

Supporting Information

Regio- and Diastereoselective Construction of 1',2'-Dihydrospiro[indoline-3,3'-pyrrol]-2'-yl)acrylates through Phosphine-catalyzed [4+1] Annulation of Morita-Baylis-Hillman Carbonates with Oxindole-Derived α,β -Unsaturated Imines

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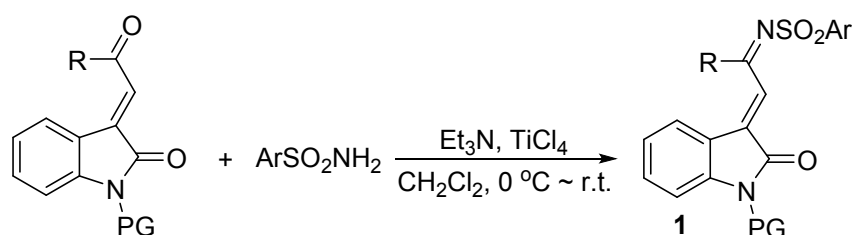
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1. General Remarks:

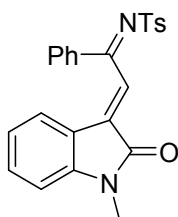
Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. Optical rotations were determined at 589 nm (sodium D line) by using a Perkin-Elmer-341 MC digital polarimeter; $[\alpha]_D$ -values are given in unit of $10 \text{ deg}^{-1} \text{ cm}^2 \text{ g}^{-1}$. ^1H 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. Chiral HPLC was performed on a SHIMADZU SPD-10A *vp* series with chiral columns (Chiralpak AD-H, OD-H, and IC columns $4.6 \times 250 \text{ mm}$, (Daicel Chemical Ind., Ltd.)) and chiral column (Phenomenex Lux 5μ Amylose-2 column $4.6 \times 250 \text{ mm}$ (PA-2), Phenomenex Lux 5μ Cellulose-2 column $4.6 \times 250 \text{ mm}$ (PC-2), (Phenomenex Ind., Ltd.)). Mass spectra were recorded by EI, ESI, MALDI and HRMS was measured on a HP-5989 instrument.

2. General Procedure for the Synthesis of Oxindole-Derived α,β -Unsaturated Imines and Spectroscopic Data of the Products.

Oxindole-derived α,β -unsaturated imines **1** were prepared according to a previous procedure in the literature.¹

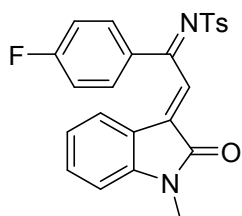
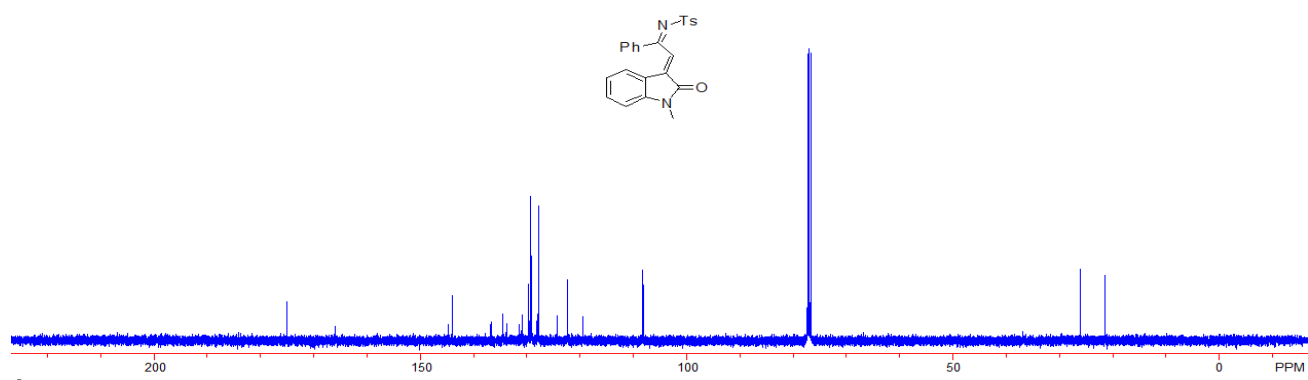
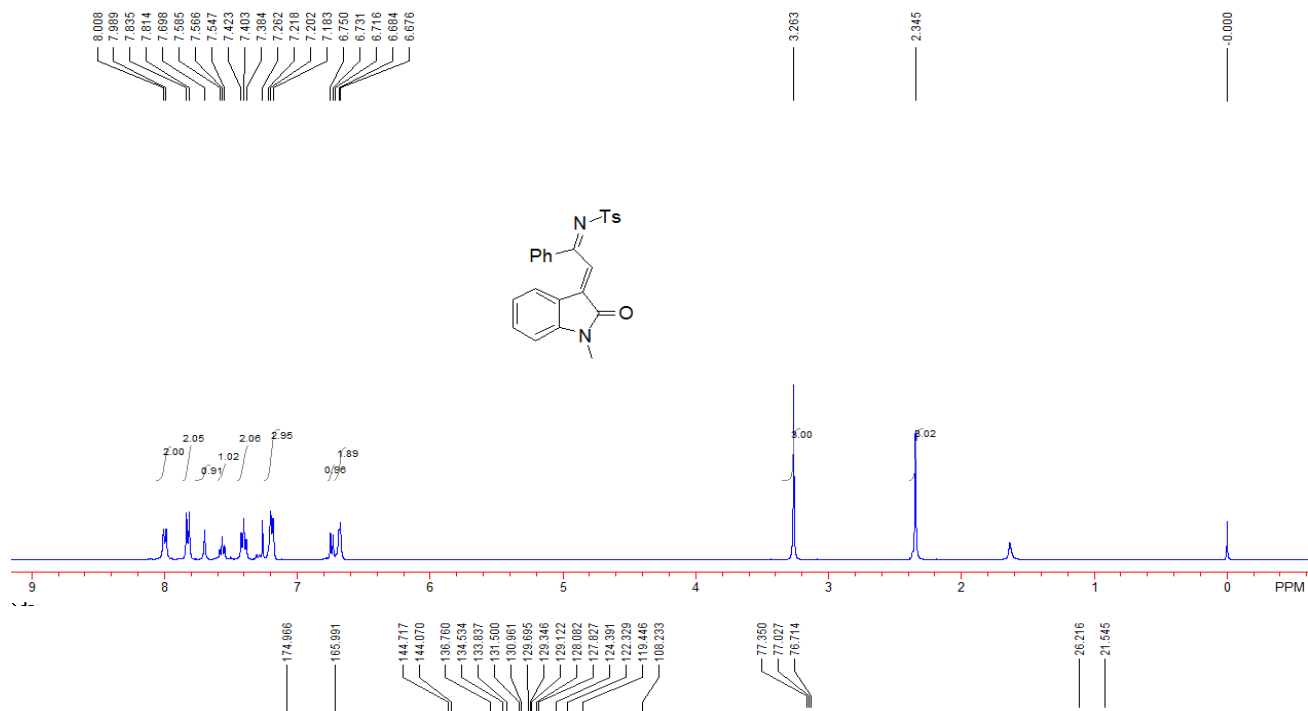


To a solution of oxindole-derived α,β -unsaturated ketones (2.0 mmol) in dry CH_2Cl_2 was added arylsulfonamide (2.0 mmol), triethylamine (4.0 mmol) and titanium tetrachloride (2.0 mmol) at 0 °C under argon, and the reaction mixture was stirred at room temperature for 12 h. The reaction was quenched by addition of brine. The aqueous phase was extracted with CH_2Cl_2 and the combined organic layers were dried over anhydrous MgSO_4 and concentrated in vacuo. Purification of the residue by column chromatography on silica gel gave the desired oxindole-derived α,β -unsaturated imines **1a-1t**.



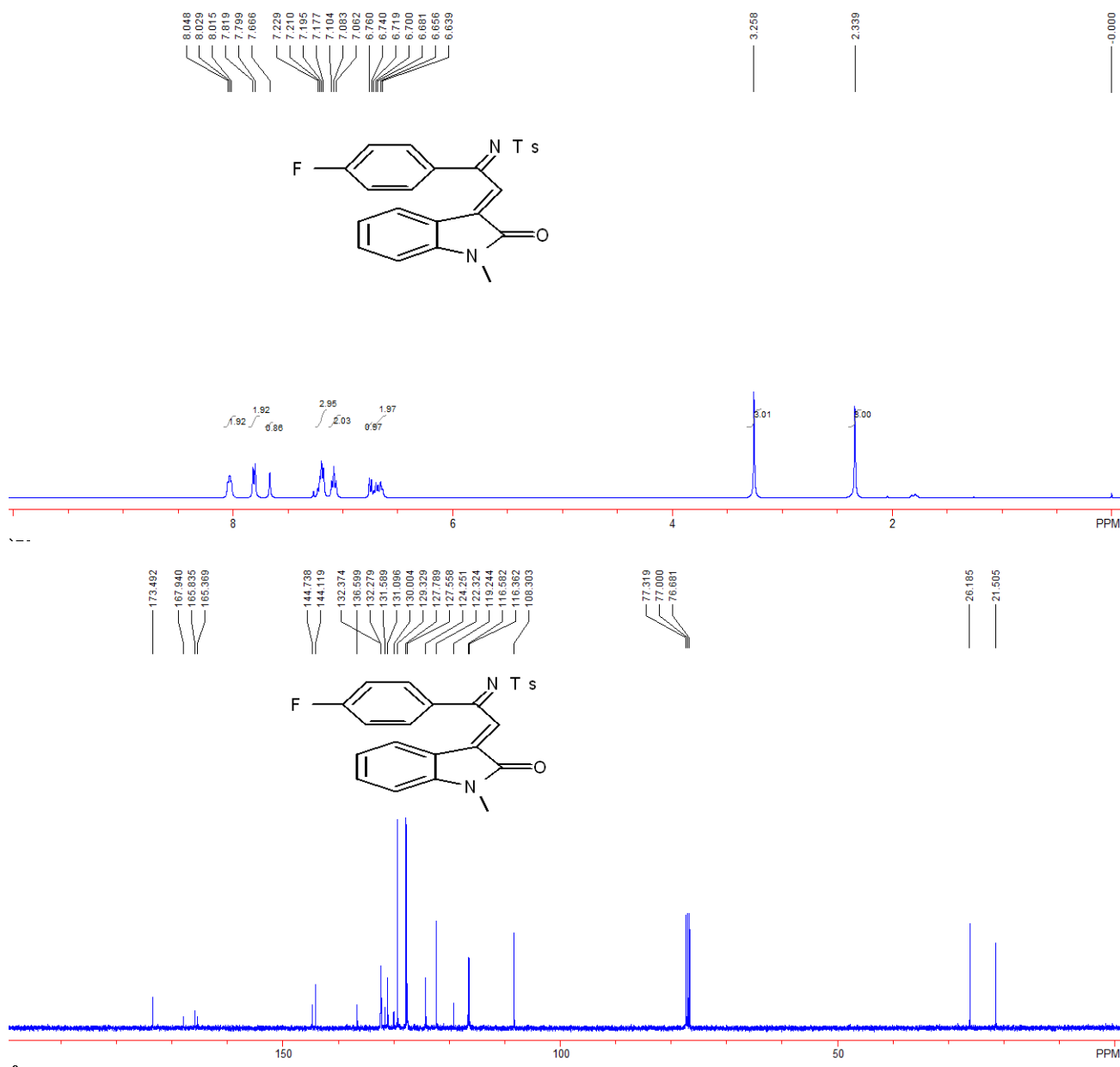
Compound 1a: A yellow solid, 400 mg, 48% yield; m.p. 98-99 °C; ^1H NMR (400 MHz, CDCl_3 , TMS): δ 2.35 (s, 3H, CH_3), 3.26 (s, 3H, CH_3), 6.68-6.72 (m, 2H, Ar), 6.74 (d, 1H, $J = 7.6$ Hz, Ar), 7.18-7.22 (m, 3H, Ar), 7.40 (t, 2H, $J = 7.6$ Hz, Ar), 7.57 (t, 1H, $J = 7.6$ Hz, Ar), 7.70 (s, 1H, =CH), 7.82 (d, 2H, $J = 7.6$ Hz, Ar), 8.00 (d, 2H, $J = 7.6$ Hz, Ar); ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 21.5, 26.2, 108.2, 119.4, 122.3, 124.4, 127.8, 128.1, 129.1, 129.3, 129.7, 131.0, 131.5, 133.8, 134.5, 136.8, 144.1, 144.7, 166.0, 175.0; HRMS (ESI) Calcd. For $\text{C}_{24}\text{H}_{21}\text{N}_2\text{O}_3\text{S}^+$ ($\text{M}+\text{H}$) $^+$ requires 417.1273,

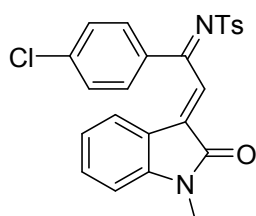
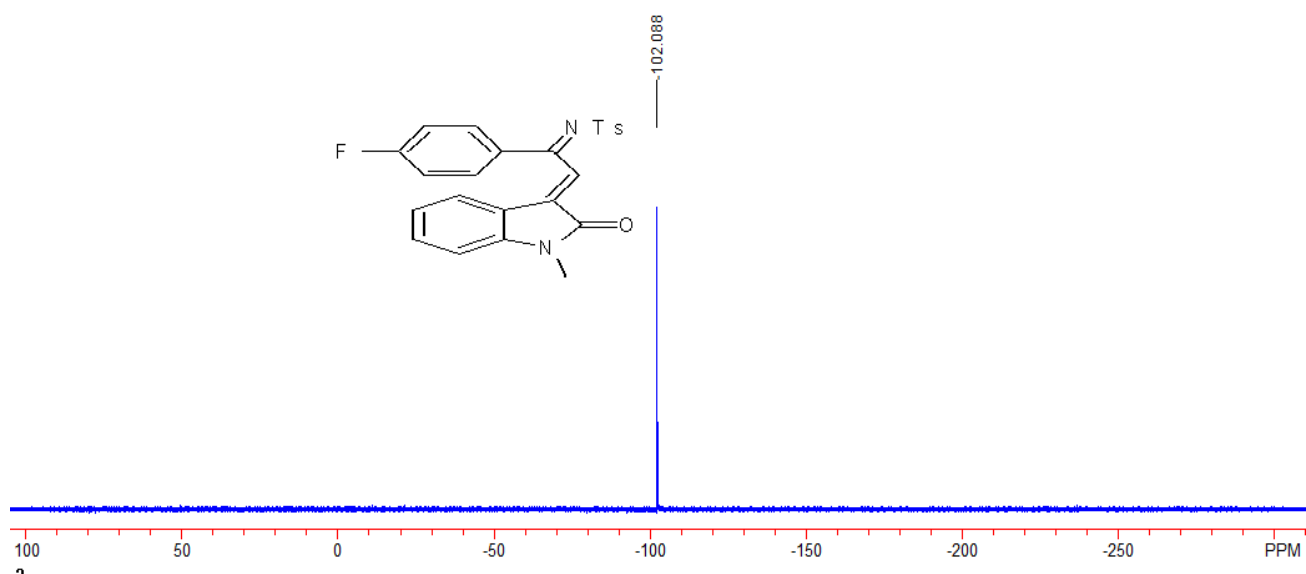
Found: 417.1265; IR (CH₂Cl₂): ν 684, 764, 773, 822, 1023, 1157, 1249, 1305, 1327, 1377, 1470, 1553, 1610, 1715, 2850, 2922 cm⁻¹.



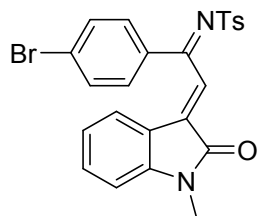
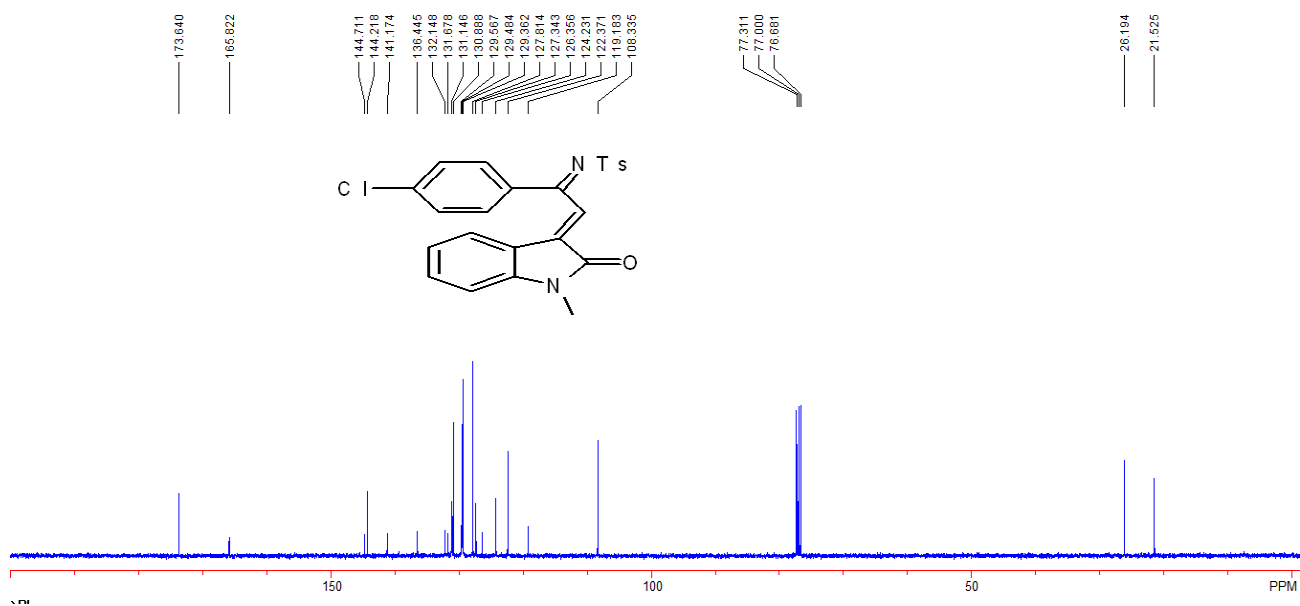
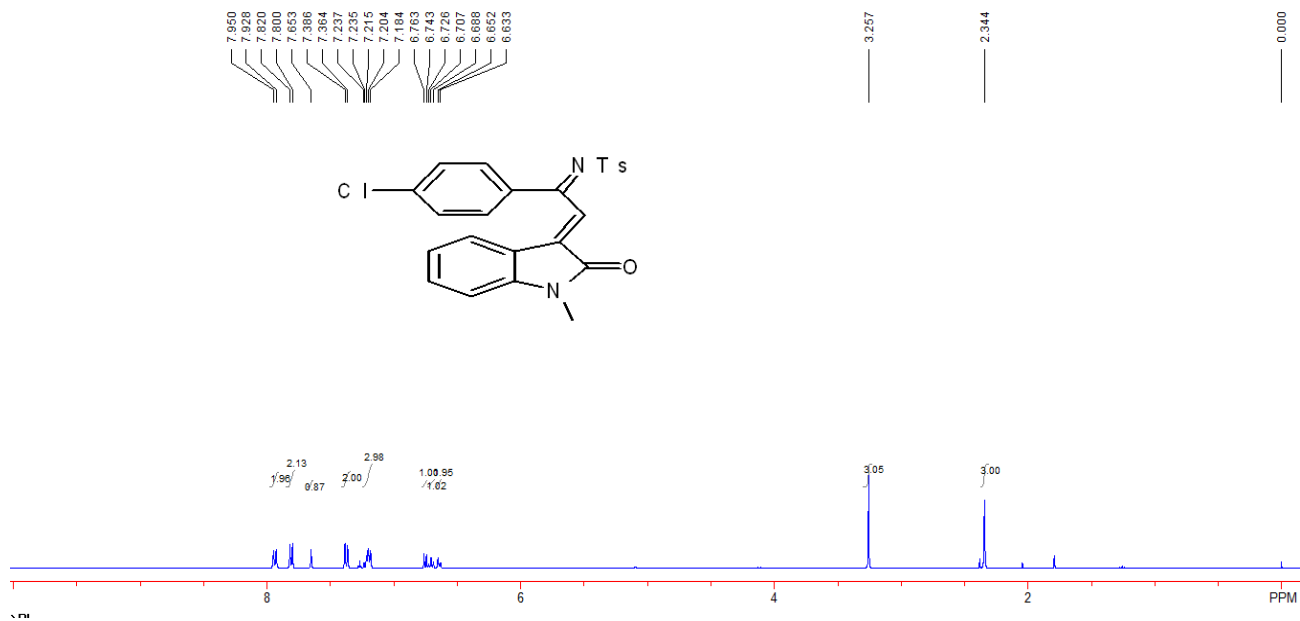
Compound 1b: A yellow solid, 408 mg, 47% yield; m.p. 169-170 °C; ¹H NMR (CDCl₃, 400 MHz, TMS): δ 2.34 (s, 3H, CH₃), 3.26 (s, 3H, CH₃), 6.64-6.76 (m, 3H, Ar), 7.08 (t, J = 8.4 Hz, 2H, Ar), 7.17-7.23 (m, 3H, Ar), 7.67 (s, 1H, =CH), 7.81 (d, J = 8.0 Hz, 2H, Ar), 8.01-8.05 (m, 2H, Ar); ¹³C

NMR (CDCl₃, 100 MHz, TMS): δ 21.5, 26.2, 108.3, 116.5 (d, $J = 22.0$ Hz), 119.2, 122.3, 124.3, 127.6, 127.8, 129.3, 130.0, 131.1, 131.6, 132.3 (d, $J = 9.5$ Hz), 136.6, 144.1, 144.7, 165.8, 166.7 (d, $J = 256.7$ Hz), 173.5; ¹⁹F NMR (CDCl₃, 376 MHz, CFC1₃): δ -102.09; HRMS (ESI) Calcd. For C₂₄H₂₃FN₃O₃S⁺ (M+NH₄)⁺ requires 452.1439, Found: 452.1451; IR (CH₂Cl₂): ν 668, 764, 769, 851, 1089, 1151, 1241, 1327, 1376, 1469, 1552, 1610, 1715, 2933, 3058 cm⁻¹.



