Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

A rhodium-catalyzed tandem reaction of *N*-sulfonyl triazoles with indoles: access to indole-substituted indanones

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Part 1: General information

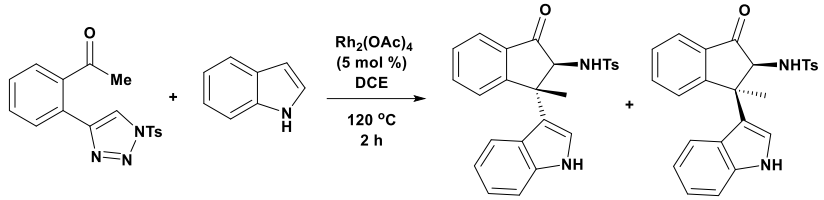
Unless otherwise noted, all reactions were carried out under a nitrogen or an argon atmosphere with dry solvents under anhydrous conditions and all the chemical reagents were purchased from commercial suppliers without further purification. Anhydrous toluene and benzene were distilled from sodium. 1, 2-DCE was distilled from calcium hydride, and $CHCl_3$ was distilled from phosphorus pentoxide. All other solvents were purchased as ACS reagents and used without further purification.

Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Tsingdao silica gel plates (60F-254) using UV light as visualizing agent and an ethanolic solution of phosphomolybdic acid and cerium sulfate, and heated as developing agents. Tsingdao silica gel (60, particle size 0.040-0.063 mm) was used for flash column chromatography.

NMR spectra were recorded on a Brüker Advance 400 (^{1}H: 400 MHz, ^{13}C: 100 MHz)，Brüker Advance 500 (^{1}H: 500 MHz, ^{13}C: 125 MHz) or Brüker Advance 300 (^{1}H: 300 MHz, ^{13}C:75 MHz) and were internally referenced to rdual protio solvent signals (note: Acetone-d6 referred to δ2.05 and 29.9 ppm respectively, CD_2Cl_2 referred to δ5.32 and 54.0 ppm respectively). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.

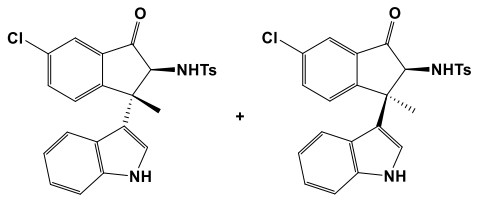
Infrared spectra (IR) were recorded on a Shimadzu IRPrestige-21 FTIR spectrometer. High resolution mass spectrometric (HRMS) data were obtained using Brüker Apex IV RTMS. All of the substrates were prepared according to our previous work.[1]

Part 2: General procedure and characteristic data for products



1a 2a 3a 3a'

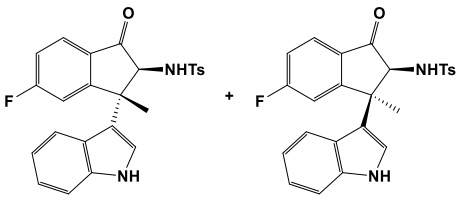
To a solution of dry DCE (4 mL) in a reaction tube (35 mL) was sequentially added triazole **1a** (68.2 mg, 0.20 mmol, 1.0 equiv), $Rh_2(OAc)_4$ (4.4 mg, 5 mol %), and indole (28.1 mg, 0.24 mmol, 1.2 equiv) under argon atmosphere at room temperature. Then, the reaction tube was sealed with a teflon screw cap and the reaction was stirred at 120 °C for 2 h (the maximum pressure resistant of the sealed tube was 6.00 atm and the pressure of the reaction system was about 2.32 atm at 120 °C). After cooled to ambient temperature, the resultant mixture was directly purified by flash column chromatography (PE: EA= 16:1 to 4:1) to afford product **3a** (65.2 mg, 0.15 mmol) in 76% yield as white solid and **3a'** (13.0 mg, 0.03 mmol) in 15% yield as white solid. **3a:** ^{1}H NMR (500 MHz, Acetone-d6) δ 10.13 (s, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.61 – 7.55 (m, 1H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.06 (dt, *J* = 10.7, 8.0 Hz, 5H), 6.99 (d, *J* = 8.5 Hz, 1H), 6.75 (t, *J* = 7.5 Hz, 1H), 6.55 (d, *J* = 8.0 Hz, 1H), 4.95 (d, *J* = 8.4 Hz, 1H), 2.35 (s, 3H), 1.54 (s, 3H); ^{13}C NMR (100 MHz, Acetone-d6) δ 200.7, 161.1, 143.3, 139.8, 138.5, 136.6, 133.3, 129.8, 129.0, 127.5, 126.4, 125.9, 124.8, 124.2, 122.2, 119.7, 119.6, 119.0, 112.7, 70.3, 46.9, 26.1, 21.5; IR ν_{max}(film): 3480, 3358, 2966, 2924, 2856, 2360, 2342, 1871, 1627, 1458, 1259, 1155, 1090, 1051, 1017, 800, 748, 475 cm^{-1}; HRMS (ESI) m/z calcd for $C_{25}H_{22}N_2O_3SNa$ $[M+Na]^+$ 453.1249, found 453.1247. **3a':** ^{1}H NMR (500 MHz, Acetone-d6) δ 10.16 (s, 1H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.76 – 7.70 (m, 2H), 7.54 (t, *J* = 7.3 Hz, 2H), 7.34 (dd, *J* = 14.7, 8.1 Hz, 3H), 7.02 – 6.95 (m, 1H), 6.77 – 6.63 (m, 3H), 6.13 (d, *J* = 8.8 Hz, 1H), 4.50 – 4.41 (m, 1H), 2.43 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, Acetone-d6) δ 201.4, 159.2, 143.7, 140.3, 138.3, 136.7, 134.8, 130.1, 129.2, 128.2, 127.1, 126.7, 125.3, 123.6, 122.0, 121.2, 119.7, 118. 7, 112.4, 70.9, 47.9, 26.2, 21.5; IR ν_{max}(film): 3694, 3425, 3299, 3082, 3027, 2924, 2856, 2366, 2336, 1871, 1782, 1693, 1589, 1531, 1479, 1354, 1238, 1130, 1072, 1004, 900, 790, 683, 488 cm^{-1}; HRMS (ESI) m/z calcd for $C_{25}H_{22}N_2O_3SNa$ $[M+Na]^+$ 453.1249, found 453.1244.



3b 3b'

3b (51.7 mg, 0.11 mmol)**:** light yellow solid, 56% yield from **1b** (75.1 mg, 0.20 mmol), ^{1}H NMR (500 MHz, Acetone-d6) δ 10.20 (s, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.53 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.18 (d, *J* = 8.3 Hz, 2H), 7.11 – 6.97 (m, 6H), 6.80 (t, *J* = 7.5 Hz, 1H), 6.64 (d, *J* = 8.1 Hz, 1H), 5.01 (d, *J* = 8.6 Hz, 1H), 2.36 (s, 3H), 1.56 (s, 3H); ^{13}C NMR (100 MHz, Acetone-d6) δ 199. 5, 162.7, 143.4, 142.2, 139.8, 138.5, 132.0, 129.8, 129.7, 127.4, 126.4, 126.1, 125.7, 125.1, 122.3, 119.9, 119.5, 118.1, 112.8, 70.2, 46.9, 25.8, 21.5; IR ν_{max}(film): 3586, 3486, 3082， 3027, 2954，2880， 2366， 1693， 1601， 1565， 1525，1439， 1384， 1304， 1238， 1194， 1112， 1034， 975， 785， 717， 696， 638， 558 cm^{-1}；HRMS (ESI) m/z calcd for $C_{25}H_{21}ClN_2O_3SNa$ $[M+Na]^+$ 487.0859, found 487.0851.

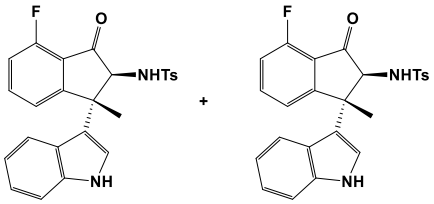
3b' (10.3 mg, 0.02 mmol): light yellow solid, 11% yield from **1b** (75.1 mg, 0.20 mmol), ^{1}H NMR (400 MHz, Acetone-d6) δ 10.24 (s, 1H), 7.77 (dd, *J* = 12.4, 8.2 Hz, 3H), 7.67 – 7.48 (m, 2H), 7.35 (dd, *J* = 8.1, 4.0 Hz, 3H), 7.00 (ddd, *J* = 8.1, 6.6, 1.5 Hz, 1H), 6.86 – 6.60 (m, 3H), 6.29 (d, *J* = 8.9 Hz, 1H), 4.60 – 4.41 (m, 1H), 2.43 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, Acetone-d6) δ 200.3, 160.9, 143.7, 142.3, 140.3, 138.3, 133.5, 130.1, 129.9, 128.1, 126.9, 126.8, 125.4, 122.1, 121.0, 119.9, 118.0, 112.5, 112.5, 70.8, 47.9, 25.9, 21.5; IR ν_{max}(film): 3504, 3455, 2924, 2849，2355, 2330, 1935, 1709, 1611, 1562, 1296, 1231, 1139, 1069, 779, 714, 493 cm^{-1}; HRMS (ESI) m/z calcd for $C_{25}H_{21}ClN_2O_3SNa$ $[M+Na]^+$ 487.0859, found 487.0851.



3c **3c'**

3c (64.0 mg, 0.14 mmol): light yellow solid, 71% yield from **1c** (71.8 mg, 0.20 mmol), ^{1}H NMR (500 MHz, Acetone-d6) δ 10.15 (s, 1H), 7.53 – 7.41 (m, 2H), 7.41 – 7.30 (m, 1H), 7.20 (d, *J* = 8.2 Hz, 2H), 7.14 – 6.97 (m, 6H), 6.82 – 6.74 (m, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 5.02 (s, 1H), 2.35 (s, 3H), 1.54 (s, 3H); ^{13}C NMR (125 MHz, Acetone-d6) δ 199.9, 163.4 (d, *J* = 246.7 Hz), 156.8, 143.4, 139.8, 138.6, 135.1 (d, *J* = 7.5 Hz), 129.8, 128.6 (d, *J* = 8.2 Hz), 127.5, 125.8, 124.8 (d, *J* = 16.0 Hz), 124.1 (d, *J* = 23.7 Hz), 123.9, 122.3, 119.7 (d, *J* = 10.0 Hz), 118.6, 112.8 (d, *J* = 5.2 Hz), 109.8 (d, *J* = 22.3 Hz), 70.7, 46.6, 26.1, 21.5; IR ν_{max}(film): 3566, 3473, 3089, 2948, 2875, 2820, 2366, 2336, 1951, 1872, 1659, 1583, 1354, 1302, 1170, 1130, 1069, 790, 717, 675, 530 cm^{-1}; HRMS (ESI) m/z calcd for $C_{25}H_{21}FN_2O_3SNa$ $[M+Na]^+$ 471.1155, found 471.1146.

3c' (13.0 mg, 0.03 mmol): light yellow solid, 15% yield from **1c** (71.8 mg, 0.20 mmol), ^{1}H NMR (400 MHz, Acetone-d6) δ 10.19 (s, 1H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.60 (dd, *J* = 8.5, 4.7 Hz, 1H), 7.52 (td, *J* = 8.9, 2.5 Hz, 1H), 7.42 (dd, *J* = 7.6, 2.4 Hz, 1H), 7.35 (t, *J* = 8.1 Hz, 3H), 7.03 – 6.95 (m, 1H), 6.76 (q, *J* = 8.3 Hz, 2H), 6.67 (d, *J* = 2.4 Hz, 1H), 6.26 (d, *J* = 8.9 Hz, 1H), 4.53 (d, *J* = 9.0 Hz, 1H), 2.93 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, Acetone-d6) δ 200.7, 163.5 (d, *J* = 247.1 Hz), 155.0, 143.7, 140.3, 138.3, 136.6 (d, *J* = 7.3 Hz), 130.1, 128.9 (d, *J* = 8.2 Hz), 128.1, 127.0, 125.3 (d, *J* = 16.2 Hz), 124.1 (d, *J* = 23.7 Hz), 122.1, 121.1, 119.8, 118.5, 112.5, 109.2 (d, *J* = 22.1 Hz), 71.3, 47.6, 26.1, 21.5; IR ν_{max}(film): 3559, 3455, 3021, 2924, 2849, 2366, 2342, 1904, 1852, 1724, 1624, 1580, 1359, 1311, 1228, 1182, 1115, 1072, 824, 797, 720, 675, 485 cm^{-1}; HRMS (ESI) m/z calcd for $C_{25}H_{21}FN_2O_3SNa$ $[M+Na]^+$ 471.1155, found 471.1154.

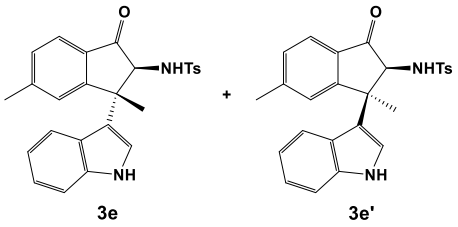


3d **3d'**

3d (52.2 mg, 0.12 mmol): white solid, 58% yield from **1d** (71.8 mg, 0.20 mmol), ^{1}H NMR (400 MHz, Acetone-d6) δ 10.11 (s, 1H), 7.67 (d, *J* = 7.5 Hz, 1H), 7.67 (d, *J* = 7.5 Hz, 1H), 7.57 (td, *J* = 7.8, 4.3 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.37 – 7.27 (m, 1H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.07 (dd, *J* = 13.2, 7.6 Hz, 4H), 6.98 (d, *J* = 2.3 Hz, 1H), 6.77 (t, *J* = 7.5 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 4.95 (d, *J* = 8.8 Hz, 1H), 2.37 (s, 3H), 1.67 (s,

3H); ^{13}C NMR (125 MHz, Acetone-d6) δ 200.0, 161.0 (d, *J* = 253.4 Hz), 145.7 (d, *J* = 14.0 Hz), 143.5, 139.8, 138.4, 136.6 (d, *J* = 3.8 Hz), 131.5 (d, *J* = 6.9 Hz), 129.9, 127.5, 126.0, 123.8, 123.5 (d, *J* = 20.5 Hz), 122.2, 120. 6 (d, *J* = 4.0 Hz), 119.7, 118.9, 118.8, 112. 8 (d, *J* = 6.5 Hz), 70.4, 45.0, 23.2, 21.5; IR ν_{max}(film): 3499, 3462, 3223, 3003, 2893, 2825, 2360, 2342, 1706, 1627, 1522, 1369, 1283, 1225, 1127, 1054, 983, 830, 787, 711, 610, 475 cm^{-1};HRMS (ESI) m/z calcd for $C_{25}H_{21}FN_2O_3SNa$ $[M+Na]^+$ 471.1155, found 471.1146.

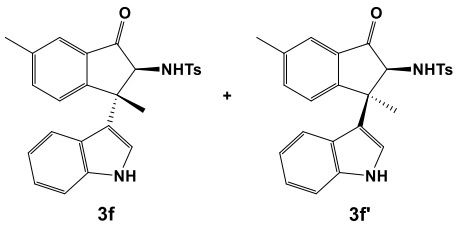
3d' (8.7 mg, 0.02 mmol): white solid, 10% yield from **1d** (71.8 mg, 0.20 mmol)**:** ^{1}H NMR (500 MHz, Acetone-d6) δ 10.23 (s, 1H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.61 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.49 – 7.41 (m, 1H), 7.36 (dd, *J* = 8.1, 4.5 Hz, 3H), 7.00 (t, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 2.3 Hz, 1H), 6.74 (dd, *J* = 11.2, 4.0 Hz, 1H), 6.63 (d, *J* = 8.2 Hz, 1H), 6.24 (d, *J* = 9.0 Hz, 1H), 4.56 (d, *J* = 9.1 Hz, 1H), 2.43 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (125 MHz, Acetone-d6) δ200.7, 161.6 (d, *J* = 252.5 Hz), 144.1 (d, *J* = 15.0 Hz), 143.8, 140.5, 138.5, 138.1 (d, *J* = 4.4 Hz), 131.8 (d, *J* = 7.0 Hz), 130.2, 128.2, 127.0, 125.4 (d, *J* = 19.7 Hz), 123.7(d, *J* = 21.0 Hz), 122.1, 120.7, 120.1 (d, *J* = 3.8 Hz), 120.0, 116.6, 112.6 (d, *J* = 6.5 Hz), 70.9 (d, *J* = 10.7 Hz), 46.9, 25.5 (d, *J* = 2.6 Hz), 21.5; IR ν_{max}(film): 3499, 3434, 2930, 2856，2366，1872， 1697， 1620， 1583， 1482， 1421， 1332， 1186, 864， 760， 537， 475 cm^{-1}； HRMS (ESI) m/z calcd for $C_{25}H_{21}FN_2O_3SNa$ $[M+Na]^+$ 471.1155, found 471.1153.



3e **3e'**

3e (53.3 mg, 0.12 mmol): white solid, 60% yield from **1e** (71.0 mg, 0.20 mmol), ^{1}H NMR (500 MHz, Acetone-d6) δ10.12 (s, 1H), 7.58 (s, 1H), 7.42 (dd, *J* = 12.7, 8.1 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.08 – 7.02 (m, 4H), 6.97 (d, *J* = 7.9 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.78 – 6.73 (m, 1H), 6.57 (d, *J* = 8.0 Hz, 1H), 4.93 (d, *J* = 8.4 Hz, 1H), 4.93 (d, *J* = 8.4 Hz, 1H), 2.41 (s, 3H), 2.35 (s, 3H), 1.52 (s, 3H); ^{13}C NMR (125 MHz, Acetone-d6) δ 200.7, 158.6, 143.4, 139.8, 139.1, 138.6, 137.7, 133.5, 129.8, 127.6, 126.2, 126.1, 124.8, 124.0, 122.2, 119.8, 119.6, 119.2, 112.7, 70.5, 46.6, 26.1, 21.5, 21.2; IR ν_{max}(film): 3511, 3455, 3107, 2924, 2856, 2366, 2336, 2269, 1818,1663, 1629, 1515, 1356, 1225, 1176, 1109, 1072, 855, 793, 717, 616, 490 cm^{-1}; HRMS (ESI) m/z calcd for $C_{26}H_{24}N_2O_3SNa$ $[M+Na]^+$ 467.1405, found 467.1397.

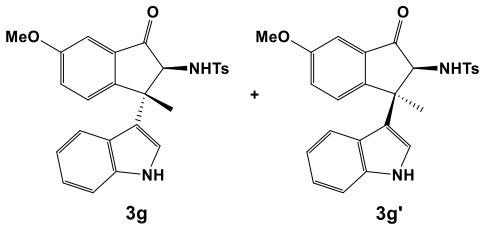
3e' (13.3 mg, 0.03 mmol): white solid, 15% yield from **1e** (74.2 mg, 0.20 mmol), ^{1}H NMR (500 MHz, Acetone-d6) δ10.12 (s, 1H), 7.58 (s, 1H), 7.42 (dd, *J* = 12.7, 8.1 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.08 – 7.02 (m, 4H), 6.97 (d, *J* = 7.9 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.78 – 6.73 (m, 1H), 6.57 (d, *J* = 8.0 Hz, 1H), 4.93 (d, *J* = 8.4 Hz, 1H), 4.93 (d, *J* = 8.4 Hz, 1H), 2.41 (s, 3H), 2.35 (s, 3H), 1.52 (s, 3H); ^{13}C NMR (125 MHz, Acetone-d6) δ 193.7, 144.2, 143.8, 138.8, 138.6, 138.3, 135.3, 131.4, 130.0, 127.9, 127.3, 126.6, 126.4, 125.4, 123.0, 122.4, 121.0, 120.4, 112.7, 63.6, 55.2, 26.9, 21.3, 20.9; IR ν_{max}(film): 3529, 3468, 3009, 2966, 2863, 2366, 2342, 1979, 1852, 1669, 1596, 1482, 1442, 1354, 1182, 1118, 812, 732, 678, 616, 537 cm^{-1}; HRMS (ESI) m/z calcd for $C_{26}H_{25}N_2O_3S$ $[M+H]^+$ 445.1586, found 445.1585.



3f **3f'**

3f (53.6 mg, 0.12 mmol): white solid, 60% yield from **1f** (71.0 mg, 0.20 mmol), ^{1}H NMR (500 MHz, Acetone-d6) δ 10.15 (s, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.31 (d, *J* = 7.9 Hz, 1H), 7.18 (d, *J* = 8.2 Hz, 2H), 7.05 (dd, *J* = 19.1, 7.8 Hz, 4H), 6.90 (d, *J* = 9.0 Hz, 2H), 6.76 (t, *J* = 7.5 Hz, 1H), 6.57 (d, *J* = 8.0 Hz, 1H), 4.92 (d, *J* = 8.4 Hz, 1H), 2.35 (s, 3H), 2.27 (s, 3H), 1.52 (s, 3H); ^{13}C NMR (100 MHz, Acetone-d6) δ 200.1, 161.5, 147.8, 143.3, 139.8, 138.5, 130.9, 130.2, 129.8, 127.5, 127.0, 126. 5, 126.0, 124.8, 124.1, 122.1, 119.7, 119.0, 112.7, 70.2, 46.7, 26.0, 22.1, 21.5; IR ν_{max}(film): 3511, 3413, 3256, 3034，2366, 2330, 1693, 1586, 1531, 1486, 1359, 1289, 1179, 1137, 1075, 975, 782, 686, 576 cm^{-1}; HRMS (ESI) m/z calcd for $C_{26}H_{24}N_2O_3SNa$ $[M+Na]^+$ 467.1405, found 467.1397.

3f' (13.4 mg, 0.03 mmol): white solid, 15% yield from **1f** (71.0 mg, 0.20 mmol), ^{1}H NMR (500 MHz, Acetone-d6) δ 10.13 (s, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.3 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 4H), 7.21 (d, *J* = 5.4 Hz, 2H), 7.11 (t, *J* = 7.6 Hz, 1H), 7.00 (dd, *J* = 17.1, 7.8 Hz, 3H), 6.28 (s, 1H), 4.51 (d, *J* = 19.1 Hz, 1H), 3.93 (d, *J* = 19.1 Hz, 1H), 2.45 (s, 3H), 2.35 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (125 MHz, Acetone-d6) δ 193.2, 146.9, 145.7, 143.9, 138.9, 138.4, 130.0, 129.4, 129.2, 128.0, 127.4, 127.1, 126.4, 125.5, 123.0, 122.4, 121.0, 120.4, 112.7, 63.6, 55.2, 26.9, 22.0, 21.3; IR ν_{max}(film): 3523, 3462, 3039, 2960, 2880, 2813, 2366, 2336, 1874, 1727, 1586, 1482, 1351, 1244, 1109, 800, 714, 537 cm^{-1}; HRMS (ESI) m/z calcd for $C_{26}H_{25}N_2O_3S$ $[M+H]^+$ 445.1586, found 445.1579.

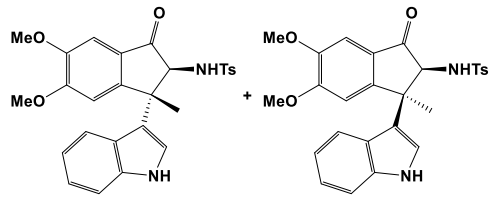


3g **3g'**

3g (43.5 mg, 0.09 mmol): white solid, 47% yield from **1g** (74.2 mg, 0.20 mmol), ^{1}H NMR (500 MHz, Acetone-d6) δ 10.14 (s, 1H), 7.73 (d, *J* = 8.5 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.11 – 6.96 (m, 5H), 6.83 – 6.69 (m, 2H), 6.59 (dd, *J* = 9.3, 5.1 Hz, 2H), 4.86 (d, *J* = 8.2 Hz, 1H), 3.70 (s, 3H), 2.35 (s, 3H), 1.55 (s, 3H); ^{13}C NMR (125 MHz, Acetone-d6) δ 198.6, 167.2, 164.2, 143.4, 139.7, 138.6, 129.9, 127. 7, 126.4, 126.2, 126.1, 124.9, 122.2, 119.8, 119.7, 119.1, 116.7, 112.7, 110.0, 70.2, 56.2, 47.0, 25.9, 21.5; IR ν_{max}(film): 3559, 3455, 3021, 2924, 2849, 2366, 2342, 1904, 1852, 1724, 1624, 1580, 1359, 1311, 1228, 1182, 1115, 1072, 824, 797, 720, 675, 485 cm^{-1}; HRMS (ESI) m/z calcd for $C_{26}H_{24}N_2O_4SNa$ $[M+Na]^+$ 483.1354, found 483.1352.

3g' (21.8 mg, 0.05 mmol): white solid, 24% yield from **1g** (74.2 mg, 0.20 mmol), ^{1}H NMR (500 MHz, Acetone-d6) δ 10.13 (s, 1H), 7.66 (d, *J* = 8.7 Hz, 1H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.93 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.83 (d, *J* = 2.3 Hz, 1H), 6.37 (s, 1H), 4.49 (d, *J* = 19.0 Hz, 1H), 3.92 (d, *J* = 19.0 Hz, 1H), 3.85 (s, 3H),

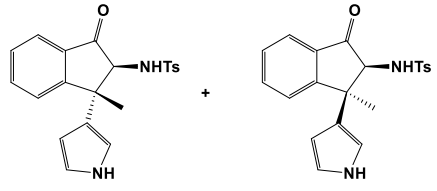
2.45 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (125 MHz, Acetone-d6) δ 192.1, 165.1, 149.4, 143.8, 138.9, 138.3, 130.0, 129.9, 128.0, 126.3, 125.4, 125.1, 122.9, 122.0, 121.0, 120.4, 113.9, 112.7, 112.1, 63.6, 56.2, 55.0, 26. 8, 21.3; IR ν_{max}(film): 3529, 3473, 3334, 3009, 2924, 2849, 2366, 2342, 1763, 1663, 1476, 1369, 1296, 1256, 1204, 1121, 1112, 852, 793, 714, 607, 534, 493 cm^{-1}; HRMS (ESI) m/z calcd for $C_{26}H_{25}N_2O_4S$ $[M+H]^+$ 461.1535, found 461.1520.



3h **3h'**

3h (37.0 mg, 0.08 mmol): white solid, 38% yield from **1h** (80.2 mg, 0.20 mmol), ^{1}H NMR (400 MHz, Acetone-d6) δ 10.13 (s, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.20 (t, *J* = 3.9 Hz, 3H), 7.06 (t, *J* = 7.5 Hz, 4H), 6.78 (dd, *J* = 15.5, 7.6 Hz, 2H), 6.67 – 6.52 (m, 2H), 4.79 (d, *J* = 7.9 Hz, 1H), 3.91 (s, 3H), 3.62 (s, 3H), 2.35 (s, 3H), 1.55 (s, 3H); ^{13}C NMR (125 MHz, Acetone-d6) δ 198.8, 157.8, 156.6, 151.4, 143.4, 139.7, 138.5, 129.9, 127.7, 126.2, 125.8, 124.8, 122.2, 119. 8, 119.6, 119.3, 112.7, 107.7, 105.0, 70.1, 70.0, 56.5, 46.7, 25.9, 21.5; IR ν_{max}(film): 3504, 3455, 3094, 2893, 2825, 2797, 2360, 2342, 1739, 1629, 1583, 1482, 1387, 1345, 1238, 1179, 1103, 996, 793, 730, 634, 488 cm^{-1}; HRMS (ESI) m/z calcd for $C_{27}H_{26}N_2O_5SNa$ $[M+Na]^+$ 513.1460, found 513.1450.

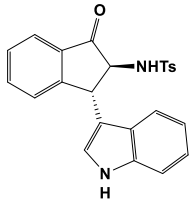
3h' (37.0 mg, 0.08 mmol): white solid, 38% yield from **1h** (80.2 mg, 0.20 mmol), ^{1}H NMR (400 MHz, Acetone-d6) δ 10.14 (s, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 7.2 Hz, 3H), 7.21 – 7.06 (m, 2H), 7.04 – 6.94 (m, 3H), 6.87 (s, 1H), 6.41 (s, 1H), 4.45 (d, *J* = 19.0 Hz, 1H), 3.94 (d, *J* = 19.0 Hz, 1H), 3.83 (s, 6H), 2.46 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, Acetone-d6) δ 192.1, 154.9, 149. 8, 143.6, 141.7, 138.8, 138.2, 130.0, 128.0, 126.3, 125.4, 124. 6, 122.8, 122.2, 121.0, 120.3, 112.7, 109.5, 109.0, 63.4, 56.4, 56.2, 54.9, 26.9, 21.3; IR ν_{max}(film): 3548, 3473, 3327, 3034, 2997, 2887, 2807, 2366, 2330, 1804, 1629, 1552, 1482, 1434, 1382, 1314, 1137, 1118, 1051, 975, 900, 845,785, 714, 600, 482 cm^{-1}; HRMS (ESI) m/z calcd for $C_{27}H_{26}N_2O_5SNa$ $[M+Na]^+$ 513.1460, found 513.1456.



3i **3i'**

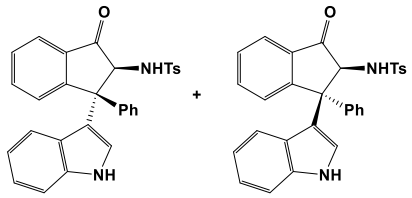
3i (33.1 mg, 0.09 mmol): white solid, 44% yield from **1a** (68.2 mg, 0.20 mmol), ^{1}H NMR (400 MHz, Acetone-d6) δ 9.82 (s, 1H), 7.46 (dd, *J* = 11.9 Hz, 7.8 Hz, 1H), 7.27-7.17 (m, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.74 (s, 1H), 6.02 (d, *J* = 2.5 Hz), 5.90 (s, 1H), 4.82 (d, *J* = 8.1 Hz), 2.39 (s, 3H), 1.45 (s, 3H); ^{13}C NMR (100 MHz, Acetone-d6) δ 200.6, 160.4, 143.4, 140.3, 136.6, 135.5, 133.1, 130.2, 129.2, 127.8, 126.4, 124.0, 118.9, 108.2, 107.6, 70.8, 47.2, 25.4, 21.5; IR ν_{max}(film): 3554, 3455, 3407, 2966, 2930, 2856, 1727, 1721, 1641, 1632, 1604, 1467, 1329, 1296, 1262, 1158, 1035, 1020, 803, 723, 668, 558 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{20}N_2O_3SNa$ $[M+Na]^+$ 403.1092, found 403.1086.

3i' (13.2 mg, 0.03 mmol): white solid, 17% yield from **1a** (68.2 mg, 0.20 mmol), ^{1}H NMR (400 MHz, Acetone-d6) δ 9.53 (s, 1H), 7.84 (d, *J* = 6.8 Hz, 2H), 7.76 (dd, *J* = 9.9, 4.2 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 7.1 Hz, 1H), 7.51 (dd, *J* = 10.6, 4.3 Hz, 1H), 7.36 (d, *J* = 7.3 Hz, 2H), 6.66 (s, 1H), 6.09 (d, *J* = 8.1 Hz, 1H), 5.86 (s, 1H), 5.10 (s, 1H), 4.36 – 4.25 (m, 1H), 2.42 (s, 3H), 1.95 (d, *J* = 1.4 Hz, 3H); ^{13}C NMR (100 MHz, Acetone-d6) δ 200.3, 157.3, 143.9, 139.7, 136.7, 134.5, 134.4, 130.2, 129.3, 128.3, 126.2, 123.8, 119.2, 108.4, 107.8, 71.1, 48.0, 23.6, 21.5; IR ν_{max}(film): 3572, 3413, 2972, 2930, 2868, 2532, 1727, 1700, 1641, 1632, 1608, 1562, 1556, 1497, 1467, 1427, 1403, 1382, 1332, 1289, 1262, 1210, 1186, 1161, 1090, 1032, 996, 882, 812,759, 730, 668, 558 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{20}N_2O_3SNa$ $[M+Na]^+$ 403.1092, found 403.1086.



3j

3j (49.0 mg, 0.12 mmol): white solid, 55% yield from **1j** (68.2 mg, 0.20 mmol), ^{1}H NMR (400 MHz, Acetone-d6) δ 10.25 (s, 1H), 8.05 (d, *J* = 7.2 Hz, 1H), 7.57 (ddd, *J* = 10.9, 8.5, 4.7 Hz, 2H), 7.46 (dd, *J* = 16.8, 8.3 Hz, 4H), 7.37 – 7.29 (m, 1H), 7.25 – 7.13 (m, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.75 (s, 1H), 6.41 (d, *J* = 1.4 Hz, 1H), 4.26 (dd, *J* = 19.1, 1.2 Hz, 1H), 3.90 (d, *J* = 19.1 Hz, 1H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, Acetone-d6) δ 192.3, 144.4, 141.6, 138.2, 137.1, 134.9, 130.9, 130.4, 128.8, 128.5, 128.0, 127.5, 126.8, 126.6, 126.5, 123.3, 120.5, 114.1, 112.6, 55.1, 50.6, 21.3; IR ν_{max}(film): 3627, 3541, 3052, 2887, 2679, 2366, 2340, 1871, 1770, 1648, 1568, 1509, 1275, 1186, 1145, 1085, 1041, 1027, 947, 882, 785, 668, 466, 433 cm^{-1}; HRMS (ESI) m/z calcd for $C_{24}H_{20}N_2O_3SNa$ $[M+Na]^+$ 439.1092, found 439.1089.

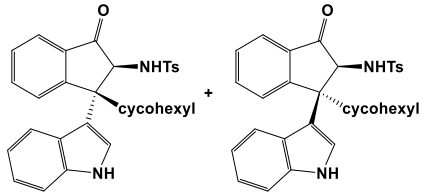


3k **3k'**

3k (70.2 mg, 0.14 mmol): yellow white solid, 71% yield from **1k** (80.6 mg, 0.20 mmol), ^{1}H NMR (500 MHz, Acetone-d6) δ 10.31 (s, 1H), 7.83 – 7.71 (m, 4H), 7.67 – 7.60 (m, 1H), 7.57 – 7.51 (m, 2H), 7.48 (d, *J* = 8.2 Hz, 1H), 7.25 (d, *J* = 8.1 Hz, 2H), 7.18 (dd, *J* = 8.2, 6.4 Hz, 1H), 7.14 – 7.06 (m, 3H), 6.83 – 6.78 (m, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 6.66 (d, *J* = 7.8 Hz, 2H), 6.30 (d, *J* = 9.6 Hz, 1H), 5.57 (d, *J* = 9.6 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, Acetone-d6) δ 200.0, 157.3, 143.6, 143.3, 140.6, 138.8, 136.6, 134.2, 130.5, 129.9, 129.5, 128.5, 128.1, 128.0, 128.0, 127.6, 125.8, 123.7, 122.3, 121.9, 119.7, 119.0, 112.8, 69. 9, 56.6, 21.5; IR ν_{max}(film): 3499, 3425, 3027, 2930, 2847, 2373, 2318, 1761, 1629, 1580, 1366, 1182, 1106, 787, 730, 530 cm^{-1}; HRMS (ESI) m/z calcd for $C_{30}H_{24}N_2O_3SNa$ $[M+Na]^+$ 515.1405, found 515.1397.

3k'(5.8 mg, 0.01 mmol): yellow white solid, 6% yield from **1k** (80.6 mg, 0.20 mmol), ^{1}H NMR (400 MHz, Acetone-d6) δ 10.35 (s, 1H), 7.75 (dd, *J* = 16.6, 6.9 Hz, 4H), 7.65 (dd, *J* = 10.8, 4.4 Hz, 1H), 7.54 (dd, *J* = 13.6, 7.5 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.22 – 7.15 (m, 1H), 7.10 (dt, *J* = 13.6, 7.9 Hz, 3H), 6.80 (t, *J* = 7.5 Hz, 1H), 6.71 (d, *J* = 8.1 Hz, 1H), 6.64 (d, *J* = 7.5 Hz, 2H), 6.34 (d, *J* = 9.6 Hz, 1H), 5.66 –

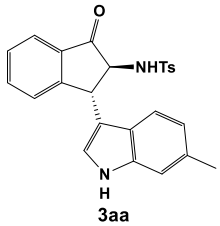
5.36 (m, 1H), 2.39 (s, 3H); ^{13}C NMR (125 MHz, Acetone-d6) δ 200.0, 157.4, 143.6, 143.3, 140.7, 138.9, 136.6, 134.3, 130.5, 129.9, 129.6, 128.6, 128.1, 128.1, 128.0, 127.6, 125.8, 123.8, 122.3, 122.0, 119.8, 119.0, 112.8, 69.9, 56.6, 21.5; IR ν_{max}(film): 3499, 3425, 3009, 2930, 2856, 2360, 2318, 1748, 1627, 1467, 1351, 1213, 1109, 806, 723, 652, 460 cm^{-1}; HRMS (ESI) m/z calcd for $C_{30}H_{24}N_2O_3SNa$ $[M+Na]^+$ 515.1405, found 515.1396.



3l **3l'**

3l (42.8 mg, 0.09 mmol): white solid, 43% yield from **1l** (81.8 mg, 0.20 mmol), ^{1}H NMR (400 MHz, Acetone-d6) δ 10.15 (s, 1H), 7.82 (d, *J* = 7.5 Hz, 1H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.27 (d, *J* = 6.9 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.04 (dd, *J* = 18.5, 11.0 Hz, 4H), 6.67 (t, *J* = 7.5 Hz, 1H), 6.26 (s, 1H), 4.53 (s, 1H), 2.58 (d, *J* = 14.7 Hz, 1H), 2.41 (d, *J* = 8.8 Hz, 1H), 2.33 (s, 3H), 1.70 (m, 1H), 1.56 (m, *2*H), 1.47 – 1.33 (m, 3H), 1.29 (s, 2H), 1.00 – 0.77 (m, 3H); ^{13}C NMR (100 MHz, Acetone-d6) δ 200.6, 154.5, 143.4, 139.1, 138.1, 135.5, 135.1, 129.8, 129.5, 129.2, 127.7, 126.5, 125.7, 123.5, 121.9, 120.1, 119.4, 112.6, 112.5, 71.8, 55.0, 42.3, 27.5, 27.3, 27.2, 21.5; IR ν_{max}(film): 3504, 3449, 3058, 2954, 2868, 2820, 2360, 2336, 1758, 1630, 1593, 1438, 1348, 1299, 1247, 1106, 1066, 1017, 861, 785, 708, 537, 445 cm^{-1}; HRMS (ESI) m/z calcd for $C_{30}H_{30}N_2O_3SNa$ $[M+Na]^+$ 521.1875, found 521.1869.

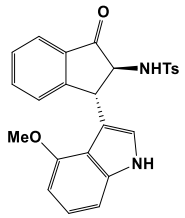
3l' (25.9 mg, 0.05 mmol): white solid, 26% yield from **1l** (81.8 mg, 0.20 mmol), ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.35 (s, 1H), 7.83 (d, *J* = 7.5 Hz, 1H), 7.67 – 7.58 (m, 1H), 7.54 (td, *J* = 7.5, 0.9 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.22 (s, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 7.0 Hz, 2H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.72 (t, *J* = 7.4 Hz, 1H), 6.15 (s, 1H), 5.32 (d, *J* = 5.8 Hz, 1H), 4.22 (d, *J* = 5.7 Hz, 1H), 2.63 (t, *J* = 11.0 Hz, 1H), 2.46 (s, 1H), 2.31 (s, 3H), 1.77 (d, *J* = 11.5 Hz, 1H), 1.65 (d, *J* = 9.3 Hz, 2H), 1.44 (ddt, *J* = 16.7, 13.1, 3.5 Hz, 3H), 1.29 (s, 1H), 1.04 – 0.89 (m, 2H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 200.6, 156.8, 154.5, 144.1, 137.4, 135.3, 134.7, 129.8, 129.2, 128.9, 127.8, 126.7, 126.2, 125.7,123.6, 122.3, 120.0, 119.7, 112.0, 71.1, 42.3, 29.7, 27.4, 27.1, 21.8, 18.3; IR ν_{max}(film): 3490, 3420, 3317, 3058, 2924, 2875, 2365, 2331, 1817, 1686, 1597, 1487, 1353, 1194, 1118, 1070, 1011, 857, 785, 732, 506 cm^{-1}; HRMS (ESI) m/z calcd for $C_{30}H_{30}N_2O_3SNa$ $[M+Na]^+$ 521.1875, found 521.1870.



3aa

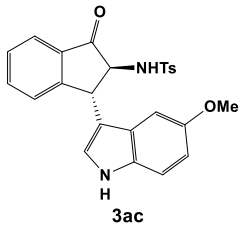
3aa (56.0 mg, 0.13 mmol): white solid, 65% yield from **1j** (65.4 mg, 0.20 mmol), ^{1}H NMR (500 MHz, Acetone-d6) δ 10.09 (s, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.56 (ddd, *J* = 14.4, 10.3, 4.6 Hz, 2H), 7.46 (dd, *J* = 15.2, 7.9 Hz, 3H), 7.38 – 7.29 (m, 1H), 7.23 (s, 1H), 7.02 (t, *J* = 8.6 Hz, 3H), 6.71 (s, 1H), 6.31 (s, 1H), 4.25 (dd, *J* = 19.0, 1.1 Hz, 1H), 3.88 (d, *J* = 19.0 Hz, 1H), 2.44 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (125 MHz, Acetone-d6) δ 192.3, 144.4, 141.8, 138.8, 137.3, 134.9, 132.9, 131.0, 130.4, 128.8, 128.5, 128.1, 126.8, 126.1, 125.6, 125.6,

122.4, 120.3, 114.2, 112.4, 55.3, 50.7, 21.9, 21.3; IR ν_{max}(film): 3469, 3414, 3041, 2924, 2885, 2379, 2310, 1713, 1578, 1178, 1099, 878, 799, 705, 530 cm^{-1}; HRMS (ESI) m/z calcd for $C_{25}H_{22}N_2O_3SNa$ $[M+Na]^+$ 453.1249, found 453.1242.



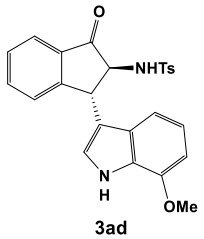
3ab

3ab (54.4 mg, 0.12 mmol): white solid, 61% yield from **1j** (65.4 mg, 0.20 mmol), ^{1}H NMR (400 MHz, Acetone-d6) δ 10.23 (s, 1H), 7.56 (dd, *J* = 10.5, 4.3 Hz, 2H), 7.41 (dd, *J* = 7.3, 5.2 Hz, 3H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.13 – 7.06 (m, 2H), 7.00 (t, *J* = 7.8 Hz, 3H), 6.60 (d, *J* = 7.7 Hz, 1H), 6.33 (s, 1H), 4.12 (d, *J* = 19.0 Hz, 1H), 4.02 (d, *J* = 19.1 Hz, 1H), 3.98 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, Acetone) δ 192.9, 155.6, 143.9, 143.1, 139.6, 137.5, 135.0, 131.1, 130.1, 128.4, 128.3, 126.6, 126.1, 125.9, 124.3, 117.5, 114.4, 105.6, 100.7, 55.3, 55.2, 50.6, 21.3; IR ν_{max}(film): 3469, 3331, 3068, 2924, 2855, 2365, 2337, 1614, 1476, 1329, 1160, 1004, 750, 667, 419 cm^{-1}; HRMS (ESI) m/z calcd for $C_{25}H_{22}N_2O_4SNa$ $[M+Na]^+$ 469.1198, found 469.1197.



3ac

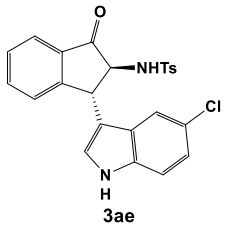
3ac (56.2 mg, 0.13 mmol): white solid, 63% yield from **1j** (68.2 mg, 0.20 mmol), ^{1}H NMR (400 MHz, Acetone-d6) δ 10.12 (s, 1H), 7.63 – 7.53 (m, 3H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.33 (dd, *J* = 8.2, 4.6 Hz, 2H), 7.04 (d, *J* = 8.2 Hz, 2H), 6.86 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.71 (s, 1H), 6.38 (s, 1H), 4.27 (d, *J* = 19.0 Hz, 1H), 3.91 (d, *J* = 19.0 Hz, 1H), 3.86 (s, 3H), 2.24 (s, 3H)；^{13}C NMR (100 MHz, Acetone-d6) δ 192.3, 155.3, 144.4, 141.7, 137.2, 134.9, 133.2, 130.9, 130.4, 128.8, 128.5, 128.0, 127.0, 126.8, 113.7, 113.5, 113.3, 113.2, 102.1, 55.9, 55.1, 50.6, 21.3; IR ν_{max}(film): 3488, 3356, 3072, 2927, 2858, 2360, 2311, 1763, 1619, 1580, 1386, 1306, 1230, 1189, 1106, 804, 690, 420 cm^{-1}; HRMS (ESI) m/z calcd for $C_{25}H_{22}N_2O_4SNa$ $[M+Na]^+$ 469.1198, found 469.1195.



3ad

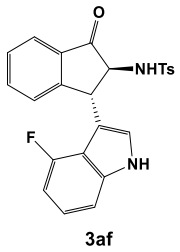
3ad (61.0 mg, 0.14 mmol): white solid, 68% yield from **1j** (65.4 mg, 0.20 mmol), ^{1}H NMR (400 MHz, Acetone-d6) δ 10.30 (s, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.56 (dd, *J* = 12.3, 4.8 Hz, 2H), 7.46 (dd, *J* = 9.8, 8.0 Hz, 3H), 7.39 – 7.28 (m, 1H), 7.09 (t, *J* = 7.9 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.76 (d, *J* = 7.7 Hz, 1H), 6.71 (s,

1H), 6.34 (d, *J* = 1.7 Hz, 1H), 4.26 (dd, *J* = 19.1, 1.1 Hz, 1H), 3.93 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, Acetone-d6) δ 192.3, 147.4, 144.3, 141.6, 137.1, 134.9, 130.9, 130.4, 129.0, 128.7, 128.5, 128.3, 128.0, 126.8, 126.0, 121.2, 114.7, 113.3, 103.4, 55.7, 55.2, 50.6, 21.3; IR ν_{max}(film): 3475, 3352, 3027, 2924, 2848, 2365, 2282, 1624, 1582, 1465, 1382, 1357, 1182, 1103, 803, 754, 672, 423 cm^{-1}; HRMS (ESI) m/z calcd for $C_{25}H_{22}N_2O_4SNa$ $[M+Na]^+$ 469.1198, found 469.1191.



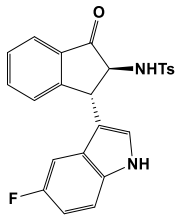
3ae

3ae (50.4 mg, 0.11 mmol): white solid, 56% yield from **1j** (81.8 mg, 0.20 mmol), ^{1}H NMR (400 MHz, Acetone-d6) δ 10.50 (s, 1H), 8.03 (d, *J* = 2.1 Hz, 1H), 7.57 (td, *J* = 7.4, 6.0 Hz, 2H), 7.52 – 7.43 (m, 4H), 7.37 – 7.31 (mv, 1H), 7.20 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.72 (s, 1H), 6.53 – 6.47 (m, 1H), 4.29 (dd, *J* = 19.1, 1.2 Hz, 1H), 3.87 (t, *J* = 31.0 Hz, 1H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, Acetone-d6) δ 192.1, 144.5, 143.1, 141.3, 137.0, 136.7, 135.0, 130.9, 130.4, 128.8, 128.6, 128.3, 128.1, 126.8, 125.9, 123.4, 119.9, 114.1, 114.0, 54.8, 50.6, 21.3; IR ν_{max}(film): 3490, 3448, 3344, 3027, 2924, 2855, 2372, 2310, 1689, 1614, 1480, 1377, 1314, 1197, 1105, 1057, 867, 767, 691, 561, 499 cm^{-1}; HRMS (ESI) m/z calcd for $C_{24}H_{19}ClN_2O_3SNa$ $[M+Na]^+$ 473.0703, found 473.0697.



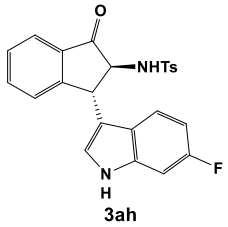
3af

3af (44.3 mg, 0.10 mmol)**:** light yellow solid, 51% yield from **1j** (65.4 mg, 0.20 mmol), ^{1}H NMR (500 MHz, Acetone-d6) δ 10.53 (s, 1H), 7.60 (td, *J* = 7.5, 1.3 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 2H), 7.36 (dd, *J* = 11.0, 4.1 Hz, 1H), 7.26 (d, *J* = 8.2 Hz, 1H), 7.16 (td, *J* = 8.0, 4.9 Hz, 1H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.89 (s, 1H), 6.84 (dd, *J* = 10.9, 7.9 Hz, 1H), 6.46 (s, 1H), 4.18 (d, *J* = 19.1, 1H), 3.97 (d, *J* = 19.1 Hz, 1H), 2.26 (s, 3H); ^{13}C NMR (125 MHz, Acetone-d6) δ 192.6, 157.8 (d, *J* = 247.7 Hz), 144.2, 142.2, 141.1 (d, *J* = 11.3 Hz), 137.2, 135.1, 131.1, 130.2, 128.6 (d, *J* = 7.5 Hz) 128.4, 127.8, 127.7, 126.8, 124.0 (d, *J* = 7.5 Hz), 116.0 (d, *J* = 20.7 Hz), 113.1, 109.0 (d, *J* = 3.8 Hz), 105.8 (d, *J* = 19.3 Hz), 55.3, 50.7, 21.3; IR ν_{max}(film): 3475, 3344, 3055, 2945, 2875, 2365, 2337, 1669, 1610, 1480, 1349, 1084, 781, 513 cm^{-1}; HRMS (ESI) m/z calcd for $C_{24}H_{20}FN_2O_3S$ $[M+H]^+$ 435.1179, found 435.1189.



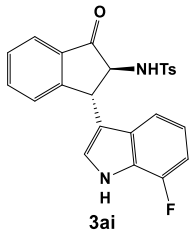
3ag

3ag (49.5 mg, 0.11 mmol): white solid, 57% yield from **1j** (65.4 mg, 0.20 mmol), ^{1}H NMR (400 MHz, Acetone-d6) δ 10.38 (s, 1H), 7.72 (dd, *J* = 9.9, 2.5 Hz, 1H), 7.56 (dd, *J* = 12.2, 4.6 Hz, 2H), 7.52 – 7.42 (m, 4H), 7.35 (d, *J* = 7.7 Hz, 1H), 7.13 – 6.93 (m, 3H), 6.71 (s, 1H), 6.52 (s, 1H), 4.29 (d, *J* = 19.1, 1H), 3.91 (d, *J* = 19.1 Hz, 1H), 2.24 (s, 3H)；^{13}C NMR (100 MHz, Acetone-d6) δ 192.1, 158.7 (d, *J* = 233.1 Hz), 144.5, 141.3, 137.0, 134.9 (d, *J* = 13.5 Hz), 130.9, 130.4, 128.8, 128.6, 128.5, 128.4, 128.0, 126.8, 114.2, 113.7 (d, *J* = 9.7 Hz), 111.4 (d, *J* = 26.6 Hz), 105.3, 105.1, 54.9, 50.5, 21.3; IR ν_{max}(film): 3490, 3349, 3007, 2924, 2855, 2379, 2317, 1755, 1631, 1377, 1304, 1232, 1225, 1149, 1094, 840, 757, 641, 550 cm^{-1}; HRMS (ESI) m/z calcd for $C_{24}H_{20}FN_2O_3S$ $[M+H]^+$ 435.1179, found 435.1171.



