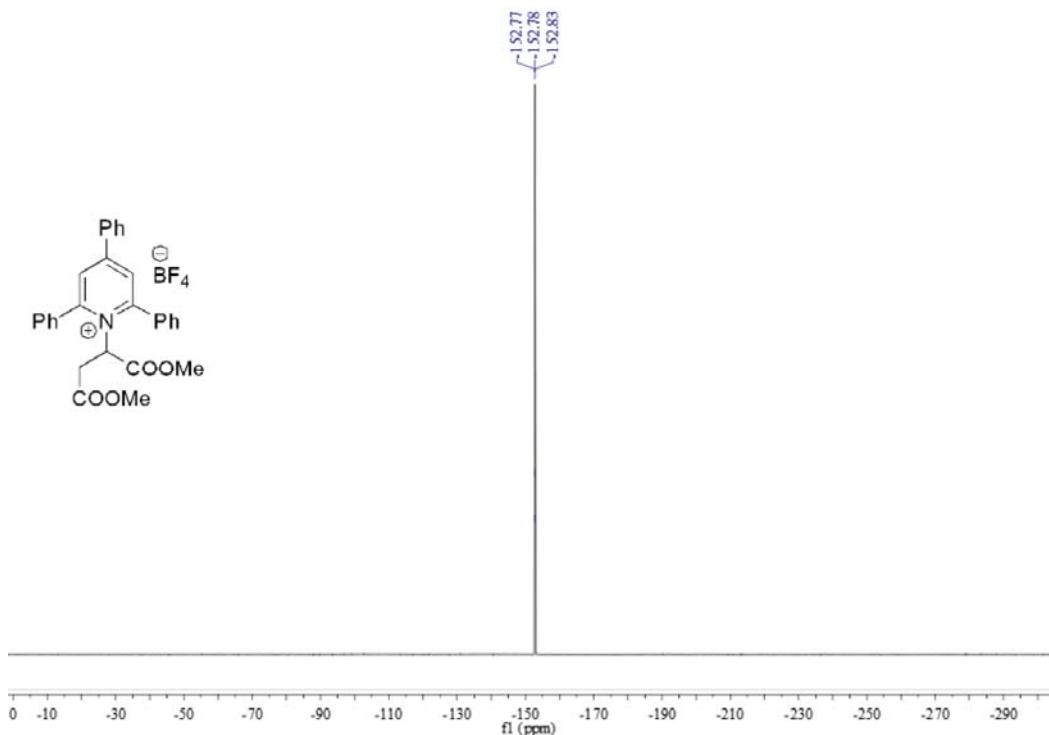
<sup>1</sup>H NMR of **2i**



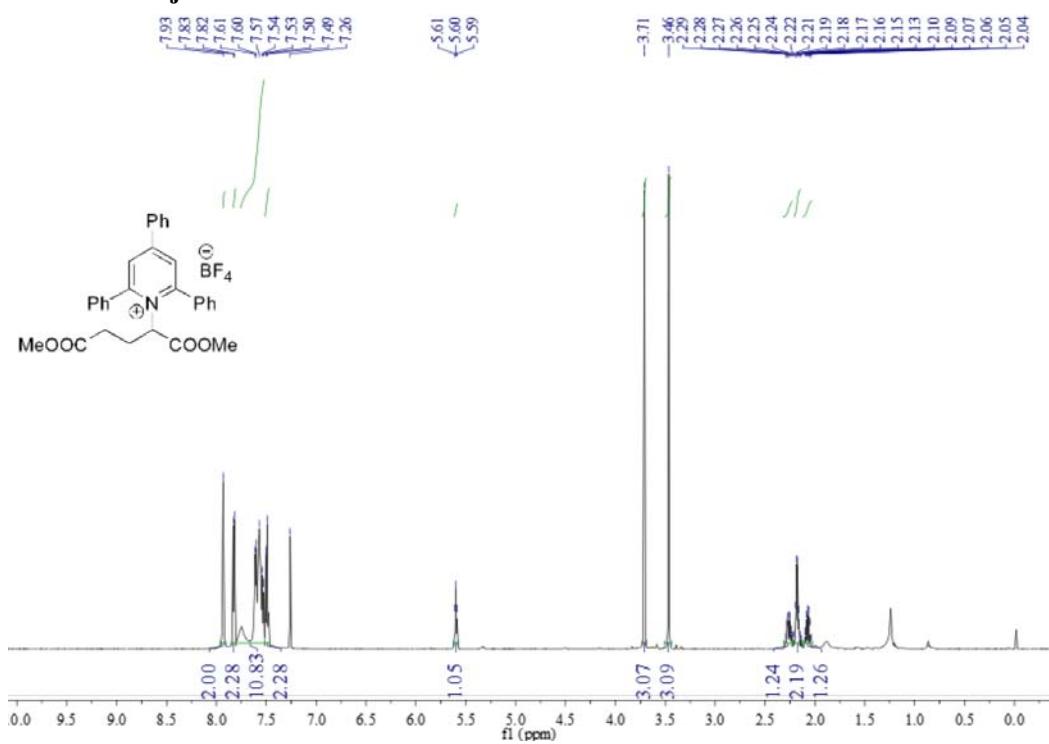
<sup>1</sup>H NMR of **2i**



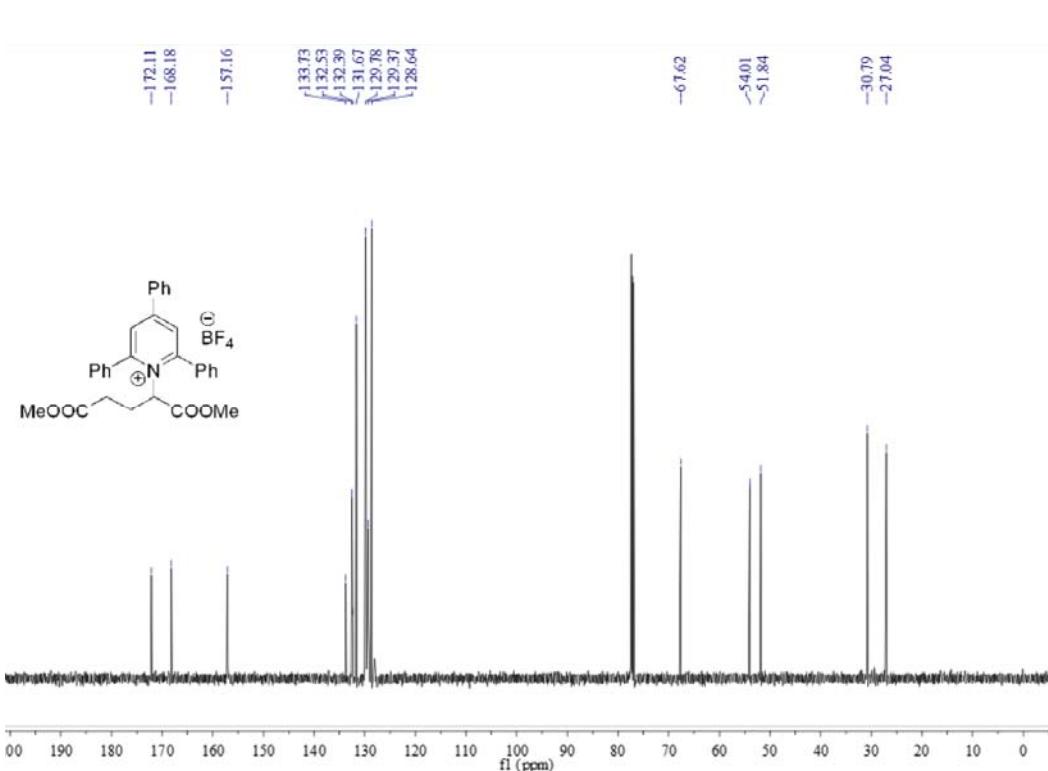
<sup>19</sup>F NMR of **2i**



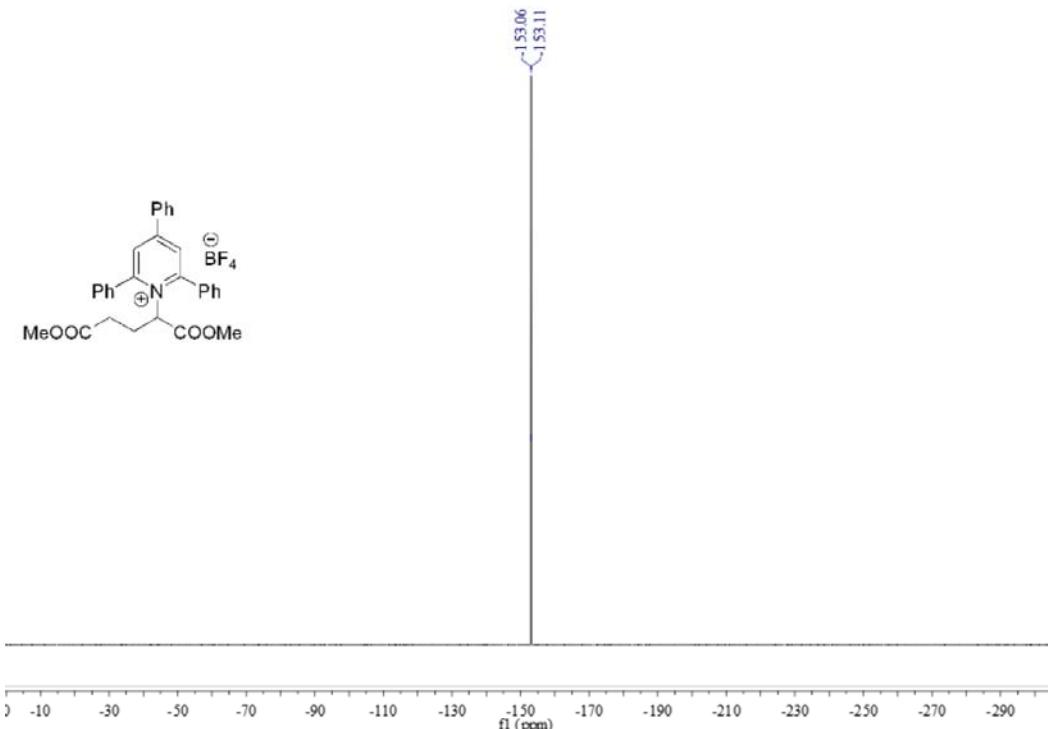
### $^1\text{H}$ NMR of **2j**



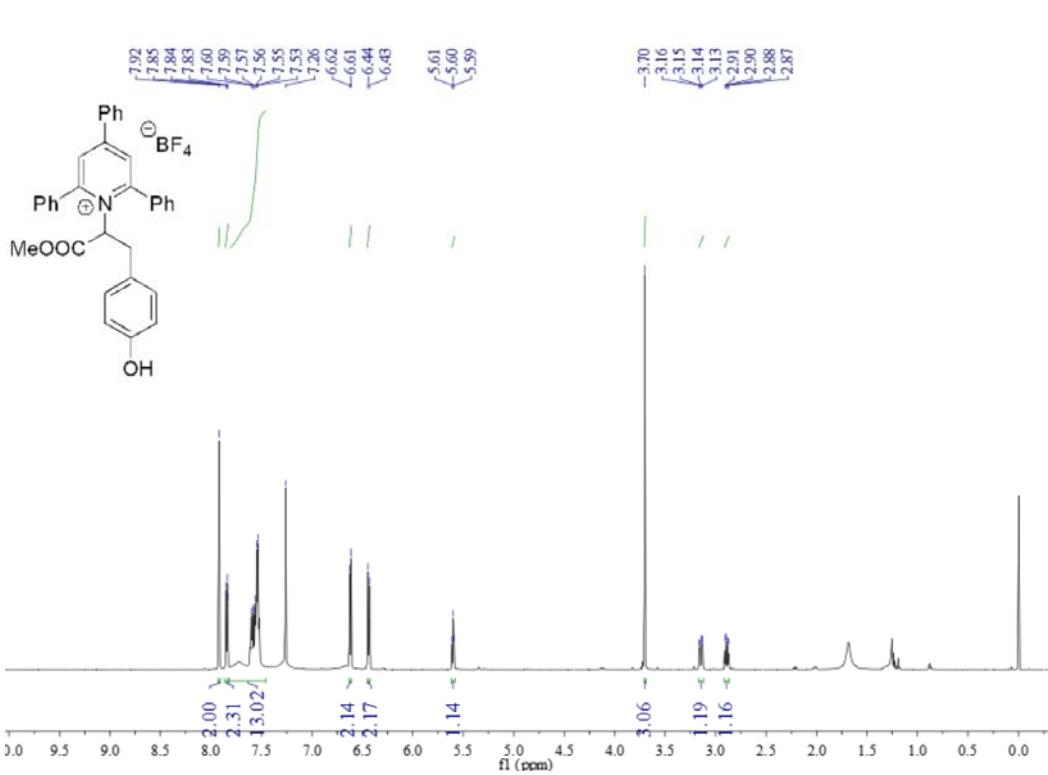
### $^{13}\text{C}$ NMR of **2j**



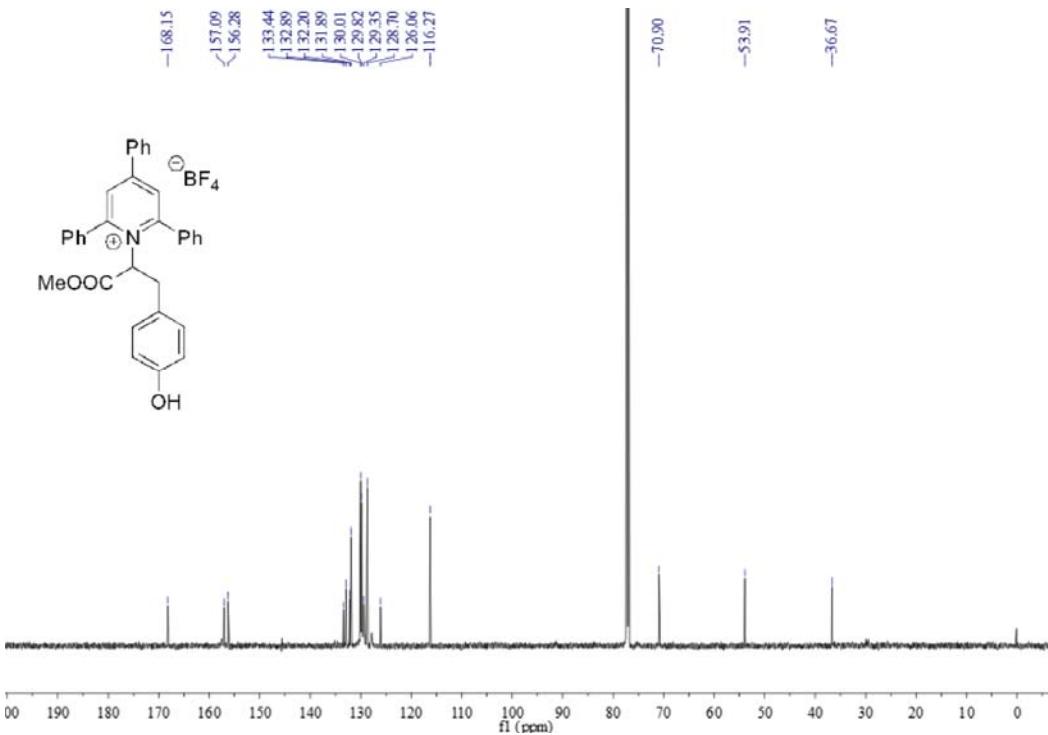
<sup>19</sup>F NMR of **2j**



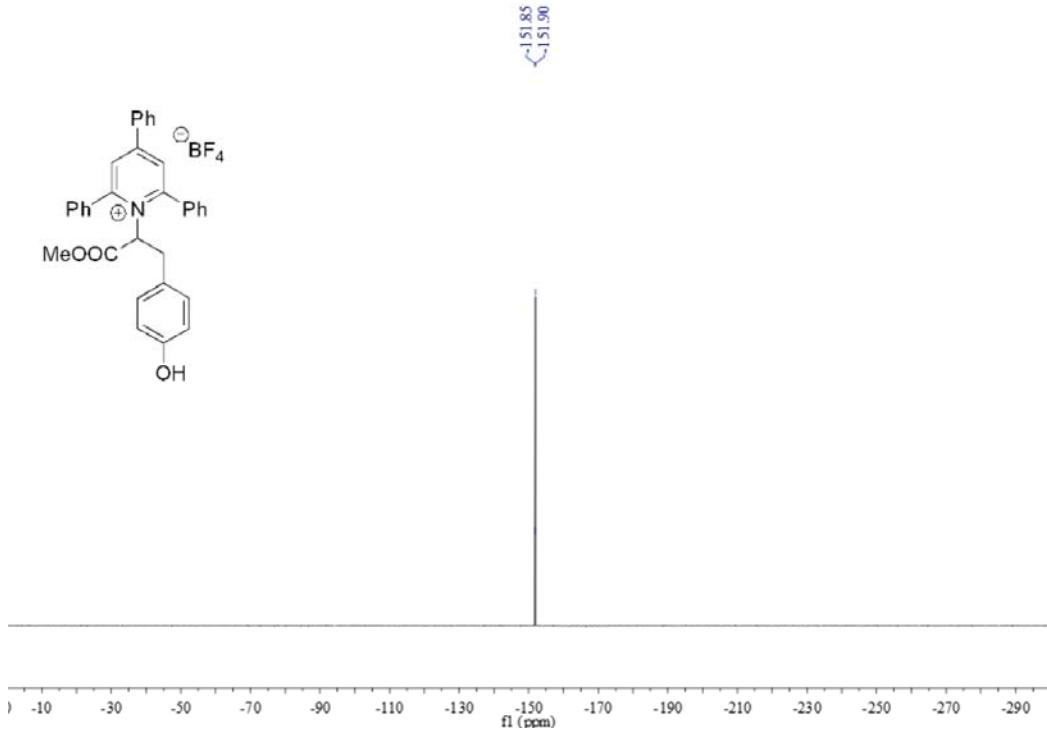
<sup>1</sup>H NMR of **2k**



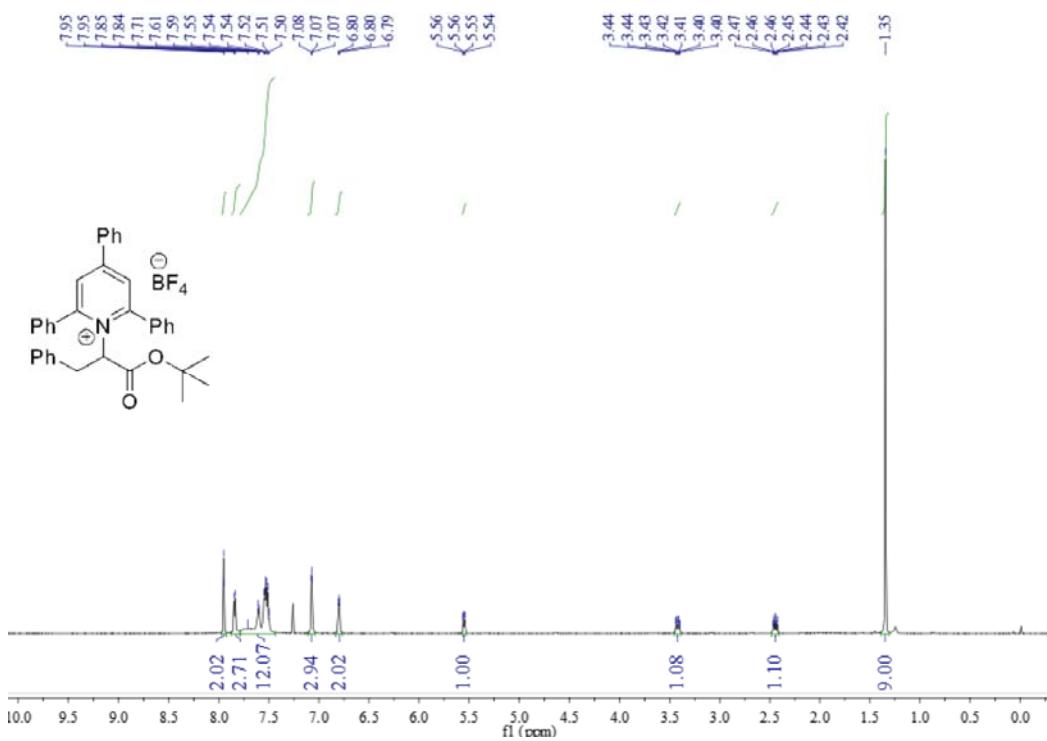
<sup>1</sup>H NMR of **2k**



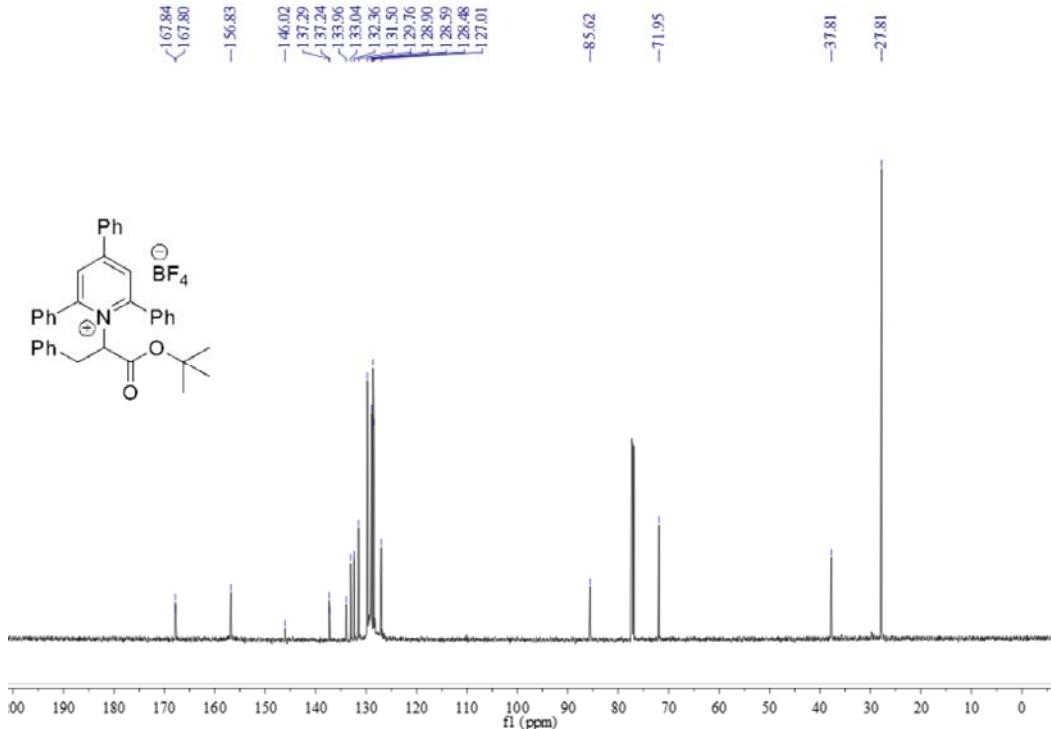
<sup>13</sup>C NMR of **2k**



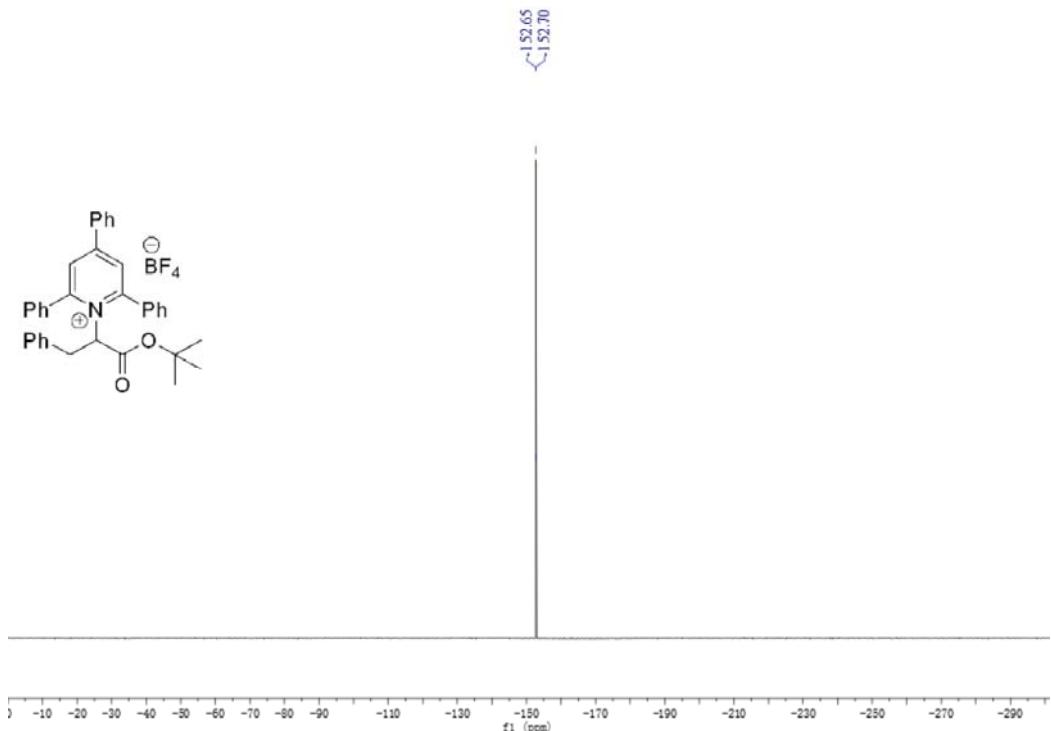
$^1\text{H}$  NMR of **2l**



