Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Gold/Scandium Bimetallic Catalyzed Formal [5+2]- and [4+2]-Annulations: Access to Tetracyclic Indoles

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1. General Information

Unless otherwise noted, all the reagents were purchased from commercial suppliers and used without further purification. All solvents and commercially available reagents were either purified via literature procedures or used without further purification.

^{1}H NMR spectra were recorded on a Bruker Avance III 400 MHz or 600 MHz. ^{13}C NMR data were collected at 100 MHz or 150 MHz with complete proton decoupling. The chemical shifts were recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration. Chemical shifts were reported in ppm from the tetramethylsilane with the solvent resonance as internal standard.

High resolution mass spectroscopy (HRMS) was recorded on TOF MS ESI^{+} mass spectrometer and acetonitrile was used to dissolve the sample. High-performance liquid chromatography (HPLC) was performed on a Shimadzu LC 20 system equipped with a variable wavelength detector using Chiralcel OD-H and AD-H column from Daicel.

Optical rotations were measured on a WZZ-3 digital polarimeter with a sodium lamp and reported as follows: $[\alpha]_{\mathrm{D}}^{\mathrm{T}\,^{\circ}\mathrm{C}}$ (*c* = g/100 mL, solvent).

UV-visible absorption and fluorescence emission spectra were recorded on commercial spectrophotometers (Shimadzu UV-2600 and HITACHI F-4600 fluorescence spectrophotometer).

Melting points were determined with a WRX-4 melting apparatus.

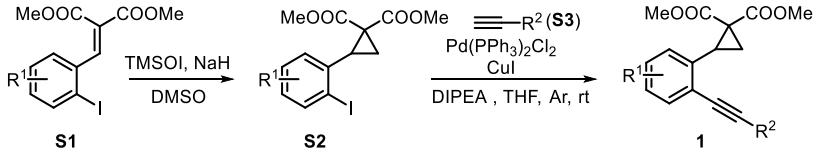
Flash Column chromatography was carried out on silica gel (200-300 mesh).

Thin layer chromatography was carried out on TLC plates coated with silica gel 60 F_{254} with fluorescence indicator. For the detection of the signals ultraviolet light (λ = 254 nm) was used.

2-Iodoarylidene malonates[1] were prepared according to the literature procedure.

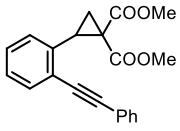
2. Experimental Procedures and Characterization Data

2.1 General procedure for the synthesis of alkynylcyclopropane 1,1-diesters 1



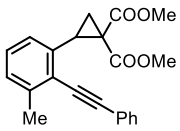
To a stirred anhydrous DMSO (30 mL) in a two-necked flask was added NaH (0.42 g, 10.5 mmol,1.05 equiv., 60% dispersion in mineral oil) at 0 °C under argon atmosphere. The mixture was stirring continued for 10 minutes at this temperature. Then, TMSOI (2.3 g, 10.5 mmol,1.05 equiv.) was added in small portions. The reaction mixture was stirred for additional 20 minutes until all the salt was dissolved. 2-Iodoarylidene malonate **S1** (10.0 mmol) solution in DMSO (10 mL) was added dropwise during 20 minutes at room temperature. The reaction mixture was stirred for 2 h at room temperature. After the reaction was completed, the reaction mixture was poured into sat. aq. NH_4Cl (100 mL) and extracted with EtOAc (2 × 100 mL), then washed with brine (2 × 100 mL). The combined organic layers were dried, concentrated to give crude 2-iodoarylcyclopropane **S2,** which was used directly in the next step without further purification.

To a solution of crude 2-iodoarylcyclopropane **S2** (containing a few amount of DMSO) in THF (30 mL), terminal alkyne **S3** (10.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.14 g, 0.2 mmol), CuI (0.095 g, 0.5 mmol), and DIPEA (30 mL) were added, respectively. The reaction mixture was stirred under an argon atmosphere at 60 °C for 12 h. Then the aqueous phases were adjusted to pH 5 and extracted with EtOAc (2 × 100 mL) and washed with brine (2 × 100 mL). The combined organic layers were dried, concentrated and purified by flash silica gel chromatography using (98:2 to 95:5 petroleum ether:EtOAc) to afford alkynylcyclopropane 1,1-diesters **1**.

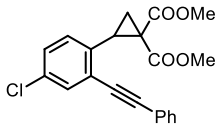


Dimethyl 2-(2-(phenylethynyl)phenyl)cyclopropane-1,1-di carbo -xylate (**1a**): white solid (52% yield, 1.7 g, 5.2 mmol); m.p. 59-60 °C; ^1H

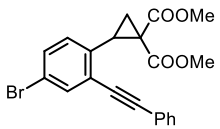
NMR (DMSO-d_6, 400 MHz) δ 7.57-7.25 (m, 3H), 7.50-7.42 (m, 3H), 7.37-7.32 (m, 2H), 7.20-7.17 (m, 1H), 3.68 (s, 3H), 3.50 (t, J = 8.8 Hz, 1H), 3.27 (s, 3H), 2.33 (dd, J = 8.0, 5.2 Hz, 1H), 1.81 (dd, J = 9.2, 5.2 Hz, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 170.0, 166.8, 136.9, 131.9, 131.7, 129.3, 129.2, 128.9, 128.1, 127.6, 124.7, 122.9, 94.6, 87.9, 53.2 (d, J = 6.7 Hz), 52.5, 37.1, 31.6 (d, J = 4.9 Hz), 18.8 (d, J = 4.3 Hz); HRMS (TOF-ESI$^+$) m/z: calcd for $C_{21}H_{18}KO_4$ $[M+K]^+$ 373.0837, found 373.0836.



Dimethyl 2-(3-chloro-2-(phenylethynyl)phenyl)cyclopropane-1,1-dicarboxylate (**1b**): white solid (24% yield, 0.84 g, 2.4 mmol); m.p. 73-75 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.56-7.53 (m, 2H), 7.38-7.33 (m, 3H), 7.14 (t, J = 2.0 Hz, 2H), 6.94-6.90 (m, 1H), 3.69 (s, 3H), 3.64 (t, J = 8.8 Hz, 1H), 3.37 (s, 3H), 2.52 (s, 3H), 2.30 (dd, J = 8.0, 4.8 Hz, 1H), 1.82 (dd, J = 9.2, 5.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.3, 167.2, 140.2, 136.6, 131.5, 128.5, 128.3, 128.2, 127.4, 125.1, 124.2, 123.6, 98.9, 86.2, 52.7 (d, J = 5.0 Hz), 52.2, 36.8, 32.9 (d, J = 5.2 Hz), 21.0 (d, J = 4.3 Hz), 19.4; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{22}H_{20}NaO_4$ $[M+Na]^+$ 371.1254, found 371.1268.

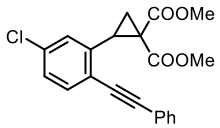


Dimethyl 2-(4-chloro-2-(phenylethynyl)phenyl)cyclopropane-1,1-dicarboxylate (**1c**): white solid (37% yield, 1.4 g, 3.7 mmol); m.p. 61-63 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.55-7.50 (m, 3H), 7.37-7.35 (m, 3H), 7.22 (dd, J = 8.4, 6.0 Hz, 1H), 7.02 (d, J = 8.4 Hz, 1H), 3.70 (s, 3H), 3.56 (t, J = 8.8 Hz, 1H), 3.41 (s, 3H), 2.27 (dd, J = 8.4, 5.2 Hz, 1H), 1.82 (dd, J = 9.2, 5.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.0, 167.1, 135.2, 133.1, 128.7, 128.4, 128.1, 126.9, 122.8, 95.8, 86.0, 52.8 (d, J = 7.8 Hz), 52,5 (d, J = 3.4 Hz), 36.8, 31.8 (d, J = 6.9 Hz), 19.2; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{21}H_{17}ClKO_4$ $[M+K]^+$ 407.0447, found 407.0448.

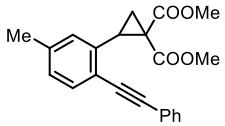


Dimethyl 2-(4-bromo-2-(phenylethynyl)phenyl)cyclopropane-1,1-dicarboxylate (**1d**): white solid (70% yield, 2.9 g, 7.0 mmol); m.p. 58-60 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.65 (d, J = 2.0 Hz, 1H), 7.54-7.52 (m, 2H), 7.38-7.35 (m, 4H), 6.95 (d, J = 8.4 Hz, 1H), 3.70 (s, 3H), 3.54 (t, J = 8.8

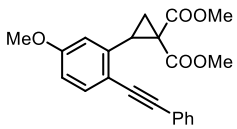
Hz, 1H), 3.41 (s, 3H), 2.27 (dd, *J* = 8.4, 5.2 Hz, 1H), 1.81 (dd, *J* = 9.2, 5.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.0, 167.0, 135.7, 134.2, 131.7, 130.9, 128.7, 128.6, 128.4, 127.2, 122.8, 121.0, 95.9, 85.9, 52.8 (d, *J* = 8.7 Hz), 52.5 (d, *J* = 3.4 Hz), 36.7, 31.8 (d, *J* = 7.4 Hz), 19.2 (d, *J* = 5.1 Hz); HRMS (TOF-ESI$^+$) m/z: calcd for $C_{21}H_{17}BrKO_4$ $[M+K]^+$ 450.9942, found 450.9942.



Dimethyl 2-(5-chloro-2-(phenylethynyl)phenyl)cyclopropane-1,1-dicarboxylate (**1e**): white solid (17% yield, 0.63 g, 1.7 mmol); m.p. 82-83 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.53 (t, *J* = 3.6 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.36-7.35 (m, 3H), 7.23 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.09 (s, 1H), 3.70 (s, 3H), 3.57 (t, *J* = 8.8 Hz, 1H), 3.42 (s, 3H), 2.27 (dd, *J* = 8.4, 5.6 Hz, 1H), 1.82 (dd, *J* = 9.2, 5.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.9, 166.9, 133.8, 132.8, 131.6, 128.5, 128.3, 127.6, 123.8, 123.0, 95.5, 86.3, 52.8 (d, *J* = 5.4 Hz), 52.4, 36.7, 31.9 (d, *J* = 5.1 Hz), 19.2; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{21}H_{17}ClNaO_4$ $[M+Na]^+$ 391.0708, found 391.0708.

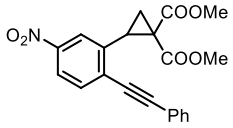


Dimethyl 2-(5-methyl-2-(phenylethynyl)phenyl)cyclopropane-1,1-dicarboxylate (**1f**): white solid (35% yield, 1.2 g, 3.5 mmol); m.p. 87-89 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.52-7.43 (m, 6H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.01 (s, 1H), 3.68 (s, 3H), 3.45 (t, *J* = 8.8 Hz, 1H), 3.29 (s, 3H), 2.33-2.32 (m, 4H), 1.79 (dd, *J* = 8.0, 5.2 Hz, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 170.0, 166.8, 138.7, 136.7, 131.8, 131.6, 129.2, 129.1, 128.7, 128.3, 123.1, 121.7, 94.0, 88.1, 53.2 (d, *J* = 4.2 Hz), 52.5, 37.0, 31.6, 21.5 (d, *J* = 3.2 Hz), 18.8; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{22}H_{20}NaO_4$ $[M+Na]^+$ 371.1254, found 371.1262.

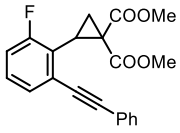


Dimethyl 2-(5-methoxy-2-(phenylethynyl)phenyl)cyclopropane-1,1-dicarboxylate (**1g**): white solid (18% yield, 0.66 g, 1.8 mmol); m.p. 80-82 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.52-7.50 (m, 2H), 7.48-7.43 (m, 4H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.01 (s, 1H), 3.68 (s, 3H), 3.46 (t, *J* = 8.4 Hz, 1H), 3.30 (s, 3H), 2.33-2.30 (m, 4H), 1.77-1.81 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.0, 166.8, 138.7, 136.8, 131.8, 131.6, 129.2, 129.1, 128.7, 128.3, 128.2, 123.1, 121.8,

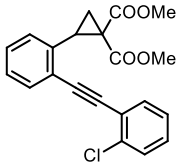
94.0, 88.1, 53.2 (d, J = 6.6 Hz), 52.5, 37.0, 31.6 (d, J = 3.9 Hz), 21.6 (d, J = 5.4 Hz), 18.8; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{22}H_{20}KO_5$ $[M+K]^+$ 403.0942, found 403.0939.



Dimethyl 2-(5-nitro-2-(phenylethynyl)phenyl)cyclopropane-1,1-dicarboxylate (**1h**): white solid (34% yield, 1.3 g, 3.4 mmol); m.p. 123-125 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.19 (dd, J = 8.4, 2.4 Hz, 1H), 8.00 (d, J = 2.4 Hz, 1H), 7.82 (d, J = 8.4 Hz, 1H), 7.60-7.57 (m, 2H), 7.52-7.49 (m, 3H), 3.68 (s, 3H), 3.53 (t, J = 8.8 Hz, 1H), 3.37 (s, 3H), 2.46 (dd, J = 8.0, 5.6 Hz, 1H), 1.90 (dd, J = 9.2, 5.6 Hz, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.5, 166.7, 147.0, 139.1, 133.2, 132.1, 131.5, 130.3, 129.4, 123.2, 122.7, 121.9, 99.6, 86.5, 53.3, 52.8, 37.1, 31.1, 19.1; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{21}H_{17}NNaO_6$ $[M+Na]^+$ 402.0948, found 402.0949.

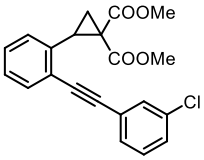


Dimethyl 2-(2-fluoro-6-(phenylethynyl)phenyl)cyclopropane-1,1-di-carboxylate (**1i**): white solid (71% yield, 2.5 g, 7.1 mmol); m.p. 61-62 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.55-7.53 (m, 2H), 7.39-7.35 (m, 3H), 7.30 (d, J =7.6 Hz, 1H), 7.23-7.17 (m, 1H), 6.69 (t, J = 9.2 Hz, 1H), 3.69 (s, 3H), 3.45 (s, 3H), 3.28 (t, J = 9.2 Hz, 1H), 2.59 (ddd, J = 8.4, 5.2, 1.2 Hz, 1H), 1.97 (dd, J = 9.2, 4.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.2, 167.7, 161.5 (d, $J_{C\text{-}F}$ = 298.0 Hz), 131.6, 128.6(3), 128.5(7), 128.4, 126.9 (d, $J_{C\text{-}F}$ = 4.8 Hz), 124.2 (d, $J_{C\text{-}F}$ = 13.2 Hz), 122.9, 115.8 (d, $J_{C\text{-}F}$ = 23.0 Hz), 95.2, 86.6, 52.8 (d, J = 5.5 Hz), 52.3 (d, J = 3.1 Hz), 35.1 (d, J = 1.6 Hz), 28.0, 22.2 (d, J = 5.3 Hz); HRMS (TOF-ESI$^+$) m/z: calcd for $C_{21}H_{17}FKO_4$ $[M+K]^+$ 391.0742, found 391.0750.

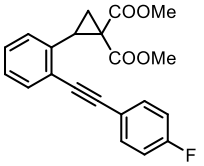


Dimethyl 2-(2-((2-chlorophenyl)ethynyl)phenyl)cyclopropane-1,1-dicarboxylate (**1j**): colorless oil (32% yield, 1.2 g, 3.2 mmol); ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.64-7.57 (m, 3H), 7.48-7.44 (m, 2H), 7.41-7.34 (m, 2H), 7.18-7.16 (m, 1H), 3.66 (s, 3H), 3.50 (t, J = 8.8 Hz, 1H), 3.38 (s, 3H), 2.32 (dd, J = 8.0, 5.2 Hz, 1H), 1.82 (dd, J = 9.2, 5.2 Hz, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.8, 166.7, 136.9, 134.9, 133.8, 132.4, 130.9, 129.8, 129.4, 128.1, 127.8, 127.4, 124.2, 122.6,

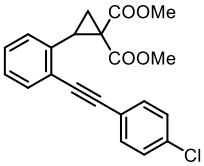
92.9, 91.0, 53.1 (d, J = 5.9 Hz), 52.5, 37.3, 31.3 (d, J = 1.6 Hz), 18.8 (d, J = 3.7 Hz); HRMS (TOF-ESI$^+$) m/z: calcd for $C_{21}H_{17}ClKO_4$ $[M+K]^+$ 407.0447, found 407.0452.



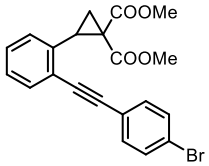
Dimethyl 2-(2-((3-chlorophenyl)ethynyl)phenyl)cyclopropane-1,1-dicarboxylate (**1k**): white solid (33% yield, 1.2 g, 3.3 mmol); m.p. 62-64 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.56-7.48 (m, 5H), 7.39-7.32 (m, 2H), 7.20 (d, J = 6.8 Hz, 1H), 3.69 (s, 3H), 3.46 (t, J = 8.8 Hz, 1H), 3.25 (s, 3H), 2.33 (dd, J = 8.0, 5.6 Hz, 1H), 1.80 (dd, J = 9.2, 5.6 Hz, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 170.0, 166.8, 137.1, 133.8, 132.0, 131.1, 130.2, 129.4, 129.3, 128.2, 127.8, 124.9, 124.2, 93.0, 89.2, 53.2 (d, J = 5.8 Hz), 52.5, 37.0, 31.6, 18.7. HRMS (TOF-ESI$^+$) m/z: calcd for $C_{21}H_{17}ClKO_4$ $[M+K]^+$ 407.0447, found 407.0454.



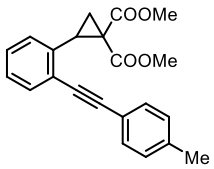
Dimethyl 2-(2-((4-fluorophenyl)ethynyl)phenyl)cyclopropane-1,1-dicarboxylate (**1l**): white solid (36% yield, 1.3 g, 3.6 mmol); m.p. 79-81 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.59-7.54 (m, 3H), 7.38-7.32 (m, 4H), 7.20-7.18 (m, 1H), 3.68 (s, 3H), 3.47 (t, J = 8.4 Hz, 1H), 3.27 (s, 3H), 2.33 (dd, J = 8.4, 5.6 Hz, 1H), 1.80 (dd, J = 9.2, 5.6 Hz, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 170.0, 166.8, 162.5 (d, $J_{C\text{-}F}$ = 246.2 Hz), 136.9, 133.9 (d, $J_{C\text{-}F}$ = 8.6 Hz), 131.8, 128.9, 128.1, 127.7, 124.6, 119.4 (d, $J_{C\text{-}F}$ = 3.2 Hz), 116.5 (d, $J_{C\text{-}F}$ = 22.1 Hz), 93.6, 87.6, 53.2 (d, J = 3.8 Hz), 52.5, 37.1, 31.6, 18.7; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{21}H_{17}FKO_4$ $[M+K]^+$ 391.0742, found 391.0747.



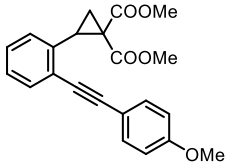
Dimethyl 2-(2-((4-chlorophenyl)ethynyl)phenyl)cyclopropane-1,1-dicarboxylate (**1m**): white solid (53% yield, 2.0 g, 5.3 mmol); m.p. 79-81 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.67-7.25 (m, 5H), 7.39-7.32 (m, 2H), 7.20 (d, J = 7.6 Hz, 1H), 3.68 (s, 3H), 3.47 (t, J = 8.8 Hz, 1H), 3.26 (s, 3H), 2.33 (dd, J = 8.0, 5.2 Hz, 1H), 1.80 (dd, J = 8.8, 5.2 Hz, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 170.0, 166.8, 137.0, 134.0, 133.3, 131.9, 129.4, 129.1, 128.1, 127.7, 124.4, 121.8, 93.4, 88.9, 53.3 (d, J = 6.1 Hz), 52.5, 37.1, 31.5, 18.7; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{21}H_{18}KO_4$ $[M+H]^+$ 369.0888, found 369.0888.



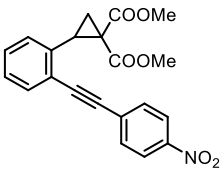
Dimethyl 2-(2-((4-bromophenyl)ethynyl)phenyl)cyclopropane-1,1-dicarboxylate (**1n**): white solid (37% yield, 1.5 g, 3.7 mmol); m.p. 81-83 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.69 (d, J = 8.4 Hz, 2H), 7.57-7.55 (m, 1H), 7.46 (d, J = 8.4 Hz, 2H), 7.39-7.32 (m, 2H), 7.20 (d, J = 6.8 Hz, 1H), 3.69 (s, 3H), 3.47 (t, J = 8.4 Hz, 1H), 3.26 (s, 3H), 2.32 (dd, J = 8.0, 5.2 Hz, 1H), 1.80 (dd, J = 9.2, 5.6 Hz, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.9, 166.8, 137.0, 133.5, 132.3, 131.9, 129.2, 128.1, 127.7, 124.4, 122.7, 122.1, 93.5, 89.1, 53.3 (d, J = 5.2 Hz), 52.5, 37.1, 31.5, 18.7; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{21}H_{17}BrKO_4$ $[M+K]^+$ 450.9942, found 450.9940.



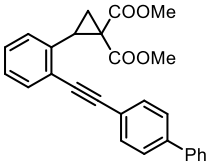
Dimethyl 2-(2-(p-tolylethynyl)phenyl)cyclopropane-1,1-dicarbo-xylate (**1o**): white solid (38% yield, 1.3 g, 3.8 mmol); m.p. 75-77 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.54-7.52 (m, 1H), 7.42 (d, J = 8.0 Hz, 2H), 7.36-7.31 (m, 2H), 7.28 (d, J = 8.0 Hz, 2H) , 7.18-7.16 (m, 1H), 3.69 (s, 3H), 3.48 (t, J = 7.6 Hz, 1H), 3.26 (s, 3H), 2.33 (dd, J = 8.0, 5.2 Hz, 1H), 1.80 (dd, J = 8.8, 5.2 Hz, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 170.0, 166.8, 139.1, 136.7, 131.8, 131.6, 129.8, 128.7, 128.1, 127.5, 124.9, 119.9, 94.9, 87.3, 53.2 (d, J = 5.1 Hz), 52.5, 37.1, 31.6, 21.6 (d, J = 4.4 Hz), 18.7; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{22}H_{21}O_4$ $[M+H]^+$ 349.1434, found 349.1435.



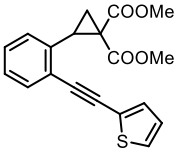
Dimethyl 2-(2-((4-methoxyphenyl)ethynyl)phenyl)cyclopropane-1,1-dicarboxylate (**1p**): white solid (45% yield, 1.6 g, 4.5 mmol); m.p. 68-69 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.52-7.50 (m, 1H), 7.46 (d, J = 8.8 Hz, 2H), 7.32 (t, J = 4.8 Hz, 2H), 7.16 (t, J = 4.0 Hz, 1H), 7.03 (d, J = 8.4 Hz, 2H), 3.82 (s, 3H), 3.70 (s, 3H), 3.48 (t, J = 8.4 Hz, 1H), 3.26 (s, 3H), 2.32 (dd, J = 8.0, 5.6 Hz, 1H), 1.80 (dd, J = 9.2, 5.6 Hz, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 170.0, 166.8, 160.1, 136.5, 133.2, 131.6, 128.4, 128.0, 127.4, 125.2, 114.9, 94.9, 84.6, 55.8 (d, J = 5.0 Hz), 53.2 (d, J = 4.2 Hz), 52.5, 37.1, 31.6, 18.7; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{22}H_{20}NaO_5$ $[M+Na]^+$ 387.1203, found 387.1203.



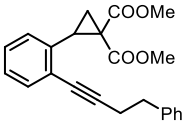
Dimethyl 2-(2-((4-nitrophenyl)ethynyl)phenyl)cyclopropane-1,1-dicarboxylate (**1q**): white solid (18% yield, 0.68 g, 1.8 mmol); m.p. 100-101 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.33 (d, J = 8.8 Hz, 2H), 7.75 (d, J = 8.8 Hz, 2H), 7.62 (d, J = 7.2 Hz, 1H), 7.43-7.35 (m, 2H), 7.23 (d, J = 7.6 Hz, 1H), 3.69 (s, 3H), 3.48 (t, J = 8.4 Hz, 1H), 3.26 (s, 3H), 2.33 (dd, J = 8.0, 5.2 Hz, 1H), 1.81 (dd, J = 9.2, 5.2 Hz Hz, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.9, 166.8, 147.4, 137.4, 132.7, 132.3, 129.9, 129.7, 128.2, 127.9, 124.5, 123.7, 92.8 (d, J = 3.3 Hz), 53.4 (d, J = 6.1 Hz), 52.5, 37.1, 31.4 (d, J = 4.1 Hz), 18.7 (d, J = 2.8 Hz); HRMS (TOF-ESI$^+$) m/z: calcd for $C_{21}H_{17}NNaO_6$ $[M+Na]^+$ 402.0948, found 402.0949.



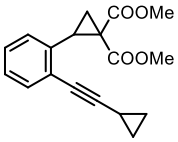
Dimethyl 2-(2-([1,1'-biphenyl]-4-ylethynyl)phenyl)cyclopropane-1,1-dicarboxylate (**1r**): white solid (28% yield, 1.1 g, 2.8 mmol); m.p. 95-97 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.80-7.74 (m, 4H), 7.62-7.57 (m, 3H), 7.51 (t, J = 7.6 Hz, 2H), 7.43-7.35 (m, 3H), 7.21-7.19 (m, 1H), 3.72 (s, 3H), 3.52 (t, J = 8.4 Hz, 1H), 3.28 (s, 3H), 2.35 (dd, J = 8.0, 5.6 Hz, 1H), 1.82 (dd, J = 9.2, 5.6 Hz, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 170.0, 166.8, 140.8, 139.6, 136.9, 132.3, 131.9, 129.5, 128.9, 128.4, 128.1, 127.6, 127.4, 127.2, 124.7, 121.9, 94.6, 88.7, 53.3 (d, J = 3.0 Hz), 52.5, 37.1, 31.6 (d, J = 1.4 Hz), 18.8; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{27}H_{22}KO_4$ $[M+K]^+$ 449.1150, found 449.1150.



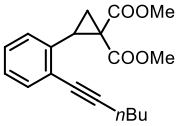
Dimethyl 2-(2-(thiophen-2-ylethynyl)phenyl)cyclopropane-1,1-dicarboxylate (**1s**): white solid (12% yield, 0.4 g, 1.2 mmol); m.p. 69-71 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.70 (d, J = 5.2 Hz, 1H), 7.55-7.52 (m, 1H), 7.38-7.32 (m, 3H), 7.20-7.15 (m, 2H), 3.71 (s, 3H), 3.42 (t, J = 8.4 Hz, 1H), 3.28 (s, 3H), 2.31 (dd, J = 8.4, 5.6 Hz, 1H), 1.79 (dd, J = 9.2, 5.6 Hz, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.8, 166.8, 136.7, 133.1, 129.6, 129.0, 128.2, 128.1, 127.7, 124.4, 122.4, 91.4, 88.0, 53.2 (d, J = 6.6 Hz), 52.5, 37.1, 31.4 (d, J = 3.1 Hz), 18.7 (d, J = 3.1 Hz); HRMS (TOF-ESI$^+$) m/z: calcd for $C_{19}H_{16}NaO_4S$ $[M+Na]^+$ 363.0662, found 363.0662.



Dimethyl 2-(2-(4-phenylbut-1-yn-1-yl)phenyl)cyclopropane-1,1-dicarboxylate (**1t**): colorless oil (70% yield, 2.5 g, 7.0 mmol); ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.35-7.32 (m, 5H), 7.27-7.22 (m, 3H), 7.08-7.06 (m, 1H), 3.72 (s, 3H), 3.40 (t, J = 8.8 Hz, 1H), 3.28 (s, 3H), 2.87 (t, J = 7.2 Hz, 2H), 2.74-2.69 (m, 2H), 2.25 (dd, J = 8.4, 5.2 Hz, 1H), 1.75 (dd, J = 9.2, 5.6 Hz, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.9, 166.8, 141.0, 136.7, 131.7, 128.9, 128.8, 128.0, 127.8, 127.0, 126.7, 125.5, 95.8, 79.5, 53.2 (d, J = 7.7 Hz), 52.5, 37.1, 34.7, 31.4 (d, J = 2.7 Hz), 21.6, 18.8 (d, J = 2.4 Hz); HRMS (TOF-ESI$^+$) m/z: calcd for $C_{23}H_{22}KO_4$ $[M+K]^+$ 401.1150, found 401.1151.

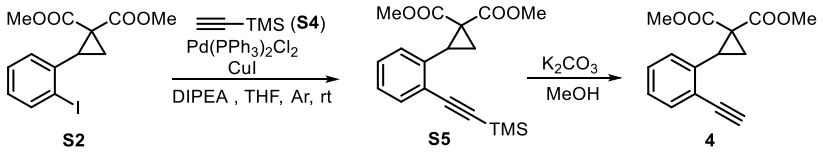


Dimethyl 2-(2-(cyclopropylethynyl)phenyl)cyclopropane-1,1-dicarboxylate (**1u**): colorless oil (39% yield, 1.2 g, 3.9 mmol); ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.37-7.35 (m, 1H), 7.25-7.23 (m, 2H), 7.07 (t, J = 3.6 Hz, 1H), 3.75 (s, 3H), 3.30 (t, J = 8.8 Hz, 1H), 3.26 (s, 3H), 2.24 (dd, J = 8.0, 5.2 Hz, 1H), 1.72 (dd, J = 9.2, 5.2 Hz, 1H), 1.57-1.50 (m, 1H), 0.93-0.88 (m, 2H), 0.73-0.70 (m, 2H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.9, 166.7, 137.8, 136.6, 131.7, 129.4, 128.7, 127.8, 127.7, 127.2, 125.8, 125.7, 99.5, 74.0, 53.2 (d, J = 8.1 Hz), 52.4, 36.9, 31.6, 18.7 (d, J = 2.2 Hz), 9.1, 8.7; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{18}H_{18}KO_4$ $[M+K]^+$ 337.0837, found 337.0846.



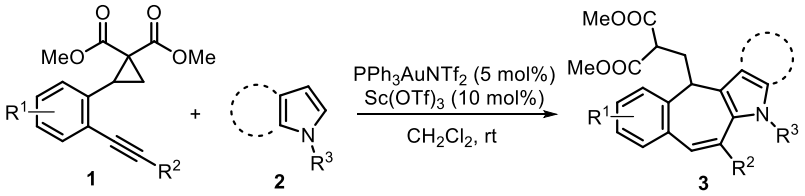
Dimethyl 2-(2-(hex-1-yn-1-yl)phenyl)cyclopropane-1,1-dicarb-oxylate (**1v**): colorless oil (41% yield, 1.3 g, 4.1 mmol); ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.37-7.34 (m, 1H), 7.25-7.22 (m, 2H), 7.06-7.04 (m, 1H), 3.71 (s, 3H), 3.25 (s, 3H), 2.41 (t, J = 6.8 Hz, 2H), 2.23 (dd, J = 8.4, 5.2 Hz, 1H), 1.73 (dd, J = 9.25.2 Hz, 1H), 1.53-1.39 (m, 4H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.8, 166.8, 136.6, 131.8, 127.9, 127.8, 127.0, 125.7, 96.3, 78.9, 53.1 (d, J = 7.7 Hz), 52.4, 37.1, 31.4 (d, J = 1.2 Hz), 30.7, 21.9, 19.0, 18.7 (d, J = 1.7 Hz), 14.0; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{19}H_{23}O_4$ $[M+H]^+$ 315.1591, found 315.1601.

Synthesis of dimethyl 2-(2-ethynylphenyl)cyclopropane-1,1-dicarboxylate 4



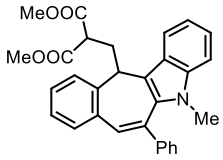
The terminal alkynylcyclopropane 1,1-diesters **4** was synthesized according to the siminal procedure by using trimethylsilylacetylene **S4** (0.98 g, 10 mmol) instead of arylacetylene. After the Sonogashira coupling reaction was completed, the solvent was removed *in vacuo* and redisolved in methanol (50 mL). After that, K_2CO_3 (2.8 g, 20 mmol) was added in one portion and the reaction mixture was stirred at room temperature for 3 h. Then, the mixture was diluted with water (30 mL), extracted with EtOAc (2 × 100 mL) and washed with brine (2 × 100 mL). The combined organic layers were dried, concentrated and purified by flash silica gel chromatography using (98:2 to 95:5 petroleum ether:EtOAc) to afford terminal alkynylcyclopropane 1,1-diesters **4** (90% yield, 2.3 g, 9 mmol). m.p. 59-61 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.47 (dd, J = 7.6, 1.6 Hz, 1H), 7.33 (td, J = 7.2, 1.2 Hz, 1H), 7.27 (td, J = 7.6, 1.6 Hz, 1H), 7.08 (d, J = 7.2 Hz, 1H), 4.40 (s, 1H), 3.72 (s, 3H), 3.73 (t, J = 8.8 Hz, 1H), 3.26 (s, 3H), 2.25 (dd, J = 8.0, 5.2 Hz, 1H), 1.75 (dd, J = 9.2, 5.6 Hz, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.7, 166.7, 137.3, 132.6, 129.0, 127.9, 127.0, 124.2, 86.0, 81.8, 53.2, 52.5, 37.2, 31.0, 18.7; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{15}H_{14}NaO_4$ $[M+Na]^+$ 281.0784, found 281.0791.

2.2 General procedure for the synthesis of cyclohepta[*b*]indole derovatives 3

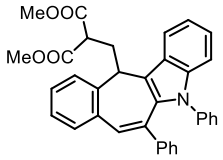


To a solution of ACP **1** (0.1 mmol) in dichloromethane (1.0 mL), indole or pyrrole derivative **2** (0.12 mmol, 1.2 equiv.), $Ph_3PAuNTf_2$ (3.7 mg, 0.005 mmol) and $Sc(OTf)_3$ (4.9 mg, 0.01 mmol) were added, respectively. The reaction was stirred at room temperature for 12

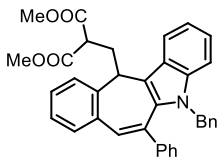
h. Then, the mixture was diluted with brine (2.0 mL) and extracted with EtOAc (2.0 mL × 2). The combined organic layers were dried, concentrated and purified by flash silica gel chromatography using (95:5 to 90:10 petroleum ether:EtOAc) to afford cyclohepta[*b*]indole **3** as a white solid.



Dimethyl 2-((5-methyl-6-phenyl-5,12-dihydrobenzo[4,5]cyclo-hepta[1,2-*b*]indol-12-yl)methyl)malonate (**3aa**): white solid (86% yield, 40.0 mg, 0.086 mmol); m.p. 173-175 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.74 (d, J = 8.0 Hz, 1H), 7.61-7.51 (m, 5H), 7.44 (d, J = 6.8 Hz, 1H), 7.39-7.35 (m, 4H), 7.32-7.28 (m, 1H), 7.21 (t, J = 7.2 Hz, 1H), 7.14 (t, J = 7.2 Hz, 1H), 4.55 (dd, J = 9.2, 6.8 Hz, 2H), 3.57 (s, 3H), 3.41 (s, 3H), 3.31 (dd, J = 8.0, 6.0 Hz, 1H), 3.07 (s, 3H), 2.36-2.29 (m, 1H), 2.15-2.07 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.7, 169.5, 142.5, 142.0, 139.4, 134.3, 133.8, 132.6, 131.3, 129.4, 129.1, 128.4, 127.9, 126.5, 126.1, 123.0, 119.7, 119.2, 118.4, 110.3, 52.8(1), 52.7(8), 52.6, 50.2, 32.6, 29.7; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{30}H_{27}KNO_4$ $[M+K]^+$ 504.1572, found 504.1572.

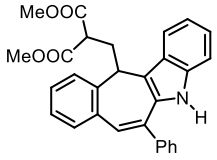


Dimethyl 2-((5,6-diphenyl-5,12-dihydrobenzo[4,5]cyclohepta-[1,2-*b*]indol-12-yl)methyl)malonate (**3ab**): white solid (46% yield, 24.2 mg, 0.046 mmol); m.p. 167-169 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.81 (d, J = 7.6 Hz, 1H), 7.63 (d, J = 7.6 Hz, 1H), 7.44-7.32 (m, 4H), 7.27 (s, 1H), 7.22-7.13 (m, 6 H), 7.10-6.94 (m, 6 H), 4.63 (t, J = 7.2 Hz, 1H), 3.57 (s, 3H), 3.45 (s, 3H), 3.33 (s, 1H), 2.40-2.32 (m, 1H), 2.19-2.12 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.7, 169.4, 142.4, 141.1, 139.4, 138.2, 134.5, 134.4, 133.1, 132.5, 131.6, 129.4, 129.2, 128.2, 127.5, 126.7, 126.6, 123.8 121.3, 120.8, 118.7, 110.6, 52.8 (d, J = 4.4 Hz), 50.2, 29.8; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{35}H_{29}NNaO_4$ $[M+Na]^+$ 550.1989, found 550.1984.

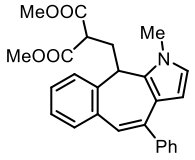


Dimethyl 2-((5-benzyl-6-phenyl-5,12-dihydrobenzo [4,5]-cyclohepta[1,2-*b*]indol-12-yl)methyl)malonate (**3ac**): colorless oil (26% yield, 14.1 mg, 0.026 mmol); ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.77-7.75 (m, 1H), 7.56 (d, J = 7.6 Hz, 1H), 7.51 (d, J = 6.8 Hz, 2H), 7.45-7.35 (m, 6H),

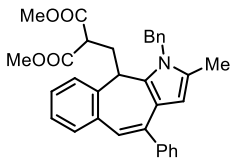
7.32-7.25 (m, 2H), 7.17-7.12 (m, 2H), 7.06-6.99 (m, 3H), 6.57 (d, *J* = 6.4 Hz, 2H), 5.11(d, *J* = 16.8 Hz, 1H), 4.57 (dd, *J* = 9.2, 6.4 Hz, 1H), 4.47 (d, *J* = 16.8 Hz, 1H), 3.57 (s, 3H), 3.42 (s, 3H), 3.33 (s, 1H), 2.41-2.34 (m, 1H), 2.17-2.10 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.7, 169.5, 142.6, 141.6, 139.3, 138.1, 134.2, 133.9, 133.0, 132.4, 131.3, 129.3, 129.1, 128.5, 127.9, 127.3, 126.7, 126.6, 126.5, 123.1, 120.3, 118.6, 111.2, 52.8 (d, *J* = 5.2 Hz), 52.6 (d, *J* = 2.8 Hz), 50.3, 47.4, 29.9; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{36}H_{31}KNO_4$ $[M+K]^+$ 580.1885, found 580.1885.



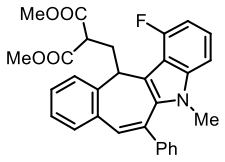
Dimethyl 2-((6-phenyl-5,12-dihydrobenzo[4,5]cyclohepta[1,2-*b*]indol-12-yl)methyl)malonate (**3ad**): white solid (51% yield, 23.0 mg, 0.051 mmol); m.p. 83-84 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 10.72 (s, 1H), 7.70-7.54 (m, 3H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.2 Hz, 2H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.39-7.38 (m, 2H), 7.31-7.29 (m, 2H), 7.20 (s, 1H), 7.13-7.05 (m, 2H), 4.55 (t, *J* = 8.8 Hz, 1H), 3.56 (s, 3H), 3.39 (s, 3H), 3.22 (t, *J* = 7.2 Hz, 1H), 2.31-2.24 (m, 1H), 2.10-1.99 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.7, 169.5, 140.9, 140.8, 137.7, 134.6, 134.4, 131.7, 131.5, 129.8, 129.3, 129.0, 128.6, 126.7, 126.5, 122.5, 119.3, 118.2, 116.7, 112.1, 52.8 (d, *J* = 5.2 Hz), 52.6, 50.0, 30.9; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{29}H_{25}NNaO_4$ $[M+Na]^+$ 474.1676 found 474.1676.



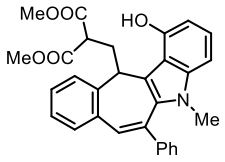
Dimethyl 2-((1-methyl-10-phenyl-1,4-dihydrobenzo[4,5]cyclo-hepta[1,2-*b*]pyrrol-4-yl)methyl)malonate (**3ae**): white solid (46% yield, 19.1 mg, 0.046 mmol); m.p. 143-145 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.52-7.48 (m, 5H), 7.42 (d, *J* = 6.8 Hz, 1H), 7.33-7.19 (m, 3H), 6.96 (s, 1H), 6.48 (d, *J* = 2.0 Hz, 1H), 5.94 (d, *J* = 2.0 Hz, 1H), 3.93 (t, *J* = 8.8 Hz, 1H), 3.59 (d, *J* = 8.0 Hz, 6H), 3.23 (t, *J* = 7.6 Hz, 1H), 2.90 (s, 3H), 2.22-2.15 (m, 1H), 2.03-1.92 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 170.0, 169.9, 169.5, 142.5, 142.1, 134.6, 134.1, 131.0, 129.2, 129.1, 128.7, 128.6, 128.3, 128.1, 126.9, 126.2, 126.0, 107.7, 52.8 (d, *J* = 3.4 Hz), 50.1, 44.2 (d, *J* = 6.2 Hz), 36.5 (d, *J* = 4.8 Hz), 29.9; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{26}H_{26}NO_4$ $[M+H]^+$ 416.1856, found 416.1844.



Dimethyl 2-((1,2-dimethyl-10-phenyl-1,4-dihydrobenzo[4,5]-cyclohepta[1,2-*b*]pyrrol-4-yl)methyl)malonate (**3af**): white solid (36% yield, 15.4 mg, 0.036 mmol); colorless oil; ^{1}H NMR (DMSO-d_6, 600 MHz) δ 7.41 (d, J = 7.8 Hz, 1H), 7.37-7.31 (m, 6H), 7.29 (t, J = 7.2 Hz, 1H), 7.23 (t, J = 7.2 Hz, 1H), 7.19 (d, J = 7.8 Hz, 1H), 7.05 (d, J = 6.6 Hz, 3H), 6.78 (s, 1H), 6.40-6.39 (m, 1H), 5.85 (s, 1H), 4.65 (d, J = 11.4 Hz, 1H), 4.26 (d, J = 10.8 Hz, 1H), 3.90 (dd, J = 9.0, 6.6 Hz, 1H), 3.60 (s, 3H), 3.58 (s, 3H), 3.26 (dd, J = 8.4, 6.6 Hz, 1H), 2.22-2.18 (m, 1H), 2.03 (s, 3H), 1.96-1.92 (m, 1H); ^{13}C NMR (DMSO-d_6, 150 MHz) δ 169.9, 169.5, 138.8, 133.5, 131.0, 129.1, 129.0, 128.6, 128.5, 128.1, 127.8, 127.1, 126.2, 125.8, 108.5, 52.8, 50.1, 47.6, 44.1, 30.0, 12.8; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{33}H_{32}NO_4$ $[M+H]^+$ 506.2326, found 506.2328.

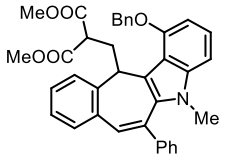


Dimethyl 2-((1-fluoro-5-methyl-6-phenyl-5,12-dihydrobenzo[4,5]cyclohepta[1,2-*b*]indol-12-yl)methyl)malonate (**3ag**): white solid (91% yield, 44.0 mg, 0.091 mmol); m.p. 190-192 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.62 (d, J = 7.2 Hz, 1H), 7.57-7.51 (m, 4H), 7.46-7.43 (m, 2H), 7.39 (t, J = 6.8 Hz, 1H), 7.32 (t, J = 7.2 Hz, 1H), 7.22-7.12 (m, 2H), 6.87 (dd, J = 11.6, 7.2Hz, 1H), 4.71 (dd, J = 9.6, 6.4 Hz, 1H), 3.59 (s, 3H), 3.41 (s, 3H), 3.31 (t, J = 7.6 Hz, 1H), 3.07 (s, 3H), 2.42-2.35 (m, 1H), 2.14-2.07 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.7, 169.2, 156.7 (d, $J_{C\text{-}F}$ = 243.7 Hz), 142.7, 141.8, 141.7, 134.1, 133.4, 133.2, 131.4, 129.7, 129.5, 128.5, 127.9, 126.7, 123.3 (d, $J_{C\text{-}F}$ = 6.9 Hz), 116.6 (d, $J_{C\text{-}F}$ = 3.8 Hz), 114.4 (d, $J_{C\text{-}F}$ = 17.6 Hz), 107.1, 105.1 (d, $J_{C\text{-}F}$ = 18.9 Hz), 52.7 (d, J = 5.7 Hz), 50.3, 41.5 (d, J = 4.2 Hz), 33.1, 29.6; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{30}H_{26}FKNO_4$ $[M+K]^+$ 522.1477, found 522.1476.

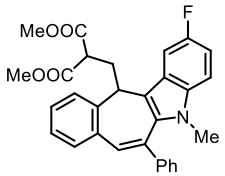


Dimethyl 2-((1-hydroxy-5-methyl-6-phenyl-5,12-dihydrobenzo[4,5]cyclohepta[1,2-*b*]indol-12-yl)methyl)malonate (**3ah**): white solid (91% yield, 43.8 mg, 0.091 mmol); m.p. 230-232 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 9.75 (s, 1H), 7.57-7.42 (m, 6H), 7.37-7.26 (m, 3H), 7.21(d, J = 7.2 Hz, 1H), 6.94 (t, J = 8.0 Hz, 1H), 6.74 (d, J = 8.0 Hz, 1H), 6.42 (d, J = 7.6 Hz, 1H), 5.18 (dd,

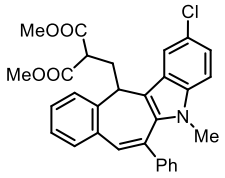
J = 9.2, 6.4 Hz, 1H), 3.60 (s, 3H), 3.44 (s, 3H), 3.26 (t, *J* = 7.6 Hz, 1H), 2.97 (s, 3H), 2.30-2.22 (m, 1H), 2.08-1.99 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 170.1, 169.2, 152.9, 143.2, 142.3, 141.5, 134.4, 133.9, 131.9, 131.1(4), 131.1(2), 129.4, 129.2, 128.2, 127.8, 126.3, 123.8, 119.7, 115.3, 104.4, 101.5, 52.7, 52.6 (d, *J* = 4.0 Hz), 50.3, 32,8 (d, *J* = 4.2 Hz), 29.7; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{30}H_{27}NNaO_5$ $[M+Na]^+$ 504.1781, found 504.1783.



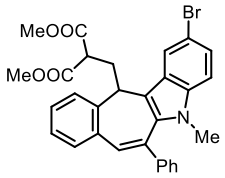
Dimethyl 2-((1-(benzyloxy)-5-methyl-6-phenyl-5,12-dihydro-benzo[4,5]cyclohepta[1,2-*b*]indol-12-yl)methyl)malonate (**3ai**): white solid (96% yield, 54.8 mg, 0.096 mmol); m.p. 71-73 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.63 (d, *J* = 7.2 Hz, 2H), 7.58-7.47 (m, 7H), 7.44-7.38 (m, 2H), 7.34 (t, *J* = 6.4 Hz, 2H), 7.27 (t, *J* = 6.8 Hz, 1H), 7.07 (t, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.69 (d, *J* = 7.6 Hz, 1H), 5.32 (dd, *J* = 23.2, 12.0 Hz, 2H), 5.16 (dd, *J* = 9.6, 6.8 Hz, 1H), 3.42 (s, 3H), 3.33 (s, 3H), 3.18 (t, *J* = 7.6 Hz, 1H), 3.00 (s, 3H), 2.33-2.26 (m, 1H), 2.07-2.00 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.8, 169.1, 153.8, 143.1, 142.1, 140.9, 137.9, 134.3, 133.8, 132.4, 131.8, 131.2, 129.4, 129.2, 129.0, 128.3, 128.0, 127.8, 126.4, 119.3, 115.8, 103.7, 101.9, 70.0, 52.6, 50.4, 41.2 (d, *J* = 4.5 Hz), 32.9 (d, *J* = 4.0 Hz), 29.6; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{37}H_{34}NO_5$ $[M+H]^+$ 572.2431, found 572.2432.



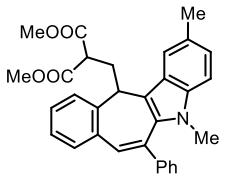
Dimethyl 2-((2-fluoro-5-methyl-6-phenyl-5,12-dihydrobenzo[4,5]cyclohepta[1,2-*b*]indol-12-yl)methyl)malonate (**3aj**): white solid (95% yield, 45.9 mg, 0.095 mmol); m.p. 179-181 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.61-7.51 (m, 6H), 7.45 (d, *J* = 7.2 Hz, 1H), 7.41-7.36 (m, 4H), 7.32-7.28 (m, 1H), 7.05 (td, *J* = 9.2, 2.4 Hz, 1H), 4.42 (dd, *J* = 9.2, 6.4 Hz, 1H), 3.56 (s, 3H), 3.38 (s, 3H), 3.33 (d, *J* = 8.0 Hz, 1H), 3.06 (s, 3H), 2.36-2.29 (m, 1H), 2.12-2.05 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.7, 169.4, 157.8 (d, *J* = 231.0 Hz), 142.5, 141.8, 136.1, 134.4, 134.2, 133.5, 133.2, 131.4, 129.5, 129.1, 128.4, 127.9, 126.5, 126.4, 126.3 (d, $J_{C\text{-}F}$ = 10.0 Hz), 119.1 (d, $J_{C\text{-}F}$ = 4.8 Hz), 111.5 (d, $J_{C\text{-}F}$ = 9.7 Hz), 111.1, 110.9, 103.3 (d, $J_{C\text{-}F}$ = 23.2 Hz), 52.8 (d, *J*= 4.1 Hz), 52.6, 50.3, 32.8, 29.8; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{30}H_{27}FNO_4$ $[M+H]^+$ 484.1919, found 484.1919.



Dimethyl 2-((2-chloro-5-methyl-6-phenyl-5,12-dihydrobenzo[4,5] cyclohepta[1,2-*b*]indol-12-yl)methyl)malonate (**3ak**): white solid (94% yield, 46.9 mg, 0.094 mmol); m.p. 146-148 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.82 (d, J = 1.6 Hz, 1H), 7.62-7.51 (m, 5H), 7.42-7.36 (m, 5H), 7.31 (t, J = 7.4 Hz, 1H), 7.20 (dd, J = 8.4, 1.6 Hz, 1H), 4.56 (dd, J = 9.2, 6.8 Hz, 1H), 3.56 (s, 3H), 3.37 (s, 3H), 3.33 (s,1H), 3.06 (s, 3H), 2.36-2.29 (m, 1H), 2.11-2.04 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.7, 169.4, 142.5, 141.7, 137.7, 134.1, 133.4, 131.4, 129.5, 129.2, 128.4, 127.9, 127.1, 126.6, 124.5, 122.7, 118.7, 117.9, 112.0, 52.8 (d, J = 3.8 Hz), 52.6, 50.3, 32.9, 29.8; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{30}H_{26}ClNNaO_4$ $[M+Na]^+$ 522.1443, found 522.1450.

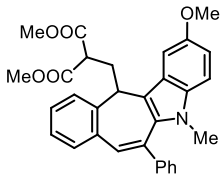


Dimethyl 2-((2-bromo-5-methyl-6-phenyl-5,12-dihydrobenzo[4,5] cyclohepta[1,2-*b*]indol-12-yl)methyl)malonate (**3al**): white solid (94% yield, 51.0 mg, 0.094 mmol); m.p. 151-153 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.96 (d, J = 1.6 Hz, 1H), 7.61-7.51 (m, 5H), 7.46-7.42 (m, 3H), 7.39-7.29 (m, 4H), 4.56 (dd, J = 9.2, 6.8 Hz, 1H), 3.56 (s, 3H), 3.37 (s, 3H), 3.33 (s, 1H), 3.06 (s, 3H), 2.36-2.28 (m, 1H), 2.10-2.03 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.7, 169.4, 142.5, 141.7, 138.0, 134.1, 133.6, 134.1, 134.0, 133.4, 133.3, 131.4, 129.5(5), 129.4(9), 128.4, 127.9, 127.8, 126.5, 125.2, 120.9, 118.6, 112.4, 112.3, 52.8 (d, J = 5.0 Hz), 52.6, 50.3, 32.8 (d, J = 3.1 Hz), 29.8; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{30}H_{26}BrKNO_4$ $[M+K]^+$ 582.0677, found 582.0666.

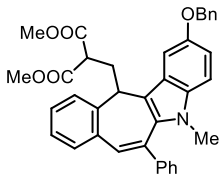


Dimethyl 2-((2,5-dimethyl-6-phenyl-5,12-dihydrobenzo[4,5]cyclo -hepta[1,2-*b*]indol-12-yl)methyl)malonate (**3am**): white solid (42% yield, 20.1 mg, 0.042 mmol); m.p. 153-155 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.60-7.43 (m, 7H), 7.37-7.35 (m, 3H), 7.33-7.28 (m, 1H), 7.25 (d, J = 8.4 Hz, 1H), 7.04 (d, J = 8.4 Hz, 1H), 4.50 (dd, J = 9.2, 6.8 Hz, 1H), 3.57 (s, 3H), 3.42 (s, 3H), 3.28 (dd, J = 8.4, 6.0 Hz, 1H), 3.04 (s, 3H), 2.46 (s, 3H), 2.30-2.27 (m, 1H), 2.12-2.05 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.7, 169.5, 142.4, 142.0, 138.0, 134.3, 133.9, 132.7, 132.3, 131.3, 129.4, 129.3, 129.1, 128.4, 127.9, 126.4, 126.3,

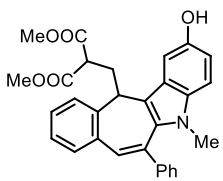
124.6, 118.7, 117.9, 110.1, 52.8 (d, *J* = 4.4 Hz), 52.7 (d, *J* = 2.3 Hz), 50.1, 32.6 (d, *J* = 2.6 Hz), 29.8, 21.7 (d, *J* = 5.1 Hz); HRMS (TOF-ESI$^+$) m/z: calcd for $C_{31}H_{29}NNaO_4$ $[M+Na]^+$ 502.1989, found 502.1988.



Dimethyl 2-((2-methoxy-5-methyl-6-phenyl-5,12-dihydrobenzo [4,5]cyclohepta[1,2-*b*]indol-12-yl)methyl)malonate (**3an**): white solid (79% yield, 39.1 mg, 0.079 mmol); m.p. 175-177 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.59-7.51 (m, 5H), 7.46-7.35 (m, 4H), 7.31-7.23 (m, 3H), 6.86 (dd, *J* = 8.8, 2.0 Hz, 1H), 4.51 (dd, *J* = 9.2, 6.4 Hz, 1H), 3.86 (s, 3H), 3.58 (s, 3H), 3.42 (s, 3H), 3.32 (dd, *J* = 8.4, 5.6 Hz, 1H), 3.03 (s, 3H), 2.35-2.28 (m, 1H), 2.13-2.06 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.8, 169.5, 154.2, 142.5, 142.0, 134.9, 134.3, 133.9, 133.2, 131.3, 129.4, 129.3, 129.1, 128.3, 127.9, 126.4, 118.9, 113.2, 111.1, 100.1, 56.0 (d, *J* = 5.4 Hz), 52.8 (d, *J* = 4.1 Hz), 52.7 (d, *J* = 2.3 Hz), 50.2, 32.6, 29.9; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{31}H_{29}KNO_5$ $[M+K]^+$ 534.1677, found 534.1677.

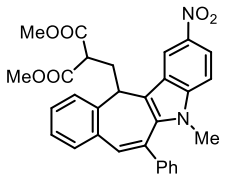


Dimethyl 2-((2-(benzyloxy)-5-methyl-6-phenyl-5,12-dihydrobenzo [4,5]cyclohepta[1,2-*b*]indol-12-yl)methyl)malonate (**3ao**): white solid (57% yield, 32.5 mg, 0.057 mmol); m.p. 159-161 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.60-7.51 (m, 7H), 7.44 (t, *J* = 7.4 Hz, 3H), 7.38-7.36 (m, 5H), 7.31-7.27 (m, 3H), 5.19 (dd, *J* = 24.8, 11.6 Hz, 2H), 4.51 (t, *J* = 8.4 Hz, 1H), 3.57 (s, 3H), 3.41 (s, 3H), 3.32 (d, *J* = 8.4 Hz, 1H), 3.03 (s, 3H), 2.34-2.2734 (m, 1H), 2.14-2.07 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.8, 169.5, 153.2, 142.5, 142.0, 138.1, 135.1, 134.3, 133.8, 133.3, 132.4, 131.3, 129.4, 129.3, 129.1, 128.9, 128.3, 128.2, 127.9, 126.4, 119.0, 113.6, 111.1, 102.1, 70.5, 52.8 (d, *J* = 5.4 Hz), 52.7 (d, *J* = 2.7 Hz), 50.3, 32.7 (d, *J* = 3.9 Hz), 29.9; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{37}H_{34}NO_5$ $[M+H]^+$ 572.2431, found 572.2440.

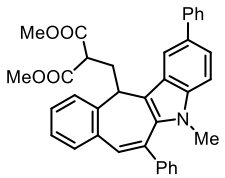


Dimethyl 2-((2-hydroxy-5-methyl-6-phenyl-5,12-dihydrobenzo[4,5] cyclohepta[1,2-*b*]indol-12-yl)methyl)malonate (**3ap**): white solid

(64% yield, 30.8 mg, 0.064 mmol); m.p. 229-230 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.90 (s, 1H), 7.58 (d, J = 7.6 Hz, 1H), 7.53-7.50 (m, 4H), 7.44 (d, J = 5.6 Hz, 1H), 7.38-7.28 (m, 4H), 7.16 (d, J = 8.8 Hz, 1H), 6.99 (s, 1H), 6.73 (d, J = 8.8 Hz, 1H), 4.37 (d, J = 8.0 Hz, 1H), 3.59 (s, 3H), 3.46 (s, 3H), 3.25 (t, J = 7.6 Hz, 1H), 3.00 (s, 3H), 2.30-2.23 (m, 1H), 2.12-2.05 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.8, 169.5, 151.6, 142.4, 142.1, 134.3, 134.0, 133.0, 132.1, 131.3, 129.4, 129.3, 129.0, 128.3, 127.9, 126.8, 126.4, 118.3, 113.5, 110.8, 102.0, 52.8 (d, J = 4.8 Hz), 52.7 (d, J = 3.3 Hz), 50.0, 32.6, 29.8; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{30}H_{27}KNO_5$ $[M+K]^+$ 520.1521, found 520.1520.

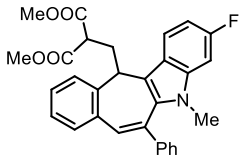


Dimethyl 2-((5-methyl-2-nitro-6-phenyl-5,12-dihydrobenzo[4,5]cyclohepta[1,2-*b*]indol-12-yl)methyl)malonate (**3aq**): colorless oil (92% yield, 46.9 mg, 0.092 mmol); ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.44 (d, J = 2.0 Hz, 1H), 7.85-7.83 (m, 2H), 7.63-7.57 (m, 4H), 7.51-7.45 (m, 4H), 7.39 (t, J = 7.2 Hz, 1H), 7.28 (t, J = 7.6 Hz, 1H), 4.93 (dd, J = 9.2, 6.8 Hz, 1H), 3.91 (s, 3H), 3.55 (s, 3H), 3.53 (s, 3H), 3.21 (dd, J = 8.4, 6.0 Hz, 1H), 2.83-2.76 (m, 1H), 2.62-2.55 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.6, 169.4, 145.2, 142.6, 135.5, 133.9, 132.6, 131.7, 129.9, 129.4, 129.3, 127.9, 127.3, 122.7, 122.2, 118.9, 118.1, 114.3, 107.6, 94.1, 88.2, 53.0 (d, J = 4.8 Hz), 52.9 (d, J = 4.4 Hz), 49.8, 37.2, 34.8, 33.5 (d, J = 7.4 Hz); HRMS (TOF-ESI$^+$) m/z: calcd for $C_{30}H_{26}N_2NaO_6$ $[M+Na]^+$ 533.1683, found 533.1677.

