

Supporting Information

Photocatalytic synthesis of 10-phenanthrenols *via* intramolecular cycloaromatization under oxidant-free conditions

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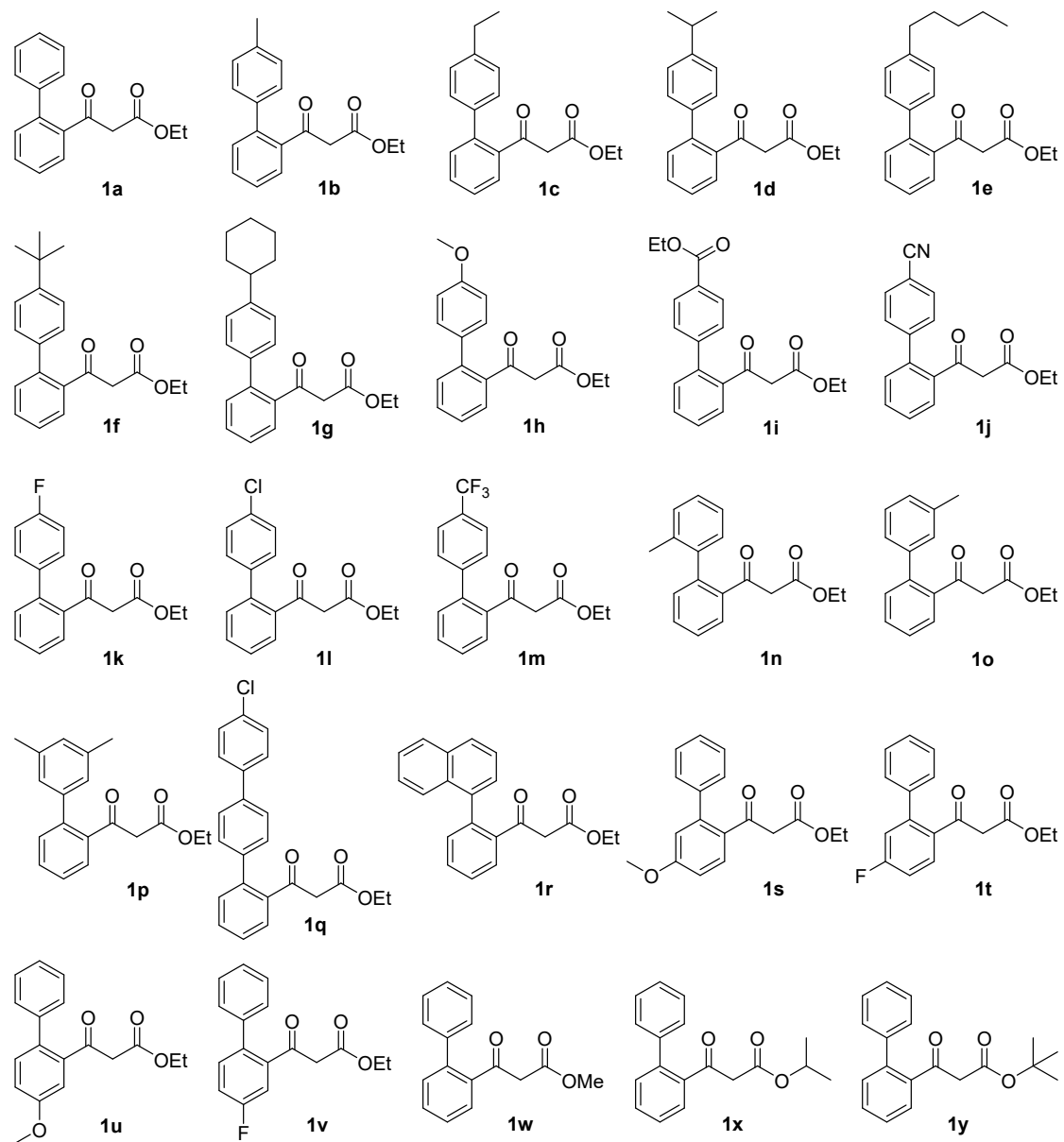
1. General Information

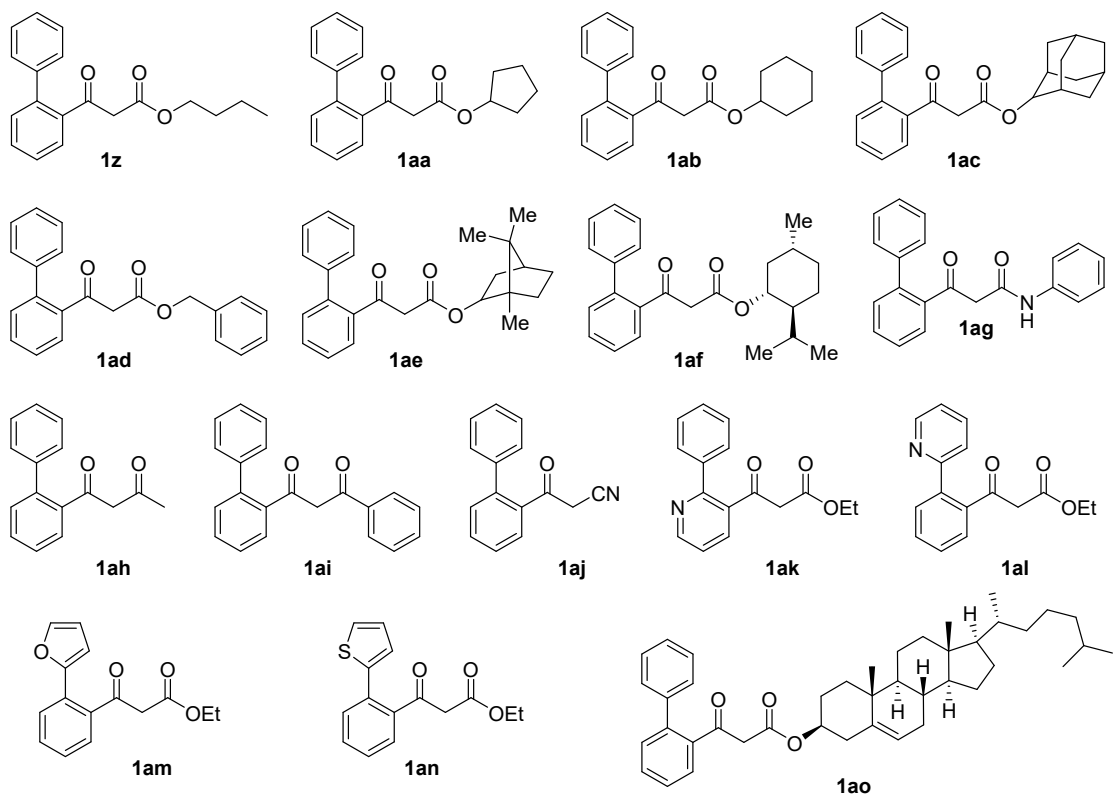
All reagents were purchased from commercial suppliers and used without further purification. Flash chromatography was carried out with silica gel (200-300 mesh). Analytical TLC was performed with silica gel GF254 plates, and the products were visualized by UV detection. ^1H NMR, ^{13}C NMR and ^{19}F NMR (400 MHz, 101 MHz and 565 MHz, respectively) spectra were measured in CDCl_3 , $\text{DMSO-}d_6$, $\text{Ethanol-}d_6$, recorded on Bruker Avance DPX 400 MHz spectrometer. All chemical shifts (δ) were reported in ppm and coupling constants (J) in Hz. NMR Spectra recorded in CDCl_3 were referenced to tetramethylsilane at 0 ppm for ^1H or referenced to residual CHCl_3 at 77.16 ppm for ^{13}C . NMR Spectra recorded in $\text{DMSO-}d_6$ were referenced to residual DMSO at 2.50 ppm for ^1H or 39.52 ppm for ^{13}C . NMR Spectra recorded in $\text{Ethanol-}d_6$ were referenced to residual ethanol at 3.56 ppm for ^1H . The following abbreviations are used: m (multiplet), s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), *etc.* Photoluminescence spectra were measured on a Horiba Fluoremax-4 PLUS spectrofluorometer (HORIBA Instruments Incorporated, Edison, USA) with a xenon lamp as an excitation light source. The high resolution mass spectra (HRMS) were measured on a Bruker Daltonics APEX II 47e spectrometer by ESI. Irradiation with blue light was performed using TaoYuan LED (3 W, $\lambda_{\text{max}} = 365 \text{ nm}$, 145 lm @1200 mA).

2. Substrates Preparation

2.1 Involved Substrates

Table S1. Involved Substrates





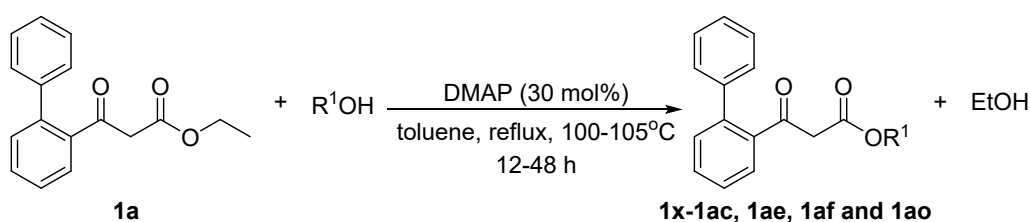
2.2 Synthesis of Compounds **1a-1w**, **1ad**, **1ag-1aj**, and **1al-1an**

All biphenyl β -ketoesters **1a-1w**, **1ad**, **1ag-1aj**, and **1al-1an** were synthesized according to the literature,¹ and the NMR spectroscopy was consisted with those data.

2.3 Synthesis of Compound **1ak**

Biphenyl β -ketoester **1ak** were synthesized according to the literature,^{1a, 2} and the analytical data of new compound **1ak** is shown as follow.

2.4 Synthesis of Compounds **1x-1ac**, **1ae**, **1af** and **1ao**



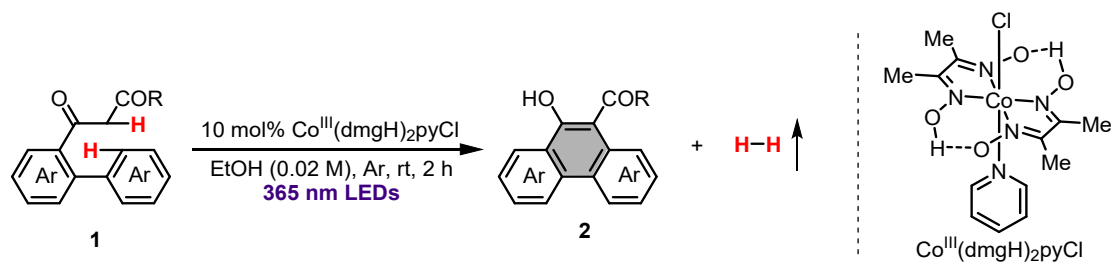
Biphenyl β -ketoesters **1x-1ac**, **1ae**, **1af** and **1ao** were prepared from the corresponding biphenyl β -ketoesters according to a slightly modified literature procedure,³ and the analytical data of new compound is shown as follow.

Ethyl 3-([1,1'-biphenyl]-2-yl)-3-oxopropanoate **1a** (1.0 mmol), corresponding alcohol (2.0 or 4.0 mmol), DMAP (0.3 mmol), and toluene (20 mL) were added in a flask equipped with a Dean-Stark trap and reflux condenser. The mixture was stirred at 100-105°C for 12-48 h, and the reaction was monitored by TLC. Upon completion of the reaction, the solvents were removed under reduced pressure and purified by flash chromatography to give the biphenyl β -ketoesters **1x-1ac**, **1ae**, **1af** and **1ao**.

2.5 Synthesis of **D₅-1a**

D₅-1a was synthesized according to the literature,^{1a} and the NMR spectroscopy was consisted with those data. ¹H NMR (400 MHz, CDCl₃): δ 12.25 (s, 0.18H, *enol*), 7.62 – 7.58 (m, 1.18H, *keto* + *enol*), 7.57 – 7.52 (m, 1H, *keto*), 7.46 – 7.36 (m, 2.54H, *keto* + *enol*), 5.06 (s, 0.18H, *enol*), 4.17 (q, $J = 7.1$ Hz, 0.36H, *enol*), 4.05 (q, $J = 7.1$ Hz, 2H, *keto*), 3.27 (s, 2H, *keto*), 1.26 (t, $J = 7.1$ Hz, 0.54H, *enol*), 1.16 (t, $J = 7.1$ Hz, 3H, *keto*).

3. General Experimental Procedure



A 10 mL Pyrex tube equipped with a magnetic stir bar was charged with substrate **1** (0.1 mmol) and $\text{Co}^{\text{III}}(\text{dmgH})_2\text{pyCl}$ (10 mol%) in EtOH (5.0 mL). The mixture was bubbled with a stream of Argon for about 0.5 h. The sample was then irradiated by 3 W UVA LEDs ($\lambda_{\text{max}} = 365 \text{ nm}$) for 2 h. Upon completion of the reaction, the solvent was removed under vacuum. The residue was purified with chromatography column on silica gel using mixtures of petroleum and ethyl acetate to give the corresponding products. The identity and purity of the product was confirmed by ^1H NMR, ^{13}C NMR or ^{19}F NMR spectroscopic analysis.

4. Mechanism Study

4.1 1a-¹H NMR (400 MHz, Ethanol-*d*₆)

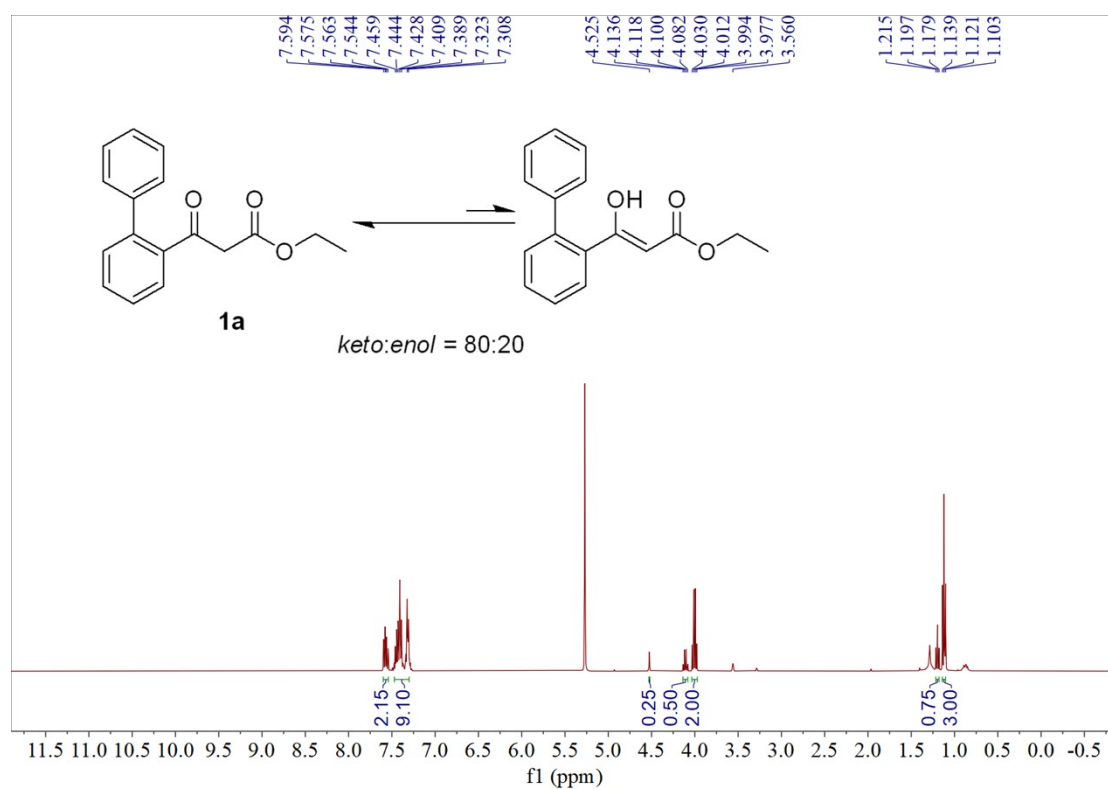


Fig. S1 ¹H NMR of **1a** in Ethanol-*d*₆.

4.2 GC Data

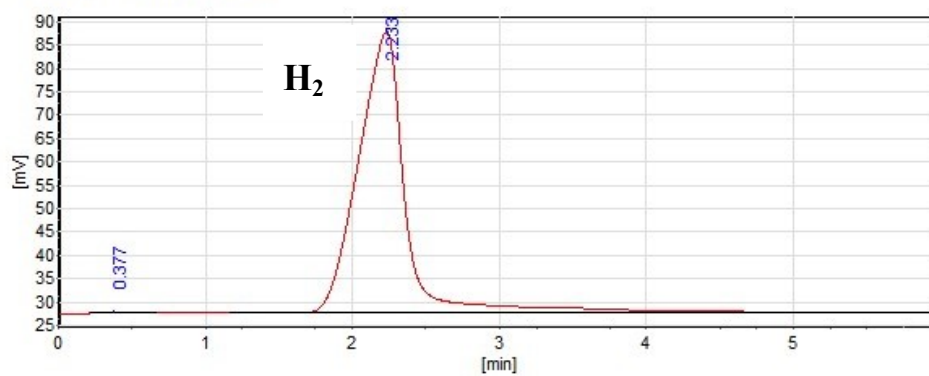


Fig. S2. GC data with **1a** (0.1 mmol) and Co(dm_gH)₂pyCl (10 mol%).

4.3 Competing Kinetic Isotope Effect (KIE) Experiments

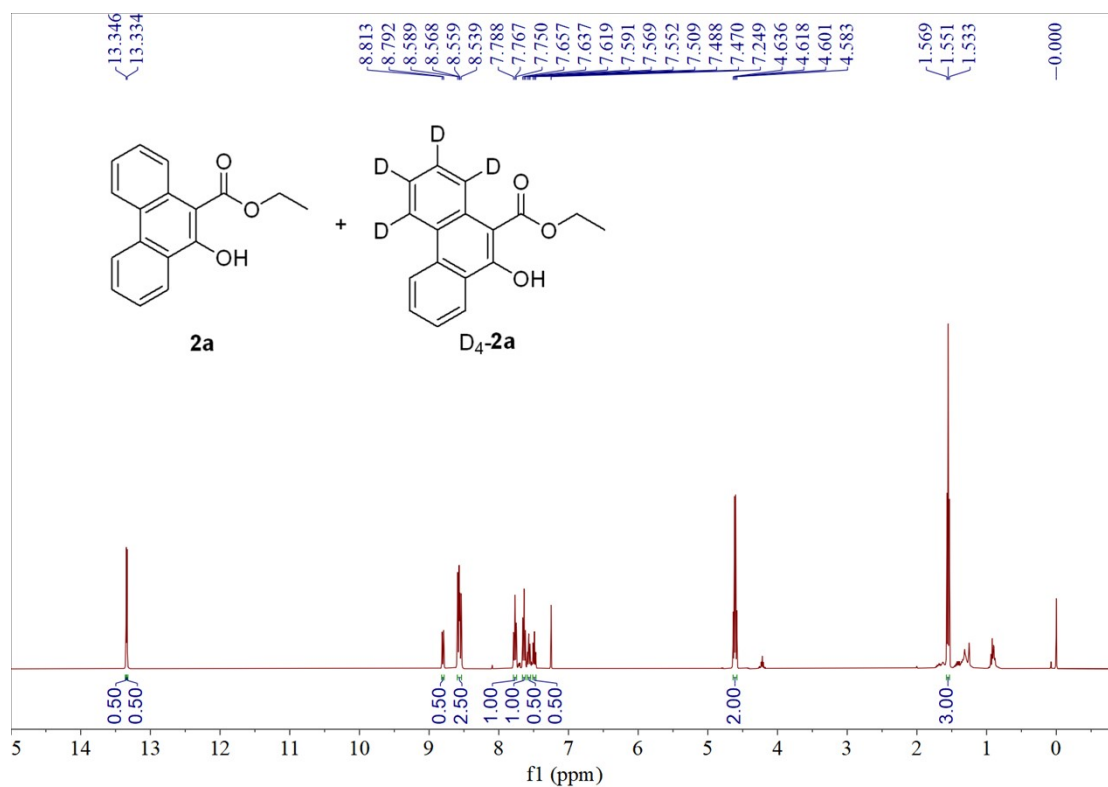
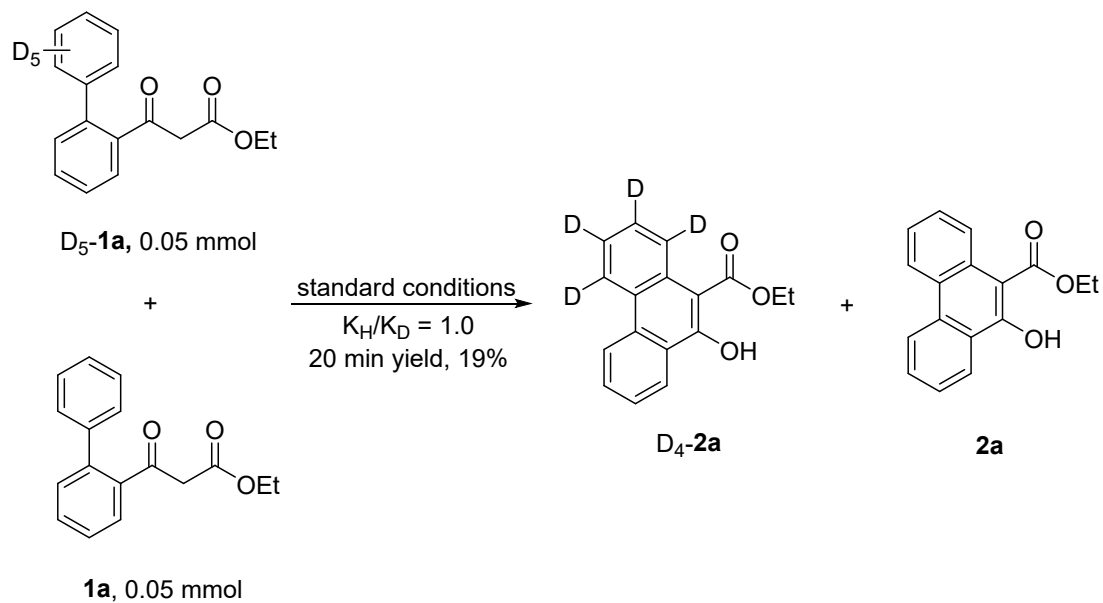


Fig. S3 Intermolecular KIE with D₅-**1a** and **1a**.

4.4 Spectroscopic Studies

a) Fluorescence emission spectrum

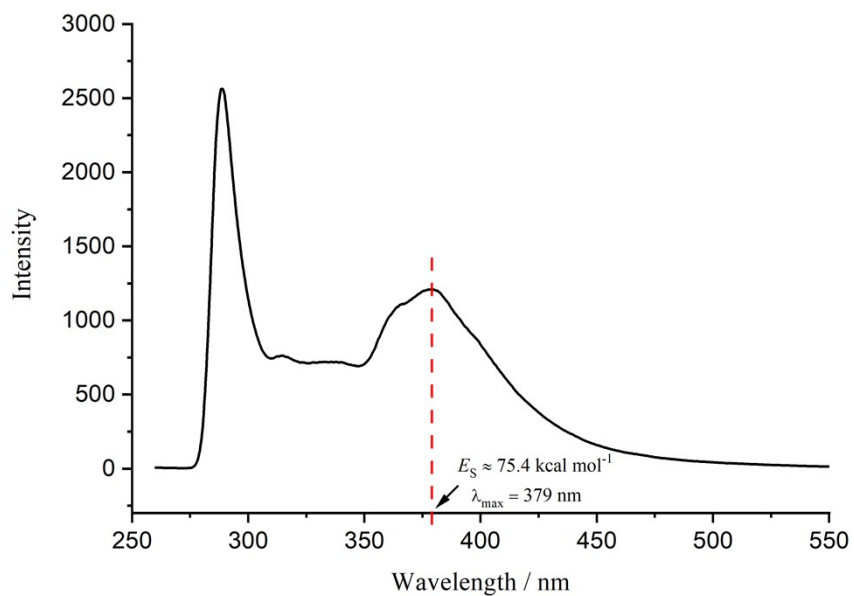


Fig. S4 Emission spectra of **1a** ($1 \times 10^{-4} \text{ M}$) in EtOH at room temperature with excitation at 286 nm.

b) Phosphorescence spectrum

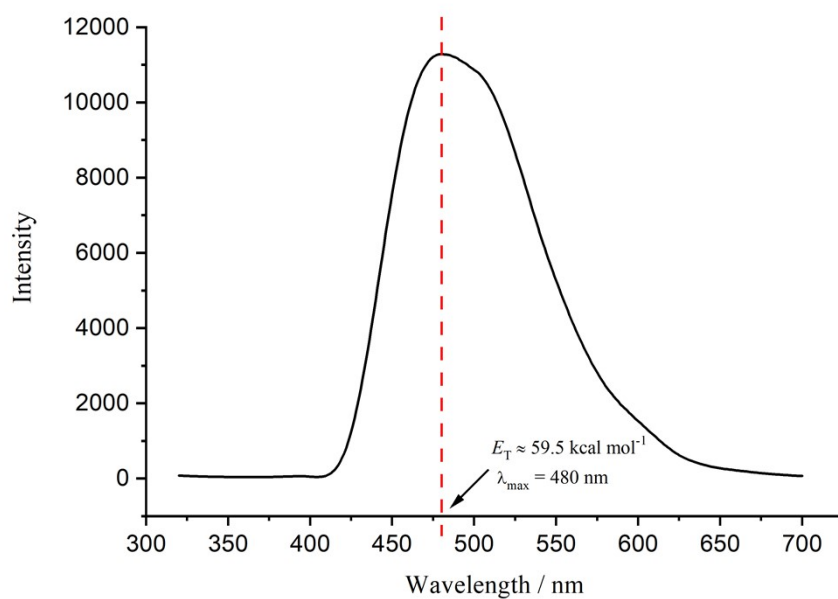


Fig. S5 Phosphorescence spectra of **1a** ($1 \times 10^{-3} \text{ M}$) in deoxygenated EtOH glass at 77 K recorded 1 ms pulsed excitation at 300 nm.

c) UV-vis absorption spectrum

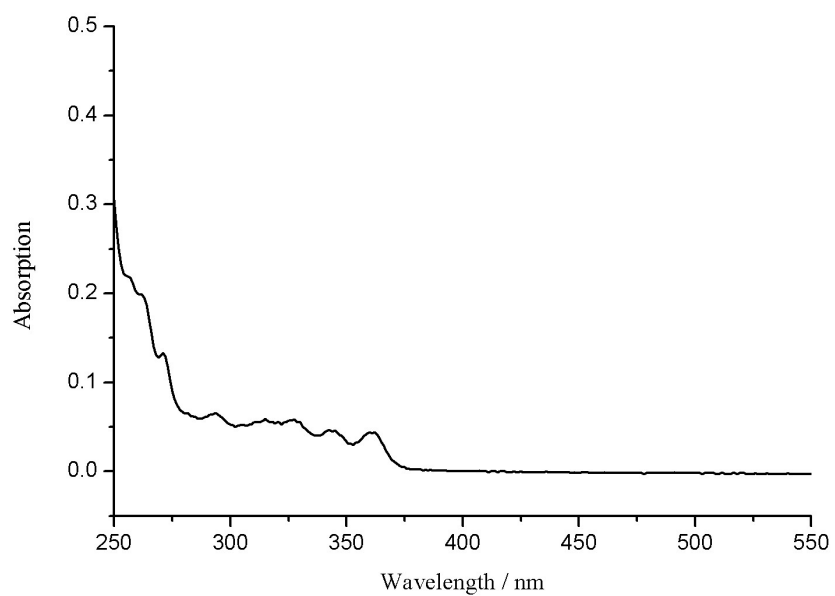


Fig. S6 UV-vis absorption spectra of **2w** (1×10^{-5} M) in EtOH.

4.5 Gram-scale Experiment

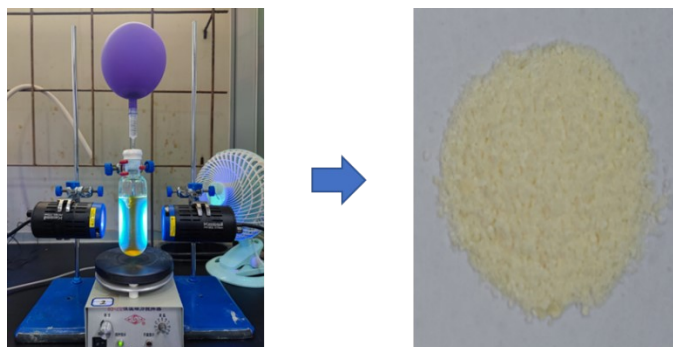
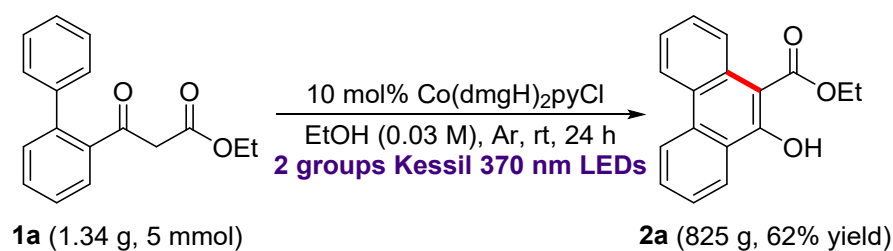
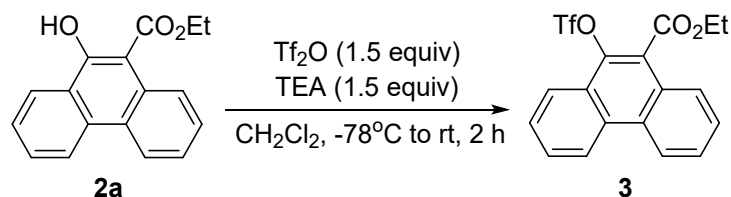


Fig. S7 Gram-scale experiment.

A 200 mL Pyrex tube equipped with a magnetic stir bar was charged with substrate **1a** (5 mmol, 1.34 g) and $\text{Co(dmgh)}_2\text{pyCl}$ (10 mol%), which were dissolved in EtOH (0.03 M, 150 mL). The mixture was bubbled with a stream of Argon for about 0.5 h. The reaction was stirred and irradiated using a Kessil LED lamp (PR160L-370 nm, 75% intensity, 3 cm away) for 24 h. Upon completion of the reaction, the solvent was then removed under vacuum. The residue was purified with chromatography column on silica gel using mixtures of petroleum ether and ethyl acetate to give the corresponding product **2a** (825 mg, 62% yield).

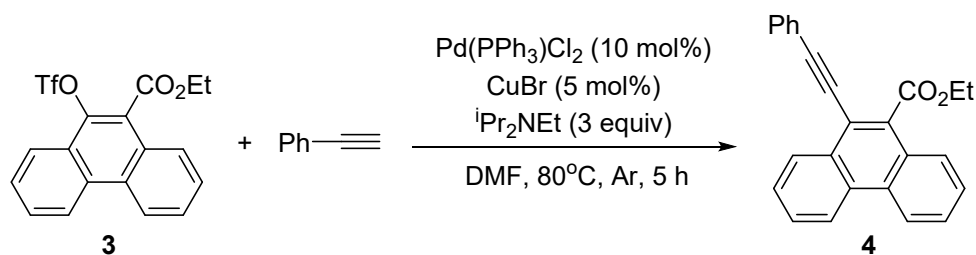
5. Application of Compound 2a by Various Transformation

Ethyl 10-(((trifluoromethyl)sulfonyl)oxy)phenanthrene-9-carboxylate (**3**)



According to relevant literature⁴: To a stirred solution of **2a** (3.0 mmol, 1.0 equiv) in CH_2Cl_2 (15.0 mL) precooled at -78°C , triethylamine (TEA, 4.5 mmol, 1.5 equiv) was added, and then trifluoromethanesulfonic anhydride (Tf_2O , 4.5 mmol, 1.5 equiv) was dropwise added within 10 minutes. After stirring at -78°C for a few minutes, the reaction mixture was then allowed to stir at room temperature for an additional 2 h until **2a** had been completely consumed as determined by TLC. Work-up: the solvent was removed under reduced pressure to get the crude product, which was purified by flash column chromatography on silica gel, eluted by petroleum ether/ethyl acetate 20:1 to get the pure product **3** as a pale yellow solid (1.18 g, 99% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.70 – 8.65 (m, 2H), 8.23 (d, $J = 7.9$ Hz, 1H), 8.13 (d, $J = 6.7$ Hz, 1H), 7.80 – 7.66 (m, 4H), 4.58 (q, $J = 7.2$ Hz, 2H), 1.49 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 165.07, 141.19, 132.36, 129.76, 129.44, 128.44, 128.30, 128.20, 127.81, 126.80, 124.89, 123.82, 123.09, 118.72 (d, $^1J_{\text{C,F}} = 321.99$ Hz), 62.78, 14.10; $^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -72.99 (s, 3F); **ESI-HRMS** Calcd for $\text{C}_{18}\text{H}_{17}\text{F}_3\text{NO}_5\text{S}^+$ [$\text{M}+\text{NH}_4$]⁺ 416.0774, found 416.0775.

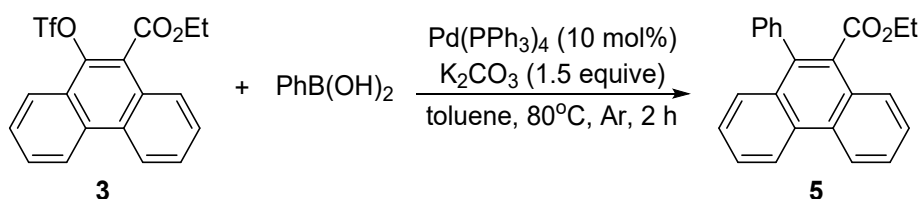
Ethyl 10-(phenylethynyl)phenanthrene-9-carboxylate (**4**)



According to relevant literature⁴: To a dried flask equipped with a magnetic stirrer was

added **3** (0.5 mmol, 1.0 equiv), phenylacetylene (1.5 mmol, 3 equiv), bis(triphenylphosphine)palladium(II) dichloride ($\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, 0.05 mmol, 0.1 equiv), copper(I) bromide (CuBr , 0.025 mmol, 0.05 equiv), diisopropylethylamine ($i\text{Pr}_2\text{NEt}$, 1.5 mmol, 3 equiv) and DMF (5.0 mL). The resulting suspension was heated at 80°C under an atmosphere of Ar for 5 h until **3** had been completely consumed as determined by TLC. Work-up: when the reaction mixture was cooled down to room temperature, the solution was extracted with ethyl acetate. Then the organic combined phase was washed with brine and dried with anhydrous sodium sulphate. Upon removal of solvent under vacuum, the crude product was purified by flash column chromatography on silica gel, eluted by petroleum ether/ethyl acetate 20:1 to furnish the pure product **4** as a yellow solid (158 mg, 90% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.68 – 8.64 (m, 2H), 8.60 – 8.56 (m, 1H), 7.89 (d, $J = 8.0$ Hz, 1H), 7.72 – 7.62 (m, 6H), 7.42 – 7.37 (m, 3H), 4.62 (q, $J = 7.1$ Hz, 2H), 1.48 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 168.98, 135.06, 131.82, 130.31, 130.21, 130.10, 128.97, 128.63, 128.19, 127.96, 127.74, 127.67, 127.62, 125.98, 123.04, 122.84, 118.01, 98.54, 85.34, 62.01, 14.57; **ESI-HRMS** Calcd for $\text{C}_{25}\text{H}_{19}\text{O}_2^+$ $[\text{M}+\text{H}]^+$ 351.1380, found 351.1383.

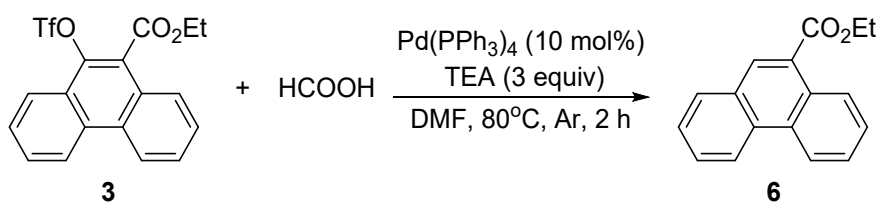
Ethyl 10-phenylphenanthrene-9-carboxylate (**5**)⁵



According to relevant literature⁴: To a stirred solution of **3** (0.5 mmol, 1.0 equiv) and phenylboronic acid (0.75 mmol, 1.5 equiv) in a toluene (5.0 mL) was added potassium carbonate (K_2CO_3 , 0.75 mmol, 1.5 equiv) and tetrakis(triphenylphosphine) palladium ($\text{Pd}(\text{PPh}_3)_4$, 0.05 mmol, 0.1 equiv). The resulting suspension was heated at 80°C under an atmosphere of Ar for 2 h. Work-up: when the reaction mixture was cooled to room temperature, the solvent was removed under vacuum to get the crude product, which was purified by flash column chromatography on silica gel, eluted by petroleum

ether/ethyl acetate 20:1 to afford the pure product **5** as a white solid (155 mg, 95% yield). **¹H NMR** (400 MHz, CDCl₃): δ 8.74 (d, *J* = 8.3 Hz, 2H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.70 – 7.62 (m, 4H), 7.51 – 7.42 (m, 6H), 4.10 (q, *J* = 7.1 Hz, 2H), 0.95 (t, *J* = 7.1 Hz, 3H); **¹³C NMR** (101 MHz, CDCl₃): δ 169.35, 138.21, 136.57, 130.92, 130.77, 130.72, 130.44, 130.01, 128.20, 128.02, 127.91, 127.56, 127.53, 127.19, 126.98, 125.99, 122.93, 122.77, 61.26, 13.84; **ESI-HRMS** Calcd for C₂₃H₁₉O₂⁺ [M+H]⁺ 327.1380, found 327.1383.

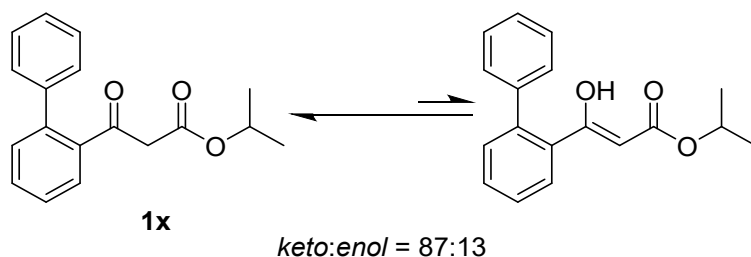
Ethyl phenanthrene-9-carboxylate (**6**)⁶



According to relevant literature⁴: To a stirred solution of **3** (0.5 mmol, 1.0 equiv) and formic acid (1.5 mmol, 3 equiv) in a DMF (5.0 mL) was added triethylamine (TEA, 0.75 mmol, 1.5 equiv) and tetrakis(triphenylphosphine) palladium (Pd(PPh₃)₄, 0.05 mmol, 0.1 equiv). The resulting suspension was heated at 80°C under an atmosphere of Ar for 2 h. Work-up: when the reaction mixture was cooled down to room temperature, the solution was extracted with ethyl acetate. Then the organic combined phase was washed with brine and dried with anhydrous sodium sulphate. Upon removal of solvent under vacuum, the crude product was purified by flash column chromatography on silica gel, eluted by petroleum ether/ethyl acetate 20:1 to afford the pure product **6** as a white solid (124 mg, 99% yield). **¹H NMR** (400 MHz, CDCl₃): δ 8.94 – 8.89 (m, 1H), 8.71 – 8.67 (m, 1H), 8.64 (d, *J* = 8.4 Hz, 1H), 8.43 (s, 1H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.72 – 7.64 (m, 3H), 7.60 (t, *J* = 6.9 Hz, 1H), 4.51 (q, *J* = 7.1 Hz, 2H), 1.48 (t, *J* = 7.1 Hz, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 167.80, 132.23, 132.18, 130.77, 130.18, 130.00, 129.16, 128.91, 127.47, 127.08, 126.96, 126.71, 126.68, 122.91, 122.73, 61.31, 14.55; **ESI-HRMS** Calcd for C₁₇H₁₅O₂⁺ [M+H]⁺ 251.1067, found 251.1065.

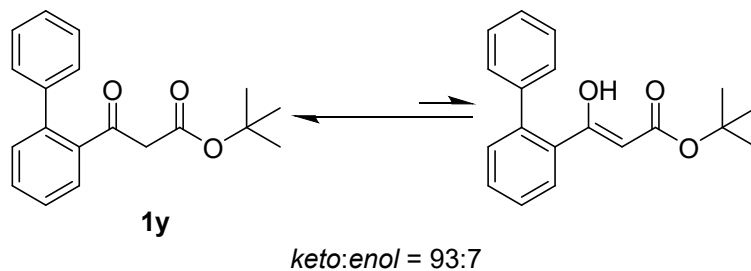
6. The Spectra Data of New Biphenyl β -ketoesters 1x-1ac, 1ae, 1af, 1ak and 1ao

Isopropyl 3-([1,1'-biphenyl]-2-yl)-3-oxopropanoate (1x) (*new compound*)



Pale yellow liquid (*keto:enol* = 87:13); R_f = 0.28 (PE/EtOAc = 20:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 12.32 (s, 0.15H, *enol*), 7.62 – 7.58 (m, 1.15H, *keto* + *enol*), 7.57 – 7.51 (m, 1.15H, *keto* + *enol*), 7.45 – 7.35 (m, 8.05H, *keto* + *enol*), 5.06 (p, J = 6.3 Hz, 0.15H, *enol*), 4.91 (p, J = 6.3 Hz, 1H, *keto*), 3.25 (s, 2H, *keto*), 1.24 (d, J = 6.1 Hz, 0.9H, *enol*), 1.13 (d, J = 6.3 Hz, 6H, *keto*); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 199.27, 174.13, 172.30, 166.66, 141.02, 140.64, 140.14, 139.48, 133.83, 131.35, 130.95, 130.43, 130.22, 129.20, 129.07, 128.97, 128.75, 128.70, 128.34, 128.24, 127.60, 127.30, 127.30, 93.18, 93.15, 68.84, 67.74, 49.20, 21.99, 21.68; **ESI-HRMS** Calcd for $\text{C}_{18}\text{H}_{19}\text{O}_3^+$ $[\text{M}+\text{H}]^+$ 283.1329, found 283.1330.

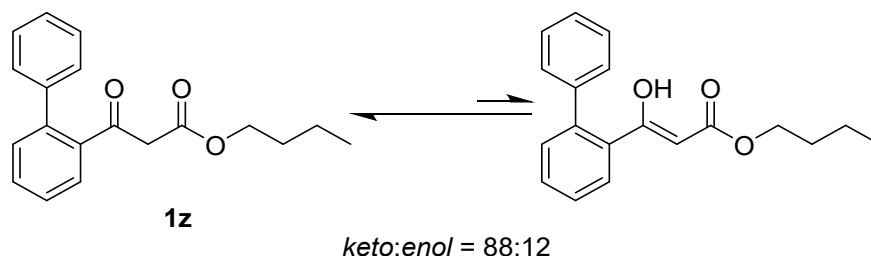
tert-Butyl 3-([1,1'-biphenyl]-2-yl)-3-oxopropanoate (1y) (*new compound*)



Pale yellow liquid (*keto:enol* = 93:7); R_f = 0.30 (PE/EtOAc = 20:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 12.36 (s, 0.07H, *enol*), 7.60 – 7.58 (m, 1.07H, *keto* + *enol*), 7.56 – 7.52 (m, 1.07H, *keto* + *enol*), 7.45 – 7.40 (m, 5.35H, *keto* + *enol*), 7.37 – 7.34 (m, 2.14H, *keto* + *enol*), 5.01 (s, 0.07H, *enol*), 3.19 (s, 2H, *keto*), 1.47 (s, 0.63H, *enol*), 1.32 (s, 9H, *keto*); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 199.75, 173.69, 172.57, 166.28, 141.07, 140.98, 140.91, 140.53, 140.16, 139.62, 134.01, 131.23, 130.89, 130.38, 130.06, 129.21, 129.07, 128.94, 128.78, 128.71, 128.29, 128.20,

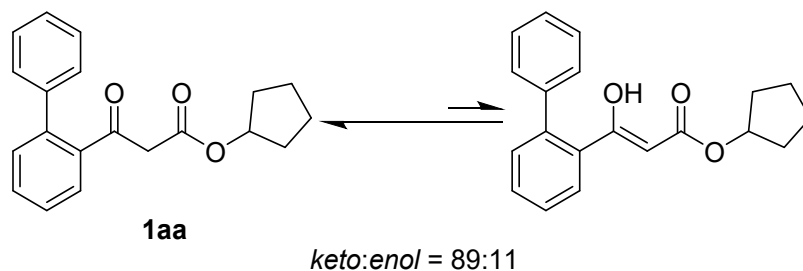
128.00, 127.97, 127.54, 127.26, 127.23, 94.18, 81.74, 81.13, 50.30, 28.40, 27.91; **ESI-HRMS** Calcd for $C_{19}H_{20}NaO_3^+$ $[M+Na]^+$ 319.1305, found 319.1302.

Butyl 3-([1,1'-biphenyl]-2-yl)-3-oxopropanoate (1z) (new compound)



Pale yellow liquid (*keto:enol* = 88:12); R_f = 0.30 (PE/EtOAc = 20:1); 1H NMR (400 MHz, $CDCl_3$) δ 12.25 (s, 0.14H, *enol*), 7.62 – 7.59 (m, 1.14H, *keto* + *enol*), 7.57 – 7.51 (m, 1.14H, *keto* + *enol*), 7.46 – 7.41 (m, 4.56H, *keto* + *enol*), 7.40 – 7.34 (m, 3.42H, *keto* + *enol*), 5.06 (s, 0.14H, *enol*), 4.11 (t, J = 6.6 Hz, 0.28H, *enol*), 4.00 (t, J = 6.6 Hz, 2H, *keto*), 3.27 (s, 2H, *keto*), 1.61 – 1.48 (m, 2.28H, *keto* + *enol*), 1.32 – 1.24 (m, 2.28H, *keto* + *enol*), 0.93 – 0.86 (m, 3.42H, *keto* + *enol*); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.17, 174.13, 172.78, 167.26, 141.05, 141.01, 140.67, 140.13, 139.44, 133.75, 131.43, 130.95, 130.46, 130.27, 129.17, 129.06, 129.01, 128.78, 128.73, 128.38, 128.29, 127.67, 127.34, 127.33, 92.86, 65.15, 64.19, 48.86, 30.71, 30.51, 19.18, 19.08, 13.84, 13.78; **ESI-HRMS** Calcd for $C_{19}H_{21}O_3^+$ $[M+H]^+$ 297.1485, found 297.1485.

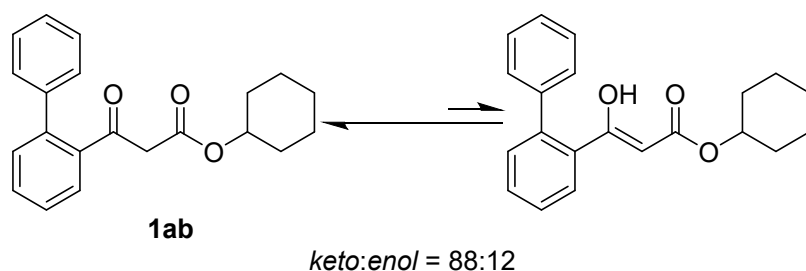
Cyclopentyl 3-([1,1'-biphenyl]-2-yl)-3-oxopropanoate (1aa) (new compound)



Pale yellow liquid (*keto:enol* = 89:11); R_f = 0.28 (PE/EtOAc = 20:1); 1H NMR (400 MHz, $CDCl_3$) δ 12.31 (s, 0.12H, *enol*), 7.60 – 7.57 (m, 1.12H, *keto* + *enol*), 7.57 – 7.51 (m, 1.12H, *keto* + *enol*), 7.45 – 7.40 (m, 4.48H, *keto* + *enol*), 7.40 – 7.34 (m, 3.36H, *keto* + *enol*), 5.22 – 5.18 (m, 0.12H, *enol*), 5.09 – 5.05 (m, 1H, *keto*), 3.24 (s, 2H, *keto*),

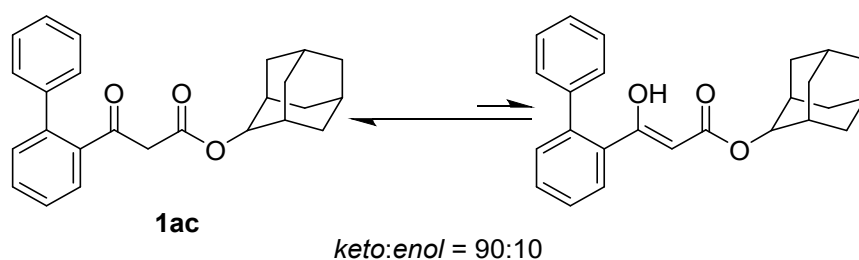
1.77 – 1.69 (m, 2.24H, *keto* + *enol*), 1.64 – 1.47 (m, 6.67H, *keto* + *enol*); ^{13}C NMR (101 MHz, CDCl_3) δ 199.31, 174.06, 172.57, 166.91, 141.01, 141.00, 140.61, 140.13, 139.48, 133.83, 131.35, 130.93, 130.43, 130.21, 129.20, 129.06, 128.97, 128.72, 128.34, 128.25, 127.62, 127.30, 127.28, 93.18, 78.18, 49.20, 32.77, 32.55, 23.81, 23.73; **ESI-HRMS** Calcd for $\text{C}_{20}\text{H}_{20}\text{NaO}_3^+$ $[\text{M}+\text{Na}]^+$ 331.1305, found 331.1307.

Cyclohexyl 3-([1,1'-biphenyl]-2-yl)-3-oxopropanoate (1ab) (*new compound*)



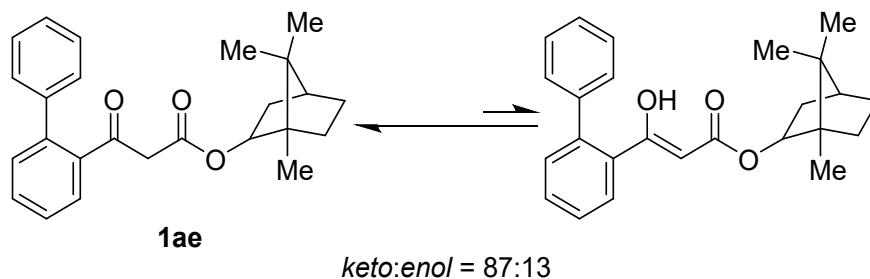
Pale yellow liquid (*keto:enol* = 88:12); R_f = 0.33 (PE/EtOAc = 20:1); ^1H NMR (400 MHz, CDCl_3) δ 12.31 (s, 0.14H, *enol*), 7.61 – 7.58 (m, 1.14H, *keto* + *enol*), 7.56 – 7.51 (m, 1.14H, *keto* + *enol*), 7.45 – 7.41 (m, 4.56H, *keto* + *enol*), 7.39 – 7.34 (m, 3.42H, *keto* + *enol*), 5.08 (s, 0.14H, *enol*), 4.82 – 4.63 (m, 1.14H, *keto* + *enol*), 3.26 (s, 2H, *keto*), 1.74 – 1.60 (m, 4.56H, *keto* + *enol*), 1.52 – 1.45 (m, 1.14H, *keto* + *enol*), 1.34 – 1.20 (m, 5.70H, *keto* + *enol*); ^{13}C NMR (101 MHz, CDCl_3) δ 199.32, 174.11, 172.25, 166.63, 141.03, 141.01, 140.64, 140.16, 139.48, 133.84, 131.35, 130.94, 130.45, 130.22, 129.22, 129.07, 128.98, 128.77, 128.71, 128.34, 128.24, 127.61, 127.30, 127.29, 93.22, 73.73, 72.72, 49.26, 31.77, 31.40, 25.43, 25.35, 23.85, 23.65; **ESI-HRMS** Calcd for $\text{C}_{21}\text{H}_{22}\text{NaO}_3^+$ $[\text{M}+\text{Na}]^+$ 345.1464, found 345.1464.

(1*r*,3*r*,5*r*,7*r*)-adamantan-2-yl 3-([1,1'-biphenyl]-2-yl)-3-oxopropanoate (1ac) (*new compound*)



Pale yellow liquid (*keto:enol* = 90:10); R_f = 0.33 (PE/EtOAc = 20:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 12.30 (s, 0.11H, *enol*), 7.63 – 7.60 (m, 1.11H, *keto* + *enol*), 7.57 – 7.52 (m, 1.11H, *keto* + *enol*), 7.45 – 7.35 (m, 7.77H, *keto* + *enol*), 5.12 (s, 0.11H, *enol*), 4.97 – 4.94 (m, 0.11H, *enol*), 4.85 – 4.82 (m, 1H, *keto*), 3.31 (s, 2H, *keto*), 1.93 – 1.88 (m, 2.22H, *keto* + *enol*), 1.84 – 1.77 (m, 6.66H, *keto* + *enol*), 1.72 – 1.67 (m, 4.44H, *keto* + *enol*), 1.53 – 1.46 (m, 2.22H, *keto* + *enol*); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 199.28, 173.96, 172.23, 166.61, 141.05, 140.67, 140.19, 139.46, 133.83, 131.38, 130.90, 130.50, 130.21, 129.20, 129.05, 128.99, 128.80, 128.72, 128.33, 128.26, 127.65, 127.31, 127.26, 93.39, 78.27, 78.24, 49.34, 37.44, 37.37, 36.39, 36.31, 31.94, 31.71, 31.65, 27.25, 27.17, 27.04, 26.97; **ESI-HRMS** Calcd for $\text{C}_{25}\text{H}_{27}\text{O}_3^+$ $[\text{M}+\text{H}]^+$ 375.1955, found 375.1959.

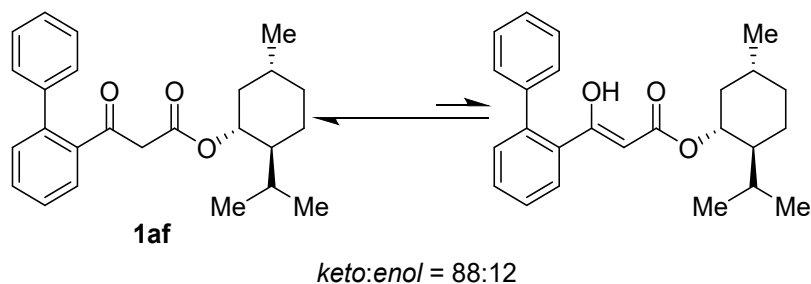
(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 3-([1,1'-biphenyl]-2-yl)-3-oxopropanoate (1ae) (new compound)



Pale yellow liquid (*keto:enol* = 87:13); R_f = 0.36 (PE/EtOAc = 20:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 12.24 (s, 0.15H, *enol*), 7.61 – 7.58 (m, 1.15H, *keto* + *enol*), 7.56 – 7.51 (m, 1.15H, *keto* + *enol*), 7.44 – 7.40 (m, 4.6H, *keto* + *enol*), 7.39 – 7.33 (m, 3.45H, *keto* + *enol*), 4.94 (s, 0.15H, *enol*), 4.71 – 4.67 (m, 0.15H, *enol*), 4.58 – 4.55 (m, 1H, *keto*), 3.24 (s, 2H, *keto*), 1.77 – 1.61 (m, 5.75H, *keto* + *enol*), 1.54 – 1.47 (m, 1.15H, *keto* + *enol*), 1.11 – 1.01 (m, 2.3H, *keto* + *enol*), 0.87 (s, 0.45H, *enol*), 0.84 (s, 3H, *keto*), 0.82 (s, 0.45H, *enol*), 0.80 (s, 3H, *keto*), 0.78 (s, 0.45H, *enol*), 0.74 (s, 3H, *keto*); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 198.97, 173.44, 172.17, 166.70, 141.14, 141.08, 140.65, 140.20, 139.43, 133.75, 131.36, 130.81, 130.47, 130.16, 129.00, 128.80 (x2), 128.27, 128.24, 127.65, 127.31, 127.26, 93.52, 82.19, 80.79, 49.18, 48.86, 48.71, 46.99, 46.95, 45.06,

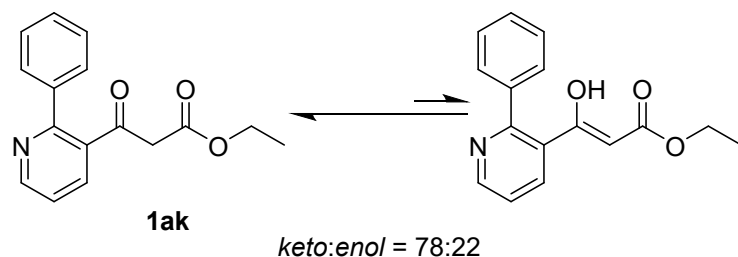
45.02, 38.79, 38.67, 33.78, 33.71, 27.12, 27.05, 20.22, 20.16, 19.94, 19.86, 11.42; **ESI-HRMS** Calcd for $C_{25}H_{28}NaO_3^+$ $[M+Na]^+$ 399.1931, found 399.1933.