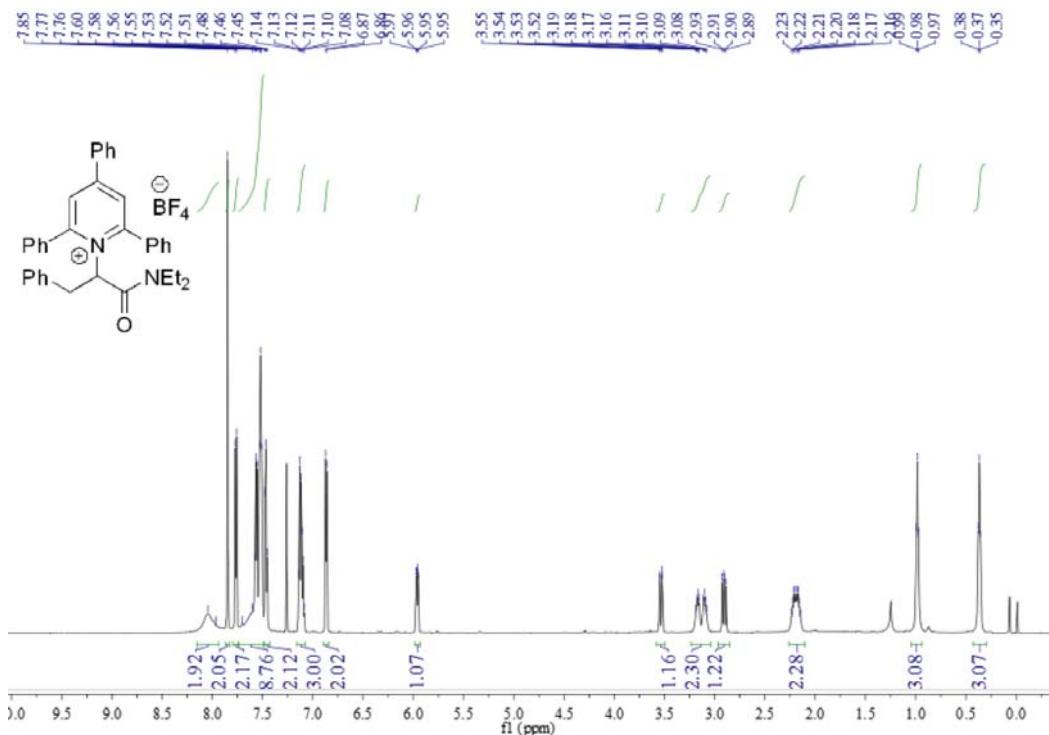
$^{12}\text{C}$  NMR of **2l**



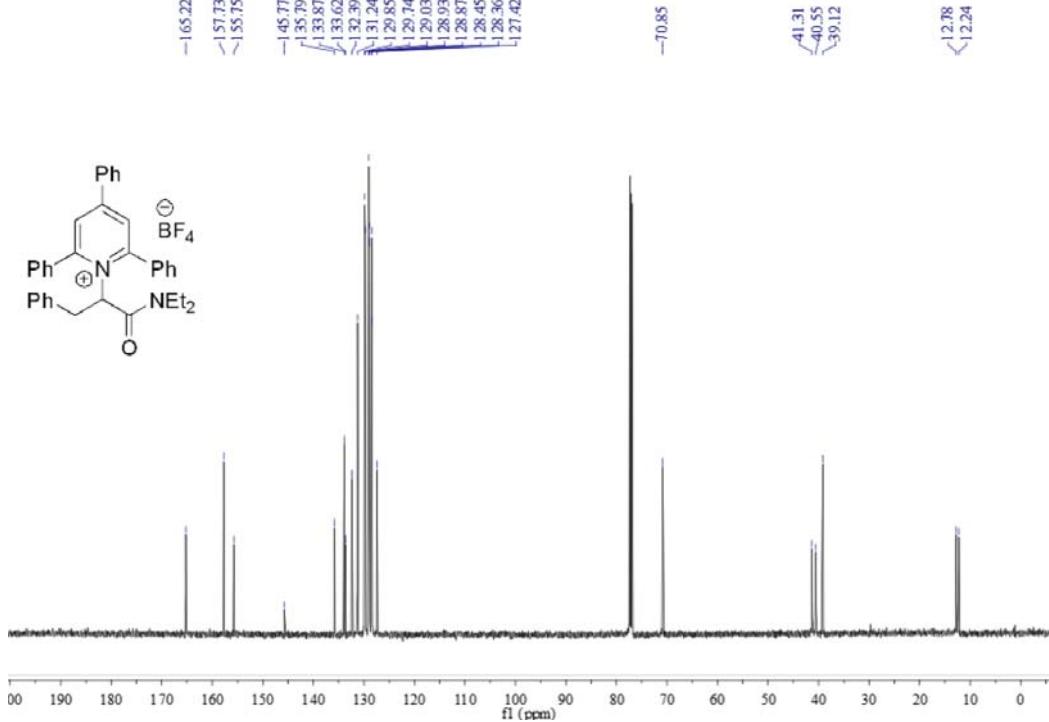
<sup>19</sup>F NMR of **2l**



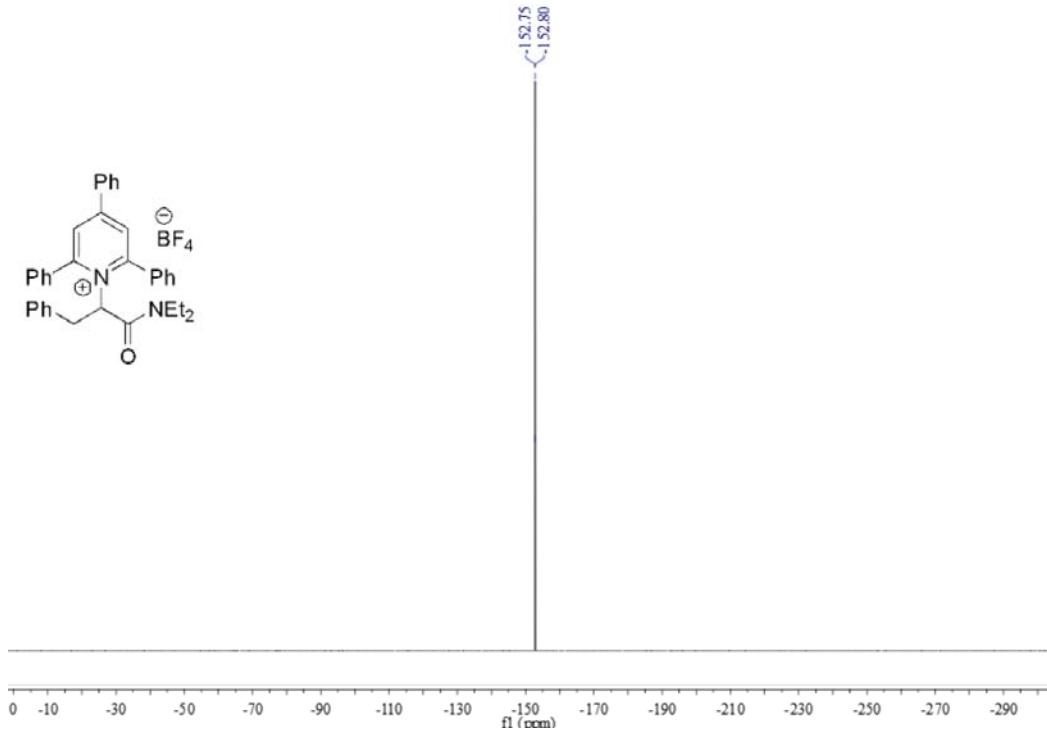
<sup>1</sup>H NMR of **2m**



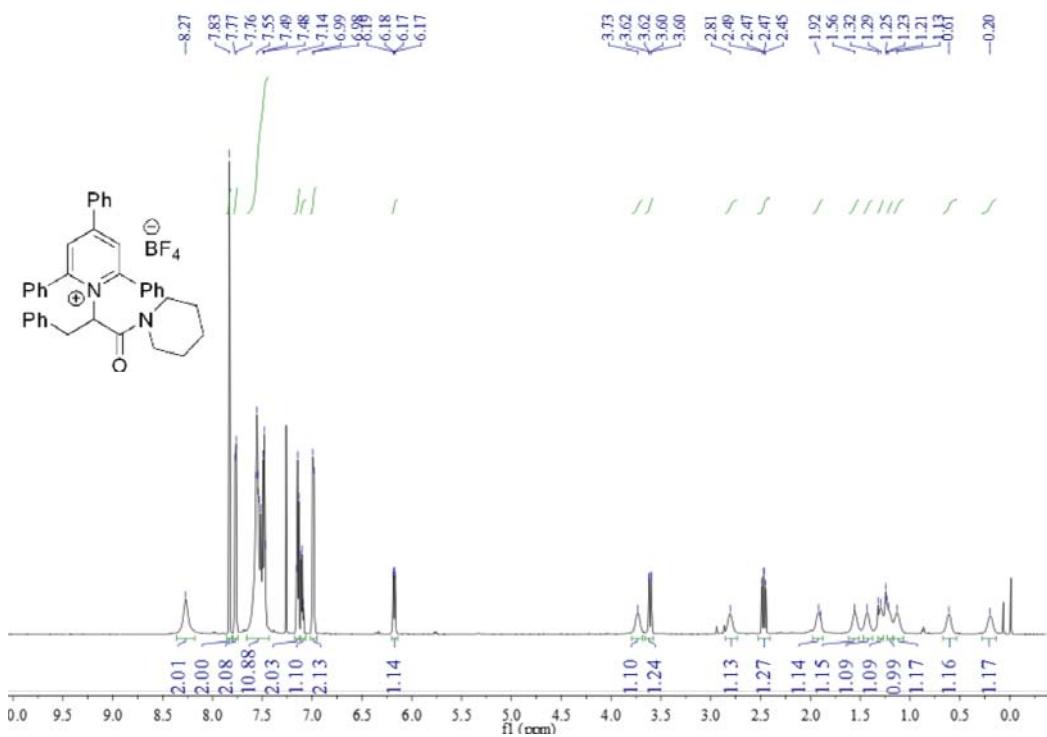
<sup>1</sup>H NMR of **2m**



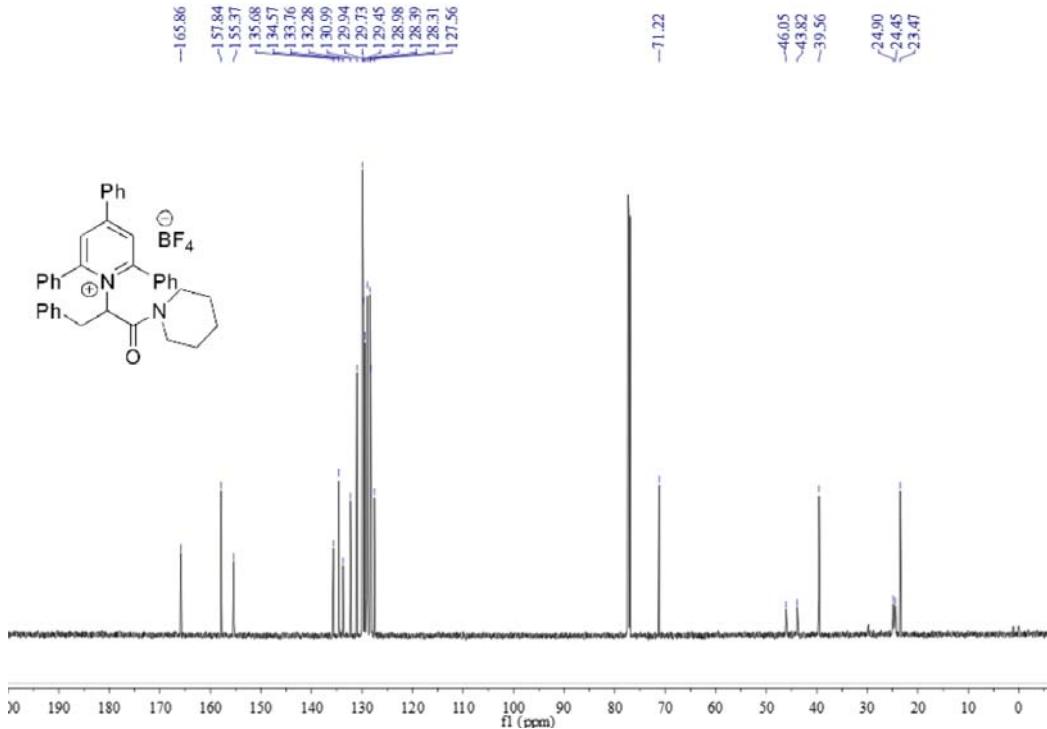
<sup>13</sup>C NMR of **2m**



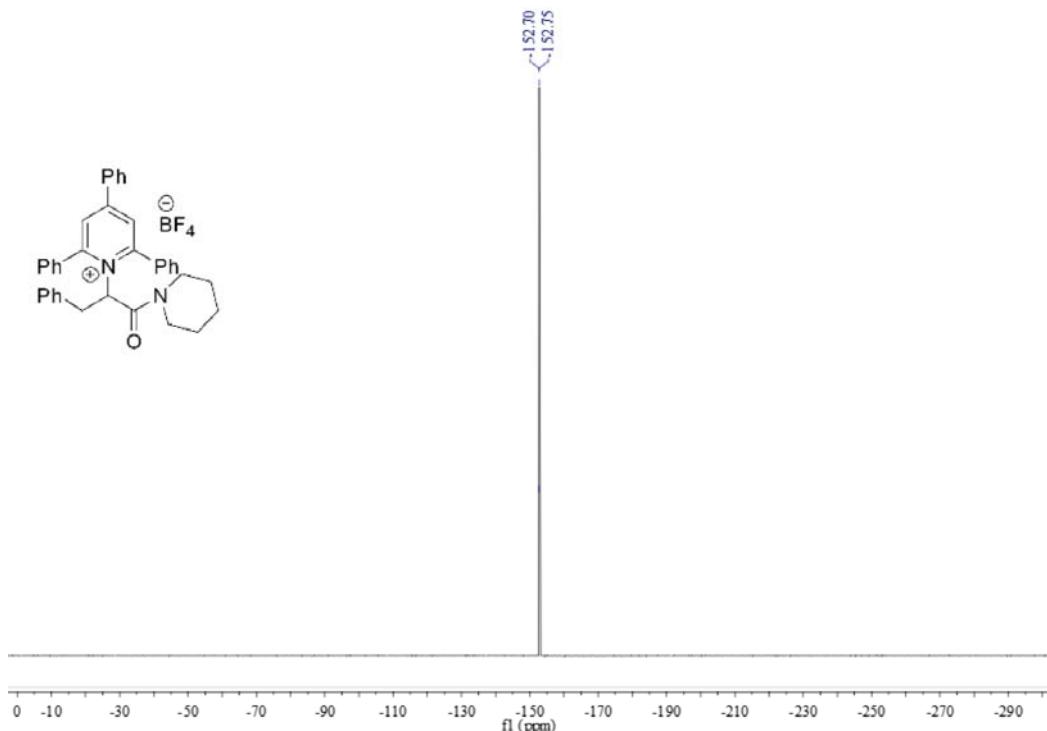
### <sup>1</sup>H NMR of **2n**



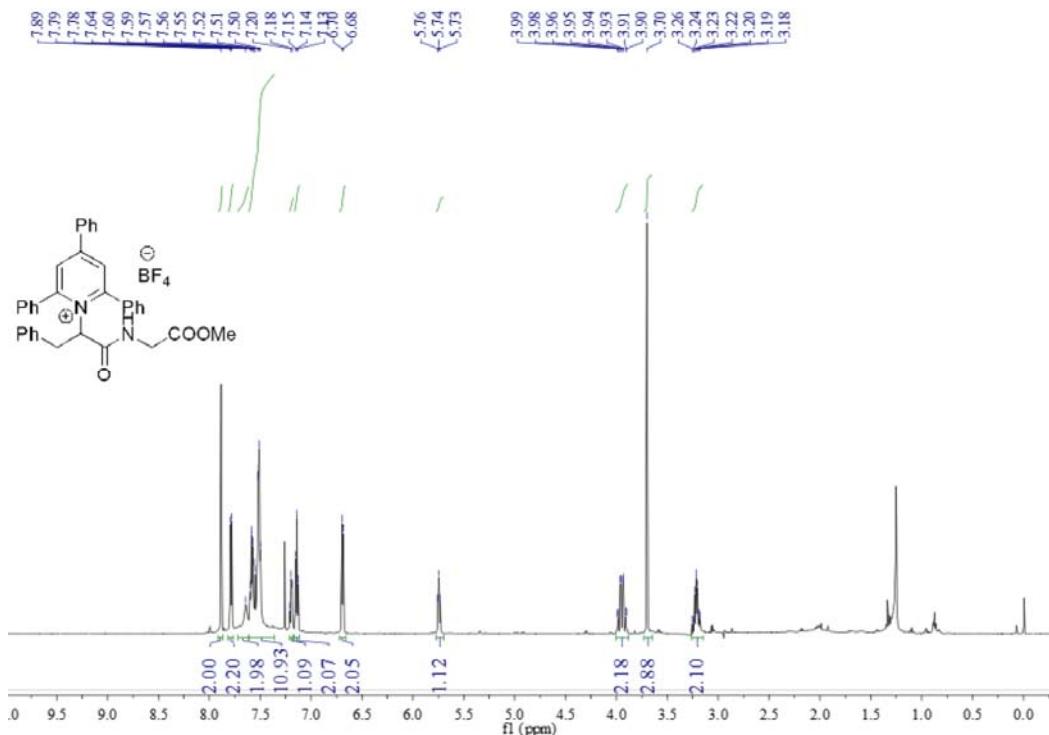
### <sup>13</sup>C NMR of **2n**



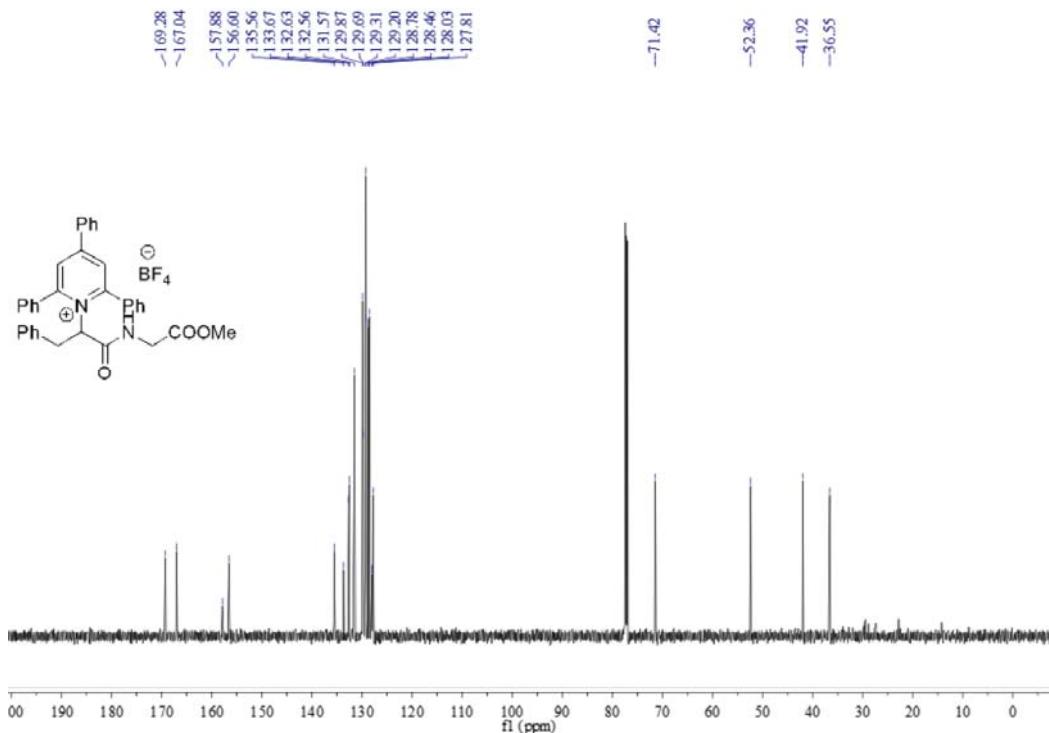
<sup>13</sup>C NMR of **2n**



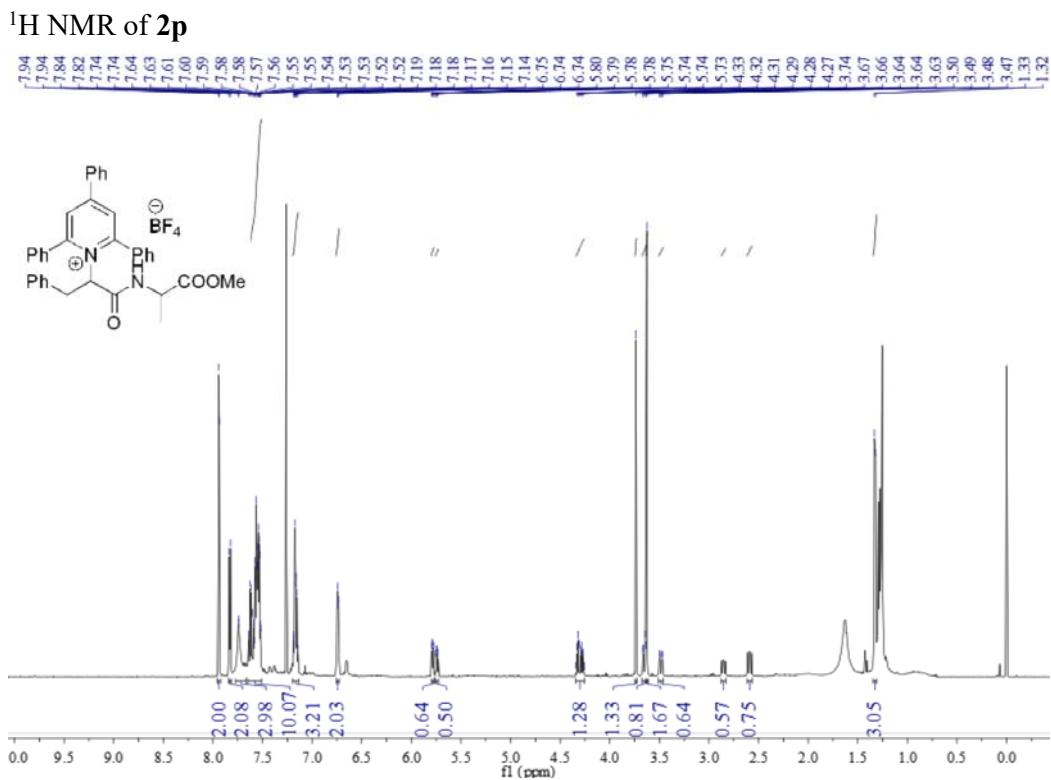
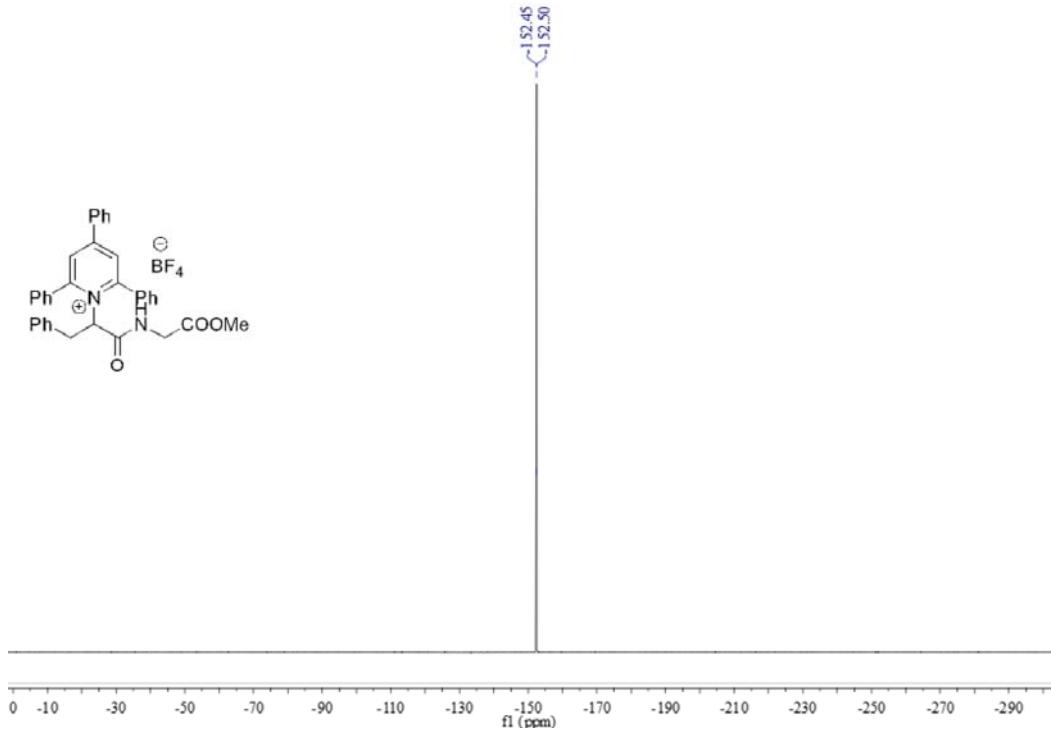
<sup>1</sup>H NMR of **2o**