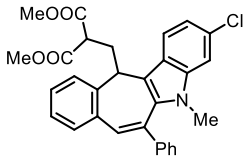


Dimethyl 2-((5-methyl-2,6-diphenyl-5,12-dihydrobenzo[4,5]cyclo-hepta[1,2-*b*]indol-12-yl)methyl)malonate (**3ar**): white solid (96% yield, 513.9 mg, 0.096 mmol); m.p. 114-116 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.03 (d, J = 1.2 Hz, 1H), 7.76 (d, J = 7.2 Hz, 2H), 7.61-7.49 (m, 8H), 7.46 (d, J = 5.6 Hz, 3H), 7.39-7.34 (m, 3H), 7.33-7.29 (m, 1H), 4.66 (dd, J = 9.2, 6.0 Hz, 1H), 3.52 (s, 3H), 3.40 (d, J = 2.8 Hz, 1H), 3.35 (s, 3H), 3.10 (s, 3H), 2.39-2.32 (m, 1H), 2.13-2.06 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.7, 169.5, 142.6, 141.9, 139.0, 134.3, 133.7, 133.4, 132.8, 132.3, 131.3, 129.5, 129.3, 128.4, 128.0,

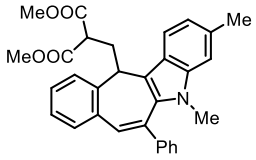
127.2, 126.7, 126.5, 122.3, 119.7, 116.7, 110.7, 52.7, 52.6, 50.4, 32.8, 29.9; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{36}H_{21}KNO_4$ $[M+K]^+$ 580.1885, found 580.1882.



Dimethyl 2-((3-fluoro-5-methyl-6-phenyl-5,12-dihydrobenzo[4,5] cyclohepta[1,2-*b*]indol-12-yl)methyl)malonate (**3as**): white solid (95% yield, 45.9 mg, 0.095 mmol); m.p. 195-197 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.74 (dd, J = 8.8, 5.6 Hz, 1H), 7.60-7.51 (m, 5H), 7.45 (t, J = 6.8 Hz, 1H), 7.37-7.35 (m, 3H), 7.32-7.28 (m, 1H), 7.25 (dd, J = 10.4, 2.0 Hz, 1H), 4.54 (dd, J = 9.2, 6.4 Hz, 1H), 3.56 (s, 3H), 3.40 (s, 3H), 3.32 (dd, J = 8.8, 6.4 Hz, 1H), 3.03 (s, 3H), 2.34-2.28 (m, 1H), 2.11-2.04 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.7, 169.4, 160.2 (d, $J_{C\text{-}F}$ = 235.0 Hz), 142.3, 141.8, 139.5 (d, $J_{C\text{-}F}$ = 12.5 Hz), 134.2, 133.5, 133.2 (d, $J_{C\text{-}F}$ = 3.6 Hz), 132.5, 131.4, 129.5, 129.1, 128.4, 128.0, 126.5, 122.9, 119.8 (d, $J_{C\text{-}F}$ = 10.4 Hz), 108.2 (d, $J_{C\text{-}F}$ = 21.8 Hz), 96.8 (d, $J_{C\text{-}F}$ = 24.0 Hz), 52.8 (d, J = 4.9 Hz), 52.6 (d, J = 2.3 Hz), 50.2, 32.9 (d, J = 3.4 Hz), 29.6; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{30}H_{26}FNNaO_4$ $[M+Na]^+$ 506.1738, found 506.1738.

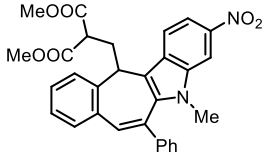


Dimethyl 2-((3-chloro-5-methyl-6-phenyl-5,12-dihydrobenzo[4,5] cyclohepta[1,2-*b*]indol-12-yl)methyl)malonate (**3at**): white solid (94% yield, 46.9 mg, 0.094 mmol); m.p. 208-210 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.75 (d, J = 8.4 Hz, 1H), 7.61-7.51 (m, 6H), 7.47-7.29 (m, 5H), 7.16 (d, J = 8.8 Hz, 1H), 4.54 (t, J = 8.8 Hz, 1H), 3.56 (s, 3H), 3.40 (s, 3H), 3.31 (t, J = 7.6 Hz, 1H), 3.06 (s, 3H), 2.35-2.28 (m, 1H), 2.12-2.05 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.7, 169.4, 142.3, 141.7, 139.7, 134.2, 133.6, 133.4, 133.1, 131.4, 129.5(4), 129.4(8), 129.1, 128.4, 127.9, 127.8, 126.6, 124.8, 120.1, 119.9, 119.1, 110.3, 52.8 (d, J = 4.3 Hz), 52.7 (d, J = 2.0 Hz), 50.2, 32.9, 29.7; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{30}H_{27}ClNO_4$ $[M+H]^+$ 500.1623, found 500.1633.

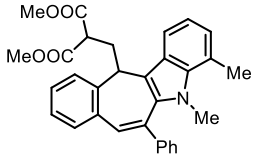


Dimethyl 2-((3,5-dimethyl-6-phenyl-5,12-dihydrobenzo[4,5] cyclohepta[1,2-*b*]indol-12-yl)methyl)malonate (**3au**): white solid (48% yield, 23.0 mg, 0.048 mmol); m.p. 169-171 °C; ^{1}H NMR

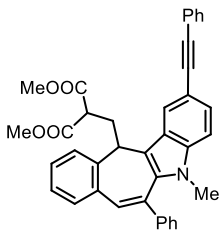
(DMSO-d_6, 400 MHz) δ 7.60-7.50 (m, 6H), 7.46-7.44 (m, 1H), 7.36-7.29 (m, 4H), 7.26 (s, 1H), 6.98 (d, J = 8.0 Hz, 1H), 4.50 (dd, J = 8.8, 6.8 Hz, 1H), 3.57 (s, 3H), 3.43 (s, 3H), 3.26 (dd, J = 8.0, 6.0 Hz, 1H), 3.03 (s, 3H), 2.43 (s, 3H), 2.30-2.27 (m, 1H), 2.11-2.04 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.7, 169.5, 142.4, 142.1, 139.9, 134.3, 133.9, 132.4, 132.0, 131.3, 129.4, 129.3, 129.1, 128.3, 127.9, 126.4, 124.1, 121.5, 119.1, 118.2, 110.1, 52.8 (d, J = 4.3 Hz), 52.7 (d, J = 2.0 Hz), 50.1, 32.6, 29.7, 22.1 (d, J = 4.8 Hz); HRMS (TOF-ESI$^+$) m/z: calcd for $C_{31}H_{29}KNO_4$ $[M+K]^+$ 518.1728, found 518.1727.



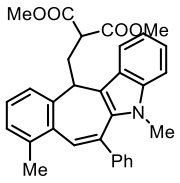
Dimethyl 2-((5-methyl-3-nitro-6-phenyl-5,12-dihydrobenzo[4,5]cyclohepta[1,2-*b*]indol-12-yl)methyl)malonate (**3av**): white solid (84% yield, 42.8 mg, 0.084 mmol); m.p. 94-96 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.53 (d, J = 2.0 Hz, 1H), 8.00 (dd, J = 8.8, 6.8 H, 1H), 7.70 (s, 1H), 7.61-7.57 (m, 4H), 7.50-7.38 (m, 5H), 7.28 (t, J = 7.6 Hz, 1H), 4.94 (t, J = 8.8 Hz, 1H), 3.85 (s, 3H), 3.53 (d, J = 3.2 Hz, 6H), 3.28 (t, J = 6.8 Hz, 1H), 2.79-2.72 (m, 1H), 2.61-2.55 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.6, 169.4, 145.1, 140.9, 139.8, 132.6, 131.8, 130.9, 130.0, 129.4, 129.2, 127.9, 127.4, 126.6, 122.6, 122.2, 120.0, 117.1, 115.8, 111.1, 94.2, 88.0, 55.4, 52.9 (t, J = 4.8 Hz), 49.9, 36.9, 34.9, 33.5 (d, J = 6.7 Hz); HRMS (TOF-ESI$^+$) m/z: calcd for $C_{30}H_{26}N_2NaO_6$ $[M+Na]^+$ 533.1683, found 533.1680.



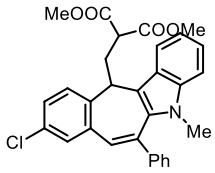
Dimethyl 2-((4,5-dimethyl-6-phenyl-5,12-dihydrobenzo[4,5]cyclohepta[1,2-*b*]indol-12-yl)methyl)malonate (**3aw**): white solid (67% yield, 32.1 mg, 0.067 mmol); m.p. 186-188 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.57 (t, J = 8.0 Hz, 3H), 7.51 (t, J = 7.4 Hz, 3H), 7.41 (t, J = 8.4 Hz, 2H), 7.37-7.32 (m, 2H), 7.31-7.27 (m, 1H), 6.99 (t, J = 7.2 Hz, 1H), 6.91 (d, J = 6.8 Hz, 1H), 4.46 (dd, J = 8.8, 7.2 Hz, 1H), 3.54 (s, 3H), 3.29 (s, 3H), 3.22 (dd, J = 8.0, 5.6 Hz, 1H), 2.60 (s, 3H), 2.27-2.21 (m, 1H), 2.11-2.04 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.7, 169.4, 142.6, 142.2, 138.7, 134.3, 133.7, 133.6, 132.6, 131.3, 129.5, 129.3, 129.1, 128.2, 127.6, 127.1, 126.5, 126.0, 121.8, 119.9, 119.8, 116.4, 52.8 (d, J = 4.9 Hz), 52.7 (d, J = 3.0 Hz), 50.1, 35.7, 29.6, 20.2; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{31}H_{29}KNO_4$ $[M+K]^+$ 518.1728, found 518.1727.



Dimethyl 2-((5-methyl-6-phenyl-2-(phenylethynyl)-5,12-dihydro benzo[4,5]cyclohepta[1,2-*b*]indol-12-yl)methyl)malonate (**3ax**): white solid (78% yield, 44.1 mg, 0.078 mmol); m.p. 166-168 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.57 (t, J = 8.0 Hz, 3H), 7.51 (t, J = 7.4 Hz, 3H), 7.41 (t, J = 8.4 Hz, 2H), 7.37-7.32 (m, 2H), 7.31-7.27 (m, 1H), 6.99 (t, J = 7.2 Hz, 1H), 6.91 (d, J = 6.8 Hz, 1H), 4.46 (dd, J = 8.8, 7.2 Hz, 1H), 3.54 (s, 3H), 3.29 (s, 3H), 3.22 (dd, J = 8.0, 5.6 Hz, 1H), 2.60 (s, 3H), 2.27-2.21 (m, 1H), 2.11-2.04 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.7, 169.4, 142.6, 142.2, 138.7, 134.3, 133.7, 133.6, 132.6, 131.3, 129.5, 129.3, 129.1, 128.2, 127.6, 127.1, 126.5, 126.0, 121.8, 119.9, 119.8, 116.4, 52.8 (d, J = 4.9 Hz), 52.7 (d, J = 3.0 Hz), 50.1, 35.7, 29.6, 20.2; HRMS (TOF-ESI^{+}) m/z: calcd for $C_{38}H_{31}KNO_4$ $[M+K]^{+}$ 604.1885, found 604.1885.

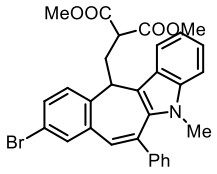


Dimethyl 2-((5,8-dimethyl-6-phenyl-5,12-dihydrobenzo[4,5]cyclo -hepta[1,2-*b*]indol-12-yl)methyl)malonate (**3ay**): white solid (70% yield, 33.5 mg, 0.07 mmol); m.p. 163-165 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.69 (d, J = 8.4 Hz, 1H), 7.54-7.52 (m, 4H), 7.46-7.44 (m, 1H), 7.35 (d, J = 9.6Hz, 2H), 7.24 (t, J = 7.2 Hz, 1H), 7.19 (t, J = 7.2 Hz, 2H), 7.14-7.11 (m, 2H), 4.49 (dd, J = 9.6, 6.6 Hz, 1H), 3.55 (s, 3H), 3.39 (s, 3H), 3.28 (dd, J = 8.4, 6.6 Hz, 1H), 3.08 (s, 3H), 2.52 (s, 3H), 2.35-2.31 (m, 1H), 2.13-2.08 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 169.8, 169.5, 143.7, 142.2, 139.2, 137.9, 133.7, 132.6, 132.5, 130.4, 129.5, 129.3, 128.5, 128.0, 127.1, 126.0, 123.0, 119.7, 119.5, 118.4, 100.2, 52.8, 52.6, 50.3, 32.4, 29.2, 21.2; HRMS (TOF-ESI^{+}) m/z: calcd for $C_{31}H_{30}NO_4$ $[M+H]^{+}$ 480.2169, found 480.2176.

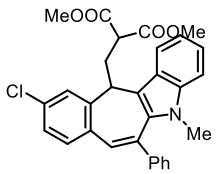


Dimethyl 2-((9-chloro-5-methyl-6-phenyl-5,12-dihydrobenzo[4,5] cyclohepta[1,2-*b*]indol-12-yl)methyl)malonate (**3az**): white solid (96% yield, 47.9 mg, 0.096 mmol); m.p. 158-160 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.74 (d, J = 7.6 Hz, 1H), 7.69 (s, 1H), 7.56-7.50 (m, 4H), 7.46-7.40 (m, 5H), 7.21(t, J = 7.6 Hz, 1H), 7.13 (t, J = 7.6 Hz, 1H), 4.57 (t, J = 8.4 Hz, 1H), 3.54 (s, 3H), 3.37 (s, 3H), 3.30 (d, J = 6.4 Hz, 1H), 3.05 (s, 3H), 2.32-2.25 (m, 1H), 2.12-2.05 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.7, 169.4, 151.4, 141.6, 141.2, 139.5, 136.3, 135.0,

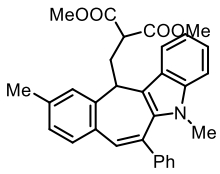
132.5, 131.0, 130.9, 130.5, 129.5, 128.8, 128.6, 128.0, 125.9, 123.2, 119.8, 119.2, 118.6, 110.4, 52.8 (d, *J* = 4.6 Hz), 52.7 (d, *J* = 2.0 Hz), 50.2, 32.6, 29.6; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{30}H_{26}ClKNO_4$ $[M+K]^+$ 538.1182, found 538.1182.



Dimethyl 2-((9-bromo-5-methyl-6-phenyl-5,12-dihydrobenzo[4,5]cyclohepta[1,2-*b*]indol-12-yl)methyl)malonate (**3ba**): white solid (88% yield, 47.8 mg, 0.088 mmol); m.p. 143-145 °C; ^{1}H NMR (DMSO-d_6, 600 MHz) δ 7.83 (d, *J* = 1.8 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.56-7.51 (m, 5H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.36-7.33 (m, 3H), 7.21(t, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 7.8 Hz, 1H), 4.56 (dd, *J* = 9.0, 7.2 Hz, 1H), 3.54 (s, 3H), 3.37 (s, 3H), 3.31 (dd, *J* = 7.8, 6.6 Hz, 1H), 3.05 (s, 3H), 2.30-2.25 (m, 1H), 2.11-2.06 (m, 1H); ^{13}C NMR (DMSO-d_6, 150 MHz) δ 169.7, 169.4, 141.6, 141.5, 139.5, 136.7, 135.0, 133.4, 132.5, 131.7, 130.9, 129.5, 128.6, 128.0, 125.9, 123.2, 119.8, 119.2(5), 119.1(9), 118.6, 110.4, 52.8, 52.7, 50.2, 39.4, 32.7, 29.3; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{30}H_{26}BrNNaO_4$ $[M+Na]^+$ 566.0937, found 566.0951.

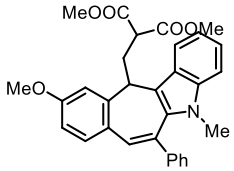


Dimethyl 2-((10-chloro-5-methyl-6-phenyl-5,12-dihydrobenzo[4,5]cyclohepta[1,2-*b*]indol-12-yl)methyl)malonate (**3bb**): white solid (83% yield, 41.4 mg, 0.083 mmol); m.p. 155-157 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.77 (d, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.50-7.56 (m, 5H), 7.46-7.42 (m, 1H), 7.37-7.34 (m, 3H), 7.21(t, *J* = 7.2 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 4.57 (dd, *J* = 9.2, 6.8 Hz, 1H), 3.55 (s, 3H), 3.37 (s, 3H), 3.33 (dd, *J* = 8.4, 6.0 Hz, 1H), 3.06 (s, 3H), 2.33-2.26 (m, 1H), 2.13-2.06 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.6, 169.4, 144.1, 141.7, 139.5, 134.3, 133.8, 133.3, 133.0, 132.6, 131.3, 129.5, 128.6, 128.5, 127.9, 126.3, 126.0, 123.2, 119.8, 118.8, 118.7, 110.3, 52.8, 52.6, 50.2, 32.6, 29.4, 19.0; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{30}H_{26}ClKNO_4$ $[M+K]^+$ 538.1182, found 538.1182.

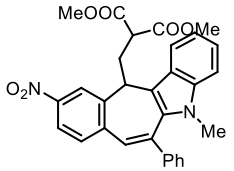


Dimethyl 2-((5,10-dimethyl-6-phenyl-5,12-dihydrobenzo[4,5]cyclo-hepta[1,2-*b*]indol-12-yl)methyl)malonate (**3bc**): white solid (77% yield, 36.9 mg, 0.077 mmol); m.p. 159-161 °C; ^{1}H NMR ($CDCl_3$, 400

MHz) δ 7.67 (d, *J* = 8.0 Hz, 1H), 7.51(d, *J* = 7.2 Hz, 2H), 7.44 (t, *J* = 7.2 Hz, 2H), 7.38-7.36 (m, 2H), 7.25-7.14 (m, 5H), 7.06 (d, *J* = 7.6 Hz, 1H), 4.51 (dd, *J* = 9.2, 6.8 Hz, 1H), 3.67 (s, 3H), 3.55 (s, 3H), 3.27 (dd, *J* = 8.8, 5.2 Hz, 1H), 3.09 (s, 3H), 2.46-2.29 (m, 1H), 2.35 (s, 3H), 2.31-2.24 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.0, 169.8, 142.3, 142.2, 139.4, 139.2, 133.2, 132.8, 132.5, 131.3, 130.8, 129.7, 128.9, 127.7, 127.6, 126.9, 126.4, 122.6, 119.4, 118.9, 118.0, 109.4, 52.4 (t, *J* = 5.7 Hz), 50.2, 49.9, 32.4, 29.5, 21.2 (d, *J* = 4.6 Hz); HRMS (TOF-ESI$^+$) m/z: calcd for $C_{31}H_{29}KNO_4$ $[M+K]^+$ 518.1728, found 518.1728.

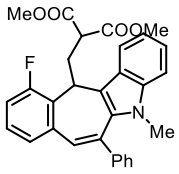


Dimethyl 2-((10-methoxy-5-methyl-6-phenyl-5,12-dihydrobenzo [4,5]cyclohepta[1,2-*b*]indol-12-yl)methyl)malonate (**3bd**): white solid (91% yield, 45.0 mg, 0.091 mmol); m.p. 160-162 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.72 (d, *J* = 8.0 Hz, 1H), 7.56-7.41 (m, 6H), 7.35 (t, *J* = 4.0 Hz, 2H), 7.23-7.19 (m, 2H), 7.16-7.11 (m, 2H), 4.49 (dd, *J* = 9.2, 6.8 Hz, 1H), 3.59 (s, 3H), 3.41 (s, 3H), 3.30 (dd, *J* = 8.0, 6.0 Hz, 1H), 3.07 (s, 3H), 2.34 (s, 3H), 2.34-2.28 (m, 1H), 2.12-2.05 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.8, 169.5, 142.4, 142.0, 139.3, 139.1, 133.0, 132.8, 132.6, 131.6, 131.4, 129.6, 129.4, 128.2, 127.9, 127.2, 126.2, 122.9, 119.7, 118.8, 118.4, 110.2, 52.8 (d, *J* = 5.3 Hz), 52.6 (d, *J* = 2.5 Hz), 50.2, 32.6 (d, *J* = 2.9 Hz), 29.9, 21.2 (d, *J* = 5.2 Hz); HRMS (TOF-ESI$^+$) m/z: calcd for $C_{31}H_{29}KNO_5$ $[M+K]^+$ 534.1677, found 434.1691.

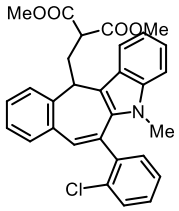


Dimethyl 2-((5-methyl-10-nitro-6-phenyl-5,12-dihydrobenzo[4,5] cyclohepta[1,2-*b*]indol-12-yl)methyl)malonate (**3be**): white solid (49% yield, 25.0 mg, 0.049 mmol); m.p. 155-157 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.39 (d, *J* = 2.0 Hz, 1H), 8.14 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.89 (dd, *J* = 10.8, 8.4 Hz, 2H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.6 Hz, 2H), 7.50 (t, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.25 (t, *J* = 7.2 Hz, 1H), 7.17 (t, *J* = 7.2 Hz, 1H), 4.88 (dd, *J* = 8.8, 6.8 Hz, 1H), 3.54 (s, 3H), 3.44 (dd, *J* = 8.8, 6.4 Hz, 1H), 3.34 (s, 3H), 2.40-2.33 (m, 1H), 2.19-2.12 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.6, 169.3, 147.6, 143.1, 141.4, 141.0, 139.8, 137.1, 132.5, 132.4, 130.5, 129.5, 129.0, 128.1, 125.8, 123.9, 123.6, 121.2, 120.0, 119.3, 119.2, 110.4, 52.8 (d, *J* = 5.4 Hz), 52.6 (d, *J* = 1.2 Hz),

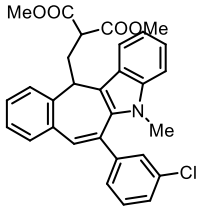
50.3, 32.7 (d, J = 3.4 Hz), 29.1; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{30}H_{26}N_2NaO_6$ $[M+Na]^+$ 533.1683, found 533.1687.



Dimethyl 2-((11-fluoro-5-methyl-6-phenyl-5,12-dihydrobenzo[4,5] cyclohepta[1,2-*b*]indol-12-yl)methyl)malonate (**3bf**): white solid (93% yield, 44.9 mg, 0.093 mmol); m.p. 196-198 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.76 (d, J = 8.4 Hz, 1H), 7.51(d, J = 6.8 Hz, 2H), 7.53 (t, J = 7.2 Hz, 2H), 7.41-7.37 (m, 1H), 7.25-7.14 (m, 6H), 7.06 (t, J = 9.2 Hz, 1H), 5.20 (t, J = 7.6 Hz, 1H), 3.65 (s, 3H), 3.56 (s, 3H), 3.30 (dd, J = 8.4, 6.4 Hz, 1H), 3.10 (s, 3H), 2.51-2.43 (m, 1H), 2.34-2.27 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.7, 169.6, 159.4 (d, J_{C-F} = 241.3 Hz), 141.9, 139.4, 136.9, 136.8 (d, J_{C-F} = 3.4 Hz), 134.9, 133.1, 131.4, 129.5, 129.4 (d, J_{C-F} = 16.2 Hz), 129.0, 128.0, 127.7, 126.6 (d, J_{C-F} = 8.6 Hz), 126.2(5), 126.1(7), 122.9, 119.7, 119.1, 118.5, 114.8 (d, J_{C-F} = 24.7 Hz), 109.4, 52.5 (d, J = 5.3 Hz), 52.4 (d, J = 4.4 Hz), 50.0, 32.4, 29.0, 28.8 (d, J = 18.6 Hz); HRMS (TOF-ESI$^+$) m/z: calcd for $C_{30}H_{26}FNNaO_4$ $[M+Na]^+$ 506.1738, found 506.1749.

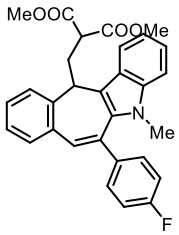


Dimethyl 2-((6-(2-chlorophenyl)-5-methyl-5,12-dihydrobenzo[4,5] cyclohepta[1,2-*b*]indol-12-yl)methyl)malonate (**3bg**): white solid (92% yield, 45.9 mg, 0.092 mmol); m.p. 159-161 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.90 (s, 1H), 7.68-7.50 (m, 5H), 7.45 (t, J = 7.2 Hz, 2H), 7.38-7.31 (m, 2H), 7.26 (s, 1H), 7.21 (t, J = 7.2 Hz, 1H), 7.13 (t, J = 7.6 Hz, 1H), 4.55 (t, J = 7.2 Hz, 1H), 3.65 (s, 3H), 3.58 (s, 3H), 3.10 -3.05 (m, 4H), 2.44-2.39 (m, 1H), 2.16-2.09 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.5, 141.8, 140.5, 139.2, 133.9, 132.8, 132.1, 131.7, 130.4, 130.0, 129.2, 126.6, 126.3, 123.1, 119.7, 118.4, 110.2, 52.9(2), 52.8(6), 49.9, 31.7, 29.2; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{30}H_{26}ClNNaO_4$ $[M+Na]^+$ 522.1443, found 522.1454.

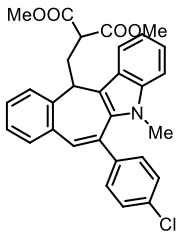


Dimethyl 2-((6-(3-chlorophenyl)-5-methyl-5,12-dihydrobenzo[4,5] cyclohepta[1,2-*b*]indol-12-yl)methyl)malonate (**3bh**): white solid (88% yield, 43.9 mg, 0.088 mmol); m.p. 167-169 °C; ^{1}H NMR ($CDCl_3$, 400

MHz) δ 7.68 (d, *J* = 7.6 Hz, 2H), 7.51 (s, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.40-7.37 (m, 3H), 7.33 (d, *J* = 4.0 Hz, 2H), 7.22 (s, 1H), 7.25-7.20 (m, 3H), 7.18-7.14 (m, 1H), 4.56 (dd, *J* = 8.2, 6.8 Hz, 1H), 3.66 (s, 3H), 3.56 (s, 3H), 3.26 (dd, *J* = 8.8, 5.6 Hz, 1H), 3.13 (s, 3H), 2.44-2.37 (m, 1H), 2.32-2.25 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.0, 169.7, 144.0, 142.3, 139.4, 134.8, 133.7, 133.1, 132.5, 132.0, 130.8, 130.2, 129.3, 129.1, 127.8, 126.2, 126.1, 122.9, 119.6, 118.1, 109.4, 52.4 (t, *J* = 4.3 Hz) , 49.8, 40.3, 32.5, 29.5; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{30}H_{26}ClNNaO_4$ $[M+Na]^+$ 522.1443, found 522.1455.

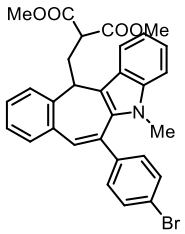


Dimethyl 2-((6-(4-fluorophenyl)-5-methyl-5,12-dihydrobenzo[4,5] cyclohepta[1,2-*b*]indol-12-yl)methyl)malonate (**3bi**): white solid (95% yield, 45.9 mg, 0.095 mmol); m.p. 162-164 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.62-7.59 (m, 3H), 7.38-7.37 (m, 6H), 7.32-7.28 (m, 1H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 4.54 (t, *J* = 8.8 Hz, 1H), 3.56 (s, 3H), 3.32 (t, *J* = 7.2 Hz, 1H), 3.09 (s, 3H), 2.35-2.29 (m, 1H), 2,10-2.03 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.8, 169.5, 162.3 (d, $J_{C\text{-}F}$ = 243.2 Hz), 142.5, 139.4, 138.3, 134.2, 132.6, 132.5, 131.3, 130.0 (d, $J_{C\text{-}F}$ = 7.5 Hz), 129.5, 129.0, 126.5, 126.1, 123.1, 119.8, 119.2, 118.5, 116.3 (d, $J_{C\text{-}F}$ = 21.2 Hz), 110.3, 52.8 (d, *J* = 3.6 Hz), 52.6, 50.2, 32.7, 29.7; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{30}H_{26}FNNaO_4$ $[M+Na]^+$ 506.1738, found 506.1751.

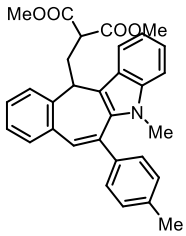


Dimethyl 2-((6-(4-chlorophenyl)-5-methyl-5,12-dihydrobenzo[4,5] cyclohepta[1,2-*b*]indol-12-yl)methyl)malonate (**3bj**): white solid (90% yield, 44.9 mg, 0.090 mmol); m.p. 177-179 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.73 (d, *J* = 7.6 Hz, 1H), 7.61-7.59 (m, 5H), 7.43 (s, 1H), 7.37 (t, *J* = 3.6 Hz, 3H), 7.32-7.28 (m, 1H), 7.22 (t, *J* = 7.2 Hz, 1H), 714 (t, *J* = 7.2 Hz, 1H), 4.54 (dd, *J* = 8.8, 6.4 Hz, 1H), 3.56 (s, 3H), 3.37 (s, 3H), 3.31 (t, *J* = 8.0 Hz, 1H), 3.10 (s, 3H), 2.60-2.33 (m, 1H), 2.10-2.003 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.7, 169.5, 142.6, 140.7, 139.4, 134.1, 133.0, 132.4, 132.2, 131.4, 129.7, 129.6, 129.5, 129.1, 126.5, 126.1, 123.1, 119.8, 119.4, 118.5, 110.3, 52.8 (d, *J* = 3.6 Hz), 52.6 (d, *J* =

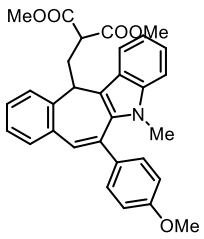
1.2 Hz), 50.2, 32.8, 29.7; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{30}H_{26}ClNNaO_4$ $[M+Na]^+$ 522.1443, found 522.1445.



Dimethyl 2-((6-(4-bromophenyl)-5-methyl-5,12-dihydrobenzo[4,5] cyclohepta[1,2-*b*]indol-12-yl)methyl)malonate (**3bk**): white solid (92% yield, 50.0 mg, 0.092 mmol); m.p. 174-176 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.73 (d, J = 8.4 Hz, 3H), 7.60 (d, J = 7.6 Hz, 1H), 7.52 (d, J = 8.0 Hz, 2H), 7.43-7.36 (m, 4H), 7.32-7.28 (m, 1H), 7.22 (t, J = 7.2 Hz, 1H), 7.14 (t, J = 7.6 Hz, 1H), 4.54 (dd, J = 8.8, 6.8 Hz, 1H), 3.56 (s, 3H), 3.30 (t, J = 7.60 Hz, 1H), 3.10 (s, 3H), 2.33-2.26 (m, 1H), 2.10-2.01 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.7, 169.5, 142.6, 141.1, 139.4, 134.1, 133.0, 132.5, 132.4, 132.1, 131.4, 130.0, 129.6, 129.1, 126.5, 126.1, 123.1, 121.6, 119.8, 119.4, 118.5, 110.3, 52.8 (d, J = 3.3 Hz), 52.6, 50.2, 32.8, 29.7; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{30}H_{26}BrNNaO_4$ $[M+Na]^+$ 566.0937, found 566.0947.

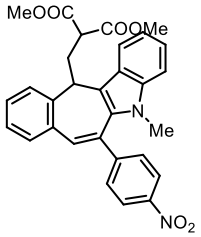


Dimethyl 2-((5-methyl-6-(p-tolyl)-5,12-dihydrobenzo[4,5]cyclohepta [1,2-*b*]indol-12-yl)methyl)malonate (**3bl**): white solid (98% yield, 46.9 mg, 0.098 mmol); m.p. 157-159 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.72 (d, J = 7.6 Hz, 1H), 7.58 (d, J = 7.2 Hz, 1H), 7.44 (d, J = 7.6 Hz, 2H), 7.36-7.27 (m, 7H), 7.21 (t, J = 7.2 Hz, 1H), 7.14 (t, J = 7.2 Hz, 1H), 4.53 (t, J = 8.8 Hz, 1H), 3.56 (s, 3H), 3.41 (s, 3H), 3.27 (t, J = 8.0 Hz, 1H), 3.08 (s, 3H), 2.40 (s, 3H), 2.33-2.26 (m, 1H), 2.13-2.05 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.7, 169.5, 142.4, 139.4, 139.1, 137.7, 134.3, 133.6, 132.7, 131.9, 131.2, 130.0, 129.3, 129.1, 127.8, 126.5, 126.1, 123.0, 119.7, 119.0, 118.4, 110.3, 52.8 (d, J = 3.9 Hz), 52.7 (d, J = 2.0 Hz), 50.2, 32.6, 29.6, 21.3 (d, J = 4.3 Hz); HRMS (TOF-ESI$^+$) m/z: calcd for $C_{31}H_{29}KNO_4$ $[M+K]^+$ 518.1728, found 318.1727.

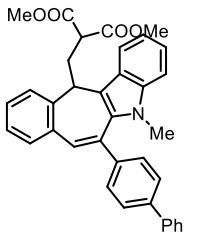


Dimethyl 2-((6-(4-methoxyphenyl)-5-methyl-5,12-dihydrobenzo[4,5] cyclohepta[1,2-*b*]indol-12-yl)methyl)malonate (**3bm**): white solid (78% yield, 38.6 mg, 0.078 mmol); m.p. 162-164 °C; ^{1}H NMR (DMSO-d_6, 400

MHz) δ 7.72 (d, *J* = 7.6 Hz, 1H), 7.57(d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.33-7.27 (m, 5H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.16-7.08 (m, 3H), 4.53 (dd, *J* = 8.8, 6.8 Hz, 1H), 3.85 (s, 3H), 3.57 (s, 3H), 3.40 (s, 3H), 3.29 (t, *J* = 7.2 Hz, 1H), 3.10 (s, 3H), 2.35-2.28 (m, 1H), 2.13-2.06 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.7, 169.5, 159.6, 142.2, 139.4, 134.4, 134.3, 133.4, 132.9, 131.3, 131.1, 129.1, 129.0, 126.4, 126.1, 123.0, 119.7, 119.0, 118.4, 114.9, 110.2, 55.8 (d, *J* = 7.5 Hz), 52.8 (d, *J* = 5.1 Hz), 52.6 (d, *J* = 2.3 Hz), 50.2, 32.6 (d, *J* = 2.4 Hz), 29.6; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{31}H_{29}KNO_5$ $[M+K]^+$ 534.1677, found 534.1676.

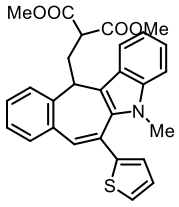


Dimethyl 2-((5-methyl-6-(4-nitrophenyl)-5,12-dihydrobenzo[4,5] cyclohepta[1,2-*b*]indol-12-yl)methyl)malonate (**3bn**): white solid (92% yield, 46.9 mg, 0.092 mmol); m.p. 72-74 °C; ^{1}H NMR (DMSO-d_6, 600 MHz) δ 8.33 (d, *J* = 9.0 Hz, 2H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.49-7.45 (m, 2H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.37 (t, *J* = 4.2 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.10 (t, *J* = 7.8 Hz, 1H), 6.93 (t, *J* = 7.8 Hz, 1H), 4.87 (t, *J* = 7.2 Hz, 1H), 3.76 (s, 3H), 3.53 (s, 3H), 3.30 (t, *J* = 6.6 Hz, 1H), 2.79-2.74 (m, 1H), 2.57-2.53 (m, 1H); ^{13}C NMR (DMSO-d_6, 150 MHz) δ 169.7, 169.5, 147.4, 146.6, 137.1, 132.9, 132.8, 137.0, 129.6, 128.1, 127.3, 127.2, 127.0, 124.6, 121.8, 121.2, 119.2, 118.7, 116.6, 110.3, 93.4, 92.2, 53.0, 52.9, 49.9, 37.5, 34.9, 32.9; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{30}H_{26}N_2NaO_6$ $[M+Na]^+$ 533.1683, found 533.1684.

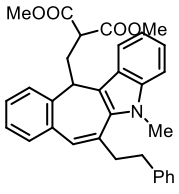


Dimethyl 2-((6-([1,1'-biphenyl]-4-yl)-5-methyl-5,12-dihydrobenzo[4,5] cyclohepta[1,2-*b*]indol-12-yl)methyl)malonate (**3bo**): white solid (96% yield, 51.9 mg, 0.096 mmol); m.p. 151-153 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 7.6 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.67-7.62 (m, 3H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.46 (s, 1H), 7.43-7.31 (m, 5H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 4.56 (t, *J* = 8.0 Hz, 1H), 3.57 (s, 3H), 3.42 (s, 3H), 3.31 (d, *J* = 7.2 Hz, 1H), 3.15 (s, 3H), 2.37-2.30 (m, 1H), 2.16-2.09 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.7, 169.5, 142.5, 141.0, 140.0, 139.4, 134.3, 133.3, 132.6, 131.4, 129.5, 129.1, 128.5, 128.1, 127.7, 127.1, 126.5, 126.1,

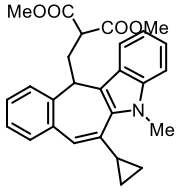
123.1, 119.8, 119.3, 118.5, 110.3, 107.6, 52.8, 52.7, 50.2, 32.8, 29.8; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{36}H_{31}KNO_4$ $[M+K]^+$ 580.1885, found 580.1886.



Dimethyl 2-((5-methyl-6-(thiophen-2-yl)-5,12-dihydrobenzo[4,5]cyclo-hepta[1,2-*b*]indol-12-yl)methyl)malonate (**3bp**): white solid (74% yield, 34.9 mg, 0.074 mmol); m.p. 163-165 °C; ^{1}H NMR (DMSO-d_6, 600 MHz) δ 7.72 (d, J = 7.8 Hz, 1H), 7.67 (d, J = 5.4 Hz, 1H), 7.53 (d, J = 7.8 Hz, 1H), 7.45 (s, 1H), 7.39 (d, J = 8.4 Hz, 1H), 7.35 (d, J = 4.2 Hz, 2H), 7.29-7.26 (m, 1H), 7.25-7.19 (m, 3H), 7.14 (t, J = 7.8 Hz, 1H), 4.53 (dd, J = 9.0, 7.2 Hz, 1H), 3.53 (s, 3H), 3.39 (s, 3H), 3.26 (dd, J = 8.4, 6.6 Hz, 1H), 3.24 (s, 3H), 2.29-2.24 (m, 1H), 2.11-2.07 (m, 1H); ^{13}C NMR (DMSO-d_6, 150 MHz) δ 169.6, 169.4, 144.3, 142.6, 139.7, 133.9, 132.4, 131.7, 131.3, 129.5, 129.1, 128.6, 127.0, 126.9, 126.8, 126.5, 125.9, 123.3, 119.9, 119.2, 118.6, 110.5, 52.8, 52.6, 50.2, 32.6, 29.5, 26.0; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{28}H_{26}NO_4S$ $[M+H]^+$ 472.1577, found 472.1573.

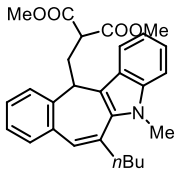


Dimethyl 2-((5-methyl-6-phenethyl-5,12-dihydrobenzo[4,5]cyclo-hepta[1,2-*b*]indol-12-yl)methyl)malonate (**3bq**): colorless oil (78% yield, 38.5 mg, 0.078 mmol); ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.62 (d, J = 8.0 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.40 (d, J = 7.6 Hz, 1H), 7.32-7.30 (m, 6H), 7.27-7.21 (m, 4H), 7.12 (t, J = 7.6 Hz, 1H), 4.42 (t, J = 9.2 Hz, 1H), 3.81 (s, 3H), 3.61 (s, 3H), 3.51 (s, 3H), 3.31 (s, 1H), 2.98-3.01 (m, 2H), 2.81 (t, J = 8.4 Hz, 2H), 2.32-2.25 (m, 1H), 2.08-2.01 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.7, 169.4, 142.1, 141.9, 139.6, 134.4, 133.6, 133.2, 131.3(1), 131.2(7), 130.7, 128.9, 128.7, 126.5, 126.4, 126.3, 122.8, 119.7, 118.4, 118.1, 110.4, 52.8(2), 52.7(8), 52.4(4), 50.0, 39.1, 36.1, 33.1 , 33.0, 29.2; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{32}H_{32}NO_4$ $[M+H]^+$ 494.2326, found 494.2325.



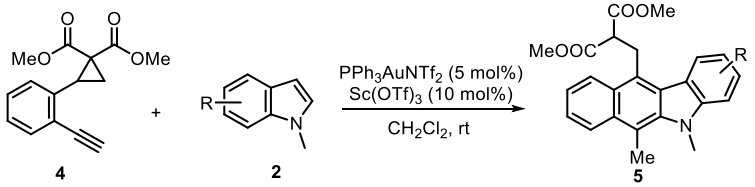
Dimethyl 2-((6-cyclopropyl-5-methyl-5,12-dihydrobenzo[4,5]cyclo-hepta[1,2-*b*]indol-12-yl)methyl)malonate (**3br**): white solid (84% yield, 36.0 mg, 0.084 mmol); m.p. 124-126 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ

7.60 (d, *J* = 8.0 Hz, 1H), 7.27-7.22 (m, 5H), 7.21-7.16 (m, 1H), 7.12 (t, *J* = 7.2 Hz, 1H), 4.42 (dd, *J* = 9.2, 7.2 Hz, 1H), 3.91 (s, 3H), 3.64 (s, 1H), 3.58 (s, 3H), 3.09 (dd, *J* = 8.8, 5.6 Hz, 1H), 2.29-2.09 (m, 3H), 1.17-1.11 (m, 1H), 0.95-0.84 (m, 2H), 0.79-0.75 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.0, 169.8, 141.5, 139.4, 134.9, 134.5, 134.1, 130.0, 129.3, 129.2, 128.8, 128.4, 126.4, 125.9, 122.3, 119.2, 117.9, 117.5, 109.2, 52.3, 49.7, 40.0, 32.7 (d, *J* = 4.8 Hz), 28.9, 16.8, 10.7, 7.32; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{27}H_{27}KNO_4$ $[M+K]^+$ 468.1572, found 468.1572.



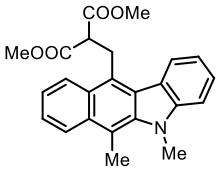
Dimethyl 2-((6-butyl-5-methyl-5,12-dihydrobenzo[4,5]cyclohepta [1,2-*b*]indol-12-yl)methyl)malonate (**3bs**): white solid (65% yield, 28.9 mg, 0.065 mmol); m.p. 107-108 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.59 (d, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.32-7.19 (m, 4H), 7.12-7.08 (m, 2H), 4.39 (dd, *J* = 9.2, 7.2 Hz, 1H), 3.76 (s, 3H), 3.60 (s, 3H), 3.53 (s, 3H), 3.16-3.08 (m, 1H), 3.01 (dd, *J* = 9.2, 5.2 Hz, 1H), 2.71-2.63 (m, 1H), 2.27-2.20 (m, 1H), 2..10-2.03 (m, 1H), 1.50-1.34 (m, 1H), 0.89 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.6, 169.4, 141.9, 139.5, 134.5, 134.0, 133.8, 130.8, 130.7, 128.9, 128.8, 126.4, 126.2, 122.8, 119.6, 118.1, 110.3, 52.9, 52.8, 49.8, 36.9, 33.0(1), 32.9(5), 32.1, 29.1, 22.6, 14.3; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{28}H_{31}KNO_4$ $[M+K]^+$ 484.1885, found 484.1886.

2.3 General procedure for the synthesis of benzo[*b*]carbazole derivatives 5

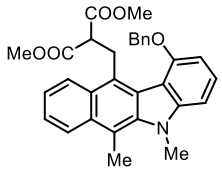


To a solution of terminal ACP **4** (25.8 mg, 0.1 mmol) in dichloromethane (1.0 mL), *N*-methyl indole derivative **2** (0.12 mmol, 1.2 equiv.), $Ph_3PAuNTf_2$ (3.7 mg, 0.005 mmol) and $Sc(OTf)_3$ (4.9 mg, 0.01 mmol) were added, respectively. The reaction was stirred at room temperature for 12 h. Then, the mixture was diluted with brine (2.0 mL) and extracted with EtOAc (2.0 mL × 2). The combined organic layers were dried over $MgSO_4$

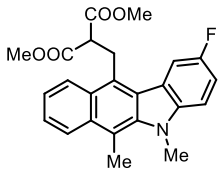
and concentrated. The crude product was then purified by flash chromatography on silica gel using (95:5 to 90:10 petroleum ether:EtOAc) to give benzo[*b*]carbazole **5** as a yellowish solid.



Dimethyl 2-((5,6-dimethyl-5*H*-benzo[*b*]carbazol-11-yl)methyl)mal-onate (**5a**): yellowish solid (87% yield, 33.8 mg, 0.087 mmol); m.p. 169-171 °C; ^{1}H NMR (DMSO-d_6, 600 MHz) δ 8.25-8.19 (m, 3H), 7.62 (d, J = 7.8 Hz, 1H), 7.59-7.54 (m, 2H), 7.47 (t, J = 7.8 Hz, 1H), 7.26 (t, J = 7.2 Hz, 1H), 4.27(d, J = 7.8 Hz, 2H), 4.13 (s, 1H), 3.88 (t, J = 7.8 Hz, 1H), 3.47 (s, 6H), 3.10 (s, 3H); ^{13}C NMR (DMSO-d_6, 150 MHz) δ 169.3, 145.6, 139.8, 132.2, 127.7, 127.0, 126.2, 125.3, 124.4, 124.0, 123.7, 123.2, 123.1, 121.9, 119.7, 112.5, 109.8, 52.9, 51.6, 34.8, 27.5, 15.0; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{24}H_{24}NO_4$ $[M+H]^+$ 390.1700, found 390.1699.

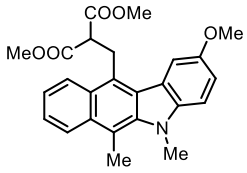


Dimethyl 2-((1-(benzyloxy)-5,6-dimethyl-5*H*-benzo[*b*]carbazol-11-yl)methyl)malonate (**5b**): yellowish solid (83% yield, 41.1 mg, 0.083 mmol); m.p. 146-147 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.21 (dd, J = 12.4, 8.8 Hz, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.50-7.38 (m, 6H), 7.33 (t, J = 7.2 Hz, 1H), 7.17 (d, J = 8.4 Hz, 1H), 6.82 (d, J = 8.0 Hz, 1H), 5.41 (s, 2H), 4.73 (s, 2H), 4.07 (s, 3H), 3.77 (t, J = 7.6 Hz, 1H), 3.27 (s, 6H), 3.07 (s, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.4, 154.0, 148.1, 140.3, 137.5, 132,2, 129.1, 129.0, 128.1, 127.5, 126.5, 125.2, 124.9, 124.7, 123.8, 123.0, 111.7, 111.4, 104.1, 103.1, 70.4, 53.8, 52.4, 35.8, 35.7, 29.1, 15.6; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{31}H_{30}NO_5$ $[M+H]^+$ 496.2118, found 496.2098.

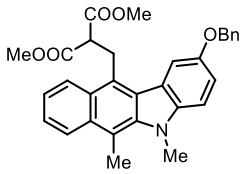


Dimethyl 2-((2-fluoro-5,6-dimethyl-5*H*-benzo[*b*]carbazol-11-yl) methyl)malonate (**5c**): yellowish solid (86% yield, 35.0 mg, 0.086 mmol); m.p. 157-159 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.22 (dd, J = 8.4, 4.0 Hz, 2H), 7.97 (dd, J = 10.4, 2.0 Hz, 1H), 7.61-7.56 (m, 2H), 7.50-7.42 (m, 2H), 4.17 (d, J = 7.6 Hz, 2H), 4.08 (s, 3H), 3.86 (t, J = 7.6 Hz, 1H), 3.49 (s, 6H), 3.05 (s, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.3, 158.0, 155.7, 142.1, 140.4,

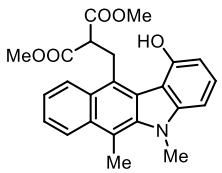
132.4, 126.8, 126.7, 125.6, 124.5, 124.0, 123.2, 122.2, 122.1, 115.0, 114.7, 112.8, 110.5, 110.4, 109.4, 109.2, 52.9 (d, J = 3.6 Hz), 51.8 (d, J = 4.4 Hz), 35.0 (d, J = 7.1 Hz), 27.3, 14.8 (d, J = 2.5 Hz); HRMS (TOF-ESI$^+$) m/z: calcd for $C_{24}H_{23}FNO_4$ $[M+H]^+$ 408.1606, found 408.1605.



Dimethyl 2-((2-methoxy-5,6-dimethyl-5*H*-benzo[*b*]carbazol-11-yl)methyl)malonate (**5d**): yellowish solid (76% yield, 31.8 mg, 0.076 mmol); m.p. 135-137 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.21 (t, J = 6.4 Hz, 2H), 7.71 (d, J = 2.0 Hz, 1H), 7.57-7.52 (m, 2H), 7.45 (t, J = 8.0 Hz, 1H), 7.23 (dd, J = 9.2, 2.4 Hz, 1H), 4.24 (d, J = 7.6 Hz, 2H), 4.07 (s, 1H), 3.87 (t, J = 9.6 Hz, 4H), 3.50 (s, 6H), 3.06 (s, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.4, 153.7, 140.5, 140.4, 132.1, 126.7, 126.3, 125.3, 124.4, 123.9, 123.6, 122.8, 122.1, 115.9, 112.4, 110.4, 106.9, 100.0, 56.0 (d, J = 7.7 Hz), 52.9 (d, J = 4.1 Hz), 51.9, 34.9 (d, J = 7.8 Hz), 27.4, 14.9 (d, J = 3.0 Hz); HRMS (TOF-ESI$^+$) m/z: calcd for $C_{25}H_{25}NNaO_5$ $[M+Na]^+$ 442.1625, found 442.1625.

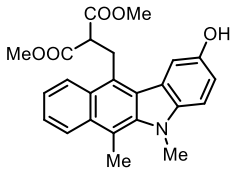


Dimethyl 2-((2-(benzyloxy)-5,6-dimethyl-5*H*-benzo[*b*]carbazol-11-yl)methyl)malonate (**5e**): yellowish solid (91% yield, 45.0 mg, 0.091 mmol); m.p. 164-166 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.22 (t, J = 9.2 Hz, 2H), 7.84 (s, 1H), 7.55-7.52 (m, 4H), 7.48-7.42 (m, 3H), 7.37 (t, J = 7.2 Hz, 1H), 7.31 (d, J = 8.4 Hz, 1H), 5.20 (s, 2H), 4.24 (d, J = 7.6 Hz, 2H), 4.06 (s, 3H), 3.90 (t, J = 7.2 Hz, 1H), 3.50 (s, 6H), 3.06 (s, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.4, 152.7, 140.7, 140.4, 137.9, 132.2, 128.9, 128.3, 126.7, 126.3, 125.3, 124.4, 123.9, 123.6, 122.9, 122.1, 116.8, 112.5, 110.4, 108.6, 70.7, 52.9 (d, J = 4.4 Hz), 51.9, 35.0, 27.4, 14.9; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{31}H_{29}KNO_5$ $[M+K]^+$ 534.1677, found 534.1677.



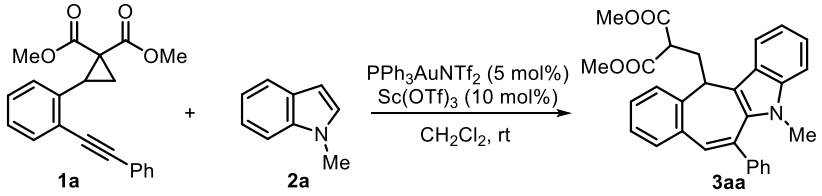
Dimethyl 2-((1-hydroxy-5,6-dimethyl-5*H*-benzo[*b*]carbazol-11-yl)methyl)malonate (**5f**): yellowish solid (57% yield, 23.1 mg, 0.057 mmol); m.p. 224-226 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 10.42 (s,

1H), 8.18 (t, *J* = 6.8 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.43-7.34 (m, 2H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.71 (d, *J* = 7.6 Hz, 1H), 4.67 (s, 2H), 4.05 (s, 3H), 3.84 (t, *J* = 7.2 Hz, 1H), 3.43 (s, 6H), 3.06 (s, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.8, 153.2, 148.4, 140.3, 132.0, 129.1, 127.6, 126.3, 125.2, 125.0, 124.6, 123.7, 122.8, 111.4, 110.0, 107.0, 100.9, 54.5 (d, *J* = 7.9 Hz), 52.5, 35.8 (d, *J* = 9.0 Hz), 29.1, 15.5 (d, *J* = 3.3 Hz); HRMS (TOF-ESI$^+$) m/z: calcd for $C_{24}H_{23}NNaO_5$ $[M+Na]^+$ 428.1468, found 428.1468.



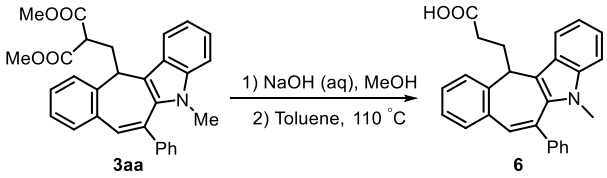
Dimethyl 2-((2-hydroxy-5,6-dimethyl-5*H*-benzo[*b*]carbazol-11-yl) methyl)malonate (**5g**): yellowish solid (59% yield, 23.9 mg, 0.059 mmol); m.p. 178-180 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 9.16 (s, 1H), 8.20 (d, *J* = 8.8 Hz, 2H), 7.59 (d, *J* = 1.2 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.08 (dd, *J* = 8.8, 2.0 Hz, 1H), 4.22 (d, *J* = 7.6 Hz, 1H), 4.06 (s,3H), 3.87 (t, *J* = 8.0 Hz, 1H), 3.50 (s, 6H), 3.07 (s, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 169.2, 151.3, 140.6, 139.8, 132.1, 126.6, 126.0, 125.2, 124.3, 123.9, 122.8, 122.5, 116.3, 112.2, 110.2, 109.1, 52.9 (d, *J* = 3.9 Hz), 51.7 (d, *J* = 5.6 Hz), 35.0 (d, *J* = 7.3 Hz), 27.3, 15.0; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{24}H_{23}KNO_5$ $[M+K]^+$ 444.1208, found 442.1207.

2.4 Experimental procedure for the scale-up reaction



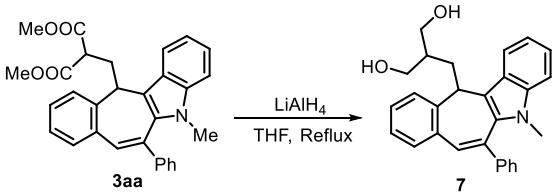
To a solution of ACP **1a** (1.0 g, 3.0 mmol) in dichloromethane (30 mL), *N*-methyl indole **2a** (0.47 g, 3.6 mmol, 1.2 equiv.), $Ph_3PAuNTf_2$ (0.11 g, 0.015 mmol) and $Sc(OTf)_3$ (0.15 g, 0.3 mmol) were added, respectively. The reaction was stirred at room temperature for 12 h. Then, the mixture was diluted with brine (50 mL) and extracted with EtOAc (100 mL × 2). The combined organic layers were dried, concentrated and purified by flash silica gel chromatography using (95:5 to 90:10 petroleum ether:EtOAc) to afford cyclohepta[*b*]indole **3aa** in 79% yield (1.1 g, 2.4 mmol).

2.5 Experimental procedure for the synthesis of acid 6



To a solution of cyclohepta[*b*]indole **3aa** (0.1 mmol, 46.5 mg) in methanol (1 mL) was added NaOH aqueous solution (0.1 M, 200 μL). The reaction mixture was stirred for 2 h at room temperature, then water was added (2 mL) and extracted with ethyl acetate (2 mL × 2). The organic phase was washed with brine, dried over Na_2SO_4. The solvent was evaporated under reduced pressure to give the residue, which was used in the next step without further purification. The residue was dissolved in toluene and heated at 110 °C for 6 h (determined to be complete by TLC). The mixture was then diluted with brine (2.0 mL) and extracted with EtOAc (2.0 mL × 2). The combined organic layers were dried, concentrated and purified by flash silica gel chromatography using (95:5 to 90:10 petroleum ether:EtOAc) to afford **6** as a white solid (64%, 26.0 mg, 0.64 mmol). m.p. 221-223 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 11.97 (s, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 7.6 Hz, 1H), 7.52 (d, J = 4.4 Hz, 4H), 7.46-7.41 (m, 1H), 7.37-7.35 (m, 4H), 7.31-7.27 (m, 1H), 7.21 (t, J = 7.2 Hz, 1H), 7.13 (t, J = 7.6 Hz, 1H), 4.55 (t, J = 8.0 Hz, 1H), 3.08 (s, 3H), 2.07 (t, J = 7.6 Hz, 2H), 2.03-1.94 (m, 1H), 1.86-1.77 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 174.7, 143.5, 142.0, 139.4, 134.2, 133.7, 132.3, 131.3, 129.5, 129.3, 129.2, 127.8, 126.4, 120.4, 118.5, 110.3, 62.5, 41.1, 32.5, 26.0 (d, J = 3.9 Hz), 25.9; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{27}H_{23}NNaO_2$ $[M+Na]^+$ 416.1621, found 416.1629.

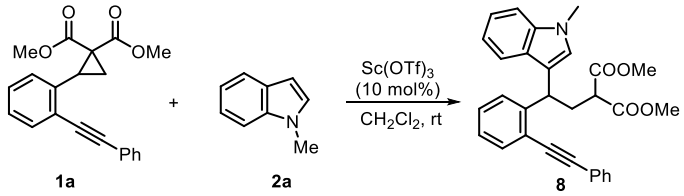
2.6 Experimental procedure for the synthesis of diol 7



To a solution of cyclohepta[*b*]indole **3aa** (0.1 mmol, 46.5 mg) in anhydrous THF (1 mL), $LiAlH_4$ (22.7 mg, 0.6 mmol, 6 equiv.) was added in small portions. The reaction mixture was stirred under refluxed for 6 h under an argon atmosphere. After cooling to 0 °C, water was added slowly to quench the excess $LiAlH_4$. After filtering out the aluminum salts, the filtrate was extracted with EtOAc (2.0 mL × 2) and washed with brine (2 mL). the combined organic layers were then dried over Na_2SO_4, filtered, concentrated and purified by flash silica gel chromatography using (90:10 to 70:30 petroleum ether:EtOAc) to afford diol **7** as a white solid (93%, 38.0 mg, 0.93 mmol). m.p. 170-172 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.86 (d, J = 7.6 Hz, 1H), 7.58-7.49 (m, 5H), 7.45-7.40 (m, 2H), 7.36-7.33 (m, 3H), 7.26 (t, J = 7.2 Hz, 1H), 7.20 (t, J = 7.2 Hz, 1H), 7.13 (t, J = 7.6 Hz, 1H), 4.62 (dd, J = 9.2, 6.8 Hz, 1H), 4.30 (t, J = 4.4 Hz, 1H), 4.22 (t, J = 5.2 Hz, 1H), 3.46-3.41 (m, 2H), 3.30-3.25 (m, 2H), 3.07 (s, 3H), 1.85-1.79 (m, 1H), 1.49-1.43 (m, 1H), 1.35-1.34 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 144.6, 142.2, 139.4, 134.3, 133.7, 132.7, 132.3, 131.2, 129.4, 129.2, 129.0, 128.2, 127.9, 126.5, 125.9, 112.8, 121.1, 119.6, 118.6, 110.2, 62.5, 61.5, 41.6, 32.5(2), 32.4(8), 29.0; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{28}H_{28}NO_2$ $[M+H]^+$ 410.2115, found 410.2116.

