SUPPORTING INFORMATION

Copper-catalyzed formal [1+2+2]-annulation of alkyne-tethered diazoacetates and pyridines: access to polycyclic indolizines

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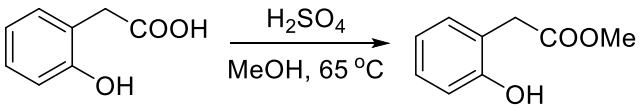
General Information

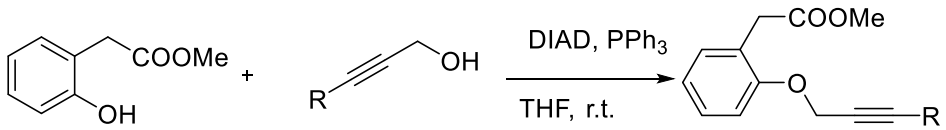
All reactions were carried out in oven-dried glassware. Flash column chromatography was performed using silica gel (300-400 mesh). Analytical thin-layer chromatography was performed using glass plates pre-coated with 200-300 mesh silica gel impregnated with a fluorescent indicator (254 nm). ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a 400 MHz spectrometer; chemical shifts are reported in ppm with the solvent signal as reference, and coupling constants (*J*) are given in Hertz. The peak information is described as: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, comp = composite. High-resolution mass spectra (HRMS) were recorded on a commercial apparatus (ESI or CI Source).

General Procedure for the Preparation of Diazo Compounds 1.



S-1 **S-2**

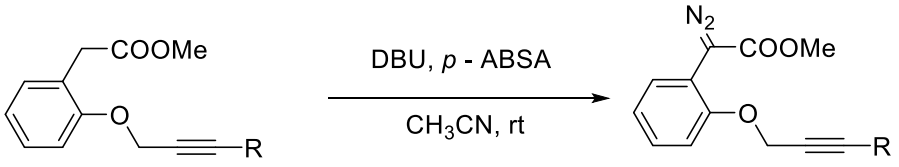
Synthesis of **S-2:** To a 250-mL oven-dried flask containing a magnetic stirring bar, **S-1** (15.2 g, 100.0 mmol) was dissolved in MeOH (75.0 mL), then added H_2SO_4 (2.6 g, 10.0 mmol) slowly, and the reaction mixture was stirred at 65 ℃ for 36 hours. Then the reaction mixture was diluted with dichloromethane (20.0 mL) and washed with saturated $NaHCO_3$ (200.0 mL). The organic phase was dried over Na_2SO_4 and the solvent was evaporated in *vacuo* after filtration to give product **S-2** in > 90% yields, which were directly used in the next step without further purification.



S-2 **S-3** **S-4**

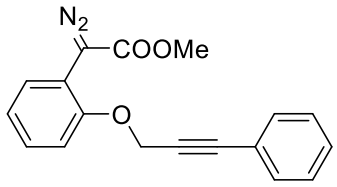
Synthesis of **S-4:** To a 50-mL oven-dried flask containing a magnetic stirring bar, **S-2** (1.7 g, 10.0 mmol), propargyl alcohol **S-3** (11.0 mmol, 1.1 equiv.), PPh_3 (3.9 g, 1.5 equiv.) in dry THF (30.0 mL), was added DIAD (3.0 g, 1.5 equiv.) slowly at 0 ℃,

and the reaction mixture was stirred at room temperature for 4-5 hours. Upon completed (monitored by TLC), the reaction mixture was filtrated through a short pad of Celite, and the filtrate was evaporated in *vacuo*. The residue was purified by column chromatography on silica gel (Hexanes : EtOAc = 20:1) to give the pure products **S-4** in > 80% yields.

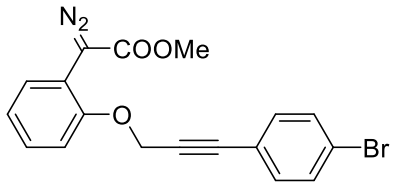


S-4 **1**

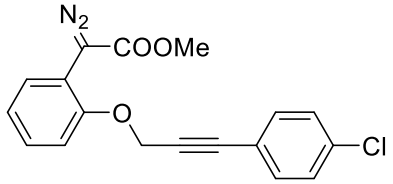
Synthesis of **1:** To a 50-mL oven-dried flask containing a magnetic stirring bar, compound **S-4** (5.0 mmol), *p*-ABSA (7.5 mmol) in dry CH_3CN (15 mL), was added DBU (10.0 mmol) in CH_3CN (5 mL) dropwise at 0℃. The resulting mixture was allowed to warm to room temperature over 30 min and stirred for additional 10 h. The reaction was quenched with aqueous NH_4Cl solution (60 mL) and then extracted with diethyl ether (20 mL), and the organic phase was dried over anhydrous Na_2SO_4. After evaporating the solvent after filtering through a short pad of Celite, the resulting residue was purified by column chromatography on silica gel (Hexanes : EtOAc = 20:1) to give pure **1** in >60% yields.



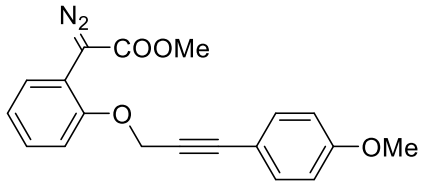
Methyl 2-diazo-2-(2-((3-phenylprop-2-yn-1-yl)oxy)phenyl)acetate (1a). Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.68 – 7.60 (m, 1H), 7.51 – 7.42 (m, 2H), 7.37 – 7.27 (comp, 4H), 7.16 – 7.05 (m, 2H), 4.96 (s, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 166.6, 153.7, 131.8, 130.3, 128.8, 128.5, 128.4, 122.2, 122.0, 114.6, 112.8, 87.6, 83.4, 57.3, 52.0; HRMS (TOF MS ESI$^+$) calculated for $C_{18}H_{14}N_2O_3Na$ $[M+Na]^+$: 329.0897, found 329.0899.



Methyl 2-(2-((3-(4-bromophenyl)prop-2-yn-1-yl)oxy)phenyl)-2-diazoacetate (1b). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.61 – 7.59 (m, 1H), 7.45 – 7.35 (m, 2H), 7.35 – 7.20 (comp, 3H), 7.08 – 7.03 (m, 2H), 4.90 (s, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 166.5, 153.6, 133.2, 131.6, 130.3, 128.5, 123.1, 122.1, 121.1, 114.6, 112.8, 86.5, 84.6, 57.2, 52.0; HRMS (TOF MS ESI$^+$) calculated for $C_{18}H_{13}BrN_2O_3Na$ $[M+Na]^+$: 407.0002, found 406.9996.

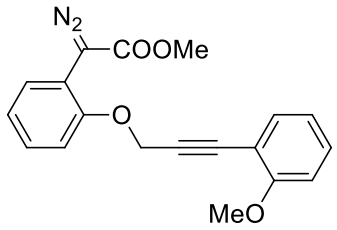


Methyl 2-(2-((3-(4-chlorophenyl)prop-2-yn-1-yl)oxy)phenyl)-2-diazoacetate (1c). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.67 – 7.56 (m, 1H), 7.40 – 7.32 (m, 2H), 7.30 – 7.25 (comp, 3H), 7.12 – 7.05 (m, 2H), 4.95 (s, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 166.7, 153.8, 135.0, 133.1, 130.4, 128.8, 128.6, 122.2, 120.7, 114.7, 112.8, 86.5, 84.4, 57.3, 52.1; HRMS (TOF MS ESI$^+$) calculated for $C_{18}H_{13}ClN_2O_3Na$ $[M+Na]^+$: 363.0507, found 363.0515.

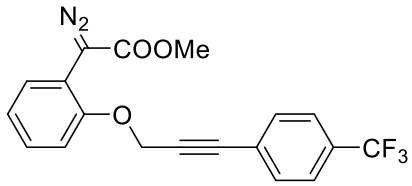


Methyl 2-diazo-2-(2-((3-(4-methoxyphenyl)prop-2-yn-1-yl)oxy)phenyl)acetate (1d). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.63 – 7.60 (m, 1H), 7.42 – 7.35 (m, 2H), 7.29 (m, 1H), 7.15 – 7.05 (m, 2H), 6.88 – 6.82 (m, 2H), 4.95 (s, 2H), 3.84 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 166.7, 160.1, 153.9, 133.4, 130.3, 128.5, 122.0, 114.6, 114.3, 114.0, 112.9, 87.6, 82.1, 57.5, 55.4, 52.1; HRMS (TOF MS ESI$^+$) calculated for $C_{19}H_{16}N_2O_4Na$ $[M+Na]^+$: 359.1002, found

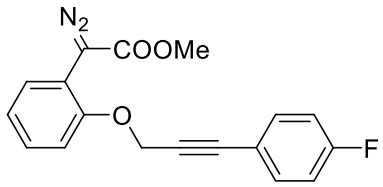
359.1004.



Methyl 2-diazo-2-(2-((3-(2-methoxyphenyl)prop-2-yn-1-yl)oxy)phenyl)acetate (1e). Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.60 – 7.57 (m, 1H), 7.38 –7.36 (m, 1H), 7.30 – 7.24 (m, 2H), 7.15 –7.13(m, 1H), 7.09 – 7.03 (m, 1H), 6.95 – 6.79 (m, 2H), 4.98 (s, 2H), 3.84 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 166.7, 160.3, 153.9, 133.9, 130.3, 130.2, 128.5, 121.9, 120.5, 114.5, 113.0, 111.4, 110.7, 87.4, 84.1, 57.6, 55.8, 52.0; HRMS (TOF MS ESI$^+$) calculated for $C_{19}H_{16}N_2O_4Na$ $[M+Na]^+$: 359.1008, found 359.1017.

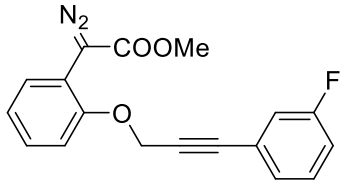


Methyl 2-diazo-2-(2-((3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-yl)oxy)phenyl) acetate (1f). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.64 – 7.49 (comp, 5H), 7.32 – 7.27 (m, 1H), 7.13 – 7.04 (m, 2H), 4.98 (s, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 166.6, 153.6, 132.0, 130.7, 130.4 (d, J = 3.1 Hz), 128.5, 125.9 (q, J = 1.5 Hz), 125.3 (q, J = 3.8 Hz), 122.5, 122.2, 114.6, 112.7, 57.1, 52.0; ^{19}F NMR (376 MHz, $CDCl_3$) (δ, ppm) -62.91. HRMS (TOF MS ESI$^+$) calculated for $C_{19}H_{13}F_3N_2O_3Na$ $[M+Na]^+$: 397.0770, found 397.0767.

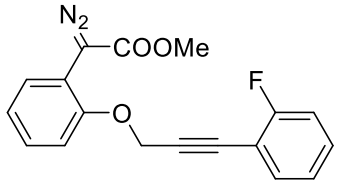


Methyl 2-diazo-2-(2-((3-(4-fluorophenyl)prop-2-yn-1-yl)oxy)phenyl)acetate (1g).

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.63 – 7.60 (m, 1H), 7.45 – 7.38 (m, 2H), 7.32 – 7.26 (m, 1H), 7.12 – 7.06 (m, 2H), 7.04 – 6.98 (m, 2H), 4.95 (s, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 166.7, 162.9 (d, *J* = 250.1 Hz), 153.8, 133.9 (d, *J* = 8.5 Hz), 130.4, 128.6, 122.4, 118.3 (d, *J* = 3.6 Hz), 115.7 (d, *J* = 22.1 Hz), 114.7, 112.9, 86.6, 83.2, 57.3, 52.1; ^{19}F NMR (376 MHz, $CDCl_3$) (δ, ppm) -110.06. HRMS (TOF MS ESI$^+$) calculated for $C_{18}H_{13}FN_2O_3Na$ $[M+Na]^+$: 347.0802, found 347.0797.

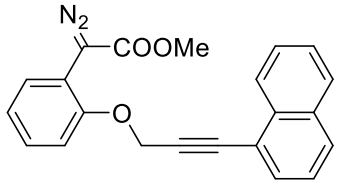


Methyl 2-diazo-2-(2-((3-(3-fluorophenyl)prop-2-yn-1-yl)oxy)phenyl)acetate (1h). Yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.63 – 7.60 (m, 1H), 7.32 – 7.25 (m, 2H), 7.23 – 7.20 (m, 1H), 7.15 – 7.03 (comp, 4H), 4.96 (s, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 166.7, 162.4 (d, *J* = 246.7 Hz), 153.8, 130.5, 130.1 (d, *J* = 8.6 Hz), 128.6, 127.8 (d, *J* = 3.1 Hz), 124.0 (d, *J* = 9.5 Hz), 122.2, 118.7 (d, *J* = 22.9 Hz), 116.29 (d, *J* = 21.1 Hz), 116.2, 114.7, 112.9, 86.4, 84.4, 57.2, 52.1.; ^{19}F NMR (376 MHz, $CDCl_3$) (δ, ppm) -112.72. HRMS (TOF MS ESI$^+$) calculated for $C_{18}H_{13}FN_2O_3Na$ $[M+Na]^+$: 347.0802, found 347.0790.

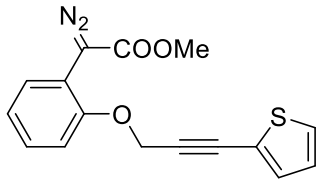


Methyl 2-diazo-2-(2-((3-(2-fluorophenyl)prop-2-yn-1-yl)oxy)phenyl)acetate (1i). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.64 – 7.61 (m, 1H), 7.46 – 7.42 (m, 1H), 7.37 – 7.28 (m, 2H), 7.18 – 7.02 (comp, 4H), 5.00 (s, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 166.6, 162.9 (d, *J* = 252.2 Hz), 153.7, 133.7, 130.6 (d, *J* = 8.0 Hz), 130.3, 128.5, 124.0 (d, *J* = 3.9 Hz), 122.1, 115.6 (d, *J* = 20.7 Hz), 114.6, 112.8, 110.7 (d, *J* = 15.6 Hz), 88.6, 81.0, 57.2, 52.0; ^{19}F NMR (376 MHz,

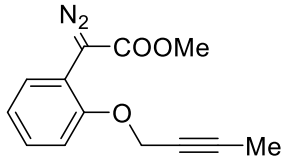
$CDCl_3$) (δ, ppm) -109.78. HRMS (TOF MS ESI^+) calculated for $C_{18}H_{13}FN_2O_3Na$ $[M+Na]^+$: 347.0802, found 347.0791.



Methyl 2-diazo-2-(2-((3-(naphthalen-1-yl)prop-2-yn-1-yl)oxy)phenyl)acetate (1j). Yellow solid; ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.25 – 8.21 (m, 1H), 7.88 – 7.83 (m, 2H), 7.70 – 7.66 (m, 2H), 7.59 – 7.50 (m, 2H), 7.44 – 7.41 (m, 1H), 7.39 – 7.30 (m, 1H), 7.21 – 7.19 (m, 1H), 7.15 – 7.11 (m, 1H), 5.12 (s, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 166.6, 153.7, 133.3, 133.1, 130.8, 130.4, 129.3, 128.5, 128.3, 127.0, 126.5, 126.1, 125.2, 122.1, 119.8, 114.8, 113.0, 88.2, 85.8, 57.4, 52.0; HRMS (TOF MS ESI^+) calculated for $C_{22}H_{16}N_2O_3Na$ $[M+Na]^+$: 379.1053, found 379.1062.

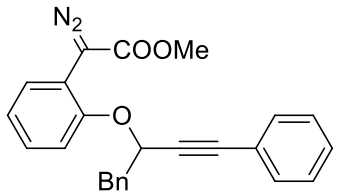


Methyl 2-diazo-2-(2-((3-(thiophen-2-yl)prop-2-yn-1-yl)oxy)phenyl)acetate (1k). Yellow solid; ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.65 – 7.63 (m, 1H), 7.36 – 7.23 (comp, 3H), 7.17 – 7.09 (m, 2H), 7.00 – 6.98 (m, 1H), 4.99 (s, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 166.6, 153.7, 133.0, 130.3, 128.5, 127.9, 127.1, 122.1, 122.0, 114.6, 112.8, 87.4, 80.9, 57.3, 52.0; HRMS (TOF MS ESI^+) calculated for $C_{16}H_{12}N_2O_3SNa$ $[M+Na]^+$: 335.0461, found 335.0460.

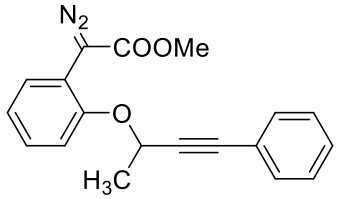


Methyl 2-(2-(but-2-yn-1-yloxy)phenyl)-2-diazoacetate (1l). Yellow oil; ^1H NMR

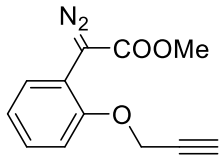
(400 MHz, $CDCl_3$) (δ, ppm) 7.62 – 7.59 (m, 1H), 7.30 – 7.25 (m, 1H), 7.16 – 6.97 (m, 2H), 4.71 (t, *J* = 2.4 Hz, 2H), 3.85 (s, 3H), 1.87 (t, *J* = 2.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 166.6, 153.8, 130.2, 128.4, 121.7, 114.3, 112.6, 84.1, 83.2, 73.6, 56.9, 51.9; HRMS (TOF MS ESI$^+$) calculated for $C_{13}H_{12}N_2O_3Na$ $[M+Na]^+$: 267.0740, found 267.0739.



Methyl 2-diazo-2-(2-((1,4-diphenylbut-3-yn-2-yl)oxy)phenyl)acetate (1m). Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.72 – 7.70 (m, 1H), 7.54 – 7.42 (comp, 6H), 7.42 – 7.32 (comp, 5H), 7.27 – 7.26 (m, 1H), 7.18 – 7.14 (m, 1H), 5.29 – 5.26 (m, 1H), 3.90 (s, 3H), 3.55 – 3.43(m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 166.5, 153.6, 136.3, 131.7, 130.4, 129.7, 128.7, 128.43, 128.39, 128.3, 127.0, 122.1, 122.0, 114.7, 114.2, 87.7, 86.5, 70.6, 51.9, 42.2; HRMS (TOF MS ESI$^+$) calculated for $C_{25}H_{20}N_2O_3Na$ $[M+Na]^+$: 419.1372, found 419.1378.

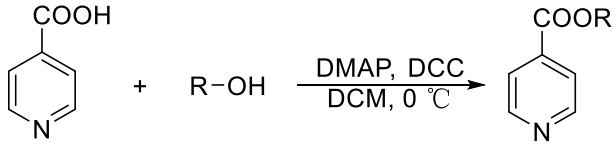


Methyl 2-diazo-2-(2-((4-phenylbut-3-yn-2-yl)oxy)phenyl)acetate (1n). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.70 – 7.61 (m, 1H), 7.47 – 7.39 (m, 2H), 7.37 – 7.27 (comp, 4H), 7.24 (d, *J* = 8.2 Hz, 1H), 7.16 – 7.04 (m, 1H), 5.15 (d, *J* = 6.5 Hz, 1H), 3.86 (s, 3H), 1.91 – 1.78 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 166.7, 153.4, 131.8, 130.1, 128.7, 128.3, 122.2, 121.9, 114.5, 113.9, 87.7, 86.1, 65.2, 52.0, 22.2; HRMS (TOF MS ESI$^+$) calculated for $C_{19}H_{16}N_2O_3Na$ $[M+Na]^+$: 343.1053, found 343.1048.



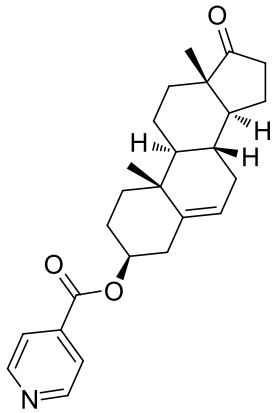
Methyl 2-diazo-2-(2-(prop-2-yn-1-yloxy)phenyl)acetate (1q). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.62 – 7.60 (m, 1H), 7.29 – 7.25 (m, 1H), 7.10 – 7.00 (m, 2H), 4.73 (d, *J* = 2.5 Hz, 2H), 3.84 (s, 3H), 2.57 (t, *J* = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 166.4, 153.3, 130.2, 128.4, 122.0, 114.4, 112.5, 77.9, 76.0, 56.2, 51.9; HRMS (TOF MS ESI$^+$) calculated for $C_{12}H_{10}N_2O_3Na$ $[M+Na]^+$: 253.0584, found 253.0579.

General Procedure for the Preparation of Pyridine Derivatives 2

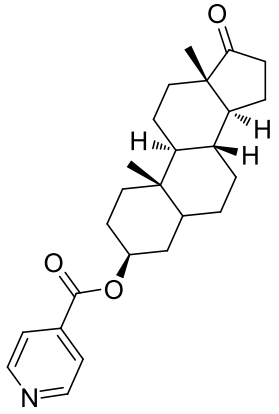


S-5 **S-6** **2**

To a 50-mL oven-dried flask containing a magnetic stirring bar, **S-5** (0.676 g, 5.5 mmol, 1.1 equiv.), and alcohol **S-6** (5.0 mmol, 1.0 equiv.) in DCM (20 mL), was added DMAP (61.0 mg, 0.5 mmol, 10.0 mol%) and DCC (1.25 g, 6.0 mmol, 1.2 equiv.) in sequence at 0 ℃. Then the reaction mixture was stirred for 4-5 hours at room temperature. Upon completed (monitored by TLC), the solvent was evaporated under vacuum after filtering through a short pad of Celite. The residue was purified by column chromatography on silica gel (Hexanes : EtOAc = 10:1) to give the pure products **2** as white solid with > 90% yields.

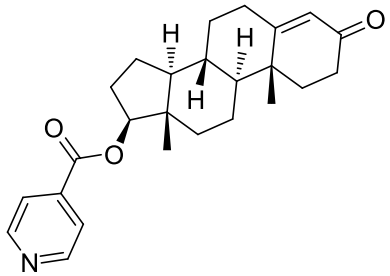


(3*S*,8*R*,9*S*,10*R*,13*S*,14*S*)-10,13-dimethyl-17-oxo-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl isonicotinate (2A). White solid; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.84 – 8.59 (m, 2H), 7.87 – 7.73 (m, 2H), 5.43 (d, *J* = 5.1 Hz, 1H), 4.90 – 4.82 (m, 1H), 2.47 – 2.40 (comp, 3H), 2.18 – 2.03 (m, 2H), 2.01 – 1.88 (comp, 3H), 1.86 – 1.78 (m, 1H), 1.76 – 1.59 (comp, 4H), 1.59 – 1.46 (m, 2H), 1.36 – 1.12 (comp, 4H), 1.07 (s, 3H), 0.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 164.5, 150.5, 139.6, 138.0, 123.0, 122.5, 75.5, 51.8, 50.2, 47.6, 38.1, 37.0, 36.8, 35.9, 31.53, 31.47, 30.9, 27.8, 22.0, 20.4, 19.5, 13.6; HRMS (TOF MS ESI$^+$) calculated for $C_{25}H_{31}NO_3Na$ $[M+Na]^+$: 416.2202, found 416.2200.

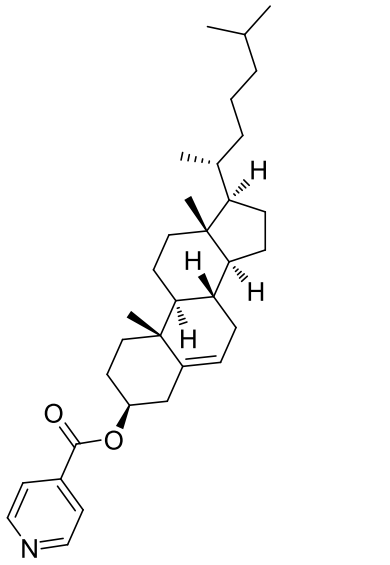


(3*S*,8*R*,9*S*,10*S*,13*S*,14*S*)-10,13-dimethyl-17-oxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl isonicotinate (2B). White solid; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.73 – 8.46 (m, 2H), 7.84 – 7.52 (m, 2H), 4.86 – 4.78(m, 1H), 2.32 – 2,25 (m, 1H), 1.97 – 1.87 (m, 1H), 1.86 – 1.75 (m, 2H), 1.72 – 1.57 (comp, 4H), 1.57 – 1.47 (m, 2H), 1.46 – 1.31 (m, 3H), 1.27 – 1.07 (comp, 6H), 1.01 – 0.93 (m, 1H), 0.91 – 0.81 (m, 1H), 0.76 (s, 3H), 0.72 (s, 3H), 0.65 – 0.56 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ,

ppm) 164.3, 150.3, 137.8, 122.6, 74.9, 54.1, 51.1, 47.5, 44.4, 36.5, 35.6, 35.5, 34.8, 33.7, 31.3, 30.6, 28.1, 27.2, 21.6, 20.3, 13.6, 12.1; HRMS (TOF MS ESI$^+$) calculated for $C_{25}H_{33}NO_3Na$ $[M+Na]^+$: 418.2358, found 413.2344.

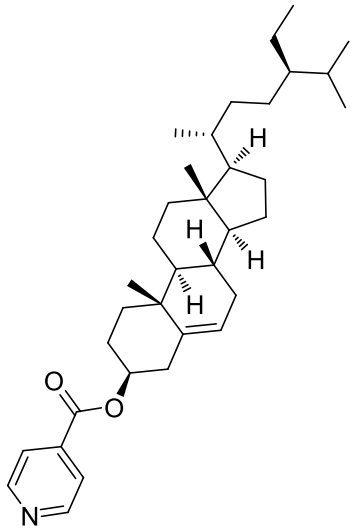


(8*R*,9*S*,10*R*,13*S*,14*S*,17*S*)-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl isonicotinate (2C). White solid; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.78 (d, *J* = 4.6 Hz, 2H), 7.90 – 7.77 (m, 2H), 5.81 – 5.66 (m, 1H), 4.89 – 4.84(m, 1H), 2.46 – 2.27 (comp, 5H), 2.05 – 2.00(m, 1H), 1.91 – 1.83 (m, 2H), 1.78 – 1.58 (comp, 5H), 1.49 – 1.38 (m, 2H), 1.32 – 1.25 (m, 1H), 1.20 (s, 3H), 1.18 – 0.99 (comp, 3H), 0.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 199.5, 170.8, 165.0, 150.5, 138.1, 124.2, 123.0, 84.1, 53.8, 50.4, 43.1, 38.7, 36.8, 35.8, 35.5, 34.0, 32.8, 31.6, 27.7, 23.7, 20.7, 17.5, 12.4; HRMS (TOF MS ESI$^+$) calculated for $C_{25}H_{33}NO_3Na$ $[M+Na]^+$: 416.2202, found 416.2212.

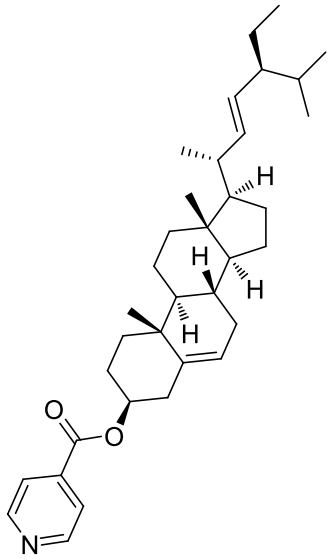


(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl

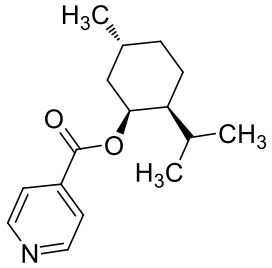
isonicotinate (2D). White solid; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.77 – 8.54 (m, 2H), 7.91 – 7.62 (m, 2H), 5.35 (d, *J* = 4.3 Hz, 1H), 4.84 – 4.76 (m, 1H), 2.40 (d, *J* = 8.0 Hz, 2H), 1.98 – 1.64 (comp, 8H), 1.55 – 1.39 (comp, 6H), 1.30 – 1.10 (comp, 8H), 1.06 – 0.92 (comp, 8H), 0.85 (d, *J* = 6.4 Hz, 3H), 0.82 – 0.79 (comp, 5H), 0.62 (d, *J* = 4.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 164.3, 150.5, 139.2, 137.9, 123.1, 122.8, 75.5, 56.6, 56.2, 50.0, 42.3, 39.5, 38.0, 36.6, 36.2, 35.8, 34.9, 31.8, 28.2, 28.0, 27.7, 25.5, 24.7, 24.3, 23.9, 22.8, 22.6, 21.0, 19.3, 18.7, 11.8; HRMS (TOF MS ESI$^+$) calculated for $C_{33}H_{49}NO_2Na$ $[M+Na]^+$: 514.3661, found 514.3673.



(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-17-((2*R*,5*R*)-5-ethyl-6-methylheptan-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl isonicotinate (2E). White solid; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.76 (d, *J* = 5.3 Hz, 2H), 7.88 – 7.82 (m, 2H), 5.45 – 5.40 (m, 1H), 4.92 – 4.88(m, 1H), 2.52 – 2.43 (m, 2H), 2.03 – 1.91 (comp, 4H), 1.86 – 1.77(m, 2H), 1.69 – 1.60 (m, 2H), 1.55 – 1.43 (comp, 5H), 1.31 – 1.14 (comp, 10H), 1.08 – 1.04 (m, 5H), 0.94 – 0.91 (comp, 4H), 0.87 – 0.81 (comp, 10H), 0.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 164.5, 150.4, 139.4, 138.3, 123.3, 123.1, 75.8, 56.8, 56.2, 50.2, 46.0, 42.5, 39.8, 38.2, 37.1, 36.8, 36.3, 34.1, 32.1, 31.99, 29.3, 28.4, 27.9, 26.2, 24.4, 23.2, 21.1, 20.0, 19.5, 19.2, 18.9, 12.1, 12.0; HRMS (TOF MS ESI$^+$) calculated for $C_{35}H_{53}NO_2Na$ $[M+Na]^+$: 542.3974, found 542.3960.



(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-17-((2*R*,5*S*,*E*)-5-ethyl-6-methylhept-3-en-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl isonicotinate (2F). White solid; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.75 (d, *J* = 5.5 Hz, 2H), 7.83 (d, *J* = 5.5 Hz, 2H), 5.41 (d, *J* = 5.1 Hz, 1H), 5.18 – 5.11(m, 1H), 5.04 – 4.98(m, 1H), 4.91 – 4.83(m, 1H), 2.46 (d, *J* = 7.5 Hz, 2H), 2.10 – 1.85 (comp, 6H), 1.79 – 1.65(m, 2H), 1.59 – 1.43 (comp, 7H), 1.28 – 1.09 (comp, 7H), 1.08 – 0.99 (comp, 8H), 0.86 – 0.78 (comp, 8H), 0.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 199.5, 170.8, 165.0, 150.5, 138.1, 124.2, 123.0, 84.1, 53.8, 50.4, 43.1, 38.7, 36.8, 35.8, 35.5, 34.0, 32.8, 31.6, 27.7, 23.7, 20.7, 17.5, 12.4; HRMS (TOF MS ESI^{+}) calculated for $C_{35}H_{51}NO_2Na$ $[M+Na]^{+}$: 540.3817, found 540.3833.

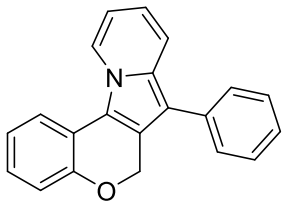


(1*S*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl isonicotinate (2G). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.81 – 8.63 (m, 2H), 7.84 – 7.72 (m, 2H), 4.94 – 4.88 (m, 1H), 2.10 – 2.04 (m, 1H), 1.91 – 1.83 (m, 1H), 1.73 – 1.65 (m, 2H), 1.57 – 1.46 (m, 2H), 1.13 – 1.03 (m, 2H), 0.93 – 0.83 (comp, 7H), 0.74 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 164.6, 150.6, 138.0, 122.9, 76.0, 47.2, 40.8,

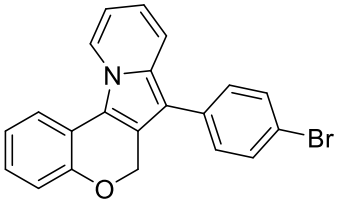
34.2, 31.5, 26.6, 23.6, 22.0, 20.8, 16.5; HRMS (TOF MS ESI$^+$) calculated for $C_{16}H_{23}NO_2Na$ $[M+Na]^+$: 284.1626, found 284.1620.

General Procedure for the Formal [1+2+2] Cycloaddition.

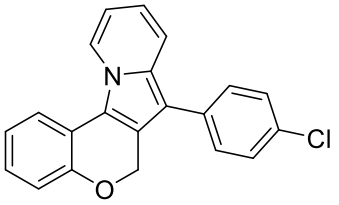
To a 10-mL oven-dried vial with a magnetic stirring bar, CuCl (1.0 mg, 5.0 mol%) in freshly distilled 1,4-dioxane (1.0 mL), was added a solution of diazo compounds **1** (0.2 mmol) and pyridine **2** (0.3 mmol) in 1,4-dioxane (1.0 mL) *via* a syringe pump at room temperature under argon atmosphere in 1 h. Then the resulting reaction mixture was stirred at 40 ℃ for additional 18 h. After the reaction was completed, the reaction mixture was directly purified by column chromatography on silica gel (eluent: Hexanes: EtOAc = 50:1 to 20:1) to give the pure products **3** in moderate to high yields.



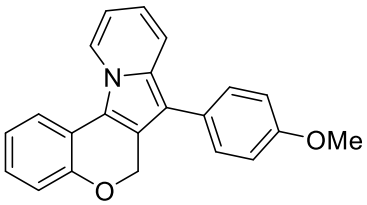
7-Phenyl-6*H*-chromeno[3,4-*b*]indolizine (3a). 44.0 mg, 74% yield. Yellow solid, mp = 166-169℃; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.50 (d, *J* = 7.1 Hz, 1H), 7.80 – 7.62 (m, 2H), 7.51 – 7.47 (m, *J* = 7.6 Hz, 2H), 7.43 – 7.37 (m, 2H), 7.36 – 7.29 (m, 1H), 7.16 – 7.09 (comp, 3H), 6,81 – 6.77 (m, 1H), 7.80 – 7.62 (m , 1H), 5.47 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 153.2, 134.3, 132.1, 129.02, 128.95, 126.6, 126.2, 123.1, 122.1, 120.8, 119.9, 119.6, 118.5, 118.1, 117.6, 116.3, 112.2, 111.4, 65.2; HRMS (TOF MS ESI$^+$) calculated for : $C_{21}H_{15}NONa$ $[M+Na]^+$: 320.1046, found 230.1044.



7-(4-Bromophenyl)-6*H*-chromeno[3,4-*b*]indolizine (3b). 51.0 mg, 68% yield. Yellow solid, mp = 165-166℃; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.50 (d, *J* = 7.1 Hz, 1H), 7.71 – 7.69 (m, 1H), 7.66 – 7.55 (comp, 3H), 7.29 – 7.21 (m, 2H), 7.21 – 7.06 (m, 3H), 6.84 – 6.80 (m, 1H), 6.73 – 6.69 (m, 1H), 5.41 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm)153.2, 133.3, 132.10, 132.08, 130.5, 126.7, 123.3, 122.2, 120.7, 120.1, 119.9, 119.4, 118.5, 118.2, 117.7, 116.6, 112.4, 110.2, 65.0; HRMS (TOF MS ESI$^+$) calculated for $C_{21}H_{14}BrNONa$ $[M+Na]^+$: 398.0156, found 398.0147.

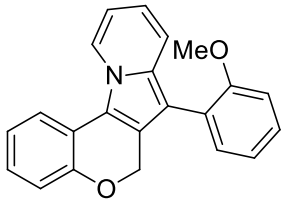


7-(4-Chlorophenyl)-6*H*-chromeno[3,4-*b*]indolizine (3c). 43.1 mg, 65% yield. Yellow solid, mp = 162-163℃; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.50 (d, *J* = 7.1 Hz, 1H), 7.71 – 7.69 (m, 1H), 7.64 – 7.61 (m, 1H), 7.50 – 7.38 (m, 2H), 7.38 – 7.28 (m, 2H), 7.19 – 7.03 (comp, 3H), 6.85 – 6.74 (m, 1H), 6.73 – 6.69 (m, 1H), 5.42 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 153.2, 132.8, 132.1, 132.0, 130.2, 129.2, 126.8, 123.2, 122.2, 120.7, 119.9, 119.5, 118.5, 118.22, 117.7, 116.5, 112.4, 110.2, 65.0; HRMS (TOF MS ESI$^+$) calculated for $C_{21}H_{14}ClNNaO$ $[M+Na]^+$: 354.0662, found 354.0670.

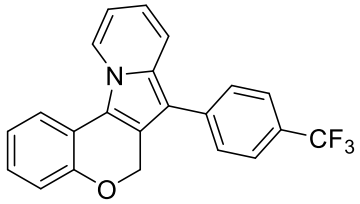


7-(4-Methoxyphenyl)-6*H*-chromeno[3,4-*b*]indolizine (3d). 39.9 mg, 61% yield. Yellow solid, mp = 133-134℃; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.48 (d, *J* = 7.1 Hz, 1H), 7.71 – 7.69 (m, 1H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.34 – 7.29 (m, 2H), 7.16 –

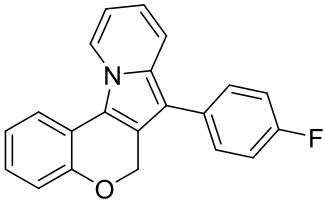
7.06 (comp, 3H), 7.05 – 6.99 (m, 2H), 6.75 (d, *J* = 9.1 Hz, 1H), 6.69 – 6.67 (m, 1H), 5.44 (s, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 158.3, 153.2, 132.0, 130.2, 126.7, 126.5, 123.1, 122.1, 120.7, 119.9, 119.7, 118.5, 117.73, 117.65, 116.1, 114.5, 112.1, 111.1, 65.2, 55.5; HRMS (TOF MS ESI$^+$) calculated for $C_{22}H_{17}NO_2Na$ $[M+Na]^+$: 350.1157, found 350.1155.



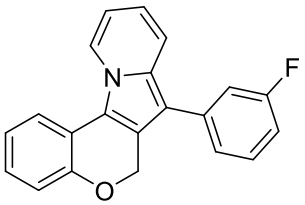
7-(2-Methoxyphenyl)-6*H*-chromeno[3,4-*b*]indolizine (3e). 47.1 mg, 72% yield. Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.50 –8.48 (m, 1H), 7.54 – 7.50 (m, 1H), 7.44 –7.41 (m, 1H), 7.37 – 7.33 (m, 1H), 7.20 – 6.92 (comp, 6H), 6.77 – 6.73 (m, 1H), 6.69 – 6.65 (m, 1H), 5.29 (s, 2H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 156.9, 153.2, 132.6, 131.5, 131.0, 128.2, 126.5, 123.1, 122.7, 122.4, 122.0, 120.9, 119.9, 118.8, 117.7, 117.6, 116.1, 112.0, 111.1, 107.0, 66.2, 55.5; HRMS (TOF MS ESI$^+$) calculated for $C_{22}H_{17}NO_2Na$ $[M+Na]^+$: 350.1157, found 350.1155.



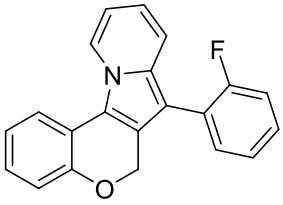
7-(4-(Trifluoromethyl)phenyl)-6*H*-chromeno[3,4-*b*]indolizine (3f). 45.3 mg, 62% yield. Yellow solid, mp = 167-168℃; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.53 (d, *J* = 7.1 Hz, 1H), 7.79 – 7.64 (comp, 4H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.21 – 7.01 (comp, 3H), 6.89 – 6.78 (m, 1H), 6.76 – 6.72 (m, 1H), 5.44 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 153.2, 138.2, 132.4, 129.0, 128.2, 127.0, 125.93 (q, *J* = 3.8 Hz), 123.4, 122.2, 120.9, 120.0, 119.3, 119.0, 118.1, 117.8, 116.9, 112.6, 110.0, 65.0; ^{19}F NMR (376 MHz, $CDCl_3$) (δ, ppm) -62.25. HRMS (TOF MS ESI$^+$) calculated for $C_{22}H_{14}F_3NONa$ $[M+Na]^+$: 388.0925, found 388.0920.



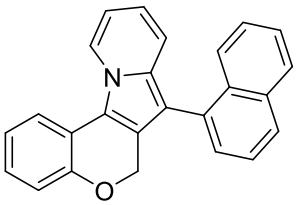
7-(4-Fluorophenyl)-6*H*-chromeno[3,4-*b*]indolizine (3g). 39.7 mg, 63% yield. Yellow solid, mp = 125-126℃; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.49 (d, *J* = 7.1 Hz, 1H), 7.71 – 7.69 (m, 1H), 7.61 (d, *J* = 9.0 Hz, 1H), 7.38 – 7.28 (m, 2H), 7.22 – 7.05 (comp, 5H), 6.81 – 6.77 (m, 1H), 6.71 – 6.68 (m, 1H), 5.41 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 161.5 (d, *J* = 245.5 Hz), 153.0, 132.0, 130.4, 130.3, 130.13 (d, *J* = 3.4 Hz), 126.6, 123.0, 122.0, 120.6, 119.8, 119.4, 118.1 (d, *J* = 4.4 Hz), 117.6, 116.2, 115.8 (d, *J* = 21.3 Hz), 112.2, 110.2, 64.92; ^{19}F NMR (376 MHz, $CDCl_3$) (δ, ppm) -116.40. HRMS (TOF MS ESI$^+$) calculated for $C_{21}H_{14}FNONa$ $[M+Na]^+$: 338.0957, found 338.0948.