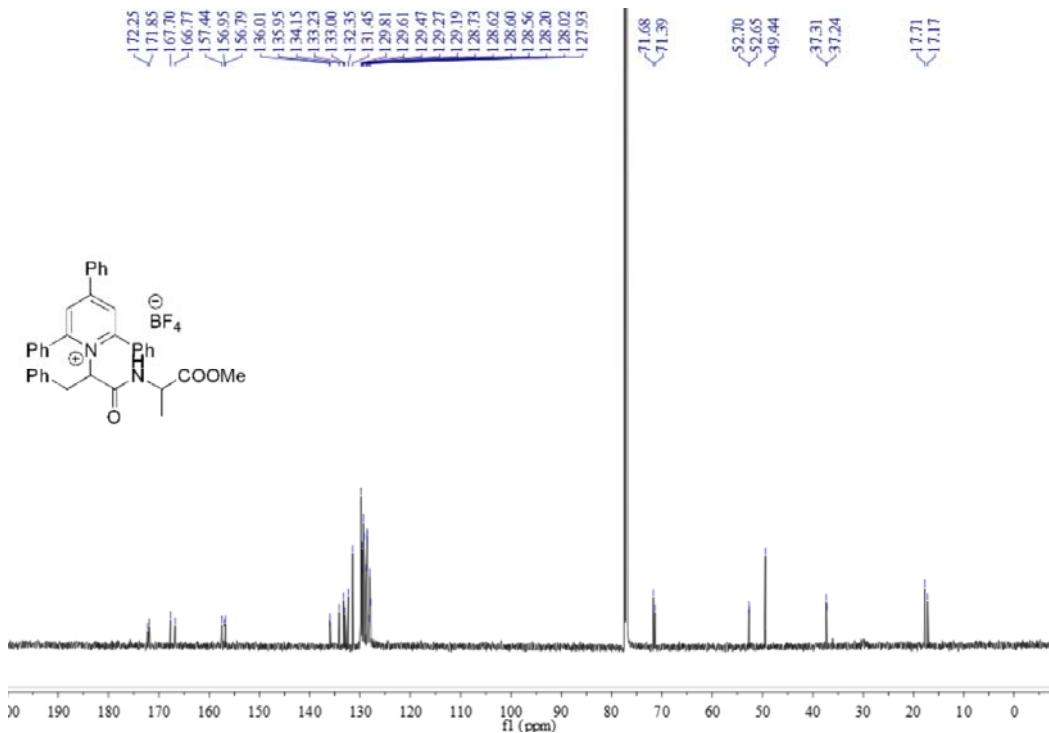


<sup>1</sup>H NMR of **2o**

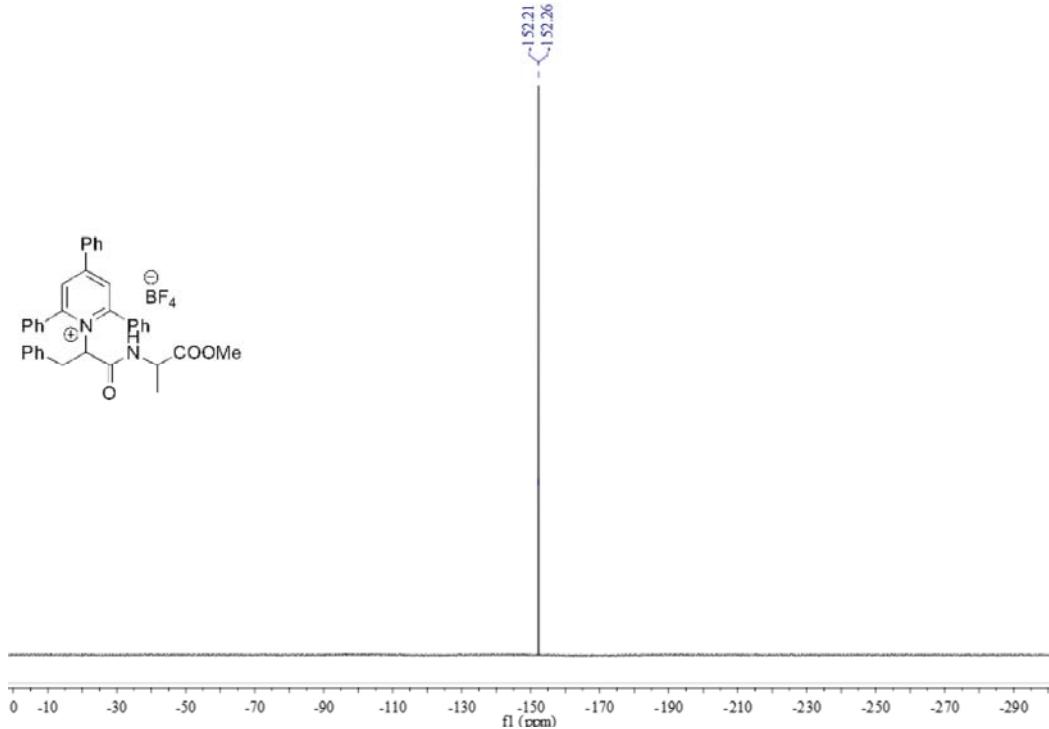


<sup>13</sup>C NMR of **2o**

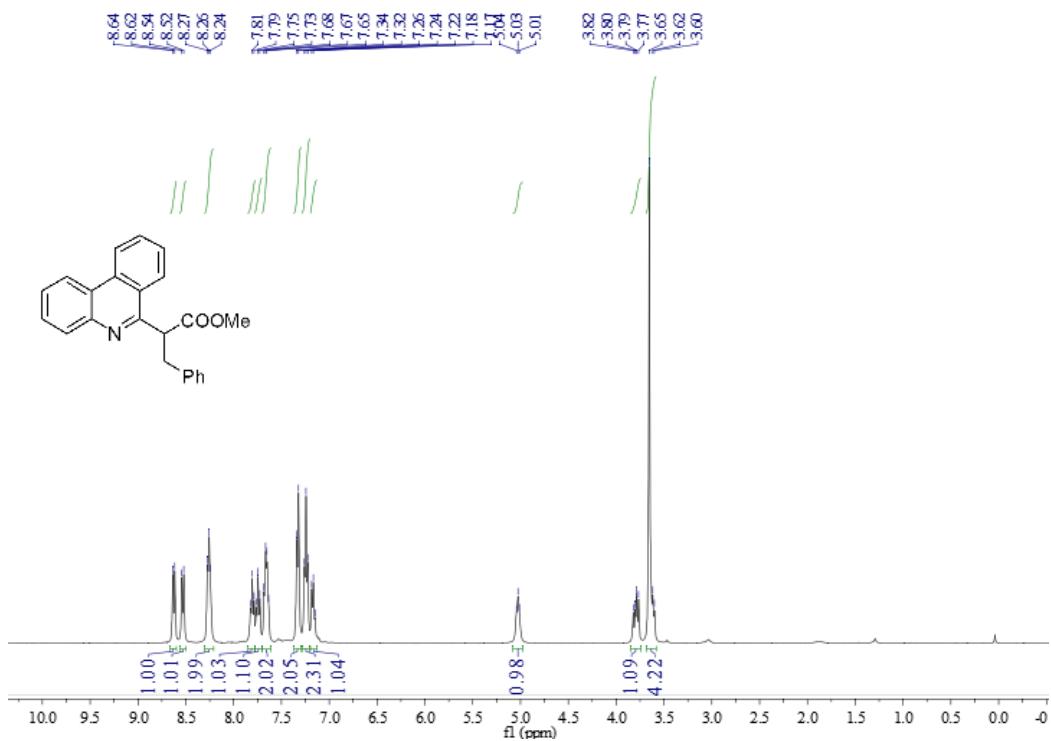




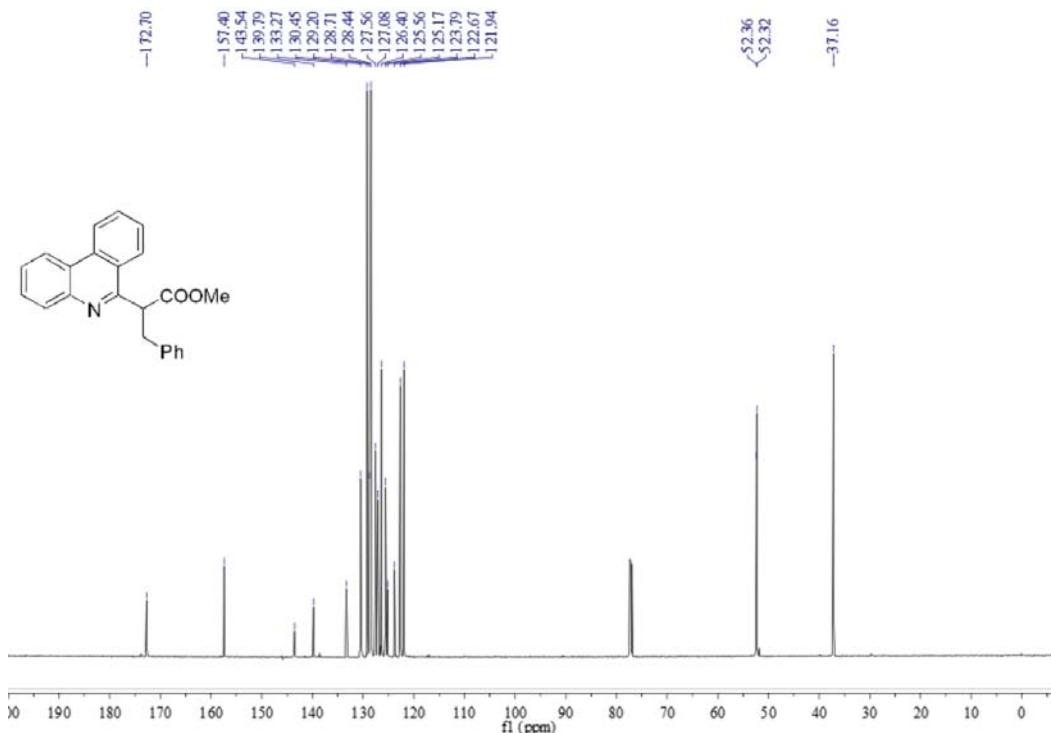
$^{13}\text{C}$  NMR of **2p**



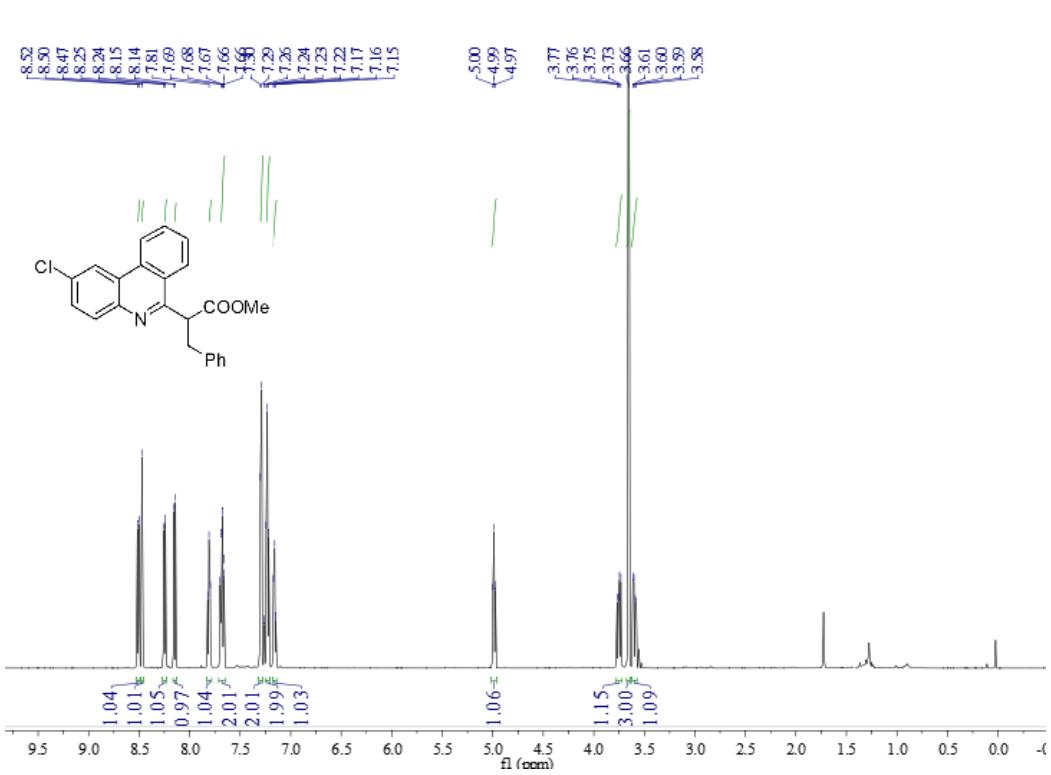
$^1\text{H}$  NMR of **3a**



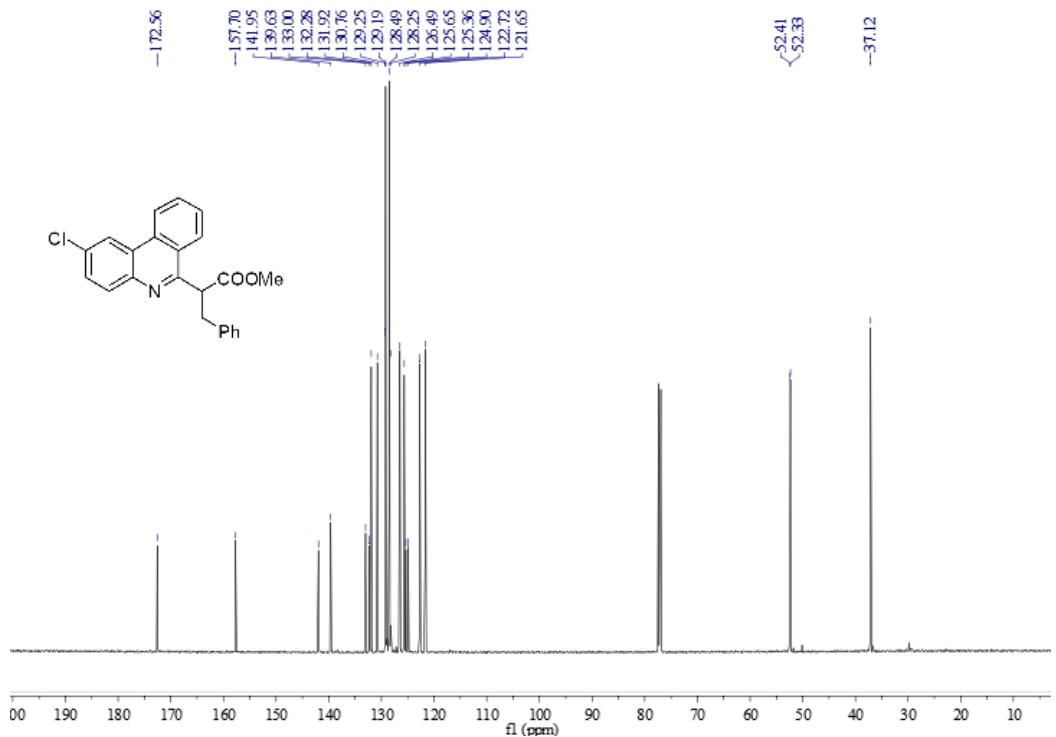
<sup>1</sup>H NMR of 3a



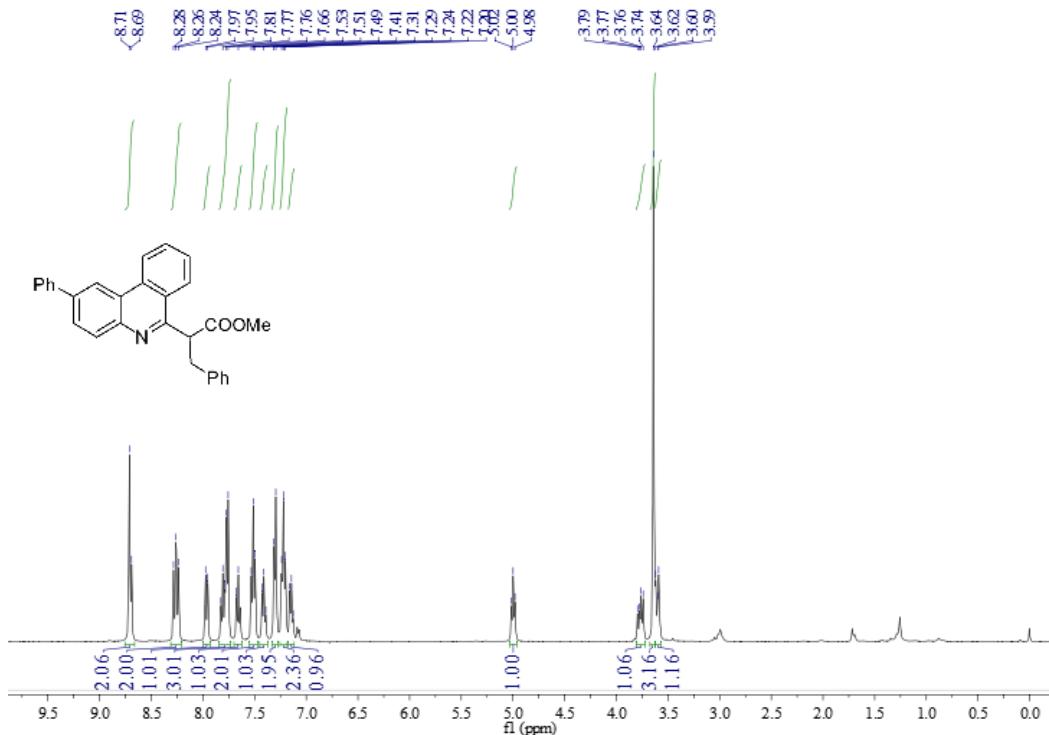
<sup>1</sup>H NMR of 3b



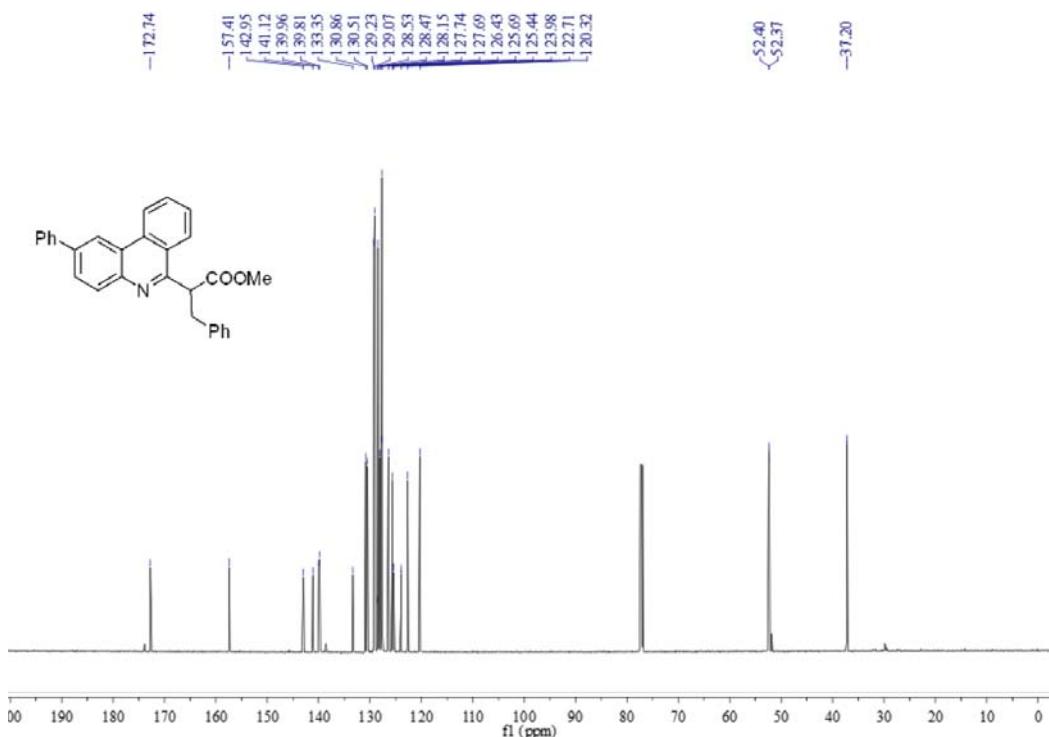
<sup>1</sup>H NMR of 3b



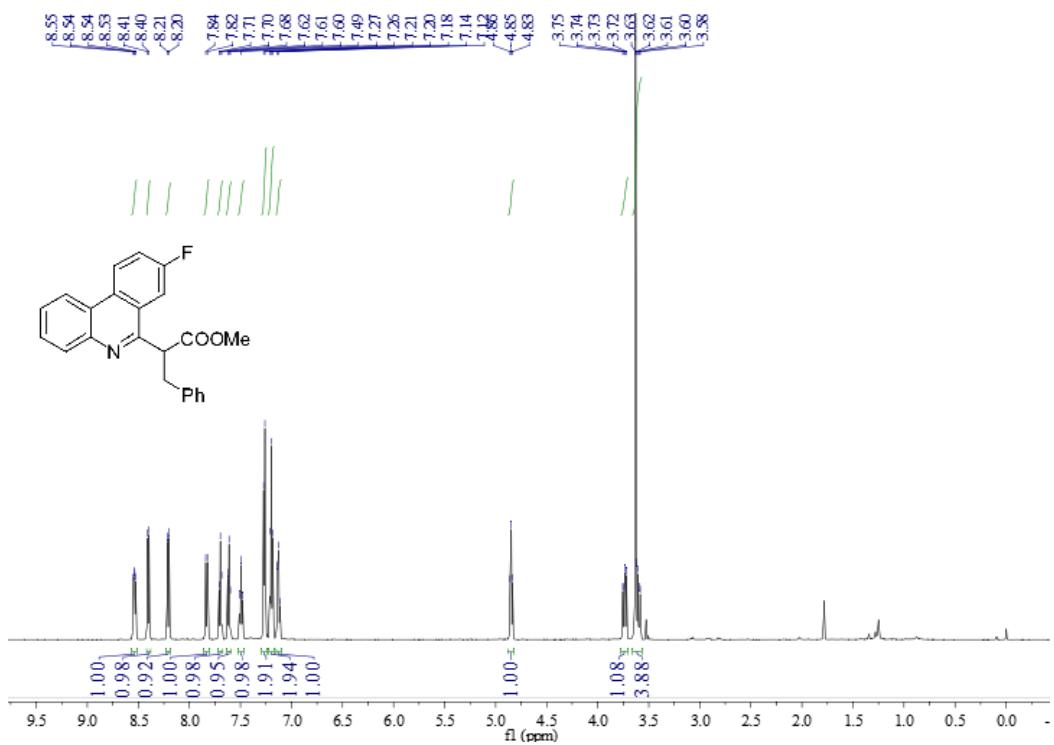
<sup>1</sup>H NMR of 3c



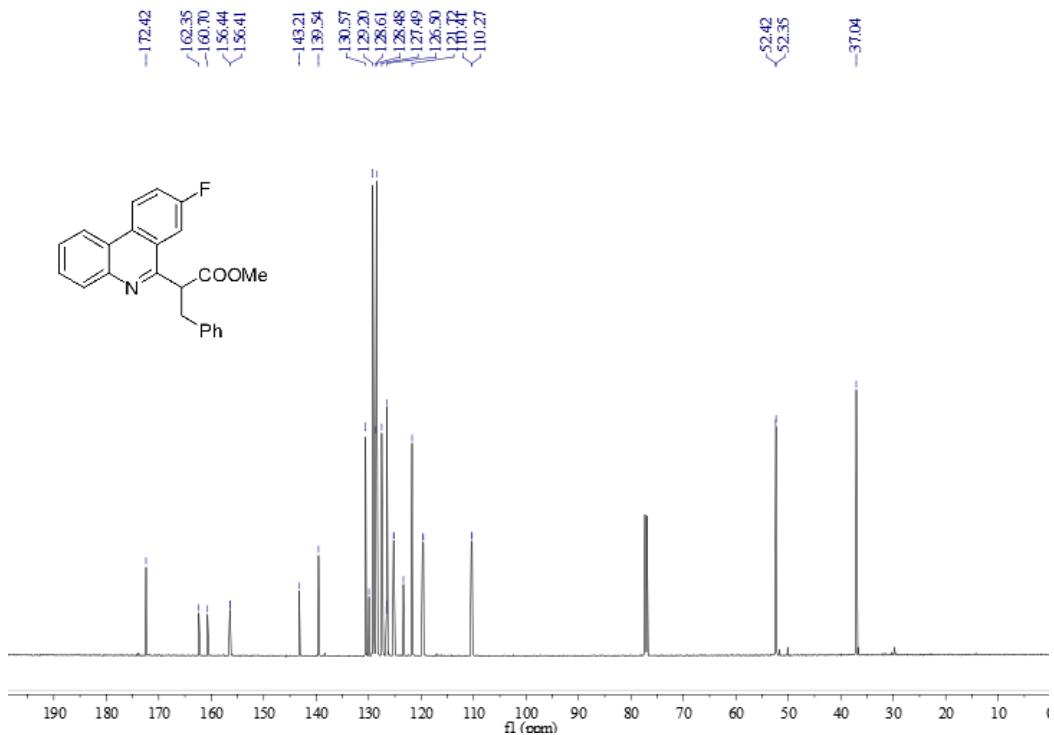
<sup>1</sup>H NMR of 3c



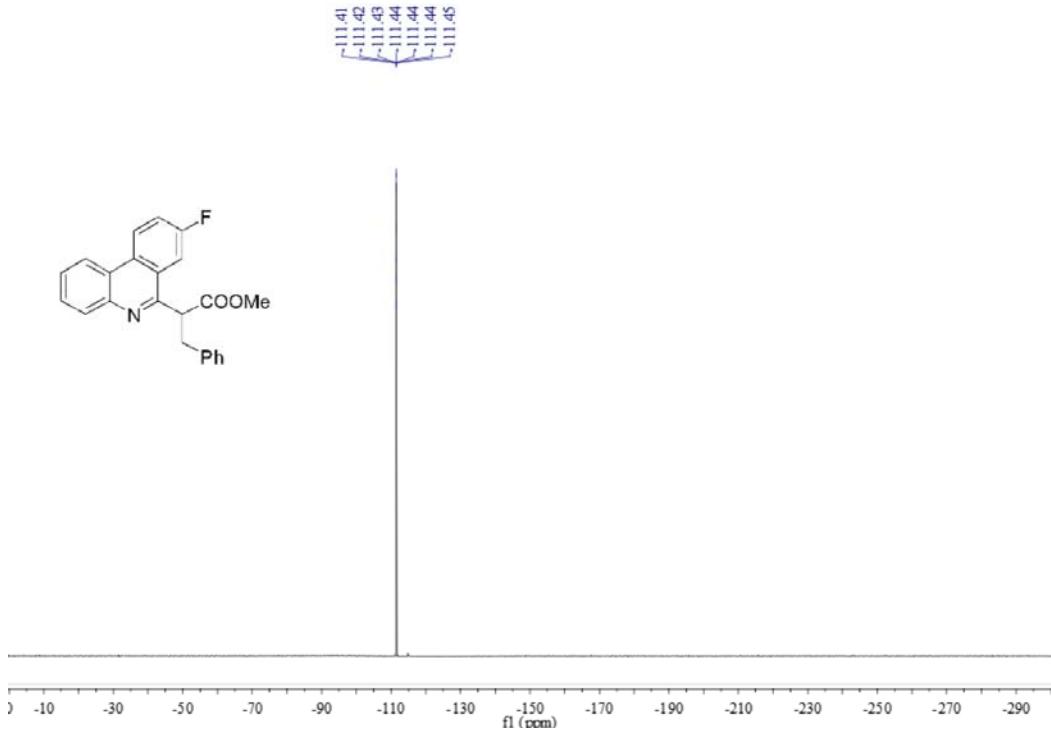
