Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Palladium-Catalyzed [4+3]-Annulations of Oxotryptamines with Allyl Dicarbonates: an Approach to Spiro[azepane-4,3'-oxindoles]

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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) was 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) was performed on a Bruker single crystal X-ray diffractometer (model of the instrument–AXS D8 Quest System).

Melting Point Apparatus

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

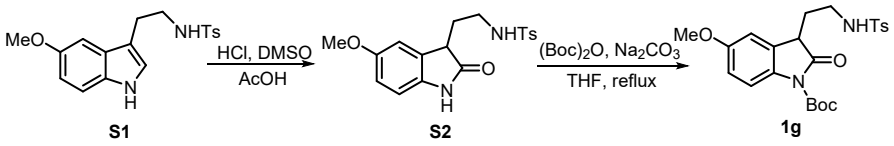
Chromatography

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

2.1 Experimental procedure for the synthesis of oxotryptamine 1g

The oxotryptamines **1**, **9** and *N*-methyl oxotryptamine **11** were prepared according to the literature procedure. [1, 2] These substrates are used directly without further characterization.



S1 **S2** **1g**

DMSO (2.5 mL, 35 mmol, 10 equiv.) was added to a suspension of **S1** (1.2 g, 3.5 mmol, 1.0 equiv.) in AcOH (35 mL, 1 M). The mixture was cooled to 0 ℃, and concentrated HCl (5.3 mL, 18 equiv., 38%) was added dropwise. The reaction was stirred for 4-5 h at this temperature. After that, it was neutralized with saturated aqueous Na_2CO_3, and extracted with EtOAc (100 mL × 2) and washed with brine (100 mL × 2). The combined organic layers were dried over anhydrous Na_2SO_4. The solvent was removed in *vacuo* to provide crude product **S2**. The crude product **S2** was used in the next step without further purification.

To a solution of newly prepared crude **S2** in THF (50 mL), di-*tert*-butyl dicarbonate (0.85 g, 3.9 mmol, 1.1 equiv.) and Na_2CO_3 (3.0 g, 28 mmol, 8.0 equiv.) were added at 0 ºC, respectively. After the reaction was stirred under the reflux conditions for 8 h, the undissolved solid was filtered off. Then 1 M HCl aqueous solution was added to adjust the pH to neutral. The mixture was extracted with EtOAc (100 mL × 2). The combined organic layers were dried over $MgSO_4$ and concentrated in *vacuo*. The residue was purified by silica gel column chromatography (EtOAc: Petroleum Ether = 1:3, V:V) to give the oxotryptamine **1g** as a white solid.

***Tert*-butyl 5-methoxy-3-(2-((4-methylphenyl)sulfonamido)ethyl)-2-oxoindoline-1-carboxylate(1g)**

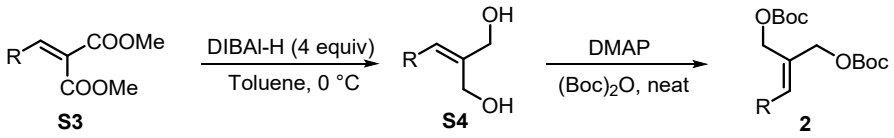
White solid; 75 % yield (1.2 g, 2.6 mmol); m.p. 112-114 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.74-7.68 (m, 3H), 7.29 (t, *J* = 8 Hz 2H), 6.83-6.77 (m, 2H), 5.03 (t, *J* = 6.4 Hz, 1H), 3.81 (s, 3H), 3.62-3.59 (m, 1H), 3.22-3.17 (m, 2H), 2.42 (s, 3H), 2.26-2.16 (m, 1H), 2.02-1.93 (m, 1H), 1.63 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 176.2, 157.0, 149.0, 143.5, 136.9, 133.2, 129.8, 128.3, 127.1, 116.0, 113.2, 109.9, 84.4, 55.7, 43.6, 40.2, 31.3, 28.1, 21.5.

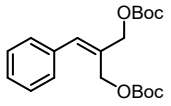
HRMS (TOF-ESI$^+$) m/z: calcd for $C_{23}H_{28}N_2O_6SNa$ $[M+Na]^+$ 483.1560, found 483.1565.

2.2 General Experimental procedure for the synthesis of allyl dicarbonates



The 2-(arylmethylene)propane-1,3-diols **S4** were prepared according to the literature procedure.[3] The allyl dicarbonates were synthesized according to the following steps: to a mixture of diols **S5** (5 mmol, 1 equiv.) and Boc_2O (20 mmol, 4 equiv.), DMAP (0.05 mmol, 1 mol%) was added. The solution was gently heated using a heat gun until effervescence was observed. After completion of the reaction (determined by TLC), the mixture was extracted with EtOAc (100 mL × 2) and washed with brine (100 mL × 2). The combined organic layers were dried, concentrated and purified by silica gel flash column chromatography (EtOAc: Petroleum Ether = 1:19～1:9, V:V) to afford allyl dicarbonates **2**.

2-Benzylidenepropane-1,3-diyl di-tert-butyl bis(carbonate) (2a)



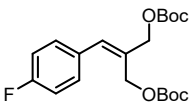
Colorless oil; 90% yield (1.6 g, 4.5 mmol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35-7.31 (m, 2H), 7.28-7.24 (m, 2H), 7.23 (s, 1H), 6.86 (s, 1H), 4.79 (s, 2H), 4.76 (s, 2H), 1.50 (s, 9H), 1.49 (s, 9H).

^{13}C NMR ($CDCl_3$, 400 MHz) δ 153.3, 153.2, 135.3, 134.8, 130.7, 128.8, 128.4, 127.8, 82.11, 82.07, 68.6, 62.9, 27.8, 27.7.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{20}H_{28}O_6Na$ $[M+Na]^+$ 387.1778, found 387.1788.

Di-*tert*-butyl (2-(4-fluorobenzylidene)propane-1,3-diyl) bis(carbonate) (2b)



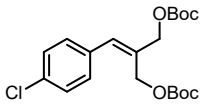
Colorless oil; 22 % yield (0.42 g, 1.1 mmol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.25-7.22 (m, 2H), 7.04 (t, J = 8.4 Hz, 2H), 6.83 (s, 1H), 4.75 (s, 4H), 1.51 (s, 9H), 1.49 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 162.3 (d, J_{C-F} = 246.3 Hz), 153.3, 153.2, 133.8, 131.3 (d, J_{C-F} = 12.8 Hz), 130.7, 130.6 (d, J_{C-F} = 8.0 Hz), 115.4 (d, J_{C-F} = 21.5 Hz), 82.4, 82.3, 68.6, 62.8, 27.8, 27.7.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{20}H_{27}FO_6Na$ $[M+Na]^+$ 405.1684, found 405.1677.

Di-*tert*-butyl (2-(4-chlorobenzylidene)propane-1,3-diyl) bis(carbonate) (2c)



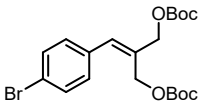
Colorless oil; 31 % yield (0.62 g, 1.6 mmol).

^{1}H NMR (DMSO-d_6, 500 MHz) δ 7.48 (d, J = 8.5 Hz, 2H), 7.32 (d, J = 8.5 Hz, 2H), 6.88 (s, 1H), 4.73 (s, 2H), 4.70 (s, 2H), 1.45 (s, 9H), 1.42 (s, 9H).

^{13}C NMR (DMSO-d_6, 125 MHz) δ 153.2, 153.1, 134.3, 133.0, 131.9, 131.0, 129.0, 82.3, 82.2, 68.7, 63.0, 27.80, 27.77.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{20}H_{27}ClO_6Na$ $[M+Na]^+$ 421.1388, found 421.1384.

2-(4-Bromobenzylidene)propane-1,3-diyl di-tert-butyl bis(carbonate)(2d)



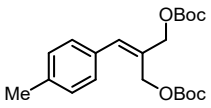
Colorless oil; 30 % yield (0.66 g, 1.5 mmol).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.51 (d, J = 8.5 Hz, 2H), 7.16 (d, J = 8.5 Hz, 2H), 6.83 (s, 1H), 4.77 (s, 2H), 4.76 (s, 2H), 1.54 (s, 9H), 1.52 (s, 9H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 153.3, 153.2, 134.2, 133.6, 131.6, 130.5, 122.1, 82.6, 82.5, 68.5, 62.8, 27.81, 27.79.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{20}H_{27}BrO_6K$ $[M+K]^+$ 481.0623, found 481.0625.

Di-*tert*-butyl (2-(4-methylbenzylidene)propane-1,3-diyl) bis(carbonate) (2e)



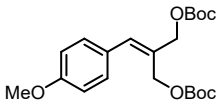
Colorless oil; 47 % yield (0.89 g, 2.4 mmol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.15 (s, 4H), 6.84 (s, 1H), 4.79 (s, 2H), 4.75 (s, 2H), 2.34 (s, 3H), 1.50 (s, 9H), 1.49 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.4, 153.3, 137.8, 135.2, 132.4, 129.8, 129.1, 128.8, 82.28, 82.26, 68.9, 63.1, 27.8, 21.2.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{21}H_{30}O_6Na$ $[M+Na]^+$ 401.1935, found 401.1937.

Di-*tert*-butyl (2-(4-methoxybenzylidene)propane-1,3-diyl) bis(carbonate) (2f)



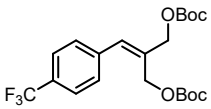
Colorless oil; 18 % yield (0.35 g, 0.90 mmol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.20 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 6.82 (s, 1H), 4.79 (s, 2H), 4.74 (s, 2H), 3.81 (s, 3H), 1.50 (s, 9H), 1.49 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.3, 153.4, 153.3, 135.2, 130.3, 128.9, 127.8, 113.9, 82.3, 82.2, 69.1, 63.2, 55.3, 27.8.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{21}H_{31}O_6Na$ $[M+Na]^+$ 417.1884, found 417.1884.

Di-*tert*-butyl (2-(4-(trifluoromethyl)benzylidene)propane-1,3-diyl) bis(carbonate) (**2g**)



Colorless oil; 38 % yield (0.82 g, 1.9 mmol).

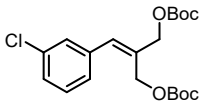
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 6.89 (s, 1H), 4.76 (s, 2H), 4.74 (s, 2H), 1.51 (s, 9H), 1.49 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.22, 153.16, 138.9, 132.8, 132.7, 129.1, 125.38, 125.35, 82.6, 82.5, 68.1, 62.6, 27.7.

^{19}F NMR ($CDCl_3$, 376 MHz) δ -62.66 (s, 3F).

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{21}H_{27}F_3O_6Na$ [M+Na]$^+$ 455.1652, found 455.1666.

Di-*tert*-butyl (2-(3-chlorobenzylidene)propane-1,3-diyl) bis(carbonate) (2h)



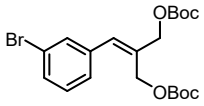
Colorless oil; 45 % yield (0.90 g, 2.3 mmol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.29-7.23 (m, 3H), 7.13 (t, *J* = 3.6 Hz, 1H), 6.81 (s, 1H), 4.75 (s, 2H), 4.74 (s, 2H), 1.51 (s, 9H), 1.49 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.3, 153.2, 137.1, 134.3, 133.1, 132.0, 129.7, 128.8, 127.9, 126.9, 82.6, 82.5, 68.2, 62.7, 27.78, 27.77.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{20}H_{27}ClO_6Na$ [M+Na]$^+$ 421.1388, found 421.1394.

2-(3-Bromobenzylidene)propane-1,3-diyl di-*tert*-butyl bis(carbonate) (2i)



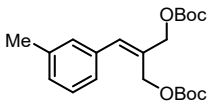
Colorless oil; 64 % yield (1.4 g, 3.2 mmol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.42 (t, *J* = 8.0 Hz, 2H), 7.24-7.17 (m, 2H), 6.80 (s, 1H), 4.74 (d, *J* = 0.8 Hz, 2H), 4.73 (s, 2H), 1.50 (s, 9H), 1.49 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.2, 153.20, 137.4, 133.0, 132.1, 131.7, 130.9, 130.0, 127.4, 122.5, 82.6, 82.5, 68.2, 62.7, 27.8.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{20}H_{27}BrO_6Na$ [M+Na]$^+$ 465.0883, found 465.0885.

Di-*tert*-butyl (2-(3-methylbenzylidene)propane-1,3-diyl) bis(carbonate) (2j)



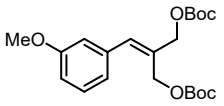
Colorless oil; 76 % yield (1.4 g, 3.8 mmol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.23 (d, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 4.0 Hz, 2H), 6.85 (s, 1H), 4.78 (s, 2H), 4.75 (s, 2H), 2.34 (s, 3H), 1.51 (s, 9H), 1.49 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.4, 153.3, 138.0, 135.25, 135.21, 130.3, 129.5, 128.6, 128.3, 125.9, 82.3, 68.7, 63.1, 27.81, 27.79, 21.4.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{21}H_{30}O_6Na$ [M+Na]$^+$ 401.1935, found 401.1939.

Di-*tert*-butyl (2-(3-methoxybenzylidene)propane-1,3-diyl) bis(carbonate) (2k)



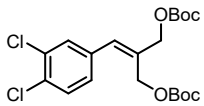
Colorless oil; 76 % yield (1.5 g, 3.8 mmol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.26 (t, *J* = 8.0 Hz, 1H), 6.85-6.81 (m, 4H), 4.78 (s, 2H), 4.75 (s, 2H), 3.79 (s, 3H), 1.51 (s, 9H), 1.49 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.5, 153.34, 153.26, 136.6, 134.9, 130.8, 129.4, 121.2, 114.0, 113.8, 82.3, 68.6, 63.0, 55.1, 27.78, 27.76.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{21}H_{30}O_6Na$ [M+Na]$^+$ 417.1884, found 417.1885.

Di-*tert*-butyl (2-(3,4-dichlorobenzylidene)propane-1,3-diyl) bis(carbonate) (**2l**)



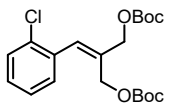
Colorless oil; 11 % yield (0.24 g, 0.55 mmol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.42 (d, J = 8.4 Hz, 1H), 7.35 (d, J = 1.6 Hz, 1H), 7.11-7.08 (m, 1H), 6.76 (s, 1H), 4.74 (s, 2H), 4.71 (s, 2H), 1.51 (s, 9H), 1.49 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.2, 153.1, 135.3, 132.61, 132.60, 132.0, 131.9, 130.6, 130.4, 128.1, 82.7, 82.5, 68.1, 62.6, 27.77, 27.75.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{20}H_{26}Cl_2O_6$ [M+Na]$^+$ 455.0999, found 455.1008.

Di-*tert*-butyl (2-(2-chlorobenzylidene)propane-1,3-diyl) bis(carbonate) (**2m**)



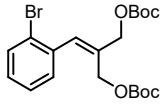
Colorless oil; 86 % yield (1.7 g, 4.3 mmol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40-7.37 (m, 1H), 7.27-7.25 (m, 3H), 6.91 (s, 1H), 4.79 (s, 2H), 4.69 (s, 2H), 1.51 (s, 9H), 1.48 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.24, 153.22, 133.9, 133.8, 132.3, 131.4, 130.6, 129.5, 129.3, 126.6, 82.43, 82.39, 67.9, 63.0, 27.79, 27.76.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{20}H_{27}ClO_6Na$ $[M+Na]^+$ 421.1388, found 421.1377.

2-(2-Bromobenzylidene)propane-1,3-diyl di-*tert*-butyl bis(carbonate) (2n)



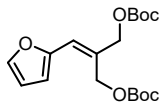
Colorless oil; 40 % yield (0.88 g, 2.0 mmol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.58 (d, J = 8.0 Hz, 1H), 7.32-7.24 (m, 2H), 7.19-7.14 (m, 1H), 6.85 (s, 1H), 4.79 (s, 2H), 4.67 (s, 2H), 1.51 (s, 9H), 1.48 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.2, 135.6, 133.6, 132.7, 132.0, 130.6, 129.4, 127.2, 124.0, 82.43, 82.39, 67.6, 62.9, 27.81, 27.77.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{20}H_{27}BrO_6Na$ $[M+Na]^+$ 465.0883, found 465.0887.

Di-*tert*-butyl (2-(furan-2-ylmethylene)propane-1,3-diyl) bis(carbonate) (2o)



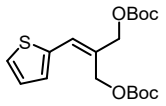
Colorless oil; 40 % yield (0.71 g, 2.0 mmol).

^{1}H NMR (DMSO-d_6, 500 MHz) δ 7.76 (d, *J* = 1.5 Hz, 1H), 6.61 (t, *J* = 3.5 Hz, 2H), 6.58-6.57 (m, 1H), 5.00 (s, 2H), 4.68 (s, 2H), 1.44 (d, *J* = 2.5 Hz, 18H).

^{13}C NMR (DMSO-d_6, 125 MHz) δ 153.4, 153.2, 150.8, 144.5, 128.0, 121.2, 113.4, 112.3, 82.1, 82.0, 68.7, 63.6, 27.8.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{18}H_{26}O_7K$ $[M+K]^+$ 393.1310, found 393.1311.

Di-*tert*-butyl (2-(thiophen-2-ylmethylene)propane-1,3-diyl) bis(carbonate) (**2p**)



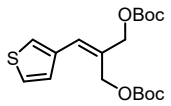
Colorless oil; 30 % yield (0.56 g, 1.5 mmol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35-7.33 (m, 1H), 7.07 (d, *J* = 3.2 Hz, 1H), 7.04-7.01 (m, 1H), 6.89 (s, 1H), 4.96 (s, 2H), 4.75 (s, 2H), 1.50 (s, 18H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.4, 153.2, 137.7, 129.3, 128.5, 127.32, 127.25, 127.2, 82.4, 82.3, 69.0, 63.3, 27.8.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{18}H_{26}O_6SK$ $[M+K]^+$ 409.1082, found 409.1088.

Di-*tert*-butyl (2-(thiophen-2-ylmethylene)propane-1,3-diyl) bis(carbonate) (2q)



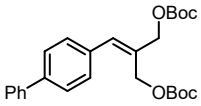
Colorless oil; 64 % yield (1.2 g, 3.2 mmol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.31-7.27 (m, 2H), 7.08 (d, *J* = 4.8 Hz, 1H), 6.78 (s, 1H), 4.84 (s, 2H), 4.74 (s, 2H), 1.50 (s, 18H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.5, 153.3, 136.3, 129.7, 129.3, 128.4, 125.8, 124.9, 82.4, 82.3, 69.0, 63.2, 27.8.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{18}H_{26}O_6SNa$ $[M+Na]^+$ 393.1342, found 393.1329.

2-([1,1'-Biphenyl]-4-ylmethylene)propane-1,3-diyl di-*tert*-butyl bis(carbonate) (2r)



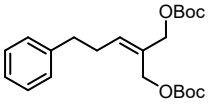
Colorless oil; 34 % yield (0.75 g, 1.7 mmol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.45-7.42 (m, 4H), 7.28 (t, *J* = 7.2 Hz, 2H), 7.20 (t, *J*=6.4 Hz, 3H), 6.76 (s, 1H), 4.73 (s, 2H), 4.66 (s, 2H), 1.39 (s, 9H), 1.37 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.3, 152.2, 139.5, 139.3, 133.4, 133.2, 129.7, 128.3, 127.8, 126.4, 126.0, 125.9, 81.15, 81.08, 67.7, 62.0, 26.71, 26.70.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{26}H_{33}O_6$ $[M+H]^+$ 441.2272, found 441.2277.

Di-*tert*-butyl (2-(3-phenylpropylidene)propane-1,3-diyl) bis(carbonate) (2s)



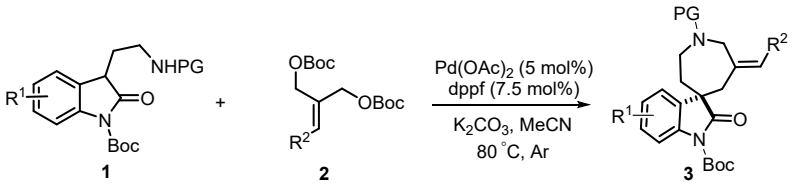
Colorless oil; 40 % yield (0.78 g, 2.0 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (s, 1H), 7.17 (d, *J* = 8.1 Hz, 4H), 5.85 (t, *J* = 7.5 Hz, 1H), 4.58 (s, 2H), 4.56 (s, 2H), 2.69 (t, *J* = 7.7 Hz, 2H), 2.51-2.45 (m, 2H), 1.48 (s, 9H), 1.47 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.4, 153.3, 141.1, 136.2, 129.4, 128.5, 128.4, 128.1, 82.2, 82.1, 69.0, 66.7, 62.0, 35.4, 29.7, 27.8.

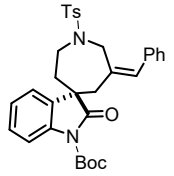
HRMS (TOF-ESI$^+$) m/z: calcd for $C_{22}H_{32}O_6Na$ $[M+Na]^+$ 415.2091, found 415.2080.

2.3 General procedure for the synthesis of spiro[azepane-4,3'-oxindoles]



To a solution of oxotryptamines **1** (0.1 mmol) and allyl dicarbonates **2** (0.15 mmol, 1.5 equiv.) in MeCN (1.0 mL), K_2CO_3 (41.4 mg, 0.3 mmol, 3 equiv.), $Pd(OAc)_2$ (1.0 mg, 0.005 mmol, 5 mol%) and DPPF (4.0 mg, 0.0075 mmol, 7.5 mol%) were added, respectively. The reaction mixture was stirred at 80 ℃ for 1 h. After completion of the reaction, the solvent was removed under reduced pressure, concentrated and purified by silica gel flash column chromatography using 1:5 Petroleum Ether/EtOAc as eluents to give spiro[azepane-4,3'-oxindoles] **3**. The product was subsequently recrystallized in *n*-hexane and DCM to afford **3** as a major isomer.

***Tert*-butyl (*Z*)-6-benzylidene-2'-oxo-1-tosylspiro[azepane-4,3'-indoline]-1'-carboxylate (3aa)**



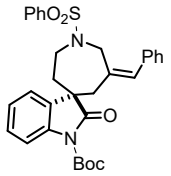
White solid; 77 % yield (43.0 mg, 0.077 mmol); *Z*/*E* = 4:1; m.p. 167-169 °C;

^{1}H NMR (DMSO-d_6, 400 MHz, major isomer) δ 7.81 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 3H), 7.30-7.24 (m, 2H), 7.18-7.12 (m,3H), 6.11 (s, 1H), 4.31 (d, *J* = 15.6 Hz, 1H), 4.23 (d, *J* = 16.8 Hz, 1H), 3.62-3.55 (m, 1H), 3.28 (d, *J* = 12.2 Hz, 1H), 2.81 (d, *J* = 13.2 Hz, 1H), 2.56 (d, *J* = 13.2 Hz, 1H), 2.40 (s, 3H), 2.14-2.07 (m, 1H), 1.87-1.82 (m, 1H), 1.58 (s, 9H).

^{13}C NMR (DMSO-d_6, 100 MHz, major isomer) δ 177.1, 149.1, 143.9, 138.5, 136.4, 135.9, 133.5, 132.3, 132.0, 130.4, 129.1, 128.8, 128.6, 127.5, 127.3, 125.1, 124.2, 114.8, 84.3, 50.6, 49.7, 45.2, 43.0, 37.0, 28.2, 21.5.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{32}H_{34}N_2O_5SNa$ [M+Na]$^+$ 581.2081, found 581.2085.

***Tert*-butyl (*Z*)-6-benzylidene-2'-oxo-1-(phenylsulfonyl)spiro[azepane-4,3'-indoline]-1'-carboxylate (3ab)**



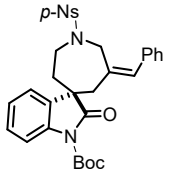
White solid; 86 % yield (46.8 mg, 0.086 mmol); *Z/E* = 3:1; m.p. 146-148 °C.

^{1}H NMR ($CDCl_3$, 400 MHz, major isomer) δ 7.90-7.82 (m, 4H), 7.55-7.51 (m, 2H), 7.35-7.28 (m, 4H), 7.17-7.12 (m, 4H), 6.22 (s, 1H), 4.47 (d, *J* = 15.6 Hz, 1H), 4.15 (d, *J* = 15.2 Hz, 1H), 3.59-3.53 (m, 1H), 3.50-3.44 (m, 1H), 2.79 (d, *J* = 13.2 Hz, 1H), 2.74 (d, *J* = 13.2 Hz, 1H), 2.20-2.15 (m, 1H), 2.03-2.00 (m, 1H), 1.65 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz, major isomer) δ 177.1, 149.3, 138.7, 138.3, 136.2, 132.8, 132.7, 132.5, 132.4, 129.3, 128.8, 128.4, 128.3, 127.1, 124.2, 123.9, 115.0, 84.5, 50.7, 49.5, 45.0, 43.6, 37.3, 28.2.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{31}H_{32}N_2O_5SNa$ [M+Na]$^+$ 567.1924, found 567.1924.

***Tert*-butyl (*Z*)-6-benzylidene-1-((4-nitrophenyl)sulfonyl)-2'-oxospiro[azepane-4,3'-indoline]-1'-carboxylate (3ac)**



White solid; 35 % yield (20.6 mg, 0.035 mmol); *Z/E* > 20:1; m.p. 147-149 °C.

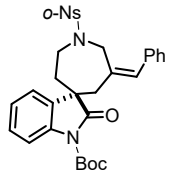
^{1}H NMR (400 MHz, $CDCl_3$, major isomer) δ 8.37 (d, *J* = 8.8 Hz, 2H), 8.00 (d, *J* = 8.8 Hz, 2H), 7.87 (d, *J* = 8.8 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 3H), 7.27 (t, *J* = 4.0 Hz, 2H), 7.19-7.12 (m, 3H), 6.25 (s, 1H), 4.46 (d, *J* = 15.6 Hz, 1H), 4.21 (d, *J* = 15.6 Hz, 1H), 3.69-3.62 (m,

1H), 3.52-3.46 (m, 1H), 2.80 (d, *J* = 13.6 Hz, 1H), 2.71 (d, *J* = 13.6 Hz, 1H), 2.21-2.15 (m, 1H), 2.10-2.03 (m, 1H), 1.65 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz, major isomer) δ 176.9, 150.1, 149.2, 144.7, 138.3, 136.0, 133.3, 132.3, 131.7, 128.7, 128.5, 128.4, 128.2, 127.4, 127.6, 124.3, 123.6, 115.1, 84.6, 50.6, 49.4, 45.1, 43.6, 37.5, 29.7, 28.1.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{31}H_{31}N_3O_7SNa$ $[M+Na]^+$ 612.1775, found 612.1783.

***Tert*-butyl (*Z*)-6-benzylidene-1-((2-nitrophenyl)sulfonyl)-2'-oxospiro[azepane-4,3'-indoline]-1'-carboxylate (3ad)**



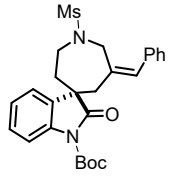
White solid; 39 % yield (23.0 mg, 0.039 mmol); *Z/E* > 20:1; m.p. 145-147 °C.

^{1}H NMR (400 MHz, $CDCl_3$, major isomer) δ7.99 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.72-7.63 (m, 3H), 7.34 (t, *J* = 7.6 Hz, 3H), 7.29-7.24 (m, 2H), 7.20-7.17 (m, 3H), 6.24 (s, 1H), 4.54 (dd, *J* = 16.4, 1.6 Hz, 1H), 4.43 (dd, *J* = 16.0, 1.6 Hz, 1H), 3.83-3.76 (m, 1H), 3.62-3.56 (m, 1H), 2.87 (d, *J* = 13.6 Hz, 1H), 2.77 (d, *J* = 13.6 Hz, 1H), 2.21-2.15 (m, 1H), 2.12-2.06 (m, 1H), 1.66 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz, major isomer) δ 176.9, 149.3, 148.3, 138.2, 136.2, 133.7, 132.8, 132.7, 132.5, 132.3, 131.7, 130.7, 128.8, 128.4, 128.3, 127.2, 124.3, 124.2, 123.7, 115.0, 84.5, 50.8, 49.5, 45.3, 43.7, 37.5, 29.7, 28.2.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{31}H_{31}N_3O_7SNa$ $[M+Na]^+$ 612.1775, found 612.1782.

***Tert*-butyl (*Z*)-6-benzylidene-1-(methylsulfonyl)-2'-oxospiro[azepane-4,3'-indoline] -1'-Carboxylate (3ae)**



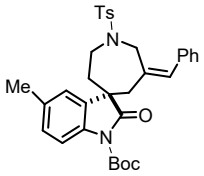
White solid; 52 % yield (25.1 mg, 0.052 mmol); *Z/E* > 20:1; m.p. 150-152 °C.

^{1}H NMR (400 MHz, $CDCl_3$, major isomer) δ 7.88 (d, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 3H), 7.33-7.27 (m, 2H), 7.20-7.16 (m, 3H), 6.26 (s, 1H), 4.45 (dd, *J* = 16.0, 1.6 Hz, 1H), 4.30 (dd, *J* = 15.6, 1.6 Hz, 1H), 4.32-4.27 (m, 1H), 3.74-3.68 (m, 1H), 3.51-3.45 (m, 1H), 2.91 (s, 3H), 2.85 (d, *J* = 13.6 Hz, 1H), 2.78 (d, *J* = 13.2 Hz, 1H), 2.19-2.13 (m, 1H), 2.07-2.00 (m, 1H), 1.67 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz, major isomer) δ 177.1, 149.3, 138.2, 136.3, 132.64, 132.58, 128.8, 128.4, 127.2, 124.3, 123.7, 115.0, 84.5, 50.2, 49.6, 44.8, 43.5, 37.5, 37.3, 28.2.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{26}H_{30}N_2O_5SK$ $[M+K]^+$ 521.1507, found 521.1507.

***Tert*-butyl (*Z*)-6-benzylidene-5'-methyl-2'-oxo-1-tosylspiro[azepane-4,3'-indoline]-1'-carboxylate (3af)**



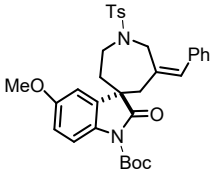
White solid; 75 % yield (42.9 mg, 0.075 mmol); *Z/E* = 4:1; m.p. 149-151 °C;

^{1}H NMR (400 MHz, $CDCl_3$, major isomer) δ 7.74-7.01 (m, 3H), 7.37-7.31 (m, 5H), 7.14 (d, *J* = 7.6 Hz, 3H), 7.04-6.99 (m, 1H), 6.21 (s, 1H), 4.45 (d, *J* = 15.6 Hz, 1H), 4.14 (dd, *J* = 16.0, 1.6 Hz, 1H), 3.55-3.48 (m, 1H), 3.46-3.40 (m, 1H), 2.74 (t, *J* = 15.6 Hz, 2H), 2.43 (s, 3H), 2.34 (s, 3H), 2.18-2.13 (m, 1H), 2.00-1.95 (m, 1H), 1.65 (s, 9H).

^{13}C NMR (DMSO-d_6, 100 MHz, major isomer) δ 177.3, 149.4, 143.5, 136.3, 135.84, 135.78, 133.8, 132.63, 132.58, 132.53, 129.9, 128.8, 128.7, 128.3, 127.14, 127.09, 124.6, 114.7, 84.3, 50.6, 49.6, 44.9, 43.5, 37.4, 28.2, 21.5, 21.2.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{33}H_{36}N_2O_5SNa$ $[M+Na]^+$ 595.2237, found 595.2243.

***Tert*-butyl (*Z*)-6-benzylidene-5'-methoxy-2'-oxo-1-tosylspiro[azepane-4,3'-indoline] -1'- carboxylate (3ag)**



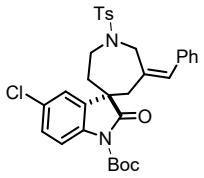
White solid; 87 % yield (51.2 mg, 0.087 mmol); *Z/E* = 8:1; m.p. 151-153 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz, major isomer) δ 7.77 (d, *J* = 8.8 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.35-7.30 (m, 4H), 7.23 (d, *J* = 7.2 Hz, 1H), 7.16 (d, *J* = 7.2 Hz, 2H), 6.91 (d, *J* = 2.4 Hz, 1H), 6.86-6.83 (m, 1H), 6.28 (s, 1H), 4.51 (d, *J* = 15.6 Hz, 1H), 4.04 (dd, *J* = 15.6, 1.2 Hz, 1H), 3.80 (s, 3H), 3.56-3.50 (m, 1H), 3.45-3.93 (m, 1H), 2.86 (d, *J* = 13.6 Hz, 1H), 2.71 (d, *J* = 13.6 Hz, 1H), 2.43 (s, 3H), 2.20-2.13 (m, 1H), 1.99-1.92 (m, 1H), 1.64 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz, major isomer) δ 177.3, 156.8, 149.4, 143.6, 136.3, 135.5, 133.8, 132.6, 132.4, 131.5, 129.9, 128.8, 128.3, 127.2, 127.1, 115.9, 113.3, 110.0, 84.2, 55.8, 50.6, 49.7, 44.9, 43.6, 36.9, 28.2, 21.5.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{33}H_{37}N_2O_6S$ $[M+H]^+$ 589.2367, found 589.2358.

***Tert*-butyl (*Z*)-6-benzylidene-5'-chloro-2'-oxo-1-tosylspiro[azepane-4,3'-indoline]-1'-carboxylate (3ah)**



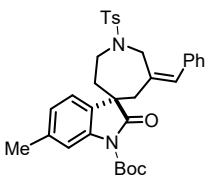
White solid; 41 % yield (24.3 mg, 0.041 mmol); *Z/E* = 5:1; m.p. 173-175 ℃;

^{1}H NMR ($CDCl_3$, 400 MHz, major isomer) δ 7.84 (d, *J* = 8.8 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.38-7.30 (m, 6H), 7.19 (d, *J* = 2.0 Hz, 1H), 7.14 (d, *J* = 7.2 Hz, 2H), 6.19 (s, 1H), 4.35 (dd, *J* = 15.6, 1.2 Hz, 1H), 4.23 (dd, *J* = 15.6, 1.6 Hz, 1H), 3.60-3.54 (m, 1H), 3.32-3.27 (m, 1H), 2.83-2.78 (m, 1H), 2.67 (d, *J* = 13.2 Hz, 1H), 2.43 (s, 3H), 2.25-2.19 (m, 1H), 1.95-1.88 (m, 1H), 1.65 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz, major isomer) δ 176.4, 149.2, 143.6, 136.9, 135.9, 135.8, 134.0, 133.3, 132.1, 129.9, 129.5, 128.8, 128.3, 127.3, 127.1, 124.4, 116.2, 84.8, 50.5, 49.7, 44.8, 43.0, 37.3, 28.1, 21.5.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{32}H_{34}ClN_2O_5S$ $[M+H]^+$ 593.1871, found 593.1883.

***Tert*-butyl (*Z*)-6-benzylidene-6'-methyl-2'-oxo-1-tosylspiro[azepane-4,3'-indoline]-1'-carboxylate (3ai)**



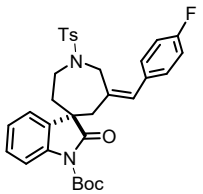
White solid; 55 % yield (31.5 mg, 0.055 mmol); *Z/E* = 1.5:1; m.p. 147-149 ℃;

^{1}H NMR ($CDCl_3$, 400 MHz, major isomer) δ 7.77-7.69 (m, 4H), 7.34-7.30 (m, 3H), 7.15 (t, *J* = 4.8 Hz, 3H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.92 (m, *J* = 1.2 Hz, 1H), 6.20 (s, 1H), 4.42 (dd, *J* = 15.6, 1.6 Hz, 1H), 4.13 (dd, *J* = 15.2, 1.6 Hz, 1H), 3.55-3.49 (m, 1H), 3.43-3.37(m, 1H), 2.75 (d, *J* = 5.2 Hz, 2H), 2.42 (s, 3H), 2.40 (s, 3H), 2.17-2.14 (m, 1H), 1.97-1.91 (m, 1H), 1.65 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz, major isomer) δ 177.5, 149.5, 143.5, 138.4, 138.3, 136.3, 135.6, 132.6, 129.8, 129.5, 128.8, 128.6, 128.3, 128.1, 127.2, 124.7, 115.7, 84.4, 50.7, 49.4, 44.9, 43.6, 37.4, 28.1, 21.9, 21.5.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{33}H_{36}N_2O_5SNa$ $[M+Na]^+$ 595.2237, found 595.2247.

***Tert*-butyl (*Z*)-6-(4-fluorobenzylidene)-2'-oxo-1-tosylspiro[azepane-4,3'-indoline]-1'-carboxylate (3aj)**



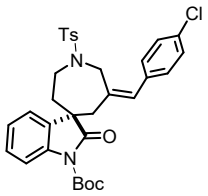
White solid; 43 % yield (24.8 mg, 0.043 mmol); *Z/E* = 4.5:1; m.p. 148-151 ℃;

^{1}H NMR ($CDCl_3$, 400 MHz, major isomer) δ 7.85 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.36-7.26 (m, 5H), 7.18-7.10 (m, 3H), 7.02 (t, *J* = 8.4 Hz, 2H), 6.19 (s, 1H), 4.44 (d, *J* = 15.6 Hz, 1H), 4.01 (d, *J* = 15.2 Hz, 1H), 3.55-3.43 (m, 2H), 2.84 (d, *J* = 13.2 Hz, 1H), 2.69 (d, *J* = 13.6 Hz, 1H), 2.44 (s, 3H), 2.18-2.12 (m, 1H), 2.05-1.98 (m, 1H), 1.65 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz, major isomer) δ 177.1, 161.8 (d, $J_{C\text{-}F}$ = 245.6 Hz), 149.3, 143.6, 138.2, 135.5, 132.67 (d, $J_{C\text{-}F}$ = 0.9 Hz), 132.6, 132.3 (d, $J_{C\text{-}F}$ = 3.2 Hz), 131.4, 130.4 (d, $J_{C\text{-}F}$ = 7.9 Hz), 129.9, 128.4, 127.1, 124.3, 123.7, 115.1 (t, $J_{C\text{-}F}$ = 21.1 Hz), 115.0, 84.5, 50.7, 49.5, 44.9, 43.7, 37.3, 28.1, 21.5.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{32}H_{34}FN_2O_5S$ $[M+H]^+$ 577.2167, found 577.2160.

***Tert*-butyl (*Z*)-6-(4-chlorobenzylidene)-2'-oxo-1-tosylspiro[azepane-4,3'-indoline]-1'-carboxylate (3ak)**



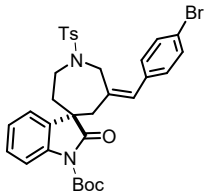
White solid; 79 % yield (46.8 mg, 0.079 mmol); *Z/E* = 4:1; m.p. 126-128 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz, major isomer) δ 7.85 (d, *J* = 8.4 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.35-7.29 (m, 6H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.18 (s, 1H), 4.44 (d, *J* = 15.6 Hz, 1H), 4.01 (d, *J* = 15.6 Hz, 1H), 3.55-3.42 (m, 2H), 2.87 (d, *J* = 13.2 Hz, 1H), 2.69 (d, *J* = 13.6 Hz, 1H), 2.44 (s, 3H), 2.17-2.11 (m, 1H), 2.05-1.98 (m, 1H), 1.65 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz, major isomer) δ 177.1, 149.3, 143.7, 138.2, 135.5, 134.7, 133.6, 132.9, 132.5, 131.1, 130.0, 129.9, 128.5, 128.4, 127.1, 124.3, 123.7, 115.0, 84.5, 50.7, 49.5, 45.0, 43.7, 37.3, 28.1, 21.6.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{32}H_{33}ClN_2O_5SK$ $[M+K]^+$ 631.1430, found 631.1430.

***Tert*-butyl (*Z*)-6-(4-bromobenzylidene)-2'-oxo-1-tosylspiro[azepane-4,3'-indoline]-1'-carboxylate (3al)**



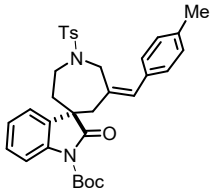
White solid; 88 % yield (56.0 mg, 0.088 mmol); *Z/E* = 4.2:1; m.p. 149-152 ℃.

^{1}H NMR (500 MHz, $CDCl_3$, major isomer) δ 7.88 (d, *J* = 8.5 Hz, 1H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.38-7.36 (m, 2H), 7.32-7.29 (m, 2H), 7.21-7.18 (m, 1H), 7.05 (d, *J* = 8.5 Hz, 2H), 6.19 (s, 1H), 4.47 (d, *J* = 15.5 Hz, 1H), 4.05 (dd, *J* = 15.5, 1.5 Hz, 1H), 3.58-3.46 (m, 2H), 2.90 (d, *J* = 13.5 Hz, 1H), 2.72 (d, *J* = 13.5 Hz, 1H), 2.48 (s, 3H), 2.21-2.15 (m, 1H), 2.08-2.02 (m, 1H), 1.68 (s, 9H).

^{13}C NMR ($CDCl_3$, 125 MHz, major isomer) δ 177.1, 149.3, 143.7, 138.2, 135.5, 135.2, 133.7, 132.5, 131.4, 131.2, 130.4, 129.9, 128.4, 127.1, 124.3, 123.7, 115.0, 84.6, 50.7, 49.5, 43.7, 37.3, 28.2, 28.1, 21.6.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{32}H_{33}BrN_2O_5SNa$ $[M+Na]^+$ 659.1186, found 659.1189.

***Tert*-butyl (Z)-6-(4-methylbenzylidene)-2'-oxo-1-tosylspiro[azepane-4,3'-indoline]-1'-carboxylate (3am)**



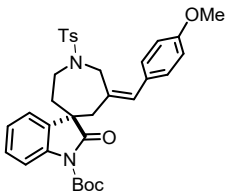
White solid; 79 % yield (45.2 mg, 0.079 mmol); *Z/E* = 9:1; m.p. 154-156 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz, major isomer) δ 7.86 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.36-7.31(m, 4H), 7.13 (t, *J* = 7.2 Hz, 3H), 7.04 (d, *J* = 7.6 Hz, 2H), 6.17 (s, 1H), 4.44 (d, *J* = 15.6 Hz, 1H), 4.12 (d, *J* = 15.6 Hz, 1H), 3.56-3.51 (m, 1H), 3.45-3.40 (m, 1H), 2.75 (s, 2H), 2.43 (s, 3H), 2.35 (s, 3H), 2.20-2.13 (m, 1H), 1.98-1.93 (m, 1H), 1.65 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz, major isomer) δ 177.2, 149.3, 143.5, 138.3, 137.0, 135.7, 133.4, 132.6, 132.5, 131.7, 129.9, 129.0, 128.7, 127.2, 124.1, 124.0, 114.9, 84.4, 50.7, 49.6, 44.9, 43.6, 37.2, 28.1, 21.5, 21.2.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{33}H_{36}N_2O_5SNa$ $[M+Na]^+$ 595.2237, found 595.2240.

***Tert*-butyl (Z)-6-(4-methoxybenzylidene)-2'-oxo-1-tosylspiro[azepane-4,3'-indoline] -1'- carboxylate (3an)**



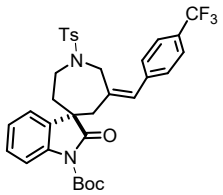
White solid; 85 % yield (50.0 mg, 0.085 mmol); *Z/E* = 3:1; m.p. 167-170℃.

^{1}H NMR ($CDCl_3$, 500 MHz, major isomer) δ 7.90 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.37-7.34 (m, 3H), 7.30 (d, *J* = 2.5 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.13 (d, *J* = 8.5 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 2H), 6.18 (s, 1H), 4.47 (d, *J* = 15.5 Hz, 1H), 4.12 (d, *J* = 15.5 Hz, 1H), 3.86 (s, 3H), 3.59-3.54 (m, 1H), 3.50-3.45 (m, 1H), 2.78 (s, 2H), 2.47 (s, 3H), 2.24-2.19 (m, 1H), 2.02-1.97 (m, 1H), 1.69 (s, 9H).

^{13}C NMR ($CDCl_3$, 125 MHz, major isomer) δ 177.4, 158.7, 149.3, 143.6, 138.3, 135.6, 132.5, 132.4, 130.7, 130.1, 129.9, 128.8, 128.3, 127.2, 124.2, 124.0, 115.0, 113.7, 84.5, 55.4, 50.8, 49.6, 44.9, 43.6, 37.2, 28.2, 21.6.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{33}H_{36}N_2O_6SK$ $[M+K]^+$ 627.1926, found 627.1926**.**

***Tert*-butyl (*Z*)-2'-oxo-1-tosyl-6-(4-(trifluoromethyl)benzylidene)spiro[azepane-4,3'-indoline]-1'-carboxylate (3ao)**



White solid; 30 % yield (18.8 mg, 0.03 mmol); *Z/E* = 5:1; m.p. 146-148 ℃.

