Supporting Information

Au(I)/Sc(III)-co-catalyzed tandem spiroannultion/cycloisomerization of 3-(2-ethynylaryl)-*N*-tosylaziridines with indoles to access 5*H*-benzo[*b*] carbazoles

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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.

NMR-Spectroscopy

^{1}H NMR spectra were recorded on a Bruker AVANCE NEO 400 MHz. ^{13}C NMR data were collected at 100 MHz with complete proton decoupling. ^{19}F NMR data were collected at 376 MHz. 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

High resolution mass spectroscopy (HRMS) were recorded on a Bruker Compact QTOF-MS mass spectrometer with an electrospray ionization (ESI) interface and acetonitrile was used to dissolve the sample.

Single Crystal X-Ray Diffraction

Single crystal X-ray diffraction (SC-XRD) were performed on a Bruker single crystal X-ray diffractometer (model of the instrument–AXS D8 Quest System).

UV-visible spectra

UV-visible absorption emission spectra were recorded on Shimadzu UV-2600 spectrophotometer.

Fluorescence emission spectra

Fluorescence emission spectra were recorded on HITACHI F-4600 fluorescence spectrophotometer.

Melting Point Apparatus

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

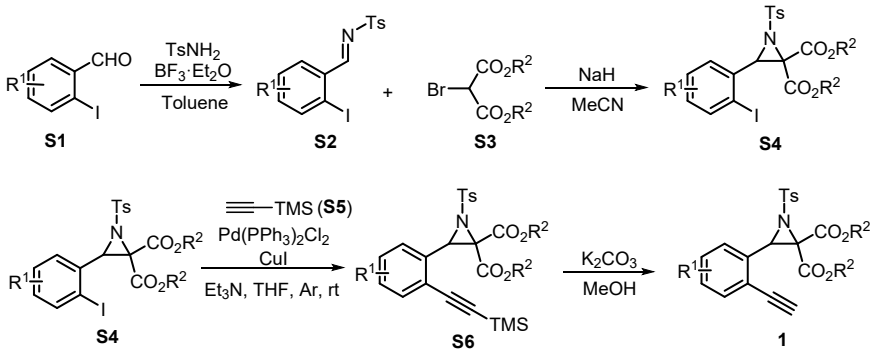
Chromatography

Flash column chromatography was carried out on silica gel (200-300 mesh). Thin layer chromatography were 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. Experimental procedures and characterization data

2.1 General experimental procedure for the synthesis of aziridines 1

Imines **S2** were known compounds and prepared according to the literatures.[1] Aziridines **1** were synthesized according to the literatures with slightly modification.[2]

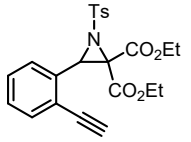


2-Iodoimine **S2** (13.2 mmol, 1.0 equiv) was dissolved in acetonitrile and stirred at 0 ℃ for 5 minutes. Then, bromomalonate **S3** (15.9 mmol, 1.2 equiv) and NaH (0.63 g, 15.9 mmol, 1.2 equiv, 60% dispersion in mineral oil) were added, respectively. The reaction was stirred at 0 ℃ for 30 minutes. After the reaction was completed, the mixture was quenched with water (10 mL), extracted with EtOAc (2 × 100 mL) and washed with brine (100 mL). The combined organic layers were dried, concentrated and purified by flash silica gel column chromatography (Petroleum Ether:EtOAc = 90:10 to 85:15) to afford 2-iodoaryl-*N*-tosylaziridines **S4**.

To a solutioin of 3-(2-iodo)aryl-*N*-tosylaziridine **S3** (12.0 mmol) in THF (50 mL), trimethylsilylacetylene **S5** (1.4g, 14.4 mmol, 1.2 equiv), $Pd(PPh_3)_2Cl_2$ (0.25 g, 0.36 mmol, 3 mol%), CuI (0.11 g, 0.6 mmol, 5 mol%) and triethylamine (50 mL) were added under argon atmosphere, respectively. The reaction mixture was stirred at room temperature for 12 h. After the reaction was completed, hydrochloric acid aqueous solution (3M, 60 mL) was added to quench the reaction. The residue was extracted with EtOAc (2 × 100 mL) and wash with brine (2 × 100 mL). The combined organic layer was dried, concentrated to give crude **S6**. The crude aziridine **S6** was

used in the next step without further purification. To a solution of newly formed aziridine **S6** in anhydrous methanol (120 mL) was added anhydrous potassium carbonate (5.0 g, 36.0 mmol, 3.0 equiv). The reaction mixture was stirred at room temperature for 12 hours. After the reaction was completed, the mixture was filtered through Celite™ and washed with EtOAc. The filtrate was extracted with EtOAc (2 × 100 mL) and washed with brine (2 × 100 mL). The combined organic layer was dried, concentrated and purified by flash silica gel column chromatography (Petroleum Ether:EtOAc = 90:10 to 85:15) to afford 3-(2-ethynylaryl)-*N*-tosylaziridine-2,2-diester **1** as white solid.

Diethyl 3-(2-ethynylphenyl)-1-tosylaziridine-2,2-dicarboxylate (1a)



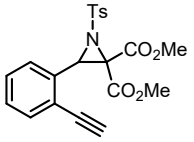
Yellow solid (81% yield, 4.3 g, 9.7 mmol); m.p. 77-78 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.46 – 7.44 (m, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.25 – 7.17 (m, 2H), 7.09 (d, *J* = 7.2 Hz, 1H), 5.21 (s, 1H), 4.43 – 4.35 (m, 2H), 3.97 – 3.88 (m, 2H), 3.45 (s, 1H), 2.44 (s, 3H), 1.37 (t, *J* = 6.8 Hz, 3H), 0.84 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 162.4, 144.9, 136.4, 133.7, 132.3, 129.8, 128.7, 128.6, 127.8, 126.4, 122.1, 83.7, 80.0, 63.2, 62.1, 57.1, 48.8, 21.7, 13.8, 13.6.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{23}H_{24}NO_6S$ $[M+H]^+$ 442.1319, found 442.1326.

Dimethyl 3-(2-ethynylphenyl)-1-tosylaziridine-2,2-dicarboxylate (**1b**)



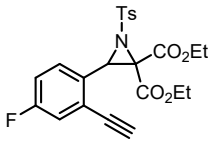
Brown solid (47% yield, 2.3 g, 5.6 mmol); m.p. 80-81 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.54 – 7.51 (m, 3H), 7.37 – 7.33 (m, 2H), 6.95 – 6.92 (m, 1H), 5.02 (s, 1H), 4.63 (s, 1H), 3.84 (s, 3H), 3.42 (s, 3H), 2.44 (s, 3H).

^{13}C NMR (100 MHz, DMSO-*d6*) δ 163.0, 162.8, 146.0, 135.6, 133.0, 132.8, 130.7, 129.7, 129.5, 127.9, 126.1, 122.2, 87.6, 80.1, 57.2, 54.5, 53.7, 48.5, 21.7.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{21}H_{19}NO_6SK$ $[M+K]^+$ 452.0565, found 452.0570.

Diethyl 3-(2-ethynyl-4-fluorophenyl)-1-tosylaziridine-2,2-dicarboxylate (**1c**)



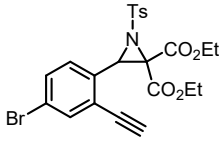
Yellow solid (60% yield, 3.3 g, 7.2 mmol); m.p. 86-87 ℃.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.44 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.23 (td, *J* = 8.4, 2.4 Hz, 1H), 6.95 (dd, *J* = 8.8, 5.6 Hz, 1H), 4.98 (s, 1H), 4.78 (s, 1H), 4.34 – 4.26 (m, 2H), 3.95 – 3.89 (m, 2H), 2.45 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H), 0.79 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, DMSO-*d6*) δ 162.4, 162.3 (d, $J_{C\text{-}F}$ = 245.1 Hz), 162.2, 145.9, 135.7, 130.7, 129.6 (d, $J_{C\text{-}F}$ = 2.9 Hz), 128.7 (d, $J_{C\text{-}F}$ = 9.3 Hz), 127.9, 124.2 (d, $J_{C\text{-}F}$ = 10.2 Hz), 119.5 (d, $J_{C\text{-}F}$ = 23.7 Hz), 116.8 (d, $J_{C\text{-}F}$ = 21.9 Hz), 88.8, 79.1, 63.5, 62.6, 57.2, 47.9, 21.6, 14.0, 13.9.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{23}H_{23}FNO_6S$ $[M+H]^+$ 460.1225, found 460.1230.

Diethyl 3-(4-bromo-2-ethynylphenyl)-1-tosylaziridine-2,2-dicarboxylate (**1d**)



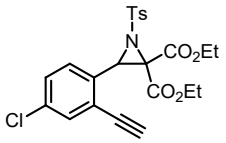
Brown solid (50% yield, 3.1 g, 6.0 mmol); m.p. 95-96 ℃.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 1.6 Hz, 1H), 7.57 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 4.96 (s, 1H), 4.78 (s, 1H), 4.33 – 4.26 (m, 2H), 3.93 (q, *J* = 6.8 Hz, 2H), 2.44 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H), 0.80 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, DMSO-*d6*) δ 162.3, 162.2, 146.0, 135.6, 134.9, 132.7, 132.5, 130.7, 128.3, 127.9, 124.3, 122.6, 89.1, 78.7, 63.6, 62.7, 57.1, 48.0, 21.7, 14.0, 13.9.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{23}H_{22}BrNO_6SNa$ $[M+Na]^+$ 542.0243, found 542.0255.

Diethyl 3-(4-chloro-2-ethynylphenyl)-1-tosylaziridine-2,2-dicarboxylate (**1e**)



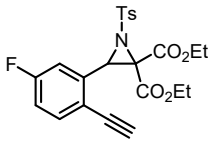
Yellow solid (88% yield, 5.0 g, 10.6 mmol); m.p. 71-72 ℃.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 2.0 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.44 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 4.97 (s, 1H), 4.79 (s, 1H), 4.33 – 4.27 (m, 2H), 3.92 (q, *J* = 6.8 Hz, 2H), 2.45 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H), 0.79 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, DMSO-*d6*) δ 162.3, 162.2, 146.0, 135.6, 134.2, 132.3, 132.1, 130.7, 129.6, 128.2, 127.9, 124.0, 89.0, 78.8, 63.6, 62.7, 57.2, 47.9, 21.7, 14.0, 13.9.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{23}H_{23}ClNO_6S$ $[M+H]^+$ 476.0929, found 476.0936.

Diethyl 3-(2-ethynyl-5-fluorophenyl)-1-tosylaziridine-2,2-dicarboxylate (**1f**)



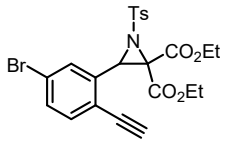
Yellow solid (64% yield, 3.5 g, 7.7 mmol); m.p. 118-119 ℃.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.60 (dd, *J* = 8.8, 5.6 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.25 (td, *J* = 8.8, 2.8 Hz, 1H), 6.62 (dd, *J* = 9.2, 2.8 Hz, 1H), 4.99 (s, 1H), 4.64 (s, 1H), 4.35 – 4.27 (m, 2H), 3.94 (q, *J* = 6.8 Hz, 2H), 2.45 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H), 0.79 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, DMSO-*d6*) δ 162.2, 162.1, 161.9 (d, *J* = 247.2 Hz), 146.1, 136.2 (d, *J* = 8.2 Hz), 135.4, 135.3, 130.7, 128.0, 118.8 (d, *J* = 3.0 Hz), 117.0 (d, *J* = 21.9 Hz), 113.7 (d, *J* = 24.6 Hz), 87.4, 79.1, 63.6, 62.7, 57.2, 47.8, 21.6, 14.0, 13.9.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{23}H_{23}FNO_6S$ $[M+H]^+$ 460.1225, found 460.1230.

Diethyl 3-(5-bromo-2-ethynylphenyl)-1-tosylaziridine-2,2-dicarboxylate (**1g**)



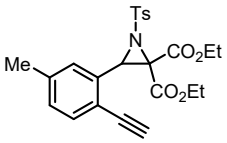
Yellow solid (62% yield, 3.9 g, 7.4 mmol); m.p. 120-121 ℃.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.59 – 7.54 (m, 3H), 7.46 (d, *J* = 8.0 Hz, 1H), 6.92 (d, *J* = 2.0 Hz, 1H), 4.95 (s, 1H), 4.75 (s, 1H), 4.34 – 4.28 (m, 2H), 3.95 (q, *J* = 7.1 Hz, 2H), 2.46 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H), 0.80 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, DMSO-*d6*) δ 162.2, 162.1, 146.2, 135.5, 135.3, 134.6, 132.6, 130.7, 129.3, 128.1, 122.5, 121.4, 88.9, 79.2, 63.6, 62.8, 57.0, 47.6, 21.7, 14.0, 13.9.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{23}H_{22}BrNO_6SNa$ $[M+Na]^+$ 542.0243, found 542.0256.

Diethyl 3-(2-ethynyl-5-methylphenyl)-1-tosylaziridine-2,2-dicarboxylate (1h)



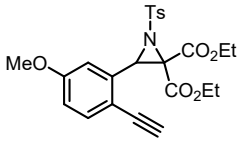
Light yellow solid (80% yield, 4.4 g, 9.6 mmol); m.p. 121-122 ℃.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 6.69 (s, 1H), 4.94 (s, 1H), 4.52 (s, 1H), 4.32 – 4.25 (m, 2H), 3.91 (q, *J* = 6.8 Hz, 2H), 2.45 (s, 3H), 2.17 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H), 0.77 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, DMSO-*d6*) δ 162.5, 162.3, 145.9, 139.1, 135.6, 133.0, 132.7, 130.6, 130.2, 128.0, 126.8, 119.4, 86.7, 80.3, 63.4, 62.5, 57.3, 48.3, 21.6, 21.5, 14.0, 13.9.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{24}H_{26}NO_6S$ $[M+H]^+$ 456.1475, found 456.1482.

Diethyl 3-(2-ethynyl-5-methoxyphenyl)-1-tosylaziridine-2,2-dicarboxylate (1i)



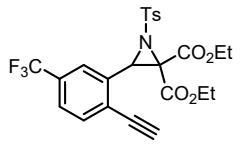
Light yellow solid (79% yield, 4.5 g, 9.5 mmol); m.p. 90-92 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 1H), 6.91 (dd, *J* = 8.4, 2.8 Hz, 1H), 6.35 (d, *J* = 2.4 Hz, 1H), 4.95 (s, 1H), 4.44 (s, 1H), 4.33 – 4.26 (m, 2H), 3.93 (q, *J* = 6.8 Hz, 2H), 3.60 (s, 3H), 2.44 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H), 0.79 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, DMSO-*d6*) δ 162.4, 162.3, 159.7, 145.9, 135.9, 134.9, 134.5, 130.7, 127.9, 115.0, 114.2, 112.2, 85.7, 80.2, 63.5, 62.5, 57.2, 55.7, 48.6, 21.6, 14.0, 13.9.

HRMS(TOF-ESI$^+$)m/z: calcd for $C_{24}H_{26}NO_7S$ $[M+H]^+$ 472.1424, found 472.1433.

Diethyl 3-(2-ethynyl-5-(trifluoromethyl)phenyl)-1-tosylaziridine-2,2-dicarboxylate (1j)



Light yellow solid (93% yield, 5.7 g, 11.2 mmol); m.p. 115-116 °C.

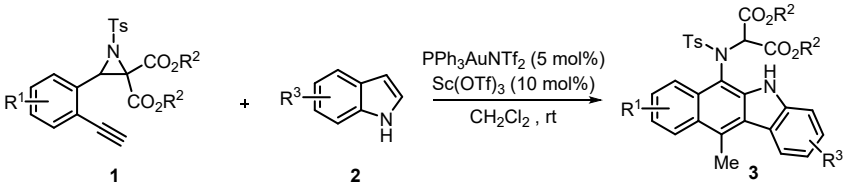
^{1}H NMR (400 MHz, DMSO-*d6*) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.75 – 7.71 (m, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 6.94 (s, 1H), 4.99 (s, 1H), 4.91 (s, 1H), 4.38 – 4.26 (m, 2H), 3.94 – 3.88 (m, 2H), 2.44 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H), 0.73 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, DMSO-*d6*) δ 162.2, 162.1, 146.3, 135.2, 134.8, 133.8, 130.7, 129.3, 129.0, 128.1, 126.4, 125.1, 123.3, 122.4, 90.6, 78.9, 63.6, 62.7, 56.8, 48.0, 21.6, 14.0, 13.7.

^{19}F NMR (376 MHz, DMSO-*d6*) δ -62.03 (s).

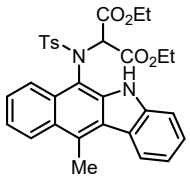
HRMS (TOF-ESI$^+$) m/z: calcd for $C_{24}H_{23}F_3NO_6S$ $[M+H]^+$ 510.1193, found 510.1201.

2.2 General experimental procedure for the synthesis of 5*H*-benzo[*b*]carbazoles 3



To a solution of 3-(2-ethynylaryl)-*N*-tosylaziridine-2,2-diester **1** (0.1 mmol) in dichloromethane (1.0 mL), indole **2** (0.12 mmol, 1.2 equiv), $Ph_3PAuNTf_2$ (3.7 mg, 0.005 mmol, 5 mol%) and $Sc(OTf)_3$ (4.9 mg, 0.01 mmol, 10 mol%) were added, respectively. The reaction was stirred at room temperature for 12 h. After the reaction was completed, 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 column chromatography (Petroleum Ether:EtOAc = 90:10 to 85:15) to afford 5*H*-benzo[*b*]carbazole **3**.

Diethyl 2-((4-methyl-*N*-(11-methyl-5*H*-benzo[*b*]carbazol-6-yl)phenyl)sulfonamido)malonate (3aa)



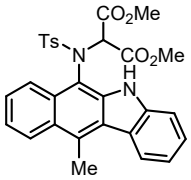
Yellow solid (88% yield, 49.1 mg, 0.088 mmol); m.p. 139-140 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.38 (s, 1H), 8.36 (d, *J* = 7.6 Hz, 1H), 8.25 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.53 – 7.48 (m, 2H), 7.36 – 7.31 (m, 3H), 7.27 – 7.24 (m, 1H), 7.18 – 7.12 (m, 3H), 5.86 (s, 1H), 4.08 – 3.94 (m, 4H), 3.18 (s, 3H), 2.24 (s, 3H), 0.94 (t, *J* = 7.0 Hz, 3H), 0.88 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 166.3, 143.9, 142.0, 140.0, 135.9, 132.0, 131.2, 128.8, 128.5, 127.6, 126.9, 125.2, 124.6, 124.1, 123.6, 123.5, 122.9, 122.4, 119.2, 110.9, 110.4, 68.5, 62.9, 62.8, 21.4, 15.8, 14.0, 13.3.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{31}H_{30}N_2O_6SNa$ $[M+Na]^+$ 581.1717, found 581.1727.

Dimethyl 2-((4-methyl-*N*-(11-methyl-5*H*-benzo[*b*]carbazol-6-yl)phenyl)sulfonamido)malonate (**3ab**)



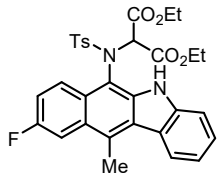
Yellow solid (60% yield, 31.8 mg, 0.060 mmol); m.p. 135-136 ℃.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.26 (s, 1H), 8.42 (d, *J* = 8.0 Hz, 1H), 8.33 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.60-7.55 (m, 2H), 7.41 (d, *J* = 8.0 Hz, 3H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.23 – 7.18 (m, 3H), 5.92 (s, 1H), 3.69 (s, 3H), 3.65 (s, 3H), 3.24 (s, 3H), 2.30 (s, 3H).

^{13}C NMR (100 MHz, DMSO-*d6*) δ 167.60, 167.56, 144.41, 142.04, 139.83, 136.15, 132.07, 131.21, 129.54, 128.49, 127.63, 127.36, 125.41, 124.75, 124.37, 124.06, 123.15, 122.77, 119.85, 111.31, 110.98, 67.79, 53.82, 53.59, 21.38, 15.98.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{29}H_{27}N_2O_6S$ $[M+H]^+$ 531.1584, found 531.1593.

Diethyl 2-((*N*-(9-fluoro-11-methyl-5*H*-benzo[*b*]carbazol-6-yl)-4-methylphenyl)sulfonamido)-malonate (**3ac**):



Yellow solid (63% yield, 36.3 mg, 0.063 mmol); m.p. 153-154 ℃.

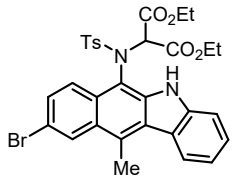
^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.47 (s, 1H), 8.36 (d, *J* = 8.0 Hz, 1H), 7.99 – 7.95 (m, 2H), 7.52 (d, *J* = 3.6 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.28 – 7.24 (m, 1H), 7.15 – 7.07 (m, 3H), 5.93 (s, 1H), 4.14 – 4.02 (m, 2H), 3.96 – 3.92 (m, 2H), 3.13 (s, 3H), 2.24 (s, 3H), 0.99 (t, *J* = 6.8 Hz, 3H), 0.81 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, DMSO-*d6*) δ 166.9, 166.4, 158.5 (d, *J* = 238.3 Hz), 144.5, 142.3, 139.7, 135.9, 131.4 (d, *J* = 5.9 Hz), 129.6, 128.8, 128.5, 127.9, 127.7 (d, *J* = 8.3 Hz), 126.2 (d, *J* = 8.7 Hz), 125.4, 124.2, 122.7, 119.8, 115.3 (d, *J* = 25.2 Hz), 111.2, 110.9, 107.9 (d, *J* = 21.6 Hz), 67.8, 62.9, 62.6, 21.4, 16.2, 13.9, 13.7.

^{19}F NMR (376 MHz, DMSO-*d6*) δ -118.7 (s).

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{31}H_{29}FN_2O_6SK$ $[M+K]^+$ 615.1362, found 615.1371.

Diethyl 2-((*N*-(9-bromo-11-methyl-5*H*-benzo[*b*]carbazol-6-yl)-4-methylphenyl)sulfonamido)-malonate (**3ad**)



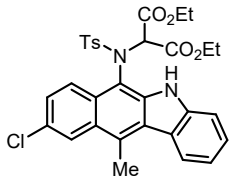
Yellow solid (58% yield, 36.9 mg, 0.058 mmol); m.p. 178-179 ℃.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.56 (s, 1H), 8.41 (d, *J* = 1.6 Hz, 1H), 8.36 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 9.2 Hz, 1H), 7.53 (d, *J* = 4.0 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.29 – 7.25 (m, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 5.94 (s, 1H), 4.15 – 4.02 (m, 2H), 3.98 – 3.89 (m, 2H), 3.15 (s, 3H), 2.24 (s, 3H), 0.99 (t, *J* = 7.2 Hz, 3H), 0.79 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, DMSO-*d6*) δ 166.9, 166.3, 144.6, 142.3, 140.3, 135.8, 131.5, 130.3, 129.6, 128.6, 128.4, 128.0, 127.9, 126.5, 125.7, 125.3, 124.3, 122.8, 120.0, 116.1, 111.1, 67.7, 62.9, 62.7, 21.4, 16.0, 13.9, 13.7.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{31}H_{29}BrN_2O_6SNa$ $[M+Na]^+$ 639.0822, found 659.0833.

Diethyl 2-((*N*-(9-chloro-11-methyl-5*H*-benzo[*b*]carbazol-6-yl)-4-methylphenyl)sulfonamido)-malonate (3ae)



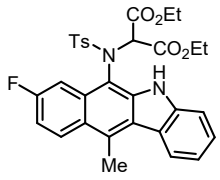
Yellow solid (68% yield, 42.9 mg, 0.068 mmol); m.p. 167-168 ℃.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.56 (s, 1H), 8.37 (d, *J* = 8.0 Hz, 1H), 8.27 (d, *J* = 2.0 Hz, 1H), 7.94 (d, *J* = 9.2 Hz, 1H), 7.53 (d, *J* = 4.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.29 – 7.25 (m, 1H), 7.17 – 7.13 (m, 3H), 5.94 (s, 1H), 4.15 – 4.02 (m, 2H), 3.97 – 3.89 (m, 2H), 3.15 (s, 3H), 2.24 (s, 3H), 0.99 (t, *J* = 6.8 Hz, 3H), 0.79 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, DMSO-*d6*) δ 166.9, 166.3, 144.6, 142.3, 140.2, 135.8, 131.5, 130.1, 129.6, 128.6, 128.0, 127.8, 127.6, 125.6, 125.5, 125.4, 124.3, 123.4, 122.8, 112.0, 111.1, 67.7, 62.9, 62.6, 21.4, 16.0, 13.9, 13.7.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{31}H_{29}ClN_2O_6SK$ $[M+K]^+$ 631.1066, found 631.1072.

Diethyl 2-((*N*-(8-fluoro-11-methyl-5*H*-benzo[*b*]carbazol-6-yl)-4-methylphenyl)sulfonamido)-malonate (3af)



Yellow solid (65% yield, 37.4 mg, 0.065 mmol); m.p. 148-149 ℃.

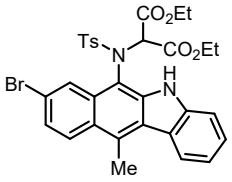
^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.58 (s, 1H), 8.36 – 8.30 (m, 2H), 7.57 – 7.50 (m, 3H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.29 – 7.24 (m, 1H), 7.22 – 7.13 (m, 3H), 5.94 (s, 1H), 4.20 – 4.04 (m, 2H), 3.98 – 3.86 (m, 2H), 3.17 (s, 3H), 2.24 (s, 3H), 1.04 (t, *J* = 7.2 Hz, 3H), 0.78 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, DMSO-*d6*) δ 167.1, 166.2, 160.0 (d, J_{C-F} = 7.2 Hz), 144.5, 142.0, 141.0, 136.0, 133.2 (d, J_{C-F} = 7.2 Hz), 132.7, 129.5, 128.5, 127.8 (d, J_{C-F} = 7.2 Hz), 127.6, 124.4, 124.0, 123.1, 112.0, 112.7 (d, J_{C-F} = 7.2 Hz), 111.0, 110.4 (d, J_{C-F} = 7.2 Hz), 106.5 (d, J_{C-F} = 7.2 Hz), 67.7, 62.9, 62.6, 40.6, 40.4, 40.2, 34.0, 39.8, 39.5, 39.3, 21.3, 16.2, 13.9, 13.6.

^{19}F NMR (376 MHz, DMSO-*d6*) δ -115.6 (s).

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{31}H_{29}FN_2O_6SK$ $[M+K]^+$ 615.1362, found 615.1371.

Diethyl 2-((*N*-(8-bromo-11-methyl-5*H*-benzo[*b*]carbazol-6-yl)-4-methylphenyl)sulfonamido)-malonate (**3ag**)



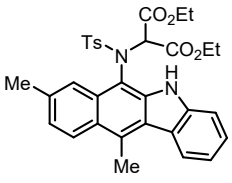
Yellow solid (58% yield, 36.9 mg, 0.058 mmol); m.p. 172-173 ℃.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.76 (s, 1H), 8.37 (d, *J* = 8.0 Hz, 1H), 8.17 (d, *J* = 9.1 Hz, 1H), 7.86 (d, *J* = 2.0 Hz, 1H), 7.61 – 7.52 (m, 2H), 7.38 – 7.34 (m, 3H), 7.30 – 7.26 (m, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 5.96 (s, 1H), 4.17 – 4.03 (m, 2H), 3.92 (q, *J* = 7.2 Hz, 2H), 3.16 (s, 3H), 2.29 (s, 3H), 1.05 (t, *J* = 6.8 Hz, 3H), 0.80 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, DMSO-*d6*) δ 166.9, 166.3, 144.7, 142.3, 140.8, 135.8, 132.6, 132.5, 129.7, 128.4, 127.9, 127.0, 125.6, 125.5, 125.0, 124.8, 124.2, 123.0, 120.1, 120.0, 111.2, 110.0, 67.6, 62.9, 62.7, 21.5, 16.0, 14.0, 13.7.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{31}H_{29}BrN_2O_6SNa$ $[M+Na]^+$ 659.0822, found 659.0834.

Diethyl 2-((*N*-(8,11-dimethyl-5*H*-benzo[*b*]carbazol-6-yl)-4-methylphenyl)sulfonamido)malonate (**3ah**)



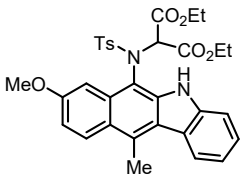
Yellow solid (70% yield, 40.0 mg, 0.070 mmol); m.p. 135-136 ℃.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.48 (s, 1H), 8.34 (d, *J* = 8.0 Hz, 1H), 8.12 (d, *J* = 8.8 Hz, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.34 (s, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.18 – 7.12 (m, 3H), 5.83 (s, 1H), 4.08 – 4.02 (m, 3H), 3.93 – 3.89 (m, 1H), 3.14 (s, 3H), 2.28 (s, 3H), 2.14 (s, 3H), 0.96-0.90 (m, 6H).

^{13}C NMR (100 MHz, DMSO-*d6*) δ 166.69, 166.56, 144.39, 142.01, 140.33, 136.42, 134.50, 131.85, 131.43, 129.51, 128.58, 127.34, 125.70, 124.87, 124.55, 123.86, 123.57, 123.35, 121.97, 119.73, 110.93, 110.43, 67.87, 62.72, 62.67, 21.56, 21.34, 15.96, 13.88, 13.78.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{32}H_{33}N_2O_6S$ $[M+H]^+$ 573.2054, found 573.2045.

Diethyl 2-((*N*-(8-methoxy-11-methyl-5*H*-benzo[*b*]carbazol-6-yl)-4-methylphenyl)sulfonamide) malonate (**3ai**).



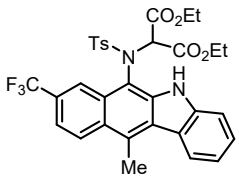
Yellow solid (75% yield, 45.3 mg, 0.075 mmol); m.p. 160-161 ℃.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.50 (s, 1H), 8.31 (d, *J* = 8.0 Hz, 1H), 8.14 (d, *J* = 9.2 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.26 – 7.22 (m, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 6.93 (dd, *J* = 9.2, 2.8 Hz, 1H), 5.79 (s, 1H), 4.24 – 4.12 (m, 2H), 3.97 – 3.88 (m, 2H), 3.51 (s, 3H), 3.13 (s, 3H), 2.25 (s, 3H), 1.09 (t, *J* = 7.2 Hz, 3H), 0.82 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, DMSO-*d6*) δ 167.5, 166.2, 157.5, 144.2, 141.8, 140.7, 136.8, 133.1, 132.1, 129.5, 128.7, 127.0, 126.5, 123.5, 123.4, 122.8, 122.3, 119.7, 115.8, 110.9, 110.6, 101.2, 68.2, 62.9, 62.5, 55.0, 21.3, 16.0, 14.0, 13.7.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{32}H_{32}N_2O_7SNa$ $[M+Na]^+$ 611.1822, found 611.1831.1

Diethyl 2-((4-methyl-*N*-(11-methyl-8-(trifluoromethyl)-5*H*-benzo[*b*]carbazol-6-yl)phenyl) sulfamido)malonate (3aj)



Yellow solid (30% yield, 18.8 mg, 0.030 mmol); m.p. 182-183 ℃.

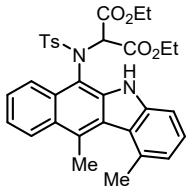
^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.99 (s, 1H), 8.43 (t, *J* = 9.2 Hz, 2H), 8.17 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.45 (dd, *J* = 9.2, 1.6 Hz, 1H), 7.33 – 7.30(m, 3H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.02 (s, 1H), 4.21 – 4.13(m, 2H), 3.83 – 3.77(m, 2H), 3.22 (s, 3H), 2.22 (s, 3H), 1.08 (t, *J* = 6.8 Hz, 3H), 0.66 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, DMSO-*d6*) δ 167.13, 165.73, 144.61, 142.60, 140.97, 135.67, 132.39, 130.37, 129.57, 128.44, 128.38, 127.90 126.42, 124.45, 122.76, 120.16, 117.47, 111.75, 111.33, 67.75, 62.84, 62.51, 21.26, 16.08, 13.95, 13.42.

^{19}F NMR (376 MHz, DMSO-*d6*) δ -60.9 (s).

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{32}H_{30}F_3N_2O_6S$ $[M+H]^+$ 627.1771, found 627.1770.

Diethyl 2-((*N*-(1,11-dimethyl-5*H*-benzo[*b*]carbazol-6-yl)-4-methylphenyl)sulfonamido)malonate (3ak)



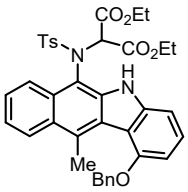
Yellow solid (66% yield, 37.8 mg, 0.066 mmol); m.p. 125-126 ℃.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.34 (s, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.40 – 7.34 (m, 3H), 7.32 – 7.26 (m, 2H), 7.18 – 7.12 (m, 3H), 7.02 (d, *J* = 7.2 Hz, 1H), 5.84 (s, 1H), 4.07 – 4.02 (m, 3H), 3.96 – 3.90 (m, 1H), 3.20 (s, 3H), 2.92 (s, 3H), 2.23 (s, 3H), 0.92 (td, *J* = 7.2, 3.2 Hz, 6H).

^{13}C NMR (100 MHz, DMSO-*d6*) δ 167.0, 166.6, 144.4, 143.1, 140.7, 136.2, 133.3, 131.3, 129.5, 128.5, 128.0, 127.9, 126.1, 125.3, 125.1, 123.3, 122.8, 122.6, 122.1, 110.6, 108.4, 68.0, 62.8, 62.7, 26.0, 21.4, 21.0, 13.9, 13.8.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{32}H_{32}N_2O_6SNa$ [M+Na]$^+$ 595.1873, found 595.1882.

Diethyl 2-((*N*-(1-(benzyloxy)-11-methyl-5*H*-benzo[*b*]carbazol-6-yl)-4-methylphenyl)sulfonamide)malonate (3al)



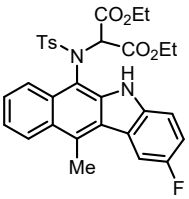
Yellow solid (62% yield, 41.2 mg, 0.062 mmol); m.p. 151-152 ℃.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.40 (s, 1H), 8.12 (d, *J* = 8.8 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.47 – 7.41 (m, 4H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.28 – 7.24 (m, 1H), 7.14 (t, *J* = 8.0 Hz, 4H), 7.05 (d, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 5.84 (s, 1H), 5.38 (s, 2H), 4.07 – 4.02 (m, 3H), 3.96 – 3.92 (m, 1H), 3.21 (s, 3H), 2.23 (s, 3H), 0.92 (td, *J* = 6.8, 4.0 Hz, 6H).

^{13}C NMR (100 MHz, DMSO-*d6*) δ 167.0, 166.7, 154.4, 144.4, 144.0, 140.2, 137.1, 136.2, 132.3, 131.0, 129.5, 129.4, 129.0, 128.9, 128.6, 128.5, 128.0, 125.2, 125.1, 125.0, 122.9, 122.6, 111.8, 110.7, 104.1, 103.5, 70.7, 68.0, 62.8, 62.7, 21.4, 19.2, 13.9, 13.8.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{38}H_{36}N_2O_7SNa$ [M+Na]$^+$ 687.2135, found 687.2148.