3ah

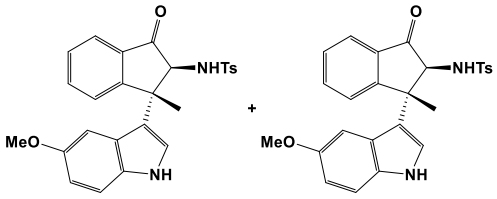
3ah (60.0 mg, 0.14 mmol): white solid, 69% yield from **1j** (65.4 mg, 0.20 mmol), ^{1}H NMR (500 MHz, Acetone-d6) δ 10.34 (s, 1H), 8.02 (dd, *J* = 8.7, 5.5 Hz, 1H), 7.62 – 7.51 (m, 2H), 7.47 (t, *J* = 8.9 Hz, 3H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.18 (dd, *J* = 9.9, 1.9 Hz, 1H), 7.09 – 6.96 (m, 3H), 6.73 (s, 1H), 6.42 (s, 1H), 4.27 (d, *J* = 19.1 Hz, 1H), 3.89 (d, *J* = 19.1 Hz, 1H), 2.24 (s, 3H); ^{13}C NMR (125 MHz, Acetone-d6) δ 192.1, 161.1 (d, *J* = 236.3 Hz), 144.5, 141.5, 138.4 (d, *J* = 12.7 Hz), 137.2, 134.9, 131.0, 130.4, 128.7 (d, *J* = 24.6 Hz), 128.1, 127.4 (d, *J* = 3.1 Hz), 127.2, 126.9, 124.3, 121.6 (d, *J* = 10.2 Hz), 114.5, 109.1 (d, *J* = 24.6 Hz), 98.6 (d, *J* = 26.3 Hz), 55.0, 50.7, 21.3; IR ν_{max}(film): 3621, 3490, 3020, 2945, 2869, 2352, 2324, 1741, 1649, 1259, 1169, 1015, 802, 667, 447 cm^{-1}; IR ν_{max}(film): 3497, 3442, 3055, 2986, 2945, 2882, 2814, 2372, 2331, 1707, 1610, 1524, 1487, 1380, 1318, 1314, 1187, 1112, 1106, 870, 778, 684, 578, 478 cm^{-1}; HRMS (ESI) m/z calcd for $C_{24}H_{20}FN_2O_3S$ $[M+H]^+$ 435.1179, found 435.1176.



3ai

3ai (56.0 mg, 0.13 mmol): white solid, 65% yield from **1j** (73.4 mg, 0.20 mmol), ^{1}H NMR (500 MHz, Acetone-d6) δ 10.70 (s, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.58 (ddd, *J* = 21.2, 10.7, 4.5 Hz, 3H), 7.51 – 7.46 (m, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.15 (td, *J* = 7.9, 4.7 Hz, 3H), 7.06 – 6.96 (m, 1H), 6.75 (s,

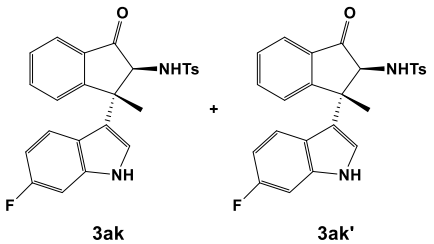
1H), 6.51 (s, 1H), 4.28 (d, *J* = 19.0, 1H), 3.92 (d, *J* = 19.1 Hz, 1H), 2.24 (s, 3H); ^{13}C NMR (125 MHz, Acetone-d6) δ 192.1, 150.6 (d, *J* = 243.2 Hz), 144.5, 141.4, 137.1, 135.0, 131.4 (d, *J* = 5.3 Hz), 131.0, 130.4, 128.7 (d, *J* = 16.1 Hz), 128.1, 127.7, 127.5, 126.9, 126.3 (d, *J* = 13.6 Hz), 121.1 (d, *J* = 6.1 Hz), 116.7 (d, *J* = 3.5 Hz), 115.4 (d, *J* = 2.3 Hz), 108.0 (d, *J* = 16.1 Hz), 55.0, 50.7, 21.3; IR ν_{max}(film): 3483, 3331, 3186, 3035, 2945, 2875, 2379, 2317, 1790, 1669, 1607, 1480, 1377,1311, 1177, 1112, 1063, 939, 850, 794, 681, 581, 485 cm^{-1}; HRMS (ESI) m/z calcd for $C_{24}H_{19}FN_2O_3SNa$ $[M+Na]^+$ 457.0998, found 457.0989.



3aj **3aj'**

3aj (46.2 mg, 0.10 mmol): white solid, 50% yield from **1a** (68.2 mg, 0.20 mmol), ^{1}H NMR (400 MHz, Acetone-d6) δ 10.02 (s, 1H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.61 (td, *J* = 7.6, 1.2 Hz, 1H), 7.50 (td, *J* = 7.5, 0.8 Hz, 1H), 7.34 (d, *J* = 8.8 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 7.7 Hz, 1H), 7.07 (d, *J* = 8.1 Hz, 2H), 7.03 – 6.95 (m, 2H), 6.74 (dd, *J* = 8.8, 2.4 Hz, 1H), 5.98 (d, *J* = 2.3 Hz, 1H), 4.92 (d, *J* = 8.3 Hz, 1H), 3.44 (s, 3H), 2.36 (s, 3H), 1.54 (s, 3H); ^{13}C NMR (100 MHz, Acetone-d6) δ 200.7, 160.8, 154.4, 143.3, 139.8, 136.5, 133.6, 133.4, 129.8, 129.0, 127.5, 126.5, 126.3, 125.5, 124.2, 118.6, 113.2, 111.8, 102.1, 70.0, 55.6, 46.8, 25.9, 21.5; IR ν_{max}(film): 3517, 3393, 3055, 2930, 2855, 2369, 2310, 1721, 1531, 1331, 1259, 1156, 977, 874, 754, 550 cm^{-1}; HRMS (ESI) m/z calcd for $C_{26}H_{24}N_2O_4SNa$ $[M+Na]^+$ 483.1354, found 483.1352.

3aj' (15.4 mg, 0.03 mmol): white solid, 17% yield from **1a** (68.2 mg, 0.20 mmol), ^{1}H NMR (400 MHz, Acetone-d6) δ 10.04 (s, 1H), 7.83 – 7.69 (m, 1H), 7.54 (td, *J* = 7.8, 1.4 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.3 Hz, 3H), 7.20 (d, *J* = 8.8 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.83 (s, 1H), 6.72 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.42 (s, 1H), 4.55 (d, *J* = 18.9 Hz, 1H), 4.13 (d, *J* = 18.9 Hz, 1H), 3.65 (s, 3H), 2.45 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, Acetone-d6) δ 193.5, 154.8, 147.8, 143.7, 139.0, 134.8, 133.2, 131.4, 130.0, 128.5, 127.7, 127.1, 126.9, 126.8, 126.2, 121.3, 113.3, 113.0, 102.6, 63.7, 55.8, 54.7, 26.3, 21.3; IR ν_{max}(film): 3483, 3472, 3048, 2925, 2855, 2379, 2331, 1673, 1618, 1317, 1222, 750, 664, 416 cm^{-1}; HRMS (ESI) m/z calcd for $C_{26}H_{24}N_2O_4SNa$ $[M+Na]^+$ 483.1354, found 483.1347.

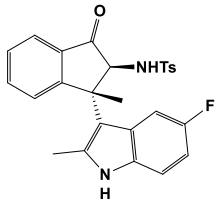


3ak **3ak'**

3ak (58.4 mg, 0.13 mmol): white solid, 65% yield from **1a** (68.2 mg, 0.20 mmol), ^{1}H NMR (500 MHz, Acetone-d6) δ 10.23 (s, 1H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.60 (td, *J* = 7.5, 1.2 Hz, 1H), 7.50 (td, *J* = 7.6, 0.9 Hz, 1H), 7.24 (dd, *J* = 8.2, 1.6 Hz, 2H), 7.17 (dd, *J* = 10.0, 2.2 Hz, 1H), 7.11 – 7.05 (m, 4H), 7.02 (d, *J* = 8.5 Hz, 1H), 6.62 – 6.56 (m, 1H), 6.53 (dd, *J* = 8.7, 5.4 Hz, 1H), 4.90 (d, *J* = 8.5 Hz, 1H), 2.37 (s, 3H), 1.53 (s, 3H); ^{13}C NMR (100 MHz, Acetone-d6) δ 200.5, 160.7, 160.4 (d, *J* = 233.0 Hz), 143.4, 139.8, 138.5 (d, *J* = 12.5 Hz), 136.6, 133.3, 129.8, 129.1, 127.5, 126.3, 125.6 (d, *J* = 3.2 Hz), 124.3, 122.7, 120.7 (d, *J* = 10.2 Hz), 119.1,

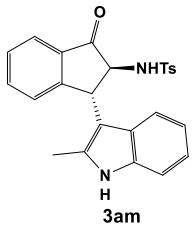
107.9 (d, *J* = 24.5 Hz), 98.6 (d, *J* = 25.7 Hz), 70.3, 46.7, 26.1, 21.5; IR ν_{max}(film): 3469, 3400, 3331, 3027, 2952, 2882, 2365, 2344, 1796, 1590, 1362, 1301, 1160, 1059, 984, 846, 750, 605, 495 cm^{-1}; HRMS (ESI) m/z calcd for $C_{25}H_{21}FN_2O_3SNa$ $[M+Na]^+$ 471.1155, found 471.1147.

3ak'(9.7 mg, 0.02 mmol): white solid, 11% yield from **1a** (68.2 mg, 0.20 mmol), ^{1}H NMR (400 MHz, Acetone-d6) δ 10.22 (s, 1H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.78 – 7.68 (m, 2H), 7.62 – 7.51 (m, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.05 (dd, *J* = 9.9, 2.3 Hz, 1H), 6.72 (dd, *J* = 8.8, 5.4 Hz, 1H), 6.64 – 6.50 (m, 2H), 6.30 (d, *J* = 8.8 Hz, 1H), 4.53 – 4.40 (m, 1H), 2.42 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, Acetone-d6) δ 201.2, 160.1 (d, *J* = 238.2 Hz), 143.7, 140.3, 138.3, 136.8, 134.8, 130.1, 129.4, 128.1, 126.7, 125.9, 124.0, 123.7, 122.4 (d, *J* = 10.0 Hz), 119.2, 108.1, 107.9, 98.2 (d, *J* = 25.6 Hz), 71.0, 47.9, 26.0, 21.5; IR ν_{max}(film): 3511, 3434, 3310, 3027, 2958, 2814, 2386, 2310, 1786, 1583, 1370, 1294, 1201, 1122, 1059, 836, 546 cm^{-1}; HRMS (ESI) m/z calcd for $C_{25}H_{21}FN_2O_3SNa$ $[M+Na]^+$ 471.1155, found 471.1147.



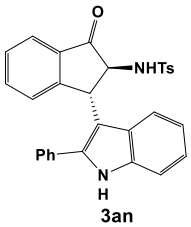
3al

3al (63.8 mg, 0.14 mmol): white solid, 69% yield from **1a** (81.8 mg, 0.20 mmol), ^{1}H NMR (400 MHz, Acetone-d6) δ 10.07 (s, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.62 (td, *J* = 7.6, 1.1 Hz, 1H), 7.51 (dd, *J* = 10.9, 4.1 Hz, 1H), 7.29 (dd, *J* = 8.7, 4.8 Hz, 1H), 7.19 (t, *J* = 7.2 Hz, 3H), 7.01 (d, *J* = 8.1 Hz, 3H), 6.76 (td, *J* = 9.1, 2.4 Hz, 1H), 6.10 (d, *J* = 9.2 Hz, 1H), 4.87 (d, *J* = 8.0 Hz, 1H), 2.33 (s, 3H), 2.27 (s, 3H), 1.67 (s, 3H); ^{13}C NMR (125 MHz, Acetone-d6) δ 200.4, 162.1, 158.0 (d, *J* = 231.1 Hz), 143.5, 139.7, 136.9, 136.7, 133.2, 132.9, 129.9, 129.1, 128.8, 127.4, 126.6, 124.4, 113.2, 112.3 (d, *J* = 10.0 Hz), 108.9 (d, *J* = 26.1 Hz), 104.6 (d, *J* = 24.5 Hz), 71.4, 48.7, 27.5, 21.4, 14.9; IR ν_{max}(film): 3480, 3413, 3315, 3045, 2960, 2880, 2366, 2342, 1813, 1593, 1486, 1345, 1200, 1127, 1069, 1008, 895, 840, 732, 678, 490 cm^{-1}; HRMS (ESI) m/z calcd for $C_{26}H_{23}FN_2O_3SNa$ $[M+Na]^+$ 485.1311, found 485.1306.



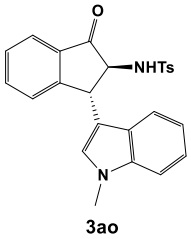
3am

3am (66.0 mg, 0.15 mmol)**:** white solid, 77% yield from **1j** (65.4 mg, 0.20 mmol), ^{1}H NMR (400 MHz, Acetone-d6) δ 9.95 (s, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.60 (td, *J* = 7.5, 1.1 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.25 (d, *J* = 8.2 Hz, 2H), 7.11 – 6.90 (m, 5H), 6.74 (t, *J* = 6.9 Hz, 1H), 6.60 (s, 1H), 4.82 – 4.48 (m, 2H), 2.33 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, Acetone-d6) δ 201.1, 154.5, 154.5, 143.1, 140.2, 140.2, 137.1, 136.4, 134.9, 129.7, 129.0, 127.0, 124.0, 121.3, 119.5, 118.6, 111.6, 111.6, 109.1, 66.6, 44.4, 21.5, 11.5; IR ν_{max}(film): 3497, 3442, 3035, 2930, 2865, 1762, 1625, 1276, 1184, 1057, 840, 798, 730, 530 cm^{-1}; HRMS (ESI) m/z calcd for $C_{25}H_{23}FN_2O_3S$ $[M+H]^+$ 431.1429, found 431.1421.



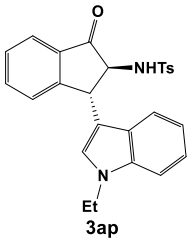
3an

3an (87.6 mg, 0.18 mmol): white solid, 89% yield from **1j** (65.4 mg, 0.20 mmol), ^{1}H NMR (500 MHz, Acetone-d6) δ 10.33 (d, *J* = 88.7 Hz, 1H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 7.0 Hz, 3H), 7.51 (t, *J* = 8.3 Hz, 2H), 7.47 – 7.35 (m, 3H), 7.24 (dd, *J* = 8.3, 1.9 Hz, 2H), 7.13 (dd, *J* = 17.5, 9.4 Hz, 3H), 6.94 (d, *J* = 7.5 Hz, 2H), 6.87 (m, 2H), 4.99 (s, 1H), 4.80 (d, *J* = 6.5 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (125 MHz, Acetone-d6) δ 201.0, 154.6, 143.1, 140.2, 140.2, 138.0, 136.5, 134.8, 133.6, 129.8, 129.7, 129.5, 129.1, 128.9, 127.2, 126.9, 124.1, 122.7, 120.2, 119.7, 112.6, 112.5, 110.0, 66.6, 44.7, 21.5； IR ν_{max}(film): 3466, 3354, 3062, 2957, 2857, 2360, 2310, 1719, 1620, 1479, 1358, 1180, 1056, 844, 785, 710, 682, 601, 477 cm^{-1}; HRMS (ESI) m/z calcd for $C_{30}H_{24}N_2O_3SNa$ $[M+Na]^+$ 515.1405, found 515.1398.



3ao

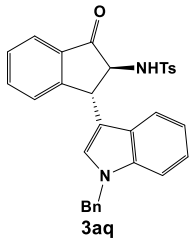
3ao (64.5 mg, 0.15 mmol): white solid, 75% yield from **1j** (65.4 mg, 0.20 mmol), ^{1}H NMR (400 MHz, Acetone-d6) δ 7.75 (d, *J* = 7.6 Hz, 1H), 7.58 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.37 (dd, *J* = 9.4, 8.6 Hz, 3H), 7.19 – 7.09 (m, 3H), 7.03 – 6.93 (m, 4H), 6.91 – 6.86 (m, 1H), 4.68 – 4.46 (m, 2H), 3.76 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, Acetone-d6) δ 201.0, 154.8, 143.0, 140.4, 138.5, 136.4, 134.6, 129.6, 129.1, 129.1, 127.4, 127.3, 127.0, 124.0, 122.3, 119.7, 119.6, 113.2, 110.5, 67.0, 44.9, 32.9, 21.5; IR ν_{max}(film): 3523, 3449, 3015, 2983, 2823, 2366, 2342, 1763, 1641, 1445, 1369, 1173, 1118, 1069, 840, 772, 714, 607, 488 cm^{-1}; HRMS (ESI) m/z calcd for $C_{25}H_{23}FN_2O_3S$ $[M+H]^+$ 431.1429, found 431.1421..



3ap

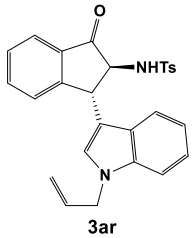
3ap (60.4 mg, 0.14 mmol): white solid, 68% yield from **1j** (65.4 mg, 0.20 mmol), ^{1}H NMR (400 MHz, Acetone-d6) δ 7.74 (d, *J* = 7.6 Hz, 1H), 7.60 (td, *J* = 7.5, 1.2 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.44 (d, *J* = 8.3 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.19 – 7.11 (m, 2H), 7.08 (s, 2H), 7.03 (d, *J* = 7.9 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.91 – 6.84 (m, 1H), 4.61 (d, *J* = 5.3 Hz, 2H), 4.19 (dt, *J* = 25.7, 7.0 Hz, 2H), 2.29 (s, 3H), 1.43 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (125 MHz, Acetone-d6) δ 201.1, 155.0, 143.1, 140.5, 137.7, 136.4, 134.7, 129.8, 129.1, 127.8, 127.4, 127.4, 127.1, 124.0, 122.3, 119.8, 119.7, 113.7, 110.6, 67.1, 45.0, 41.5, 21.5, 15.8; IR ν_{max}(film):

3523, 3449, 3015, 2983, 2823, 2366, 2342, 1763, 1641, 1445, 1369, 1173, 1118, 1069, 840, 772, 714, 607, 488 cm^{-1}; HRMS (ESI) m/z calcd for $C_{26}H_{24}N_2O_3SNa$ $[M+Na]^+$ 467.1405, found 467.1403.



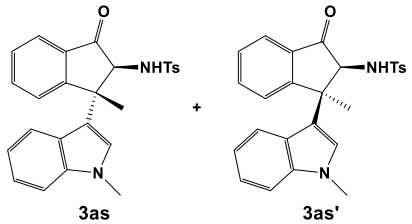
3aq

3aq (65.8 mg, 0.13 mmol): white solid, 65% yield from **1j** (65.4 mg, 0.20 mmol), ^{1}H NMR (400 MHz, Acetone-d6) δ 7.75 (d, *J* = 7.6 Hz, 1H), 7.61 (td, *J* = 7.5, 1.2 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.44 – 7.38 (m, 3H), 7.36 – 7.30 (m, 2H), 7.29 – 7.24 (m, 3H), 7.21 – 7.15 (m, 2H), 7.14 – 7.06 (m, 2H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.88 (ddd, *J* = 7.9, 7.1, 0.9 Hz, 1H), 5.40 (q, *J* = 16.0 Hz, 2H), 4.73 – 4.54 (m, 2H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, Acetone-d6) δ 201.0, 154.9, 143.2, 140.4, 139.2, 138.0, 136.5, 134.6, 129.8, 129.5, 129.1, 128.8, 128.3, 128.0, 127.9, 127.4, 127.1, 124.0, 122.5, 119.8, 114.2, 111.1, 67.0, 50.5, 45.0, 21.5; IR ν_{max}(film): 3486, 3431, 3034, 2924, 2856, 2366, 2336, 1761, 1638, 1586, 1486, 1302, 1186, 1124, 1086, 837, 775, 717, 485 cm^{-1}; HRMS (ESI) m/z calcd for $C_{31}H_{26}N_2O_3SNa$ $[M+Na]^+$ 529.1562, found 529.1552.



3ar

3ar (62.9 mg, 0.14 mmol): white solid, 69% yield from **1j** (81.8 mg, 0.20 mmol), ^{1}H NMR (400 MHz, Acetone-d6) δ 7.75 (d, *J* = 7.3 Hz, 1H), 7.60 (d, *J* = 6.4 Hz, 1H), 7.50 (d, *J* = 7.3 Hz, 1H), 7.41 (d, *J* = 7.9 Hz, 3H), 7.13 (dd, *J* = 16.5, 7.9 Hz, 3H), 7.07 – 6.96 (m, 4H), 6.93 – 6.83 (m, 1H), 6.15 – 5.94 (m, 1H), 5.25 – 5.04 (m, 2H), 4.79 (dd, *J* = 15.7, 4.1 Hz, 2H), 4.62 (s, 2H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, Acetone-d6) δ 201.0, 154.9, 143.1, 140.5, 137.9, 136.4, 135.1, 134.6, 129.8, 129.1, 128.2, 127.7, 127.4, 127.1, 124.0, 122.4, 119.9, 119.7, 117.3, 113.9, 111.0, 67.0, 49.2, 44.9, 21.5; IR ν_{max}(film): 3517, 3455, 3290, 3015, 2930, 2856, 2366, 2318, 1727, 1635, 1519, 1461, 1359, 1231, 1176, 1130, 1051, 949, 852, 775, 717, 693, 610, 482 cm^{-1}; HRMS (ESI) m/z calcd for $C_{27}H_{25}N_2O_3S$ $[M+H]^+$ 457.1586, found 457.1578.



3as **3as'**

3as (63.0 mg, 0.14 mmol): white solid, 71% yield from **1a** (68.2 mg, 0.20 mmol), ^{1}H NMR (500 MHz, Acetone-d6) δ 7.79 (d, *J* = 7.6 Hz, 1H), 7.64 – 7.54 (m, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.40 (d, *J* = 8.3 Hz, 1H), 7.20 – 7.16 (m, 2H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.06 (dd, *J* = 7.4, 4.7 Hz, 4H), 6.87 (d, *J* = 3.3 Hz, 1H), 6.79 (t, *J* = 7.5 Hz, 1H), 6.57 (d, *J* = 8.0 Hz, 1H), 4.98 (d, *J* = 8.5 Hz, 1H), 3.79 (s, 1H), 2.40 (s, 3H), 1.51 (s, 3H); ^{13}C NMR

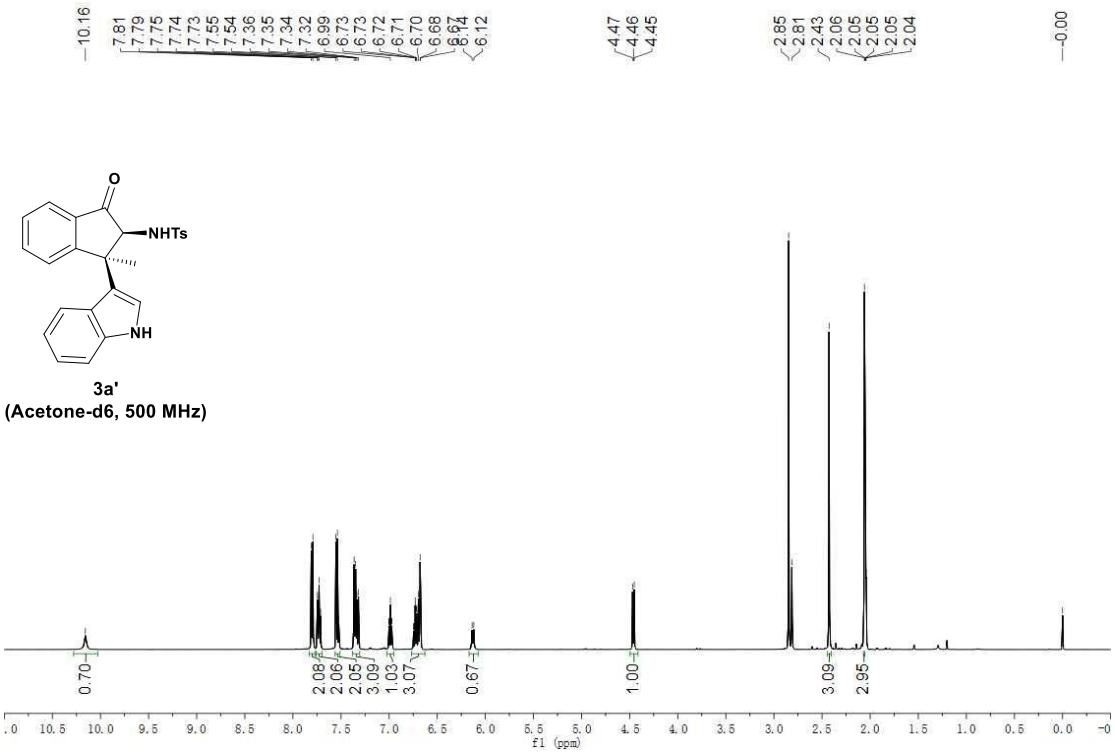
(125 MHz, Acetone-d6) δ 200.6, 160.9, 143.2, 140.1, 138.9, 136.5, 133.3, 129.7, 129.1, 129.0, 127.4, 126.8, 126.3, 124.2, 122.1, 119.9, 119.6, 117.9, 110.6, 70.4, 46.7, 33.1, 26.1, 21.6; IR ν_{max}(film): 3480, 3431, 3064, 2948, 2880, 2820, 2360, 2336, 1831, 1663, 1613, 1445, 1299, 1207, 1186, 1139, 1069, 931, 840, 775, 720, 493 cm^{-1}; HRMS (ESI) m/z calcd for $C_{26}H_{25}N_2O_3S$ $[M+H]^+$ 445.1586, found 445.1582.

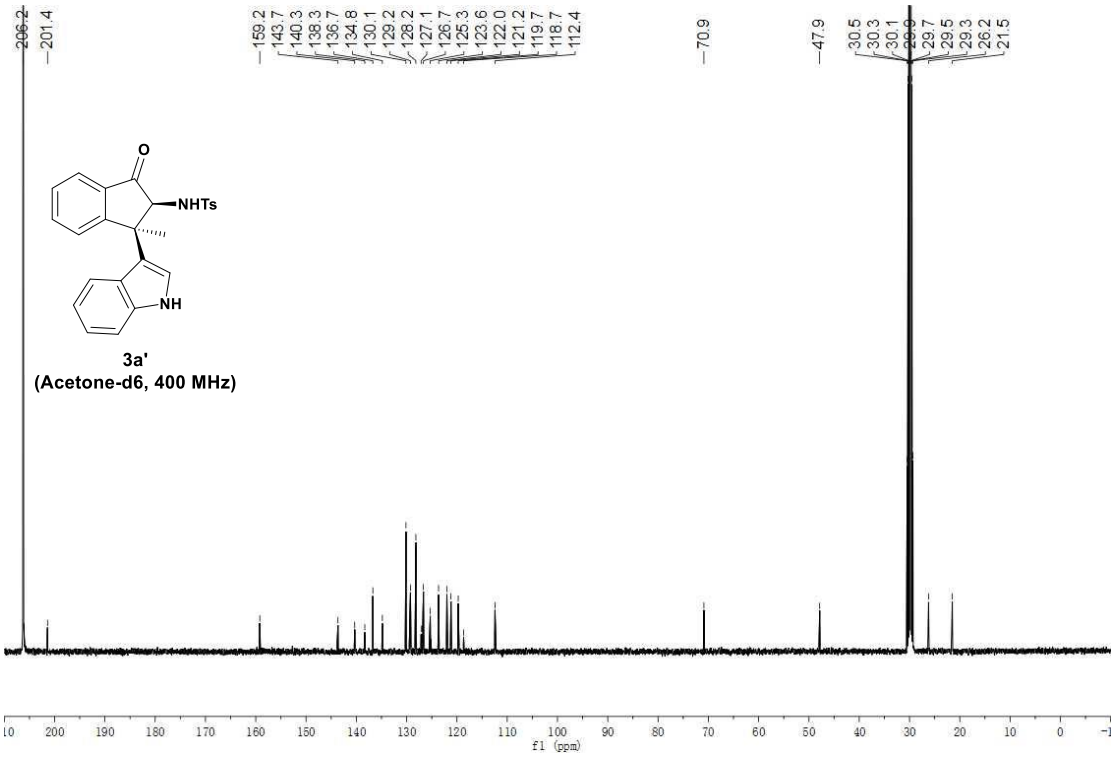
3as' (21.3 mg, 0.05 mmol): white solid, 24% yield from **1a** (68.2 mg, 0.20 mmol), ^{1}H NMR (400 MHz, Acetone-d6) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.73 (ddd, *J* = 8.8, 5.0, 1.2 Hz, 2H), 7.58 – 7.51 (m, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 1H), 7.08 – 7.02 (m, 1H), 6.77 – 6.70 (m, 1H), 6.63 (d, *J* = 8.2 Hz, 1H), 6.56 (s, 1H), 6.15 (d, *J* = 8.7 Hz, 1H), 4.47 (d, *J* = 8.9 Hz, 1H), 3.71 (s, 3H), 2.44 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (125 MHz, Acetone-d6) δ 201.4, 159.2, 143.7, 140.5, 138.8, 136.8, 134.9, 130.2, 129.6, 129.3, 128.2, 127.6, 126.7, 123.7, 122.0, 121.3, 119.8, 117.6, 110.4, 70.9, 47.9, 32.9, 26.4, 21.5; IR ν_{max}(film): 3541, 3425, 3241, 3045, 2954, 2887, 2366, 2342, 1761, 1687, 1583, 1482, 1356, 1262, 1192, 1121, 1072, 980, 858, 790, 683, 482 cm^{-1}; HRMS (ESI) m/z calcd for $C_{26}H_{23}FN_2O_3SNa$ $[M+Na]^+$ 485.1311, found 485.1306, HRMS (ESI) m/z calcd for $C_{26}H_{24}N_2O_3SNa$ $[M+Na]^+$ 467.1405, found 467.1382.

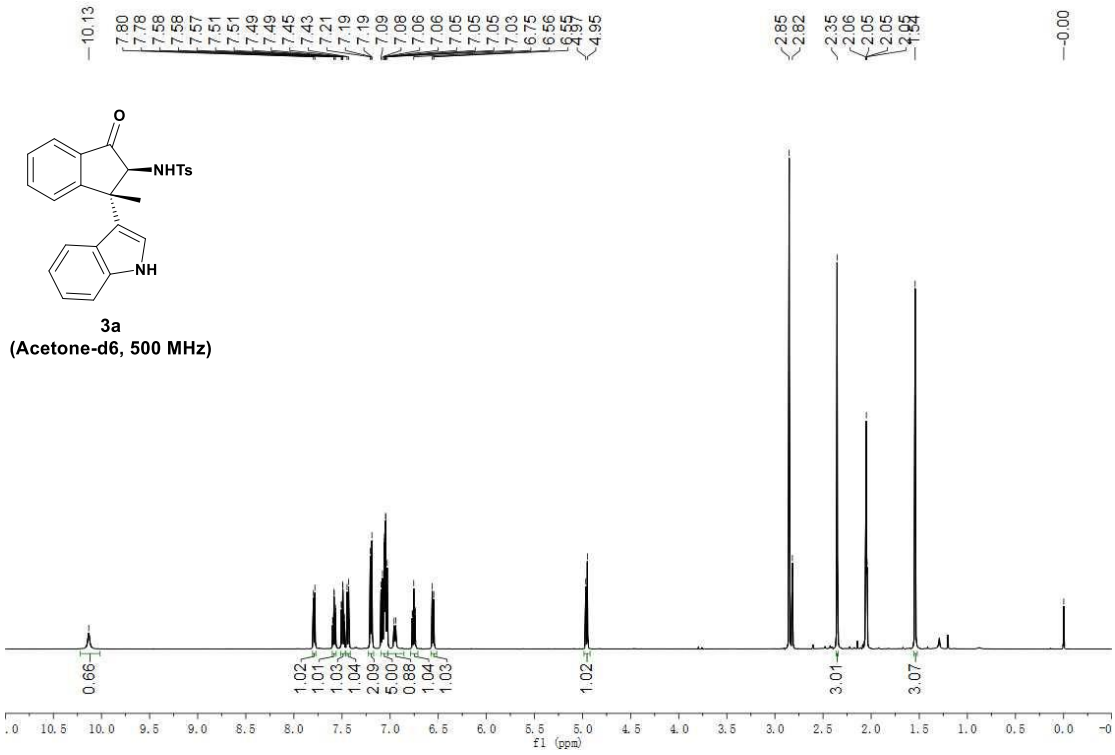
Part 5: Reference

(1) H. Yuan, J. Gong and Z. Yang, *Org. Lett*. 2016, **18**, 5500.

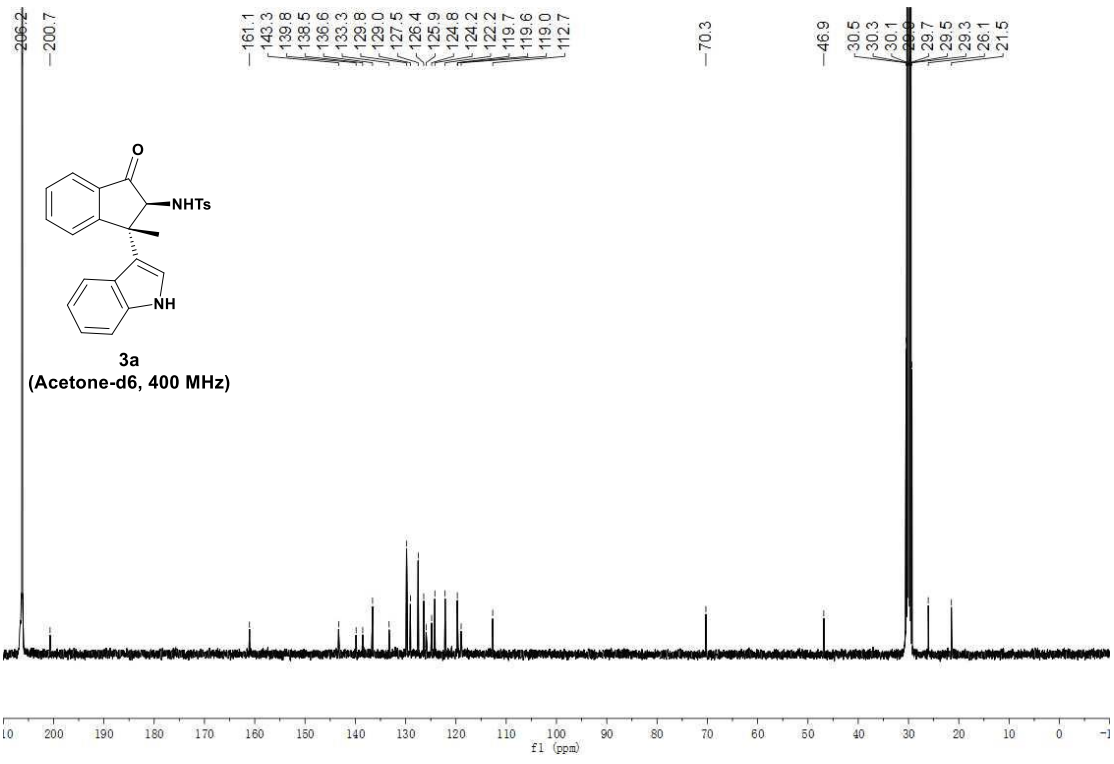
Part 4: NMR spectra data of products:



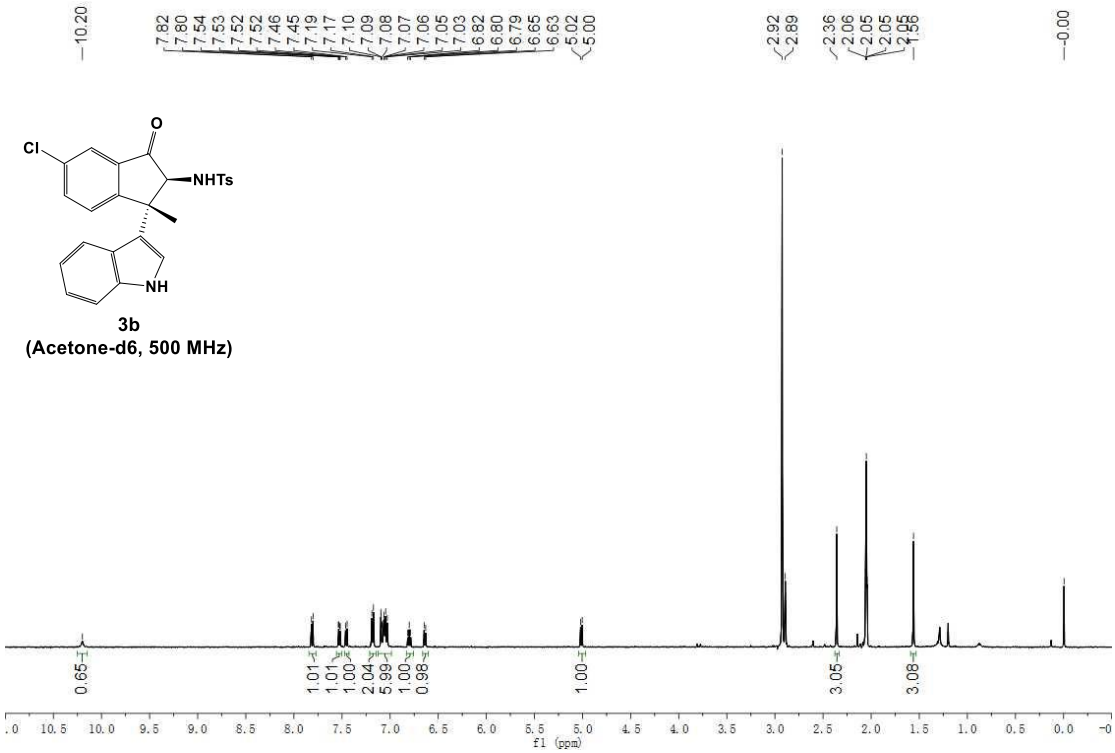




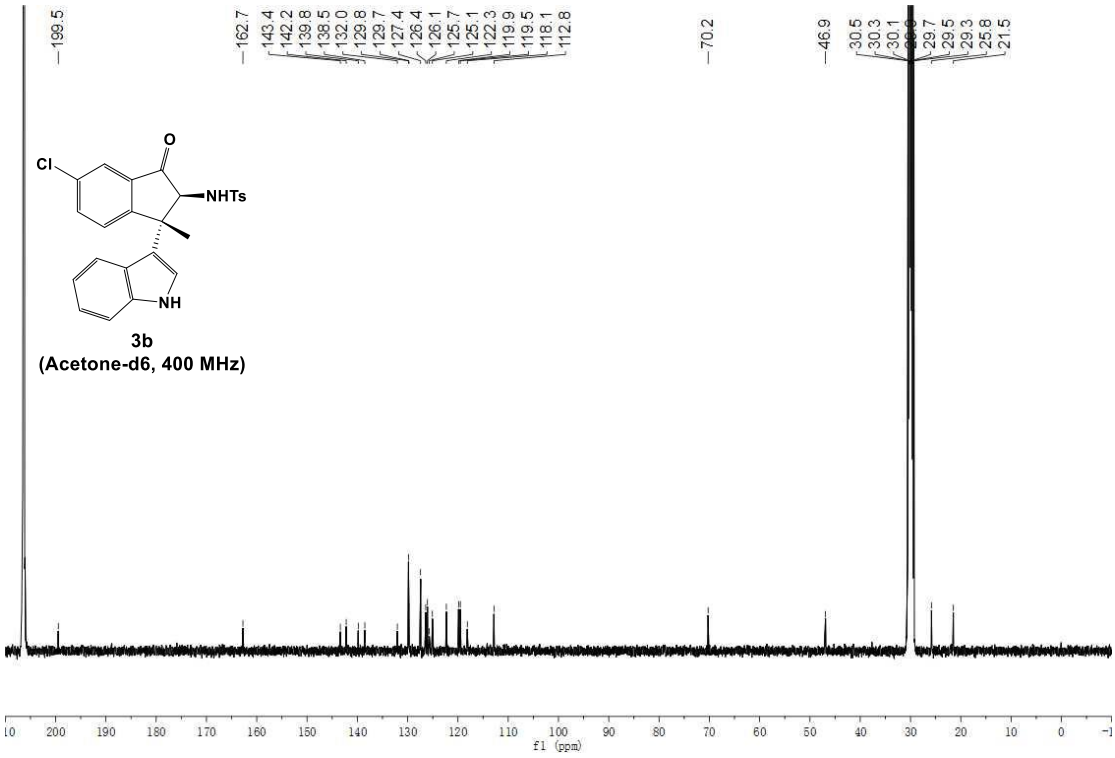
3a
(Acetone-d6, 500 MHz)



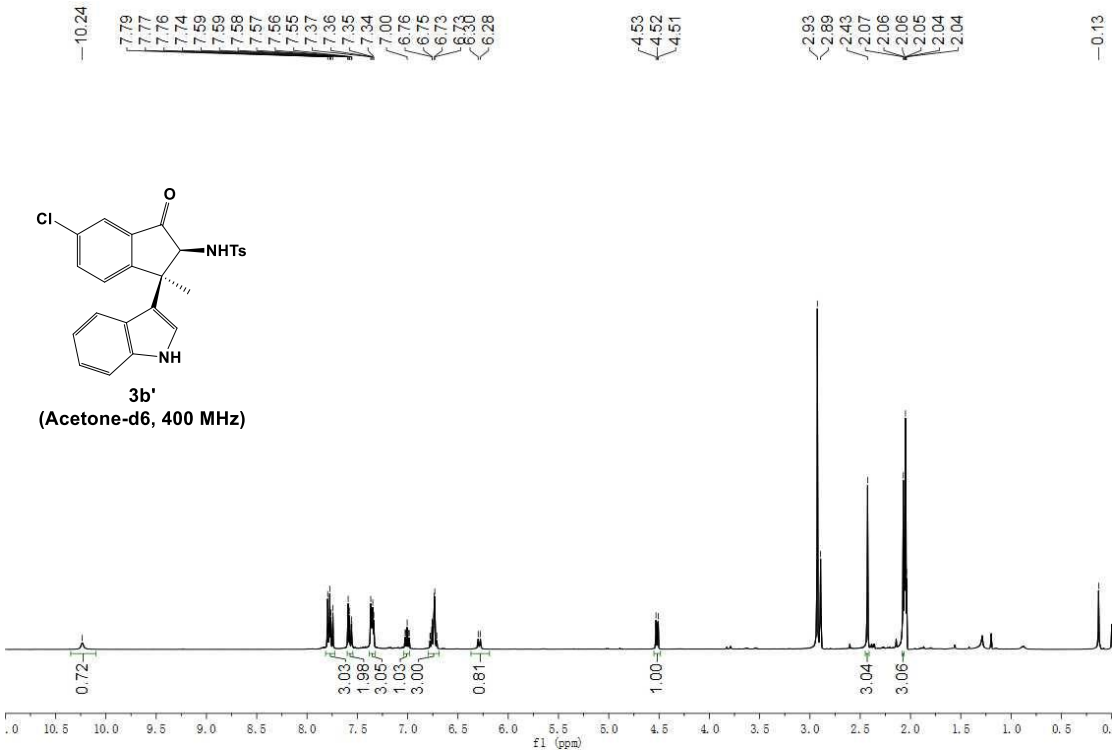
3a
(Acetone-d6, 400 MHz)



3b
(Acetone-d6, 500 MHz)



3b
(Acetone-d6, 400 MHz)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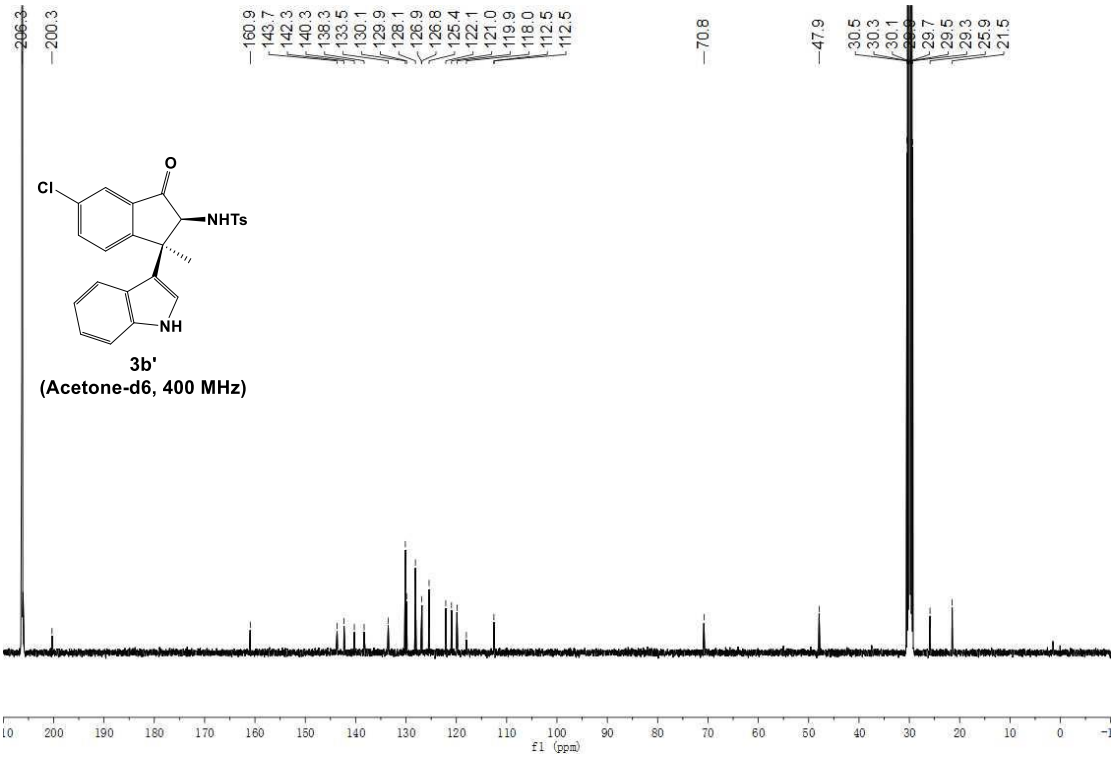
7.77
7.76
7.74
7.59
7.59
7.58
7.57
7.56
7.55
7.37
7.36
7.35
7.34
7.00
6.76
6.75
6.73
6.33
6.30
6.28
4.53
4.52
4.51
2.93
2.89
2.43
2.07
2.06
2.06
2.05
2.04
2.04
0.13
Cl
O
NHTs
NH
3b'
(Acetone-d6, 400 MHz)
0.72
3.03
1.98
3.05
1.03
3.00
0.81
1.00
3.04
3.06
f1 (ppm)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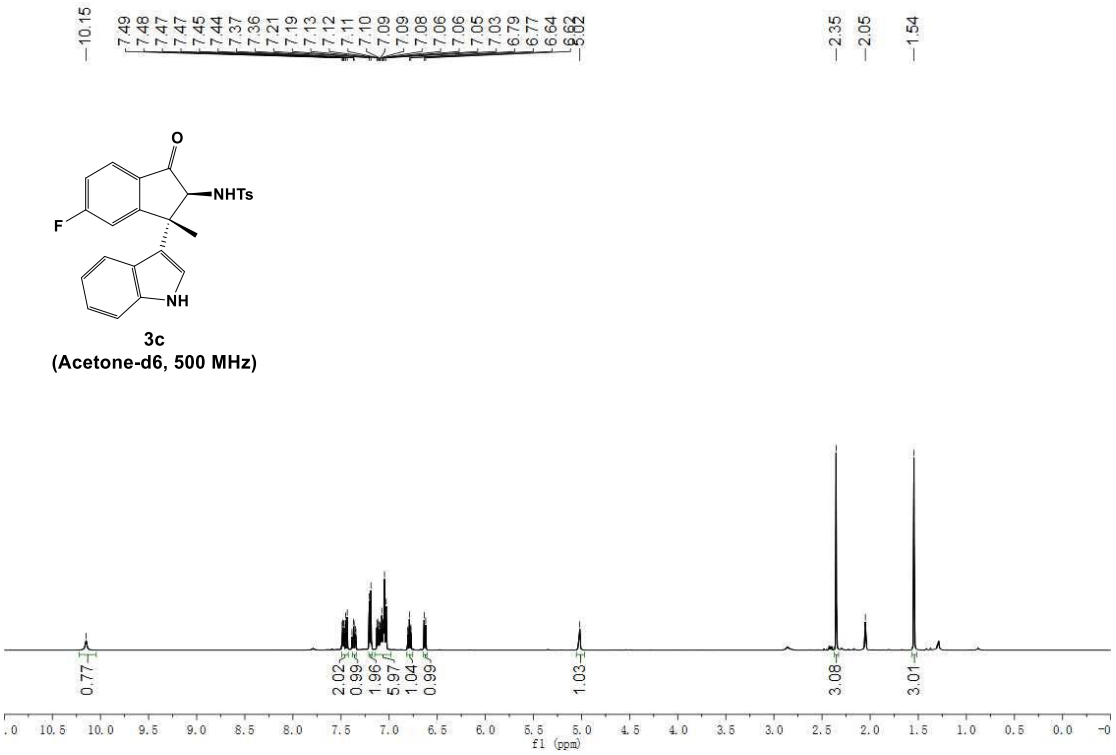
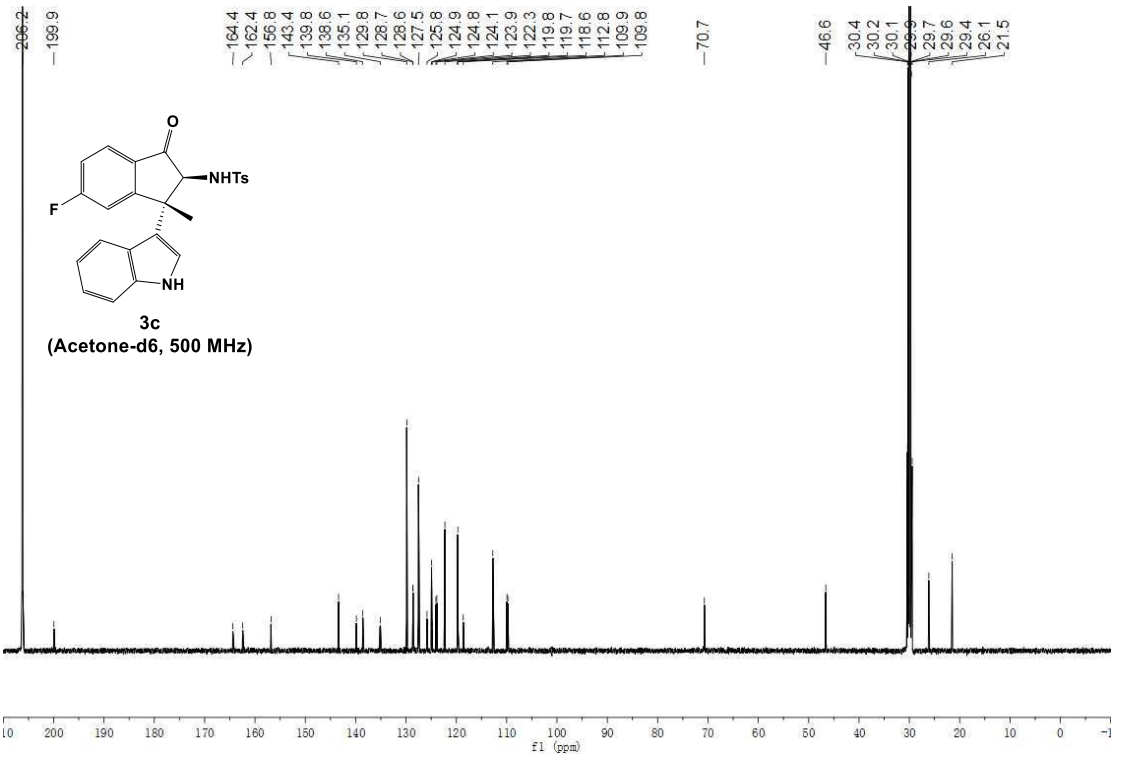
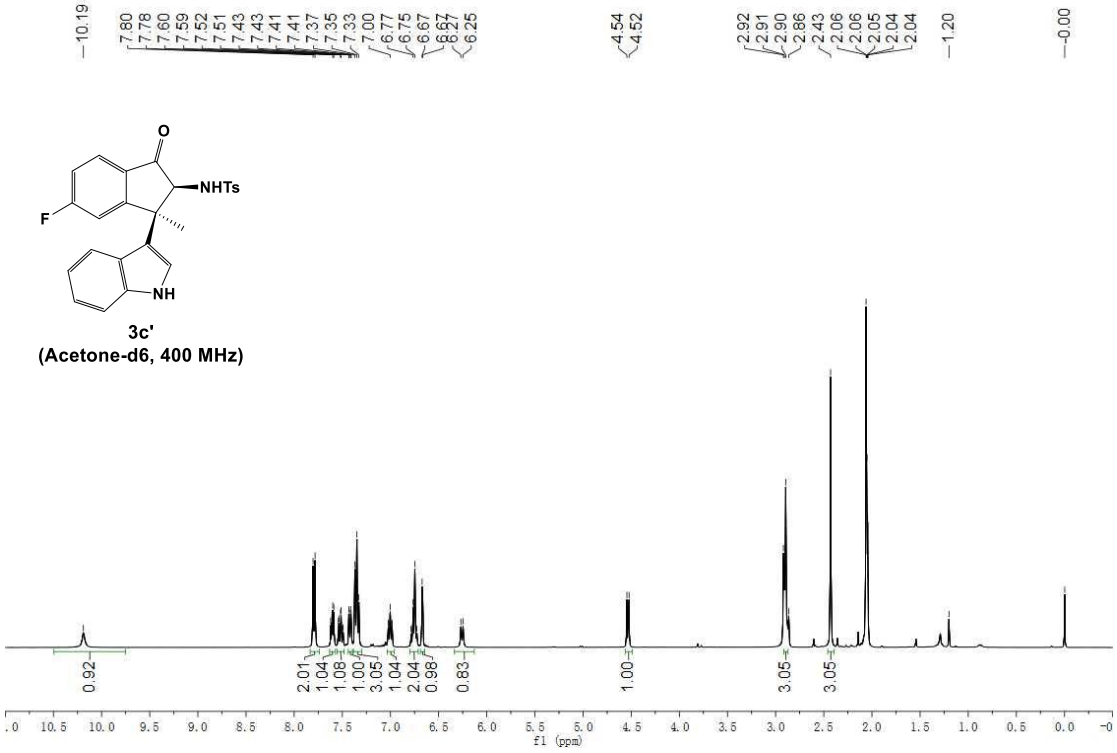
200.3
160.9
143.7
142.3
140.3
138.3
133.5
130.1
129.9
128.1
126.9
126.8
125.4
122.1
121.0
119.9
118.0
112.5
112.5
70.8
47.9
30.5
30.3
30.1
29.7
29.5
29.3
25.9
21.5
Cl
O
NHTs
NH
3b'
(Acetone-d6, 400 MHz)
f1 (ppm)