<sup>1</sup>H NMR of 3d



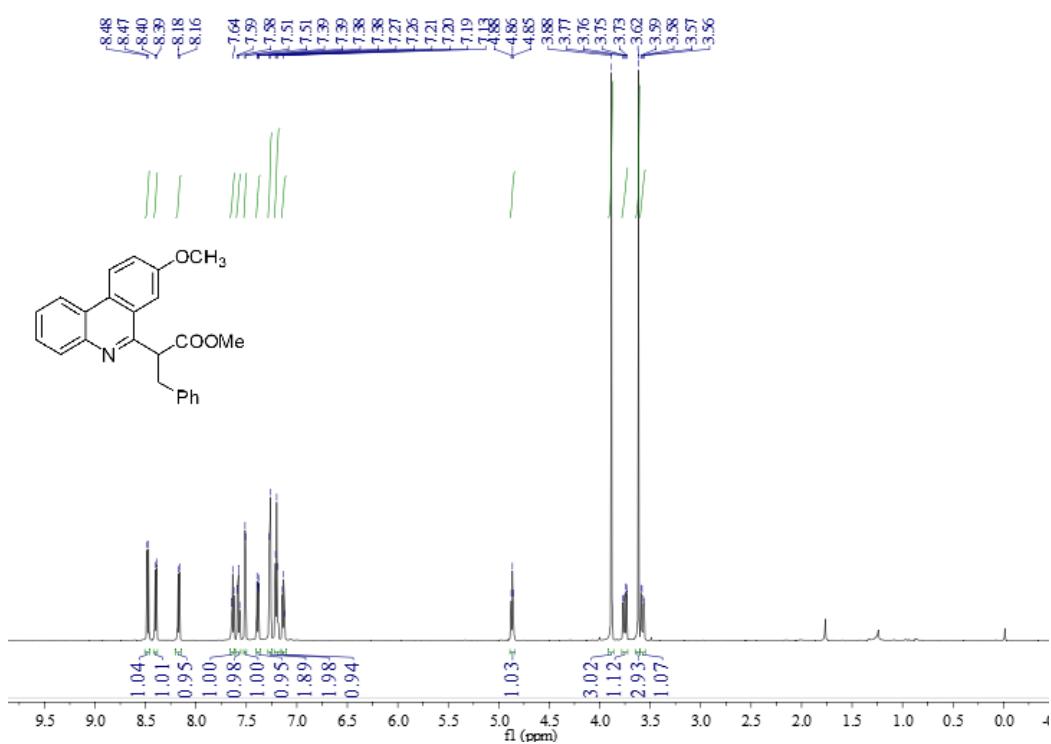
<sup>1</sup>H NMR of **3d**



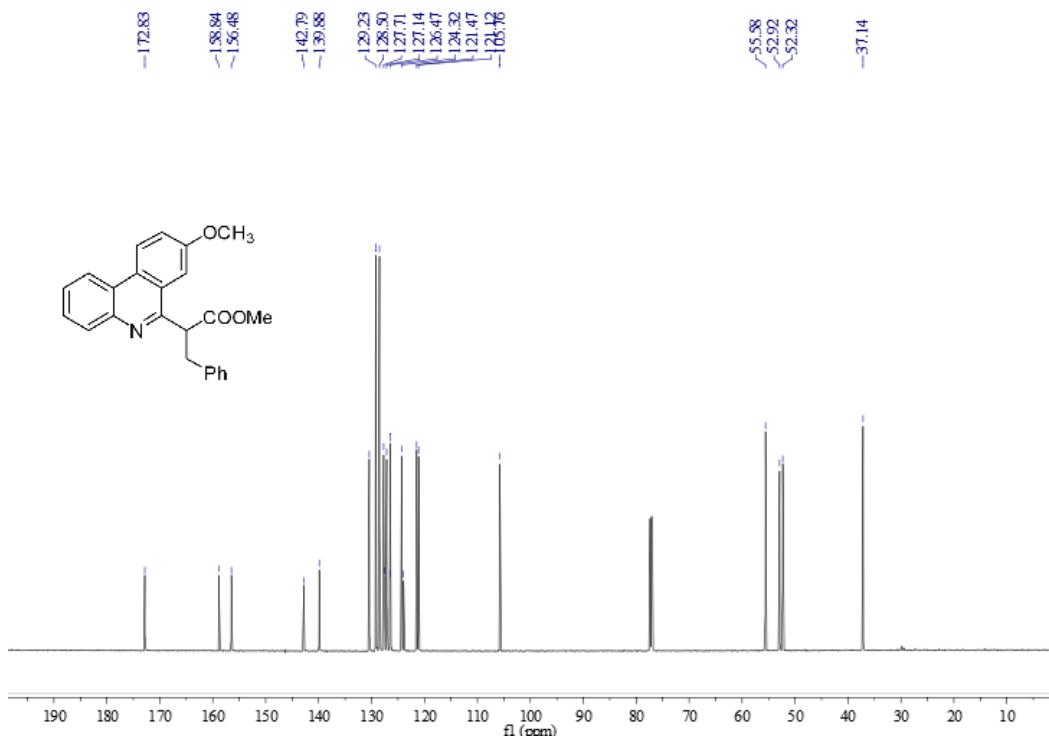
<sup>19</sup>F NMR of **3d**



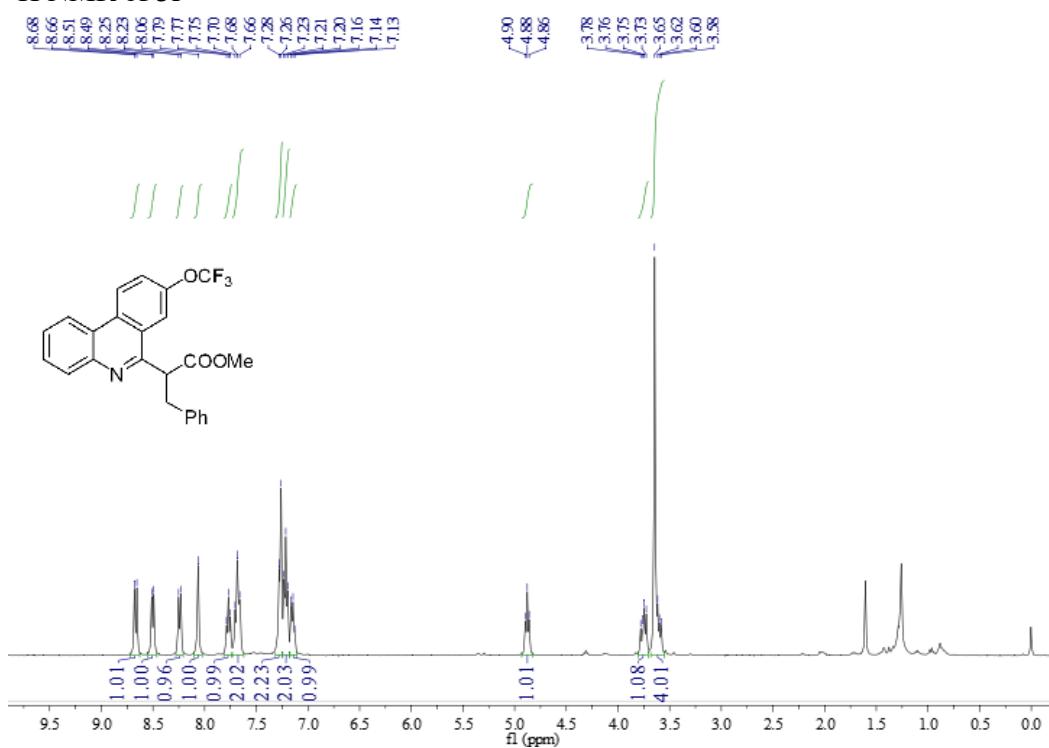
$^1\text{H}$  NMR of **3e**



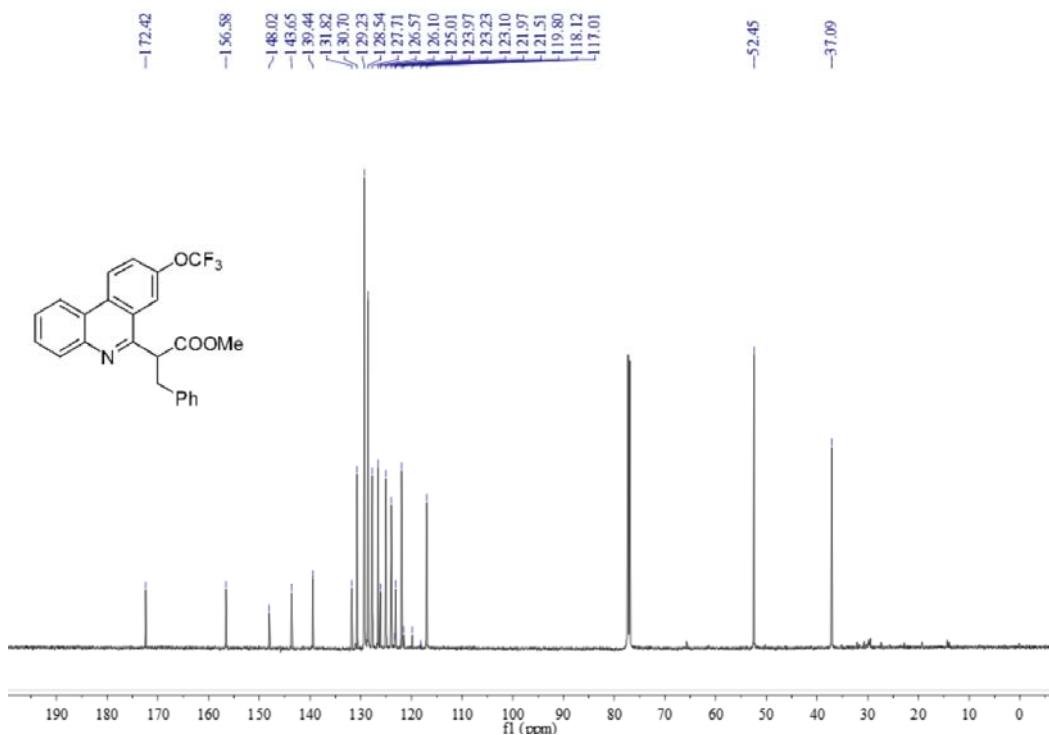
$^{13}\text{C}$  NMR of **3e**



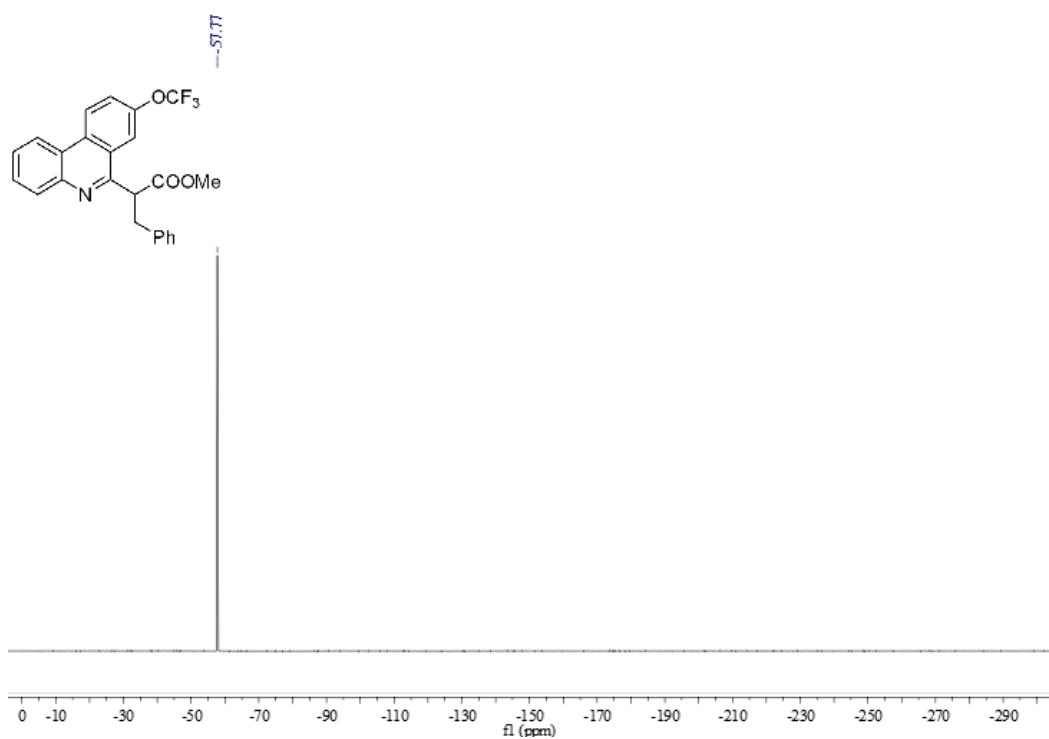
### <sup>1</sup>H NMR of 3f



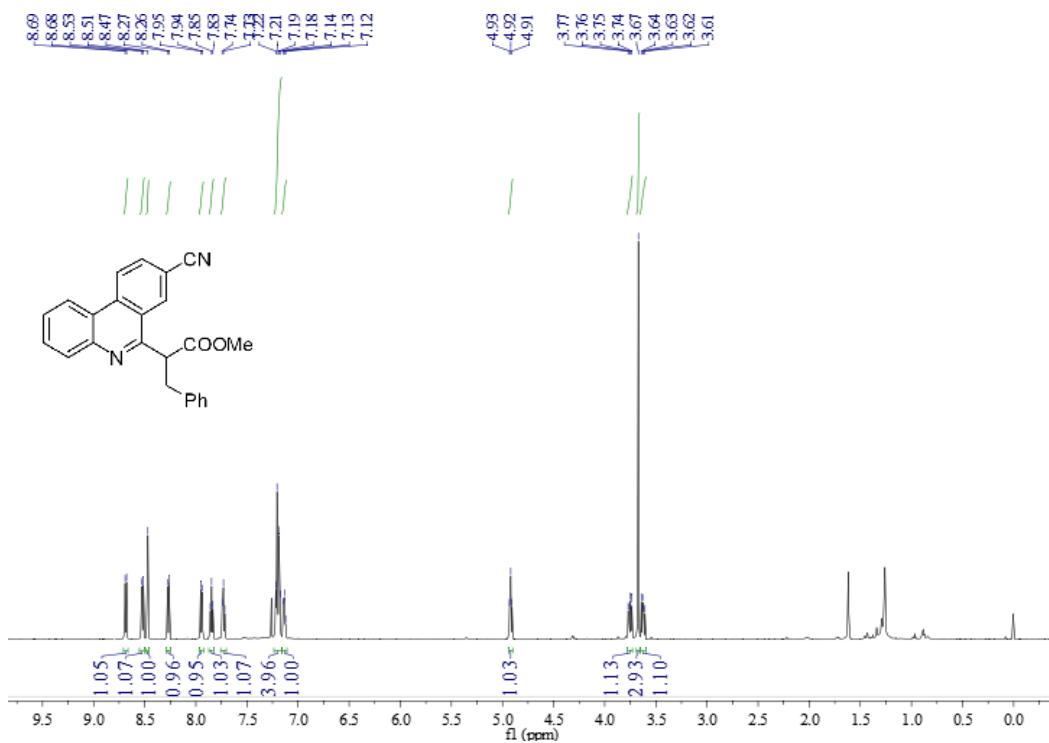
### <sup>13</sup>C NMR of 3f



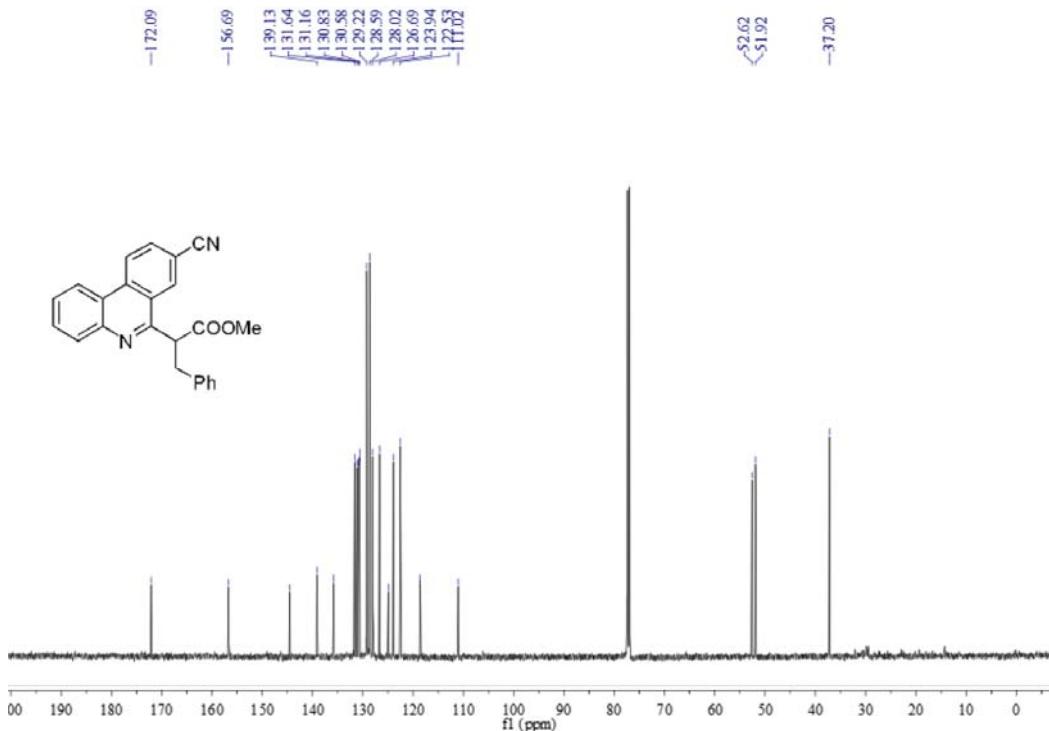
<sup>19</sup>F NMR of **3f**



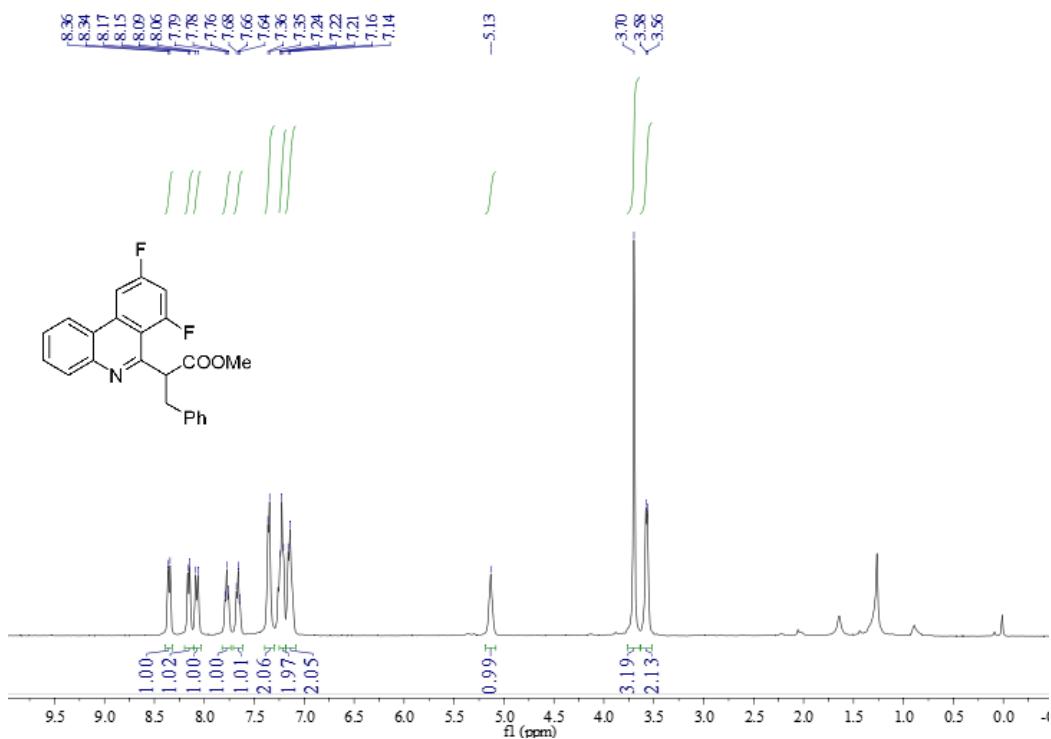
<sup>1</sup>H NMR of **3g**



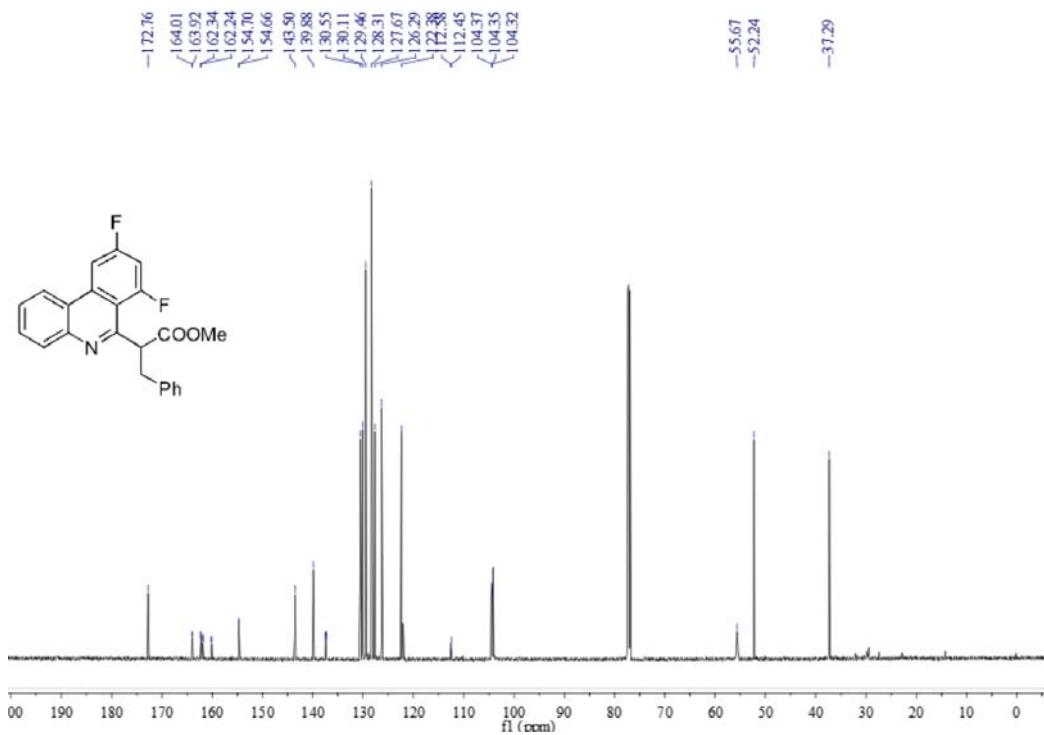
<sup>1</sup>H NMR of **3g**



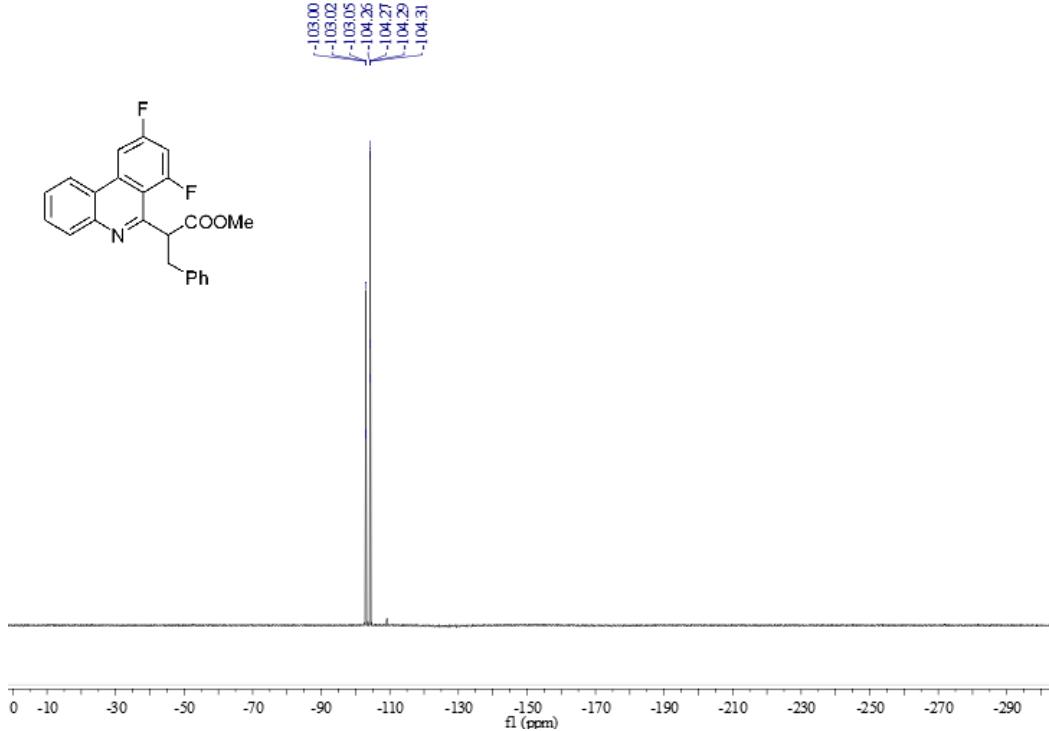