Diethyl 2-((*N*-(2-fluoro-11-methyl-5*H*-benzo[*b*]carbazol-6-yl)-4-methylphenyl)sulfonamido)malonate (3am)



Yellow solid (61% yield, 35.1 mg, 0.061 mmol); m.p. 148-149 ℃.

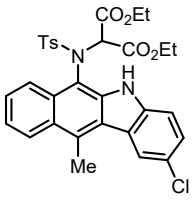
^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.46 (s, 1H), 8.26 (d, *J* = 8.8 Hz, 1H), 8.14 (dd, *J* = 10.0, 2.4 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.55 (dd, *J* = 8.8, 4.8 Hz 1H), 7.40 – 7.35 (m, 2H), 7.34 – 7.31 (m, 2H), 7.18 – 7.12 (m, 3H), 5.87 (s, 1H), 4.10 – 3.94 (m, 4H), 3.15 (s, 3H), 2.24 (s, 3H), 0.95 (t, *J* = 6.8 Hz, 3H), 0.85 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 166.2, 157.1 (d, $J_{C\text{-}F}$ = 232.9 Hz), 143.9, 140.8, 138.2, 135.8, 132.5, 131.5, 128.8, 128.4, 127.4, 125.5, 124.2, 123.9 (d, $J_{C\text{-}F}$ = 9.4 Hz), 122.9, 122.5, 114.2 (d, $J_{C\text{-}F}$ = 24.8 Hz), 111.1, 110.6 (d, $J_{C\text{-}F}$ = 8.8 Hz), 109.7 (d, $J_{C\text{-}F}$ = 25.0 Hz), 68.4, 63.0, 62.8, 21.4, 15.7, 14.0, 13.3.

^{19}F NMR (376 MHz, DMSO-*d6*) δ -124.15 (s).

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{31}H_{29}FN_2O_6SNa$ $[M+Na]^+$ 599.1623, found 599.1633.

Diethyl 2-((*N*-(2-chloro-11-methyl-5*H*-benzo[*b*]carbazol-6-yl)-4-methylphenyl)sulfonamido) malonate (**3an**)



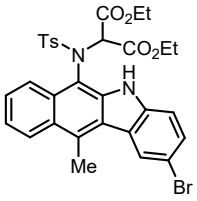
Yellow solid (60% yield, 35.5 mg, 0.060 mmol); m.p. 171-172 ℃.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.61 (s, 1H), 8.33 – 8.26 (m, 2H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.59 – 7.52 (m, 2H), 7.35 – 7.32 (m, 3H), 7.19 – 7.12 (m, 3H), 5.89 (s, 1H), 4.10 – 3.91 (m, 4H), 3.16 (s, 3H), 2.24 (s, 3H), 0.96 (t, *J* = 7.2 Hz, 3H), 0.81 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 166.1, 144.0, 140.3, 140.2, 135.8, 132.6, 131.5, 128.9, 128.4, 127.6, 126.8, 125.6, 124.7, 124.4, 124.2, 123.7, 123.3, 123.0, 122.7, 111.1, 111.2, 68.4, 63.0, 62.8, 21.4, 15.8, 14.0, 13.3.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{31}H_{30}ClN_2O_6S$ $[M+H]^+$ 593.1508, found 593.1500.

Diethyl 2-((*N*-(2-bromo-11-methyl-5*H*-benzo[*b*]carbazol-6-yl)-4-methylphenyl)sulfonamido) malonate (**3ao**)



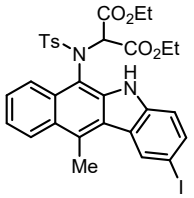
Light yellow solid (55% yield, 35.0 mg, 0.055 mmol); m.p. 152-153 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (s, 1H), 8.30 – 8.21 (m, 3H), 7.59 – 7.57 (m, 1H), 7.45 – 7.42 (m, 1H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.26 (s, 1H), 7.10 (t, *J* = 8.4 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 2H), 5.46 (s, 1H), 4.47 – 4.37 (m, 2H), 4.00 – 3.92 (m, 1H), 3.82 – 3.73 (m, 1H), 3.20 (s, 3H), 2.22 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H), 0.84 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 165.9, 144.0, 140.6, 139.2, 135.7, 132.7, 131.9, 129.1, 129.0, 128.4, 128.0, 125.8, 124.8, 124.5, 124.1, 123.7, 123.0, 122.4, 120.2, 111.5, 103.7, 68.1, 62.9, 62.8, 21.4, 15.8, 14.0, 13.3.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{31}H_{29}BrN_2O_6SNa$ $[M+Na]^+$ 659.0822, found 659.0833.

Diethyl 2-((*N*-(2-iodo-11-methyl-5*H*-benzo[*b*]carbazol-6-yl)-4-methylphenyl)sulfonamido) malonate (**3ap**)



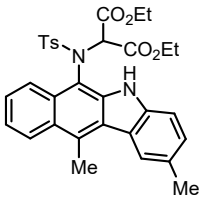
Light yellow solid (68% yield, 46.5 mg, 0.068 mmol); m.p. 180-181 ℃.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.59 (s, 1H), 8.60 (s, 1H), 8.26 (d, *J* = 8.8 Hz, 1H), 7.88 (d, *J* = 8.8 Hz, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 3H), 7.18 (d, *J* = 8.4 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 5.89 (s, 1H), 4.12 – 4.00 (m, 2H), 3.95 – 3.91 (m, 2H), 3.15 (s, 3H), 2.24 (s, 3H), 0.96 (t, *J* = 7.2 Hz, 3H), 0.81 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, DMSO-*d6*) δ 166.7, 166.4, 144.4, 141.4, 139.9, 136.1, 135.6, 132.8, 131.9, 129.5, 128.6, 127.4, 125.8, 125.6, 124.7, 123.4, 123.0, 113.4, 111.2, 82.4, 67.8, 62.8, 62.6, 21.4, 16.0, 13.9, 13.7.

HRMS(TOF-ESI$^+$)m/z: calcd for $C_{31}H_{29}IN_2O_6SK$ $[M+K]^+$ 723.0423, found 723.0430.

Diethyl 2-((*N*-(2,11-dimethyl-5*H*-benzo[*b*]carbazol-6-yl)-4-methylphenyl)sulfonamido) malonate (**3aq**)



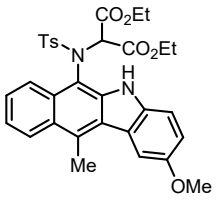
Yellow solid (75% yield, 45.8 mg, 0.075 mmol); m.p. 157-158 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (s, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 8.10 (s, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.32 – 7.24 (m, 4H), 6.96 (d, *J* = 8.0 Hz, 2H), 5.30 (s, 1H), 4.45 – 4.36 (m, 2H), 4.03 – 3.95 (m, 1H), 3.85 – 3.77 (m, 1H), 3.20 (s, 3H), 2.55 (s, 3H), 2.22 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H), 0.87 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.85, 166.33, 143.83, 140.25, 140.13, 135.97, 131.91, 131.12, 128.81, 128.47 ,128.38, 128.01, 127.45, 125.19, 124.59, 124.08, 123.80, 123.70, 122.83, 122.24, 110.87, 110.08, 68.58, 62.84, 62.76, 21.68, 21.42, 15.88, 14.04, 13.37.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{32}H_{32}N_2O_6SK$ $[M+K]^+$ 611.1613, found 611.1618.

Diethyl 2-((*N*-(2-methoxy-11-methyl-5*H*-benzo[*b*]carbazol-6-yl)-4-methylphenyl)sulfonamido) malonate (**3ar**)



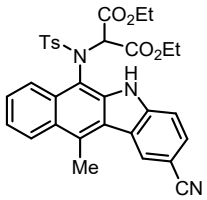
Brown solid (80% yield, 47.0 mg, 0.080 mmol); m.p. 162-163 ℃.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.17 (s, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 7.86 – 7.84 (m, 2H), 7.44 (d, *J* = 8.8 Hz, 1H), 7.36 – 7.28 (m, 3H), 7.18 – 7.12 (m, 4H), 5.82 (s, 1H), 4.06 – 3.94 (m, 4H), 3.90 (s, 3H), 3.17 (s, 3H), 2.24 (s, 3H), 0.94-0.89 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.87, 166.30, 153.48, 143.83, 140.67, 136.84, 135.93, 132.07, 131.24, 128.80, 128.45, 127.23, 125.29, 124.64, 124.09, 122.80, 122.21, 114.46, 110.88, 110.67, 108.59, 68.54, 62.84, 62.76, 56.42, 21.42, 15.75, 14.02, 13.35.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{32}H_{32}N_2O_7SNa$ $[M+Na]^+$ 611.1822, found 611.1835.

Diethyl 2-((*N*-(2-cyano-11-methyl-5*H*-benzo[*b*]carbazol-6-yl)-4-methylphenyl)sulfonamido) malonate (3as)



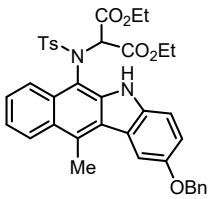
Light yellow solid (36% yield, 21.0 mg, 0.036 mmol); m.p. 197-198 ℃.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 11.11 (s, 1H), 8.79 (s, 1H), 8.31 (d, *J* = 8.4 Hz, 1H), 7.92 – 7.88 (m, 2H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.40 – 7.33 (m, 3H), 7.21 – 7.12 (m, 3H), 5.95 (s, 1H), 4.14 – 4.02 (m, 2H), 3.89 – 3.82 (m, 2H), 3.20 (s, 3H), 2.24 (s, 3H), 1.00 (t, *J* = 7.2 Hz, 3H), 0.71 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, DMSO-*d6*) δ 166.8, 166.0, 144.5, 140.3, 135.9, 133.5, 132.2, 131.2, 129.6, 128.6, 127.8, 125.9, 124.9, 123.5, 123.4, 122.9, 120.9, 111.9, 111.8, 101.5, 67.6, 62.8, 62.6, 21.4, 16.1, 13.9, 13.6.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{32}H_{30}N_3O_6S$ $[M+H]^+$ 584.1850, found 584.1851.

Diethyl 2-((*N*-(2-(benzyloxy)-11-methyl-5*H*-benzo[*b*]carbazol-6-yl)-4-methylphenyl)sulfon amido)malonate (3at)



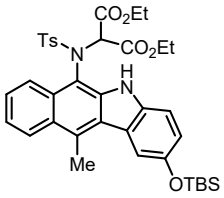
Brown solid (60% yield, 39.8 mg, 0.060 mmol); m.p. 157-158 ℃.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.19 (s, 1H), 8.24 (d, *J* = 8.8 Hz, 1H), 7.93 (d, *J* = 2.0 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.54 (d, *J* = 6.8 Hz, 2H), 7.45 – 7.40 (m, 3H), 7.35 (d, *J* = 8.0 Hz, 3H), 7.29 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.24 (dd, *J* = 8.8, 2.4 Hz, 1H),, 7.14 (t, *J* = 9.6 Hz, 3H), 5.82 (s, 1H), 5.25 (s, 2H), 4.06 – 4.02 (m, 2H), 4.01 – 3.95 (m, 2H), 3.14 (s, 3H), 2.24 (s, 3H), 0.94-0.89 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.87, 166.30, 152.57, 143.83, 140.68, 137.53, 137.04, 135.93, 132.09, 131.24, 128.81, 128.63, 128.45, 127.97, 127.70, 127.25, 125.29, 124.63, 124.09, 124.06, 122.78, 122.22, 115.53, 110.88, 110.62, 110.25, 71.63, 68.53, 62.84, 62.76, 21.42, 15.72, 14.02, 13.36.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{38}H_{36}N_2O_7SNa$ $[M+Na]^+$ 687.2135, found 687.2135.

Diethyl 2-((*N*-(2-((tert-butyldimethylsilyl)oxy)-11-methyl-5*H*-benzo[*b*]carbazol-6-yl)-4-methylphenyl)sulfonamido)malonate (3au)



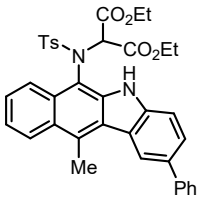
Yellow solid (72% yield, 49.5 mg, 0.072 mmol); m.p. 137-138 ℃.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.24 (s, 1H), 8.23 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.75 (d, *J* = 2.0 Hz, 1H), 7.42 (d, *J* = 8.8 Hz, 1H), 7.36 – 7.29 (m, 3H), 7.14 (t, *J* = 8.8 Hz, 3H), 7.06 (dd, *J* = 8.4, 2.0 Hz, 1H), 5.83 (s, 1H), 4.08 – 3.95 (m, 4H), 3.12 (s, 3H), 2.24 (s, 3H), 1.02 (s, 9H), 0.95 (t, *J* = 7.2 Hz, 3H), 0.91 (t, *J* = 7.2 Hz, 3H), 0.26 (s, 6H).

^{13}C NMR (100 MHz, DMSO-*d6*) δ 166.8, 166.7, 148.6, 144.3, 140.7, 137.2, 136.2, 132.1, 131.6, 129.5, 128.5, 127.0, 125.2, 124.6, 124.2, 123.7, 123.1, 122.6, 120.3, 114.5, 111.3, 110.9, 67.9, 62.8, 62.6, 26.2, 21.4, 18.6, 15.8, 13.8, -3.9.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{37}H_{44}N_2O_7SSiK$ $[M+K]^+$ 727.2270, found 727.2274.

Diethyl 2-((4-methyl-*N*-(11-methyl-2-phenyl-5*H*-benzo[*b*]carbazol-6-yl)phenyl)sulfonamido) malonate (3av)



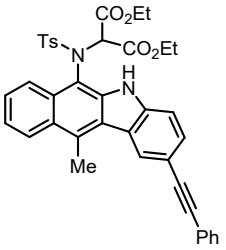
Light yellow solid (68% yield, 43.1 mg, 0.068 mmol); m.p. 176-177 ℃.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.50 (s, 1H), 8.55 (d, *J* = 0.8 Hz, 1H), 8.28 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.83 – 7.80 (m, 3H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.38 – 7.32 (m, 4H), 7.19 – 7.14 (m, 3H), 5.89 (s, 1H), 4.10 – 3.96 (m, 4H), 3.25 (s, 3H), 2.25 (s, 3H), 0.95 (t, *J* = 7.2 Hz, 3H), 0.88 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 166.2, 143.9, 142.3, 141.5, 140.4, 135.9, 132.8, 132.2, 131.3, 128.9, 128.5, 127.6, 127.4, 126.6, 126.5, 125.4, 124.6, 124.2, 122.9, 122.5, 122.4, 111.1, 110.6, 68.5, 62.9, 62.8, 21.4, 16.0, 14.0, 13.4.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{37}H_{34}N_2O_6SK$ $[M+K]^+$ 673.1769, found 673.1770.

Diethyl 2-((4-methyl-*N*-(11-methyl-2-(phenylethynyl)-5*H*-benzo[*b*]carbazol-6- yl)phenyl) sulfonamido)malonate (3aw)



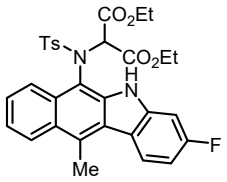
Yellow solid (60% yield, 39.5 mg, 0.060 mmol); m.p. 234-3-235 ℃.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.73 (s, 1H), 8.52 (s, 1H), 8.29 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.70 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.64 – 7.58 (m, 3H), 7.46 – 7.42 (m, 3H), 7.35 (d, *J* = 8.4 Hz, 3H), 7.15 (t, *J* = 7.2 Hz, 3H), 5.91 (s, 1H), 4.12 – 4.01 (m, 2H), 3.97 – 3.91 (m, 2H), 3.21 (s, 3H), 2.25 (s, 3H), 0.98 (t, *J* = 7.2 Hz, 3H), 0.81 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, CDCl3) δ 168.1, 166.1, 144.0, 141.7, 140.2, 135.8, 132.6, 131.5, 131.4, 130.6, 128.9, 128.5, 128.4, 127.9, 127.8, 127.1, 125.6, 124.2, 123.9, 123.8, 123.7, 123.0, 122.7, 113.7, 111.2, 110.4, 90.9, 87.6, 68.4, 63.0, 62.9, 21.4, 15.9, 14.0, 13.3.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{39}H_{34}N_2O_6SNa$ [M+Na]$^+$ 681.2030, found 681.2039.

Diethyl 2-((*N*-(3-fluoro-11-methyl-5*H*-benzo[*b*]carbazol-6-yl)-4-methylphenyl)sulfonamido) malonate (**3ax**)



Light yellow solid (65% yield, 37.4 mg, 0.065 mmol); m.p. 150-151 ℃.

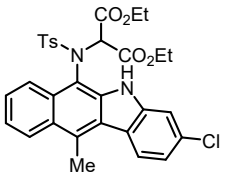
^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.58 (s, 1H), 8.34 (dd, *J* = 8.8, 5.6 Hz, 1H), 8.25 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.41 (dd, *J* = 9.6, 2.0 Hz, 1H), 7.37 – 7.31 (m, 3H), 7.15 (t, *J* = 9.6 Hz, 3H), 7.07 (td, J = 9.2, 2.4 Hz, 1H), 5.86 (s, 1H), 4.10 – 3.97 (m, 4H), 3.14 (s, 3H), 2.25 (s, 3H), 0.95 (t, *J* = 7.2 Hz, 3H), 0.85 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, DMSO-*d6*) δ 166.7, 166.5, 162.3 (d, J_{C-F} = 240.2 Hz), 144.4, 143.3 (d, J_{C-F} = 13.0 Hz), 140.6, 136.1, 131.6, 131.3, 129.5, 128.5, 127.5, 125.4 (d, J_{C-F} = 10.6 Hz), 125.2, 124.6, 123.7, 123.3, 123.0, 119.9, 111.2, 107.2 (d, J_{C-F} = 23.5 Hz), 97.9 (d, J_{C-F} = 26.4 Hz), 67.8, 62.8, 62.6, 21.4, 15.9, 13.9, 13.8.

^{19}F NMR (376 MHz, DMSO-*d6*) δ -113.53 (s).

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{31}H_{29}FN_2O_6SK$ [M+K]$^+$ 615.1362, found 615.1366.

Diethyl 2-((*N*-(3-chloro-11-methyl-5*H*-benzo[*b*]carbazol-6-yl)-4-methylphenyl)sulfonamido) malonate (**3ay**)



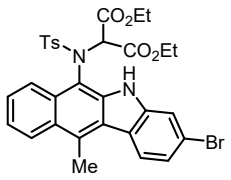
Yellow solid (62% yield, 36.7 mg, 0.062 mmol); m.p. 159-160 ℃.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.56 (s, 1H), 8.34 (d, *J* = 8.4 Hz, 1H), 8.26 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.8 Hz, 1H), 7.64 (d, *J* = 1.6 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 3H), 7.27 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.15 (dd, *J* = 14.4, 8.0 Hz, 3H), 5.86 (s, 1H), 4.09 – 3.93 (m, 4H), 3.15 (s, 3H), 2.25 (s, 3H), 0.96 (t, *J* = 7.2 Hz, 3H), 0.84 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 166.0, 144.0, 142.6, 140.2, 135.8, 132.7, 132.0, 131.4, 128.9, 128.4, 127.8, 125.5, 124.2, 124.1, 123.8, 123.1, 122.7, 122.2, 119.6, 111.1, 110.5, 68.3, 63.0, 62.8, 21.4, 15.8, 14.0, 13.3.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{31}H_{30}ClN_2O_6S$ $[M+H]^+$ 593.1508, found 593.1501.

Diethyl 2-((*N*-(3-bromo-11-methyl-5*H*-benzo[*b*]carbazol-6-yl)-4-methylphenyl)sulfonamido) malonate (**3az**)



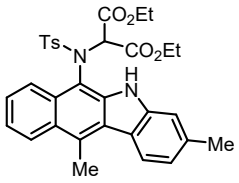
Yellow solid (68% yield, 43.2 mg, 0.068 mmol); m.p. 166-167 ℃.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.54 (s, 1H), 8.27 (t, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 8.8Hz, 1H), 7.77 (d, *J* = 1.6 Hz, 1H), 7.40 – 7.32 (m, 4H), 7.19 – 7.13 (m, 3H), 5.86 (s, 1H), 4.07 – 3.96 (m, 4H), 3.14 (s, 3H), 2.25 (s, 3H), 0.95 (t, *J* = 7.2 Hz, 3H), 0.84 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 166.0, 144.1, 142.8, 140.0, 135.8, 132.2, 131.5, 128.9, 128.4, 127.8, 125.5, 124.6, 124.1, 123.8, 123.1, 122.7, 122.6, 122.3, 120.6, 113.4, 111.1, 68.3, 63.0, 62.8, 21.4, 15.9, 14.0, 13.3.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{31}H_{29}BrN_2O_6SNa$ $[M+Na]^+$ 659.0822, found 659.0834.

Diethyl 2-((*N*-(3,11-dimethyl-5*H*-benzo[*b*]carbazol-6-yl)-4-methylphenyl)sulfonamido)malon ate (**3ba**)



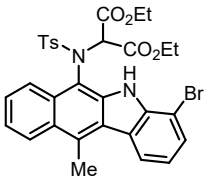
Yellow solid (60% yield, 34.3 mg, 0.060 mmol); m.p. 153-154 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.72 (s, 1H), 8.20 – 8.15 (m, 2H), 7.95 (d, *J* = 8.5 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.34 – 7.30 (m, 1H), 7.26 (d, *J* = 6.0 Hz, 1H), 7.17 (s, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 2H), 5.30 (s, 1H), 4.44 – 4.37 (m, 2H), 4.01 – 3.96 (m, 1H), 3.82 – 3.78 (m, 1H), 3.18 (s, 3H), 2.53 (s, 3H), 2.23 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H), 0.86 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, CD_3CN) δ 162.5, 161.0, 138.5, 137.1, 134.8, 132.0, 130.6, 126.0, 125.6, 123.5, 123.1, 122.3, 119.7, 119.4, 118.7, 117.9, 117.5, 117.0, 115.8, 115.3, 105.6, 105.5, 63.2, 57.5, 57.4, 16.6, 16.1, 10.5, 8.7, 8.0.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{32}H_{32}N_2O_6SNa$ $[M+Na]^+$ 595.1873, found 595.1882.

Diethyl 2-((*N*-(4-bromo-11-methyl-5*H*-benzo[*b*]carbazol-6-yl)-4-methylphenyl)sulfonamido) malonate (**3bb**)



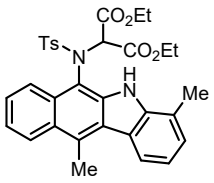
Light yellow solid (62% yield, 39.4 mg, 0.062 mmol); m.p. 154-155 ℃.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.01 (s, 1H), 8.35 (dd, *J* = 16.8, 8.0 Hz, 2H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.45 – 7.41 (m, 1H), 7.37 – 7.32 (m, 3H), 7.21 (t, *J* = 8.0 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 5.82 (s, 1H), 4.38 – 4.29 (m, 2H), 4.02 – 3.94 (m, 1H), 3.87 – 3.79 (m, 1H), 3.18 (s, 3H), 2.22 (s, 3H), 1.26 (t, *J* = 8.0 Hz, 3H), 0.81 (t, *J* = 8.0 Hz, 3H).

^{13}C NMR (100 MHz, DMSO-*d6*) δ 168.10, 166.66, 144.45, 140.16, 139.17, 135.93, 133.16, 131.82, 129.73, 128.34, 127.92, 125.94, 124.92, 124.78, 124.21, 123.55, 123.39, 121.37, 112.06, 103.26, 68.08, 63.03, 62.99, 21.40, 15.93, 14.30, 13.67.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{31}H_{29}BrN_2O_6SNa$ $[M+Na]^+$ 659.0822, found 659.0833.

Diethyl 2-((*N*-(4,11-dimethyl-5*H*-benzo[*b*]carbazol-6-yl)-4-methylphenyl)sulfonamido)malonate (3bc)



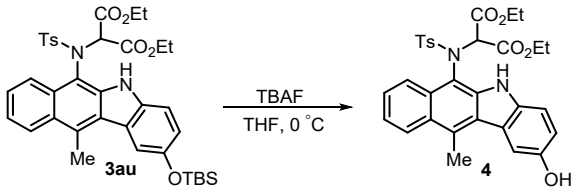
Brown solid (70% yield, 40.0 mg, 0.070 mmol); m.p. 127-128 ℃.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 9.91 (s, 1H), 8.29 (d, *J* = 8.4 Hz, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.41 – 7.30 (m, 5H), 7.18-7.12 (m, 3H), 5.85 (s, 1H), 4.32 – 4.26 (m, 2H), 3.98 – 3.94 (m, 1H), 3.82 – 3.77 (m, 1H), 3.17 (s, 3H), 2.41 (s, 3H), 2.21 (s, 3H), 1.21 (t, *J* = 6.8 Hz, 3H), 0.79 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, DMSO-*d6*) δ 168.2, 166.7, 144.4, 140.9, 139.6, 136.3, 132.1, 131.6, 129.5, 128.5, 128.0, 127.6, 125.4, 124.7, 124.6, 123.6, 122.9, 122.7, 121.7, 120.0, 119.3, 111.3, 68.1, 63.0, 26.0, 21.3, 16.5, 15.9, 14.2, 13.6.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{32}H_{32}N_2O_6SNa$ $[M+Na]^+$ 595.1873, found 595.1885.

2.3 Experimental procedure for the synthesis of 5*H*-benzo[*b*]carbazole 4



To a solution of 5*H*-benzo[*b*]carbazole **3au** (68.8 mg, 0.1 mmol, 1.0 equiv) in THF, tetrabutylammonium fluoride (40.0mg, 0.15mmol, 1.5 equiv) was added at 0 ℃ under argon atmosphere. The mixture was stirred at 0 ℃ for 2 hours. After the reaction was completed, the mixture was quenched with HCl (aq., 3 M), extracted with EtOAc (2.0 mL × 2) and washed with brine (2.0 mL × 2). The combined organic layers were dried, concentrated and purified by flash

silica gel column chromatography (Petroleum Ether:EtOAc = 95:5 to 75:25) to yield 5*H*-benzo[*b*]carbazole **4** in 86% yield (49.4 mg, 0.086 mmol).

Diethyl 2-((*N*-(2-hydroxy-11-methyl-5*H*-benzo[*b*]carbazol-6-yl)-4-methylphenyl)sulfonamido) malonate (4)

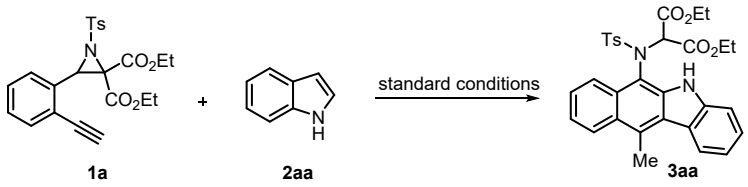
White solid (86% yield, 49.4 mg, 0.086 mmol); m.p. 261-262 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.61 (s, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.65 (d, *J* = 2.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.24 – 7.17 (m, 2H), 7.09 (d, *J* = 8.4 Hz, 1H), 6.91 – 6.88 (m, 3H), 5.24 (s, 1H), 4.37 – 4.30 (m, 2H), 3.95 – 3.91 (m, 1H), 3.78 – 3.72 (m, 1H), 3.01 (s, 3H), 2.16 (s, 3H), 1.98 (s, 1H), 1.29 (t, *J* = 7.2 Hz, 3H), 0.82 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.86, 165.30, 148.00, 142.85, 139.67, 135.63, 134.89, 131.14, 130.19, 127.80, 127.43, 126.17, 124.24, 123.11, 123.07, 121.71, 121.14, 114.25, 109.73, 109.62, 108.77, 67.50, 61.81 (d, *J* = 6.0 Hz), 28.68, 20.38, 14.58, 12.98, 12.23.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{31}H_{31}N_2O_7S$ $[M+H]^+$ 575.1846, found 575.1854.

2.4 Gram-scale synthesis of 5*H*-benzo[*b*]carbazole 3aa



To a solution of 3-(2-ethynylaryl)-*N*-tosylaziridine-2,2-diester **1** (1.0 g, 2.3 mmol) in dichloromethane (23.0 mL), indole **2** (0.32 g, 2.7 mmol, 1.2 equiv), $Ph_3PAuNTf_2$ (0.021 g, 0.011 mmol, 5 mol%) and $Sc(OTf)_3$ (0.11 g, 0.23 mmol, 10 mol%) were added, respectively. The reaction was stirred at room temperature for 12 h. After the reaction was completed, the mixture was diluted with brine (50 mL) and extracted with EtOAc (50 mL × 2). The combined organic layers were dried, concentrated and purified by flash silica gel column chromatography (Petroleum Ether:EtOAc = 90:10 to 85:15) to afford 5*H*-benzo[*b*]carbazole **3** in 72% yield (0.91 g, 1.6 mmol).

2.5 Photophysical properties

Absorption and fluorescence spectra were measured at 25 °C for solutions of **3am**, **3aq**, **3av**, **3ar, 3au, 4** in acetonitrile (MeCN) with a concentration of 10^{-4} M, using 10 × 45 mmcuvettes. The quantum yields of **3am**, **3aq**, **3av**, **3ar, 3au, 4** were determined according to references[1] by using a solution of 7-diethylamino-4-methyl coumarin in ethanol (Φ = 0.5) as a standard.

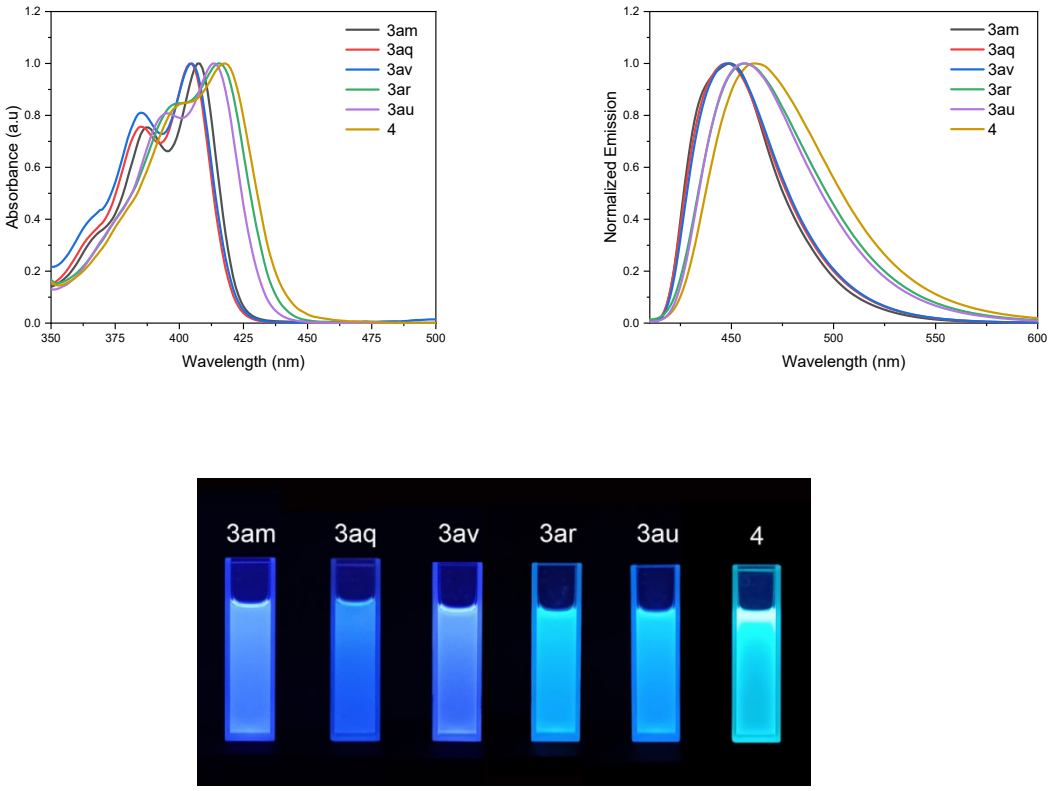


Figure S1. Normalized absorption and normalized fluorescence spectra of **3am**, **3aq**, **3av**, **3ar, 3au, 4** in MeCN

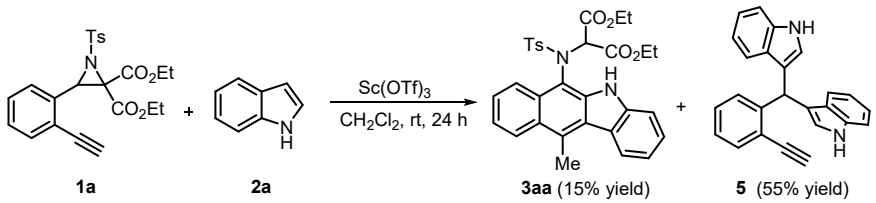
Table S1. Photopysical properties of selected compounds

Compound	λ_{abs} (nm)	λ_{em} (nm)	$\Phi_{F(x)}$ (%)	Stocks shift (nm)
3am	408	449	55	41
3aq	404	447	32	43
3av	405	448	45	43

3ar	415	466	36	51
3au	413	461	43	48
4	418	471	71	53

2.6 Control experiments

(1) Transformation of aziridine 1a with indole 2a enabled by scandium(III) catalysis



To a solution of 3-(2-ethynylaryl)-*N*-tosylaziridine-2,2-diester **1a** (44.1 mg, 0.1 mmol) in dichloromethane (1.0 mL), indole **2a** (14.0 mg, 0.12 mmol, 1.2 equiv) and $Sc(OTf)_3$ (4.9 mg, 0.01 mmol, 10 mol%) were added, respectively. The reaction was stirred at room temperature for 24 h. After the reaction was completed, 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 column chromatography (Petroleum Ether:EtOAc = 90:10 to 85:15) to afford 5*H*-benzo[*b*]carbazole **3aa** and bisindole **5** in 15% (8.4 mg, 0.015 mmol) and 55% (19.0 mg, 0.055 mmol) yield, respectively.

3,3'-((2-Ethynylphenyl)methylene)bis(1*H*-indole) (5)

Yellow solid (55% yield, 19.0 mg, 0.055 mmol); m.p. 220-221 ℃.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.89 (d, *J* = 1.2 Hz, 2H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.41 – 7.35 (m, 4H), 7.32 – 7.30 (m, 2H), 7.28 – 7.24 (m, 1H), 7.09 (t, *J* = 8.0 Hz, 2H), 6.93 (t, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 2.0 Hz, 2H), 6.40 (s, 1H), 4.43 (s, 1H)

^{13}C NMR (100 MHz, DMSO-*d6*) δ 147.4, 137.0, 132.8, 129.3, 129.1, 127.1, 126.5, 124.2, 121.4, 121.3, 119.2, 118.8, 117.9, 112.0, 85.1, 82.8, 37.5.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{25}H_{19}N_2$ $[M+H]^+$ 347.1543, found 347.1547.

