Supporting Information

Construction of Spirothioureas Having an Amino Quaternary Stereogenic Center *via* a [3+2] Annulation of 3-Isothiocyanato Oxindoles with 2-Aminoacrylates

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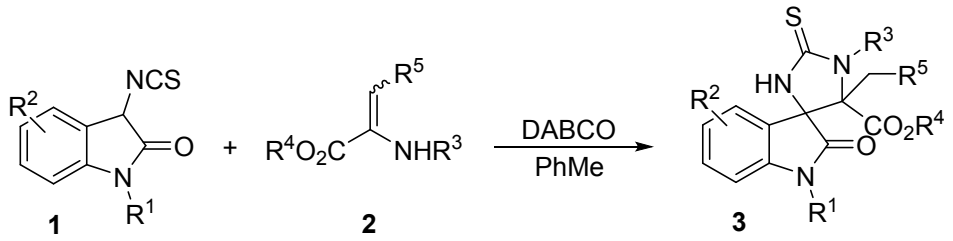
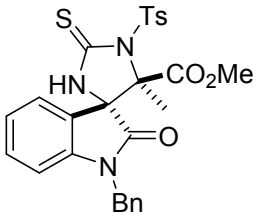
1. General Remarks: Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. ^{1}H NMR spectra were recorded on a Varian Mercury-300 and 400 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard; coupling constants *J* are given in Hz. ^{13}C NMR spectra were recorded on a Varian Mercury-300 and 400 spectrophotometers (75 or 100 MHz) with complete proton decoupling spectrophotometers ($CDCl_3$: 77.0 ppm). Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Flash column chromatography was performed using 300-400 mesh silica gel. For thin-layer chromatography (TLC), silica gel plates (Huanghai GF254) were used. Mass spectra were recorded by ESI. HRMS was measured on a HP-5989 instrument.

2. General Procedure for the Synthesis of 3



To a 20 mL flame-dried tube was charged with 3-isothiocyanato **1** (0.24 mmol, 1.2 equiv), 2-aminoacrylates **2** (0.2 mmol, 1.0 equiv) and DABCO (0.02 mmol, 0.1 equiv). Then, 2.5 mL PhMe was added into the tube. The reaction mixture was stirred at room temperature for 12 h. The solvent was removed under reduced pressure, and the residue was purified by a flash column chromatography (SiO_2) to give the corresponding crude products **3**.

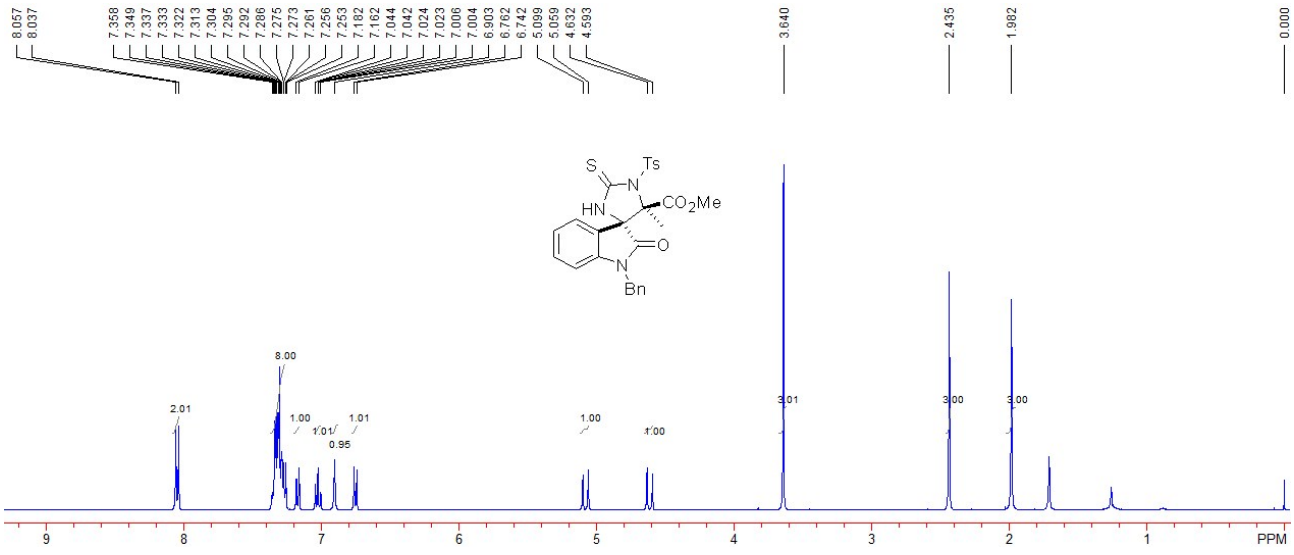
3. Characterization and Spectra Charts for Compounds 3 and 3'

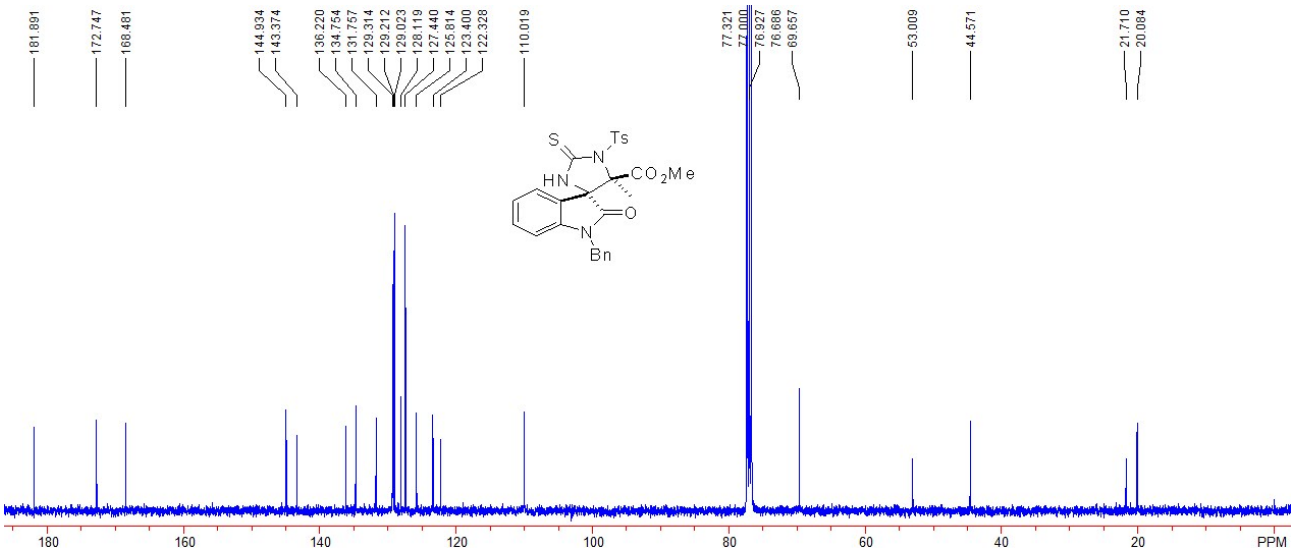


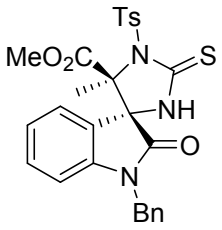
Methyl-1'-benzyl-5-methyl-2'-oxo-2-thioxo-1-tosylspiro[imidazolidine-4,3'-indoline]-5-carboxylate (3aa)

A white solid, 100 mg, 97 % yield; *dr* = 24:1; m. p. 205-207 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.05 (d, *J* = 8.0 Hz, 2H), 7.36-7.25 (m, 8H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.02 (td, *J* = 0.8, 8.0 Hz, 1H), 6.90 (s, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 5.08 (d, *J* = 16.0 Hz, 1H), 4.61 (d, *J* = 15.6 Hz, 1H), 3.64 (s, 3H), 2.44 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 181.9, 172.7, 168.5, 144.9, 143.4, 136.2, 134.7, 131.8, 129.3, 129.2, 129.0, 128.1, 127.4, 125.8, 123.4, 122.3, 110.0, 76.9, 69.6, 53.0, 44.6, 21.7, 20.1; IR (neat): ν 3123, 2953, 1713, 1609, 1497, 1468, 1362, 1086, 1037, 802, 754, 688, 667 cm^{-1}; HRMS (ESI) Calcd. For $C_{27}H_{29}N_4O_5S_2^+$ $(M+NH_4)^+$ requires 553.1574, found: 553.1564.

For asymmetric study: A white solid, 52 mg, 98 % yield; *dr* = 1:1; m. p. 159-162 °C; $[\alpha]^{20}_D$ = 111.9 (c 1.00, CH_2Cl_2).

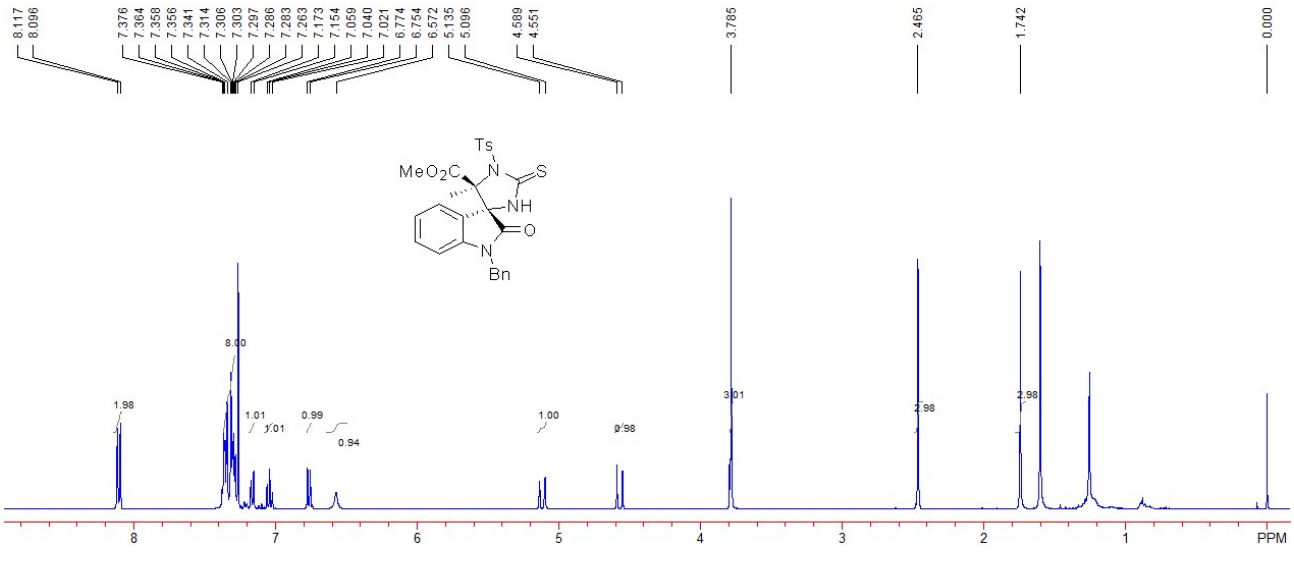


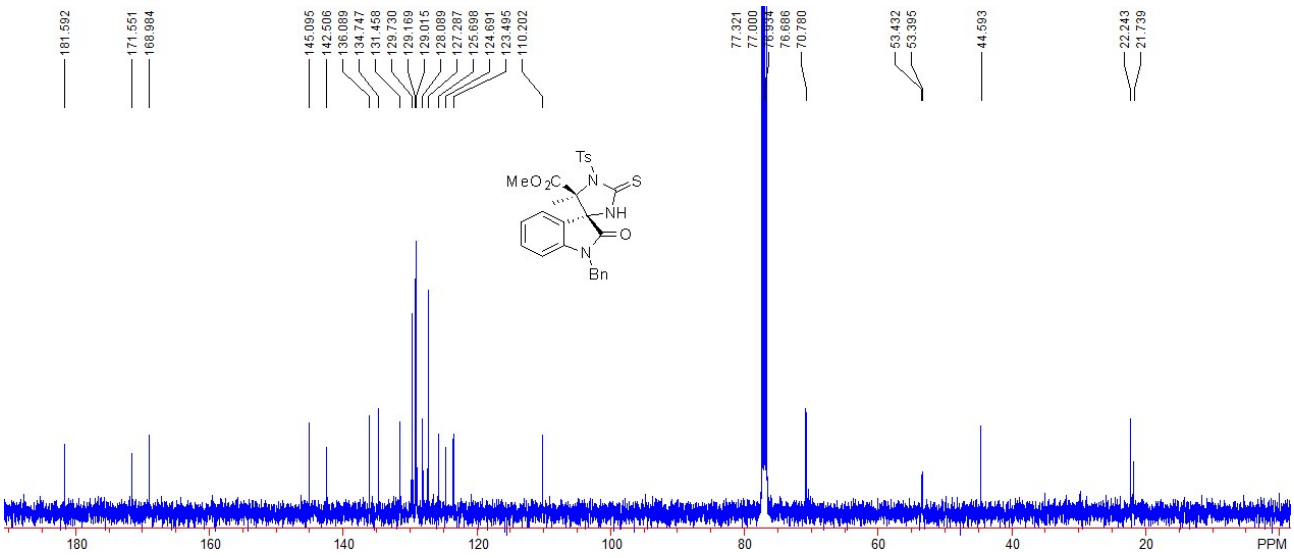


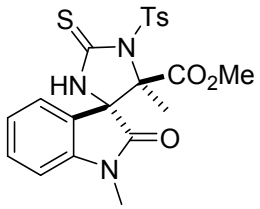


Methyl(4R,5S)-1'-benzyl-5-methyl-2'-oxo-2-thioxo-1-tosylspiro[imidazolidine-4,3'-indoline]-5-carboxylate (3aa')

A white solid, 52 mg, 98 % yield; *dr* = 1:1; m. p. 104-107 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.11 (d, *J* = 8.4 Hz, 2H), 7.38-7.28 (m, 8H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.04 (td, *J* = 0.8, 7.6 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 6.57 (s, 1H), 5.12 (d, *J* = 15.6 Hz, 1H), 4.57 (d, *J* = 15.2 Hz, 1H), 3.79 (s, 3H), 2.47 (s, 3H), 1.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 181.6, 171.6, 169.0, 145.1, 142.5, 136.1, 134.7, 131.5, 129.7, 129.2, 129.0, 128.1, 127.3, 125.7, 124.7, 123.5, 110.2, 76.9, 70.8, 53.4 (d, *J* = 3.7 Hz), 44.6, 22.2, 21.7; IR (neat): ν 3092, 2924, 1752, 1722, 1486, 1468, 1366, 1167, 1131, 1039, 751, 740, 664 cm^{-1}; HRMS (ESI) Calcd. For $C_{27}H_{29}N_4O_5S_2^+$ $(M+NH_4)^+$ requires 553.1574, found: 553.1566; $[\alpha]^{20}_D$ = 15.8 (c 1.00, CH_2Cl_2).





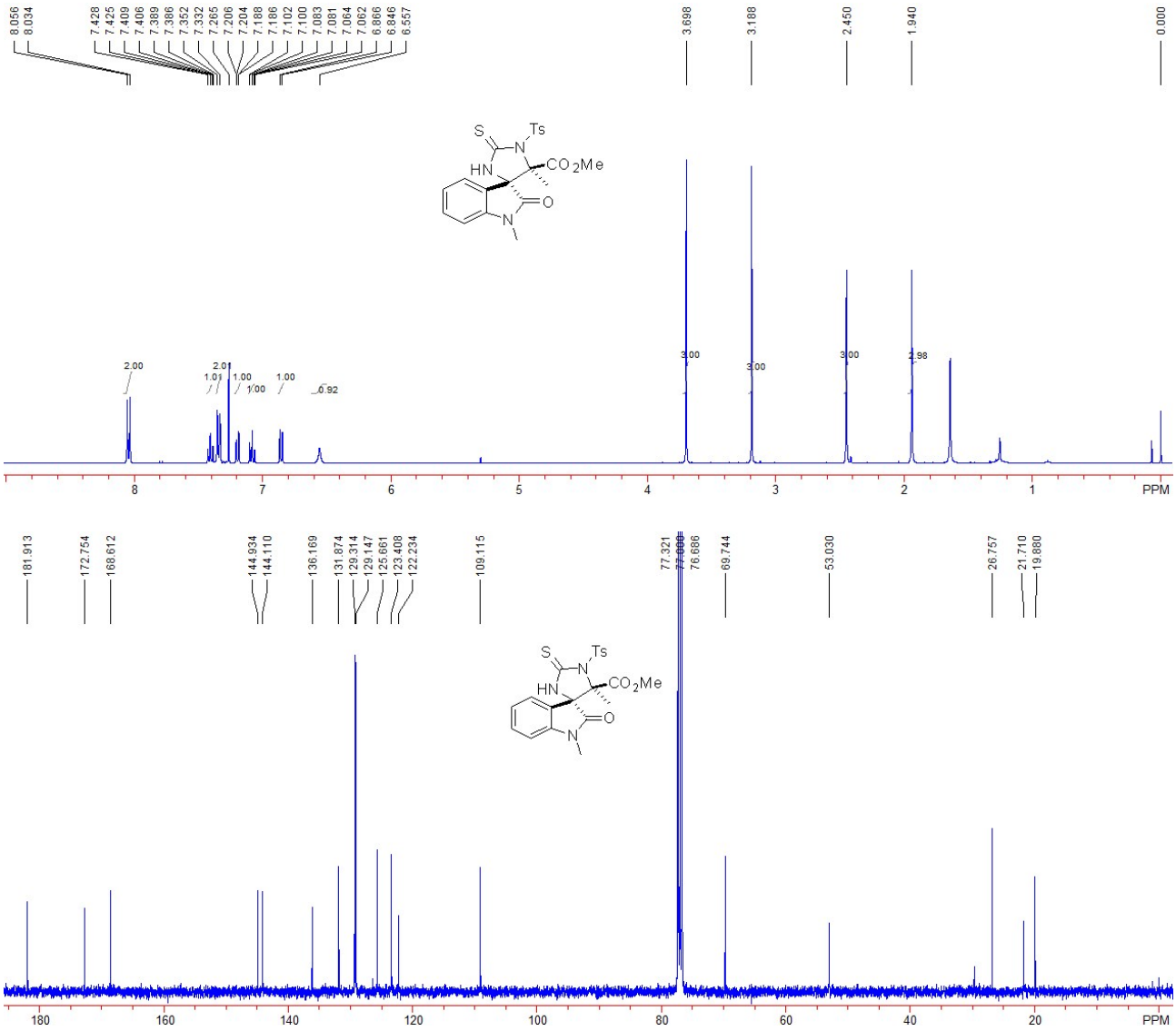


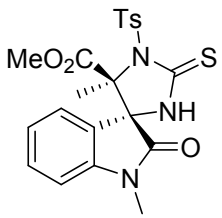
Methyl-1',5-dimethyl-2'-oxo-2-thioxo-1-tosylspiro[imidazolidine-4,3'-indoline]-5-carboxylate (3ba)

A white solid, 74 mg, 90 % yield; *dr* = 9:1; m. p. 208-211 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.05 (d, *J* = 8.4 Hz, 2H), 7.41 (td, *J* = 1.2, 7.6 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.19 (dd, *J* = 0.8, 7.2 Hz, 1H), 7.08 (td, *J* = 0.8, 7.6 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.56 (s, 1H), 3.70 (s, 3H), 3.19 (s, 3H), 2.45 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 181.9, 172.8, 168.6, 144.9,

144.1, 136.2, 131.9, 129.3, 129.1, 125.7, 123.4, 122.2, 109.1, 69.7, 53.0, 26.8, 21.7, 19.9; IR (neat): ν 3113, 2964, 1752, 1721, 1519, 1349, 1082, 1040, 762, 730, 693, 674, 662 cm^{-1}; HRMS (ESI) Calcd. For $C_{21}H_{22}N_3O_5S_2^+$ $(M+H)^+$ requires 460.0995, found: 460.0986.

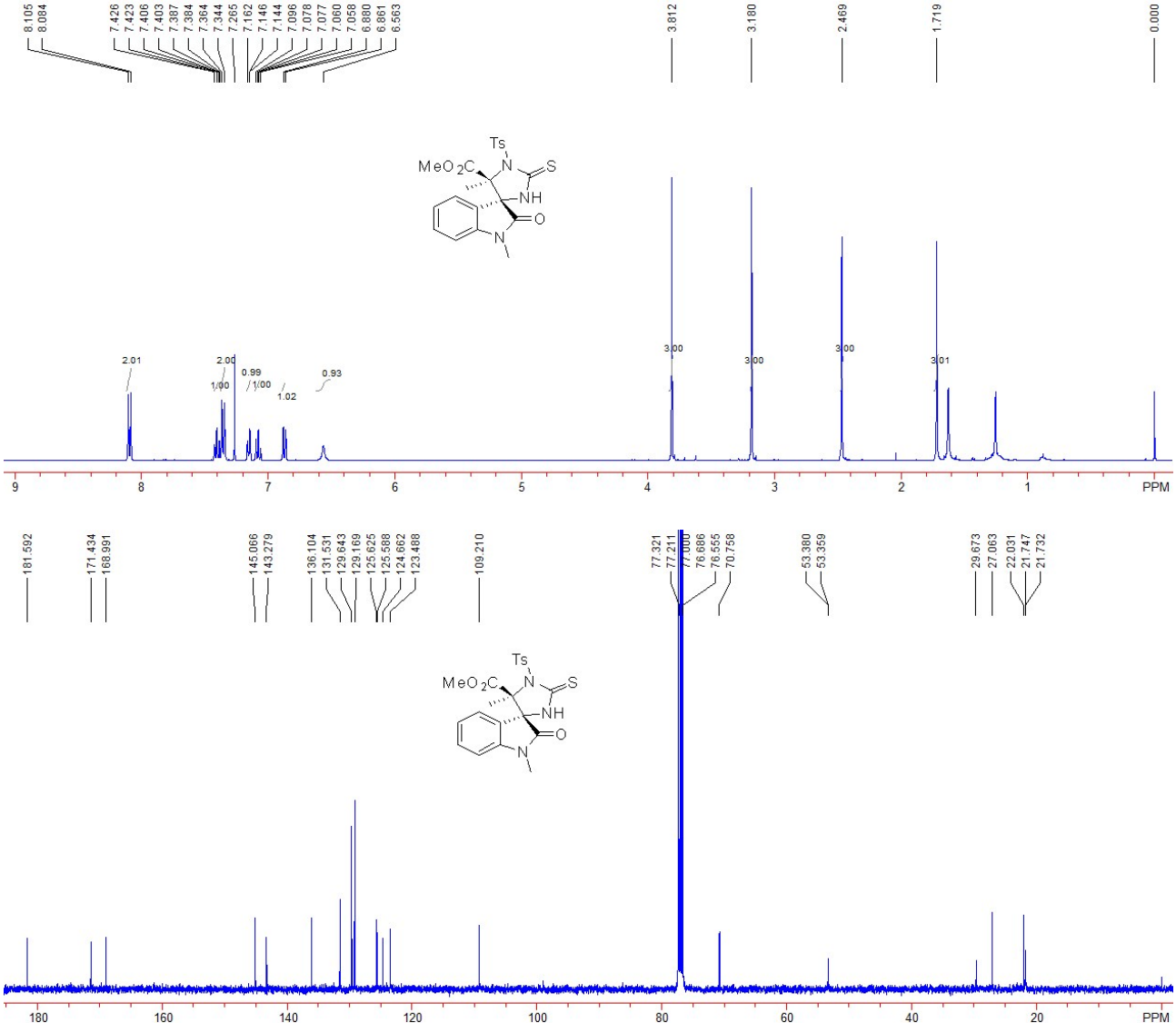
For asymmetric study: A white solid, 56 mg, 92 % yield; *dr* = 2:1; m. p. 149-151 °C; $[\alpha]^{20}_D$ = 186.1 (c 1.00, CH_2Cl_2).