<sup>1</sup>H NMR of **3h**



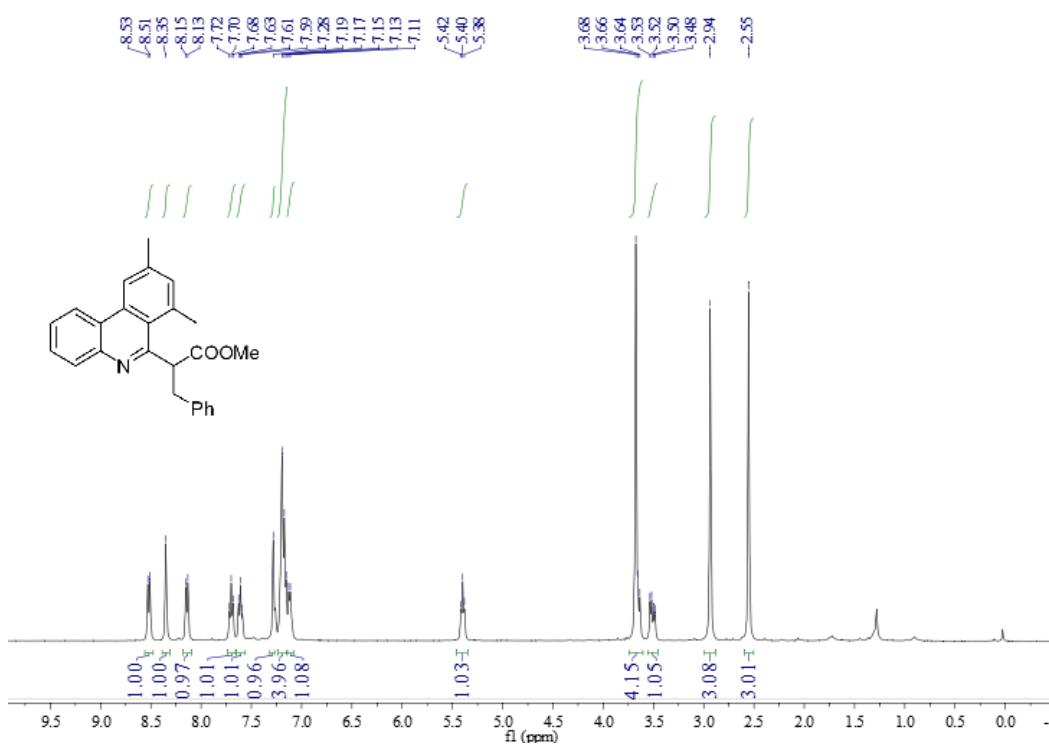
<sup>13</sup>C NMR of **3h**



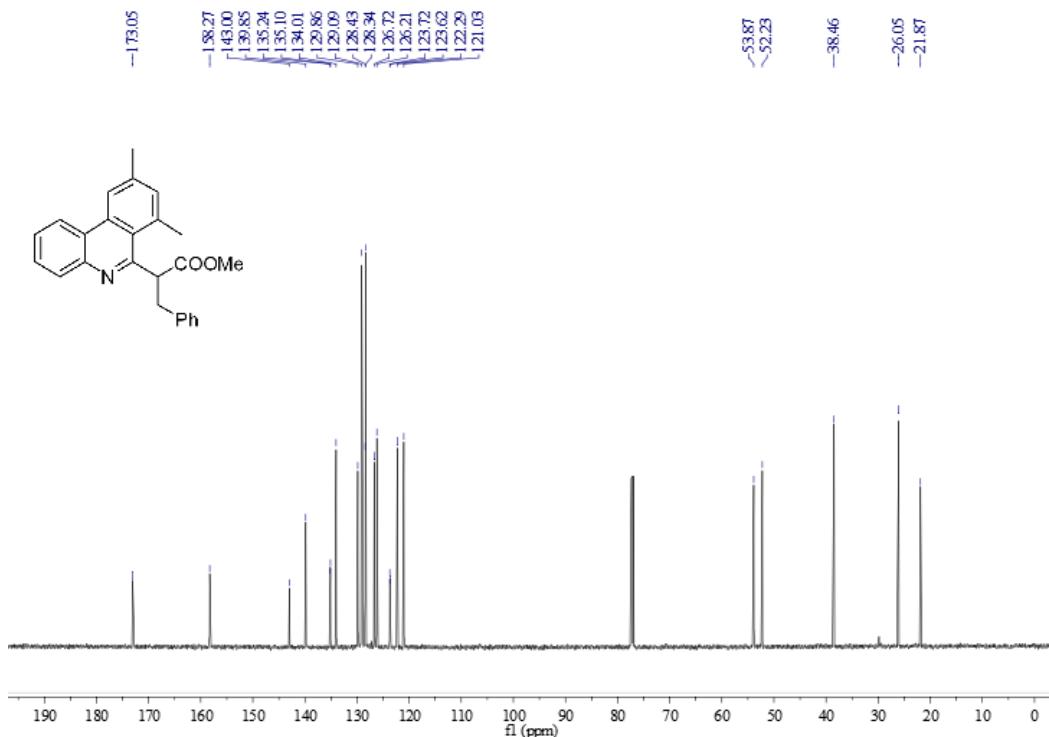
<sup>19</sup>F NMR of **3h**



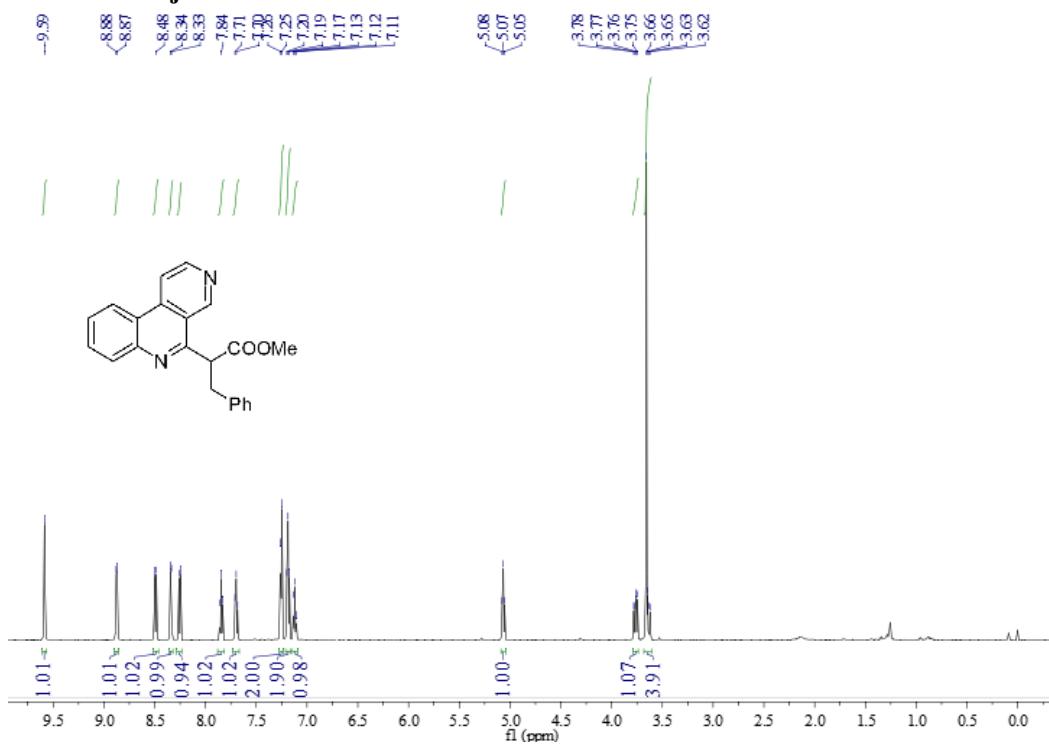
<sup>1</sup>H NMR of **3i**



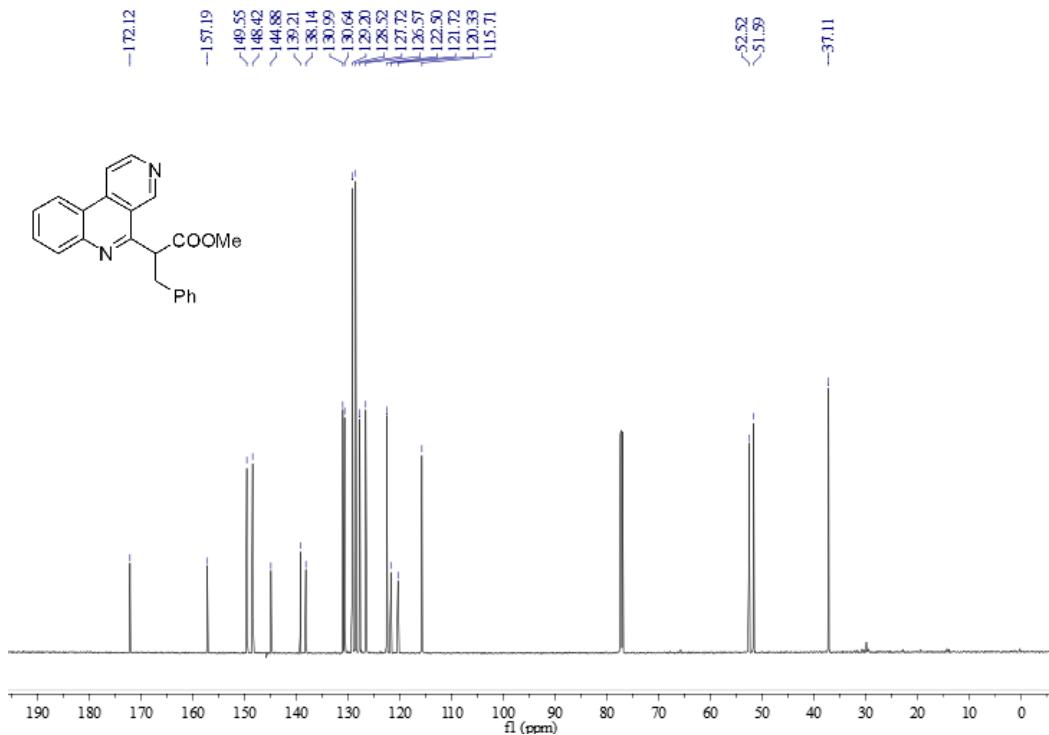
<sup>13</sup>C NMR of **3i**



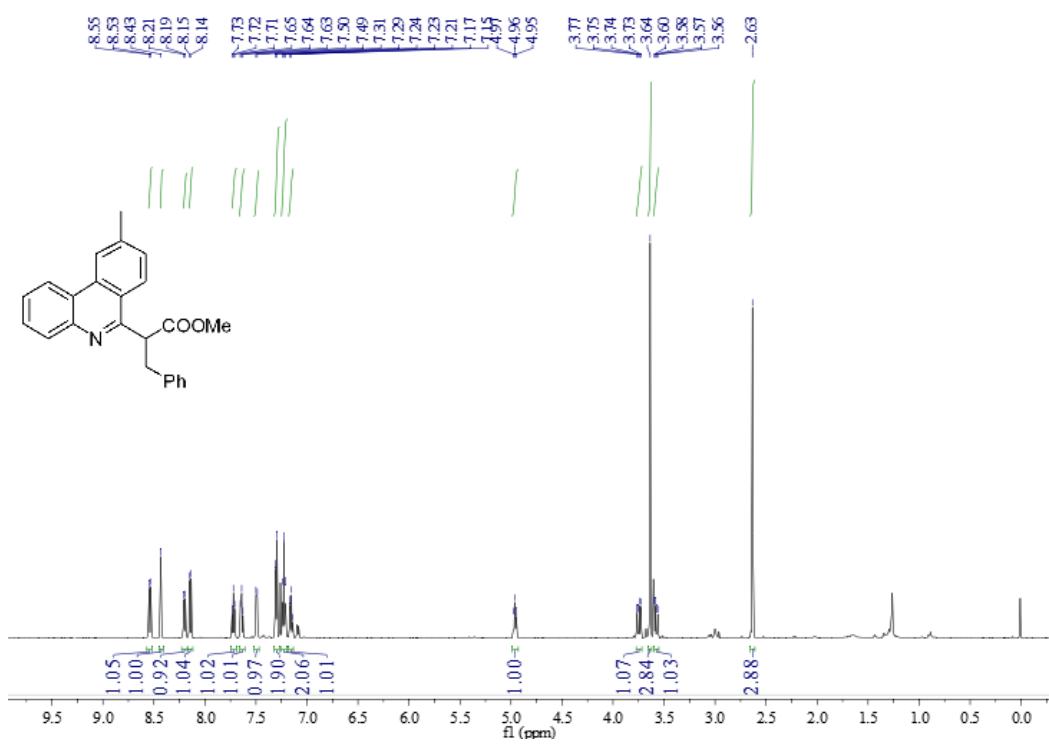
<sup>1</sup>H NMR of 3j



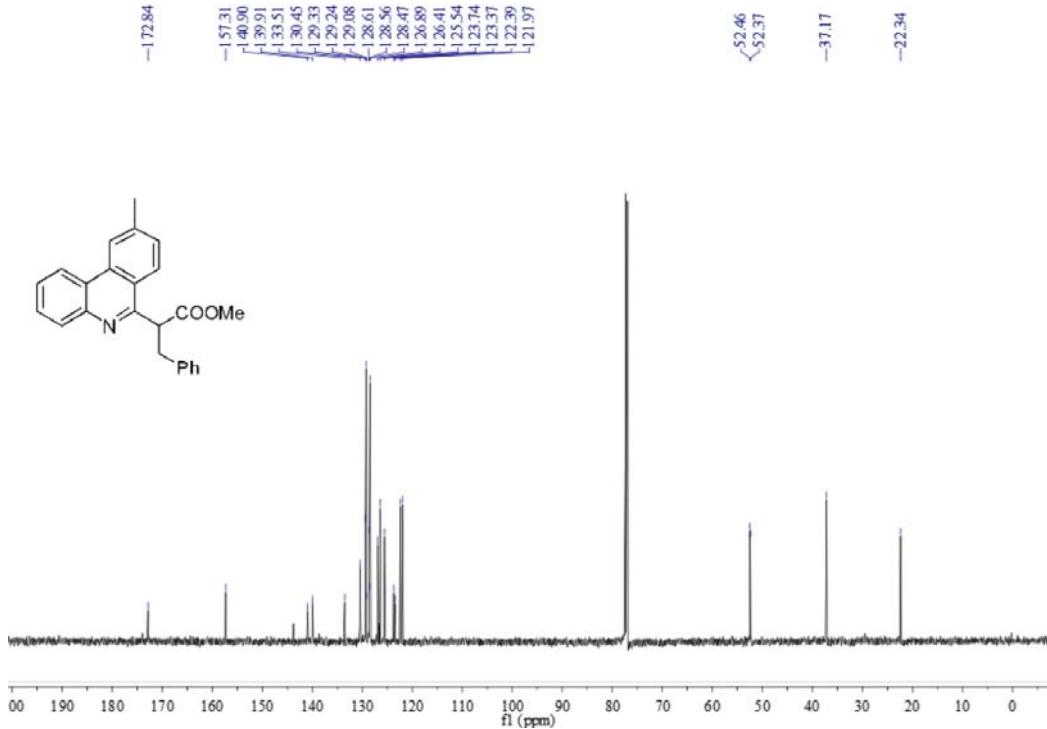
<sup>13</sup>C NMR of 3j



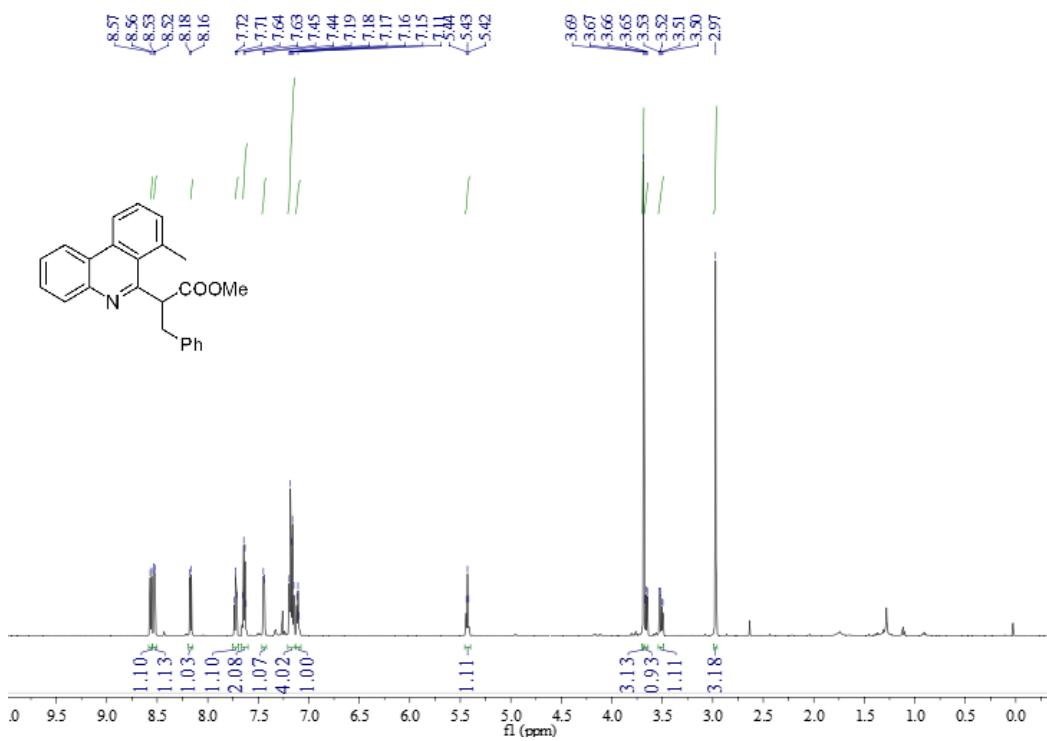
<sup>1</sup>H NMR of **3k**



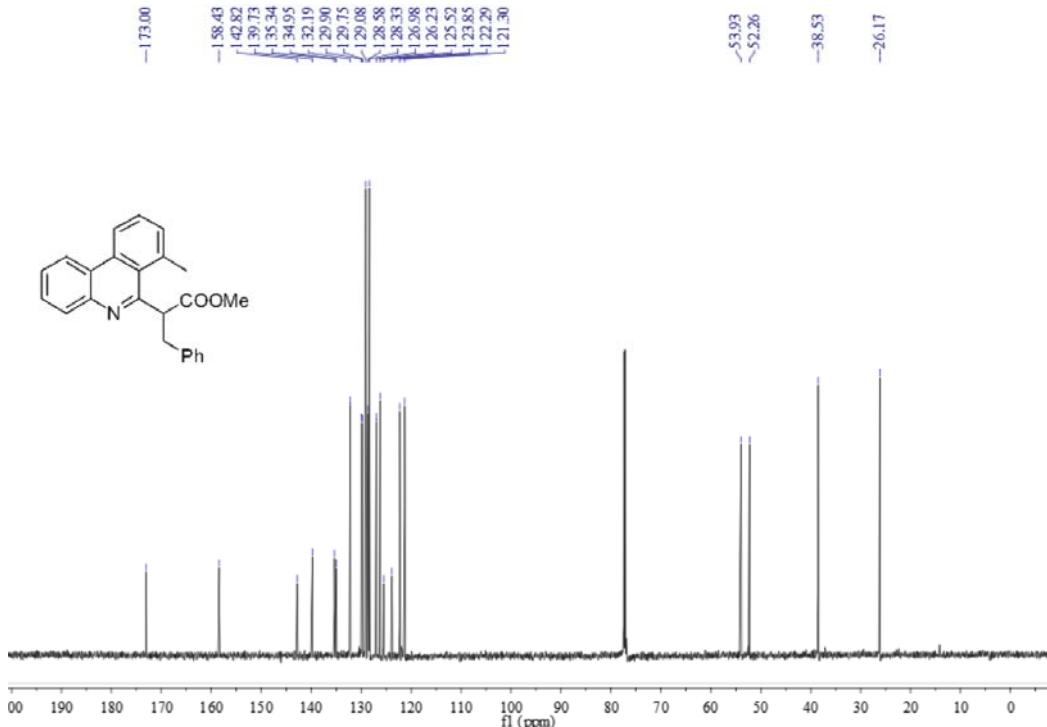
<sup>13</sup>C NMR of **3k**



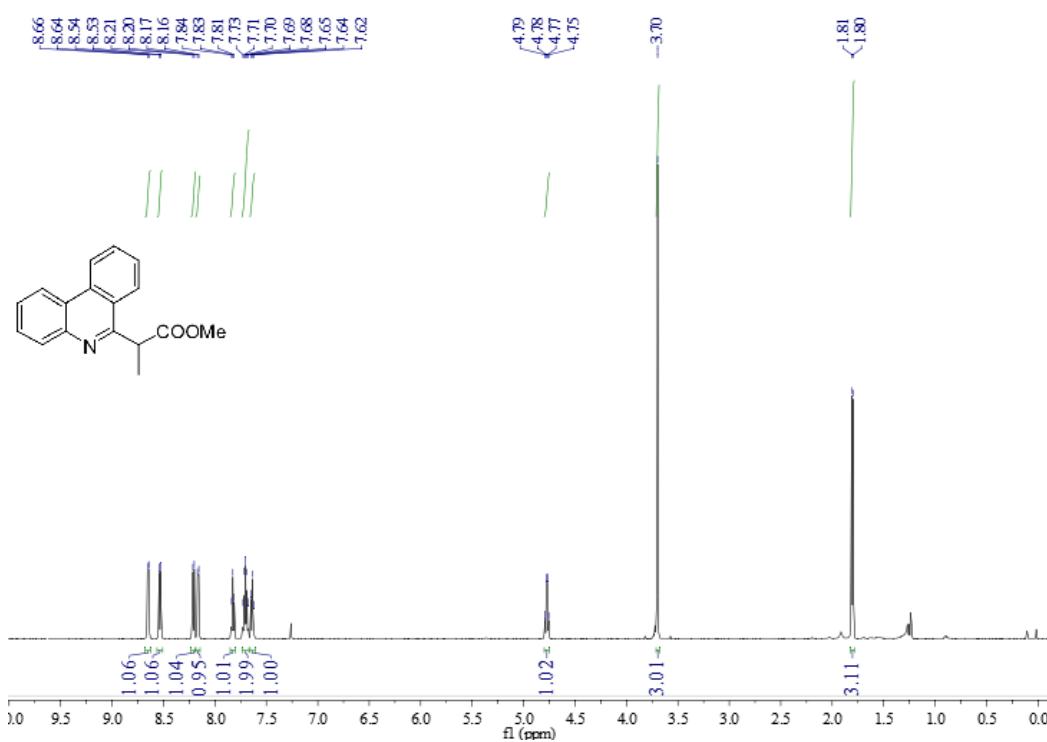
<sup>1</sup>H NMR of **3k'**



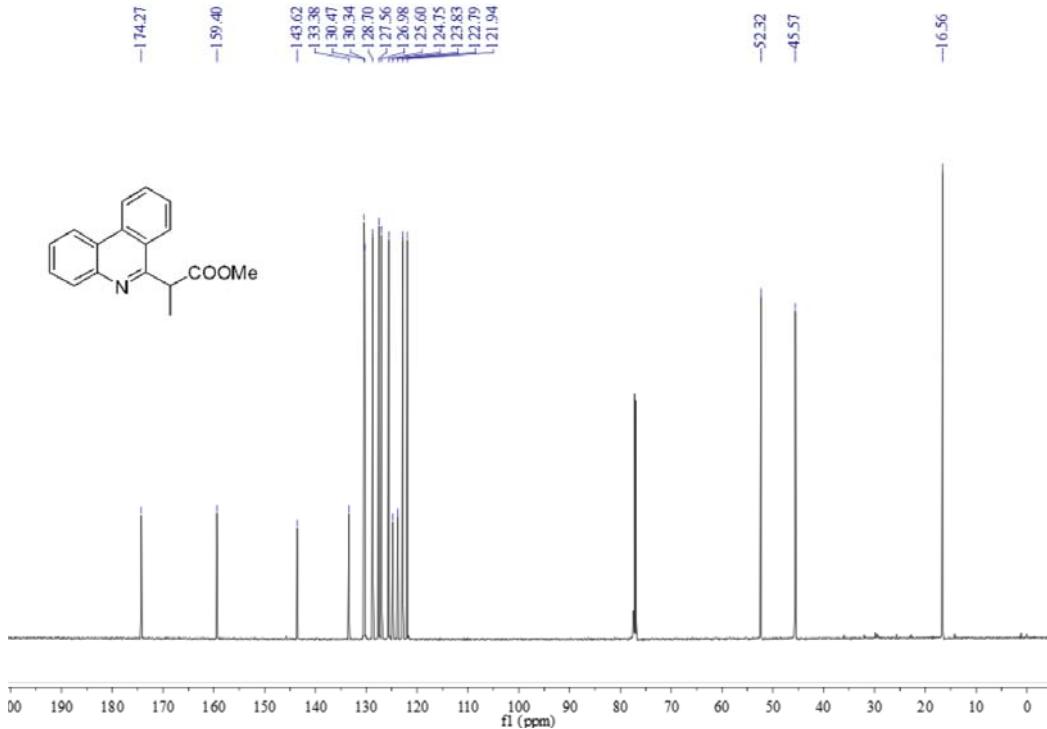