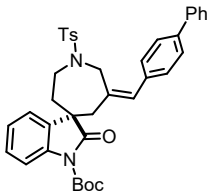
^{1}H NMR ($CDCl_3$, 500 MHz, major isomer) δ 7.89 (d, *J* = 8.5 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.39-7.35 (m, 3H), 7.33 (d, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 6.0 Hz, 3H), 7.21 (t, *J* = 7.5 Hz, 1H), 6.30 (s, 1H), 4.52 (d, *J* = 16.0 Hz, 1H), 4.06 (dd, *J* = 16.0, 1.5 Hz, 1H), 3.61-3.56 (m, 1H), 3.50-3.45 (m, 1H), 2.98 (d, *J* = 13.5 Hz, 1H), 2.73 (d, *J* = 13.5 Hz, 1H), 2.47 (s, 3H), 2.19-2.14 (m, 1H), 2.11-2.06 (m, 1H), 1.69 (s, 9H).

^{13}C NMR ($CDCl_3$, 125 MHz, major isomer) δ 177.0, 149.3, 143.8, 139.9, 138.2, 135.4, 135.3, 132.5, 130.8, 130.0, 129.0, 128.5, 127.1, 125.2 (t, J_{C-F} = 3.6 Hz), 124.4, 123.6, 115.0, 84.6, 50.7, 49.5, 45.0, 43.8, 37.3, 28.2, 21.6.

^{19}F NMR ($CDCl_3$, 376 MHz) δ -62.51 (s, 3F).

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{33}H_{33}F_3N_2O_5SNa$ $[M+Na]^+$ 649.1954, found 649.1961.

***Tert*-butyl (*Z*)-6-([1,1'-biphenyl]-4-ylmethylene)-2'-oxo-1-tosylspiro[azepane-4,3'-indoline]-1'-carboxylate (3ap)**



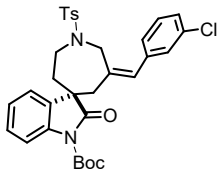
White solid; 87 % yield (55.2 mg, 0.087 mmol); *Z/E* > 20:1; m.p. 92-95 ℃;

^{1}H NMR (400 MHz, $CDCl_3$, major isomer) δ 7.87 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.61-7.56 (m, 4H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.38-7.31 (m, 5H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.16 (t, *J* = 7.6 Hz, 1H), 6.25 (s, 1H), 4.52 (d, *J* = 15.6 Hz, 1H), 4.17 (d, *J* = 15.6 Hz, 1H), 3.57-3.44 (m, 2H), 2.83 (d, *J* = 13.2 Hz, 1H), 2.76 (d, *J* = 13.6 Hz, 1H), 2.41 (s, 3H), 2.23-2.16 (m, 1H), 2.02-1.96 (m, 1H), 1.66 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz, major isomer) δ 177.2, 149.3, 143.6, 140.6, 139.9, 138.3, 135.6, 135.2, 132.8, 132.5, 132.2, 129.9, 129.3, 128.9, 128.4, 127.5, 127.2, 127.02, 126.97, 124.2, 124.0, 115.0, 84.5, 50.8, 49.6, 45.0, 43.7, 37.3, 28.2, 21.5.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{38}H_{38}N_2O_5SNa$ [M+Na]$^+$ 657.2394, found 657.2407.

***Tert*-butyl (Z)-6-(3-chlorobenzylidene)-2'-oxo-1-tosylspiro[azepane-4,3'-indoline]-1'-carboxylate (3aq)**



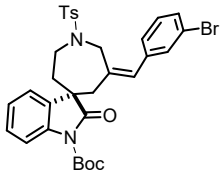
White solid; 78 % yield (46.2 mg, 0.078 mmol); *Z/E* > 20:1; m.p. 96-98 ℃.

^{1}H NMR (400 MHz, $CDCl_3$, major isomer) δ 7.85 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 3H), 7.29-7.26 (m, 2H), 7.24 (d, *J* = 5.6 Hz, 1H), 7.19-7.14 (m, 2H), 7.03 (d, *J* = 7.2 Hz, 1H), 6.16 (s, 1H), 4.45 (d, *J* = 15.6 Hz, 1H), 4.03 (dd, *J* = 16.0, 1.6 Hz, 1H), 3.55-3.40 (m, 2H), 2.90 (d, *J* = 13.2 Hz, 1H), 2.68 (d, *J* = 13.6 Hz, 1H), 2.43 (s, 3H), 2.16-2.11 (m, 1H), 2.06-1.99 (m, 1H), 1.65 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz, major isomer) δ 177.0, 149.3, 143.7, 138.2, 138.1, 135.3, 134.4, 134.2, 132.5, 130.7, 129.9, 129.5, 128.7, 128.4, 127.2, 127.1, 126.9, 124.3, 123.7, 115.0, 84.5, 50.8, 49.5, 45.0, 43.6, 37.2, 28.2, 21.6.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{32}H_{33}ClN_2O_5SNa$ [M+Na]$^+$ 615.1691, found 615.1699.

***Tert*-butyl (Z)-6-(3-bromobenzylidene)-2'-oxo-1-tosylspiro[azepane-4,3'-indoline]-1'-carboxylate (3ar)**



White solid; 17 % yield (10.8 mg, 0.017 mmol); *Z/E* = 3:1; m.p. 64-66 ℃.

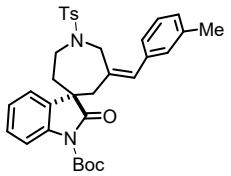
^{1}H NMR (400 MHz, $CDCl_3$, major isomer) δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.38-7.32 (m, 5H), 7.29 (d, *J* = 5.6 Hz, 2H), 7.19 (t, *J* = 3.6 Hz, 1H), 7.08 (d, *J* = 7.2 Hz, 1H), 6.16 (s, 1H), 4.45 (d, *J* = 15.6 Hz, 1H), 4.02 (dd, *J* = 15.6, 1.6 Hz, 1H), 3.54-3.48

(m, 1H), 3.46-3.40 (m, 1H), 2.90 (d, *J* = 13.2 Hz, 1H), 2.68 (d, *J* = 13.2 Hz, 1H), 2.43 (s, 3H), 2.13-2.10 (m, 1H), 2.05-2.02 (m, 1H), 1.65 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz, major isomer) δ 176.9, 149.3, 143.7, 138.3, 138.2, 135.3, 134.5, 132.5, 131.6, 130.6, 130.1, 129.9, 129.8, 128.4, 127.4, 127.1, 124.4, 123.7, 122.4, 115.0, 84.5, 50.8, 49.5, 45.1, 43.6, 37.2, 28.2, 21.6.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{32}H_{33}BrN_2O_5SNa$ $[M+Na]^+$ 659.1186, found 659.1196.

***Tert*-butyl (*Z*)-6-(3-methylbenzylidene)-2'-oxo-1-tosylspiro[azepane-4,3'-indoline]-1'-Carboxylate (3as)**



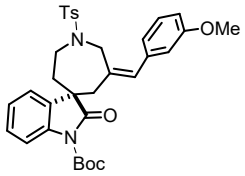
White solid; 80 % yield (45.8 mg, 0.08 mmol); *Z/E* = 7:1; m.p. 88-91 ℃.

^{1}H NMR (400 MHz, $CDCl_3$, major isomer) δ 7.86 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.35-7.29 (m, 4H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 7.6 Hz, 1H), 6.97 (t, *J* = 8.8 Hz), 2H), 6.19(s, 1H), 4.45 (d, *J* = 15.6 Hz, 1H), 4.09 (d, *J* = 15.6 Hz, 1H), 3.53-3.42 (m, 2H), 2.76 (dd, *J* = 21.2, 13.6 Hz, 2H), 2.42 (s, 3H), 2.35 (s, 3H), 2.20-2.15 (m, 1H), 2.00-1.95 (m, 1H), 1.65 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz, major isomer) δ 177.2, 149.3, 143.5, 138.3, 137.9, 136.2, 135.5, 132.8, 132.5, 132.2, 129.8, 129.5, 128.3, 128.2, 127.9, 127.2, 125.9, 124.2, 123.9, 114.9, 84.4, 50.9, 49.5, 45.0, 43.6, 37.3, 28.2, 21.5, 21.4.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{33}H_{36}N_2O_5SNa$ $[M+Na]^+$ 595.2237, found 595.2238.

***Tert*-butyl (Z)-6-(3-methoxybenzylidene)-2'-oxo-1-tosylspiro[azepane-4,3'-indoline]-1'- carboxylate (3at)**



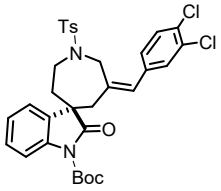
White solid; 85 % yield (50.0 mg, 0.085 mmol); *Z/E* = 3.5:1; m.p. 121-123 ℃.

^{1}H NMR (400 MHz, $CDCl_3$, major isomer) δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.35-7.28 (m, 4H), 7.23 (s, 1H), 7.16 (t, *J* = 7.2 Hz, 1H), 6.82-6.79 (m, 1H), 6.73 (s, 1H), 6.68 (s, 1H), 6.19 (s, 1H), 4.45 (d, *J* = 15.6 Hz, 1H), 4.11 (d, *J* = 15.6 Hz, 1H), 3.81 (s, 3H), 3.52-3.41 (m, 2H), 2.77 (dd, *J* = 19.6, 13.6 Hz, 2H), 2.43 (s, 3H), 2.20-2.16 (m, 1H), 2.00-1.94 (m, 1H), 1.65 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz, major isomer) δ 177.2, 159.5, 149.3, 143.6, 138.3, 137.6, 135.5, 132.8, 132.5, 129.9, 129.3, 128.3, 127.2, 124.2, 124.0, 121.3, 115.0, 114.1, 112.9, 84.5, 55.2, 50.8, 49.5, 45.0, 43.5, 37.2, 28.1, 21.5.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{33}H_{36}N_2O_6SNa$ $[M+Na]^+$ 611.2186, found 611.2185.

***Tert*-butyl (*Z*)-6-(3,4-dichlorobenzylidene)-2'-oxo-1-tosylspiro[azepane-4,3'-indoline] -1'-Carboxylate (3au)**



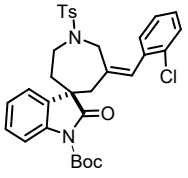
White solid; 90 % yield (56.3 mg, 0.09 mmol); *Z/E* = 6:1; m.p. 66-68 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz, major isomer) δ 7.85 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.40-7.31 (m, 5H), 7.24 (d, *J* = 1.6 Hz, 1H), 7.18 (d, *J* = 7.2 Hz, 1H), 7.00-6.98 (m, 1H), 6.14 (s, 1H), 4.46 (d, *J* = 15.8 Hz, 1H), 3.98 (dd, *J* = 15.6, 5.2 Hz, 1H), 3.59-3.53 (m, 1H), 3.43-3.37 (m, 1H), 2.95 (d, *J* = 13.6 Hz, 1H), 2.65 (d, *J* = 13.6 Hz, 1H), 2.44 (s, 3H), 2.11-2.04 (m, 2H), 1.65 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz, major isomer) δ 176.9, 149.2, 143.8, 138.2, 136.3, 135.3, 135.2, 132.5, 132.4, 131.0, 130.5, 130.2, 130.0, 129.6, 128.5, 128.1, 127.1, 124.4, 123.5, 115.0, 84.6, 50.8, 49.4, 45.1, 43.7, 37.2, 28.1, 21.6.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{32}H_{32}Cl_2N_2O_5SNa$ $[M+Na]^+$ 649.1301, found 649.1305.

***Tert*-butyl (*Z*)-6-(2-chlorobenzylidene)-2'-oxo-1-tosylspiro[azepane-4,3'-indoline]-1'-carboxylate (3av)**



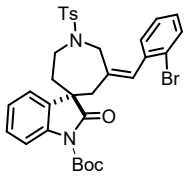
White solid; 64 % yield (37.9 mg, 0.064 mmol); *Z/E* = 1:1; m.p. 62-64 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.38-7.28 (m, 5H), 7.25-7.20 (m, 3H), 7.16 (t, *J* = 7.6 Hz, 1H), 6.32 (s, 1H), 4.38 (d, *J* = 15.6 Hz, 1H), 3.97 (d, *J* = 15.6 Hz, 1H), 3.54 (t, *J* = 5.6 Hz, 2H), 2.85 (d, *J* = 13.6 Hz, 1H), 2.73 (d, *J* = 13.6 Hz, 1H), 2.42 (s, 3H), 2.18-2.12 (m, 1H), 2.09-2.02 (m, 1H), 1.64 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 176.9, 149.3, 143.5, 138.1, 135.7, 134.6, 133.7, 132.7, 130.4, 129.8, 129.6, 129.4, 128.7, 128.3, 127.1, 126.5, 124.5, 123.7, 115.0, 84.5, 50.7, 49.3, 44.8, 43.7, 37.7, 28.1, 21.5.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{32}H_{33}ClN_2O_5SNa$ $[M+Na]^+$ 615.1691, found 615.1700.

***Tert*-butyl (*Z*)-6-(2-bromobenzylidene)-2'-oxo-1-tosylspiro[azepane-4,3'-indoline]-1'-Carboxylate (3aw)**



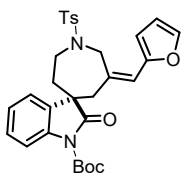
White solid; 69 % yield (43.9 mg, 0.069 mmol); *Z/E* = 1:1; m.p. 62-65 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.45-7.43 (m, 1H), 7.38-7.29 (m, 5H), 7.15-7.09 (m, 2H), 7.06-7.02 (m, 1H), 6.50 (s, 1H), 4.63 (d, *J* = 16.0 Hz, 1H), 4.07 (dd, *J* = 15.6, 1.2 Hz, 1H), 3.62-3.55 (m, 2H), 2.73 (dd, *J* = 16.4, 14.4 Hz, 2H), 2.46 (s, 3H), 2.15-2.09 (m, 2H), 1.62 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 176.7, 149.2, 143.6, 137.9, 136.7, 136.0, 135.3, 134.5, 132.7, 132.5, 131.4, 130.4, 129.9, 129.8, 128.5, 128.2, 127.1, 124.7, 123.2, 114.9, 84.5, 54.7, 49.1, 44.9, 37.9, 36.8, 28.1, 21.6.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{32}H_{33}BrN_2O_5SNa$ $[M+Na]^+$ 659.1186, found 659.1195.

***Tert*-butyl (*Z*)-6-(furan-2-ylmethylene)-2'-oxo-1-tosylspiro[azepane-4,3'-indoline]-1'-carboxylate (3ax)**



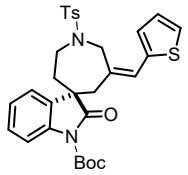
White solid; 44 % yield (24.1 mg, 0.044 mmol); *Z/E* = 3:1; m.p. 68-70 ℃.

^{1}H NMR (400 MHz, $CDCl_3$, major isomer) δ 7.83 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 4H), 7.15 (t, *J* = 7.2 Hz, 1H), 6.40 (d, *J* = 2.0 Hz, 1H), 6.25 (s, 1H), 6.15 (d, *J* = 3.2 Hz, 1H), 6.03 (s, 1H), 4.67 (d, *J* = 17.2 Hz, 1H), 4.25 (d, *J* = 18.4 Hz, 1H), 3.68-3.59 (m, 2H), 2.96-2.92 (m, 1H), 2.66 (d, *J* = 13.6 Hz, 1H), 2.46 (s, 3H), 2.15-2.09 (m, 1H), 2.00-1.96 (m, 1H), 1.63 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz, major isomer) δ 176.9, 152.0, 149.3, 143.6, 142.1, 138.2, 135.7, 132.5, 132.1, 129.9, 128.3, 127.2, 124.5, 123.7, 118.1, 114.9, 111.4 ,110.1, 84.5, 51.5, 49.6, 45.5, 43.6, 36.8, 28.1, 21.6.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{30}H_{32}N_2O_6SNa$ $[M+Na]^+$ 571.1873，found 571.1875.

Tert-butyl (_Z_)-2'-oxo-6-(thiophen-2-ylmethylene)-1-tosylspiro[azepane-4,3'-indoline] -1'- carboxylat (3ay)



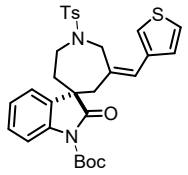
White solid; 30 % yield (16.9 mg, 0.03 mmol); *Z/E* > 20;1; m.p. 114-116 ℃.

^{1}H NMR ($CDCl_3$, 500 MHz, major isomer) δ 7.88 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.37-7.33 (m, 3H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.08-7.06 (m, 1H), 6.92 (d, *J* = 3.5 Hz, 1H), 6.42 (s, 1H), 4.58 (d, *J* = 16.5 Hz, 1H), 4.20 (d, *J* = 16.5 Hz, 1H), 3.61-3.56 (m, 1H), 3.53-3.48 (m, 1H), 2.99 (d, *J* = 13.5 Hz, 1H), 2.77 (d, *J* = 14.0 Hz, 1H), 2.50 (s, 3H), 2.21-2.16 (m, 1H), 2.01-1.96 m, 1H), 1.67 (s, 9H).

^{13}C NMR ($CDCl_3$, 125 MHz, major isomer) δ 177.0, 149.3, 143.7, 139.2, 138.3, 135.2, 132.3, 131.9, 130.0, 128.4, 127.8, 127.3, 126.0, 124.5, 123.9, 123.4, 115.0, 84.5, 51.6, 49.6, 45.6, 43.6, 36.8, 28.1, 21.6.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{30}H_{32}NaN_2O_5S_2$ $[M+Na]^+$ 587.1645, found 587.1645.

Tert-butyl (_Z_)-2'-oxo-6-(thiophen-3-ylmethylene)-1-tosylspiro[azepane-4,3'-indoline] -1'-Carboxylate (3az)



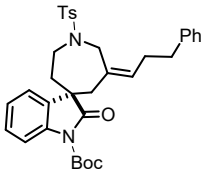
White solid; 96 % yield (54.1 mg, 0.096 mmol); *Z/E* = 5:1; m.p. 114-116 ℃.

^{1}H NMR ($CDCl_3$, 500 MHz, major isomer) δ 7.88 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.37-7.33 (m, 1H), 7.33-7.30 (m, 2H), 7.19-7.16 (m, 1H), 7.00-6.98 (m, 1H), 6.22 (s, 1H), 4.54 (dd, *J* = 15.5, 1.0 Hz, 1H), 4.14 (dd, *J* = 15.5, 1.5 Hz, 1H), 3.58-3.52 (m, 2H), 2.86 (d, *J* = 13.5 Hz, 1H), 2.76 (d, *J* = 14.0 Hz, 1H), 2.49 (s, 3H), 2.22-2.16 (m, 1H), 2.03-1.97 (m, 1H), 1.68 (s, 9H).

^{13}C NMR ($CDCl_3$, 125 MHz, major isomer) δ 177.2, 149.3, 143.7, 138.3, 137.4, 135.5, 132.5, 132.3, 130.0, 128.8, 128.3, 127.2, 125.9, 125.3, 124.3, 123.9, 123.5, 115.0, 84.5, 51.3, 49.5, 46.2, 43.7, 37.1, 28.2, 21.6.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{30}H_{32}N_2O_5S_2Na$ $[M+Na]^+$ 587.1645, found 587.1662.

***Tert*-butyl (*Z*)-2'-oxo-6-(3-phenylpropylidene)-1-tosylspiro[azepane-4,3'-indoline]-1'-Carboxylate (3ba)**



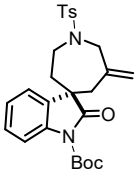
White solid; 59 % yield (34.6 mg, 0.059 mmol); *Z/E* = 4:1; m.p. 117-119 ℃.

^{1}H NMR (400 MHz, $CDCl_3$, major isomer) δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 3.6 Hz, 2H), 7.35-7.33 (m, 9H), 7.15 (d, *J* = 7.2 Hz, 4H), 6.21 (s, 1H), 4.45 (d, *J* = 15.2 Hz, 1H), 4.12 (d, *J* = 15.6 Hz, 1H), 3.58-3.48 (m, 2H), 3.48-3.40 (m, 2H), 2.77 (d, *J* = 8.4 Hz, 2H), 2.42 (s, 3H), 2.34-2.28 (m, 1H), 2.20-2.15 (m, 1H), 2.05-1.97 (m, 2H), 1.65 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz, major isomer) δ 177.1, 149.3, 143.5, 141.6, 138.1, 135.8, 132.9, 131.2, 131.0, 129.9, 128.8, 128.5, 128.1, 127.1, 126.0, 124.3, 123.5, 114.8, 84.3, 49.6, 49.4, 45.1, 43.5, 37.1, 35.2, 29.6, 28.1, 21.6.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{34}H_{38}N_2O_5SK$ $[M+K]^+$ 625.2133, found 625.2120.

***Tert*-butyl 6-methylene-2'-oxo-1-tosylspiro[azepane-4,3'-indoline]-1'-carboxylate (3bb)**



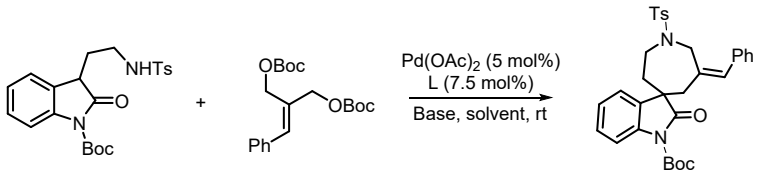
White solid; 80 % yield (38.6 mg, 0.08 mmol); m.p. 115-117 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.83 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.30-7.27 (m, 2H), 5.10 (s, 1H), 4.80 (s, 1H), 4.72 (d, *J* = 14.8 Hz, 1H), 3.86 (d, *J* = 14.8 Hz, 1H), 3.56-3.52 (m, 2H), 2.68 (d, *J* = 13.6 Hz, 1H), 2.55 (d, *J* = 13.2 Hz, 1H), 2.45 (s, 3H), 2.16-2.10 (m, 1H), 2.06-2.00 (m, 1H), 1.63 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 177.0, 149.3, 143.5, 139.4, 138.1, 135.8, 132.7, 129.8, 128.3, 127.1, 124.3, 123.5, 117.9, 114.9, 84.4, 54.1, 48.9, 44.3, 42.3, 38.0, 28.1, 21.5.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{26}H_{30}N_2NaO_5S$ $[M+Na]^+$ 505.1768, found 505.1763.

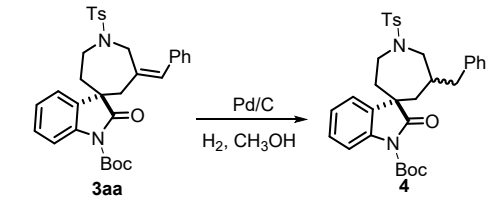
2.4 Gram-scale synthesis of spiro[azepane-4,3'-oxindole] 3aa



To a solution of **1a** (1.0 g, 2.3 mmol) and **2a** (1.3 g, 3.5 mmol, 1.5 equiv.) in MeCN (20 mL), K_2CO_3 (0.92 g, 7.0 mmol, 3 equiv), $Pd(OAc)_2$ (23.0 mg, 0.12 mmol, 5 mol%) and DPPF (93.0 mg, 0.16 mmol, 7.5 mol%) were added, respectively. The reaction mixture was stirred at 80 ℃ for 1 h. After completion of the reaction, the solvent was removed under reduced pressure, concentrated and purified by flash silica gel column chromatography using 1:5 Petroleum Ether/EtOAc as eluents to give **3aa** in 85% yield (1.1 g, *Z*/*E*= 3:1).

2.5 Derivatizations of spiro[azepane-4,3'-oxindole] 3aa

Hydrogenation of 3aa



3aa
major isomer (>20:1 *Z*/*E*)

4
99% yield, 5:1 *dr*

To a solution of **3aa** (55.8 mg, 0.1 mmol) and palladium on activated carbon (5.6 mg, 10% on activated carbon, wetted with ca.55% water) in CH_3OH (4 mL) was degassed, and charged with a hydrogen balloon and stirred at ambient temperature. After 12 h, the mixture was filtered, concentrated and purified by flash column chromatography (Petroleum Ether/EtOAc = 5:1, V:V) to give the product **4** in 99 % yield (55.4 mg, dr = 5:1).

Colorless oil; 83% yield (46.2 mg, 0.083 mmol); major diastereomer of **4**.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.72 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.30-7.22 (m, 5H), 7.18-7.13 (m, 4H), 3.76-3.71 (m, 1H), 3.48-3.42 (m, 2H), 3.17-3.12 (m, 1H), 3.06-2.96 (m, 1H), 2.71-2.66 (m, 1H), 2.51-2.46 (m, 1H), 2.43 (s, 3H), 2.17-2.08 (m, 2H), 2.01-1.96 (m, 1H), 1.65 (s, 1H), 1.62 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 178.2, 149.1, 143.3, 139.1, 137.7, 135.8, 134.0, 129.8, 129.1, 128.4, 128.1, 127.0, 126.2, 124.8, 122.6, 114.9, 84.4, 52.3, 47.9, 43.5, 41.0, 40.3, 38.5, 32.8, 28.1, 21.5.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{32}H_{36}N_2O_5S$ $[M+H]^+$ 561.2418, found 561.2419.

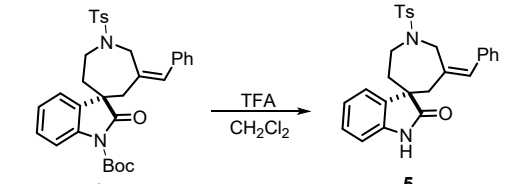
White solid; 16% yield (9.2 mg, 0.016 mmol); m.p. 135-137 ℃; minor diastereomer of **4**.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.80 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.31-7.21 (m, 5H), 7.18-7.11 (m, 2H), 7.06 (d, *J* = 7.2 Hz, 2H), 3.92 (d, *J* = 13.2 Hz, 1H), 3.81-3.75 (m, 1H), 3.23-3.17 (m, 1H), 2.70-2.60 (m, 2H), 2.56-2.50 (m, 1H), 2.43 (s, 3H), 2.22-2.15 (m, 1H), 2.02-1.91 (m, 2H), 1.62 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 179.6, 149.2, 143.4, 138.6, 138.3, 135.6, 132.0, 129.8, 129.1, 128.5, 128.2, 127.2, 126.4, 124.7, 124.5, 115.0, 84.6, 53.6, 49.8, 44.7, 42.0, 41.0, 38.7, 36.0, 28.1, 21.6.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{32}H_{36}N_2O_5SK$ $[M+K]^+$ 599.1977, found 599.1978.

Deportection of 3aa



3aa
major isomer (>20:1 *Z*/*E*)

5
99% yield, >20:1 *Z*/*E*

To a solution of **3aa** (55.8 mg, 0.1 mmol) in dichloromethane (1.0 mL) was added TFA (171.0 mg, 1.5 mmol, 15 equiv.). The reaction mixture was stirred at room temperature for 2 h. After completion of the reaction, the mixture was diluted with EtOAc (5 mL), washed with saturated sodium bicarbonate (5 mL × 2) and brine (5 mL × 2). The combined organic layers were dried with Na_2SO_4, concentrated and purified by flash silica gel column chromatography using 1:3 Petroleum Ether/EtOAc as eluents to give deprotected spirooxindole **5**.

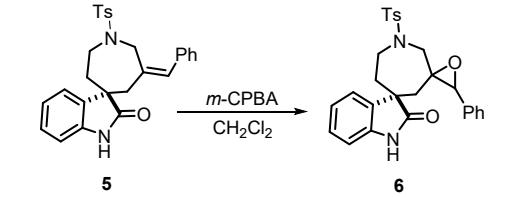
White solid; 99% yield (45.3 mg, 0.099 mmol); *Z*/*E* > 20:1; m.p. 75-78 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz, major isomer) δ 8.75 (s, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 4H), 7.26-7.18 (m, 4H), 7.14 (d, *J* = 7.2 Hz, 2H), 7.01-6.98 (m, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.20 (s, 1H), 4.38-4.27 (m, 2H), 3.68-3.62 (m, 1H), 3.34-3.27 (m, 1H), 2.88 (d, *J* = 13.2 Hz, 1H), 2.66 (d, *J* = 13.2 Hz, 1H), 2.43 (s, 3H), 2.27-2.21 (m, 1H), 1.93-1.88 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz, major isomer) δ 181.5, 143.5, 139.9, 136.3, 135.7, 133.8, 133.0, 132.4, 129.9, 128.8, 128.3, 128.1, 127.2, 127.1, 124.7, 122.0, 110.1, 50.8, 50.0, 45.0, 42.4, 37.0, 21.6.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{27}H_{26}N_2O_3SNa$ $[M+Na]^+$ 481.1556, found 481.1565.

Synthesis of epoxide 6



5
99% yield, >20:1 *Z*/*E*

6
42% yield, >20:1 *dr*

To a solution of **5** (45.1 mg, 0.1 mmol) in dichloromethane (1.0 mL) was added *m*-CPBA (34.5 mg, 0.2 mmol, 2 equiv., 85%). The reaction mixture was stirred at room temperature for 20 h. After completion of the reaction, the mixture was diluted with EtOAc (5 mL), washed with saturated sodium bicarbonate (5 mL × 2) and brine (5 mL × 2). The combined organic layers were dried with Na_2SO_4, concentrated and purified by flash

silica gel column chromatography using 1:5 Petroleum Ether/EtOAc as eluents to give epoxide **6**.

White solid; 42% yield (19.9 mg, 0.042 mmol); *dr* > 20:1; m.p. 168-169 ℃.

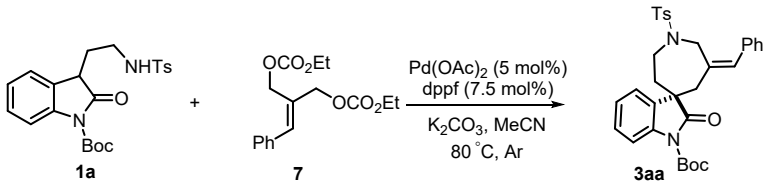
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (s, 1H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 3H), 7.36-7.30 (m, 3H), 7.24-7.20 (m, 2H), 7.10-7.06 (m, 1H), 6.90 (d, *J* = 7.6 Hz, 1H), 4.06 (s, 1H), 3.83-3.73 (m, 2H), 3.28-3.22 (m, 1H), 3.00 (d, *J* = 14.8 Hz, 1H), 2.84 (d, *J* = 14.4 Hz, 1H), 2.39 (s, 3H), 2.14-2.08 (m, 1H), 2.02-1.98 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 181.6, 143.5, 139.5, 136.0, 134.8, 134.3, 129.8, 128.30, 128.27, 127.8, 127.1, 126.8, 124.0, 123.1, 109.9, 84.5, 82.5, 50.0, 48.4, 45.0, 41.8, 36.6, 21.5.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{27}H_{26}N_2NaO_4S$ $[M+Na]^+$ 497.1505, found 497.1517.

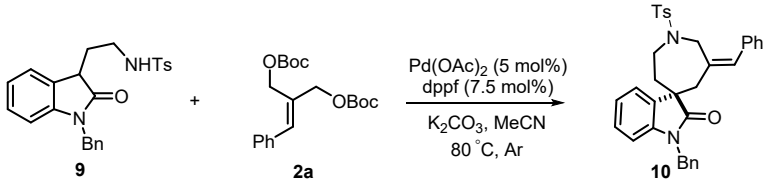
2.6 Control experiments

[4+3]-annulation of oxotryptamine 1a with 2-benzylidenepropane-1,3-diyl diethyl bis (carbonate) 7



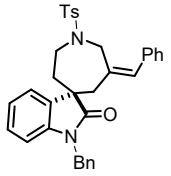
To a solution of oxotryptamine **1a** (43.0 mg, 0.1 mmol) and 2-benzylidenepropane-1,3-diyl diethyl bis(carbonate) **7** (0.15 mmol, 1.5 equiv.) in MeCN (1.0 mL), K_2CO_3 (41.4 mg, 0.3 mmol, 3 equiv.), $Pd(OAc)_2$ (1.0 mg, 0.005 mmol, 5 mol%) and DPPF (4.0 mg, 0.0075 mmol, 7.5 mol%) were added, respectively. The reaction mixture was stirred at 80 ℃ for 1 h. After completion of the reaction, the solvent was removed under reduced pressure, concentrated and purified by silica gel flash column chromatography using 1:5 Petroleum Ether/EtOAc as eluents to give **3aa** in 44% yield (24.6 mg, 0.044 mmol) with 6:1 *Z/E* ratio.

[4+3]-annulation of *N*-Benzyl oxotryptamine 9 with allyl dicarbonate 2a



To a solution of *N*-benzyl oxotryptamines **9** (42.0 mg, 0.1 mmol) and allyl dicarbonate **2a** (54.6 mg, 0.15 mmol, 1.5 equiv.) in MeCN (1.0 mL), K_2CO_3 (41.4 mg, 0.3 mmol, 3 equiv.), $Pd(OAc)_2$ (1.0 mg, 0.005 mmol, 5 mol%) and DPPF (4.0 mg, 0.0075 mmol, 7.5 mol%) were added, respectively. The reaction mixture was stirred at 80 ℃ for 1 h. After completion of the reaction, the solvent was removed under reduced pressure, concentrated and purified by silica gel flash column chromatography using 1:5 Petroleum Ether/EtOAc as eluents to give the desired product **10**.

(*Z*)-1'-benzyl-6-benzylidene-1-tosylspiro[azepane-4,3'-indolin]-2'-one (10)



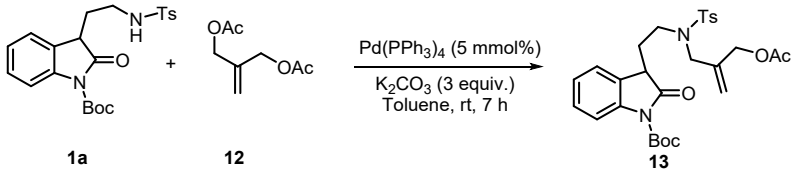
White solid; 75% yield (41.1 mg, 0.075 mmol); *Z/E* = 5:1; m.p. 102-104 ℃.

^{1}H NMR (400 MHz, $CDCl_3$, major isomer) δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.35-7.27 (m, 9H), 7.24-7.14 (m, 5H), 7.01-6.97 (m, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 6.20 (s, 1H), 4.95 (d, *J* = 15.6 Hz, 1H), 4.86 (d, *J* = 15.6 Hz, 1H), 4.43 (dd, *J* = 15.6, 1.6 Hz, 1H), 4.23 (dd, *J* = 15.2, 1.6 Hz, 1H), 3.69-3.63 (m, 1H), 3.44-3.38 (m, 1H), 2.84 (d, *J* = 13.4 Hz, 1H), 2.72 (d, *J* = 13.4 Hz, 1H), 2.43 (s, 3H), 2.26-2.20 (m, 1H), 1.97-1.92 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz, major isomer) δ 179.0, 143.5, 141.7, 136.4, 136.1, 135.8, 133.5, 133.2, 132.2, 129.8, 128.84, 128.78, 128.3, 128.0, 127.7, 127.24, 127.19, 127.1, 124.3, 122.2, 109.1, 50.9, 49.4, 45.1, 43.6, 43.0, 37.0, 21.5.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{34}H_{32}N_2O_3S$ $[M+K]^+$ 587.1765, found 587.1773.

Synthesis of *N*-alkylation product 13



1a **12** **13**

To a solution of oxotryptamine **1a** (43.0 mg, 0.1 mmol) and allyl diacetate **12** (20.6 mg, 0.12 mmol, 1.2 equiv.) in toluene (1.0 mL), K_2CO_3 (41.4 mg, 0.3 mmol, 3 equiv.), and $Pd(PPh_3)_4$ (5.7 mg, 0.005 mmol, 5 mol%) were added, respectively. The reaction mixture was stirred at room temperature for 7 h. After completion of the reaction, the solvent was

removed under reduced pressure, concentrated and purified by silica gel flash column chromatography using CH_2Cl_2 as eluent to give the desired product **13**.

Colorless oil; 55% yield (29.8 mg, 0.055 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.4 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.34-7.29 (m, 1H), 7.23-7.16 (m, 4H), 4.92 (s, 1H), 4.76 (s, 1H), 4.53 (t, *J* = 6.0 Hz, 1H), 3.90 (dd, *J* = 18.4, 13.6 Hz, 2H), 2.71-2.61 (m, 3H), 2.49 (d, *J* = 13.6 Hz, 1H), 2.40 (s, 3H), 2.26-2.18 (m, 1H), 2.08-2.03 (m, 1H), 2.00 (s, 3H), 1.62 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 177.6, 170.3, 148.8, 143.4, 139.8, 138.0, 136.5, 129.7, 128.9, 127.0, 124.7, 122.9, 117.8, 115.4, 84.6, 66.8, 52.1, 41.8, 39.1, 37.9, 28.1, 21.5, 20.8.

HRMS (TOF-ESI$^+$) m/z: calcd for $C_{28}H_{34}N_2NaO_7S$ $[M+Na]^+$ 565.1979, found 565.1962.

3. References

1 T. Cong, H. Wang, X. Li, H. Wu and J. Zhang, Chiral bifunctional bisphosphine enabled enantioselective tandem Michael addition of tryptamine-derived oxindoles to ynones, *Chem. Commun.*, 2019, **55**, 9176-9179.

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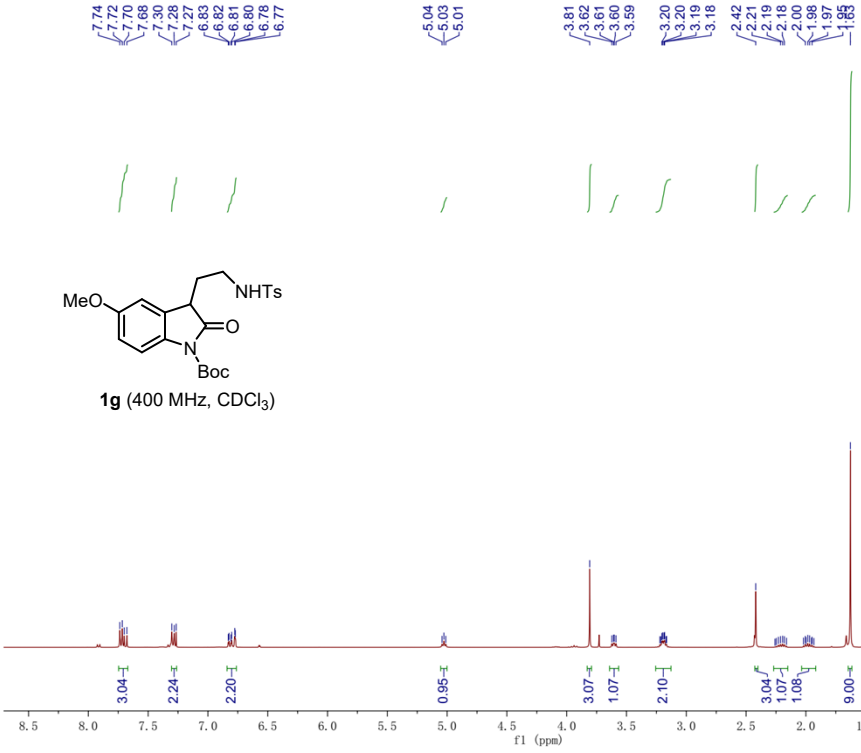
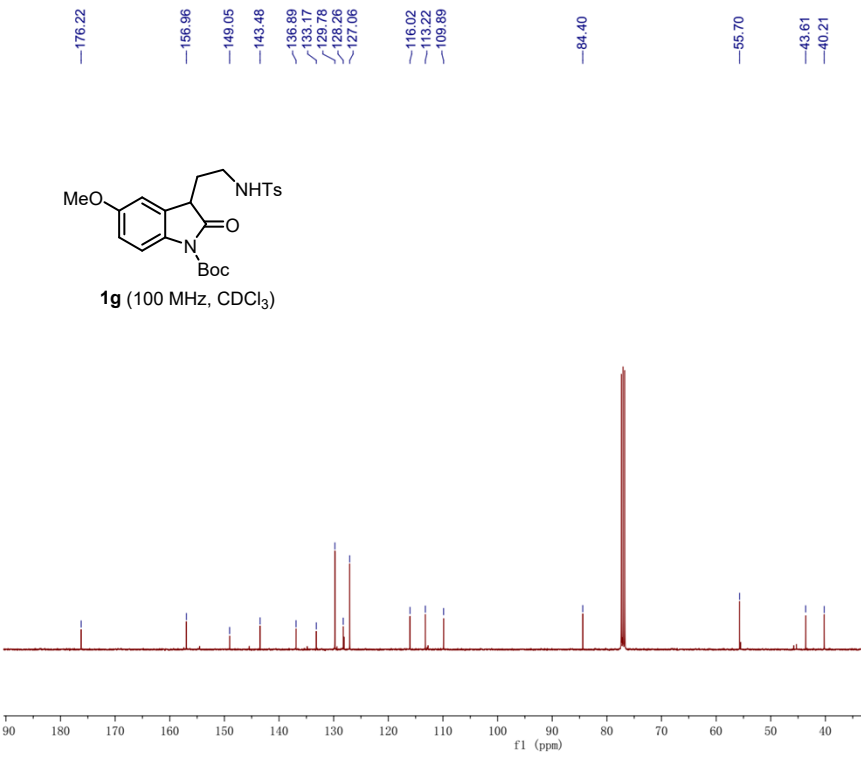
3 (a) M. Gao, Y. Zhao, C. Zhong, S. Liu, P. Liu, Q. Yin and L. Hu, General [4 + 1] Cyclization Approach To Access 2,2-Disubstituted Tetrahydrofurans Enabled by Electrophilic Bifunctional Peroxides, *Org. Lett.*, 2019, **21**, 5679-5684; (b) R. Shintani, K. Moriya and T. Hayashi, Guiding the nitrogen nucleophile to the middle: palladium-catalyzed decarboxylative cyclopropanation of 2-alkylidenetrimethylene carbonates with isocyanates, *Chem. Commun.*, 2011, **47**, 3057-3059.

4 J. Xu, W. Shi, M. Liu, J. Liao, W. Wang, Y. Wu and H. Guo, Palladium-Catalyzed [4+2] Cycloaddition of Hydroxy-Tethered Allylic Carbonates with Alkenes: Synthesis of Functionalized Tetrahydropyrans, *Adv. Synth. Catal.*, 2022, **364**, 2060-2066.