(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl **3-([1,1'-biphenyl]-2-yl)-3-oxopropanoate (1af) (new compound)**



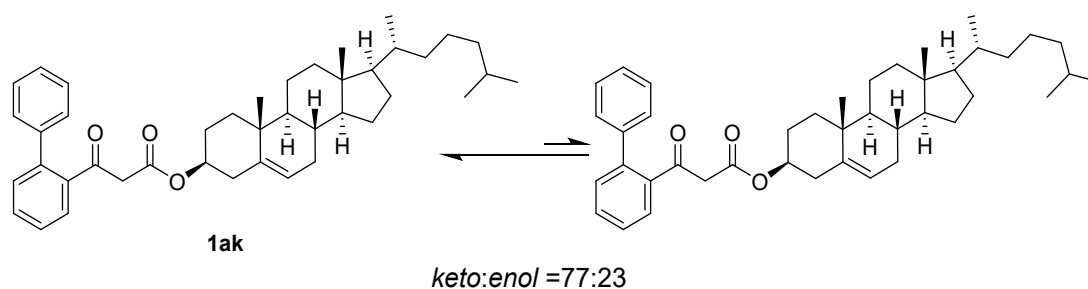
Pale yellow liquid (*keto:enol* = 88:12); R_f = 0.41 (PE/EtOAc = 20:1); **¹H NMR** (400 MHz, $CDCl_3$) δ 12.32 (s, 0.14H, *enol*), 7.61 – 7.57 (m, 1.14H, *keto* + *enol*), 7.56 – 7.52 (m, 1.14H, *keto* + *enol*), 7.45 – 7.41 (m, 4.56H, *keto* + *enol*), 7.40 – 7.35 (m, 3.42H, *keto* + *enol*), 4.95 (s, 0.14H, *enol*), 4.74 – 4.55 (m, 1.14H, *keto* + *enol*), 3.27 (d, J = 2.5 Hz, 2H, *keto*), 1.90 – 1.82 (m, 1.14H, *keto* + *enol*), 1.66 – 1.59 (m, 3.42H, *keto* + *enol*), 1.44 – 1.35 (m, 1.14H, *keto* + *enol*), 1.28 – 1.22 (m, 1.14H, *keto* + *enol*), 1.03 – 0.95 (m, 1.14H, *keto* + *enol*), 0.90 (d, J = 6.4 Hz, 0.42H, *enol*), 0.87 – 0.80 (m, 8.7H, *keto* + *enol*), 0.73 (d, J = 6.8 Hz, 0.42H, *enol*), 0.65 (d, J = 6.9 Hz, 3H, *keto*); **¹³C NMR** (101 MHz, $CDCl_3$) δ 199.20, 173.67, 172.32, 166.73, 141.11, 141.02, 140.66, 140.17, 139.42, 133.84, 131.36, 130.86, 130.46, 130.21, 129.07, 128.98, 128.81, 128.79, 128.31, 128.22, 127.62, 127.35, 127.27, 93.47, 75.30, 74.11, 49.33, 47.08, 46.91, 41.02, 40.60, 34.31, 34.22, 31.49, 31.40, 26.42, 25.89, 23.76, 23.21, 22.14, 22.08, 20.93, 20.74, 16.73, 16.12; **ESI-HRMS** Calcd for $C_{25}H_{30}NaO_3^+$ $[M+Na]^+$ 401.2087, found 401.2085.

Ethyl 3-oxo-3-(2-phenylpyridin-3-yl)propanoate (1ak) (new compound)



Pale yellow solid (*keto:enol* = 78:22); R_f = 0.42 (PE/EtOAc = 2:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 12.35 (s, 0.28H, *enol*), 8.81 – 8.73 (m, 1.28H, *keto* + *enol*), 7.94 – 7.85 (m, 1.28H, *keto* + *enol*), 7.65 – 7.57 (m, 2.56H, *keto* + *enol*), 7.51 – 7.31 (m, 5.12H, *keto* + *enol*), 5.13 (s, 0.28H, *enol*), 4.19 (q, J = 7.2 Hz, 0.56H, *enol*), 4.05 (q, J = 7.2 Hz, 2H, *keto*), 3.33 (s, 2H, *keto*), 1.27 (t, J = 7.1 Hz, 0.84H, *enol*), 1.16 (t, J = 7.1 Hz, 3H, *keto*); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 198.30, 172.41, 166.76, 157.40, 157.05, 151.45, 150.94, 150.46, 139.60, 139.11, 137.41, 137.18, 135.13, 129.82, 129.58, 129.33, 129.18, 129.09, 128.86, 128.86, 128.80, 128.42, 122.05, 121.74, 93.41, 61.40, 60.55, 48.47, 14.25, 14.03; **ESI-HRMS** Calcd for $\text{C}_{16}\text{H}_{15}\text{NaO}_3^+$ $[\text{M}+\text{Na}]^+$ 292.0944, found 292.0945.

(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 3-([1,1'-biphenyl]-2-yl)-3-oxopropanoate (1ao)
(new compound)

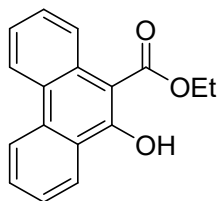


Pale yellow solid (*keto:enol* = 77:23); R_f = 0.41 (PE/EtOAc = 20:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 12.30 (s, 0.30H, *enol*), 7.61 – 7.57 (m, 1.30H, *keto* + *enol*), 7.55 – 7.51 (m, 1H, *keto*), 7.45 – 7.40 (m, 5.5H, *keto* + *enol*), 7.38 – 7.35 (m, 3.9H, *keto* + *enol*), 5.38 – 5.31 (m, 1.3H, *keto* + *enol*), 5.06 (s, 0.3H, *enol*), 4.71 – 4.61 (m, 0.3H, *enol*), 4.56 – 4.46 (m, 1H, *keto*), 3.25 (s, 2H, *keto*), 2.33 – 2.31 (m, 0.6H, *enol*), 2.21 – 2.16

(m, 2H, *keto*), 2.02 – 1.95 (m, 2.6H, *keto + enol*), 1.85 – 1.75 (m, 3.9H, *keto + enol*), 1.53 – 1.30 (m, 15.6H, *keto + enol*), 1.15 – 1.07 (m, 7.8H, *keto + enol*), 1.03 – 1.0 (m, 3.9H, *keto + enol*), 0.98 – 0.96 (m, 3.9H, *keto + enol*), 0.92 – 0.90 (m, 3.9H, *keto + enol*), 0.87 – 0.85 (m, 7.8H, *keto + enol*), 0.67 – 0.65 (m, 3.9H, *keto + enol*); ¹³C NMR (101 MHz, CDCl₃) δ 199.21, 174.25, 172.21, 166.52, 141.05, 140.67, 140.18, 139.69, 139.52, 139.48, 133.85, 131.35, 130.97, 130.45, 130.22, 129.22, 129.10, 128.99, 128.80, 128.74, 128.36, 128.25, 127.61, 127.32, 122.90, 122.90, 93.09, 77.36, 75.02, 73.99, 56.77, 56.23, 50.13, 50.07, 49.23, 42.41, 39.82, 39.63, 38.29, 37.89, 37.09, 36.97, 36.69, 36.63, 36.30, 35.91, 32.02, 31.98, 31.93, 28.35, 28.13, 27.94, 27.60, 24.39, 23.95, 22.96, 22.70, 21.12, 19.43, 19.40, 18.84, 11.97; **ESI-HRMS** Calcd for C₄₂H₅₆NaO₃⁺ [M+Na]⁺ 631.4122, found 631.4123.

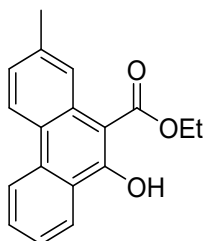
7. The Spectra Data of Products

Ethyl 10-hydroxyphenanthrene-9-carboxylate (2a)¹



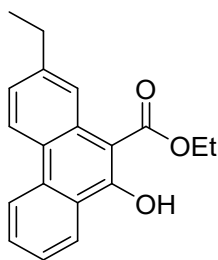
White solid; yield 20.0 mg, 75%; R_f = 0.44 (PE/EtOAc = 50:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 13.32 (s, 1H), 8.77 (d, J = 8.5 Hz, 1H), 8.55 – 8.51 (m, 3H), 7.75 – 7.71 (m, 1H), 7.63 – 7.59 (m, 1H), 7.57 – 7.52 (m, 1H), 7.46 (t, J = 7.6 Hz, 1H), 4.57 (t, J = 7.1 Hz, 2H), 1.53 (t, J = 7.1 Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 173.03, 162.83, 133.75, 130.52, 129.56, 127.69, 126.95, 126.16, 126.08, 125.35, 125.06, 124.31, 122.95, 122.52, 101.65, 62.16, 14.47; **ESI-HRMS** Calcd for $\text{C}_{17}\text{H}_{15}\text{O}_3^+$ $[\text{M}+\text{H}]^+$ 267.1016, found 267.1020.

Ethyl 10-hydroxy-7-methylphenanthrene-9-carboxylate (2b)¹



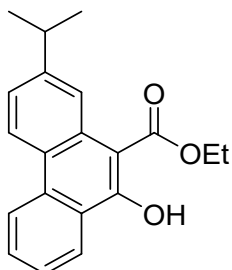
White solid; yield 21.3 mg, 76%; R_f = 0.44 (PE/EtOAc = 50:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 13.25 (s, 1H), 8.56 (s, 1H), 8.49 (dd, J = 8.3, 4.2 Hz, 2H), 8.41 (d, J = 8.4 Hz, 1H), 7.71 (t, J = 7.7 Hz, 1H), 7.57 (t, J = 7.6 Hz, 1H), 7.28 (d, J = 8.3 Hz, 1H), 4.57 (q, J = 7.1 Hz, 2H), 2.51 (s, 3H), 1.53 (t, J = 7.1 Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 173.01, 162.82, 137.35, 133.82, 130.44, 129.62, 126.48, 126.07, 125.81, 125.02, 124.95, 123.97, 122.83, 122.32, 101.46, 62.07, 22.28, 14.39; **ESI-HRMS** Calcd for $\text{C}_{18}\text{H}_{17}\text{O}_3^+$ $[\text{M}+\text{H}]^+$ 281.1172, found 281.1177.

Ethyl 7-ethyl-10-hydroxyphenanthrene-9-carboxylate (2c)¹



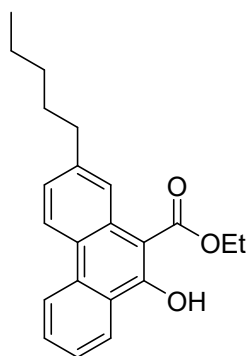
White solid; yield 22.7 mg, 77%; $R_f = 0.44$ (PE/EtOAc = 50:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 13.27 (s, 1H), 8.62 (s, 1H), 8.50 (d, $J = 9.6$ Hz, 2H), 8.44 (d, $J = 8.4$ Hz, 1H), 7.73 – 7.69 (m, 1H), 7.58 (t, $J = 8.1$ Hz, 1H), 7.32 (d, $J = 8.4$ Hz, 1H), 4.58 (q, $J = 7.2$ Hz, 2H), 2.83 (q, $J = 7.6$ Hz, 2H), 1.55 (t, $J = 7.1$ Hz, 3H), 1.35 (t, $J = 7.6$ Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 173.09, 162.87, 143.55, 133.84, 130.46, 129.68, 126.50, 125.03, 124.98, 124.80, 124.79, 124.21, 122.88, 122.36, 101.58, 62.07, 29.45, 15.51, 14.41; **ESI-HRMS** Calcd for $\text{C}_{19}\text{H}_{19}\text{O}_3^+$ $[\text{M}+\text{H}]^+$ 295.1329, found 295.1334.

Ethyl 10-hydroxy-7-isopropylphenanthrene-9-carboxylate (2d)¹



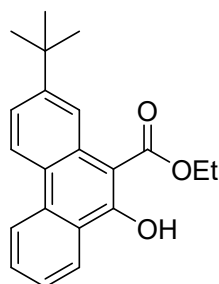
White solid; yield 24.7 mg, 80%; $R_f = 0.44$ (PE/EtOAc = 50:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 13.31 (s, 1H), 8.69 (s, 1H), 8.51 (dd, $J = 8.2, 1.4$ Hz, 2H), 8.46 (d, $J = 8.5$ Hz, 1H), 7.74 – 7.69 (m, 1H), 7.60 – 7.56 (m, 1H), 7.36 (d, $J = 8.6$ Hz, 1H), 4.58 (q, $J = 7.1$ Hz, 2H), 3.08 (p, $J = 6.9$ Hz, 1H), 1.56 (t, $J = 7.1$ Hz, 3H), 1.36 (d, $J = 7.0$ Hz, 6H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 173.17, 162.96, 148.16, 133.84, 130.48, 129.66, 126.52, 125.04, 125.04, 124.36, 123.63, 123.37, 122.91, 122.37, 101.66, 62.06, 34.63, 24.22, 14.45; **ESI-HRMS** Calcd for $\text{C}_{20}\text{H}_{21}\text{O}_3^+$ $[\text{M}+\text{H}]^+$ 309.1485, found 309.1489.

Ethyl 10-hydroxy-7-pentylphenanthrene-9-carboxylate (2e)¹



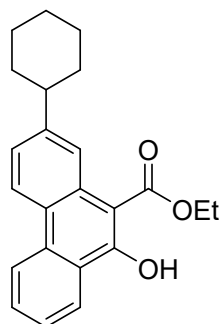
White solid; yield 24.2 mg, 72%; $R_f = 0.40$ (PE/EtOAc = 50:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 13.26 (s, 1H), 8.60 (s, 1H), 8.51 (d, $J = 8.4$ Hz, 2H), 8.45 (d, $J = 8.4$ Hz, 1H), 7.71 (t, $J = 7.7$ Hz, 1H), 7.58 (t, $J = 7.4$ Hz, 1H), 7.30 (d, $J = 6.7$ Hz, 1H), 4.58 (q, $J = 7.2$ Hz, 2H), 2.77 (t, $J = 7.7$ Hz, 2H), 1.77 – 1.70 (m, 2H), 1.54 (t, $J = 7.1$ Hz, 3H), 1.41 – 1.35 (m, 4H), 0.93 – 0.89 (m, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 173.09, 162.84, 142.32, 133.86, 130.46, 129.60, 126.50, 125.51, 125.25, 125.04, 124.98, 124.21, 122.83, 122.36, 101.59, 62.06, 36.55, 31.67, 31.14, 22.75, 14.40, 14.20; **ESI-HRMS** Calcd for $\text{C}_{22}\text{H}_{24}\text{NaO}_3^+$ $[\text{M}+\text{Na}]^+$ 359.1618, found 359.1621.

Ethyl 7-(*tert*-butyl)-10-hydroxyphenanthrene-9-carboxylate (2f)¹



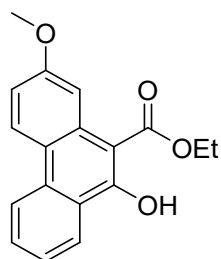
White solid; yield 22.9 mg, 71%; $R_f = 0.43$ (PE/EtOAc = 50:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 13.37 (s, 1H), 8.86 (s, 1H), 8.52 (d, $J = 8.5$ Hz, 2H), 8.48 (d, $J = 8.7$ Hz, 1H), 7.75 – 7.70 (m, 1H), 7.61 – 7.53 (m, 2H), 4.58 (q, $J = 7.1$ Hz, 2H), 1.57 (t, $J = 7.1$ Hz, 3H), 1.44 (s, 9H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 173.30, 163.10, 150.38, 133.73, 130.50, 129.34, 126.56, 125.11, 125.07, 123.95, 122.68, 122.44 (x2), 122.39, 101.78, 62.08, 35.34, 31.60, 14.55; **ESI-HRMS** Calcd for $\text{C}_{21}\text{H}_{22}\text{NaO}_3^+$ $[\text{M}+\text{Na}]^+$ 345.1461, found 345.1464.

Ethyl 7-cyclohexyl-10-hydroxyphenanthrene-9-carboxylate (2g)¹



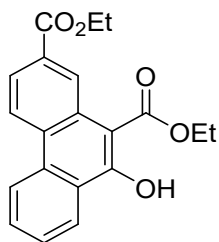
White solid; yield 26.1 mg, 75%; R_f = 0.36 (PE/EtOAc = 50:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 13.27 (s, 1H), 8.66 (s, 1H), 8.51 (d, J = 8.6 Hz, 2H), 8.45 (d, J = 8.5 Hz, 1H), 7.70 (d, J = 6.6 Hz, 1H), 7.57 (t, J = 7.8 Hz, 1H), 7.34 (d, J = 8.4 Hz, 1H), 4.59 (q, J = 7.2 Hz, 2H), 2.69 – 2.63 (m, 1H), 1.95 (dd, J = 43.2 Hz J = 12 Hz, 4H), 1.80 (d, J = 14.1 Hz, 1H), 1.57 (t, J = 7.2 Hz, 3H), 1.51 – 1.42 (m, 3H), 1.36 – 1.23 (m, 2H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 173.12, 162.87, 147.40, 133.85, 130.45, 129.65, 126.49, 125.03, 125.00, 124.38, 124.01, 123.77, 122.84, 122.37, 101.69, 62.05, 45.06, 34.76, 27.11, 26.45, 14.49; **ESI-HRMS** Calcd for $\text{C}_{23}\text{H}_{24}\text{NaO}_3^+$ $[\text{M}+\text{Na}]^+$ 371.1618, found 371.1621.

Ethyl 10-methoxy-7-hydroxyphenanthrene-9-carboxylate (2h)¹



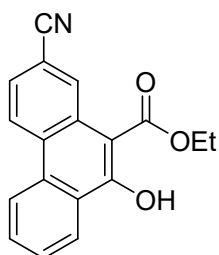
White solid; yield 16.0 mg, 54%; R_f = 0.36 (PE/EtOAc = 20:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 13.44 (s, 1H), 8.49 (d, J = 8.2 Hz, 1H), 8.44 (d, J = 9.2 Hz, 2H), 8.31 (d, J = 2.6 Hz, 1H), 7.71 (t, J = 7.0 Hz, 1H), 7.55 (t, J = 7.0 Hz, 1H), 7.09 (dd, J = 9.1, 2.6 Hz, 1H), 4.58 (q, J = 7.1 Hz, 2H), 3.92 (s, 3H), 1.55 (t, J = 7.1 Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 173.09, 163.78, 159.12, 133.92, 131.09, 130.63, 125.88, 125.10, 124.36, 124.23, 122.01, 120.27, 113.66, 108.08, 101.21, 62.06, 55.23, 14.44; **ESI-HRMS** Calcd for $\text{C}_{18}\text{H}_{16}\text{NaO}_4^+$ $[\text{M}+\text{Na}]^+$ 319.0941, found 319.0941.

Diethyl 9-hydroxyphenanthrene-2,10-dicarboxylate (2i)¹



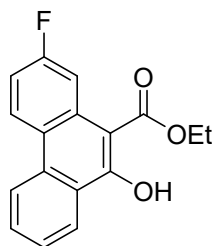
White solid; yield 21.7 mg, 64%; $R_f = 0.28$ (PE/EtOAc = 20:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 13.43 (s, 1H), 9.48 (s, 1H), 8.47 (t, $J = 8.8$ Hz, 3H), 8.01 (d, $J = 8.6$ Hz, 1H), 7.76 – 7.71 (m, 1H), 7.66 – 7.62 (m, 1H), 4.57 (q, $J = 7.1$ Hz, 2H), 4.44 (q, $J = 7.1$ Hz, 2H), 1.60 (t, $J = 7.1$ Hz, 3H), 1.46 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 172.75, 167.03, 163.35, 132.88, 130.70, 129.04, 128.96 (x2), 128.27, 127.87, 126.10, 125.14, 124.32, 123.06, 122.87, 101.41, 62.40, 61.15, 14.57, 14.27; **ESI-HRMS** Calcd for $\text{C}_{20}\text{H}_{18}\text{NaO}_5^+$ $[\text{M}+\text{Na}]^+$ 361.1046, found 361.1048.

Ethyl 7-cyano-10-hydroxyphenanthrene-9-carboxylate (2j)¹



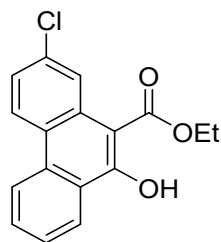
White solid; yield 15.4 mg, 53%; $R_f = 0.38$ (PE/EtOAc = 10:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 13.55 (s, 1H), 9.08 (d, $J = 1.7$ Hz, 1H), 8.53 – 8.45 (m, 3H), 7.80 (t, $J = 6.9$ Hz, 1H), 7.70 (t, $J = 7.0$ Hz, 1H), 7.60 (dd, $J = 8.5, 1.7$ Hz, 1H), 4.62 (q, $J = 7.1$ Hz, 2H), 1.57 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 172.30, 164.14, 132.40, 131.20, 131.08, 129.35, 128.66, 128.57, 126.26, 125.91, 125.37, 123.77, 122.99, 119.76, 110.99, 100.53, 62.81, 14.41; **ESI-HRMS** Calcd for $\text{C}_{18}\text{H}_{13}\text{NNaO}_3^+$ $[\text{M}+\text{Na}]^+$ 314.0788, found 314.0790.

Ethyl 7-fluoro-10-hydroxyphenanthrene-9-carboxylate (2k)¹



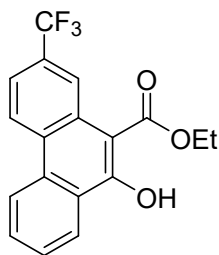
White solid; yield 9.4 mg, 33%; $R_f = 0.43$ (PE/EtOAc = 50:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 13.50 (s, 1H), 8.47 – 8.34 (m, 4H), 7.69 (t, $J = 6.9$ Hz, 1H), 7.56 (t, $J = 7.6$ Hz, 1H), 7.17 – 7.11 (m, 1H), 4.57 (q, $J = 7.1$ Hz, 2H), 1.54 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 172.75, 164.08, 162.27(d, $^1J_{\text{C,F}} = 244.7$ Hz), 133.36, 131.21 (d, $^3J_{\text{C,F}} = 10.3$ Hz), 130.80, 126.66, 125.15, 124.91, 124.82, 124.79, 122.59 (d, $^4J_{\text{C,F}} = 1.9$ Hz), 122.27, 112.56 (d, $^2J_{\text{C,F}} = 23.5$ Hz), 111.53 (d, $^2J_{\text{C,F}} = 25.8$ Hz), 100.97 (d, $^4J_{\text{C,F}} = 3.3$ Hz), 62.38, 14.39; $^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -112.75 (s, 1F); **ESI-HRMS** Calcd for $\text{C}_{17}\text{H}_{14}\text{FO}_3^+ [\text{M}+\text{H}]^+$ 285.0921, found 285.0921.

Ethyl 7-chloro-10-hydroxyphenanthrene-9-carboxylate (2l)¹



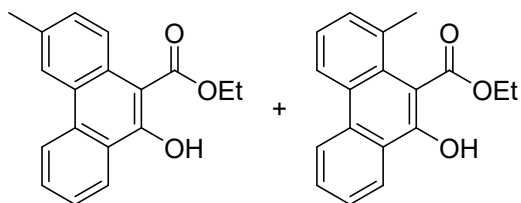
White solid; yield 10.5 mg, 35%; $R_f = 0.44$ (PE/EtOAc = 50:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 13.43 (s, 1H), 8.71 (d, $J = 2.2$ Hz, 1H), 8.44 (d, $J = 8.2$ Hz, 1H), 8.33 (dd, $J = 15.7, 8.6$ Hz, 2H), 7.69 (t, $J = 7.0$ Hz, 1H), 7.58 (t, $J = 7.0$ Hz, 1H), 7.33 (dd, $J = 8.8, 2.2$ Hz, 1H), 4.56 (q, $J = 7.1$ Hz, 2H), 1.55 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 172.59, 163.78, 133.76, 133.09, 130.78, 130.60, 127.11, 125.58, 125.56, 125.13, 124.44, 124.34, 124.20, 122.34, 100.61, 62.43, 14.33; **ESI-HRMS** Calcd for $\text{C}_{17}\text{H}_{13}\text{ClNaO}_3^+ [\text{M}+\text{Na}]^+$ 323.0445, found 323.0445.

Ethyl 10-hydroxy-7-(trifluoromethyl)phenanthrene-9-carboxylate (2m)¹



White solid; yield 12.4 mg, 37%; $R_f = 0.44$ (PE/EtOAc = 50:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 13.50 (s, 1H), 9.18 (s, 1H), 8.61 (d, $J = 8.6$ Hz, 1H), 8.55 (d, $J = 8.2$ Hz, 2H), 7.83 – 7.78 (m, 1H), 7.72 – 7.64 (m, 2H), 4.61 (q, $J = 7.1$ Hz, 2H), 1.58 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 172.49, 163.80, 132.60, 130.84, 129.01, 128.89 (d, $^2J_{\text{C,F}} = 32.2$ Hz), 127.95, 127.87, 125.86, 125.14, 124.74 (d, $^1J_{\text{C,F}} = 276.0$ Hz), 123.39 (x2), 122.72, 120.04 (d, $^4J_{\text{C,F}} = 3.7$ Hz), 100.98, 62.52, 14.06; $^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -62.41 (s, 3F); **ESI-HRMS** Calcd for $\text{C}_{18}\text{H}_{13}\text{F}_3\text{NaO}_3^+$ $[\text{M}+\text{Na}]^+$ 357.0709, found 357.0705.

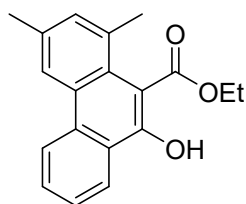
Ethyl 10-hydroxy-8-methylphenanthrene-9-carboxylate and ethyl 10-hydroxy-6-methylphenanthrene-9-carboxylate (2o)¹



2o:2o' = 1.7:1

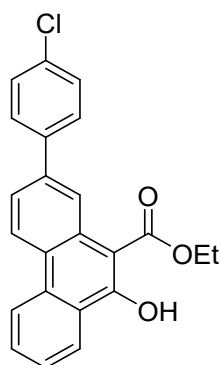
Pale yellow solid; yield 16.3 mg, 58%; $R_f = 0.41, 0.31$ (PE/EtOAc = 50:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 13.23 (s, 1H), 10.88 (s, 0.6H), 8.66 (d, $J = 8.6$ Hz, 1H), 8.56 – 8.51 (m, 2.6H), 8.43 (d, $J = 6.6$ Hz, 0.6H), 8.38 (d, $J = 5.6$ Hz, 0.6H), 8.33 (s, 1H), 7.74 – 7.68 (m, 1.6H), 7.62 – 7.58 (m, 1.6H), 7.42 – 7.36 (m, 2.2H), 4.58 (q, $J = 7.1$ Hz, 2H), 4.43 (q, $J = 7.2$ Hz, 1.2H), 2.54 (s, 3H), 2.50 (s, 1.8H), 1.53 (t, $J = 7.1$ Hz, 3H), 1.34 (t, $J = 7.1$ Hz, 1.8H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 173.06, 171.82, 162.19, 158.35, 134.26, 133.84, 133.71, 133.54, 130.55, 130.34, 130.12, 129.28, 128.87, 127.30, 127.21, 126.95, 126.82, 126.25, 125.99, 125.45, 125.04, 124.64, 124.64 (x2), 122.86 (x2), 122.51, 120.39, 103.71, 101.63, 62.08, 61.89, 23.08, 21.61, 14.48, 14.25; **ESI-HRMS** Calcd for $\text{C}_{18}\text{H}_{16}\text{NaO}_3^+$ $[\text{M}+\text{Na}]^+$ 303.0992, found 303.0995.

Ethyl 10-hydroxy-6,8-dimethylphenanthrene-9-carboxylate (2p)¹



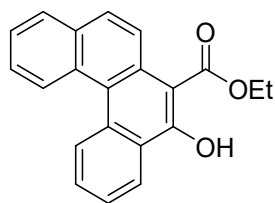
Pale yellow solid; yield 15.0 mg, 51%; R_f = 0.31 (PE/EtOAc = 50:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 10.80 (s, 1H), 8.53 (d, J = 8.3 Hz, 1H), 8.42 (d, J = 8.1 Hz, 1H), 8.19 (s, 1H), 7.71 – 7.67 (m, 1H), 7.60 – 7.56 (m, 1H), 7.23 (d, J = 1.8 Hz, 1H), 4.42 (q, J = 7.2 Hz, 2H), 2.51 (s, 3H), 2.47 (s, 3H), 1.34 (t, J = 7.2 Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 171.87, 157.75, 134.06 (x2), 133.64, 132.16, 129.94, 127.41, 126.83, 126.63, 124.75, 124.60, 122.85, 120.44, 103.72, 61.83, 22.92, 21.58, 14.26; **ESI-HRMS** Calcd for $\text{C}_{19}\text{H}_{18}\text{NaO}_3^+$ $[\text{M}+\text{Na}]^+$ 317.1148, found 317.1147.

Ethyl 7-(4-chlorophenyl)-10-hydroxyphenanthrene-9-carboxylate (2q)¹



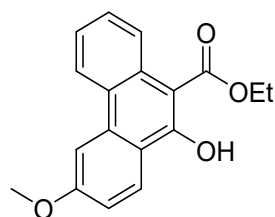
White solid; yield 20.7 mg, 55%; R_f = 0.36 (PE/EtOAc = 50:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 13.39 (s, 1H), 8.97 (s, 1H), 8.48 (t, J = 8.3 Hz, 3H), 7.70 (d, J = 6.7 Hz, 1H), 7.61 – 7.57 (m, 4H), 7.43 (d, J = 8.5 Hz, 2H), 4.54 (q, J = 7.1 Hz, 2H), 1.52 (t, J = 7.1 Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 172.93, 163.43, 139.96, 138.65, 133.59, 133.41, 130.67, 129.86, 129.12, 128.52, 127.04, 125.41, 125.36, 125.16, 124.47, 123.53, 122.90, 122.53, 101.43, 62.21, 14.42; **ESI-HRMS** Calcd for $\text{C}_{23}\text{H}_{17}\text{ClNaO}_3^+$ $[\text{M}+\text{Na}]^+$ 399.0758, found 399.0754.

Ethyl 5-hydroxybenzo[*c*]phenanthrene-6-carboxylate (2r)¹



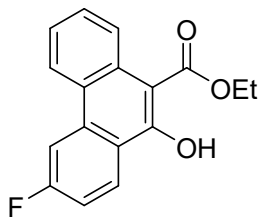
Pale yellow solid; yield 18.7 mg, 59%; R_f = 0.38 (PE/EtOAc = 50:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 12.99 (s, 1H), 8.81 (dd, J = 15.3, 8.3 Hz, 2H), 8.70 (d, J = 9.1 Hz, 1H), 8.60 (d, J = 6.7 Hz, 1H), 7.92 (d, J = 7.6 Hz, 1H), 7.82 (d, J = 9.2 Hz, 1H), 7.70 (t, J = 6.9 Hz, 1H), 7.61 (t, J = 7.5 Hz, 1H), 7.57 – 7.50 (m, 2H), 4.58 (q, J = 7.1 Hz, 2H), 1.52 (t, J = 7.1 Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 172.71, 161.80, 133.25, 131.80, 129.97, 129.43, 128.48, 128.41, 127.98, 127.92, 127.57, 126.26, 126.02, 125.72, 125.36, 124.56, 124.03, 122.77, 102.69, 62.28, 14.46; **ESI-HRMS** Calcd for $\text{C}_{21}\text{H}_{16}\text{NaO}_3^+$ $[\text{M}+\text{Na}]^+$ 339.0992, found 339.0993.

Ethyl 10-hydroxy-3-methoxyphenanthrene-9-carboxylate (2s)¹



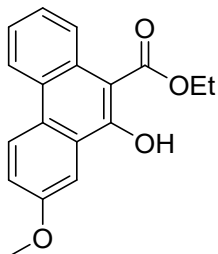
White solid; yield 18.4 mg, 62%; R_f = 0.42 (PE/EtOAc = 20:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 13.31 (s, 1H), 8.74 (d, J = 8.4 Hz, 1H), 8.42 (dd, J = 7.9, 4.2 Hz, 2H), 7.83 (d, J = 2.8 Hz, 1H), 7.46 (dt, J = 23.1, 7.2 Hz, 2H), 7.33 (dd, J = 9.1, 2.8 Hz, 1H), 4.58 (q, J = 7.2 Hz, 2H), 3.95 (s, 3H), 1.53 (t, J = 7.2 Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 173.15, 162.12, 158.67, 128.42, 128.00, 126.69, 126.53, 126.25, 126.02, 124.33, 124.25, 122.41, 121.18, 104.66, 102.01, 62.16, 55.63, 14.46; **ESI-HRMS** Calcd for $\text{C}_{18}\text{H}_{16}\text{NaO}_4^+$ $[\text{M}+\text{Na}]^+$ 319.0941, found 319.0943.

Ethyl 3-fluoro-10-hydroxyphenanthrene-9-carboxylate (2t)¹



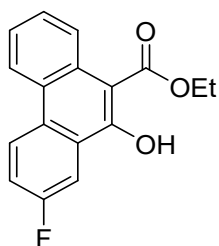
Pale yellow solid; yield 17.6 mg, 62%; $R_f = 0.40$ (PE/EtOAc = 50:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 13.35 (s, 1H), 8.72 (d, $J = 8.6$ Hz, 1H), 8.45 (dd, $J = 9.0, 6.1$ Hz, 1H), 8.30 (d, $J = 8.3$ Hz, 1H), 8.05 (dd, $J = 11.2, 2.5$ Hz, 1H), 7.55 – 7.50 (m, 1H), 7.44 – 7.39 (m, 1H), 7.31 – 7.25 (m, 1H), 4.57 (q, $J = 7.2$ Hz, 2H), 1.53 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 172.94, 164.25 (d, $^1J_{\text{C},\text{F}} = 251.3$ Hz), 162.48, 135.93 (d, $^3J_{\text{C},\text{F}} = 9.1$ Hz), 130.03, 128.27, 127.93 (d, $^3J_{\text{C},\text{F}} = 9.6$ Hz), 126.12, 125.29 (d, $^4J_{\text{C},\text{F}} = 3.8$ Hz), 124.29, 123.07, 121.90 (d, $^4J_{\text{C},\text{F}} = 1.5$ Hz), 115.70 (d, $^2J_{\text{C},\text{F}} = 23.6$ Hz), 107.86 (d, $^2J_{\text{C},\text{F}} = 23.0$ Hz), 100.99, 62.20, 14.44; $^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -108.13 (s, 1F); **ESI-HRMS** Calcd for $\text{C}_{17}\text{H}_{14}\text{FO}_3^+$ $[\text{M}+\text{H}]^+$ 285.0921, found 285.0916.

Ethyl 10-hydroxy-2-methoxyphenanthrene-9-carboxylate (2u)¹



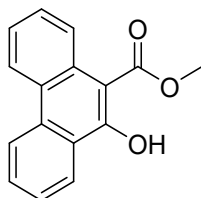
White solid; yield 21.0 mg, 71%; $R_f = 0.42$ (PE/EtOAc = 20:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 13.42 (s, 1H), 8.77 (d, $J = 8.5$ Hz, 1H), 8.42 (d, $J = 9.0$ Hz, 2H), 7.85 (d, $J = 2.4$ Hz, 1H), 7.53 (t, $J = 7.7$ Hz, 1H), 7.42 (t, $J = 7.6$ Hz, 1H), 7.19 (dd, $J = 9.0, 2.4$ Hz, 1H), 4.57 (q, $J = 7.1$ Hz, 2H), 3.98 (s, 3H), 1.53 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 173.14, 163.23, 161.59, 135.79, 130.24, 127.82, 127.03, 126.15, 125.59, 123.92, 122.94, 119.52, 116.40, 104.20, 99.76, 61.96, 55.55, 14.50; **ESI-HRMS** Calcd for $\text{C}_{18}\text{H}_{17}\text{O}_4^+$ $[\text{M}+\text{H}]^+$ 297.1121, found 297.1120.

Ethyl 2-fluoro-10-hydroxyphenanthrene-9-carboxylate (2v)¹



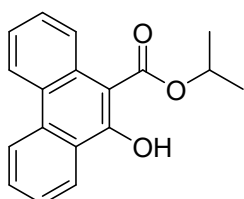
Pale yellow solid; yield 19.3 mg, 68%; R_f = 0.39 (PE/EtOAc = 50:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 13.21 (s, 1H), 8.78 (d, J = 8.5 Hz, 1H), 8.54 (dd, J = 9.2, 5.2 Hz, 1H), 8.48 (d, J = 8.2 Hz, 1H), 8.14 (dd, J = 9.9, 2.8 Hz, 1H), 7.55 (t, J = 7.0 Hz, 1H), 7.50 – 7.45 (m, 2H), 4.61 (q, J = 7.2 Hz, 2H), 1.55 (t, J = 7.1 Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 172.79, 161.61 (d, $^1J_{\text{C, F}}$ = 247.8 Hz), 161.59 (d, $^4J_{\text{C, F}}$ = 3.5 Hz), 130.18 (d, $^4J_{\text{C, F}}$ = 2.1 Hz), 128.95, 127.45, 126.81 (d, $^3J_{\text{C, F}}$ = 8.7 Hz), 126.11, 125.74, 124.94 (d, $^3J_{\text{C, F}}$ = 8.3 Hz), 124.55, 122.68, 119.17 (d, $^2J_{\text{C, F}}$ = 23.7 Hz), 109.77 (d, $^2J_{\text{C, F}}$ = 22.7 Hz), 102.47, 62.32, 14.43; $^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -113.76 (s, 1F); **ESI-HRMS** Calcd for $\text{C}_{17}\text{H}_{14}\text{FO}_3^+$ $[\text{M}+\text{H}]^+$ 285.0921, found 285.0917.

Methyl 10-hydroxyphenanthrene-9-carboxylate (2w)⁷



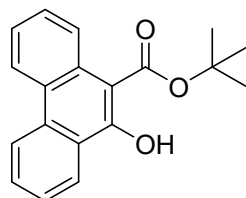
White solid; yield 14.1 mg, 56%; R_f = 0.35 (PE/EtOAc = 50:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 13.23 (s, 1H), 8.70 (d, J = 8.5 Hz, 1H), 8.53 (d, J = 8.3 Hz, 3H), 7.73 (t, J = 7.7 Hz, 1H), 7.60 (t, J = 7.7 Hz, 1H), 7.56 – 7.51 (m, 1H), 7.45 (t, J = 7.6 Hz, 1H), 4.09 (s, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 173.46, 162.86, 133.78, 130.58, 129.37, 127.73, 126.96, 126.14, 126.10, 125.27, 125.09, 124.37, 122.95, 122.52, 101.54, 52.62; **ESI-HRMS** Calcd for $\text{C}_{16}\text{H}_{12}\text{NaO}_3^+$ $[\text{M}+\text{Na}]^+$ 275.0679, found 275.0676.

Isopropyl 10-hydroxyphenanthrene-9-carboxylate (2x) (new compound)



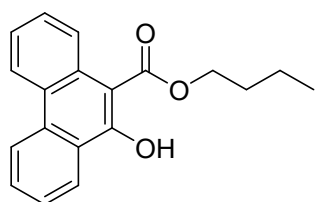
White solid; yield 18.2 mg, 65%; $R_f = 0.43$ (PE/EtOAc = 50:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 13.37 (s, 1H), 8.81 (d, $J = 8.1$ Hz, 1H), 8.56 (dd, $J = 14.1, 8.3$ Hz, 3H), 7.76 (t, $J = 7.4$ Hz, 1H), 7.64 (t, $J = 7.6$ Hz, 1H), 7.57 (t, $J = 7.7$ Hz, 1H), 7.49 (t, $J = 7.6$ Hz, 1H), 5.51 (p, $J = 6.3$ Hz, 1H), 1.53 (d, $J = 6.3$ Hz, 6H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 172.52, 162.67, 133.71, 130.45, 129.68, 127.63, 126.94, 126.18, 126.07, 125.40, 125.02, 124.26, 122.94, 122.52, 101.92, 70.34, 22.20; **ESI-HRMS** Calcd for $\text{C}_{18}\text{H}_{16}\text{NaO}_3^+$ $[\text{M}+\text{Na}]^+$ 303.0992, found 303.0989.

***tert*-Butyl 10-hydroxyphenanthrene-9-carboxylate (2y) (new compound)**



White solid; yield 15.6 mg, 53%; $R_f = 0.48$ (PE/EtOAc = 50:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 13.40 (s, 1H), 8.78 (d, $J = 8.4$ Hz, 1H), 8.56 – 8.52 (m, 3H), 7.73 (t, $J = 7.0$ Hz, 1H), 7.61 (t, $J = 7.1$ Hz, 1H), 7.54 (t, $J = 7.1$ Hz, 1H), 7.45 (t, $J = 6.9$ Hz, 1H), 1.74 (s, 9H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 172.38, 162.38, 133.55, 130.28, 129.81, 127.46, 126.90, 126.16, 126.11, 125.51, 124.93, 124.14, 122.92, 122.49, 102.80, 84.31, 28.69; **ESI-HRMS** Calcd for $\text{C}_{19}\text{H}_{18}\text{NaO}_3^+$ $[\text{M}+\text{Na}]^+$ 317.1148, found 317.1146.

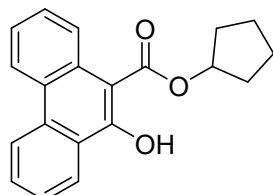
Butyl 10-hydroxyphenanthrene-9-carboxylate (2z) (new compound)



White solid; yield 15.6 mg, 53%; $R_f = 0.46$ (PE/EtOAc = 50:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 13.34 (s, 1H), 8.78 (d, $J = 8.6$ Hz, 1H), 8.59 – 8.53 (m, 3H), 7.76 (t, $J = 7.0$ Hz, 1H), 7.63 (t, $J = 7.0$ Hz, 1H), 7.56 (t, $J = 7.0$ Hz, 1H), 7.48 (t, $J = 6.9$ Hz, 1H), 4.54 (t, $J = 6.7$ Hz, 2H), 1.93 – 1.86 (m, 2H), 1.59 – 1.53 (m, 2H), 1.02 (t, $J = 7.4$ Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 173.15, 162.83, 133.74, 130.52, 129.58, 127.67,

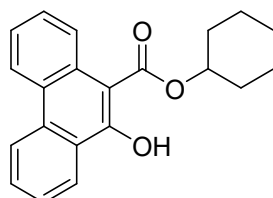
126.95, 126.15, 126.09, 125.36, 125.07, 124.30, 122.95, 122.51, 101.70, 66.05, 30.76, 19.58, 13.90; **ESI-HRMS** Calcd for $C_{19}H_{18}NaO_3^+$ $[M+Na]^+$ 317.1148, found 317.1148.

Cyclopentyl 10-hydroxyphenanthrene-9-carboxylate (2aa) (new compound)



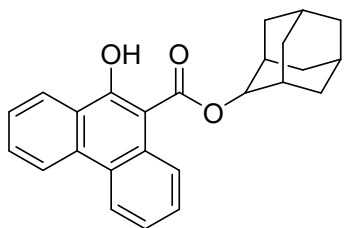
White solid; yield 22.1 mg, 72%; $R_f = 0.38$ (PE/EtOAc = 50:1); **1H NMR** (400 MHz, $CDCl_3$) δ 13.41 (s, 1H), 8.76 (d, $J = 8.4$ Hz, 1H), 8.56 (dd, $J = 12.8, 8.2$ Hz, 3H), 7.76 (t, $J = 7.7$ Hz, 1H), 7.64 (t, $J = 7.6$ Hz, 1H), 7.56 (t, $J = 7.0$ Hz, 1H), 7.48 (t, $J = 7.6$ Hz, 1H), 5.68 – 5.63 (m, 1H), 2.04 (d, $J = 7.2$ Hz, 4H), 1.90 (dd, $J = 7.5, 4.6$ Hz, 2H), 1.80 – 1.72 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.80, 162.73, 133.68, 130.44, 129.66, 127.60, 126.93, 126.13, 125.91, 125.38, 125.02, 124.22, 122.94, 122.49, 101.89, 79.55, 33.00, 23.92; **ESI-HRMS** Calcd for $C_{20}H_{18}NaO_3^+$ $[M+Na]^+$ 329.1148, found 329.1148.

Cyclohexyl 10-hydroxyphenanthrene-9-carboxylate (2ab) (new compound)



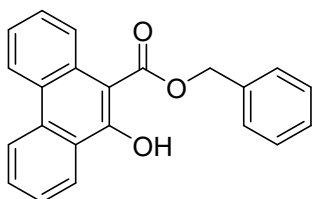
White solid; yield 19.2 mg, 60%; $R_f = 0.47$ (PE/EtOAc = 50:1); **1H NMR** (400 MHz, $CDCl_3$) δ 13.39 (s, 1H), 8.83 (d, $J = 8.5$ Hz, 1H), 8.56 – 8.51 (m, 3H), 7.75 – 7.71 (m, 1H), 7.63 – 7.59 (m, 1H), 7.57 – 7.53 (m, 1H), 7.46 (t, $J = 7.6$ Hz, 1H), 5.29 (tt, $J = 8.4, 3.8$ Hz, 1H), 2.08 (s, 2H), 1.87 – 1.72 (m, 4H), 1.63 – 1.40 (m, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.45, 162.70, 133.69, 130.43, 129.69, 127.61, 126.93, 126.17, 125.41, 125.01, 124.24, 122.93, 122.51, 101.98, 75.08, 31.78, 25.51, 23.87; **ESI-HRMS** Calcd for $C_{21}H_{20}NaO_3^+$ $[M+Na]^+$ 343.1305, found 343.1305.

Adamantan-2-yl 10-hydroxyphenanthrene-9-carboxylate (2ac) (new compound)



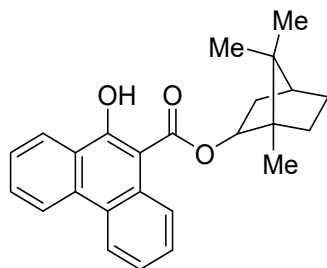
White solid; yield 21.6 mg, 58%; R_f = 0.34 (PE/EtOAc = 80:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 13.47 (s, 1H), 8.96 (d, J = 8.5 Hz, 1H), 8.57 (dd, J = 14.3, 8.4 Hz, 3H), 7.79 – 7.74 (m, 1H), 7.64 (t, J = 7.6 Hz, 1H), 7.61 – 7.56 (m, 1H), 7.49 (t, J = 7.6 Hz, 1H), 5.46 (s, 1H), 2.31 (s, 2H), 2.22 (d, J = 12.9 Hz, 2H), 1.93 (d, J = 20.9 Hz, 6H), 1.81 (s, 2H), 1.72 (d, J = 12.6 Hz, 2H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 172.54, 162.82, 133.69, 130.46, 129.70, 127.56, 126.95, 126.29, 126.15, 125.47, 125.05, 124.25, 122.96, 122.51, 102.14, 80.23, 37.53, 36.59, 32.36, 32.12, 27.36, 27.17; **ESI-HRMS** Calcd for $\text{C}_{25}\text{H}_{24}\text{NaO}_3^+$ $[\text{M}+\text{Na}]^+$ 395.1618, found 395.1615.

Benzyl 10-hydroxyphenanthrene-9-carboxylate (2ad)¹



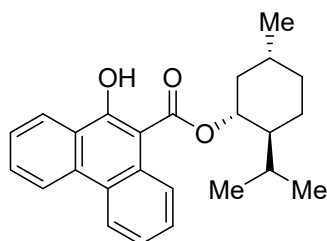
White solid; yield 13.1 mg, 40%; R_f = 0.43 (PE/EtOAc = 50:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 13.21 (s, 1H), 8.77 (d, J = 8.6 Hz, 1H), 8.54 (d, J = 8.3 Hz, 3H), 7.76 – 7.71 (m, 1H), 7.63 – 7.59 (m, 1H), 7.52 – 7.34 (m, 7H), 5.56 (s, 2H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 172.79, 163.05, 135.38, 133.86, 130.65, 129.45, 128.89, 128.68, 128.52, 127.78, 127.00, 126.19 (x2), 125.30, 125.13, 124.38, 122.96, 122.55, 101.56, 67.73; **ESI-HRMS** Calcd for $\text{C}_{22}\text{H}_{16}\text{NaO}_3^+$ $[\text{M}+\text{Na}]^+$ 351.0992, found 351.0991.

(1*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 10-hydroxyphenanthrene-9-carboxylate (2ae) (new compound)



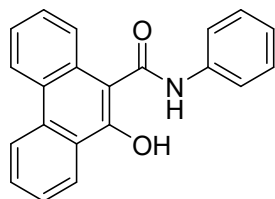
White solid; yield 25.1 mg, 67%; $R_f = 0.46$ (PE/EtOAc = 50:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 13.48 (s, 1H), 8.83 (d, $J = 7.9$ Hz, 1H), 8.54 (d, $J = 8.3$ Hz, 3H), 7.73 (t, $J = 7.5$ Hz, 1H), 7.61 (t, $J = 7.6$ Hz, 1H), 7.53 (t, $J = 7.7$ Hz, 1H), 7.46 (t, $J = 6.9$ Hz, 1H), 5.11 (dd, $J = 7.3, 4.5$ Hz, 1H), 2.04 (d, $J = 7.2$ Hz, 2H), 1.80 (d, $J = 16.7$ Hz, 2H), 1.70 – 1.63 (m, 1H), 1.30 – 1.18 (m, 2H), 1.09 (d, $J = 5.0$ Hz, 6H), 0.91 (s, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 172.88, 162.82, 133.67, 130.47, 129.51, 127.32, 126.94, 126.32, 126.01, 125.47, 125.08, 124.27, 122.88, 122.47, 102.09, 84.26, 49.14, 47.25, 45.07, 39.51, 34.37, 27.12, 20.53, 20.26, 12.57; **ESI-HRMS** Calcd for $\text{C}_{25}\text{H}_{26}\text{NaO}_3^+$ $[\text{M}+\text{Na}]^+$ 397.1774, found 397.1774.

(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 10-hydroxyphenanthrene-9-carboxylate (2af) (new compound)



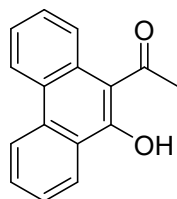
White solid; yield 25.6 mg, 68%; $R_f = 0.42$ (PE/EtOAc = 80:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 13.51 (s, 1H), 8.84 (d, $J = 8.5$ Hz, 1H), 8.58 – 8.54 (m, 3H), 7.77 – 7.72 (m, 1H), 7.65 – 7.60 (m, 1H), 7.59 – 7.54 (m, 1H), 7.50 – 7.45 (m, 1H), 5.25 (td, $J = 10.8, 4.4$ Hz, 1H), 2.29 (d, $J = 11.9$ Hz, 1H), 2.07 – 1.99 (m, 1H), 1.80 – 1.56 (m, 4H), 1.36 – 1.27 (m, 1H), 1.22 – 1.12 (m, 1H), 0.97 (d, $J = 6.4$ Hz, 4H), 0.92 (d, $J = 7.0$ Hz, 3H), 0.82 (d, $J = 6.9$ Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 172.74, 162.91, 133.73, 130.49, 129.81, 127.68, 126.97, 126.20, 126.14, 125.47, 125.06, 124.24, 122.98, 122.53, 101.81, 76.63, 47.41, 41.27, 34.30, 31.75, 26.56, 23.53, 22.19, 21.03, 16.41; **ESI-HRMS** Calcd for $\text{C}_{25}\text{H}_{28}\text{NaO}_3^+$ $[\text{M}+\text{Na}]^+$ 399.1931, found 399.1928.

10-hydroxy-*N*-phenylphenanthrene-9-carboxamide (2ag)¹



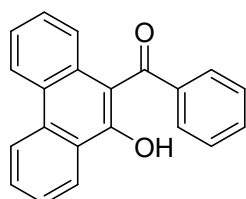
White solid; yield 18.2 mg, 58%; $R_f = 0.42$ (PE/EtOAc = 8:1); $^1\text{H NMR}$ (400 MHz, DMSO- d_6) δ 10.58 (s, 1H), 10.11 (s, 1H), 8.86 (d, $J = 8.0$ Hz, 1H), 8.79 (d, $J = 8.1$ Hz, 1H), 8.41 (d, $J = 7.9$ Hz, 1H), 7.85 (d, $J = 8.0$ Hz, 2H), 7.75 (d, $J = 19.3$ Hz, 3H), 7.57 (dd, $J = 14.6, 7.7$ Hz, 2H), 7.38 (t, $J = 7.7$ Hz, 2H), 7.12 (t, $J = 7.4$ Hz, 1H); $^{13}\text{C NMR}$ (101 MHz, DMSO- d_6) δ 166.02, 147.19, 139.64, 130.97, 130.04, 128.72, 127.91, 127.46, 126.84, 126.14, 125.54, 124.37, 124.23, 123.48, 123.22, 123.07, 119.63, 116.78; **ESI-HRMS** Calcd for $\text{C}_{21}\text{H}_{16}\text{NO}_2^+$ $[\text{M}+\text{H}]^+$ 314.1176, found 314.1177.

1-(10-hydroxyphenanthren-9-yl)ethan-1-one (2ah)¹



Pale yellow solid; yield 8.0 mg, 34%; $R_f = 0.42$ (PE/EtOAc = 20:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 14.71 (s, 1H), 8.54 – 8.48 (m, 3H), 7.96 (d, $J = 8.3$ Hz, 1H), 7.77 – 7.72 (m, 1H), 7.63 – 7.58 (m, 1H), 7.56 – 7.51 (m, 1H), 7.50 – 7.45 (m, 1H), 2.80 (s, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 204.09, 163.06, 134.21, 131.12, 129.83, 127.32, 127.22, 126.24, 125.55 (x2), 125.50, 124.63, 123.45, 122.55, 112.17, 31.85; **ESI-HRMS** Calcd for $\text{C}_{16}\text{H}_{13}\text{O}_2^+$ $[\text{M}+\text{H}]^+$ 237.0910, found 237.0911.