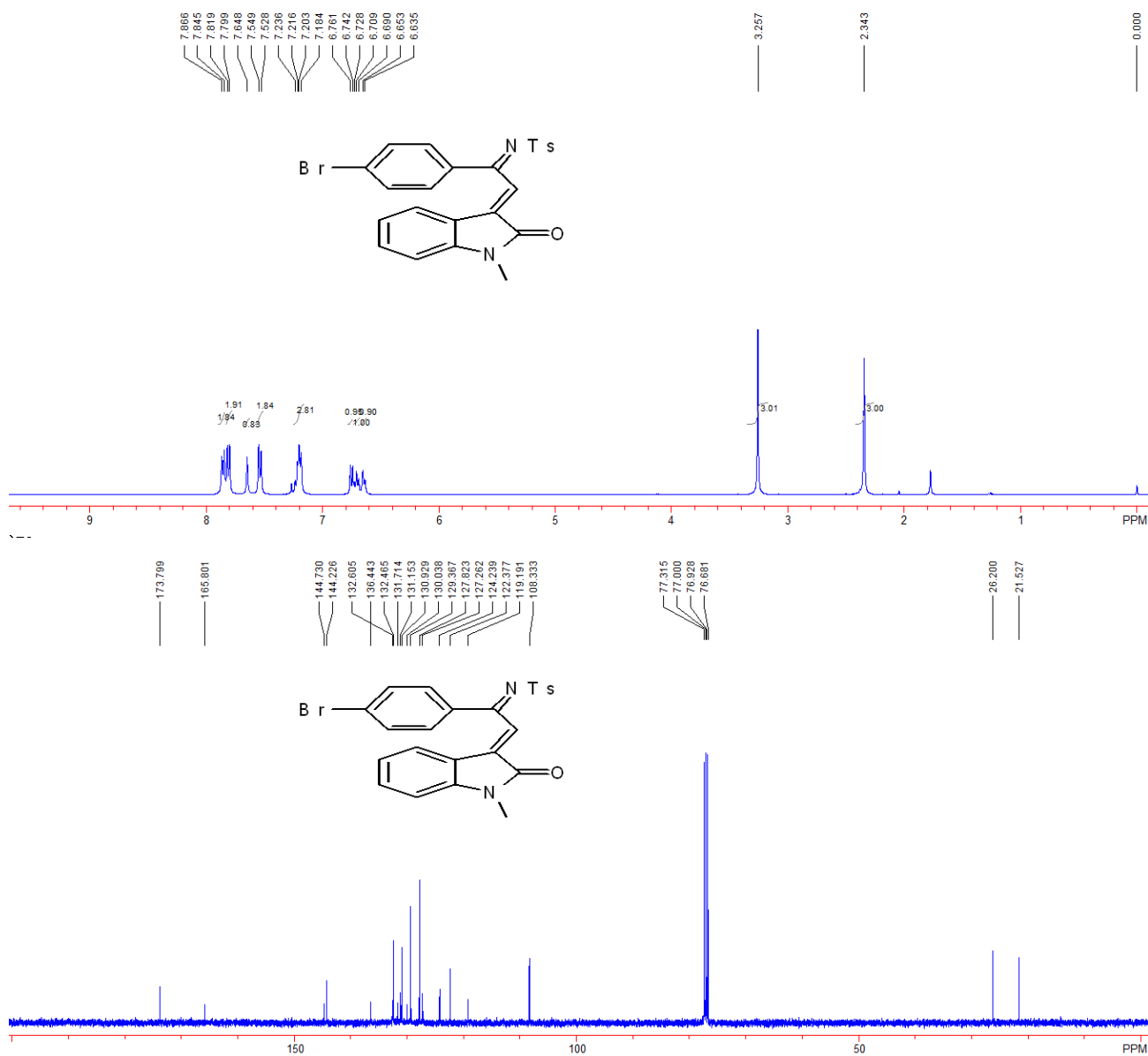


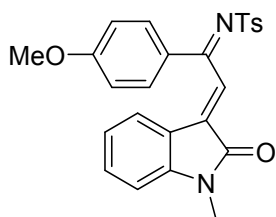
Compound 1c: A yellow solid, 459 mg, 51% yield; m.p. 173-174 °C; ^1H NMR (CDCl_3 , 400 MHz, TMS): δ 2.34 (s, 3H, CH_3), 3.26 (s, 3H, CH_3), 6.64 (d, $J = 7.6$ Hz, 1H, Ar), 6.71 (t, $J = 7.6$ Hz, 1H, Ar), 6.75 (d, $J = 8.0$ Hz, 1H, Ar), 7.18-7.24 (m, 3H, Ar), 7.38 (d, $J = 8.8$ Hz, 2H, Ar), 7.65 (s, 1H, =CH), 7.81 (d, $J = 8.0$ Hz, 2H, Ar), 7.95 (d, $J = 8.8$ Hz); ^{13}C NMR (CDCl_3 , 100 MHz, TMS): δ 21.5, 26.2, 108.3, 119.2, 122.4, 124.2, 126.4, 127.3, 127.8, 129.4, 129.5, 129.6, 130.9, 131.1, 131.7, 132.1, 136.4, 141.2, 144.2, 144.7, 165.8, 173.6; HRMS (ESI) Calcd. For $\text{C}_{24}\text{H}_{23}\text{ClN}_3\text{O}_3\text{S}^+$ ($\text{M}+\text{NH}_4$) $^+$ requires 468.1143, Found: 468.1148; IR (CH_2Cl_2): ν 699, 729, 746, 776, 1012, 1089, 1158, 1331, 1469, 1577, 1610, 1715, 2919 cm^{-1} .



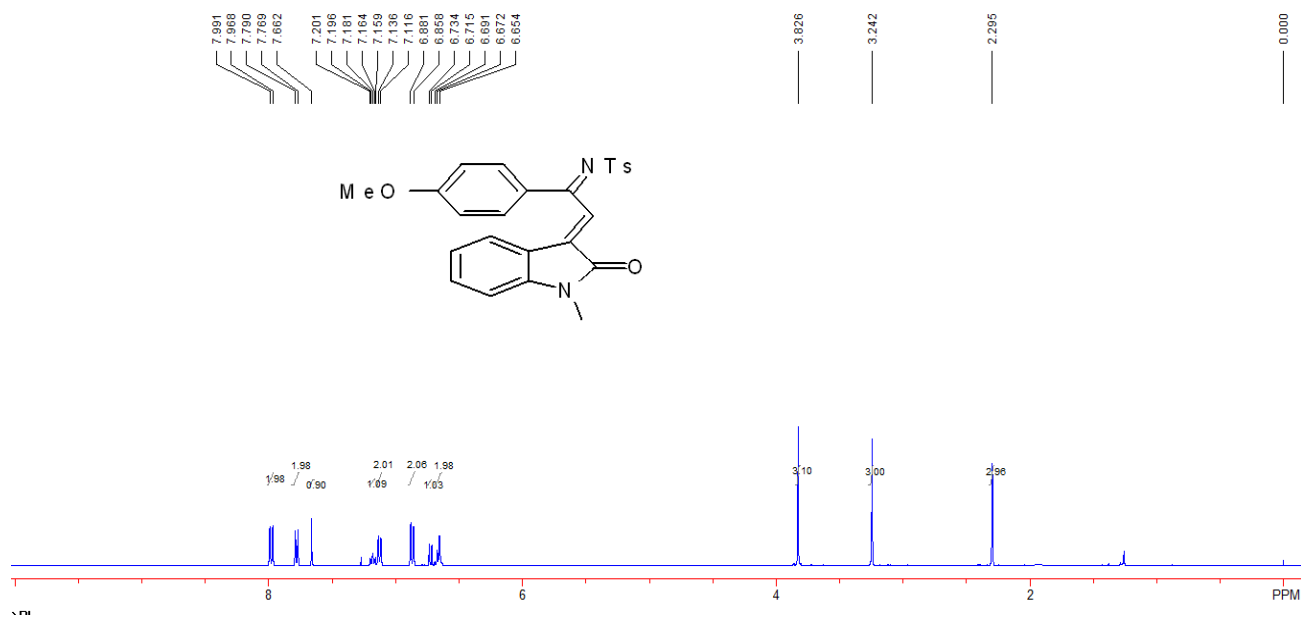
Compound 1d: A yellow solid, 523 mg, 53% yield; m.p. 185-186 °C; ¹H NMR (CDCl₃, 400 MHz, TMS): δ 2.34 (s, 3H, CH₃), 3.26 (s, 3H, CH₃), 6.64 (d, *J* = 7.2 Hz, 1H, Ar), 6.71 (t, *J* = 7.6 Hz, 1H, Ar), 6.75 (d, *J* = 7.6 Hz, 1H, Ar), 7.18-7.24 (m, 3H, Ar), 7.54 (d, *J* = 8.4 Hz, 2H, Ar), 7.65 (s, 1H,

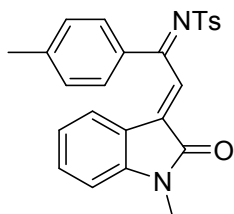
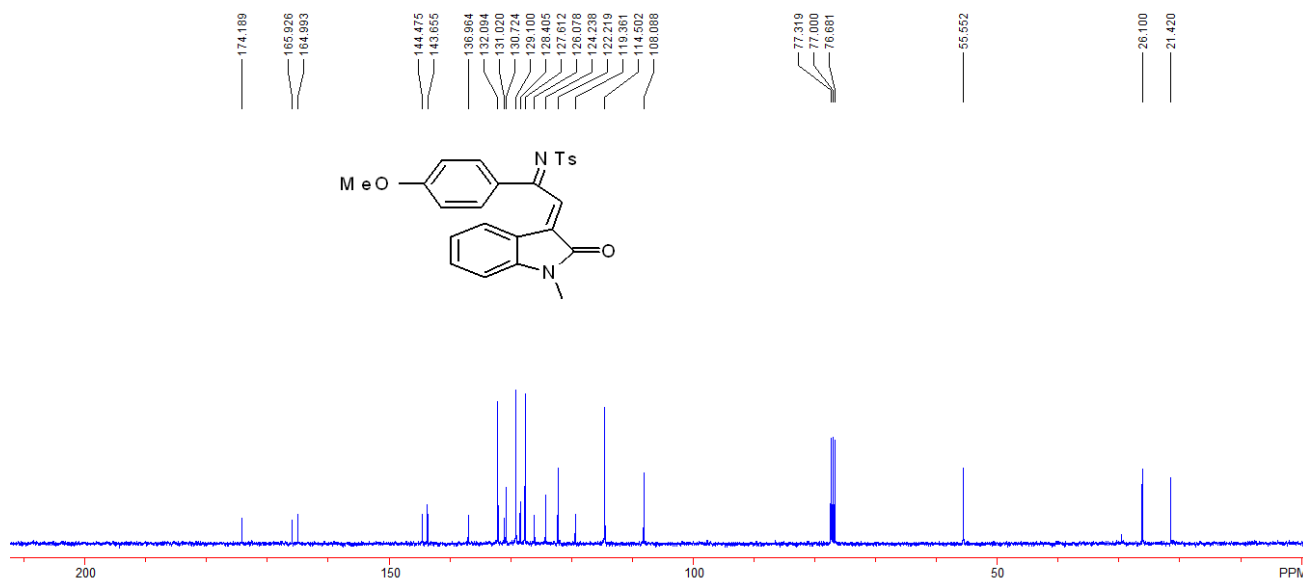
=CH), 7.81 (d, $J = 8.0$ Hz, 2H, Ar), 7.86 (d, $J = 8.4$ Hz); ^{13}C NMR (CDCl_3 , 100 MHz, TMS): δ 21.5, 26.2, 108.3, 119.2, 122.4, 124.2, 127.2, 127.8, 129.4, 130.0, 130.9, 131.2, 131.7, 132.5, 132.6, 136.4, 144.2, 144.7, 165.8, 173.8; HRMS (ESI) Calcd. For $\text{C}_{24}\text{H}_{23}\text{BrN}_3\text{O}_3\text{S}^+$ ($\text{M}+\text{NH}_4$) $^+$ requires 512.0638, Found: 512.0642; IR (CH_2Cl_2) ν 693, 745, 775, 818, 1008, 1089, 1158, 1329, 1469, 1542, 1610, 1713, 2926, 3054 cm^{-1} .



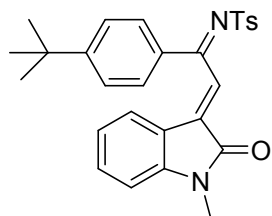
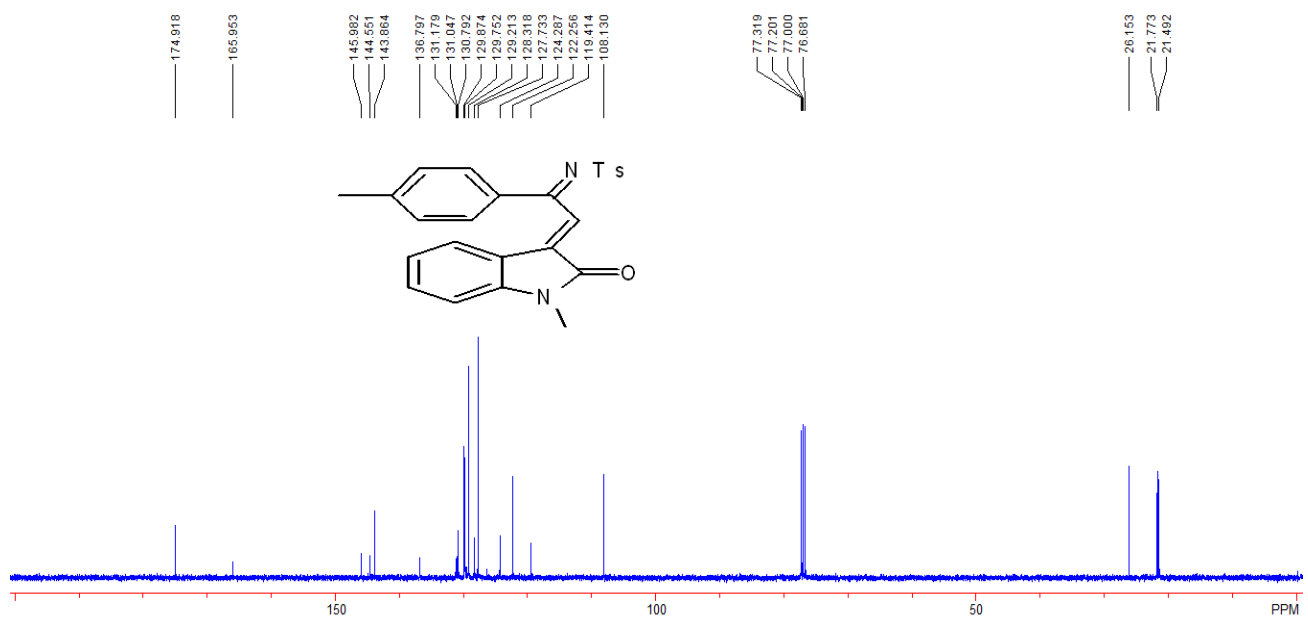
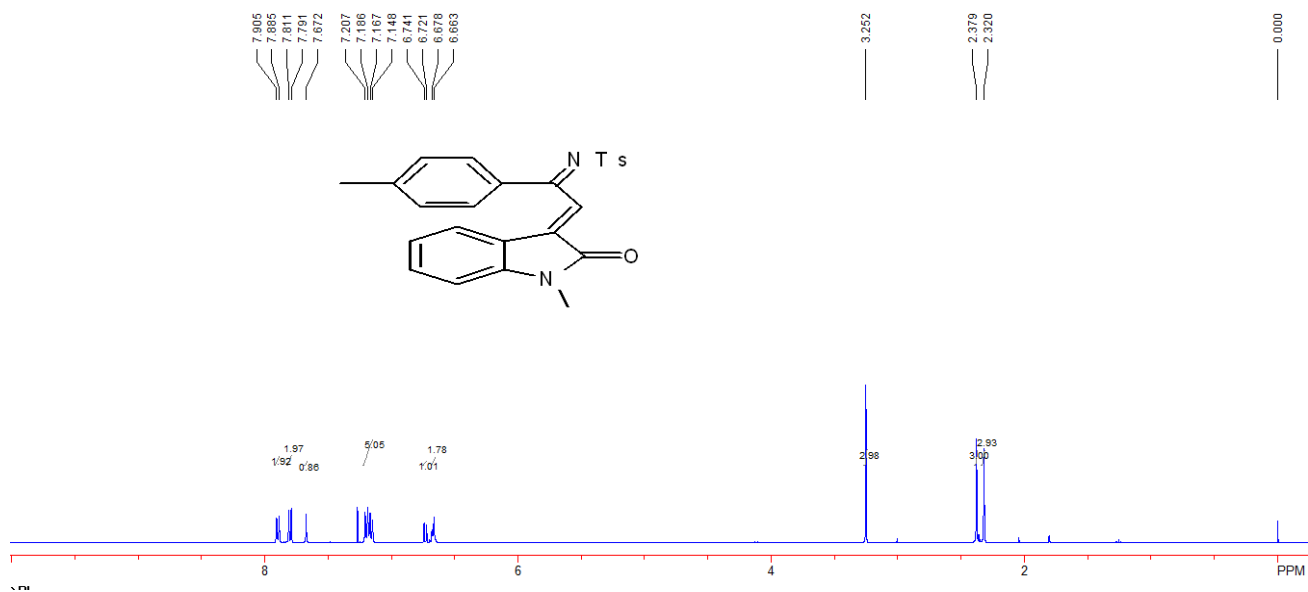


Compound 1e: A yellow solid, 410 mg, 46% yield; m.p. 188-189 °C; ^1H NMR (CDCl_3 , 400 MHz, TMS): δ 2.30 (s, 3H, CH_3), 3.24 (s, 3H, CH_3), 3.83 (s, 3H, CH_3), 6.67 (t, $J = 7.6$ Hz, 2H, Ar), 6.72 (d, $J = 7.6$ Hz, 1H, Ar), 6.87 (d, $J = 9.2$ Hz, 2H, Ar), 7.11-7.21 (m, 3H, Ar), 7.66 (s, 1H, =CH), 7.78 (d, $J = 8.2$ Hz, 2H, Ar), 7.98 (d, $J = 9.2$ Hz, 2H, Ar); ^{13}C NMR (CDCl_3 , 100 MHz, TMS): δ 21.4, 26.1, 55.5, 108.1, 114.5, 119.4, 122.2, 124.2, 126.1, 127.6, 128.4, 129.1, 130.7, 131.0, 132.1, 137.0, 143.7, 144.5, 165.0, 165.9, 174.2; HRMS (ESI) Calcd. For $\text{C}_{25}\text{H}_{23}\text{N}_2\text{O}_4\text{S}^+$ ($\text{M}+\text{H}$) $^+$ requires 447.1373, Found: 447.1379; IR (CH_2Cl_2) ν 746, 767, 823, 842, 1089, 1153, 1172, 1261, 1318, 1469, 1536, 1609, 1713, 2927, 3056 cm^{-1} .



