Supplementary Information

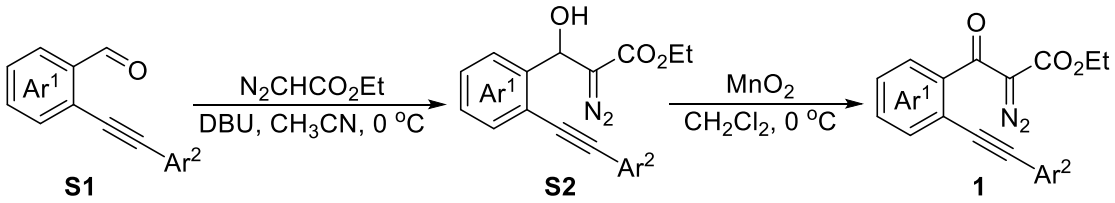
Gold(I)-Catalyzed Intramolecular Cyclization/Intermolecular Cycloaddition Cascade: Fast Track to Polycarbocycles and Mechanistic Insights

Cheng Zhang *et al.*

General Information

All the reactions were carried out under argon atmosphere using oven-dried glassware. Dichloroethane (DCE), ethyl diazoacetate, olefins, phosphine ligands, and metal catalysts were purchased from chemical companies and were used without further treatment. Flash column chromatography was performed using a silica gel (300-400 mesh). Analytical thin-layer chromatography was performed using glass plates precoated with 200-300 mesh silica gel impregnated with a fluorescent indicator (254 nm). All the new compounds were fully characterized. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 using a 300/400/500/600 MHz spectrometer, and chemical shifts were reported in ppm with the solvent signals as the reference, and coupling constants (*J*) were given in Hz. The peak information was described as: s = singlet, br = broad, d = doublet, t = triplet, q = quartet, m = multiplet, and comp = composite. High-resolution mass spectra (HRMS) were recorded using a commercial apparatus (ESI+ Source, CI+ or EI Source).

General Procedure for the Preparation of Diazo Compounds 1



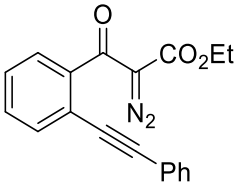
All of the materials **S1** were prepared were prepared according to literature procedures[1].

Synthesis of **S2**: To a solution of ethyl diazoacetate (EDA, 1.37 g, 12.0 mmol) in CH_3CN (10.0 mL), **S1** (10.0 mmol) and 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU, 0.15 g, 1.0 mmol) were added at 0 ℃ in sequence. After the mixture was stirred at 25 ºC for 12.0 hours, the reaction was quenched with saturated aqueous NH_4Cl (15 mL) and then extracted with CH_2Cl_2 (3 × 20.0 mL). The combined organic phase was dried over Na_2SO_4 and the solvent was evaporated under vacuum after filtration. The obtained product **S2** was directly used for the next step without further purification.

Synthesis of **1**: To a 50-mL oven-dried flask containing a magnetic stirring bar, the above obtained product **S2** in DCM (20.0 mL), was added manganese dioxide (MnO_2, 8.70 g, 100.0 mmol) slowly at 25 ºC. The reaction mixture was stirred at overnight and then the solvent was evaporated under vacuum after filtering through a pad of Celite, and the resulting residue was purified by column chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 10:1) to give the pure diazoacetates **1** in good to high yields.

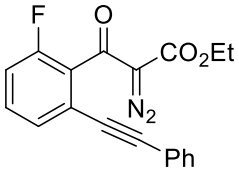
Characterization of Diazoacetates 1.

Ethyl 2-diazo-3-oxo-3-(2-(phenylethynyl)phenyl)propanoate (1a).



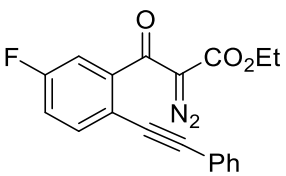
Yellow solid, 2.64 g, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.58 – 7.53 (m, 1H), 7.49 – 7.45 (comp, 2H), 7.45 – 7.36 (comp, 3H), 7.37 – 7.29 (comp, 3H), 4.15 (q, *J* = 7.1 Hz, 2H), 1.09 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 187.1, 160.9, 140.5, 132.0, 131.5, 130.4, 128.7, 128.4, 128.2, 127.1, 122.6, 121.0, 94.0, 86.6, 61.6, 13.9. HRMS (TOF MS ESI$^+$) calculated for $C_{19}H_{14}N_2NaO_3^+$ $[M+Na]^+$: 341.0897, found: 341.0902.

Ethyl 2-diazo-3-(2-fluoro-6-(phenylethynyl)phenyl)-3-oxopropanoate (**1b**).



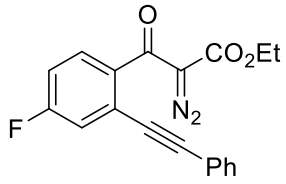
Yellow solid, 2.52 g, 75% yield. ^{1}H NMR (300 MHz, $CDCl_3$) (δ, ppm) 7.50 – 7.43 (comp, 2H), 7.42 – 7.29 (comp, 5H), 7.14 – 7.05 (m, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 1.13 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 182.9 (d, *J* = 1.3 Hz), 160.4, 157.1, 131.7, 131.2 (d, *J* = 9.1 Hz), 129.0, 128.5, 128.0 (d, *J* = 3.2 Hz), 122.7 (d, *J* = 4.9 Hz), 122.4, 115.8 (d, *J* = 21.5 Hz), 94.4, 85.4 (d, *J* = 4.0 Hz), 61.8, 14.0; ^{19}F NMR (283 MHz, $CDCl_3$) (δ, ppm) -115.68. HRMS (TOF MS ESI$^+$) calculated for $C_{19}H_{13}FN_2NaO_3^+$ $[M+Na]^+$: 359.0802, found: 359.0831.

Ethyl 2-diazo-3-(5-fluoro-2-(phenylethynyl)phenyl)-3-oxopropanoate (**1c**).



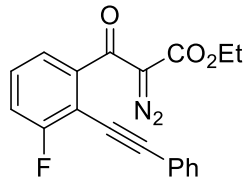
Yellow solid, 2.93 g, 87% yield. ^{1}H NMR (300 MHz, $CDCl_3$) (δ, ppm) 7.61 – 7.53 (m, 1H), 7.52 – 7.45 (comp, 2H), 7.43 – 7.31 (comp, 3H), 7.28 – 7.07 (m, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 1.15 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 185.8 (d, *J* = 2.0 Hz), 162.0 (d, *J* = 251.7 Hz), 160.7, 142.5 (d, *J* = 7.3 Hz), 134.0 (d, *J* = 8.1 Hz), 131.5, 128.8, 128. 5, 122.5, 117.6 (d, *J* = 22.0 Hz), 117.3 (d, *J* = 3.7 Hz), 114.6 (d, *J* = 24.1 Hz), 93.7 (d, *J* = 1.6 Hz), 85.6, 61.8, 14.0; ^{19}F NMR (283 MHz, $CDCl_3$) (δ, ppm) -109.87. HRMS (TOF MS ESI$^+$) calculated for $C_{19}H_{13}FN_2NaO_3^+$ $[M+Na]^+$: 359.0802, found: 359.0812.

Ethyl 2-diazo-3-(4-fluoro-2-(phenylethynyl)phenyl)-3-oxopropanoate (**1d**).



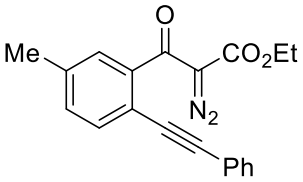
Yellow solid, 2.69 g, 80% yield. ^{1}H NMR (300 MHz, $CDCl_3$) (δ, ppm) 7.54 – 7.42 (comp, 3H), 7.42 – 7.31 (comp, 3H), 7.30 – 7.22 (m, 1H), 7.16 – 7.06 (m, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 1.14 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 186.1, 163.4 (d, *J* = 251.6 Hz), 160.9, 136.8 (d, *J* = 3.4 Hz), 131.6, 129.1, 129.7 (d, *J* = 9.4 Hz), 128.5, 123.6 (d, *J* = 10.3 Hz), 122.1, 118.8 (d, *J* = 23.5 Hz), 115.7 (d, *J* = 22.0 Hz), 95.0, 85.6 (d, *J* = 3.0 Hz), 61.7, 14.9; ^{19}F NMR (283 MHz, $CDCl_3$) (δ, ppm) -109.03. HRMS (TOF MS ESI$^+$) calculated for $C_{19}H_{13}FN_2NaO_3^+$ [M+Na]$^+$: 359.0802, found: 359.0808.

Ethyl 2-diazo-3-(3-fluoro-2-(phenylethynyl)phenyl)-3-oxopropanoate (**1e**).



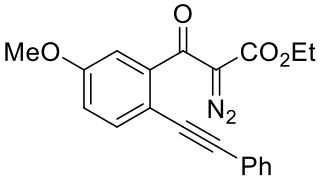
Yellow solid, 2.39 g, 71% yield. ^{1}H NMR (300 MHz, $CDCl_3$) (δ, ppm) 7.54 – 7.44 (comp, 2H), 7.42 – 7.29 (comp, 4H), 7.25 – 7.06 (m, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 1.11 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 185.9 (d, *J* = 3.2 Hz), 162.1 (d, *J* = 253.0 Hz), 160.7, 142.4, 131.7, 129.7 (d, *J* = 8.3 Hz), 129.1, 128.5, 122.8 (d, *J* = 3.6 Hz), 117.4 (d, *J* = 21.5 Hz), 110.2 (d, *J* = 17.9 Hz), 99.1 (d, *J* = 3.7 Hz), 80.0 (d, *J* = 0.6 Hz) , 61.8, 14.0; ^{19}F NMR (283 MHz, $CDCl_3$) (δ, ppm) -109.16. HRMS (TOF MS ESI$^+$) calculated for $C_{19}H_{13}FN_2NaO_3^+$ [M+Na]$^+$: 359.0802, found: 359.0822.

Ethyl 2-diazo-3-(5-methyl-2-(phenylethynyl)phenyl)-3-oxopropanoate (**1f**).



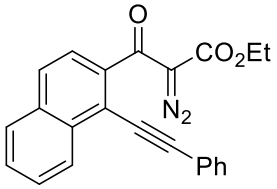
Yellow solid, 2.69 g, 81% yield. ^{1}H NMR (300 MHz, $CDCl_3$) (δ, ppm) 7.52 – 7.43 (comp, 2H), 7.42 – 7.26 (comp, 5H), 7.24 – 7.16 (m, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 2.37 (s, 3H), 1.11 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 187.1, 161.0, 140.9, 137.8, 132.6, 131.5, 129.2, 128.6, 128.4, 127.5, 122.8, 121.1, 93.6, 86.9, 61.6, 21.2, 14.0. HRMS (TOF MS ESI$^+$) calculated for $C_{20}H_{16}N_2NaO_3^+$ [M+Na]$^+$: 355.1053, found: 355.1070.

Ethyl 2-diazo-3-(5-methoxy-2-(phenylethynyl)phenyl)-3-oxopropanoate (**1g**).



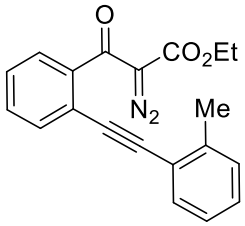
2.54 g, 73% yield. ^{1}H NMR (300 MHz, $CDCl_3$) (δ, ppm) 7.53 – 7.40 (comp, 3H), 7.38 – 7.26 (comp, 3H), 7.03 – 6.93 (m, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 186.9, 160.9, 159.5, 141.9, 133.5, 131.3, 128.4 128.3, 123.0, 116.6, 113.2, 112.4, 92.6, 86.6, 61.7, 55.5, 14.0. HRMS (TOF MS ESI$^+$) calculated for $C_{20}H_{16}N_2NaO_4^+$ [M+Na]$^+$: 371.1002, found: 371.1000.

Ethyl 2-diazo-3-oxo-3-(1-(phenylethynyl)naphthalen-2-yl)propanoate (**1h**).



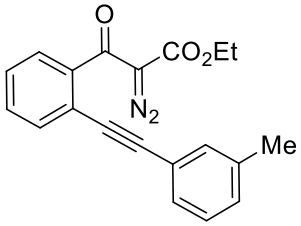
Yellow solid, 2.57 g, 70% yield. ^{1}H NMR (300 MHz, $CDCl_3$) (δ, ppm) 8.70 – 8.33 (m, 1H), 8.01 – 7.85 (comp, 2H), 7.73 – 7.54 (comp, 4H), 7.54 – 7.48 (m, 1H), 7.47 – 7.26 (comp, 3H), 4.13 (q, *J* = 7.1 Hz, 2H), 1.01 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 187.8, 161.1, 138.9, 133.9, 132.7, 131.7, 129.0, 128.8, 128.6, 128.4, 127.8, 127.7, 127.0, 123.8, 122.9, 119.1, 99.9, 84.8, 61.8, 14.0. HRMS (TOF MS ESI$^+$) calculated for $C_{23}H_{16}N_2NaO_3^+$ [M+Na]$^+$: 391.1053, found: 391.1060.

Ethyl 2-diazo-3-oxo-3-(2-(*o*-tolylethynyl)phenyl)propanoate (**1i**).



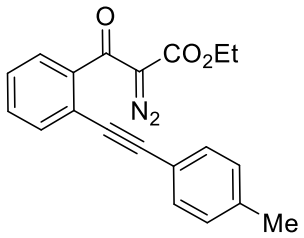
Yellow solid, 2.69 g, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.59 (d, *J* = 7.4 Hz, 1H), 7.54 – 7.31 (comp, 4H), 7.30 – 7.22 (comp, 2H), 7.22 – 7.11 (m, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.48 (s, 3H), 1.12 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 187.5, 160.8, 140.6, 140.1, 132.2, 132.1, 130.3, 129.6, 128.8, 128.2, 126.9, 125.7, 122.6, 121.2, 93.0, 90.5, 61.7, 20.6, 14.1. HRMS (TOF MS ESI$^+$) calculated for $C_{20}H_{16}N_2NaO_3^+$ [M+Na]$^+$: 355.1053, found: 355.1062.

Ethyl 2-diazo-3-oxo-3-(2-(*m*-tolylethynyl)phenyl)propanoate (**1j**).



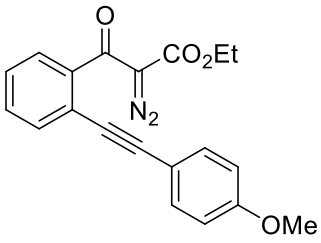
Yellow solid, 2.63 g, 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.64 – 7.56 (m, 1H), 7.52 – 7.40 (comp, 3H), 7.38 – 7.24 (comp, 3H), 7.23 – 7.16 (m, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 2.38 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 187.3, 160.9, 140.6, 138.1, 132.1, 132.0, 130.4, 129.6, 128.7, 128.3, 128.2, 127.2, 122.5, 121.1, 94.3, 86.3, 61.7, 21.2, 14.0. HRMS (TOF MS ESI$^+$) calculated for $C_{20}H_{16}N_2NaO_3^+$ [M+Na]$^+$: 355.1053, found: 355.1060

Ethyl 2-diazo-3-oxo-3-(2-(*p*-tolylethynyl)phenyl)propanoate (**1k**).



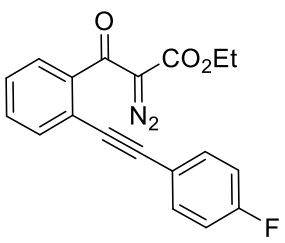
Yellow solid, 2.49 g, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.55 – 7.51 (m, 1H), 7.45 – 7.34 (comp, 5H), 7.18 – 7.10 (comp, 2H), 4.14 (q, *J* = 7.2 Hz, 3H), 2.35 (s, 3H), 1.09 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 187.3, 161.0, 140.5, 138.9, 131.9, 131.4, 130.4, 129.2, 128.1, 127.2, 121.3, 119.6, 94.3, 86.0, 61.6, 21.5, 14.0. HRMS (TOF MS ESI$^+$) calculated for $C_{20}H_{16}N_2NaO_3^+$ [M+Na]$^+$: 355.1053, found: 355.1065.

Ethyl 2-diazo-3-(2-((4-methoxyphenyl)ethynyl)phenyl)-3-oxopropanoate (**1l**).



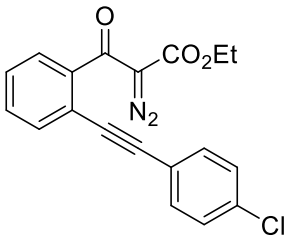
Yellow solid, 2.96 g, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.53 (d, *J* = 7.5 Hz, 1H), 7.49 – 7.29 (comp, 5H), 6.93 – 6.83 (comp, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 1H), 1.10 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 187.4, 161.1, 160. 0, 140.4, 133.1, 131.9, 130.5, 128.0, 127.2, 121.5, 114.8, 114.1, 94.3, 85.5, 61.7, 55.3, 14.0. HRMS (TOF MS ESI$^+$) calculated for $C_{20}H_{16}N_2NaO_4^+$ [M+Na]$^+$:371.1002, found: 371.1031.

Ethyl 2-diazo-3-(2-((4-fluorophenyl)ethynyl)phenyl)-3-oxopropanoate (**1m**).



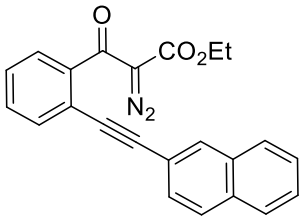
Yellow solid, 2.46 g, 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.54 – 7.47 (m, 1H), 7.46 – 7.33 (comp, 5H), 7.05 – 6.95 (comp, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 1.06 (t, *J* = 7.1 Hz, 3H) ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 187.0, 162.6 (d, *J* = 250.4 Hz), 160.8, 140.5, 133.4 (d, *J* = 8.4 Hz), 131.9, 130.3, 128.2, 127.2, 120.7, 118.7 (d, *J* = 3.5 Hz), 115.7 (d, *J* = 22.1 Hz), 92.8, 86.3, 61.6, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$) (δ, ppm) -110.07. HRMS (TOF MS ESI$^+$) calculated for $C_{19}H_{13}FN_2NaO_3^+$ [M+Na]$^+$: 359.0802, found: 359.0822

Ethyl 3-(2-((4-chlorophenyl)ethynyl)phenyl)-2-diazo-3-oxopropanoate (**1n**).



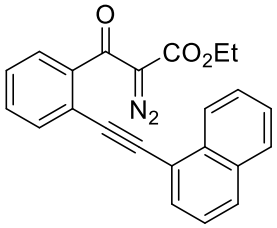
Yellow solid, 2.47 g, 70% yield. ^{1}H NMR (300 MHz, $CDCl_3$) (δ, ppm) 7.57 – 7.50 (m, 1H), 7.48 – 7.34 (comp, 5H), 7.35 – 7.26 (comp, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 1.09 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 187.1, 161.0, 140.6, 134.8, 132.8, 132.1, 130.5, 128.8, 128.5, 127.3, 121.2, 120.7, 92.8, 87.7, 61.8, 14.0. HRMS (TOF MS ESI$^+$) calculated for $C_{19}H_{13}ClN_2NaO_3^+$ [M+Na]$^+$: 375.0507, found: 375.0512.

Ethyl 2-diazo-3-(2-(naphthalen-2-ylethynyl)phenyl)-3-oxopropanoate (**1o**).



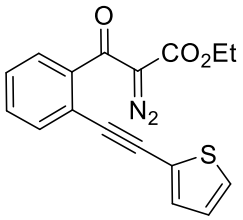
Yellow solid, 2.62 g, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.01 (s, 1H), 7.87 – 7.78 (comp, 3H), 7.65 – 7.59 (m, 1H), 7.56 – 7.40 (comp, 6H), 4.18 (q, *J* = 7.1 Hz, 2H), 1.11 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 187.4, 161.0, 140.7, 133.03, 132.98, 132.2, 131.7, 130.5, 128.4, 128.20, 128.16, 127.91, 127.87, 127.3, 127.0, 126.8, 121.2, 120.0, 94.5, 87.1, 61.8, 14.1. HRMS (TOF MS ESI$^+$) calculated for $C_{23}H_{16}N_2NaO_3^+$ [M+Na]$^+$: 391.1053, found 391.1051.

Ethyl 2-diazo-3-(2-(naphthalen-1-ylethynyl)phenyl)-3-oxopropanoate (**1p**).



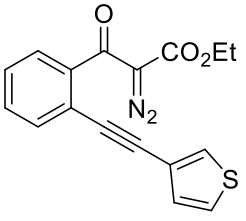
Yellow solid, 2.69 g, 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.31 (d, *J* = 8.3 Hz, 1H), 7.94 – 7.81 (comp, 2H), 7.77 – 7.66 (comp, 2H), 7.64 – 7.58 (m, 1H), 7.58 – 7.41 (comp, 5H), 4.12 (q, *J* = 7.1 Hz, 2H), 1.04 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 187.6, 160.8, 140.8, 133.31, 133.26, 132.3, 130.7, 130.5, 129.3, 128.5, 128.4, 127.1, 126.6, 126.1, 125.4, 121.2, 120.5, 92.3, 91.6, 61.7, 14.0. HRMS (TOF MS ESI$^+$) calculated for $C_{23}H_{16}N_2NaO_3^+$ [M+Na]$^+$: 391.1053, found: 391.1062.

Ethyl 2-diazo-3-oxo-3-(2-(thiophen-2-ylethynyl)phenyl)propanoate (**1q**).



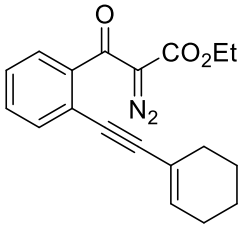
Yellow solid, 2.63 g, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.57 – 7.49 (m, 1H), 7.46 – 7.37 (comp, 3H), 7.33 – 7.27 (m, 1H), 7.25 – 7.19 (m, 1H), 7.03 – 6.96 (m, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 1.11 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 187.2, 160.9, 140.5, 132.4, 131.6, 130.5, 128.5, 128.0, 127.3, 122.6, 120.8, 90.5, 87.3, 61.7, 14.0. HRMS (TOF MS ESI$^+$) calculated for $C_{17}H_{12}N_2NaO_3S^+$ [M+Na]$^+$: 347.0461, found: 347.0464.

Ethyl 2-diazo-3-oxo-3-(2-(thiophen-3-ylethynyl)phenyl)propanoate (**1r**).



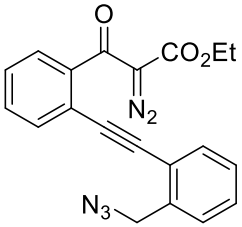
Yellow solid, 2.69 g, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.58 – 7.50 (comp, 2H), 7.47 – 7.38 (comp, 3H), 7.34 – 7.29 (m, 1H), 7.17 – 7.13 (m, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 1.11 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 187.1, 160.9, 140.5, 131.8, 130.4, 129.6, 129.2, 128.2, 127.2, 125.6, 121.6, 121.0, 89.2, 86.2, 61.6, 13.9. HRMS (TOF MS ESI$^+$) calculated for $C_{17}H_{12}N_2NaO_3S^+$ [M+Na]$^+$: 347.0461, found: 347.0469.

Ethyl 3-(2-(cyclohex-1-en-1-ylethynyl)phenyl)-2-diazo-3-oxopropanoate (**1s**).



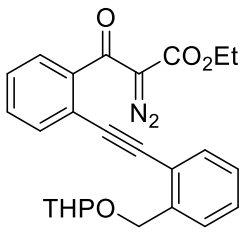
Yellow solid, 2.51 g, 78% yield. ^{1}H NMR (300 MHz, $CDCl_3$) (δ, ppm) 7.47 – 7.33 (comp, 4H), 6.24 – 6.14 (m, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.22 – 2.10 (comp, 4H), 1.75 – 1.59 (comp, 4H), 1.15 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 187.5, 161.1, 140.5, 136.1, 131.8, 130.4, 127.8, 127.1, 121.7, 120.5, 96.2, 84.1, 61.7, 29.0, 25.9, 22.3, 21.5, 14.1. HRMS (TOF MS ESI$^+$) calculated for $C_{19}H_{18}N_2NaO_3^+$ $[M+Na]^+$: 345.1210, found: 345.1212.

Ethyl 3-(2-((2-(azidomethyl)phenyl)ethynyl)phenyl)-2-diazo-3-oxopropanoate (**1t**).



Yellow solid, 2.57 g, 69% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.60 (d, *J* = 7.1 Hz, 1H), 7.55 – 7.49 (m, 1H), 7.49 – 7.43 (m, 1H), 7.43 – 7.26 (comp, 5H), 4.54 (s, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 1.12 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 187.0, 160.5, 140.4, 137.0, 132.5, 132.2, 130.2, 129.1, 128.6, 128.3, 128.2, 126.9, 122.2, 120.3, 91.4, 90.8, 61.5, 52.8, 13.9. HRMS (TOF MS ESI$^+$) calculated for $C_{20}H_{15}N_5NaO_3^+$ $[M+Na]^+$: 396.1067, found: 396.1071.

Ethyl 2-diazo-3-oxo-3-(2-((2-(((tetrahydro-2*H*-pyran-2-yl)oxy)methyl)phenyl)ethynyl)phenyl) propanoate (**1u**).



Yellow solid, 3.11 g, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.59 – 7.42 (comp, 2H), 7.41 – 7.34 (comp, 2H), 7.33 – 7.23 (comp, 3H), 7.22 – 7.15 (m, 1H), 4.75 (dd, *J* = 81.3, 13.0 Hz, 2H), 4.70 (t, *J* = 3.5 Hz, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.89 – 3.80 (m, 1H), 3.52 – 3.41 (m, 1H), 1.88 – 1.74 (m, 1H), 1.68 – 1.58 (m, 2H), 1.50 – 1.43 (m, 2H), 1.22 – 1.15 (m, 1H), 1.02 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 187.3, 160.9, 140.6, 140.5, 132.3, 132.3, 130.4, 129.0, 128.3, 127.6, 127.3, 127.1, 121.2, 121.1, 98.5, 91.7, 91.1, 67.2, 62.3, 61.7, 30.7, 25.6, 19.5, 14.1. HRMS (TOF MS ESI$^+$) calculated for $C_{25}H_{24}N_2NaO_5^+$ $[M+Na]^+$: 455.1577, found: 455.1574.

General Procedure for the Preparation of Au(I)-Catalysts

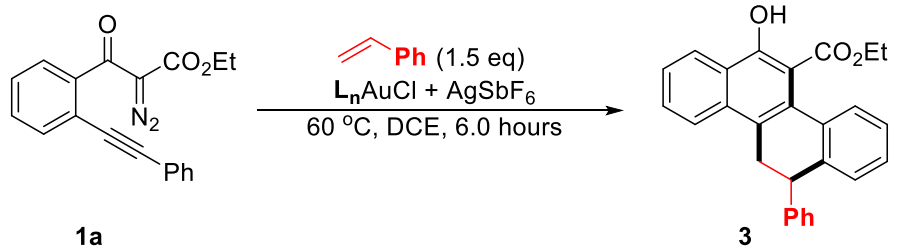
L1AuCl – **L7**AuCl were prepared according to literature procedures[2].

Preparation of $(Me_2N)_3PAuCl$: To a solution of the tris(dimethylamino)phosphine (163.2 mg, 1.0 mmol) in CH_2Cl_2 (5.0 mL), $(Me_2S)AuCl$ (294.6 mg, 1.0 mmol) was added under argon in the absence of light at 25 ºC, and the solution was stirring for 6 hours. After TLC indicated complete consumption of the starting materials, the reaction solution was removed under reduced pressure to give 395.0 mg $(Me_2N)_3PAuCl$ complex in quantitative yield, which was pure enough and used directly without additional treatment (stored in the glove box). The analysis of NMR is consistent with the literature[3]. ^{1}H NMR (300 MHz, $CDCl_3$) (δ, ppm) 2.66 (d, J = 11.7 Hz, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 37.8 (d, J = 9.2 Hz); ^{31}P NMR (122 MHz, $CDCl_3$) (δ, ppm) 110.75 (s).

Optimization of the Reaction Conditions

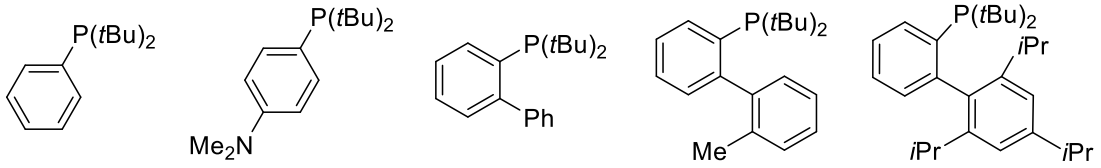
To a 10-mL oven-dried vial containing a magnetic stirring bar, the **Ln**AuCl complex (0.01 mmol), $AgSbF_6$ (3.34 mg, 0.01 mmol), and DCE (0.5 mL) were added in sequence in a nitrogen-filled glove-box. The reaction was stirred at 25 ºC for 2.0 hours. The solvent was removed and the residue was dissolved in DCE (0.5 mL). The mixture was filtered through a pad of Celite. The filtrate was added into a solution of **1a** (63.6 mg, 0.2 mmol) and styrene (31.3 mg, 35.0 μL) in DCE (0.5 mL) at 60 ℃, and the resulting reaction mixture was stirred under these conditions for 6.0 hours. Then, the crude the reaction mixture was subjected to ^{1}H NMR analysis with mesitylene as internal standard for the determination of the yields, and the results are summarized in Fig. S1a. Moreover, these optimization results have shown good correlation with the calculated parameters of Au-Cl bond distance of gold-complexes with corresponding ligands (see Fig. S1b).

a)

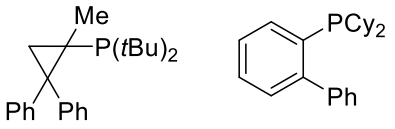


1a **3**

$(p\text{-}CF_3C_6H_4)_3P$	Ph_3P	$(p\text{-}OMeC_6H_4)_3P$	$(o\text{-}MeC_6H_4)_3P$	$(o\text{-}PhC_6H_4)PPh_2$
< 2%	< 2%	9%	< 2%	< 2%
Ph_2MeP	Me_3P	Cy_3P	$(t\text{Bu})_2MeP$	$(t\text{Bu})_3P$
< 2%	< 2%	36%	27%	29%



L1, < 2% **L2**, 58% **L3**, (90%)84% **L4**, 52% **L5**, 41%

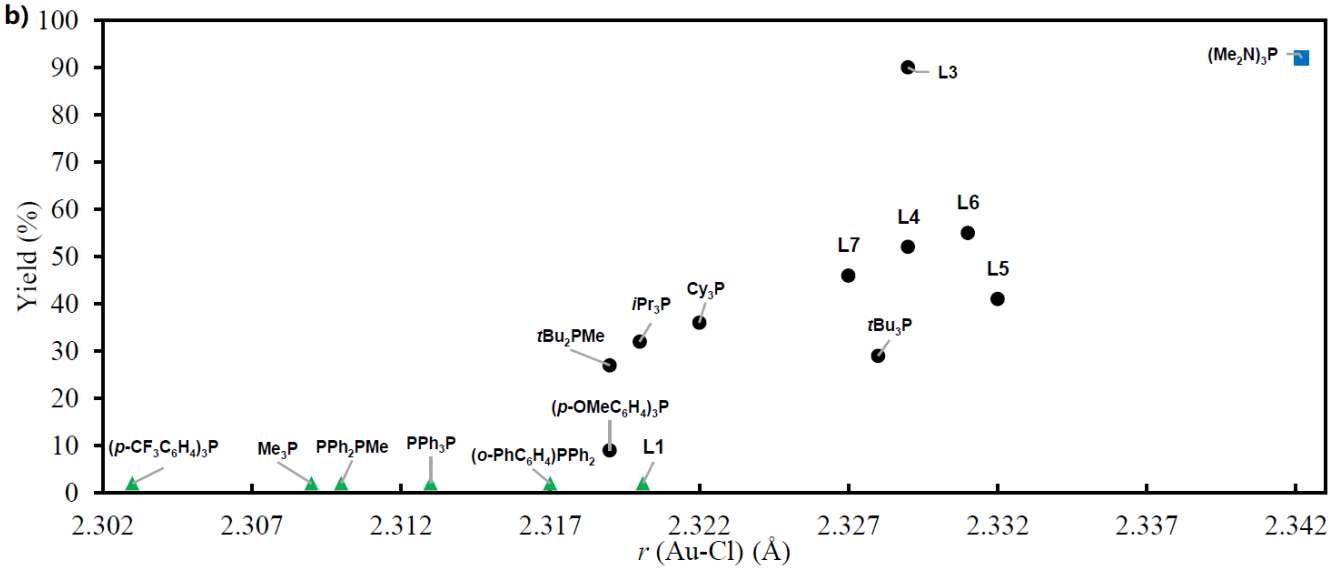


L6, 55% **L7**, 46%

iPr_3P 32%

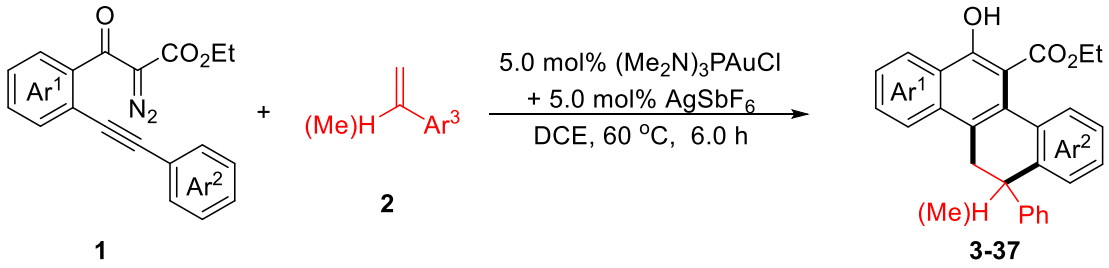
$(Me_2N)_3P$ (92%) 89%

b)



Supplementary Fig. S1 a) Screening of phosphine ligands. **b**) Plot of yield versus distance of Au-Cl (*L*). *Note*: the calculated distance of Au-Cl bond may not correspond with the same absolute values as those reported in the literature[4].

General Procedure for the Gold-Catalyzed Formal [4+2] Cycloaddition

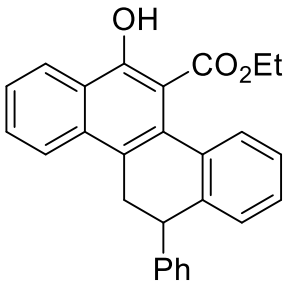


To a 10-mL oven-dried vial containing a magnetic stirring bar, $(Me_2N)_3PAuCl$ (3.95 mg, 0.01 mmol), $AgSbF_6$ (3.43 mg, 0.01 mmol), and DCE (0.5 mL) were added in sequence in a nitrogen-filled glove-box. The reaction mixture was stirred at 25 °C for 2.0 hours. The solvent was removed and the residue was dissolved in DCE (0.5 mL). Then the mixture was filtered through a pad of Celite. The filtrate was added into a solution of **1** (0.2 mmol) and **2** (olefin, 0.3 mmol) in DCE (0.5 mL) at 60 °C, and the resulting reaction mixture was stirred under these conditions for 6.0 hours. Then, the solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel (eluent: Ethyl acetate/light petroleum ether =1/30~1/10) to afford the polycyclic compounds **3** – **37** in good to high yields.

Note: 6.0 mL DCE was used in preparation of compound **30** and **31**.

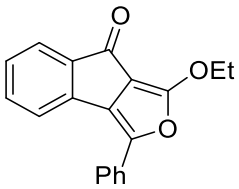
Characterization of [4+2] Cycloaddition Products 3-31

Ethyl 6-hydroxy-12-phenyl-11,12-dihydrochrysene-5-carboxylate (3).



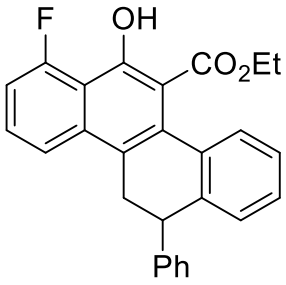
Yellow solid; m.p. 168.0 – 170.0 °C. 70.2 mg, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 11.13 (s, 1H), 8.55 – 8.35 (m, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.60 – 7.53 (m, 1H), 7.50 – 7.44 (m, 1H), 7.39 – 7.16 (comp, 8H), 7.04 (d, *J* = 7.3 Hz, 1H), 4.47 – 4.08 (comp, 3H), 3.68 – 3.11 (m, 2H), 1.08 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.1, 158.6, 142.8, 139.0, 135.5, 134.2, 131.2, 129.6, 129.4, 128.7, 128.4, 127.02, 126.98, 126.6, 125.81, 125.76, 124.5, 124.4, 123.2, 104.9, 61.4, 44.2, 32.3, 13.7. HRMS (TOF MS ESI$^+$) calculated for $C_{27}H_{22}NaO_3^+$ $[M+Na]^+$: 417.1461, found: 417.1450.

1-Ethoxy-3-phenyl-8*H*-indeno[1,2-*c*]furan-8-one (3').



Yellow solid; m.p. 128.0 – 130.0 °C. 51.7 mg, 89% yield. ^{1}H NMR (300 MHz, $CDCl_3$) (δ, ppm) 7.82 – 7.72 (comp, 4H), 7.55 – 7.46 (comp, 3H), 7.42 – 7.30 (m, 2H), 4.90 (q, *J* = 7.1 Hz, 2H), 1.53 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) (δ, ppm) 182.6, 157.4, 142.1, 138.2, 137.3, 133.5, 129.8, 129.0, 128.5, 128.3, 125.5, 125.3, 124.8, 122.5, 101.1, 70.9, 15.1. HRMS (TOF MS ESI$^+$) calculated for $C_{19}H_{14}NaO_3^+$ $[M+Na]^+$: 313.0835, found: 313.0850.

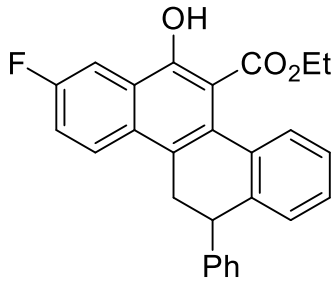
Ethyl 7-fluoro-6-hydroxy-12-phenyl-11,12-dihydrochrysene-5-carboxylate (4).



Yellow solid; m.p. 143.0 – 145.0 °C. 75.0 mg, 91% yield. ^{1}H NMR (300 MHz, $CDCl_3$) (δ, ppm) 11.12 (d, *J* = 2.1 Hz, 1H), 7.60 (d, *J* = 8.5 Hz, 1H), 7.36 – 7.28 (m, 1H), 7.21 – 7.07 (comp, 8H), 7.00 – 6.90 (comp, 2H), 4.25 – 4.04 (comp, 3H), 3.22 (d, *J* = 6.8 Hz, 2H), 0.94 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 171.7, 161.0 (d, *J* = 260.6 Hz), 158.1 (d, *J* = 3.9 Hz), 142.6, 139.0, 136.6 (d, *J* = 2.5 Hz), 135.2, 132.5 (d, *J* = 1.6 Hz), 129.7 (d, *J* = 9.6 Hz), 129.2, 128.7, 128.4, 127.4, 127.2, 126.7, 126.0, 125.4 (d, *J* = 2.4 Hz), 119.2 (d, *J* = 4.4 Hz), 114.3 (d, *J* = 8.8 Hz), 111.9 (d, *J* = 22.5 Hz), 106.3 (d, *J* = 1.9 Hz),

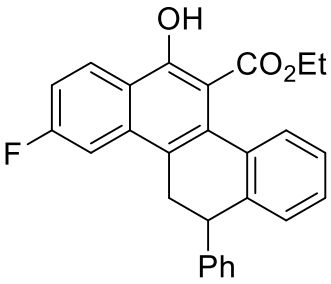
61.6, 44.1, 32.9, 13.6; ^{19}F NMR (283 MHz, $CDCl_3$) (δ, ppm) -109.47. HRMS (TOF MS ESI$^+$) calculated for $C_{27}H_{21}FNaO_3^+$ [M+Na]$^+$: 435.1367, found: 435.1370.

Ethyl 8-fluoro-6-hydroxy-12-phenyl-11,12-dihydrochrysene-5-carboxylate (5).



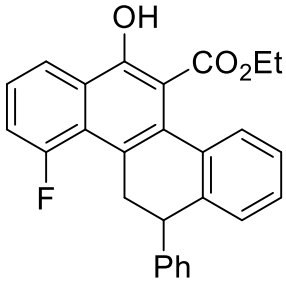
Yellow solid; m.p. 161.0 – 163.0 ℃. 76.6 mg, 93% yield. ^{1}H NMR (300 MHz, $CDCl_3$) (δ, ppm) 10.83 (s, 1H), 7.86 (dd, *J* = 9.9, 2.7 Hz, 1H), 7.76 (dd, *J* = 9.3, 5.3 Hz, 1H), 7.20 – 7.03 (comp, 9H), 6.93 – 6.86 (m, 1H), 4.28 – 3.97 (comp, 3H), 3.19 (d, *J* = 6.9 Hz, 2H), 0.95 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 171.9, 160.7 (d, *J* = 246.9 Hz), 157.5 (d, *J* = 4.8 Hz), 142.6, 138.9, 135.3, 131.1 (d, *J* = 1.4 Hz), 130.6 (d, *J* = 2.6 Hz), 129.3, 128.7, 128.5, 127.1, 126.7, 125.9, 125.8, 125.7, 125.6, 125.5, 119.2 (d, *J* = 24.6 Hz), 108.7 (d, *J* = 22.4 Hz), 105.9, 61.6, 44.1, 32.5, 13.7; ^{19}F NMR (283 MHz, $CDCl_3$) (δ, ppm) -114.12. HRMS (TOF MS ESI$^+$) calculated for $C_{27}H_{21}FNaO_3^+$ [M+Na]$^+$: 435.1367, found: 435.1377.

Ethyl 9-fluoro-6-hydroxy-12-phenyl-11,12-dihydrochrysene-5-carboxylate (6).



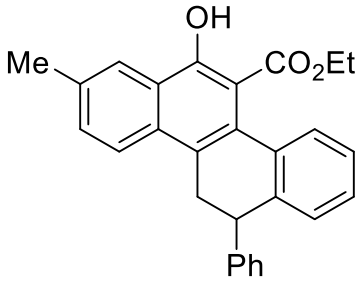
Yellow solid; m.p. 141.0 – 143.0 ℃. 71.7 mg, 87% yield. ^{1}H NMR (300 MHz, $CDCl_3$) (δ, ppm) 11.01 (s, 1H), 8.23 (dd, *J* = 9.1, 6.0 Hz, 1H), 7.38 (dd, *J* = 11.2, 2.4 Hz, 1H), 7.18 – 7.00 (comp, 9H), 6.94 – 6.87 (m, 1H), 4.22 – 4.02 (comp, 3H), 3.12 (d, *J* = 6.8 Hz, 2H), 0.94 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 171.9, 163.6 (d, *J* = 249.6 Hz), 158.6 (d, *J* = 1.1 Hz), 142.5, 139.0, 136.0 (d, *J* = 9.2 Hz), 135.3, 132.7, 129.6, 128.7, 128.4, 127.5 (d, *J* = 9.7 Hz), 127.3, 127.2, 126.7, 125.9, 125.0 (d, *J* = 4.8 Hz), 121.3 (d, *J* = 1.1 Hz), 115.3 (d, *J* = 24.6 Hz), 107.6 (d, *J* = 22.2 Hz), 104.4 (d, *J* = 2.0 Hz), 61.5, 44.0, 32.5, 13.7; ^{19}F NMR (283 MHz, $CDCl_3$) (δ, ppm) -108.83. HRMS (TOF MS ESI$^+$) calculated for $C_{27}H_{21}FNaO_3^+$ [M+Na]$^+$: 435.1367, found: 435.1361.

Ethyl 10-fluoro-6-hydroxy-12-phenyl-11,12-dihydrochrysene-5-carboxylate (7).



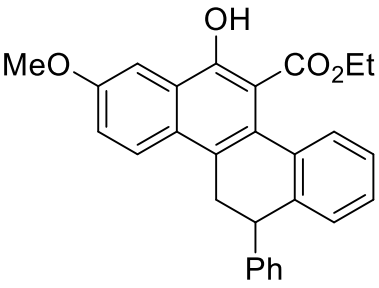
Yellow solid; m.p. 158.0 – 160.0 ℃. 67.6 mg, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 10.90 (s, 1H), 8.03 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.18 – 6.99 (comp, 10H), 6.95 – 6.86 (m, 1H), 4.20 – 3.99 (comp, 3H), 3.71 – 3.38 (m, 2H), 0.91 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 171.8, 160.2 (d, *J* = 252.8 Hz), 157.7 (d, *J* = 4.1 Hz), 142.8, 138.9, 135.4, 132.8 (d, *J* = 1.6 Hz), 129.3, 128.8, 128.3, 127.3, 126.9, 126.8 (d, *J* = 5.3 Hz), 126.5, 125.9, 125.5 (d, *J* = 9.1 Hz), 124.5 (d, *J* = 11.1 Hz), 124.2 (d, *J* = 5.0 Hz), 120.6 (d, *J* = 4.1 Hz), 115.4 (d, *J* = 24.0 Hz), 106.0 (d, *J* = 1.4 Hz), 61.6, 44.0 (d, *J* = 2.8 Hz), 34.6 (d, *J* = 16.0 Hz), 13.6; ^{19}F NMR (283 MHz, $CDCl_3$) (δ, ppm) -109.08. HRMS (TOF MS ESI$^+$) calculated for $C_{27}H_{21}FNaO_3^+$ [M+Na]$^+$: 435.1367, found: 435.1365.

Ethyl 6-hydroxy-8-methyl-12-phenyl-11,12-dihydrochrysene-5-carboxylate (8).



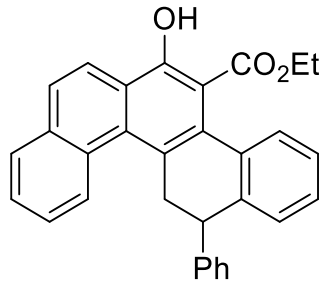
Yellow solid; m.p. 90.0 – 92.0 ℃. 73.5 mg, 90% yield. ^{1}H NMR (300 MHz, $CDCl_3$) (δ, ppm) 11.07 (s, 1H), 8.27 (d, *J* = 8.5 Hz, 1H), 7.71 (s, 1H), 7.33 – 7.12 (comp, 9H), 7.02 – 6.92 (m, 1H), 4.32 – 4.11 (comp, 3H), 3.43 – 3.24 (m, 2H), 2.47 (s, 3H), 1.04 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 172.2, 158.8, 142.9, 139.9, 139.1, 135.7, 134.5, 131.4, 129.4, 128.8, 128.5, 127.9, 127.0, 126.9, 126.7, 125.8, 125.4, 124.5, 122.7, 122.5, 104.2, 61.3, 44.3, 32.4, 22.3, 13.7. HRMS (TOF MS ESI$^+$) calculated for $C_{28}H_{24}NaO_3^+$ [M+Na]$^+$: 431.1618, found: 431.1623.

Ethyl 6-hydroxy-8-methoxy-12-phenyl-11,12-dihydrochrysene-5-carboxylate (9).



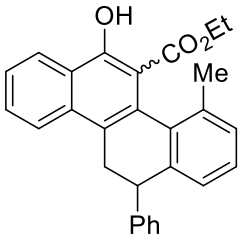
Yellow solid; m.p. 138.0 – 142.0 ℃. 78.1 mg, 92% yield. ^{1}H NMR (300 MHz, $CDCl_3$) (δ, ppm) 10.89 (s, 1H), 7.69 (d, *J* = 9.2 Hz, 1H), 7.56 (d, *J* = 2.7 Hz, 1H), 7.21 – 7.00 (comp, 9H), 6.87 (d, *J* = 7.3 Hz, 1H), 4.22 – 4.01 (comp, 3H), 3.78 (s, 3H), 3.28 – 3.04 (m, 2H), 0.95 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 172.2, 157.8, 157.3, 142.8, 138.8, 135.6, 129.3, 129.2, 128.9, 128.8, 128.4, 127.0, 126.63, 126.60, 125.9, 125.8, 125.5, 125.0, 121.6, 105.5, 103.1, 61.4, 55.5, 44.3, 32.5, 13.7. HRMS (TOF MS ESI$^+$) calculated for $C_{28}H_{24}NaO_4^+$ [M+Na]$^+$: 447.1567, found: 447.1558.

Ethyl 14-hydroxy-8-phenyl-7,8-dihydrobenzo[*c*]chrysene-13-carboxylate (10).



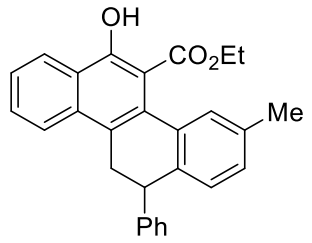
Yellow solid; m.p. 168.0 – 170.0 ℃. 47.1 mg, 53% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 12.18 (s, 1H), 8.39 (d, *J* = 9.0 Hz, 1H), 7.90 – 7.80 (comp, 2H), 7.57 – 7.51 (m, 1H), 7.39 – 7.27 (comp, 3H), 7.24 – 7.13 (comp, 5H), 7.04 – 6.96 (comp, 2H), 6.87 – 6.73 (m, 1H), 4.46 (t, *J* = 6.9 Hz, 1H), 3.93 (q, *J* = 7.2 Hz, 2H), 3.15 – 3.09 (m, 2H), 0.69 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) (δ, ppm) 172.1, 158.8, 144.3, 142.1, 138.9, 138.0, 133.2, 131.8, 129.2, 129.0, 128.5, 128.3, 128.2, 127.8, 127.5, 126.61, 126.59, 126.55, 126.5, 126.0, 123.4, 121.3, 120.9, 108.5, 61.0, 44.9, 34.0, 13.1. HRMS (TOF MS ESI$^+$) calculated for $C_{31}H_{24}NaO_3^+$ [M+Na]$^+$: 467.1618, found: 467.1630.

Ethyl 6-hydroxy-4-methyl-12-phenyl-11,12-dihydrochrysene-5-carboxylate (11).

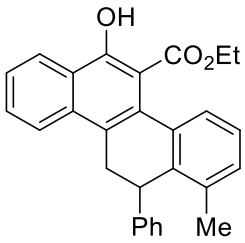


Yellow solid; m.p. 113.0 – 115.0 ℃. 61.3 mg, 75% yield, *dr* = 3:2. ^{1}H NMR (300 MHz, $CDCl_3$) (δ, ppm) *with two isomers together*, 11.88 and 11.65 (s, 1H), 8.60 – 8.41 (comp, 1H), 8.09 – 8.02 (comp, 1H), 7.70 – 7.43 (comp, 4H), 7.31 – 7.26 (comp, 1H), 7.26 – 7.17 (comp, 2H), 7.12 – 7.00 (comp, 3H), 6.70 – 6.49 (comp, 1H), 4.45 – 4.07 (comp, 3H), 3.88 – 3.50 (comp, 1H), 3.26 – 2.99 (comp, 1H), 2.34 and 2.33 (s, 3H), 1.10 and 1.01 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) *with two isomers together*, 172.0 and 171.8, 158.2 and 157.9, 143.0 and 142.5, 142.0 and 139.3, 136.7 and 135.7, 135.8 and 135.0, 134.8 and 134.0, 130.8 and 130.2, *129.7 – 123.2 included 25 peaks*: (129.7, 129.5, 129.4, 129.1, 128.8, 128.6, 128.1, 127.8, 127.0, 126.9, 126.5, 125.90, 125.86, 125.81, 125.77, 125.5, 124.6, 124.5, 124.2, 124.1, 123.5, 123.4, 123.3), 106.9 and 106.7, 61.6 and 61.5, 46.9 and 44.0, 32.7 and 32.1, 20.84, 13.6 and 13.4. HRMS (TOF MS ESI$^+$) calculated for $C_{28}H_{24}NaO_3^+$ [M+Na]$^+$: 431.1618, found: 431.1611.

Ethyl 6-hydroxy-3-methyl-12-phenyl-11,12-dihydrochrysene-5-carboxylate (**12a**) &
Ethyl 6-hydroxy-1-methyl-12-phenyl-11,12-dihydrochrysene-5-carboxylate (**12b**).



12a

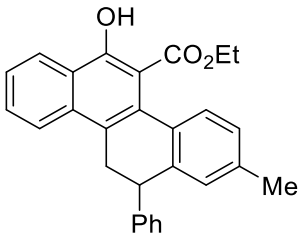


12b

Yellow oil, combined 77.6 mg in total with 95% yield, **12a**:**12b** = 63:37. **12a**: ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 11.03 (s, 1H), 8.35 (d, *J* = 8.3 Hz, 1H), 7.89 – 7.82 (m, 1H), 7.51 – 7.42 (comp, 2H), 7.40 – 7.31 (m, 1H), 7.23 – 6.92 (comp, 6H), 6.84 (d, *J* = 7.5 Hz, 1H) 4.28 – 4.07 (comp, 3H), 3.32 – 3.22 (m, 2H) 2.28 (s, 3H), 1.04 – 0.97 (m, 3H); **12b**: ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 10.86 (s, 1H), 8.29 (d, *J* = 8.3 Hz, 1H), 7.89 – 7.82 (m, 1H), 7.40 – 7.31 (comp, 2H), 7.23 – 6.92 (comp, 8H), 4.51 (d, *J* = 5.9 Hz, 1H), 4.24 – 4.07 (m, 2H), 3.66 (d, *J* = 16.3 Hz, 1H), 3.09 (dd, *J* = 16.2, 6.2

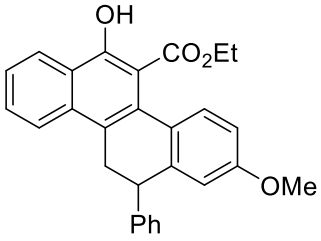
Hz, 1H), 2.23 (s, 3H), 1.04 – 0.97 (m, 3H); *Combined two isomers*: ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.2 and 172.1, 158.5 and 158.2, 143.00 and 141.9,(34 carbon signals were crossed from 123.1 to 136.4) 136.4, 136.24, 136.22, 136.1, 135.4, 135.1, 135.0, 134.4, 134.2, 131.9, 131.3, 130.1, 129.6, 129.4, 129.0, 128.7, 128.4, 128.2, 128.0, 127.7, 127.5, 126.9, 126.6, 126.2, 125.7, 125.5, 124.5, 124.44, 124.37, 124.3, 124.0, 123.2, 123.1, 105.2 and 104.9, 61.3 and 61.2, 43.9 and 38.9, 32.5 and 32.4, 21.3 and 19.4, 13.69 and 13.66. HRMS (TOF MS ESI$^+$) calculated for $C_{28}H_{24}NaO_3^+$ $[M+Na]^+$: 431.1618, found: 431.1611.

Ethyl 6-hydroxy-2-methyl-12-phenyl-11,12-dihydrochrysene-5-carboxylate (13).



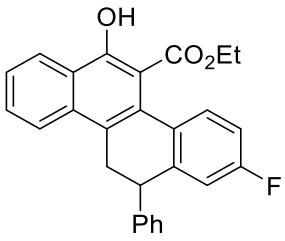
Yellow solid; m.p. 143.0 – 145.0 ℃. 68.6 mg, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 11.05 (s, 1H), 8.48 – 8.39 (m, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.62 – 7.56 (m, 1H), 7.52 – 7.46 (m, 1H), 7.36 – 7.32 (comp, 2H), 7.31 – 7.26 (comp, 2H), 7.25 – 7.19 (m, 1H), 7.16 – 7.07 (comp, 2H), 6.88 (s, 1H), 4.37 – 4.20 (comp, 3H), 3.47 – 3.34 (m, 2H), 2.34 (s, 3H), 1.12 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.2, 158.4, 143.0, 138.8, 136.9, 134.3, 132.9, 131.3, 129.6, 129.4, 128.7, 128.4, 127.8, 126.7, 126.6, 125.6, 125.2, 124.6, 124.3, 123.2, 105.0, 61.4, 44.2, 32.5, 21.4, 13.8. HRMS (TOF MS ESI$^+$) calculated for $C_{28}H_{24}NaO_3^+$ $[M+Na]^+$: 431.1618, found: 431.1613.

Ethyl 12-(2-chlorophenyl)-6-hydroxy-2-methoxy-11,12-dihydrochrysene-5-carboxylate (14).



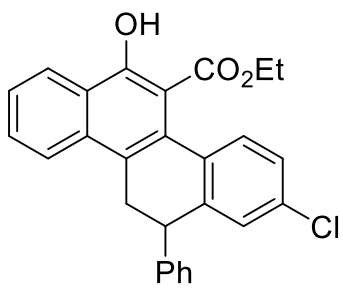
Yellow solid; m.p. 174.0 – 176.0 ℃. 76.4 mg, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 11.10 (s, 1H), 8.43 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.61 – 7.55 (m, 1H), 7.50 – 7.44 (m, 1H), 7.38 – 7.33 (comp, 2H), 7.33 – 7.27 (comp, 2H), 7.26 – 7.21 (m, 1H), 7.17 (d, *J* = 8.5 Hz, 1H), 6.87 – 6.80 (m, 1H), 6.62 (s, 1H), 4.38 – 4.22 (comp, 3H), 3.79 (s, 3H), 3.47 – 3.29 (m, 2H), 1.15 (t, *J* = 7.1 Hz, 3H) ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.2, 158.8, 158.5, 142.7, 140.8, 134.3, 131.0, 130.7, 129.6, 128.71, 128.65, 128.4, 126.7, 125.4, 124.5, 124.0, 123.0, 112.5, 111.4, 104.9, 61.4, 55.3, 44.6, 32.3, 13.9. HRMS (TOF MS ESI$^+$) calculated for $C_{28}H_{24}NaO_4^+$ $[M+Na]^+$: 447.1567, found: 447.1588.

Ethyl 2-fluoro-6-hydroxy-12-phenyl-11,12-dihydrochrysene-5-carboxylate (15).



Yellow solid; m.p. 120.0 – 122.0 ℃. 33.8 mg, 41% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 11.16 (s, 1H), 8.43 (d, *J* = 7.7 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.62 – 7.58 (m, 1H), 7.53 – 7.48 (m, 1H), 7.37 – 7.30 (comp, 4H), 7.23 – 7.12 (comp, 2H), 6.97 – 6.92 (m, 1H), 6.76 – 6.66 (m, 1H), 4.36 – 4.16 (comp, 3H), 3.46 – 3.29 (comp, 2H), 1.11 (t, *J* = 7.1 Hz, 3H) ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.0, 161.9 (d, *J* = 246.9 Hz), 158.9, 142.0, 134.2, 131.7 (d, *J* = 3.2 Hz), 130.9 (d, *J* = 8.1 Hz), 130.3, 129.9, 128.76, 128.67, 127.0, 125.9, 124.7, 124.4, 123.2, 113.9 (d, *J* = 22.2 Hz), 112.7 (d, *J* = 21.7 Hz), 104.7, 61.5, 44.5, 32.1, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$) (δ, ppm) -114.89. HRMS (TOF MS ESI$^+$) calculated for $C_{27}H_{21}FNaO_3^+$ $[M+Na]^+$: 435.1367, found: 435.1379.

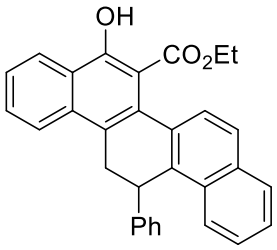
Ethyl 2-chloro-6-hydroxy-12-phenyl-11,12-dihydrochrysene-5-carboxylate (16).



Yellow solid; m.p. 176.0 – 178.0 ℃. 46.3 mg, 54% yield. ^{1}H NMR (300 MHz, $CDCl_3$) (δ, ppm) 11.18 (s, 1H), 8.49 – 8.37 (m, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.64 – 7.58 (m, 1H), 7.54 – 7.47 (m, 1H), 7.34 – 7.29 (comp, 4H), 7.26 – 7.20 (comp, 2H), 7.15 – 7.11 (m, 1H), 7.03 – 6.96 (m, 1H), 4.40 – 4.16 (comp, 3H), 3.46 – 3.29 (m, 2H), 1.12 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.8, 159.0, 141.9, 141.0, 134.2, 132.7, 130.7, 130.2, 129.9, 128.7, 127.1, 127.0, 126.1, 125.9, 124.7, 124.6,

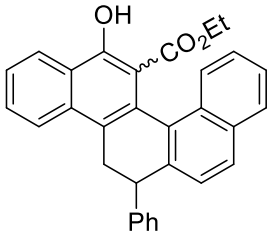
123.3, 104.6, 61.6, 44.3, 32.2, 13.8. HRMS (TOF MS ESI$^+$) calculated for $C_{27}H_{21}ClNaO_3^+$ [M+Na]$^+$: 451.1071, found: 451.1080.

Ethyl 14-hydroxy-6-phenyl-5,6-dihydrobenzo[*c*]tetraphene-13-carboxylate (17).



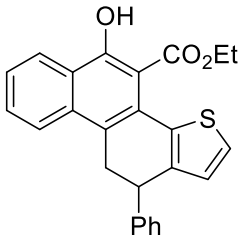
Yellow solid; m.p. 182.0 – 184.0 ℃. 75.6 mg, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 11.17 (s, 1H), 8.51 – 8.30 (m, 1H), 8.11 – 8.03 (m, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.93 – 7.89 (m, 1H), 7.82 (d, *J* = 8.6 Hz, 1H), 7.64 – 7.57 (m, 1H), 7.53 – 7.48 (comp, 3H), 7.46 (s, 1H), 7.37 – 7.32 (comp, 2H), 7.15 – 7.05 (comp, 3H), 5.19 (d, *J* = 6.1 Hz, 1H), 4.40 – 4.31 (m, 1H), 4.22 – 4.14 (m, 1H), 3.88 (d, *J* = 16.4, 1H), 3.29 (dd, *J* = 16.4, 6.1 Hz, 1H), 0.99 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.9, 158.7, 142.0, 134.5, 133.9, 133.2, 132.9, 132.0, 131.3, 129.6, 128.4, 128.21, 128.15, 127.9, 126.5, 126.3, 125.80, 125.75, 125.7, 124. 6, 124.5, 124.1, 123.9, 123.2, 105.0, 61.4, 38.5, 32.5, 13.7. HRMS (TOF MS ESI$^+$) calculated for $C_{31}H_{24}NaO_3^+$ [M+Na]$^+$: 467.1618, found: 467.1604.

Ethyl 8-hydroxy-14-phenyl-13,14-dihydrobenzo[c]chrysene-7-carboxylate (18).



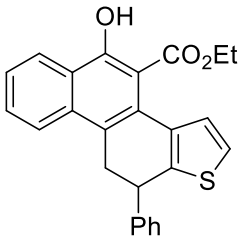
The desired product was isolated as a mixture of two diastereoisomers. Yellow solid; m.p. 165.0 – 170.0 ℃. 70.2 mg, 79% yield, *dr* = 1:1. *One diastereoisomer*: ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 11.66 (s, 1H), 8.55 (d, *J* = 8.4 Hz, 1H), 8.09 – 8.00 (comp, 2H), 7.82 – 7.77 (m, 1H), 7.67 – 7.62 (comp, 2H), 7.59 – 7.55 (m, 1H), 7.50 – 7.37 (comp, 7H), 6.92 (d, *J* = 8.4 Hz, 1H), 4.24 (dd, *J* = 14.9, 4.1 Hz, 1H), 3.68 – 3.55 (comp, 2H), 3.37 – 3.27 (m, 1H), 3.06 (t, *J* = 15.0 Hz, 1H), 0.47 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.7, 157.9, 143.0, 138.9, 134.1, 132.8, 132.4, 131.9, 129.7, 129.1, 129.0, 128.6, 128.5, 127.2, 127.0, 126.5, 125.9, 125.0, 124.7, 124.6, 124.4, 123.8, 123.7, 107.6, 61.2, 46.7, 33.3, 12.6. *The other diastereoisomer*: ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 11.43 (s, 1H), 8.43 (d, *J* = 8.3 Hz, 1H), 8.13 – 8.05 (comp, 2H), 7.90 – 7.86 (m, 1H), 7.82 – 7.80 (m, 1H), 7.60 – 7.57 (m, 1H), 7.51 – 7.44 (comp, 4H), 7.22 – 7.17 (commp, 2H), 7.08 – 6.98 (comp, 3H), 4.50 (d, *J* = 4.9 Hz, 1H), 3.88 – 3.78 (m, 2H), 3.32 – 3.27 (m, 1H), 3.24 – 3.16 (m, 1H), 0.43 (t, *J* = 7.2 Hz, 3H); *Combined two isomers*: ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.5, 157.5, 142.0, 136.7, 134.9, 134.0, 133.0, 132.1, 129.5, 129.0, 128.6, 128.2, 128.0, 127.7, 126.8, 126.6, 126.1, 125.8, 125.7, 125.1, 124.5, 124.3, 123.7, 123.5, 107.5, 61.1, 44.1, 32.5, 12.9. HRMS (TOF MS ESI$^+$) calculated for $C_{31}H_{24}NaO_3^+$ [M+Na]$^+$: 467.1618, found: 467.1613.

Ethyl 5-hydroxy-11-phenyl-10,11-dihydrophenanthro[1,2-*b*]thiophene-4-carboxy late (19).



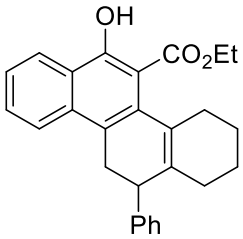
Yellow solid; m.p. 161.0 – 163.0 ℃. 69.7 mg, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 10.94 (s, 1H), 8.47 – 8.39 (m, 1H), 7.97 (d, *J* = 8.5 Hz, 1H), 7.64 – 7.56 (m, 1H), 7.53 – 7.46 (m, 1H), 7.46 – 7.41 (comp, 2H), 7.40 – 7.33 (comp, 2H), 7.33 – 7.25 (comp, 2H), 6.68 (d, *J* = 5.1 Hz, 1H), 4.54 – 4.37 (comp, 3H), 3.54 (dd, *J* = 16.2, 6.4 Hz, 1H), 3.32 (dd, *J* = 16.2, 10.6 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.0, 158.1, 143.3, 139.8, 136.8, 134.5, 129.8, 128.6, 128.4, 126.9, 126.8, 126.0, 125.6, 124.8, 124.7, 124.1, 124.0, 123.5, 104.9, 61.9, 41.2, 33.9, 13.9. HRMS (TOF MS ESI$^+$) calculated for $C_{25}H_{20}NaO_3S^+$ [M+Na]$^+$: 423.1025, found 423.1020.

Ethyl 5-hydroxy-11-phenyl-10,11-dihydrophenanthro[2,1-*b*]thiophene-4-carboxy late (20).

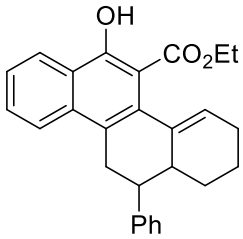


Yellow solid; m.p. 125.0 – 127.0 ℃. 72.9 mg, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 11.06 (s, 1H), 8.42 (d, *J* = 7.9 Hz, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.61 – 7.54 (m, 1H), 7.52 – 7.40 (comp, 3H), 7.39 – 7.27 (comp, 3H), 7.08 (d, *J* = 5.2 Hz, 1H), 6.99 (d, *J* = 5.2 Hz, 1H), 4.48 (dd, *J* = 10.6, 6.1 Hz, 1H), 4.43 – 4.29 (m, 2H), 3.56 (dd, *J* = 16.0, 6.1 Hz, 1H), 3.33 (dd, *J* = 16.0, 10.7 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.7, 158.3, 142.8, 140.7, 136.4, 134.7, 129.7, 128.7, 128.3, 128.1, 127.4, 125.4, 124.6, 123.9, 123. 6, 123. 3, 121.1, 105.0, 61.7, 40.9, 34.2, 13.9. HRMS (TOF MS ESI$^+$) calculated for $C_{25}H_{20}NaO_3S^+$ $[M+Na]^+$: 423.1025, found: 423.1018.

Ethyl 6-hydroxy-12-phenyl-1,2,3,11,12,12a-hexahydrochrysene-5-carboxylate (**22b**) &
Ethyl 6-hydroxy-12-phenyl-1,2,3,4,11,12-hexahydrochrysene-5-car boxylate (**22a**).



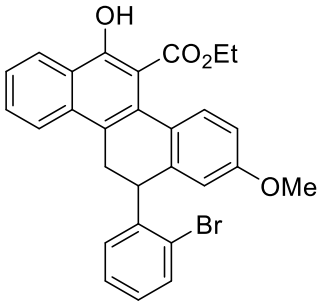
21a



21b

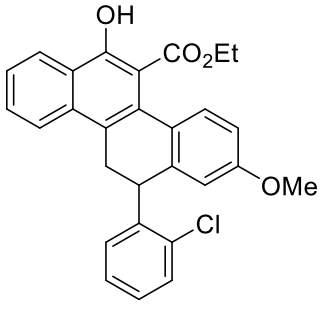
Yellow solid; combined 66.2 mg in total with 83% yield, **21a**:**21b** (*dr* = 1.7:1) = 40:60. *Combined three isomers*: ^{1}H NMR (300 MHz, $CDCl_3$) (δ, ppm) 10.99 – 10.21 (comp, 1H), 8.38 – 8.04 (comp, 1H), 7.86 – 7.49 (comp, 1H), 7.43 – 6.78 (comp, 7H), 5.63 – 0.64 (comp, 16H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.7, 172.4, 171.6, 157.6, 156.99, 156.98, 145.5, 144.0, 142.2, 137.6, 137.0, 134.9, 134.7, 134.3, 134.2, 133.8, 133.6, 133.5, 132.4, 129.29, 129.28, 129.2, 128.8, 128.7, 128.5, 128.4, 128.14, 128.06, 127.9, 126.63, 126.57, 126.3, 126.2, 125.3, 125.1, 124.8, 124.4, 124.3, 124.2, 124.1, 123.9, 123.4, 123.3, 123.23, 123.18, 123.0, 122.5, 106.3, 106.2, 105.3, 61.6, 61.2, 61.1, 49.3, 45.2, 44.0, 38.9, 35.3, 32.6, 30.3, 29.2, 29.0, 28.3, 27.0, 26.3, 26.0, 23.9, 23.4, 22.7, 21.8, 20.1, 14.2, 14.14, 14.12. HRMS (TOF MS ESI$^+$) calculated for $C_{27}H_{26}NaO_3^+$ $[M+Na]^+$: 421.1774, found: 421.1778.

Ethyl 12-(2-bromophenyl)-6-hydroxy-2-methoxy-11,12-dihydrochrysene-5-carboxylate (22).



Yellow solid; m.p. 182.0 – 184.0 ℃. 91.6 mg, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 11.02 (s, 1H), 8.47 – 8.34 (m, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.64 – 7.53 (comp, 2H), 7.50 – 7.41 (m, 1H), 7.26 – 7.21 (m, 1H), 7.20 (d, *J* = 8.5 Hz, 1H), 7.09 – 6.98 (comp, 2H), 6.90 – 6.83 (m, 1H), 6.68 (d, *J* = 2.5 Hz, 1H), 4.78 (t, *J* = 5.4 Hz, 1H), 4.44 – 4.33 (m, 1H), 4.31 – 4.21 (m, 1H), 3.81 (s, 3H), 3.67 (dd, *J* = 16.2, 5.4 Hz, 1H), 3.27 (dd, *J* = 16.2, 6.0 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.1, 159.0, 158.5, 141.1, 139.3, 134.4, 133.1, 131.0, 130.7, 129.6, 129.3, 128.1, 127.2, 125.5, 124.8, 124.5, 124.1, 123.7, 123.1, 112.6, 112.3, 104.8, 61.4, 55.4, 43.6, 30.4, 13.9. HRMS (TOF MS ESI$^+$) calculated for $C_{28}H_{23}BrNaO_4^+$ $[M+Na]^+$: 525.0672, found: 525.0696.

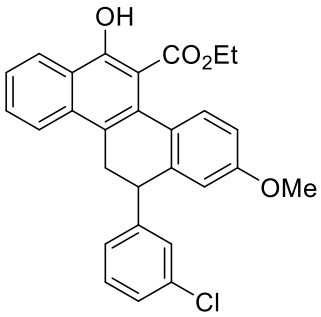
Ethyl 12-(2-chlorophenyl)-6-hydroxy-2-methoxy-11,12-dihydrochrysene-5-carboxylate (23).



Yellow solid; m.p. 193.0 – 195.0 ℃. 71.6 mg, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 11.02 (s, 1H), 8.41 – 8.36 (m, 1H), 7.93 (d, *J* = 8.5 Hz, 1H), 7.59 – 7.54 (m, 1H), 7.47 – 7.43 (m, 1H), 7.40 – 7.36 (m, 1H), 7.24 – 7.17 (m, 2H), 7.12 – 7.06 (m, 1H), 7.00 (t, *J* = 7.2 Hz, 1H), 6.89 – 6.83 (m, 1H), 6.68 (d, *J* = 2.5 Hz, 1H), 4.81 (t, *J* = 5.6 Hz, 1H), 4.44 – 4.20 (m, 2H), 3.81 (s, 3H), 3.66 (dd, *J* = 16.2, 5.5 Hz, 1H), 3.27 (dd, *J* = 16.2, 6.0 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.1, 159.0, 158.5, 139.5, 139.3, 134.5, 134.1, 131.0, 130.8, 130.6, 129.8, 129.6, 129.4, 127.8, 126.5, 125.5, 124.5, 124.1, 123.8, 123.1, 112.5, 112.2, 104.8, 61.4, 55.4,

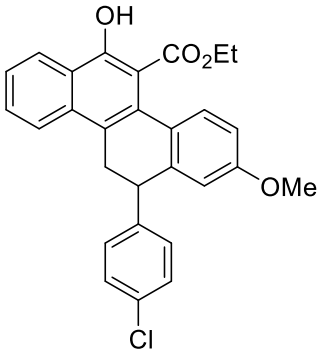
41.1, 30.2, 13.9. HRMS (TOF MS ESI$^+$) calculated for $C_{28}H_{23}ClNaO_4^+$ [M+Na]$^+$: 481.1177, found: 481.1186.

Ethyl 12-(3-chlorophenyl)-6-hydroxy-2-methoxy-11,12-dihydrochrysene-5-carboxylate (24).



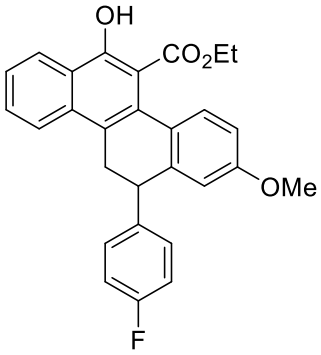
Yellow solid; m.p. 178.0 – 180.0 ℃. 65.2 mg, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 11.10 (s, 1H), 8.43 – 8.38 (m, 1H), 7.92 (d, *J* = 8.5 Hz, 1H), 7.62 – 7.54 (m, 1H), 7.53 – 7.42 (m, 1H), 7.27 – 7.21 (comp, 2H), 7.20 – 7.13 (comp, 3H), 6.91 – 6.78 (m, 1H), 6.65 (d, *J* = 2.4 Hz, 1H), 4.34 – 4.25 (comp, 3H), 3.81 (s, 3H), 3.43 (dd, *J* = 16.0, 6.5 Hz, 1H), 3.32 (dd, *J* = 16.0, 5.6 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.1, 158.9, 158.6, 144.9, 139.5, 134.3, 134.2, 131.0, 130.9, 129.7, 129.6, 128.8, 128.7, 126.8, 126.7, 125.5, 124.6, 124.1, 123.7, 123.0, 112.6, 111.9, 104.8, 61.6, 55.4, 44.1, 32.3, 13.9. HRMS (TOF MS ESI$^+$) calculated for $C_{28}H_{23}ClNaO_4^+$ [M+Na]$^+$: 481.1177, found: 481.1169.

Ethyl 12-(4-chlorophenyl)-6-hydroxy-2-methoxy-11,12-dihydrochrysene-5-carboxylate (25).



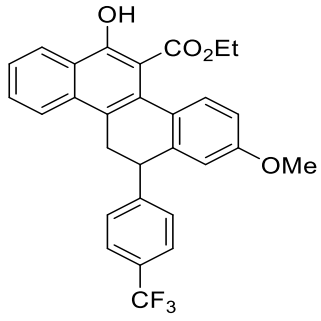
Yellow solid; m.p. 180.0 – 182.0 ℃. 80.8 mg, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 11.08 (s, 1H), 8.42 (d, *J* = 8.2 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.61 – 7.53 (m, 1H), 7.51 – 7.41 (m, 1H), 7.27 – 7.21 (comp, 4H), 7.17 (d, *J* = 8.6 Hz, 1H), 6.89 – 6.81 (m, 1H), 6.62 (d, *J* = 2.0 Hz, 1H), 4.39 – 4.22 (comp, 3H), 3.80 (s, 3H), 3.40 – 3.28 (m, 2H), 1.14 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.0, 158.9, 158.5, 141.2, 140.0, 134.2, 132.3, 131.0, 130.8, 130.0, 129.7, 128.6, 128.5, 125.5, 124.6, 124.0, 123.9, 122.9, 112.5, 111.6, 104.8, 61.4, 55.4, 43.9, 32.2, 13.9. HRMS (TOF MS ESI$^+$) calculated for $C_{28}H_{23}ClNaO_4^+$ [M+Na]$^+$: 481.1177, found: 481.1163.

Ethyl 12-(4-fluorophenyl)-6-hydroxy-2-methoxy-11,12-dihydrochrysene-5-carboxylate (26).



Yellow solid; m.p. 109.0 – 111.0 ℃. 54.0 mg, 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 11.03 (s, 1H), 8.40 (d, *J* = 7.5 Hz, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.61 – 7.56 (m, 1H), 7.49 – 7.44 (m, 1H), 7.30 – 7.25 (comp, 2H), 7.14 (d, *J* = 8.5 Hz, 1H), 6.98 – 6.91 (comp, 2H), 6.86 – 6.79 (m, 1H), 6.58 (d, *J* = 2.3 Hz, 1H), 4.36 – 4.18 (comp, 3H), 3.78 (s, 3H), 3.48 – 3.16 (m, 2H), 1.11 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.1, 158.7 (d, *J* = 35.0 Hz), 140.5, 138.3 (d, *J* = 3.1 Hz), 134.3, 131.0, 130.8, 130.1 (d, *J* = 8.0 Hz), 129.7, 128.6, 125.5, 124.6, 124.2, 124.1, 123.0, 115.4, 115.1, 112.5, 111.6, 104.9, 61.5, 55.4, 43.9, 32.5, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$) (δ, ppm) -116.66. HRMS (TOF MS ESI$^+$) calculated for $C_{28}H_{23}FNaO_4^+$ [M+Na]$^+$: 465.1473, found: 465.1481.

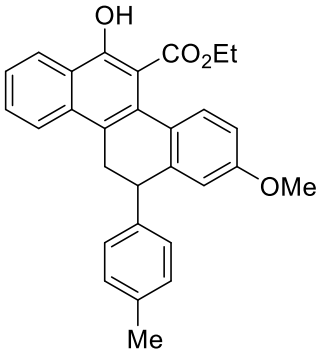
Ethyl 6-hydroxy-2-methoxy-12-(4-(trifluoromethyl)phenyl)-11,12-dihydrochrysene-5-carboxylate (27).



Yellow solid; m.p. 138.0 – 140.0 ℃. 85.7 mg, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 11.05 (s, 1H), 8.45 – 8.36 (m, 1H), 7.92 (d, *J* = 8.5 Hz, 1H), 7.62 – 7.56 (m, 1H), 7.51 – 7.40 (comp, 5H), 7.18 (d, *J* = 8.5 Hz, 1H), 6.89 – 6.82 (m, 1H), 6.61 (d, *J* = 2.2 Hz, 1H), 4.38 – 4.20 (comp, 3H), 3.80 (s, 3H), 3.48 – 3.32 (m, 2H), 1.14 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.0, 159.0, 158.6, 146.9, 139.5, 134.3, 131.0, 130.9, 129.8, 129.0, 128.9 (q, *J* = 32.4 Hz), 128.7, 125.6, 125.3 (q, *J* = 3.6 Hz), 124.7, 124.3 (d, *J* = 272.0 Hz), 124.1, 122.9, 112.7, 111.8, 104.8, 61.5, 55.4, 44.3, 32.3, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$) (δ, ppm) -62.38. HRMS (TOF MS ESI$^+$)

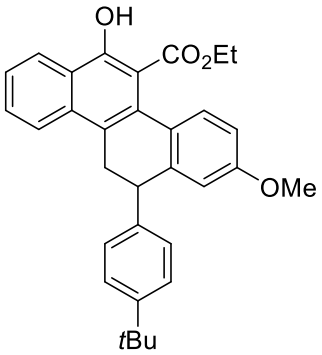
calculated for $C_{29}H_{23}F_3NaO_4^+$ $[M+Na]^+$: 515.1441, found: 515.1419.

Ethyl 6-hydroxy-2-methoxy-12-(*p*-tolyl)-11,12-dihydrochrysene-5-carboxylate (28).



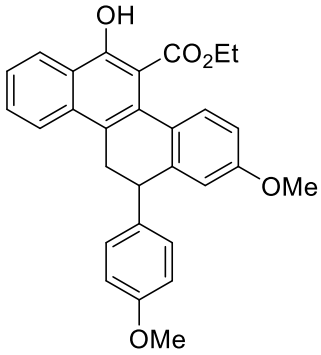
Yellow solid; m.p. 178.0 – 180.0 ℃.71.0 mg, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 11.08 (s, 1H), 8.43 – 8.39 (m, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.59 – 7.54 (m, 1H), 7.48 – 7.43 (m, 1H), 7.24 – 7.21 (comp, 2H), 7.16 – 7.13 (m, 1H), 7.11 – 7.07 (comp, 2H), 6.83 – 6.79 (m, 1H), 6.63 – 6.59 (m, 1H), 4.35 – 4.23 (comp, 3H), 3.77 (s, 3H), 3.40 – 3.29 (m, 2H), 2.31 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.2, 158.8, 158.5, 141.0, 139.6, 136.2, 134.3, 131.1, 130.7, 129.6, 129.2, 128.7, 128.6, 125.4, 124.6, 124.5, 124.0, 123.1, 112.5, 111.4, 104.9, 61.4, 55.3, 44.2, 32.4, 21.1, 13.9. HRMS (TOF MS ESI$^+$) calculated for $C_{29}H_{26}NaO_4^+$ $[M+Na]^+$: 461.1723, found: 461.1686.

Ethyl 12-(4-(*tert*-butyl)phenyl)-6-hydroxy-2-methoxy-11,12-dihydrochrysene-5- carboxylate (29).