4. NMR spectra



1g (400 MHz, $CDCl_3$)



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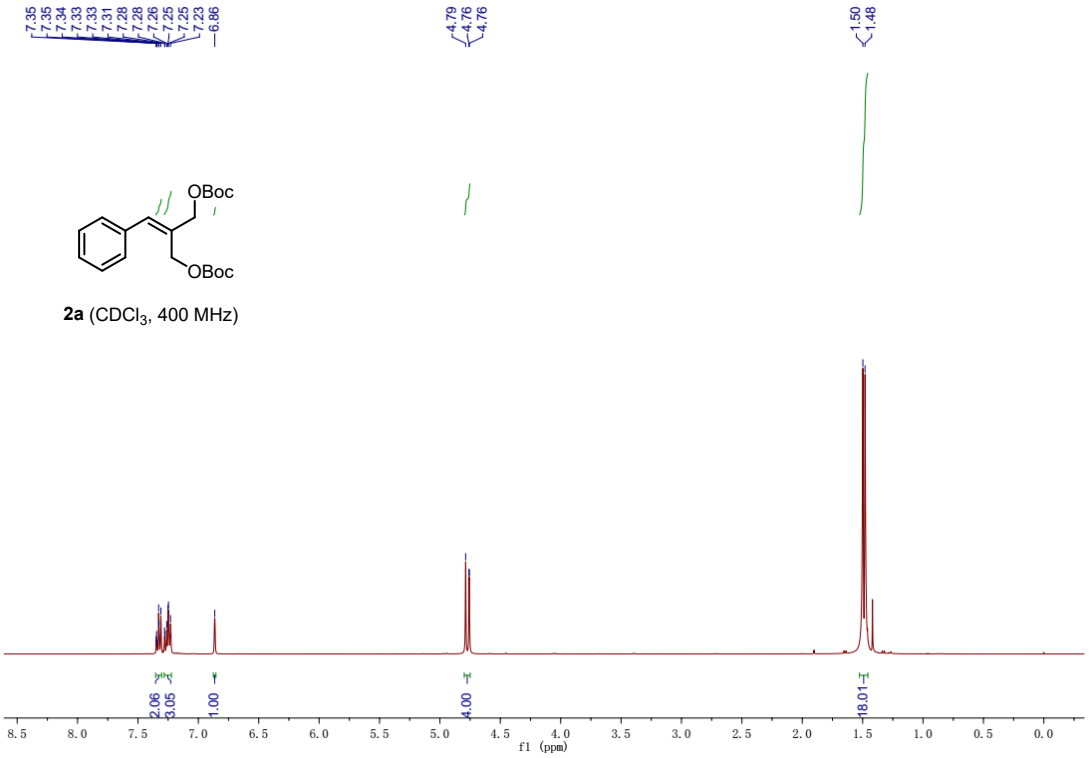
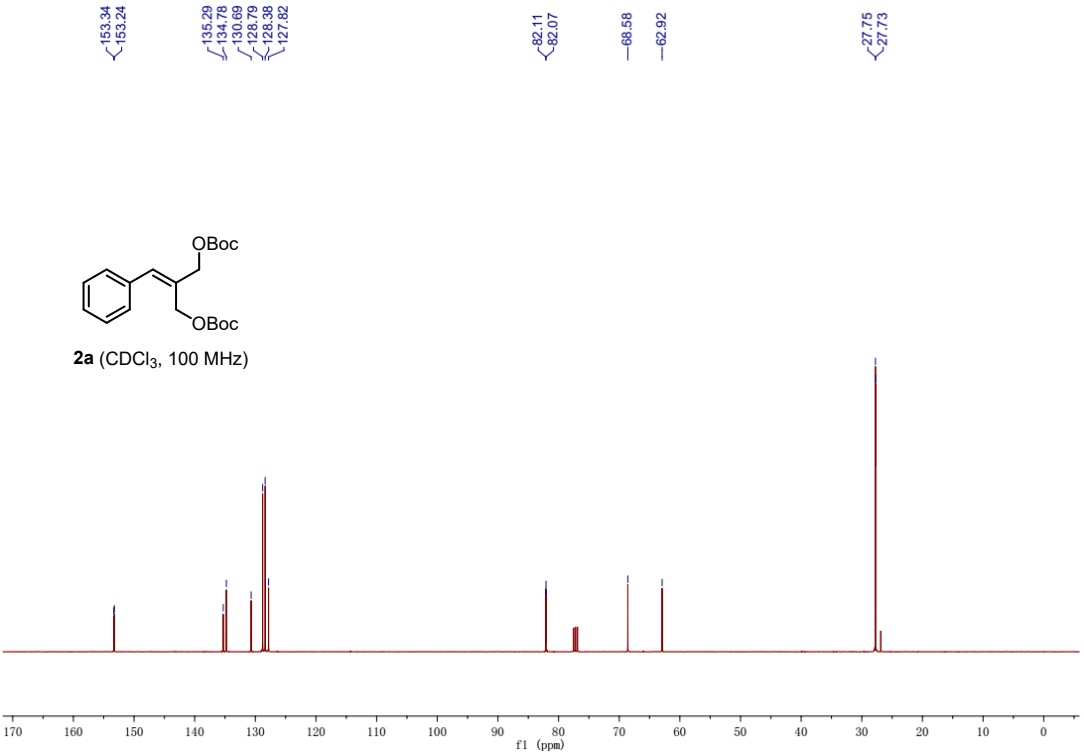


2a ($CDCl_3$, 400 MHz)



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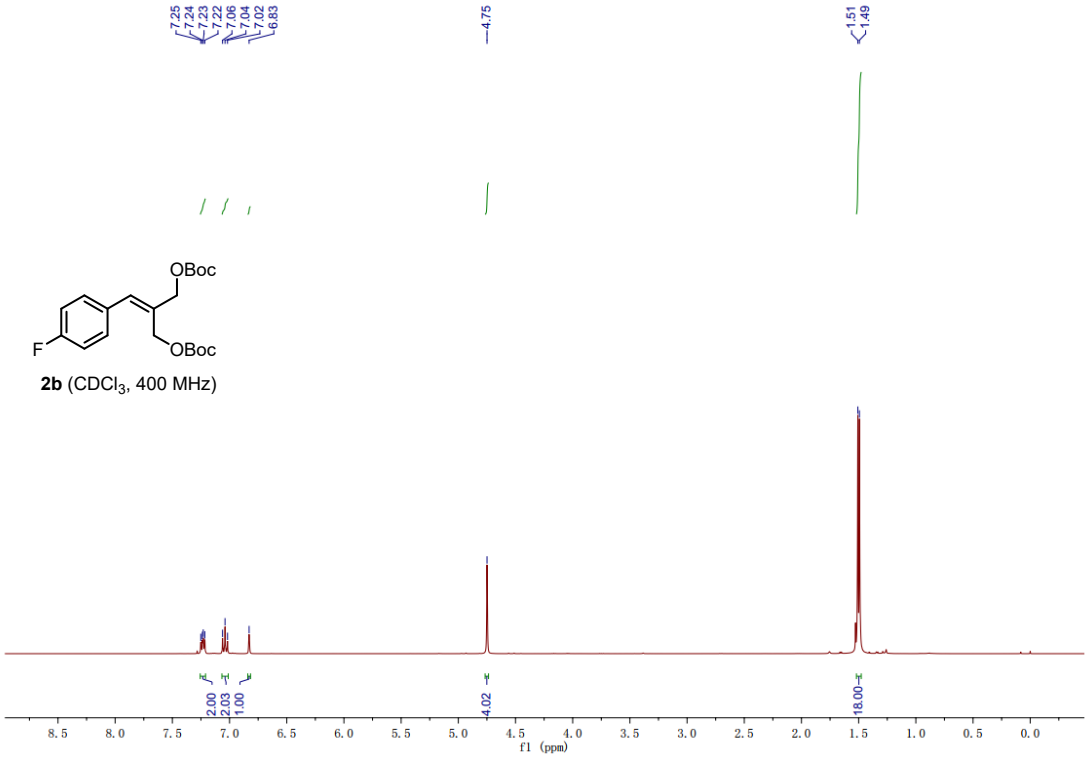
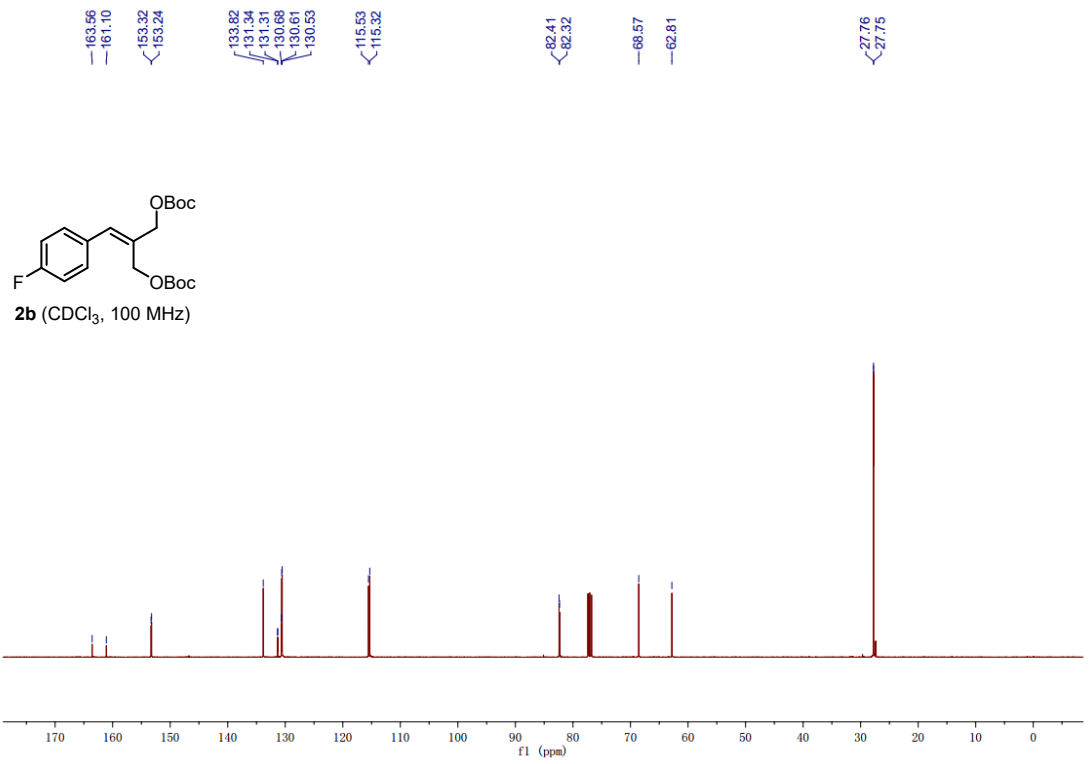
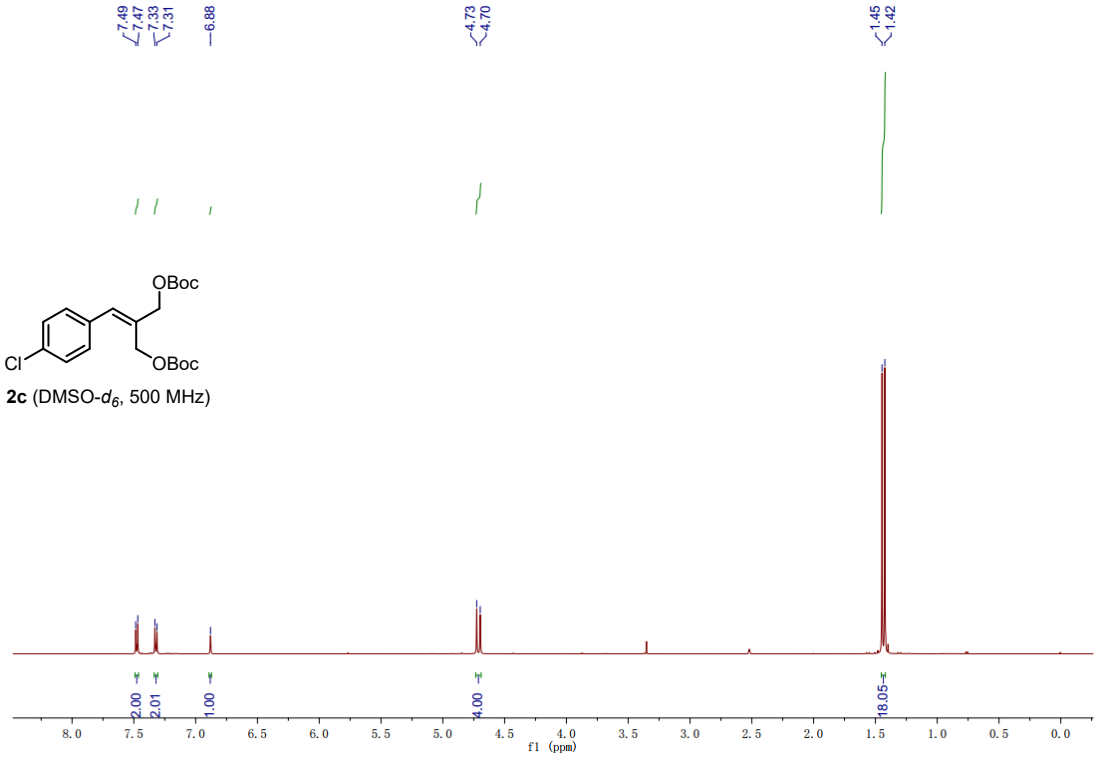


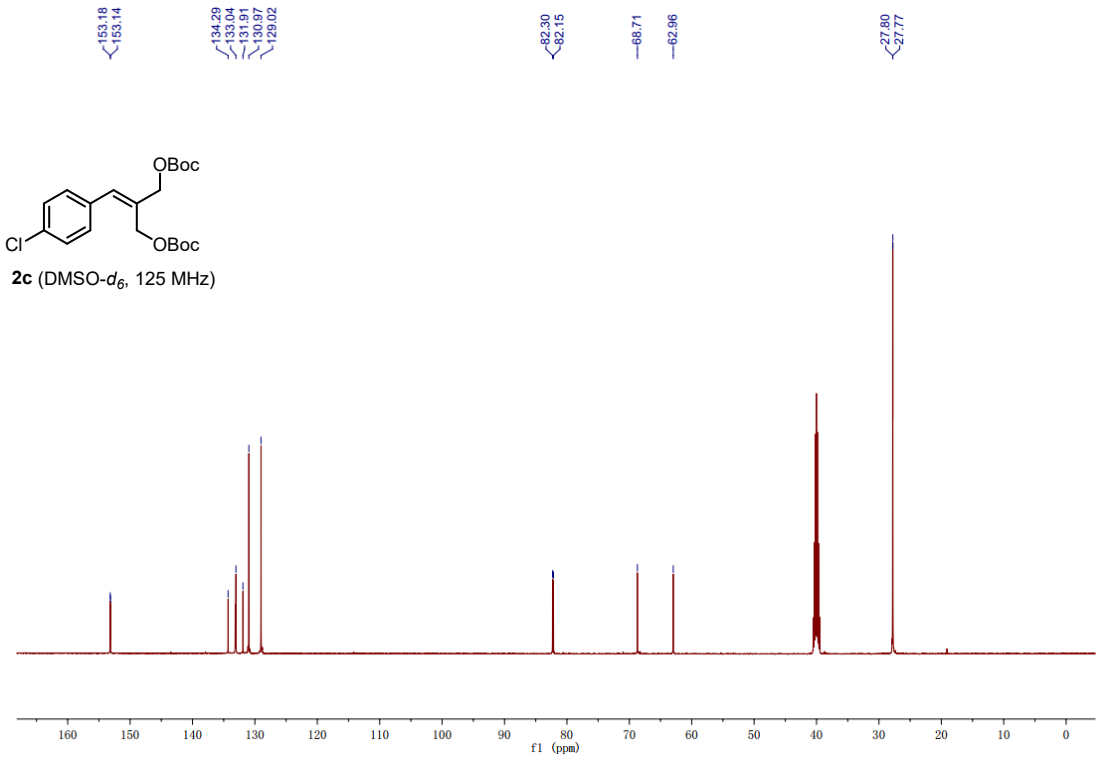
2b ($CDCl_3$, 400 MHz)



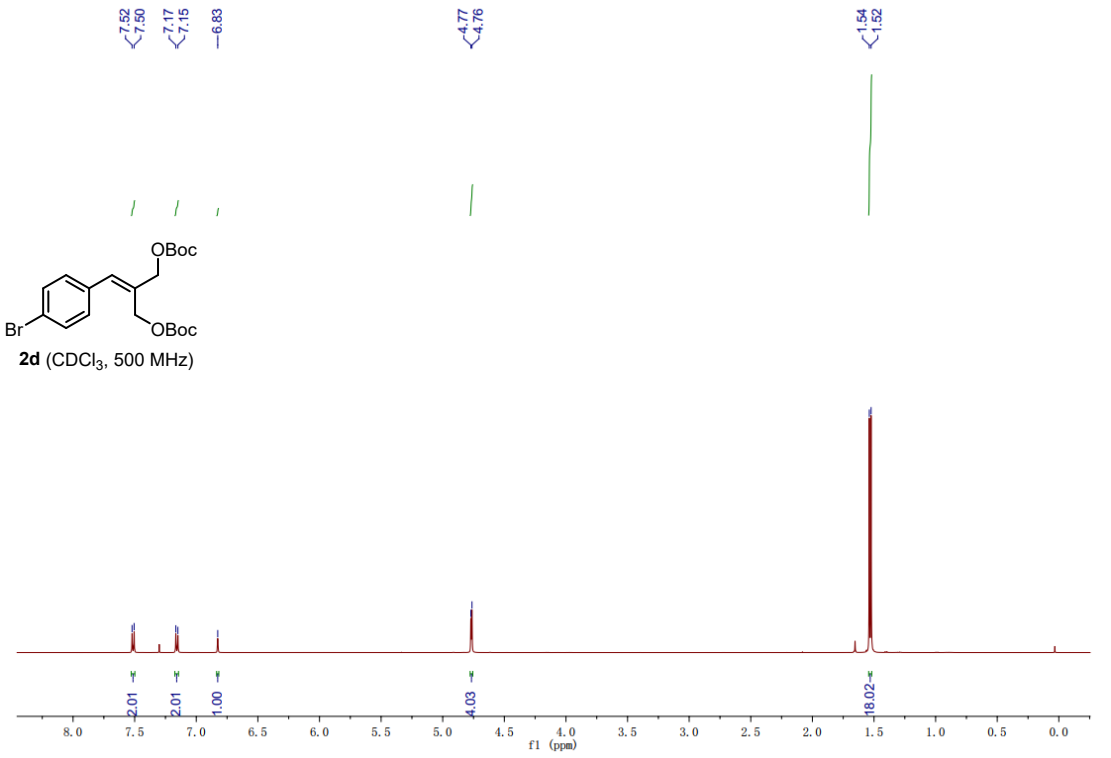
2b ($CDCl_3$, 100 MHz)



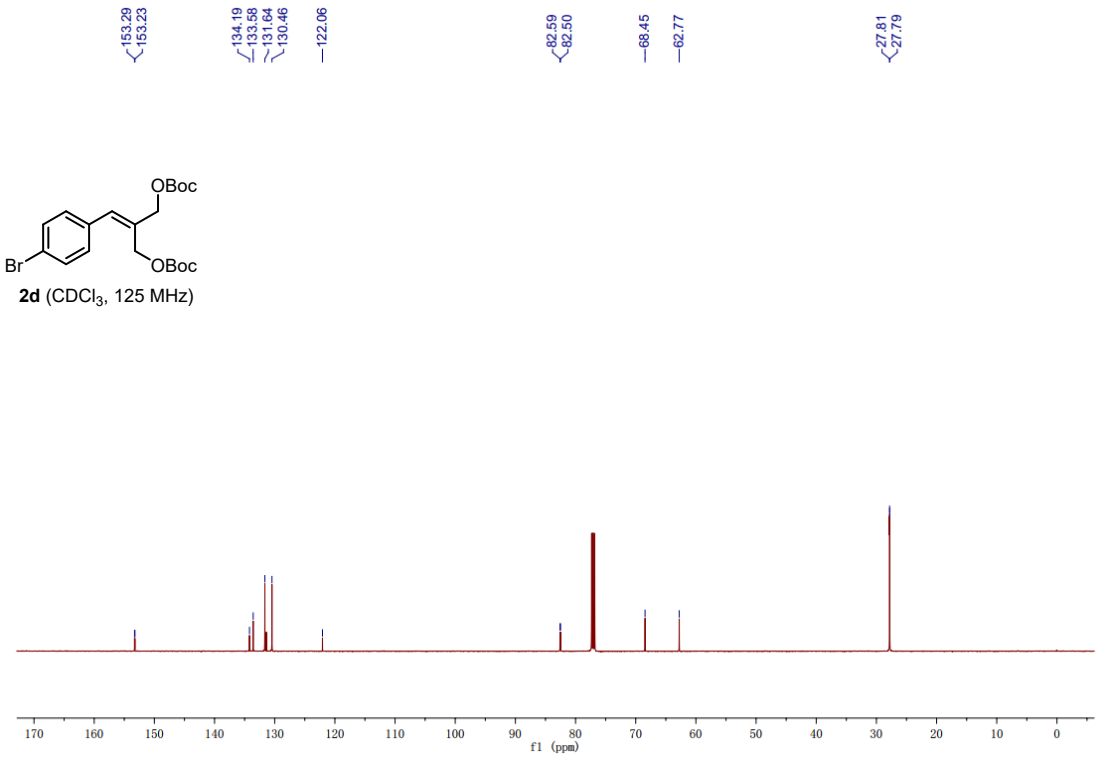
2c (DMSO-d_6, 500 MHz)



2c (DMSO-d_6, 125 MHz)



2d ($CDCl_3$, 500 MHz)



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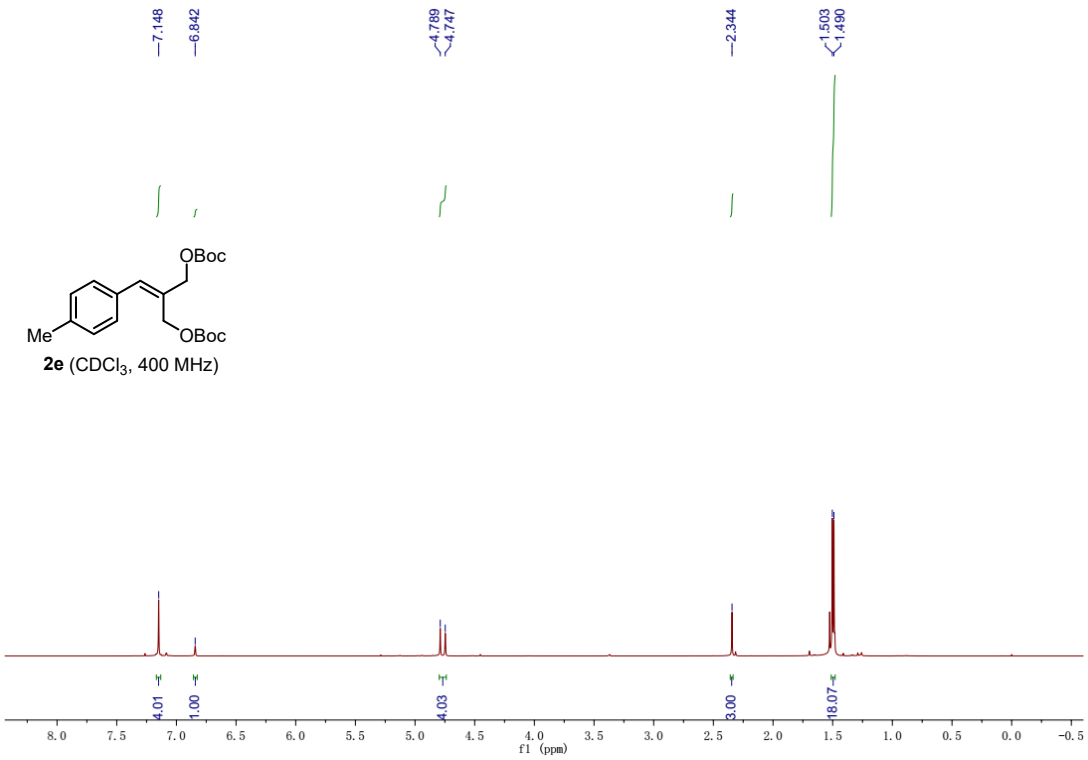

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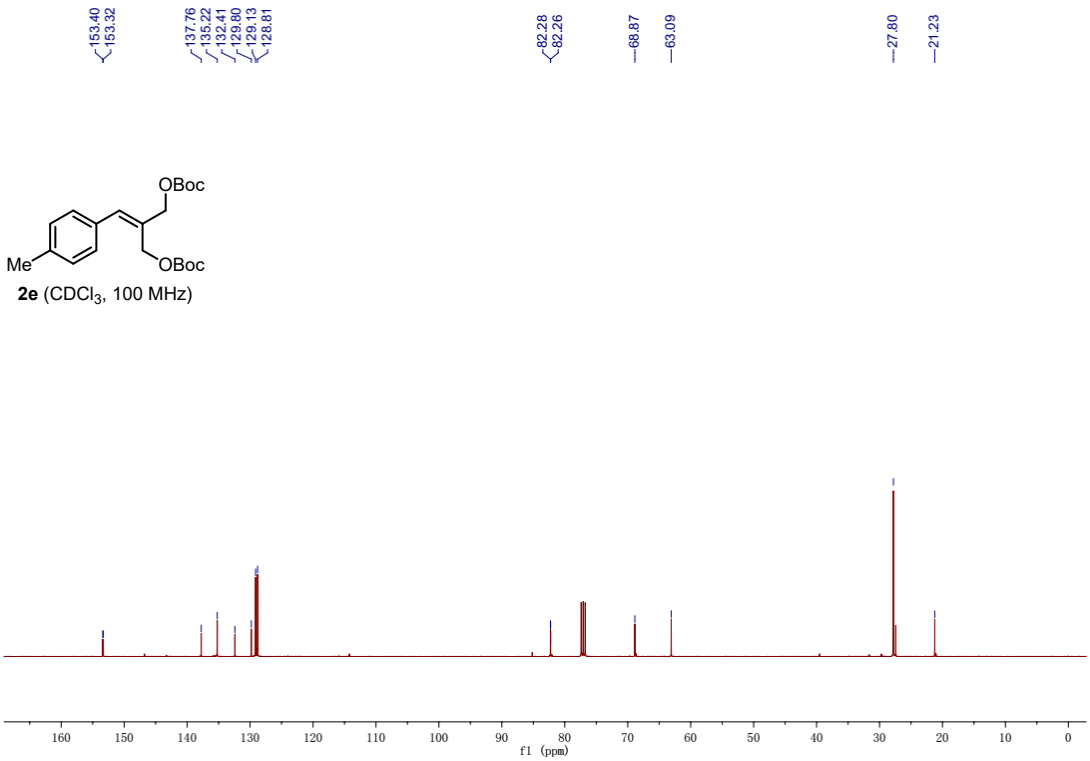

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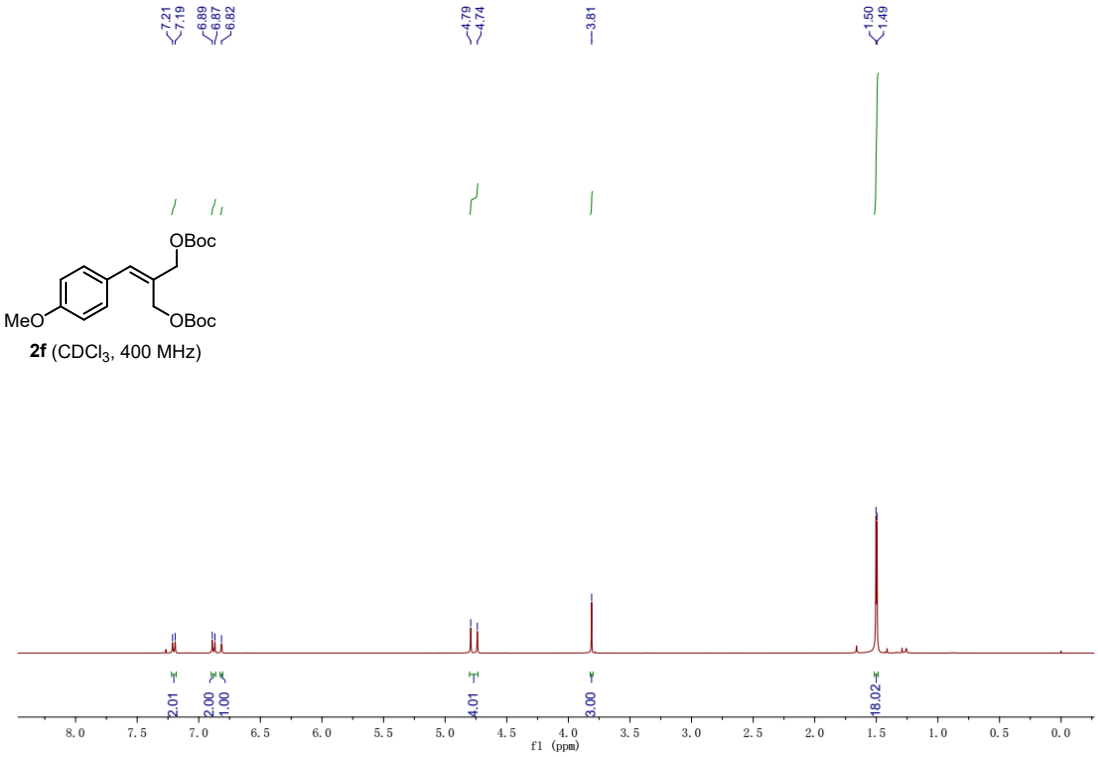

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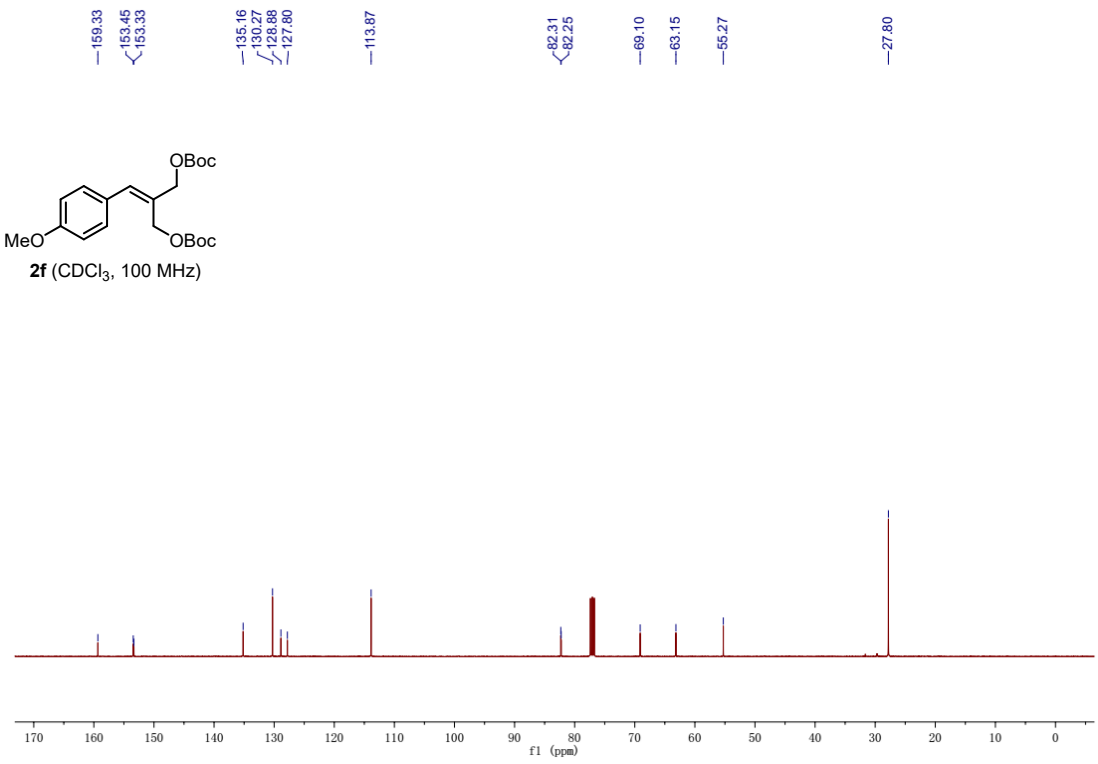

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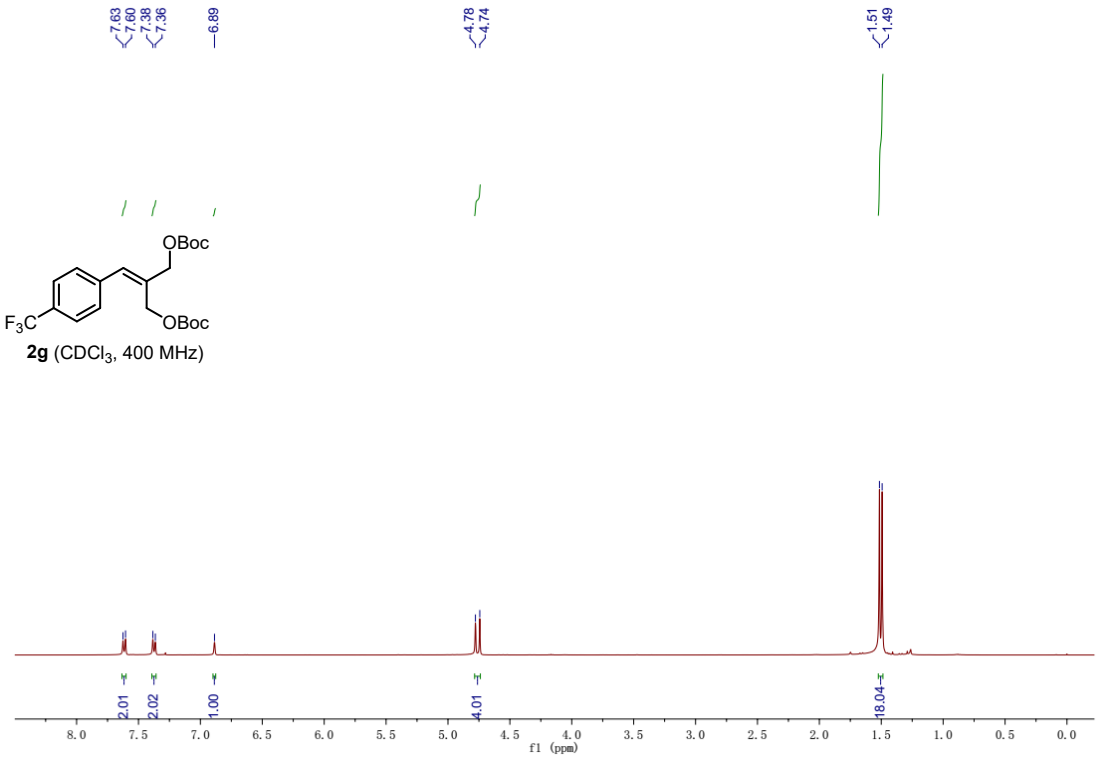
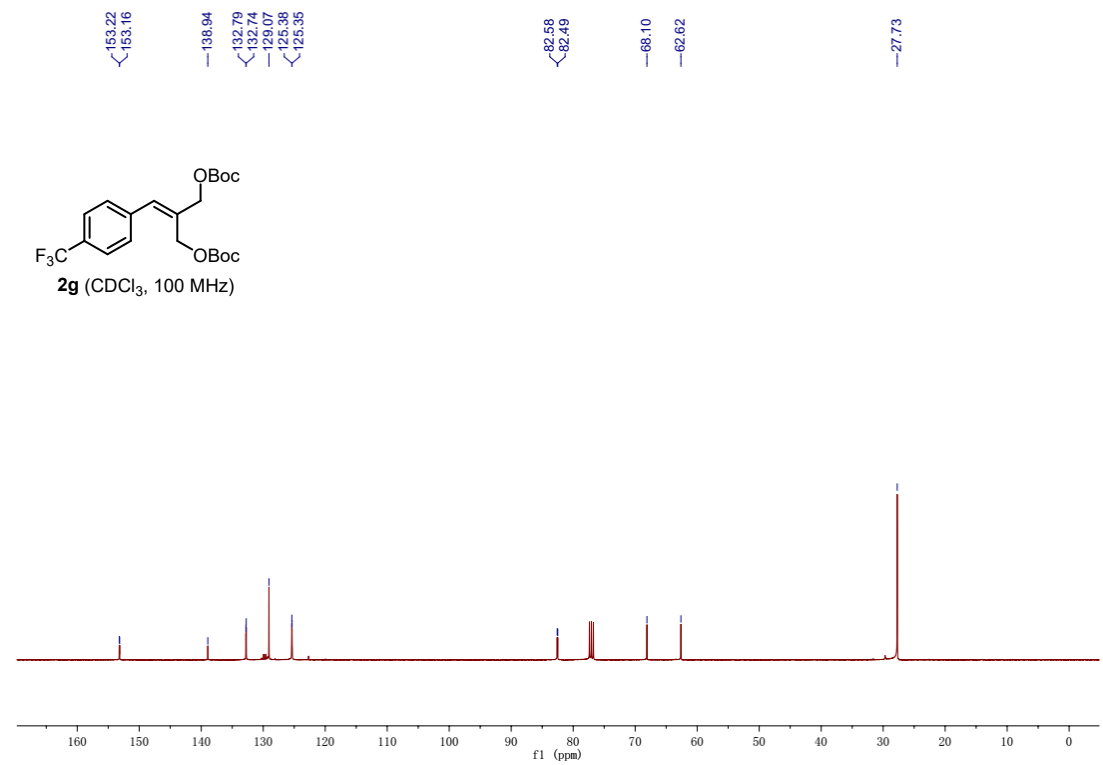


2g ($CDCl_3$, 400 MHz)



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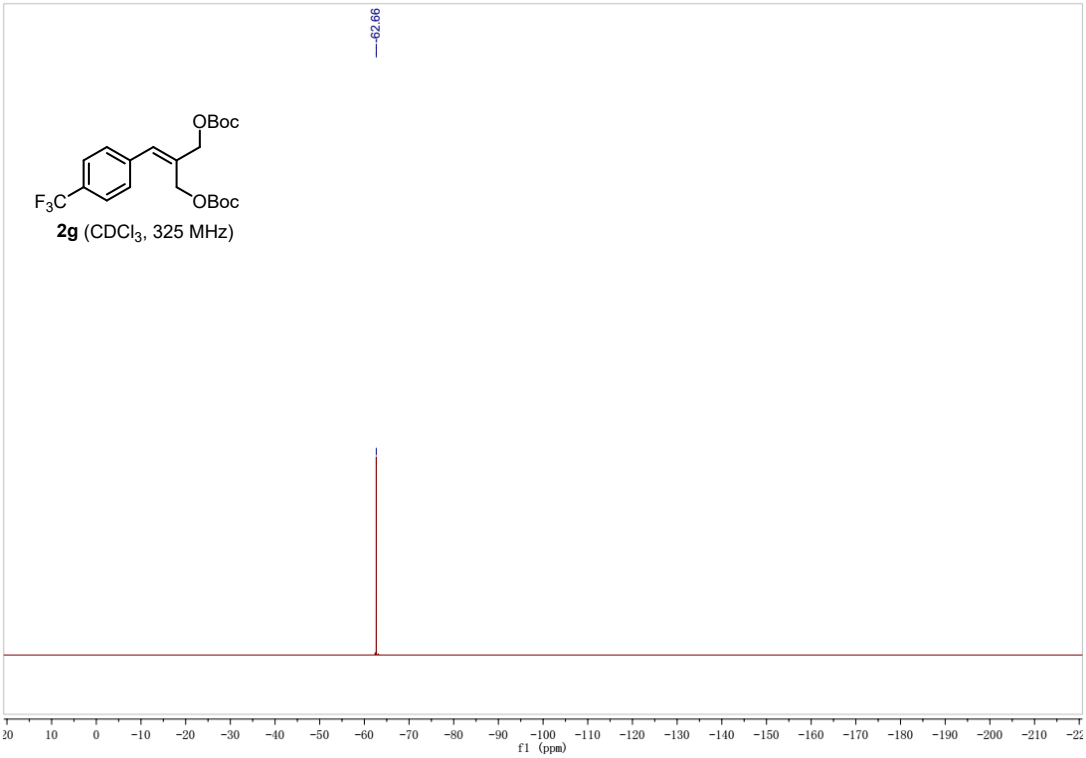

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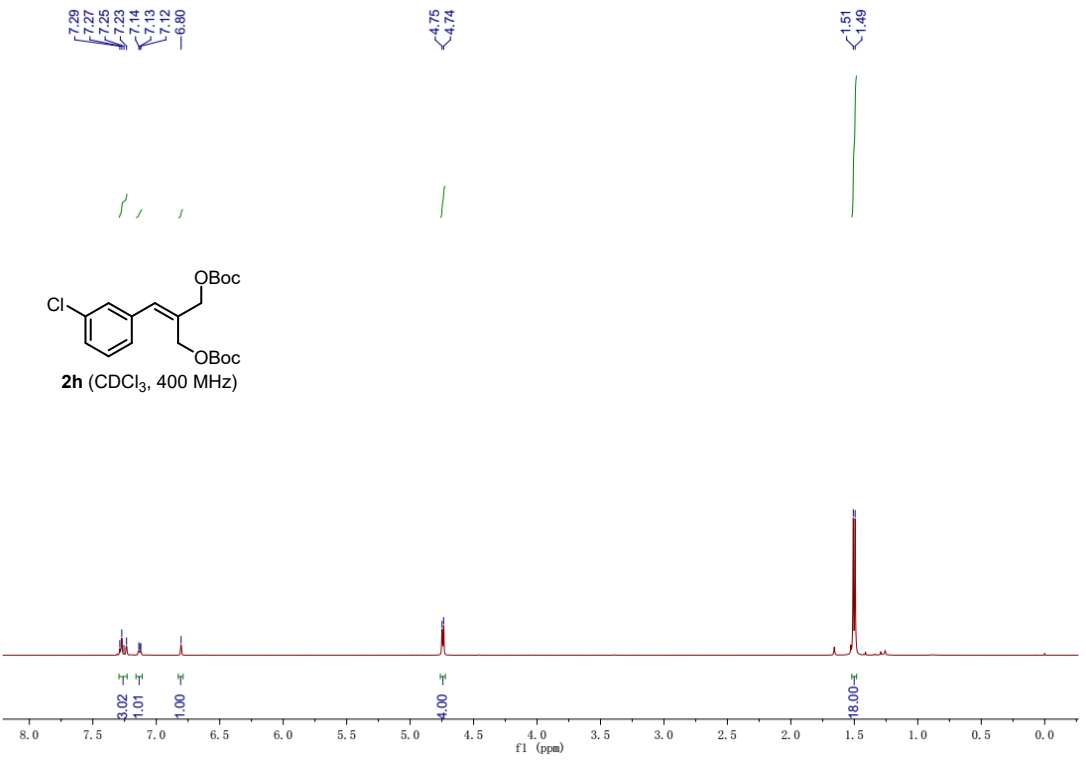
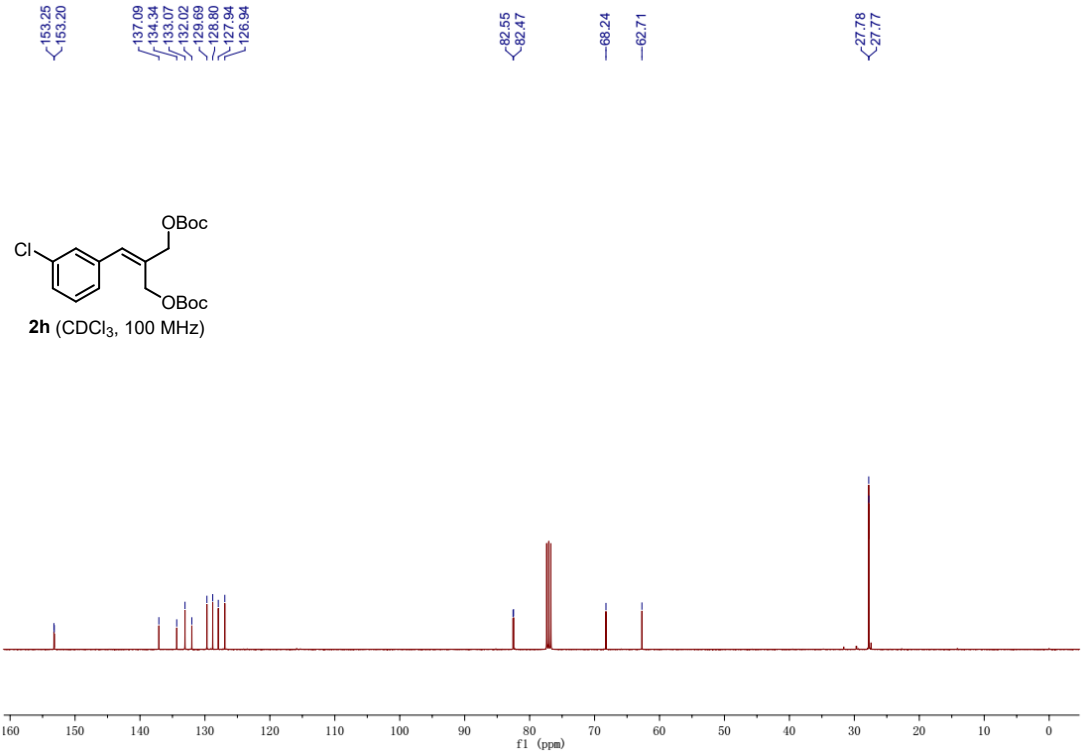


2h ($CDCl_3$, 400 MHz)