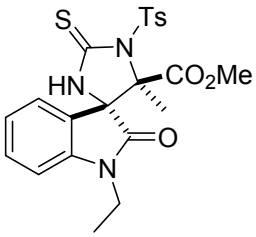




Methyl(4R,5S)-1',5-dimethyl-2'-oxo-2-thioxo-1-tosylspiro[imidazolidine-4,3'-indoline]-5-carboxylate (3ba')

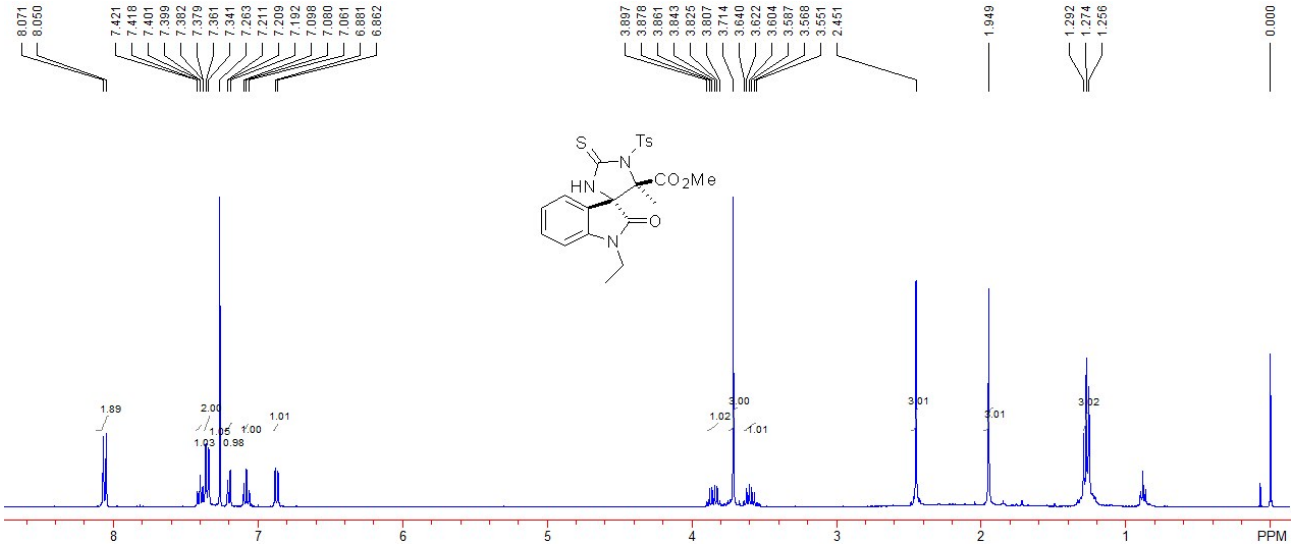
A white solid, 28 mg, 92 % yield; *dr* = 2:1; m. p. 110-113 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.09 (d, *J* = 8.4 Hz, 2H), 7.40 (td, *J* = 1.2, 8.0 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 7.2 Hz, 1H), 7.08 (td, *J* = 0.8, 7.2 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.56 (s, 1H), 3.81 (s, 3H), 3.18 (s, 3H), 2.47 (s, 3H), 1.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 181.6, 171.4, 169.0, 145.1, 143.3, 136.1, 131.5, 129.6, 129.2, 125.6, 124.7, 123.5, 109.2, 70.8, 53.4 (d, *J* = 2.1 Hz), 27.1, 22.0, 21.7 (d, *J* = 1.5 Hz); IR (neat): ν 3120, 2965, 1751, 1721, 1607, 1349, 1083, 761, 692, 674, 662 cm^{-1}; HRMS (ESI) Calcd. For $C_{21}H_{25}N_4O_5S_2^+$ $(M+NH_4)^+$ requires 477.1261, found: 477.1253; $[\alpha]^{20}_D$ = -51.4 (c 1.00, CH_2Cl_2).

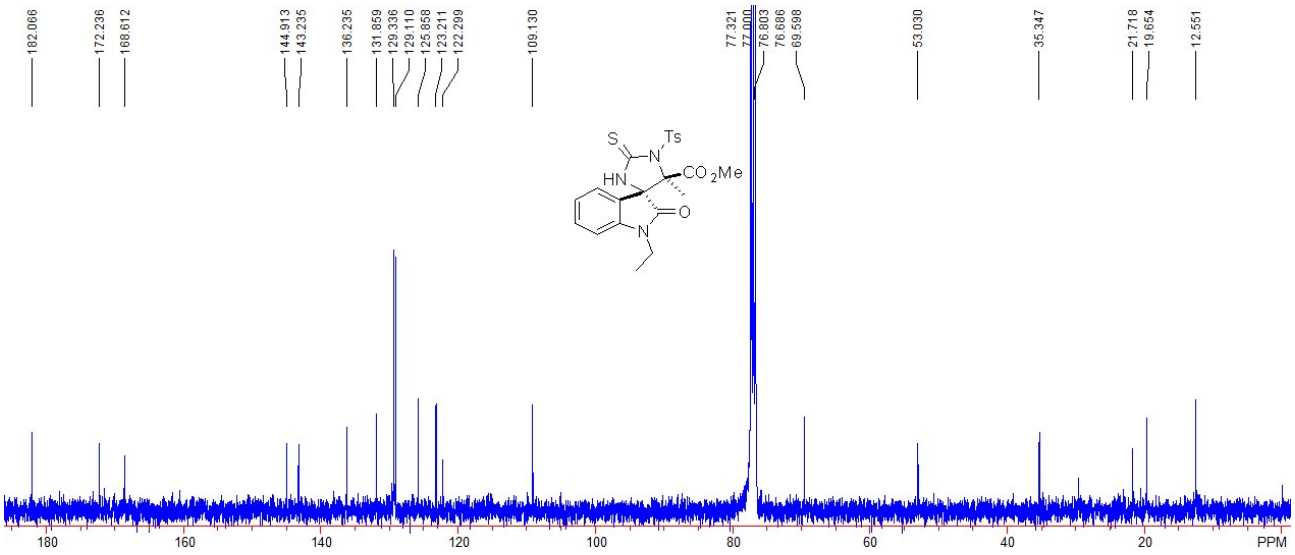


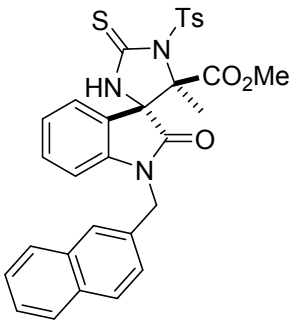


Methyl-1'-ethyl-5-methyl-2'-oxo-2-thioxo-1-tosylspiro[imidazolidine-4,3'-indoline]-5-carboxylate (3ca)

A white solid, 56 mg, 90 % yield; *dr* = 10:1; m. p. 206-208 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.06 (d, *J* = 8.4 Hz, 2H), 7.40 (td, *J* = 1.2, 8.4 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.26 (s, 1H), 7.20 (dd, *J* = 0.8, 7.6 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 7.6 Hz, 1H), 3.85 (qd, *J* = 7.2, 14.4 Hz, 1H), 3.71 (s, 3H), 3.59 (qd, *J* = 7.2, 14.4 Hz, 1H), 2.45 (s, 3H), 1.95 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 182.0, 172.2, 168.6, 144.9, 143.2, 136.2, 131.9, 129.3, 129.1, 125.9, 123.2, 122.3, 109.1, 76.8, 69.6, 53.0, 35.3, 21.7, 19.7, 12.6; IR (neat): ν 2919, 1716, 1609, 1467, 1366, 1356, 1258, 1124, 1085, 758, 688, 669 cm^{-1}; HRMS (ESI) Calcd. For $C_{22}H_{24}N_3O_5S_2^+$ $(M+H)^+$ requires 474.1152, found: 474.1146.

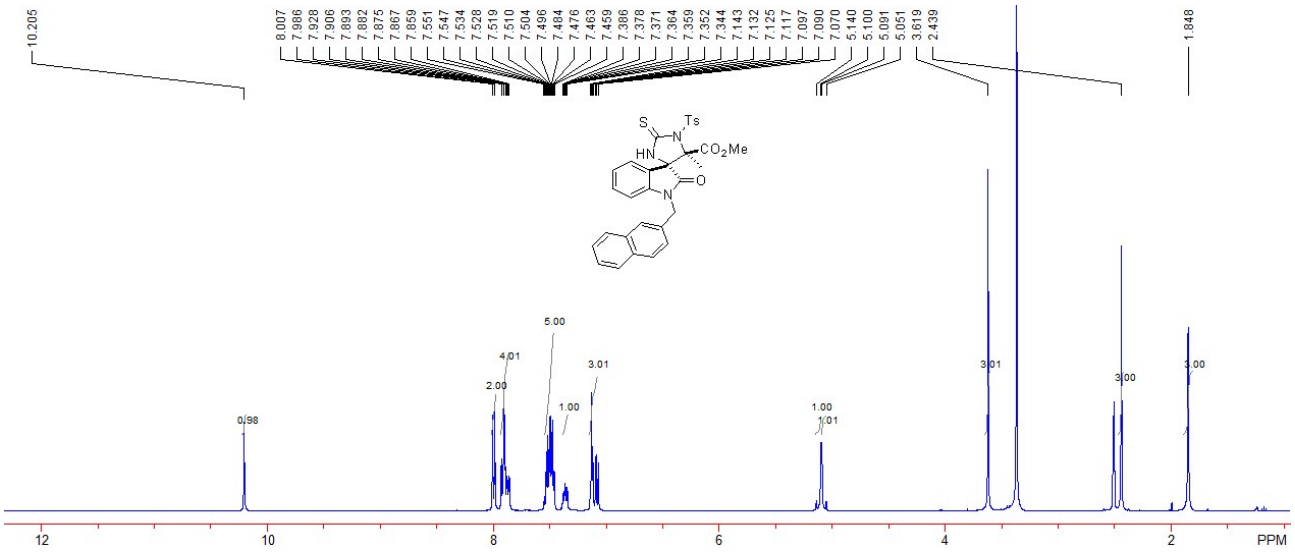


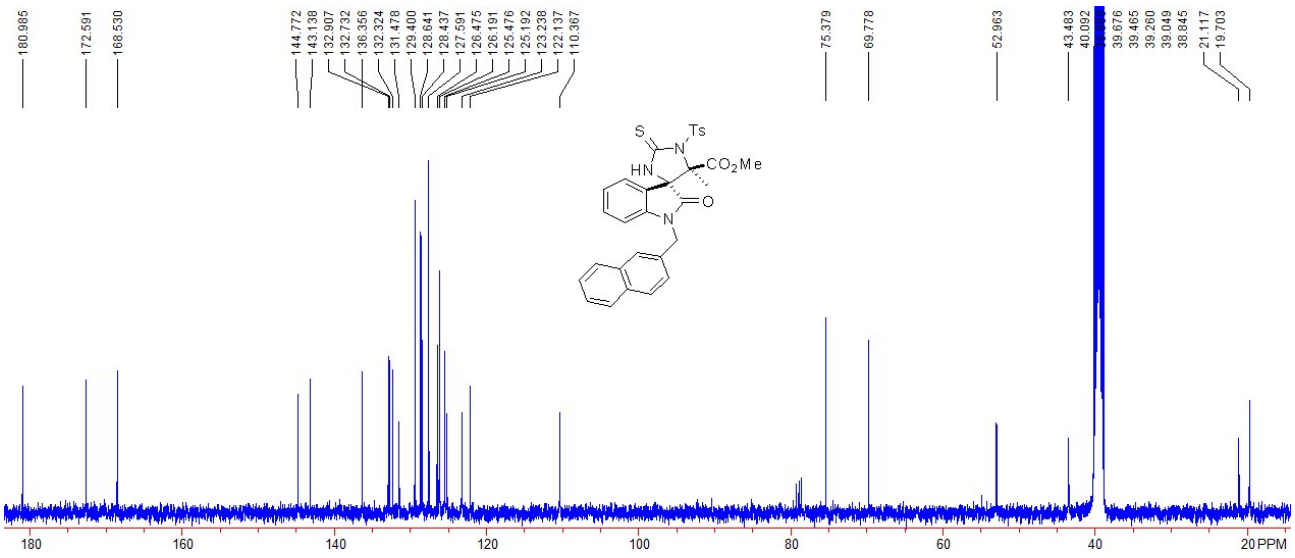


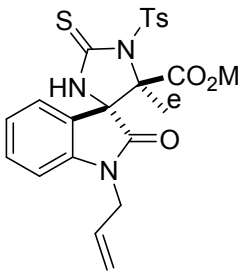


Methyl-5-methyl-1'-(naphthalen-2-ylmethyl)-2'-oxo-2-thioxo-1-tosylspiro[imidazolidine-4,3'-indoline]-5-carboxylate (3da)

A white solid, 92 mg, 85 % yield; *dr* = 12:1; m. p. 225-228 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ 10.21 (s, 1H), 8.00 (d, *J* = 8.4 Hz, 2H), 7.93-7.86 (m, 4H), 7.55-7.46 (m, 5H), 7.39-7.34 (m, 1H), 7.14-7.07 (m, 3H), 5.12 (d, *J* = 16.0 Hz, 1H), 5.07 (d, *J* = 16.0 Hz, 1H), 3.62 (s, 3H), 2.44 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, TMS) δ 181.0, 172.6, 168.5, 144.8, 143.1, 136.4, 132.9, 132.7, 132.3, 131.5, 129.4, 128.6, 128.4, 127.6, 126.5, 126.2, 125.5, 125.2, 123.2, 122.1, 110.4, 75.4, 69.8, 53.0, 43.5, 21.1, 19.7; IR (neat): ν 3131, 2927, 2854, 1746, 1716, 1609, 1497, 1468, 1366, 1189, 1161, 984, 814, 748, 689, 668 cm^{-1}; HRMS (ESI) Calcd. For $C_{31}H_{28}N_3O_5S_2^+$ $(M+H)^+$ requires 586.1465, found: 586.1460.



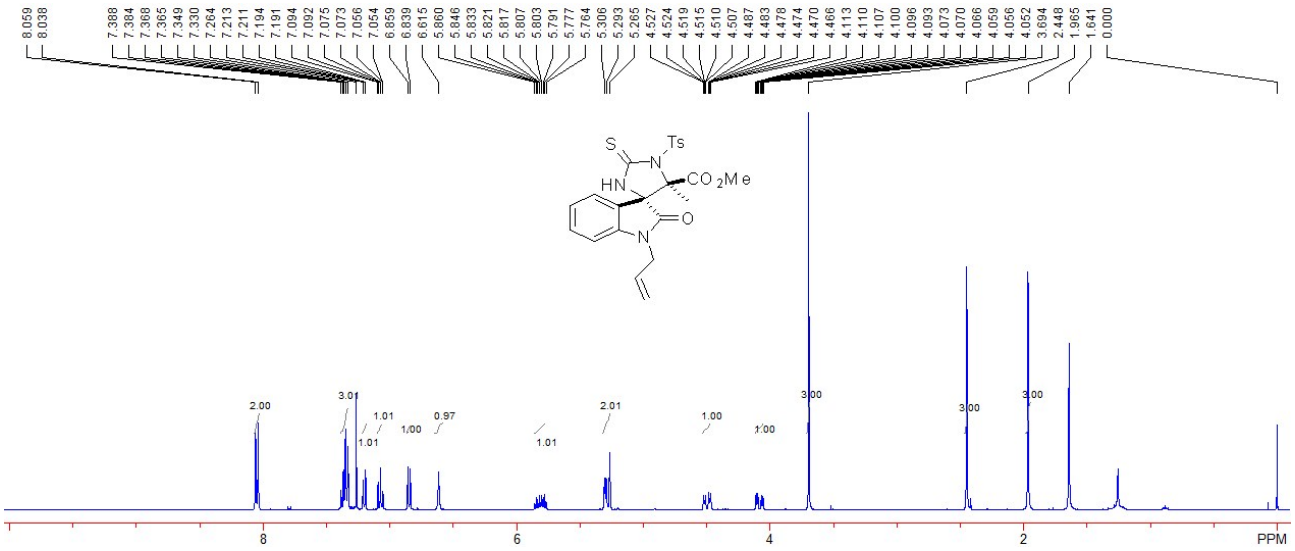


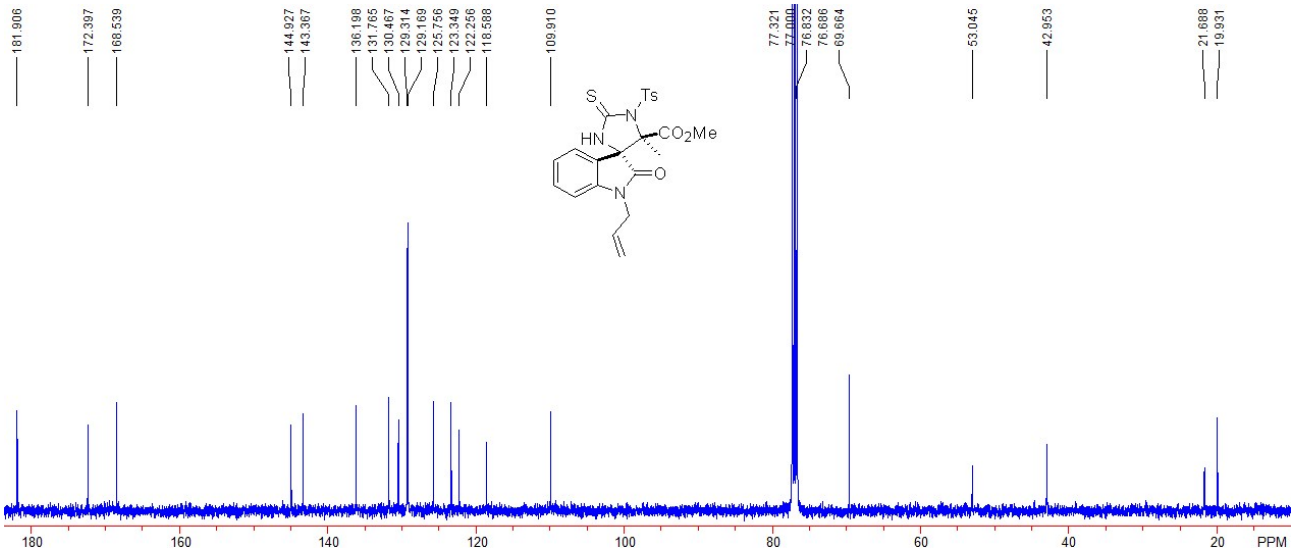


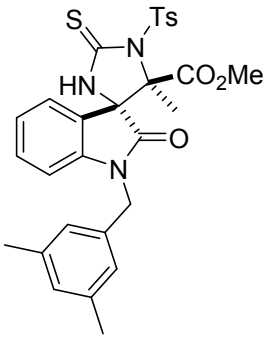
Methyl-1'-allyl-5-methyl-2'-oxo-2-thioxo-1-tosylspiro[imidazolidine-4,3'-indoline]-5-carboxylate (3ea)

A white solid, 86 mg, 95 % yield; *dr* = 13:1; m. p. 228-231 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.05 (d, *J* = 8.4 Hz, 2H), 7.39-7.33 (m, 3H), 7.20 (dd, *J* = 0.8, 7.6 Hz, 1H), 7.07 (td, *J* = 0.8, 7.6 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.62 (s, 1H), 5.86-5.76 (m, 1H), 5.31-5.27 (m, 2H), 4.50 (ddt, *J* = 1.6, 5.6, 16.0 Hz, 1H), 4.08 (ddt, *J* = 1.6, 5.6, 16.0 Hz, 1H), 3.69 (s, 3H), 2.45 (s, 3H), 1.97 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 181.9, 172.4, 168.5, 144.9, 143.4, 136.2, 131.8, 130.5, 129.3, 129.2, 125.8, 123.3, 122.3, 118.6, 109.9, 76.8, 69.7, 53.0, 43.0, 21.7, 19.9; IR (neat): ν 3136, 2953, 1754, 1712, 1611, 1492, 1364, 1261, 1192, 1164, 1087, 1034, 807, 748, 687, 669, 660 cm^{-1}; HRMS (ESI) Calcd. For $C_{23}H_{24}N_3O_5S_2^+$ $(M+H)^+$ requires 486.1152, found: 486.1142.

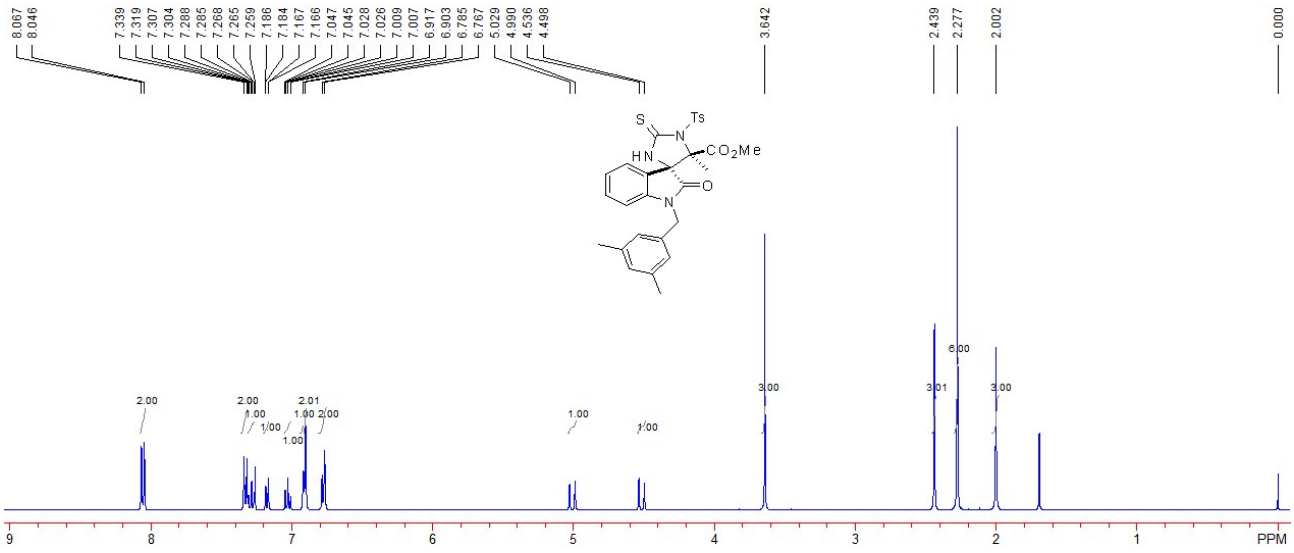


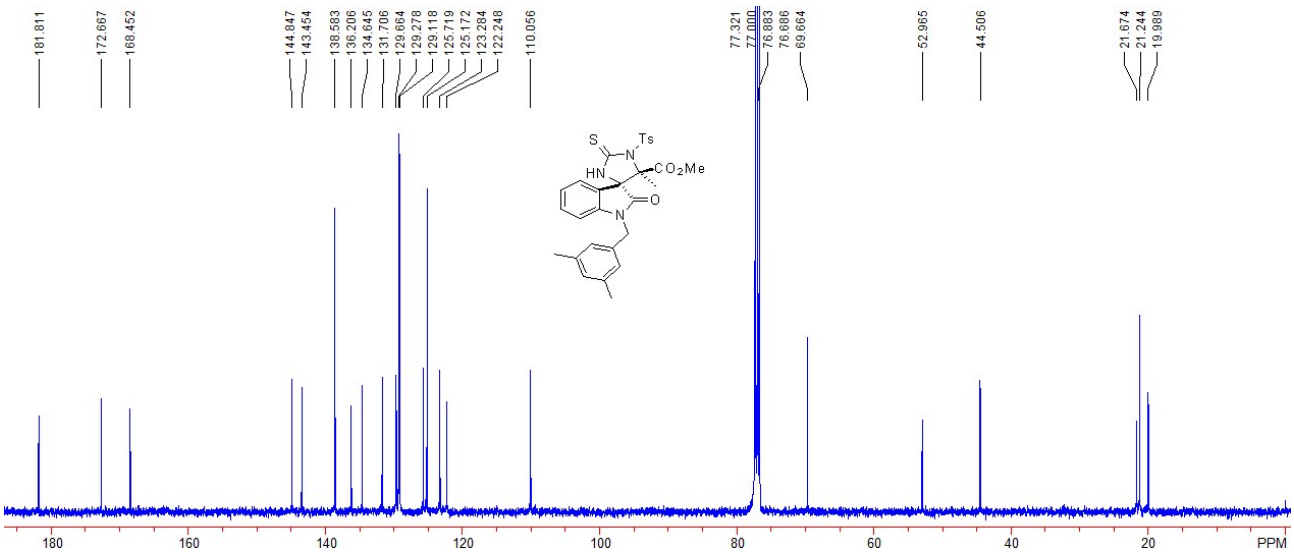


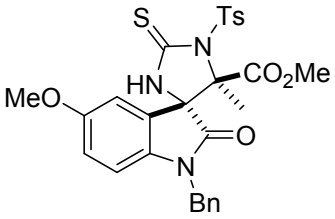


Methyl-1'-(3,5-dimethylbenzyl)-5-methyl-2'-oxo-2-thioxo-1-tosylspiro[imidazolidine-4,3'-indoline]-5-carboxylate (3fa)

A white solid, 104 mg, 97 % yield; *dr* = 19:1; m. p. 136-138 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.06 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.29 (td, *J* = 1.2, 7.6 Hz, 1H), 7.18 (dd, *J* = 0.8, 7.6 Hz, 1H), 7.03 (td, *J* = 0.8, 7.6 Hz, 1H), 6.92 (s, 1H), 6.90 (s, 2H), 6.79-6.77 (m, 2H), 5.01 (d, *J* = 15.6 Hz, 1H), 4.52 (d, *J* = 15.2 Hz, 1H), 3.64 (s, 3H), 2.44 (s, 3H), 2.28 (s, 6H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 181.8, 172.7, 168.5, 144.8, 143.5, 138.6, 136.2, 134.6, 131.7, 129.7, 129.3, 129.1, 125.7, 125.2, 123.3, 122.2, 110.0, 76.9, 69.7, 53.0, 44.5, 21.7, 21.2, 20.0; IR (neat): ν 3314, 2948, 1727, 1609, 1359, 1160, 1086, 1037, 801, 750, 667 cm^{-1}; HRMS (ESI) Calcd. For $C_{29}H_{30}N_3O_5S_2^+$ $(M+H)^+$ requires 564.1621, found: 564.1616.