(2) Two-step procedure of scandium(III) catalysis followed by gold(I) catalysis

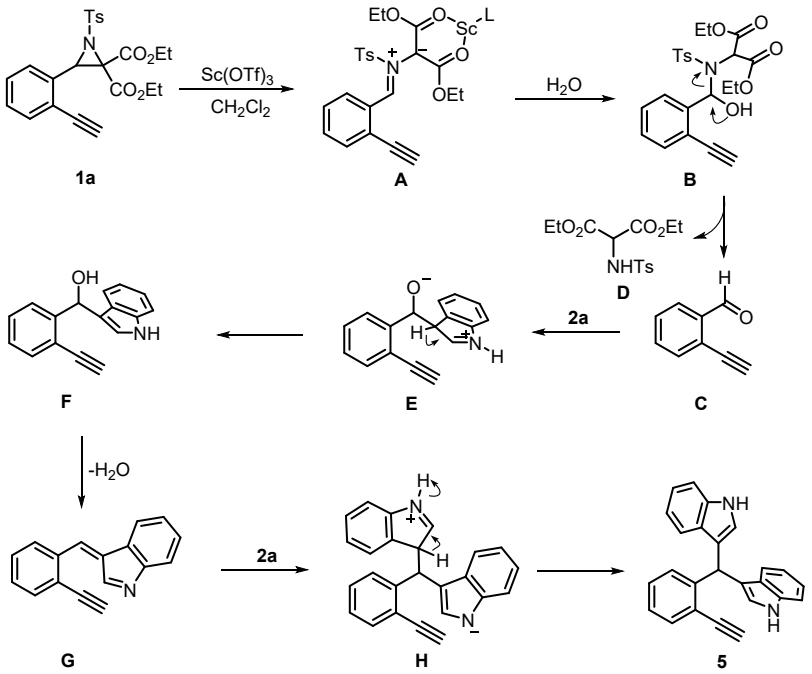
To a solution of 3-(2-ethynylaryl)-*N*-tosylaziridine-2,2-diester **1a** (44.1 mg, 0.1 mmol) in dichloromethane (1.0 mL), indole **2a** (14.0 mg, 0.12 mmol, 1.2 equiv) and $Sc(OTf)_3$ (4.9 mg, 0.01 mmol, 10 mol%) were added, respectively. The reaction was stirred at room temperature for 24 h. Then, $Ph_3PAuNTf_2$ (3.7 mg, 0.005 mmol, 5 mol%) was added to the mixture and stirred for another 12 h. 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 column chromatography (Petroleum Ether:EtOAc = 90:10 to 85:15) to afford 5*H*-benzo[*b*]carbazole **3aa** in 18% yield (10.0 mg, 0.018 mmol).

(3) Two-step procedure of gold(I) catalysis followed by scandium(III) catalysis

To a solution of 3-(2-ethynylaryl)-*N*-tosylaziridine-2,2-diester **1a** (44.1 mg, 0.1 mmol) in dichloromethane (1.0 mL), indole **2a** (14.0 mg, 0.12 mmol, 1.2 equiv) and $Ph_3PAuNTf_2$ (3.7 mg, 0.005 mmol, 5 mol%) were added, respectively. The reaction was stirred at room temperature for 12 h. Then, $Sc(OTf)_3$ (4.9 mg, 0.01 mmol, 10 mol%) was added to the mixture and stirred for another 24 h. 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 column chromatography (Petroleum Ether:EtOAc = 90:10 to 85:15) to afford 5*H*-benzo[*b*]carbazole **3** in 45% yield (25.1 mg, 0.045 mmol).

2.7 Proposed mechanism of the synthesis of bisindole 5

A proposed mechanism of the synthesis of bisindole **5** is depicted in Scheme S1. First, the coordination of scandium triflate with carbonyl groups of *N*-tosylaziridine **1a** afforded 1,3-dipole intermediate **A**. Subsequently, hydrolysis of intermediate **A** gives aldehyde **C** and sulfonamide **D**. The 2-ethynylbenzaldehyde **C** undergoes Friedel-Crafts reaction with indole **2a** to deliver alcohol **F**. Finally, the intermediate **F** undergoes dehydration, C3-nucleophilic attack of indole **2a** and hydrogen migration to generate bisindole **5**.



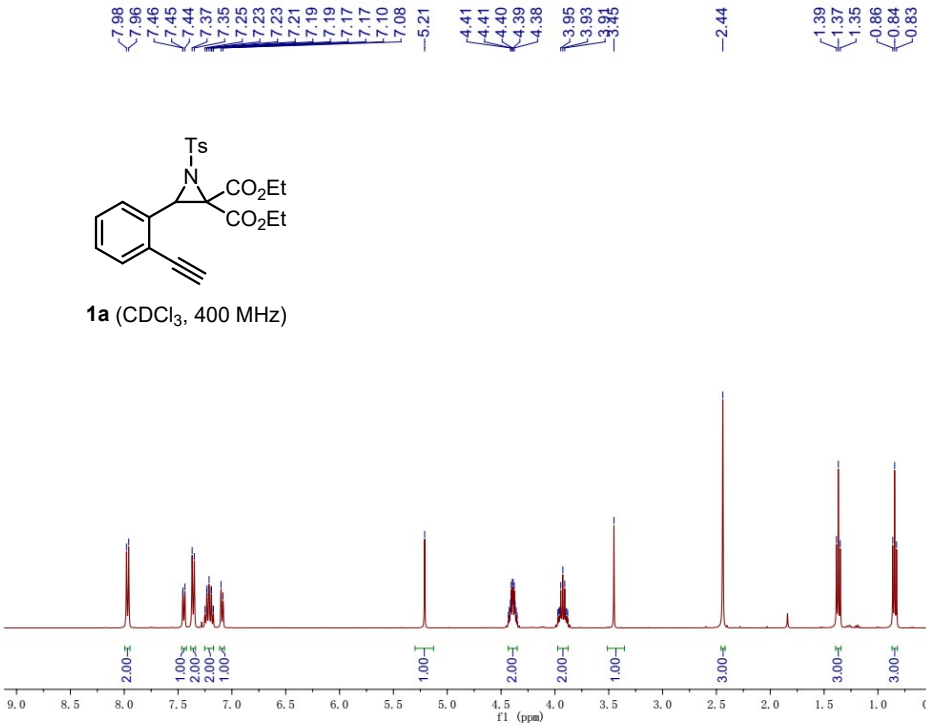
Scheme S1 Proposed mechanism of the synthesis of **5**

3. References

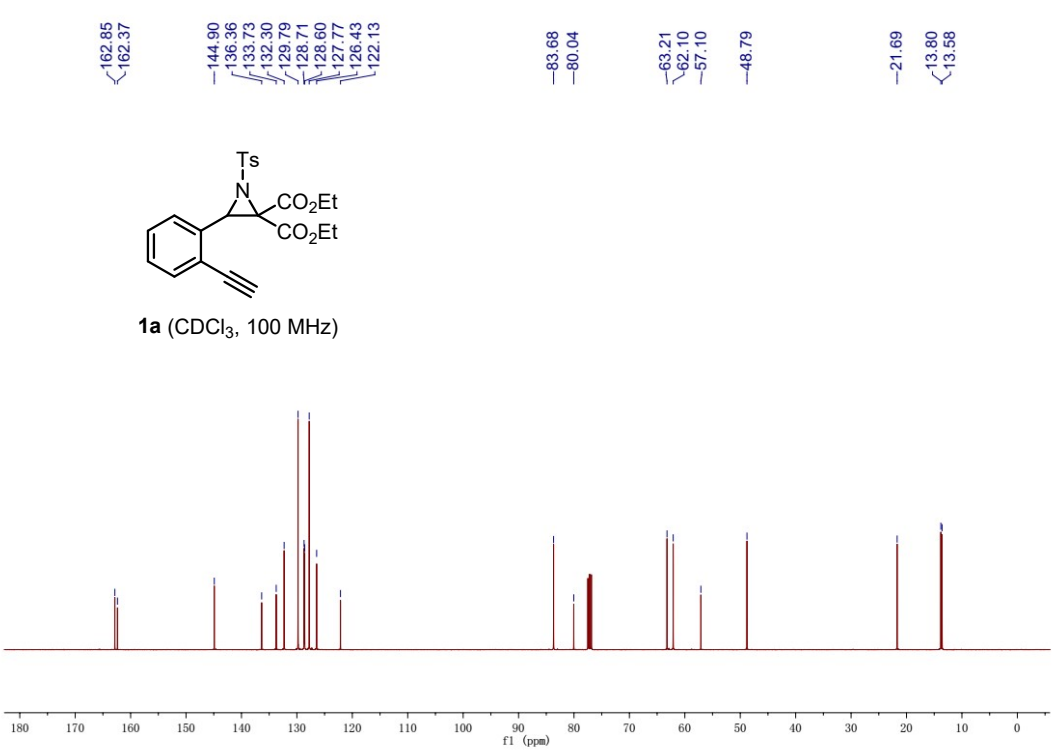
1 Stark, D. G.; O Riordan, T. J. C.; Smith, A. D., Synthesis of Di-, Tri-, and Tetrasubstituted Pyridines from (Phenylthio)carboxylic Acids and 2-[Aryl(tosylimino)methyl]acrylates. *Org. Lett.* **2014,** 16, (24), 6496-6499.

2 (a) Zhan, Y.; Liu, T.; Ren, J.; Wang, Z., Lewis Acid-Catalyzed Intramolecular [3+2] Cross-Cycloaddition of Aziridine 2,2-Diesters with Conjugated Dienes for Construction of Aza-[n.2.1] Skeletons. *Chem. Eur. J.* **2017,** 23, (71), 17862-17866; (b) Chen, L.; Tian, J.; Zhan, Y.; Ren, J.; Wang, Z., Lewis Acid-Catalyzed Intramolecular [3+2] Cross-Cycloaddition of Donor- Acceptor Epoxides with Alkenes for Construction of Oxa-[n.2.1] Skeletons. *Chin. J. Chem.* **2019, 7**, (37), 695-699.

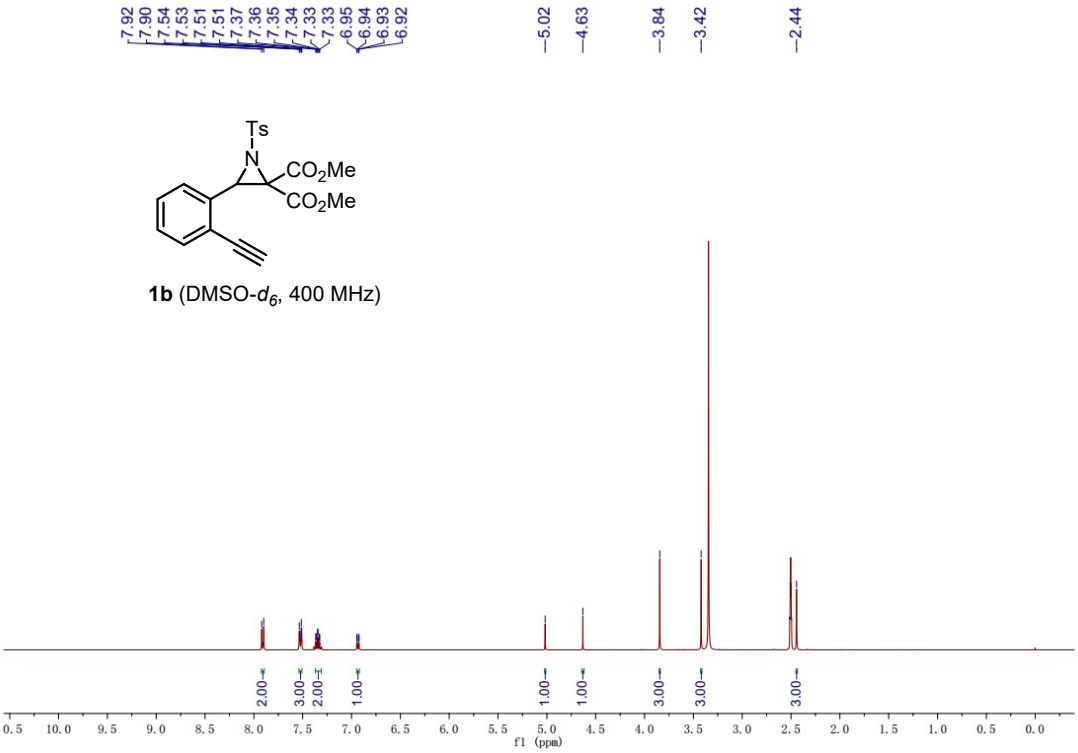
4. NMR spectra



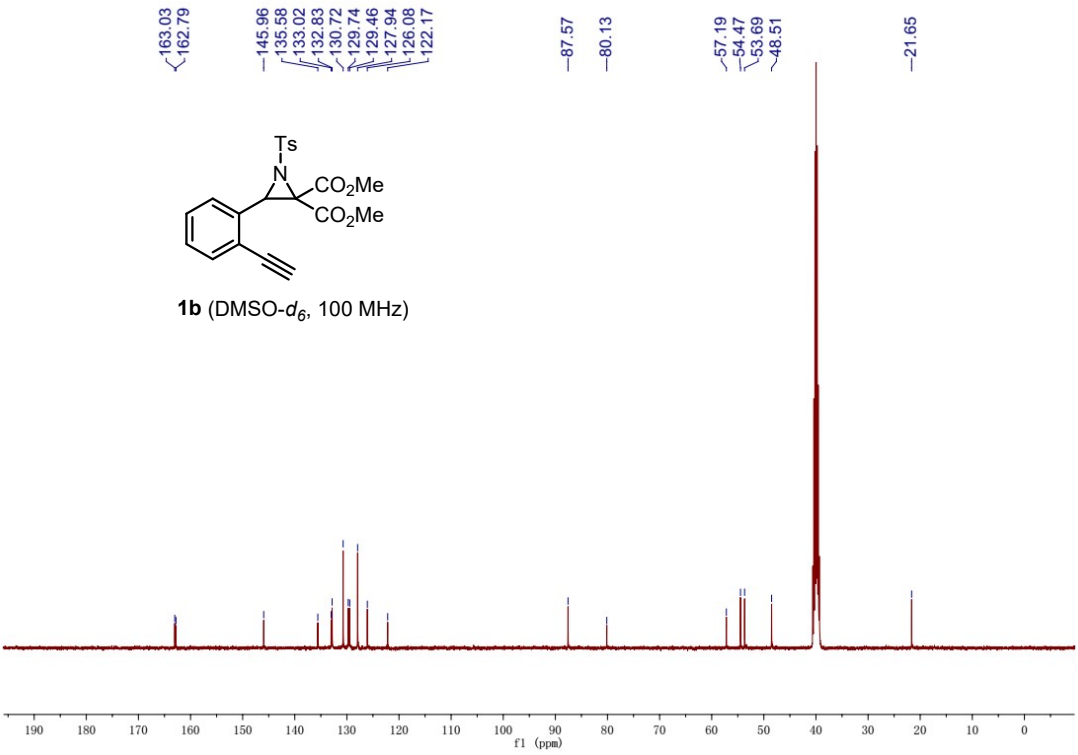
1a ($CDCl_3$, 400 MHz)



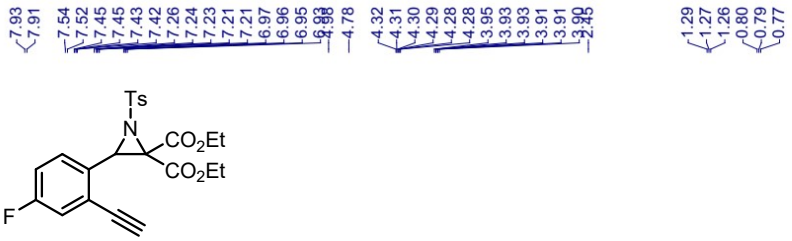
1a ($CDCl_3$, 100 MHz)



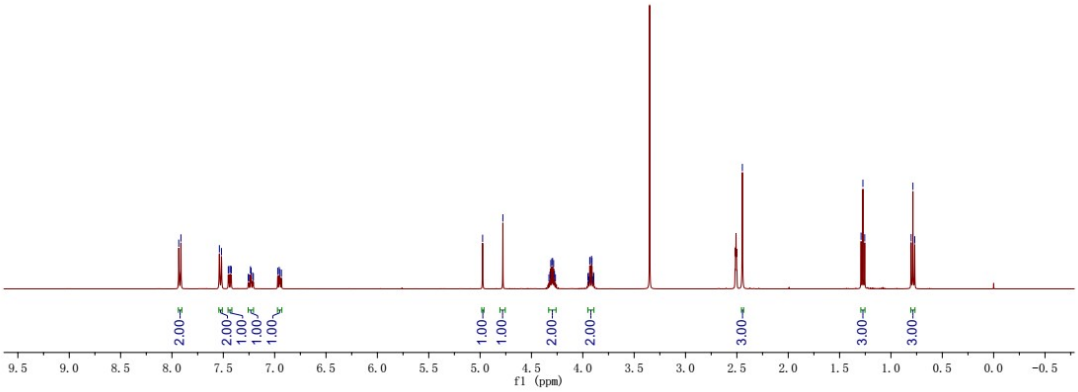
1b (DMSO-d_6, 400 MHz)

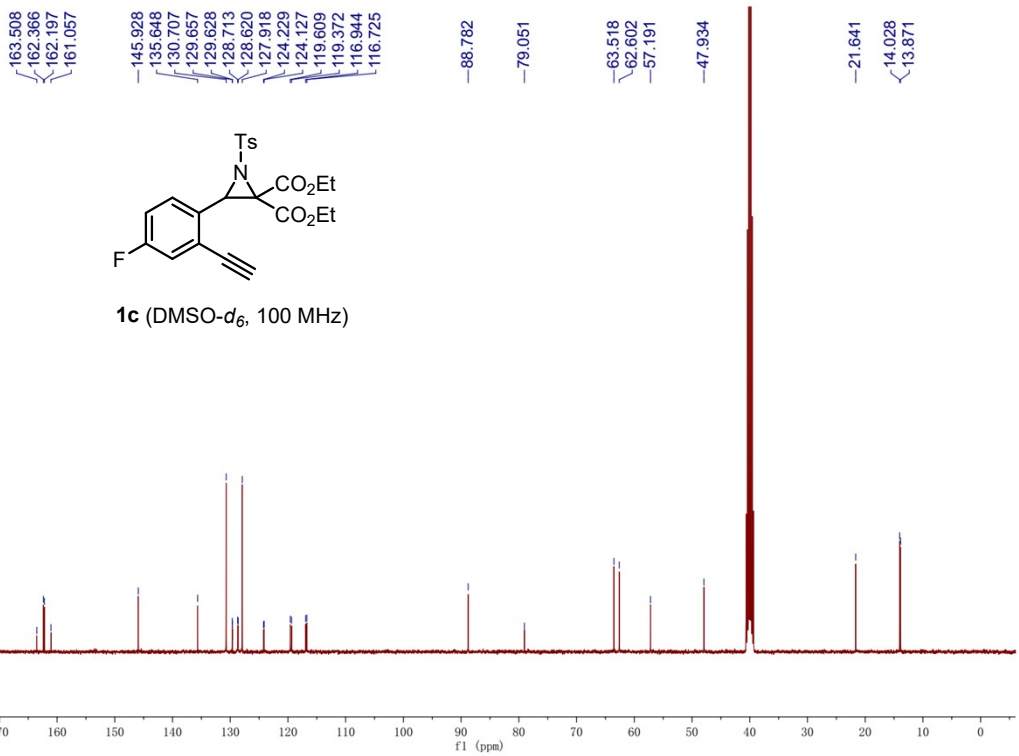


1b (DMSO-d_6, 100 MHz)



1c (DMSO-d_6, 400 MHz)





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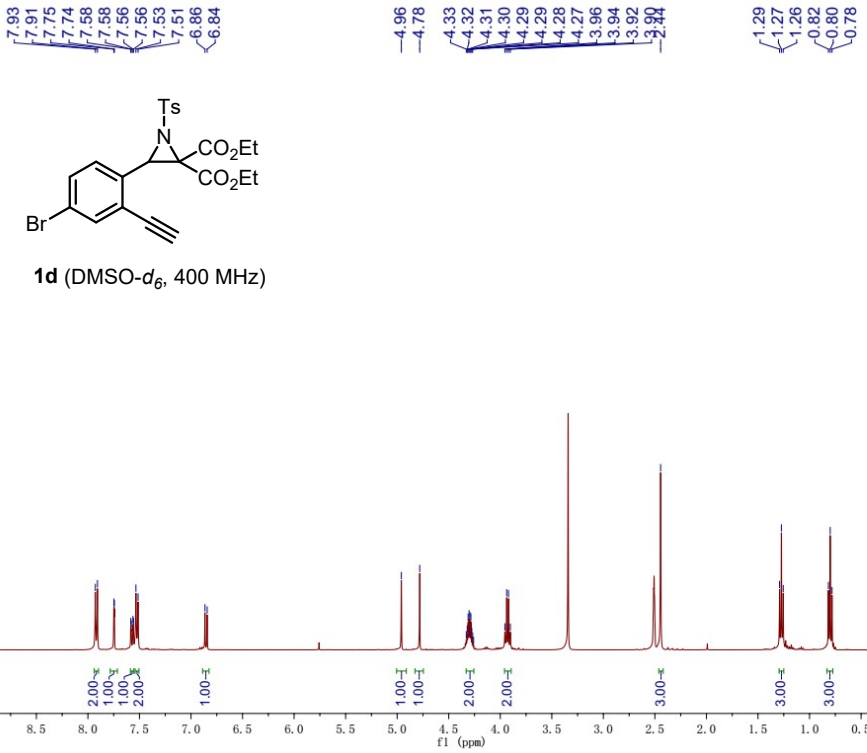
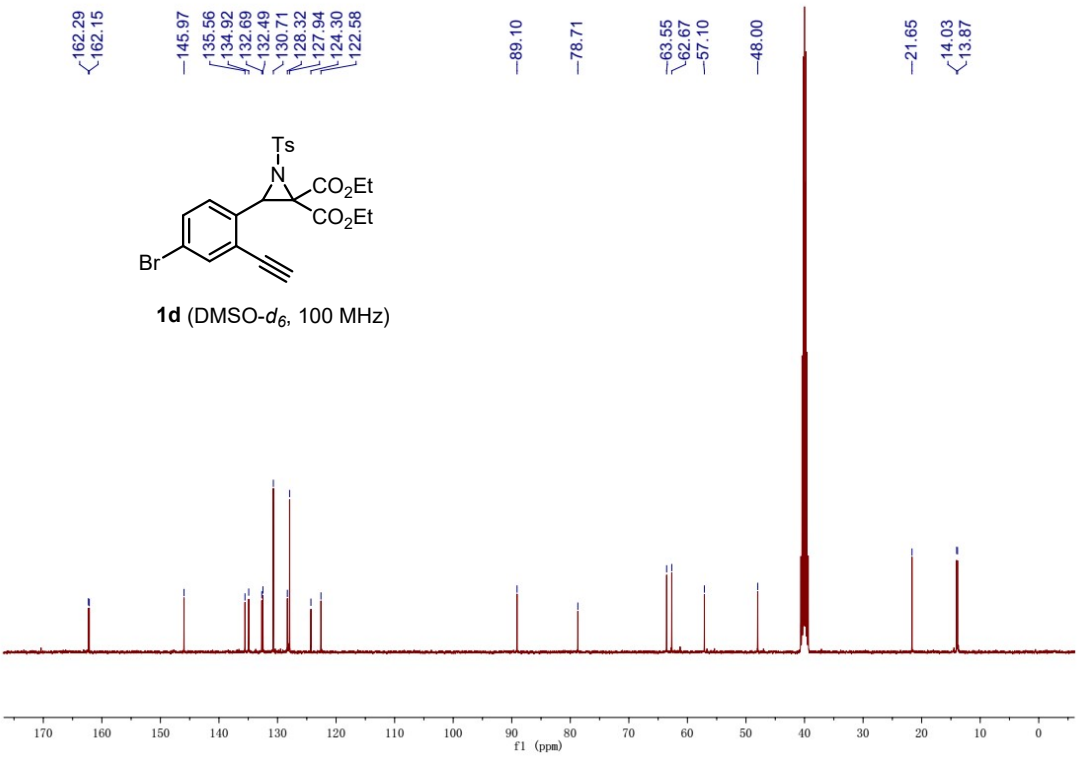
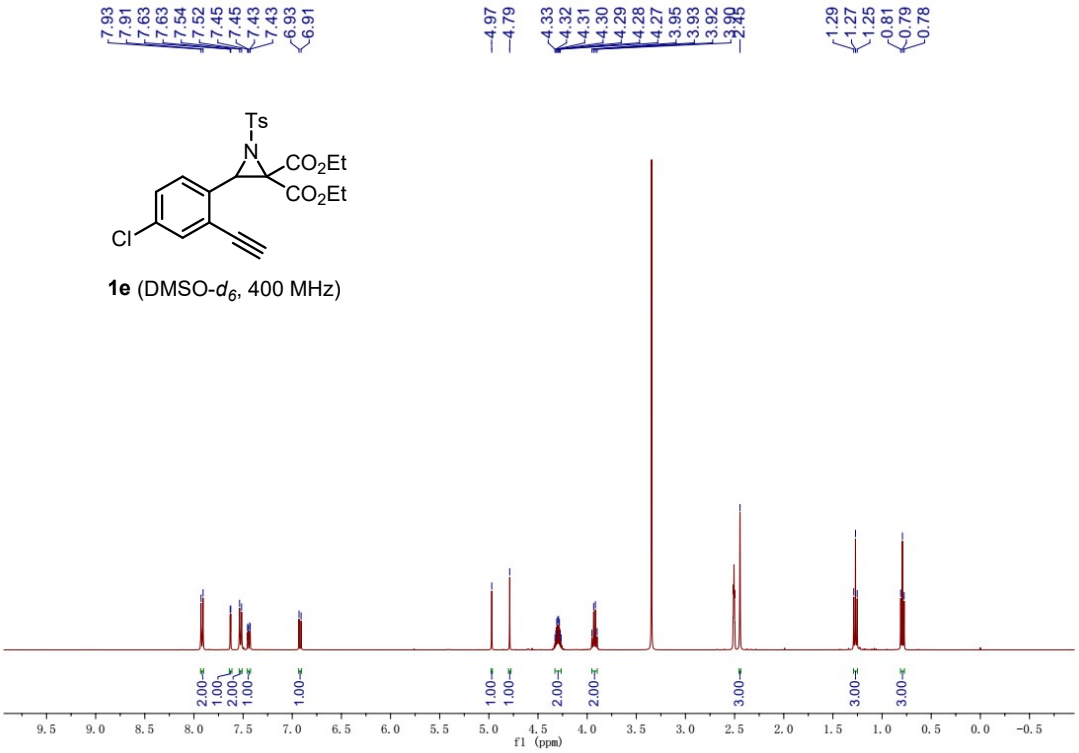


1d (DMSO-d_6, 400 MHz)



1d (DMSO-d_6, 100 MHz)



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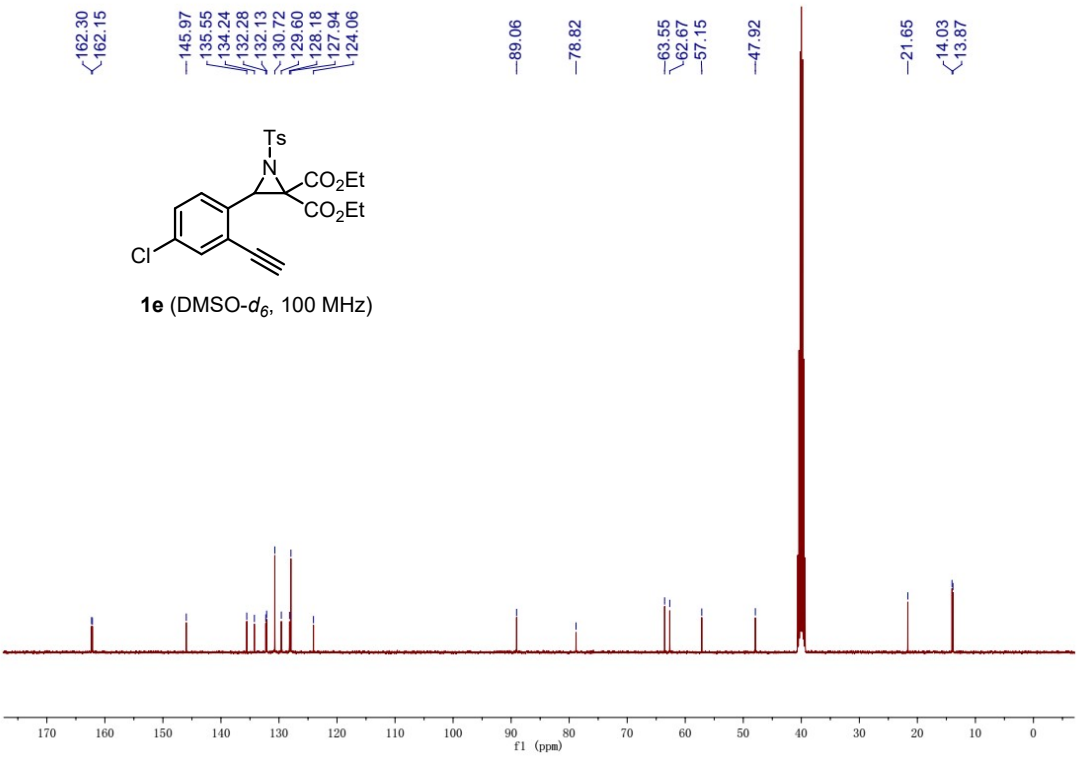
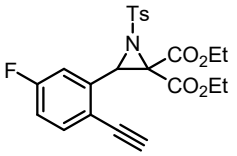


1e (DMSO-d_6, 100 MHz)



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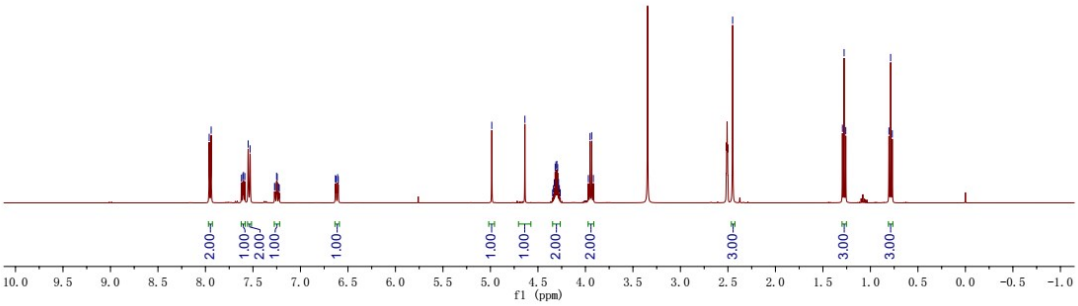
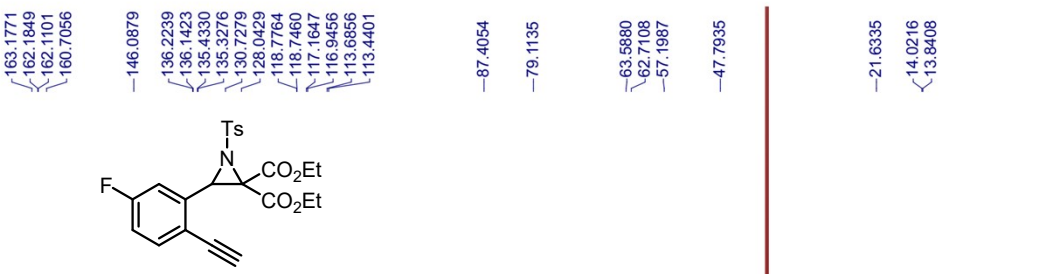
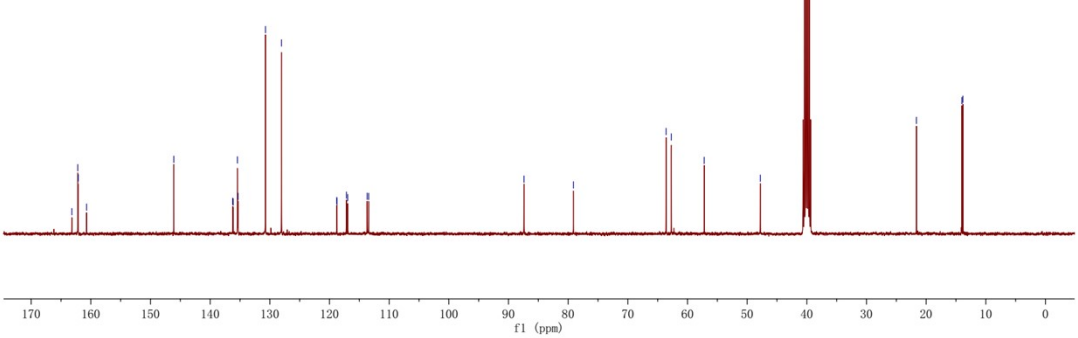
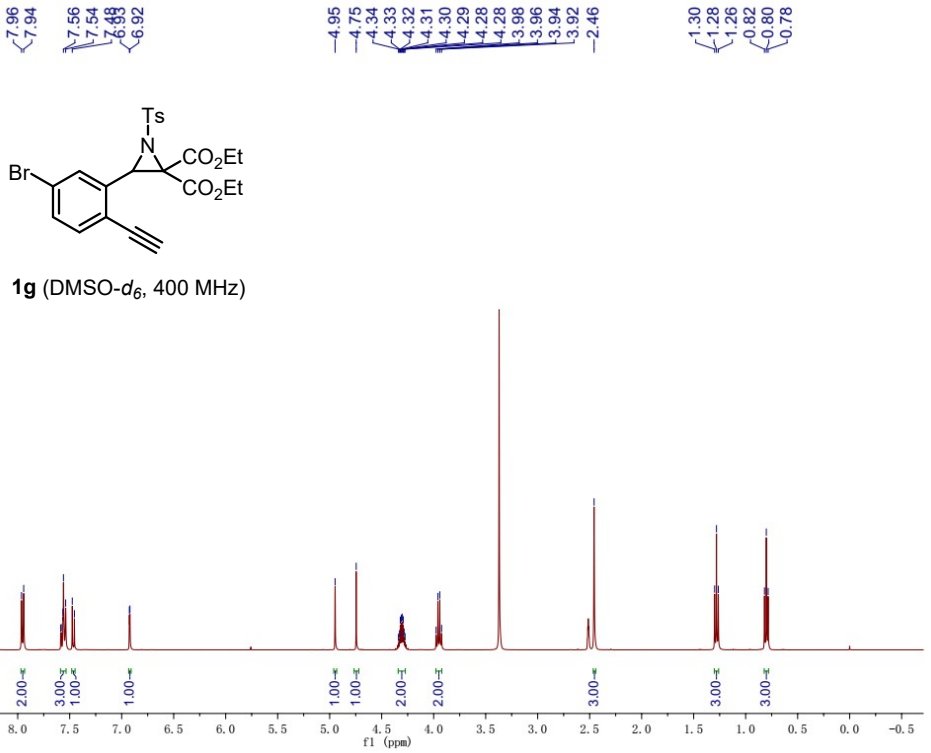