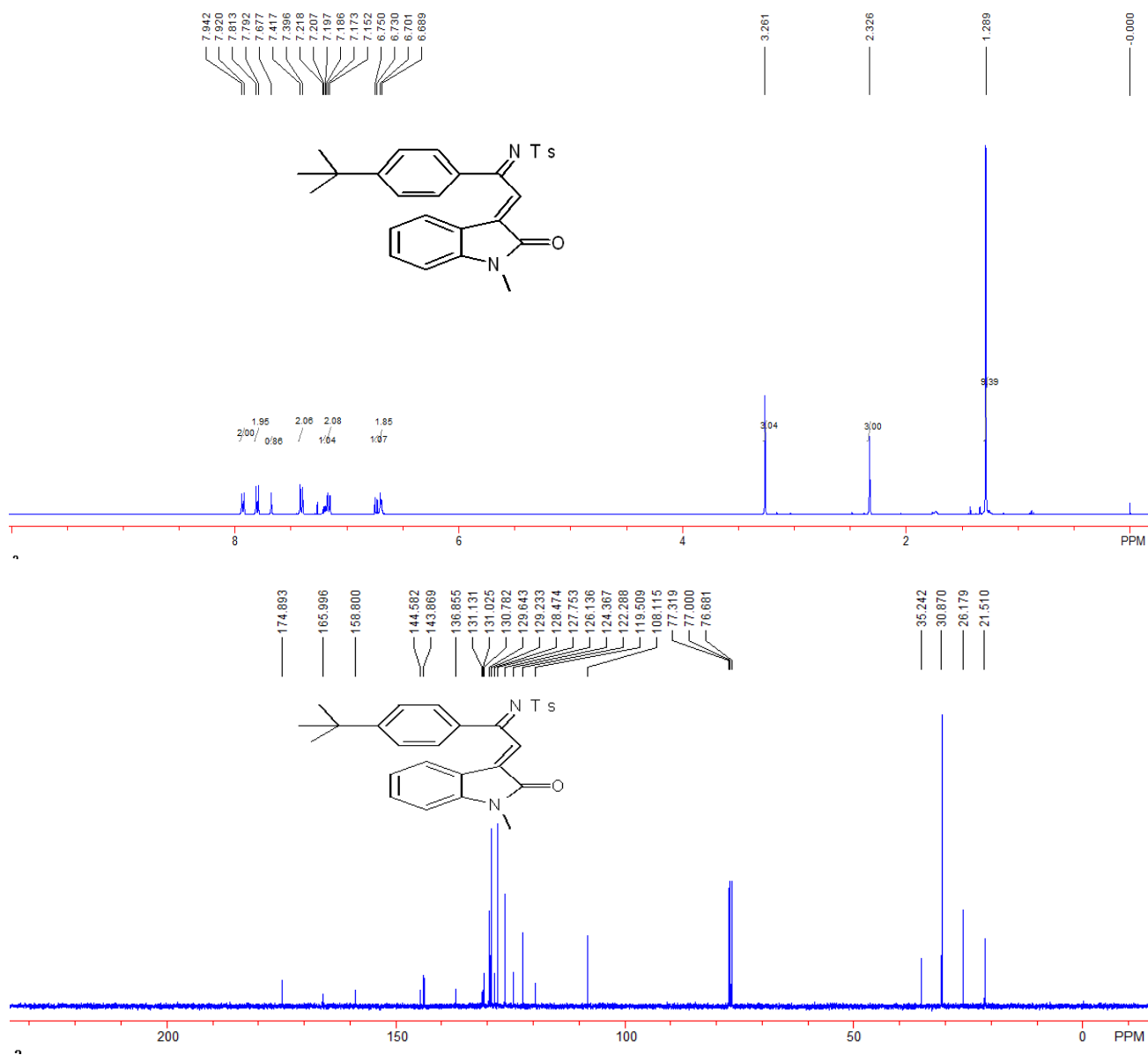


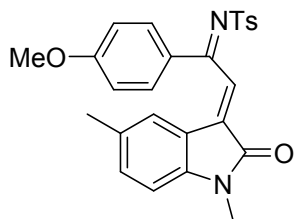
Compound 1f: A yellow solid, 361 mg, 42% yield; m.p. 178-179 °C; ^1H NMR (CDCl_3 , 400 MHz, TMS): δ 2.32 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 3.25 (s, 3H, CH_3), 6.67 (d, $J = 6.0$ Hz, 2H, Ar), 6.73 (d, $J = 8.0$ Hz, 1H, Ar), 7.14-7.21 (m, 5H, Ar), 7.67 (s, 1H, =CH), 7.80 (d, $J = 8.0$ Hz, 2H, Ar), 7.90 (d, $J = 8.0$ Hz, 2H, Ar); ^{13}C NMR (CDCl_3 , 100 MHz, TMS): δ 21.5, 21.8, 26.2, 108.1, 119.4, 122.3, 124.3, 127.7, 128.3, 129.2, 129.8, 129.9, 130.8, 131.0, 131.2, 136.8, 143.9, 144.6, 146.0, 166.0, 174.9; HRMS (ESI) Calcd. For $\text{C}_{25}\text{H}_{23}\text{N}_2\text{O}_3\text{S}^+$ ($\text{M}+\text{H}$) $^+$ requires 431.1424, Found: 431.1427; IR (CH_2Cl_2): ν 666, 746, 773, 814, 1089, 1158, 1332, 1469, 1544, 1609, 1701, 3259, 3348 cm^{-1} .



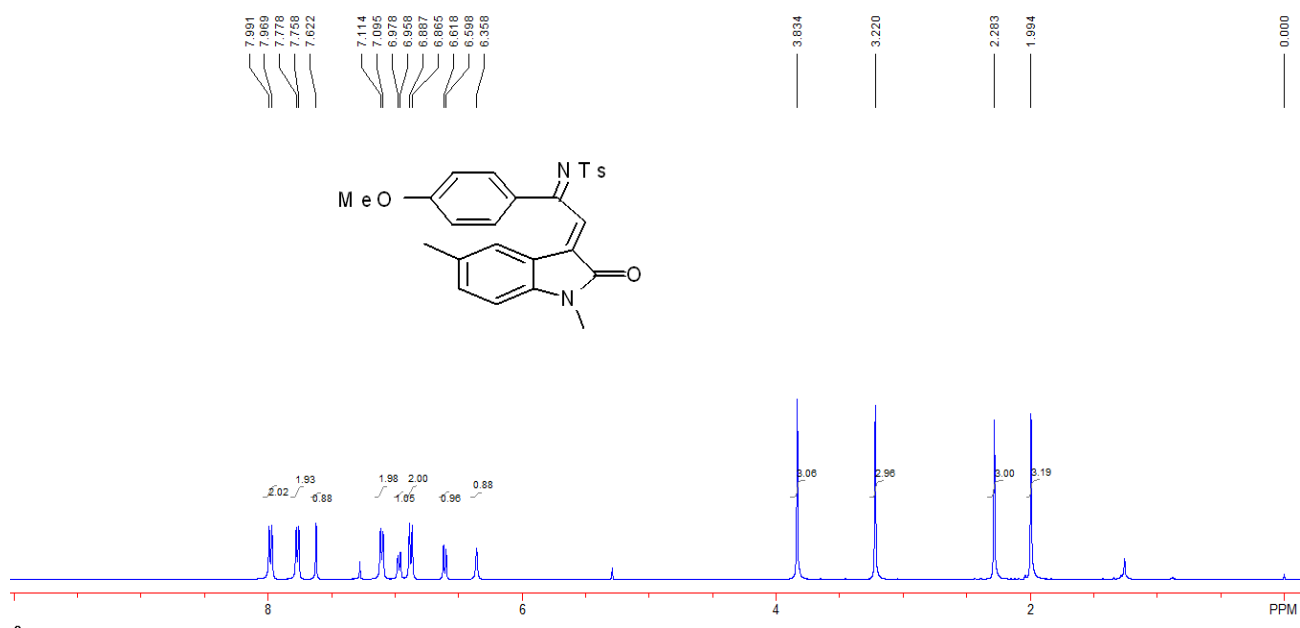
Compound 1g: A yellow solid, 349 mg, 37% yield; m.p. 180-181 °C; ¹H NMR (CDCl₃, 400 MHz, TMS): δ 1.29 (s, 9H, CH₃), 2.33 (s, 3H, CH₃), 3.26 (s, 3H, CH₃), 6.70 (d, *J* = 4.8 Hz, 2H, Ar), 6.74 (d, *J* = 8.0 Hz, 1H, Ar), 7.16 (d, *J* = 8.4 Hz, 2H, Ar), 7.20 (dd, *J*₁ = 8.4Hz, *J*₂ = 4.4Hz, 1H, Ar), 7.41

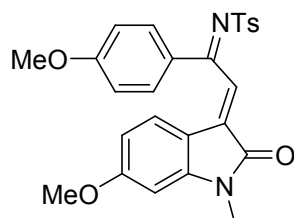
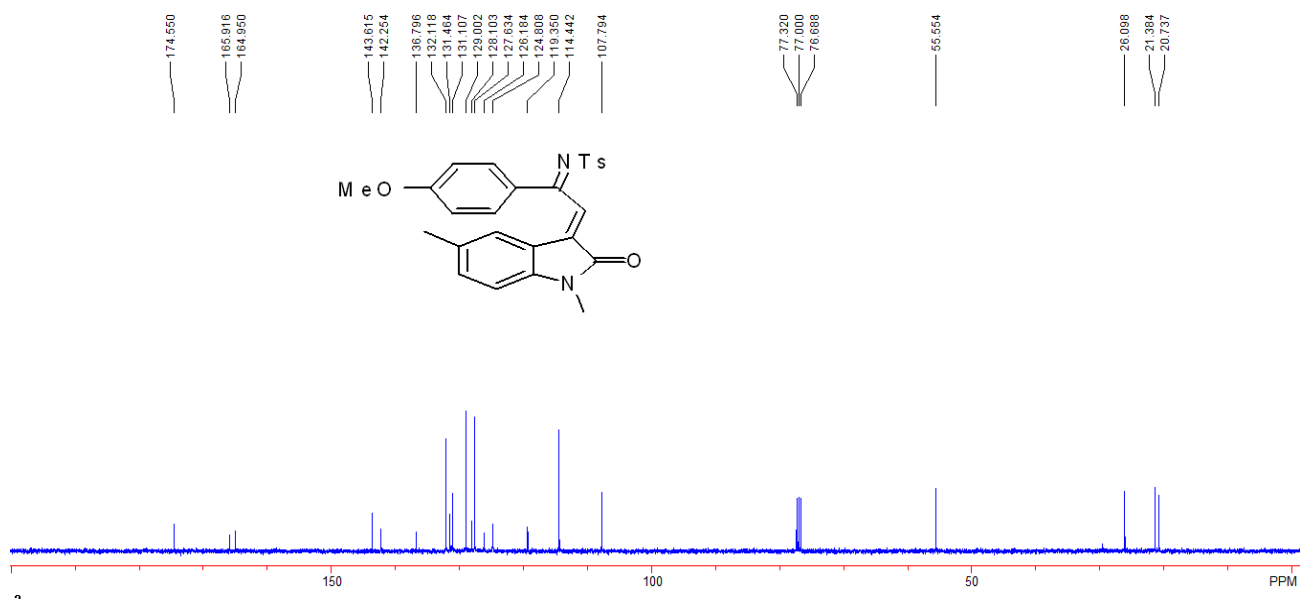
(d, $J = 8.4$ Hz, 2H, Ar), 7.68 (s, 1H, =CH), 7.80 (d, $J = 8.4$ Hz, 2H, Ar), 7.93 (d, $J = 8.8$ Hz, 2H, Ar); ^{13}C NMR (CDCl_3 , 100 MHz, TMS): δ 21.5, 26.2, 30.9, 35.2, 108.1, 119.5, 122.3, 124.4, 126.1, 127.8, 128.5, 129.2, 129.6, 130.8, 131.0, 131.1, 136.9, 143.9, 144.6, 158.8, 166.0, 174.9; HRMS (ESI) Calcd. For $\text{C}_{28}\text{H}_{29}\text{N}_2\text{O}_3\text{S}^+$ ($\text{M}+\text{H}$) $^+$ requires 473.1893, Found: 473.1891; IR (CH_2Cl_2): ν 746, 1090, 1159, 1332, 1376, 1469, 1542, 1574, 1610, 1716, 2926, 2955 cm^{-1} .



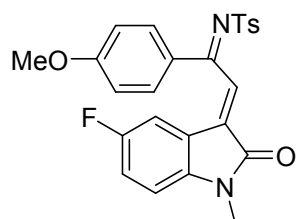
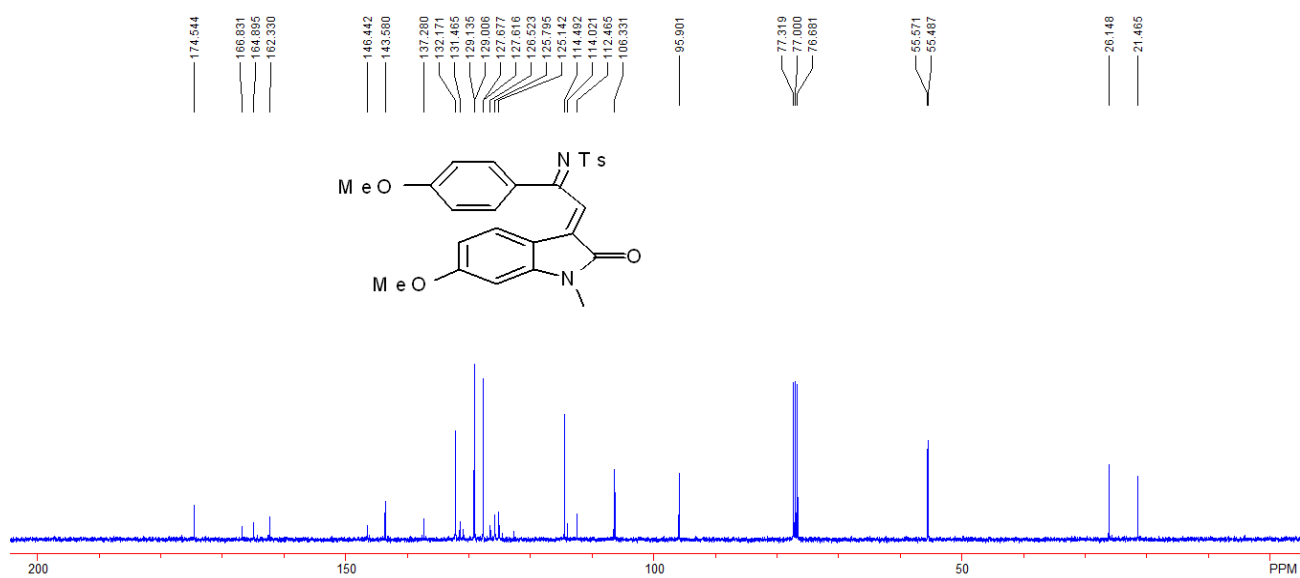
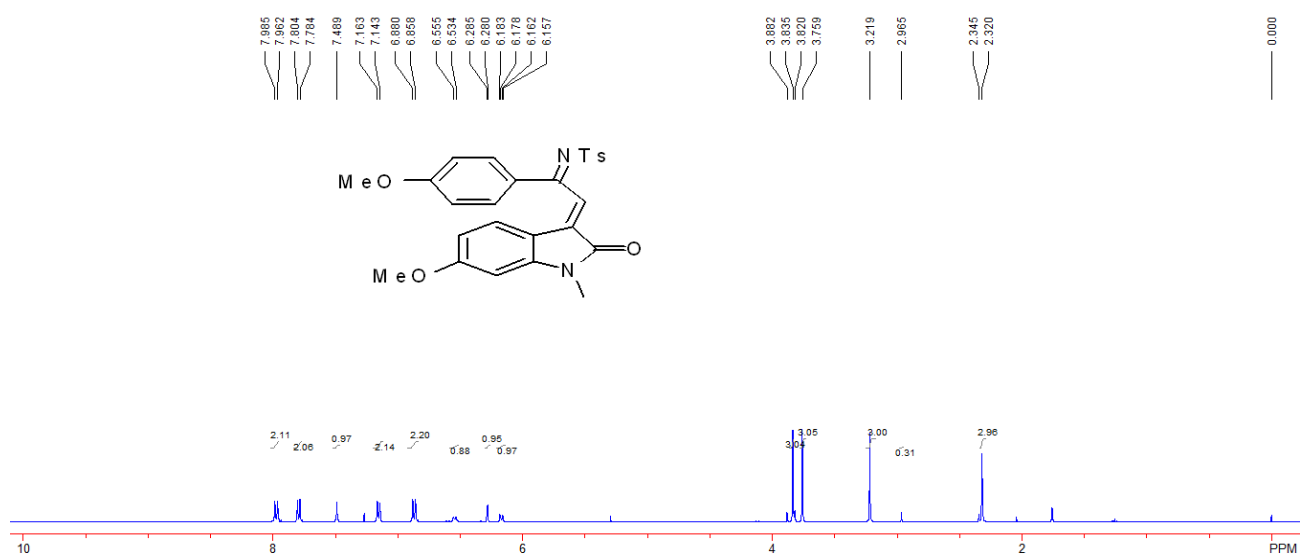


Compound 1h: A yellow solid, 377 mg, 41% yield; m.p. 192-193 °C; ^1H NMR (CDCl_3 , 400 MHz, TMS): δ 1.99 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 3.22 (s, 3H, CH_3), 3.83 (s, 3H, CH_3), 6.36 (s, 1H, Ar), 6.61 (d, $J = 8.0$ Hz, 1H, Ar), 6.88 (d, $J = 8.8$ Hz, 2H, Ar), 6.97 (d, $J = 8.0$ Hz, 1H, Ar), 7.10 (d, $J = 7.6$ Hz, 2H, Ar), 7.62 (s, 1H, =CH), 7.77 (d, $J = 8.0$ Hz, 2H, Ar), 7.98 (d, $J = 8.8$ Hz, 2H, Ar); ^{13}C NMR (CDCl_3 , 100 MHz, TMS): δ 20.7, 21.4, 26.1, 55.6, 107.8, 114.4, 119.4, 124.8, 126.2, 127.6, 128.1, 129.0, 131.1, 131.5, 132.1, 136.8, 142.2, 143.6, 165.0, 165.9, 174.6; HRMS (ESI) Calcd. For $\text{C}_{26}\text{H}_{25}\text{N}_2\text{O}_4\text{S}^+$ ($\text{M}+\text{H}$) $^+$ requires 461.1530, Found: 461.1535; IR (CH_2Cl_2): ν 668, 735, 765, 807, 1015, 1089, 1155, 1171, 1259, 1319, 1533, 1710, 2922 cm^{-1} .