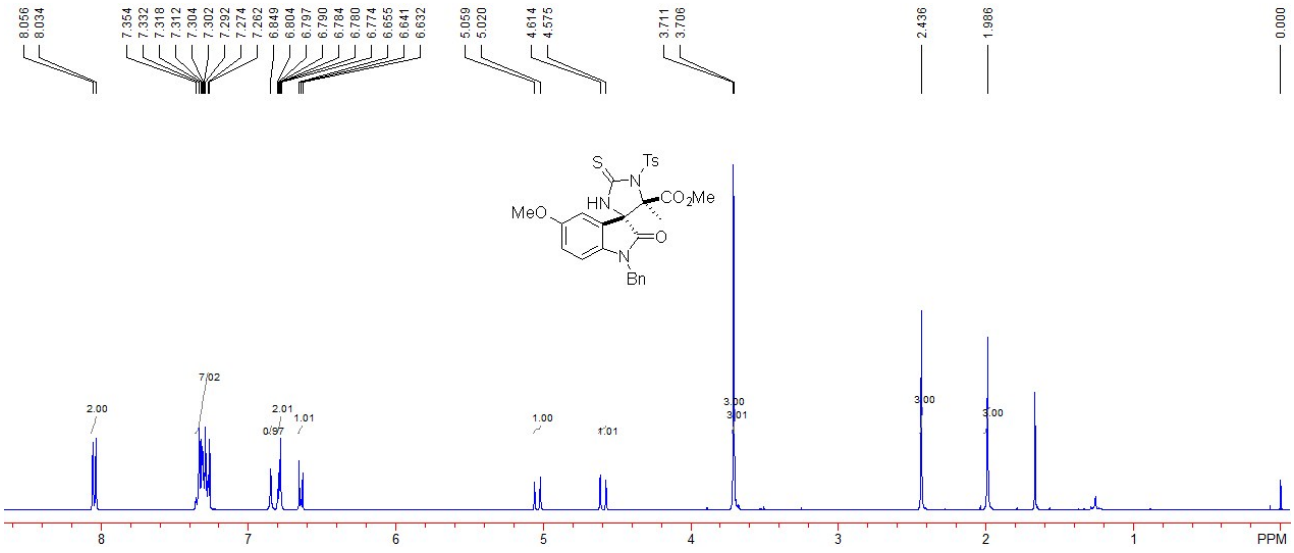


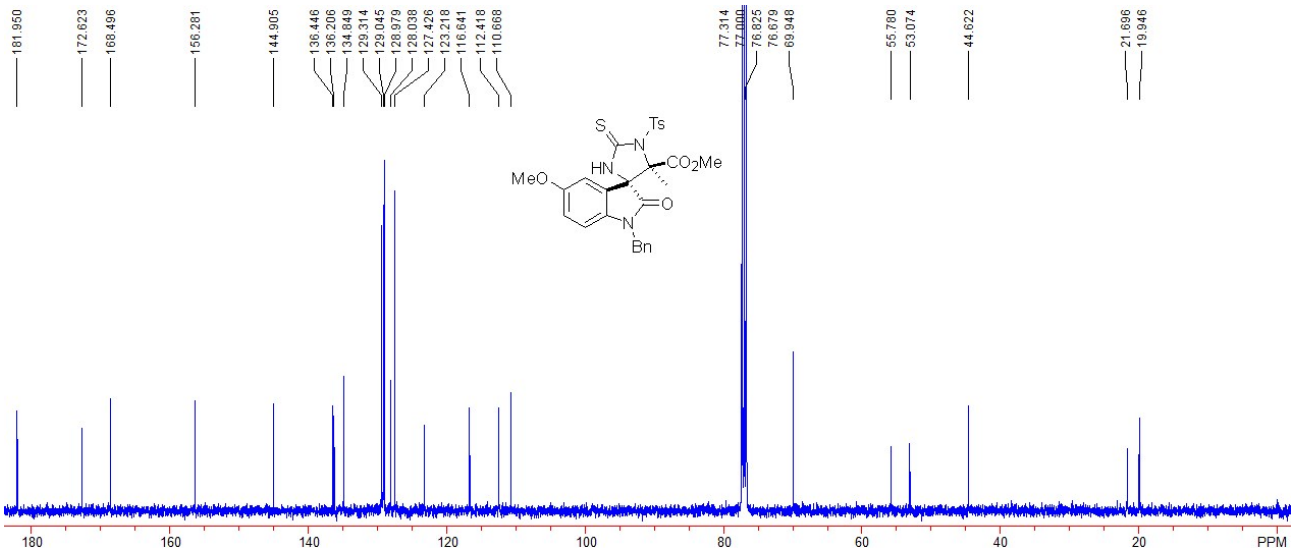


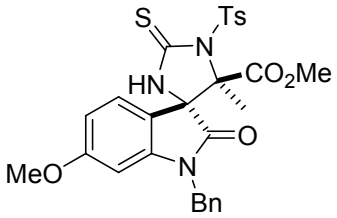


Methyl-1'-benzyl-5'-methoxy-5-methyl-2'-oxo-2-thioxo-1-tosylspiro[imidazolidine-4,3'-indoline]-5-carboxylate (3ga)

A white solid, 101 mg, 95 % yield; *dr* = 15:1; m. p. 167-169 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.05 (d, *J* = 8.8 Hz, 2H), 7.35-7.26 (m, 7H), 6.85 (s, 1H), 6.80-6.77 (m, 2H), 6.66-6.63 (m, 1H), 5.04 (d, *J* = 15.6 Hz, 1H), 4.60 (d, *J* = 15.6 Hz, 1H), 3.711 (s, 3H), 3.706 (s, 3H), 2.44 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 182.0, 172.6, 168.5, 156.3, 144.9, 136.4, 136.2, 134.8, 129.3, 129.05, 128.98, 128.0, 127.4, 123.2, 116.6, 112.4, 110.7, 76.8, 69.9, 55.8, 53.1, 44.6, 21.7, 19.9; IR (neat): ν 3149, 2956, 1702, 1495, 1361, 1235, 1184, 1160, 1127, 826, 801, 727, 702, 672 cm^{-1}; HRMS (ESI) Calcd. For $C_{28}H_{28}N_3O_6S_2^+$ $(M+H)^+$ requires 566.1414, found: 566.1409.

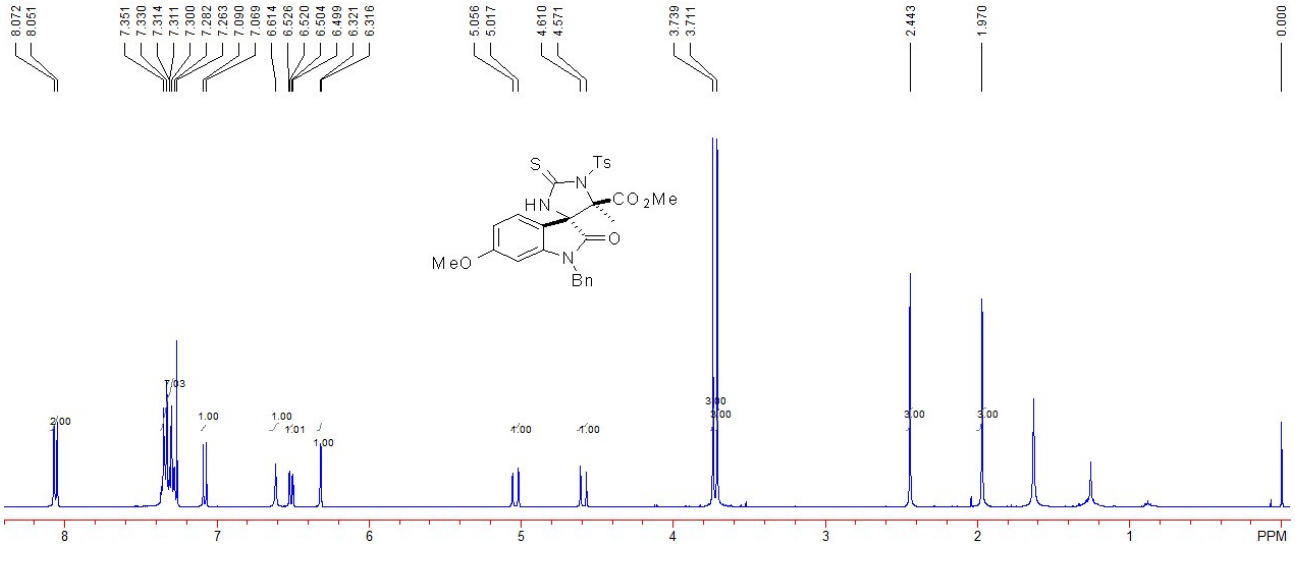


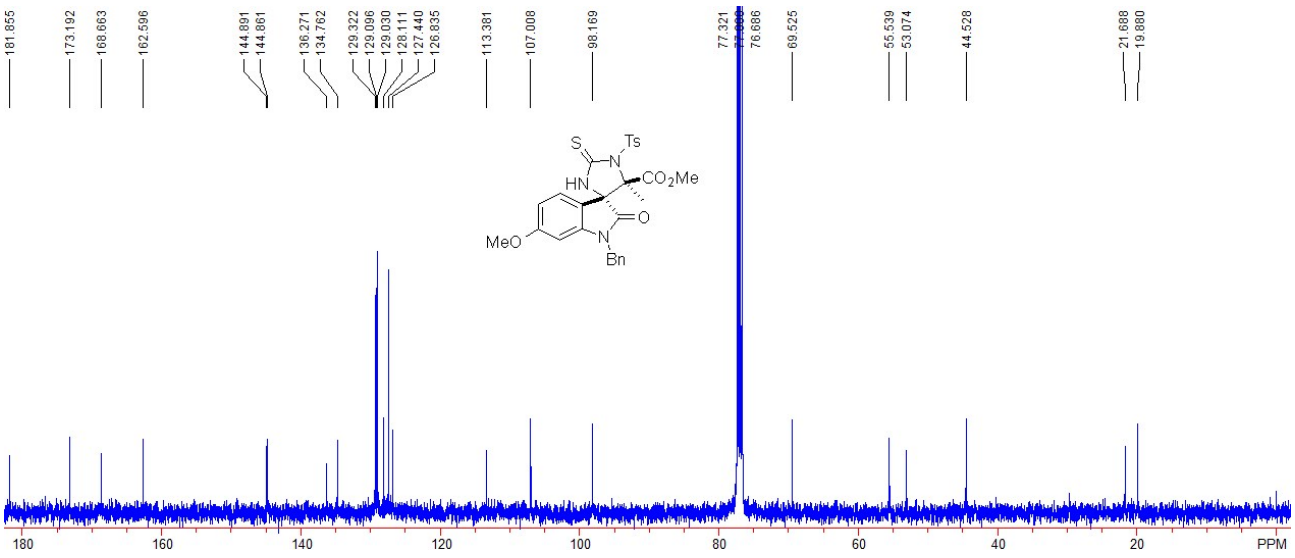


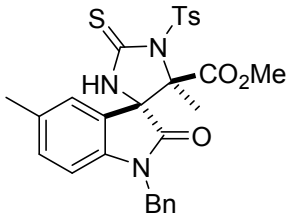


Methyl-1'-benzyl-6'-methoxy-5-methyl-2'-oxo-2-thioxo-1-tosylspiro[imidazolidine-4,3'-indoline]-5-carboxylate (3ha)

A white solid, 106 mg, 98 % yield; *dr* = 21:1; m. p. 171-173 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.06 (d, *J* = 8.4 Hz, 2H), 7.35-7.28 (m, 7H), 7.08 (d, *J* = 8.4 Hz, 1H), 6.61 (s, 1H), 6.51 (dd, *J* = 2.4, 8.4 Hz, 1H), 6.32 (d, *J* = 2.0 Hz, 1H), 5.04 (d, *J* = 15.6 Hz, 1H), 4.59 (d, *J* = 15.6 Hz, 1H), 3.74 (s, 3H), 3.71 (s, 3H), 2.44 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 181.9, 173.2, 168.7, 162.6, 144.89, 144.86, 136.3, 134.8, 129.3, 129.1, 129.0, 128.1, 127.4, 126.8, 113.4, 107.0, 98.2, 76.7, 69.5, 55.5, 53.1, 44.5, 21.7, 19.9; IR (neat): ν 3257, 2924, 1726, 1626, 1454, 1377, 1358, 1259, 1190, 1164, 1132, 1087, 1040, 1024, 834, 668 cm^{-1}; HRMS (ESI) Calcd. For $C_{28}H_{28}N_3O_6S_2^+$ $(M+H)^+$ requires 566.1414, found: 566.1406.



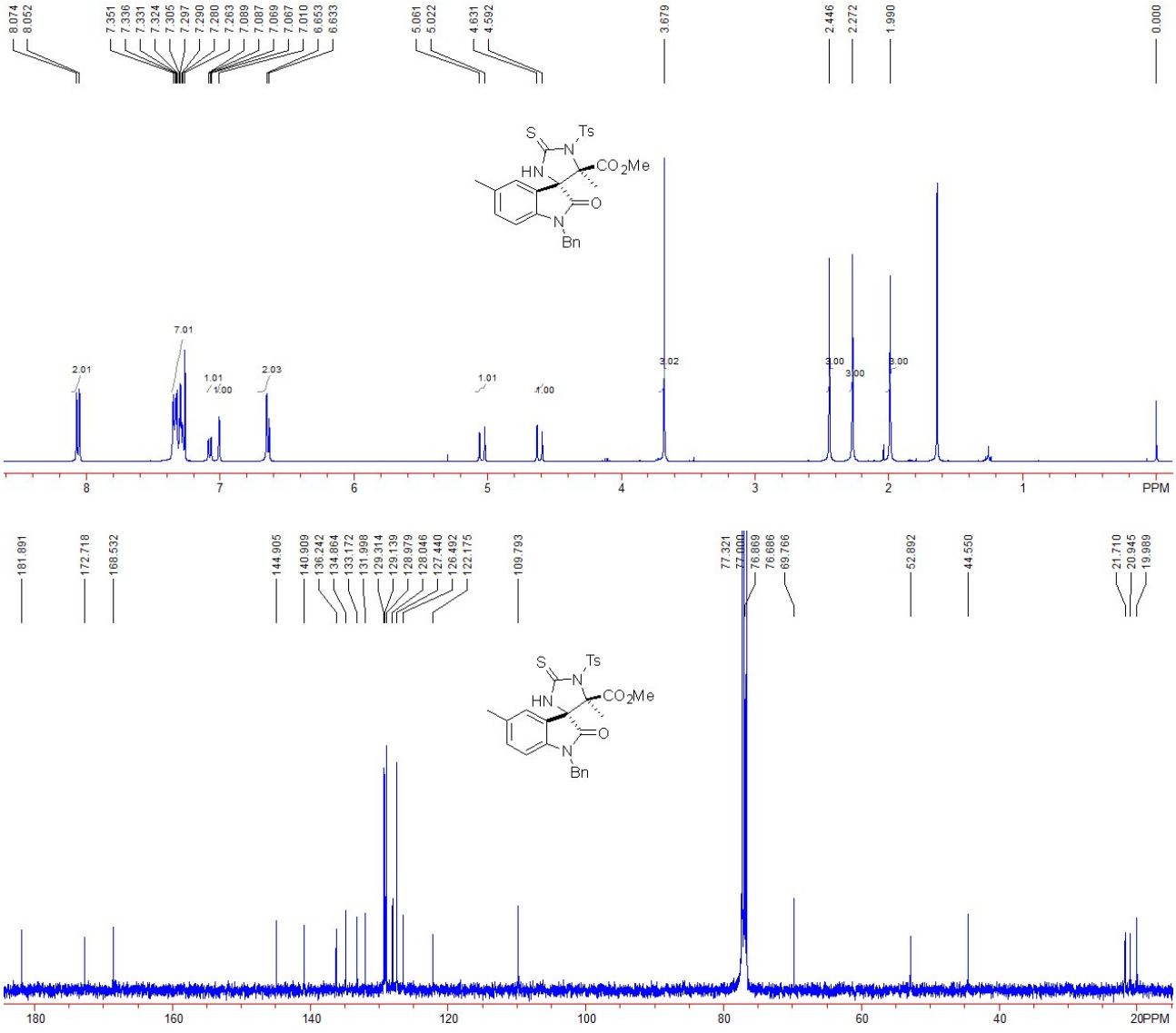


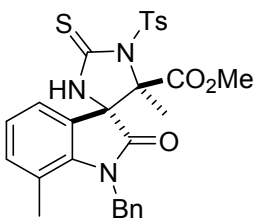


Methyl-1'-benzyl-5,5'-dimethyl-2'-oxo-2-thioxo-1-tosylspiro[imidazolidine-4,3'-indoline]-5-carboxylate (3ia)

A white solid, 99 mg, 95 % yield; *dr* = 18:1; m. p. 203-205 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.06 (d, *J* = 8.8 Hz, 2H), 7.35-7.26 (m, 7H), 7.08 (dd, *J* = 0.8, 8.0 Hz, 1H), 7.01 (s, 1H), 6.65-6.63 (m, 2H), 5.04 (d, *J* = 15.6 Hz, 1H), 4.61 (d, *J* = 15.6 Hz, 1H), 3.68 (s, 3H), 2.45 (s, 3H), 2.27 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 181.9, 172.7, 168.5, 144.9, 140.9, 136.2,

134.9, 133.2, 132.0, 129.3, 129.1, 129.0, 128.0, 127.4, 126.5, 122.2, 109.8, 76.9, 69.8, 52.9, 44.6, 21.7, 20.9, 20.0; IR (neat): ν 3147, 2951, 1707, 1497, 1363, 1341, 1222, 1160, 1034, 820, 804, 697, 670 cm^{-1}; HRMS (ESI) Calcd. For $C_{28}H_{28}N_3O_5S_2^+$ $(M+H)^+$ requires 550.1465, found: 550.1461.



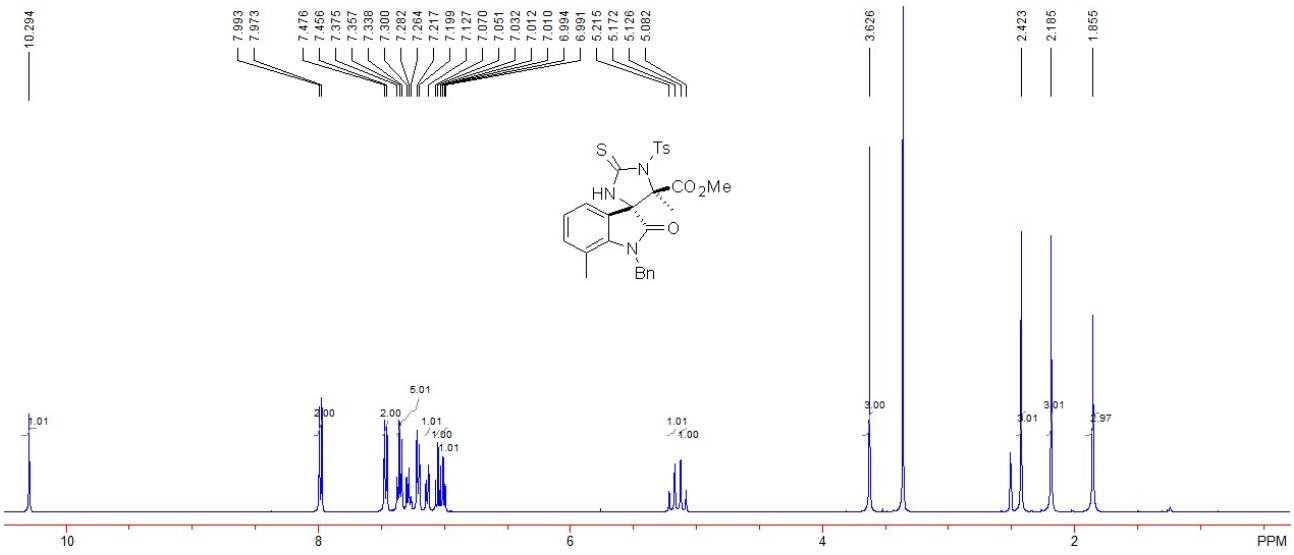


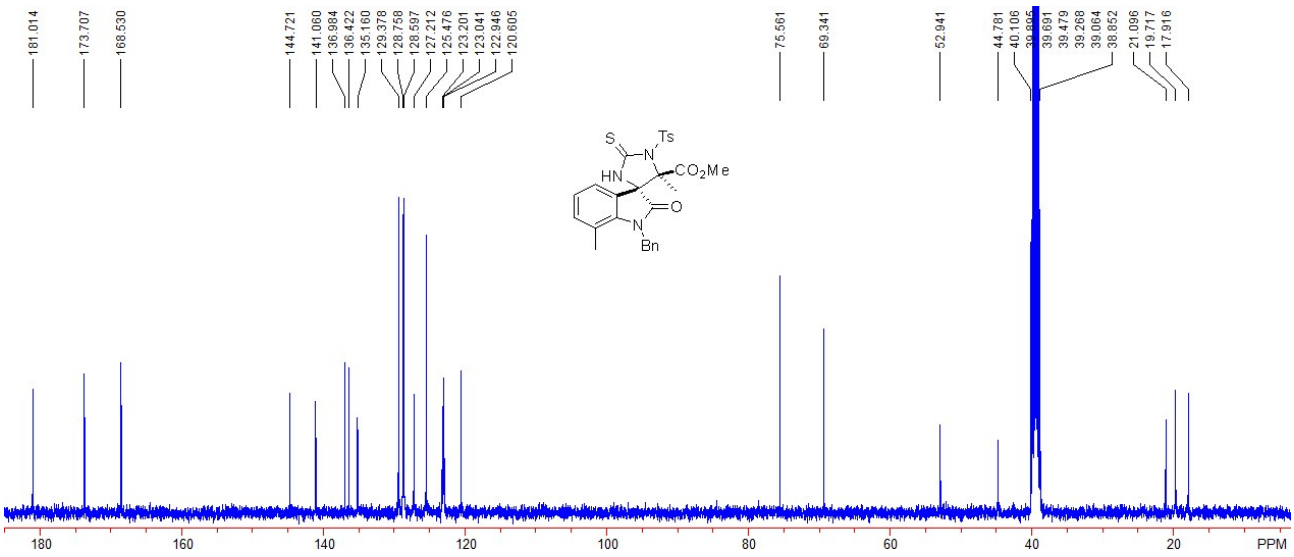
Methyl-1'-benzyl-5,7'-dimethyl-2'-oxo-2-thioxo-1-tosylspiro[imidazolidine-4,3'-indoline]-5-carboxylate (3ja)

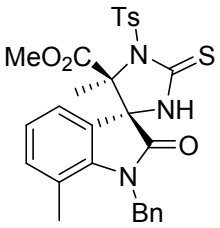
A white solid, 97 mg, 93 % yield; *dr* = 19:1; m. p. 224-226 °C; ^{1}H NMR (400 MHz, DMSO-d_6,

TMS) δ 10.29 (s, 1H), 7.98 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.38-7.13 (m, 5H), 7.05 (t, *J* = 7.6 Hz, 1H), 7.01 (dd, *J* = 3.2, 7.6 Hz, 1H), 5.19 (d, *J* = 17.2 Hz, 1H), 5.10 (d, *J* = 17.6 Hz, 1H), 3.63 (s, 3H), 2.42 (s, 3H), 2.19 (s, 3H), 1.86 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, TMS) δ 181.0, 173.7, 168.5, 144.7, 141.1, 137.0, 136.4, 135.2, 129.4, 128.8, 128.6, 127.2, 125.5, 123.2, 123.0, 122.9, 120.6, 75.6, 69.3, 52.9, 44.8, 21.1, 19.7, 17.9; IR (neat): ν 3134, 2979, 1712, 1511, 1448, 1356, 1227, 1174, 1126, 1082, 858, 733, 671 cm^{-1}; HRMS (ESI) Calcd. For $C_{28}H_{28}N_3O_5S_2^+$ $(M+H)^+$ requires 550.1465, found: 550.1460.

For asymmetric study: A white solid, 52 mg, 95 % yield; *dr* = 1:1; m. p. 186-188 °C; $[\alpha]^{20}_D$ = 67.0 (c 1.00, CH_2Cl_2).