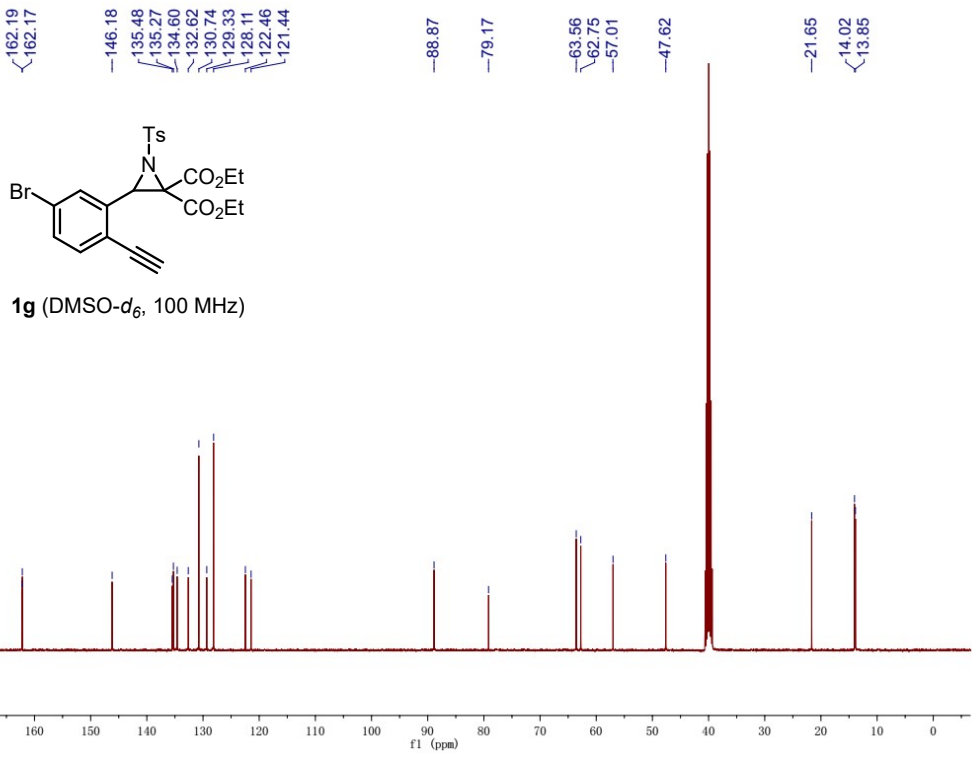


1f (DMSO-d_6, 100 MHz)

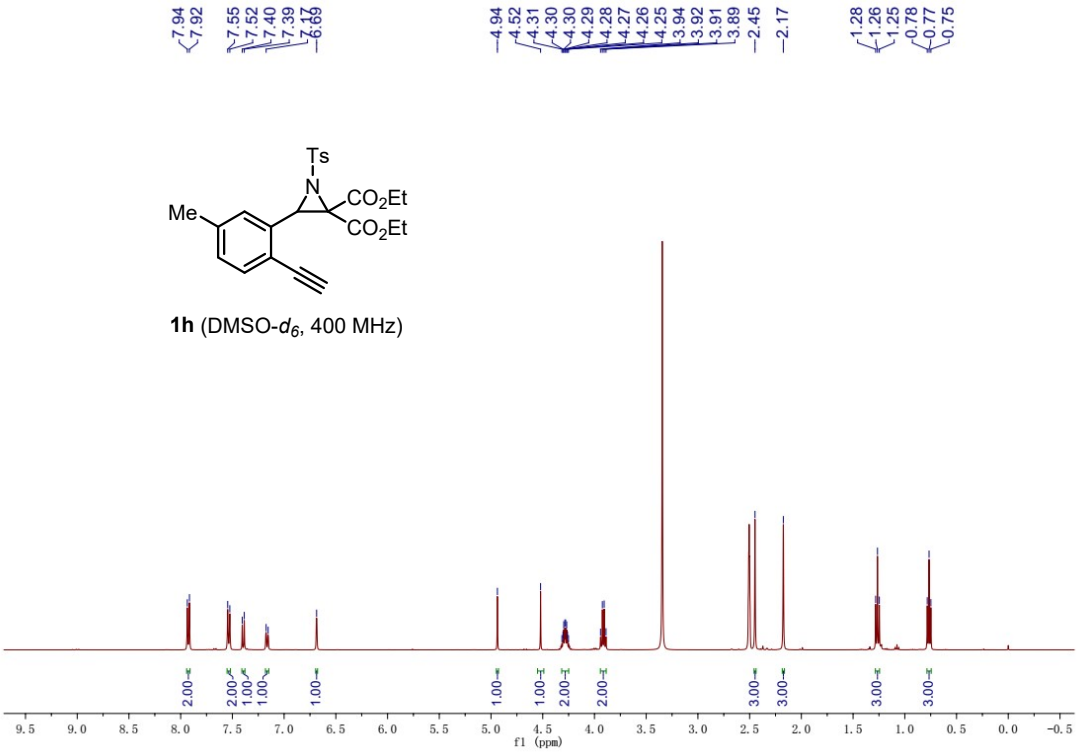




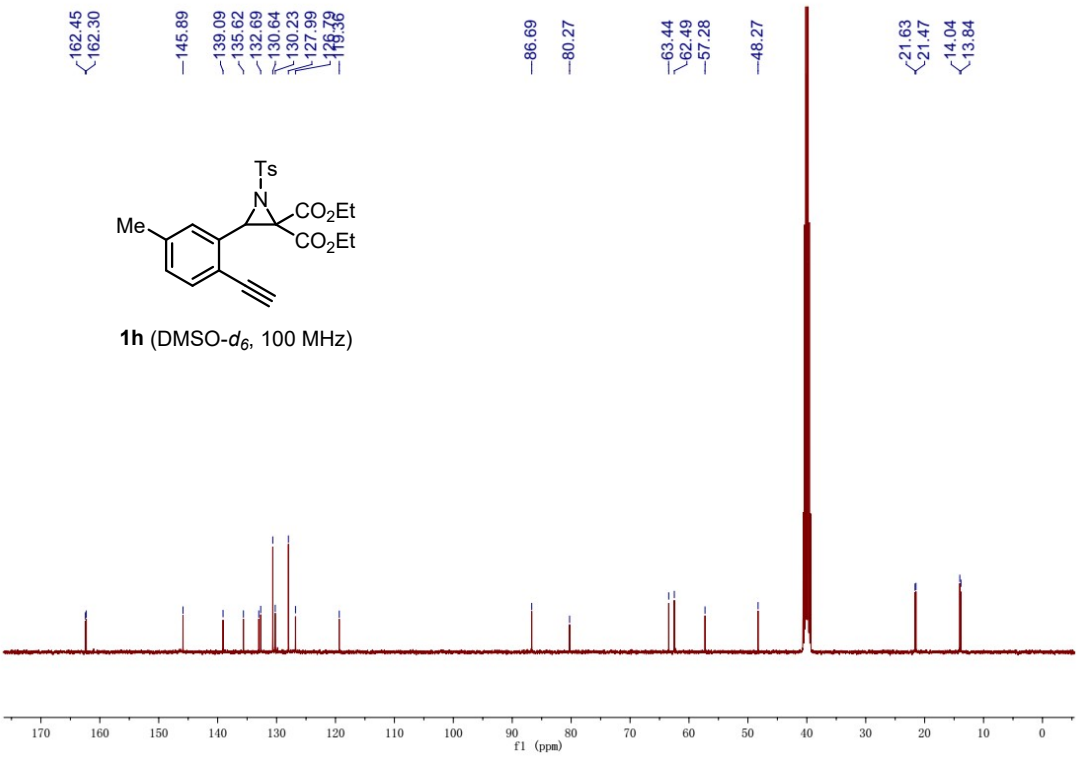
1g (DMSO-d_6, 400 MHz)



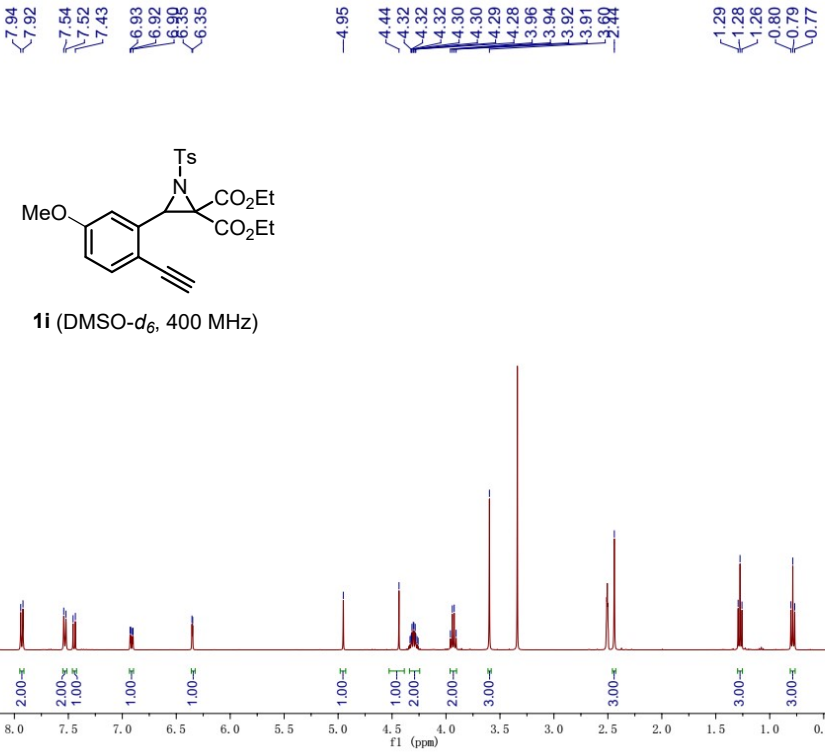
1g (DMSO-d_6, 100 MHz)



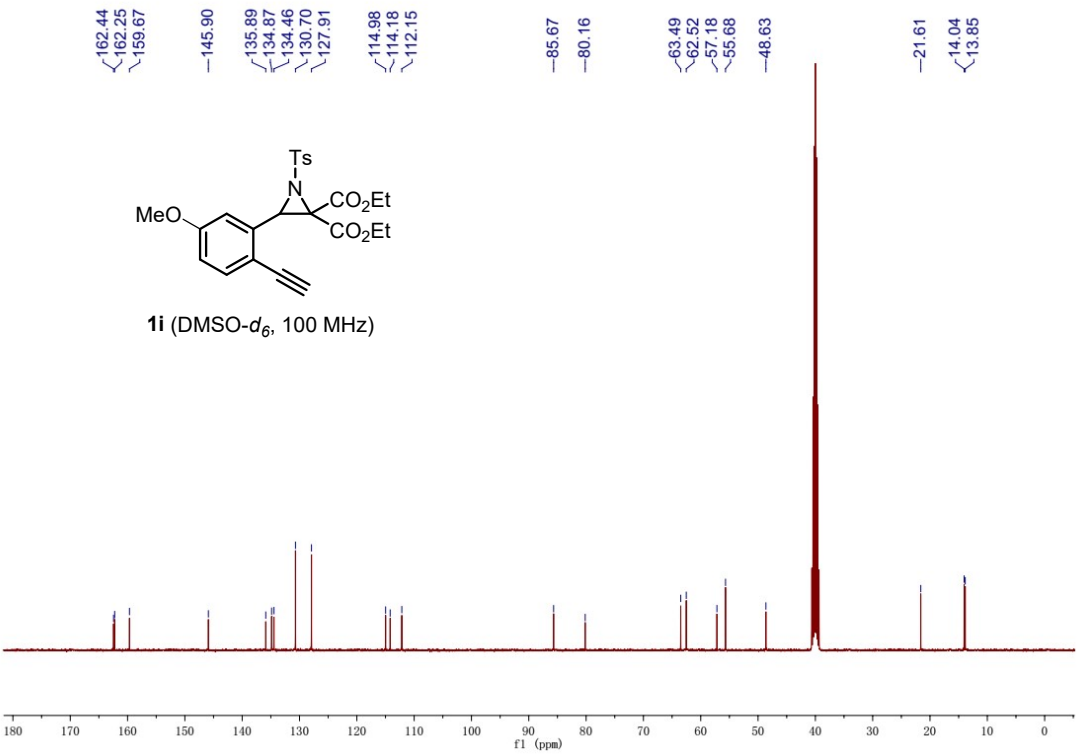
1h (DMSO-d_6, 400 MHz)



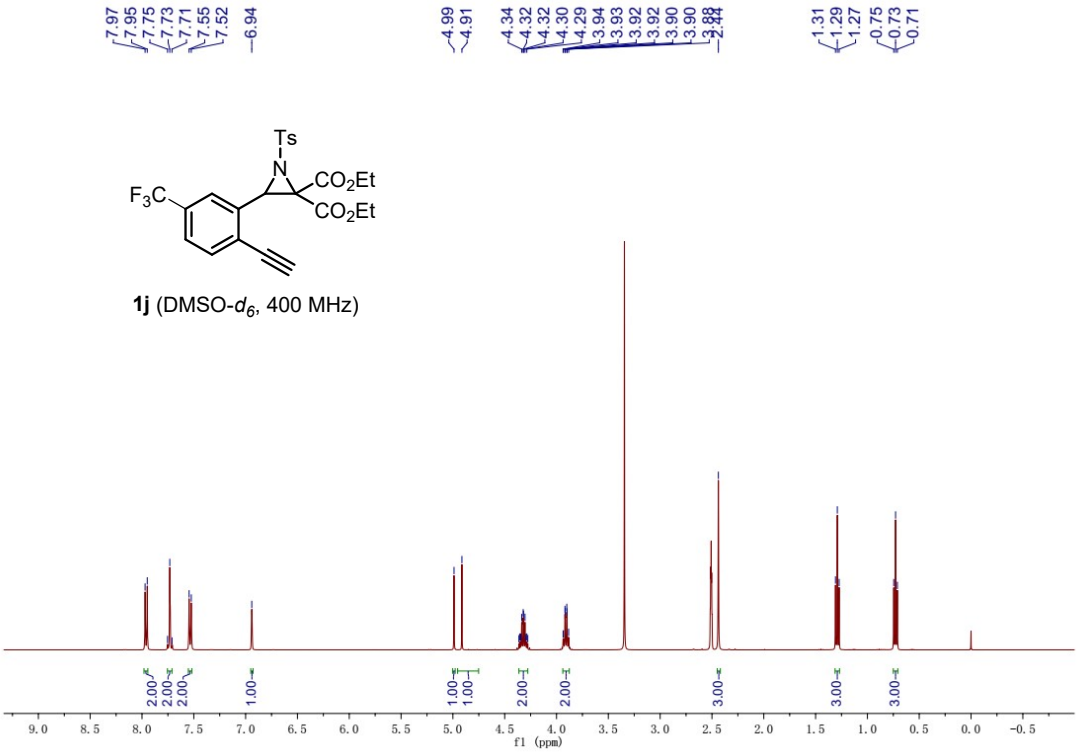
1h (DMSO-d_6, 100 MHz)



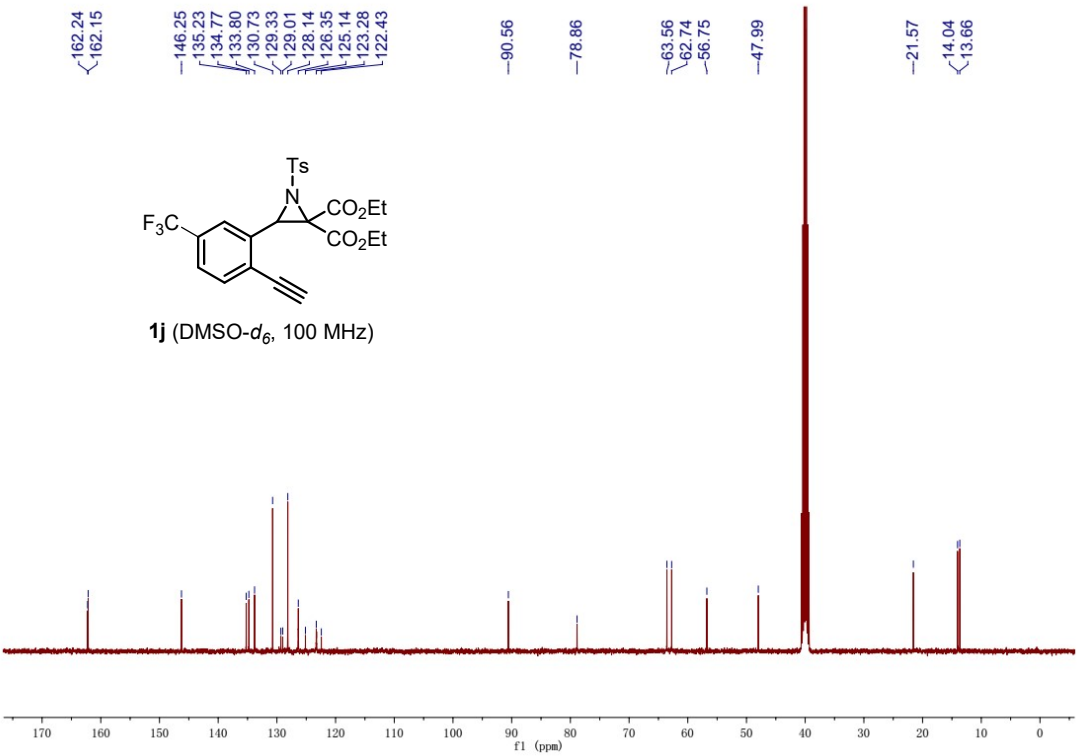
1i (DMSO-d_6, 400 MHz)



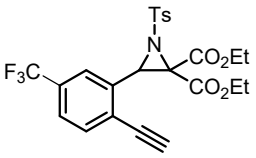
1i (DMSO-d_6, 100 MHz)



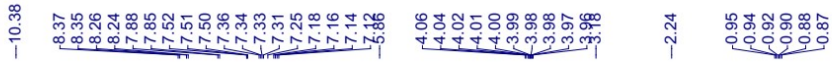
1j (DMSO-d_6, 400 MHz)

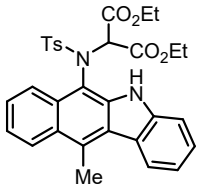


1j (DMSO-d_6, 100 MHz)

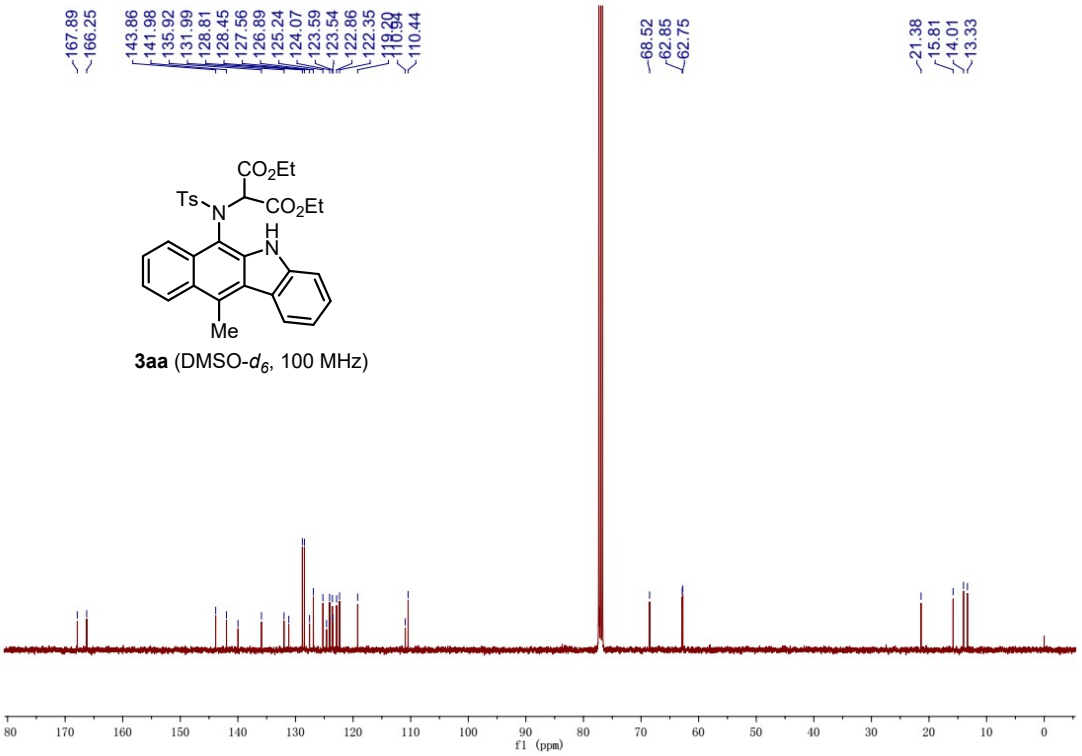


1j (DMSO-d_6, 376 MHz)

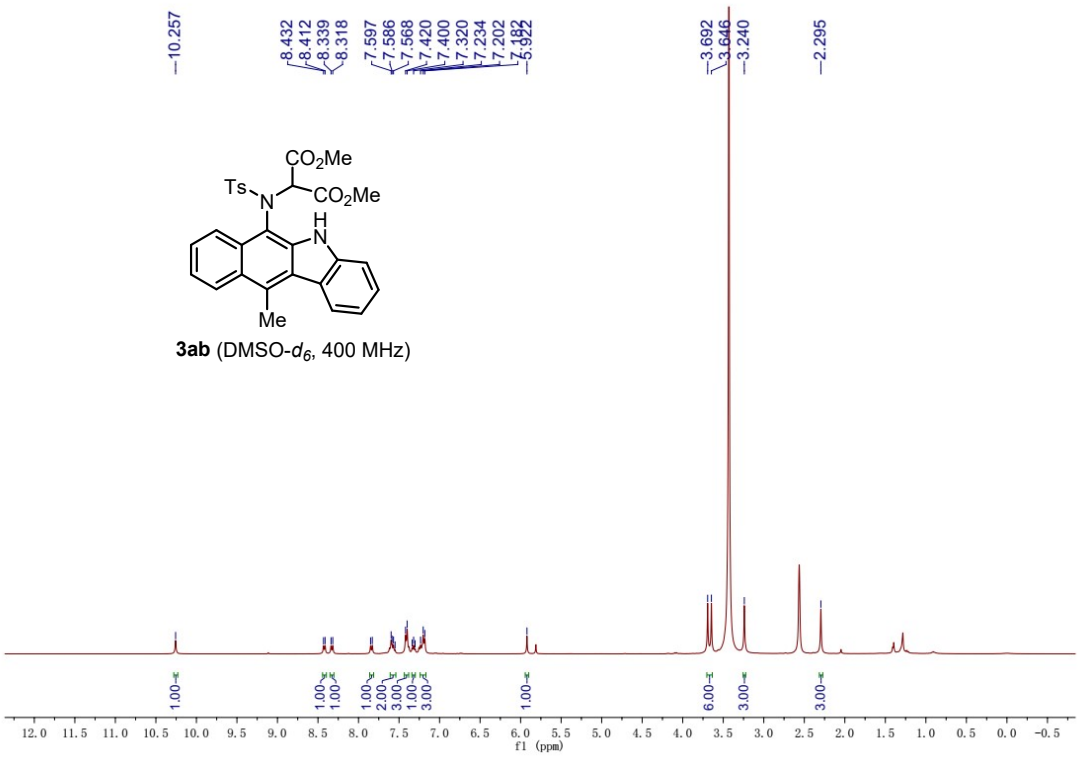




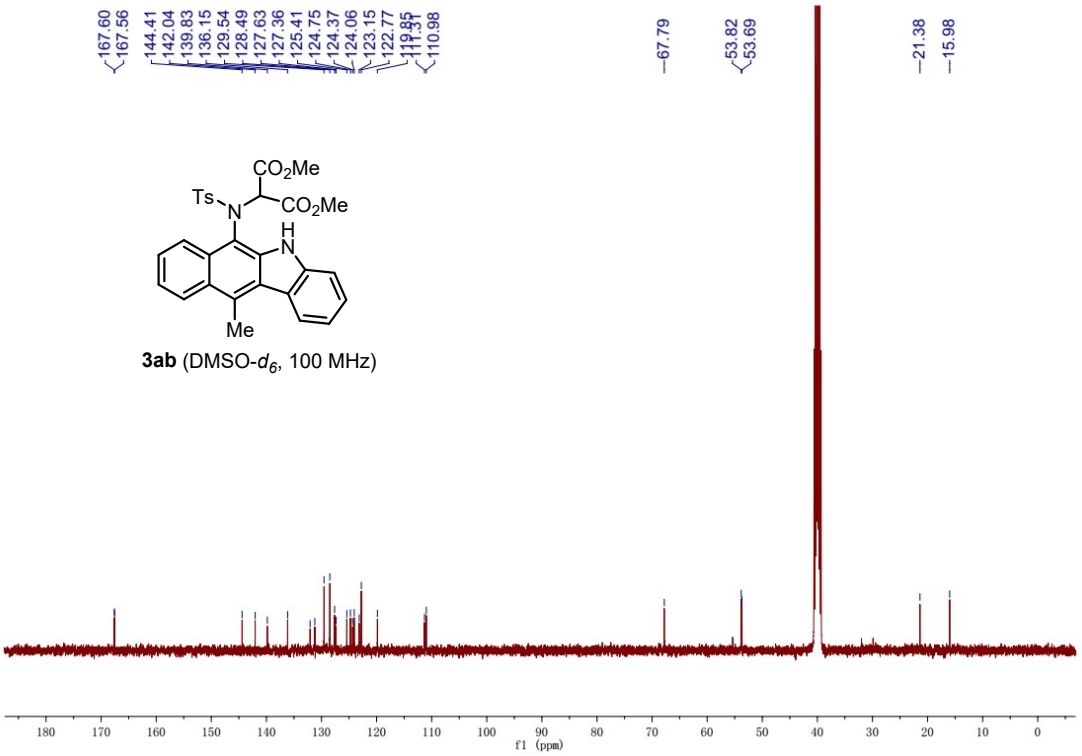
3aa (DMSO-d_6, 400 MHz)



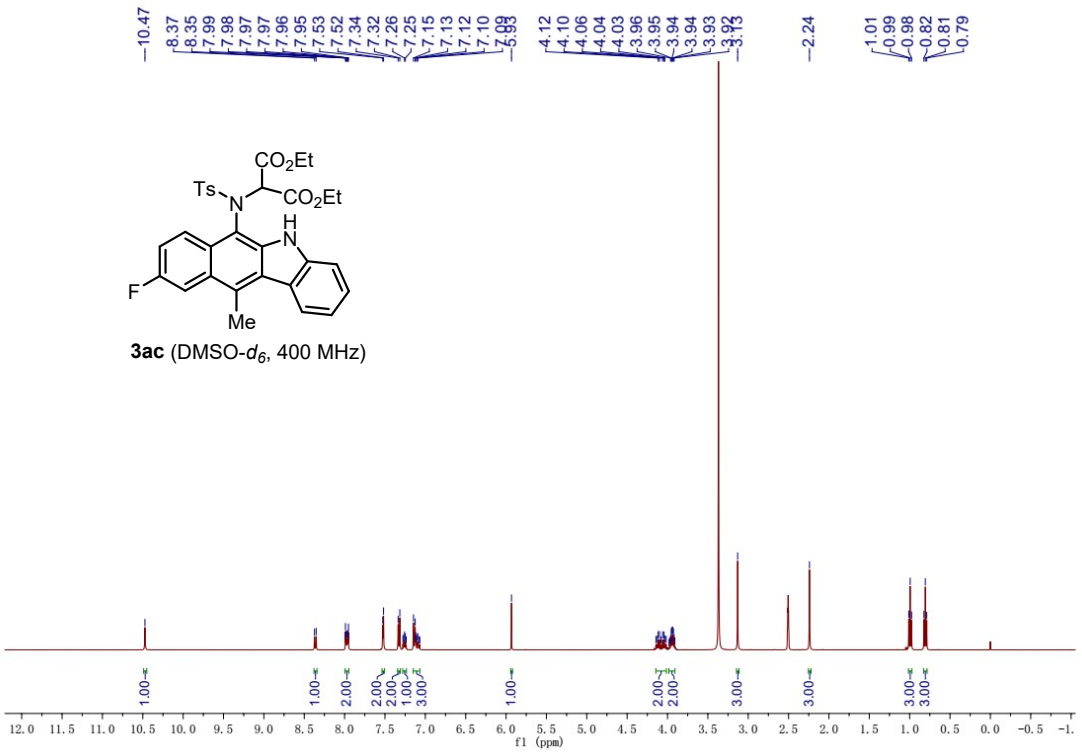
3aa (DMSO-d_6, 100 MHz)



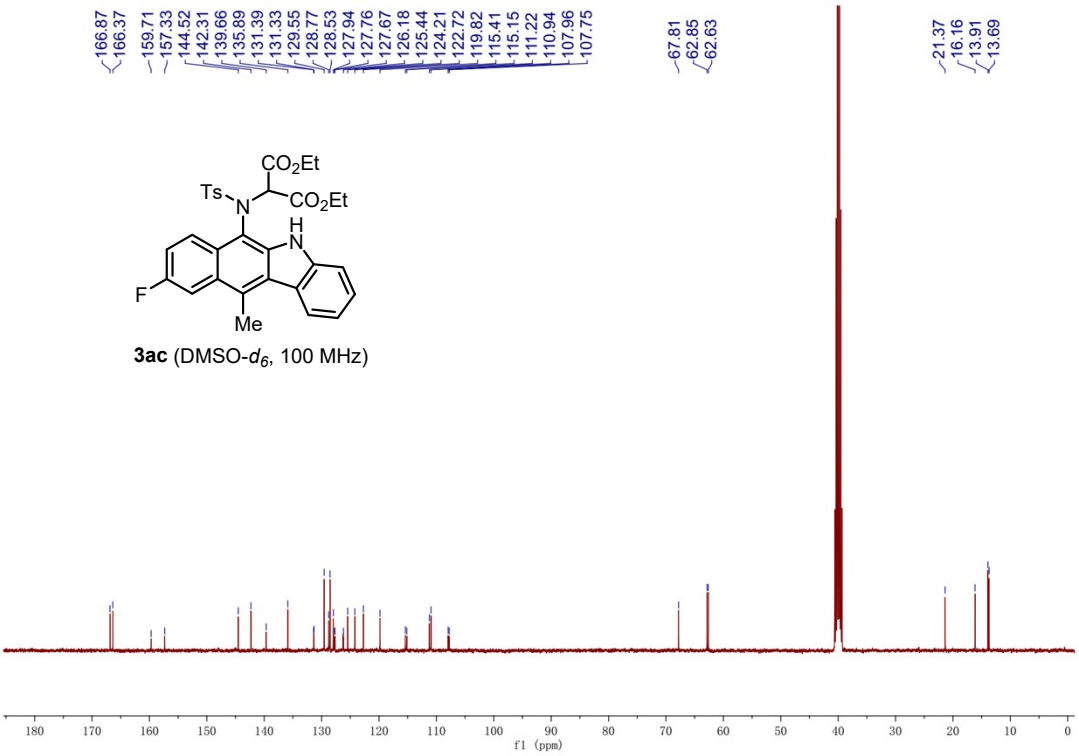
3ab (DMSO-d_6, 400 MHz)



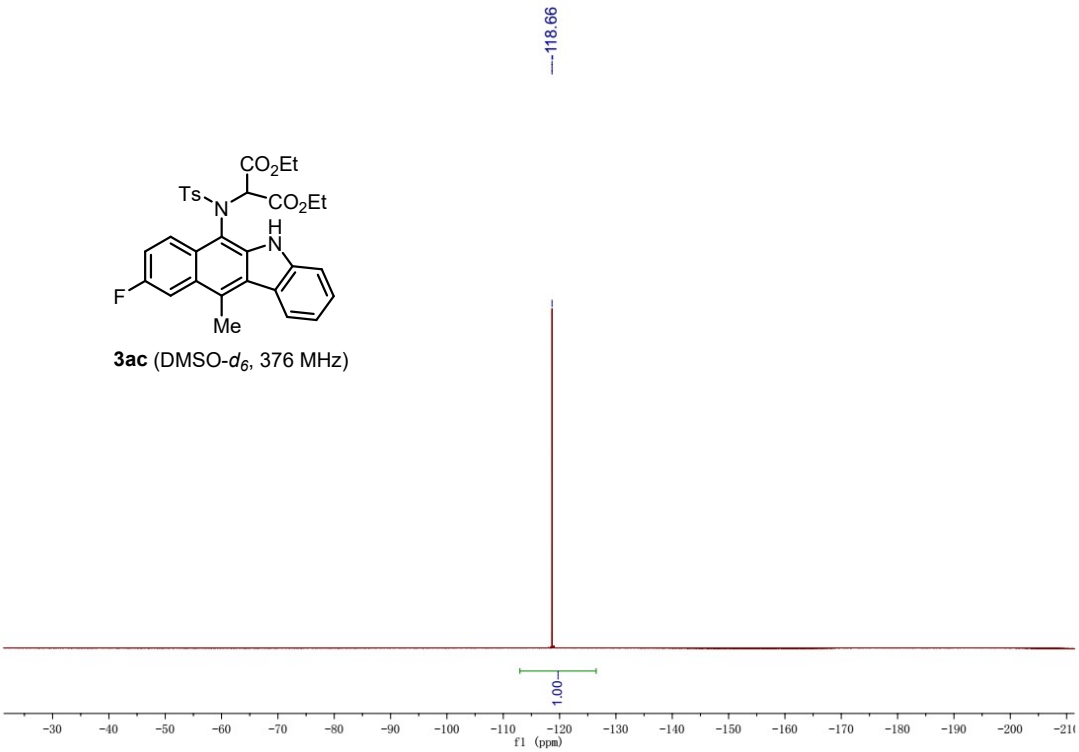
3ab (DMSO-d_6, 100 MHz)



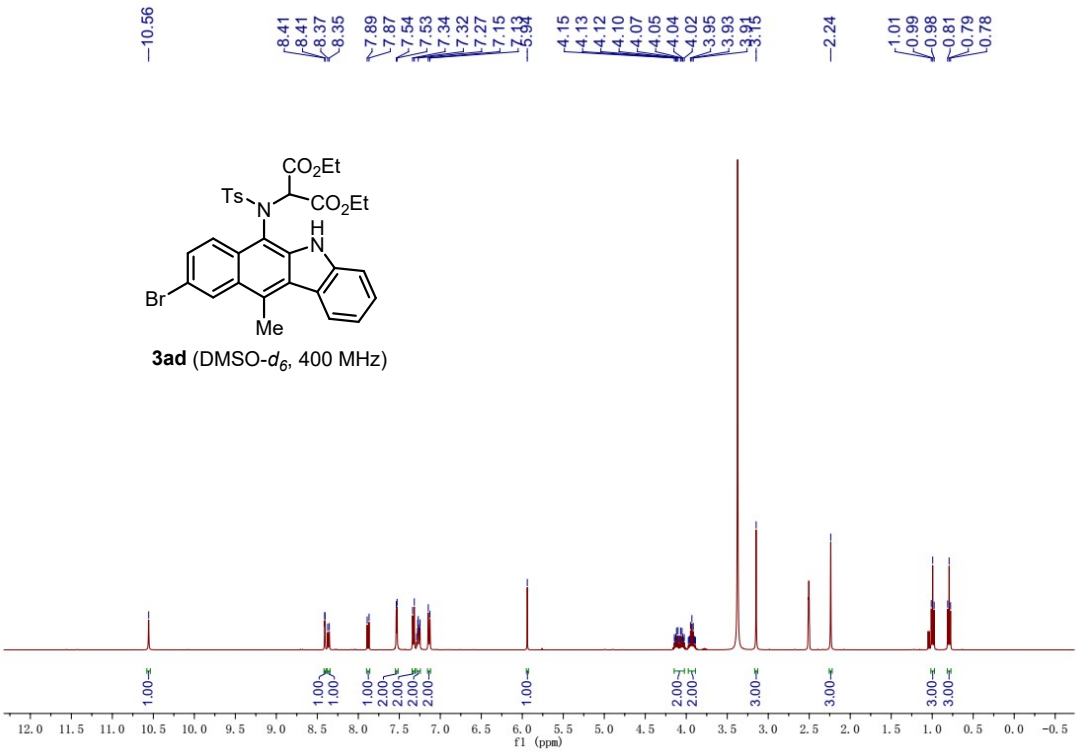
3ac (DMSO-d_6, 400 MHz)