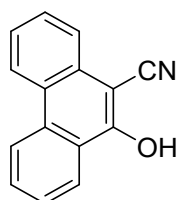
(10-hydroxyphenanthren-9-yl)(phenyl)methanone (2ai)¹



Pale yellow solid; yield 13.7 mg, 46%; $R_f = 0.42$ (PE/EtOAc = 20:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 12.76 (s, 1H), 8.58 (dd, $J = 8.3, 3.2$ Hz, 2H), 8.51 (d, $J = 8.3$ Hz, 1H),

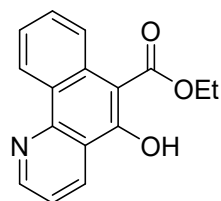
7.80 (t, $J = 7.7$ Hz, 1H), 7.67 (t, $J = 7.6$ Hz, 1H), 7.61 (d, $J = 7.4$ Hz, 2H), 7.52 (t, $J = 7.5$ Hz, 1H), 7.40 – 7.31 (m, 4H), 7.15 (t, $J = 7.7$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 200.34, 160.81, 140.45, 134.11, 132.56, 130.76, 130.35, 129.55, 128.60, 127.79, 127.23, 126.26, 126.00, 125.31, 125.18, 124.54, 122.97, 122.73, 111.06; **ESI-HRMS** Calcd for $\text{C}_{21}\text{H}_{15}\text{O}_2^+$ $[\text{M}+\text{H}]^+$ 299.1067, found 299.1066.

10-hydroxyphenanthrene-9-carbonitrile (2aj)¹



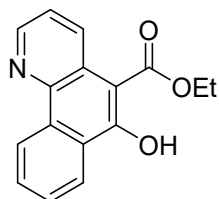
Cream solid; yield 9.6 mg, 44%; $R_f = 0.25$ (PE/EtOAc = 5:1); ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 11.90 (s, 1H), 8.88 (d, $J = 8.3$ Hz, 1H), 8.80 (d, $J = 8.3$ Hz, 1H), 8.49 (d, $J = 7.7$ Hz, 1H), 7.99 (d, $J = 7.7$ Hz, 1H), 7.90 (d, $J = 6.8$ Hz, 1H), 7.82 – 7.75 (m, 2H), 7.63 (d, $J = 7.0$ Hz, 1H); ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ 158.79, 132.48, 130.46, 129.36, 128.68, 127.53, 125.57, 125.29, 124.78, 123.76, 123.65, 123.56, 123.53, 116.54, 90.18; **ESI-HRMS** Calcd for $\text{C}_{15}\text{H}_9\text{NNaO}^+$ $[\text{M}+\text{Na}]^+$ 242.0576, found 242.0575.

Ethyl 5-hydroxybenzo[*h*]quinoline-6-carboxylate (2ak) (new compound)



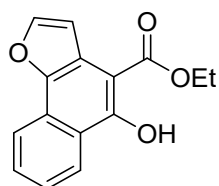
Pale yellow solid; yield 18.7 mg, 70%; $R_f = 0.41$ (petroleum ether/ethyl acetate 10:1); ^1H NMR (400 MHz, CDCl_3) δ 13.30 (s, 1H), 9.23 (d, $J = 8.2$ Hz, 1H), 9.03 (dd, $J = 4.4, 1.8$ Hz, 1H), 8.77 – 8.71 (m, 2H), 7.63 (t, $J = 7.8$ Hz, 1H), 7.56 – 7.50 (m, 2H), 4.60 (q, $J = 7.1$ Hz, 2H), 1.55 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.82, 162.05, 152.16, 149.15, 132.98, 130.81, 129.40, 127.43, 125.44, 124.86, 124.67, 122.01, 120.24, 102.21, 62.37, 14.44; **ESI-HRMS** Calcd for $\text{C}_{16}\text{H}_{12}\text{NO}_3^-$ $[\text{M}-\text{H}]^-$ 266.0823, found 266.0821.

Ethyl 6-hydroxybenzo[*h*]quinoline-5-carboxylate (2al)¹



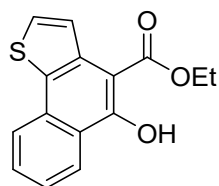
White solid; yield 5.6 mg, 21%; $R_f = 0.37$ (petroleum ether/ethyl acetate 10:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 13.53 (s, 1H), 9.21 (d, $J = 8.2$ Hz, 1H), 9.06 (d, $J = 8.7$ Hz, 1H), 8.77 (d, $J = 2.7$ Hz, 1H), 8.50 (d, $J = 8.1$ Hz, 1H), 7.84 (t, $J = 7.0$ Hz, 1H), 7.73 (t, $J = 7.6$ Hz, 1H), 7.45 (dd, $J = 8.6, 4.3$ Hz, 1H), 4.59 (q, $J = 7.1$ Hz, 2H), 1.54 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 172.69, 163.75, 145.93, 142.32, 134.84, 133.70, 130.98, 128.63, 126.73, 124.71, 124.37, 122.42, 99.89, 62.35, 14.46; **ESI-HRMS** Calcd for $\text{C}_{16}\text{H}_{12}\text{NO}_3^-$ $[\text{M-H}]^-$ 266.0823, found 266.0824.

Ethyl 5-hydroxynaphtho[1,2-*b*]furan-4-carboxylate (2am)¹



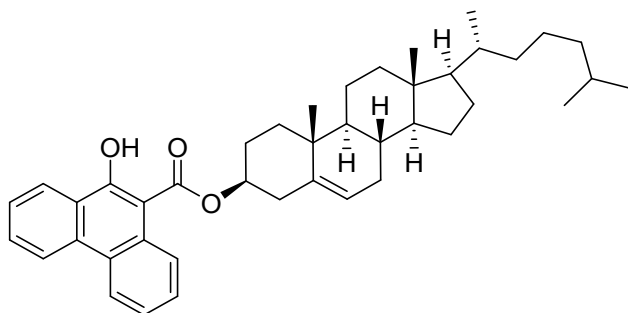
Pale yellow solid; yield 15.6 mg, 61%; $R_f = 0.43$ (petroleum ether/ethyl acetate 50:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 12.35 (s, 1H), 8.46 (d, $J = 8.4$ Hz, 1H), 8.19 (d, $J = 8.2$ Hz, 1H), 7.72 – 7.68 (m, 2H), 7.54 – 7.50 (m, 1H), 7.20 (s, 1H), 4.52 (q, $J = 7.2$ Hz, 2H), 1.53 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 171.73, 159.41, 144.46, 144.33, 130.10, 125.16, 125.02, 124.93, 123.06, 119.92, 119.88, 109.43, 99.44, 61.67, 14.43; **ESI-HRMS** Calcd for $\text{C}_{15}\text{H}_{11}\text{O}_4^-$ $[\text{M-H}]^-$ 255.0663, found 255.0664.

Ethyl 5-hydroxynaphtho[1,2-*b*]thiophene-4-carboxylate (2an)¹



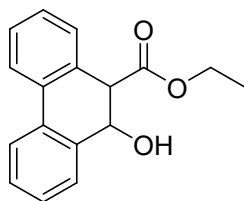
White solid; yield 15.2 mg, 56%; R_f = 0.50 (PE/EtOAc = 20:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 12.89 (s, 1H), 8.43 (d, J = 7.2 Hz, 1H), 7.97 – 7.94 (m, 2H), 7.61 (t, J = 7.6 Hz, 1H), 7.48 (t, J = 7.7 Hz, 1H), 7.44 (d, J = 5.4 Hz, 1H), 4.51 (q, J = 7.1 Hz, 2H), 1.51 (t, J = 7.1 Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 172.03, 161.91, 133.67, 131.75, 130.37, 130.30, 126.61, 125.68, 125.35 (x2), 123.45, 123.40, 101.81, 61.92, 14.41; **ESI-HRMS** Calcd for $\text{C}_{15}\text{H}_{13}\text{O}_3\text{S}^+$ $[\text{M}+\text{H}]^+$ 273.0585, found 273.0584.

(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 10-hydroxyphenanthrene-9-carboxylate (2a0)
(new compound)



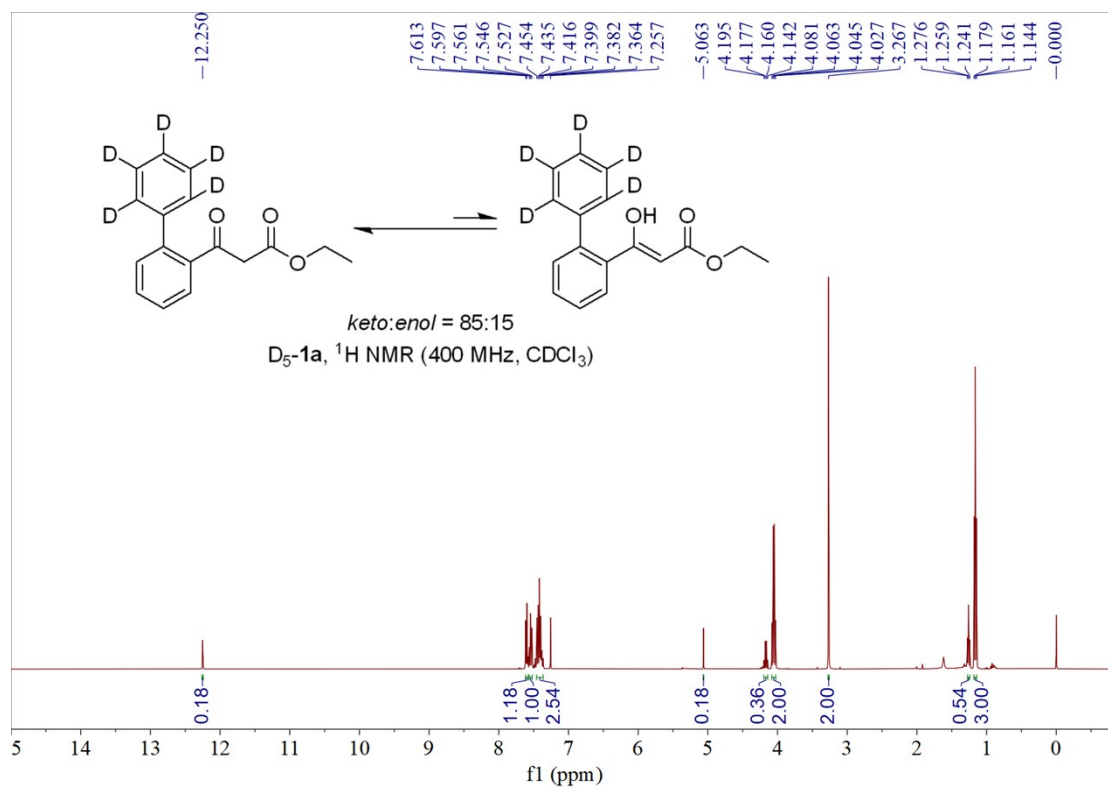
White solid; yield 35.8 mg, 59%; R_f = 0.39 (PE/EtOAc = 80:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 13.35 (s, 1H), 8.80 (d, J = 8.6 Hz, 1H), 8.57 – 8.52 (m, 3H), 7.74 (t, J = 7.0 Hz, 1H), 7.62 (t, J = 7.6 Hz, 1H), 7.56 (t, J = 7.7 Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H), 5.46 (d, J = 4.7 Hz, 1H), 5.08 (s, 1H), 2.62 (d, J = 7.9 Hz, 2H), 2.14 (s, 1H), 1.96 (s, 5H), 1.51 (s, 7H), 1.33 (s, 7H), 1.08 (s, 5H), 0.98 (s, 3H), 0.92 (d, J = 6.5 Hz, 3H), 0.87 (dd, J = 6.6, 1.8 Hz, 7H), 0.68 (s, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 172.44, 162.76, 139.43, 133.75, 130.49, 129.70, 127.70, 126.96, 126.21, 126.15, 125.43, 125.08, 124.29, 123.38, 122.97, 122.54, 101.88, 76.49, 56.78, 56.26, 50.16, 42.44, 39.83, 39.67, 38.48, 37.19, 36.81, 36.33, 35.94, 32.04, 31.96, 28.38, 28.18, 24.41, 24.01, 22.99, 22.73, 21.19, 19.55, 18.86, 12.00; **ESI-HRMS** Calcd for $\text{C}_{42}\text{H}_{53}\text{O}_3^-$ $[\text{M}-\text{H}]^-$ 605.4000, found 607.4000.

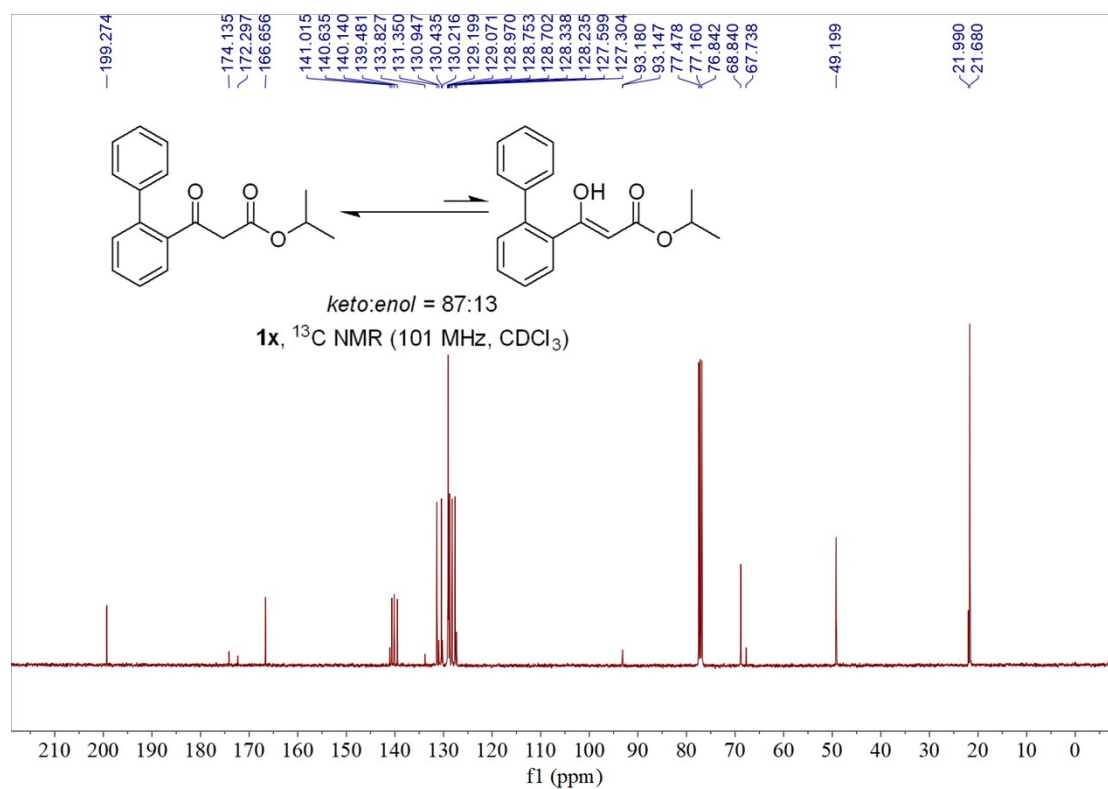
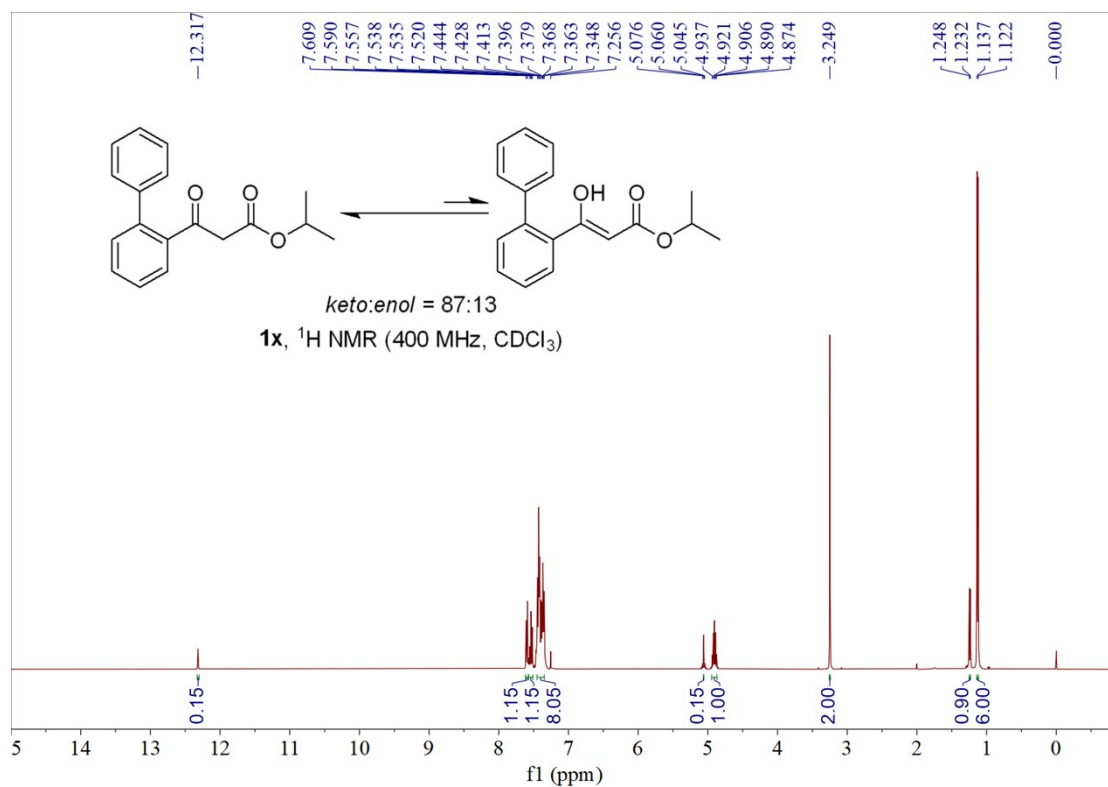
Ethyl 10-hydroxy-9,10-dihydrophenanthrene-9-carboxylate (8) *(new compound)*

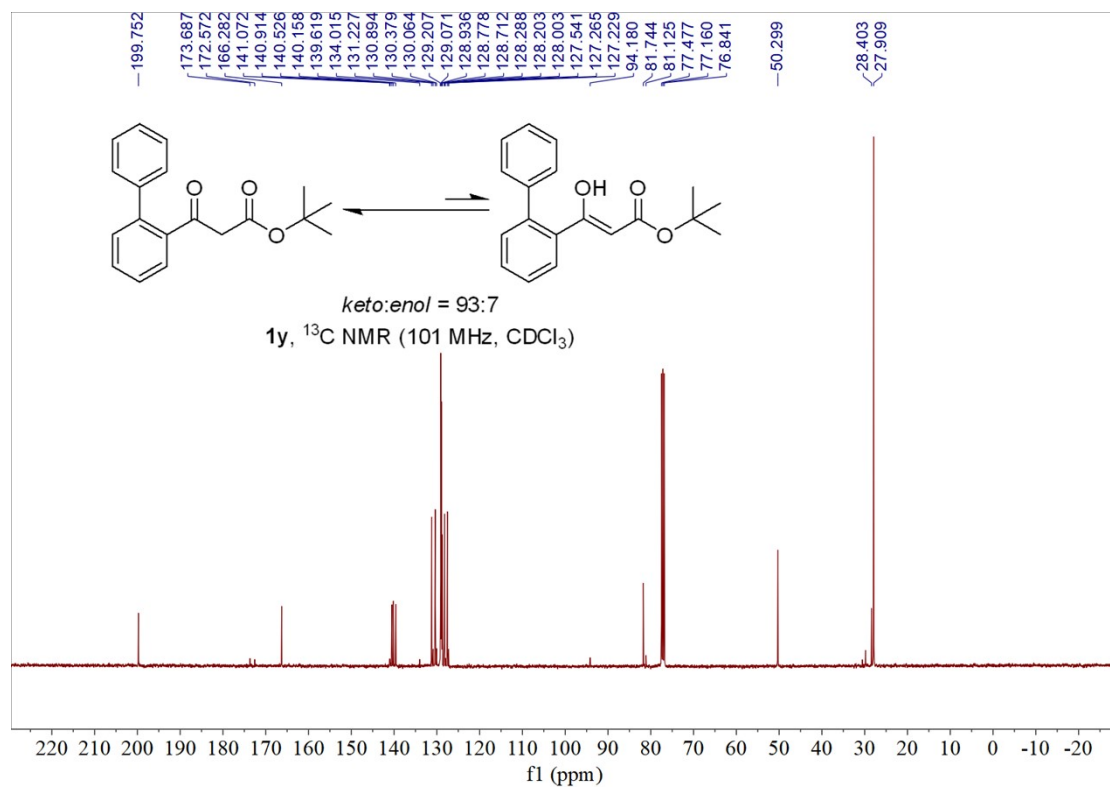
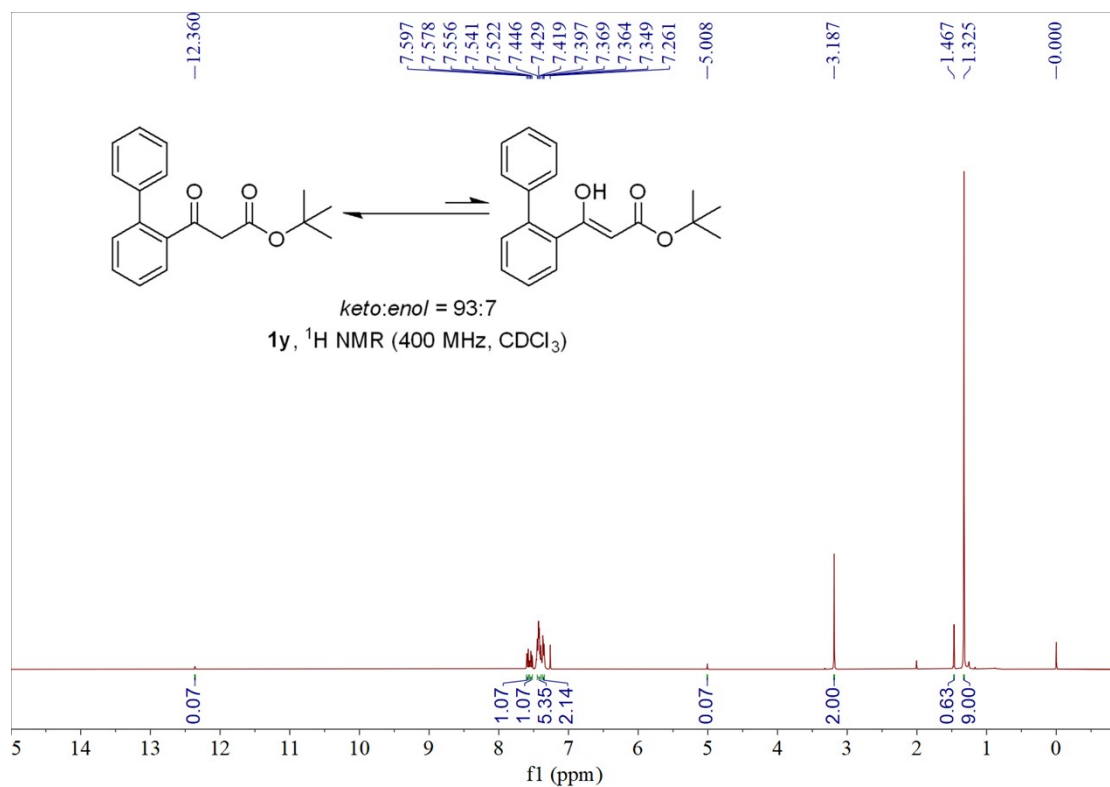


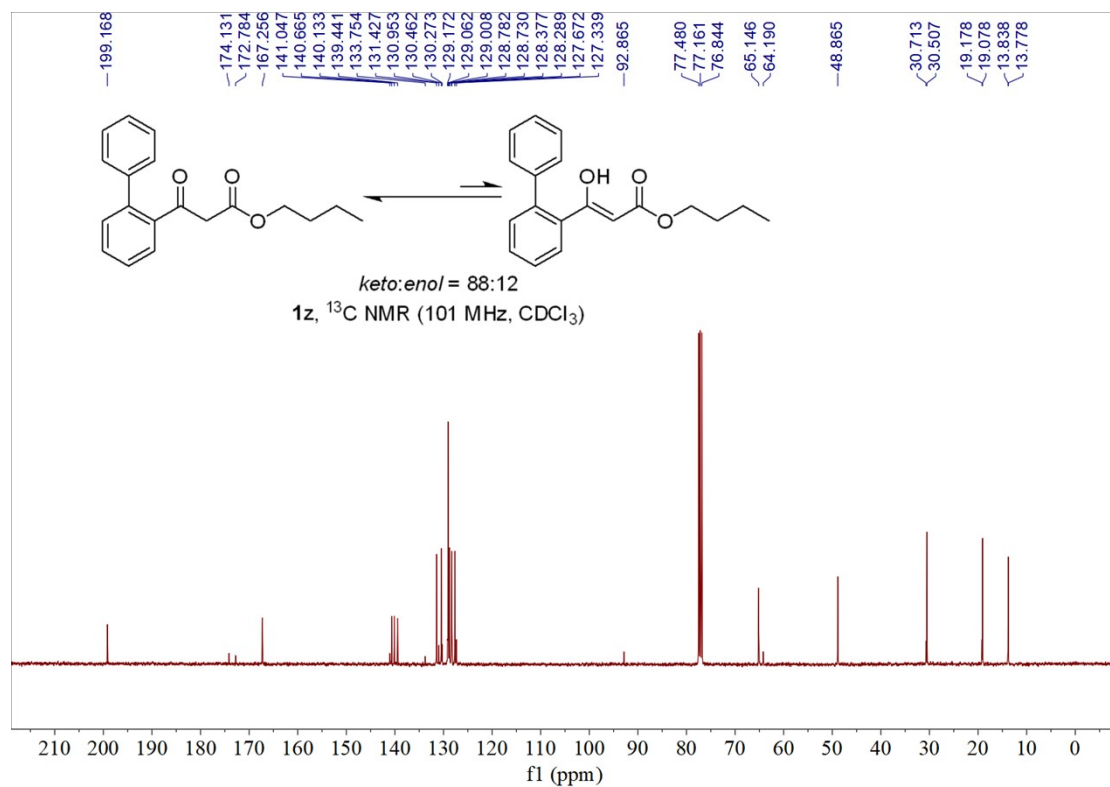
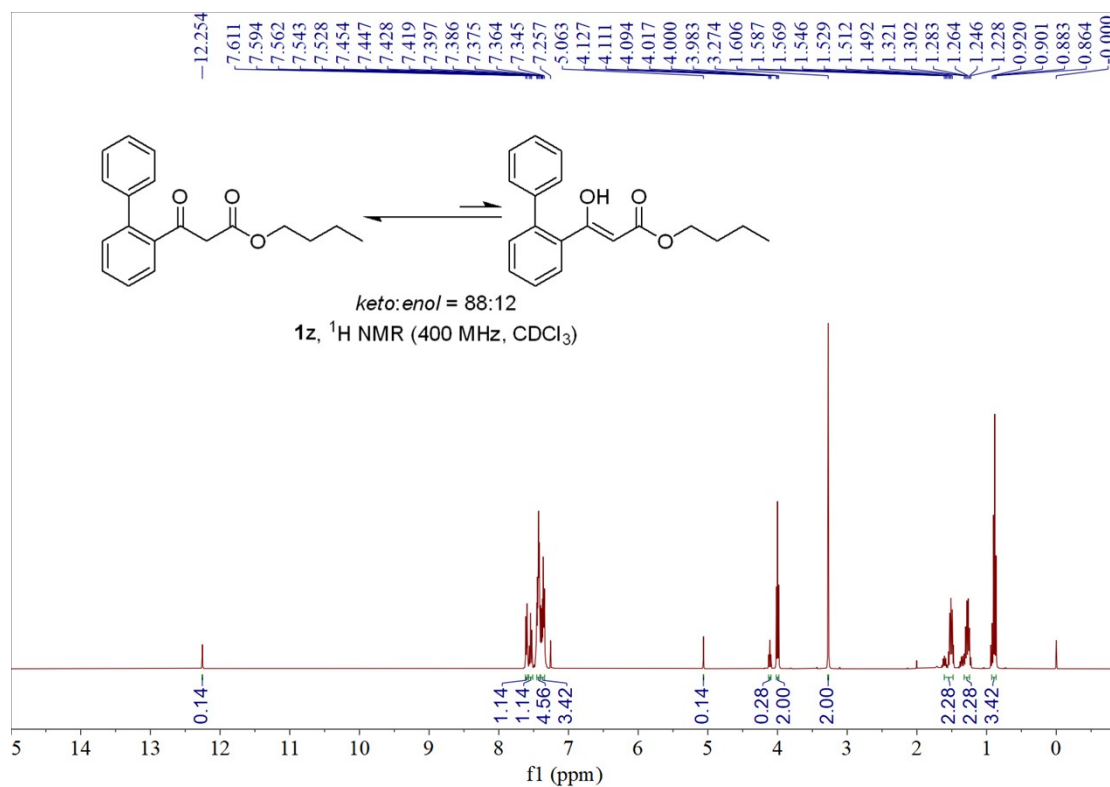
Pale yellow solid; yield 9.1 mg, 34%; $R_f = 0.39$ (PE/EtOAc = 3:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.75 (dd, $J = 12.3, 7.8$ Hz, 2H), 7.52 (d, $J = 7.5$ Hz, 1H), 7.39 – 7.21 (m, 5H), 5.14 (d, $J = 7.7$ Hz, 1H), 4.15 (q, $J = 6.8$ Hz, 2H), 3.99 (d, $J = 7.7$ Hz, 1H), 2.52 (s, 1H), 1.18 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 172.03, 136.55, 133.25, 132.57, 131.19, 128.84, 128.74, 128.46, 128.34, 128.22, 126.67, 124.07, 123.99, 69.94, 61.25, 53.58, 14.19; **ESI-HRMS** Calcd for $\text{C}_{17}\text{H}_{20}\text{NO}_3^+$ $[\text{M}+\text{NH}_4]^+$ 286.1438, found 286.1439.

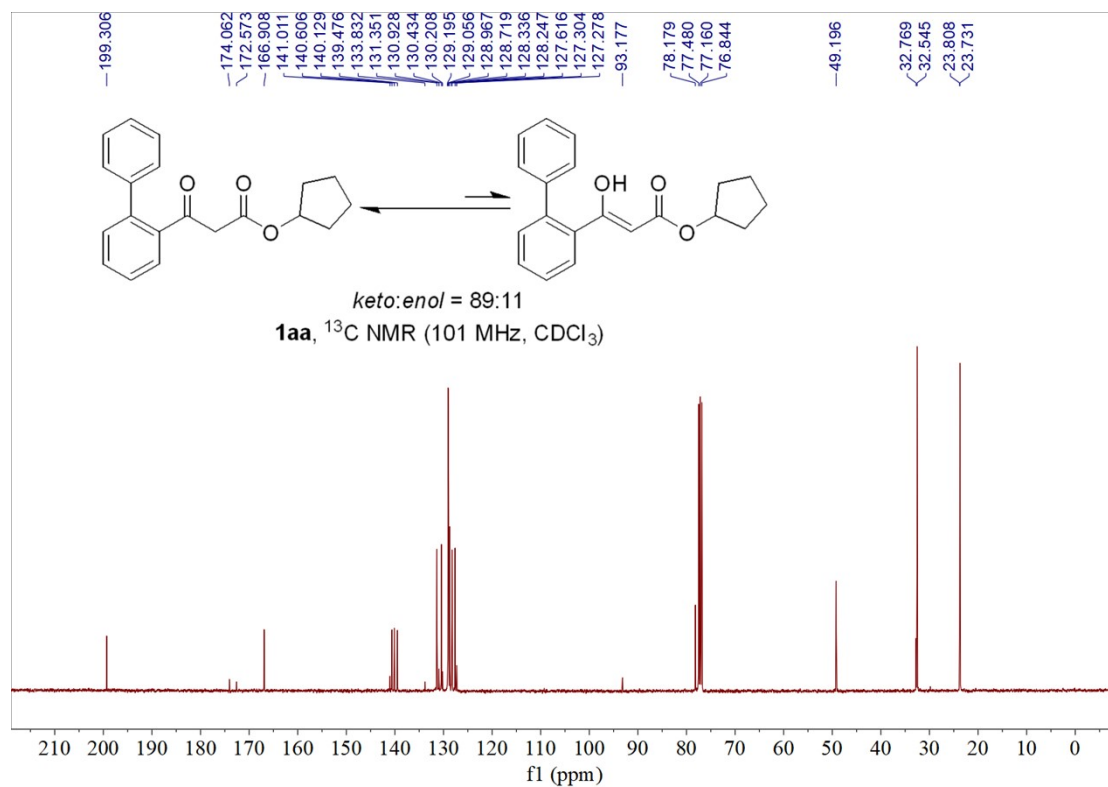
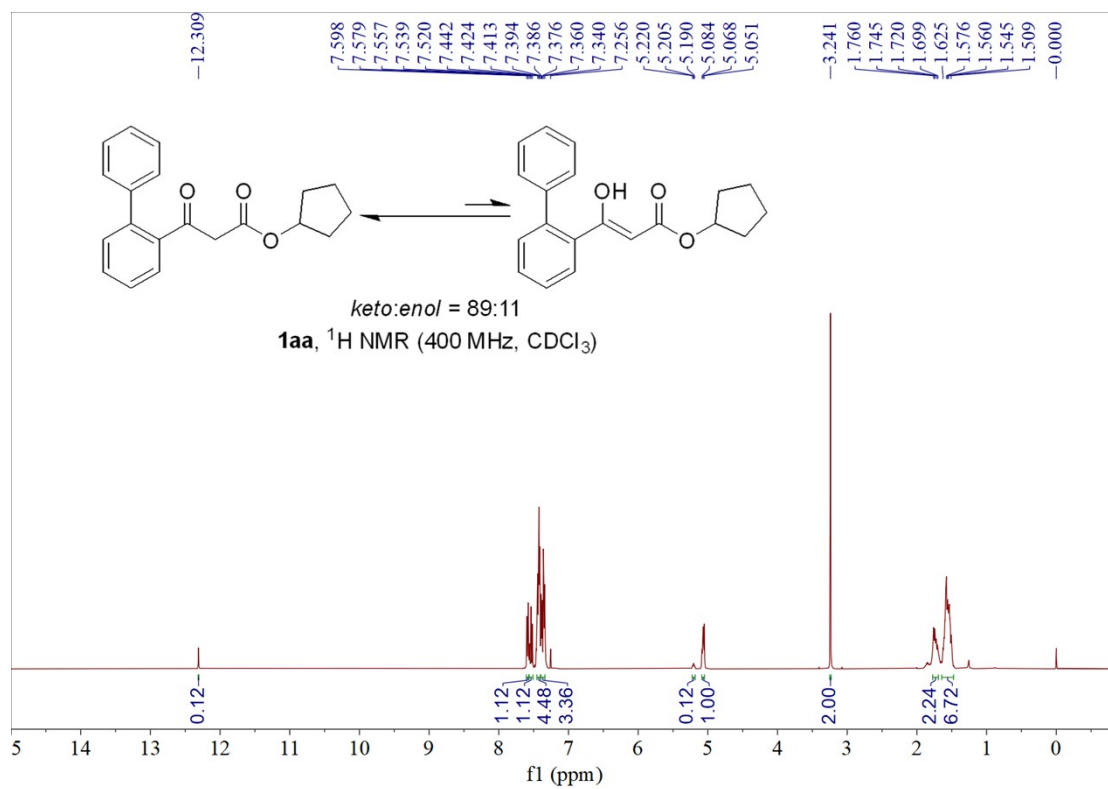
8. Copies of ^1H NMR, ^{13}C NMR and ^{19}F NMR

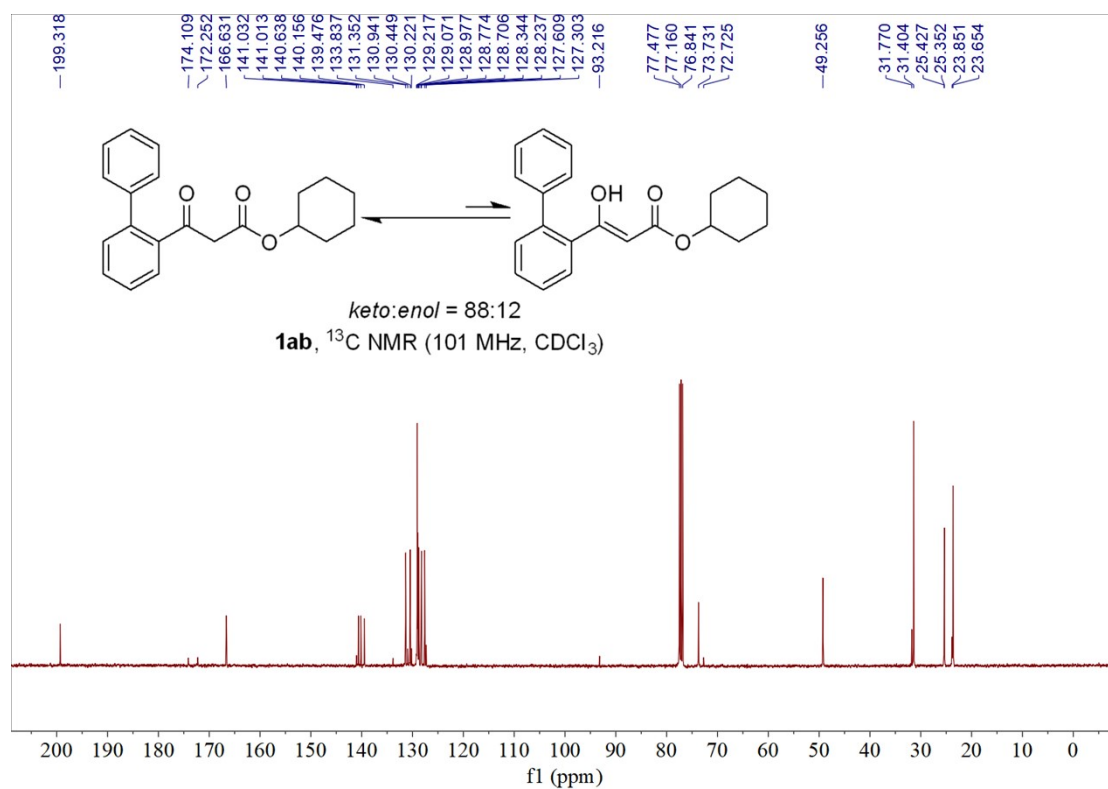
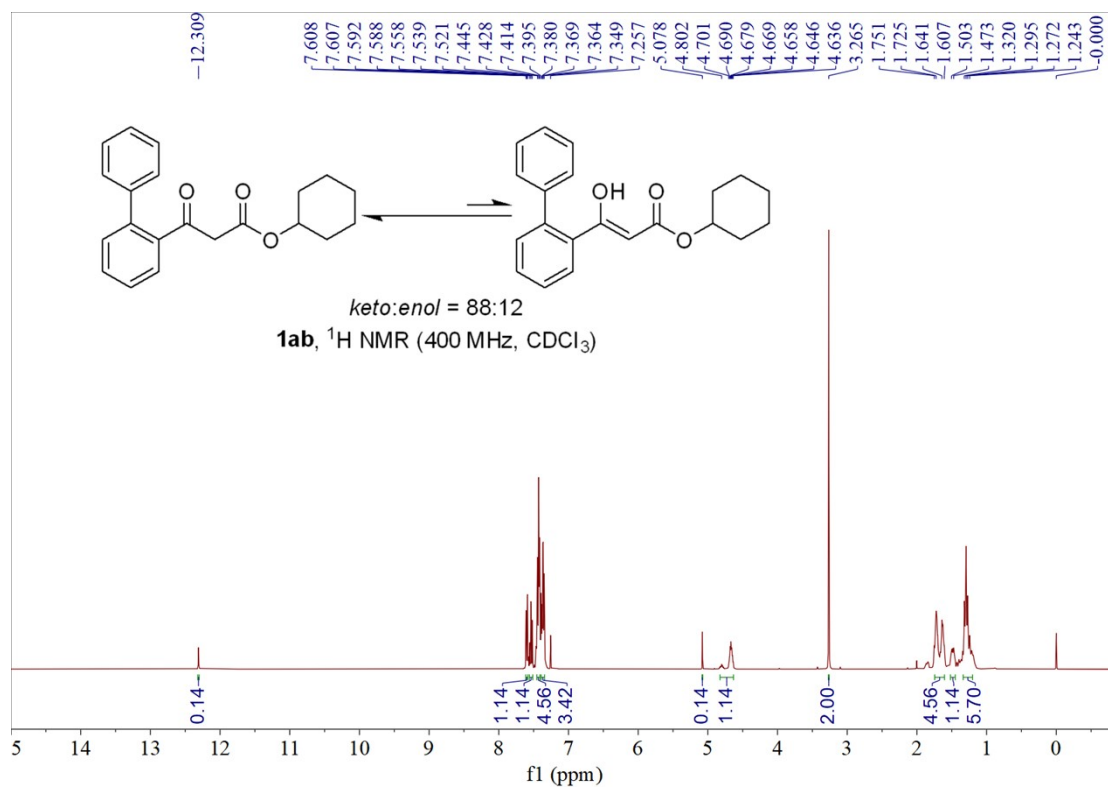


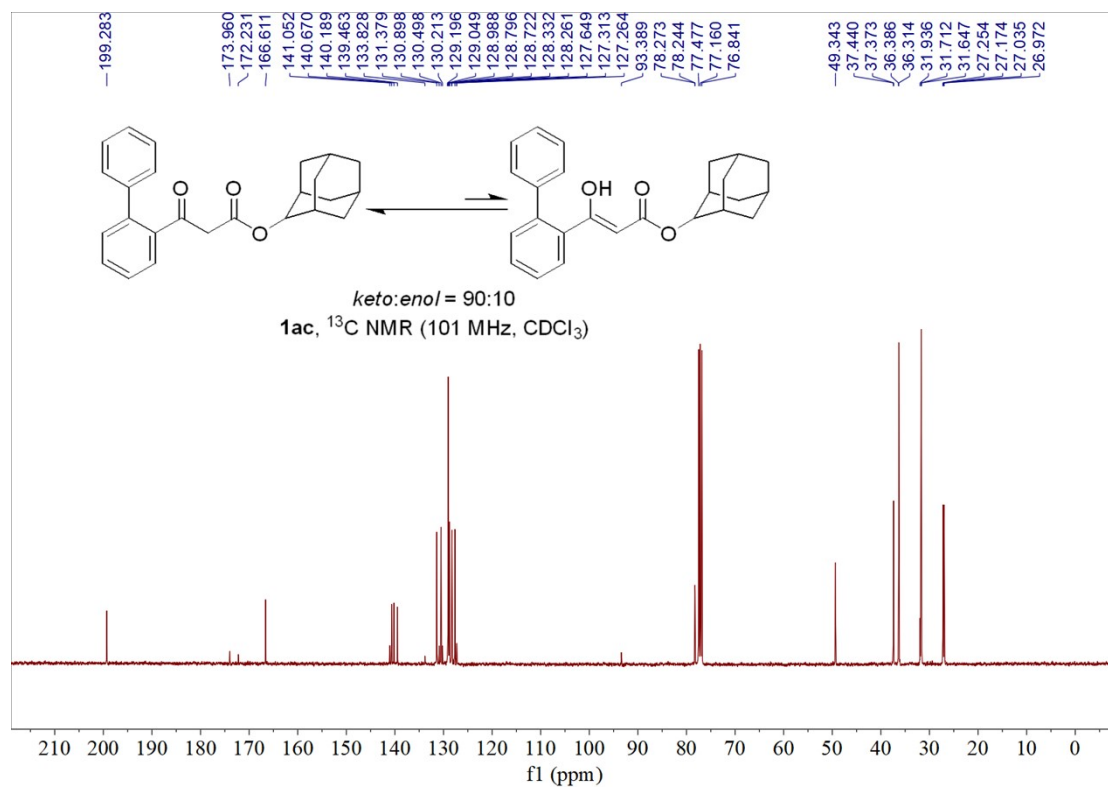
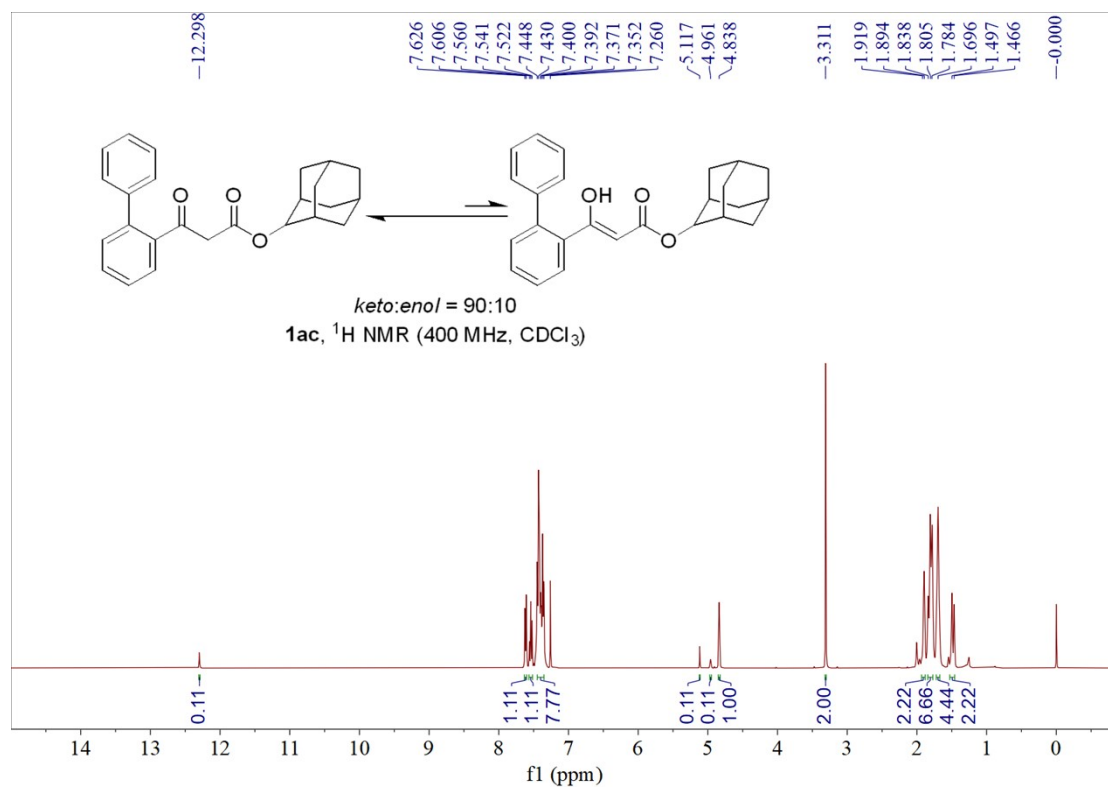


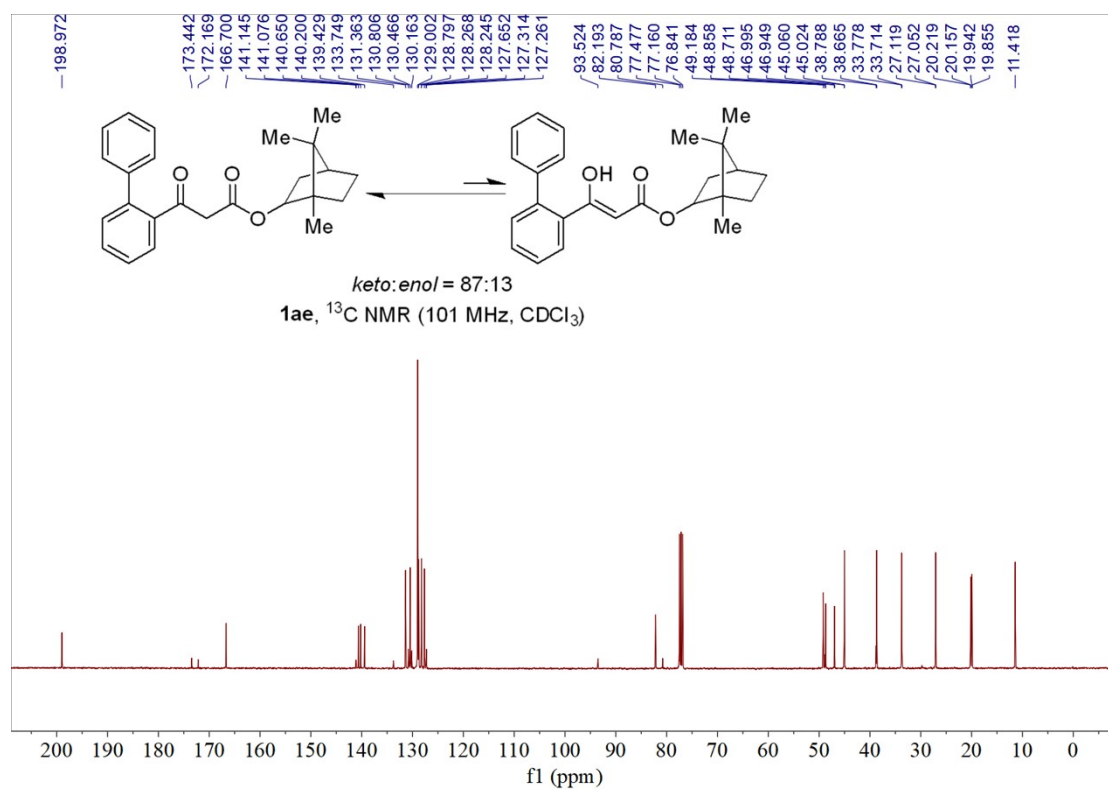
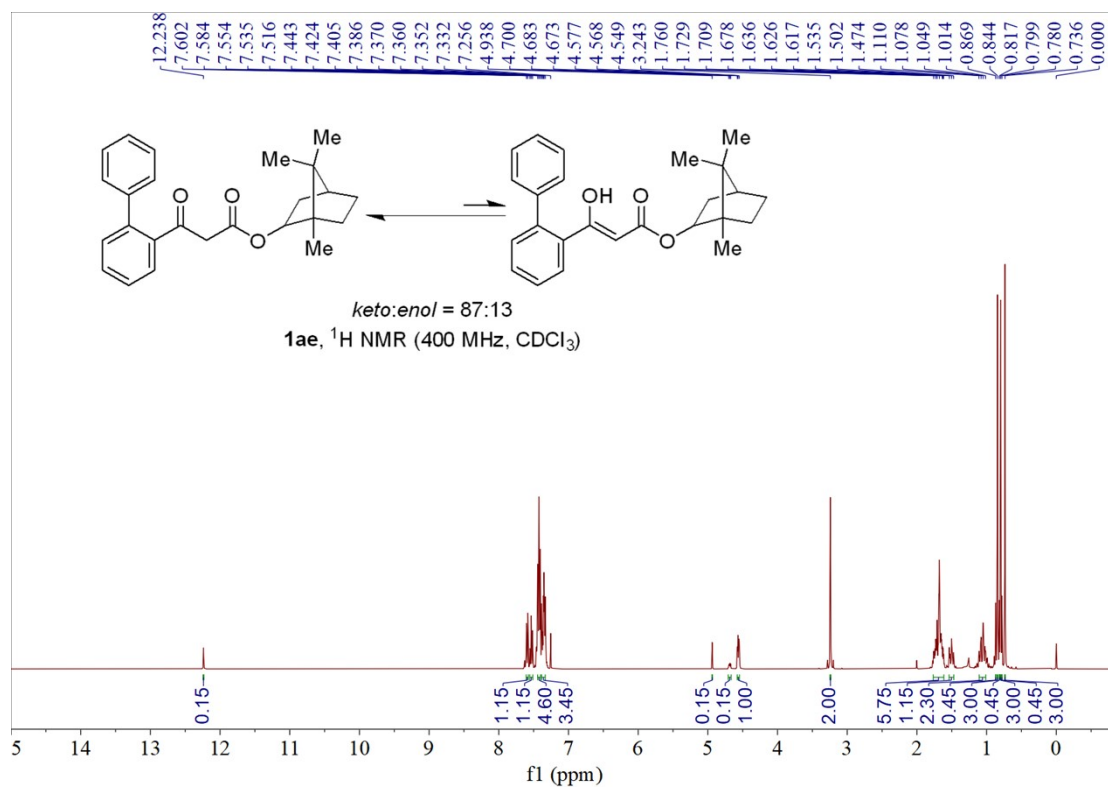


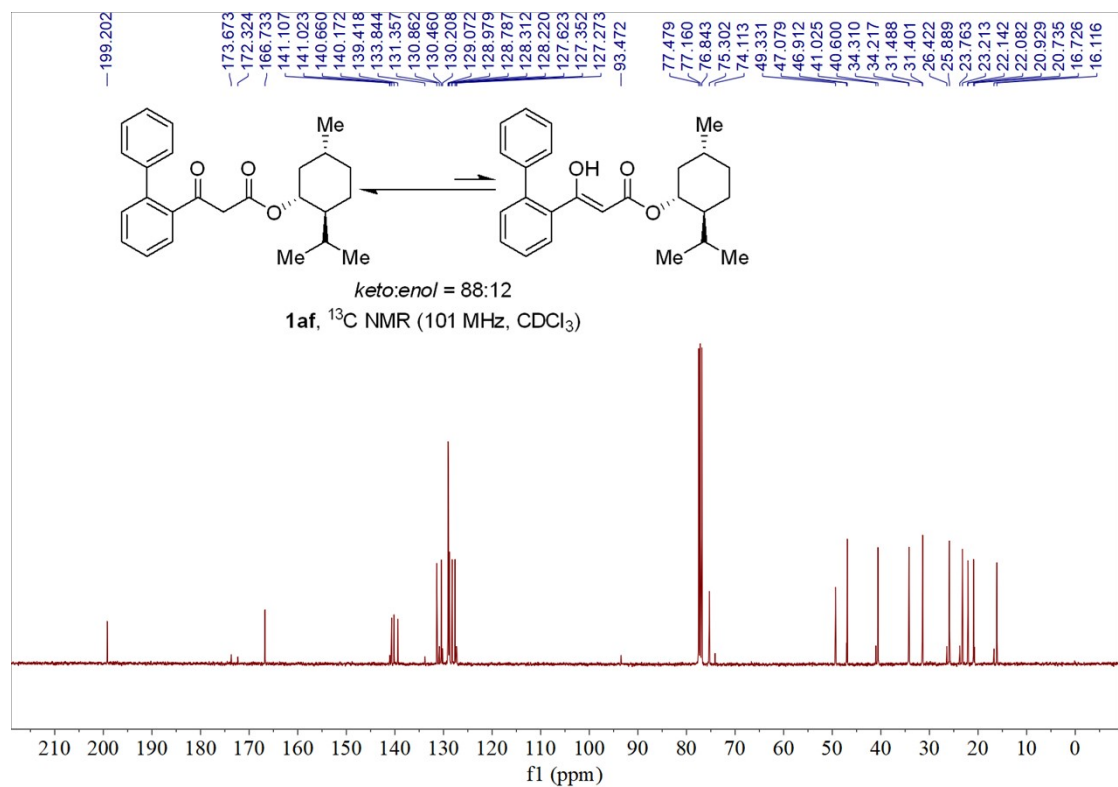
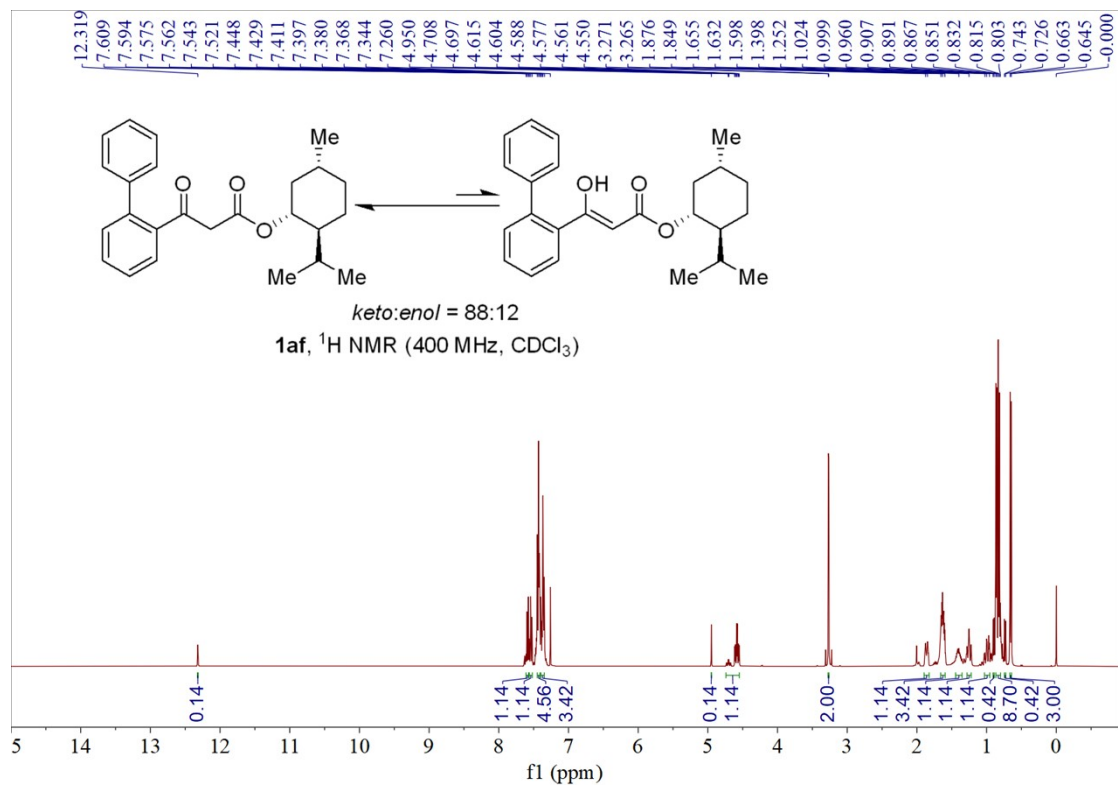