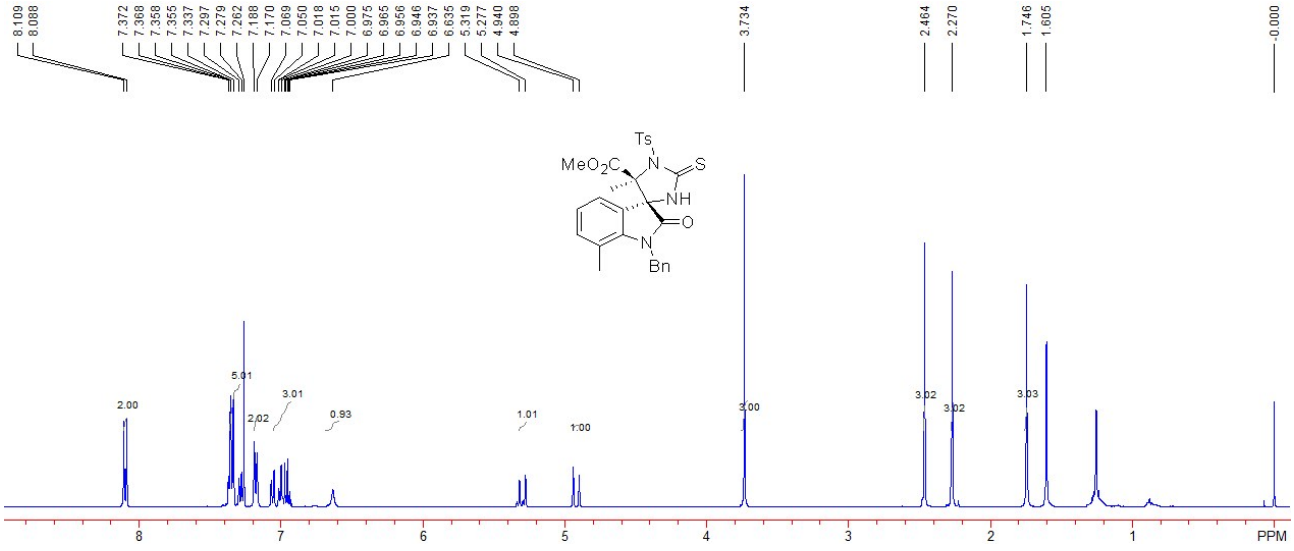


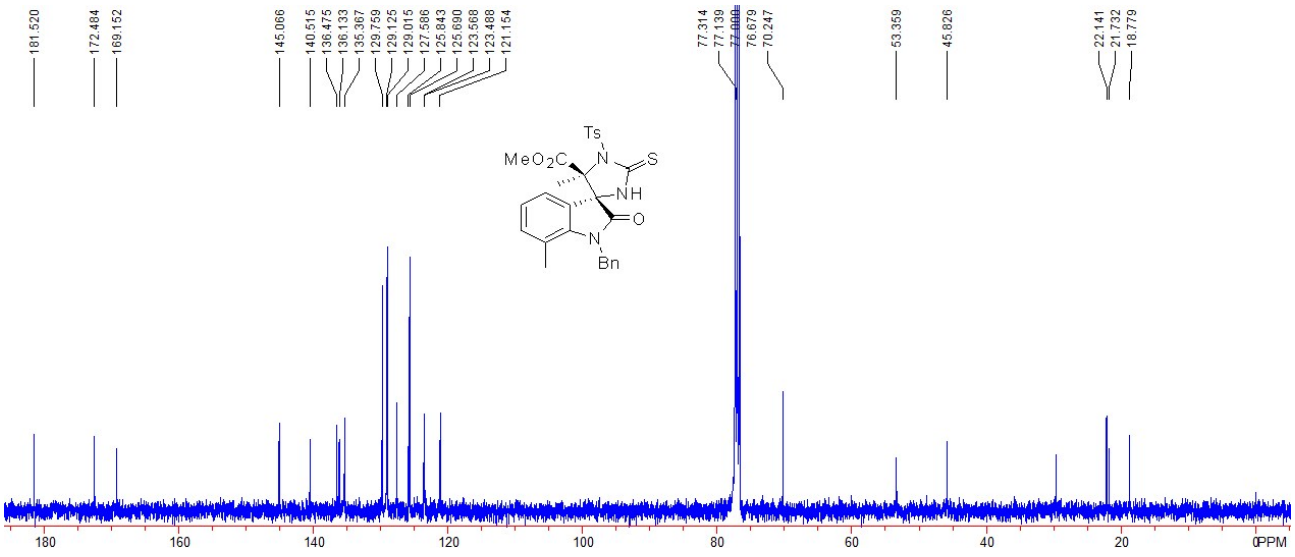


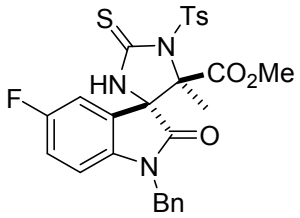


Methyl(4R,5S)-1'-benzyl-5,7'-dimethyl-2'-oxo-2-thioxo-1-tosylspiro[imidazolidine-4,3'-indoline]-5-carboxylate (3ja')

A white solid, 52 mg, 95 % yield; *dr* = 1:1; m. p. 123-125 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.10 (d, *J* = 8.4 Hz, 2H), 7.37-7.28 (m, 5H), 7.18 (d, *J* = 7.2 Hz, 2H), 7.07-6.94 (m, 3H), 6.64 (s, 1H), 5.30 (d, *J* = 16.8 Hz, 1H), 4.92 (d, *J* = 16.8 Hz, 1H), 3.73 (s, 3H), 2.46 (s, 3H), 2.27 (s, 3H), 1.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 181.5, 172.5, 169.2, 145.1, 140.5, 136.5, 136.1, 135.4, 129.8, 129.1, 129.0, 127.6, 125.8, 125.7, 123.6, 123.5, 121.2, 77.1, 70.2, 53.4, 45.8, 22.1, 21.7, 18.8; IR (neat): ν 3150, 2975, 1742, 1713, 1508, 1449, 1364, 1356, 1226, 1126, 1082, 733, 672 cm^{-1}; HRMS (ESI) Calcd. For $C_{28}H_{31}N_4O_5S_2^+$ $(M+H)^+$ requires 567.1730, found: 567.1723; $[\alpha]^{20}_D$ = 15.2 (c 1.00, CH_2Cl_2).

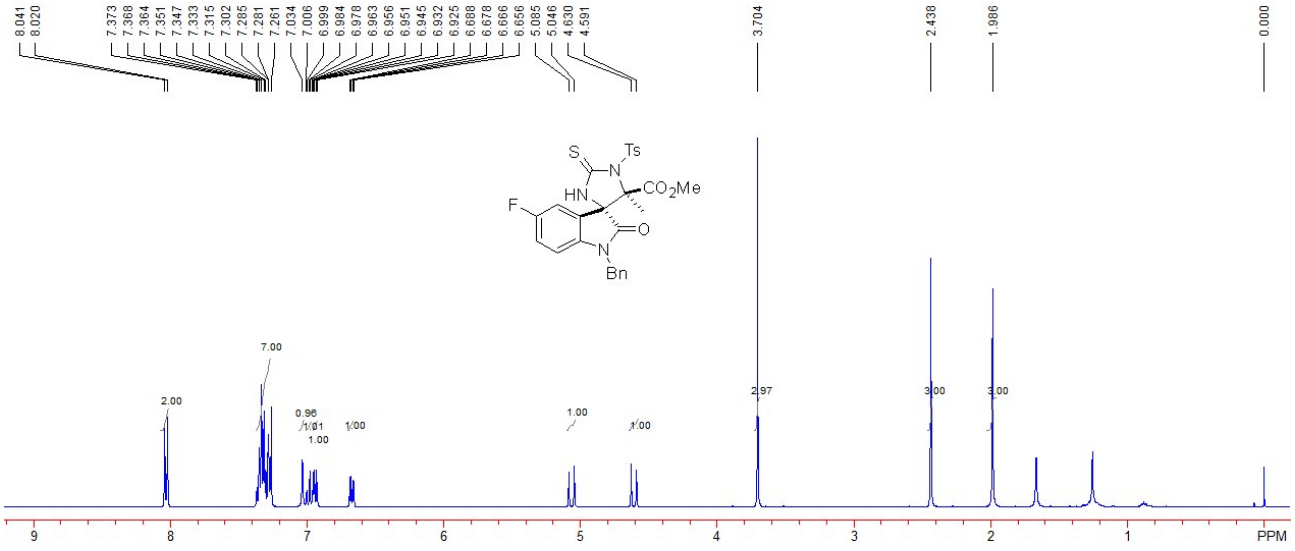






Methyl-1'-benzyl-5'-fluoro-5-methyl-2'-oxo-2-thioxo-1-tosylspiro[imidazolidine-4,3'-indoline]-5-carboxylate (3ka)

A white solid, 82 mg, 83 % yield; *dr* = 8:1; m. p. 175-177 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.37-7.26 (m, 7H), 7.03 (s, 1H), 6.98 (td, *J* = 2.8, 8.4 Hz, 1H), 6.94 (dd, *J* = 2.8, 8.0 Hz, 1H), 6.67 (dd, *J* = 4.0, 8.8 Hz, 1H), 5.07 (d, *J* = 15.6 Hz, 1H), 4.61 (d, *J* = 15.6 Hz, 1H), 3.70 (s, 3H), 2.44 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 181.8, 172.6, 168.4, 159.1 (d, *J* = 242.1 Hz), 139.3 (d, *J* = 2.2 Hz), 136.0, 134.5, 129.3, 129.1, 128.1, 127.3, 123.8 (d, *J* = 8.0 Hz), 118.2 (d, *J* = 23.3 Hz), 113.9 (d, *J* = 25.5 Hz), 110.9 (d, *J* = 8.0 Hz), 76.7, 69.7 (d, *J* = 1.5 Hz), 53.1, 44.7, 21.7, 20.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ -117.95; IR (neat): ν 3309, 2950, 1727, 1491, 1360, 1221, 1083, 1036, 811, 701, 670 cm^{-1}; HRMS (ESI) Calcd. For $C_{27}H_{25}FN_3O_5S_2^+$ $(M+H)^+$ requires 554.1214, found: 554.1210.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6.656
5.085
5.046
4.630
4.591
3.704
2.438
1.986
0.000
Ts
S
N
CO2Me
HN
F
O
N
Bn
7.00
2.00
0.96
1.01
1.00
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3.00
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7
6
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2
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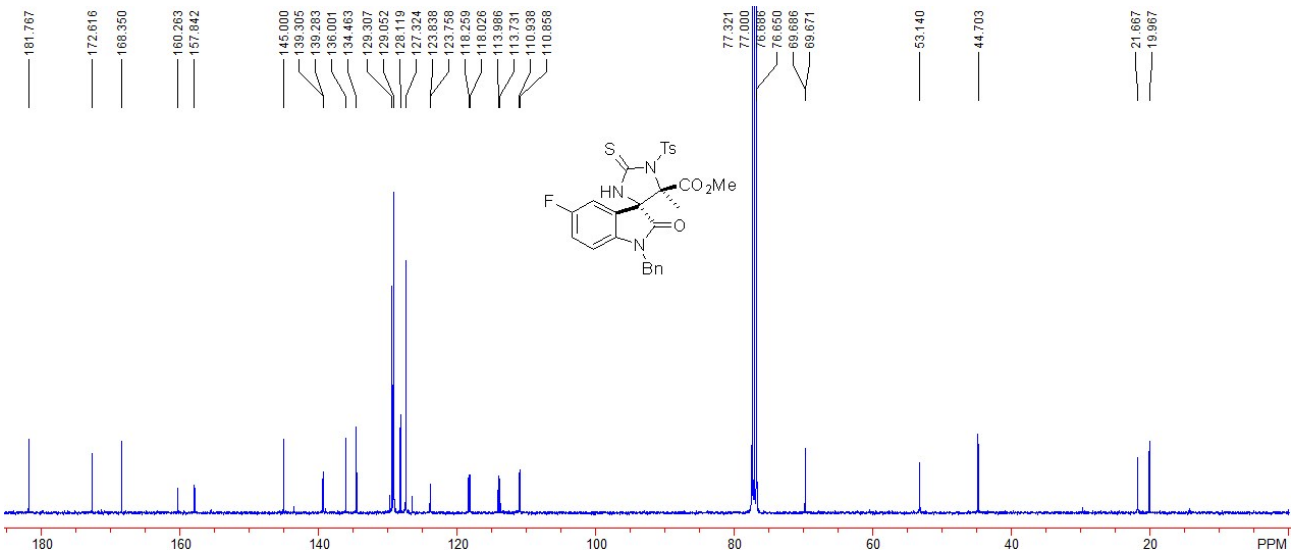
PPM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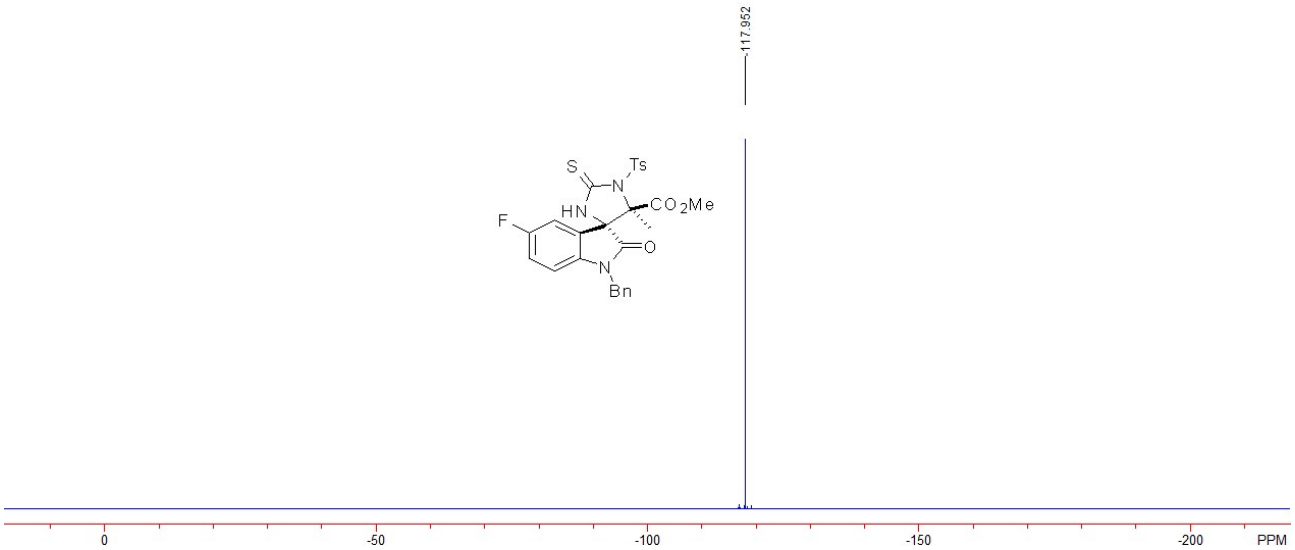
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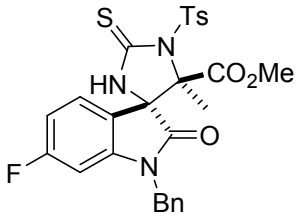
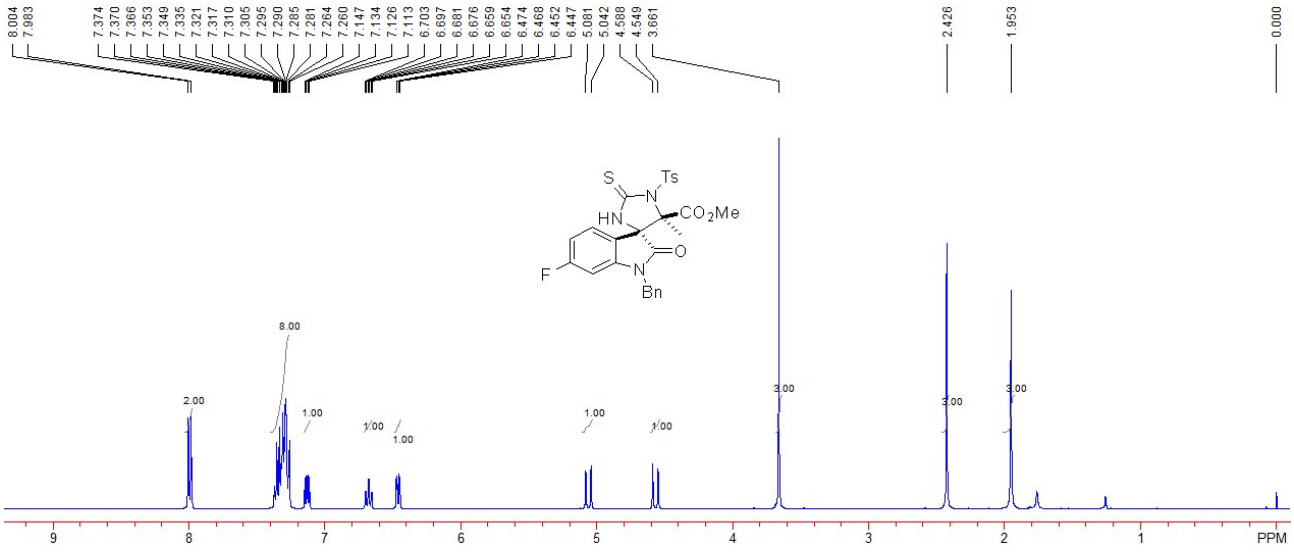
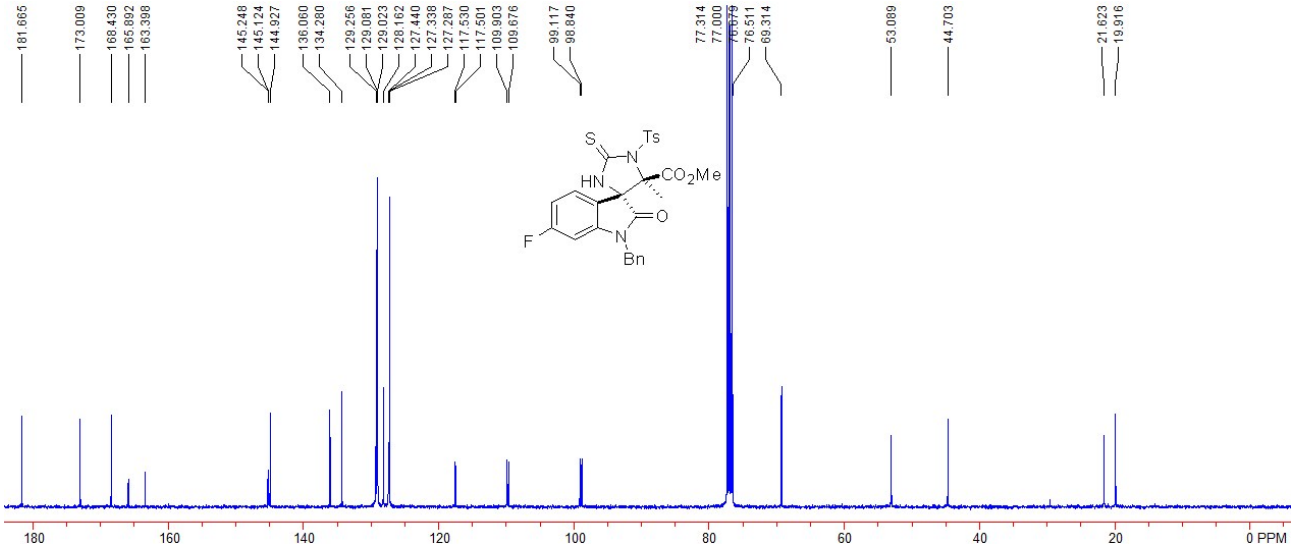
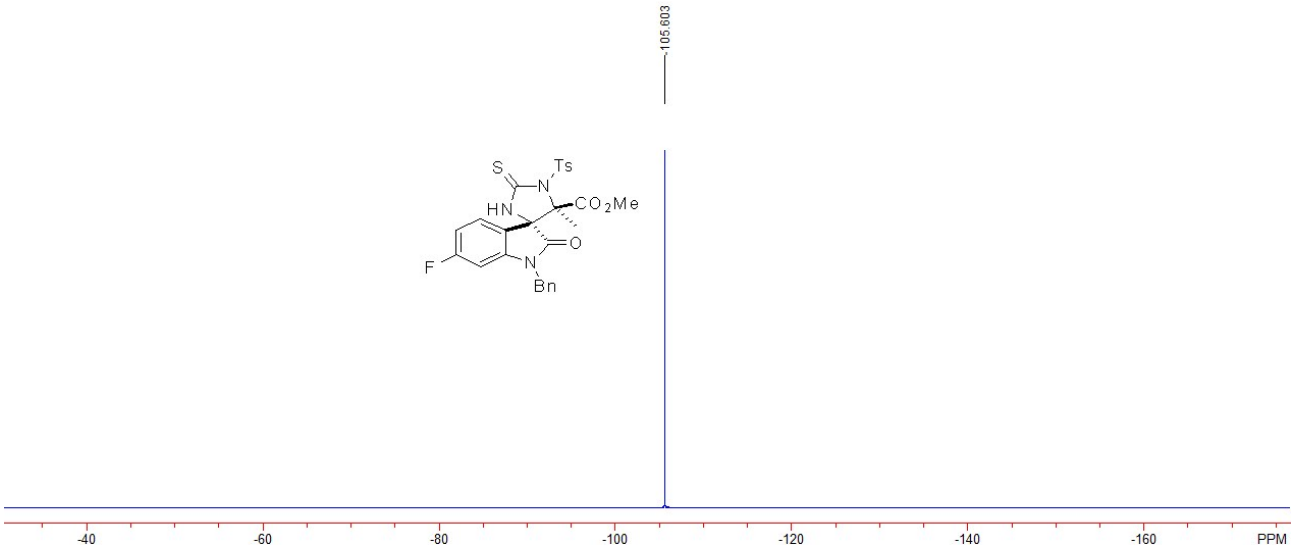


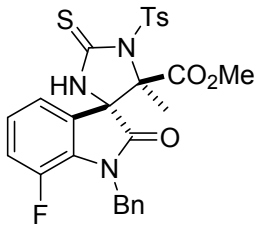
Methyl-1'-benzyl-6'-fluoro-5-methyl-2'-oxo-2-thioxo-1-tosylspiro[imidazolidine-4,3'-indoline]-5-carboxylate (3la)

A white solid, 92 mg, 90 % yield; *dr* = 12:1; m. p. 165-167 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.37-7.26 (m, 8H), 7.13 (dd, *J* = 5.2, 8.4 Hz, 1H), 6.68 (td, *J* = 2.4, 8.8 Hz, 1H), 6.46 (dd, *J* = 2.4, 8.8 Hz, 1H), 5.06 (d, *J* = 15.6 Hz, 1H), 4.57 (d, *J* = 15.6 Hz, 1H), 3.66 (s, 3H), 2.43 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 181.7, 173.0, 168.4, 164.6 (d, *J* = 249.4 Hz), 145.2 (d, *J* = 12.4 Hz), 144.9, 136.0, 134.3, 129.3, 129.1, 129.0, 128.2, 127.4 (d, *J* = 10.2 Hz), 127.3, 117.5 (d, *J* = 2.9 Hz), 109.8 (d, *J* = 22.7 Hz), 99.0 (d, *J* = 27.7 Hz), 76.5, 69.3, 53.1, 44.7, 21.6, 19.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ -105.60; IR (neat): ν 3139, 2951, 1746, 1716, 1614, 1495, 1455, 1223, 1160, 1114, 1082, 1035, 984, 805, 702, 669 cm^{-1}; HRMS (ESI) Calcd. For $C_{27}H_{25}FN_3O_5S_2^+$ $(M+H)^+$ requires 554.1214, found: 554.1209.