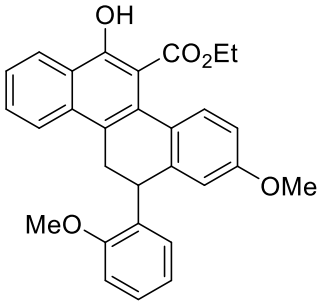
Yellow solid; m.p. 232.0 – 234.0 ℃. 81.7 mg, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 11.10 (s, 1H), 8.43 (d, *J* = 8.3 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.61 – 7.54 (m, 1H), 7.49 – 7.44 (m, 1H), 7.34 – 7.25 (comp, 4H), 7.16 (d, *J* = 8.5 Hz, 1H), 6.88 – 6.77 (m, 1H), 6.63 (s, 1H), 4.37 – 4.23 (comp, 3H), 3.79 (s, 3H), 3.43 – 3.28 (m, 2H), 1.33 (s, 9H), 1.16 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.2, 158.8, 158.5, 149.4, 141.1, 139.5, 134.4, 131.1, 130.7, 129.6, 128.7, 128.4, 125.4, 124.8, 124.5, 124.0, 123.1, 112.7, 111.2, 104.9, 61.4, 55.4, 44.2, 34.5, 32.4, 31.5, 13.9. HRMS (TOF MS ESI$^+$) calculated for $C_{32}H_{32}NaO_4^+$ $[M+Na]^+$: 503.2193, found: 503.2171.

Ethyl 6-hydroxy-2-methoxy-12-(4-methoxyphenyl)-11,12-dihydrochrysene-5-carboxylate (30).



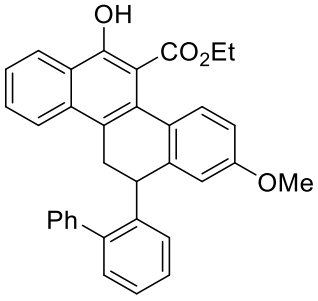
Yellow solid; m.p. 167.0 – 169.0 ℃. 49.1 mg, 54% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 11.03 (s, 1H), 8.39 (d, *J* = 7.9 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.26 – 7.22 (comp, 3H), 7.13 (d, *J* = 8.4 Hz, 1H), 6.84 – 6.77 (comp, 3H), 6.57 (s, 1H), 4.31 – 4.20 (comp, 3H), 3.77 (comp, 6H), 3.38 – 3.28 (m, 2H), 1.11 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.2, 158.8, 158.5, 158.4, 134.7, 134.4, 131.1, 130.7, 129.7, 129.6, 128.6, 125.4, 124.7, 124.6, 124.1, 123.1, 113.9, 112.4, 111.4, 104.9, 61.4, 55.41, 55.37, 43.9, 32.5, 13.9. HRMS (TOF MS ESI$^+$) calculated for $C_{29}H_{26}NaO_5^+$ $[M+Na]^+$: 477.1672, found: 477.1675

Ethyl 6-hydroxy-2-methoxy-12-(2-methoxyphenyl)-11,12-dihydrochrysene-5-carboxylate (31).



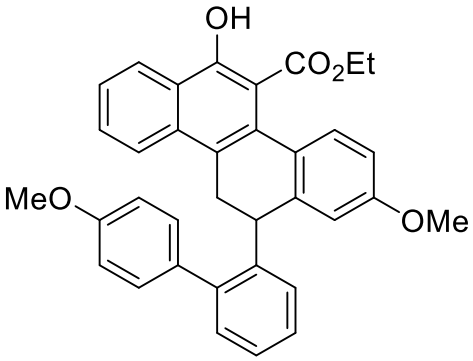
Yellow solid; m.p. 158.0 – 159.0 ℃. 73.7 mg, 81% yield. ^{1}H NMR (300 MHz, $CDCl_3$) (δ, ppm) 11.03 (s, 1H), 8.40 (dd, *J* = 8.4, 0.9 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.60 – 7.52 (m, 1H), 7.48 – 7.40 (m, 1H), 7.20 – 7.07 (comp, 3H), 6.90 (d, *J* = 7.7 Hz, 1H), 6.83 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.75 (t, *J* = 7.5 Hz, 1H), 6.68 (d, *J* = 2.6 Hz, 1H), 4.77 (t, *J* = 6.0 Hz, 1H), 4.42 – 4.20 (m, 2H), 3.93 (s, 3H), 3.80 (s, 3H), 3.59 (dd, *J* = 16.1, 6.2 Hz, 1H), 3.23 (dd, *J* = 16.1, 6.0 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 172.2, 158.9, 158.3, 157.4, 140.6, 134.6, 131.0, 130.6, 130.4, 129.9, 129.4, 127.6, 125.2, 124.9, 124.5, 124.0, 123.2, 120.3, 112.4, 111.8, 110.5, 104.9, 61.4, 55.6, 55.4, 37.9, 30.4, 13.9. HRMS (EI) calculated for $C_{29}H_{26}O_5$ (*m/z*): 454.1780, found: 454.1791

Ethyl 12-([1,1'-biphenyl]-2-yl)-6-hydroxy-2-methoxy-11,12-dihydrochrysene-5-carboxylate (32).



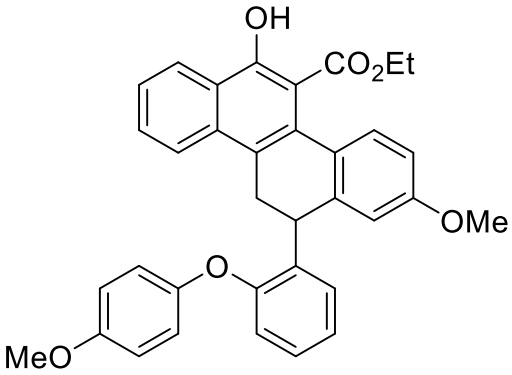
Yellow solid; m.p. 185.0 – 186.0 ℃. 93.1 mg, 93% yield. ^{1}H NMR (300 MHz, $CDCl_3$) (δ, ppm) 11.17 (s, 1H), 8.46 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.59 – 7.36 (comp, 11H), 7.20 (d, *J* = 8.5 Hz, 1H), 6.89 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.70 (d, *J* = 2.3 Hz, 1H), 4.70 – 4.53 (m, 1H), 4.43 – 4.27 (m, 2H), 3.83 (d, *J* = 8.3 Hz, 3H), 3.38 – 3.07 (m, 2H), 1.19 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 172.0, 158.8, 158.3, 142.7, 141.9, 141.7, 139.8, 134.0, 130.9, 130.6, 130.5, 129.4, 129.2, 128.91, 128.85, 128.2, 127.5, 127.1, 126.6, 125.2, 125.1, 124.4, 123.8, 122.9, 112.8, 110.7, 104.8, 61.2, 55.2, 40.9, 31.9, 13.7. HRMS (EI) calculated for $C_{34}H_{28}O_4$ (*m/z*): 500.1988, found: 500.1200

Ethyl 12-(2-chlorophenyl)-6-hydroxy-2-methoxy-11,12-dihydrochrysene-5-carboxylate (33).



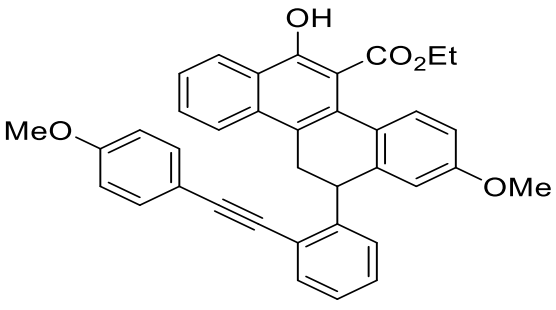
Yellow solid; m.p. 188.0 – 190.0 ℃. 99.8 mg, 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 11.08 (s, 1H), 8.48 – 8.37 (m, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.58 – 7.52 (m, 1H), 7.49 – 7.42 (comp, 2H), 7.40 – 7.28 (comp, 5H), 7.15 (d, *J* = 8.4 Hz, 1H), 7.00 – 6.87 (comp, 2H) 6.86 – 6.78 (m, 1H), 6.62 (d, *J* = 2.5 Hz, 1H), 4.60 – 4.48 (m, 1H), 4.36 – 4.23 (m, 2H), 3.88 – 3.74 (comp, 6H), 3.38 – 3.04 (m, 2H), 1.15 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.1, 158.80, 158.77, 158.4, 142.4, 142.1, 140.0, 134.1, 134.0, 131.0, 130.7, 130.5, 130.2, 129.5, 128.9, 127.3, 126.6, 125.3, 124.5, 123.9, 123.0, 113.7, 112.8, 110.7, 104.8, 61.2, 55.32, 55.25, 41.0, 32.0, 13.8. HRMS (TOF MS ESI$^+$) calculated for $C_{35}H_{30}NaO_5^+$ $[M+Na]^+$: 553.1985, found: 553.1985.

Ethyl 6-hydroxy-2-methoxy-12-(2-(4-methoxyphenoxy)phenyl)-11,12-dihydrochrysene-5- carboxylate (34).



Yellow solid; m.p. 148.0 – 150.0 ℃. 90.7 mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 11.16 (s, 1H), 8.50 (d, *J* = 7.6 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.65 – 7.60 (m, 1H), 7.55 – 7.50 (m, 1H), 7.32 – 7.27 (comp, 2H), 7.18 – 7.09 (comp, 3H), 7.04 – 6.99 (comp, 2H), 6.98 – 6.88 (comp, 4H), 4.95 (t, *J* = 5.3 Hz, 1H), 4.53 – 4.44 (m, 1H), 4.42 – 4.32 (m, 1H), 3.94 – 3.87 (comp, 6H), 3.87 – 3.79 (m, 1H), 3.31 (dd, *J* = 16.1, 5.8 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.1, 158.9, 158.3, 155.9, 155.7, 151.1, 139.9, 134.5, 132.6, 131.0, 130.6, 130.5, 129.4, 129.3, 127.6, 125.2, 124.4, 124.2, 124.0, 123.1, 122.6, 120.0, 117.8, 115.0, 112.6, 111.9, 104.8, 61.3, 55.7, 55.3, 30.5, 13.8. HRMS (TOF MS ESI$^+$) calculated for $C_{35}H_{30}NaO_6^+$ $[M+Na]^+$: 569.1935, found: 569.1933.

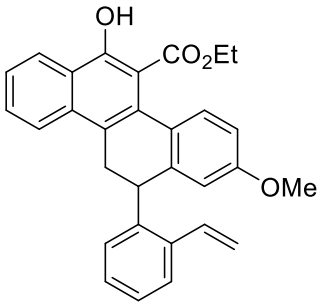
Ethyl 6-hydroxy-2-methoxy-12-(2-((4-methoxyphenyl)ethynyl)phenyl)-11,12-dihydrochrysene-5-carboxylate (35).



Yellow solid; m.p. 82.0 – 84.0 ℃. 54.4 mg, 49% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 11.01 (s, 1H), 8.39 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.58 – 7.41 (comp, 5H), 7.24 – 7.05 (comp, 4H), 6.93 – 6.82 (comp, 3H), 6.72 (d, *J* = 2.2 Hz, 1H), 4.94 (t, *J* = 5.8 Hz, 1H), 4.44 – 4.31 (m, 1H), 4.29 – 4.20 (m, 1H), 3.88 – 3.75 (comp, 7H), 3.35 (dd, *J* = 16.1, 5.8 Hz, 1H), 1.14 (t, *J* = 7.1

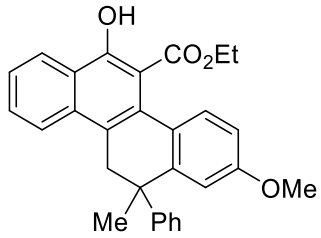
Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.2, 159.9, 159.0, 158.4, 144.0, 140.0, 134.5, 133.1, 132.4, 131.1, 130.6, 129.6, 129.3, 128.9, 127.9, 126.4, 125.4, 124.5, 124.3, 124.1, 123.22, 123.20, 115.6, 114.2, 112.5, 112.1, 104.9, 94.5, 87.1, 61.4, 55.5, 55.4, 42.6, 30.8, 13.9. HRMS (TOF MS ESI$^+$) calculated for $C_{37}H_{30}NaO_5^+$ [M+Na]$^+$: 577.1985, found: 577.1962.

Ethyl 6-hydroxy-2-methoxy-12-(2-vinylphenyl)-11,12-dihydrochrysene-5-carbox ylate (36).



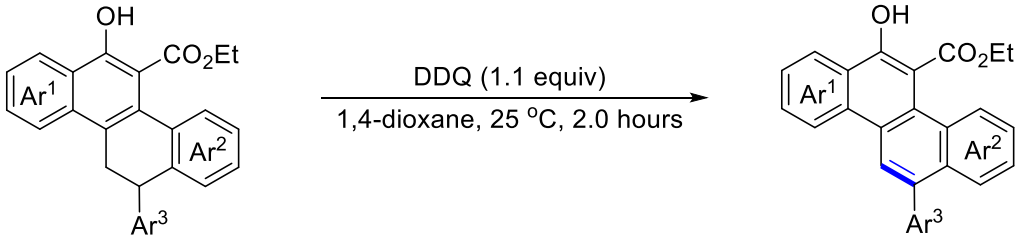
Yellow solid; m.p. 148.0 – 150.0 ℃. 73.0 mg, 81% yield, *dr* 1:1. *Two diastereoisomers:* ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 11.08 and 11.06 (two singlets, 1H), 8.45 – 8.36 (comp, 1H), 7.98 – 7.92 (comp, 1H), 7.60 – 7.55 (comp, 1H), 7.49 – 7.44 (comp, 1H), 7.38 – 7.32 (comp, 1H), 7.32 – 7.27 (comp, 2H), 7.26 – 7.23 (comp, 1H), 7.17 – 7.14 (comp, 1H), 6.83 – 6.80 (comp, 1H), 6.70 – 6.64 (comp, 1H), 6.62 – 6.59 (comp, 1H), 5.73 – 5.67 (comp, 1H), 5.23 – 5.18 (comp, 1H), 4.34 – 4.22 (comp, 3H), 3.78 and 3.77 (two singlets, 2H), 3.44 – 3.31 (comp, 2H), 1.138 and 1.135 (two triplets, *t, J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.24 and 172.18, 158.8, 158.6 and 158.5, 142.95 and 142.40, 140.7 and 140.6, 137.8 and 136.1, 137.0 and 136.6, 134.32, 131.1 and 131.0, 130.8 and 130.7, 129.7, 128.9, 128.66 and 128.63, 128.3 and 126.8, 126.3, 125.4, 124.58 and 124.55, 124.06 and 124.05, 123.09 and 123.05, 114.0 and 113.5, 112.53 and 112.48, 111.54 and 111.50,104.87 and 104.86, 61.5 and 61.4, 55.40 and 55.39, 44.7 and 44.4, 32.34 and 32.33, 13.9. HRMS (TOF MS ESI$^+$) calculated for $C_{30}H_{26}NaO_4^+$ [M+Na]$^+$: 473.1723, found: 473.1717.

Ethyl 6-hydroxy-2-methoxy-12-methyl-12-phenyl-11,12-dihydrochrysene-5-carb oxylate (37).



Yellow solid; m.p. 152.0 – 154.0 ℃. 66.7 mg, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 10.99 (s, 1H), 8.37 (d, *J* = 8.3 Hz, 1H), 8.06 (d, *J* = 8.3 Hz, 1H), 7.67 – 7.58 (m, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.23 – 7.17 (comp, 2H), 7.16 – 7.12 (m, 1H), 7.11 – 7.00 (comp, 4H), 6.89 – 6.83 (m, 1H), 4.27 – 4.10 (m, 2H), 3.92 – 3.82 (comp, 4H), 2.94 (d, *J* = 16.1 Hz, 1H), 1.87 (s, 3H), 1.14 – 1.01 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.0, 158.9, 158.2, 146.9, 144.6, 134.2, 131.5, 131.1, 129.6, 129.1, 127.7, 126.8, 125.9, 125.2, 124.5, 124.4, 123.9, 122.8, 111.4, 110.6, 104.7, 61.1, 55.5, 42.4, 38.7, 28.7, 13.8. HRMS (TOF MS ESI$^+$) calculated for $C_{29}H_{26}NaO_4^+$ [M+Na]$^+$: 461.1723, found: 461.1714.

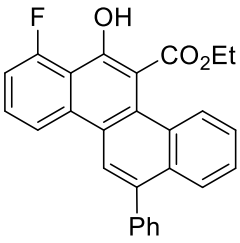
General Procedure for the Synthesis of Polycyclic Aromatic Hydrocarbons



To a 10-mL oven-dried flask equipped with a magnetic stirring bar, the above prepared polycyclic products (0.10 mmol), 2,3-Dicyano-5,6-dichlorobenzoquinone (DDQ, 25.0 mg, 0.11 mmol), and 1,4-dioxane (6.0 mL) were added in sequence. The reaction mixture was stirred at 25 ºC for 12.0 hours. Then, the solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20:1) to give the polycyclic aromatic hydrocarbons **38**-**53** in high to excellent yields.

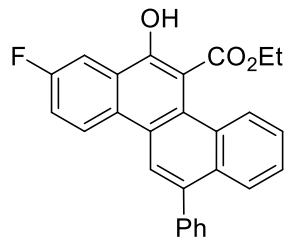
Characterization of the polycyclic aromatic hydrocarbons 38-53.

Ethyl 7-fluoro-6-hydroxy-12-phenylchrysene-5-carboxylate (38).



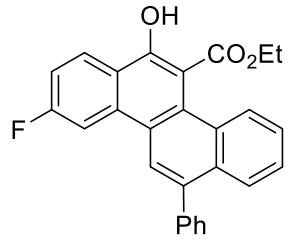
Yellow solid, m.p. 157 – 158 ℃. 39.4 mg, 96% yield. ^{1}H NMR (300 MHz, $CDCl_3$) (δ, ppm) 11.20 (s, 1H), 8.46 – 8.26 (comp, 2H), 8.17 – 8.03 (m, 1H), 8.01 – 7.87 (m, 1H), 7.81 – 7.39 (comp, 8H), 7.32 – 7.24 (m, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 172.2, 161.1 (d, *J* = 260.0 Hz), 157.7 (d, *J* = 3.8 Hz), 140.8, 138.3, 135.7 (d, *J* = 2.1 Hz), 132.0, 130.28 (d, *J* = 9.7 Hz), 130.26, 129.7, 129.2, 128.5, 127.6, 127.0 (d, *J* = 1.0 Hz), 126.6, 126.2, 124.6, 122.9 (d, *J* = 2.5 Hz), 121.3, 119.2 (d, *J* = 4.2 Hz), 114.4 (d, *J* = 8.3 Hz), 113.5 (d, *J* = 22.6 Hz), 105.2 (d, *J* = 1.9 Hz), 62.0, 13.9; ^{19}F NMR (283 MHz, $CDCl_3$) (δ, ppm) -109.46. HRMS (EI) calculated for $C_{27}H_{19}FO_3$ (*m/z*): 410.1318, found 410.1324.

Ethyl 8-fluoro-6-hydroxy-12-phenylchrysene-5-carboxylate (**39**).



Yellow solid, m.p. 178 – 179 ℃. 37.8 mg, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 11.06 (s, 1H), 8.61 (dd, *J* = 9.2, 5.1 Hz, 1H), 8.38 (s, 1H), 8.17 (dd, *J* = 9.7, 2.8 Hz, 1H), 8.08 – 8.00 (m, 1H), 7.98 – 7.92 (m, 1H), 7.68 – 7.61 (m, 2H), 7.59 – 7.54 (m, 2H), 7.53 – 7.45 (comp, 4H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.19 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.5, 161.6 (d, *J* = 247.7 Hz), 157.7 (d, *J* = 4.0 Hz), 140.9, 138.4, 131.7, 130.3, 130.0, 129.9 (d, *J* = 1.9 Hz), 129.3, 128.6, 127.6, 126.5 (d, *J* = 8.7 Hz), 126.3 (d, *J* = 1.5 Hz), 125.9 (d, *J* = 1.6 Hz), 125.7 (d, *J* = 8.5 Hz), 124.5, 123.4 (d, *J* = 0.5 Hz), 121.0, 119.2 (d, *J* = 23.9 Hz), 109.6 (d, *J* = 22.6 Hz), 104.9, 62.1, 13.9; ^{19}F NMR (283 MHz, $CDCl_3$) (δ, ppm) -113.28. HRMS (EI) calculated for $C_{27}H_{19}FO_3$ (*m/z*): 410.1318, found 410.1314.

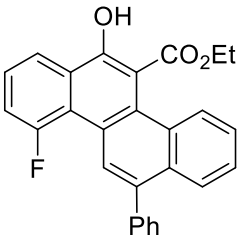
Ethyl 9-fluoro-6-hydroxy-12-phenylchrysene-5-carboxylate (**40**).



Yellow solid, m.p. 198 – 199 ℃. 36.9 mg, 90% yield. ^{1}H NMR (300 MHz, $CDCl_3$) (δ, ppm) 11.26 (s, 1H), 8.55 (dd, *J* = 9.0, 6.0 Hz, 1H), 8.26 (s, 1H), 8.19 (dd, *J* = 11.1, 2.4 Hz, 1H), 8.10 – 8.00 (m, 1H), 7.99 – 7.89 (m, 1H), 7.67 – 7.45 (comp, 7H), 7.42 – 7.32 (m, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.19 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.5, 164.2 (d, *J* = 250.0 Hz), 158.7, 140.8, 138.1, 135.4 (d, *J* = 9.2 Hz), 132.1, 130.3, 130.0, 129.6, 128.6, 127.7 (d, *J* = 9.6 Hz), 127.6, 127.4, 126.6, 126.3, 124.4, 122.9 (d, *J* = 4.1 Hz), 121.6 (d, *J* = 1.3 Hz), 121.1, 116.0 (d, *J* = 23.8 Hz), 108.4 (d, *J* = 22.9 Hz), 103.3 (d, *J* = 1.7 Hz), 61.9, 14.0; ^{19}F NMR (283 MHz, $CDCl_3$) (δ, ppm) -108.13. HRMS (EI) calculated for $C_{27}H_{19}FO_3$ (*m/z*):

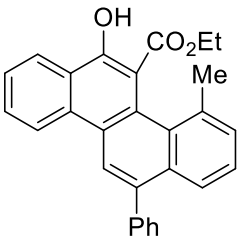
410.1318, found 410.1328.

Ethyl 10-fluoro-6-hydroxy-12-phenylchrysene-5-carboxylate (41).



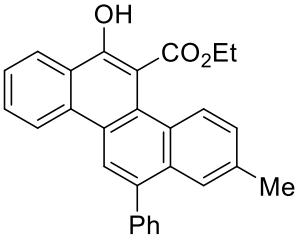
Yellow solid, m.p. 182 – 183 ℃. 38.2 mg, 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 11.22 (s, 1H), 8.97 (d, *J* = 3.7 Hz, 1H), 8.48 – 8.37 (m, 1H), 8.07 – 8.01 (m, 1H), 8.01 – 7.95 (m, 1H), 7.69 – 7.64 (comp, 2H), 7.62 – 7.54 (comp, 3H), 7.52 – 7.45 (comp, 4H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.17 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.5, 160.9 (d, *J* = 253.4 Hz), 158.0 (d, *J* = 4.2 Hz), 141.1, 137.9 (d, *J* = 2.3 Hz), 131.5 (d, *J* = 1.9 Hz), 130.4, 129.8, 129.6, 128.5, 127.430 (d, *J* = 4.8 Hz), 127.429, 127.1 (d, *J* = 9.9 Hz), 127.0 (d, *J* = 0.6 Hz), 126.5, 126.0, 125.1 (d, *J* = 26.0 Hz), 124.2, 122.5 (d, *J* = 9.1 Hz), 122.1 (d, *J* = 5.9 Hz), 121.0 (d, *J* = 3.7 Hz), 117.2 (d, *J* = 25.3 Hz), 104.6 (d, *J* = 0.6 Hz), 62.0, 13.9; ^{19}F NMR (283 MHz, $CDCl_3$) (δ, ppm) -108.61. HRMS (EI) calculated for $C_{27}H_{19}FO_3$ (*m/z*): 410.1318, found 410.1304.

Ethyl 6-hydroxy-4-methyl-12-phenylchrysene-5-carboxylate (**42**).



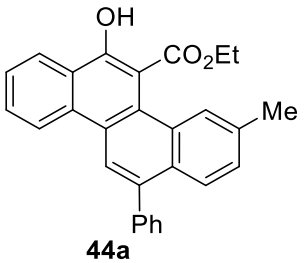
Yellow solid, m.p. 151 – 153 ℃. 32.9 mg, 81% yield. ^{1}H NMR (300 MHz, $CDCl_3$) (δ, ppm) 12.31 (s, 1H), 8.71 – 8.57 (comp, 2H), 8.38 (s, 1H), 7.83 – 7.75 (comp, 2H), 7.72 – 7.63 (comp, 3H), 7.61 – 7.50 (comp, 3H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 6.9 Hz, 1H), 4.33 – 4.15 (m, 2H), 2.70 (s, 3H), 1.04 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 172.3, 158.6, 141.3, 138.0, 136.8, 133.4, 132.3, 131.8, 130.4, 130.3, 128.4, 127.6, 127.4, 126.8, 125.9, 125.1, 124.94, 124.86, 124.3, 123.6, 123.2, 120.6, 106.0, 61.7, 22.8, 13.6. HRMS (EI) calculated for $C_{28}H_{22}O_3$ (*m/z*): 406.1569, found 406.1564.

Ethyl 6-hydroxy-2-methyl-12-phenylchrysene-5-carboxylate (**43**).

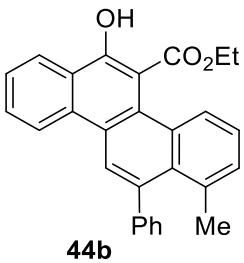


Yellow solid, m.p. 154.0 – 155.0 ℃. 34.6 mg, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 11.16 (s, 1H), 8.62 (d, *J* = 8.4 Hz, 1H), 8.56 – 8.54 (m, 1H), 8.43 (s, 1H), 7.95 (d, *J* = 8.6 Hz, 1H), 7.79 – 7.75 (m, 1H), 7.71 (d, *J* = 1.6 Hz, 1H), 7.68 – 7.62 (comp, 3H), 7.59 – 7.54 (m, 2H), 7.52 – 7.48 (m, 1H), 7.32 (dd, *J* = 8.6, 1.8 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 2.47 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.7, 158.8, 141.2, 137.6, 136.1, 133.4, 132.0, 130.4, 130.2, 129.4, 128.5, 128.1, 127.4, 126.8, 126.5, 126.3, 125.4, 124.8, 124.8, 123.1, 123.0, 121.3, 103.8, 61.9, 21.9, 14.1. HRMS (TOF MS CI$^+$) calculated for $C_{28}H_{23}O_3^+$ $[M+H]^+$: 407.1642, found 407.1635.

Ethyl 6-hydroxy-3-methyl- 12-phenylchrysene-5-carboxylate (**44a**) &
Ethyl 6-hydroxy-1-methyl-12-phenylchrysene-5-carboxylate (**44b**).



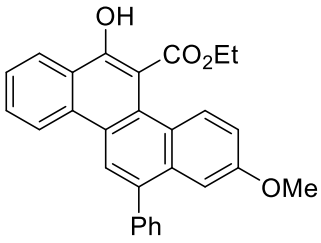
44a



44b

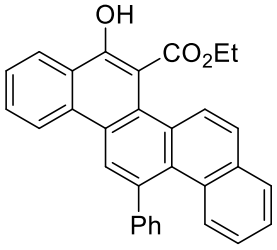
Yellow solid. Combined 32.1 mg in total with 79% yield, **42a**:**42b** = 4:1. *Combined two isomers*: ^{1}H NMR (300 MHz, $CDCl_3$) (δ, ppm) 11.27 – 11.01 (comp, 1H), 8.54 – 8.39 (comp, 2H), 8.31 – 8.17 (comp, 1H), 7.82 – 7.16 (comp, 10H), 4.37 – 4.17 (comp, 2H), 2.46 – 1.98 (comp, 3H), 1.14 – 1.03 (comp, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 172.8, 172.7, 159.0, 158.7, 141.2, 137.8, 137.7, 133.7, 133.4, 130.3, 130.2, 130.2, 130.1, 130.0, 129.7, 129.0, 128.5, 128.1, 127.9, 127.5, 127.0, 126.9, 126.1, 126.0, 124.9, 124.8, 124.8, 123.94, 123.86, 123.8, 123.1, 120.4, 104.0, 1038, 61.8, 25.6, 22.0, 14.0, 13.9. HRMS (EI) calculated for $C_{28}H_{22}O_3$ (*m/z*): 406.1569, found 406.1577.

Ethyl 6-hydroxy-2-methoxy-12-phenylchrysene-5-carboxylate (**45**).



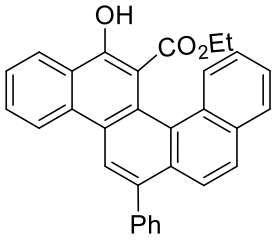
Yellow solid, m.p. 173.0 – 174.0 ℃. 38.6 mg, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 11.24 (s, 1H), 8.63 – 8.50 (m, 2H), 8.44 (s, 1H), 7.97 (d, *J* = 9.2 Hz, 1H), 7.77 – 7.73 (m, 1H), 7.68 – 7.61 (comp, 3H), 7.59 – 7.53 (m, 2H), 7.53 – 7.46 (m, 1H), 7.32 (d, *J* = 2.7 Hz, 1H), 7.15 (dd, *J* = 9.2, 2.7 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.7, 159.0, 157.9, 141.2, 137.2, 133.5, 133.3, 131.0, 130.2, 130.2, 128.6, 127.5, 126.6, 126.5, 124.9, 124.8, 124.5, 122.8, 122.3, 121.9, 115.5, 105.6, 103.5, 61.9, 55.4, 14.1. HRMS (TOF MS CI$^+$) calculated for $C_{28}H_{23}O_4^+$ $[M+H]^+$: 423.1591, found 423.1588.

Ethyl 5-hydroxy-13-phenylpicene-6-carboxylate (**46**).



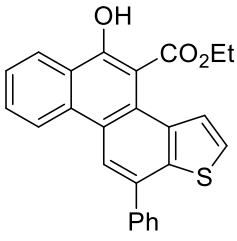
Yellow solid, m.p. 191.0 – 193.0 ℃. 38.0 mg, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 11.49 (s, 1H), 8.64 (d, *J* = 8.3 Hz, 1H), 8.58 – 8.56 (m, 1H), 8.47 (s, 1H), 7.95 (d, *J* = 9.0 Hz, 1H), 7.88 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.82 – 7.65 (comp, 4H), 7.56 – 7.41 (comp, 6H), 7.16 – 7.12 (m, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 1.09 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.7, 159.7, 145.6, 137.7, 133.2, 133.0, 130.5, 130.2, 129.9, 129.6, 129.09, 129.06, 128.9, 127.9, 127.8, 127.3, 127.2, 126.7, 126.2, 125.1, 125.0, 124.8, 124.6, 124.1, 123.2, 103.5, 61.9, 14.0. HRMS (TOF MS CI$^+$) calculated for $C_{31}H_{23}O_3^+$ $[M+H]^+$: 443.1642, found 443.1650.

Ethyl 8-hydroxy-14-phenylbenzo[*c*]chrysene-7-carboxylate (**47**).



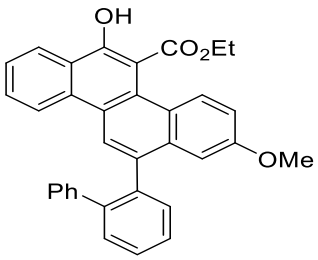
Yellow solid, m.p. 186 – 187 ℃. 43.4 mg, 98% yield. ^{1}H NMR (300 MHz, $CDCl_3$) (δ, ppm) 12.02 (s, 1H), 8.88 – 8.70 (m, 1H), 8.72 – 8.60 (comp, 2H), 8.58 (s, 1H), 7.97 – 7.87 (comp, 2H), 7.83 – 7.51 (comp, 10H), 3.78 – 3.67 (m, 1H), 3.36 – 3.24 (m, 1H), 0.42 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 172.0, 158.9, 141.1, 137.6, 133.3, 133.1, 131.4, 130.6, 130.3, 129.7, 128.5, 128.0, 127.5, 127.12, 127.08, 126.3, 126.1, 125.8, 125.2, 125.1, 125.0, 124.6, 124.2, 123.2, 122.0, 106.0, 61.4, 12.9. HRMS (EI) calculated for $C_{31}H_{22}O_3$ (*m/z*): 442.1569, found 442.1562.

Ethyl 5-hydroxy-11-phenylphenanthro[2,1-*b*]thiophene-4-carboxylate (**48**).



Yellow solid, m.p. 155 – 156 ℃. 33.8 mg, 84% yield. ^{1}H NMR (500 MHz, $CDCl_3$) (δ, ppm) 11.17 (s, 1H), 8.67 (d, *J* = 8.4 Hz, 1H), 8.53 (d, *J* = 8.1 Hz, 1H), 8.50 (s, 1H), 7.86 (d, *J* = 7.6 Hz, 2H), 7.78 (t, *J* = 7.6 Hz, 1H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.63 – 7.54 (comp, 3H), 7.54 – 7.44 (comp, 2H), 4.50 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) (δ, ppm) 171.9, 158.9, 140.8, 139.9, 135.8, 134.2, 133.9, 130.4, 129.0, 128.7, 128.3, 126.8, 126.7, 124.9, 124.52, 124.47, 124.3, 124.2, 123.1, 119.0, 103.6, 62.0, 14.2. HRMS (EI) calculated for $C_{25}H_{18}O_3S$ (*m/z*): 398.0977, found 398.0989.

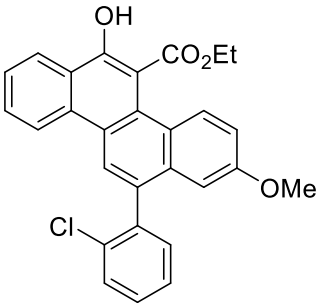
Ethyl 12-([1,1'-biphenyl]-2-yl)-6-hydroxy-2-methoxychrysene-5-carboxylate (**49**).



Yellow solid, m.p. 138 – 139 ℃. 44.4 mg, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 11.15 (s, 1H), 8.51 (dd, *J* = 8.2, 1.0 Hz, 1H), 8.39 (d, *J* = 8.2 Hz, 1H), 8.33 (s, 1H), 7.83 (d, *J* = 9.1 Hz, 1H), 7.74 – 7.49 (comp, 6H), 7.19 – 7.12 (m, 2H), 7.07 – 6.90 (comp, 5H), 4.60 – 4.14 (m, 2H), 3.74 (s, 3H), 1.11 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.6, 158.8, 157.6, 142.1, 141.5, 139.4, 136.4, 133.5, 133.4, 131.9, 130.6, 130.4, 130.1, 129.1, 128.2, 127.8, 127.6, 126.6, 126.4, 124.78, 124.77,

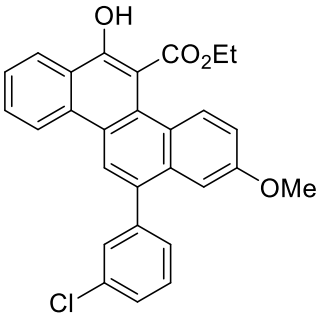
124.4, 123.2, 122.8, 122.1, 115.4, 105.5, 103.6, 61.6, 55.3, 13.9. HRMS (EI) calculated for $C_{34}H_{26}O_4$ (*m/z*): 498.1831, found 498.1834.

Ethyl 12-(2-chlorophenyl)-6-hydroxy-2-methoxychrysene-5-carboxylate (**50**).



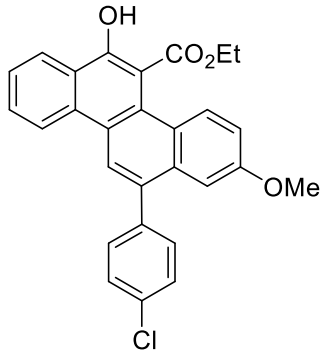
Yellow solid, m.p. 207 – 209 ℃. 41.8 mg, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 11.24 (s, 1H), 8.61 – 8.49 (m, 2H), 8.42 (s, 1H), 7.98 (d, *J* = 9.2 Hz, 1H), 7.77 – 7.73 (m, 1H), 7.66 – 7.60 (m, 2H), 7.55 – 7.50 (m, 1H), 7.48 – 7.41 (m, 2H), 7.15 (dd, *J* = 9.2, 2.7 Hz, 1H), 6.89 (d, *J* = 2.6 Hz, 1H), 4.39 (t, *J* = 7.2 Hz, 2H), 3.79 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.7, 159.2, 157.9, 139.7, 134.5, 134.4, 133.5, 133.2, 132.5, 131.0, 130.3, 129.9, 129.3, 127.1, 127.0, 126.6, 124.8, 124.6, 124.5, 122.8, 122.4, 122.1, 115.5, 105.5, 103.6, 61.8, 55.3, 14.1. HRMS (TOF MS CI$^+$) calculated for $C_{28}H_{22}ClO_4^+$ $[M+H]^+$: 457.1201, found 457.1208.

Ethyl 12-(3-chlorophenyl)-6-hydroxy-2-methoxychrysene-5-carboxylate (**51**).



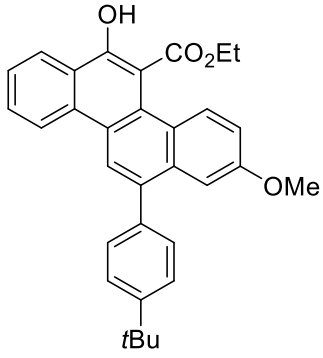
Yellow solid, m.p. 214 – 216 ℃. 43.0 mg, 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 11.25 (s, 1H), 8.63 – 8.49 (m, 2H), 8.40 (s, 1H), 7.95 (d, *J* = 9.2 Hz, 1H), 7.79 – 7.74 (m, 1H), 7.70 – 7.59 (m, 2H), 7.57 – 7.45 (comp, 3H), 7.24 (d, *J* = 2.7 Hz, 1H), 7.15 (dd, *J* = 9.2, 2.7 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.6, 159.3, 158.0, 143.0, 135.6, 134.6, 133.4, 133.0, 131.2, 130.4, 130.2, 129.8, 128.4, 127.7, 127.0, 126.7, 124.94, 124.89, 124.5, 122.8, 122.1, 122.0, 115.6, 105.3, 103.4, 61.9, 55.4, 14.1. HRMS (TOF MS CI$^+$) calculated for $C_{28}H_{22}ClO_4^+$ $[M+H]^+$: 457.1201, found 457.1212.

Ethyl 12-(4-chlorophenyl)-6-hydroxy-2-methoxychrysene-5-carboxylate (**52**).



Yellow solid, m.p. 107 – 109 ℃. 40.7 mg, 89% yield. ^{1}H NMR (300 MHz, $CDCl_3$) (δ, ppm) 11.25 (s, 1H), 8.62 – 8.47 (comp, 2H), 8.37 (s, 1H), 7.95 (d, *J* = 9.2 Hz, 1H), 7.78 – 7.70 (m, 1H), 7.65 – 7.50 (comp, 5H), 7.23 (d, *J* = 2.6 Hz, 1H), 7.15 (dd, *J* = 9.2, 2.6 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 172.6, 159.2, 158.0, 139.7, 135.8, 133.54, 133.35, 133.0, 131.5, 131.1, 130.3, 128.8, 126.8, 126.6, 124.93, 124.86 124.5, 122.7, 122.1, 121.9, 115.6, 105.3, 103.4, 61.9, 55.4, 14.1. HRMS (EI) calculated for $C_{28}H_{21}ClO_4$ (*m/z*): 456.1128, found 456.1622.

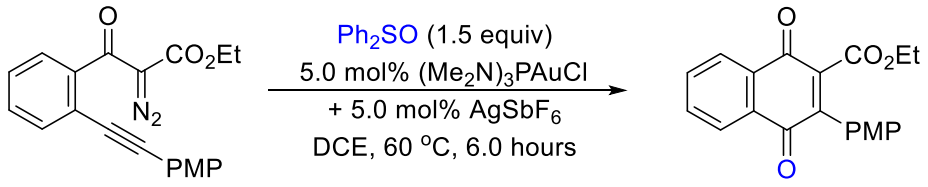
Ethyl 12-(4-(*tert*-butyl)phenyl)-6-hydroxy-2-methoxychrysene-5-carboxylate (**53**).



Yellow solid, m.p. 193 – 194 ℃. 45.2 mg, 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 11.23 (s, 1H), 8.65 – 8.51 (m, 2H), 8.44 (s, 1H), 7.97 (d, *J* = 9.2 Hz, 1H), 7.77 – 7.72 (m, 1H), 7.68 – 7.54 (comp, 5H), 7.40 (d, *J* = 2.7 Hz, 1H), 7.16 (dd, *J* = 9.2, 2.7 Hz, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 1.47 (s, 9H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.7, 158.9, 157.8, 150.4, 138.2, 137.1, 133.5, 133.4, 131.0, 130.2, 129.8, 126.5, 126.4, 125.5, 125.0, 124.8, 124.5, 122.8, 122.3, 121.9, 115.2, 106.0, 103.5, 61.8, 55.4, 34.8, 31.6, 14.1. HRMS (TOF MS CI$^+$) calculated for $C_{32}H_{31}O_4^+$ $[M+H]^+$: 479.2217, found 479.2224.

Control Experiments

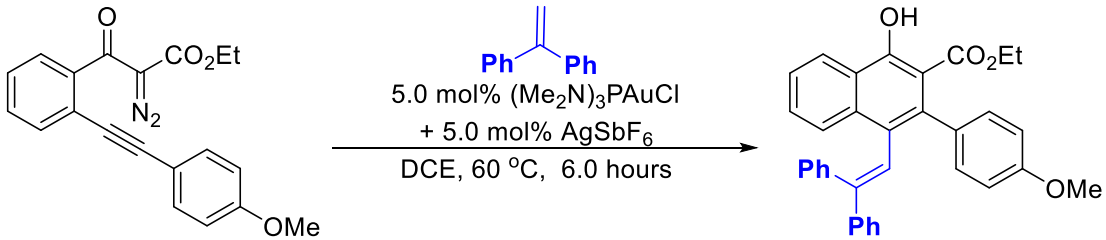
Synthesis of 54



1l **54**, 84 % yield

To a 10-mL oven-dried vial containing a magnetic stirring bar, $(Me_2N)_3PAuCl$ (3.95 mg, 0.01 mmol), $AgSbF_6$ (3.43 mg, 0.01 mmol), and DCE (0.5 mL) were added in sequence in a nitrogen-filled glove-box. The reaction mixture was stirred at 25 °C for 2.0 hours. The solvent was removed and the residue was dissolved in DCE (0.5 mL). Then the mixture was filtered through a pad of Celite. The filtrate was added into a solution of **1l** (69.9 mg, 0.2 mmol) and phenyl sulfoxide (60.7 mg, 0.3 mmol) in DCE (0.5 mL) at 60 °C, and the resulting reaction mixture was stirred under these conditions for 6.0 hours. Then, the solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel (solvents: petroleum ether/ethyl acetate = 10: 1) to give 56.5 mg **54** in 84% yield. White solid; m. p. 55.0 – 57.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.16 – 8.10 (comp, 2H), 7.80 – 7.75 (comp, 2H), 7.39 – 7.34 (comp, 2H), 6.97 – 6.93 (m, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 184.5, 182.2, 164.6, 161.1, 144.1, 138.8, 134.3, 134.3, 131.8, 131.6, 131.3, 127.1, 126.4, 123.7, 113.8, 62.0, 55.5, 14.0. HRMS (TOF MS ESI$^+$) calculated for $C_{20}H_{16}NaO_5^+$ $[M+Na]^+$: 359.0890, found: 359.0894.

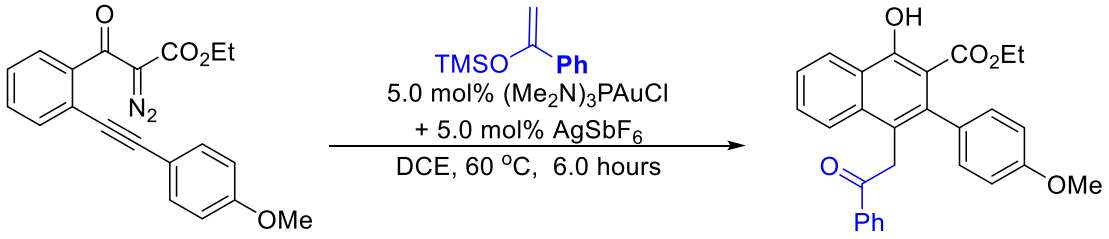
Synthesis of 55



1l **55**, 71%

To a 10-mL oven-dried vial containing a magnetic stirring bar, $(Me_2N)_3PAuCl$ (3.95 mg, 0.01 mmol), $AgSbF_6$ (3.43 mg, 0.01 mmol), and DCE (0.5 mL) were added in sequence in a nitrogen-filled glove-box. The reaction mixture was stirred at 25 °C for 2.0 hours. The solvent was removed and the residue was dissolved in DCE (0.5 mL). Then the mixture was filtered through a pad of Celite. The filtrate was added into a solution of **1l** (69.9 mg, 0.2 mmol) and 1,1-diphenylethylene (54.0 mg, 0.3 mmol) in DCE (0.5 mL) at 60 °C, and the resulting reaction mixture was stirred under these conditions for 6.0 hours. Then, the solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel (solvents: petroleum ether/ethyl acetate = 10: 1) to give 71.1 mg **55** in 71% yield. White solid; m. p. 155.0 – 157.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 12.11 (s, 1H), 8.47 (d, *J* = 8.0 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.64 – 7.47 (comp, 2H), 7.34 – 7.26 (comp, 3H), 7.22 – 7.08 (comp, 3H), 7.05 – 6.99 (m, 1H), 6.99 – 6.82 (comp, 3H), 6.81 (s, 1H), 6.70 – 6.44 (comp, 3H), 6.39 – 6.27 (m, 1H), 3.91 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 0.72 (t, *J* = 7.1 Hz, 3H) ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.2, 160.3, 158.1, 145.1, 143.8, 139.8, 136.7, 135.4, 134.7, 130.1, 129.8, 128.5, 128.1, 127.4, 127.0, 126.9, 126.3, 126.1, 125.7, 124.2, 124.1, 112.7, 107.3, 61.1, 55.5, 13.2. HRMS (TOF MS ESI$^+$) calculated for $C_{34}H_{28}NaO_4^+$ $[M+Na]^+$: 523.1880, found: 523.1877.

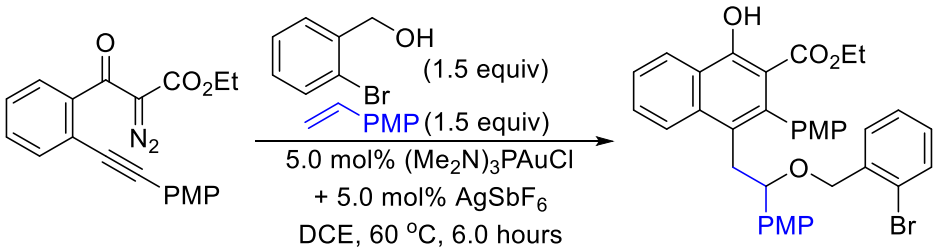
Synthesis of 56



1l **56**, 80 % yield

To a 10-mL oven-dried vial containing a magnetic stirring bar, $(Me_2N)_3PAuCl$ (3.95 mg, 0.01 mmol), $AgSbF_6$ (3.43 mg, 0.01 mmol), and DCE (0.5 mL) were added in sequence in a nitrogen-filled glove-box. The reaction mixture was stirred at 25 °C for 2.0 hours. The solvent was removed and the residue was dissolved in DCE (0.5 mL). Then the mixture was filtered through a pad of Celite. The filtrate was added into a solution of **1l** (69.9 mg, 0.2 mmol) and 1-phenyl-1-trimethylsiloxyethene (57.7 mg, 0.3 mmol) in DCE (0.5 mL) at 60 °C, and the resulting reaction mixture was stirred under these conditions for 6.0 hours. Then, the solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel (solvents: petroleum ether/ethyl acetate = 10: 1) to give 70.5 mg **56** in 80% yield. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 12.49 (s, 1H), 8.53 (d, *J* = 8.1 Hz, 1H), 7.94 – 7.87 (comp, 2H), 7.60 – 7.50 (comp, 4H), 7.48 – 7.42 (comp, 2H), 7.13 – 7.02 (comp, 2H), 6.86 – 6.77 (comp, 2H), 4.42 (s, 2H), 3.96 (q, *J* = 7.2 Hz, 2H), 3.78 (d, *J* = 2.6 Hz, 3H), 0.76 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 198.2, 172.2, 160.9, 158.6, 138.8, 136.9, 135.4, 135.0, 133.3, 130.3, 129.9, 128.7, 128.2, 125.6, 124.84, 124.75, 124.3, 121.9, 113.3, 107.0, 61.1, 55.5, 40.1, 13.3. HRMS (TOF MS ESI$^+$) calculated for $C_{28}H_{24}NaO_5^+$ $[M+Na]^+$: 463.1516, found: 463.1529.

Synthesis of 57

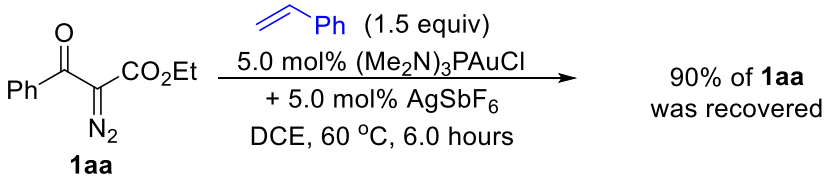


1l **57**, 79 % yield

To a 10-mL oven-dried vial containing a magnetic stirring bar, $(Me_2N)_3PAuCl$ (3.95 mg, 0.01 mmol), $AgSbF_6$ (3.43 mg, 0.01 mmol), and DCE (0.5 mL) were added in sequence in a nitrogen-filled glove-box. The reaction mixture was stirred at 25 °C for 2.0 hours. The solvent was removed and the residue was dissolved in DCE (0.5 mL). Then the mixture was filtered through a pad of Celite. The filtrate was added into a solution of **1l** (69.9 mg, 0.2 mmol), 2-bromobenzyl alcohol (56.1 mg, 0.3 mmol), and 4-methoxystyrene (40.2 mg, 0.3 mmol) in DCE (0.5 mL) at 60 °C, and the resulting reaction mixture was stirred under these conditions for 6.0 hours. Then, the solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel (solvents: petroleum ether/ethyl acetate = 10: 1) to give 101.4 mg **57** in 79% yield. White solid; m. p. 86.0 – 88.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 12.31 (s, 1H), 8.54 – 8.49 (m, 1H), 8.23 – 8.07 (m, 1H), 7.66 – 7.60 (m, 1H), 7.56 – 7.51 (m, 1H), 7.43 – 7.38 (m, 1H), 7.15 – 7.10 (m, 1H), 7.07 – 7.01 (comp, 2H), 6.94 – 6.86 (comp, 4H), 6.82 – 6.75 (comp, 3H), 6.64 – 6.49 (m, 1H), 4.41 (dd, *J* = 8.0, 5.6 Hz, 1H), 4.20 (dd, *J* = 85.6, 13.4 Hz, 2H), 3.93 (q, *J* = 7.1 Hz, 2H), 3.88 (s, 3H), 3.79 (s, 3H), 3.45 (dd, *J* = 14.4, 8.0 Hz, 1H), 3.08 (dd, *J* = 14.4, 5.6 Hz, 1H), 0.76 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.3, 159.9, 159.1, 158.4, 138.2, 138.0, 135.8, 134.7, 134.2, 132.2, 130.7, 130.6,

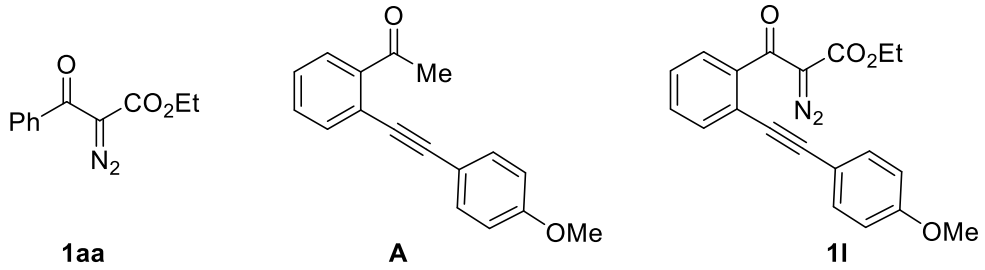
129.4, 129.3, 128.6, 127.6, 127.1, 125.5, 125.4, 125.0, 124.7, 124.3, 122.6, 113.8, 113.0, 113.0, 107.2, 81.9, 69.9, 61.0, 55.6, 55.4, 37.8, 13.3. HRMS (TOF MS ESI$^+$) calculated for $C_{36}H_{33}BrNaO_6^+$ [M+Na]$^+$: 663.1353, found: 663.1351.

Control experiment of diazo compound 1aa with styrene:



To a 10-mL oven-dried vial containing a magnetic stirring bar, $(Me_2N)_3PAuCl$ (3.95 mg, 0.01 mmol), $AgSbF_6$ (3.43 mg, 0.01 mmol), and DCE (0.5 mL) were added in sequence in a nitrogen-filled glove-box. The reaction mixture was stirred at 25 °C for 2.0 hours. The solvent was removed and the residue was dissolved in DCE (0.5 mL). Then the mixture was filtered through a pad of Celite. The filtrate was added into a solution of **1aa** (43.6 mg, 0.2 mmol) and styrene (31.2 mg, 0.3 mmol) in DCE (0.5 mL) at 60 °C, and the resulting reaction mixture was stirred under these conditions for 6.0 hours. Then, the solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel (solvents: petroleum ether/ethyl acetate = 10: 1) to recover 39.3 mg of **1aa** (90%).

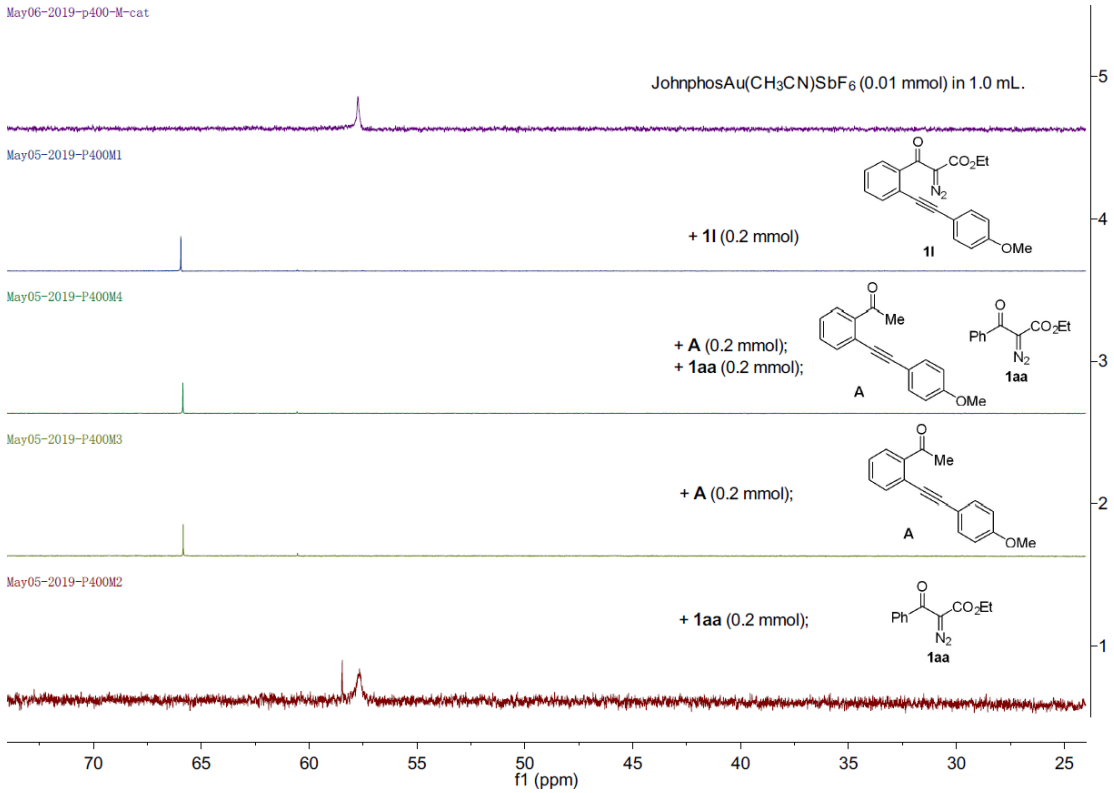
^{31}P NMR Spectra of gold-complex with 1aa, A, or 1l:



In order to explore the initiation step of this gold-catalyzed [4+2] cycloaddition, diazo compound **1aa** without the alkyne species, internal alkyne **A**, and **l1** were selected to mix with the gold catalyst. Considering the stability of the catalyst, JohnphosAu$(CH_3CN)SbF_6$ was chosen as the catalyst.

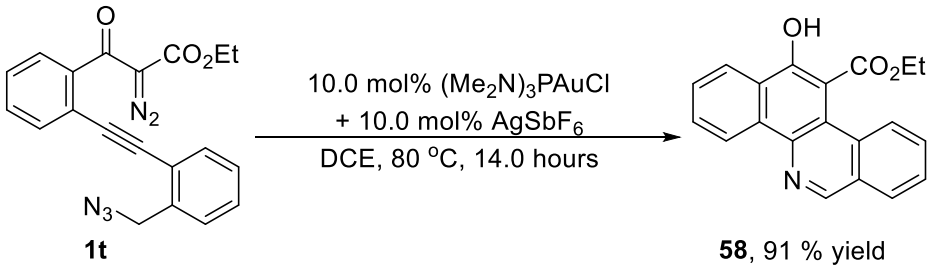
Experimental procedure: To a dried NMR tube, **1aa** (43.6 mg, 0.2 mmol) in $CDCl_3$ (1.0 mL) was added JohnphosAu$(CH_3CN)SbF_6$ (7.6 mg, 0.01 mmol, 5.0 mol%). Then the mixture was subjected to ^{31}P NMR analysis after 3.5 minutes at 25 °C (Fig. S2-1). The experimental procedure with **A** (Fig. S2-2), with **1aa** and **A** (Fig. S2-3), or with **1l** (Fig. S2-4) were similar to that of **1aa** (Fig. S5-1). For the ^{31}P NMR of JohnphosAu$(CH_3CN)SbF_6$, see Fig. S2-5. In all these ^{31}P NMR spectra, the external 85% phosphoric acid was used as ^{31}P standard.

These results implied that the gold catalyst first coordinated with the alkynyl group, instead of direct decomposition of the diazo species.



Supplementary Fig. S2 The ^{31}P NMR spectra of gold catalyst with **1l**, **A**, or **1aa**, separately or in combination.

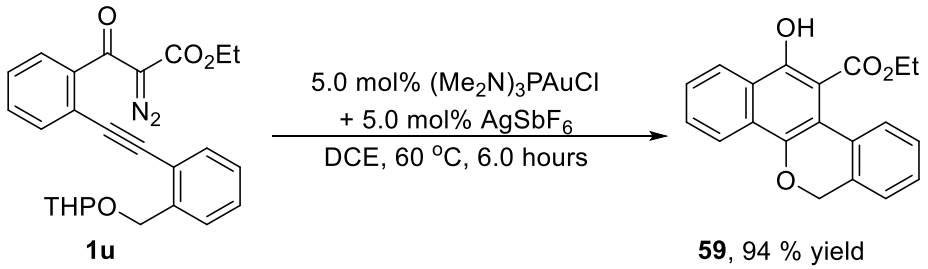
Synthesis of 58



1t **58**, 91 % yield

To a 10-mL oven-dried vial containing a magnetic stirring bar, $(Me_2N)_3PAuCl$ (3.95 mg, 0.01 mmol), $AgSbF_6$ (3.43 mg, 0.01 mmol), and DCE (0.5 mL) were added in sequence in a nitrogen-filled glove-box. The reaction mixture was stirred at 25 °C for 2.0 hours. The solvent was removed and the residue was dissolved in DCE (0.5 mL). Then the mixture was filtered through a pad of Celite. The filtrate was added into a solution of **1t** (74.6 mg, 0.2 mmol) in DCE (0.5 mL) at 80 °C, and the resulting reaction mixture was stirred under these conditions for 14 hours. Then, the solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel (solvents: petroleum ether/ethyl acetate = 5: 1) to give 57.8 mg **58** in 91% yield. White solid; m. p. 221.0 – 223.0 °C. ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm) 11.34 (s, 1H), 9.46 – 9.10 (comp, 2H), 8.50 (d, J = 8.1 Hz, 1H), 8.06 (d, J = 7.3 Hz, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.92 – 7.79 (m, 1H), 7.78 – 7.55 (comp, 3H), 4.40 (q, J = 7.1 Hz, 2H), 1.19 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.9, 159.7, 150.3, 137.6, 134.9, 132.3, 130.6, 128.4, 127.9, 127.8, 127.7, 126.9, 125.5, 124.9, 124.1, 119.6, 102.2, 61.9, 13.9. HRMS (TOF MS ESI$^+$) calculated for $C_{20}H_{15}NNaO_3^+$ $[M+Na]^+$: 340.0944, found: 340.0947.

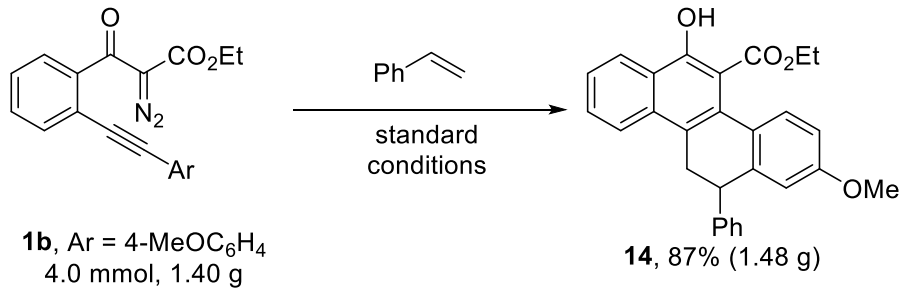
Synthesis of 59



To a 10-mL oven-dried vial containing a magnetic stirring bar, $(Me_2N)_3PAuCl$ (3.95 mg, 0.01 mmol), $AgSbF_6$ (3.43 mg, 0.01 mmol), and DCE (0.5 mL) were added in sequence in a nitrogen-filled glove-box. The reaction mixture was stirred at 25 °C for 2.0 hours. The solvent was removed and the residue was dissolved in DCE (0.5 mL). Then the mixture was filtered through a pad of Celite. The filtrate was added into a solution of **1u** (86.4 mg, 0.2 mmol) in DCE (0.5 mL) at 60 °C, and the resulting reaction mixture was stirred under these conditions for 6.0 hours. Then, the solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel (solvents: petroleum ether/ethyl acetate = 10: 1) to give 60.2 mg **59** in 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 11.30 (s, 1H), 8.45 – 8.27 (m, 1H), 8.26 – 8.03 (m, 1H), 7.65 – 7.58 (m, 1H), 7.58 – 7.52 (m, 1H), 7.31 – 7.26 (m, 1H), 7.26 – 7.23 (comp, 2H), 7.15 (d, *J* = 7.3 Hz, 1H), 5.16 (s, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.16 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.6, 156.1, 145.8, 131.0, 130.5, 129.7, 128.4, 127.4, 127.3, 127.2, 126.7, 125.7, 124.6, 124.3, 122.2, 115.1, 102.8, 69.5, 61.6, 13.9. HRMS (TOF MS ESI$^+$) calculated for $C_{20}H_{16}NaO_4^+$ $[M+Na]^+$: 343.0941, found: 343.0947. The analysis of NMR is consistent with the literature.[4]

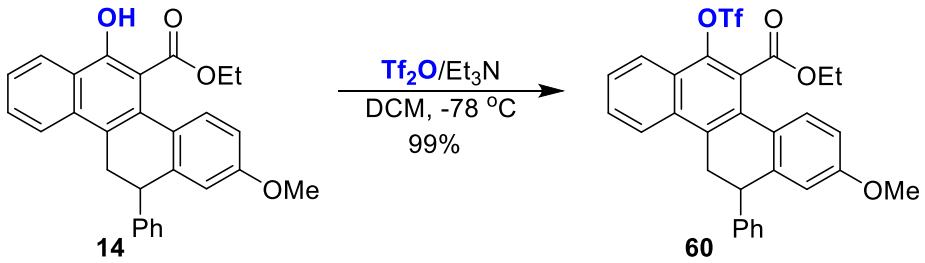
Synthetic Transformations

Gram-scale



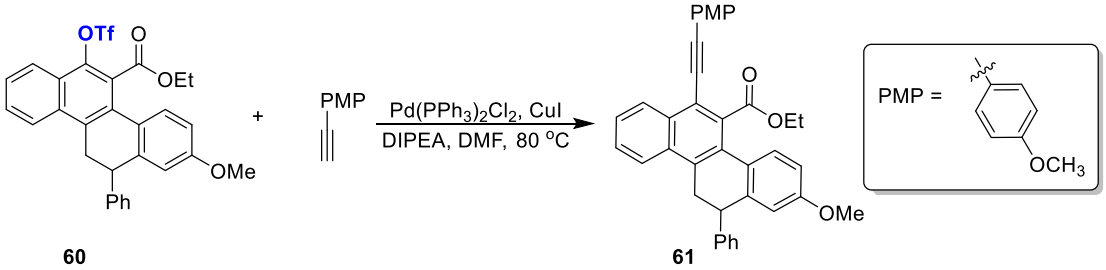
To a 10-mL oven-dried vial containing a magnetic stirring bar, $(Me_2N)_3PAuCl$ (79 mg, 0.2 mmol), $AgSbF_6$ (68.63 mg, 0.2 mmol), and DCE (10 mL) were added in sequence in a nitrogen-filled glove-box. The reaction mixture was stirred at 25 °C for 2.0 hours. The solvent was removed and the residue was dissolved in DCE (10 mL). Then the mixture was filtered through a pad of Celite. The filtrate was added into a solution of **1b** (1.40 g, 4.0 mmol) and **2a** (0.624 g, 6.0 mmol) in DCE (10 mL) at 60 °C, and the resulting reaction mixture was stirred under these conditions for 6.0 hours. Then, the solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel (eluent: Ethyl acetate/light petroleum ether =1/30~1/10) to afford 1.48 g **14** in 87% yield.

Synthesis of 60



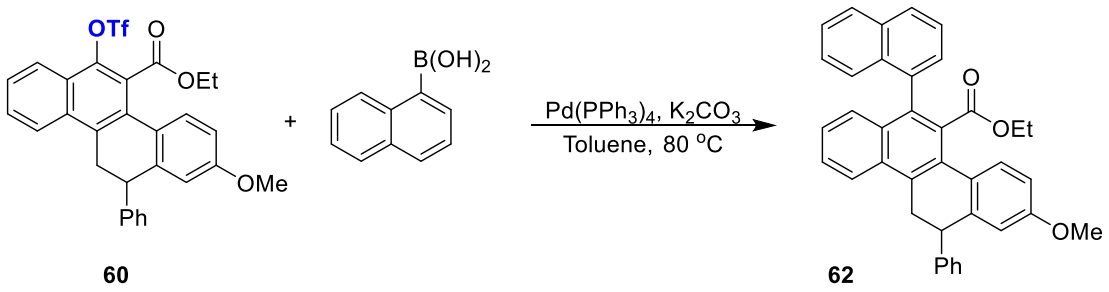
To a 10-mL oven-dried vial containing a magnetic stirring bar, triethylamine (Et_3N, 253.0 μL, 1.5 mmol), and **14** (424.5 mg, 1.0 mmol) in dry dichloromethane (DCM, 3.0 mL), was added trifluoromethanesulfonic anhydride (Tf_2O, 208.0 μL, 1.5 mmol) in 10 minutes *via* a syringe at -78 ℃. The reaction mixture was warmed to room temperature slowly in 3.0 hours. Until **14** was completely consumed (determined by TLC), the solvent was removed under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent: ethyl acetate/hexane = 1:100) to give 551.0 mg pure product **60** in 99% yield. ^{1}H NMR (300 MHz, $CDCl_3$) (δ, ppm) 8.21 – 8.05 (comp, 2H), 7.65 – 7.56 (comp, 2H), 7.43 (d, *J* = 8.6 Hz, 1H), 7.38 – 7.26 (comp, 5H), 6.82 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.50 (d, *J* = 2.2 Hz, 1H), 4.44 – 4.22 (comp, 3H), 3.74 (s, 3H), 3.51 (ddd, *J* = 26.6, 15.8, 8.0 Hz, 2H), 1.24 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) (δ, ppm) 166.7, 159.7, 142.4, 141.84, 141.78, 134.5, 133.2, 130.6, 128.9, 128.83, 128.79, 128.1, 127.7, 127.2, 126.6, 125.3, 123.6, 123.2, 122.8, 113.5, 111.8, 62.5, 55.4, 44.5, 33.1, 13.8; ^{19}F NMR (283 MHz, $CDCl_3$) (δ, ppm) -72.9. HRMS (TOF MS ESI$^+$) calculated for $C_{29}H_{24}F_3O_6S^+$ [M+H]$^+$: 557.1240, found 557.1237.

Synthesis of 61



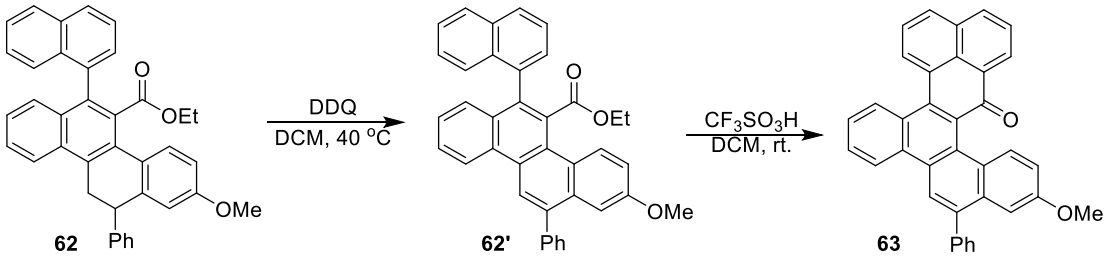
To a 10-mL oven-dried vial containing a magnetic stirring bar, **60** (55.6 mg, 0.1 mmol), 4-ethynylanisole (20.0 mg, 0.15 mmol), $Pd(PPh_3)_2Cl_2$ (7.0 mg, 0.01 mmol), CuI (1.0 mg, 0.005 mmol), diisopropylethylamine (DIPEA, 52.0 μL, 0.3 mmol), and DMF (1.0 mL) were added in sequence under argon atmosphere. The reaction was stirred at 80 ℃ for 12.0 hours until **60** was completely consumed (determined by TLC). The reaction mixture was purified by flash column chromatography on silica gel without additional treatment (eluent: ethyl acetate/hexane = 1:40) to give 50.0 mg **61** in 93% yield. White solid; m. p. 190.0 – 192.0 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) (δ, ppm) 8.51 (d, *J* = 7.5 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.6 Hz, 1H), 7.59 (d, *J* = 8.3 Hz, 2H), 7.57 – 7.51 (comp, 2H), 7.33 – 7.27 (comp, 4H), 7.26 – 7.23 (m, 1H), 6.94 (d, *J* = 8.3 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 1H), 6.54 (s, 1H), 4.52 – 4.39 (m, 2H), 4.25 (dd, *J* = 9.5, 4.8 Hz, 1H), 3.86 (s, 3H), 3.75 (s, 3H), 3.61 (dd, *J* = 15.6, 4.8 Hz, 1H), 3.50 (dd, *J* = 15.6, 10.1 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) (δ, ppm) 170.4, 160.0, 159.4, 142.31, 142.29, 133.8, 133.3, 132.8, 131.8, 131.7, 129.5, 128.73, 128.70, 127.8, 127.73, 127.68, 127.2, 126.9, 126.8, 123.8, 119.4, 115.5, 114.2, 113.6, 111.9, 98.6, 84.2, 61.8, 55.5, 55.3, 44.7, 33.0, 14.3. HRMS (TOF MS ESI$^+$) calculated for $C_{37}H_{31}O_4^+$ [M+H]$^+$: 539.2217, found: 539.2210.

Synthesis of 62



To a 10-mL oven-dried vial containing a magnetic stirring bar, **60** (111.2 mg, 0.2 mmol), 1-naphthylboronic acid (51.6 mg, 0.3 mmol), $Pd(PPh_3)_4$ (23.1 mg, 0.02 mmol), K_2CO_3 (55.3mg, 0.4 mmol), and toluene (2.0 mL) were added in sequence under argon atmosphere. The reaction was stirred at 80 ℃ for 6.0 hours until **60** was completely consumed (determined by TLC). The reaction mixture was purified by flash column chromatography on silica gel without additional treatment (eluent: ethyl acetate/hexane = 1:40) to give 104.8 mg **62** in 98% yield. White solid; m. p. 217.5 – 219.5 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) (δ, ppm) with three diastereoisomers: 8.17 – 6.48 (comp, 17H), 4.42 – 3.44 (comp, 8H), 1.31 – 0.52 (comp, 3H), ^{13}C NMR (125 MHz, $CDCl_3$) (δ, ppm) with three diastereoisomers: (170.9, 170.28, 170.25), (159.23, 159.22, 159.17), 143.0, 142.6, 142.52, 142.48, 142.2, 141.7, 136.4, 136.10, 136.07, 135.9, 133.7, 133.6, 133.5, 133.4, 133.32, 133.30, 132.9, 132.6, 131.8, 131.7, 131.6, 131.5, 130.8, 130.6, 130.4, 129.6, 129.4, 129.27, 129.26, 129.1, 128.81, 128.79, 128.76, 128.7, 128.63, 128.58, 128.3, 128.2, 128.1, 128.04, 128.01, 127.99, 127.97, 127.8, 127.7, 127.44, 127.41, 127.21, 127.20, 127.10, 127.0, 126.9, 126.8, 126.2, 126.12, 126.05, 125.94, 125.89, 125.3, 125.2, (123.63, 123.56, 123.5), (113.7, 113.5, 113.2), (111.8, 111.6, 111.3), (61.5, 60.8, 60.7), (55.32, 55.29, 55.2), (45.2, 44.8, 44.7), (33.1, 33.0, 32.8), (14.2, 13.3, 13.2). HRMS (TOF MS ESI$^+$) calculated for $C_{38}H_{31}O_3^+$ $[M+H]^+$: 535.2268, found: 535.2260.

Synthesis of 63



To a 10-mL oven-dried flask equipped with a magnetic stirring bar, **62** (53.5 mg, 0.1 mmol), DDQ (45.4 mg, 0.20 mmol), and DCM (3.0 mL) were added in sequence. The reaction mixture was stirred at 40 ℃ for 12 hours. Upon completion (monitored by TLC), the solvent was evaporated under vacuum after filtering through a pad of Celite. The obtained crude **62'** was directly used for the next step without further purification.

To a 10-mL oven-dried round-bottom flask containing a magnetic stirring bar, the above obtained **62'**, trifluoromethanesulfonic acid (87.0 μL, 1.0 mmol), and DCM (1.0 mL) were added in sequence under argon at 25 °C. Then the reaction mixture was stirred for 12 hours. Then, water (50 mL) was added to the reaction mixture and stirred for 1-2 hours. The yellow solid precipitated out and was filtered under vacuum. The crude product was purified by column chromatography on silica gel (ethyl acetate/petroleum ether = 1/3) to give 39.9 mg **63** in 82% yield based on **62**. Yellow solid; m. p. 279.0 – 281.0 ℃. ^{1}H NMR (500 MHz, $Cl_2CDCDCl_2$) (δ, ppm) 9.70 (s, 1H), 9.04 (d, *J* = 7.6 Hz, 1H), 8.83 (d, *J* = 5.7 Hz, 1H), 8.72 (d, *J* = 6.4 Hz, 1H), 8.67 (d, *J* = 8.6 Hz, 1H), 8.59 (s, 1H), 8.47 (d, *J* = 7.9 Hz, 1H), 8.06 (d, *J* = 5.1 Hz, 1H), 7.97 (d, *J* = 7.9 Hz, 1H), 7.91 (t, *J* = 6.7 Hz, 1H), 7.78 – 7.71 (comp, 2H), 7.69 – 7.56 (comp,

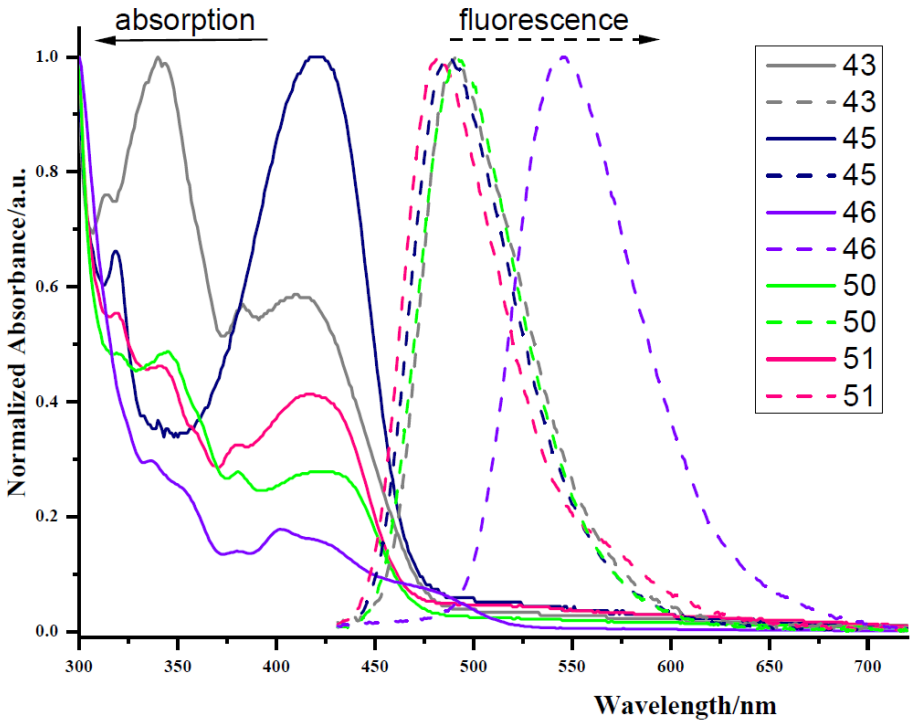
5H), 7.47 – 7.36 (comp, 2H), 3.86 (s, 3H); ^{13}C NMR (125 MHz, $Cl_2CDCDCl_2$) (δ, ppm) 183.6, 158.2, 140.7, 140.4, 137.0, 136.7, 132.6, 129.9, 129.8, 129.5, 129.4, 129.0, 128.7, 128.6, 128.2, 128.1, 128.0, 127.9, 127.8, 127.1, 127.02, 126.96, 126.9, 126.6, 125.5, 124.8, 124.5, 122.8, 122.3, 117.9, 107.5, 55.4. HRMS (TOF MS ESI$^+$) calculated for $C_{36}H_{23}O_2^+$ $[M+H]^+$: 487.1693, found 487.1676.

References

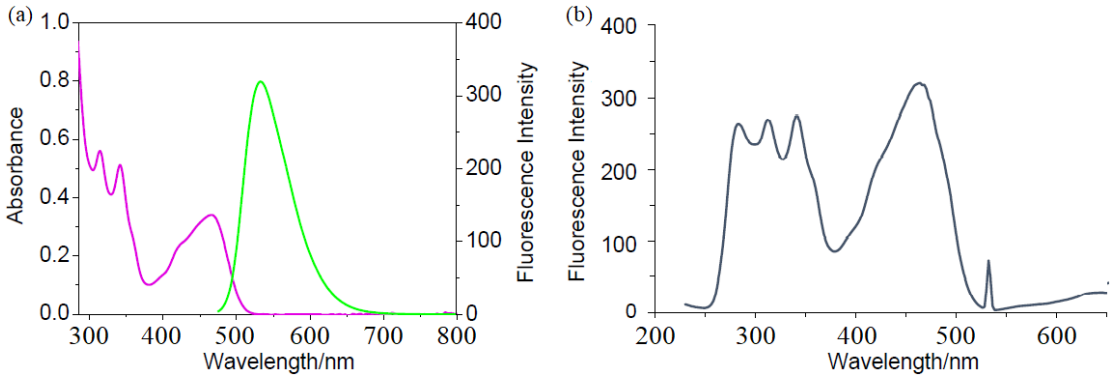
1. Wang, J. et al. Facile synthesis of halogenated spiroketals *via* a tandem iodocyclization. *Org. Lett.* **16**, 2236–2239 (2014).
2. Zhang, C. et al. Gold(I)-catalyzed aromatization: expeditious synthesis of polyfunctionalized naphthalenes. *iScience* **21**, 499–508 (2019).
3. Bauer, A. et al. Tris(dimethylamino)phosphane as a new ligand in gold(I) chemistry: synthesis and crystal structures of $[(Me_2N)_3P]AuCl$, $\{[(Me_2N)_3PAu]_3O\}^+BF_4^-$, $\{[Me_2N)_3PAu]_3NP(NMe_2)_3\}^{2+}\{BF_4^-\}_2$ and the precursor molecule $(Me_2N)_3PNSiMe_3$. *Chem. Ber.* **130**, 323−328 (1997).
4. Jover, J. et al. Expansion of the ligand knowledge base for monodentate P-donor ligands (LKB-P). *Organometallics* **29**, 6245−6258 (2010).

Optical and Photophysical Properties

The optical and photophysical properties of these obtained π-conjugated polycyclic hydrocarbons (CPHs) **43**, **45**, **46**, **50**, and **51** were examined in DMSO solution (0.2–0.3 mg/L, in quartz cuvettes with a layer thickness of 1 cm). The UV-vis absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. The f and excitation spectra were measured on a Shimadzu RF-5301PC spectroscope (Fig. S3).