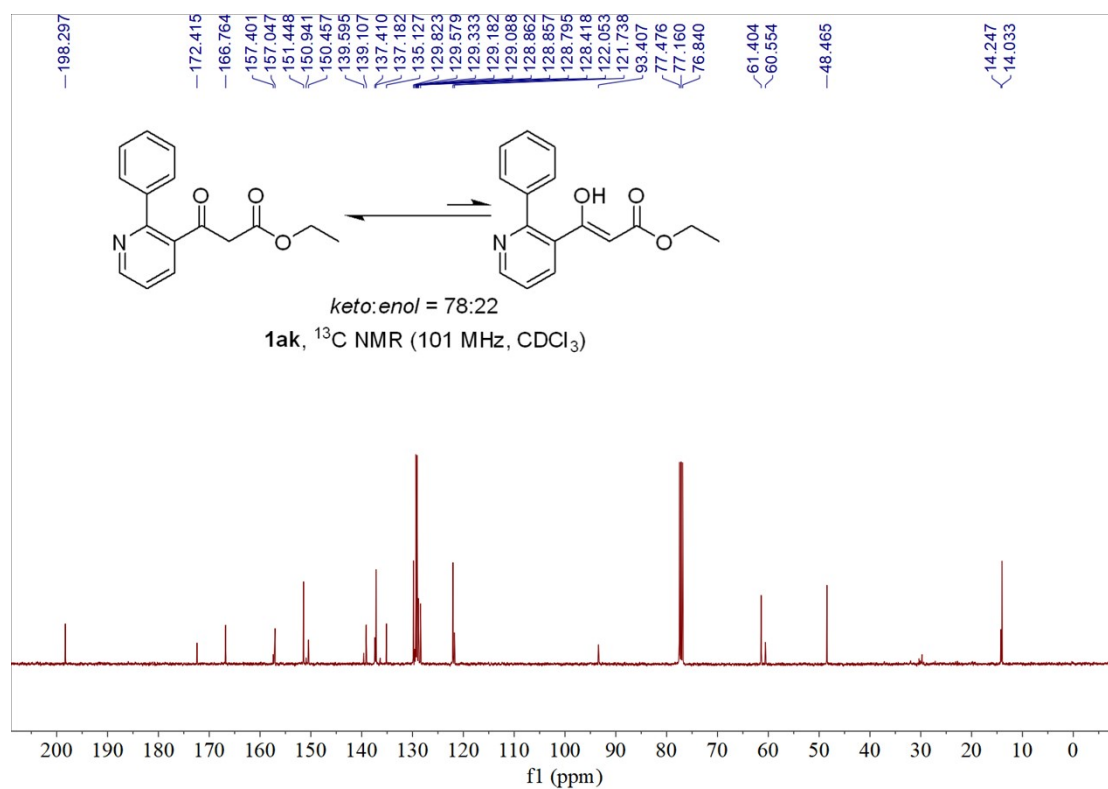
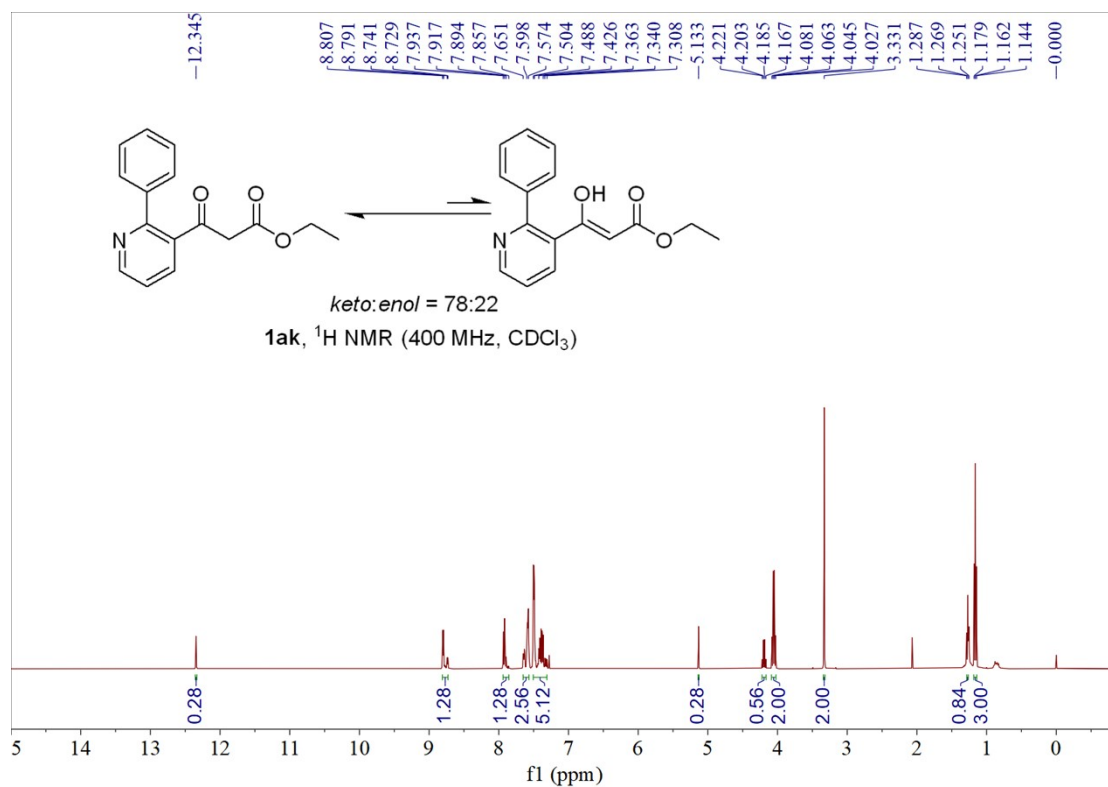


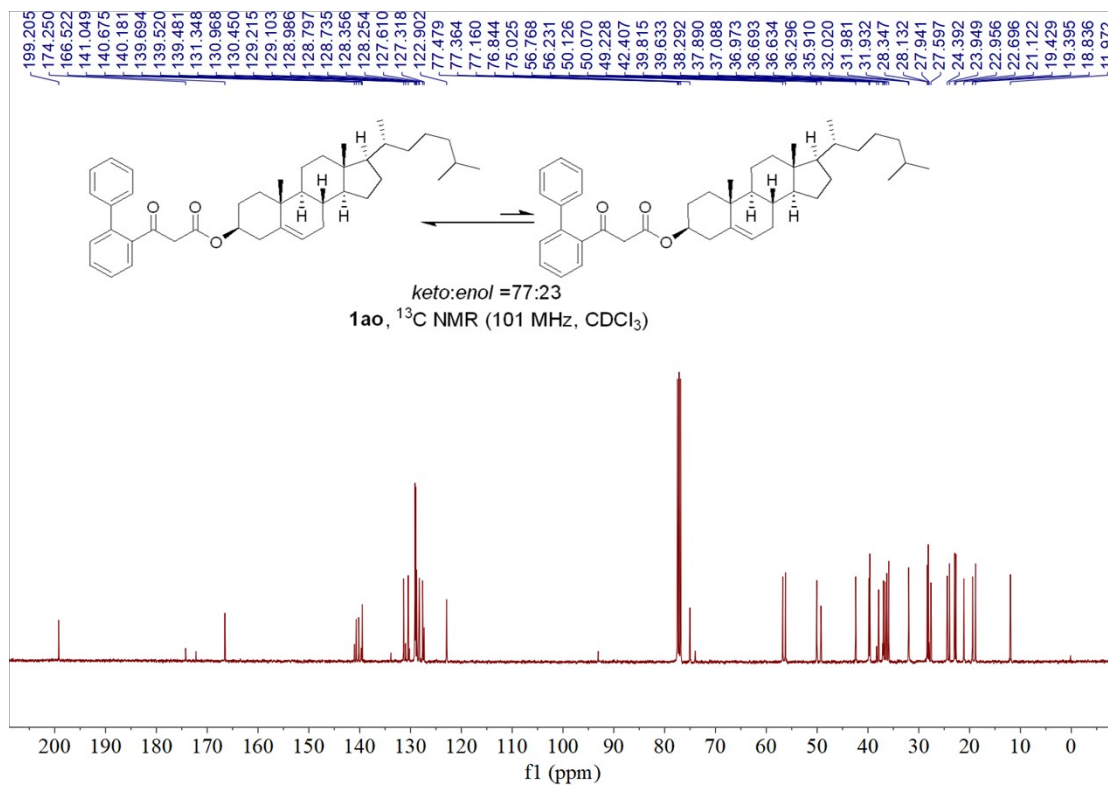
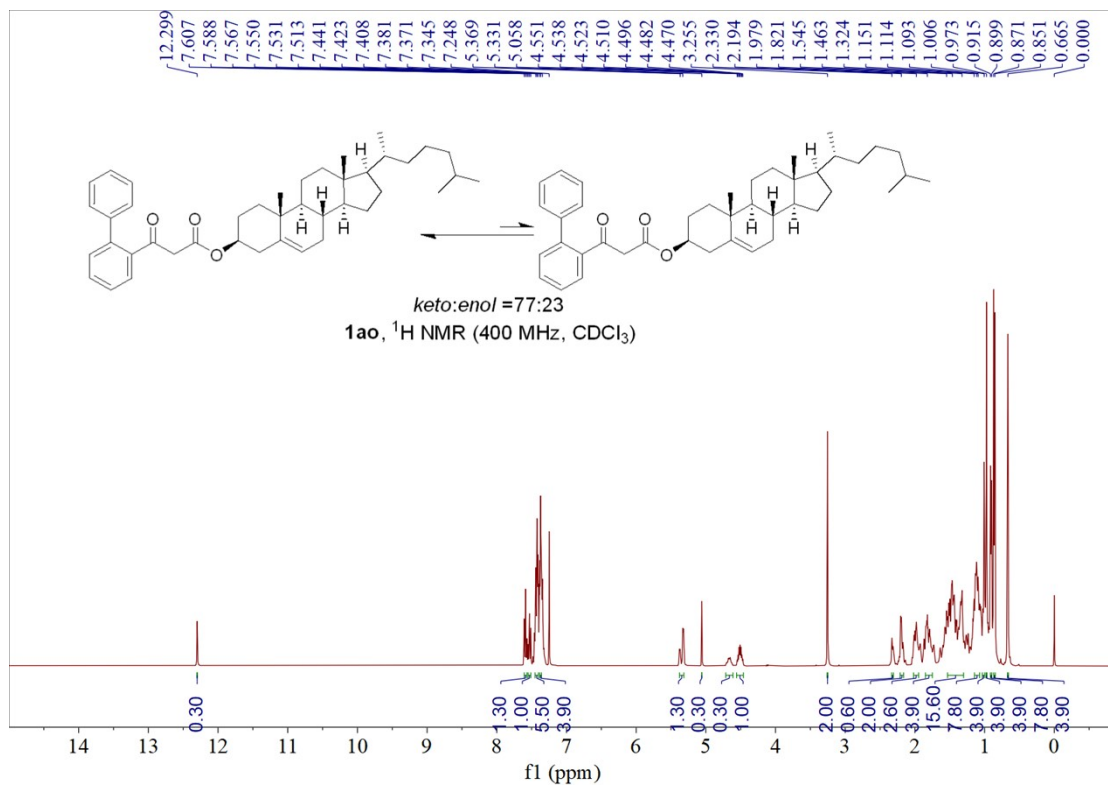


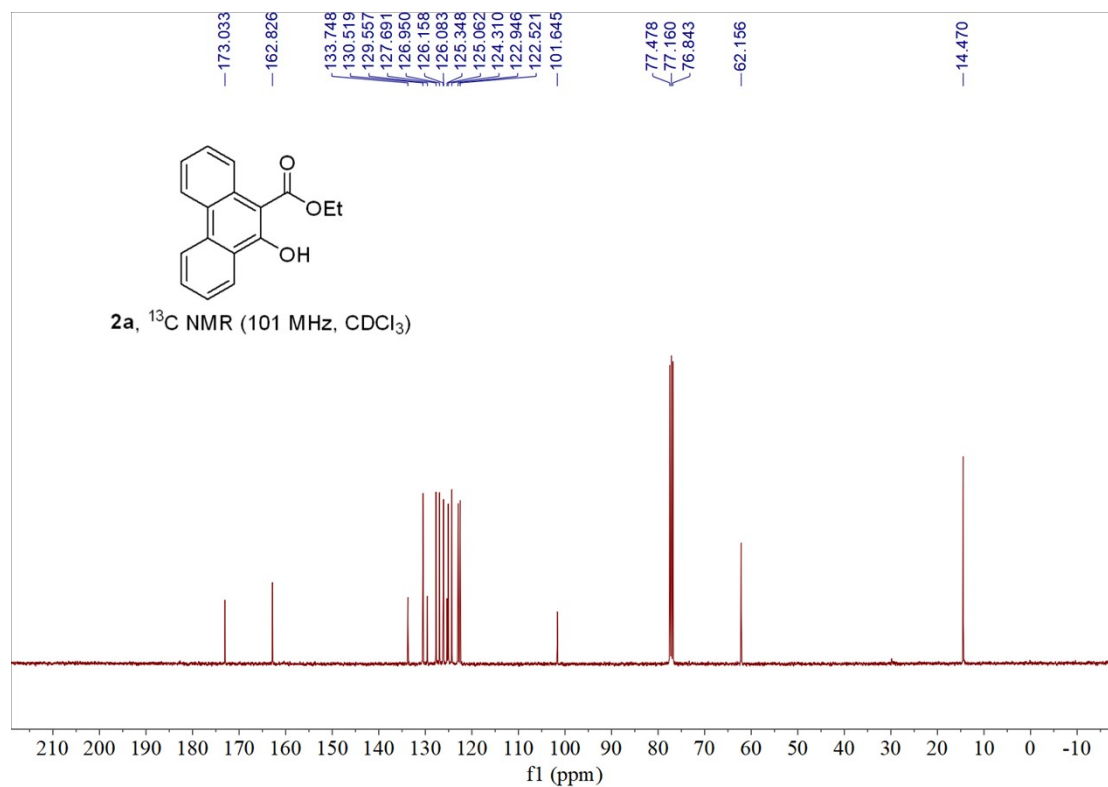
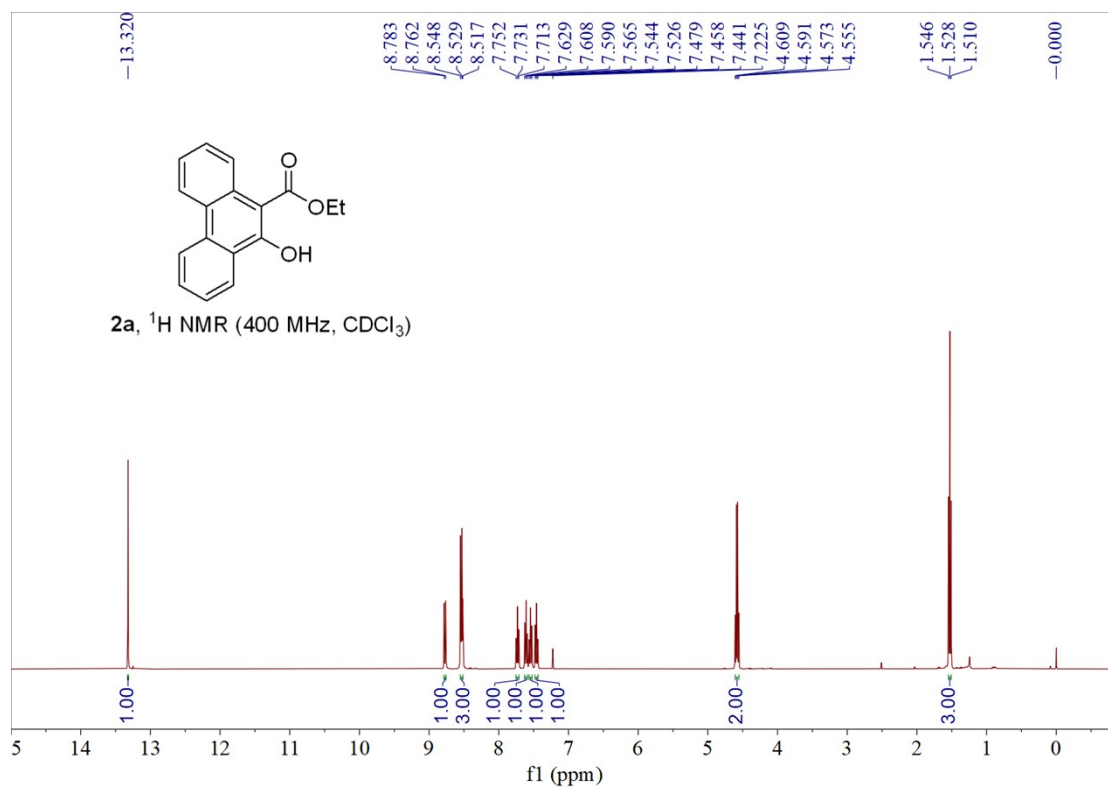


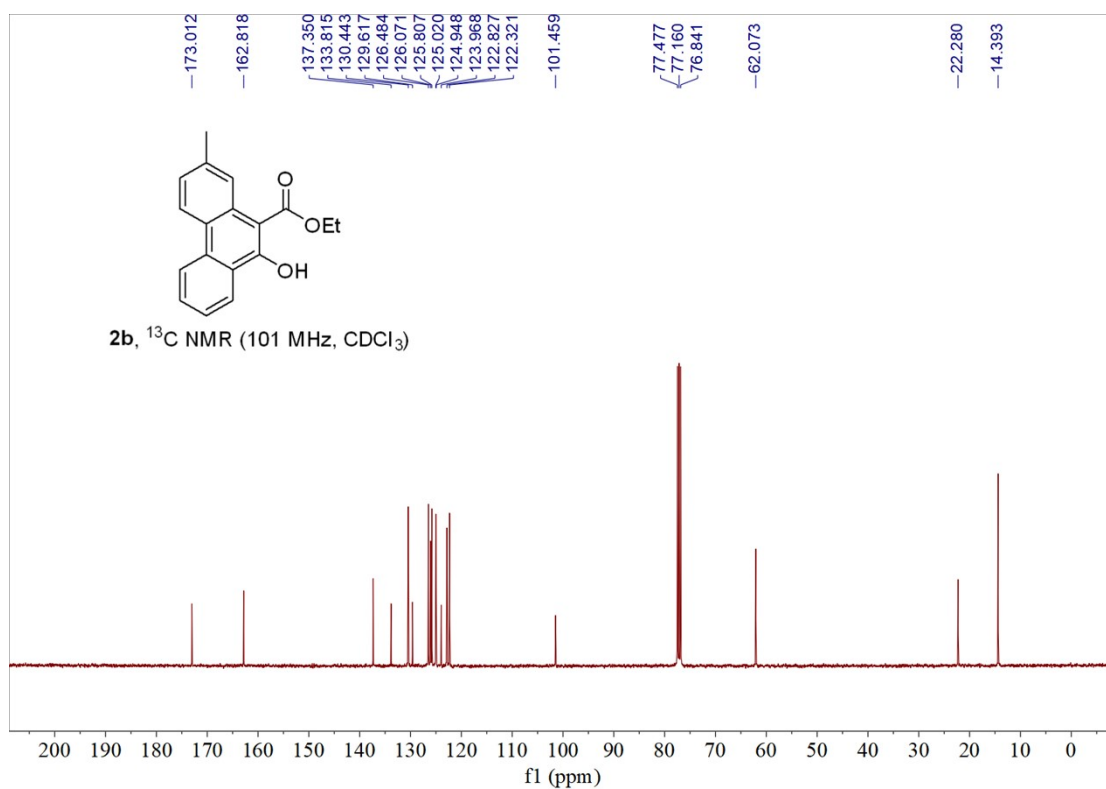
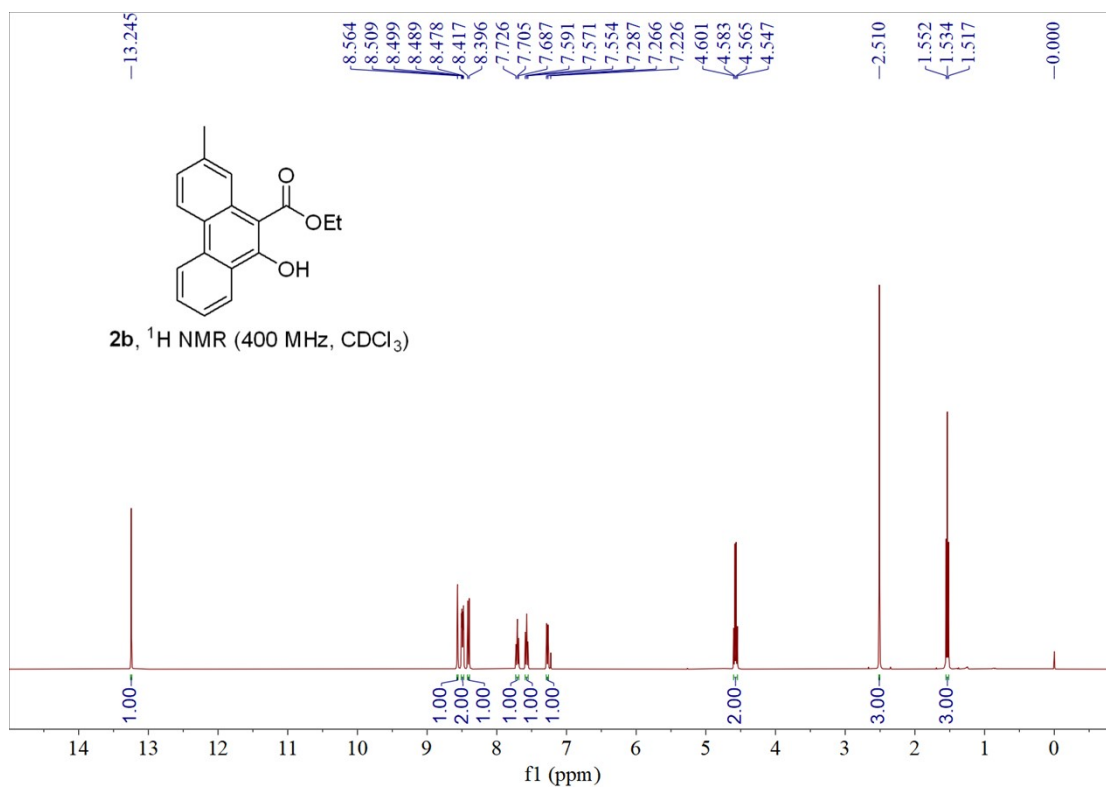


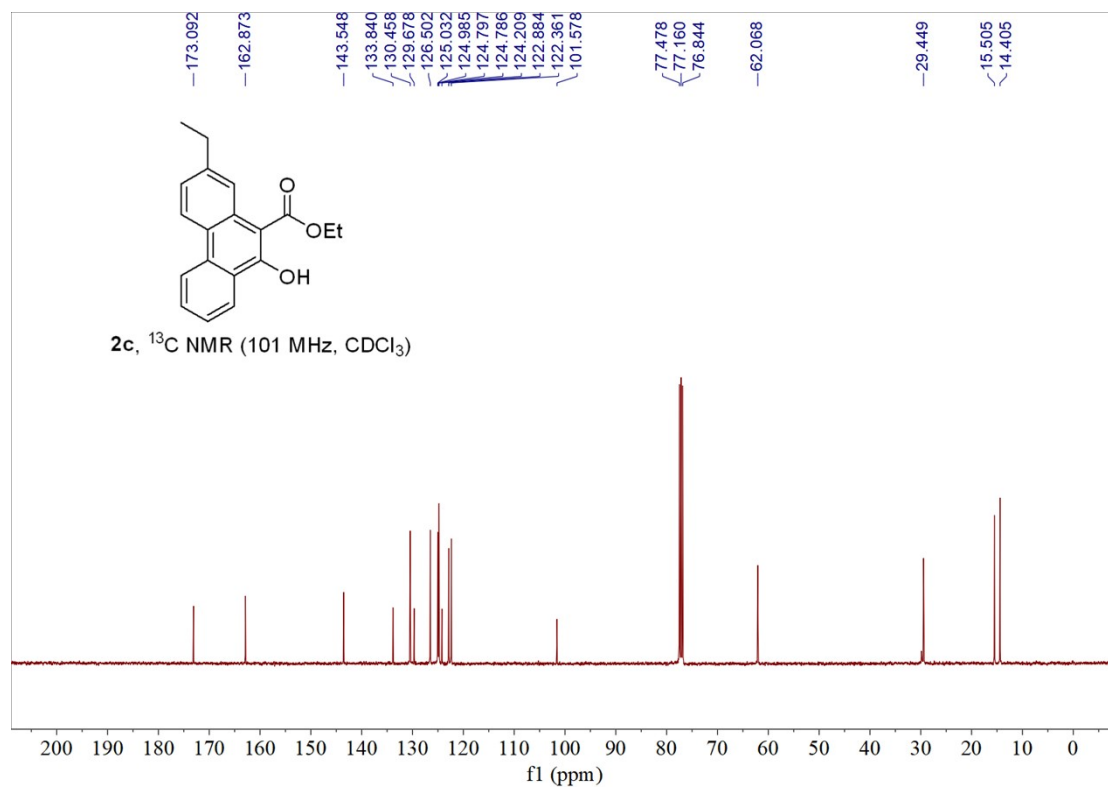
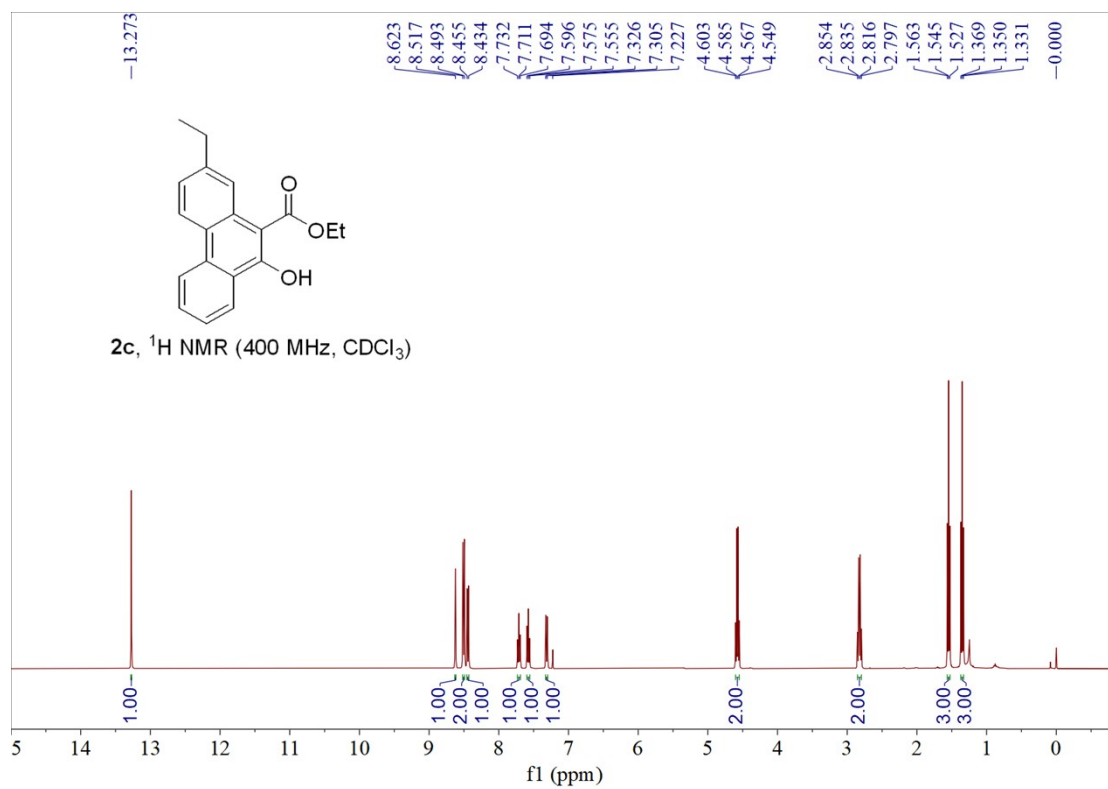


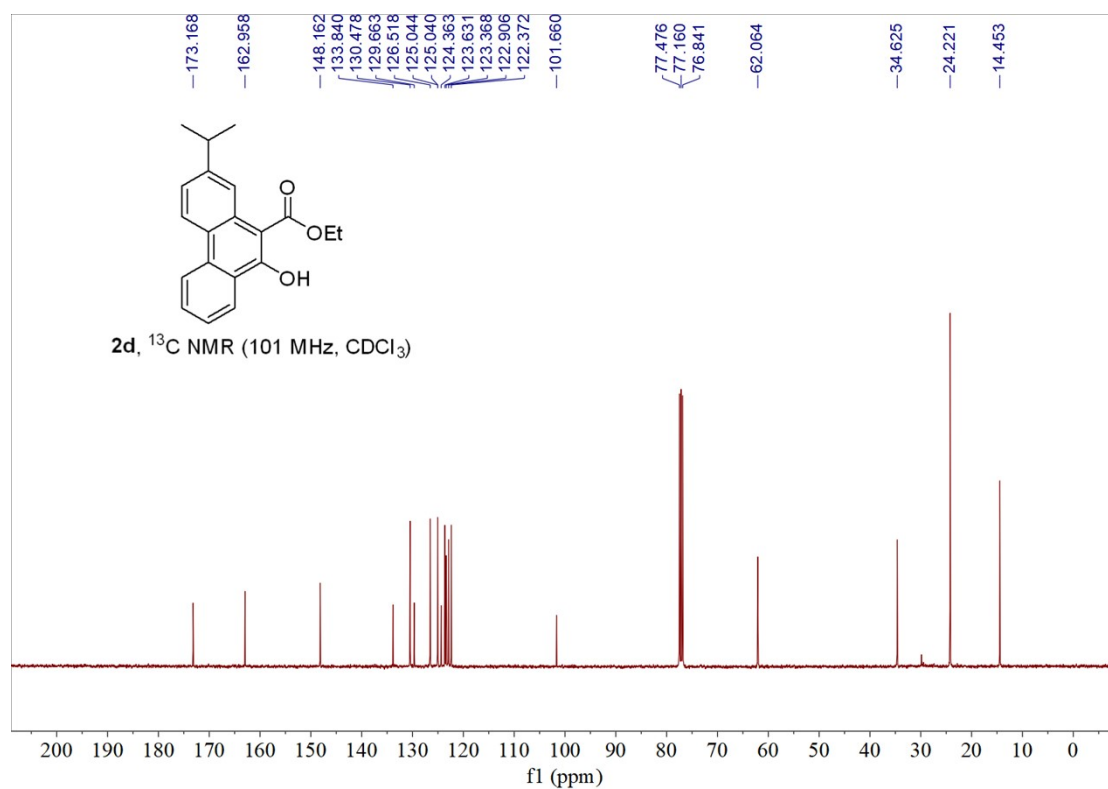
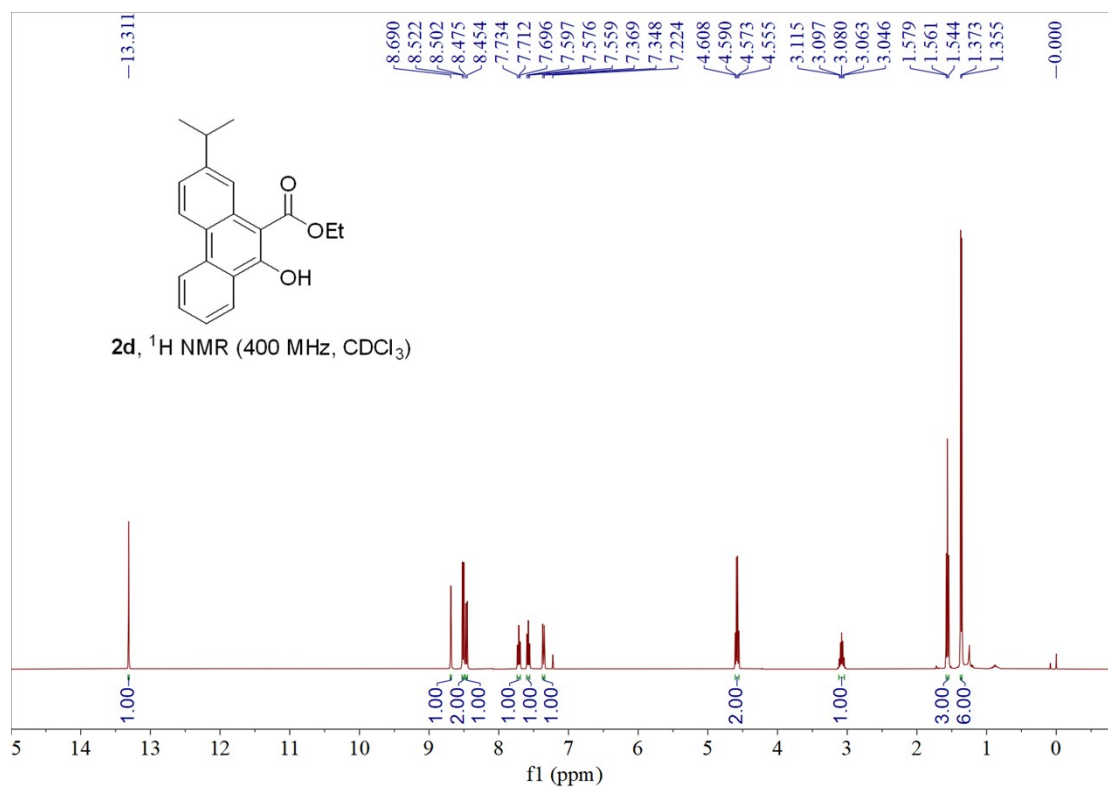


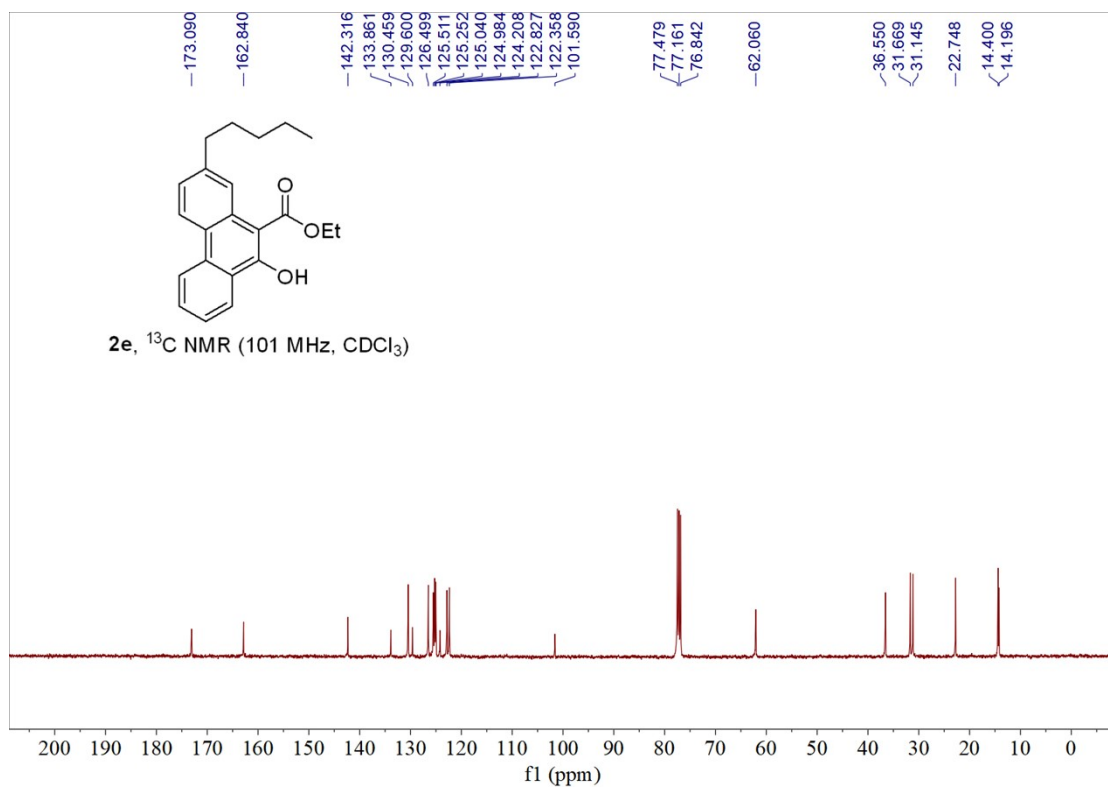
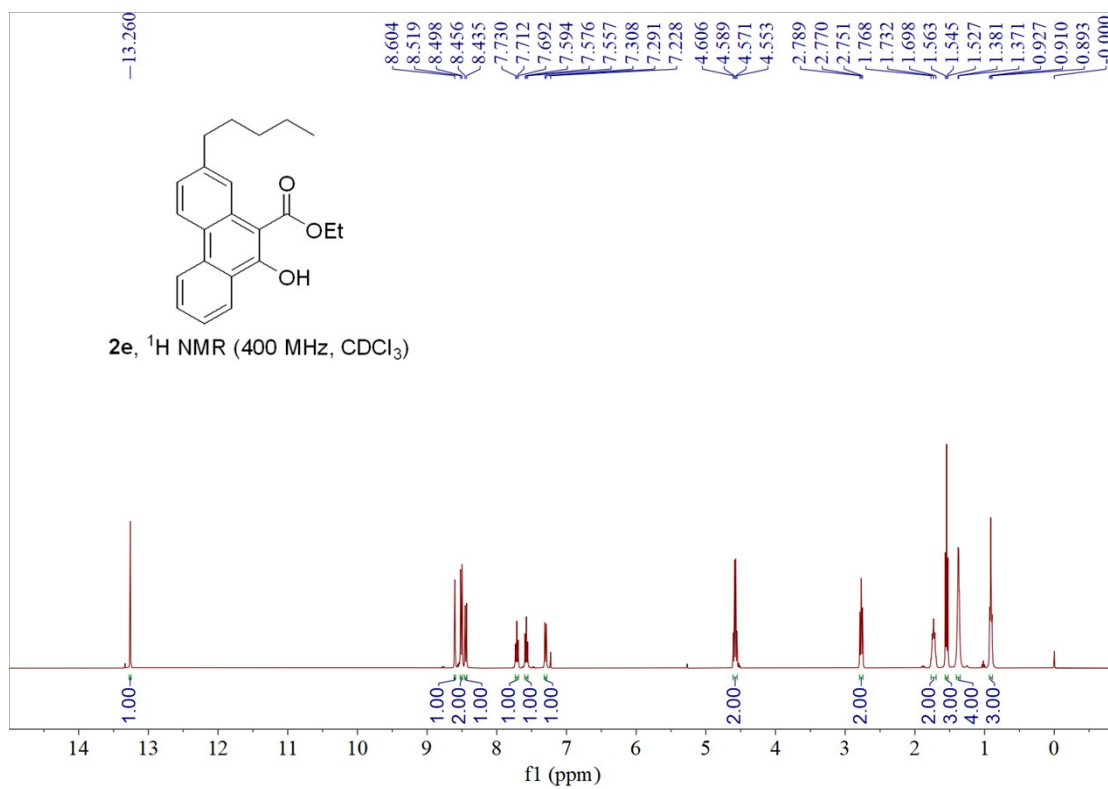


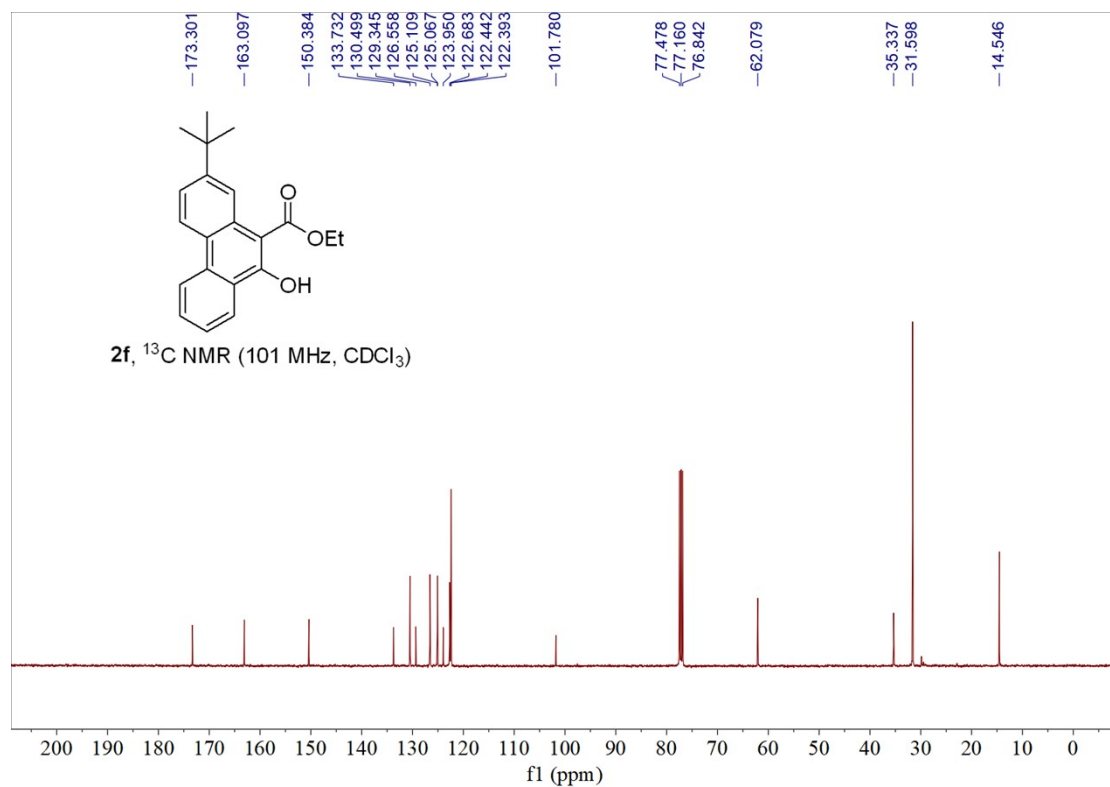
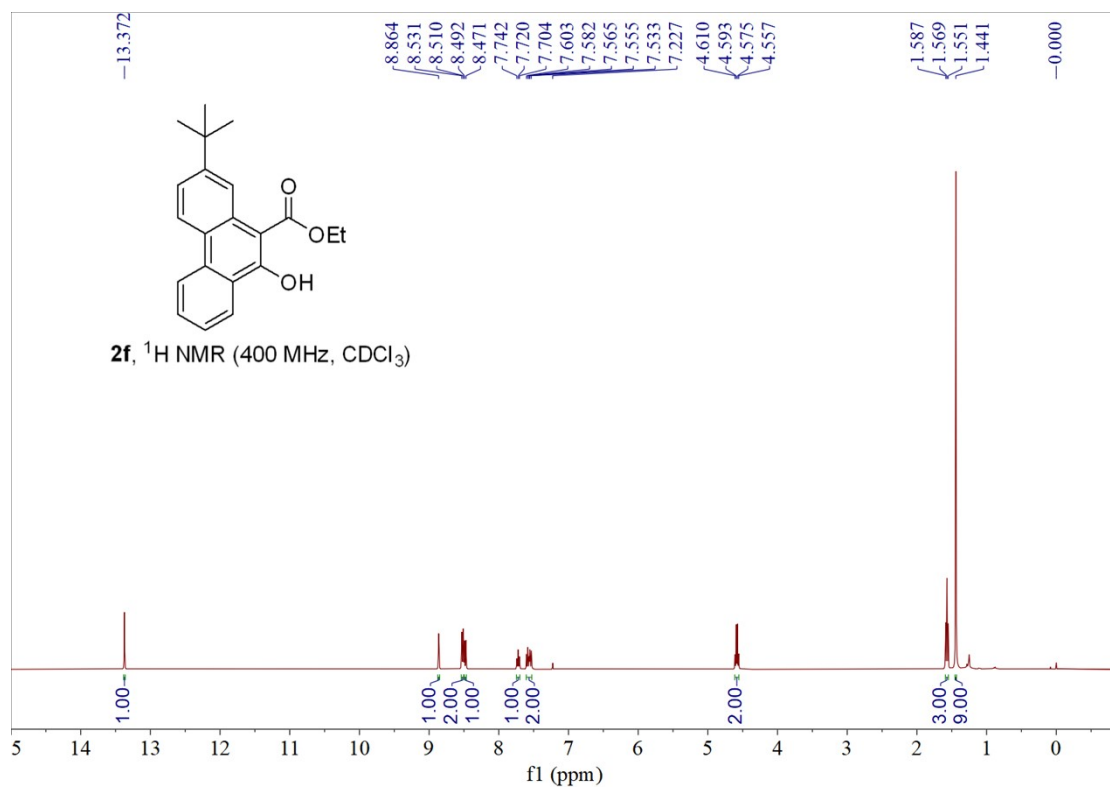


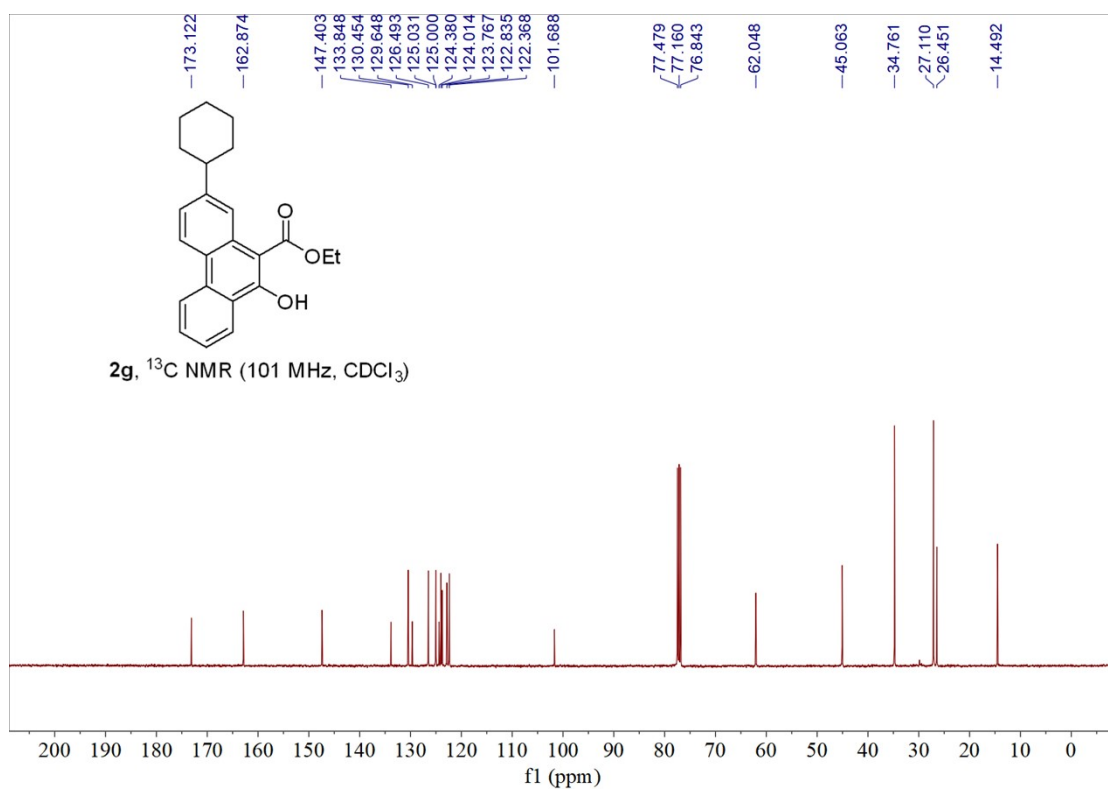
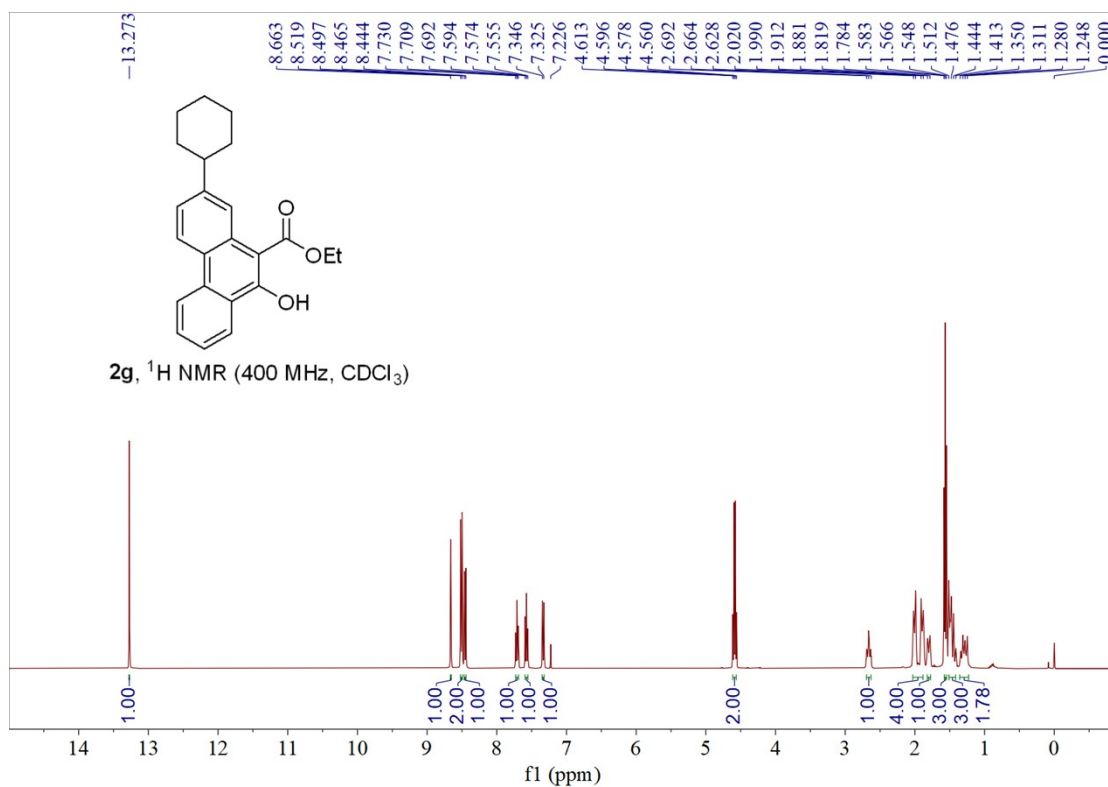


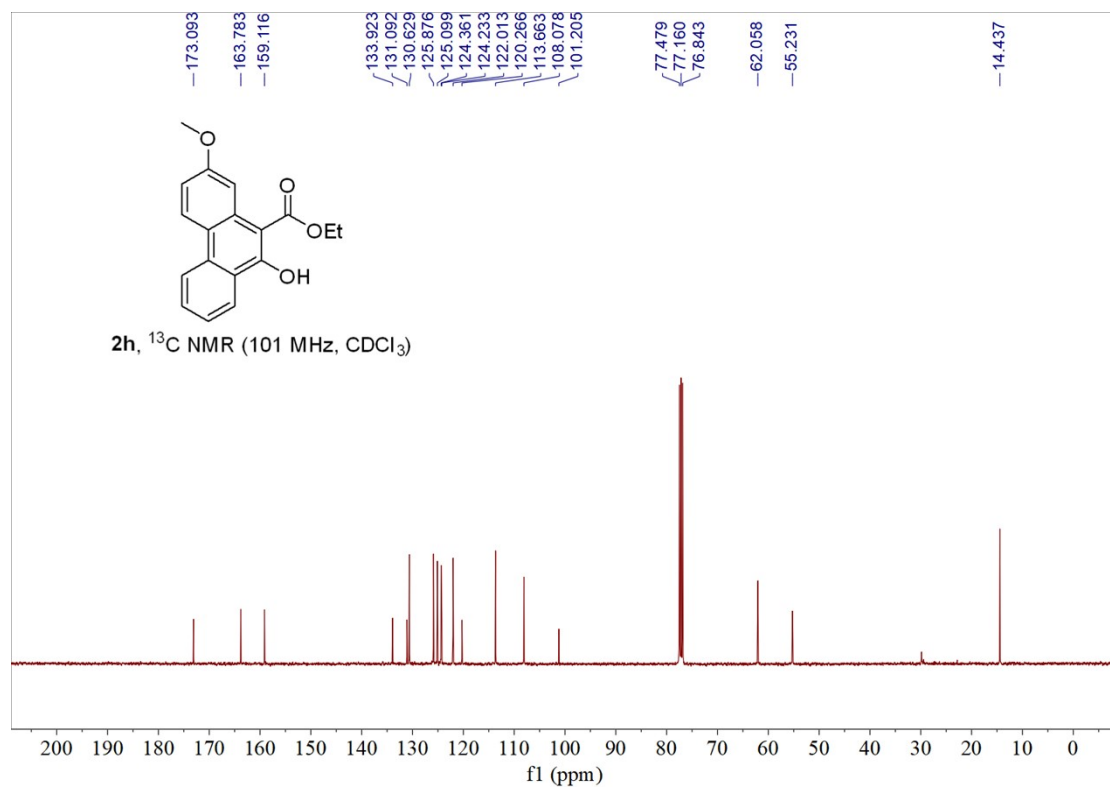
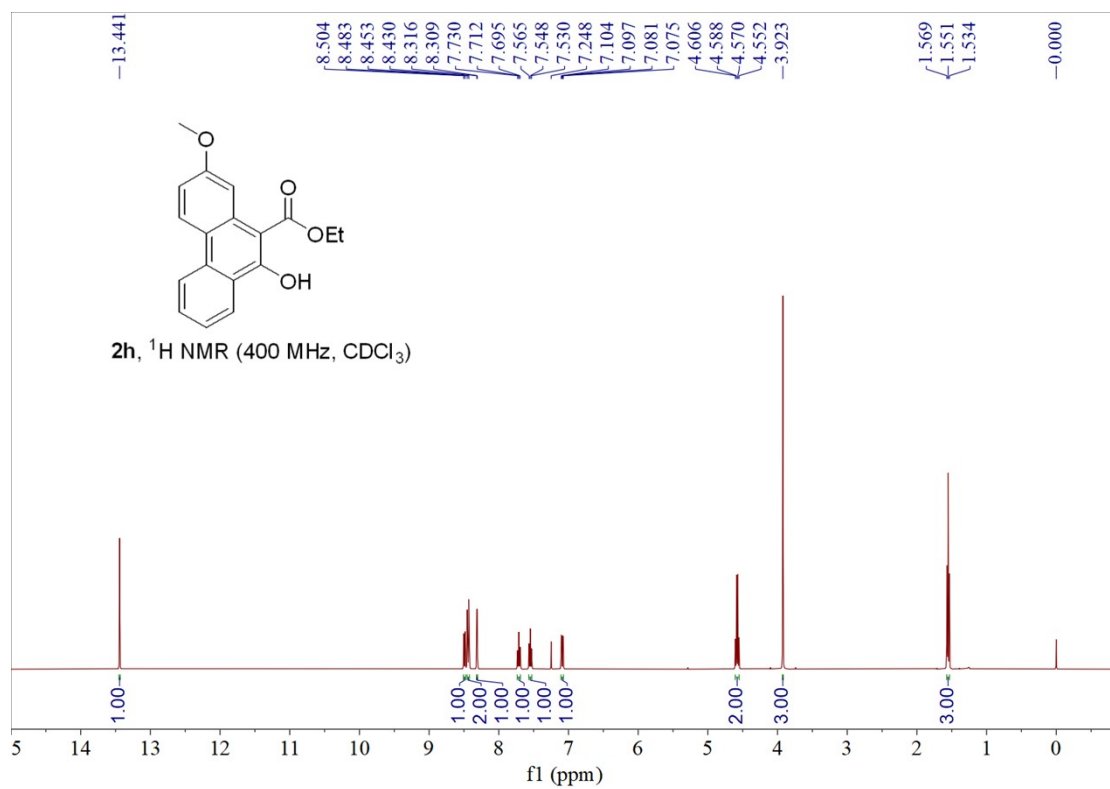