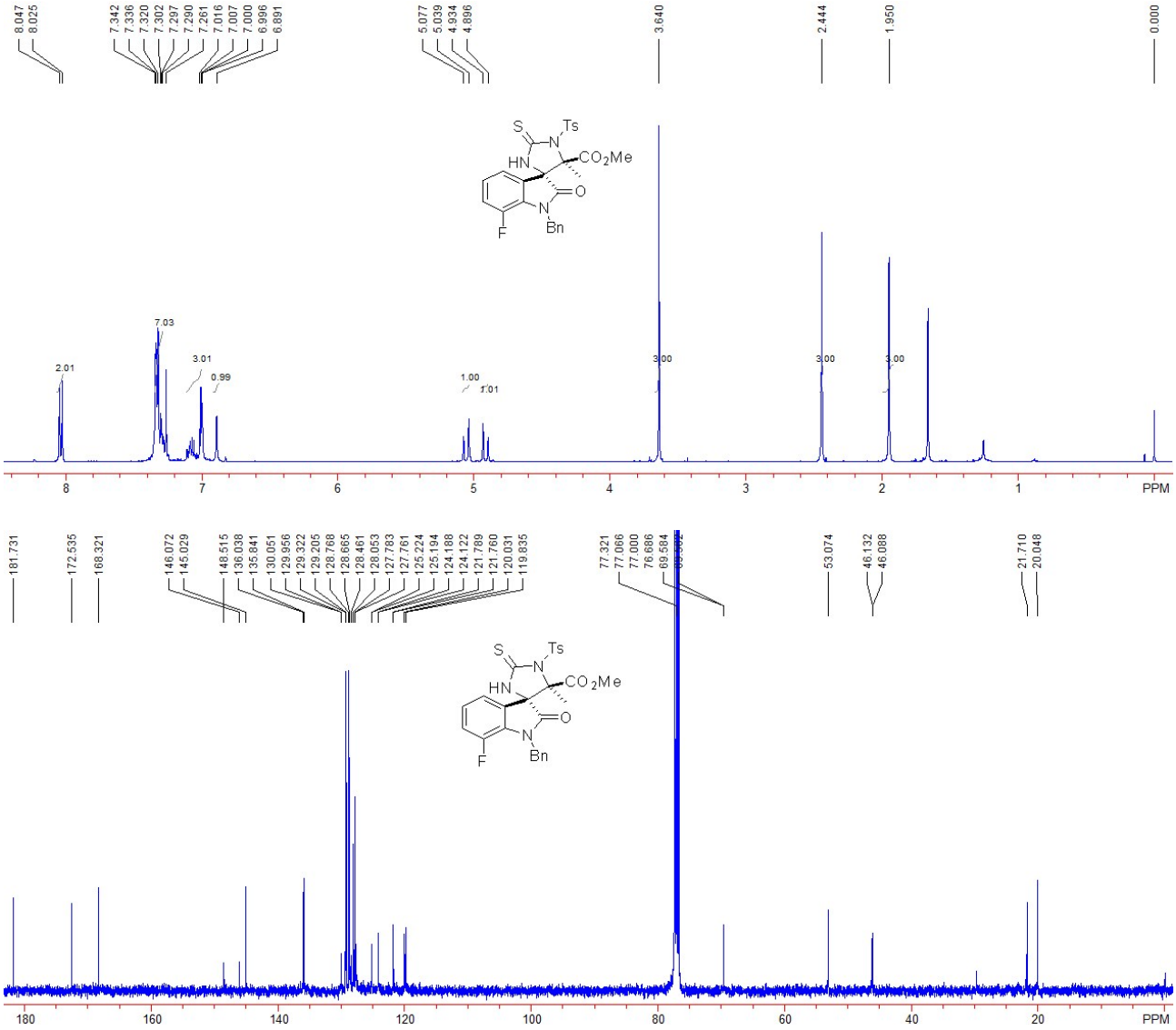


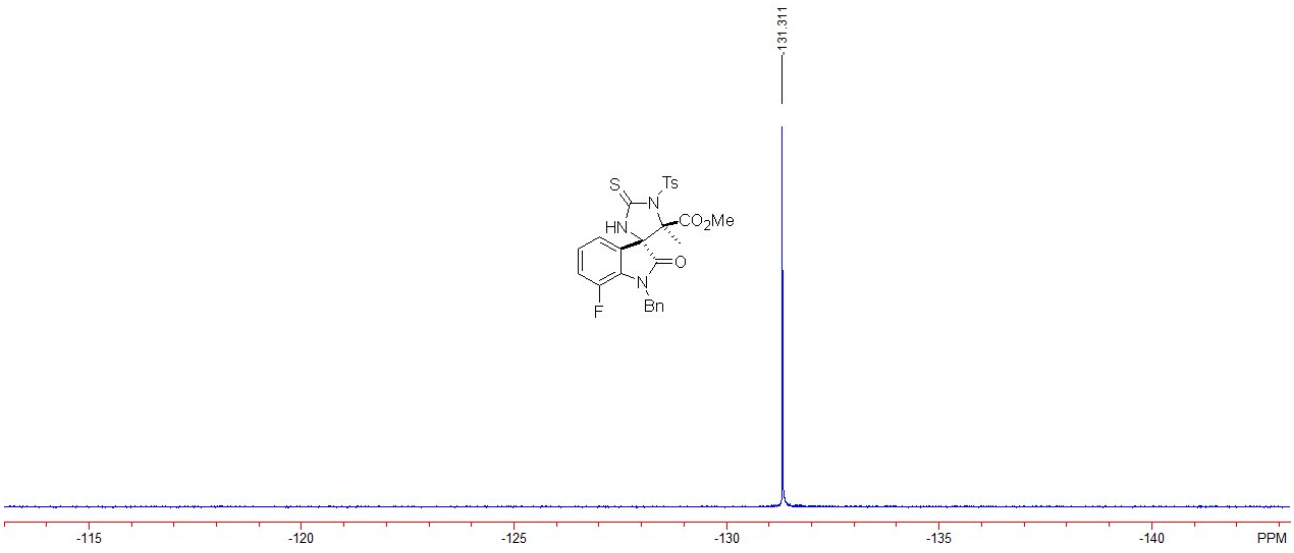


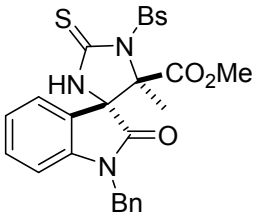
Methyl-1'-benzyl-7'-fluoro-5-methyl-2'-oxo-2-thioxo-1-tosylspiro[imidazolidine-4,3'-indoline]-5-carboxylate (3ma)

A white solid, 96 mg, 95 % yield; *dr* = 11:1; m. p. 145-147 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.04 (d, *J* = 8.8 Hz, 2H), 7.34-7.29 (m, 7H), 7.02-7.00 (m, 3H), 6.89 (s, 1H), 5.06 (d, *J* = 15.2 Hz, 1H), 4.92 (d, *J* = 15.2 Hz, 1H), 3.64 (s, 3H), 2.44 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 181.7, 172.5, 168.3, 147.3 (d, *J* = 244.3 Hz), 145.0, 136.0, 135.8, 130.0 (d, *J* = 9.5 Hz),

129.3, 129.2, 128.8, 128.6 (d, J = 20.4 Hz), 128.0, 127.8 (d, J = 2.2 Hz), 125.2 (d, J = 3.0 Hz), 124.2 (d, J = 6.6 Hz), 121.7 (d, J = 2.9 Hz), 119.9 (d, J = 19.6 Hz), 77.1, 69.6 (d, J = 2.2 Hz), 53.1, 46.1 (d, J = 4.4 Hz), 21.7, 20.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ -131.31; IR (neat): ν 3309, 2945, 1732, 1353, 1163, 1129, 1084, 1038, 812, 796, 725, 701 cm^{-1}; HRMS (ESI) Calcd. For $C_{27}H_{25}FN_3O_5S_2^+$ $(M+H)^+$ requires 554.1214, found: 554.1209.



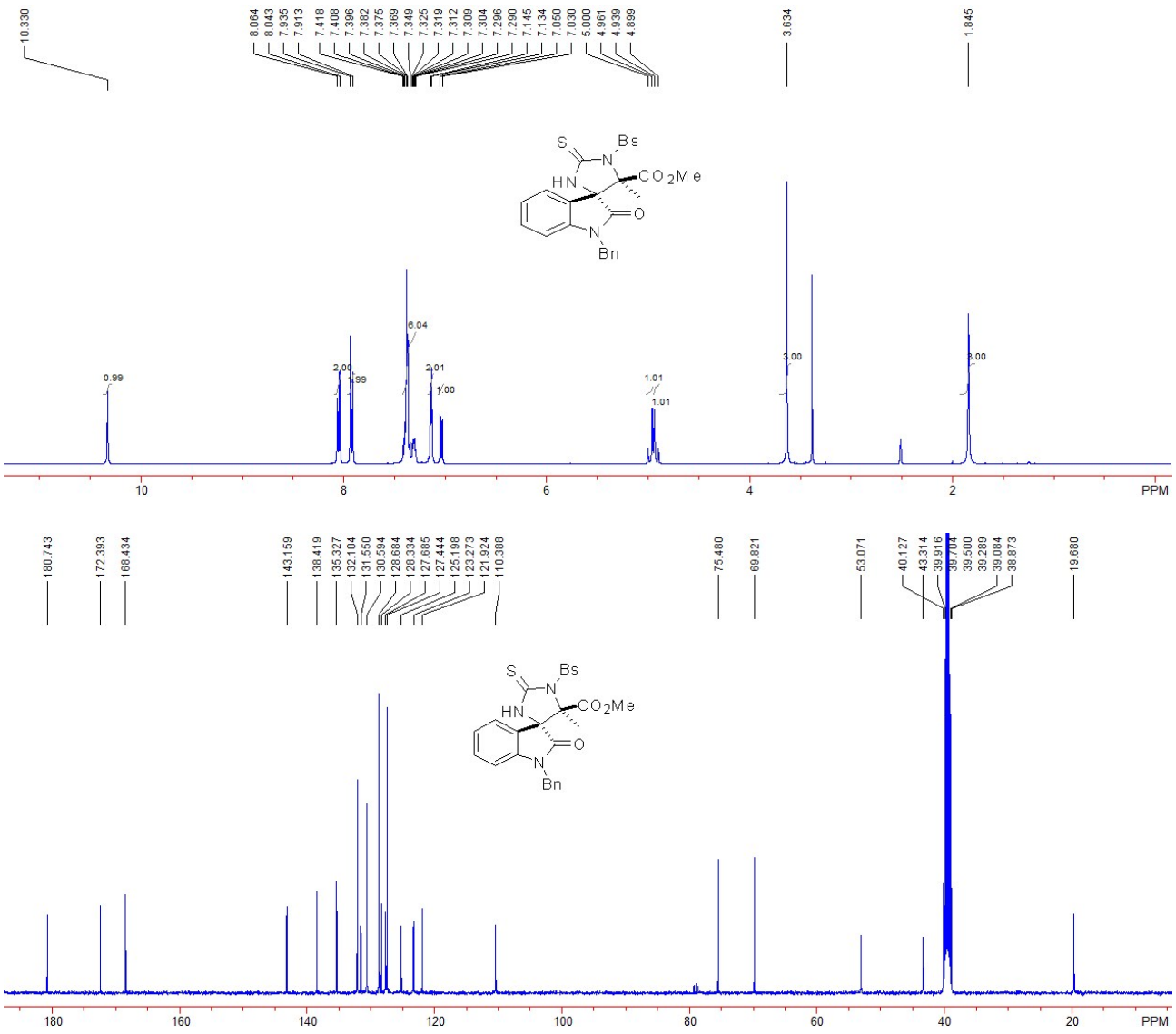


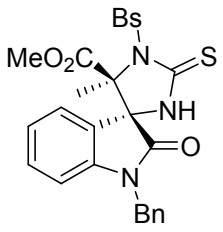


Methyl-1'-benzyl-1-((4-bromophenyl)sulfonyl)-5-methyl-2'-oxo-2-thioxospiro[imidazolidine-4,3'-indoline]-5-carboxylate (3ab)

A white solid, 111 mg, 97 % yield; *dr* = 19:1; m. p. 244-246 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ 10.33 (s, 1H), 8.05 (d, *J* = 8.4 Hz, 2H), 7.92 (d, *J* = 8.8 Hz, 2H), 7.42-7.30 (m, 6H), 7.14 (d, *J* = 4.4 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 1H), 4.98 (d, *J* = 15.6 Hz, 1H), 4.92 (d, *J* = 16.0 Hz, 1H), 3.63 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, TMS) δ 180.7, 172.4, 168.4, 143.2, 138.4, 135.3, 132.1, 131.6, 130.6, 128.7, 128.3, 127.7, 127.4, 125.2, 123.3, 121.9, 110.4, 75.5, 69.8, 53.1, 43.3, 19.7; IR (neat): ν 3403, 2922, 1715, 1481, 1465, 1363, 1039, 1025, 998, 988, 743, 736 cm^{-1}; HRMS (ESI) Calcd. For $C_{26}H_{26}BrN_4O_5S_2^+$ $(M+NH_4)^+$ requires 617.0523, found: 617.0522.

For asymmetric study: A white solid, 74 mg, 92 % yield; *dr* = 2:1; m. p. 193-195 ^{o}C; $[\alpha]^{20}_{D}$ = 179.0 (c 1.00, CH_2Cl_2).

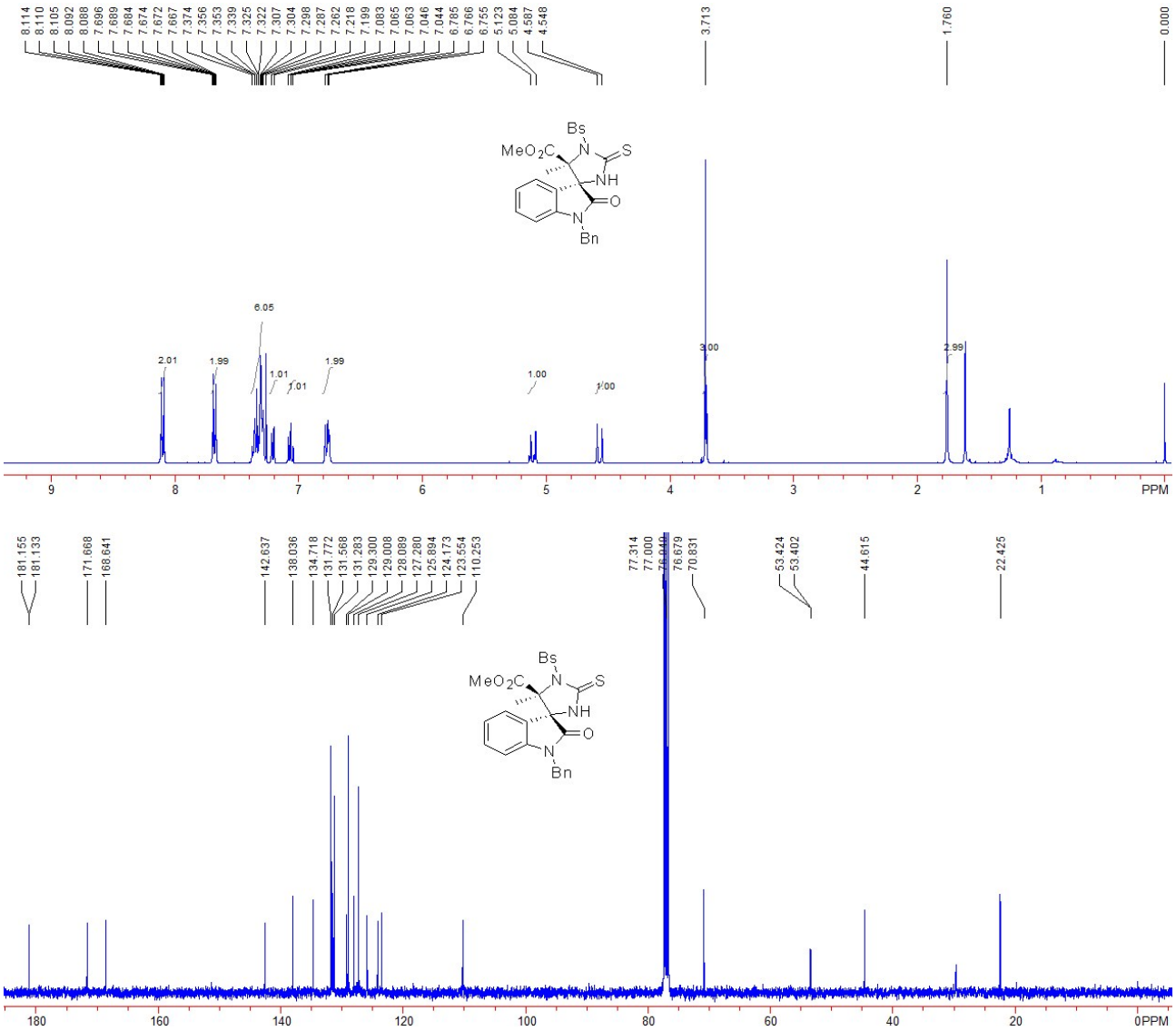


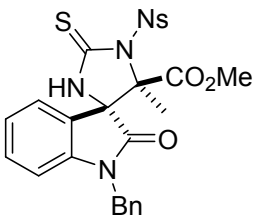


Methyl(4R,5S)-1'-benzyl-1-((4-bromophenyl)sulfonyl)-5-methyl-2'-oxo-2-thioxospiro[imidazolidine-4,3'-indoline]-5-carboxylate (3ab')

A white solid, 37 mg, 92% yield, *dr* = 2:1; m. p. 139-142 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.11-8.09 (m, 2H), 7.70-7.67 (m, 2H), 7.37-7.29 (m, 6H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.06 (td, *J* = 0.8, 7.6 Hz, 1H), 6.79-6.76 (m, 2H), 5.10 (d, *J* = 15.6 Hz, 1H), 4.57 (d, *J* = 15.6 Hz, 1H), 3.71 (s, 3H), 1.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 181.2, 171.7, 168.6, 142.6, 138.0, 134.7, 131.8,

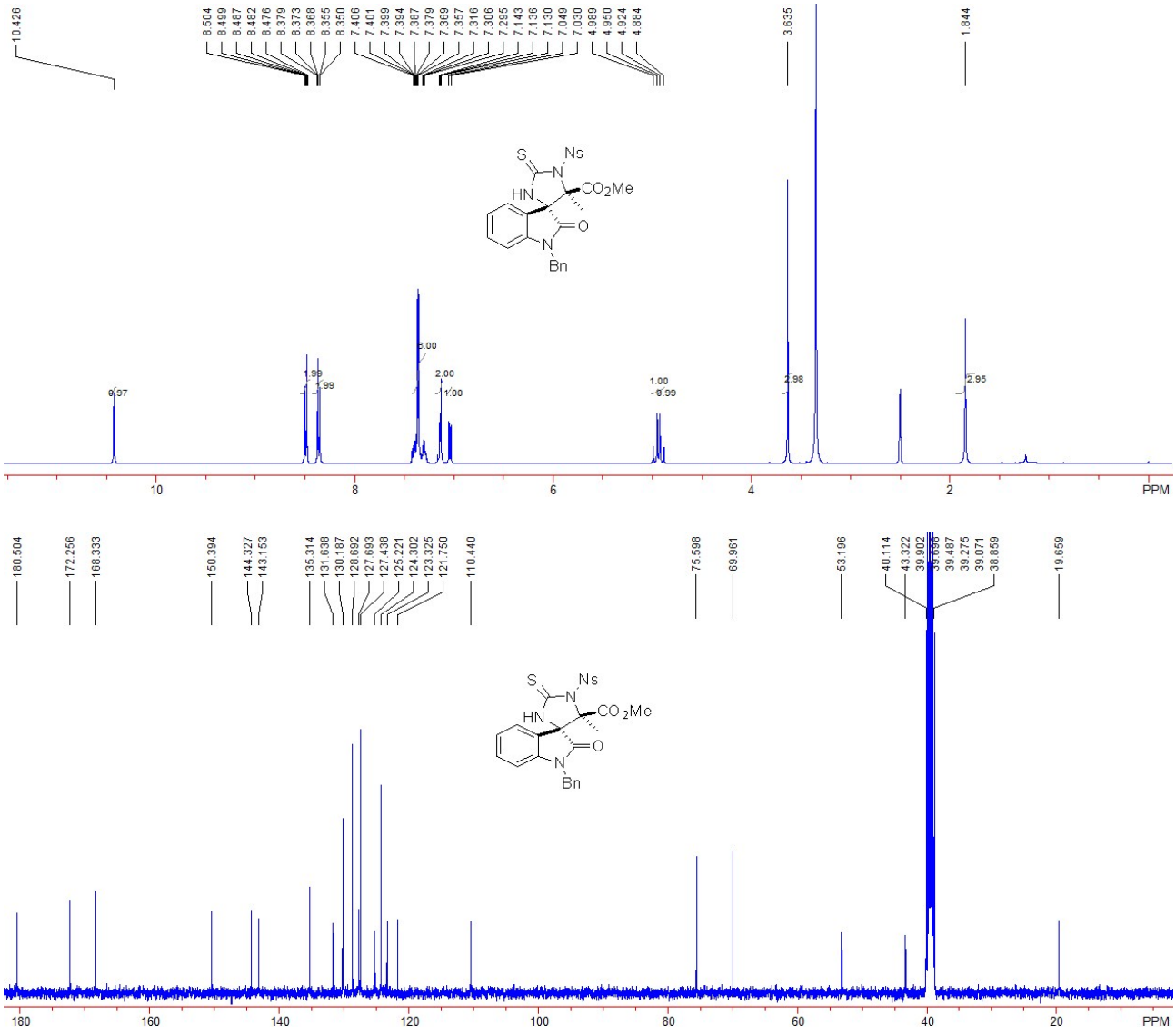
131.6, 131.3, 129.3, 129.0, 128.1, 127.3, 125.9, 124.2, 123.6, 110.3, 76.9, 70.8, 53.4 (d, J = 2.2 Hz), 44.6, 22.4; IR (neat): ν 2919, 2846, 1749, 1719, 1697, 1467, 1083, 1068, 1008, 818, 742, 701 cm^{-1}; HRMS (ESI) Calcd. For $C_{26}H_{26}BrN_4O_5S_2^+$ $(M+NH_4)^+$ requires 617.0523, found: 617.0519; $[\alpha]^{20}_D$ = 27.4 (c 1.00, CH_2Cl_2).

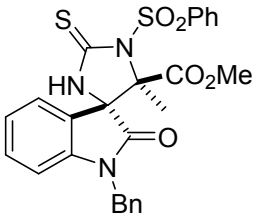




Methyl-1'-benzyl-5-methyl-1-((4-nitrophenyl)sulfonyl)-2'-oxo-2-thioxospiro[imidazolidine-4,3'-indoline]-5-carboxylate (3ac)

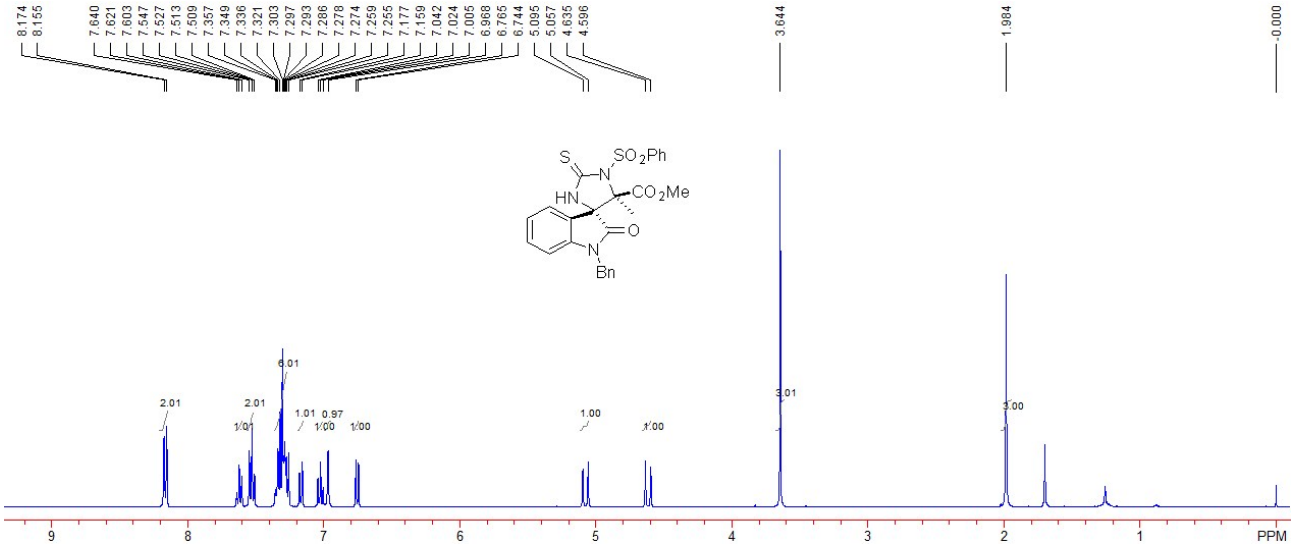
A white solid, 100 mg, 96 % yield; *dr* = 11:1; m. p. 238-240 °C; ^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ 10.43 (s, 1H), 8.50-8.48 (m, 2H), 8.38-8.35 (m, 2H), 7.41-7.30 (m, 6H), 7.14-7.13 (m, 2H), 7.04 (d, *J* = 7.6 Hz, 1H), 4.97 (d, *J* = 15.6 Hz, 1H), 4.90 (d, *J* = 16.0 Hz, 1H), 3.64 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, TMS) δ 180.5, 172.3, 168.3, 150.4, 144.3, 143.2, 135.3, 131.6, 130.2, 128.7, 127.7, 127.4, 125.2, 124.3, 123.3, 121.8, 110.4, 75.6, 70.0, 53.2, 43.3, 19.7; IR (neat): ν 3322, 3100, 2953, 1724, 1531, 1467, 1363, 1344, 1179, 853, 740, 680 cm^{-1}; HRMS (ESI) Calcd. For $C_{26}H_{26}N_5O_7S_2^+$ $(M+NH_4)^+$ requires 584.1268, found: 584.1271.

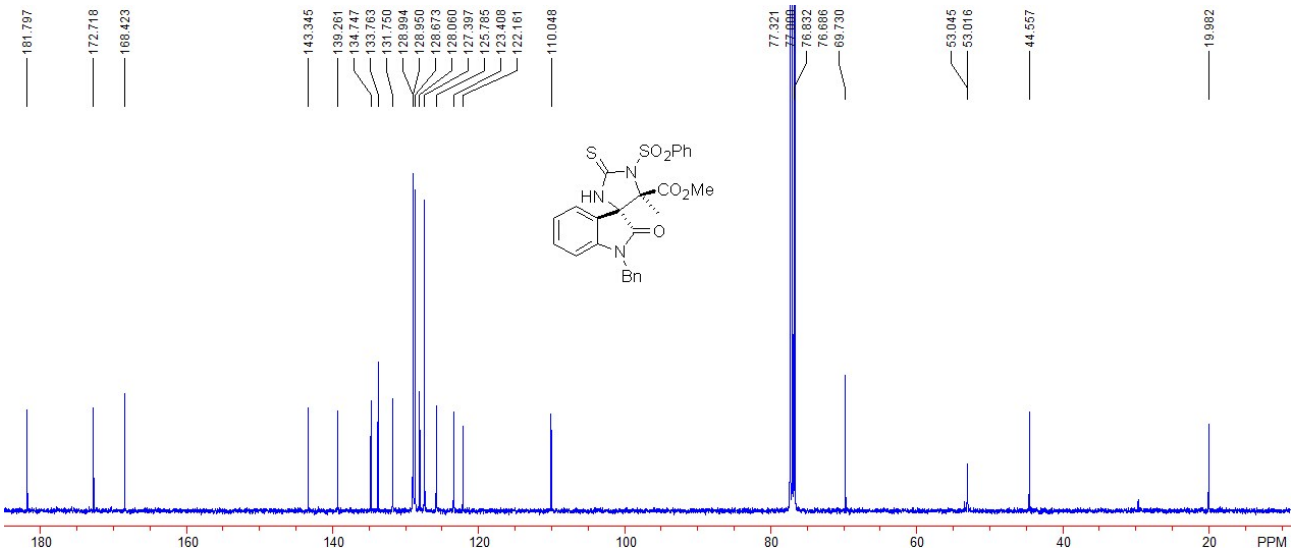


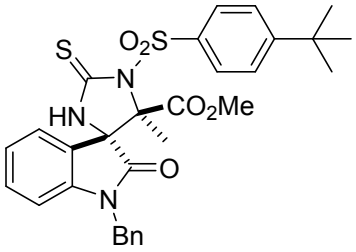


Methyl-1'-benzyl-5-methyl-2'-oxo-1-(phenylsulfonyl)-2-thioxospiro[imidazolidine-4,3'-indoline]-5-carboxylate (3ad)

A white solid, 87 mg, 89 % yield; *dr* = 15:1; m. p. 212-214 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.17 (d, *J* = 7.6 Hz, 2H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.55-7.51 (m, 2H), 7.36-7.26 (m, 6H), 7.17 (d, *J* = 7.2 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.97 (s, 1H), 6.76 (d, *J* = 7.6 Hz, 1H), 5.08 (d, *J* = 15.2 Hz, 1H), 4.62 (d, *J* = 15.6 Hz, 1H), 3.64 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 181.8, 172.7, 168.4, 143.3, 139.3, 134.7, 133.8, 131.8, 128.99, 128.95, 128.7, 128.1, 127.4, 125.8, 123.4, 122.2, 110.0, 76.8, 69.7, 53.0 (d, *J* = 2.9 Hz), 44.6, 20.0; IR (neat): ν 3314, 2927, 1741, 1723, 1482, 1467, 1153, 1083, 802, 752, 729, 700, 678 cm^{-1}; HRMS (ESI) Calcd. For $C_{26}H_{24}N_3O_5S_2^+$ $(M+H)^+$ requires 522.1152, found: 522.1148.