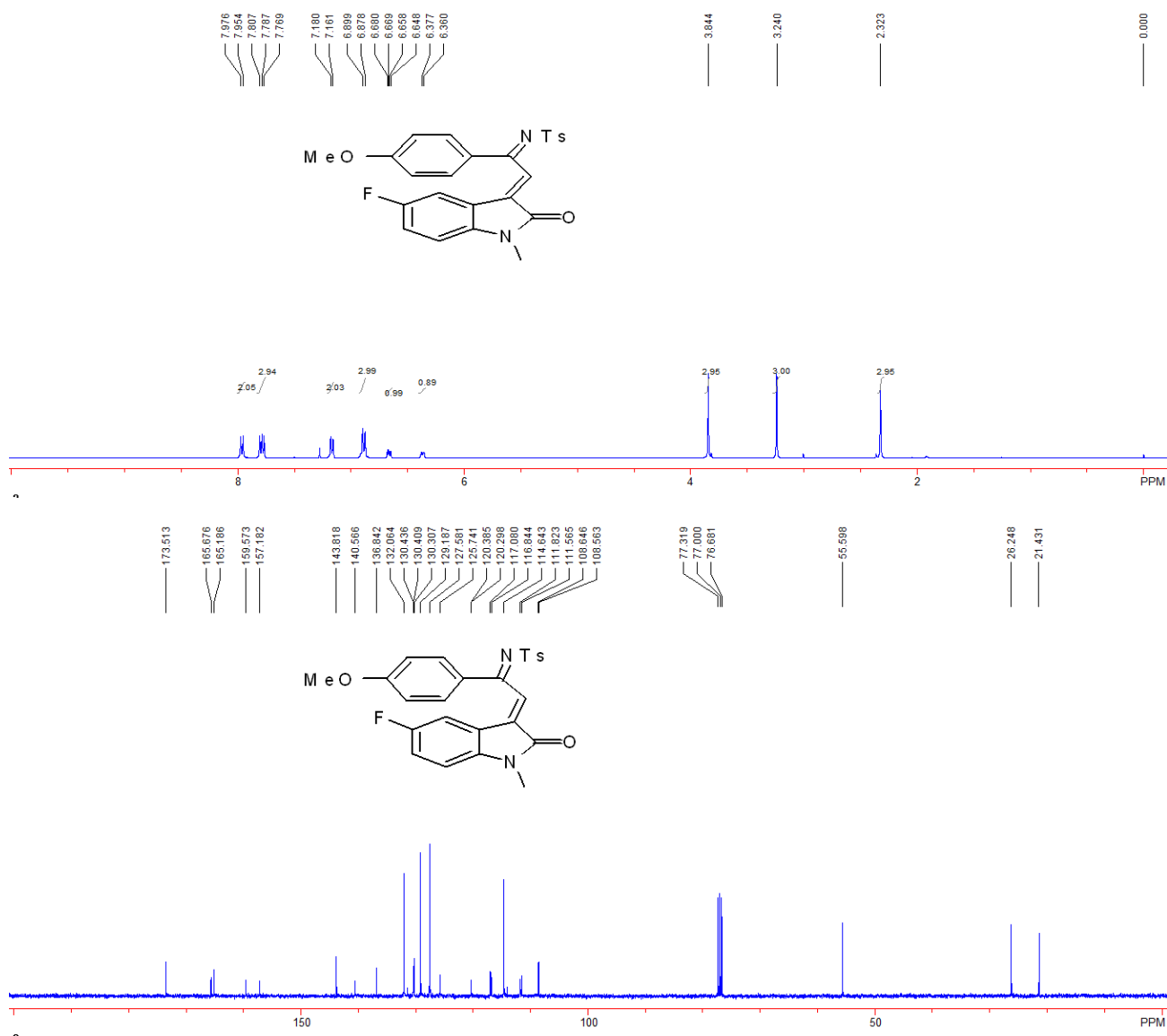


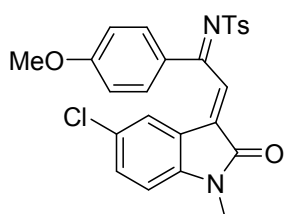
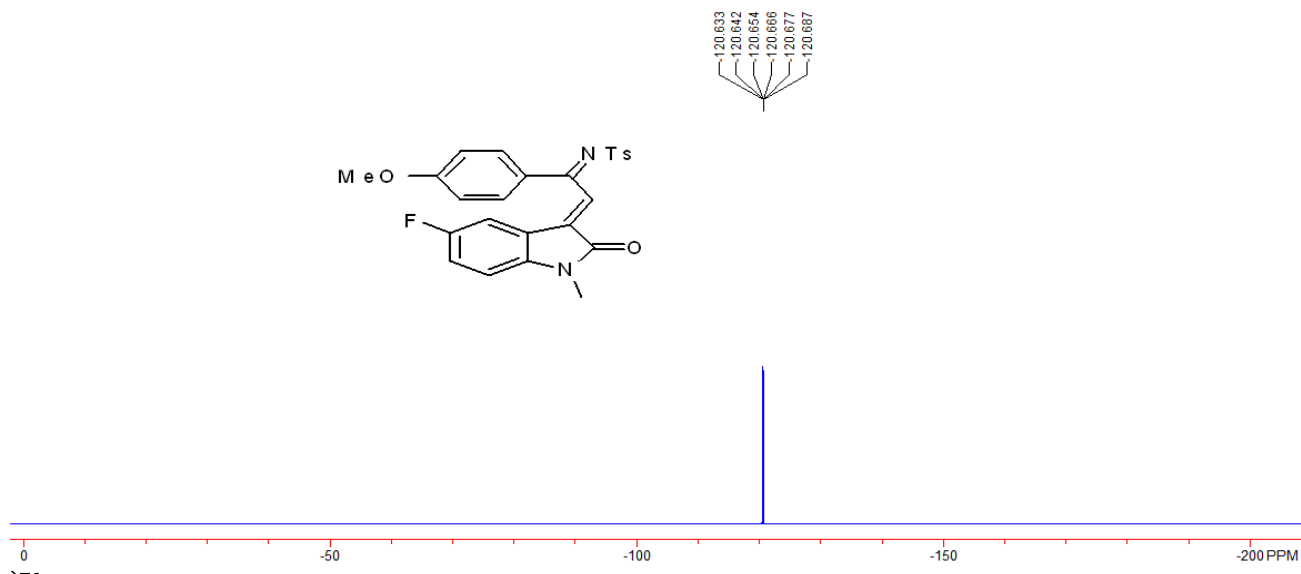
Compound 1i: A yellow solid, 428 mg, 45% yield; m.p. 201-202 °C; ^1H NMR (CDCl_3 , 400 MHz, TMS): δ 2.32 (s, 3H, CH_3), 3.22 (s, 3H, CH_3), 3.76 (s, 3H, CH_3), 3.84 (s, 3H, CH_3), 6.17 (dd, $J_1 = 8.4$ Hz, $J_2 = 2.0$ Hz, 1H, Ar), 6.28 (d, $J = 2.0$ Hz, 1H, Ar), 6.54 (d, $J = 8.4$ Hz, 1H, Ar), 6.87 (d, $J = 8.8$ Hz, 2H, Ar), 7.15 (d, $J = 8.0$ Hz, 2H, Ar), 7.49 (s, 1H, =CH), 7.79 (d, $J = 8.0$ Hz, 2H, Ar), 7.97 (d, $J = 9.2$ Hz, 2H, Ar); ^{13}C NMR (CDCl_3 , 100 MHz, TMS): δ 21.5, 26.1, 55.5, 55.6, 95.9, 106.3, 112.5, 114.0, 114.5, 125.1, 125.8, 126.5, 127.6, 127.7, 129.0, 129.1, 131.5, 132.2, 137.3, 143.6, 146.4, 162.3, 164.9, 166.8, 174.5; HRMS (ESI) Calcd. For $\text{C}_{26}\text{H}_{25}\text{N}_2\text{O}_5\text{S}^+$ ($\text{M}+\text{H}$) $^+$ requires 477.1479, Found: 477.1468; IR (CH_2Cl_2): ν 668, 760, 801, 843, 1019, 1089, 1107, 1154, 1171, 1260, 1316, 1380, 1530, 1621, 1715, 2838, 2922 cm^{-1} .



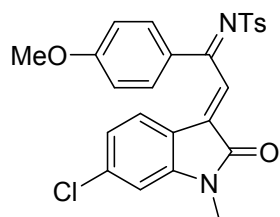
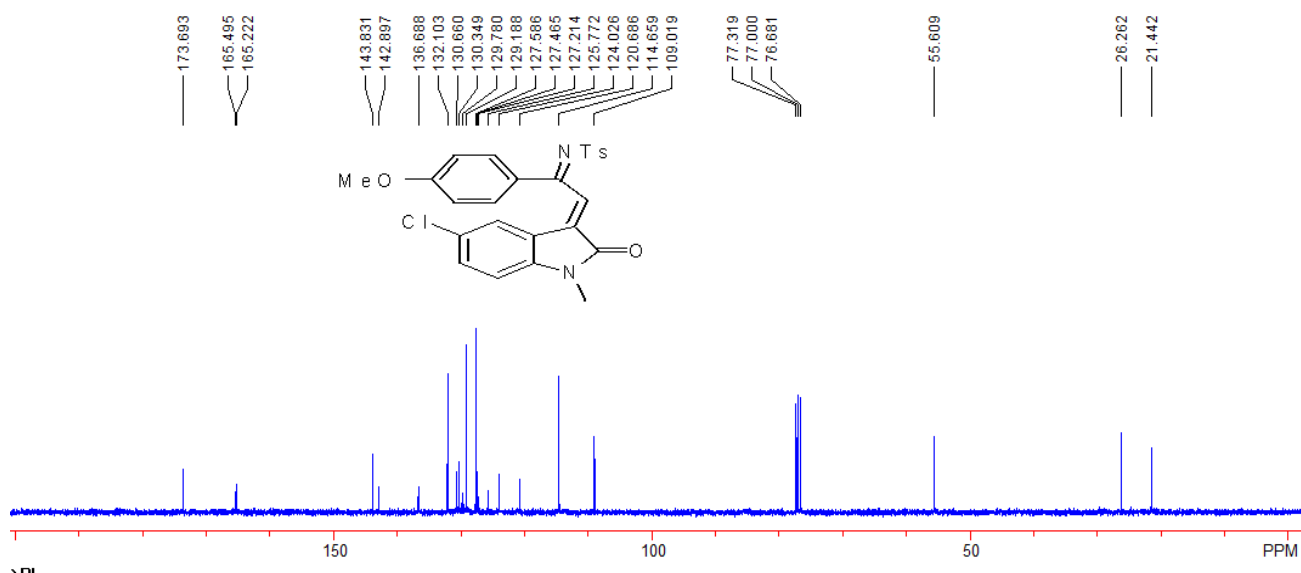
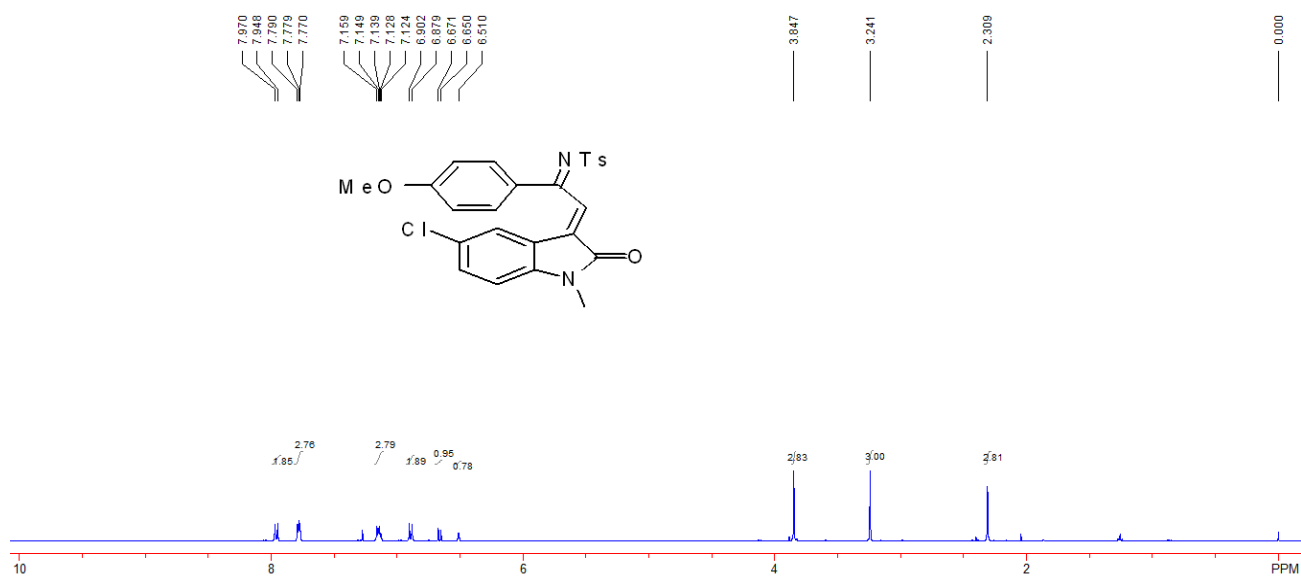
Compound 1j: A yellow solid, 389 mg, 42% yield; m.p. 183-184 °C; ¹H NMR (CDCl₃, 400 MHz, TMS): δ 2.32 (s, 3H, CH₃), 3.24 (s, 3H, CH₃), 3.84 (s, 3H, CH₃), 6.38 (d, *J* = 6.8 Hz, 1H, Ar), 6.66 (dd, *J*₁ = 8.8 Hz, *J*₂ = 4.0 Hz, 1H, Ar), 6.89 (d, *J* = 8.4 Hz, 3H, Ar), 7.17 (d, *J* = 7.6 Hz, 2H, Ar), 7.77 (s, 1H, =CH), 7.80 (d, *J* = 8.0 Hz, 2H, Ar), 7.97 (d, *J* = 8.8 Hz, 2H, Ar); ¹³C NMR (CDCl₃, 100 MHz, TMS): δ 21.4, 26.2, 55.6, 108.6 (d, *J* = 8.3 Hz), 111.7 (d, *J* = 25.8 Hz), 114.1, 114.6, 117.0 (d, *J* =

23.6 Hz), 120.3 (d, $J = 8.7$ Hz), 125.7, 127.6, 129.2, 130.3, 130.4 (d, $J = 2.7$ Hz), 132.1, 136.8, 140.6, 143.8, 158.4 (d, $J = 239.1$ Hz), 165.2, 165.7, 173.5; ^{19}F NMR (CDCl_3 , 376 MHz, CFCl_3): δ -120.69 - 120.63(m); HRMS (ESI) Calcd. For $\text{C}_{25}\text{H}_{22}\text{FN}_2\text{O}_4\text{S}^+$ ($\text{M}+\text{H}$) $^+$ requires 465.1279, Found: 465.1278. IR (CH_2Cl_2): ν 668, 737, 775, 808, 1089, 1155, 1172, 1262, 1317, 1468, 1487, 1534, 1602, 1714, 2922, 2955 cm^{-1} .



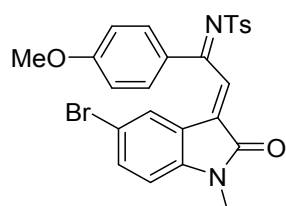
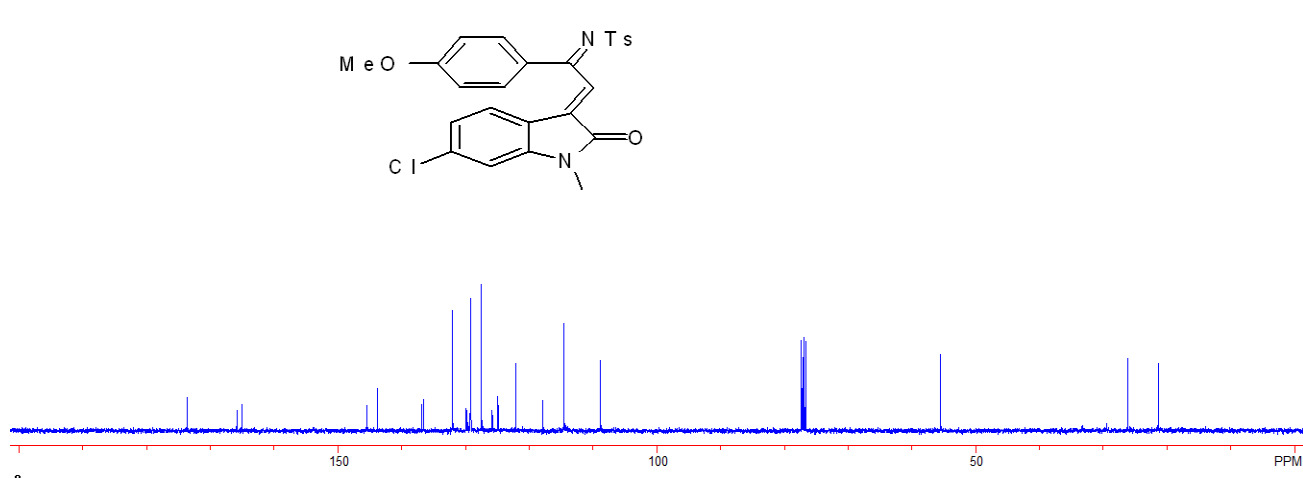
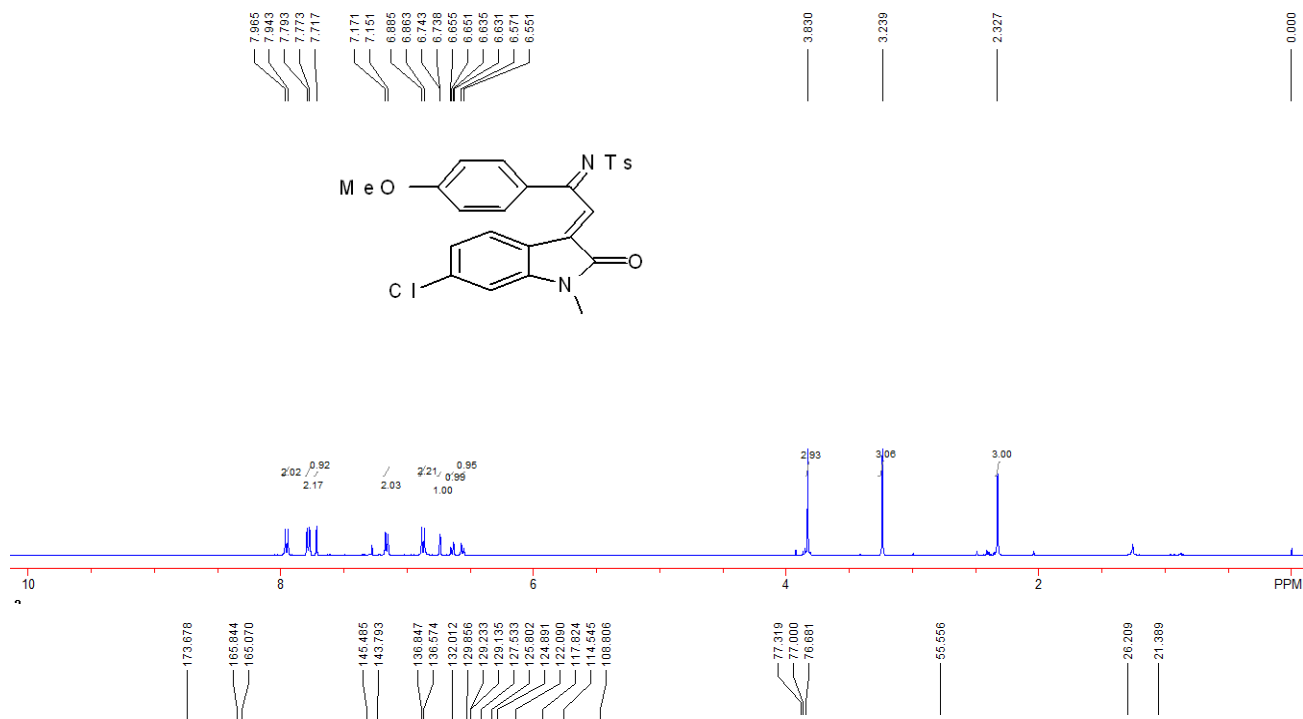


Compound 1k: A yellow solid, 451 mg, 47% yield; m.p. 194-195 °C; ^1H NMR (CDCl_3 , 400 MHz, TMS): δ 2.31 (s, 3H, CH_3), 3.24 (s, 3H, CH_3), 3.85 (s, 3H, CH_3), 6.51 (s, 1H, Ar), 6.66 (d, $J = 8.4$ Hz, 1H, Ar), 6.89 (d, $J = 9.2$ Hz, 2H, Ar), 7.12-7.16 (m, 3H, Ar), 7.77-7.79 (m, 3H, Ar, =CH), 7.96 (d, $J = 8.8$ Hz, 2H, Ar); ^{13}C NMR (CDCl_3 , 100 MHz, TMS): δ 21.4, 26.3, 55.6, 109.0, 114.7, 120.7, 124.0, 125.8, 127.2, 127.5, 127.6, 129.2, 129.8, 130.3, 130.7, 132.1, 136.7, 142.9, 143.8, 165.2, 165.5, 173.7; HRMS (ESI) Calcd. For $\text{C}_{25}\text{H}_{22}\text{ClN}_2\text{O}_4\text{S}^+$ ($\text{M}+\text{H}$) $^+$ requires 481.0983, Found: 481.0975; IR (CH_2Cl_2): ν 669, 742, 763, 1017, 1088, 1154, 1171, 1262, 1319, 1533, 1606, 1716, 2926 cm^{-1} .