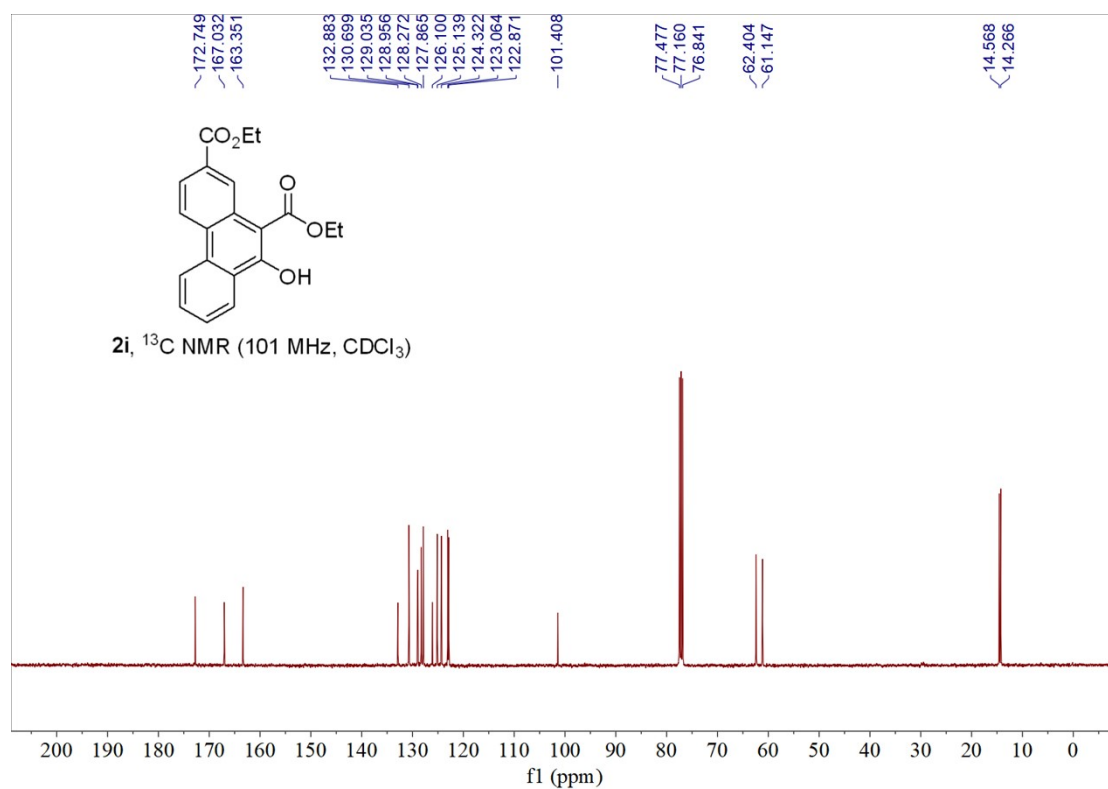
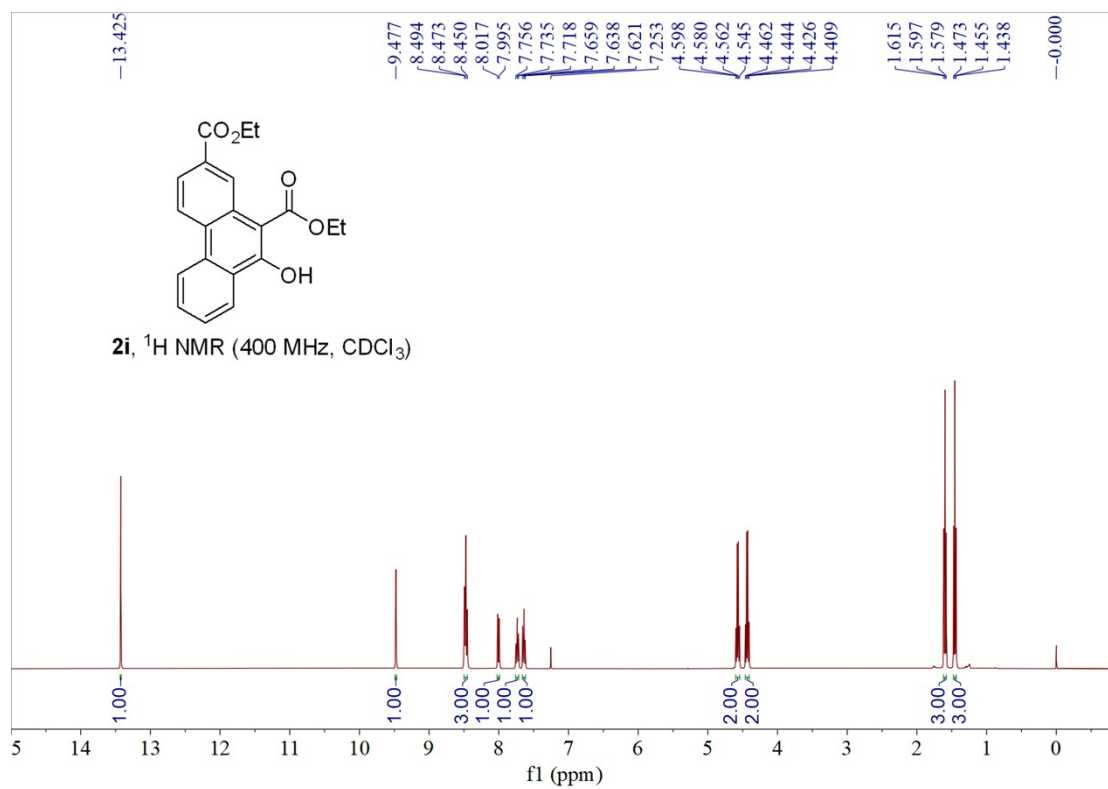


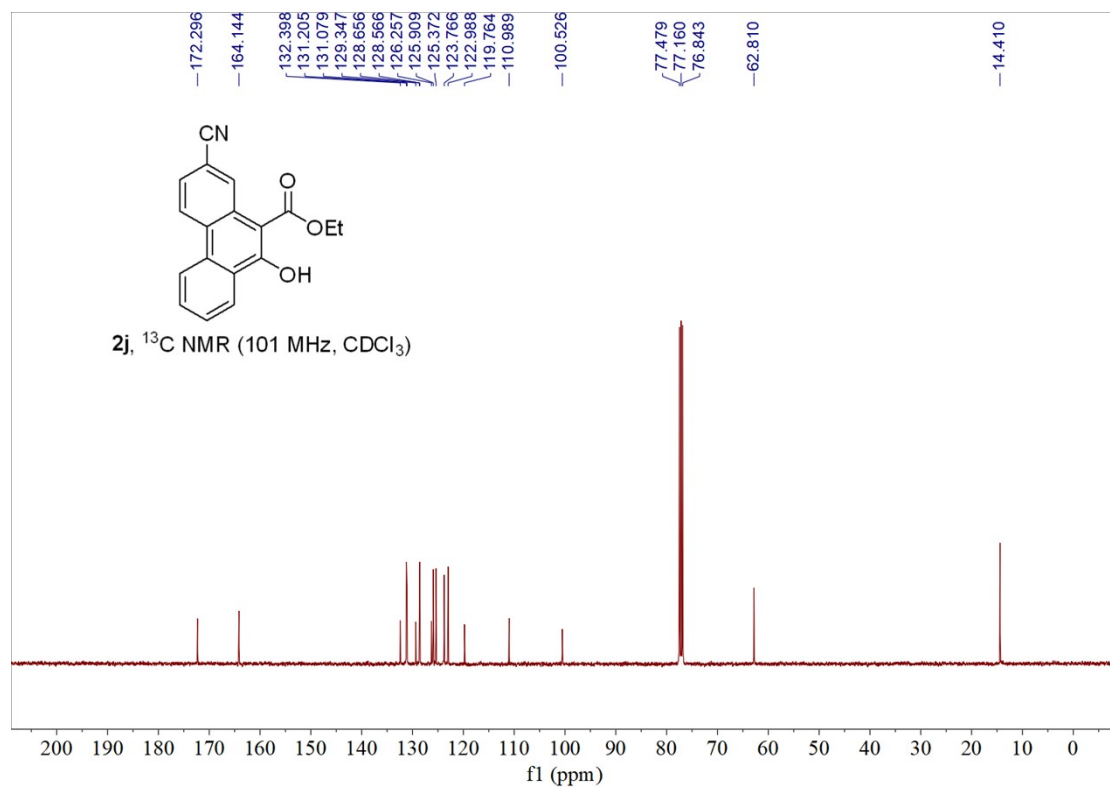
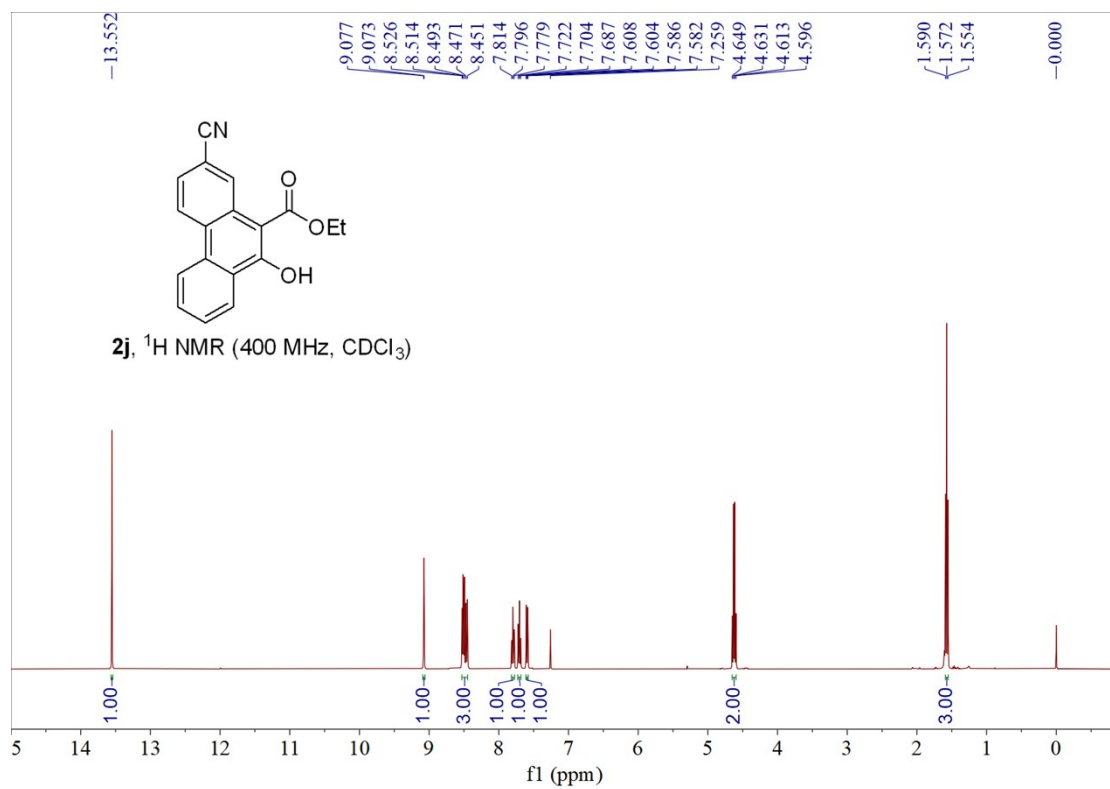


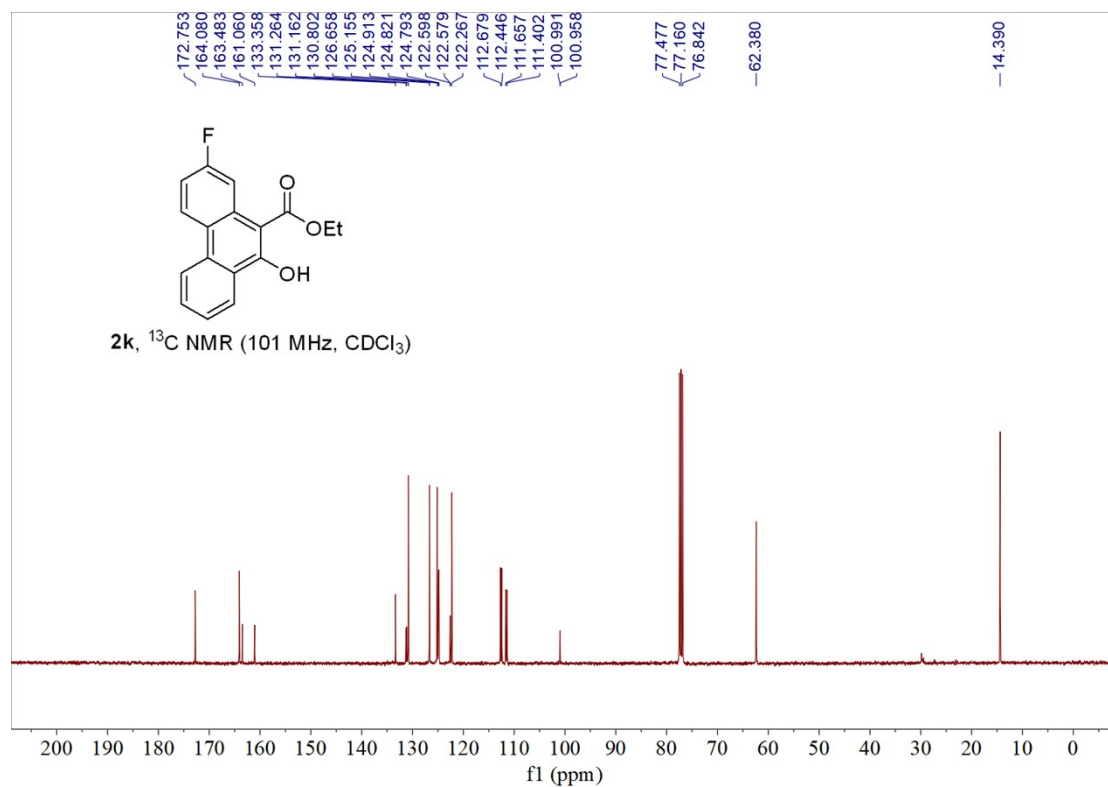
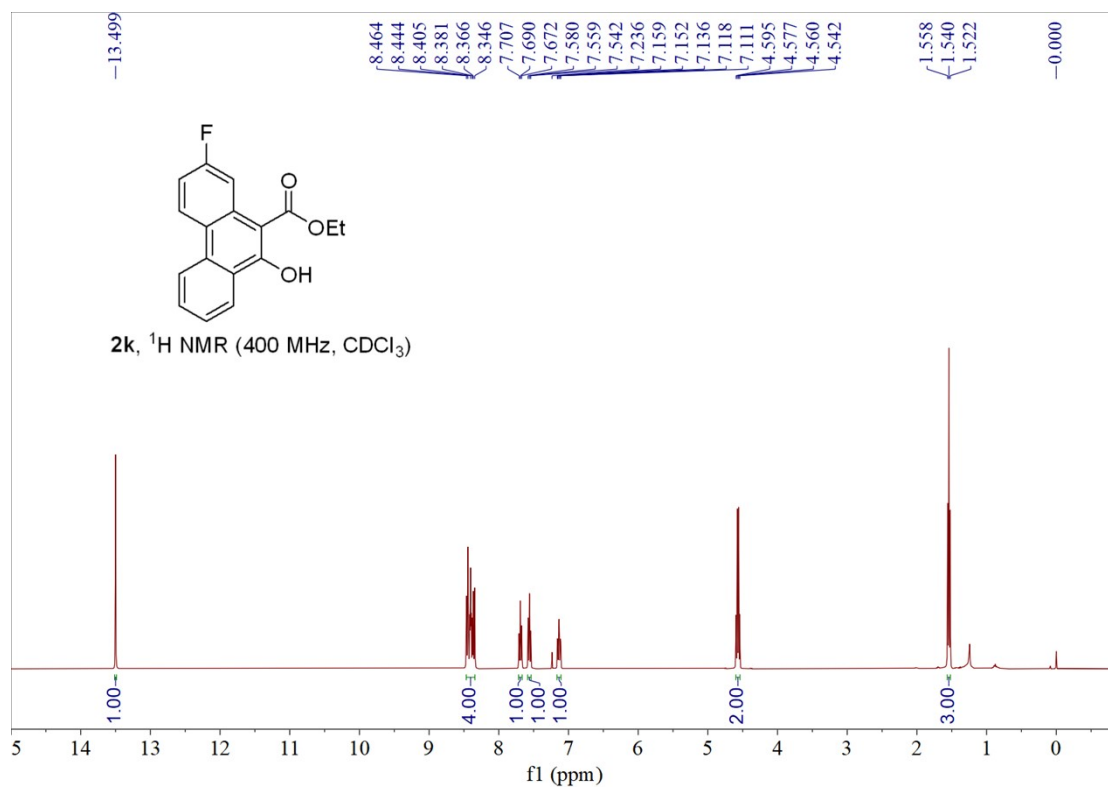


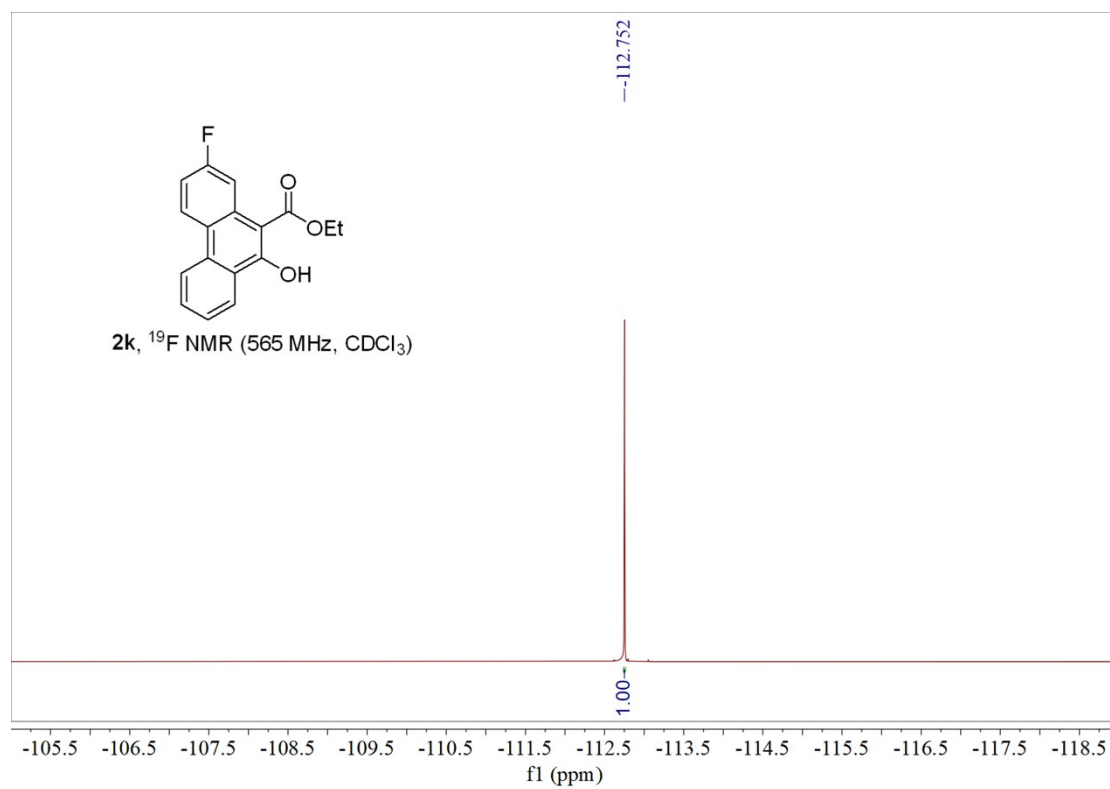


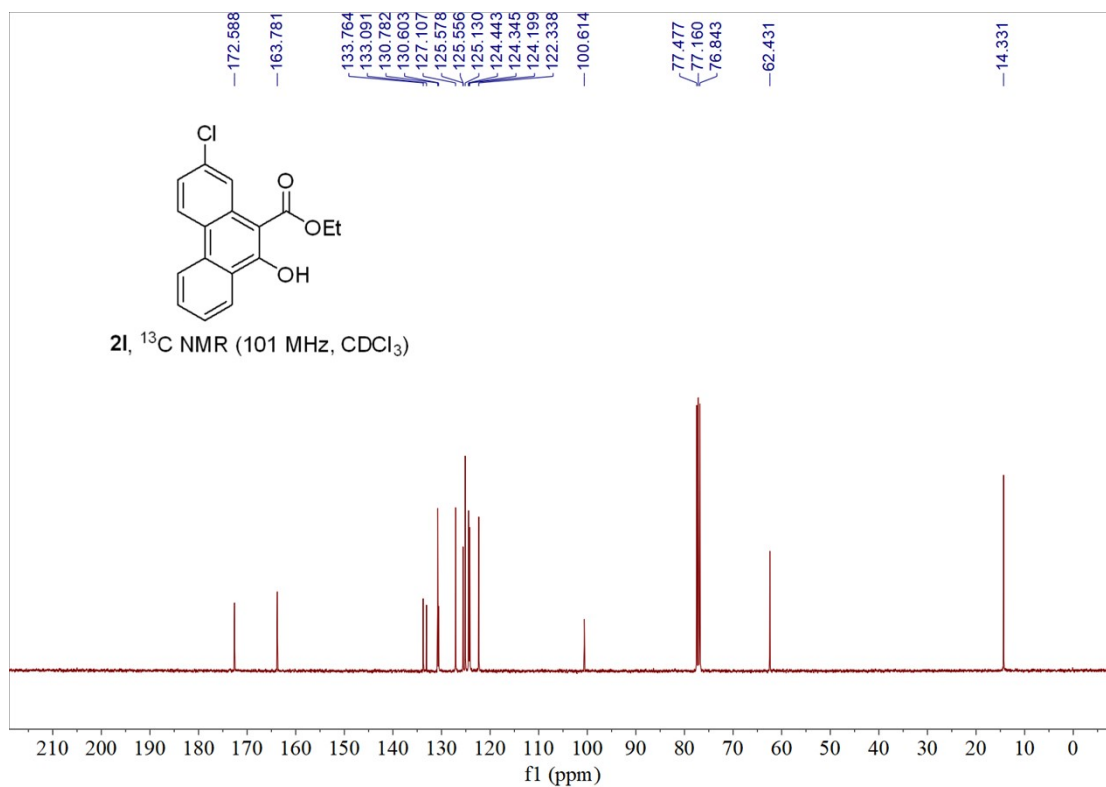
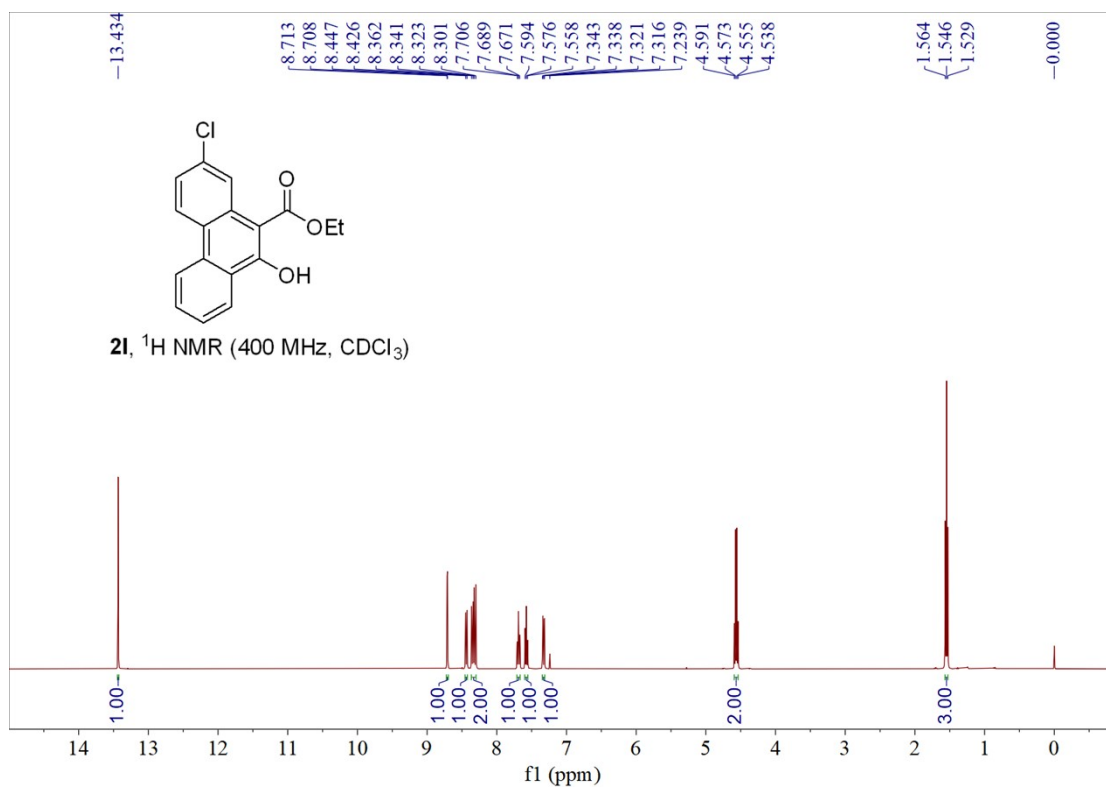


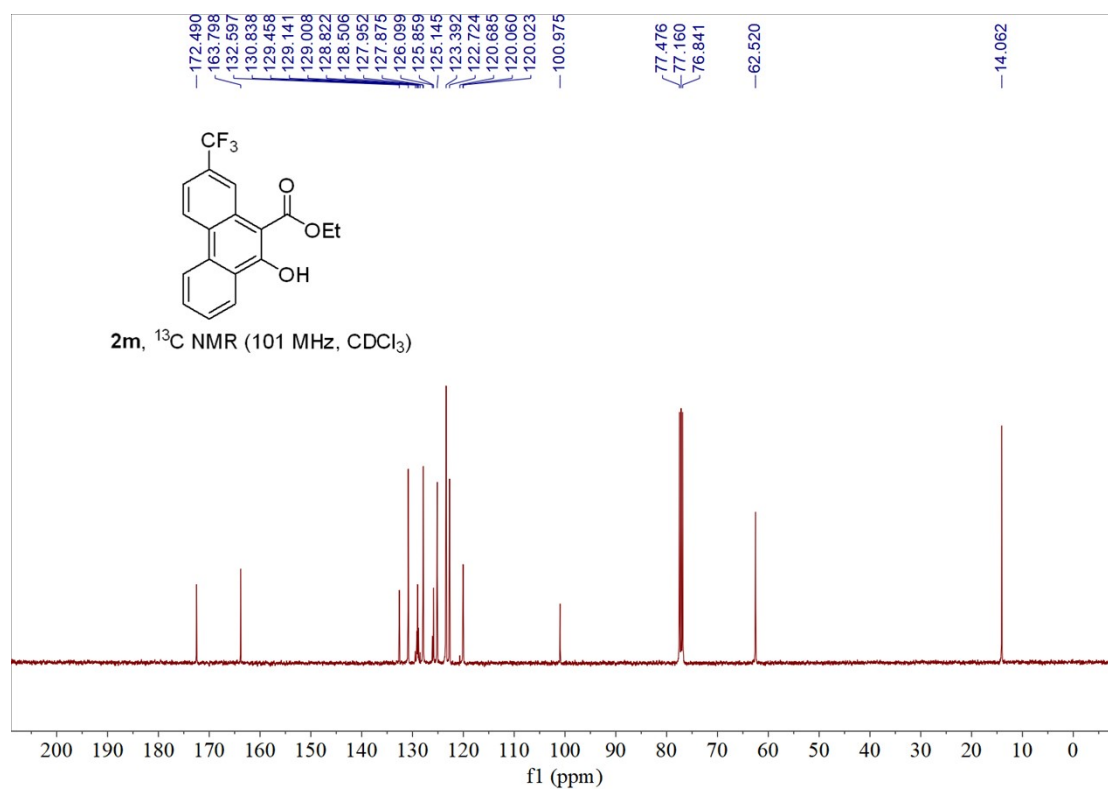
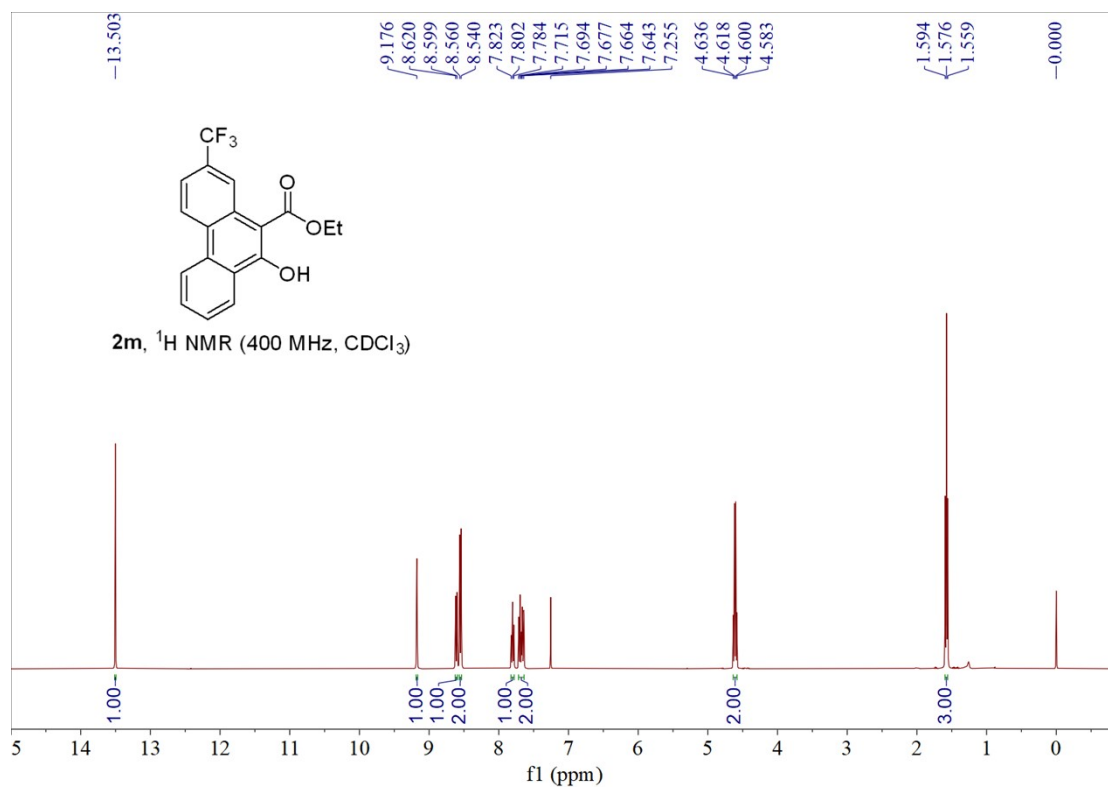


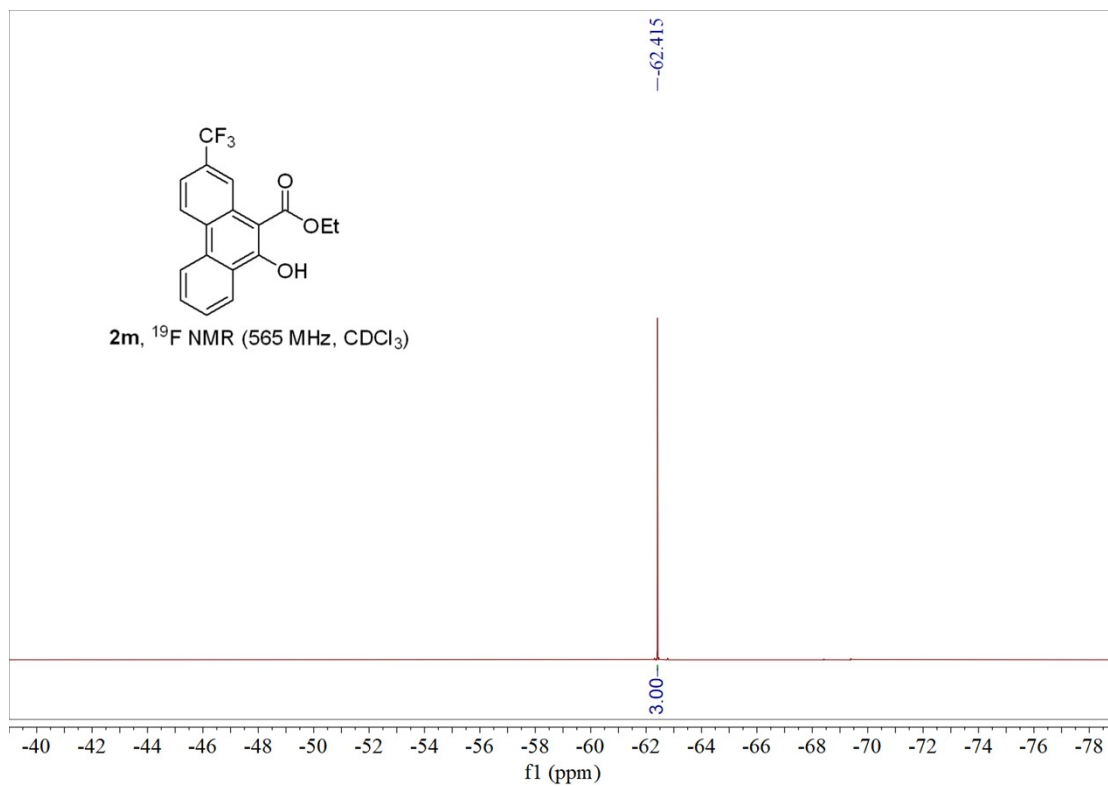


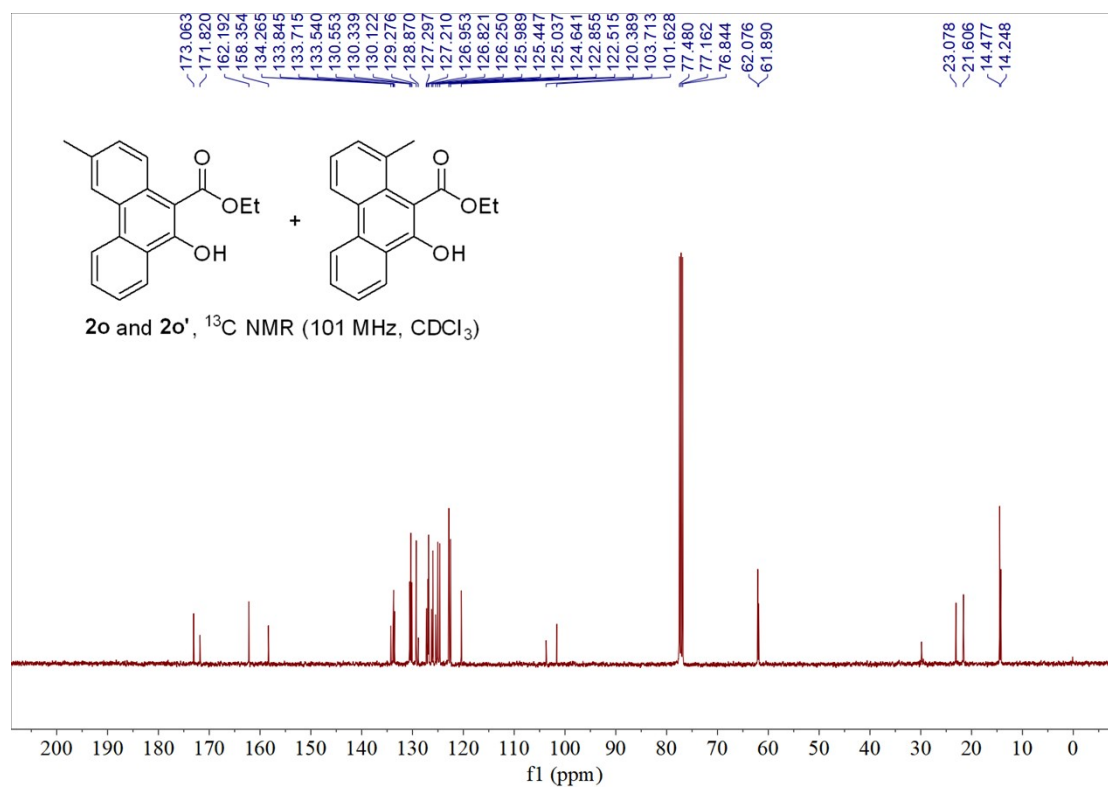
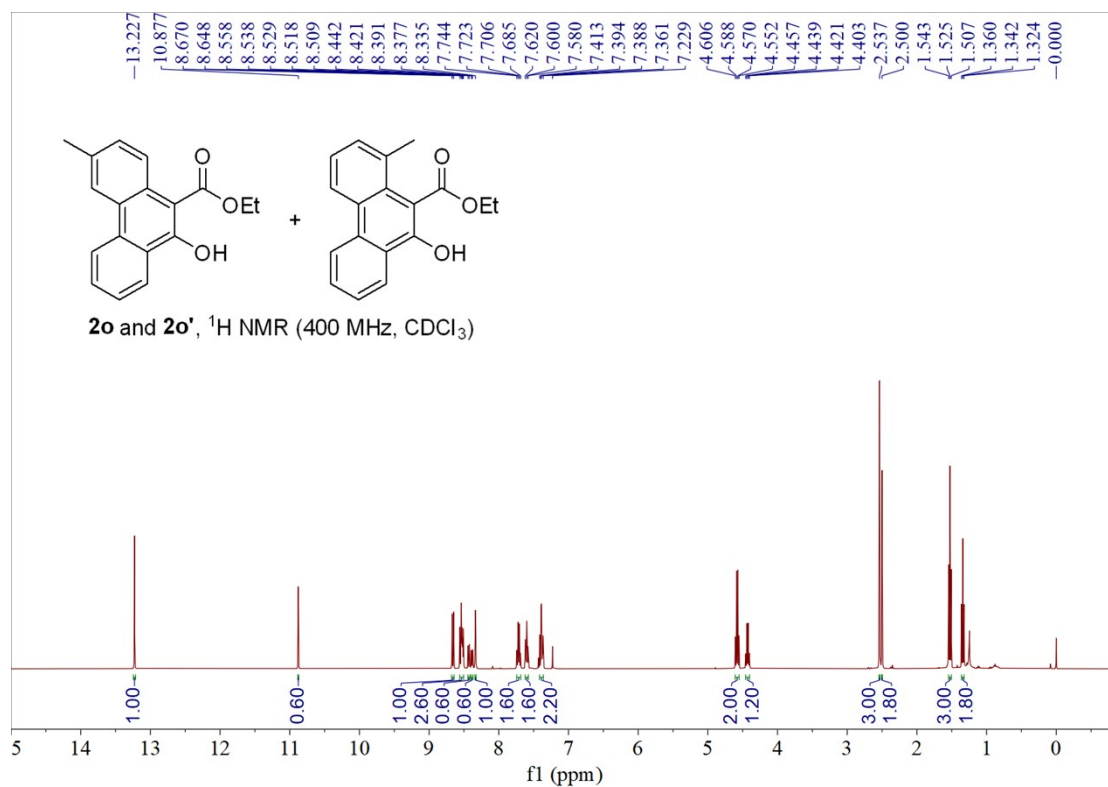


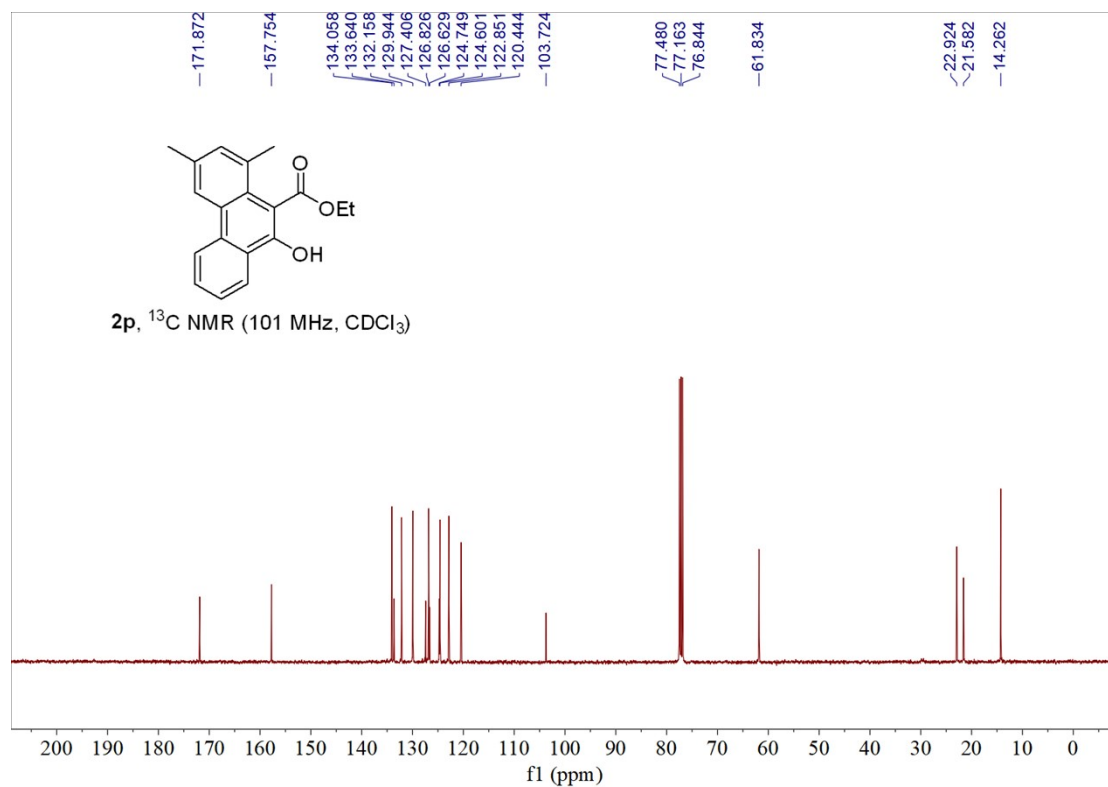
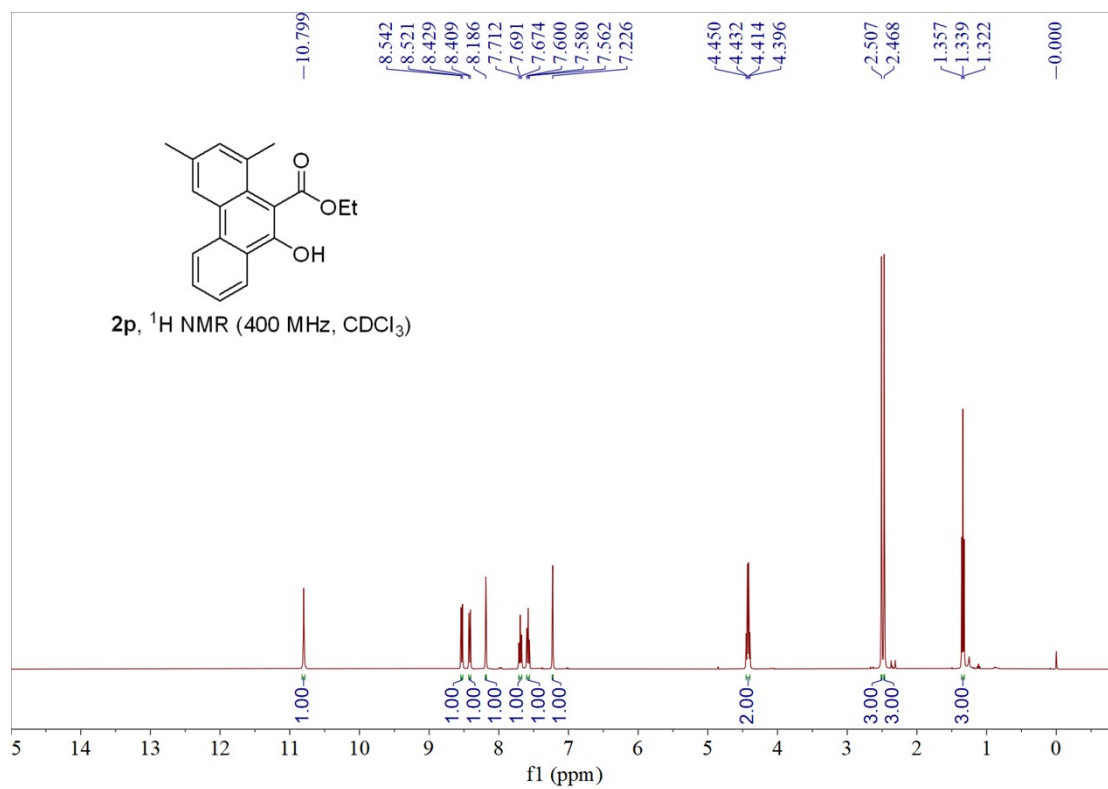


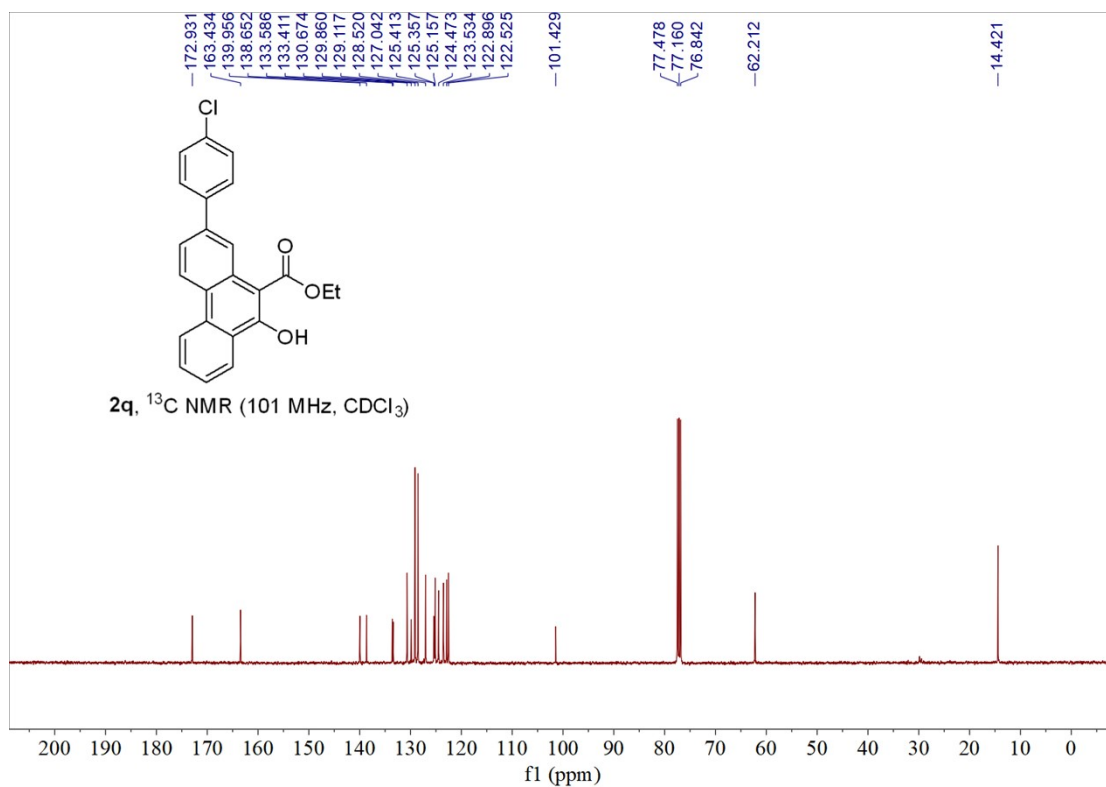
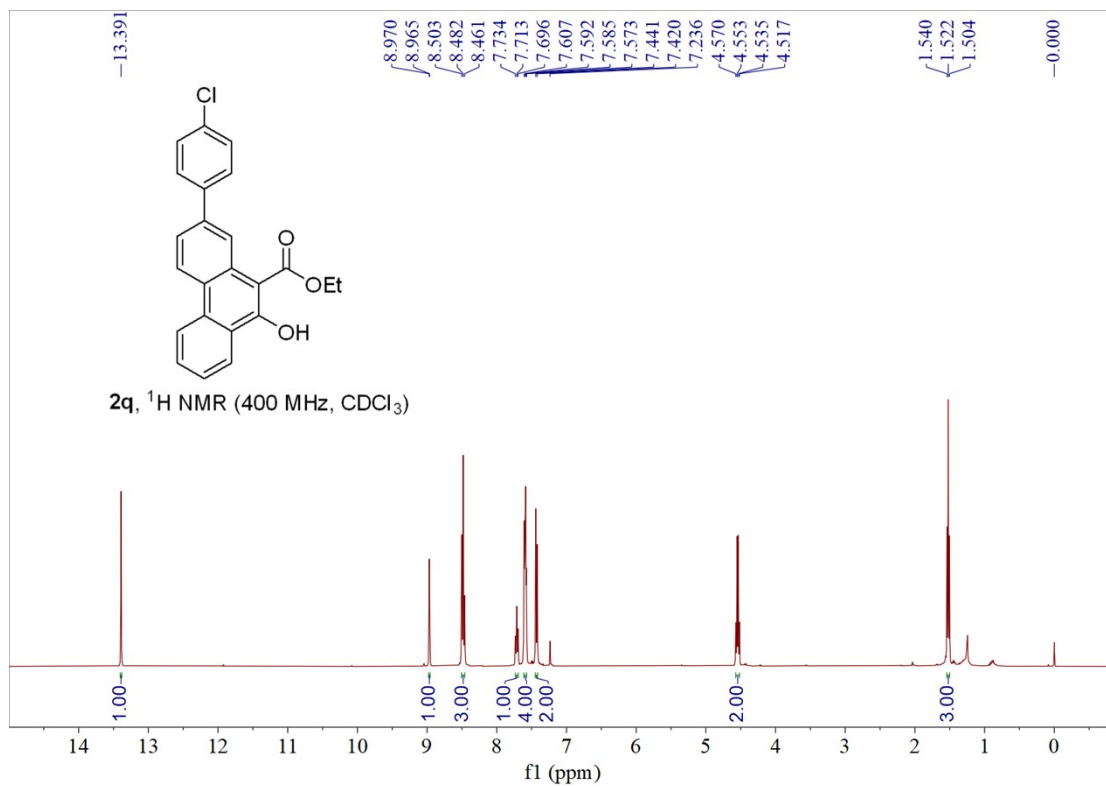


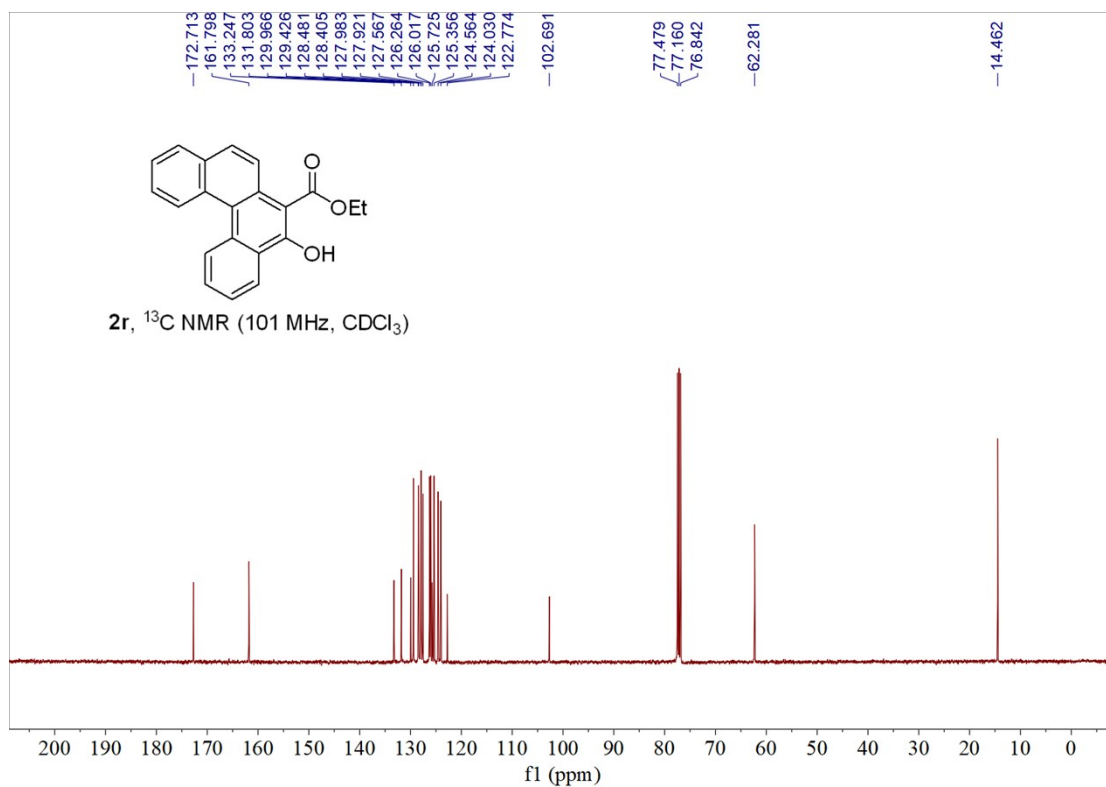
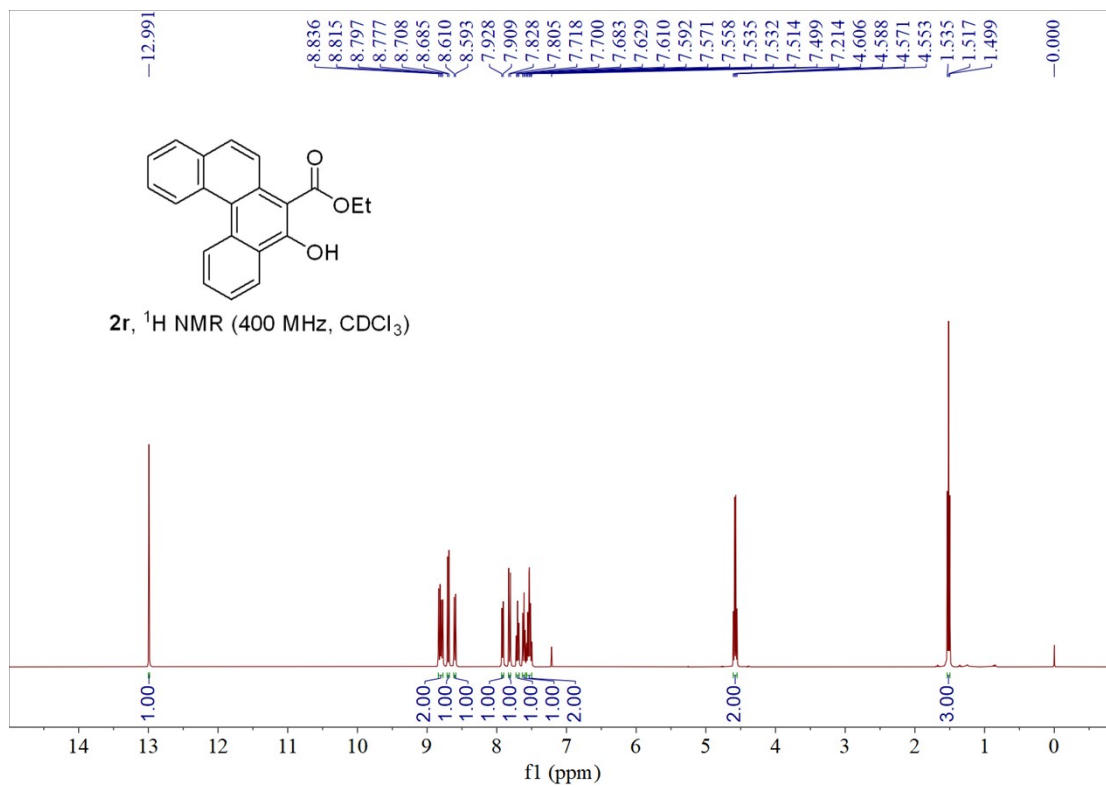