2.7 Experimental procedure for the control experiments

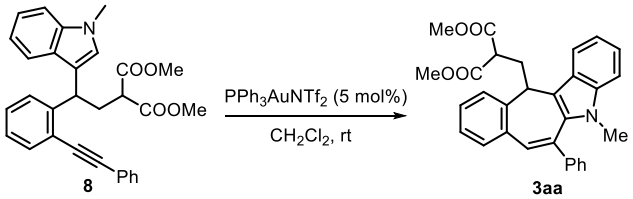
Synthesis of C-3 arylation product 8



To a solution of ACP **1a** (33.4 mg, 0.1 mmol) in dichloromethane (1.0 mL), *N*-methyl indole **2** (15.7 mg, 0.12 mmol, 1.2 equiv.), $Sc(OTf)_3$ (4.9 mg, 0.01 mmol, 10 mol%) were added, respectively. The reaction was stirred at room temperature for 12 h. Then, the mixture was diluted with brine (2.0 mL) and extracted with EtOAc (2.0 mL × 2). The combined organic layers were dried, concentrated and purified by flash silica gel chromatography using (95:5 to 90:10 petroleum ether:EtOAc) to afford **8** as a colorless oil (97%, 45.1 mg, 0.97 mmol). ^{1}H NMR (DMSO-d_6, 600 MHz) δ 7.59 (d, J = 6.6 Hz, 2H), 7.55 (d, J = 7.8

Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.48-7.44 (m, 4H), 7.37-7.34 (m, 3H), 7.24 (t, *J* = 7.8 Hz, 1H), 7.10 (t, *J* = 7.8Hz, 1H), 6.92 (t, *J* = 7.8 Hz, 1H), 4.88 (dd, *J* = 9.0, 6.6 Hz, 1H), 3.75 (s, 3H), 3.54 (s, 3H), 3.51 (s, 3H), 3.27 (dd, *J* = 8.4, 6.0 Hz, 1H), 2.79-2.74 (m, 1H), 2.54-2.51 (m, 1H); ^{13}C NMR (DMSO-d_6, 150 MHz) δ 169.7, 169.5, 137.1, 132.4, 131.7, 129.8, 129.4, 129.3, 127.9, 127.0, 126.9, 122.8, 121.8, 119.1, 118.8, 116.9, 110.2, 93.8, 88.4, 52.9, 52.8, 49.9, 37.3, 35.0, 32.9; HRMS (TOF-ESI$^+$) m/z: calcd for $C_{30}H_{28}NO_4$ $[M+H]^+$ 466.2013, found 466.2022.

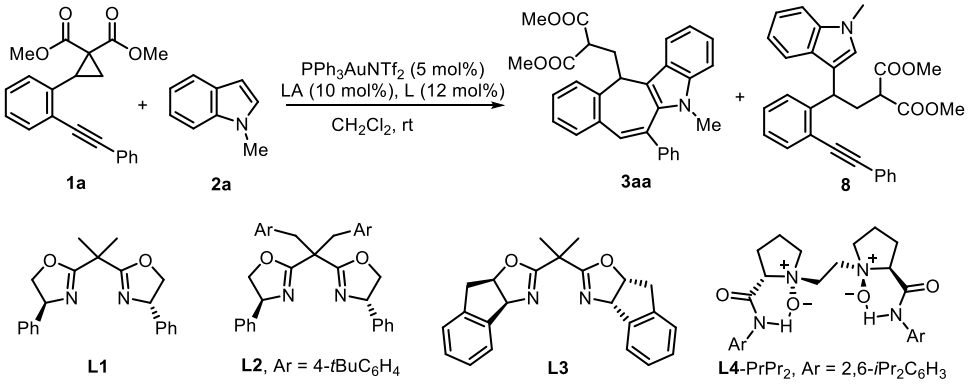
***Synthesis of* cyclohepta[*b*]indole 3aa *via* gold-catalyzed 6-*endo*-*dig* cyclization**



To a solution of **8** (46.5 mg, 0.1 mmol) in dichloromethane (1.0 mL) was added PPh_3AuNTf_2 (3.7 mg, 0.005 mmol, 5 mol%). The reaction was stirred at room temperature for 12 h. Then, the mixture was diluted with brine (2.0 mL) and extracted with EtOAc (2.0 mL × 2). The combined organic layers were dried, concentrated and purified by flash silica gel chromatography using (95:5 to 90:10 petroleum ether:EtOAc) to afford cyclohep-ta[*b*]indole **3aa** as a white solid (91%, 42.3 mg).

2.8 Exploration of the asymmetric tandem [5+2]-cycloaddition

Table S1. Reaction optimization of asymmetric tandem [5+2]-cycloaddition



Entry	LA (10 mol%)	L (12 mol%)	Yield of **3aa**/**8** (%) [a]	Ee (**3aa**/**8**) (%) [b]
1	$Cu(OTf)_2$	L1	80/nd	4
2	$Cu(OTf)_2$	L2	64/nd	24
3	$Cu(OTf)_2$	L3	69/nd	6
4	$Ni(OTf)_2$	L3	NR	-
5	$Cu(OTf)_2$	L4	trace	-
6	$Ni(OTf)_2$	L4	NR	-
7	$Sc(OTf)_3$	L4	65/15	6/7

[a] Isolated yield. [b] Determined by chiral HPLC.

Experimental procedure

To a solution of ACP **1a** (33.4 mg, 0.1 mmol) in dichloromethane (1 mL), *N*-methyl indole **2a** (15.7 mg, 0.12 mmol, 1.2 equiv.), $Ph_3PAuNTf_2$ (3.7 mg, 0.005 mmol, 5 mol%), ligand (0.012 mmol, 12 mol%) and Lewis acid (0.01 mmol, 10 mol%) were added, respectively. The reaction was stirred at room temperature for 12 h. Then, the mixture was diluted with brine (2.0 mL) and extracted with EtOAc (2.0 mL × 2). The combined organic layers were dried, concentrated and purified by flash silica gel chromatography using (95:5 to 90:10 petroleum ether:EtOAc) to afford cyclohepta[*b*]indole **3aa** and **8**.

HPLC analysis of **3aa**: Daicel Chiralpak OD-H (*i*-PrOH: *n*-Hexane = 80:20; flow rate: 1 mL/min; λ = 254 nm; t_{major} = 4.7 min, t_{minorr} = 6.0 min. $[\alpha]_D^{25}$ +5.4 °(c 0.01, CH_2Cl_2)

HPLC analysis of **8**: Daicel Chiralpak OD-H (*i*-PrOH: *n*-Hexane = 80:20; flow rate: 1 mL/min; λ = 254 nm; t_{major} = 6.3 min, t_{minorr} = 8.6 min.

2.9 Photopysical properties

Absorption and fluorescence spectra were measured at 25 °C for solutions of **3an**, **3ao**, **3ar**, **3bf, 5a, 6**, **7** in acetonitrile (MeCN) with a concentration of 10^{-4} M, using 10 × 45 mm cuvettes. The quantum yields of **3an**, **3ao**, **3ar**, **3bf, 6** and diol **7** were determined according to references[2] by using a solution of 7-diethylamino-4-methyl coumarin in ethanol

(Φ = 0.73) as a standard. The quantum yield of **5a** was determined according to references[2] by using a solution of fluorescein in ethanol (Φ = 0.79) as a standard.

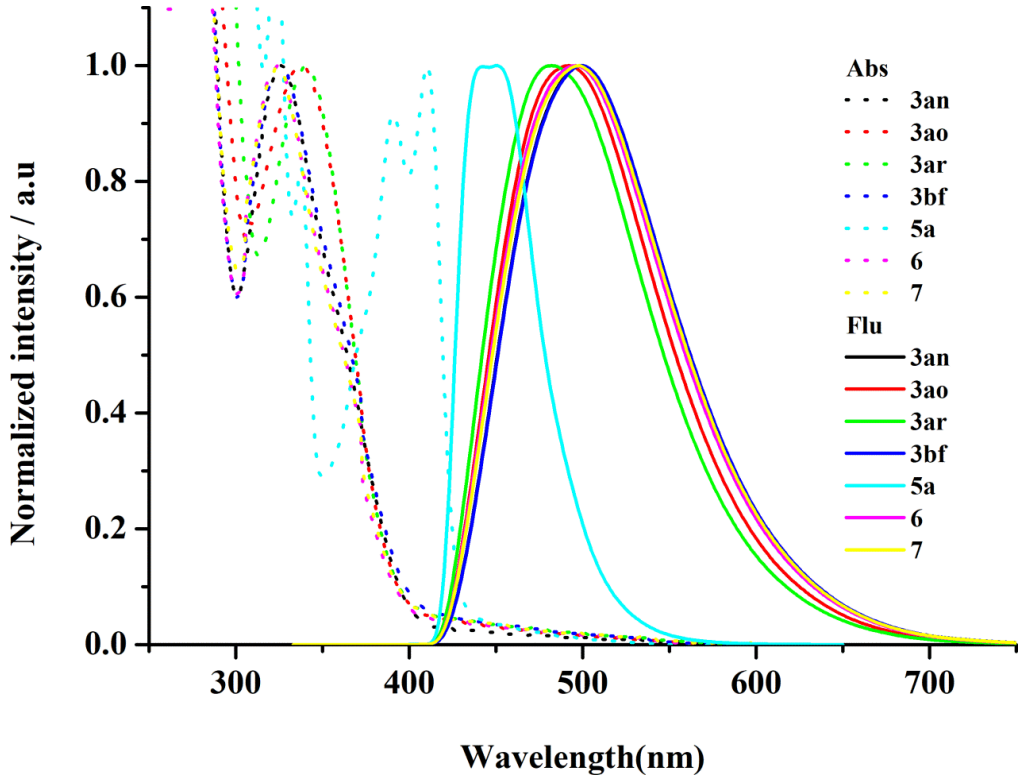


Figure S1. Normalized absorption (dashed lines) and normalized fluorescence (solid lines) spectra of of **3an**, **3ao**, **3ar**, **3bf**, **5a**, **6** and **7** in MeCN

Table S2. Photopysical properties of selected compounds

Compound	λ_{abs} (nm)	λ_{em} (nm)	$\Phi_{F(x)}$ (%)	SS[a] (nm)
3an	324	498	10	173
3ao	337	492	10	155
3ar	341	482	11	141
3bf	325	499	14	175
4aa	391, 410	451	51	41
6	324	496	14	172
7	323	498	13	175

[a]Stokes shifts

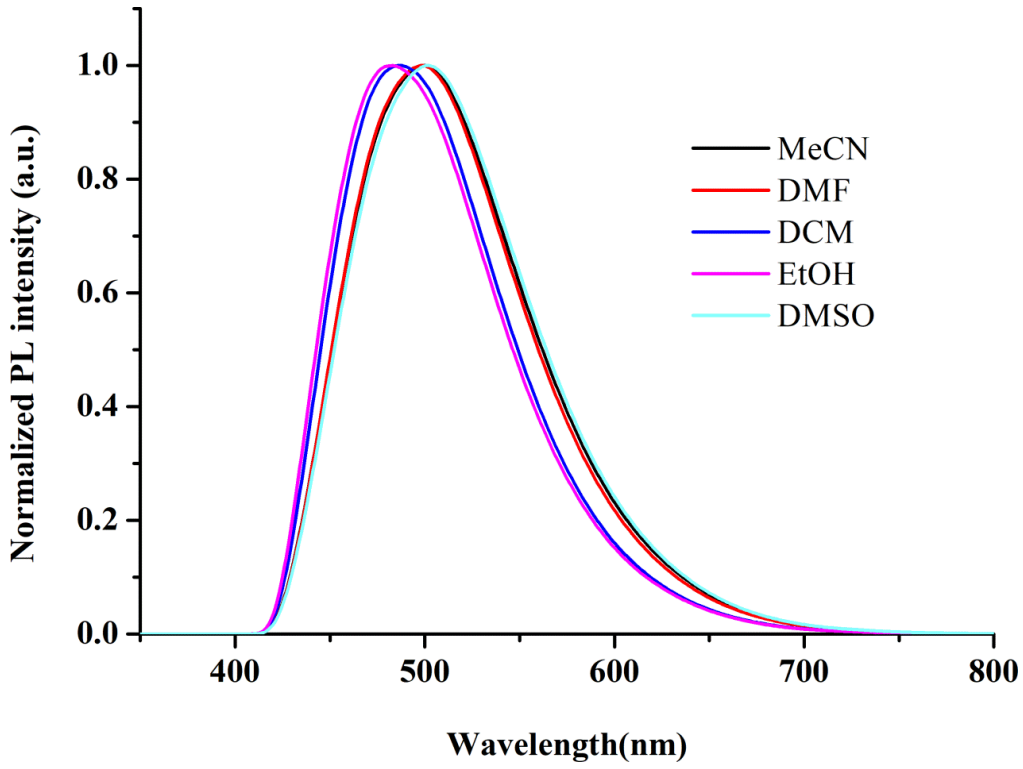


Figure S2. Fluorescence spectra of **3bf** obtained in various solvents

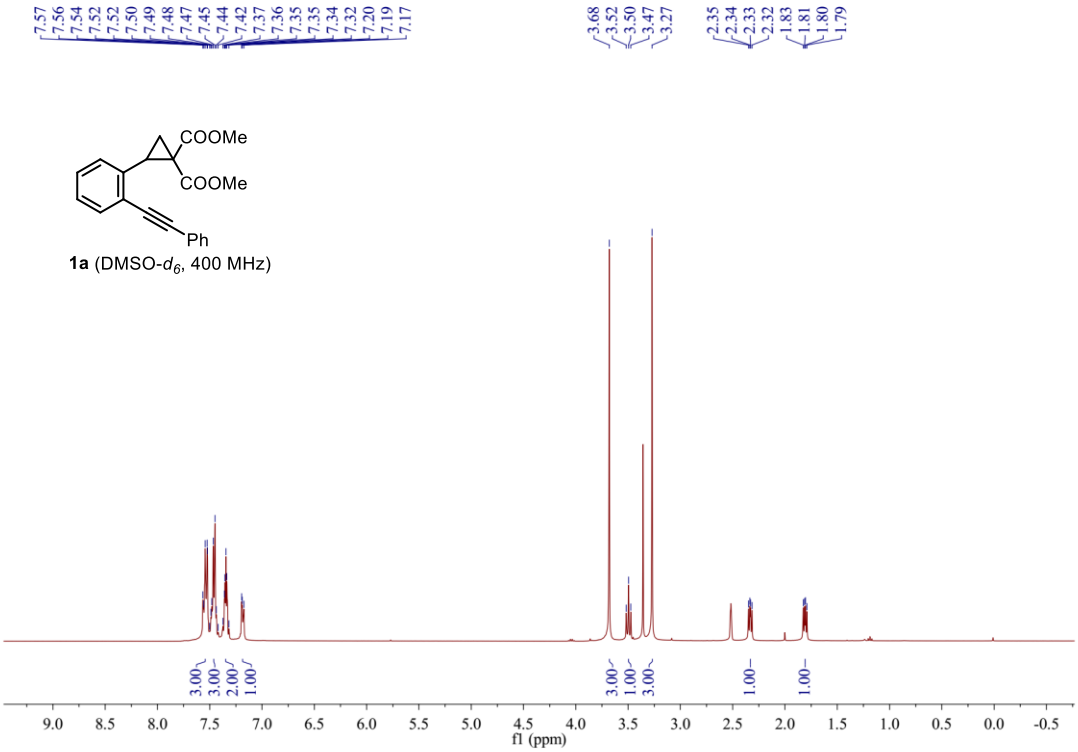
Table S3. Photopysical properties of **3bf** in various solvents

Solvent	MeCN	DMF	DCM	EtOH	DMSO
λ_{abs}/nm	324	325	326	327	328
λ_{em}/nm	499	499	486	482	501
SS (nm)	175	174	160	155	172

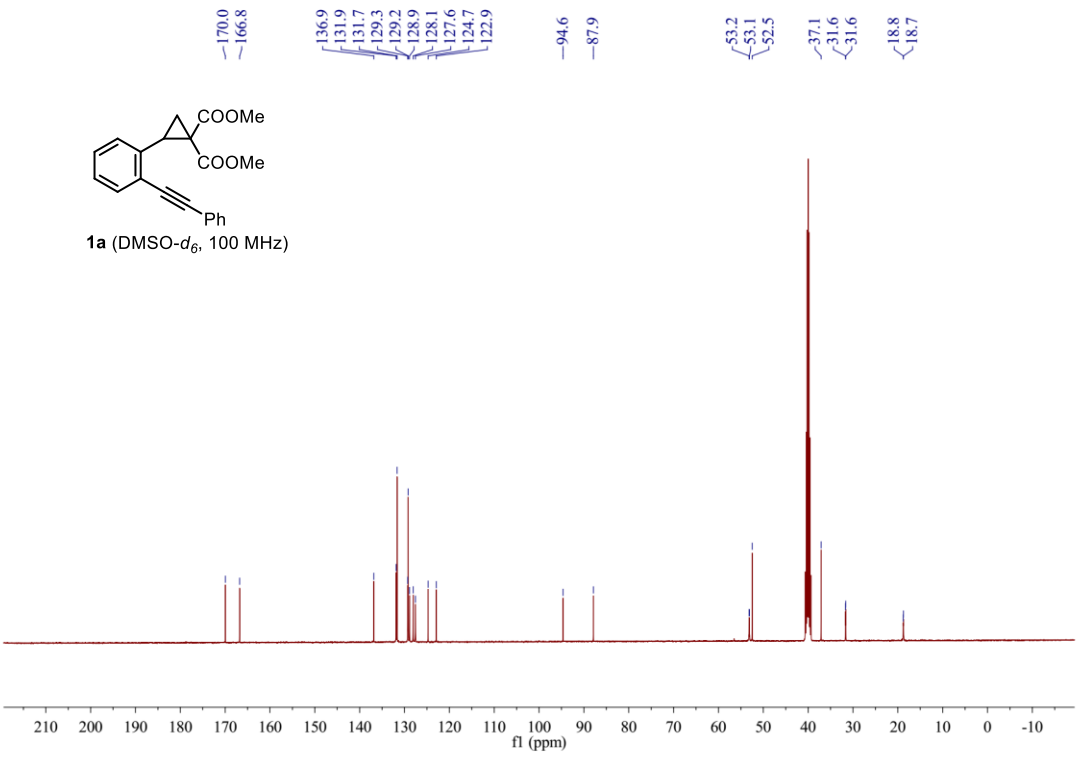
3. References

[1] (a) Kulandai Raj, A. S.; Narode, A. S.; Liu, R., Gold(I)-Catalyzed Reactions between N-(o-Alkynylphenyl)imines and Vinyldiazo Ketones to Form 3-(Furan-2-ylmethyl)-1H-indoles via Postulated Azallyl Gold and Allylic Cation Intermediates. *Org. Lett.* **2021**, 23, (4), 1378-1382; (b) Poulsen, P. H.; Li, Y.; Lauridsen, V. H.; Jørgensen, D. K. B.; Palazzo, T. A.; Meazza, M.; Jørgensen, K. A., Organocatalytic Formation of Chiral Trisubstituted Allenes and Chiral Furan Derivatives. *Angew. Chem. Int. Ed.* **2018**, 57, (33), 10661-10665.

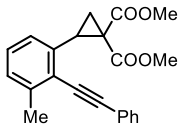
4. NMR Spectra



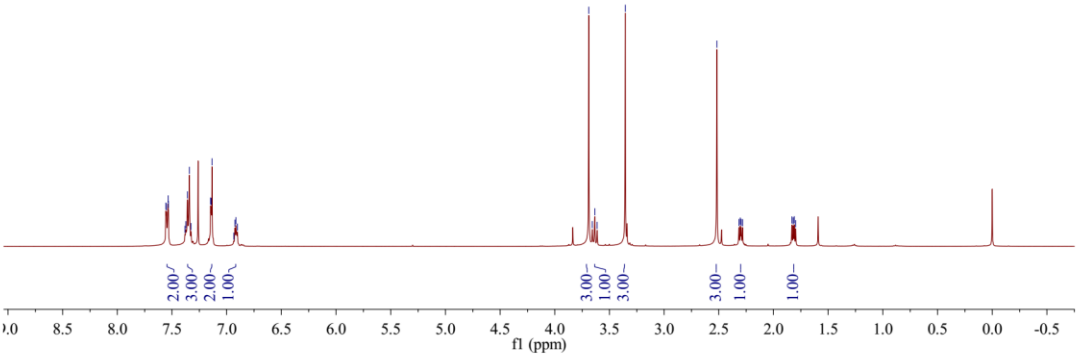
1a (DMSO-d_6, 400 MHz)

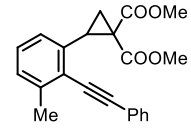


1a (DMSO-d_6, 100 MHz)

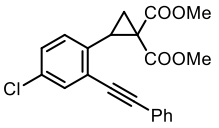


1b ($CDCl_3$, 400 MHz)

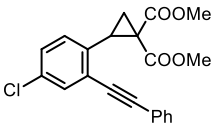




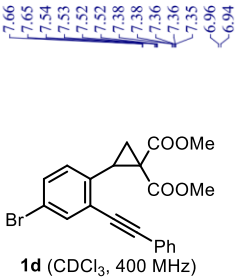
1b ($CDCl_3$, 100 MHz)



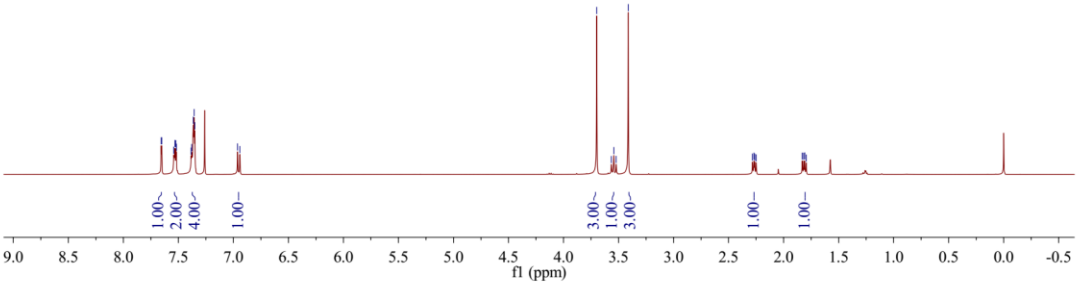
1c ($CDCl_3$, 400 MHz)

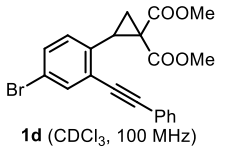


1c ($CDCl_3$, 100 MHz)



1d ($CDCl_3$, 400 MHz)





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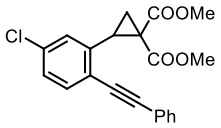

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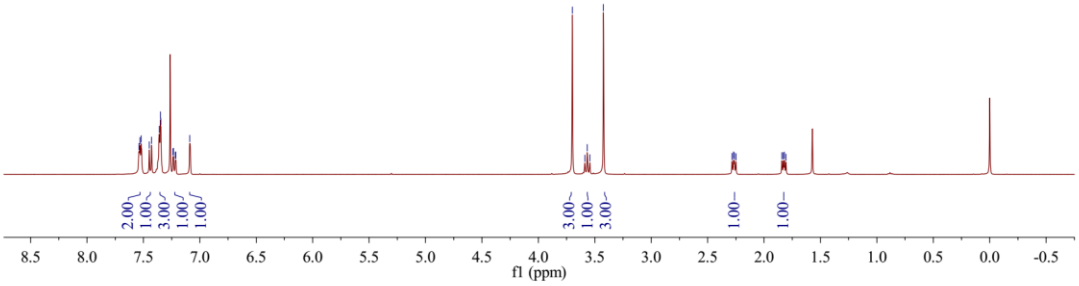
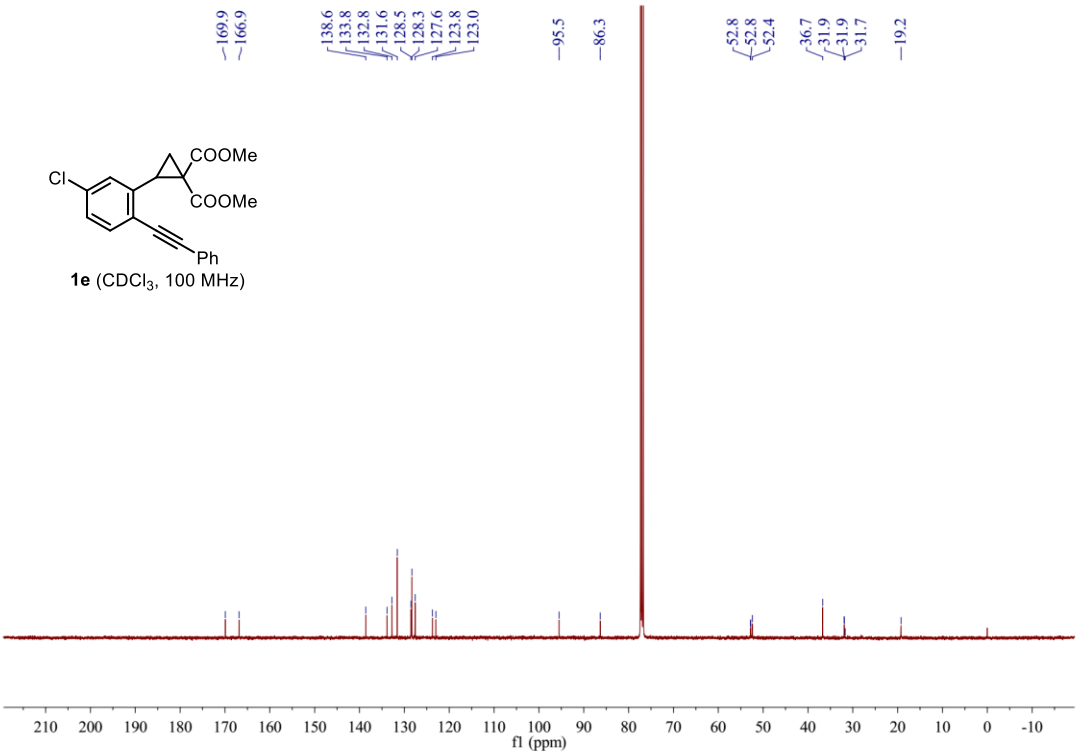
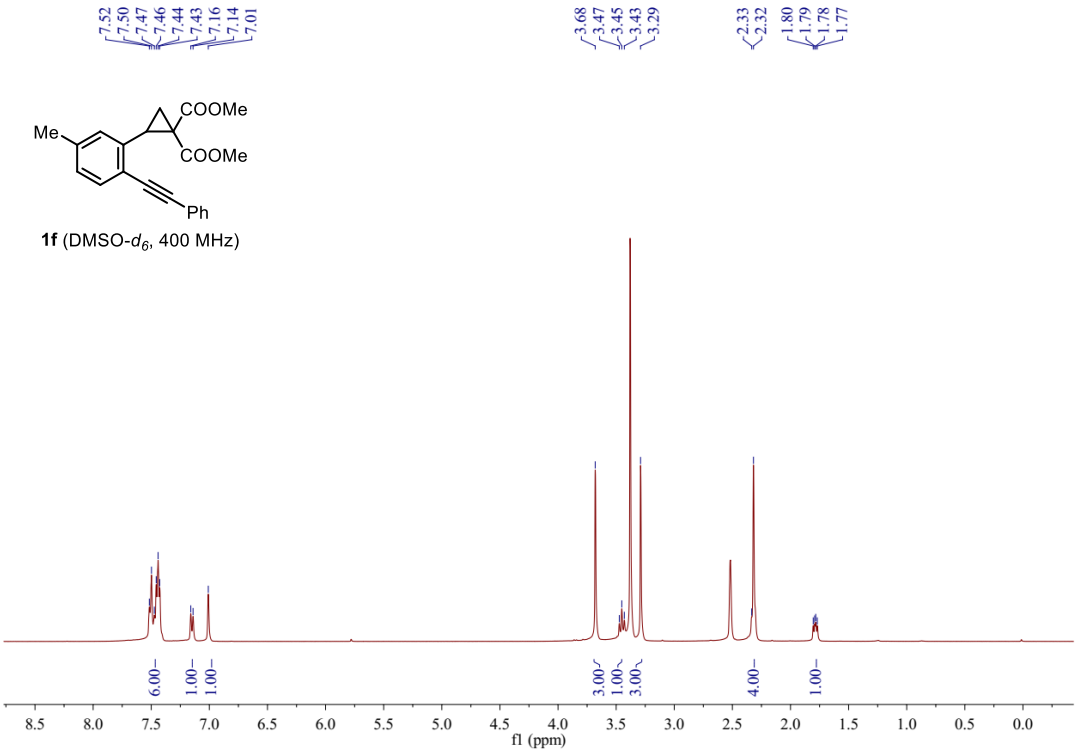
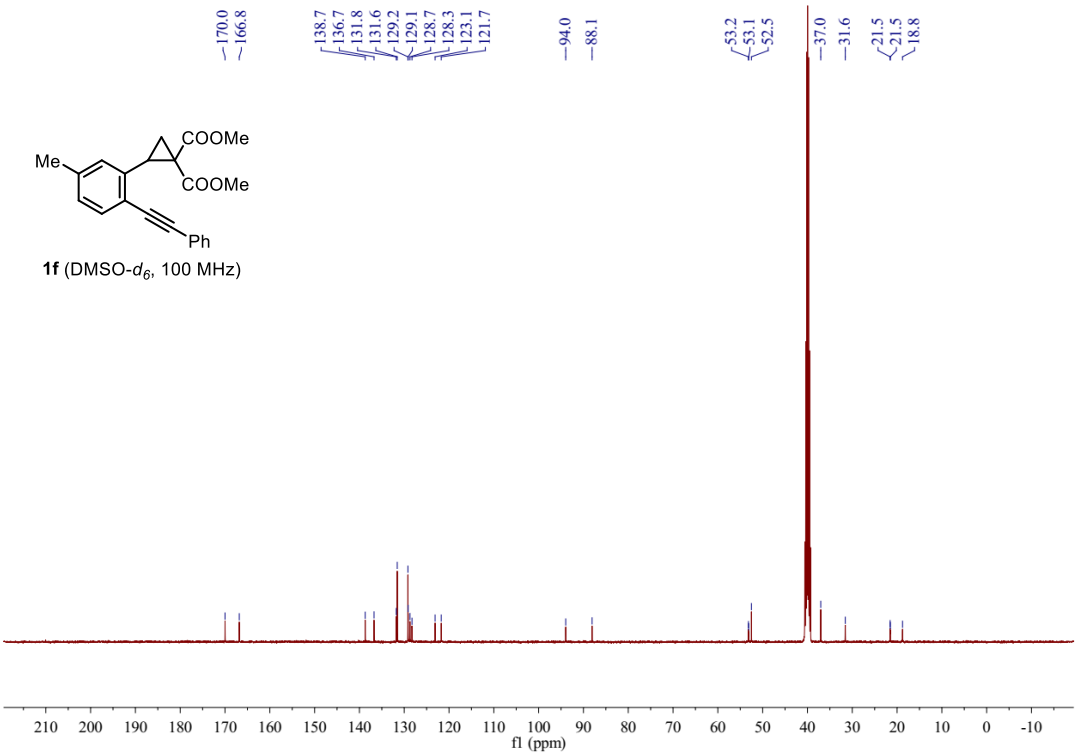




1e ($CDCl_3$, 100 MHz)



1f (DMSO-d_6, 400 MHz)



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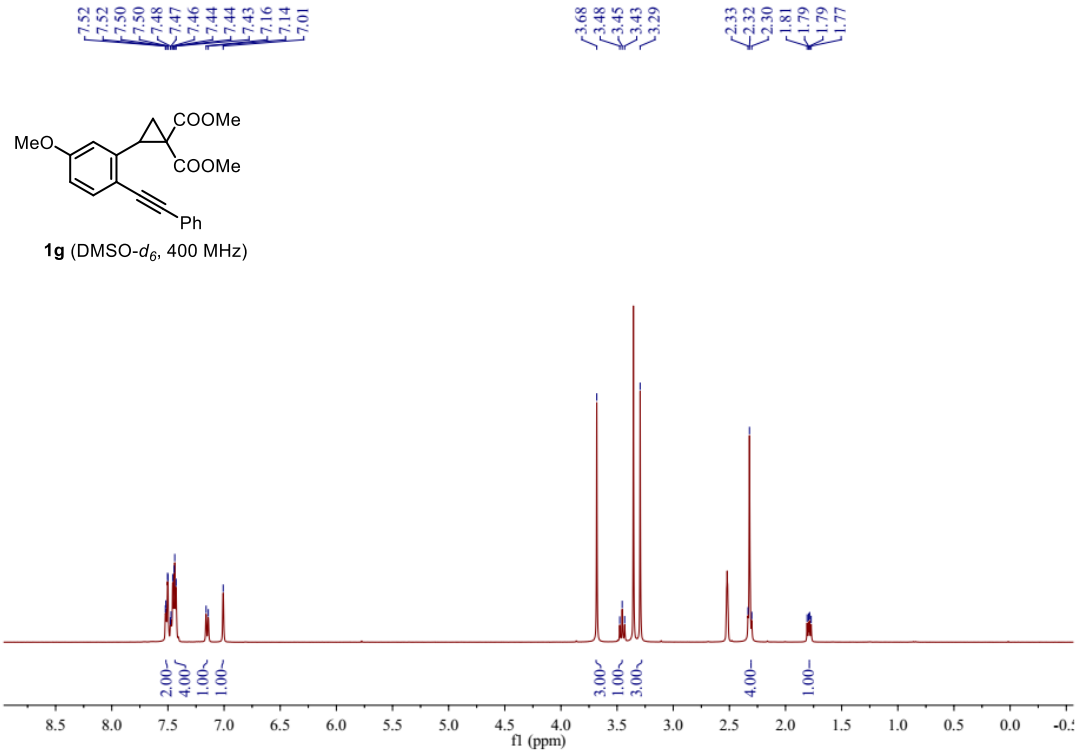
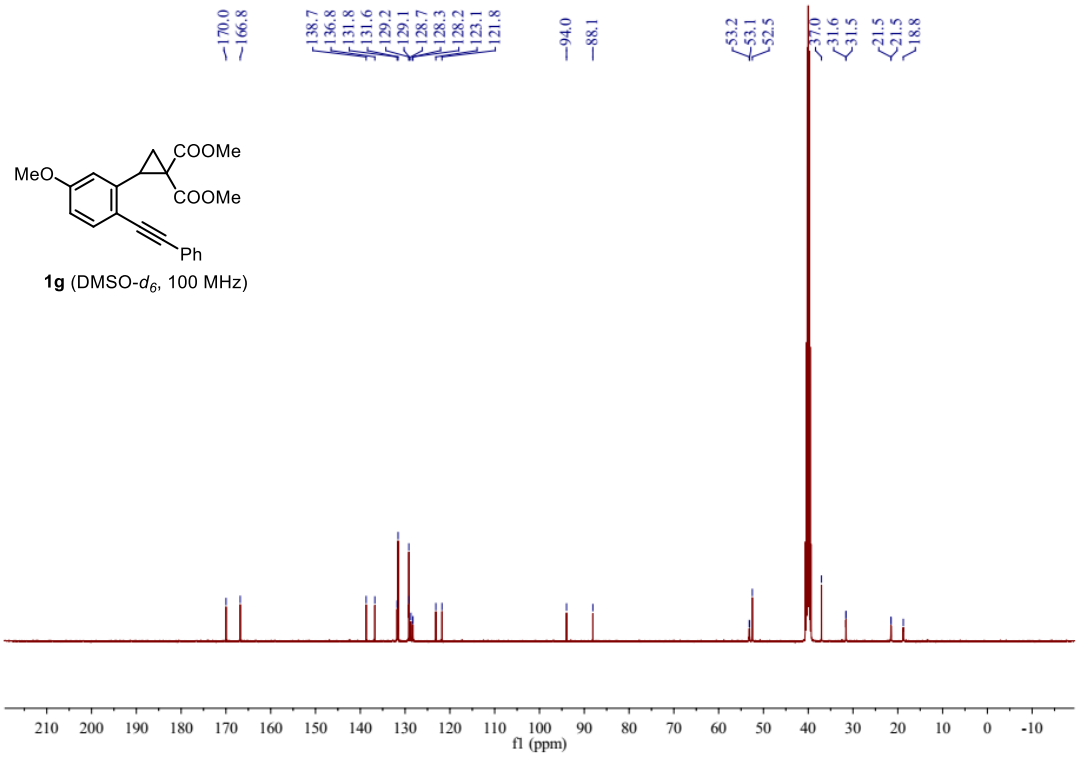


1g (DMSO-d_6, 400 MHz)



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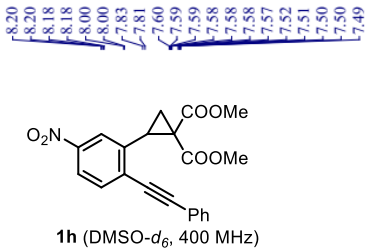
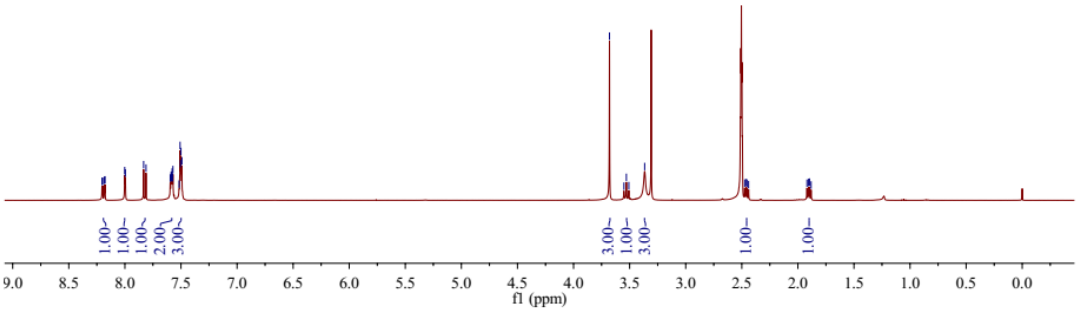
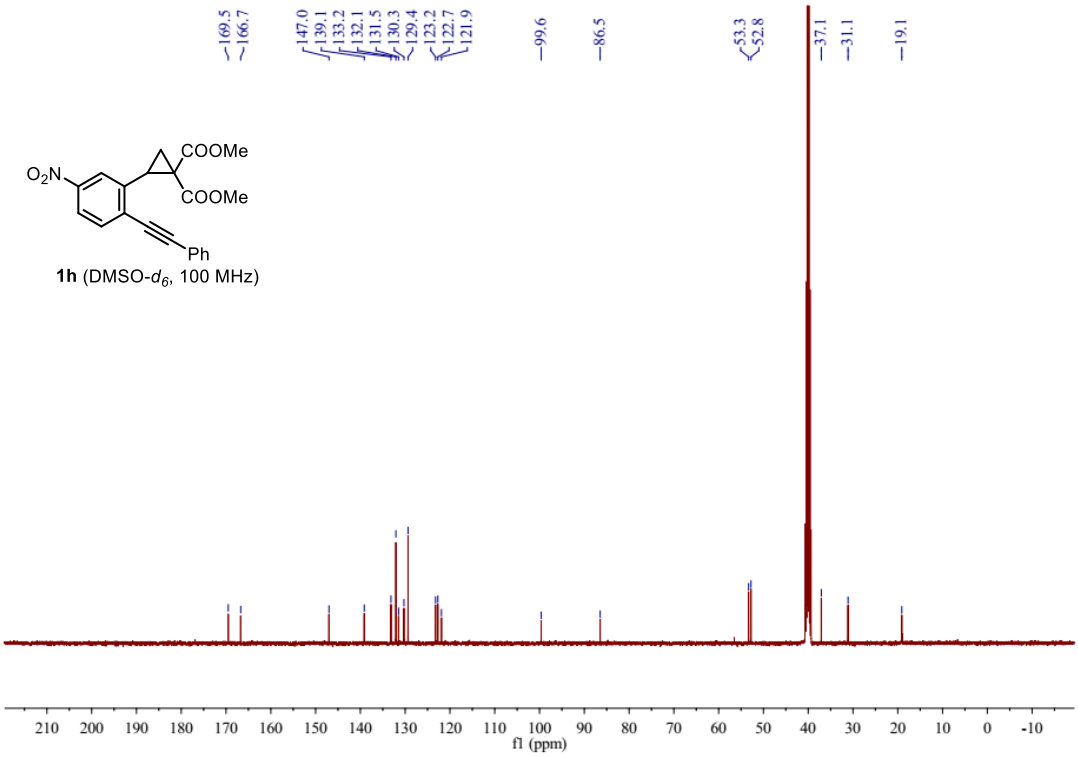
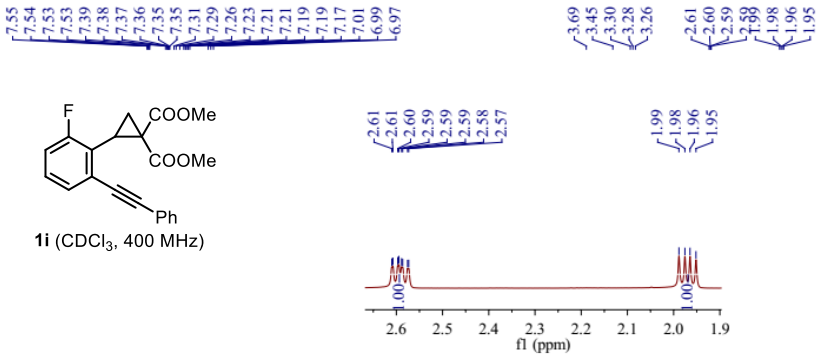


1h (DMSO-d_6, 400 MHz)

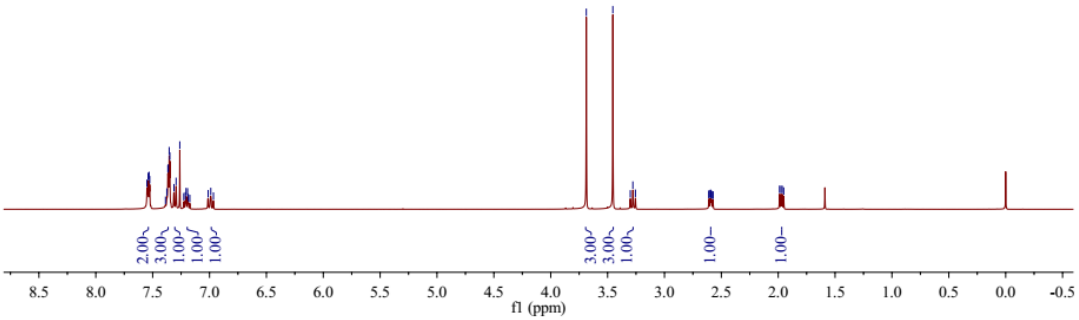


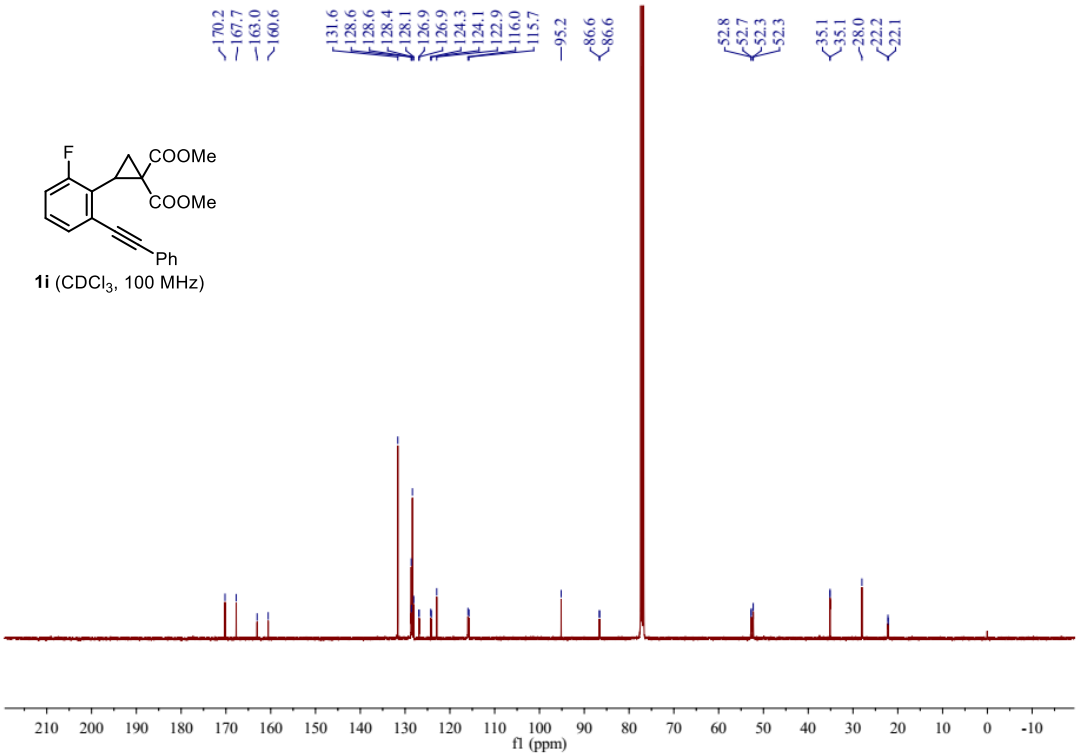


1h (DMSO-d_6, 100 MHz)

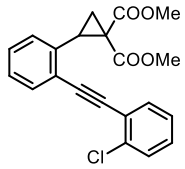


1i ($CDCl_3$, 400 MHz)

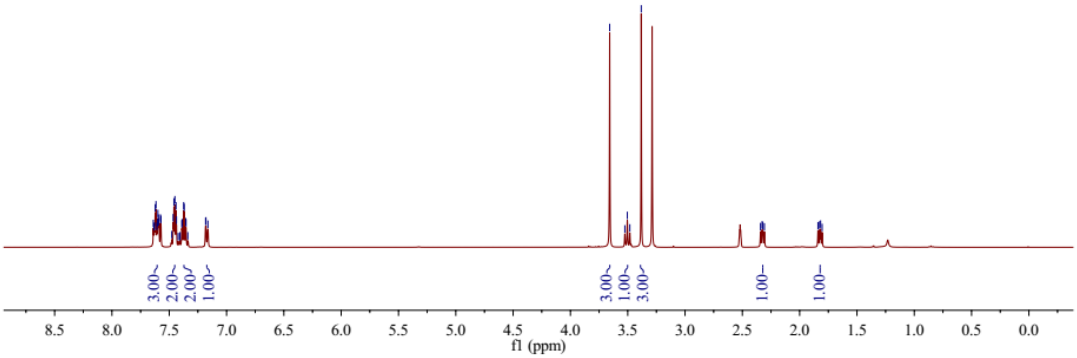


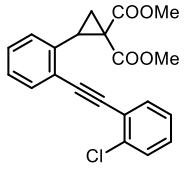


1i ($CDCl_3$, 100 MHz)

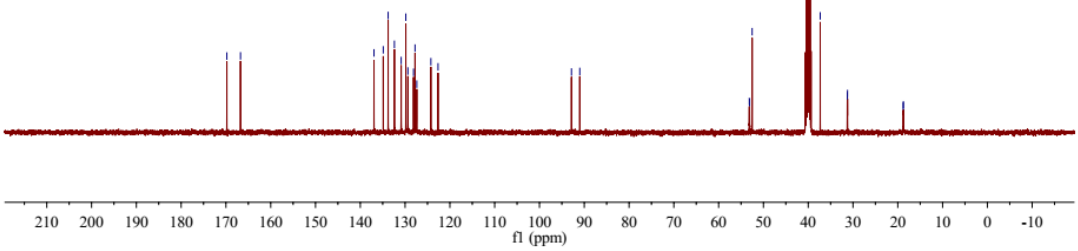


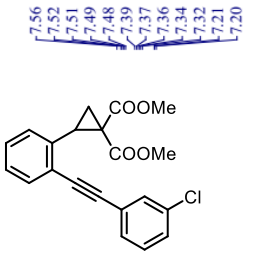
1j (DMSO-d_6, 400 MHz)



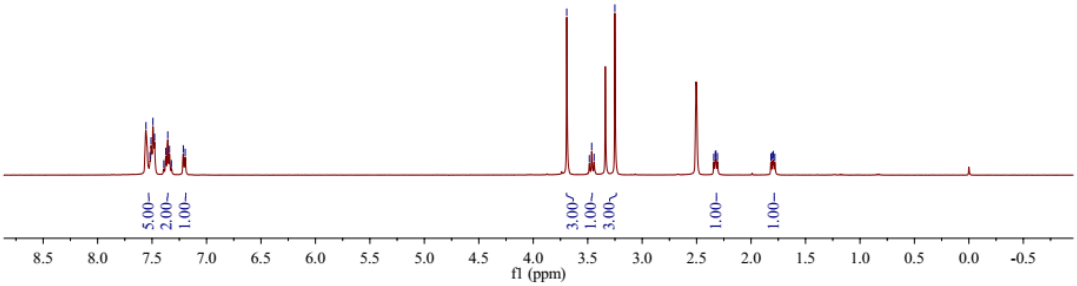


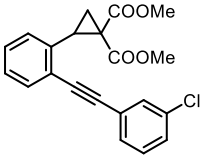
1j (DMSO-d_6, 100 MHz)



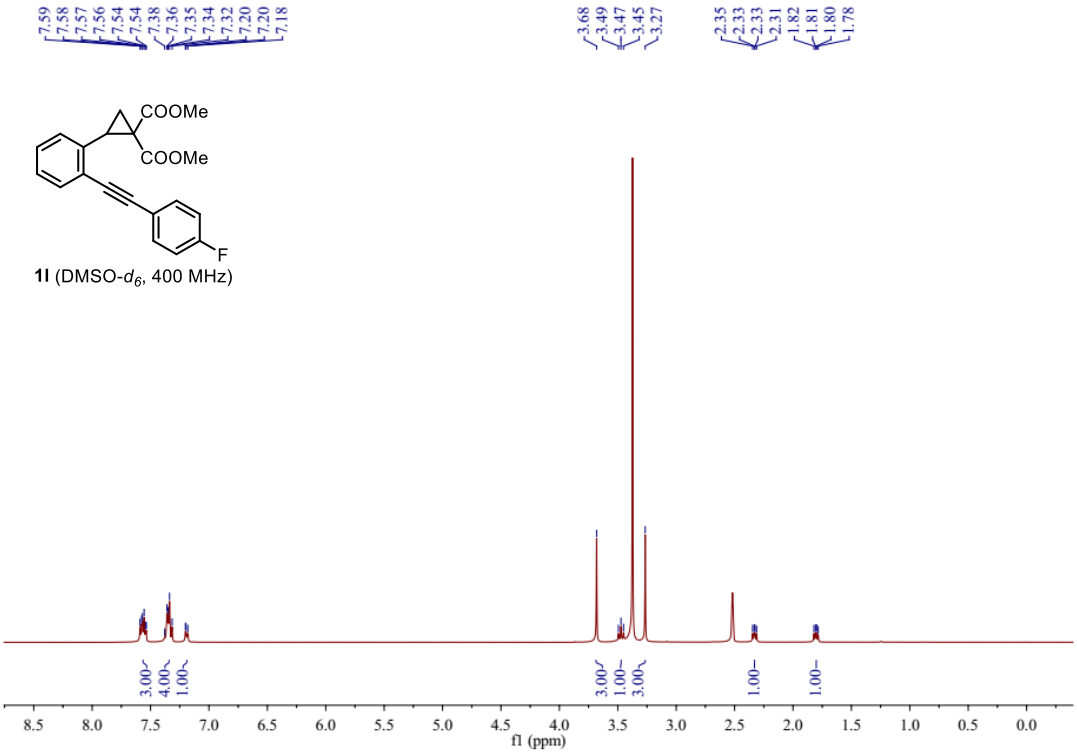


1k (DMSO-d_6, 400 MHz)

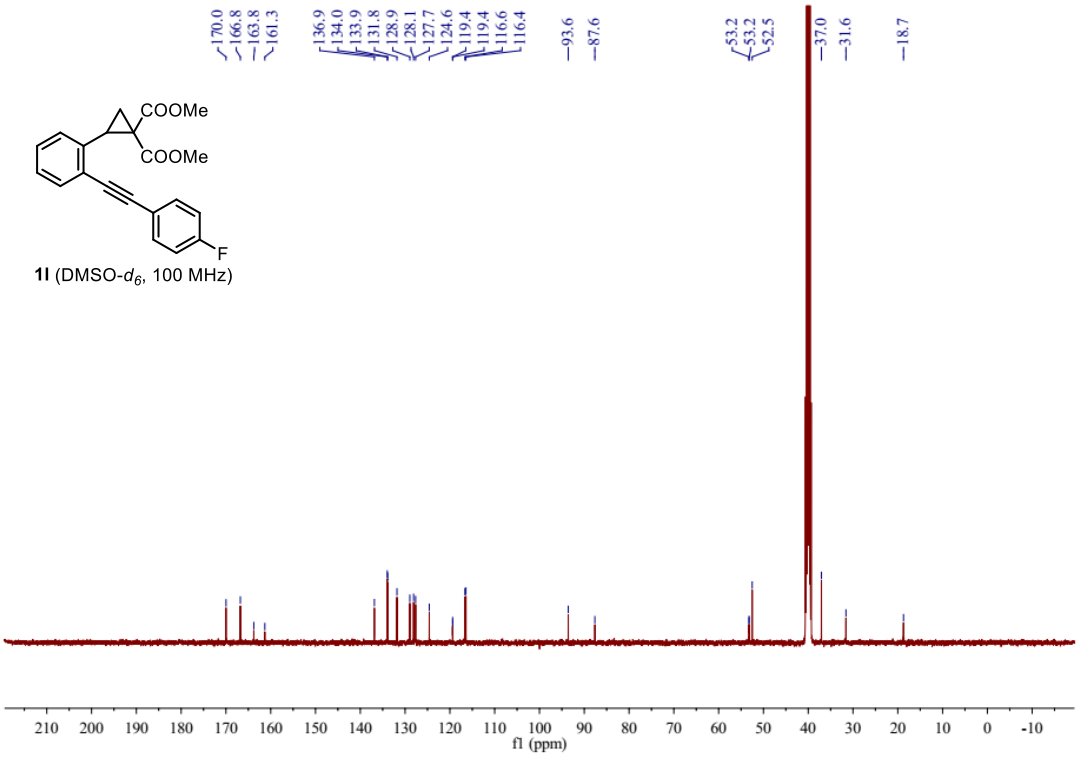




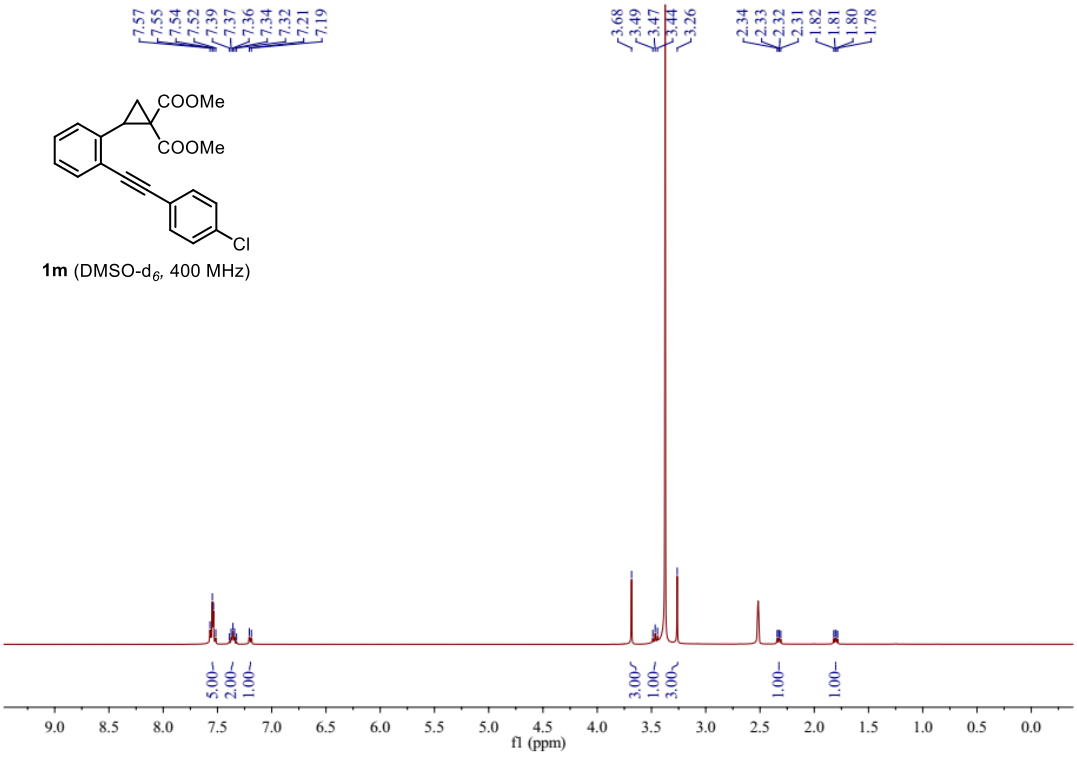
1k (DMSO-d_6, 100 MHz)



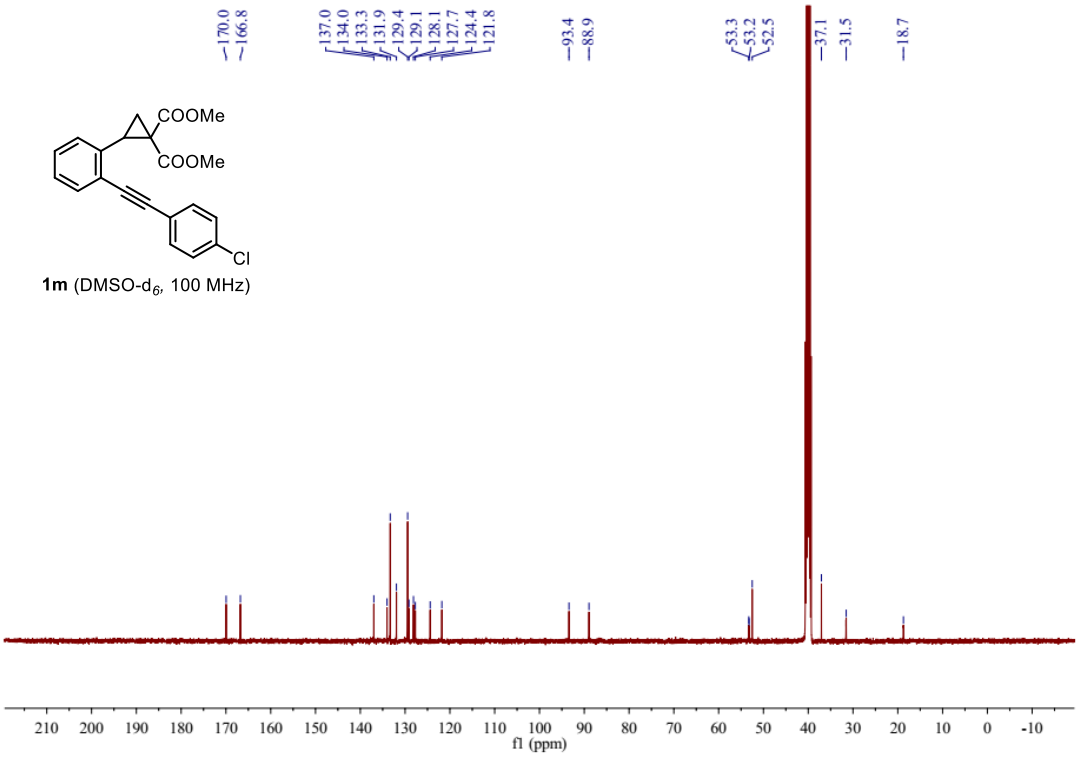
1l (DMSO-d_6, 400 MHz)