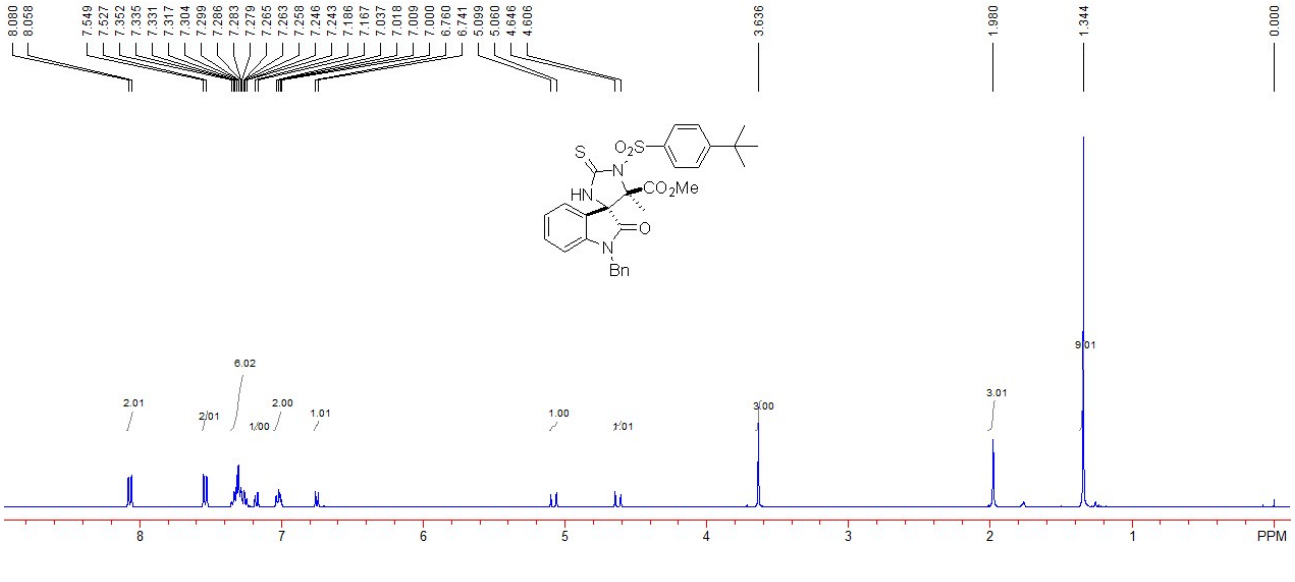


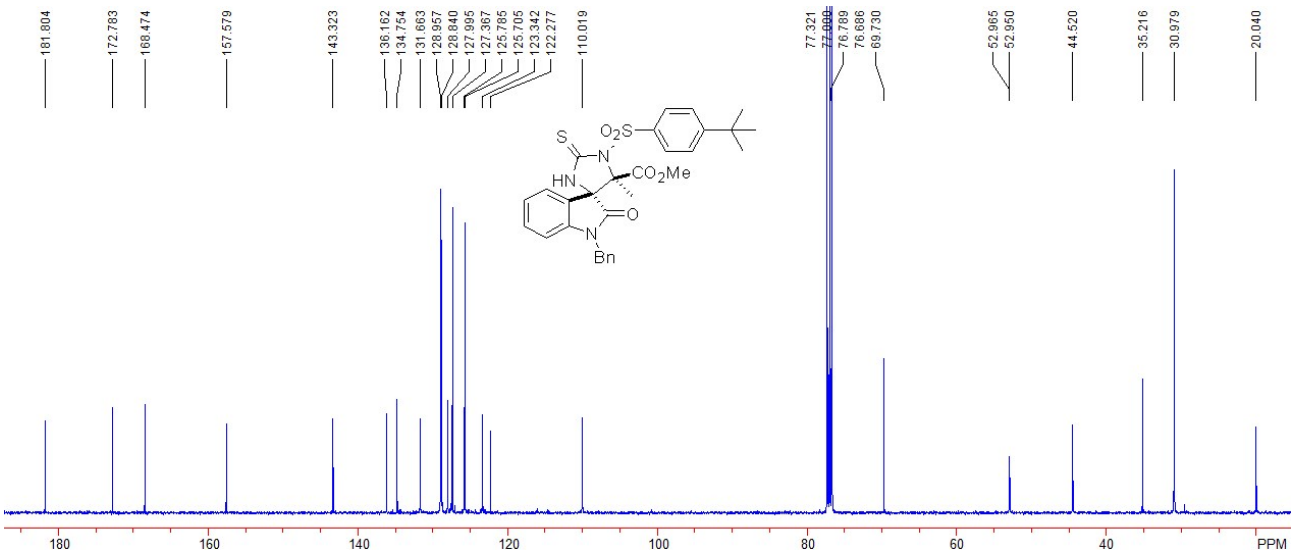


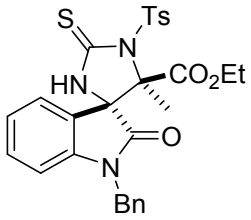


Methyl-1'-benzyl-1-((4-(tert-butyl)phenyl)sulfonyl)-5-methyl-2'-oxo-2-thioxospiro[imidazolidine-4,3'-indoline]-5-carboxylate (3ae)

A white solid, 95 mg, 89 % yield; *dr* = 12:1; m. p. 255-257 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.07 (d, *J* = 8.8 Hz, 2H), 7.54 (d, *J* = 8.8 Hz, 2H), 7.35-7.24 (m, 6H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.04-7.00 (m, 2H), 6.75 (d, *J* = 7.6 Hz, 1H), 5.08 (d, *J* = 15.6 Hz, 1H), 4.63 (d, *J* = 16.0 Hz, 1H), 3.63 (s, 3H), 1.98 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 181.8, 172.8, 168.5, 157.6, 143.3, 136.2, 134.8, 131.7, 128.99, 128.9, 128.8, 128.0, 127.4, 125.8, 125.7, 123.3, 122.3, 110.0, 76.8, 69.7, 53.0 (d, *J* = 1.5 Hz), 44.5, 35.2, 31.0, 20.0; IR (neat): ν 3317, 2964, 1765, 1728, 1481, 1350, 1339, 1177, 1128, 788, 747, 735, 697, 662 cm^{-1}; HRMS (ESI) Calcd. For $C_{30}H_{32}N_3O_5S_2^+$ $(M+H)^+$ requires 578.1778, found: 578.1772.



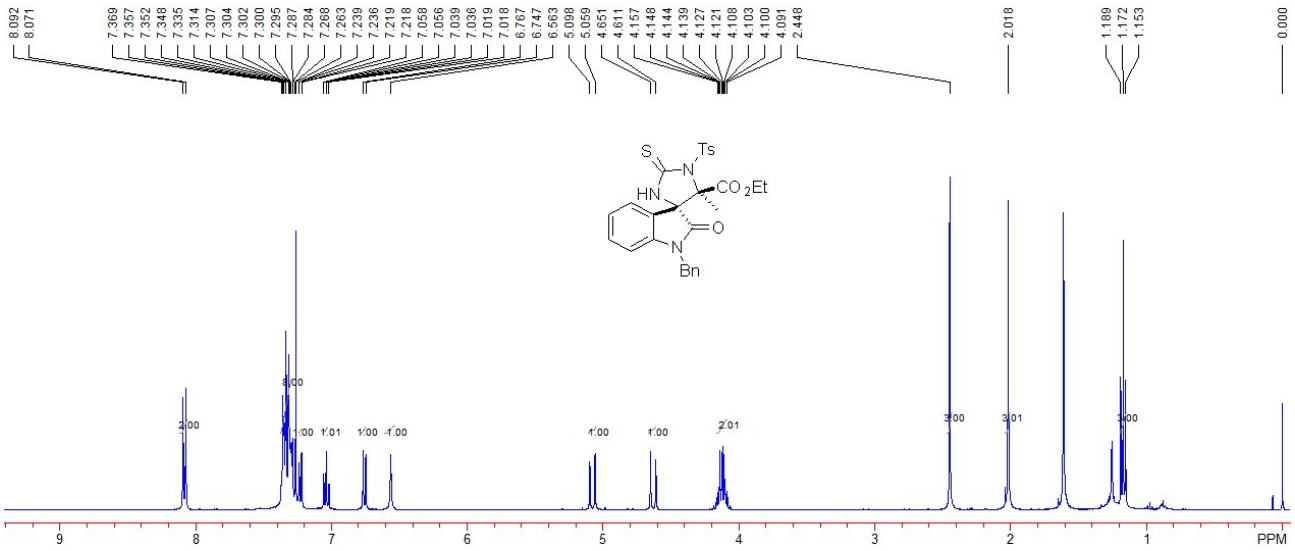


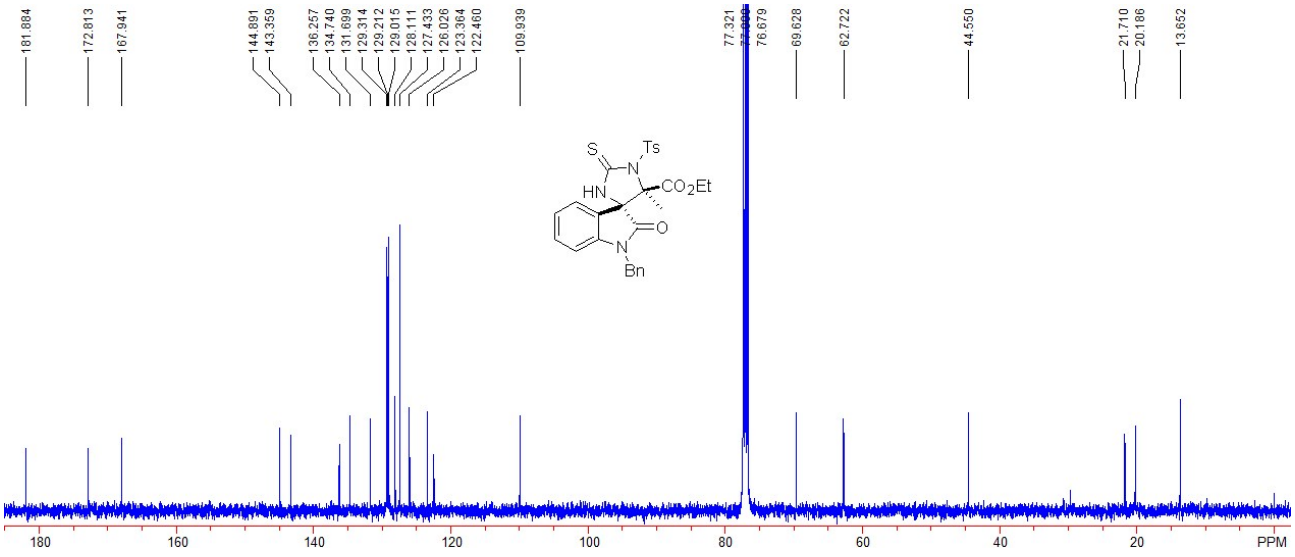


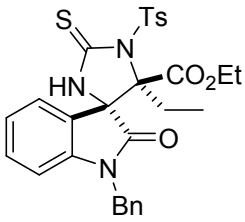
Ethyl-1'-benzyl-2'-oxo-5-phenethyl-2-thioxo-1-tosylspiro[imidazolidine-4,3'-indoline]-5-carboxylate (3ag)

A white solid, 91 mg, 88 % yield; *dr* = 16:1; m. p. 177-180 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.08 (d, *J* = 8.4 Hz, 2H), 7.37-7.28 (m, 8H), 7.23 (dd, *J* = 1.2, 8.0 Hz, 1H), 7.04 (td, *J* = 1.2, 8.0 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 6.56 (s, 1H), 5.08 (d, *J* = 15.6 Hz, 1H), 4.63 (d, *J* = 16.0 Hz, 1H), 4.16-4.09 (m, 2H), 2.45 (s, 3H), 2.02 (s, 3H), 1.17 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$,

TMS) δ 181.9, 172.8, 167.9, 144.9, 143.4, 136.3, 134.7, 131.7, 129.3, 129.2, 129.0, 128.1, 127.4, 126.0, 123.4, 122.5, 109.9, 69.6, 62.7, 44.6, 21.7, 20.2, 13.7; IR (neat): ν 3147, 2919, 2848, 1713, 1610, 1504, 1363, 1179, 1082, 811, 756, 701, 691, 666 cm^{-1}; HRMS (ESI) Calcd. For $C_{28}H_{28}N_3O_5S_2^+$ $(M+H)^+$ requires 550.1461, found: 550.1465.

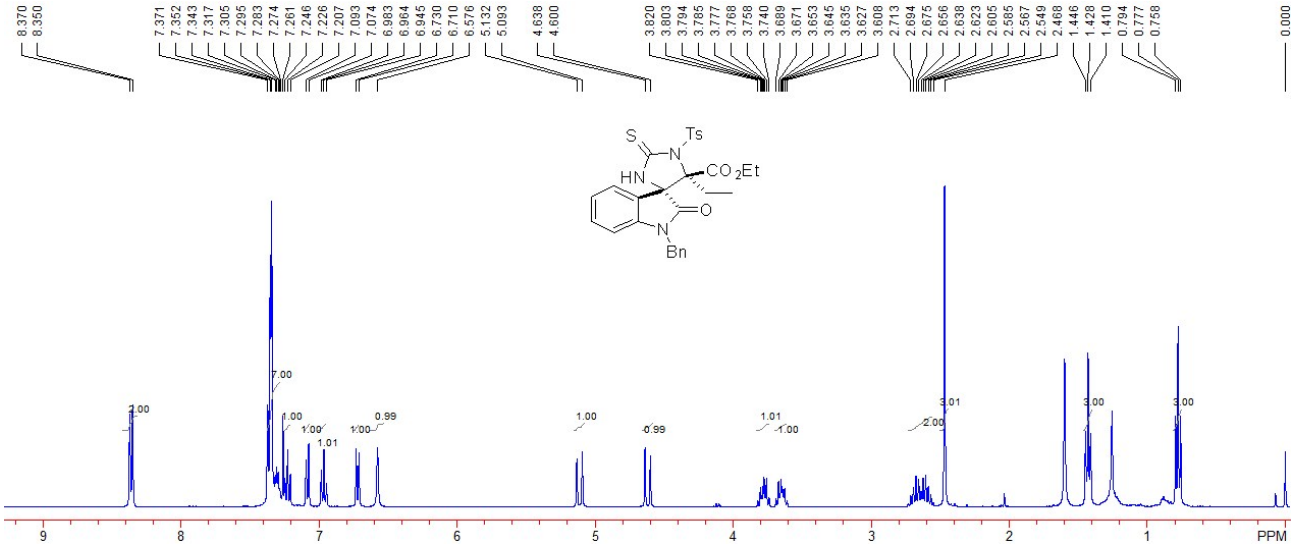


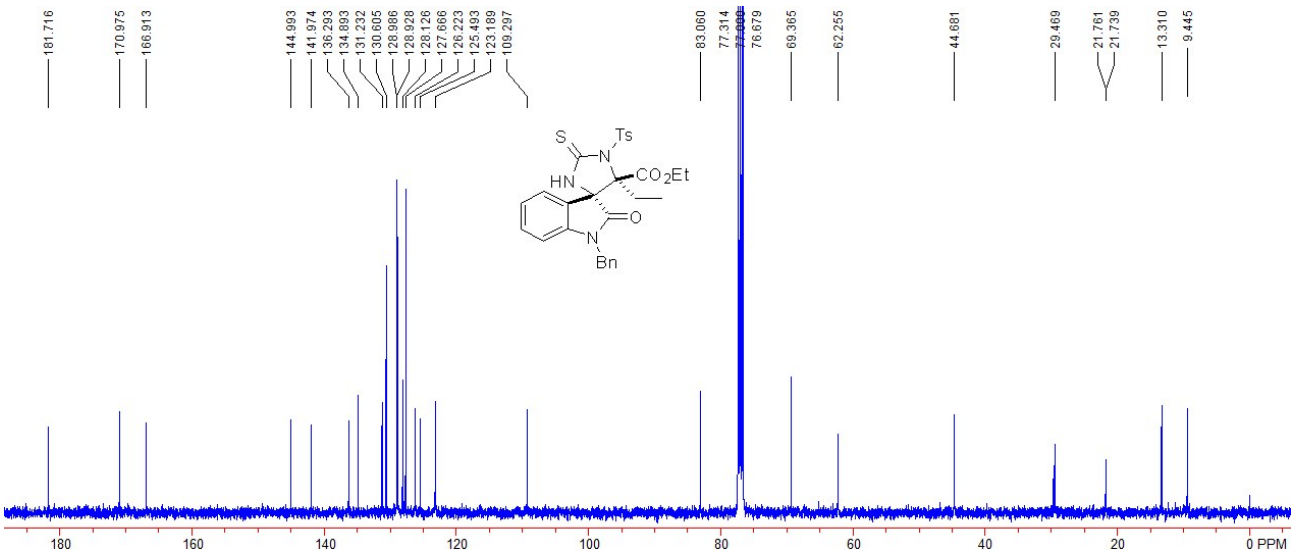


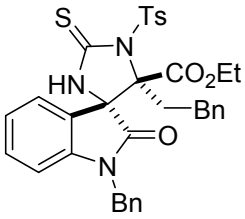


Ethyl-1'-benzyl-5-ethyl-2'-oxo-2-thioxo-1-tosylspiro[imidazolidine-4,3'-indoline]-5-carboxylate (3ah)

A white solid, 55 mg, 52 % yield; *dr* = 14:1; m. p. 167-169 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.36 (d, *J* = 8.0 Hz, 2H), 7.37-7.27 (m, 7H), 7.23 (t, *J* = 8.0 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 6.58 (s, 1H), 5.11 (d, *J* = 15.6 Hz, 1H), 4.62 (d, *J* = 15.2 Hz, 1H), 3.82-3.74 (m, 1H), 3.69-3.61 (m, 1H), 2.71-2.55 (m, 2H), 2.47 (s, 3H), 1.43 (t, *J* = 7.2 Hz, 3H), 0.78 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 181.7, 171.0, 166.9, 145.0, 142.0, 136.3, 134.9, 131.2, 130.6, 129.0, 128.9, 128.1, 127.7, 126.2, 125.5, 123.2, 109.3, 83.1, 69.4, 62.3, 44.7, 29.5, 21.7 (d, *J* = 2.2 Hz), 13.3, 9.4; IR (neat): ν 3301, 2924, 1728, 1611, 1485, 1467, 1355, 1238, 1170, 1082, 813, 752, 702, 665 cm^{-1}; HRMS (ESI) Calcd. For $C_{29}H_{30}N_3O_5S_2^+$ $(M+H)^+$ requires 564.1621, found: 564.1615.

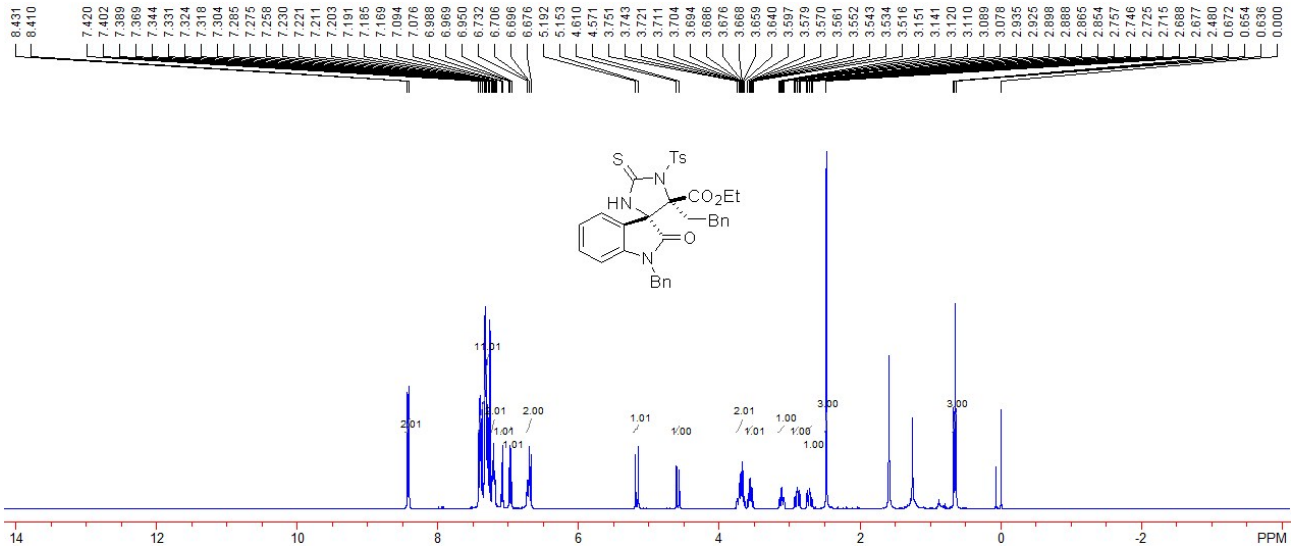


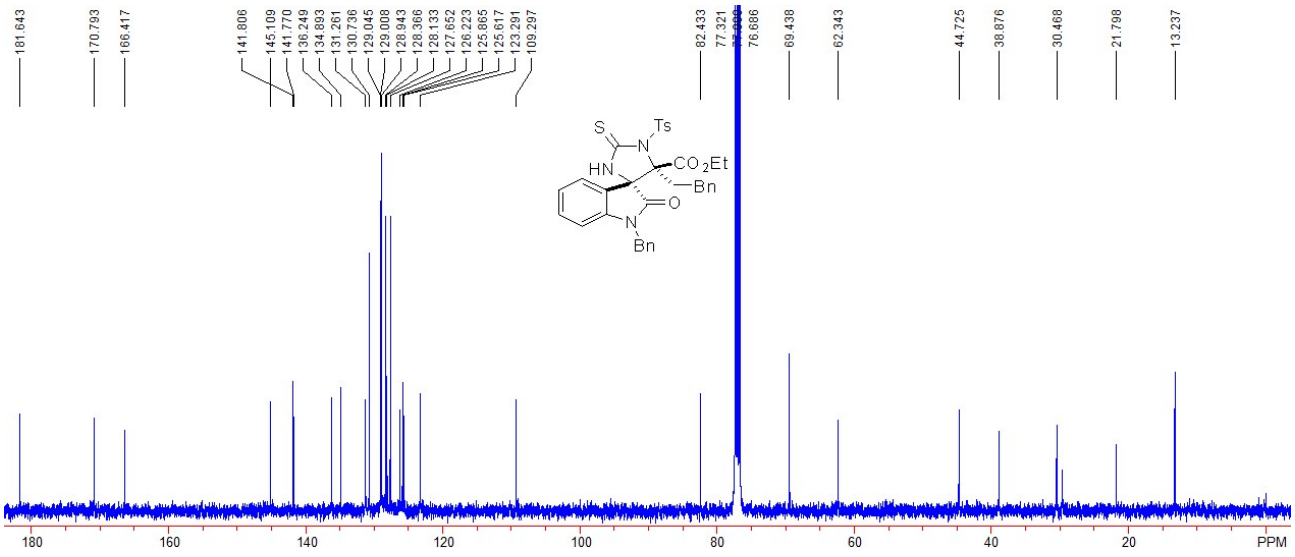




Ethyl-1'-benzyl-2'-oxo-5-phenethyl-2-thioxo-1-tosylspiro[imidazolidine-4,3'-indoline]-5-carboxylate (3aj)

A white solid, 65 mg, 58 % yield; *dr* = 7:1; m. p. 169-171 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.42 (d, *J* = 8.4 Hz, 2H), 7.42-7.28 (m, 11H), 7.23-7.19 (m, 2H), 7.08 (d, *J* = 7.2 Hz, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.73-6.68 (m, 2H), 5.17 (d, *J* = 15.6 Hz, 1H), 4.59 (d, *J* = 15.6 Hz, 1H), 3.75-3.64 (m, 2H), 3.60-3.52 (m, 1H), 3.12 (td, *J* = 4.0, 12.4 Hz, 1H), 2.89 (td, *J* = 4.0, 13.2 Hz, 1H), 2.72 (td, *J* = 4.0, 12.8 Hz, 1H), 2.48 (s, 3H), 0.65 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 181.6, 170.8, 166.4, 145.1, 141.81, 141.77, 136.2, 134.9, 131.3, 130.7, 129.05, 129.01, 128.9, 128.4, 128.1, 127.7, 126.2, 125.9, 125.6, 123.3, 109.3, 82.4, 69.4, 62.3, 44.7, 38.9, 30.5, 21.8, 13.2; IR (neat): ν 3293, 2924, 1757, 1732, 1457, 1339, 1235, 1166, 1079, 751, 730, 700, 667 cm^{-1}; HRMS (ESI) Calcd. For $C_{35}H_{34}N_3O_5S_2^+$ $(M+H)^+$ requires 640.1934, found: 640.1932.