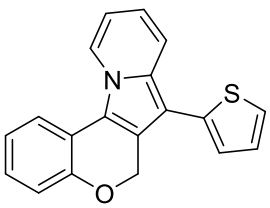
7-(3-Fluorophenyl)-6*H*-chromeno[3,4-*b*]indolizine (3h). 34.7 mg, 55% yield. Yellow solid, mp = 129 - 130℃; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.52 – 8.49 (m, 1H), 7.78 – 7.63 (m, 2H), 7.45 – 7.39 (m, 1H), 7.21 – 7.05 (comp, 5H), 7.05 – 6.98 (m, 1H), 6.88 – 6.79 (m, 1H), 6.75 – 6.65 (m, 1H), 5.44 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 163.3 (d, *J* = 245.7 Hz), 153.2, 136.6 (d, *J* = 8.2 Hz), 132.2, 130.4 (d, *J* = 8.7 Hz), 126.8, 124.7 (d, *J* = 2.6 Hz), 123.3, 122.2, 120.8, 119.9, 119.4, 118.5 (d, *J* = 37.0 Hz), 117.7, 116.6, 115.7, 115.5, 113.0 (d, *J* = 21.2 Hz), 112.4, 110.2, 65.0; ^{19}F NMR (376 MHz, CDCl3) (δ, ppm) -112.84. HRMS (TOF MS ESI$^+$) calculated for $C_{21}H_{14}FNONa$ $[M+Na]^+$: 338.0957, found 338.0955.



7-(2-Fluorophenyl)-6*H*-chromeno[3,4-*b*]indolizine (3i). 38.4 mg, 61% yield. Yellow solid, mp = 94-95℃; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.51 (d, *J* = 7.1 Hz, 1H), 7.72 – 7.70 (m, 1H), 7.54 – 7.51 (m, 1H), 7.47 – 7.42 (m, 1H), 7.34 – 7.30 (m, 1H), 7.27 – 7.19 (m, 2H), 7.18 – 7.06 (comp, 3H), 6.83 –6.79 (m, 1H), 6.73 – 6.69 (m, 1H), 5.36 (d, *J* = 1.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 156.0 (d, *J* = 245.5 Hz), 153.2, 132.6, 131.6 (d, *J* = 3.7 Hz), 128.4 (d, *J* = 8.1 Hz), 126.7, 124.4 (d, *J* = 3.6 Hz), 123.2, 122.1, 119.9, 119.6, 118.6 (d, *J* = 2.1 Hz), 118.3, 117.7, 116.3, 116.1, 112.3, 104.4, 65.5; ^{19}F NMR (376 MHz, $CDCl_3$) (δ, ppm) -115.59. HRMS (TOF MS ESI$^+$) calculated for $C_{21}H_{14}FNONa$ $[M+Na]^+$: 338.0957, found 338.0966.

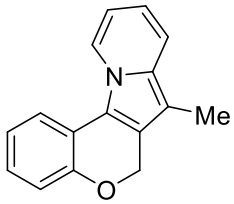


7-(Naphthalen-1-yl)-6*H*-chromeno[3,4-*b*]indolizine (3j). 43.8 mg, 63% yield. Yellow solid, mp = 94-95℃; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.45 (d, *J* = 4.8 Hz, 1H), 7.84 – 7.78 (comp, 2H), 7.71 – 7.65 (comp, 2H), 7.48 – 7.38 (comp, 3H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.18 – 7.14 (m, 1H), 7.04 – 6.97 (comp, 3H), 6.62 – 6.59 (m, 1H), 5.18 – 5.07 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 151.9, 133.0, 132.1, 131.6, 130.3, 127.4, 126.5, 125.4, 125.1, 124.8, 124.5, 121.9, 121.1, 120.9, 118.7, 118.6, 117.7, 116.5, 111.0, 108.1, 64.4.; HRMS (TOF MS ESI$^+$) calculated for $C_{25}H_{17}NONa$ $[M+Na]^+$: 370.1208, found 370.1215.

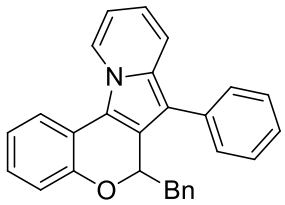


7-(Thiophen-2-yl)-6*H*-chromeno[3,4-*b*]indolizine (3k). 35.8 mg, 59% yield. Yellow

solid, mp = 96-97℃; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.49 – 8.47 (m, 1H), 7.85 – 7.82 (m, 1H), 7.69 – 7.67 (m, 1H), 7.33 – 7.31 (m, 1H), 7.17 – 7.13 (m, 2H), 7.11 – 7.07 (m, 2H), 7.00 – 6.98 (m, 1H), 6.86 – 6.82 (m, 1H), 6.73 – 6.69 (m, 1H), 5.52 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 153.1, 136.0, 132.4, 127.8, 126.8, 124.5, 123.9, 123.2, 122.1, 120.9, 119.8, 119.3, 118.8, 118.6, 117.7, 116.5, 112.5, 104.4, 65.2; HRMS (TOF MS ESI$^+$) calculated for $C_{19}H_{13}NOSNa$ $[M+Na]^+$: 326.0616, found 326.0612.

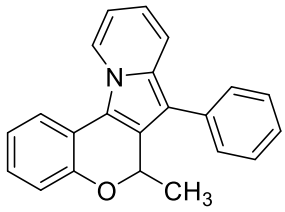


7-Methyl-6*H*-chromeno[3,4-*b*]indolizine (3l). 22.6 mg, 48% yield. Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.39 – 8.36 (m, 1H), 7.64 – 7.62 (m, 1H), 7.36 – 7.39 (m, 1H), 7.14 – 7.00 (comp, 3H), 6.70 – 6.66 (m, 1H), 6.61 – 6.57 (m, 1H), 5.38 (s, 2H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 152.7, 132.8, 126.1, 122.9, 122.0, 121.7, 119.9, 119.5, 117.7, 117.5, 115.8, 115.1, 111.4, 104.1, 65.1, 29.8; HRMS (TOF MS ESI$^+$) calculated for $C_{16}H_{13}NONa$ $[M+Na]^+$: 258.0895, found 258.0890.

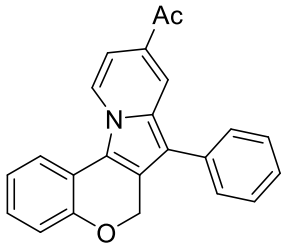


6-Benzyl-7-phenyl-6*H*-chromeno[3,4-*b*]indolizine (3m). 58.9 mg, 76% yield. Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.54 (d, *J* = 6.4 Hz, 1H), 7.76 (d, *J* = 7.7 Hz, 1H), 7.59 (d, *J* = 9.1 Hz, 1H), 7.50 – 7.45 (comp, 4H), 7.37 – 7.33 (m, 1H), 7.26 – 7.16 (comp, 4H), 7.14 – 7.10 (m, 1H), 7.09 – 7.04 (comp, 3H), 6.78 (s, 1H), 6.75 – 6.66 (m, 1H), 5.91 –5.88 (m, 1H), 3.17 – 3.13 (m, 1H), 2.87 – 2.82(m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 150.8, 138.1, 134.3, 132.6, 129.42, 129.41, 128.9, 128.3, 126.8, 126.48, 126.46, 124.0, 123.4, 121.8, 119.8, 119.3, 118.9, 118.6, 118.1,

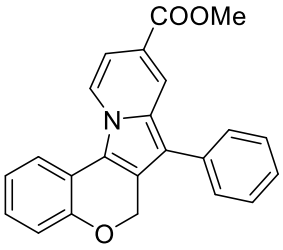
115.4, 112.3, 111.4, 76.7, 41.8; HRMS (TOF MS ESI$^+$) calculated for $C_{28}H_{21}NONa$ $[M+Na]^+$: 410.1521, found 410.1515.



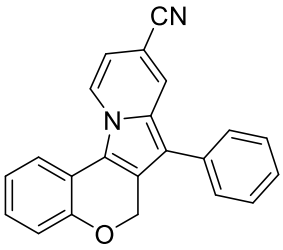
6-Methyl-7-phenyl-6*H*-chromeno[3,4-*b*]indolizine (3n). 43.0 mg, 69% yield. Yellow solid, mp = 150.5-153.0℃; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.52 (d, *J* = 7.1 Hz, 1H), 7.77 – 7.72 (m, 1H), 7.55 (d, *J* = 8.9 Hz, 1H), 7.52 – 7.45 (comp, 4H), 7.36 – 7.32 (m, 1H), 7.18 – 7.05 (comp, 3H), 6.78 – 6.74 (m, 1H), 6.70 – 6.67 (m, 1H), 5.82 (q, *J* = 6.5 Hz, 1H), 1.47 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 151.2, 134.5, 132.6, 129.6, 128.8, 126.6, 126.5, 125.5, 123.2, 121.7, 119.7, 119.1, 118.5, 118.4, 117.9, 115.1, 112.2, 111.1, 71.9, 21.8; HRMS (TOF MS ESI$^+$) calculated for $C_{22}H_{17}NONa$ $[M+Na]^+$: 334.1208, found 334.1200.



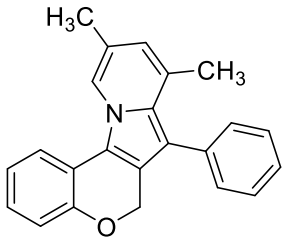
1-(7-Phenyl-6*H*-chromeno[3,4-*b*]indolizin-9-yl)ethan-1-one (3o). 52.3 mg, 77% yield. Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.40 – 8.37 (m, 1H), 8.23 – 8.22 (m, 1H), 7.73 – 7.70 (m, 1H), 7.54 – 7.50 (m, 2H), 7.41 – 7.37 (comp, 3H), 7.27 – 7.24 (m, 1H), 7.22 – 7.18 (m, 1H), 7.13 – 7.07 (m, 2H), 5.40 (d, *J* = 1.3 Hz, 2H), 2.54 (d, *J* = 1.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 195.4, 153.9, 133.2, 130.6, 129.3, 129.2, 128.1, 127.2, 126.4, 122.4, 122.3, 122.2, 121.6, 120.8, 119.6, 118.5, 118.0, 117.4, 110.1, 64.8, 25.9; HRMS (TOF MS ESI$^+$) calculated for $C_{23}H_{17}NO_2Na$ $[M+Na]^+$: 362.1157, found 362.1149.



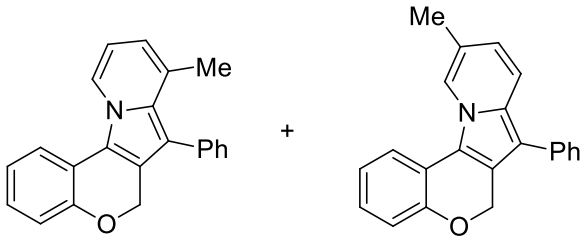
Methyl 7-phenyl-6*H*-chromeno[3,4-*b*]indolizine-9-carboxylate (3p). 51.2 mg, 72% yield. Yellow solid, mp = 129-130℃; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.41 – 8.37 (m, 2H), 7.72 – 7.70(m, 1H), 7.52 – 7.48 (m, 2H), 7.39 – 7.37 (comp, 3H), 7.25 – 7.20 (m, 2H), 7.12 – 7.07 (m, 2H), 5.41 (s, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 166.3, 153.8, 133.2, 131.0, 129.3, 129.2, 127.9, 127.0, 122.3, 122.21, 122.17, 122.0, 120.7, 119.1, 118.71, 118.67, 118.0, 116.5, 111.4, 64.9, 52.2; HRMS (TOF MS ESI$^+$) calculated for $C_{23}H_{17}NO_3Na$ $[M+Na]^+$: 378.1106, found 378.1100.



7-Phenyl-6*H*-chromeno[3,4-*b*]indolizine-9-carbonitrile (3q). 42.6 mg, 66% yield. Yellow solid, mp = 142-143℃; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.46 (d, *J* = 7.4 Hz, 1H), 8.02 – 8.01(m, 1H), 7.72 – 7.70 (m, 1H), 7.55 – 7.48 (m, 2H), 7.43 – 7.39 (m, 1H), 7.38 – 7.34 (m, 2H), 7.24 – 7.22 (m, 1H), 7.17 – 7.07 (m, 2H), 6.78 – 6.75(m, 1H), 5.43 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 154.0, 132.5, 130.1, 129.3, 129.2, 128.6, 127.6, 125.7, 122.9, 122.8, 122.4, 120.8, 120.1, 118.2, 118.1, 116.7, 111.9, 99.3, 64.7; HRMS (TOF MS ESI$^+$) calculated for $C_{22}H_{14}N_2ONa$ $[M+Na]^+$: 345.1004, found 345.1008.

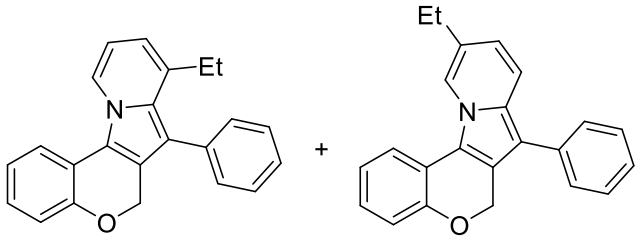


8,10-Dimethyl-7-phenyl-6*H*-chromeno[3,4-*b*]indolizine (3r). 44.2 mg, 68% yield. Yellow solid, mp = 70-71℃; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.23 (s, 1H), 7.76 – 7.73 (m, 1H), 7.42 – 7.31 (comp, 5H), 7.14 – 7.05 (comp, 3H), 6.40 (d, *J* = 1.4 Hz, 1H), 5.20 (s, 2H), 2.30 (d, *J* = 1.2 Hz, 3H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm)153.1, 135.7, 131.3, 130.6, 129.0, 127.6, 126.7, 126.3, 122.0, 121.9, 121.7, 120.8, 120.0, 119.9, 118.9, 117.6, 115.2, 112.2, 65.2, 20.7, 18.6; HRMS (TOF MS ESI$^+$) calculated for $C_{23}H_{19}NONa$ $[M+Na]^+$:348.1364, found 348.1358.



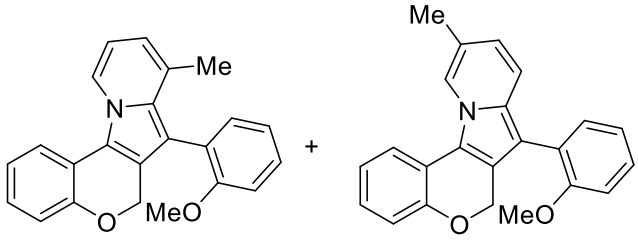
3s **3s'**

8-Methyl-7-phenyl-6*H*-chromeno[3,4-*b*]indolizine (3s) and 10-Methyl-7-phenyl-6*H*-chromeno[3,4-*b*]indolizine (**3s'**)**.** Combined in 63% yield, 39.2 mg (**3s** : **3s'** = 6 : 1). Green oil; composited NMR signals of **3s** and **3s'**; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.43 (d, *J* = 7.1 Hz, 1H), 8.30 (d, *J* = 0.9 Hz, 0.19H), 7.76 – 7.71 (m, 1H), 7.63 (d, *J* = 9.1 Hz, 0.19H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.44 – 7.31 (comp, 5.55H), 7.16 – 7.08 (comp, 3.54H), 6.69 – 6.66(m, 0.19H), 6.61 (t, *J* = 6.9 Hz, 1H), 6.51 (d, *J* = 6.7 Hz, 1H), 5.46 (s, 0.36H), 5.23 (s, 2H), 2.35 (s, 0.55H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 153.2, 135.6, 134.5, 131.6, 131.4, 131.1, 129.7, 128.94, 128.91, 127.6, 126.8, 126.43, 126.37, 126.0, 122.2, 122.0, 121.6, 121.4, 121.2, 120.8, 120.3, 119.9, 119.8, 119.7, 118.5, 117.8, 117.63, 117.59, 116.0, 115.5, 112.4, 111.5, 65.2, 65.1, 22.8, 20.9; HRMS (TOF MS ESI$^+$) calculated for $C_{22}H_{17}NONa$ $[M+Na]^+$: 334.1208, found 334.1218.



3t **3t'**

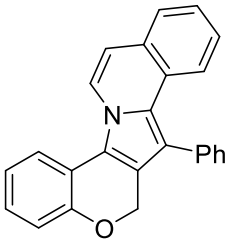
8-Ethyl-7-phenyl-6*H*-chromeno[3,4-*b*]indolizine (3t) and 10-Ethyl-7-phenyl-6*H*-chromeno[3,4-*b*]indolizine (3t'). Combined in 65% yield, 42.3 mg (**3t** : **3t'** = 4 : 1). Green oil; composited NMR signals of **3t** and **3t'**; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.44 (d, *J* = 7.0 Hz, 1H), 8.32 (s, 0.17H), 7.78 – 7.73(comp, 1.33H), 7.59 – 7.54(m, 0.18H), 7.50 – 7.33 (comp, 1.81H), 7.29 – 7.26(m, 1H), 7.16 – 6.69 (comp, 8.36H), 6.69 – 6.60 (comp, 1.18H), 6.53 (s, 1H), 5.31 – 5.13 (comp, 2.34H), 3.85 (s, 0.52H), 3.81 (s, 3.00H), 2.36 (s, 0.52H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 153.2, 153.1, 135.9, 134.5, 131.3, 131.1, 131.0, 129.0, 128.9, 128.0, 127.8, 126.9, 126.42, 126.38, 126.0, 122.3, 122.1, 122.0, 121.2, 120.5, 120.4, 120.1, 119.90, 119.88, 119.8, 119.7, 118.1, 117.7, 116.4, 116.1, 115.6, 112.0, 111.6, 111.1, 65.22, 65.15, 26.5, 25.9, 15.3, 13.9; HRMS (TOF MS ESI$^+$) calculated for $C_{24}H_{19}NONa$ $[M+Na]^+$: 348.1364, found 348.1378.



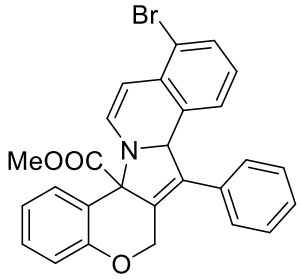
3u **3u'**

7-(2-Methoxyphenyl)-8-methyl-6*H*-chromeno[3,4-*b*]indolizine (3u) and 7-(2-Methoxyphenyl)-10-methyl-6*H*-chromeno[3,4-*b*]indolizine (3u'). Combined in 50% yield, 34.1 mg (**3u** : **3u'** = 6 : 1). Green oil; composited NMR signals of **3y** and **3y'**; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.44 (d, *J* = 7.0 Hz, 1H), 8.32 (s, 0.17H), 7.78 – 7.73(comp, 1.33H), 7.59 – 7.54(m, 0.18H), 7.50 – 7.33 (comp, 1.81H), 7.29 – 7.26(m, 1H), 7.16 – 6.69 (comp, 8.36H), 6.69 – 6.60 (comp, 1.18H), 6.53 (s,

1H), 5.31 – 5.13 (comp, 2.34H), 3.85 (s, 0.52H), 3.81 (s, 3.00H), 2.36 (s, 0.52H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 158.0, 153.1, 133.5, 132.1, 131.6, 131.5, 131.0, 129.8, 128.9, 128.7, 128.1, 126.3, 124.9, 124.1, 122.7, 121.9, 121.4, 120.9, 120,0 119.9, 119.8, 118.3, 118.3, 118.2, 117.5, 115.7, 111.4, 111.1, 110.5, 107.5, 68.3, 66.2, 65.5, 55.5, 29.8, 20.0; HRMS (TOF MS ESI$^+$) calculated for $C_{23}H_{19}NO_2Na$ $[M+Na]^+$: 364.1313, found 364.1306.

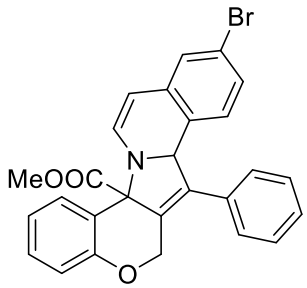


7-Phenyl-6*H*-chromeno[3',4':4,5]pyrrolo[2,1-*a*]isoquinoline (3v). 50.0 mg, 72% yield. Yellow solid, mp = 120-121℃; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.36 (d, *J* = 7.5 Hz, 1H), 7.76 – 7.71 (m, 2H), 7.57 – 7.55 (m, 1H), 7.52 – 7.41 (comp, 5H), 7.32 – 7.28 (m, 1H), 7.20 – 7.14 (m, 2H), 7.12 – 7.07 (m, 2H), 6.88 (d, *J* = 7.5 Hz, 1H), 5.21 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 153.6, 135.6, 130.5, 129.0, 127.5, 127.4, 127.2, 127.1, 126.98, 126.96, 125.8, 122.9, 122.5, 122.1, 120.9, 120.3, 119.4, 118.1, 117.9, 115.5, 112.1, 65.0; HRMS (TOF MS ESI$^+$) calculated for $C_{25}H_{17}NONa$ $[M+Na]^+$: 370.1208, found 370.1200.

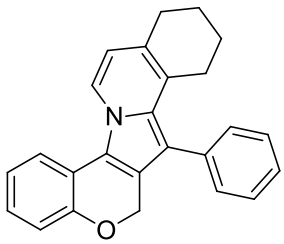


Methyl 11-bromo-7-phenyl-6,7a-dihydro-14a*H*-chromeno[3',4':4,5]pyrrolo[2,1-*a*] isoquinoline-14a-carboxylate (3w). 74.9 mg, 77% yield. Yellow solid, mp = 138-139℃; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.47 – 7.38 (comp, 4H), 7.32 – 7.23 (comp, 4H), 7.03 – 6.93 (comp, 3H), 6.61 (t, *J* = 7.8 Hz, 1H), 6.36 (d, *J* = 7.6 Hz, 1H), 6.11 (d, *J* = 7.6 Hz, 1H), 5.91 (d, *J* = 2.8 Hz, 1H), 5.08 – 4.94 (m, 2H), 3.83 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.1, 154.3, 138.3, 134.3, 133.6, 133.2, 131.2, 130.7, 130.0, 129.1, 128.7, 128.2, 126.7, 125.9, 123.5, 123.3, 121.5, 119.1, 118.0, 102.5, 72.0, 69.3, 62.6, 53.4; HRMS (TOF MS ESI$^+$) calculated for $C_{27}H_{20}BrNO_3Na$ $[M+Na]^+$: 508.0524, found 508.0511.

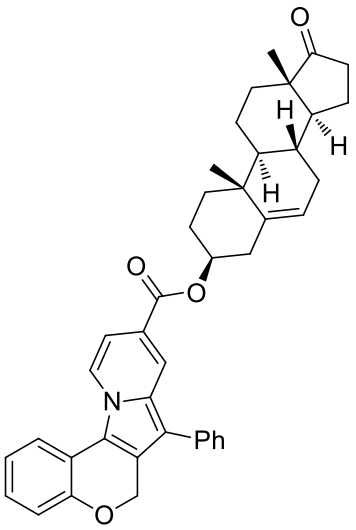


Methyl 10-bromo-7-phenyl-6,7a-dihydro-14a*H*-chromeno[3',4':4,5]pyrrolo[2,1-*a*] isoquinoline-14a-carboxylate (3x). 71.0 mg, 73% yield. Yellow solid, mp = 135-136℃; ^{1}H NMR (400 MHz, $CDCl_3$) 7.44 – 7.34 (comp, 4H), 7.27 – 7.19 (comp, 3H), 7.09 (d, *J* = 2.1 Hz, 1H), 6.95 – 6.89 (comp, 3H), 6.85 – 6.82 (m, 1H), 6.20 (d, *J* = 8.2 Hz, 1H), 5.84 (d, *J* = 2.8 Hz, 1H), 5.64 (d, *J* = 7.4 Hz, 1H), 5.03 – 4.90 (m, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.2, 154.3, 138.5, 136.0, 133.7, 133.6, 130.5, 130.0, 129.1, 128.7, 128.2, 127.6, 127.0, 126.7, 126.0, 125.9, 123.3, 121.4, 121.2, 118.1, 72.1, 68.7, 62.6, 53.3; HRMS (TOF MS ESI$^+$) calculated for $C_{27}H_{20}BrNO_3Na$ $[M+Na]^+$: 508.0524, found 508.0526.

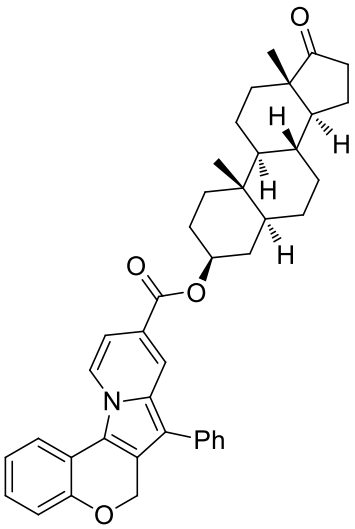


7-Phenyl-8,9,10,11-tetrahydro-6*H*-chromeno[3',4':4,5]pyrrolo[2,1-*a*]isoquinoline (3y). 35.1 mg, 50% yield. Yellow solid, mp = 122-123℃; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.32 (s, 1H), 7.67 (d, *J* = 6.9 Hz, 1H), 7.43 – 7.28 (comp, 5H), 7.09 – 7.03 (comp, 3H), 6.41 (d, *J* = 7.1 Hz, 1H), 5.17 (s, 2H), 2.68 (s, 2H), 2.34 (t, *J* = 6.3 Hz, 2H), 1.79 –1.73 (m, 2H), 1.65 – 1.57 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 153.0, 136.1, 134.5, 131.4, 131.3, 127.6, 127.4, 126.6, 126.1, 122.2, 122.0, 120.9,

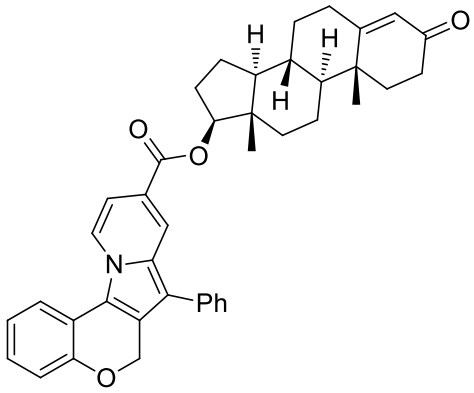
119.8, 119.7, 117.6, 114.3, 111.3, 65.2, 29.1, 27.5, 22.8, 22.6; HRMS (TOF MS ESI$^+$) calculated for $C_{25}H_{22}NO$ $[M+H]^+$: 352.1701, found 352.1710.



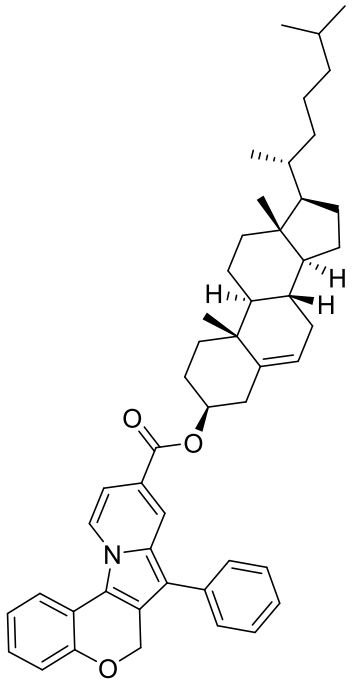
(3*S*,8*R*,9*S*,10*R*,13*S*,14*S*)-10,13-Dimethyl-17-oxo-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 7-phenyl-6*H*-chromeno[3,4-*b*]indolizine-9-carboxylate (3A). 77.0 mg, 63% yield. Yellow solid, mp =145-146 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.42 (d, *J* = 7.5 Hz, 1H), 8.39 (d, *J* = 1.8 Hz, 1H), 7.74 – 7.72 (m, 1H), 7.53 – 7.49 (comp, 2H), 7.43 – 7.35 (comp, 3H), 7.27 – 7.22 (m, 1H), 7.22 – 7.18 (m, 1H), 7.16 – 7.04 (m, 2H), 5.43 (s, 2H), 4.91 – 4.78 (m, 1H), 2.52 – 2.43 (m, 2H), 2.19 – 2.00 (comp, 3H), 1.97 – 1.81 (comp, 3H), 1.72 – 1.64 (comp, 3H), 1.55 – 1.41 (m, 2H), 1.39 – 1.21 (comp, 7H), 1.09 (s, 3H), 0.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 165.3, 153.8, 140.1, 133.3, 131.0, 129.2, 129.1, 127.8, 127.0, 122.3, 122.2, 122.1, 122.0, 121.9, 120.6, 119.3, 119.0, 118.7, 118.0, 116.3, 111.5, 74.6, 64.9, 51.8, 50.2, 47.6, 38.3, 37.1, 36.9, 35.9, 31.6, 31.5, 30.9, 27.9, 22.0, 20.5, 19.5, 13.7; HRMS (TOF MS ESI$^+$) calculated for $C_{41}H_{41}NO_4Na$ $[M+Na]^+$: 634.2933, found 634.2950.



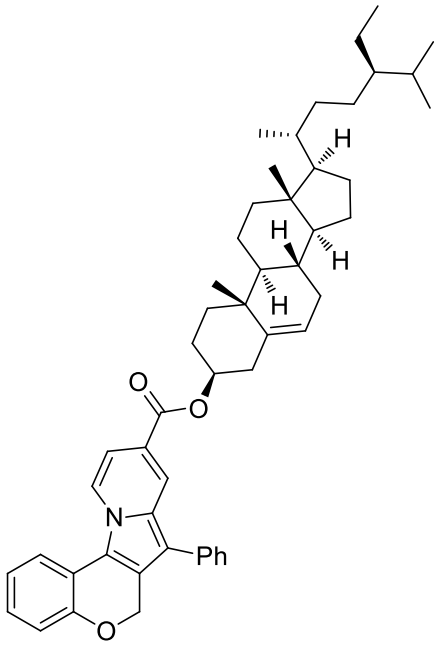
(3*S*,5*S*,8*R*,9*S*,10*S*,13*S*,14*S*)-10,13-Dimethyl-17-oxohexadecahydro-1*H*-cyclopenta[a]phenanthren-3-yl 7-phenyl-6*H*-chromeno[3,4-*b*]indolizine-9-carboxylate (3B). 68.7 mg, 56% yield. Yellow solid, mp =93-94 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.44 (d, *J* = 7.4 Hz, 1H), 8.38 (d, *J* = 1.9 Hz, 1H), 7.75 – 7.73 (m, 1H), 7.53 – 7.49 (m, 2H), 7.42 – 7.36 (comp, 3H), 7.25 (d, *J* = 6.4 Hz, 1H), 7.22 – 7.18 (m, 1H), 7.16 – 7.08 (m, 2H), 5.44 (s, 2H), 4.89 – 4.80 (m, 1H), 2.52 – 2.43 (m, 1H), 2.13 – 2.02 (m, 1H), 1.98–1.90 (m, 2H), 1.82 – 1.76 (comp, 3H), 1.73 – 1.62 (comp, 3H), 1.61 – 1.45 (comp, 4H), 1.36 – 1.32 (m, 2H), 1.25 (s, 3H), 1.16 – 1.07 (m, 1H), 1.06 – 0.97 (m, 1H), 0.90 (s, 3H), 0.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 165.5, 153.8, 133.4, 131.1, 129.3, 129.2, 127.9, 127.0, 122.3, 122.2, 122.0, 121.9, 120.6, 119.5, 119.0, 118.8, 118.0, 116.3, 111.5, 74.4, 64.9, 54.5, 51.5, 47.9, 44.9, 36.9, 36.0, 35.9, 35.2, 34.2, 31.7, 31.0, 28.5, 27.7, 21.9, 20.6, 14.0, 12.5; HRMS (TOF MS ESI^{+}) calculated for $C_{41}H_{43}NO_4Na$ $[M+Na]^{+}$: 636.3090, found 636.3084.



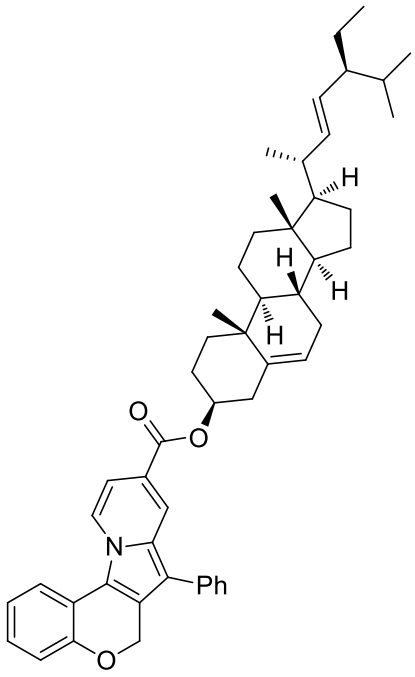
(8*R*,9*S*,10*R*,13*S*,14*S*,17*S*)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-17-yl 7-phenyl-6*H*-chromeno [3,4-*b*]indolizine-9-carboxylate (3C). 74.6 mg, 61% yield. Yellow solid, mp = 99-100 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.50 – 8.38 (m, 2H), 7.76 – 7.74 (m, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.44 – 7.36 (comp, 3H), 7.26 – 7.18 (m, 2H), 7.16 – 7.08 (m, 2H), 5.75 (d, *J* = 1.6 Hz, 1H), 5.45 (s, 2H), 4.87–4.83 (m, 1H), 2.43 – 2.36 (comp, 3H), 2.33 – 2.18 (comp, 3H), 2.05 – 2.00 (m, 1H), 1.91 – 1.86 (m, 2H), 1.75 –1.65 (comp, 3H), 1.64 – 1.57 (m, 2H), 1.46 – 1.39 (m, 2H), 1.31 – 1.23 (comp, 3H), 1.21 (s, 3H), 0.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 199.6, 171.1, 165.7, 153.8, 133.3, 131.0, 129.13, 129.14, 127.9, 127.0, 124.1, 122.3, 122.2, 122.0, 120.6, 119.2, 119.1, 118.7, 118.0, 116.4, 111.4, 83.1, 64.9, 53.8, 50.4, 43.0, 38.7, 36.9, 35.8, 35.5, 34.0, 32.9, 31.6, 27.9, 23.7, 20.7, 17.5, 12.4; HRMS (TOF MS ESI$^+$) calculated for $C_{41}H_{41}NO_4Na$ $[M+Na]^+$: 634.2933, found 634.2930.



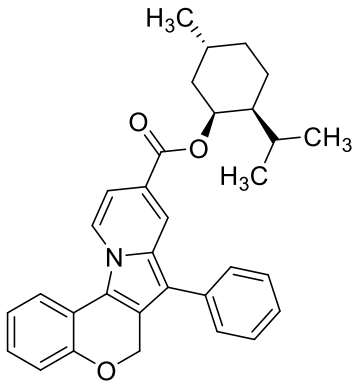
(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 7-phenyl-6*H*-chromeno[3,4-*b*]indolizine-9-carboxylate (3D). 82.4 mg, 58% yield. Yellow solid, mp = 164-165 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.40 – 8.37 (m, 2H), 7.70 (d, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.40 – 7.34 (comp, 3H), 7.24 – 7.22 (m, 1H), 7.20 – 7.15 (m, 1H), 7.11 – 7.06 (m, 2H), 5.41 (s, 2H), 4.86 – 4.80 (m, 1H), 2.45 (d, *J* = 7.3 Hz, 2H), 2.03 – 1.94 (comp, 3H), 1.92 – 1.87 (m, 1H), 1.74 – 1.66 (m, 1H), 1.61 – 1.39 (comp, 6H), 1.38 – 1.29 (comp, 4H), 1.29 – 1.22 (m, 3H), 1.16 – 1.10 (comp, 5H), 1.07 – 1.05 (comp, 4H), 1.02 – 0.95 (comp, 3H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.88 – 0.86 (comp, 6H), 0.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 165.3, 153.8, 139.8, 133.3, 131.0, 129.2, 129.1, 127.8, 126.9, 122.9, 122.2, 122.1, 122.0, 121.8, 120.6, 119.5, 118.9, 118.7, 117.9, 116.3, 111.5, 74.8, 64.9, 56.8, 56.3, 50.2, 42.4, 39.9, 39.6, 38.4, 36.8, 36.3, 35.9, 32.1, 32.0, 28.4, 28.1, 28.0, 24.4, 24.0, 23.0, 22.7, 21.2, 19.5, 18.8, 12.0; HRMS (TOF MS ESI$^+$) calculated for $C_{49}H_{60}NO_3[M+H]^+$: 710.4573, found 710.4571.



(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-17-((2*R*,5*R*)-5-Ethyl-6-methylheptan-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 7-phenyl-6*H*-chromeno[3,4-*b*]indolizine-9-carboxylate (3E). 80.0 mg, 54% yield. Yellow solid, mp =85-86 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.44 (d, *J* = 7.5 Hz, 1H), 8.40–8.38 (m, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.44 – 7.36 (comp, 3H), 7.27 – 7.24 (m, 2H), 7.23 – 7.18 (m, 1H), 7.16 – 7.08 (m, 2H), 5.43 (d, *J* = 4.9 Hz, 2H), 4.89–4.81 (m, 1H), 2.47 (d, *J* = 7.5 Hz, 1H), 2.05 – 1.96 (comp, 3H), 1.87 – 1.67 (comp, 4H), 1.38 – 1.21 (comp, 10H), 1.15 – 0.99 (comp, 10H), 0.96 –0.91(comp, 6H), 0.87–0.77 (comp, 11H), 0.69 (d, *J* = 5.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 165.3, 153.9, 139.8, 133.4, 131.1, 129.3, 129.2, 127.8, 127.0, 122.9, 122.3, 122.2, 122.1, 121.9, 120.6, 119.5, 119.0, 118.8, 118.0, 116.3, 111.5, 74.9, 64.9, 56.8, 56.2, 50.2, 46.0, 42.5, 39.9, 38.4, 37.2, 36.8, 36.3, 34.1, 32.1, 32.0, 29.3, 28.4, 28.1, 26.2, 24.5, 23.2, 21.2, 20.0, 19.6, 19.2, 18.9, 12.1, 12.0; HRMS (TOF MS ESI^{+}) calculated for $C_{51}H_{63}NO_3Na$ $[M+Na]^{+}$: 760.4706, found 760.4700.



(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-17-((2*R*,5*S*,*E*)-5-Ethyl-6-methylhept-3-en-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 7-phenyl-6*H*-chromeno[3,4-*b*]indolizine-9-carboxylate (3F). 86.9 mg, 59% yield. Yellow solid, mp = 101-102 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.44 (d, *J* = 7.5 Hz, 1H), 8.40 (d, *J* = 1.8 Hz, 1H), 7.76 – 7.73 (m, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.44 – 7.35 (comp, 3H), 7.28 – 7.24 (m, 2H), 7.22 – 7.18 (m, 1H), 7.16 – 7.08 (m, 2H), 5.44 (s, 2H), 5.19 –5.13(m, 1H), 5.05 – 4.99(m, 1H), 4.88 – 4.82(m, 1H), 2.47 (d, *J* = 8.0 Hz, 2H), 1.98 (comp, 5H), 1.72 (comp, 3H), 1.59 – 1.42 (comp, 8H), 1.33 – 1.16 (comp, 7H), 1.10 – 1.01 (comp, 7H), 0.87 – 0.79 (comp, 9H), 0.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 165.4, 153.8, 139.9, 138.5, 133.4, 131.1, 129.4, 129.3, 129.2, 127.9, 127.0, 122.9, 122.3, 122.2, 122.1, 121.9, 120.6, 119.5, 119.0, 118.8, 118.0, 116.4, 111.6, 74.9, 65.0, 57.0, 56.1, 51.4, 50.2, 42.4, 40.7, 39.8, 38.4, 37.2, 36.8, 32.1, 32.0, 29.1, 28.1, 25.6, 24.5, 21.4, 21.3, 21.2, 19.6, 19.2, 12.4, 12.2; HRMS (TOF MS ESI$^+$) calculated for $C_{51}H_{61}NO_3Na$ $[M+Na]^+$: 758.4549, found 758.4540.



(1*S*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 7-phenyl-6*H*-chromeno[3,4-*b*] indolizine-9-carboxylate (3G). 59.5 mg, 62% yield. Yellow solid, mp =85-86 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.44 – 8.41 (m, 2H), 7.74 – 7.71 (m, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.41 – 7.34 (comp, 3H), 7.26 – 7.24 (m, 1H), 7.21 – 7.17 (m, 1H), 7.13 – 7.07 (m, 2H), 5.43 (d, *J* = 1.2 Hz, 2H), 4.92 (td, *J* = 10.9, 4.5 Hz, 1H), 2.17 – 2.08 (m, 1H), 1.98 – 1.93 (m, 1H), 1.75 – 1.70 (m, 2H), 1.58 – 1.51 (m, 2H), 1.28 – 1.24 (m, 1H), 1.17 – 1.06 (m, 2H), 0.93 (d, *J* = 6.8 Hz, 6H), 0.83 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 165.4, 153.8, 133.4, 131.1, 129.2, 129.1, 127.8, 127.0, 122.3, 122.14, 122.12, 121.9, 120.6, 119.5, 118.9, 118.8, 118.0, 116.3, 111.5, 75.1, 64.9, 47.4, 41.2, 34.5, 31.6, 27.0, 24.1, 22.2, 20.8, 17.0; HRMS (TOF MS ESI$^+$) calculated for $C_{32}H_{33}NO_3Na$ $[M+Na]^+$: 502.2358, found 502.2355.