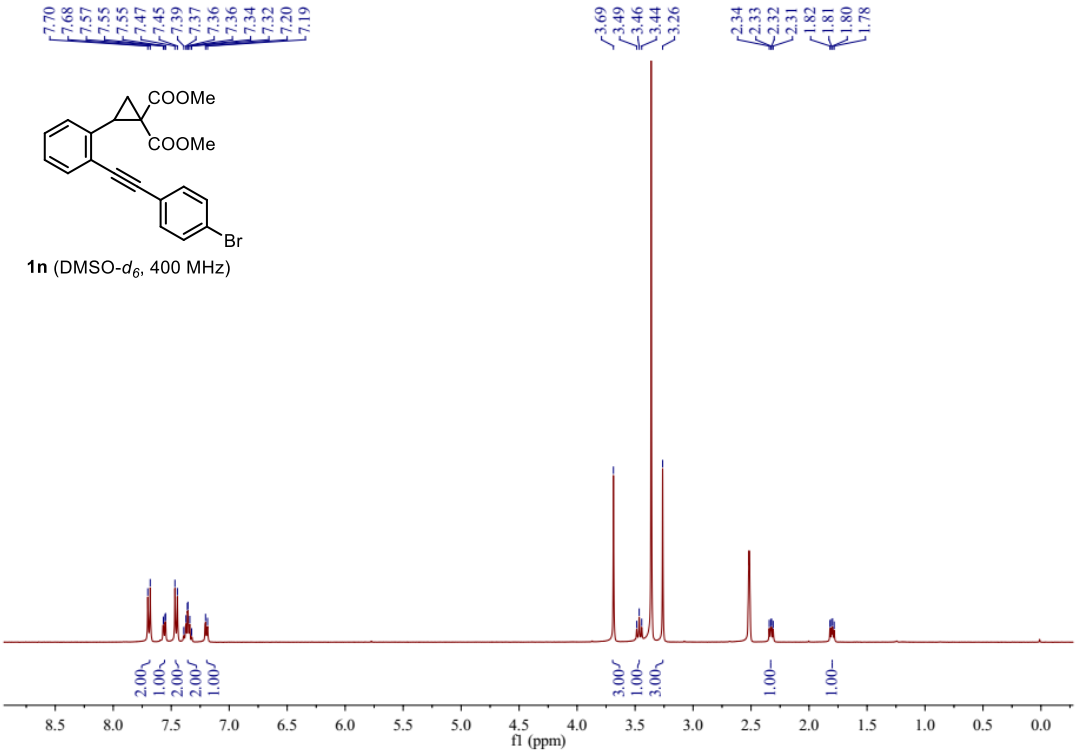
1l (DMSO-d_6, 100 MHz)



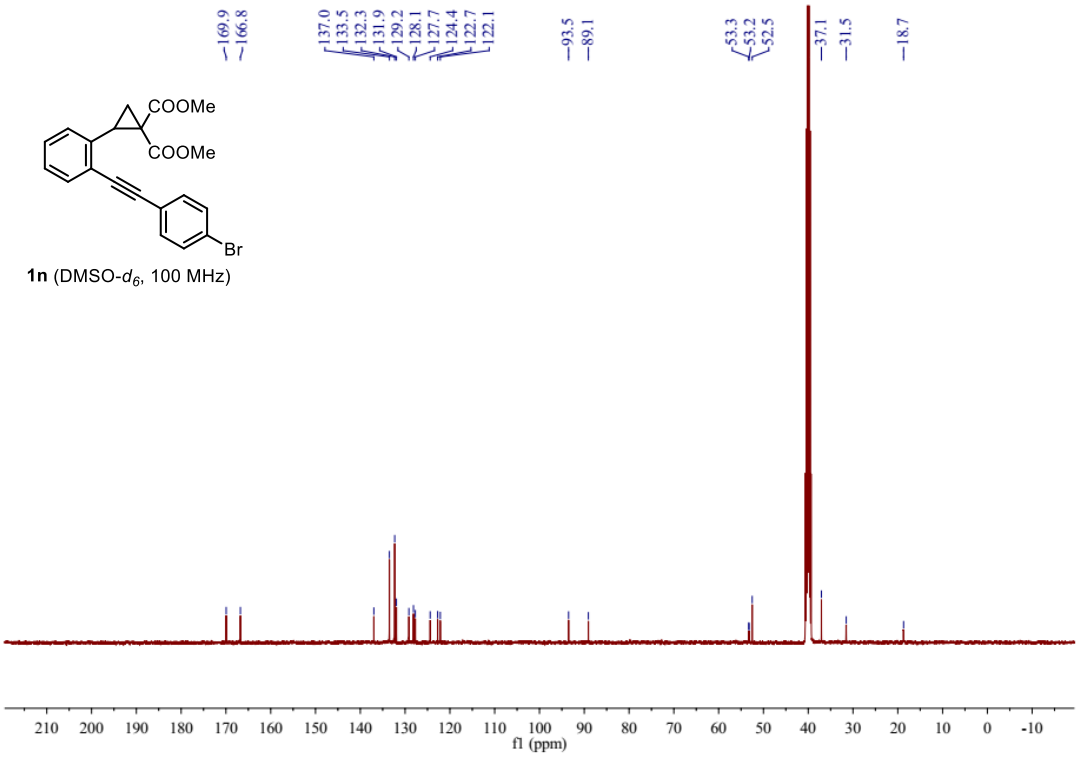
1m (DMSO-d_6, 400 MHz)



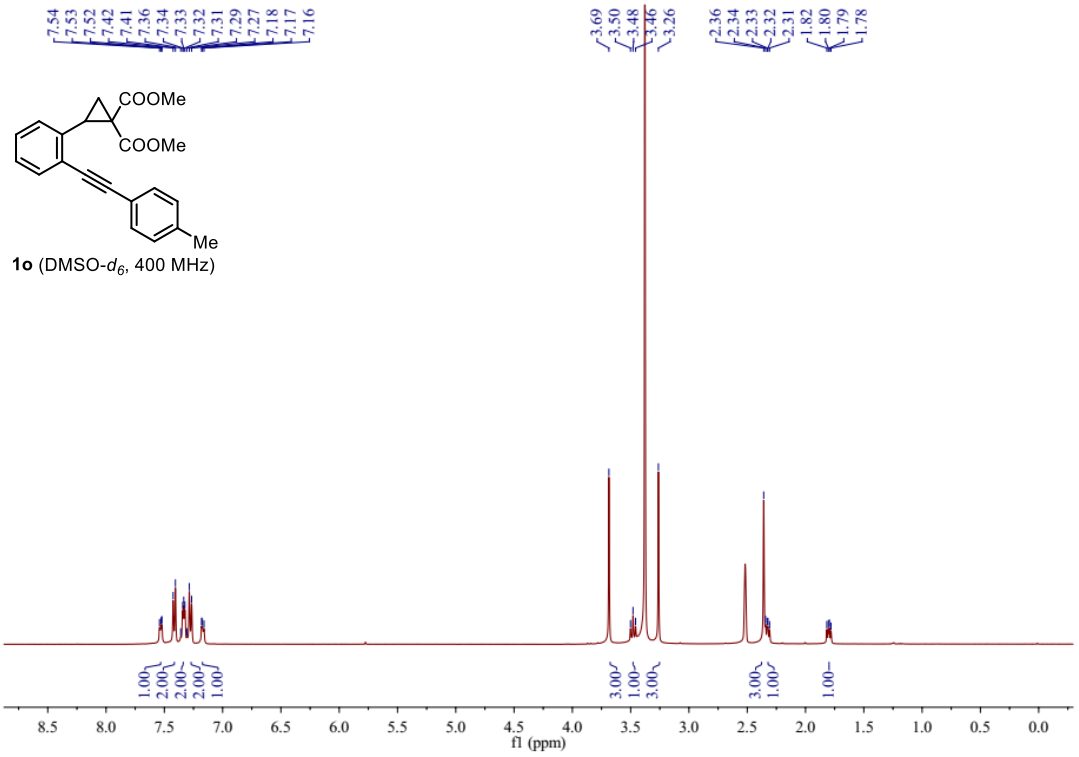
1m (DMSO-d_6, 100 MHz)



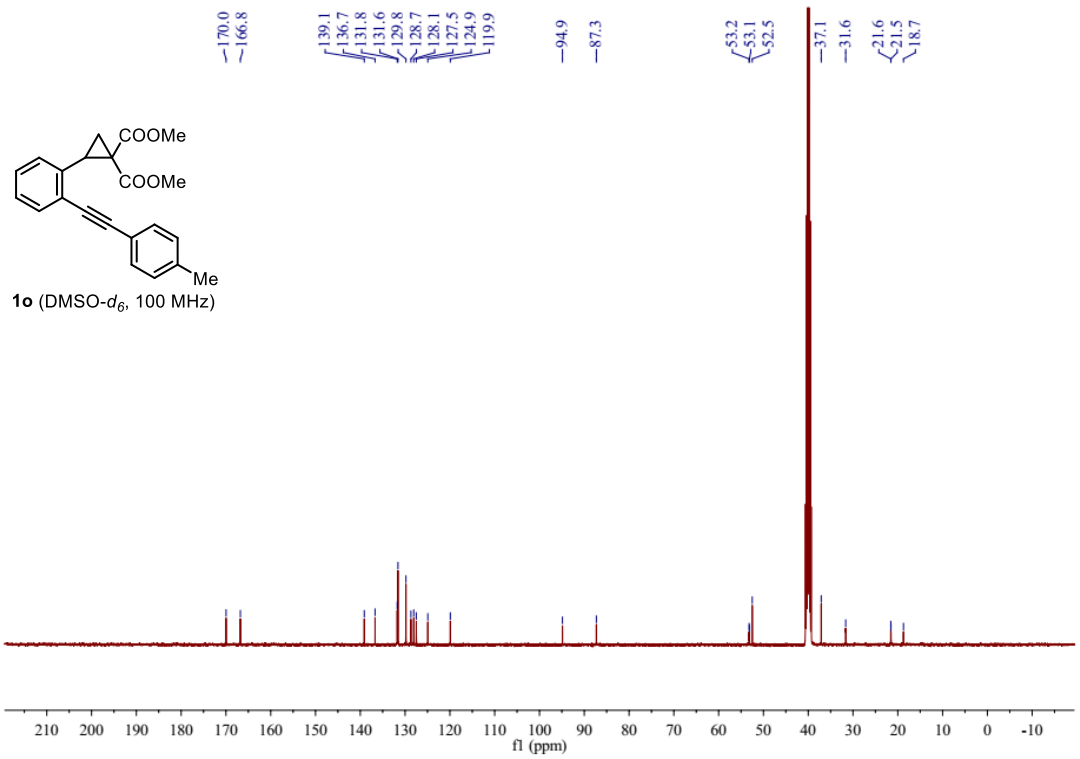
1n (DMSO-d_6, 400 MHz)



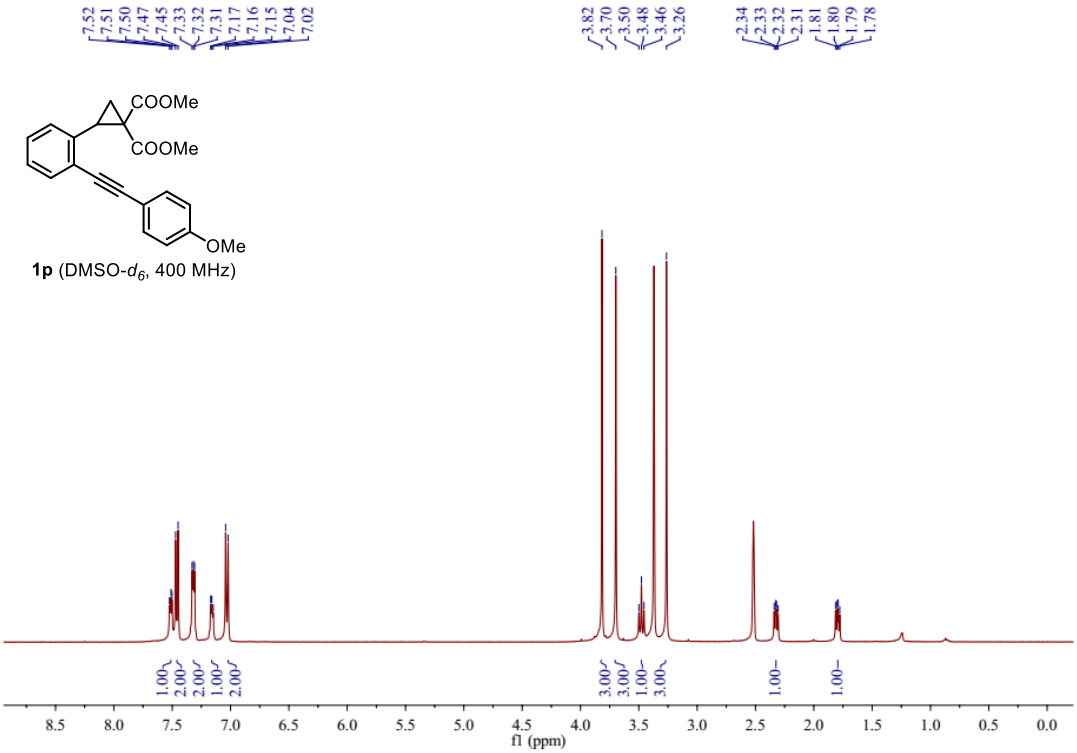
1n (DMSO-d_6, 100 MHz)



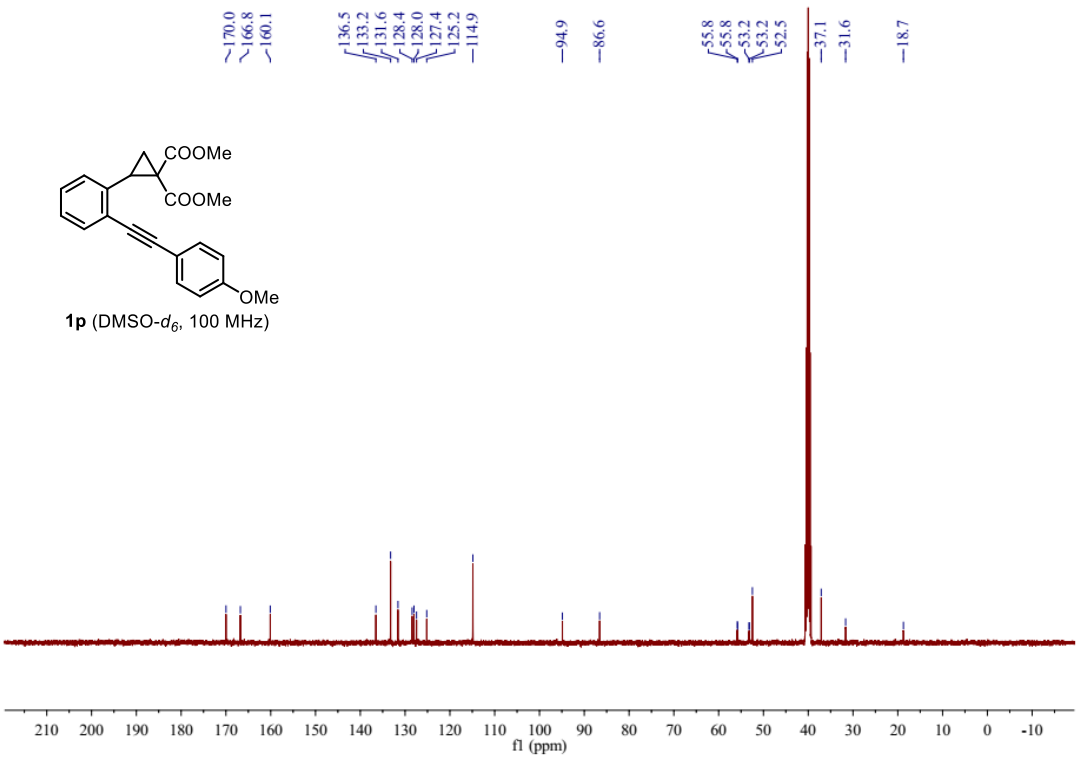
1o (DMSO-d_6, 400 MHz)



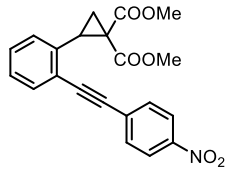
1o (DMSO-d_6, 100 MHz)



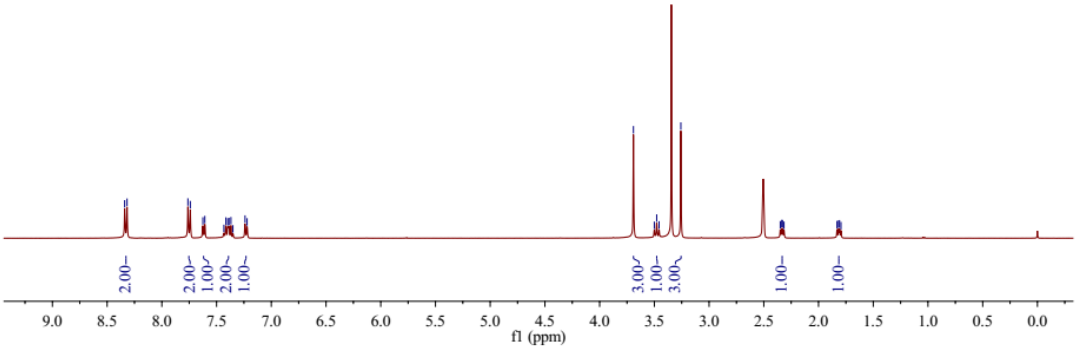
1p (DMSO-d_6, 400 MHz)

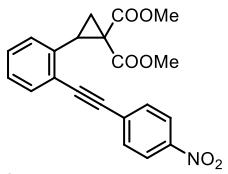


1p (DMSO-d_6, 100 MHz)

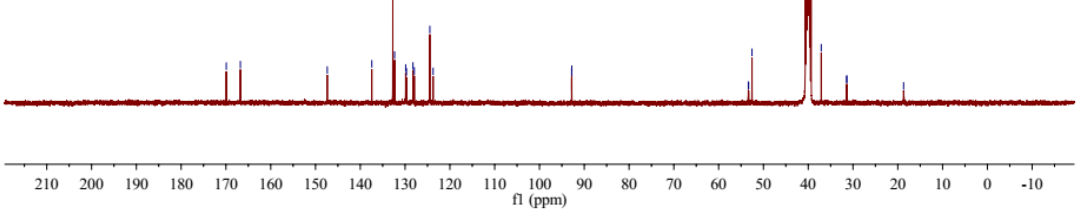


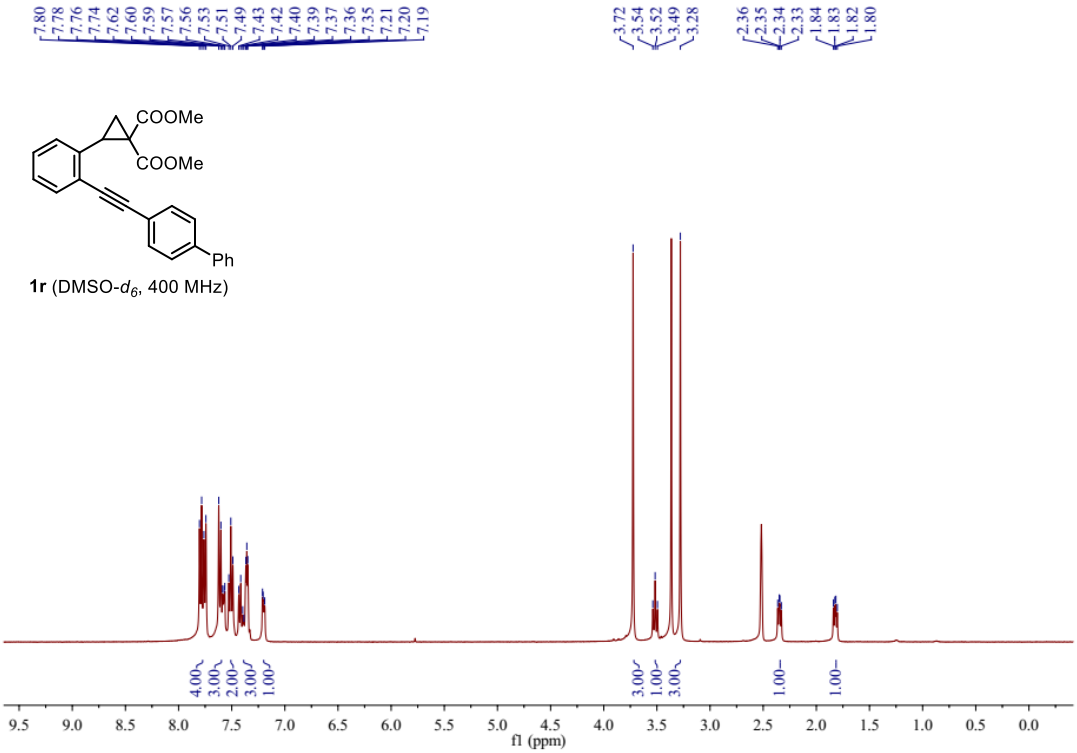
1q (DMSO-d_6, 400 MHz)



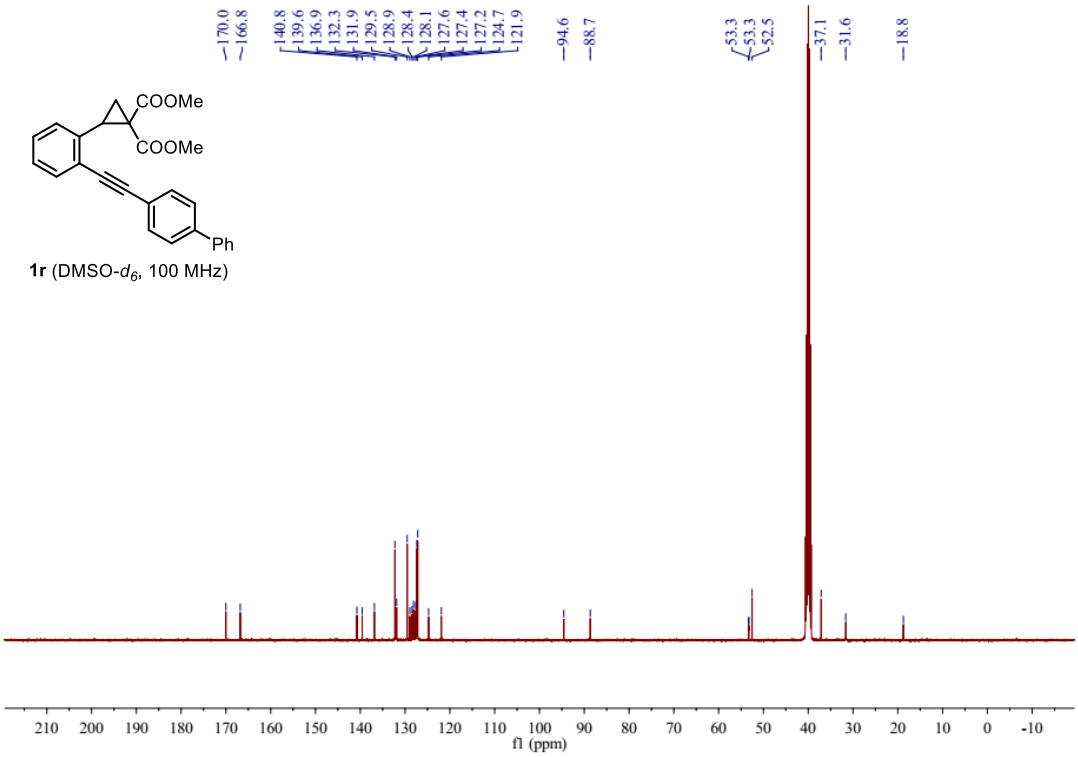


1q (DMSO-d_6, 100 MHz)

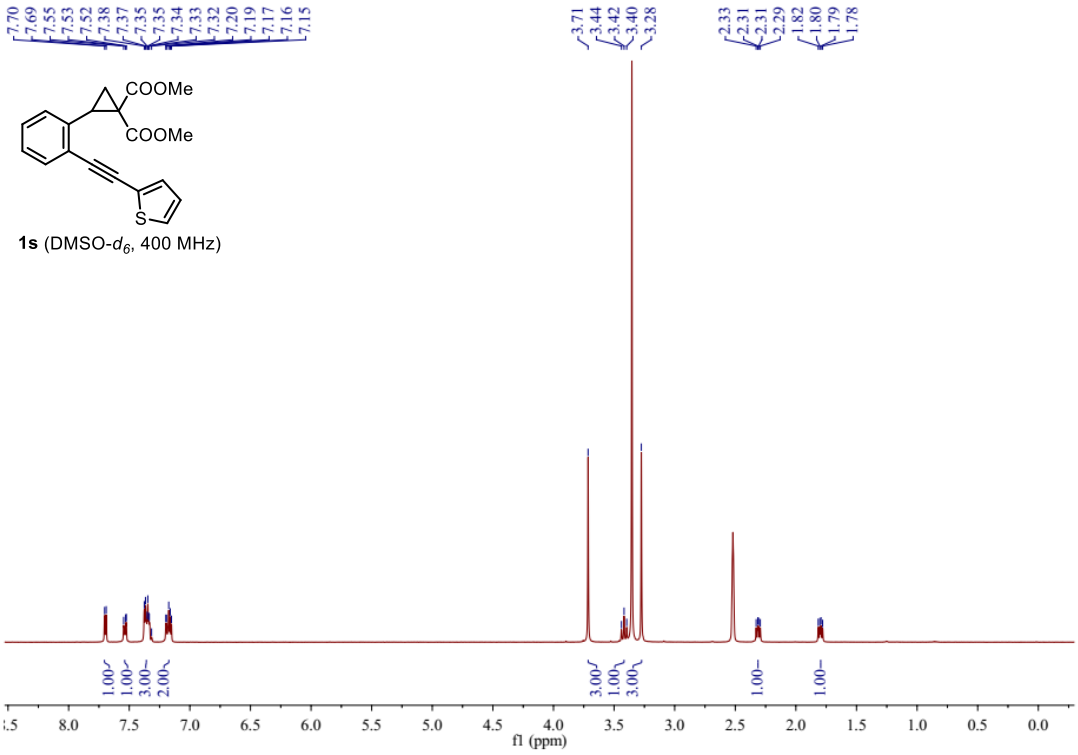




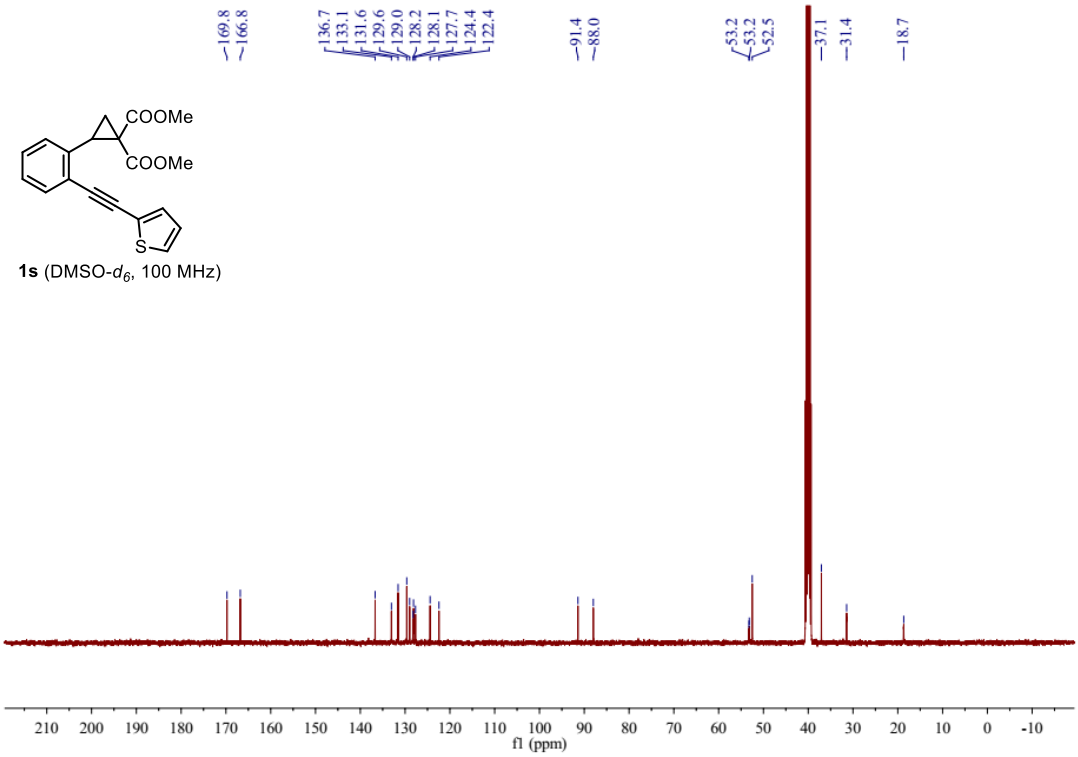
1r (DMSO-d_6, 400 MHz)



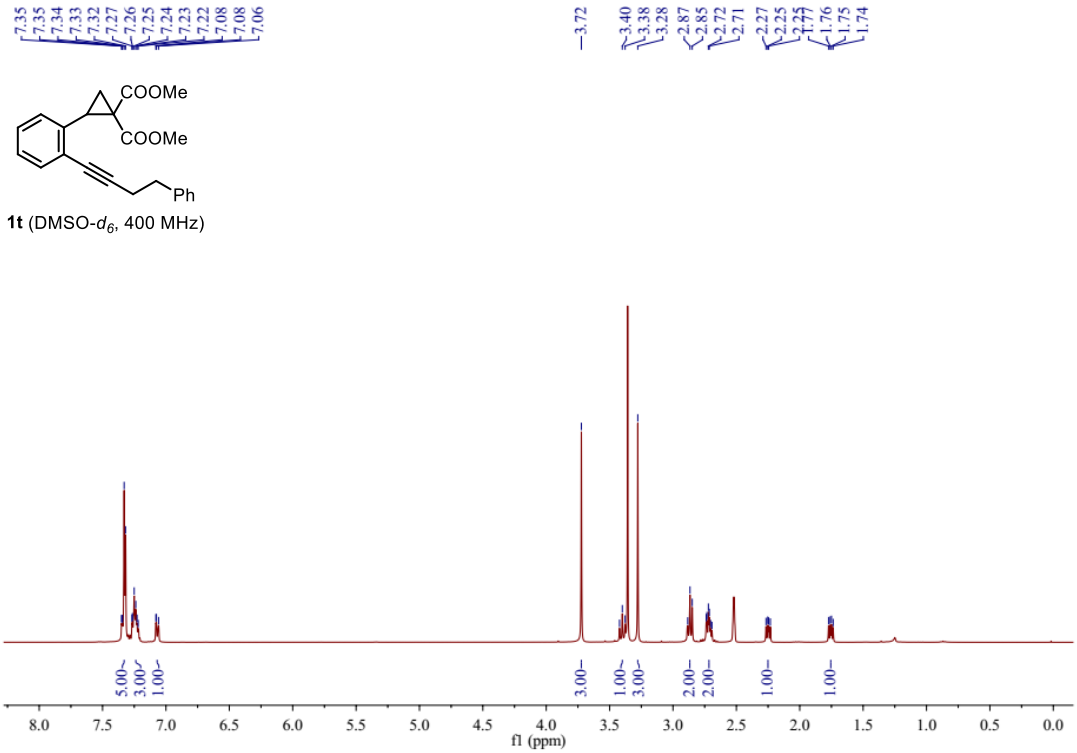
1r (DMSO-d_6, 100 MHz)



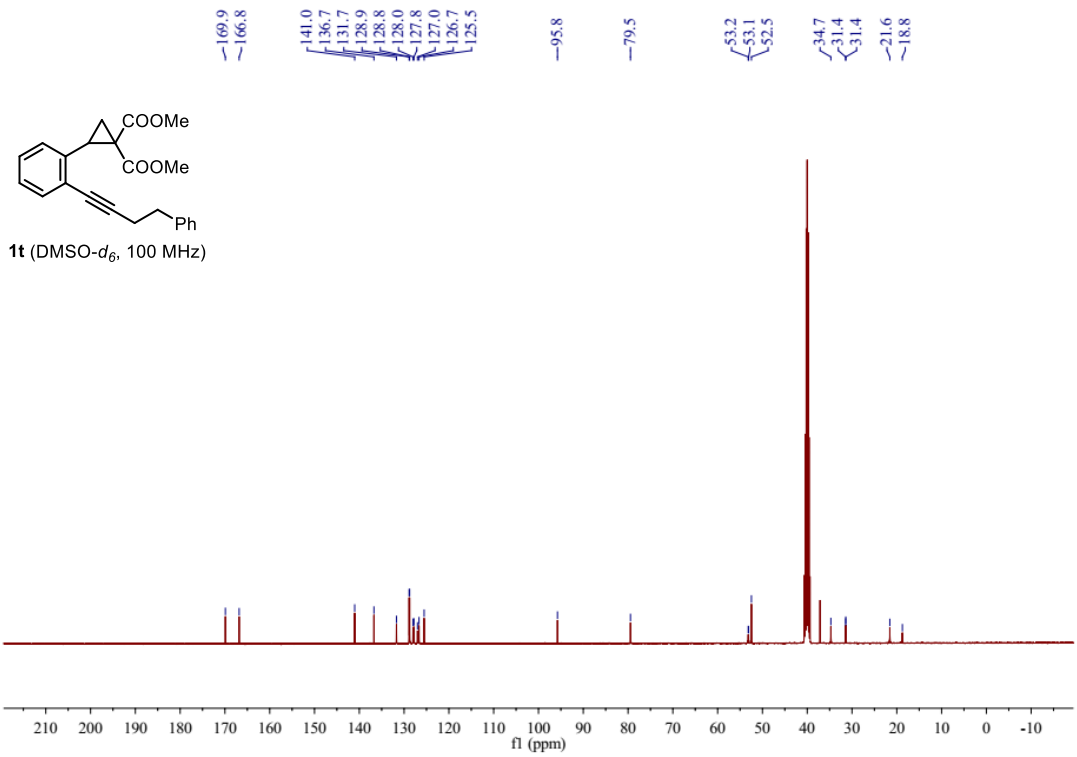
1s (DMSO-d_6, 400 MHz)



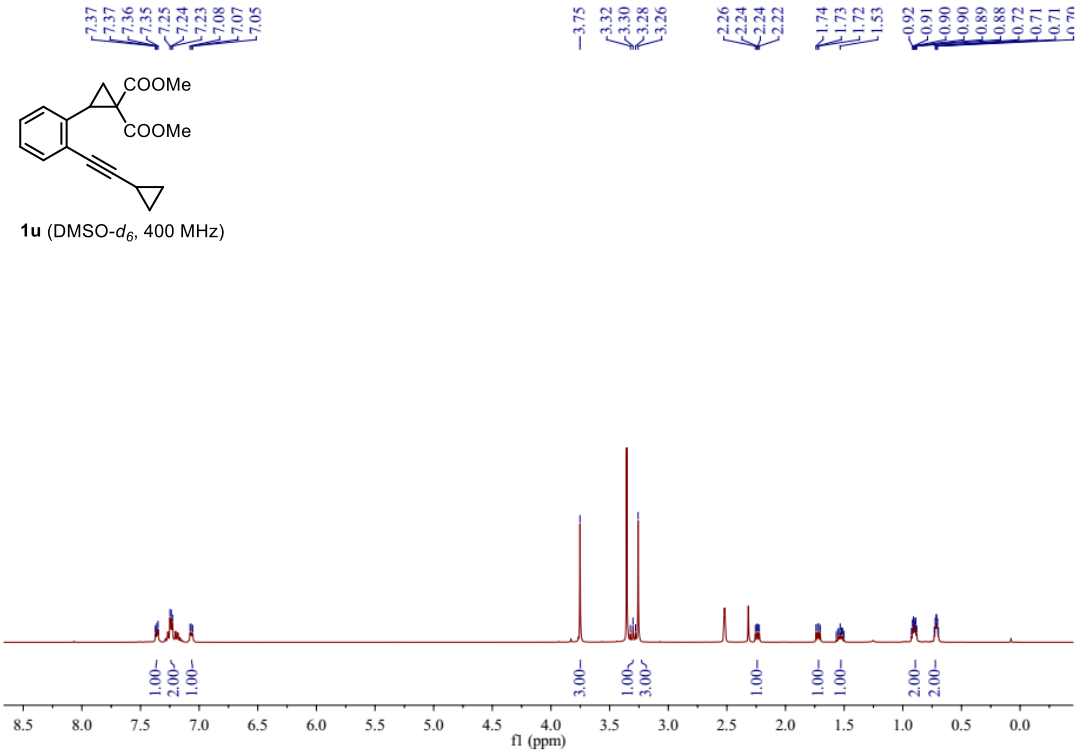
1s (DMSO-d_6, 100 MHz)



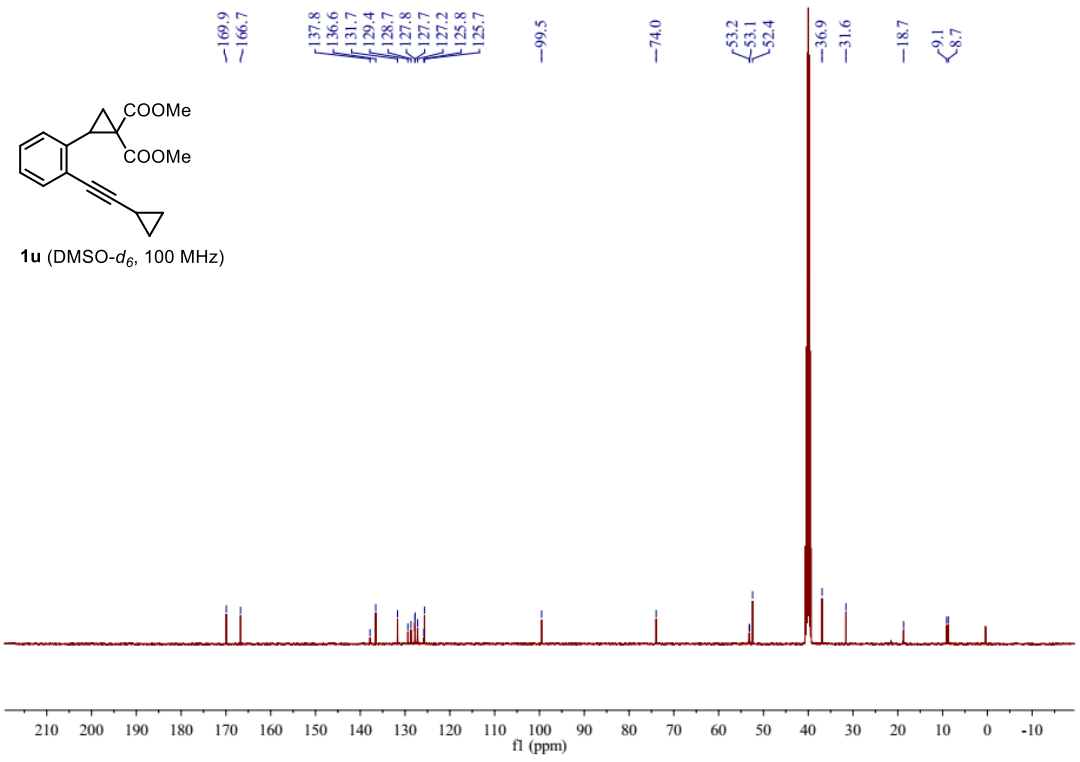
1t (DMSO-d_6, 400 MHz)



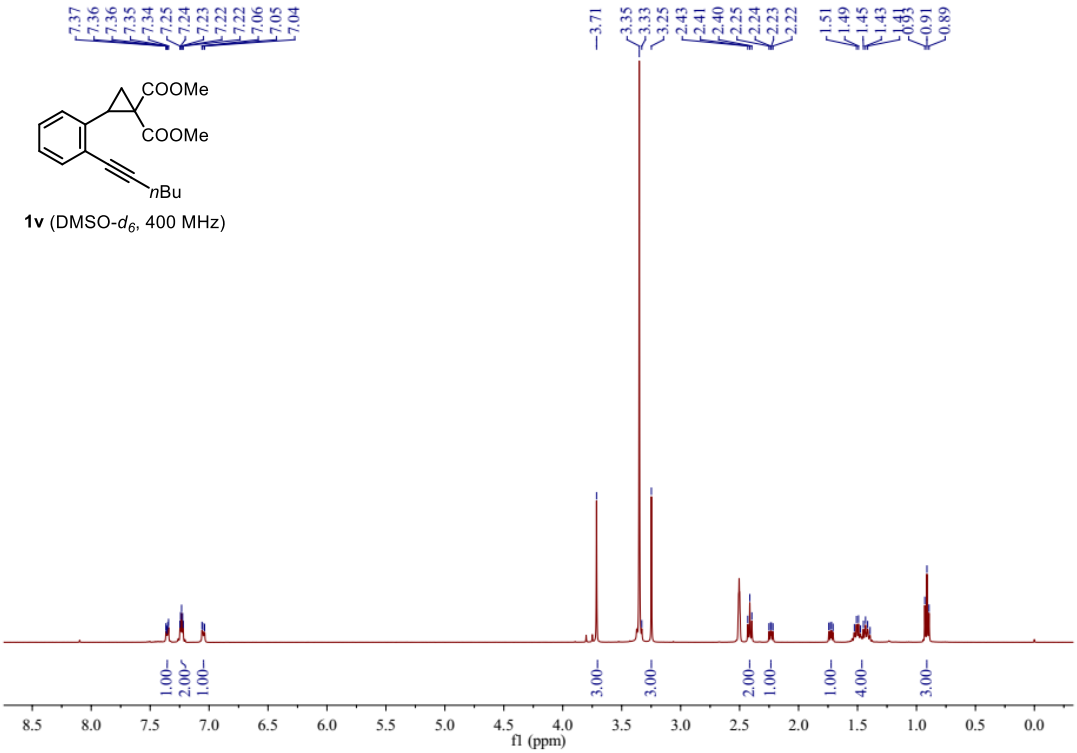
1t (DMSO-d_6, 100 MHz)



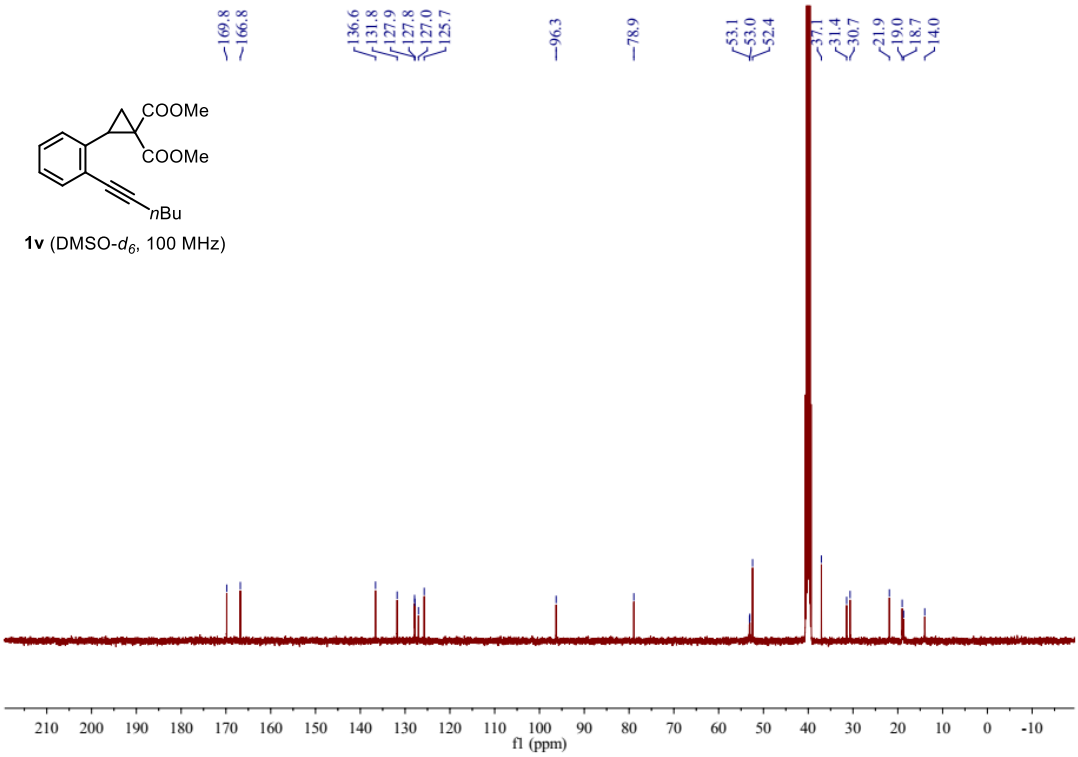
1u (DMSO-d_6, 400 MHz)



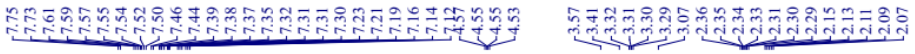
1u (DMSO-d_6, 100 MHz)

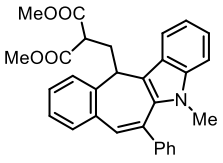


1v (DMSO-d_6, 400 MHz)

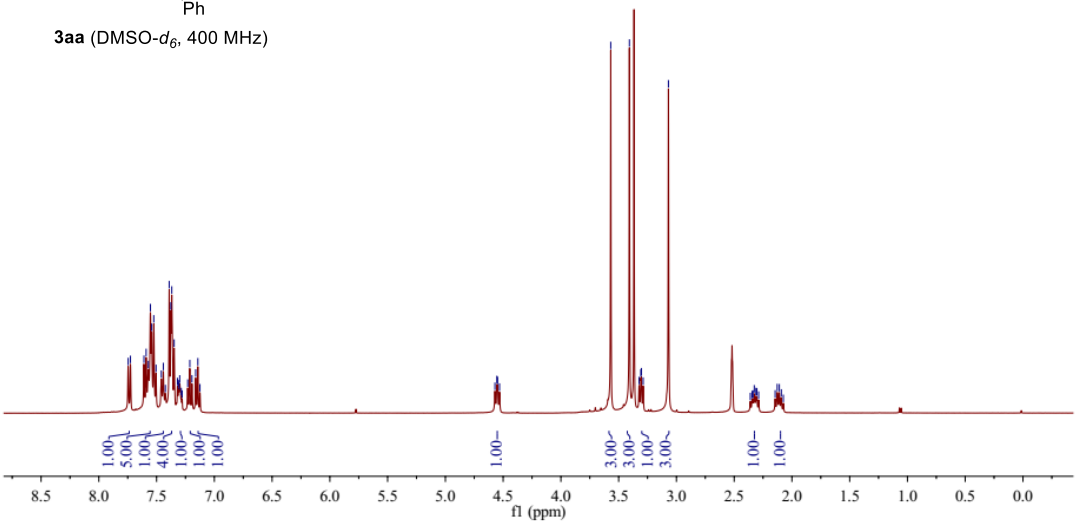


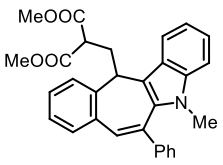
1v (DMSO-d_6, 100 MHz)



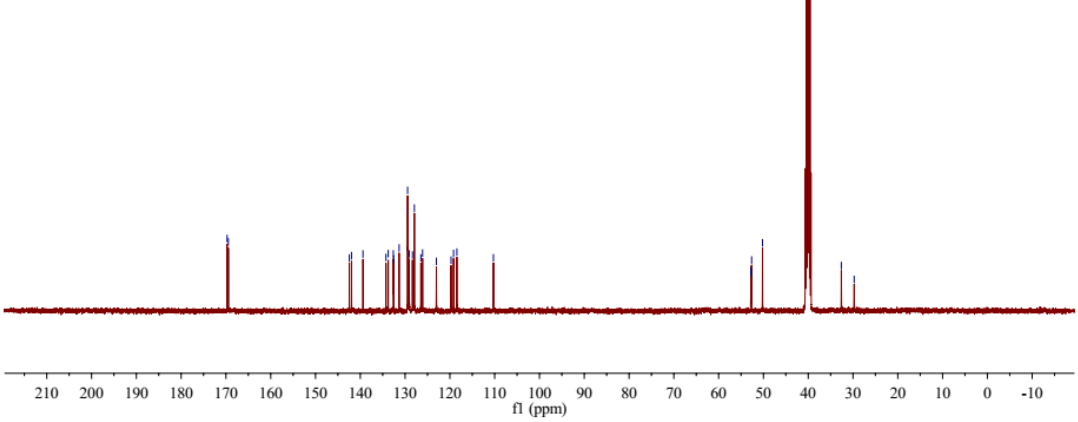


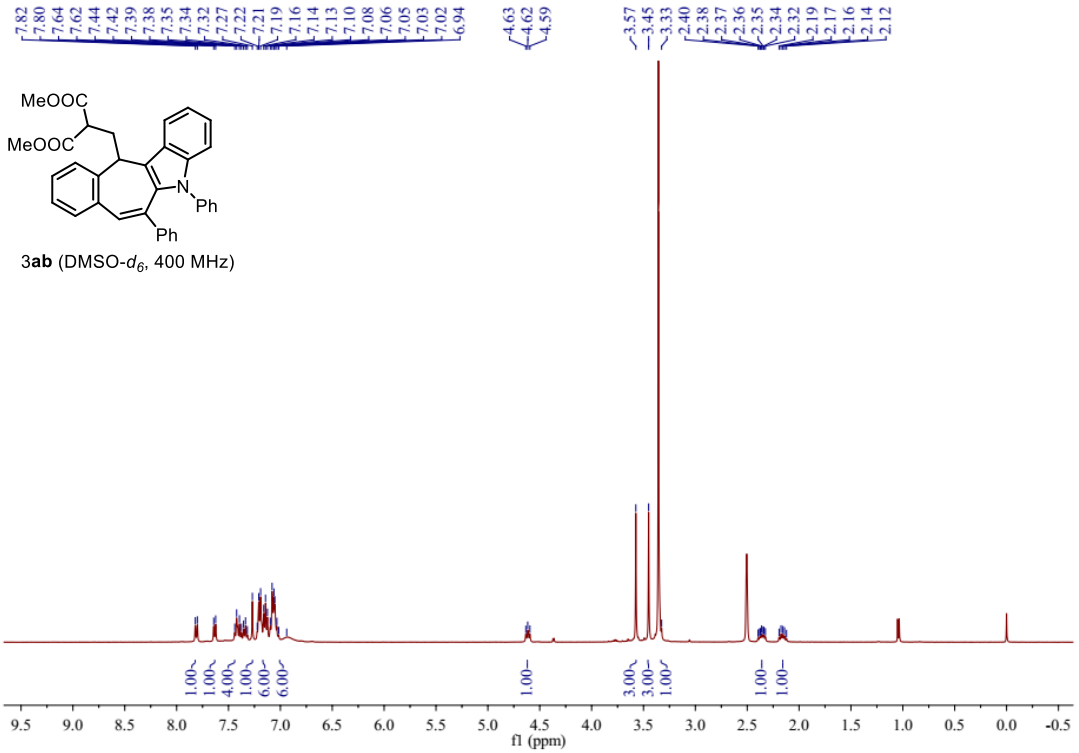
3aa (DMSO-d_6, 400 MHz)



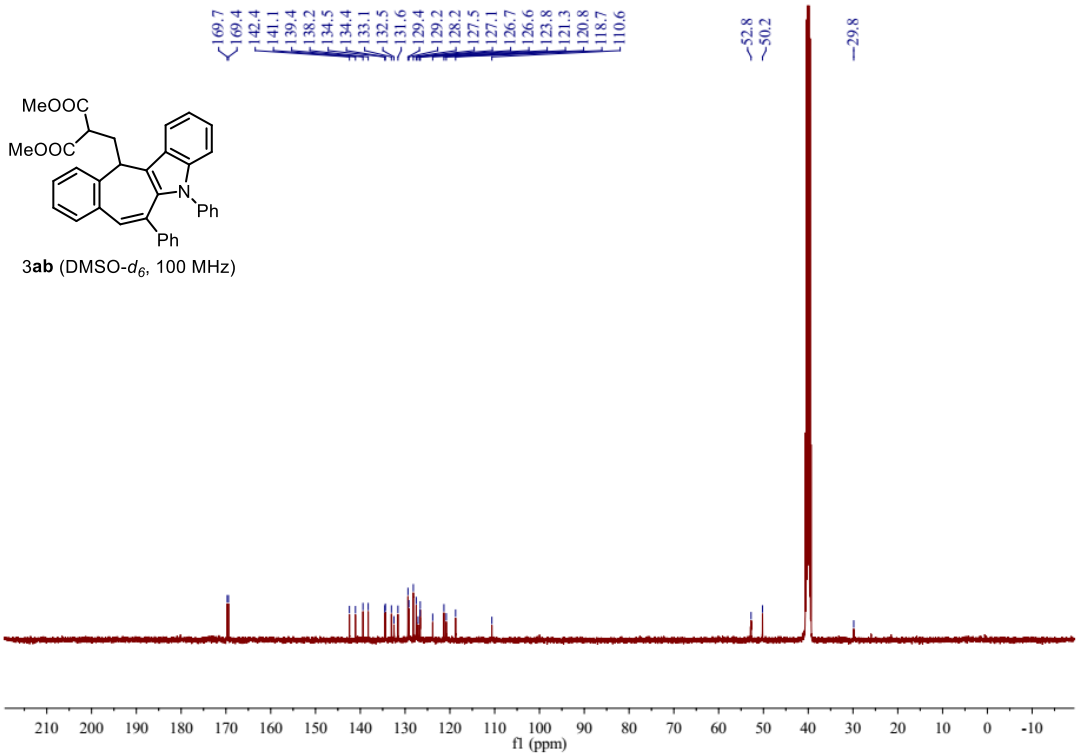


3aa (DMSO-d_6, 100 MHz)

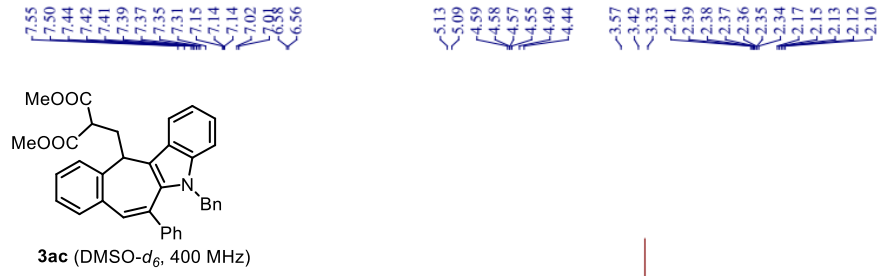




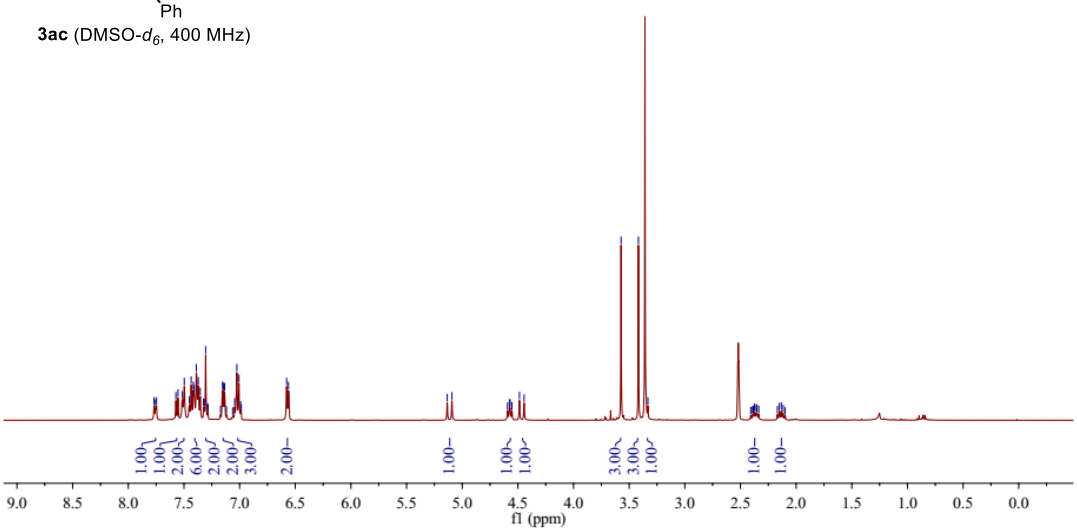
3ab (DMSO-d_6, 400 MHz)



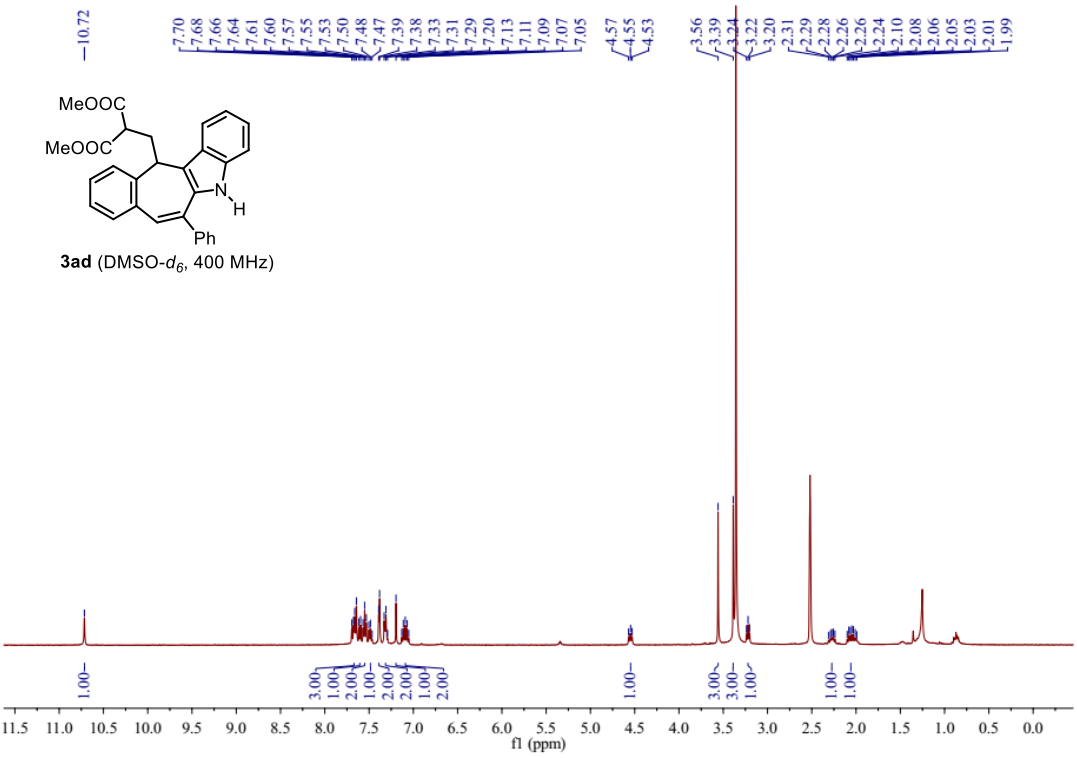
3ab (DMSO-d_6, 100 MHz)