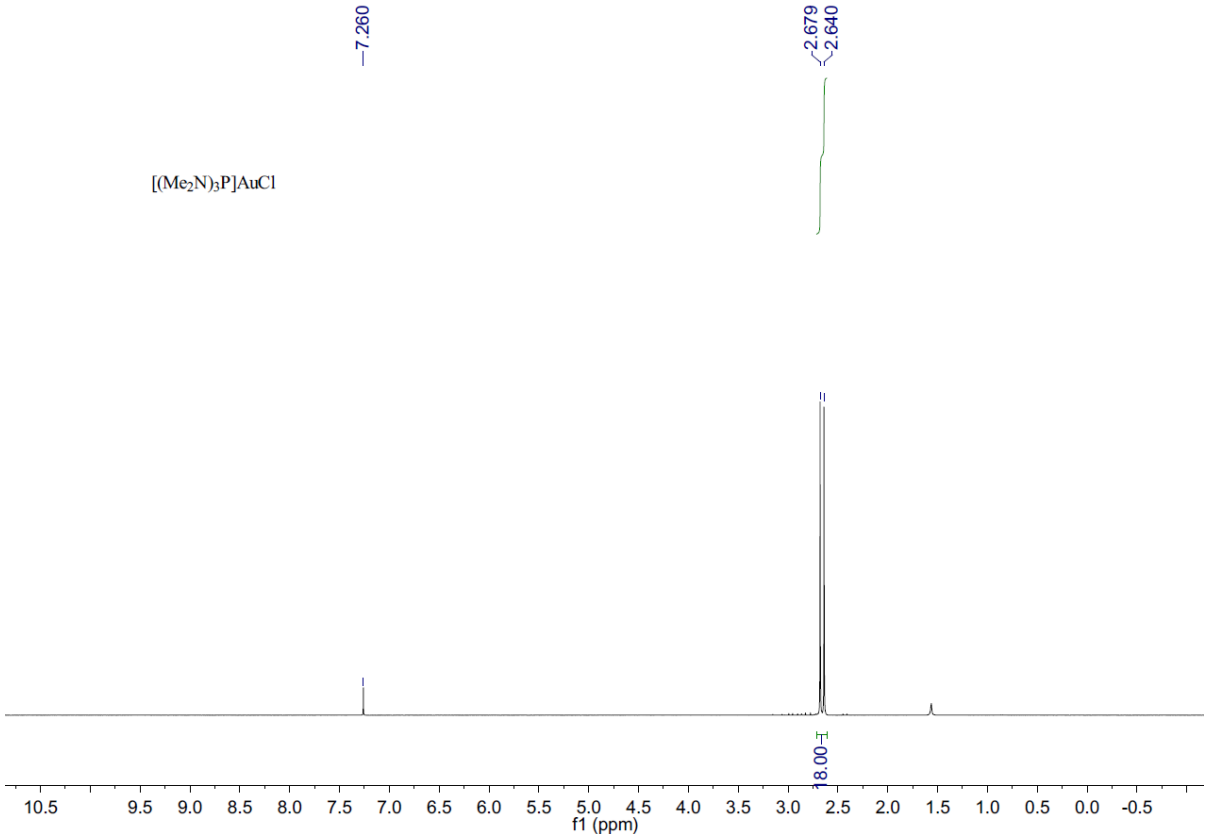


Supplementary Fig. S3 The UV/Vis absorption (solid lines) and emission spectra (broken lines) in DMSO.

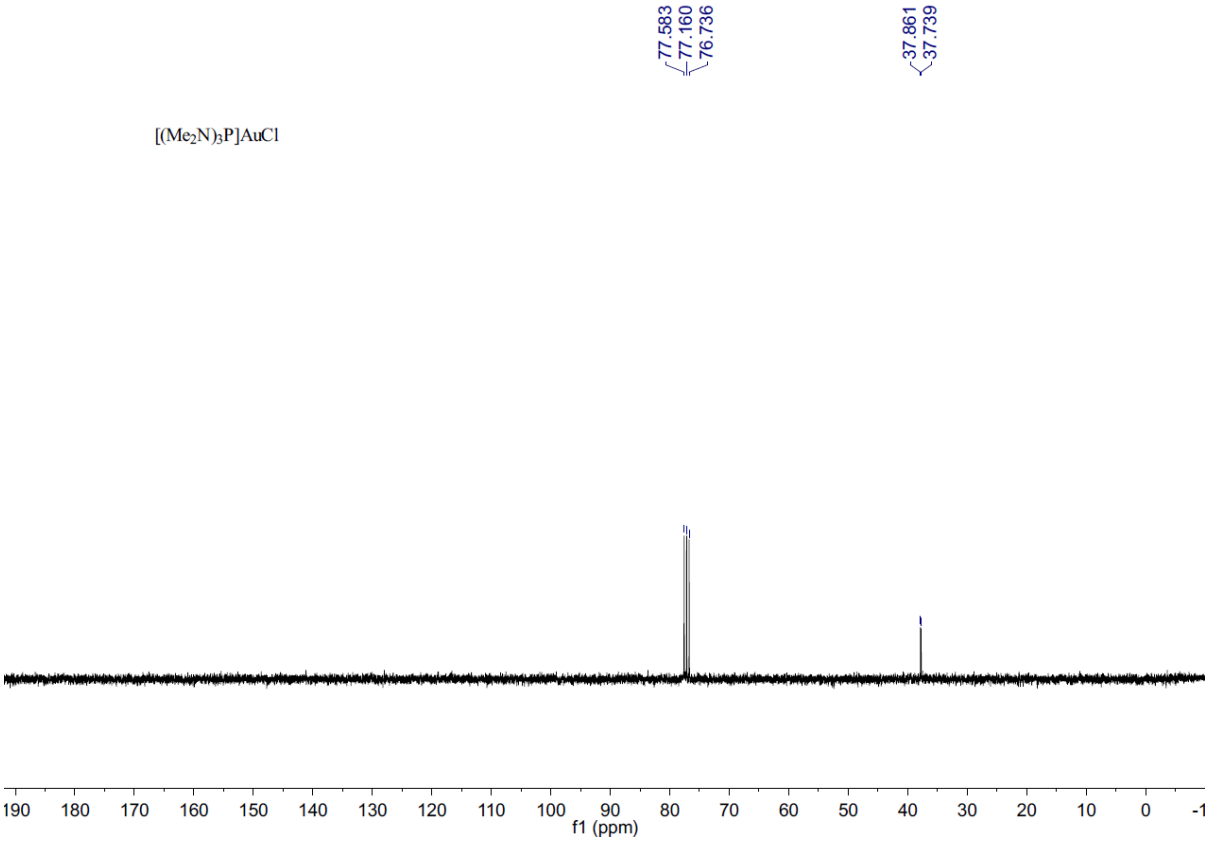


Supplementary Fig. 4 (a) UV/Vis absorption and fluorescence emission spectra of compound **63** in TCE at room temperature. **(b)** Fluorescence excitation spectra of compound **63** in TCE at room temperature. λ_{ex} = 465 nm; λ_{em} = 533 nm; bandwidth: 3 nm.

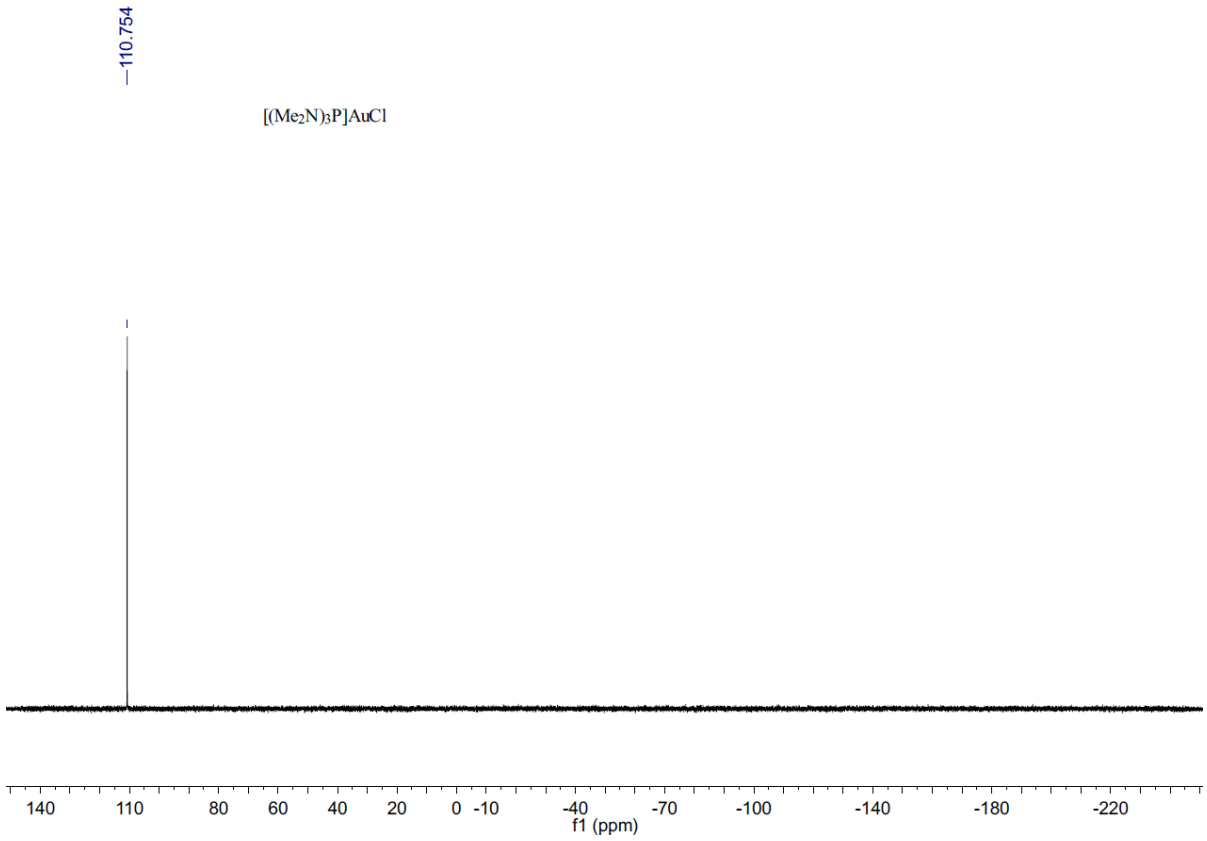
NMR spectra of new compounds



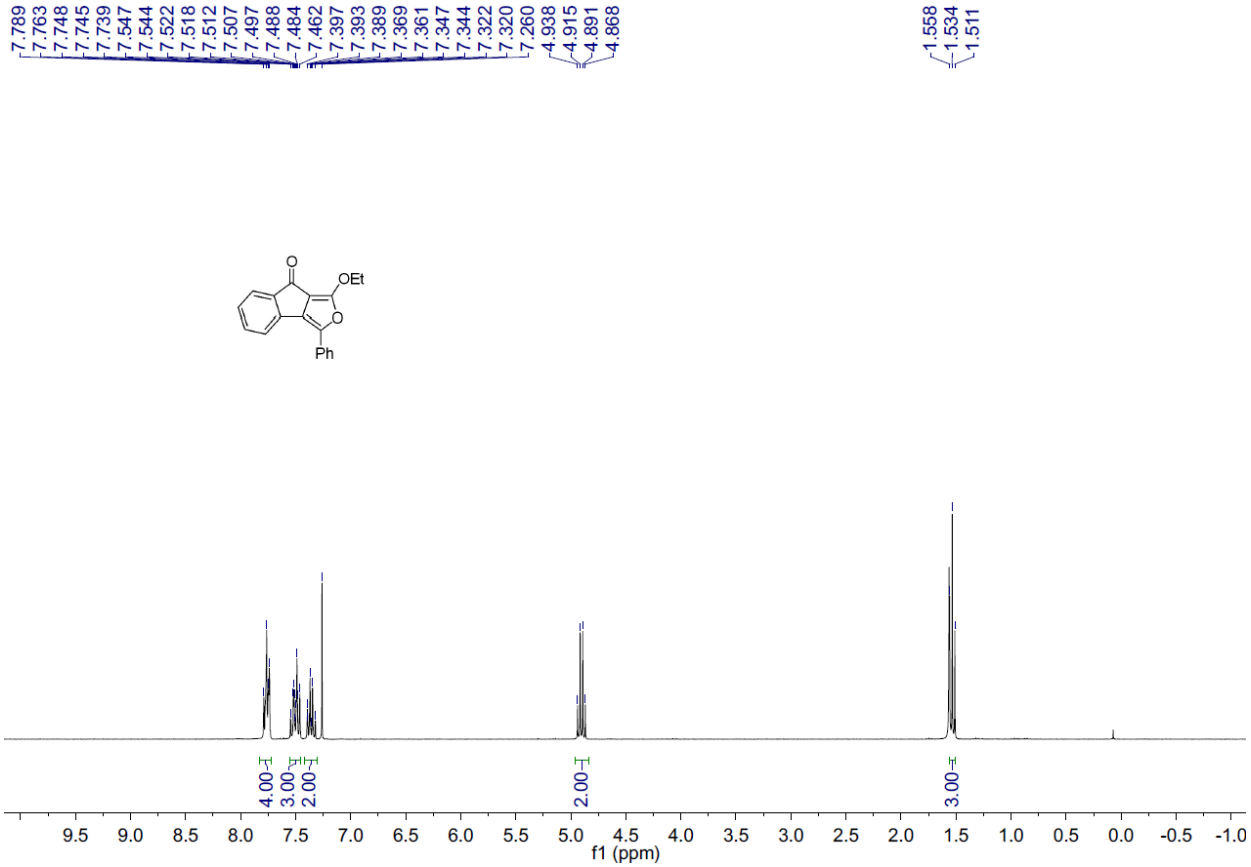
Supplementary Fig. 5 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum for $(Me_2N)_3PAuCl$.



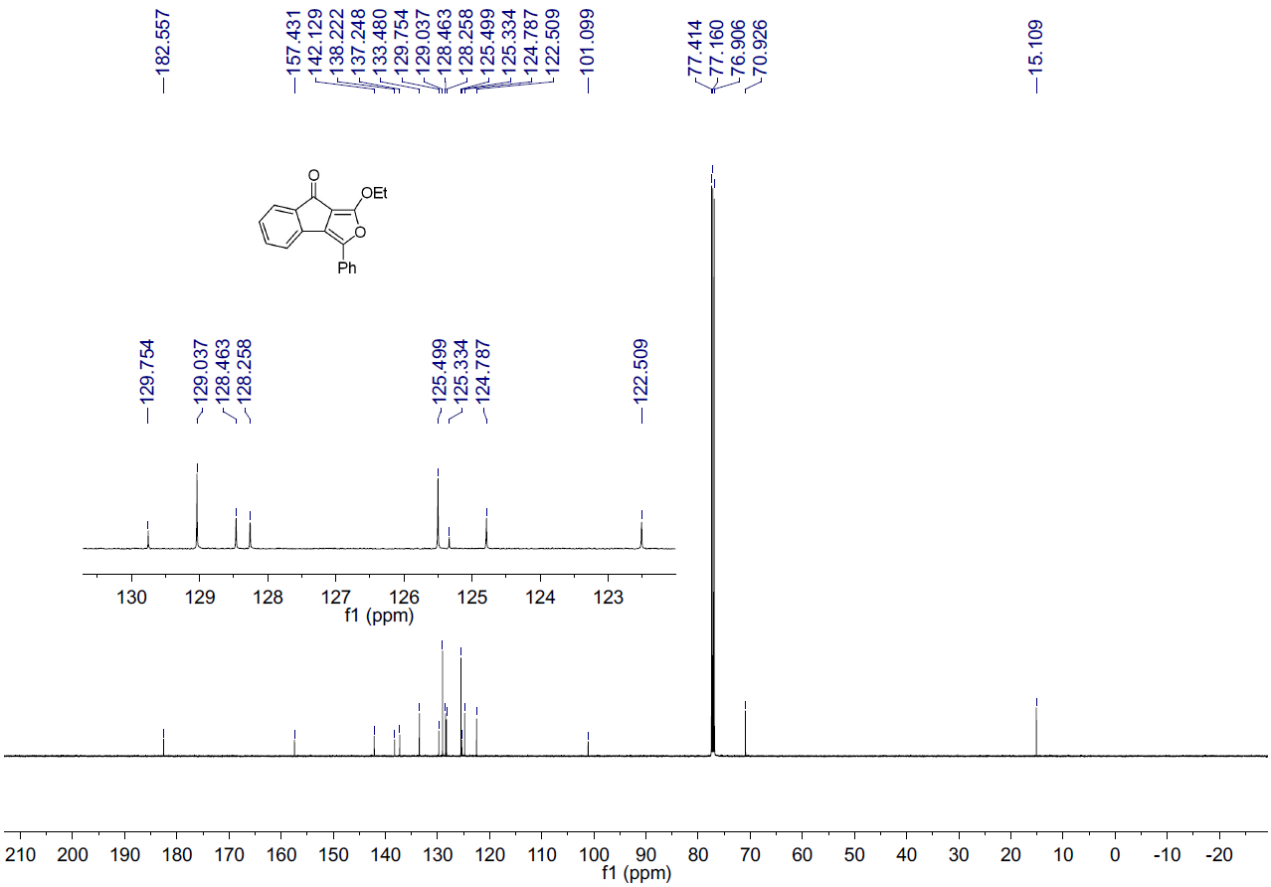
Supplementary Fig. 6 ^{13}C NMR (75 MHz, $CDCl_3$) spectrum for $(Me_2N)_3PAuCl$.



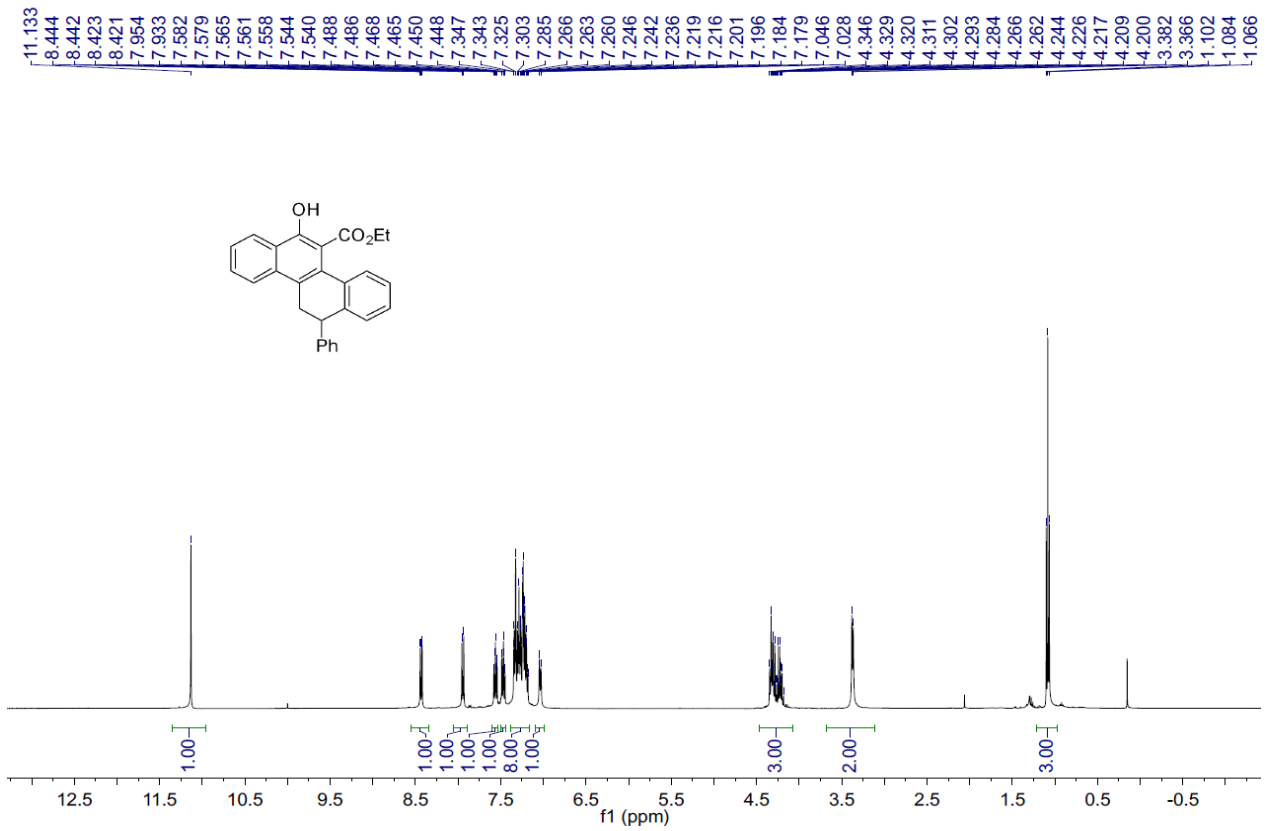
Supplementary Fig. 7 ^{13}C NMR (75 MHz, $CDCl_3$) spectrum for $(Me_2N)_3PAuCl$.



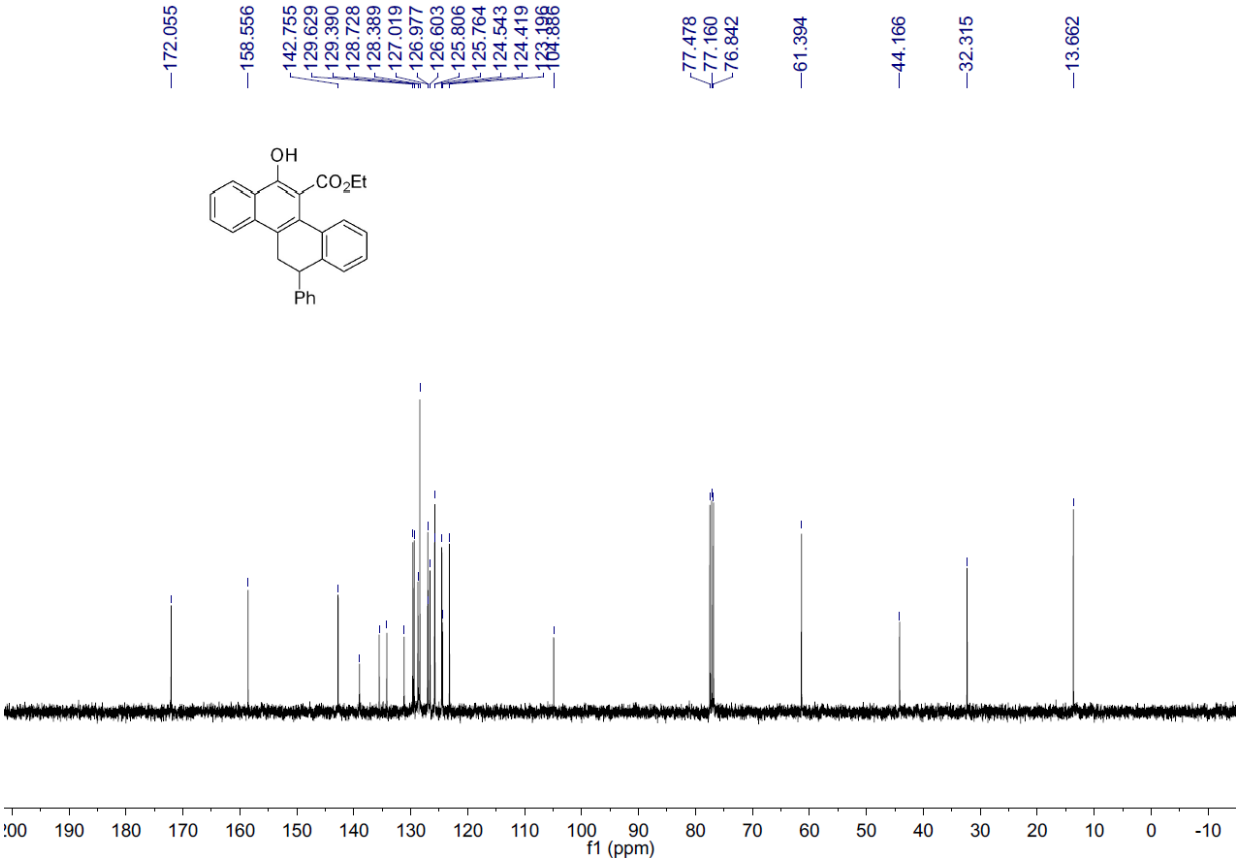
Supplementary Fig. 8 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum for 3'.



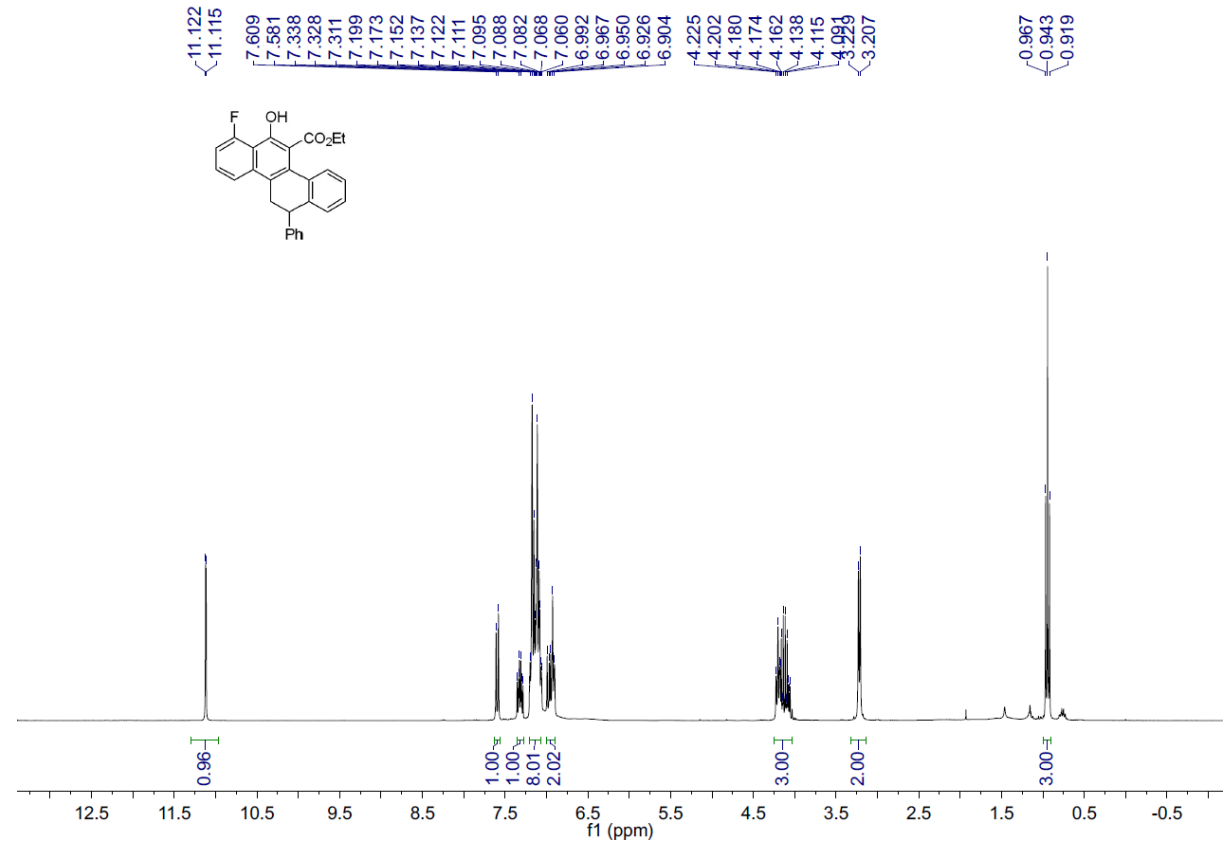
Supplementary Fig. 9 ^{13}C NMR (125 MHz, $CDCl_3$) spectrum for 3'.



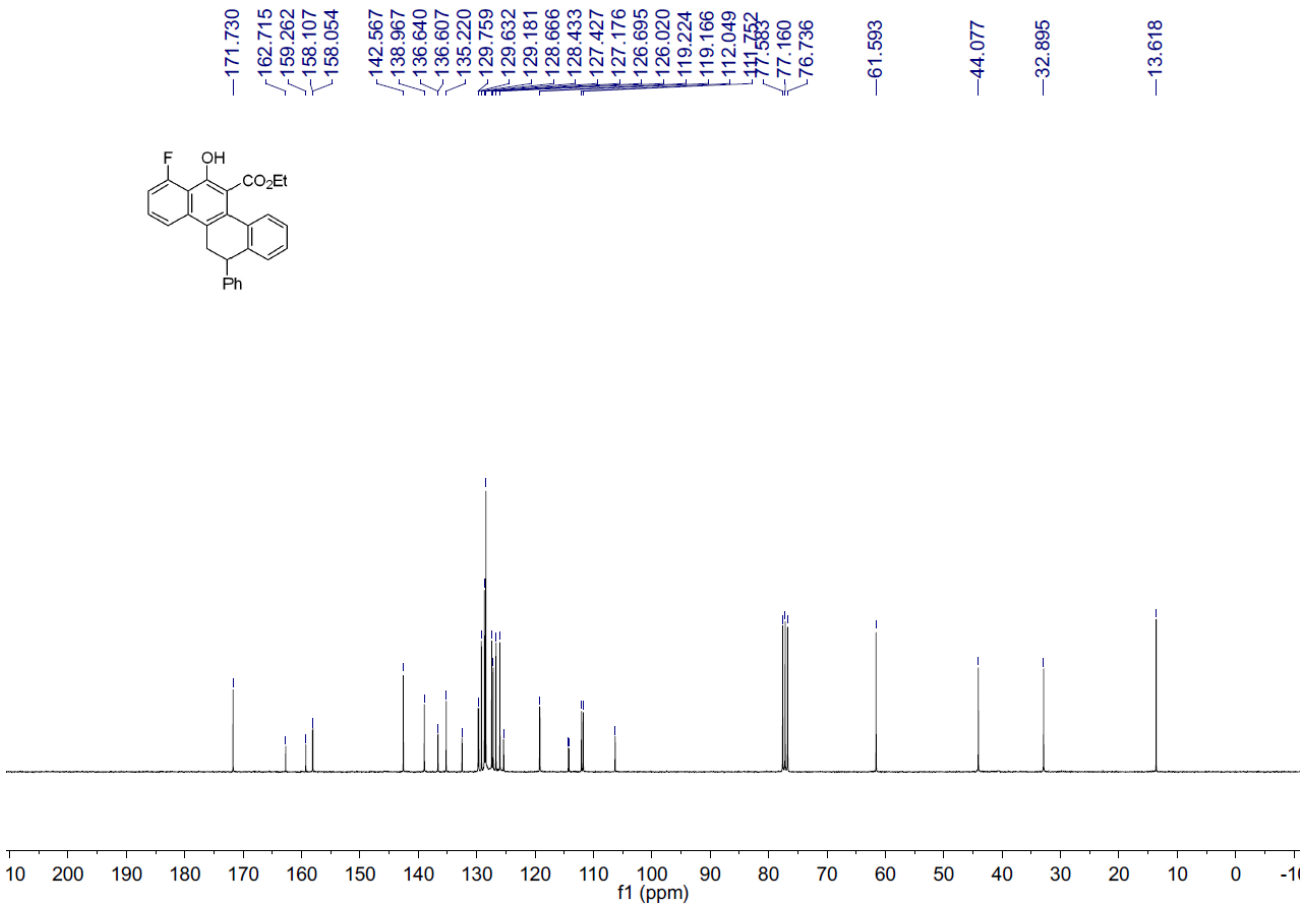
Supplementary Fig. 10 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3.



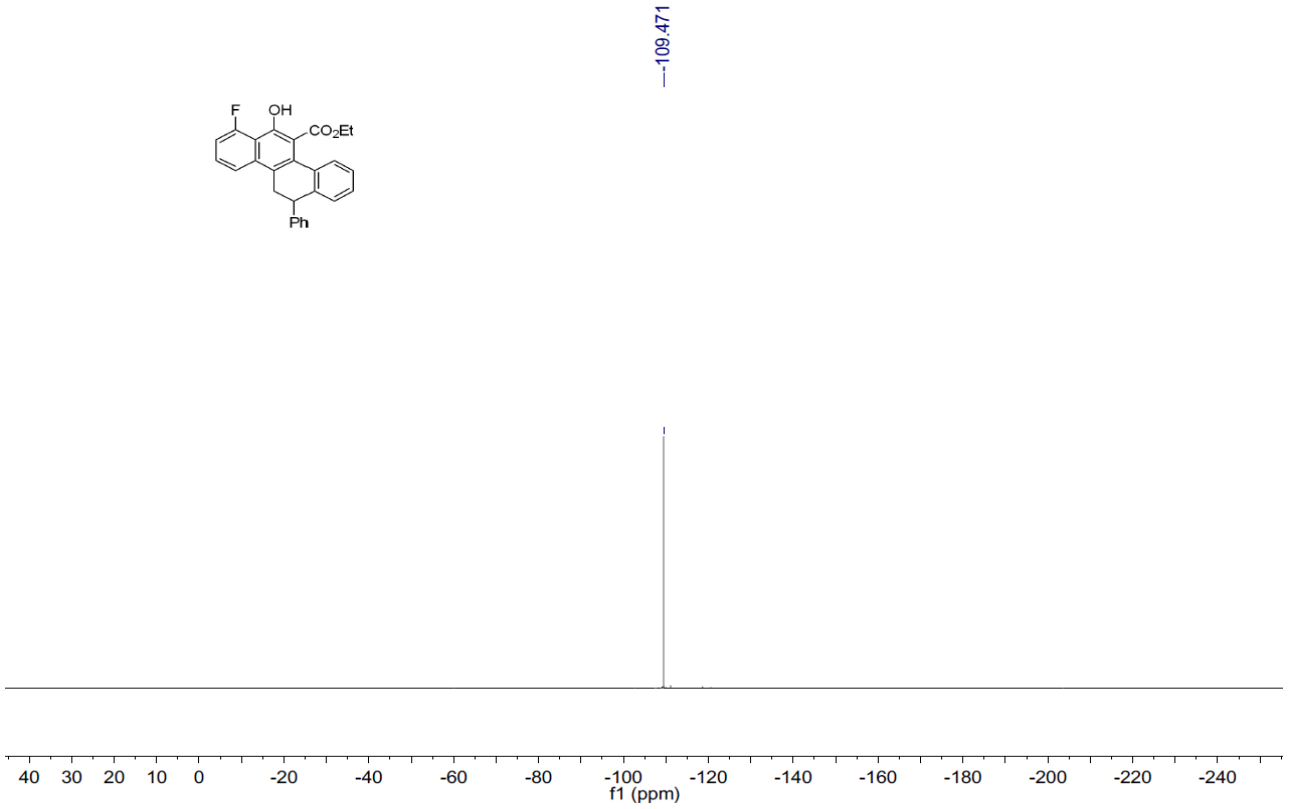
Supplementary Fig. 11 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 3.



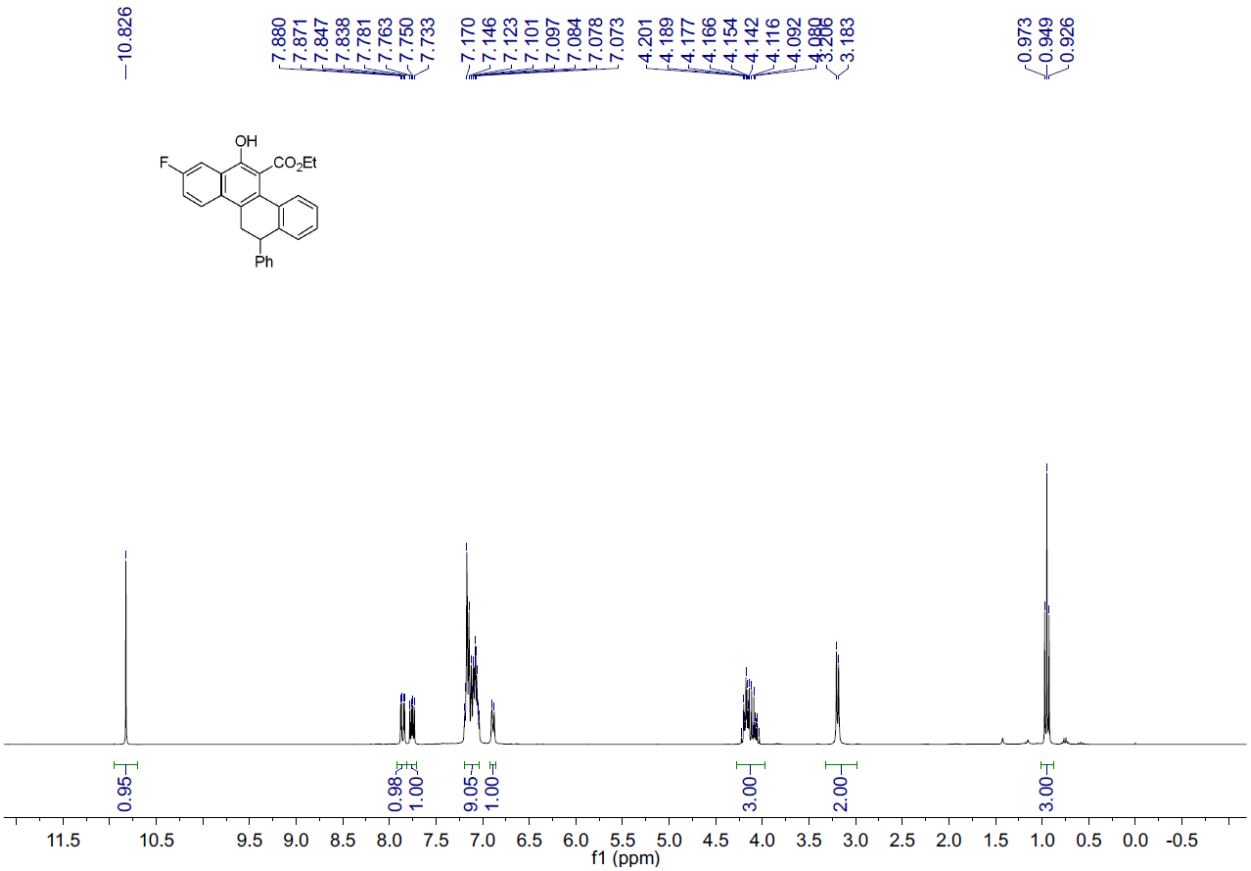
Supplementary Fig. 12 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum for 4.



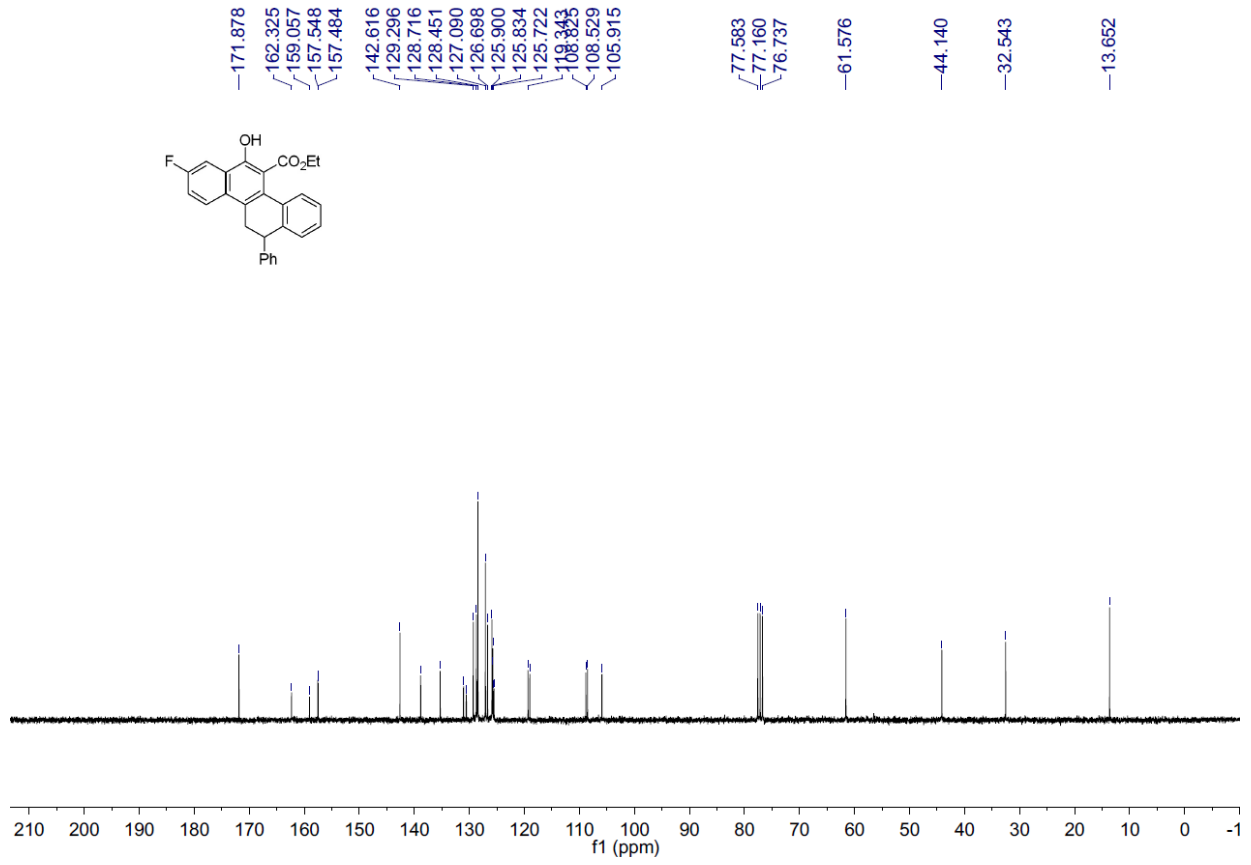
Supplementary Fig. 13 ^{13}C NMR (75 MHz, $CDCl_3$) spectrum for 4.



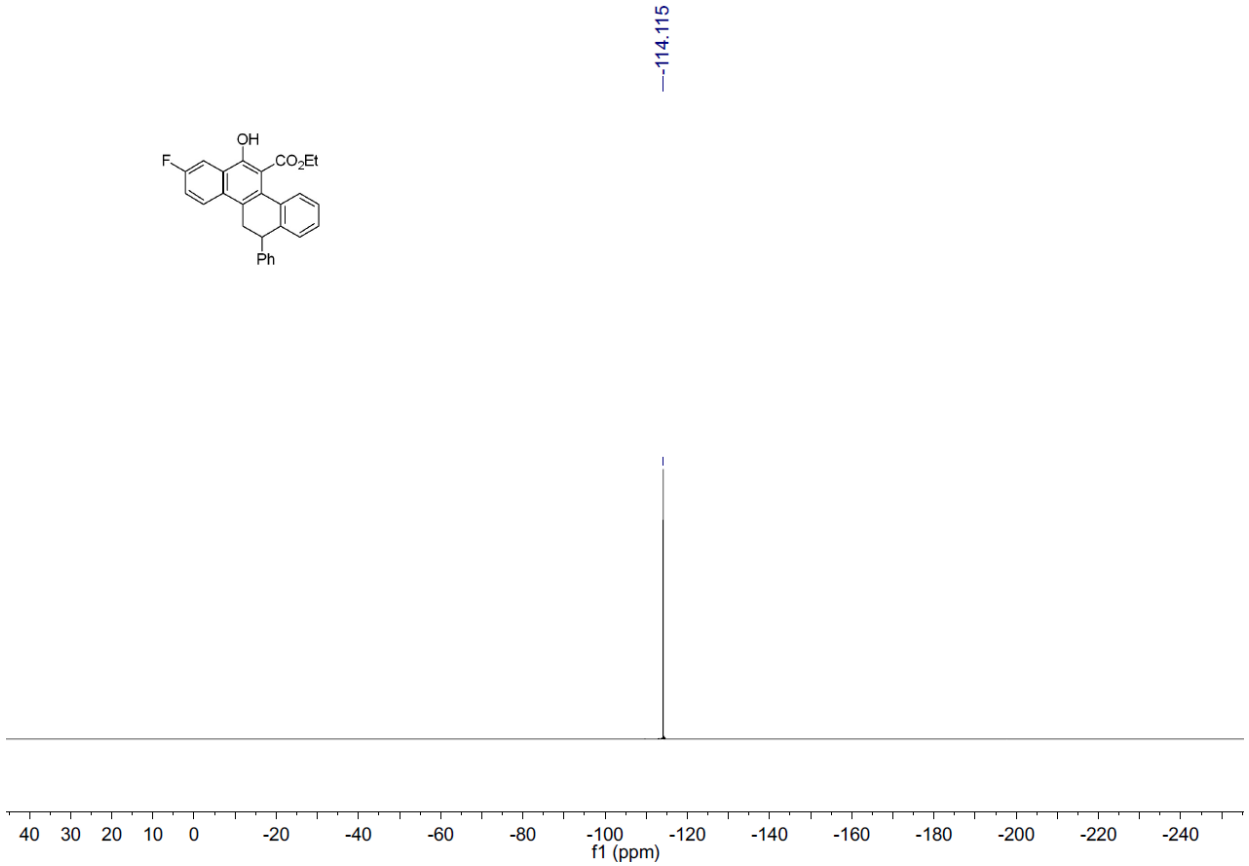
Supplementary Fig. 14 ^{19}F NMR (283 MHz, $CDCl_3$) spectrum for 4.



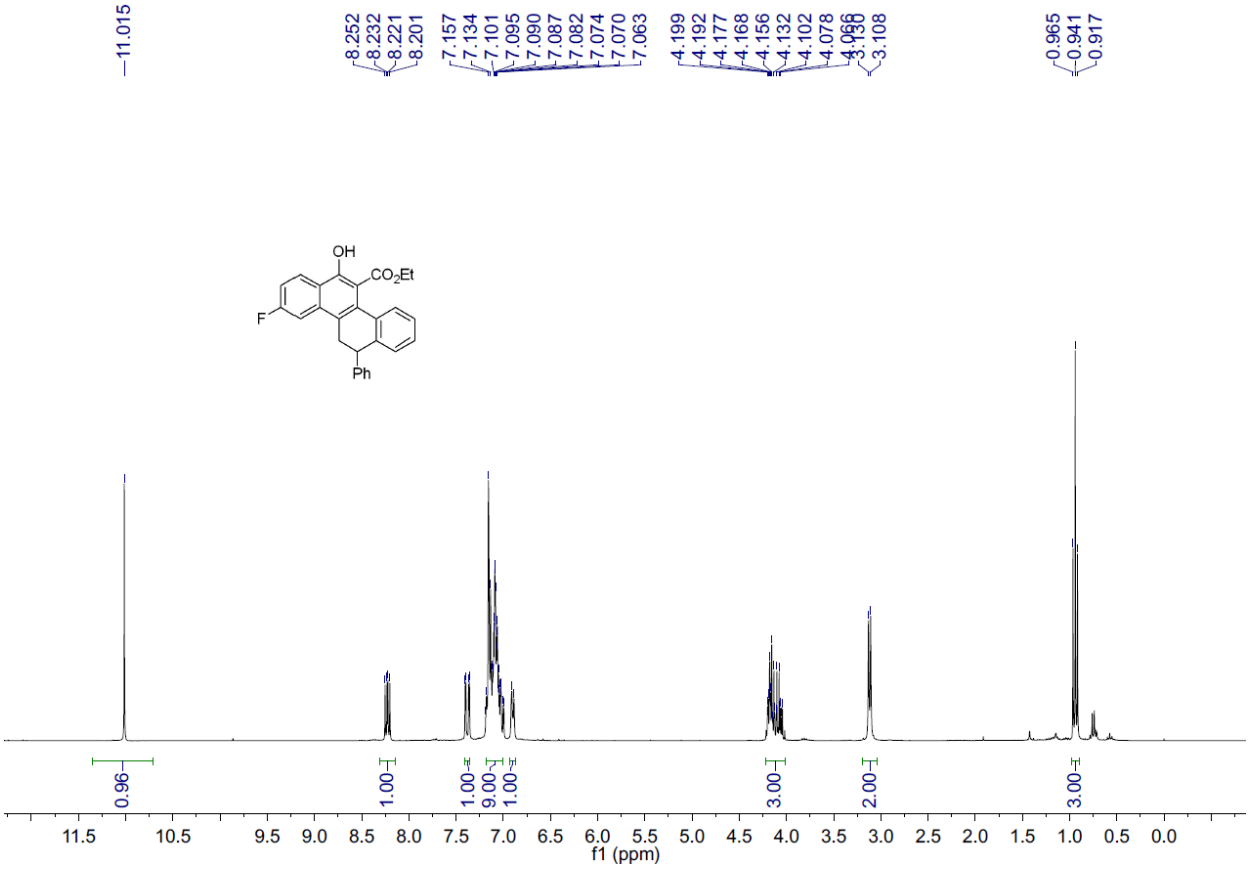
Supplementary Fig. 15 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum for 5.



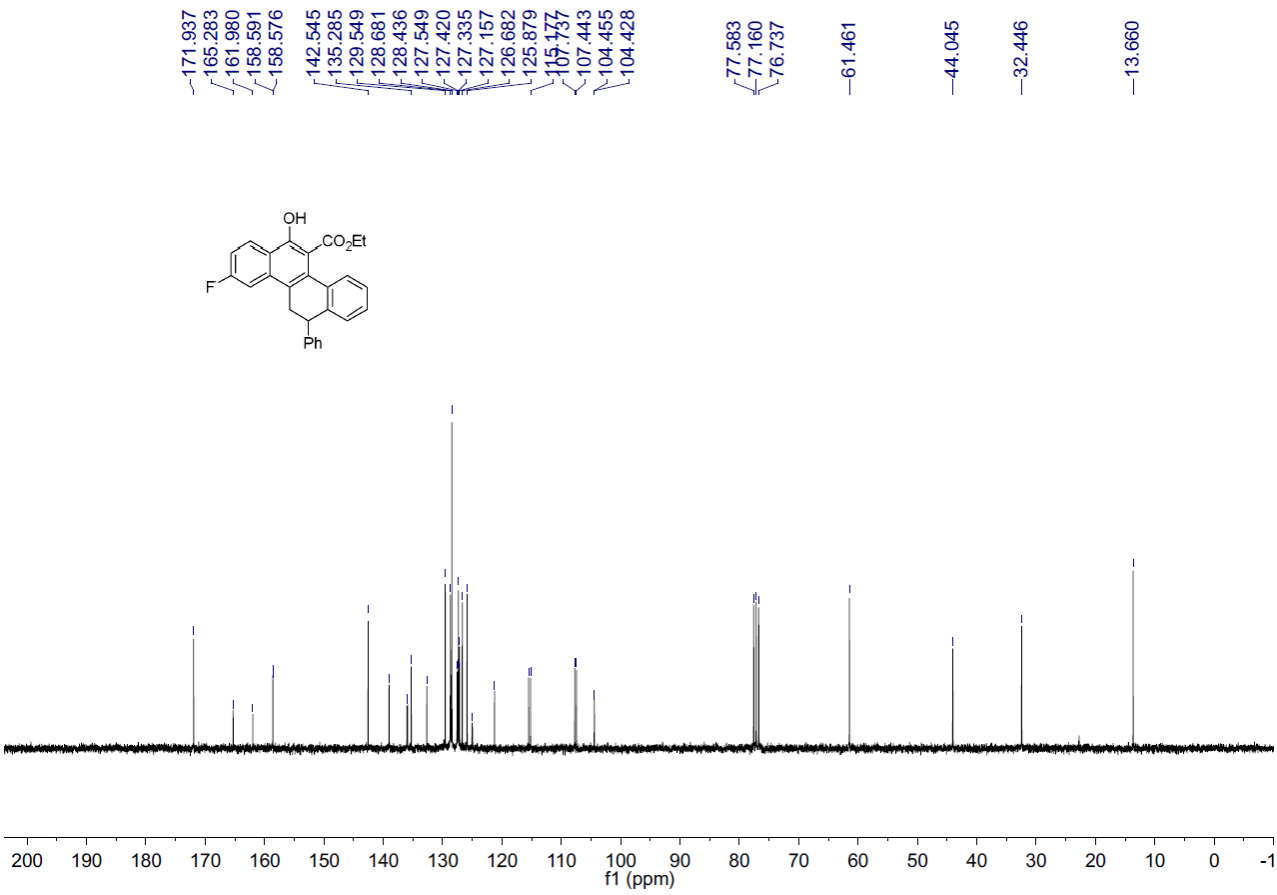
Supplementary Fig. 16 ^{13}C NMR (75 MHz, $CDCl_3$) spectrum for 5.



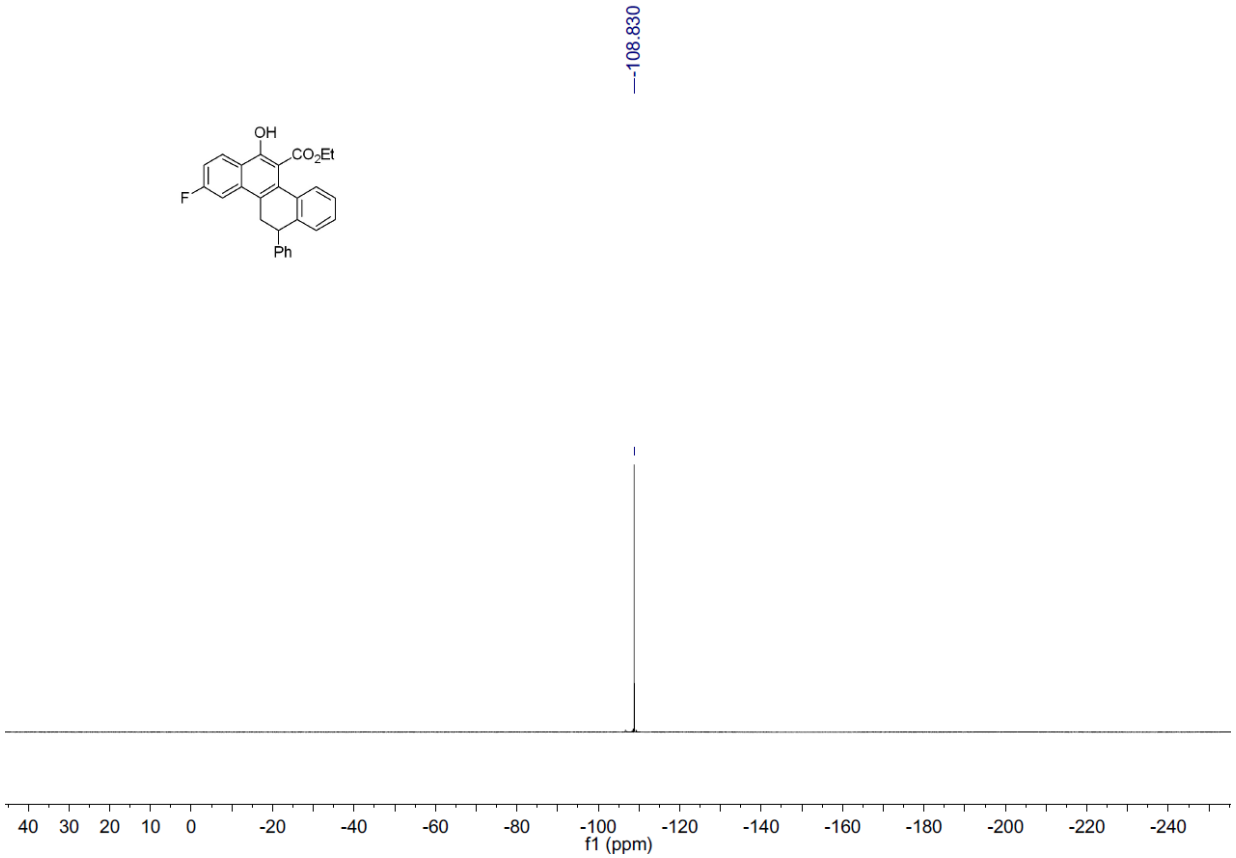
Supplementary Fig. 17 ^{19}F NMR (283 MHz, $CDCl_3$) spectrum for 5.



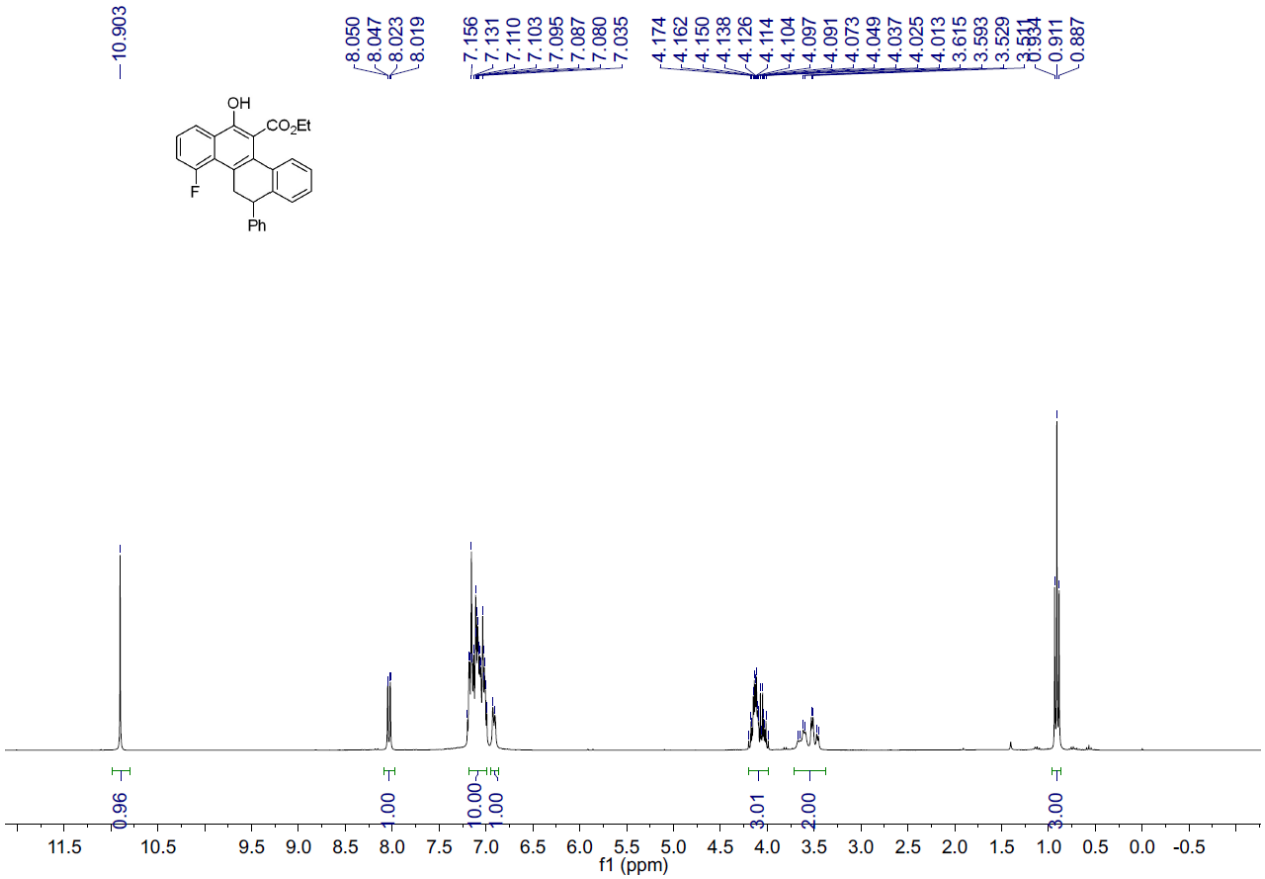
Supplementary Fig. 18 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum for 6.



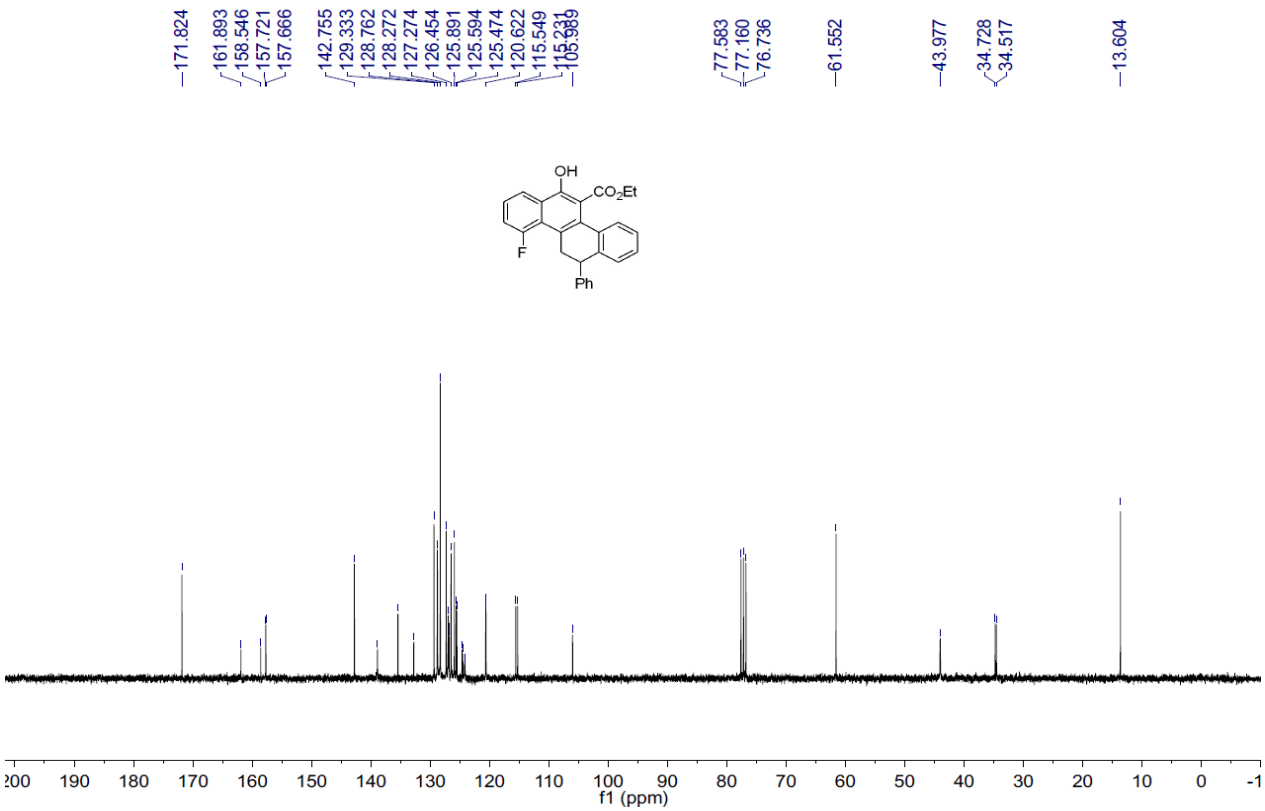
Supplementary Fig. 19 ^{13}C NMR (75 MHz, $CDCl_3$) spectrum for 6.



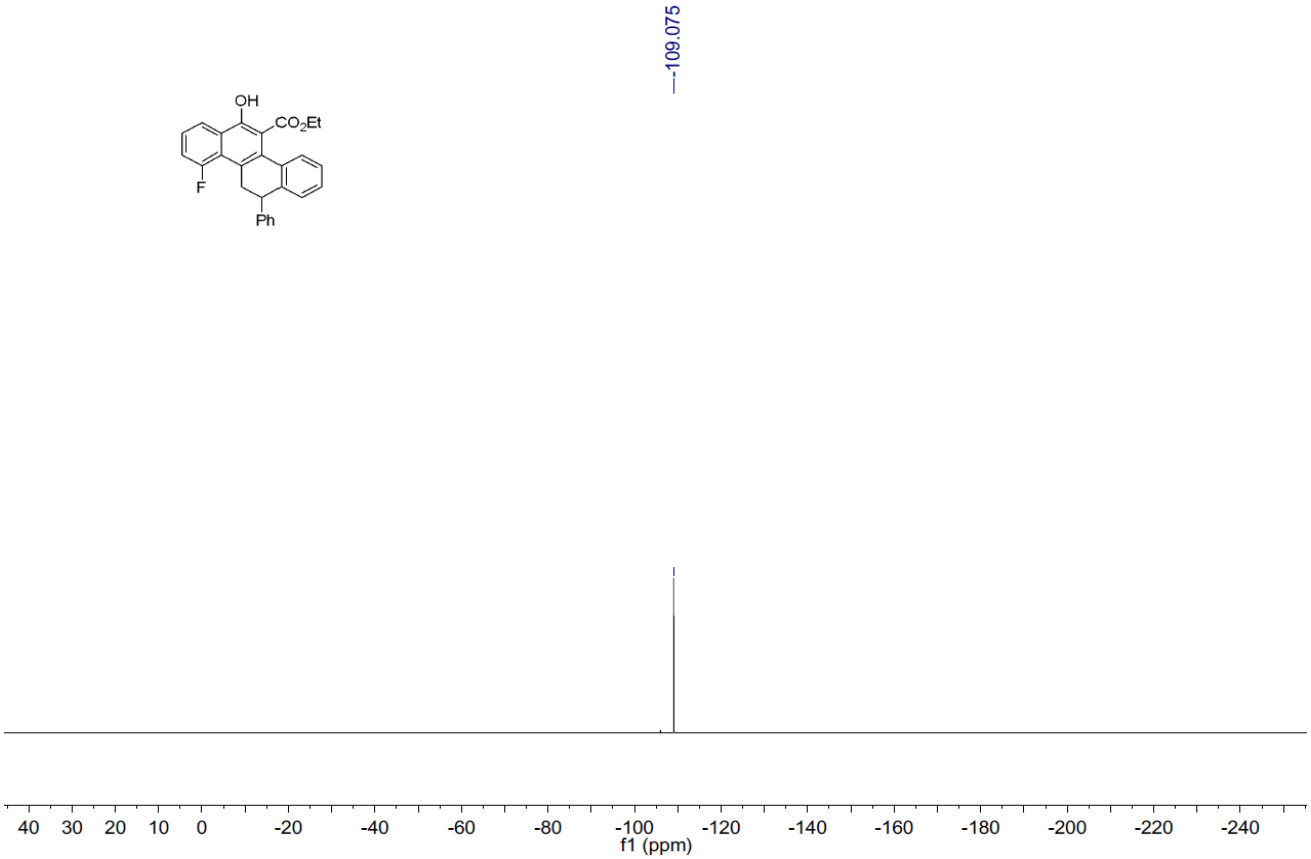
Supplementary Fig. 20 ^{19}F NMR (283 MHz, $CDCl_3$) spectrum for 6.



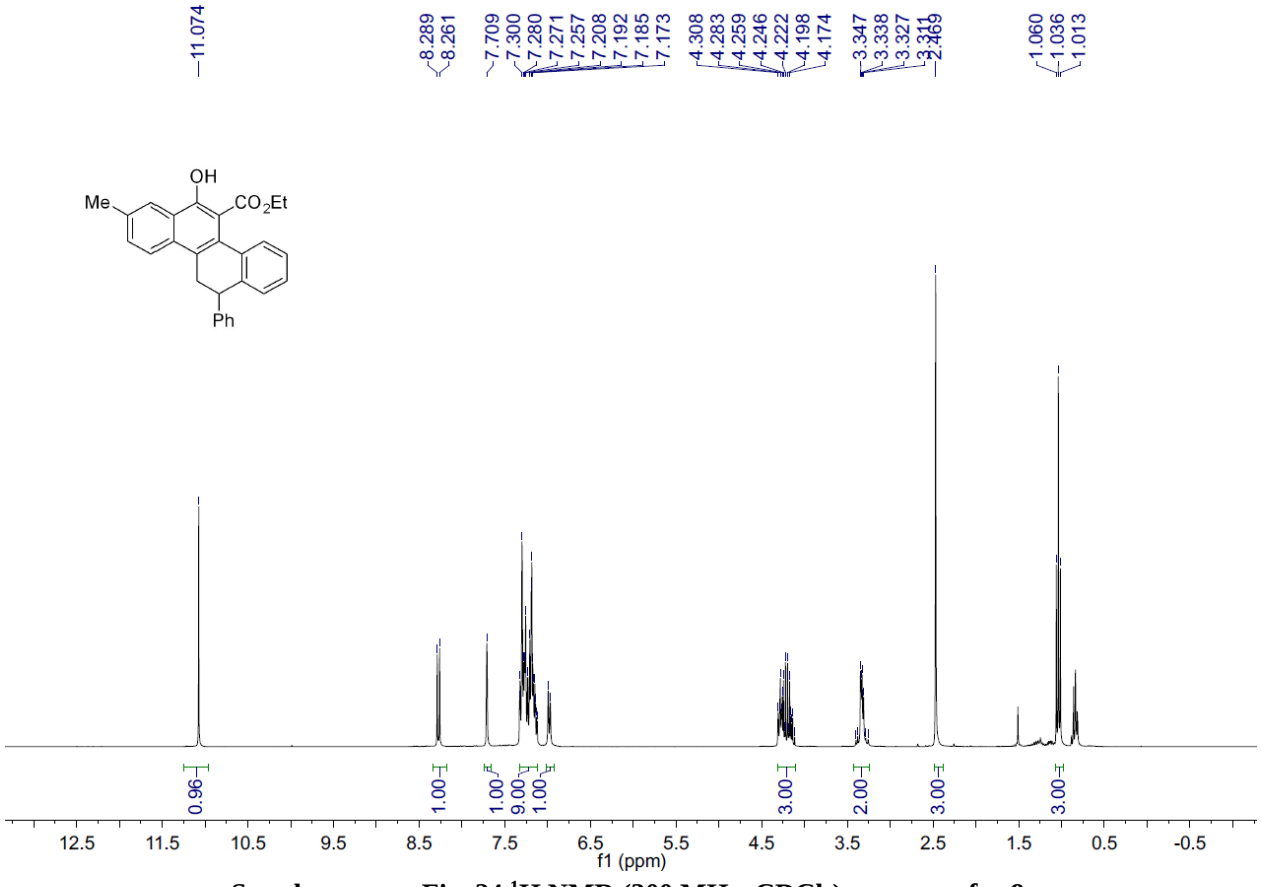
Supplementary Fig. 21 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 7.



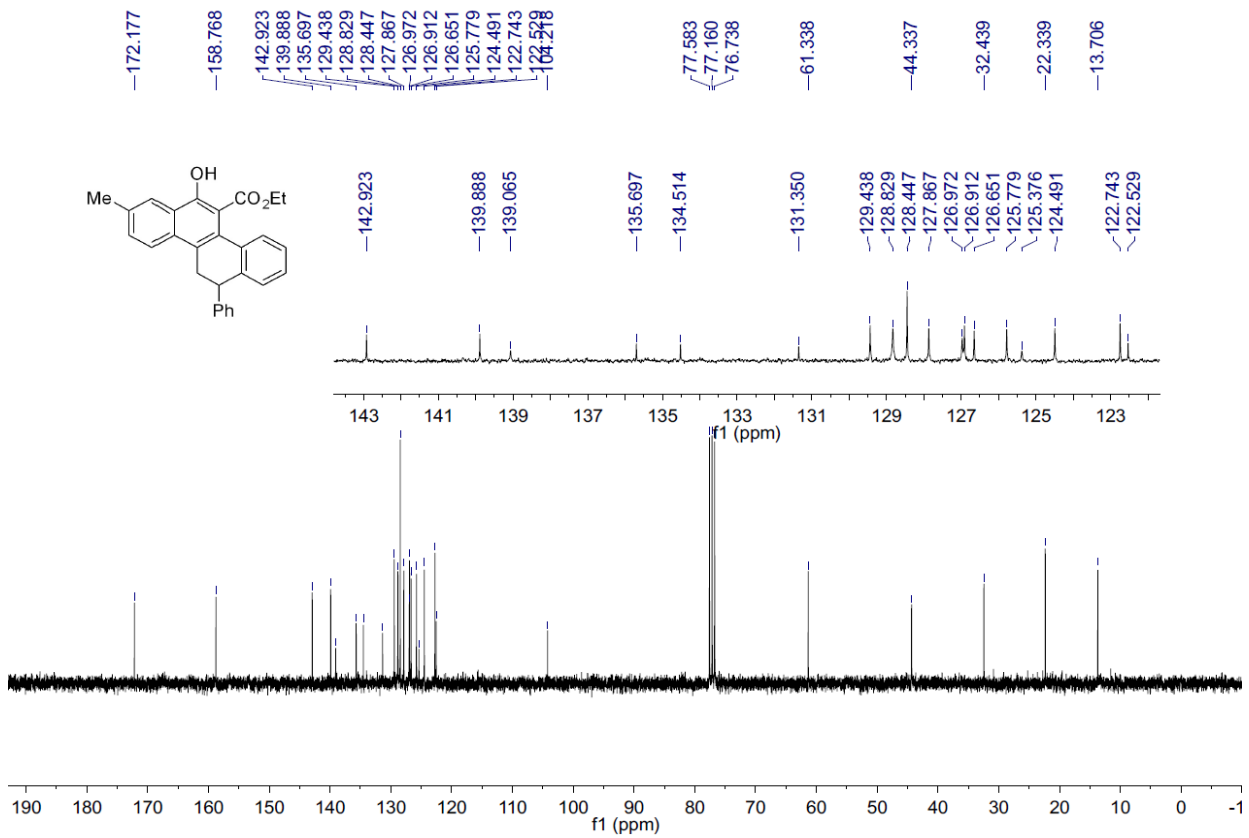
Supplementary Fig. 22 ^{13}C NMR (75 MHz, $CDCl_3$) spectrum for 7.



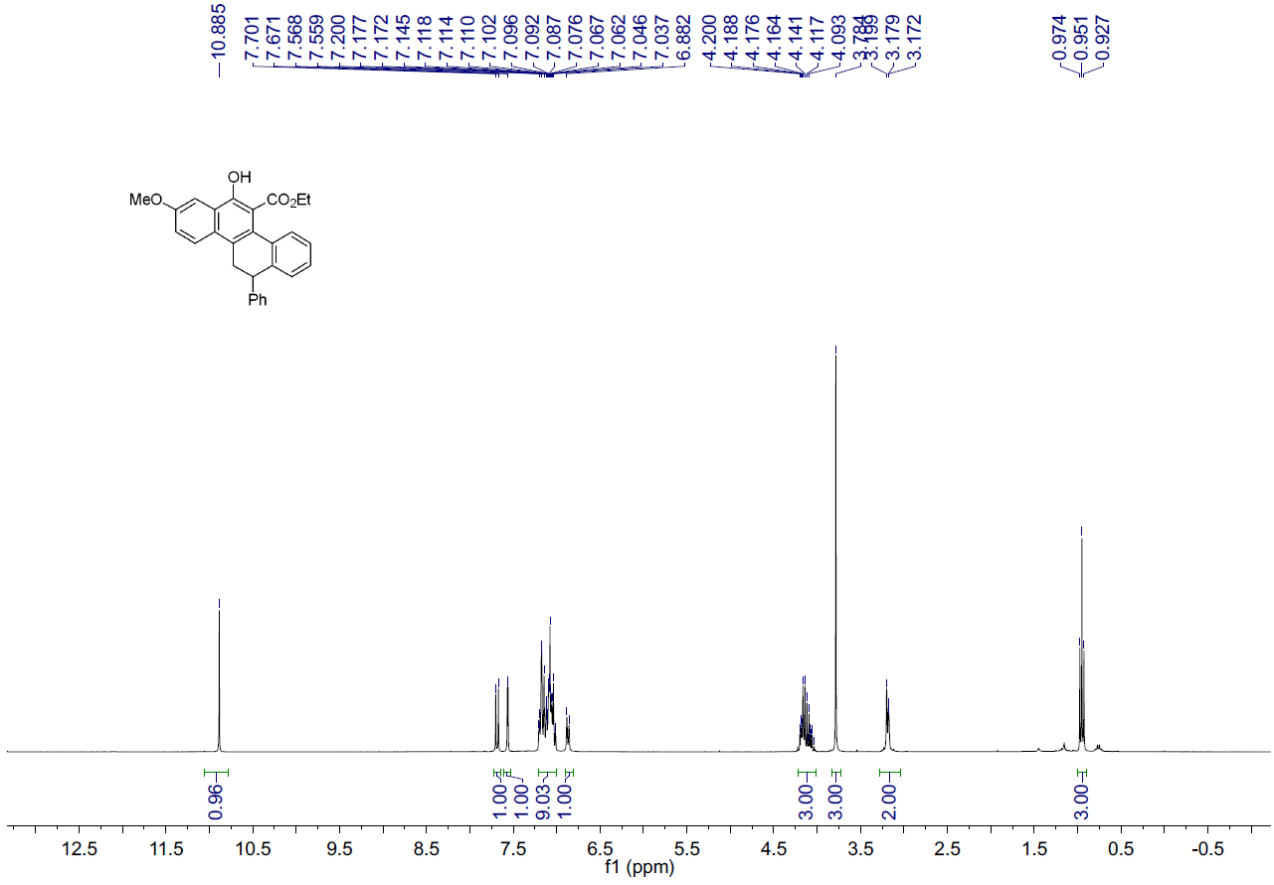
Supplementary Fig. 23 ^{19}F NMR (283 MHz, $CDCl_3$) spectrum for 7.



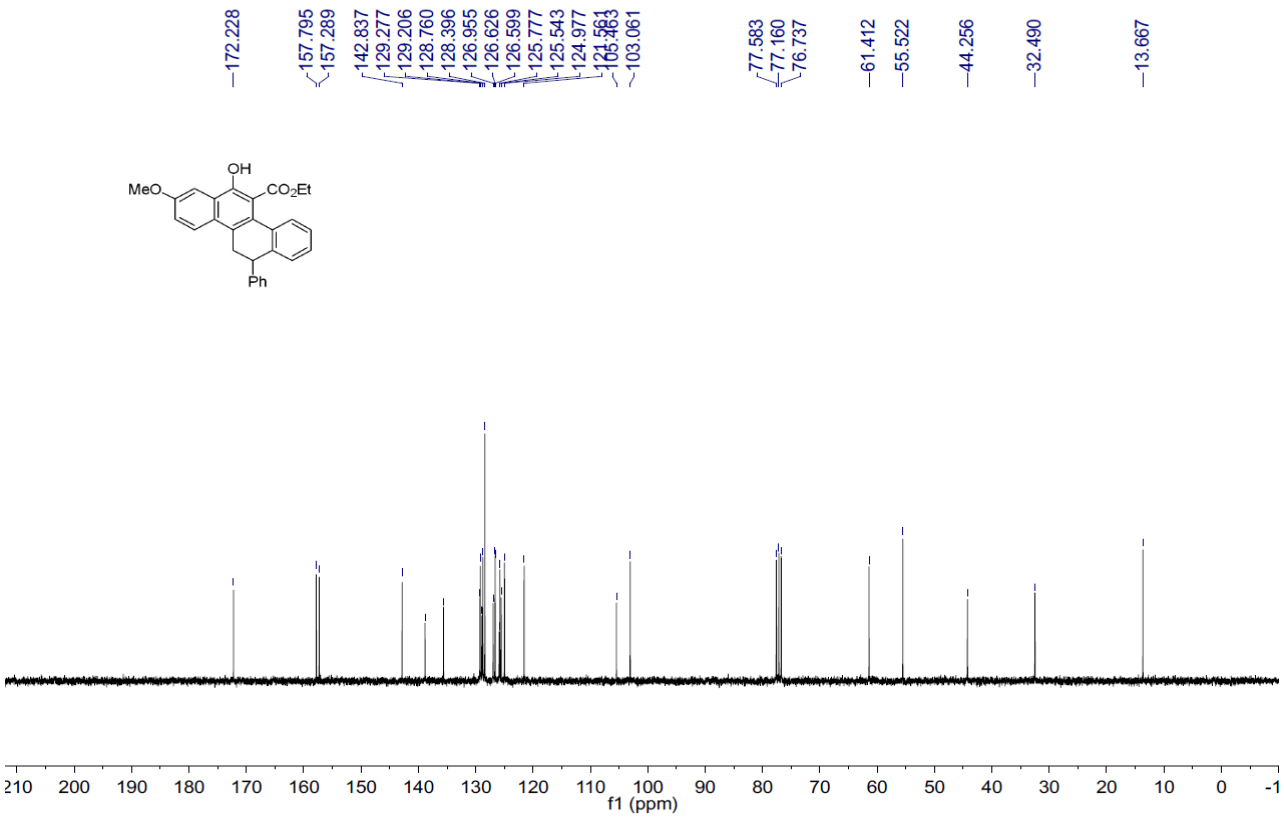
Supplementary Fig. 24 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum for 8.



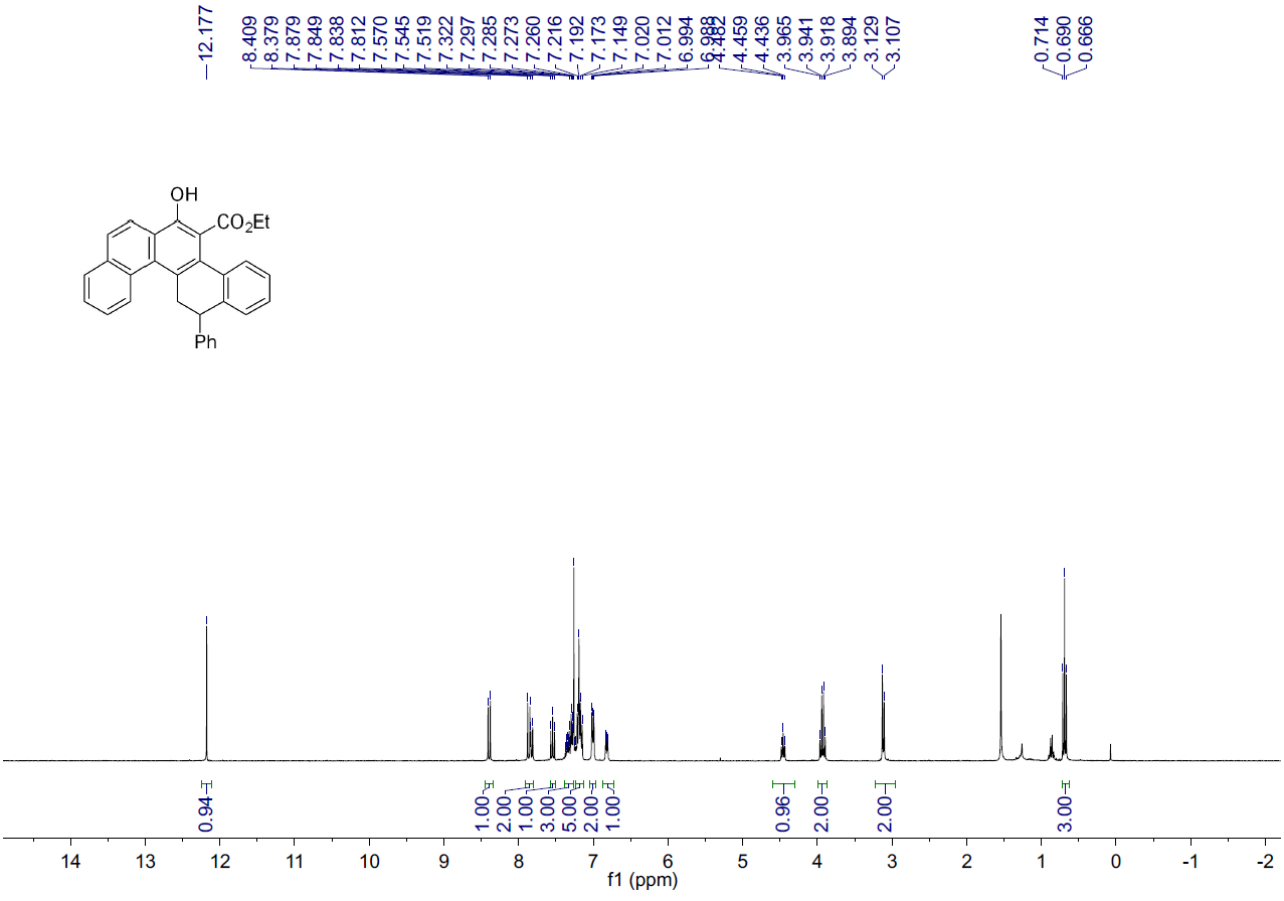
Supplementary Fig. 25 ^{13}C NMR (75 MHz, $CDCl_3$) spectrum for 8.