1D-NOE NMR Analysis:

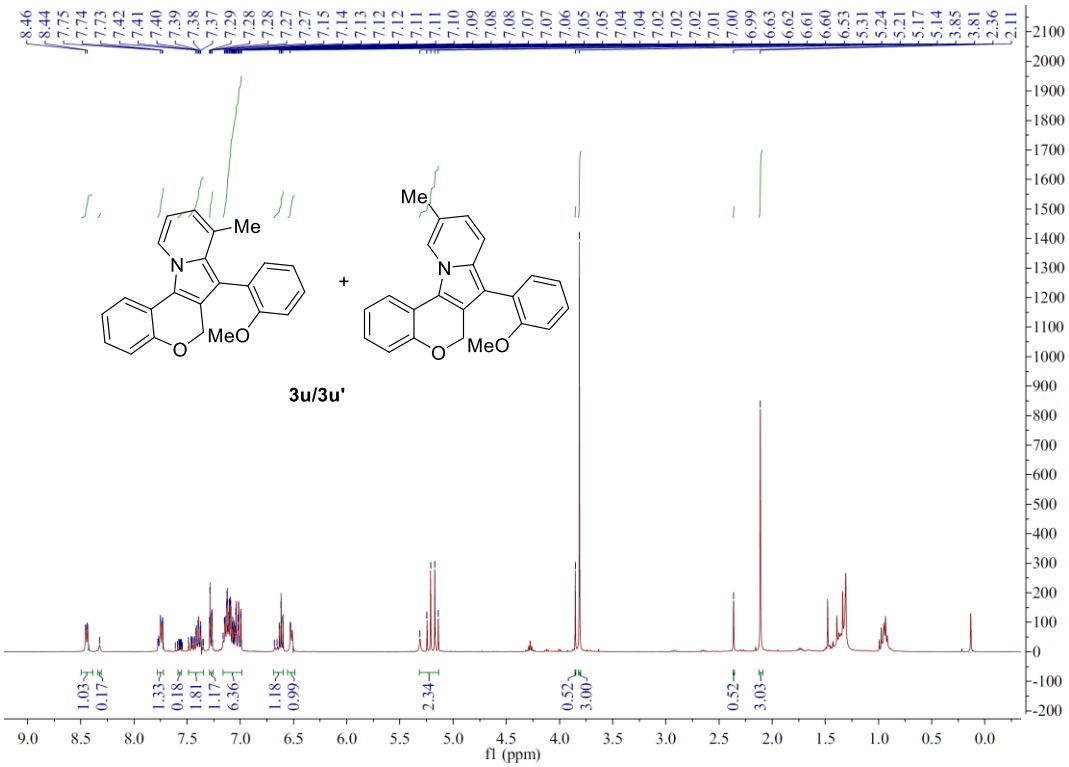


Figure S1. Proton NMR spectra of mixture of **3y** and **3y'**.

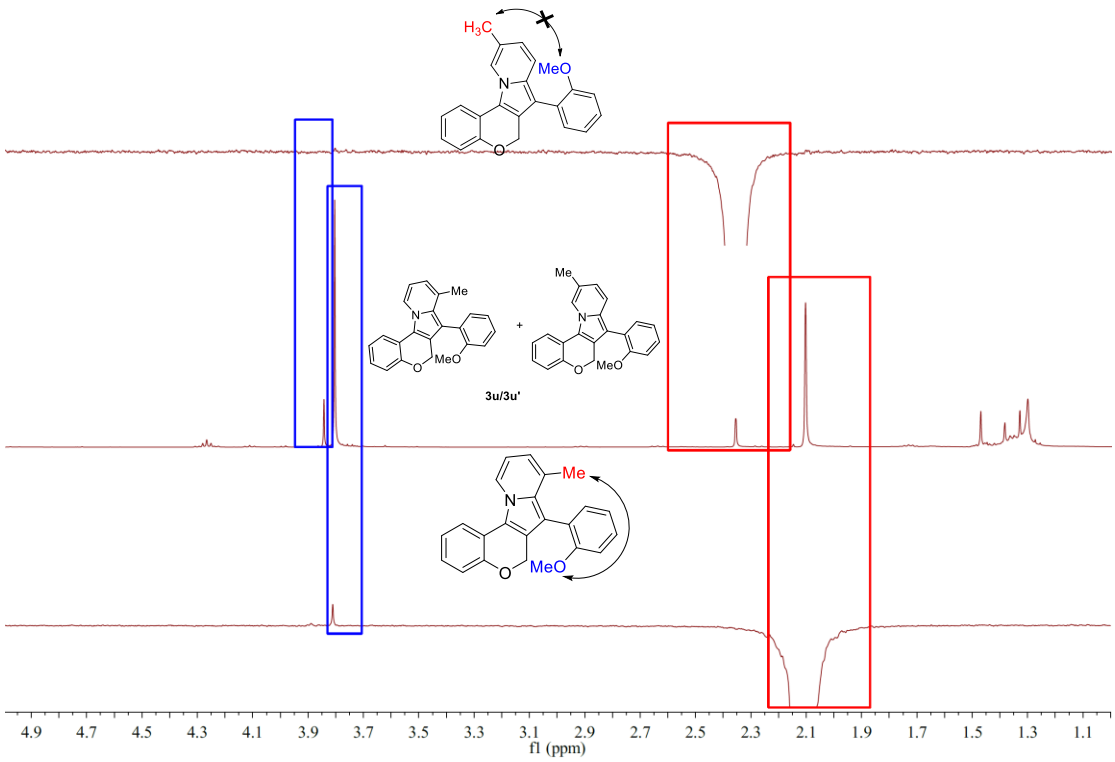
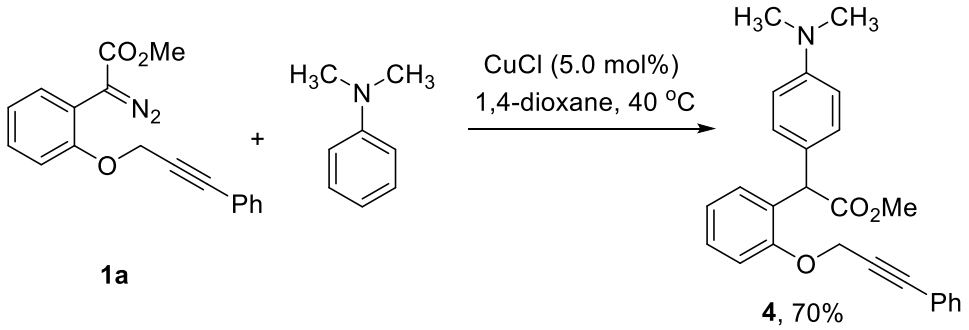
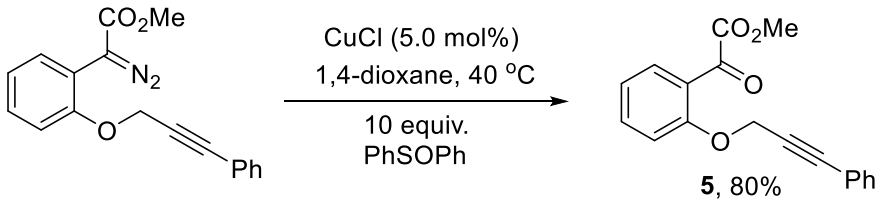


Figure S2. NOE NMR spectra of **3y** and **3y'**.

Control Experiments



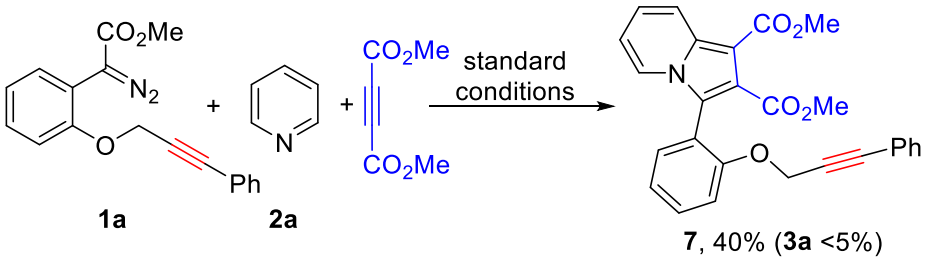
To a 10-mL oven-dried vial with a magnetic stirring bar, CuCl (1.0 mg, 5.0 mol%) and *N*,*N*-dimethylaniline (72.6 mg, 0.6 mmol) in freshly distilled 1,4-dioxane (1.0 mL), was added the solution of diazo **1a** (0.2 mmol) in 1,4-dioxane (1.0 mL) *via* a syringe in 1 hour at room temperature. The reaction mixture was heated at 40 ℃ under argon atmosphere for 18 h, After the reaction was completed, the solvent was evaporated in *vacuo*, then the crude mixture was purified by column chromatography to give product **4** as white solid, 70% yield, mp = 133.4-136.0 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.50 – 7.44 (comp, 2H), 7.38 – 7.32 (comp, 3H), 7.29 – 7.24 (comp, 3H), 7.09 (d, *J* = 7.7 Hz, 2H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.77 (d, *J* = 7.9 Hz, 2H), 5.28 (s, 1H), 4.95 (s, 2H), 3.75 (s, 3H), 2.97 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 174.0, 155.4, 131.9, 130.0, 129.5, 129.4, 128.8, 128.4, 128.3, 122.5, 121.5, 113.0, 112.3, 87.1, 57.3, 52.3, 50.4, 40.9; HRMS (TOF MS ESI$^+$) calculated for $C_{26}H_{25}NO_3Na$ $[M+Na]^+$: 422.1727, found 422.1715.



To a 10-mL oven-dried vial with a magnetic stirring bar, CuCl (1.0 mg, 5.0 mol%) and diphenyl sulfoxide (404 mg, 2.0 mmol) in freshly distilled 1,4-dioxane (1.0 mL), was added the solution of diazo **1a** (0.2 mmol) in 1,4-dioxane (1.0 mL) *via* a syringe in 1 hour at room temperature. The reaction mixture was heated at 40℃ under argon atmosphere for 18 h, After the reaction was completed, the solvent was evaporated in

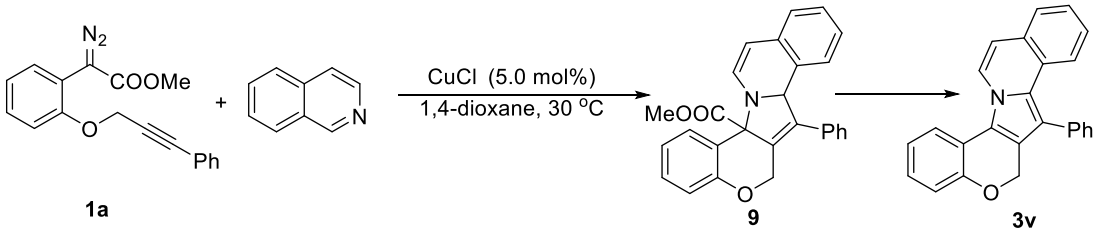
vacuo, then the crude mixture was purified by column chromatography to give product **5** as yellow oil, 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.92 – 7.90 (m, 1H), 7.66 – 7.55 (m, 1H), 7.47 – 7.42 (comp, 2H), 7.38 – 7.29 (comp, 3H), 7.16 – 7.12 (comp, 2H), 4.96 (s, 2H), 3.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 186.4, 165.7, 158.7, 136.3, 131.9, 131.1, 129.2, 128.6, 123.6, 122.2, 122.0, 113.4, 88.2, 82.6, 58.0, 52.7; HRMS (TOF MS ESI$^+$) calculated for $C_{18}H_{14}O_4Na$ $[M+Na]^+$: 317.0784, found 317.0780.

Control experiment in the presence of dimethyl but-2-ynedioate.



To a 10-mL oven-dried vial with a magnetic stirring bar, CuCl (1.0 mg, 5.0 mol%) and dimethyl but-2-ynedioate (142.1 mg, 1.0 mmol) in freshly distilled 1,4-dioxane (1.0 mL), was added the solution of diazo **1a** (0.2 mmol) and pyridine **2a** (0.3 mmol) in 1,4-dioxane (1.0 mL) *via* a syringe in 1 hour at room temperature. The reaction mixture was heated at 40 ℃ under argon atmosphere for 18 h, After the reaction was completed, the solvent was evaporated in *vacuo*, then the crude mixture was purified by column chromatography to give product **7** as white solid, 40% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 9.44 (d, J = 7.2 Hz, 1H), 7.53 – 7.47 (m, 1H), 7.41 – 7.34 (comp, 4H), 7.32 – 7.28 (comp, 3H), 7.24 (d, J = 7.6 Hz, 1H), 7.11 – 7.01 (comp, 2H), 6.91 – 6.87 (m, 1H), 4.83 (s, 2H), 3.90 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 167.0, 161.2, 155.3, 135.0, 132.0, 131.8, 128.9, 128.8, 128.4, 127.5, 127.4, 122.8, 122.5, 122.2, 121.7, 119.4, 114.4, 113.5, 111.7, 111.1, 87.3, 84.2, 56.8, 52.5, 51.7.

Proton NMR observation of the reaction intermediate.



To a 10-mL oven-dried vial with a magnetic stirring bar, CuCl (1.0 mg, 5.0 mol%) in freshly distilled 1,4-dioxane (1.0 mL), was added the solution of diazo compound **1a** (61.2 mg, 0.2 mmol) and isoquinoline (38.7 mg, 0.3 mmol) in 1,4-dioxane (1.0 mL) *via* a syringe in 1 hour at room temperature under argon atmosphere. The reaction mixture was heated at 40℃ for corresponding period of time (1.0 h, 1.5 h, 24.0 h), then the reaction mixture (0.25 mL) was filtered and the filtrate was evaporated in *vacuo* and the residue was directly subjected to proton NMR analysis with $CDCl_3$ as the solvent without any further purification. See Figure S3 for these spectra.

Discussion: From this study, the compound **9** is confirmed as the intermediate in this transformation.

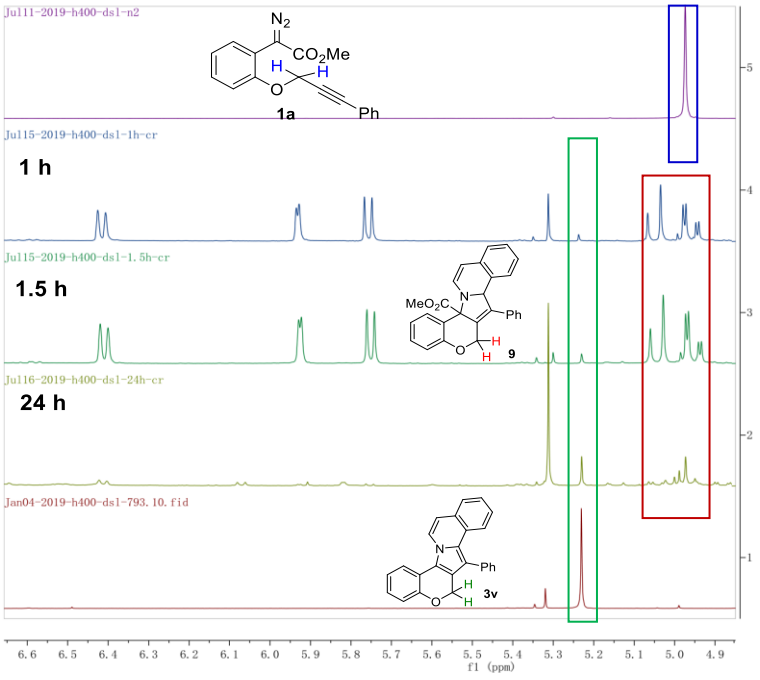
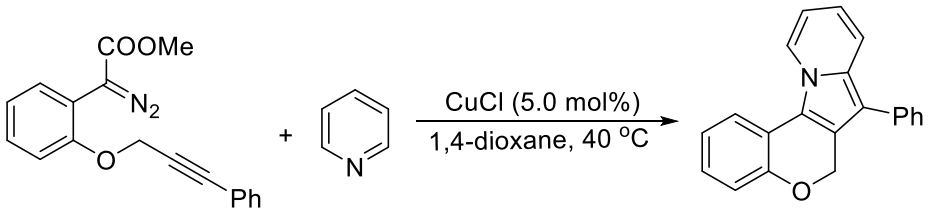


Figure S3. Proton NMR spectra monitoring of the reaction mixture.

General Procedure for Scale up

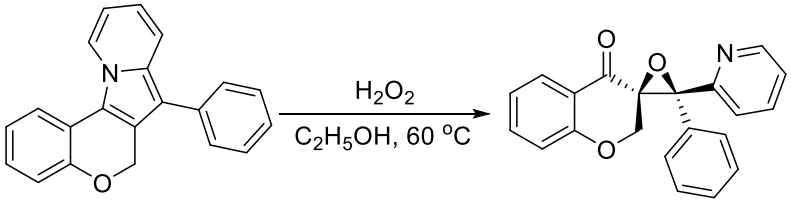


1a 8.0 mmol, 2.45 g | **2a** 12.0 mmol, 0.95 g | **3a** 1.43 g, 60% yield

To a 50-mL oven-dried round-bottom flask with a magnetic stirring bar, diazo compound **1a** (2.45 g, 8.0 mmol), pyridine (0.95 g, 12.0 mmol), CuCl (39.6 mg, 5.0 mol%), and anhydrous 1,4-dioxane (30.0 mL) was added in sequence under atmosphere of argon, and the reaction mixture was stirred at 40 ℃ for 24 hours. When the reaction was completed (monitored by TLC), the most of the solvent was evaporated in *vacuo*, the reaction mixture was purified by flash column chromatography on silica gel (Hexanes : EtOAc = 50:1 to 20:1) to give 1.43 g pure **3a** (60% yield).

Derivatizations:

Procedure for the Preparation of 10.[1]

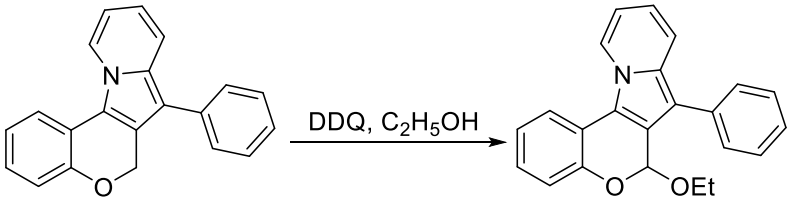


3a | **10**, 65%

To a 10-mL oven-dried round-bottom flask with a magnetic stirring bar, **3a** (29.7 mg, 0.1 mmol), H_2O_2 (2.0 mmol, 10.0 equiv.), and CH_3CH_2OH (2.0 mL) were added in sequence. Then the reaction mixture was stirred at 60℃ for 12 hours. After the reaction completed, the reaction mixture was quenched with saturated brine (10.0 mL) and extracted with EtOAc (3×10.0 mL) The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure after filtration. The obtained residue was purified by flash column chromatography on silica gel (hexanes : EtOAc = 15:1 to 8:1) to give 21.4 mg pure product **10** as white solid, 65% yield, mp = 90.4 - 90.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.45 – 8.32 (m, 1H), 7.78 – 7.62

(comp, 5H), 7.52 – 7.48 (m, 1H), 7.43 – 7.33 (comp, 3H), 7.16 – 7.12 (m, 1H), 7.02 (t, *J* = 7.9 Hz, 2H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.03 (d, *J* = 11.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 187.3, 161.5, 156.0, 148.6, 136.7, 136.5, 135.2, 128.9, 128.6, 127.6, 127.4, 123.0, 122.8, 122.3, 122.0, 118.3, 74.3, 68.2, 65.2; HRMS (TOF MS ESI$^+$) calculated for $C_{21}H_{15}NO_3Na$ [M+Na]$^+$: 352.0950, found 352.0944.

Procedure for the Preparation of 11.[2]



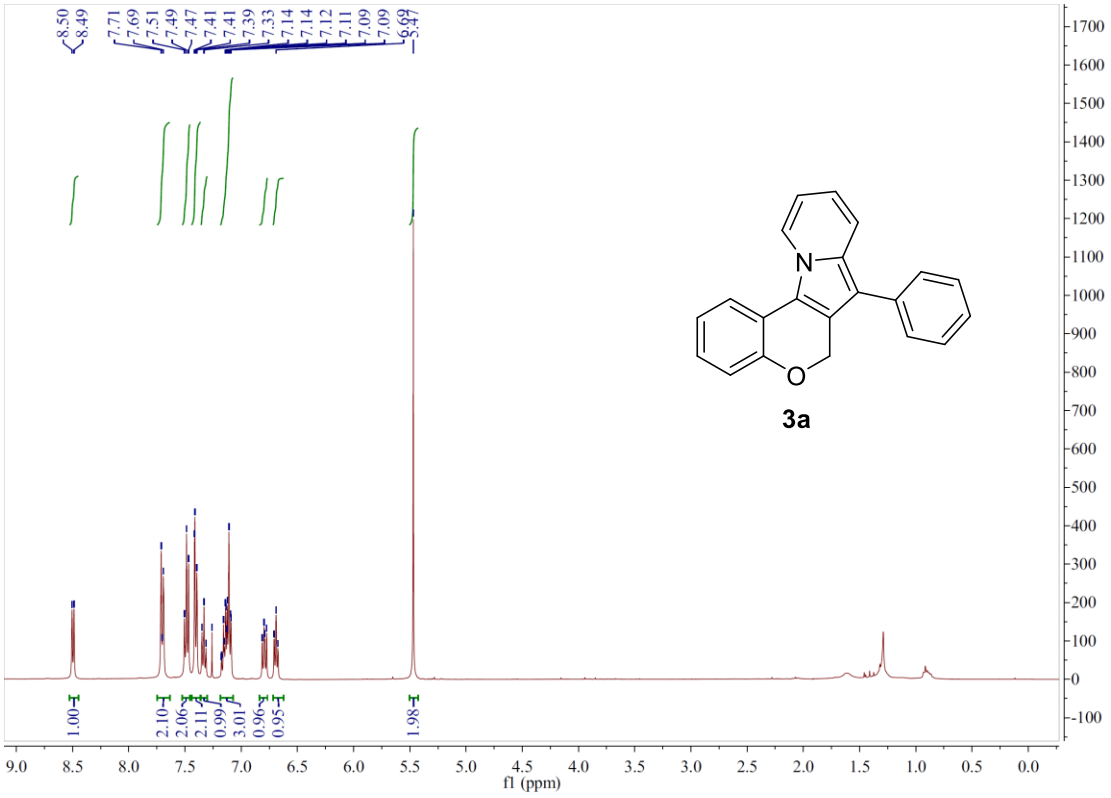
3a **11**, 84%

To a 10-mL oven-dried vial with a magnetic stirring bar, **3a** (29.7 mg, 0.1 mmol), DDQ (0.2 mmol, 2.0 equiv.), and anhydrous C_2H_5OH (2.0 mL) were added in sequence, and the reaction mixture was stirred for 2 hours at room temperature. When the reaction was completed (monitored by TLC), the crude reaction mixture was purified by flash column chromatography on silica gel (Hexanes : EtOAc = 50:1) to give 28.6 mg pure product **11** as yellow solid, 84% yield, mp = 122.4 -122.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.58 (d, *J* = 7.2 Hz, 1H), 7.88 – 7.82 (m, 1H), 7.77 – 7.74 (m, 1H), 7.70 – 7.62 (m, 2H), 7.51 (t, *J* = 7.7 Hz, 2H), 7.38 – 7.33 (m, 1H), 7.28 – 7.14 (comp, 3H), 6.84 – 6.80(m, 1H), 6.74 – 6.71 (m, 1H), 4.11 – 4.03 (m, 1H), 3.97 – 3.81 (m, 1H), 1.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 145.0, 134.2, 132.2, 131.9, 129.3, 128.9, 126.6, 126.4, 123.7, 122.2, 120.3, 119.9, 119.1, 118.5, 118.4, 118.3, 112.5, 111.6, 95.8, 64.0, 15.41; HRMS (TOF MS ESI$^+$) calculated for $C_{23}H_{19}NO_2Na$ [M+Na]$^+$: 364.1313, found 364.1310.

References:

1 Y. He, X. Zhang, L. Cui, J. Wang and X. Fan, *Green Chem.*, **2012**, *14*, 3429.

2 F. Yang, Y. Li, P. E. Floreancig, X. Li and L. Liu, *Org. Biomol. Chem.*, **2018**, *16*, 5144.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7.41
7.41
7.39
7.33
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7.11
7.09
7.09
6.69
5.47
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2.06
2.11
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3.01
0.96
0.95
1.98
fl (ppm)
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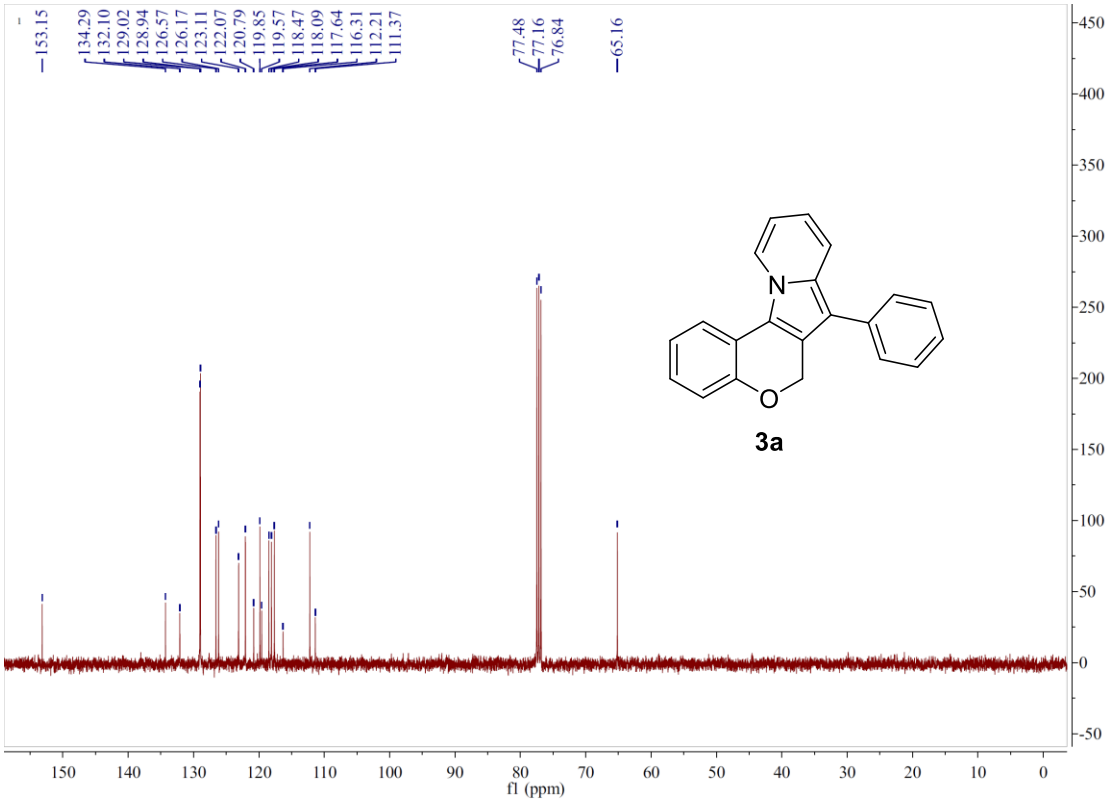
O
3a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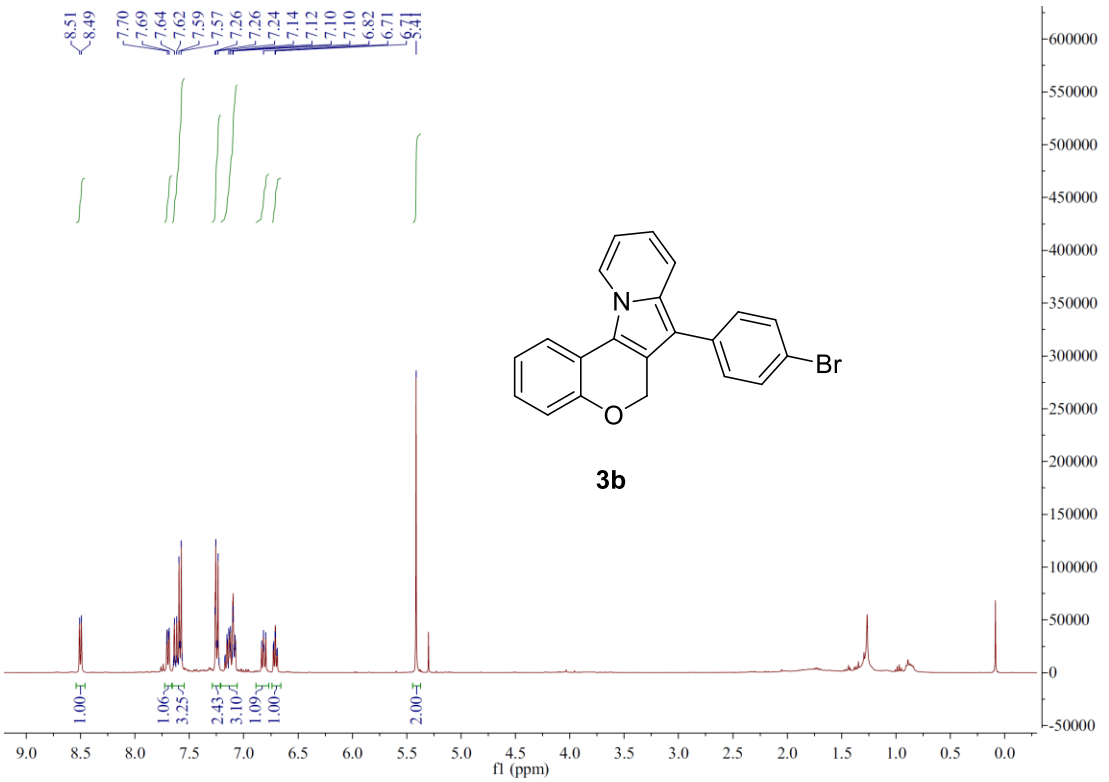
65.16
fl (ppm)
N
O
3a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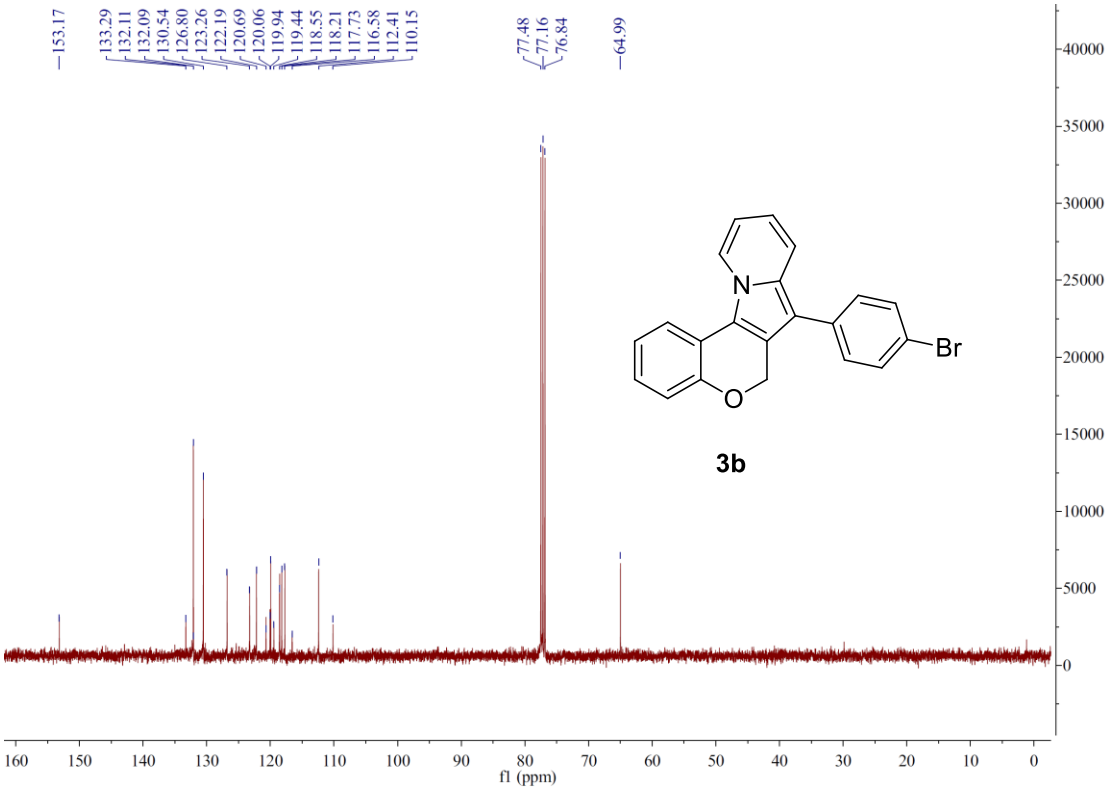
f1 (ppm)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64.99
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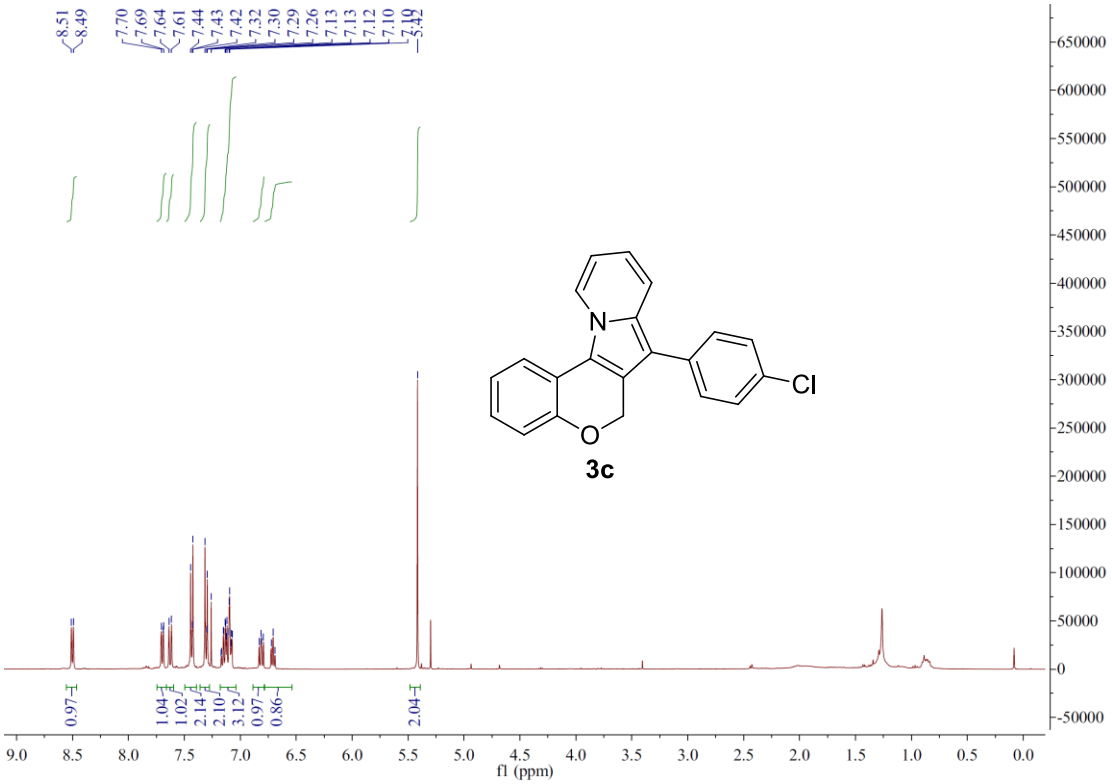
3b
f1 (ppm)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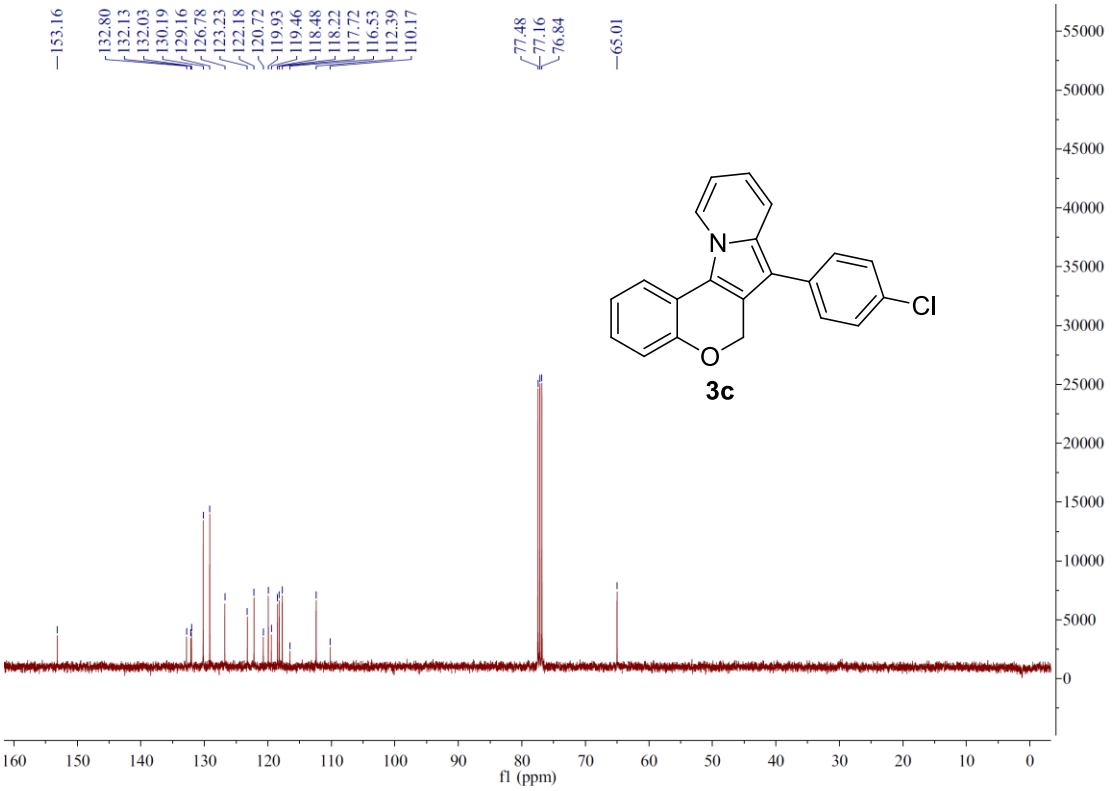
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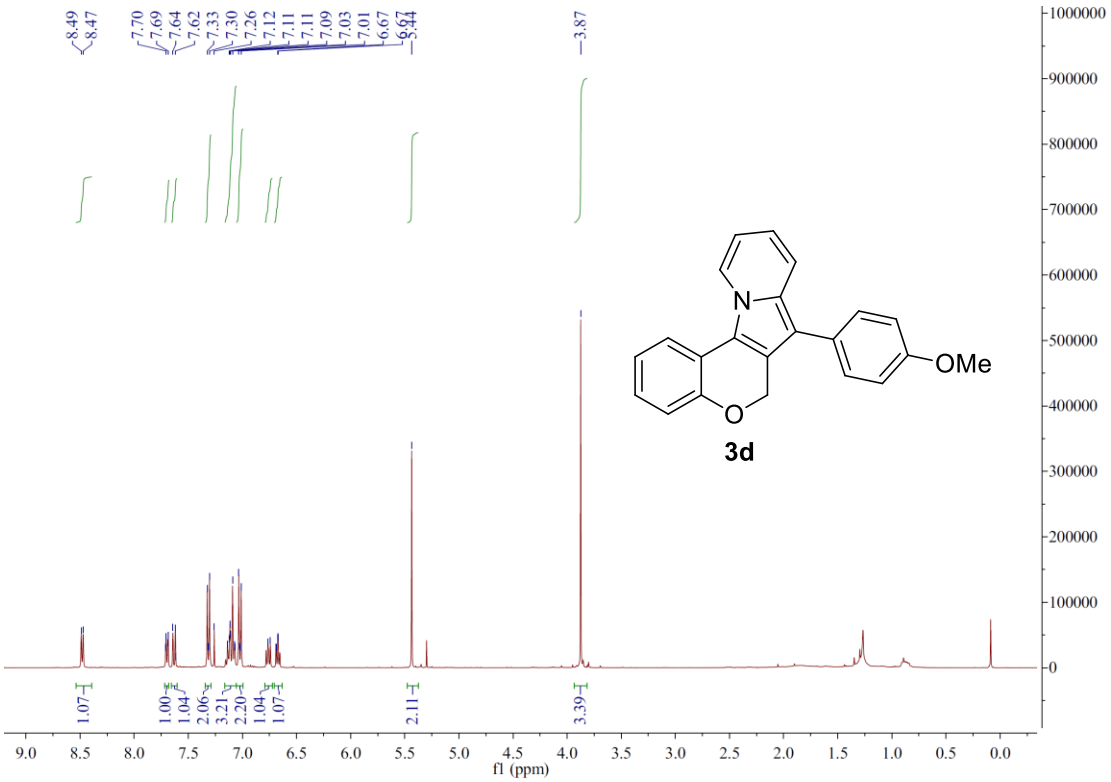
O
3c
f1 (ppm)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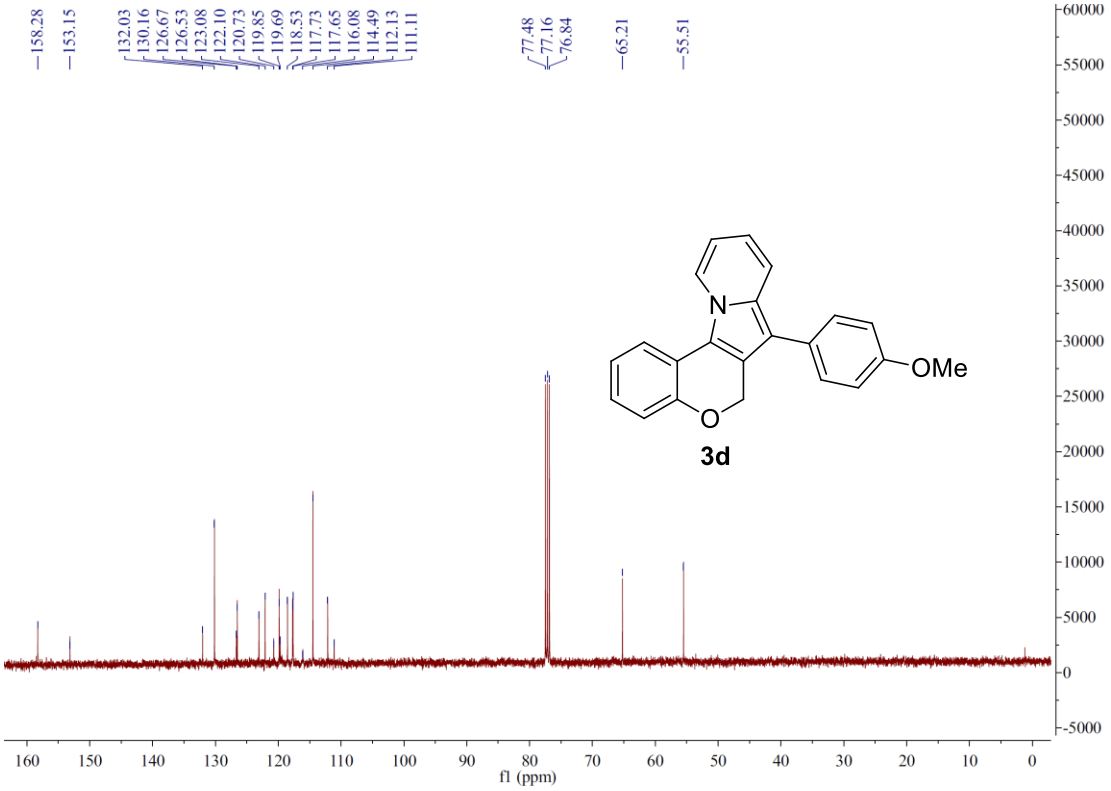
OMe
3d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fl (ppm)
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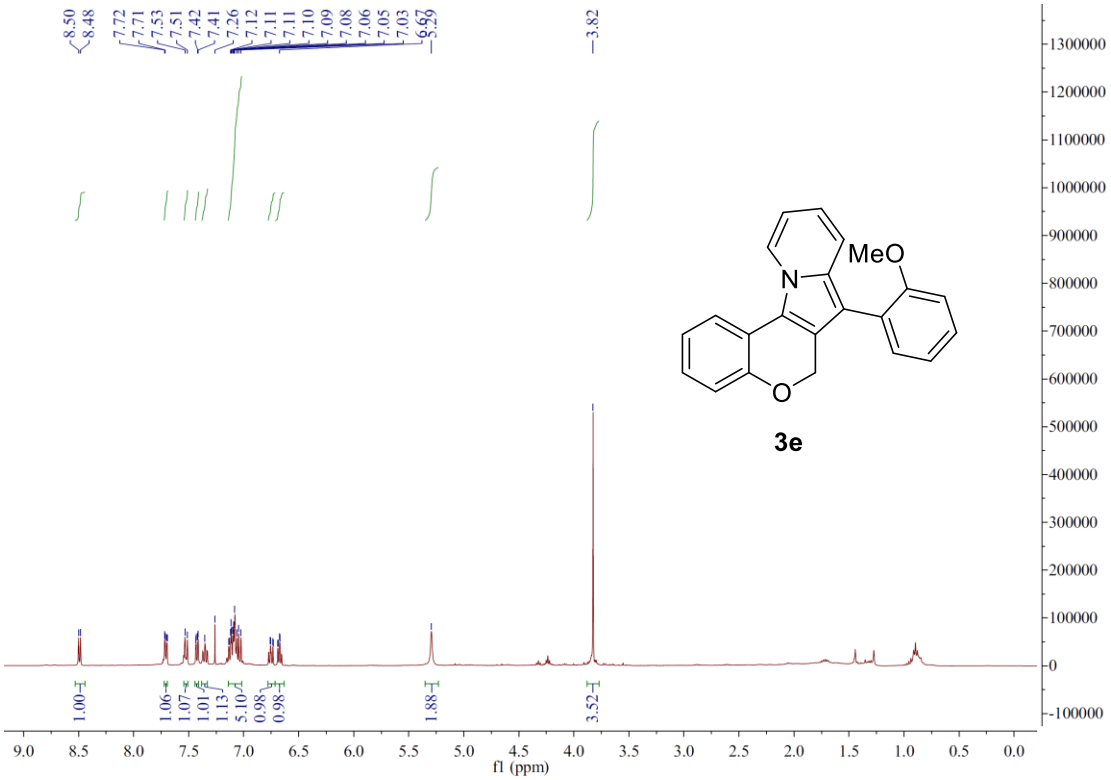
O
OMe
3d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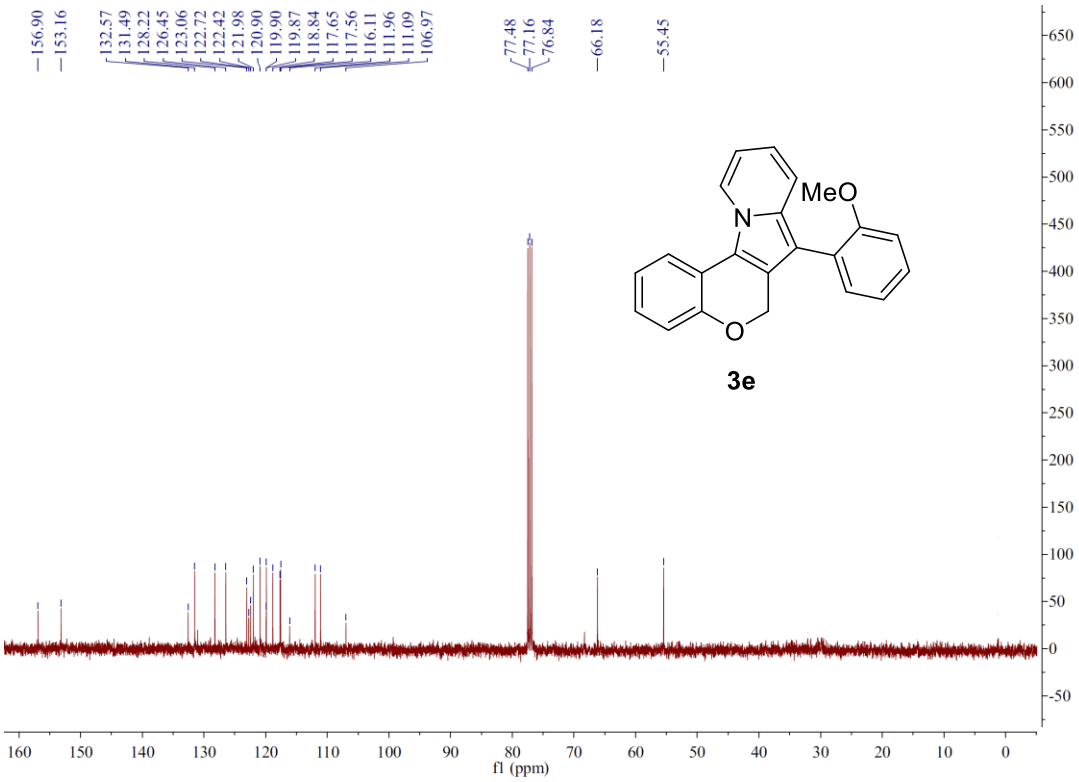
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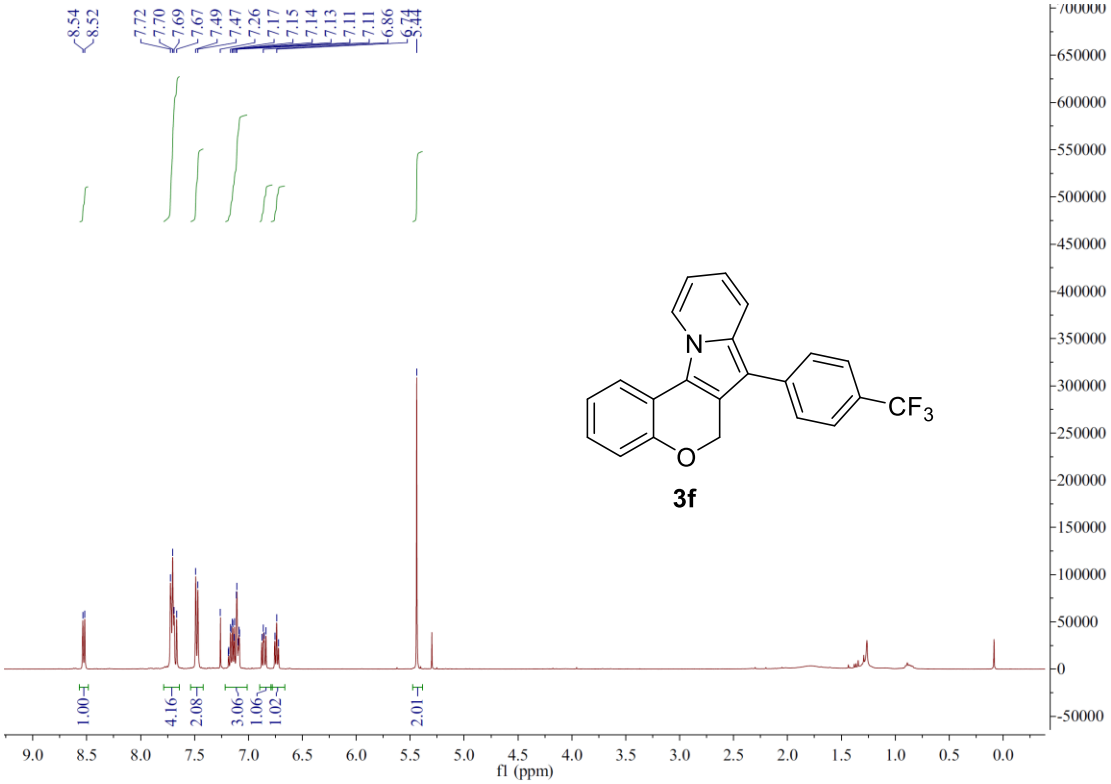
fl (ppm)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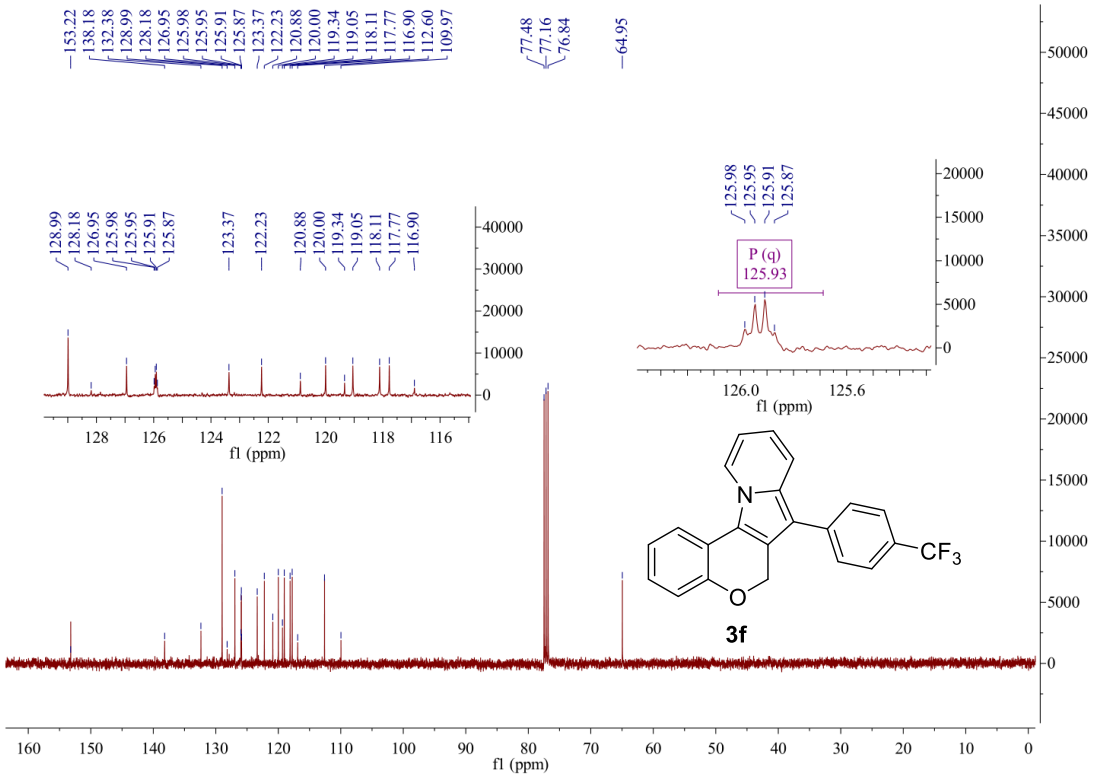
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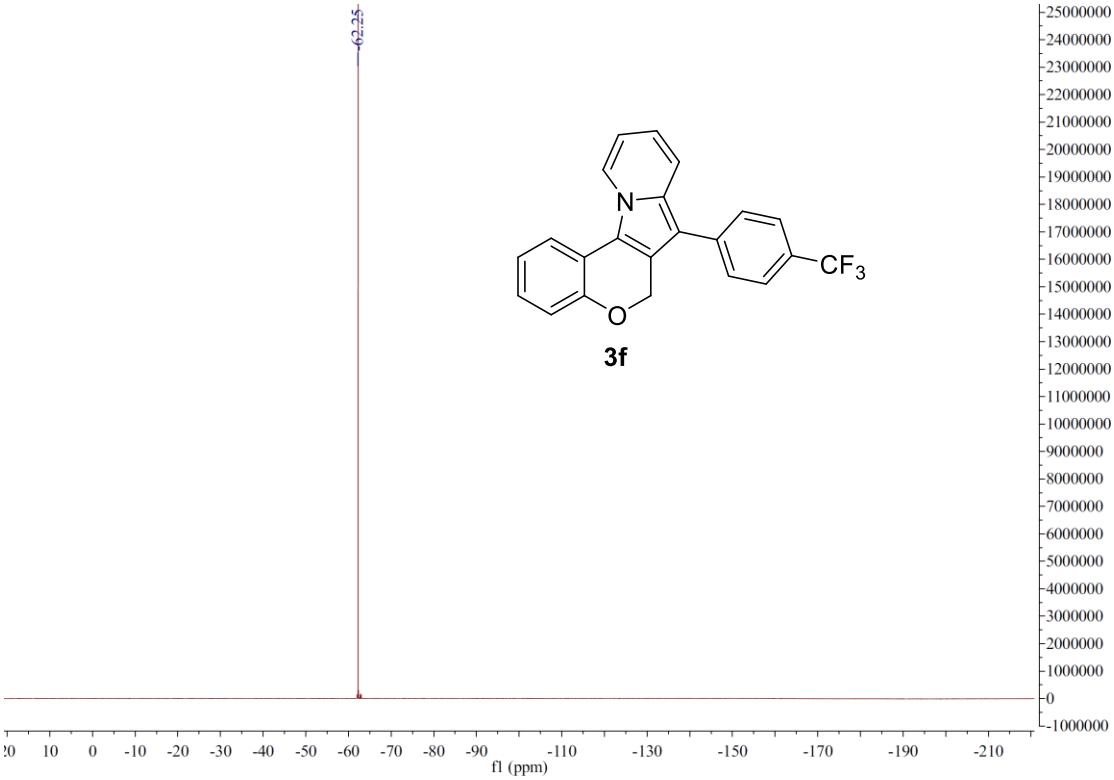
CF3
3f
f1 (ppm)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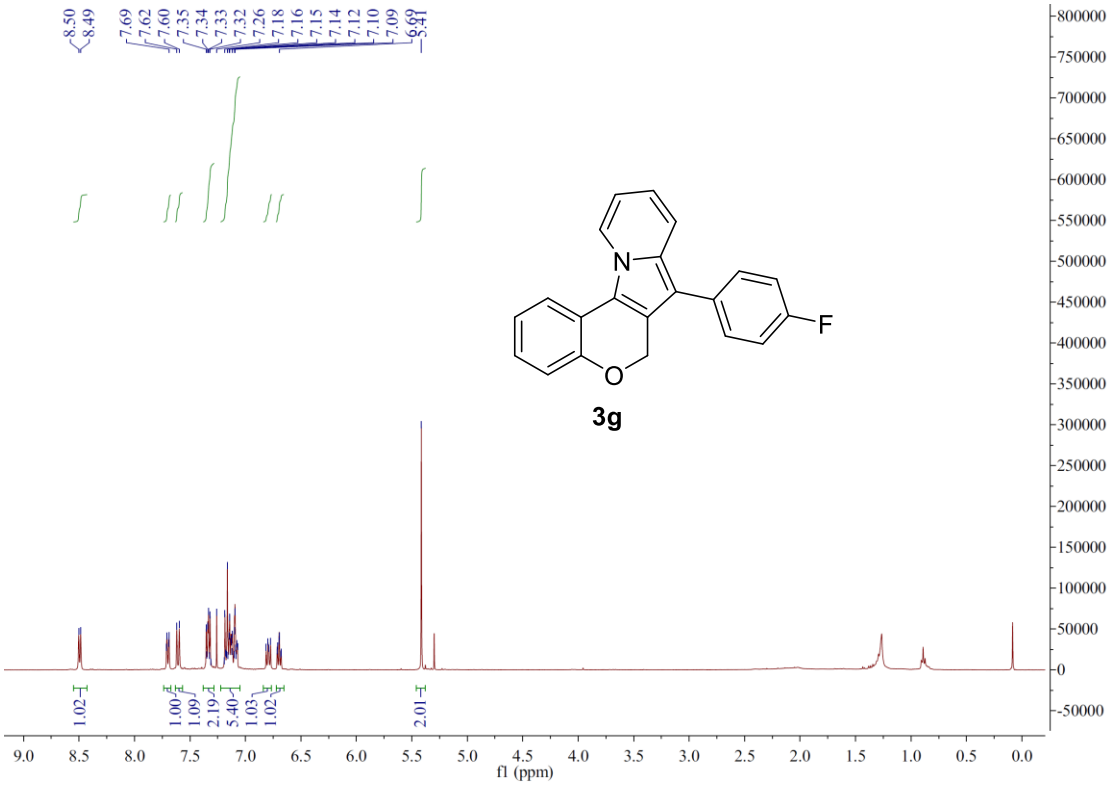
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2.01
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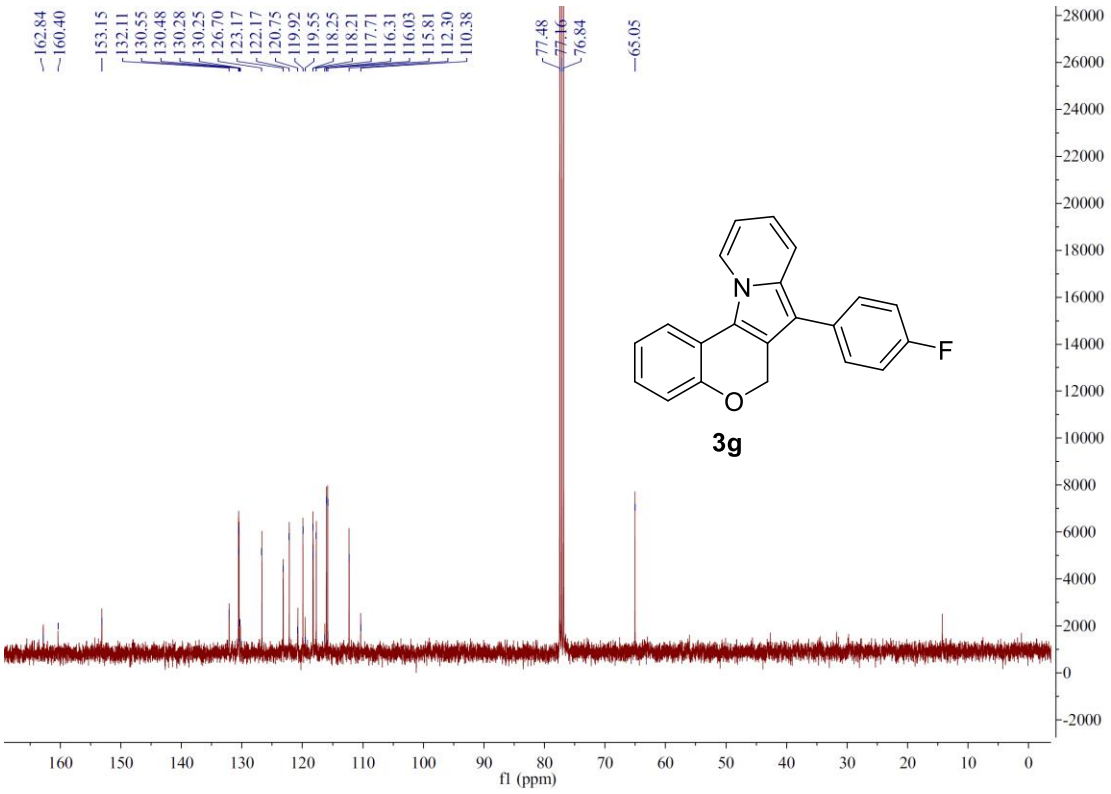
O
F
3g
f1 (ppm)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116.31
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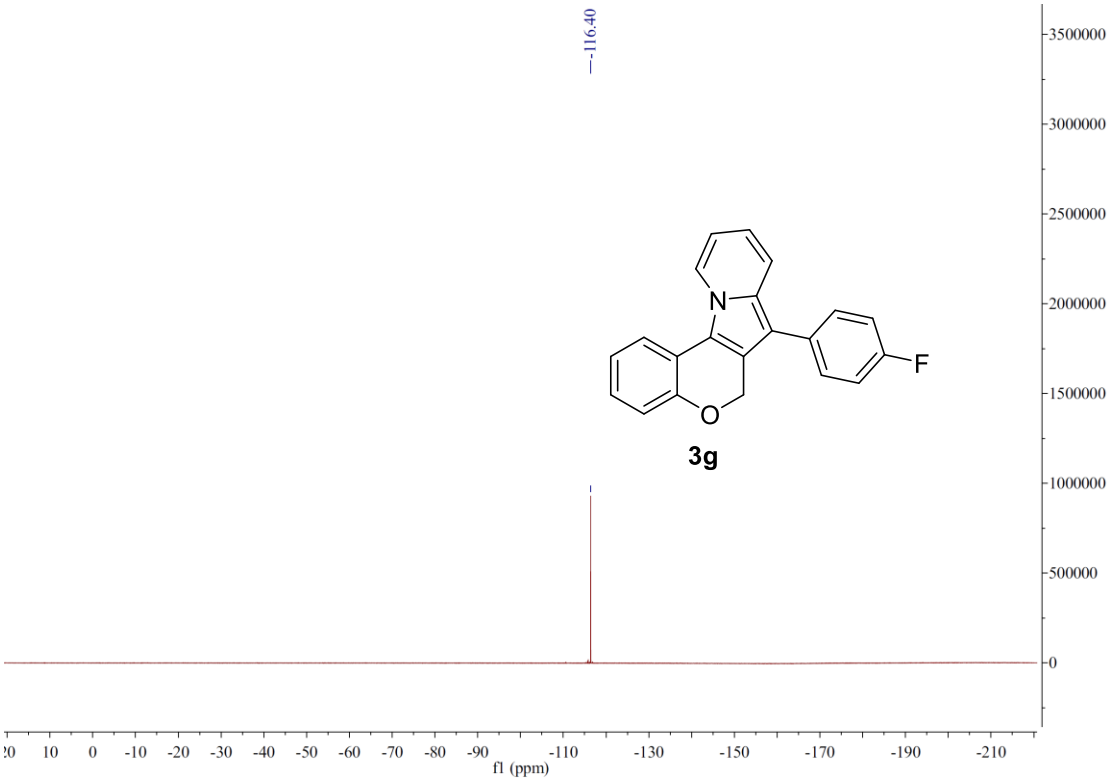
N
F
O
3g
f1 (ppm)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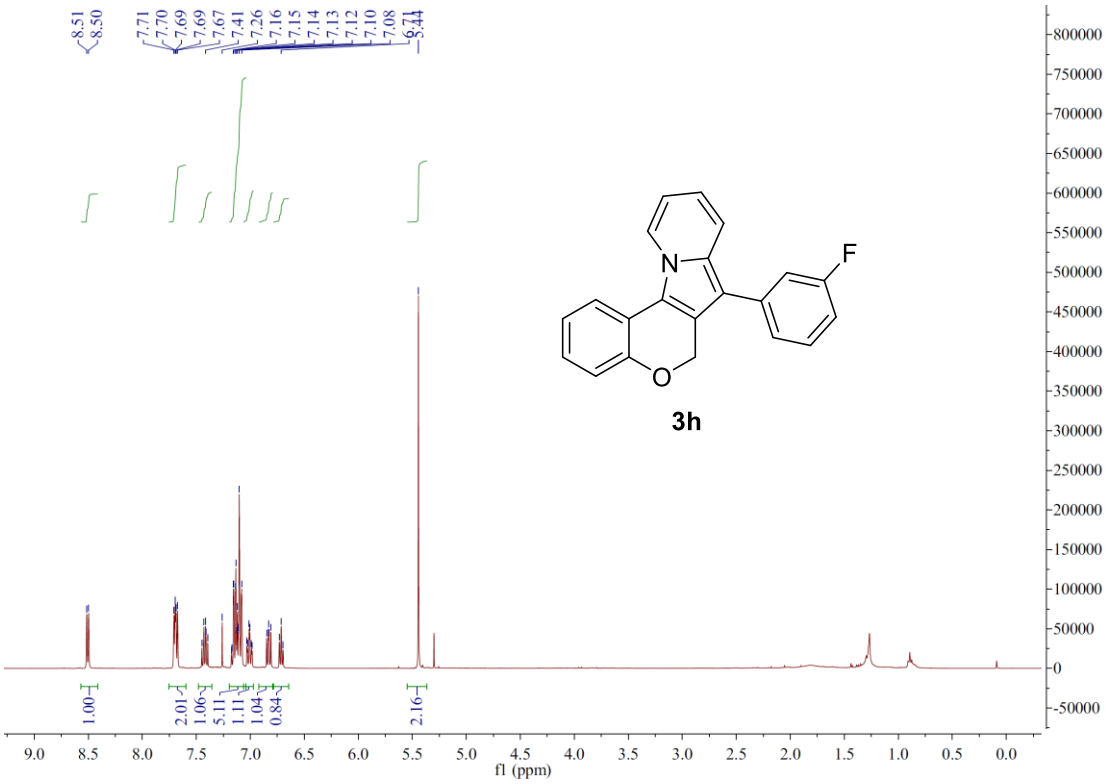
3g
f1 (ppm)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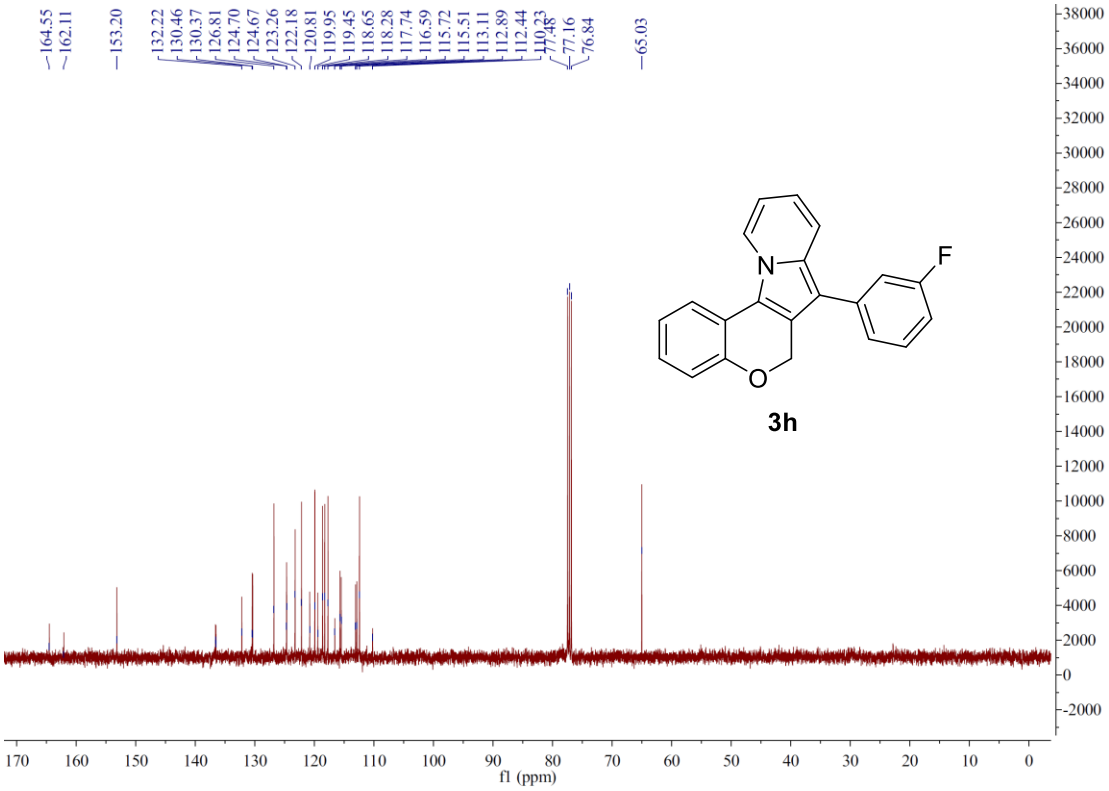
7.69
7.69
7.67
7.41
7.26
7.16
7.15
7.14
7.13
7.12
7.10
7.08
6.71
6.71
1.00
2.01
1.06
5.11
1.11
1.04
0.84
2.16
F
N
O
3h
fl (ppm)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130.37
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124.70
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123.26
122.18
120.81
119.95
119.45
118.65
118.28
117.74
116.59
115.72
115.51
113.11
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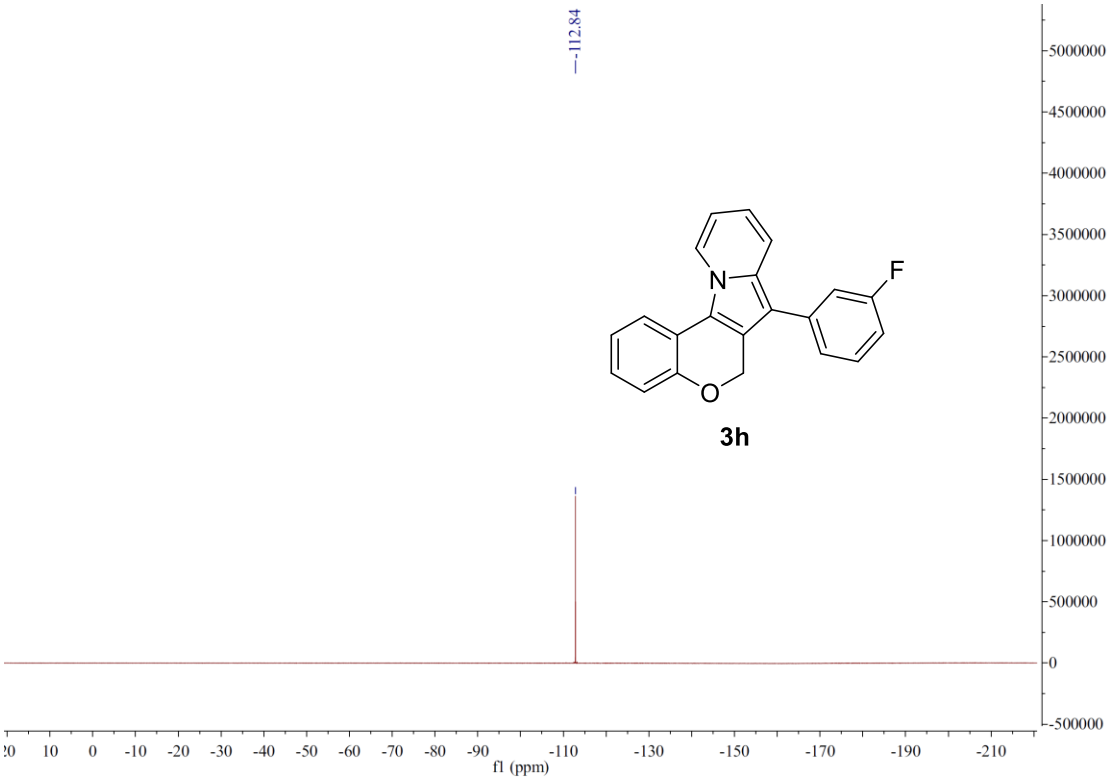
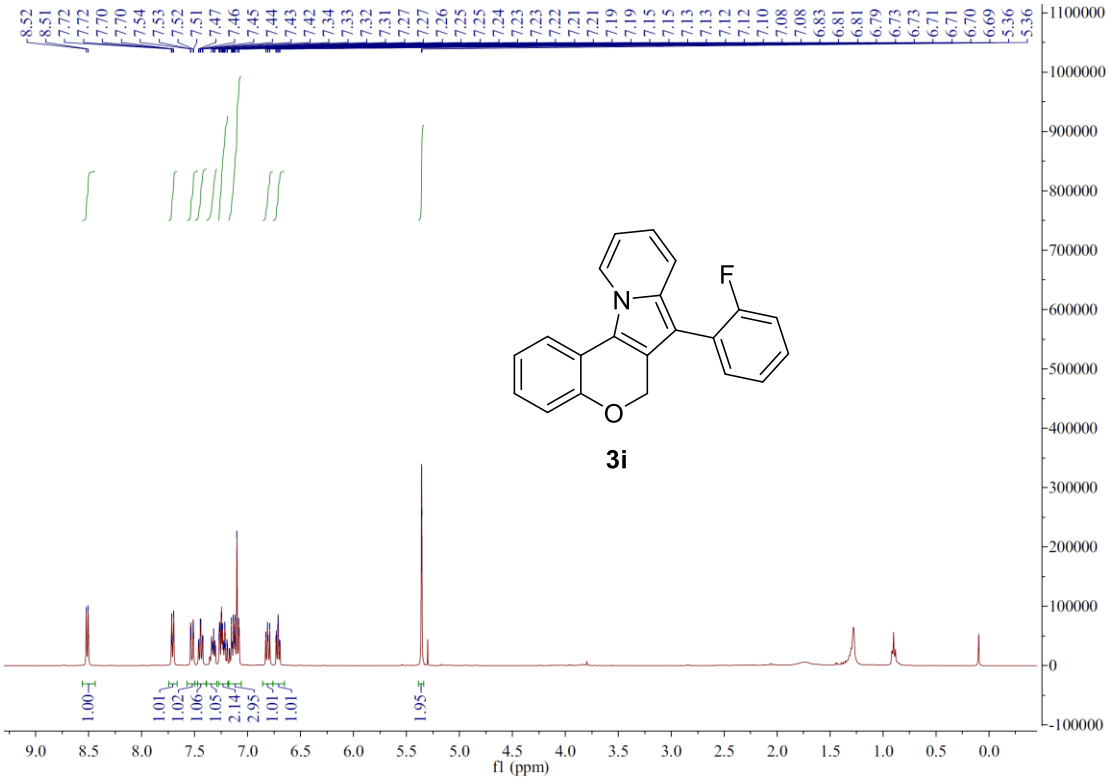
112.44
110.23
77.48
77.16
76.84
65.03
F
N
O
3h
fl (ppm)