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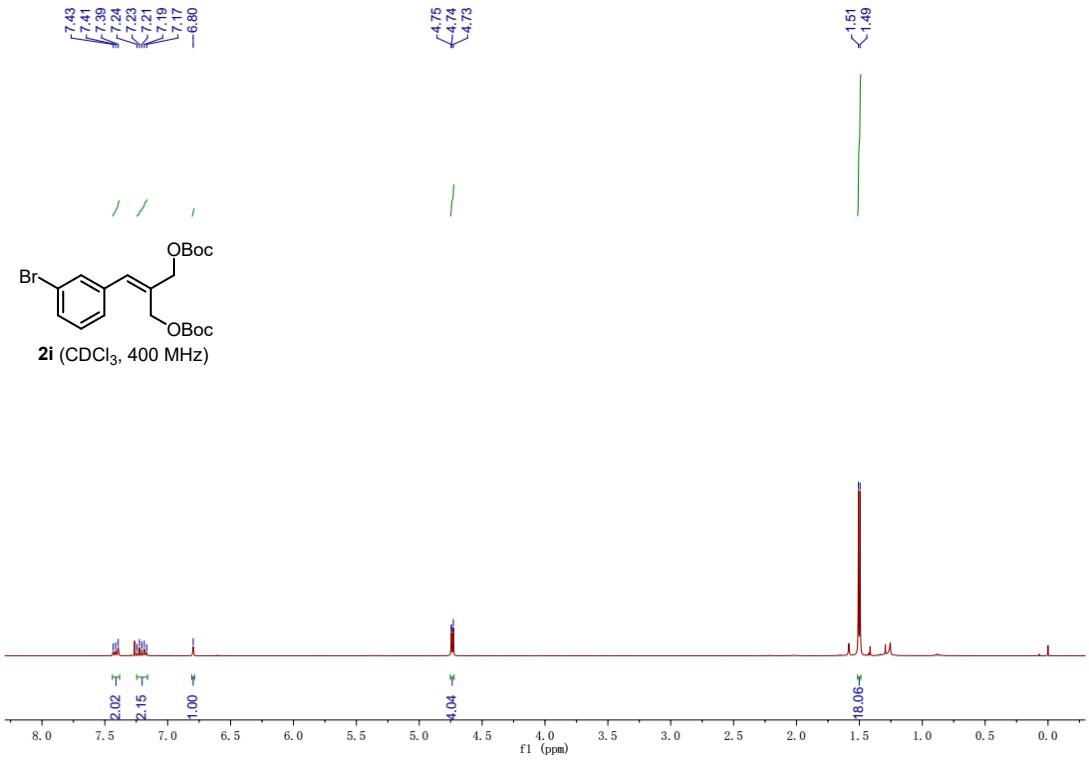
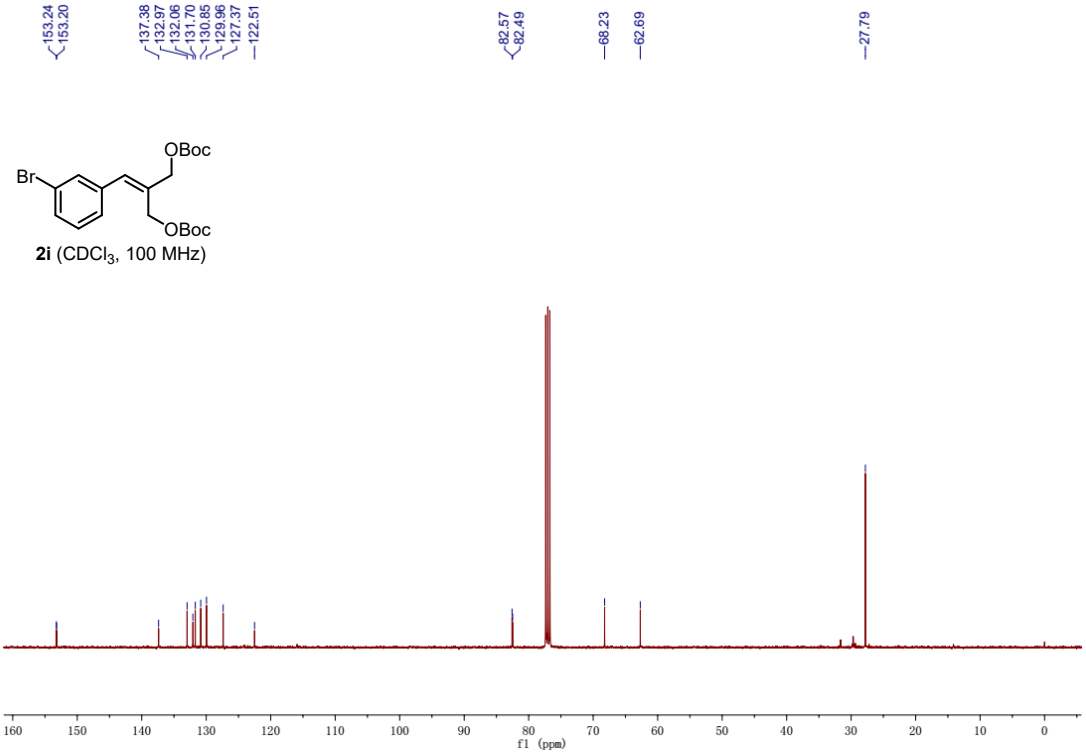


2i ($CDCl_3$, 400 MHz)



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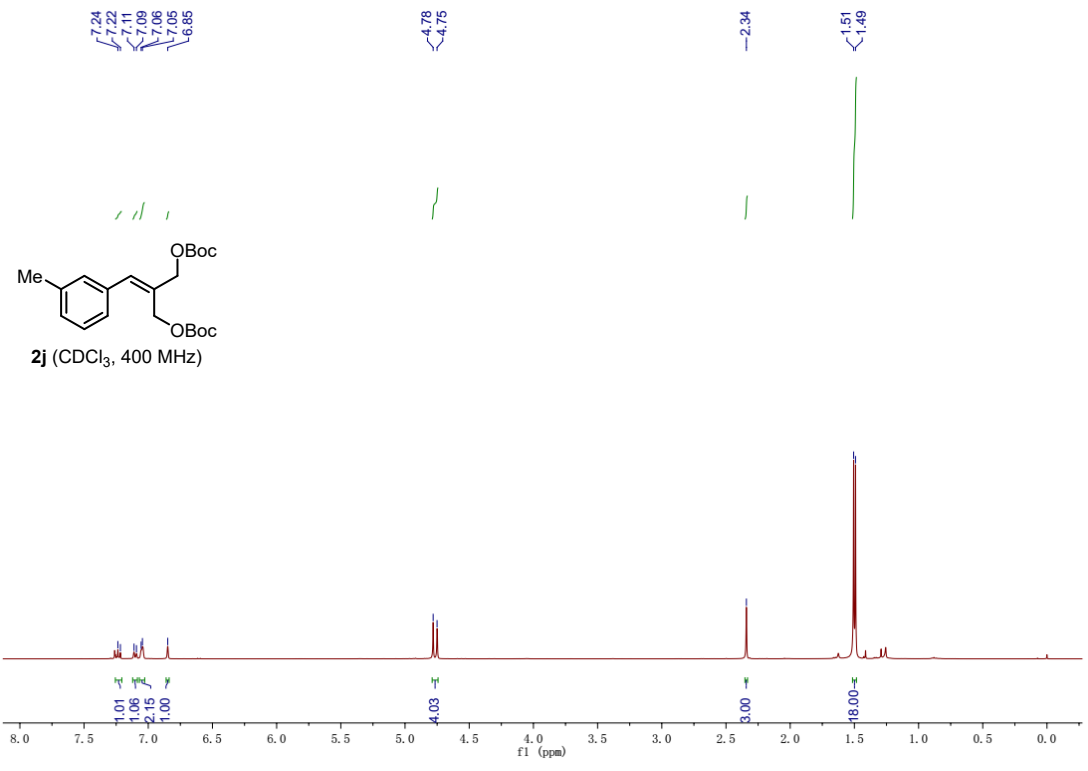

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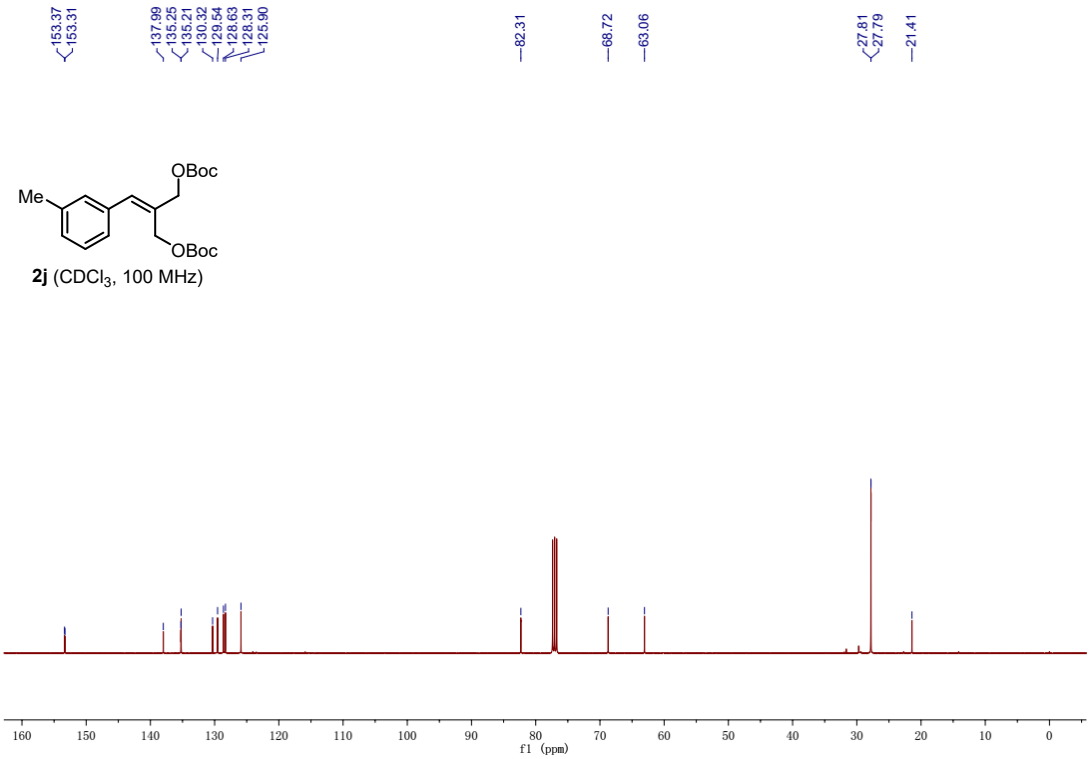

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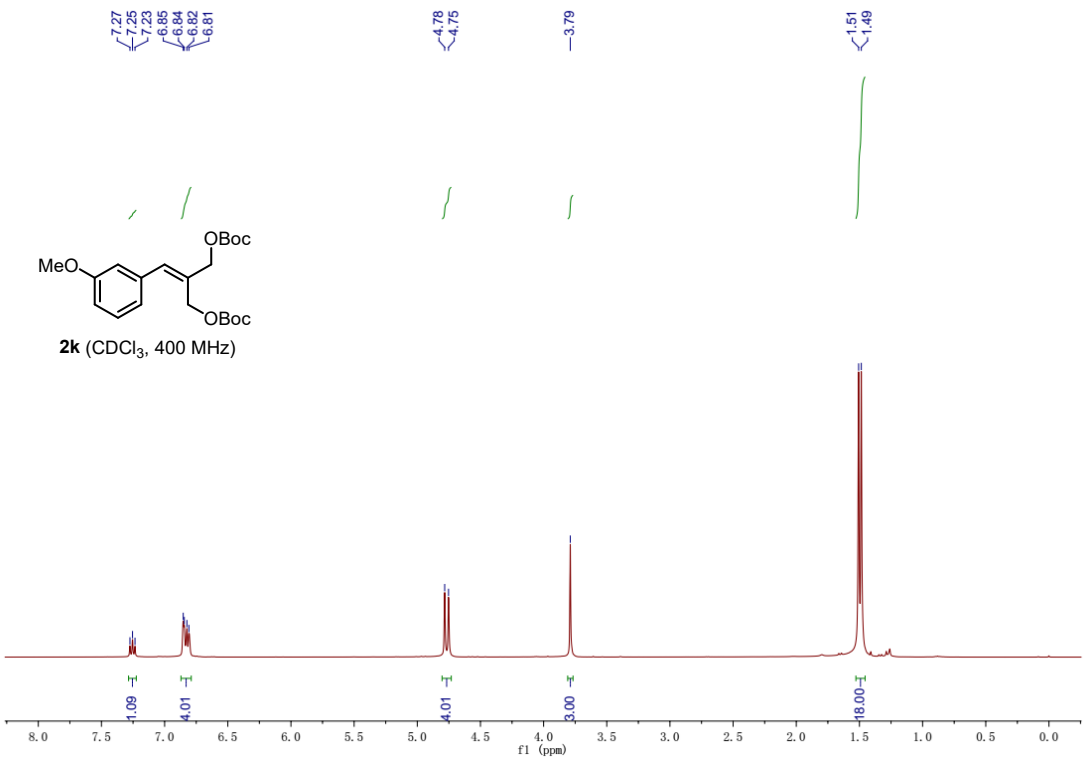

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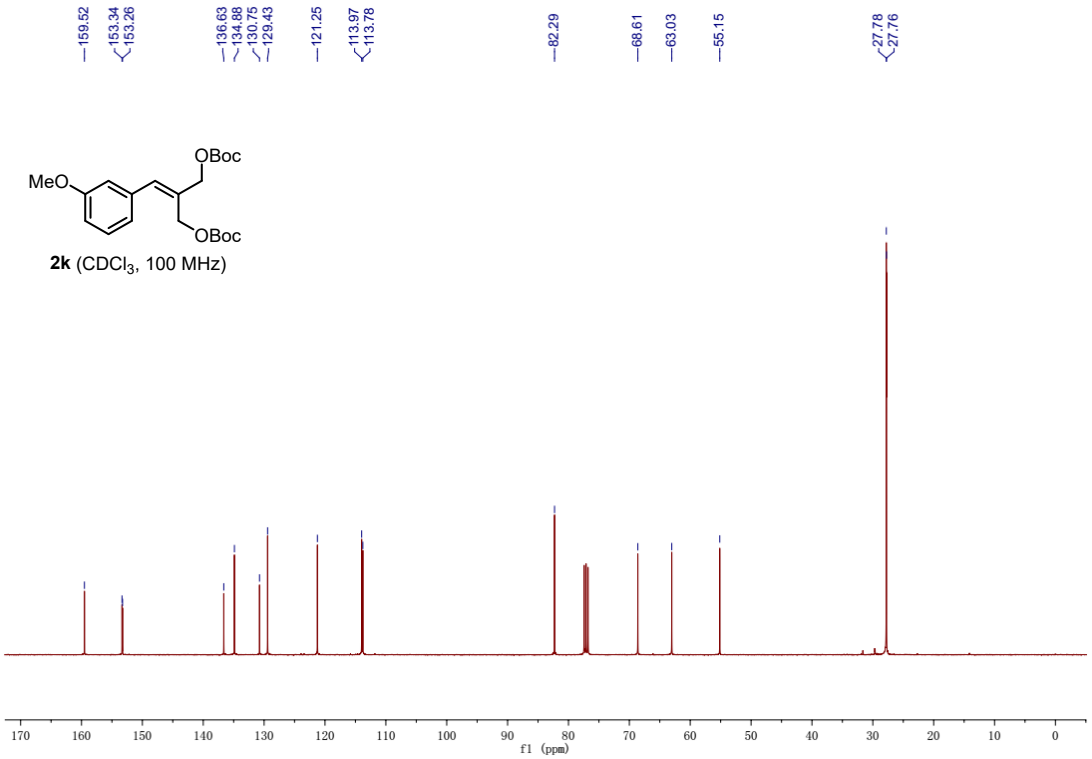

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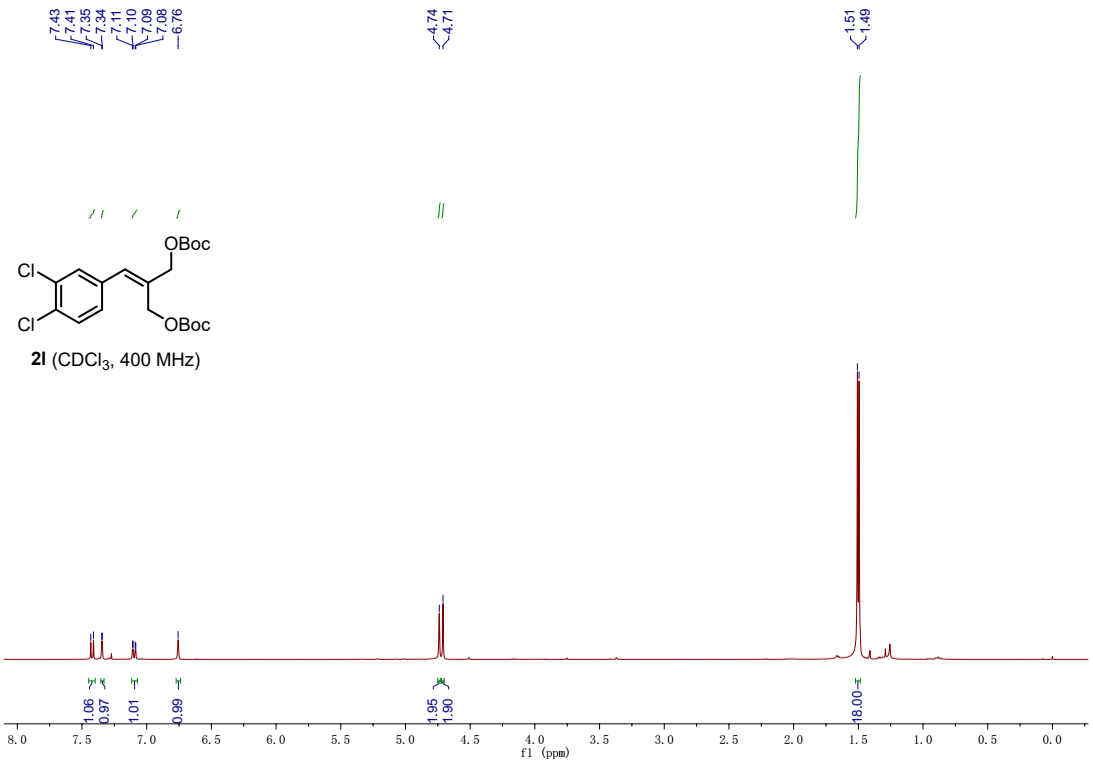

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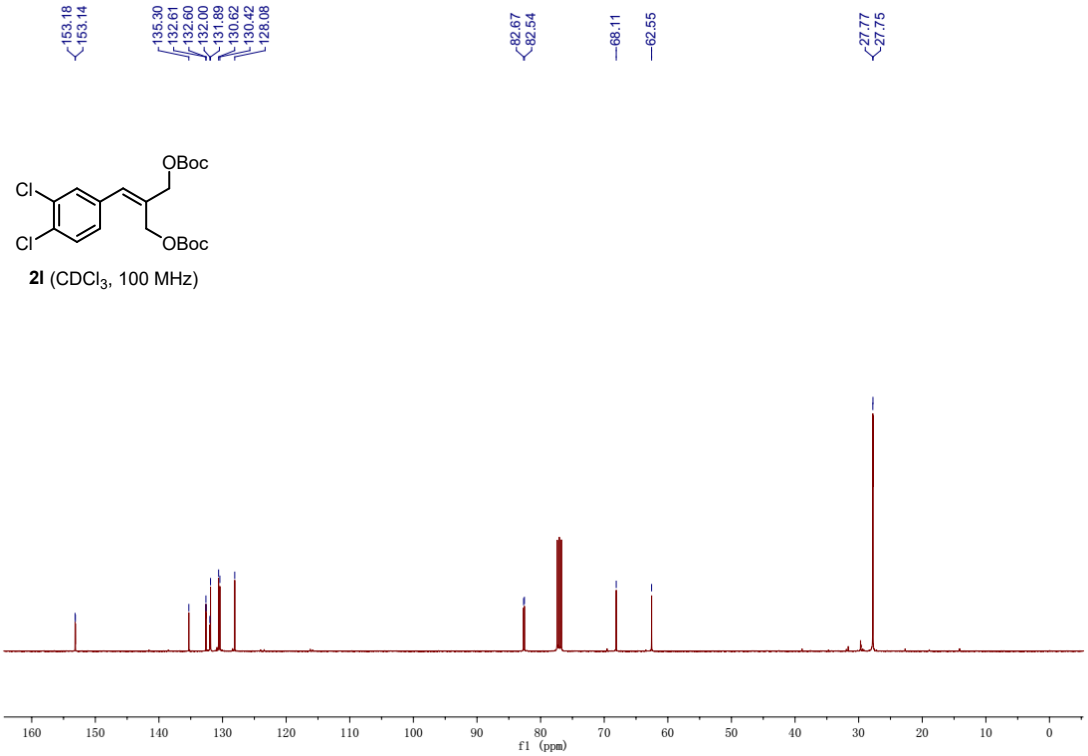

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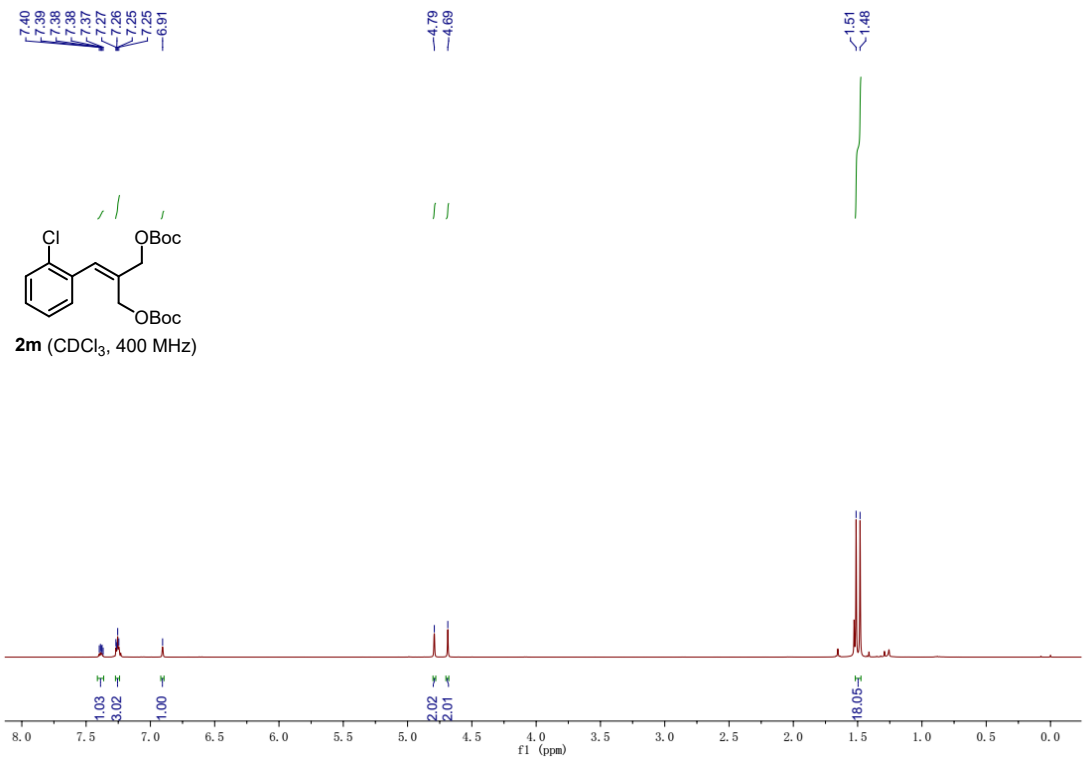

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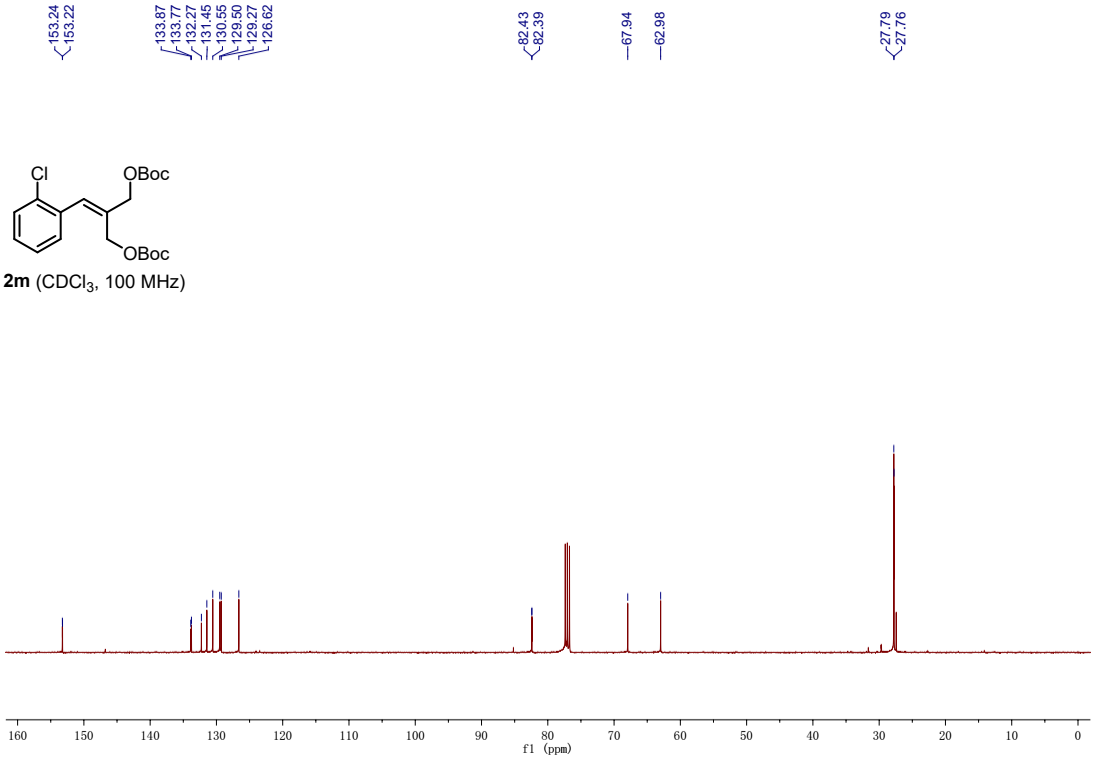

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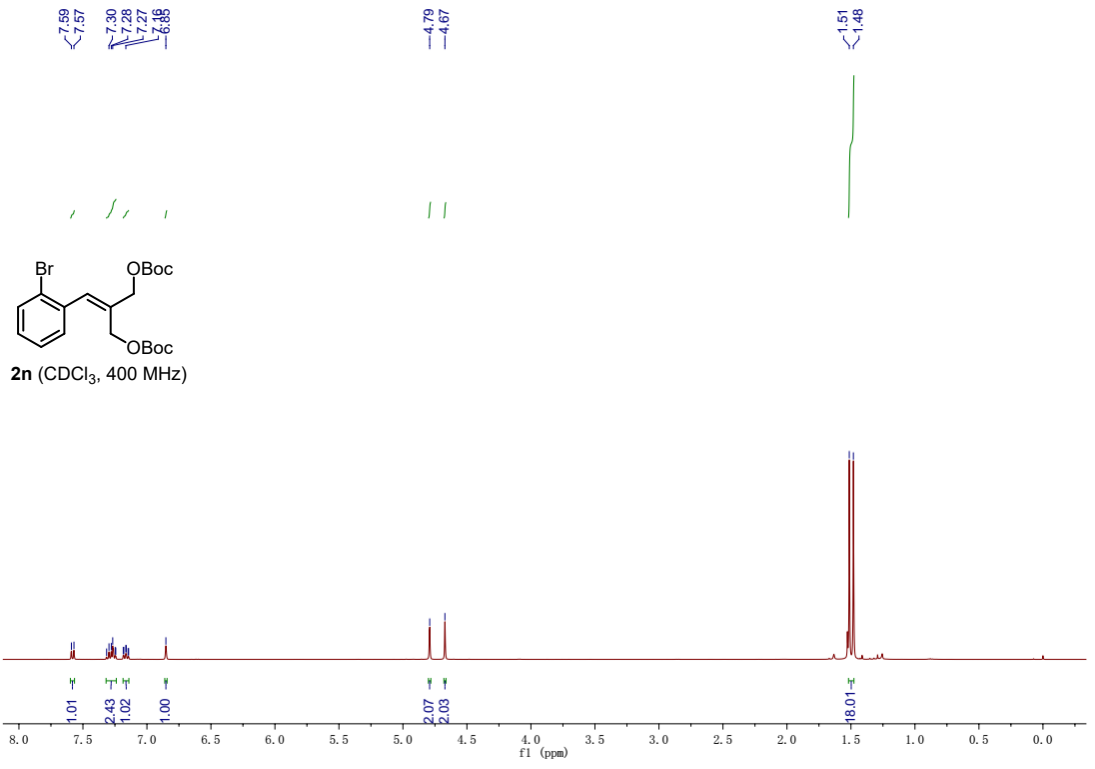

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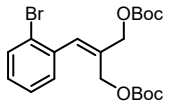

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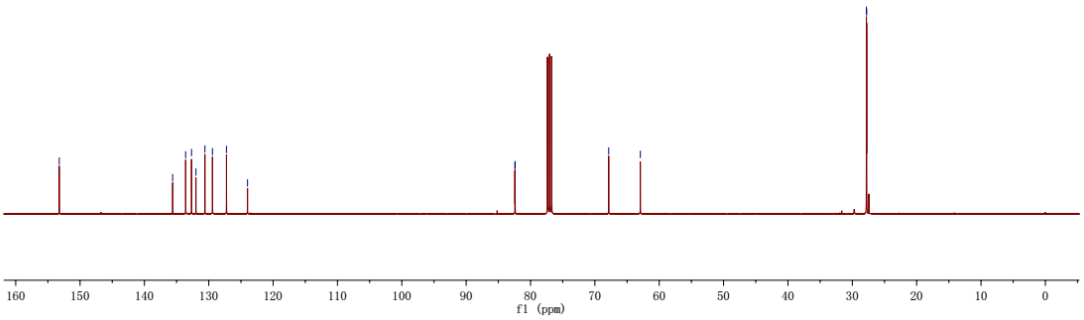

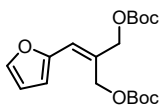

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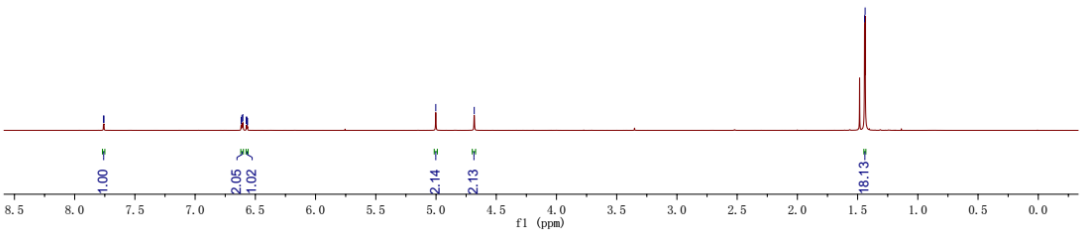
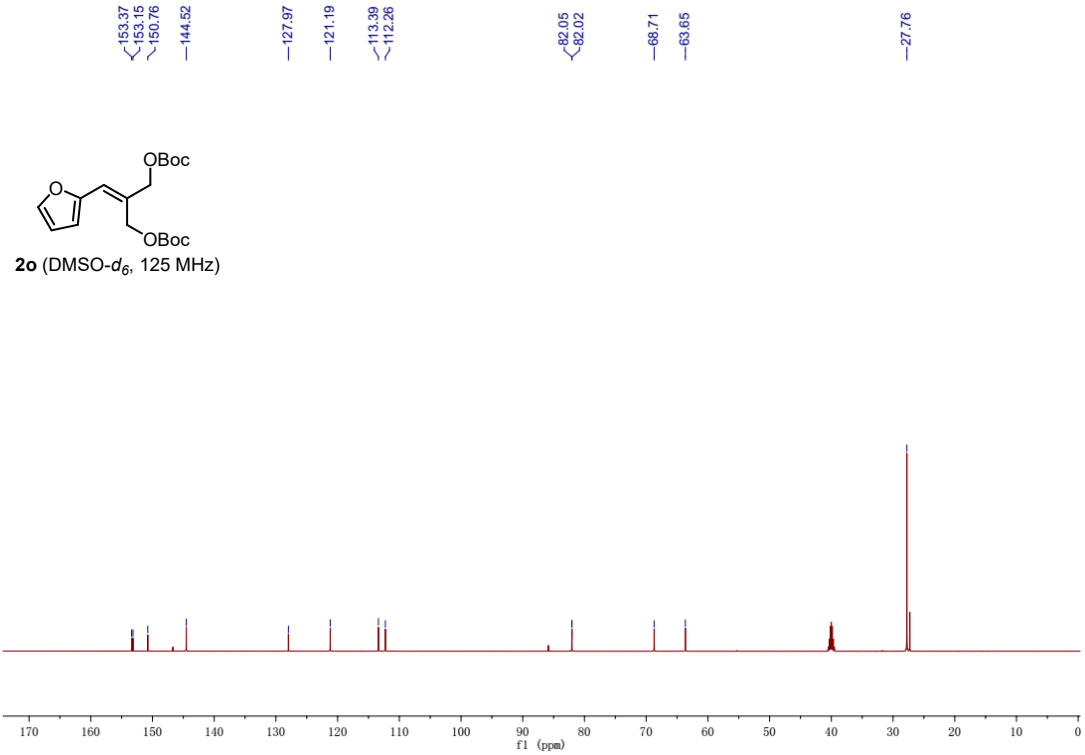
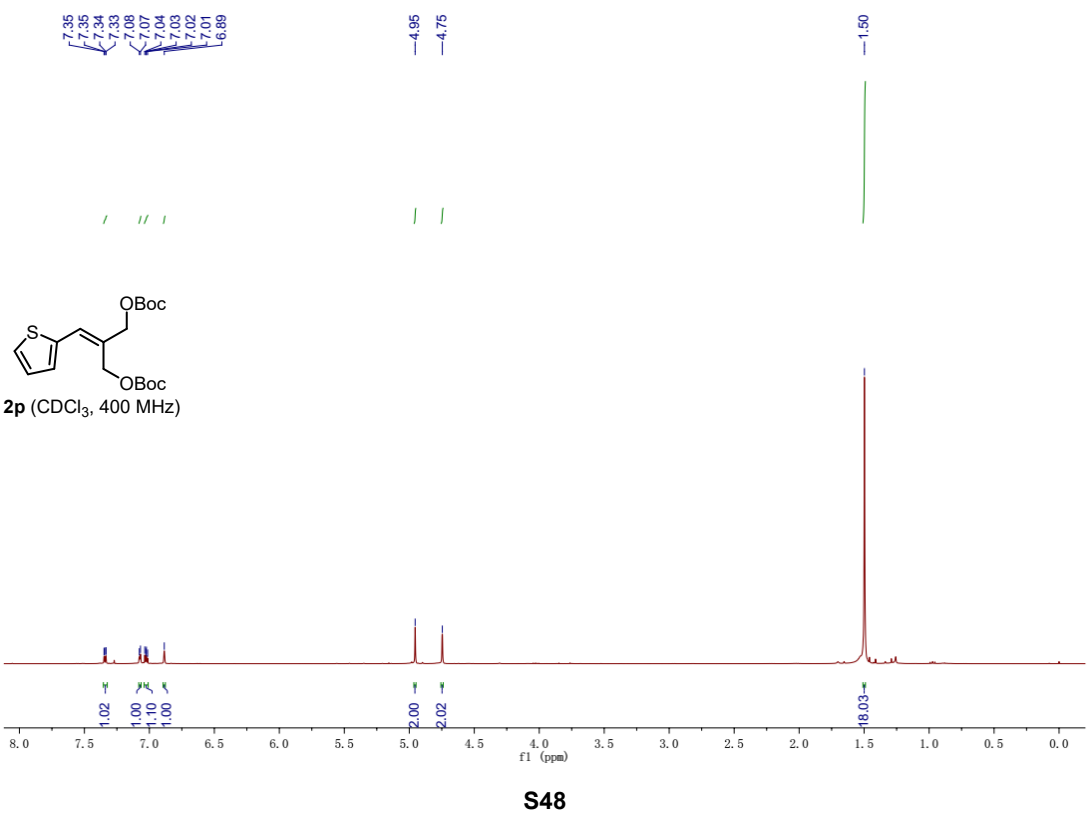
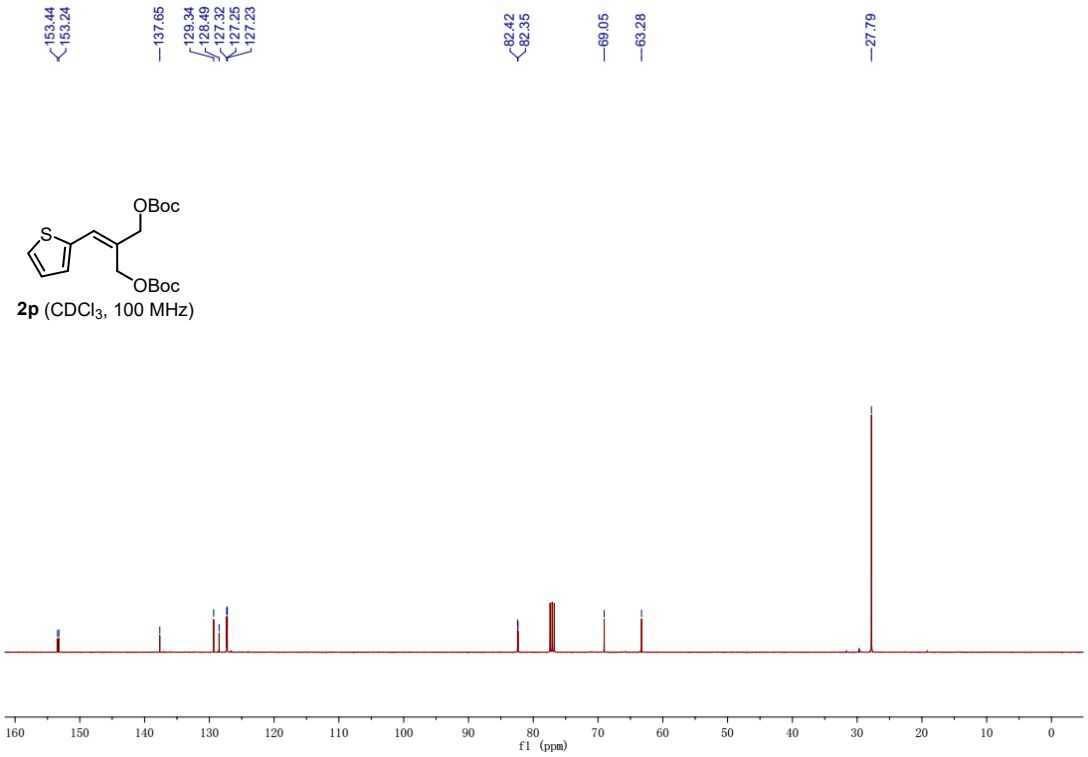




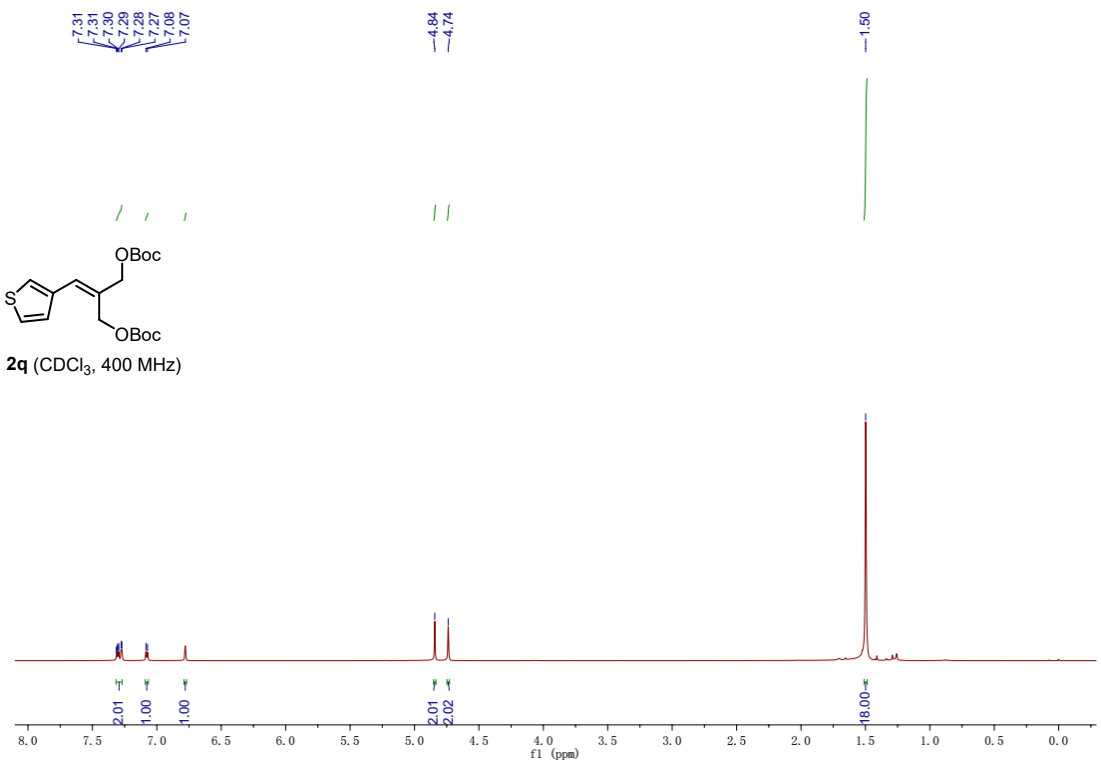
2o (DMSO-d_6, 125 MHz)



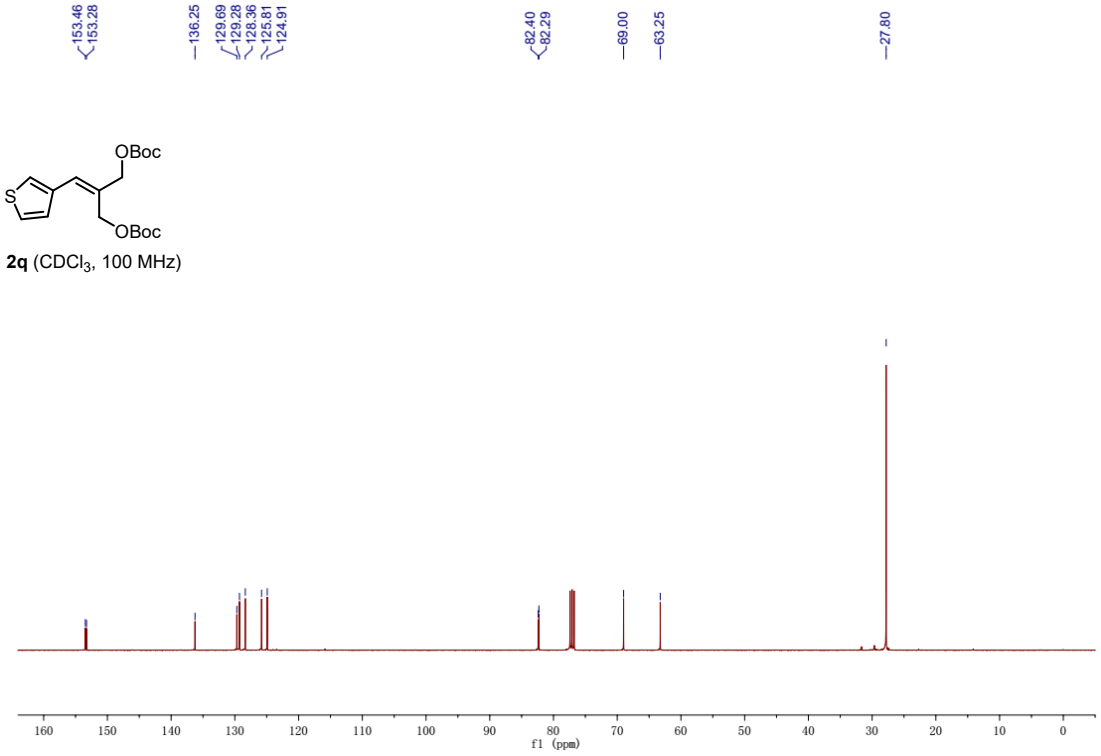
2p ($CDCl_3$, 400 MHz)



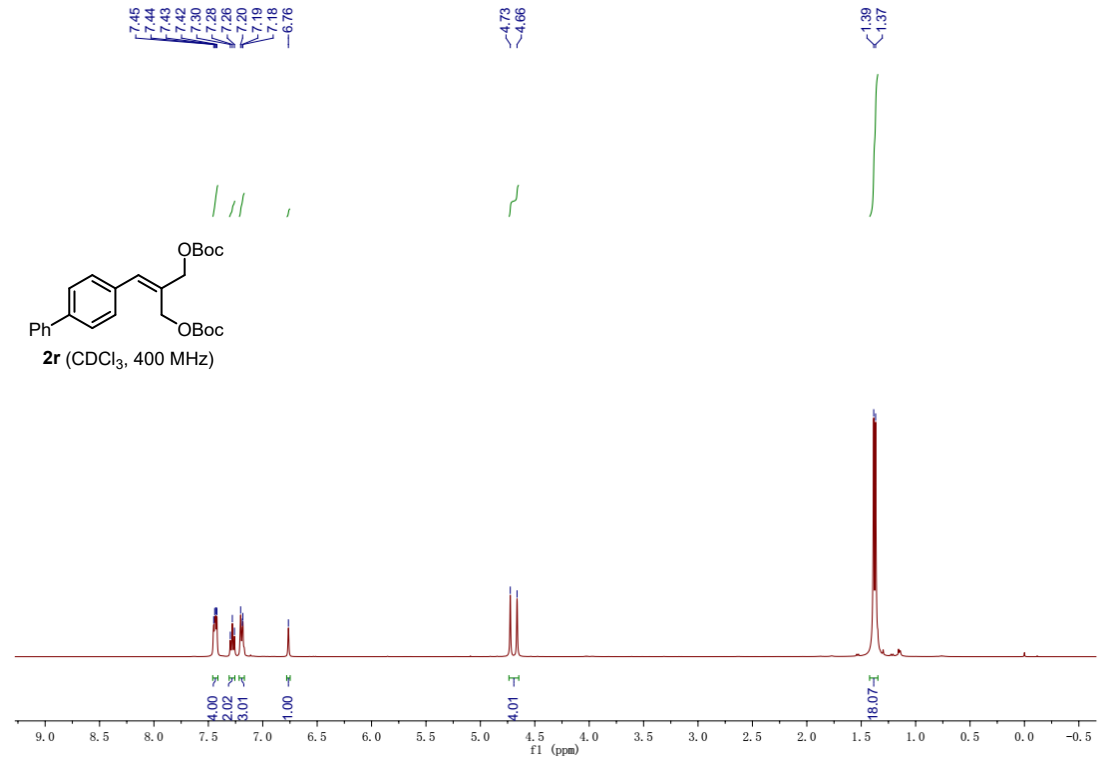
2p ($CDCl_3$, 100 MHz)