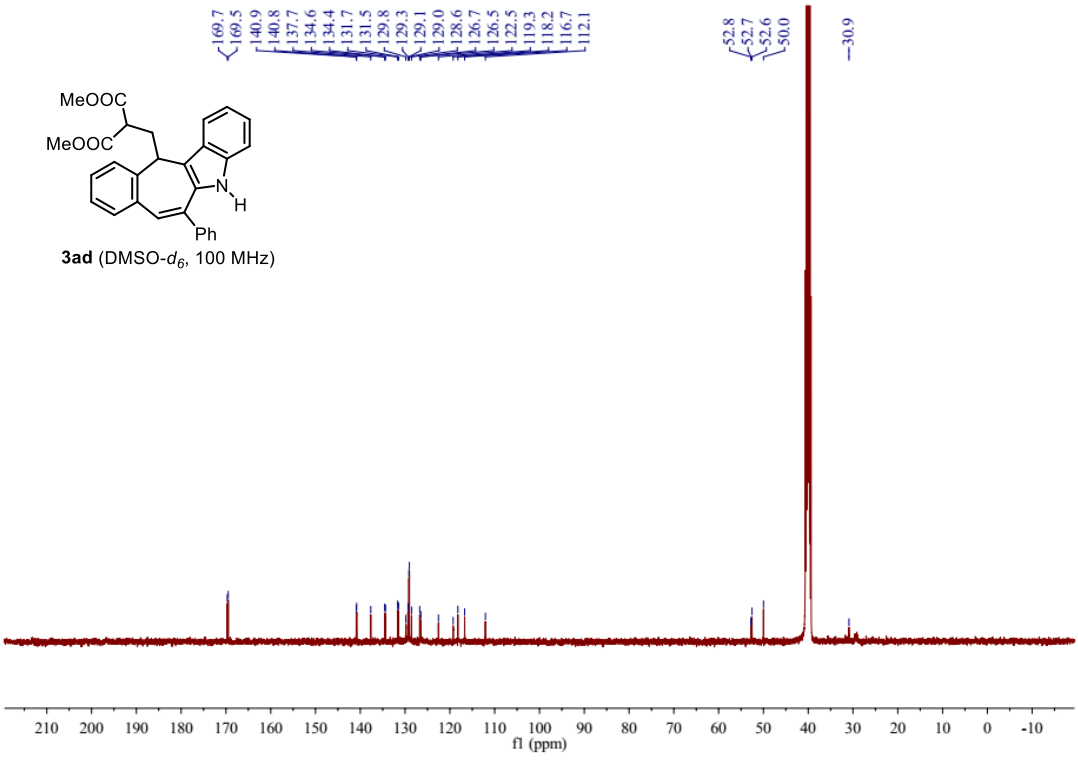
3ac (DMSO-d_6, 400 MHz)



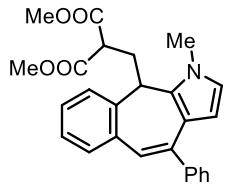
3ac (DMSO-d_6, 100 MHz)



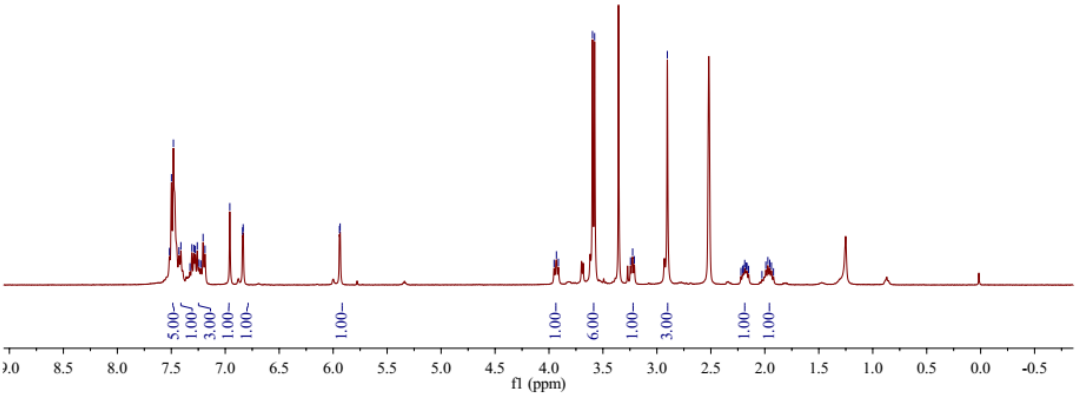
3ad (DMSO-d_6, 400 MHz)

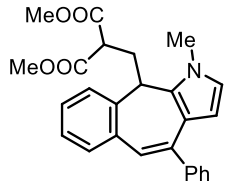


3ad (DMSO-d_6, 100 MHz)

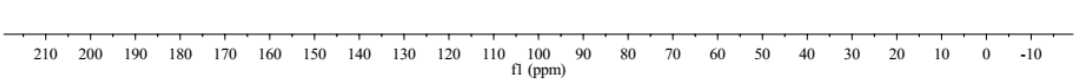


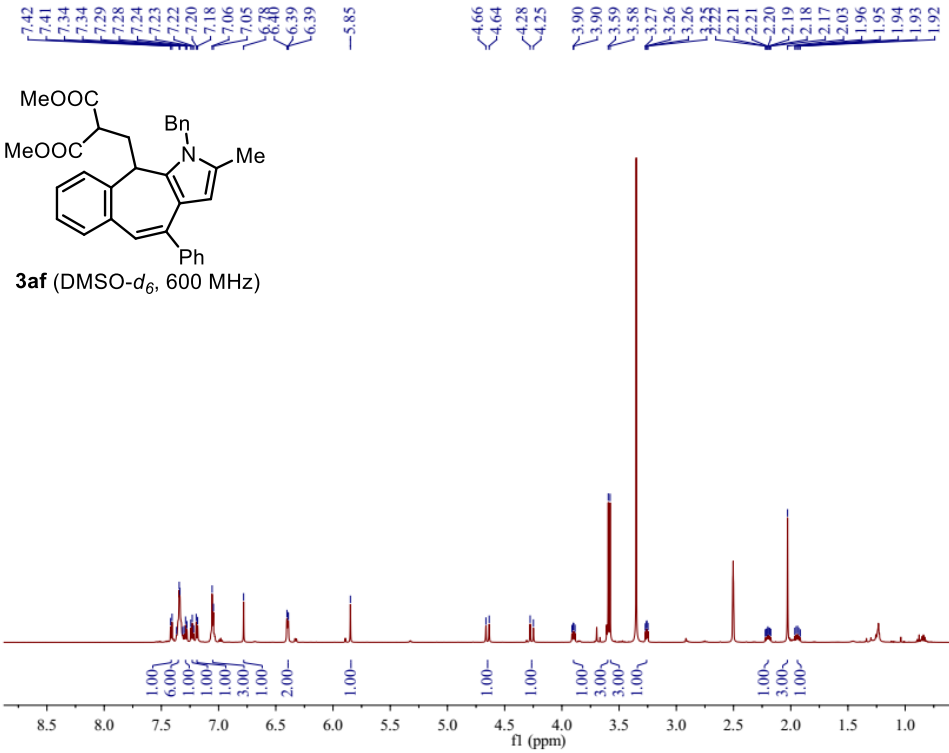
3ae (DMSO-d_6, 400 MHz)



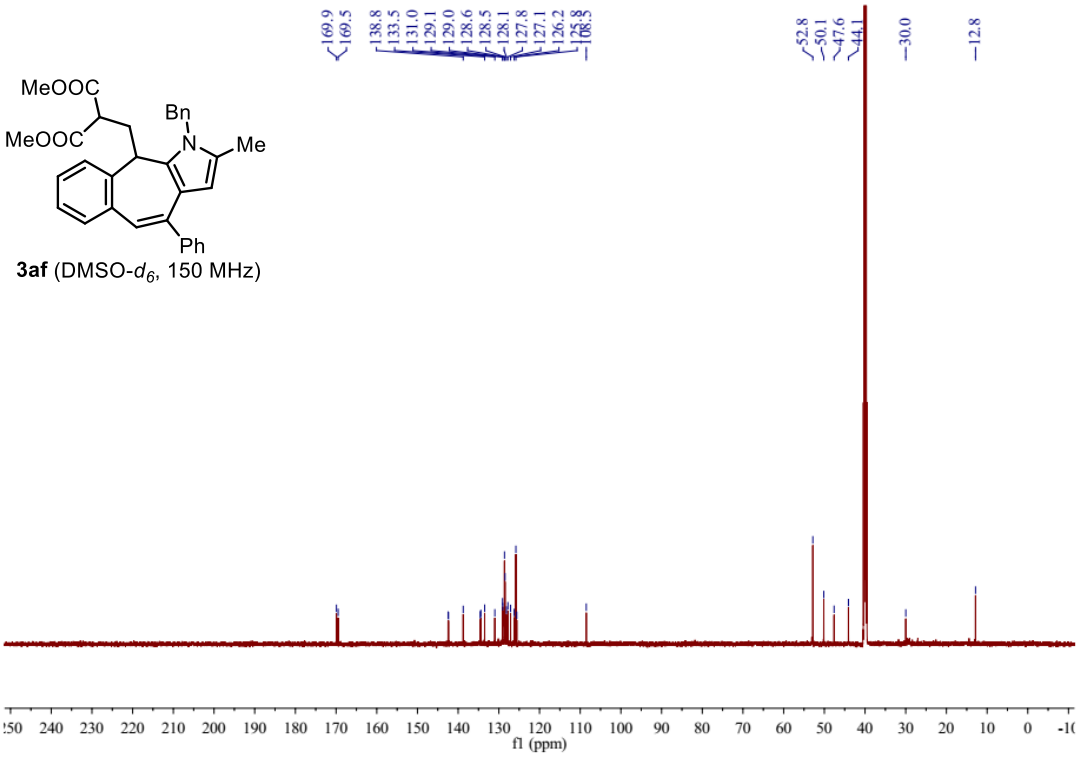


3ae (DMSO-d_6, 100 MHz)

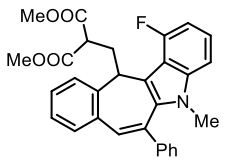




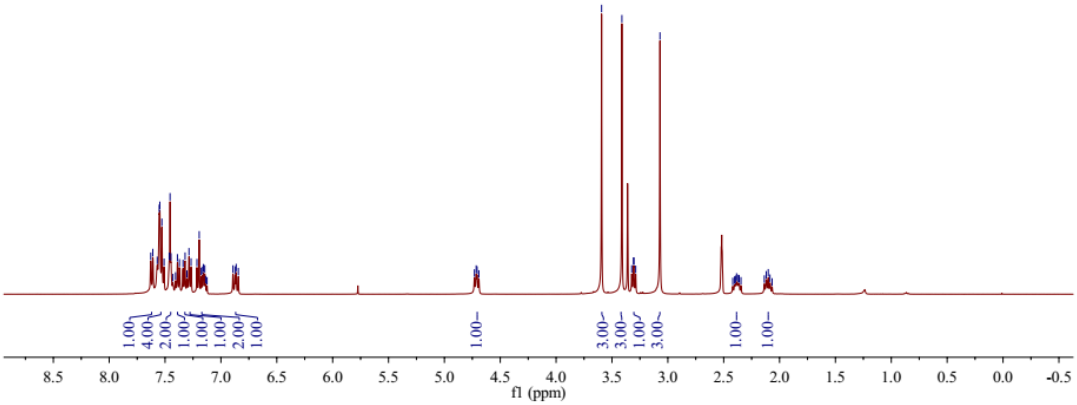
3af (DMSO-d_6, 600 MHz)

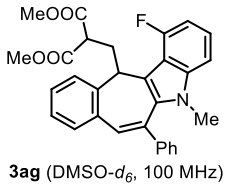


3af (DMSO-d_6, 150 MHz)

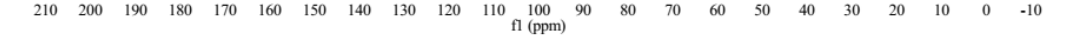


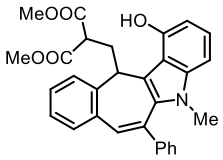
3ag (DMSO-d_6, 400 MHz)



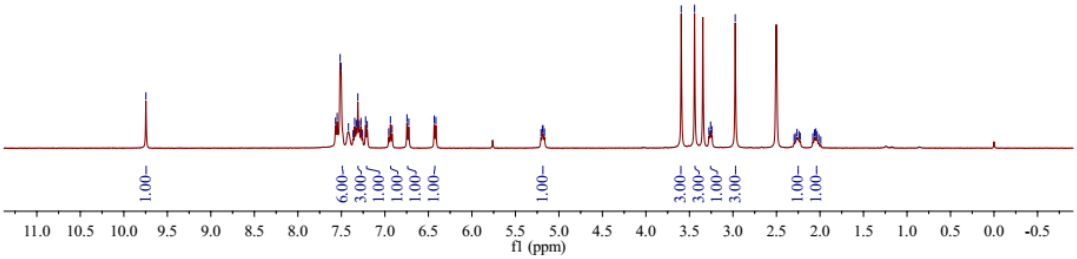


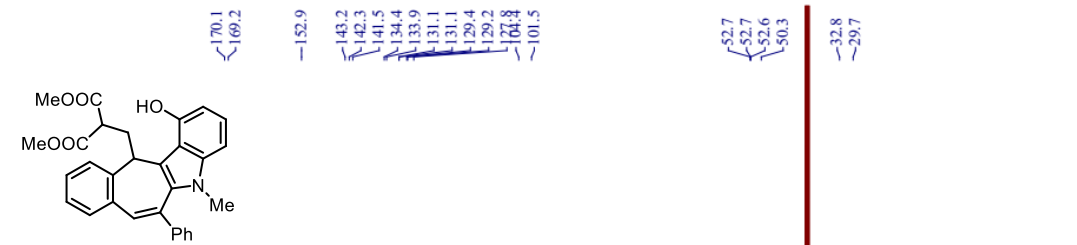
3ag (DMSO-d_6, 100 MHz)



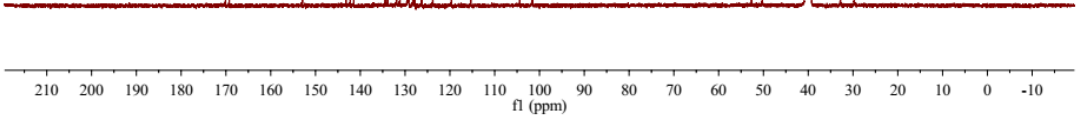


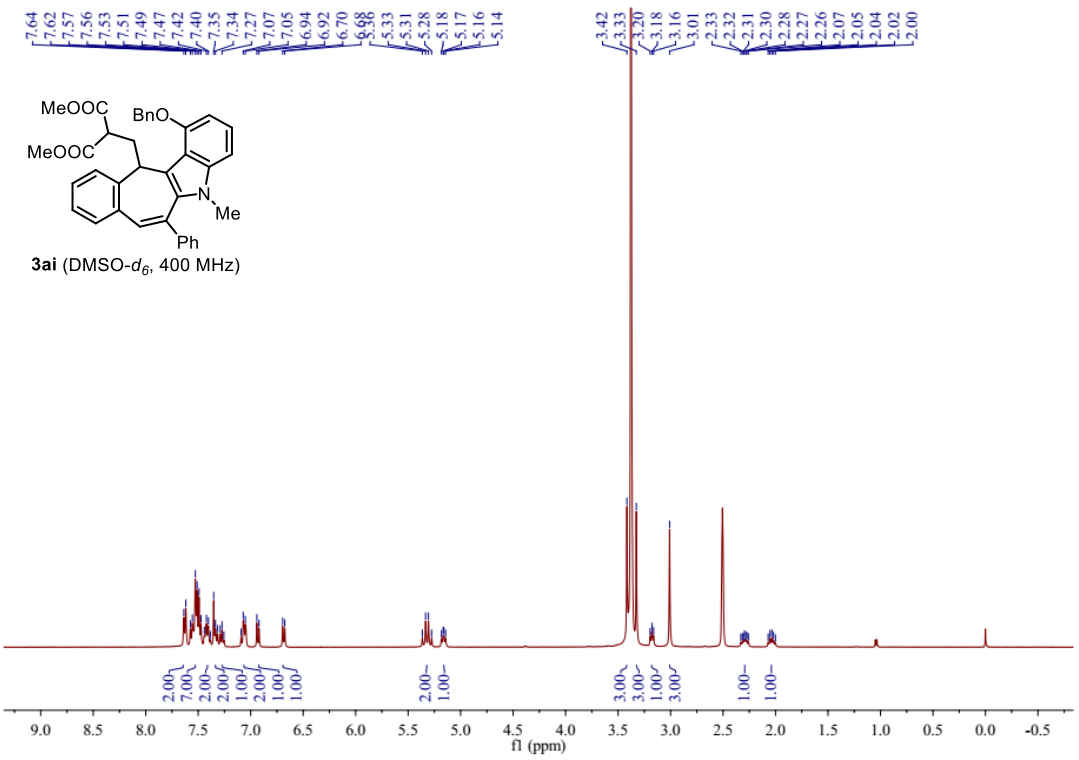
3ah (DMSO-d_6, 400 MHz)



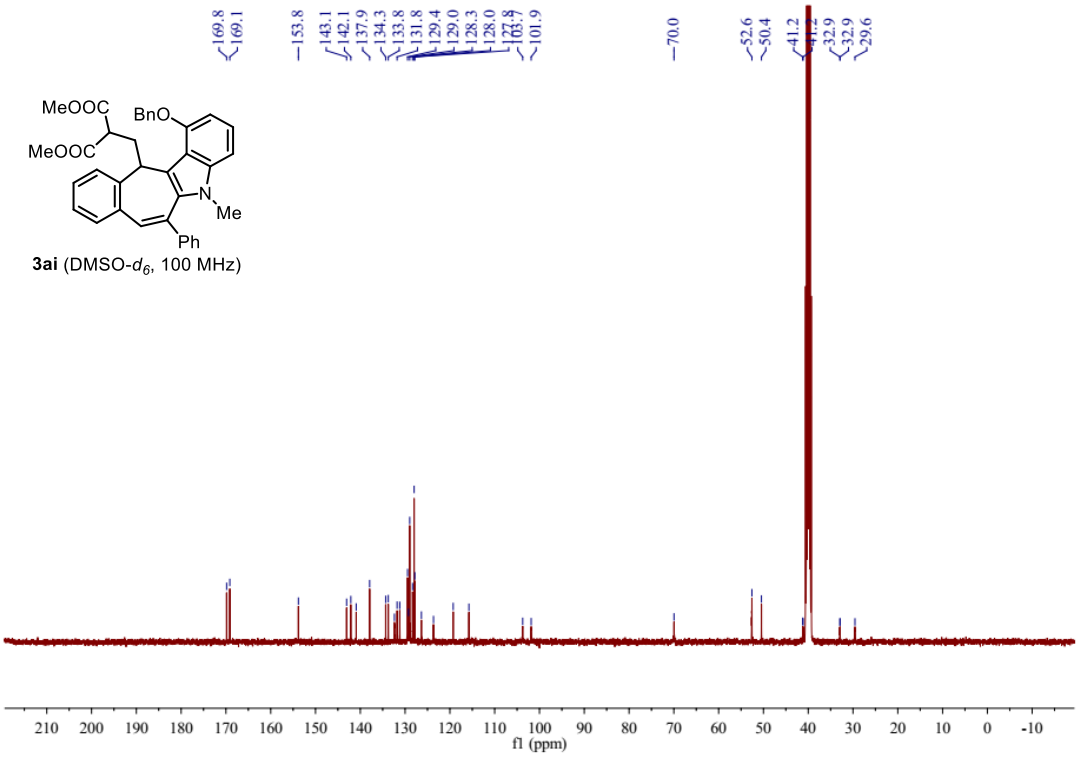


3ah (DMSO-d_6, 100 MHz)

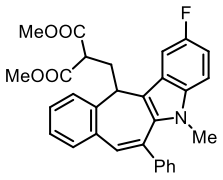




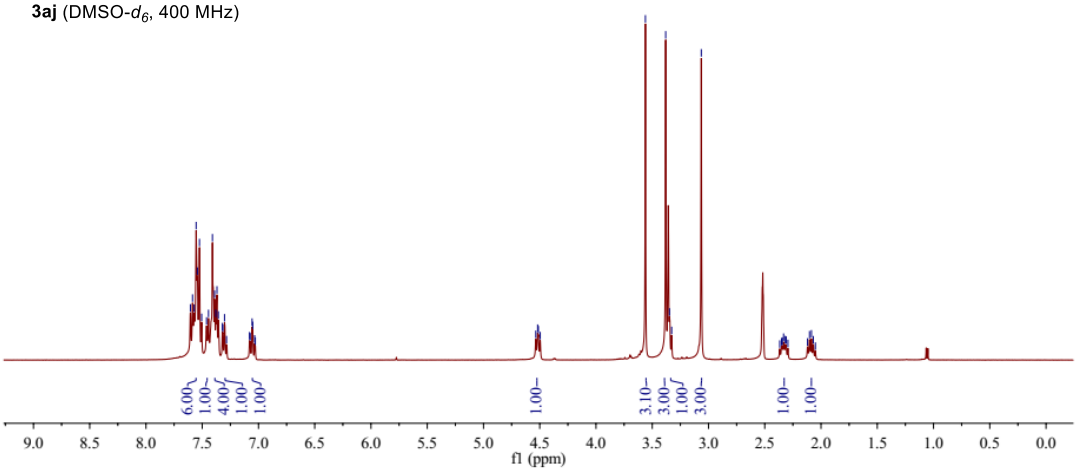
3ai (DMSO-d_6, 400 MHz)

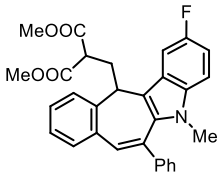


3ai (DMSO-d_6, 100 MHz)

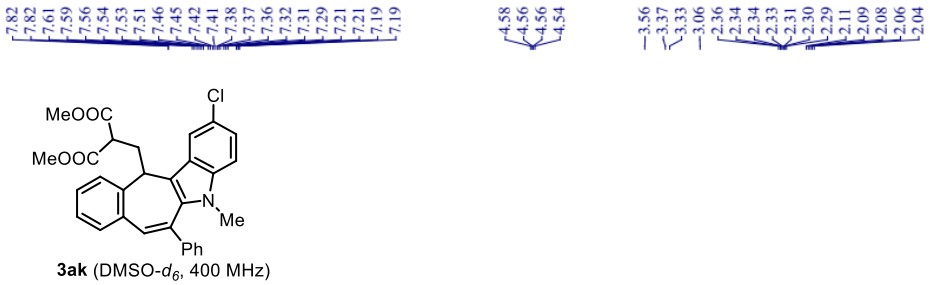


3aj (DMSO-d_6, 400 MHz)

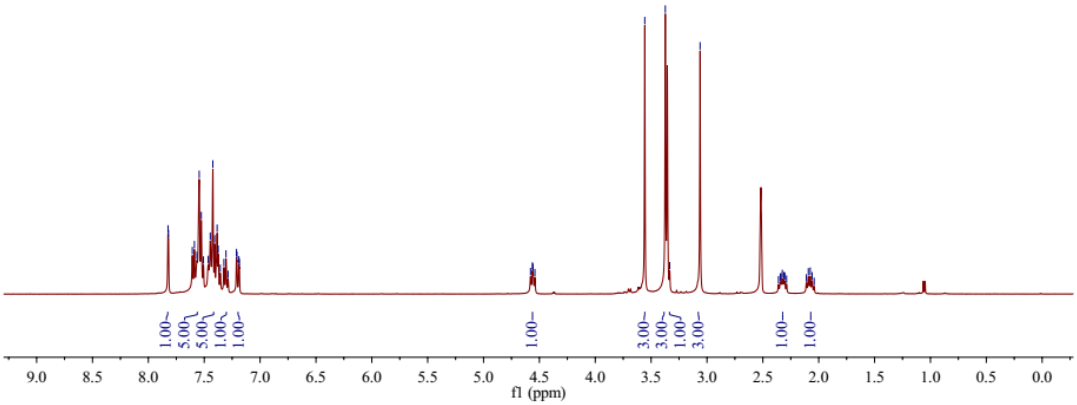


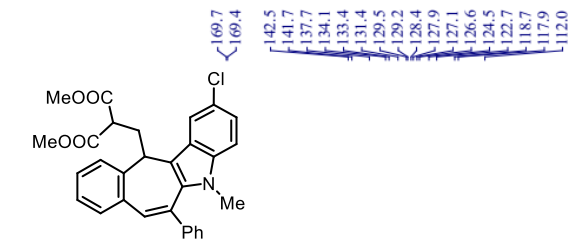


3aj (DMSO-d_6, 100 MHz)

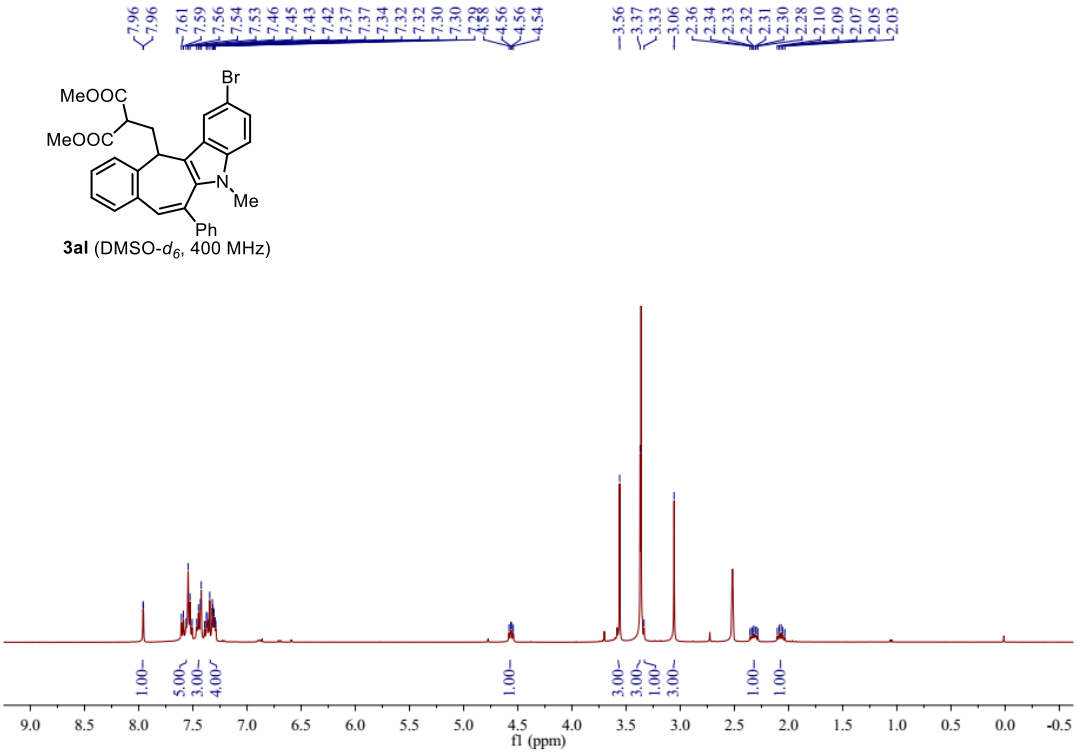


3ak (DMSO-d_6, 400 MHz)

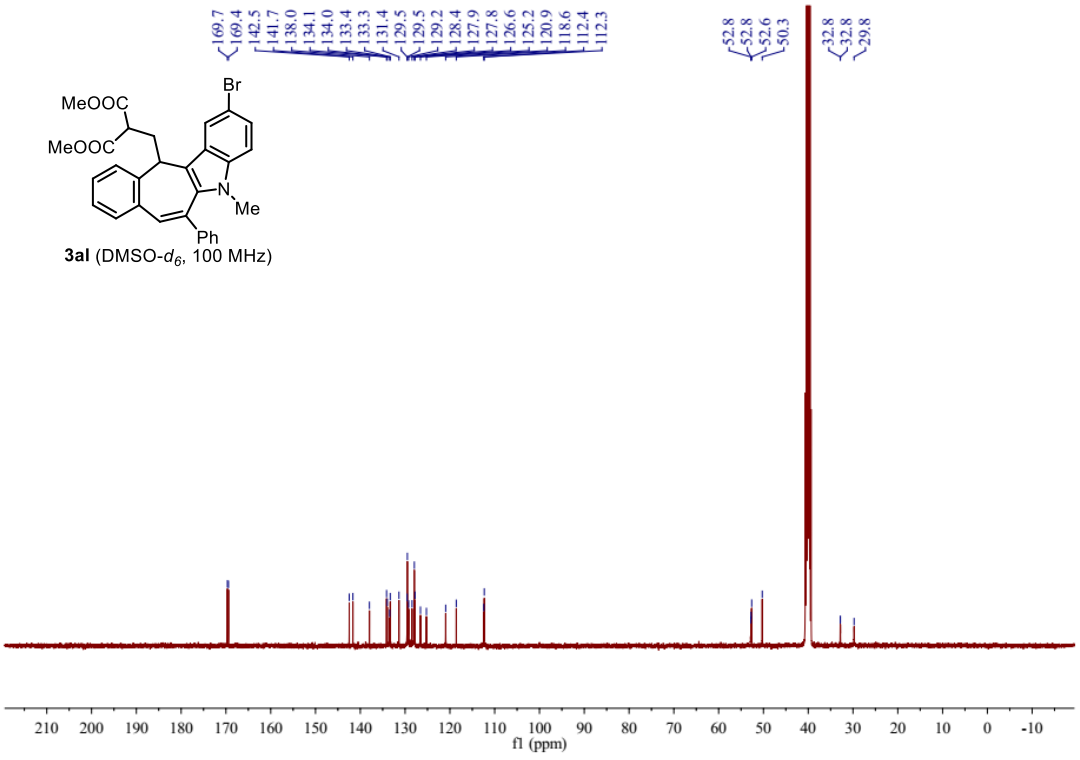




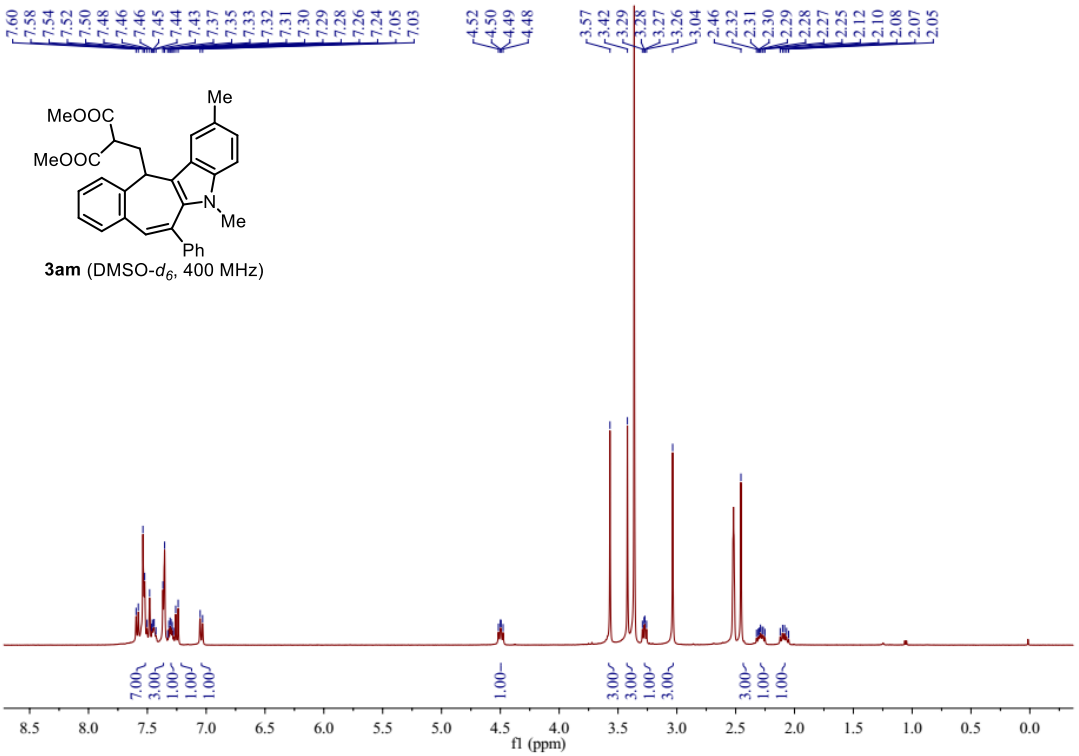
3ak (DMSO-d_6, 100 MHz)



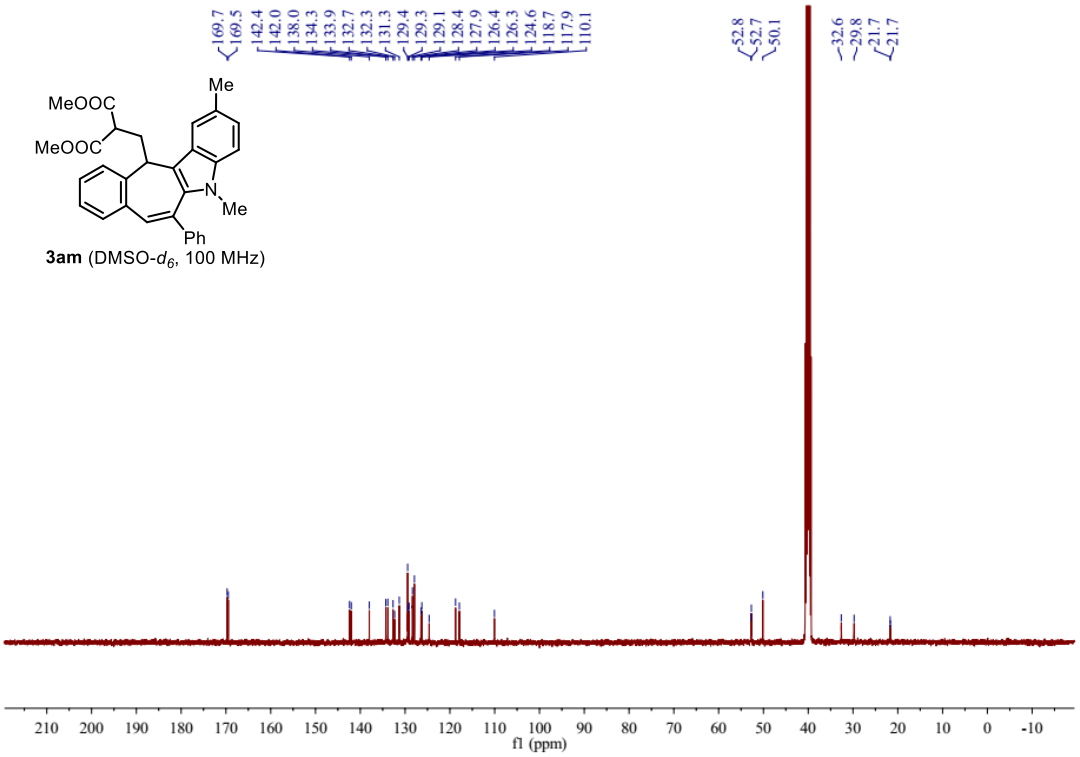
3al (DMSO-d_6, 400 MHz)



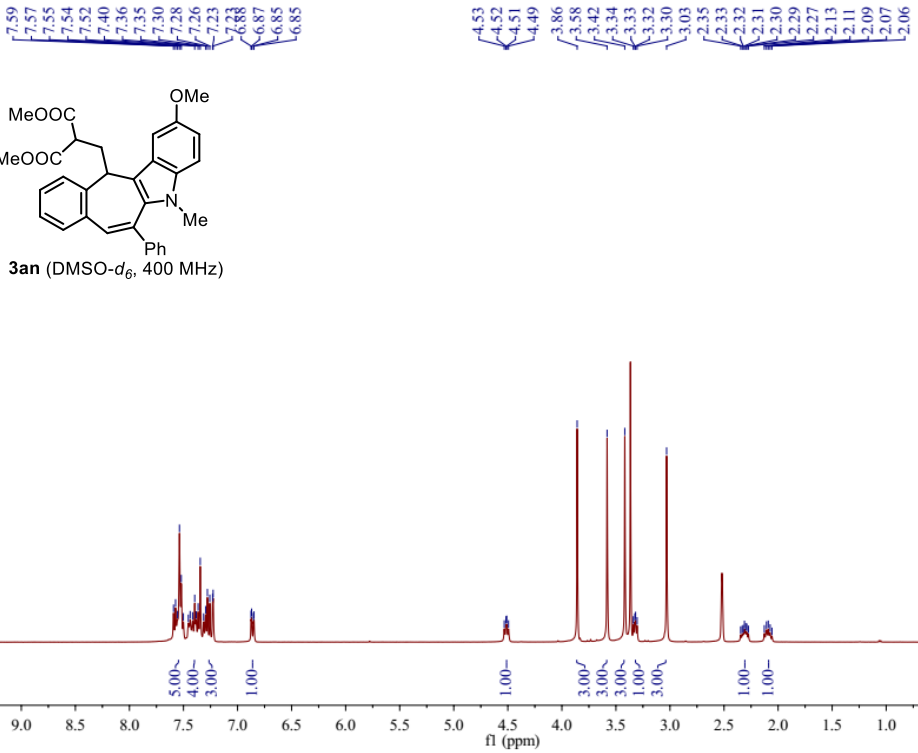
3al (DMSO-d_6, 100 MHz)



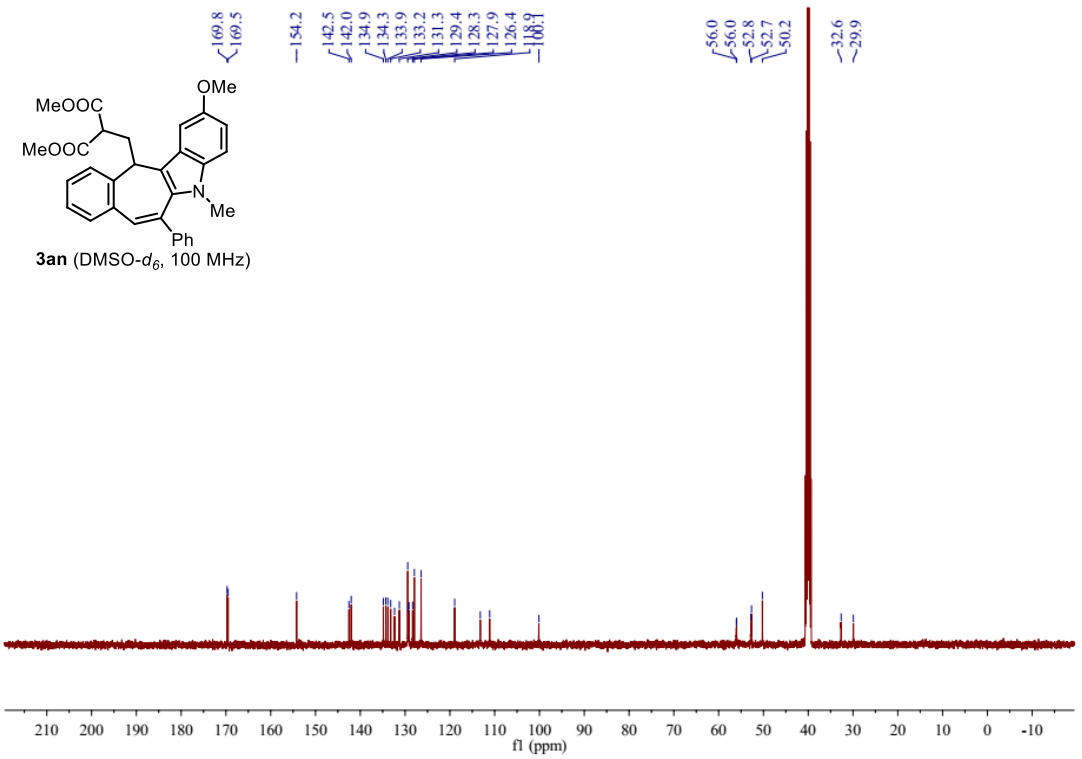
3am (DMSO-d_6, 400 MHz)



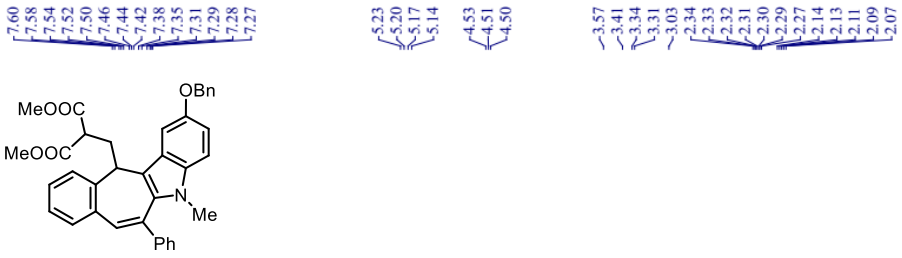
3am (DMSO-d_6, 100 MHz)



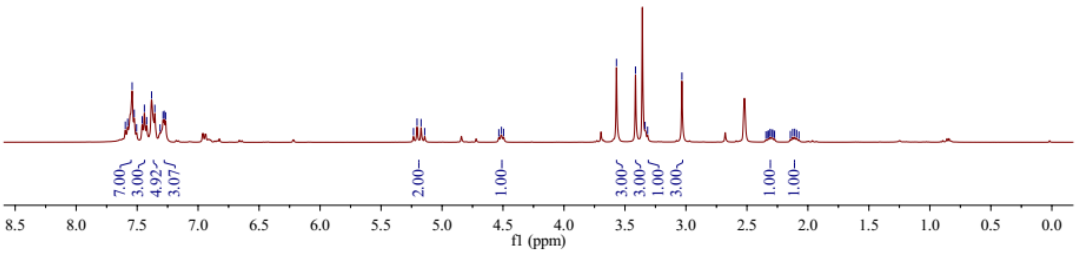
3an (DMSO-d_6, 400 MHz)

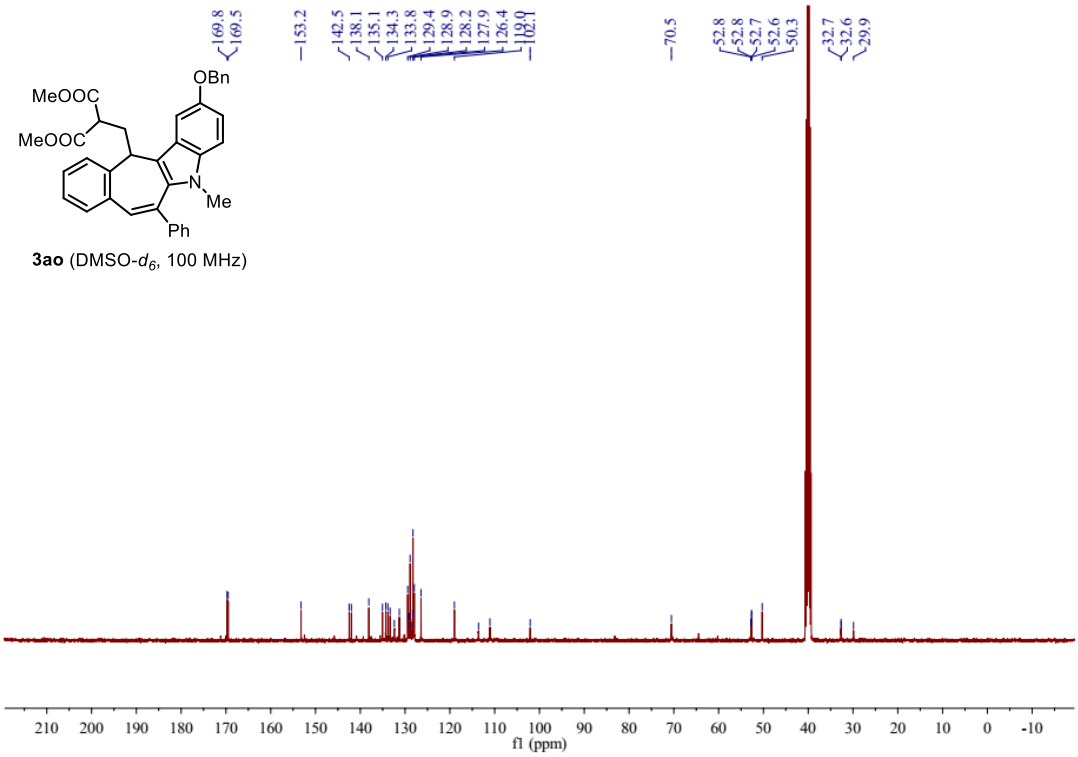


3an (DMSO-d_6, 100 MHz)

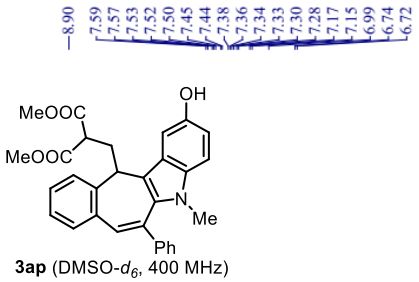


3ao (DMSO-d_6, 400 MHz)

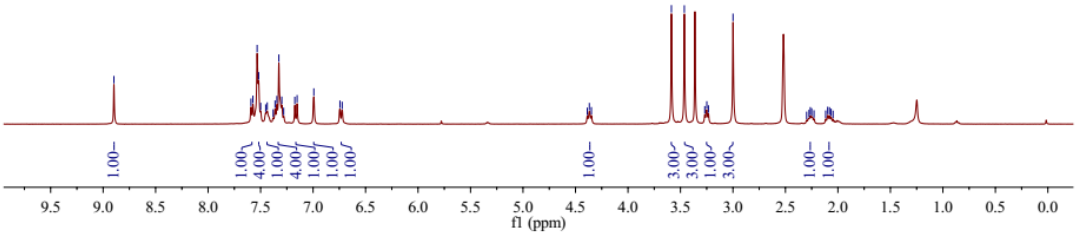


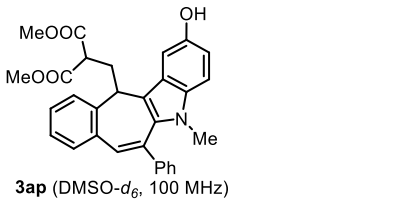


3ao (DMSO-d_6, 100 MHz)

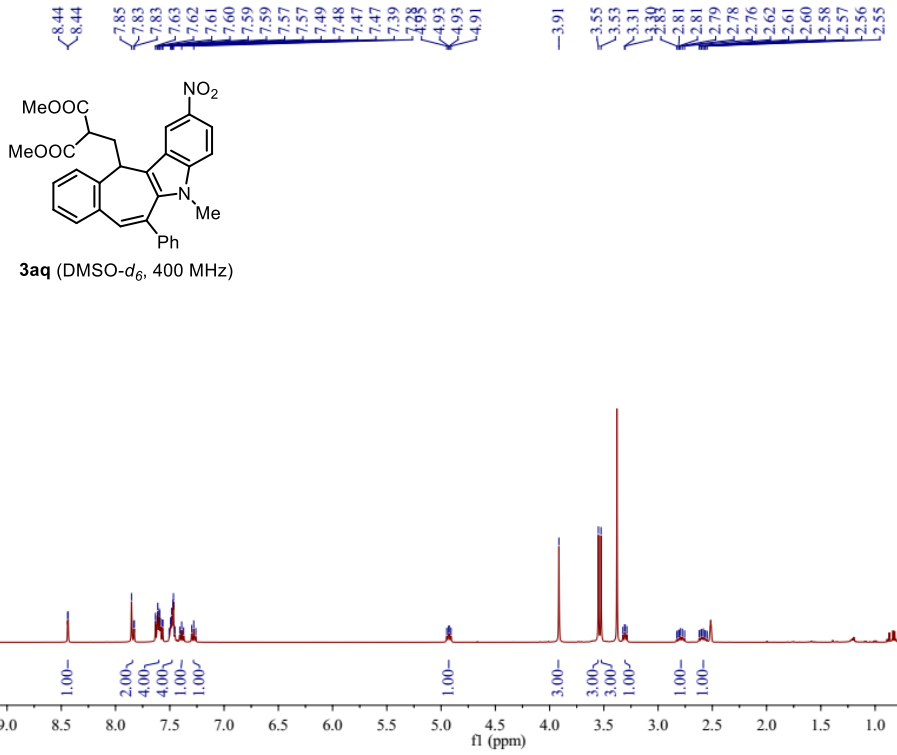


3ap (DMSO-d_6, 400 MHz)

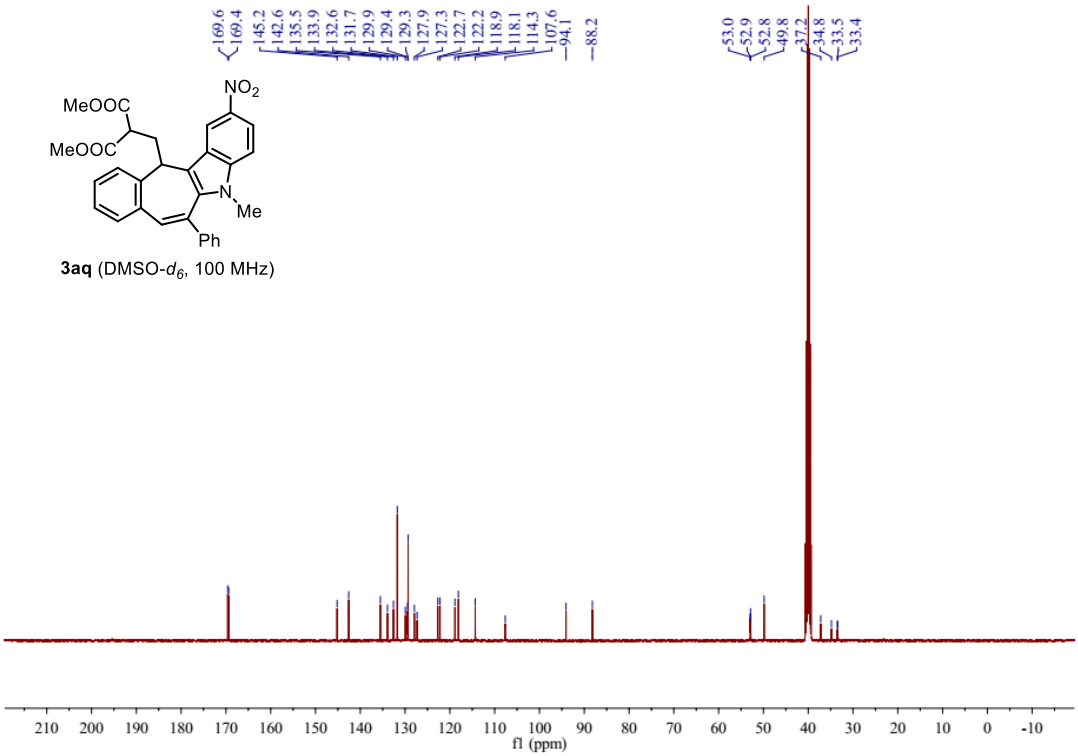




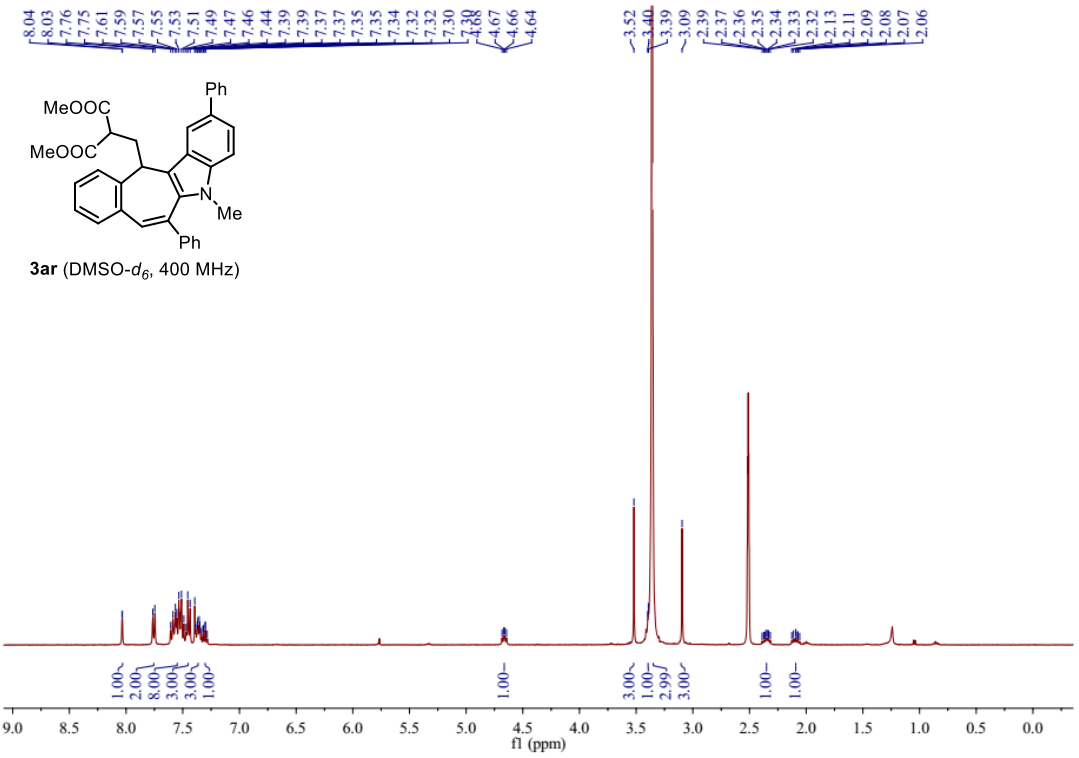
3ap (DMSO-d_6, 100 MHz)



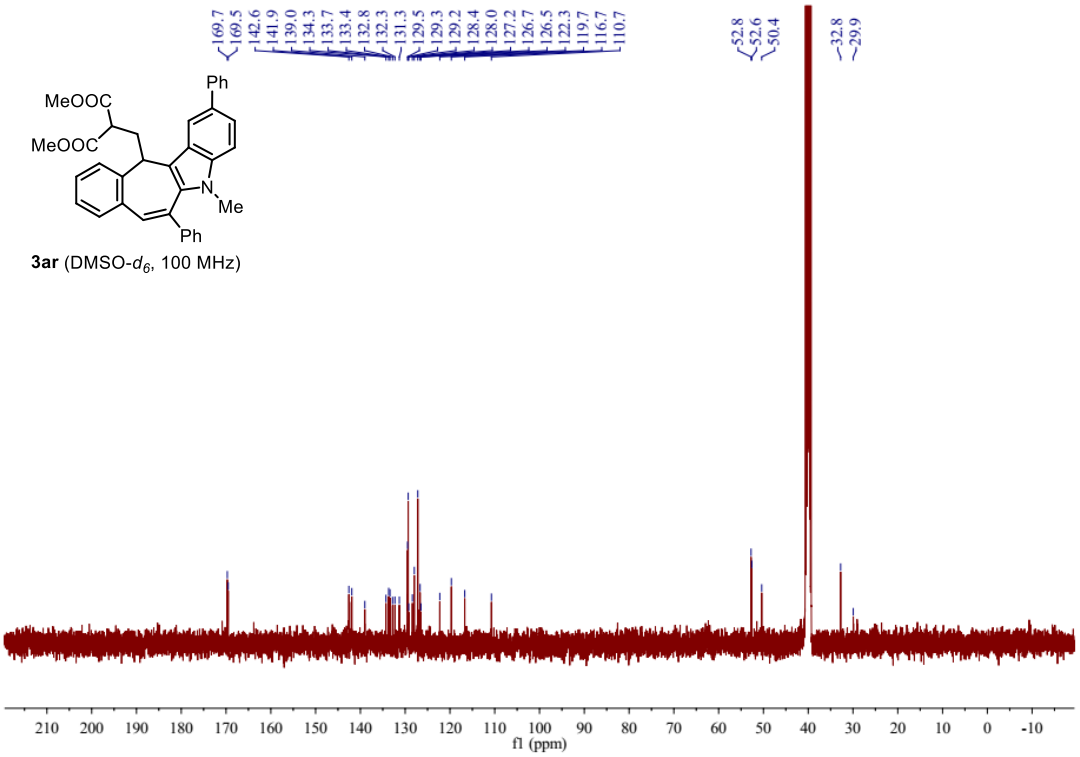
3aq (DMSO-d_6, 400 MHz)



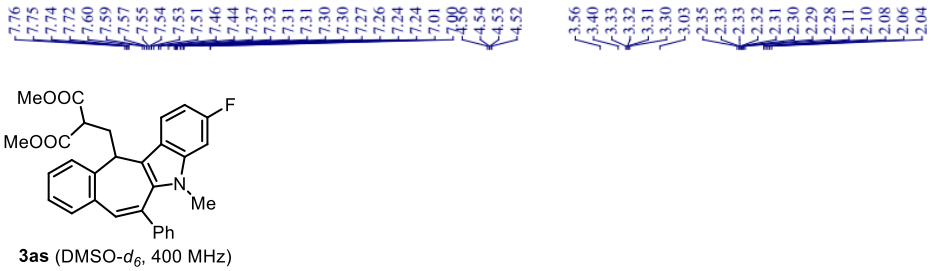
3aq (DMSO-d_6, 100 MHz)



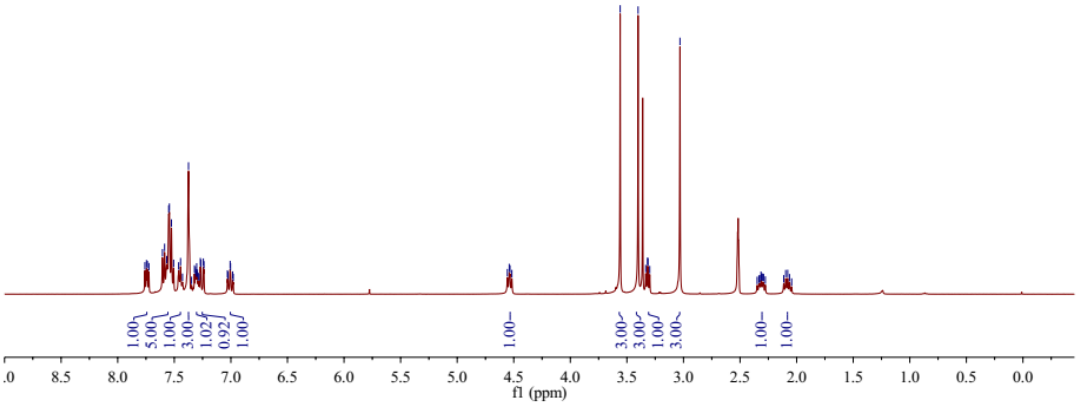
3ar (DMSO-d_6, 400 MHz)