-112.84
F
N
O
3h
f1 (ppm)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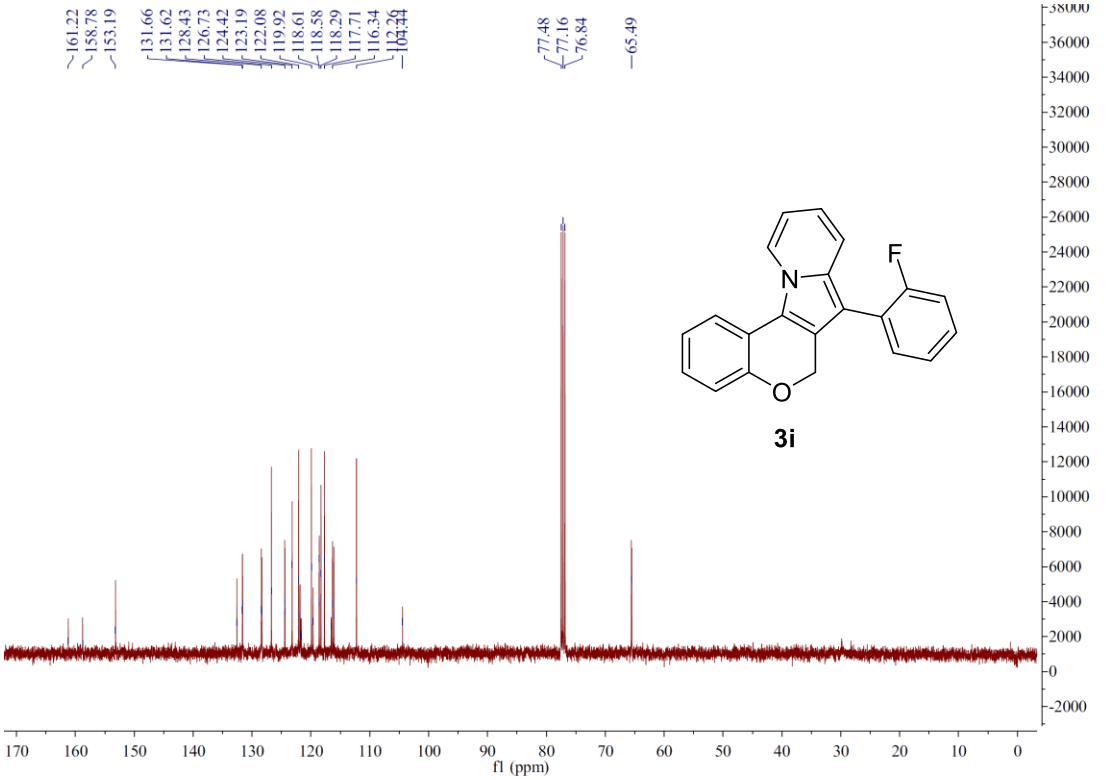
7.46
7.45
7.44
7.43
7.42
7.34
7.33
7.32
7.31
7.27
7.27
7.26
7.25
7.25
7.24
7.23
7.23
7.22
7.21
7.21
7.19
7.19
7.15
7.15
7.13
7.13
7.12
7.12
7.10
7.08
7.08
6.83
6.81
6.81
6.79
6.73
6.73
6.71
6.71
6.70
6.69
5.36
5.36
F
N
O
3i
1.00
1.01
1.02
1.06
1.05
2.14
2.95
1.01
1.01
1.95
f1 (ppm)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122.08
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118.61
118.58
118.29
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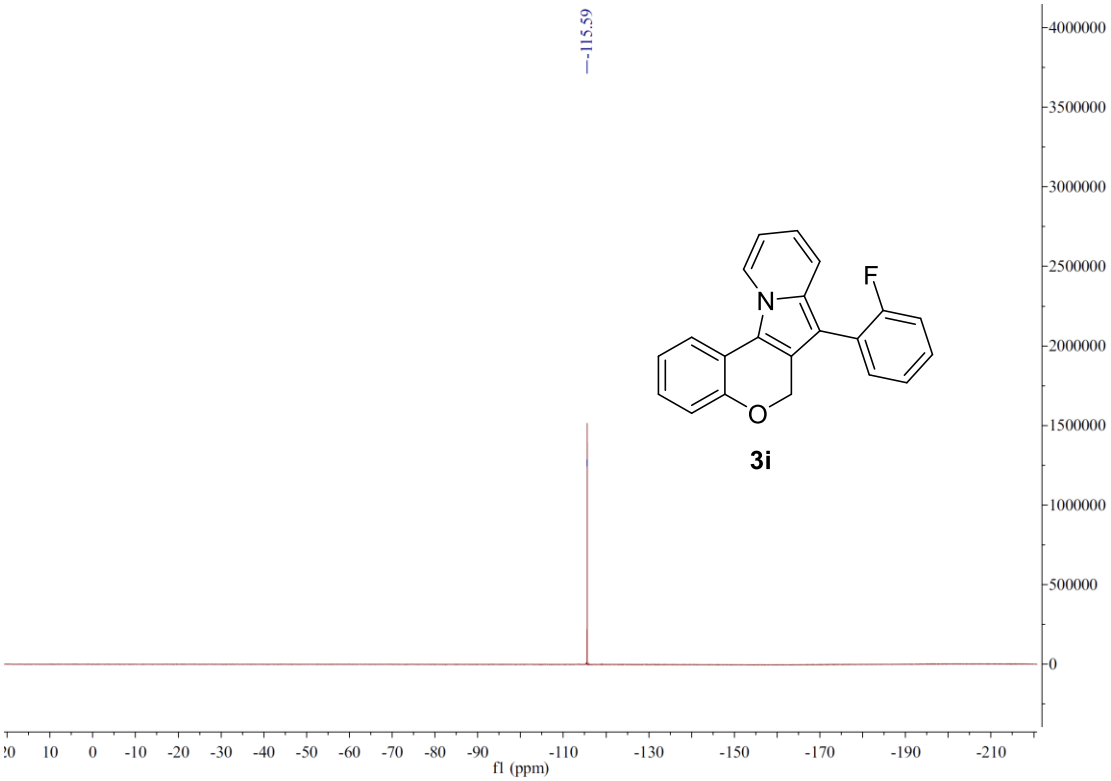
112.26
104.44
77.48
77.16
76.84
65.49
F
N
O
3i
fl (ppm)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F
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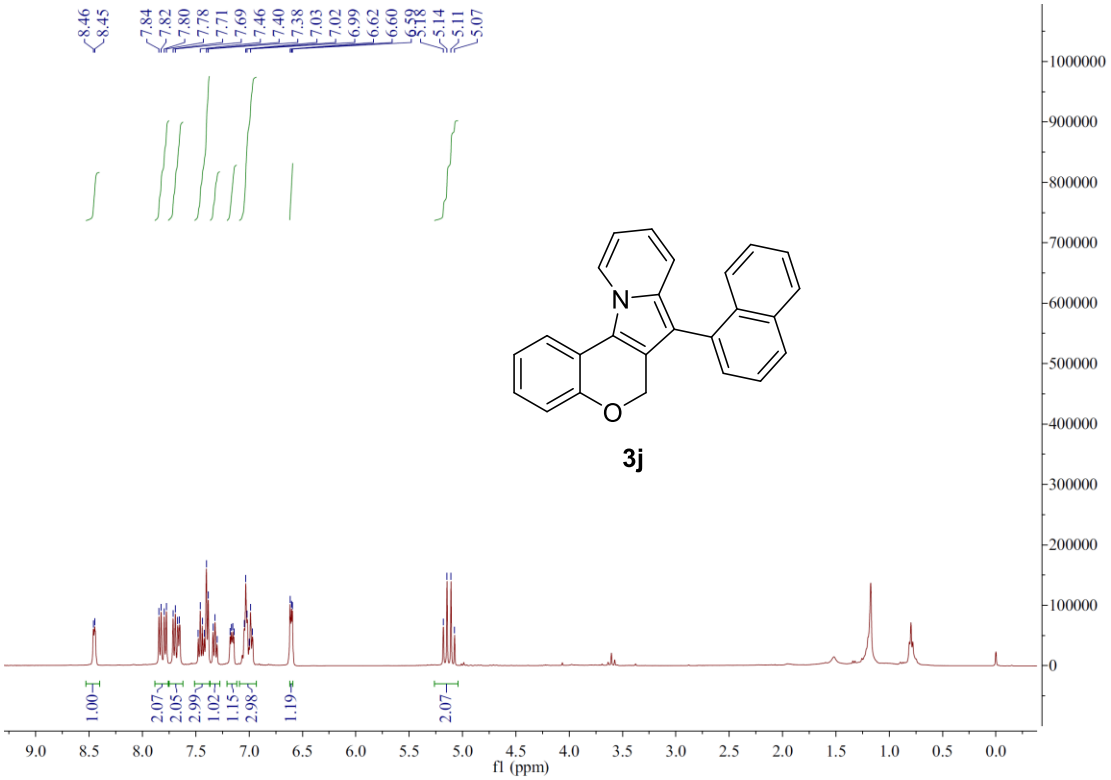
O
3i
fl (ppm)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8.45
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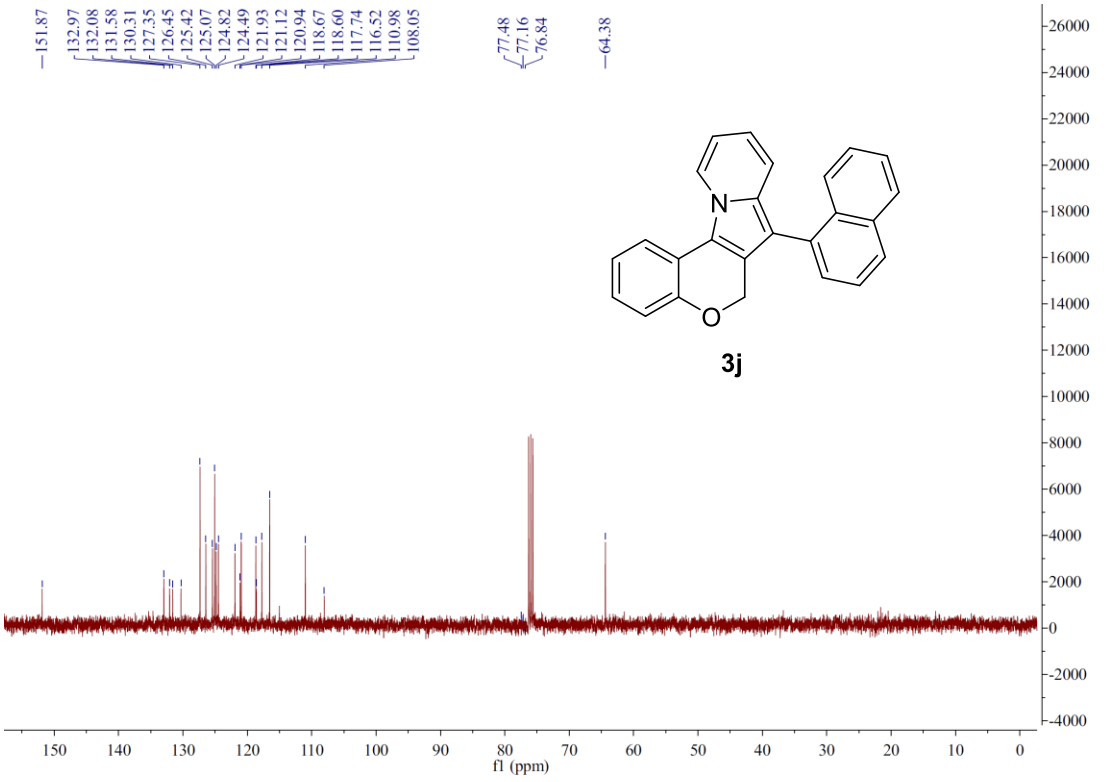
7.78
7.71
7.69
7.46
7.40
7.38
7.03
7.02
6.99
6.62
6.60
5.18
5.14
5.11
5.07
N
O
3j
1.00
2.07
2.05
2.99
1.02
1.15
2.98
1.19
2.07
f1 (ppm)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126.45
125.42
125.07
124.82
124.49
121.93
121.12
120.94
118.67
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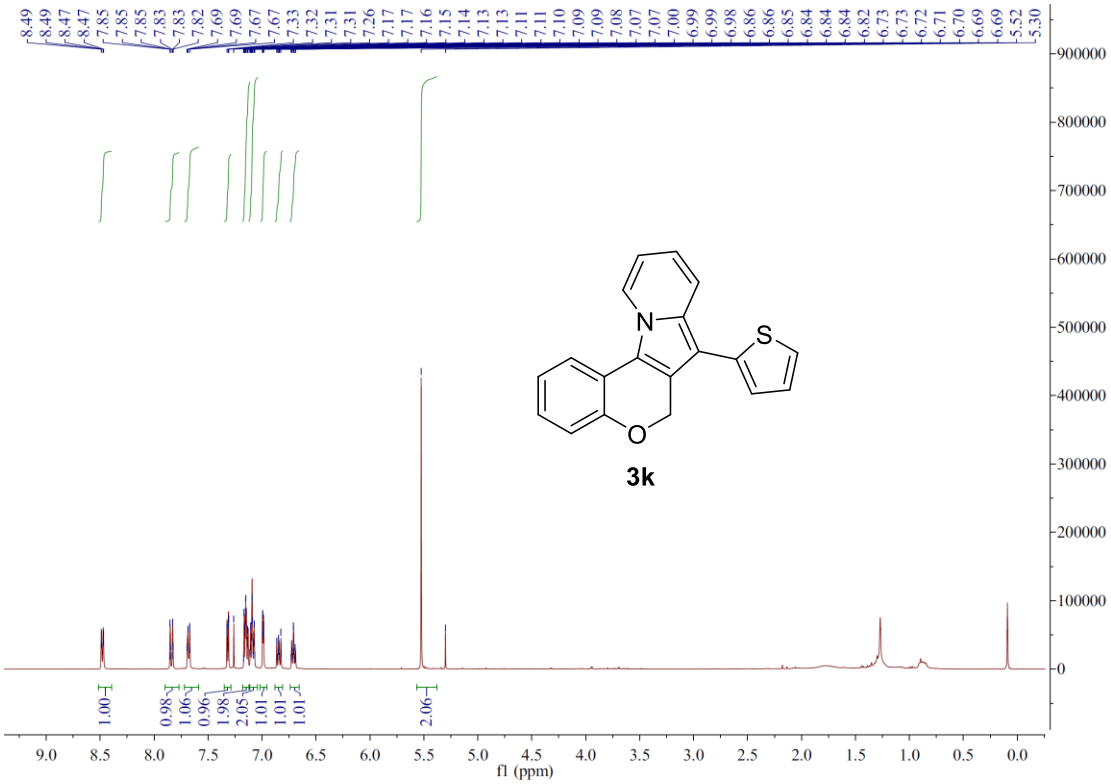
110.98
108.05
77.48
77.16
76.84
64.38
N
O
3j
f1 (ppm)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7.85
7.85
7.83
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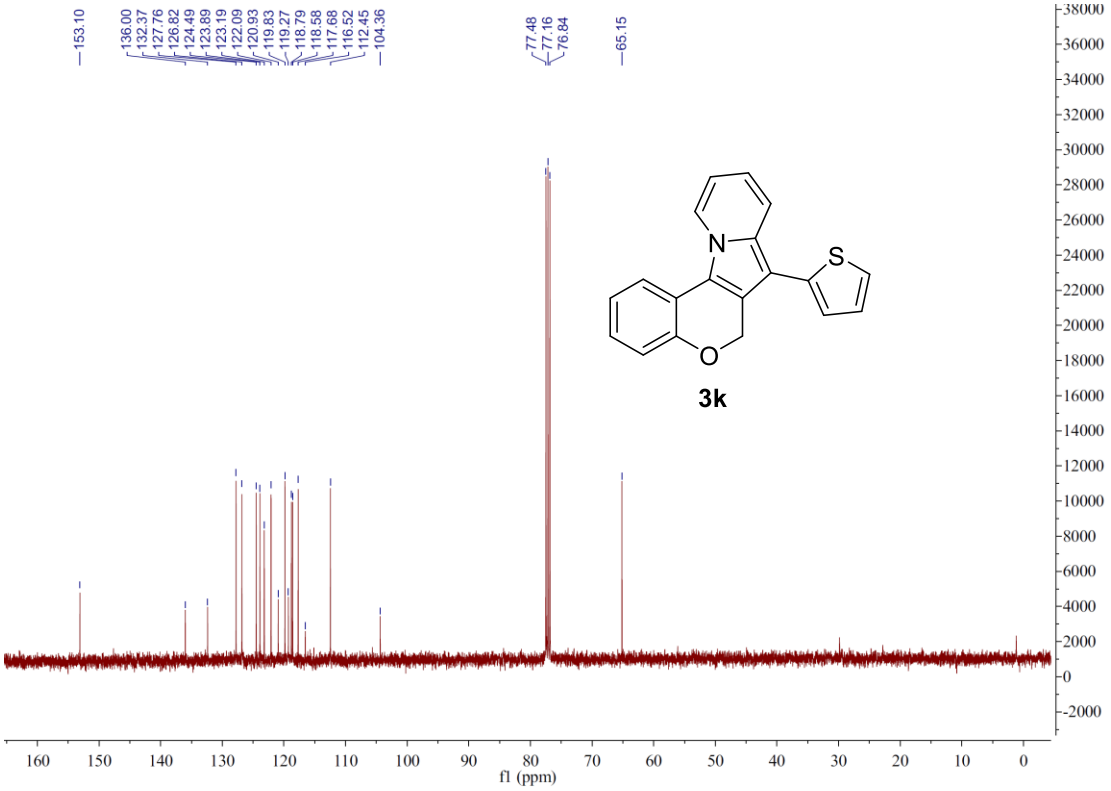
7.82
7.69
7.69
7.67
7.67
7.33
7.32
7.31
7.31
7.26
7.17
7.17
7.16
7.15
7.14
7.13
7.13
7.11
7.11
7.10
7.09
7.09
7.08
7.07
7.07
7.00
6.99
6.99
6.98
6.86
6.86
6.85
6.84
6.84
6.84
6.82
6.73
6.73
6.72
6.71
6.70
6.69
6.69
5.52
5.30
N
S
O
3k
1.00
0.98
1.06
0.96
1.98
2.05
1.01
1.01
1.01
2.06
f1 (ppm)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120.93
119.83
119.27
118.79
118.58
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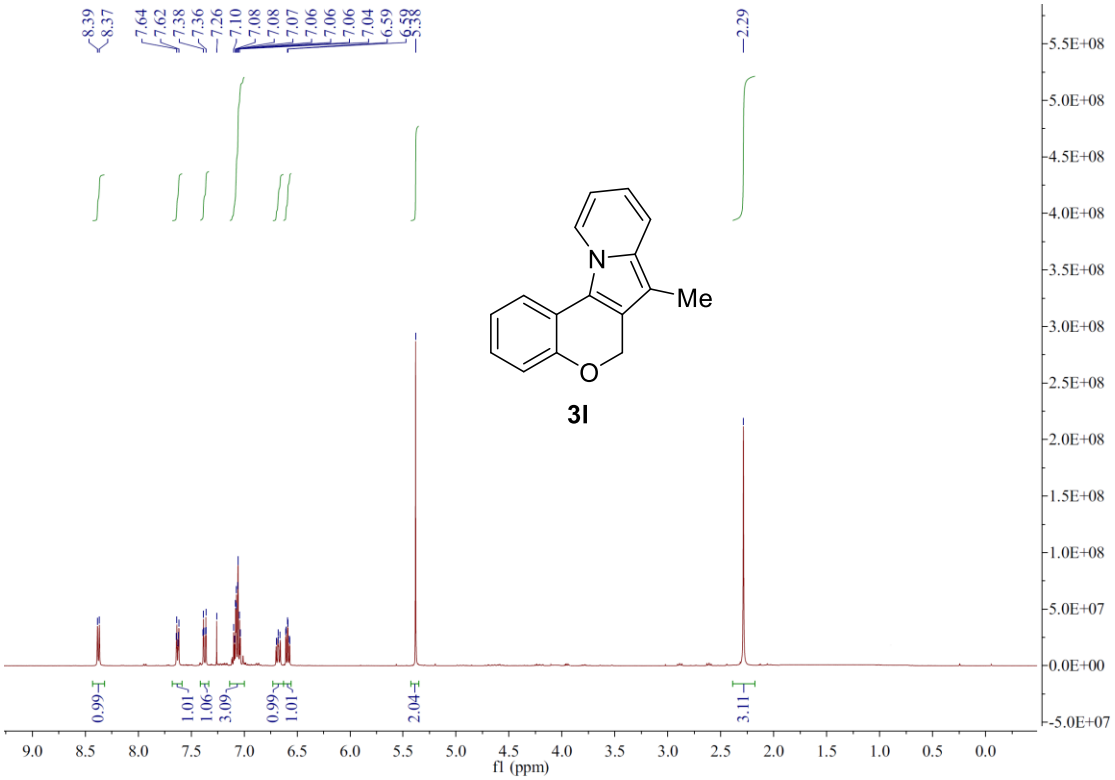
116.52
112.45
104.36
77.48
77.16
76.84
65.15
N
S
O
3k
f1 (ppm)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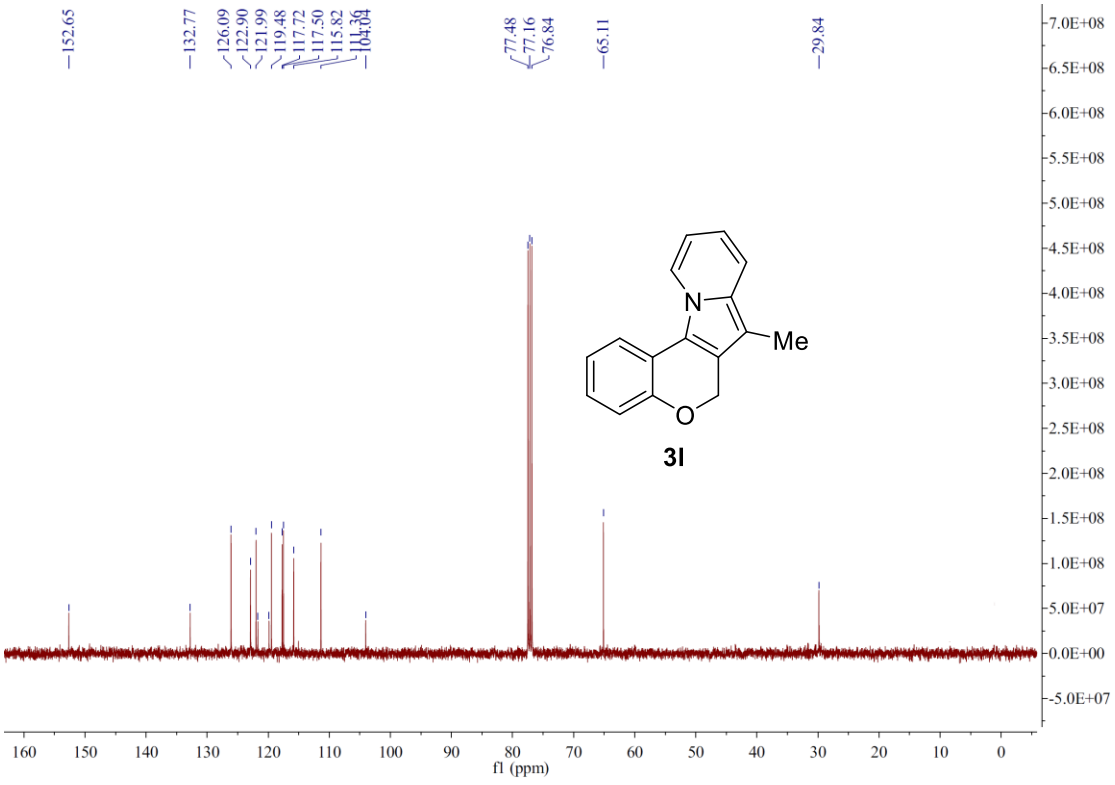
7.38
7.36
7.26
7.10
7.08
7.08
7.07
7.06
7.06
7.06
7.04
6.59
6.58
2.29
N
Me
O
3l
0.99
1.01
1.06
3.09
0.99
1.01
2.04
3.11
fl (ppm)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117.50
115.82
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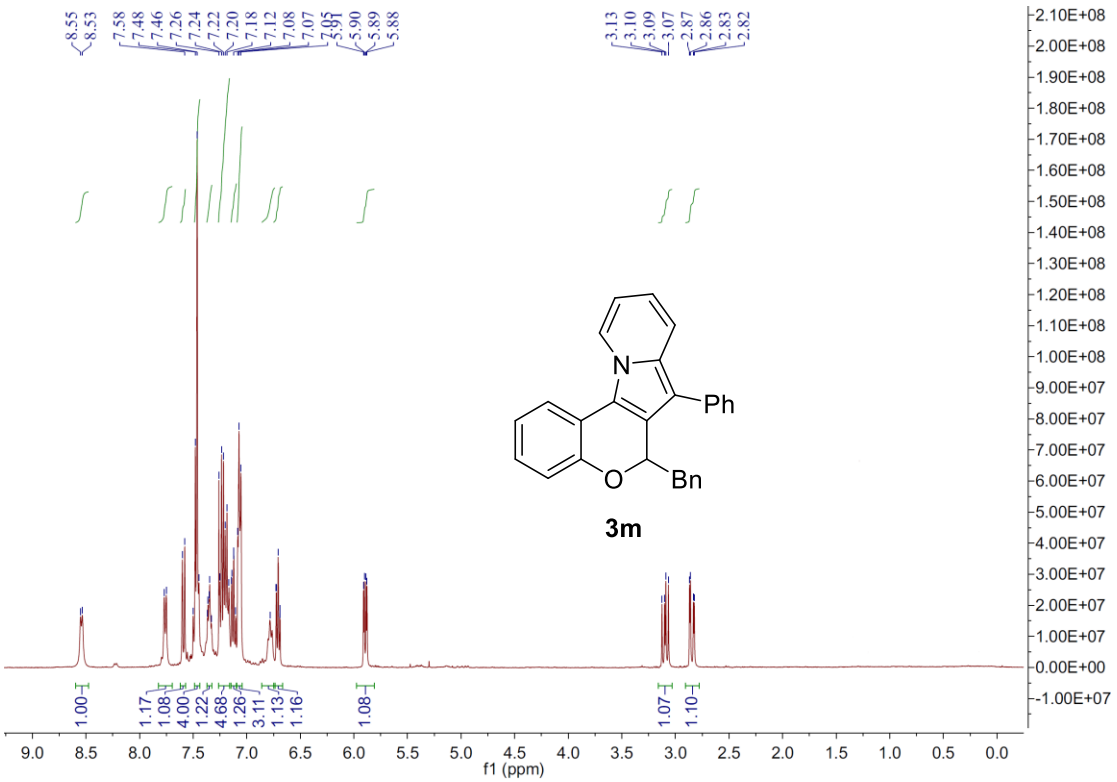
104.04
77.48
77.16
76.84
65.11
29.84
N
Me
O
3l
fl (ppm)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8.53
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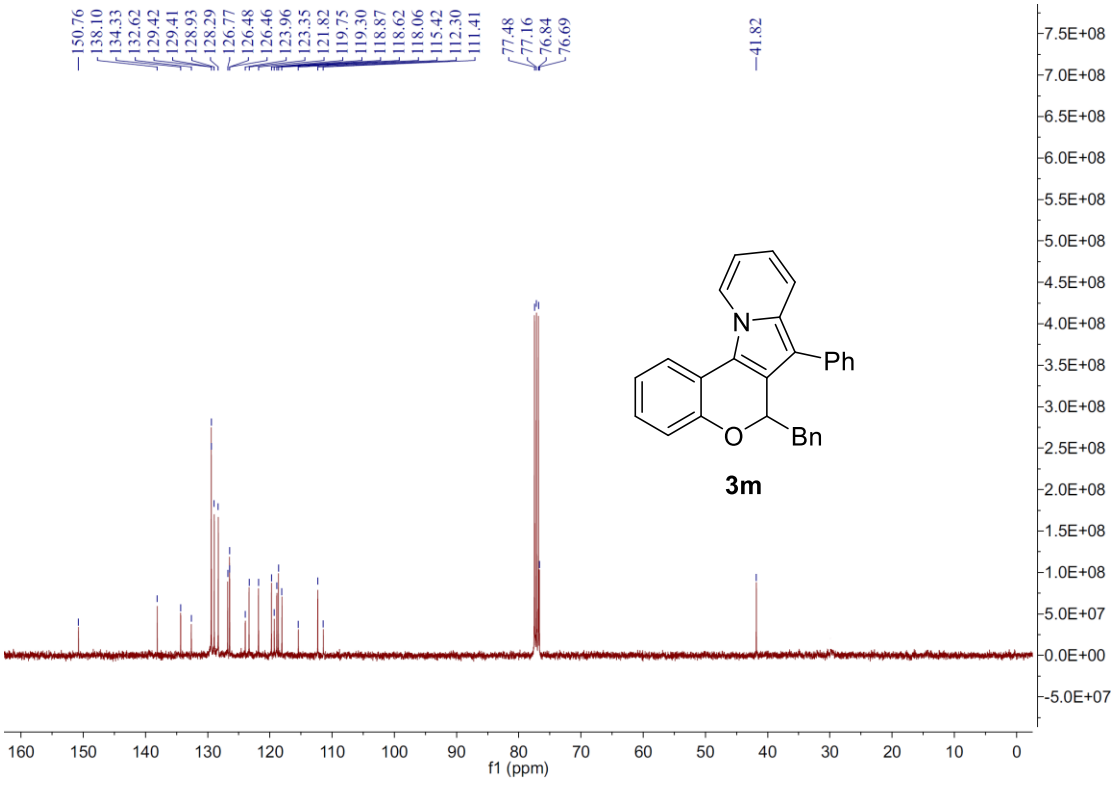
7.22
7.20
7.18
7.12
7.08
7.07
5.91
5.90
5.89
5.88
3.13
3.10
3.09
3.07
2.87
2.86
2.83
2.82
N
Ph
O
Bn
3m
1.00
1.17
1.08
4.00
1.22
4.68
1.26
3.11
1.13
1.16
1.08
1.07
1.10
f1 (ppm)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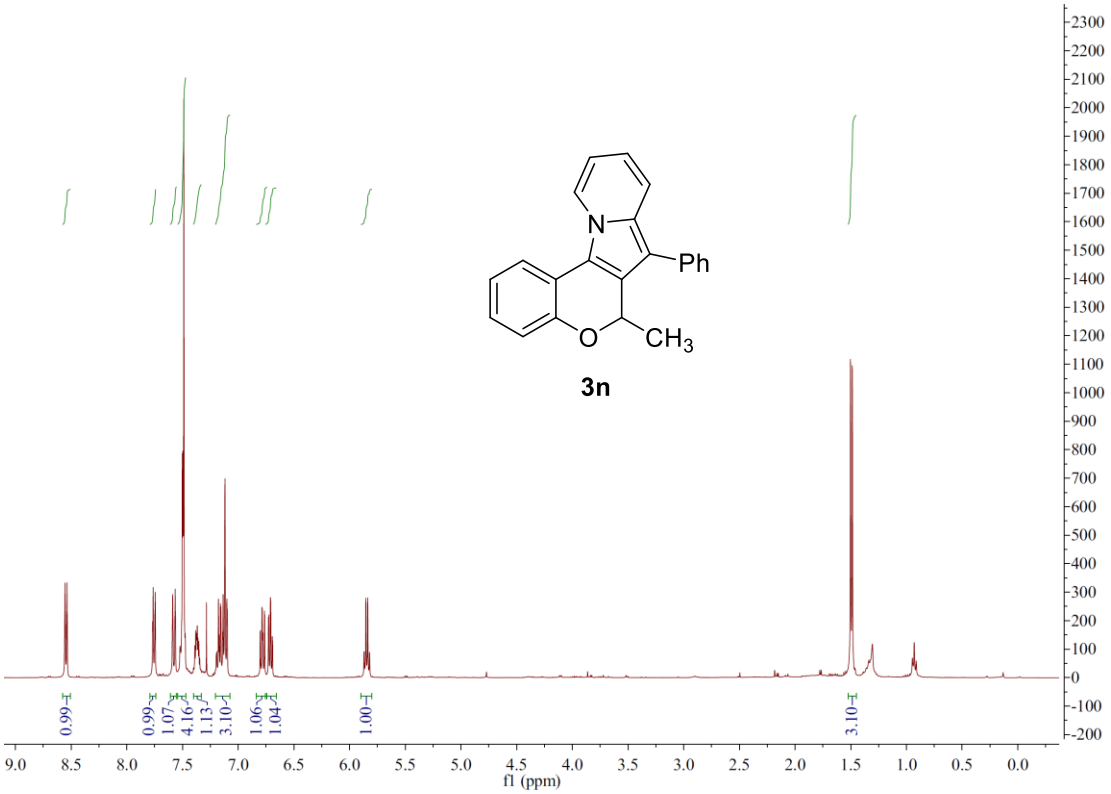
129.41
128.93
128.29
126.77
126.48
126.46
123.96
123.35
121.82
119.75
119.30
118.87
118.62
118.06
115.42
112.30
111.41
77.48
77.16
76.84
76.69
41.82
N
Ph
O
Bn
3m
f1 (ppm)


N
Ph
O
CH3
3n
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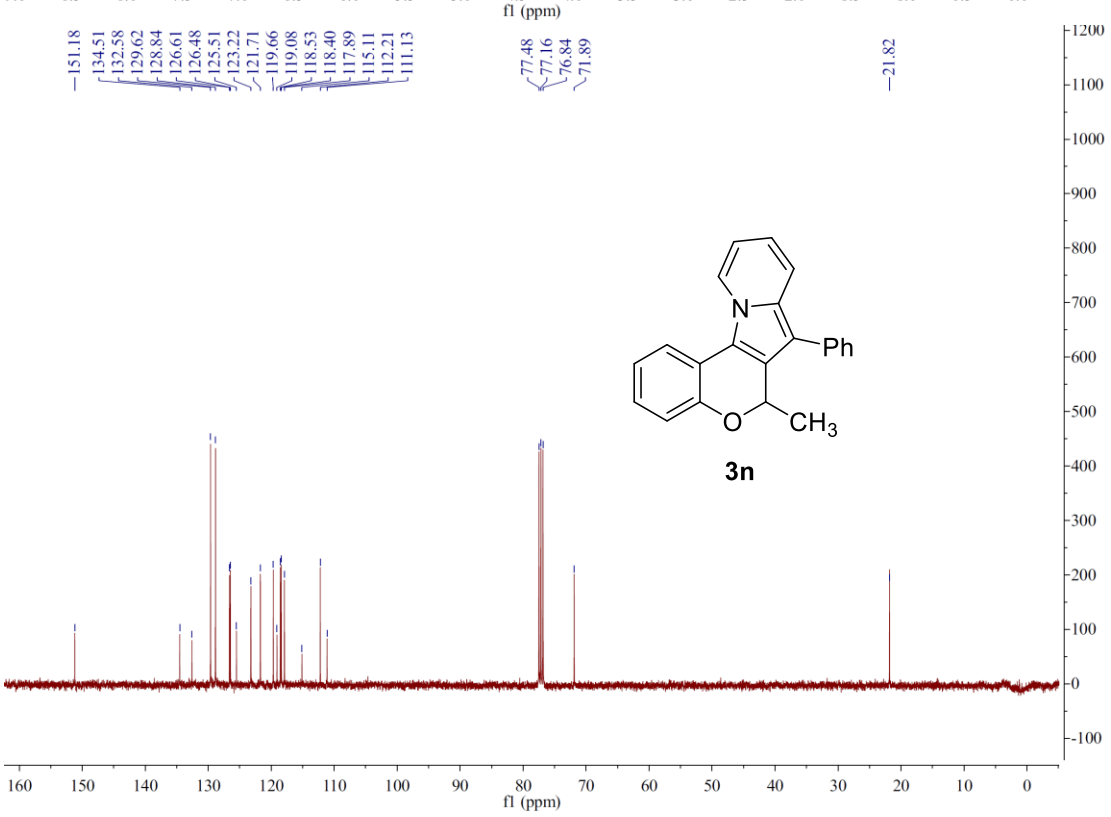
0.99
1.07
4.16
1.13
3.10
1.06
1.04
1.00
3.10
f1 (ppm)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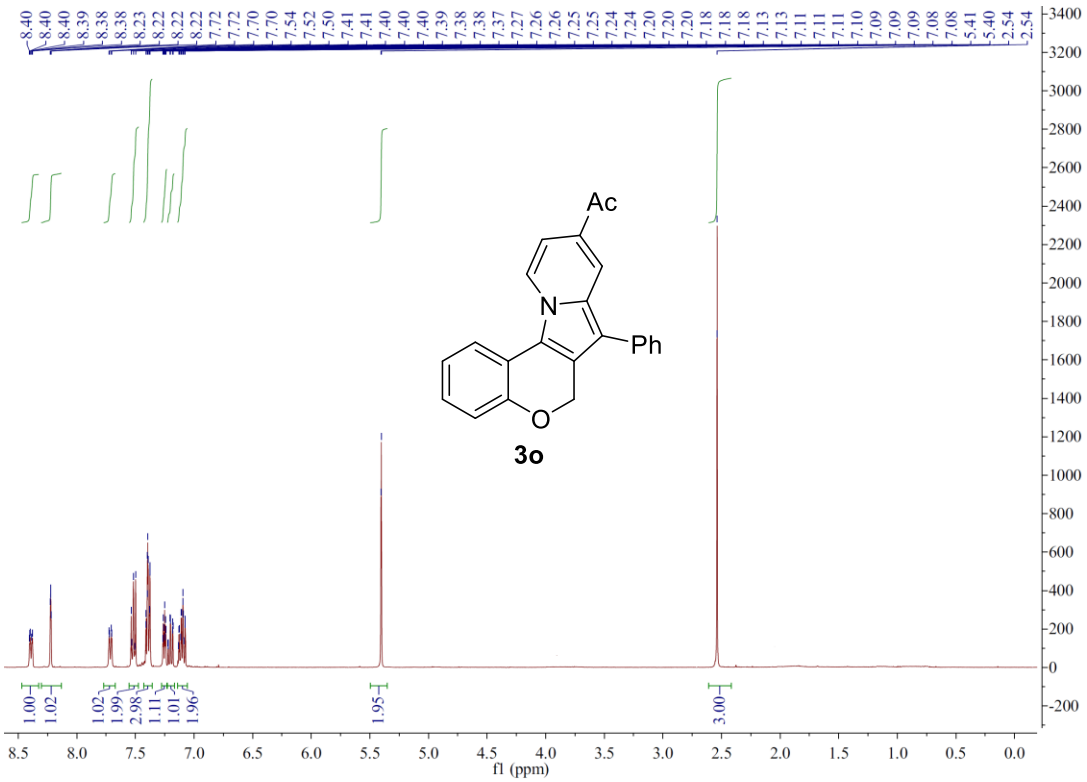
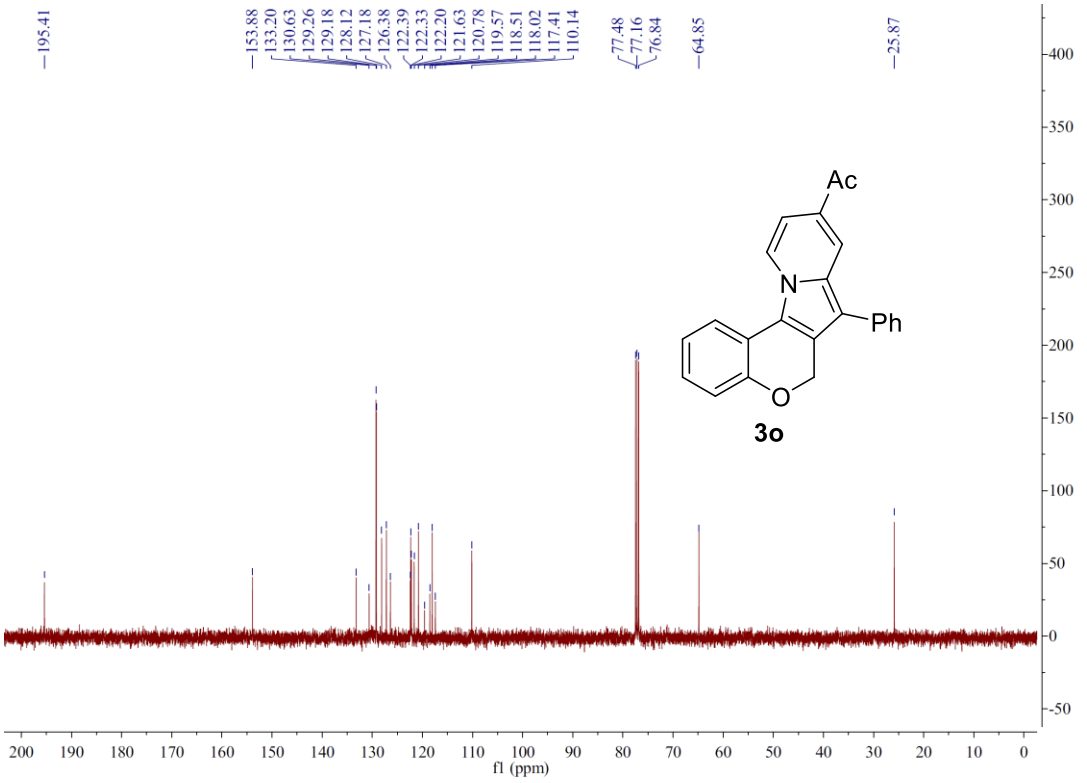
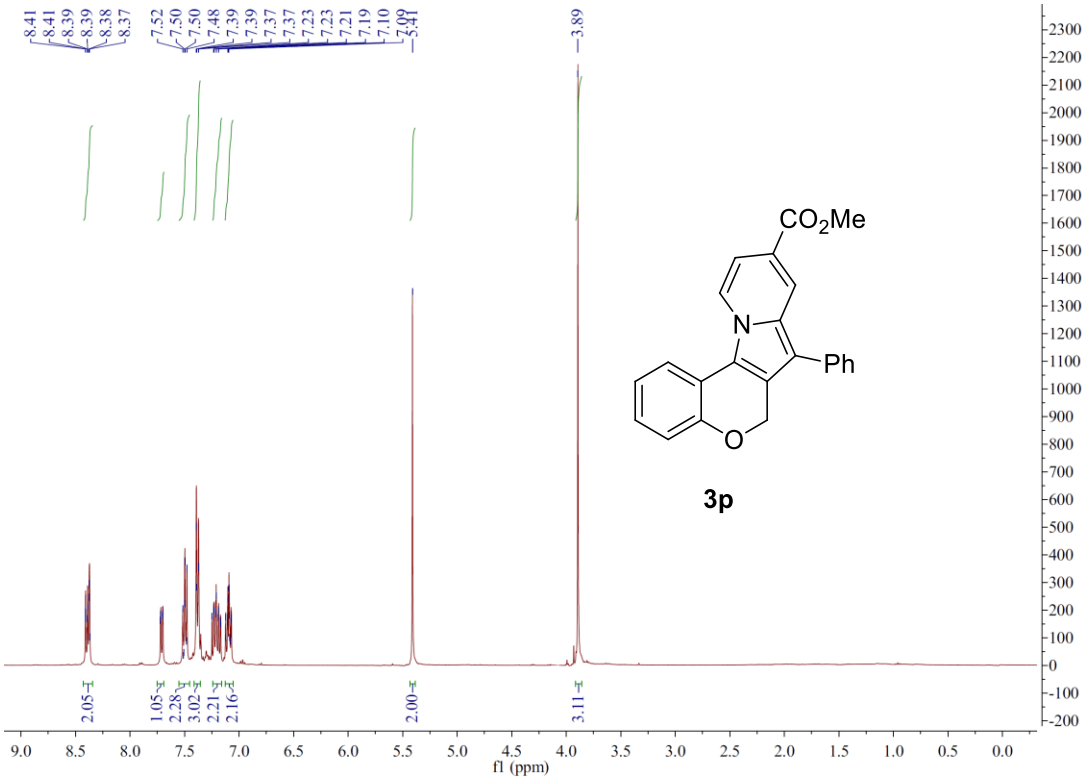
121.71
119.66
119.08
118.53
118.40
117.89
115.11
112.21
111.13
77.48
77.16
76.84
71.89
21.82
N
Ph
O
CH3
3n
f1 (ppm)


Ac
N
Ph
O
3o
fl (ppm)