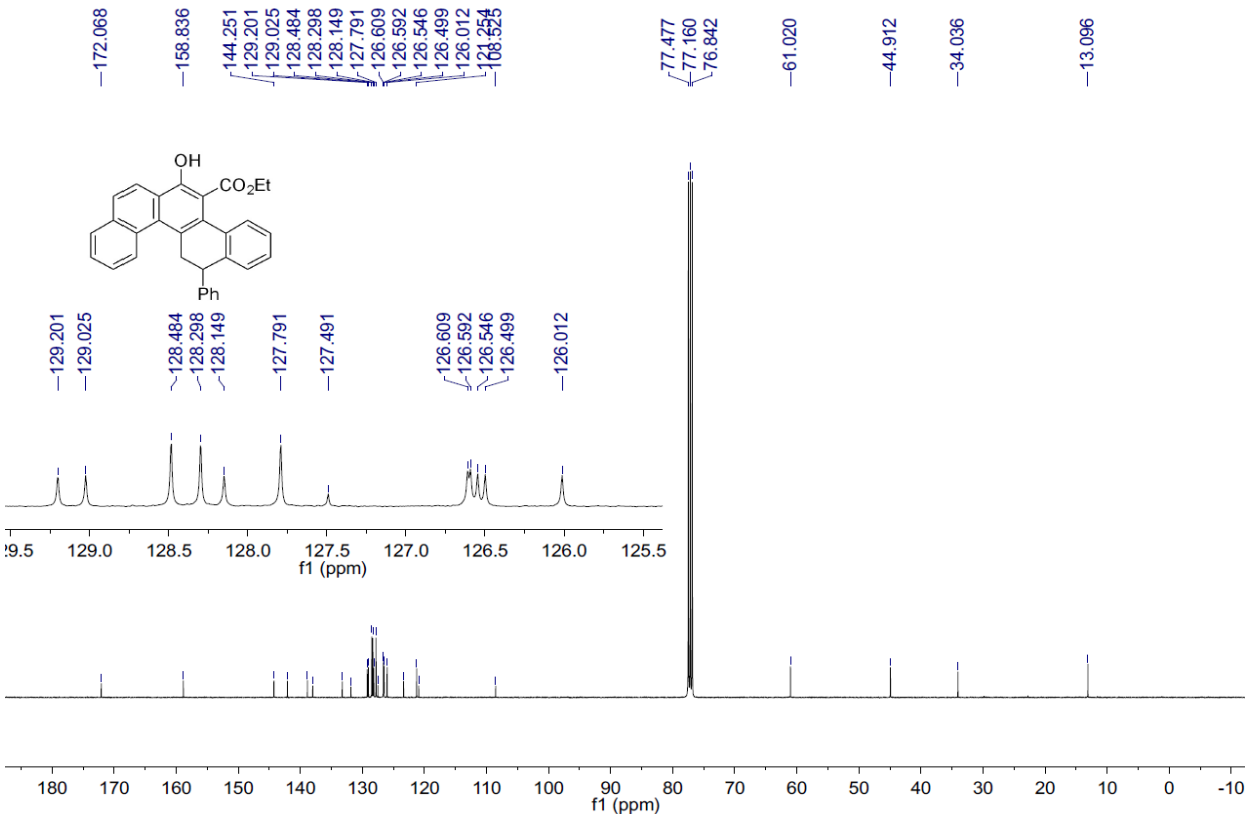
Supplementary Fig. 26 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum for 9.



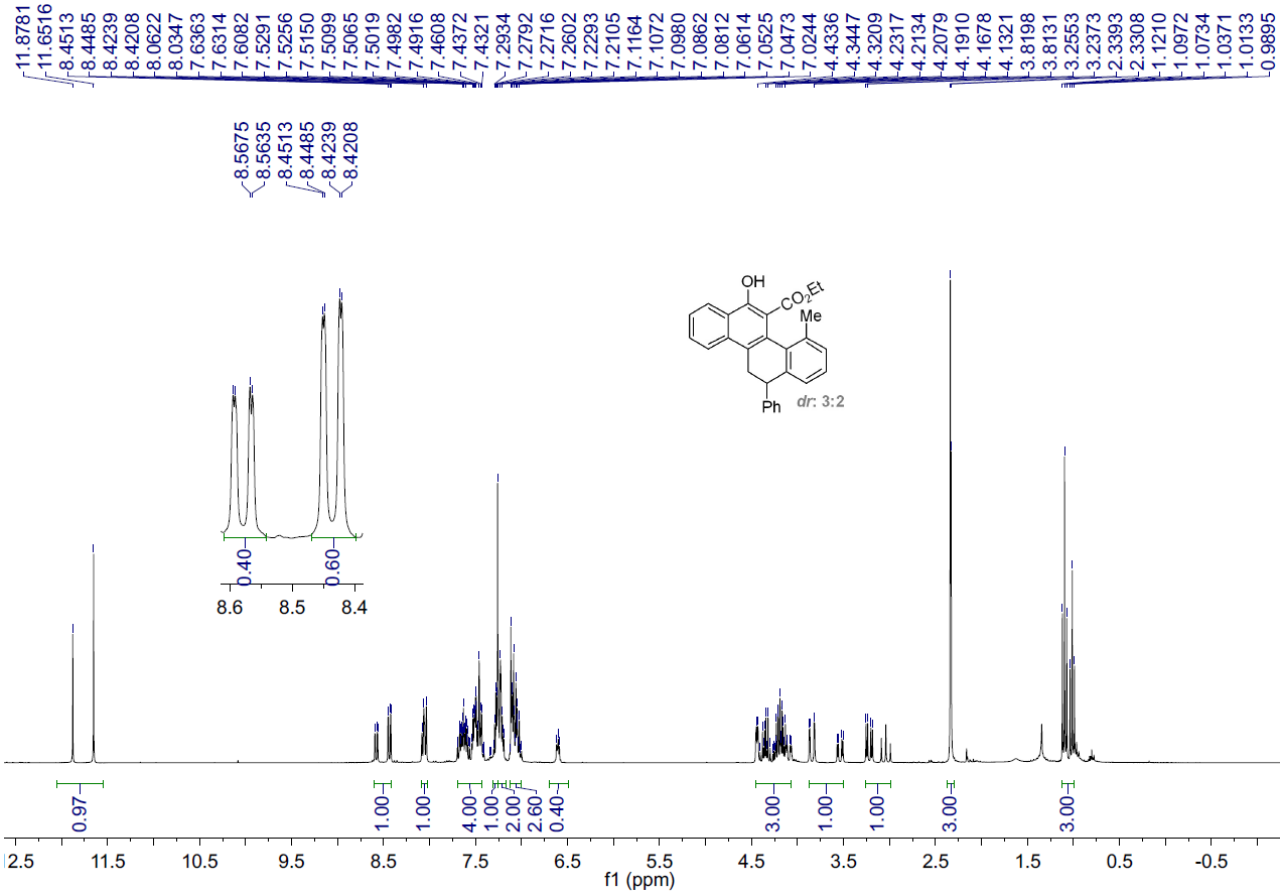
Supplementary Fig. 27 ^{13}C NMR (75 MHz, $CDCl_3$) spectrum for 9.



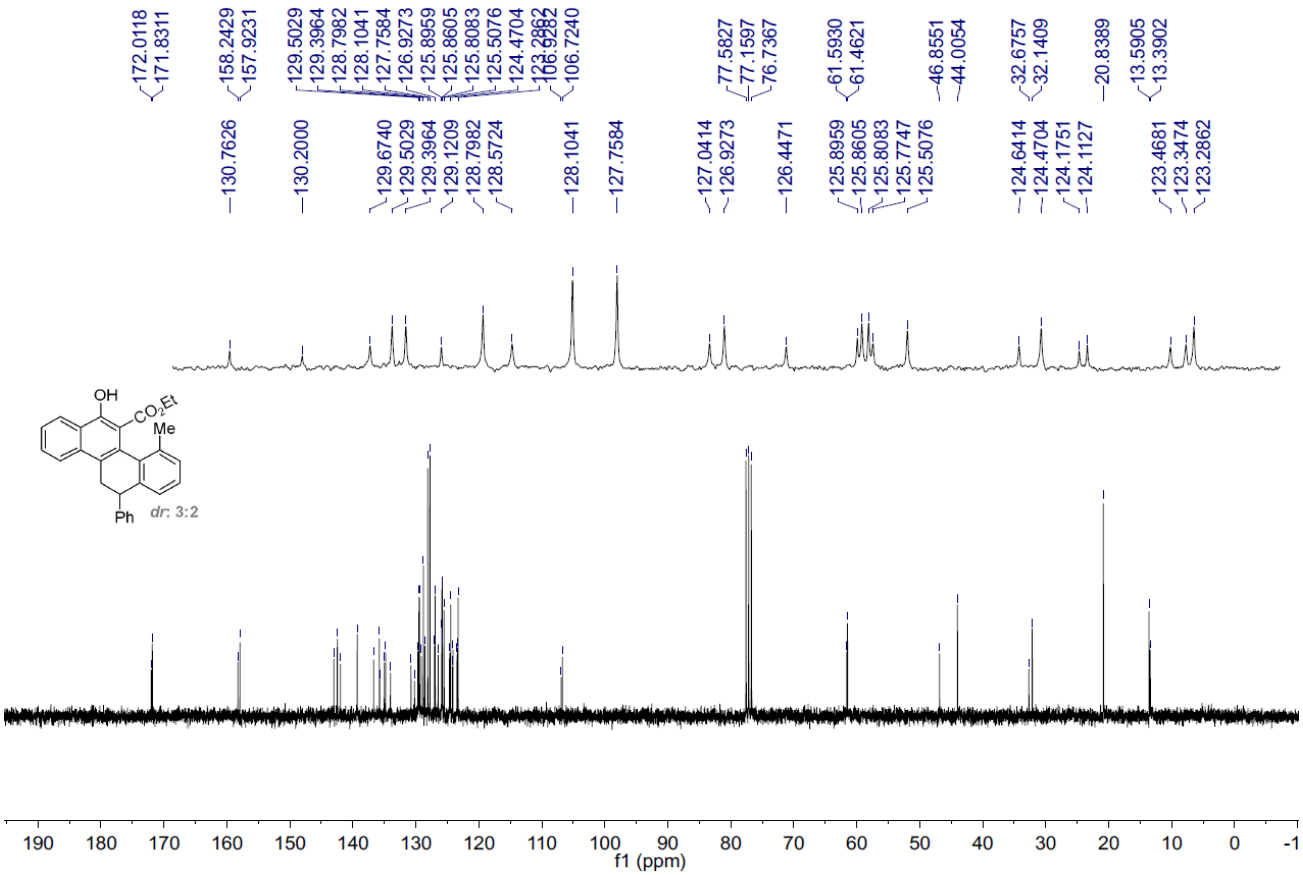
Supplementary Fig. 28 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 10.



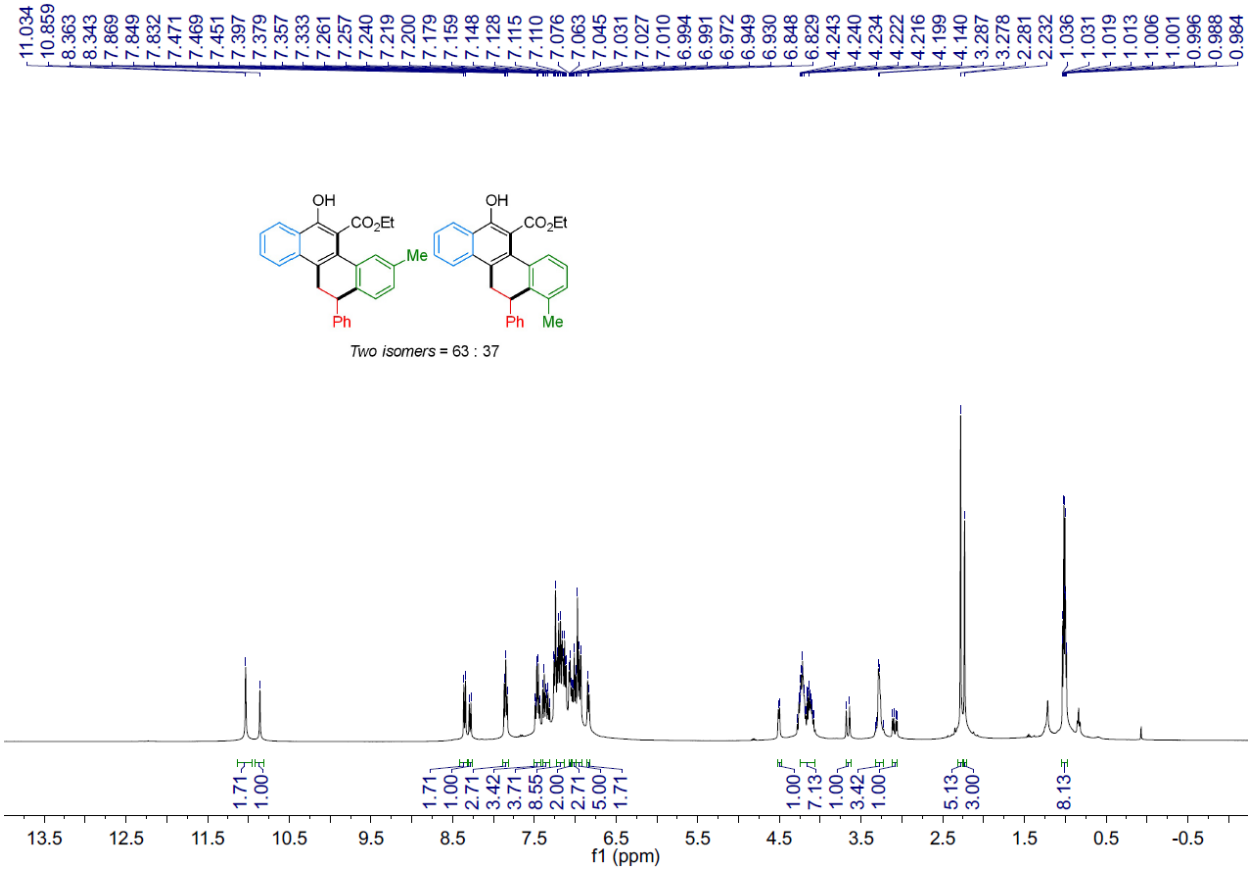
Supplementary Fig. 29 ^{13}C NMR (125 MHz, $CDCl_3$) spectrum for 10.



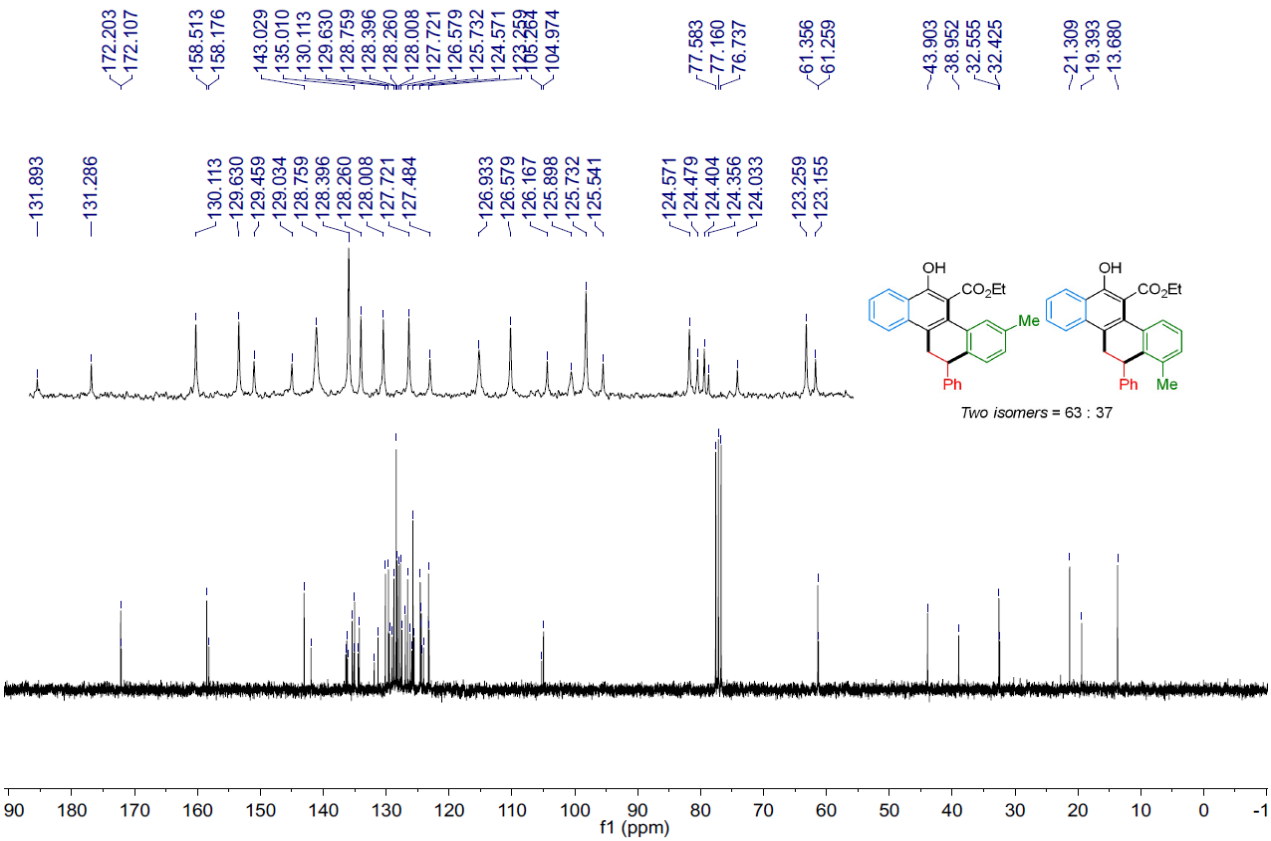
Supplementary Fig. 30 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum for 11.



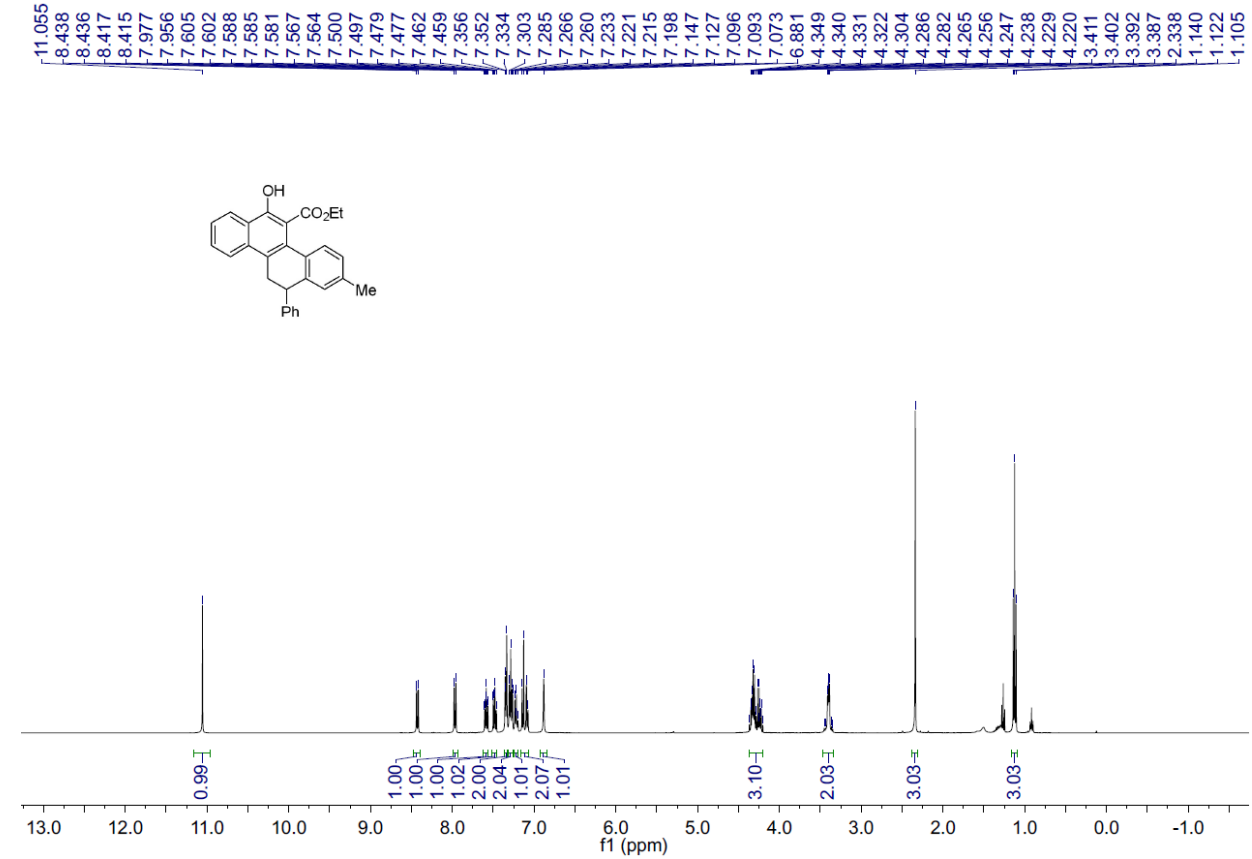
Supplementary Fig. 31 ^{13}C NMR (75 MHz, $CDCl_3$) spectrum for 11.



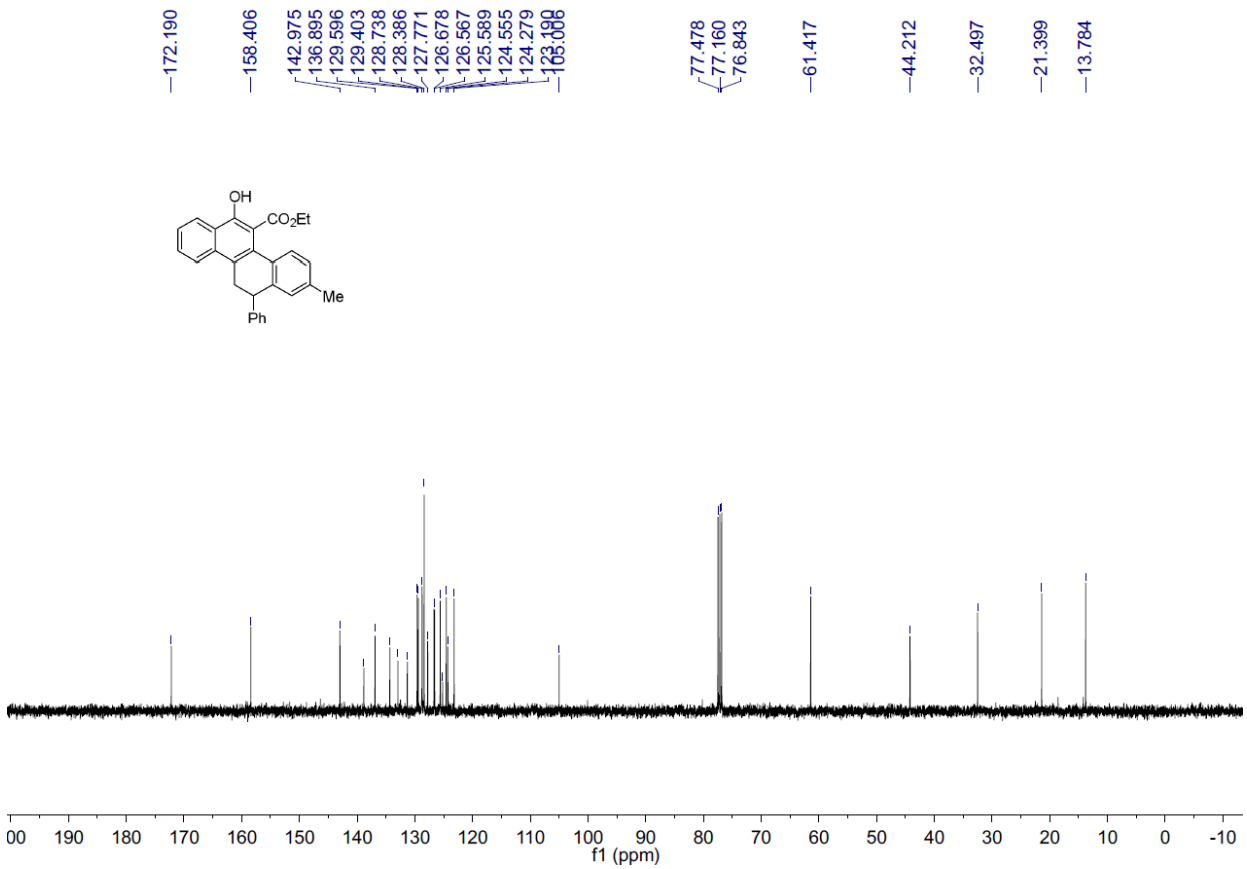
Supplementary Fig. 32 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 12.



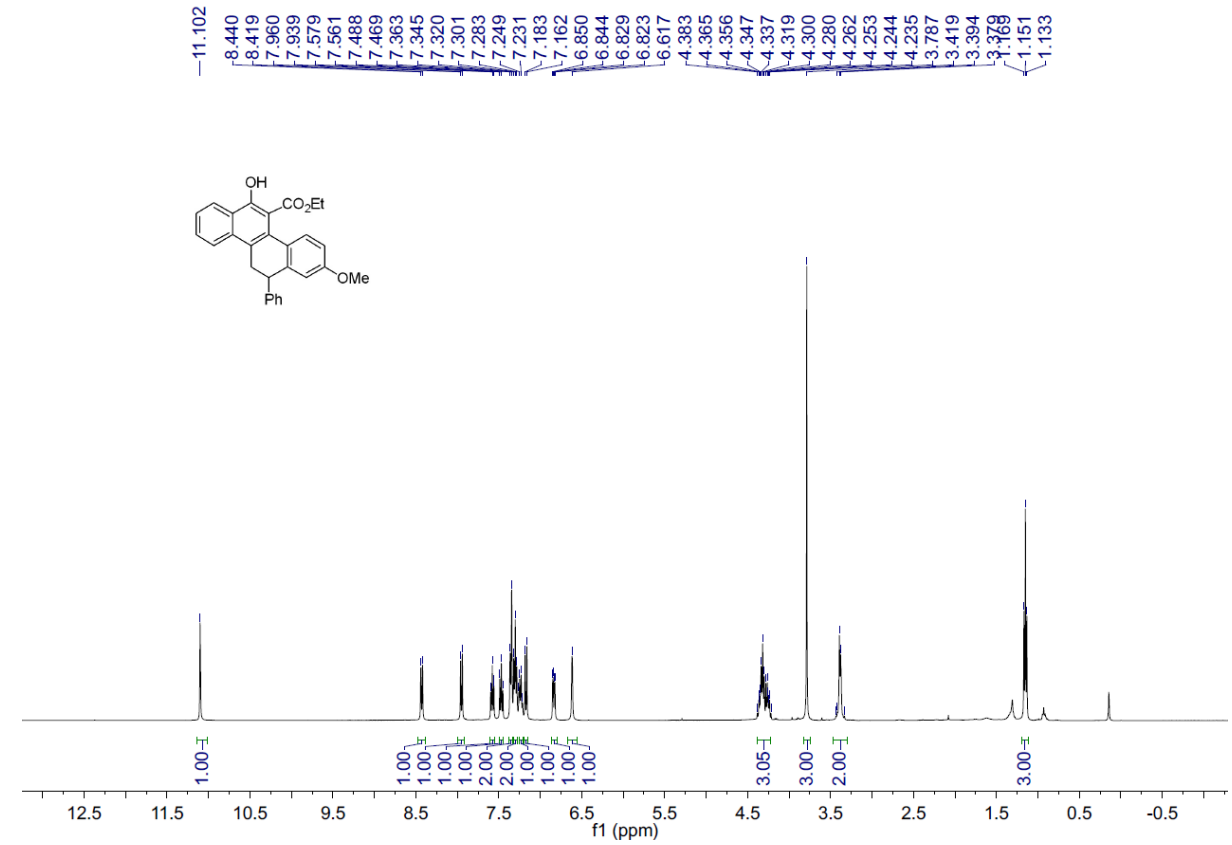
Supplementary Fig. 33 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 12.



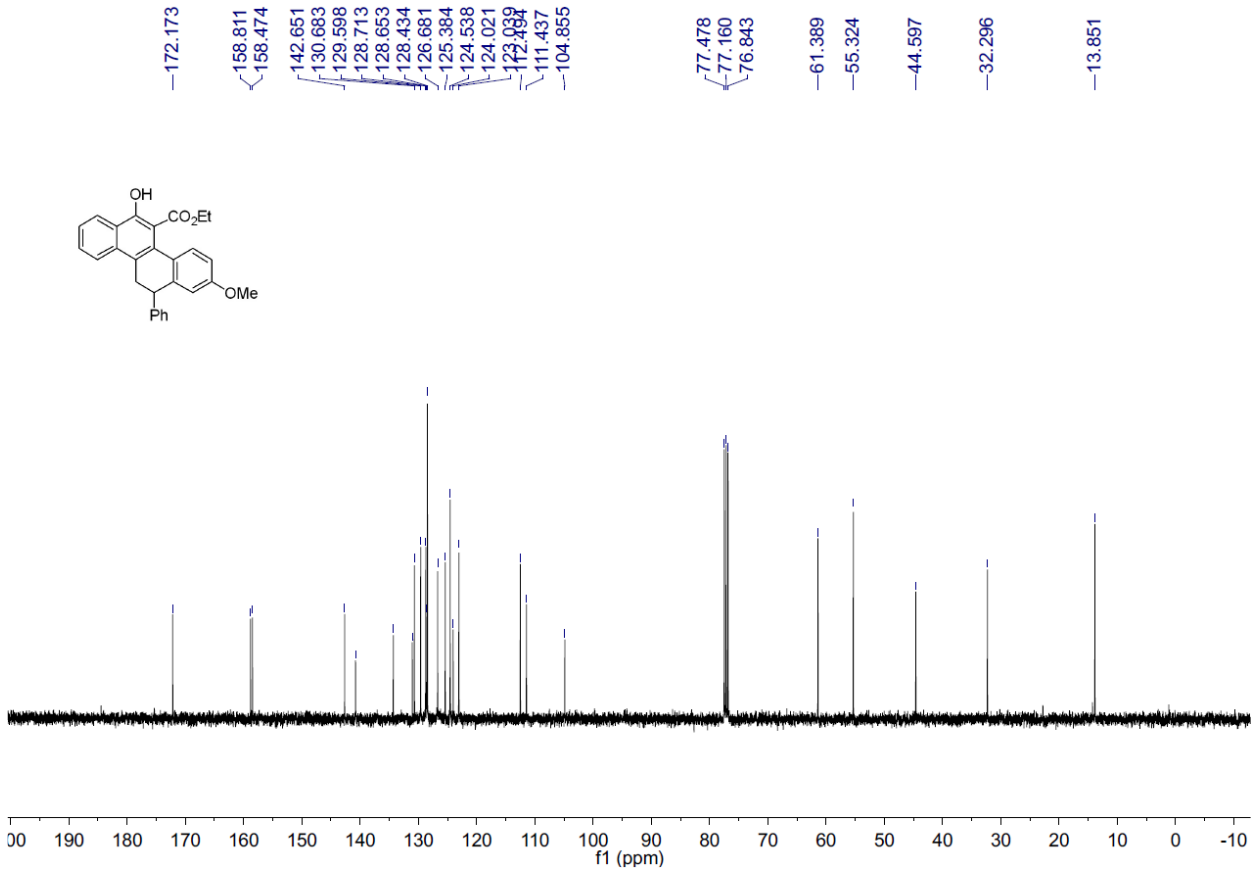
Supplementary Fig. 34 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 13.



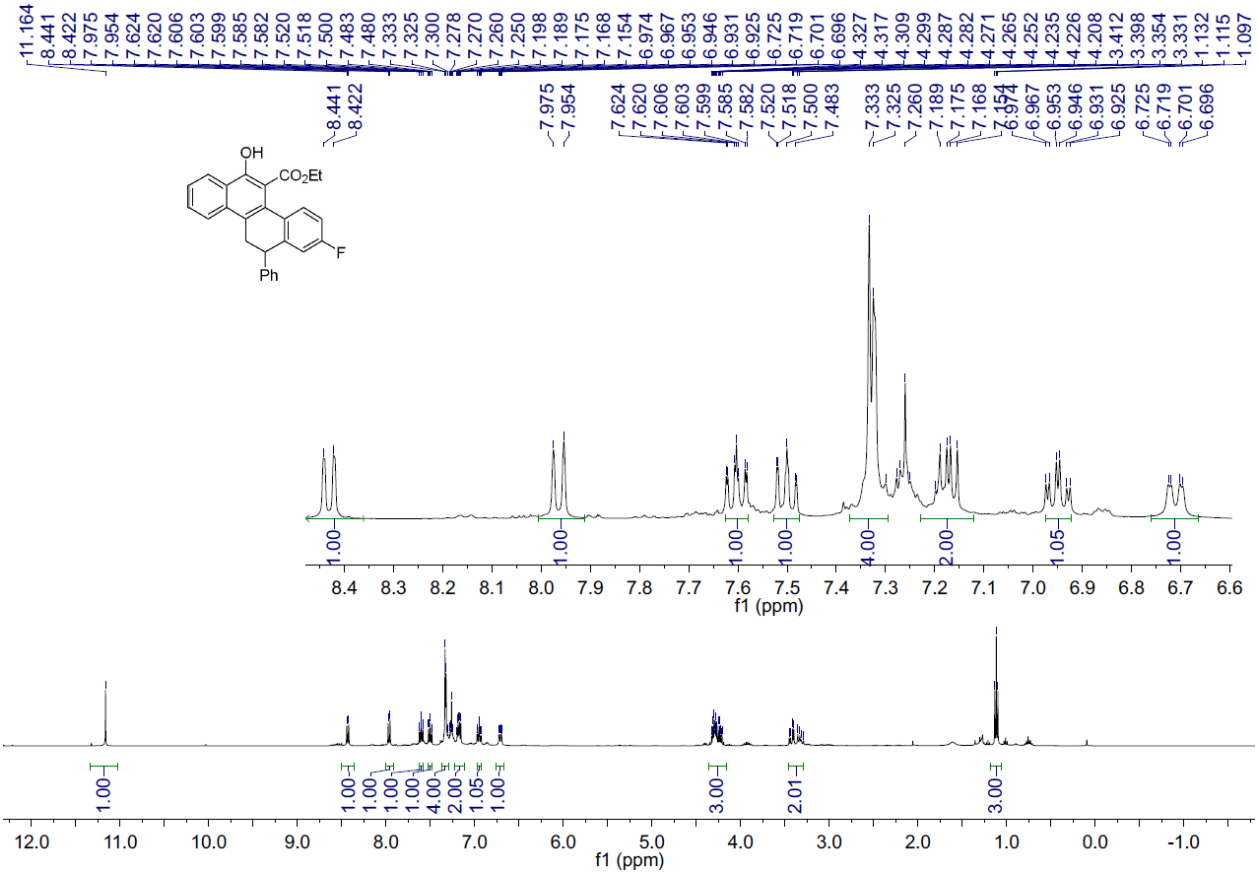
Supplementary Fig. 35 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 13.



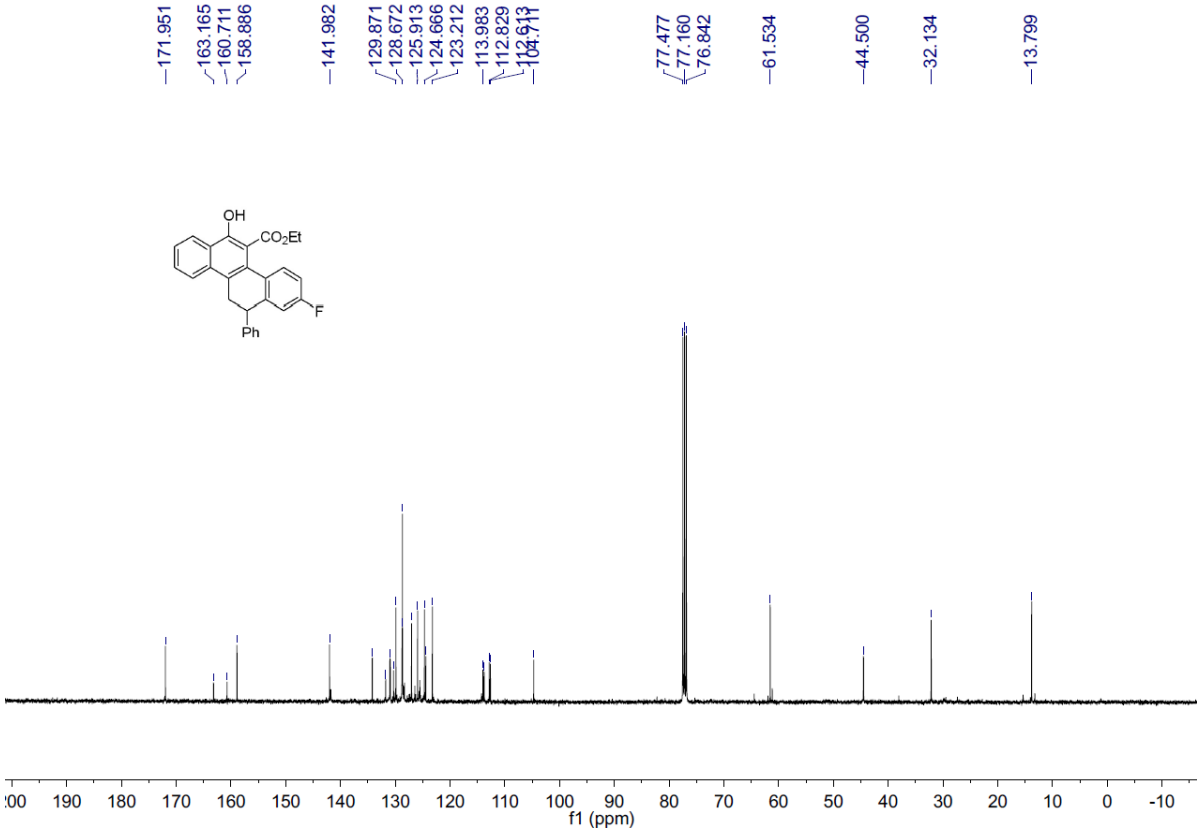
Supplementary Fig. 36 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 14.



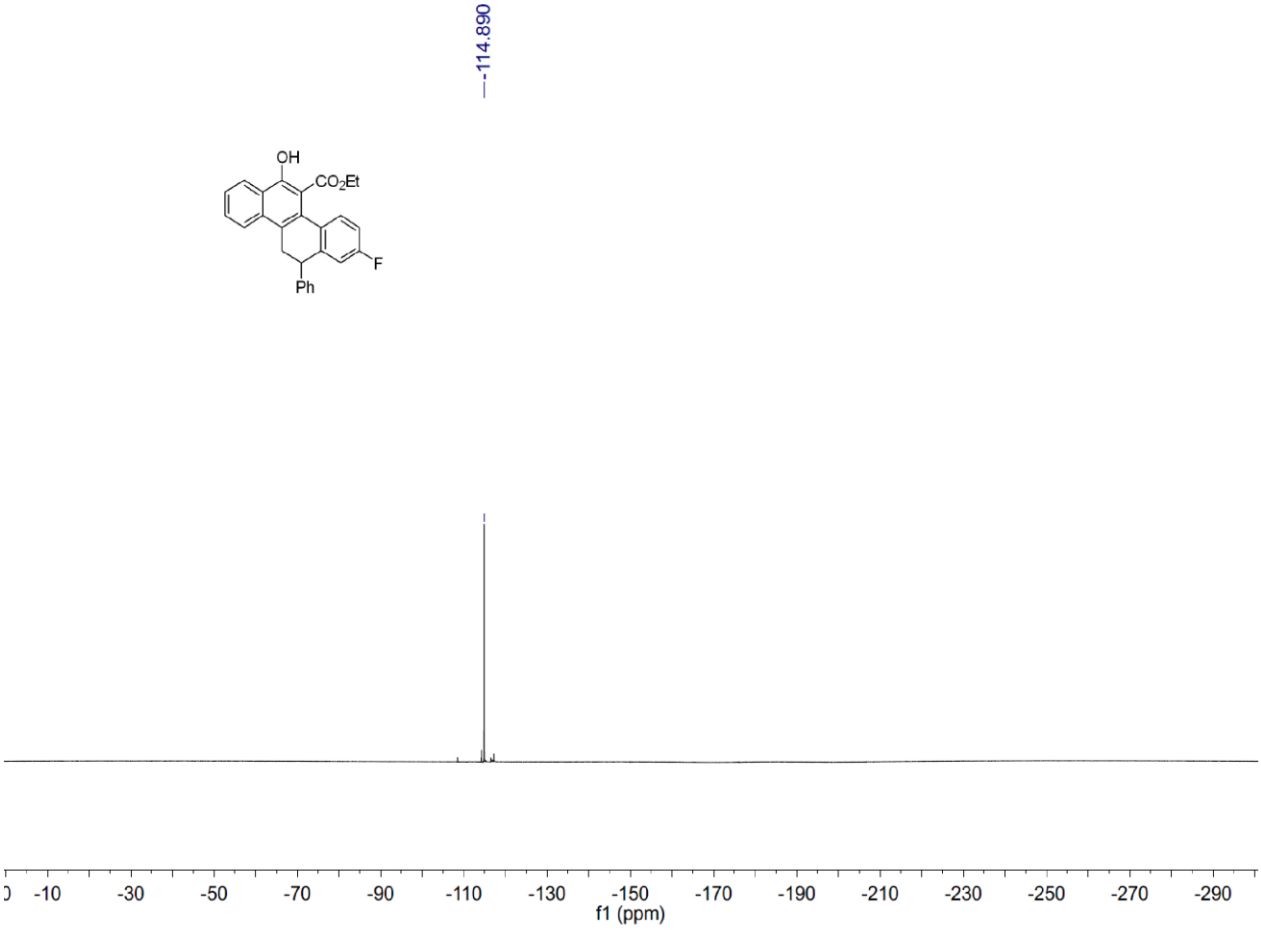
Supplementary Fig. 37 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 14.



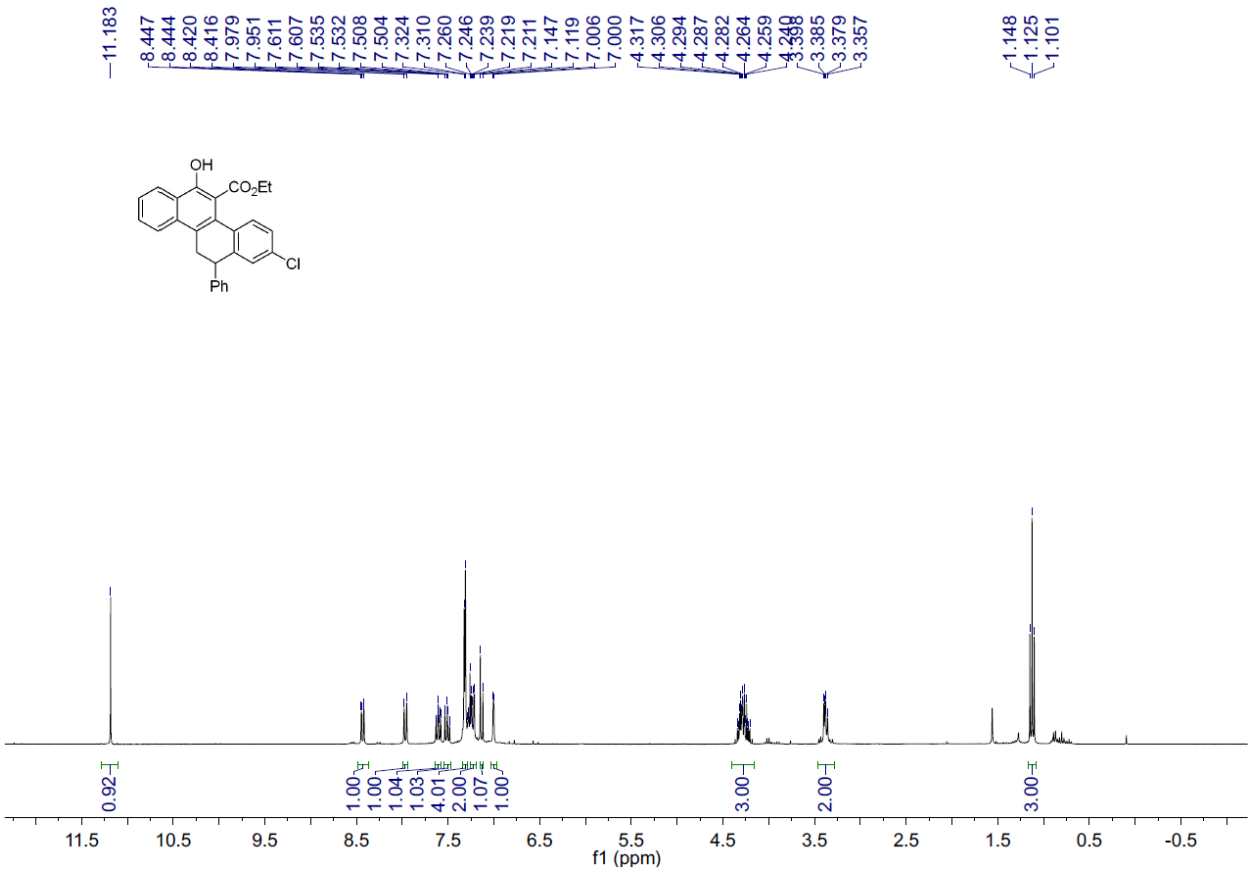
Supplementary Fig. 38 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 15.



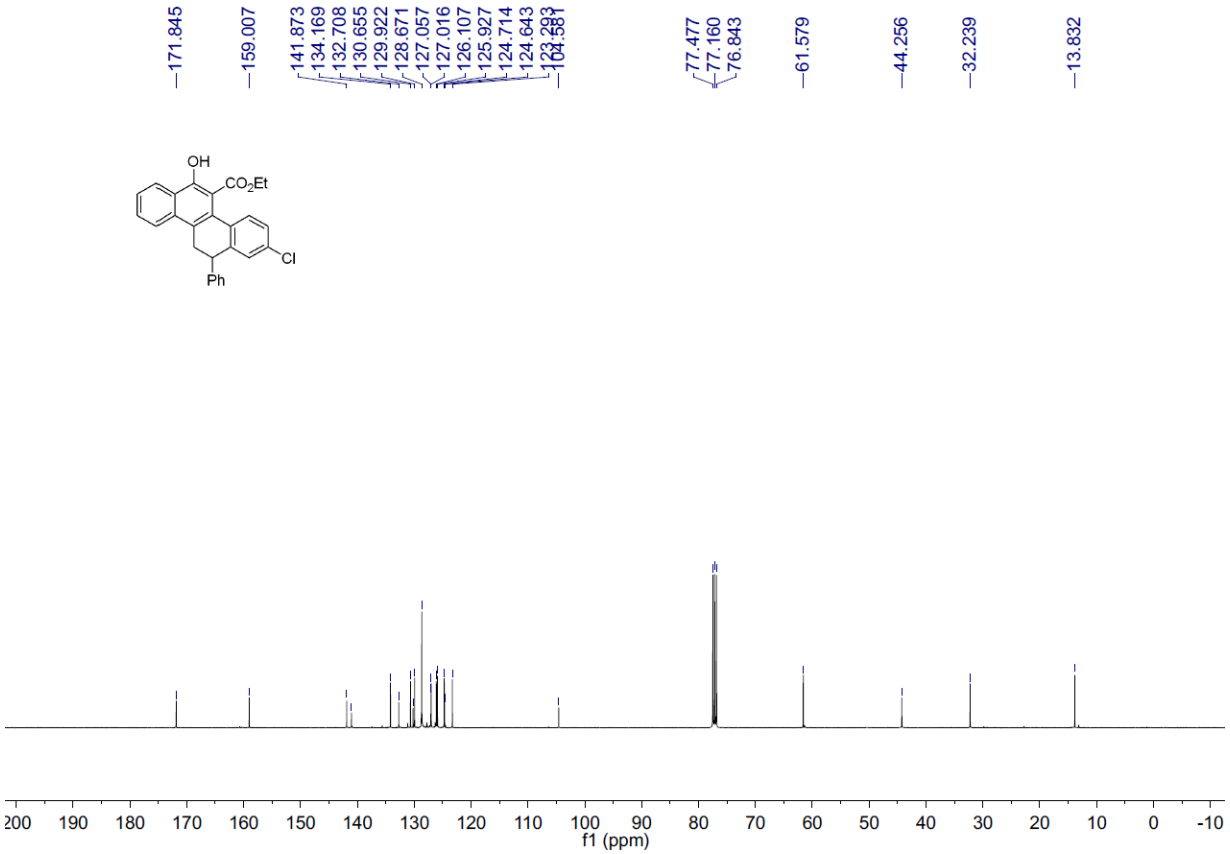
Supplementary Fig. 39 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 15.



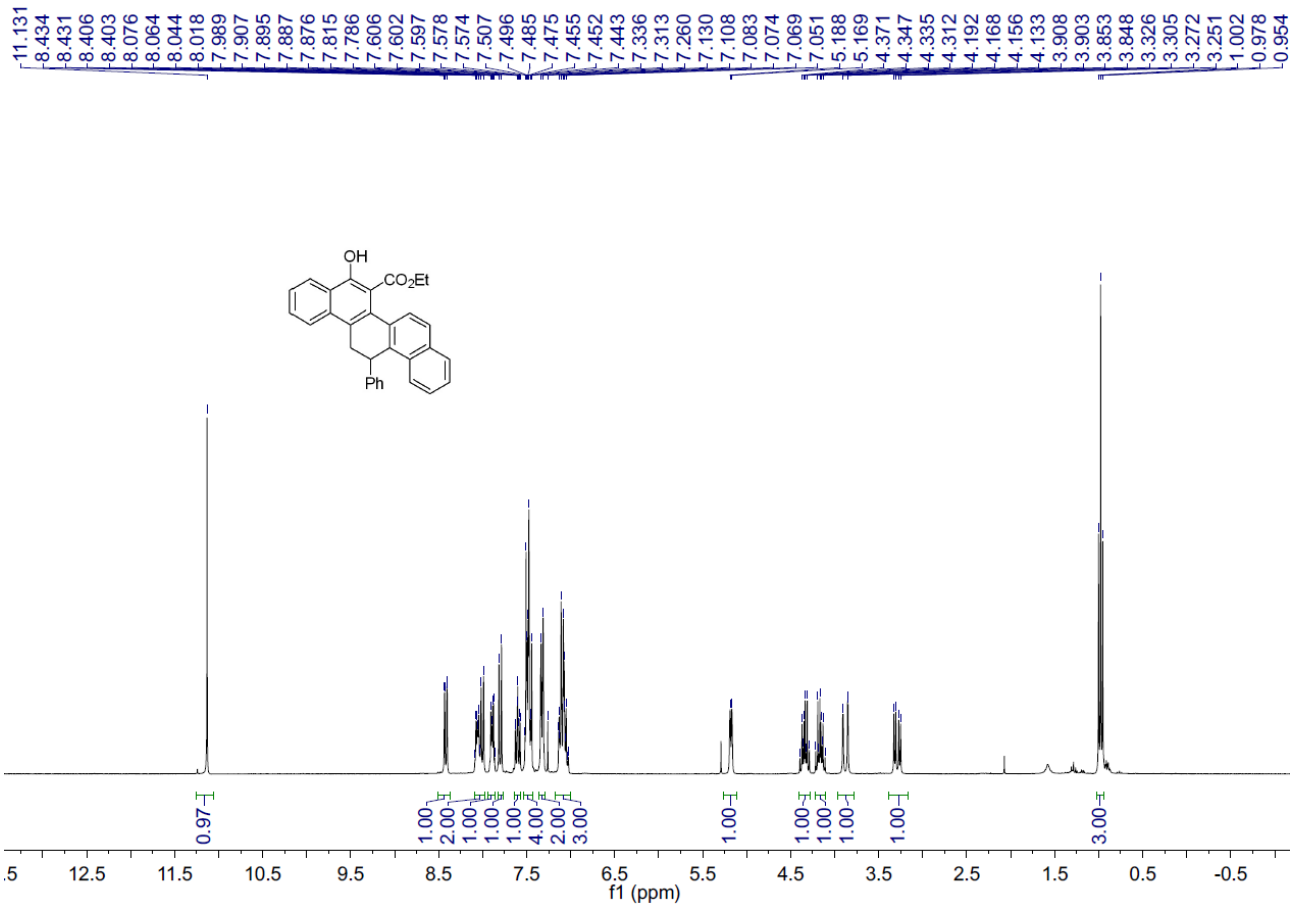
Supplementary Fig. 40 ^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 15.



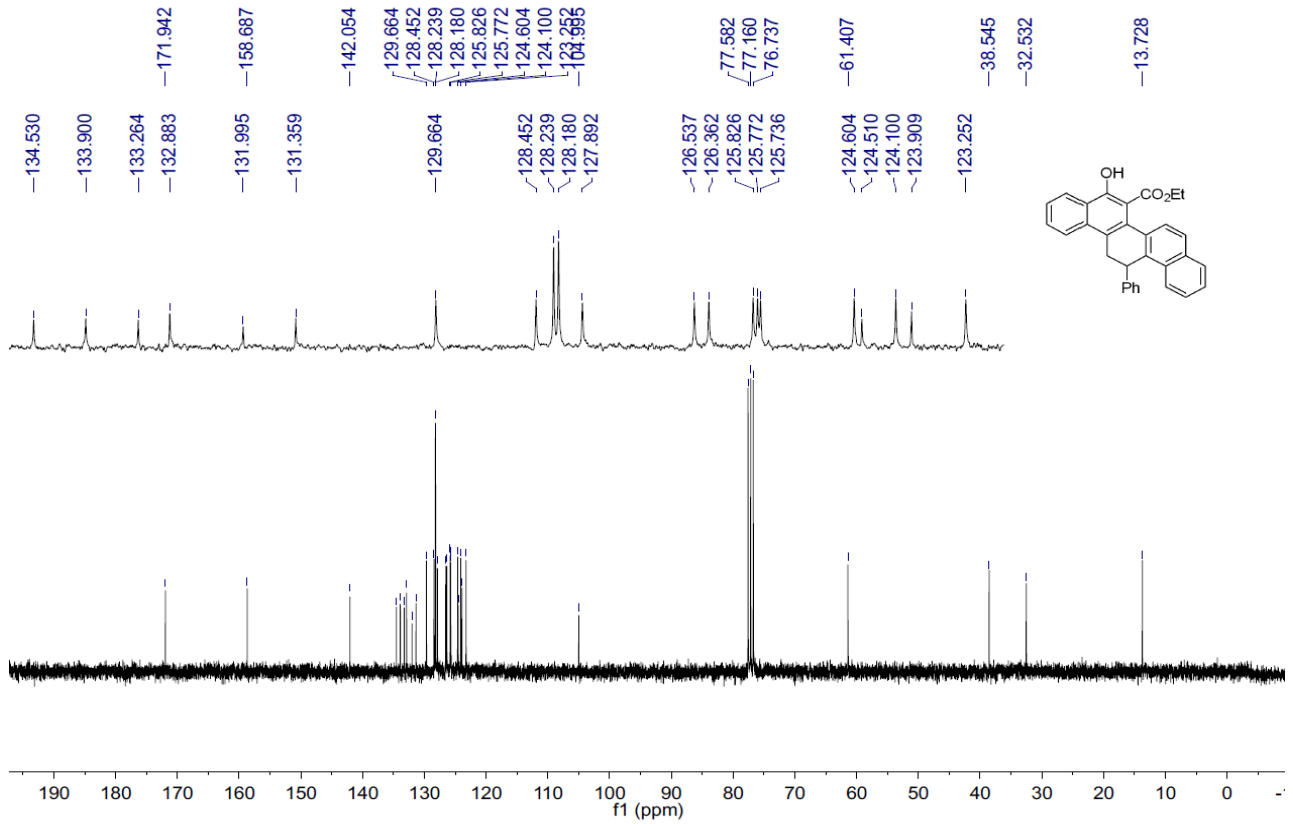
Supplementary Fig. 41 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum for 16.



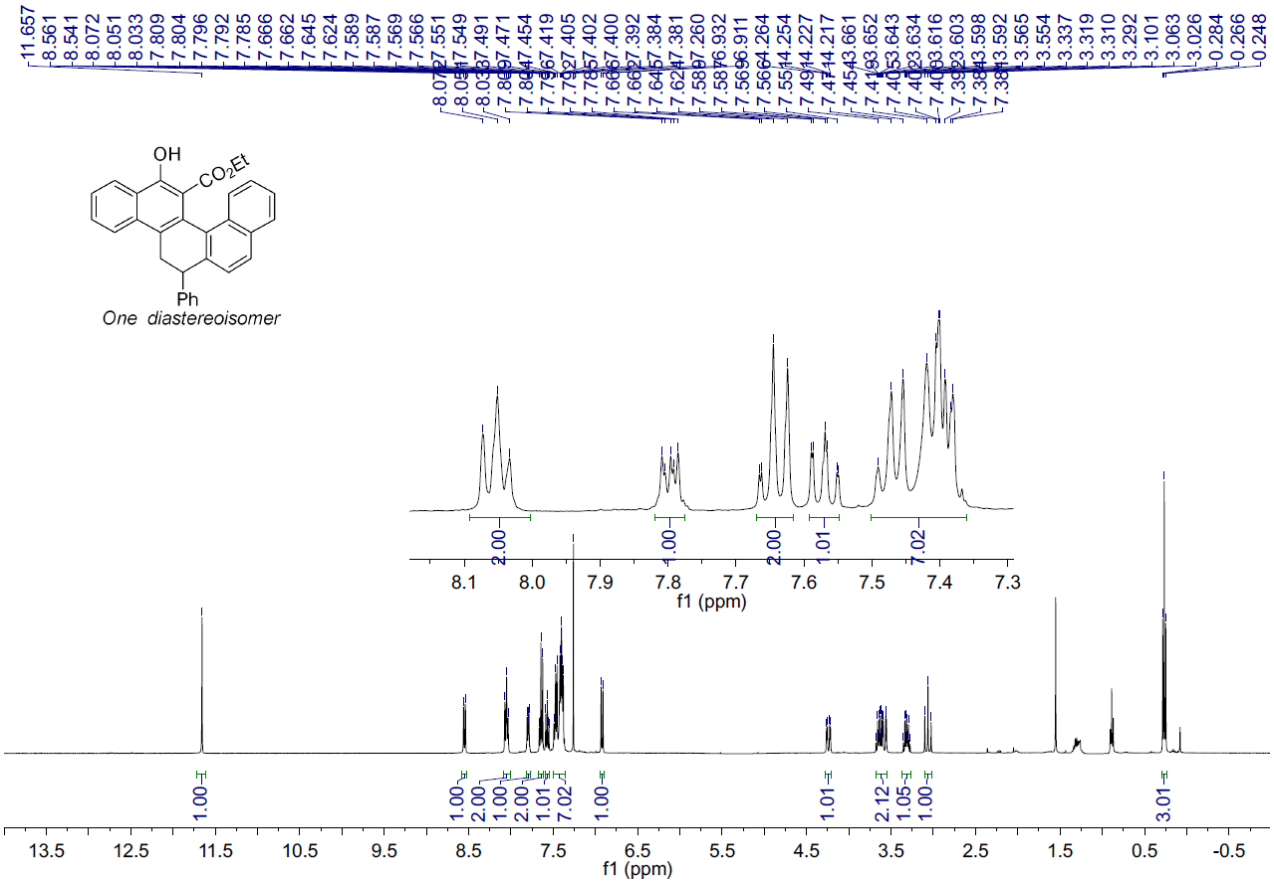
Supplementary Fig. 42 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 16.



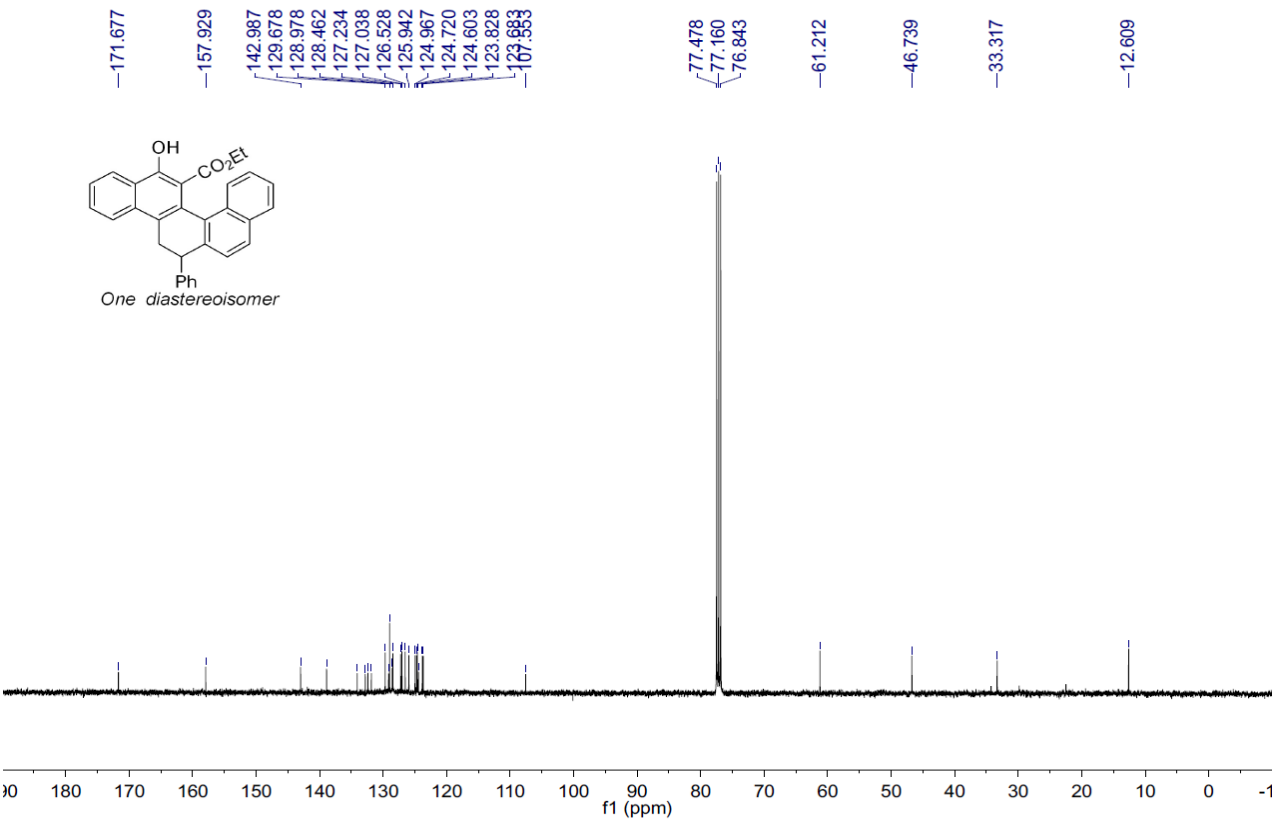
Supplementary Fig. 43 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 17.



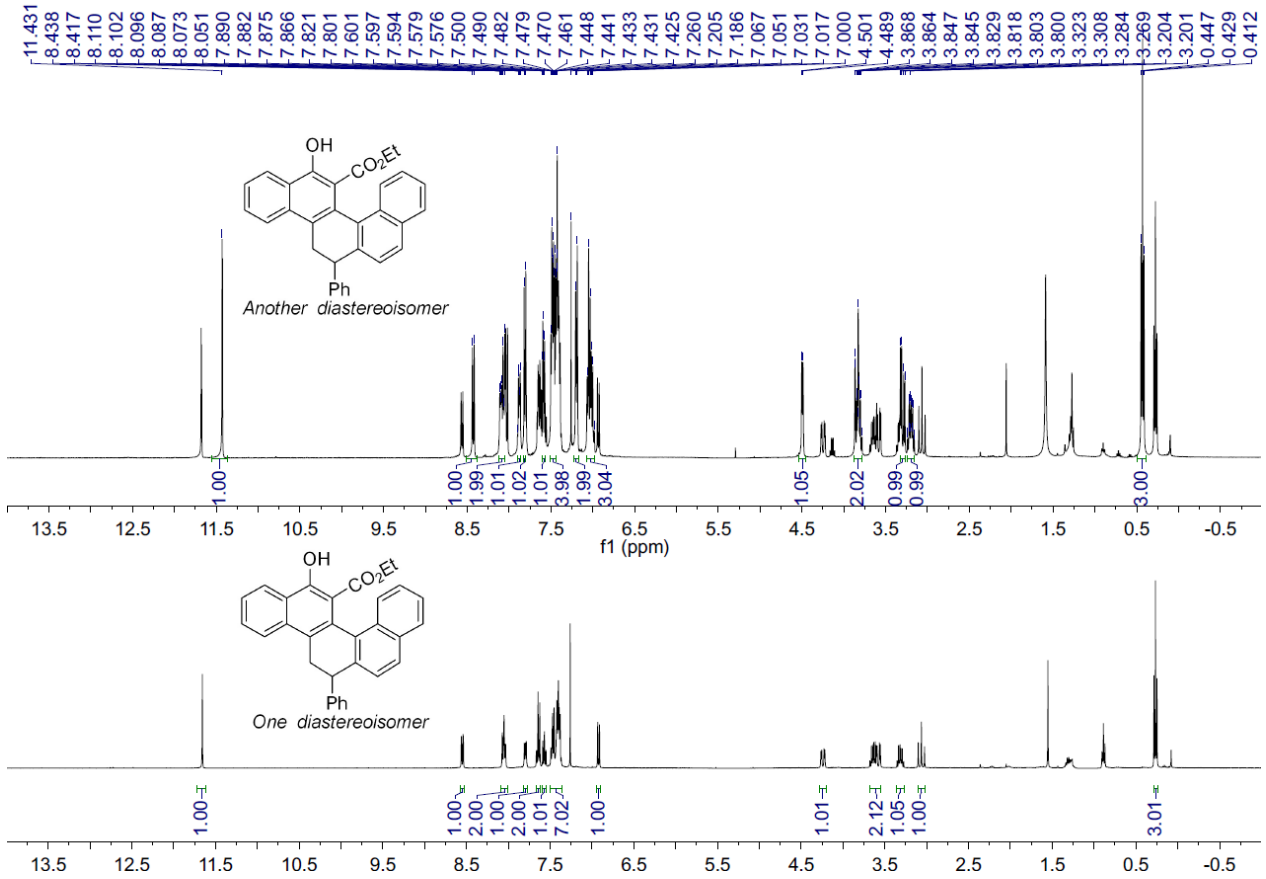
Supplementary Fig. 44 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 17.



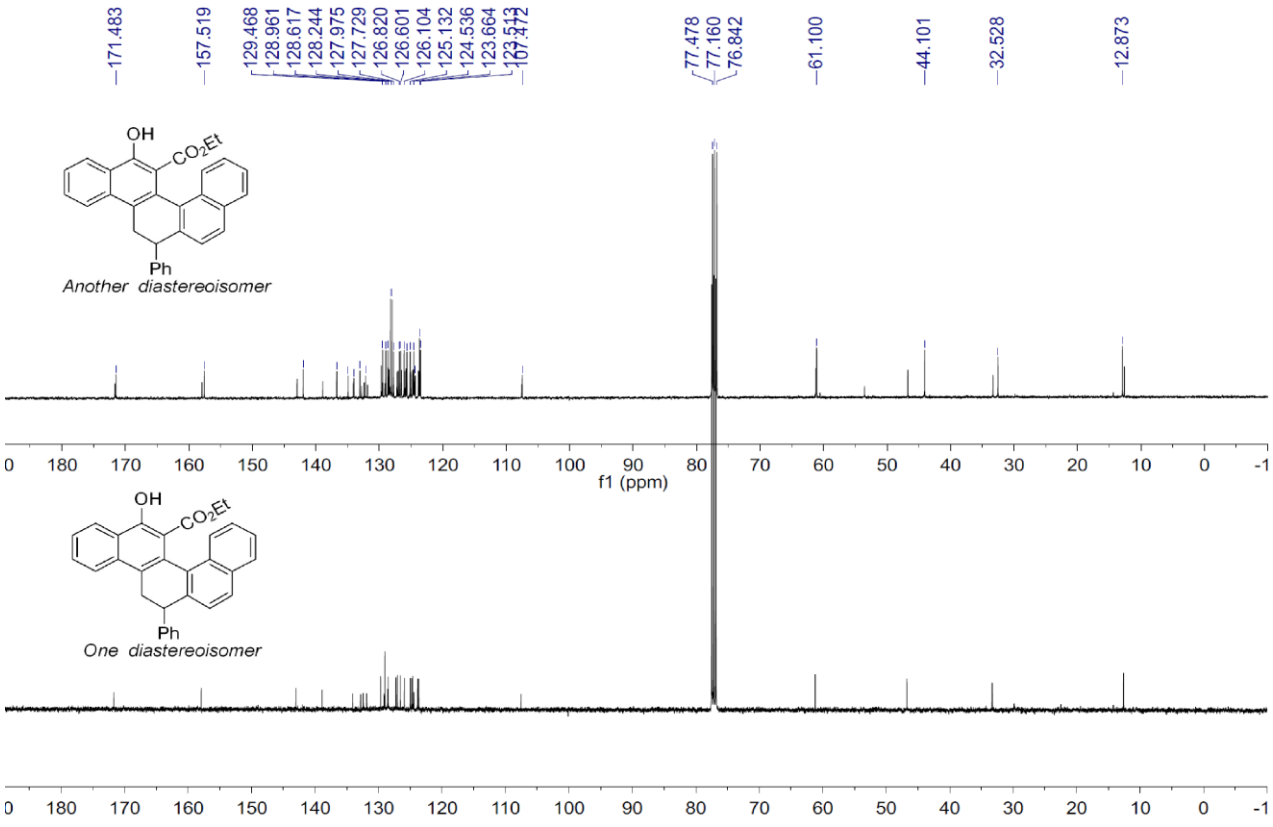
Supplementary Fig. 45 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 18.



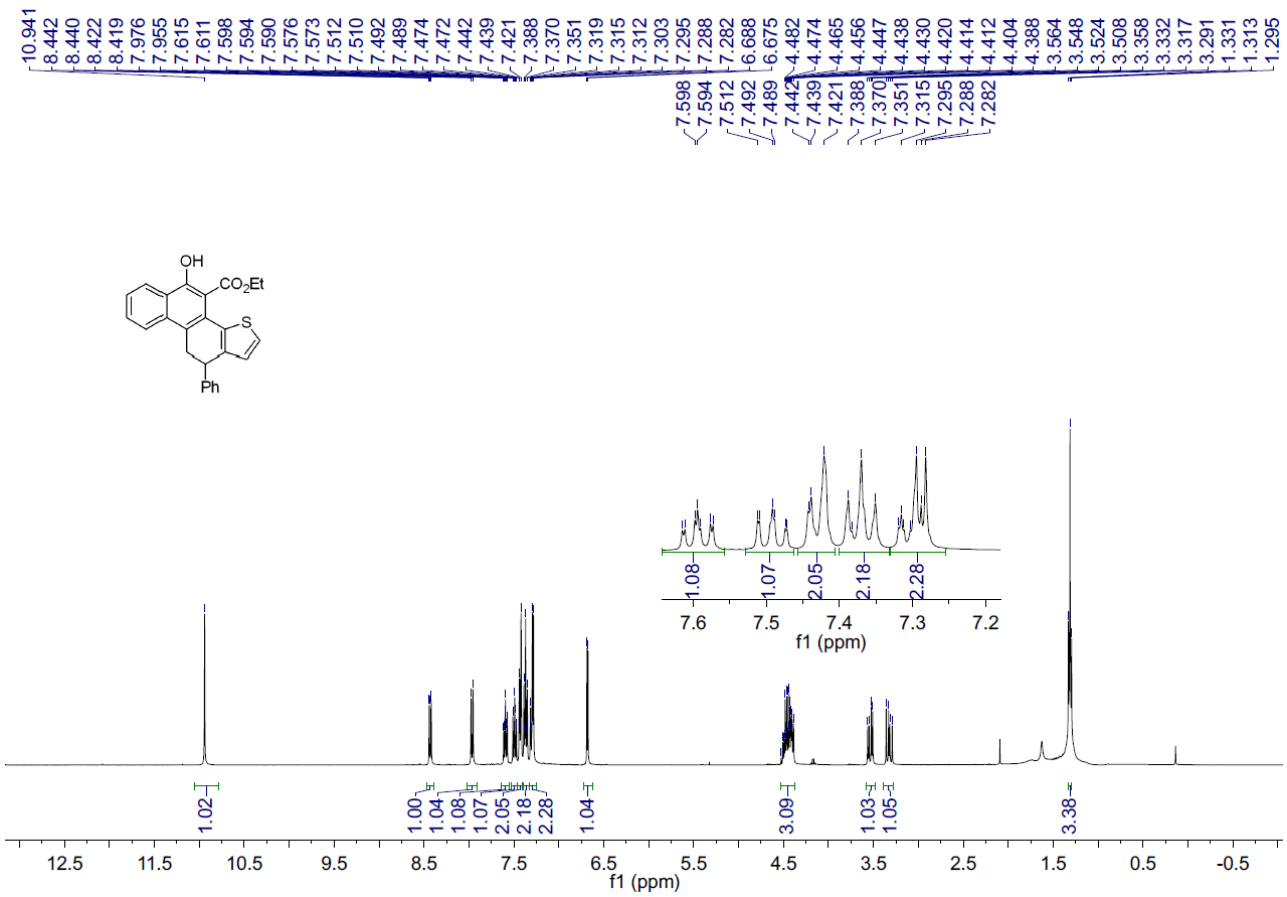
Supplementary Fig. 46 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 18.



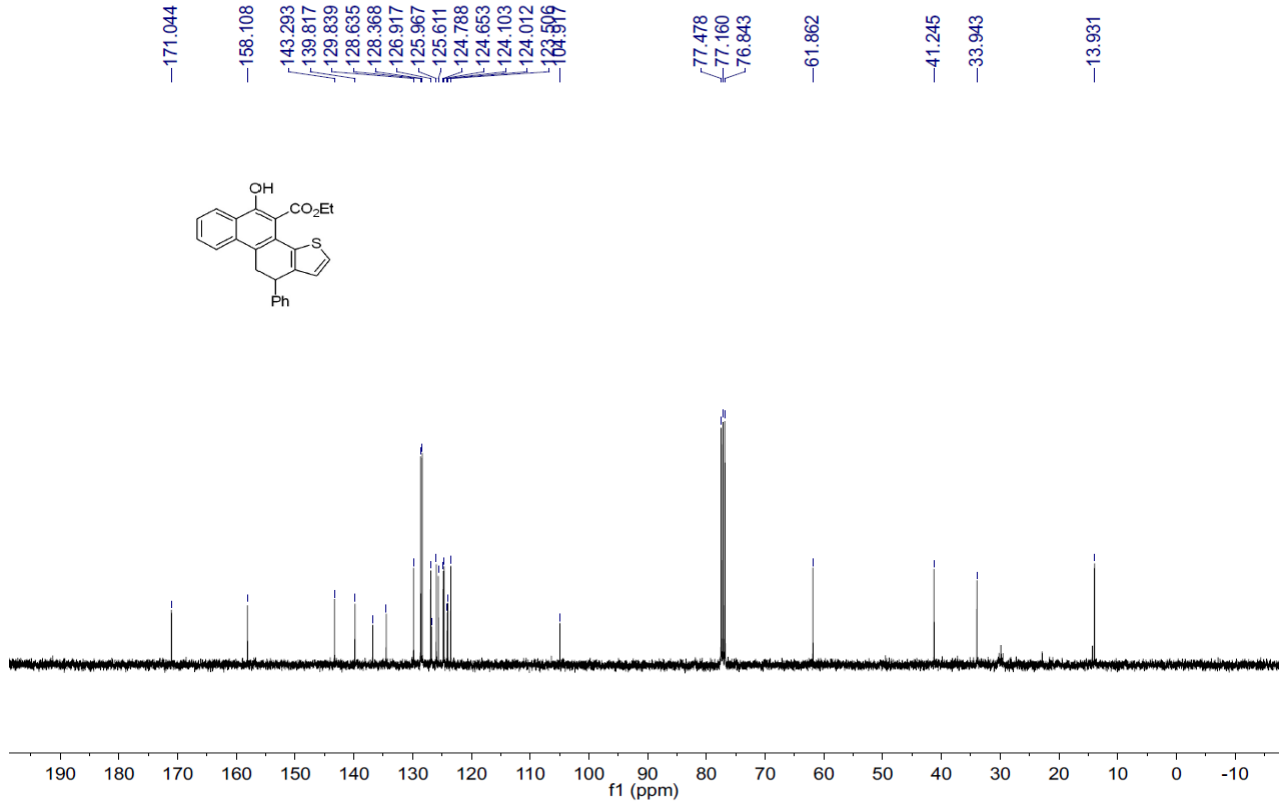
Supplementary Fig. 47 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 18.



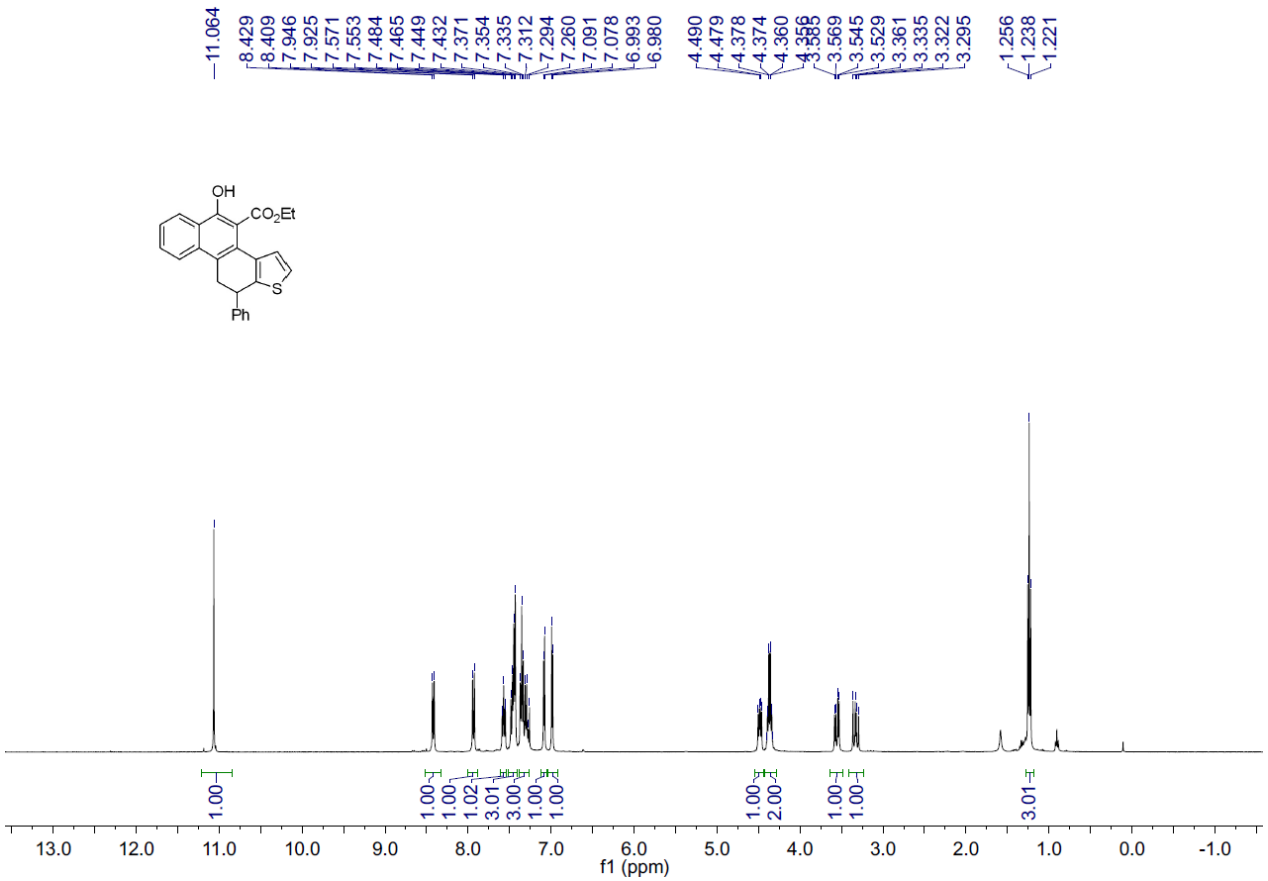
Supplementary Fig. 48 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 18.



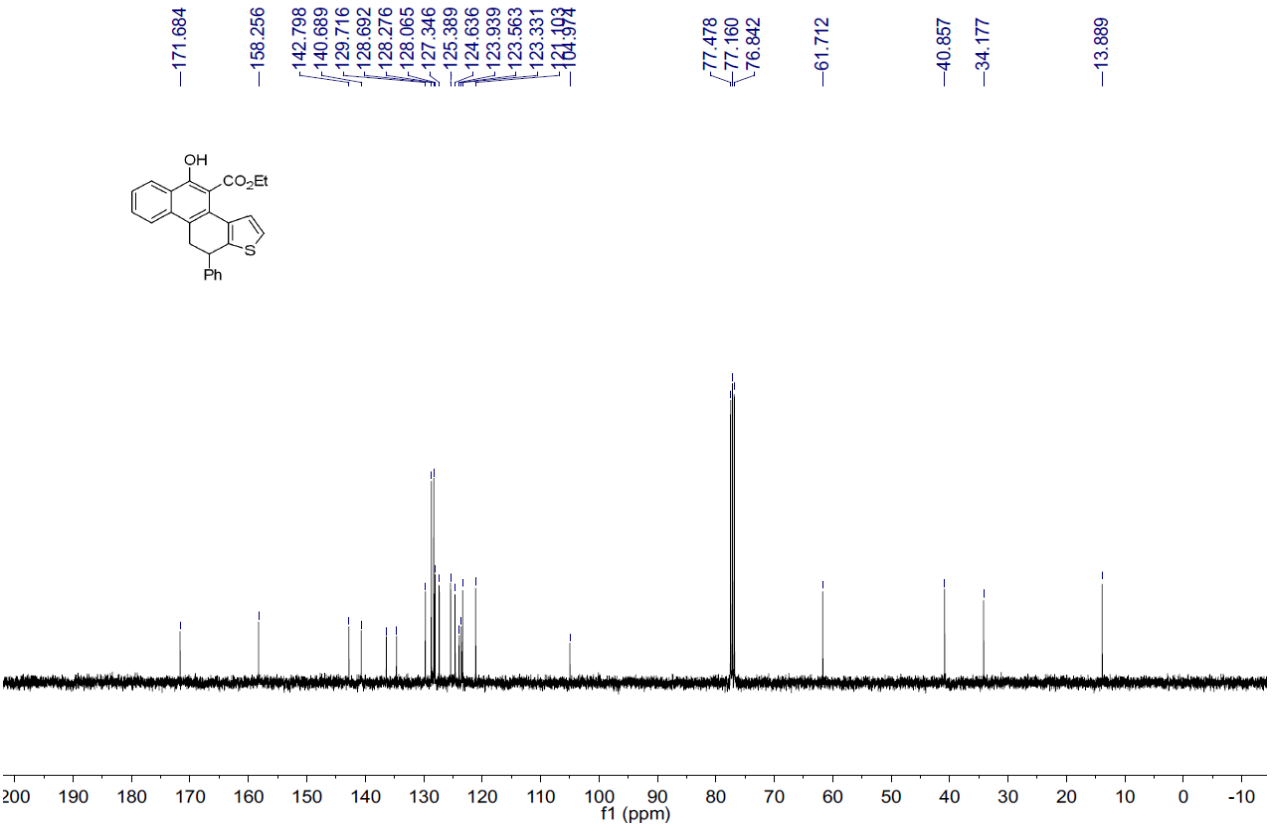
Supplementary Fig. 49 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 19.