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62.343
44.725
38.876
30.468
21.798
13.237
S
Ts
N
HN
CO2Et
Bn
O
N
Bn
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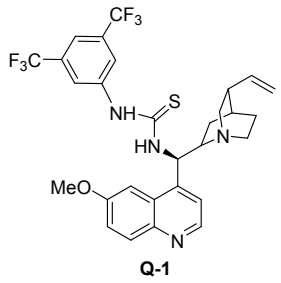
160
140
120
100
80
60
40
20
PPM

4. Asymmetric Study for the Reaction and HPLC Spectra

Table S1. Screening of chiral catalysts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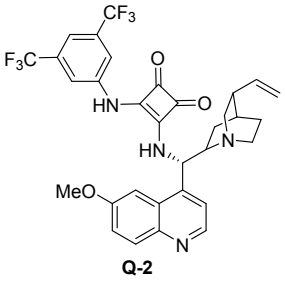
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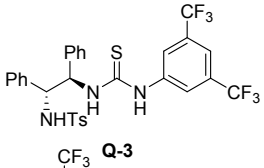
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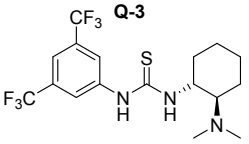
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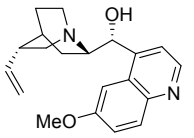
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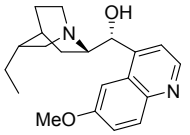
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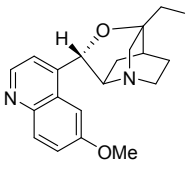
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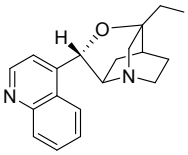
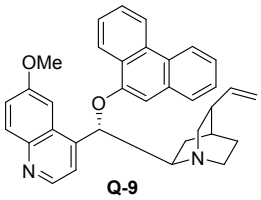
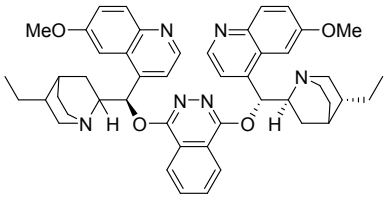
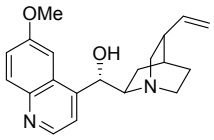
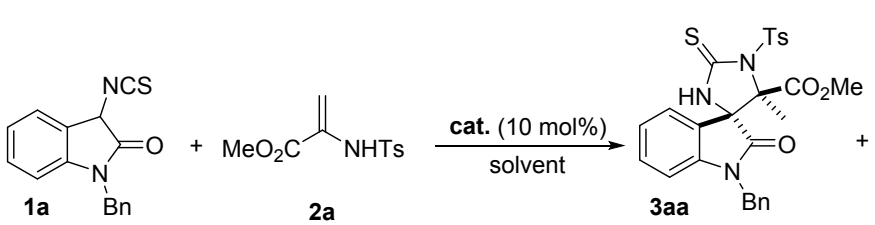

Q-8


Q-9


Q-10

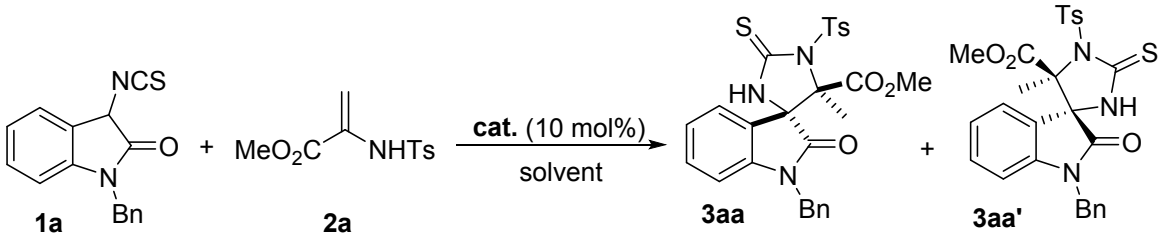

Q-11


1a 2a 3aa 3aa'

entry[a]	cat.	solvent	dr[b]	yield (%)[c]	**3aa** e.r.[d]
1	**Q-1**	THF	1:1	97	13:87
2	**Q-2**	THF	2:1	98	53:47
3	**Q-3**	THF	2:1	98	83:17
4	**Q-4**	PhMe	1:1	93	73:27
5	**Q-5**	PhMe	16:1	94	37:63
6	**Q-6**	PhMe	21:1	95	36:64
7	**Q-7**	PhMe	8:1	81	46:54
8	**Q-8**	PhMe	23:1	93	70:30
9	**Q-9**	PhMe	11:1	94	69:31
10	**Q-10**	PhMe	0.6:1	87	52:48
11	**Q-11**	PhMe	18:1	95	62:38

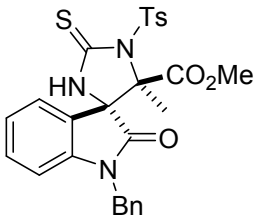
[a]Unless otherwise indicated, all reactions were carried out with **1a** (0.24 mmol), **2a** (0.2 mmol), **cat.** (10 mol %) in solvent (2.5 mL) at room temperature in a reaction tube. [b]Isolated yield. [c]d.r. values were determined by ^{1}H NMR spectroscopy. [d]Determined by chiral HPLC.

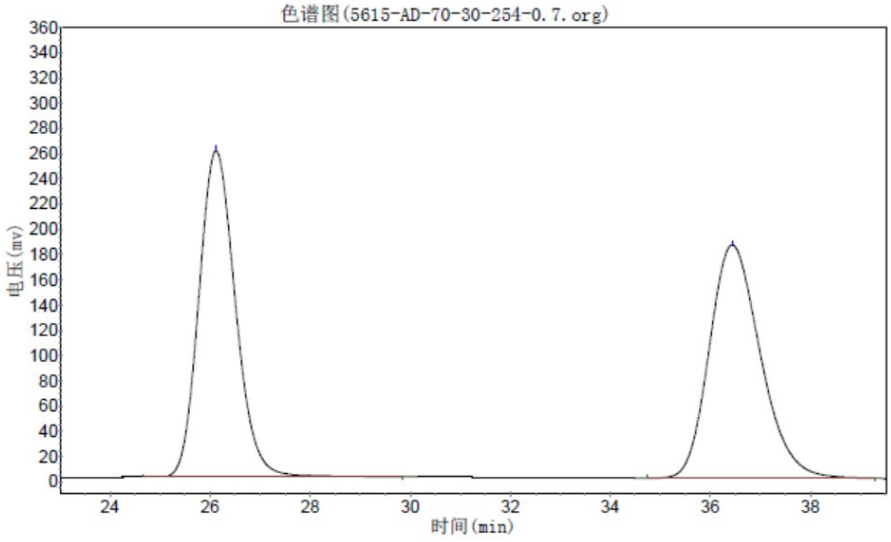
Table S2. Screening of solvents



entry[a]	cat.	solvent	d.r.[b]	yield (%)[c]	**3aa** e.r.[d]
1	**Q-1**	THF	1:1	97	12.5:87.5
2	**Q-1**	DCM	1:1	96	24:76
3	**Q-1**	PhMe	1:1	98	41:59
4	**Q-1**	MeCN	1:1	98	5:95
5[e]	**Q-1**	MeCN	1:1	97	5.5:95.5
6	**Q-8**	PhMe	23:1	96	70:30
7	**Q-8**	THF	1:1	94	68.5:31.5
8	**Q-8**	DCM	5:1	93	70.5:29.5
9	**Q-8**	MeCN	0.8:1	95	61:39

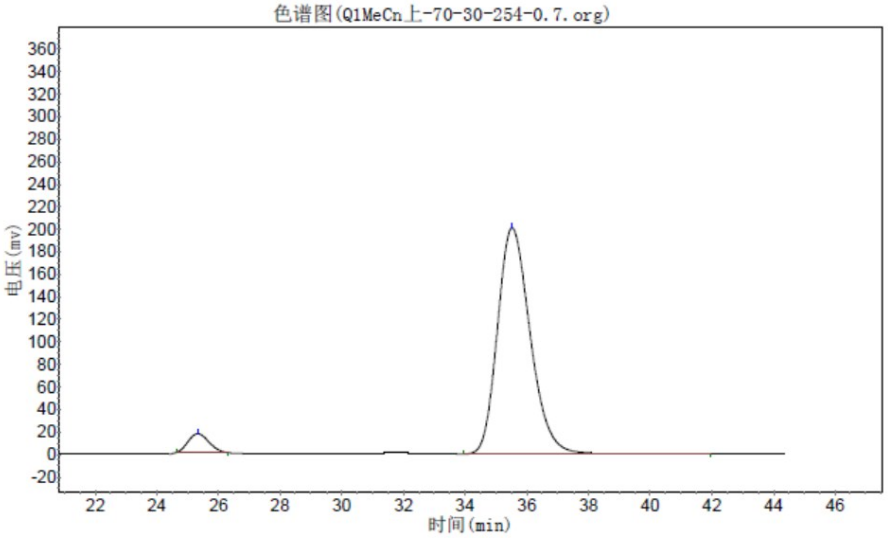
[a]Unless otherwise indicated, all reactions were carried out with **1a** (0.24 mmol), **2a** (0.2 mmol), **cat.** (10 mol %) in solvent (2.5 mL) at room temperature in a reaction tube. [b]Isolated yield. [c]d.r. values were determined by ^{1}H NMR spectroscopy. [d]Determined by chiral HPLC.[e]Reaction conducted at 0 ^{o}C





分析结果表

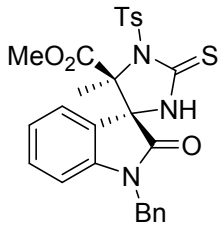
峰号	峰名	保留时间	峰高	峰面积	含量
1		26.123	258484.234	13120137.000	50.1077
2		36.440	184614.422	13063721.000	49.8923
总计			443098.656	26183858.000	100.0000

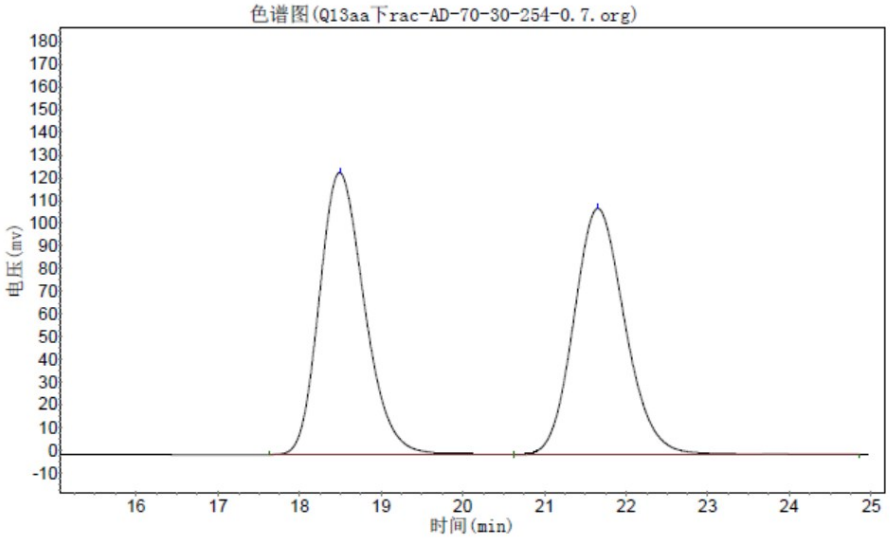


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		25.323	16795.848	789174.375	5.0761
2		35.512	200687.109	14757623.000	94.9239
总计			217482.957	15546797.375	100.0000

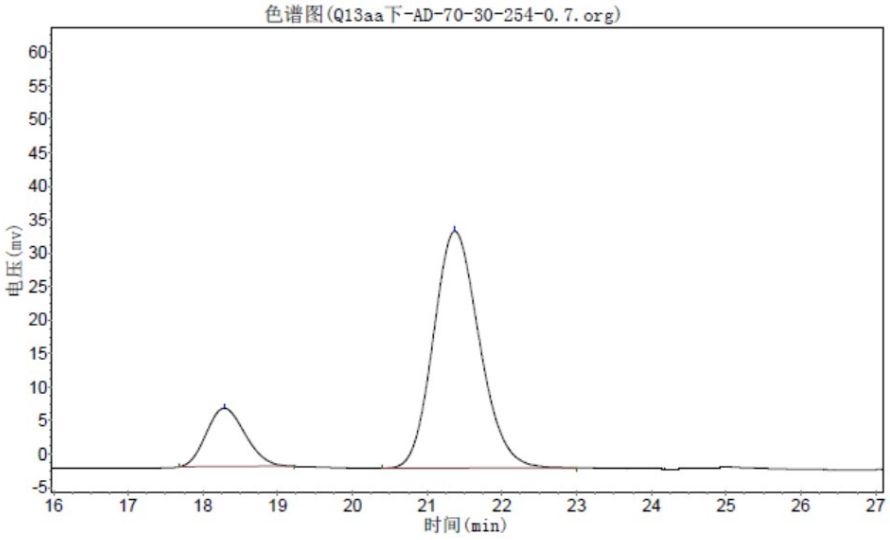
Translation: Chiralcel AD-H column [λ = 254 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.7 mL/min; t_{minor} = 25.32 min, t_{major} = 35.51 min; e.r = 95:5].





分析结果表

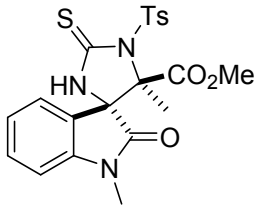
峰号	峰名	保留时间	峰高	峰面积	含量
1		18.490	123805.250	4755670.000	50.2738
2		21.657	108154.234	4703878.000	49.7262
总计			231959.484	9459548.000	100.0000

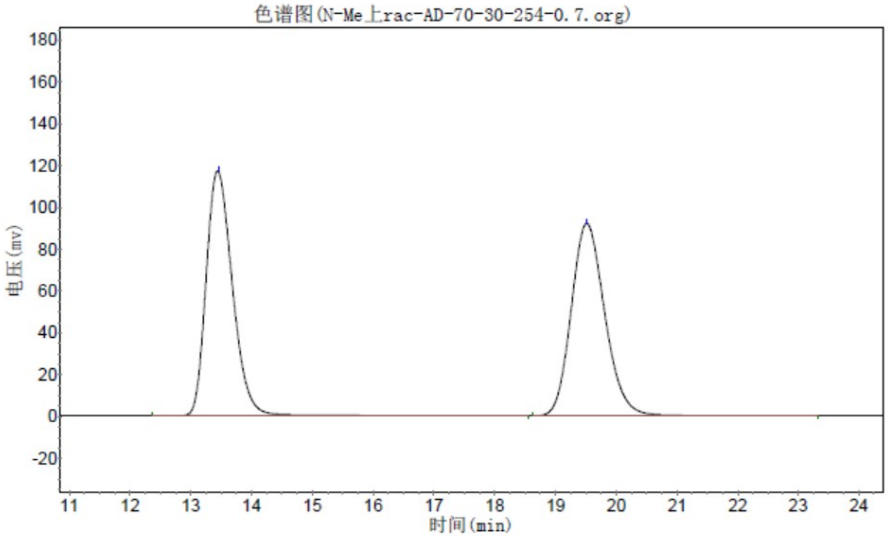


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		18.283	8728.824	316037.000	17.3058
2		21.370	35368.078	1510155.500	82.6942
总计			44096.902	1826192.500	100.0000

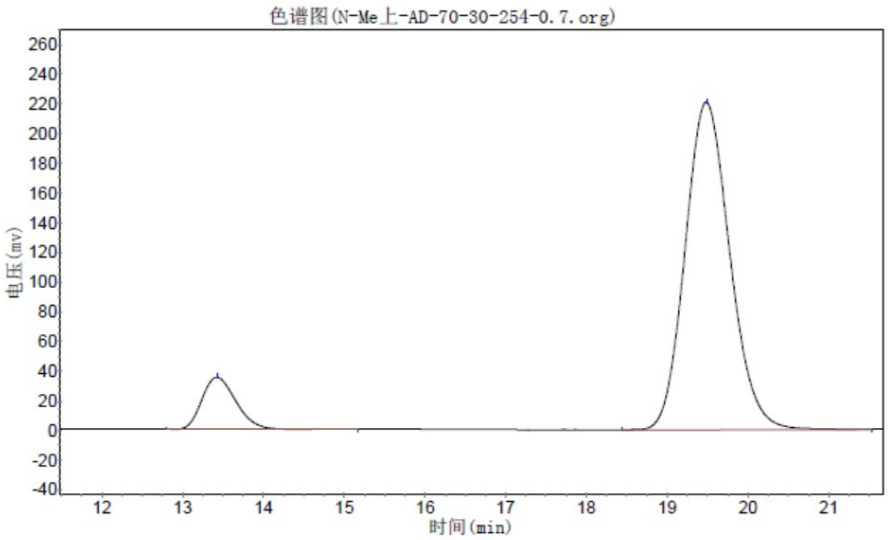
Translation: Chiralcel AD-H column [λ = 254 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.7 mL/min; t_{minor} = 18.28 min, t_{major} = 21.37 min; e.r = 83:17].





分析结果表

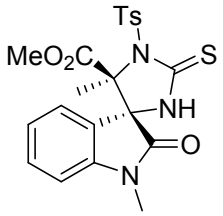
峰号	峰名	保留时间	峰高	峰面积	含量
1		13.457	116953.391	3536312.250	50.0441
2		19.523	91898.008	3530082.250	49.9559
总计			208851.398	7066394.500	100.0000

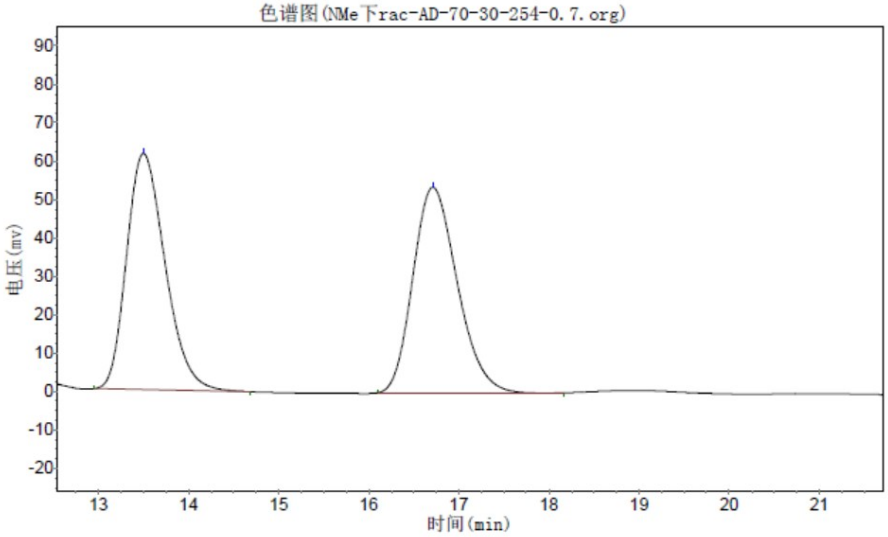


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		13.432	35377.168	1053041.250	11.0224
2		19.498	220737.641	8500618.000	88.9776
总计			256114.809	9553659.250	100.0000

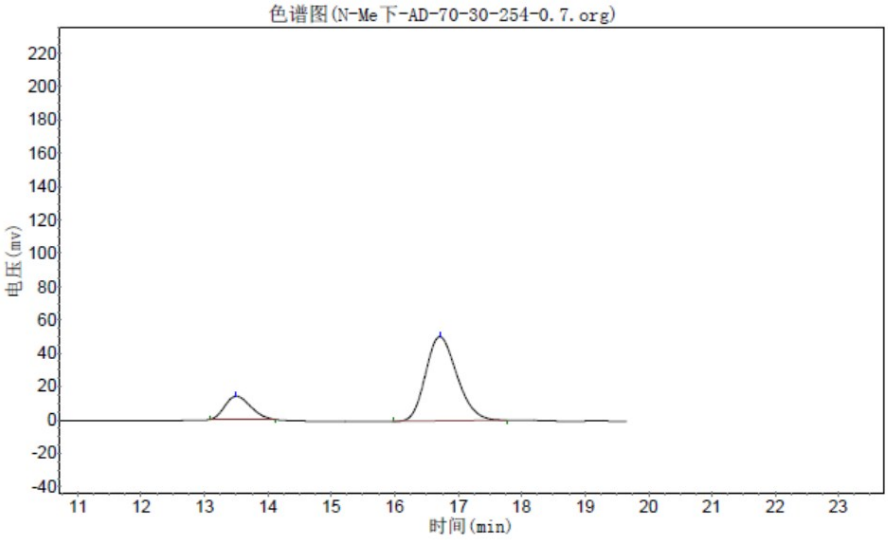
Translation: Chiralcel AD-H column [λ = 254 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.7 mL/min; t_{minor} = 13.43 min, t_{major} = 19.50 min; e.r = 89:11].





分析结果表

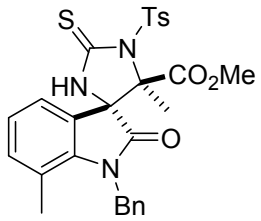
峰号	峰名	保留时间	峰高	峰面积	含量
1		13.500	61537.117	1831125.875	50.0713
2		16.710	53528.652	1825911.250	49.9287
总计			115065.770	3657037.125	100.0000

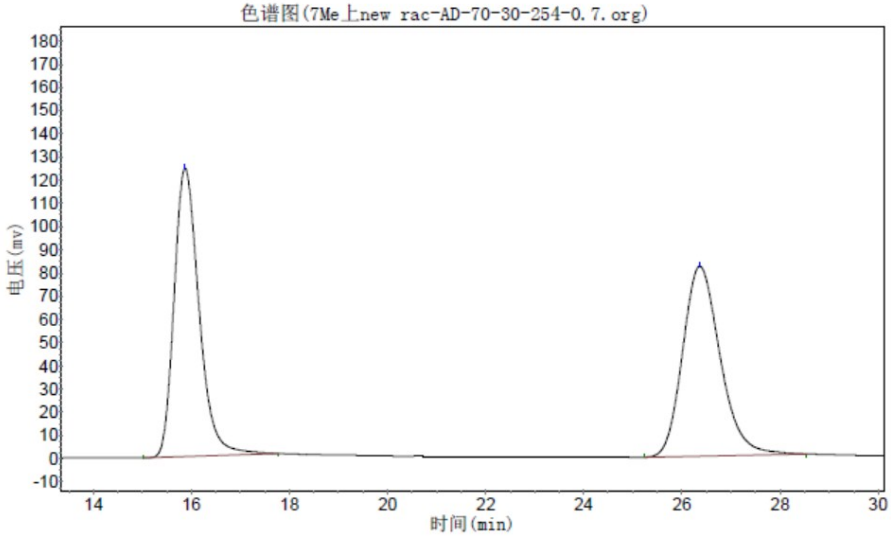


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		13.500	13984.070	395168.219	18.6091
2		16.708	50465.961	1728356.375	81.3909
总计			64450.031	2123524.594	100.0000

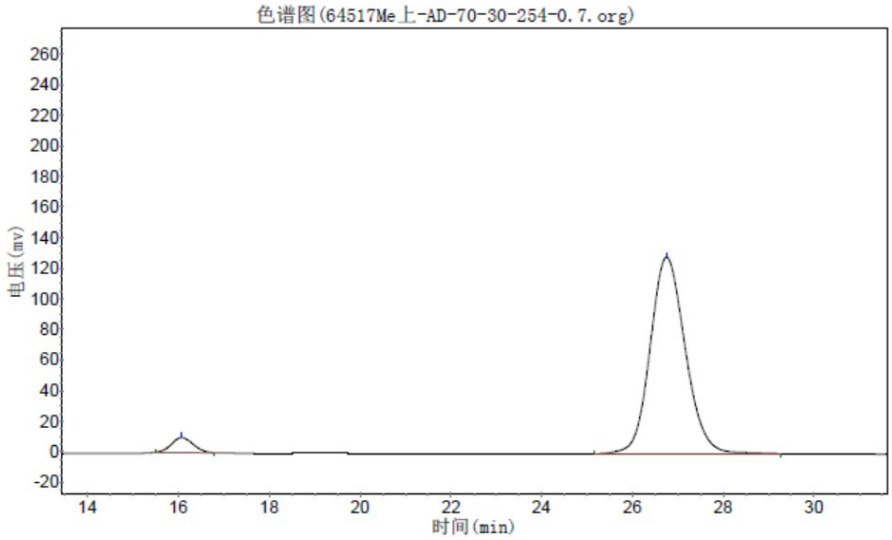
Translation: Chiralcel AD-H column [λ = 254 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.7 mL/min; t_{minor} = 13.50 min, t_{major} = 16.71 min; e.r = 81:19].