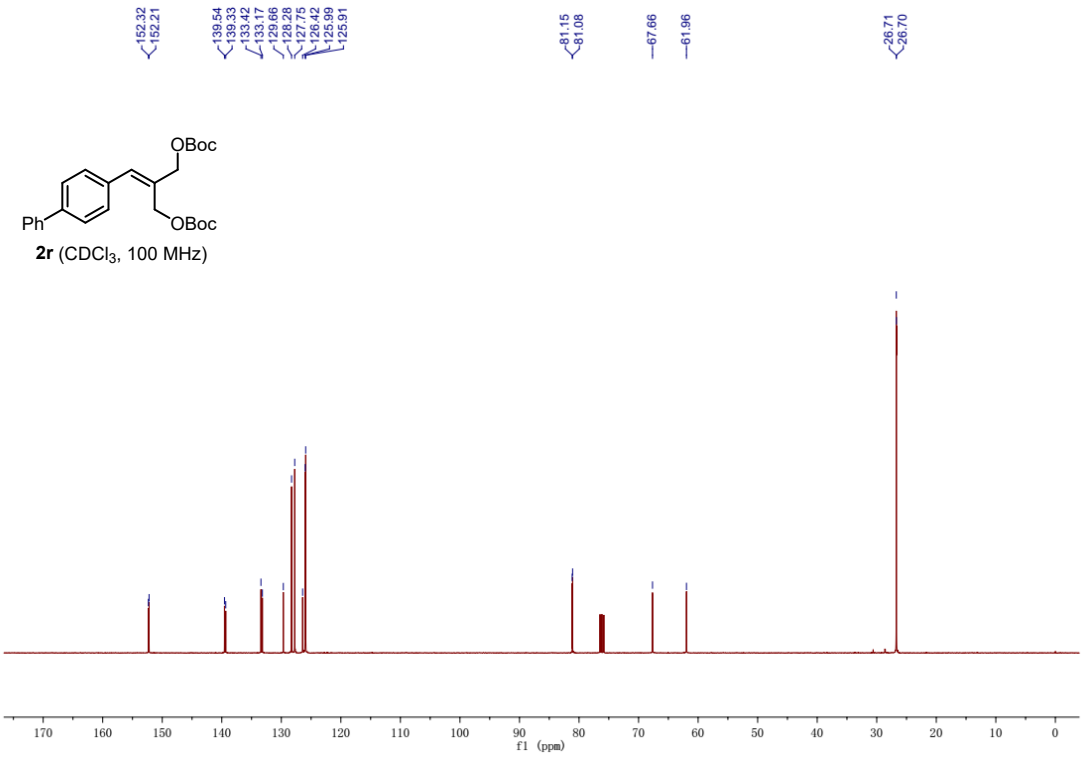
2q ($CDCl_3$, 400 MHz)



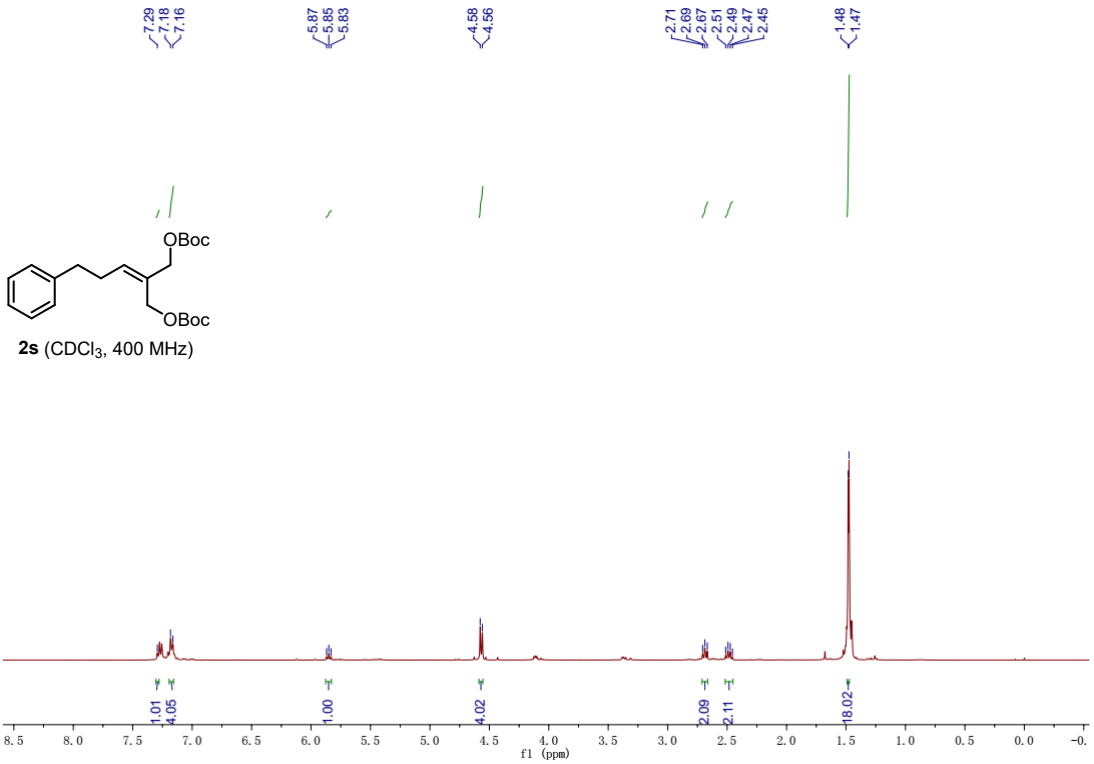
2q ($CDCl_3$, 100 MHz)



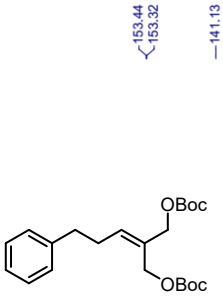
2r ($CDCl_3$, 400 MHz)



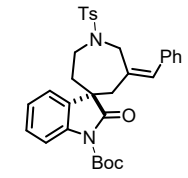
2r ($CDCl_3$, 100 MHz)



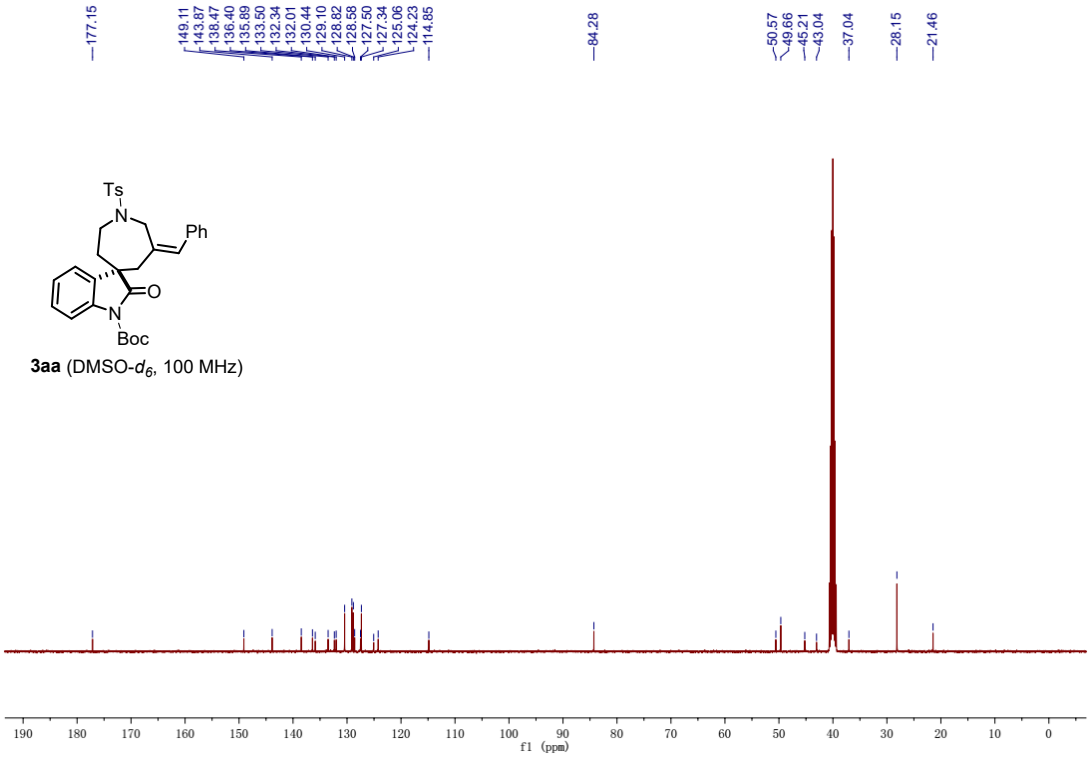
2s ($CDCl_3$, 400 MHz)



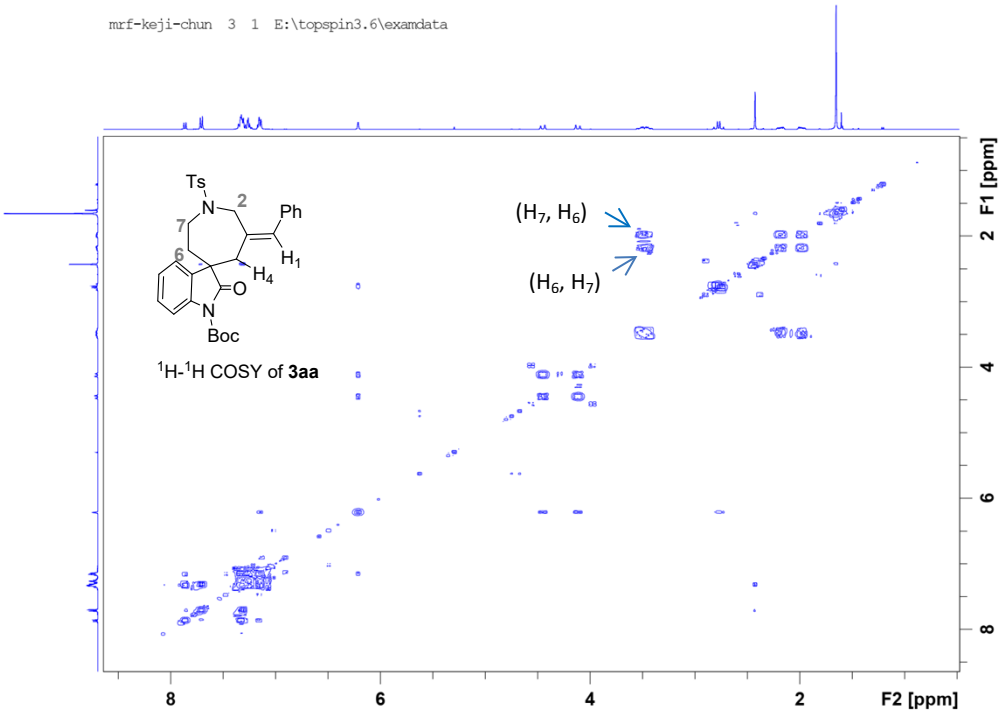
2s ($CDCl_3$, 100 MHz)



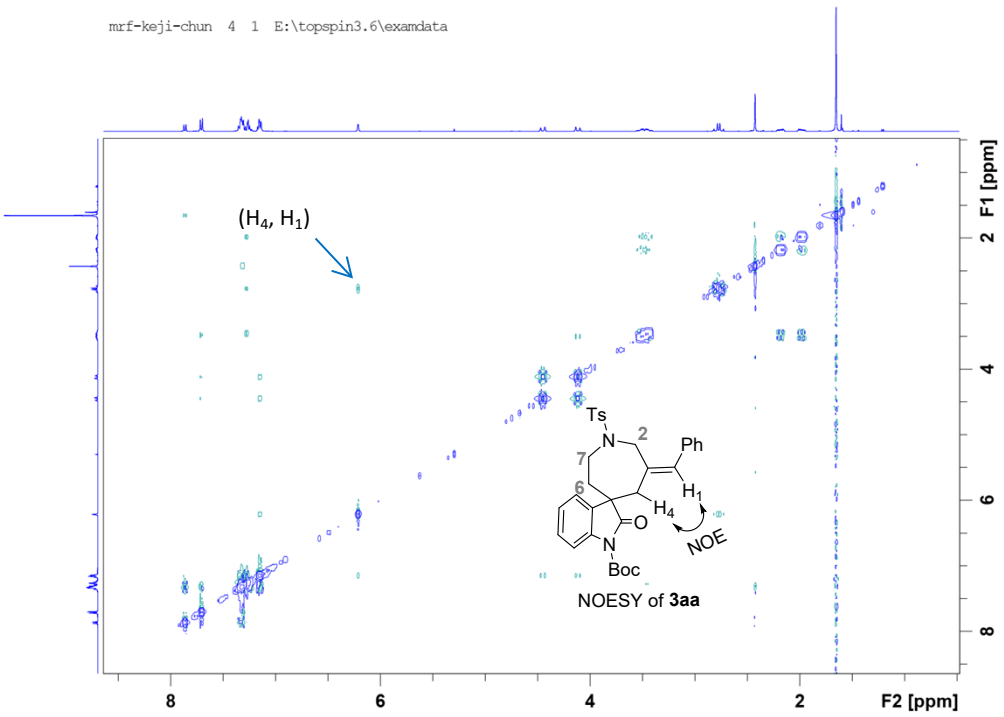
3aa (DMSO-d_6, 400 MHz)

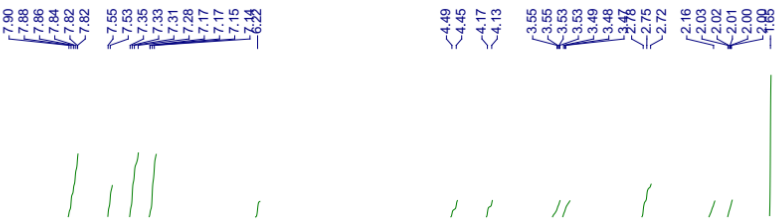


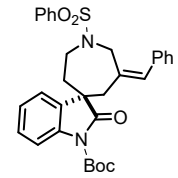
3aa (DMSO-d_6, 100 MHz)



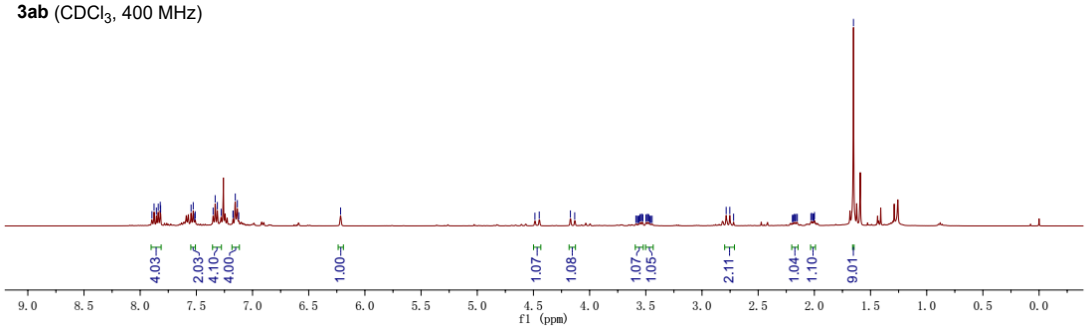
^{1}H-^{1}H COSY of **3aa**

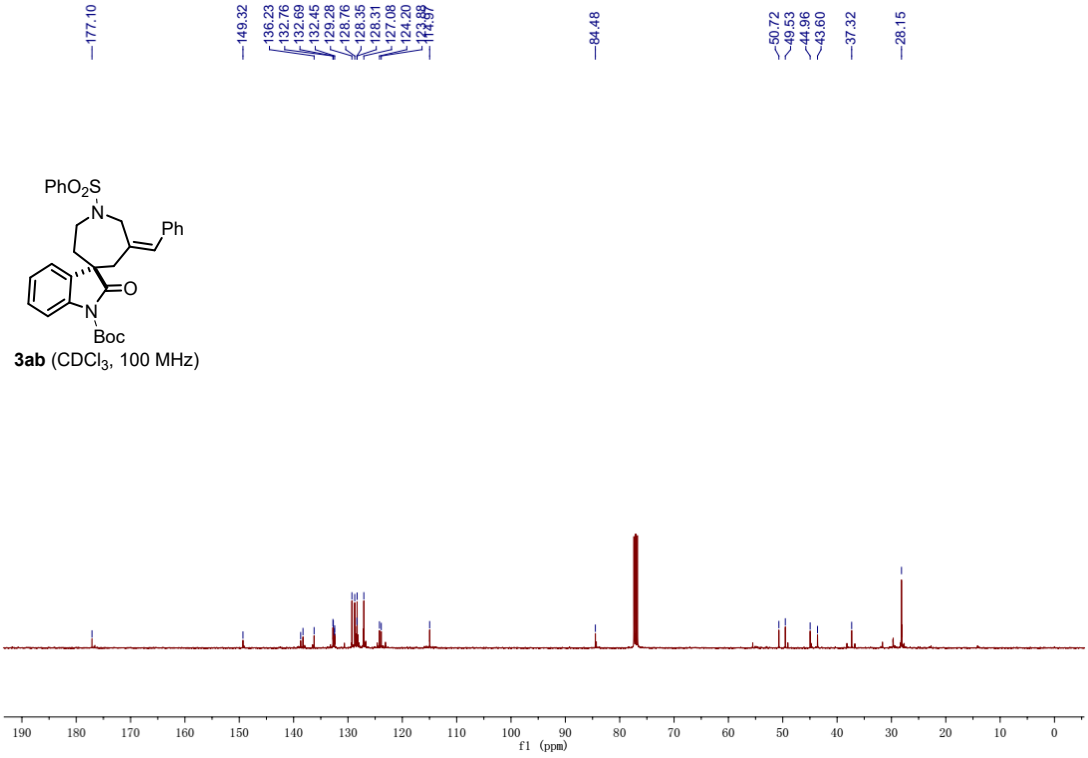




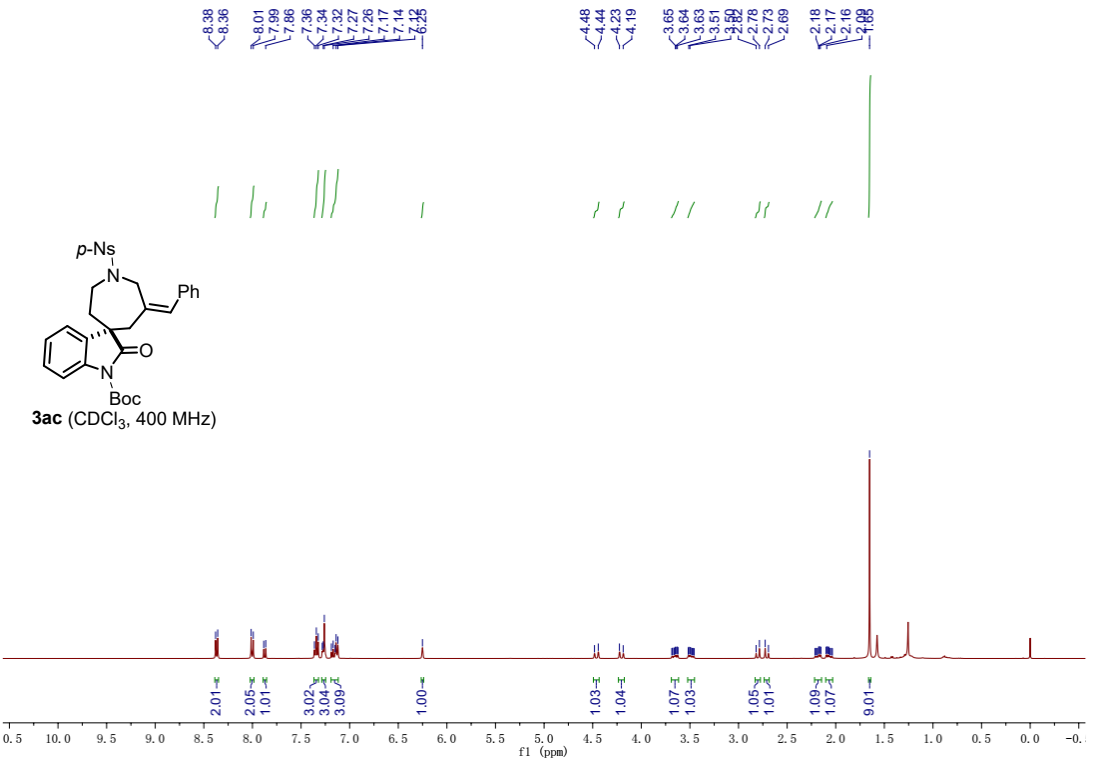


3ab ($CDCl_3$, 400 MHz)

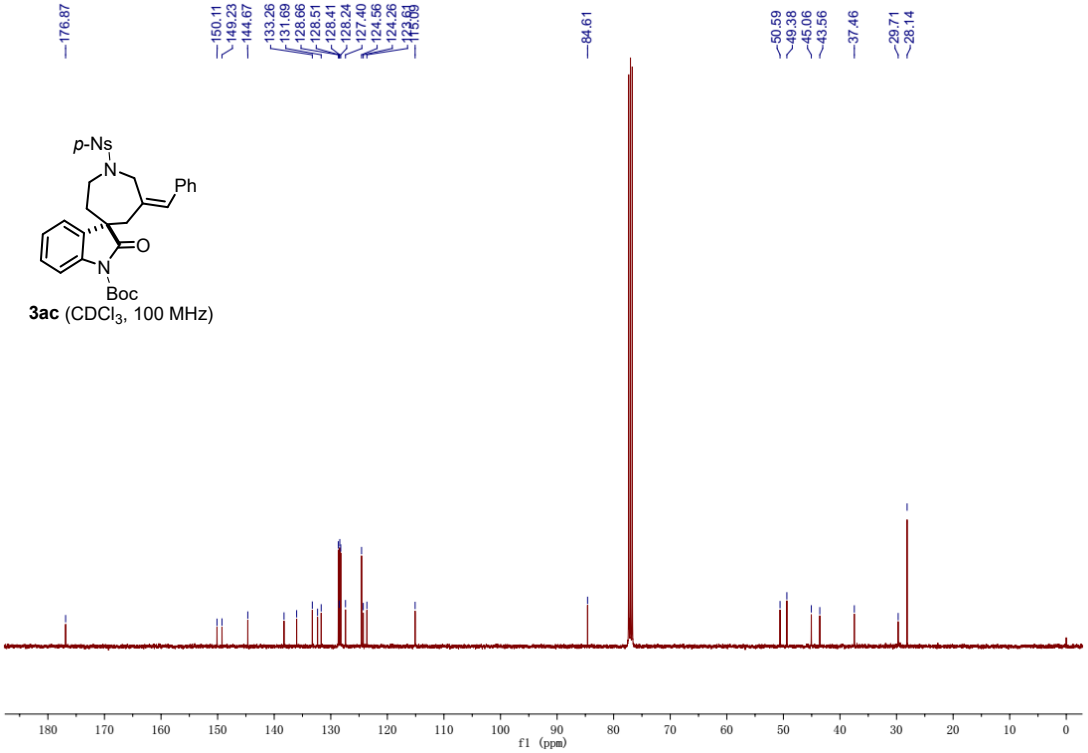




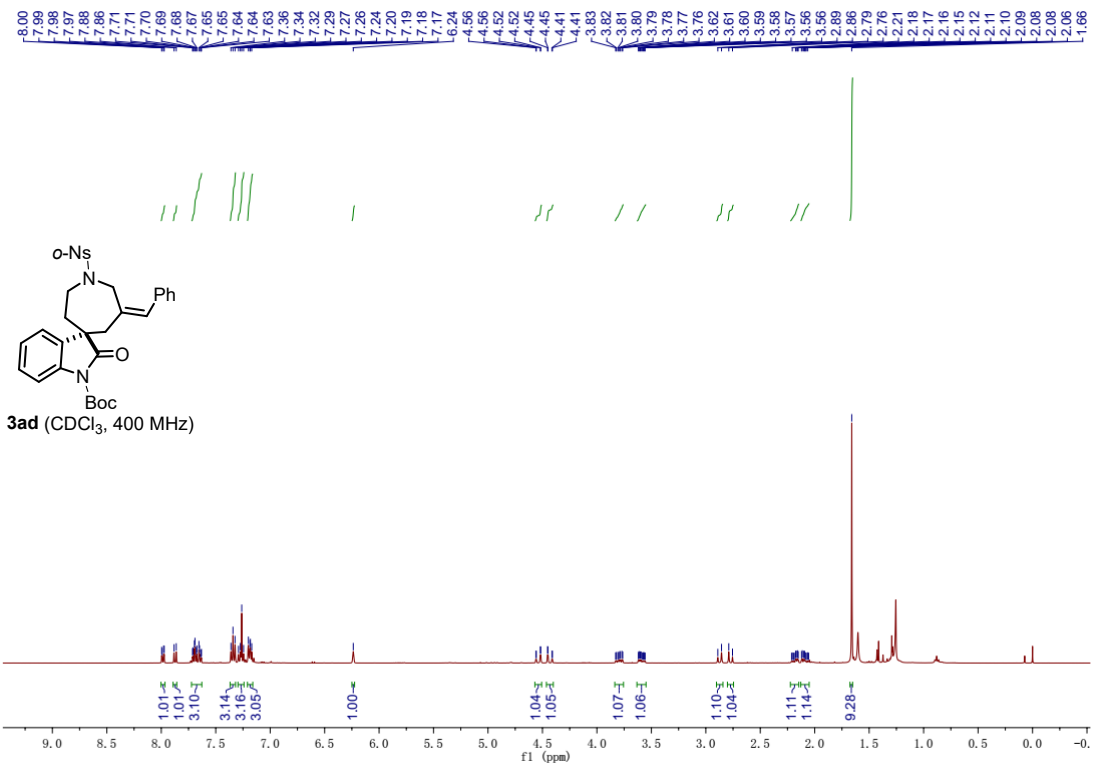
3ab ($CDCl_3$, 100 MHz)



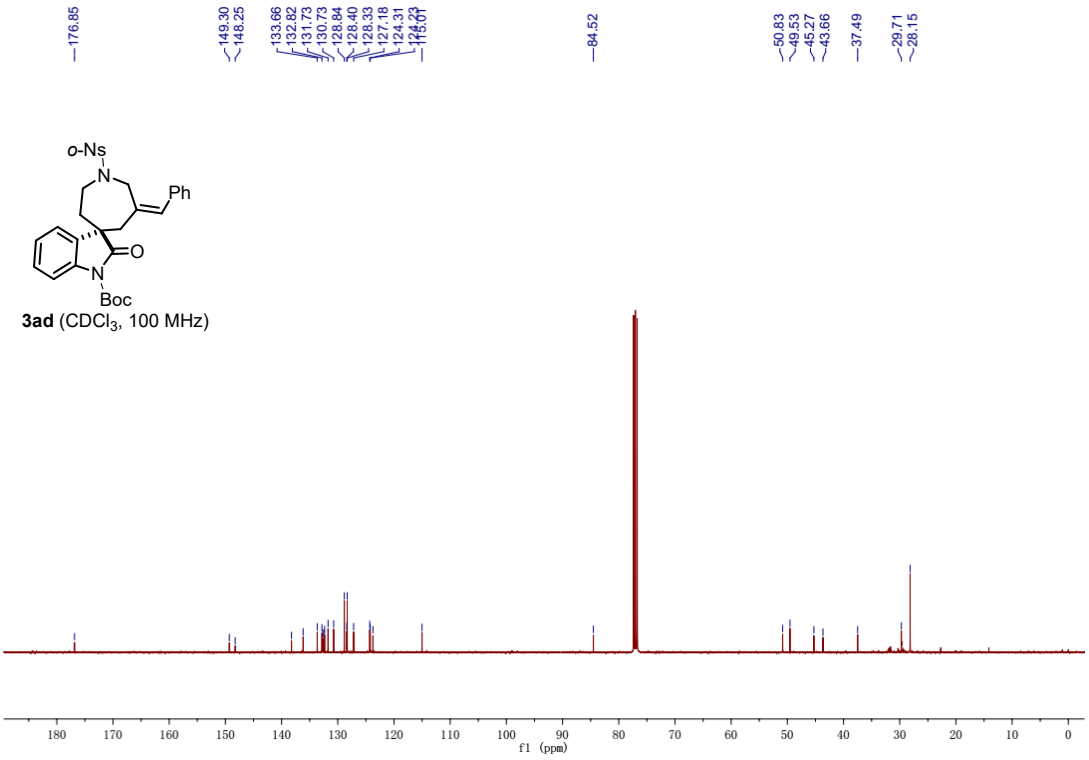
3ac ($CDCl_3$, 400 MHz)



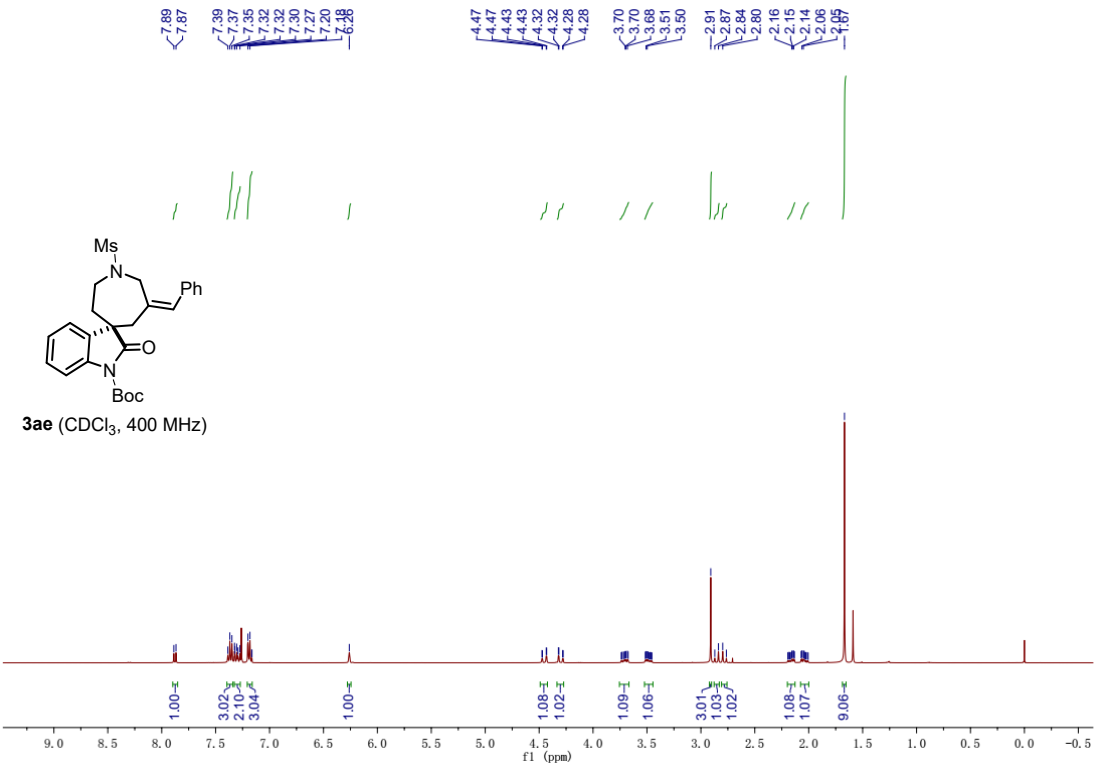
3ac ($CDCl_3$, 100 MHz)



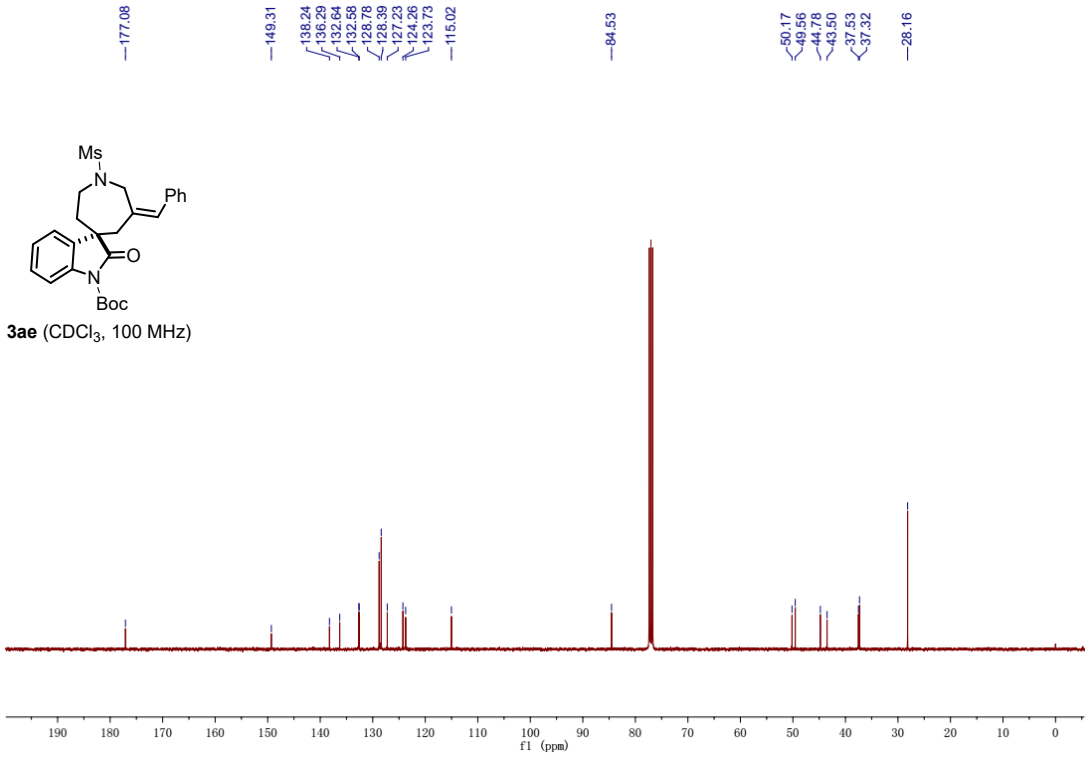
3ad ($CDCl_3$, 400 MHz)



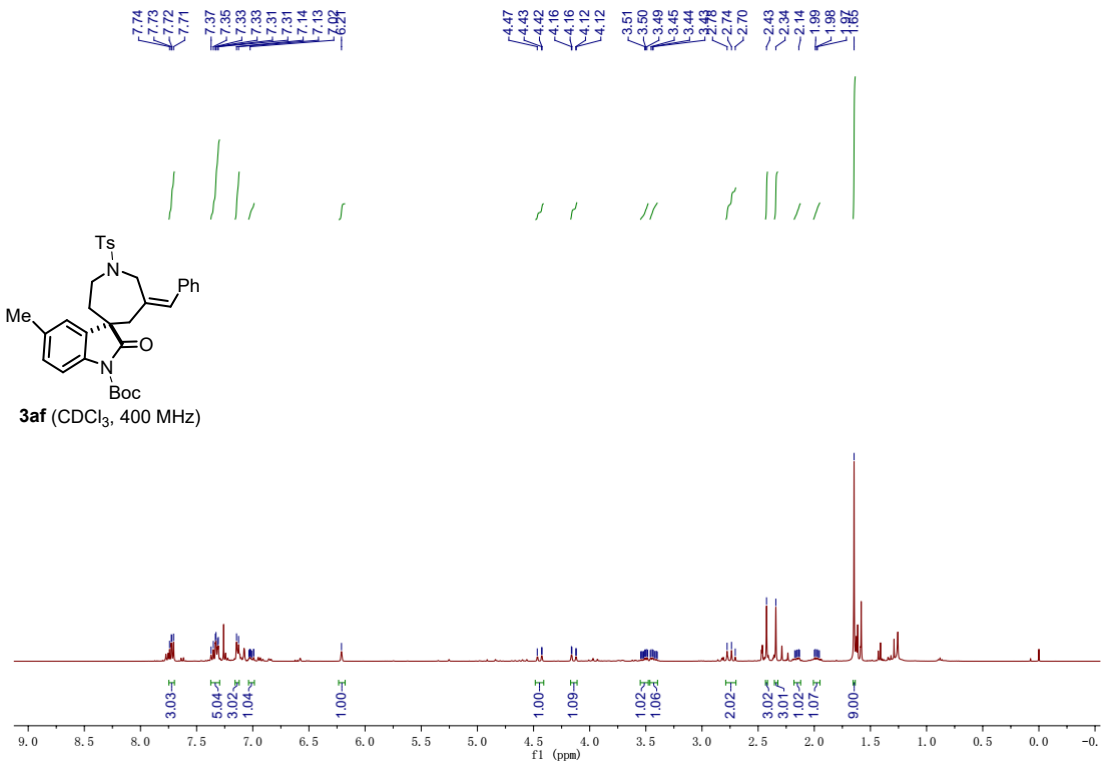
3ad ($CDCl_3$, 100 MHz)



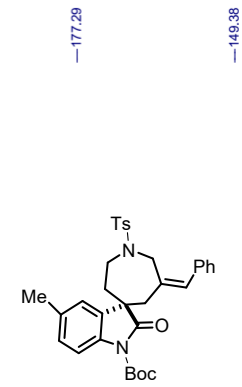
3ae ($CDCl_3$, 400 MHz)



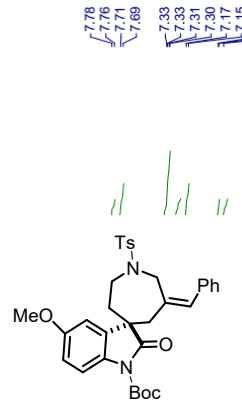
3ae ($CDCl_3$, 100 MHz)



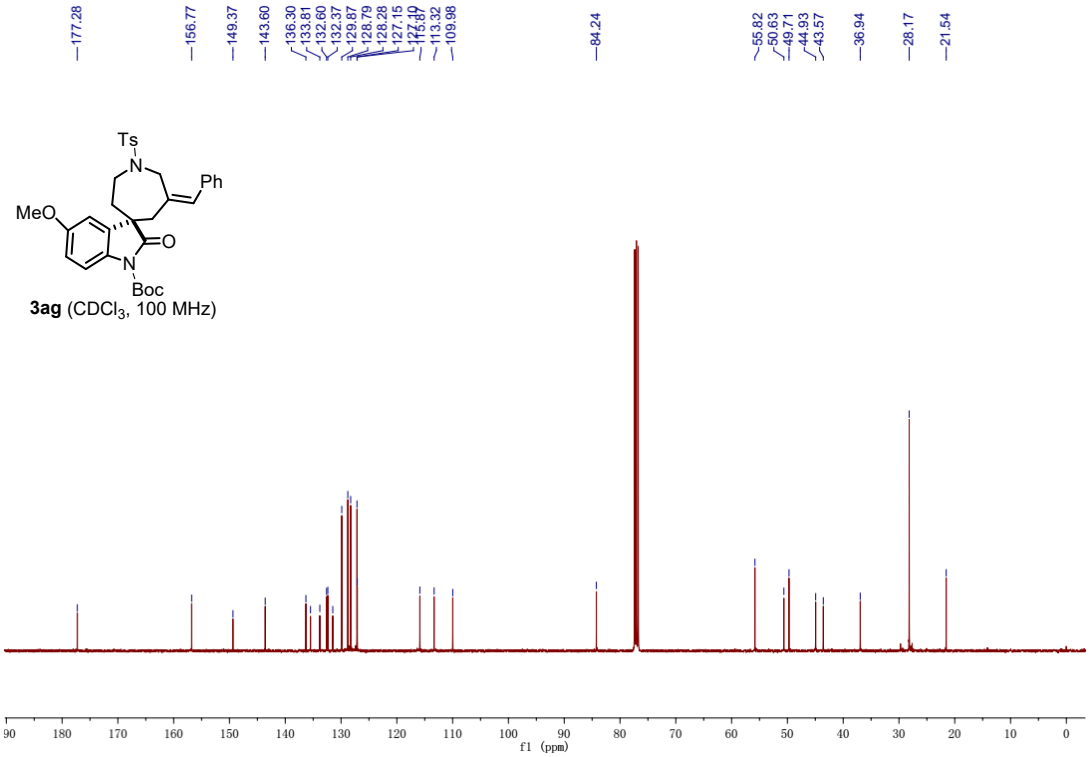
3af ($CDCl_3$, 400 MHz)



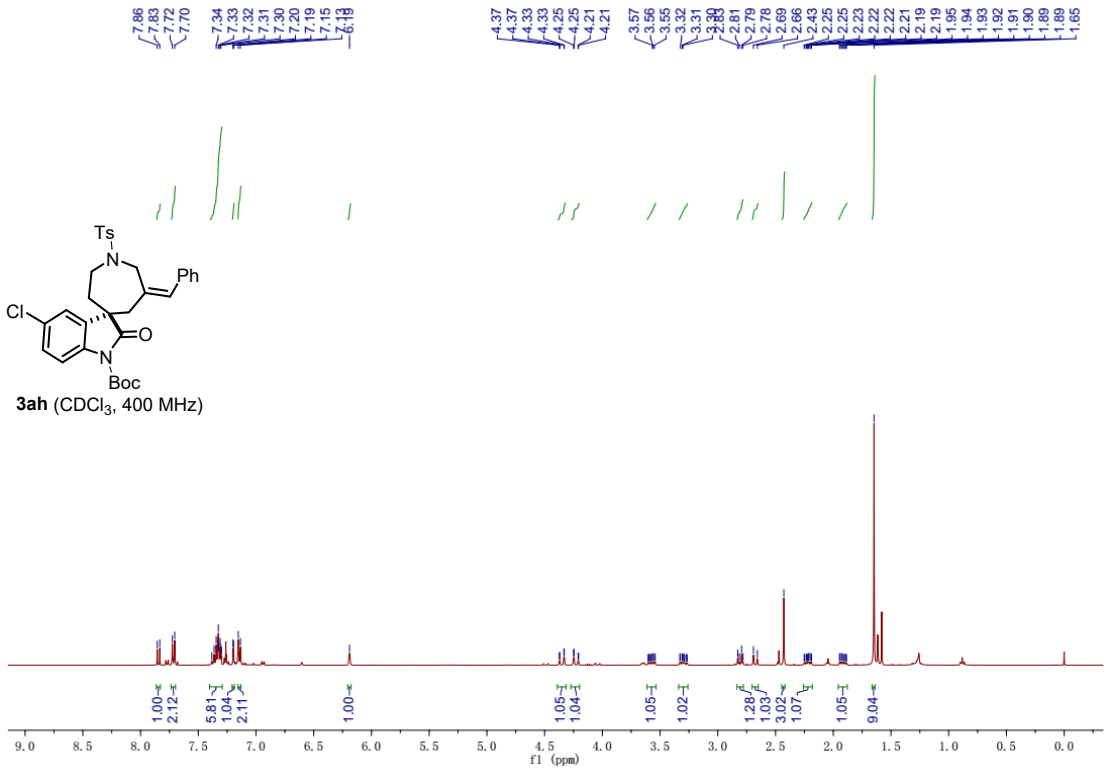
3af ($CDCl_3$, 100 MHz)



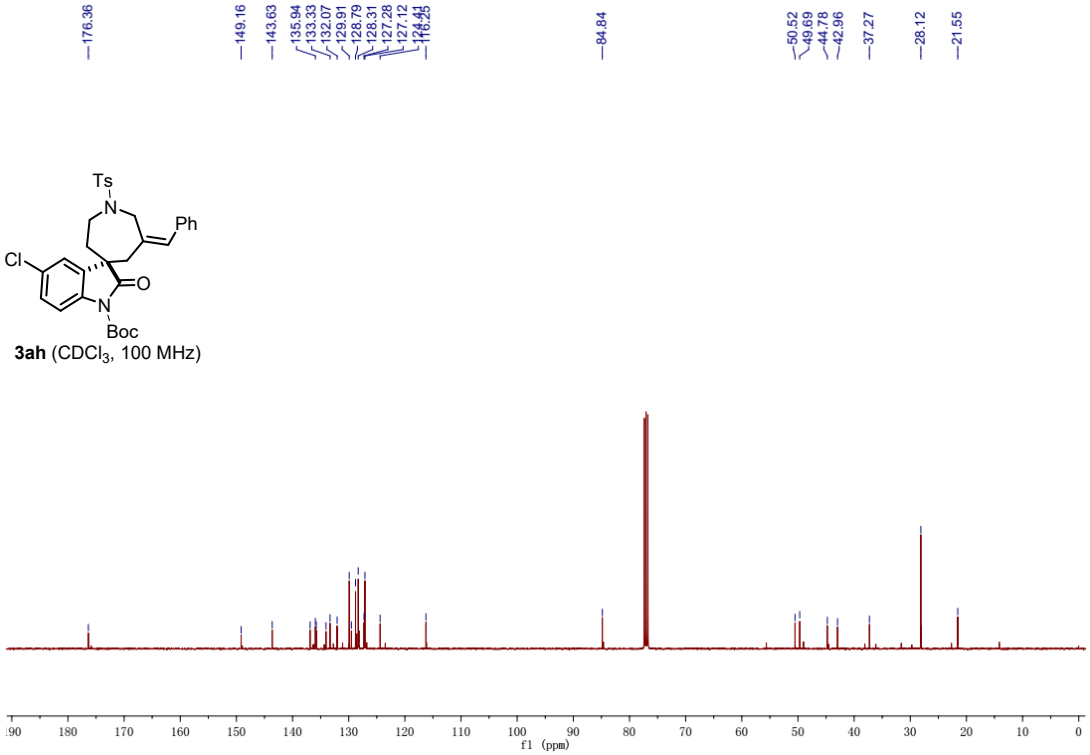
3ag ($CDCl_3$, 400 MHz)