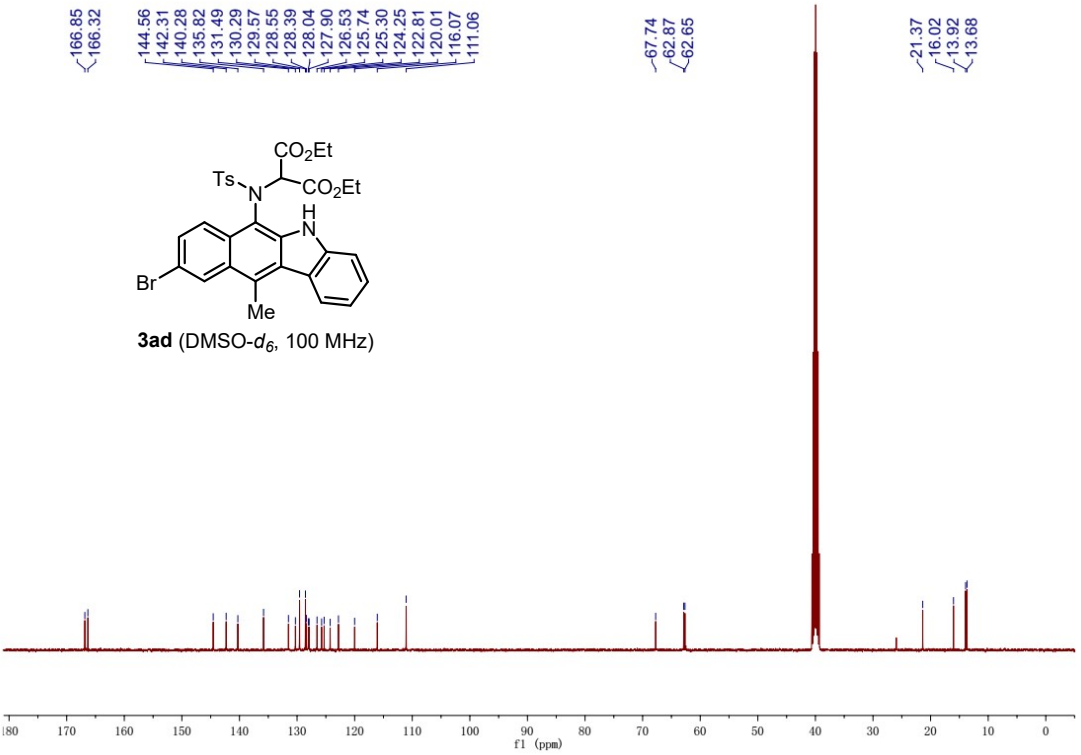
3ac (DMSO-d_6, 100 MHz)



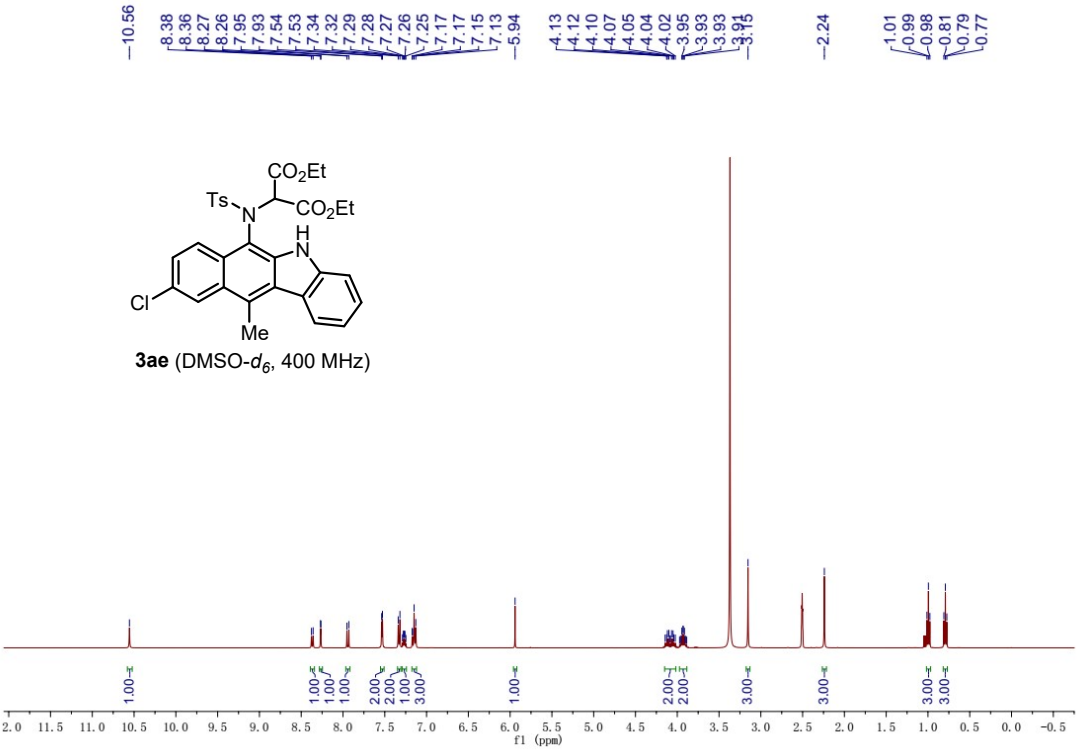
3ac (DMSO-d_6, 376 MHz)



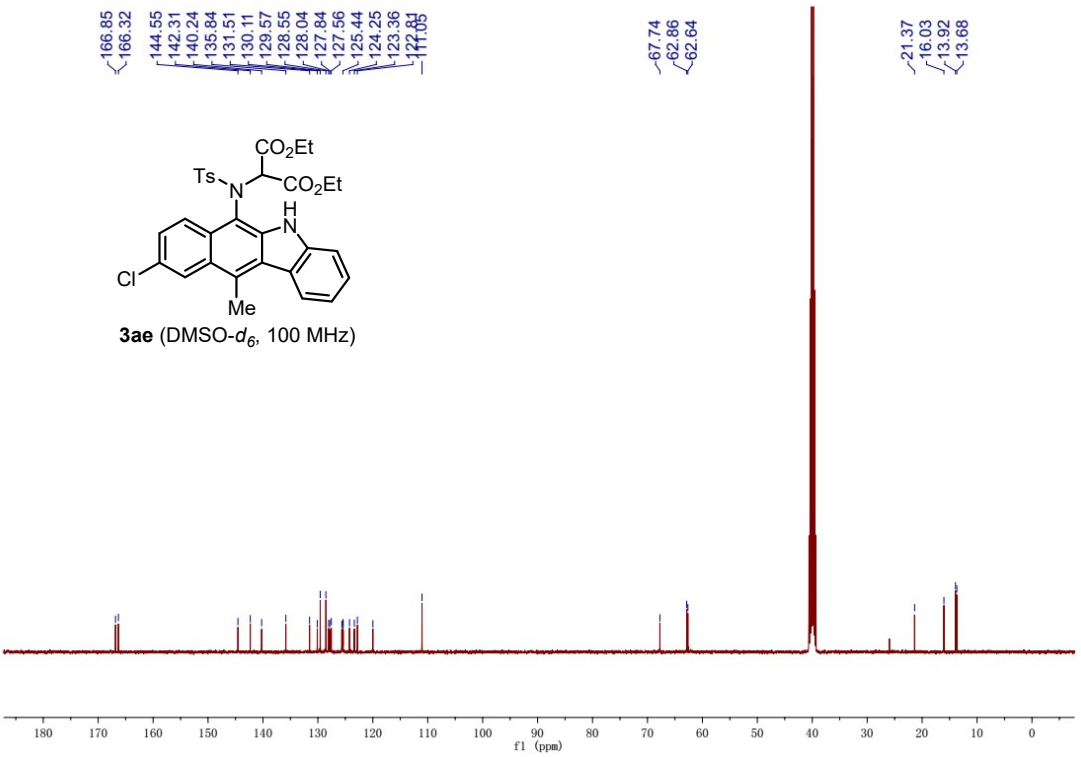
3ad (DMSO-d_6, 400 MHz)



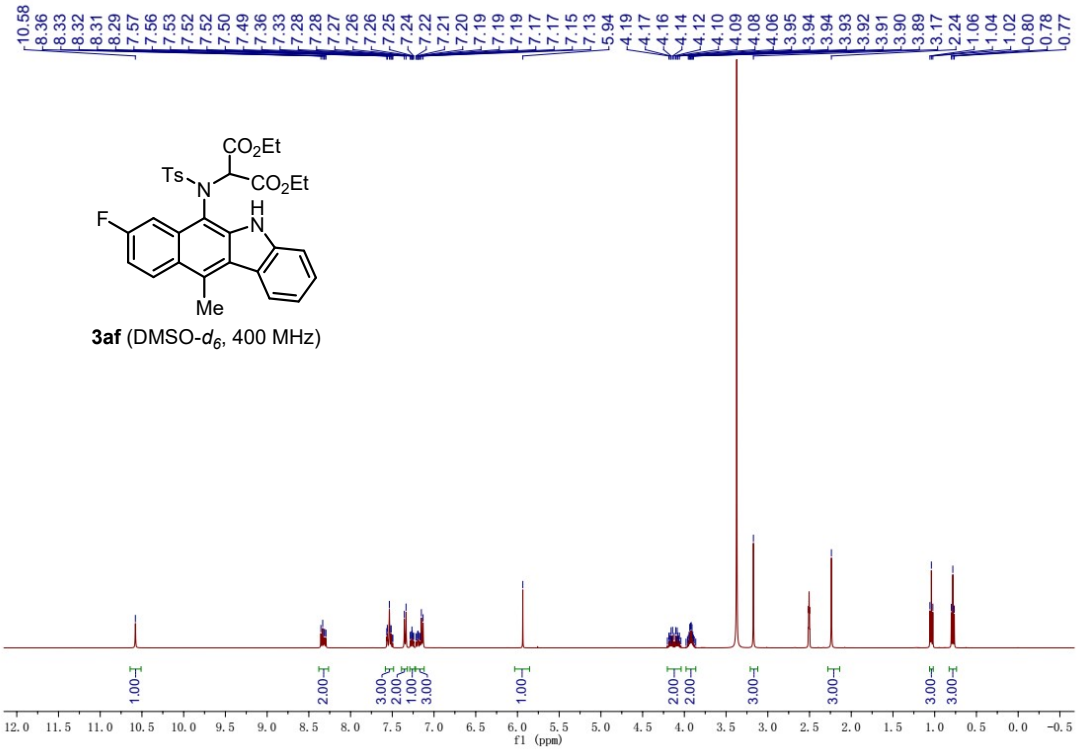
3ad (DMSO-d_6, 100 MHz)



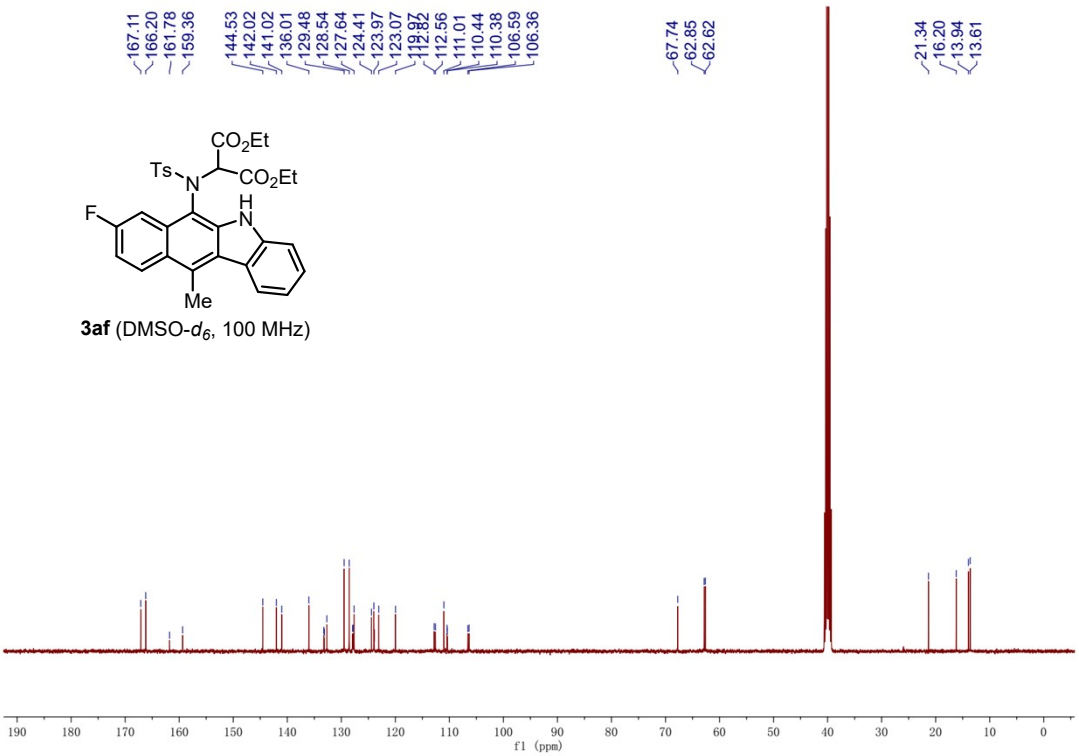
3ae (DMSO-d_6, 400 MHz)



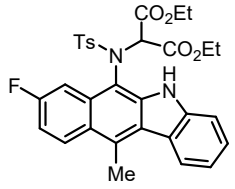
3ae (DMSO-d_6, 100 MHz)



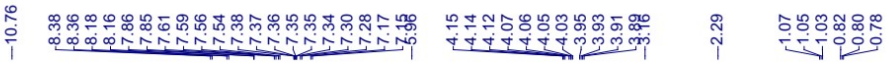
3af (DMSO-d_6, 400 MHz)

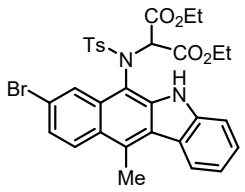


3af (DMSO-d_6, 100 MHz)

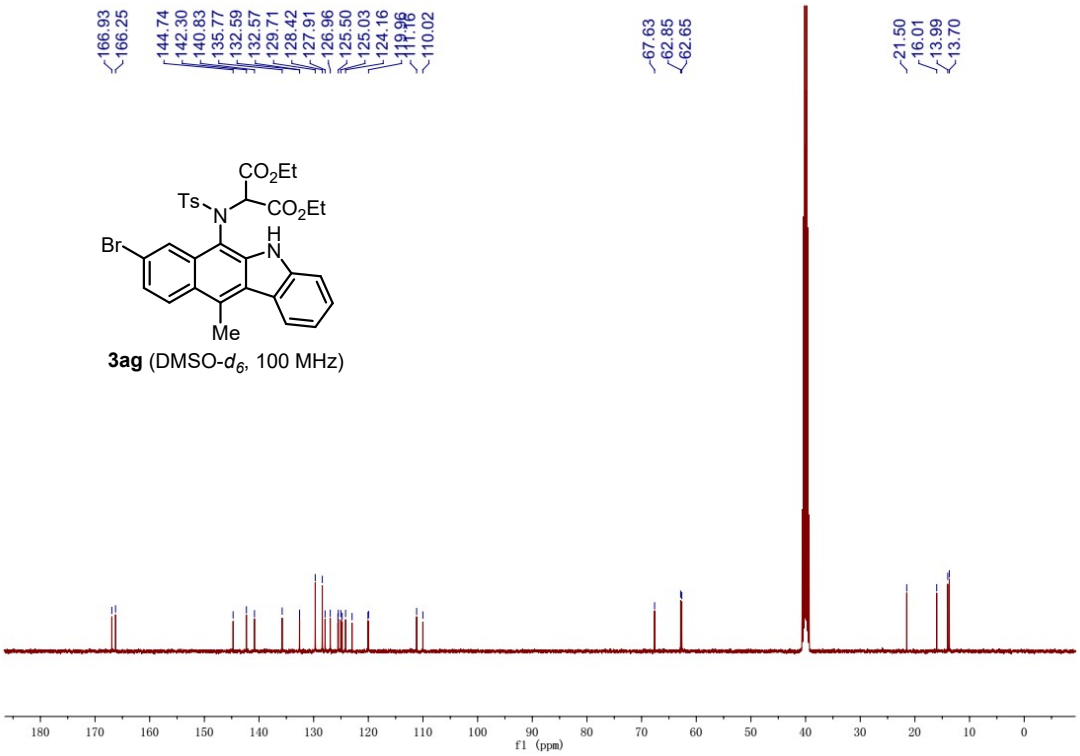


3af (DMSO-d_6, 376 MHz)

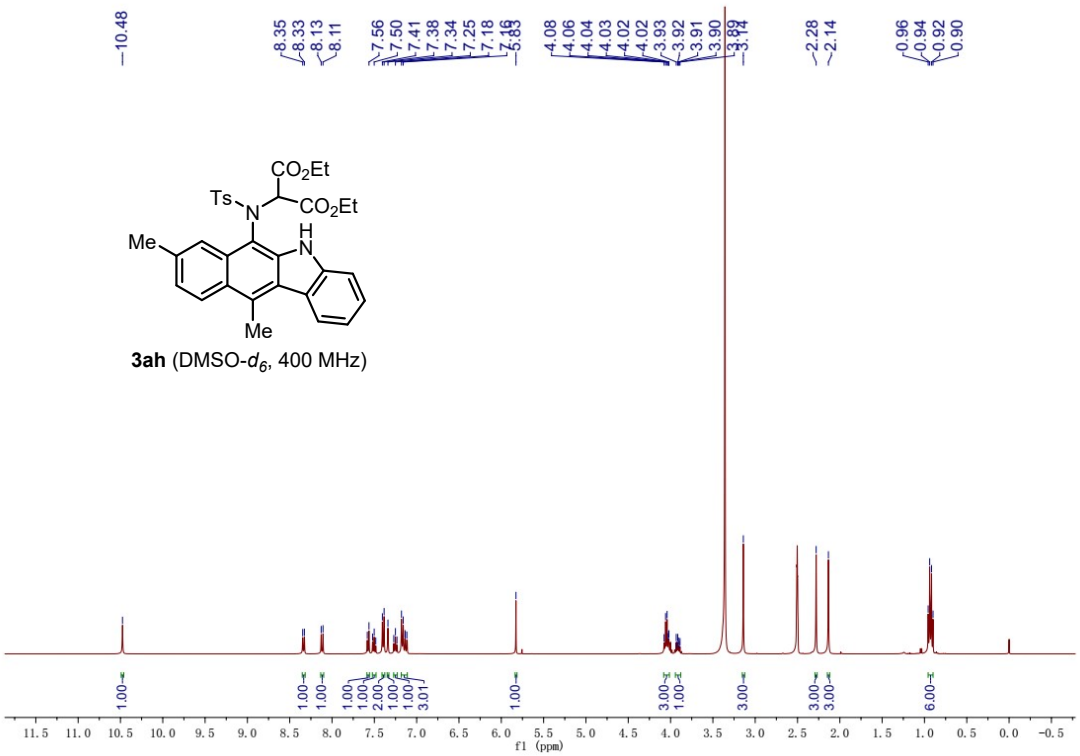




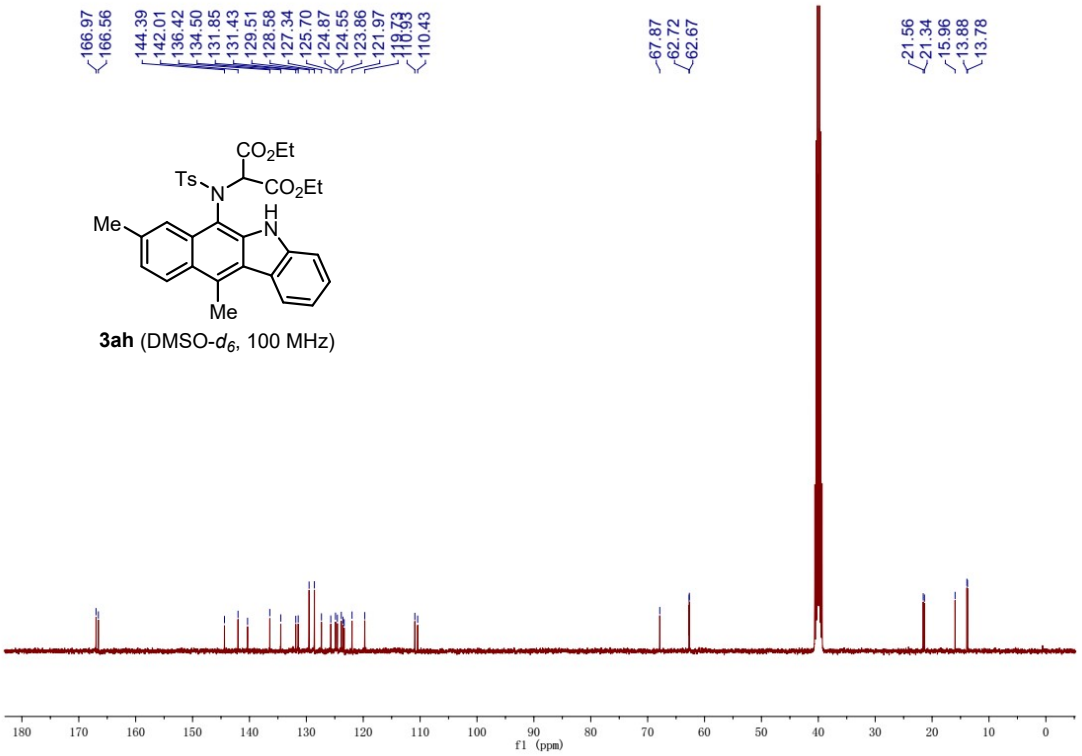
3ag (DMSO-d_6, 400 MHz)



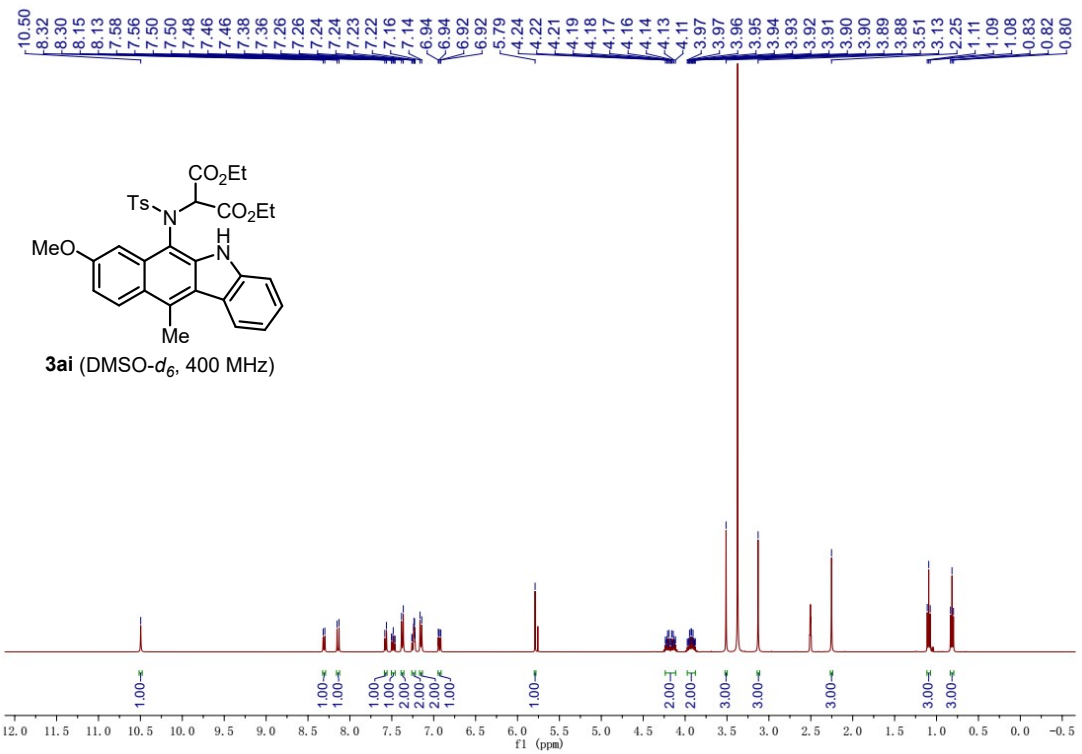
3ag (DMSO-d_6, 100 MHz)



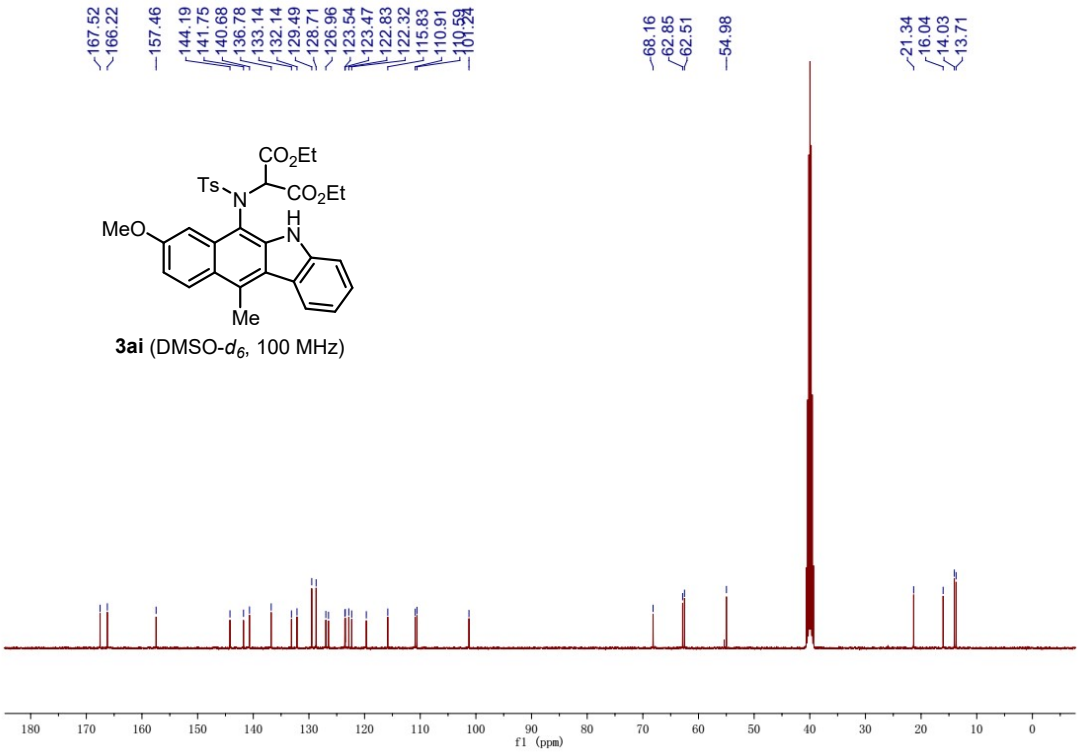
3ah (DMSO-d_6, 400 MHz)



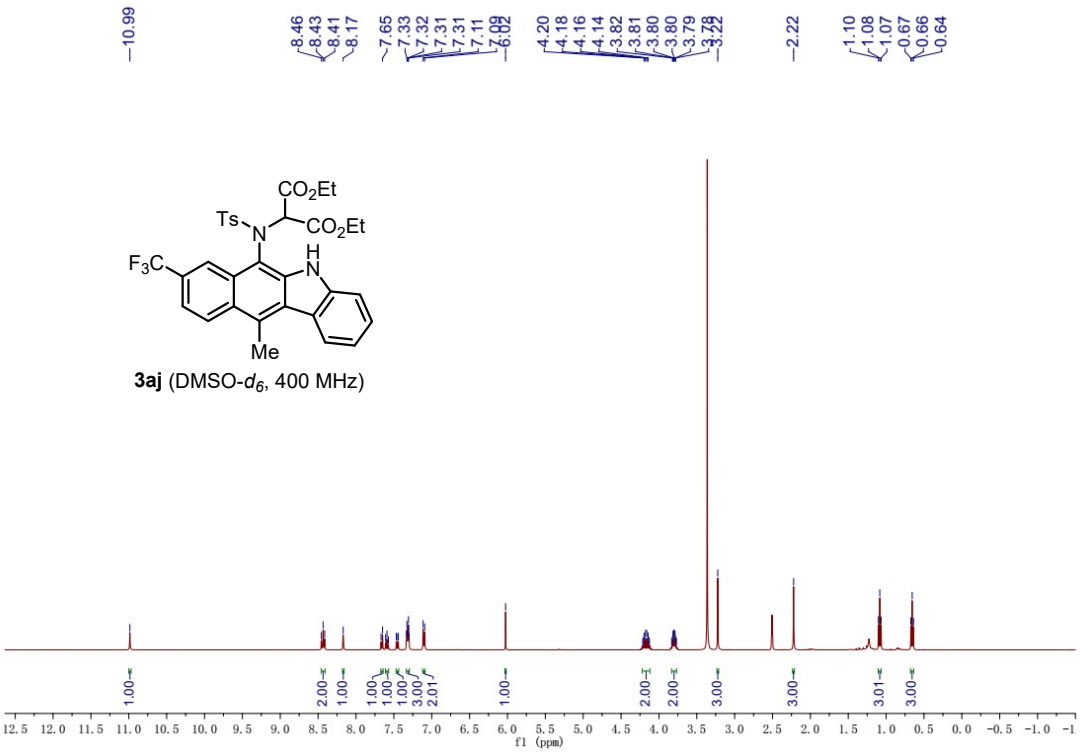
3ah (DMSO-d_6, 100 MHz)



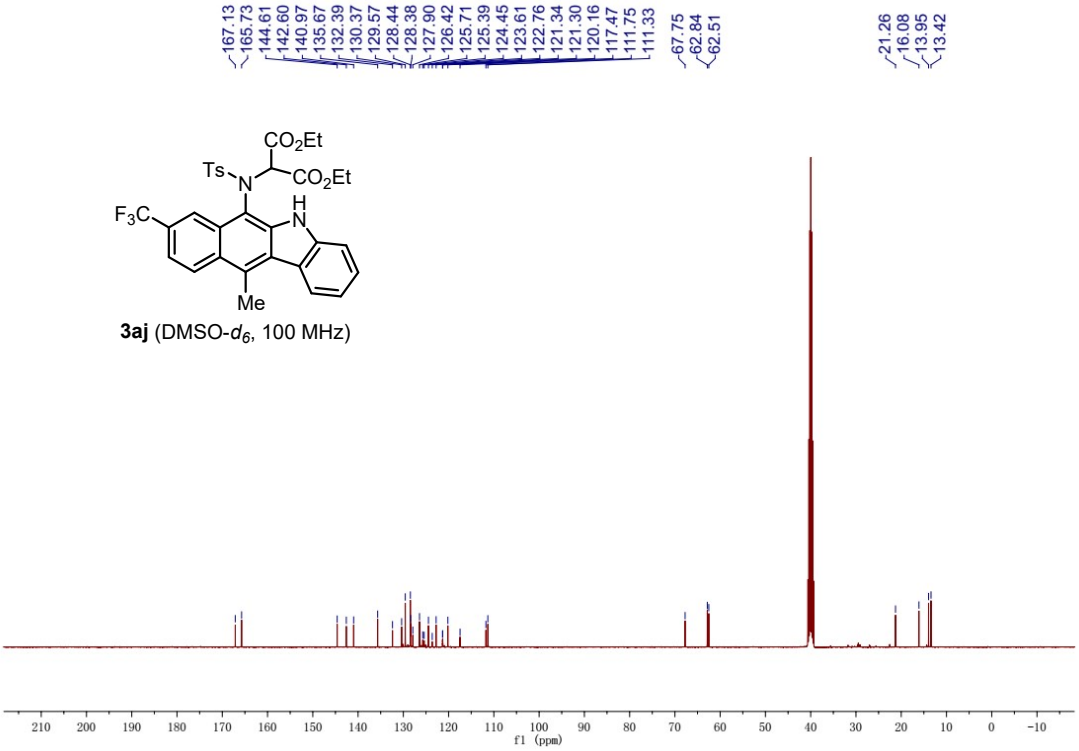
3ai (DMSO-d_6, 400 MHz)



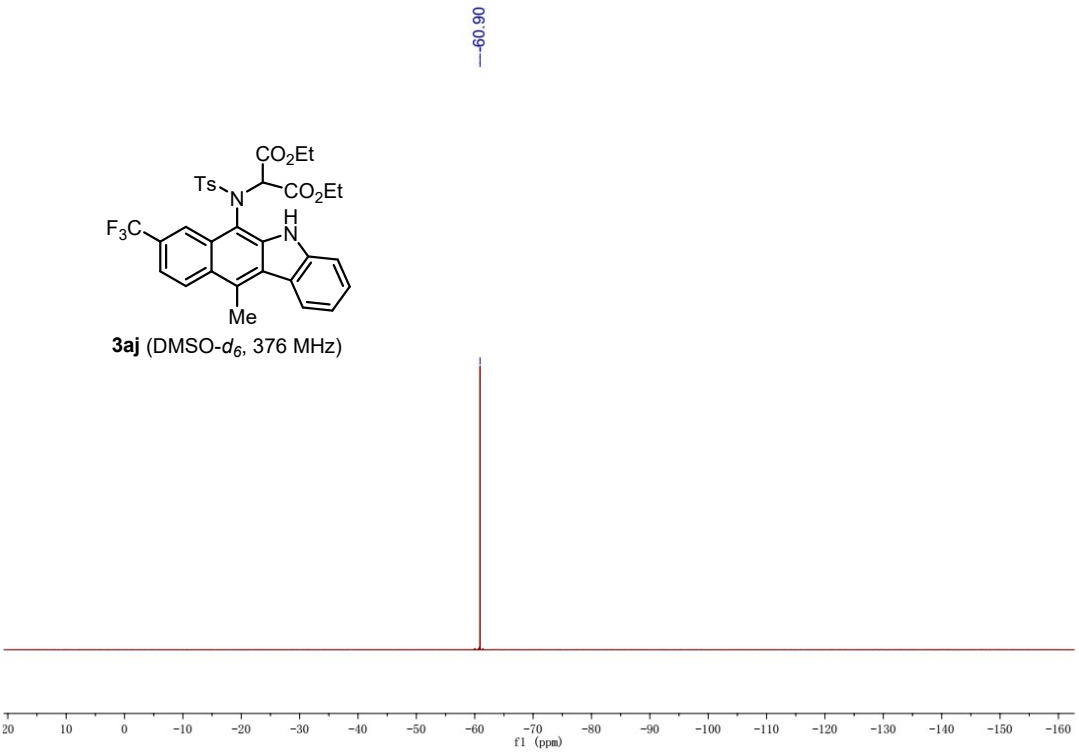
3ai (DMSO-d_6, 100 MHz)