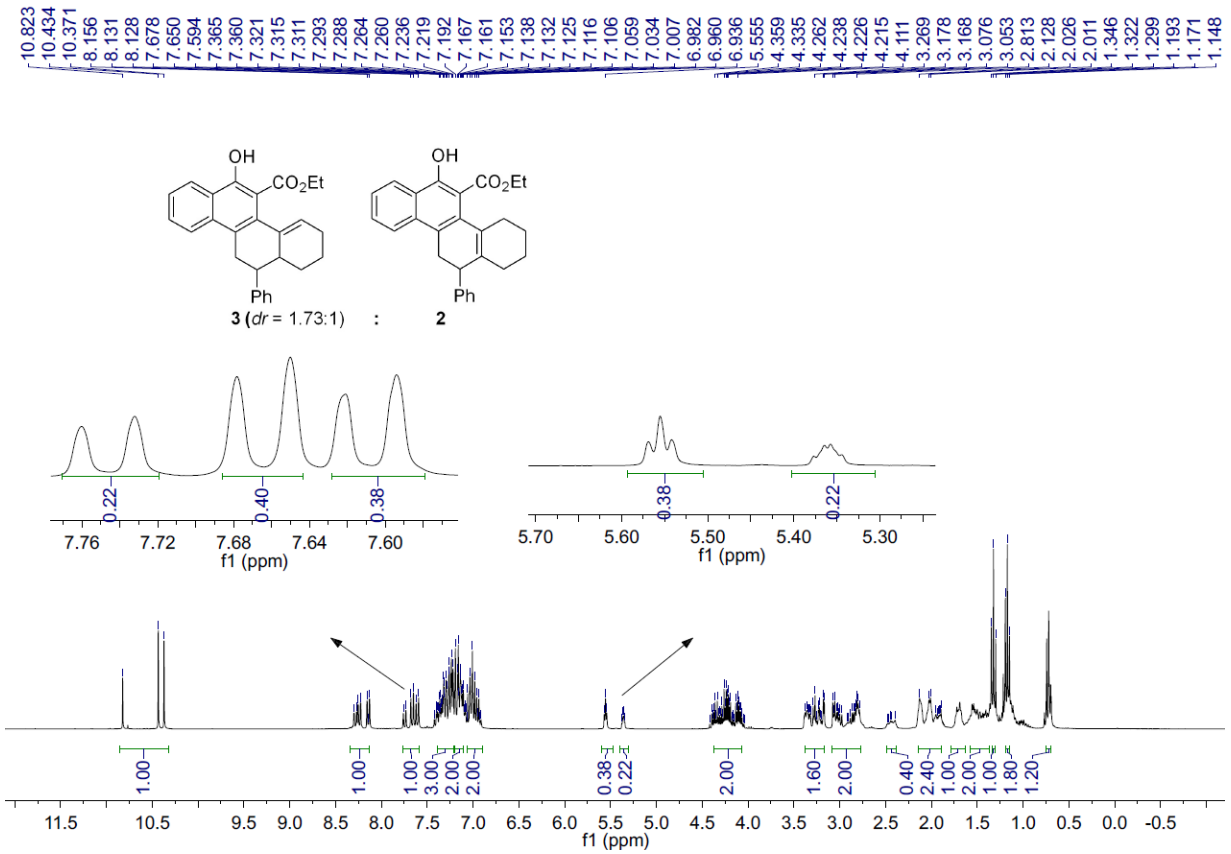
Supplementary Fig. 50 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 19.



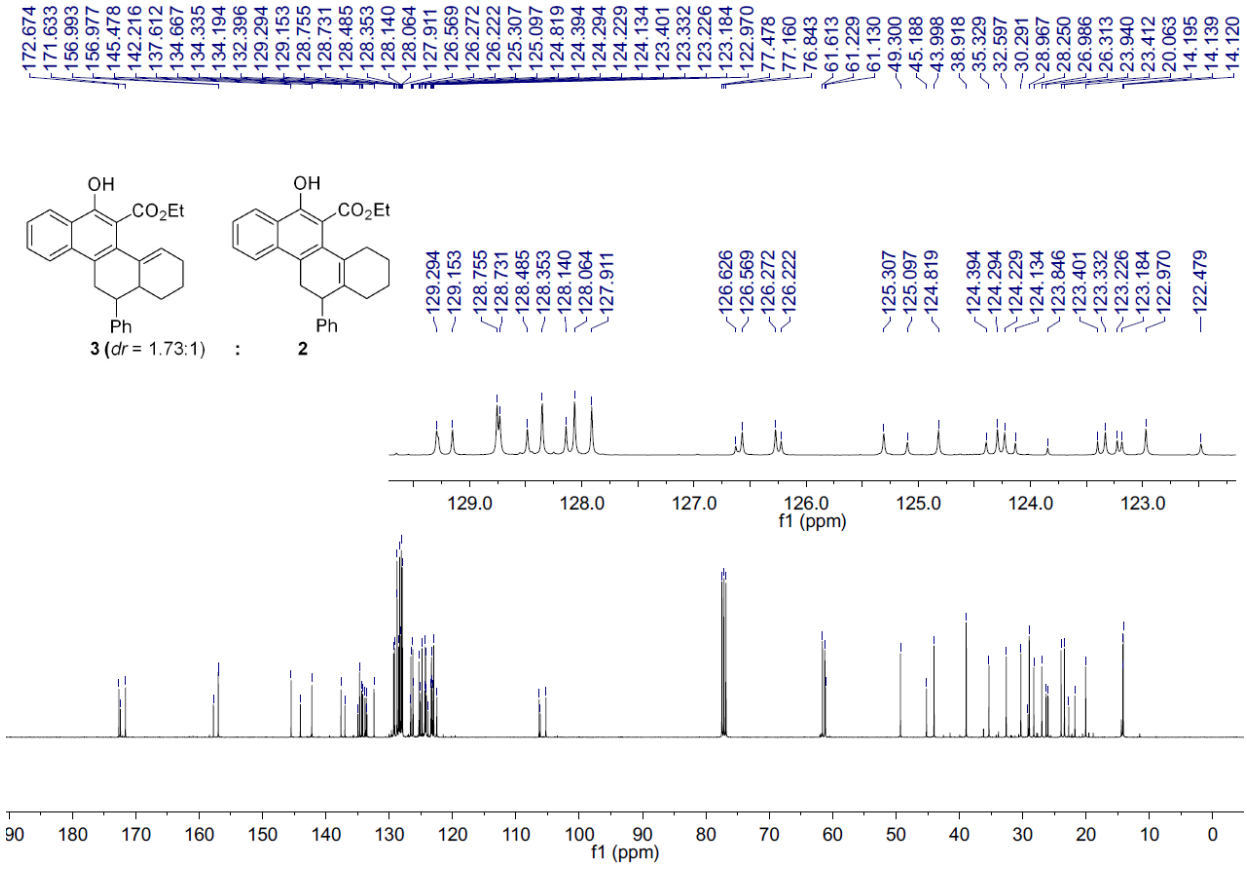
Supplementary Fig. 51 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 20.



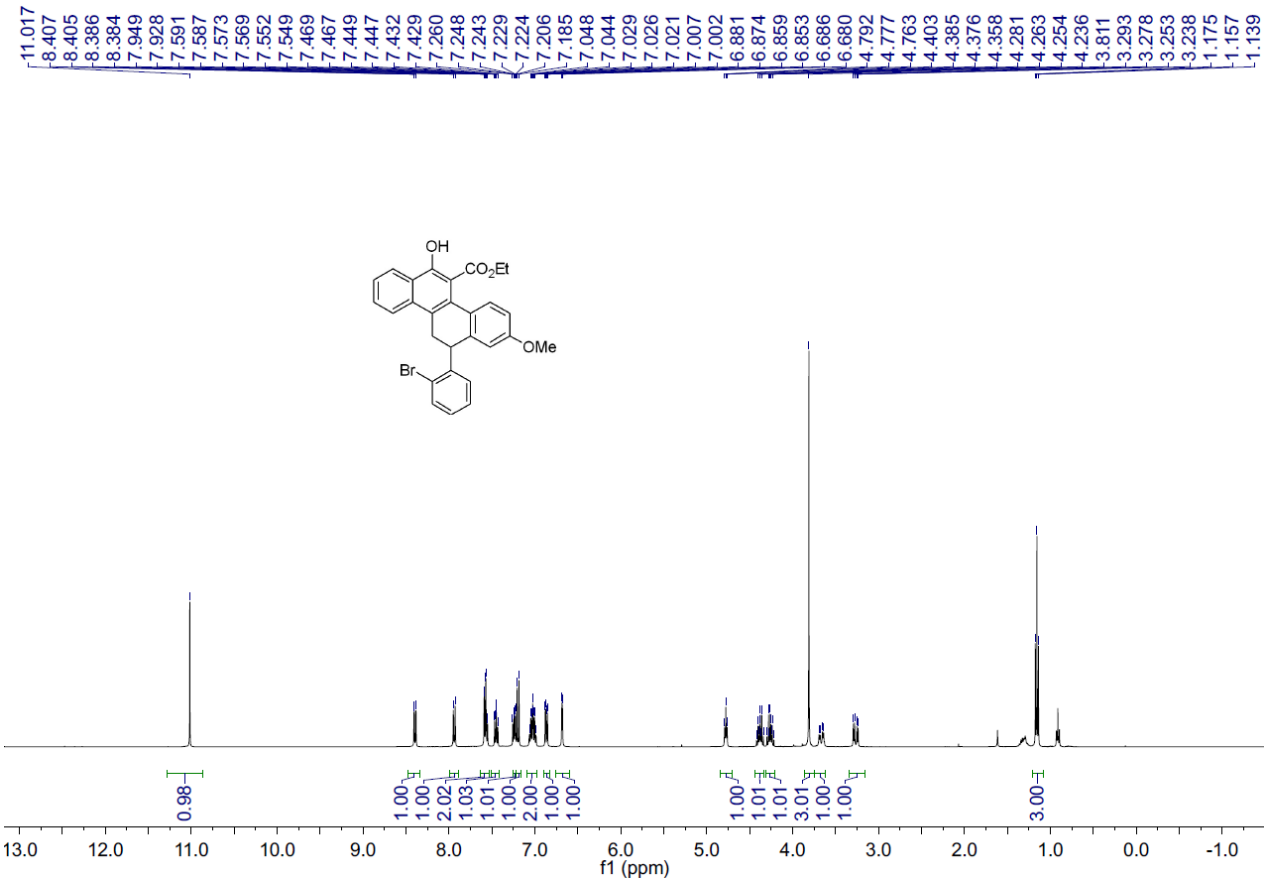
Supplementary Fig. 52 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 20.



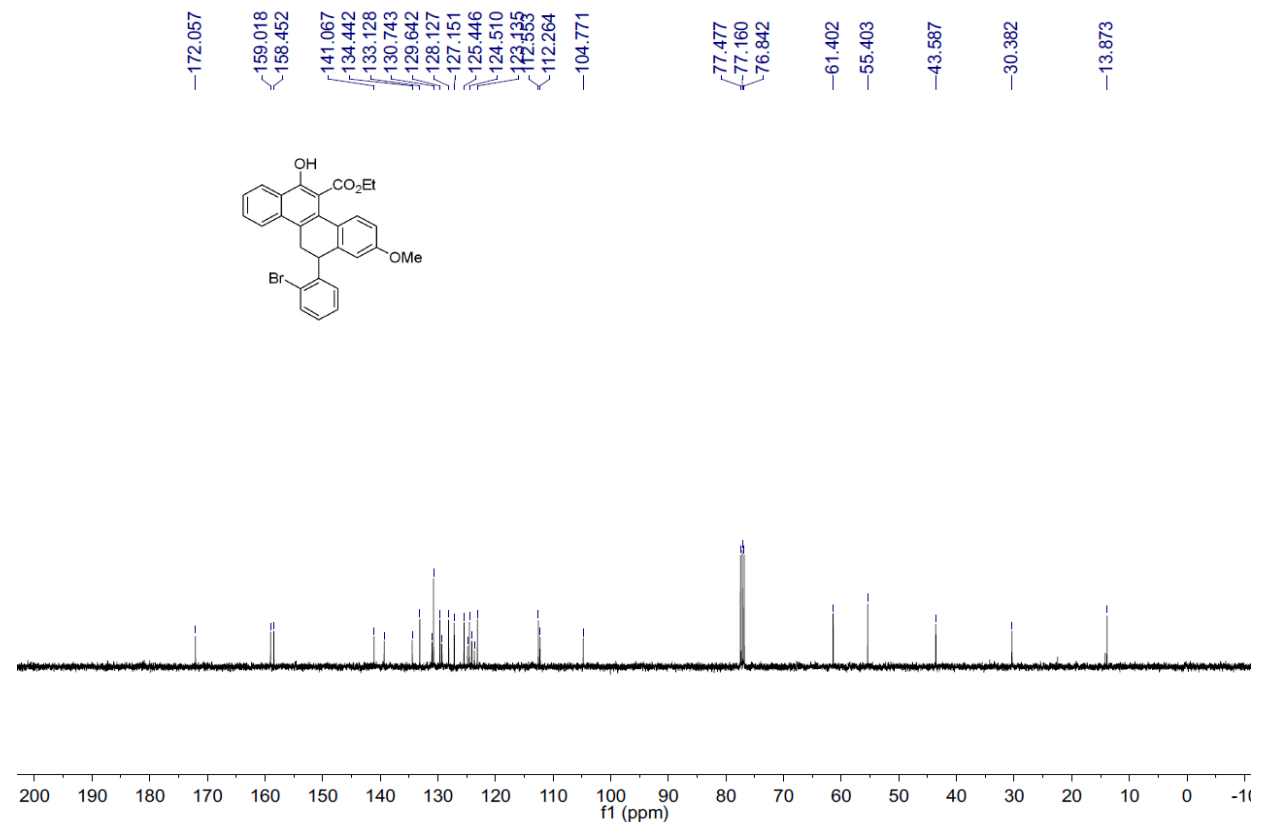
Supplementary Fig. 53 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum for 21.



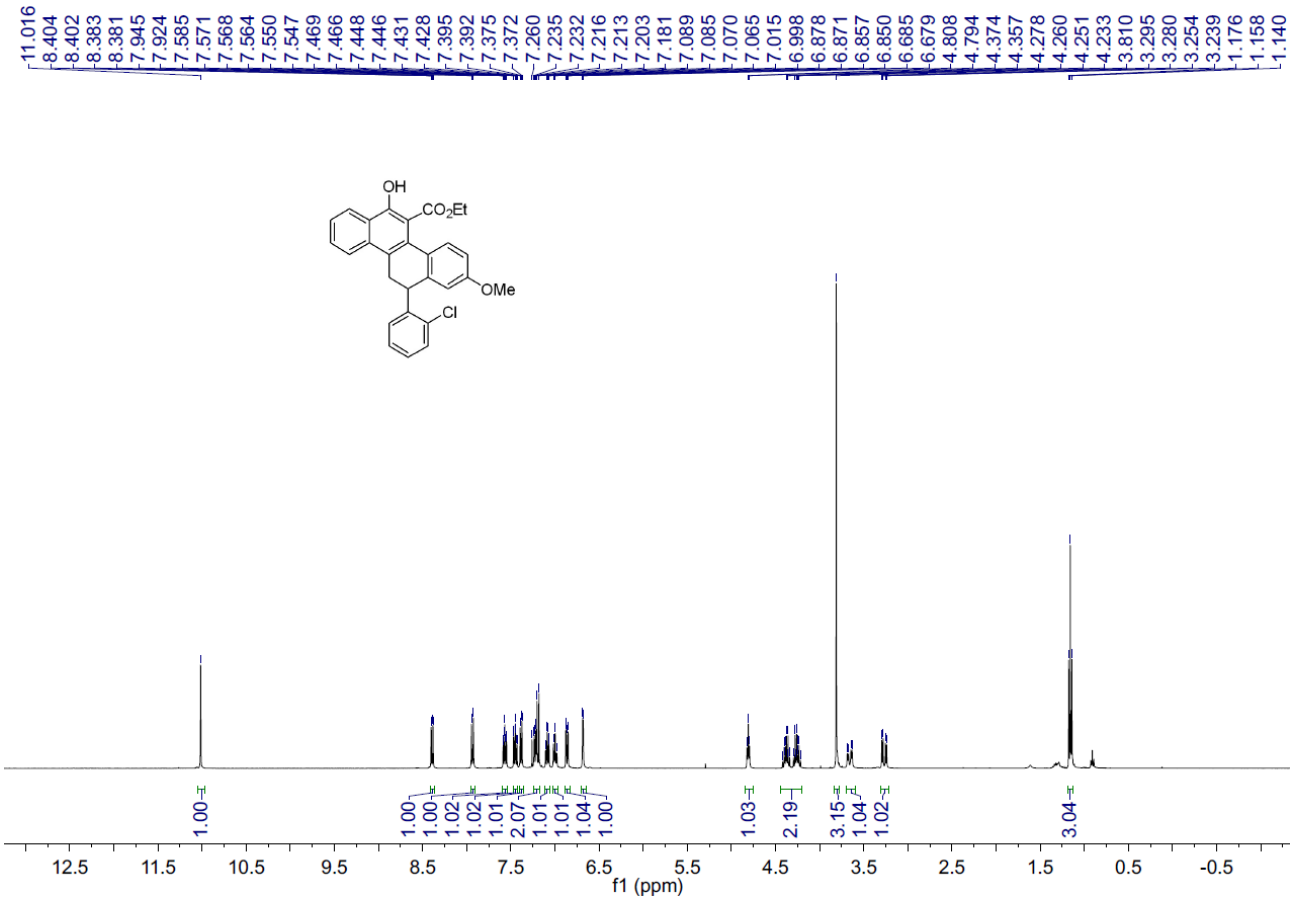
Supplementary Fig. 54 ^{13}C NMR (75 MHz, $CDCl_3$) spectrum for 21.



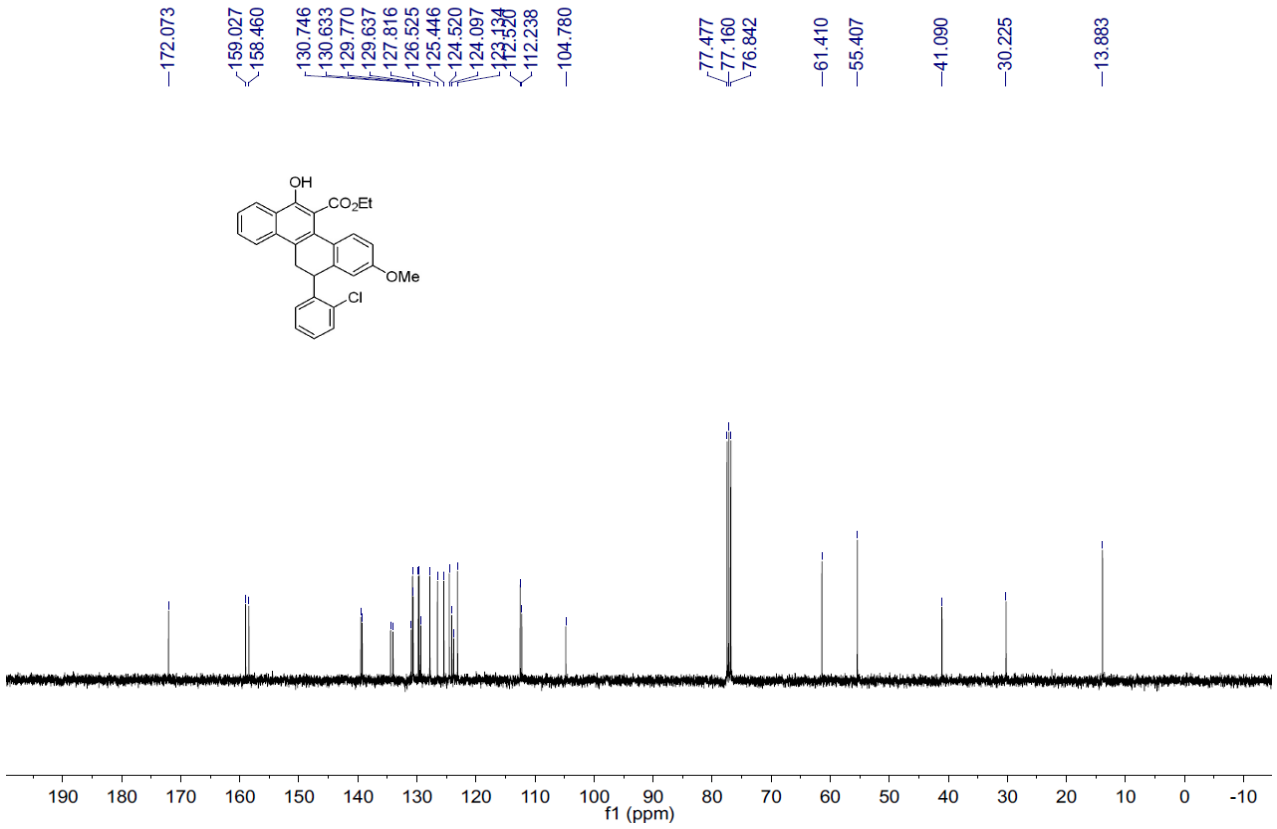
Supplementary Fig. 55 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 22.



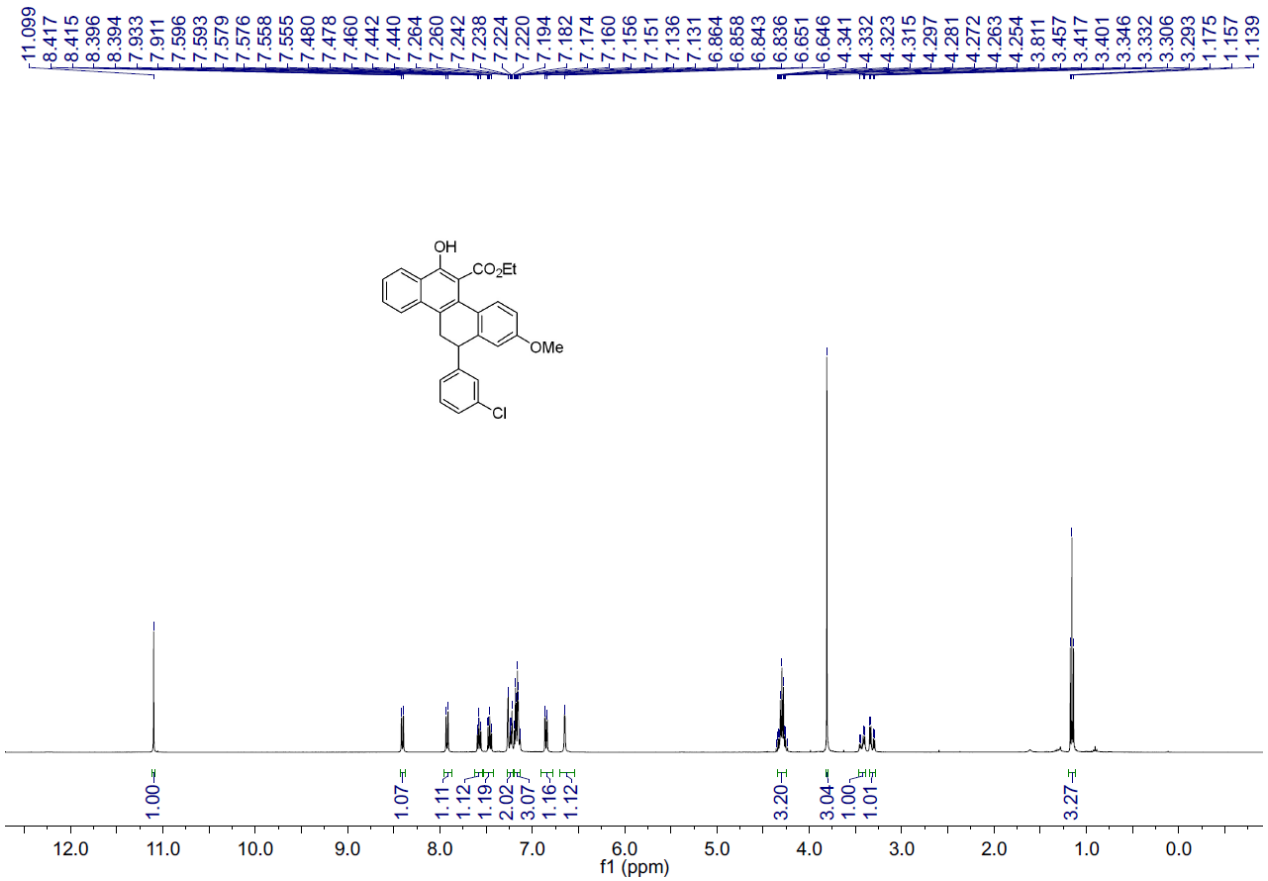
Supplementary Fig. 56 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 22.



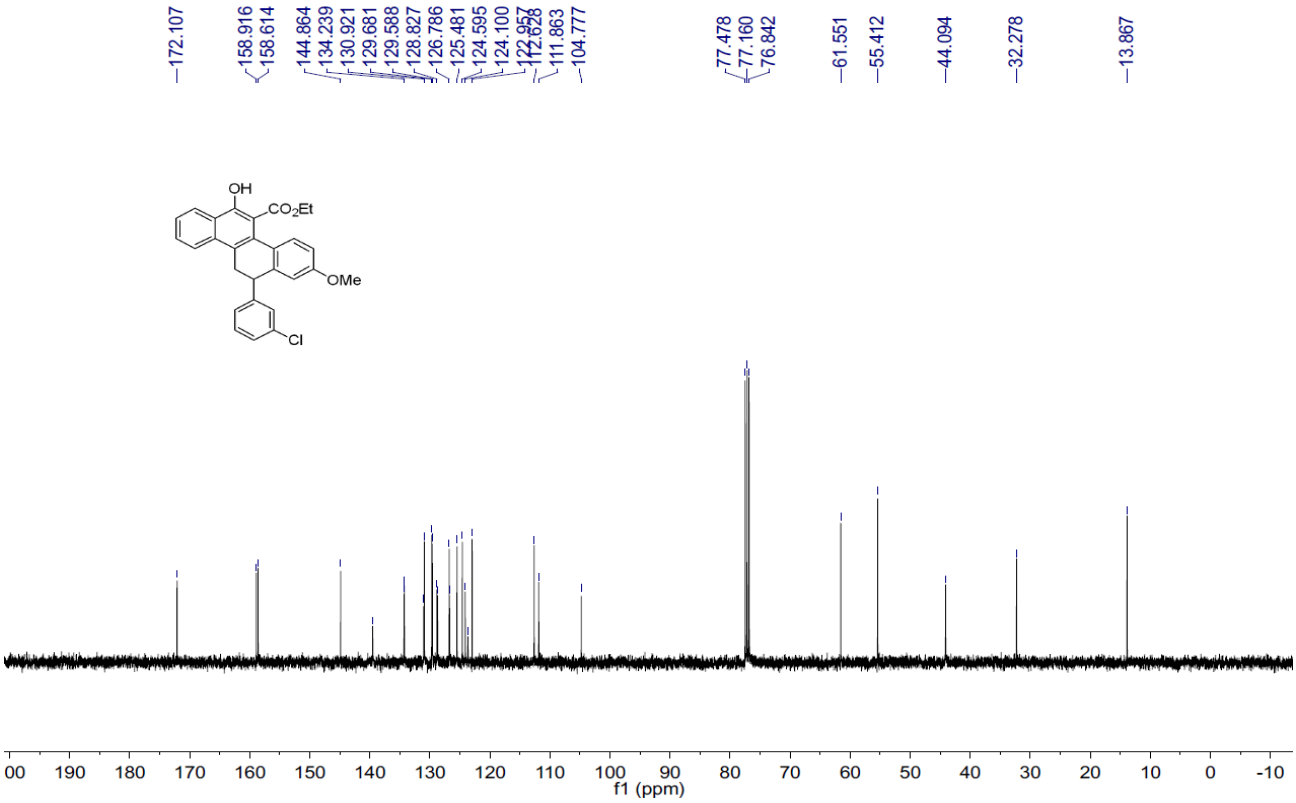
Supplementary Fig. 57 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 23.



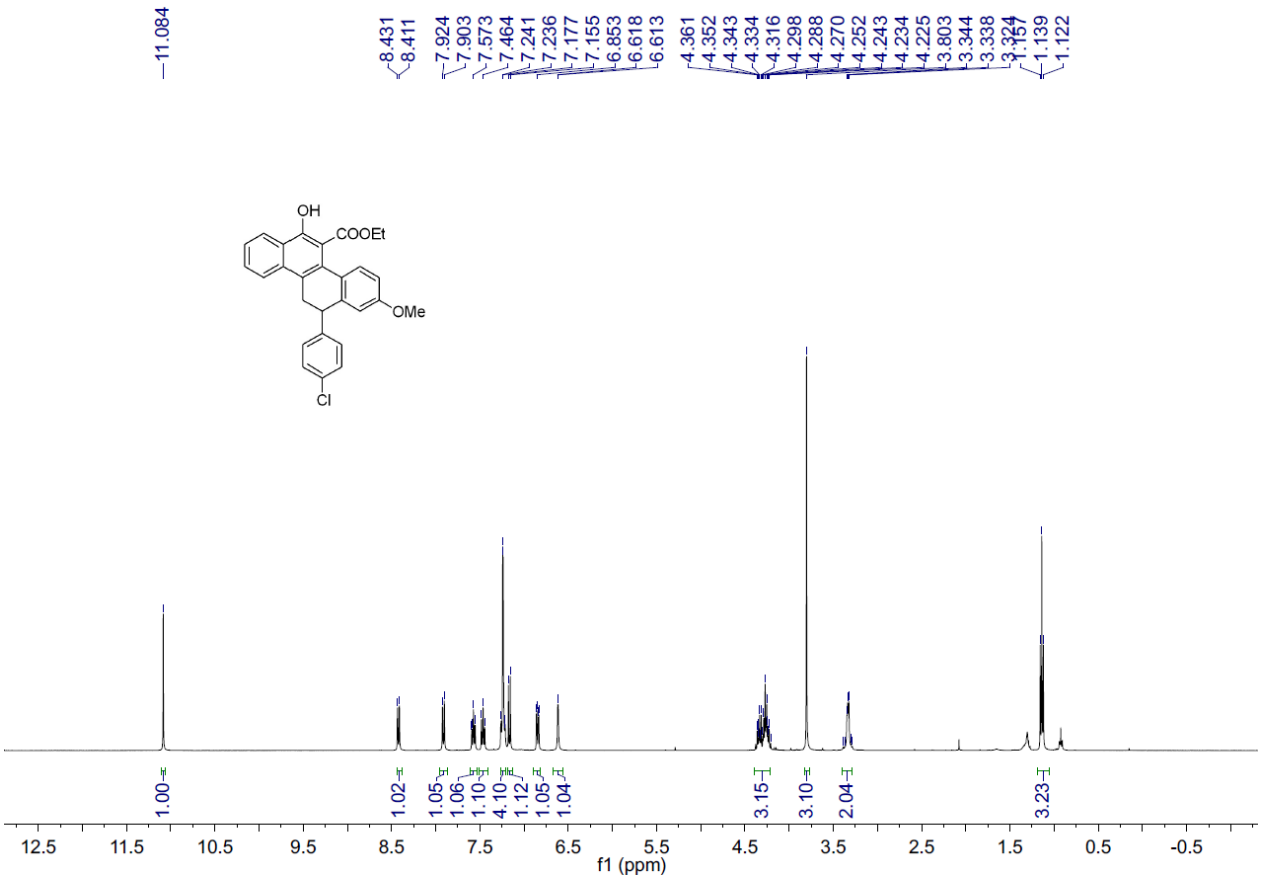
Supplementary Fig. 58 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 23.



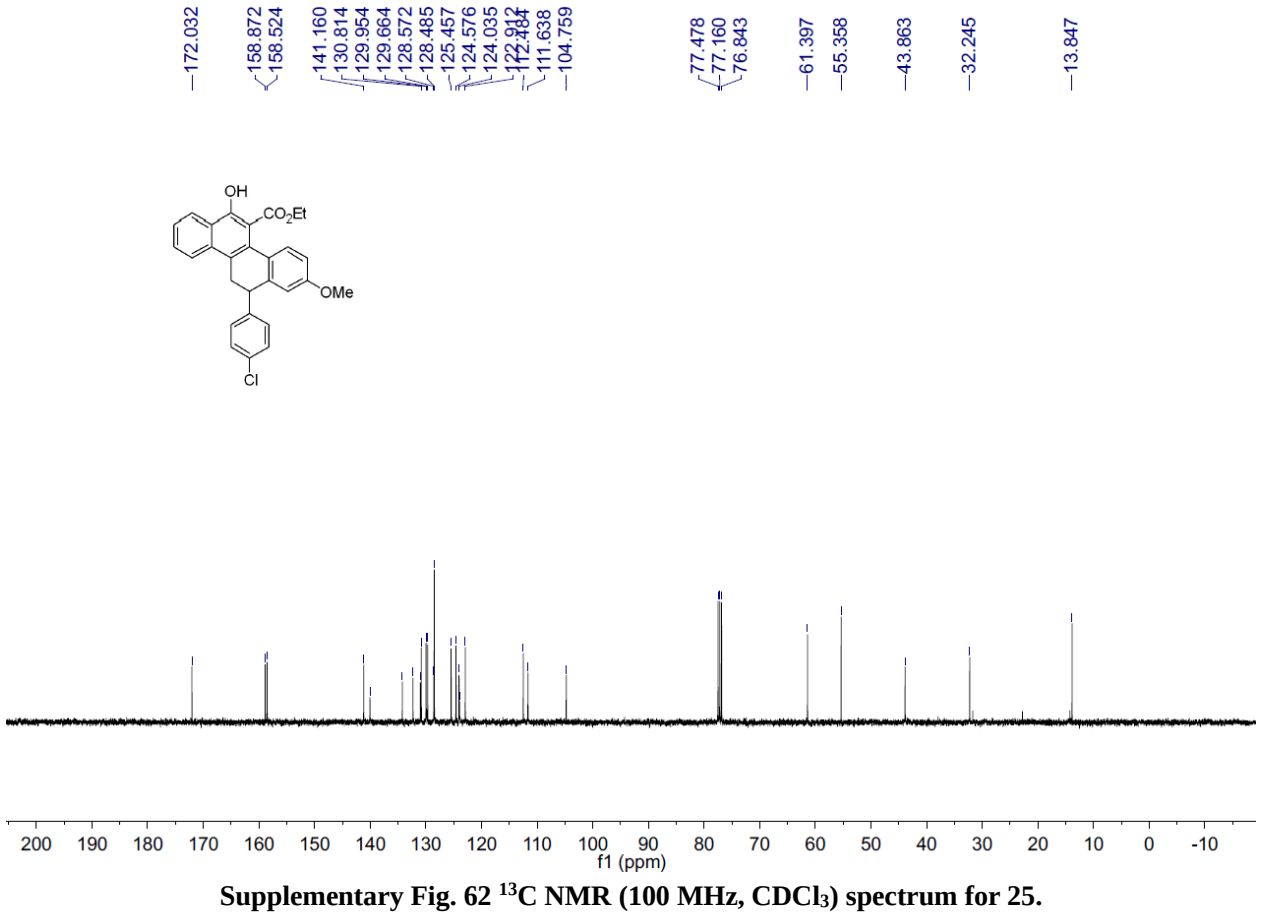
Supplementary Fig. 59 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 24.



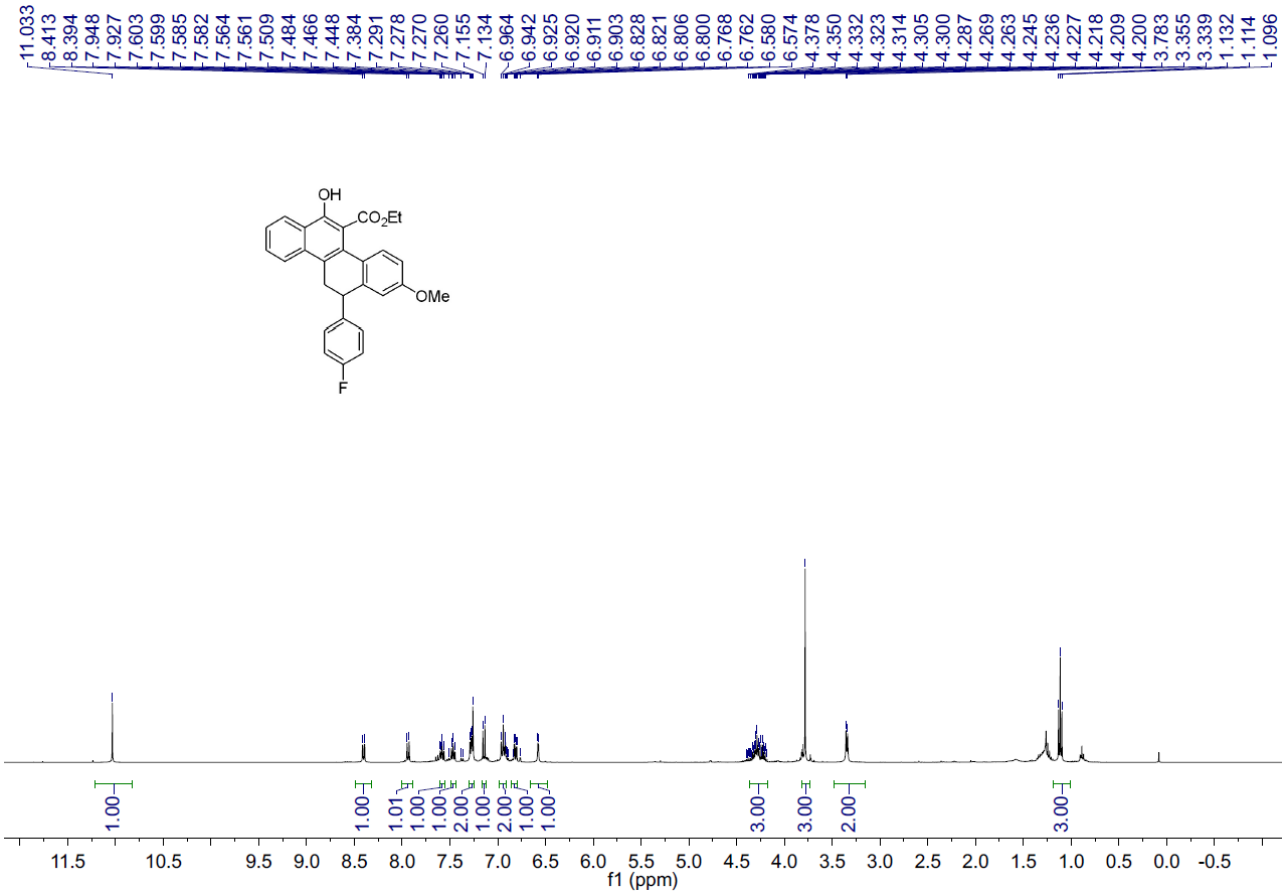
Supplementary Fig. 60 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 24.



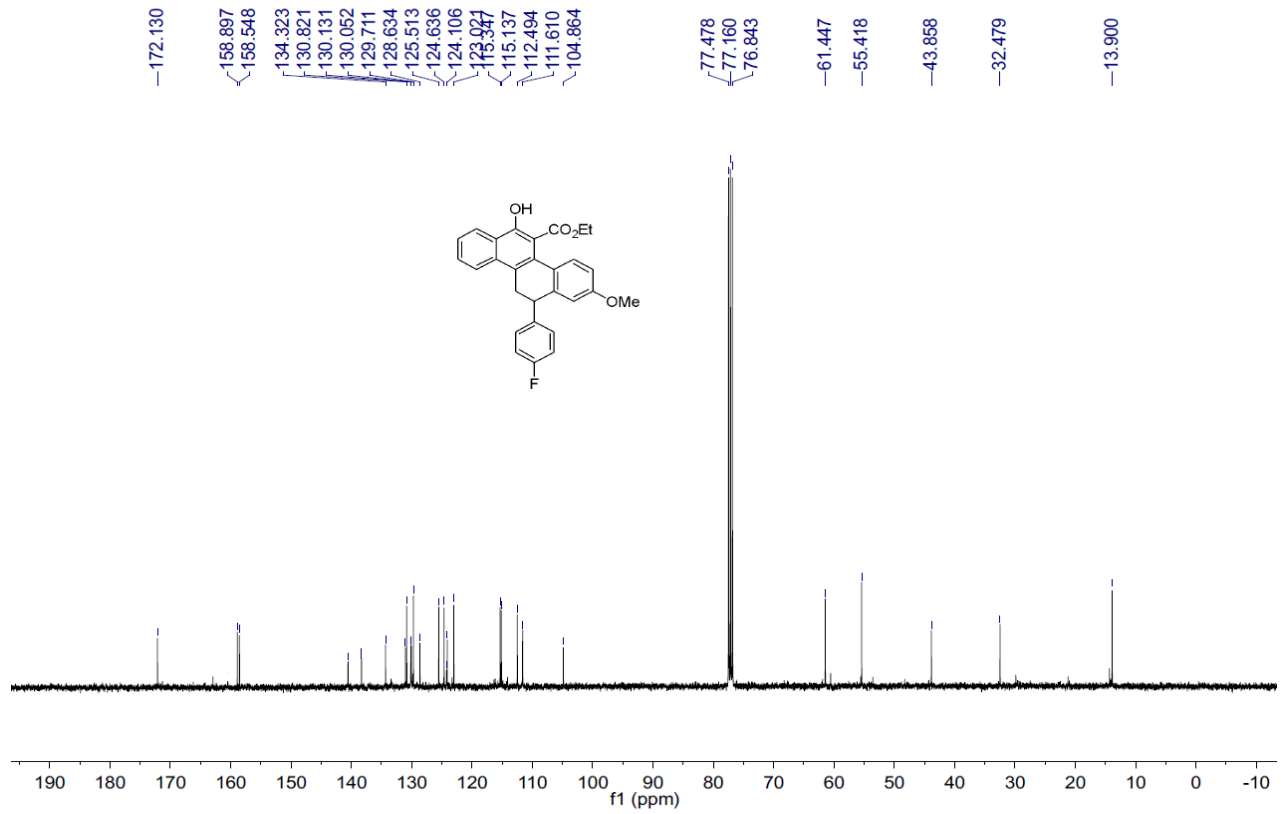
Supplementary Fig. 61 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 25.



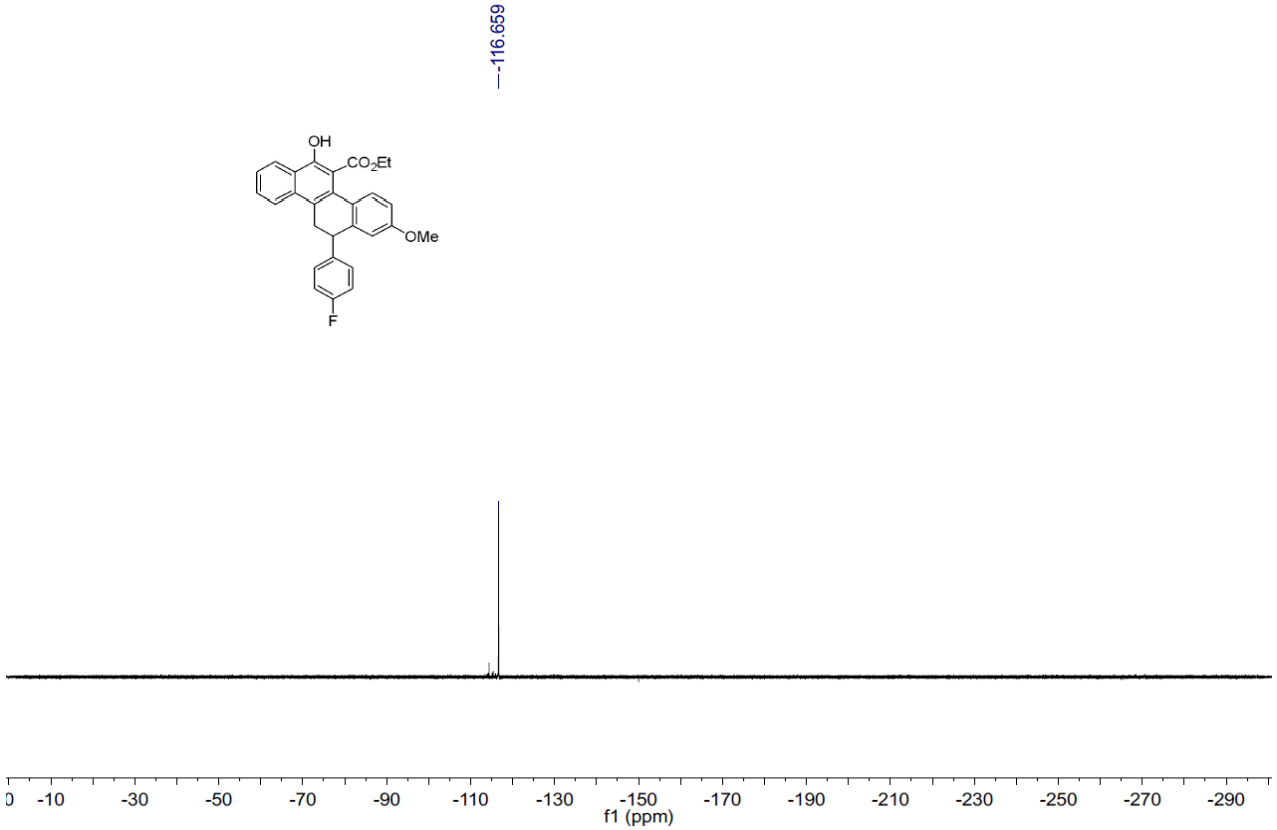
Supplementary Fig. 62 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 25.



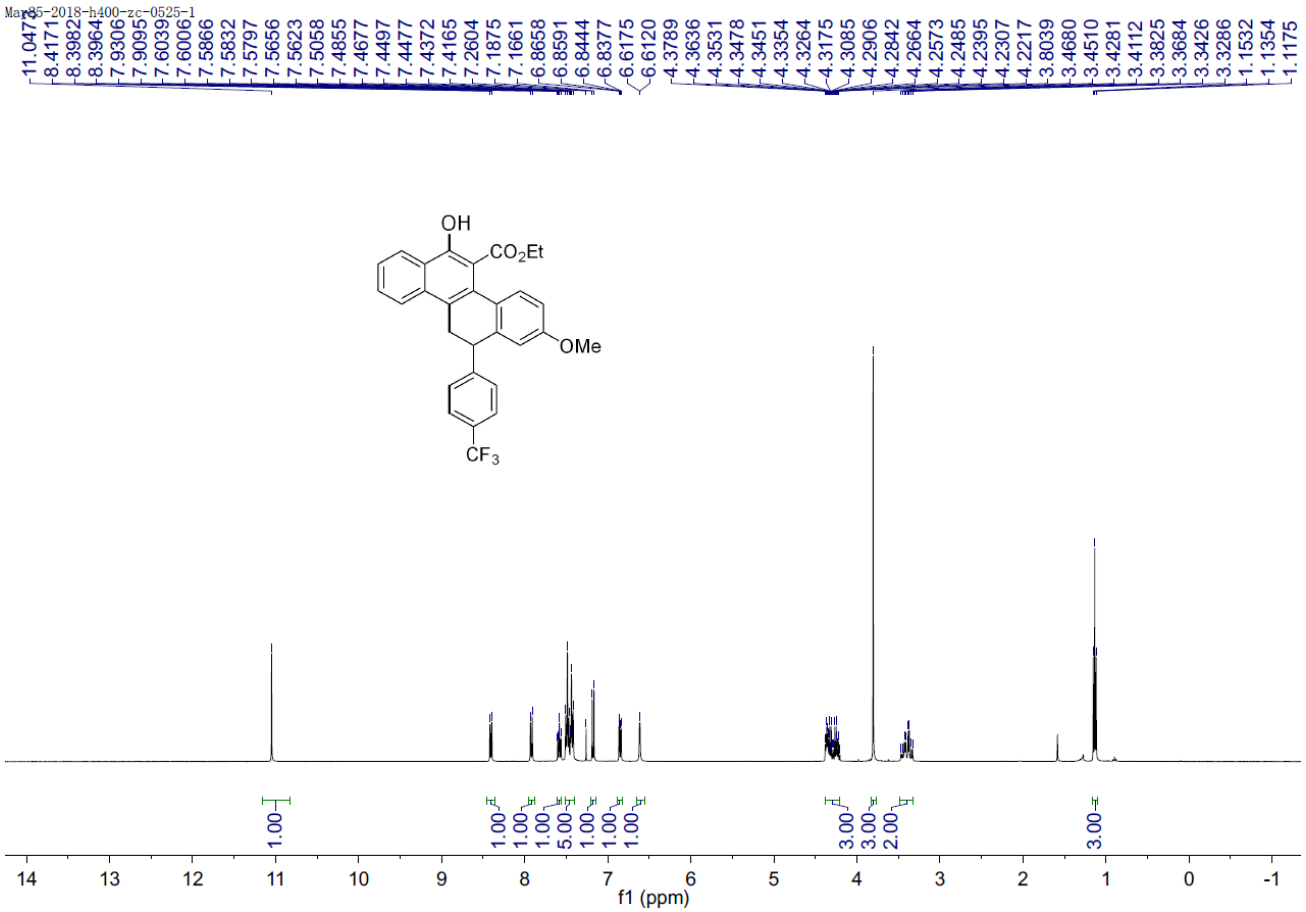
Supplementary Fig. 63 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 26.



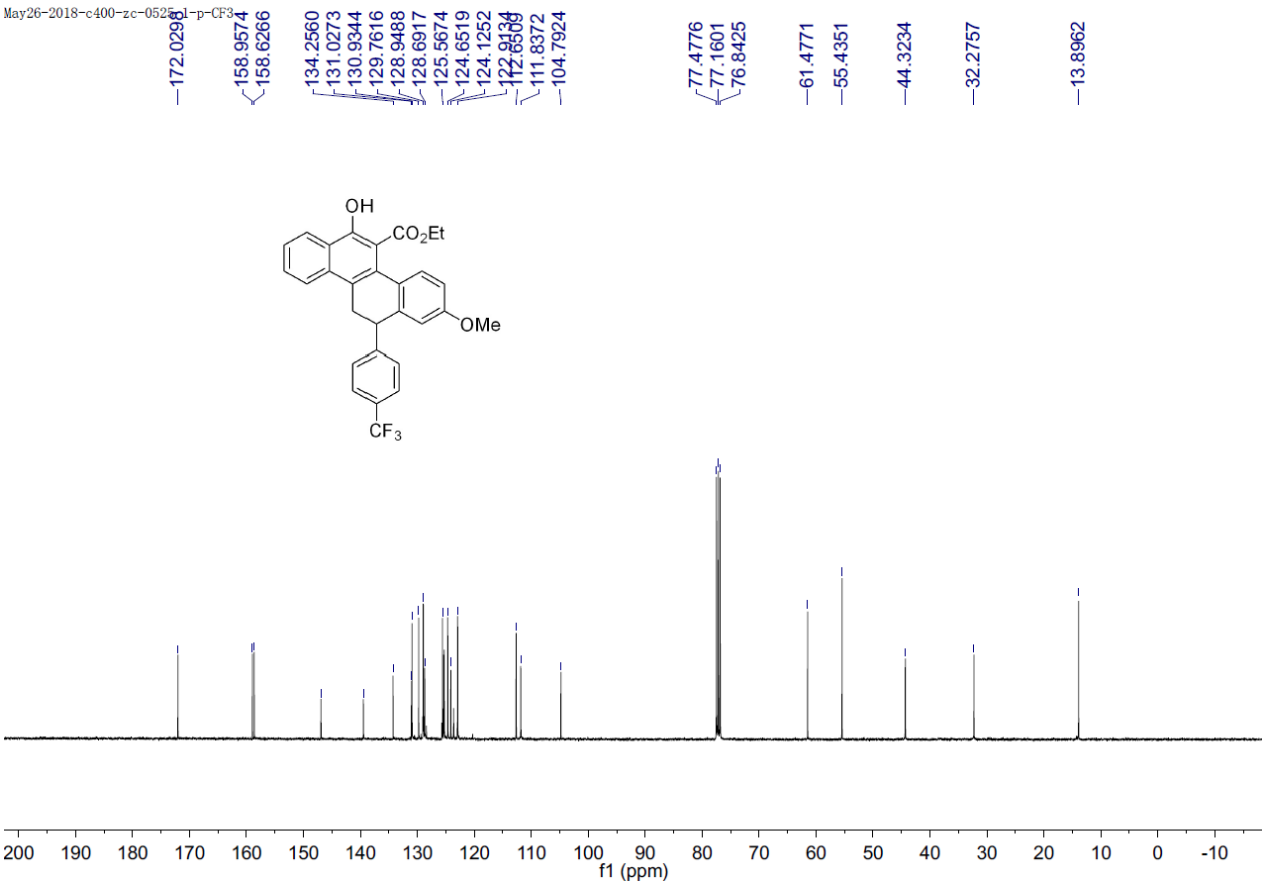
Supplementary Fig. 64 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 26.



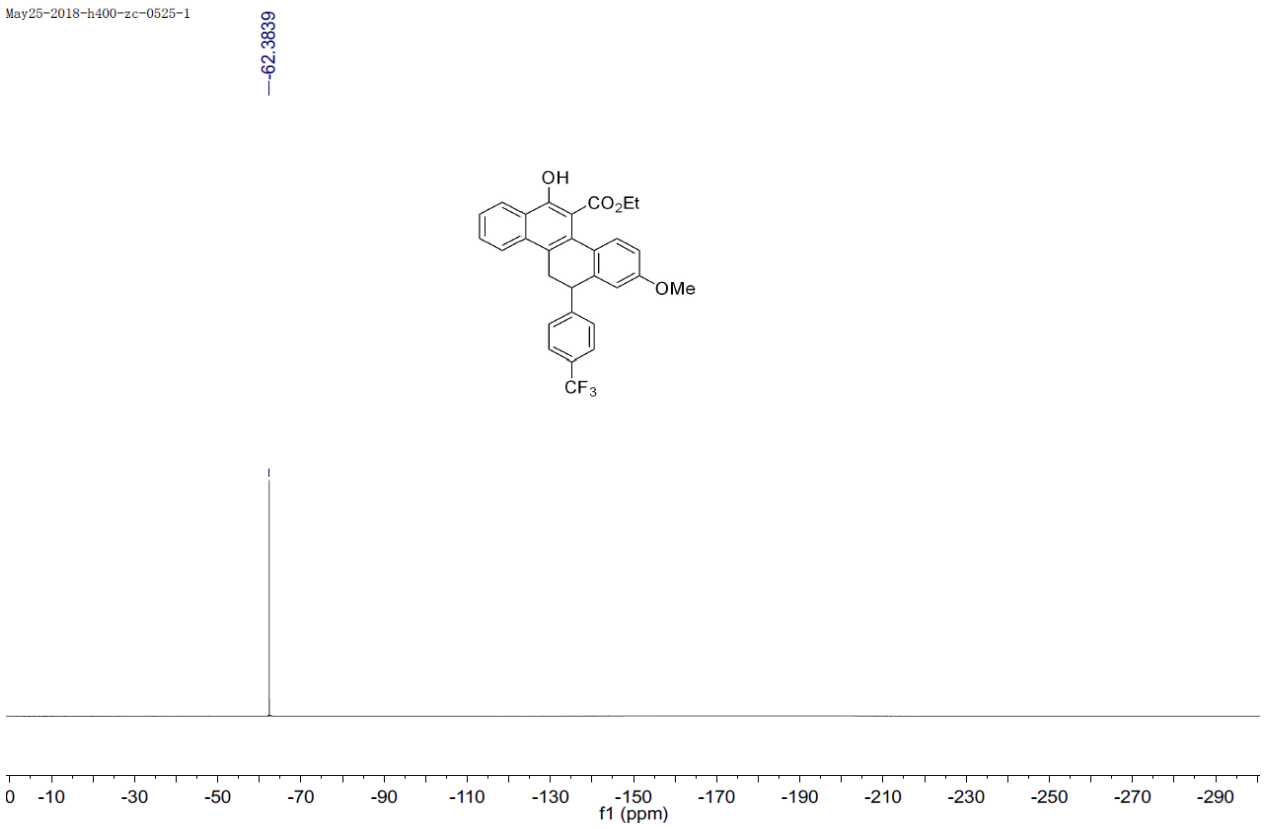
Supplementary Fig. 65 ^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 26.



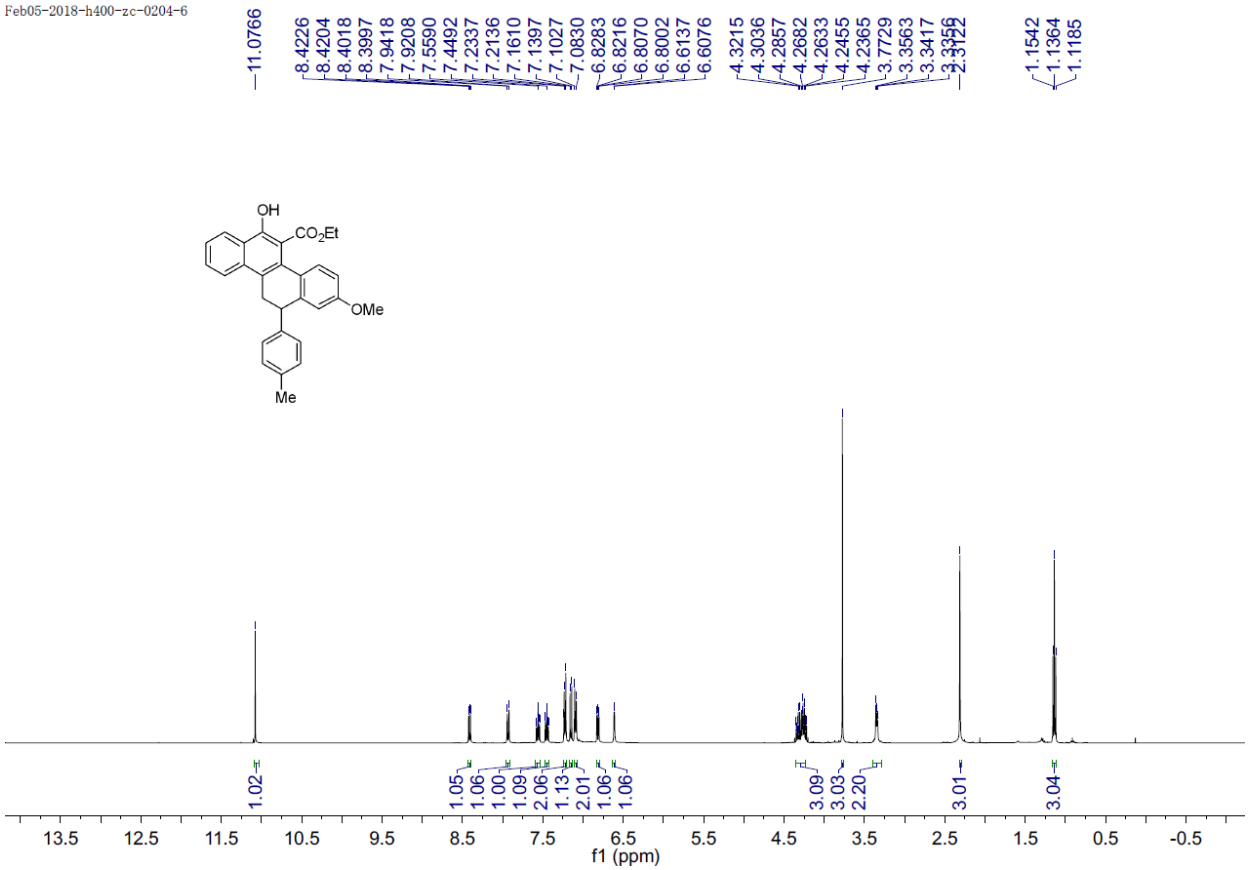
Supplementary Fig. 66 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 27.



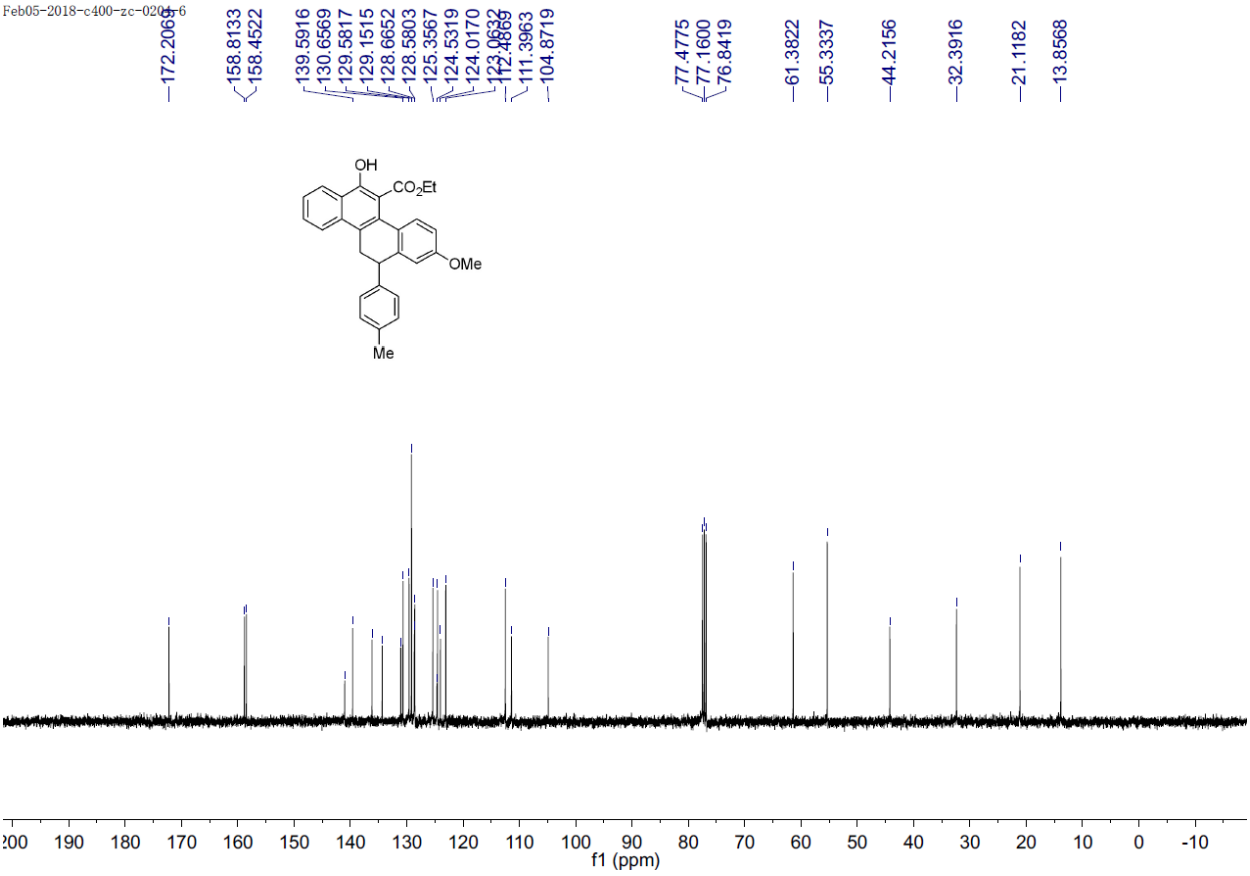
Supplementary Fig. 67 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 27.



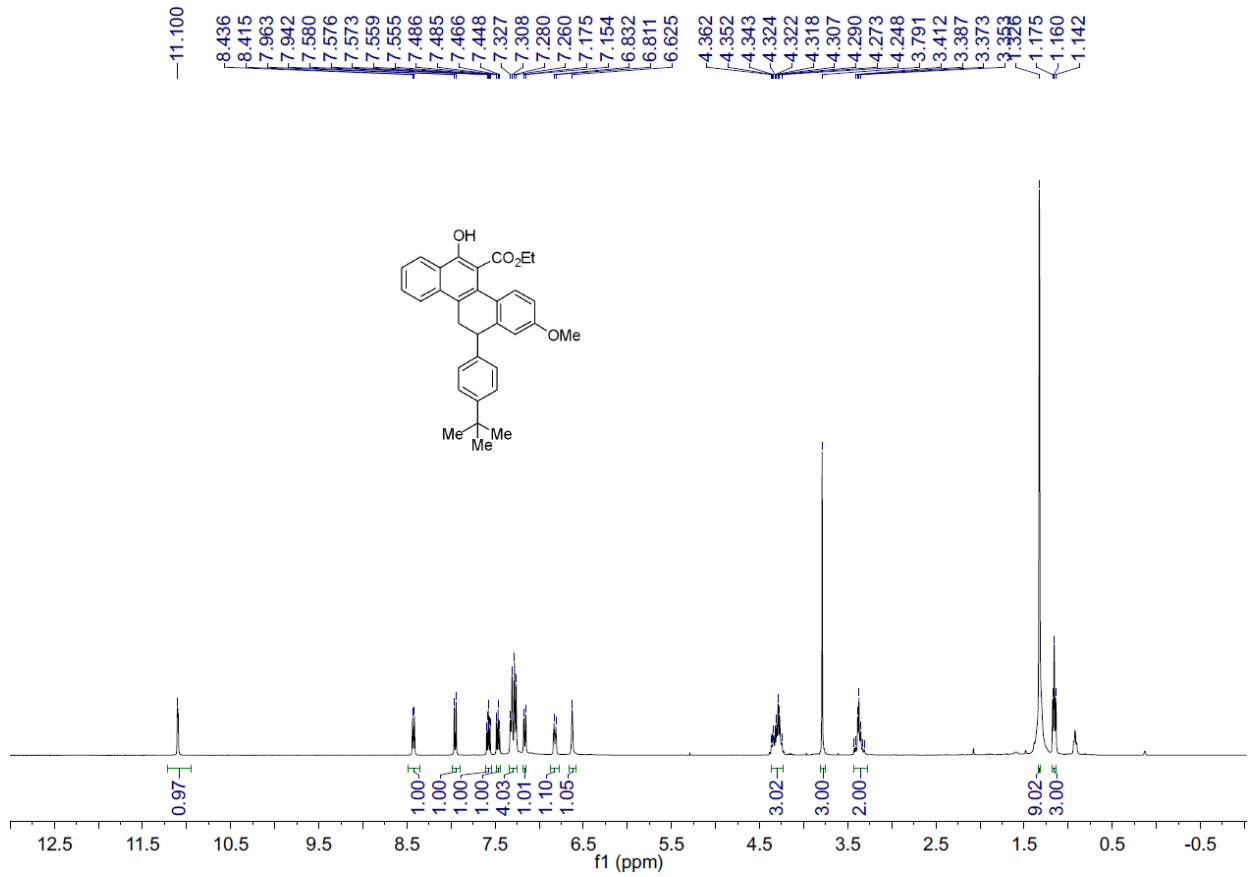
Supplementary Fig. 68 ^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 27.



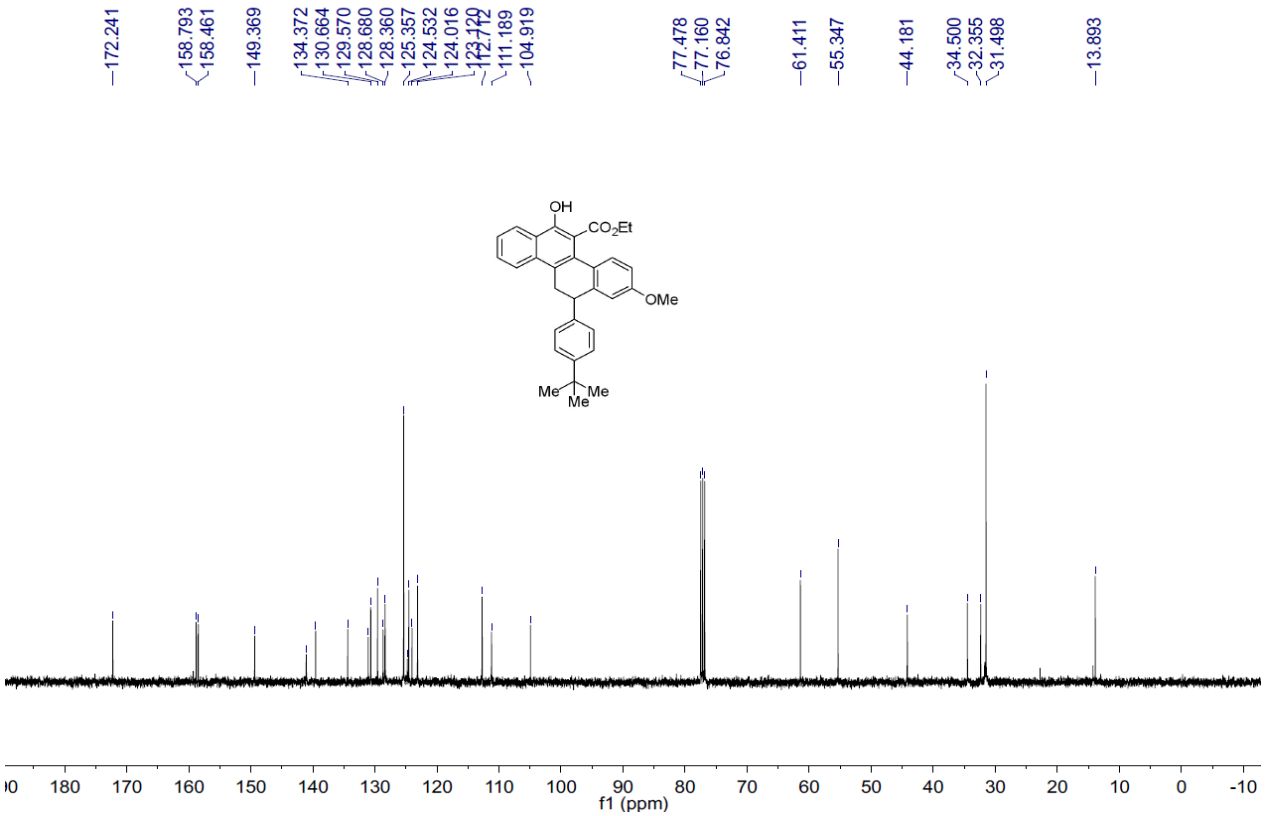
Supplementary Fig. 69 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 28.



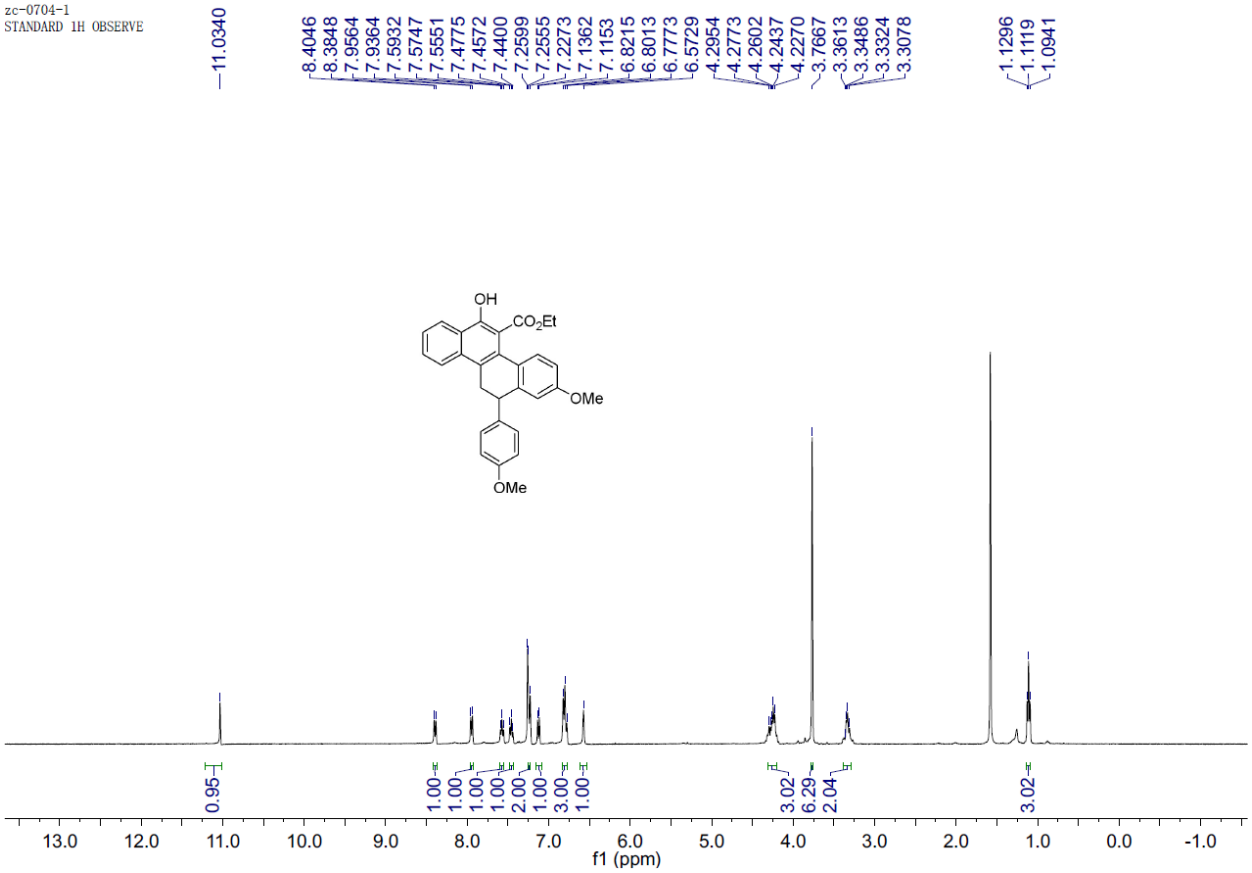
Supplementary Fig. 70 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 28.



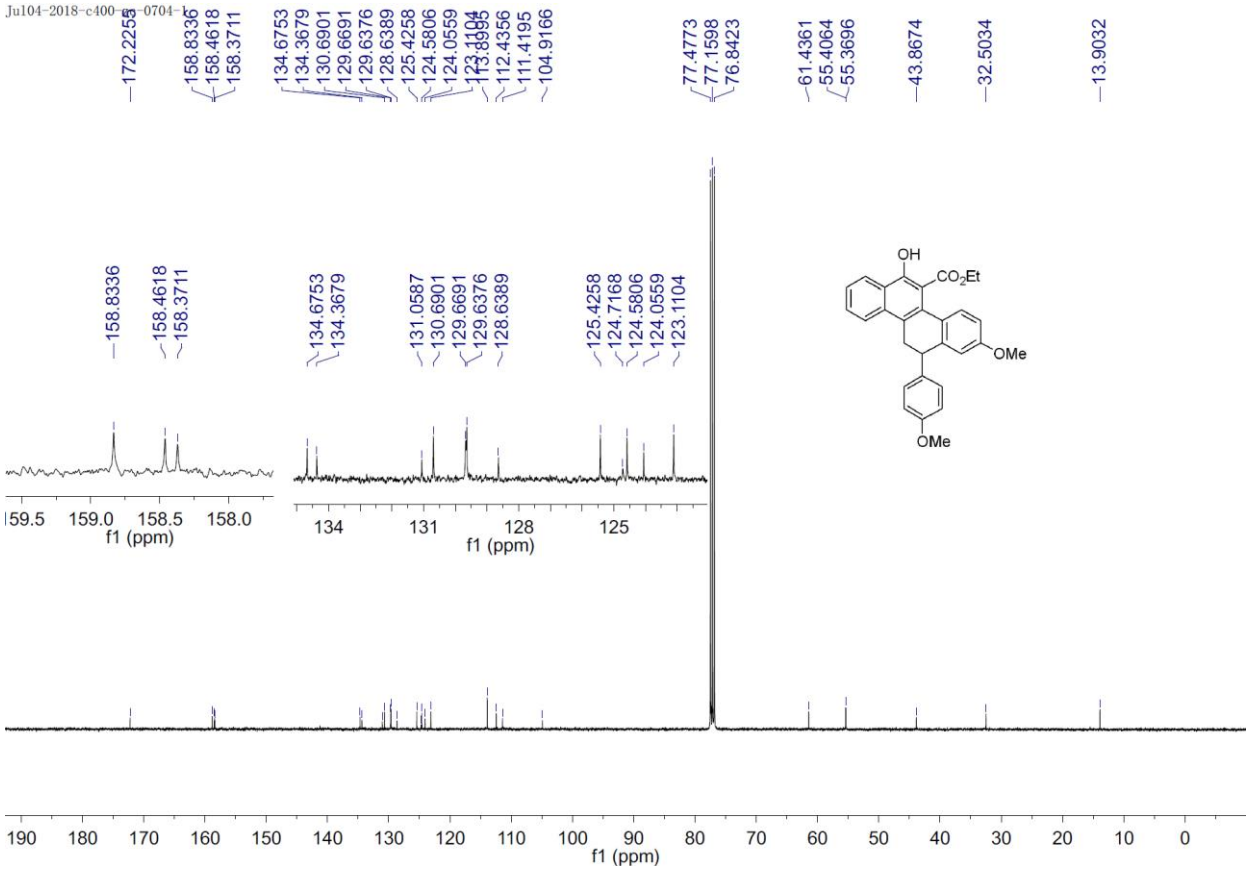
Supplementary Fig. 71 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 29.



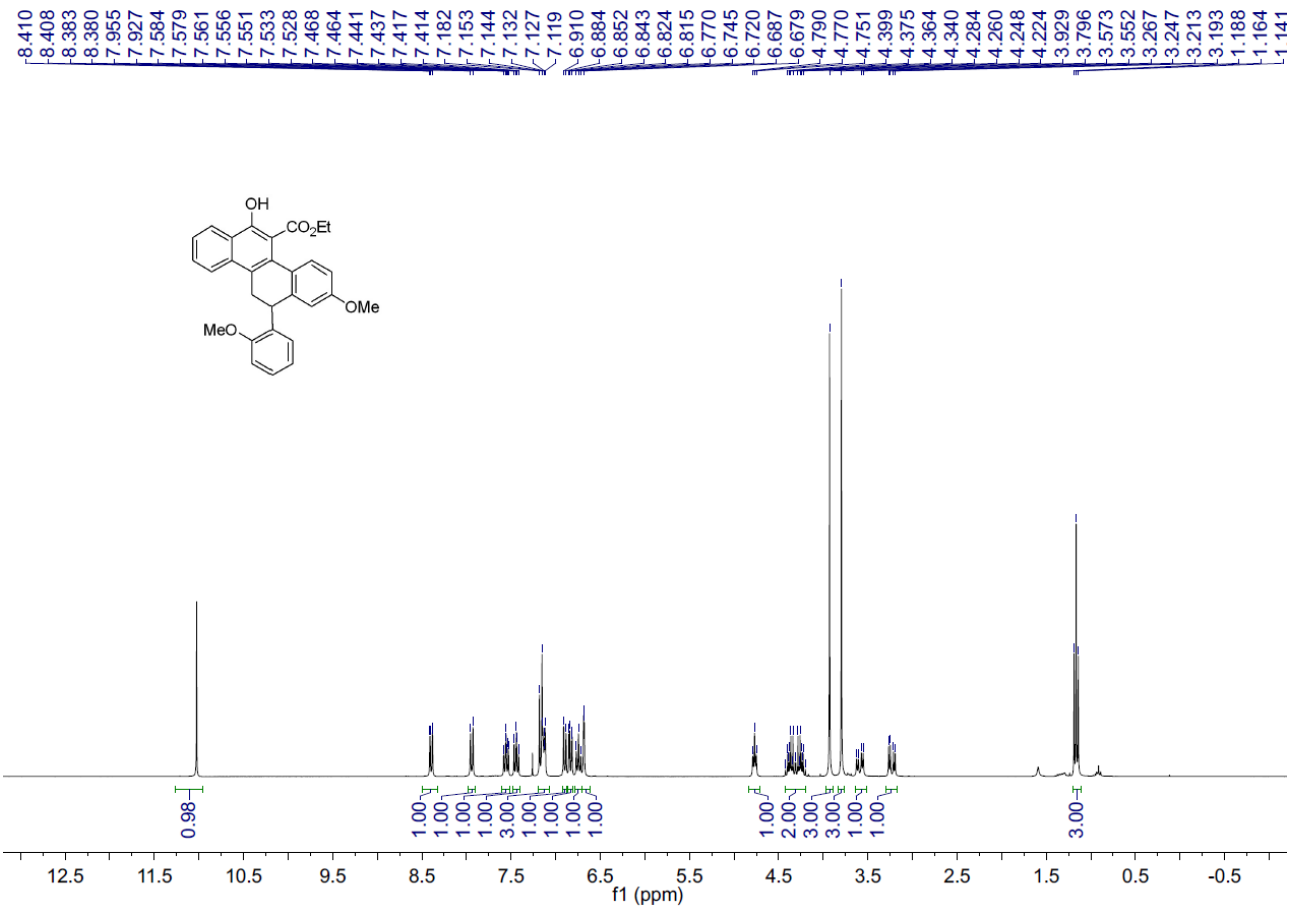
Supplementary Fig. 72 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 29.