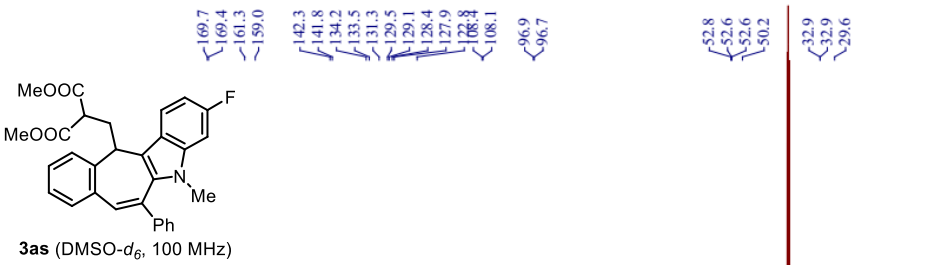


3ar (DMSO-d_6, 100 MHz)

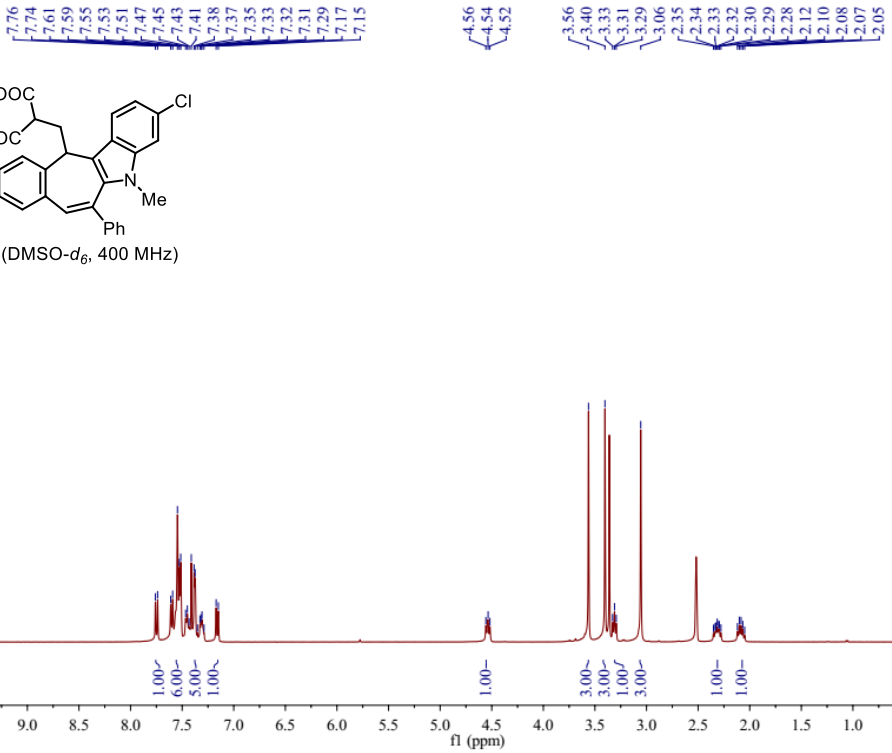


3as (DMSO-d_6, 400 MHz)

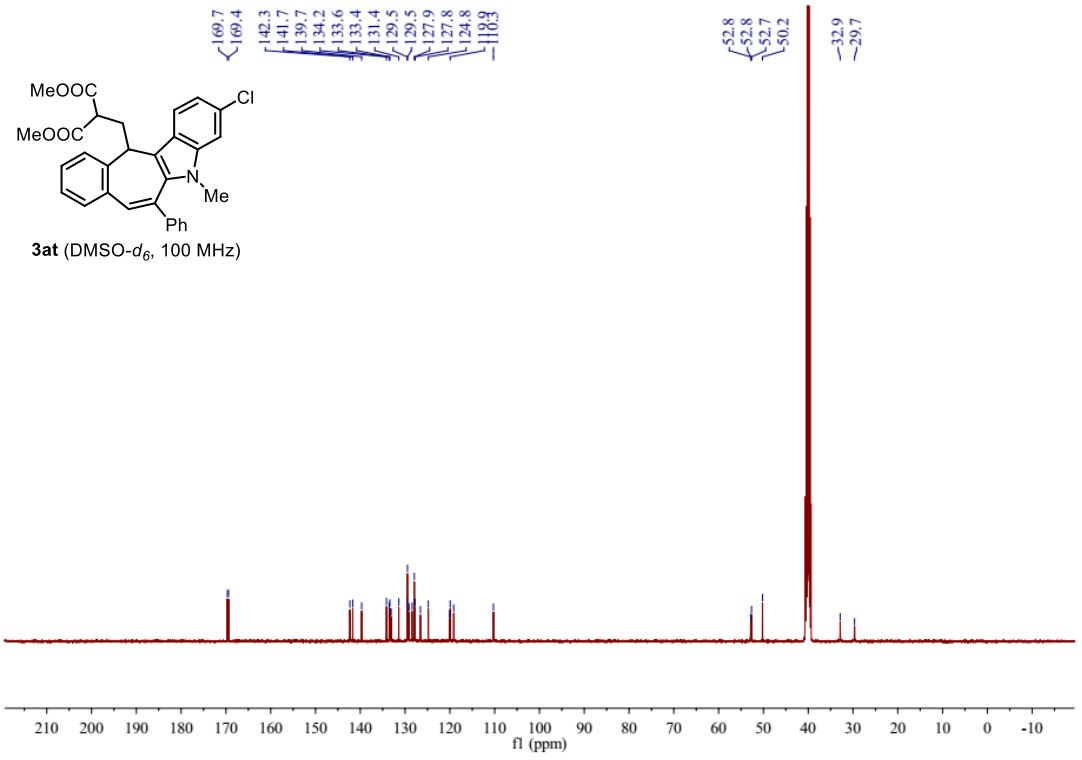




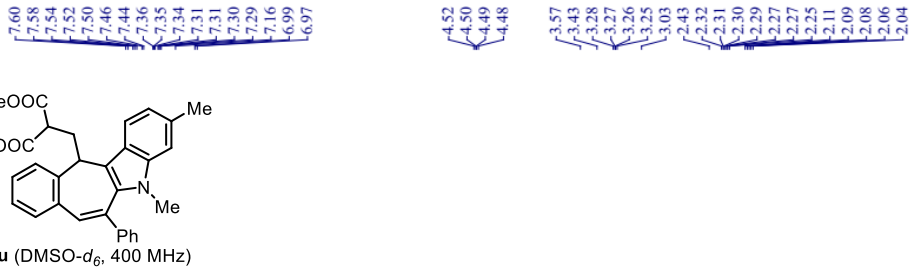
3as (DMSO-d_6, 100 MHz)



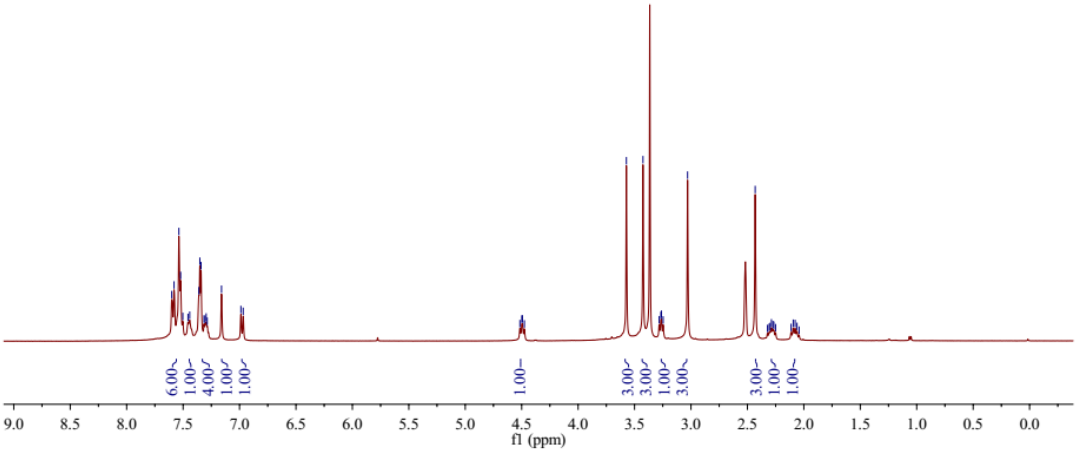
3at (DMSO-d_6, 400 MHz)

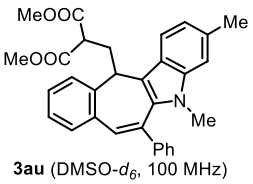


3at (DMSO-d_6, 100 MHz)

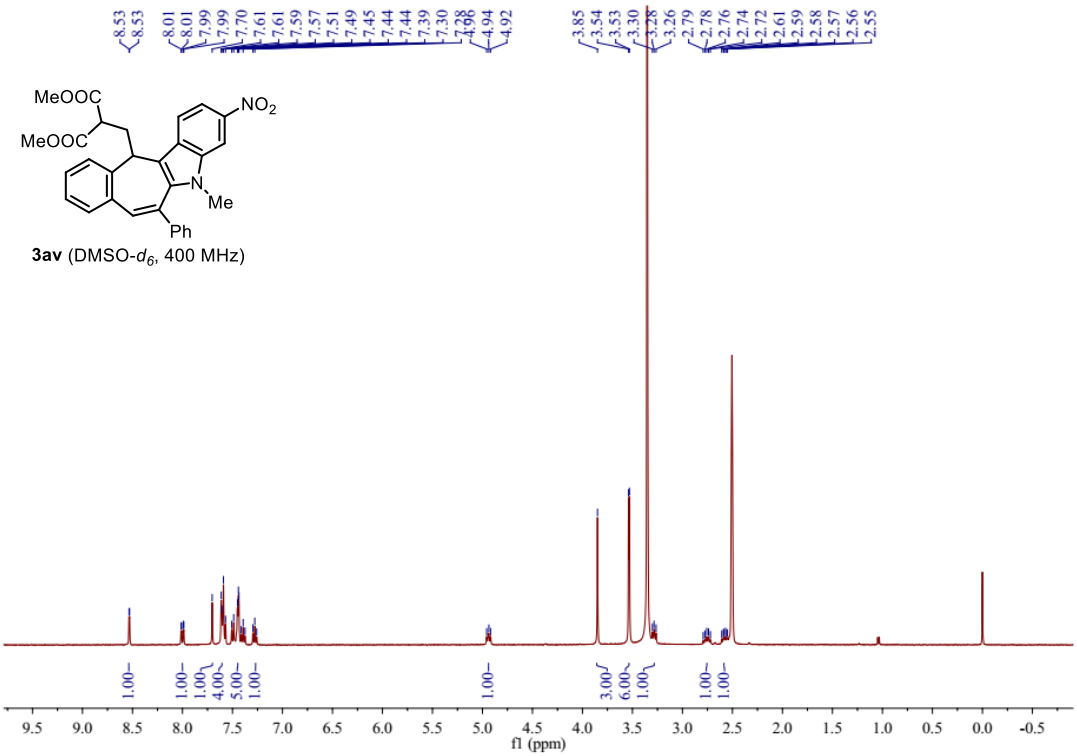


3au (DMSO-d_6, 400 MHz)

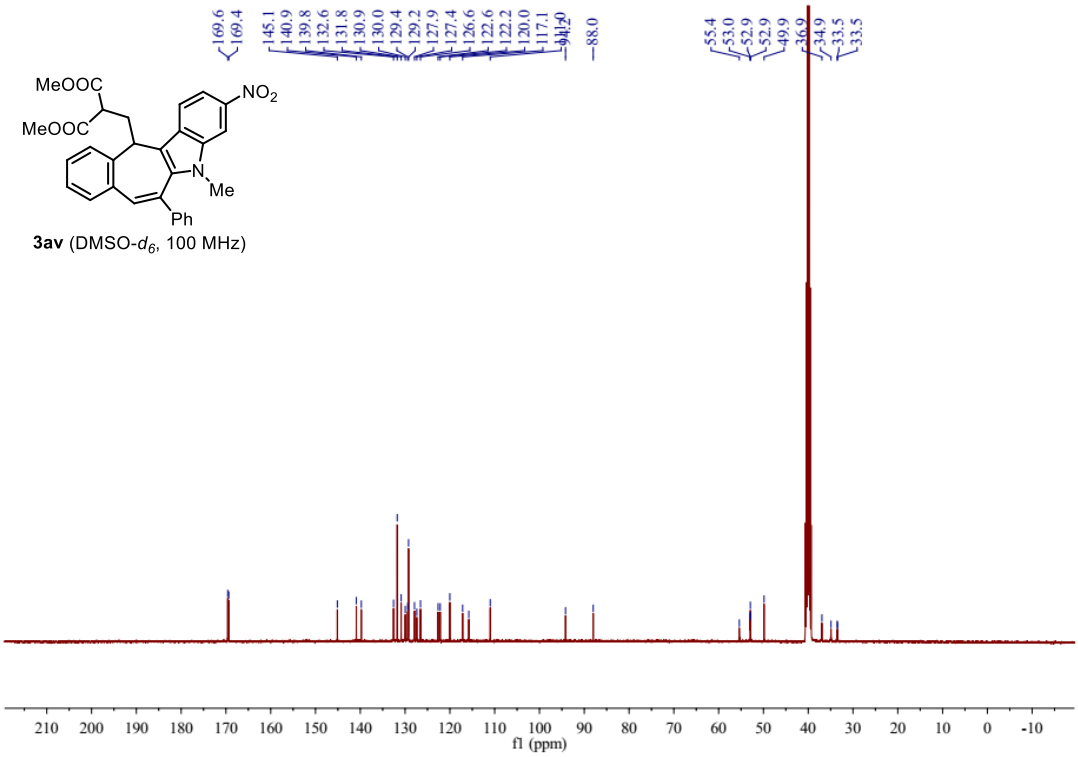




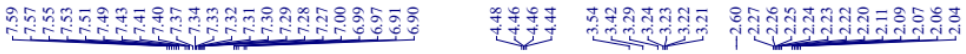
3au (DMSO-d_6, 100 MHz)

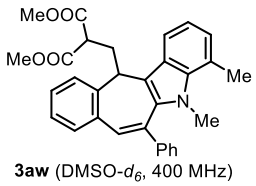


3av (DMSO-d_6, 400 MHz)

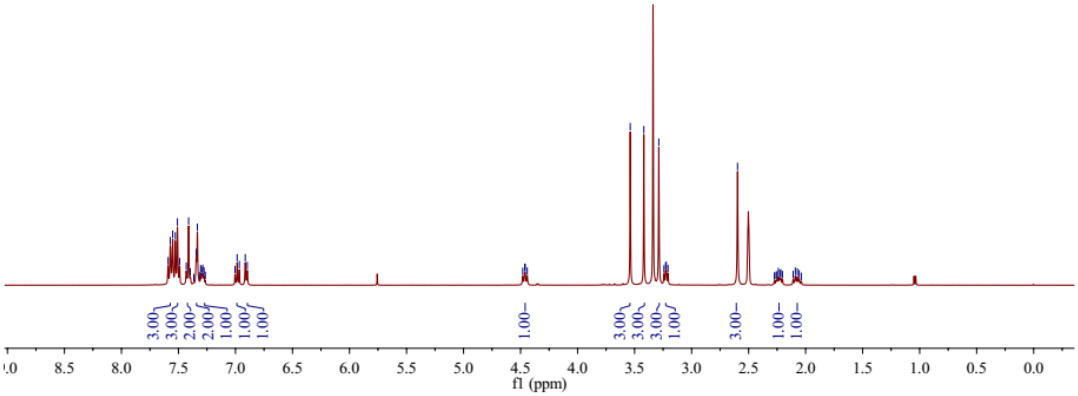


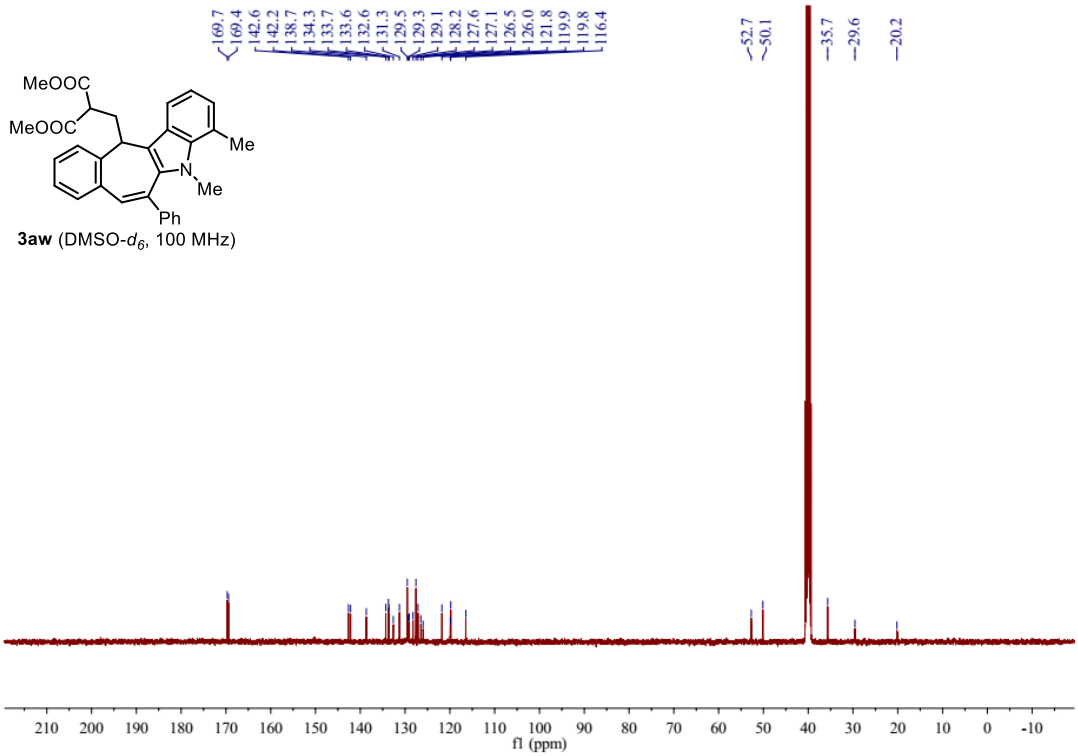
3av (DMSO-d_6, 100 MHz)



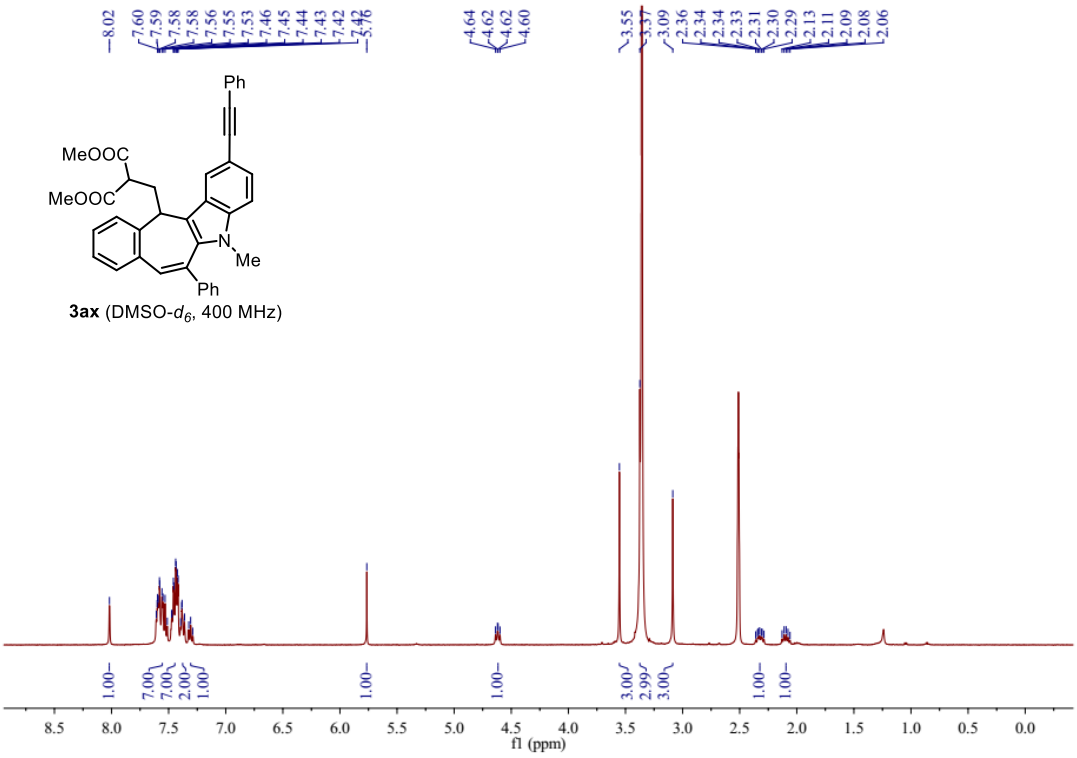


3aw (DMSO-d_6, 400 MHz)

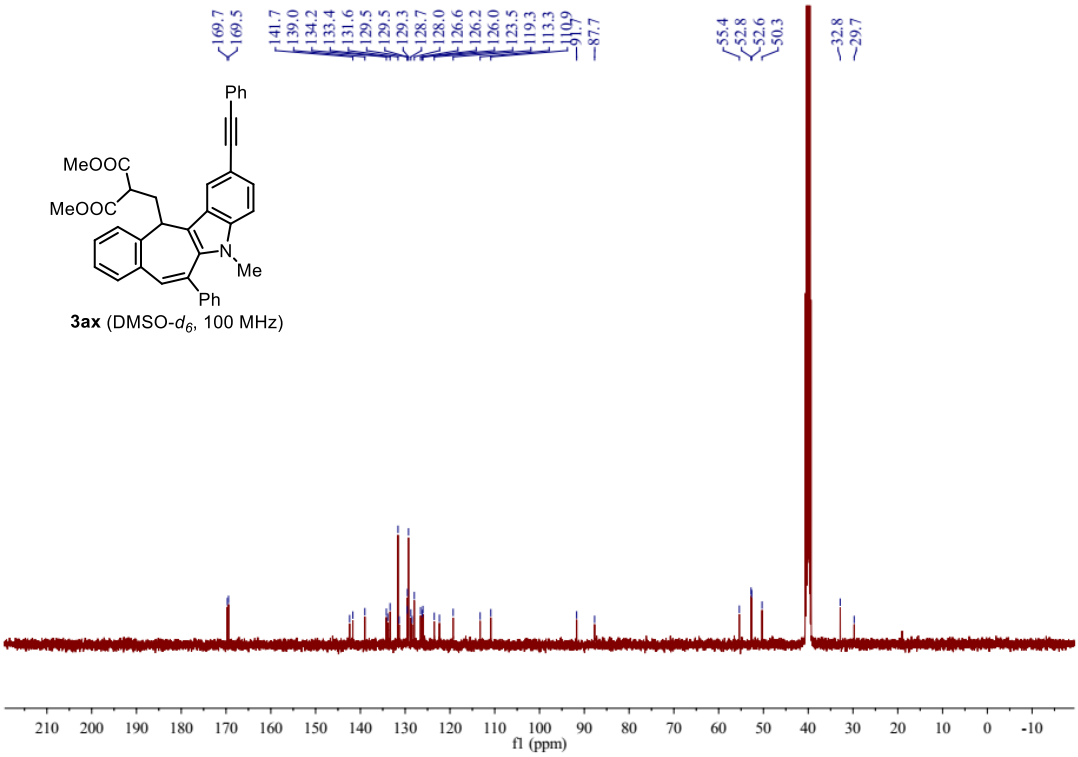




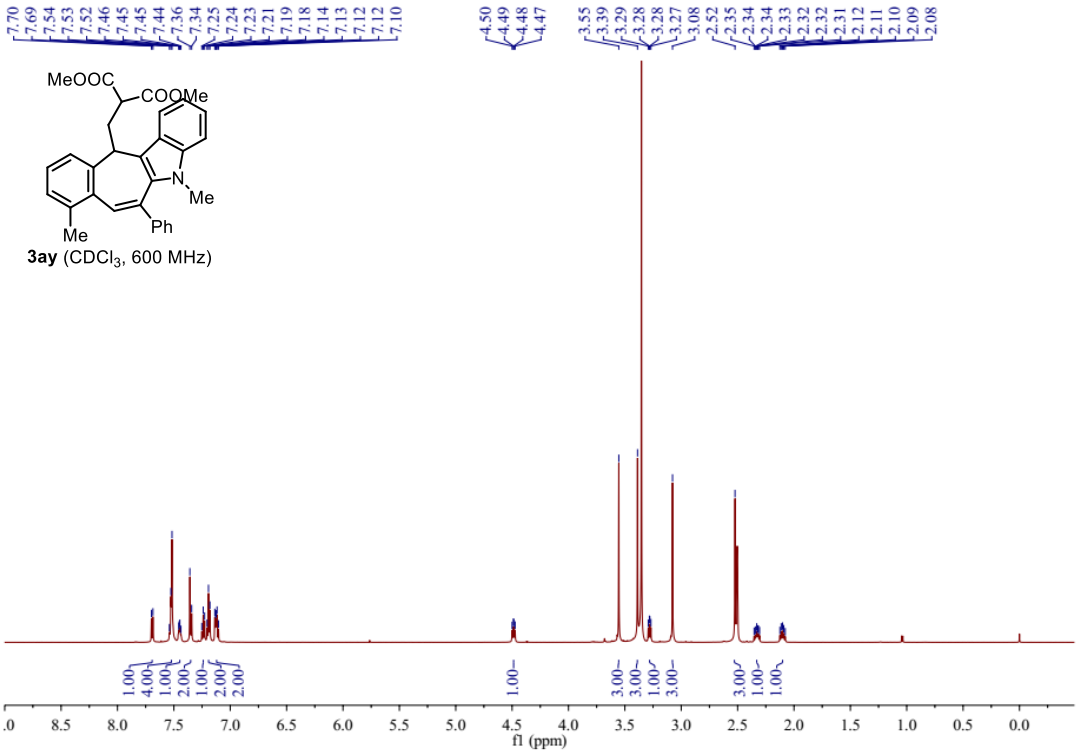
3aw (DMSO-d_6, 100 MHz)



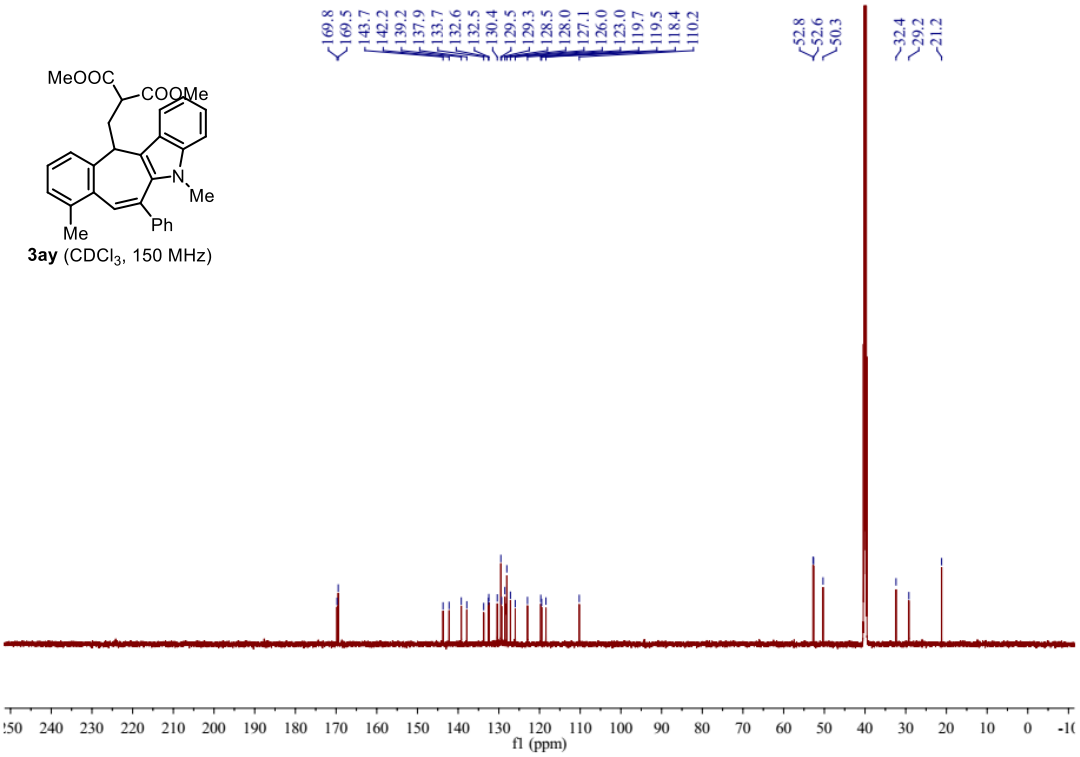
3ax (DMSO-d_6, 400 MHz)



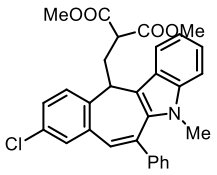
3ax (DMSO-d_6, 100 MHz)



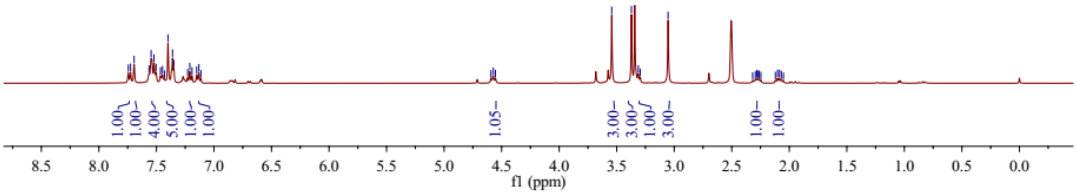
3ay ($CDCl_3$, 600 MHz)

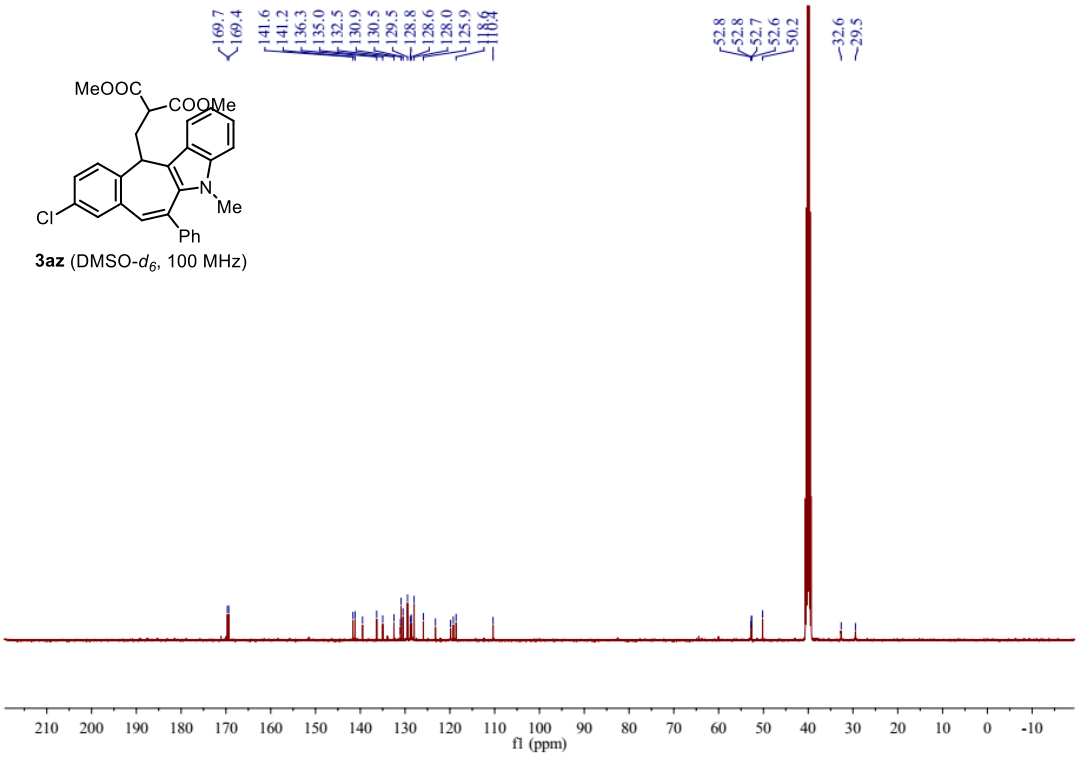


3ay ($CDCl_3$, 150 MHz)

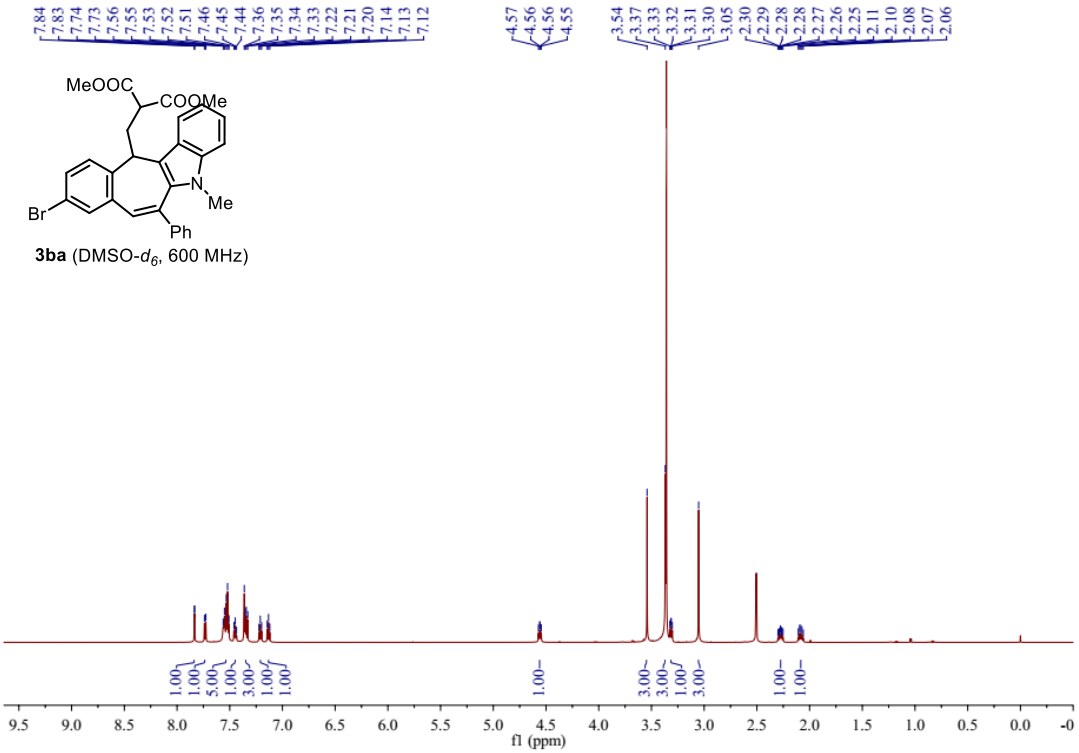


3az (DMSO-d_6, 400 MHz)

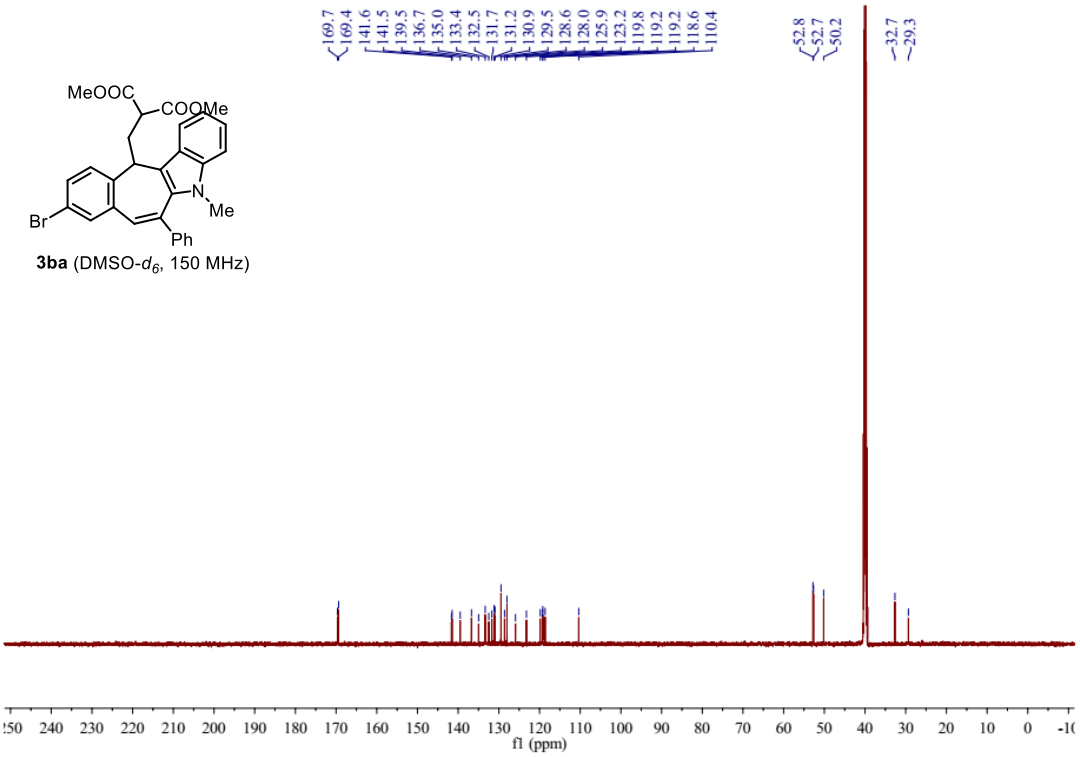




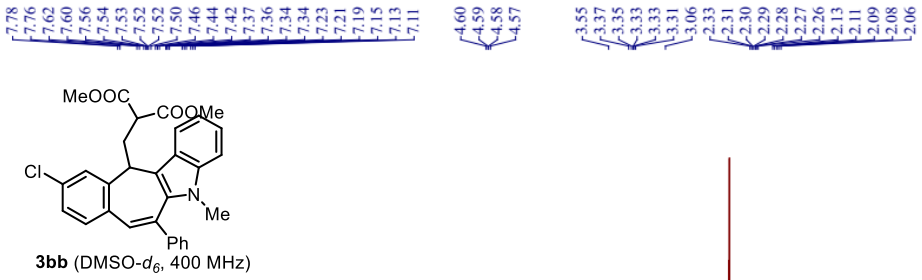
3az (DMSO-d_6, 100 MHz)



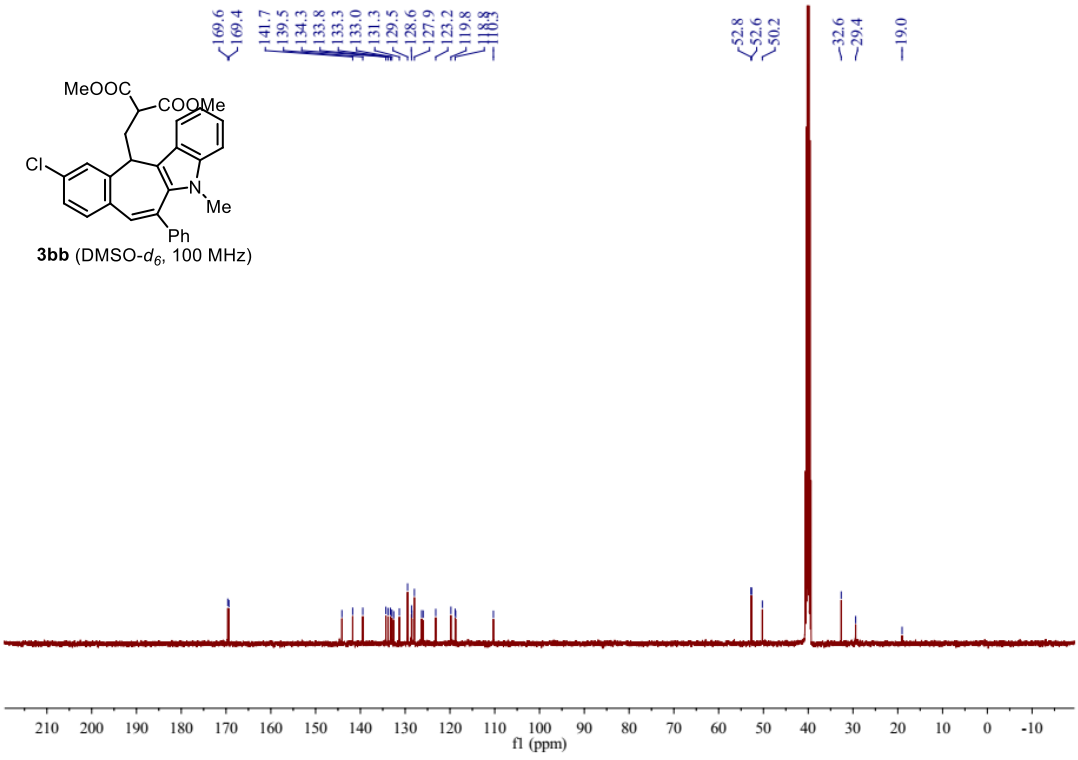
3ba (DMSO-d_6, 600 MHz)



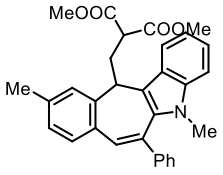
3ba (DMSO-d_6, 150 MHz)



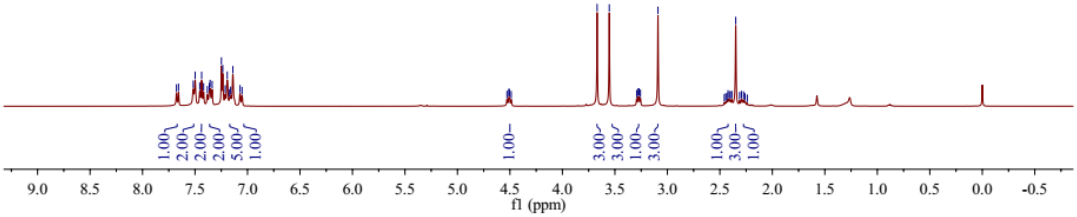
3bb (DMSO-d_6, 400 MHz)

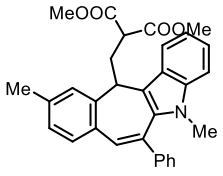


3bb (DMSO-d_6, 100 MHz)

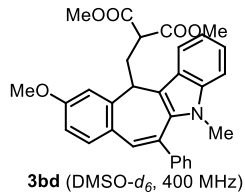


3bc ($CDCl_3$, 400 MHz)

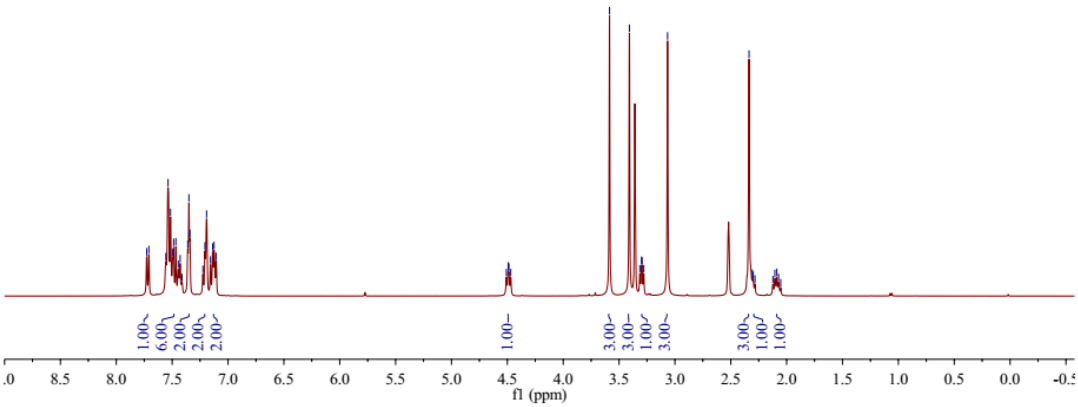


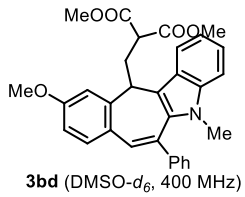


3bc ($CDCl_3$,100 MHz)

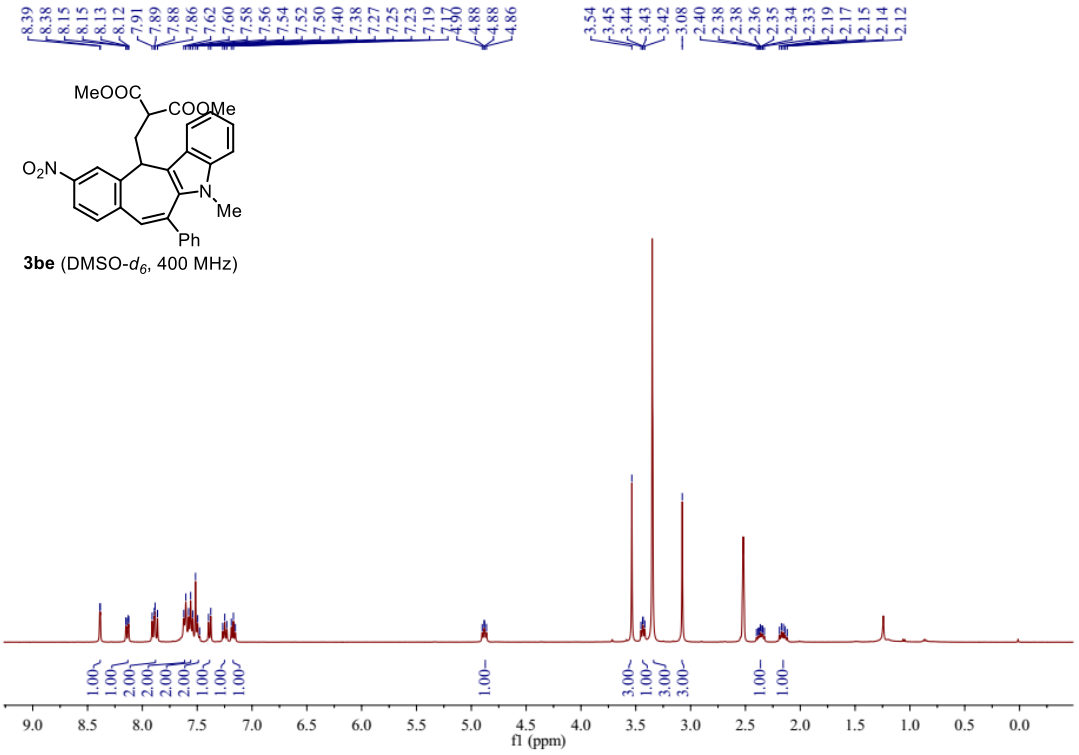


3bd (DMSO-d_6, 400 MHz)

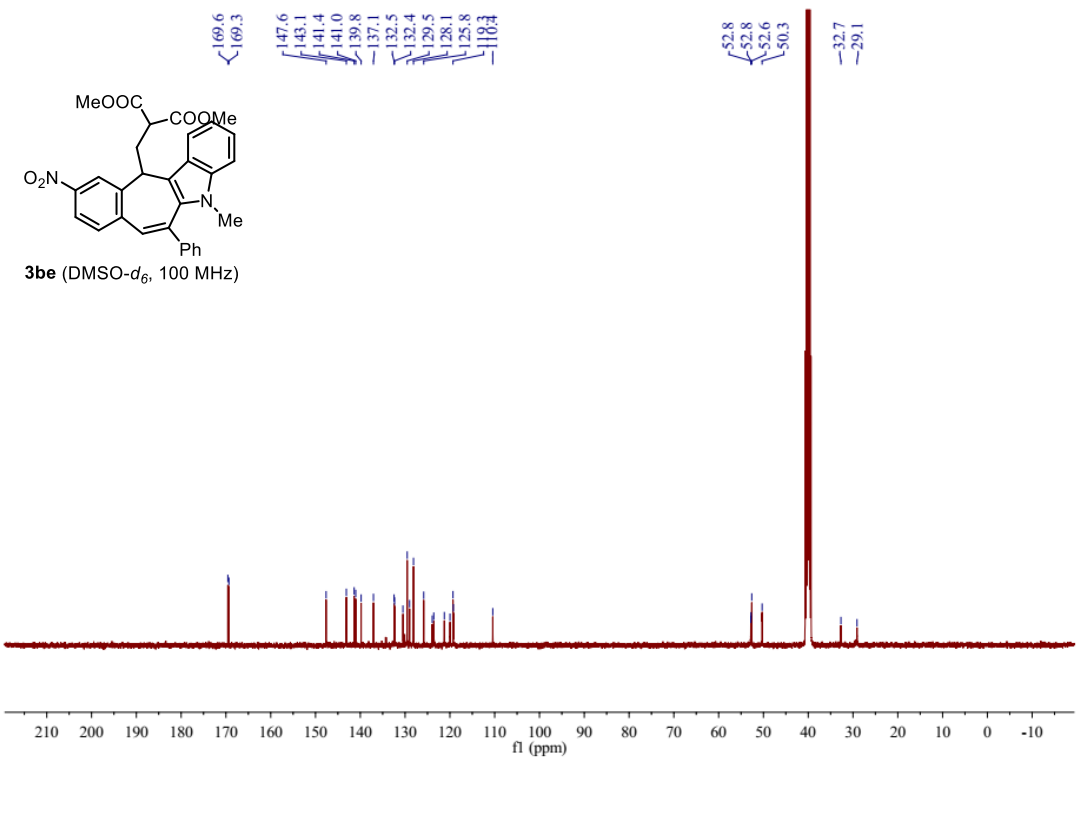




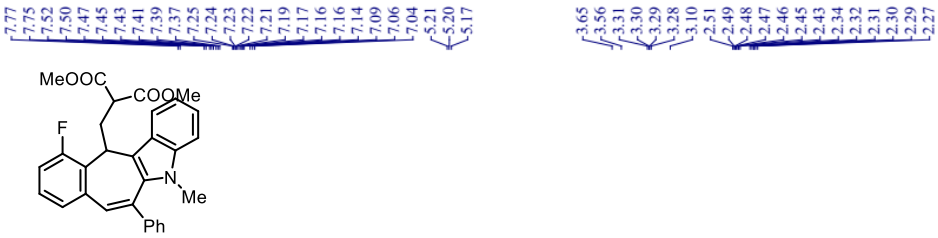
3bd (DMSO-d_6, 400 MHz)



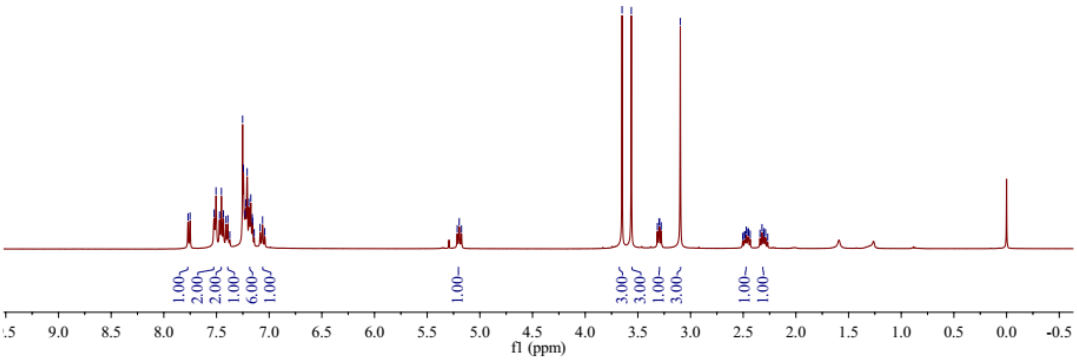
3be (DMSO-d_6, 400 MHz)

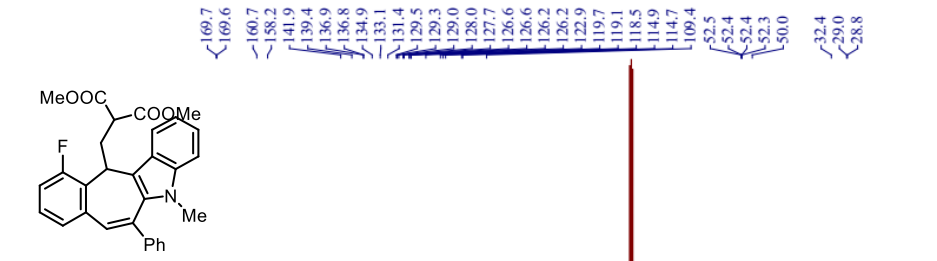


3be (DMSO-d_6, 100 MHz)

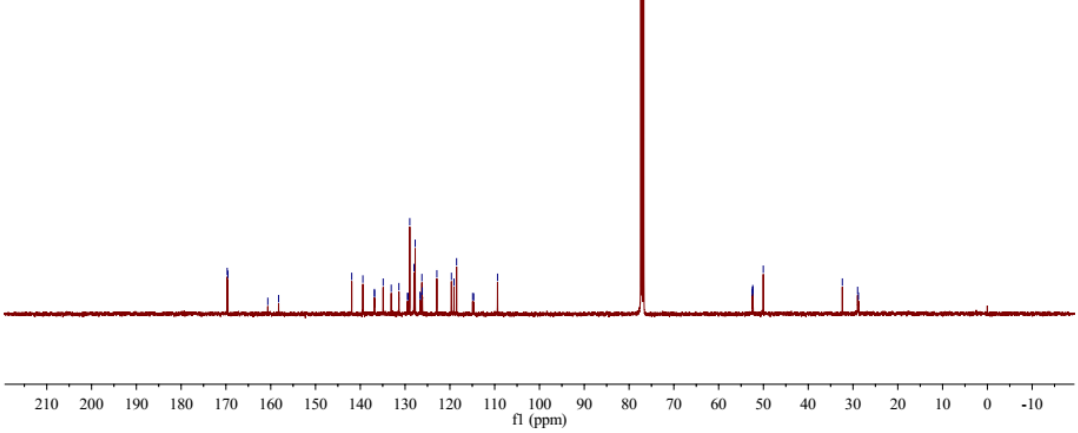


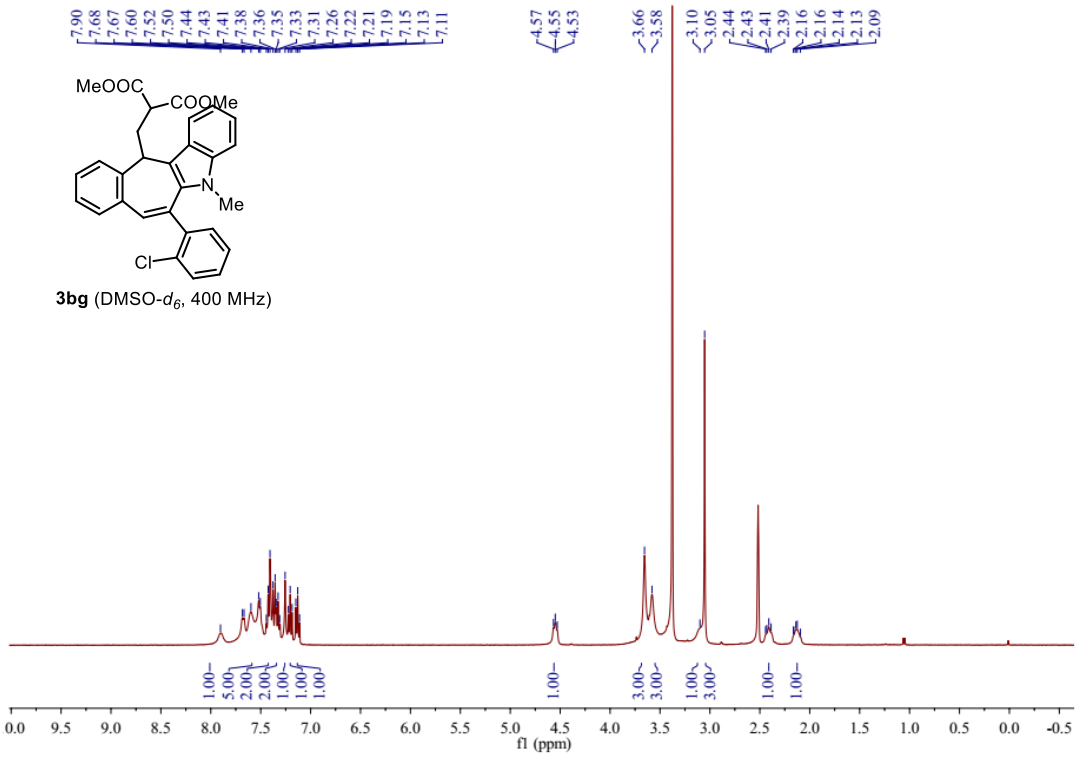
3bf ($CDCl_3$, 400 MHz)



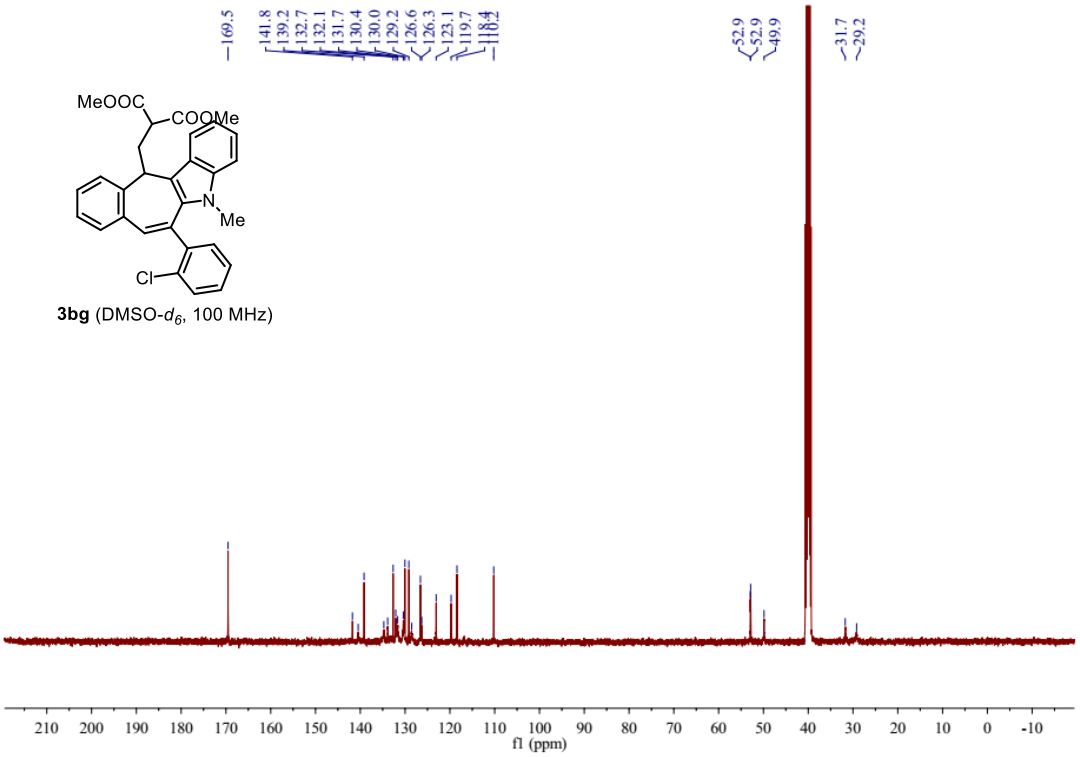


3bf ($CDCl_3$, 100 MHz)