3c
(Acetone-d6, 500 MHz)



3c
(Acetone-d6, 500 MHz)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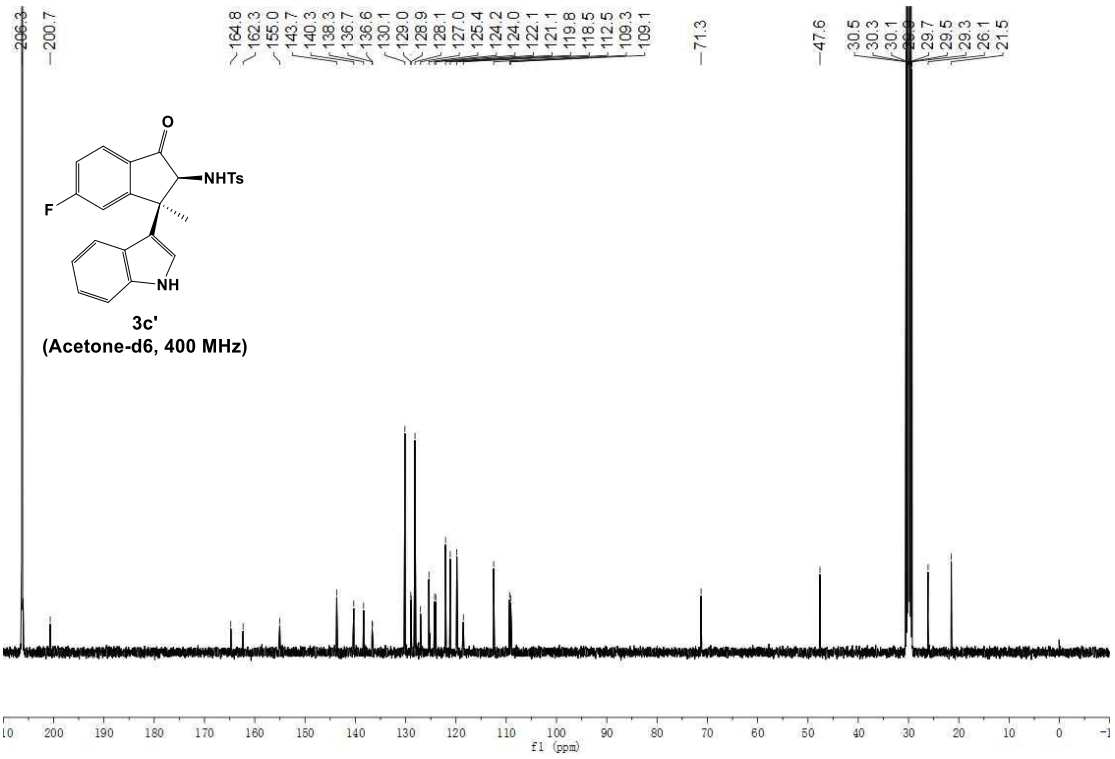
7.60
7.59
7.52
7.51
7.43
7.43
7.41
7.41
7.37
7.35
7.33
7.00
6.77
6.75
6.67
6.67
6.25
4.54
4.52
2.92
2.91
2.90
2.86
2.43
2.06
2.06
2.05
2.04
2.04
1.20
0.00
O
NHTs
F
NH
3c'
(Acetone-d6, 400 MHz)
0.92
2.01
1.04
1.08
1.00
3.05
1.04
2.04
0.98
0.83
1.00
3.05
3.05
f1 (ppm)


206.3
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140.3
138.3
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136.6
130.1
129.0
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128.1
127.0
125.4
124.2
124.0
122.1
121.1
119.8
118.5
112.5
109.3
109.1
71.3
47.6
30.5
30.3
30.1
29.7
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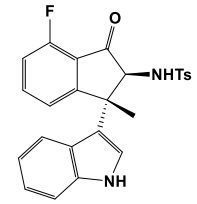
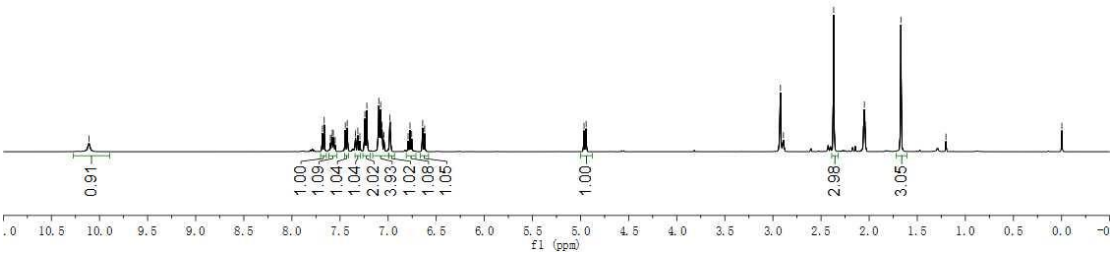
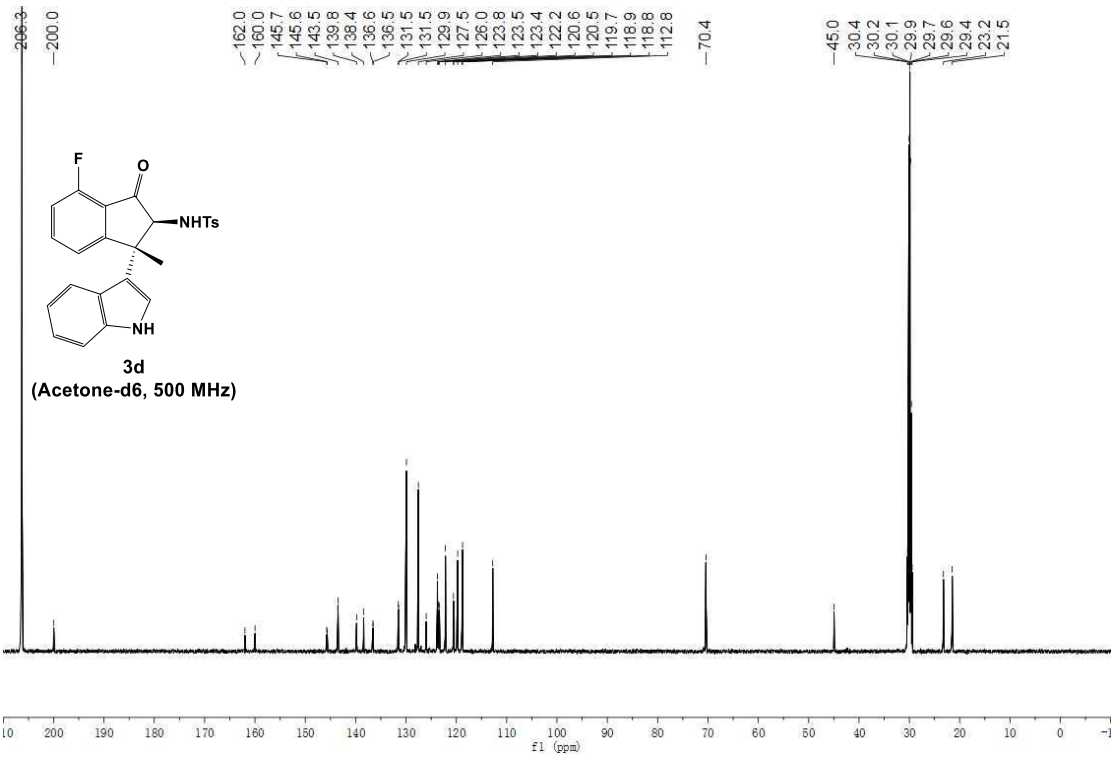
21.5
O
NHTs
F
NH
3c'
(Acetone-d6, 400 MHz)
f1 (ppm)

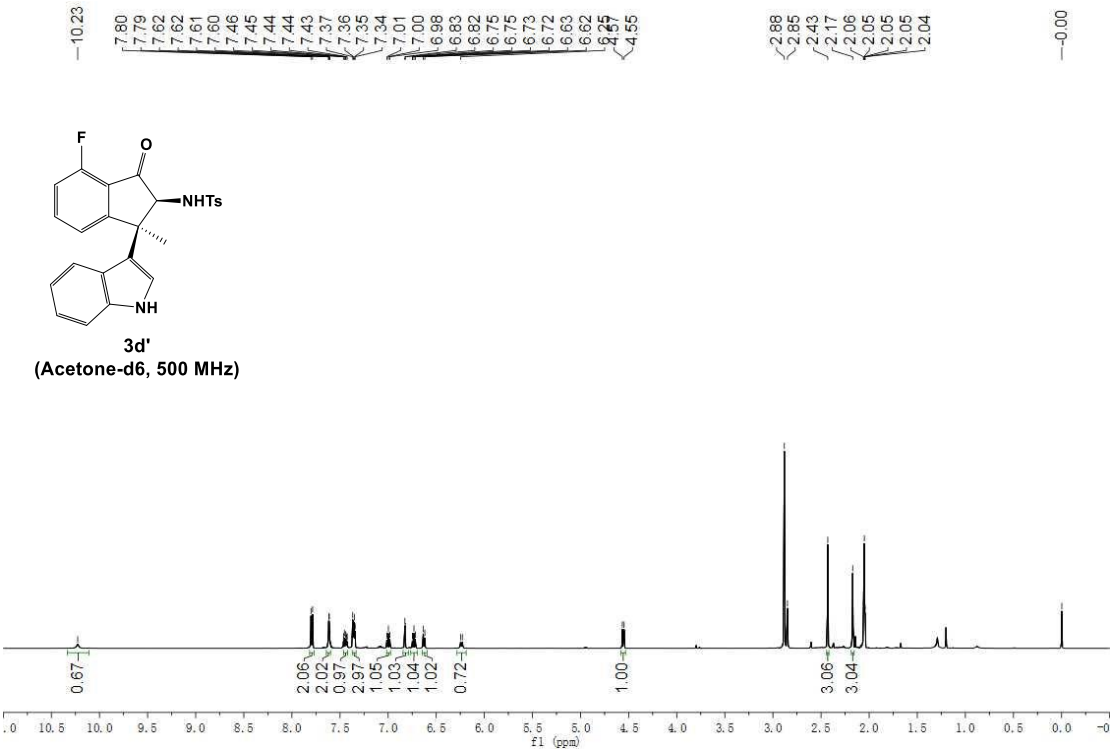


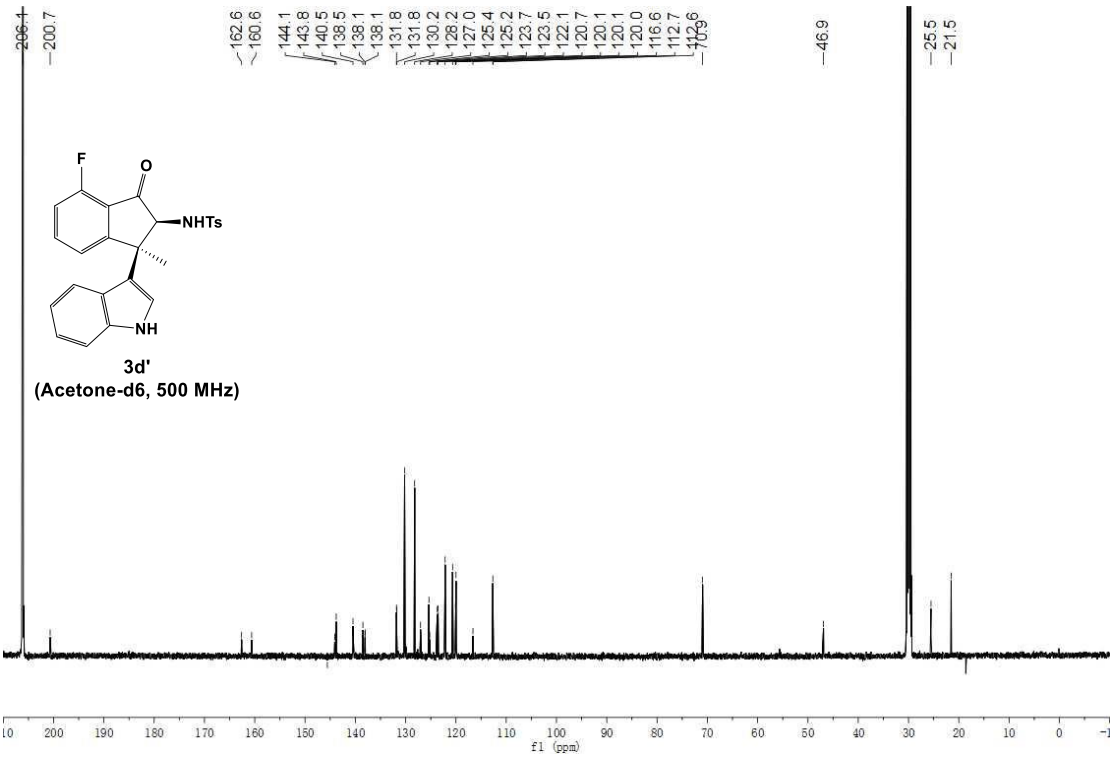
3d
(Acetone-d6, 400 MHz)

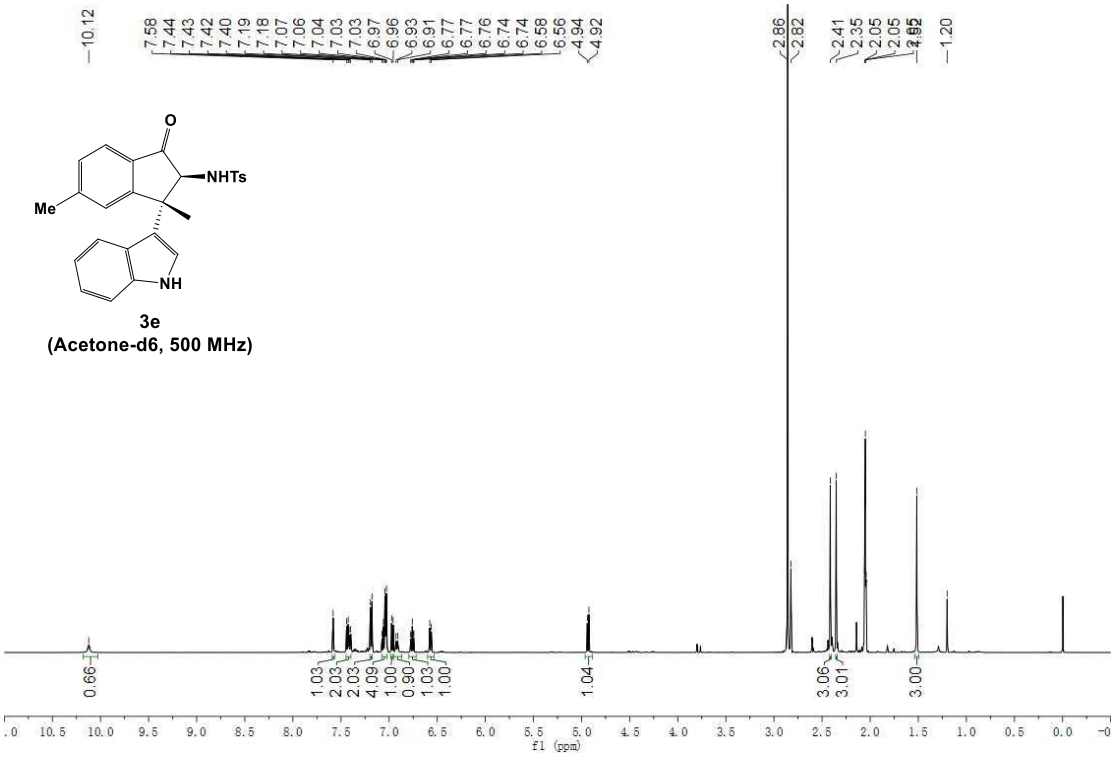




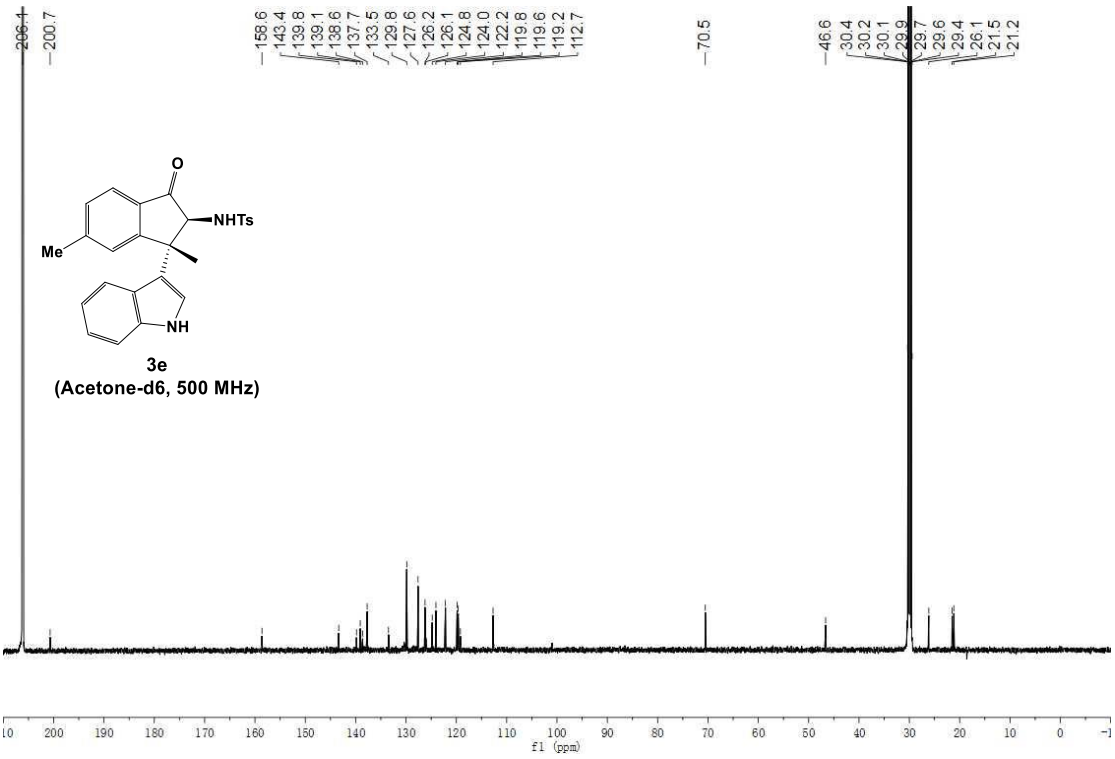
3d
(Acetone-d6, 500 MHz)


F
O
NHTs
NH
3d'
(Acetone-d6, 500 MHz)
f1 (ppm)

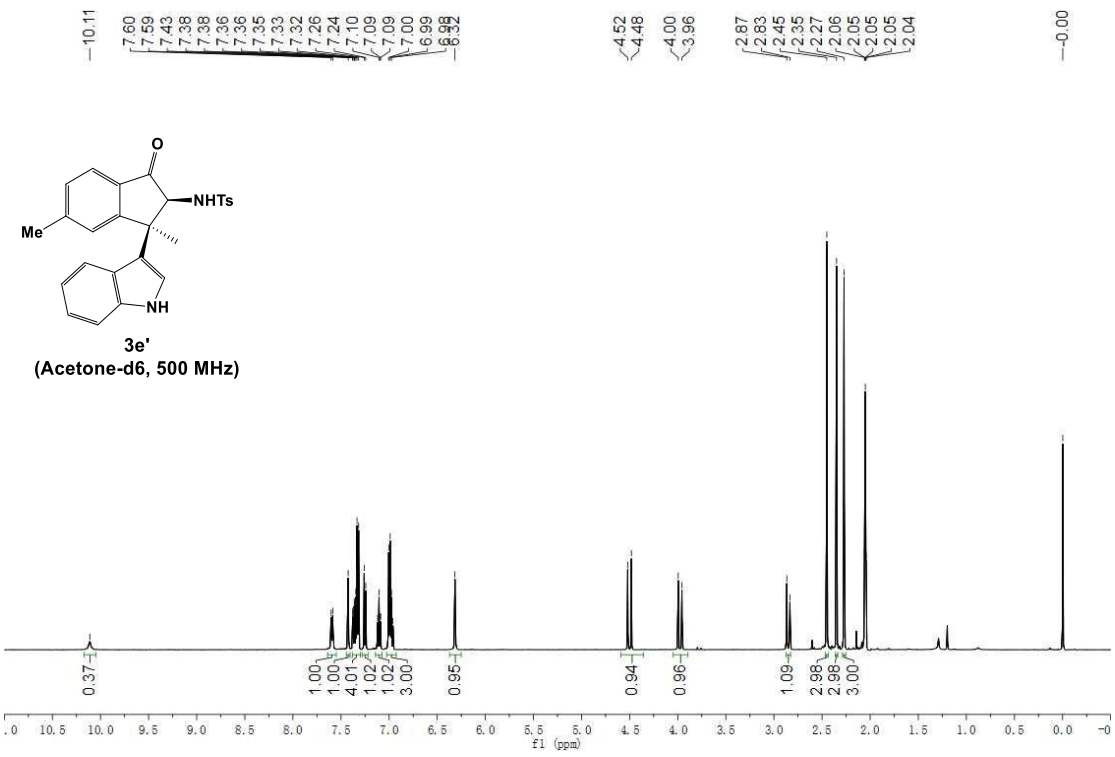

F
O
NHTs
NH
3d'
(Acetone-d6, 500 MHz)
f1 (ppm)



3e
(Acetone-d6, 500 MHz)



3e
(Acetone-d6, 500 MHz)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7.59
7.43
7.38
7.38
7.36
7.36
7.35
7.33
7.32
7.26
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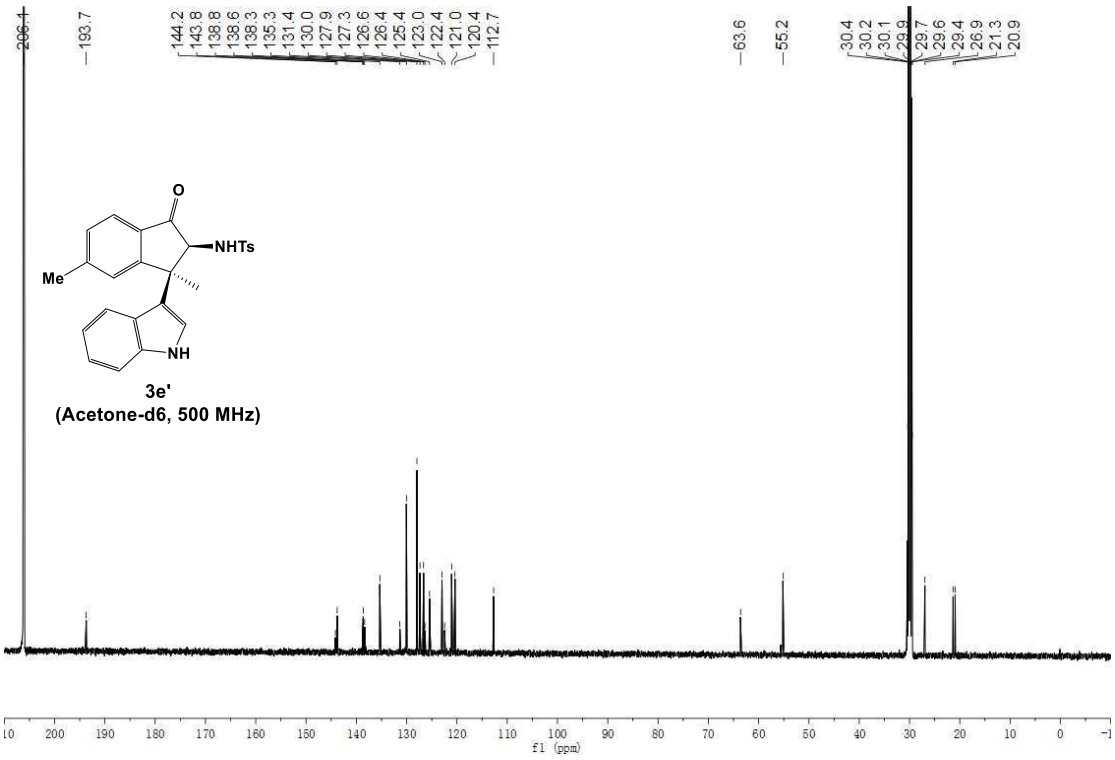
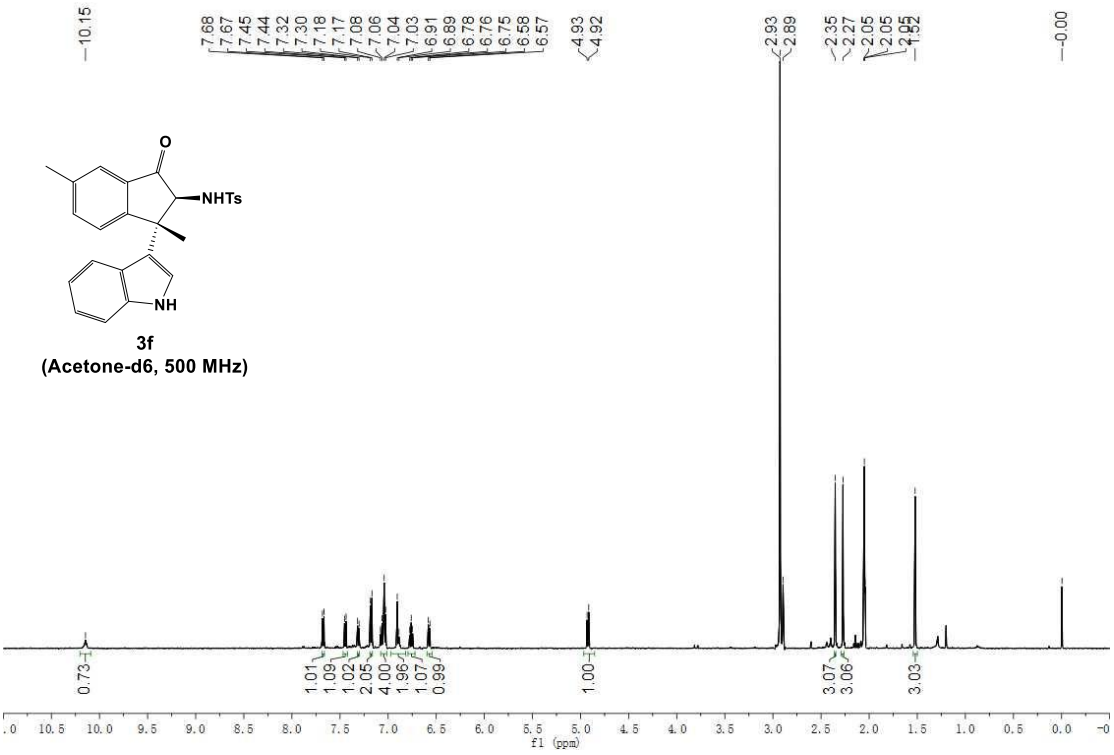
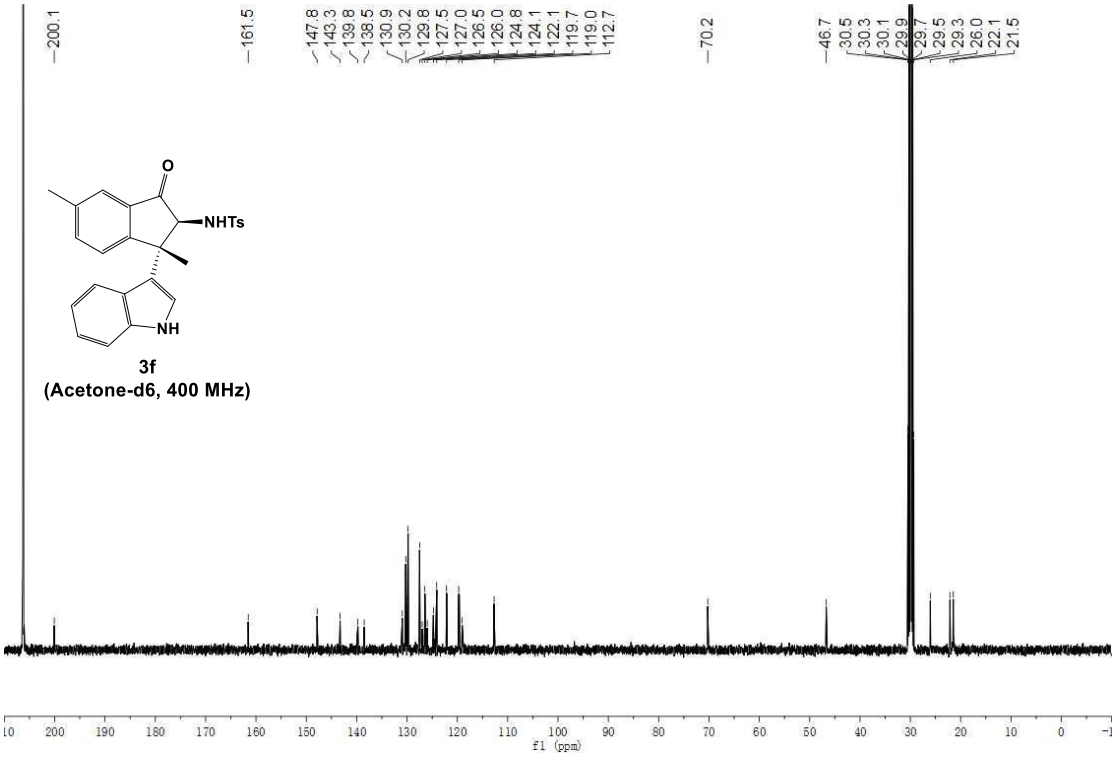
7.10
7.09
7.09
7.00
6.99
6.98
6.92
4.52
4.48
4.00
3.96
2.87
2.83
2.45
2.35
2.27
2.06
2.05
2.05
2.05
2.04
0.00
O
NHTs
Me
NH
3e'
(Acetone-d6, 500 MHz)
0.37
1.00
1.00
4.01
1.02
1.02
3.00
0.95
0.94
0.96
1.09
2.98
2.98
3.00
f1 (ppm)

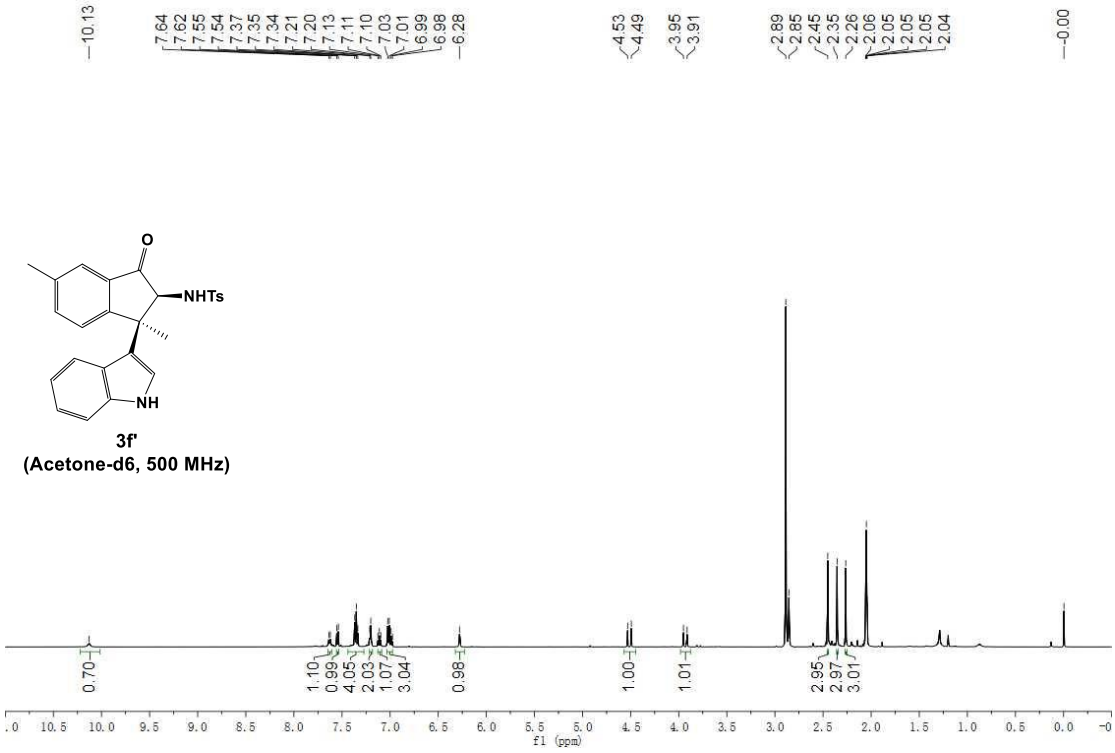

206.1
193.7
144.2
143.8
138.8
138.6
138.3
135.3
131.4
130.0
127.9
127.3
126.6
126.4
125.4
123.0
122.4
121.0
120.4
112.7
63.6
55.2
30.4
30.2
30.1
29.9
29.7
29.6
29.4
26.9
21.3
20.9
O
NHTs
Me
NH
3e'
(Acetone-d6, 500 MHz)
f1 (ppm)

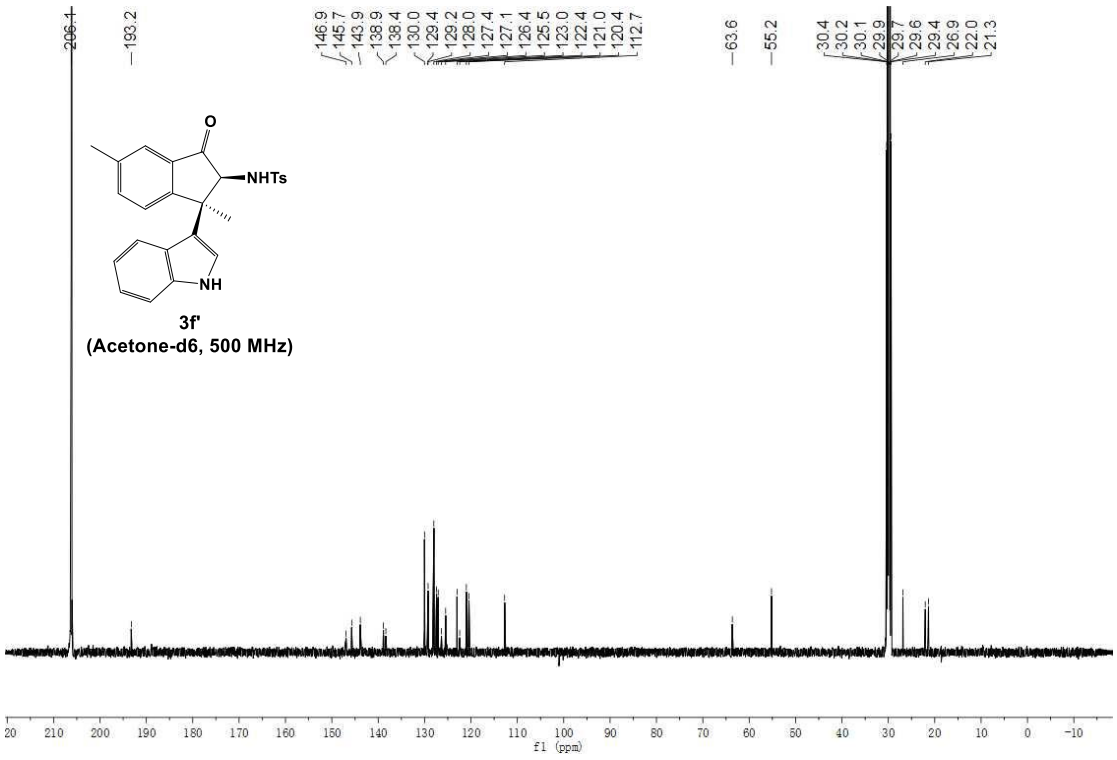


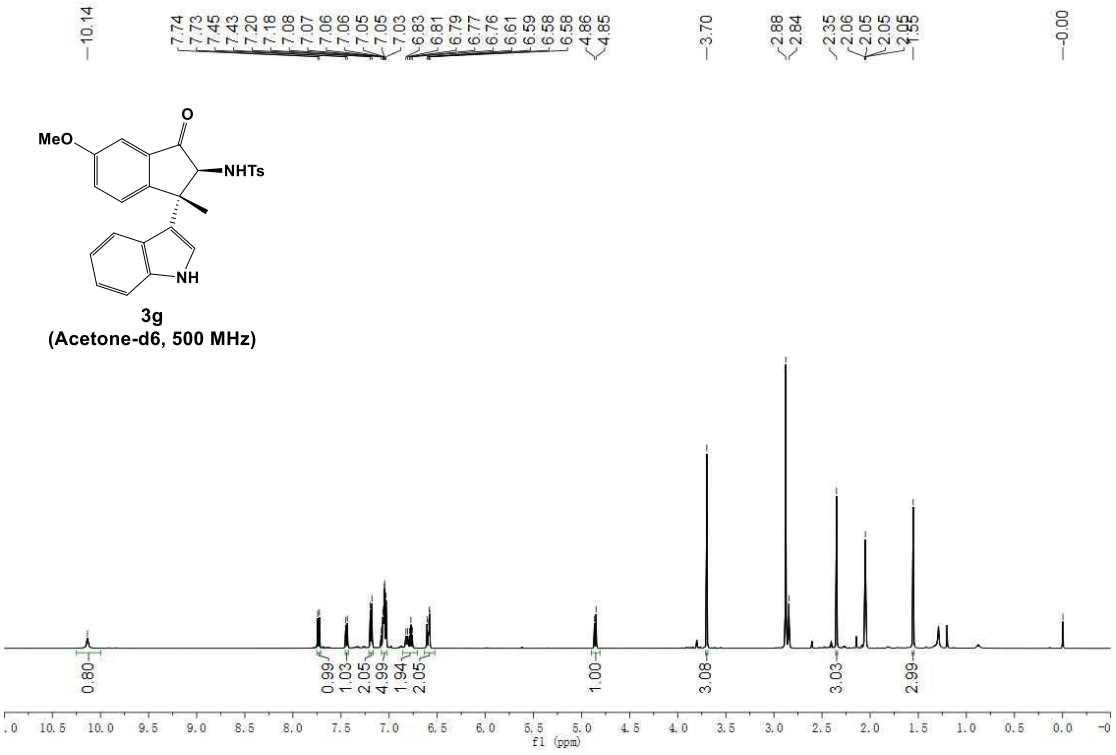
3f
(Acetone-d6, 500 MHz)



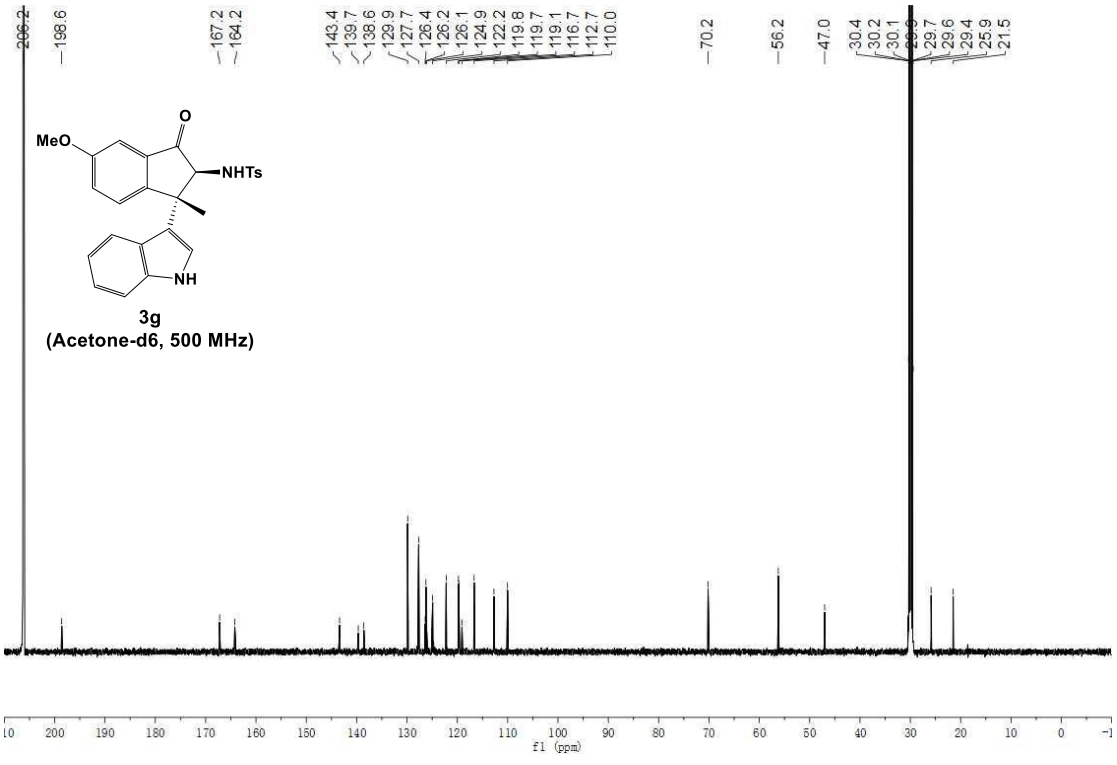
3f
(Acetone-d6, 400 MHz)


10.13
7.64
7.62
7.55
7.54
7.37
7.35
7.34
7.21
7.20
7.13
7.11
7.10
7.03
7.01
6.99
6.98
6.28
4.53
4.49
3.95
3.91
2.89
2.85
2.45
2.35
2.26
2.06
2.05
2.05
2.05
2.04
0.00
O
NHTs
NH
3f'
(Acetone-d6, 500 MHz)
0.70
1.10
0.99
4.05
2.03
1.07
3.04
0.98
1.00
1.01
2.95
2.97
3.01
f1 (ppm)

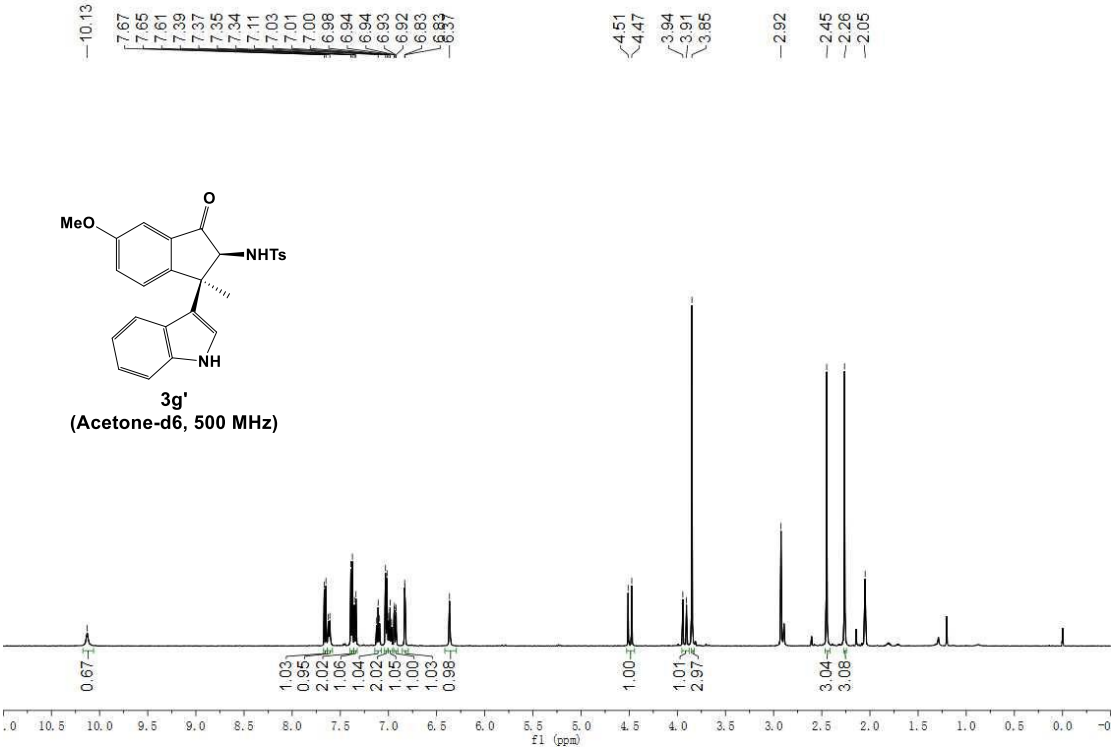

206.1
193.2
146.9
145.7
143.9
138.9
138.4
130.0
129.4
129.2
128.0
127.4
127.1
126.4
125.5
123.0
122.4
121.0
120.4
112.7
63.6
55.2
30.4
30.2
30.1
29.9
29.7
29.6
29.4
26.9
22.0
21.3
O
NHTs
NH
3f'
(Acetone-d6, 500 MHz)
f1 (ppm)