Ac
N
Ph
O
3o
fl (ppm)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7.48
7.39
7.39
7.37
7.37
7.23
7.21
7.19
7.10
7.09
5.41
3.89
2.05
1.05
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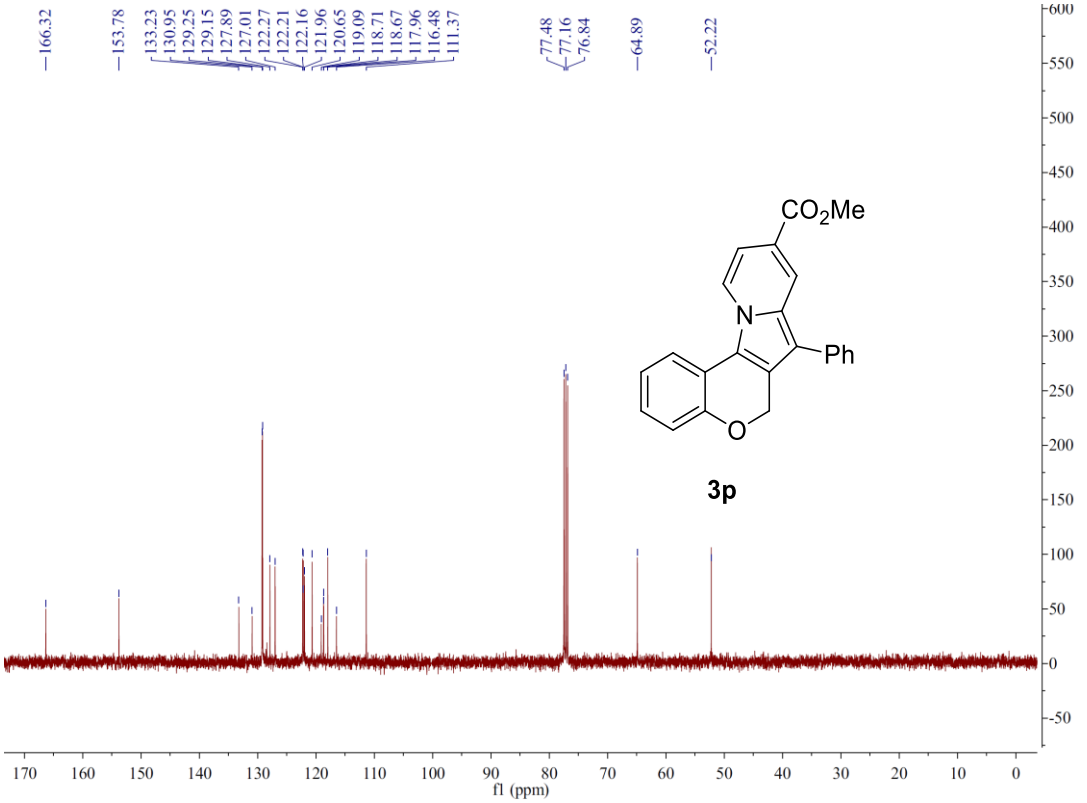
3.02
2.21
2.16
2.00
3.11
CO2Me
N
Ph
O
3p
f1 (ppm)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122.21
122.16
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120.65
119.09
118.71
118.67
117.96
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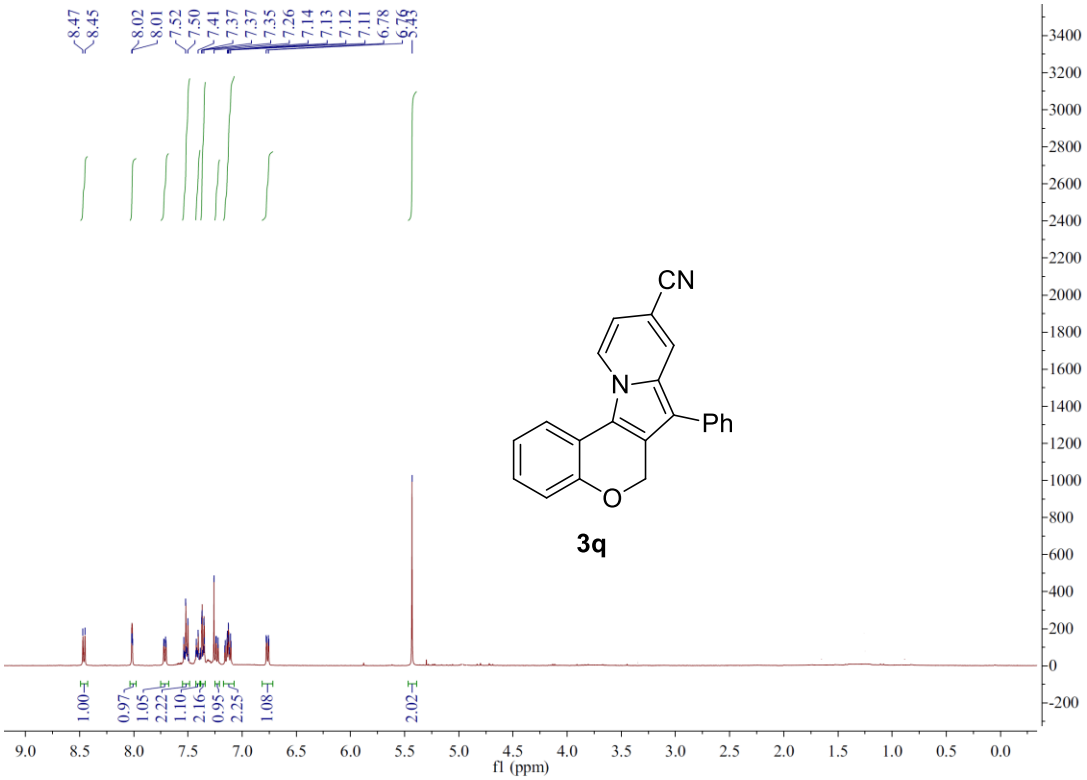
77.48
77.16
76.84
64.89
52.22
CO2Me
N
Ph
O
3p
f1 (ppm)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8.01
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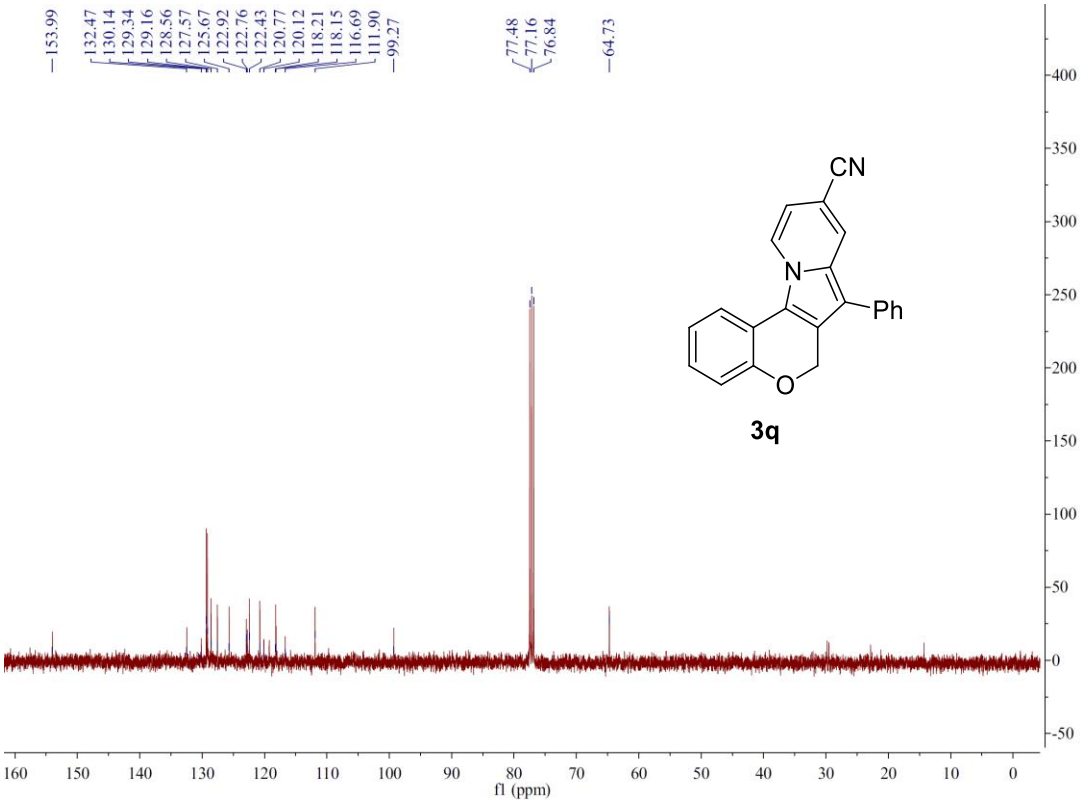
7.50
7.41
7.37
7.37
7.35
7.26
7.14
7.13
7.12
7.11
6.78
6.76
5.43
CN
N
Ph
O
3q
1.00
0.97
1.05
2.22
1.10
2.16
0.95
2.25
1.08
2.02
f1 (ppm)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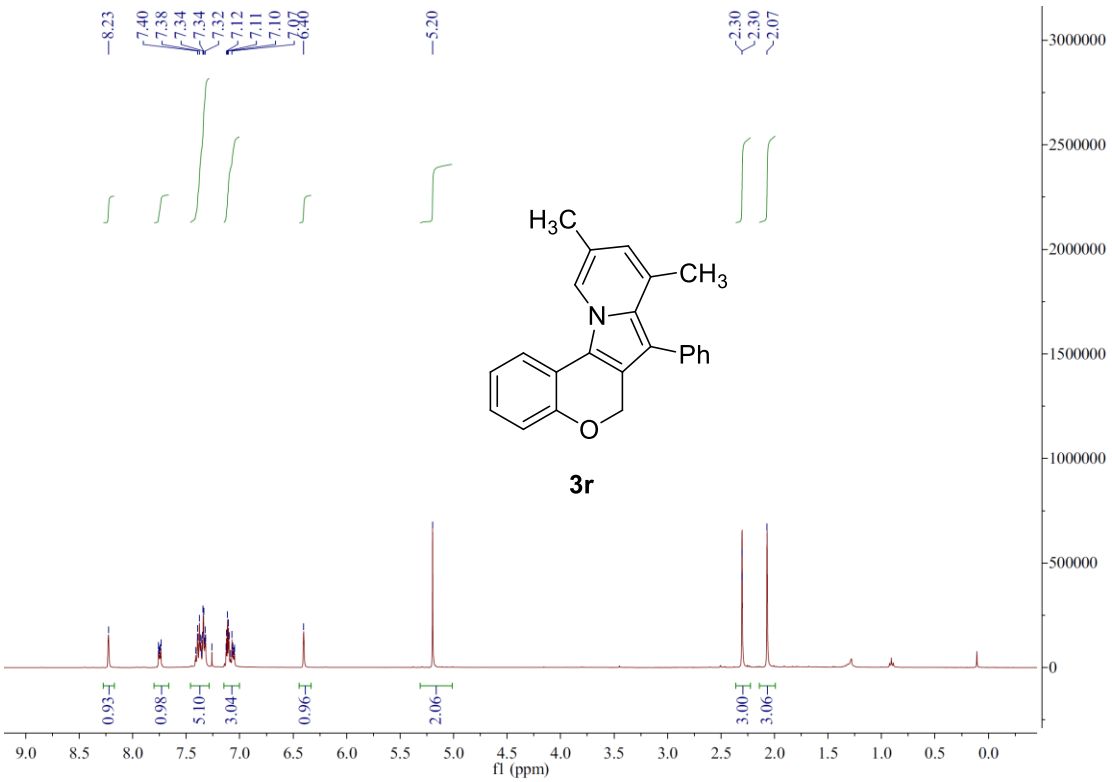
125.67
122.92
122.76
122.43
120.77
120.12
118.21
118.15
116.69
111.90
99.27
77.48
77.16
76.84
64.73
CN
N
Ph
O
3q
f1 (ppm)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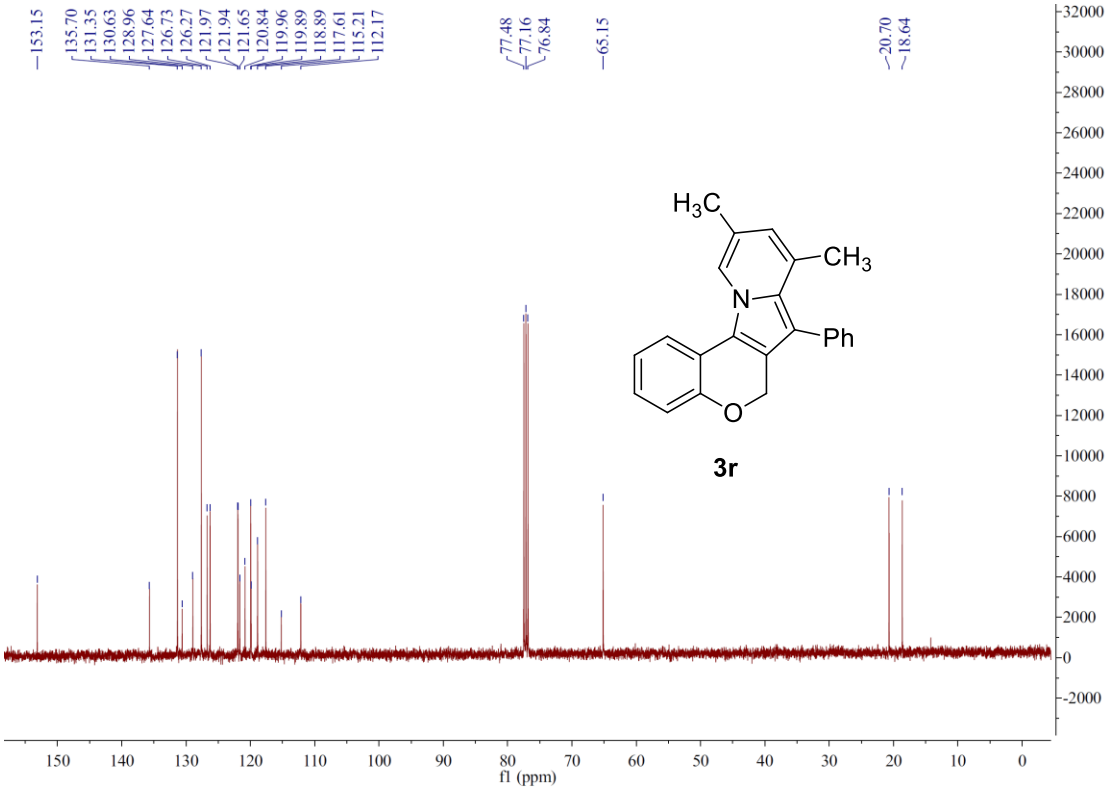
7.34
7.32
7.12
7.11
7.10
7.07
6.46
5.20
2.30
2.30
2.07
H3C
CH3
N
Ph
O
3r
0.93
0.98
5.10
3.04
0.96
2.06
3.00
3.06
fl (ppm)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118.89
117.61
115.21
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76.84
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18.64
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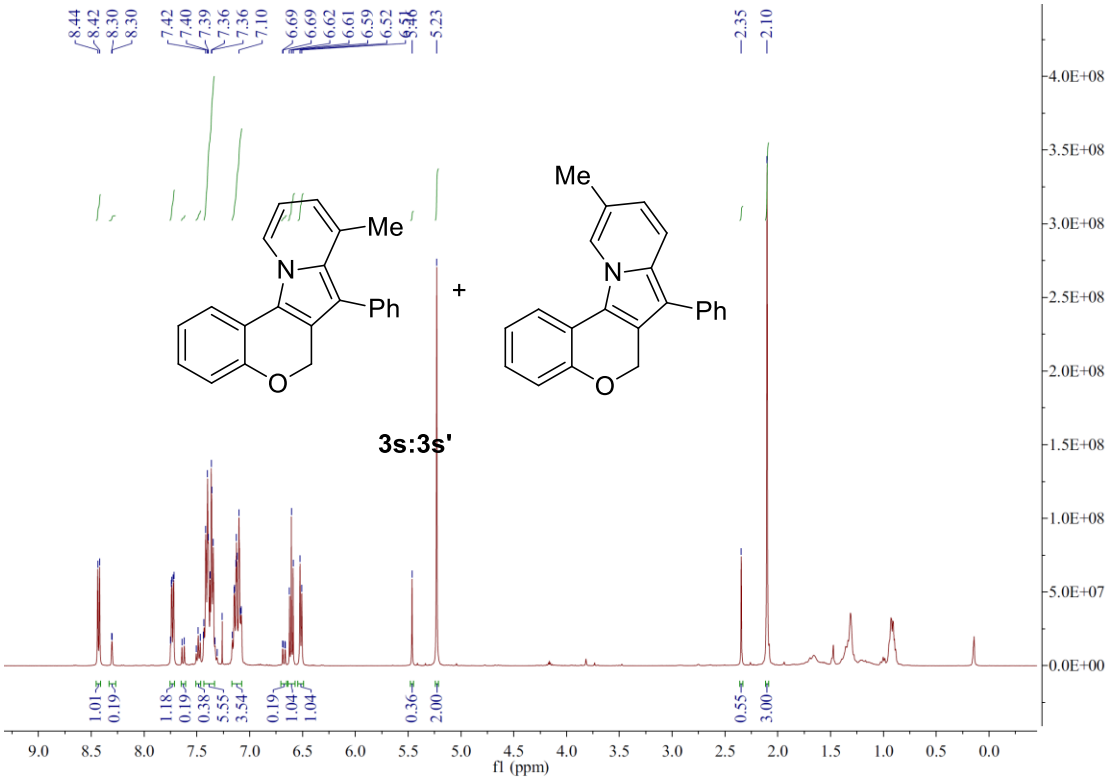
CH3
N
Ph
O
3r
fl (ppm)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7.10
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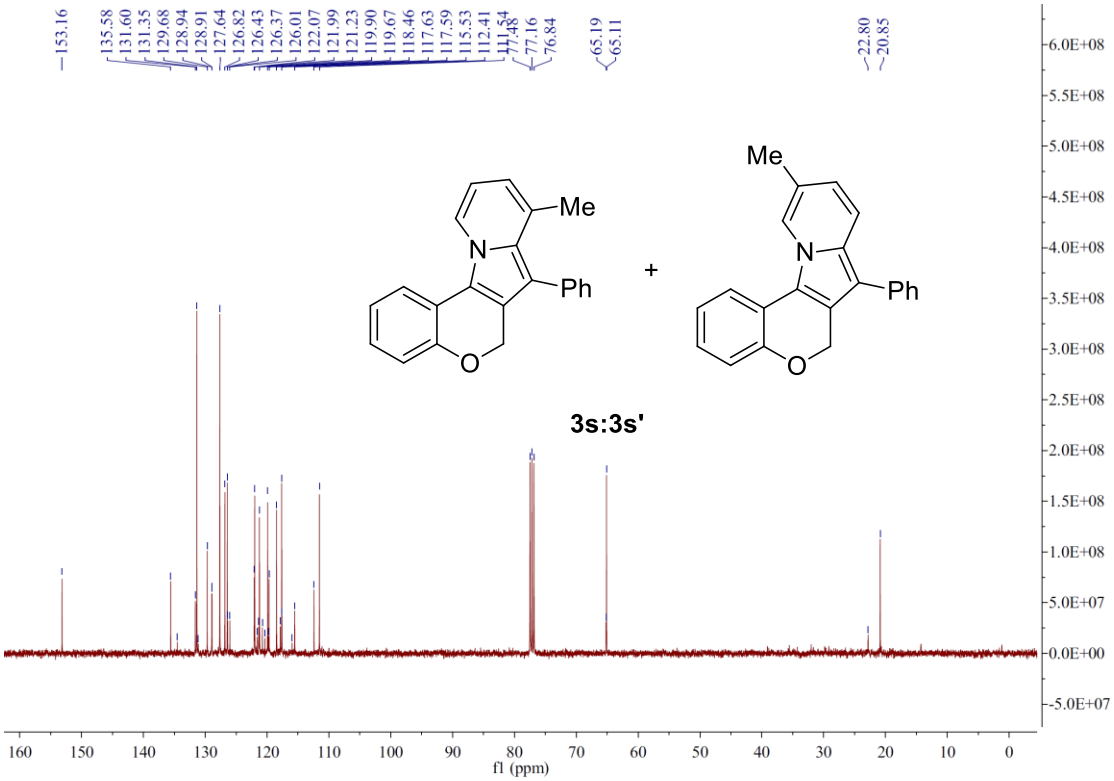
6.69
6.62
6.61
6.59
6.52
5.23
2.35
2.10
Me
N
Ph
O
+
Me
N
Ph
O
3s:3s'
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
1.01
0.19
1.18
0.19
0.38
5.55
3.54
0.19
1.04
1.04
0.36
2.00
0.55
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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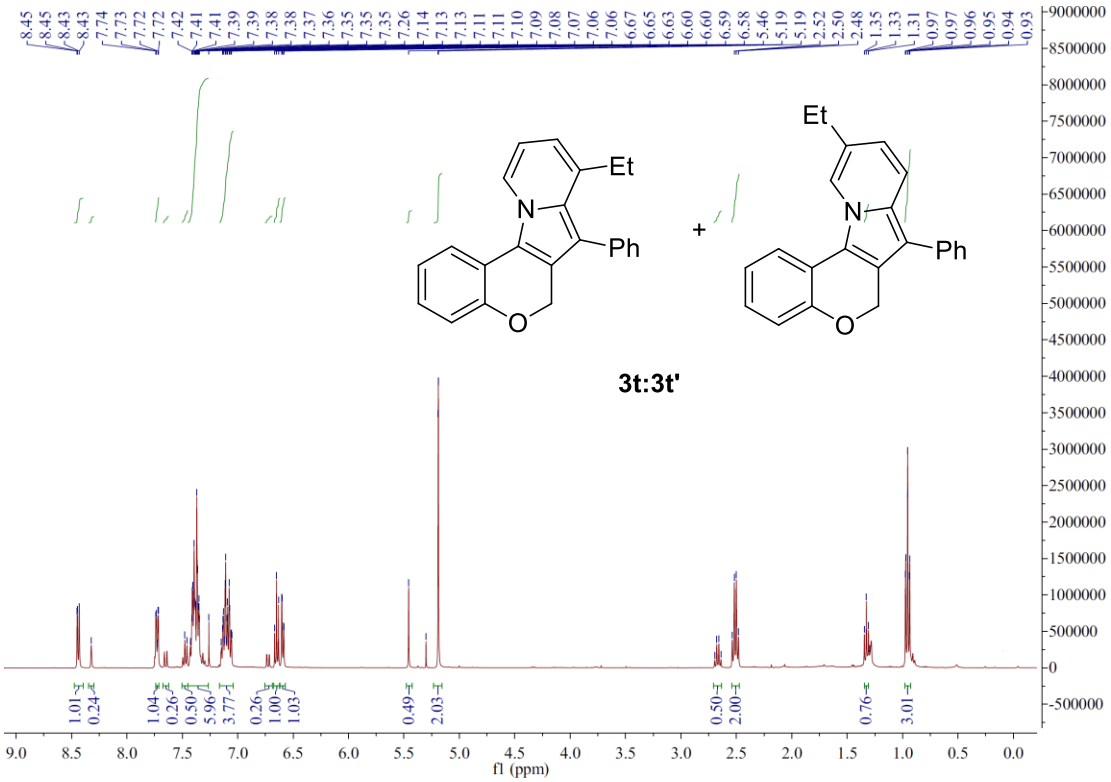
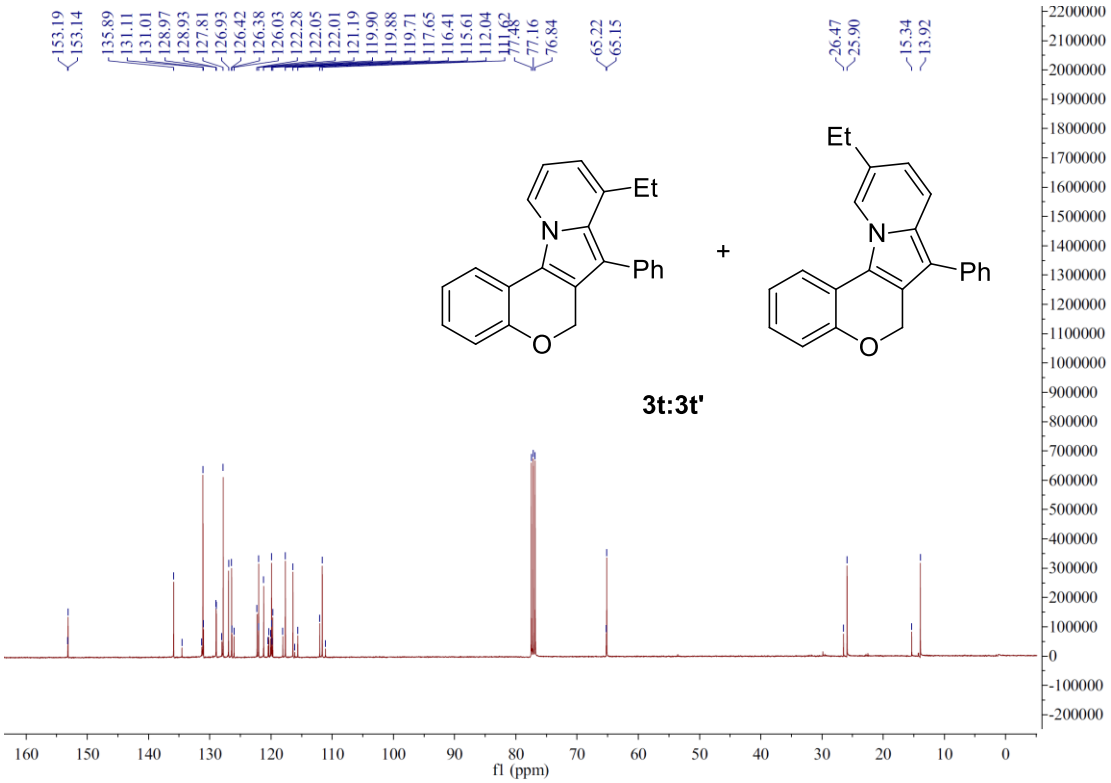
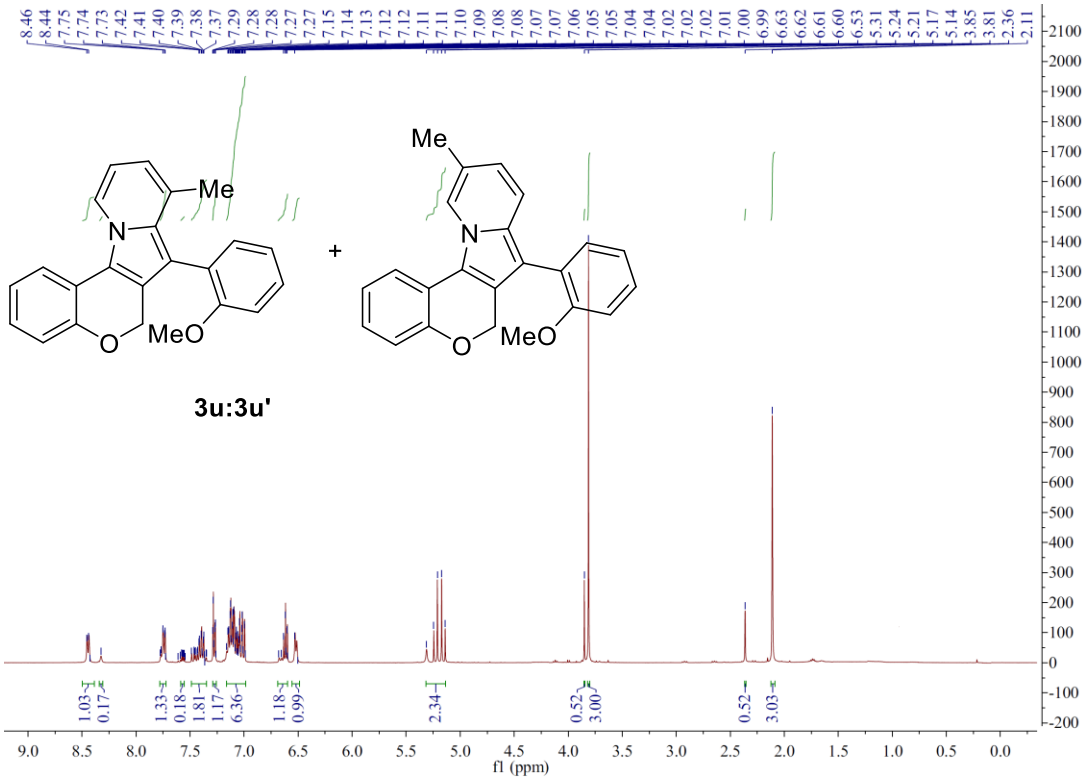
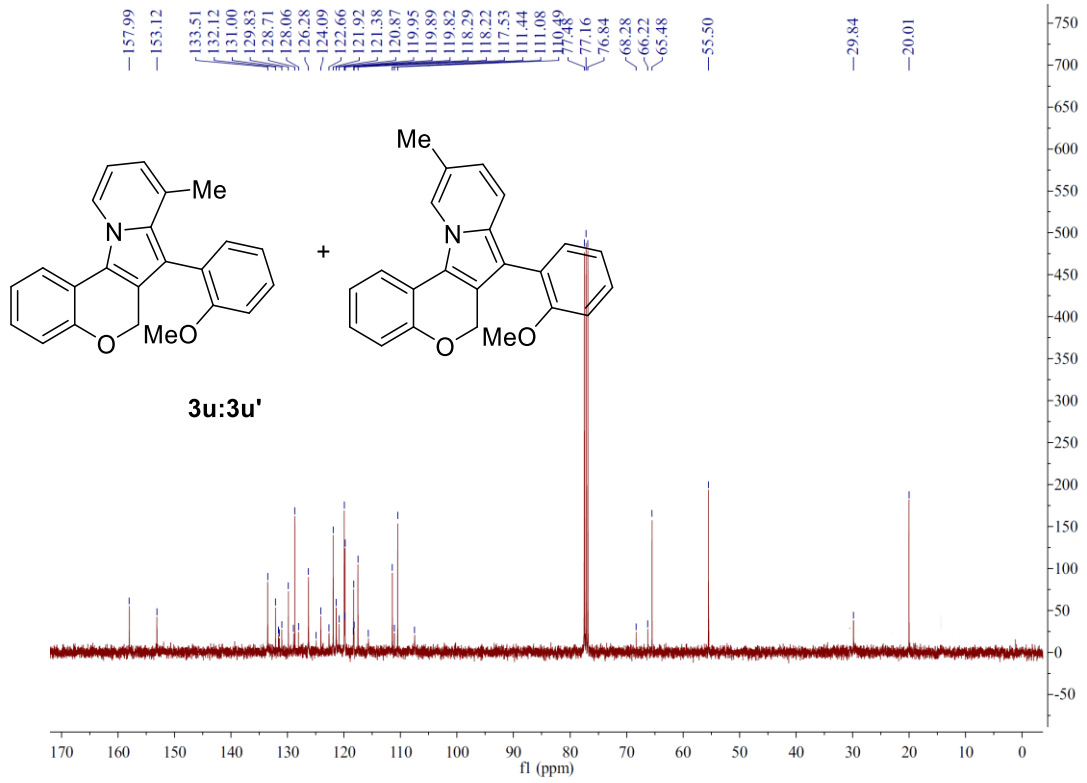
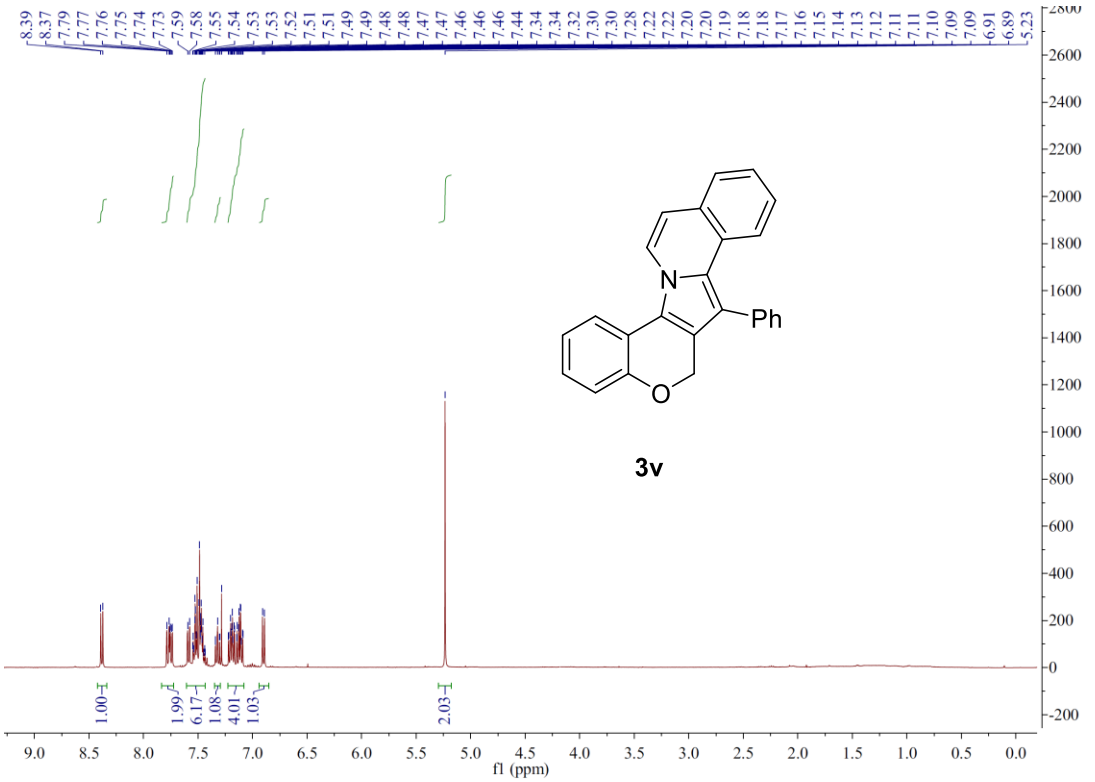
127.64
126.82
126.43
126.37
126.01
122.07
121.99
121.23
119.90
119.67
118.46
117.63
117.59
115.53
112.41
111.54
111.48
77.16
76.84
65.19
65.11
22.80
20.85
Me
N
Ph
O
+
Me
N
Ph
O
3s:3s'
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Et
N
Ph
O
+
3t:3t'
fl (ppm)


Et
N
Ph
O
+
3t:3t'
fl (ppm)


Me
N
MeO
O
+
Me
N
MeO
O
3u:3u'
fl (ppm)