<sup>13</sup>C NMR of **3k'**



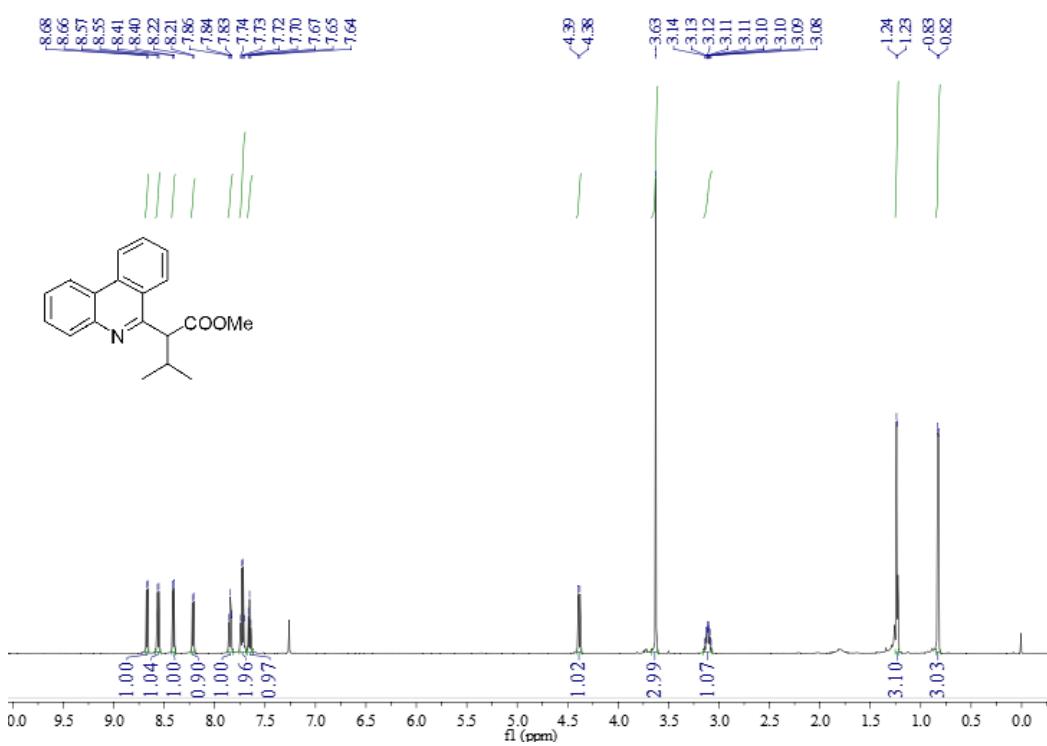
<sup>1</sup>H NMR of **4a**



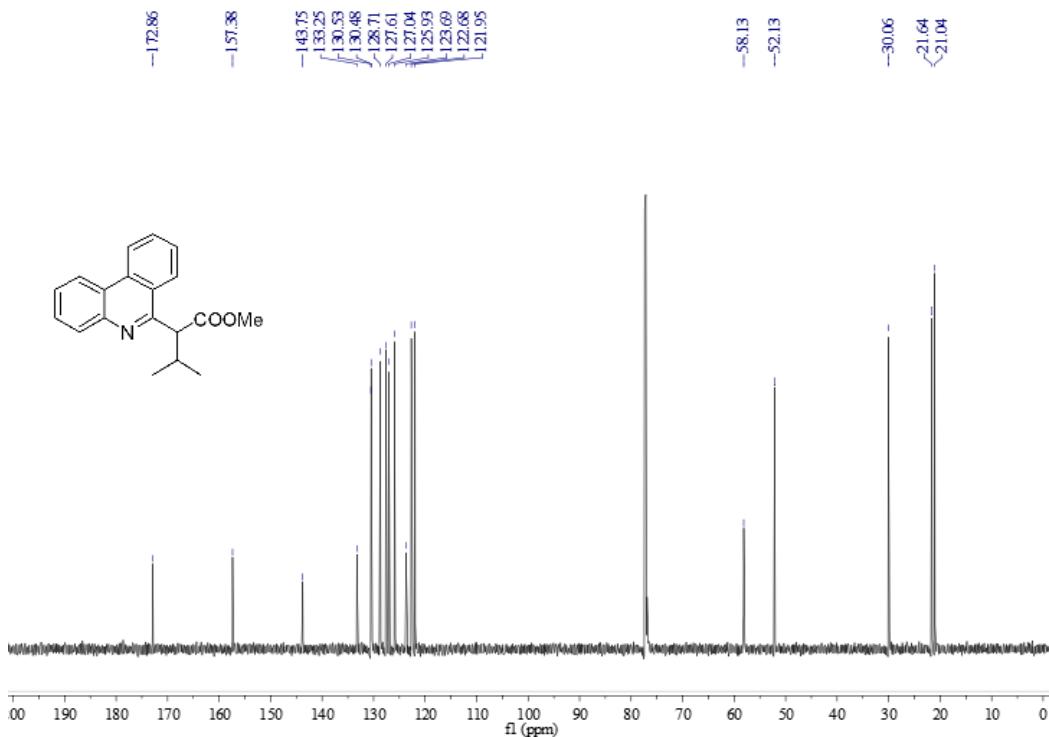
<sup>13</sup>C NMR of **4a**



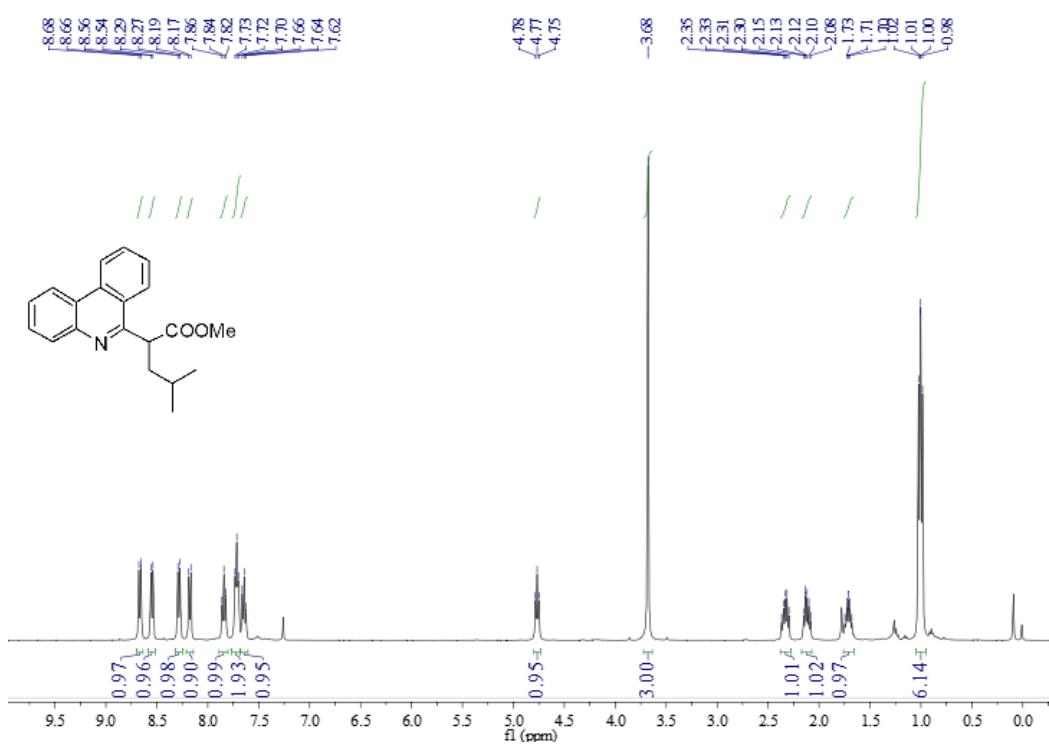
<sup>1</sup>H NMR of **4b**



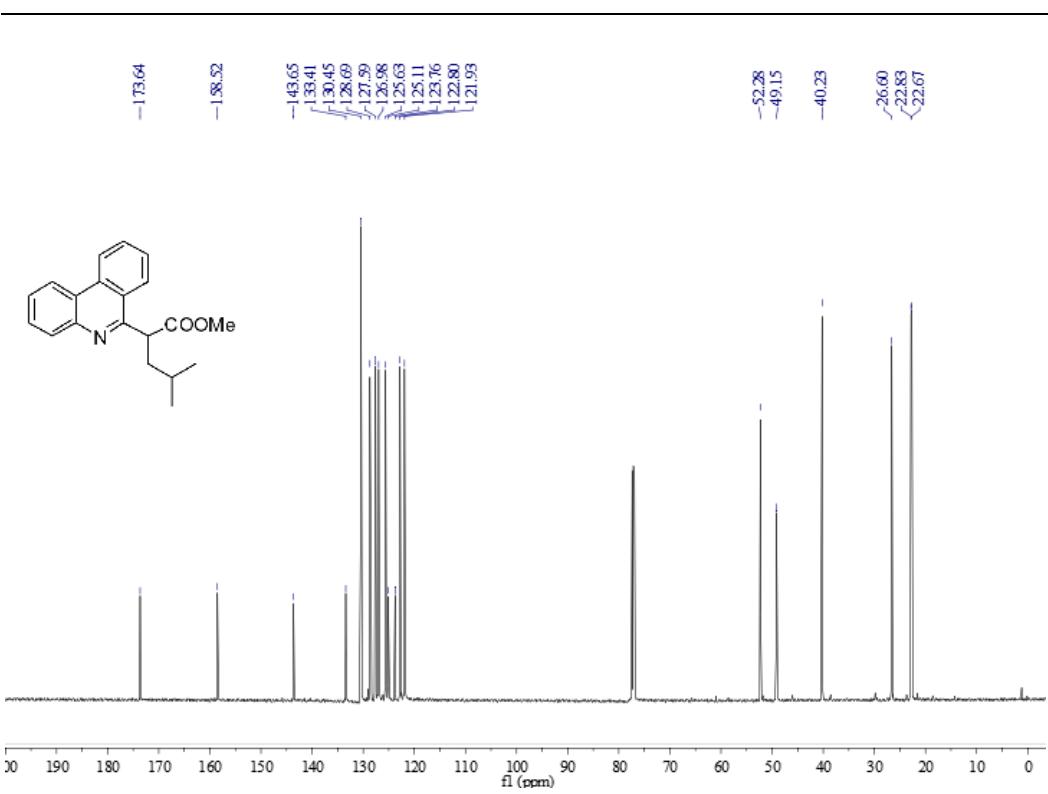
<sup>13</sup>C NMR of **4b**



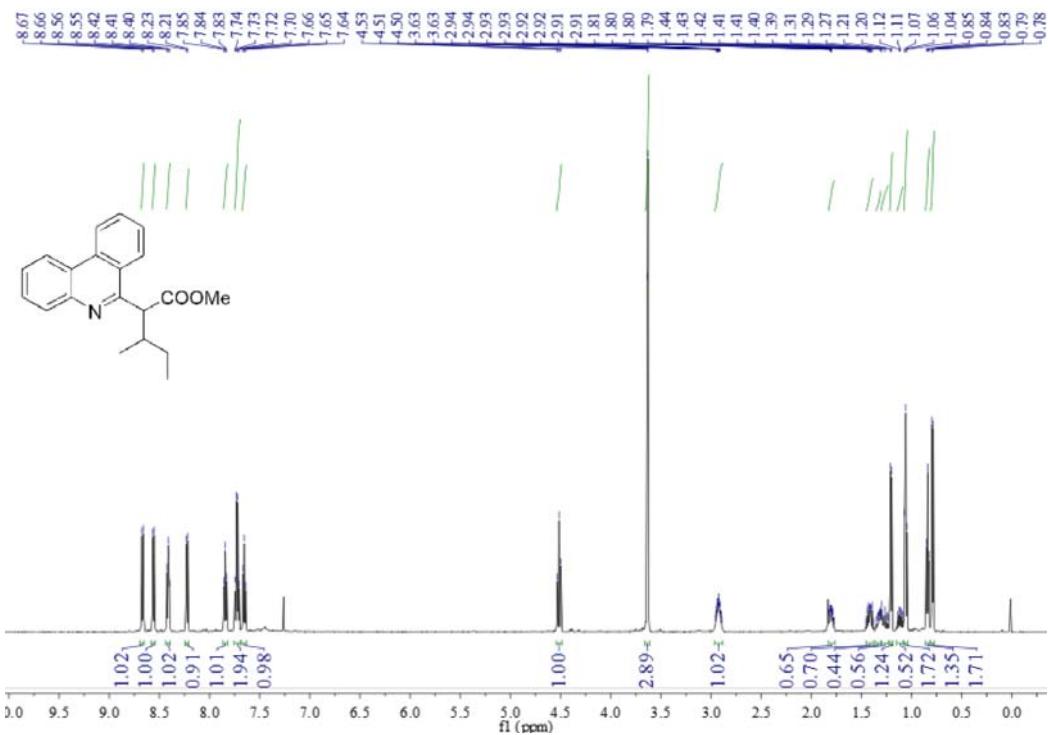
<sup>1</sup>H NMR of 4c



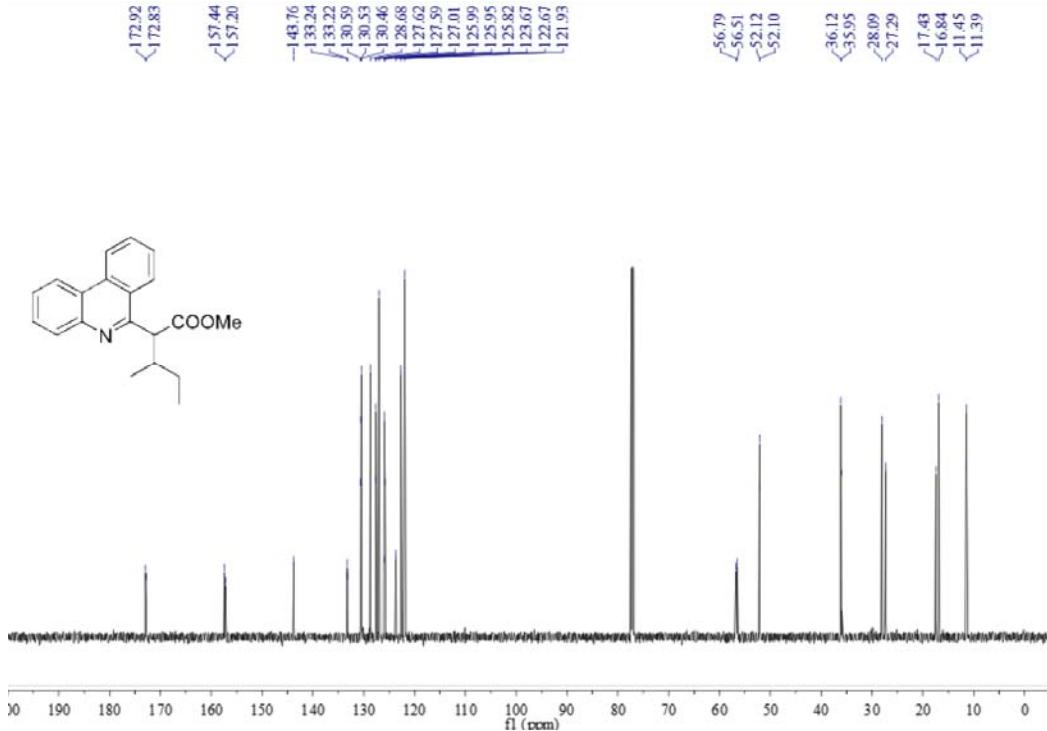
<sup>13</sup>C NMR of 4c



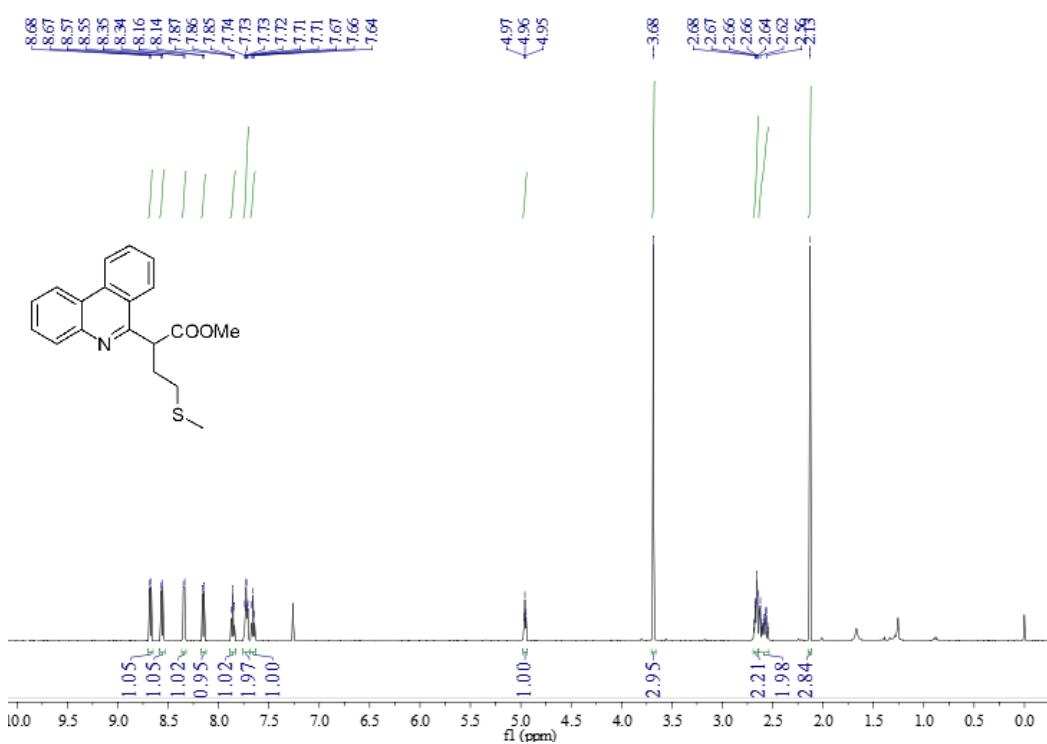
<sup>1</sup>H NMR of **4d**



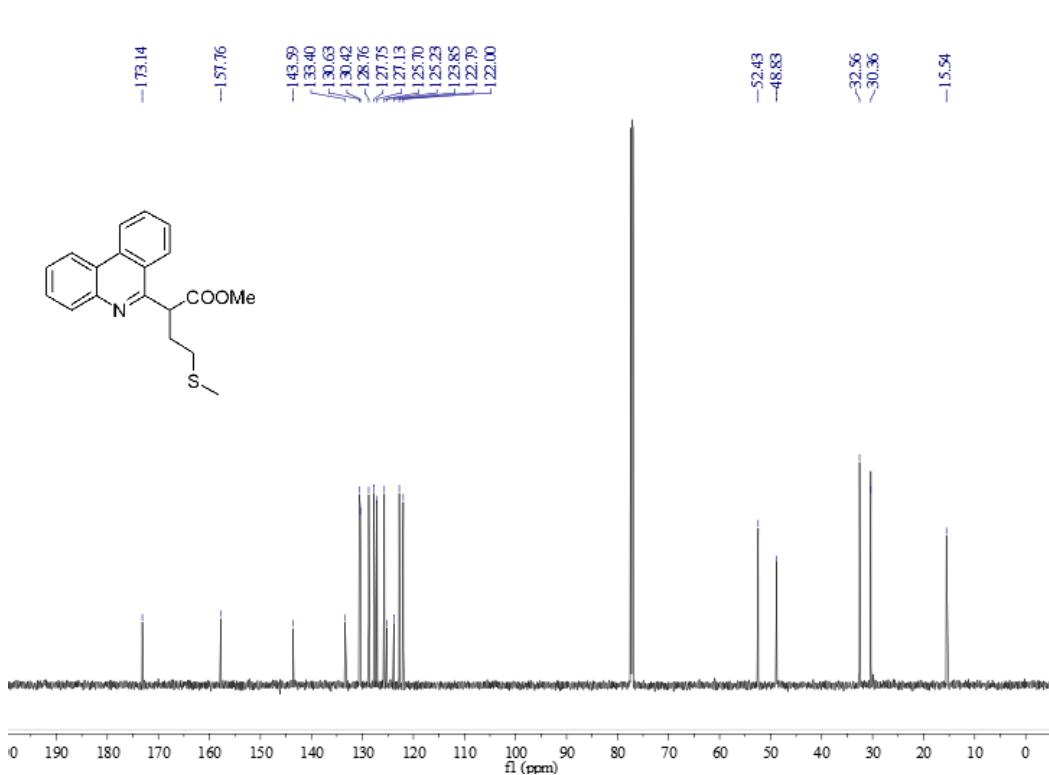
<sup>13</sup>C NMR of **4d**



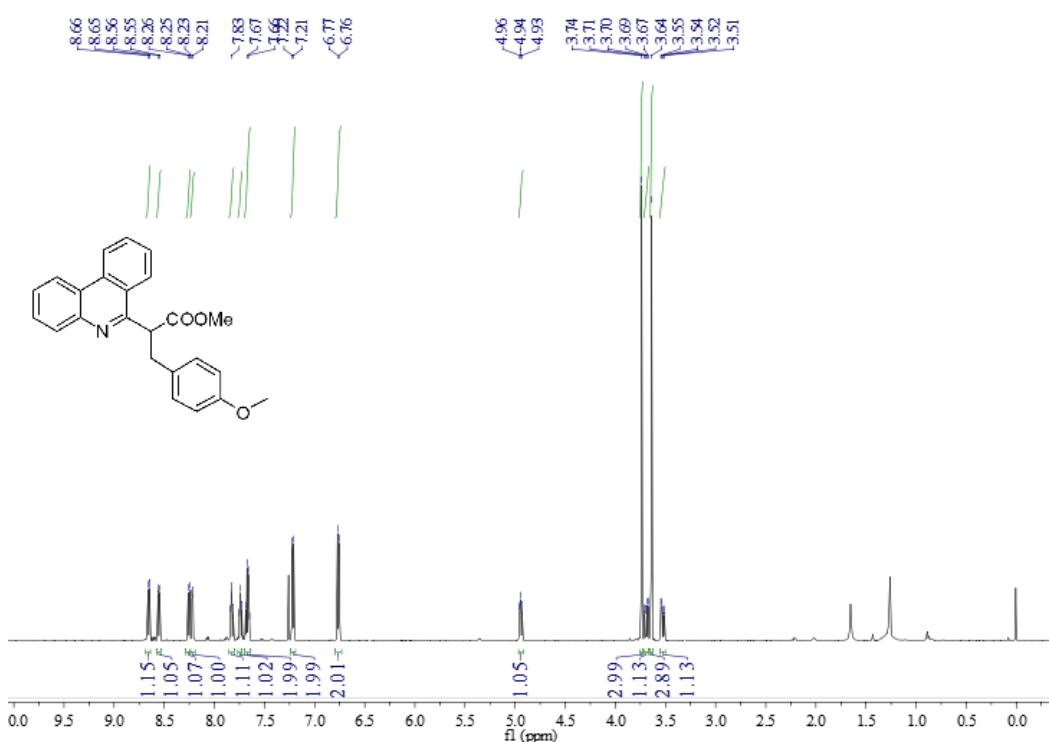
<sup>1</sup>H NMR of 4e



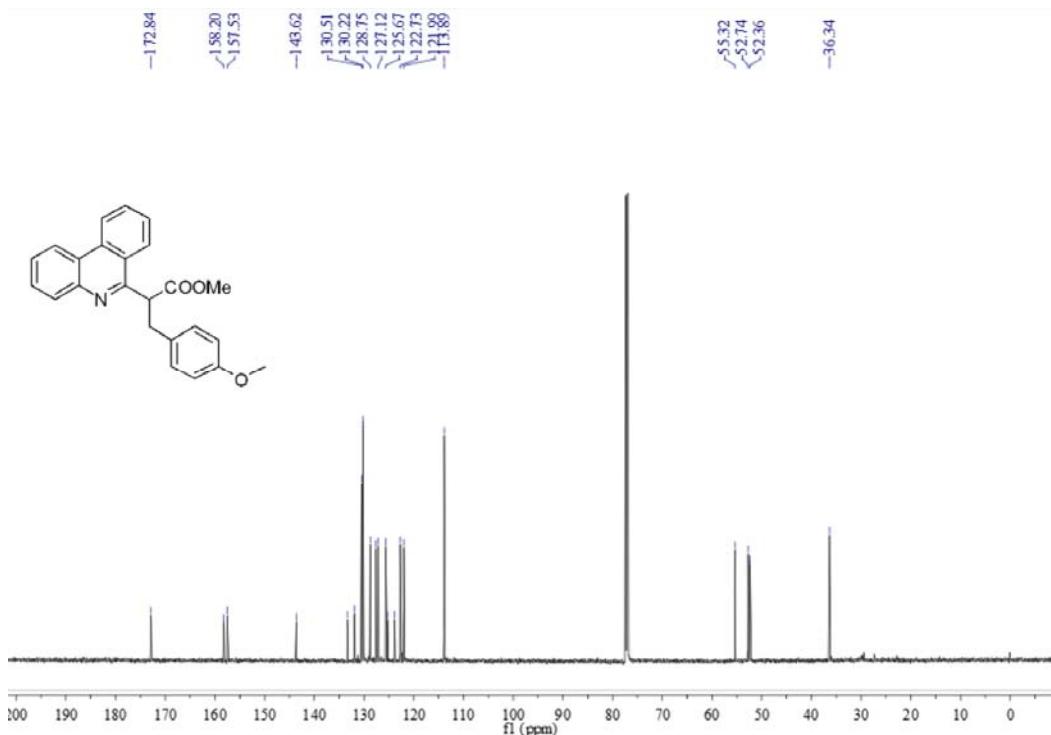
<sup>13</sup>C NMR of 4e