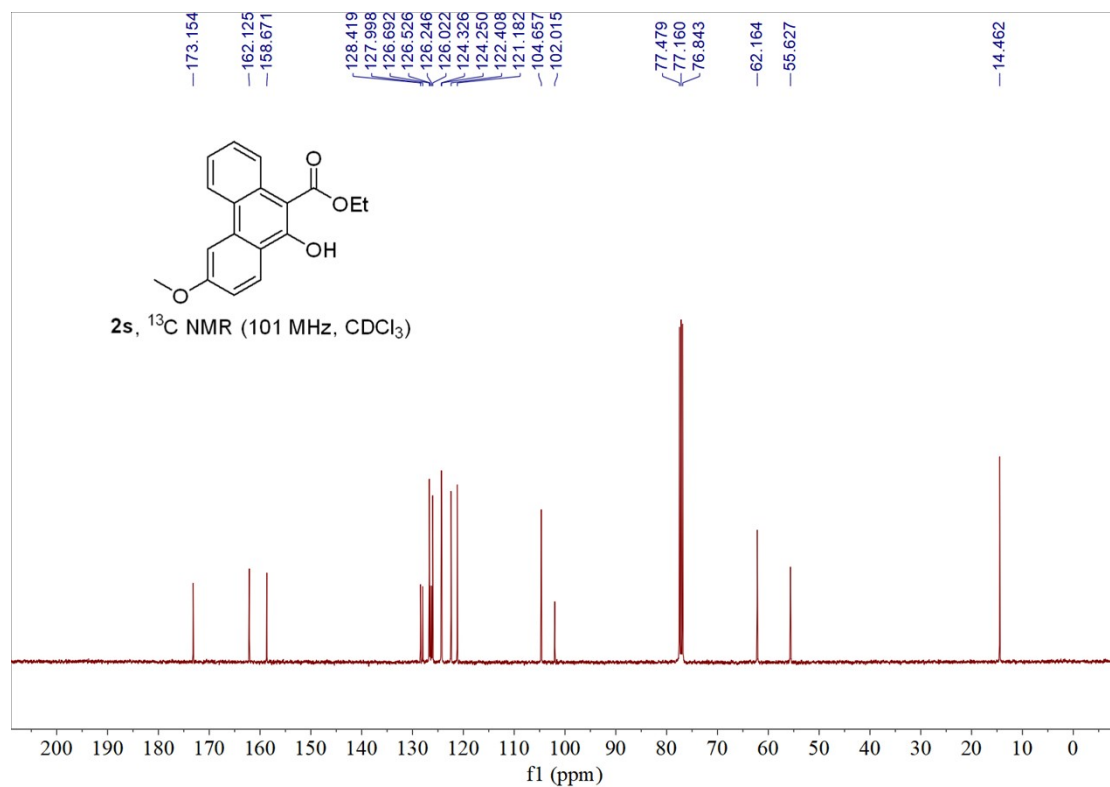
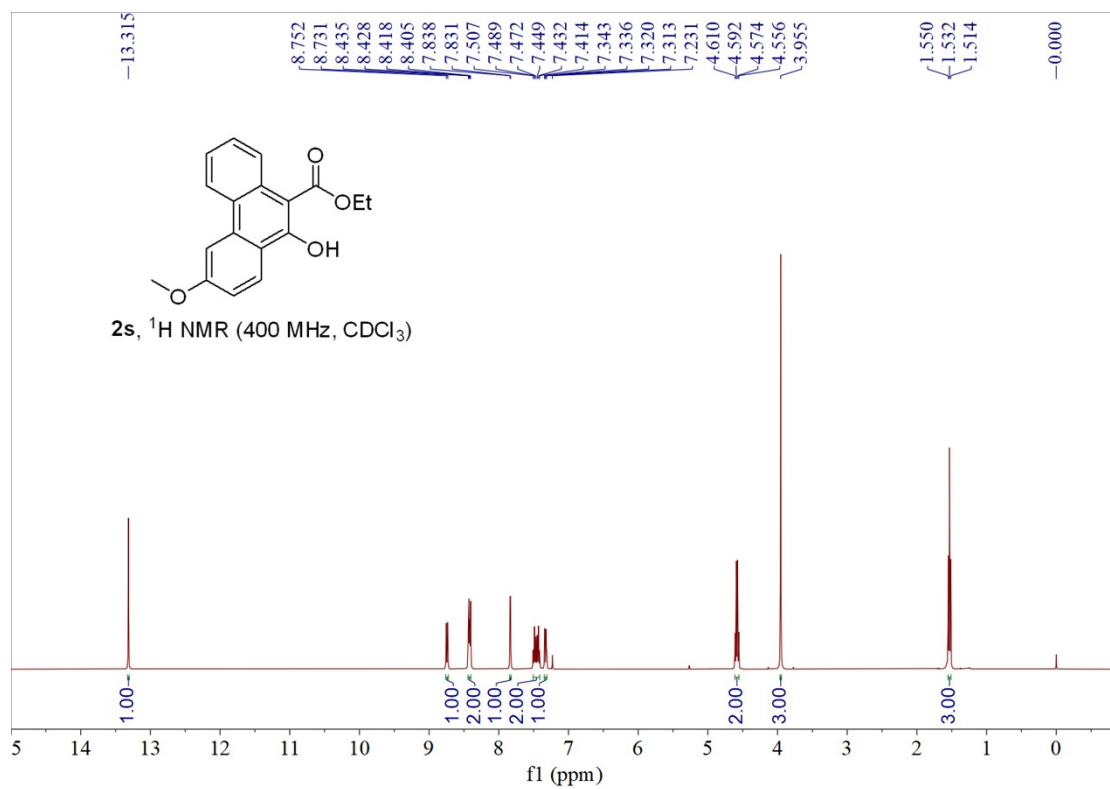


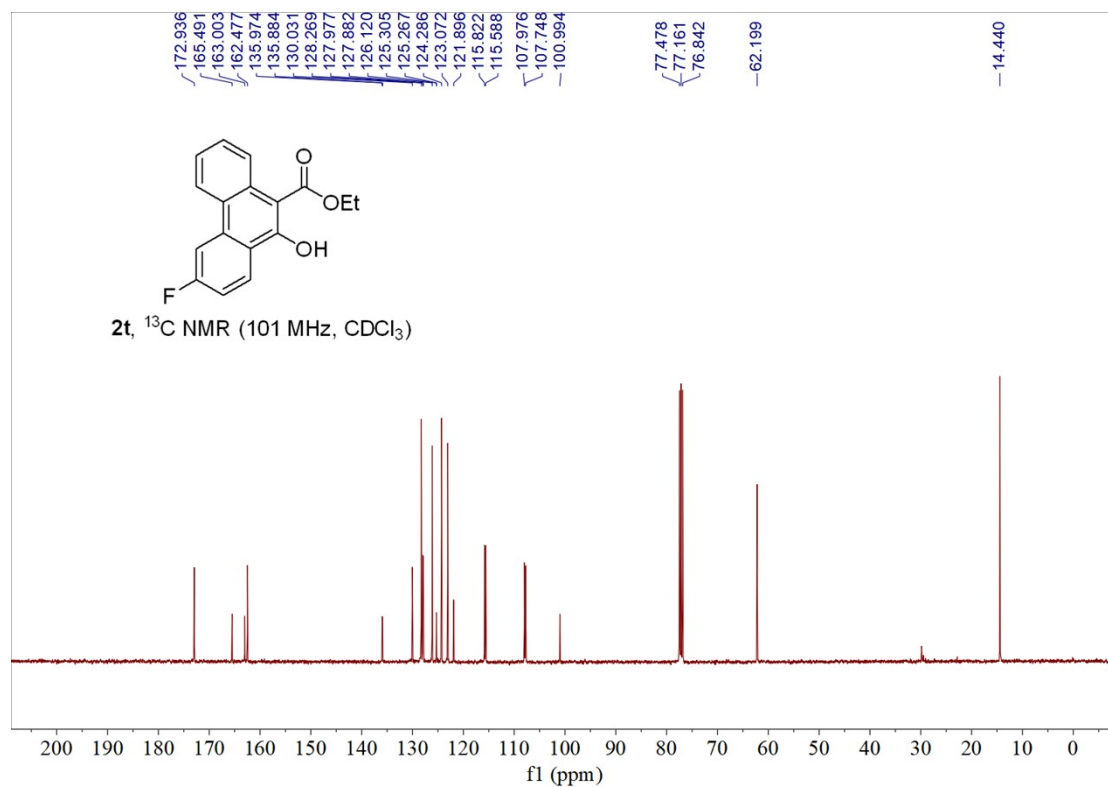
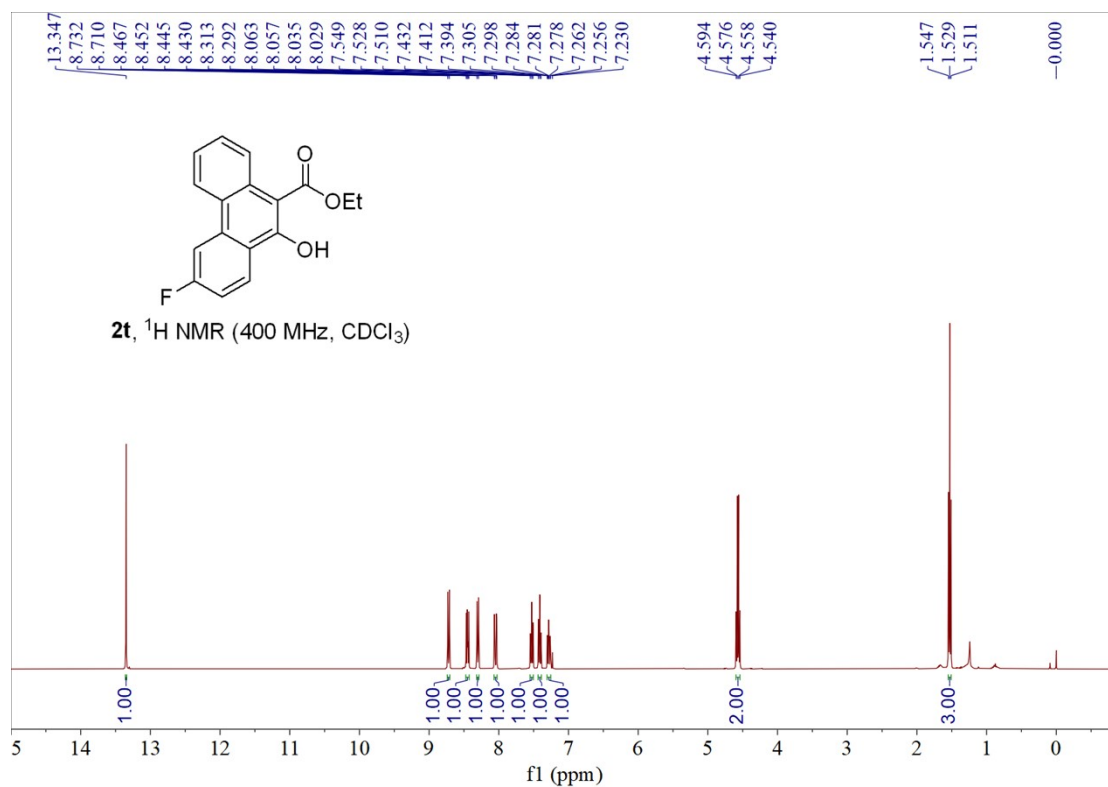


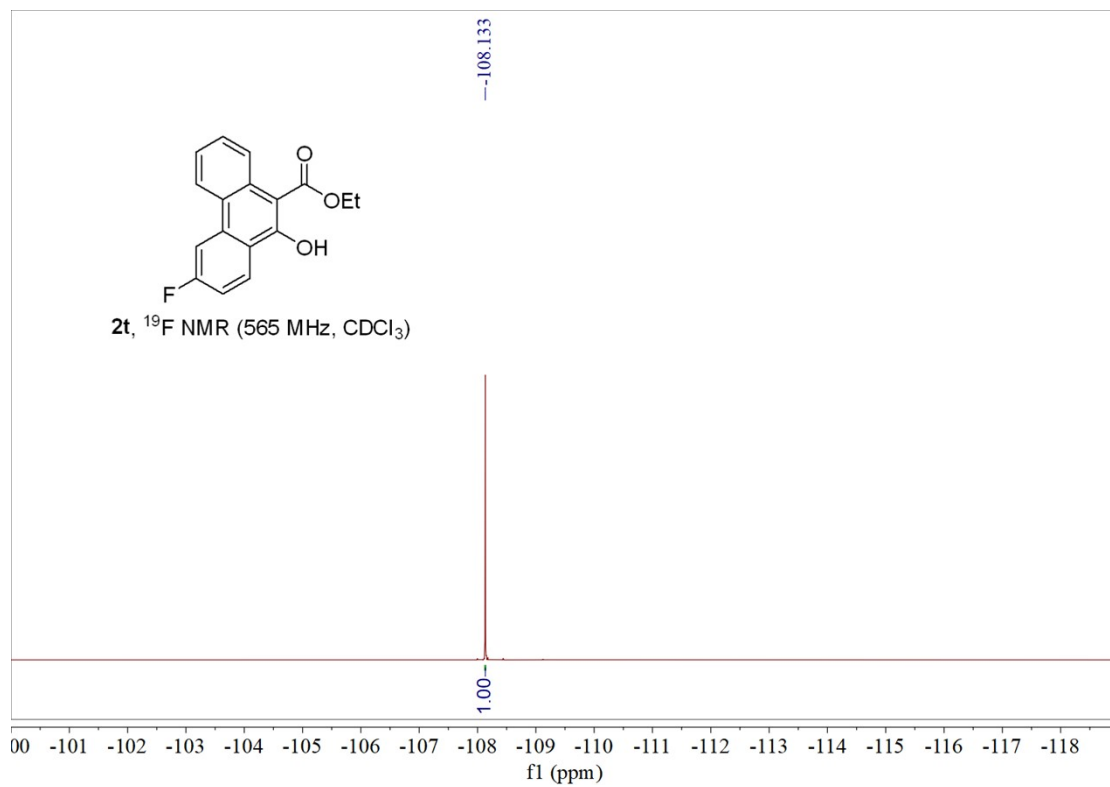


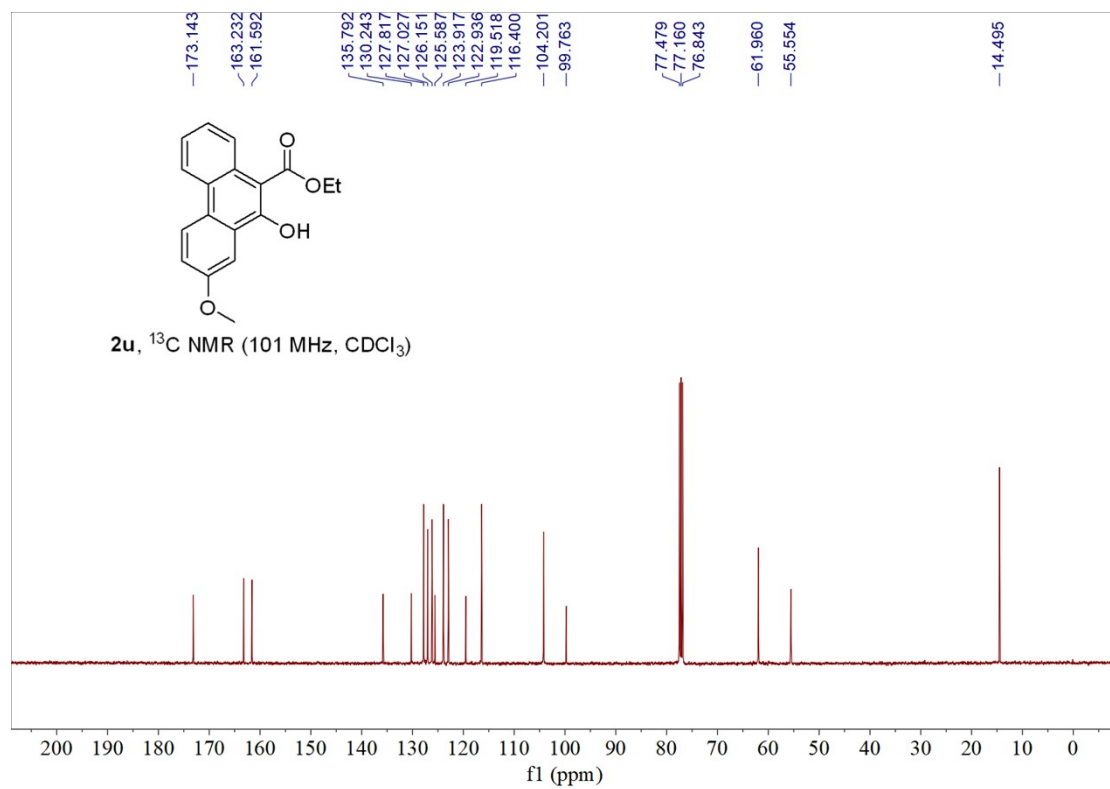
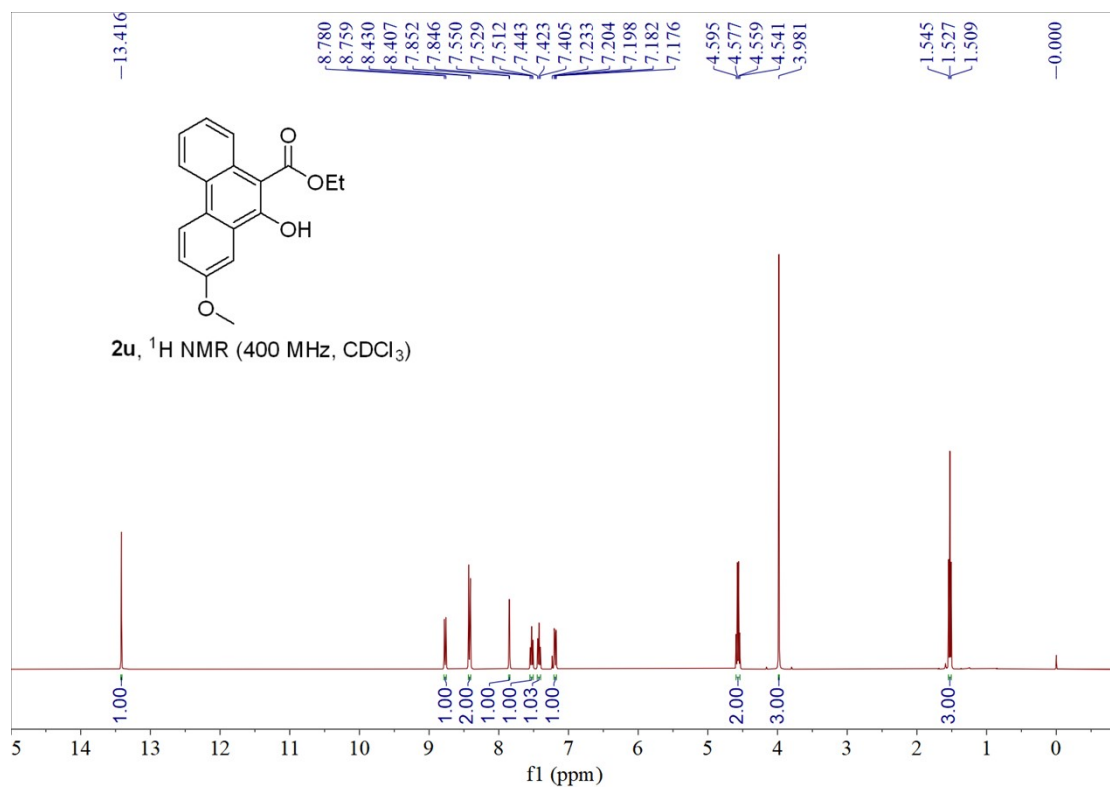


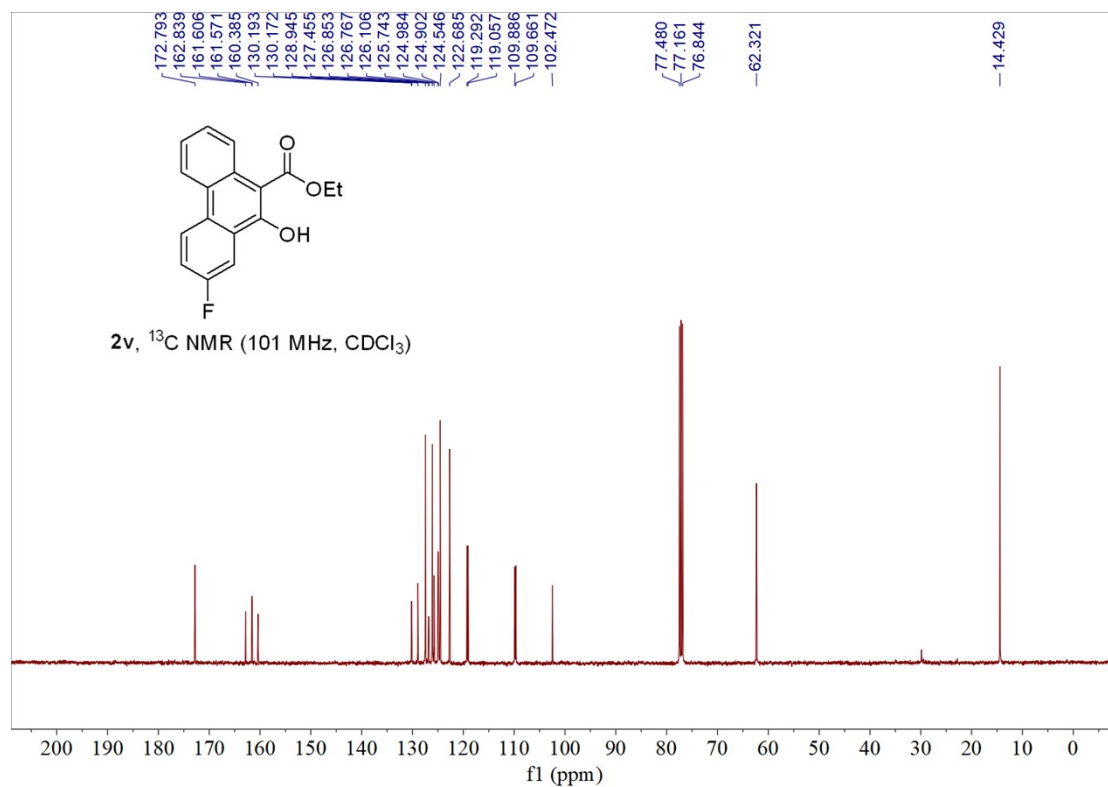
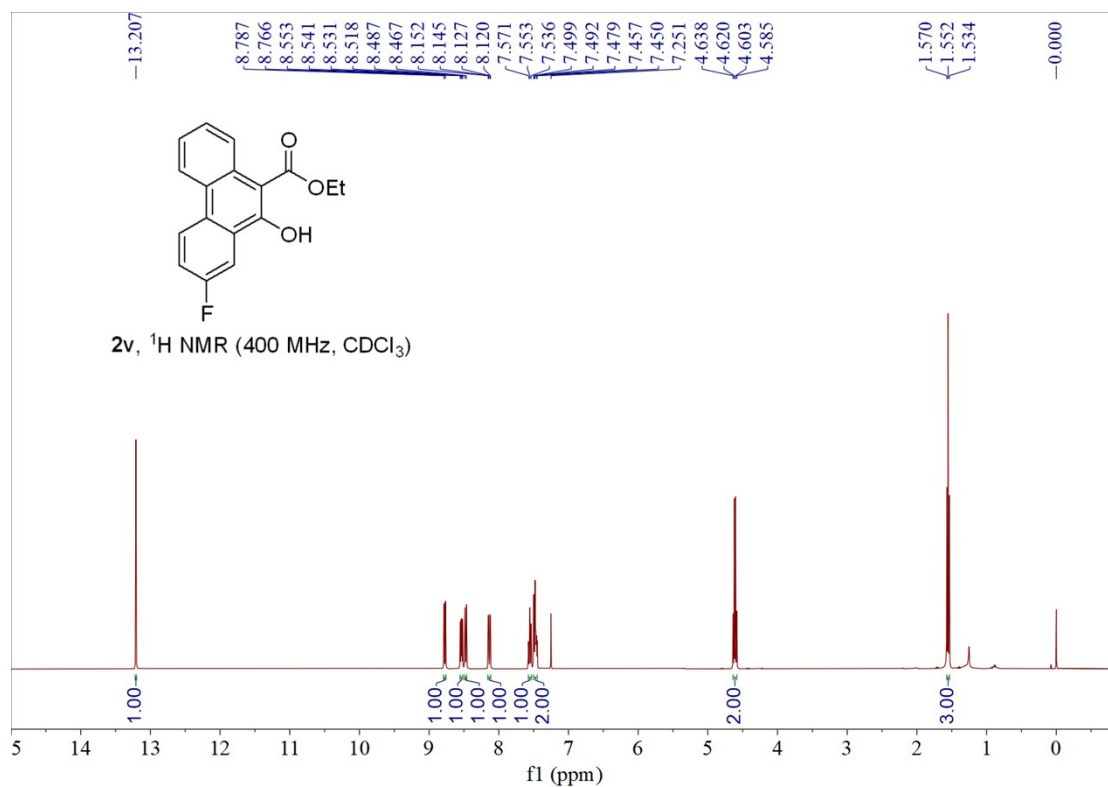


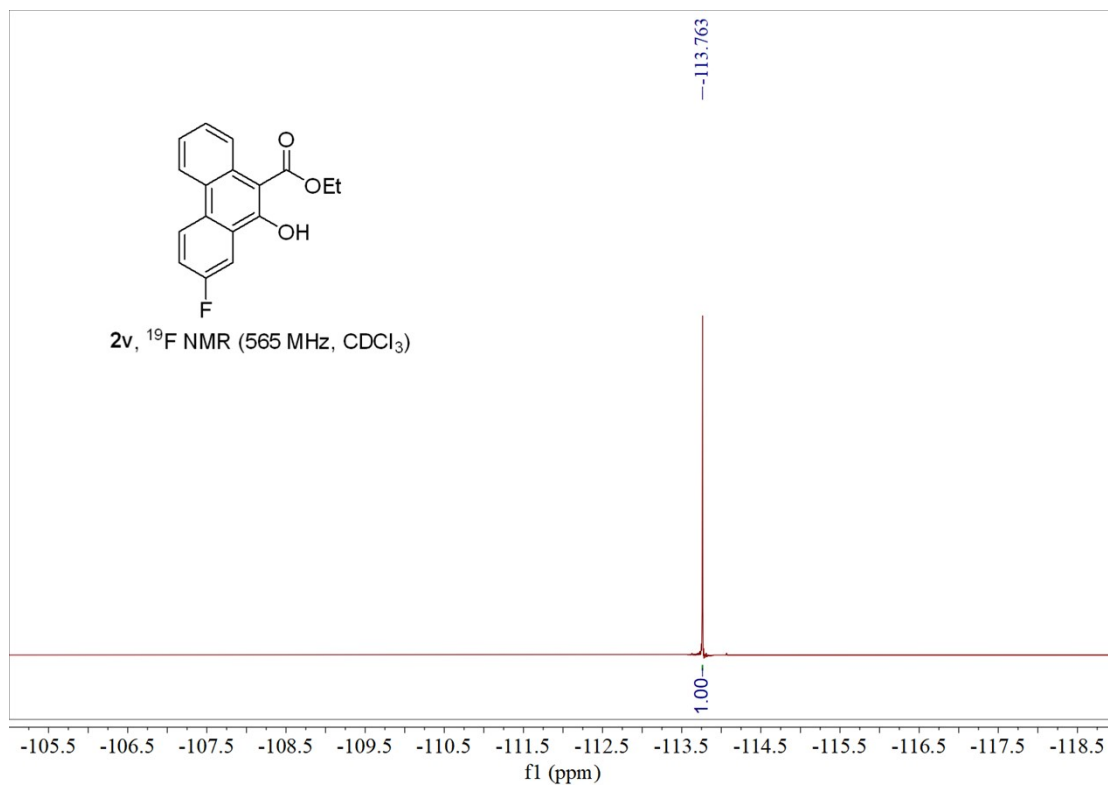


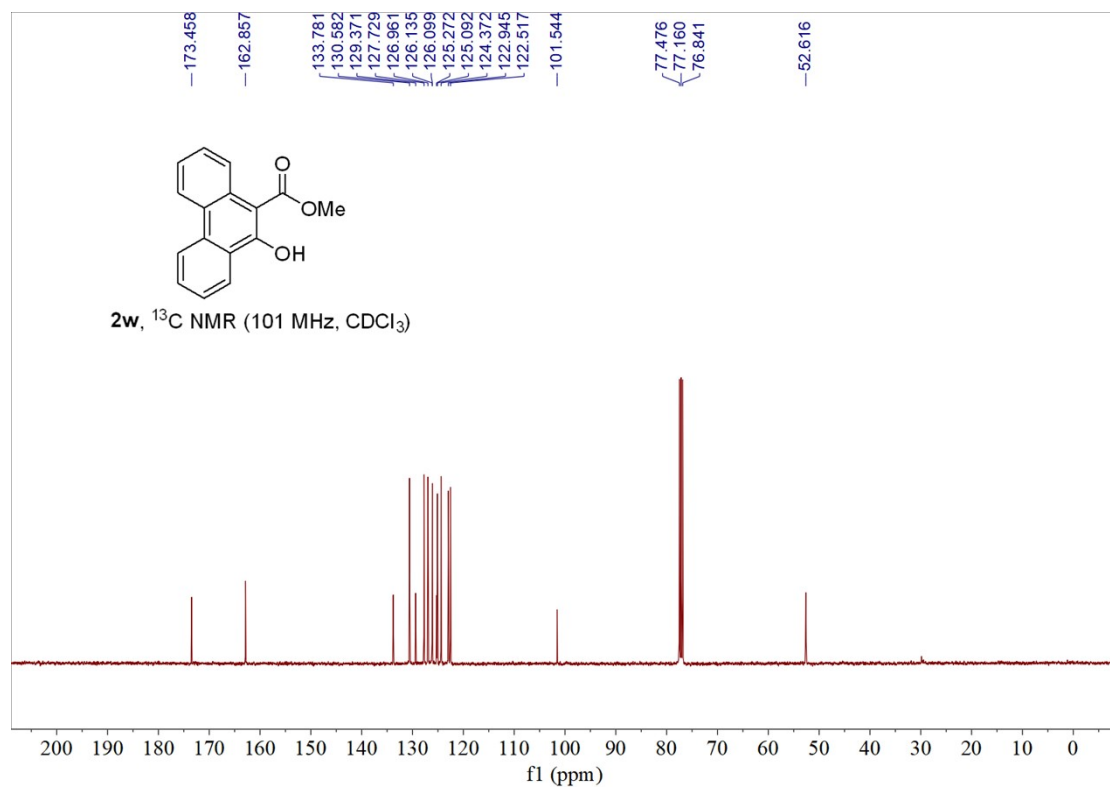
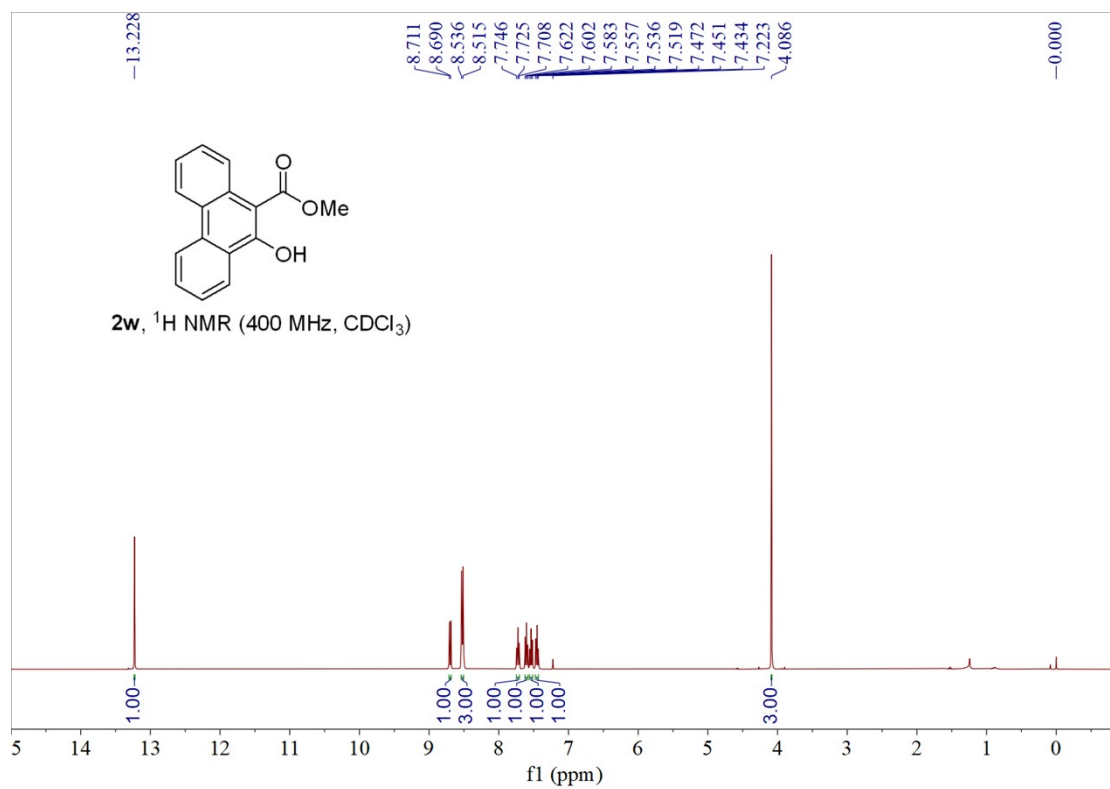


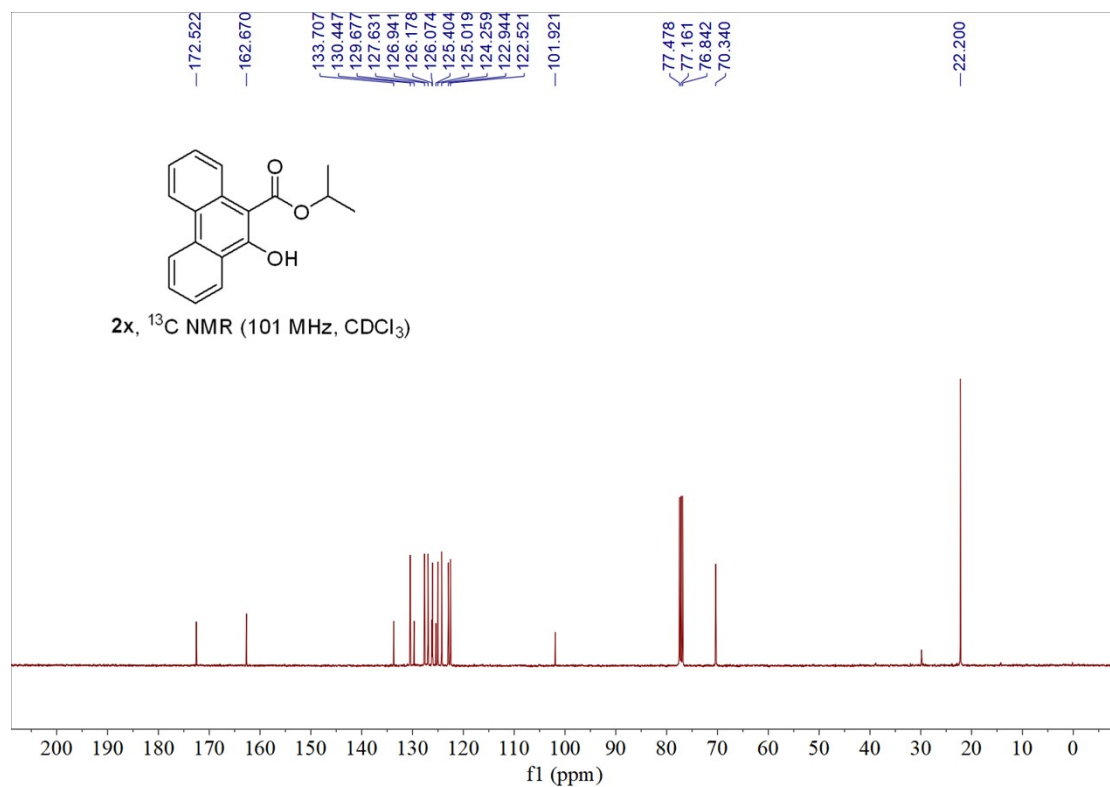
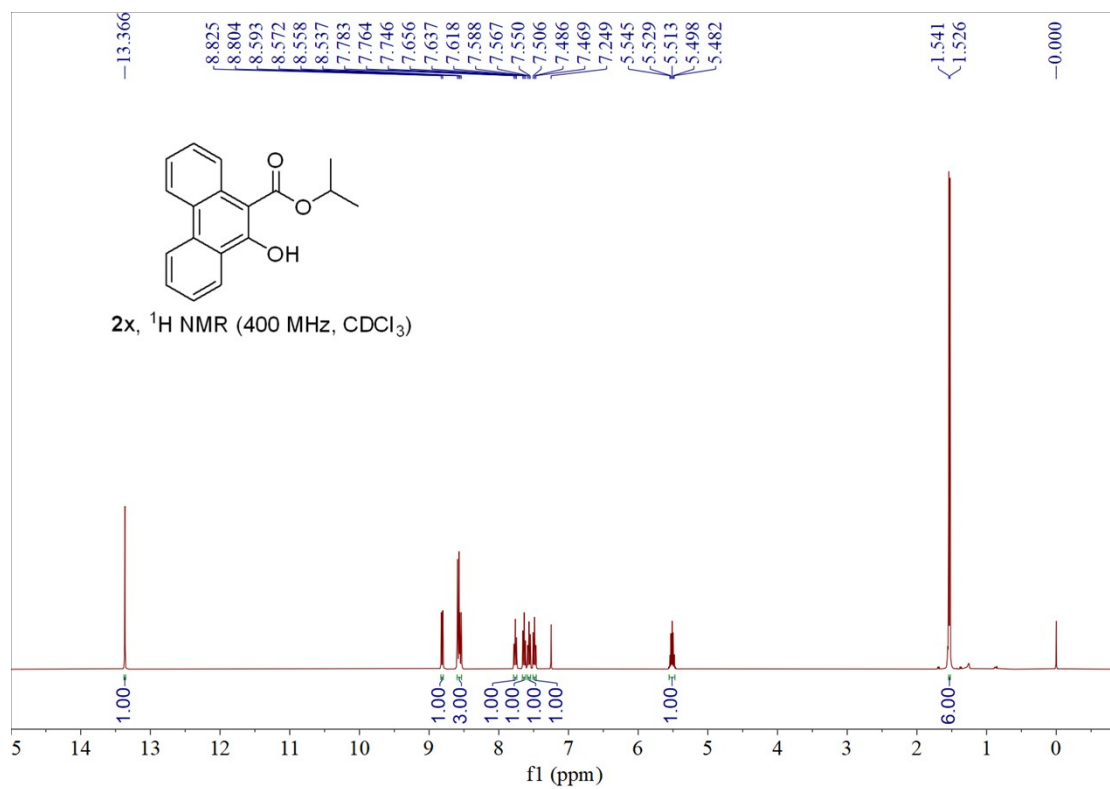


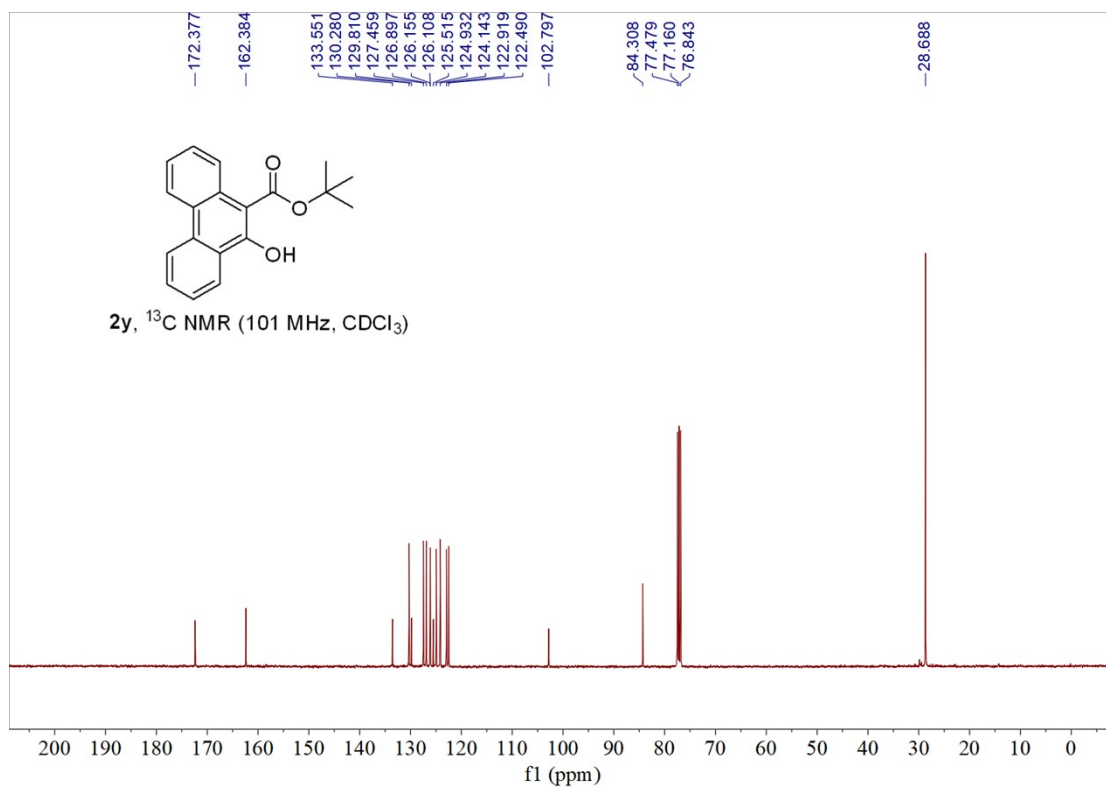
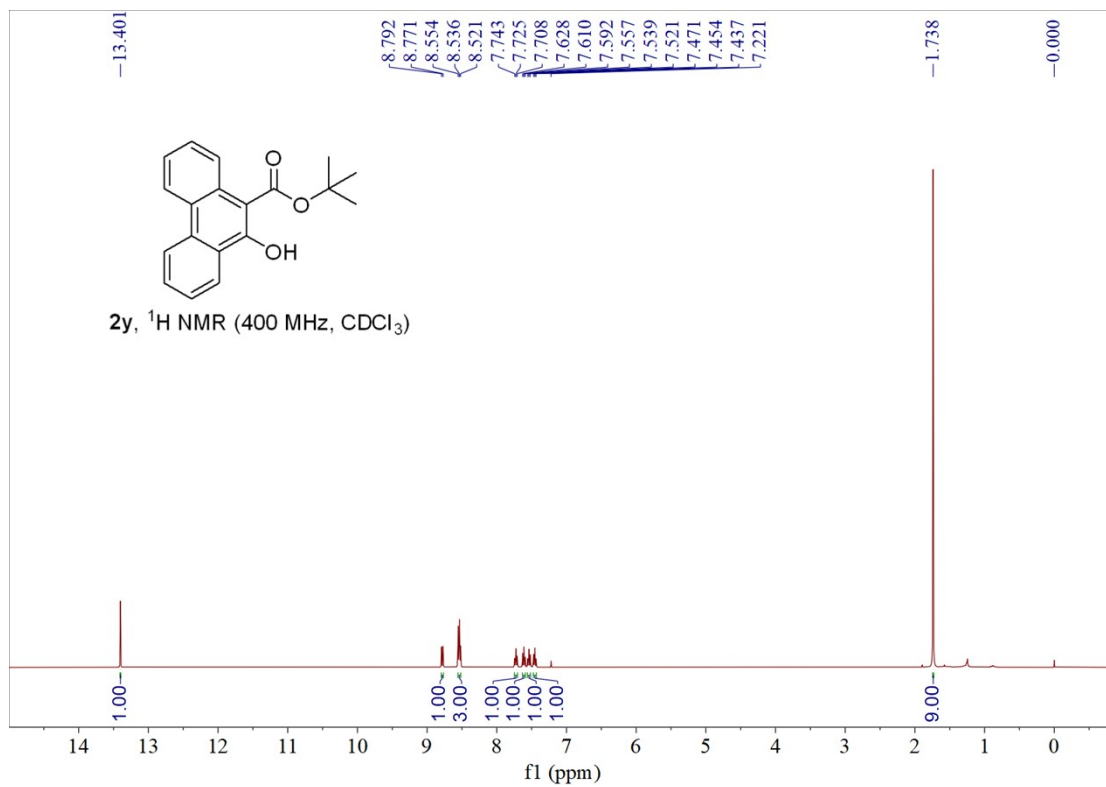


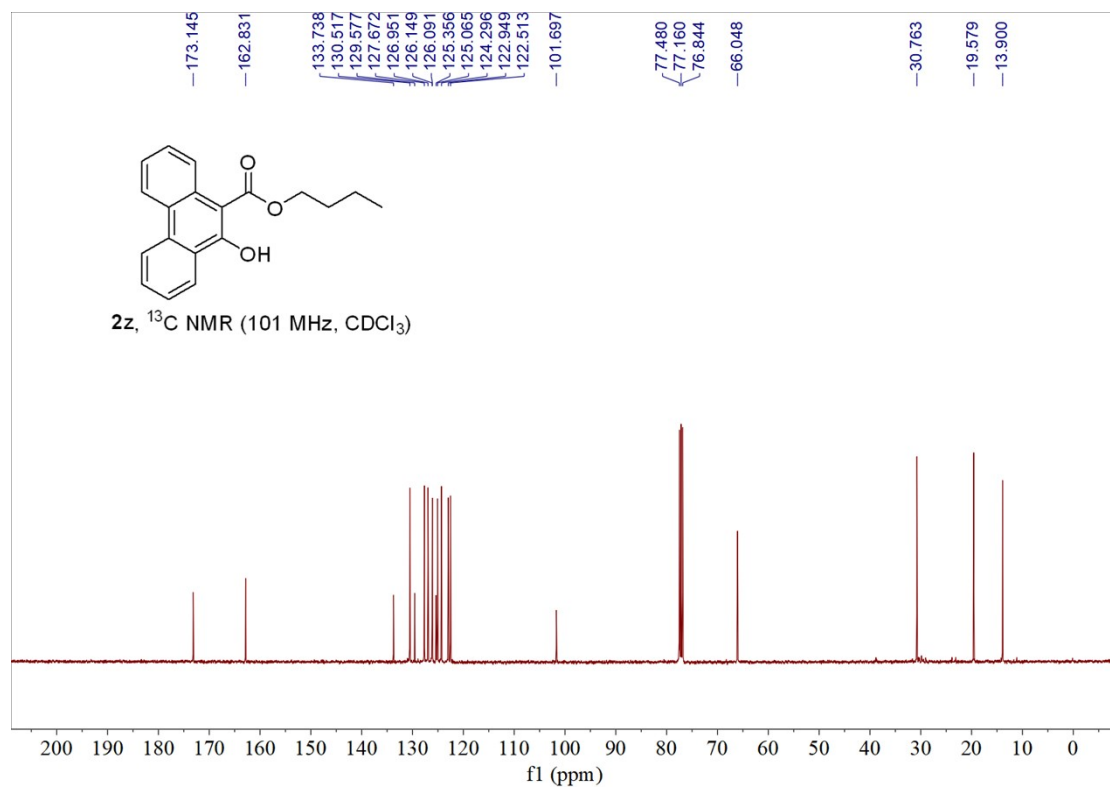
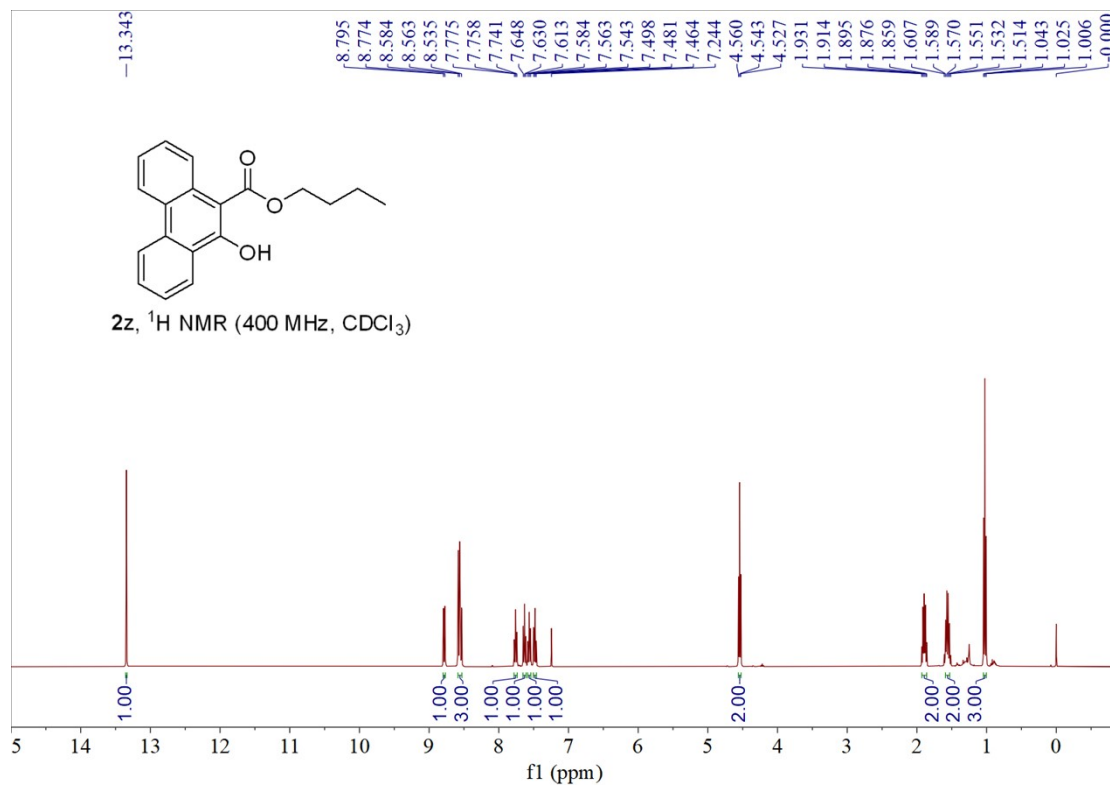


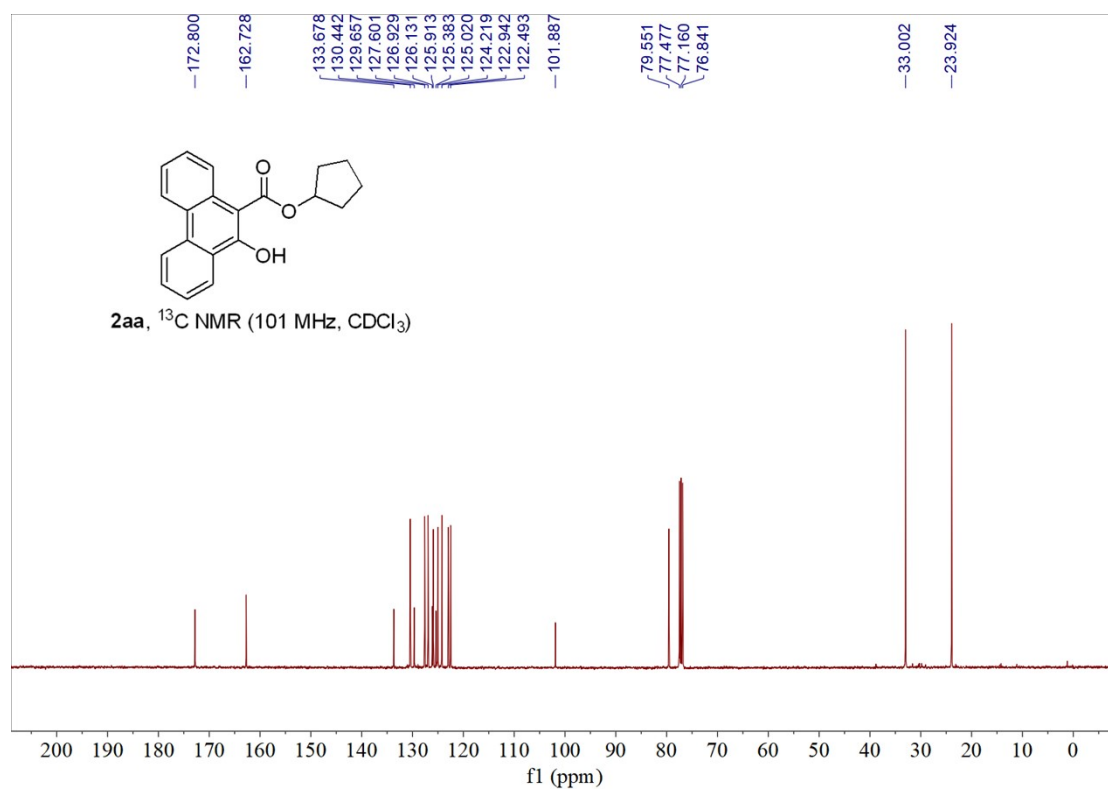
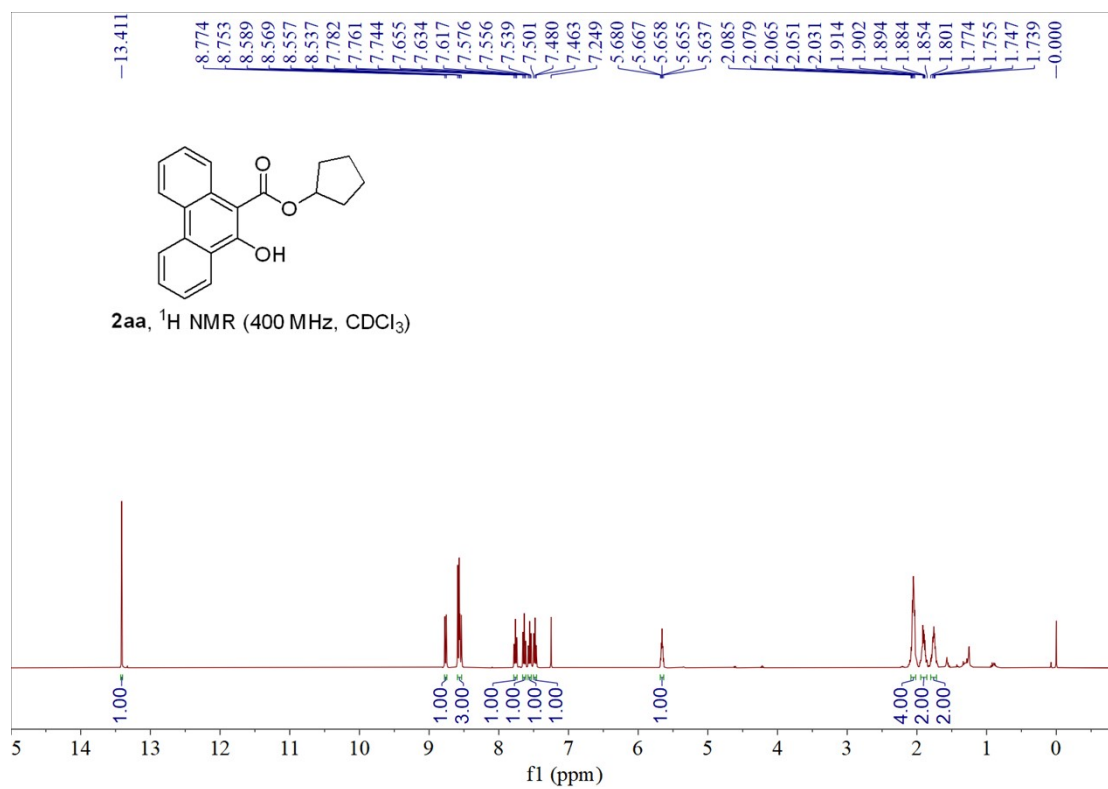