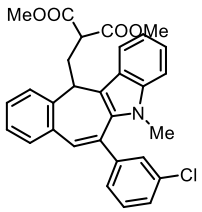




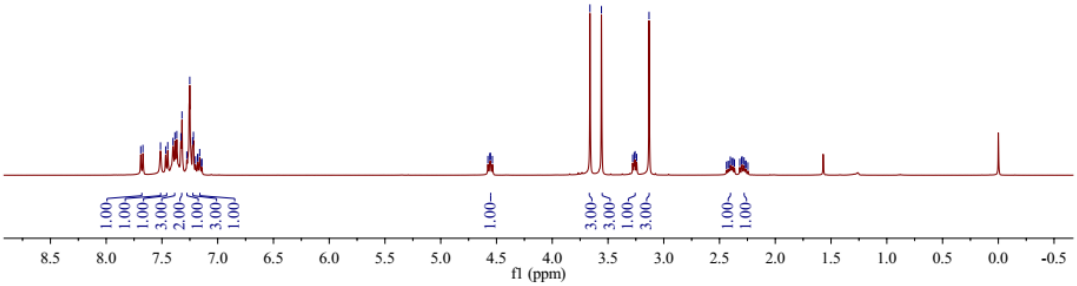
3bg (DMSO-d_6, 400 MHz)

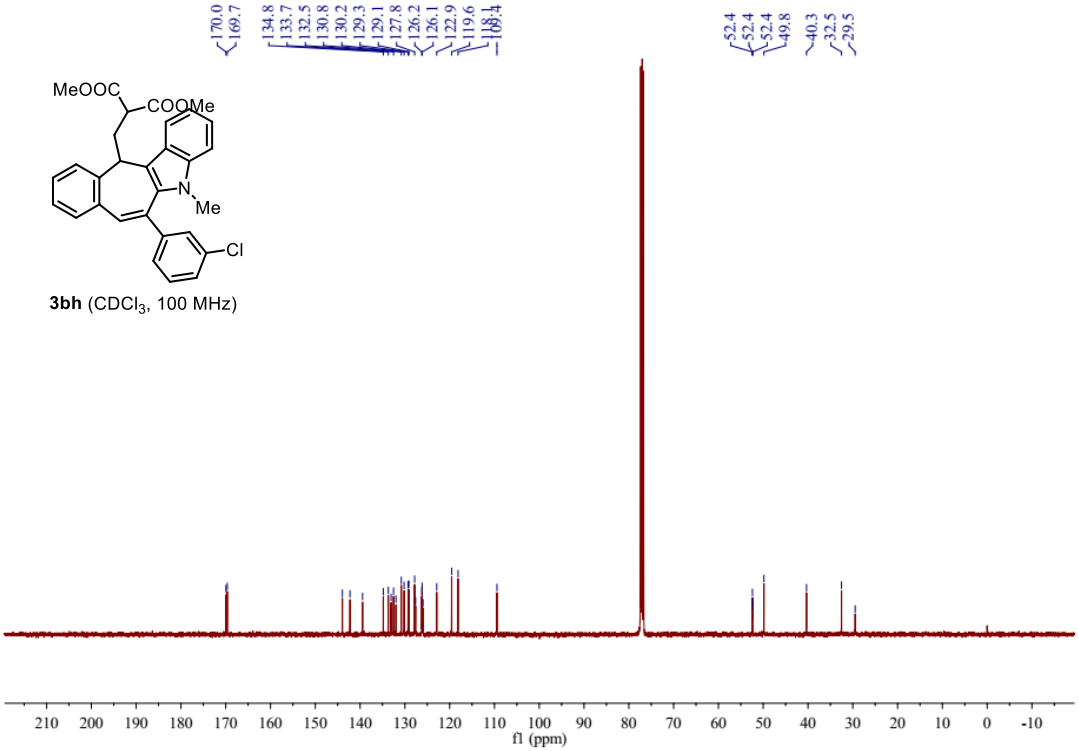


3bg (DMSO-d_6, 100 MHz)

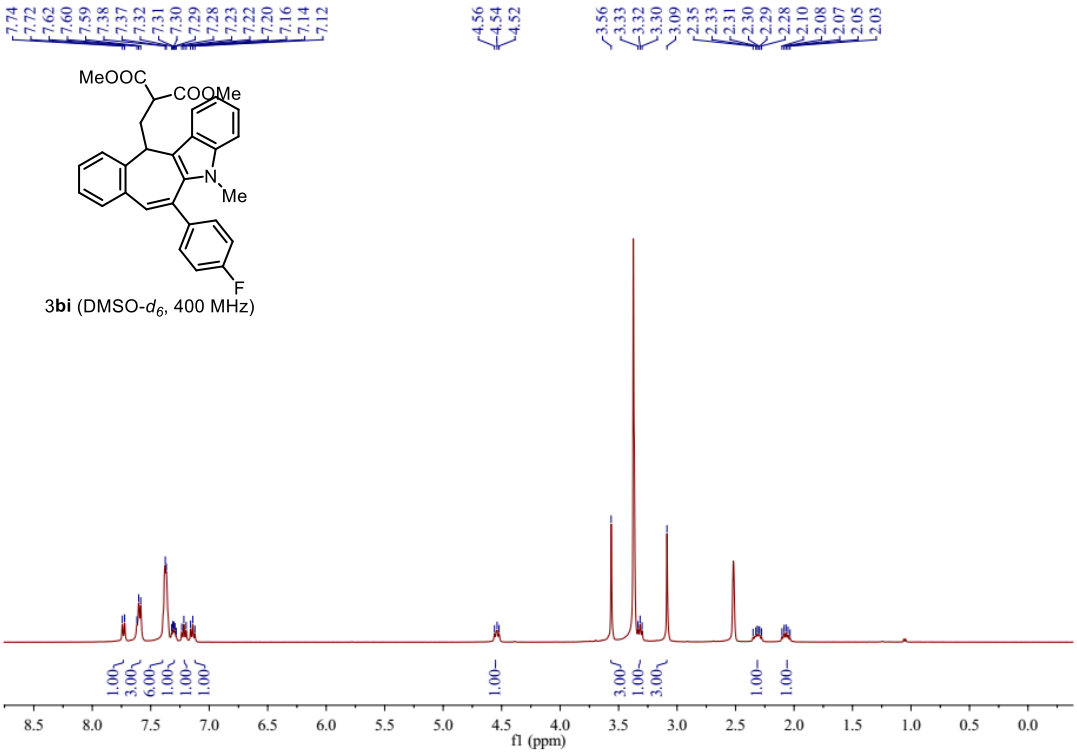


3bh ($CDCl_3$, 400 MHz)

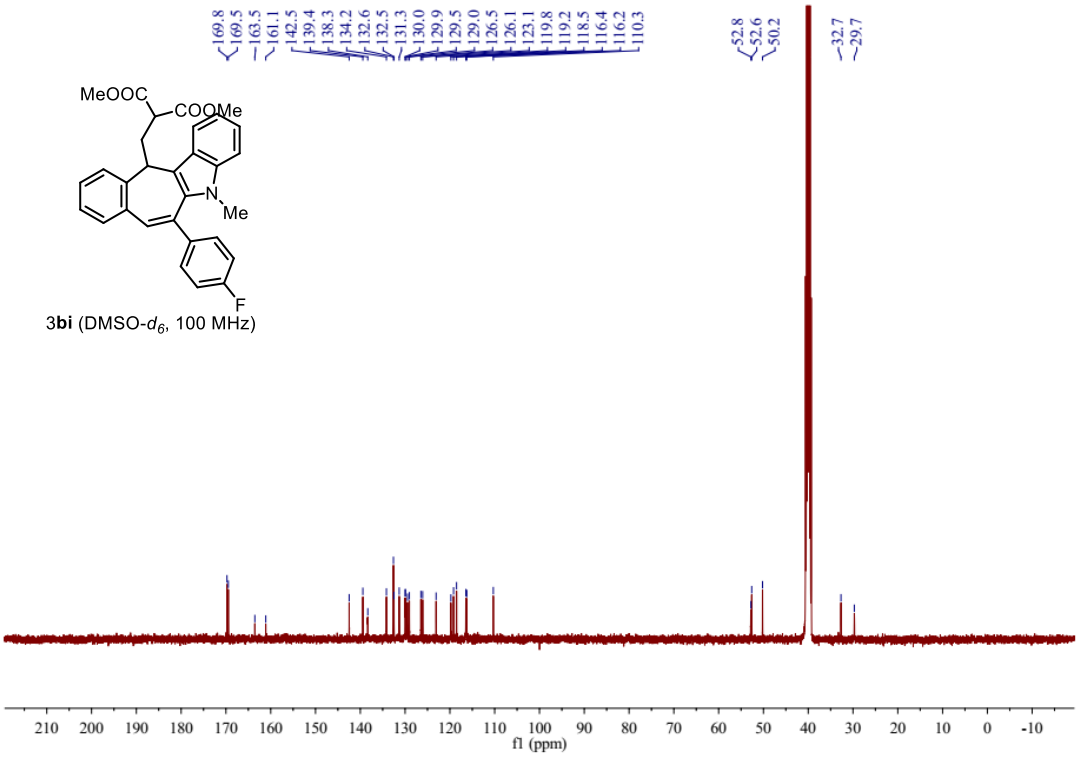




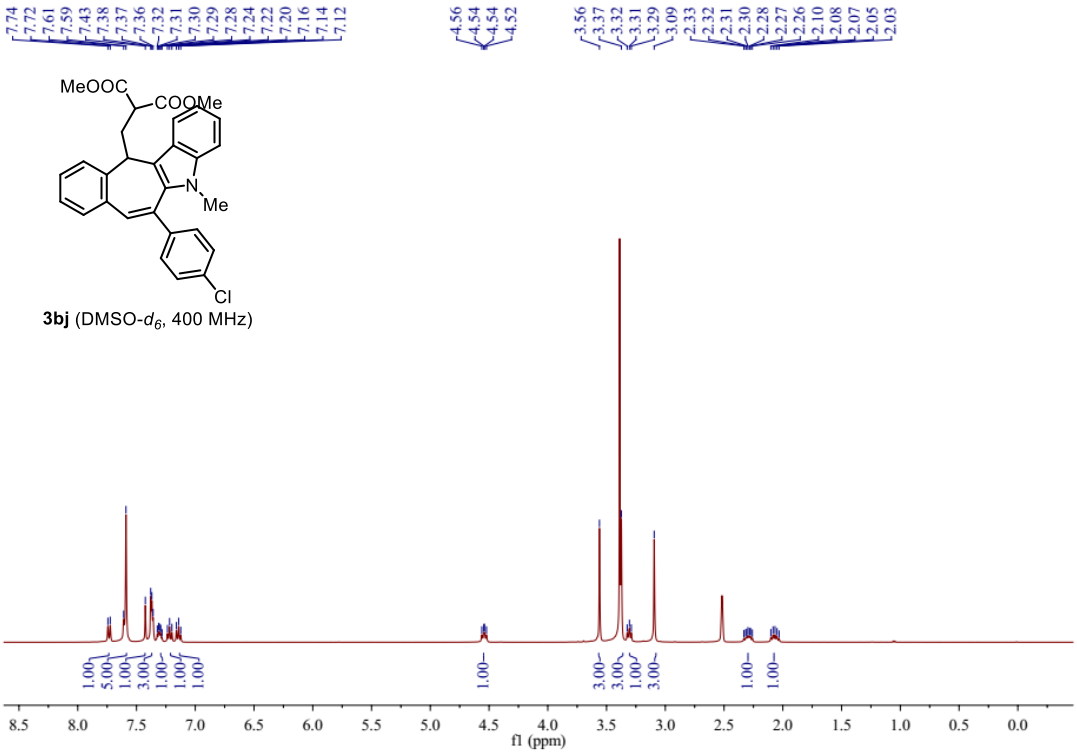
3bh ($CDCl_3$, 100 MHz)



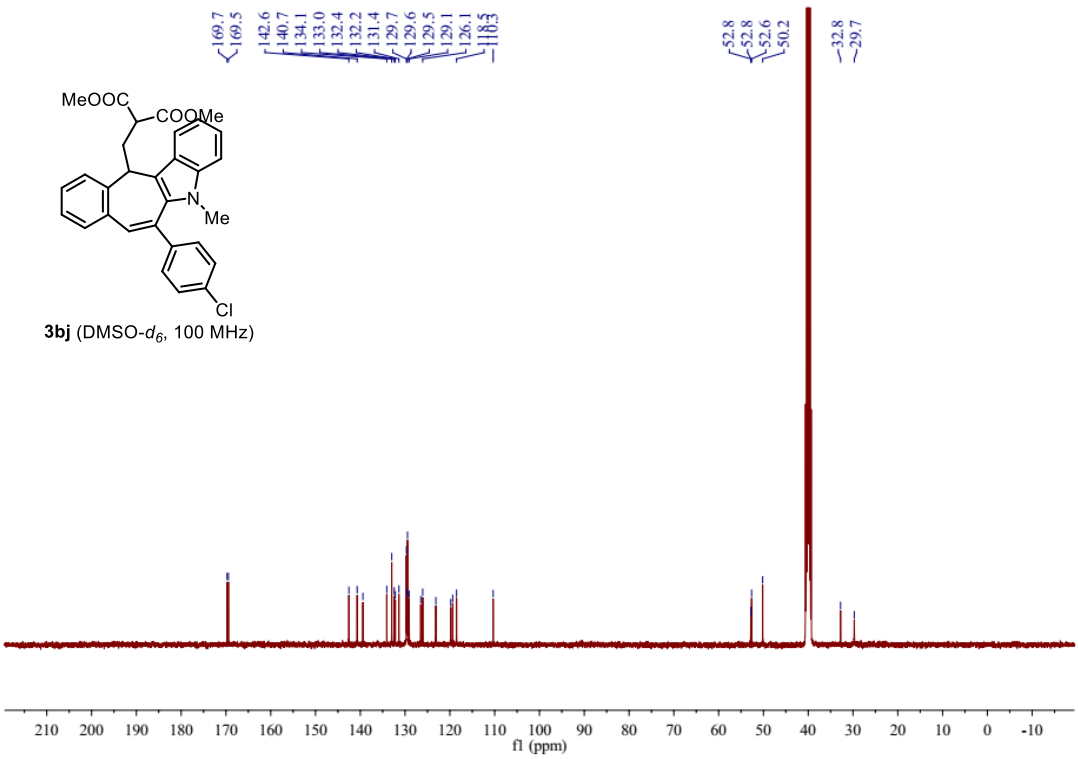
3**bi** (DMSO-d_6, 400 MHz)



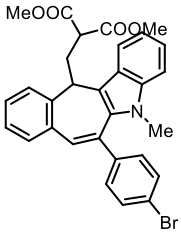
3**bi** (DMSO-d_6, 100 MHz)



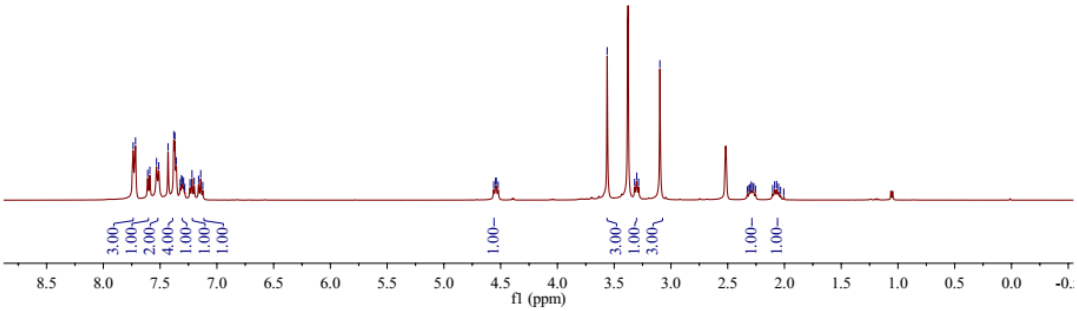
3bj (DMSO-d_6, 400 MHz)

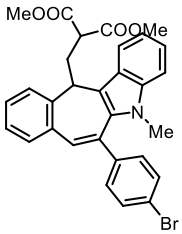


3bj (DMSO-d_6, 100 MHz)

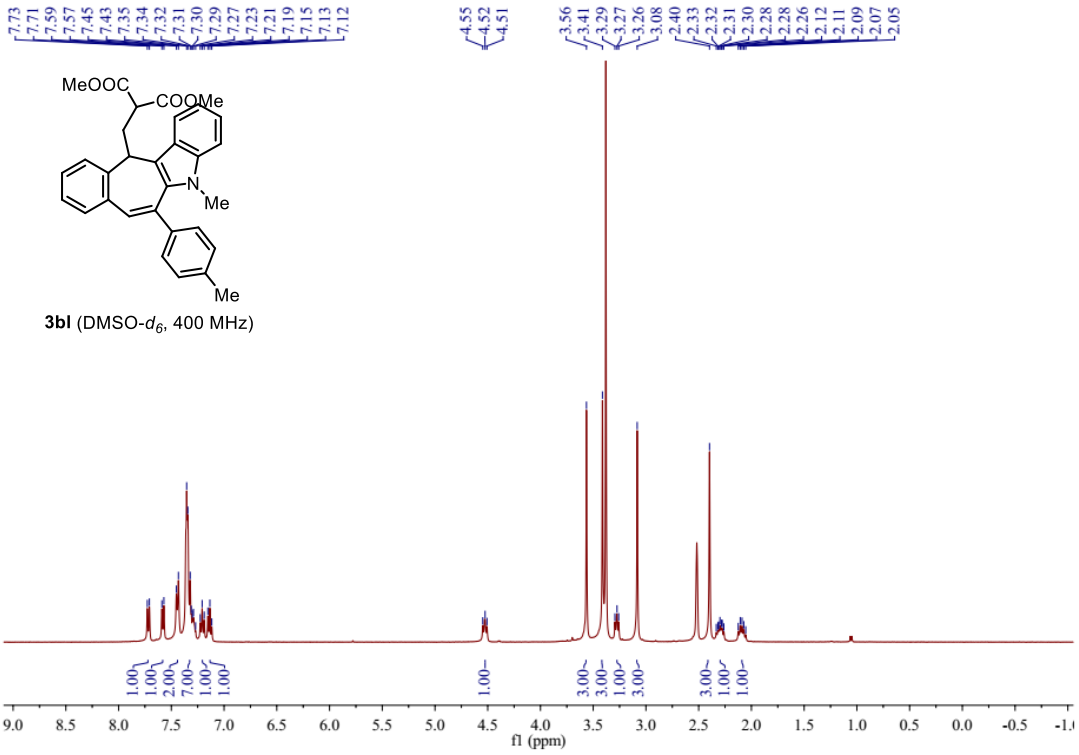


3bk (DMSO-d_6, 400 MHz)

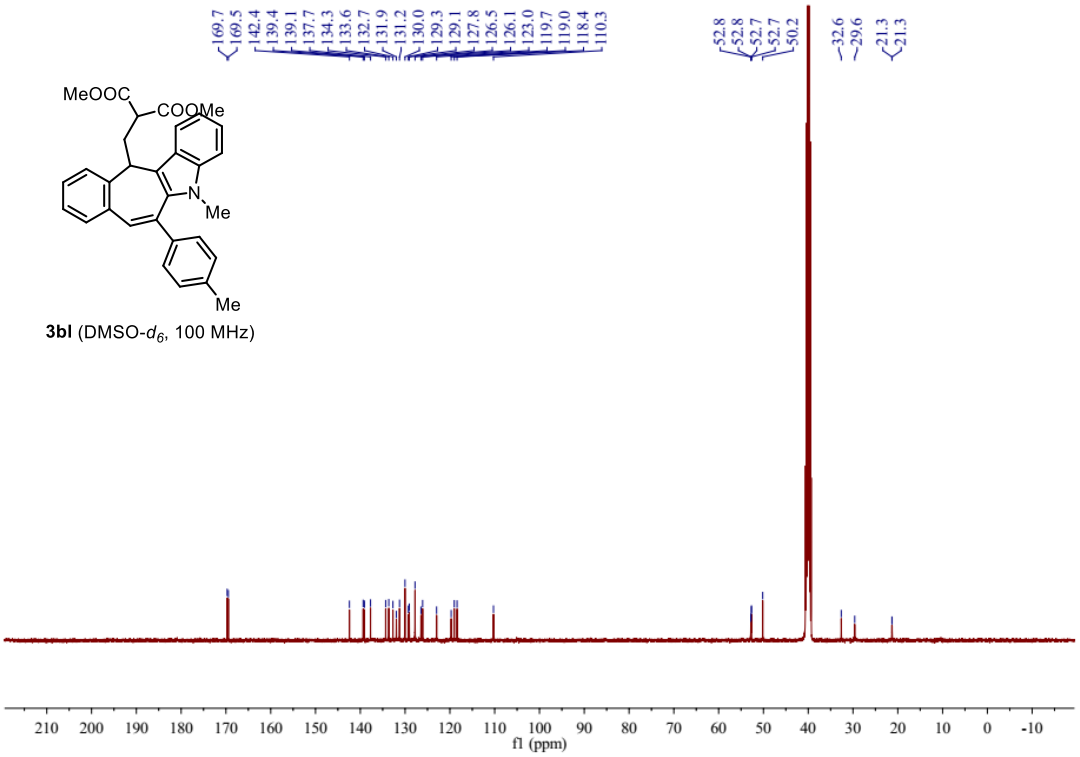




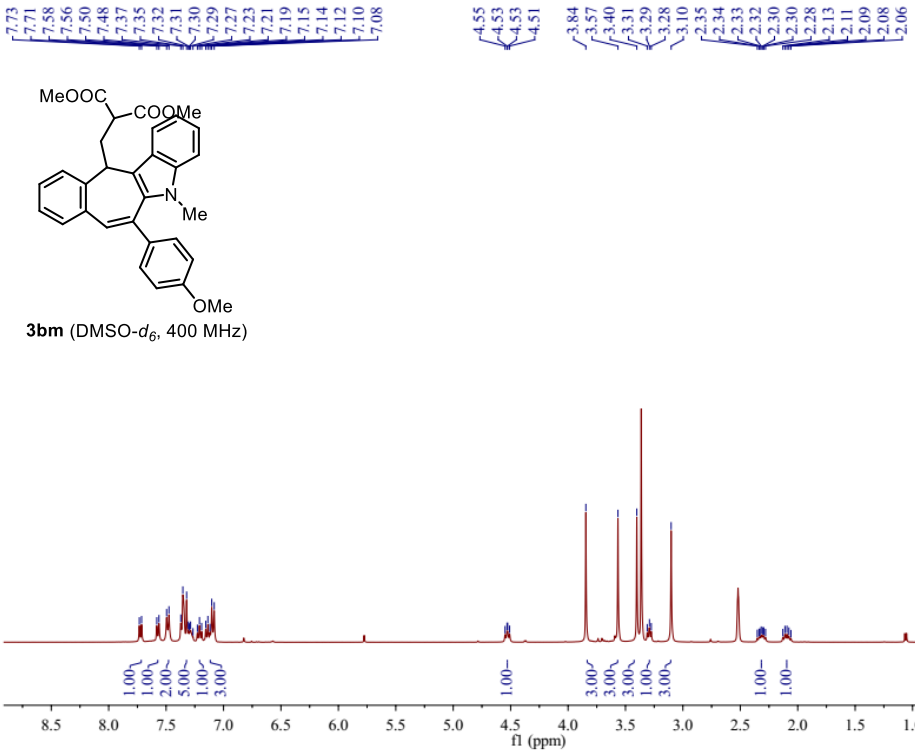
3bk (DMSO-d_6, 100 MHz)



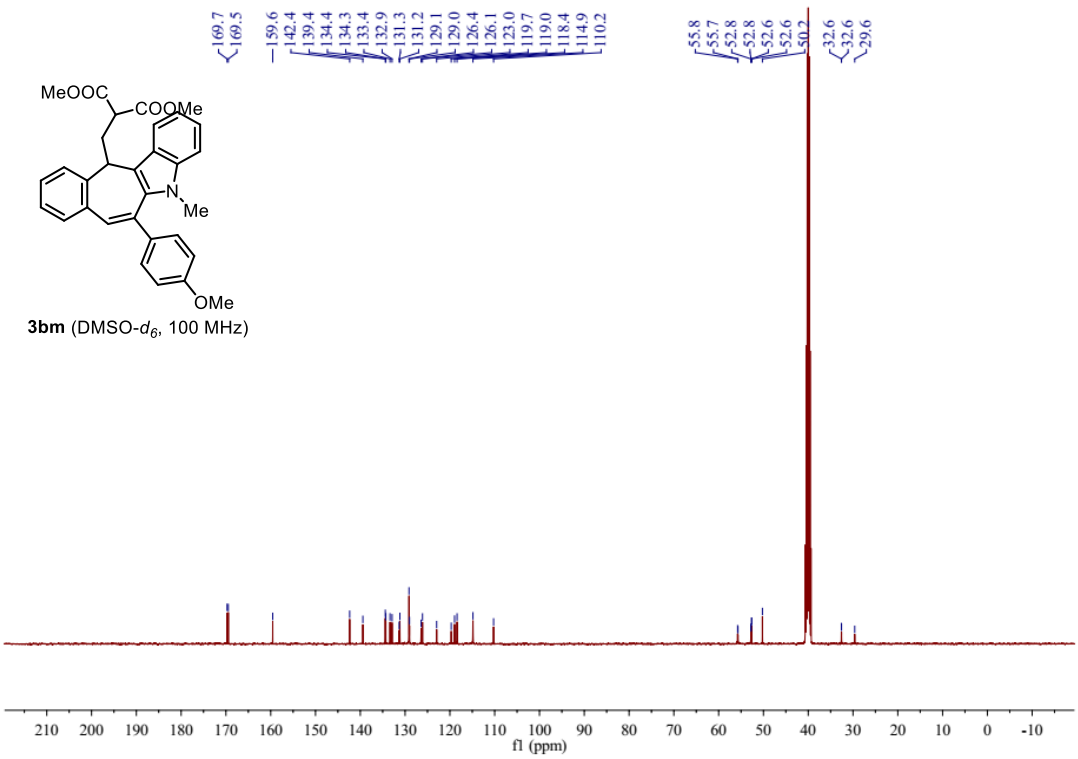
3bl (DMSO-d_6, 400 MHz)



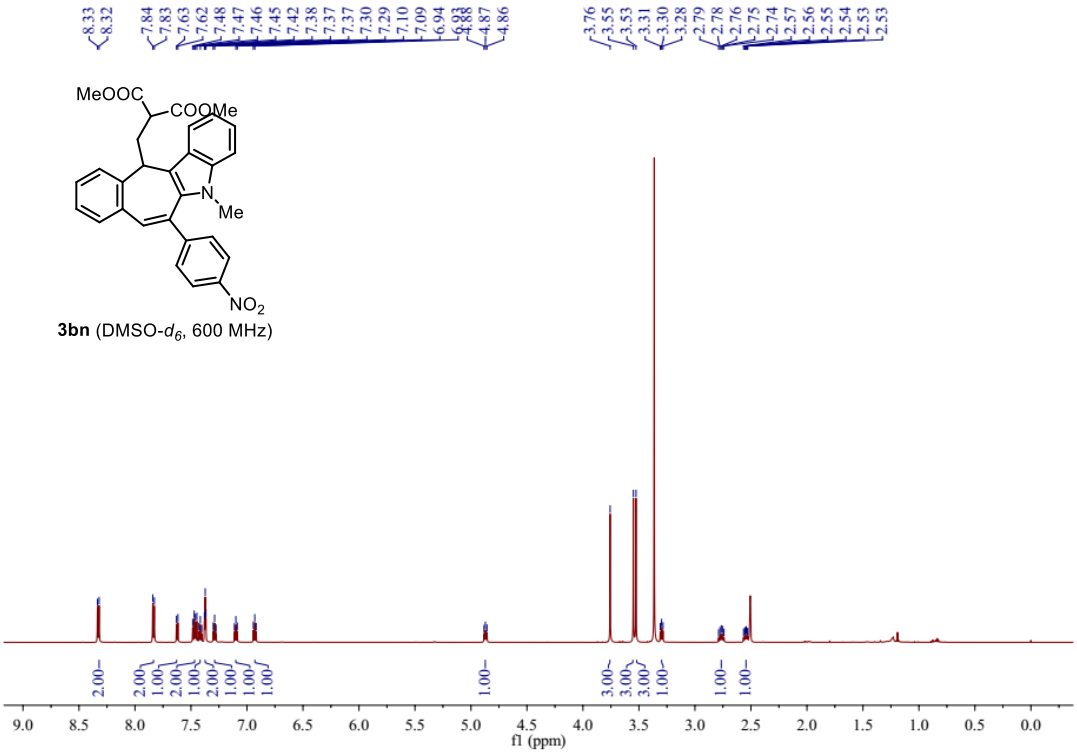
3bl (DMSO-d_6, 100 MHz)



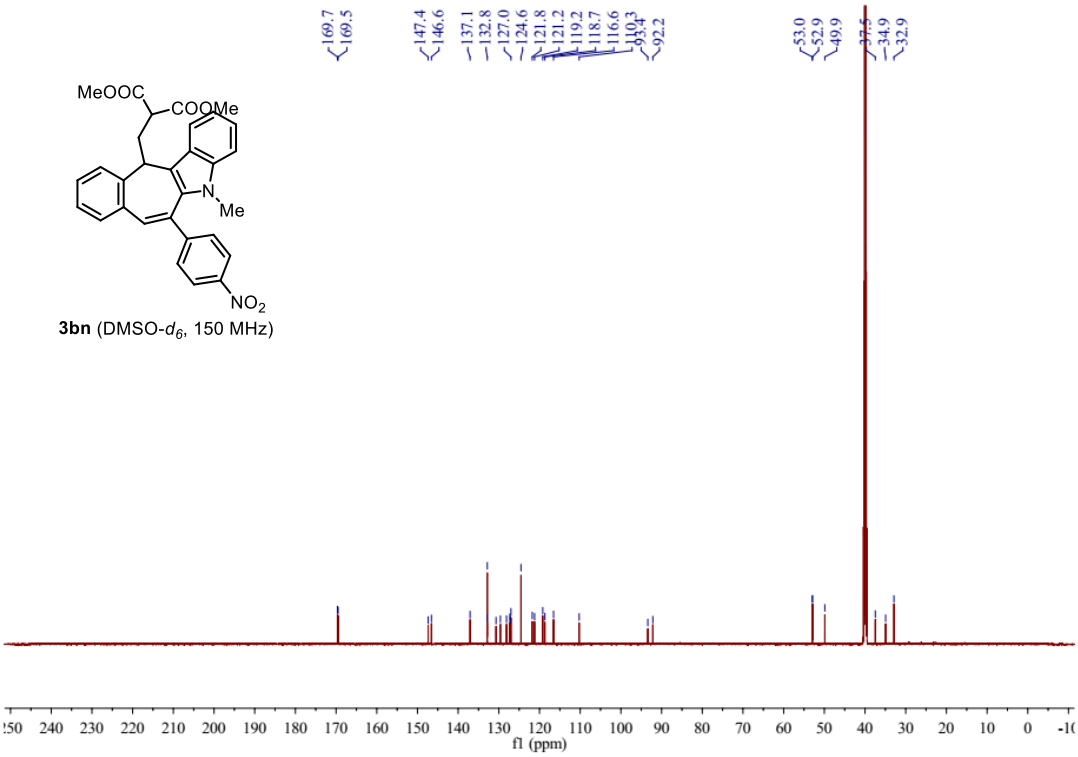
3bm (DMSO-d_6, 400 MHz)



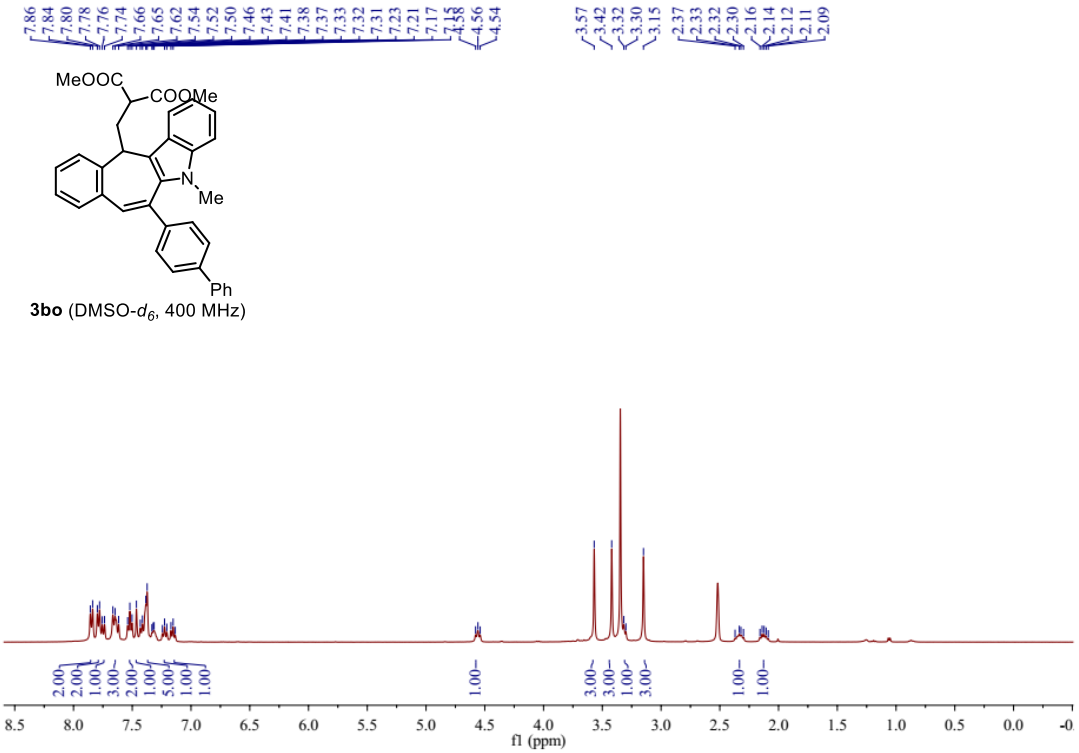
3bm (DMSO-d_6, 100 MHz)



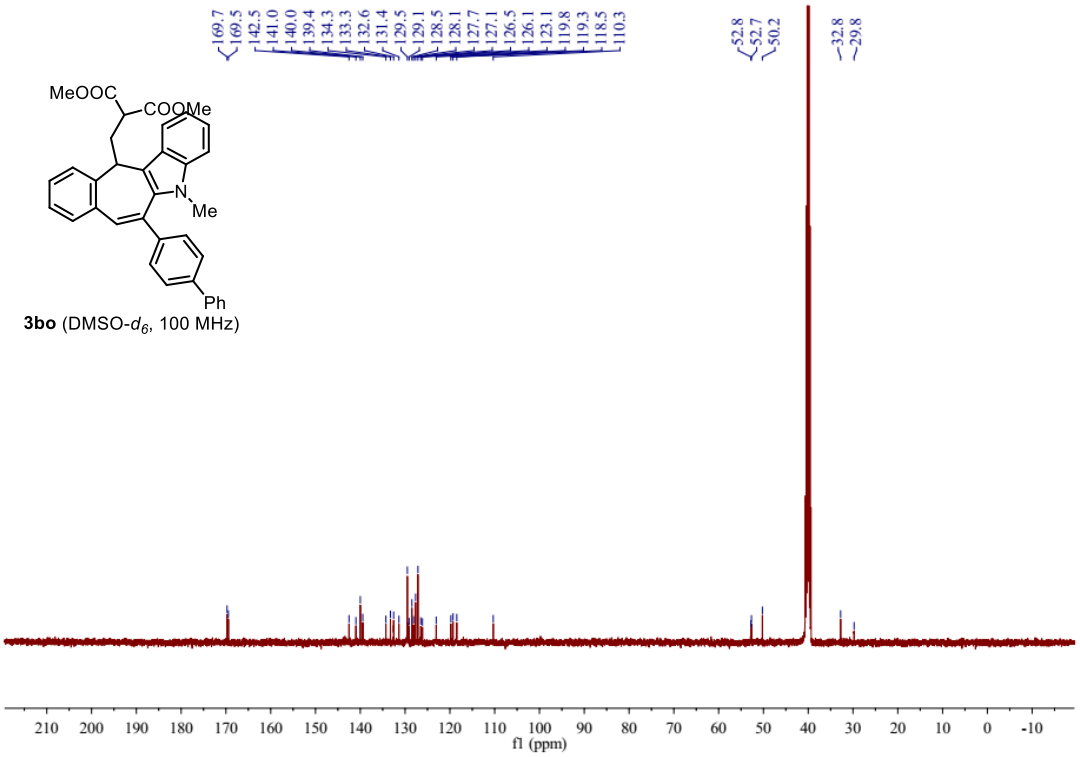
3bn (DMSO-d_6, 600 MHz)



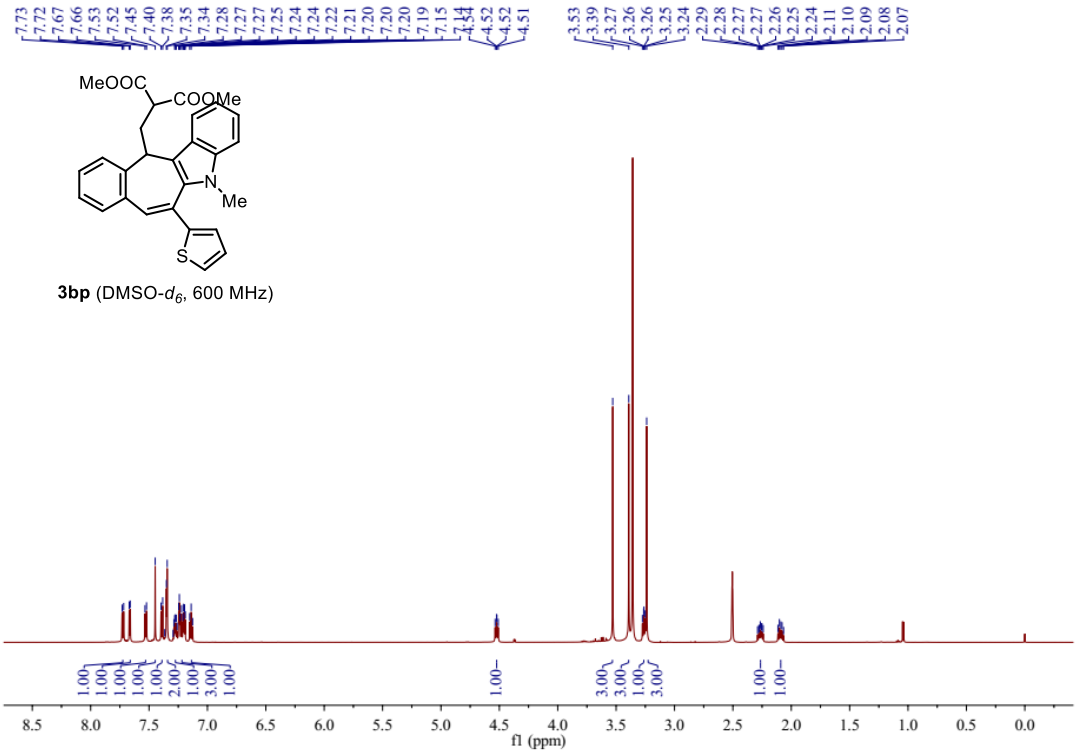
3bn (DMSO-d_6, 150 MHz)



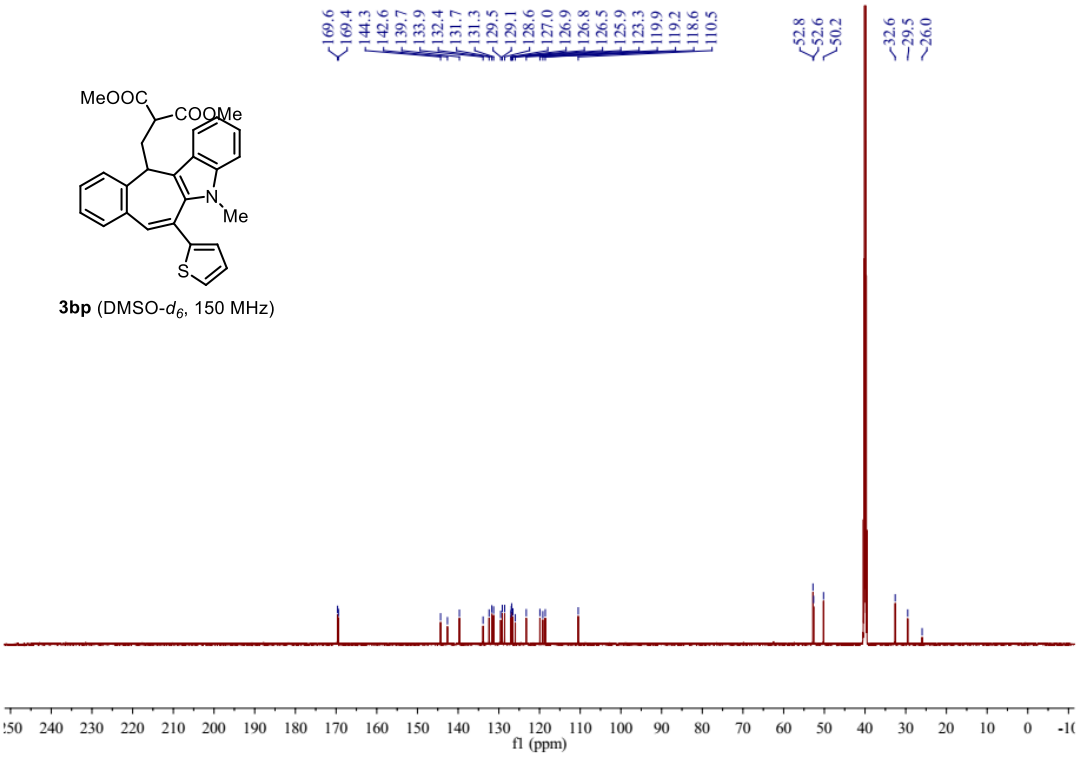
3bo (DMSO-d_6, 400 MHz)



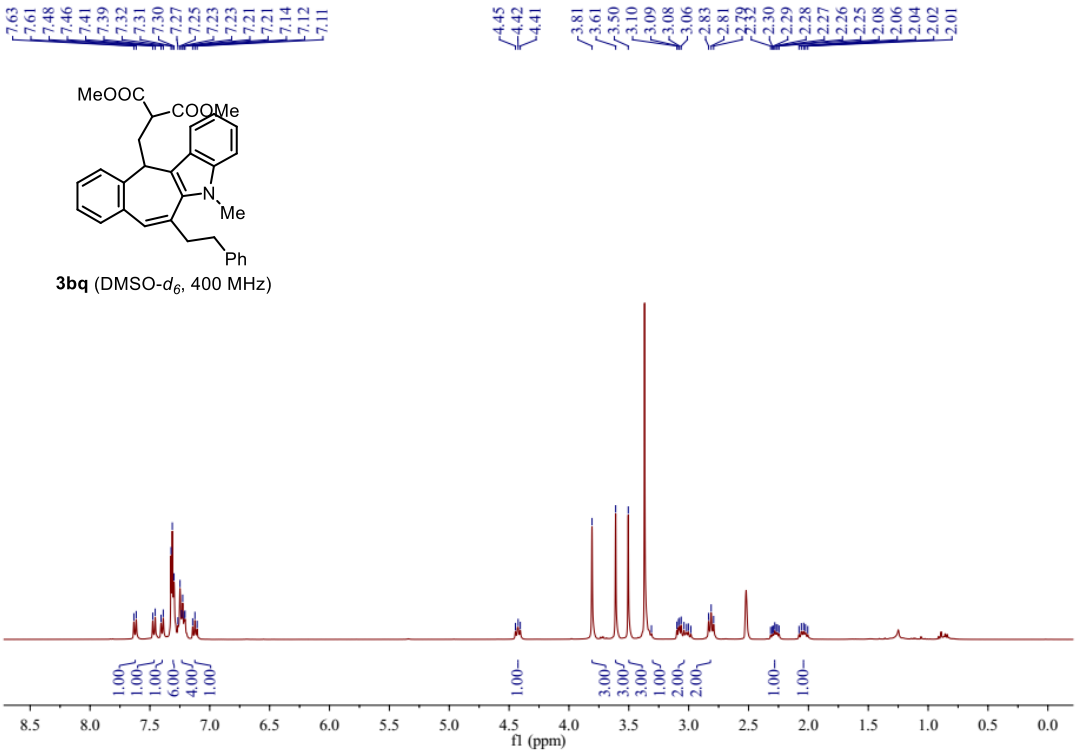
3bo (DMSO-d_6, 100 MHz)



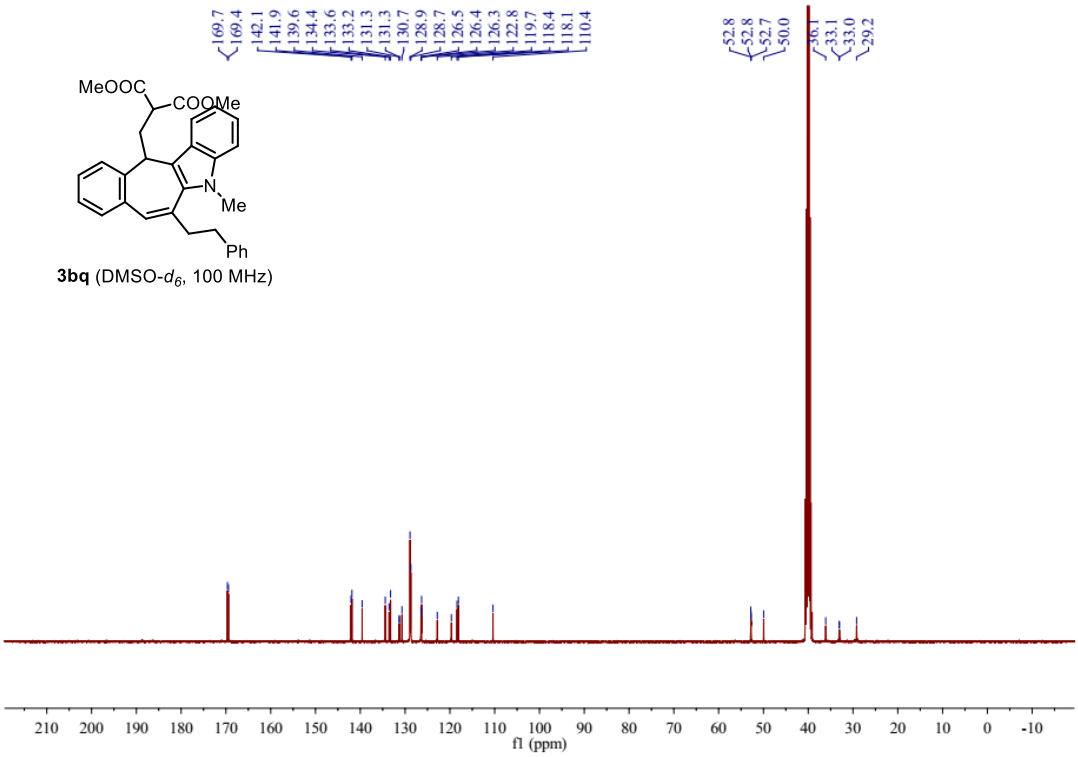
3bp (DMSO-d_6, 600 MHz)



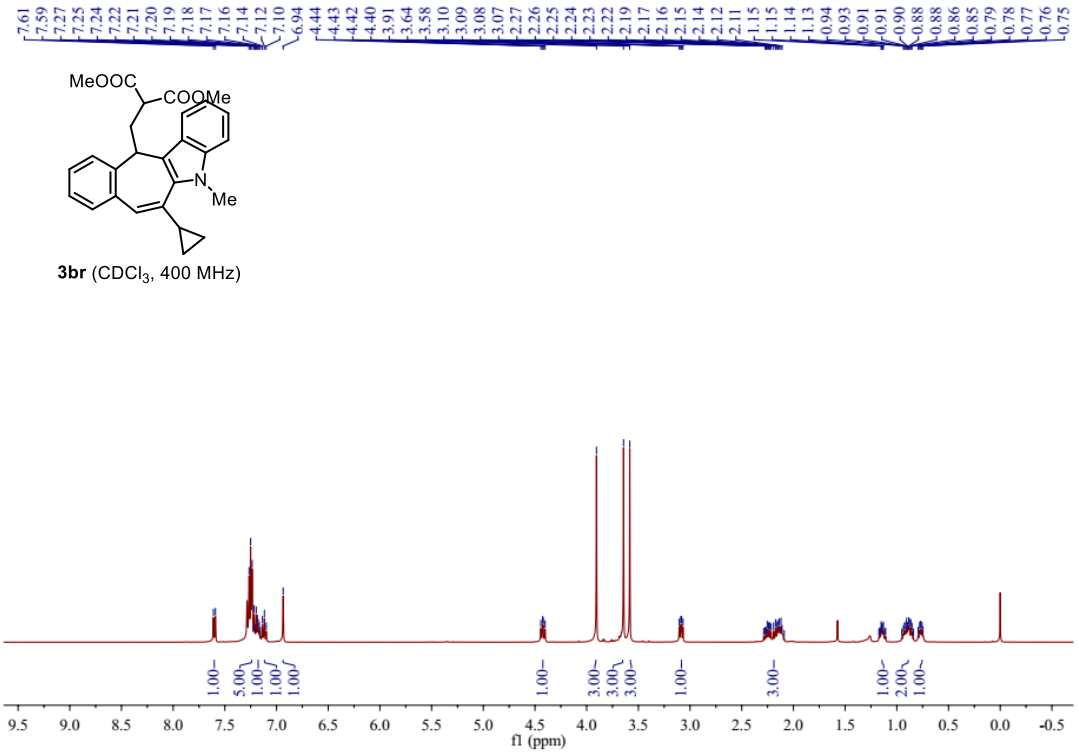
3bp (DMSO-d_6, 150 MHz)



3bq (DMSO-d_6, 400 MHz)

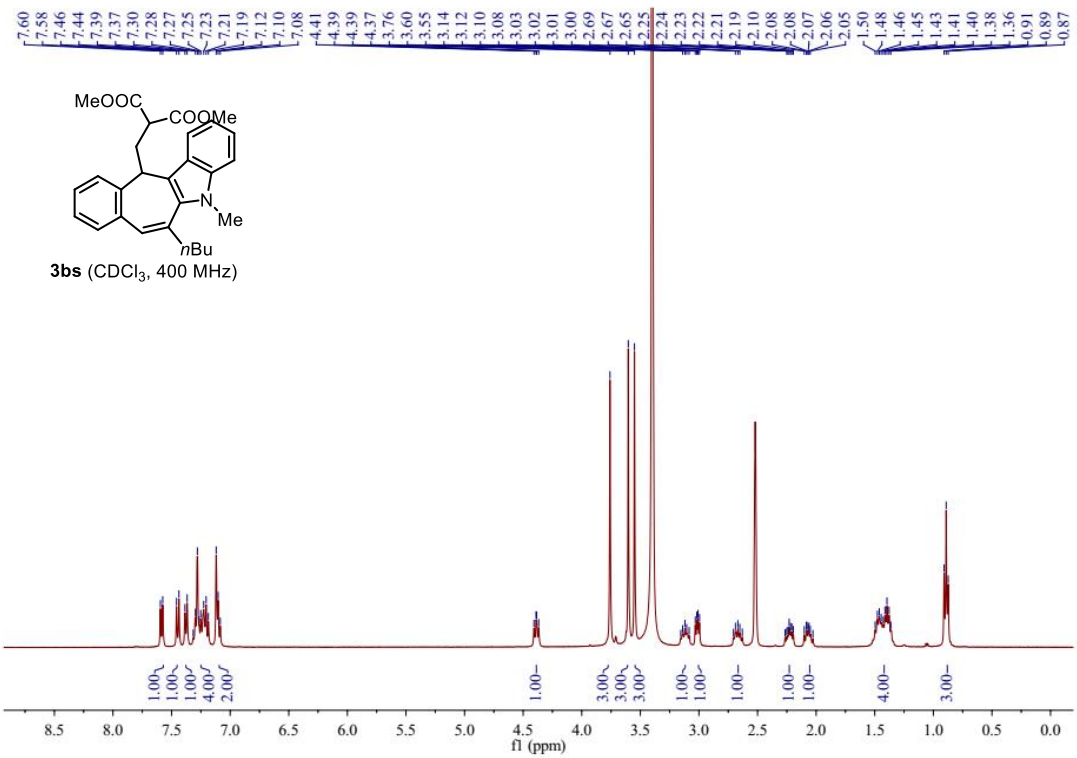


3bq (DMSO-d_6, 100 MHz)

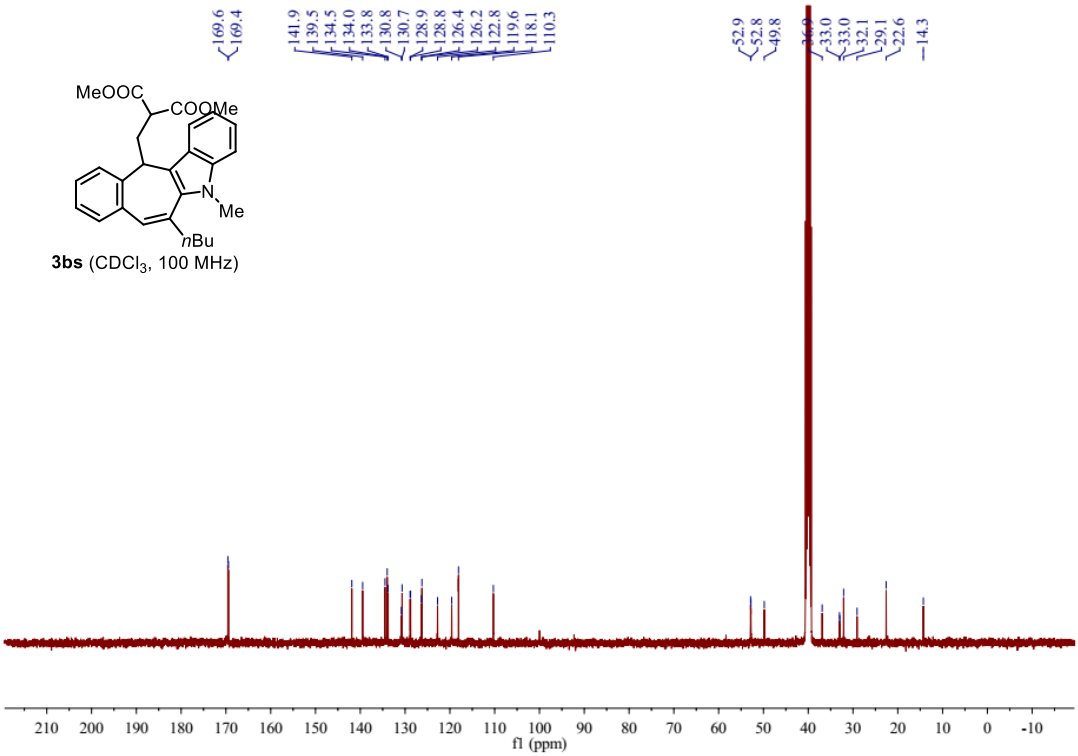


3br ($CDCl_3$, 400 MHz)

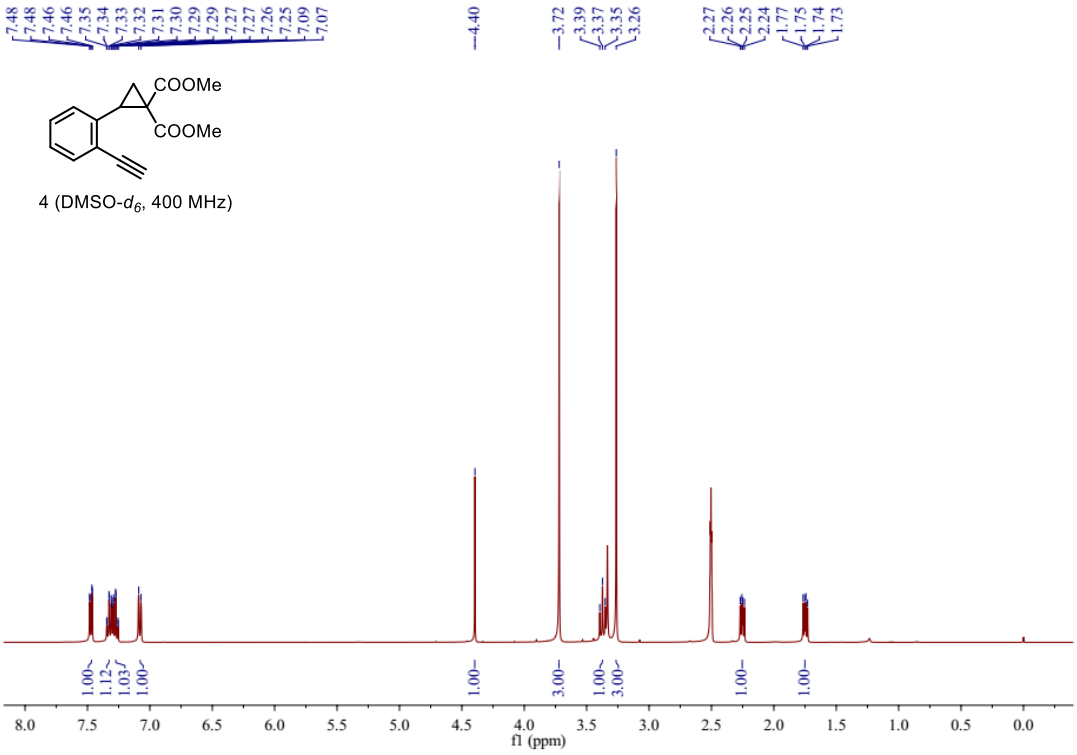
3br ($CDCl_3$, 100 MHz)



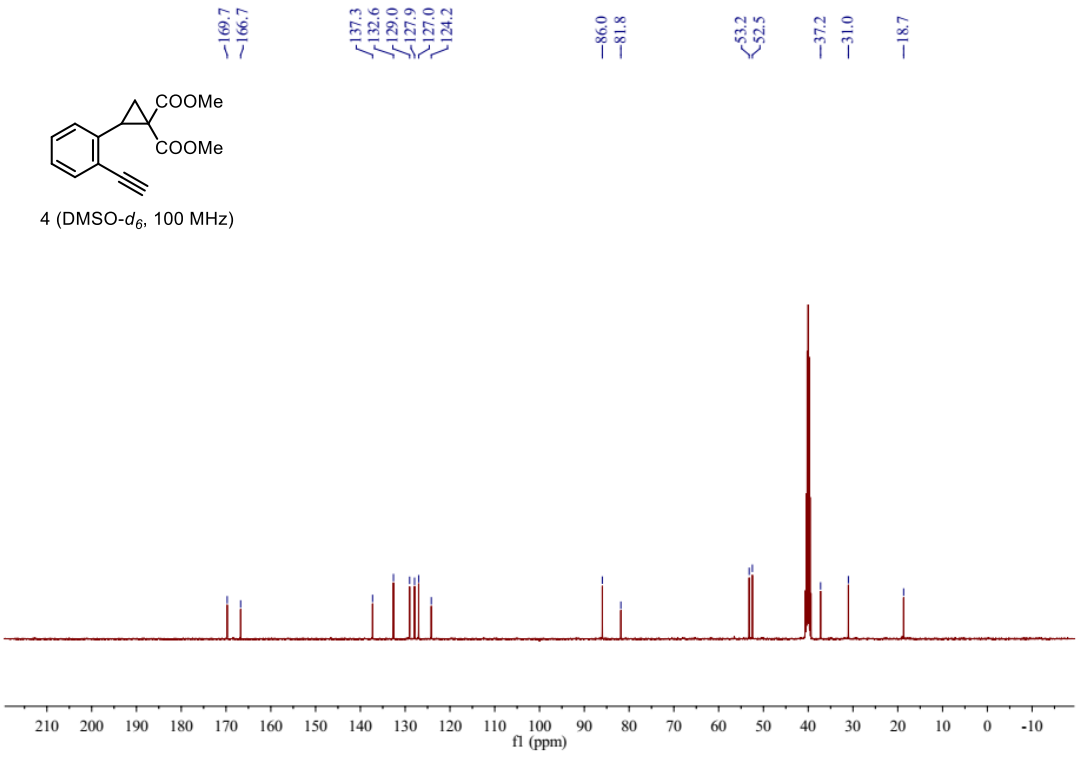
3bs ($CDCl_3$, 400 MHz)