Me
N
MeO
O
+
Me
N
MeO
O
3u:3u'
fl (ppm)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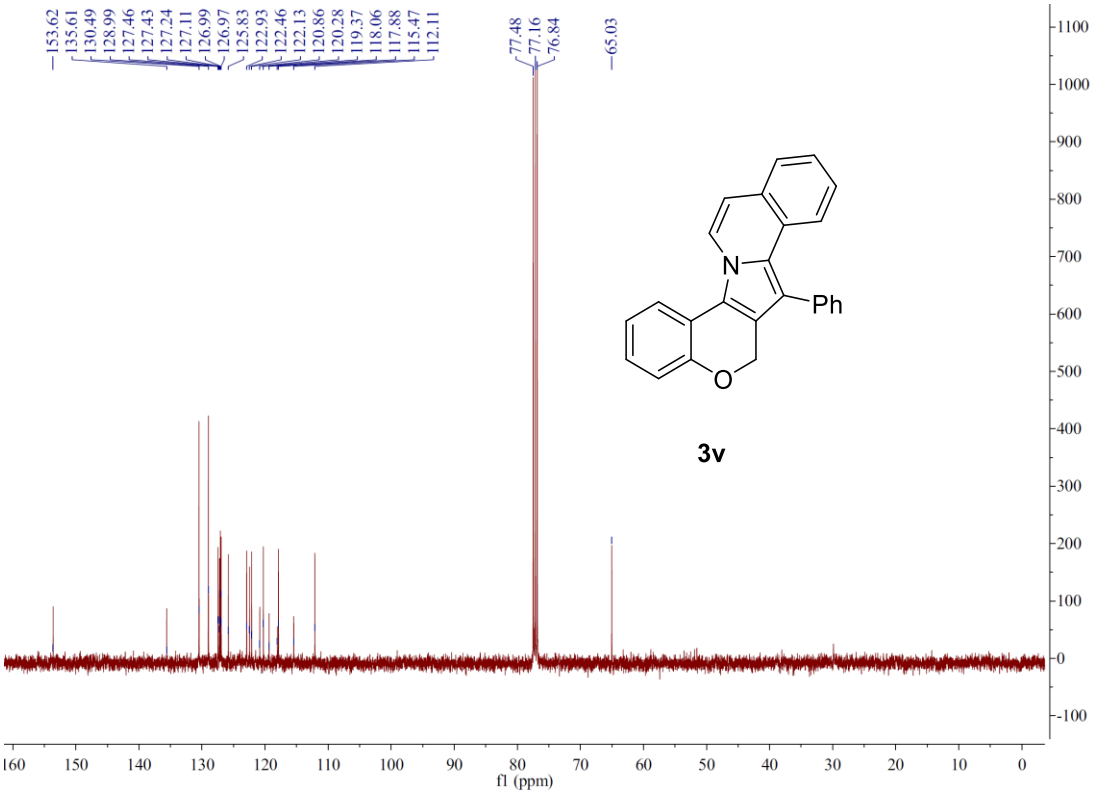
4.01
1.03
2.03
f1 (ppm)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65.03
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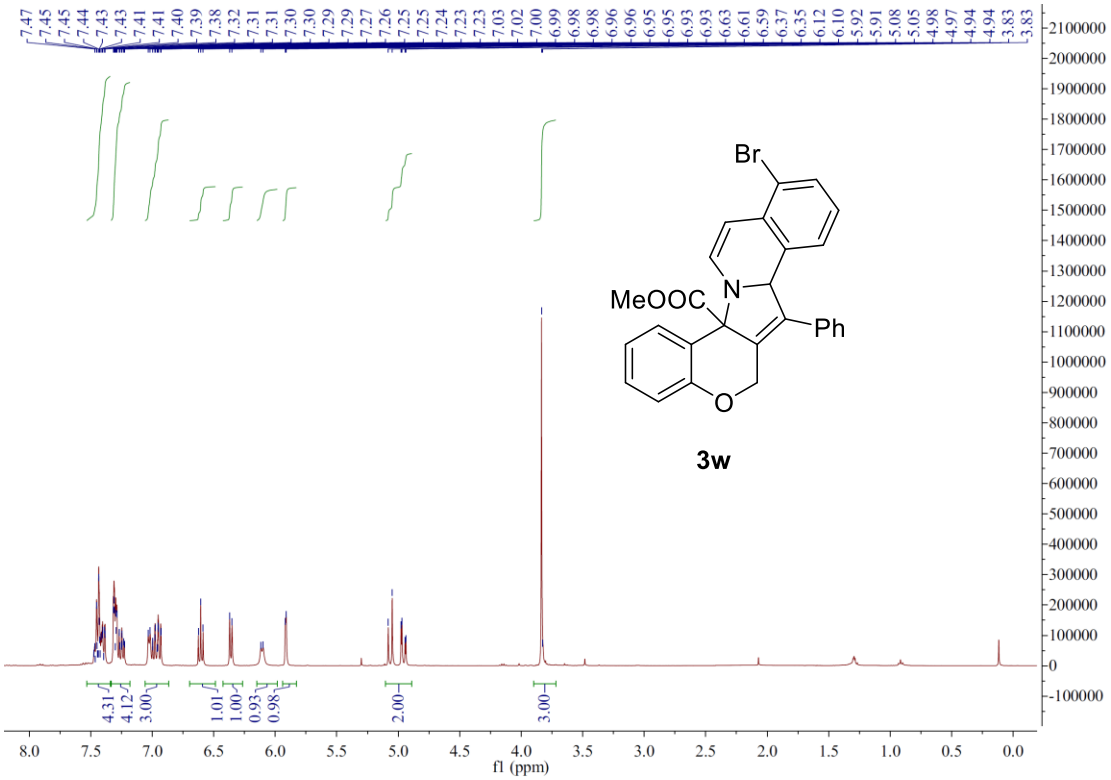
Ph
O
3v
f1 (ppm)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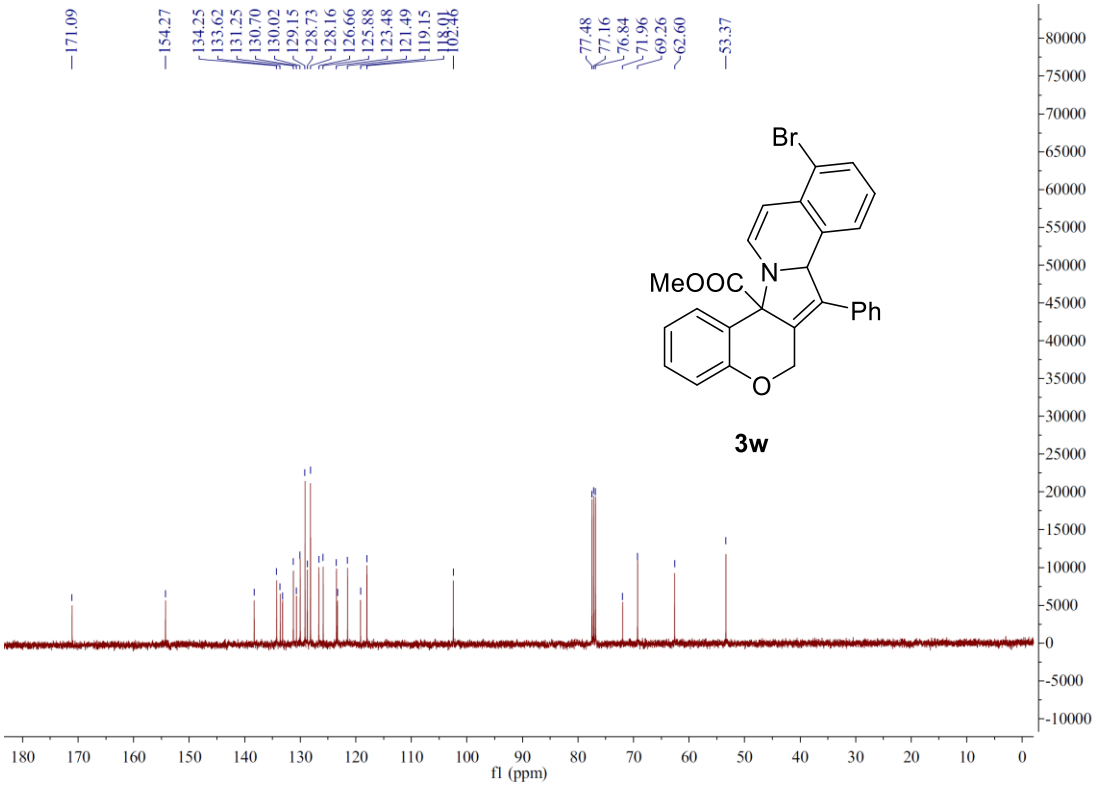
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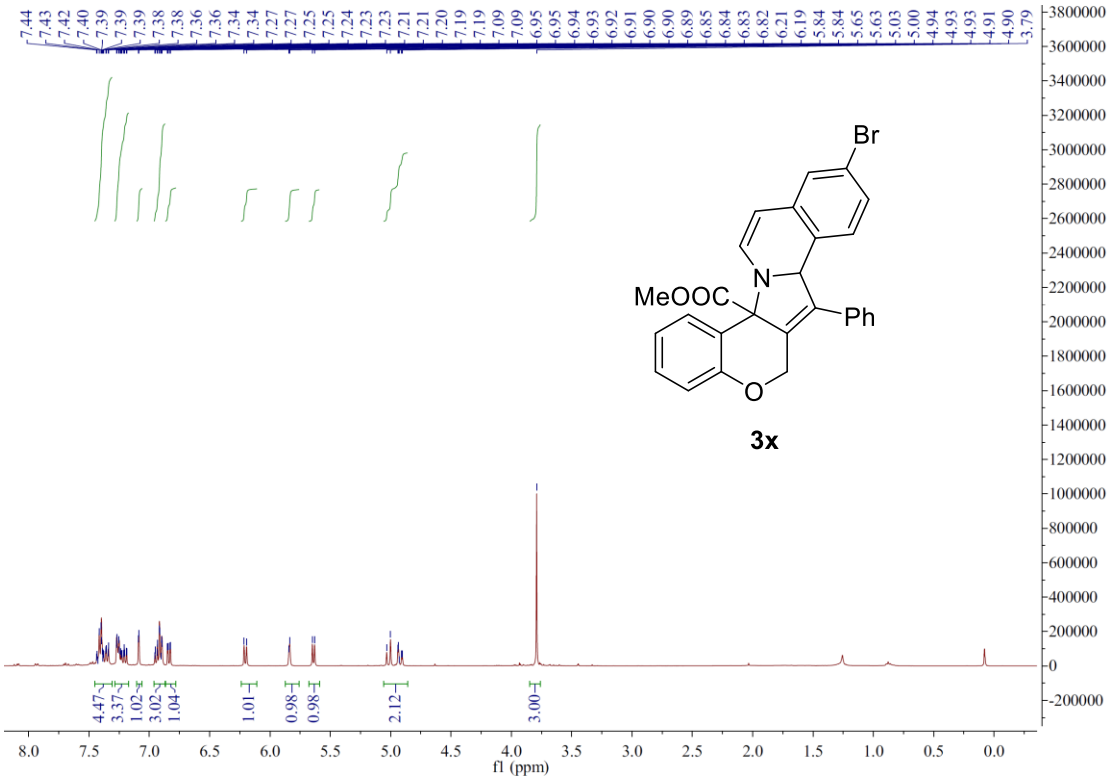
Ph
O
3w
fl (ppm)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Ph
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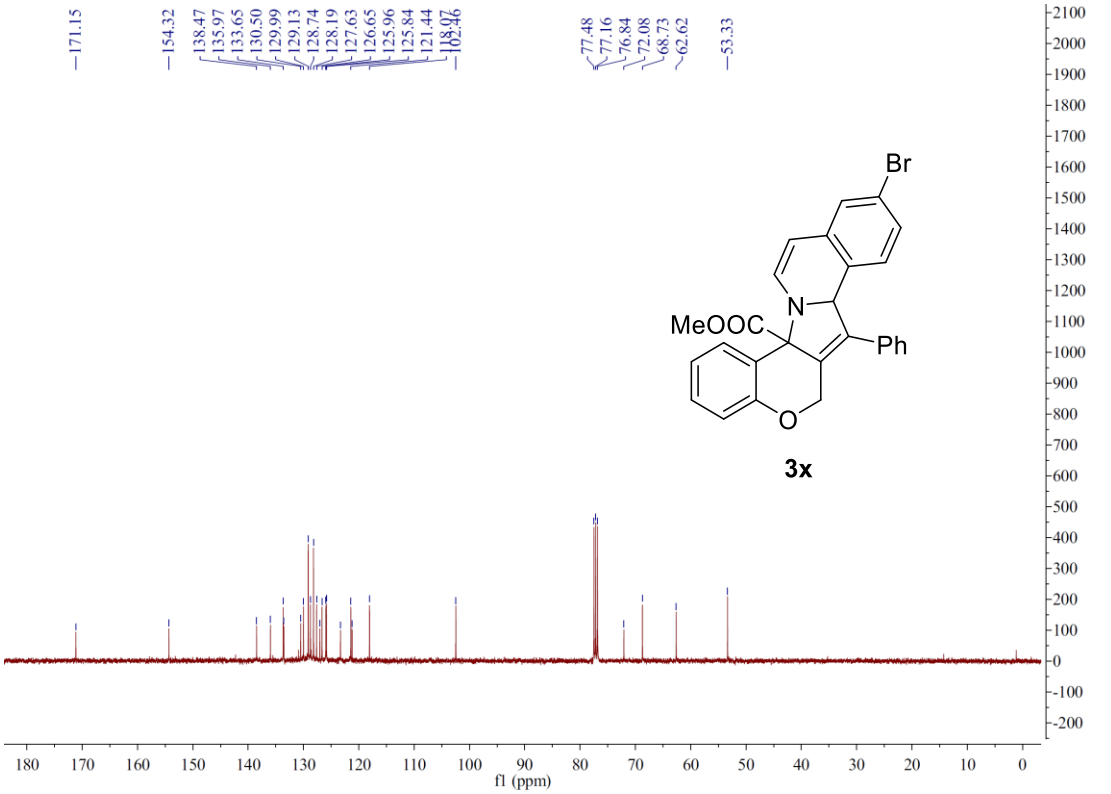
3x
fl (ppm)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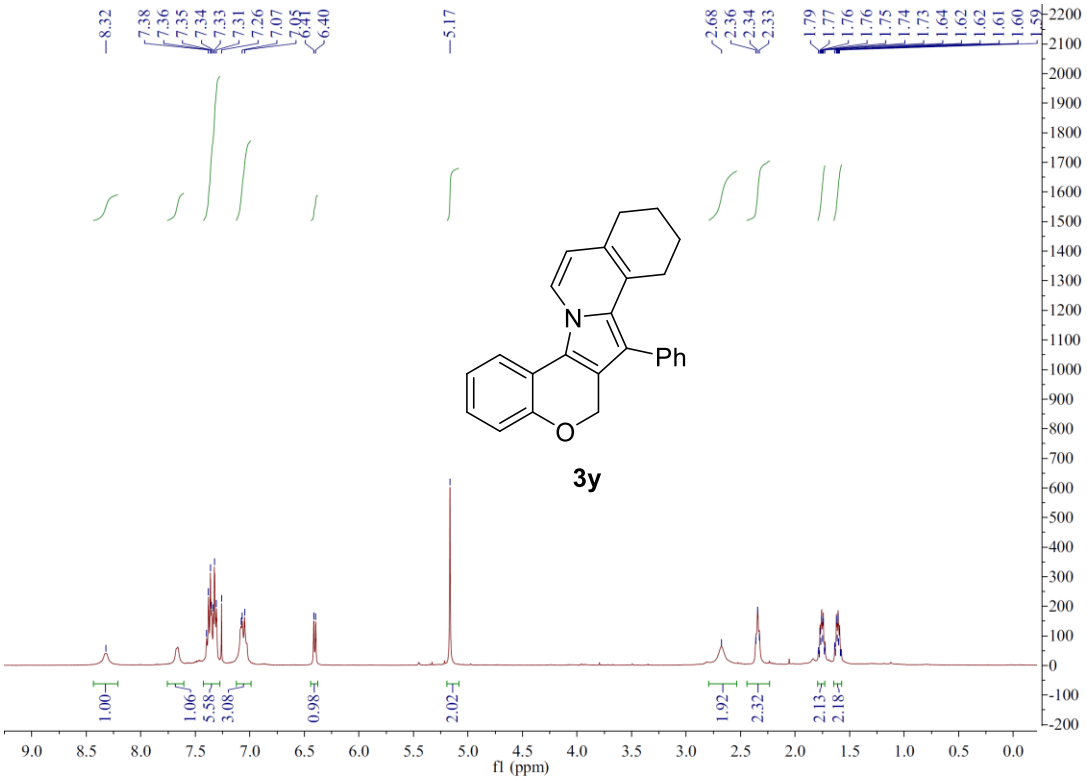
MeOOC
Ph
O
3x
fl (ppm)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2.34
2.33
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1.74
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1.64
1.62
1.62
1.61
1.60
1.59
N
Ph
O
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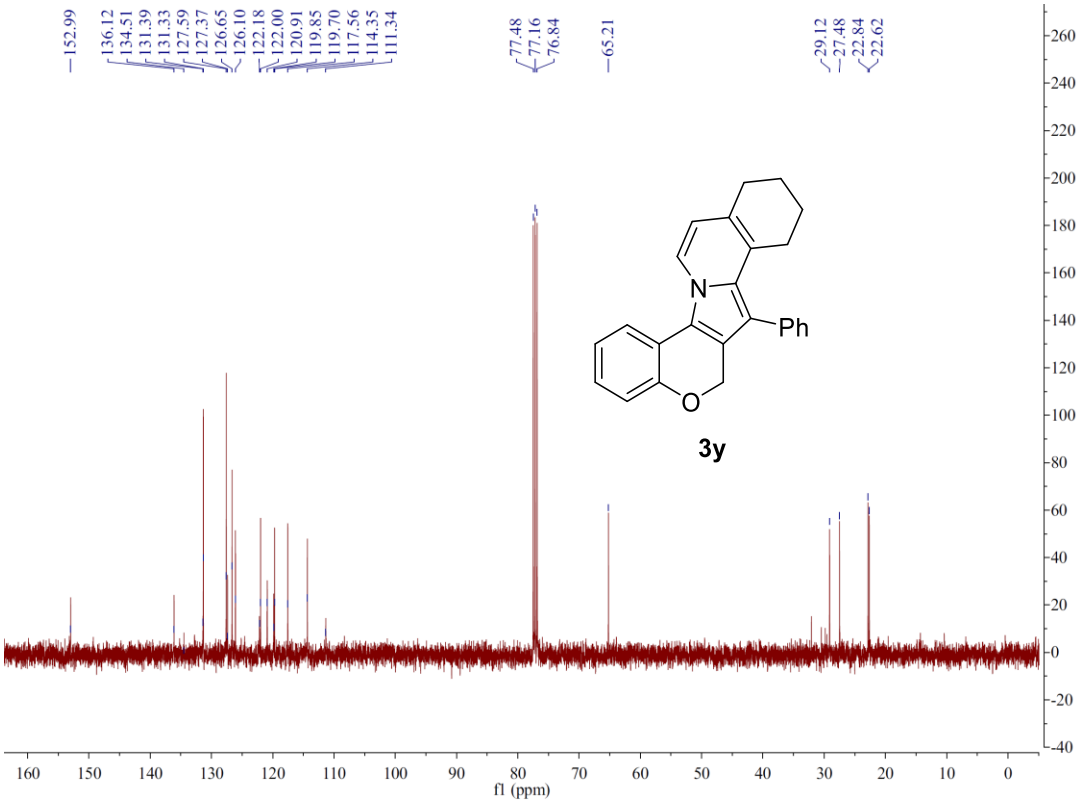
1.92
2.32
2.13
2.18
f1 (ppm)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22.62
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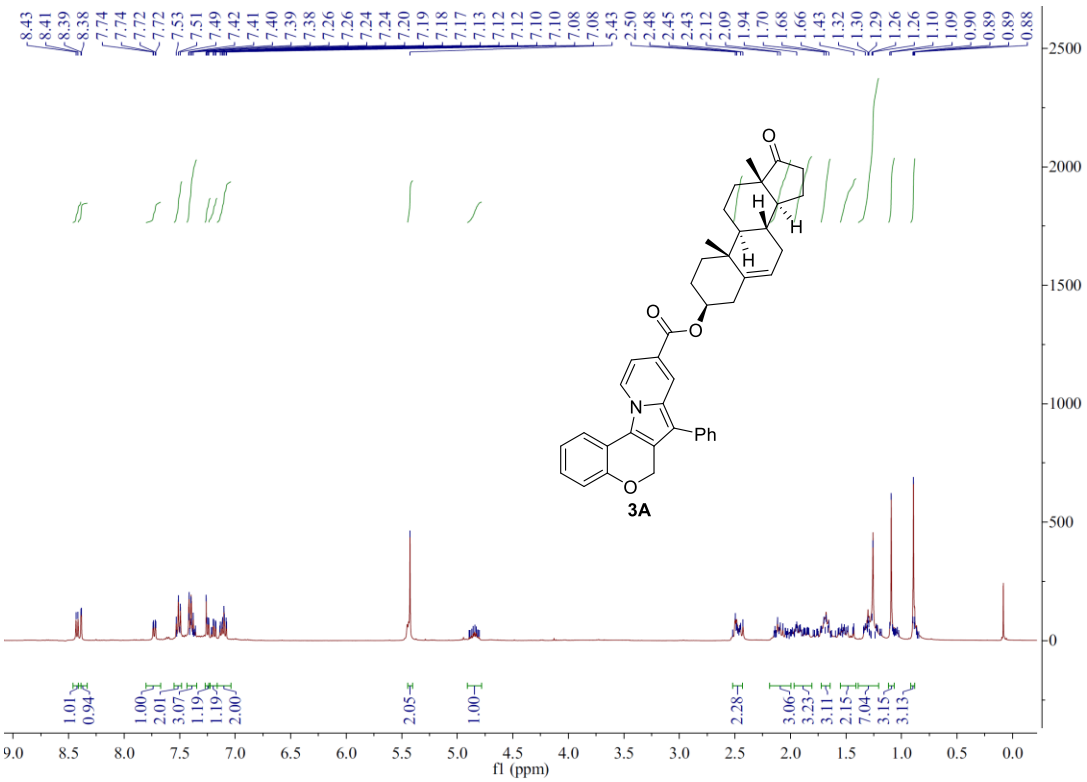
Ph
O
3y
f1 (ppm)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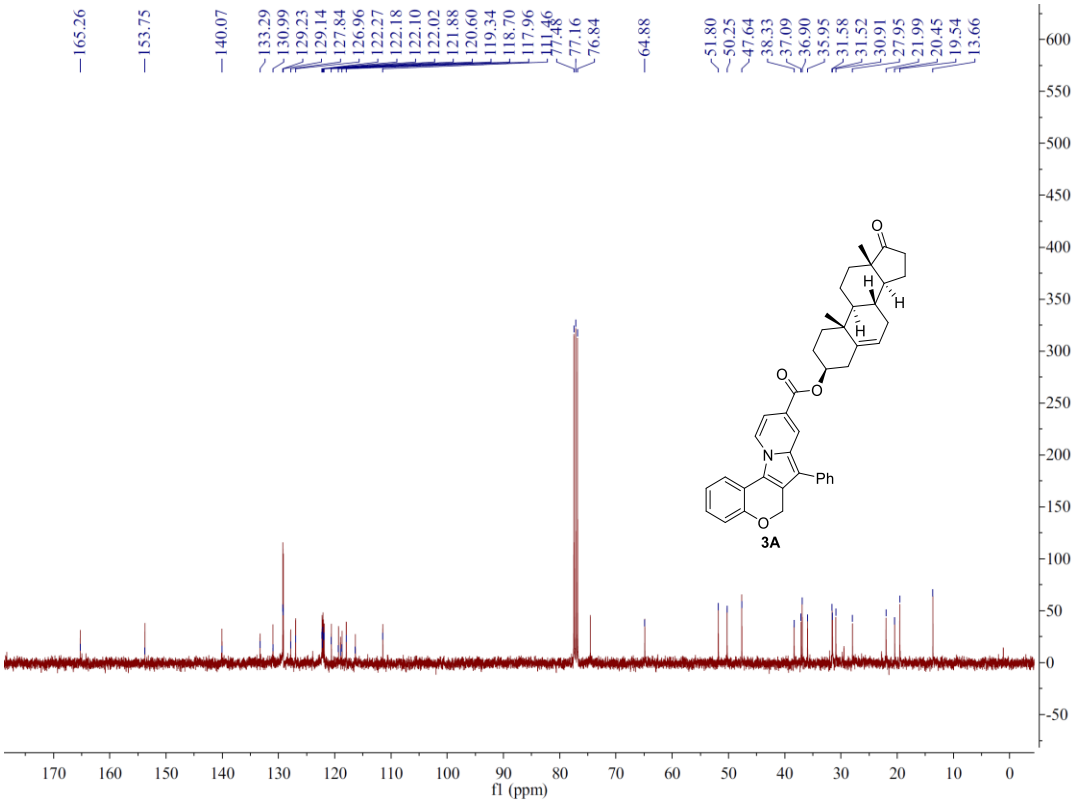
O
H
H
H
O
O
N
Ph
O
3A
1.01 0.94 1.00 2.01 3.07 1.19 1.19 2.00 2.05 1.00 2.28 3.06 3.23 3.11 2.15 7.04 3.15 3.13
fl (ppm)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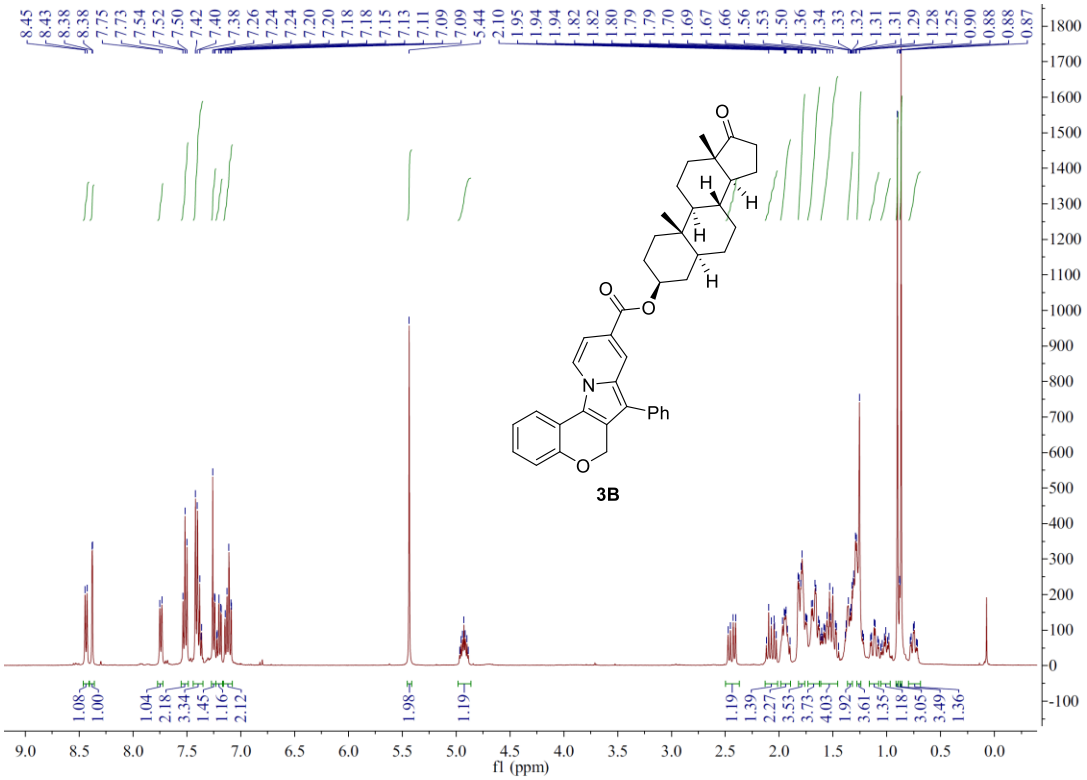
O
H
H
H
O
O
N
Ph
O
3A
fl (ppm)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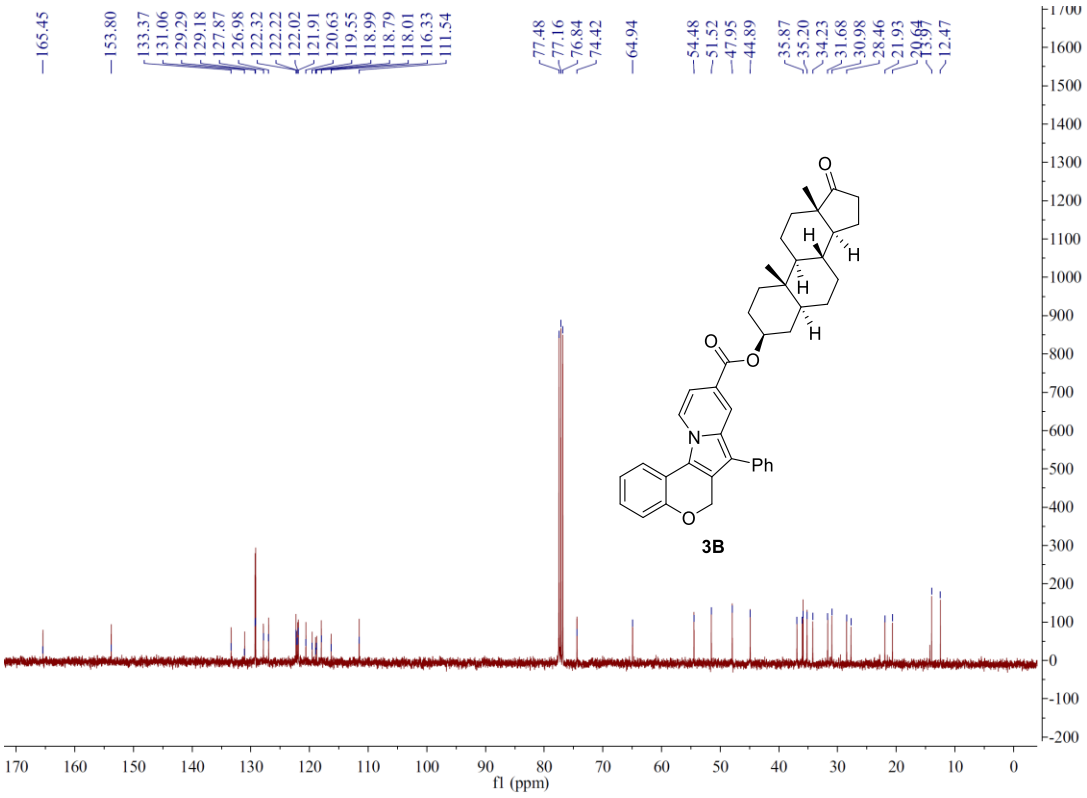
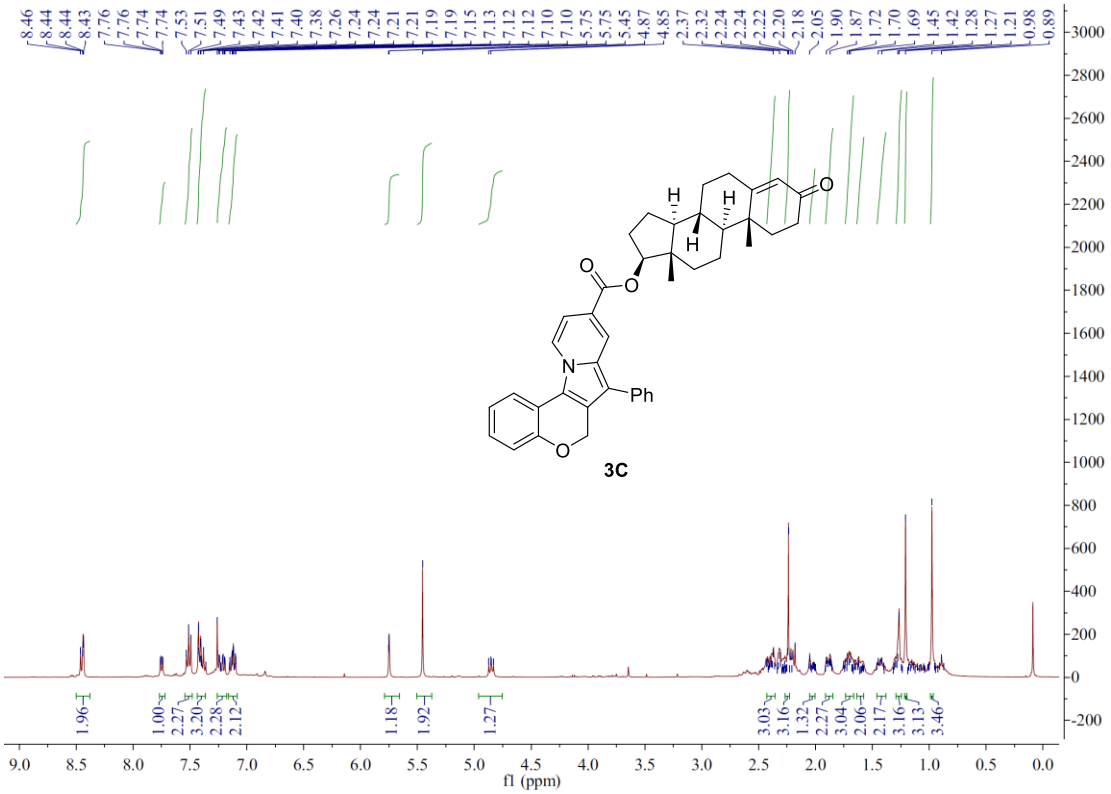
1.08 1.00 1.04 2.18 3.34 1.45 1.16 2.12 1.98 1.19 1.19 1.39 2.27 3.53 3.73 4.03 1.92 3.61 1.35 1.18 3.05 3.49 1.36
f1 (ppm)
3B