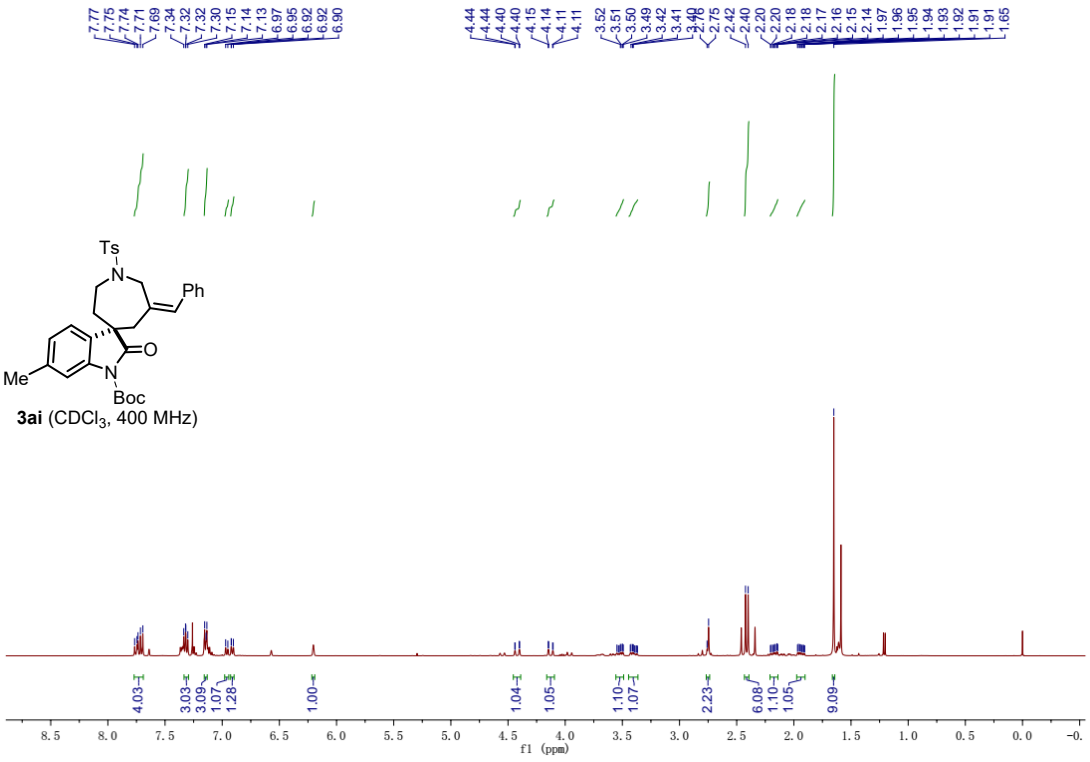
3ag ($CDCl_3$, 100 MHz)



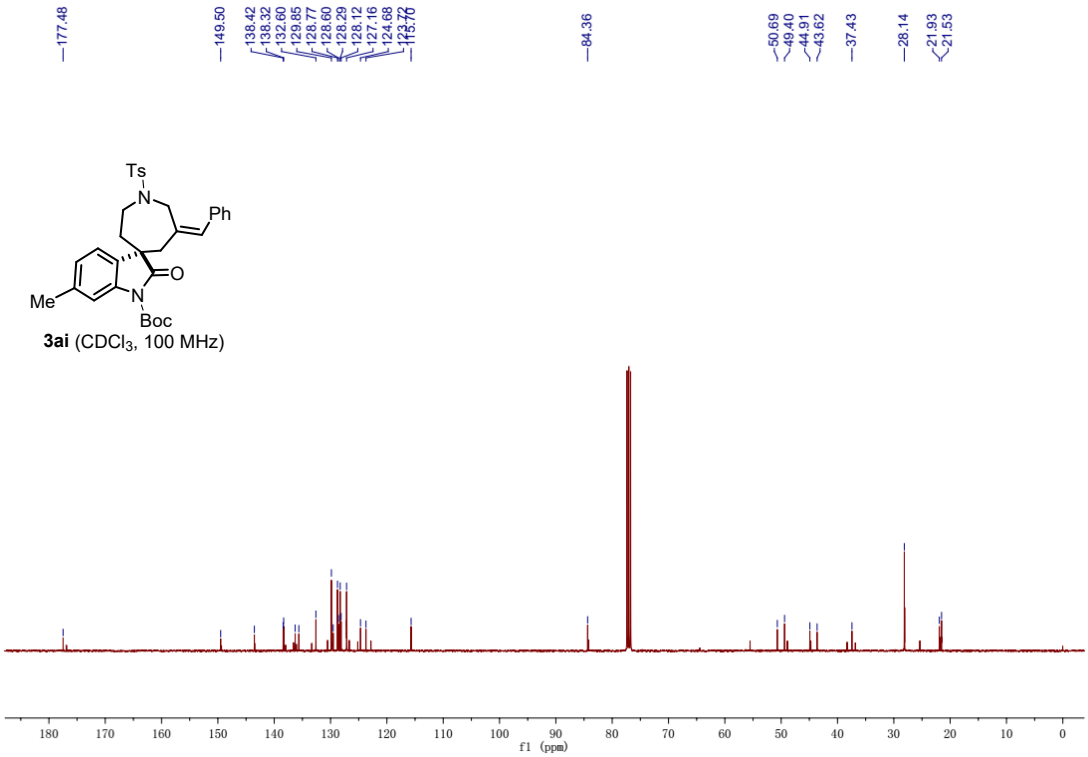
3ah ($CDCl_3$, 400 MHz)



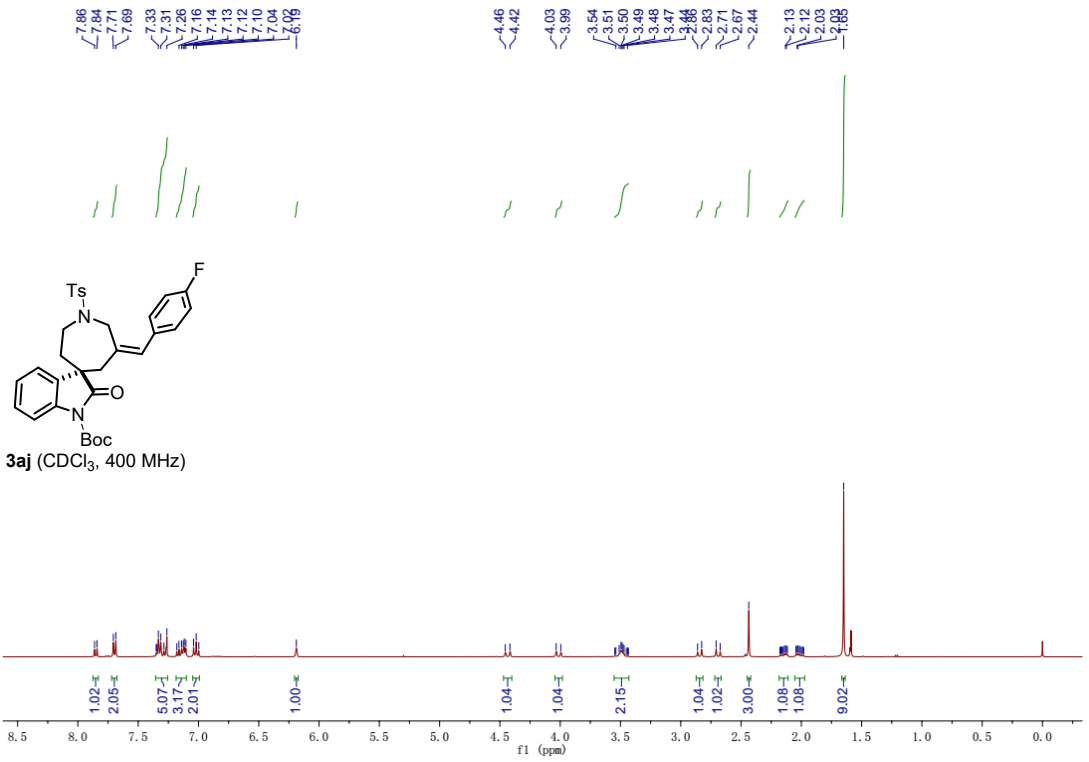
3ah ($CDCl_3$, 100 MHz)



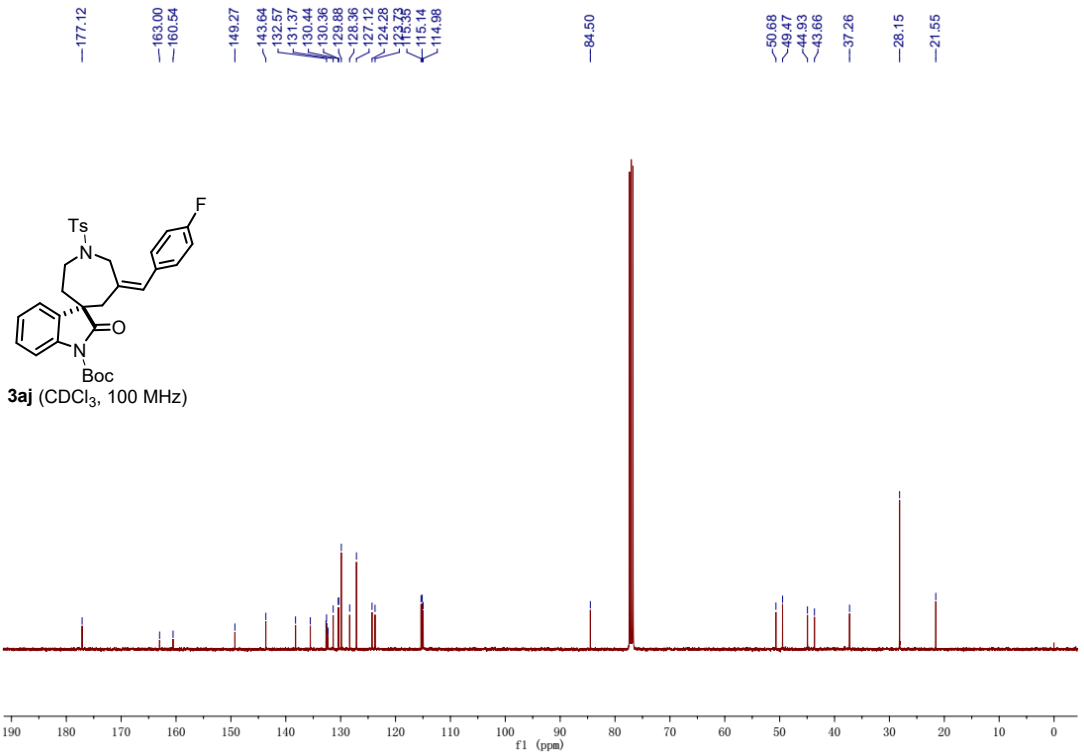
3ai ($CDCl_3$, 400 MHz)



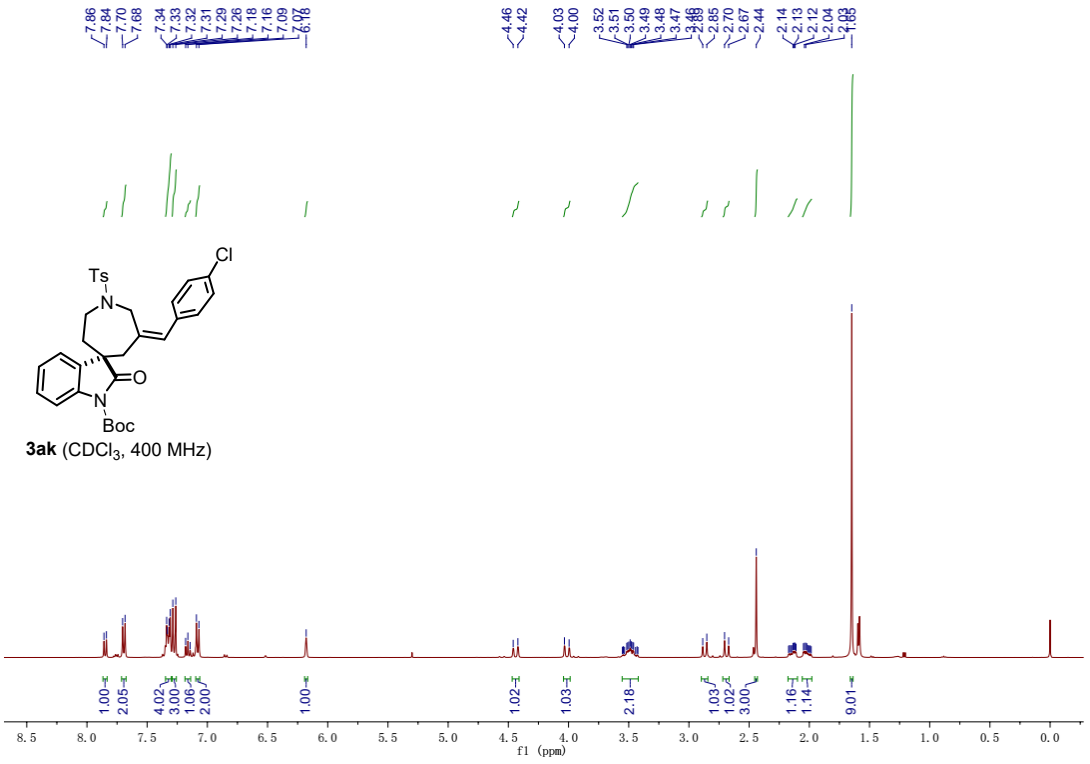
3ai ($CDCl_3$, 100 MHz)



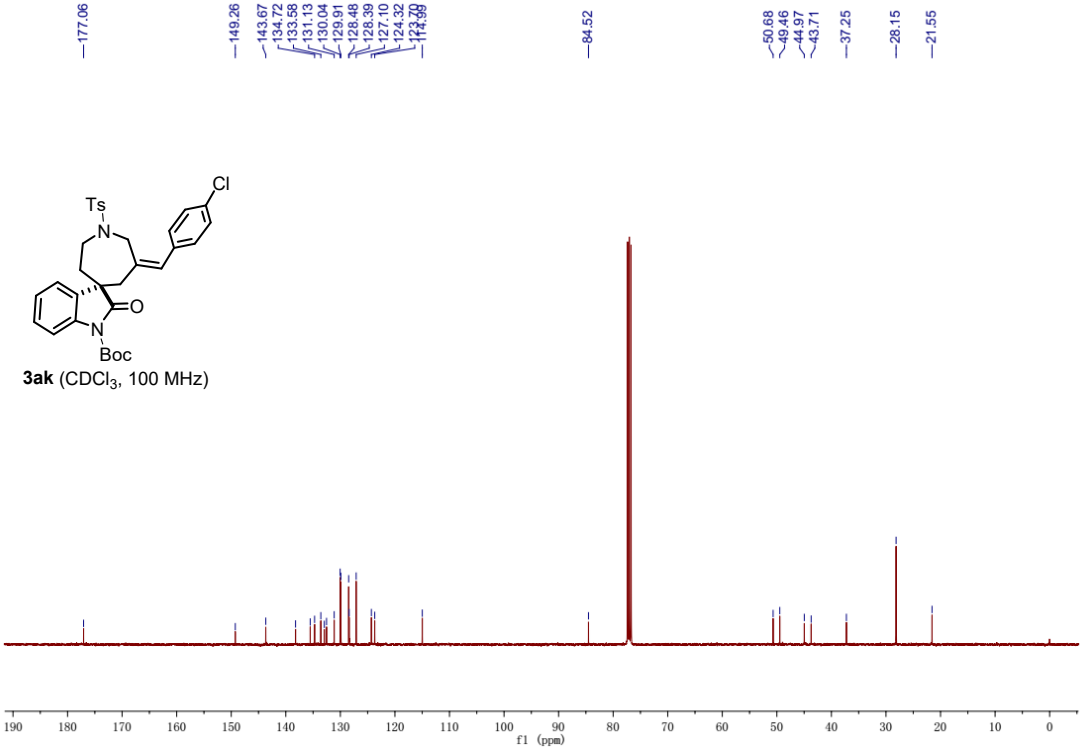
3aj ($CDCl_3$, 400 MHz)



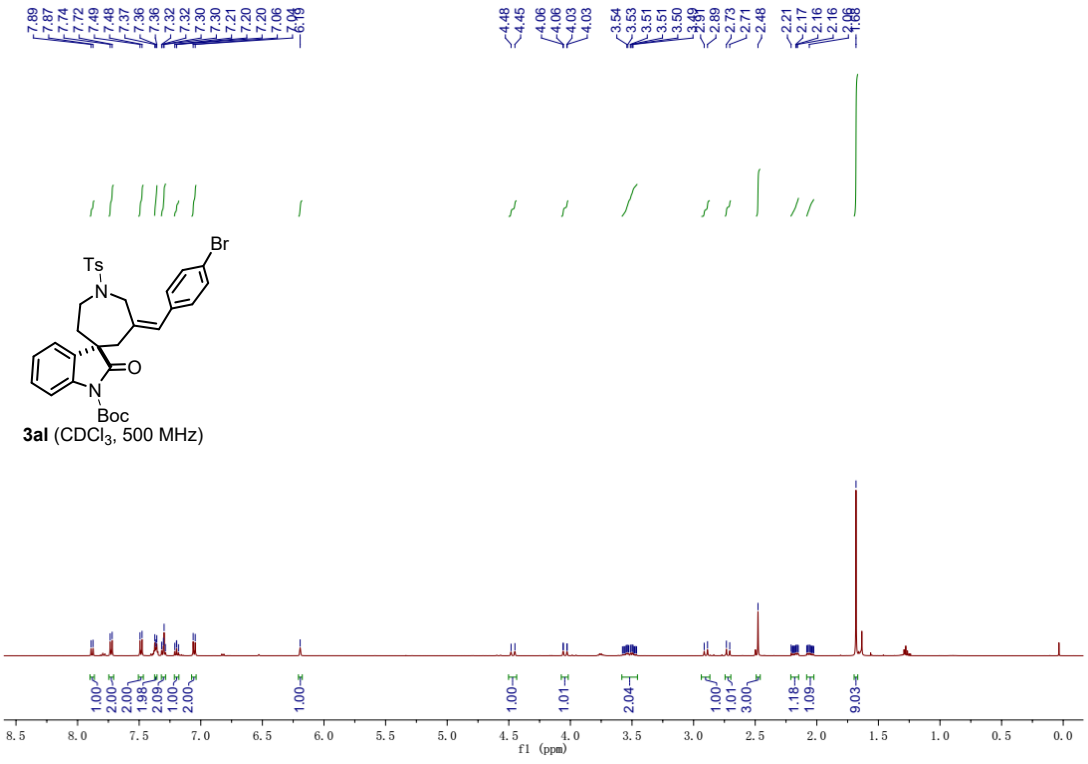
3aj ($CDCl_3$, 100 MHz)



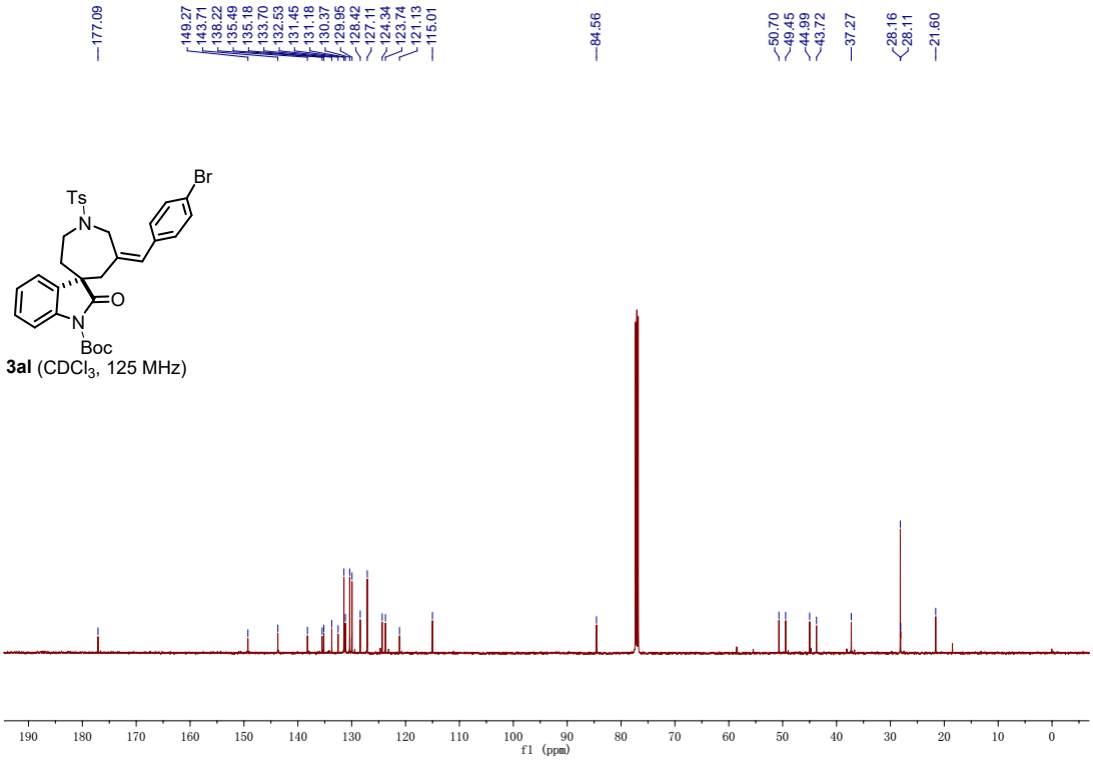
3ak ($CDCl_3$, 400 MHz)



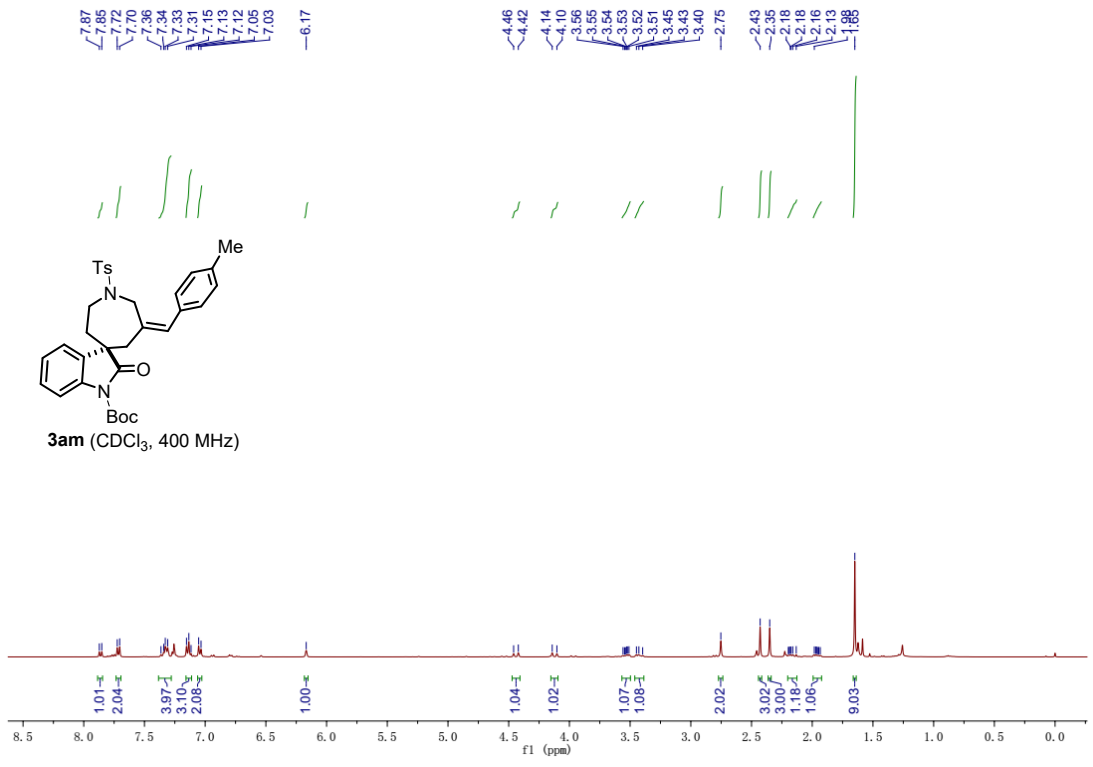
3ak ($CDCl_3$, 100 MHz)



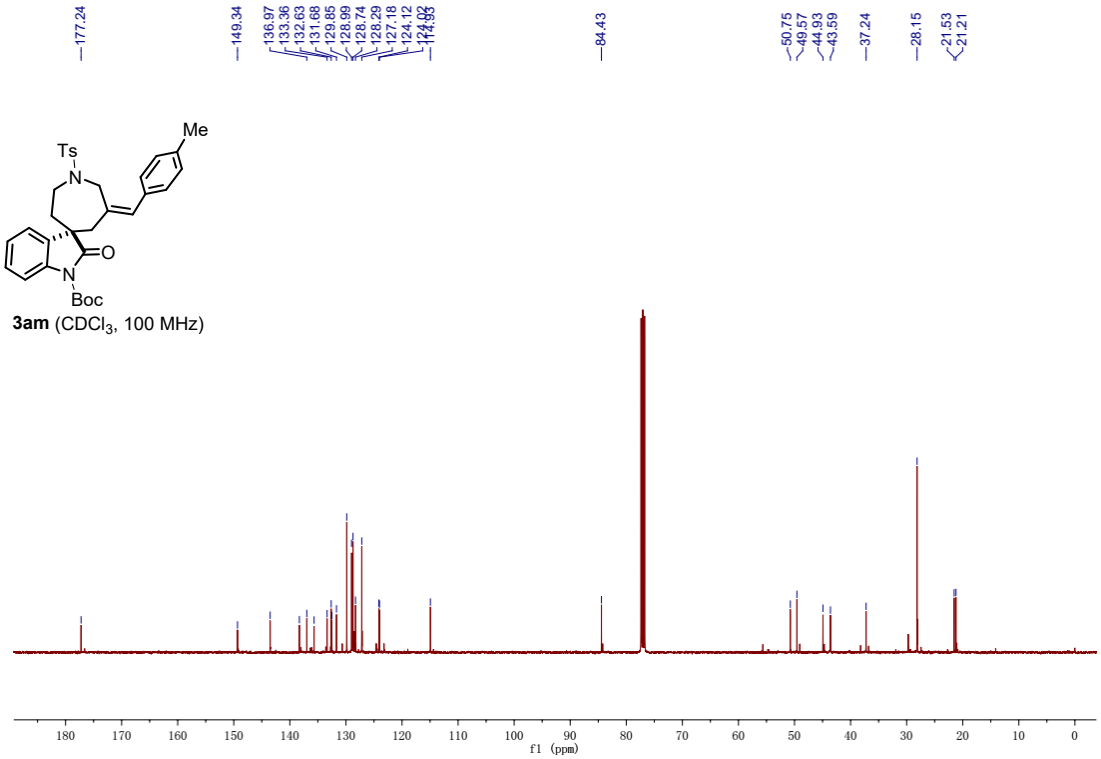
3al ($CDCl_3$, 500 MHz)



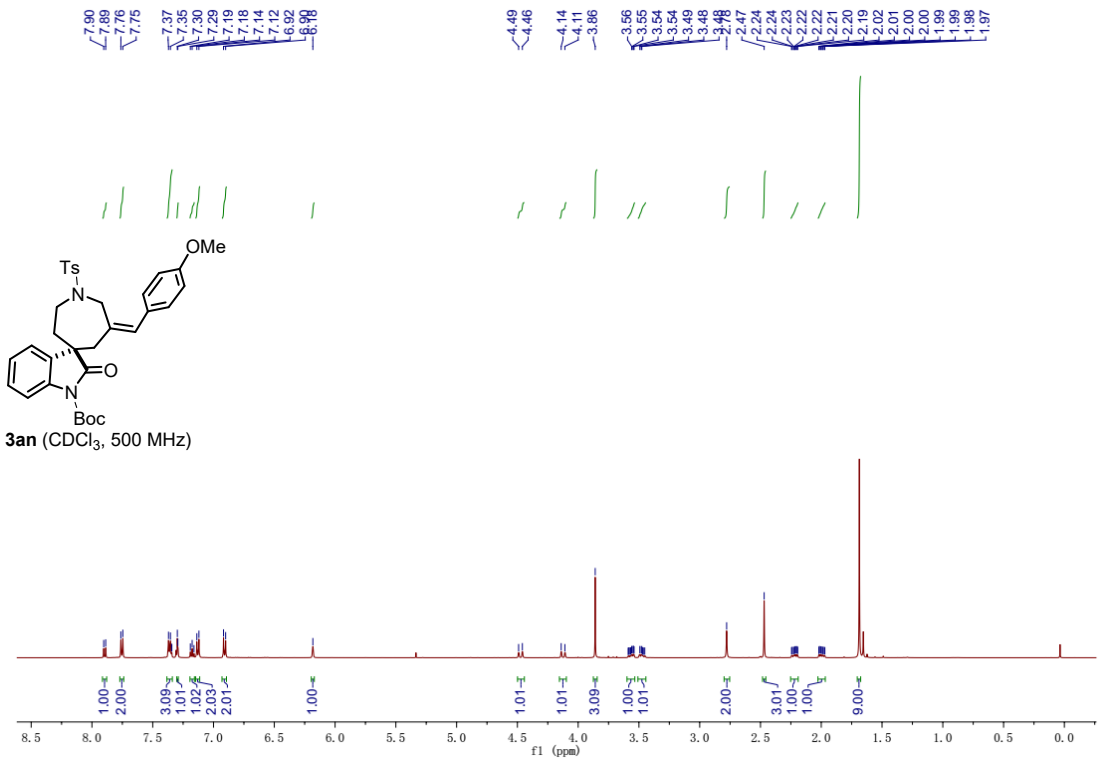
3al ($CDCl_3$, 125 MHz)



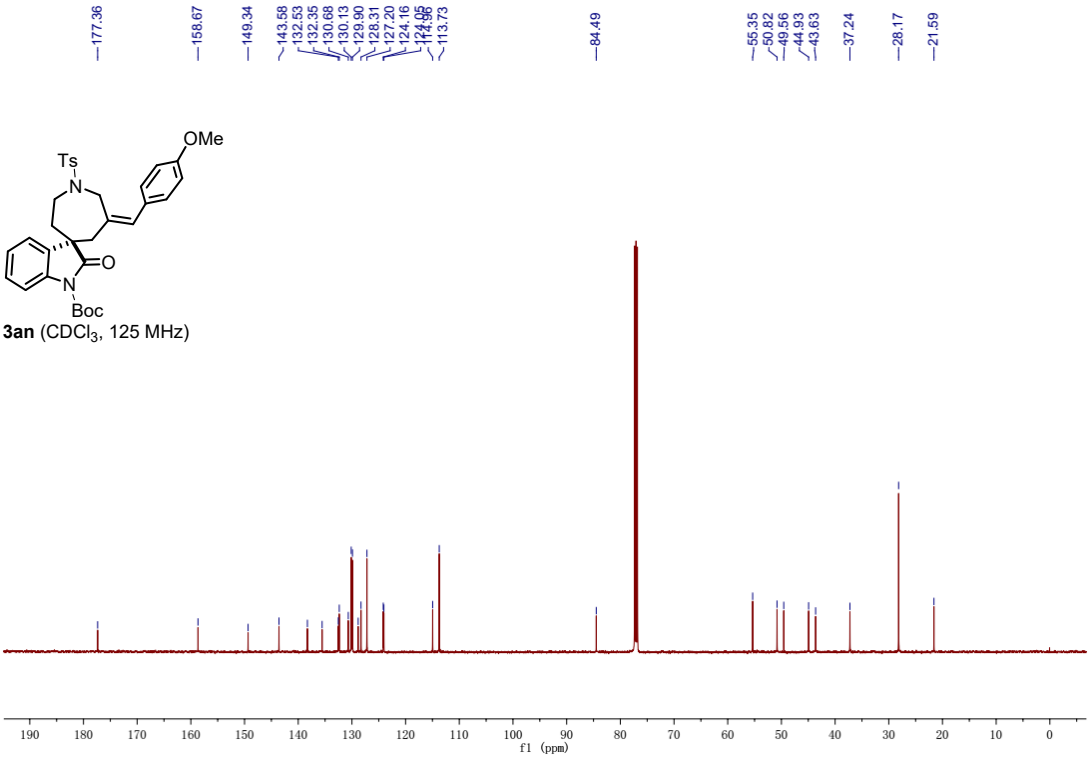
3am ($CDCl_3$, 400 MHz)



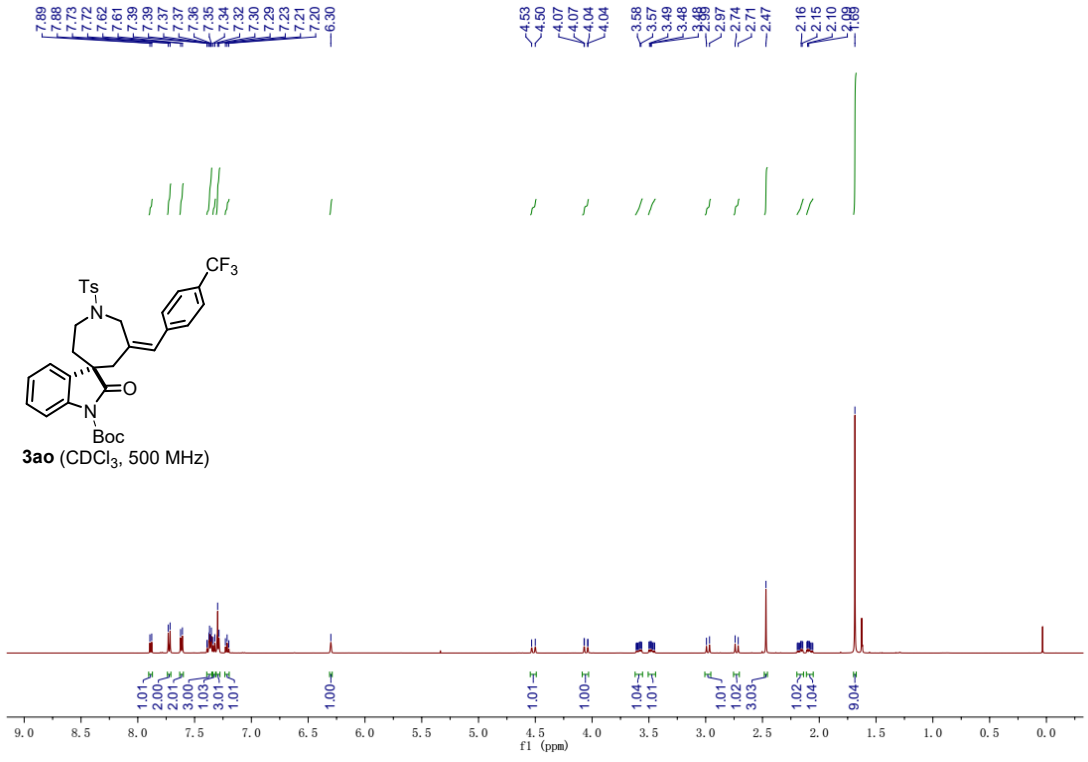
3am ($CDCl_3$, 100 MHz)



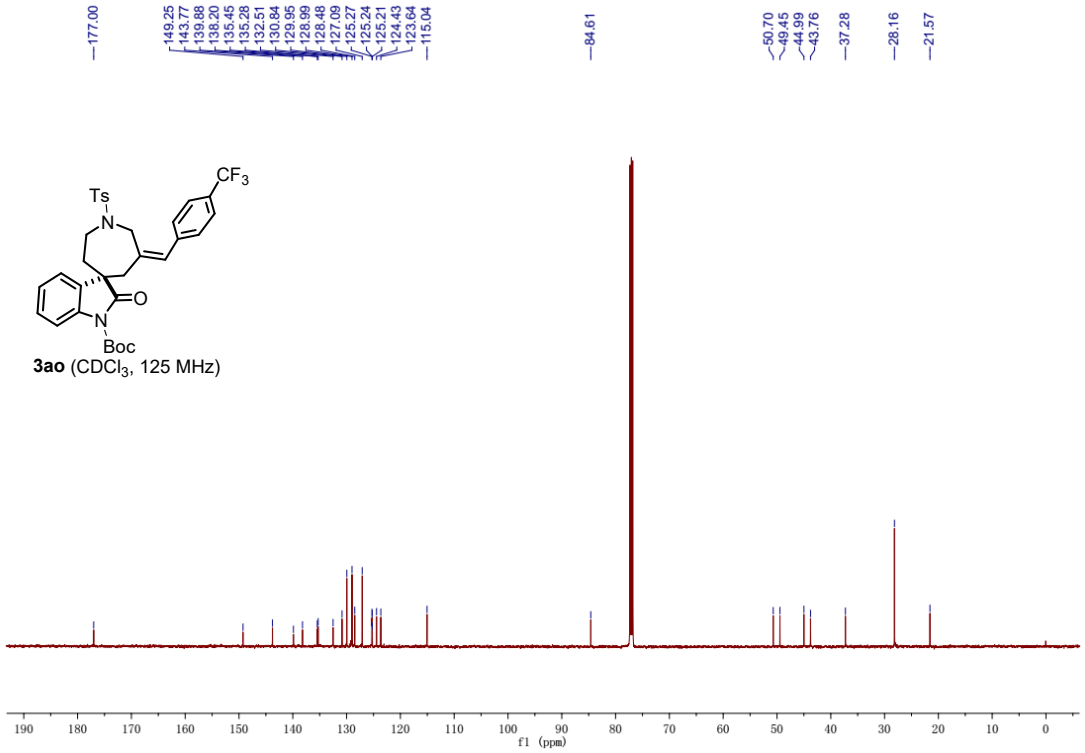
3an ($CDCl_3$, 500 MHz)



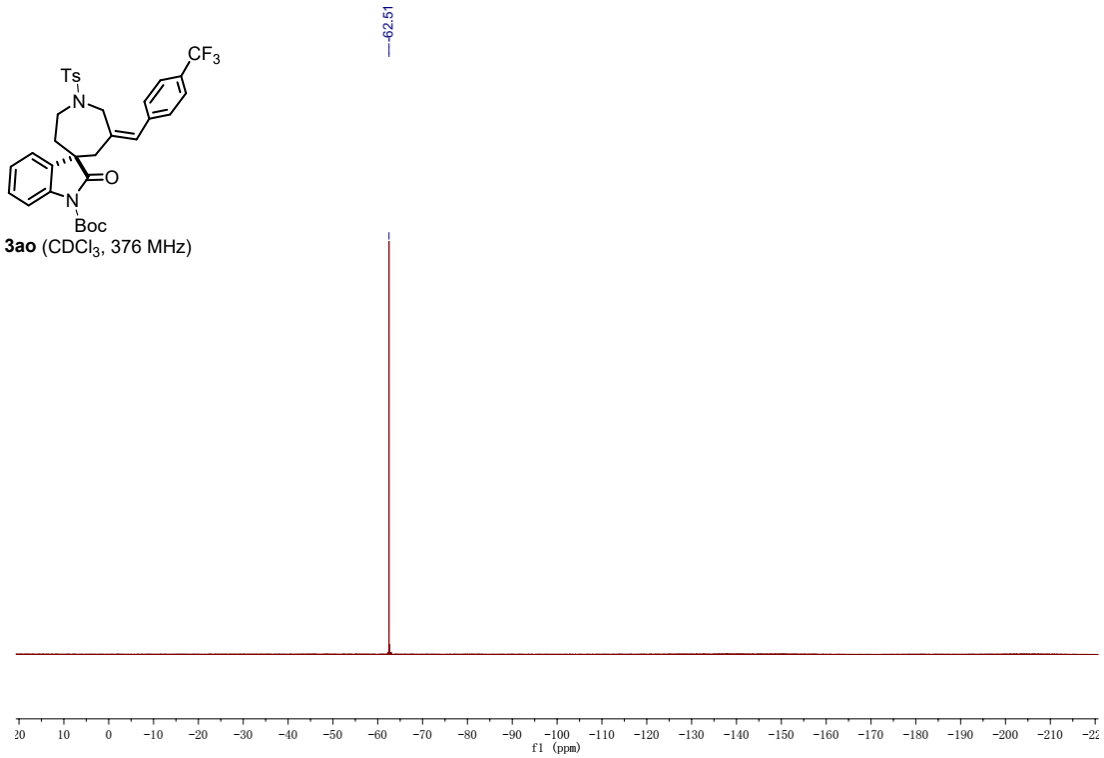
3an ($CDCl_3$, 125 MHz)



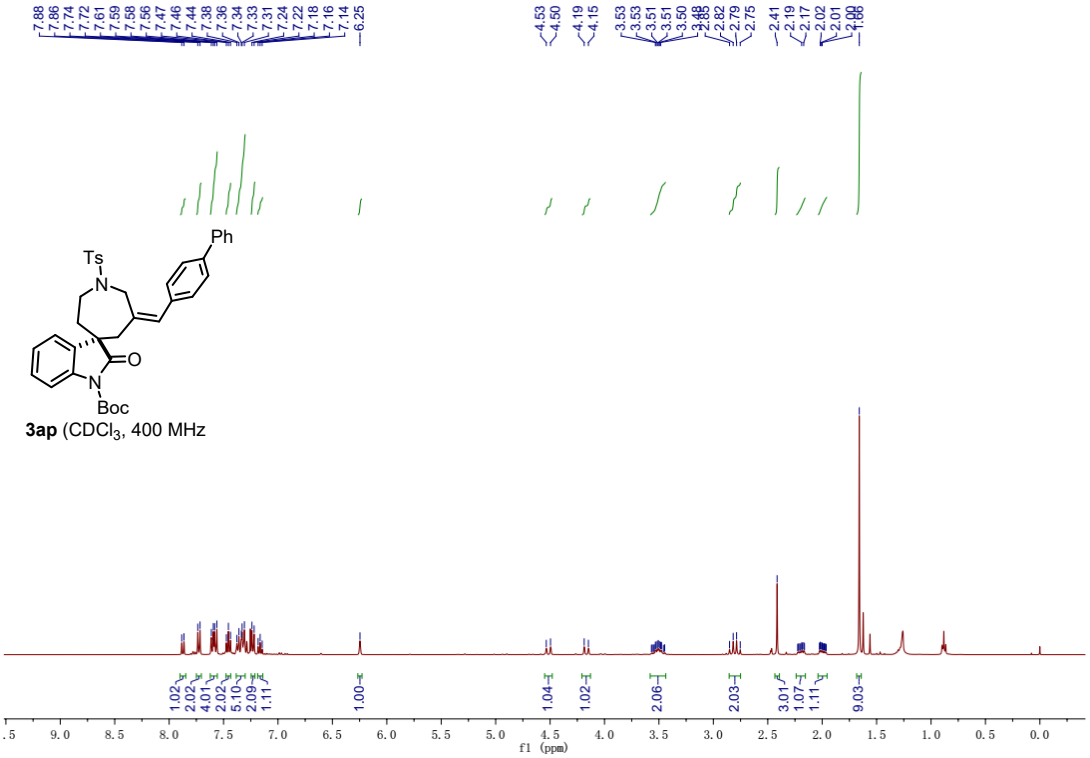
3ao ($CDCl_3$, 500 MHz)