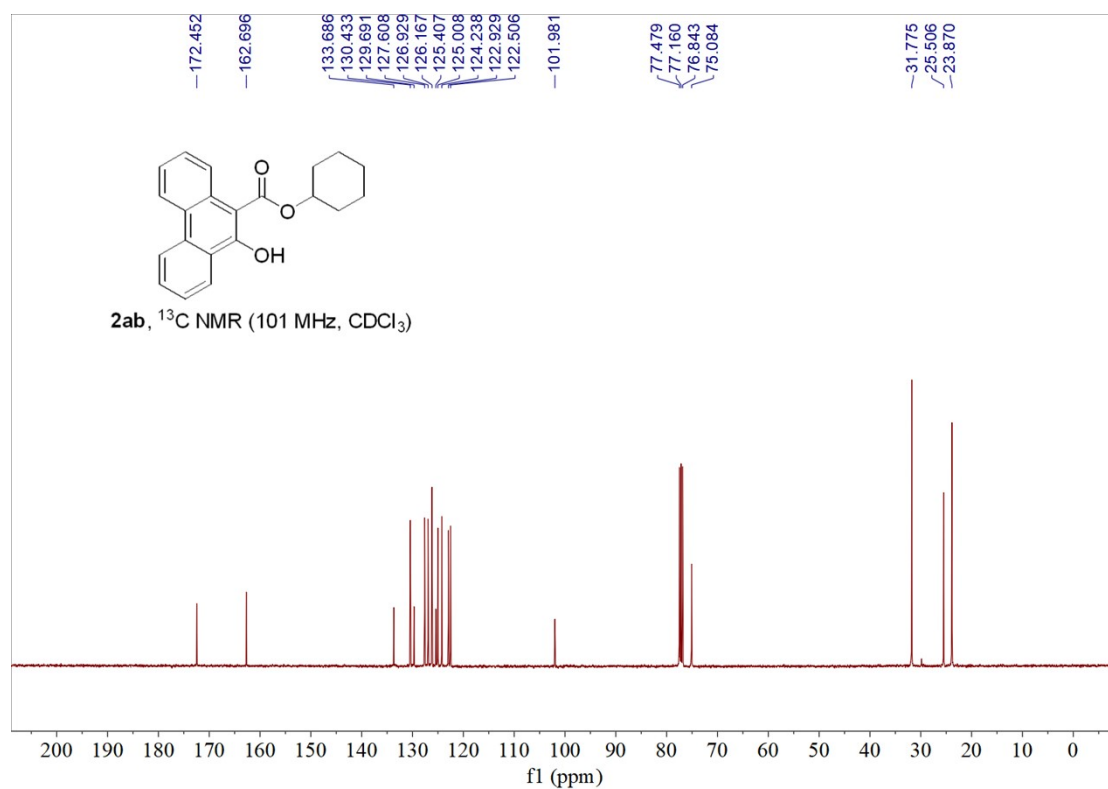
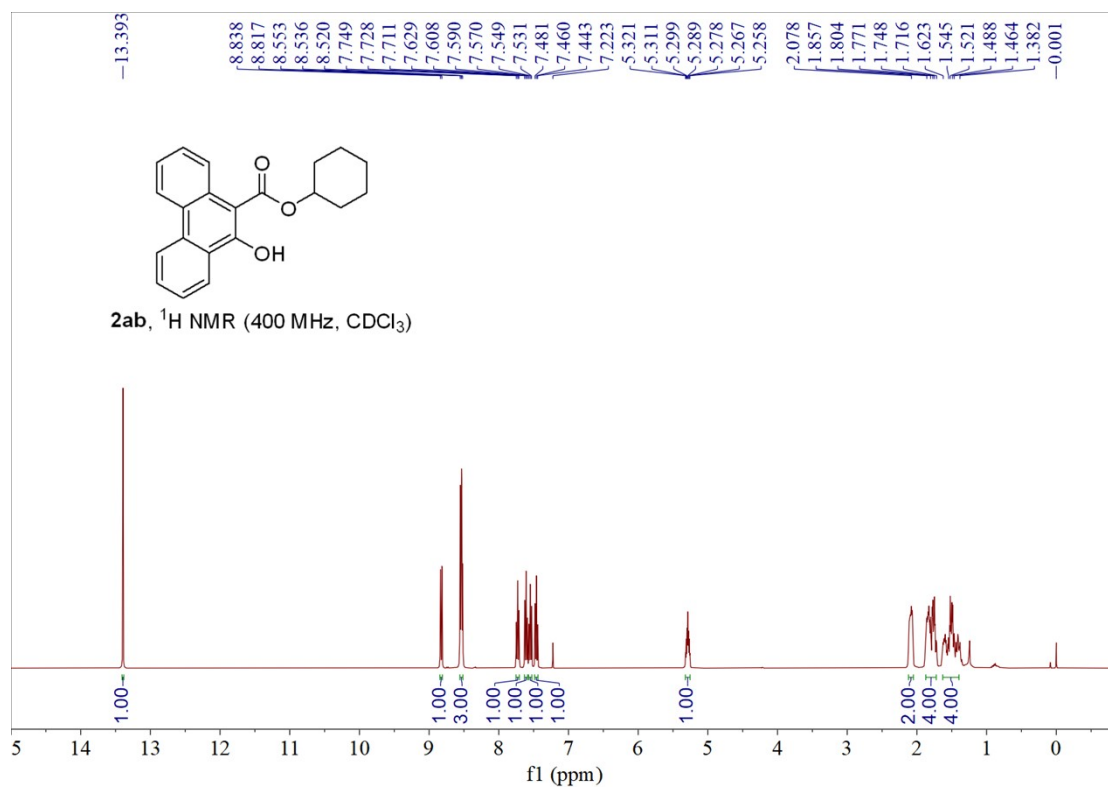


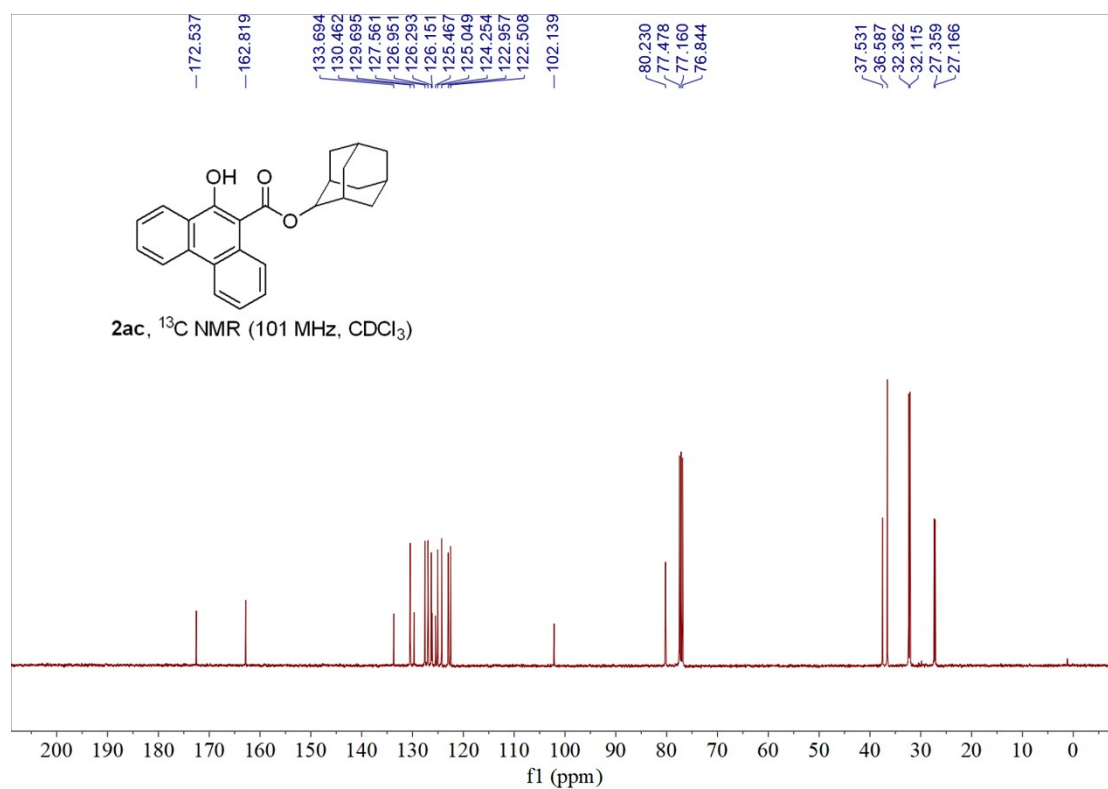
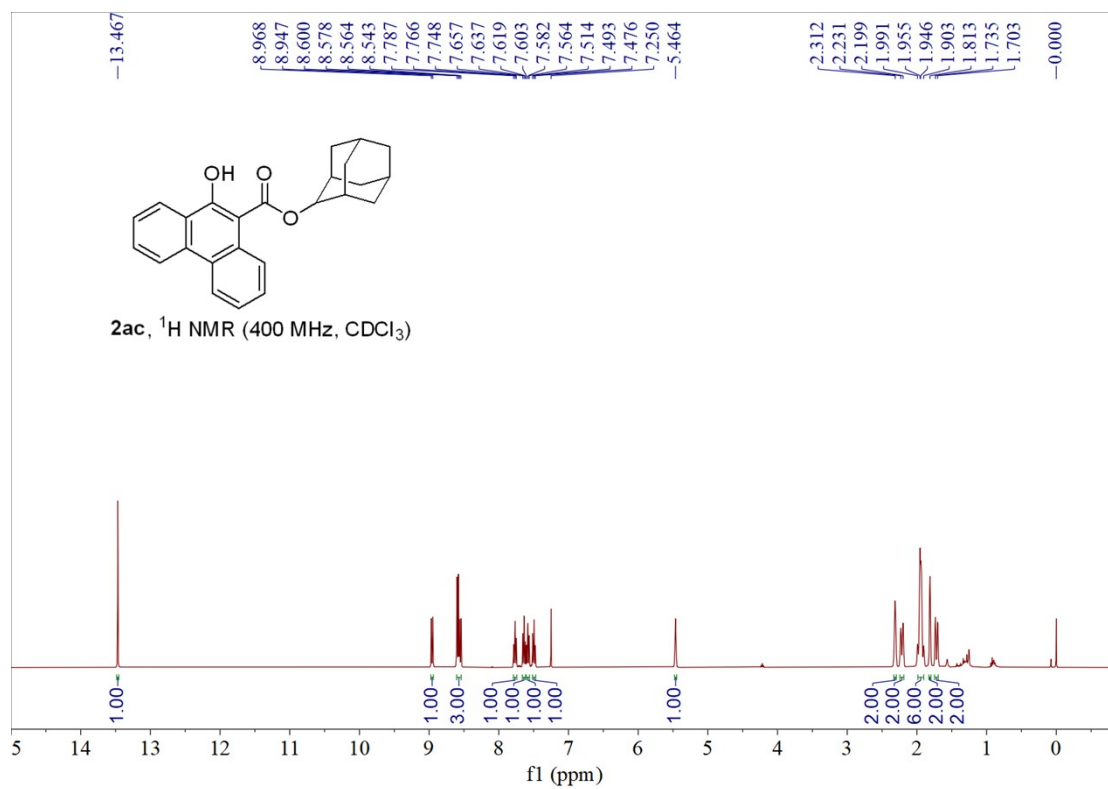


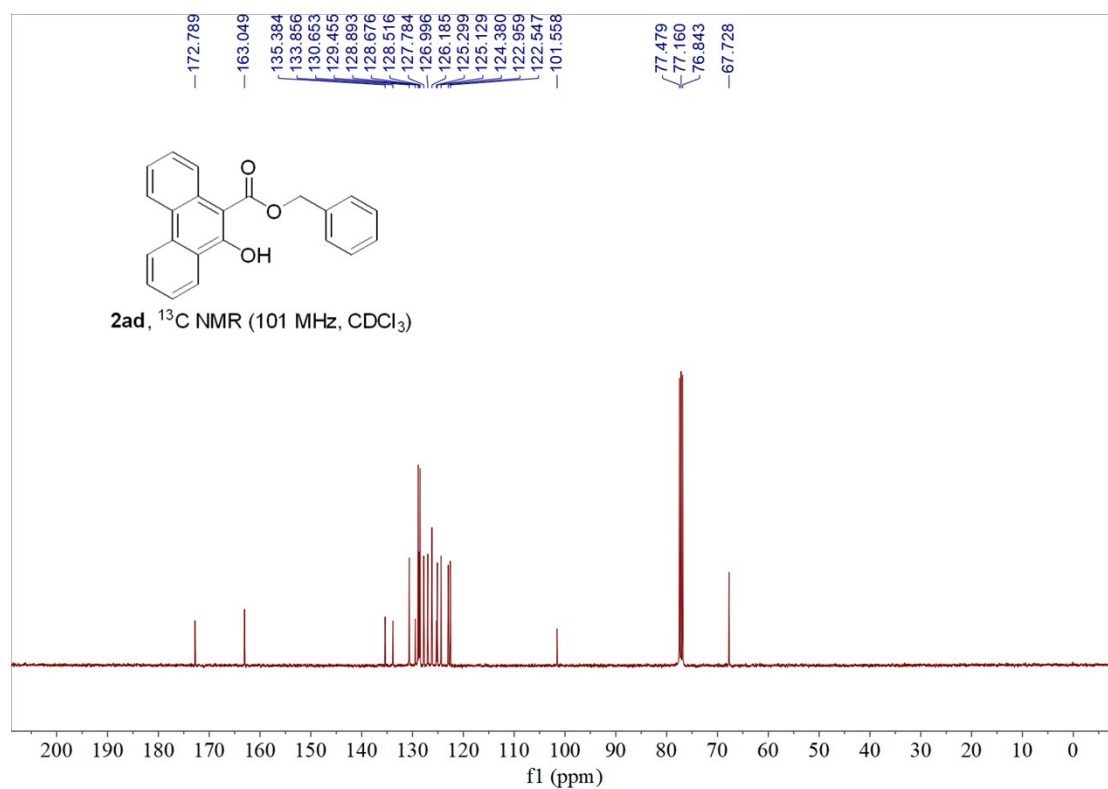
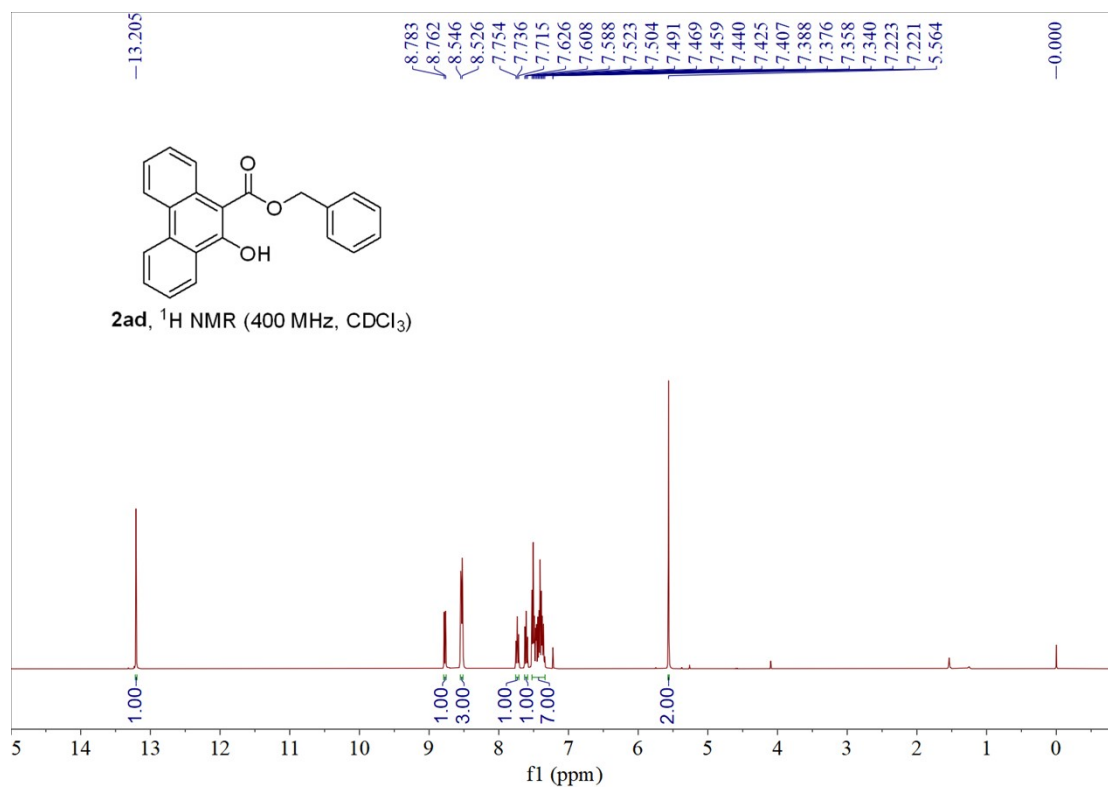


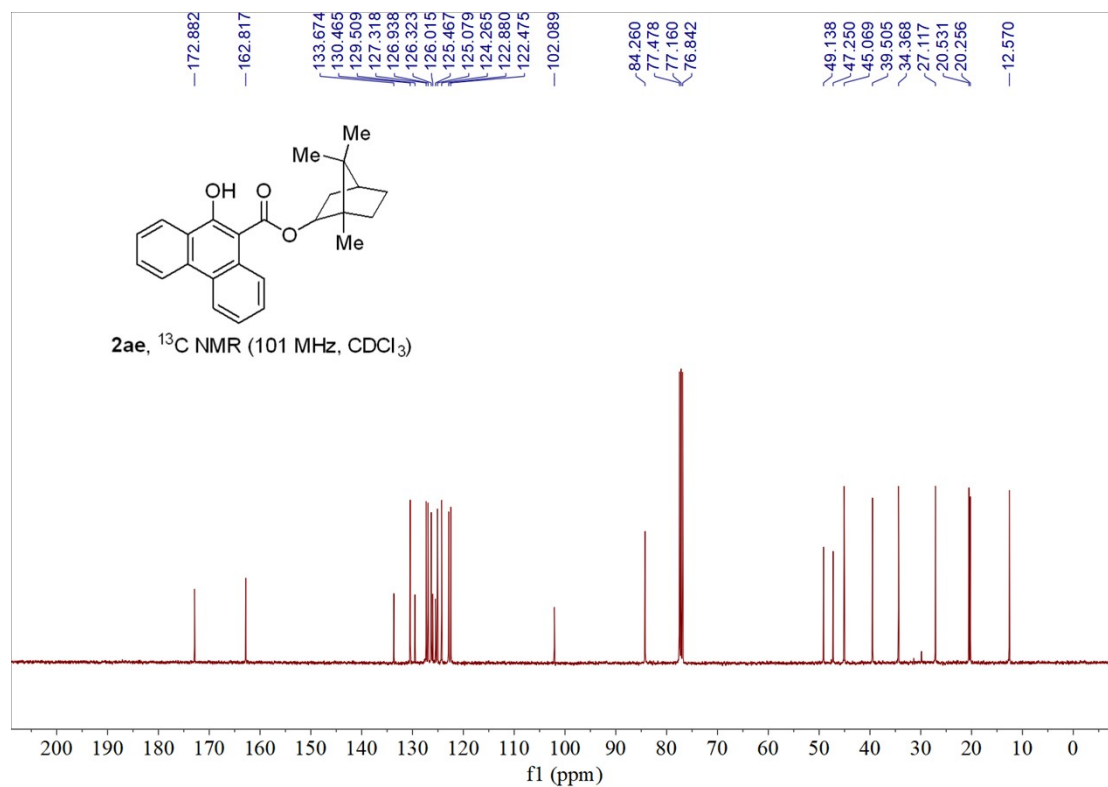
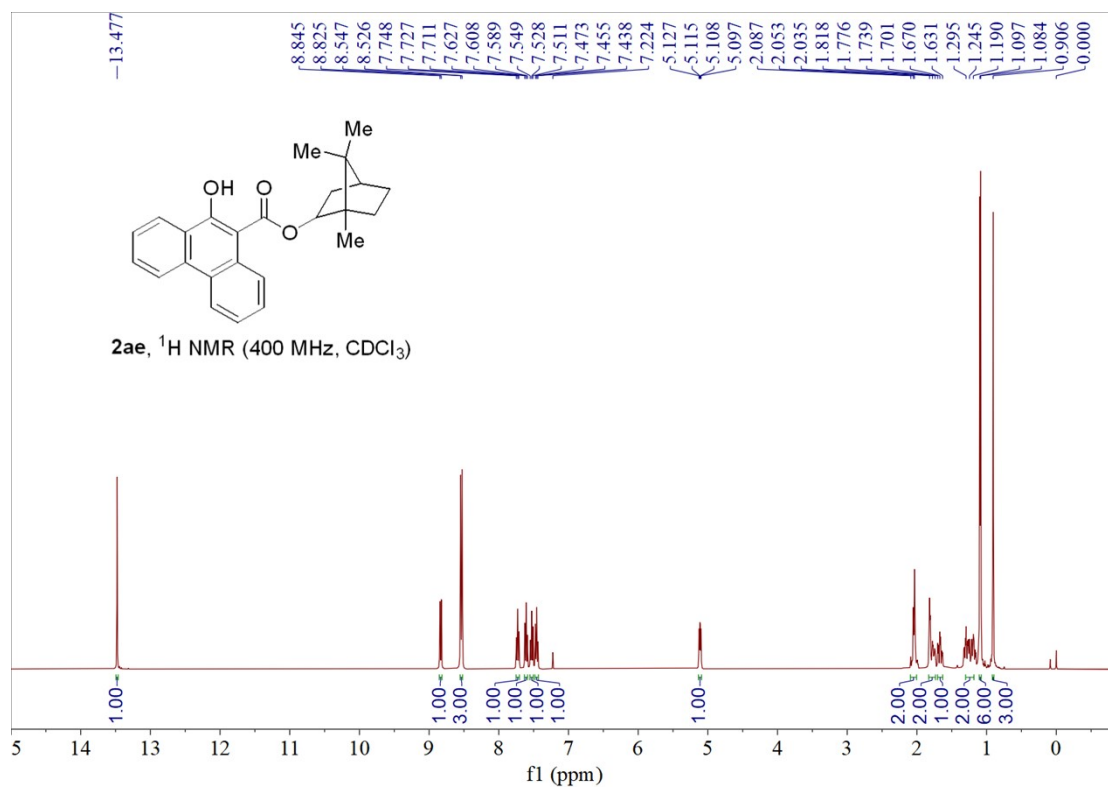


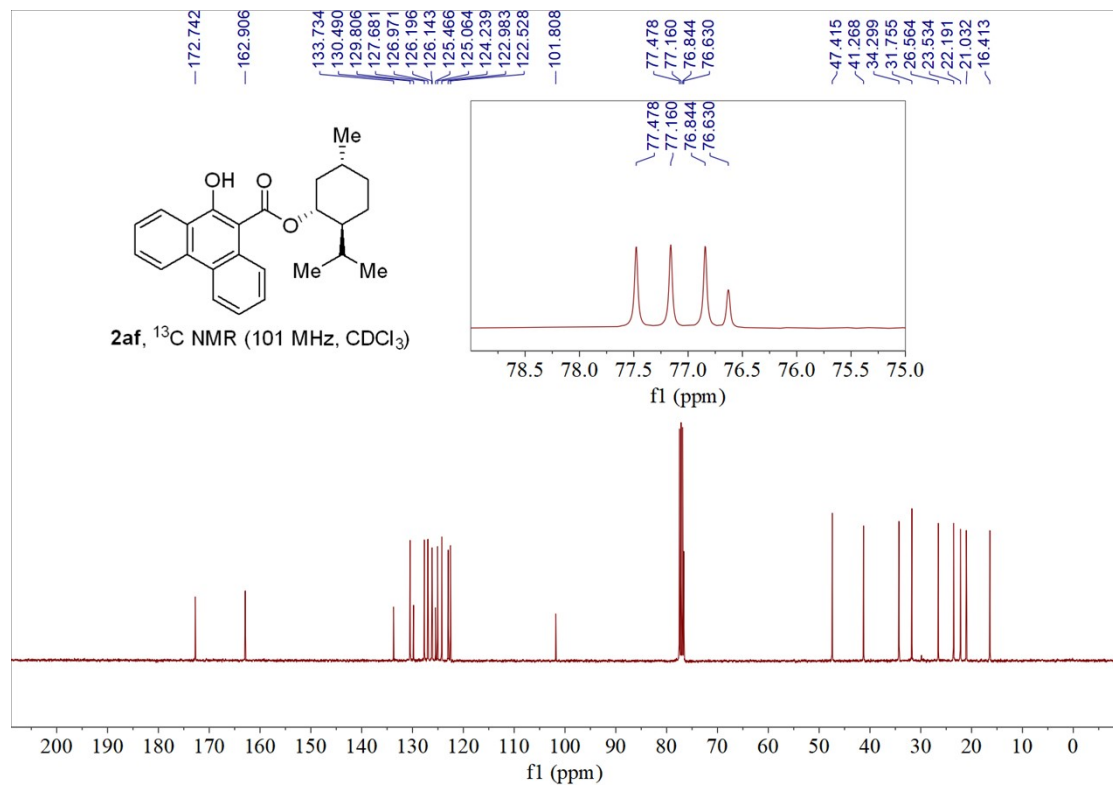
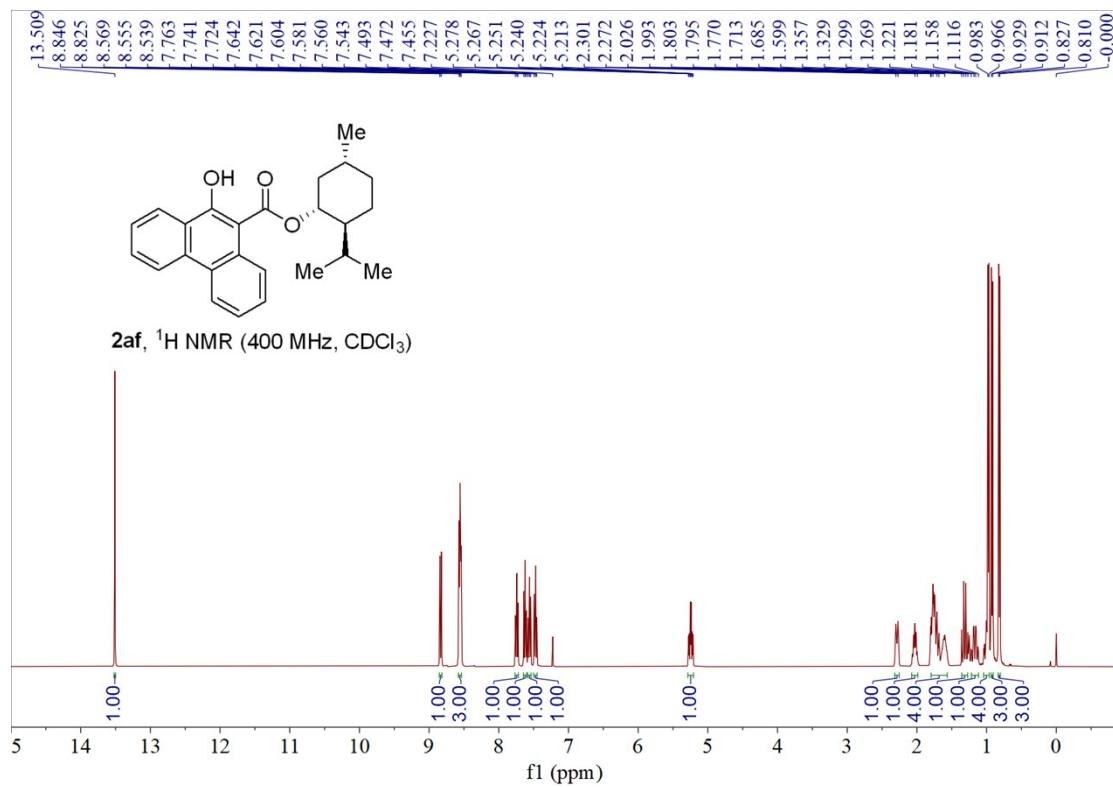


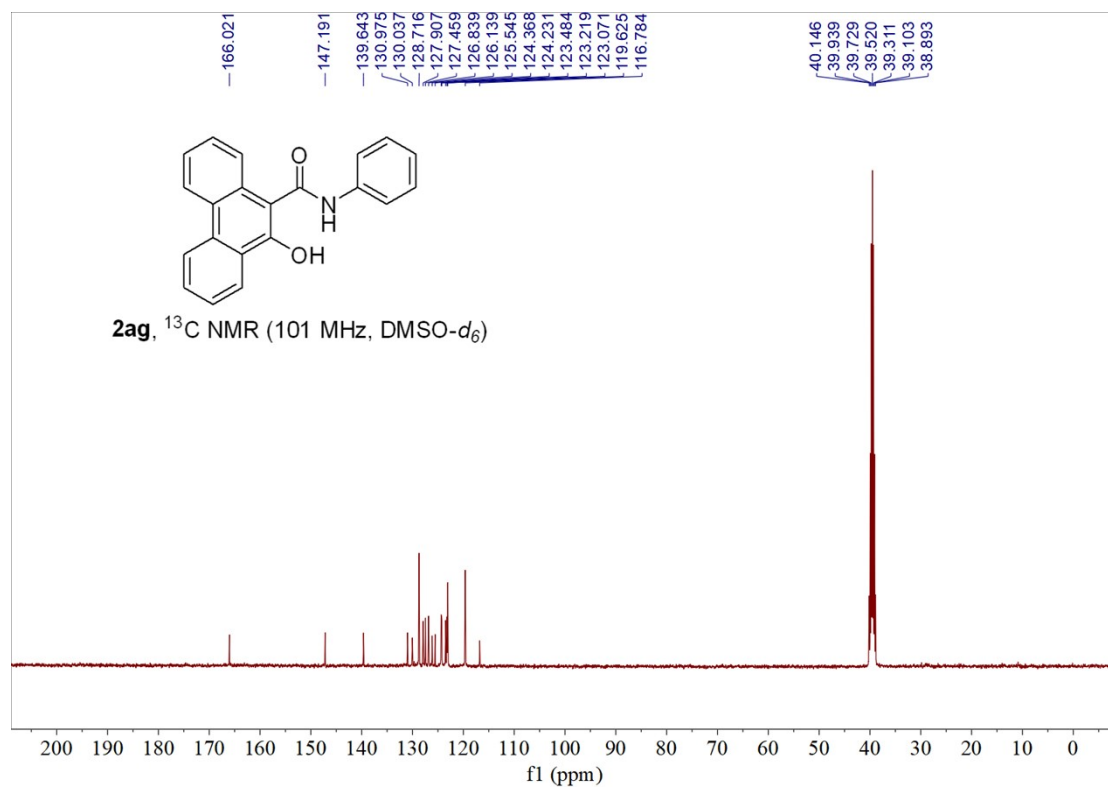
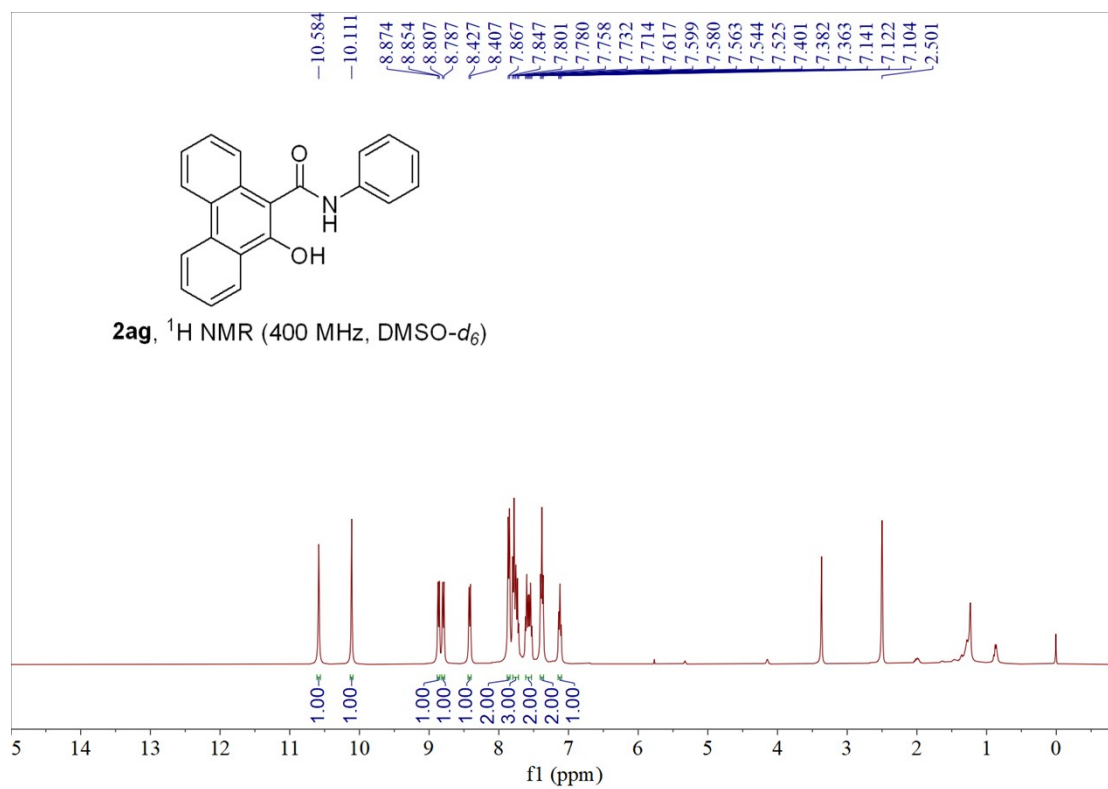


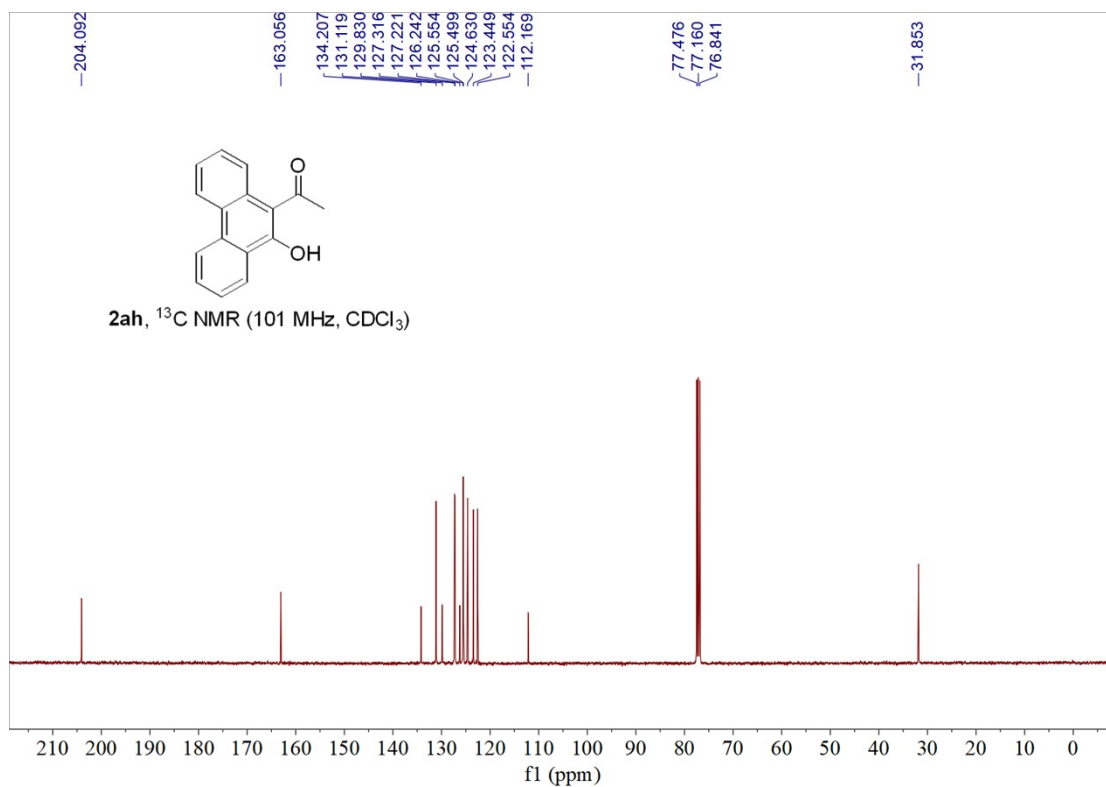
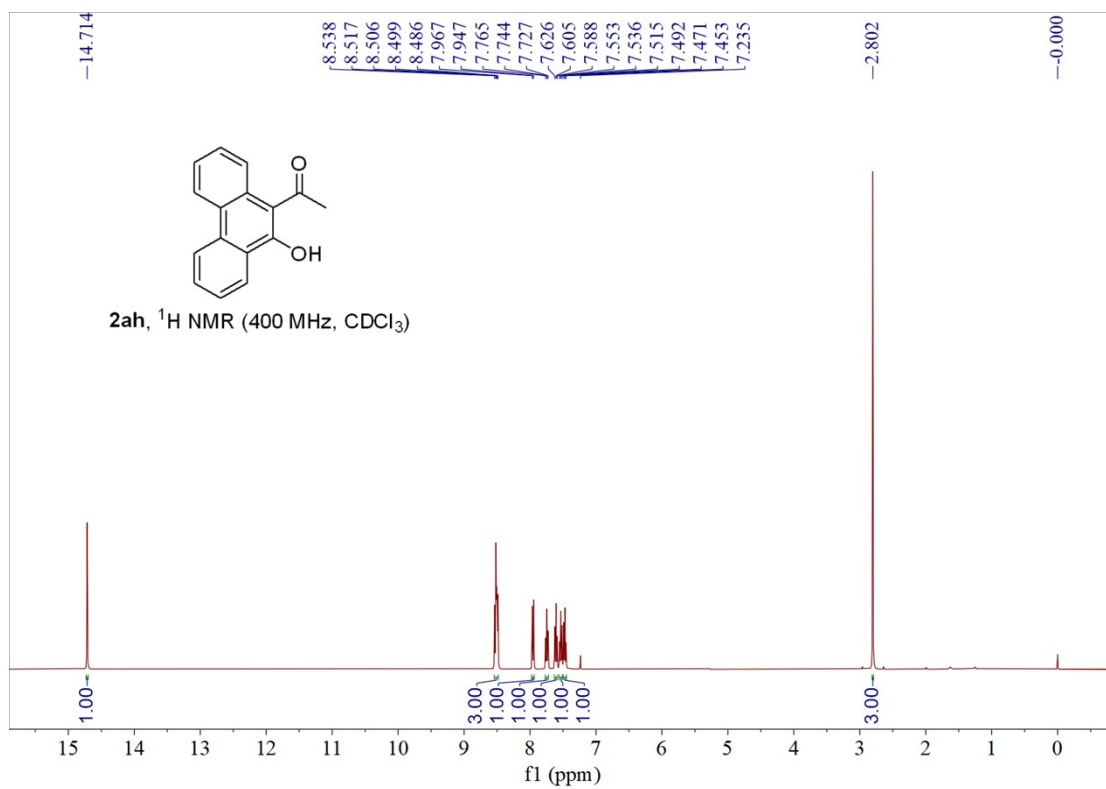


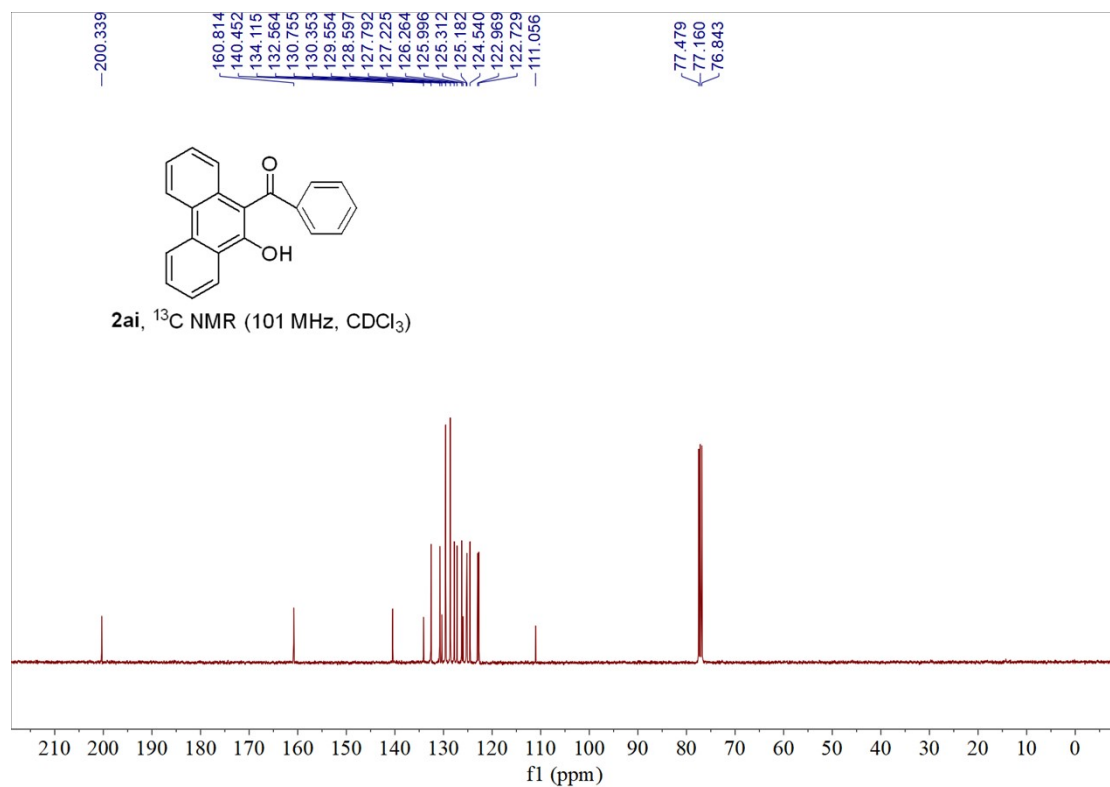
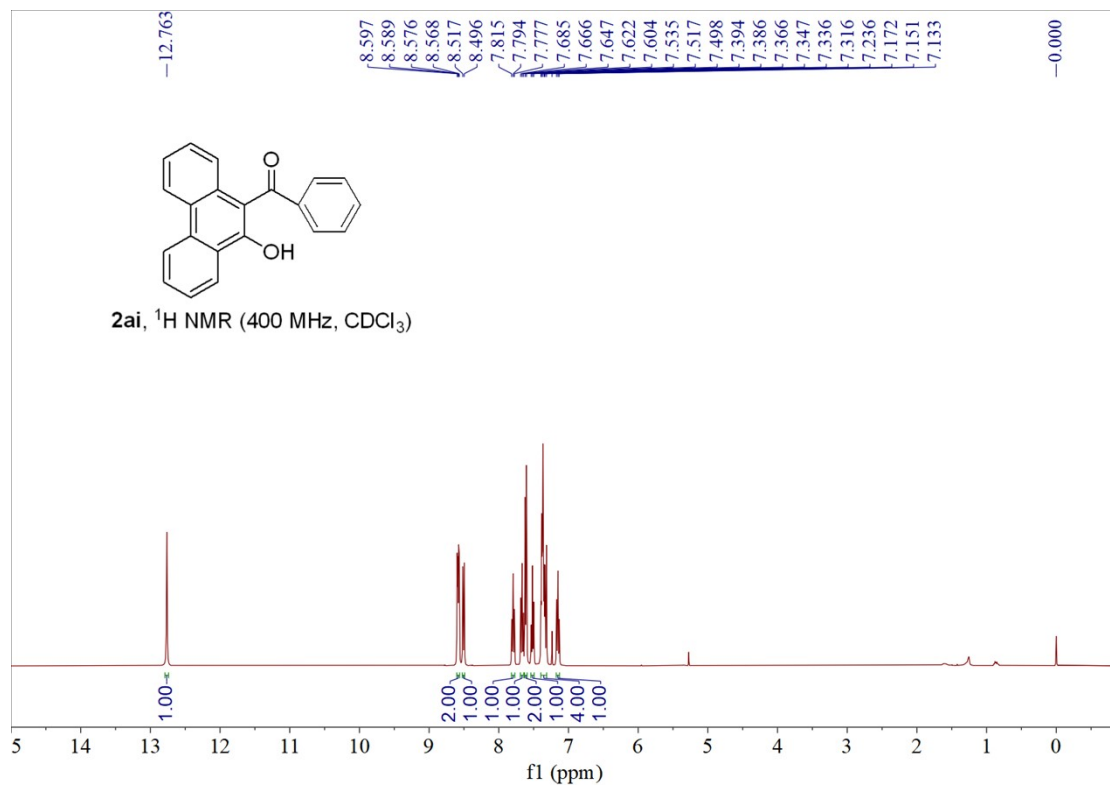


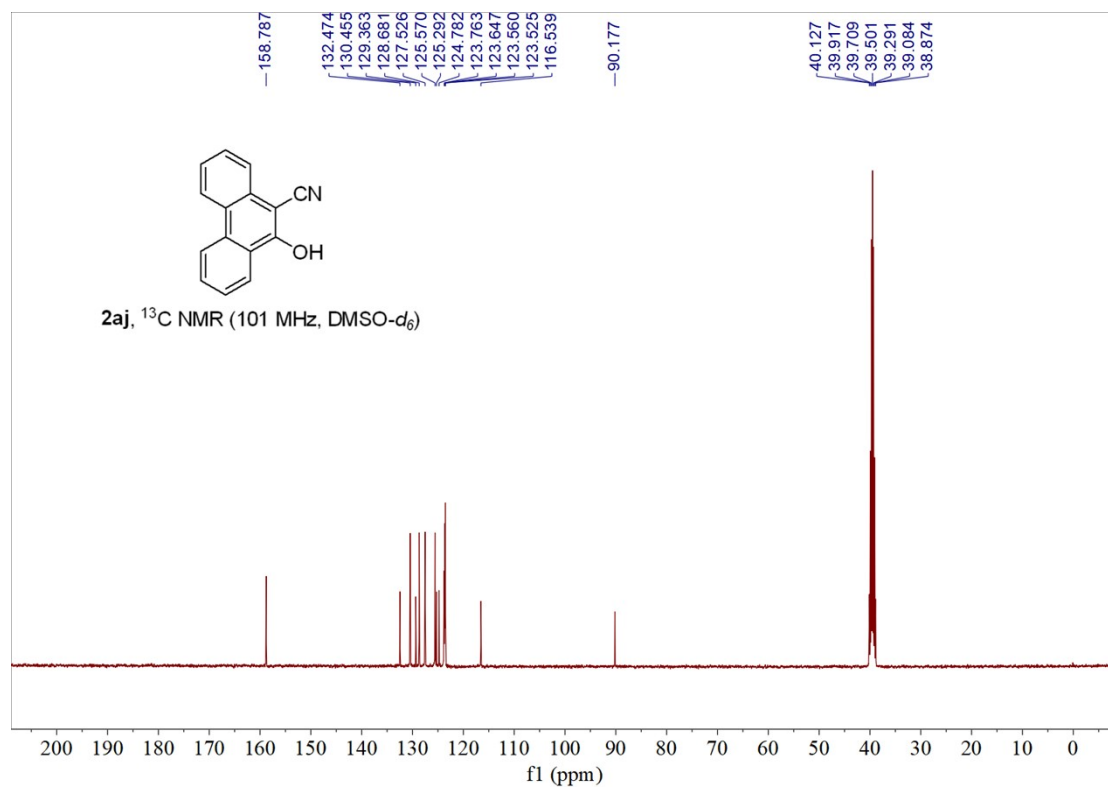
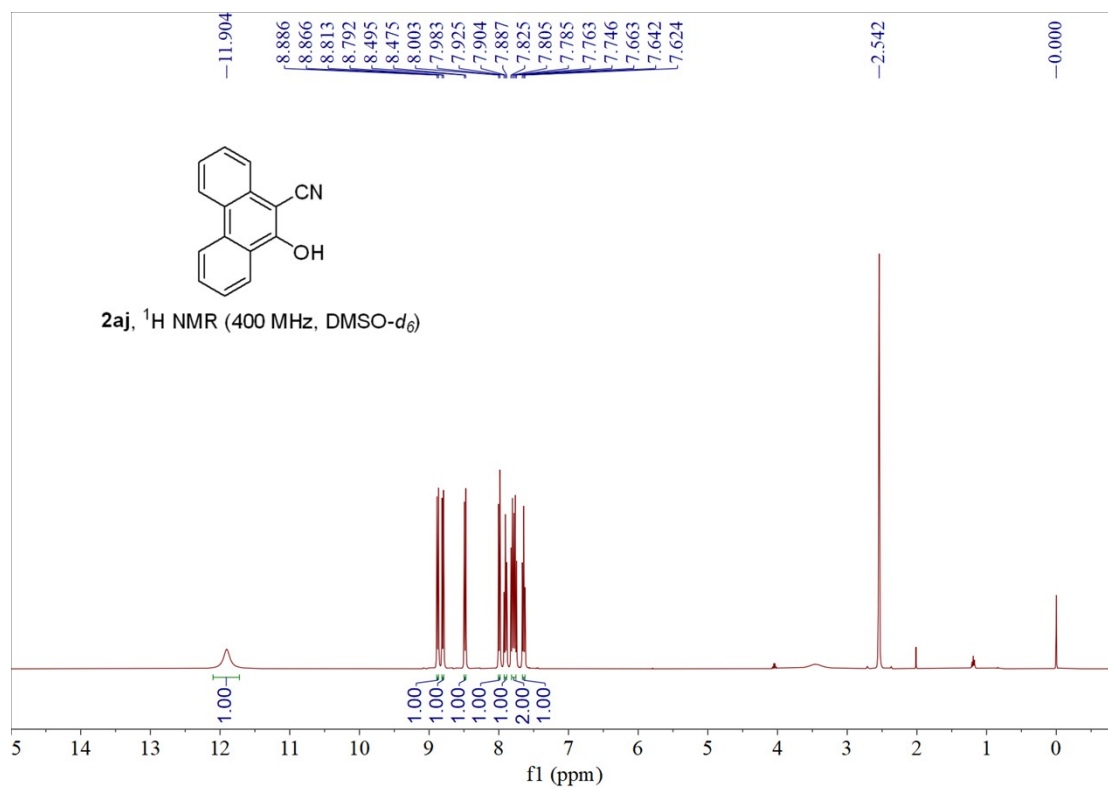


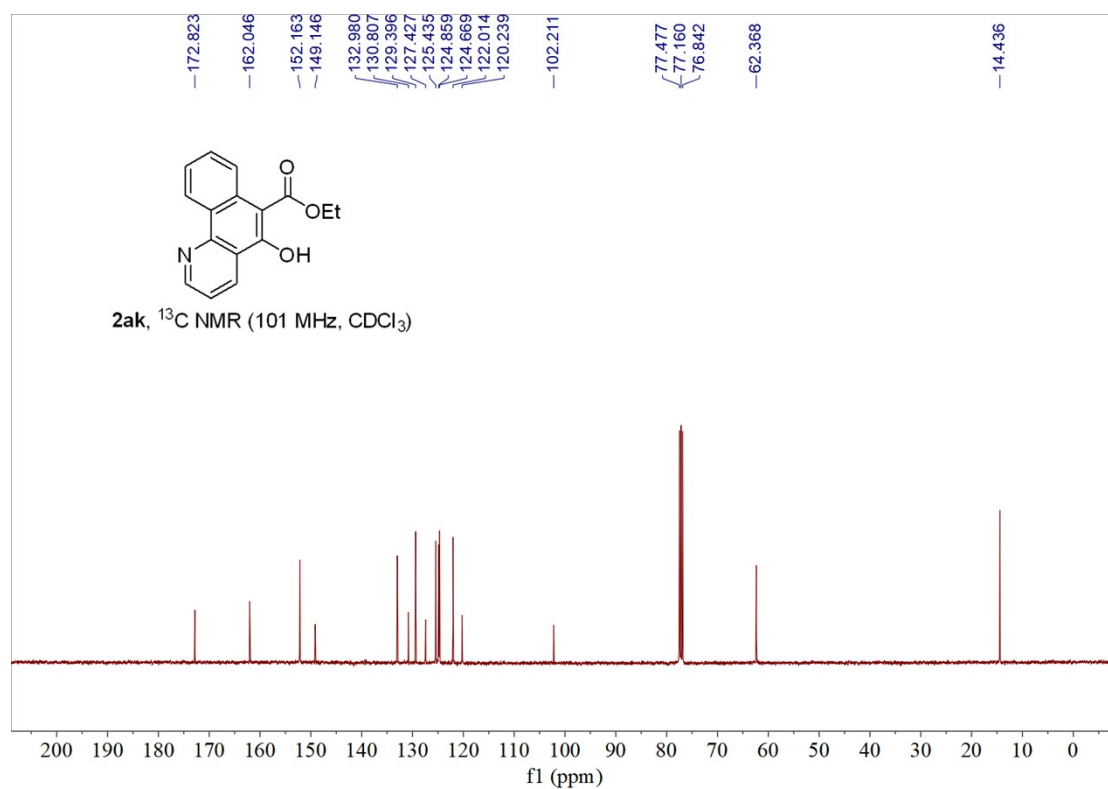
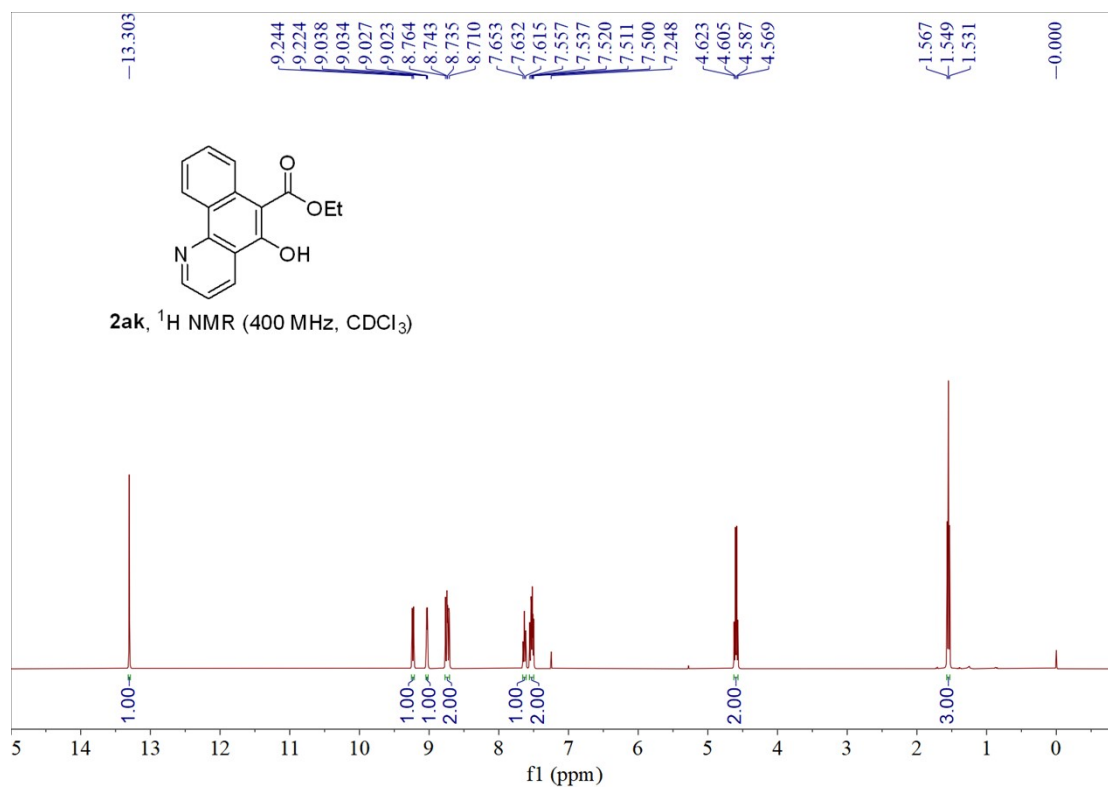