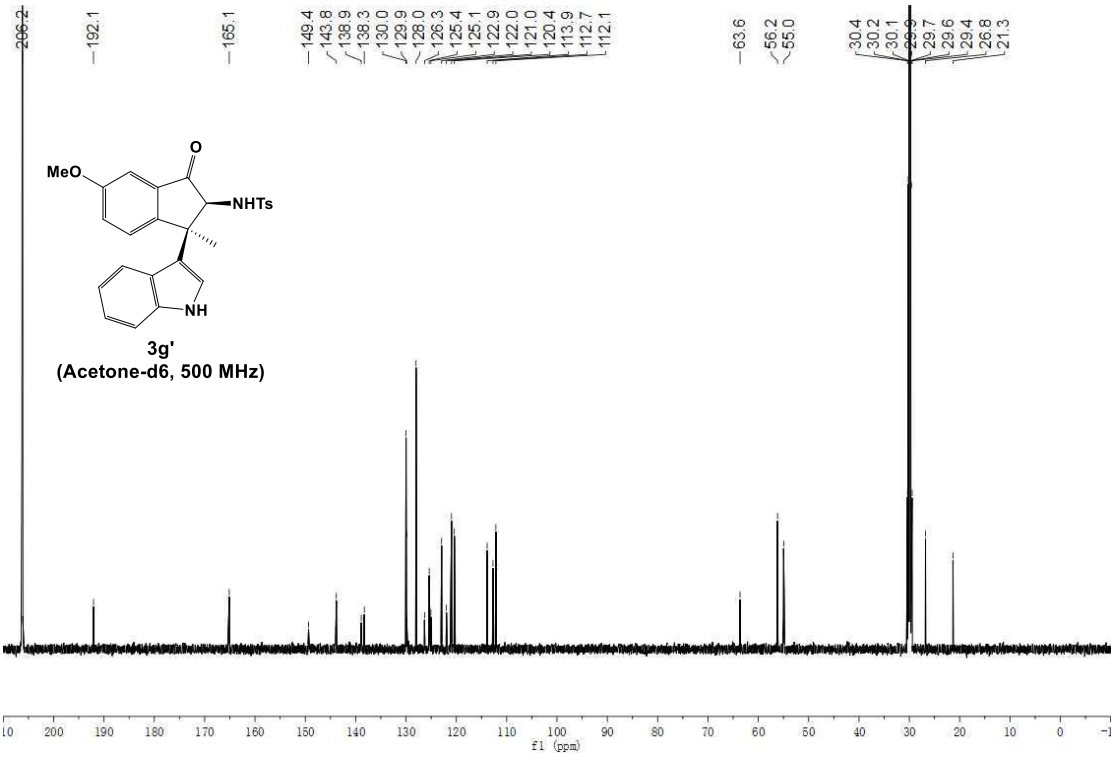


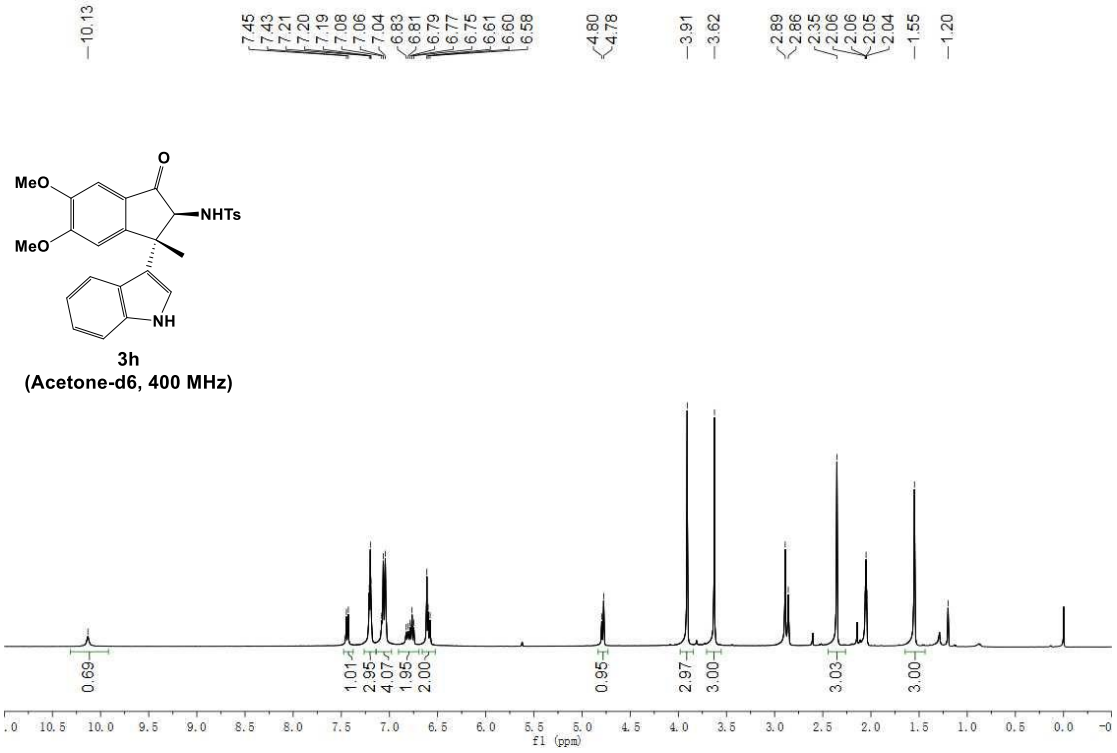
3g
(Acetone-d6, 500 MHz)



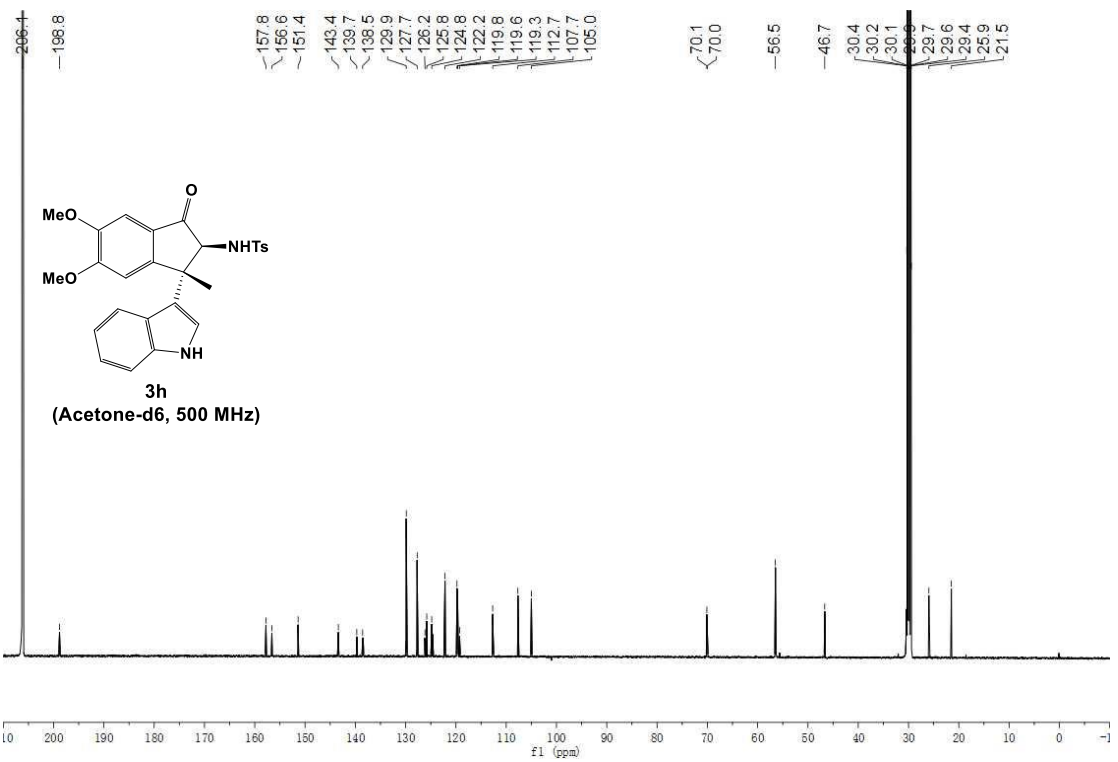
3g
(Acetone-d6, 500 MHz)


10.13
7.67
7.65
7.61
7.39
7.37
7.35
7.34
7.11
7.03
7.01
7.00
6.98
6.94
6.94
6.93
6.92
6.83
6.83
6.81
4.51
4.47
3.94
3.91
3.85
2.92
2.45
2.26
2.05
MeO
O
NHTs
NH
3g'
(Acetone-d6, 500 MHz)
0.67
1.03
0.95
2.02
1.06
1.04
2.02
1.05
1.00
1.03
0.98
1.00
1.01
2.97
3.04
3.08
f1 (ppm)

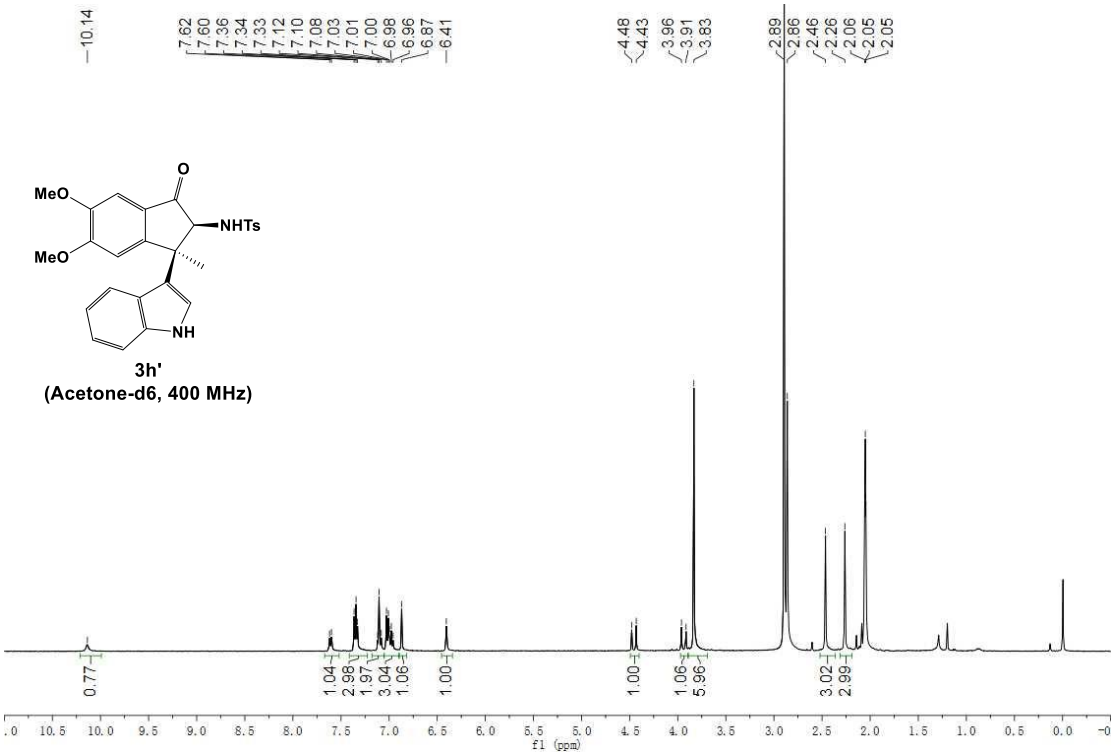

206.2
192.1
165.1
149.4
143.8
138.9
138.3
130.0
129.9
128.0
126.3
125.4
125.1
122.9
122.0
121.0
120.4
113.9
112.7
112.1
63.6
56.2
55.0
30.4
30.2
30.1
29.9
29.7
29.6
29.4
26.8
21.3
MeO
O
NHTs
NH
3g'
(Acetone-d6, 500 MHz)
f1 (ppm)

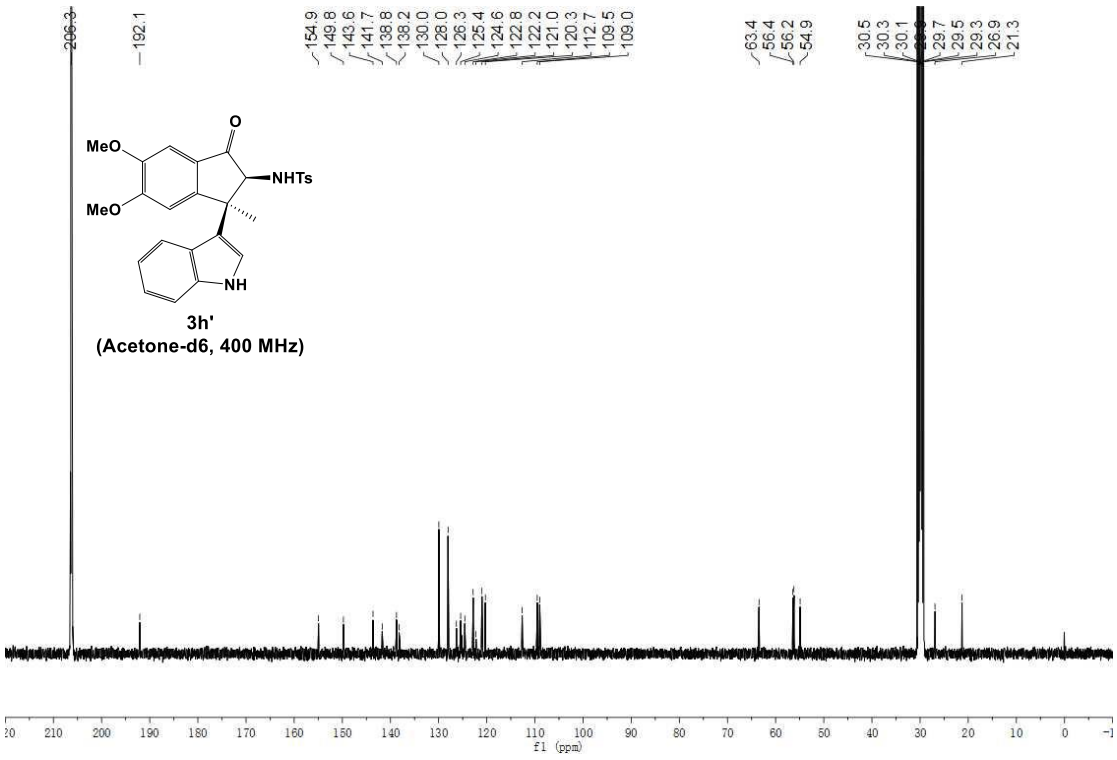


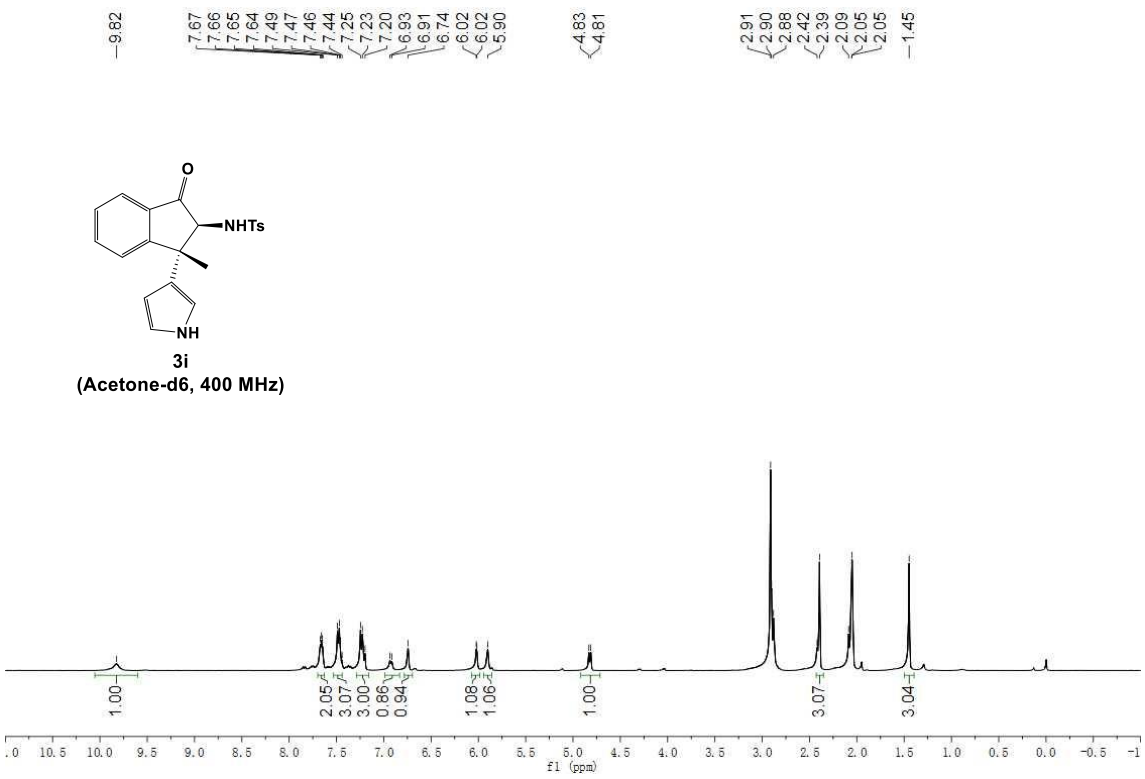
3h
(Acetone-d6, 400 MHz)

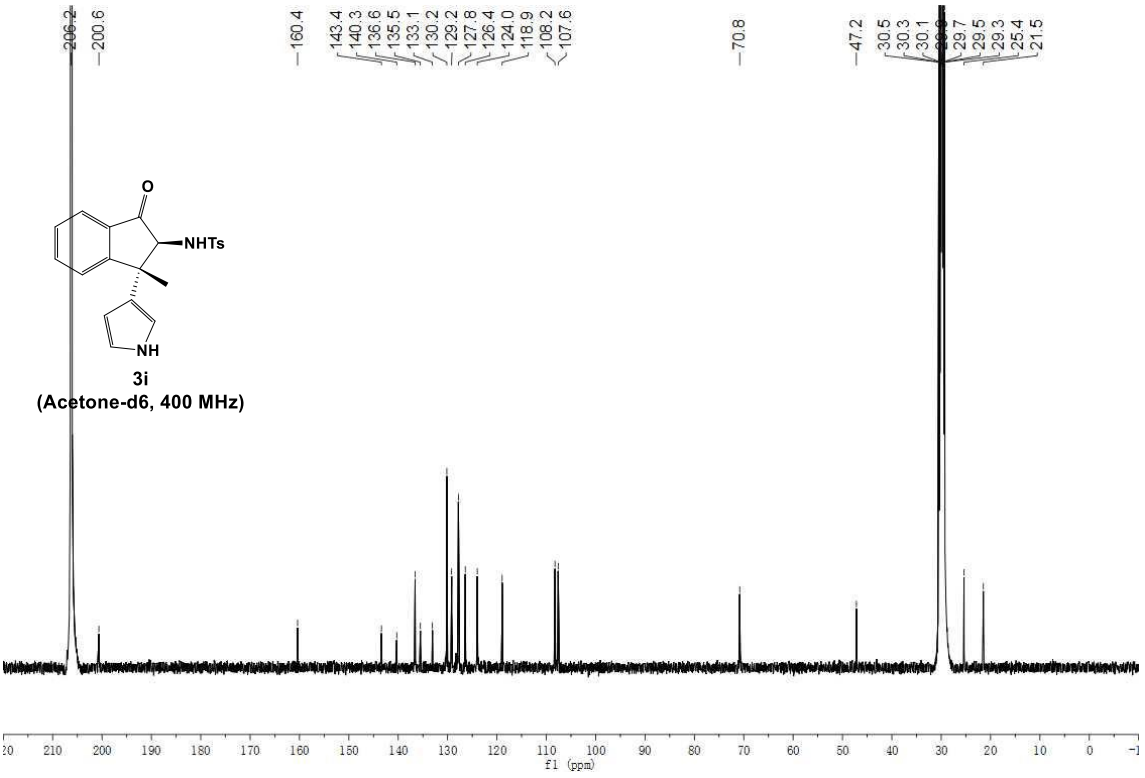


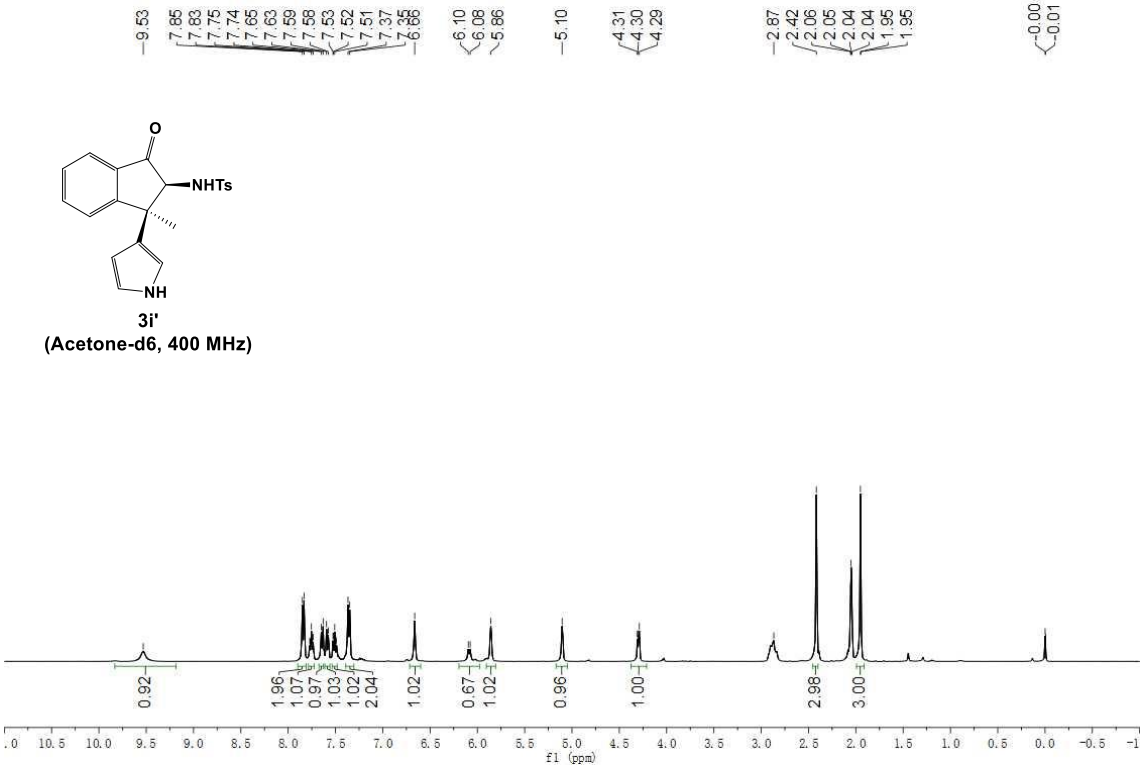
3h
(Acetone-d6, 500 MHz)

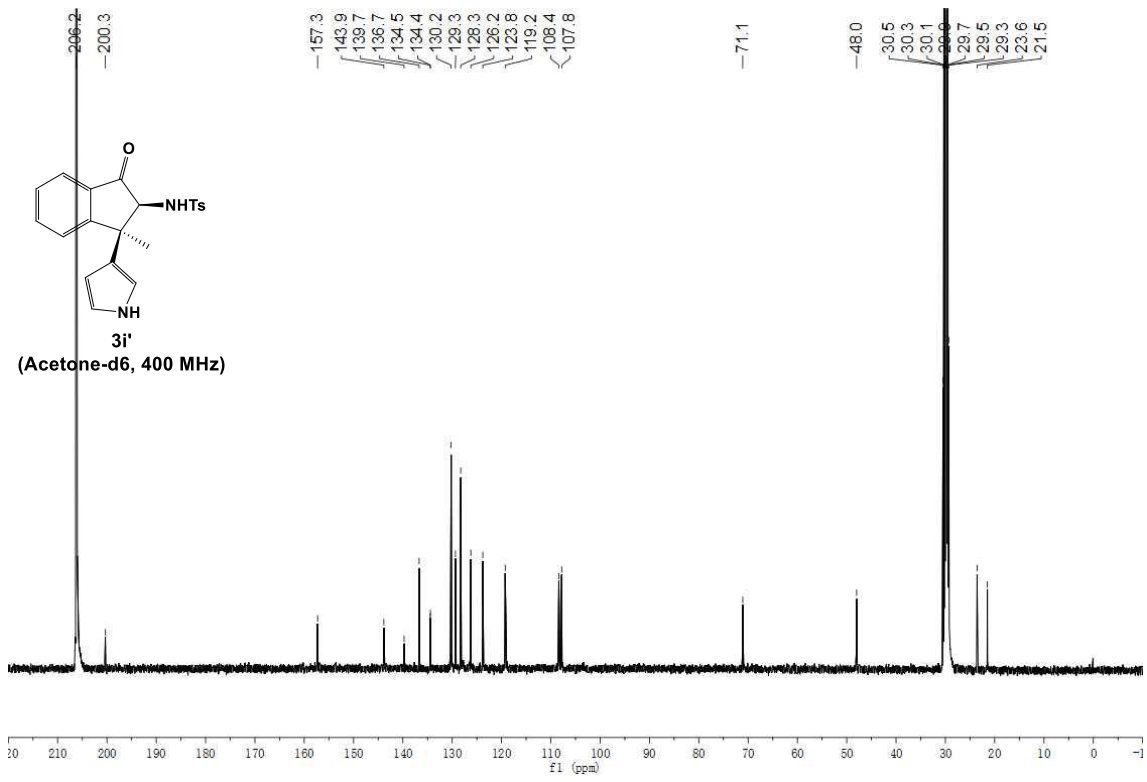

MeO
MeO
O
NHTs
NH
3h'
(Acetone-d6, 400 MHz)
f1 (ppm)

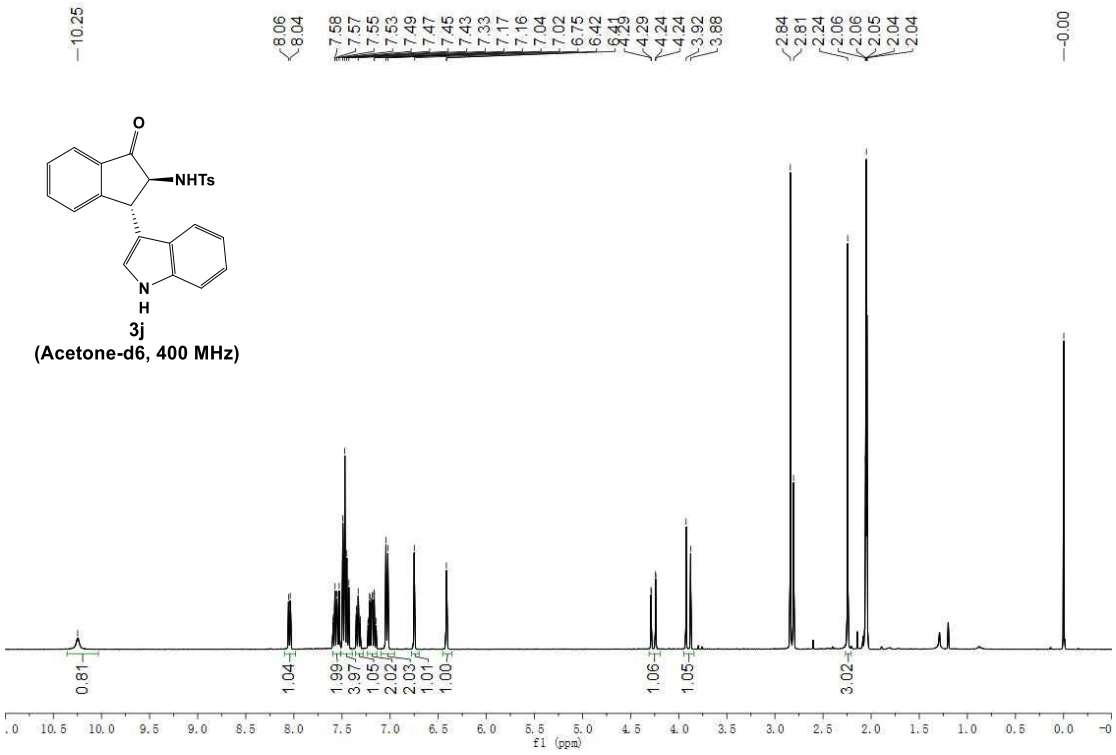

MeO
MeO
O
NHTs
NH
3h'
(Acetone-d6, 400 MHz)
f1 (ppm)

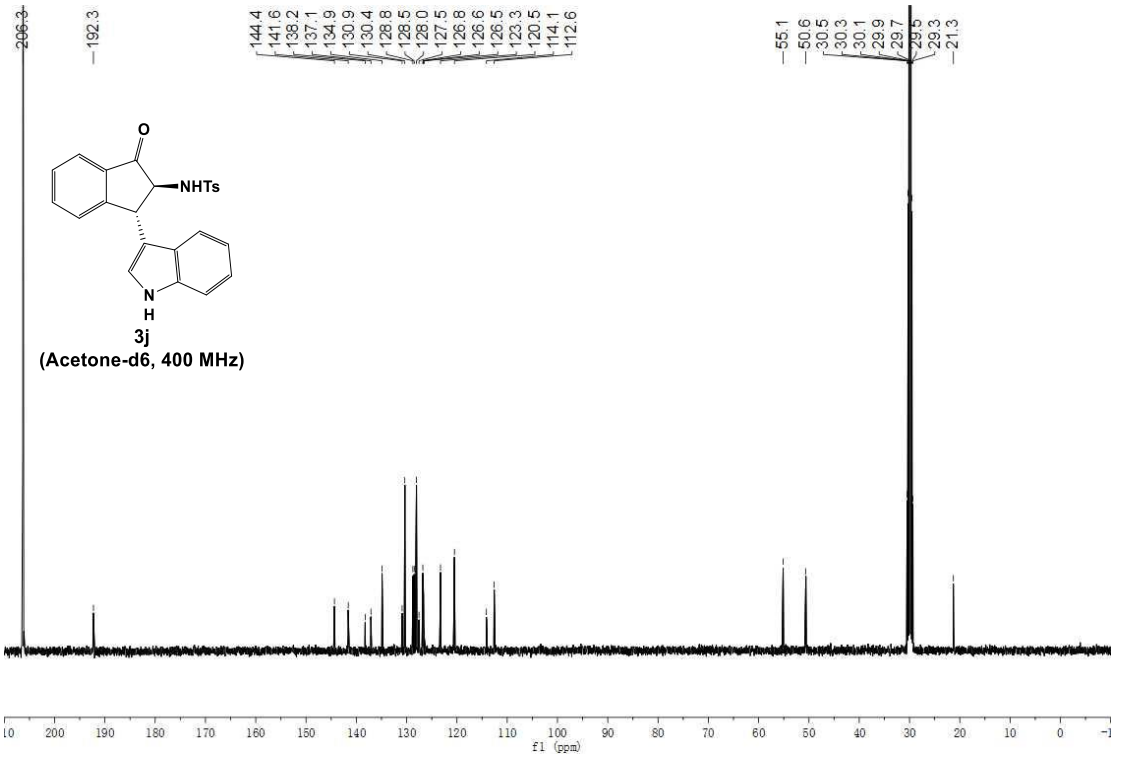

9.82
7.67
7.66
7.65
7.64
7.49
7.47
7.46
7.44
7.25
7.23
7.20
6.93
6.91
6.74
6.02
6.02
5.90
4.83
4.81
2.91
2.90
2.88
2.42
2.39
2.09
2.05
2.05
1.45
O
NHTs
NH
3i
(Acetone-d6, 400 MHz)
1.00
2.05
3.07
3.00
0.86
0.94
1.08
1.06
1.00
3.07
3.04
f1 (ppm)

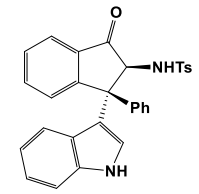

206.2
200.6
160.4
143.4
140.3
136.6
135.5
133.1
130.2
129.2
127.8
126.4
124.0
118.9
108.2
107.6
70.8
47.2
30.5
30.3
30.1
29.7
29.5
29.3
25.4
21.5
O
NHTs
NH
3i
(Acetone-d6, 400 MHz)
f1 (ppm)


9.53
7.85
7.83
7.75
7.74
7.65
7.63
7.59
7.58
7.53
7.52
7.51
7.37
7.35
6.86
6.10
6.08
5.86
5.10
4.31
4.30
4.29
2.87
2.42
2.06
2.05
2.04
2.04
1.95
1.95
0.00
-0.01
O
NHTs
NH
3i'
(Acetone-d6, 400 MHz)
0.92
1.96
1.07
0.97
1.03
1.02
2.04
1.02
0.67
1.02
0.96
1.00
2.98
3.00
f1 (ppm)

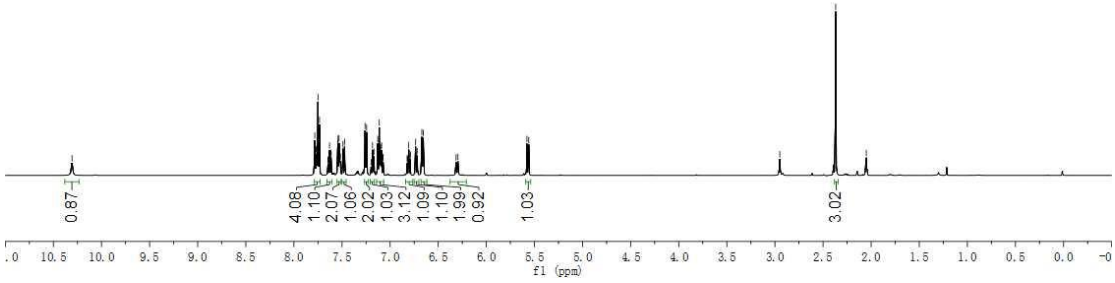

206.2
200.3
157.3
143.9
139.7
136.7
134.5
134.4
130.2
129.3
128.3
126.2
123.8
119.2
108.4
107.8
71.1
48.0
30.5
30.3
30.1
29.7
29.5
29.3
23.6
21.5
O
NHTs
NH
3i'
(Acetone-d6, 400 MHz)
f1 (ppm)

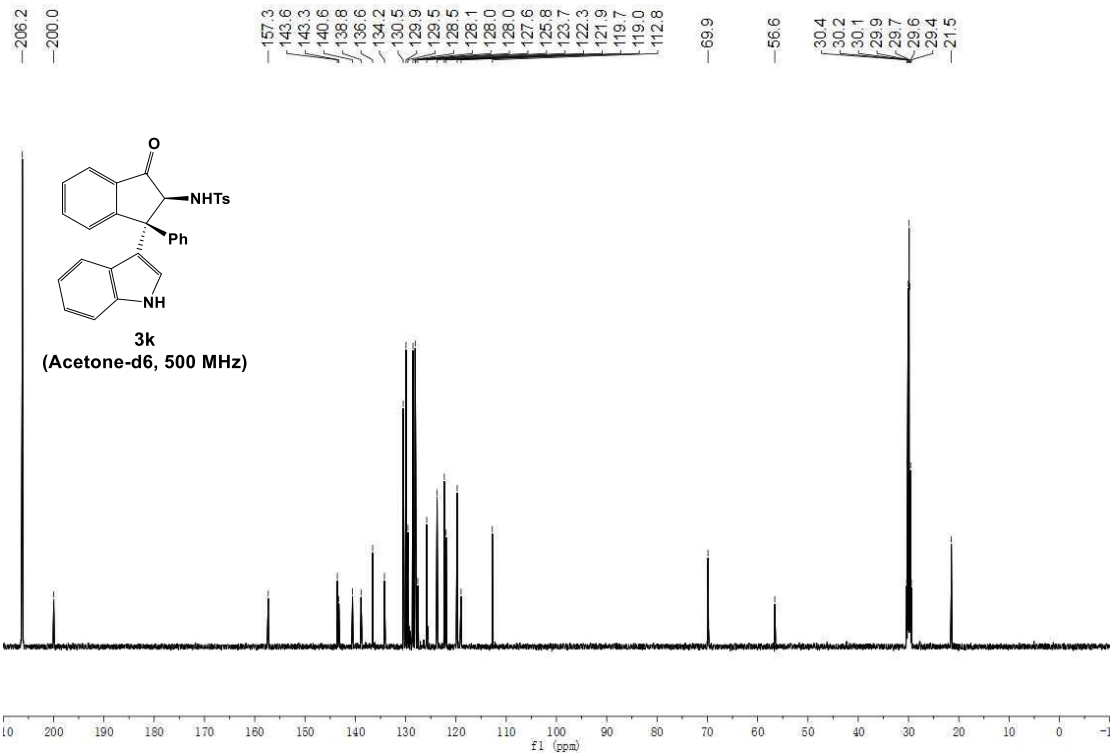

10.25
8.06
8.04
7.58
7.57
7.55
7.53
7.49
7.47
7.45
7.43
7.33
7.17
7.16
7.04
7.02
6.75
6.42
6.41
4.29
4.24
4.24
3.92
3.88
2.84
2.81
2.24
2.06
2.06
2.05
2.04
2.04
0.00
O
NHTs
N
H
3j
(Acetone-d6, 400 MHz)
0.81
1.04
1.99
3.97
1.05
2.02
2.03
1.01
1.00
1.06
1.05
3.02
f1 (ppm)


206.2
192.3
144.4
141.6
138.2
137.1
134.9
130.9
130.4
128.8
128.5
128.0
127.5
126.8
126.6
126.5
123.3
120.5
114.1
112.6
55.1
50.6
30.5
30.3
30.1
29.9
29.7
29.5
29.3
21.3
O
NHTs
N
H
3j
(Acetone-d6, 400 MHz)
f1 (ppm)

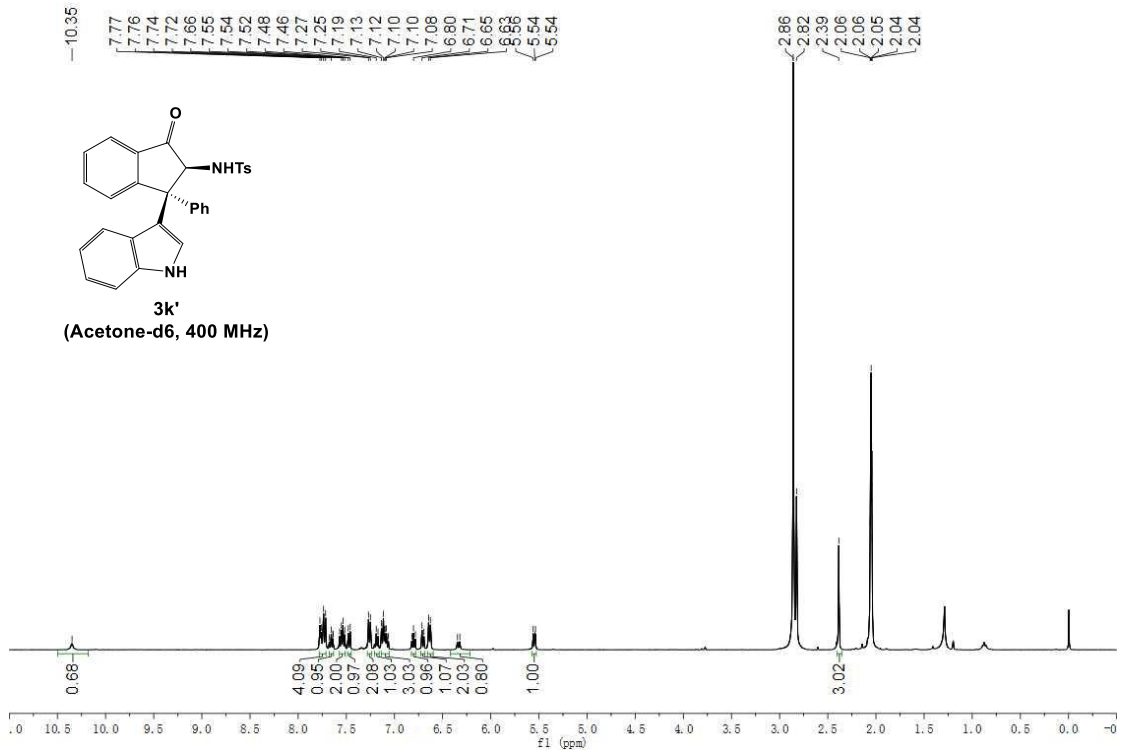


3k
(Acetone-d6, 500 MHz)

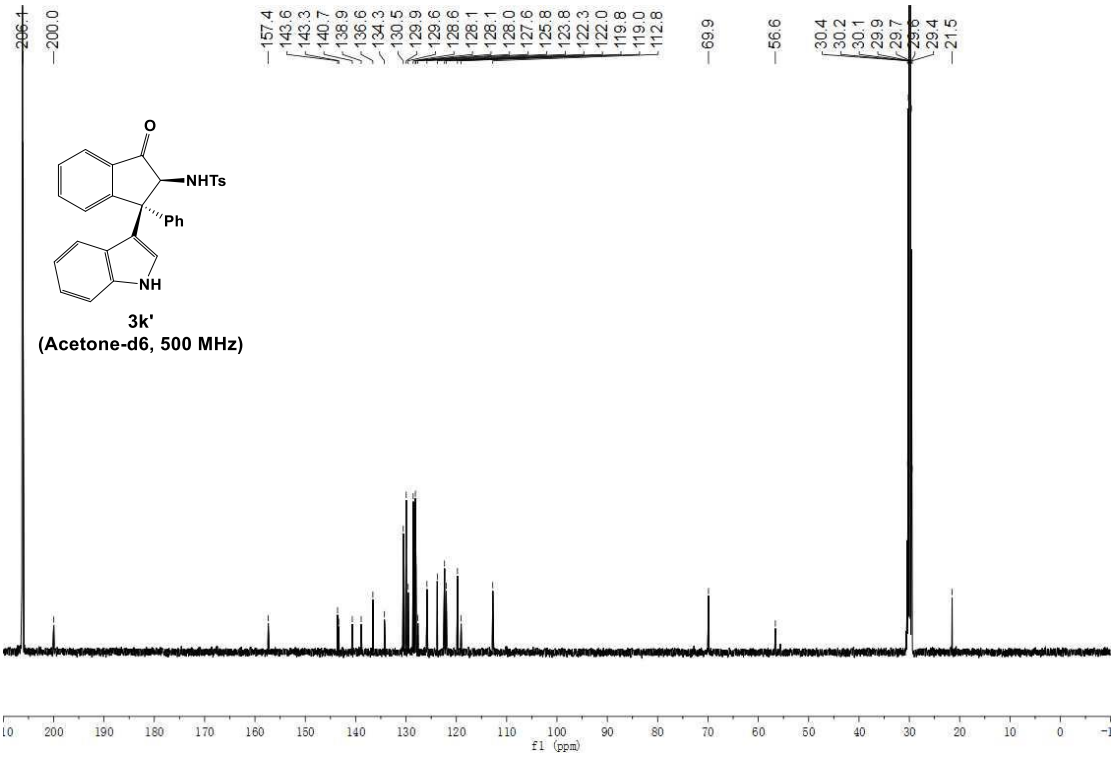




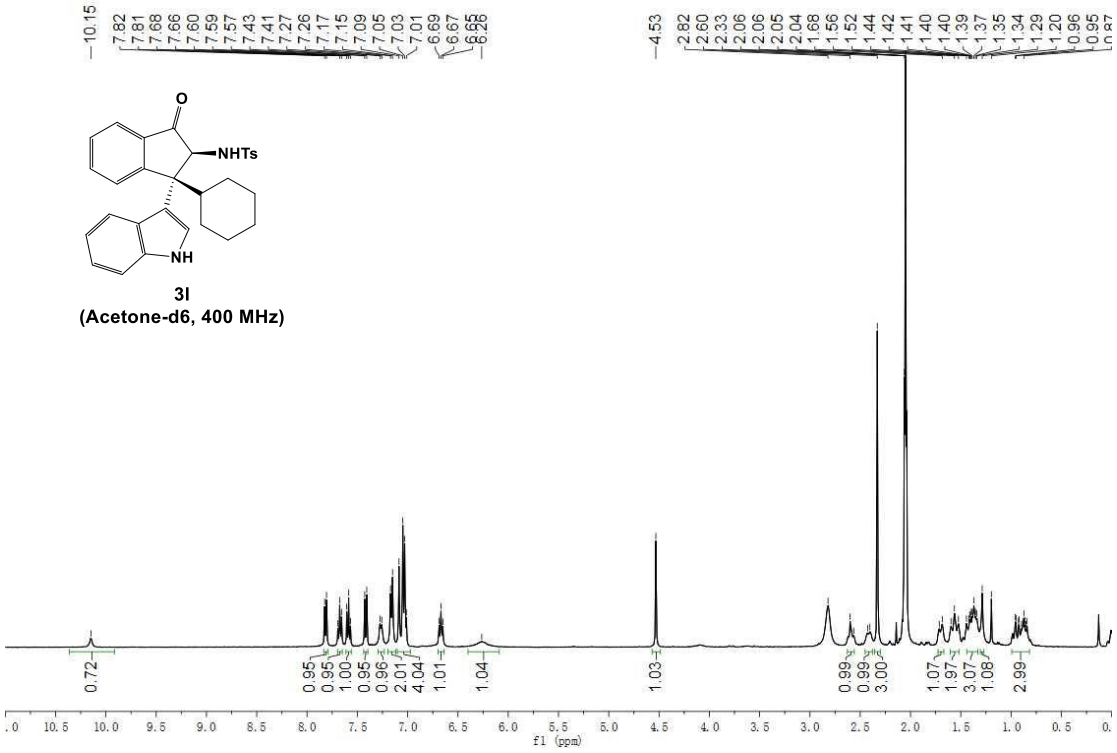
3k
(Acetone-d6, 500 MHz)

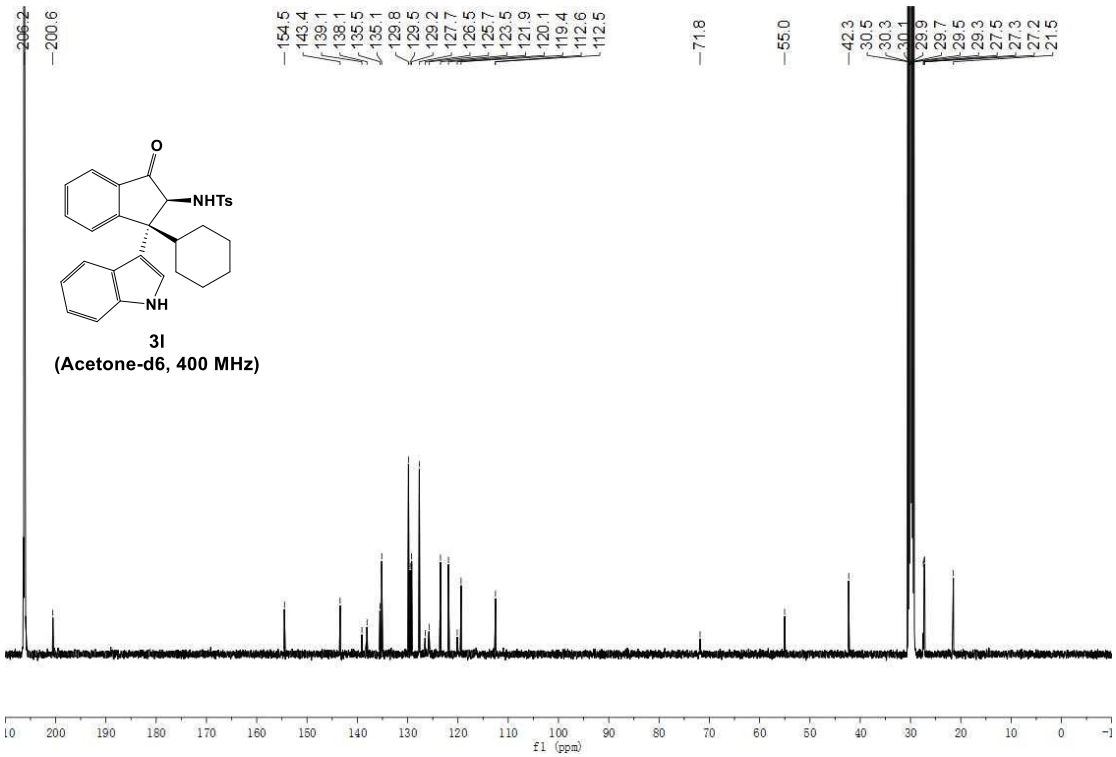


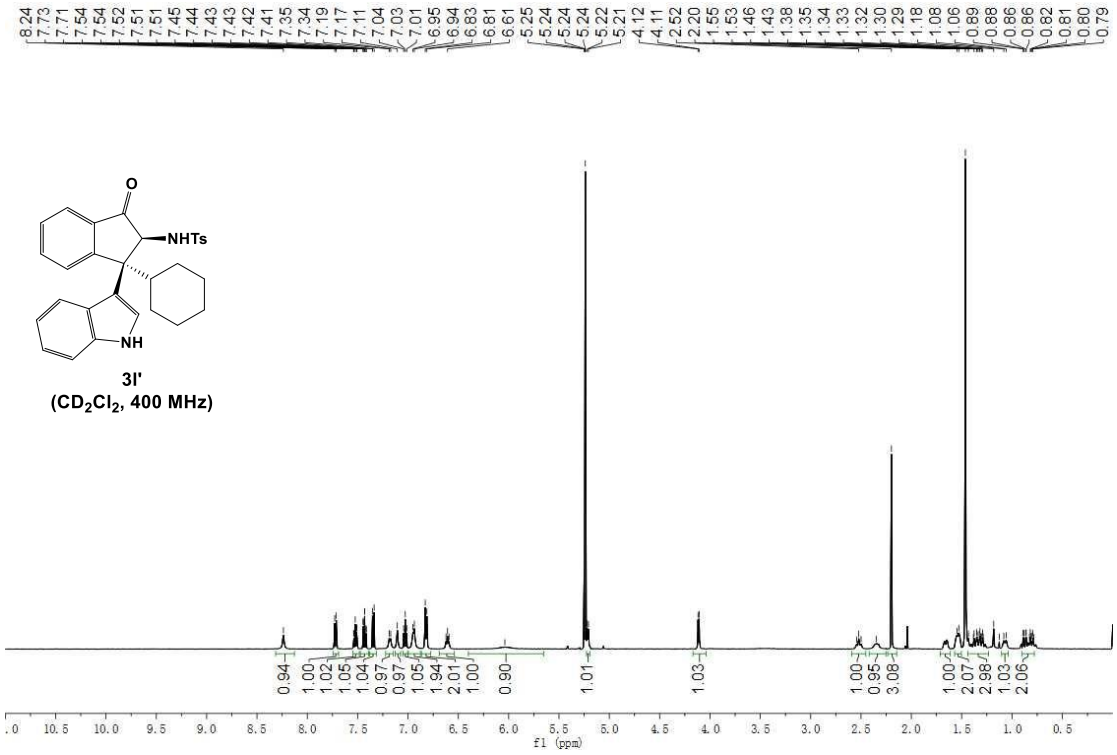
3k'
(Acetone-d6, 400 MHz)