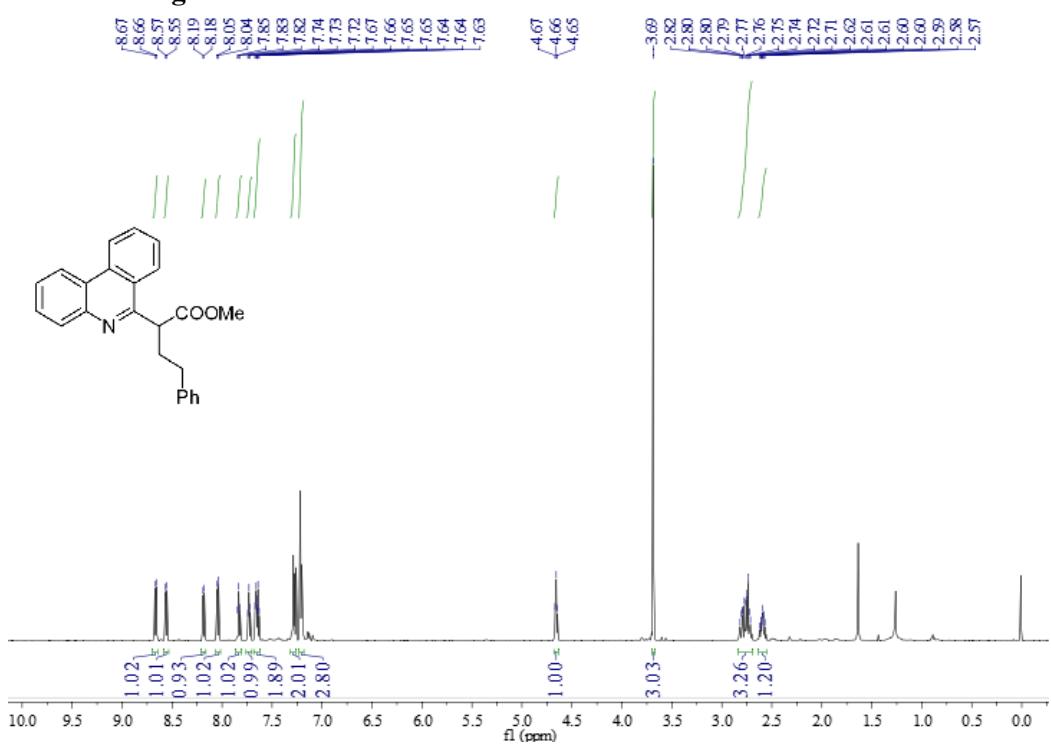
<sup>1</sup>H NMR of 4f



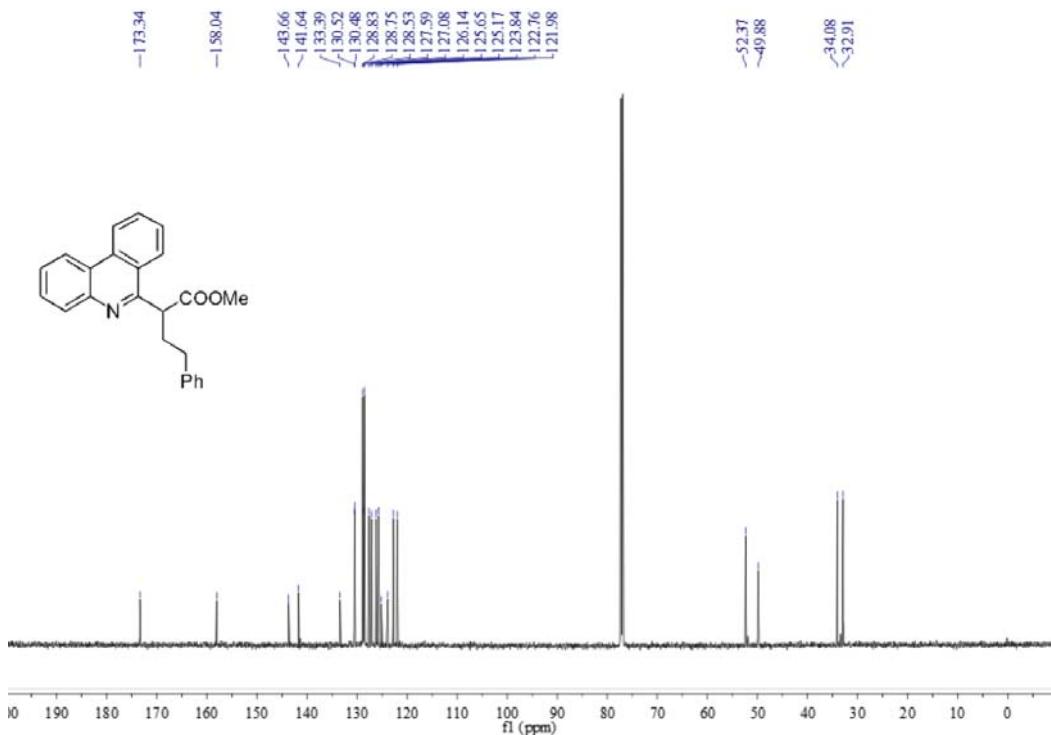
<sup>13</sup>C NMR of 4f



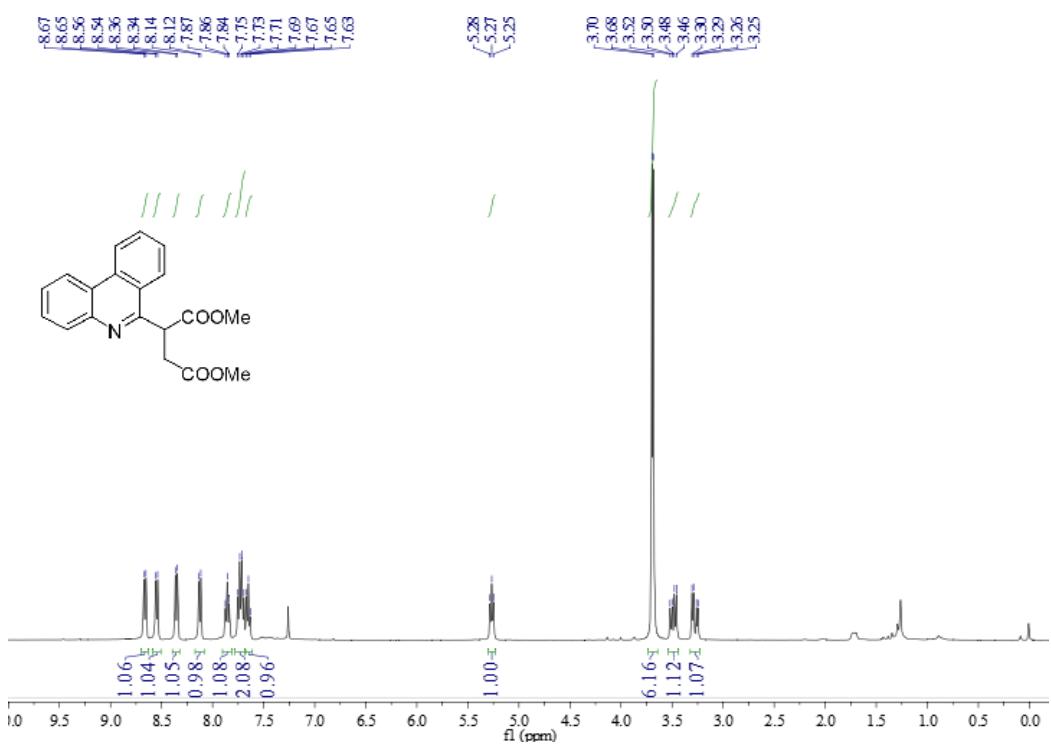
<sup>1</sup>H NMR of 4g



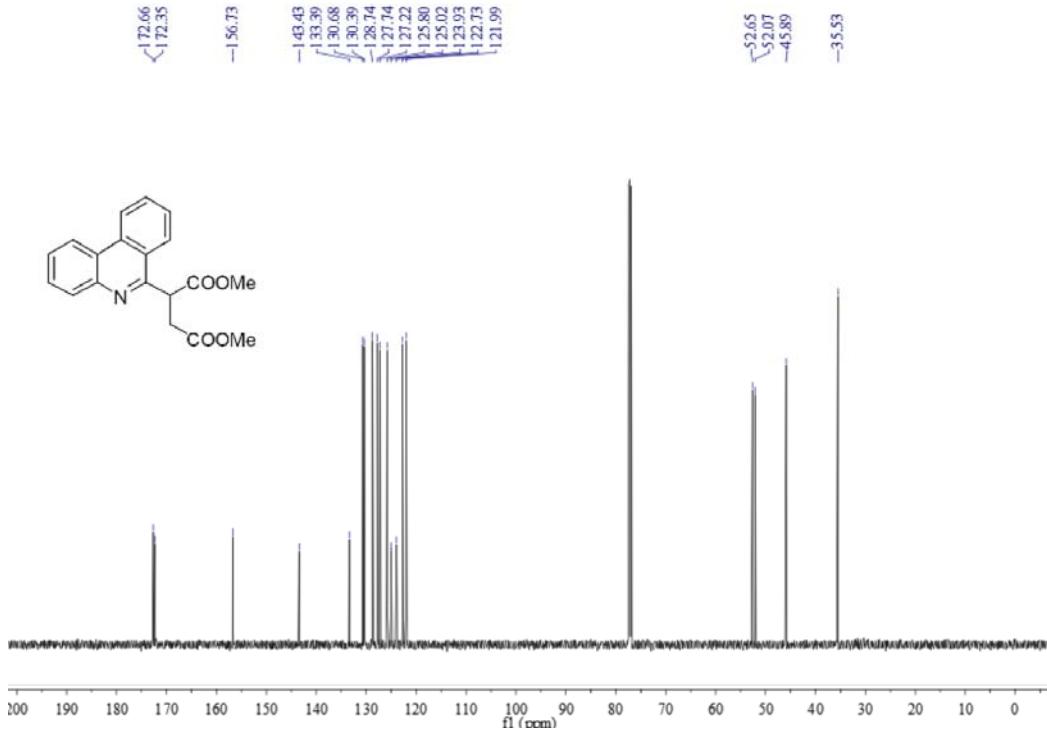
<sup>13</sup>C NMR of 4g



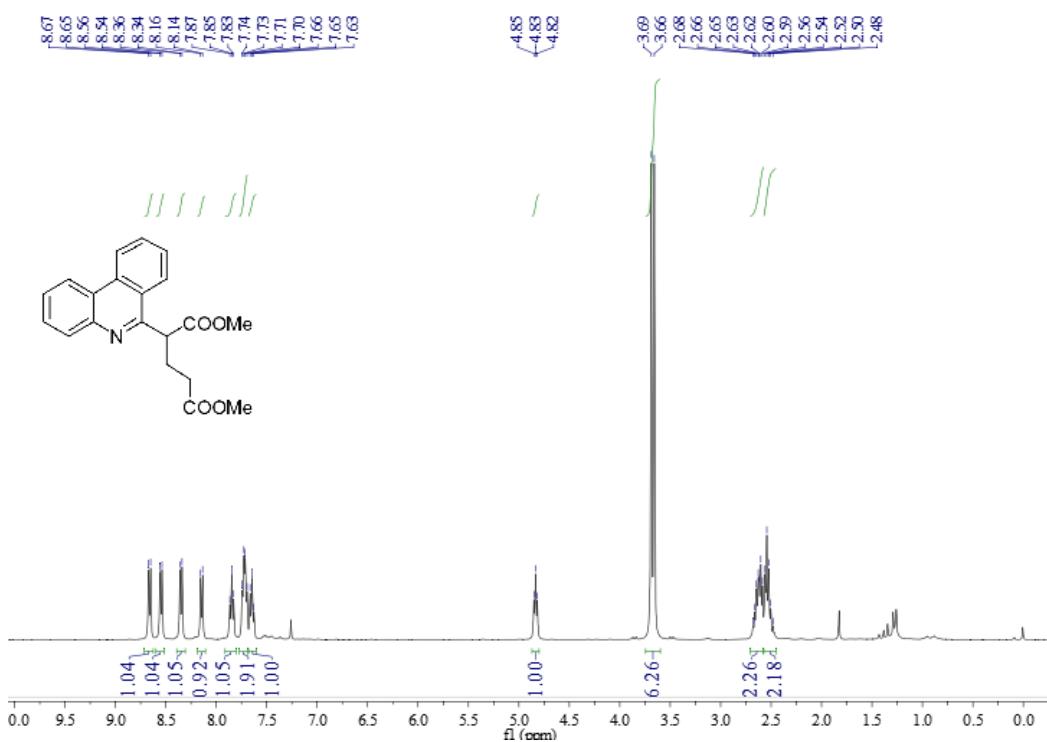
### <sup>1</sup>H NMR of 4h



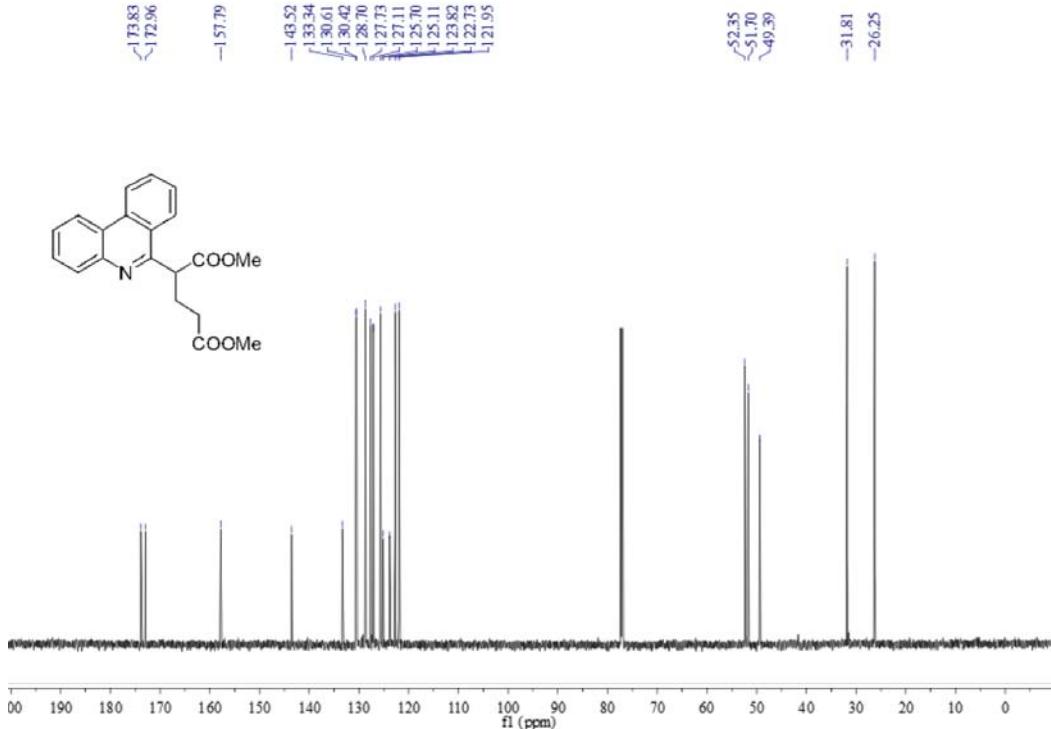
### <sup>13</sup>C NMR of 4h



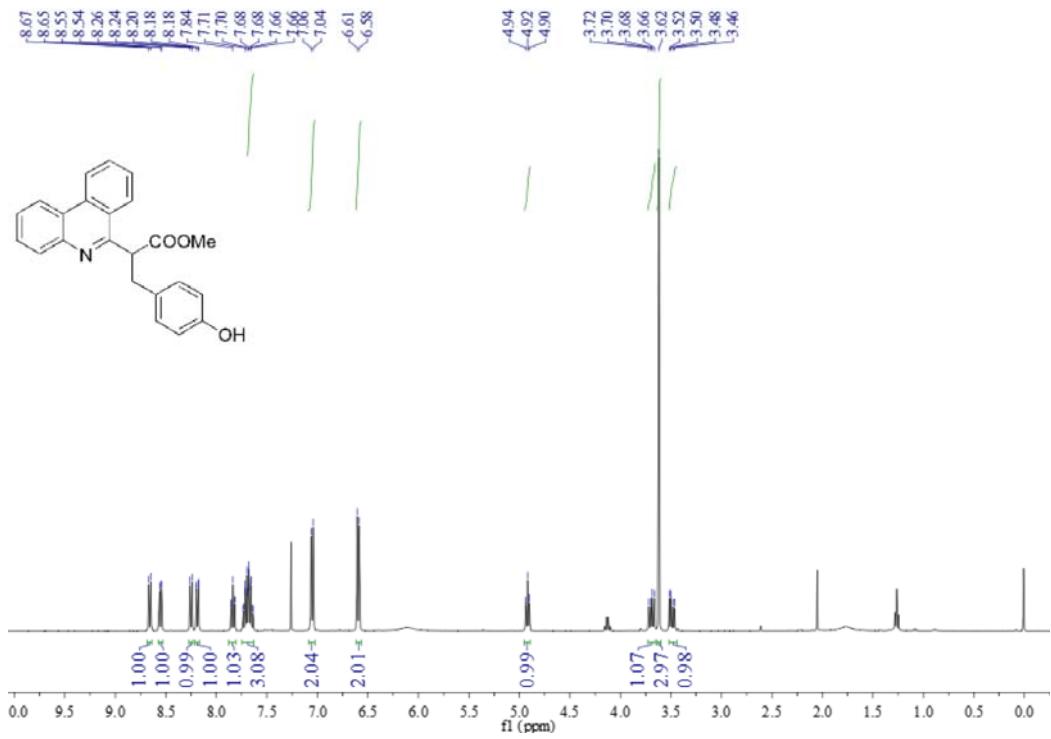
$^1\text{H}$  NMR of **4i**



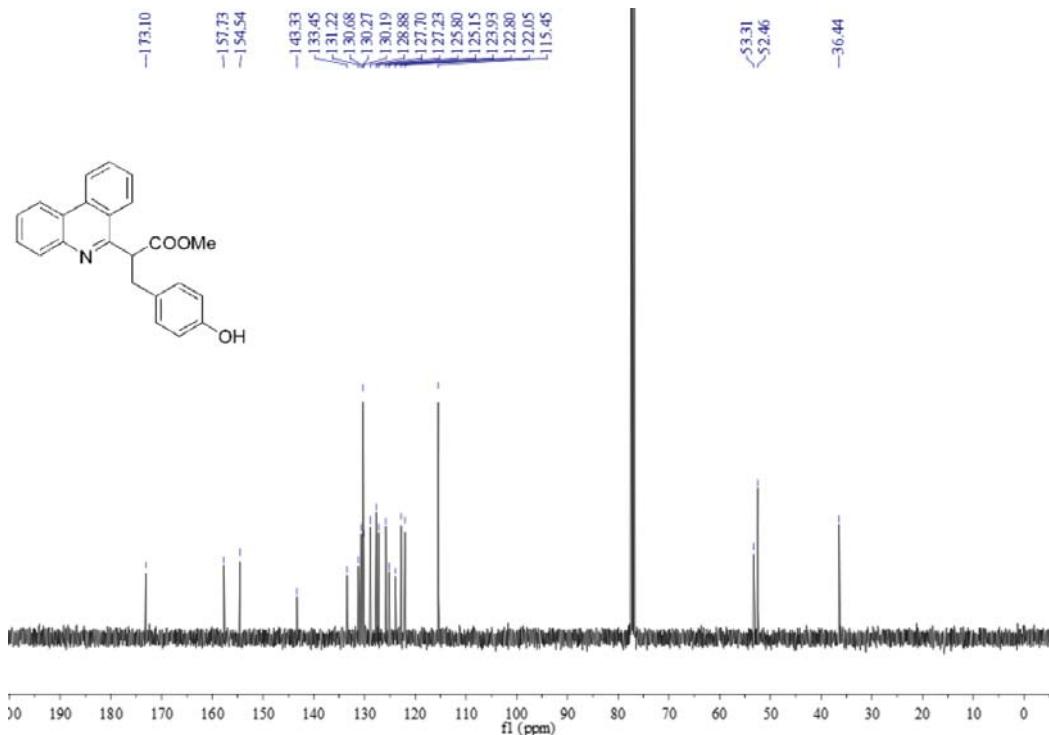
$^{13}\text{C}$  NMR of **4i**



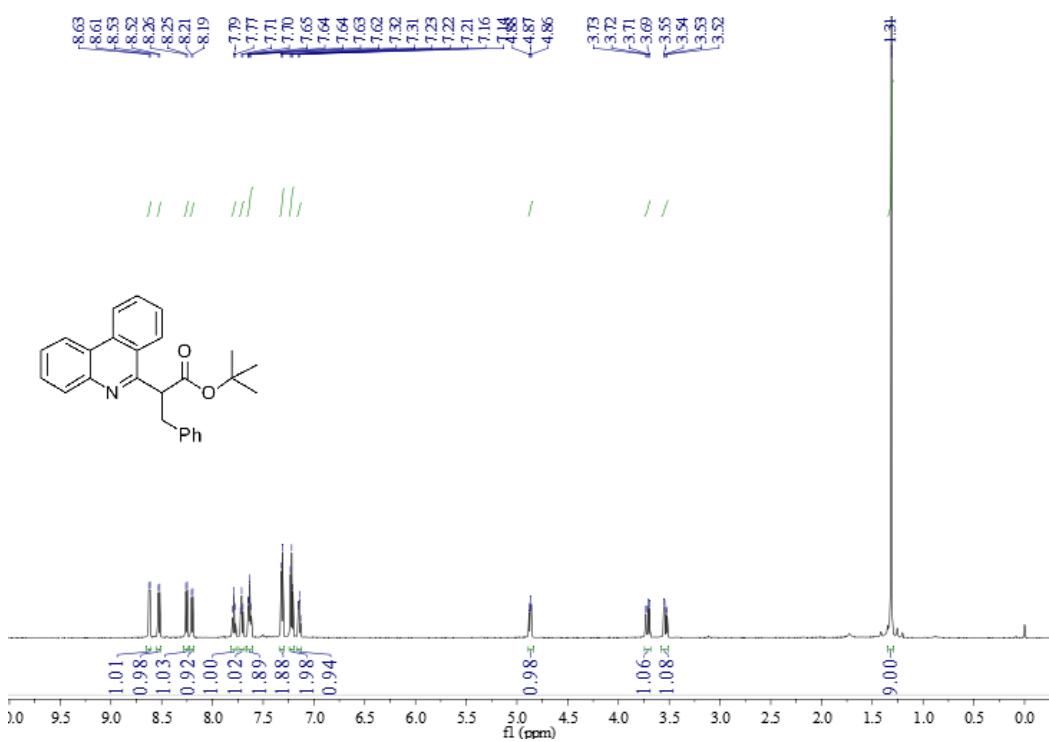
<sup>1</sup>H NMR of 4j



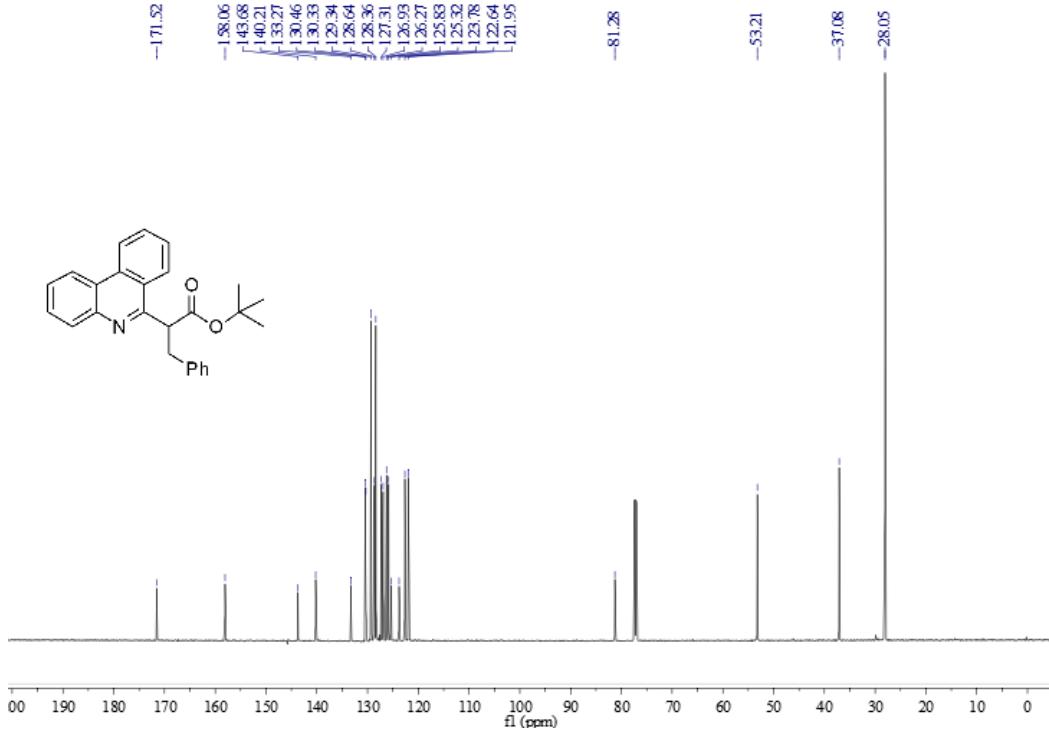
<sup>13</sup>C NMR of 4j