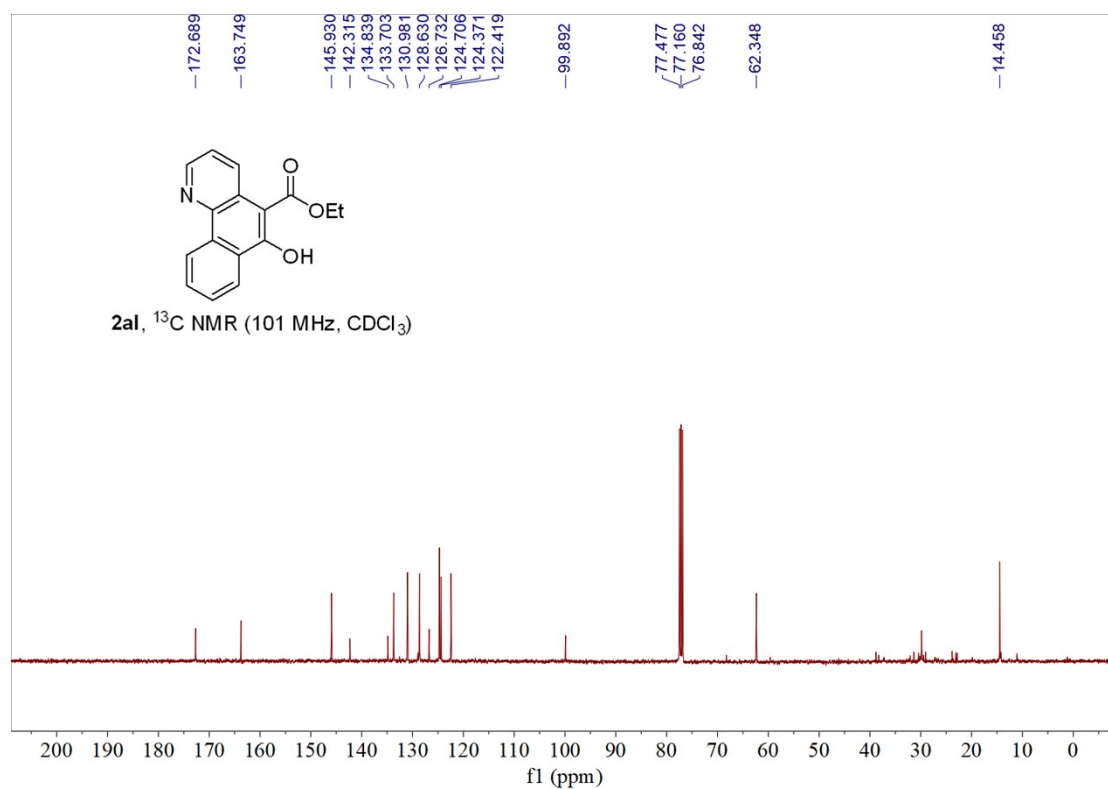
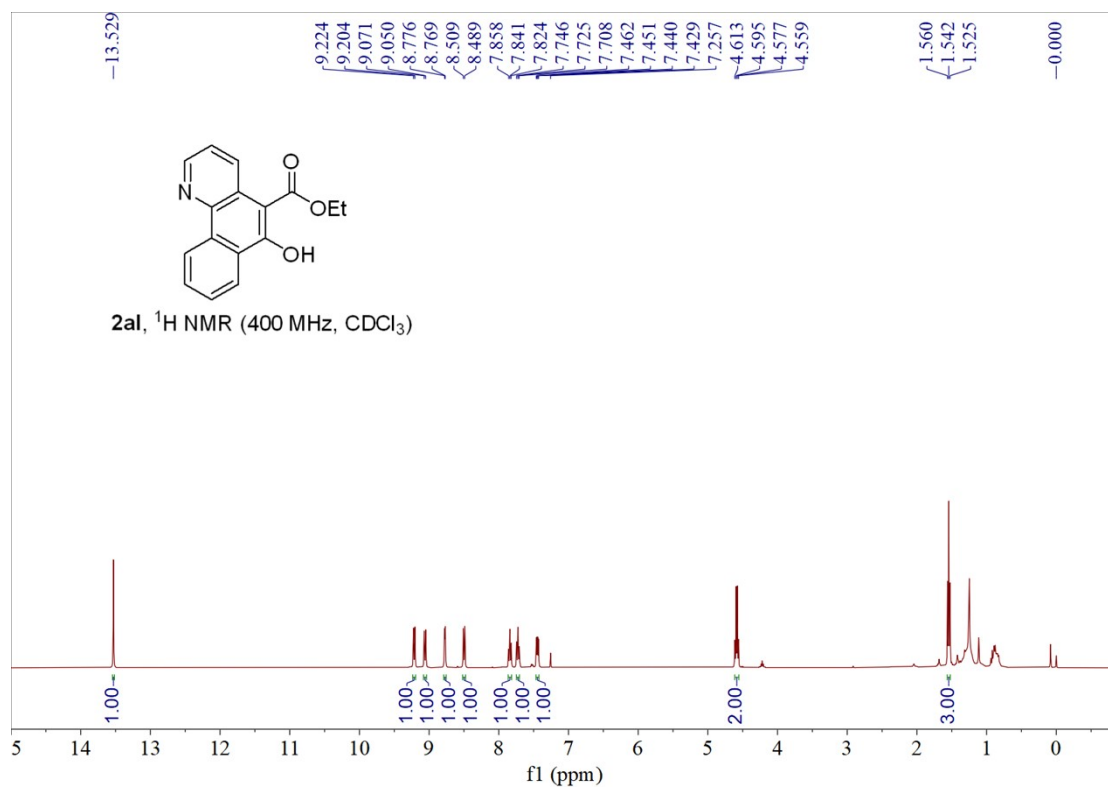


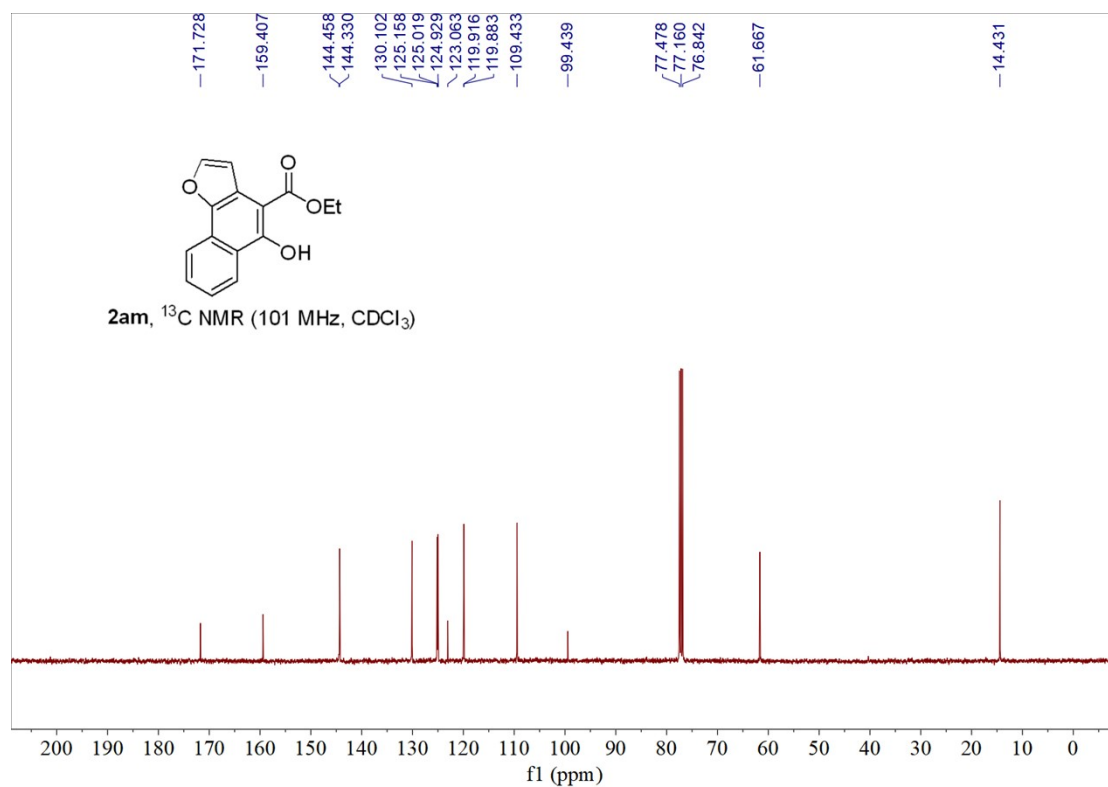
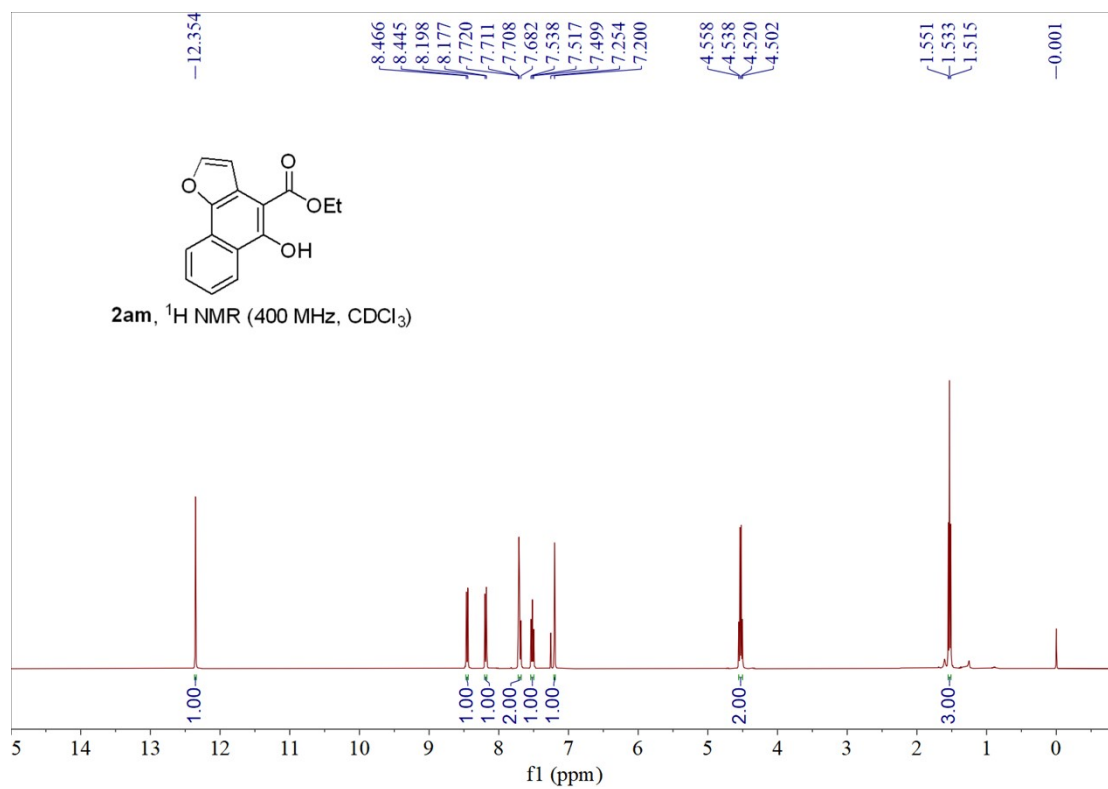


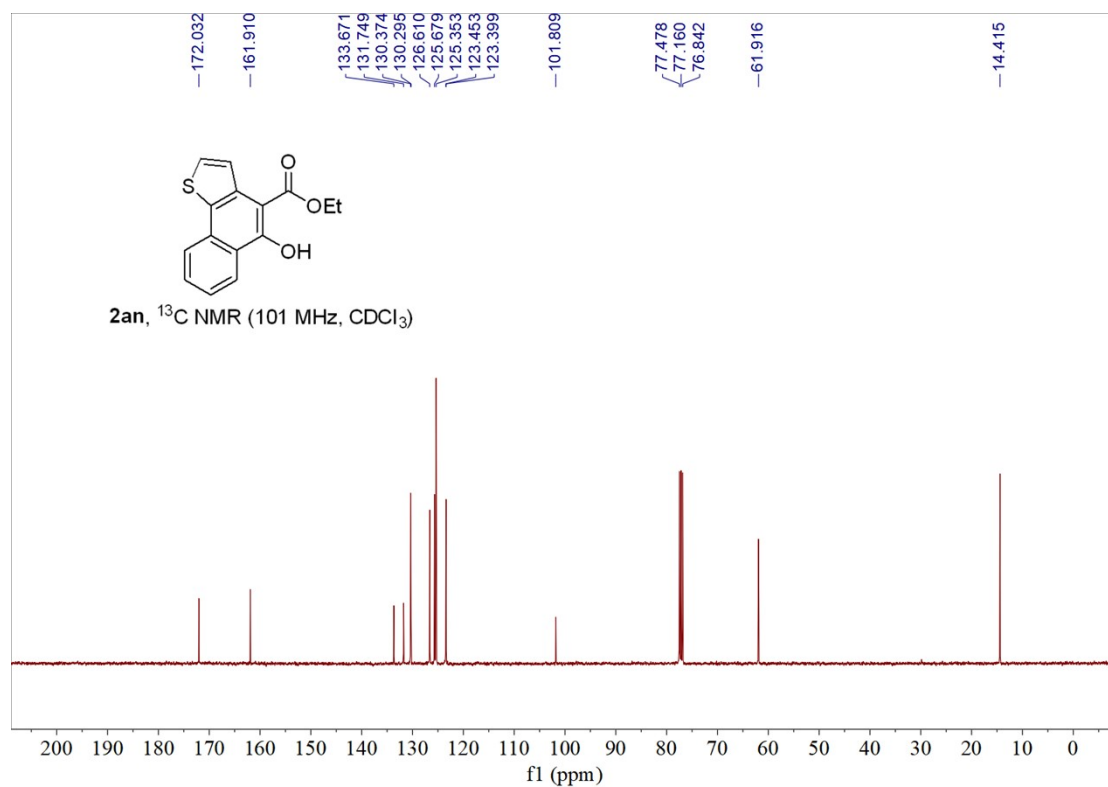
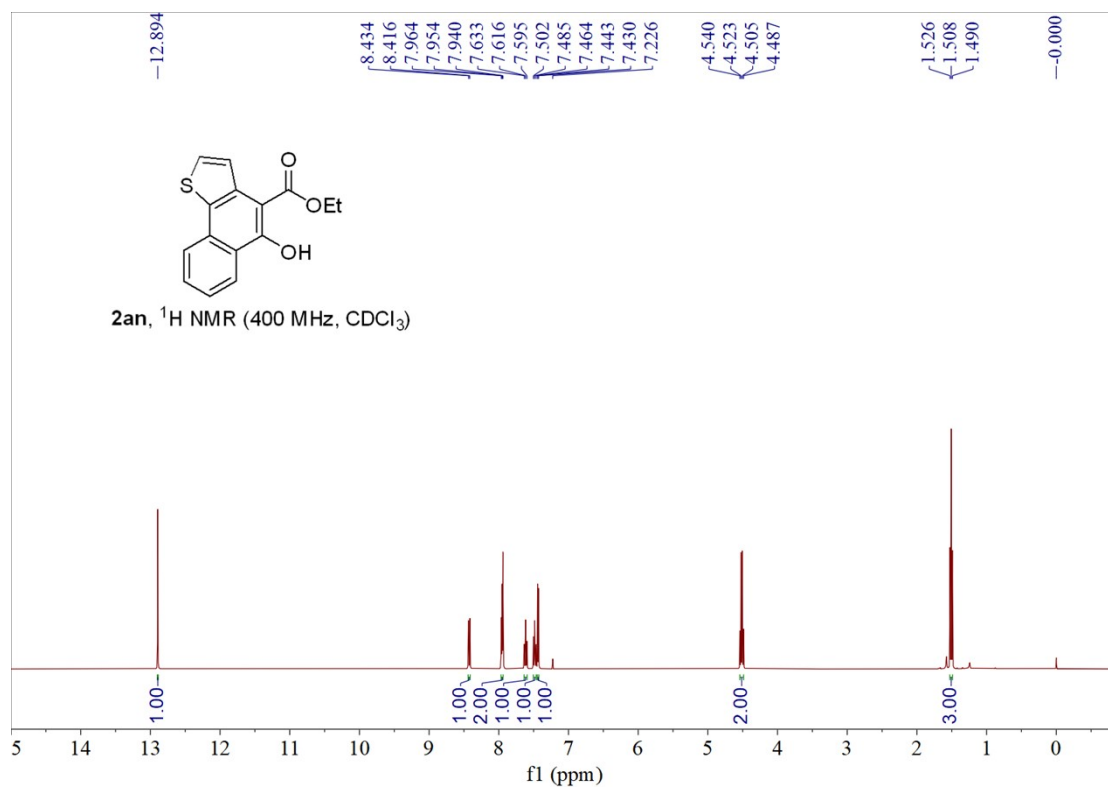


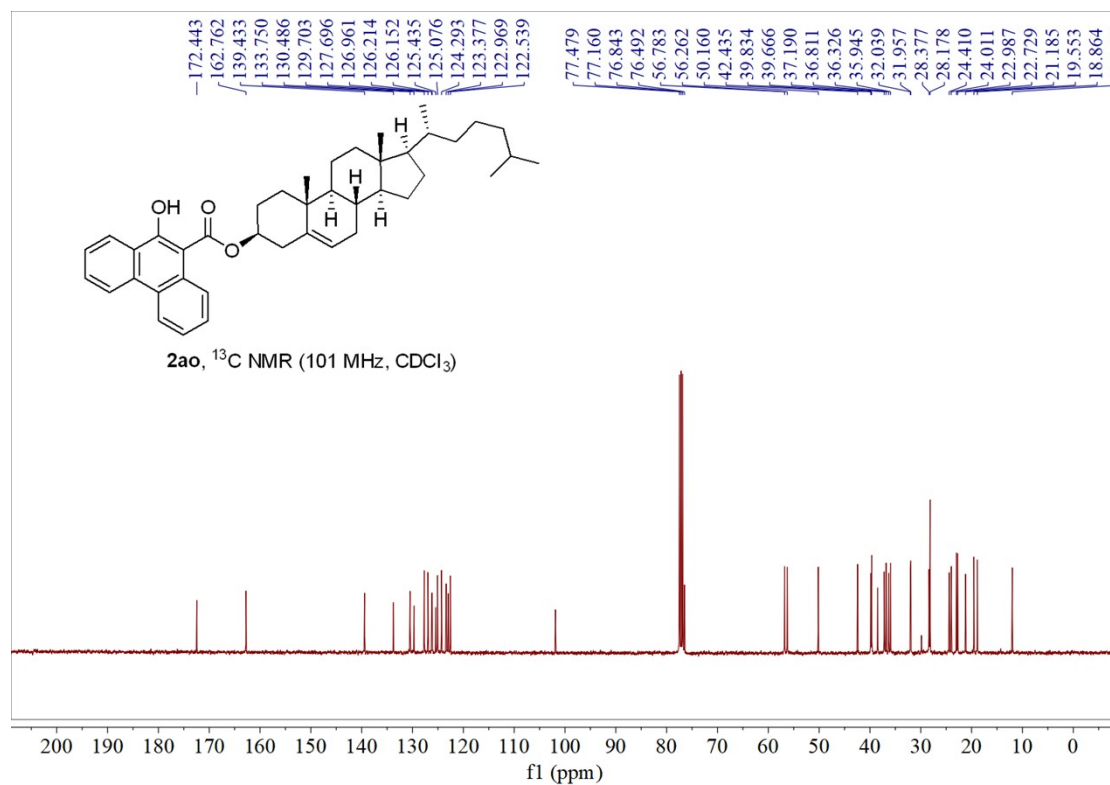
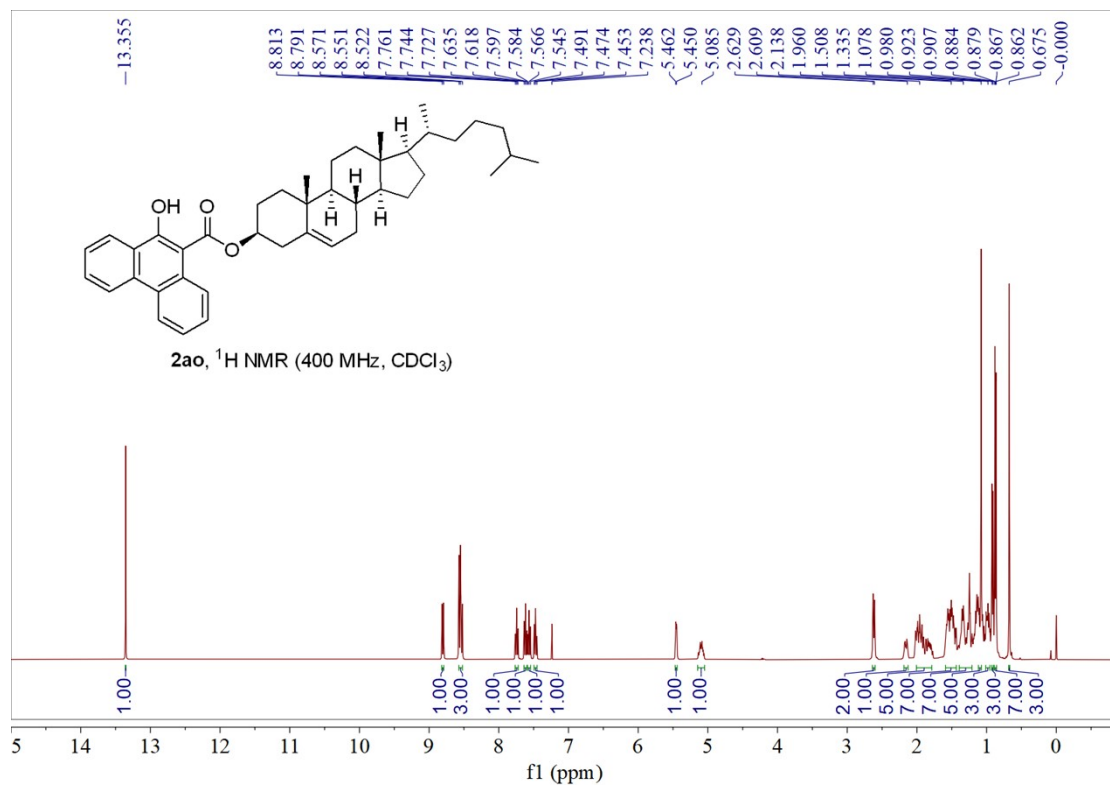


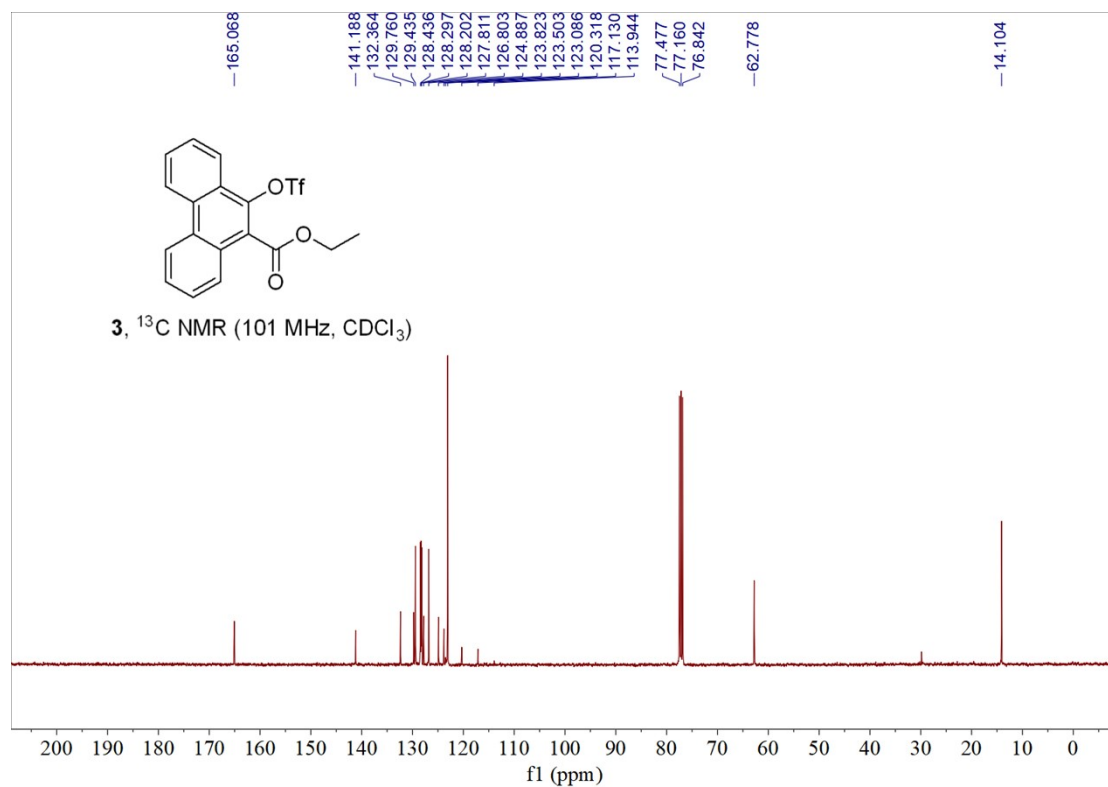
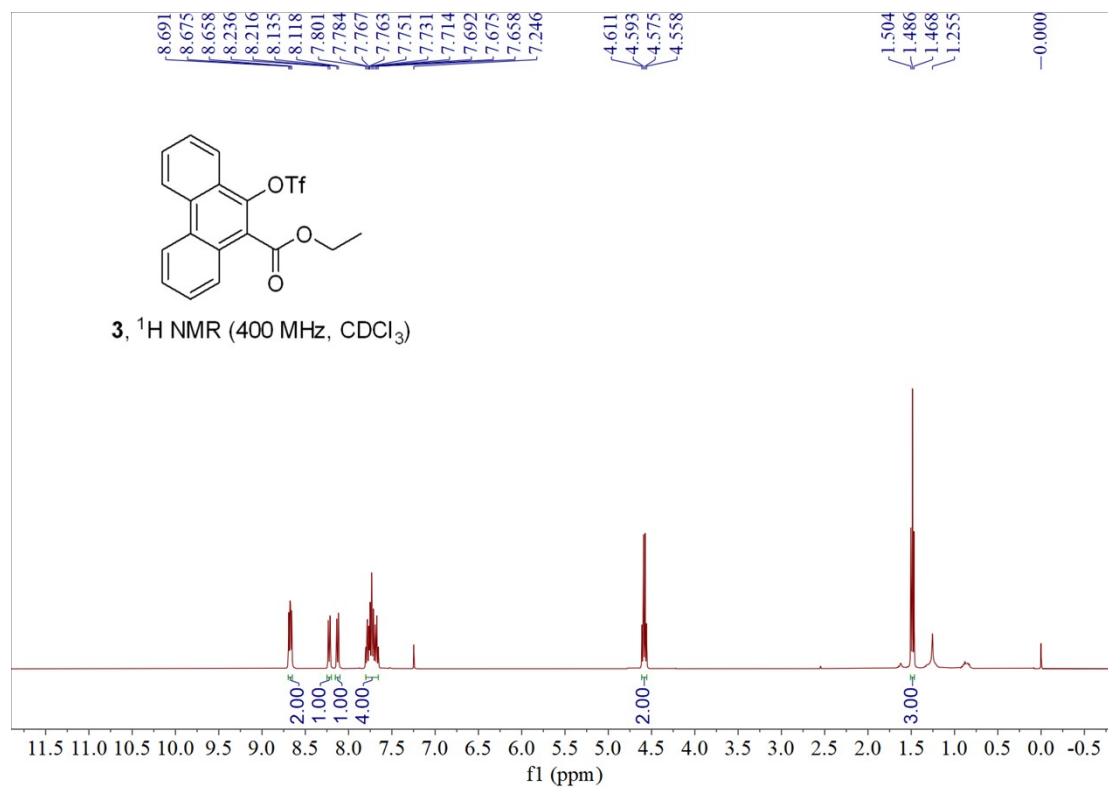


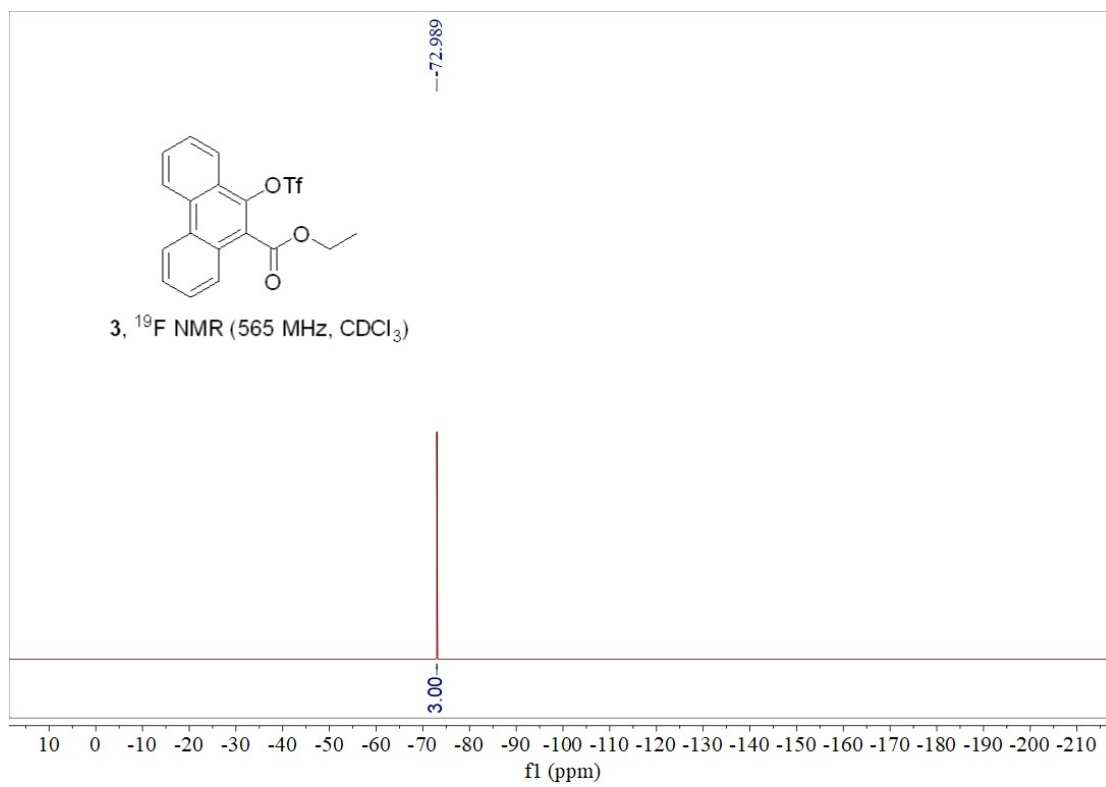


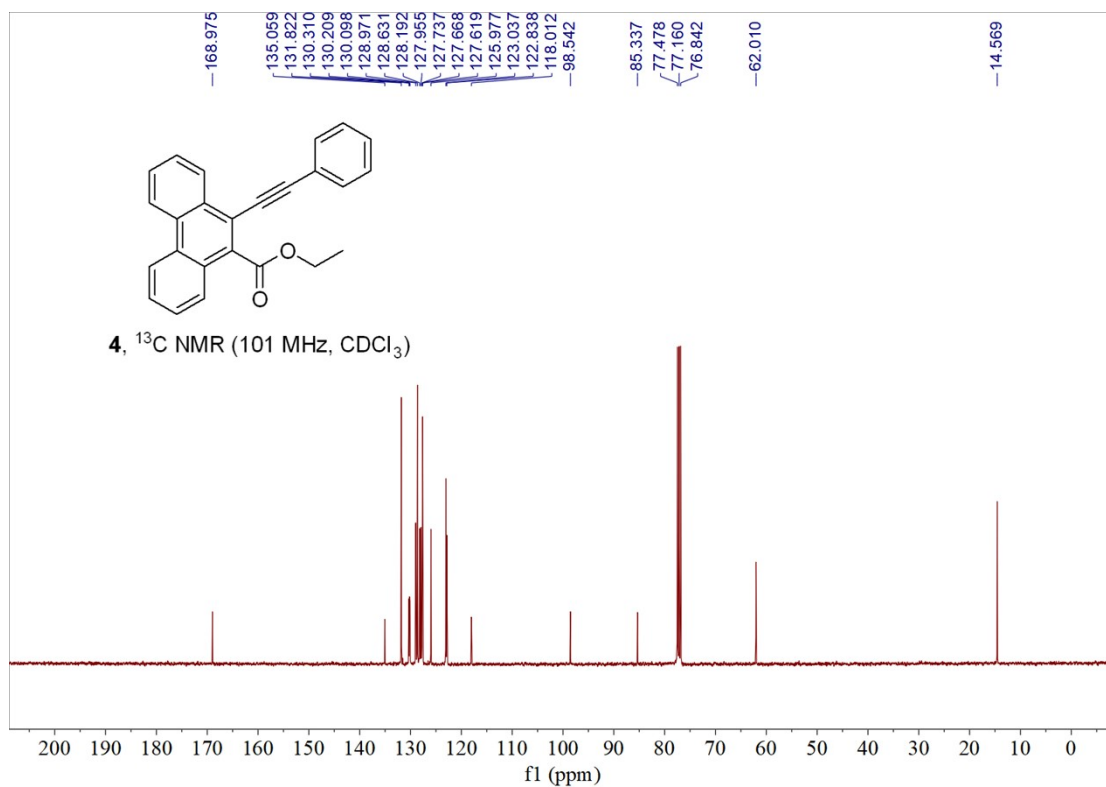
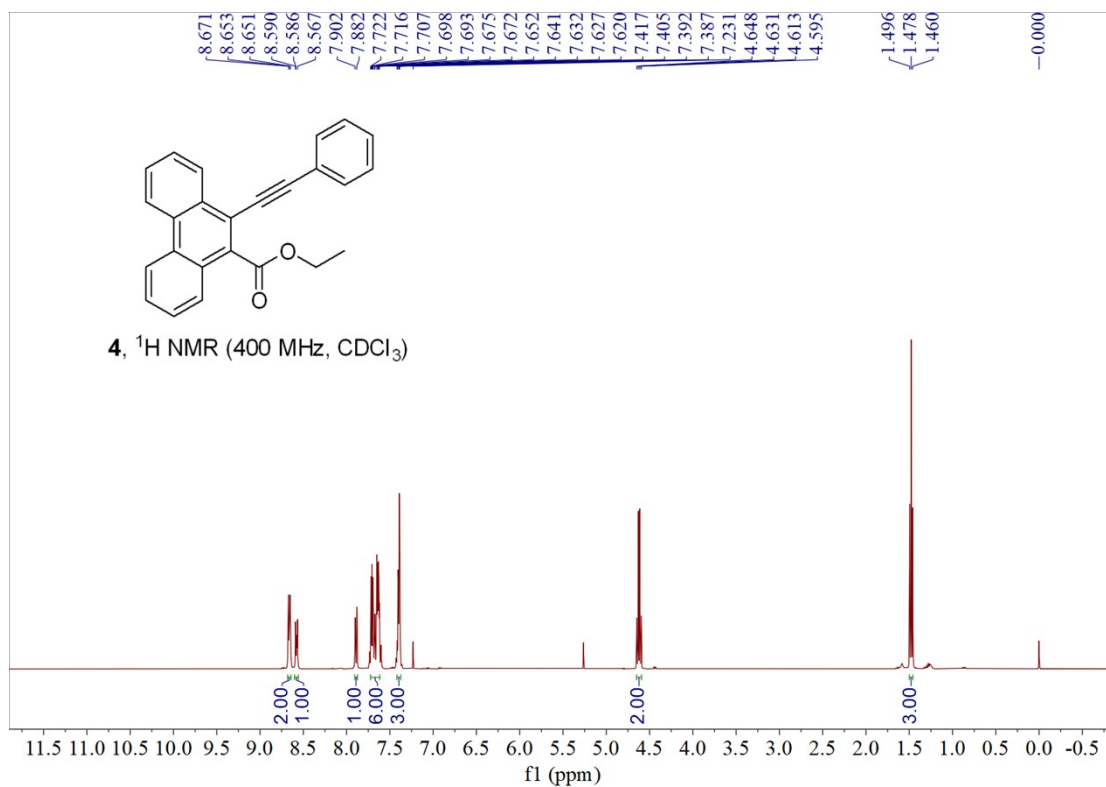


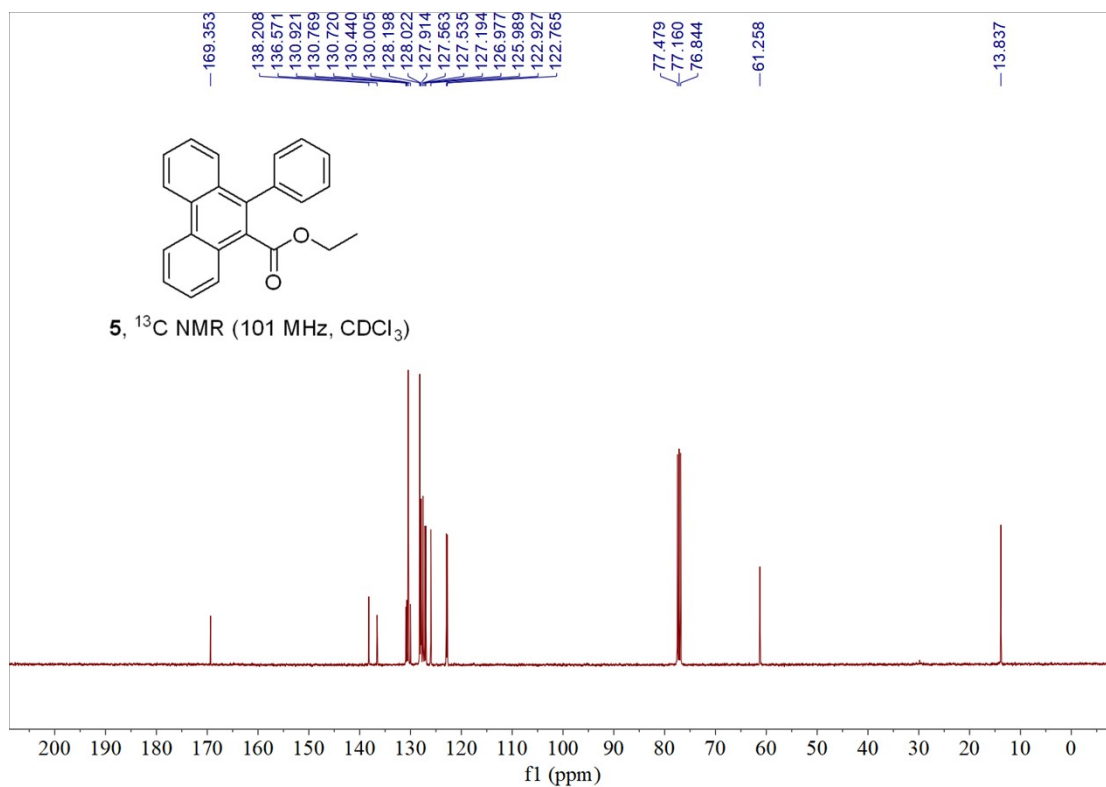
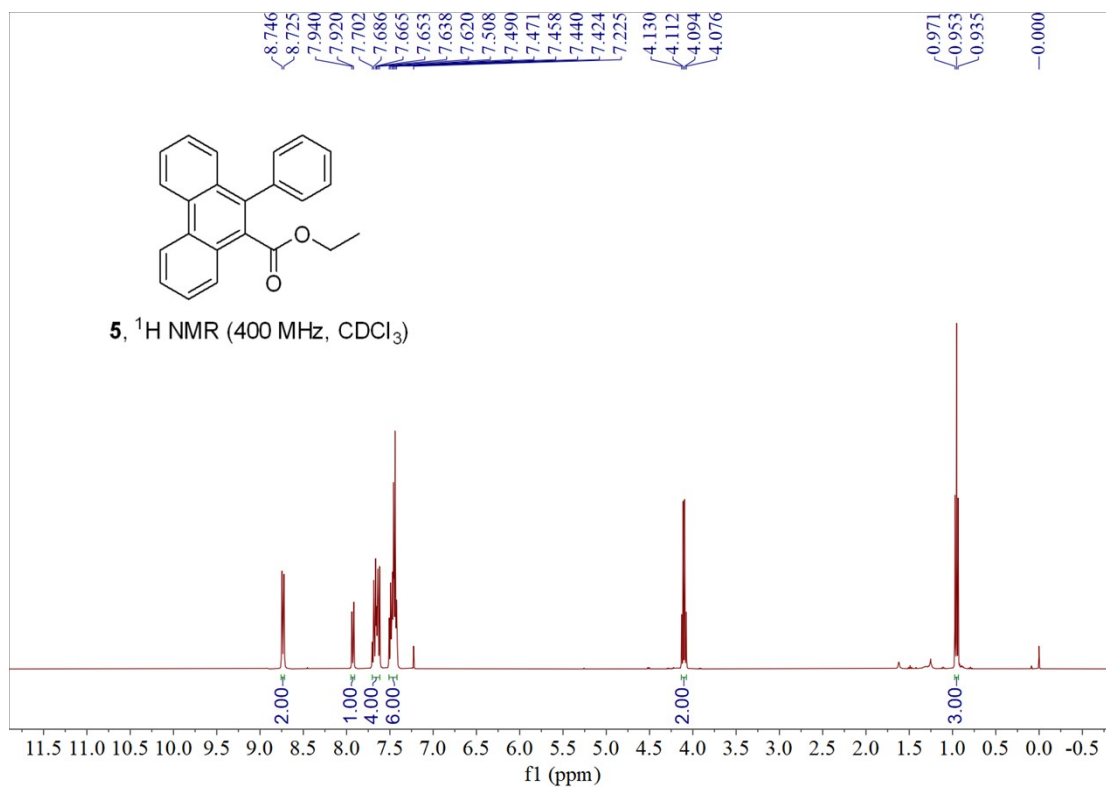


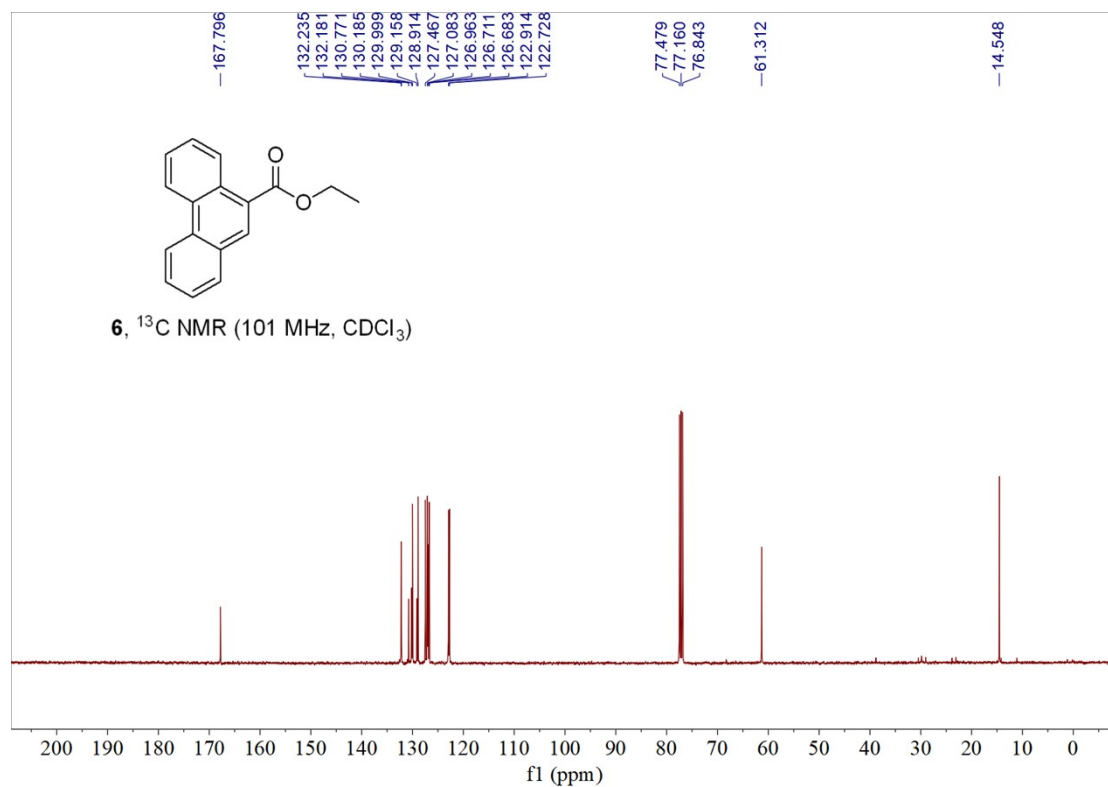
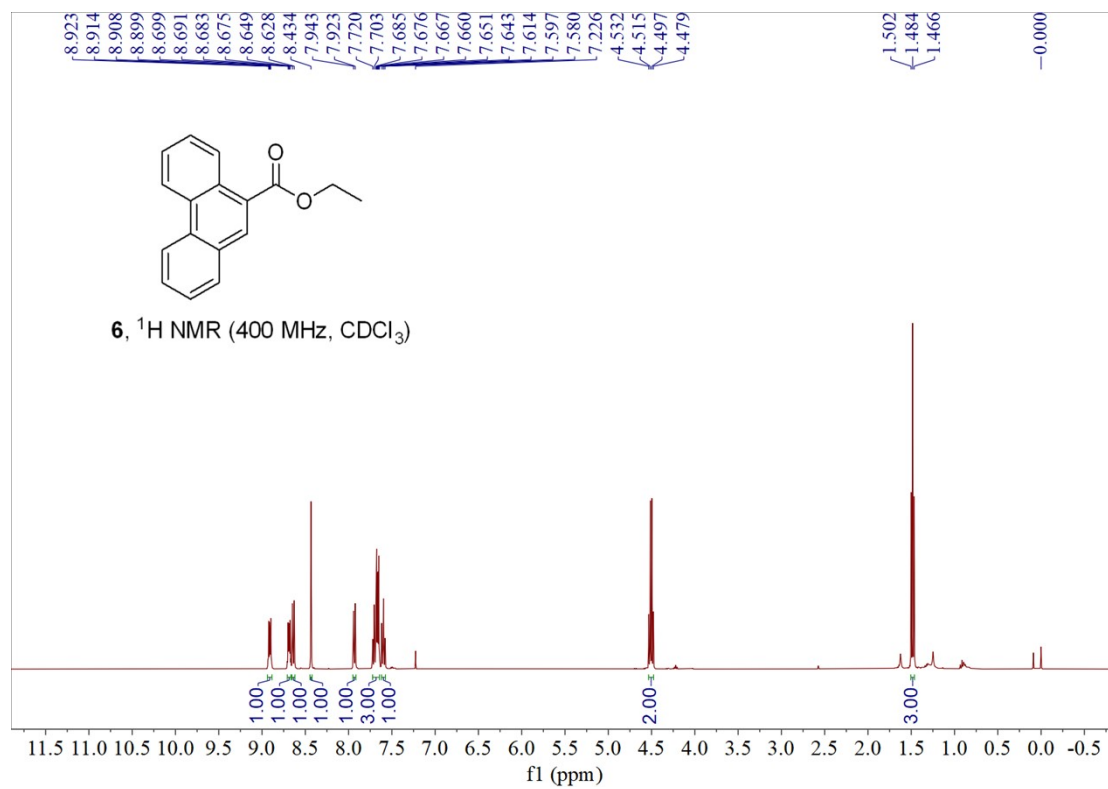


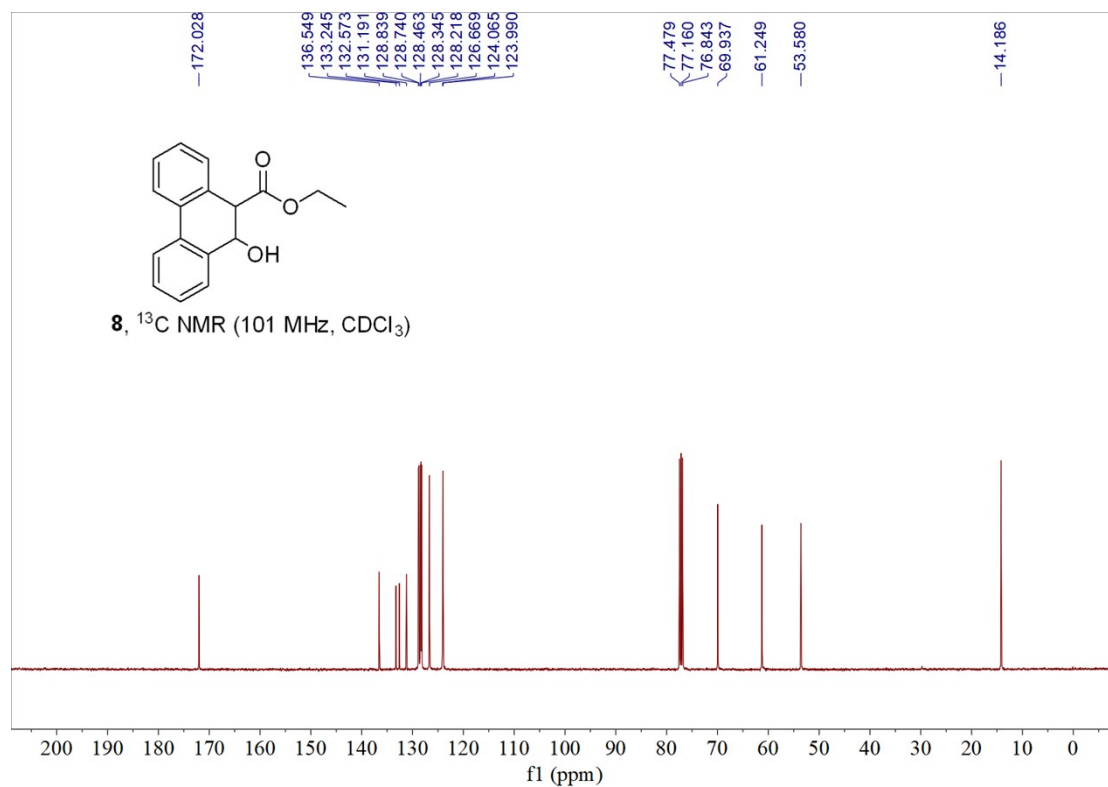
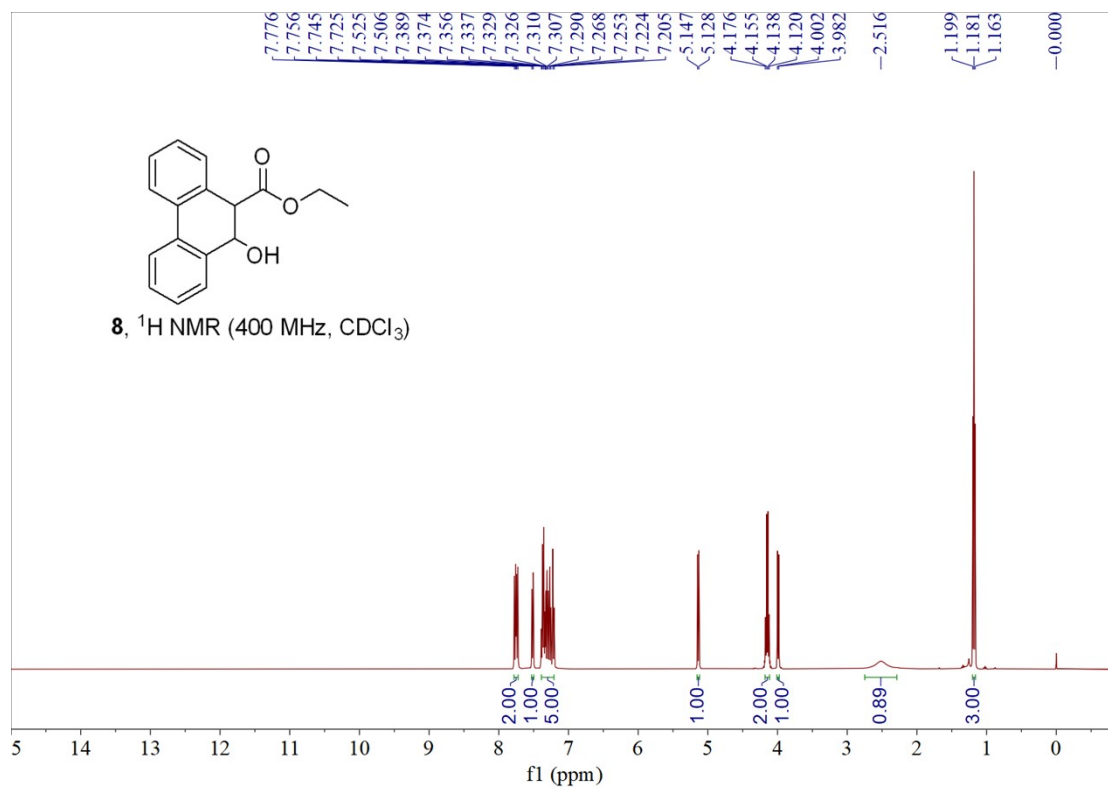












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