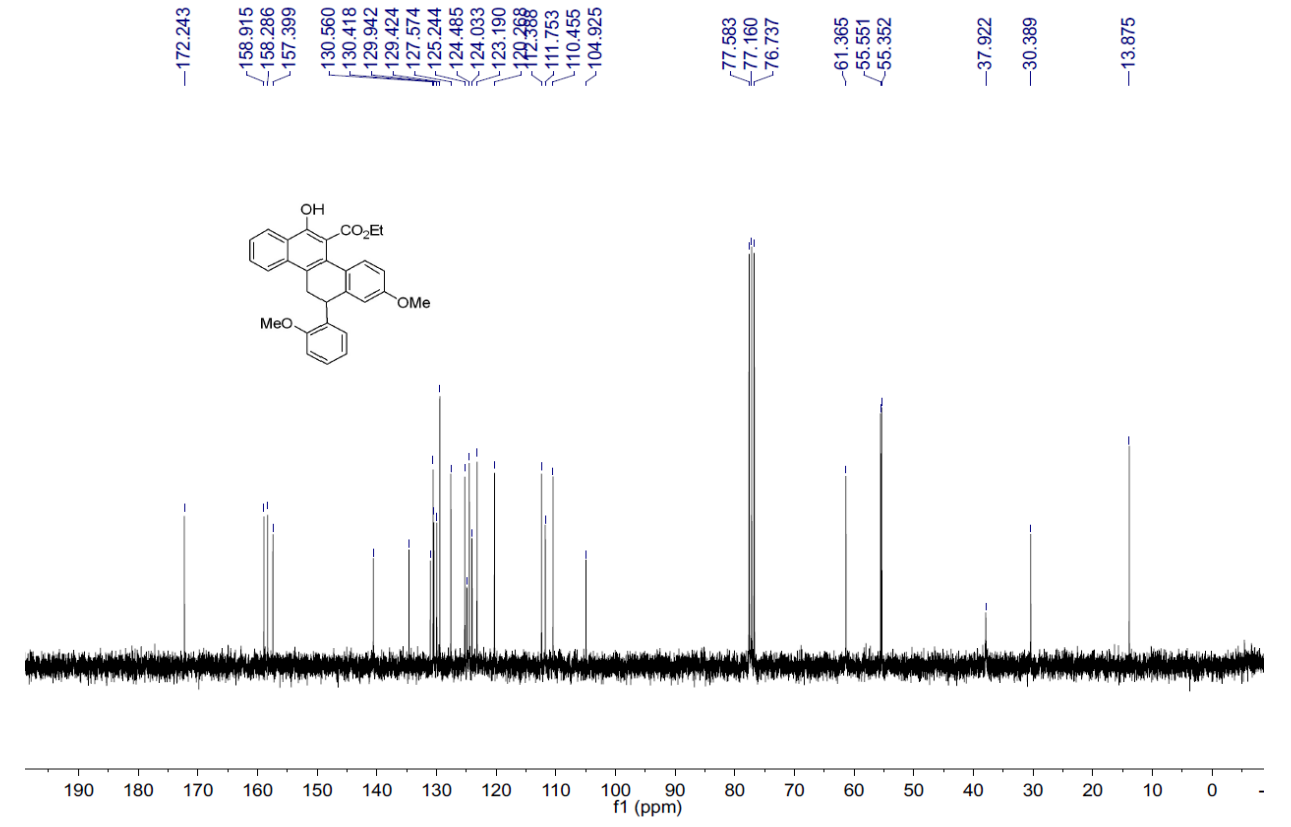
Supplementary Fig. 73 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 30.



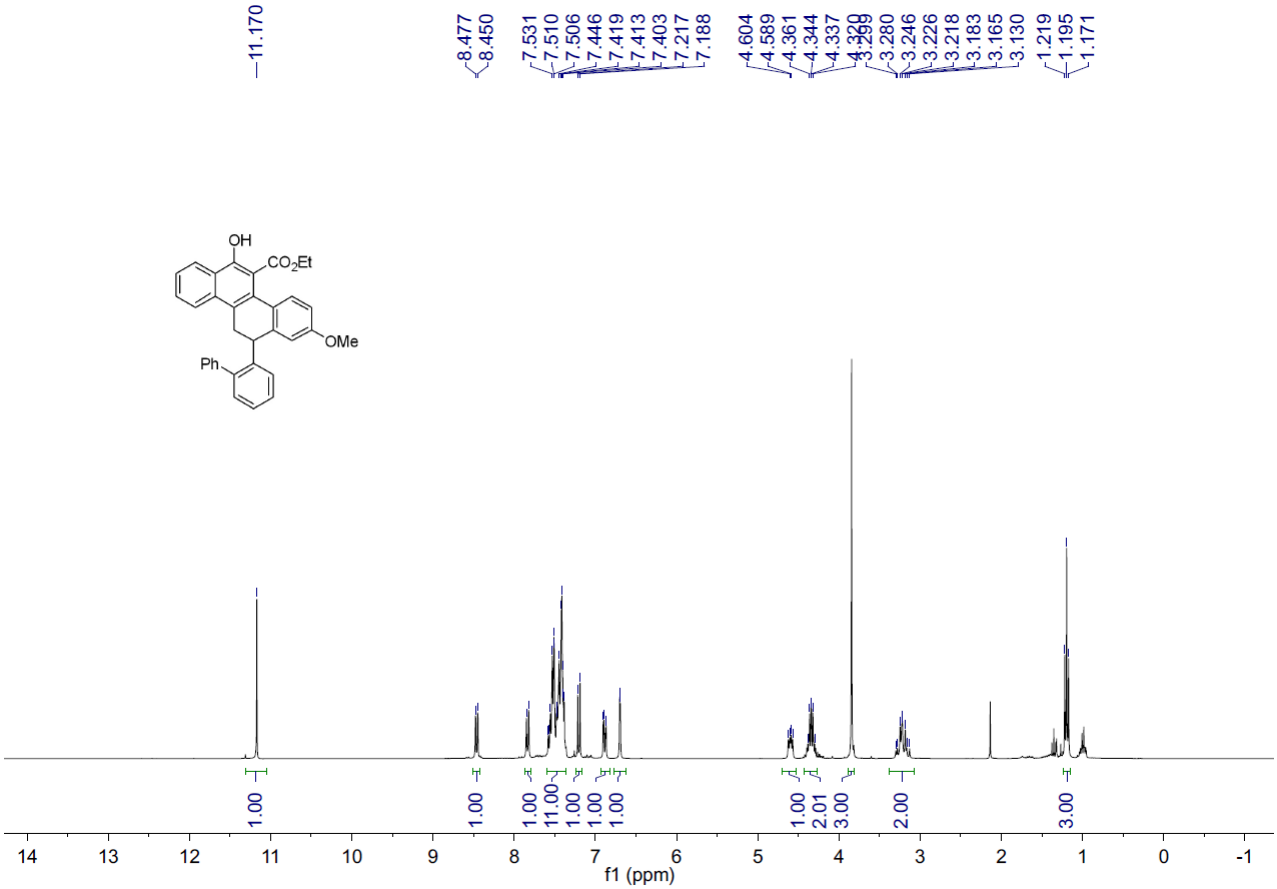
Supplementary Fig. 74 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 30.



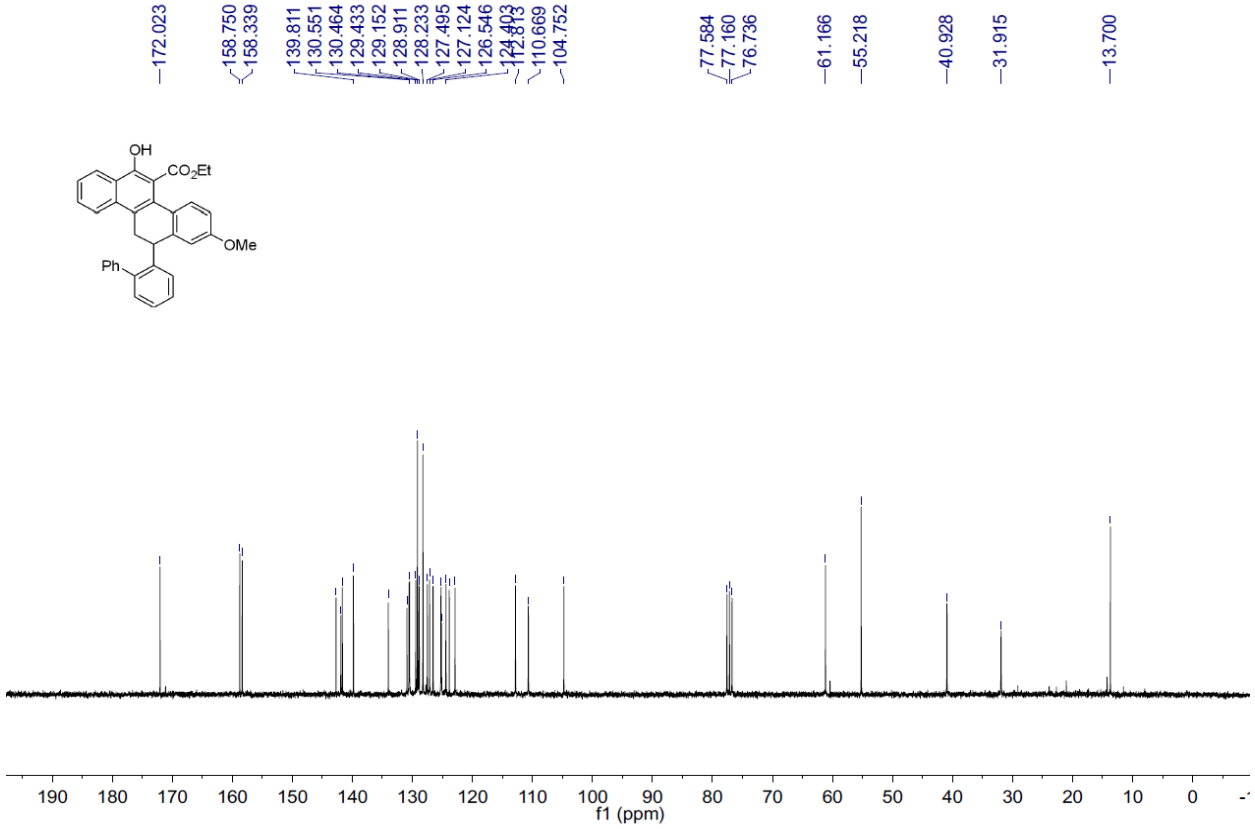
Supplementary Fig. 75 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum for 31.



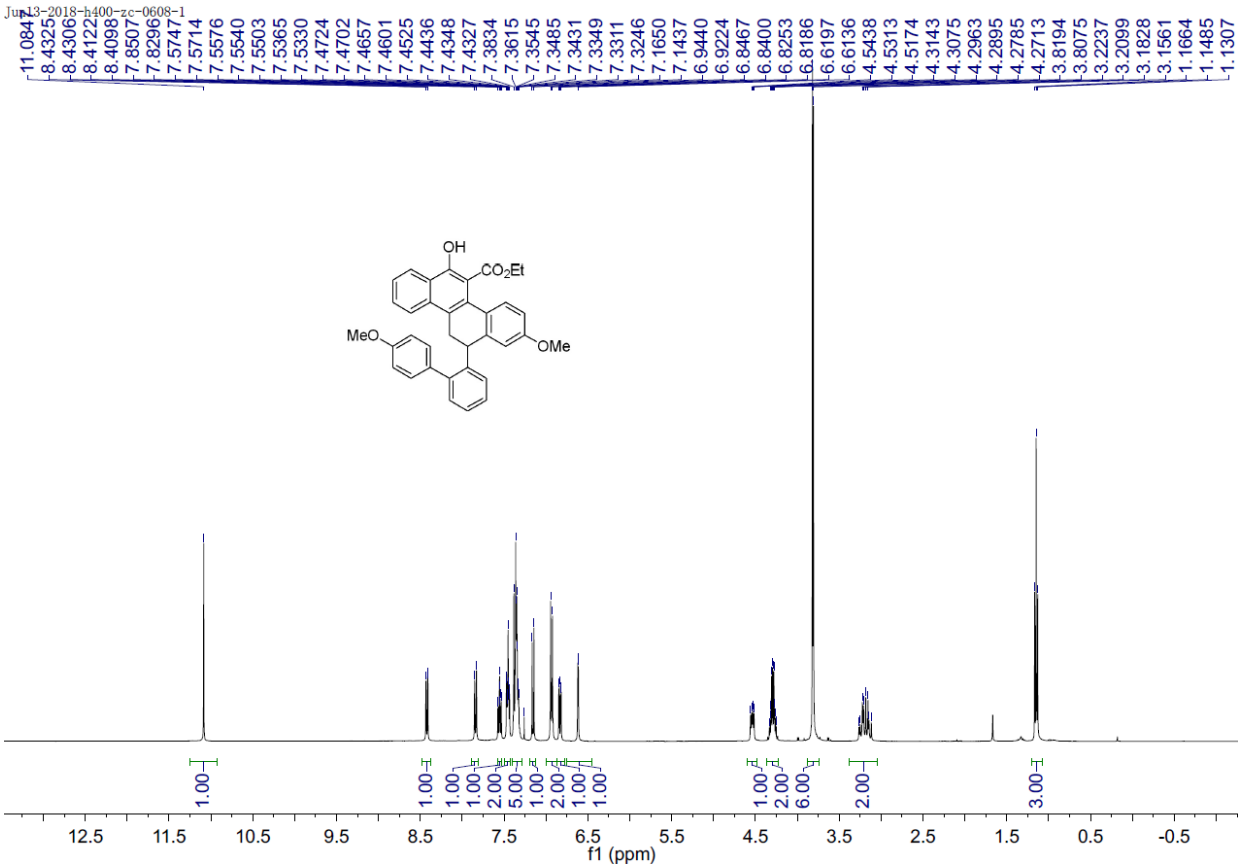
Supplementary Fig. 76 ^{13}C NMR (75 MHz, $CDCl_3$) spectrum for 31.



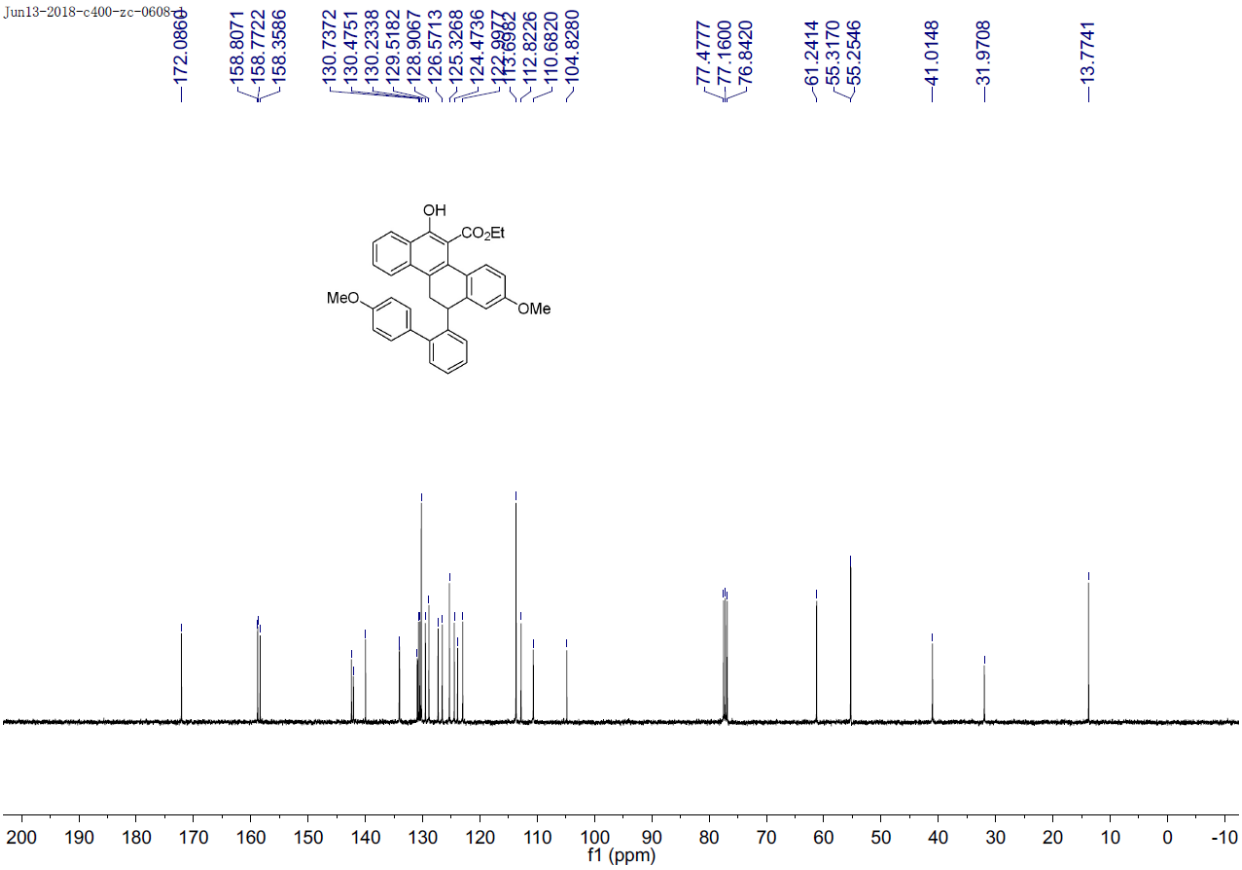
Supplementary Fig. 77 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum for 32.



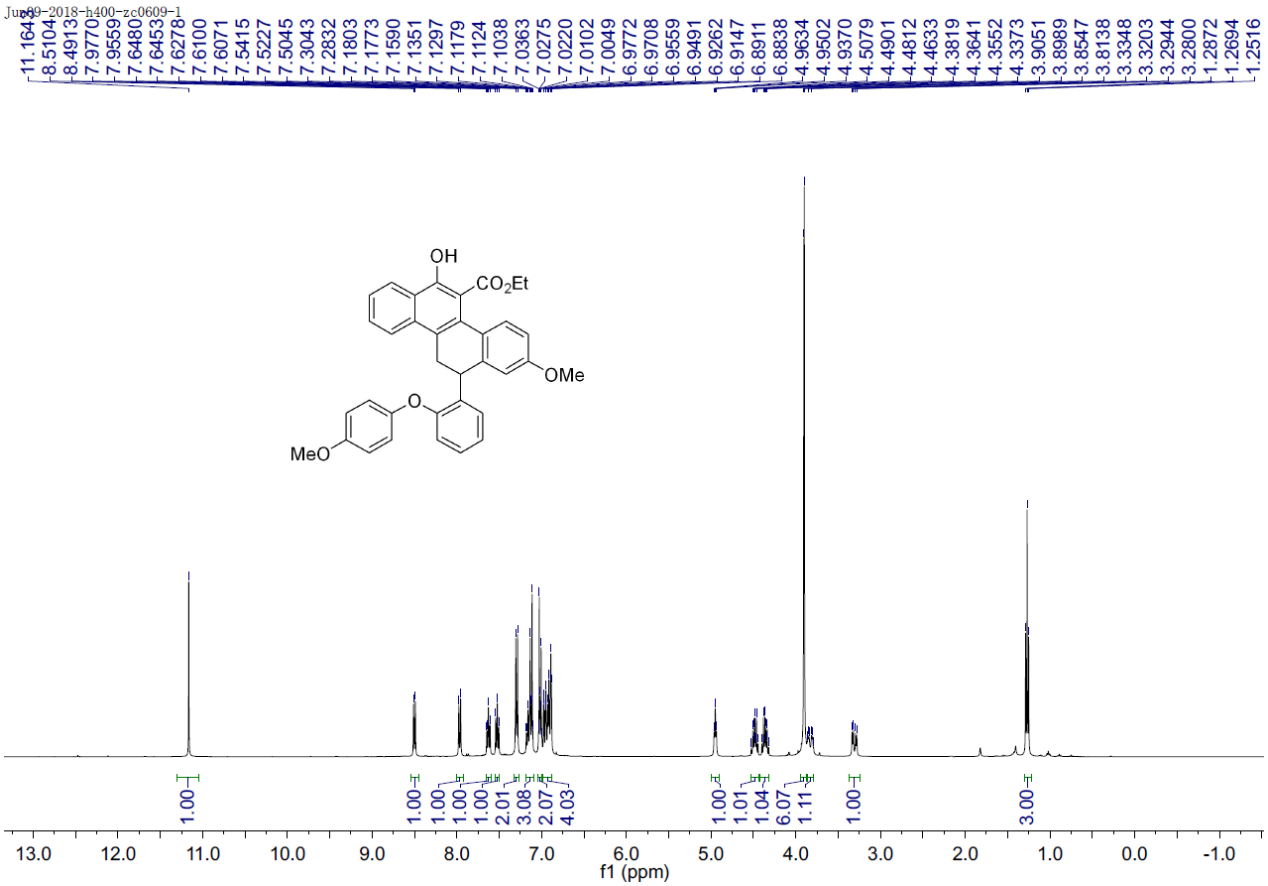
Supplementary Fig. 78 ^{13}C NMR (75 MHz, $CDCl_3$) spectrum for 32.



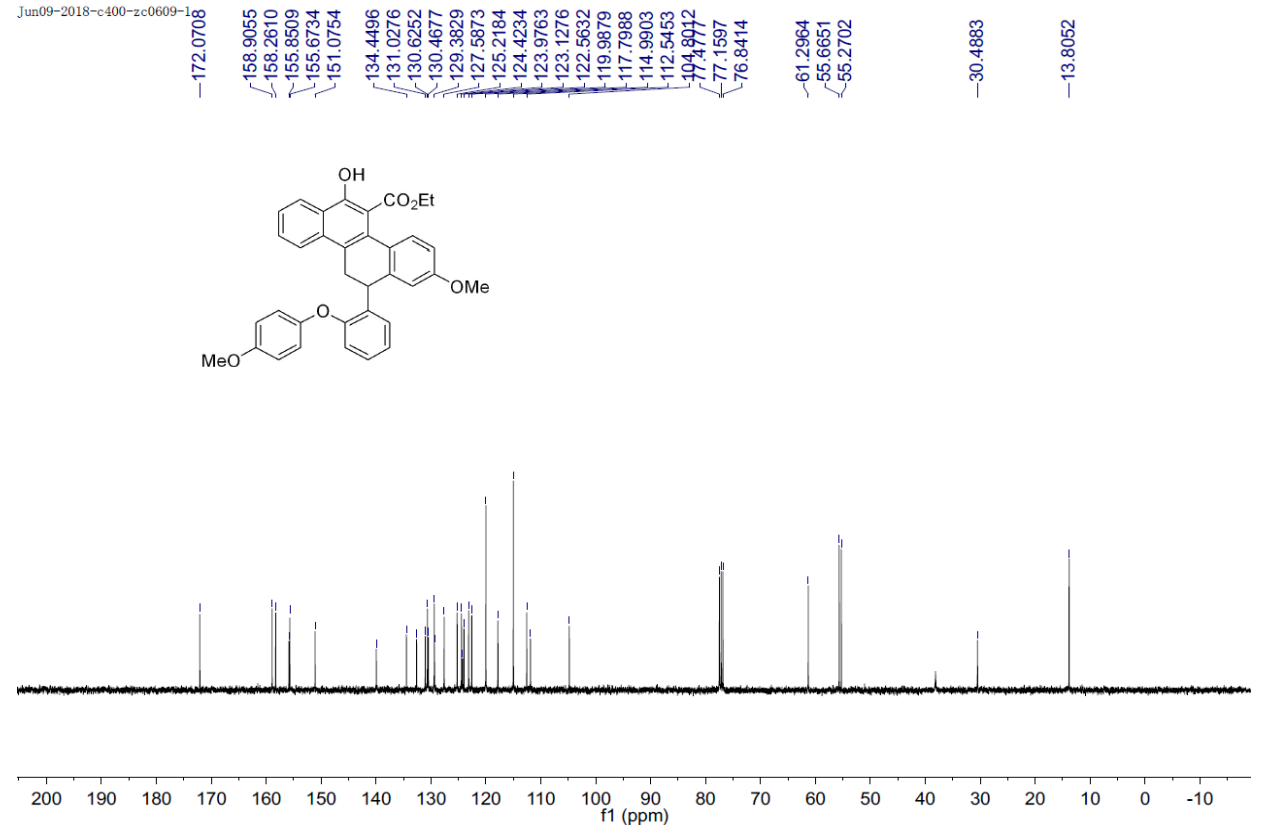
Supplementary Fig. 79 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 33.



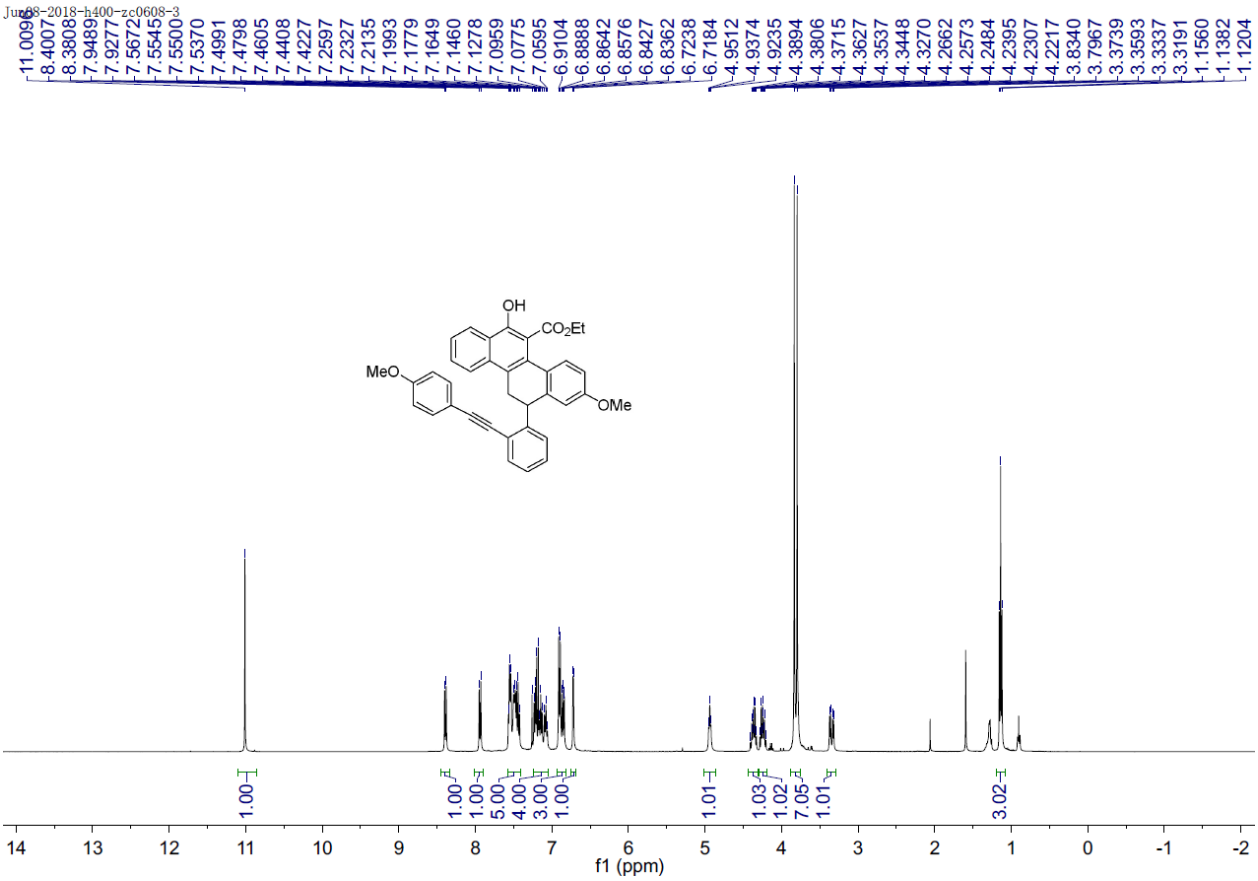
Supplementary Fig. 80 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 33.



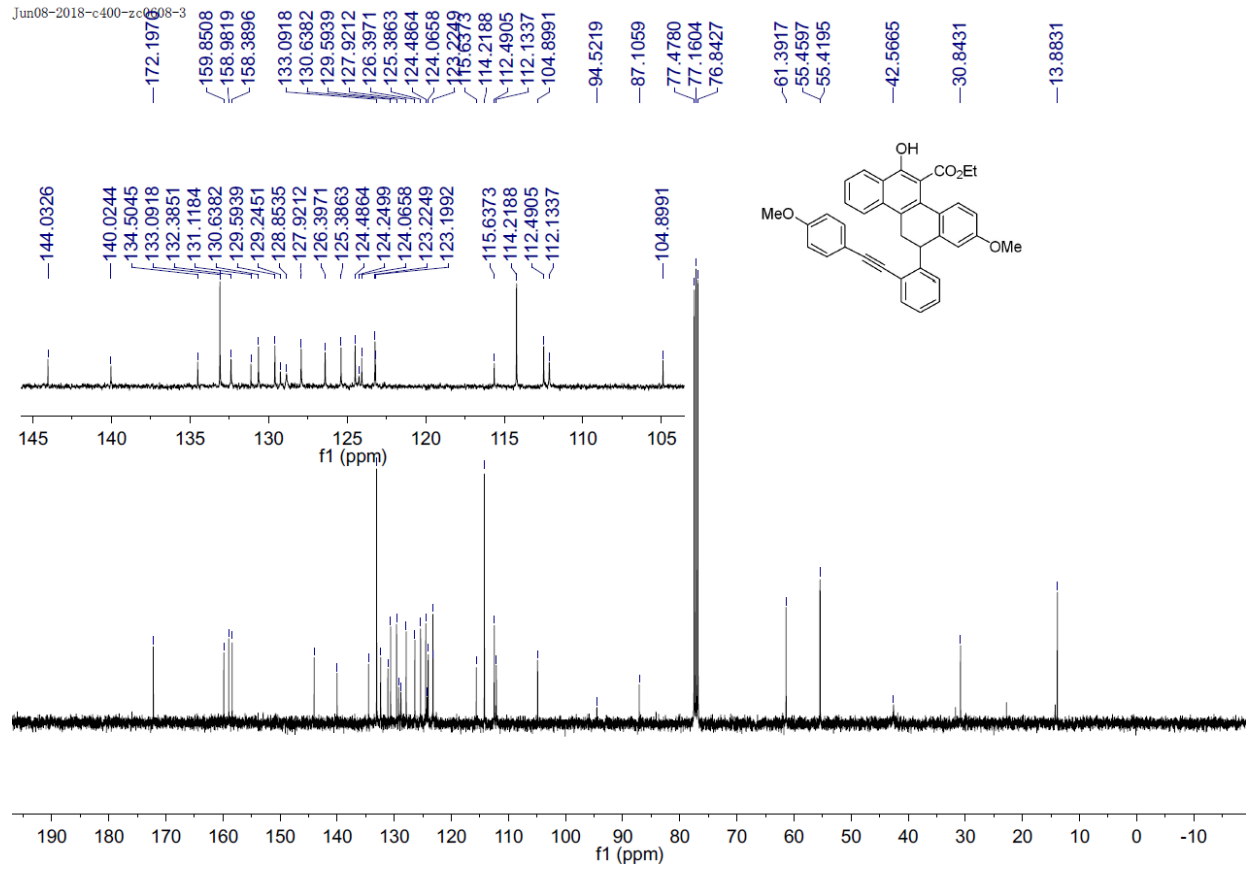
Supplementary Fig. 81 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 34.



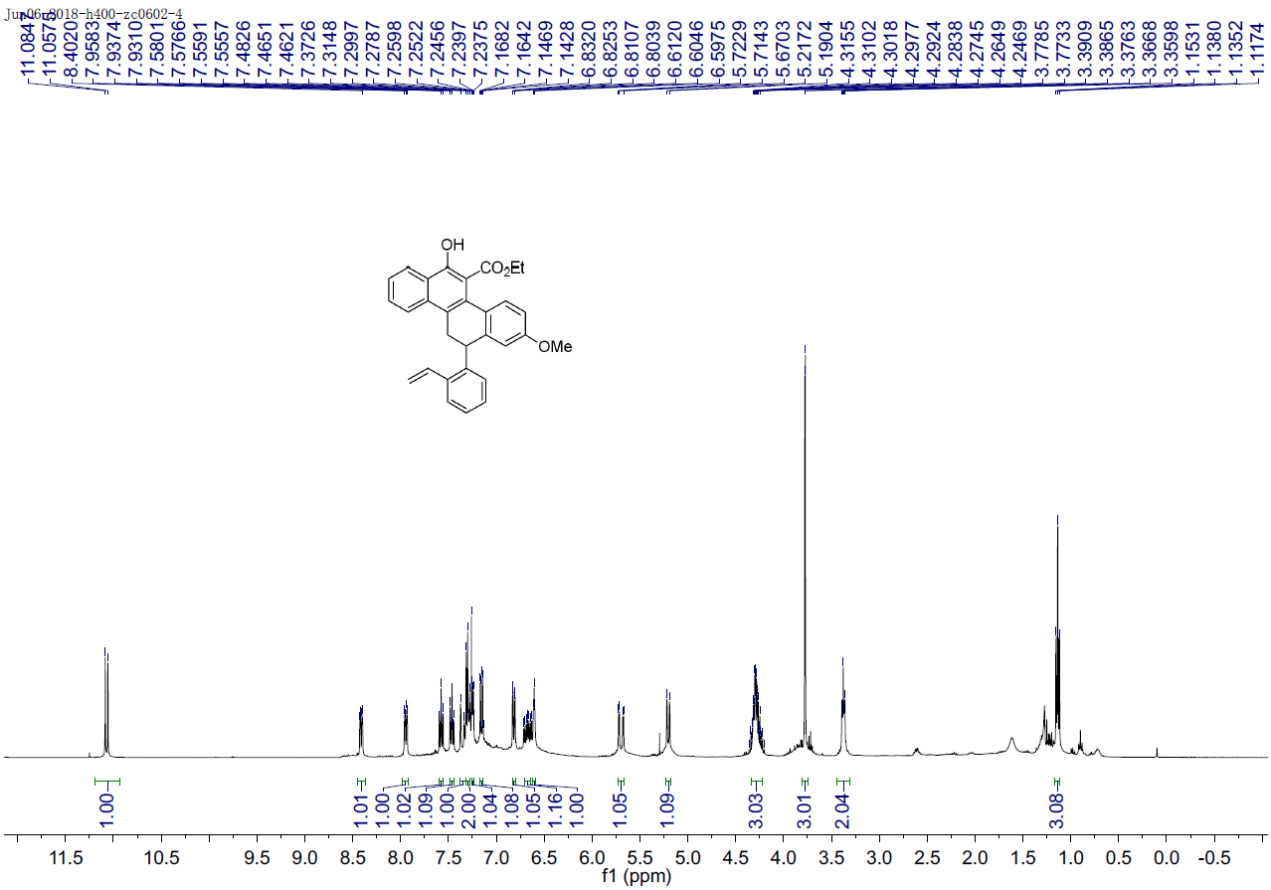
Supplementary Fig. 82 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 34.



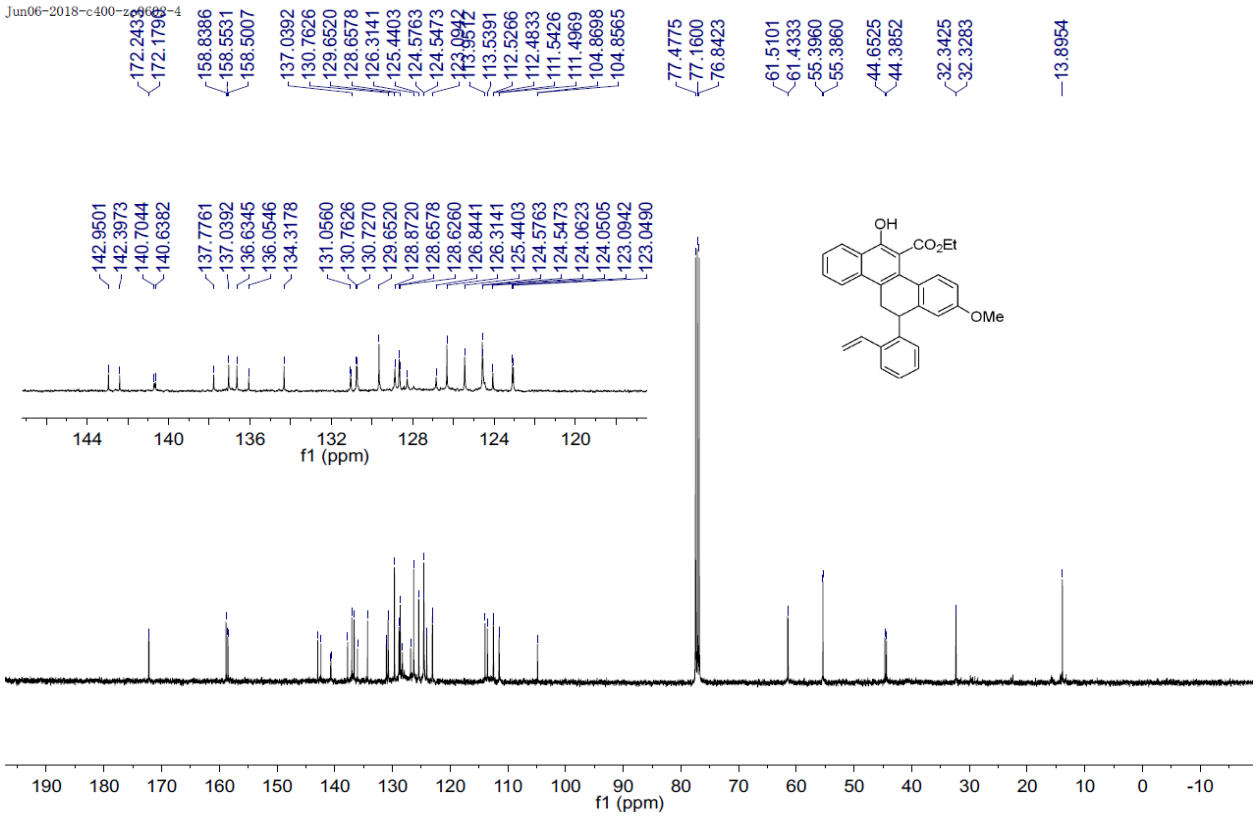
Supplementary Fig. 83 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 35.



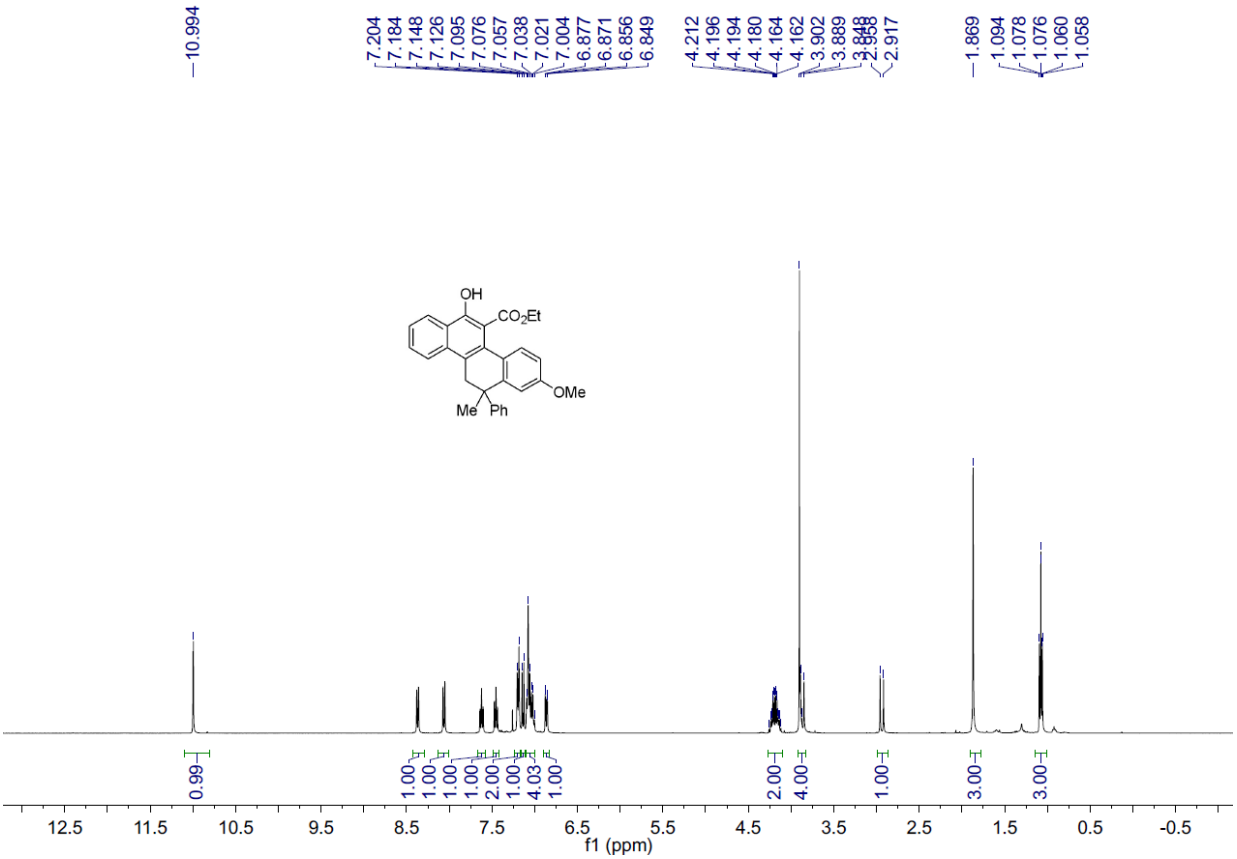
Supplementary Fig. 84 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 35.



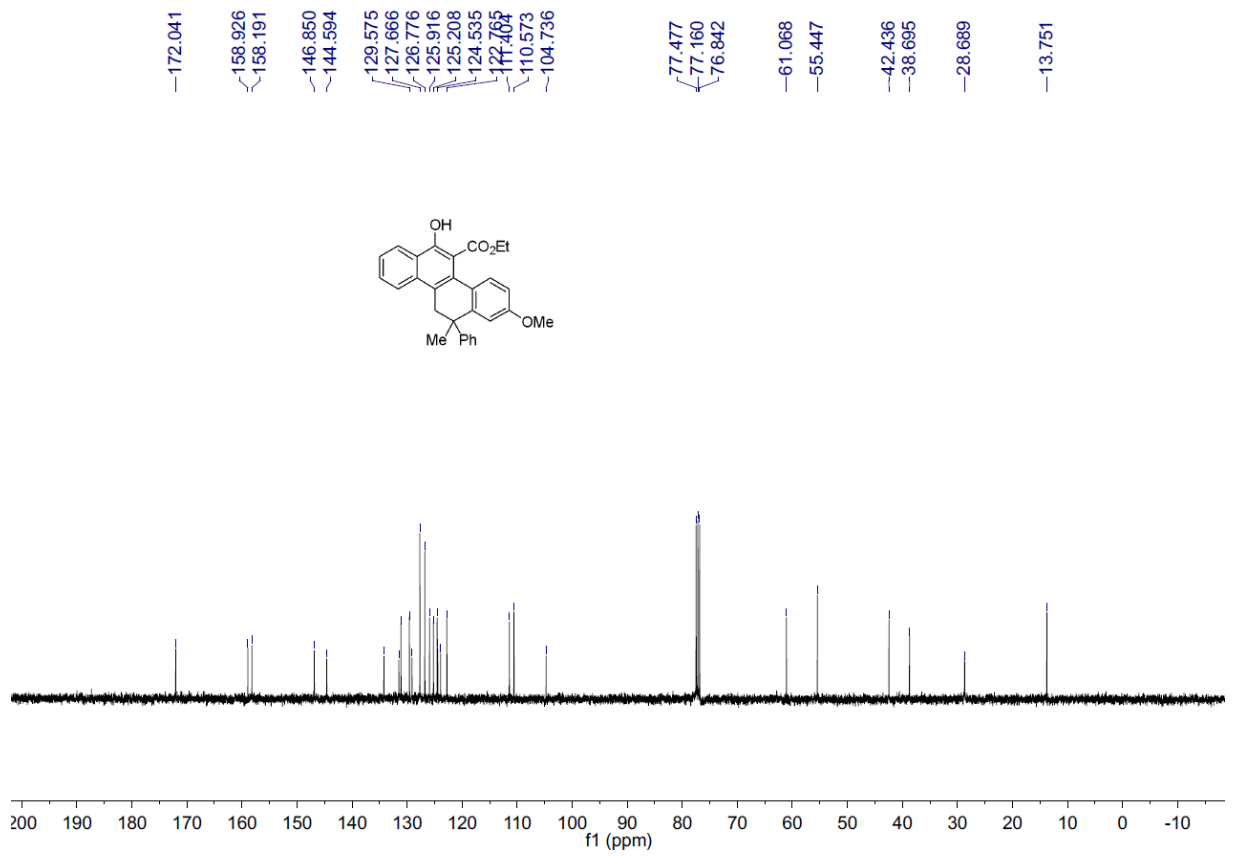
Supplementary Fig. 85 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 36.



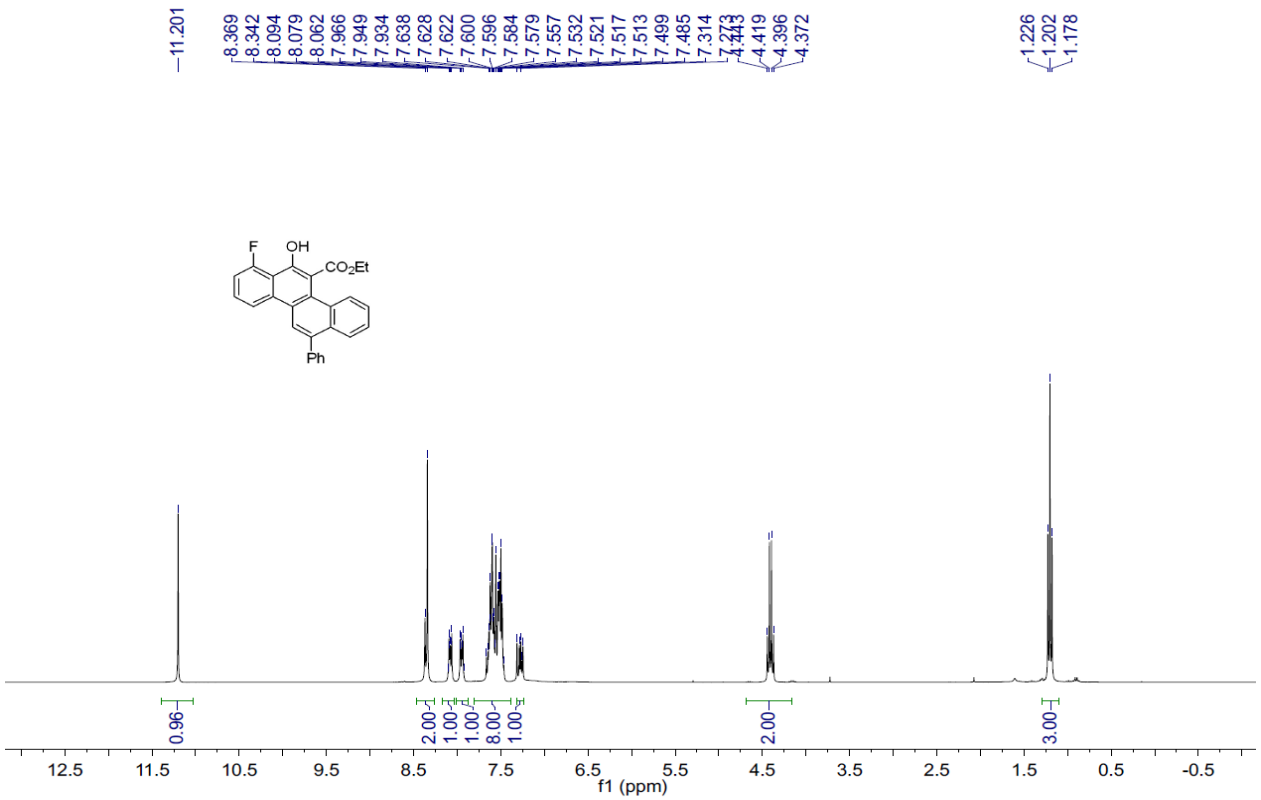
Supplementary Fig. 86 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 36.



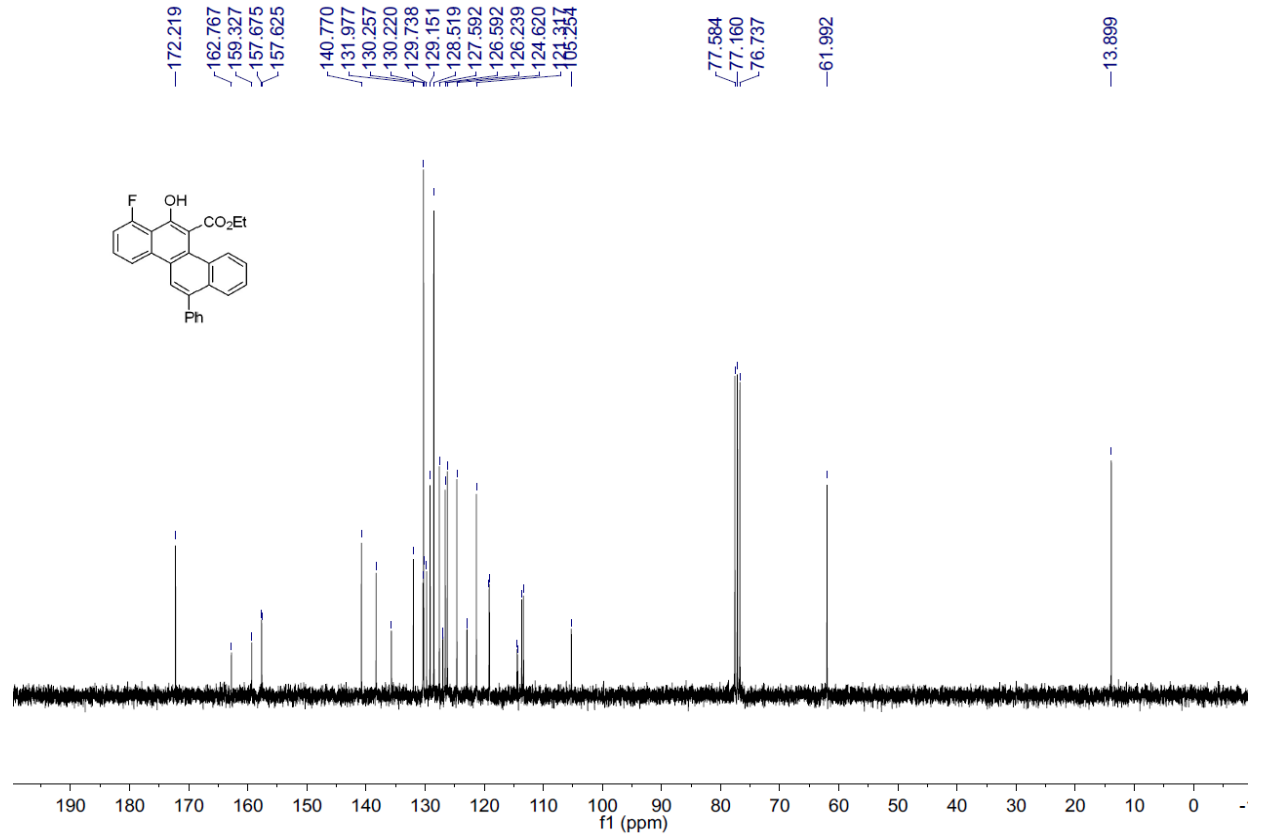
Supplementary Fig. 87 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 37.



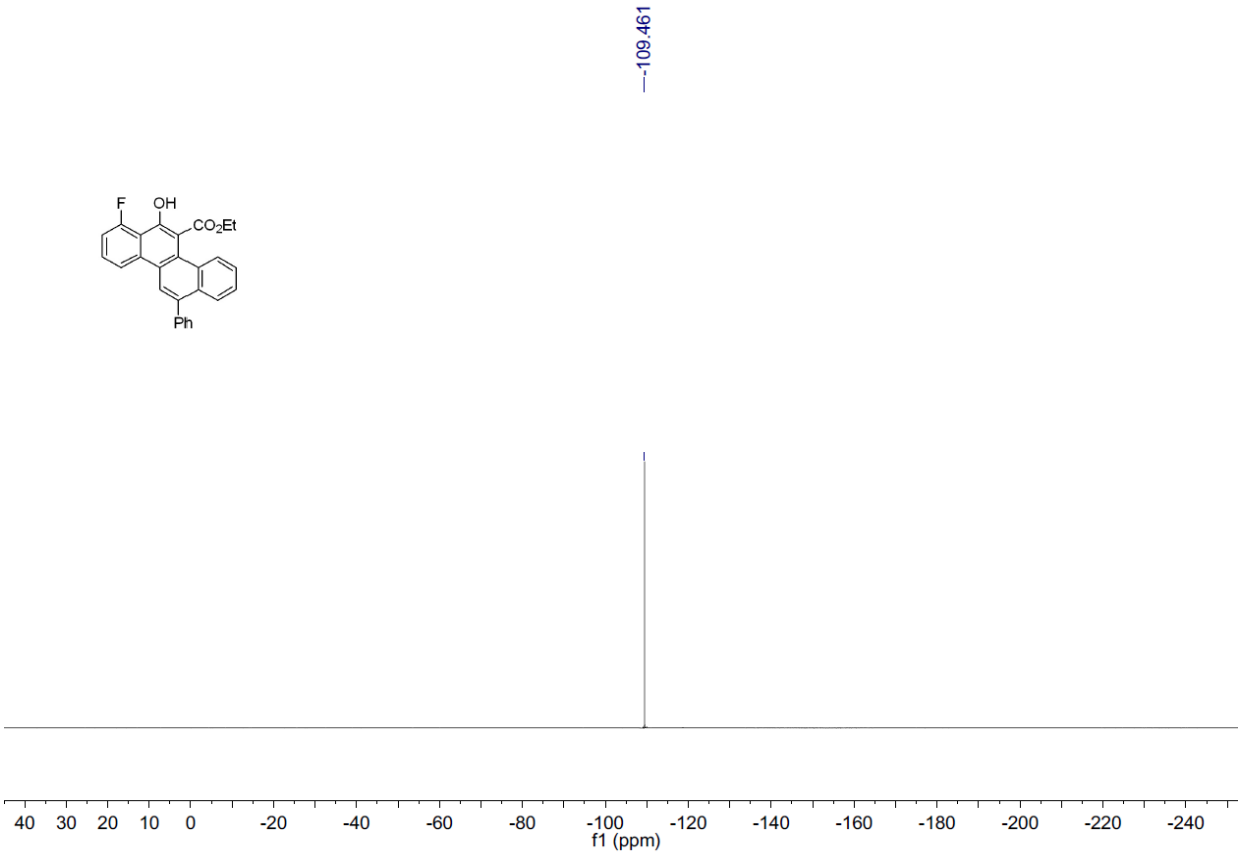
Supplementary Fig. 88 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 37.



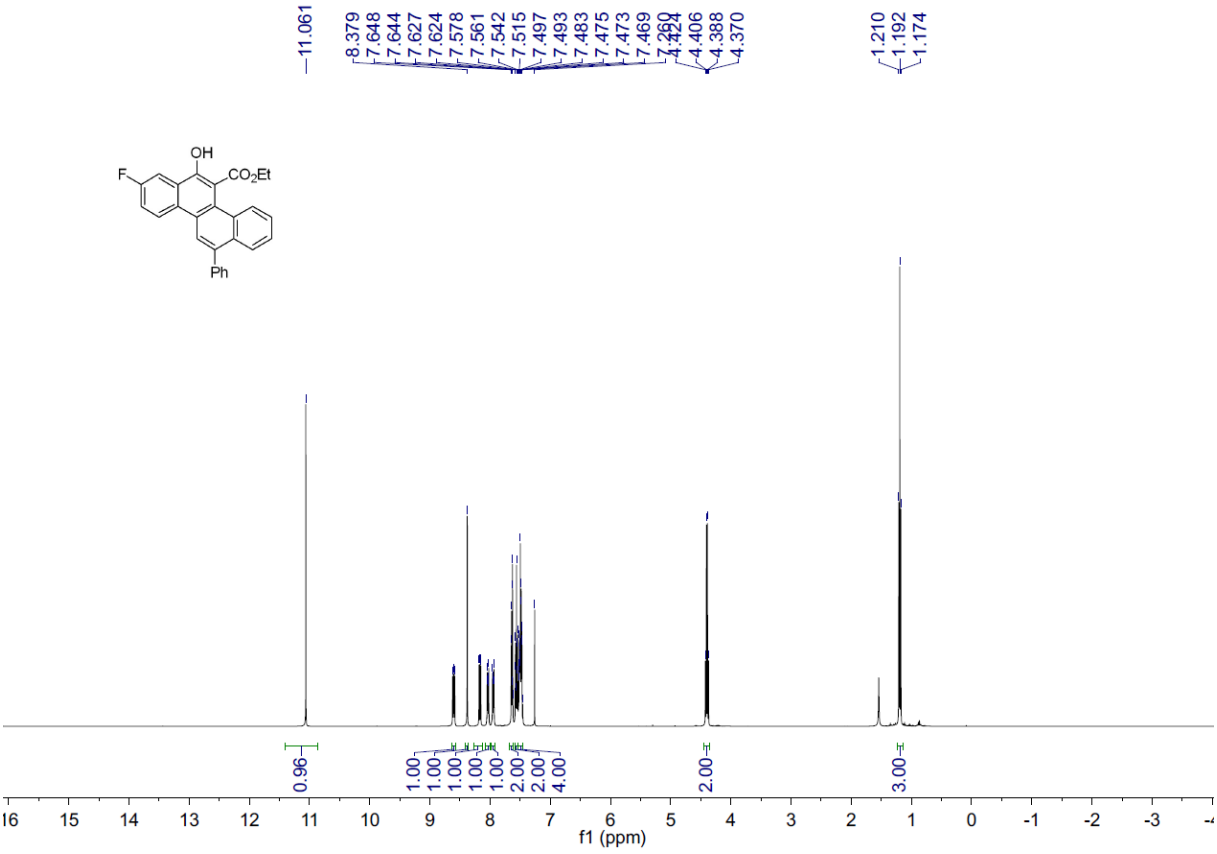
Supplementary Fig. 89 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum for 38.



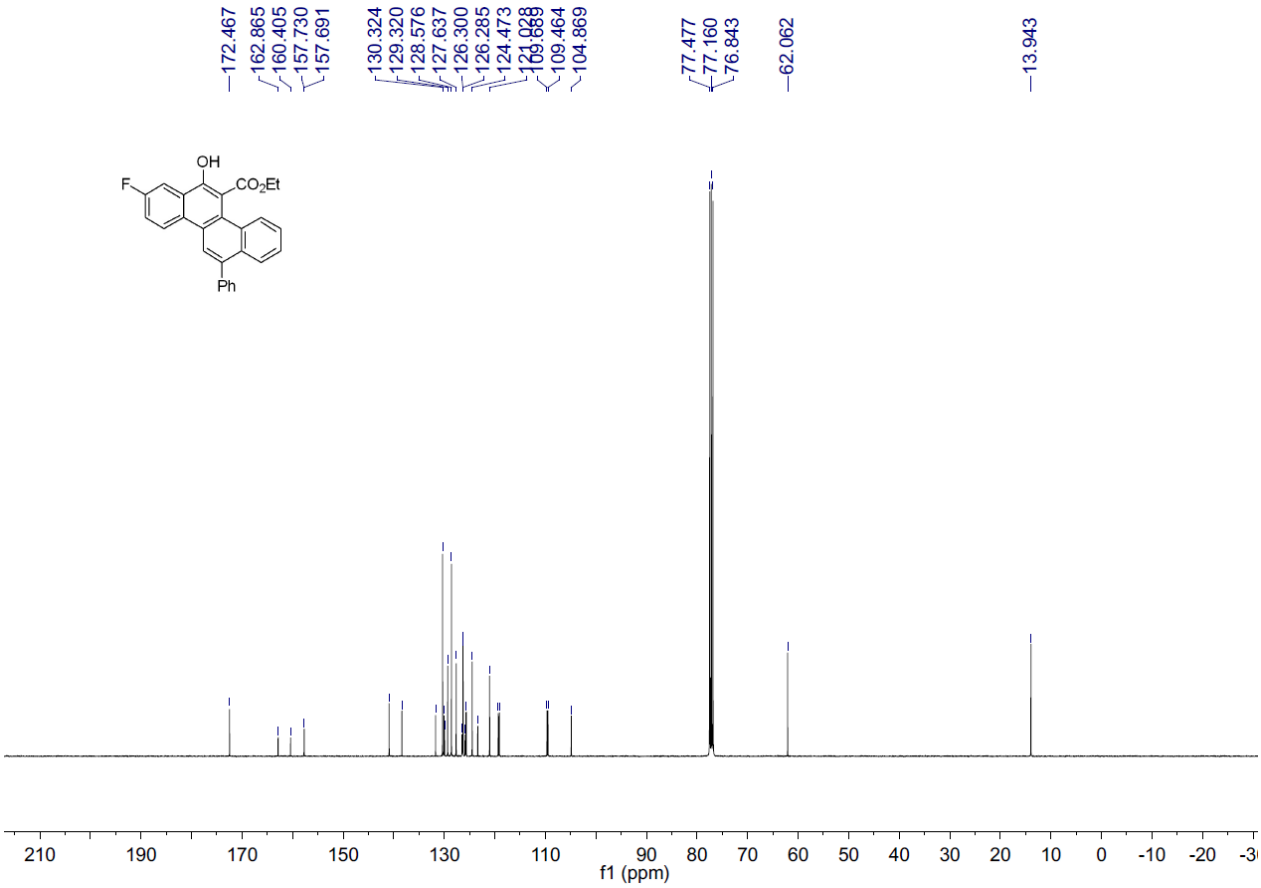
Supplementary Fig. 90 ^{13}C NMR (75 MHz, $CDCl_3$) spectrum for 38.



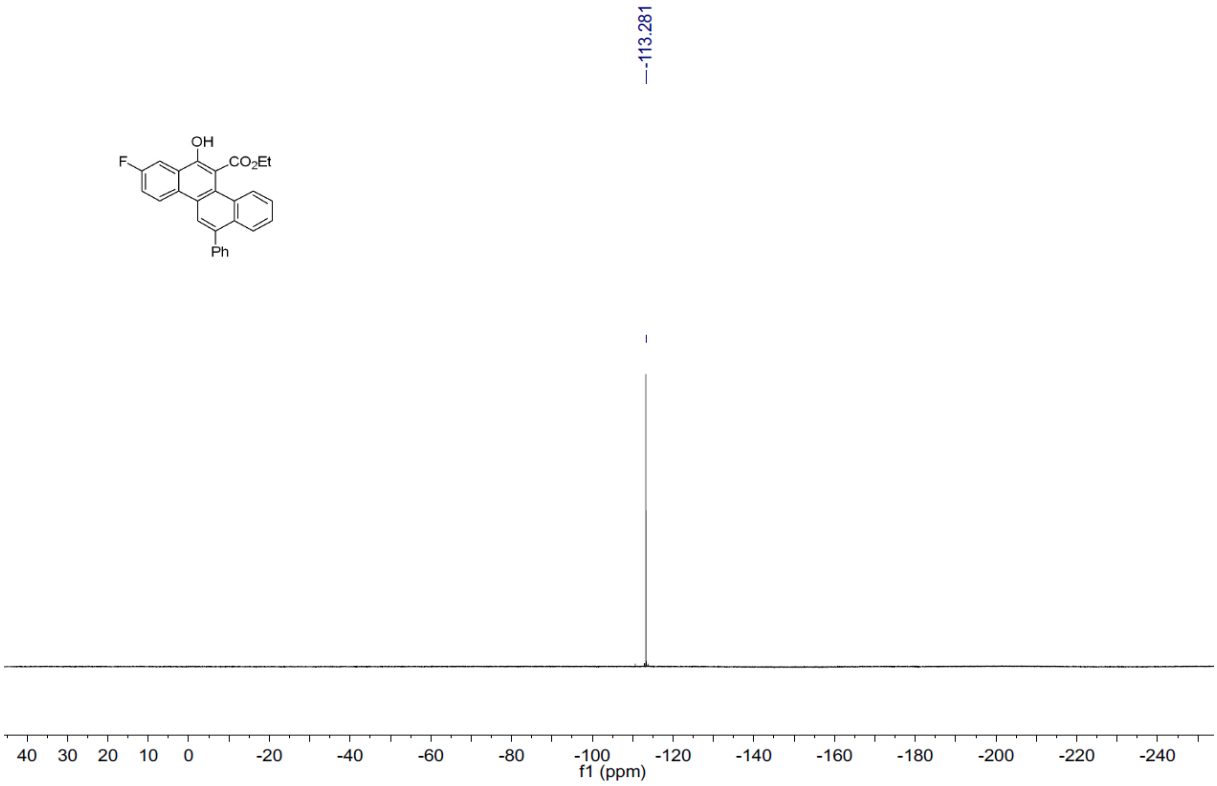
Supplementary Fig. 91 ^{19}F NMR (283 MHz, $CDCl_3$) spectrum for 38.



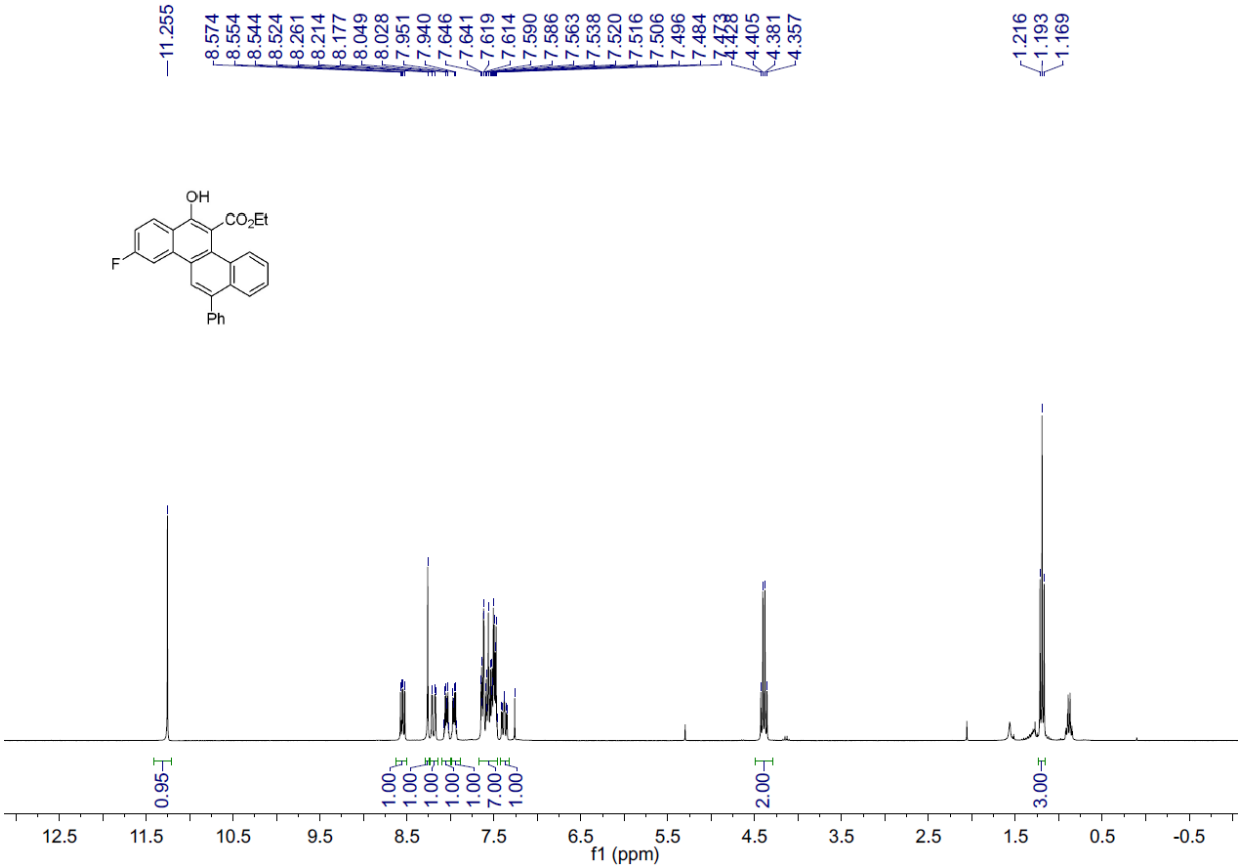
Supplementary Fig. 92 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 39.



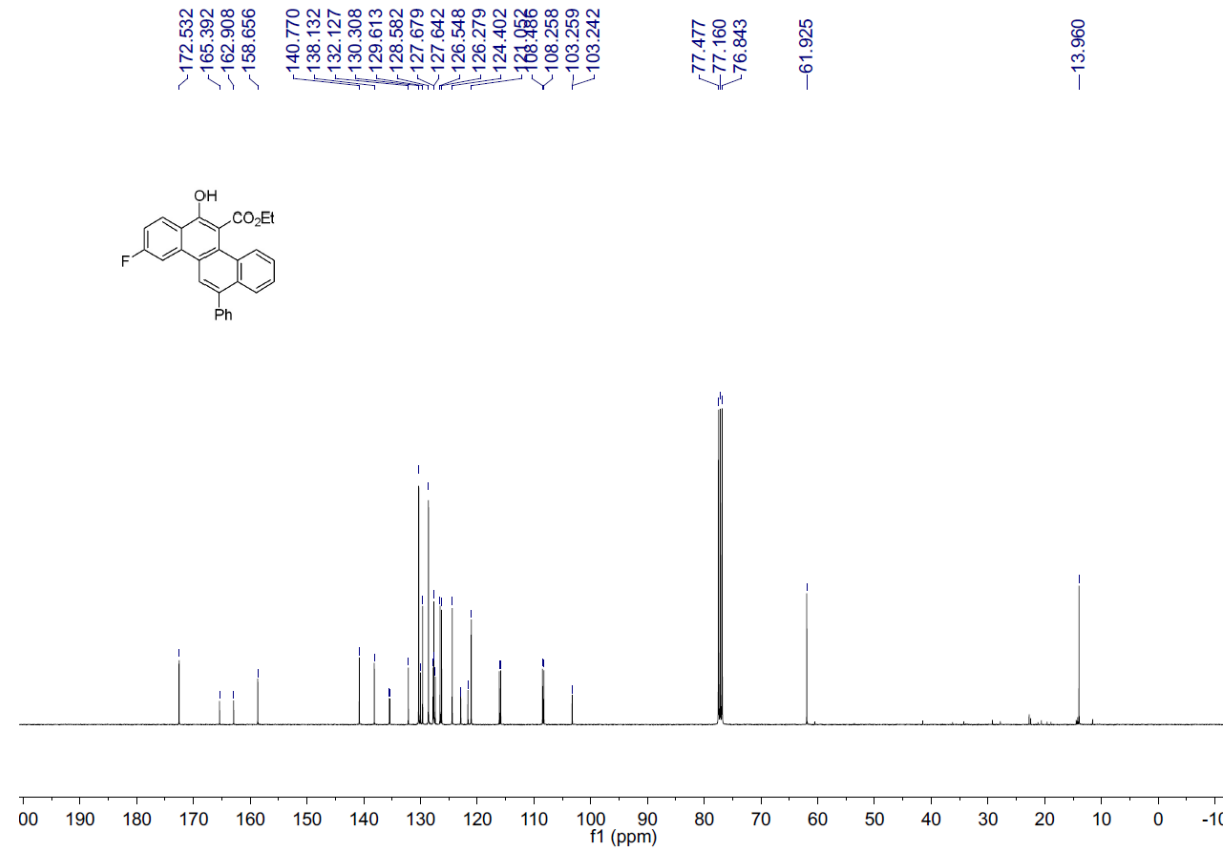
Supplementary Fig. 93 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 39.



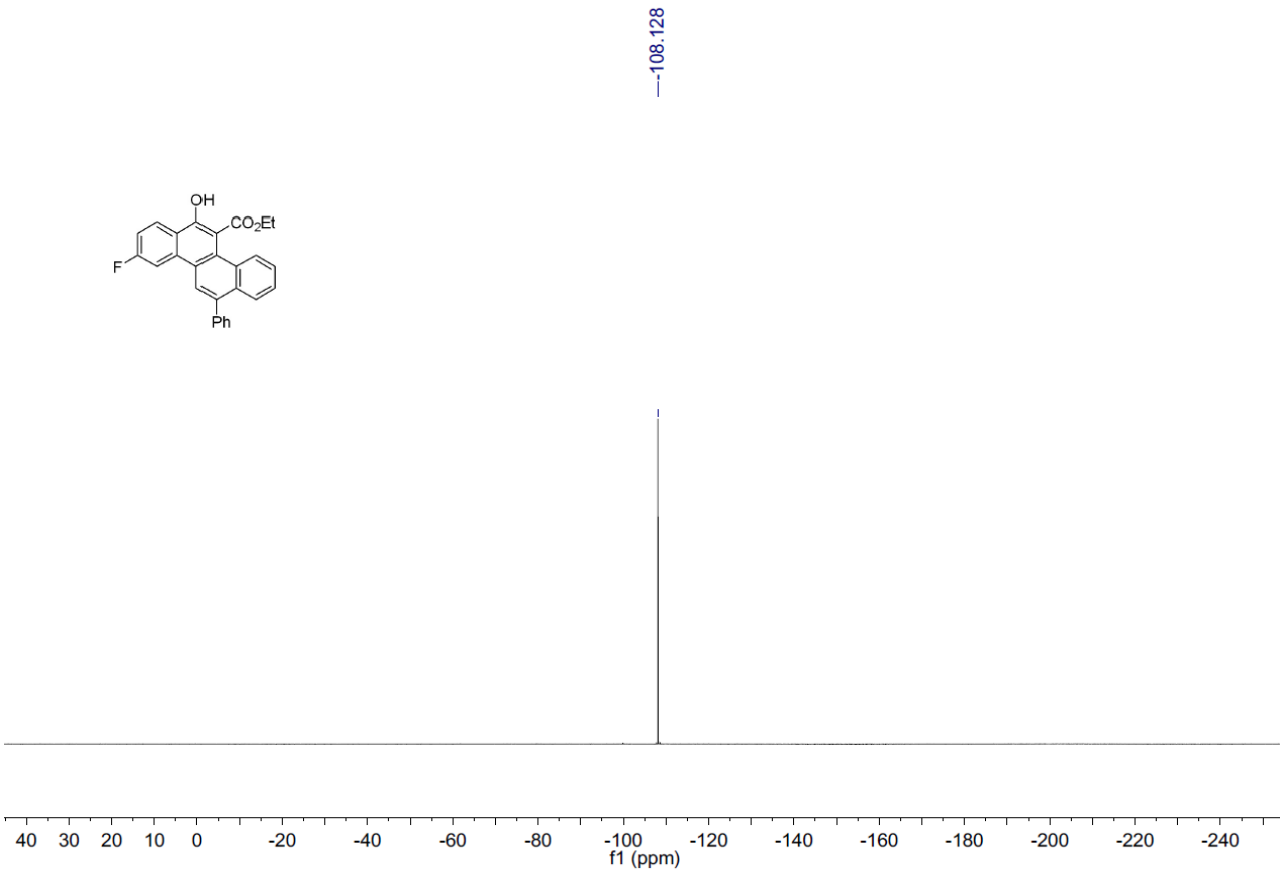
Supplementary Fig. 94 ^{19}F NMR (283 MHz, $CDCl_3$) spectrum for 39.



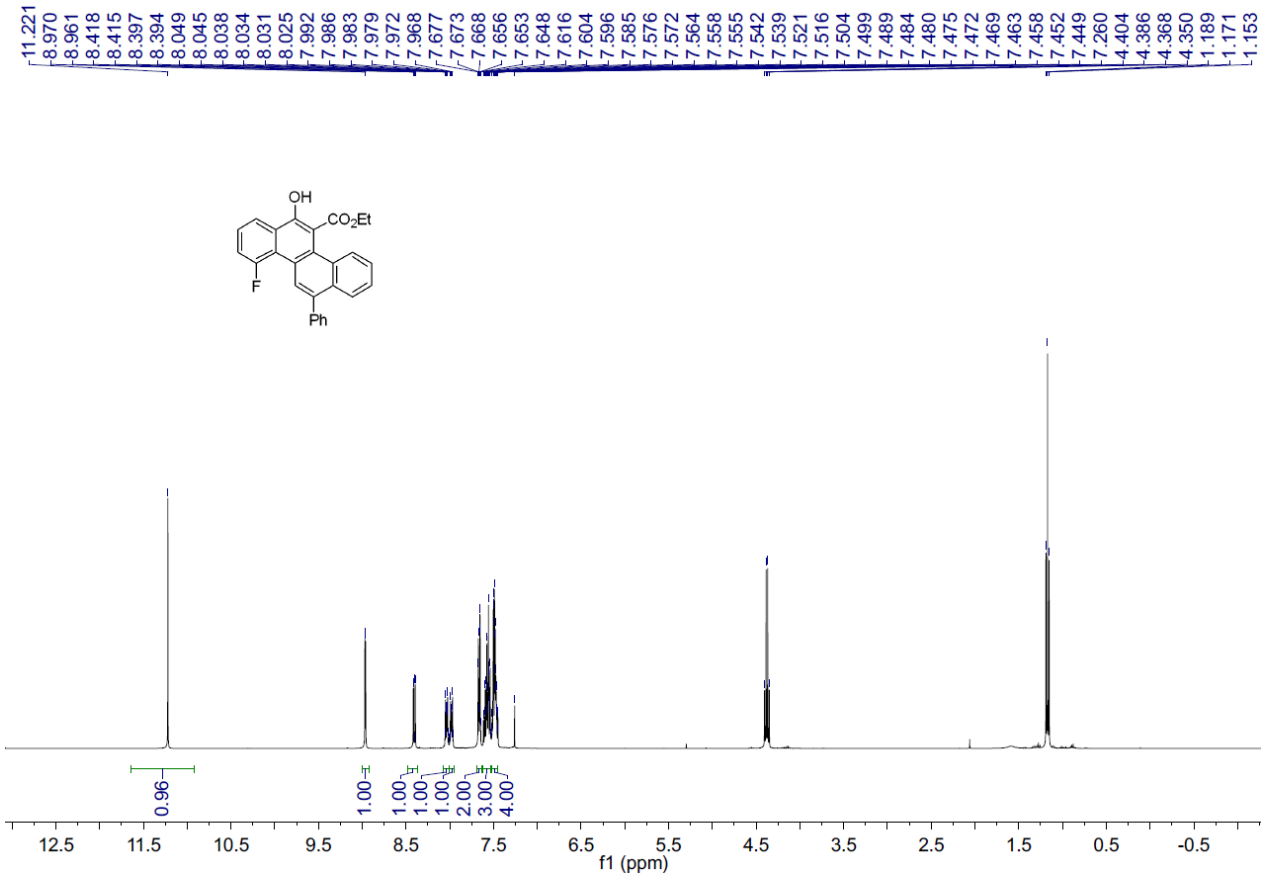
Supplementary Fig. 95 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum for 40.



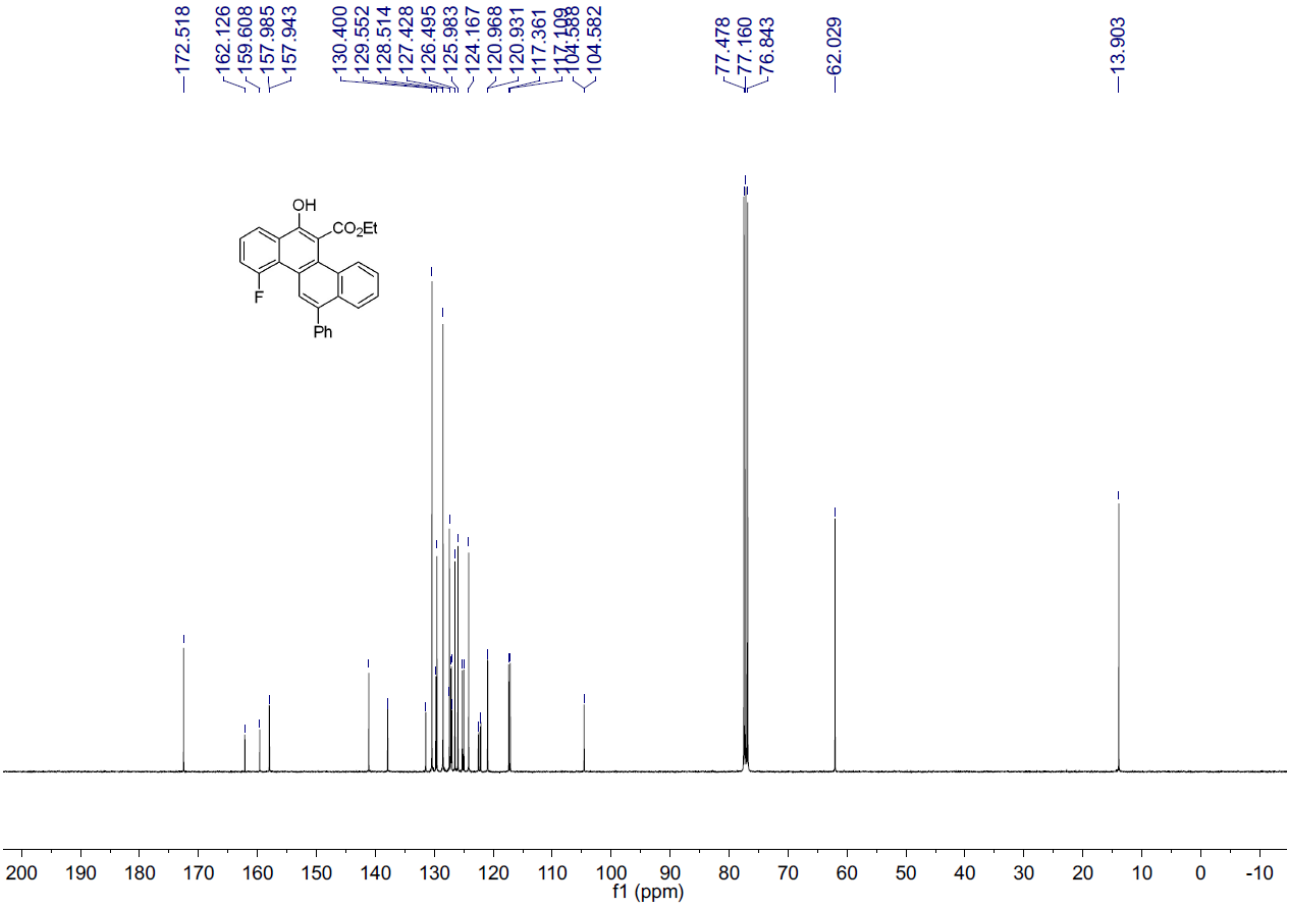
Supplementary Fig. 96 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 40.