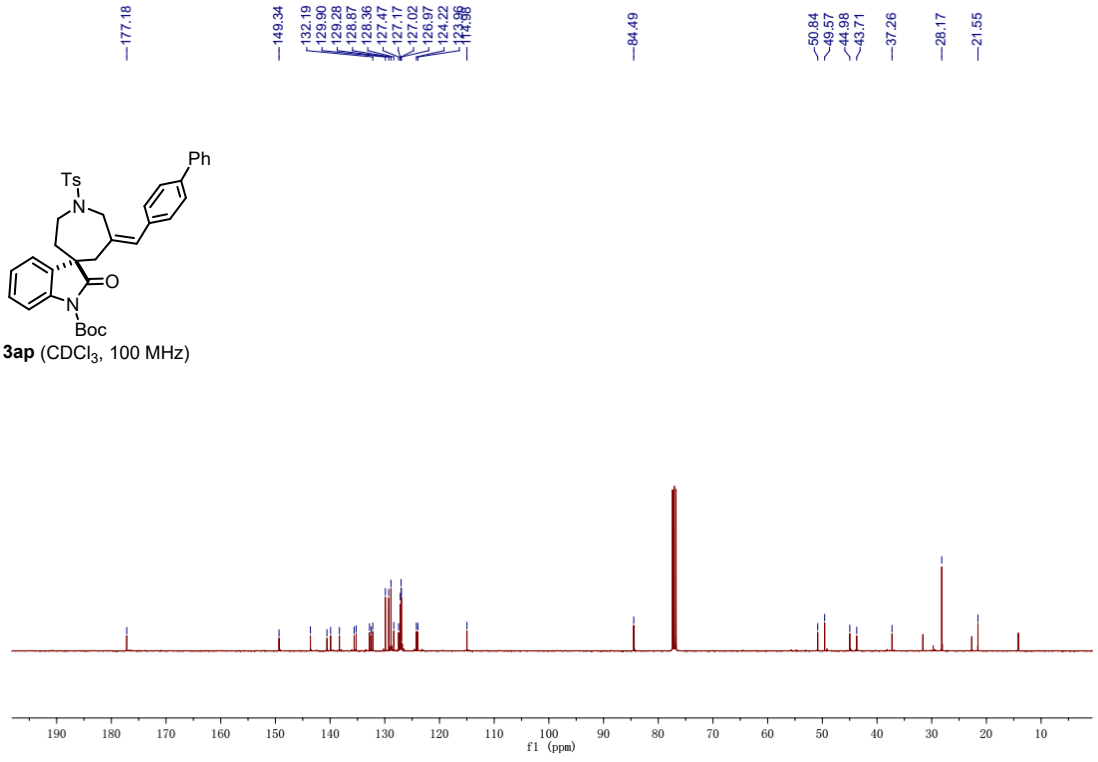
3ao ($CDCl_3$, 125 MHz)



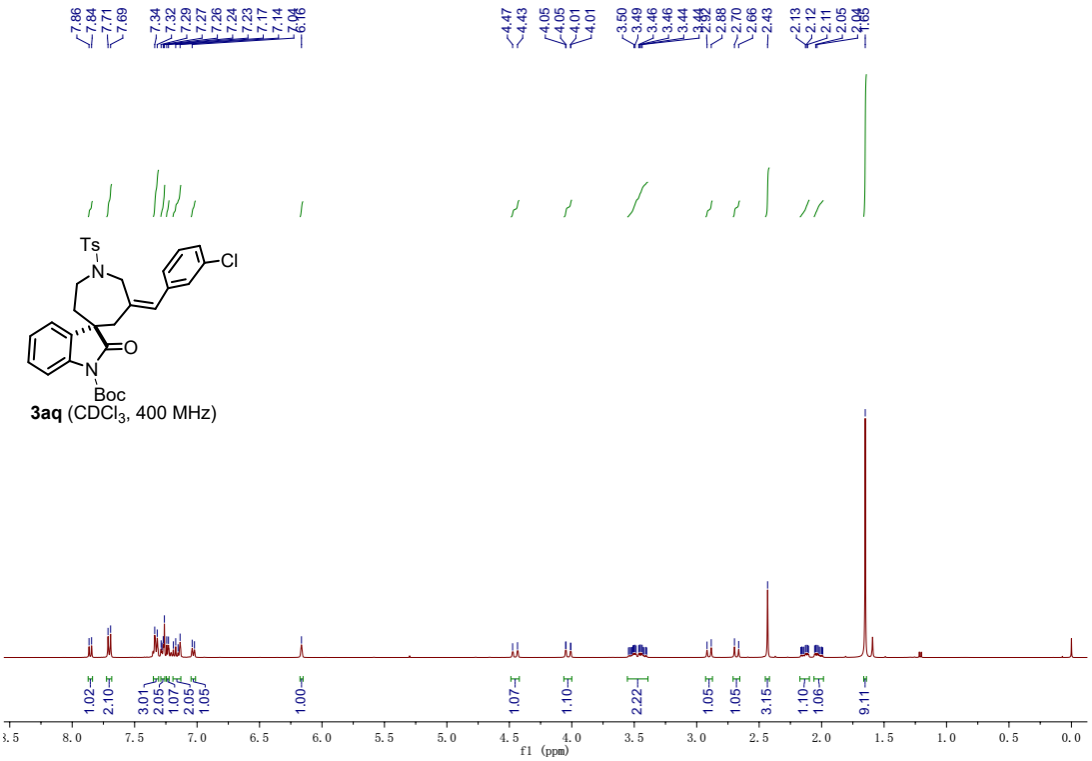
3ao ($CDCl_3$, 376 MHz)



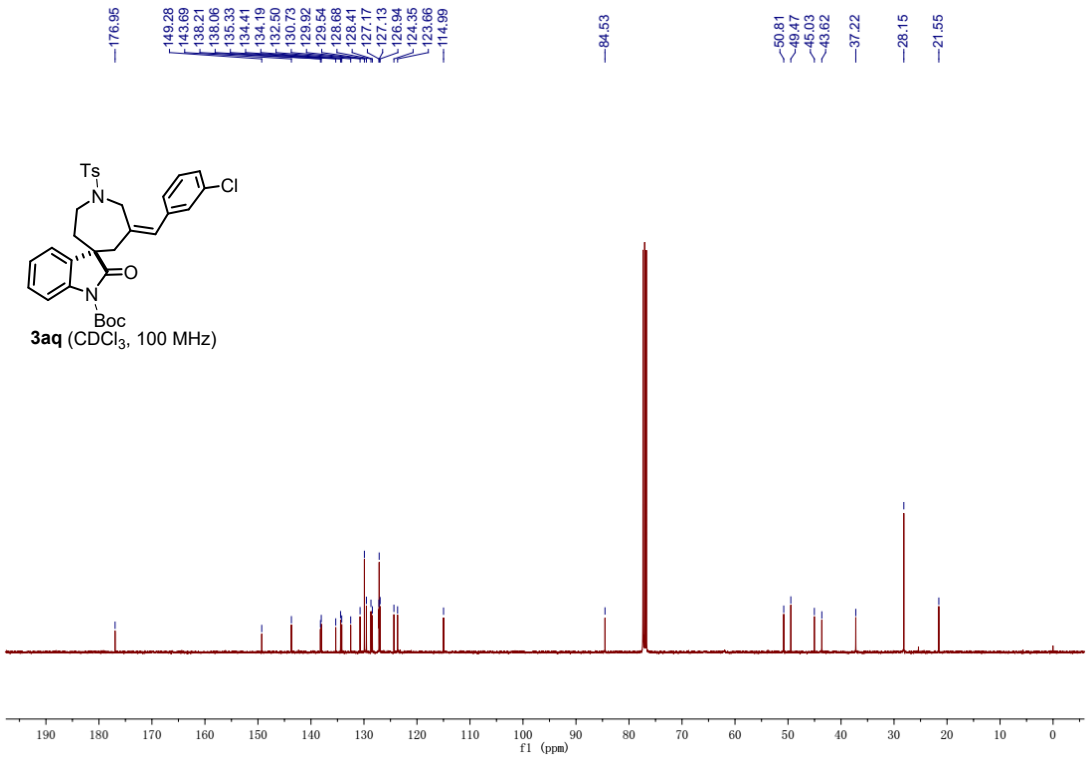
3ap ($CDCl_3$, 400 MHz



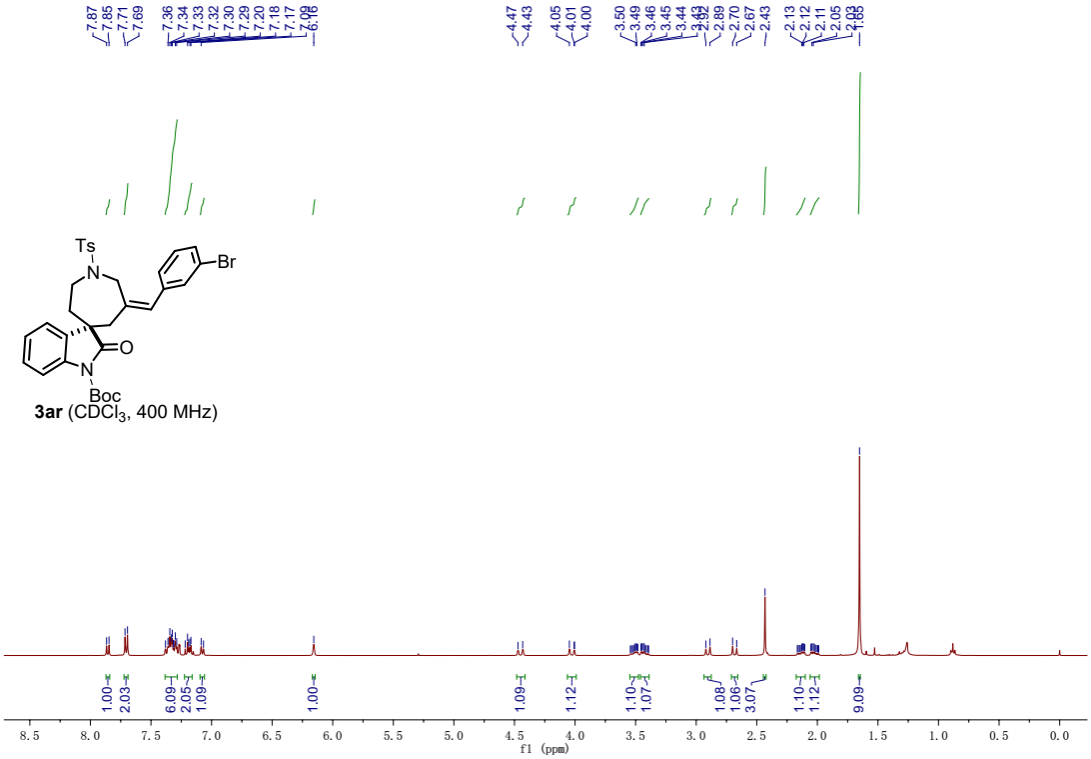
3ap ($CDCl_3$, 100 MHz)



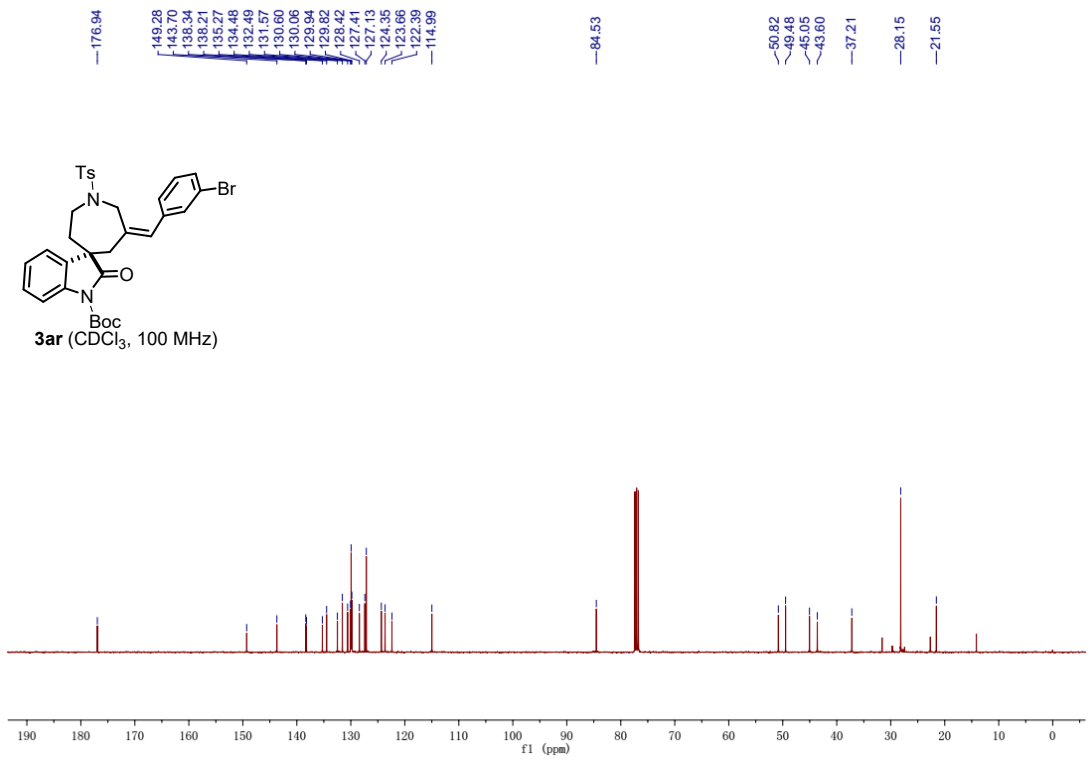
3aq ($CDCl_3$, 400 MHz)



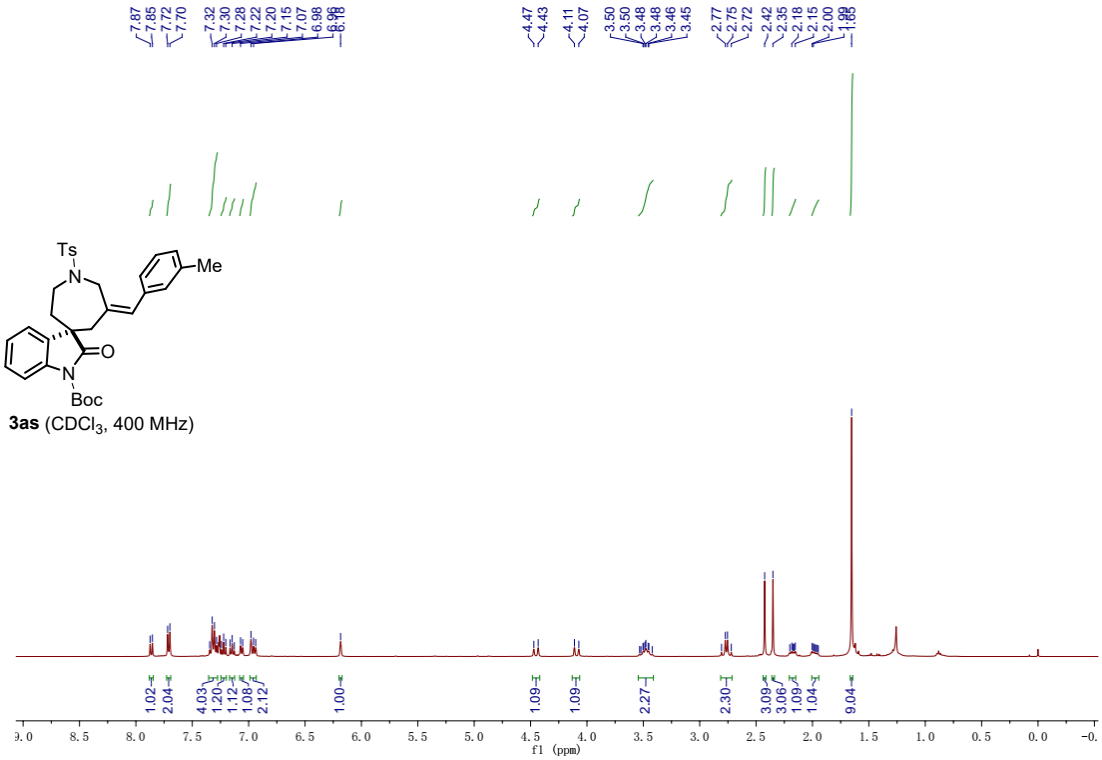
3aq ($CDCl_3$, 100 MHz)



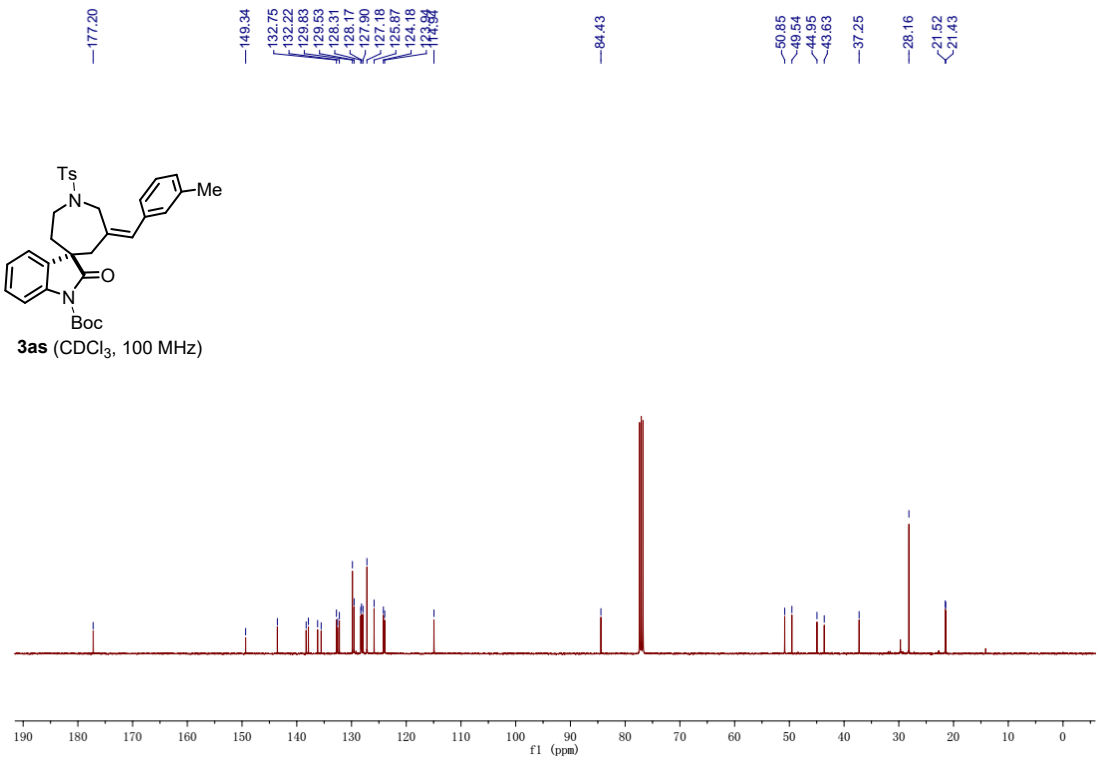
3ar ($CDCl_3$, 400 MHz)



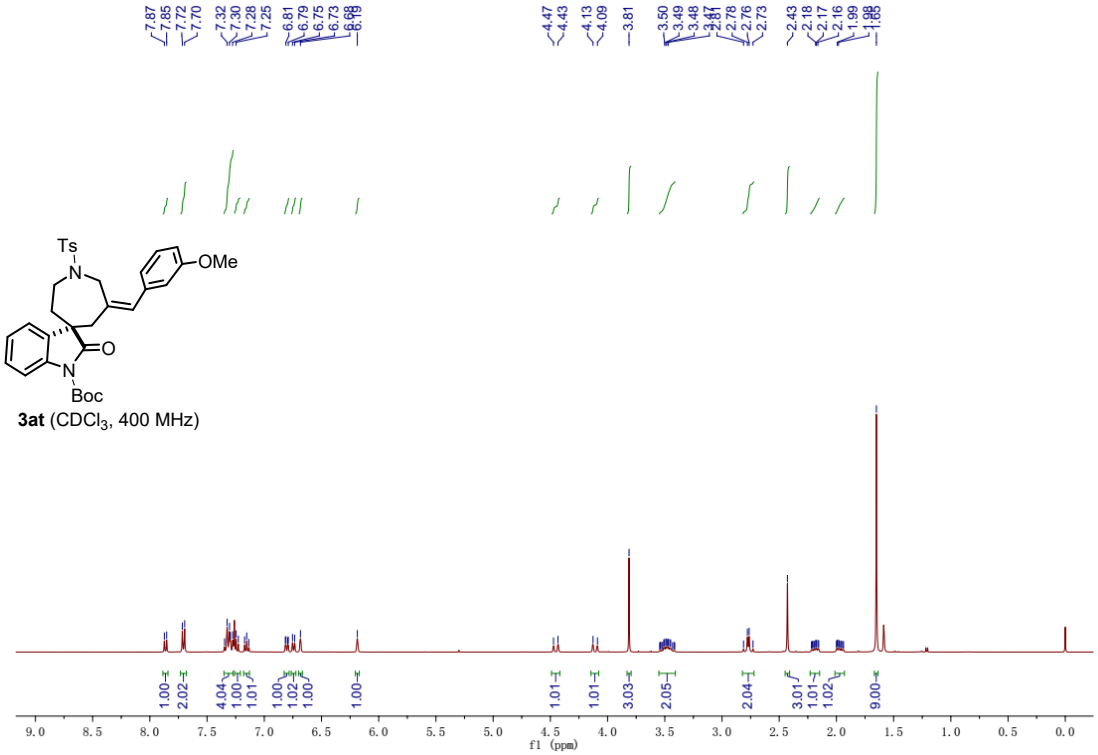
3ar ($CDCl_3$, 100 MHz)



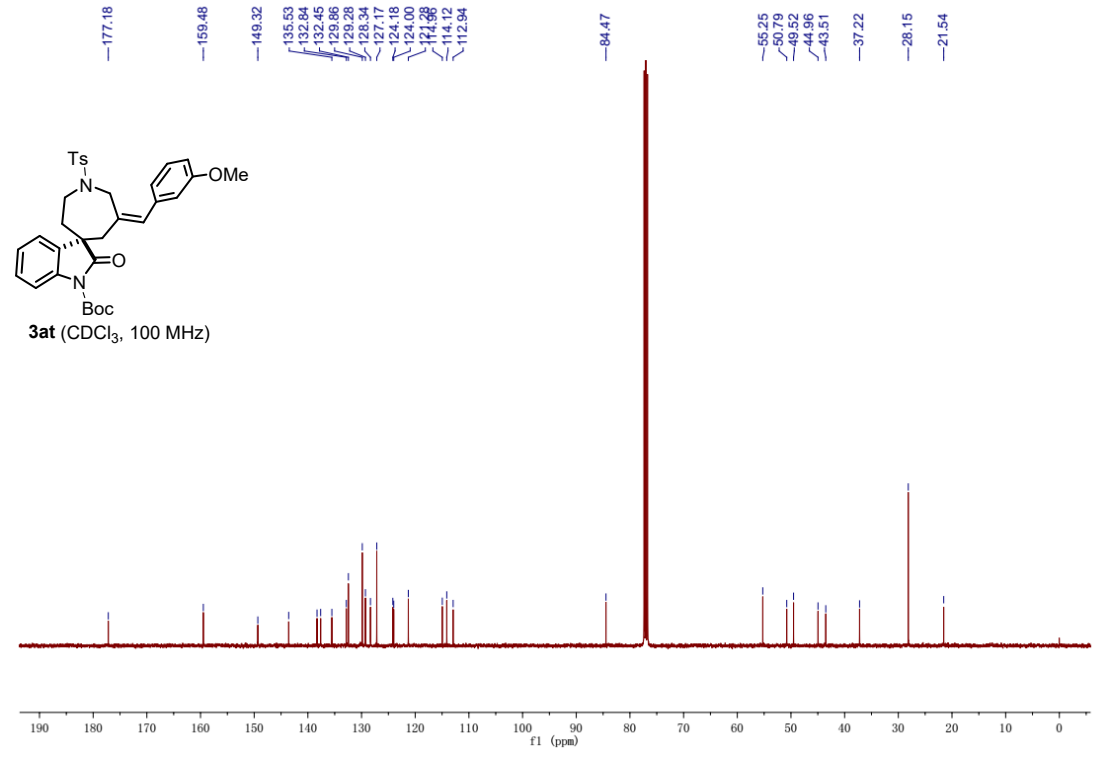
3as ($CDCl_3$, 400 MHz)



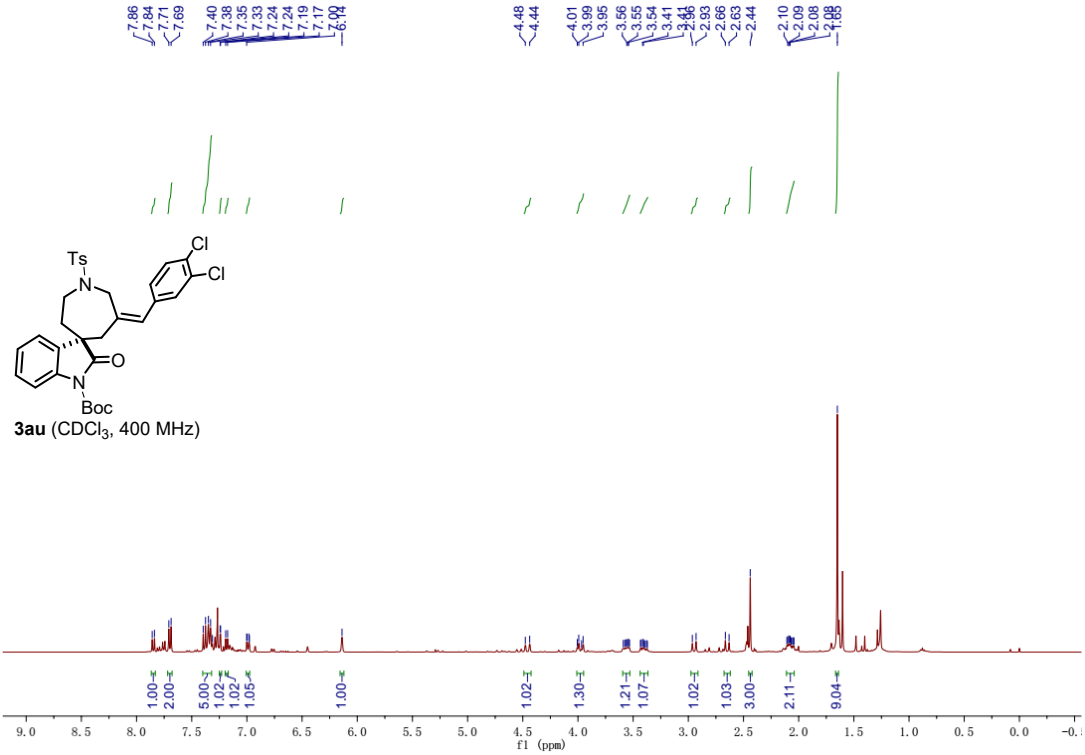
3as ($CDCl_3$, 100 MHz)



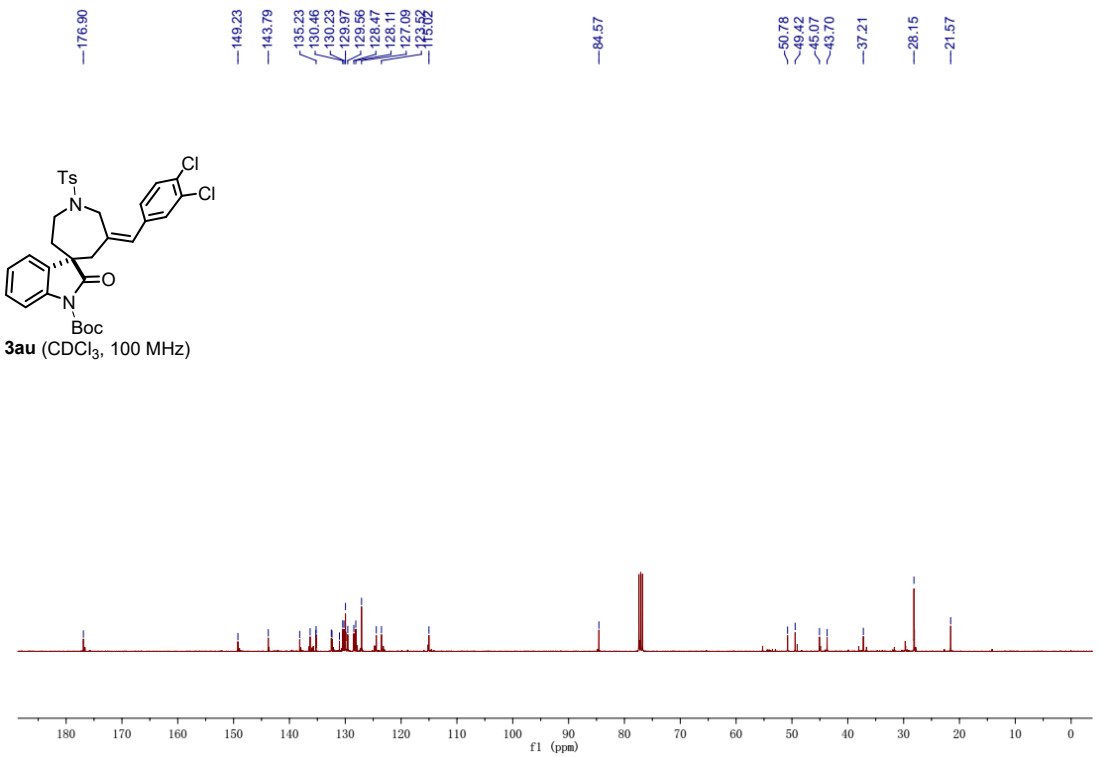
3at ($CDCl_3$, 400 MHz)



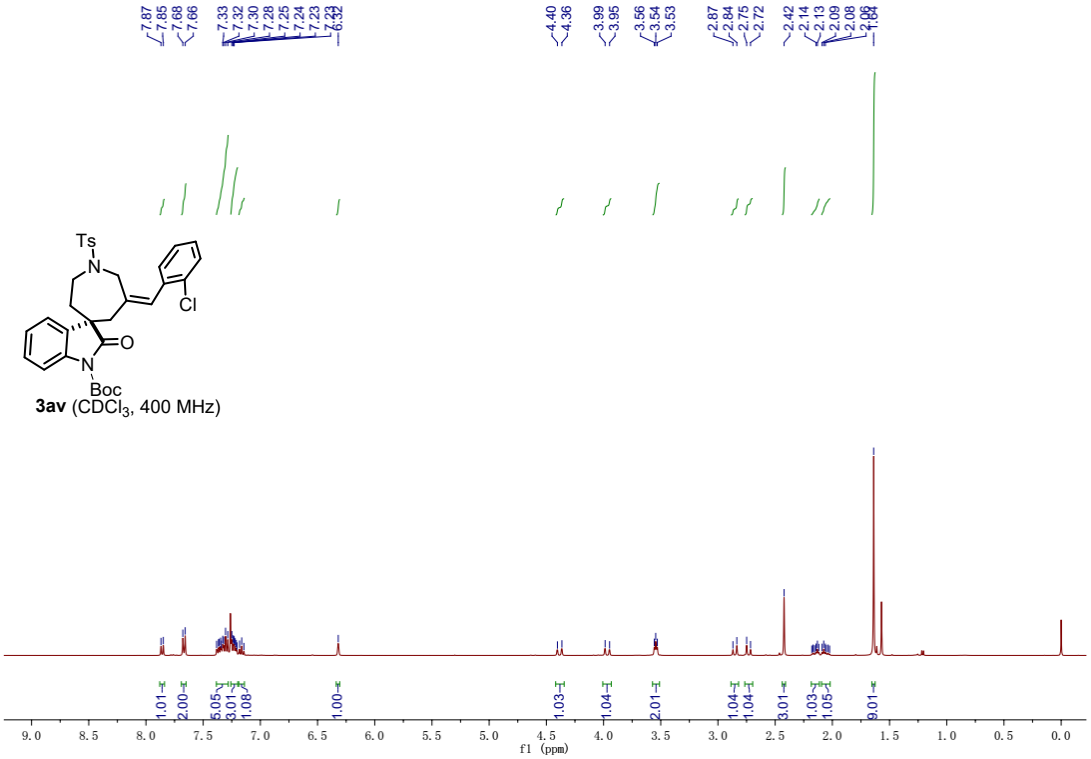
3at ($CDCl_3$, 100 MHz)



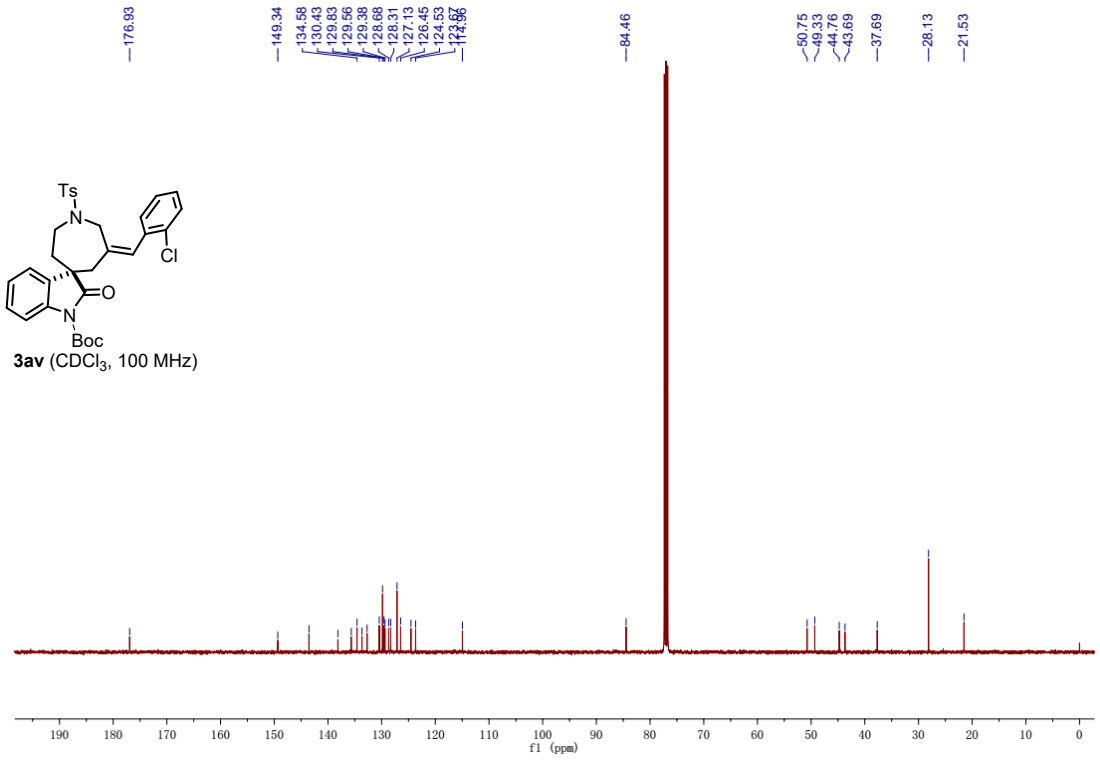
3au ($CDCl_3$, 400 MHz)



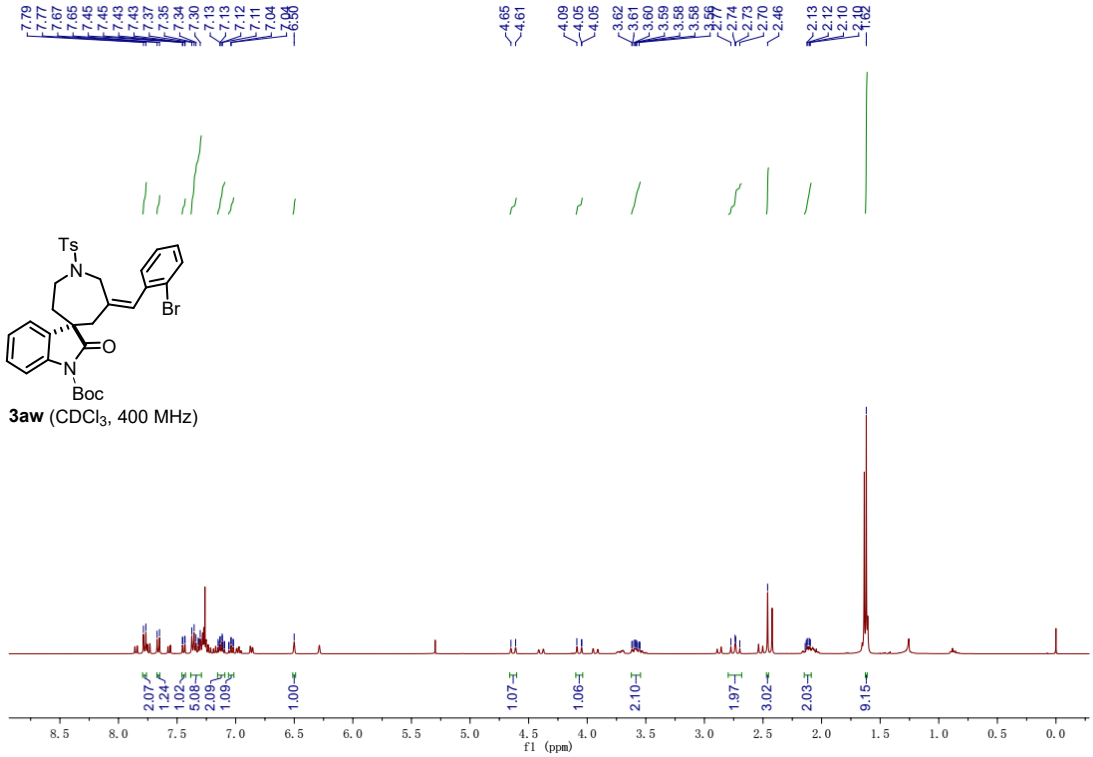
3au ($CDCl_3$, 100 MHz)



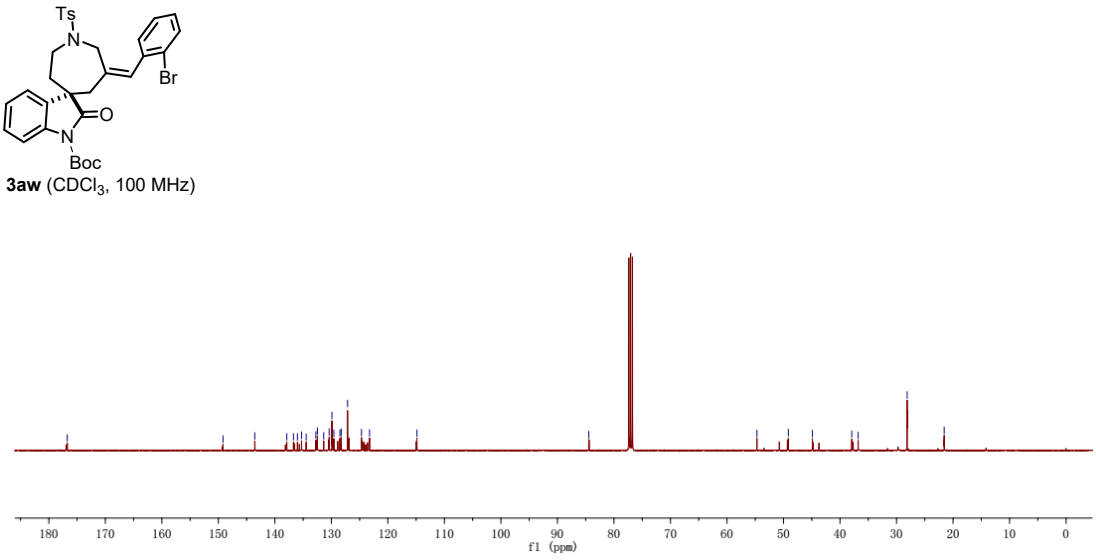
3av ($CDCl_3$, 400 MHz)



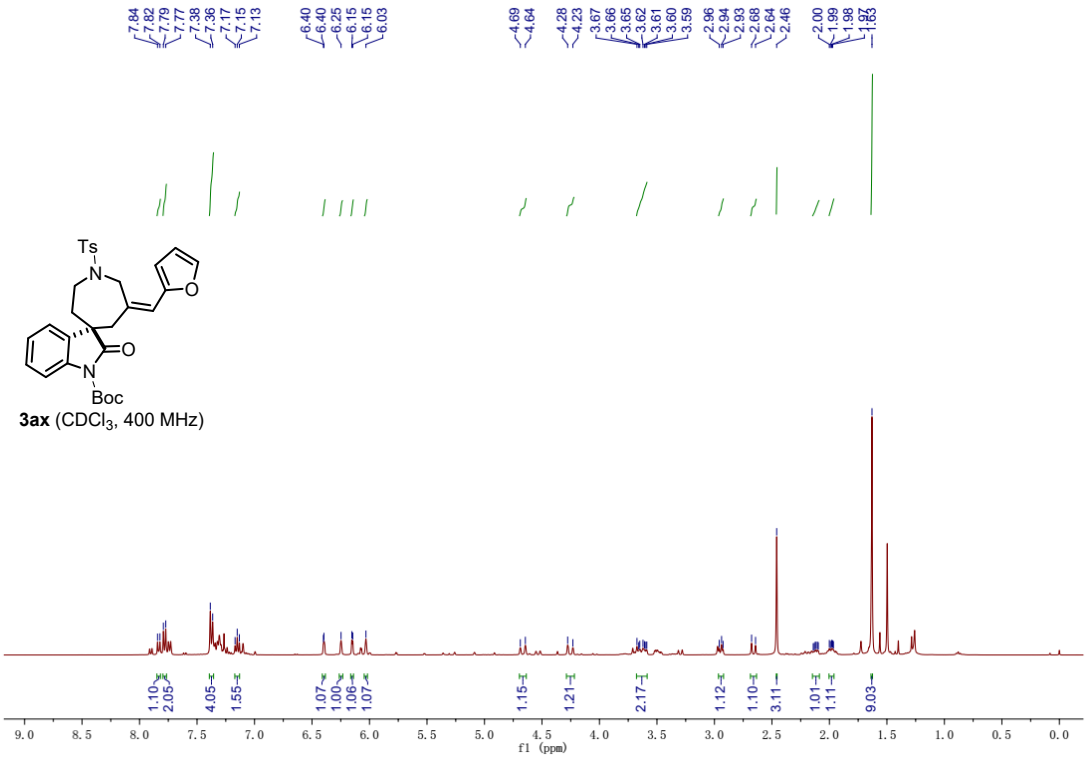
3av ($CDCl_3$, 100 MHz)



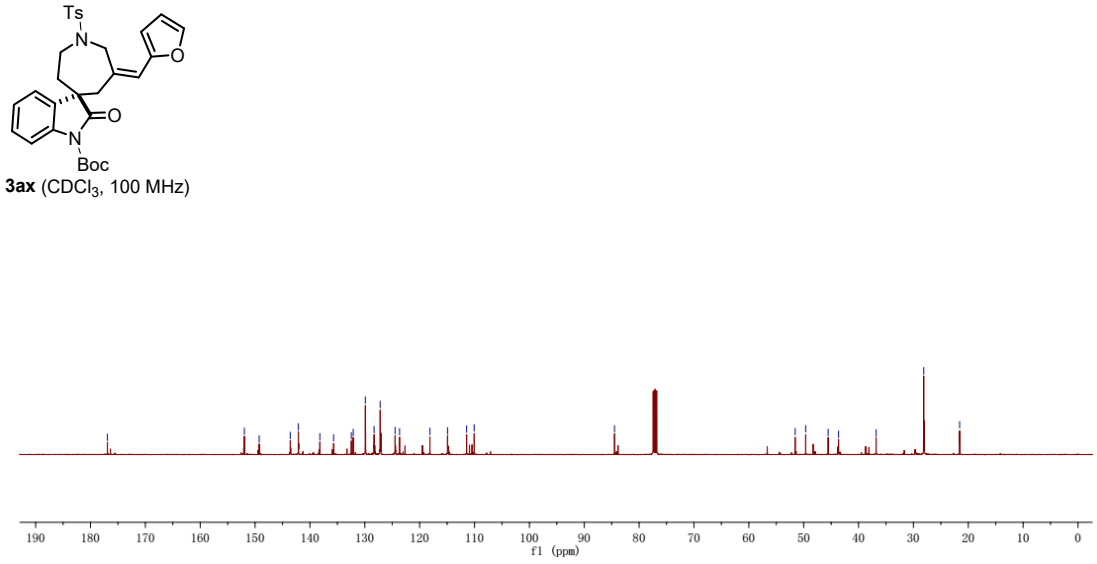
3aw ($CDCl_3$, 400 MHz)