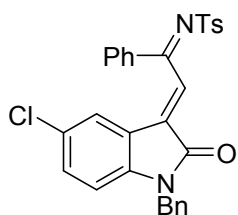
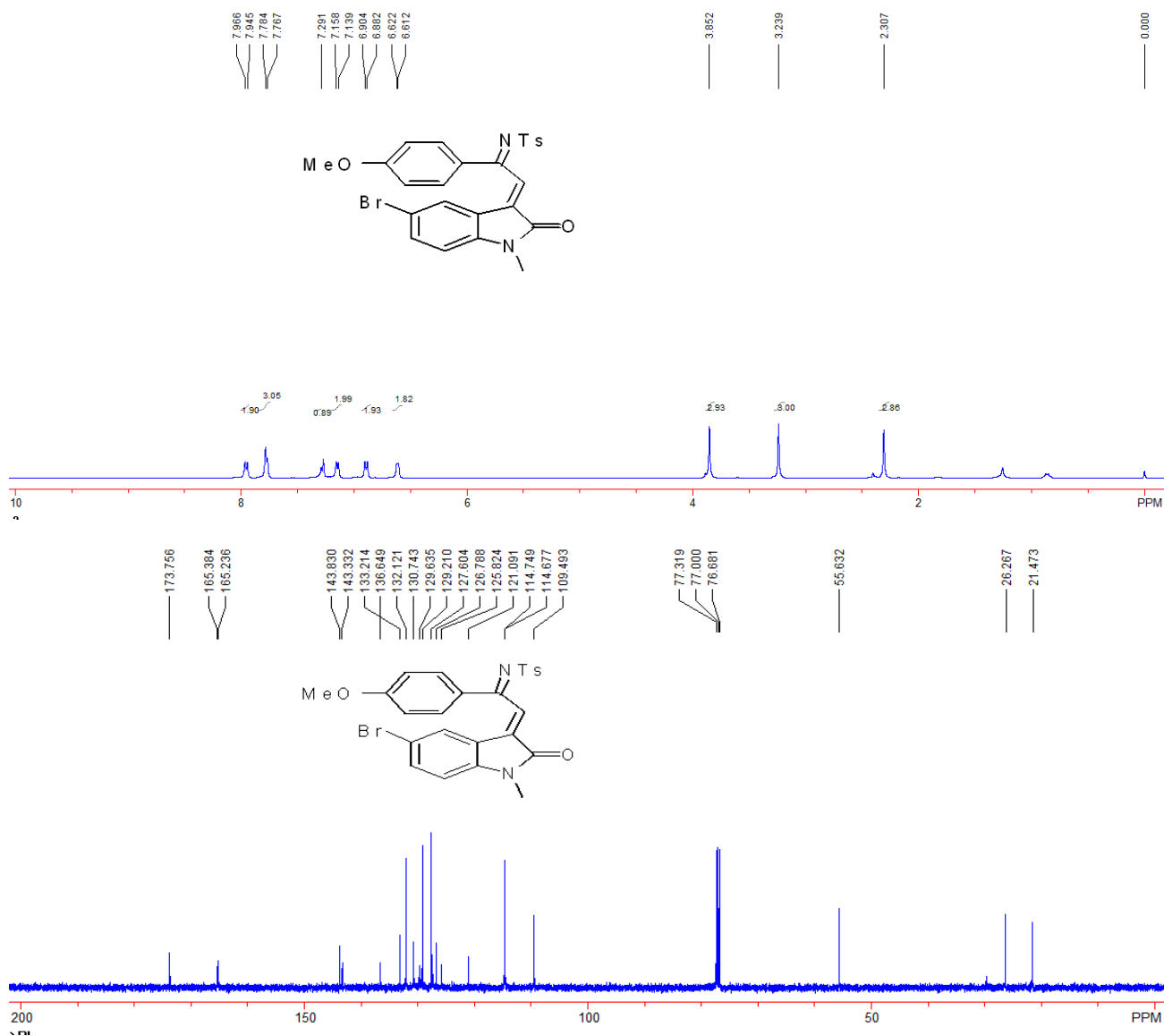
Compound 11: A yellow solid, 432 mg, 45% yield; m.p. 186-187 °C; ^1H NMR (CDCl_3 , 400 MHz, TMS): δ 2.33 (s, 3H, CH_3), 3.24 (s, 3H, CH_3), 3.83 (s, 3H, CH_3), 6.56 (d, $J = 8.0$ Hz, 1H, Ar), 6.64 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.6$ Hz, 1H, Ar), 6.74 (d, $J = 2.0$ Hz, 1H, Ar), 6.87 (d, $J = 8.8$ Hz, 2H, Ar), 7.16 (d, $J = 8.0$ Hz, 2H, Ar), 7.72 (s, 1H, =CH), 7.78 (d, $J = 8.0$ Hz, 2H, Ar), 7.95 (d, $J = 8.8$ Hz, 2H, Ar); ^{13}C NMR (CDCl_3 , 100 MHz, TMS): δ 21.4, 26.2, 55.6, 108.8, 114.5, 117.8, 122.1, 124.9, 125.8,

127.5, 129.1, 129.2, 129.9, 132.0, 136.6, 136.8, 143.8, 145.5, 165.1, 165.8, 173.7; HRMS (ESI) Calcd. For $C_{25}H_{22}ClN_2O_4S^+$ (M+H)⁺ requires 481.0983, Found: 481.0982; IR (CH₂Cl₂): ν 667, 742, 763, 1017, 1087, 1153, 1171, 1260, 1292, 1318, 1373, 1537, 1606, 1716, 2931 cm⁻¹.

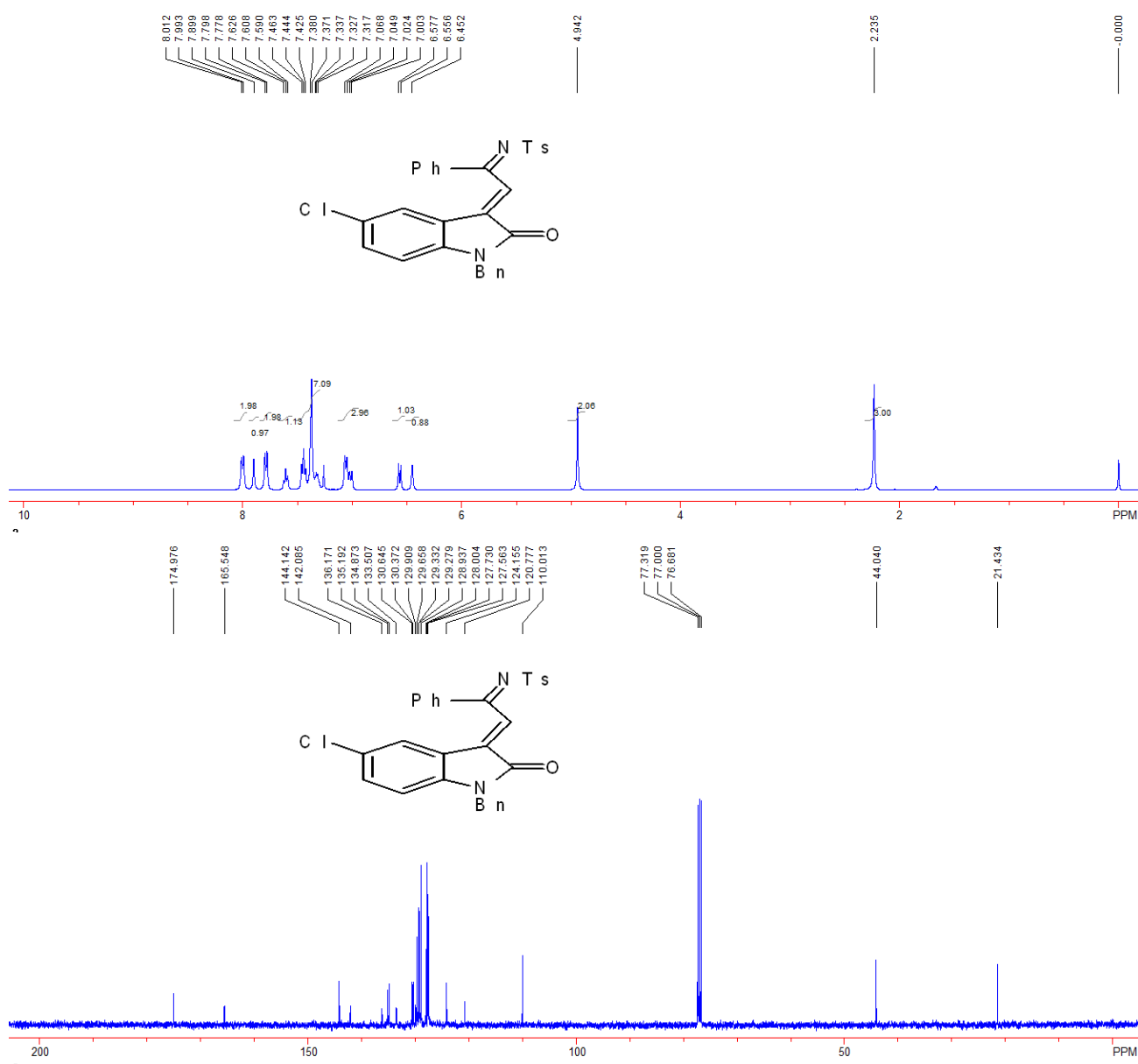


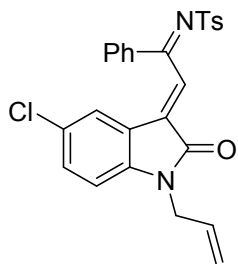
Compound 1m: A yellow solid, 377 mg, 36% yield; m.p. 206-207 °C; ¹H NMR (CDCl₃, 400 MHz, TMS): δ 2.31 (s, 3H, CH₃), 3.24 (s, 3H, CH₃), 3.85 (s, 3H, CH₃), 6.62 (d, J = 4.0 Hz, 2H, Ar), 6.89

(d, $J = 8.8$ Hz, 2H, Ar), 7.15 (d, $J = 7.6$ Hz, 2H, Ar), 7.29 (s, 1H, Ar), 7.76-7.79 (m, 3H, Ar, =CH), 7.96 (d, $J = 8.4$ Hz, 2H, Ar); ^{13}C NMR (CDCl_3 , 100 MHz, TMS): δ 21.5, 26.3, 55.6, 109.5, 114.68, 114.75, 122.1, 125.8, 126.8, 127.6, 129.2, 129.6, 130.7, 132.1, 133.2, 136.6, 143.3, 143.8, 165.2, 165.4, 173.8; HRMS (ESI) Calcd. For $\text{C}_{25}\text{H}_{22}\text{BrN}_2\text{O}_4\text{S}^+$ ($\text{M}+\text{H}$) $^+$ requires 525.0478, Found: 525.0473; IR (CH_2Cl_2): ν 669, 763, 1019, 1089, 1155, 1171, 1262, 1320, 1537, 1604, 1719, 2919 cm^{-1} .

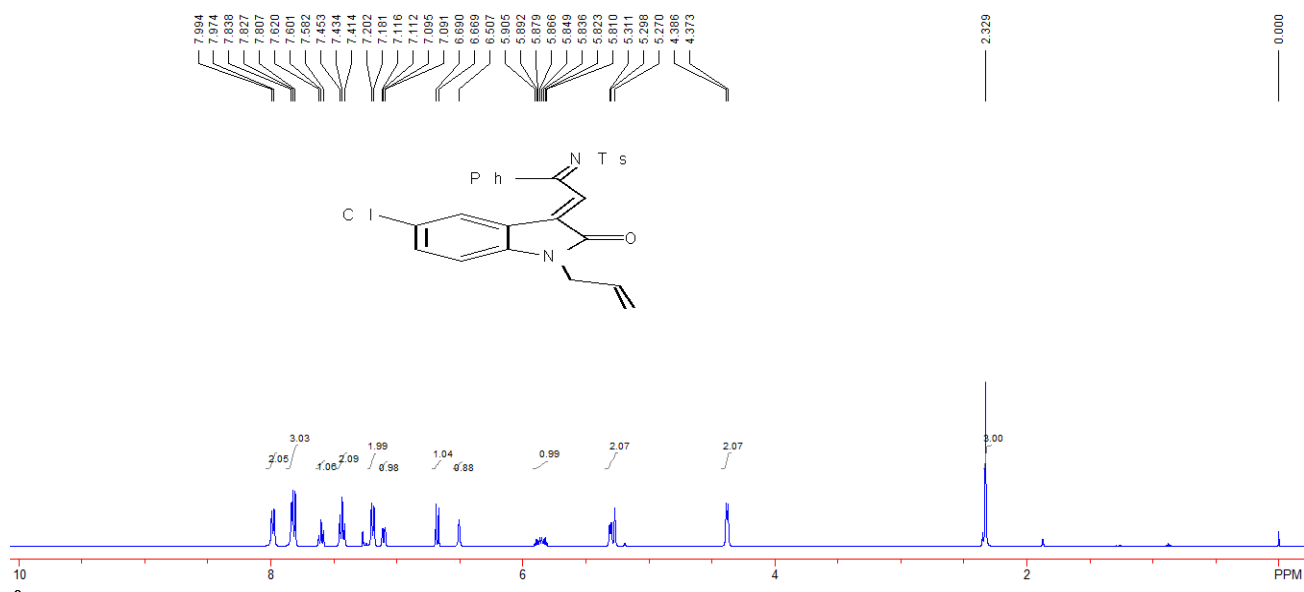


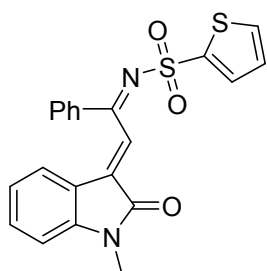
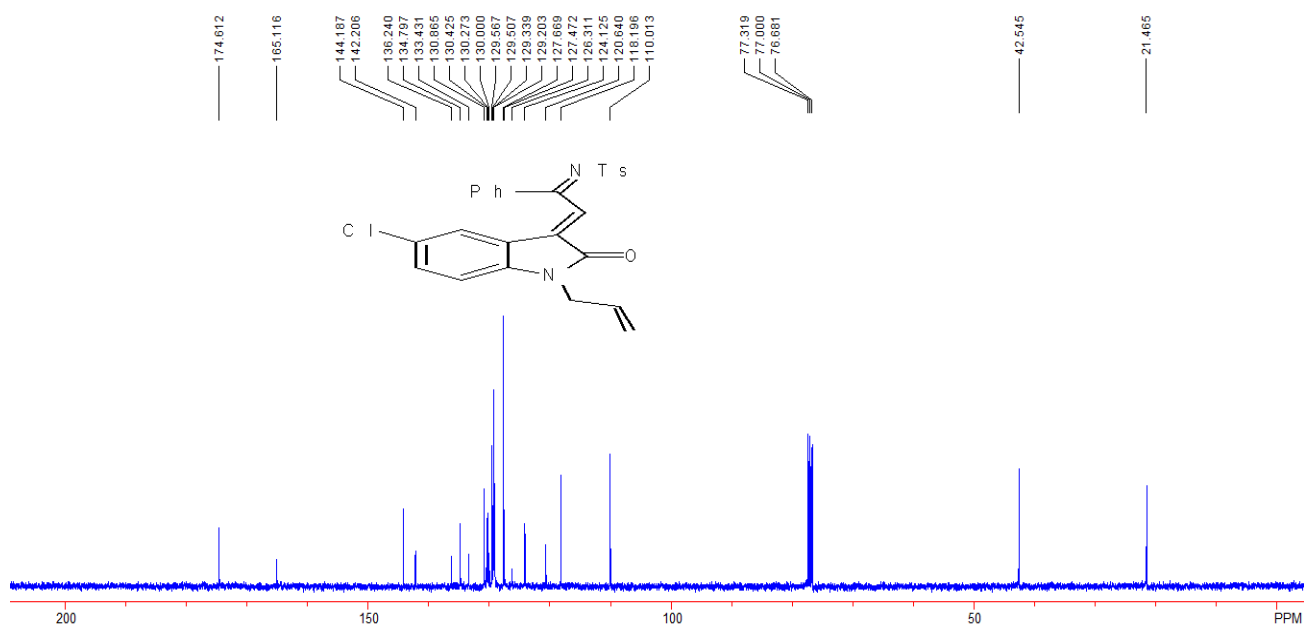
Compound 1n: A yellow solid, 368 mg, 35% yield; m.p. 177-178 °C; ¹H NMR (CDCl₃, 400 MHz, TMS): δ 2.24 (s, 3H, CH₃), 4.94 (s, 2H, CH₂), 6.45 (s, 1H, Ar), 6.57 (d, *J* = 8.4 Hz, 1H, Ar), 7.01 (d, *J* = 8.4 Hz, 1H, Ar), 7.06 (d, *J* = 7.6 Hz, 2H, Ar), 7.31-7.47 (m, 7H, Ar), 7.61 (t, *J* = 7.2 Hz, 1H, Ar), 7.79 (d, *J* = 8.0 Hz, 2H, Ar), 7.90 (s, 1H, =CH), 8.00 (d, *J* = 7.6 Hz, 2H, Ar); ¹³C NMR (CDCl₃, 100 MHz, TMS): δ 21.4, 44.0, 110.0, 120.8, 124.2, 127.6, 127.7, 128.0, 128.9, 129.28, 129.33, 129.7, 129.9, 130.4, 130.6, 133.5, 134.9, 135.2, 136.2, 142.1, 144.1, 165.5, 175.0; HRMS (ESI) Calcd. For C₃₀H₂₇ClN₃O₃S⁺ (M+NH₄)⁺ requires 544.1456, Found: 544.1453; IR (CH₂Cl₂): ν 685, 758, 815, 1089, 1158, 1327, 1475, 1548, 1716, 2920, 2954 cm⁻¹.