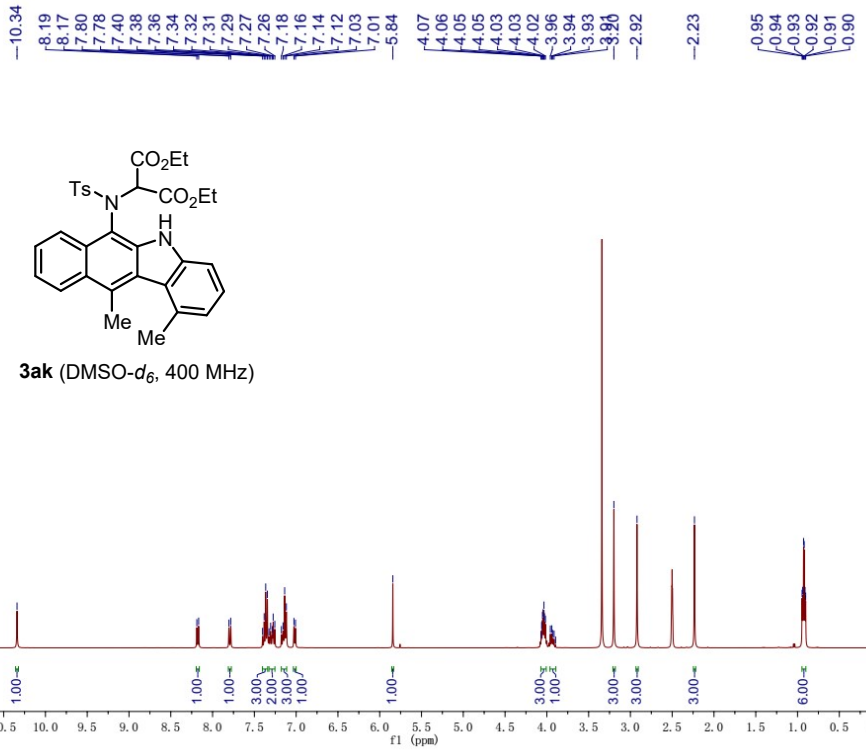
3aj (DMSO-d_6, 400 MHz)



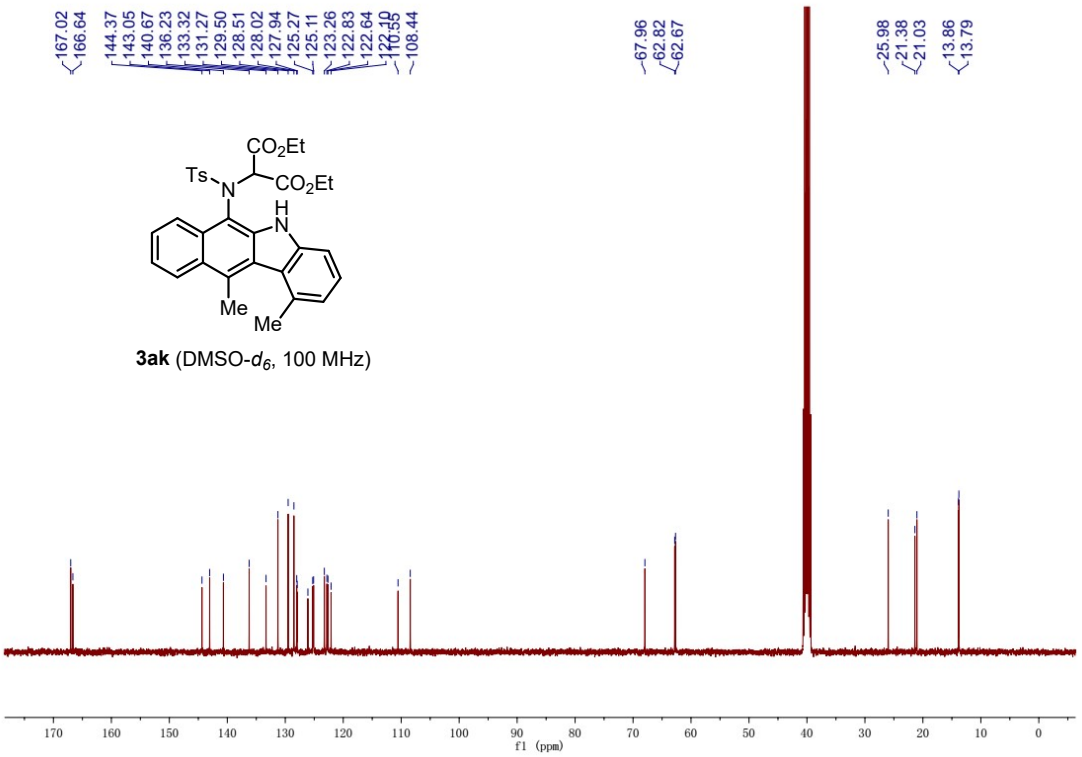
3aj (DMSO-d_6, 100 MHz)



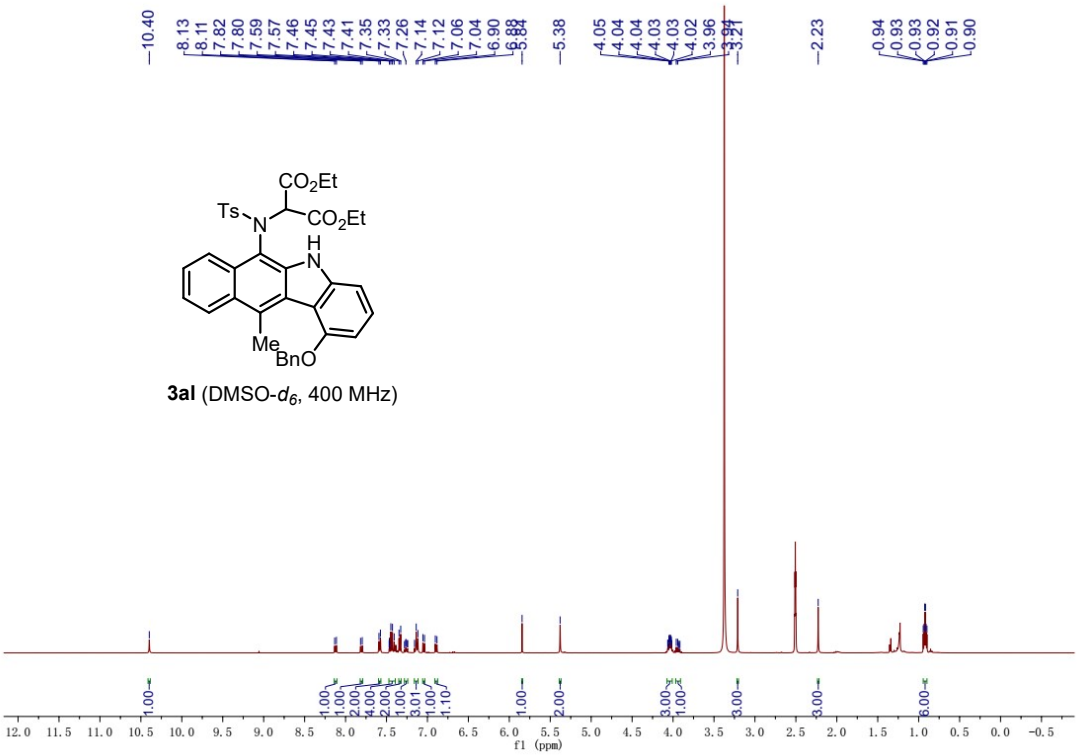
3aj (DMSO-d_6, 376 MHz)



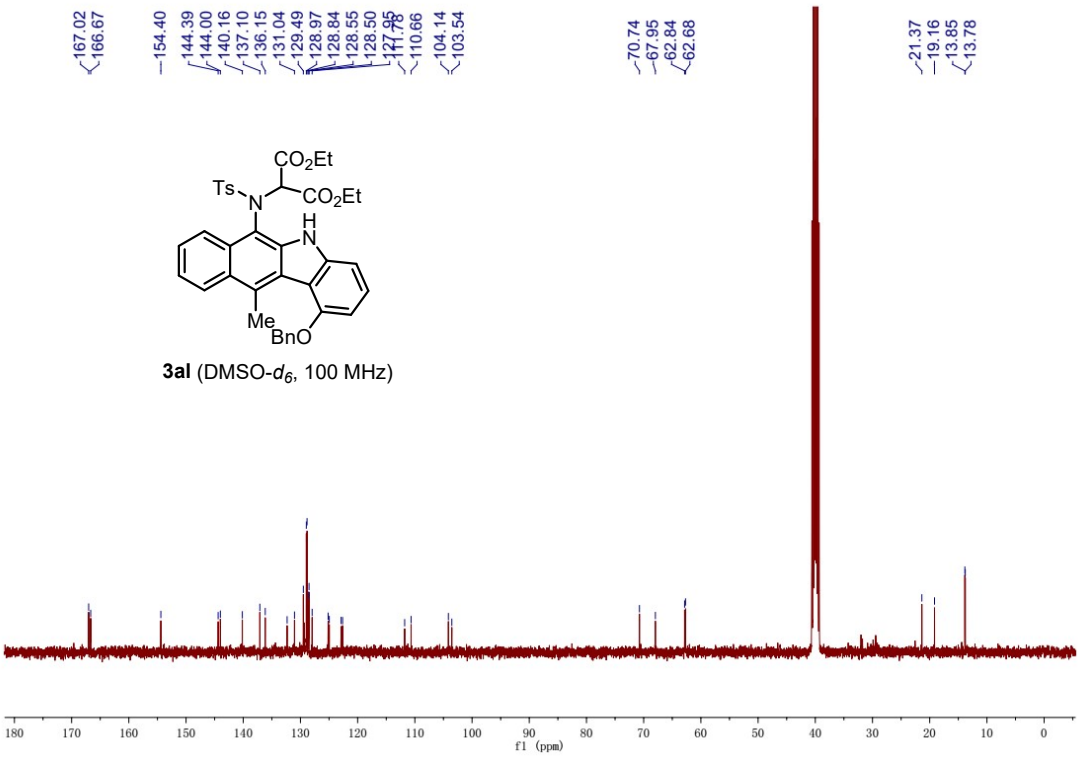
3ak (DMSO-d_6, 400 MHz)



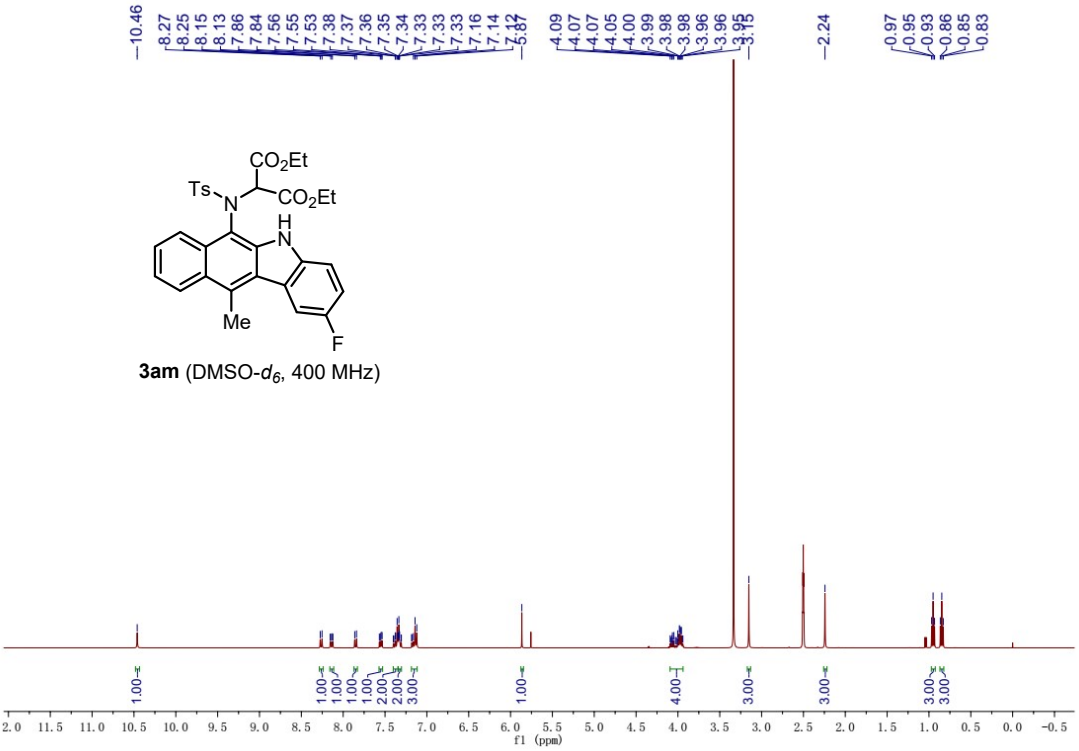
3ak (DMSO-d_6, 100 MHz)



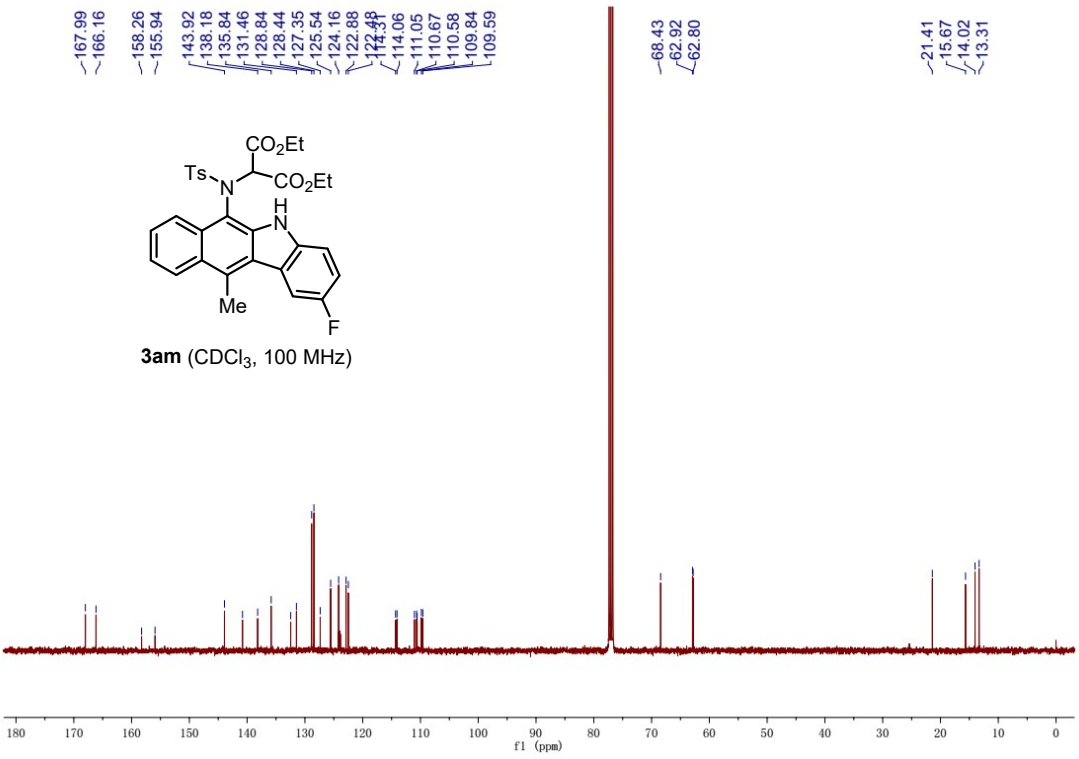
3al (DMSO-d_6, 400 MHz)



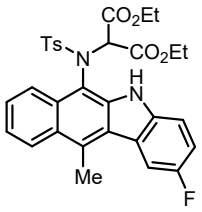
3al (DMSO-d_6, 100 MHz)



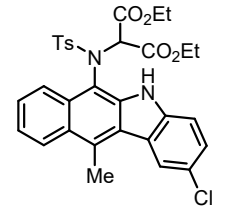
3am (DMSO-d_6, 400 MHz)



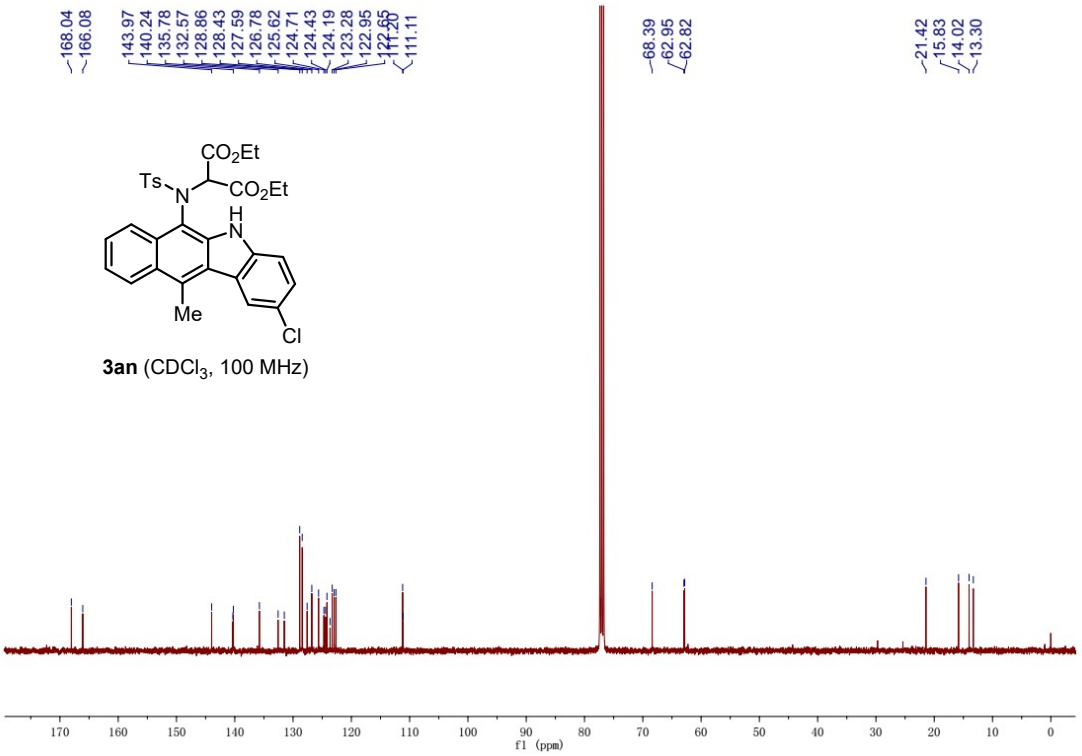
3am ($CDCl_3$, 100 MHz)



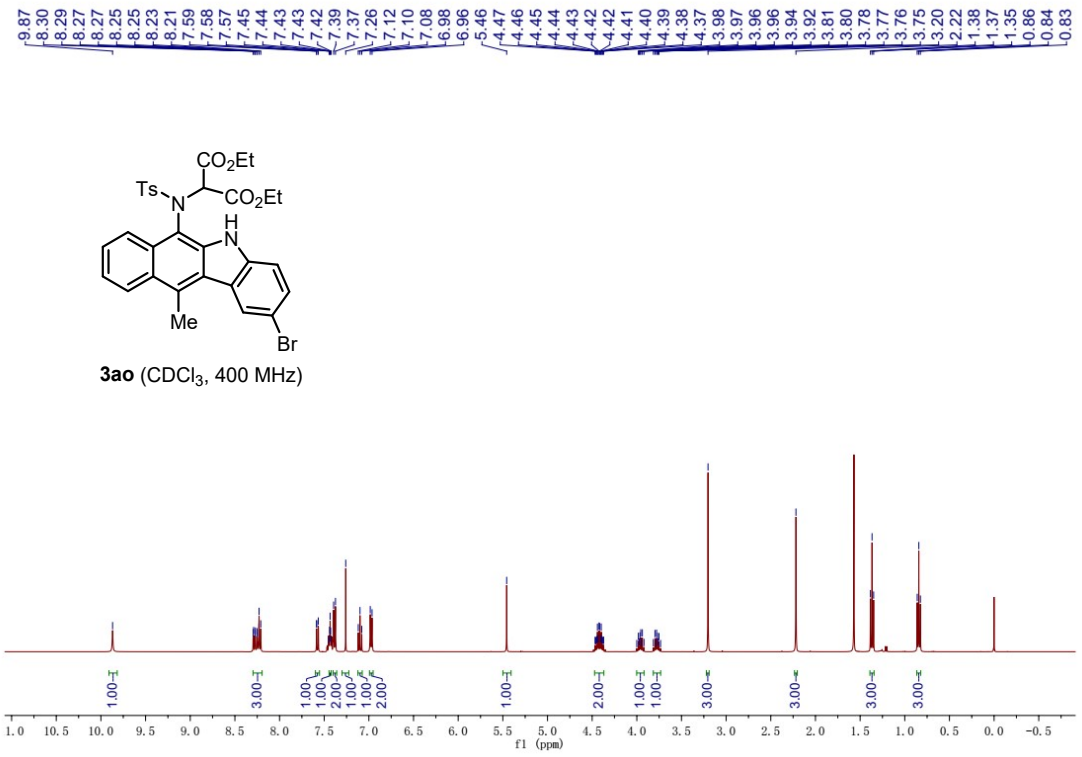
3am (DMSO-d_6, 376 MHz)



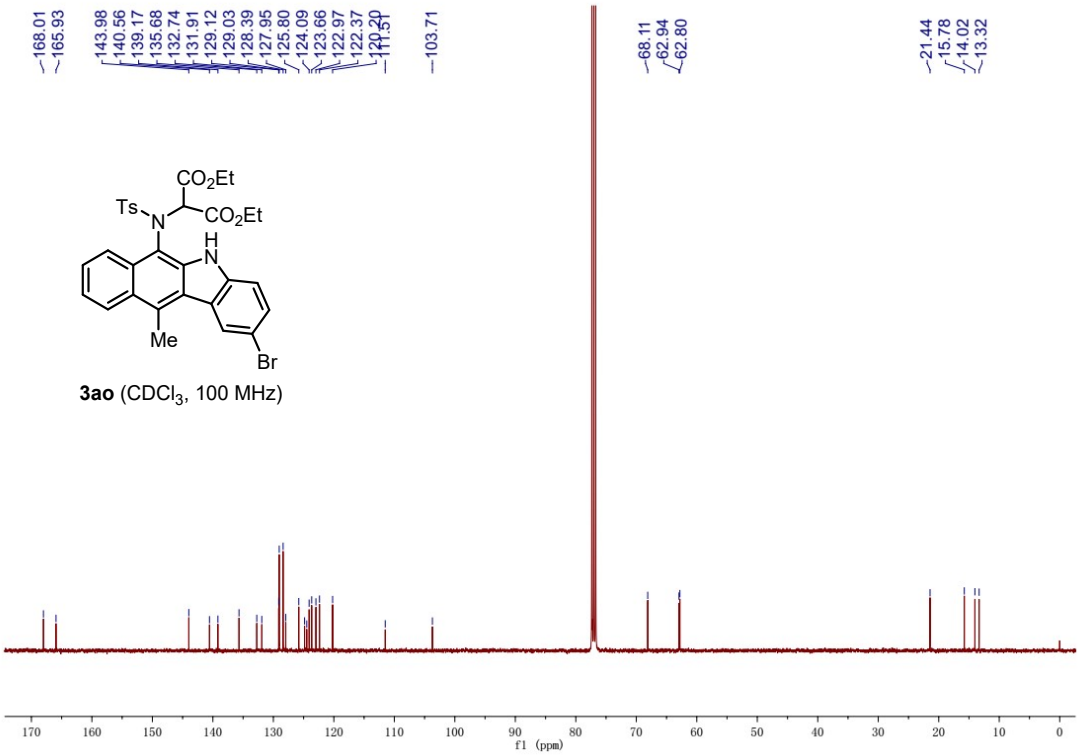
3an (DMSO-d_6, 400 MHz)



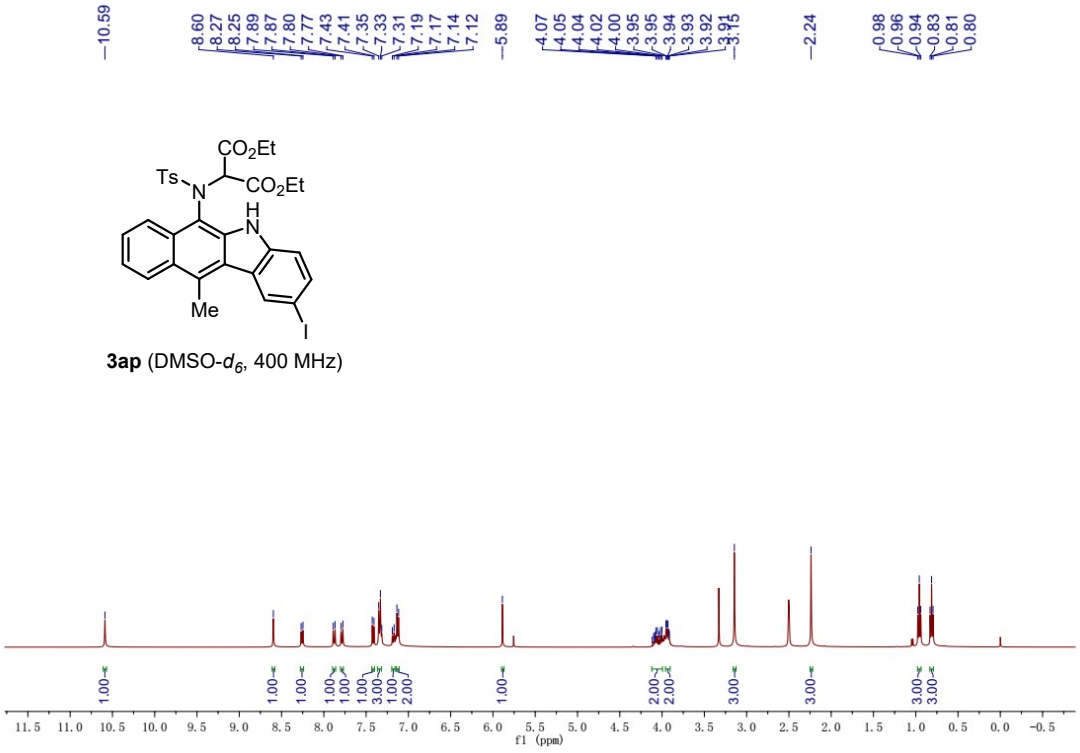
3an ($CDCl_3$, 100 MHz)



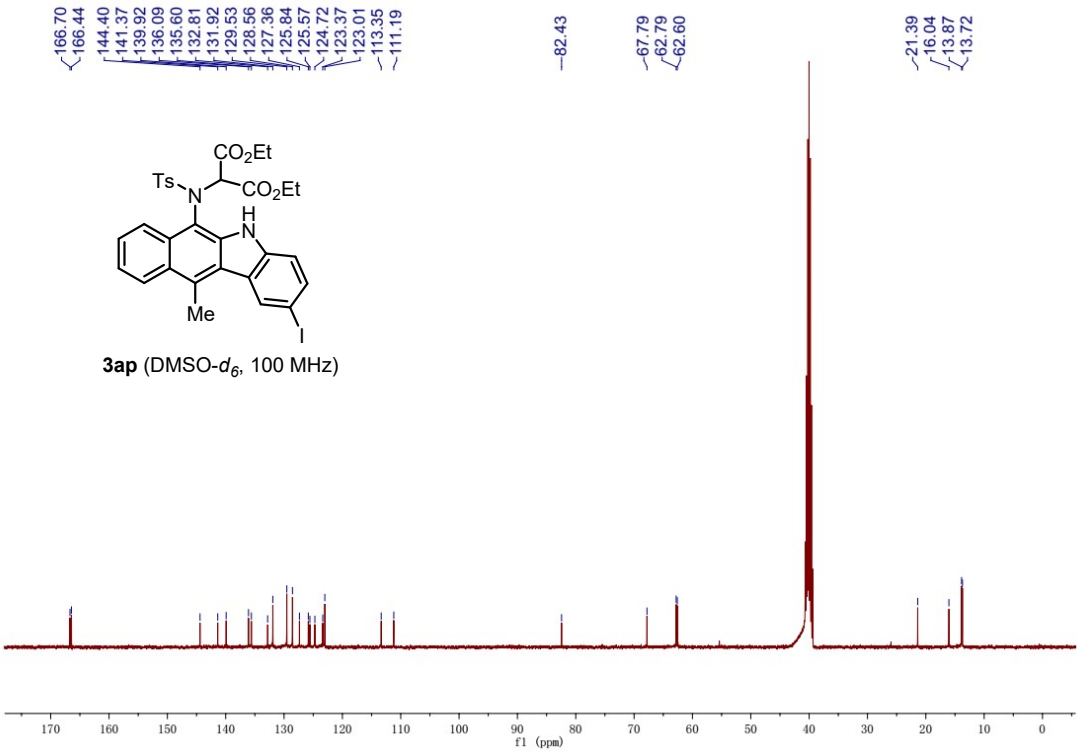
3ao ($CDCl_3$, 400 MHz)



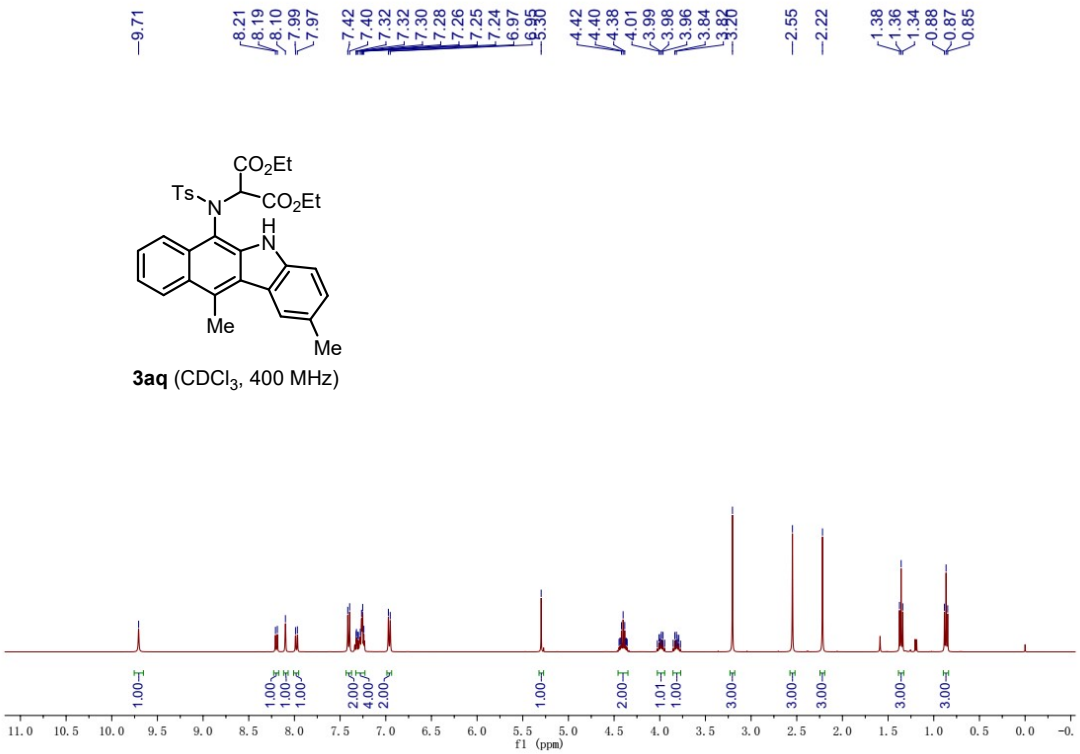
3ao ($CDCl_3$, 100 MHz)



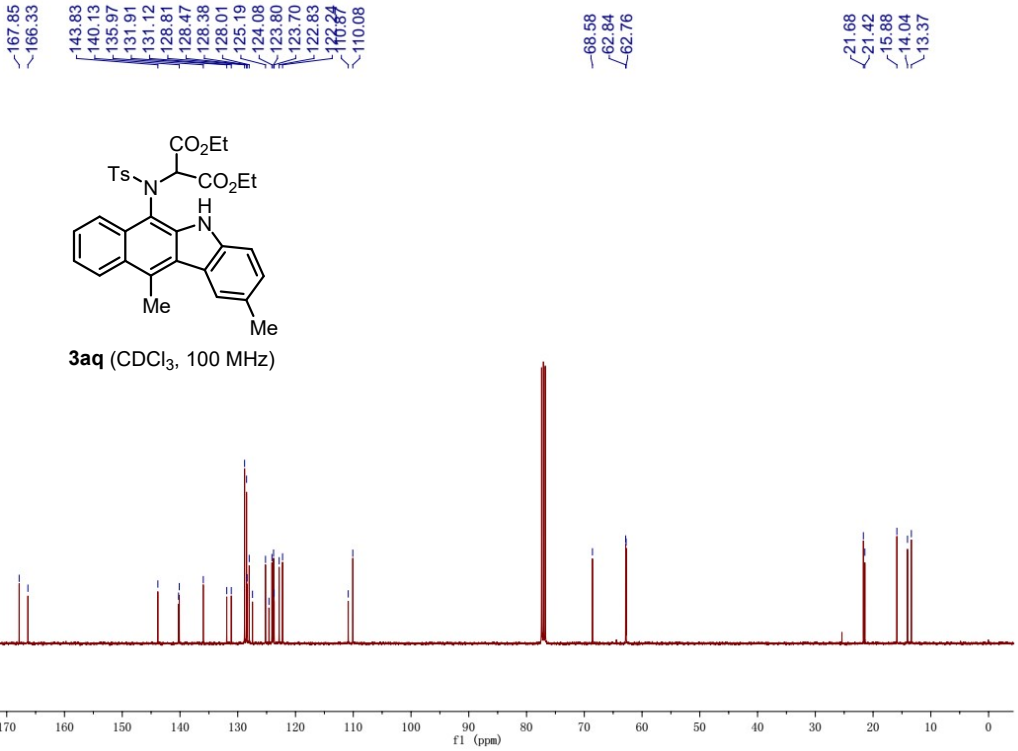
3ap (DMSO-d_6, 400 MHz)



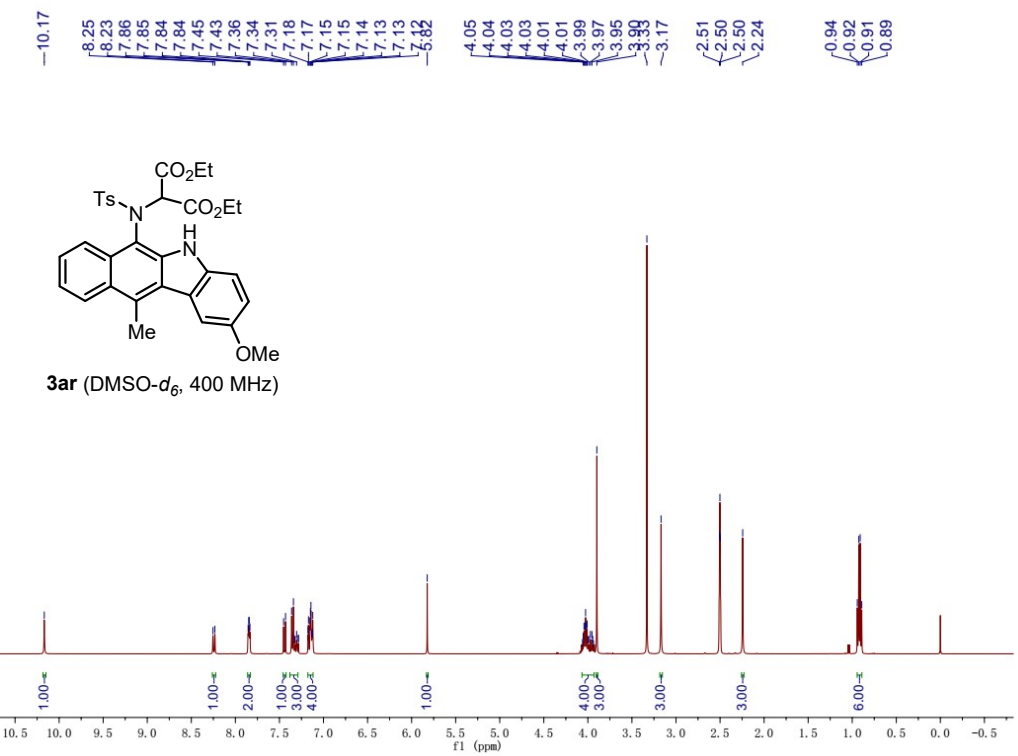
3ap (DMSO-d_6, 100 MHz)