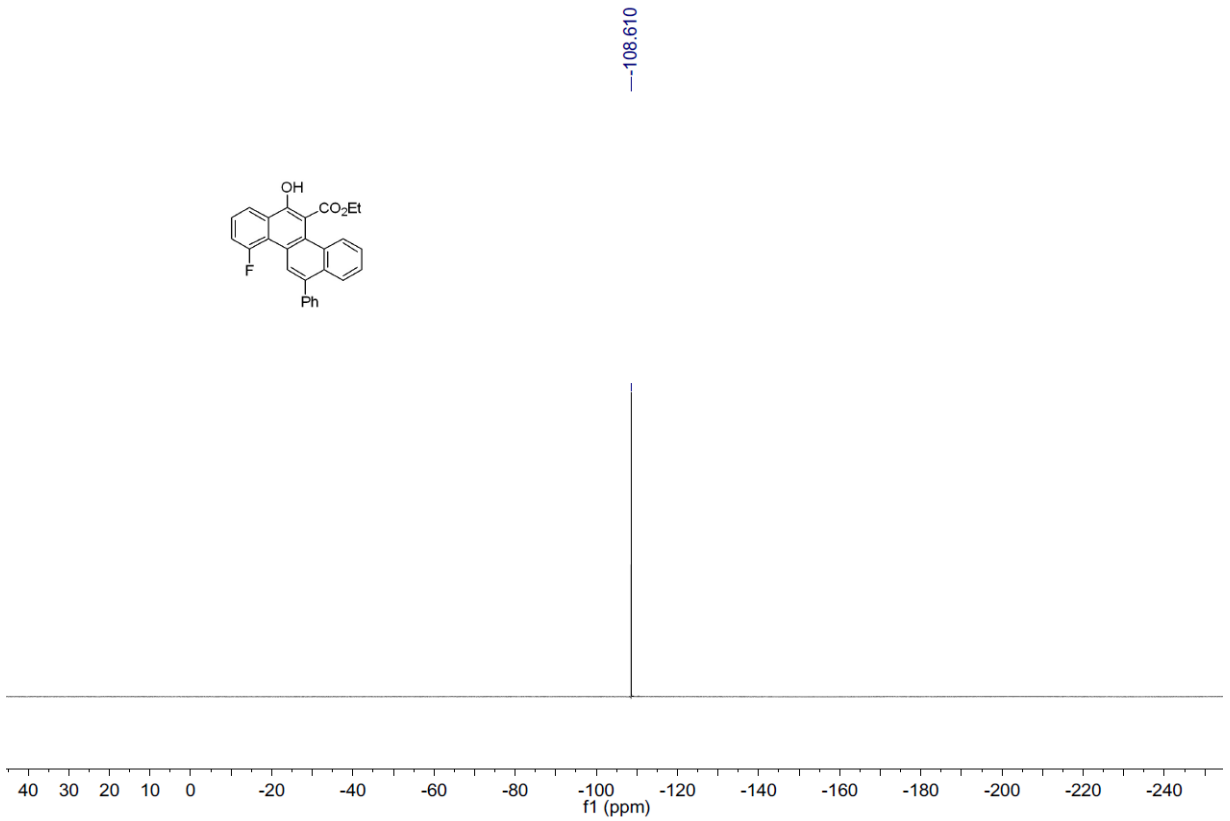
Supplementary Fig. 97 ^{19}F NMR (283 MHz, $CDCl_3$) spectrum for 40.



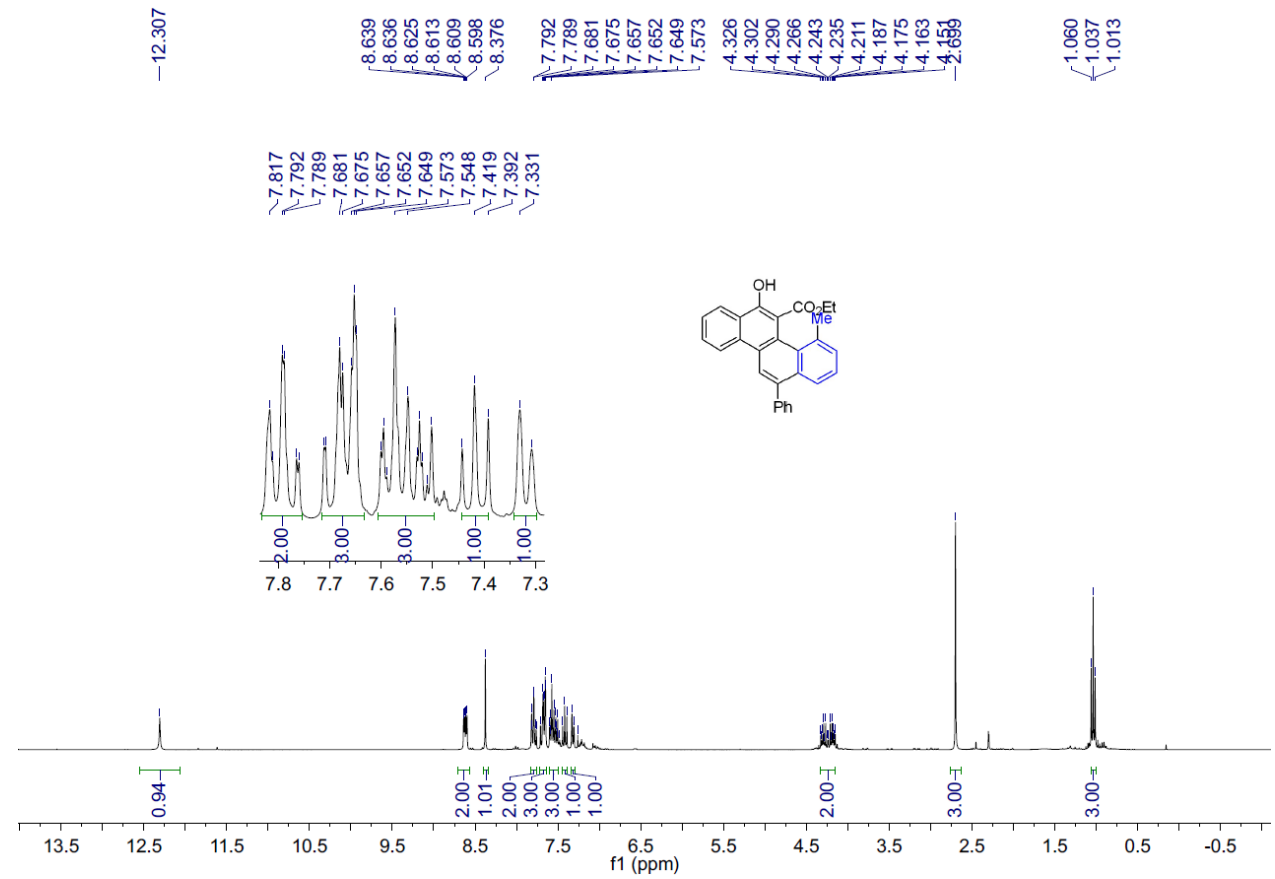
Supplementary Fig. 98 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 41.



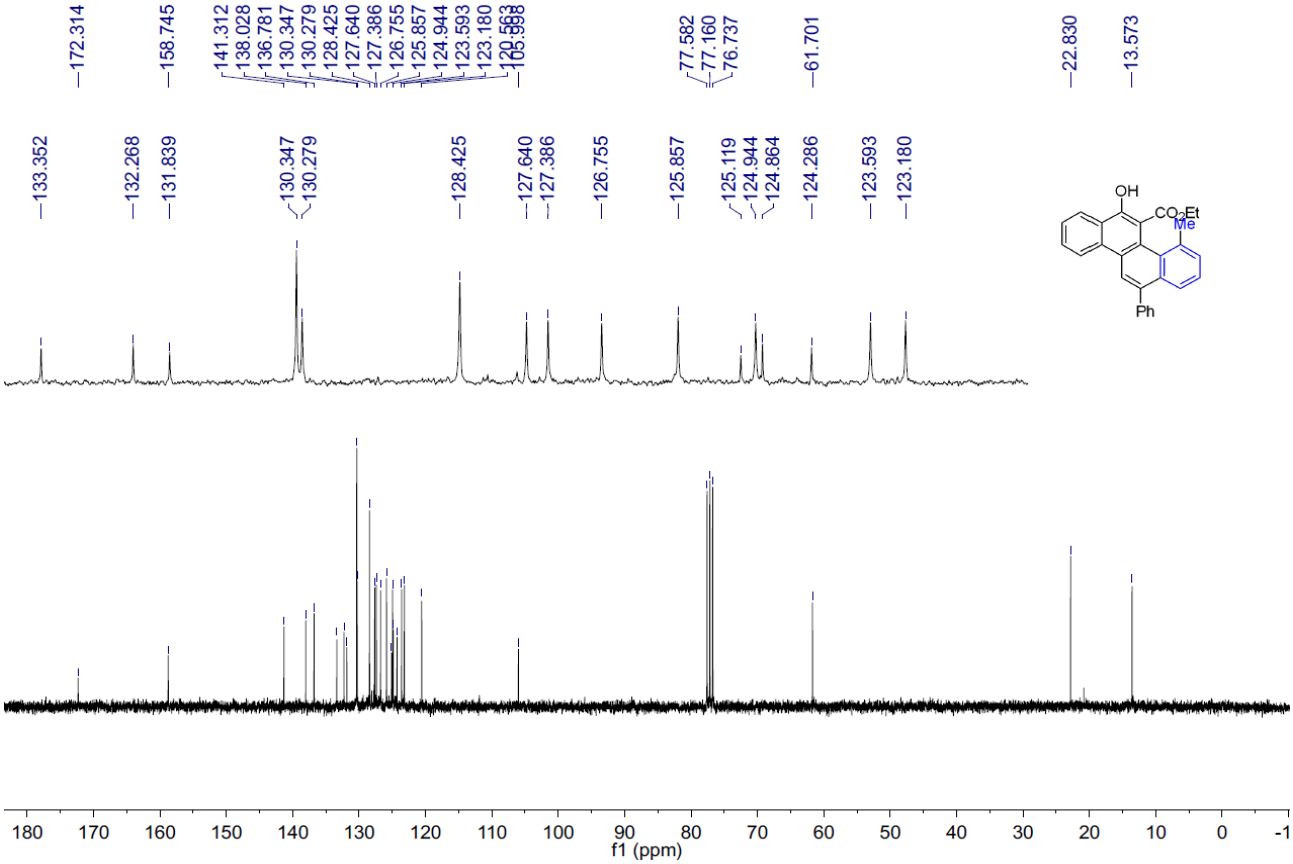
Supplementary Fig. 99 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 41.



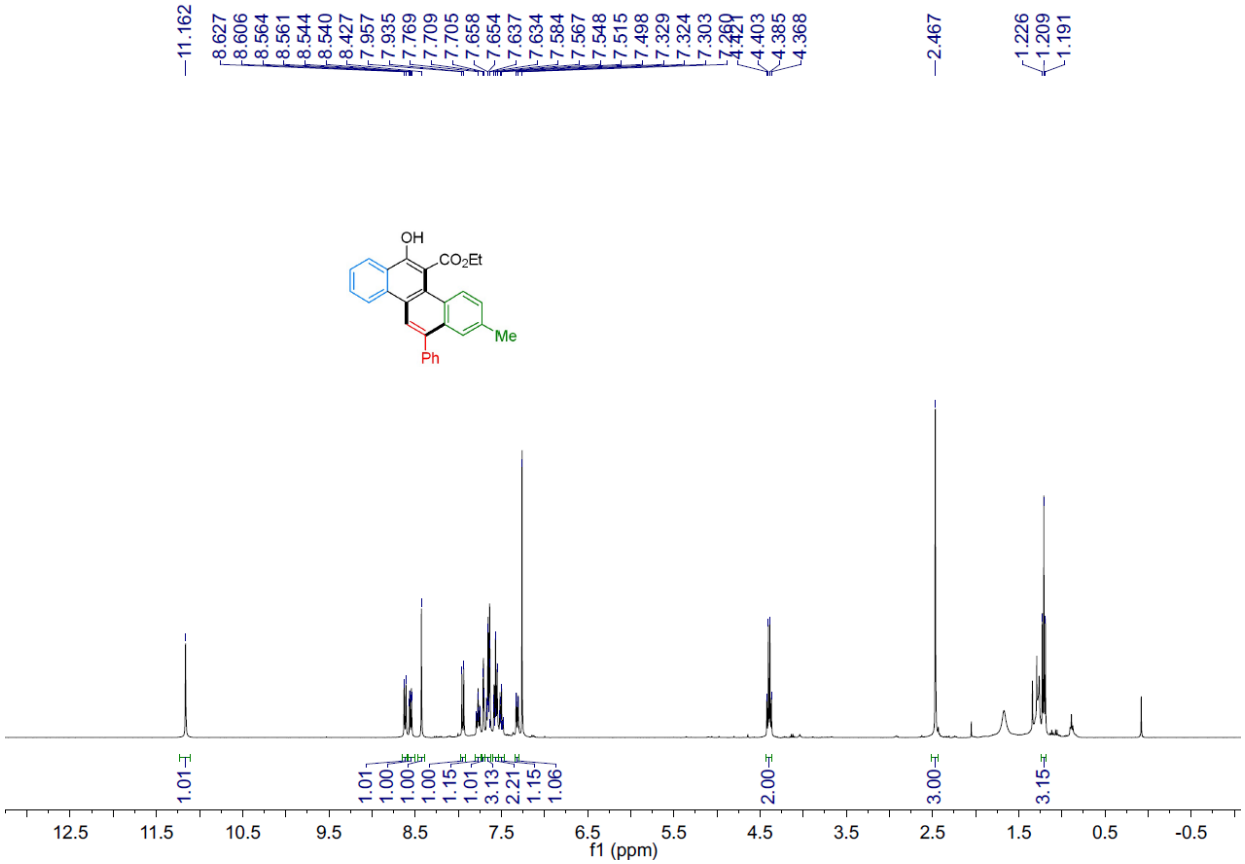
Supplementary Fig. 100 ^{19}F NMR (283 MHz, $CDCl_3$) spectrum for 41.



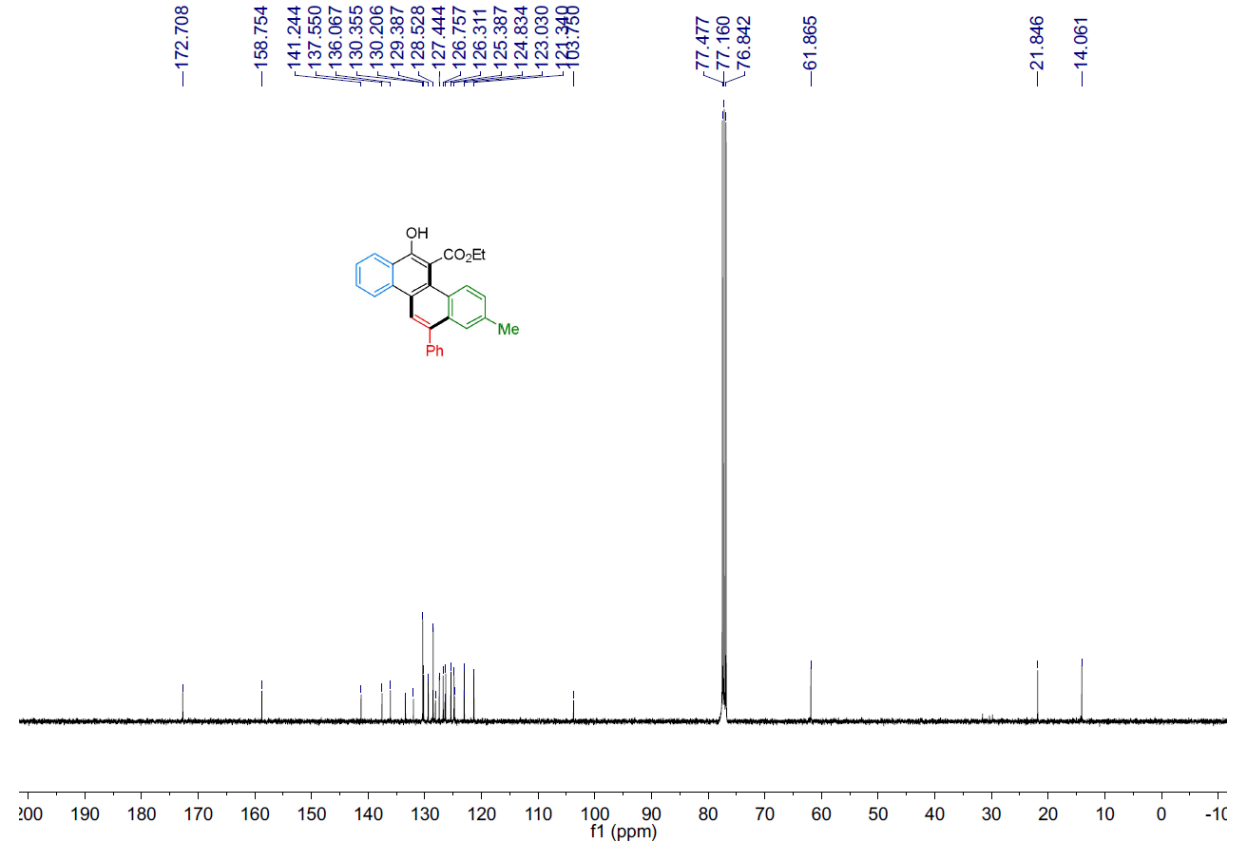
Supplementary Fig. 101 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum for 42.



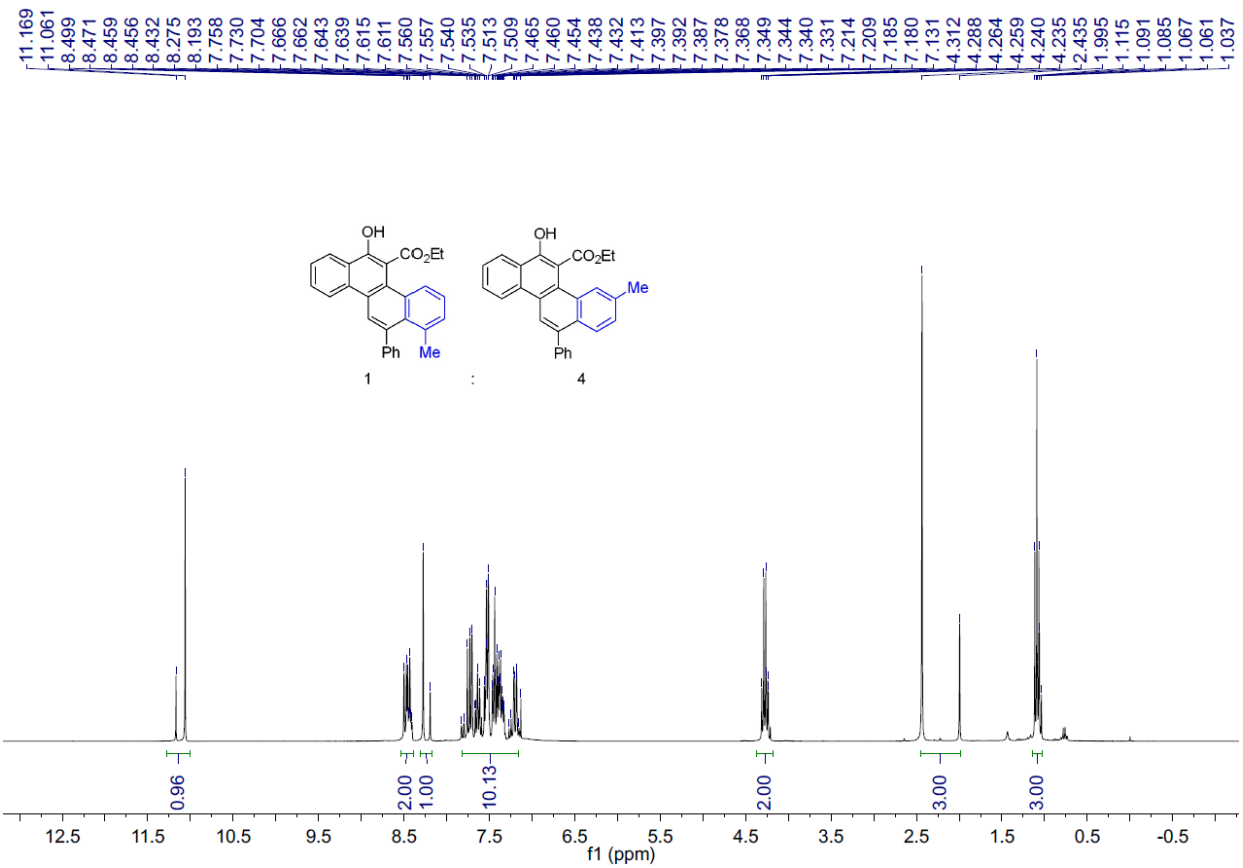
Supplementary Fig. 102 ^{13}C NMR (75 MHz, $CDCl_3$) spectrum for 42.



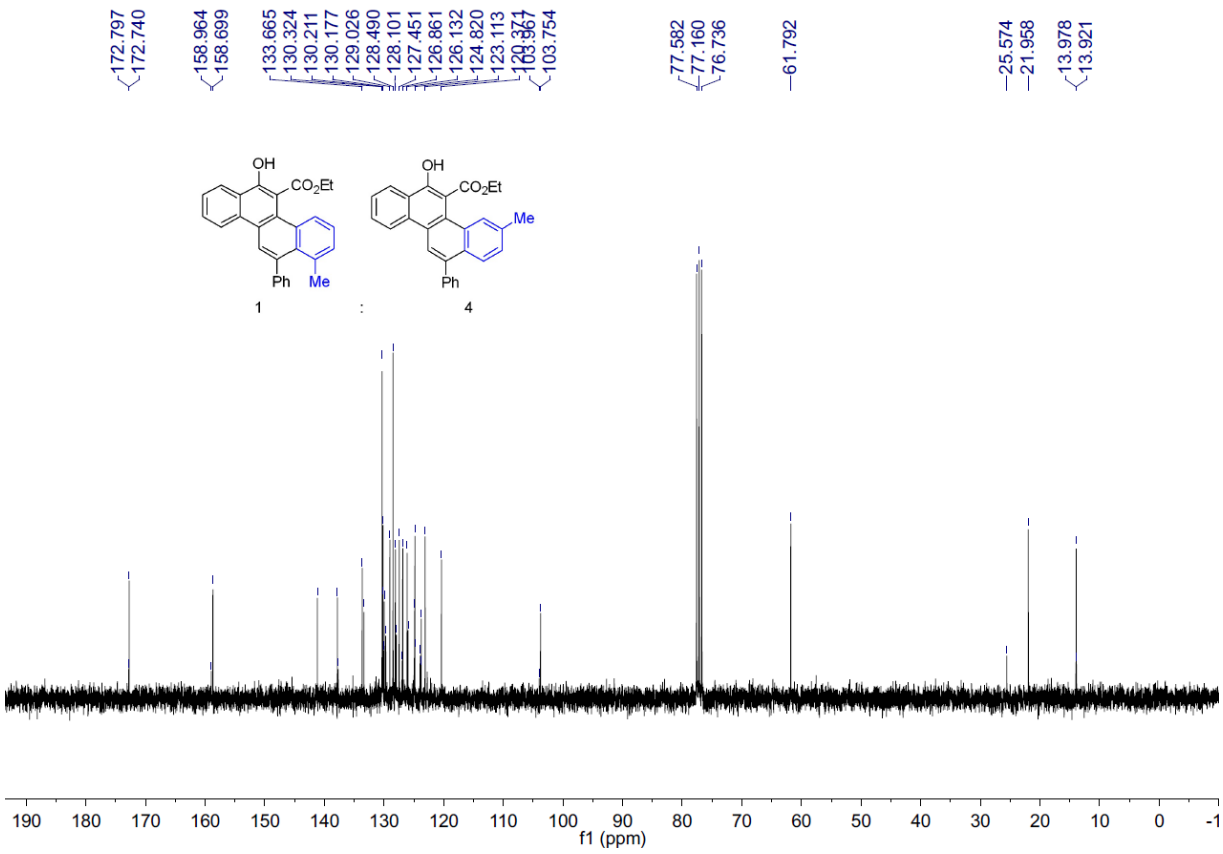
Supplementary Fig. 103 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 43.



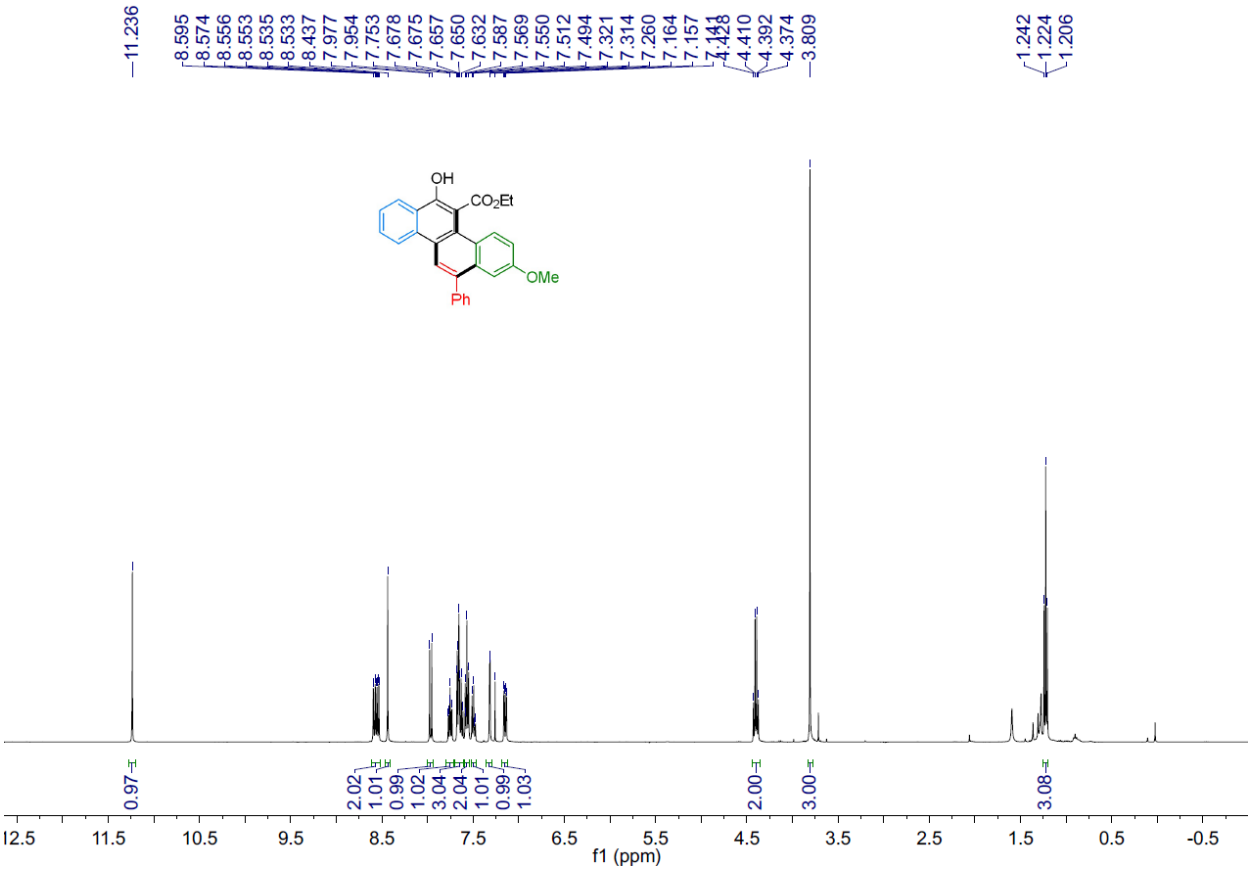
Supplementary Fig. 104 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 43.



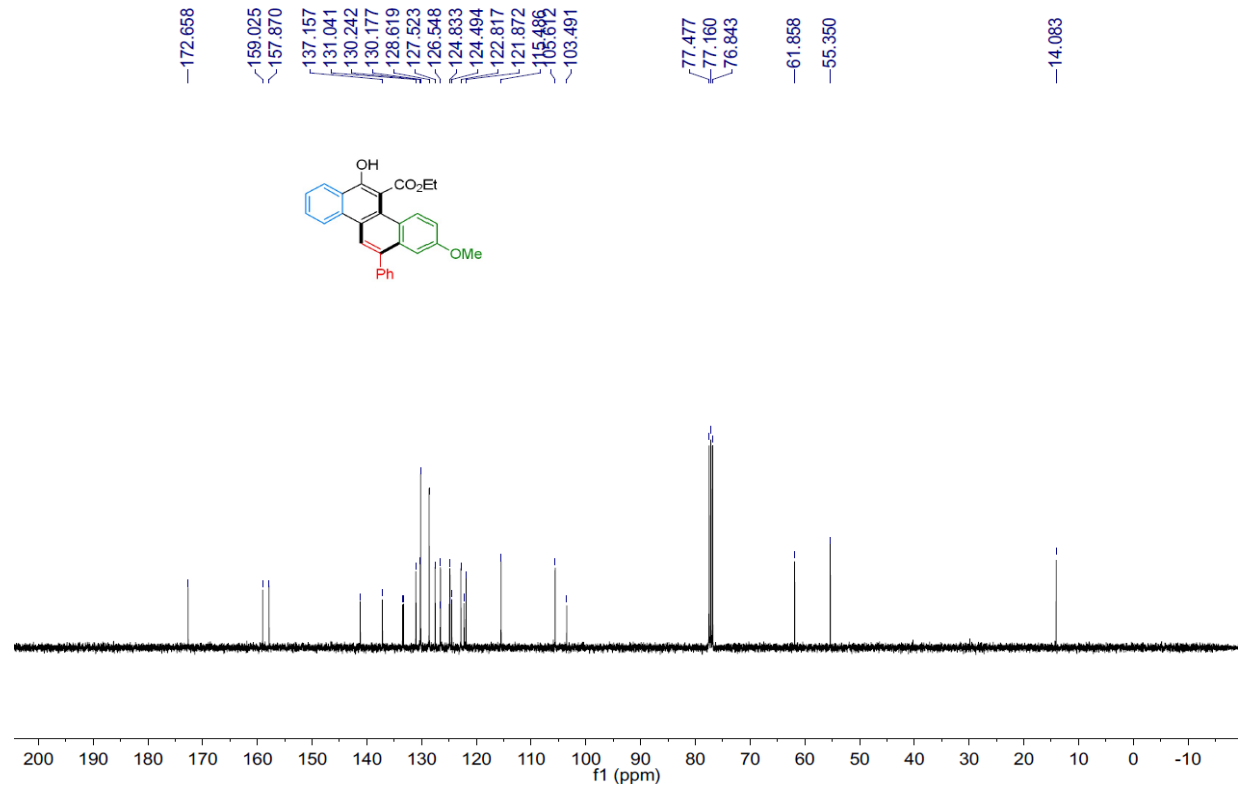
Supplementary Fig. 105 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum for 44.



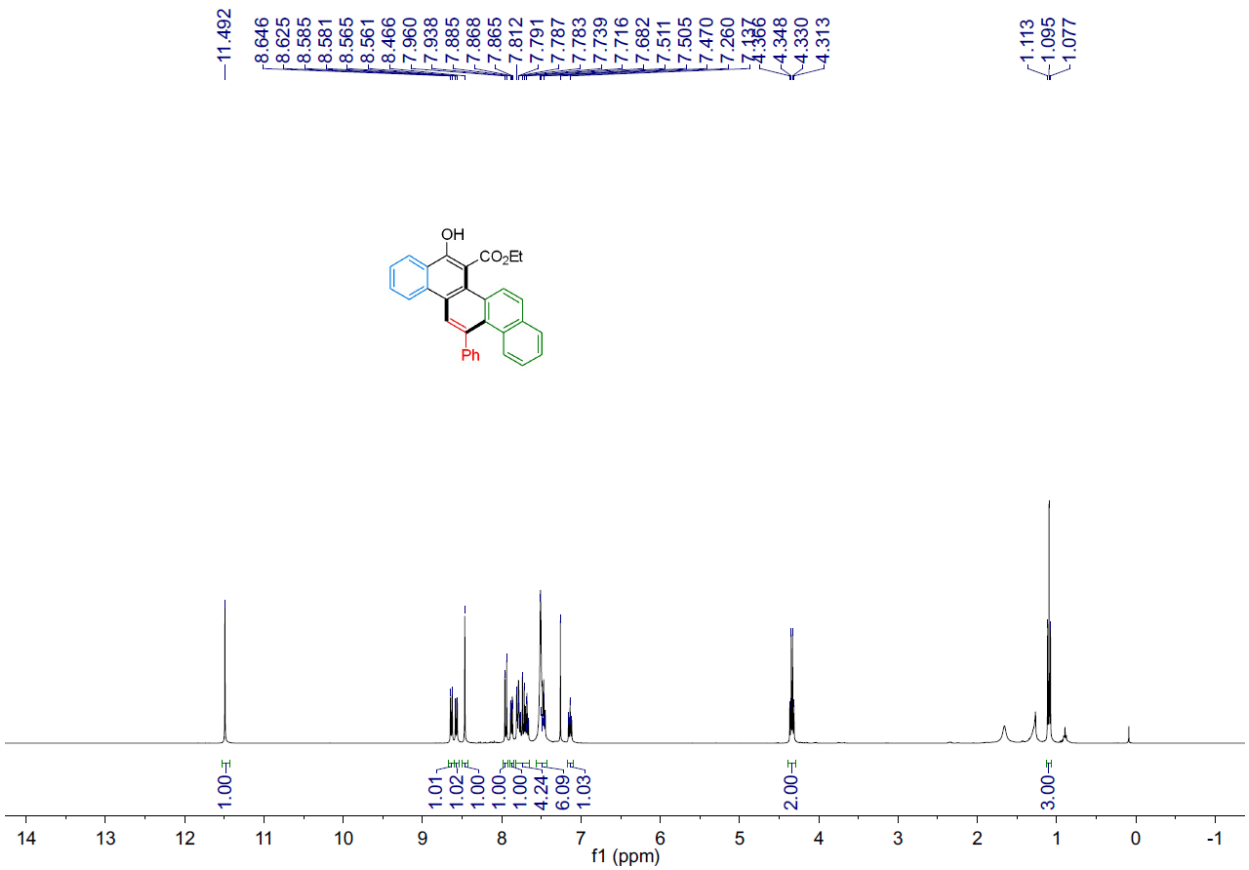
Supplementary Fig. 106 ^{13}C NMR (75 MHz, $CDCl_3$) spectrum for 44.



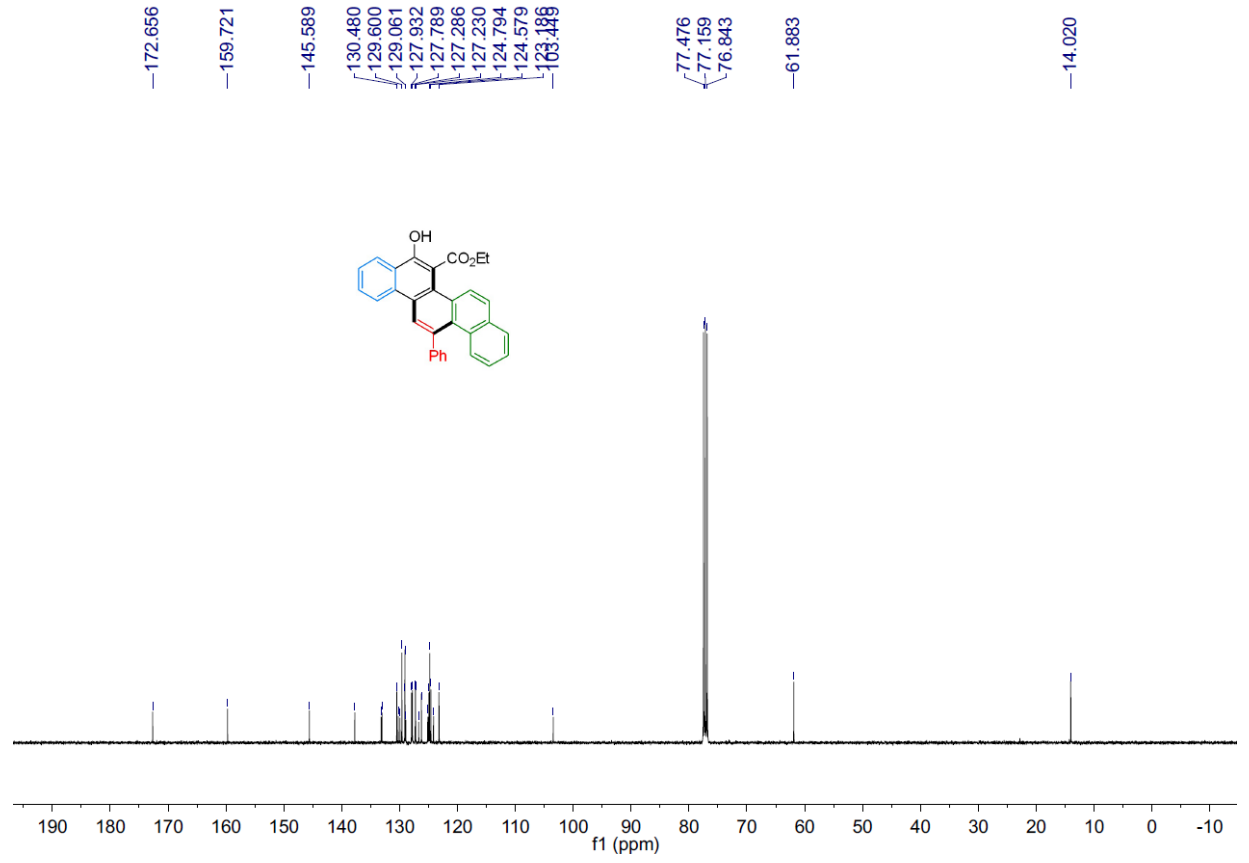
Supplementary Fig. 107 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 45.



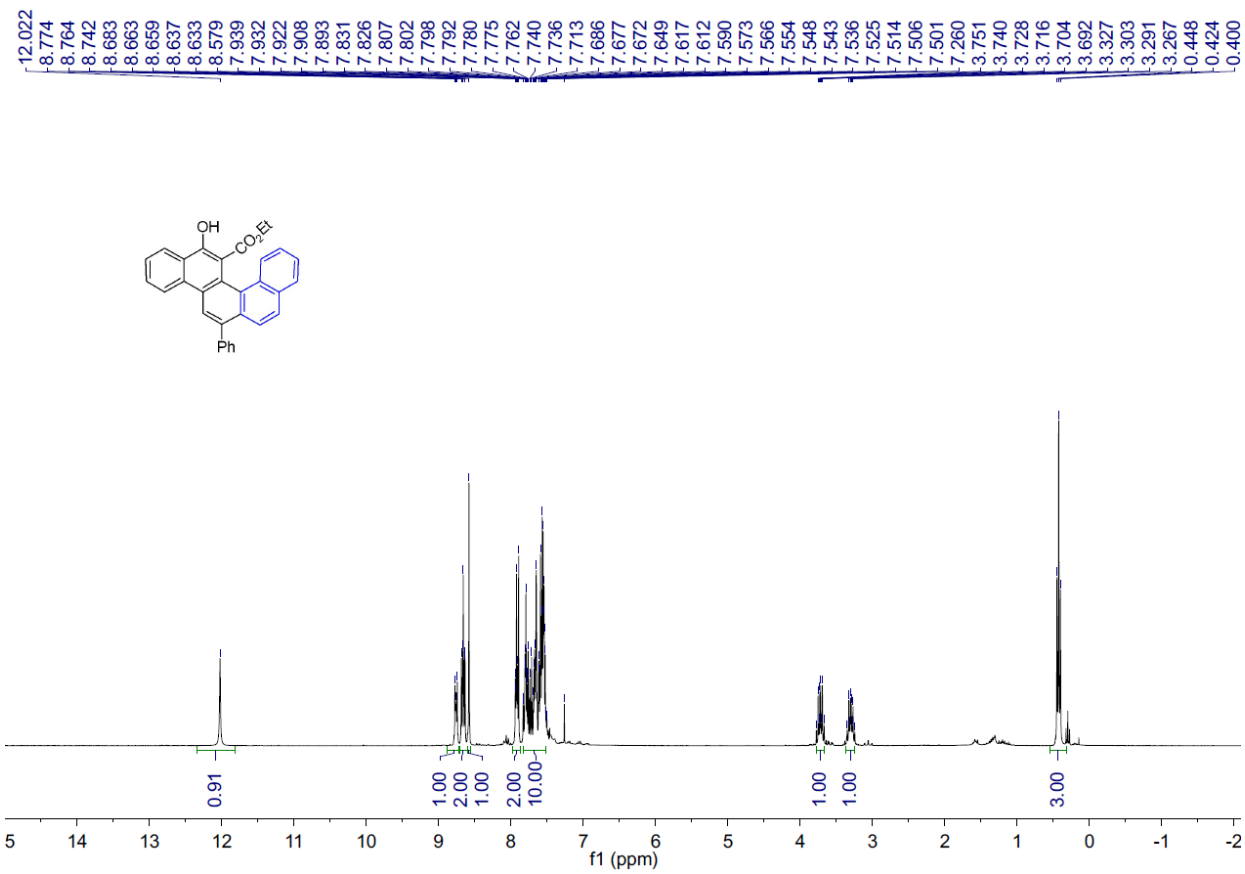
Supplementary Fig. 108 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 45.



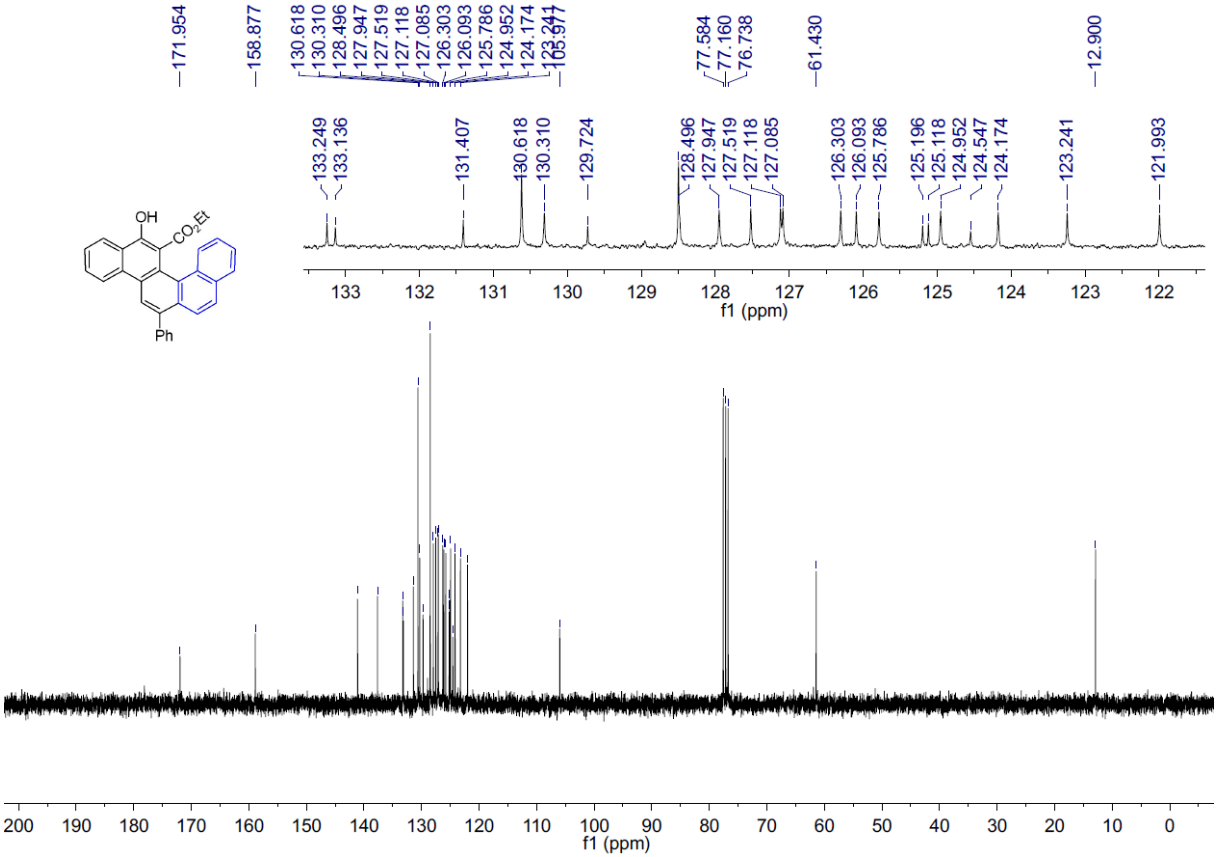
Supplementary Fig. 109 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 46.



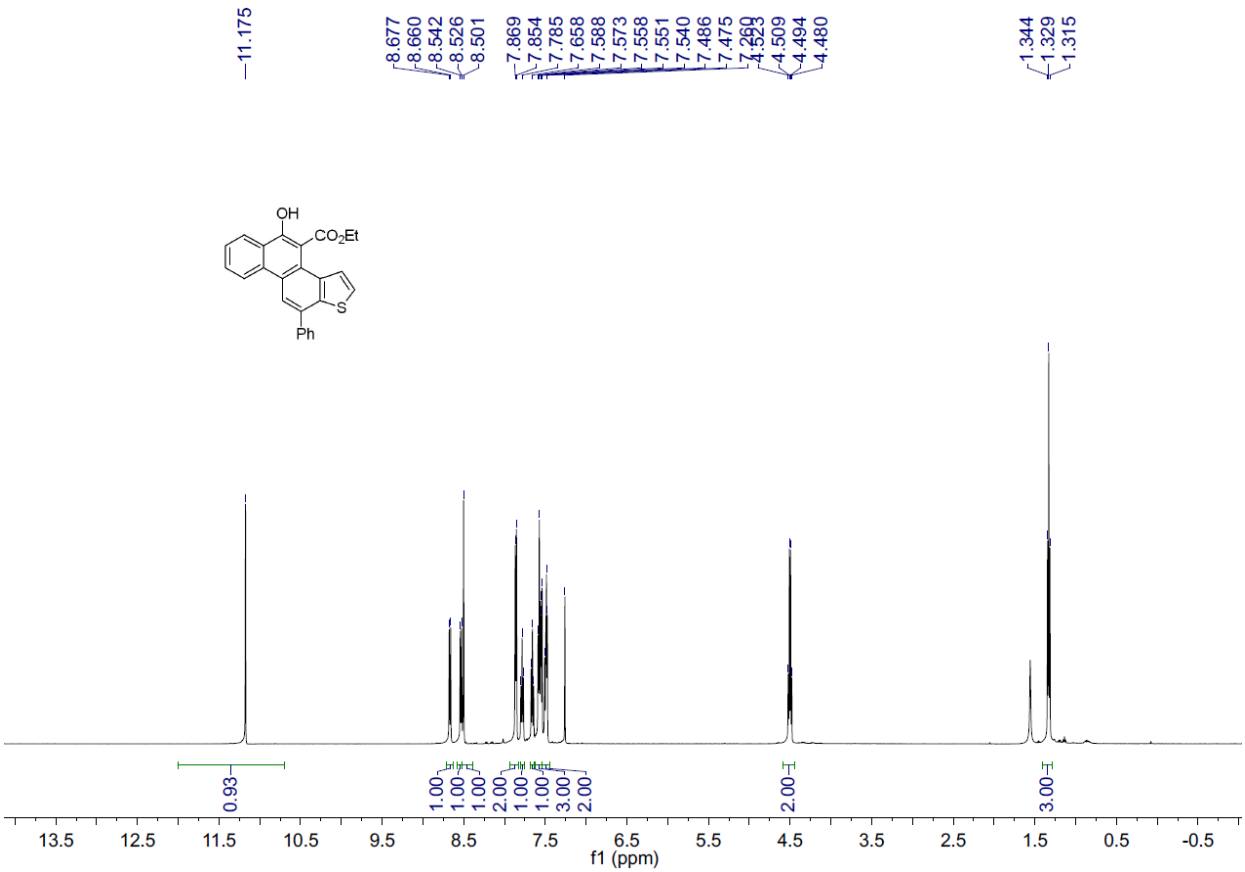
Supplementary Fig. 110 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 46.



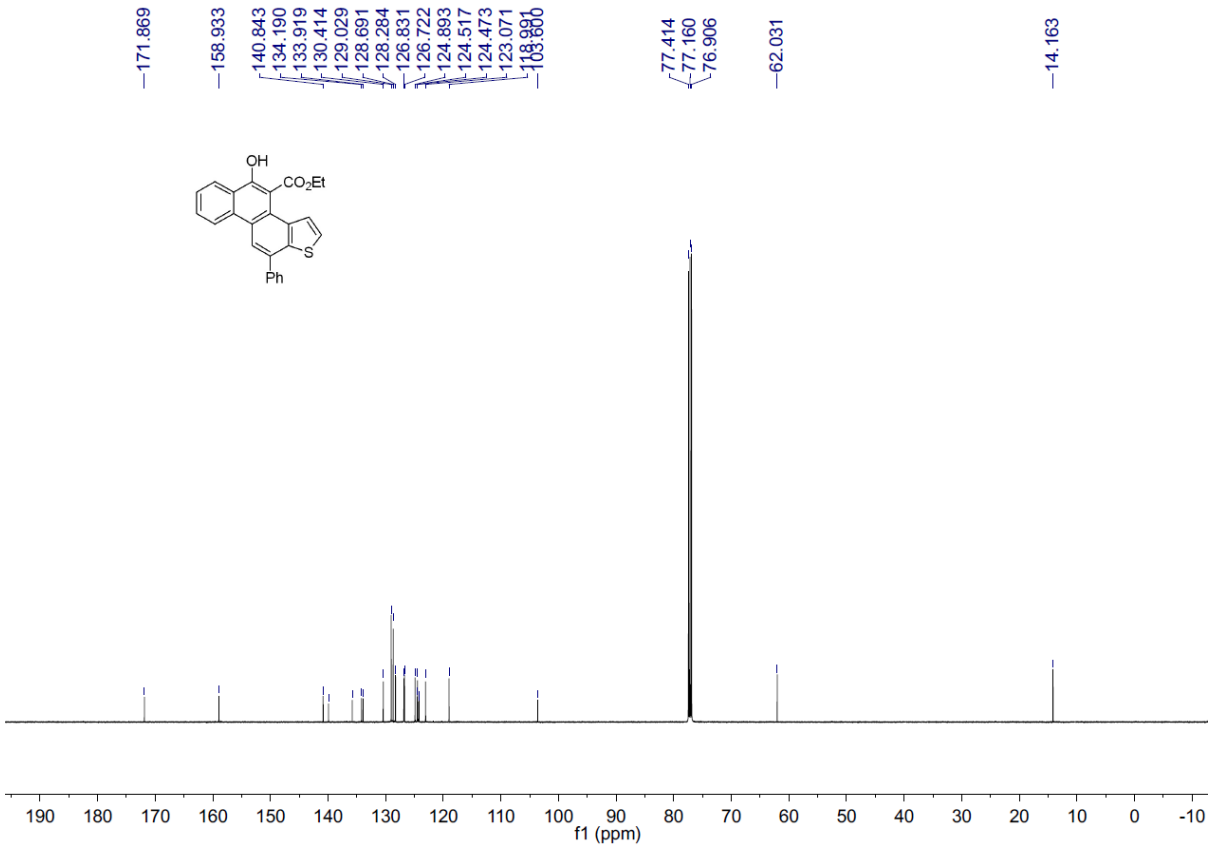
Supplementary Fig. 111 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum for 47.



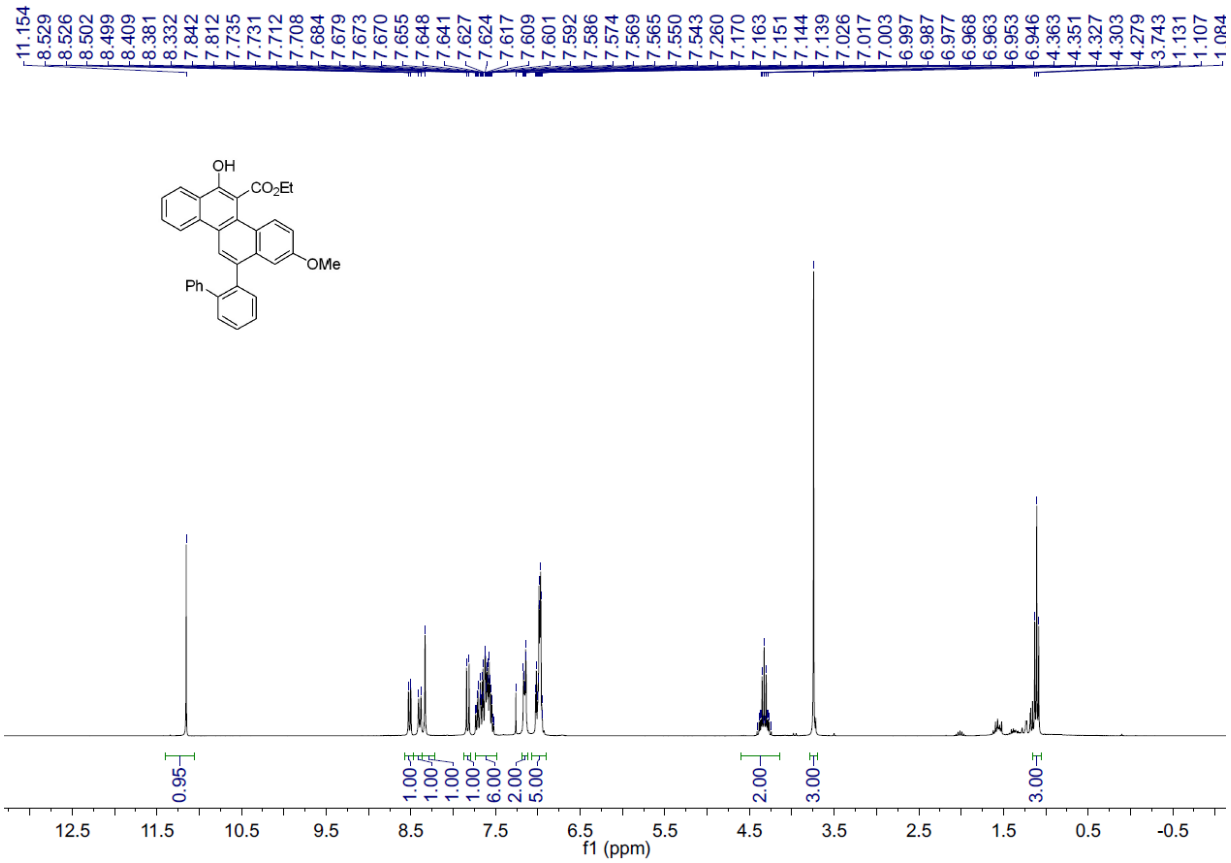
Supplementary Fig. 112 ^{13}C NMR (75 MHz, $CDCl_3$) spectrum for 47.



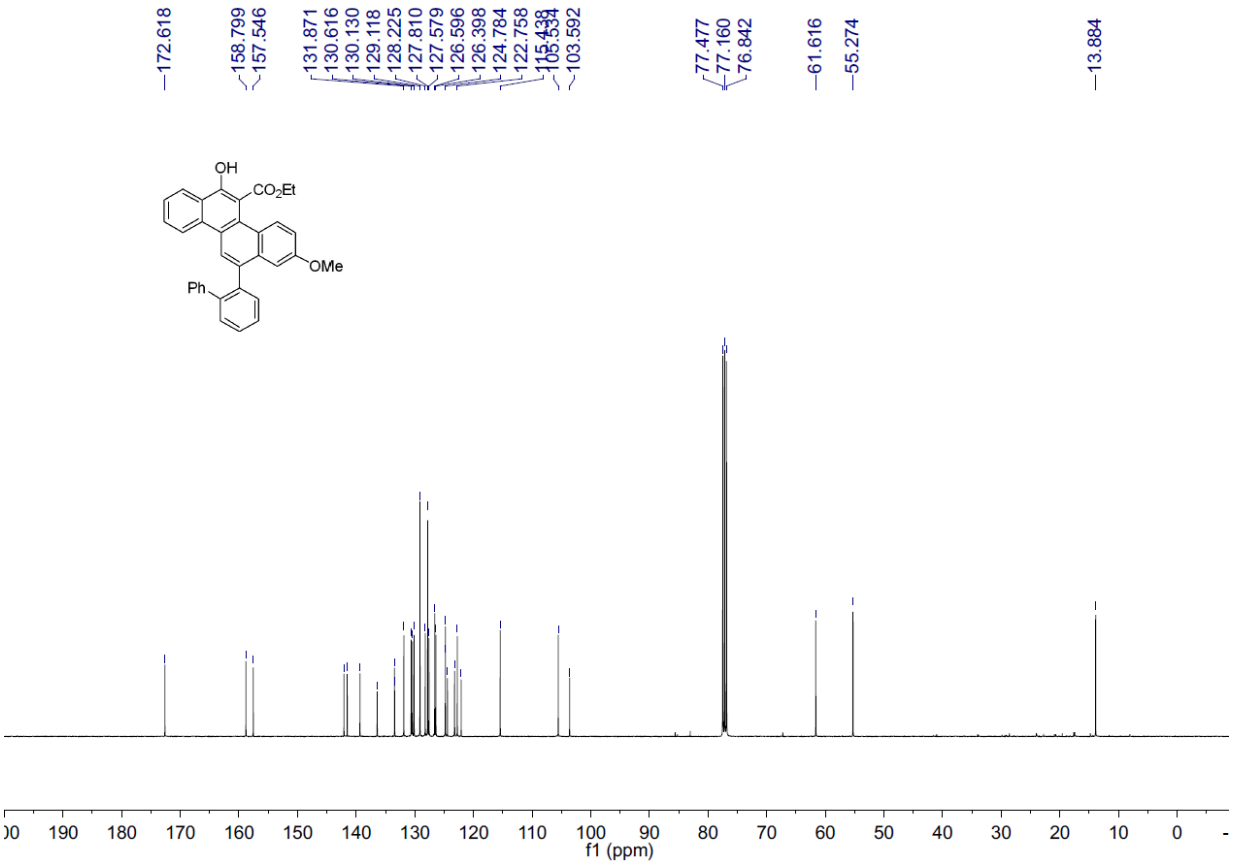
Supplementary Fig. 113 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum for 48.



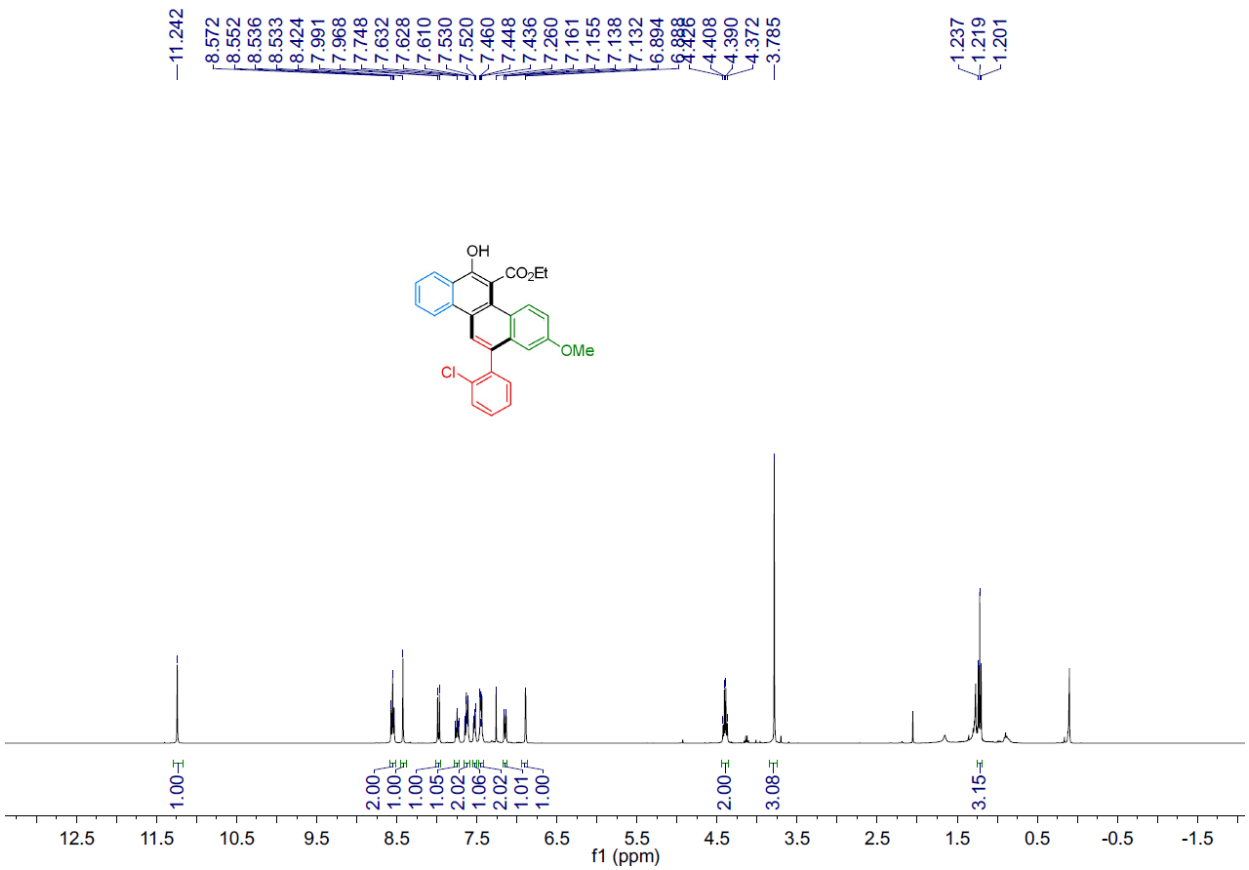
Supplementary Fig. 114 ^{13}C NMR (125 MHz, $CDCl_3$) spectrum for 48.



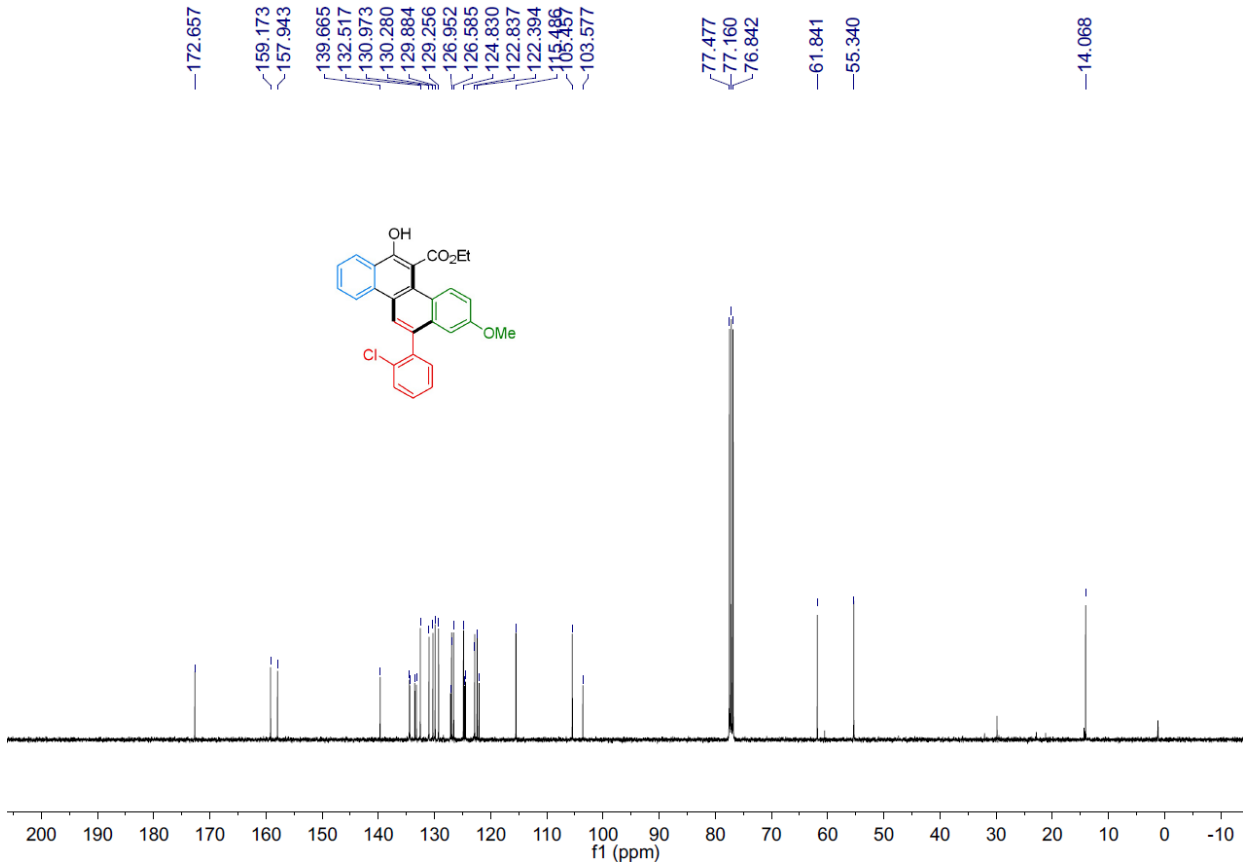
Supplementary Fig. 115 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 49.



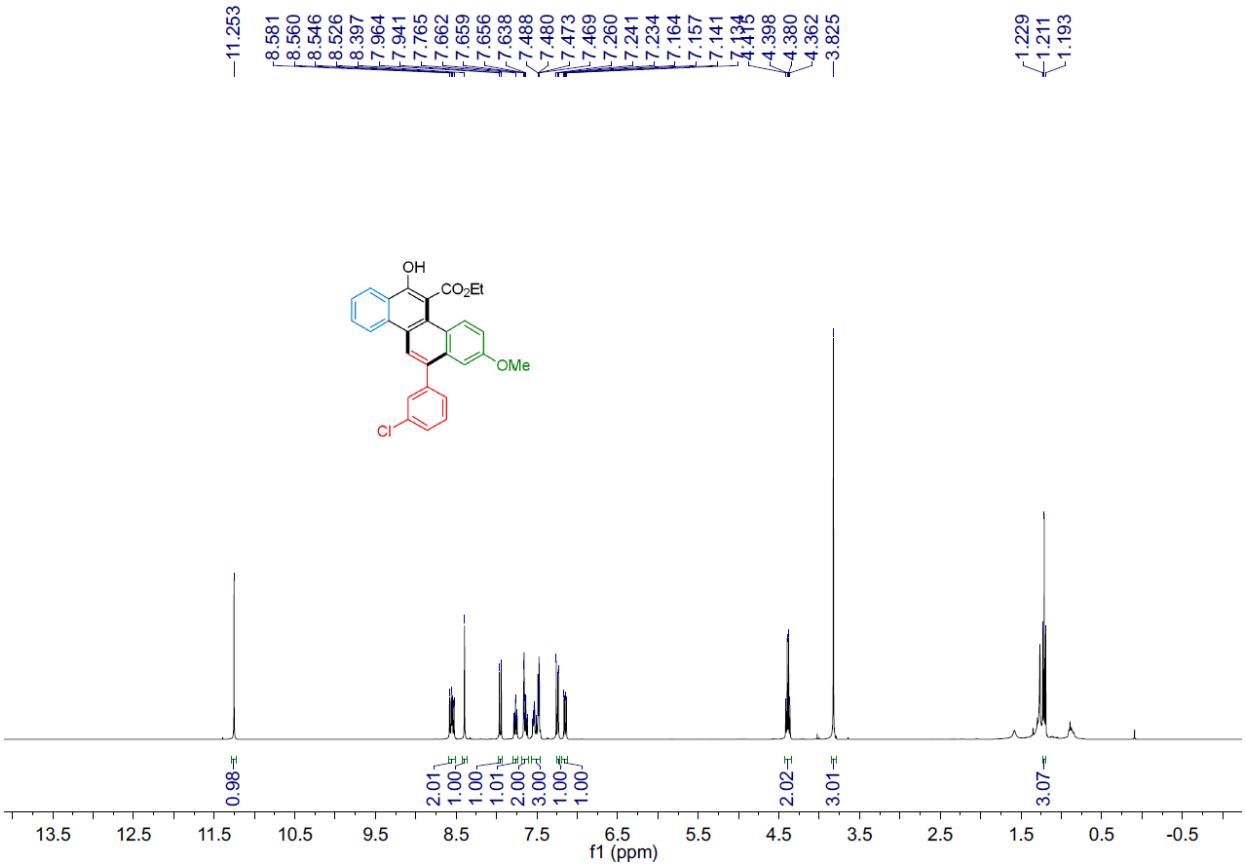
Supplementary Fig. 116 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 49.



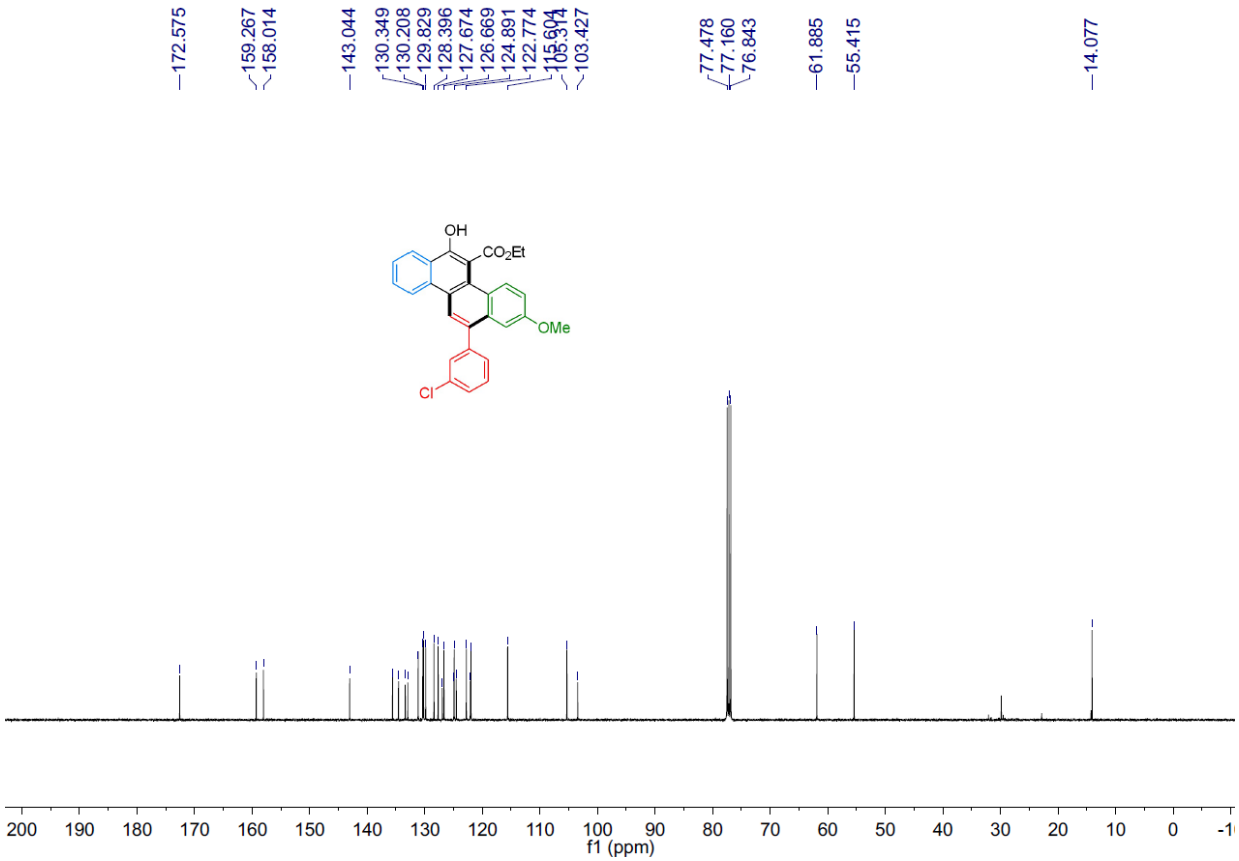
Supplementary Fig. 117 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 50.



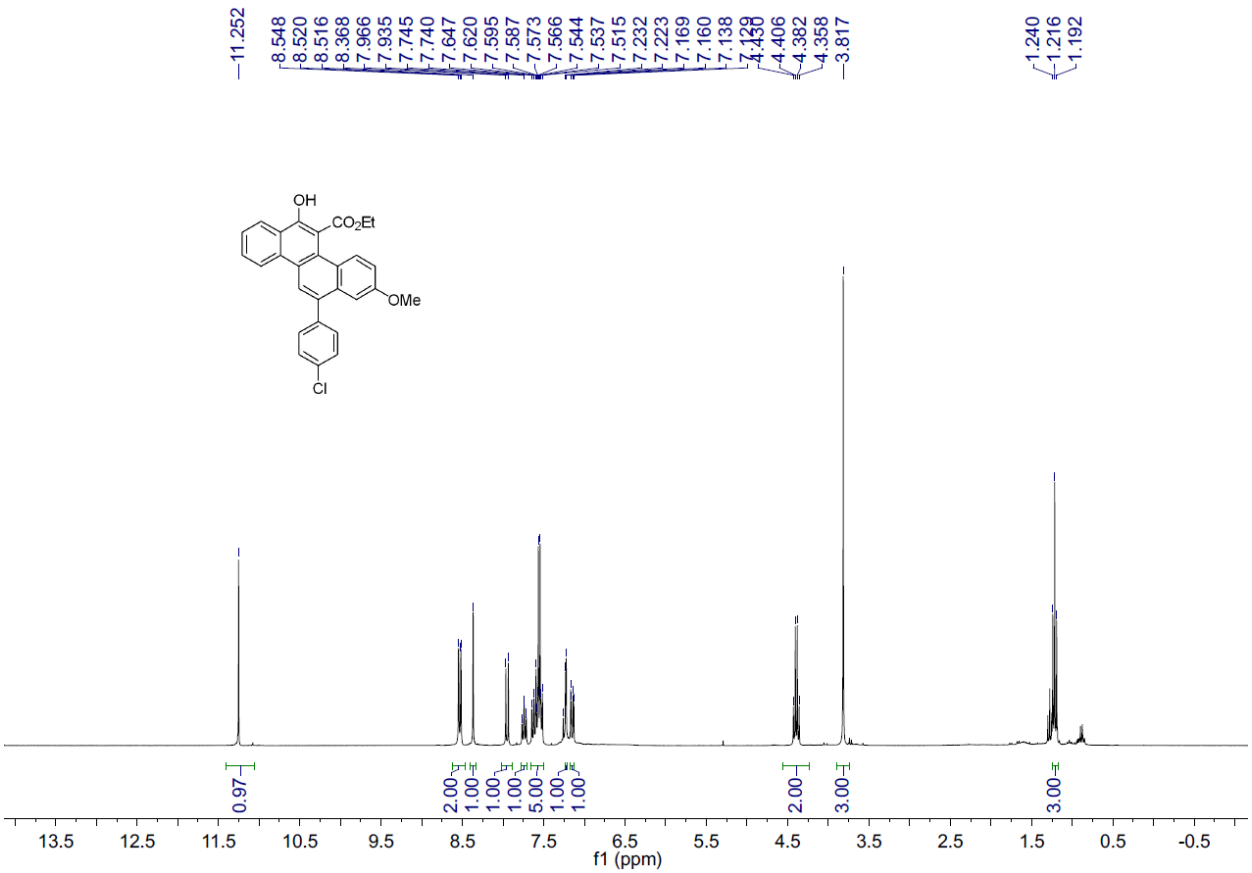
Supplementary Fig. 118 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 50.



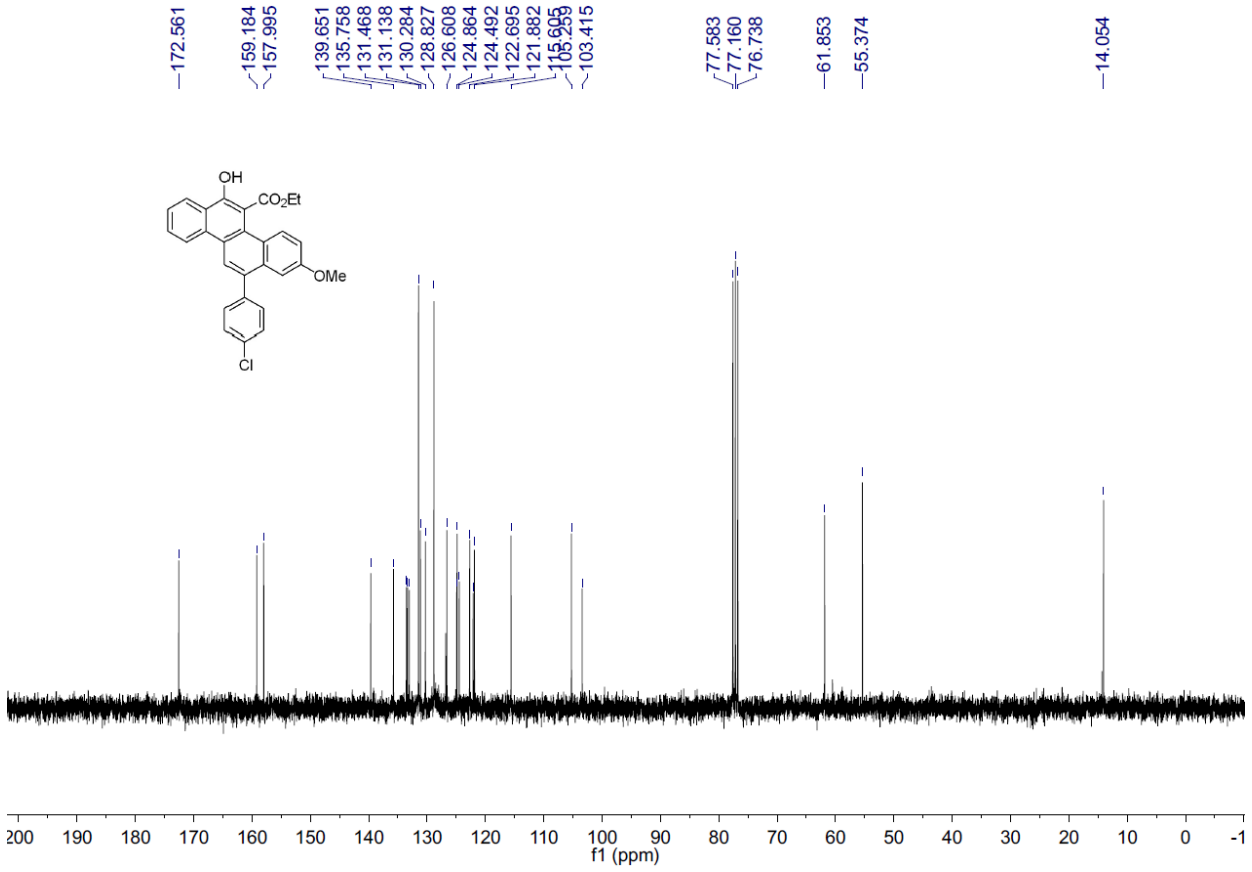
Supplementary Fig. 119 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 51.



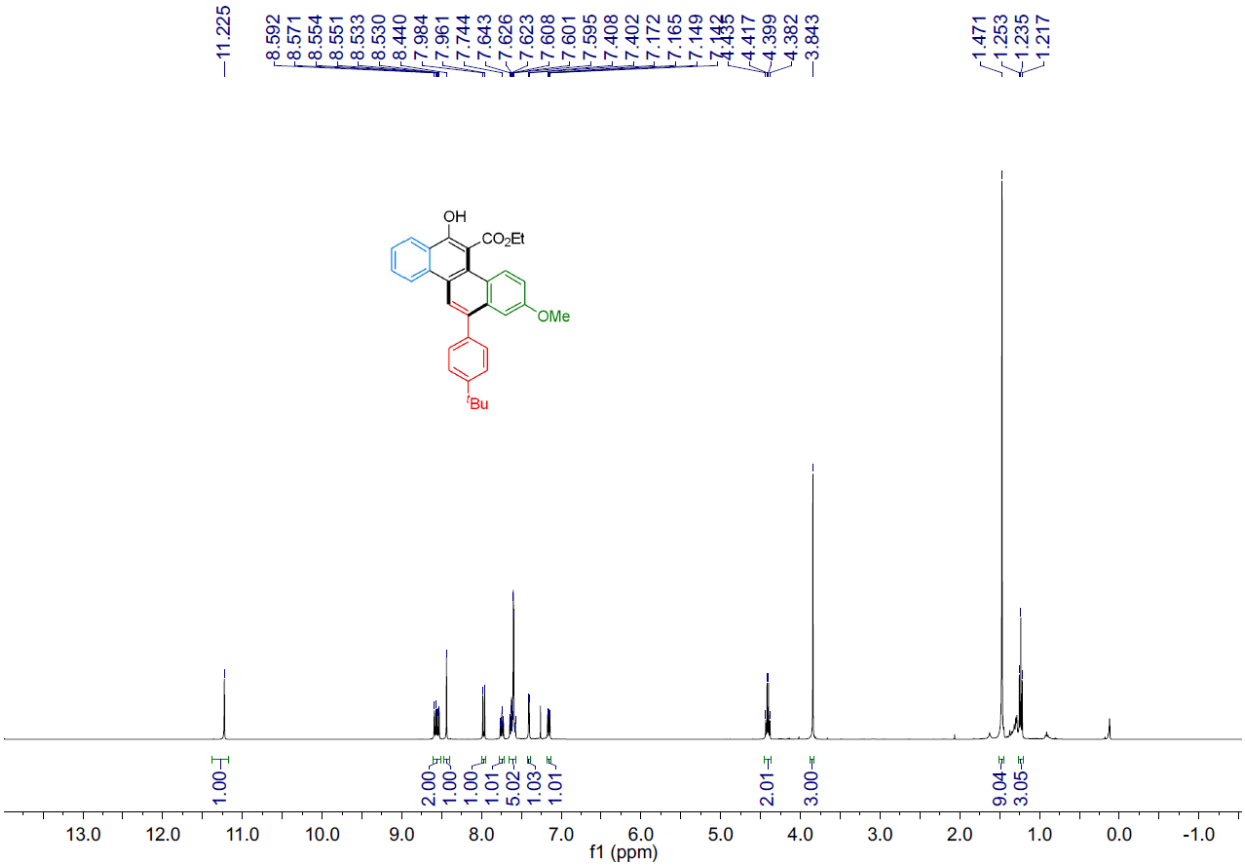
Supplementary Fig. 120 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 51.



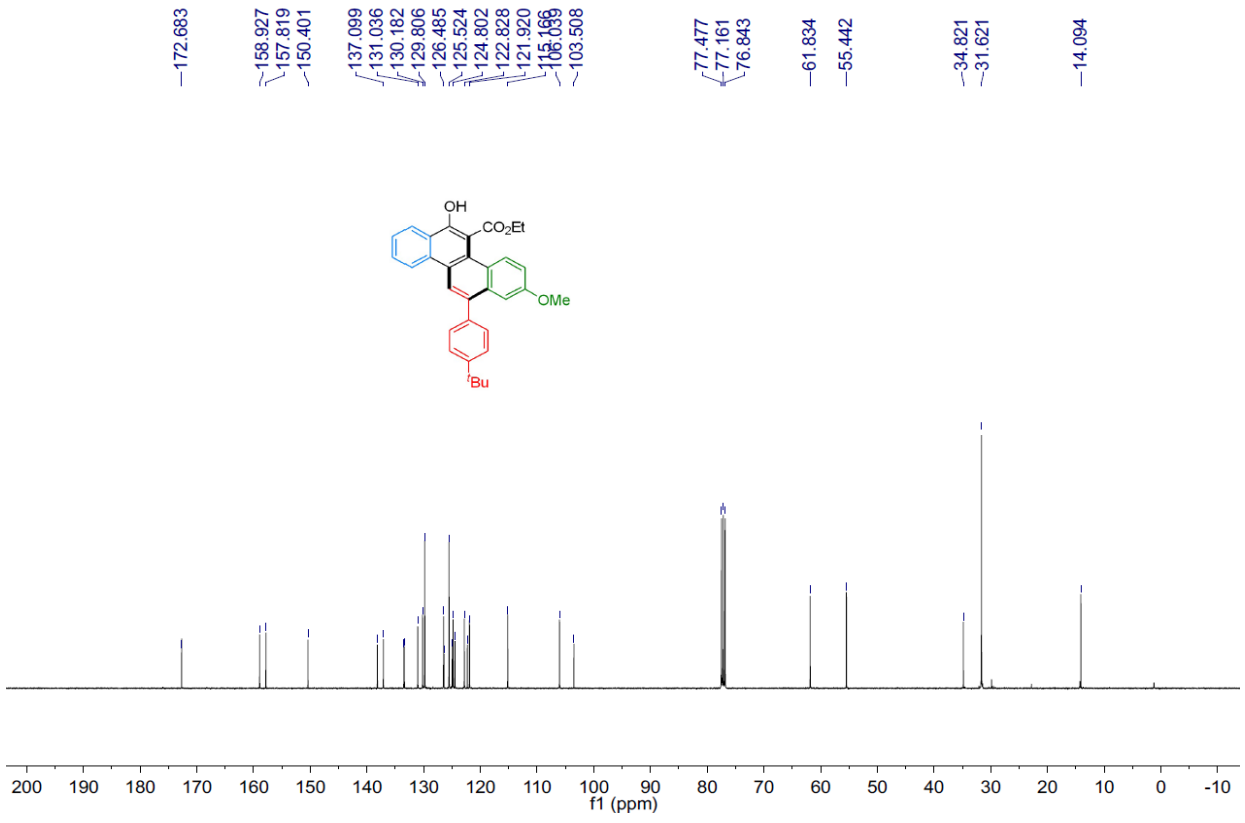
Supplementary Fig. 121 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum for 52.