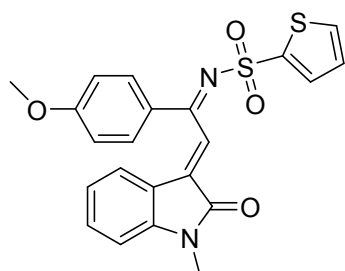
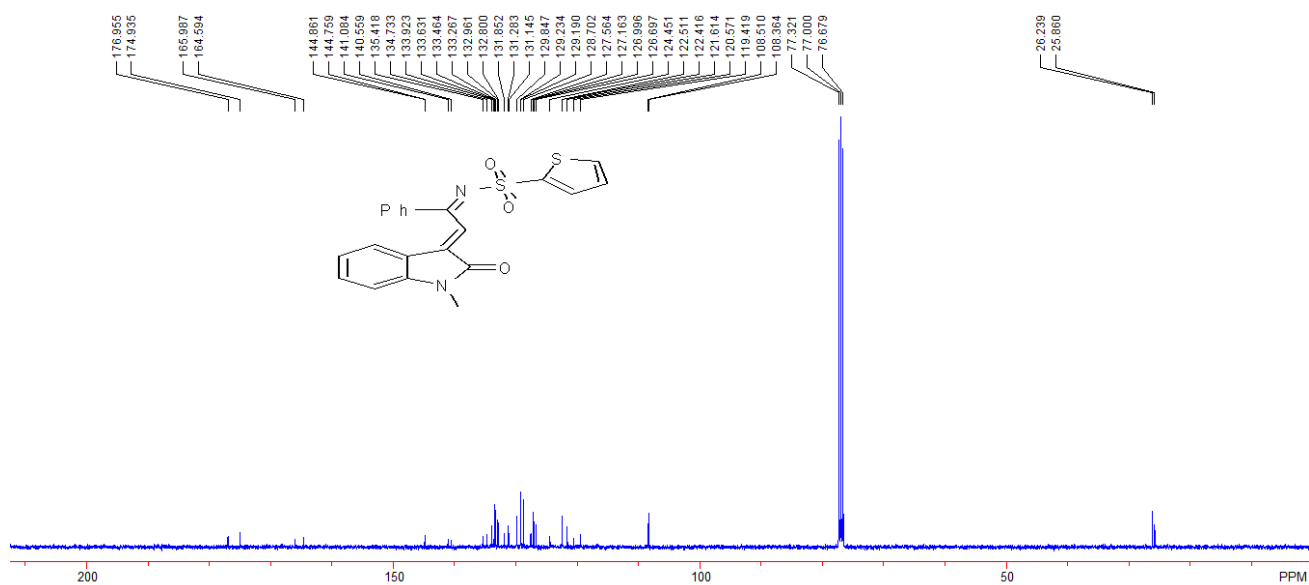
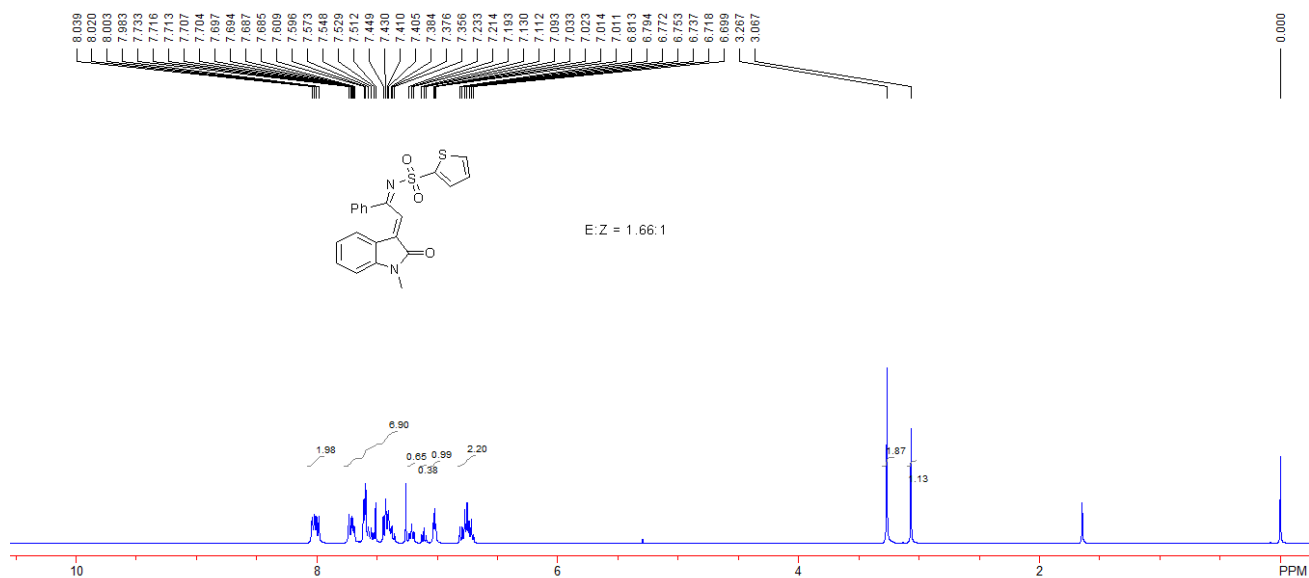


Compound 10: A yellow solid, 426 mg, 37% yield; m.p. 168-169 °C; ^1H NMR (CDCl_3 , 400 MHz, TMS): δ 2.33 (s, 3H, CH_3), 4.38 (d, $J = 5.2$ Hz, 2H, CH_2), 5.27 (s, 1H, $=\text{CH}_2$), 5.30 (d, $J = 5.2$ Hz, 1H, $=\text{CH}_2$), 5.81-5.91 (m, 1H, $=\text{CH}$), 6.51 (s, 1H, Ar), 6.68 (d, $J = 8.4$ Hz, 1H, Ar), 7.10 (dd, $J_1 = 8.4$ Hz, $J_2 = 1.6$ Hz, 1H, Ar), 7.19 (d, $J = 8.4$ Hz, 2H, Ar), 7.43 (t, $J = 7.6$ Hz, 2H, Ar), 7.60 (t, $J = 7.6$ Hz, 1H, Ar), 7.82 (d, $J = 8.0$ Hz, 2H, Ar), 7.84 (s, 1H, $=\text{CH}$), 7.98 (d, $J = 8.0$ Hz, 2H, Ar); ^{13}C NMR (CDCl_3 , 100 MHz, TMS): δ 21.5, 42.5, 110.0, 118.2, 120.6, 124.1, 126.3, 127.5, 127.7, 129.2, 129.3, 129.5, 129.6, 130.0, 130.3, 130.4, 130.9, 133.4, 134.8, 136.2, 142.2, 144.2, 165.1, 174.6; HRMS (ESI) Calcd. For $\text{C}_{26}\text{H}_{22}\text{ClN}_2\text{O}_3\text{S}^+$ ($\text{M}+\text{H}$) $^+$ requires 477.1034, Found: 477.1031; IR (CH_2Cl_2): ν 684, 749, 765, 812, 1089, 1157, 1325, 1475, 1551, 1605, 1716, 2921, 2954 cm^{-1} .



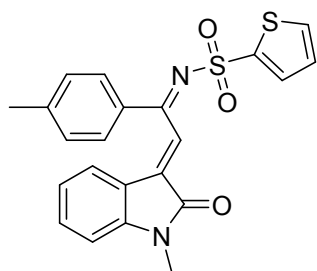
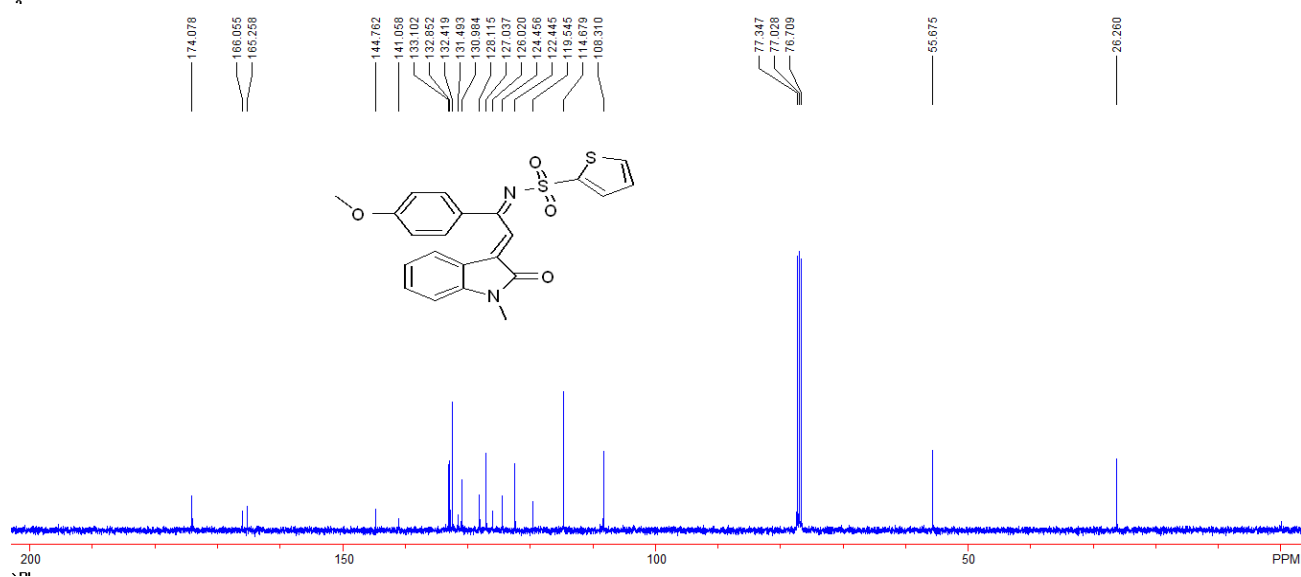
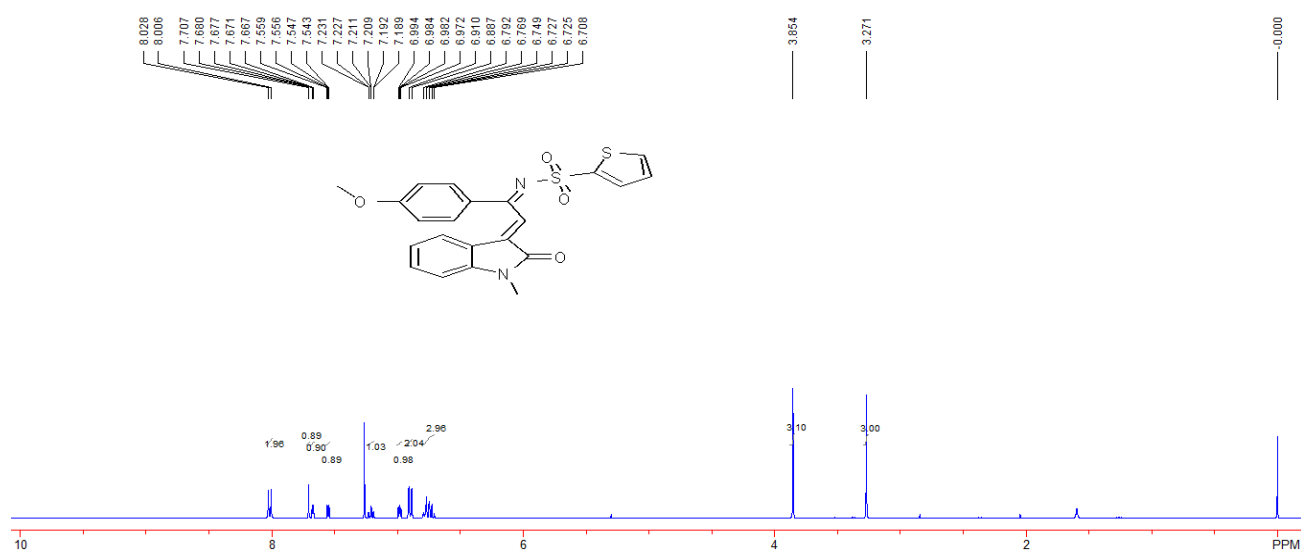


Compound 1p: A yellow solid, 350 mg, 43% yield (E:Z = 1.66:1); m.p. 161-162 °C; ¹H NMR (CDCl₃, 400 MHz, TMS): δ 3.07 (s, 1.13H, CH₃), 3.27 (s, 1.87H, CH₃), 6.70-6.82 (m, 2H, Ar), 7.02 (t, *J* = 4.4 Hz, 1H, Ar), 7.11 (t, *J* = 7.6 Hz, 0.38H, Ar), 7.21 (t, *J* = 7.6 Hz, 0.65H, Ar), 7.35-7.74 (m, 7H, Ar, =CH), 7.99 (d, *J* = 8.0 Hz, 1H, Ar), 8.03 (d, *J* = 7.6 Hz, 1H, Ar); ¹³C NMR (CDCl₃, 100 MHz, TMS): δ 25.9, 26.2, 108.4, 108.5, 119.4, 120.6, 121.6, 122.4, 122.5, 124.5, 126.7, 127.0, 127.2, 127.6, 128.7, 129.19, 129.23, 129.8, 131.1, 131.3, 131.9, 132.8, 133.0, 133.3, 133.5, 133.6, 133.9, 134.7, 135.4, 140.6, 141.1, 144.8, 144.9, 164.6, 166.0, 174.9, 177.0; HRMS (ESI) Calcd. For C₂₁H₁₇N₂O₃S₂⁺ (M+H)⁺ requires 409.0675, Found: 409.0676; IR (CH₂Cl₂): ν 683, 747, 790, 812, 856, 1019, 1095, 1152, 1260, 1332, 1376, 1489, 1556, 1611, 1712, 2927, 3053 cm⁻¹.

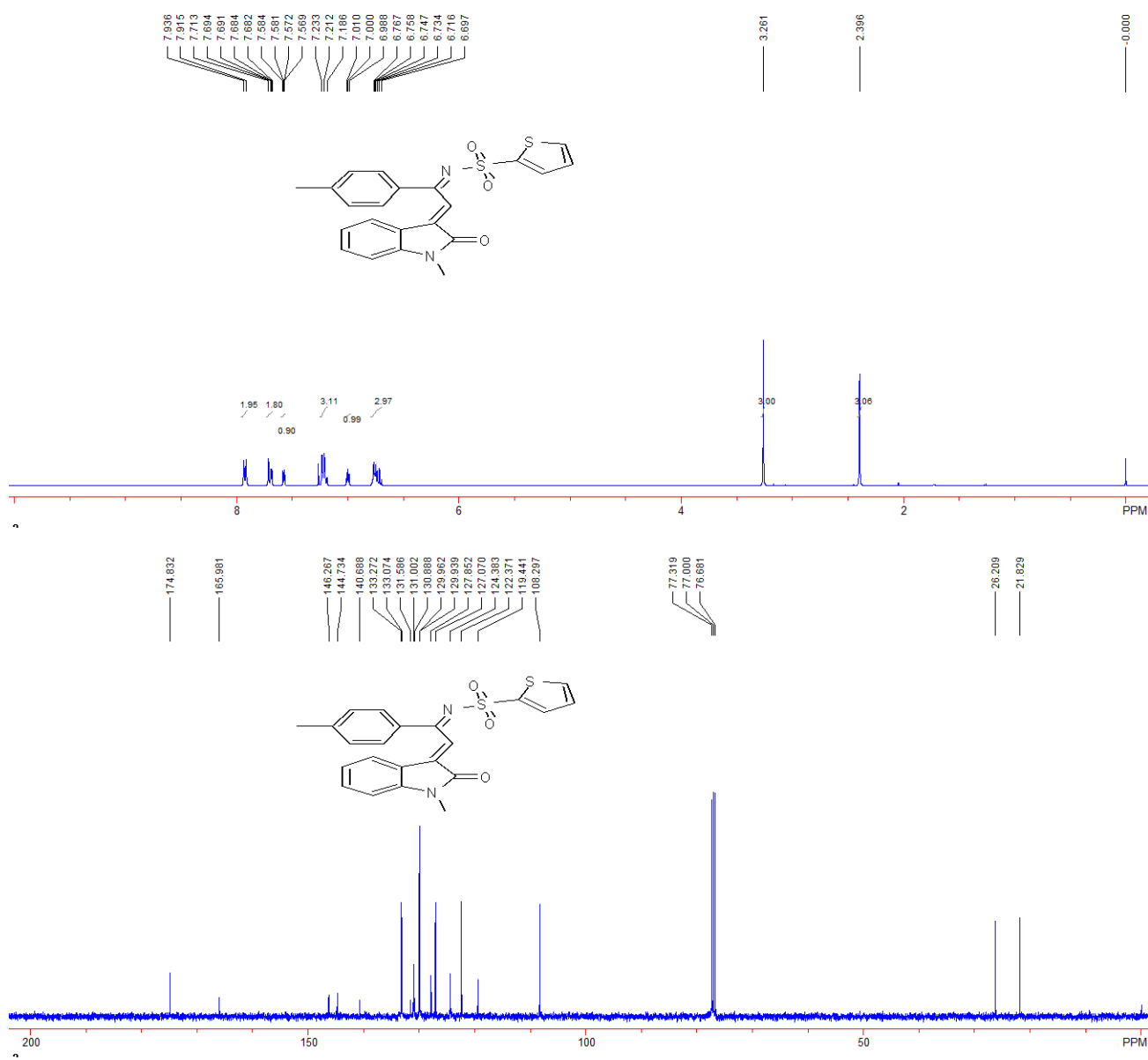


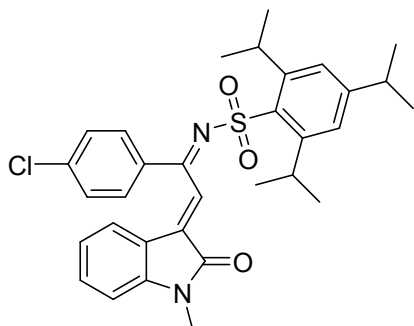
Compound 1q: A yellow solid, 341 mg, 39% yield; m.p. 196-197 °C; ¹H NMR (CDCl₃, 400 MHz, TMS): δ 3.27 (s, 3H, CH₃), 3.85 (s, 3H, CH₃), 6.70-6.80 (m, 3H, Ar), 6.90 (d, *J* = 9.2 Hz, 2H, Ar), 6.98 (dd, *J*₁ = 4.8 Hz, *J*₂ = 4.0 Hz, 1H, Ar), 7.21 (dt, *J*₁ = 8.0 Hz, *J*₂ = 1.2 Hz, 1H, Ar), 7.55 (dd, *J*₁ =

4.8 Hz, $J_2 = 1.2$ Hz, 1H, Ar), 7.67 (dd, $J_1 = 3.6$ Hz, $J_2 = 1.2$ Hz, 1H, Ar), 7.71 (s, 1H, =CH), 8.02 (d, $J = 8.8$ Hz, 2H, Ar); ^{13}C NMR (CDCl_3 , 100 MHz, TMS): δ 26.3, 55.7, 108.3, 114.7, 119.5, 122.4, 124.5, 126.0, 127.0, 128.1, 131.0, 131.5, 132.4, 132.9, 133.1, 141.1, 144.8, 165.3, 166.1, 174.1; HRMS (ESI) Calcd. For $\text{C}_{22}\text{H}_{19}\text{N}_2\text{O}_4\text{S}_2^+$ ($\text{M}+\text{H}$) $^+$ requires 439.0781, Found: 439.0780; IR (CH_2Cl_2): ν 745, 769, 784, 1017, 1149, 1173, 1262, 1327, 1376, 1468, 1538, 1609, 1714, 2921, 2954 cm^{-1} .