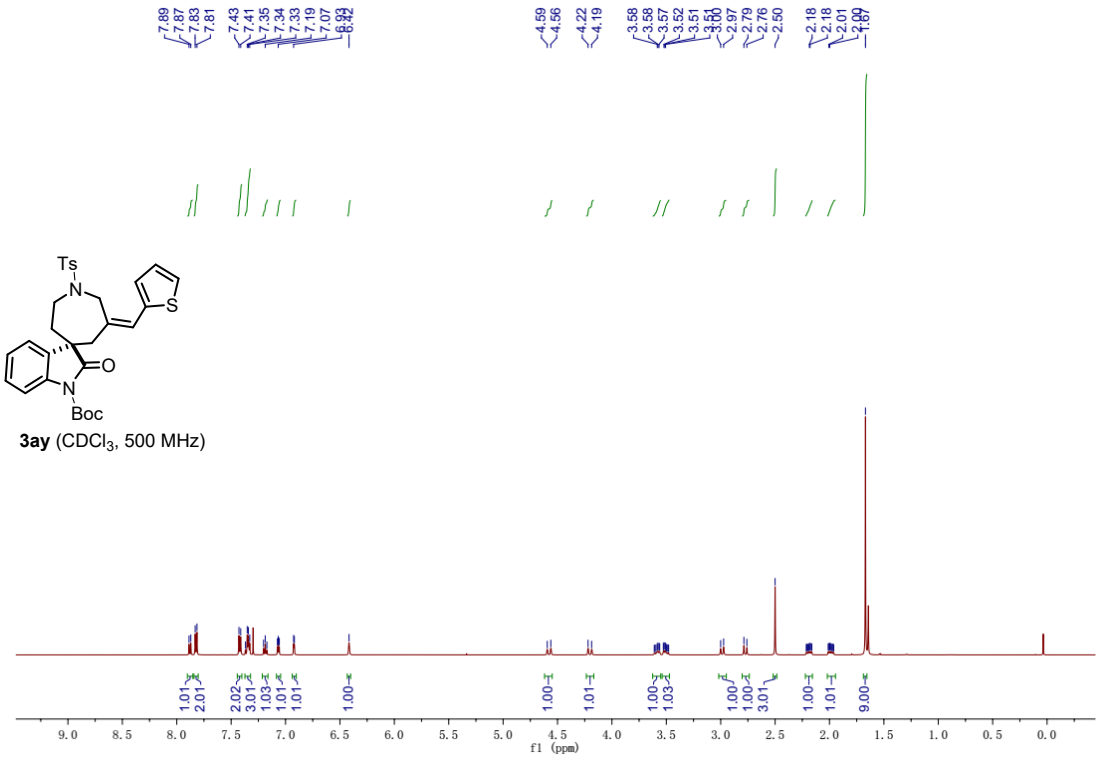
3aw ($CDCl_3$, 100 MHz)



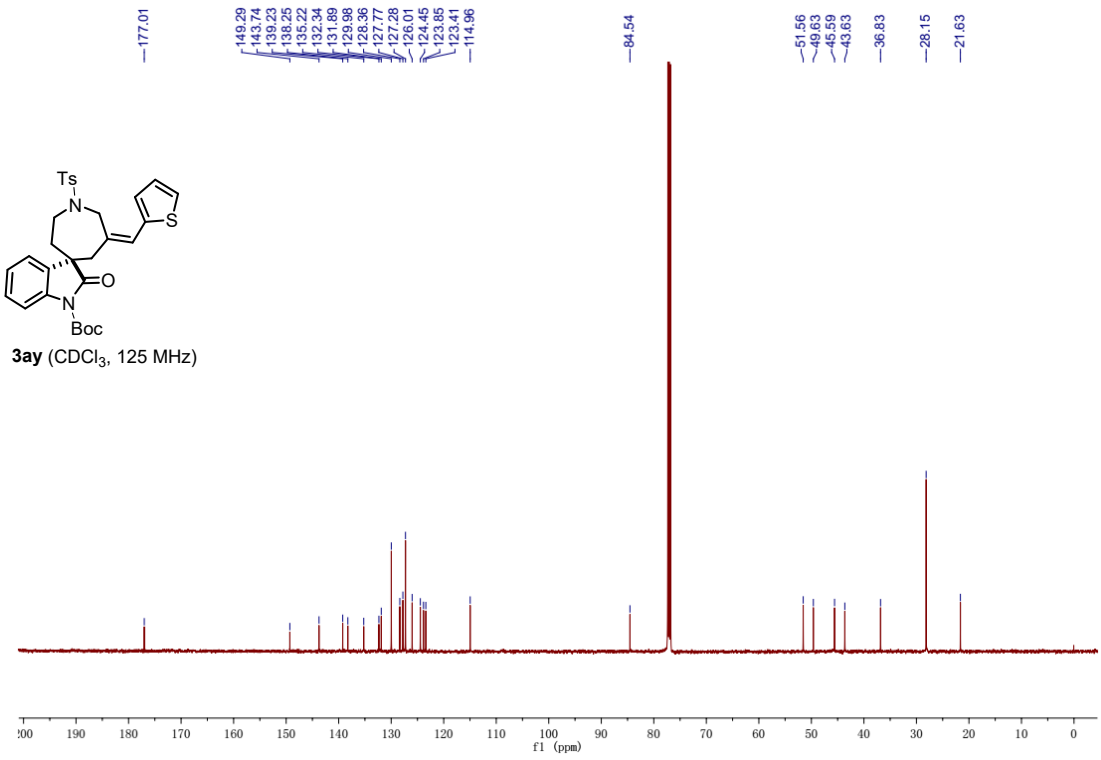
3ax ($CDCl_3$, 400 MHz)



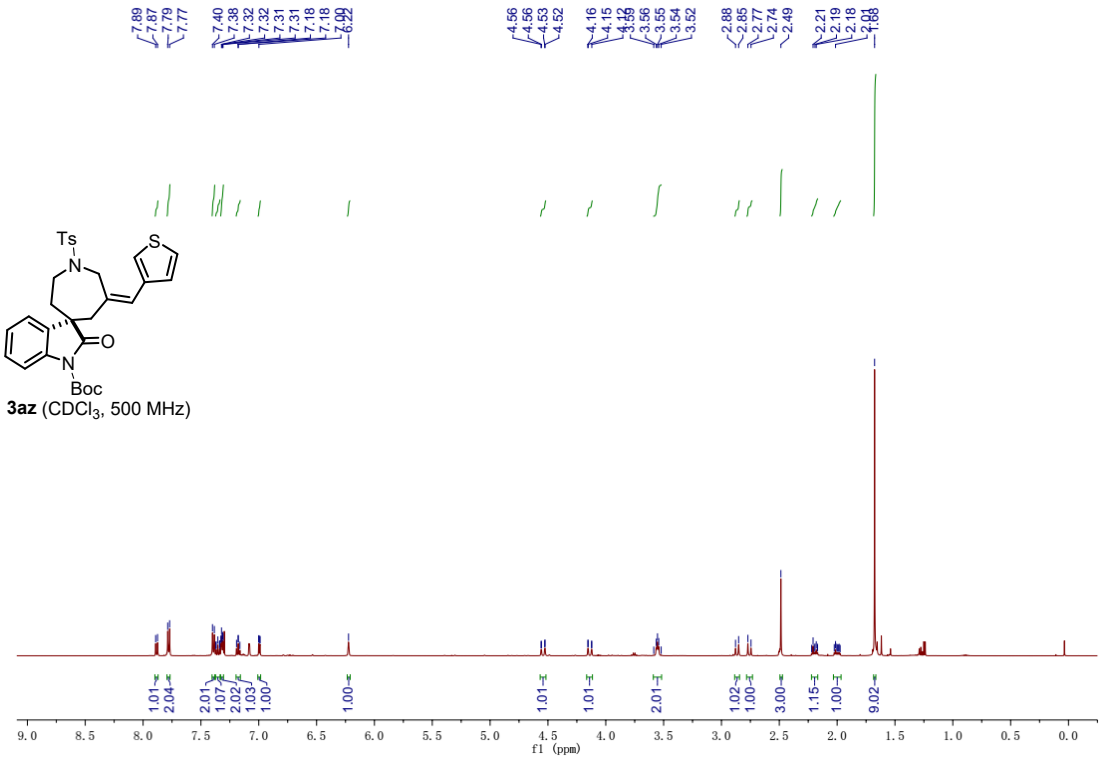
3ax ($CDCl_3$, 100 MHz)



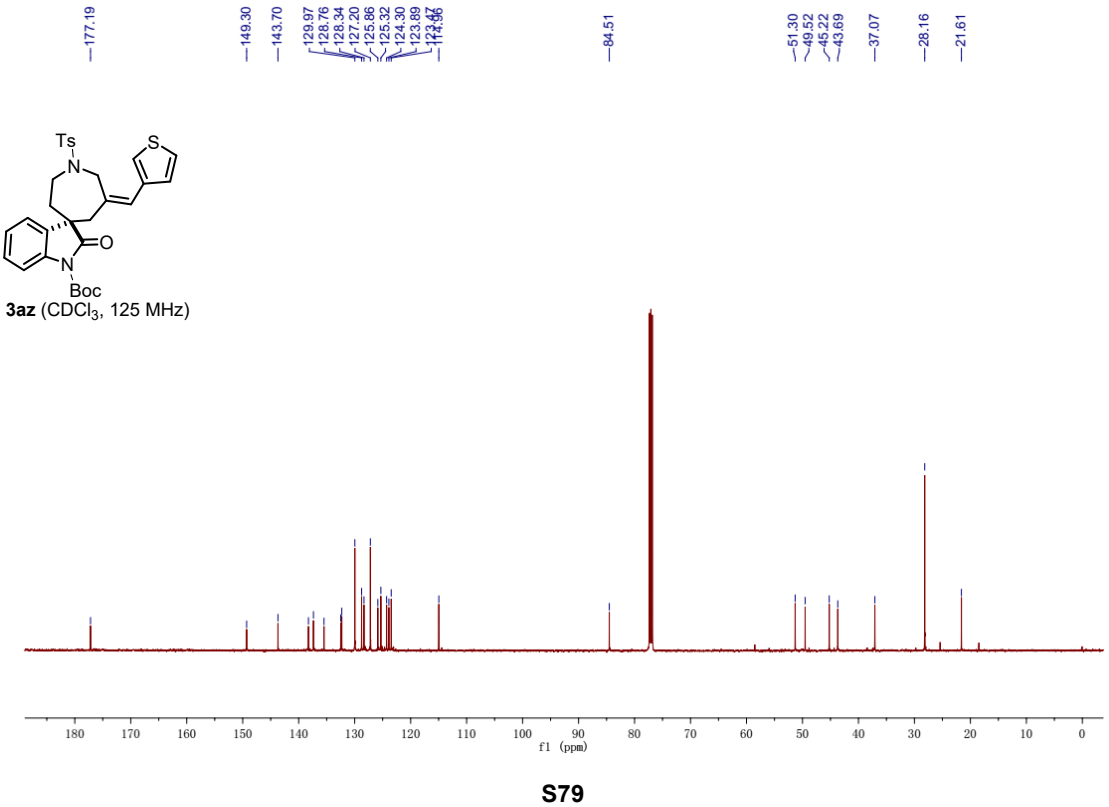
3ay ($CDCl_3$, 500 MHz)



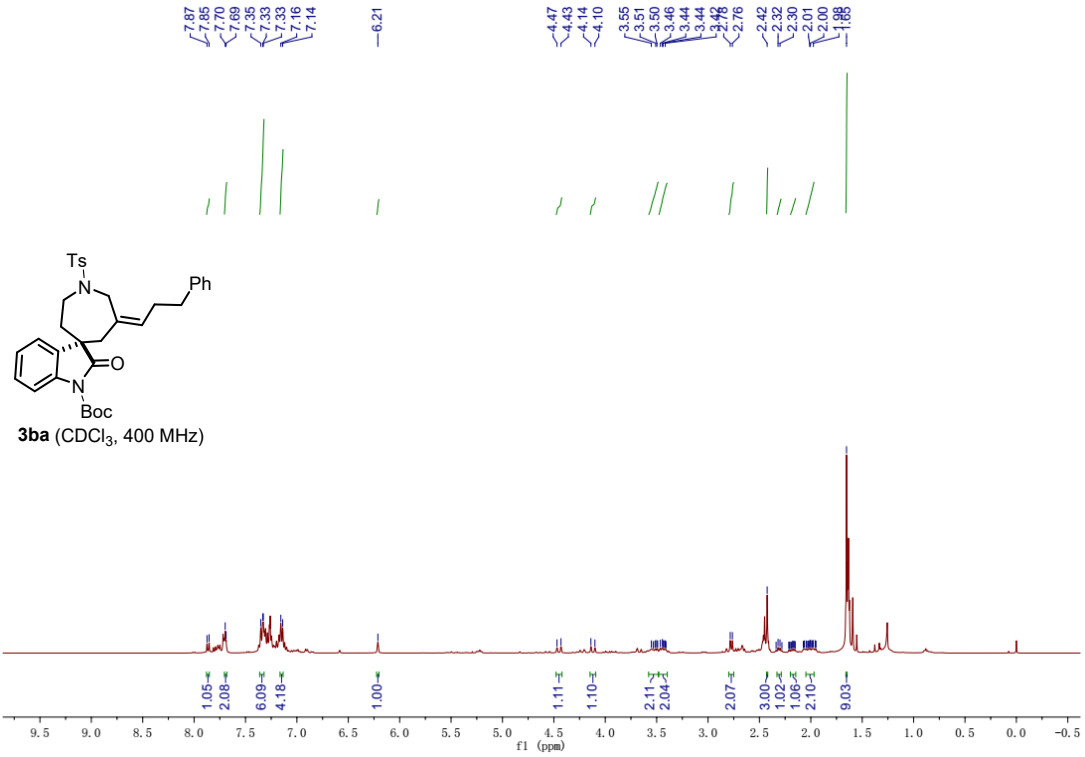
3ay ($CDCl_3$, 125 MHz)



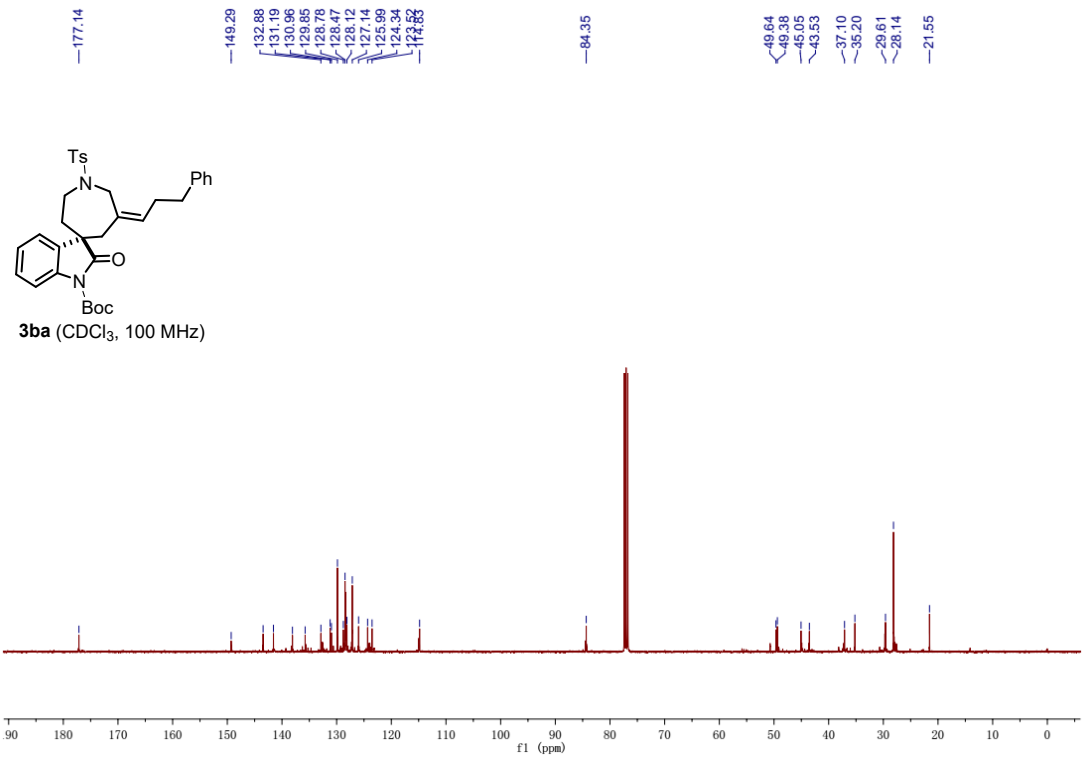
3az ($CDCl_3$, 500 MHz)



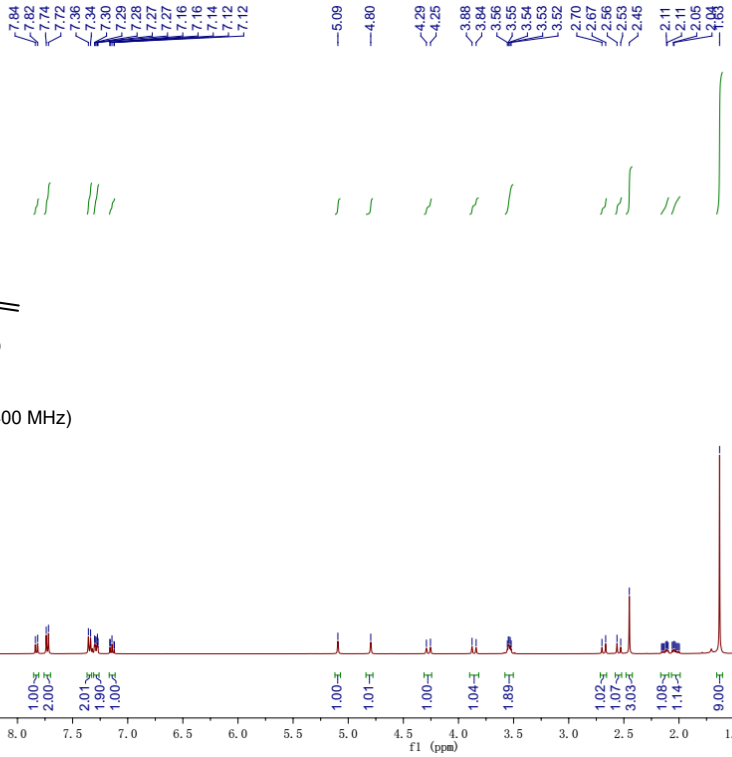
3az ($CDCl_3$, 125 MHz)



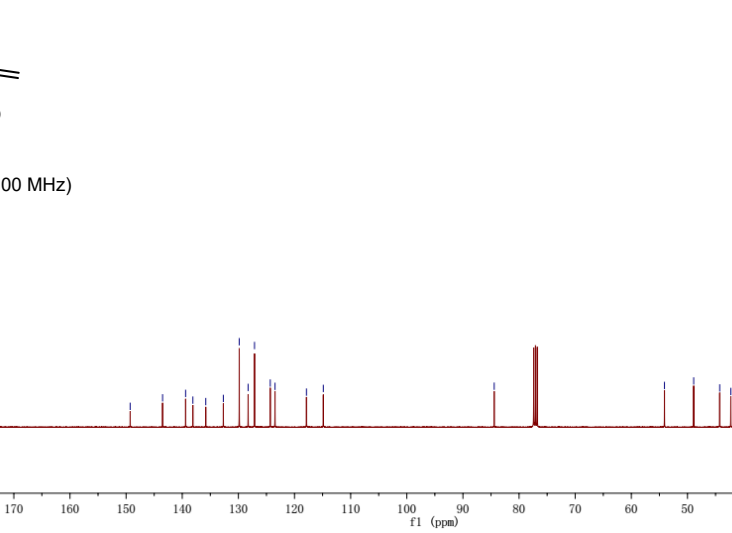
3ba ($CDCl_3$, 400 MHz)



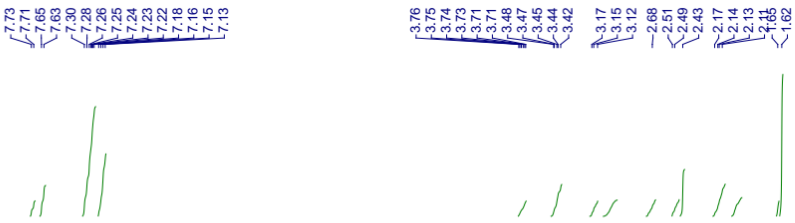
3ba ($CDCl_3$, 100 MHz)

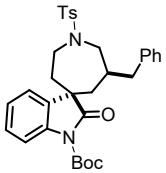


3bb ($CDCl_3$, 400 MHz)

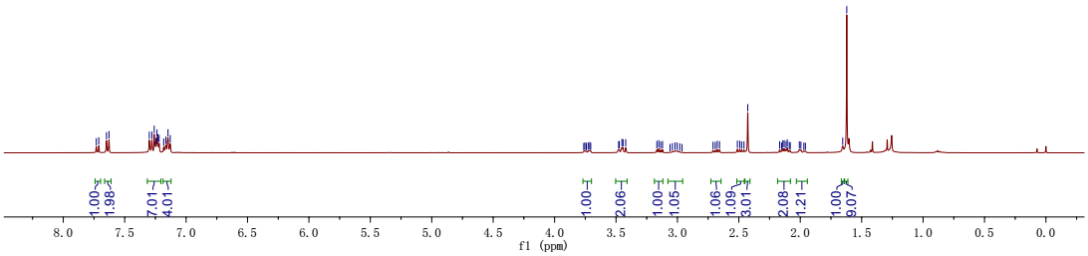


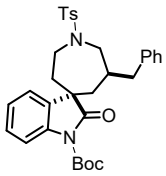
3bb ($CDCl_3$, 100 MHz)



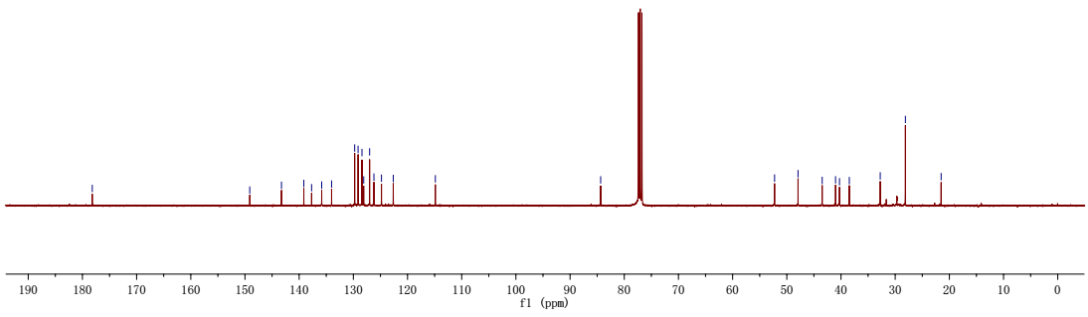


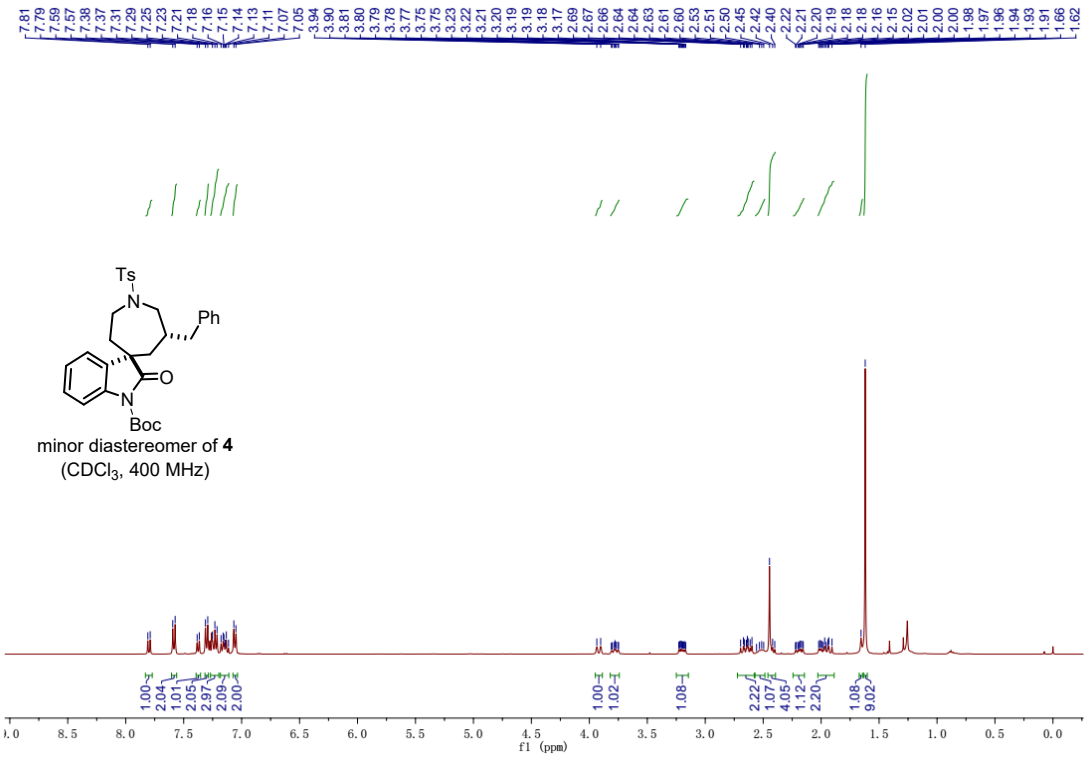
major diastereomer of **4**
($CDCl_3$, 400 MHz)



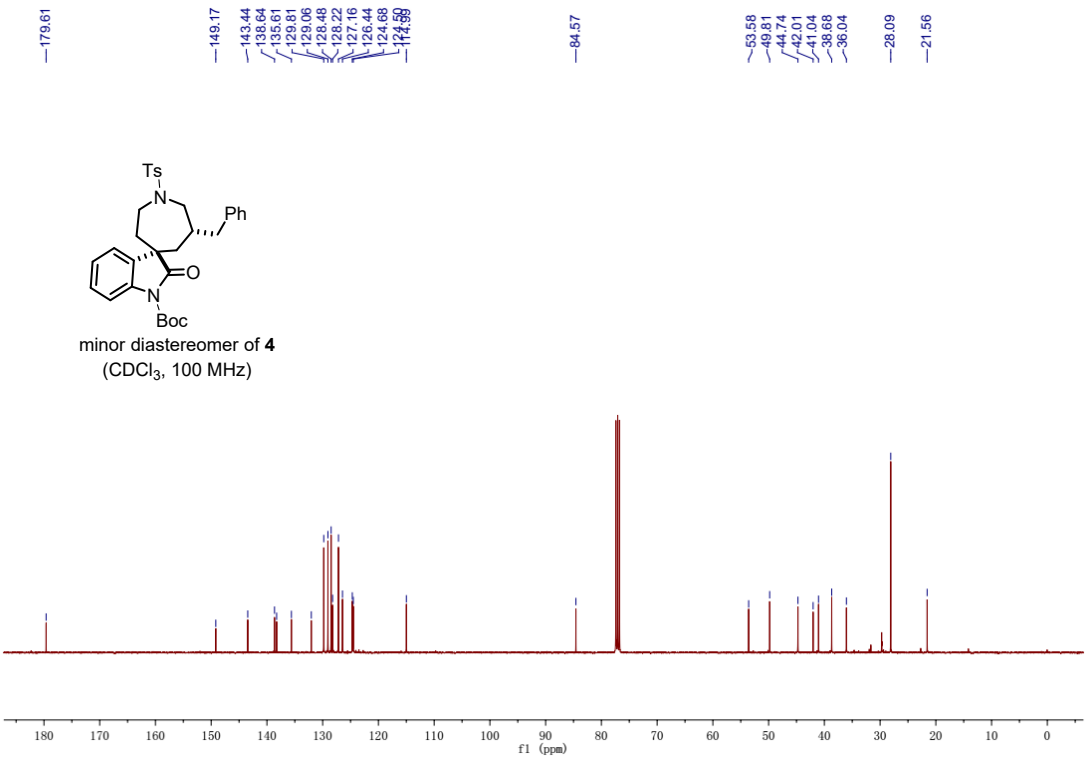


major diastereomer of **4**
($CDCl_3$, 100 MHz)

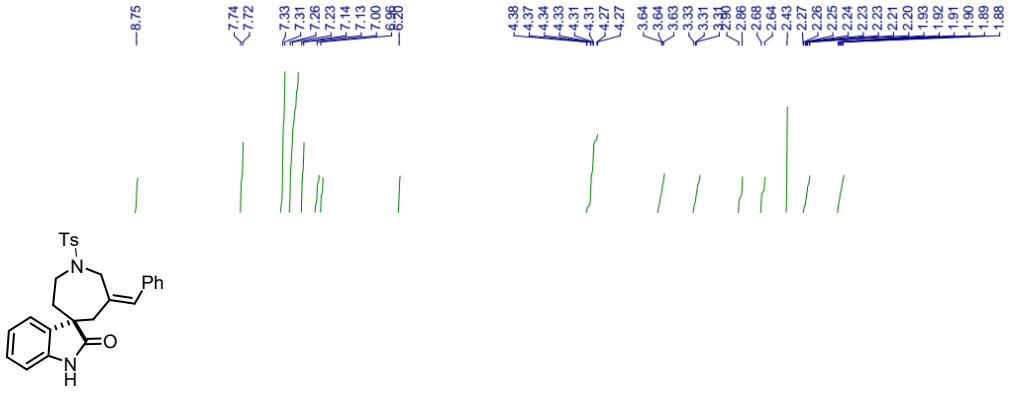




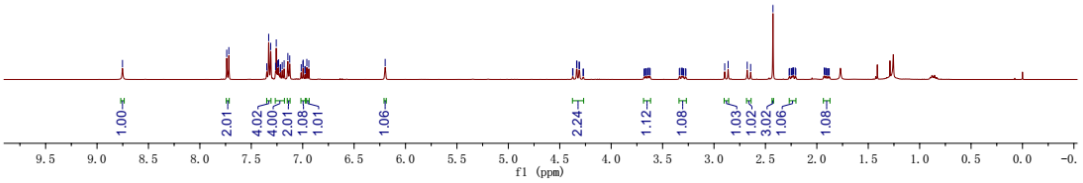
minor diastereomer of **4**
($CDCl_3$, 400 MHz)

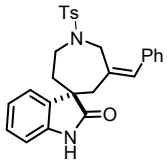


minor diastereomer of **4**
($CDCl_3$, 100 MHz)

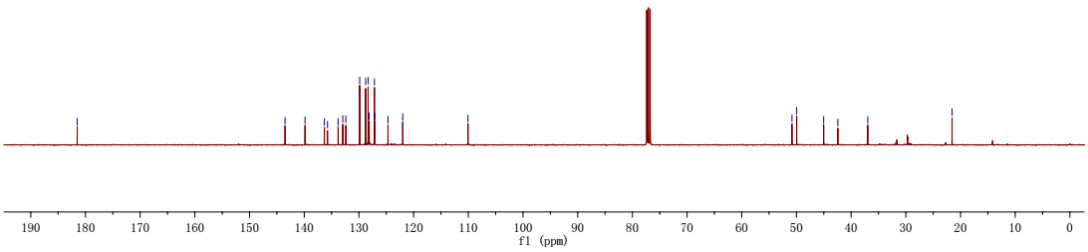


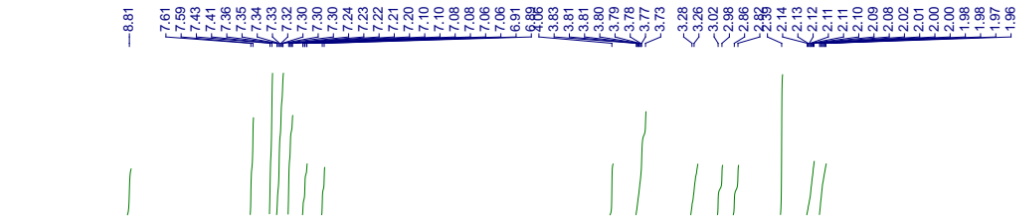
5 ($CDCl_3$, 400 MHz)

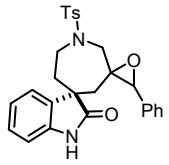




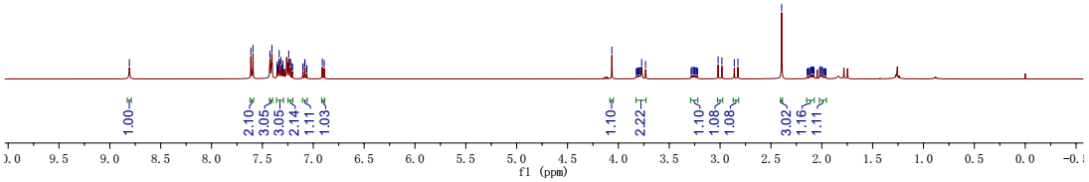
5 ($CDCl_3$, 100 MHz)

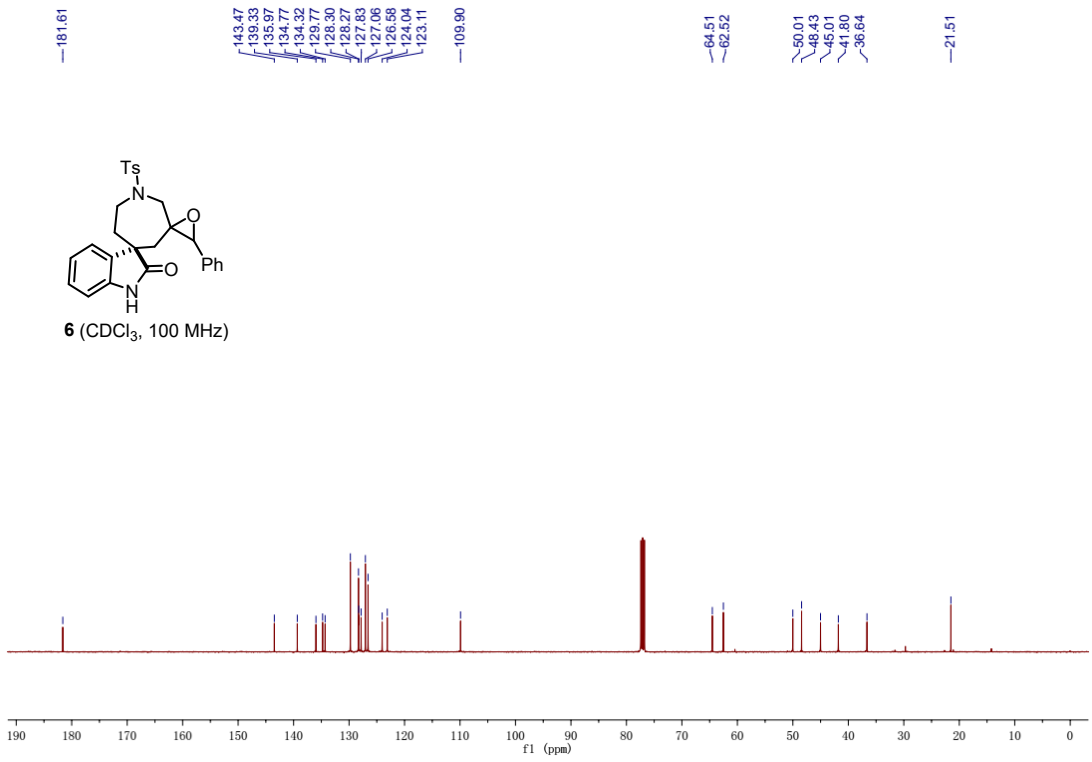




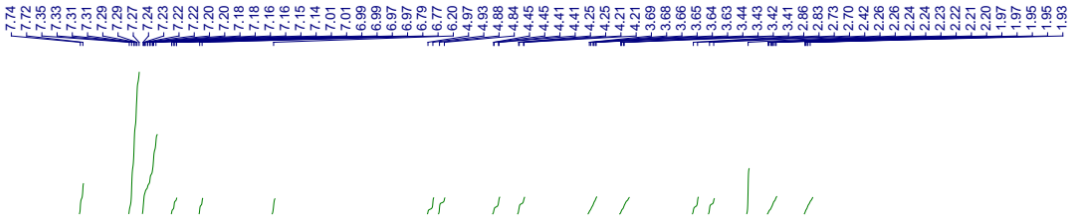


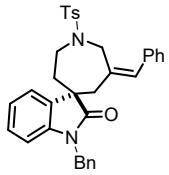
6 ($CDCl_3$, 400 MHz)



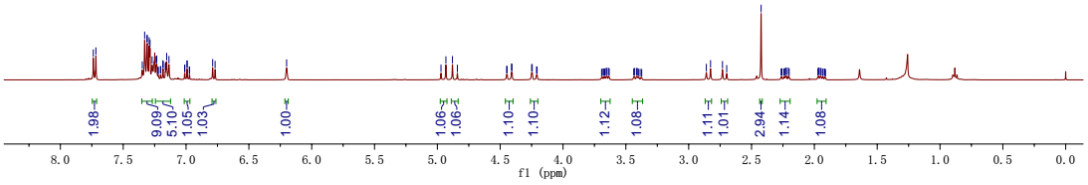


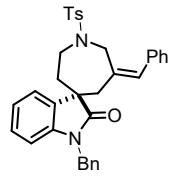
6 ($CDCl_3$, 100 MHz)



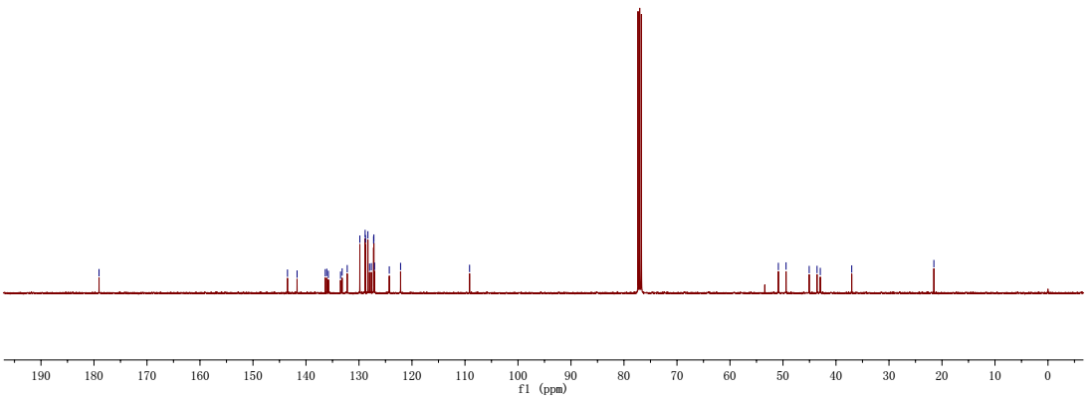


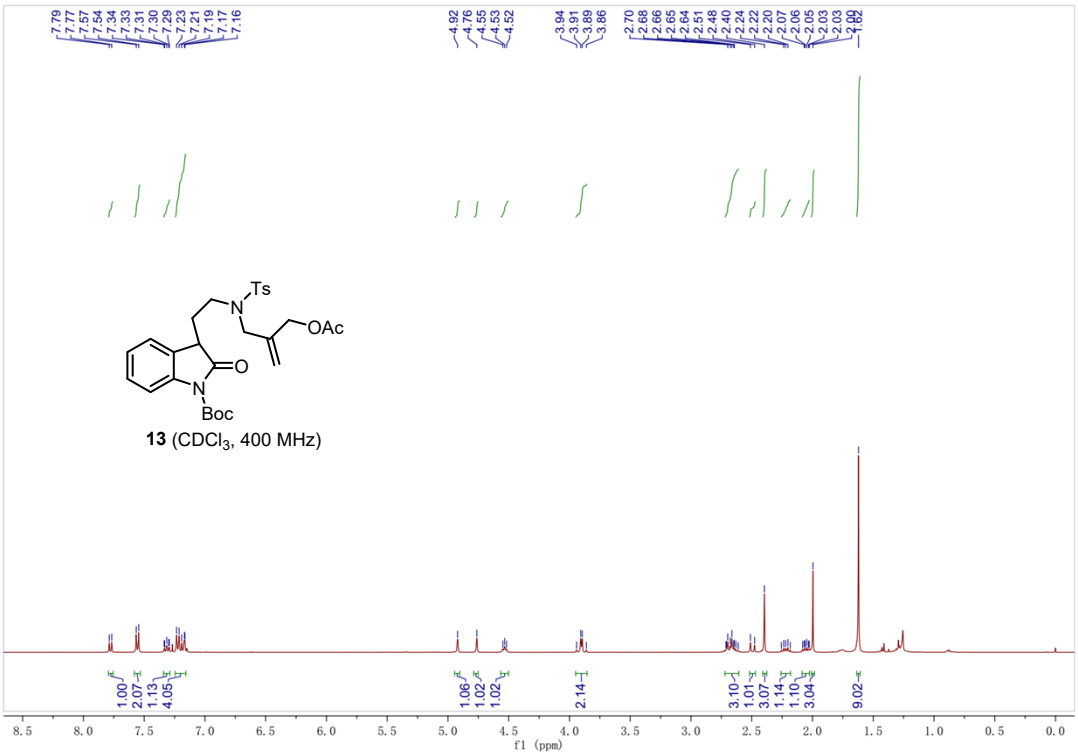
10 ($CDCl_3$, 400 MHz)



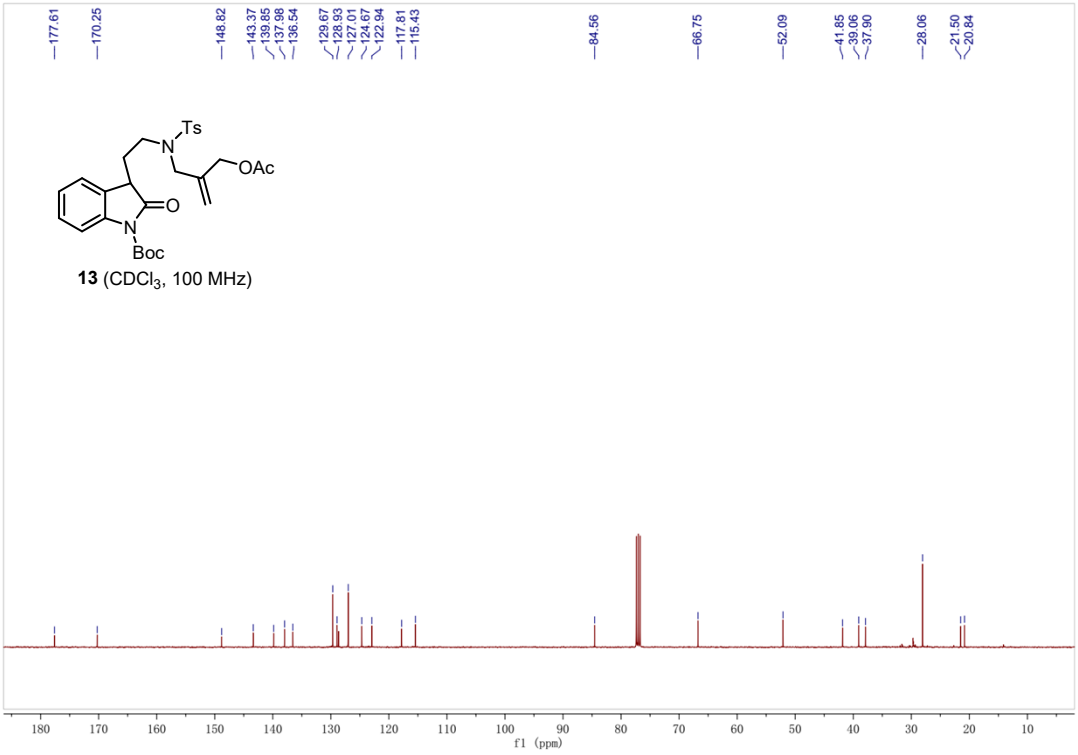


10 ($CDCl_3$, 100 MHz)





13 ($CDCl_3$, 400 MHz)



13 ($CDCl_3$, 100 MHz)

5. X-ray crystal structures

The crystal was obtained by slow evaporation of **3as** in isopropanol. The direct method was used to resolve the crystal structure using the free OLEX2 program embedded with SHELX-2014.

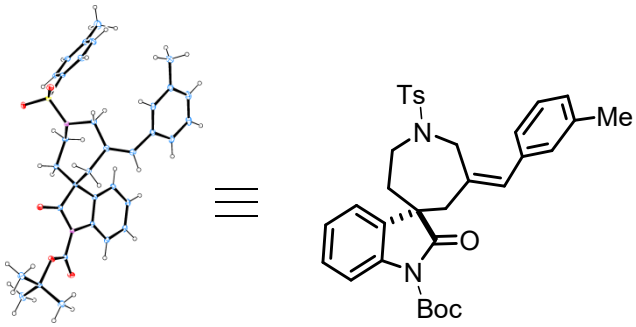


Figure S3. X-ray structure of **3as** (with 15% probability level)

Compound 3as		**CCDC:** 2254812
Bond precision: C-C = 0.0041 Å		Wavelength = 0.71073
a = 9.9541(13)	b = 9.6812(13)	a = 9.9541(13)
alpha = 90	beta = 91.103(3)	alpha = 90
Cell setting: Monoclinic		Moiety formula: $C_{33}H_{36}N_2O_5S$
Cell volume = 2979.5(7)		Space group: P21/c
Data completeness = 0.980		Theta(max) = 27.620
R(reflections) =0.0602(4014)		WR2(reflections) = 0.1661(6779)
S = 1.009		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