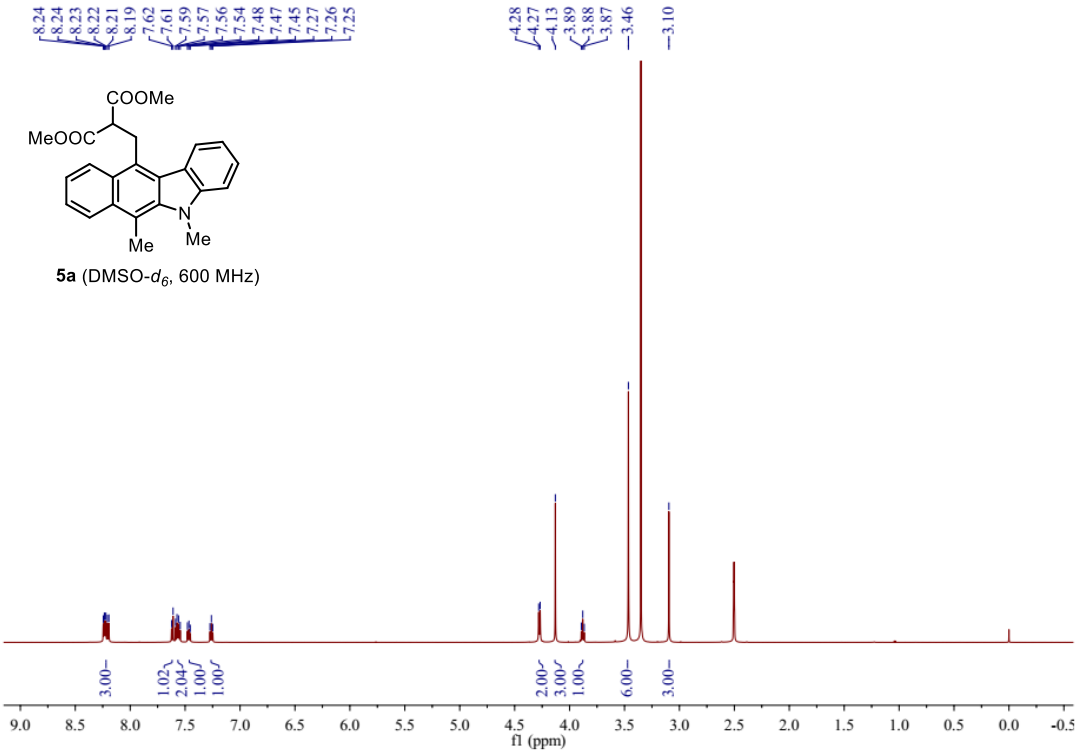
3bs ($CDCl_3$, 100 MHz)



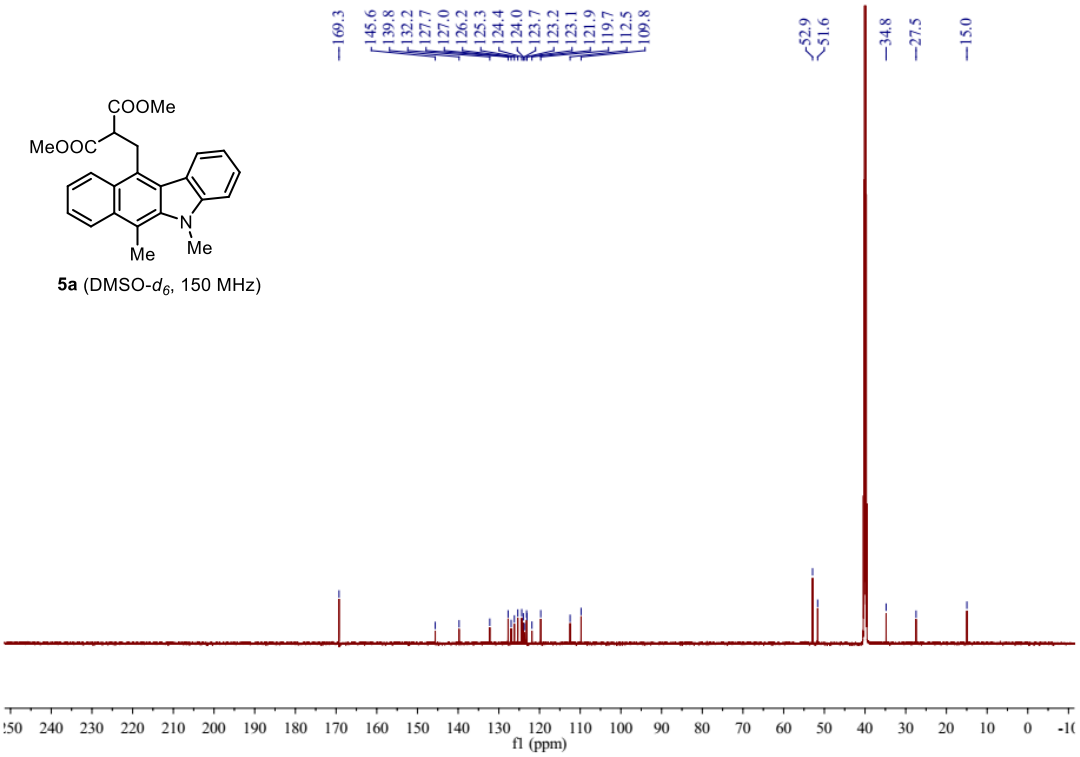
4 (DMSO-d_6, 400 MHz)



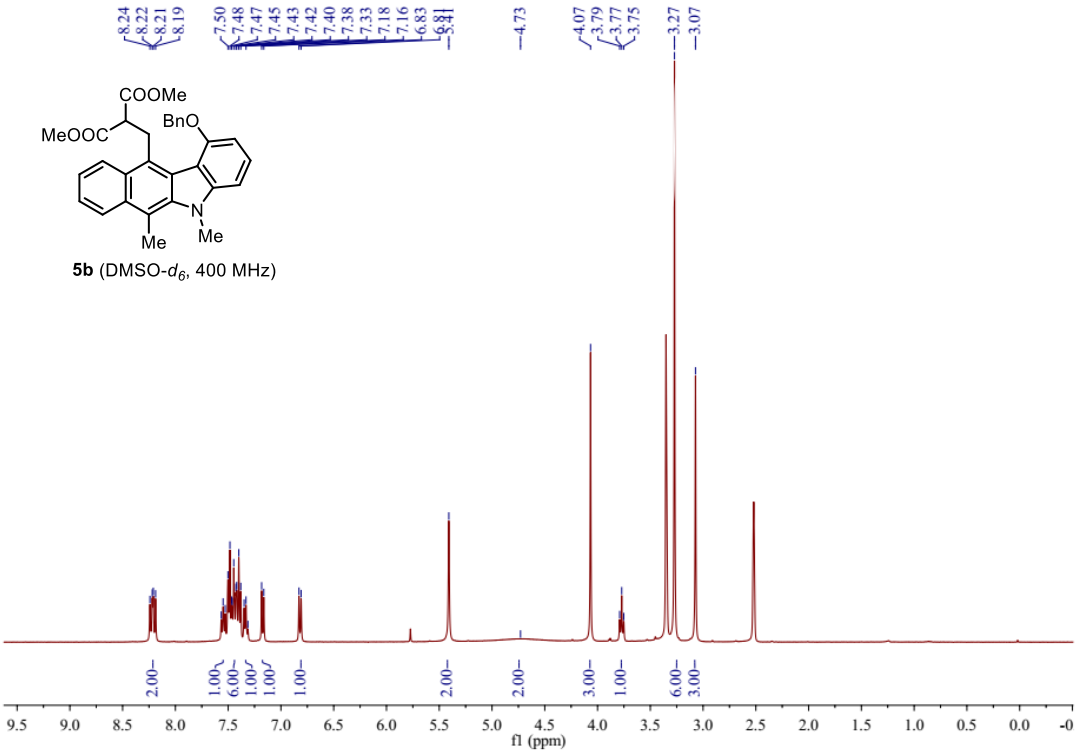
4 (DMSO-d_6, 100 MHz)



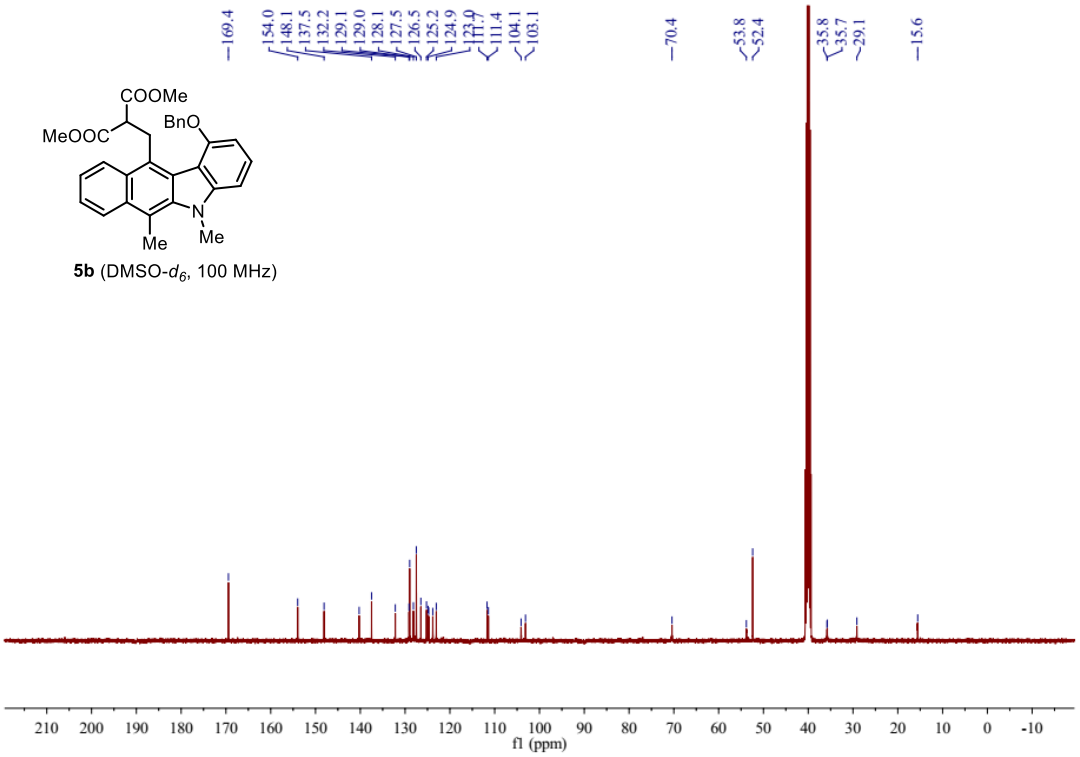
5a (DMSO-d_6, 600 MHz)



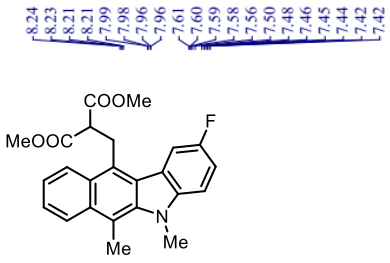
5a (DMSO-d_6, 150 MHz)



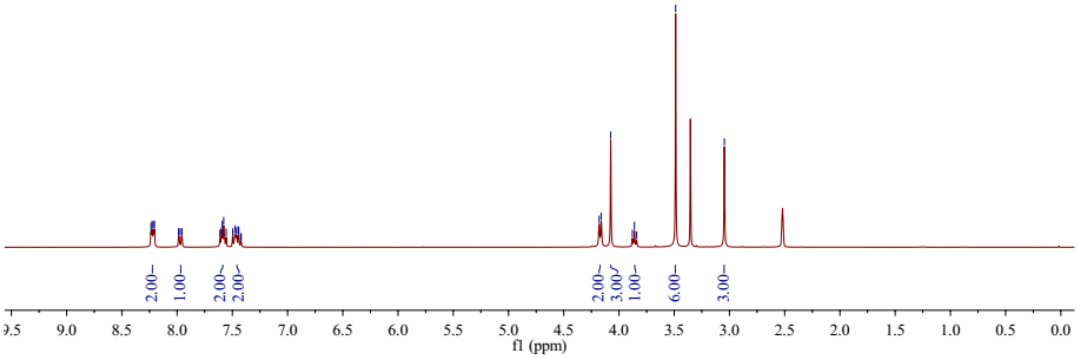
5b (DMSO-d_6, 400 MHz)

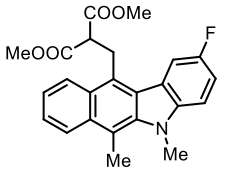


5b (DMSO-d_6, 100 MHz)

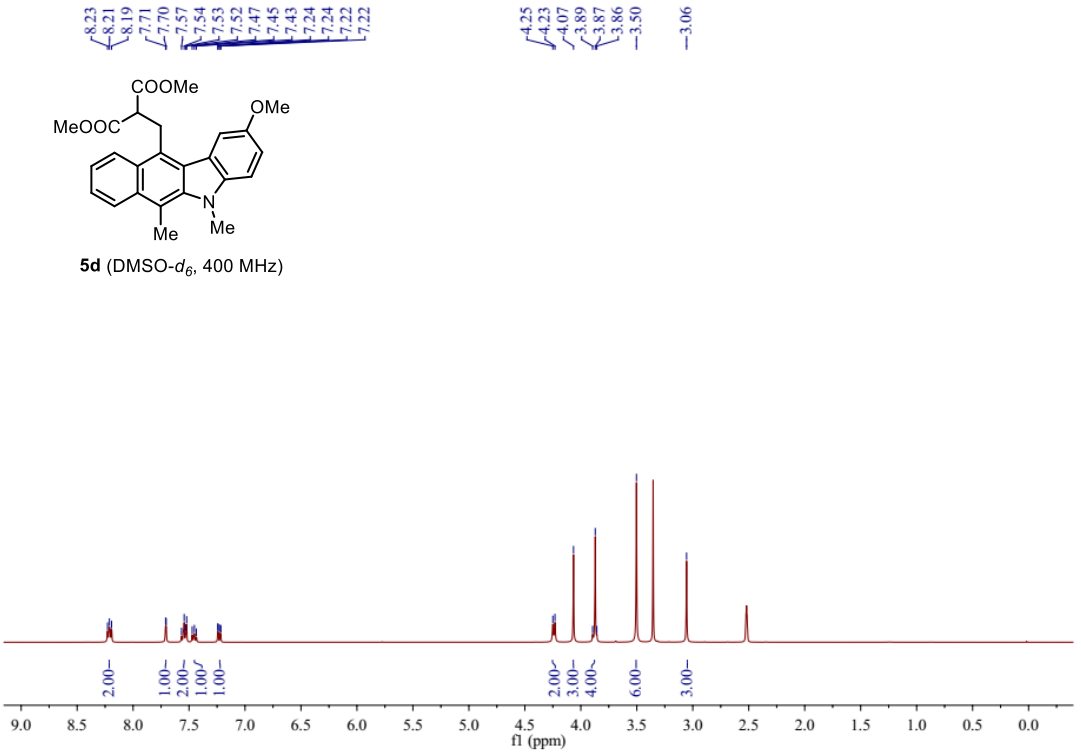


5c (DMSO-d_6, 400 MHz)

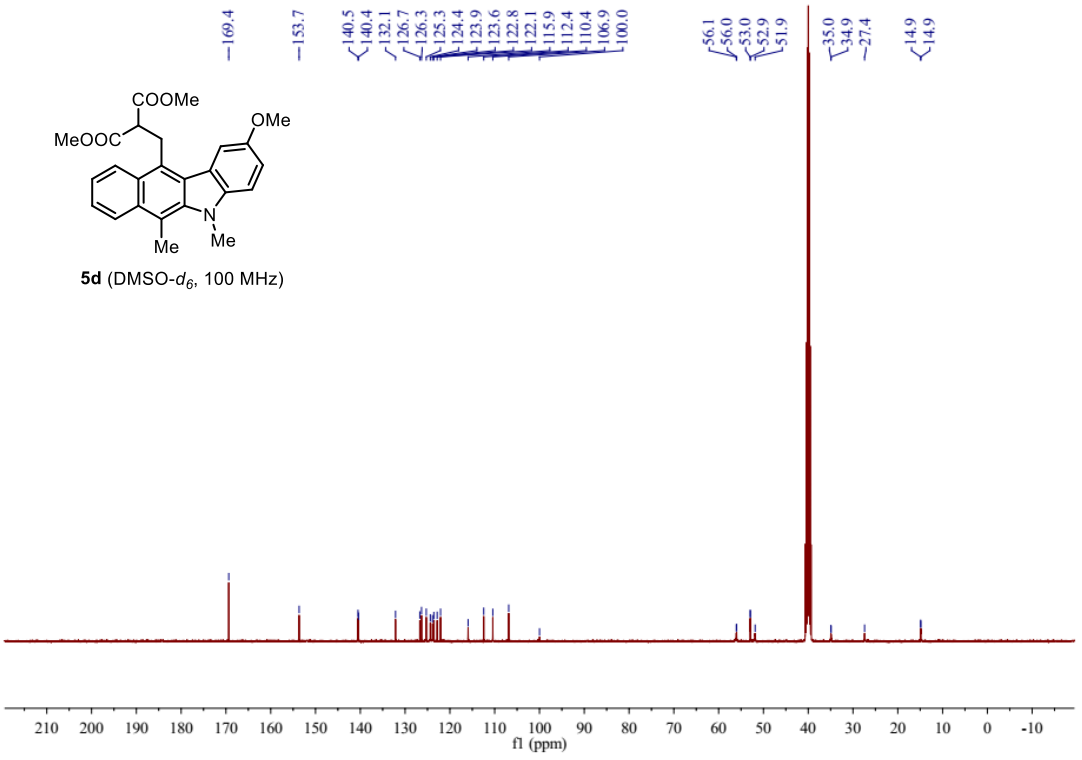




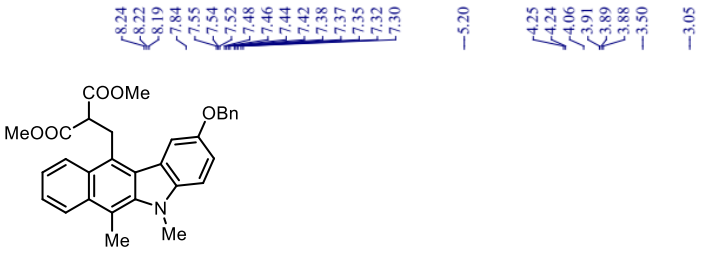
5c (DMSO-d_6, 100 MHz)



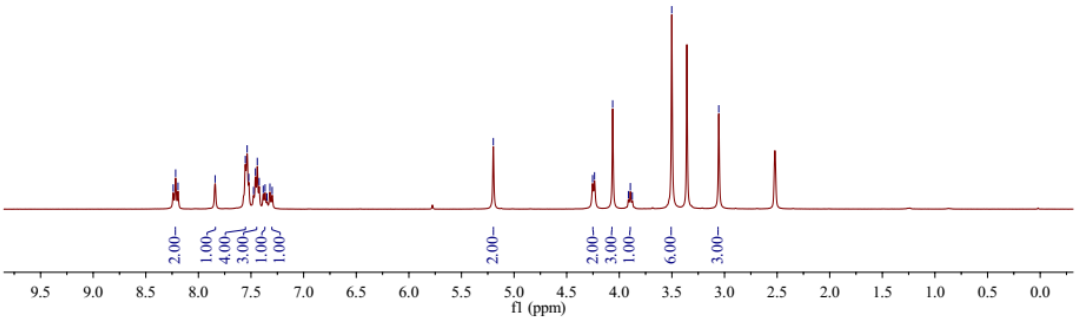
5d (DMSO-d_6, 400 MHz)

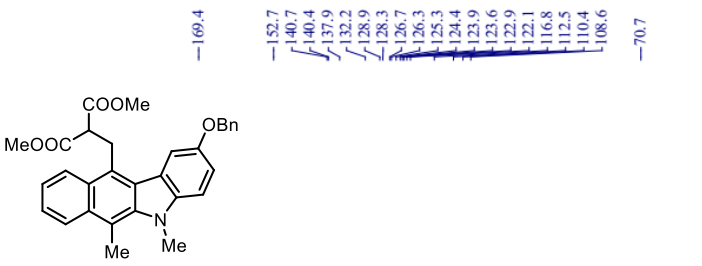


5d (DMSO-d_6, 100 MHz)

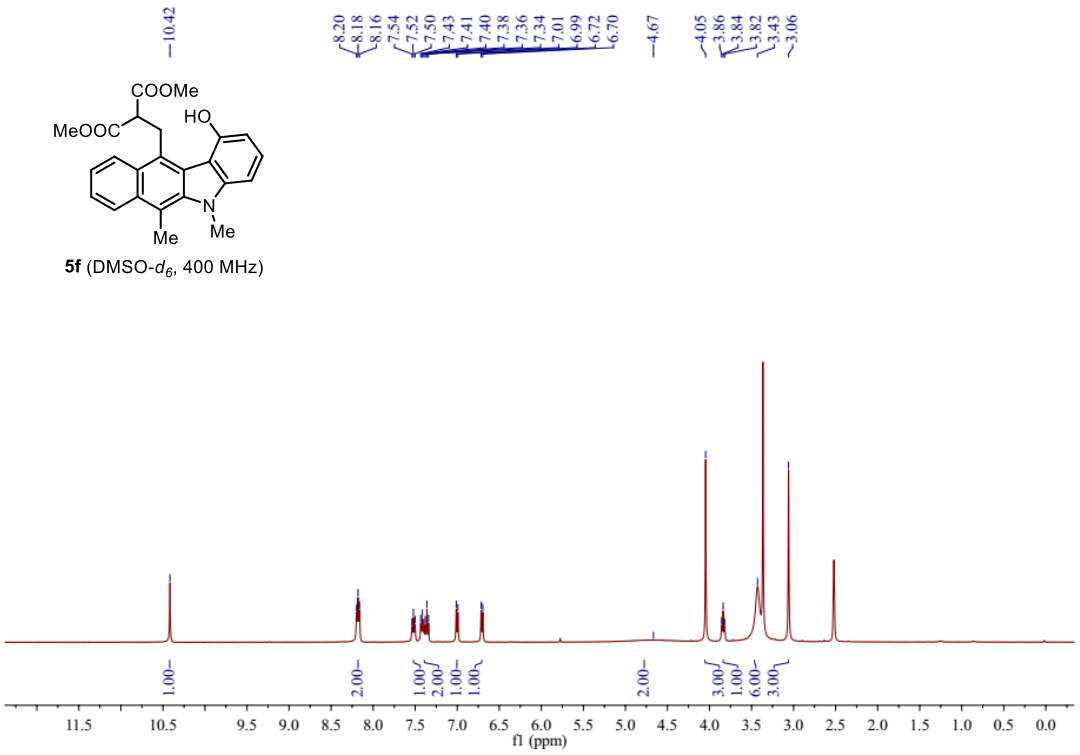


5e (DMSO-d_6, 400 MHz)

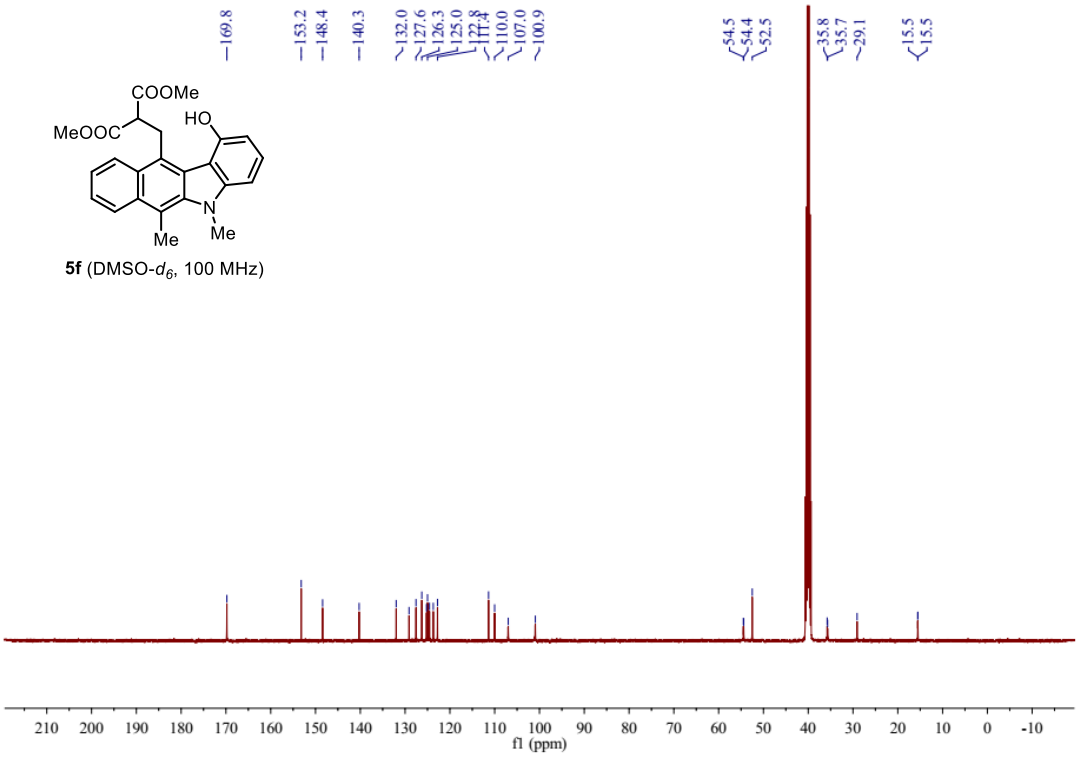




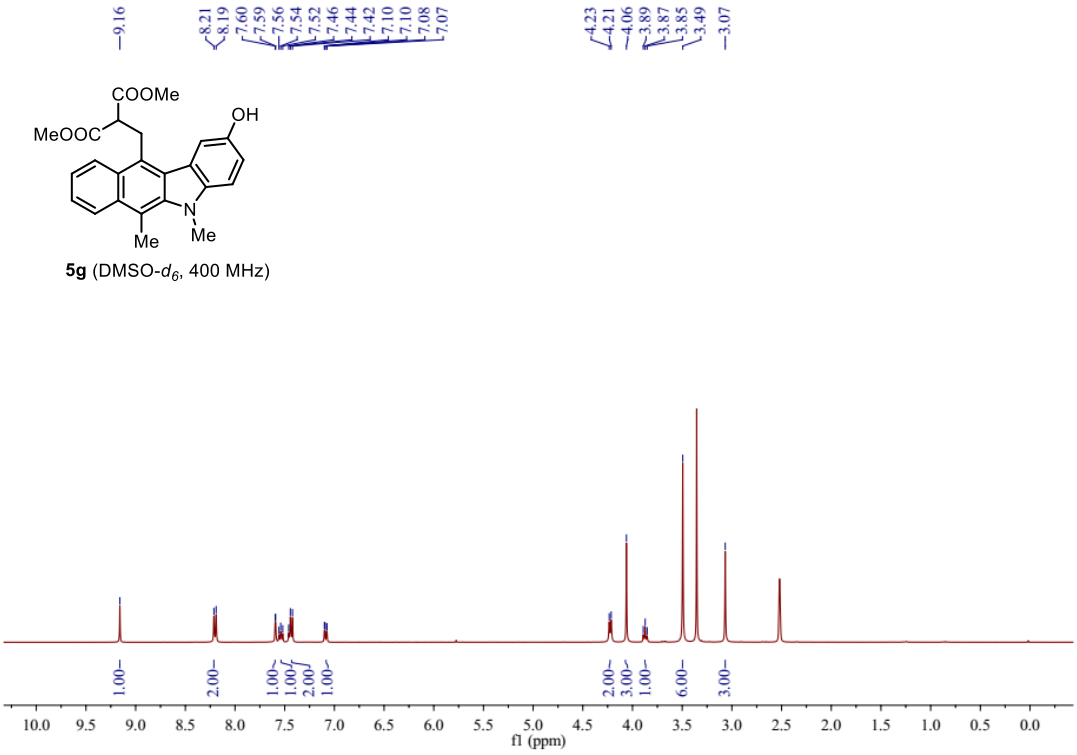
5e (DMSO-d_6, 100 MHz)



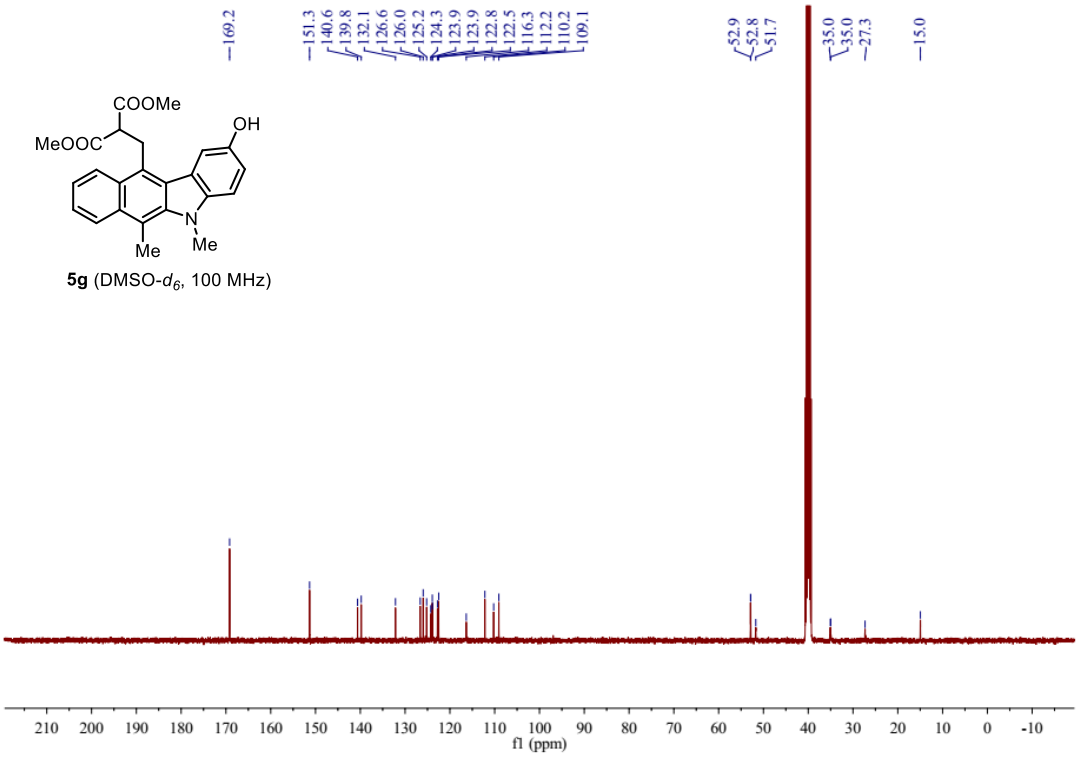
5f (DMSO-d_6, 400 MHz)



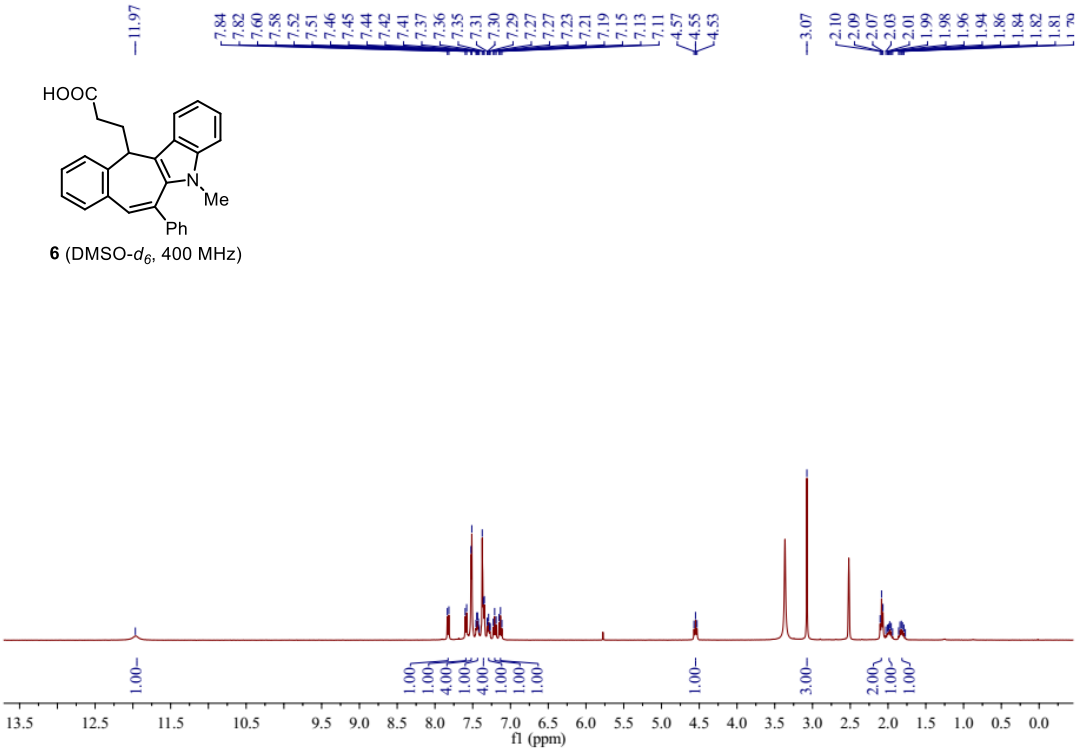
5f (DMSO-d_6, 100 MHz)



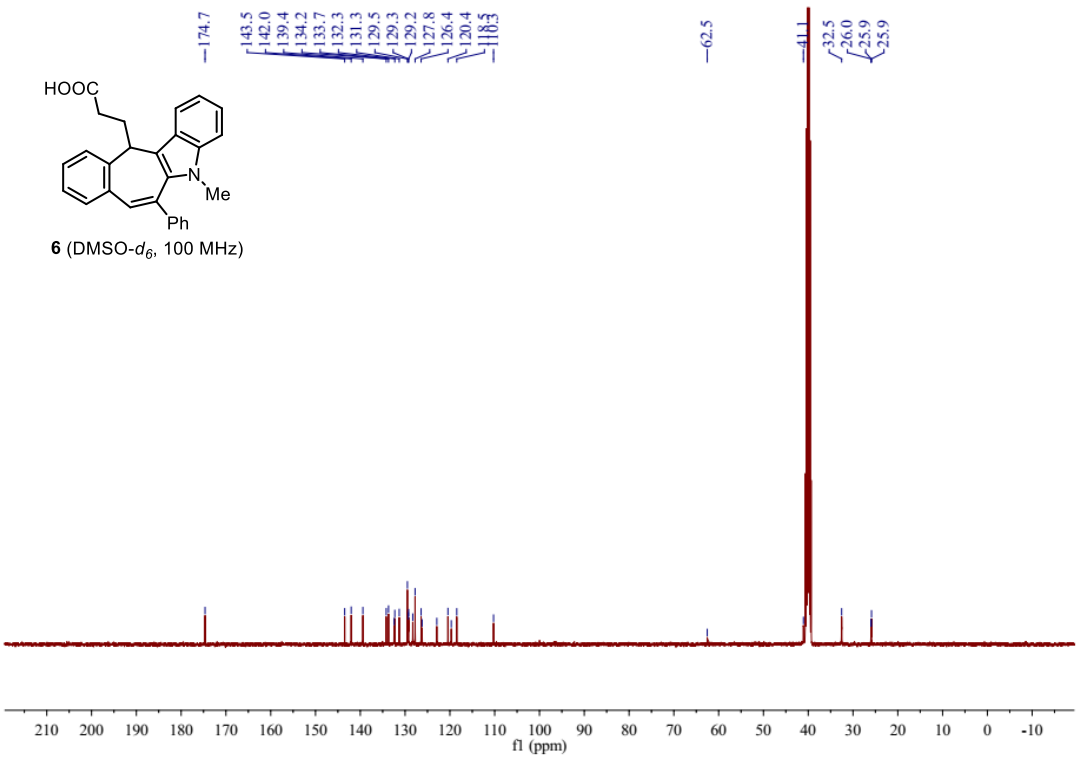
5g (DMSO-d_6, 400 MHz)



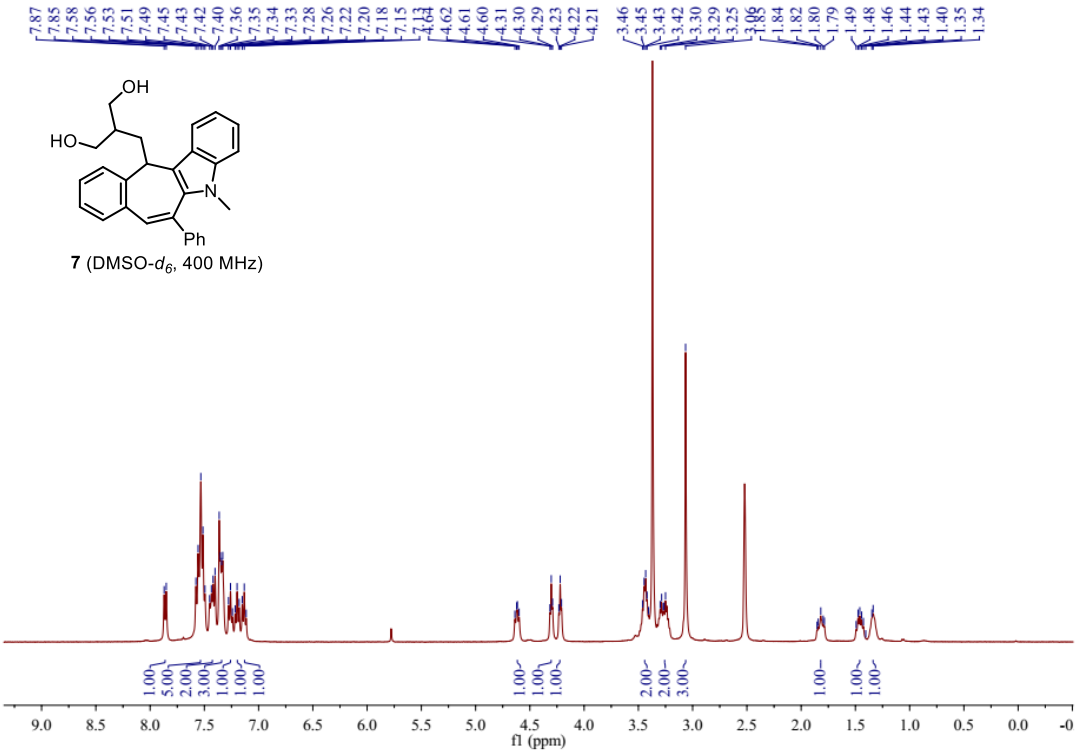
5g (DMSO-d_6, 100 MHz)



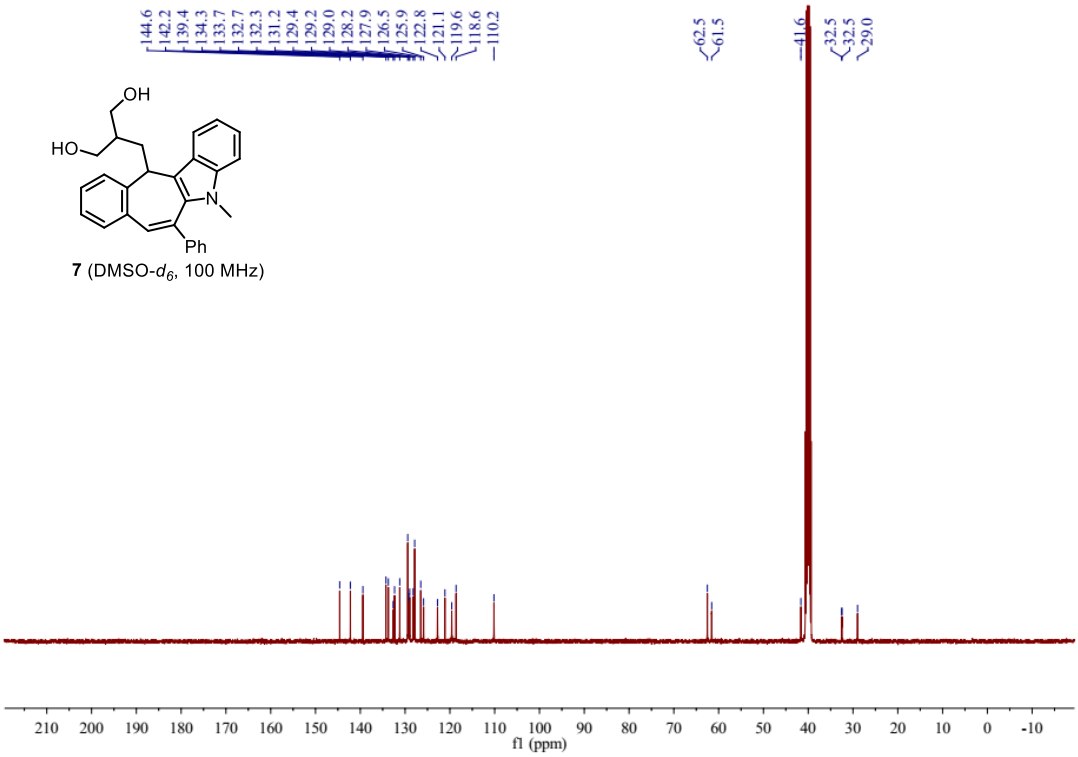
6 (DMSO-d_6, 400 MHz)



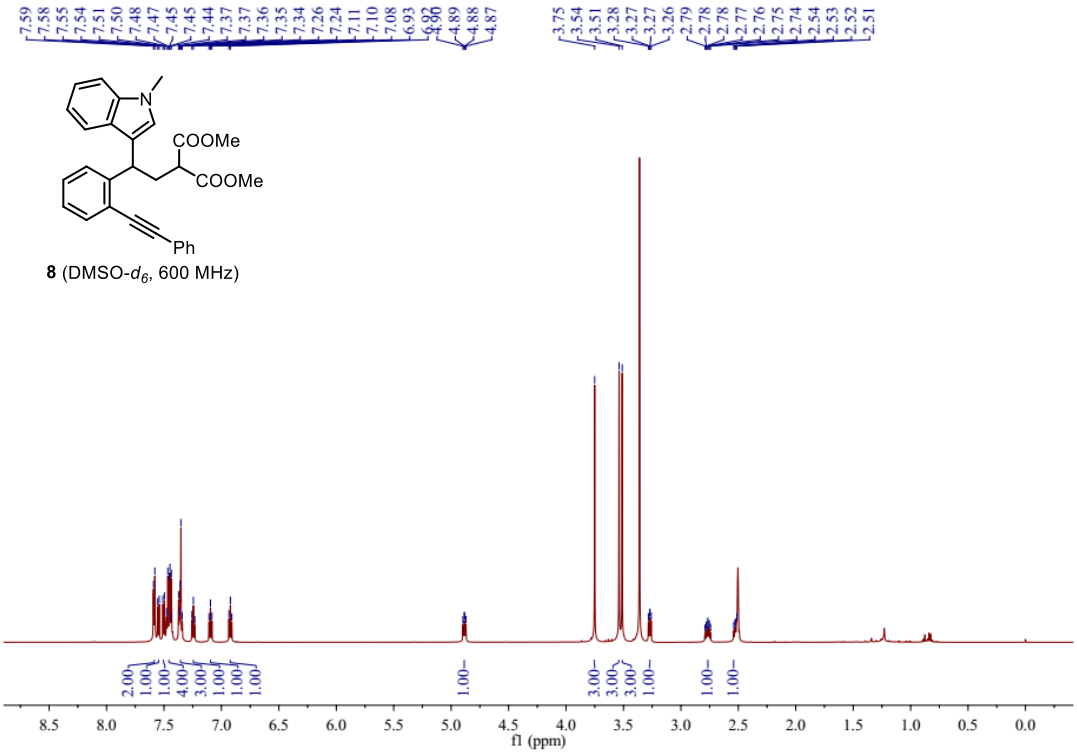
6 (DMSO-d_6, 100 MHz)



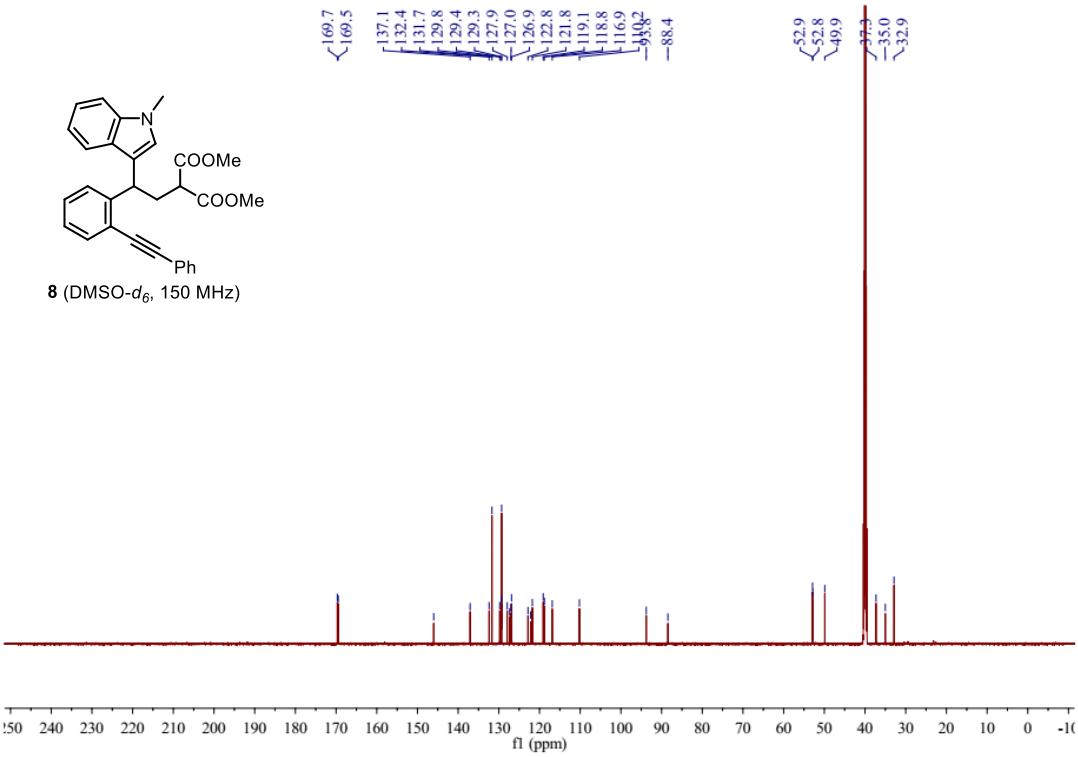
7 (DMSO-d_6, 400 MHz)



7 (DMSO-d_6, 100 MHz)



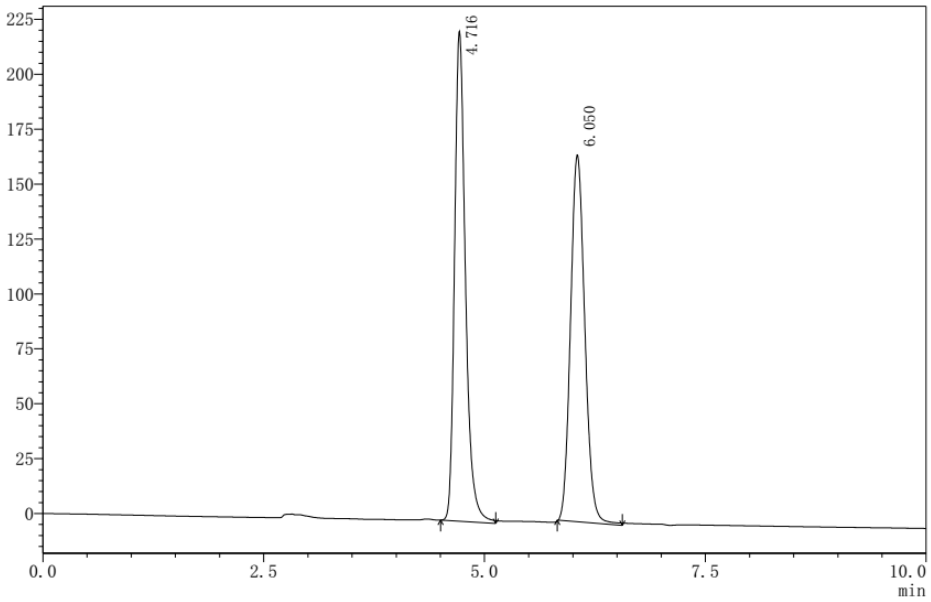
8 (DMSO-d_6, 600 MHz)



8 (DMSO-d_6, 150 MHz)

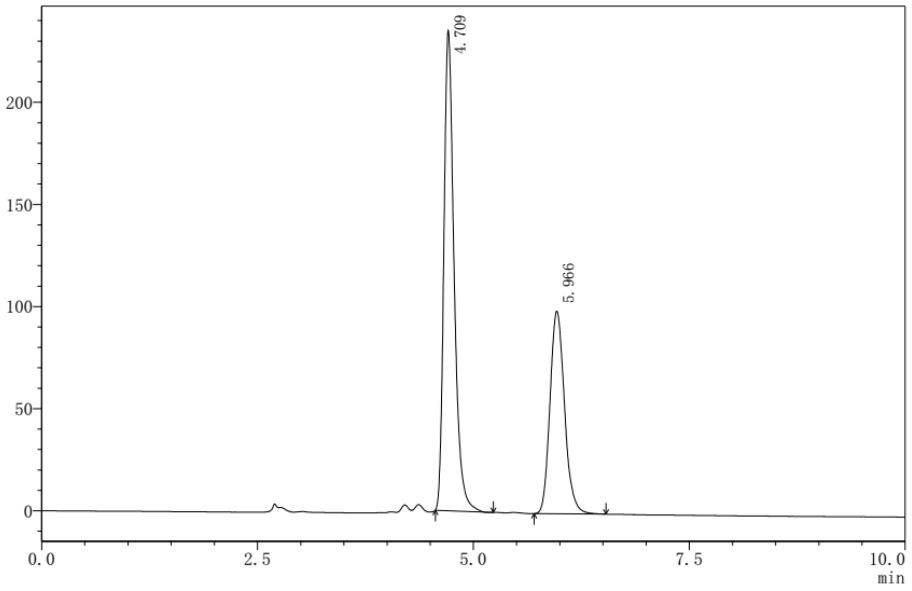
5. HPLC Spectra

HPLC spectra of *racemic*-**3aa**



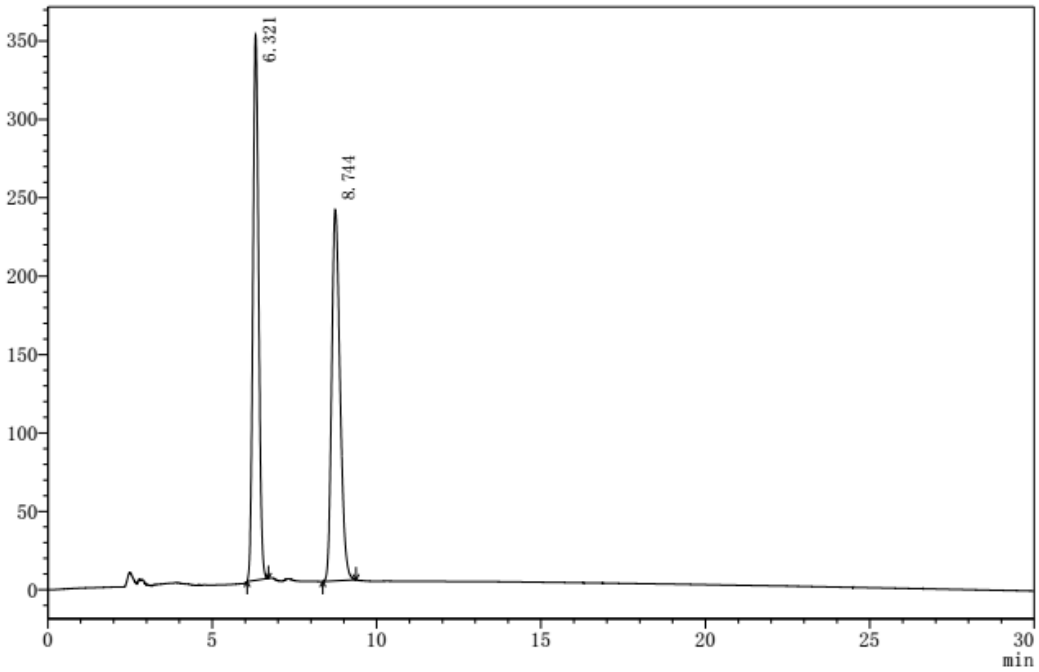
Peak	RetTime	Area	Height	Area%
1	4.716	1911291	222711	50.490
2	6.050	1874184	166794	49.510

HPLC spectra of enantioenriched-**3aa**



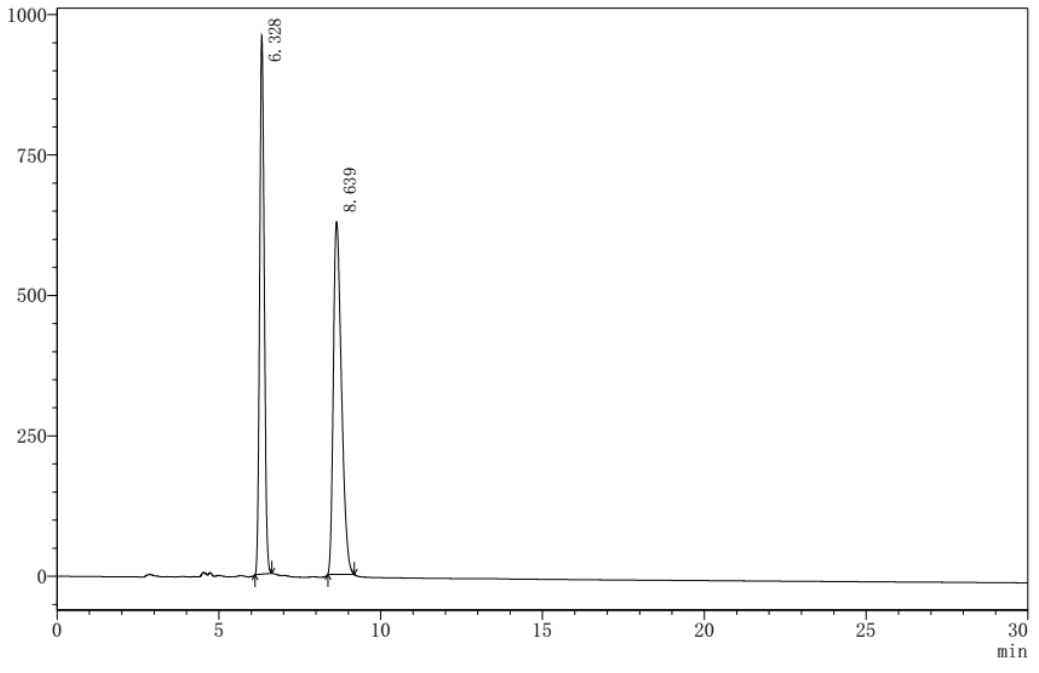
Peak	RetTime	Area	Height	Area%
1	4.709	1934270	234915	62.443
2	5.966	1163409	99255	37.557

HPLC spectra of *racemic*-**8**



Peak	RetTime	Area	Height	Area%
1	6.321	4194474	347607	50.096
2	8.744	4178448	236708	49.904

HPLC spectra of **enantioenriched**-**8**



Peak	RetTime	Area	Height	Area%
1	6.328	9465008	957709	46.276
2	8.639	10988340	627829	53.724

6. X-Ray Crystal Structures

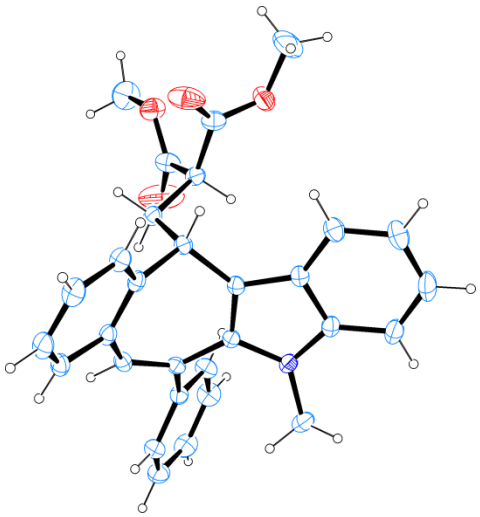


Figure S3. X-ray structure of **3aa** (with the 10% probability level)

Compound 3aa		**CCDC:** 2041332
Bond precision: C-C = 0.0025 Å		Wavelength = 0.71076
a = 8.891(2)	b = 11.712(3)	c = 11.924(3)
alpha = 90.530(8)	beta = 91.989(8)	gamma = 94.978(8)
Cell setting: Triclinic		Moiety formula: $C_{30}H_{27}NO_4$
Cell volume = 1236.1(5)		Space group: P-1
Data completeness = 0.995		Theta(max) = 27.610
R(reflections) = 0.0549(3781)		WR2(reflections) = 0.1512(5728)
S = 1.023		Radiation type: MoK\a
Measurement device type: CCD area detector		Measurement method: phi and omega scans
Structure solution: SHELXS-97		Structure refinement: SHELXL-97
Solution primary: direct		Solution secondary: difmap
Solution hydrogens: geom		Hydrogen treatment: mixed

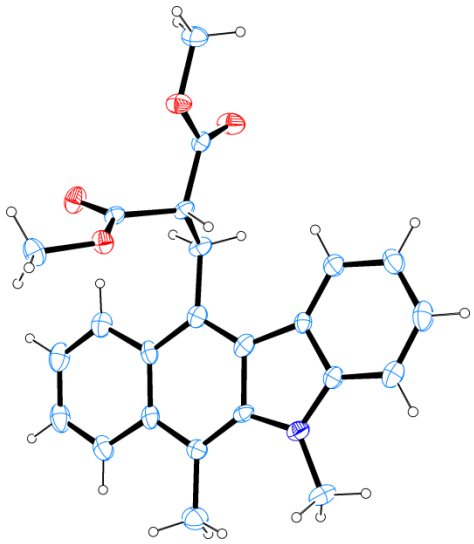


Figure S4. X-ray structure of **5a** (with the 10% probability level)

Compound 5a		**CCDC:** 2085610
Bond precision: C-C =0.0042 Å		Wavelength = 0.71073
a = 11.5856(7)	b = 7.9134(5)	c = 21.1647(13)
alpha = 90.00	beta = 96.028(2)	gamma = 90.00
Cell setting: Monoclinic		Moiety formula: $C_{24}H_{23}NO_4$
Cell volume = 1929.7(2)		Space group: P2(1)/c
Data completeness = 0.999		Theta(max) = 27.520
R(reflections) = 0.0689(2310)		WR2(reflections) = 0.1790(4440)
S = 1.011		Radiation type: MoK\a
Measurement device type: CCD area detector		Measurement method: phi and omega scans
Structure solution: SHELXS-97		Structure refinement: SHELXL-97
Solution primary: direct		Solution secondary: difmap
Solution hydrogens: geom		Hydrogen treatment: mixed