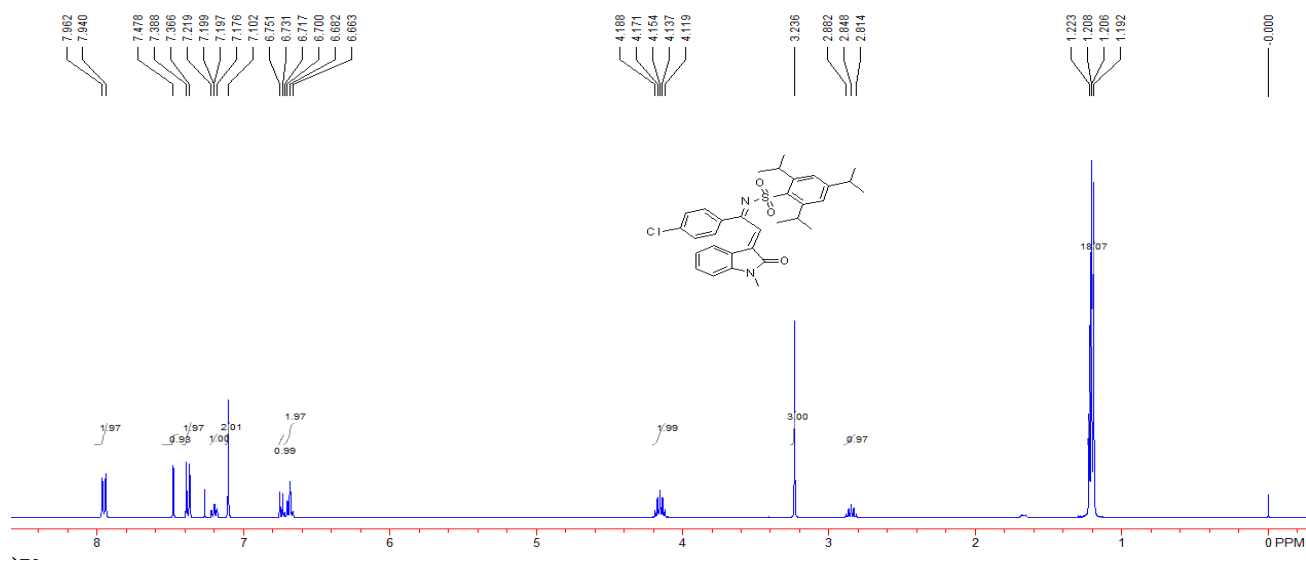


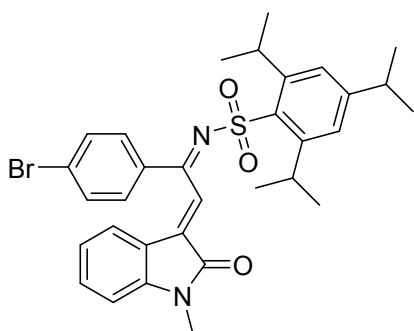
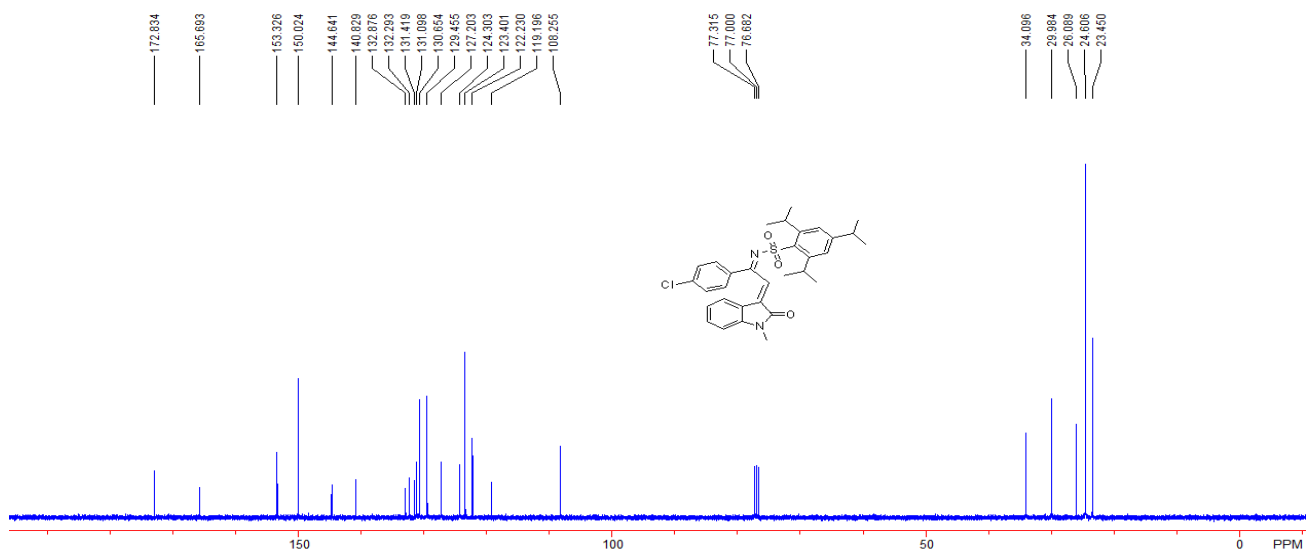
Compound 1r: A yellow solid, 303 mg, 36% yield; m.p. 173-174 °C; ¹H NMR (CDCl₃, 400 MHz, TMS): δ 2.40 (s, 3H, CH₃), 3.26 (s, 3H, CH₃), 6.69-6.77 (m, 3H, Ar), 7.00 (dd, *J*₁ = 8.8 Hz, *J*₂ = 4.0 Hz, 1H, Ar), 7.18-7.24 (m, 3H, Ar), 7.58 (dd, *J*₁ = 4.8 Hz, *J*₂ = 1.2 Hz, 1H, Ar), 7.69 (dd, *J*₁ = 4.0 Hz, *J*₂ = 1.2 Hz, 1H, Ar), 7.71 (s, 1H, =CH), 7.93 (d, *J* = 8.4 Hz, 2H, Ar); ¹³C NMR (CDCl₃, 100 MHz, TMS): δ 21.8, 26.2, 108.3, 119.4, 122.4, 124.4, 127.1, 127.9, 129.9, 130.0, 130.9, 131.0, 131.6, 133.1, 133.3, 140.7, 144.7, 146.3, 166.0, 174.8; HRMS (ESI) Calcd. For C₂₂H₁₉N₂O₃S₂⁺ (M+H)⁺ requires 423.0832, Found: 423.0826; IR (CH₂Cl₂): ν 669, 744, 775, 1016, 1152, 1332, 1376, 1469, 1540, 1610, 1715, 2923, 2954 cm⁻¹.



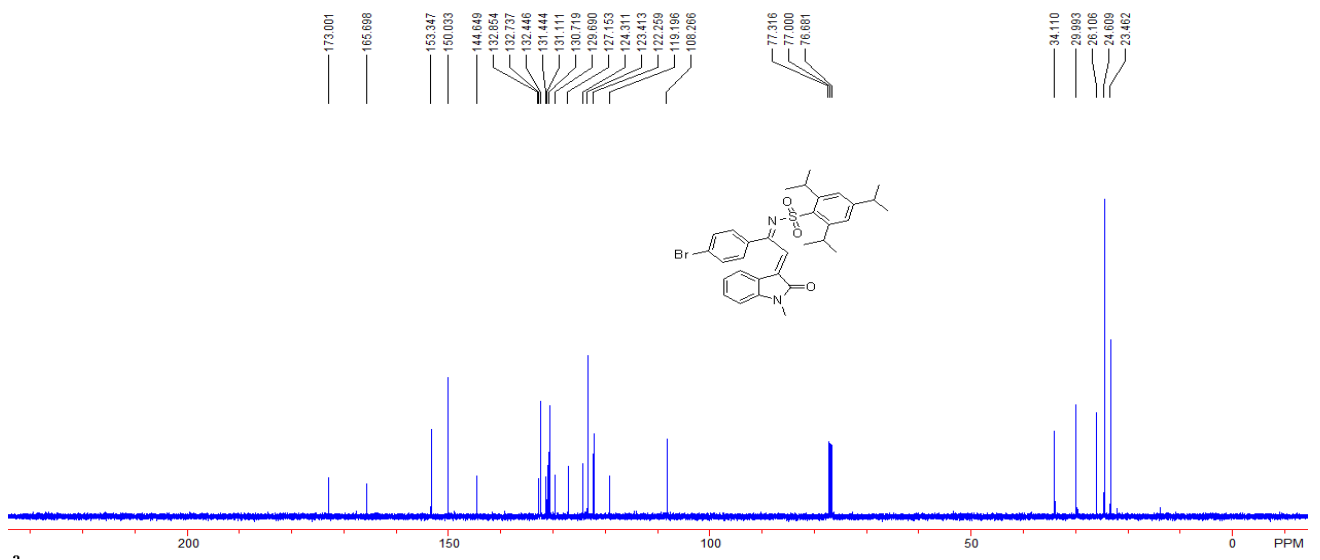
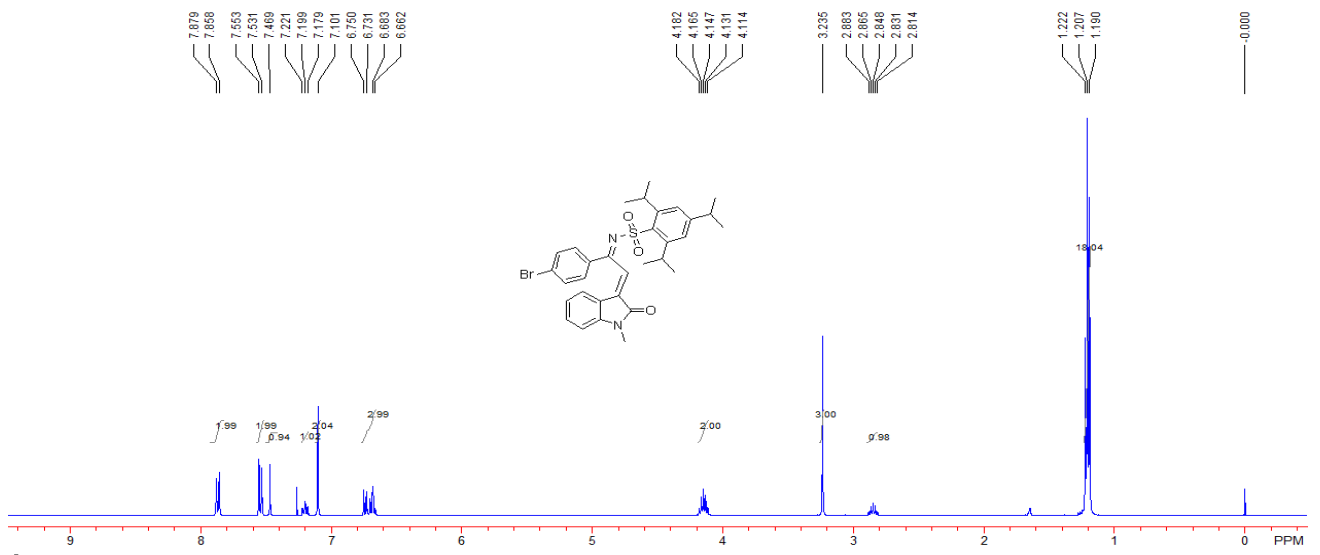


Compound 1s: A yellow solid, 505 mg, 45% yield; m. p. 230-231 °C; ^1H NMR (400 MHz, CDCl_3 , TMS): δ 1.19-1.22 (m, 18H, 6 CH_3), 2.81-2.88 (m, 1H, CH), 3.24 (s, 3H, CH_3), 4.12-4.19 (m, 2H, 2CH), 6.66-6.72 (m, 2H, Ar), 6.74 (d, 1H, $J = 8.0$ Hz, Ar), 7.10 (s, 2H, Ar), 7.18-7.22 (m, 1H, Ar), 7.38 (d, 2H, $J = 8.8$ Hz, Ar), 7.48 (s, 1H, =CH), 7.95 (d, 2H, $J = 8.8$ Hz, Ar); ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 23.5, 24.6, 26.1, 30.0, 34.1, 108.3, 119.2, 122.2, 123.4, 124.3, 127.2, 129.5, 130.7, 131.1, 131.4, 132.3, 132.9, 140.8, 144.6, 150.0, 153.3, 165.7, 172.8; HRMS (ESI) Calcd. For $\text{C}_{32}\text{H}_{36}\text{ClN}_2\text{O}_3\text{S}^+$ ($\text{M}+\text{H}$) $^+$ requires 563.2135, Found: 563.2119; IR (CH_2Cl_2): ν 667, 775, 882, 1101, 1150, 1320, 1470, 1552, 1597, 1610, 1716, 2869, 2959 cm^{-1} .



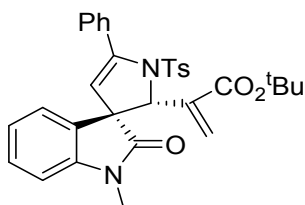


Compound 1t: A yellow solid, 412 mg, 34% yield; m. p. 231-232 °C; ¹H NMR (400 MHz, CDCl₃, TMS): δ 1.19-1.22 (m, 18H, 6CH₃), 2.81-2.88 (m, 1H, CH), 3.24 (s, 3H, CH₃), 4.11-4.18 (m, 2H, 2CH), 6.66-6.75 (m, 3H, Ar), 7.10 (s, 2H, Ar), 7.18-7.22 (m, 1H, Ar), 7.47 (s, 1H, =CH), 7.54 (d, 2H, *J* = 8.4 Hz, Ar), 7.87 (d, 2H, *J* = 8.4 Hz, Ar); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 23.5, 24.6, 26.1, 30.0, 34.1, 108.3, 119.2, 122.3, 123.4, 124.3, 127.2, 129.7, 130.7, 131.1, 131.4, 132.4, 132.7, 132.9, 144.6, 150.0, 153.3, 165.7, 173.0; HRMS (ESI) Calcd. For C₃₂H₃₆BrN₂O₃S⁺ (M+H)⁺ requires 607.1630, Found: 607.1609; IR (CH₂Cl₂): ν 669, 692, 776, 1073, 1152, 1322, 1376, 1470, 1544, 1574, 1611, 1717, 2959, 3726 cm⁻¹.

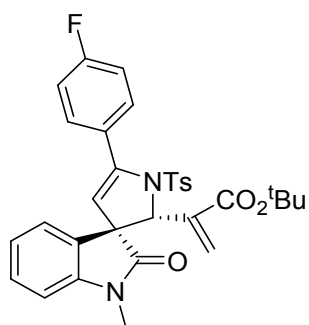
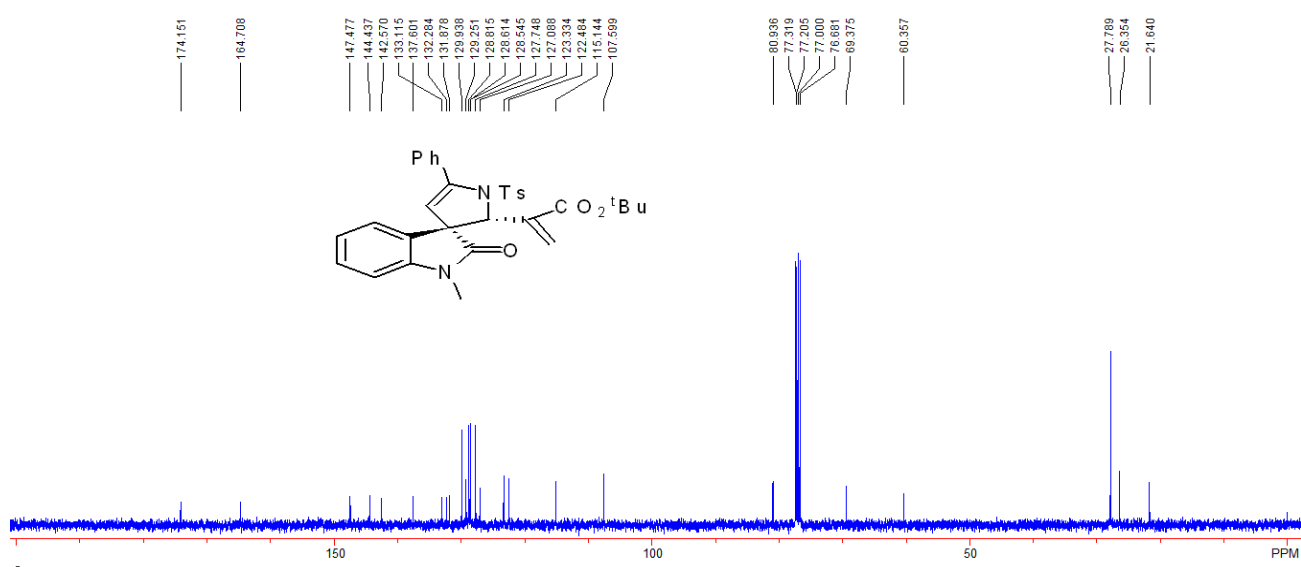
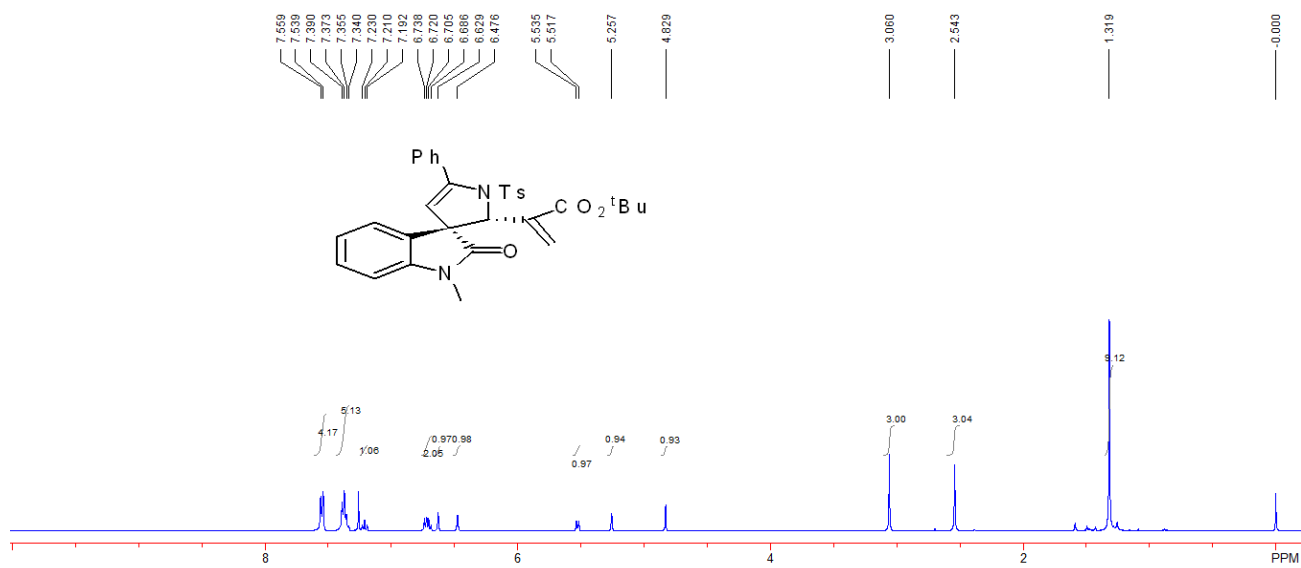


3. General Procedure for the [4+1] annulations of α,β -unsaturated ketones **1** with MBH Carbonates **2** and Spectroscopic Data of the Products.