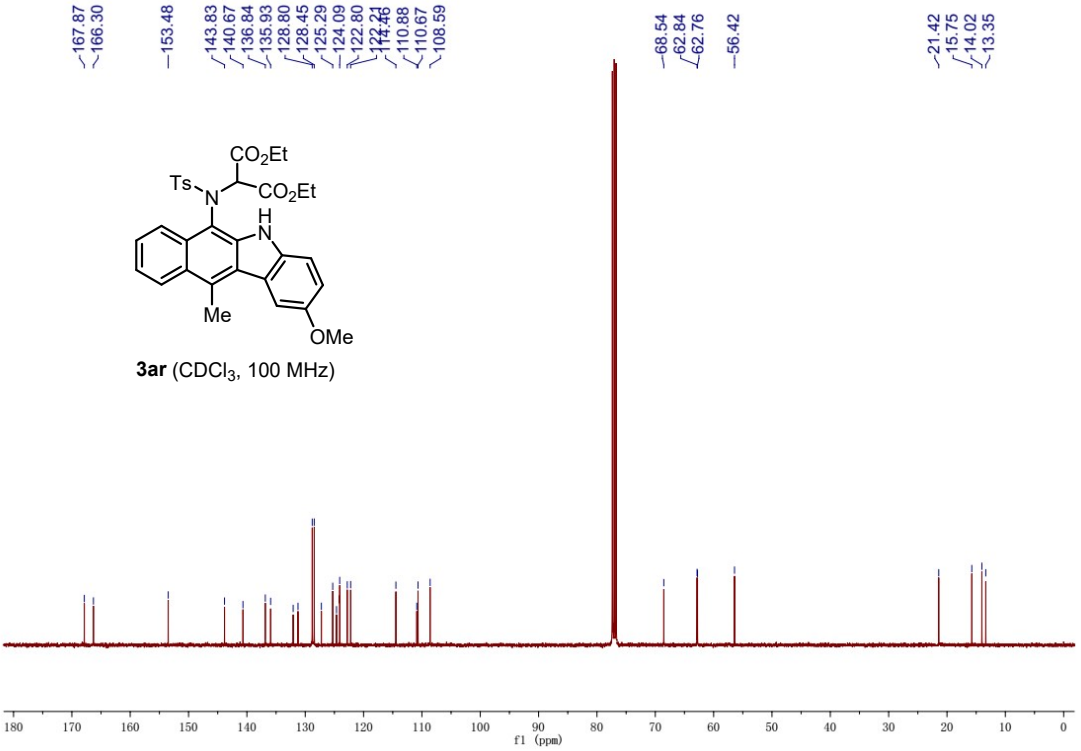
3aq ($CDCl_3$, 400 MHz)



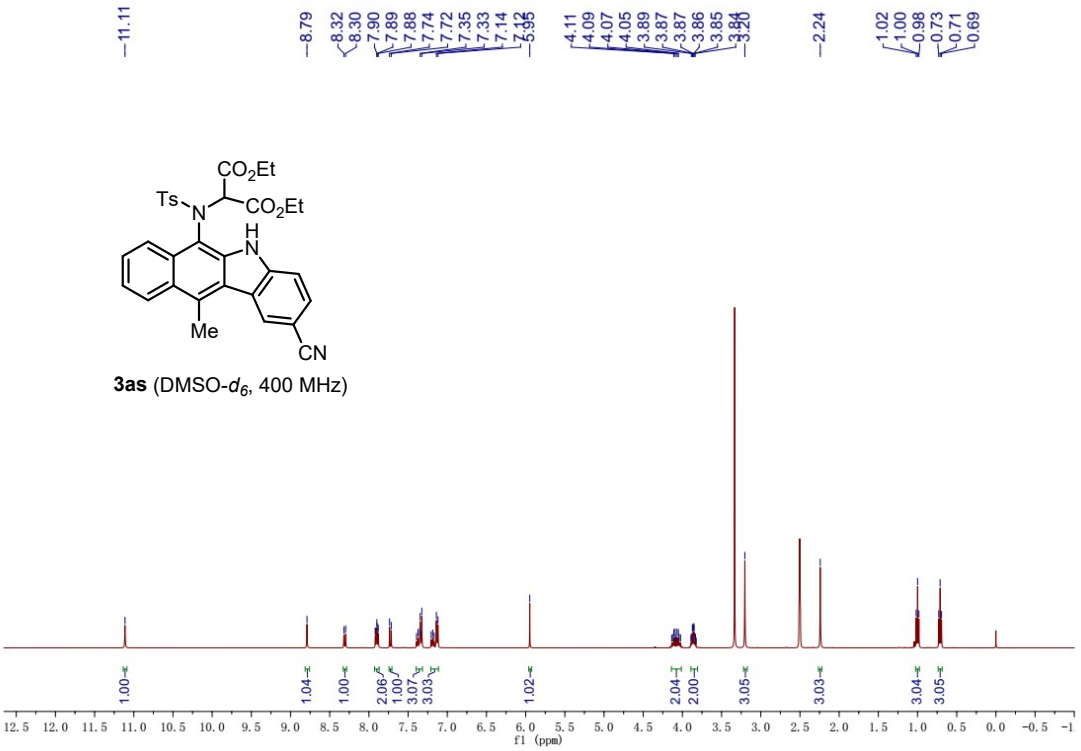
3aq ($CDCl_3$, 100 MHz)



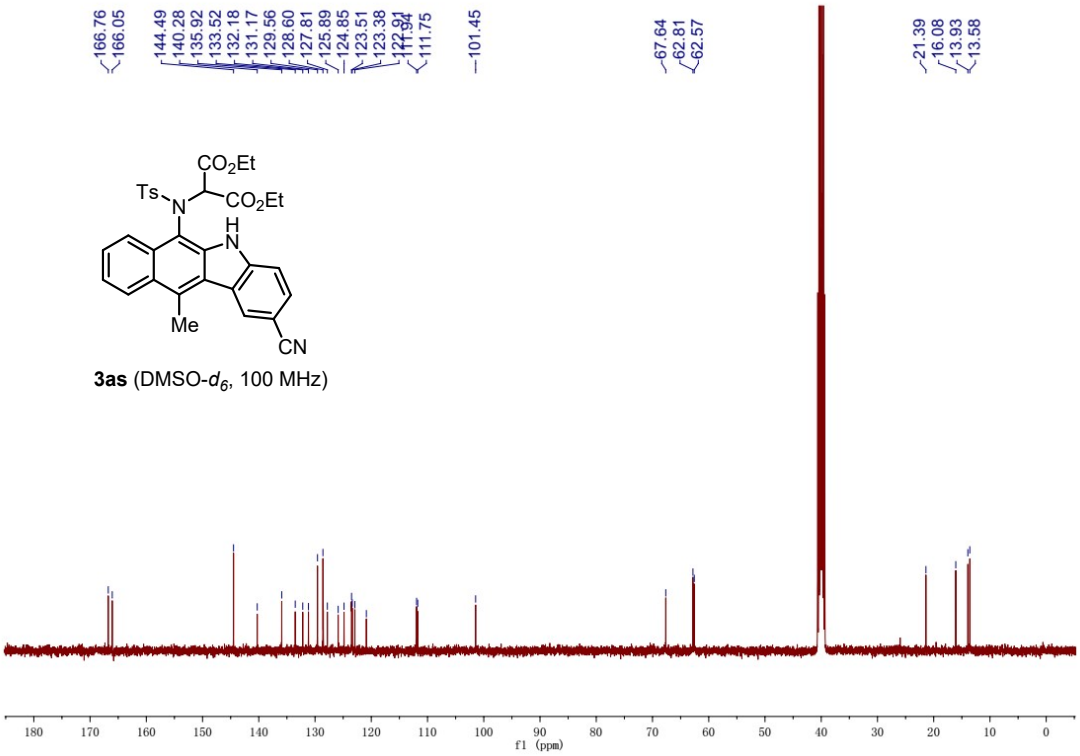
3ar (DMSO-d_6, 400 MHz)



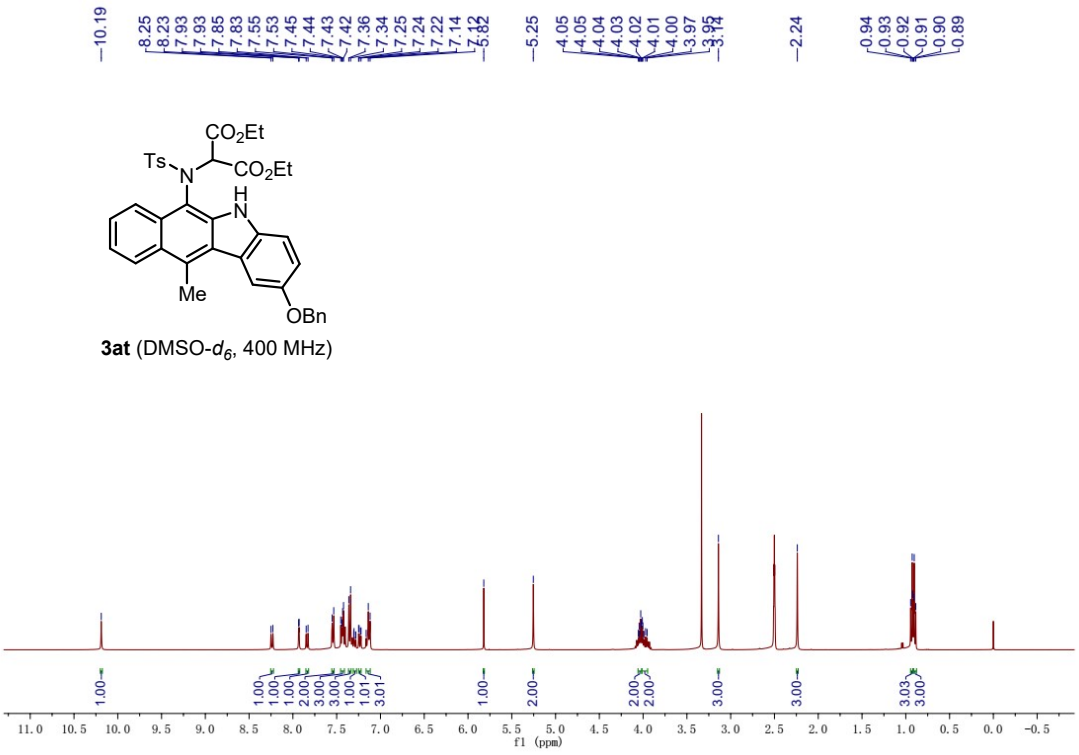
3ar ($CDCl_3$, 100 MHz)



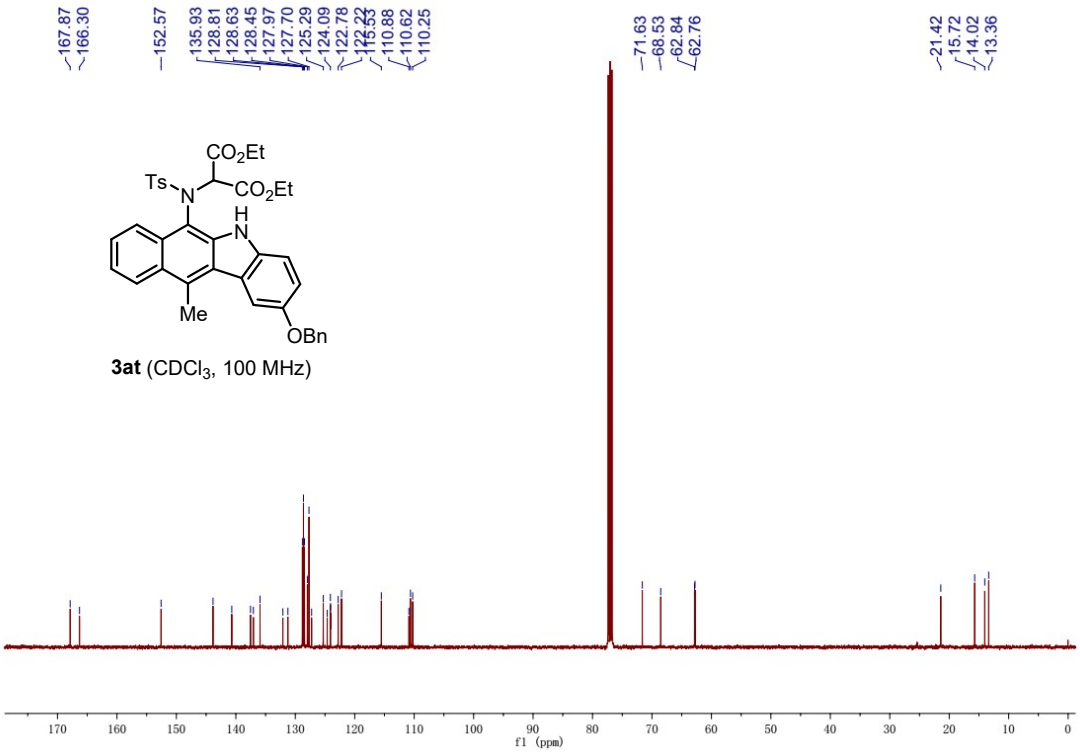
3as (DMSO-d_6, 400 MHz)



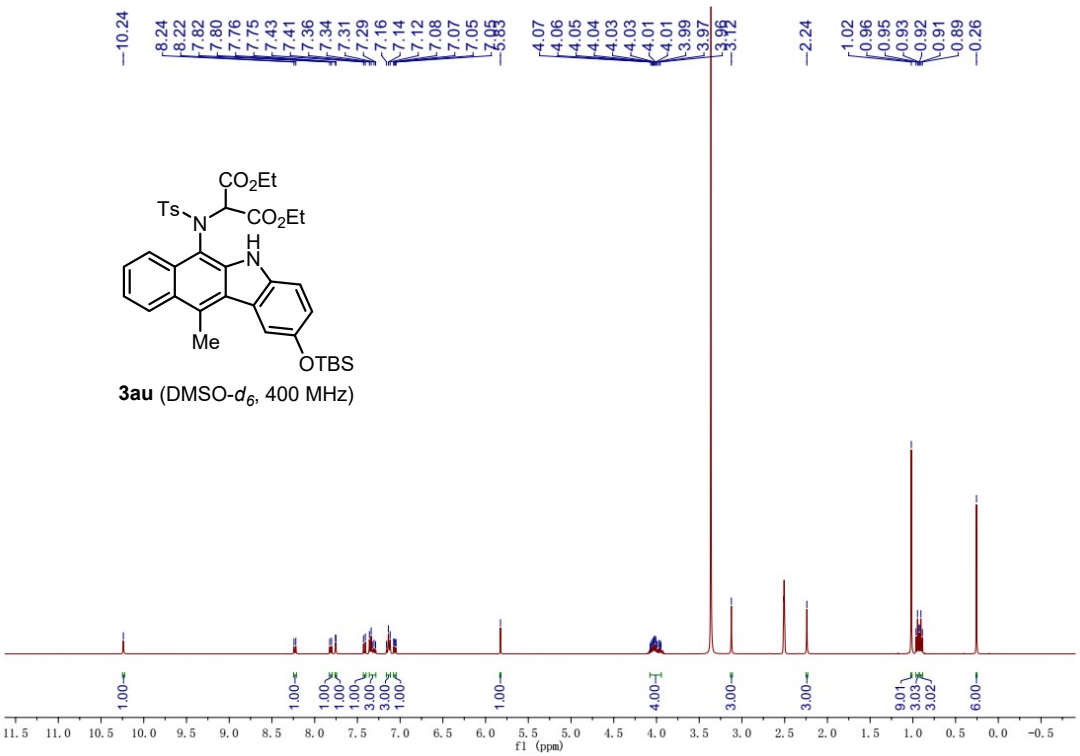
3as (DMSO-d_6, 100 MHz)



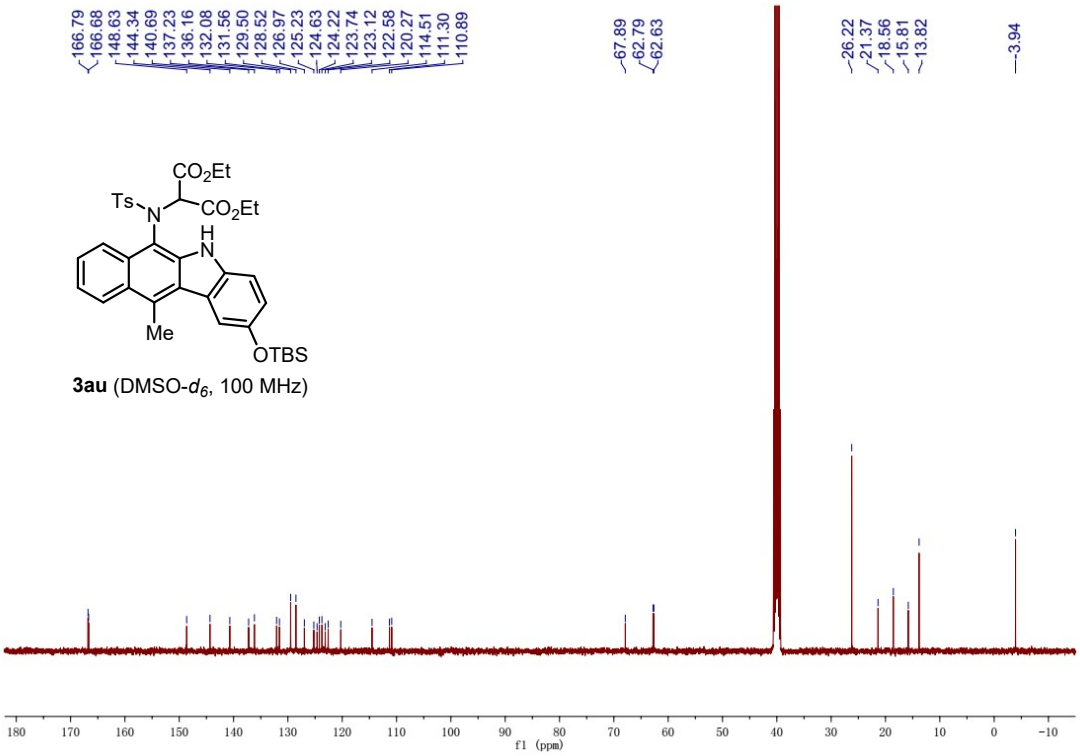
3at (DMSO-d_6, 400 MHz)



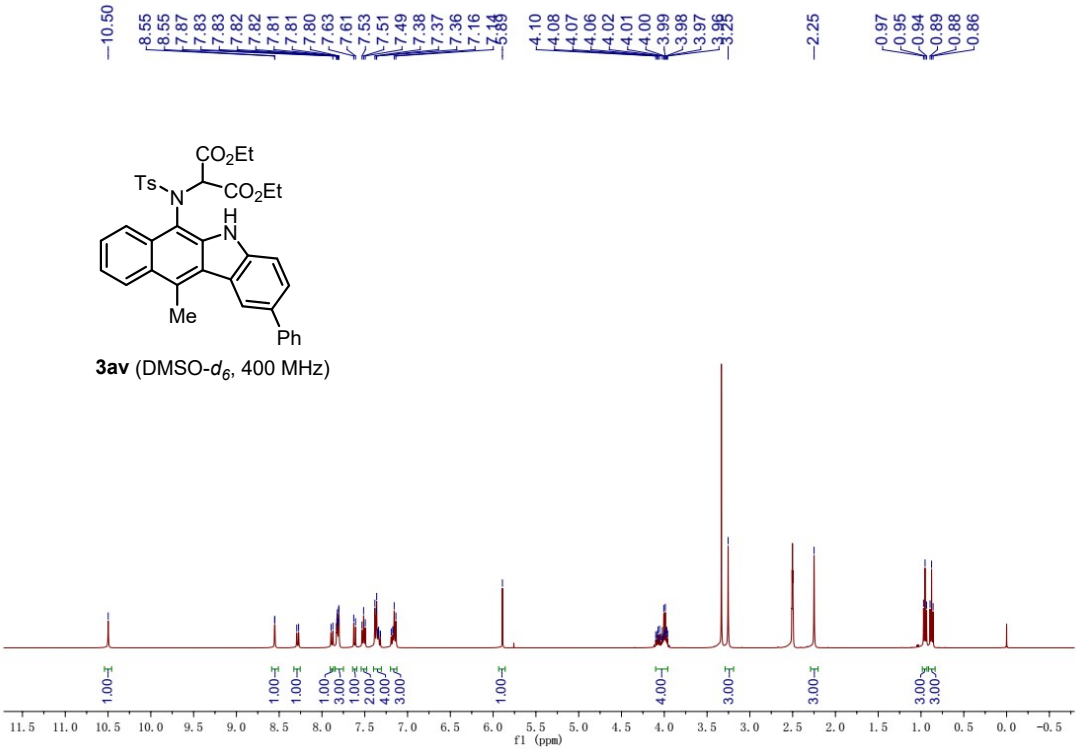
3at ($CDCl_3$, 100 MHz)



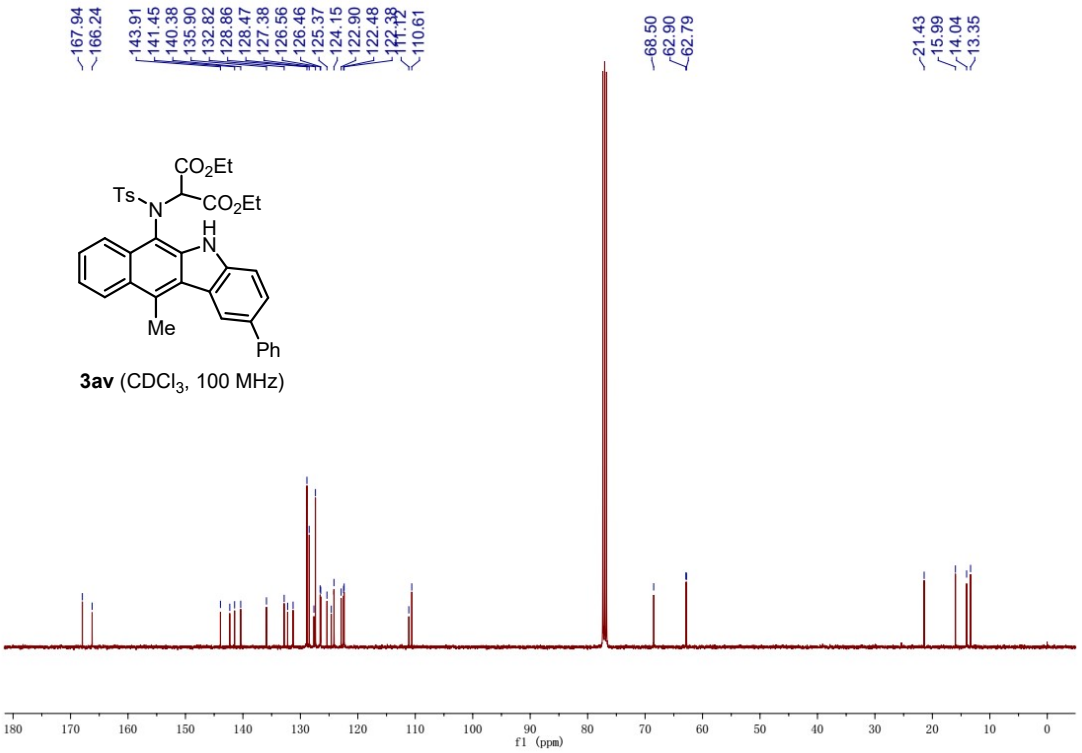
3au (DMSO-d_6, 400 MHz)



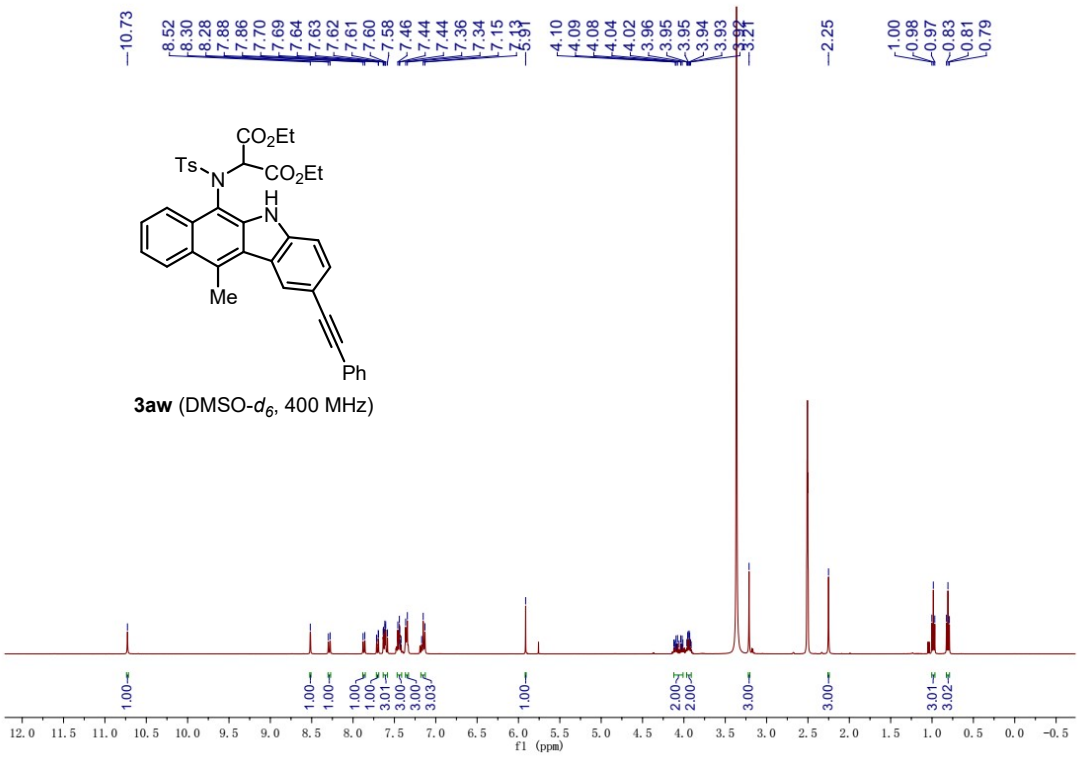
3au (DMSO-d_6, 100 MHz)



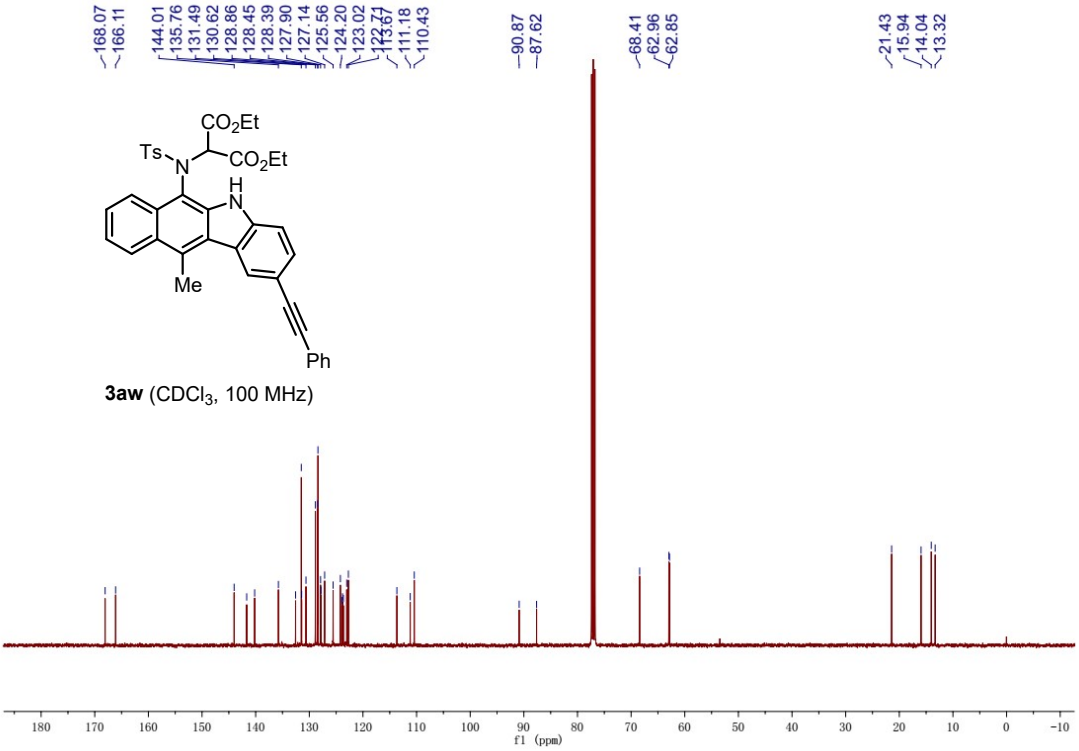
3av (DMSO-d_6, 400 MHz)



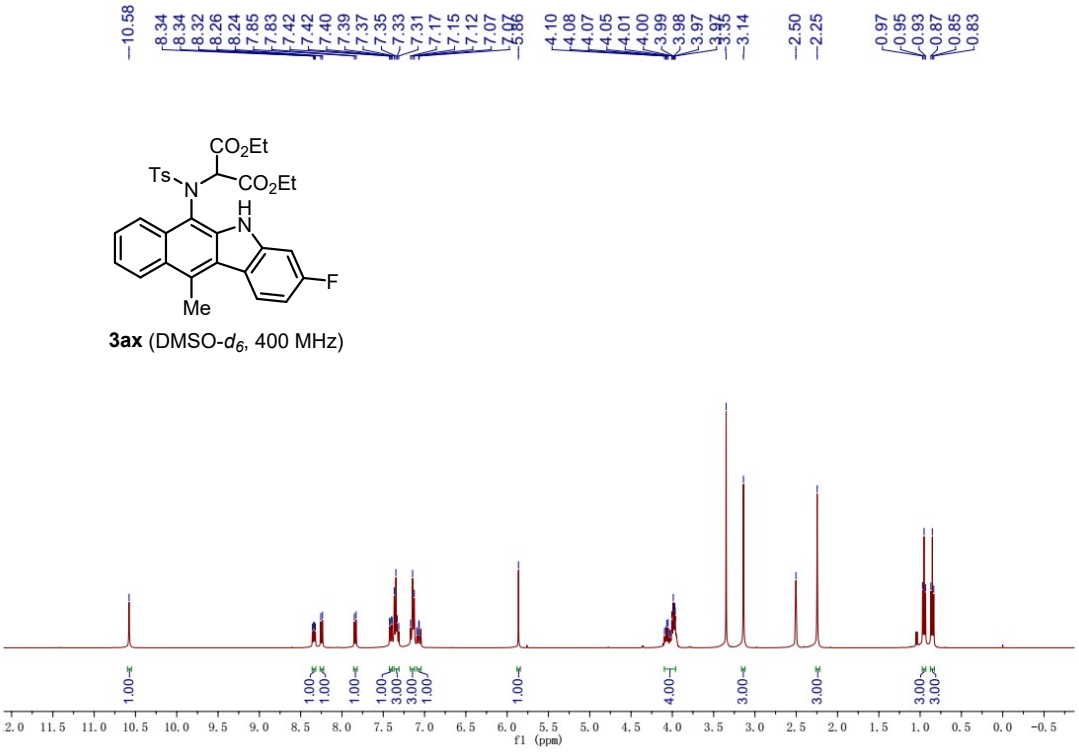
3av ($CDCl_3$, 100 MHz)



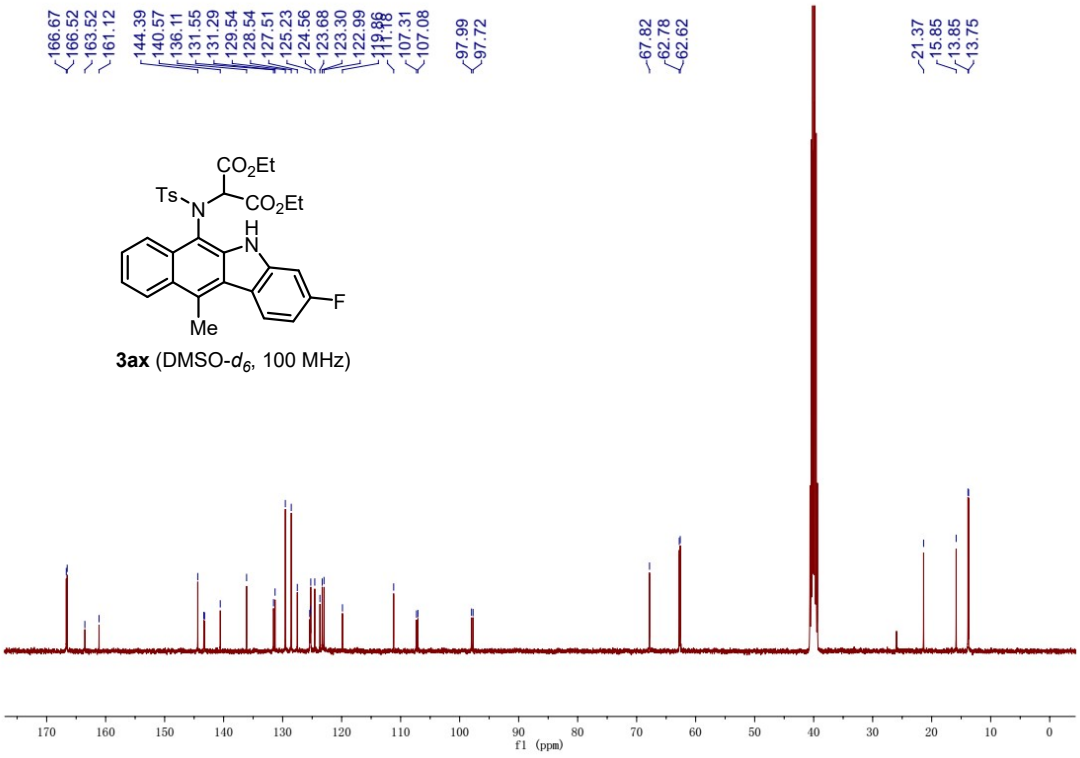
3aw (DMSO-d_6, 400 MHz)