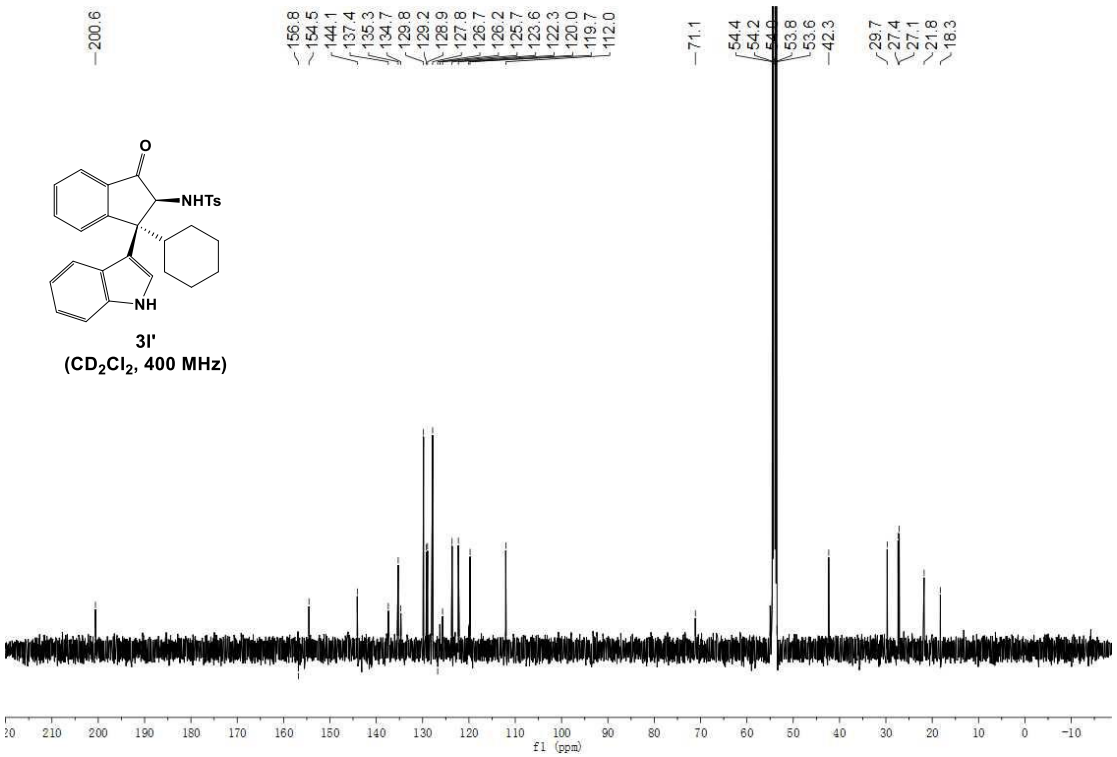


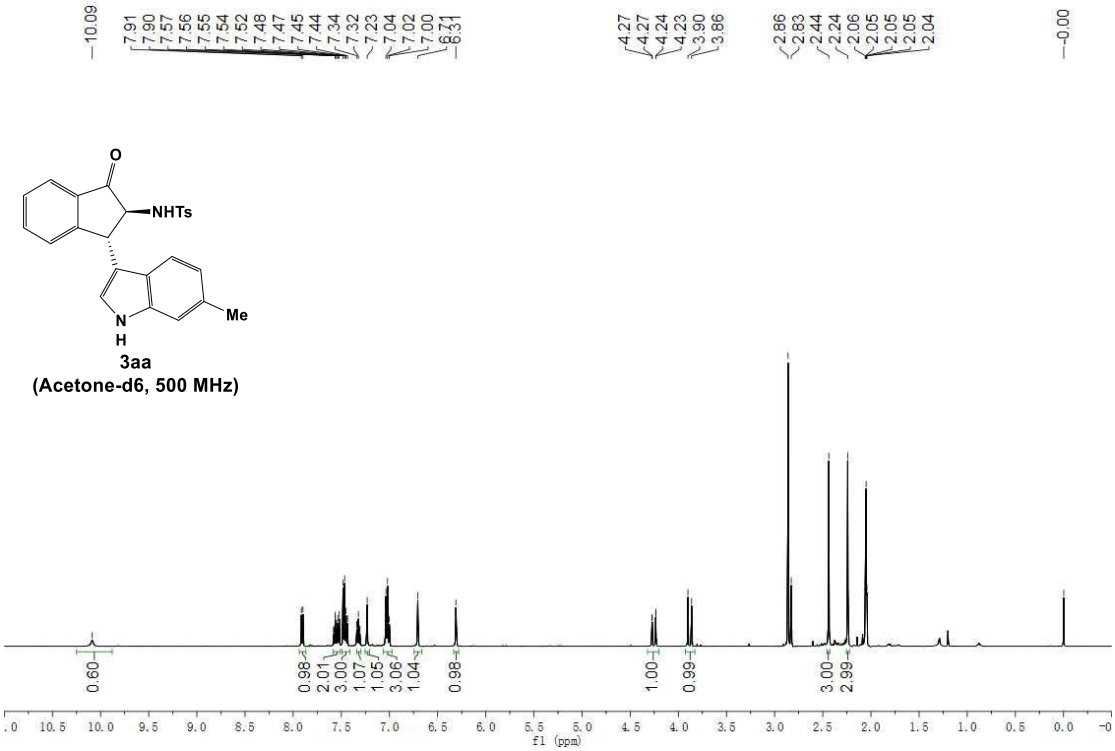
3k'
(Acetone-d6, 500 MHz)

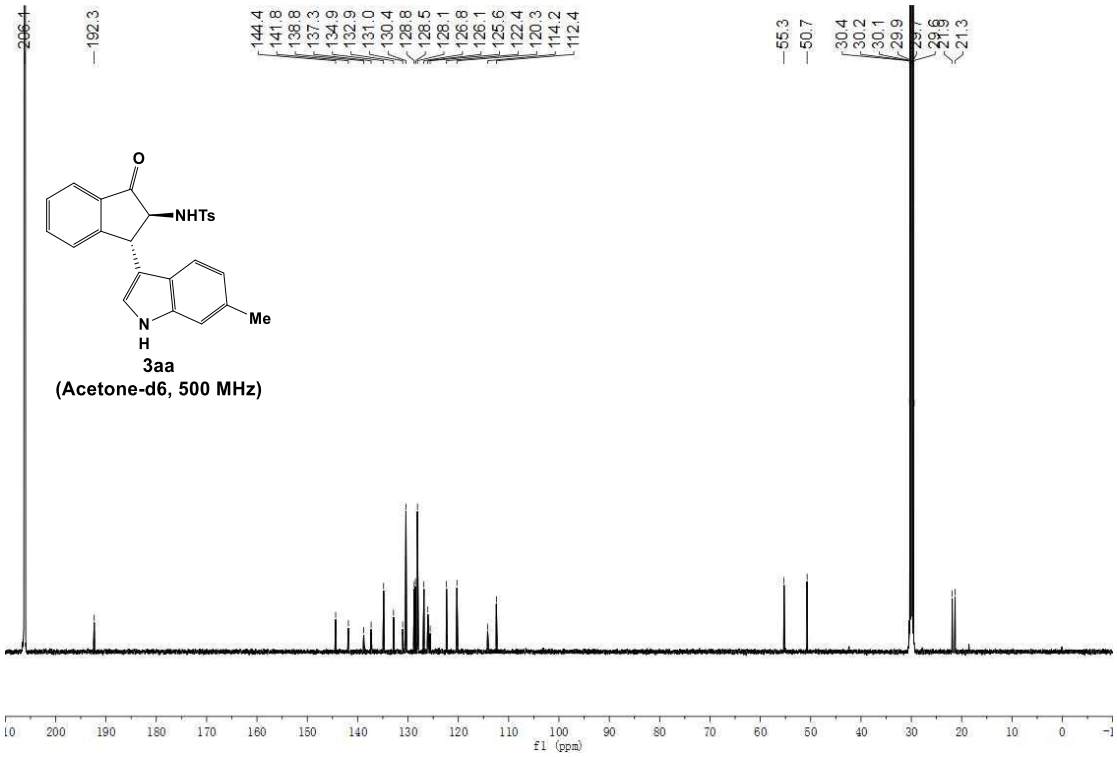

O
NHTs
NH
3l
(Acetone-d6, 400 MHz)
f1 (ppm)

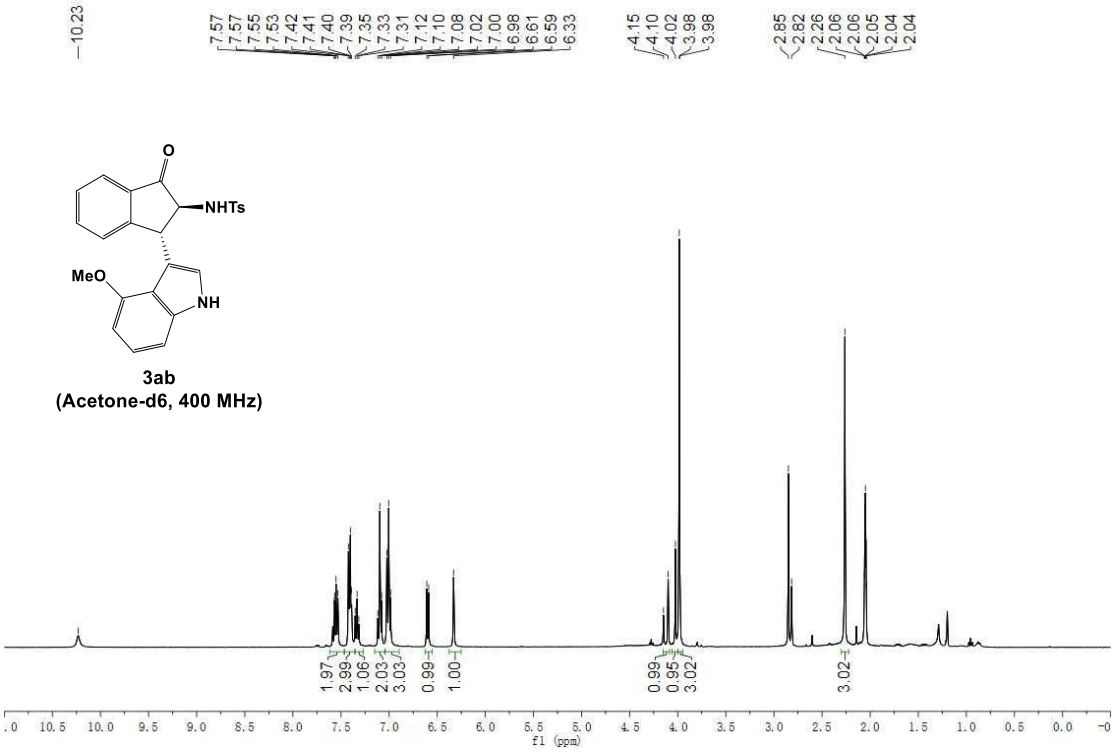

O
NHTs
NH
3l
(Acetone-d6, 400 MHz)
f1 (ppm)


O
NHTs
NH
3l'
(CD2Cl2, 400 MHz)
f1 (ppm)

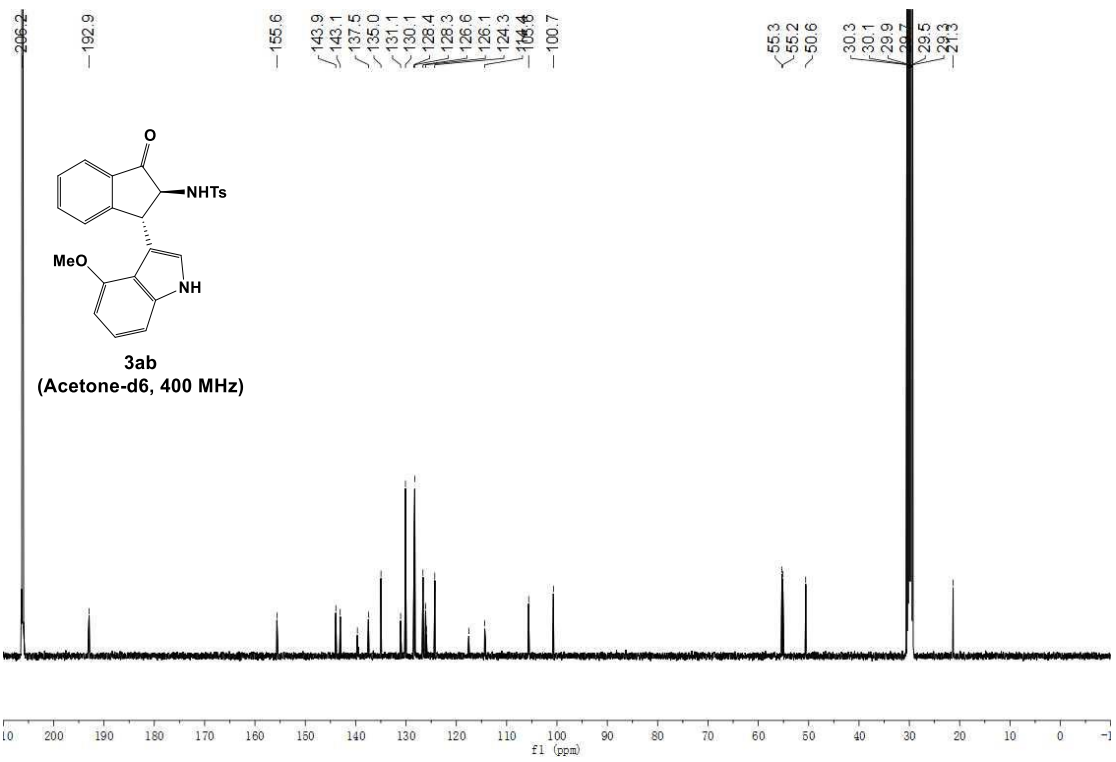

O
NHTs
NH
3l'
(CD2Cl2, 400 MHz)
f1 (ppm)


10.09
7.91
7.90
7.57
7.56
7.55
7.54
7.52
7.48
7.47
7.45
7.44
7.34
7.32
7.23
7.04
7.02
7.00
6.31
4.27
4.27
4.24
4.23
3.90
3.86
2.86
2.83
2.44
2.24
2.06
2.05
2.05
2.05
2.04
0.00
O
NHTs
N
H
Me
3aa
(Acetone-d6, 500 MHz)
0.60
0.98
2.01
3.00
1.07
1.05
3.06
1.04
0.98
1.00
0.99
3.00
2.99
f1 (ppm)

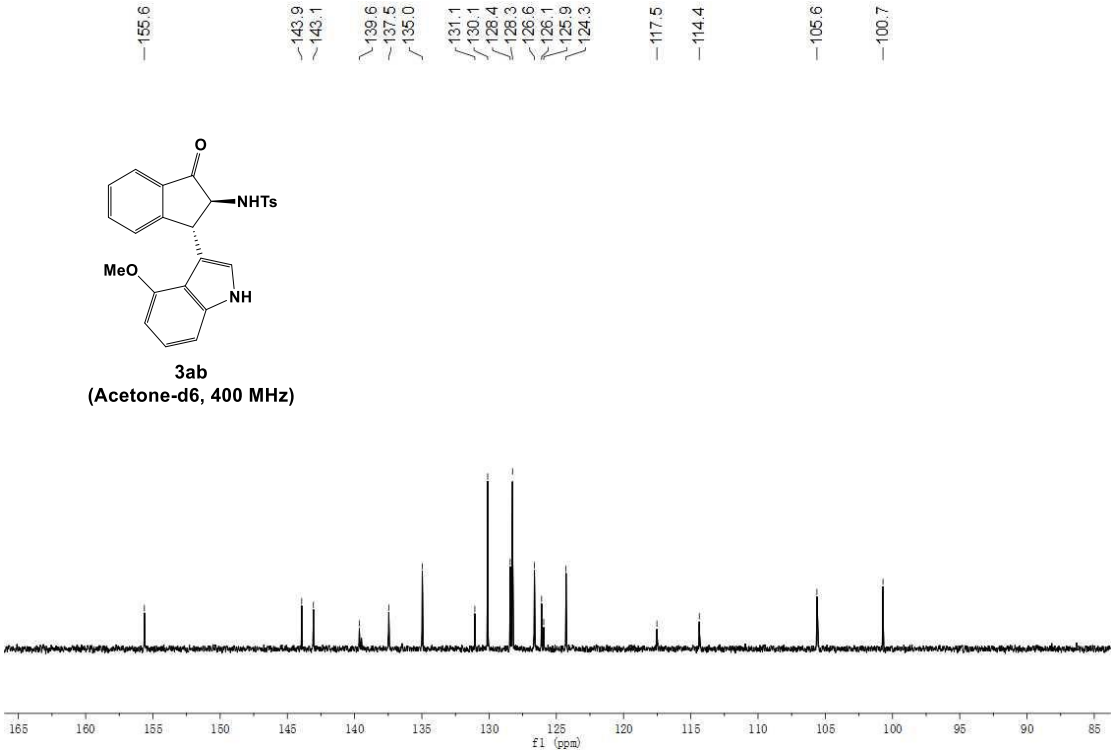

206.1
192.3
144.4
141.8
138.8
137.3
134.9
132.9
131.0
130.4
128.8
128.5
128.1
126.8
126.1
125.6
122.4
120.3
114.2
112.4
55.3
50.7
30.4
30.2
30.1
29.9
21.9
21.3
O
NHTs
N
H
Me
3aa
(Acetone-d6, 500 MHz)
f1 (ppm)



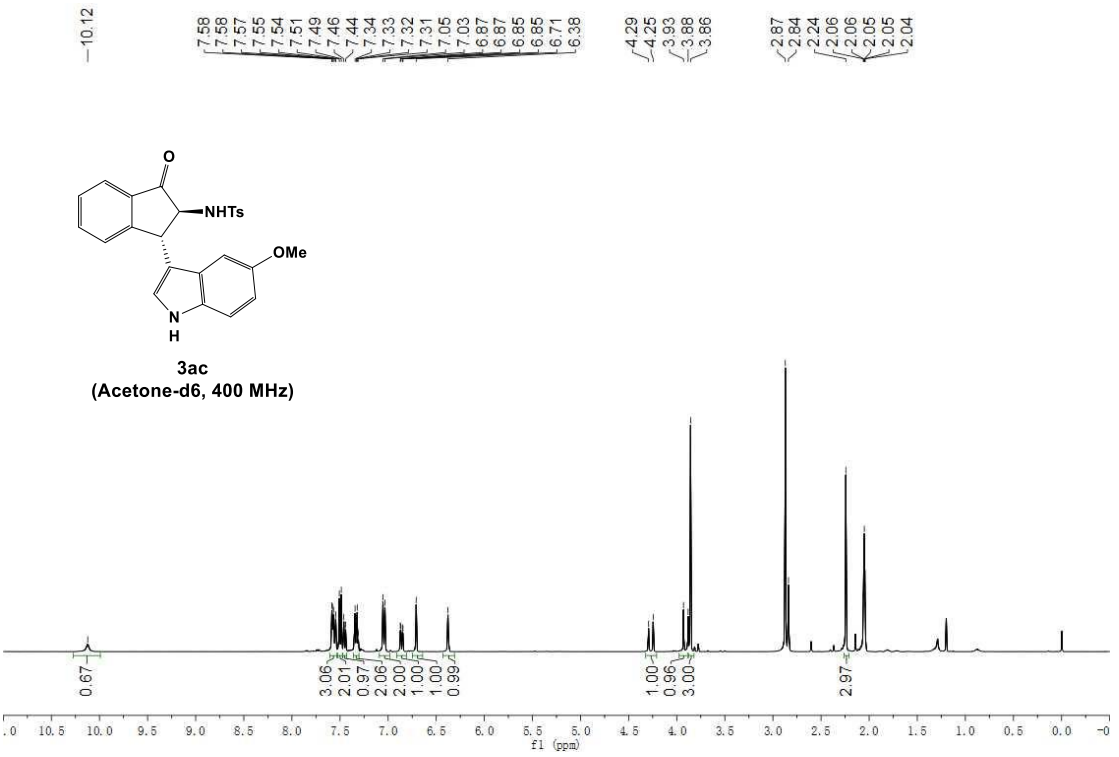
3ab
(Acetone-d6, 400 MHz)



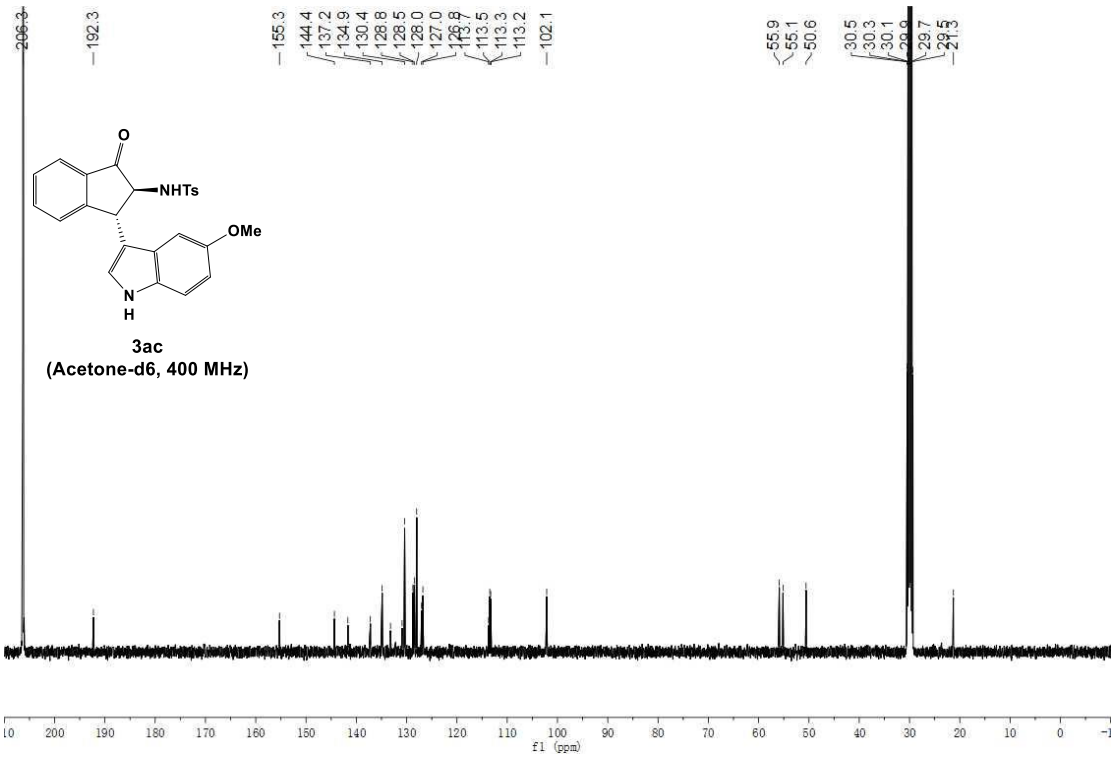
3ab
(Acetone-d6, 400 MHz)



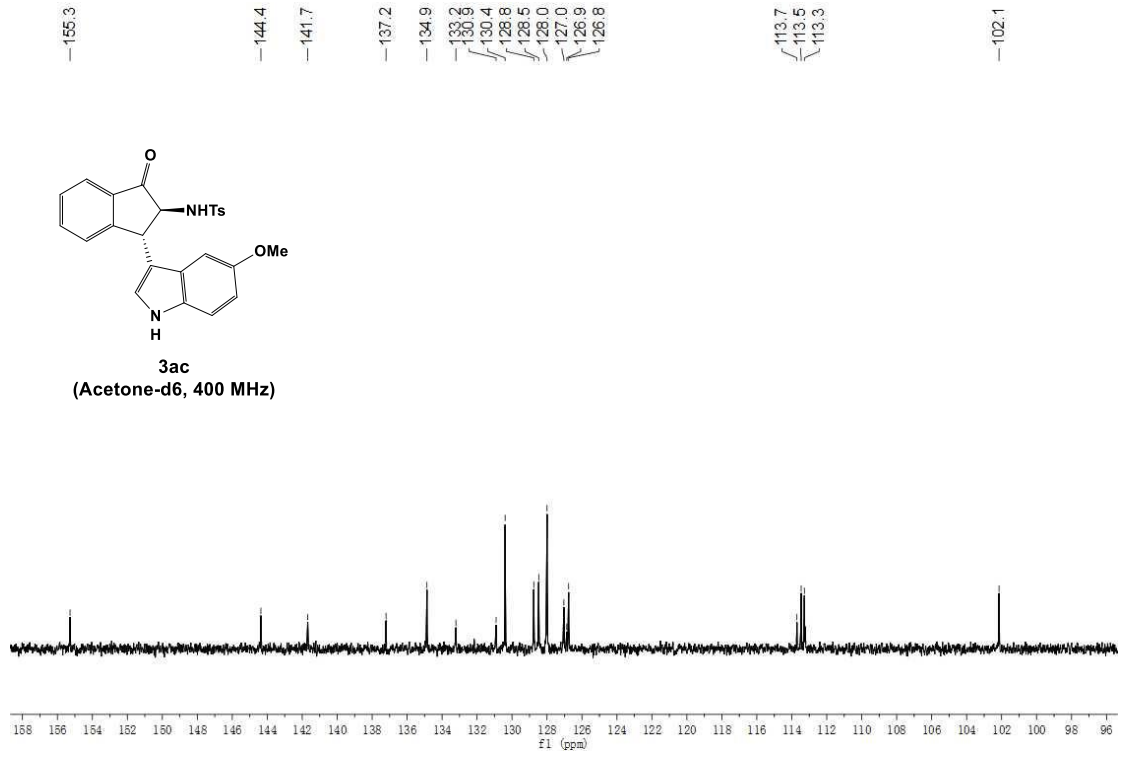
3ab
(Acetone-d6, 400 MHz)



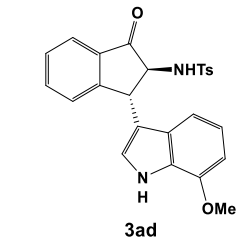
3ac
(Acetone-d6, 400 MHz)



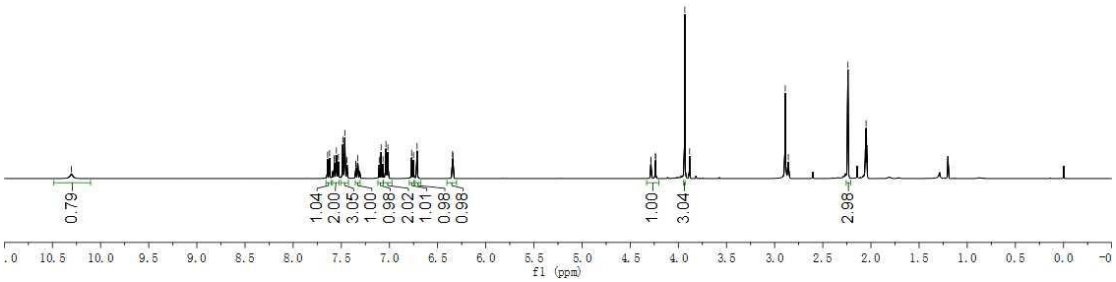
3ac
(Acetone-d6, 400 MHz)

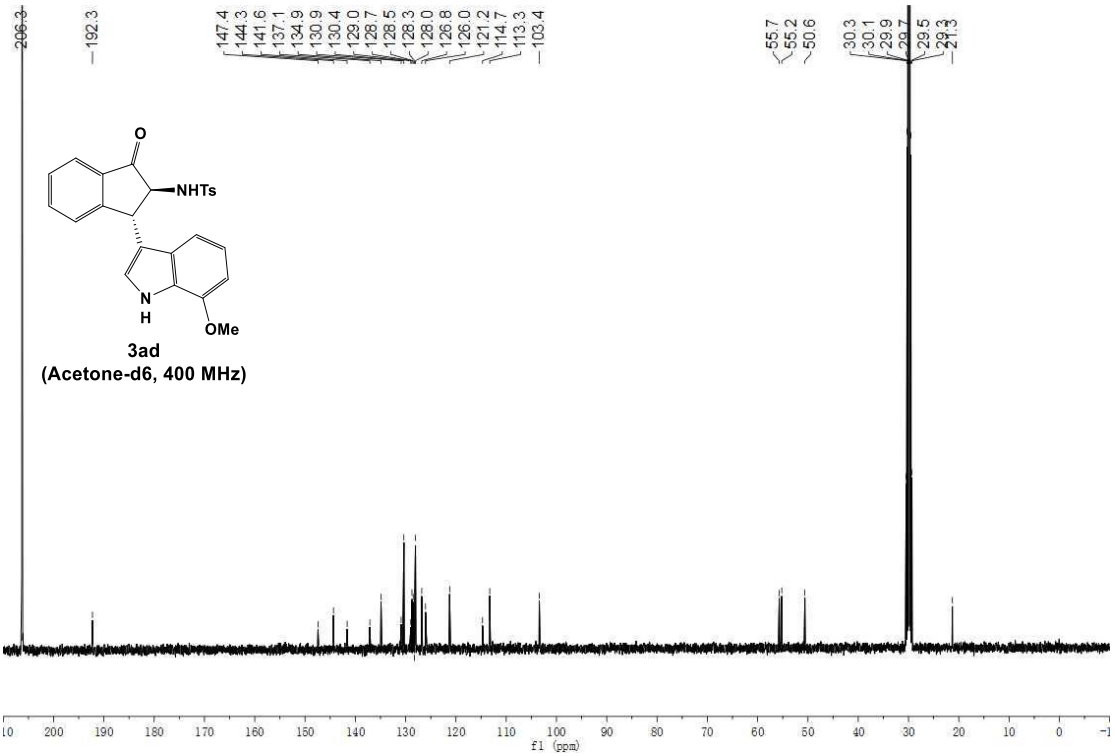


3ac
(Acetone-d6, 400 MHz)

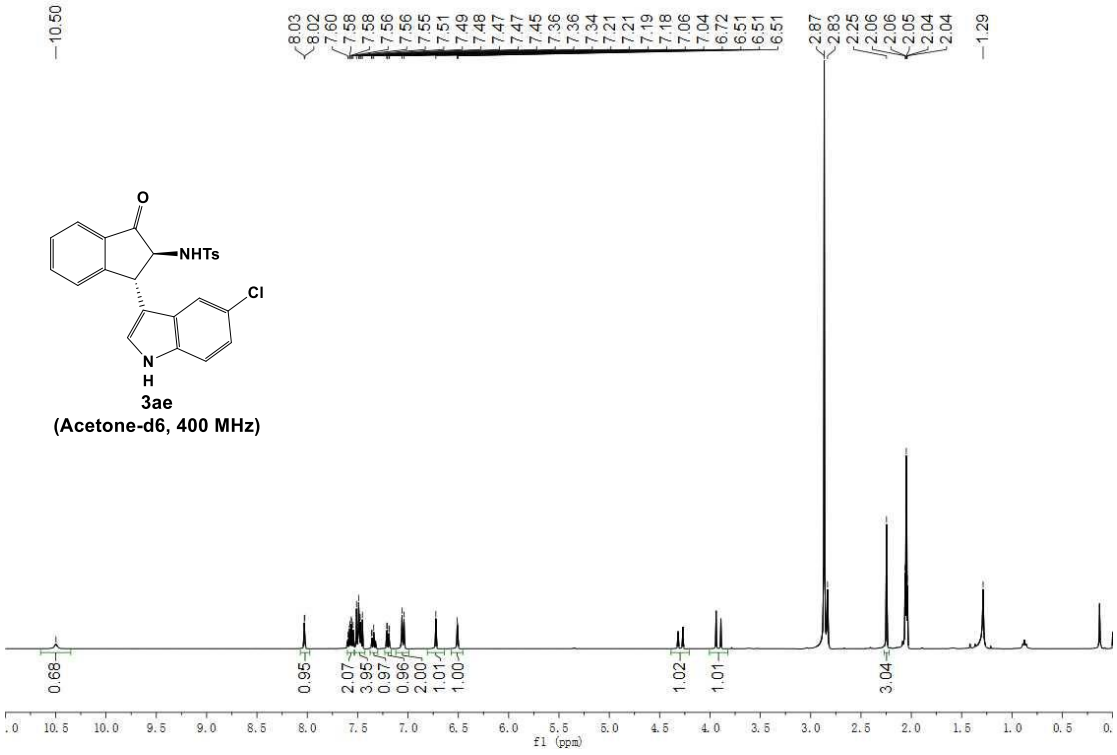


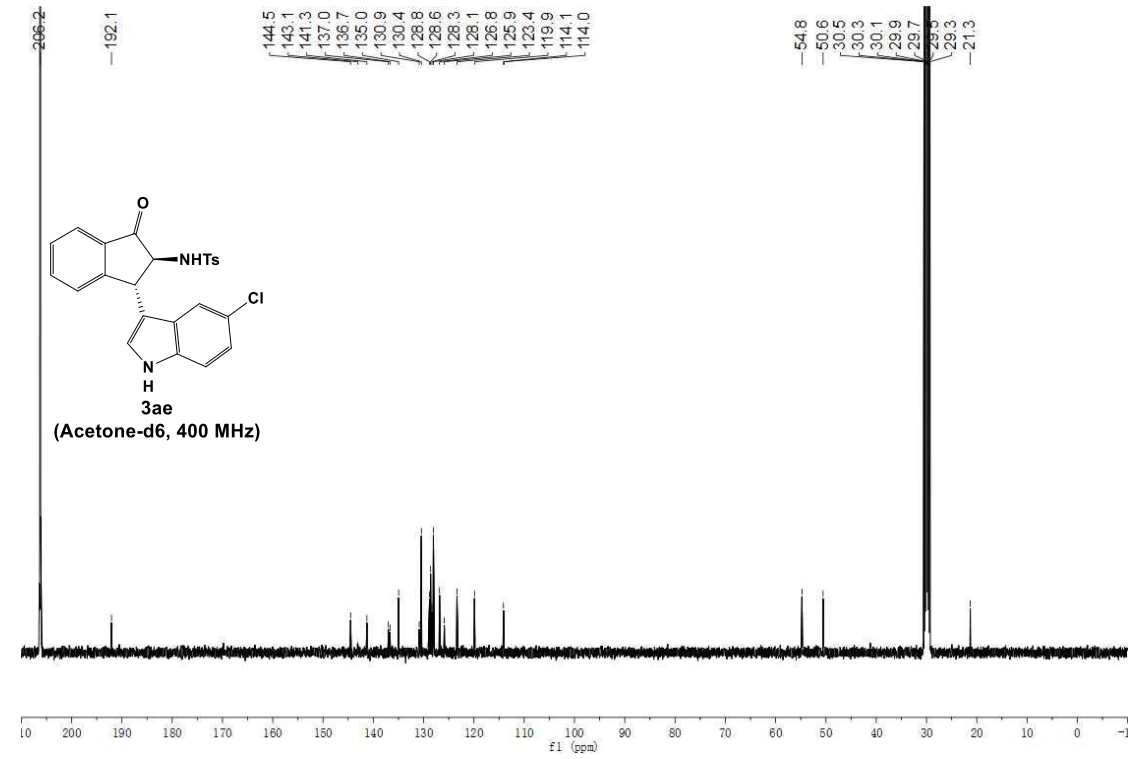
3ad
(Acetone-d6, 400 MHz)

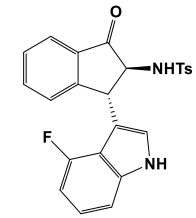




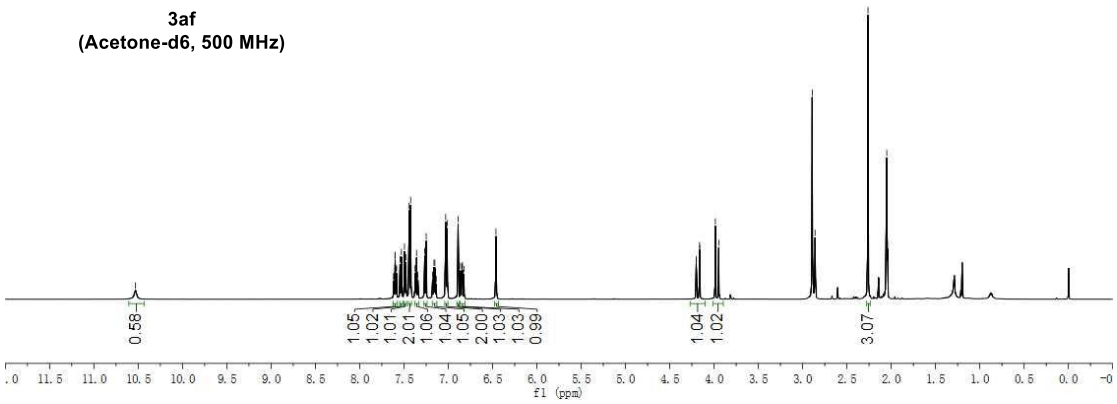
3ad
(Acetone-d6, 400 MHz)

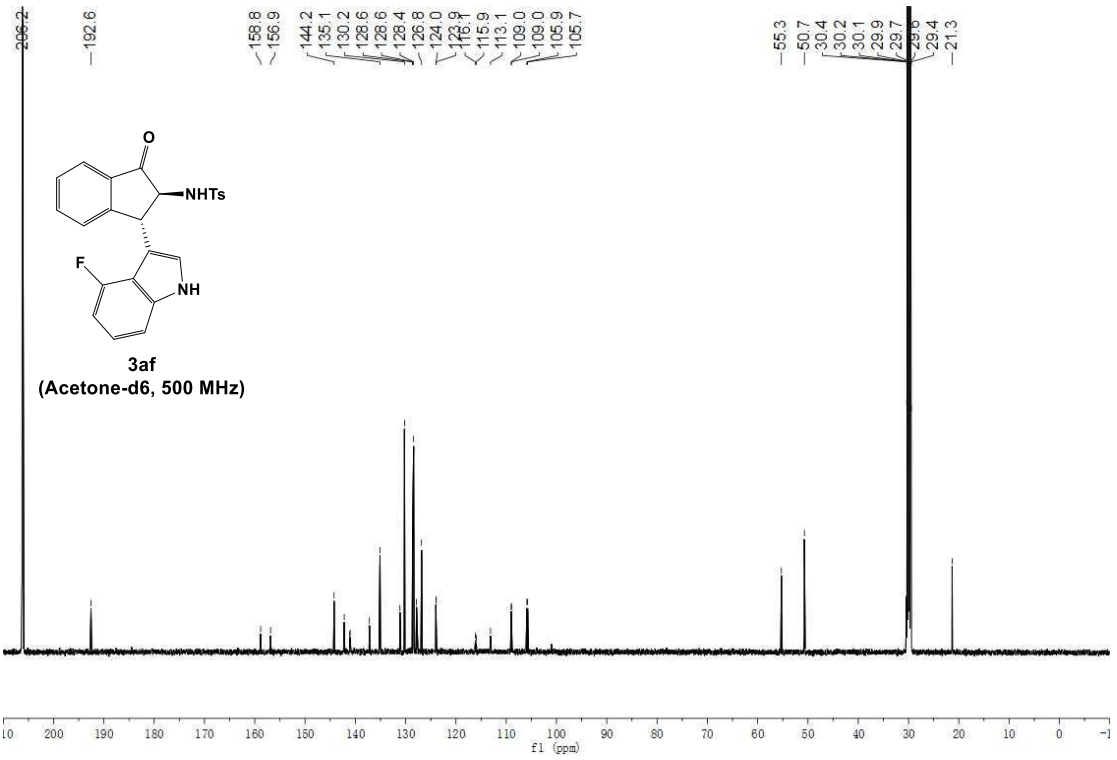

10.50
8.03
8.02
7.60
7.58
7.58
7.56
7.56
7.55
7.51
7.49
7.48
7.47
7.47
7.45
7.36
7.36
7.34
7.21
7.21
7.19
7.18
7.06
7.04
6.72
6.51
6.51
6.51
2.87
2.83
2.25
2.06
2.06
2.05
2.04
2.04
1.29
O
NHTs
Cl
N
H
3ae
(Acetone-d6, 400 MHz)
0.68
0.95
2.07
3.95
0.97
0.96
2.00
1.01
1.00
1.02
1.01
3.04
f1 (ppm)


206.2
192.1
144.5
143.1
141.3
137.0
136.7
135.0
130.9
130.4
128.8
128.6
128.3
128.1
126.8
125.9
123.4
119.9
114.1
114.0
54.8
50.6
30.5
30.3
30.1
29.9
29.7
29.5
29.3
21.3
O
NHTs
Cl
N
H
3ae
(Acetone-d6, 400 MHz)
f1 (ppm)

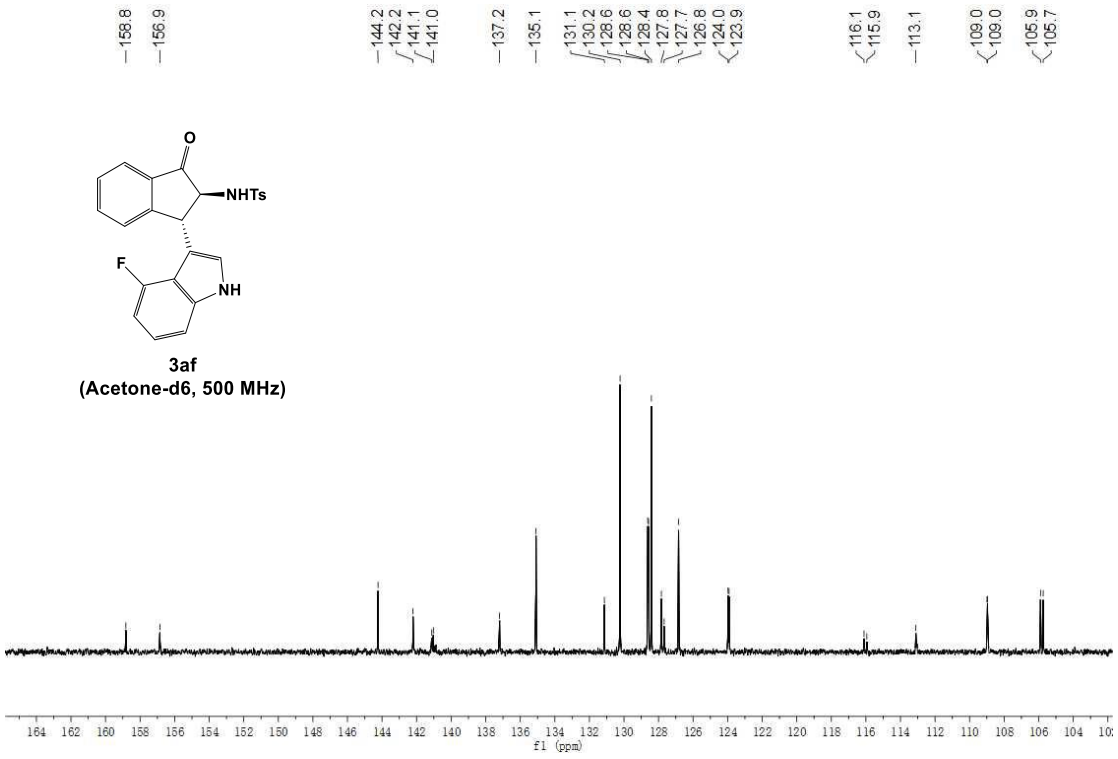


3af
(Acetone-d6, 500 MHz)

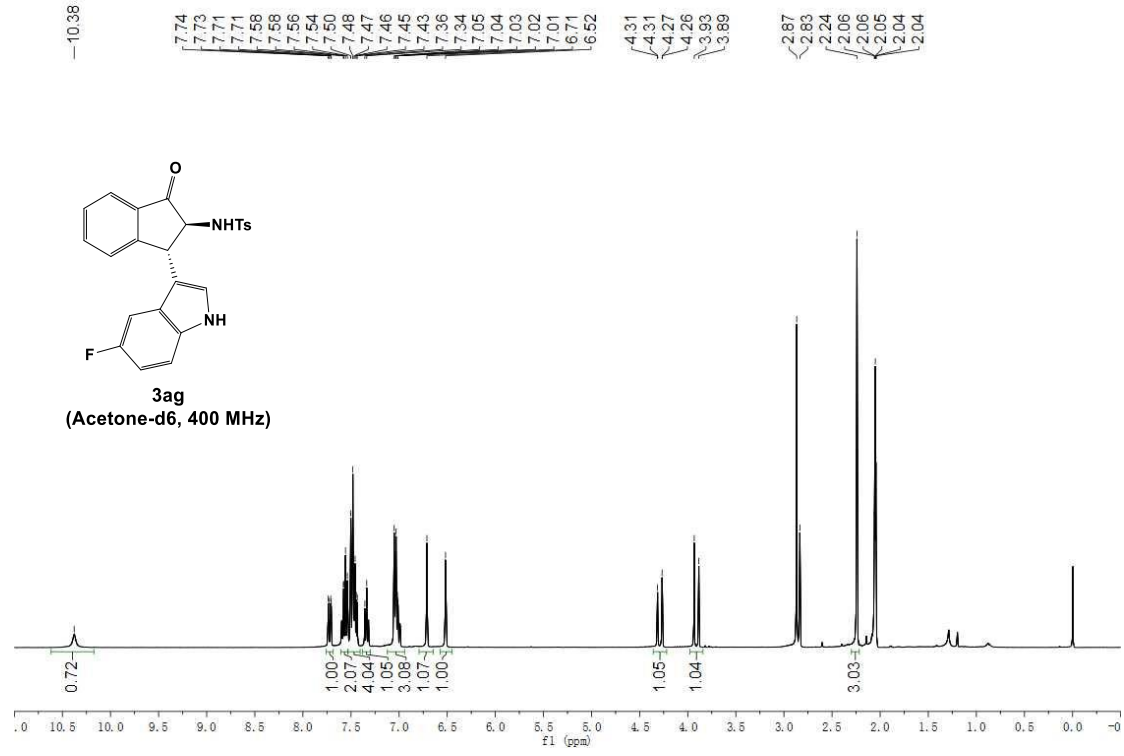




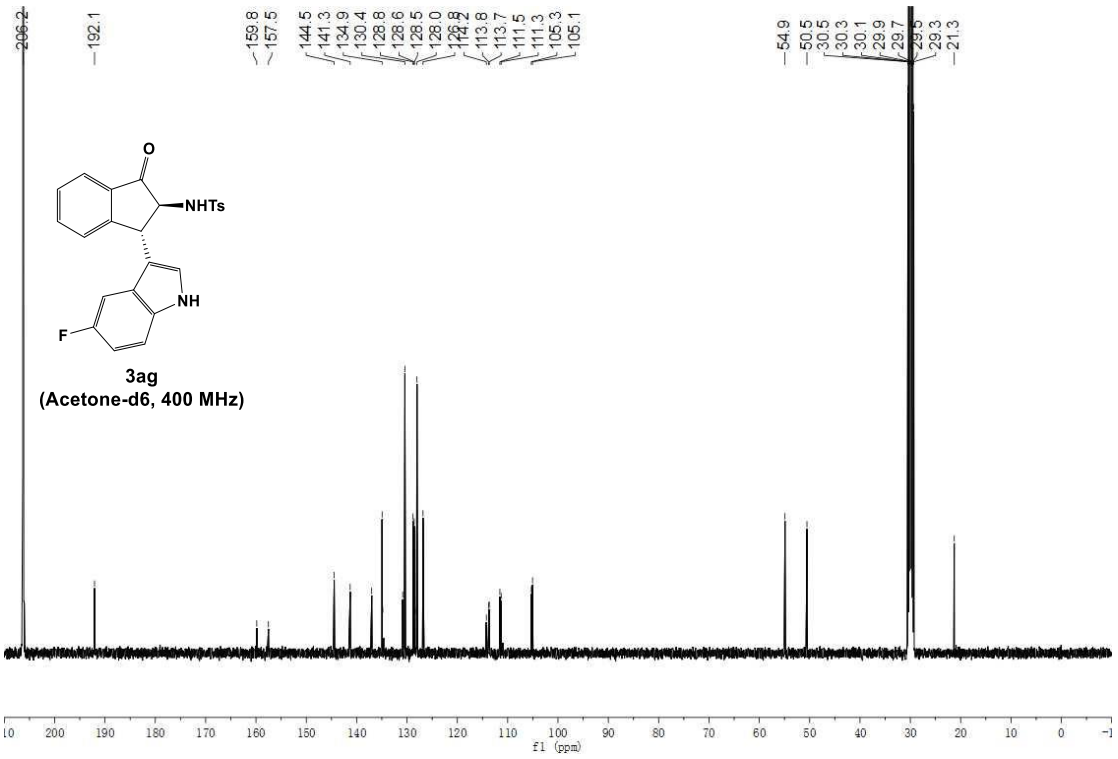
3af
(Acetone-d6, 500 MHz)



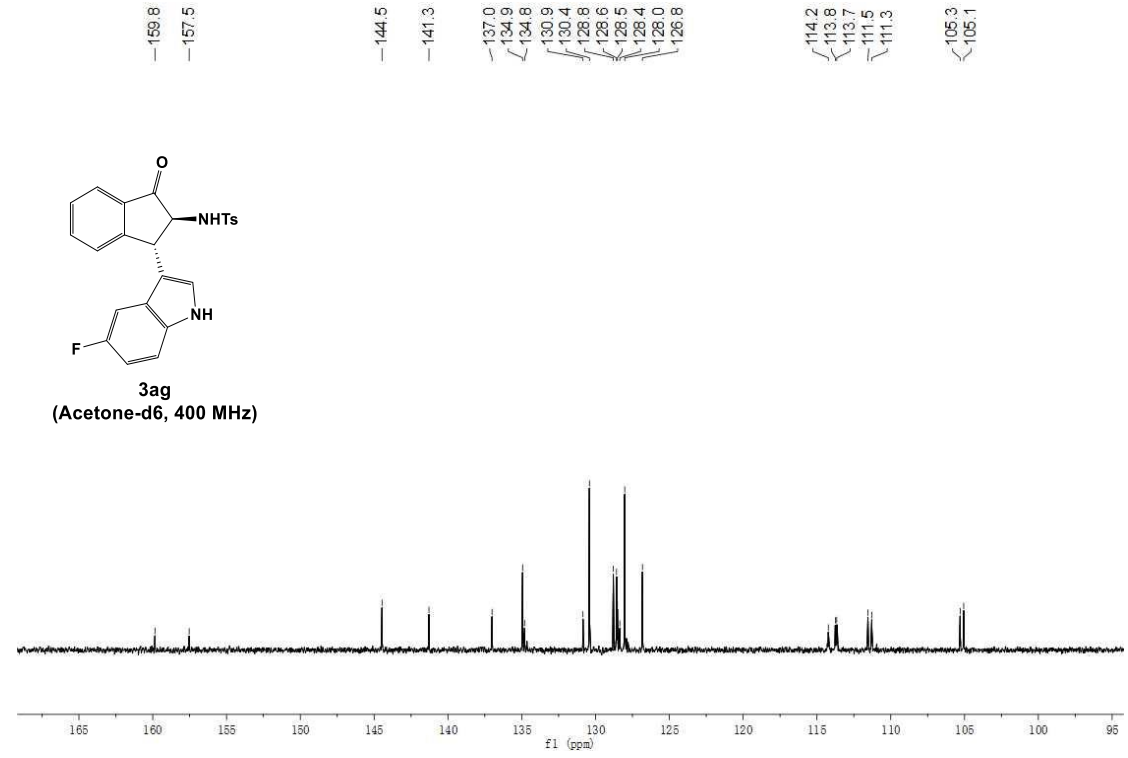
3af
(Acetone-d6, 500 MHz)



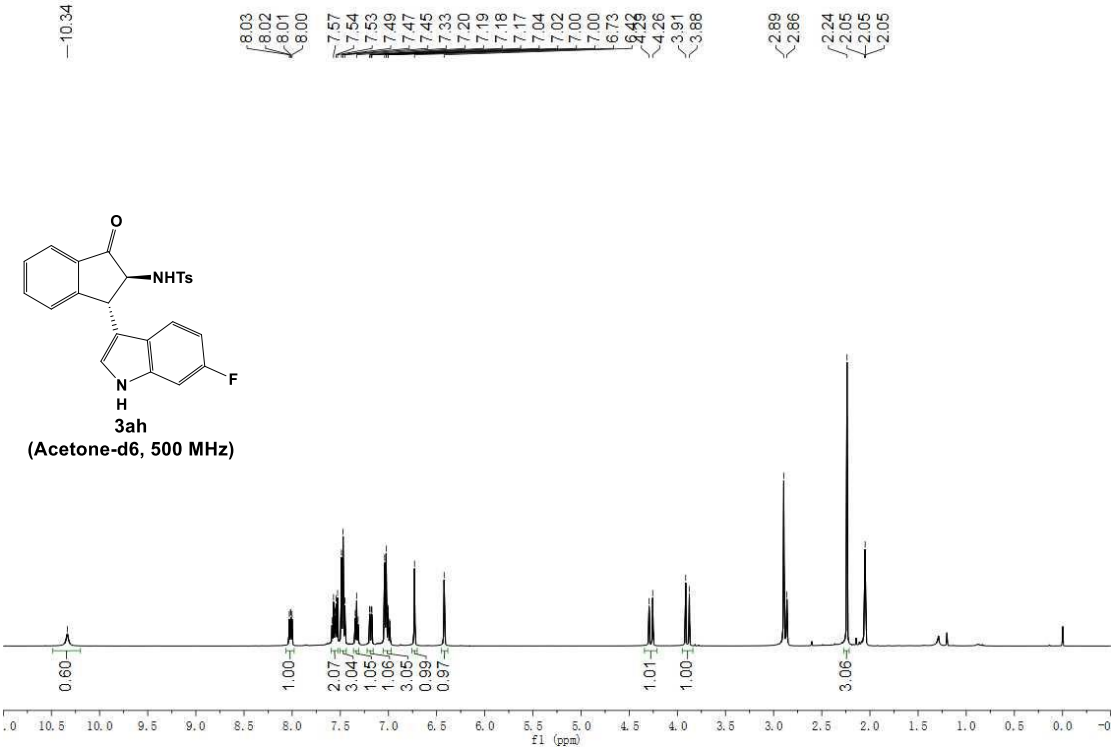
3ag
(Acetone-d6, 400 MHz)