分析结果表

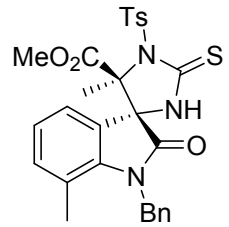
峰号	峰名	保留时间	峰高	峰面积	含量
1		15.868	124159.219	4387451.000	50.2325
2		26.360	81791.281	4346835.500	49.7675
总计			205950.500	8734286.500	100.0000

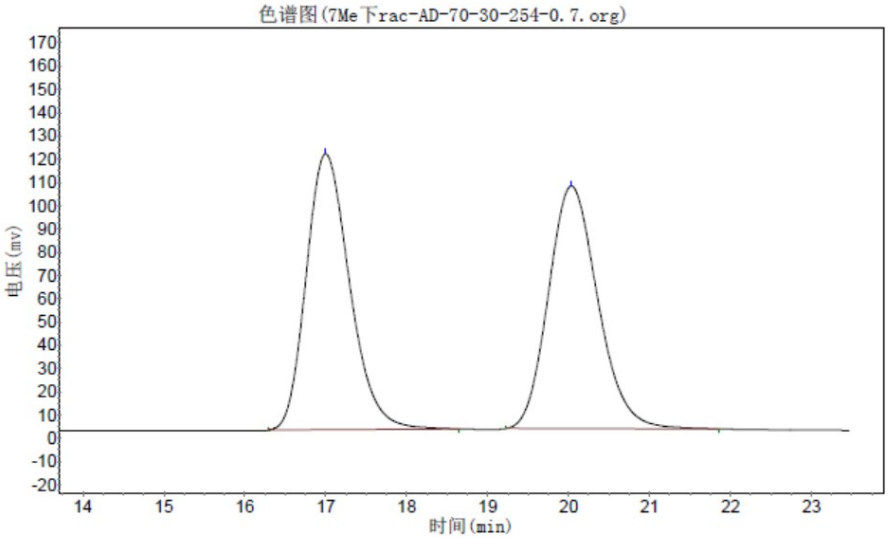


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		16.067	9654.987	318058.594	4.3877
2		26.753	128676.422	6930734.000	95.6123
总计			138331.409	7248792.594	100.0000

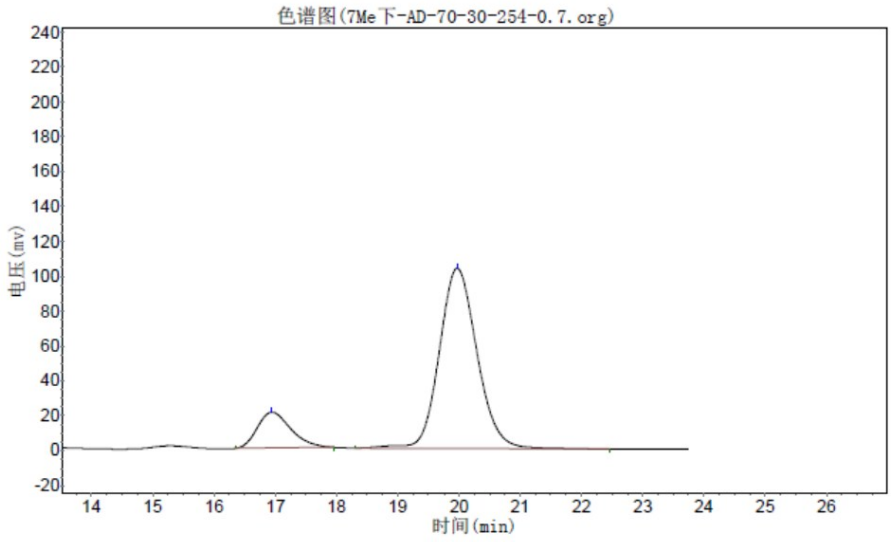
Translation: Chiralcel AD-H column [λ = 254 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.7 mL/min; t_{minor} = 16.07 min, t_{major} = 26.75 min; e.r = 96:4].





分析结果表

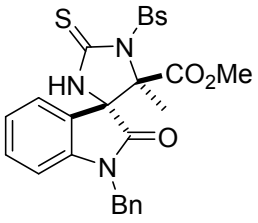
峰号	峰名	保留时间	峰高	峰面积	含量
1		16.998	118721.219	4433601.500	50.0354
2		20.033	104346.133	4427324.500	49.9646
总计			223067.352	8860926.000	100.0000

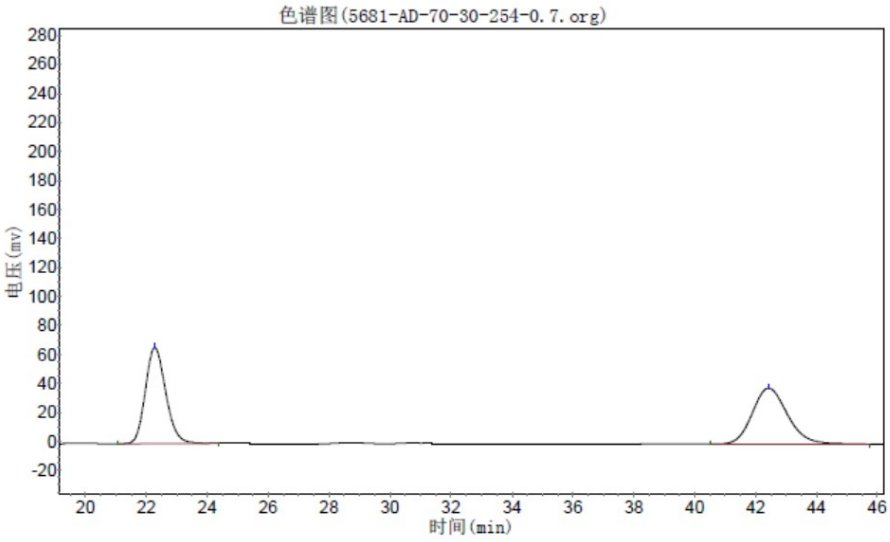


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		16.943	20586.145	783665.375	15.0813
2		19.968	103302.484	4412615.000	84.9187
总计			123888.629	5196280.375	100.0000

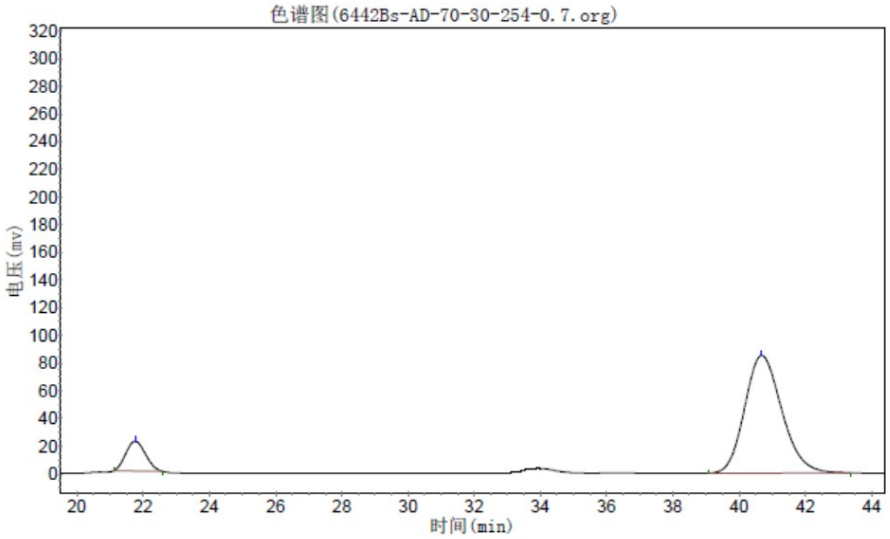
Translation: Chiralcel AD-H column [λ = 254 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.7 mL/min; t_{minor} = 16.94 min, t_{major} = 19.97 min; e.r = 85:15].





分析结果表

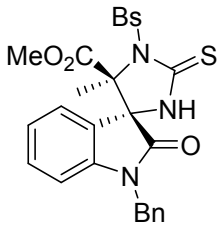
峰号	峰名	保留时间	峰高	峰面积	含量
1		22.273	66131.313	3069440.750	49.9730
2		42.422	38496.453	3072752.250	50.0270
总计			104627.766	6142193.000	100.0000

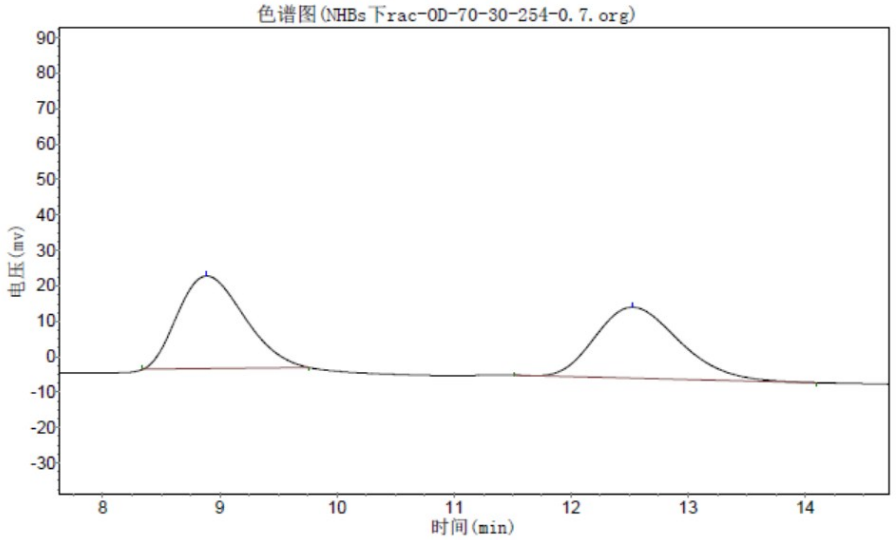


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		21.765	21594.873	891129.625	11.8610
2		40.672	85090.578	6621970.500	88.1390
总计			106685.451	7513100.125	100.0000

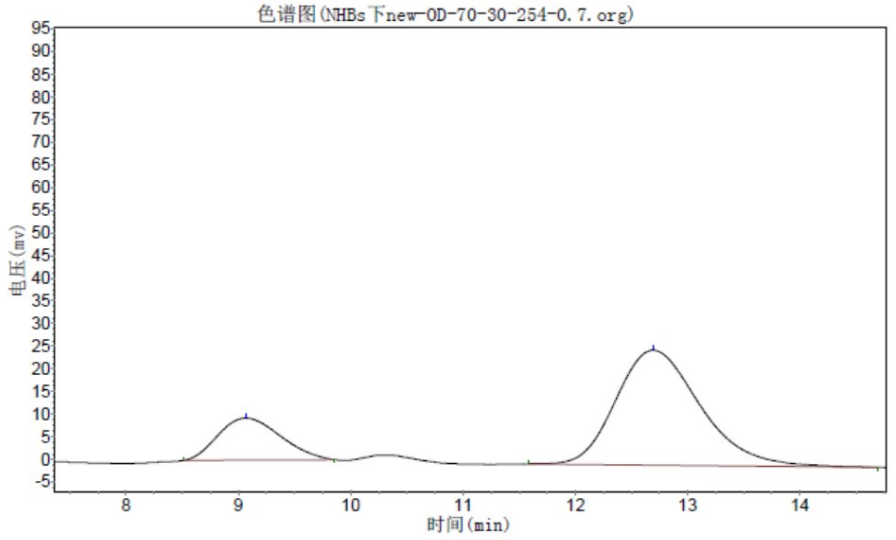
Translation: Chiralcel AD-H column [λ = 254 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.7 mL/min; t_{minor} = 21.77 min, t_{major} = 40.67 min; e.r = 88:12].





分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		8.887	26127.932	1030489.188	50.9156
2		12.523	20021.100	993426.625	49.0844
总计			46149.031	2023915.813	100.0000

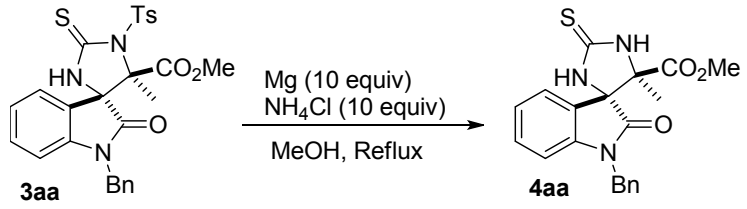


分析结果表

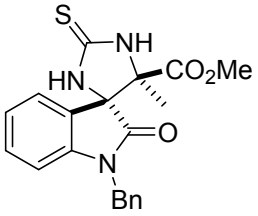
峰号	峰名	保留时间	峰高	峰面积	含量
1		9.063	9253.216	355858.719	21.2360
2		12.690	25334.645	1319873.500	78.7640
总计			34587.860	1675732.219	100.0000

Translation: Chiralcel OD-H column [λ = 254 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.7 mL/min; t_{minor} = 9.06 min, t_{major} = 12.69 min; e.r = 79:21].

5. General Procedure for the Synthesis of 4aa and Its Spectra Charts

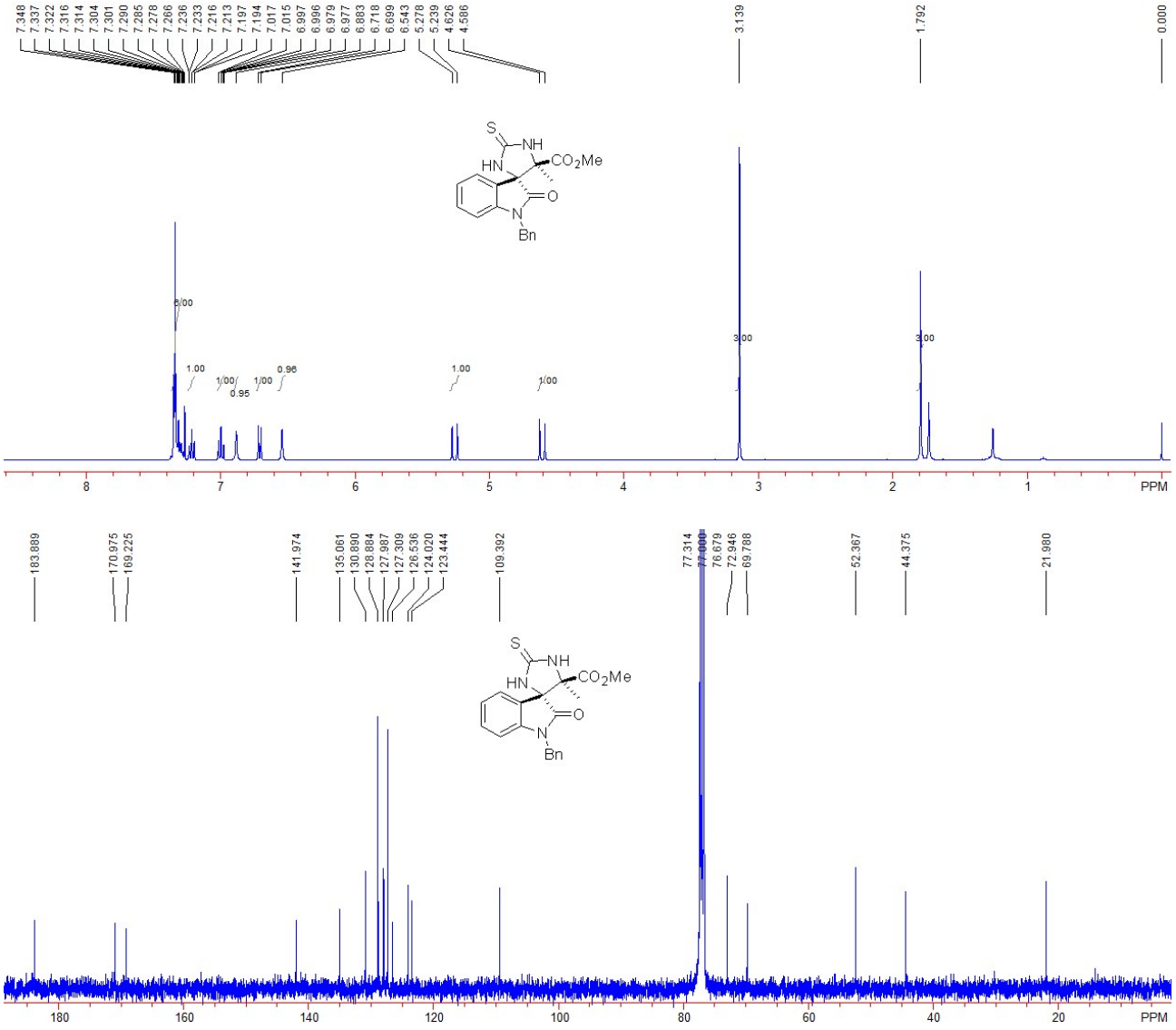


Magnesium dust (24 mg, 1.0 mmol) and NH_4Cl (5.3 mg, 1.0 mmol) were added in one portion to a suspension of **3aa** (54 mg, 0.1 mmol) in MeOH (2.0 mL). The reaction mixture was heated to reflux for 4 h. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography on silica gel to give the corresponding product **4aa** in 58% yield.



Methyl-1'-benzyl-5-methyl-2'-oxo-2-thioxospiro[imidazolidine-4,3'-indoline]-5-carboxylate (4aa)

A white solid, 22 mg, 58 % yield; m. p. 123-125 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.34-7.28 (m, 6H), 7.21 (td, *J* = 1.2, 8.0 Hz, 1H), 7.00 (td, *J* = 0.8, 7.6 Hz, 1H), 6.88 (s, 1H), 6.71 (d, *J* = 7.6 Hz, 1H), 6.54 (s, 1H), 5.26 (d, *J* = 15.6 Hz, 1H), 4.61 (d, *J* = 16.0 Hz, 1H), 3.14 (s, 3H), 1.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 183.9, 171.0, 169.2, 142.0, 135.1, 130.9, 128.9, 128.0, 127.3, 126.5, 124.0, 123.4, 109.4, 72.9, 69.8, 52.4, 44.4, 22.0; IR (neat): ν 3170, 2924, 1720, 1612, 1487, 1365, 1175, 1129, 909, 754, 731, 697 cm^{-1}; HRMS (ESI) Calcd. For $C_{20}H_{20}N_3O_3S^+$ $(M+H)^+$ requires 382.1220, Found: 382.1216.


7.348
7.337
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7.314
7.304
7.301
7.290
7.285
7.278
7.266
7.236
7.233
7.216
7.213
7.197
7.194
7.017
7.015
6.997
6.996
6.979
6.977
6.883
6.718
6.699
6.543
5.278
5.239
4.626
4.586
3.139
1.792
0.000
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NH
HN
CO2Me
O
N
Bn
3.00
1.00
1.00
0.95
1.00
0.96
1.00
1.00
3.00
3.00
8
7
6
5
4
3
2
1
PPM
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130.890
128.884
127.987
127.309
126.536
124.020
123.444
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77.000
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69.788
52.367
44.375
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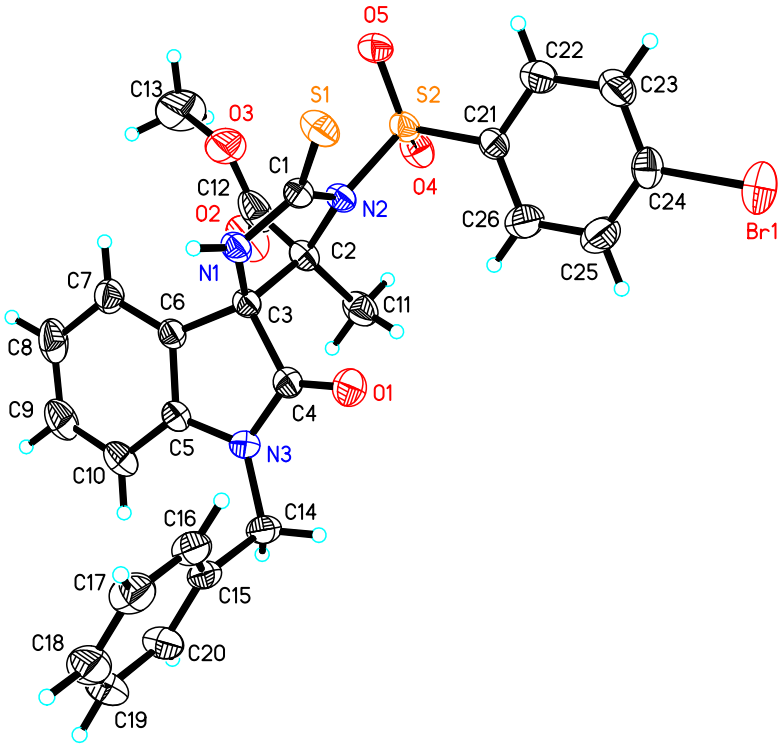
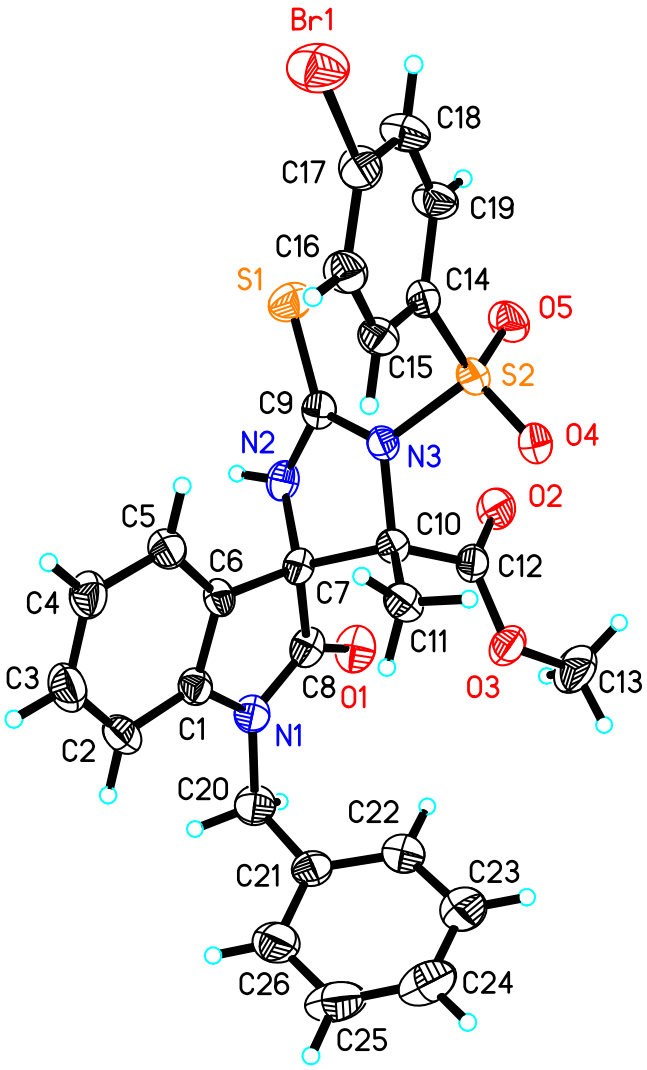
S
NH
HN
CO2Me
O
N
Bn
180
160
140
120
100
80
60
40
20
PPM

6. X-ray Data of 3ab and 3ab'



The crystal data of **3ab** have been deposited in CCDC with number 1838515. Empirical Formula: $C_{26}H_{22}BrN_3O_5S_2$; Formula Weight: 600.49; Crystal Color, colorless; Crystal Dimensions: 0.200 x 0.170 x 0.130 mm^3; Crystal System: Triclinic; Lattice Parameters: a = 11.1459(3)Å, b = 12.2398(4)Å, c = 12.4710(4)Å, α = 67.3830(10)°, β = 76.8290(10)°, γ = 77.6170(10)°, V = 1513.89(8)$Å^3$; Space group: P -1; Z = 2; D_{calc} = 1.317 g/cm^3; F_{000} = 612; Final R indices [I>2sigma(I)] R1 = 0.0521, wR2 = 0.1544.



The crystal data of **3ab'** have been deposited in CCDC with number 1867790. Empirical Formula: $C_{29}H_{28}BrN_3O_6S_2$; Formula Weight: 658.57; Crystal Color, colorless; Crystal Dimensions: 0.180 x 0.150 x 0.120 mm^3; Crystal System: Monoclinic; Lattice Parameters: a = 10.6362(13)Å, b = 13.2220(16)Å, c = 11.2568(14)Å, α = 90°, β = 105.849(2)°, γ = 90°, V = 1522.9(3)$Å^3$; Space group: P 21; Z = 2; D_{calc} = 1.436 g/cm^3; F_{000} = 676; Final R indices [I>2sigma(I)] R1 = 0.0530, wR2 = 0.1374.