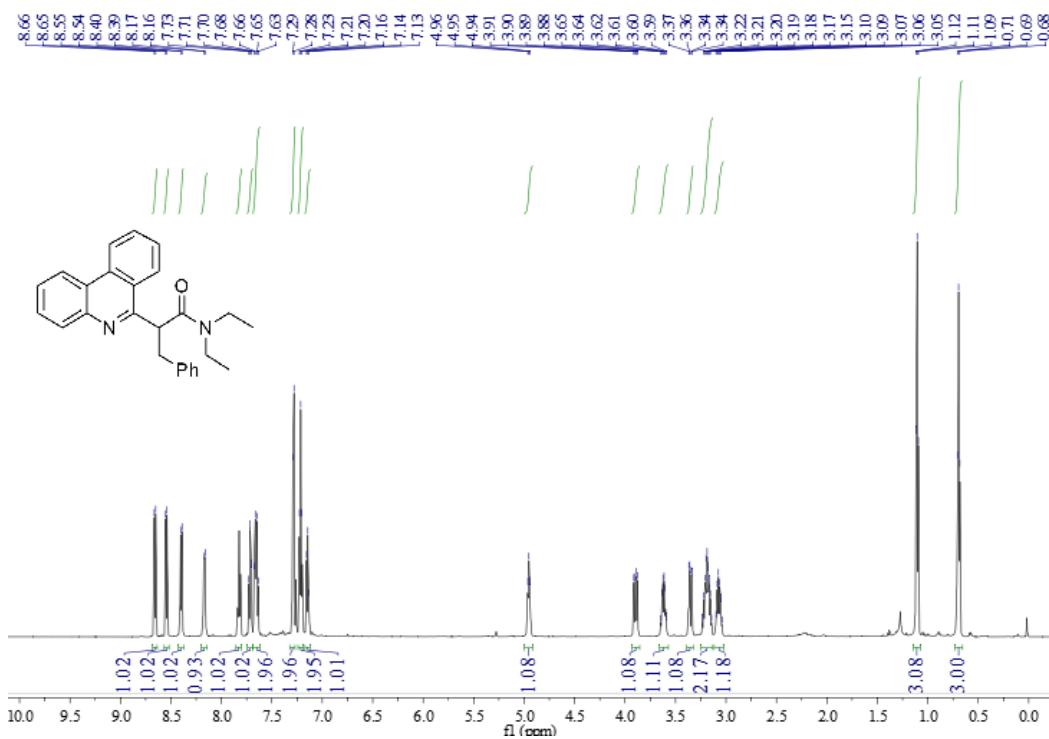
### <sup>1</sup>H NMR of 4k



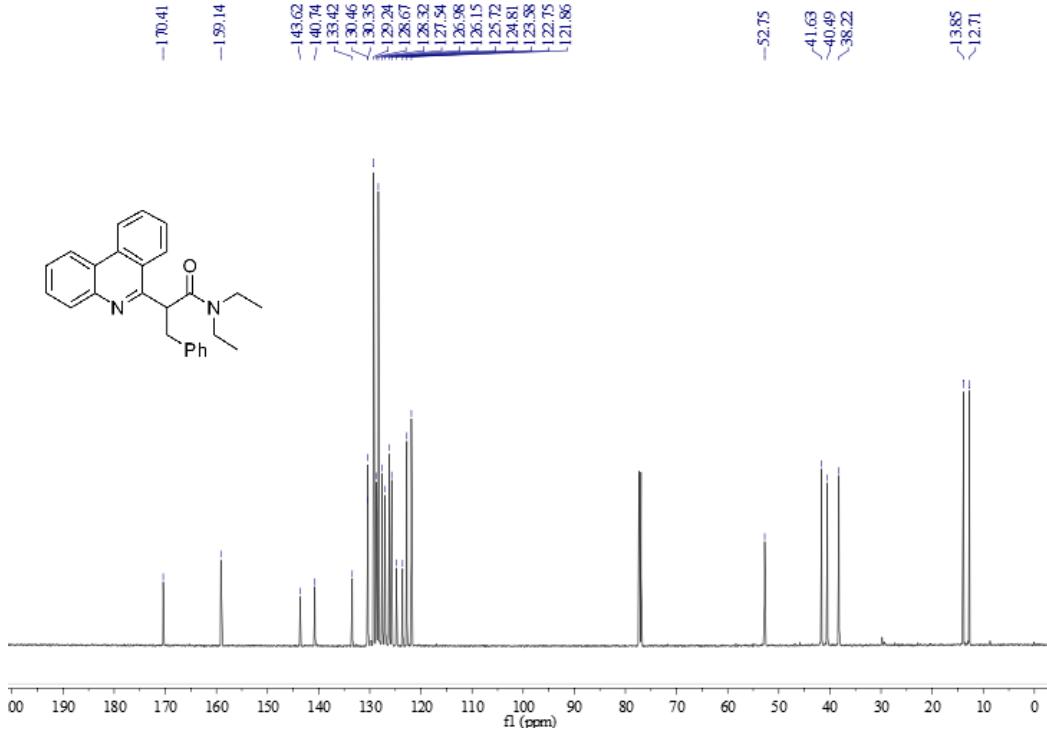
### <sup>13</sup>C NMR of 4k



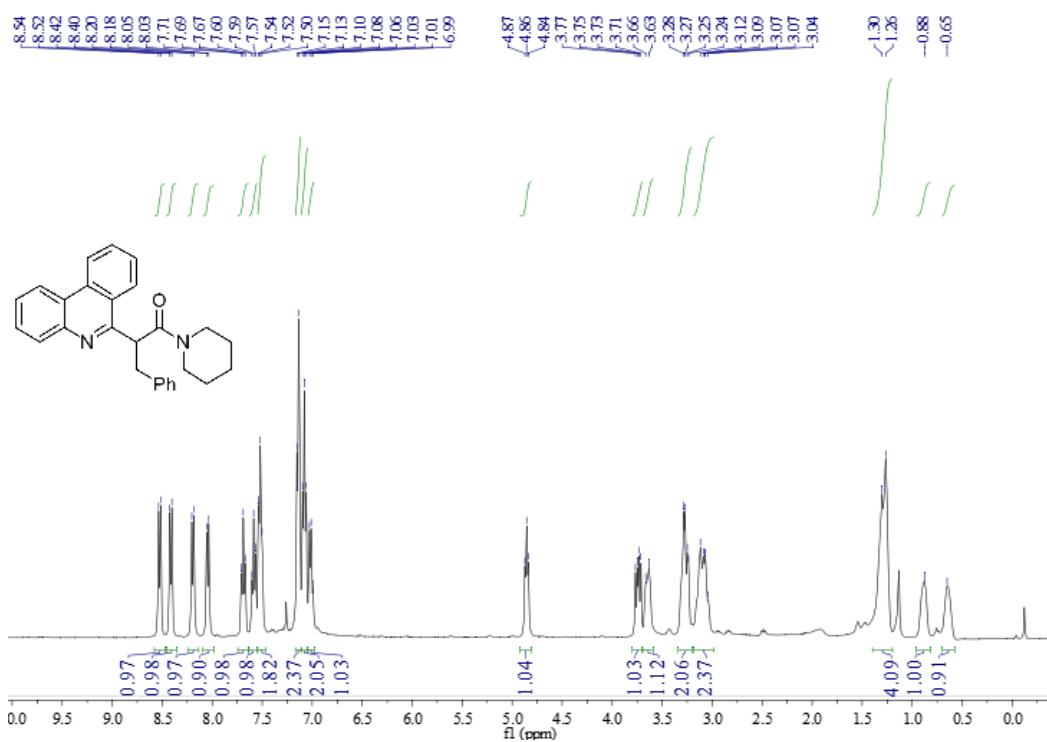
<sup>1</sup>H NMR of 4I



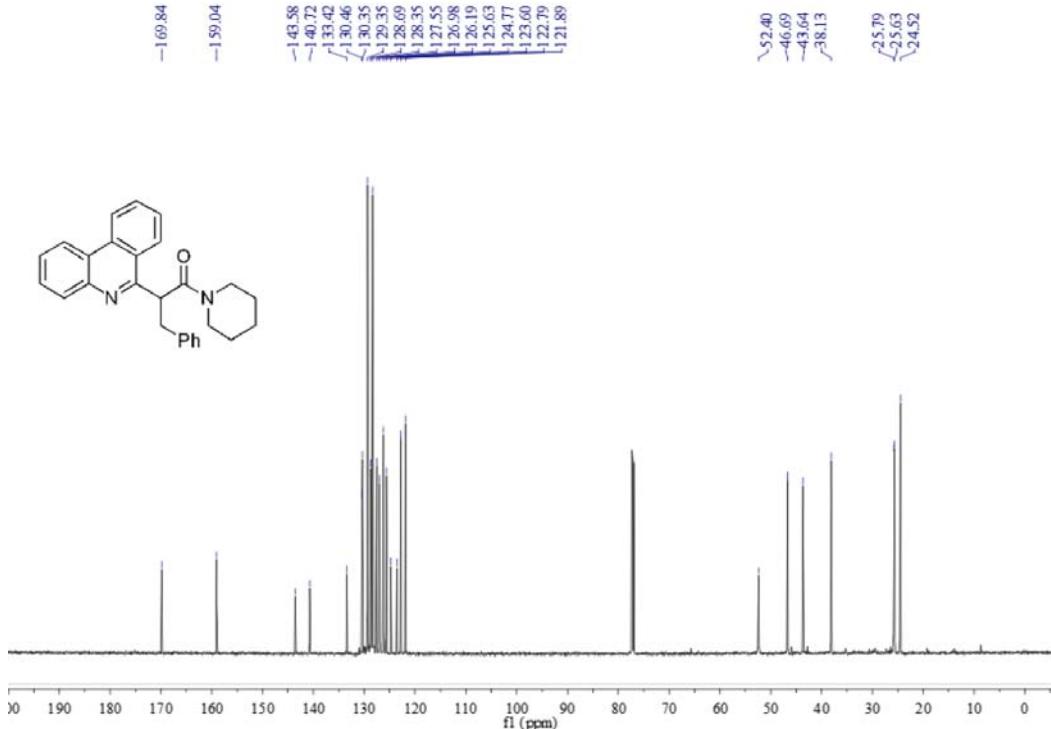
<sup>13</sup>C NMR of 4I



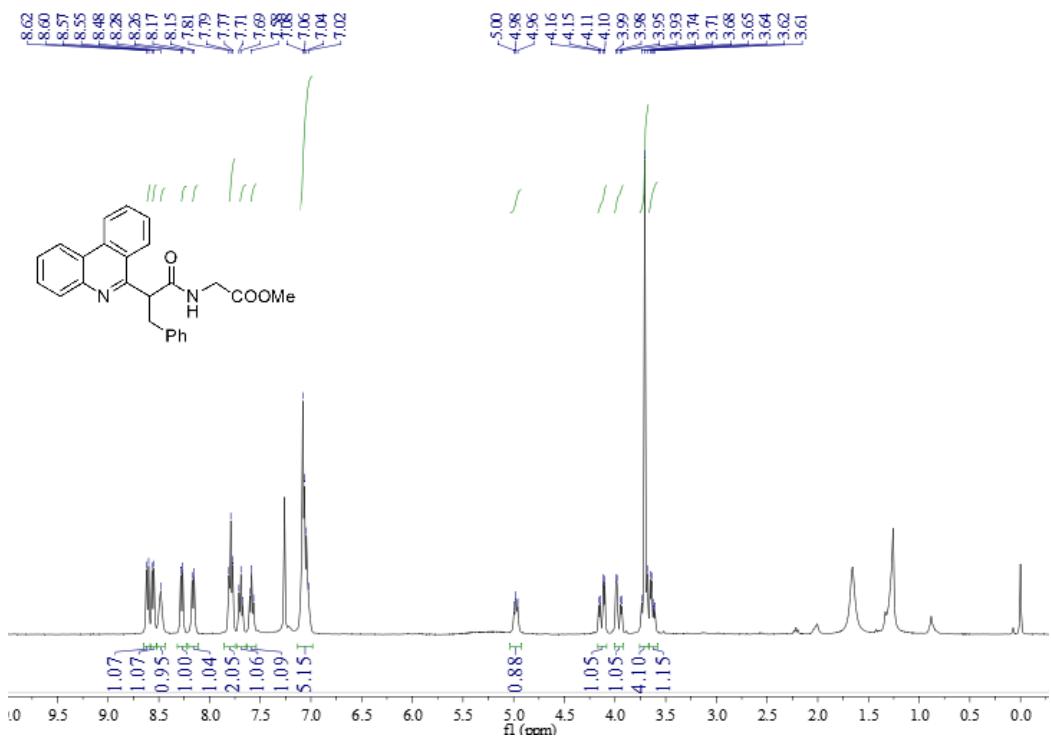
### <sup>1</sup>H NMR of **4m**



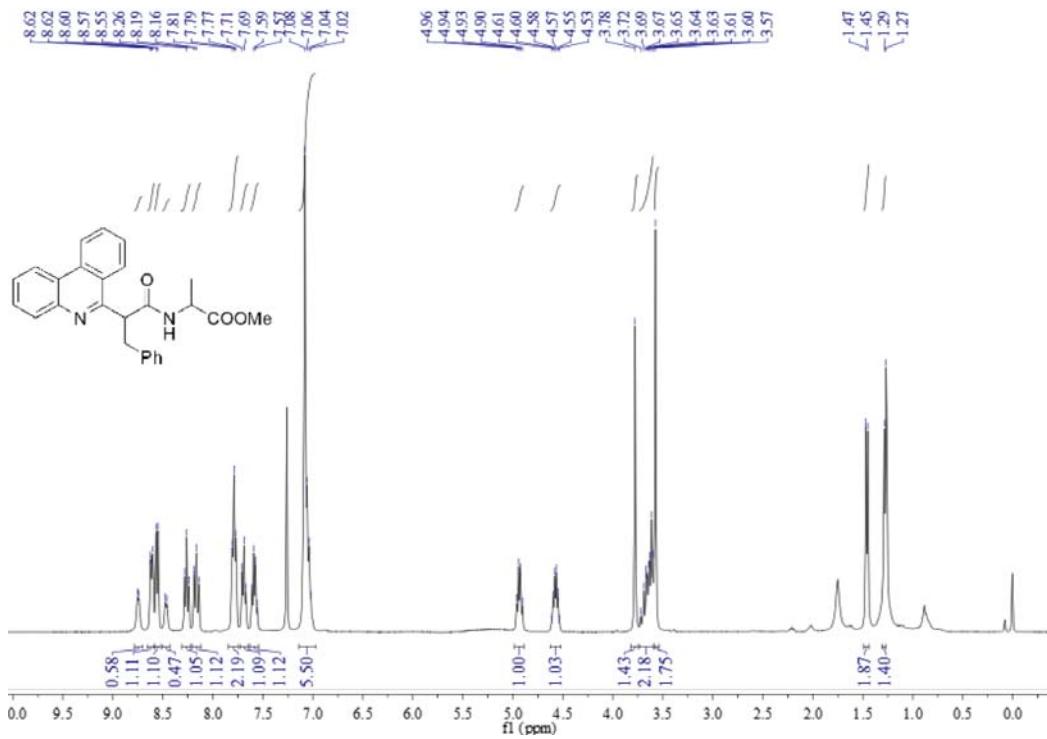
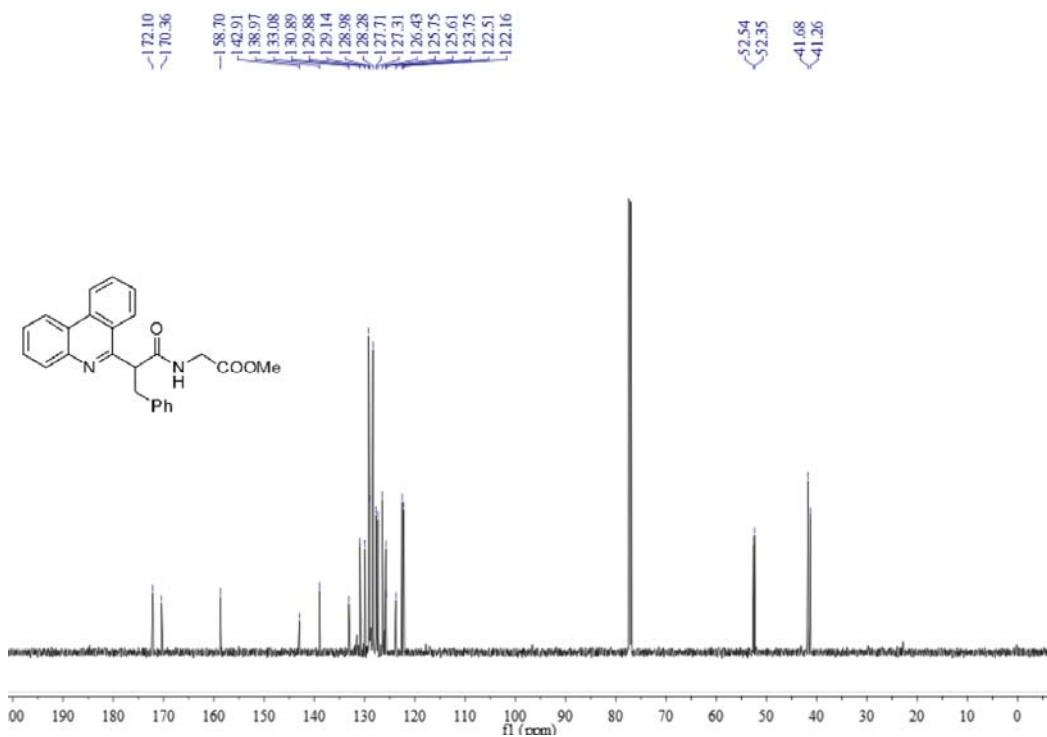
### <sup>13</sup>C NMR of **4m**



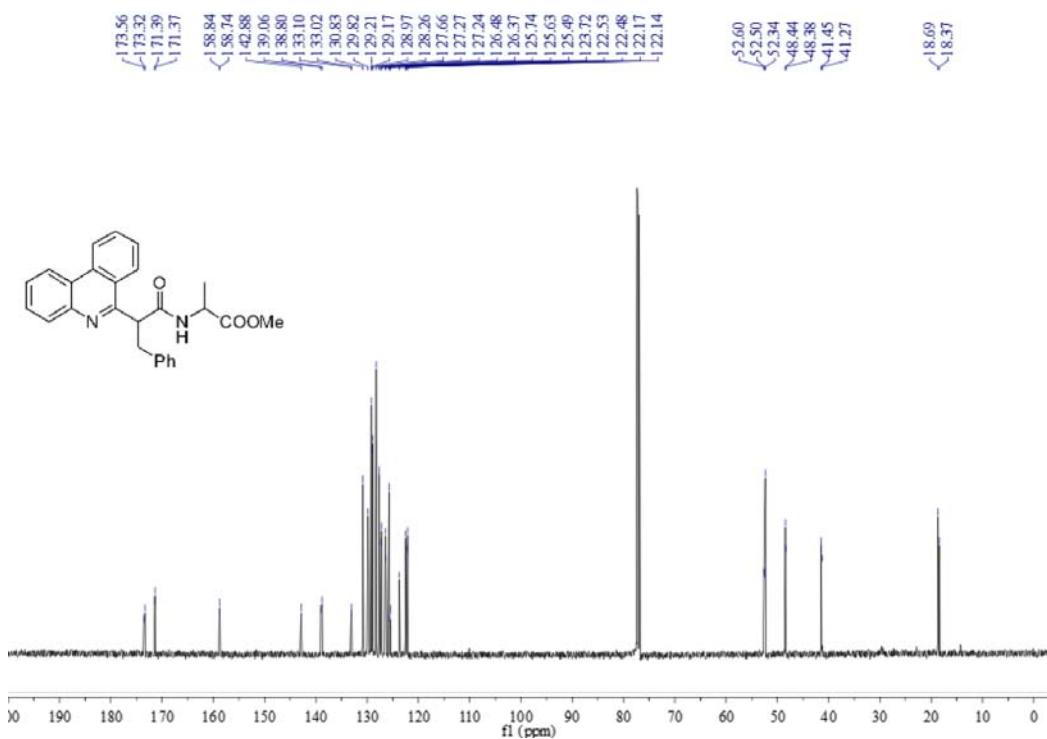
### 1H NMR of 4n



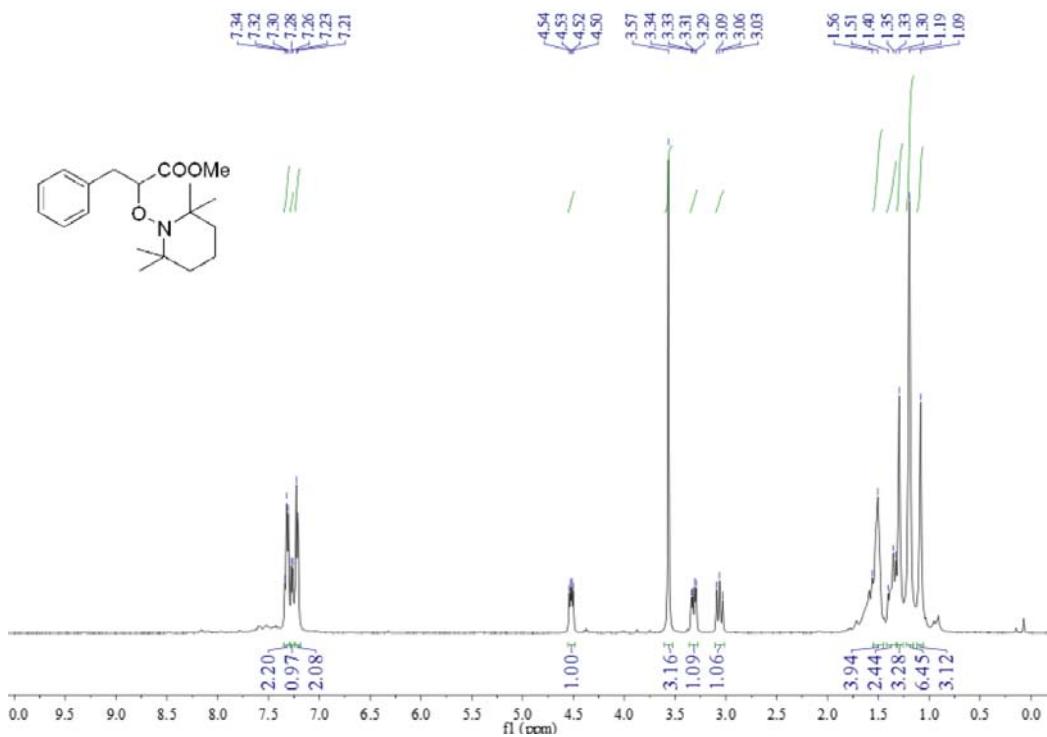
<sup>13</sup>C NMR of 4n



<sup>13</sup>C NMR of **4o**



<sup>1</sup>H NMR of TEMPO-trapped product



<sup>13</sup>C NMR of TEMPO-trapped product