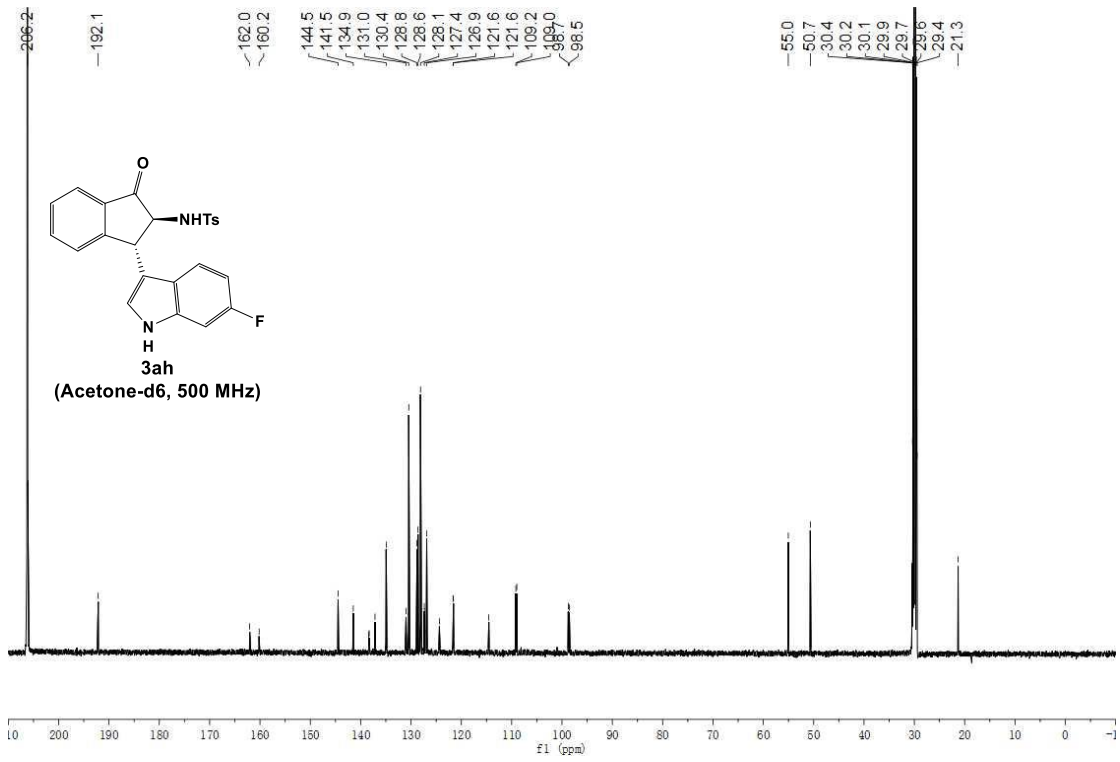


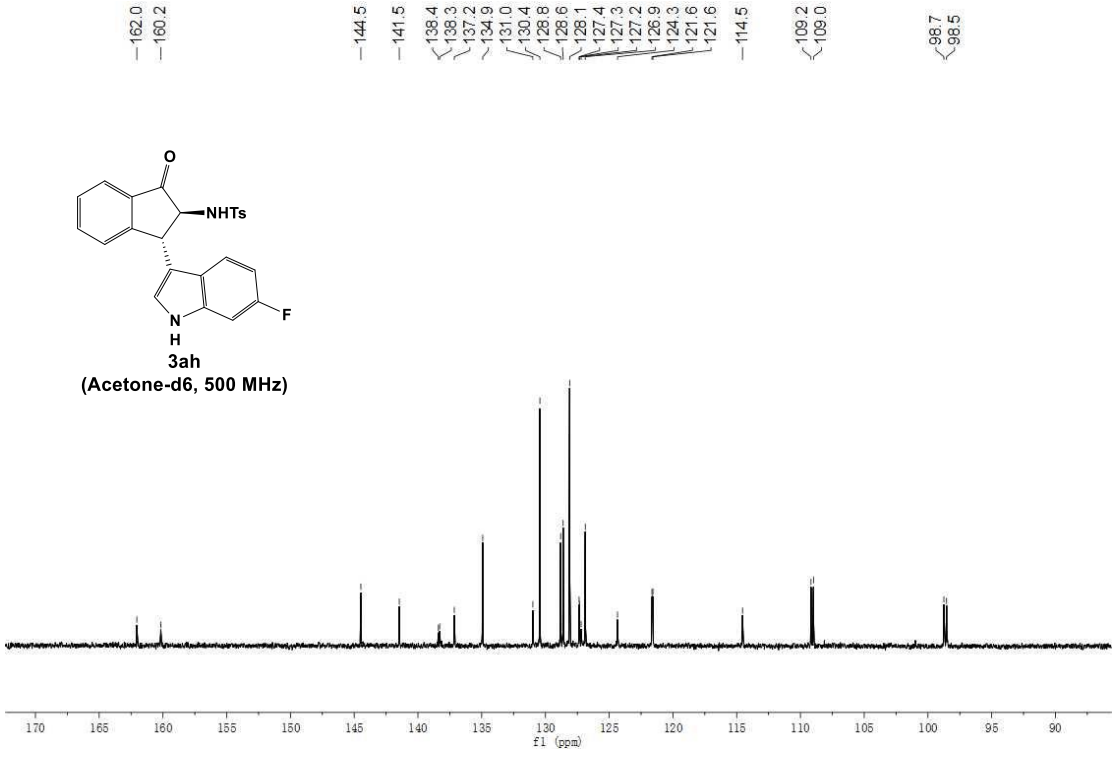
3ag
(Acetone-d6, 400 MHz)

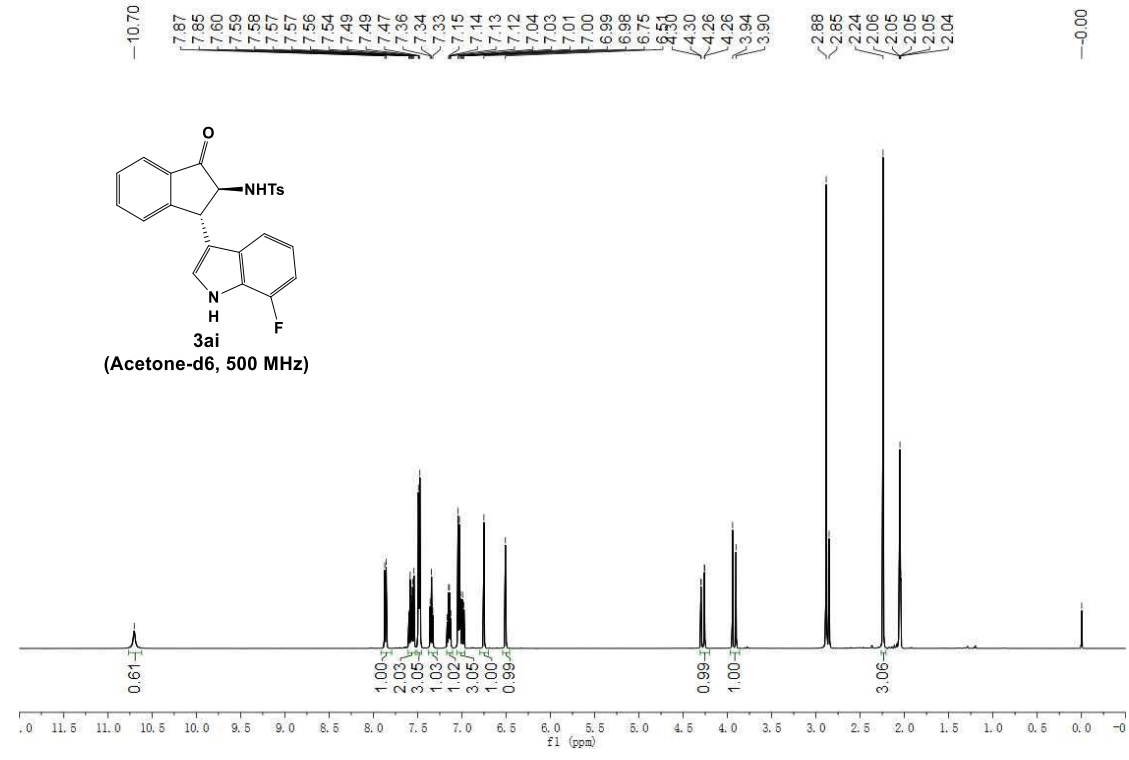


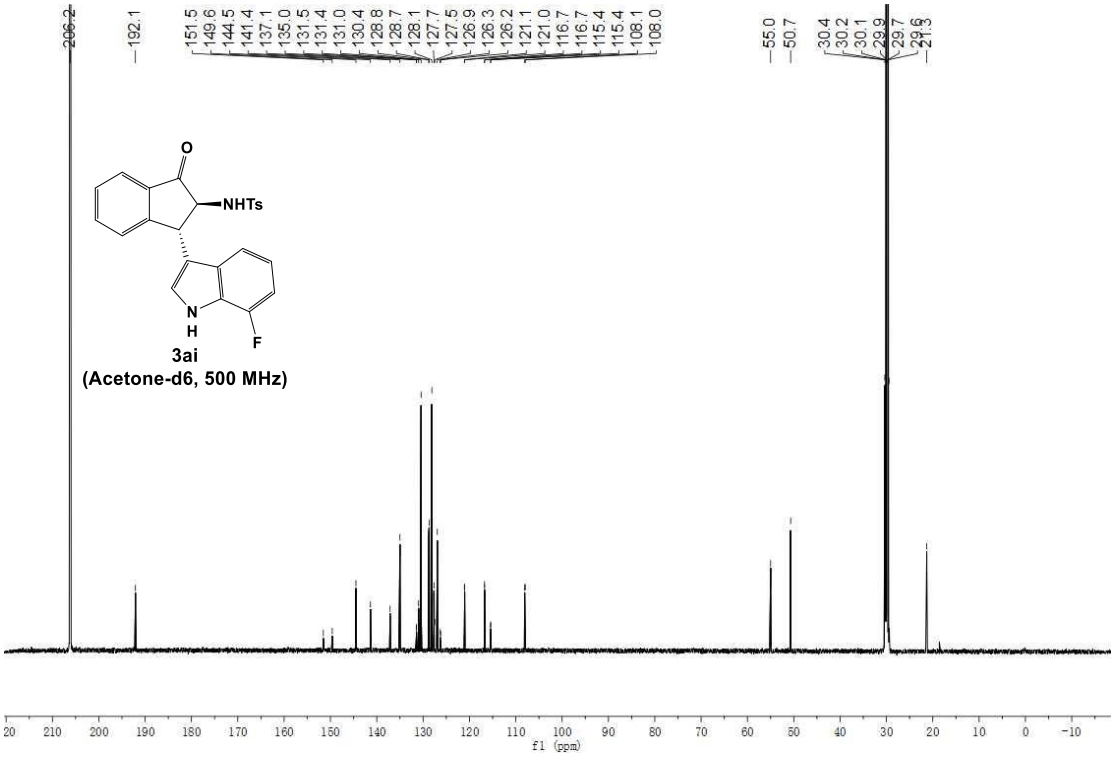
3ag
(Acetone-d6, 400 MHz)

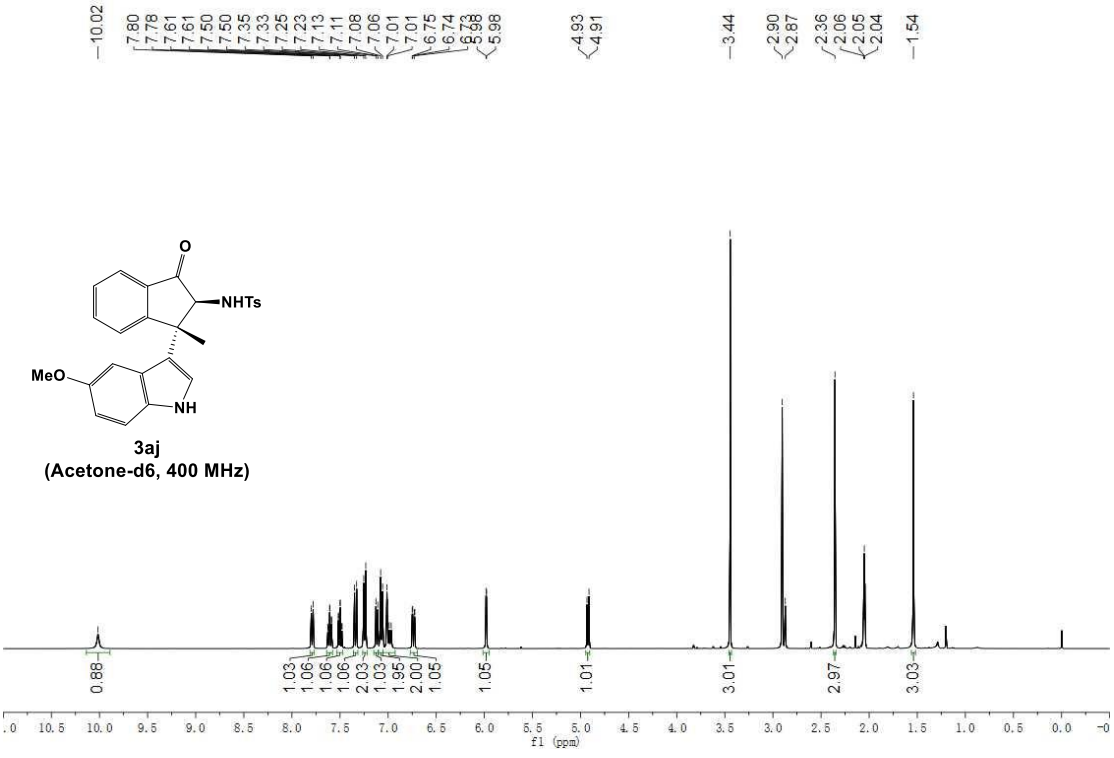

10.34
8.03
8.02
8.01
8.00
7.57
7.54
7.53
7.49
7.47
7.45
7.33
7.20
7.19
7.18
7.17
7.04
7.02
7.00
7.00
6.73
4.29
4.26
3.91
3.88
2.89
2.86
2.24
2.05
2.05
2.05
O
NHTs
N
H
F
3ah
(Acetone-d6, 500 MHz)
0.60
1.00
2.07
3.04
1.05
1.06
3.05
0.99
0.97
1.01
1.00
3.06
f1 (ppm)

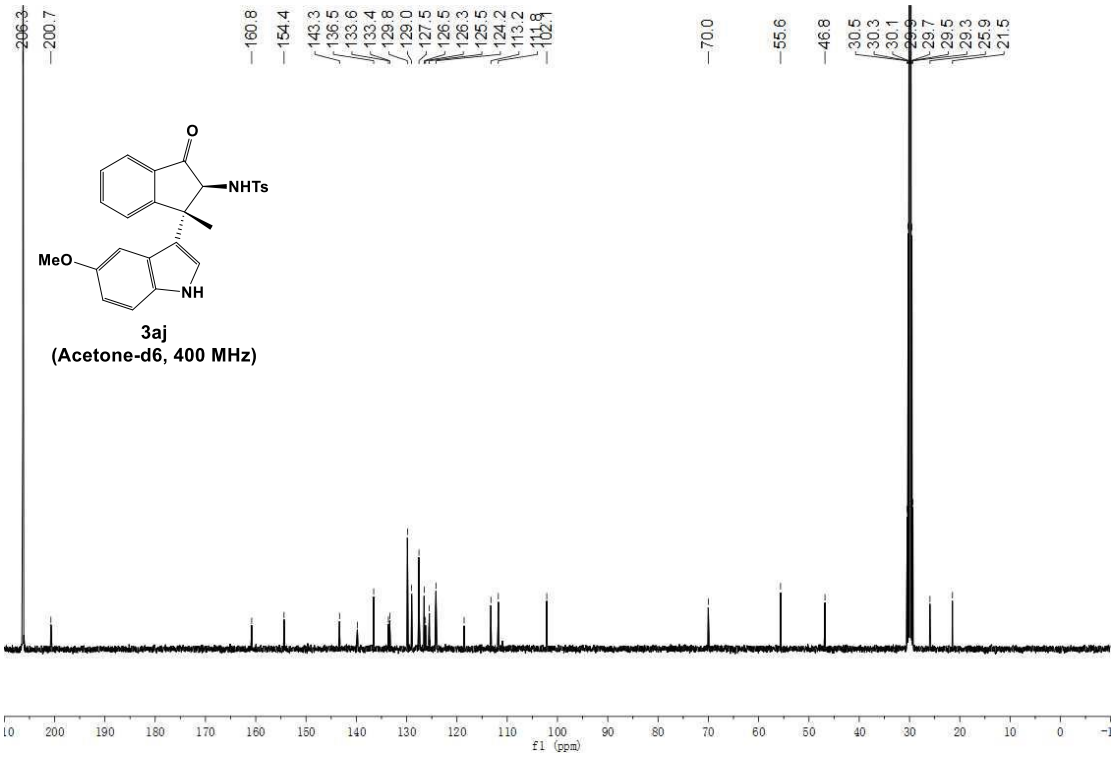

206.2
192.1
162.0
160.2
144.5
141.5
134.9
131.0
130.4
128.8
128.6
128.1
127.4
126.9
121.6
121.6
109.2
109.0
98.7
98.5
55.0
50.7
30.4
30.2
30.1
29.9
29.7
29.6
29.4
21.3
O
NHTs
N
H
F
3ah
(Acetone-d6, 500 MHz)
f1 (ppm)


162.0
160.2
144.5
141.5
138.4
138.3
137.2
134.9
131.0
130.4
128.8
128.6
128.1
127.4
127.3
127.2
126.9
124.3
121.6
121.6
114.5
109.2
109.0
98.7
98.5
O
NHTs
N
H
F
3ah
(Acetone-d6, 500 MHz)
f1 (ppm)

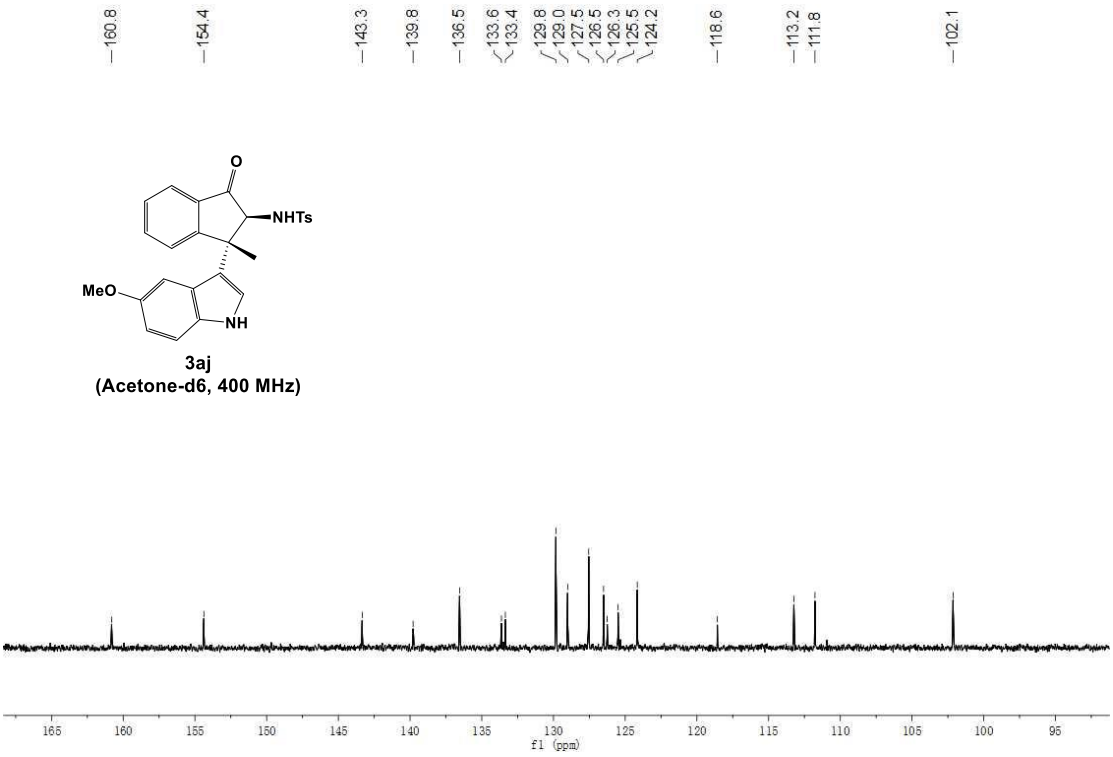

10.70
7.87
7.85
7.60
7.59
7.58
7.57
7.57
7.56
7.54
7.49
7.49
7.47
7.36
7.34
7.33
7.15
7.14
7.13
7.12
7.04
7.03
7.01
7.00
6.99
6.98
6.75
6.51
4.30
4.30
4.26
4.26
3.94
3.90
2.88
2.85
2.24
2.06
2.05
2.05
2.05
2.04
0.00
O
NHTs
N
H
F
3ai
(Acetone-d6, 500 MHz)
0.61
1.00
2.03
3.05
1.03
1.02
3.05
1.00
0.99
0.99
1.00
3.06
f1 (ppm)


206.2
192.1
151.5
149.6
144.5
141.4
137.1
135.0
131.5
131.4
131.0
130.4
128.8
128.7
128.1
127.7
127.5
126.9
126.3
126.2
121.1
121.0
116.7
116.7
115.4
108.1
108.0
55.0
50.7
30.4
30.2
30.1
29.9
29.7
29.6
21.3
O
NHTs
N
H
F
3ai
(Acetone-d6, 500 MHz)
f1 (ppm)

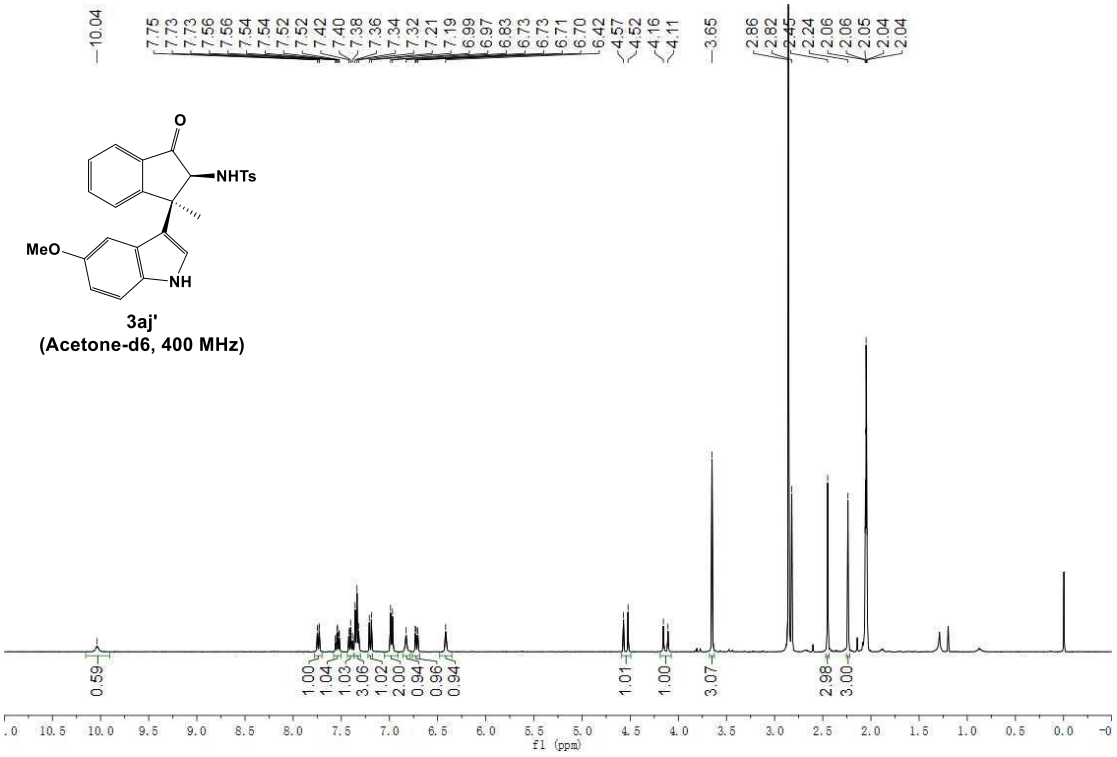

10.02
7.80
7.78
7.61
7.61
7.50
7.50
7.35
7.33
7.25
7.23
7.13
7.11
7.08
7.06
7.01
7.01
6.75
6.74
6.73
6.73
5.98
4.93
4.91
3.44
2.90
2.87
2.36
2.06
2.05
2.04
1.54
O
NHTs
MeO
NH
3aj
(Acetone-d6, 400 MHz)
0.88
1.03
1.06
1.06
1.06
2.03
1.03
1.95
2.00
1.05
1.05
1.01
3.01
2.97
3.03
f1 (ppm)



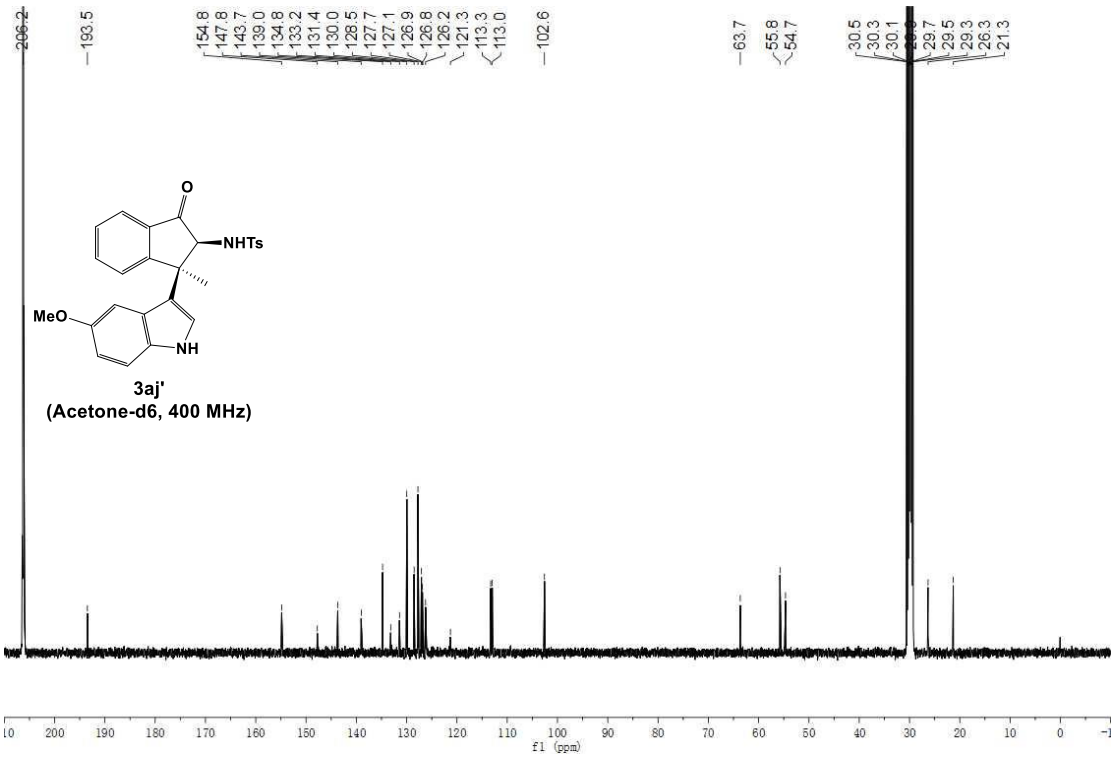
3aj
(Acetone-d6, 400 MHz)



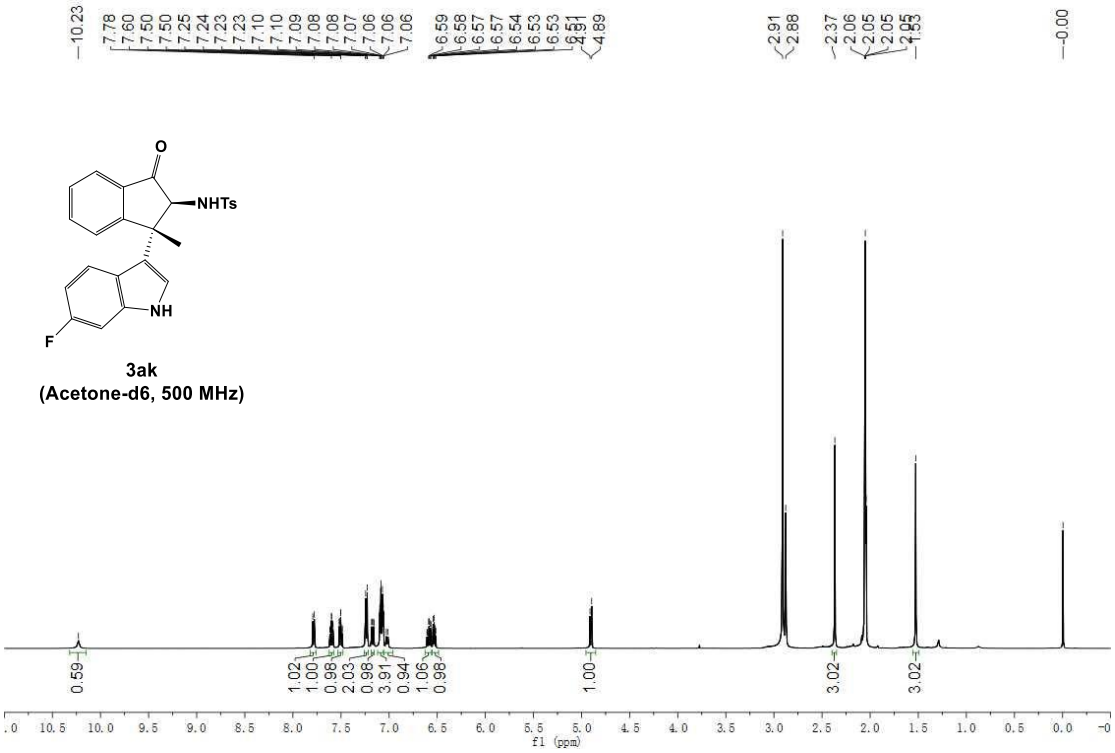
3aj
(Acetone-d6, 400 MHz)

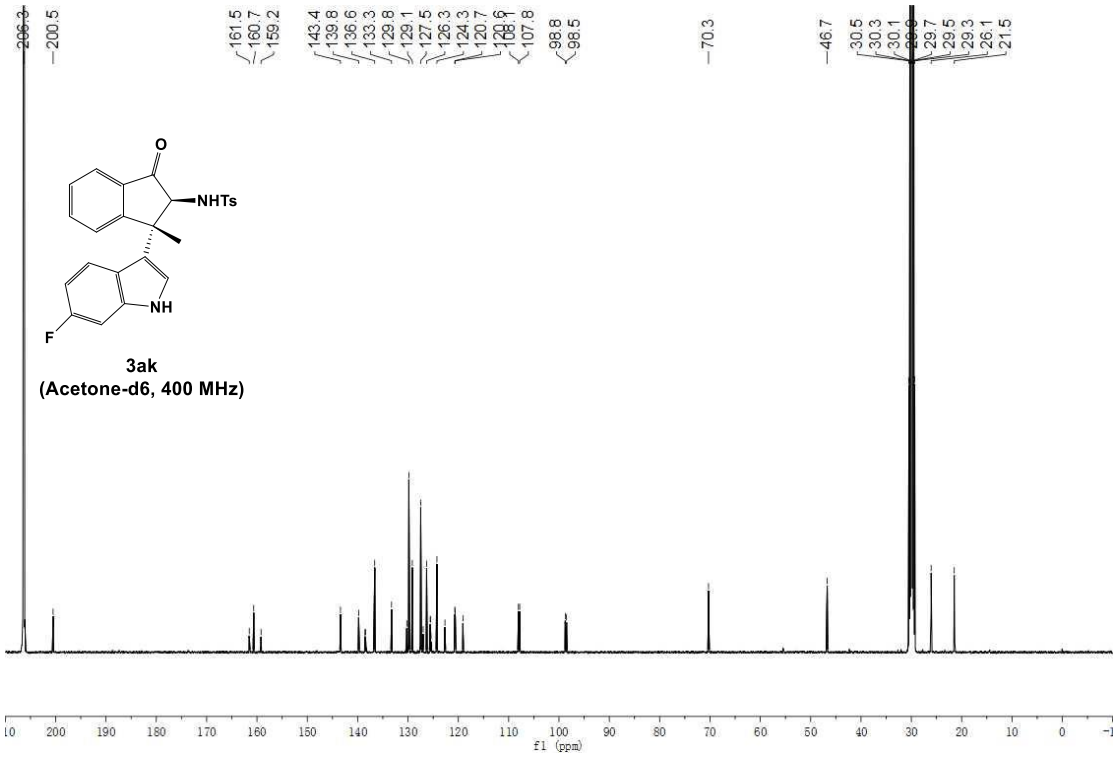


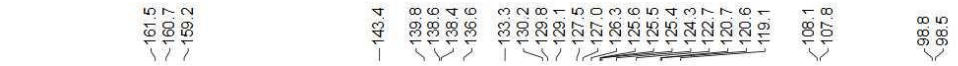
3aj'
(Acetone-d6, 400 MHz)

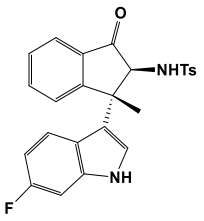


3aj'
(Acetone-d6, 400 MHz)

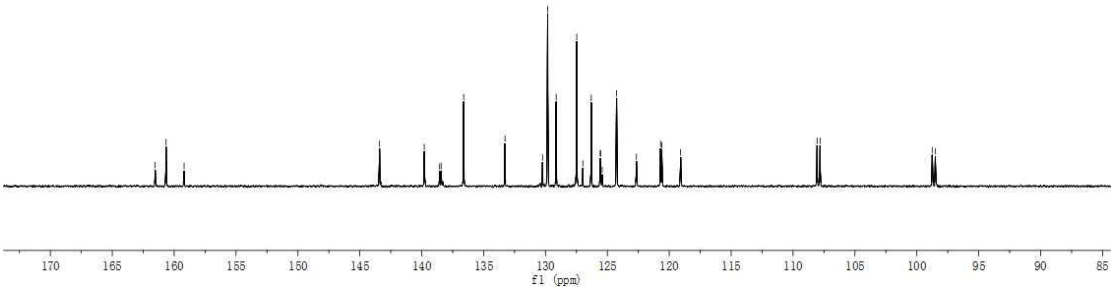

O
NHTs
NH
F
3ak
(Acetone-d6, 500 MHz)
f1 (ppm)

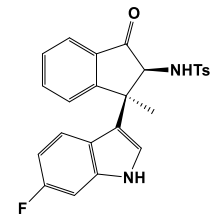

O
NHTs
NH
F
3ak
(Acetone-d6, 400 MHz)
f1 (ppm)



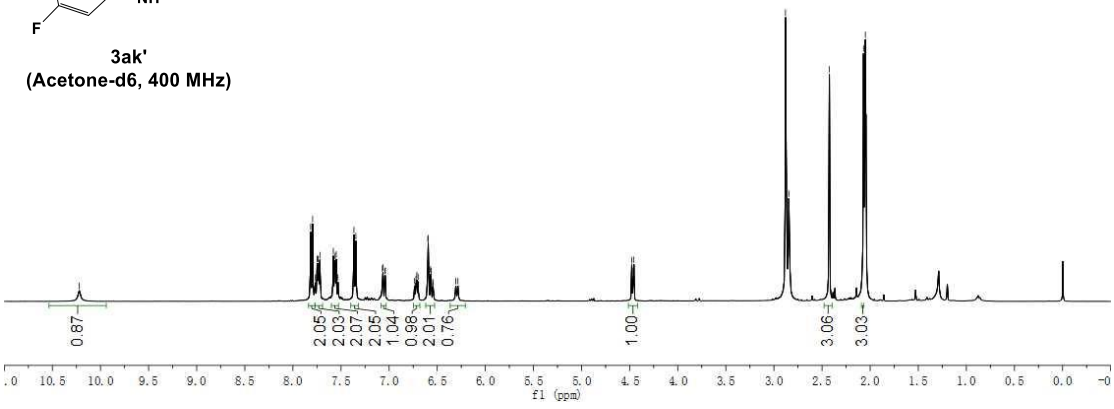


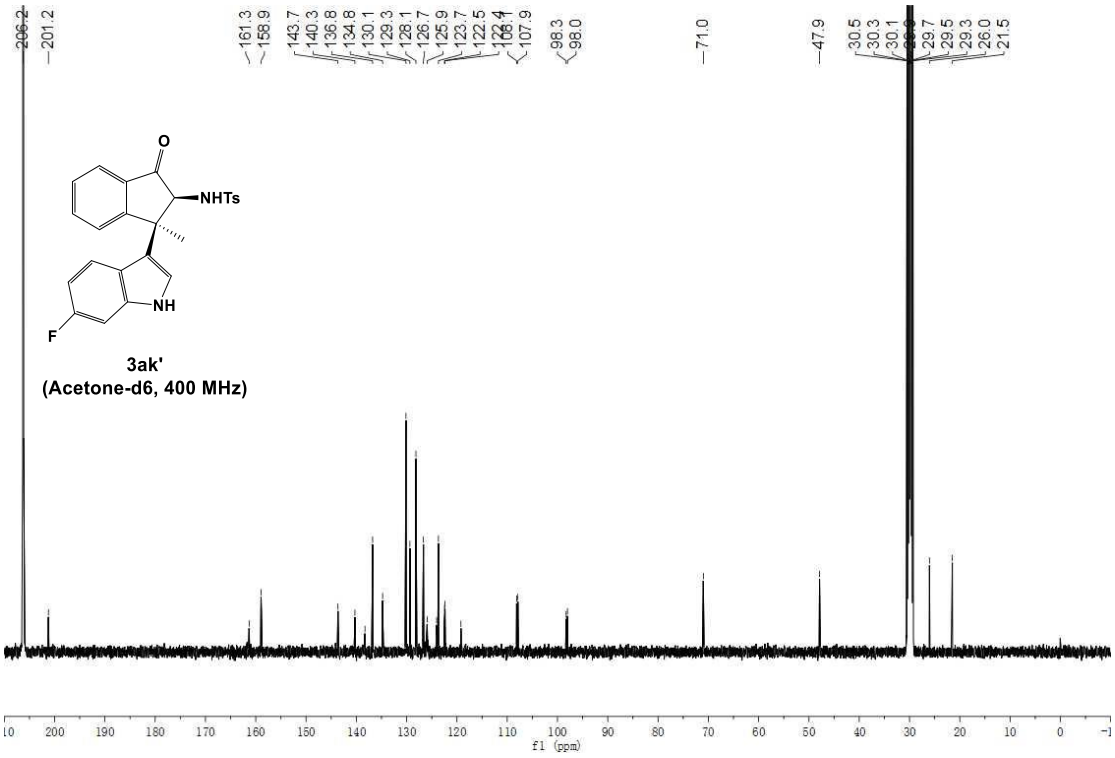
3ak
(Acetone-d6, 400 MHz)

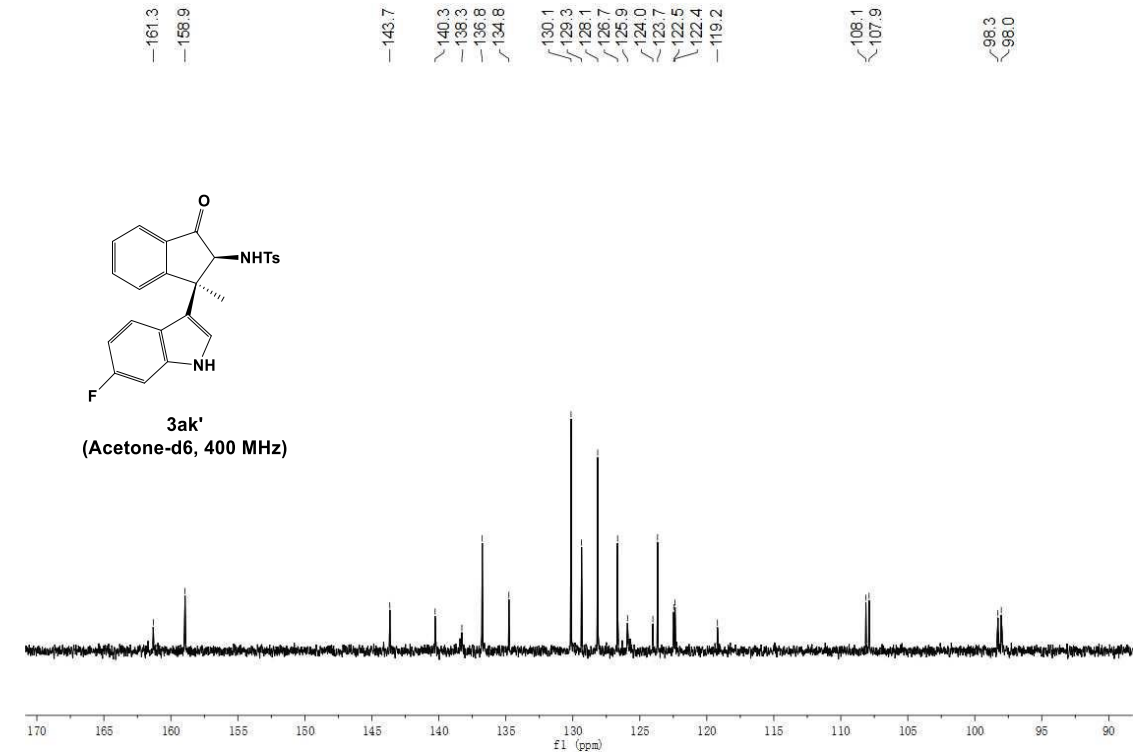


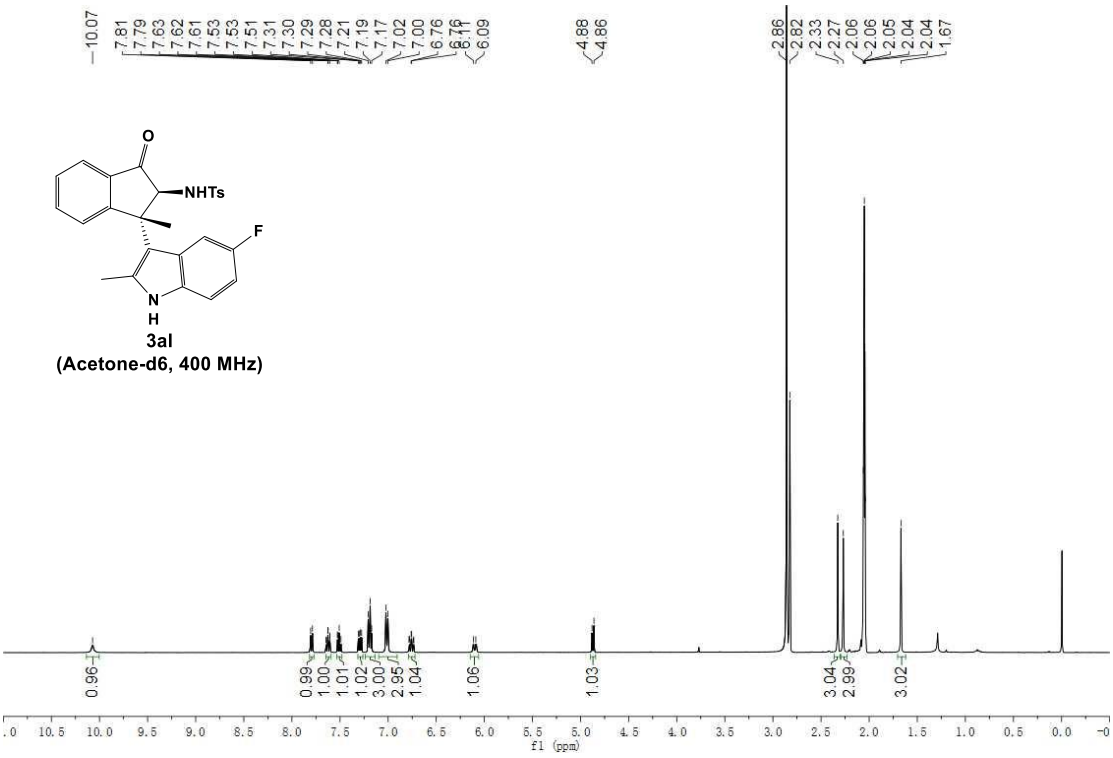


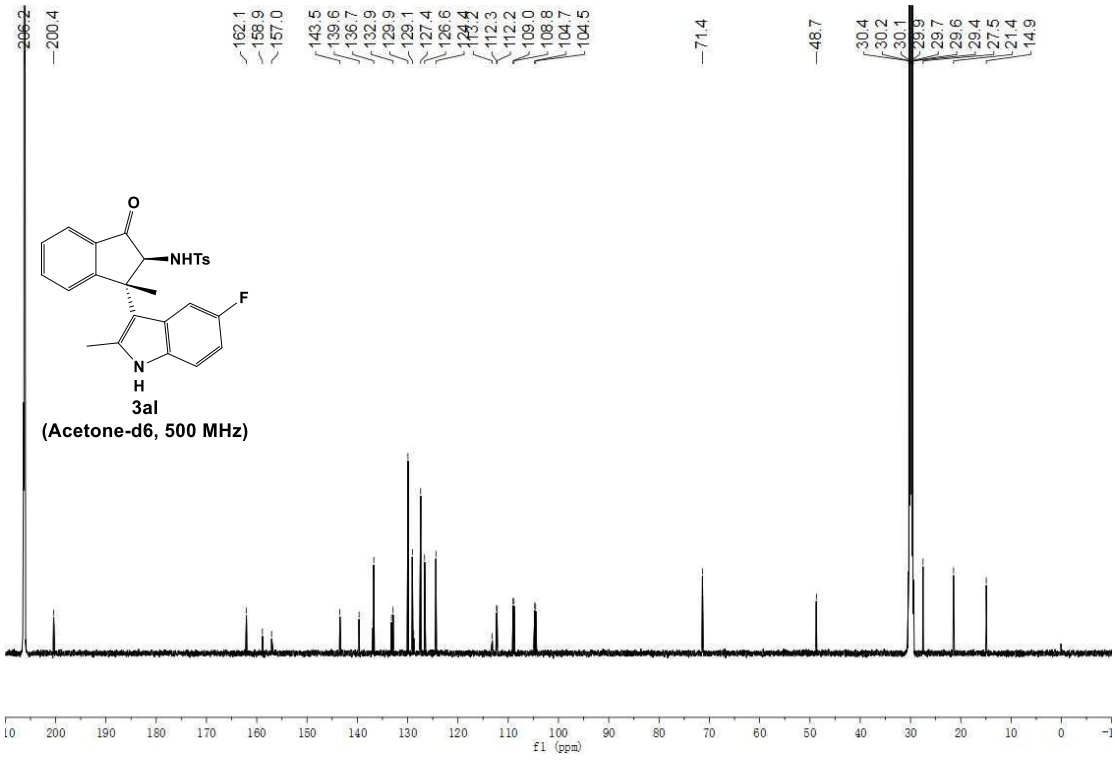
3ak'
(Acetone-d6, 400 MHz)

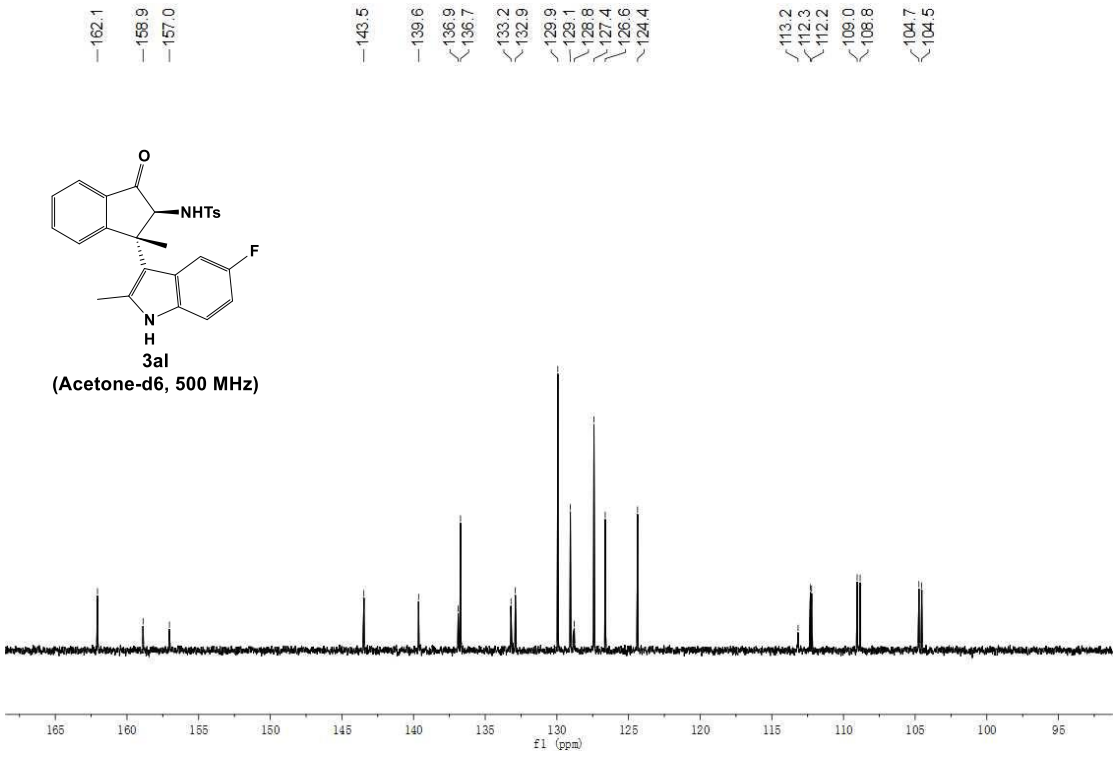



206.2
201.2
161.3
158.9
143.7
140.3
136.8
134.8
130.1
129.3
128.1
126.7
125.9
123.7
122.5
122.4
108.1
107.9
98.3
98.0
71.0
47.9
30.5
30.3
30.1
29.7
29.5
29.3
26.0
21.5
O
NHTs
NH
F
3ak'
(Acetone-d6, 400 MHz)
f1 (ppm)