165.45 153.80 133.37 131.06 129.29 129.18 127.87 126.98 122.32 122.22 122.02 121.91 120.63 119.55 118.99 118.79 118.01 116.33 111.54 77.48 77.16 76.84 74.42 64.94 54.48 51.52 47.95 44.89 35.87 35.20 34.23 31.68 30.98 28.46 21.93 20.64 13.97 12.47
f1 (ppm)
3B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7.12
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7.10
7.10
5.75
5.75
5.45
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2.37
2.32
2.24
2.24
2.22
2.20
2.18
2.05
1.90
1.87
1.72
1.70
1.69
1.45
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1.28
1.27
1.21
0.98
0.89
H
H
H
O
O
O
N
Ph
3C
1.96
1.00
2.27
3.20
2.28
2.12
1.18
1.92
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3.03
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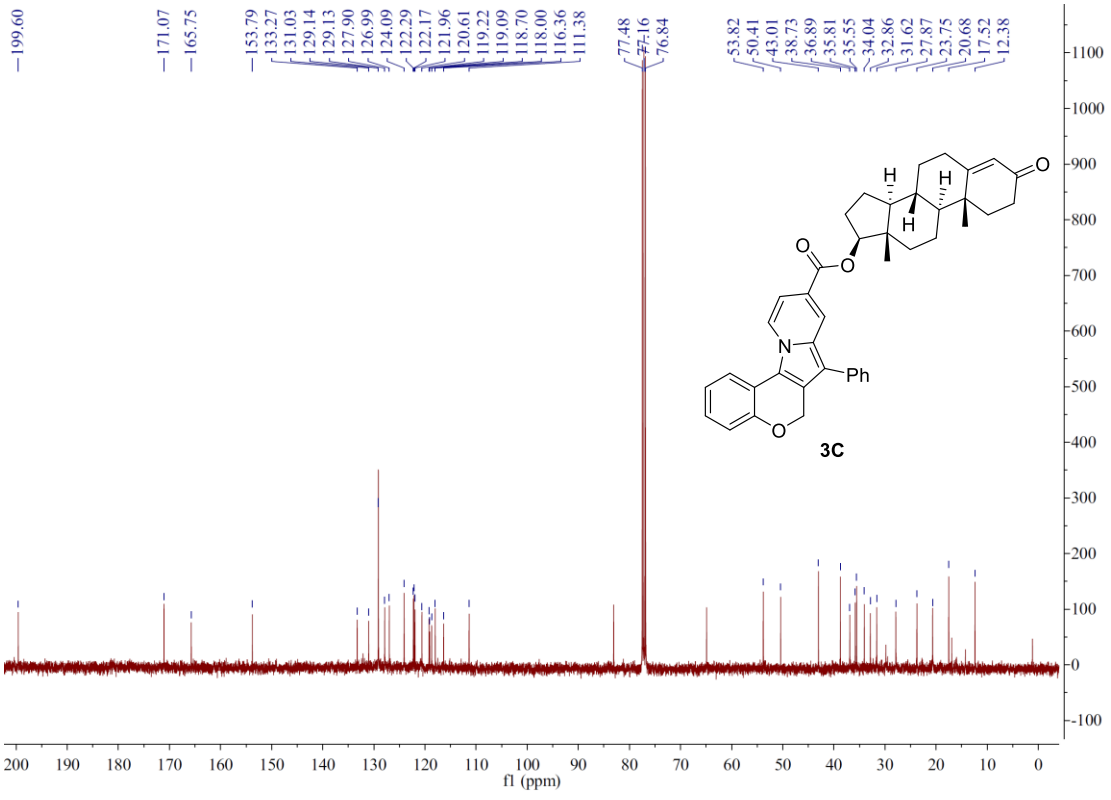
3.04
2.06
2.17
3.16
3.13
3.46
f1 (ppm)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119.22
119.09
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77.16
76.84
53.82
50.41
43.01
38.73
36.89
35.81
35.55
34.04
32.86
31.62
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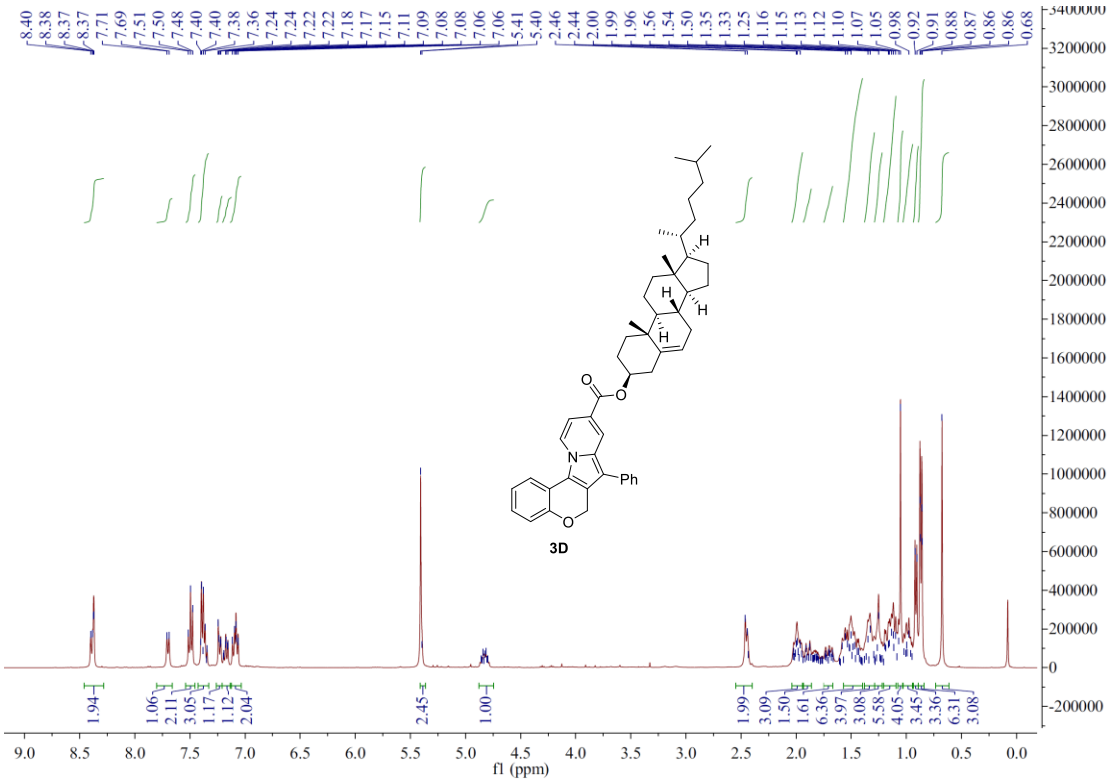
20.68
17.52
12.38
H
H
H
O
O
O
N
Ph
3C
f1 (ppm)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1.25
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1.12
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0.86
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3D
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2.04
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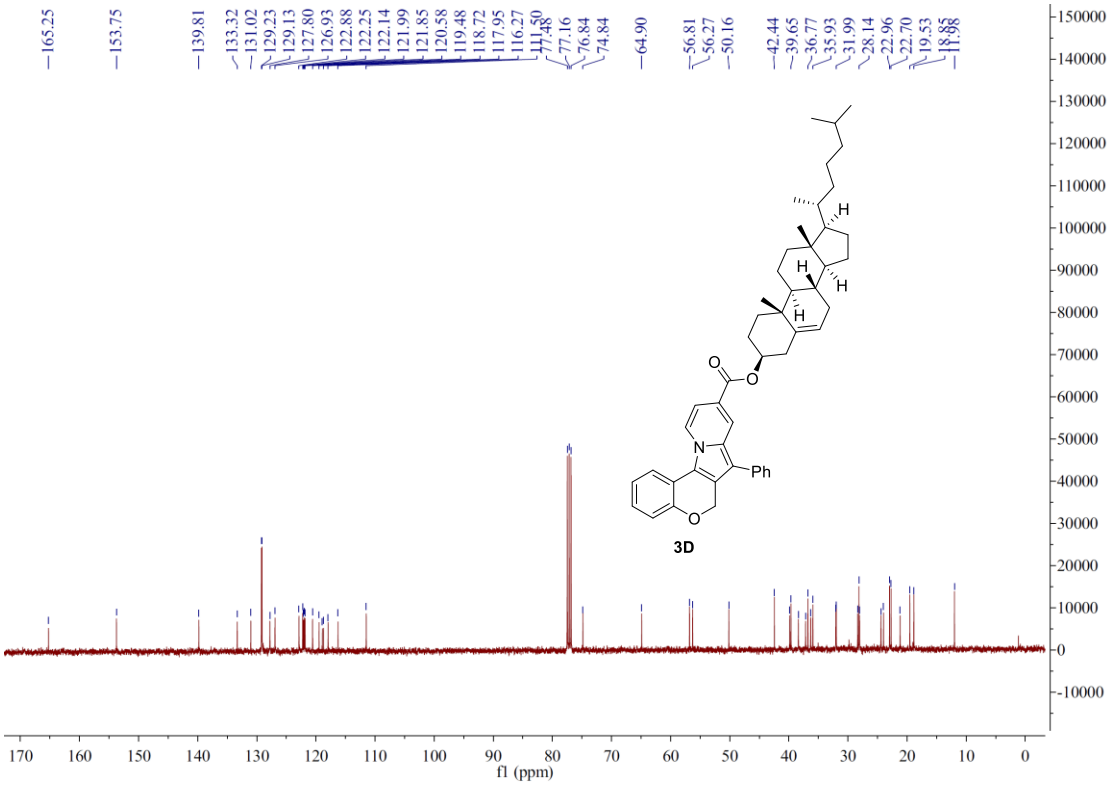
3.08
f1 (ppm)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120.58
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77.16
76.84
74.84
64.90
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56.27
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28.14
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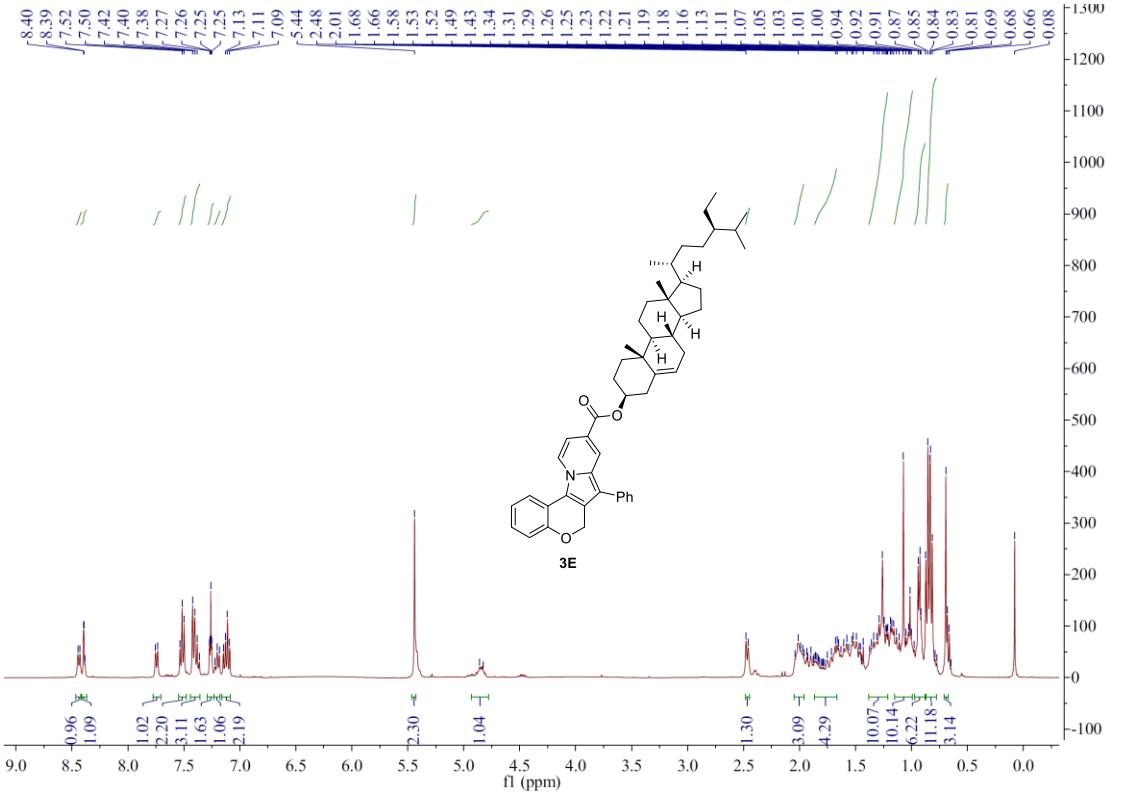
3D
f1 (ppm)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1.29
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1.25
1.23
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1.00
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0.08
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1.09
1.02
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3.11
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11.18
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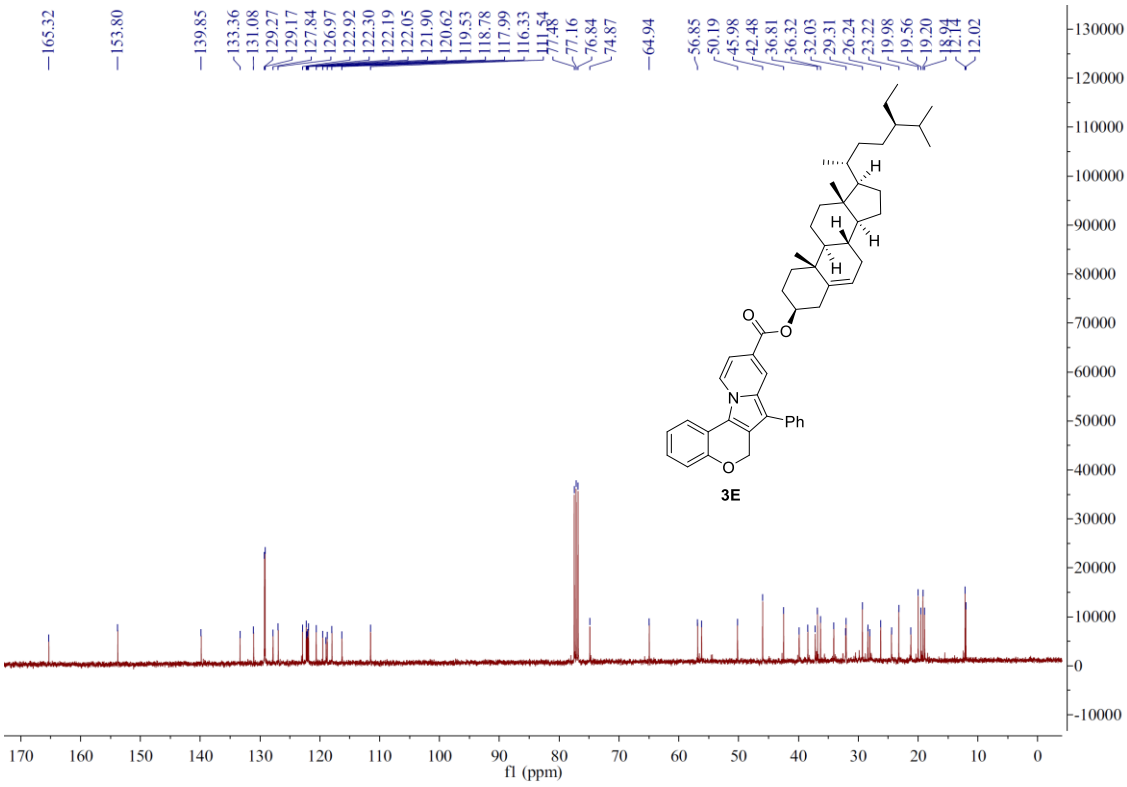
3E
Ph
f1 (ppm)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122.19
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120.62
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74.87
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56.85
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45.98
42.48
36.81
36.32
32.03
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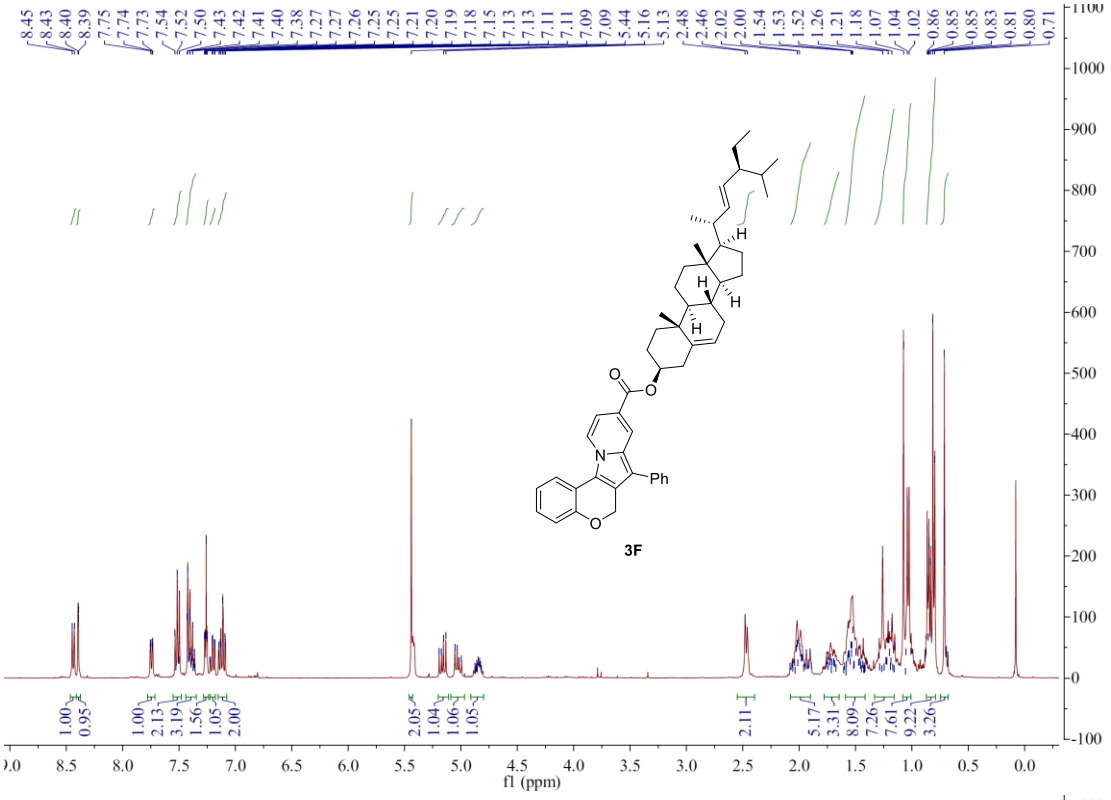
18.94
12.14
12.02
3E
Ph
f1 (ppm)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7.11
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7.09
7.09
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5.13
2.48
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2.00
2.05
1.04
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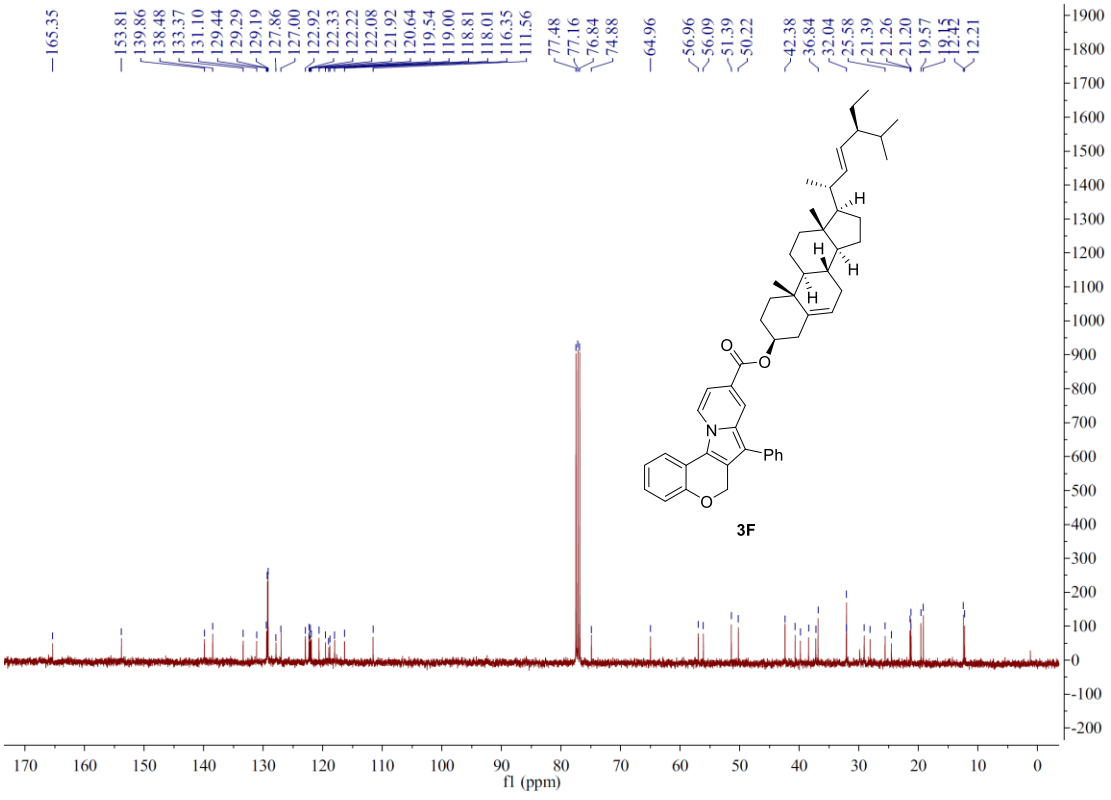
f1 (ppm)
3F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119.00
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118.01
116.35
111.56
77.48
77.16
76.84
74.88
64.96
56.96
56.09
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50.22
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21.26
21.20
19.57
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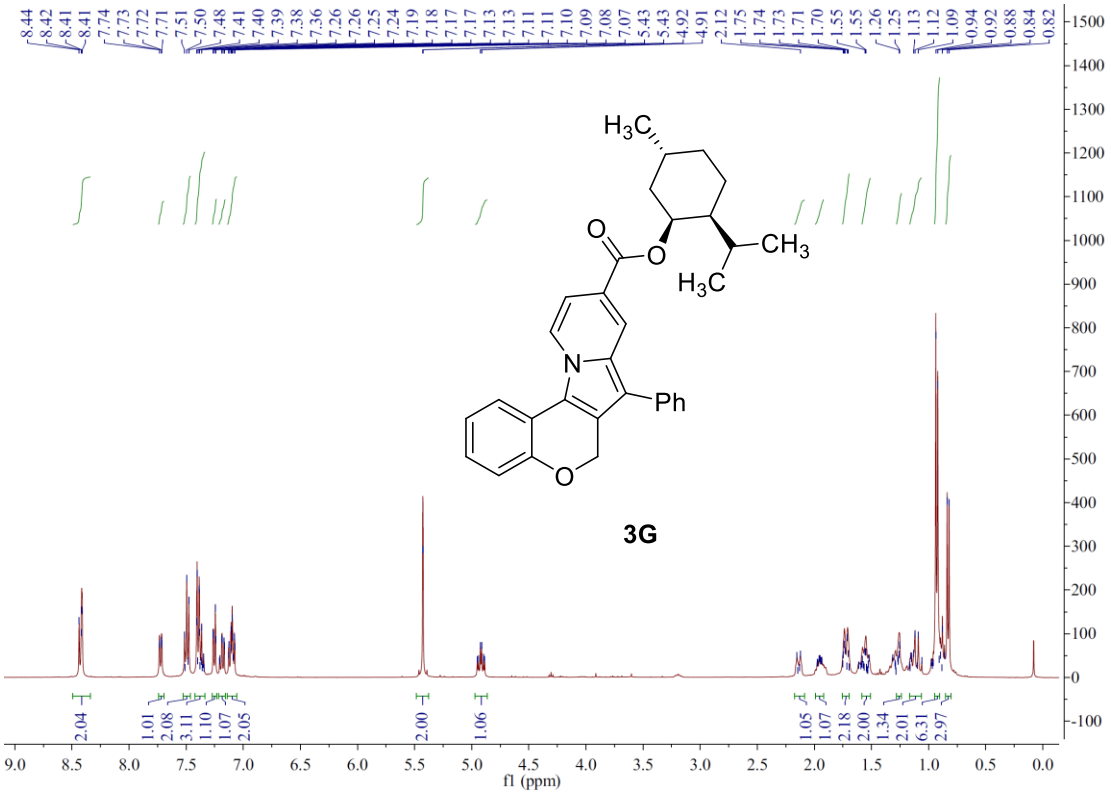
f1 (ppm)
3F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7.08
7.07
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O
O
CH3
H3C
N
Ph
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3G
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2.08
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1.07
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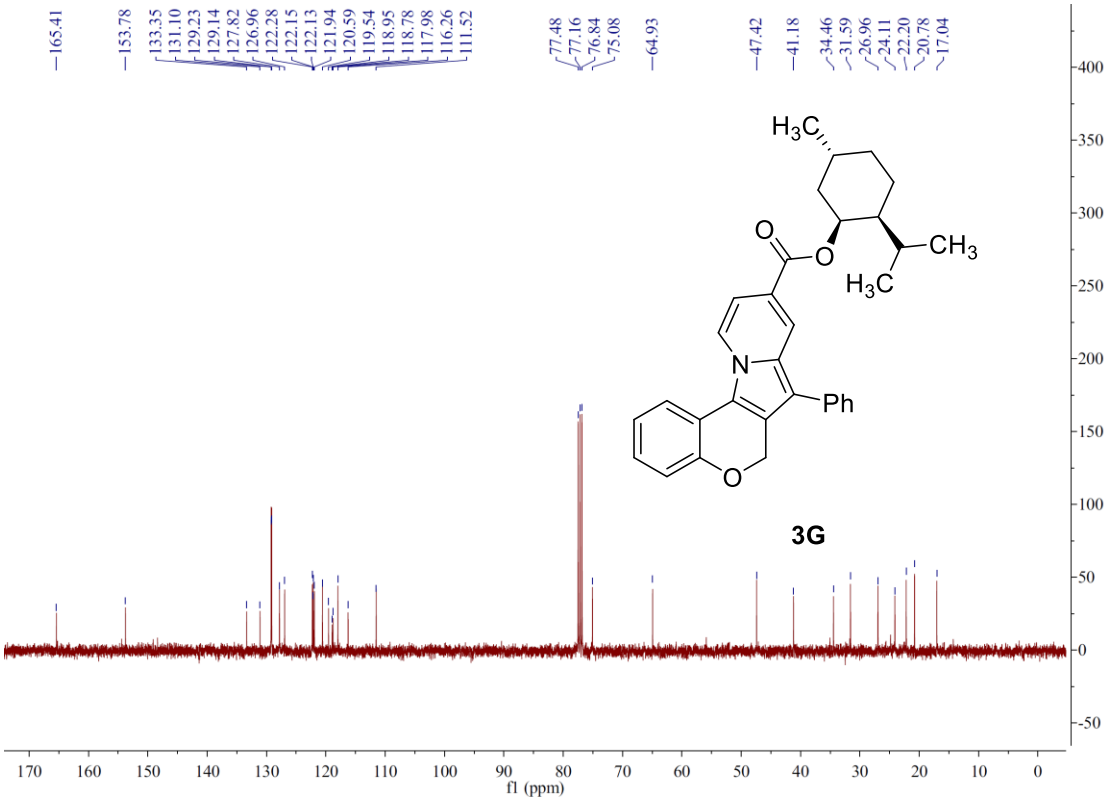
fl (ppm)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118.95
118.78
117.98
116.26
111.52
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77.16
76.84
75.08
64.93
47.42
41.18
34.46
31.59
26.96
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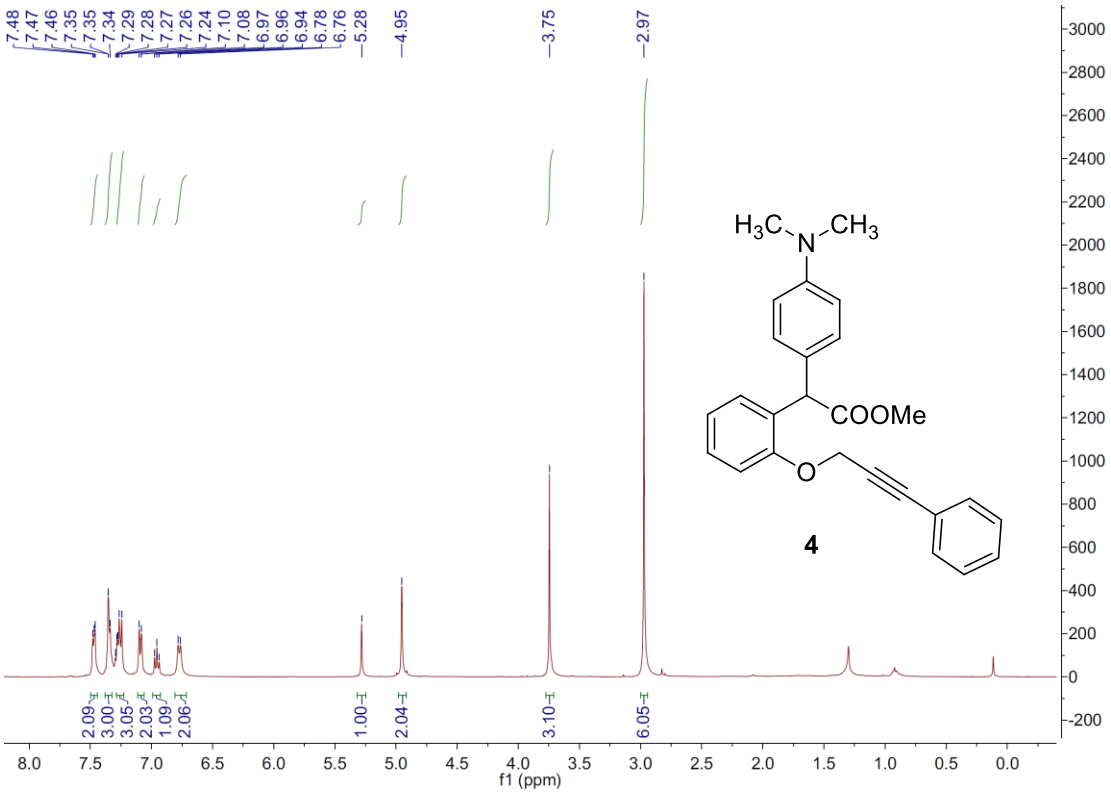
20.78
17.04
H3C
O
O
CH3
H3C
N
Ph
O
3G
fl (ppm)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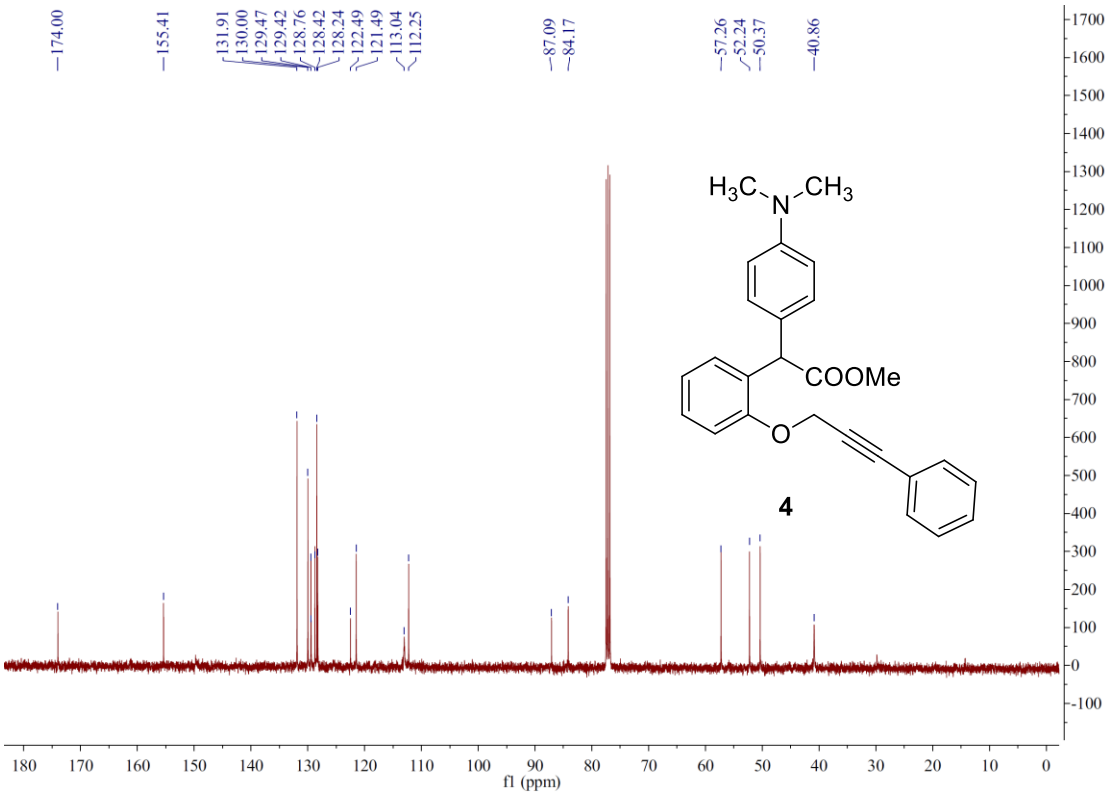
6.97
6.96
6.94
6.78
6.76
5.28
4.95
3.75
2.97
2.09
3.00
3.05
2.03
1.09
2.06
1.00
2.04
3.10
6.05
f1 (ppm)
H3C
N
CH3
COOMe
O
4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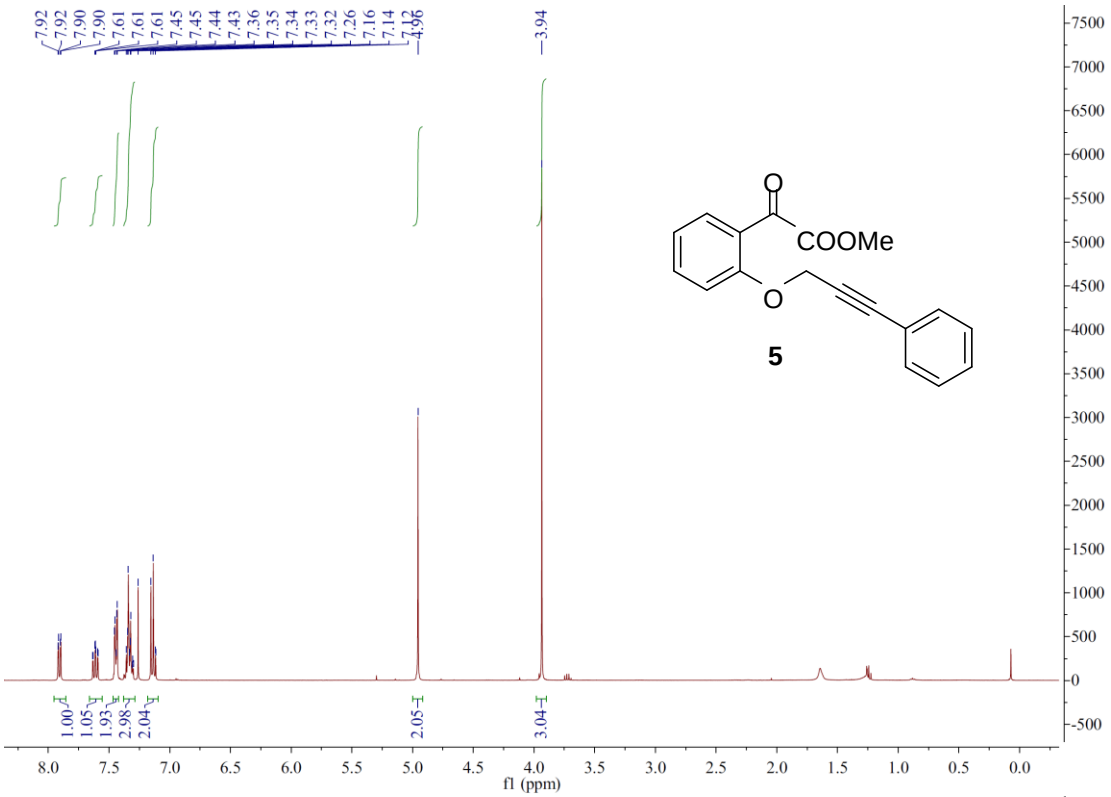
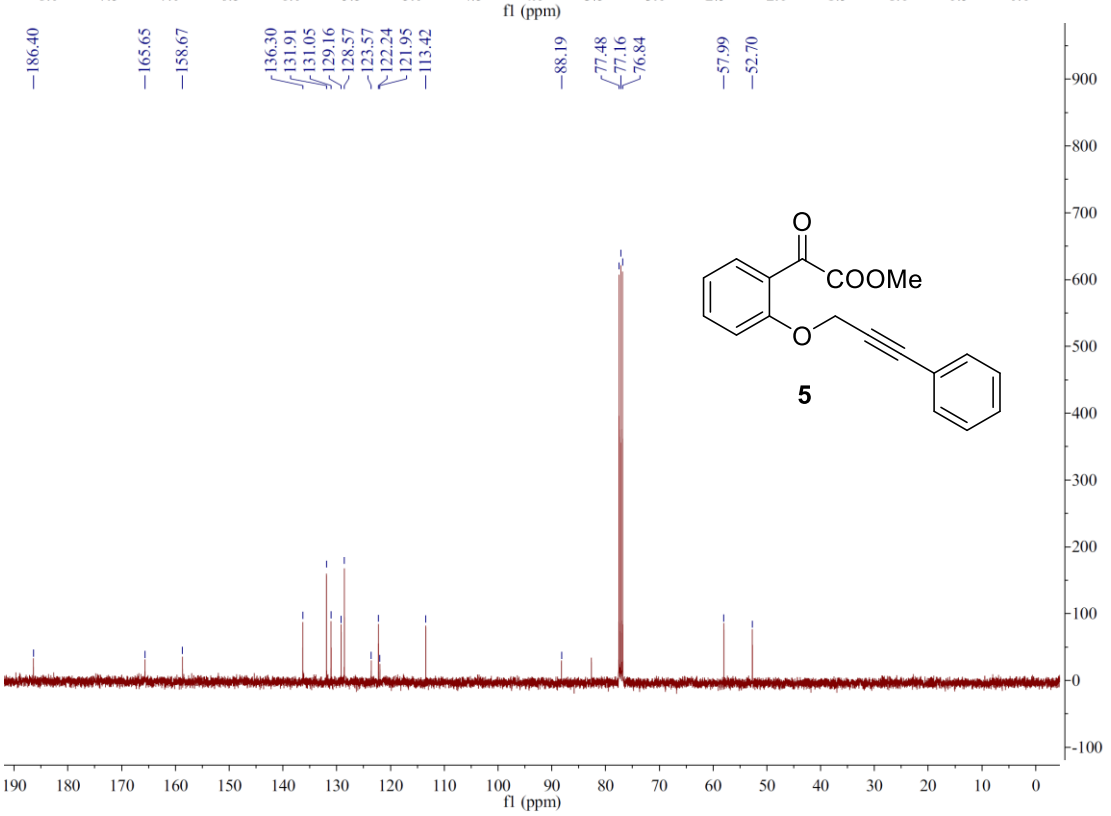
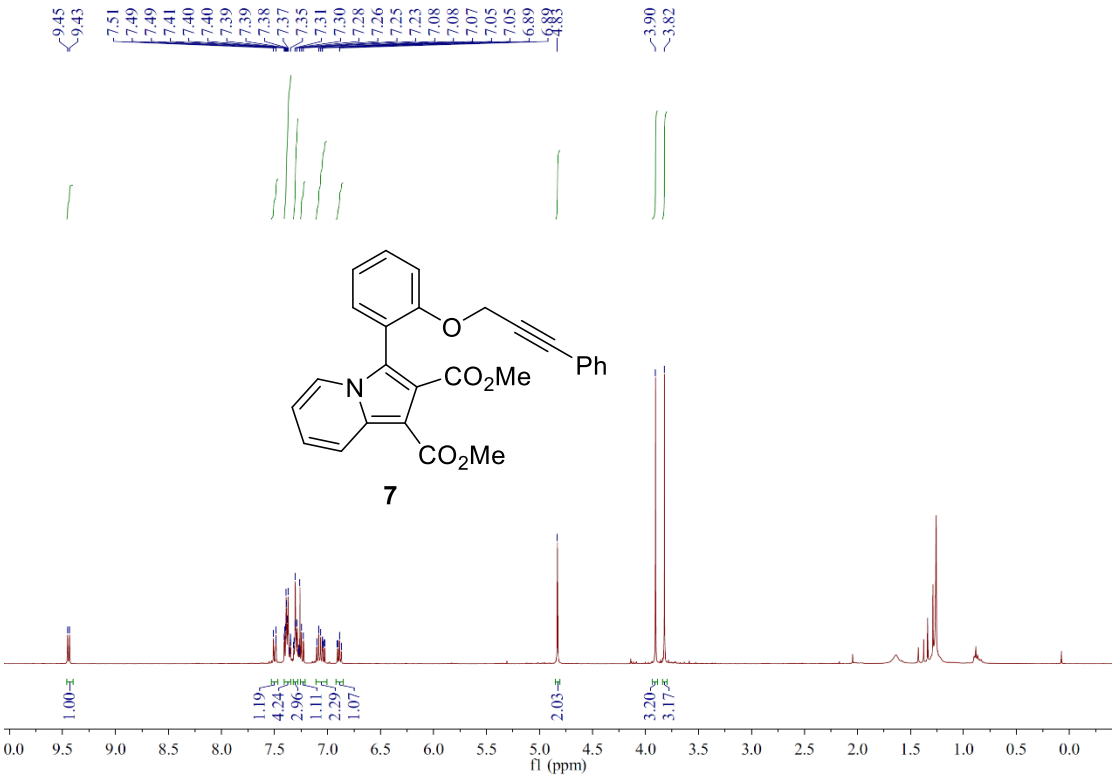
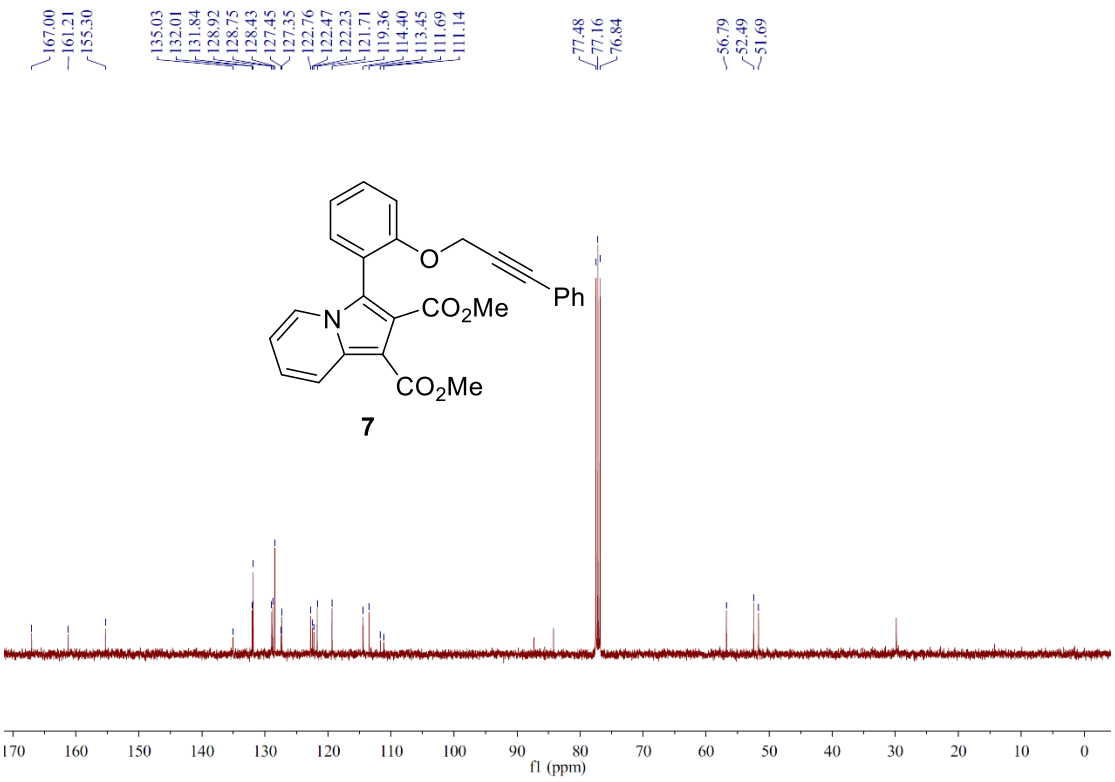
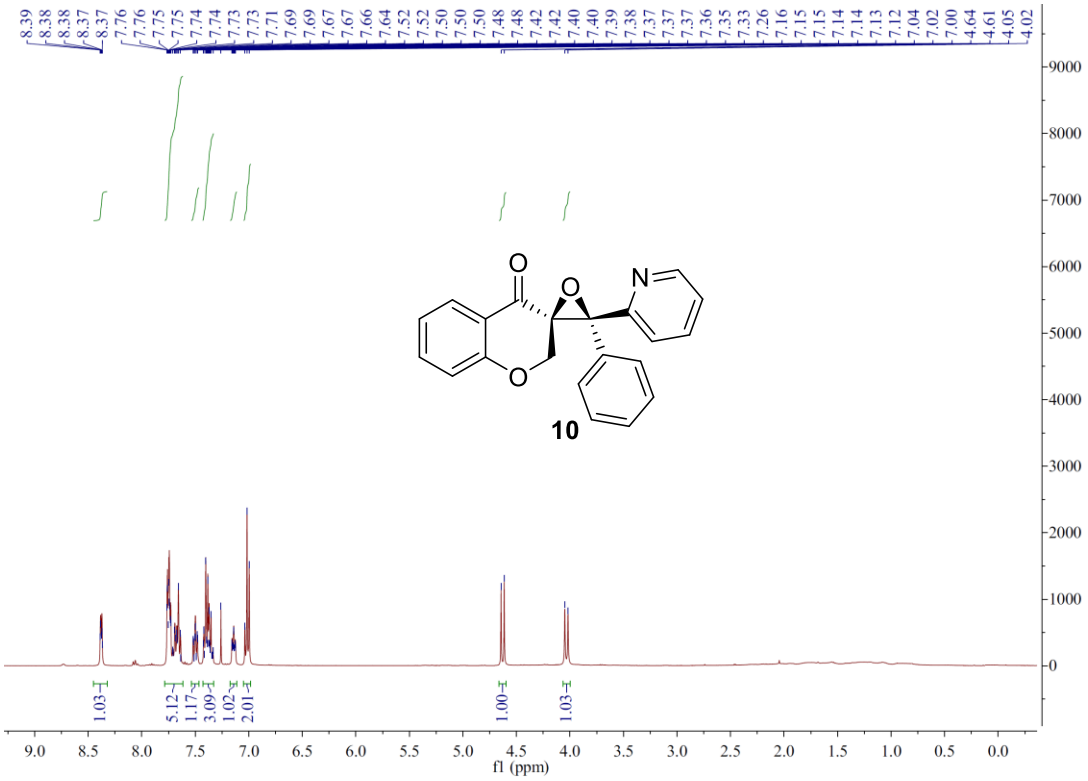
122.49
121.49
113.04
112.25
87.09
84.17
57.26
52.24
50.37
40.86
f1 (ppm)
H3C
N
CH3
COOMe
O
4

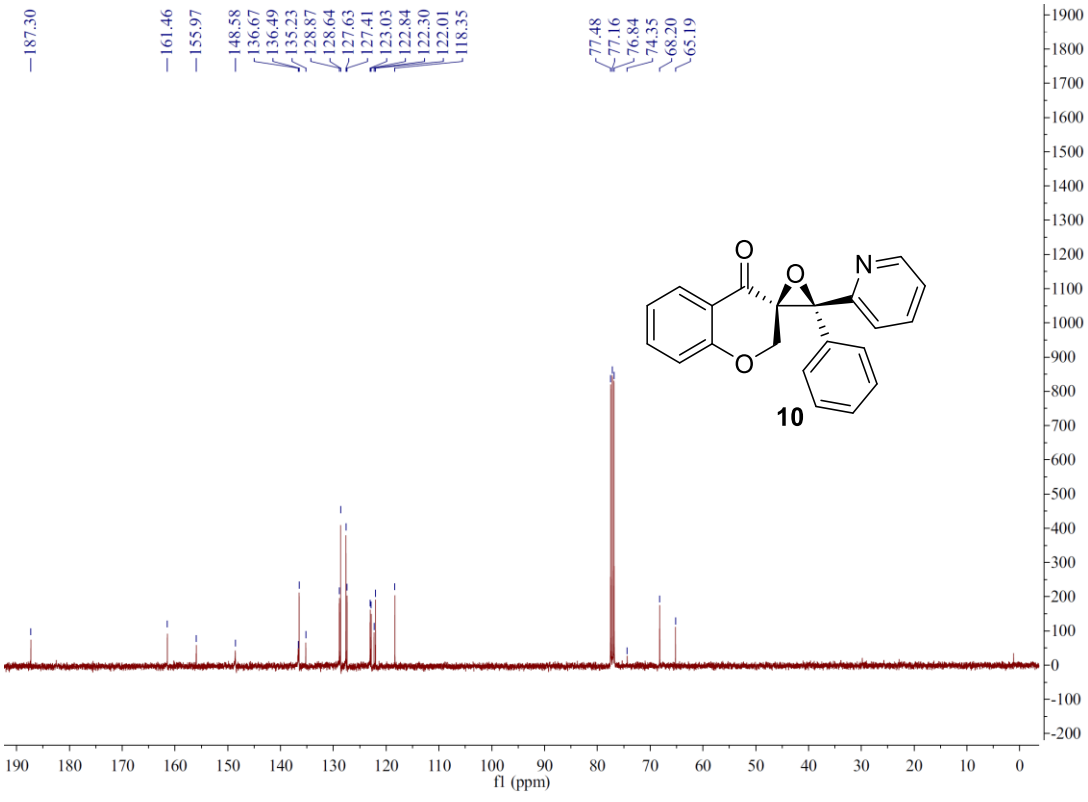

7.92
7.92
7.90
7.90
7.61
7.61
7.61
7.45
7.45
7.44
7.43
7.36
7.35
7.34
7.33
7.32
7.26
7.16
7.14
7.12
4.96
3.94
1.00
1.05
1.93
2.98
2.04
2.05
3.04
O
COOMe
O
5
fl (ppm)

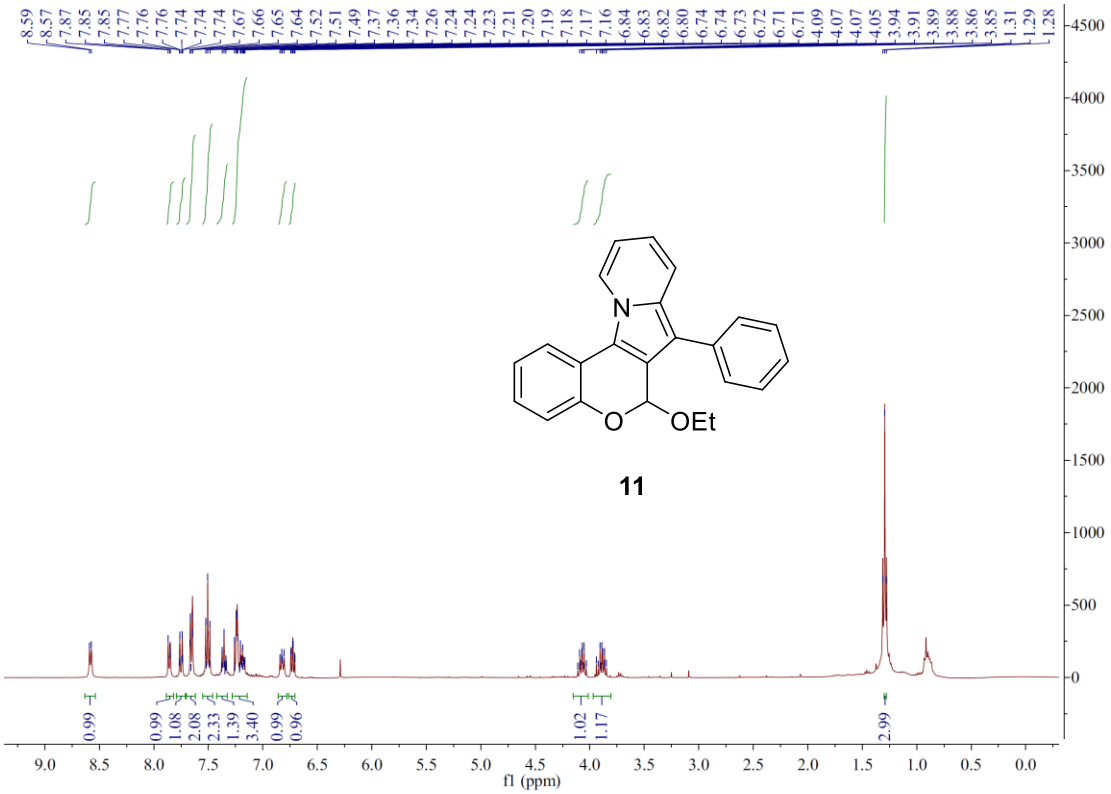

186.40
165.65
158.67
136.30
131.91
131.05
129.16
128.57
123.57
122.24
121.95
113.42
88.19
77.48
77.16
76.84
57.99
52.70
O
COOMe
O
5
fl (ppm)


9.45
9.43
7.51
7.49
7.49
7.41
7.40
7.40
7.39
7.38
7.37
7.35
7.31
7.30
7.28
7.26
7.25
7.23
7.08
7.08
7.07
7.05
7.05
6.89
6.89
4.83
3.90
3.82
O
Ph
N
CO2Me
CO2Me
7
1.00
1.19
4.24
2.96
1.11
2.29
1.07
2.03
3.20
3.17
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

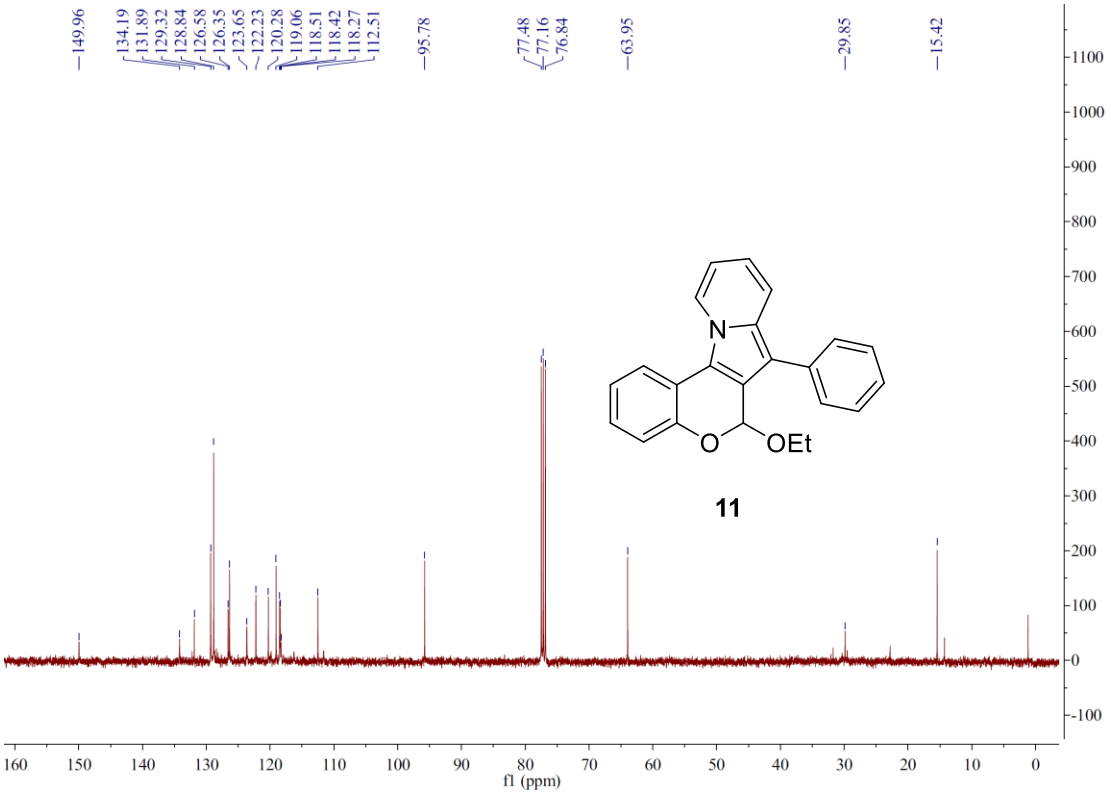

167.00
161.21
155.30
135.03
132.01
131.84
128.92
128.75
128.43
127.45
127.35
122.76
122.47
122.23
121.71
119.36
114.40
113.45
111.69
111.14
77.48
77.16
76.84
56.79
52.49
51.69
O
Ph
N
CO2Me
CO2Me
7
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.39 8.38 8.38 8.37 8.37 7.76 7.76 7.75 7.75 7.74 7.74 7.73 7.73 7.71 7.69 7.69 7.67 7.67 7.66 7.64 7.52 7.52 7.50 7.50 7.50 7.48 7.48 7.42 7.42 7.40 7.40 7.39 7.38 7.37 7.37 7.37 7.36 7.35 7.33 7.26 7.16 7.15 7.15 7.14 7.14 7.13 7.12 7.04 7.02 7.00 4.64 4.61 4.05 4.02
1.03 5.12 1.17 3.09 1.02 2.01 1.00 1.03
fl (ppm)
10


187.30 161.46 155.97 148.58 136.67 136.49 135.23 128.87 128.64 127.63 127.41 123.03 122.84 122.30 122.01 118.35 77.48 77.16 76.84 74.35 68.20 65.19
fl (ppm)
10

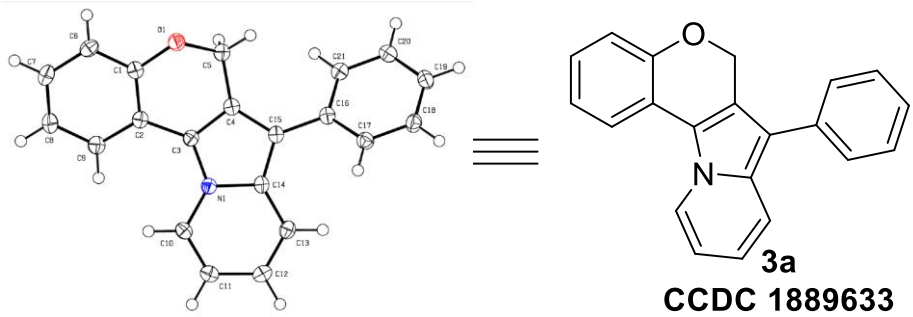


11



11

Crystallographic Data for Compound 3a



CCDC 1889633

Bond precision: C-C = 0.0020 A Wavelength=0.71073

Cell: a=9.4156(5) b=14.0062(6) c=11.1540(6)
alpha=90 beta=104.097(2) gamma=90
Temperature: 120 K

	Calculated	Reported
Volume	1426.66(12)	1426.66(12)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C21 H15 N O	?
Sum formula	C21 H15 N O	C21 H15 N O
Mr	297.34	297.34
Dx,g cm-3	1.384	1.384
Z	4	4
Mu (mm-1)	0.085	0.085
F000	624.0	624.0
F000'	624.25	
h,k,lmax	12,18,14	12,18,14
Nref	3278	3268
Tmin,Tmax	0.985,0.990	0.559,0.746
Tmin'	0.983	

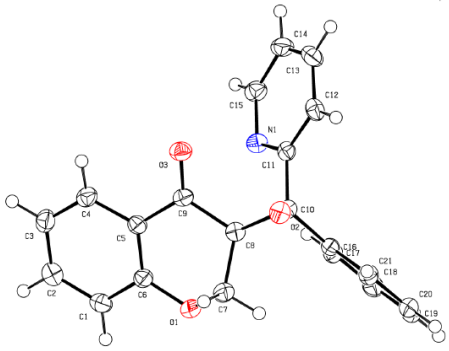
Correction method= # Reported T Limits: Tmin=0.559 Tmax=0.746
AbsCorr = MULTI-SCAN

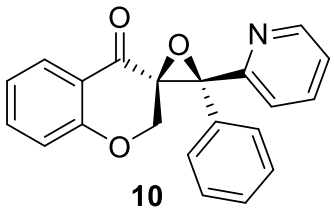
Data completeness= 0.997 Theta(max)= 27.511

R(reflections)= 0.0402(2589) wR2(reflections)= 0.1001(3268)

S = 1.038 Npar= 208

Crystallographic Data for Compound 9





10

CCDC 1908849

Bond precision: C-C = 0.0027 A Wavelength=0.71073

Cell: a=13.6852(16) b=7.2265(6) c=32.525(3)
alpha=90 beta=90 gamma=90

Temperature: 120 K

	Calculated	Reported
Volume	3216.6(5)	3216.6(5)
Space group	P b c a	P b c a
Hall group	-P 2ac 2ab	-P 2ac 2ab
Moiety formula	C21 H15 N O3	C21 H15 N O3
Sum formula	C21 H15 N O3	C21 H15 N O3
Mr	329.34	329.34
Dx,g cm-3	1.360	1.360
Z	8	8
Mu (mm-1)	0.092	0.092
F000	1376.0	1376.0
F000'	1376.66	
h,k,lmax	17,9,42	17,9,42
Nref	3693	3673
Tmin,Tmax	0.982,0.986	0.654,0.746
Tmin'	0.982	

Correction method= # Reported T Limits: Tmin=0.654 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.995 Theta(max)= 27.500

R(reflections)= 0.0451(2507) wR2(reflections)= 0.1173(3673)

S = 1.065 Npar= 226