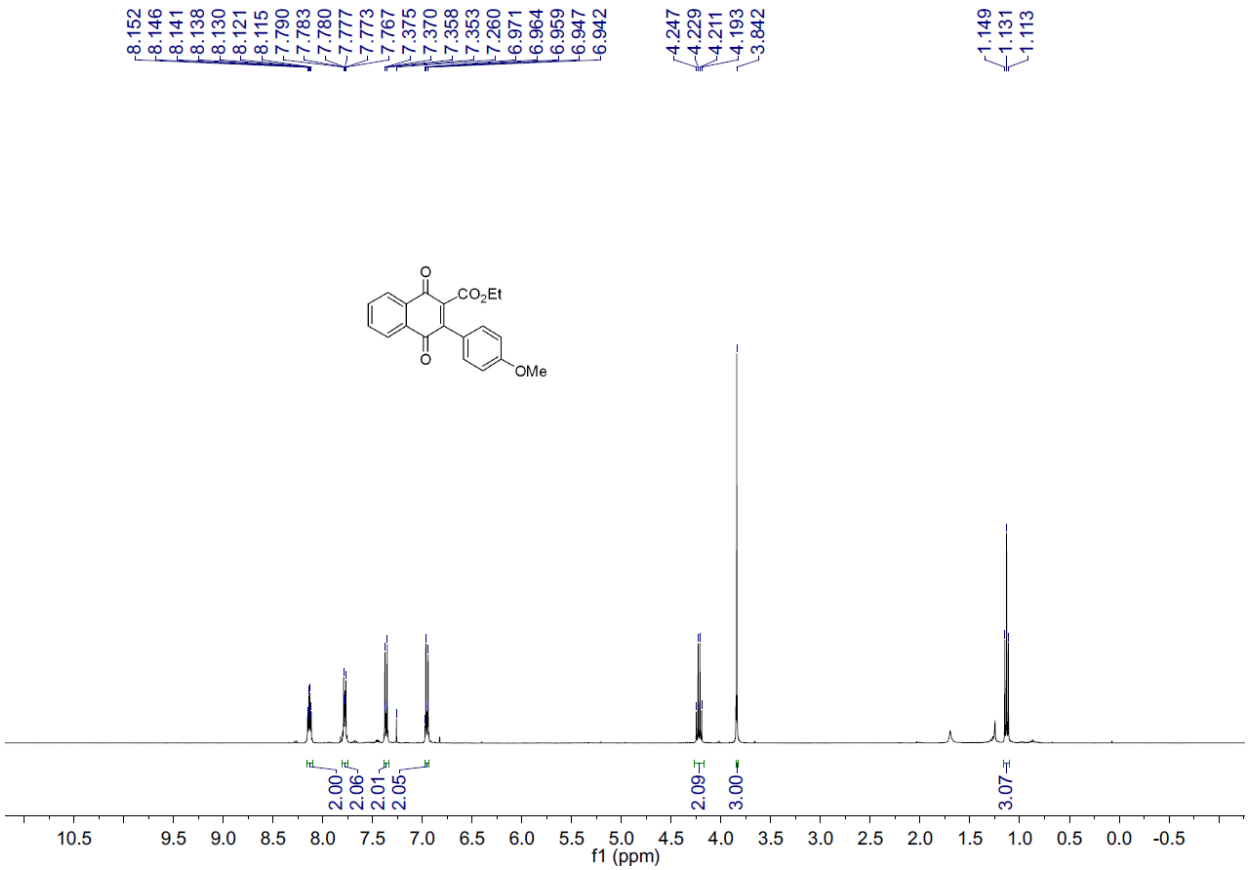
Supplementary Fig. 122 ^{13}C NMR (75 MHz, $CDCl_3$) spectrum for 52.



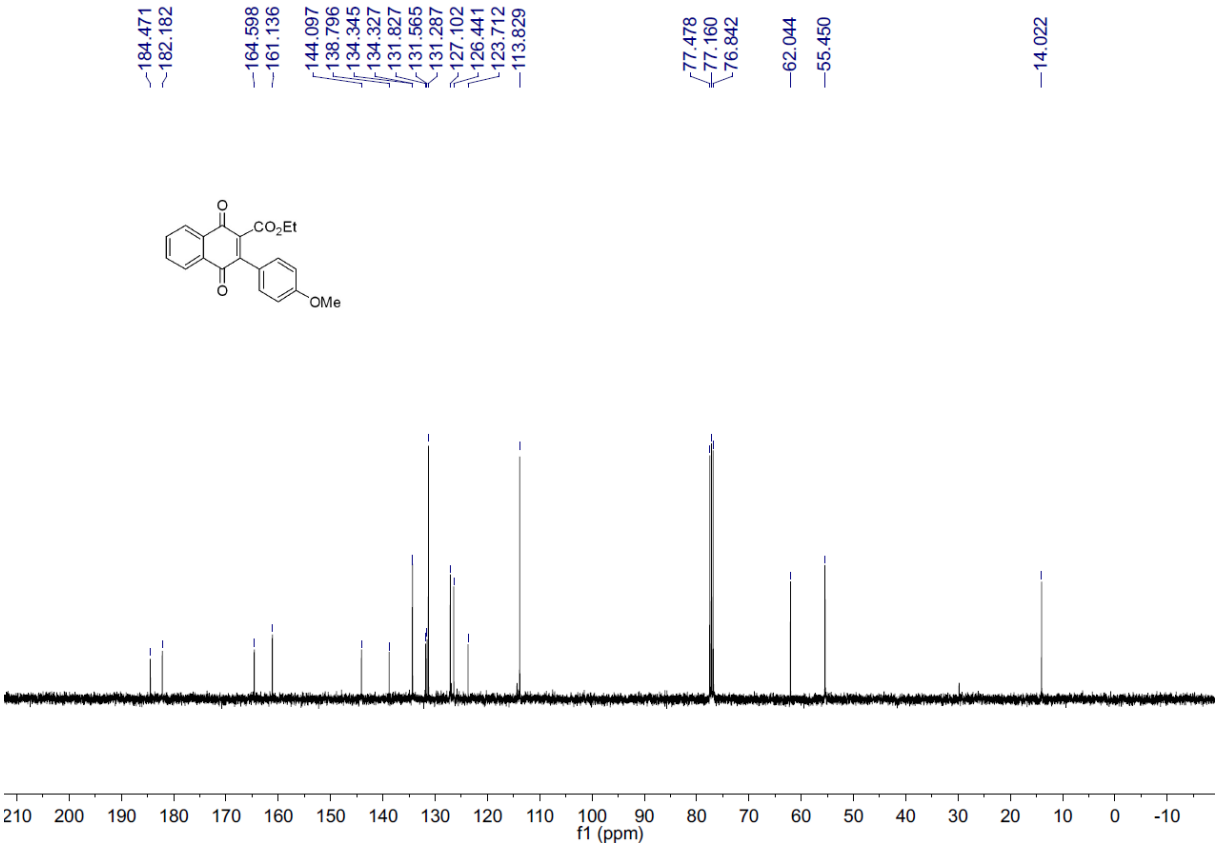
Supplementary Fig. 123 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 53.



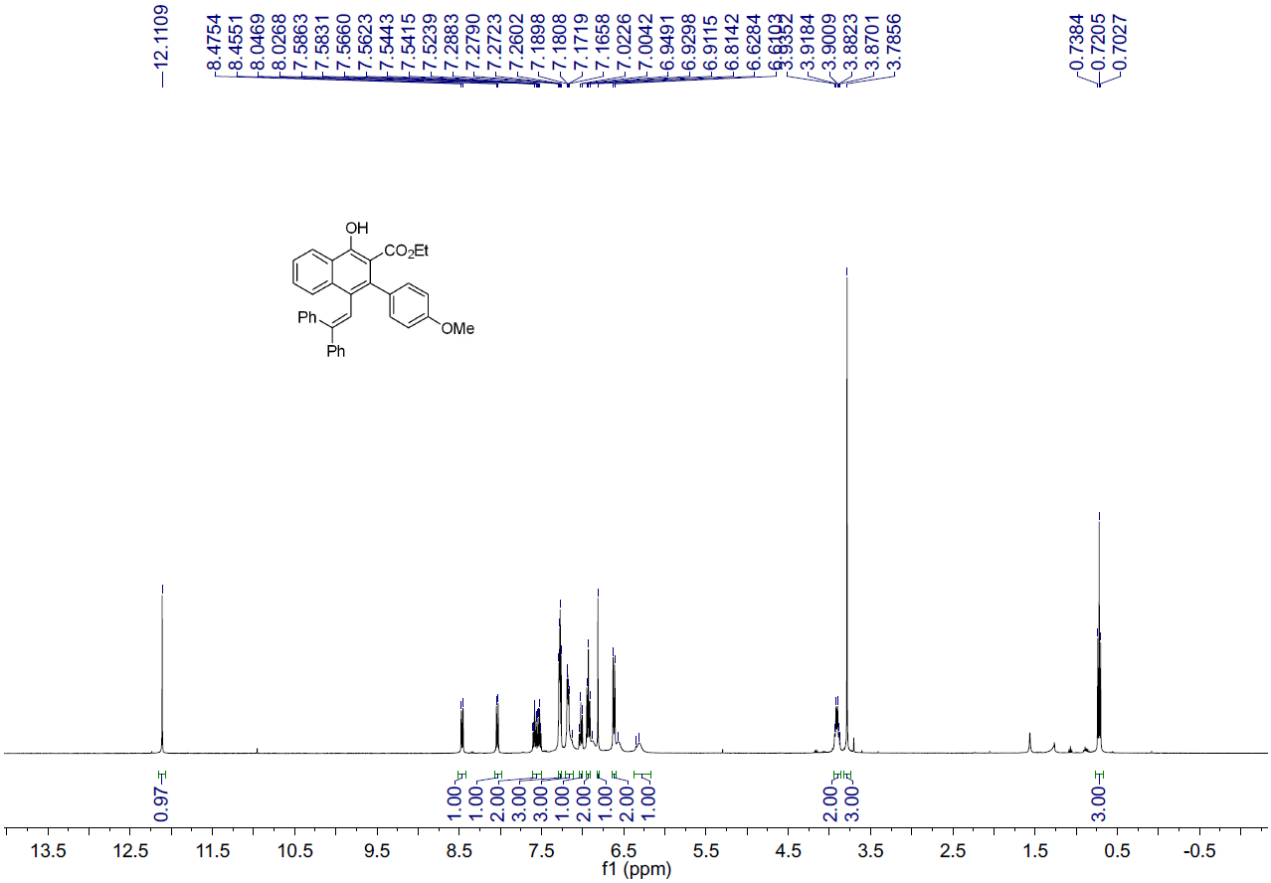
Supplementary Fig. 124 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 53.



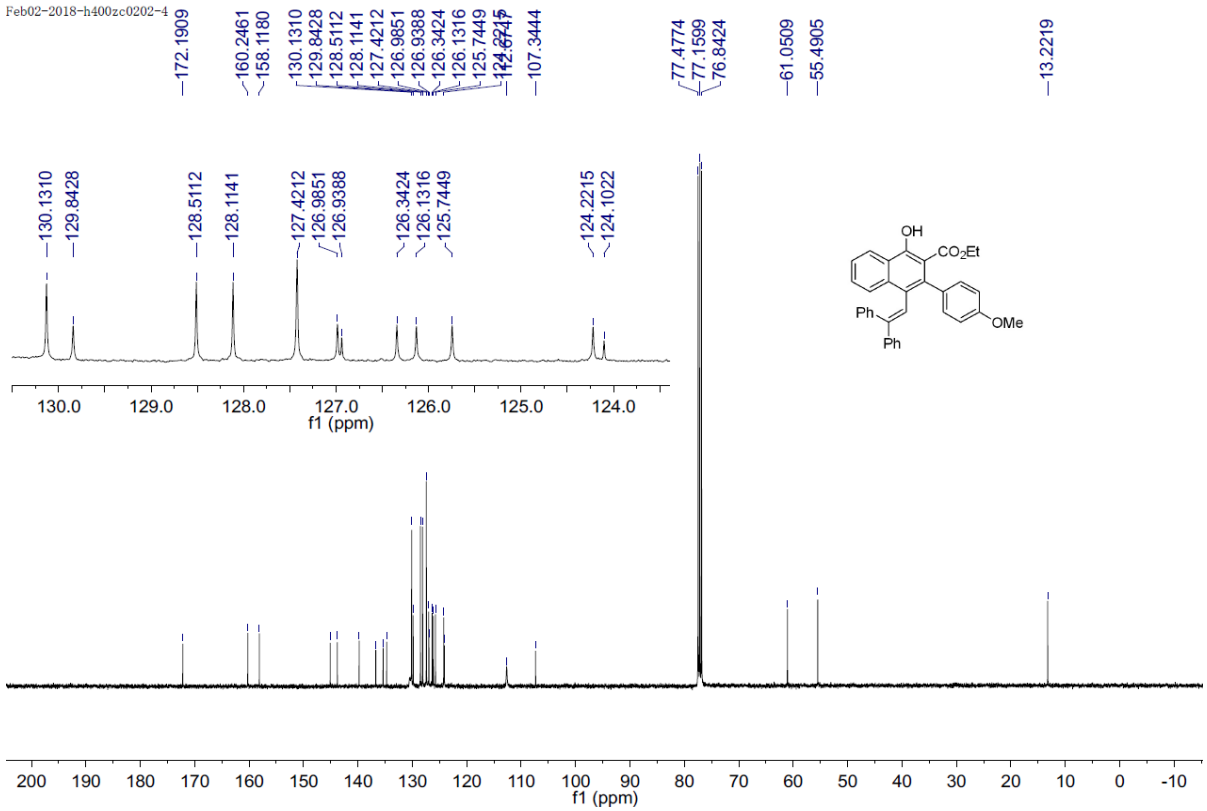
Supplementary Fig. 125 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 54.



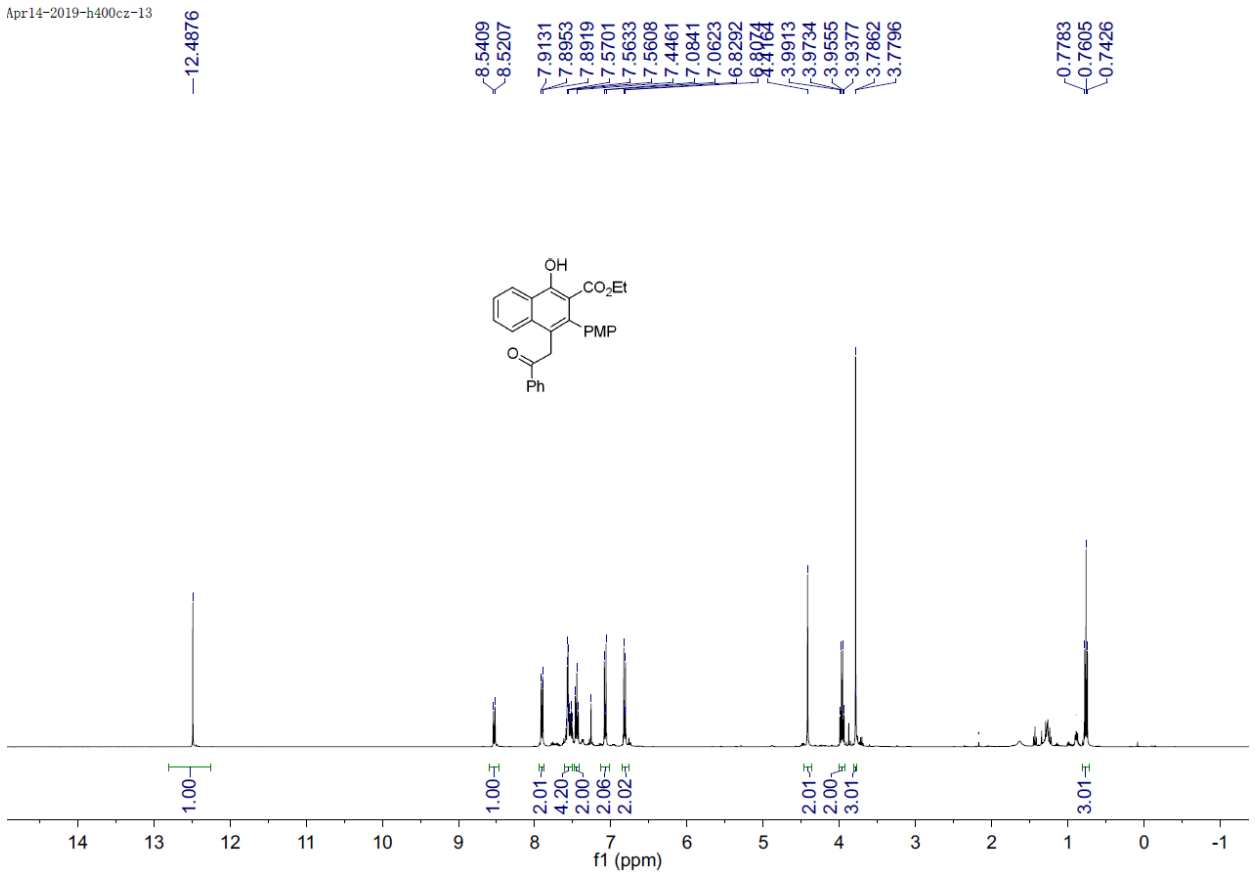
Supplementary Fig. 126 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 54.



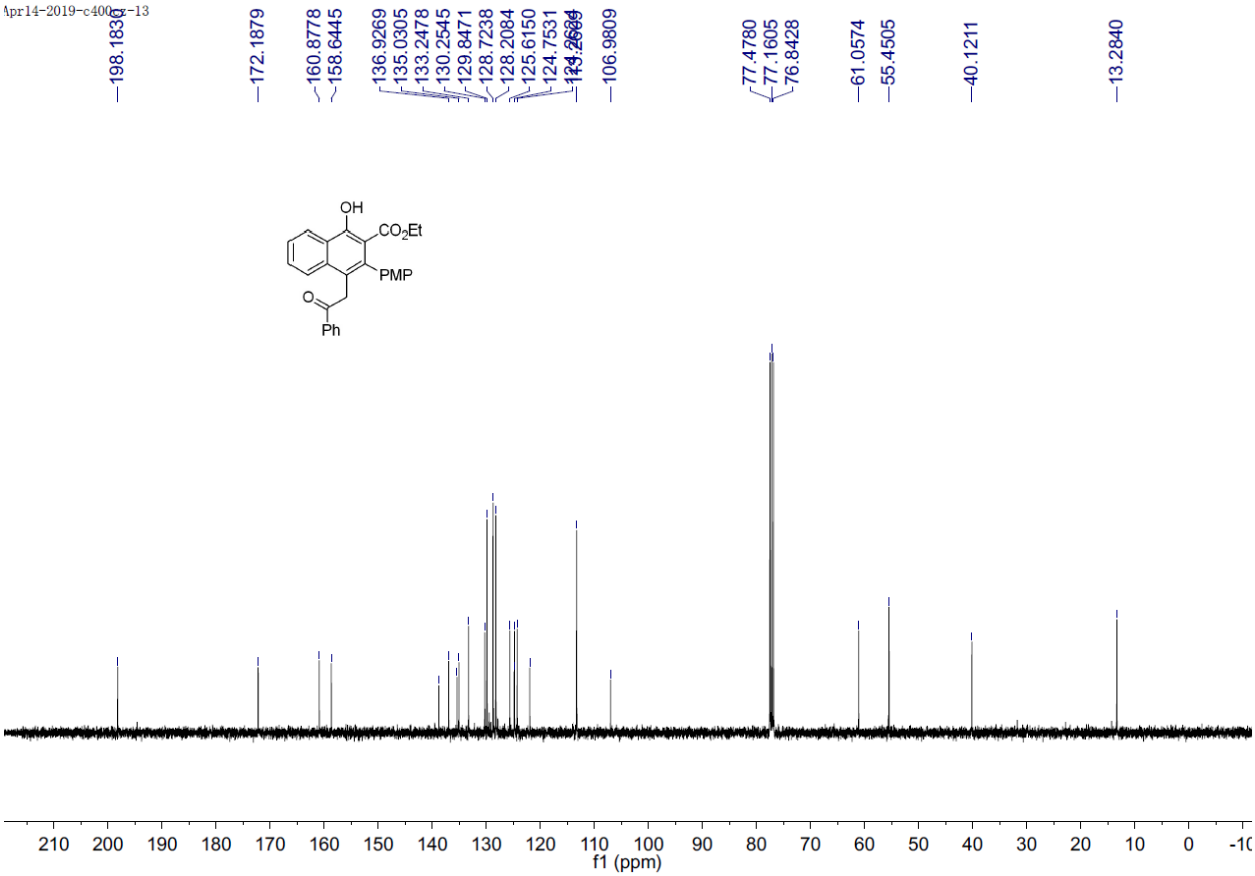
Supplementary Fig. 127 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 55.



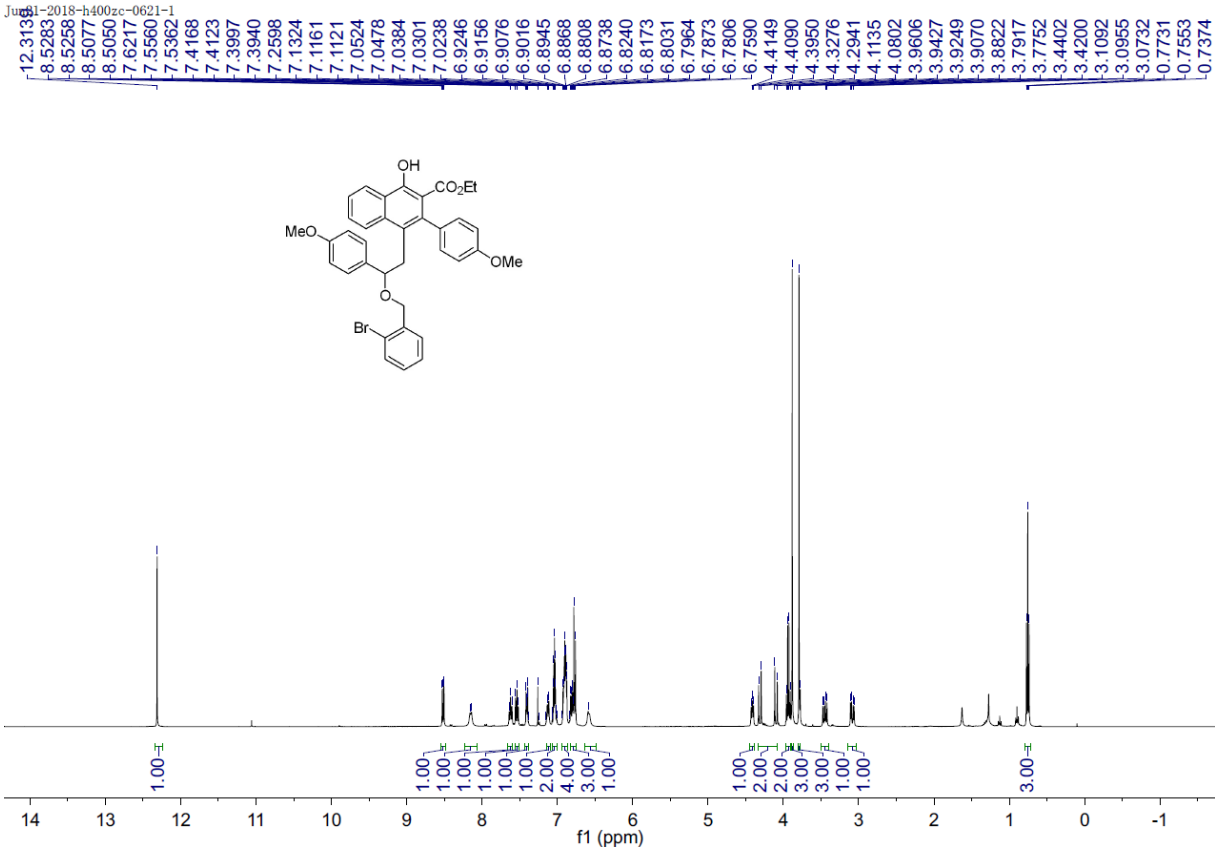
Supplementary Fig. 128 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 55.



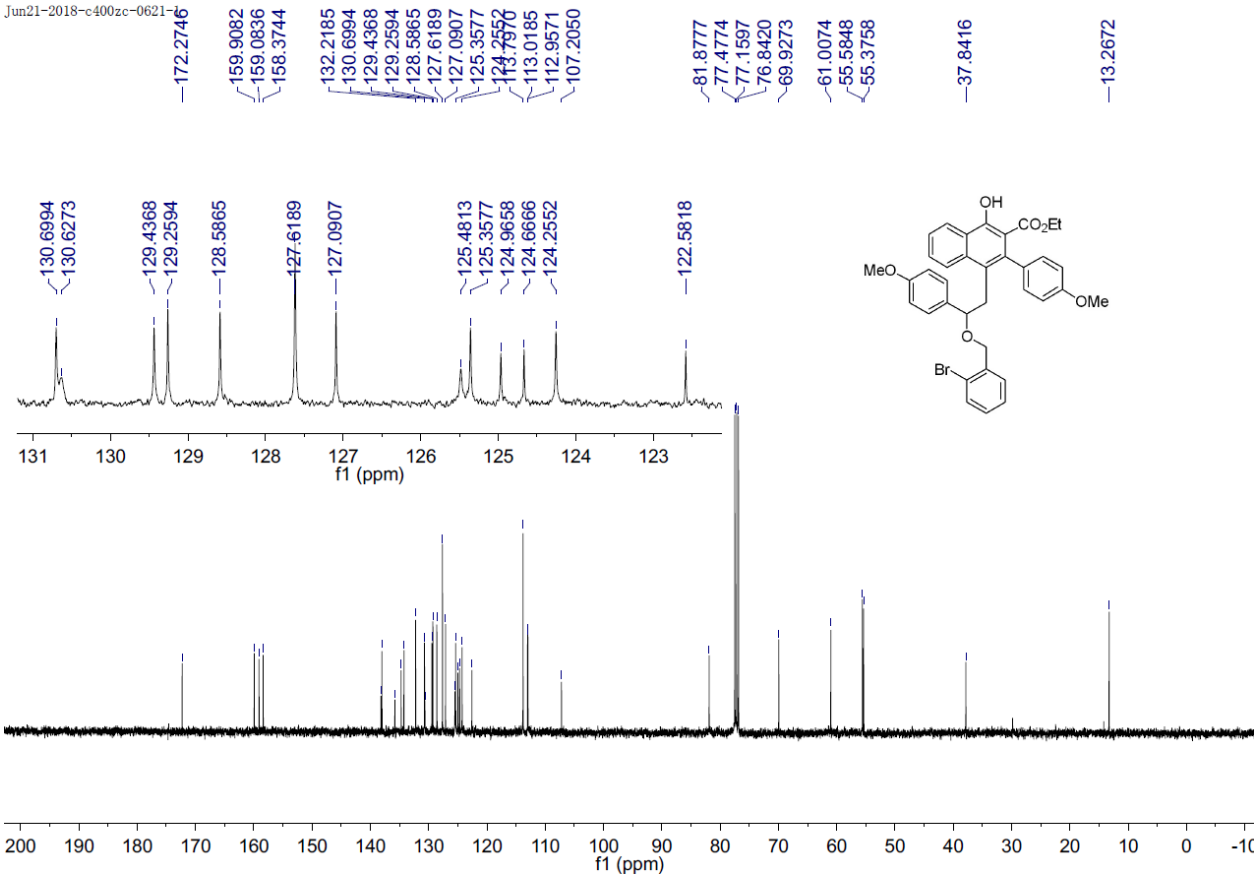
Supplementary Fig. 129 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 56.



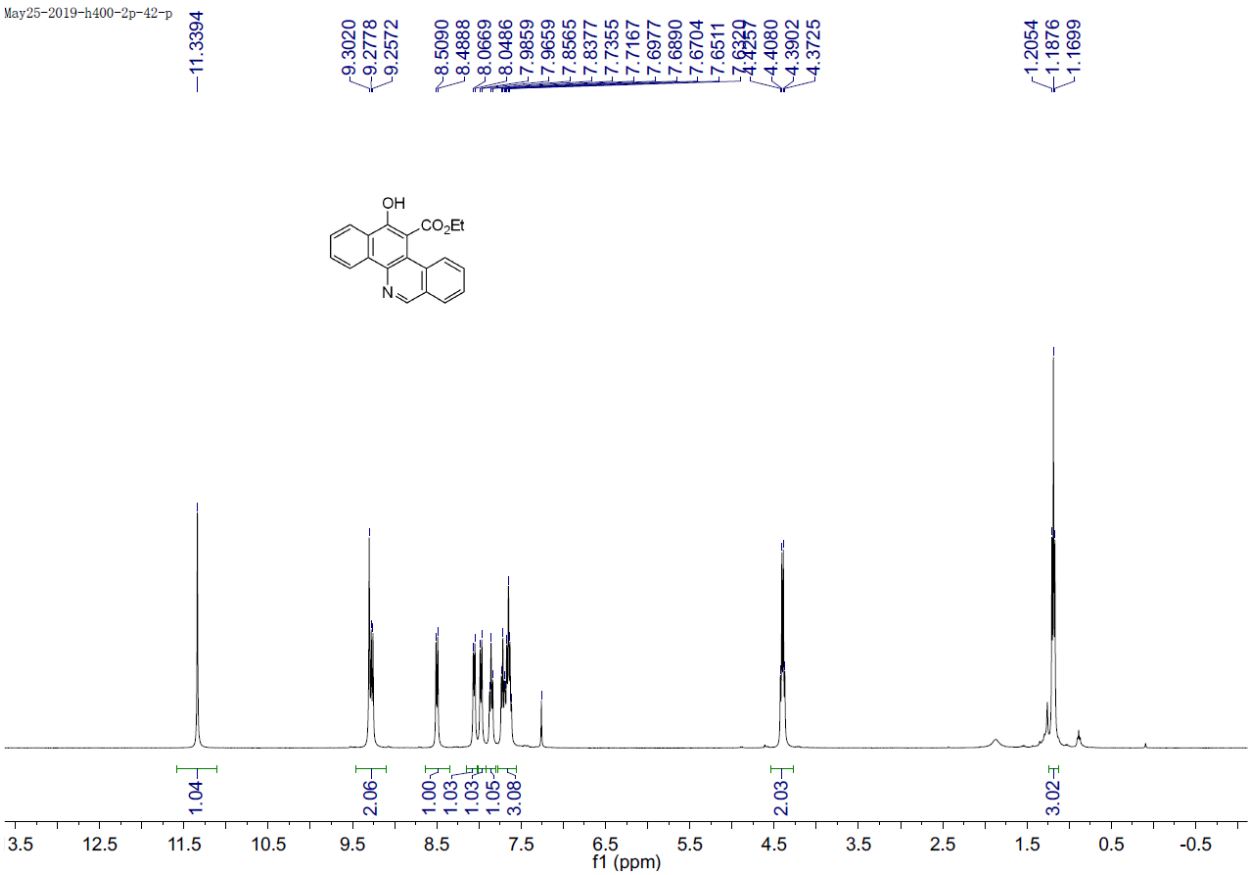
Supplementary Fig. 130 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 56.



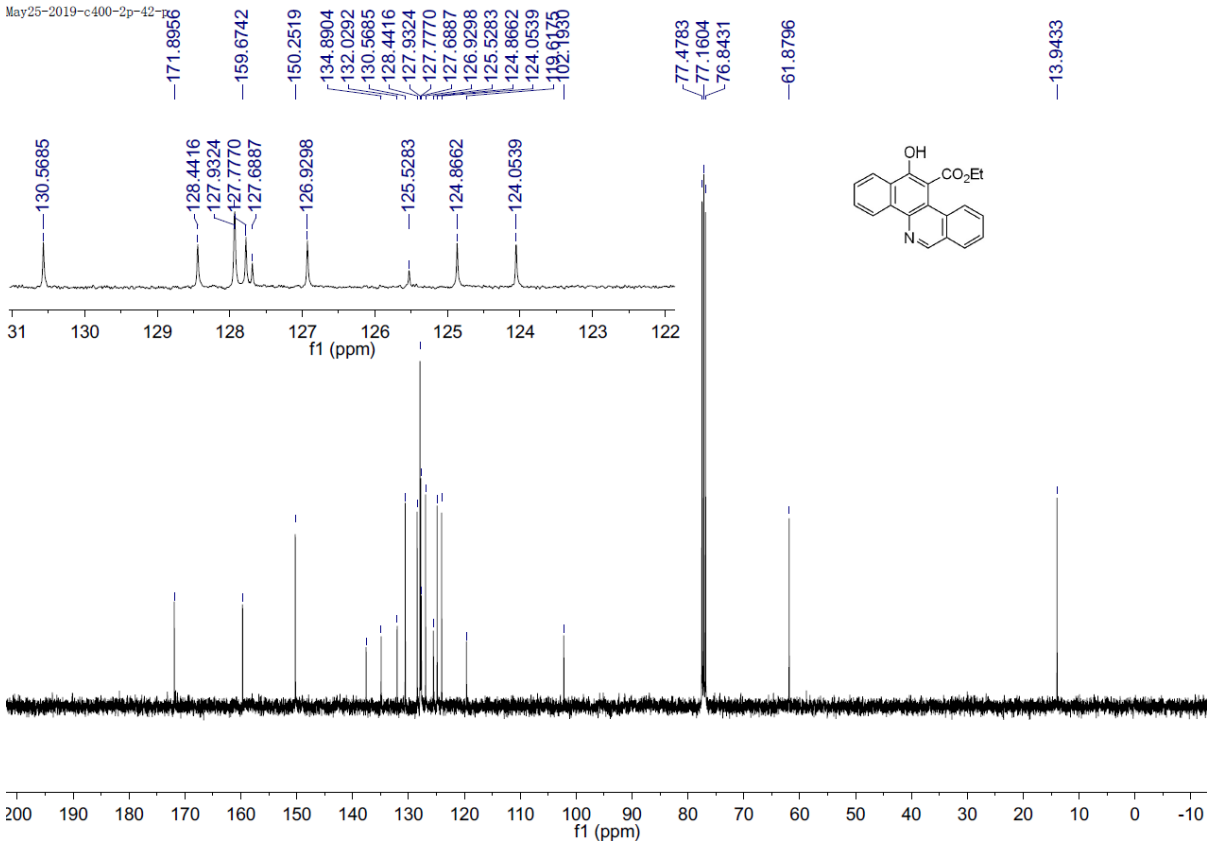
Supplementary Fig. 131 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 57.



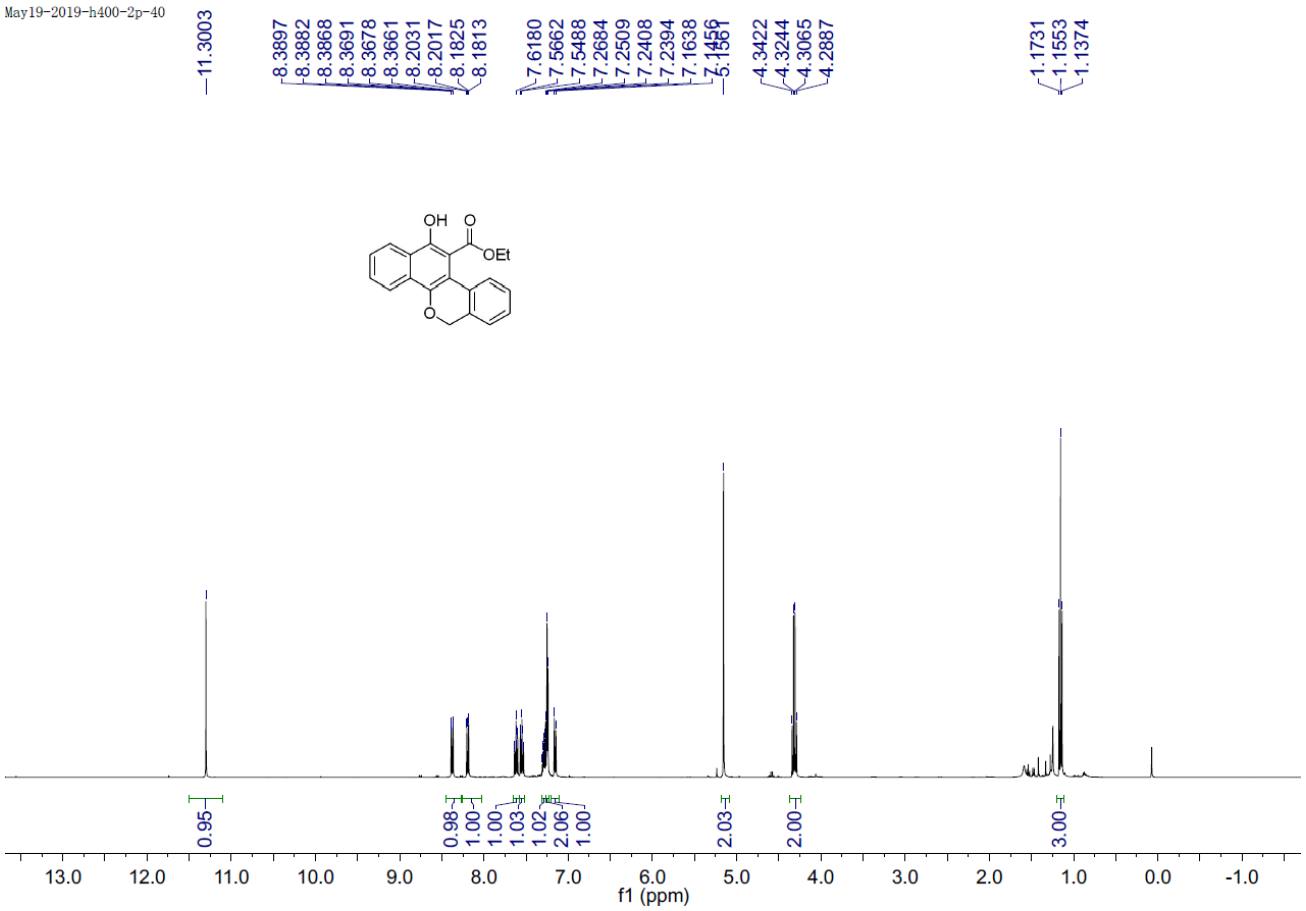
Supplementary Fig. 132 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 57.



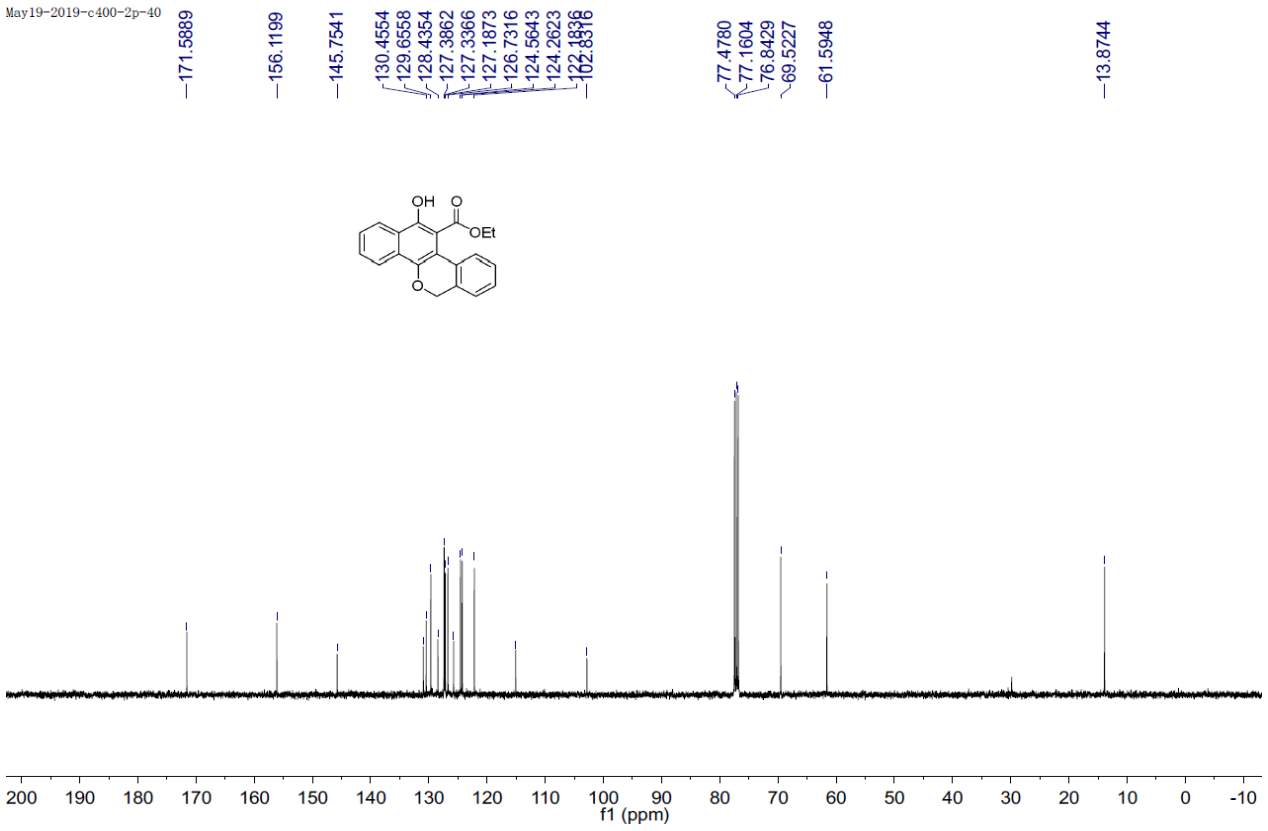
Supplementary Fig. 133 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 58.



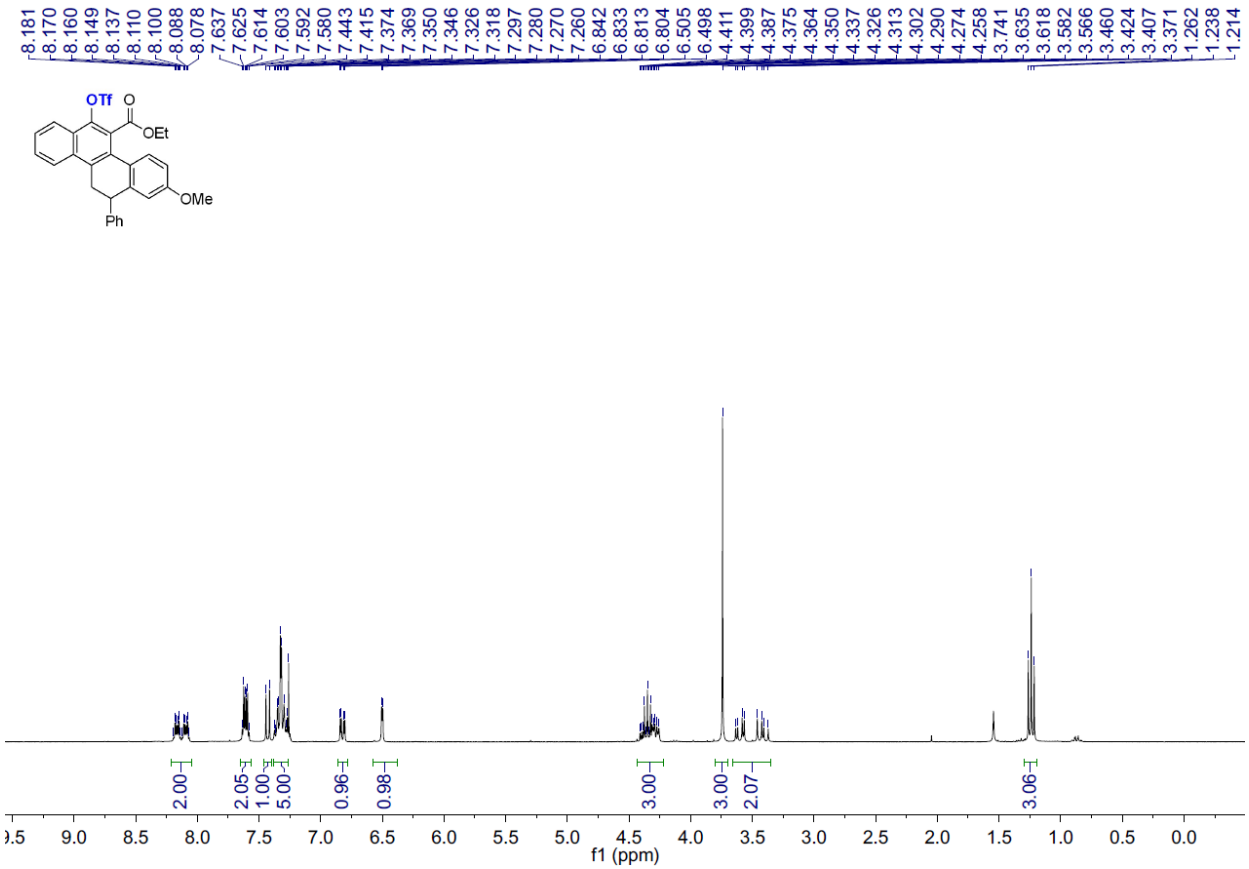
Supplementary Fig. 134 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 58.



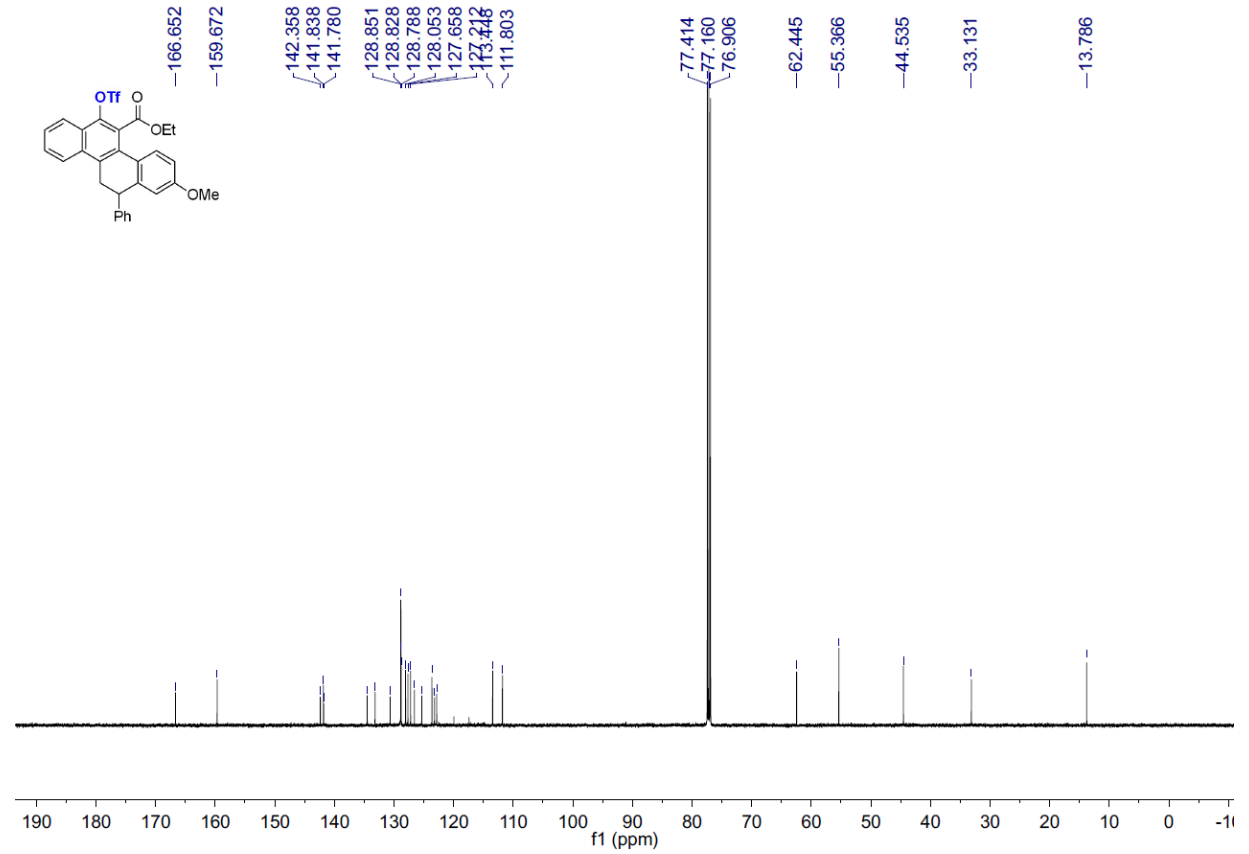
Supplementary Fig. 135 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 59.



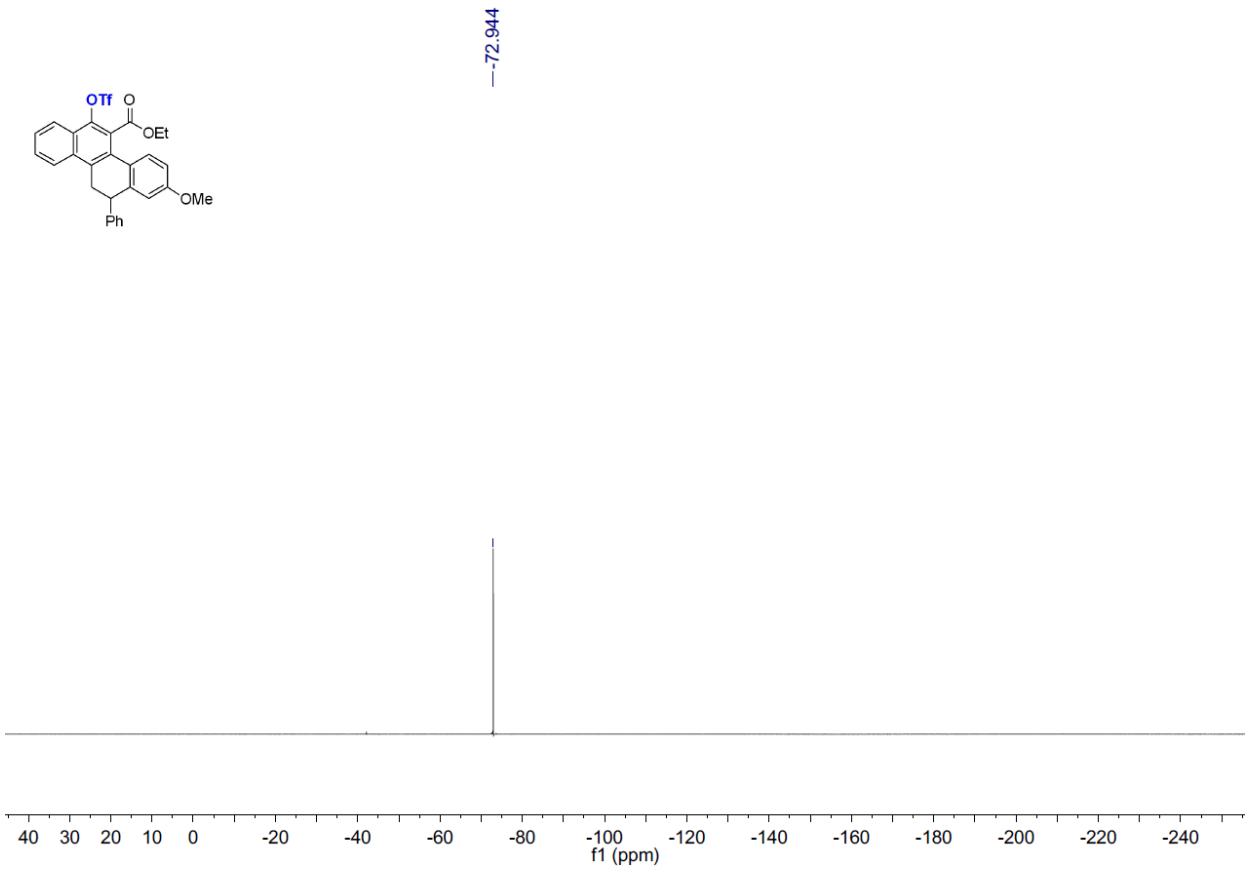
Supplementary Fig. 136 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 59.



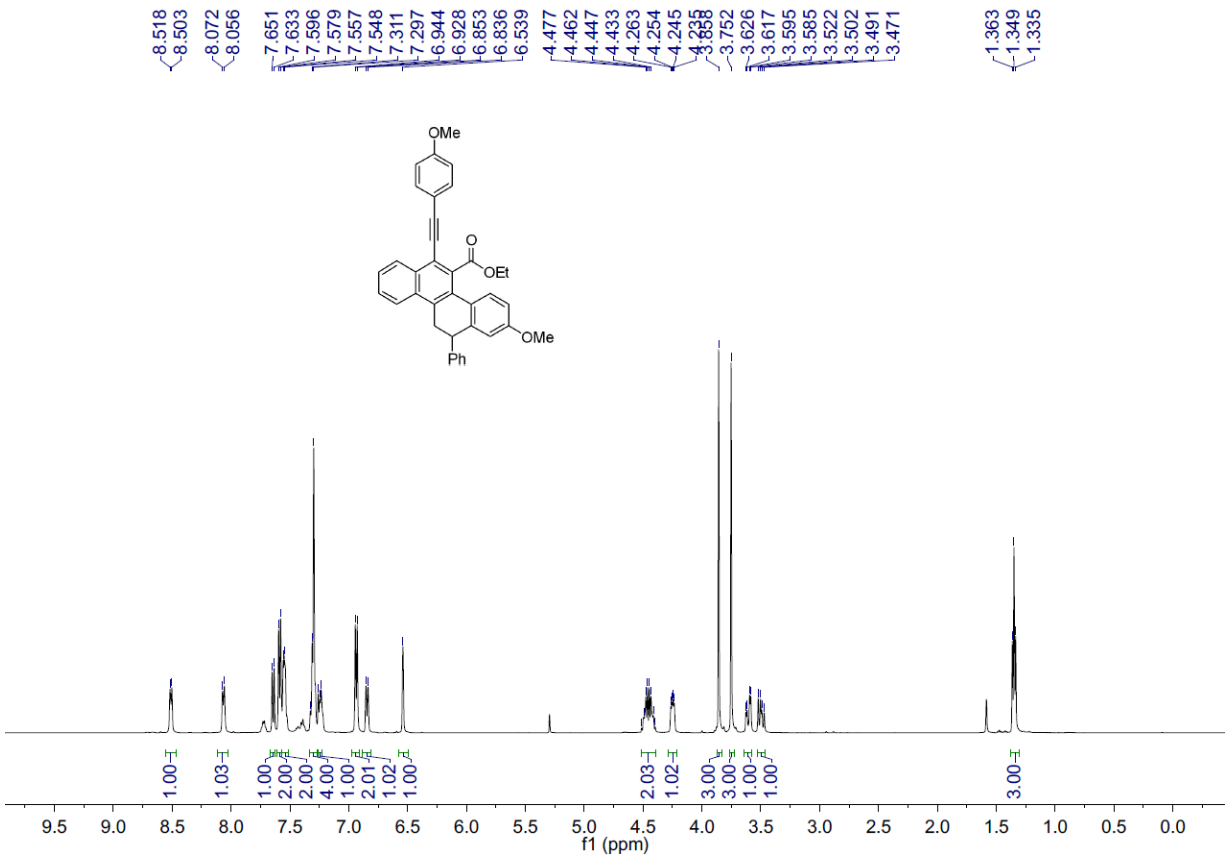
Supplementary Fig. 137 ^{1}H NMR (300 MHz, $CDCl_3$) spectrum for 60.



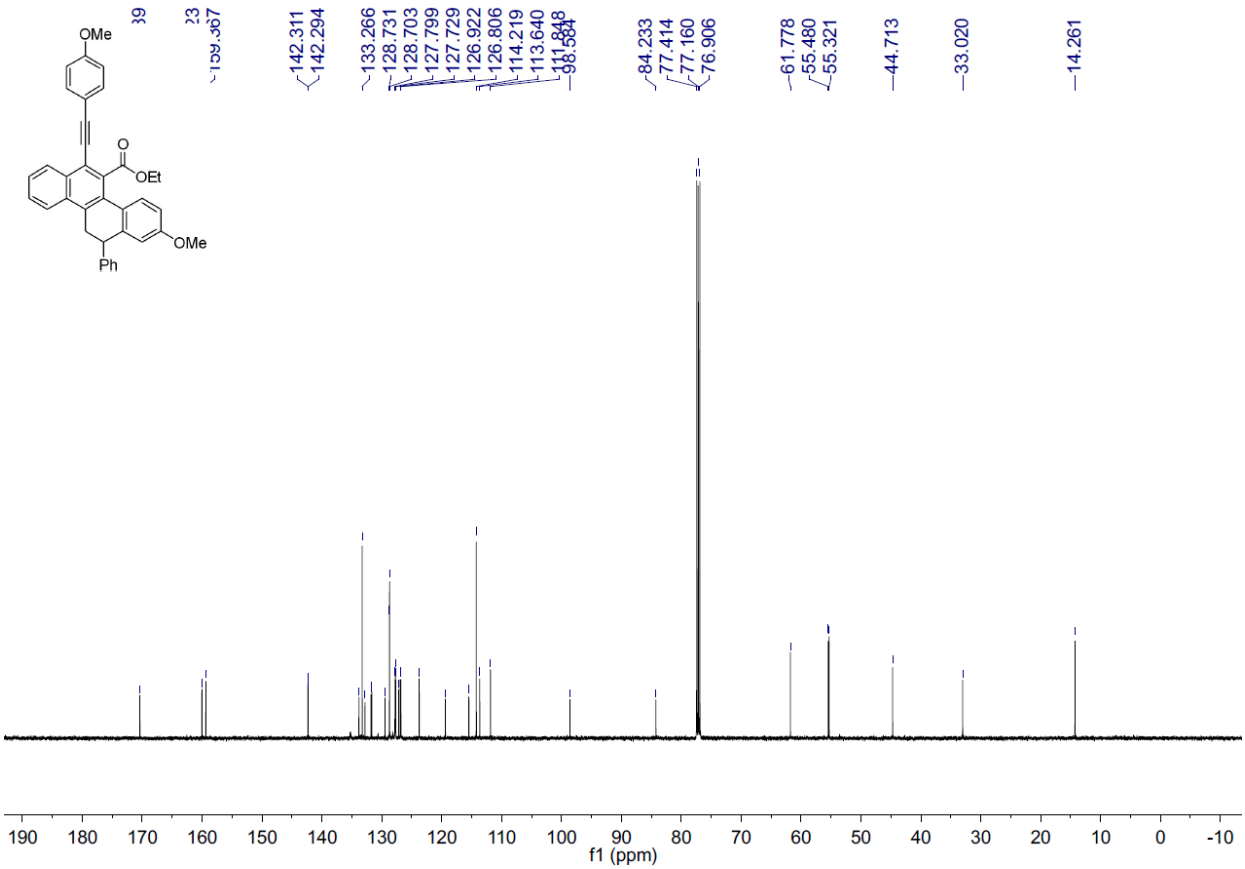
Supplementary Fig. 138 ^{13}C NMR (125 MHz, $CDCl_3$) spectrum for 60.



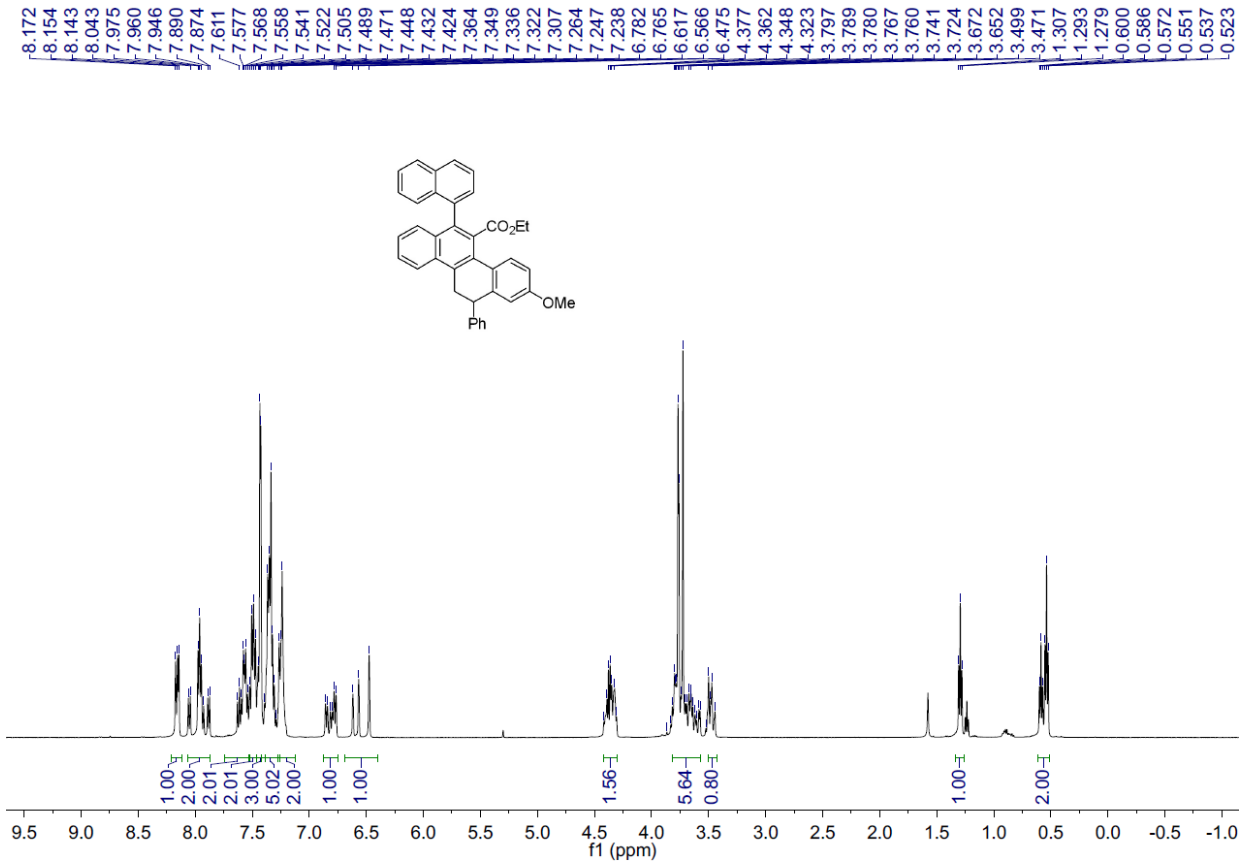
Supplementary Fig. 139 ^{19}F NMR (283 MHz, $CDCl_3$) spectrum for 60.



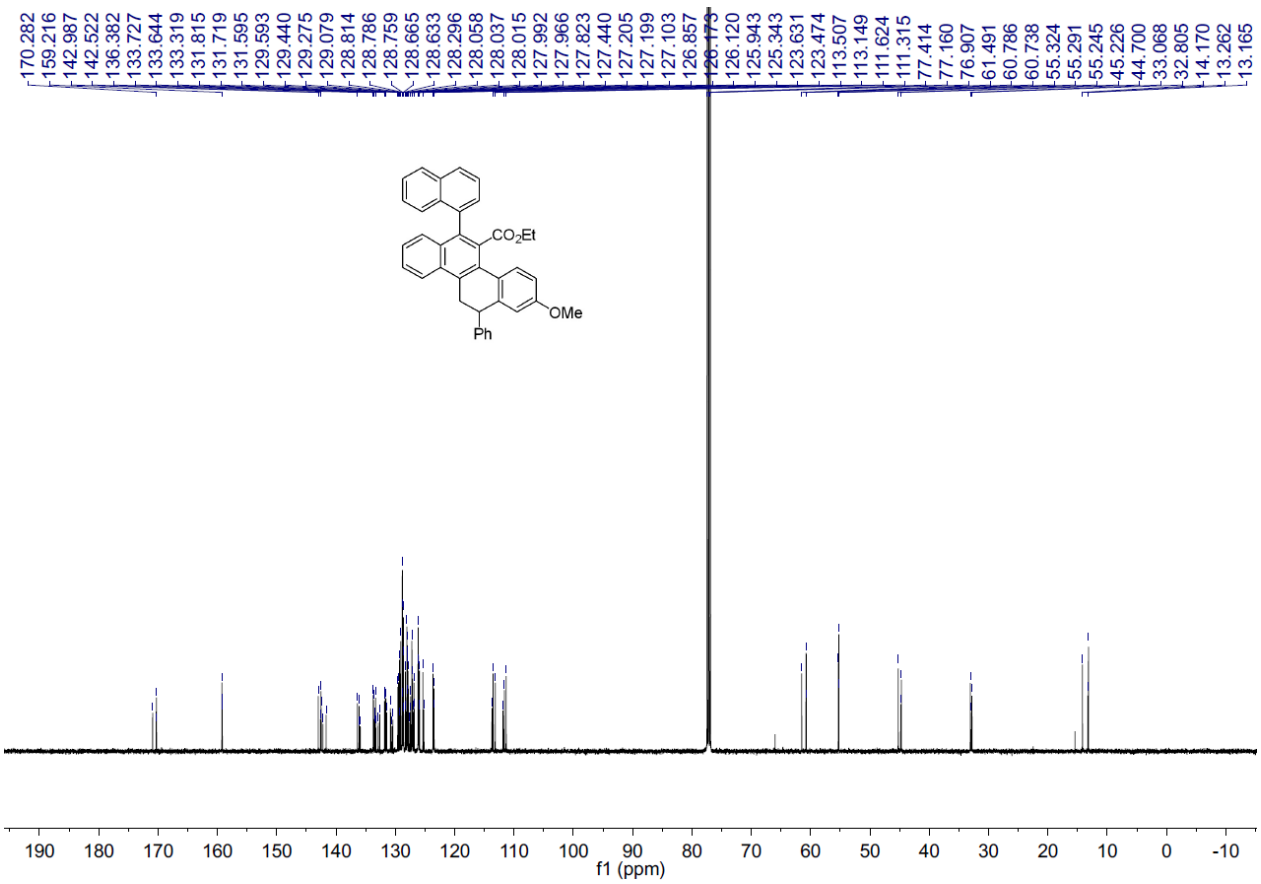
Supplementary Fig. 140 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum for 61.



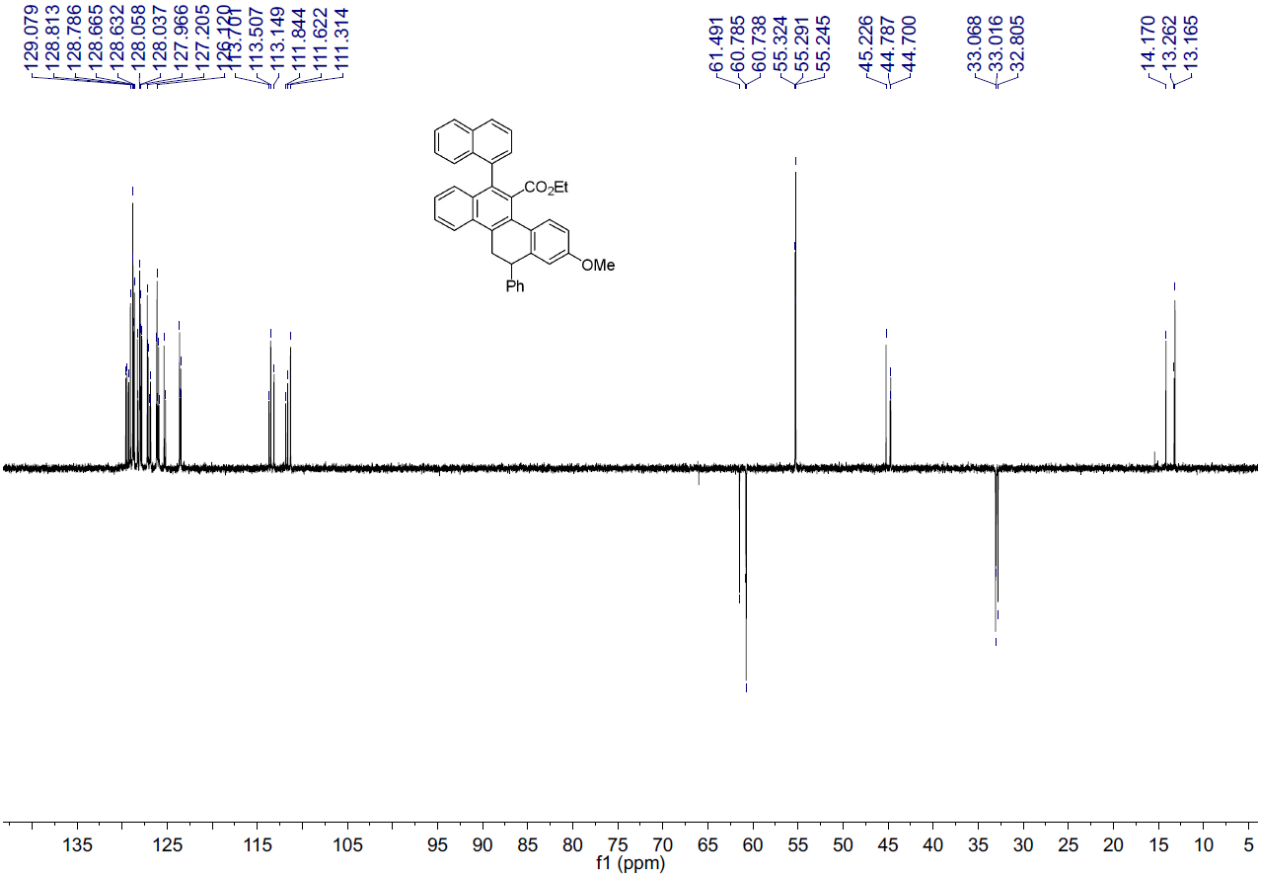
Supplementary Fig. 141 ^{13}C NMR (125 MHz, $CDCl_3$) spectrum for 61.



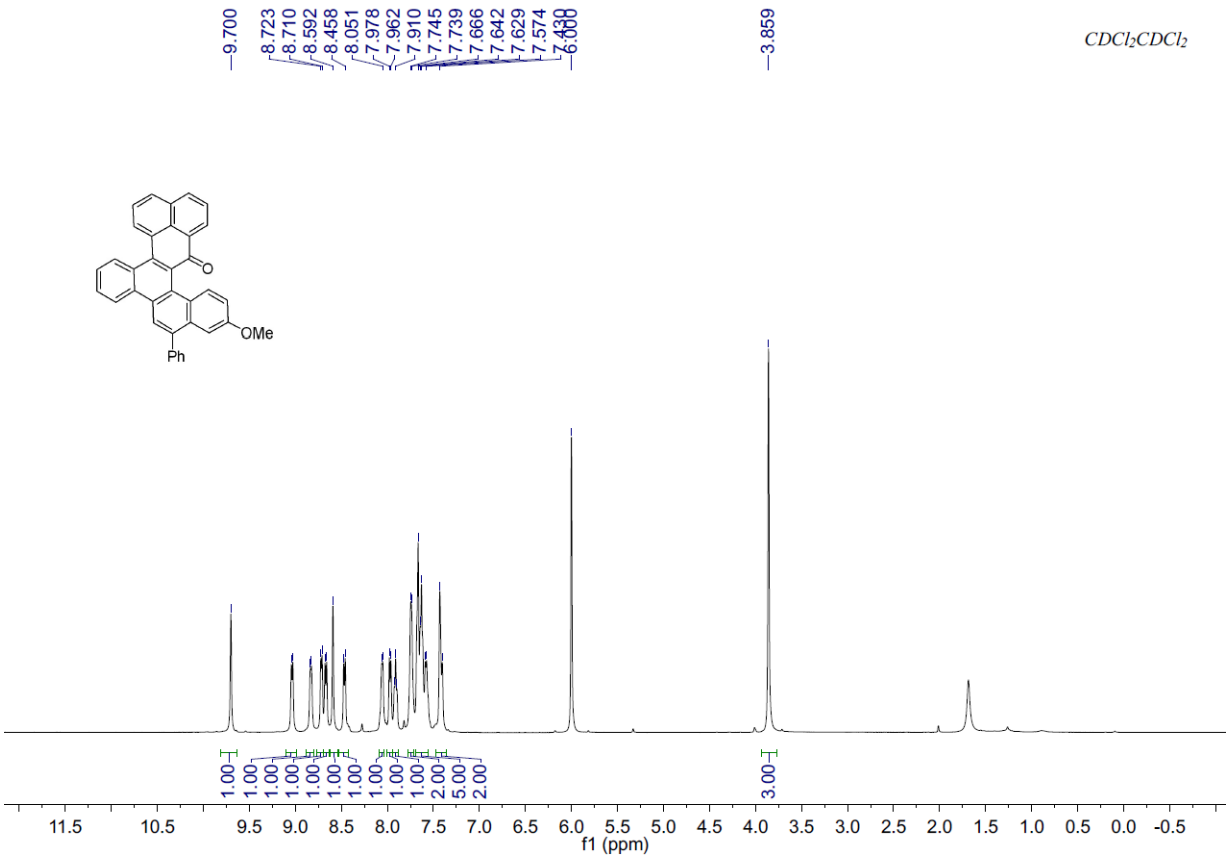
Supplementary Fig. 142 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum for 62.



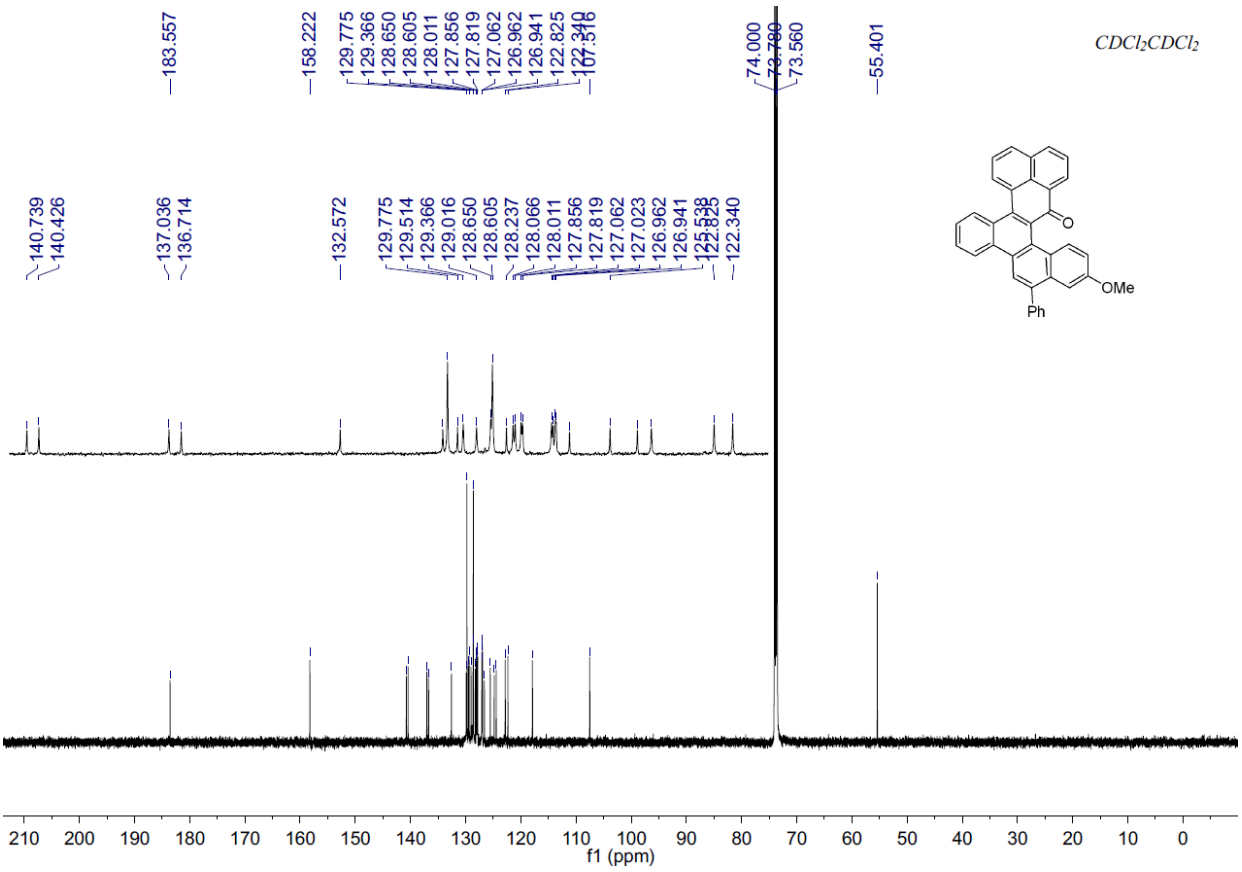
Supplementary Fig. 143 ^{13}C NMR (125 MHz, $CDCl_3$) spectrum for 62.



Supplementary Fig. 144 Dept 135 NMR (125 MHz, $CDCl_3$) spectrum for 62.

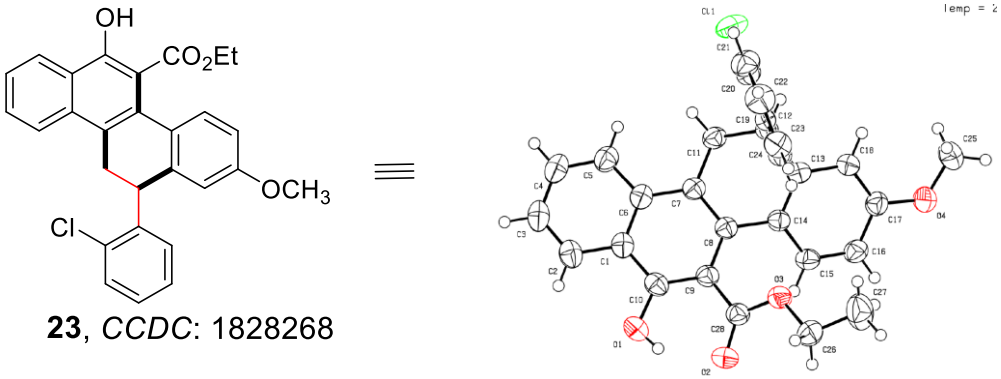


Supplementary Fig. 145 ^{1}H NMR (500 MHz, $CDCl_2CDCl_2$) spectrum for 63.



Supplementary Fig. 146 ^{13}C NMR (125 MHz, $CDCl_2CDCl_2$) spectrum for 63.

Single-crystal X-ray diffractions

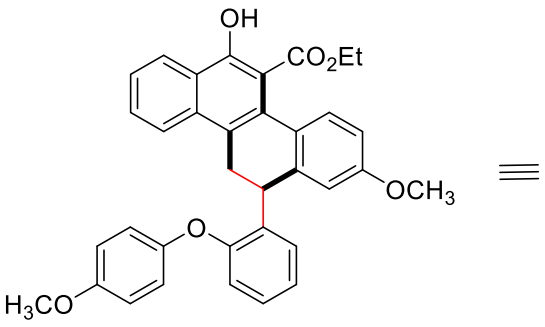


23, *CCDC*: 1828268

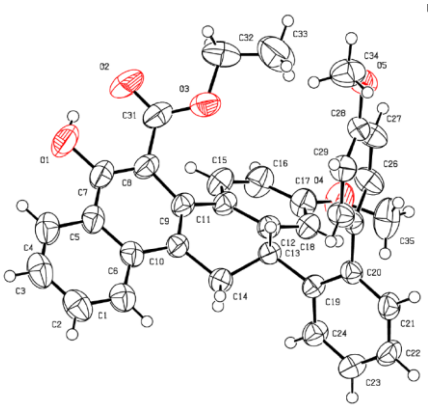
Datablock: cu_zc0207a_1_0m

```
Bond precision:  C-C = 0.0022 A          Wavelength=1.54178

Cell:            a=14.510(2)     b=7.7110(11)        c=19.858(3)
                 alpha=90        beta=91.260(6)      gamma=90
Temperature:     290 K

                 Calculated                Reported
Volume           2221.3(6)                 2221.4(6)
Space group      P 21/c                    P 1 21/c 1
Hall group       -P 2ybc                   -P 2ybc
Moiety formula   C28 H23 Cl O4             C28 H23 Cl O4
Sum formula      C28 H23 Cl O4             C28 H23 Cl O4
Mr               458.91                    458.91
Dx,g cm-3        1.372                     1.372
Z                4                         4
Mu (mm-1)        1.799                     1.799
F000             960.0                     960.0
F000'            964.18
h,k,lmax         17,9,24                   17,9,23
Nref             4131                      4042
Tmin,Tmax        0.682,0.698               0.530,0.753
Tmin'            0.464

Correction method= # Reported T Limits: Tmin=0.530 Tmax=0.753
AbsCorr = MULTI-SCAN

Data completeness= 0.978          Theta(max)= 68.992

R(reflections)= 0.0385( 3699)     wR2(reflections)= 0.1129( 4042)

S = 1.063                 Npar= 301
```

Supplementary Fig. 147 Crystallographic Data for 23.



34, *CCDC*: 1849634



Datablock: t

Bond precision: C-C = 0.0041 A Wavelength=0.71073

Cell: a=9.29800 b=19.00800 c=15.95600
alpha=90 beta=96.7100 gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	2800.689	2801
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C35 H30 O5	?
Sum formula	C35 H30 O5	C35 H30 O5
Mr	530.59	530.59
Dx,g cm-3	1.258	1.258
Z	4	4
Mu (mm-1)	0.083	0.083
F000	1120.0	1120.0
F000'	1120.54	
h,k,lmax	11,22,18	11,22,18
Nref	4930	4904
Tmin,Tmax		
Tmin'		

Correction method= Not given

Data completeness= 0.995 Theta(max)= 24.997

R(reflections)= 0.0751(4120) wR2(reflections)= 0.1561(4904)

S = 1.147 Npar= 365

Supplementary Fig. 148 Crystallographic Data for 34.