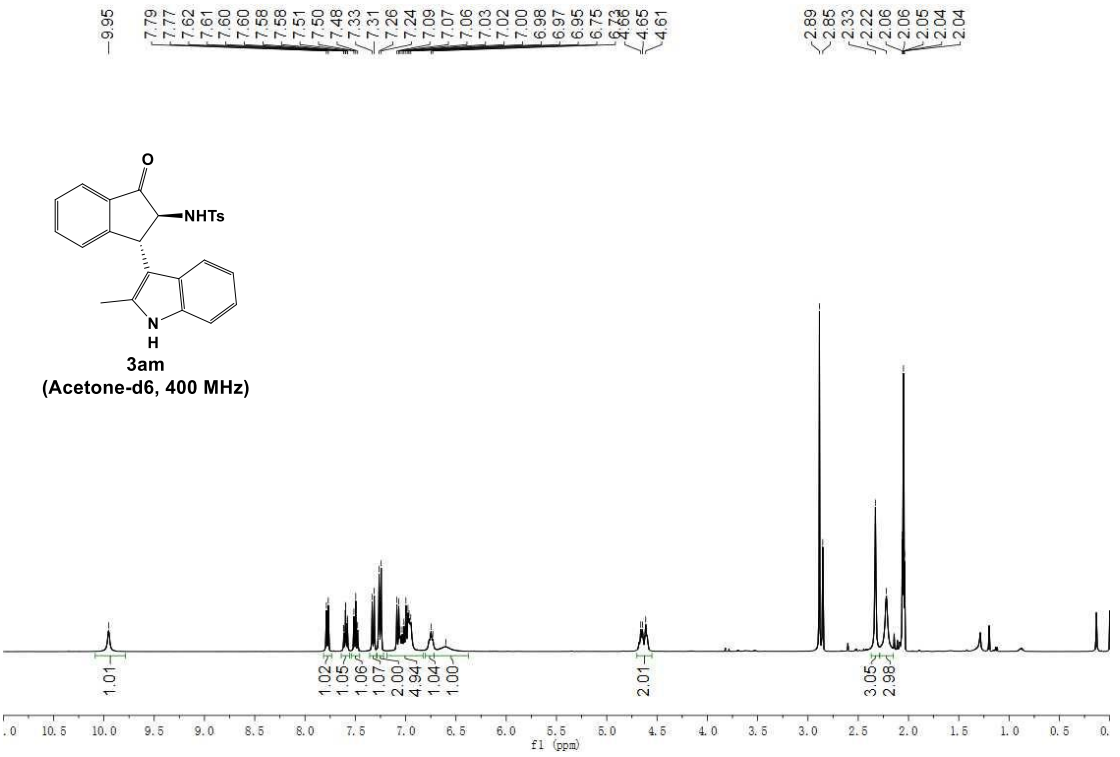

161.3
158.9
143.7
140.3
138.3
136.8
134.8
130.1
129.3
128.1
126.7
125.9
124.0
123.7
122.5
122.4
119.2
108.1
107.9
98.3
98.0
O
NHTs
NH
F
3ak'
(Acetone-d6, 400 MHz)
f1 (ppm)


O
NHTs
F
N
H
3al
(Acetone-d6, 400 MHz)
f1 (ppm)

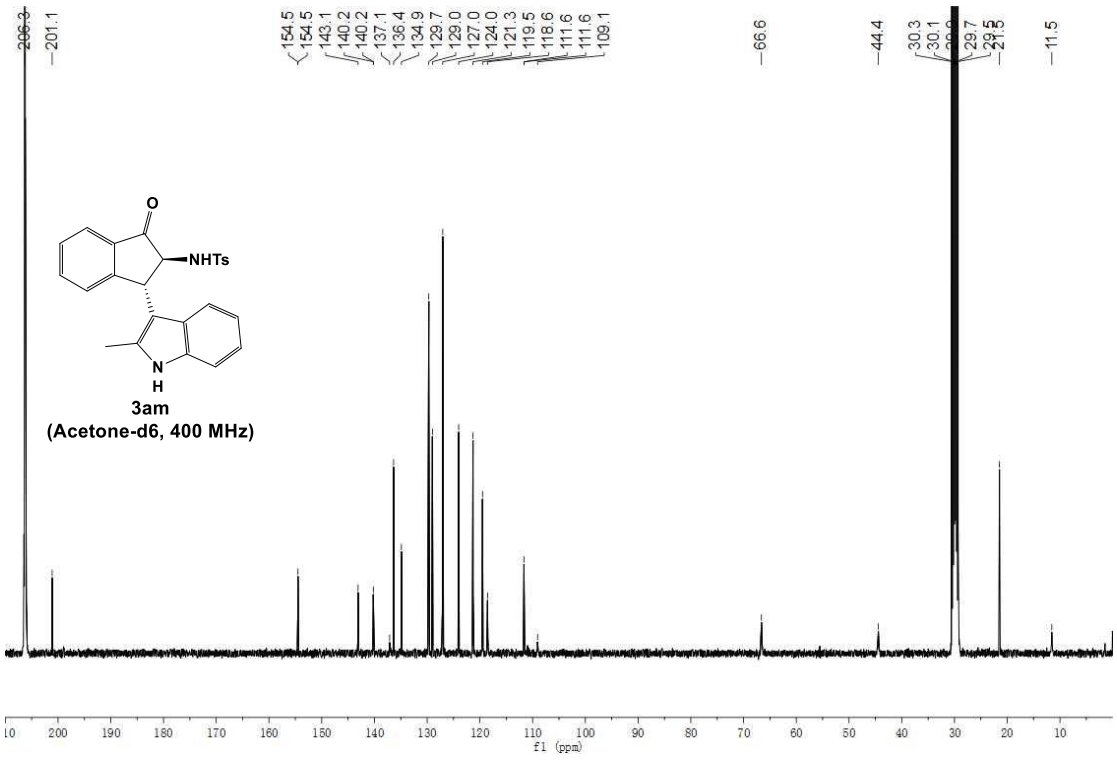

O
NHTs
F
N
H
3al
(Acetone-d6, 500 MHz)
f1 (ppm)

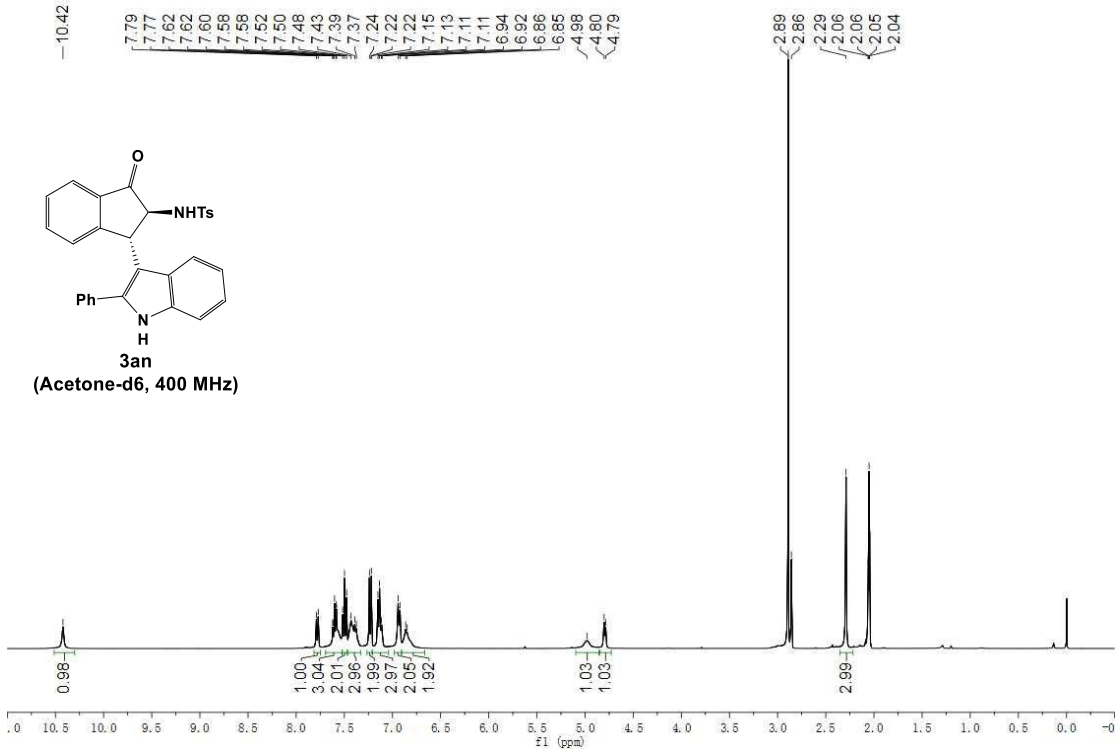


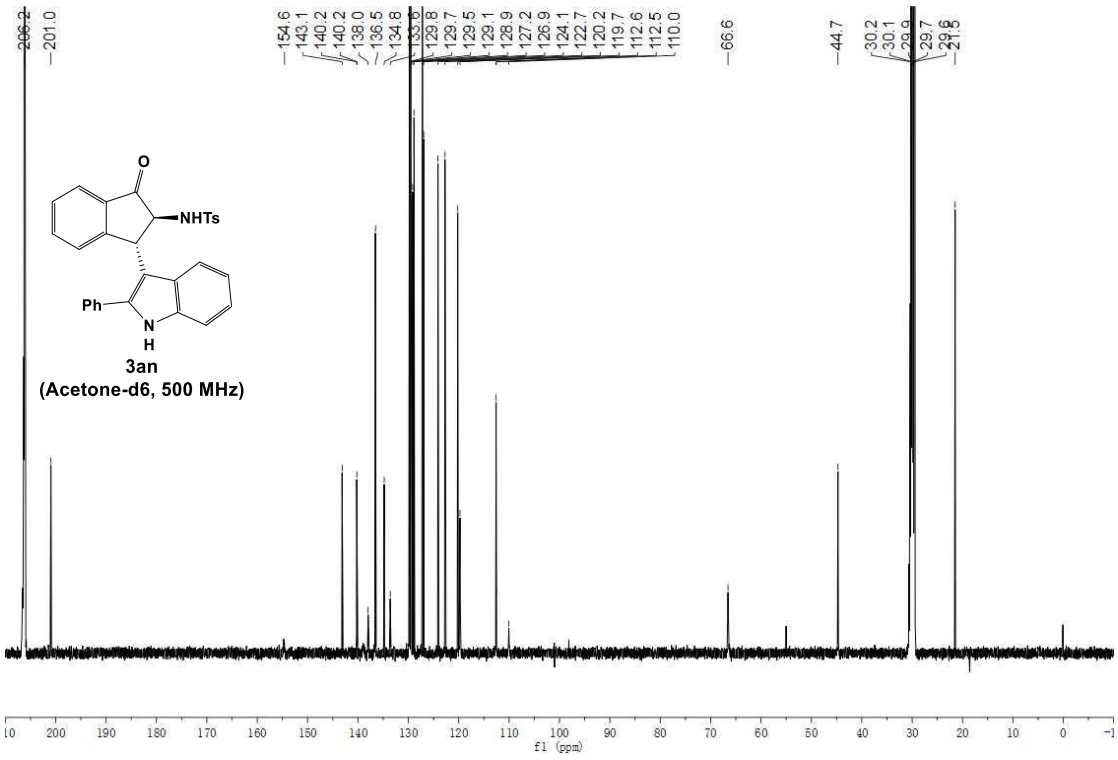
3al
(Acetone-d6, 500 MHz)

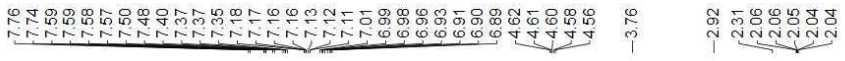


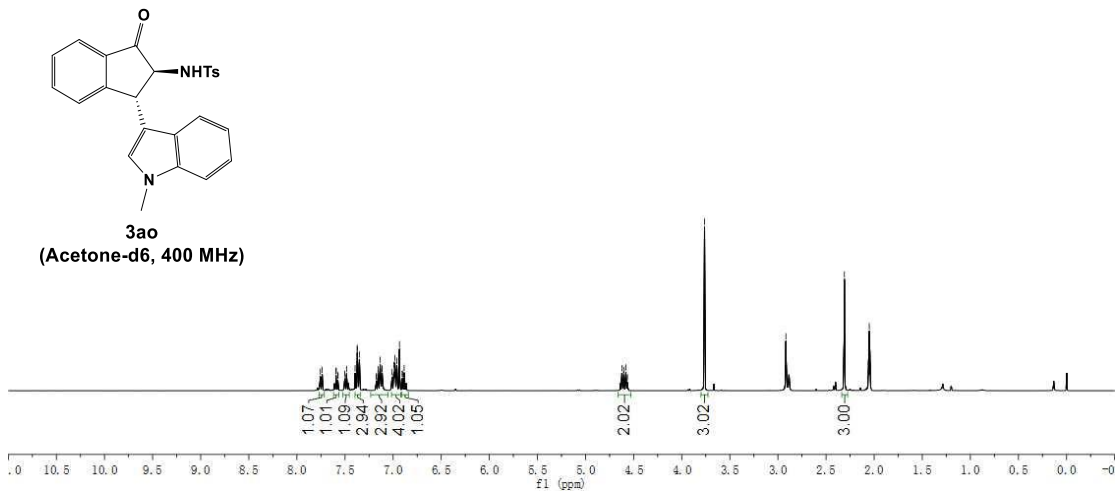
3am
(Acetone-d6, 400 MHz)

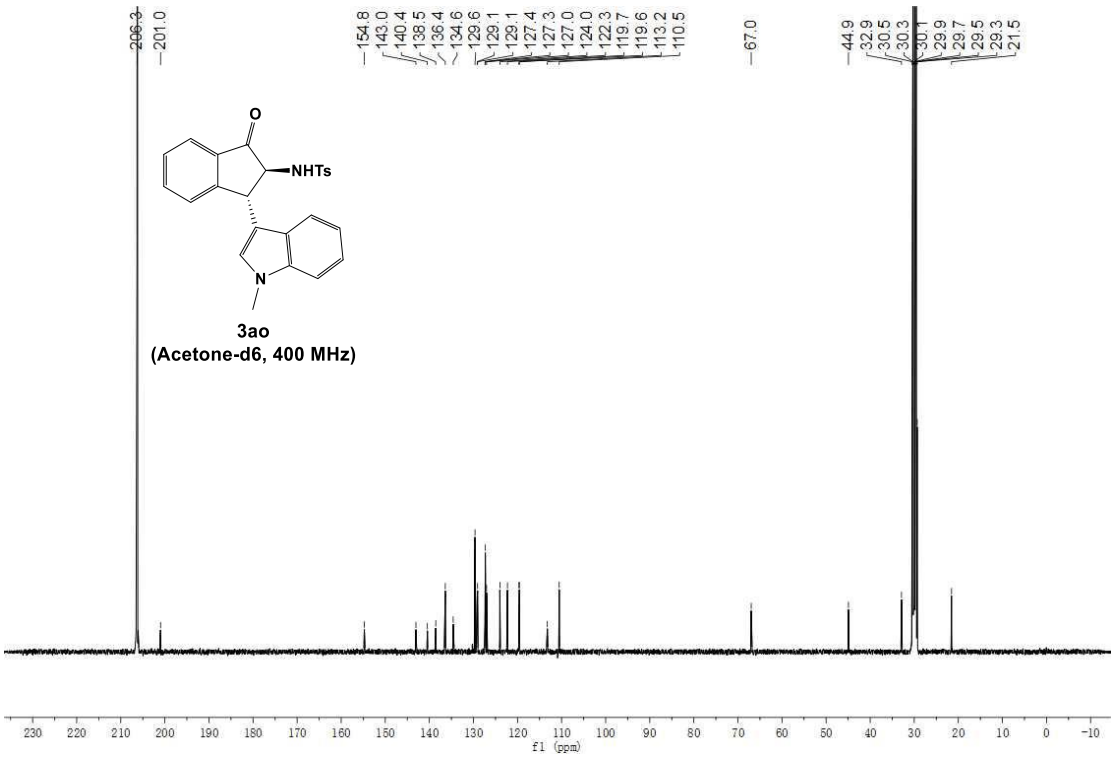

O
NHTs
N
H
3am
(Acetone-d6, 400 MHz)
206.3
201.1
154.5
154.5
143.1
140.2
140.2
137.1
136.4
134.9
129.7
129.0
127.0
124.0
121.3
119.5
118.6
111.6
111.6
109.1
66.6
44.4
30.3
30.1
29.7
29.5
21.5
11.5
f1 (ppm)


O
NHTs
Ph
N
H
3an
(Acetone-d6, 400 MHz)
10.42
7.79
7.77
7.62
7.62
7.60
7.58
7.58
7.52
7.50
7.48
7.43
7.39
7.37
7.24
7.22
7.22
7.15
7.13
7.11
7.11
6.94
6.92
6.86
6.85
4.98
4.80
4.79
2.89
2.86
2.29
2.06
2.06
2.05
2.04
0.98
1.00
3.04
2.01
2.96
1.99
2.97
2.05
1.92
1.03
1.03
2.99
f1 (ppm)

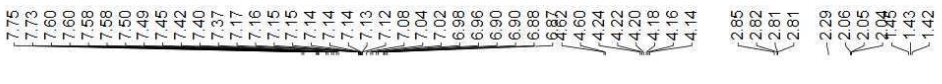

O
NHTs
Ph
N
H
3an
(Acetone-d6, 500 MHz)
206.2
201.0
154.6
143.1
140.2
140.2
138.0
136.5
134.8
133.6
129.8
129.7
129.5
129.1
128.9
127.2
126.9
124.1
122.7
120.2
119.7
112.6
112.5
110.0
66.6
44.7
30.2
30.1
29.9
29.7
29.6
21.5
f1 (ppm)

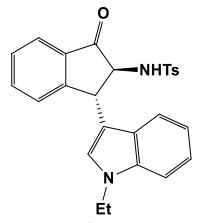

7.76
7.74
7.59
7.59
7.58
7.57
7.50
7.48
7.40
7.37
7.37
7.35
7.18
7.17
7.16
7.16
7.13
7.12
7.11
7.01
6.99
6.98
6.96
6.93
6.91
6.90
6.89
4.62
4.61
4.60
4.58
4.56
3.76
2.92
2.31
2.06
2.06
2.05
2.04
2.04


O
NHTs
N
3ao
(Acetone-d6, 400 MHz)
1.07
1.01
1.09
2.94
2.92
4.02
1.05
2.02
3.02
3.00
f1 (ppm)

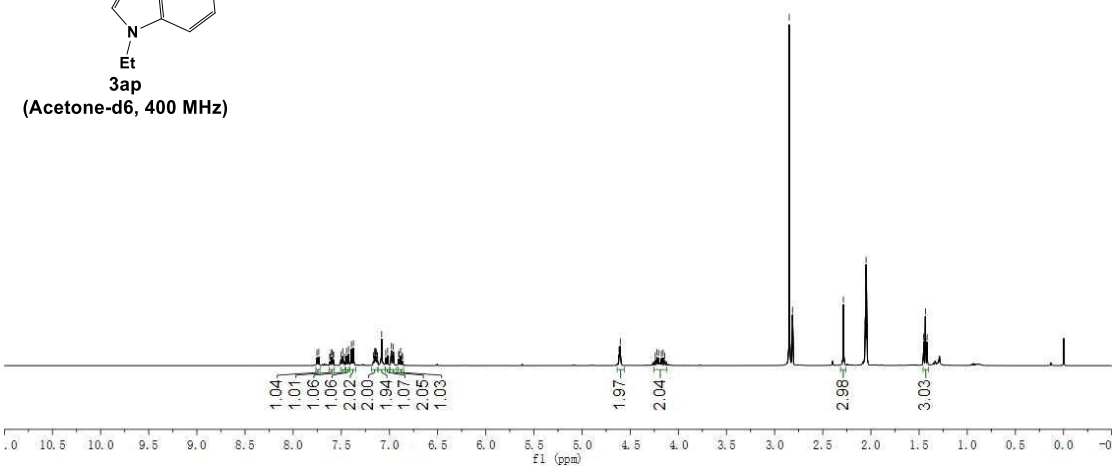


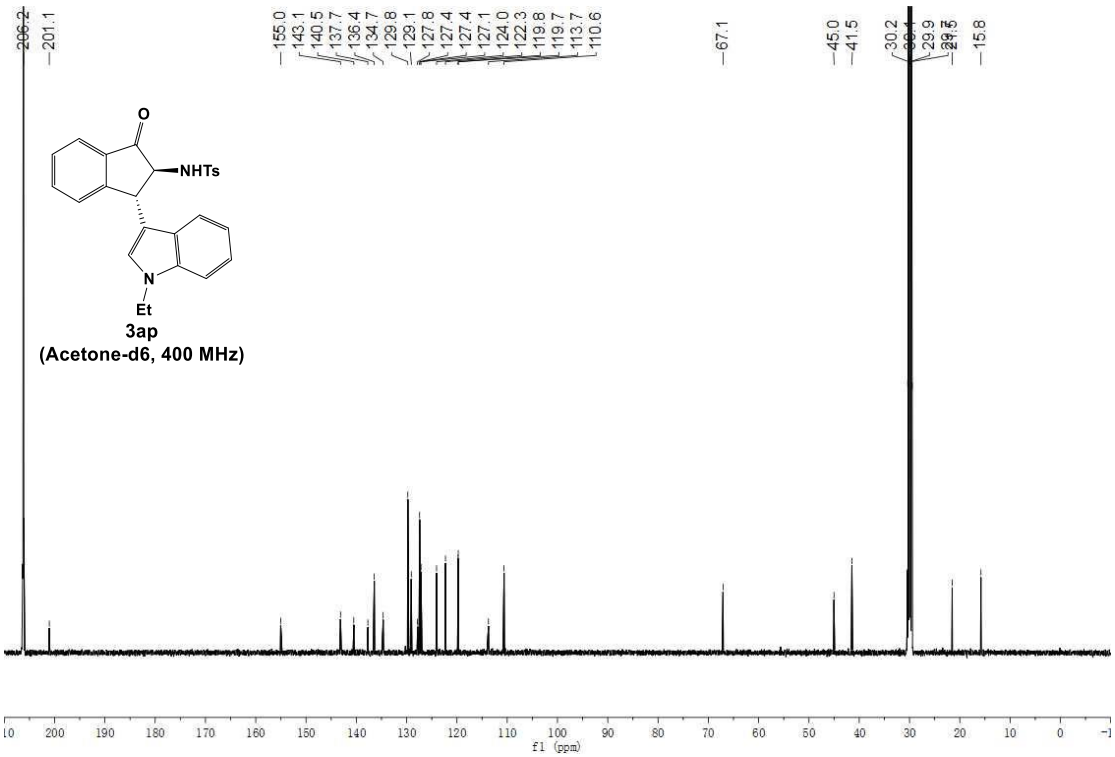
3ao
(Acetone-d6, 400 MHz)

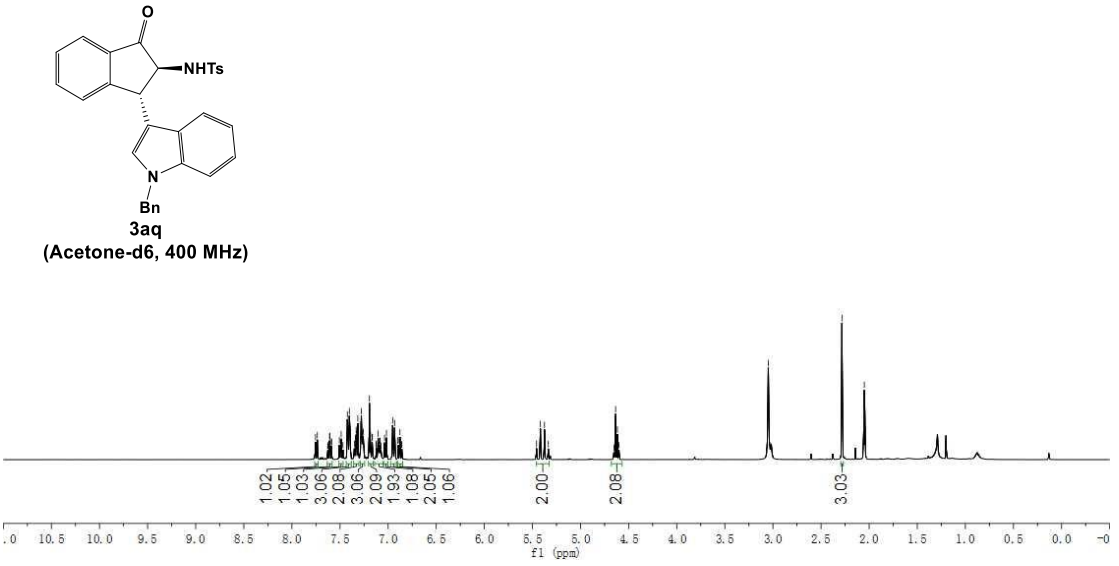


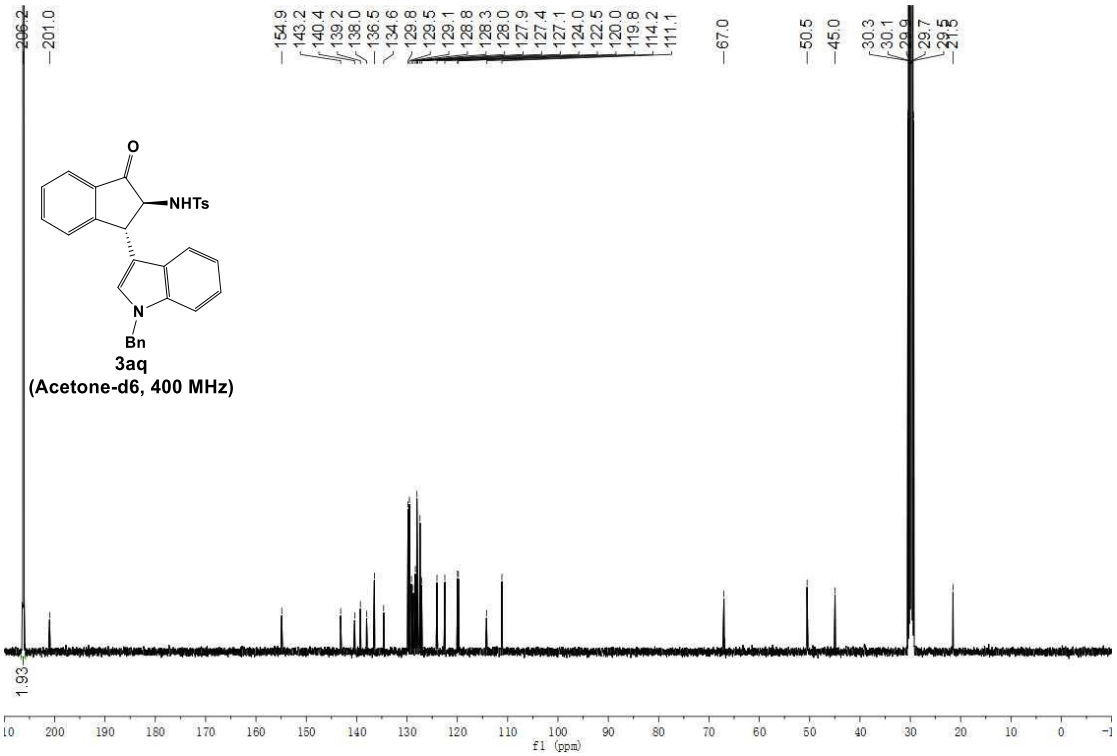


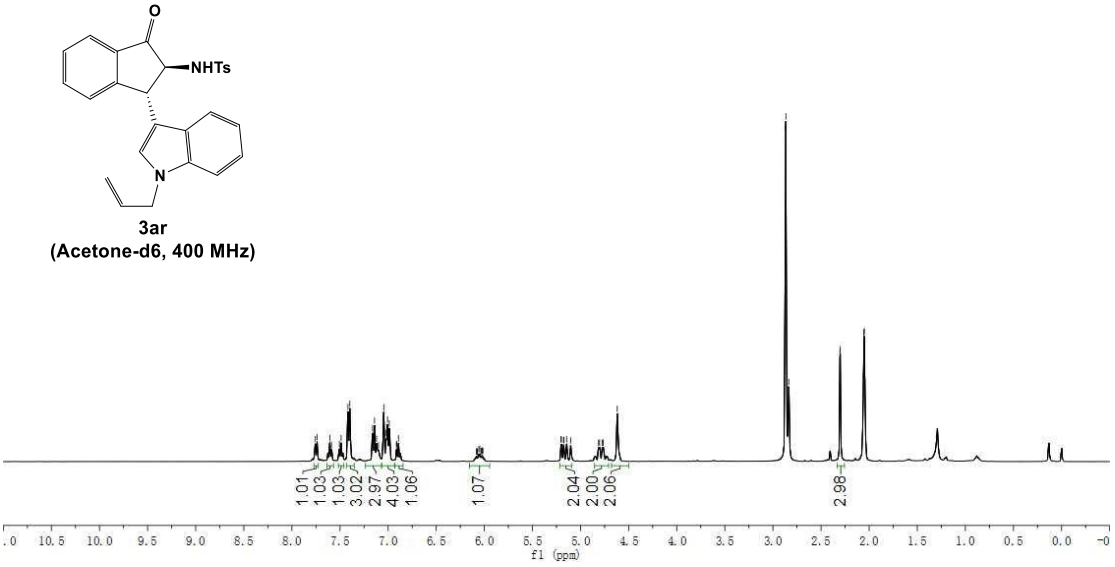
3ap
(Acetone-d6, 400 MHz)

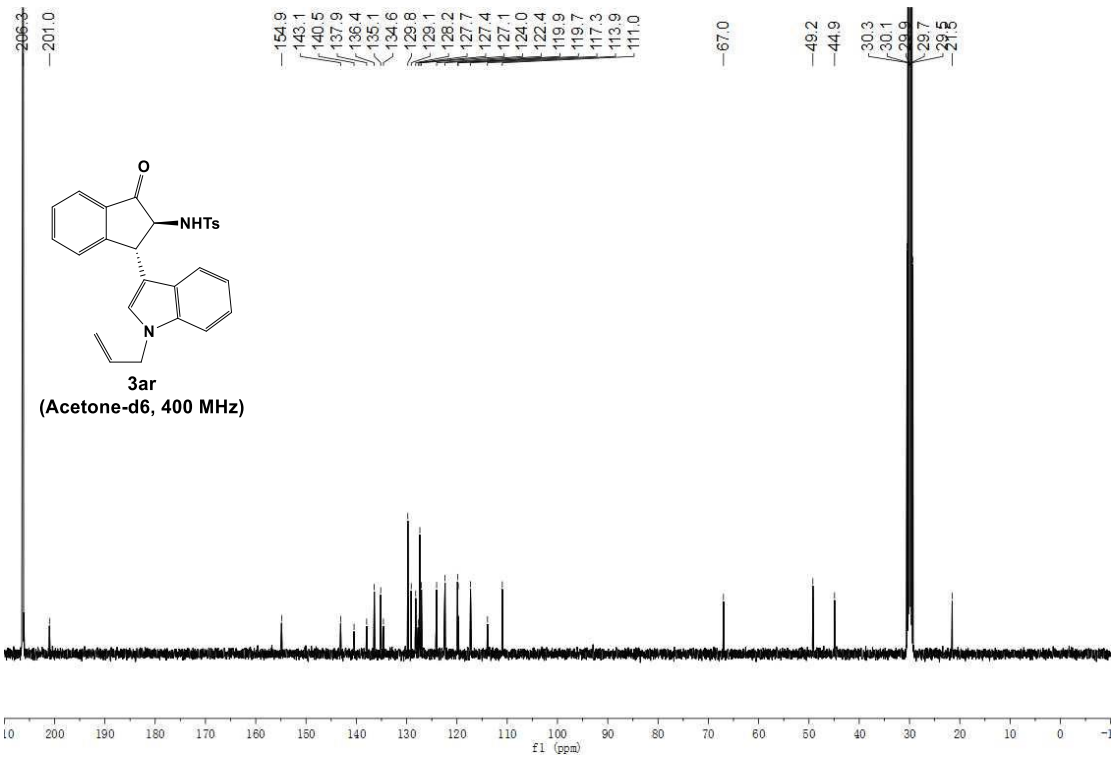


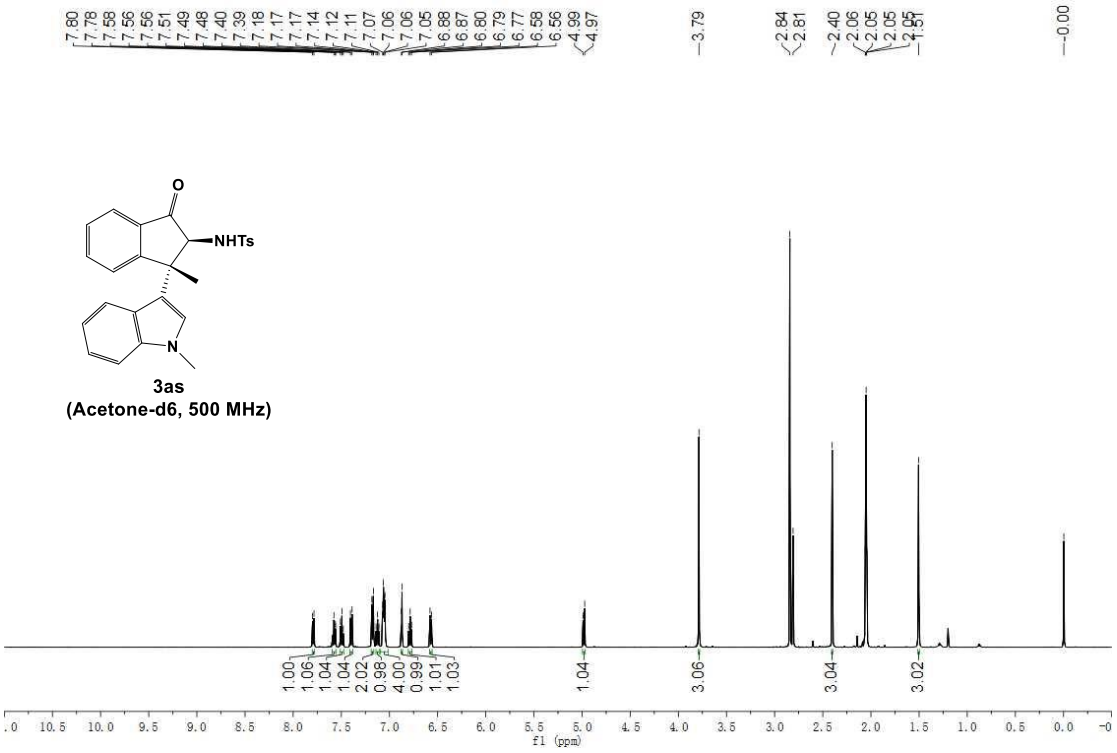

O
NHTs
N
Et
3ap
(Acetone-d6, 400 MHz)
f1 (ppm)

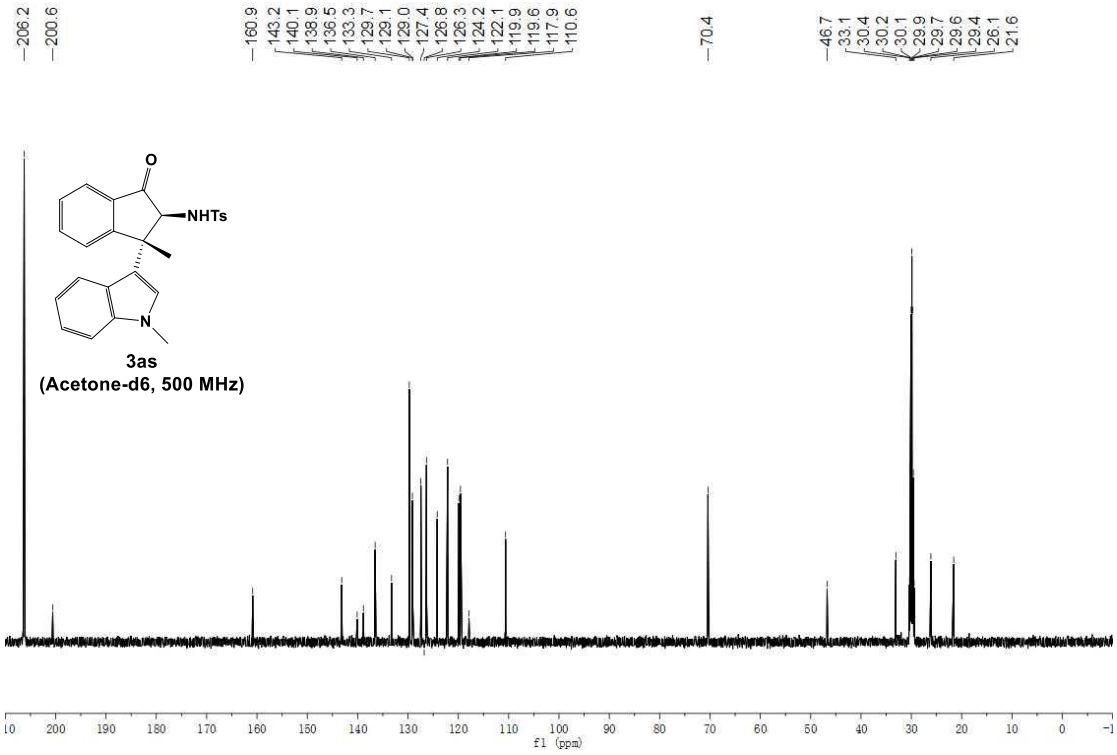

O
NHTs
N
Bn
3aq
(Acetone-d6, 400 MHz)
f1 (ppm)

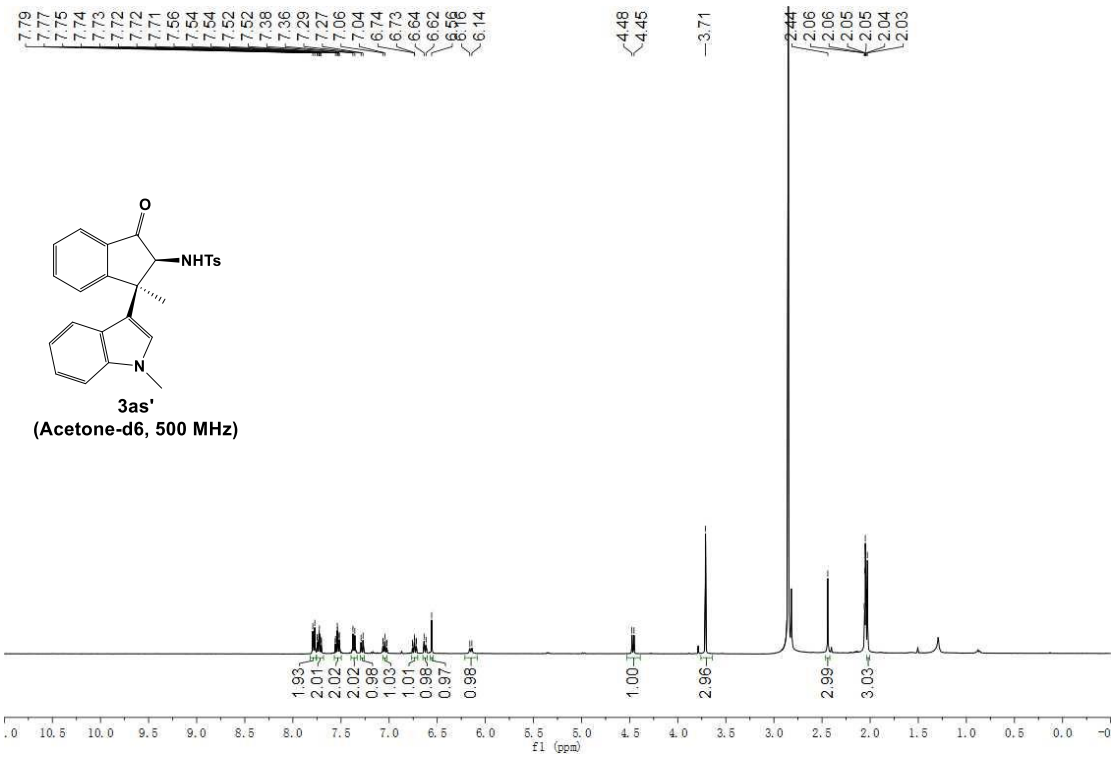

O
NHTs
N
Bn
3aq
(Acetone-d6, 400 MHz)
f1 (ppm)

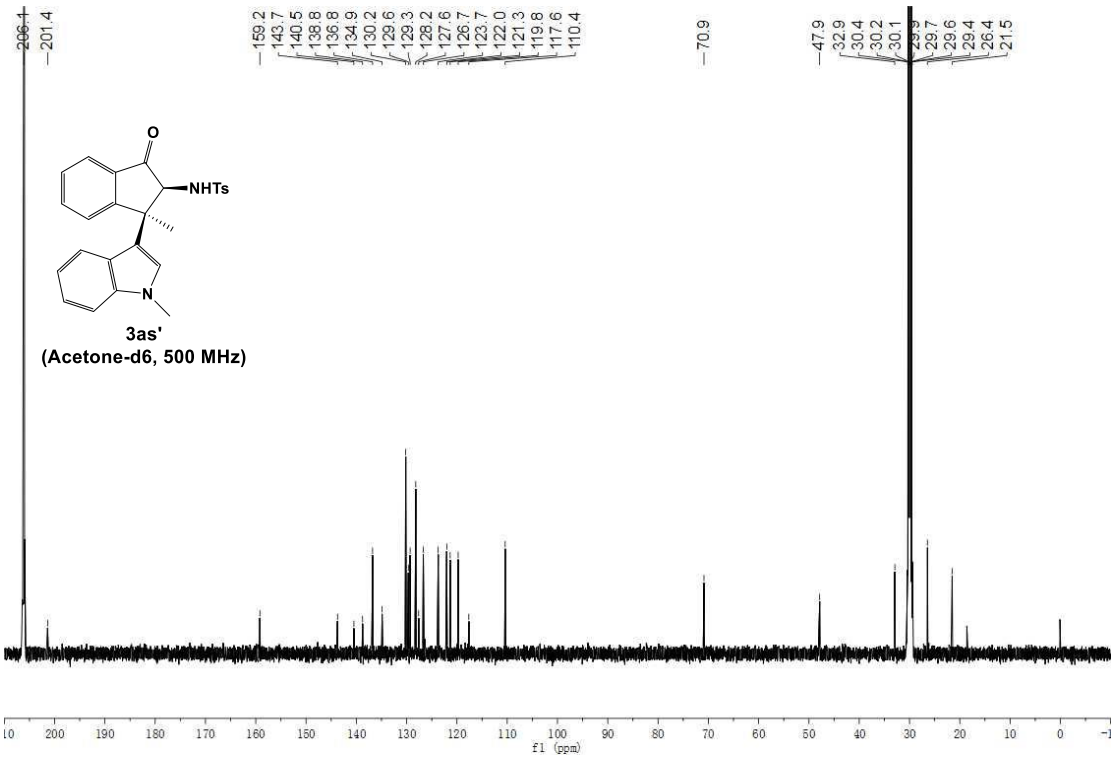

O
NHTs
N
3ar
(Acetone-d6, 400 MHz)
f1 (ppm)


O
NHTs
N
3ar
(Acetone-d6, 400 MHz)
f1 (ppm)


O
NHTs
N
3as
(Acetone-d6, 500 MHz)
f1 (ppm)

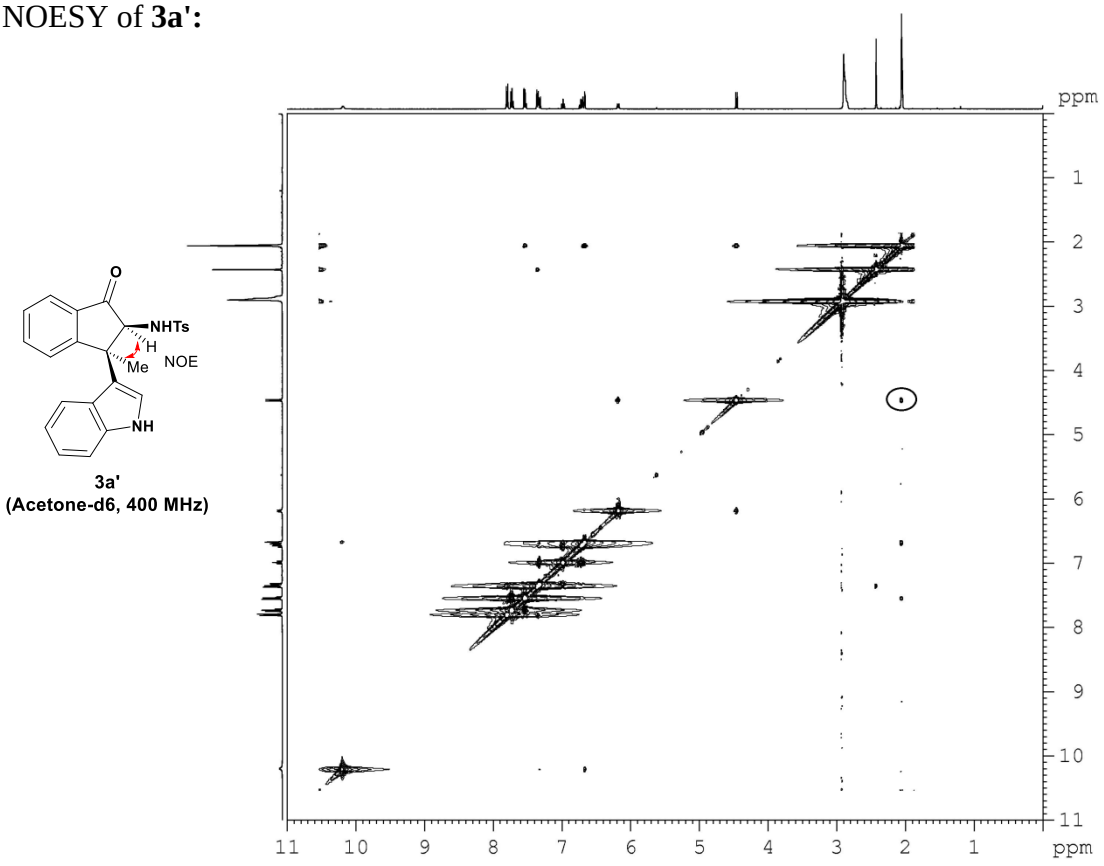

206.2
200.6
160.9
143.2
140.1
138.9
136.5
133.3
129.7
129.1
129.0
127.4
126.8
126.3
124.2
122.1
119.9
119.6
117.9
110.6
70.4
46.7
33.1
30.4
30.2
30.1
29.9
29.7
29.6
29.4
26.1
21.6
O
NHTs
N
3as
(Acetone-d6, 500 MHz)
f1 (ppm)


7.79
7.77
7.75
7.74
7.73
7.72
7.72
7.71
7.56
7.54
7.54
7.52
7.52
7.38
7.36
7.29
7.27
7.06
7.04
6.74
6.73
6.64
6.62
6.56
6.16
6.14
4.48
4.45
3.71
2.44
2.06
2.06
2.05
2.05
2.04
2.03
O
NHTs
N
3as'
(Acetone-d6, 500 MHz)
1.93
2.01
2.02
2.02
0.98
1.03
1.01
0.98
0.97
0.98
1.00
2.96
2.99
3.03
f1 (ppm)


206.4
201.4
159.2
143.7
140.5
138.8
136.8
134.9
130.2
129.6
129.3
128.2
127.6
126.7
123.7
122.0
121.3
119.8
117.6
110.4
70.9
47.9
32.9
30.4
30.2
30.1
29.9
29.7
29.6
29.4
26.4
21.5
O
NHTs
N
3as'
(Acetone-d6, 500 MHz)
f1 (ppm)

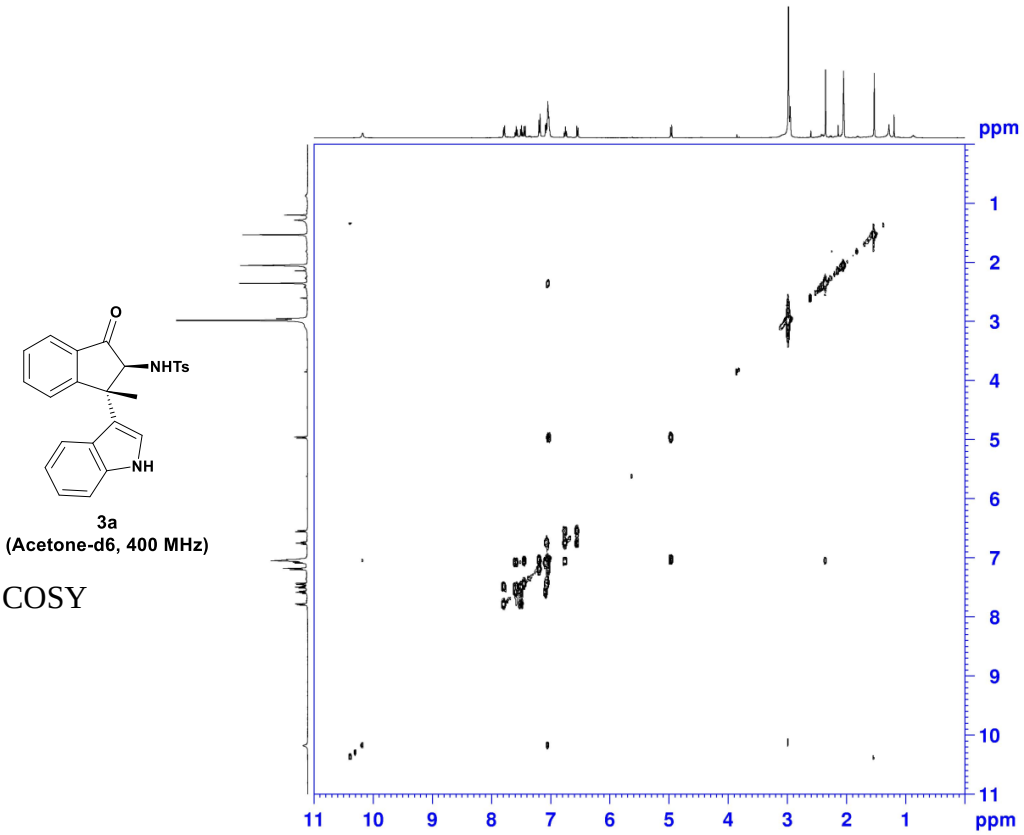
Part 5: 2D NMR spectra of some products

NOESY of **3a':**



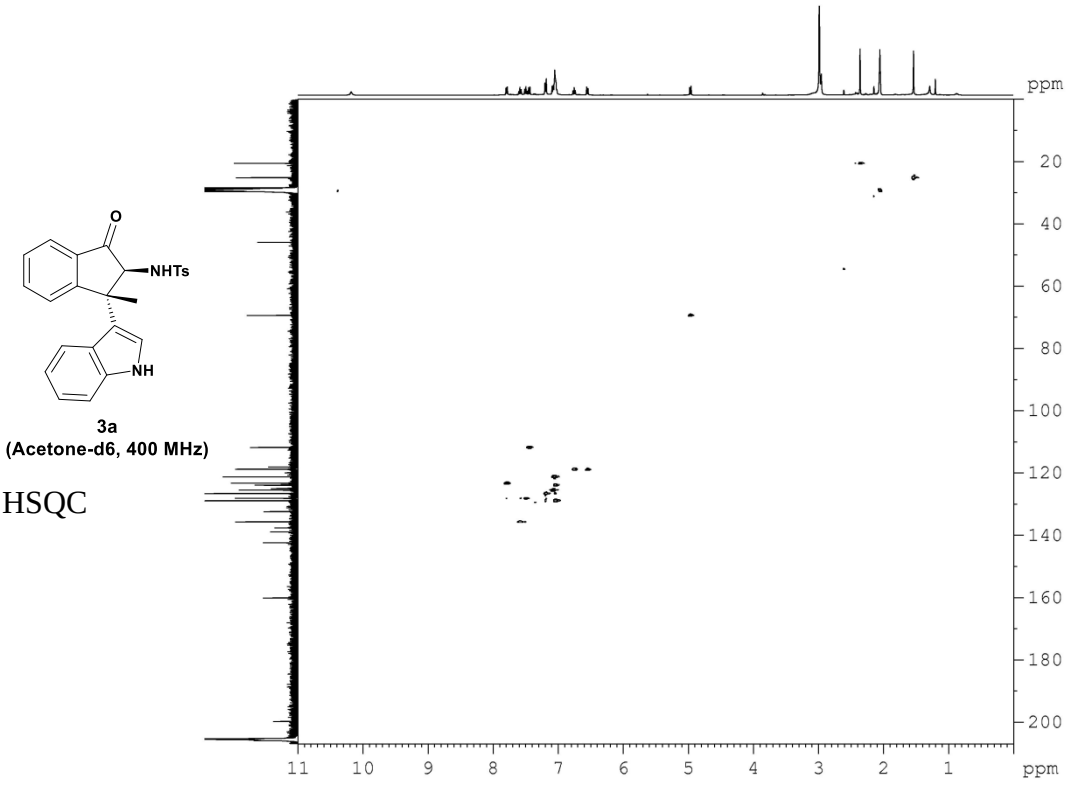
3a'
(Acetone-d6, 400 MHz)