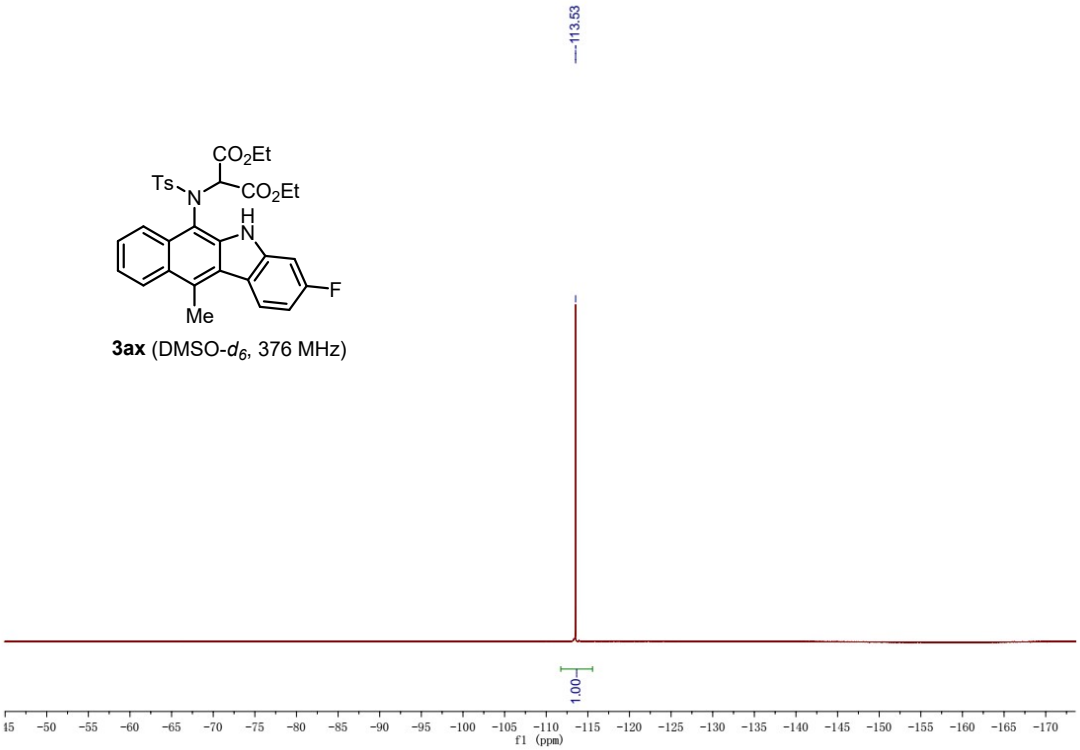
3aw ($CDCl_3$, 100 MHz)



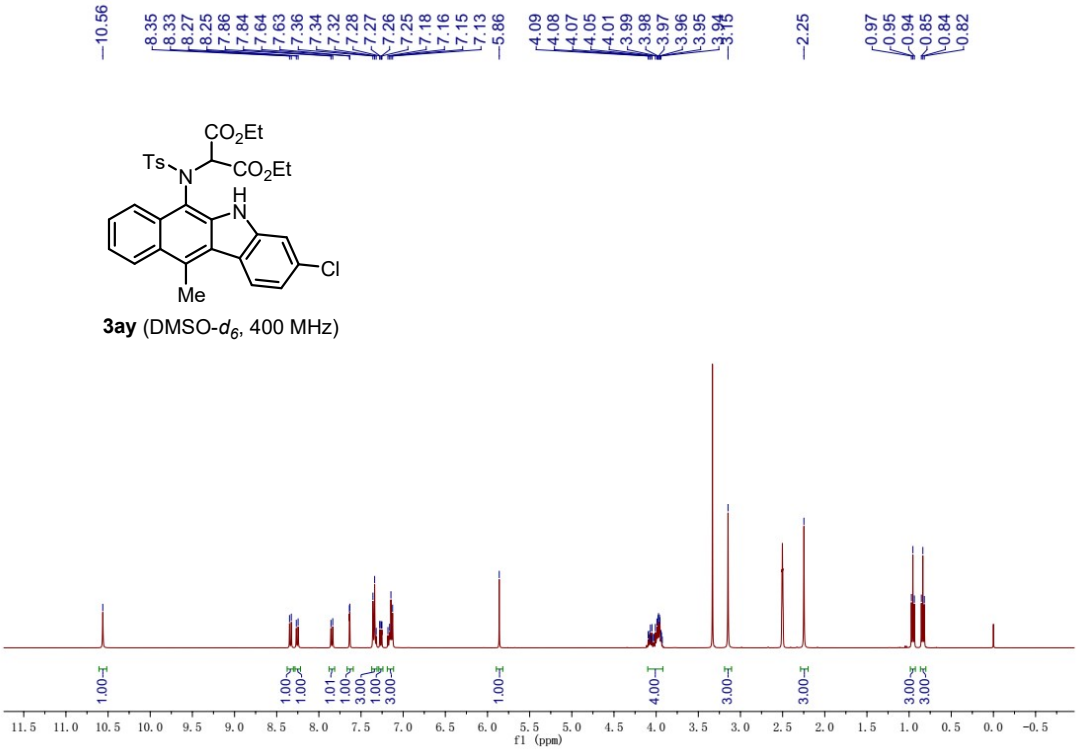
3ax (DMSO-d_6, 400 MHz)



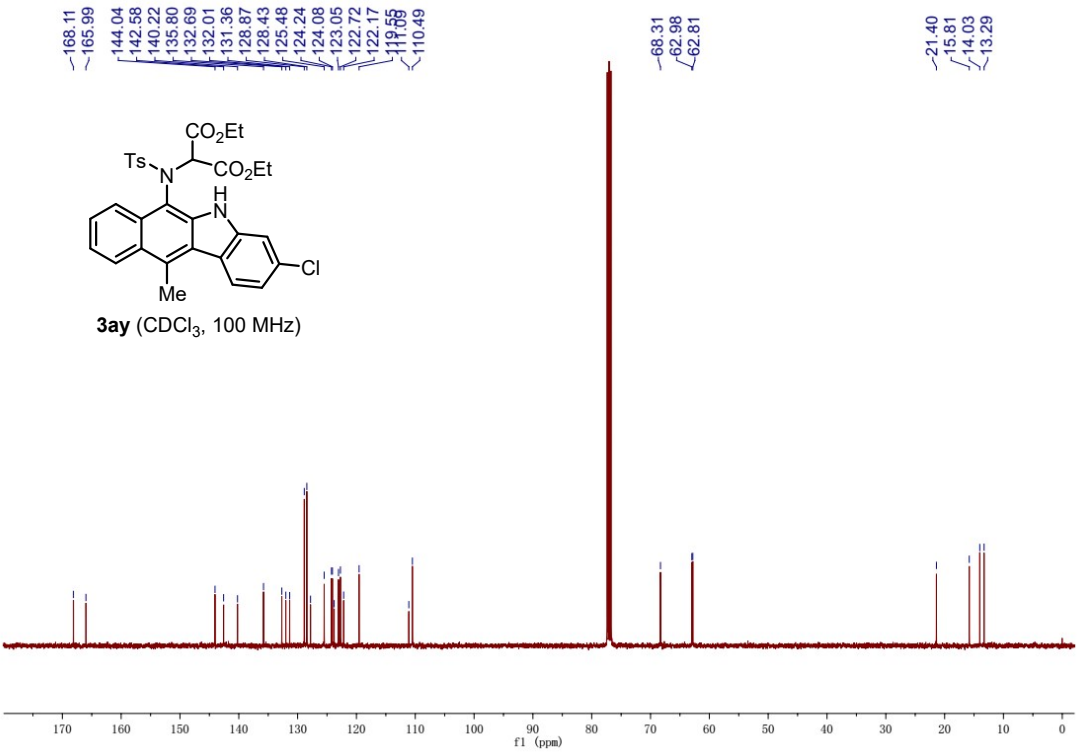
3ax (DMSO-d_6, 100 MHz)



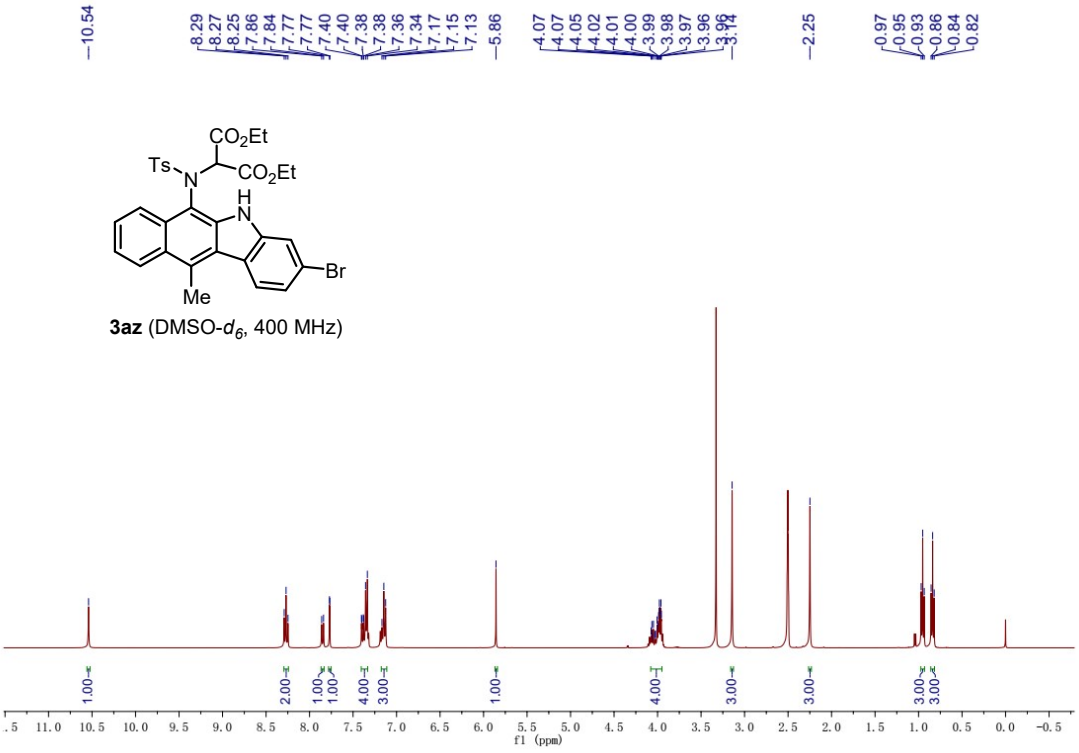
3ax (DMSO-d_6, 376 MHz)



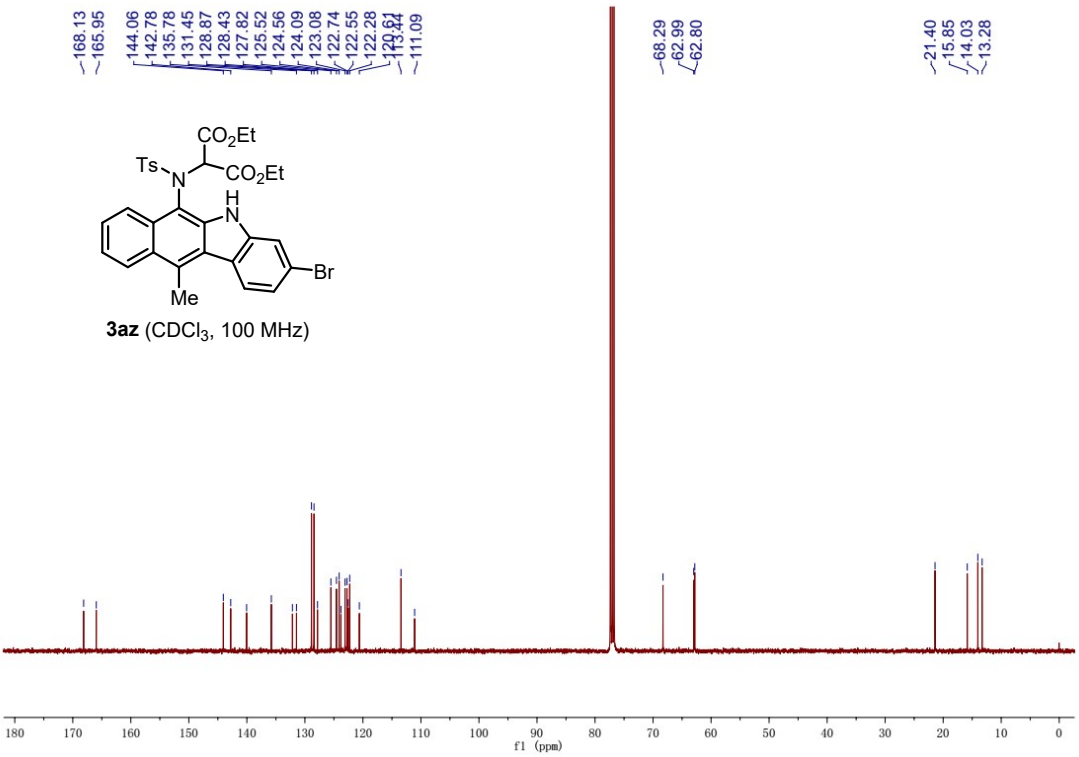
3ay (DMSO-d_6, 400 MHz)



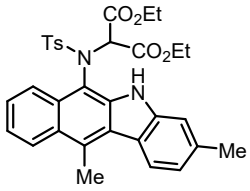
3ay ($CDCl_3$, 100 MHz)



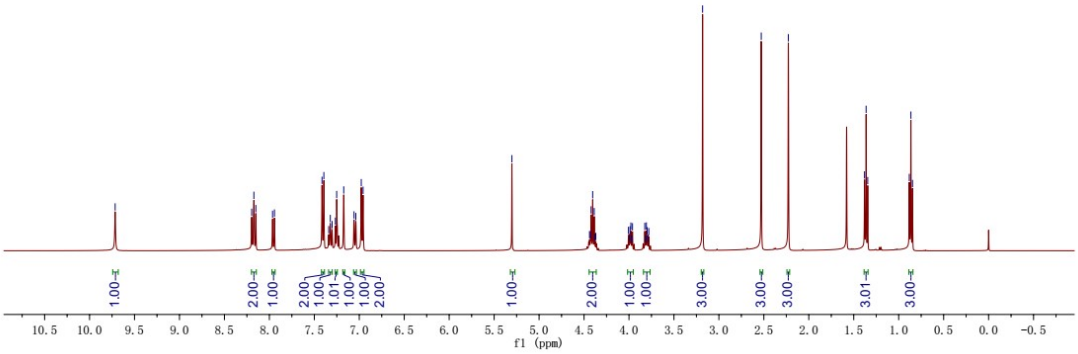
3az (DMSO-d_6, 400 MHz)

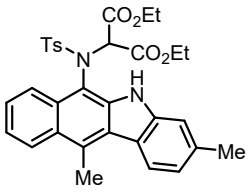


3az ($CDCl_3$, 100 MHz)

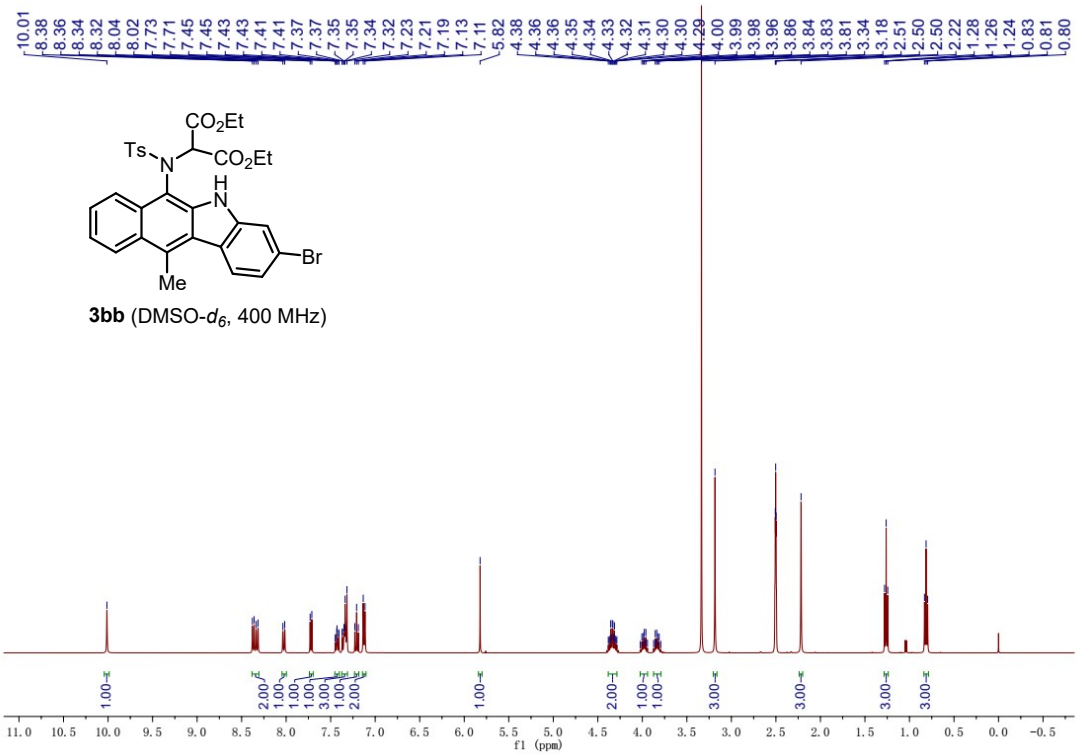


3ba ($CDCl_3$, 400 MHz)

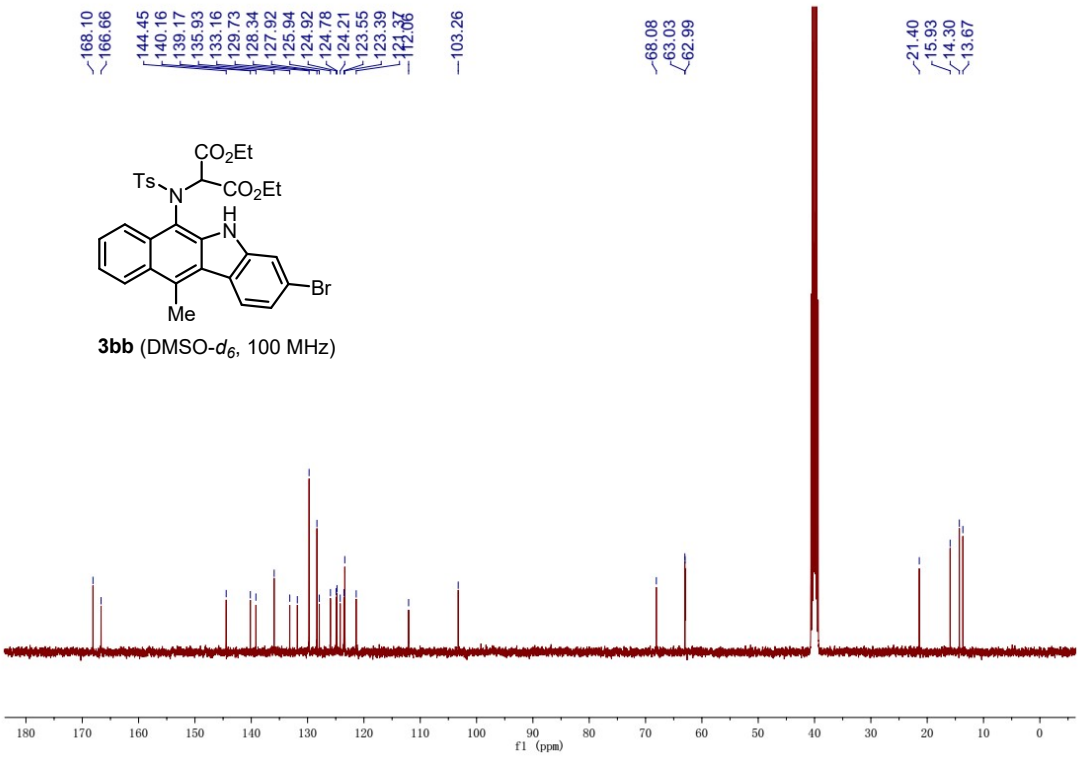




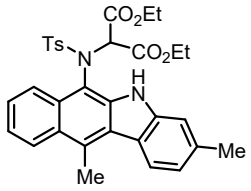
3ba ($CDCl_3$, 100 MHz)



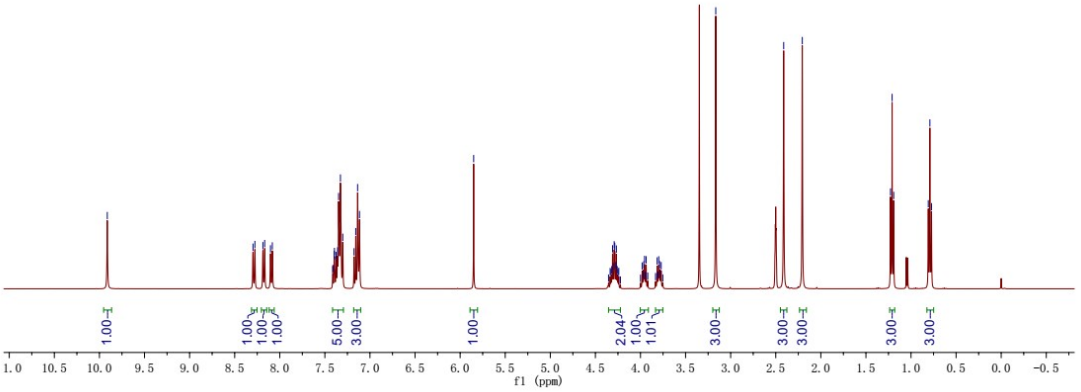
3bb (DMSO-d_6, 400 MHz)

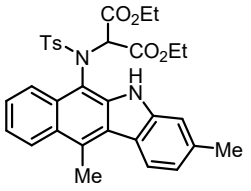


3bb (DMSO-d_6, 100 MHz)

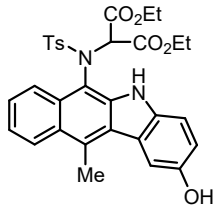


3bc (DMSO-d_6, 400 MHz)

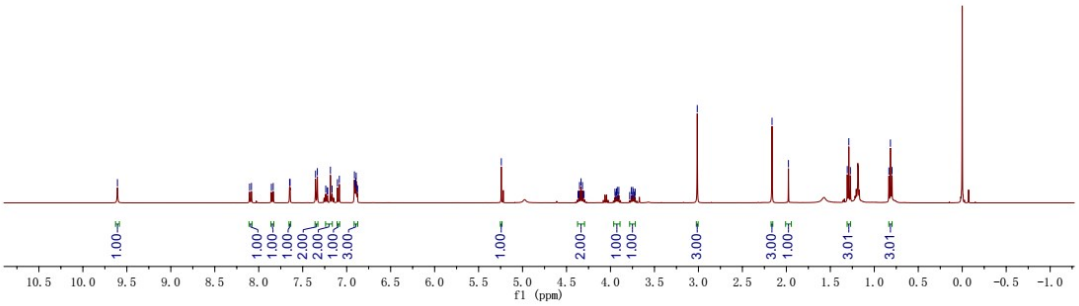


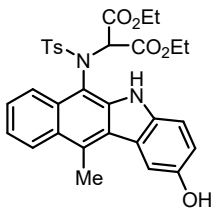


3bc (DMSO-d_6, 100 MHz)

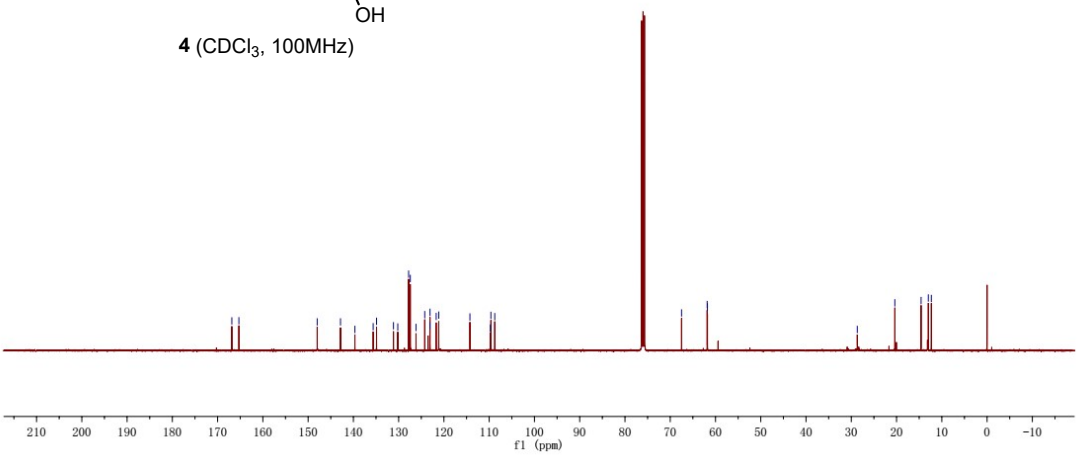


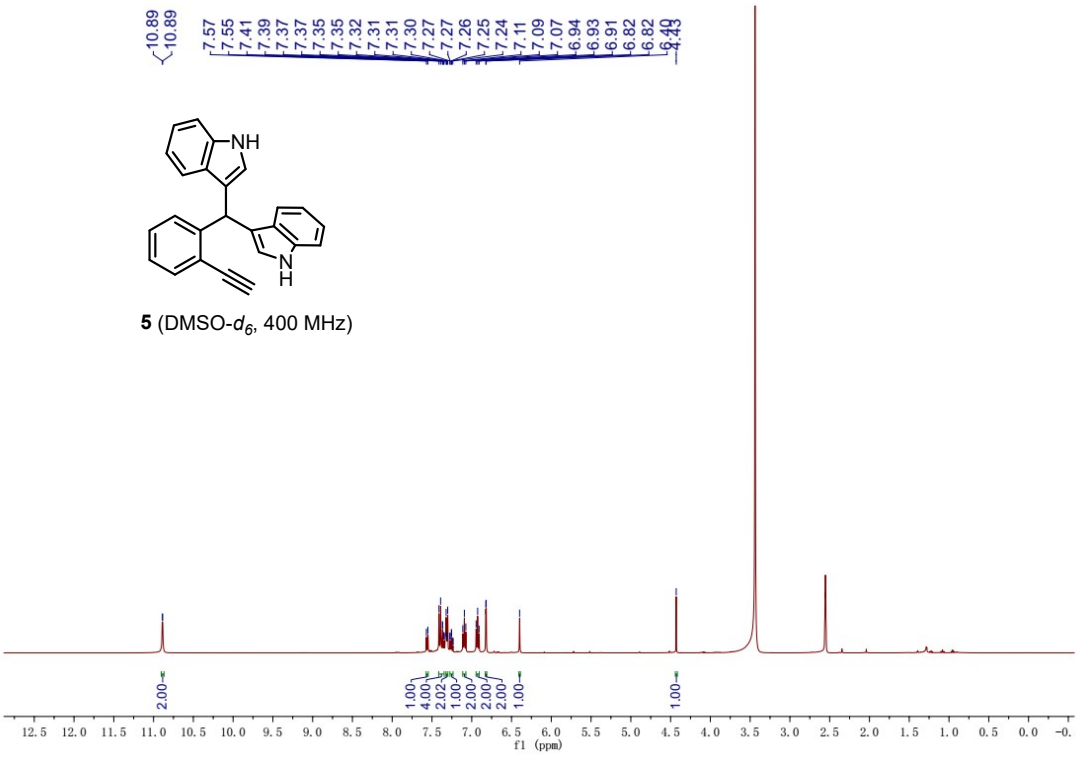
4 ($CDCl_3$, 400MHz)



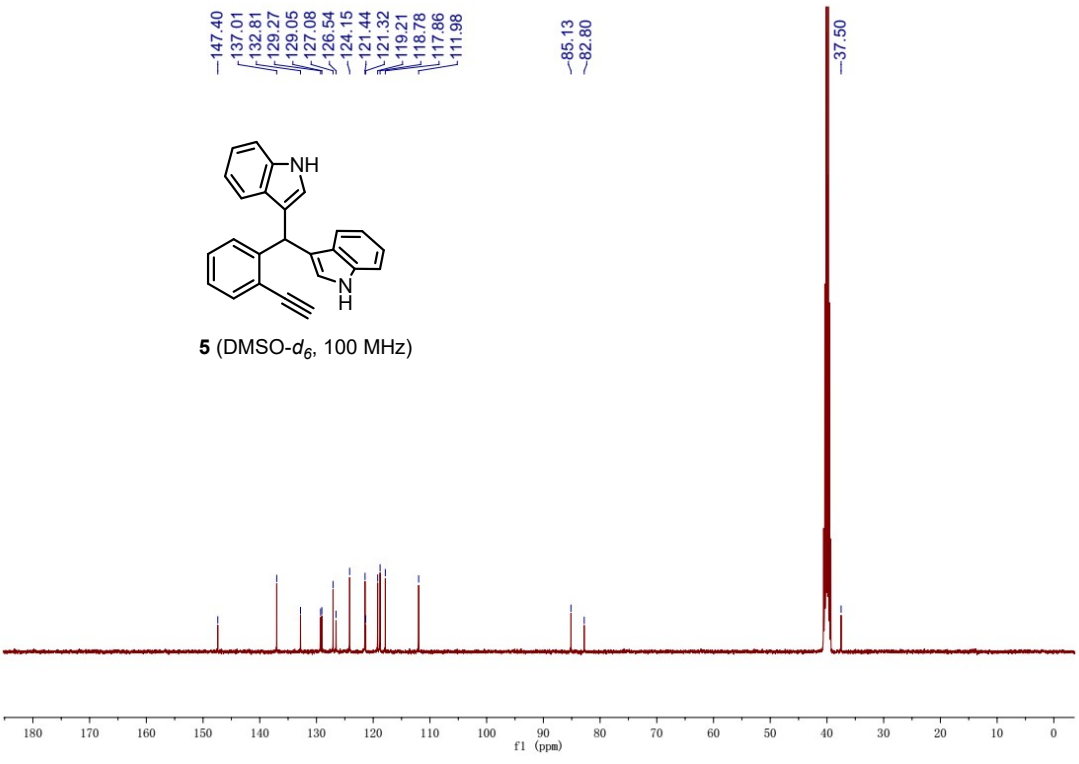


4 ($CDCl_3$, 100MHz)





5 (DMSO-d_6, 400 MHz)



5 (DMSO-d_6, 100 MHz)

5. X-ray crystal structures

The crystal was obtained by slow evaporation of **3ai, 3ax** or **5** in CH_2Cl_2/*n*-Hexane = 1:3. The direct method was used to resolve the crystal structure using the free OLEX2 program embedded with SHELX-2014.

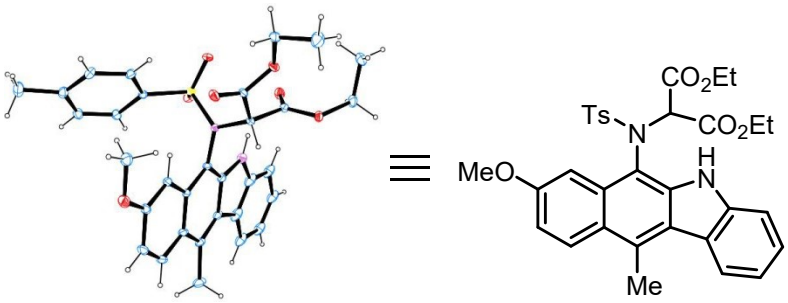


Figure S2. X-ray structure of **3ai** (with the 10% probability level)

Compound 3ai		**CCDC:**2314005
Bond precision: C-C =0.0066 Å		Wavelength = 0.71073
a=9.4792(14)	b=13.0255(19)	c=15.078(2)
alpha=66.132(2)	beta=81.509(3)	gamma=69.931(3)
Cell setting: Monoclinic		Moiety formula: $C_{32}H_{32}N_2O_7S$
Cell Volume = 1599.0(4)		Space group: P-1
Data completeness = 0.993		Theta(max) = 25.030
R(reflections) = 0.0692(3584)		WR2(reflections) = 0.2199(5617)
S = 1.094		Radiation type: MoK\a
Measurement device type: CCD area detector		Measurement method: phi and omega scans
Structure solution: SHELXS-2014		Structure refinement: SHELXL-2014

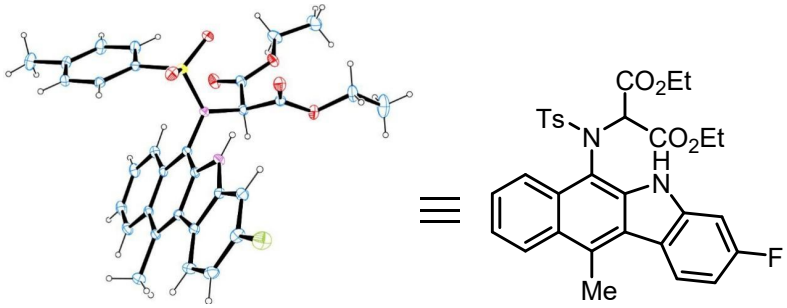


Figure S3. X-ray structure of **3ax** (with the 10% probability level)

Compound 3ax		**CCDC:**2301357
Bond precision: C-C =0.0043 Å		Wavelength = 0.71076
a=12.9151(17)	b=15.309(2)	c=14.3386(18)
alpha=90	beta=98.673(2)	gamma=90
Cell setting: Monoclinic		Moiety formula: $C_{31}H_{29}FN_2O_6S$
Cell Volume = 2802.6(6)		Space group: P 21/c
Data completeness = 0.983		Theta(max) = 27.560
R(reflections) = 0.0609(3579)		WR2(reflections) = 0.1768(6361)
S = 1.051		Radiation type: MoK\a
Measurement device type: CCD area detector		Measurement method: phi and omega scans
Structure solution: SHELXS-2014		Structure refinement: SHELXL-2014

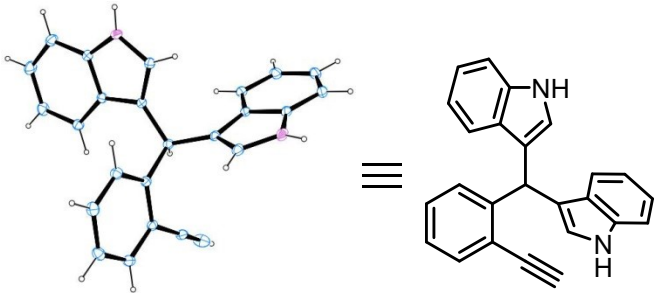


Figure S4. X-ray structure of **5** (with the 10% probability level)

Compound 5		**CCDC:**2327200
Bond precision: C-C =0.0031 Å		Wavelength = 0.71073
a=8.2463(10)	b=10.1584(13)	c=12.5010(15)
alpha=67.384(1)	beta=76.173(2)	gamma=84.943(2)
Cell setting: Monoclinic		Moiety formula: $C_{25}H_{18}N_2$
Cell Volume = 938.7(2)		Space group: P-1
Data completeness = 0.992		Theta(max) = 25.680
R(reflections) = 0.0426(2384)		WR2(reflections) = 0.1364(3535)
S = 1.005		Radiation type: MoK\a
Measurement device type: CCD area detector		Measurement method: phi and omega scans
Structure solution: SHELXS-2014		Structure refinement: SHELXL-2014