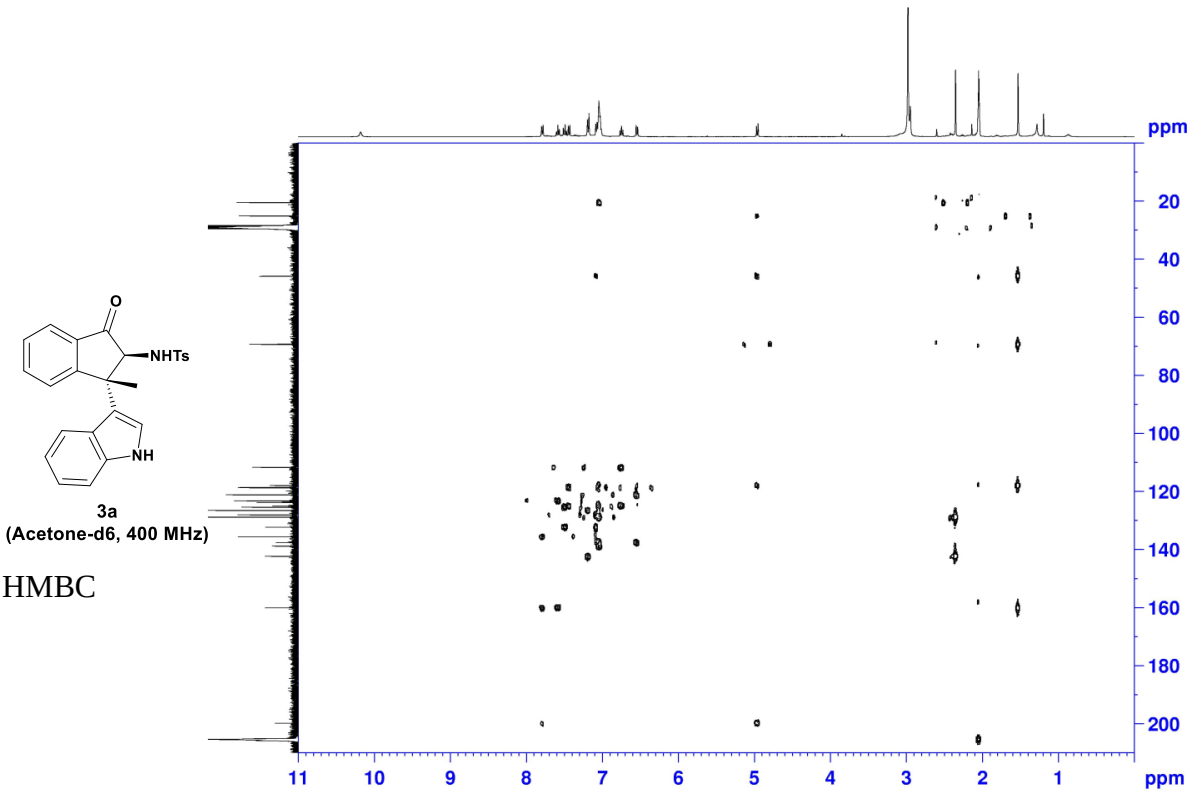
2D NMR of **3a:**

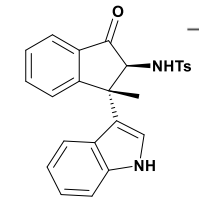


3a
(Acetone-d6, 400 MHz)

COSY

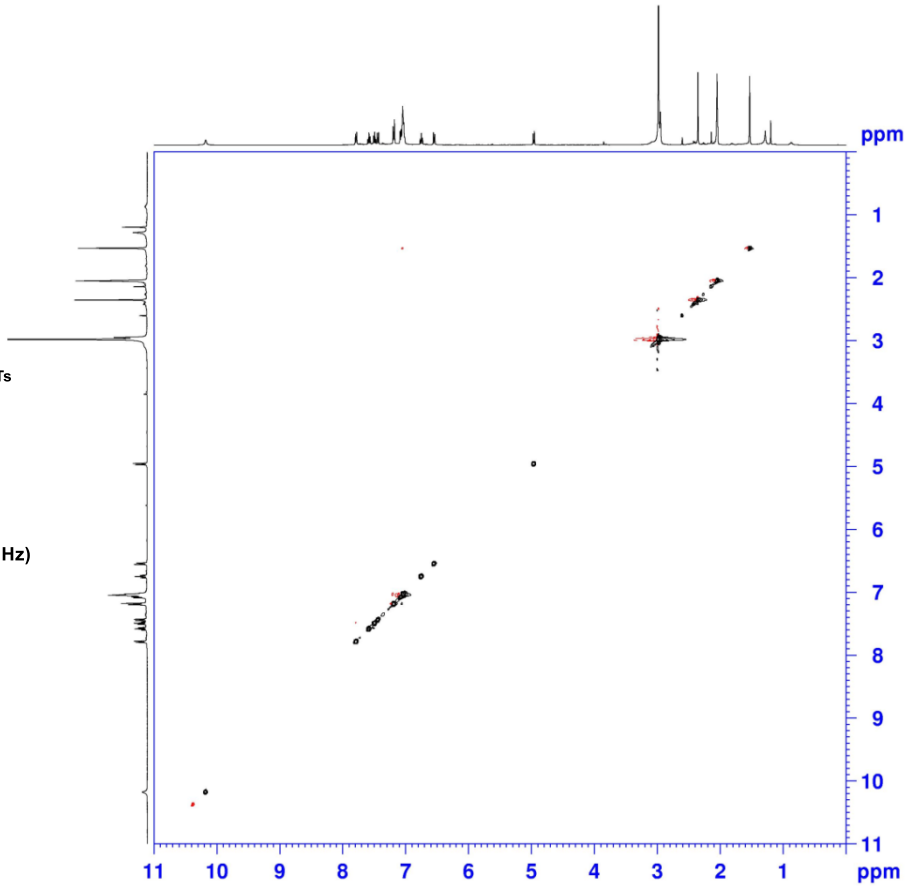

O
NHTs
NH
3a
(Acetone-d6, 400 MHz)
HSQC
ppm
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
ppm


O
NHTs
NH
3a
(Acetone-d6, 400 MHz)
HMBC
ppm
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
ppm

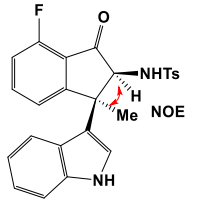


3a
(Acetone-d6, 400 MHz)

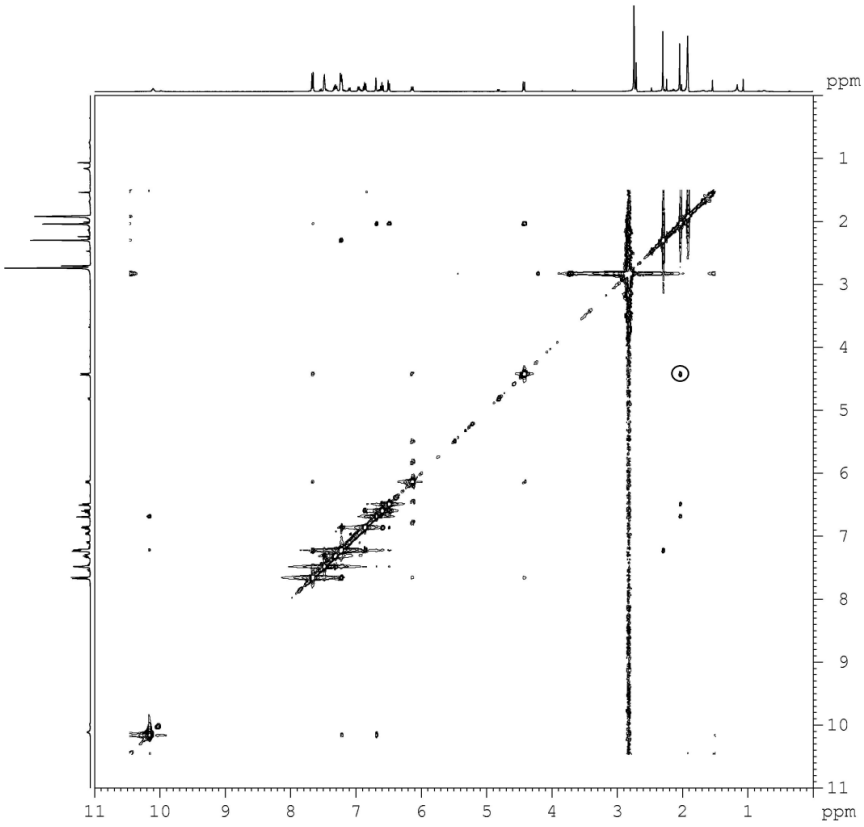
NOESY



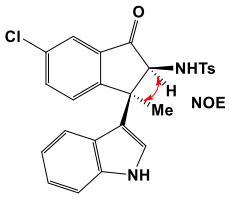
NOESY of **3b'**:



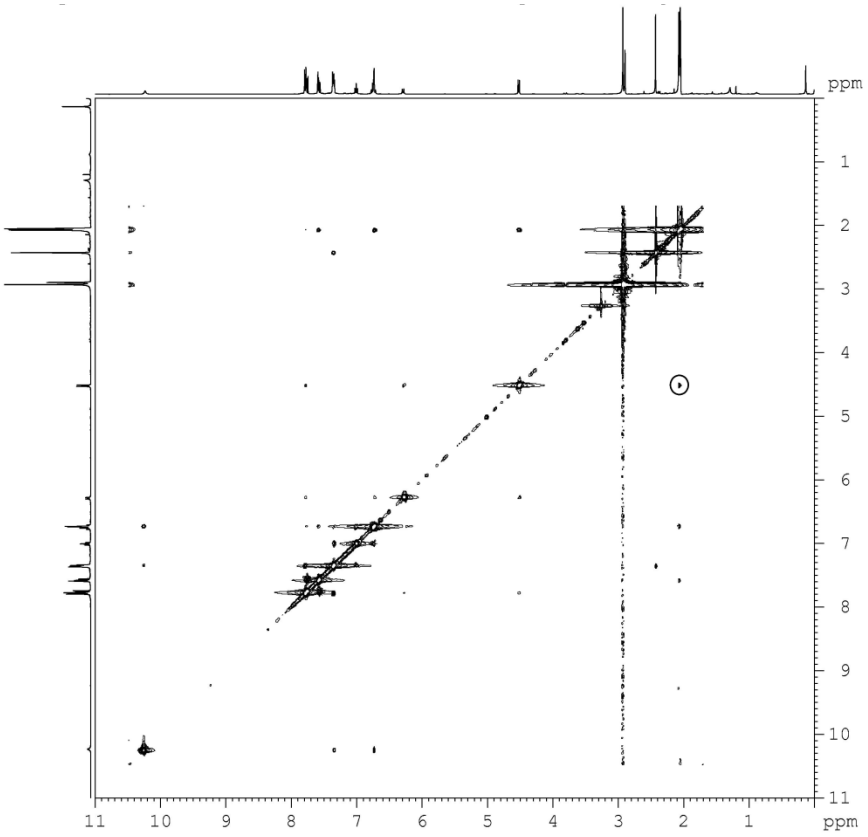
3b'
(Acetone-d6, 500 MHz)



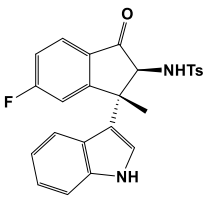
NOESY of **3c'**:



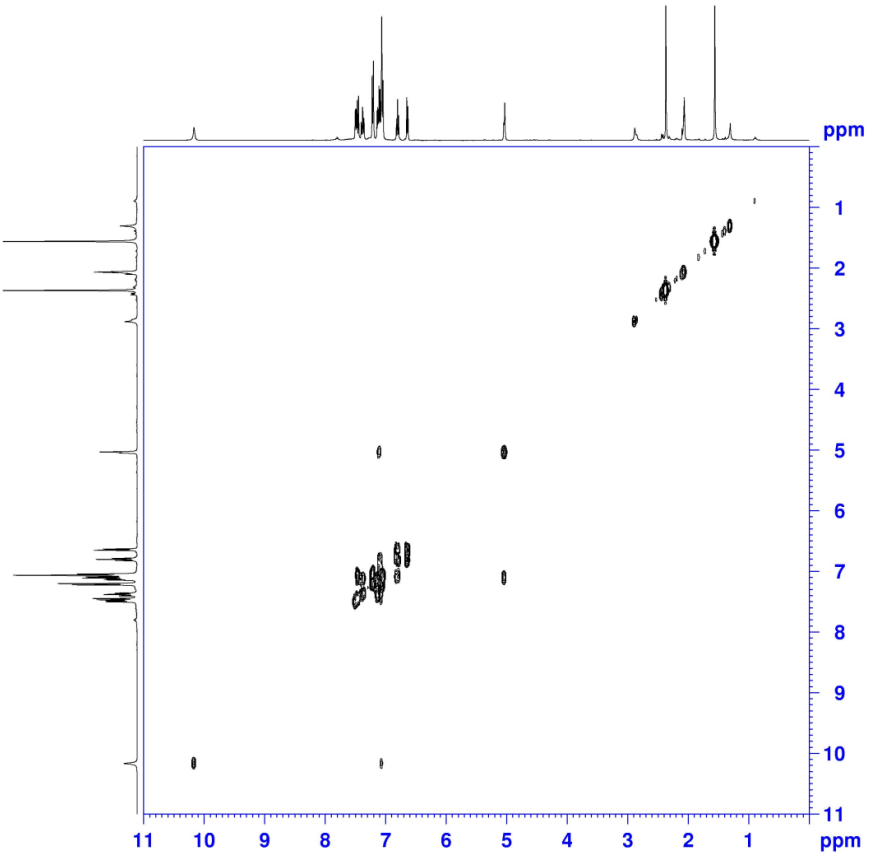
3c'
(Acetone-d6, 400 MHz)



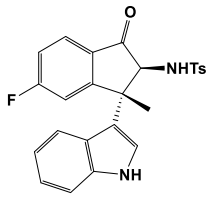
2D NMR of **3c:**



3c
(Acetone-d6, 400 MHz)

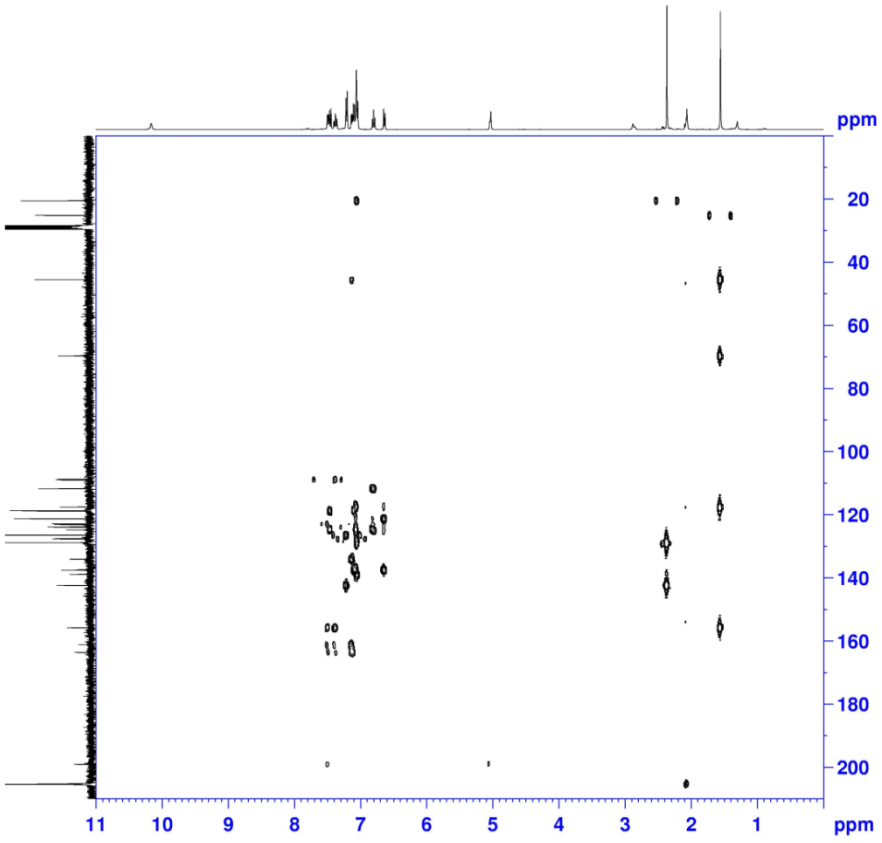


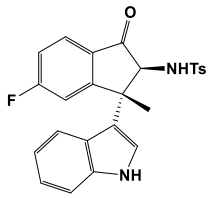
COSY



3c
(Acetone-d6, 400 MHz)

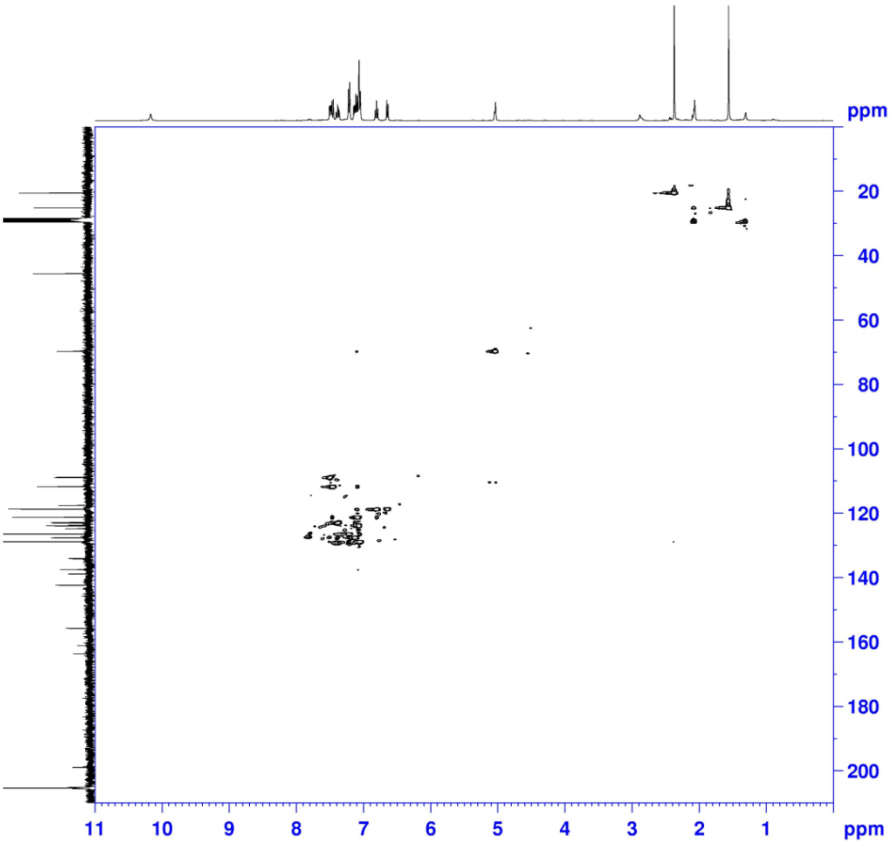
HMBC

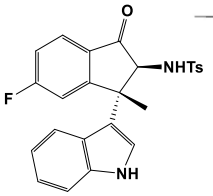




3c
(Acetone-d6, 400 MHz)

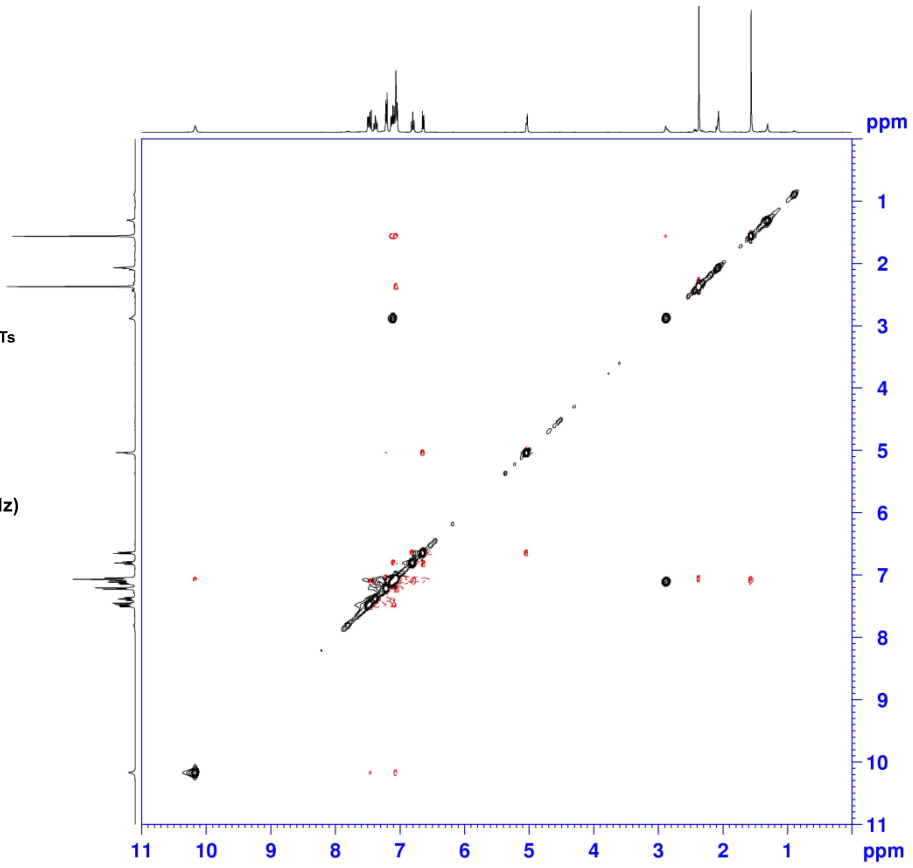
HSQC



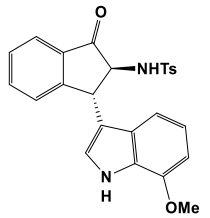


3c
(Acetone-d6, 400 MHz)

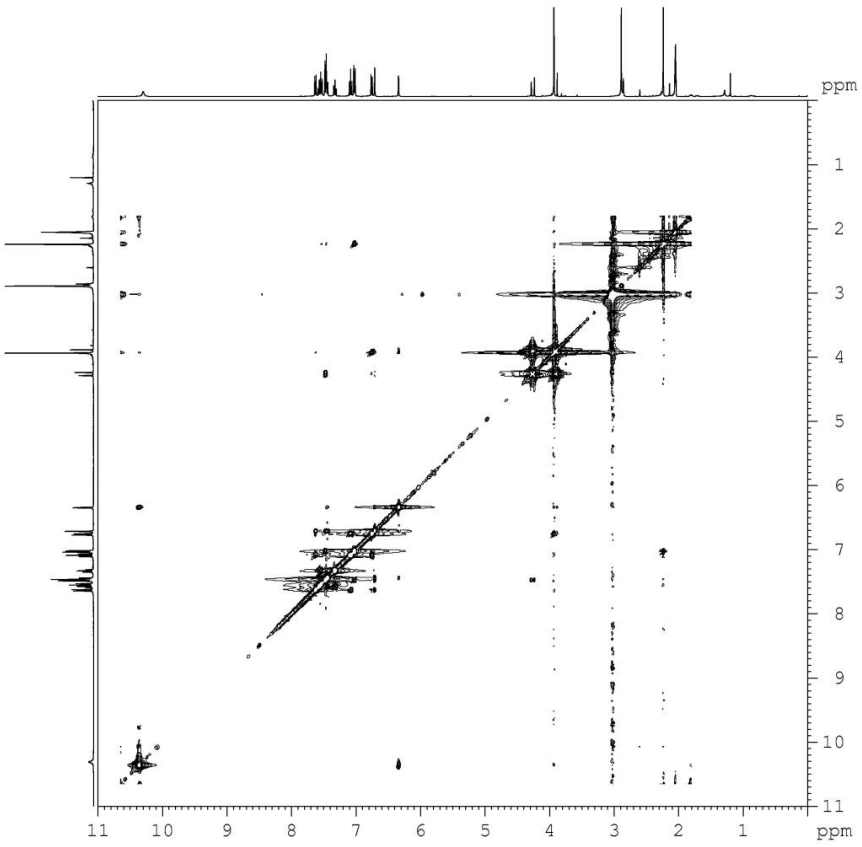
NOESY



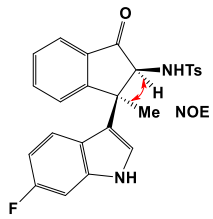
NOESY of **3ad:**



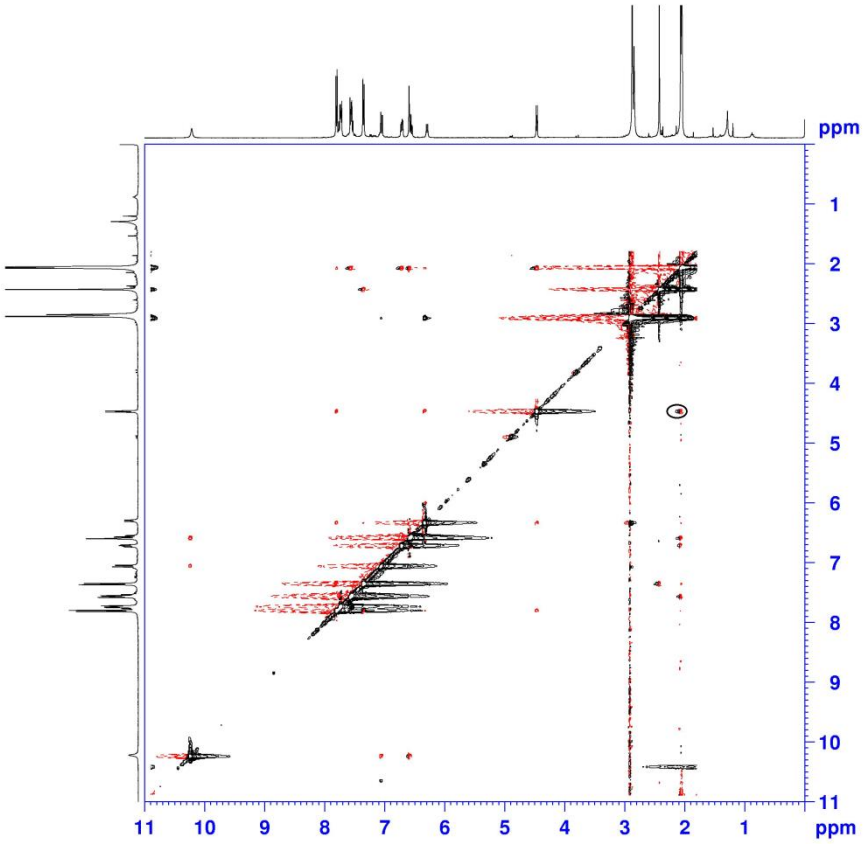
3ad
(Acetone-d6, 400 MHz)



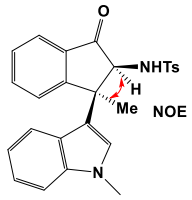
NOESY of **3ak':**



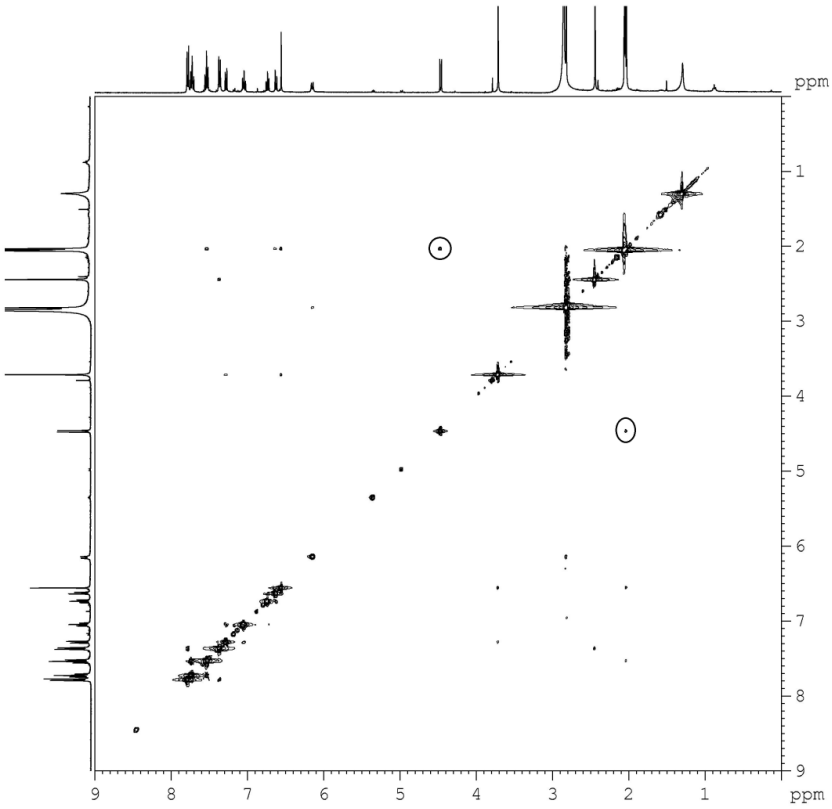
3ak'
(Acetone-d6, 400 MHz)



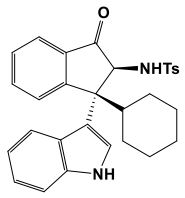
NOESY of **3as':**



3as'
(Acetone-d6, 400 MHz)

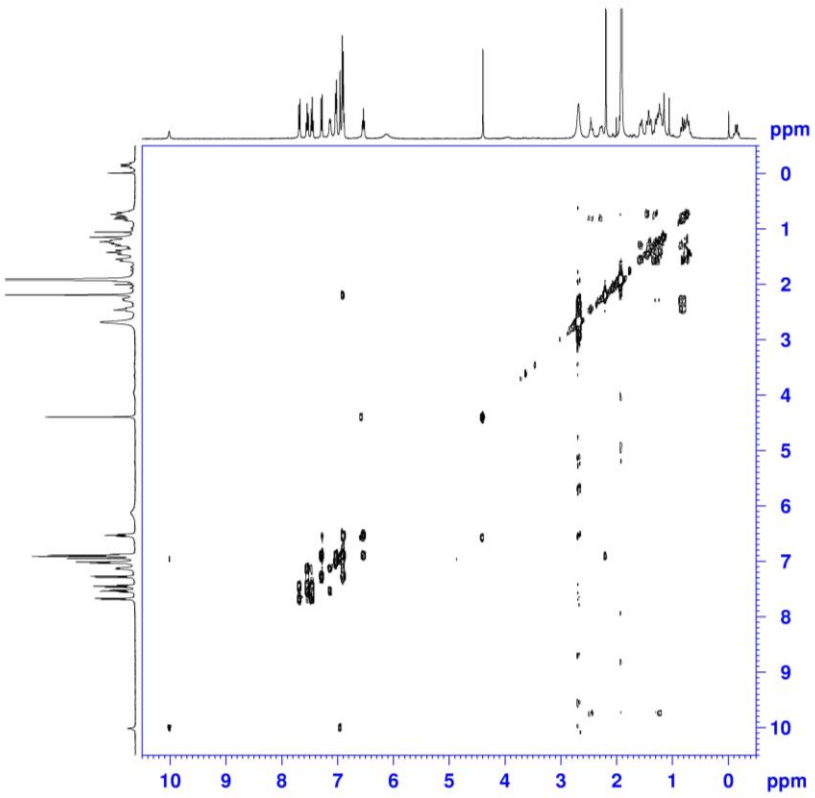


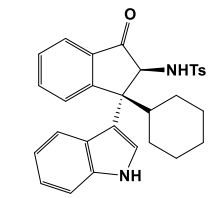
2D NMR of **3l:**



3l
(Acetone-d6, 400 MHz)

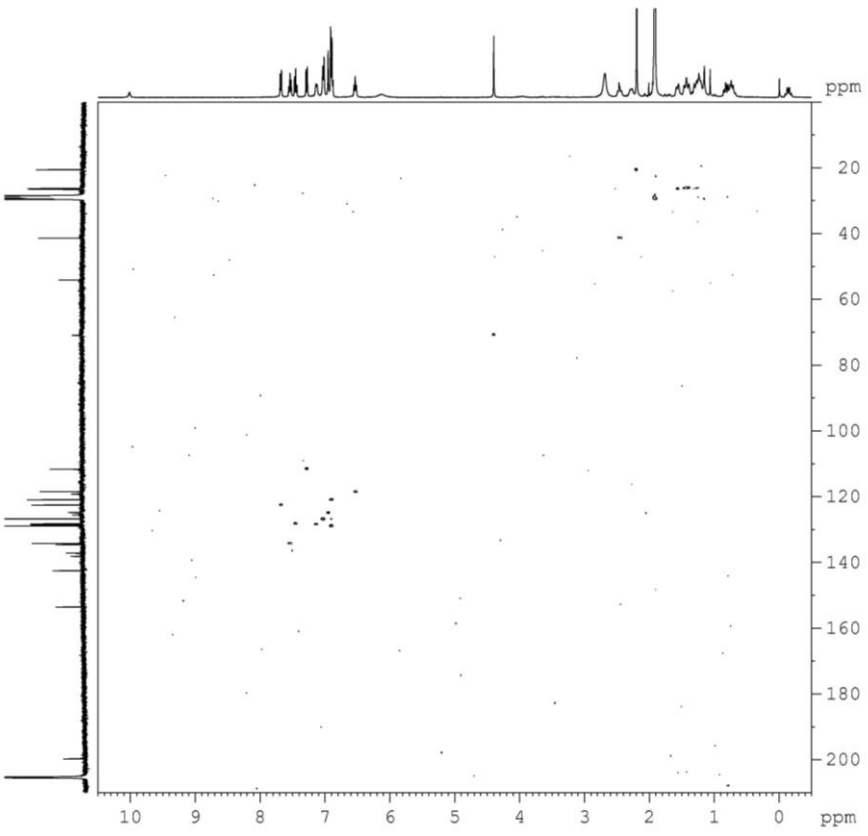
COSY

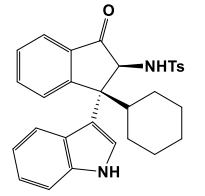




3l
(Acetone-d6, 400 MHz)

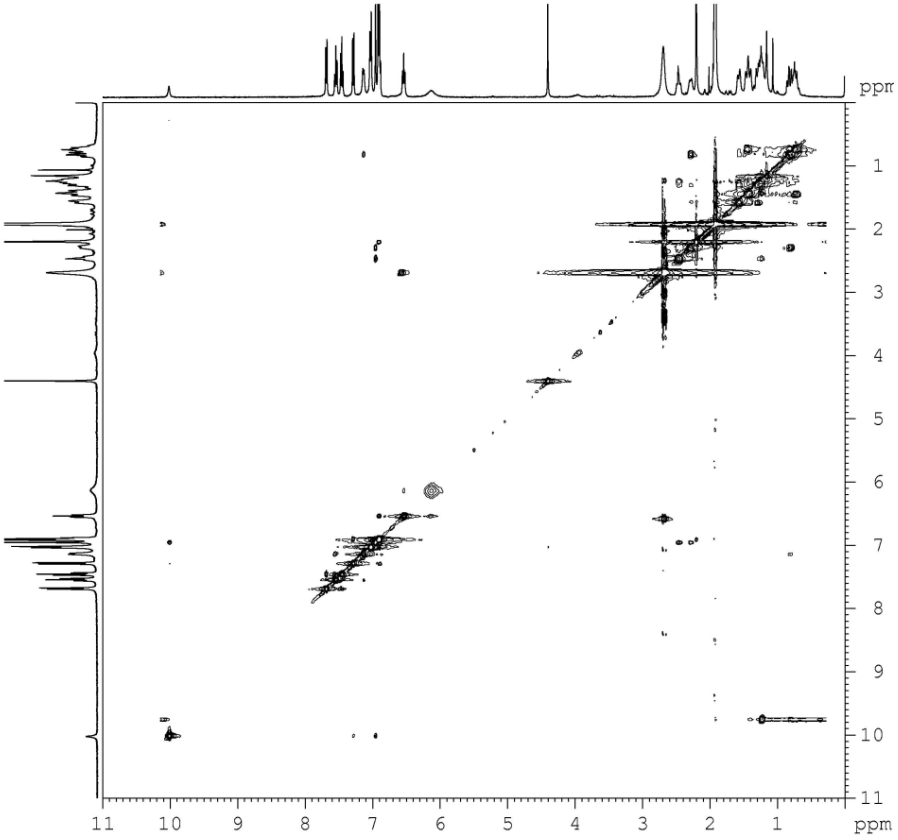
HSQC





3l
(Acetone-d6, 400 MHz)

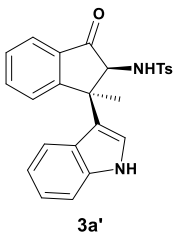
NOESY



Part 6: X-ray Crystal Images

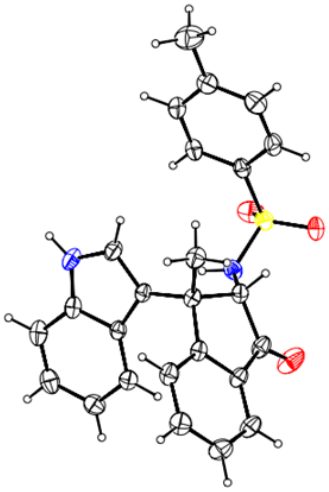
CCDC 1537759 and1537761contain the supplementary crystallographic data for compound **3a**, **3a'**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Figure 1. Crystal structure of the compound **3a'** (CCDC 1537759)



3a'

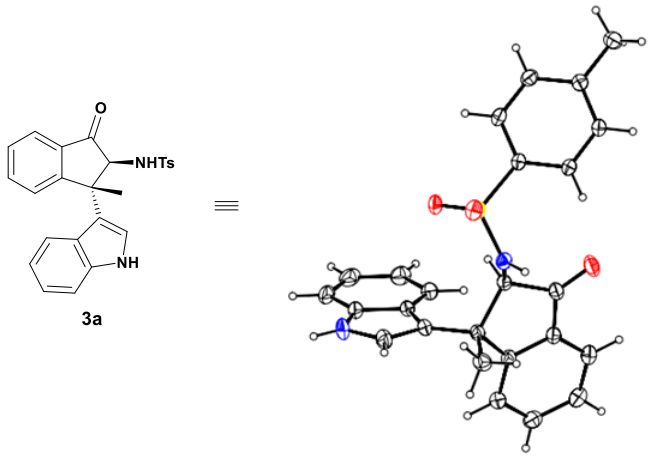
≡



Datablock: shelx

```
Bond precision:  C-C = 0.0045 A          Wavelength=1.54178

Cell:            a=19.827(7)     b=7.782(3)          c=14.742(6)
                 alpha=90        beta=107.923(7)     gamma=90
Temperature:     293 K

                Calculated                Reported
Volume          2164.2(14)                2164.3(14)
Space group     P 21/c                    P 21/c
Hall group      -P 2ybc                   -P 2ybc
Moiety formula  C25 H22 N2 O3 S           C25 H22 N2 O3 S
Sum formula     C25 H22 N2 O3 S           C25 H22 N2 O3 S
Mr              430.51                    430.50
Dx,g cm-3       1.321                     1.321
Z               4                         4
Mu (mm-1)       1.569                     1.569
F000            904.0                     904.0
F000'           907.85
h,k,lmax        23,9,17                   23,9,17
Nref            3956                      3817
Tmin,Tmax       0.767,0.731               0.578,1.000
Tmin'           0.696

Correction method= # Reported T Limits: Tmin=0.578 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.965          Theta(max)= 68.160

R(reflections)= 0.0697( 2806)     wR2(reflections)= 0.2291( 3817)

S = 1.149                 Npar= 288
```

Figure 2. Crystal structure of the compound **3a** (CCDC 1537761)

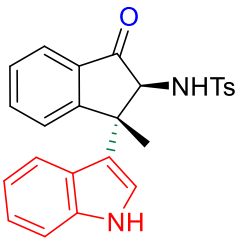


Datablock: shelx

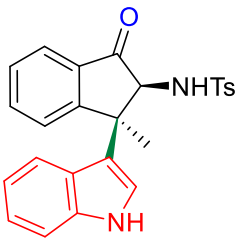
```
Bond precision:  C-C = 0.0031 A          Wavelength=1.54178

Cell:            a=12.2496(9)     b=15.4498(4)        c=11.5317(3)
                 alpha=90         beta=103.677(7)     gamma=90
Temperature:     293 K

                 Calculated                Reported
Volume           2120.53(19)               2120.53(18)
Space group      P 21/c                    P 21/c
Hall group       -P 2ybc                   -P 2ybc
Moiety formula   C25 H22 N2 O3 S           ?
Sum formula      C25 H22 N2 O3 S           C25 H22 N2 O3 S
Mr               430.51                    430.50
Dx,g cm-3        1.349                     1.348
Z                4                         4
Mu (mm-1)        1.601                     1.601
F000             904.0                     904.0
F000'            907.85
h,k,lmax         14,18,13                  14,18,13
Nref             3865                      3833
Tmin,Tmax        0.762,0.726               0.768,1.000
Tmin'            0.691

Correction method= # Reported T Limits: Tmin=0.768 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.992          Theta(max)= 68.001

R(reflections)= 0.0409( 3168)     wR2(reflections)= 0.1086( 3833)

S = 1.042                 Npar= 289
```

Part 7: DFT study of 3a and 3a'

Figure 3. Comparison between optimized 3a and 3a'. Relative free energies (*energies*) are in kcal/mol.



3a



3a'

$\Delta G_{sov}(\Delta E_{sov})$ kcal/mol	0.0(*0.0*)	2.0(*2.5*)

Computational Methods

All the calculations were performed with Gaussian 09 package.[1] Geometry optimization of all stationary points was conducted by density functional theory B3LYP-D3[2] in solvent (solvent = 1,2-dichloroethane) using SMD[3] solvation model. The 6-31G(d) basis set[4] was used for all the atoms. Frequency calculations at the same level of theory were also performed to verify the stationary points as minima (no imaginary frequency). Single-point energy calculation was calculated with SMD model and B3LYP-D3 method with 6-311++G(d, p) basis set[5]. All relative energies (corrected with zero point energy) and Gibbs free energies (at 298.15 K and 1 atm) are reported in kcalmol^{-1}.

References

1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A.; Jr. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Lyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Rev. D.01, Gaussian, Inc.: Wallingford, CT, 2010.
2. (a) A. D. Becke, *Phys. Rev. A: Gen. Phys.* 1988, **38**, 3098; (b) A. D. Becke, *J. Chem. Phys.* 1993, **98**, 5648; c) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B* 1988, **37**, 785; (d) S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.* 2010, **132**, 154104.
3. A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B* 2009, **113**, 6378.
4. (a) R. Ditchfield, W. J. Hehre and J. A. Pople, *J. Chem. Phys.* 1971, **54**, 724; (b) P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta.* 1973, **28**, 213.
5. (a) F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.* 2005, **7**, 3297; (b) R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.* 1980, **72**, 650; (c) T. Clark, J. Chandrasekhar, G. W. Spitznagel and P. V. R. Schleyer, *J. Comp. Chem.* 1983, **4**, 294; (d) The basis sets were obtained from the Gaussian Basis Set Library EMSL at https://bse.pnl.gov/bse/portal.

Energies and Cartesian Coordinates of Optimized Structures

Table S1. ZPE and thermal correction from B3LYP-D3/6-31G(d) frequency calculation in solvent (1,2-dichloroethane) and single point energies of related structures (single point energy were calculated at the B3LYP-D3/6-311++G(d,p) level at 298.15 K and 1 atm.

Geometry	ZPE	H correction	G correction	E
3a	0.421398	0.448349	0.365583	-1699.706162
3a'	0.420906	0.448036	0.364348	-1699.701661

Cartesian coordinates (in Å) of related structures which calculated at the B3LYP-D3/6-31G(d) level of theory.

3a

S	1.224891	-2.545915	-0.905834
O	1.707234	-3.919321	-0.689110
O	1.122400	-2.010478	-2.269337
O	-1.916574	-2.518560	2.063296
N	-0.313303	-2.525776	-0.217721
H	-0.350453	-3.219752	0.532921
C	4.323427	1.454716	2.475139
H	4.605796	1.045799	3.450135
H	5.231369	1.816960	1.978188
H	3.679956	2.327692	2.644962
C	3.609471	0.433381	1.625980
C	3.250400	-0.821596	2.142440
H	3.513638	-1.075044	3.165909
C	2.554239	-1.745754	1.365820
H	2.277854	-2.712247	1.776503
C	2.215840	-1.408011	0.052169
C	-0.906384	-1.268051	0.223575
H	-0.166977	-0.639808	0.743063
C	-1.627971	-0.373550	-0.847611
C	3.266636	0.738702	0.300134
H	3.525969	1.710350	-0.109830
C	2.565110	-0.168825	-0.489733
H	2.278254	0.080101	-1.504651
C	-1.974624	-1.578511	1.285130
C	-3.008347	-0.545995	1.156657
C	-2.792993	0.180577	-0.021734
C	-3.635755	1.243200	-0.342865
H	-3.472317	1.824681	-1.245458
C	-4.690872	1.545977	0.522114
H	-5.355670	2.372038	0.283634
C	-4.910487	0.803964	1.696627
C	-4.067781	-0.254661	2.024432
H	-4.210672	-0.836059	2.930838
C	-2.197725	-1.247353	-1.982694
H	-1.388168	-1.712462	-2.550042
H	-2.825484	-2.043416	-1.569873
H	-2.808988	-0.638232	-2.656543
H	-5.737932	1.065474	2.349882
C	-0.736793	0.725673	-1.374755
C	-0.129343	1.789067	-0.604111
C	-0.298624	0.889988	-2.668675
C	0.669963	2.553014	-1.503268
C	-0.155837	2.158632	0.753910
N	0.543328	1.978234	-2.749368
H	-0.503105	0.297592	-3.547756
C	1.426293	3.654699	-1.087385
H	-0.757986	1.600632	1.464720
C	0.600283	3.248118	1.174536
H	0.989630	2.306899	-3.594510
H	2.026691	4.220296	-1.794800
C	1.383162	3.990441	0.263086
H	0.587212	3.537277	2.222154
H	1.960747	4.838471	0.621217

3a'

S	1.200809	-2.486629	-0.808206
O	1.659900	-2.935825	-2.133280
O	0.923108	-3.476132	0.248046
N	-0.164445	-1.547080	-1.113008
C	2.372942	-1.309641	-0.158027
H	-0.512348	-1.782830	-2.045917
C	-1.244108	-1.533821	-0.134858
C	2.703996	-0.188473	-0.926498
C	2.960615	-1.537433	1.084308
H	-1.337436	-2.519285	0.344860
C	-1.203346	-0.461659	1.018497
C	-2.582588	-1.328134	-0.862980
C	3.625067	0.721207	-0.422659
H	2.229267	-0.017642	-1.886953
C	3.882441	-0.609490	1.574861
H	2.692408	-2.415787	1.661184
C	-0.336247	0.746212	0.715985
C	-2.678910	-0.046349	1.093308
C	-0.776478	-1.132265	2.339784
O	-2.823659	-1.741638	-1.987172
C	-3.441342	-0.545299	0.030761
C	4.221381	0.531292	0.836510
H	3.873432	1.604554	-1.005150
H	4.338315	-0.774693	2.547543
C	-0.355168	1.612891	-0.445491
C	0.615621	1.268281	1.564918
C	-3.284842	0.764703	2.053205
H	0.257884	-1.484216	2.279529
H	-1.418356	-1.993385	2.551817
H	-0.859225	-0.437468	3.181089
C	-4.802242	-0.248477	-0.113335
C	5.176202	1.563511	1.381524
C	0.621489	2.628507	-0.220641
C	-1.065856	1.638974	-1.661873
N	1.181171	2.395096	1.014769
H	0.951055	0.918065	2.529266
H	-2.708273	1.176438	2.876623
C	-4.645094	1.055712	1.924800
C	-5.403178	0.554733	0.850766
H	-5.362083	-0.642022	-0.956912
H	5.987167	1.769098	0.672522
H	5.621454	1.242472	2.328179
H	4.657538	2.515480	1.557746
C	0.903665	3.631610	-1.155279
C	-0.792747	2.634964	-2.593337
H	-1.815823	0.889364	-1.886700
H	1.949206	2.913713	1.417056
H	-5.127343	1.688158	2.665544
H	-6.458189	0.802025	0.776188
H	1.661214	4.384052	-0.952564
C	0.184789	3.622827	-2.345741
H	-1.339646	2.650954	-3.532400
H	0.378608	4.385372	-3.095371