General Procedure: Under argon atmosphere, to a solution of oxindole-derived α,β -unsaturated imines **1** (0.2 mmol) and catalyst (0.04 mmol) in toluene (1.0 mL) was added the corresponding vinyl ketones **2** (0.3 mmol), and the reaction mixture was stirred at 0 °C until the reaction completed (monitoring by TLC). Then the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography to afford the desired cyclic products **3**.

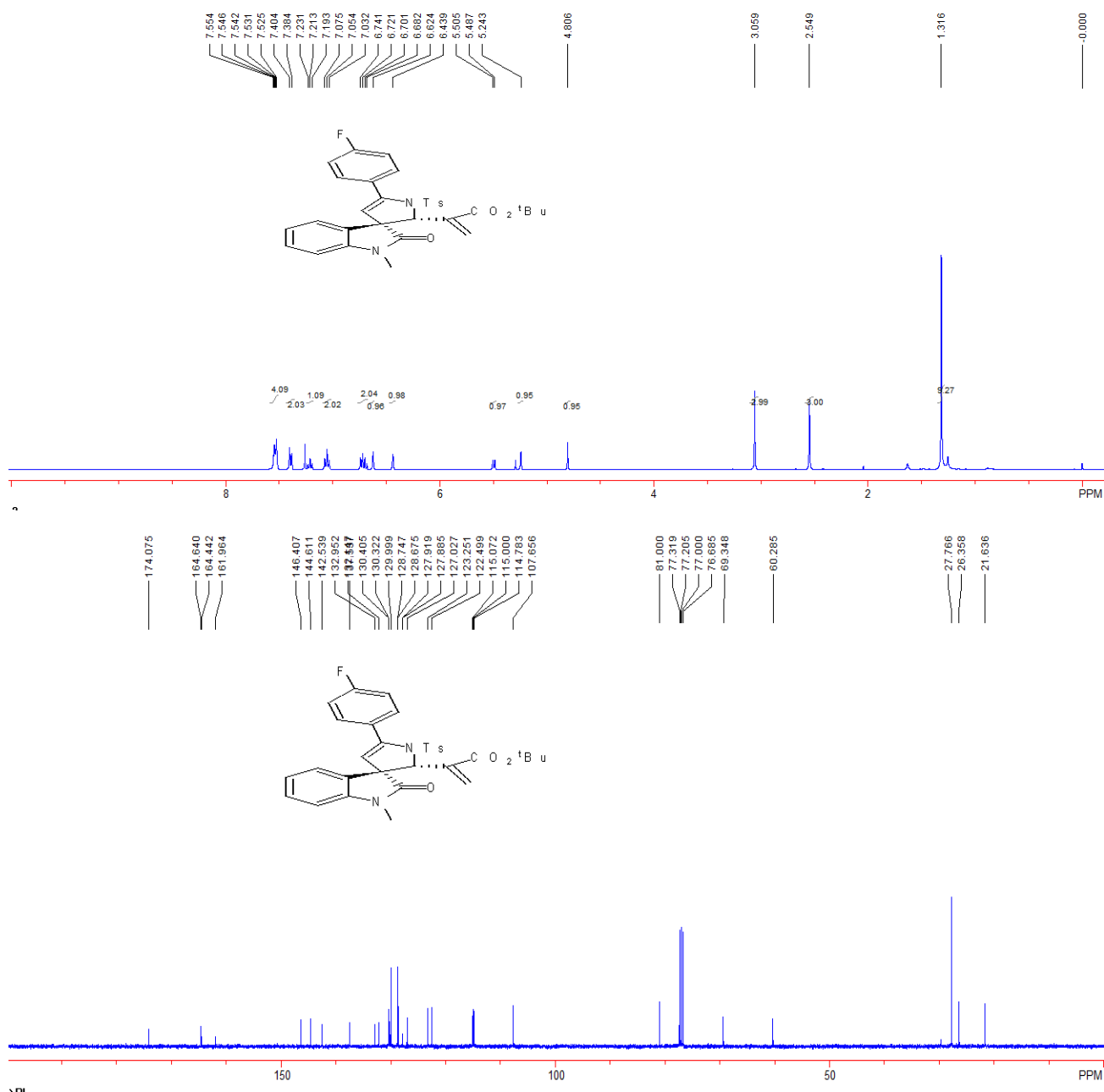


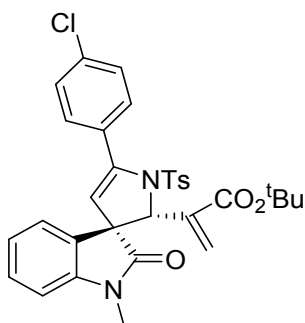
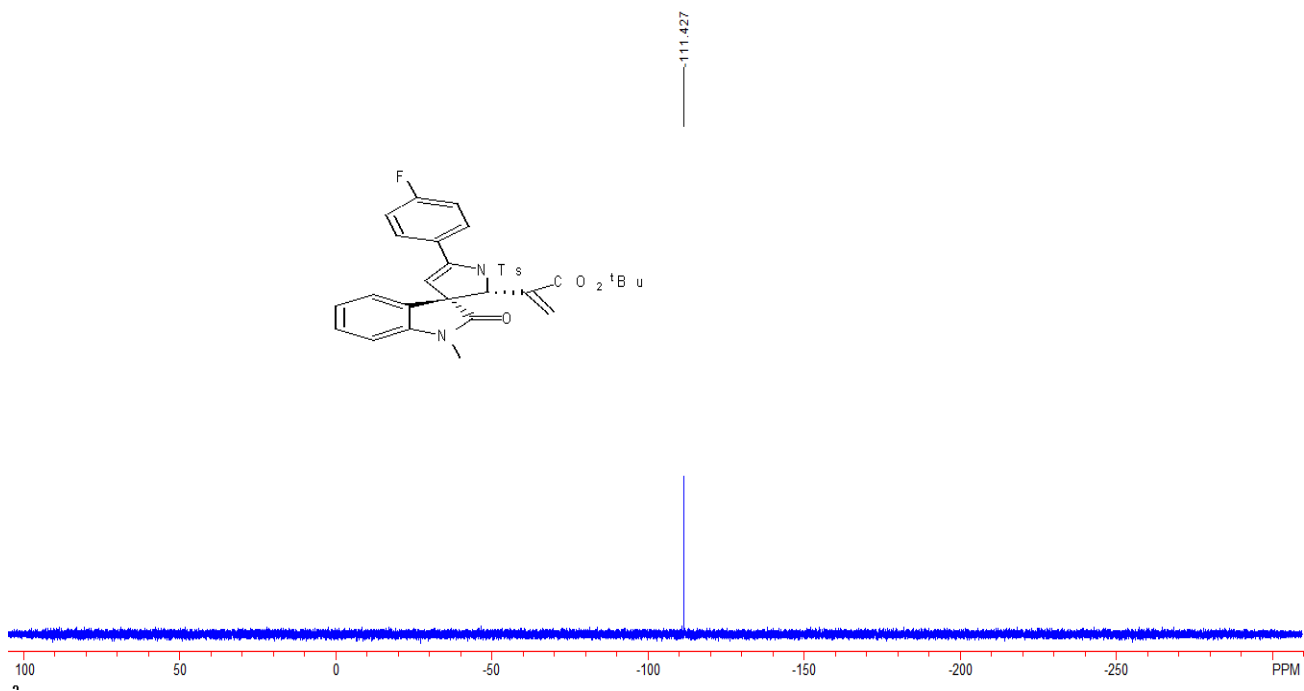
Compound 3a: A pale yellow solid, 98 mg, 88% yield; m.p. 104-105 °C; ^1H NMR (CDCl_3 , 400 MHz, TMS): δ 1.32 (s, 9H, 3 CH_3), 2.54 (s, 3H, CH_3), 3.06 (s, 3H, CH_3), 4.83 (s, 1H, CH), 5.26 (s, 1H, =CH), 5.53 (d, $J = 7.2$ Hz, 1H, Ar), 6.48 (s, 1H, = CH_2), 6.63 (s, 1H, = CH_2), 6.68-6.74 (m, 2H, Ar), 7.21 (t, $J = 8.4$ Hz, 1H, Ar), 7.34-7.39 (m, 5H, Ar), 7.53-7.56 (m, 4H, Ar); ^{13}C NMR (CDCl_3 , 100 MHz, TMS): δ 21.6, 26.4, 27.8, 60.4, 69.4, 80.9, 107.6, 115.1, 122.5, 123.3, 127.1, 127.7, 128.5, 128.6, 128.8, 129.3, 129.9, 131.9, 132.3, 133.1, 137.6, 142.6, 144.4, 147.5, 164.7, 174.2; HRMS (ESI) Calcd. For $\text{C}_{32}\text{H}_{33}\text{N}_2\text{O}_5\text{S}^+$ ($\text{M}+\text{H}$) $^+$ requires 557.2015, Found: 557.2013; IR (CH_2Cl_2): ν 669, 752, 1086, 1150, 1171, 1366, 1467, 1611, 1719, 2923, 2954 cm^{-1} .



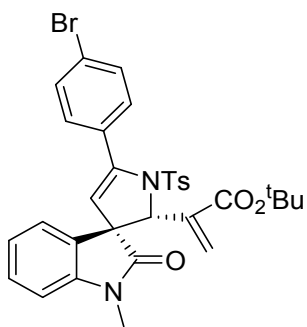
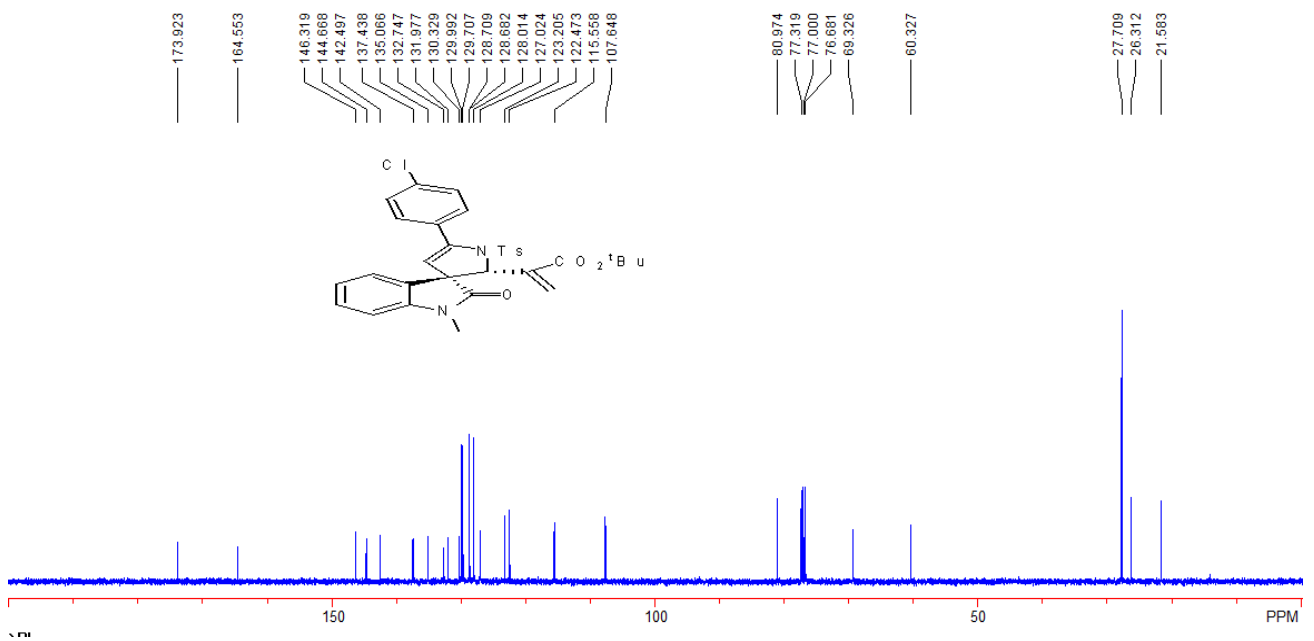
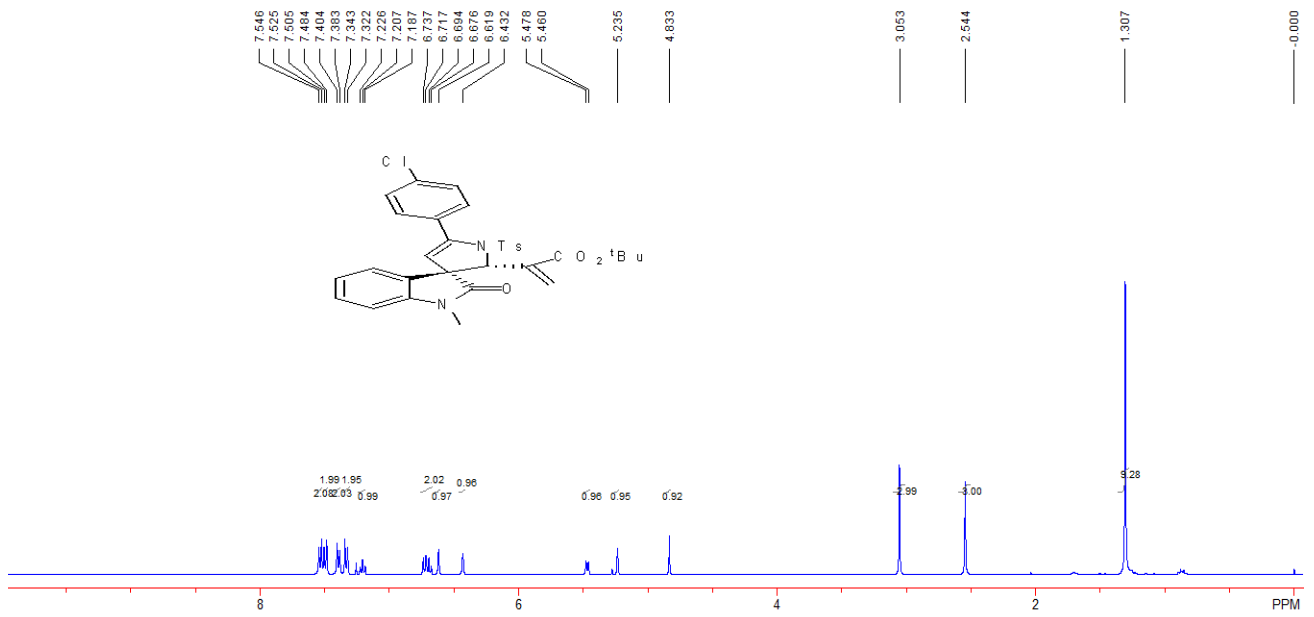
Compound 3b: A pale yellow solid, 82 mg, 72% yield; m.p. 125-126 °C; ¹H NMR (CDCl₃, 400 MHz, TMS): δ 1.32 (s, 9H, 3CH₃), 2.55 (s, 3H, CH₃), 3.06 (s, 3H, CH₃), 4.81 (s, 1H, CH), 5.24 (s, 1H, =CH), 5.50 (d, *J* = 7.2 Hz, 1H, Ar), 6.44 (s, 1H, =CH₂), 6.62 (s, 1H, =CH₂), 6.68-6.74 (m, 2H,

Ar), 7.05 (t, $J = 8.4$ Hz, 2H, Ar), 7.21 (t, $J = 8.0$ Hz, 1H, Ar), 7.39 (d, $J = 8.0$ Hz, 2H, Ar), 7.52-7.56 (m, 4H, Ar); ^{13}C NMR (CDCl_3 , 100 MHz, TMS): δ 21.6, 26.4, 27.8, 60.3, 69.3, 81.0, 107.7, 114.9 (d, $J = 21.7$ Hz), 115.1, 122.5, 123.3, 127.0, 127.9 (d, $J = 3.4$ Hz), 128.68, 128.75, 130.0, 130.3 (d, $J = 8.3$ Hz), 132.1, 133.0, 137.5, 142.5, 144.6, 146.4, 163.3 (d, $J = 247.8$ Hz), 164.4, 174.1; ^{19}F NMR (CDCl_3 , 376 MHz, CFCl_3): δ -111.43; HRMS (ESI) Calcd. For $\text{C}_{32}\text{H}_{32}\text{FN}_2\text{O}_5\text{S}^+$ ($\text{M}+\text{H}$) $^+$ requires 575.2017, Found: 575.2024; IR (CH_2Cl_2): ν 680, 716, 750, 815, 843, 1087, 1150, 1171, 1365, 1492, 1507, 1611, 1718, 2927, 2974 cm^{-1} .

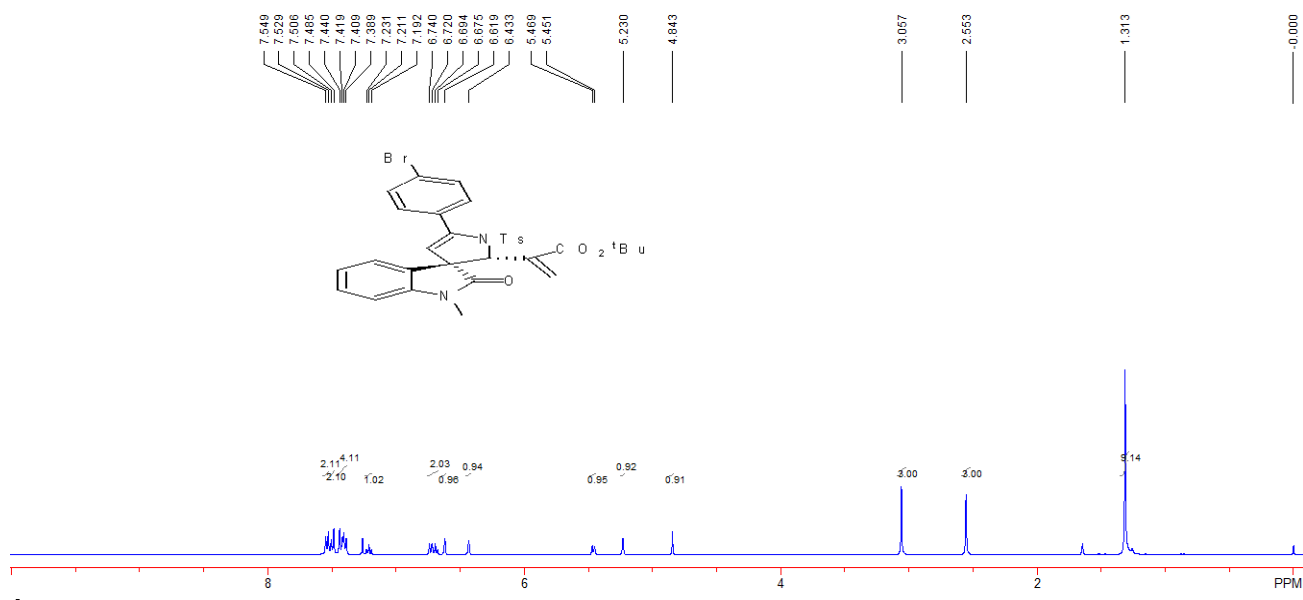


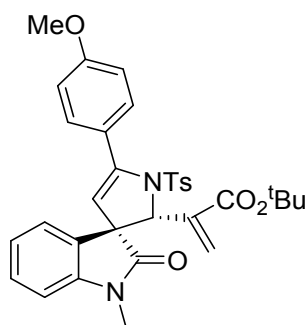
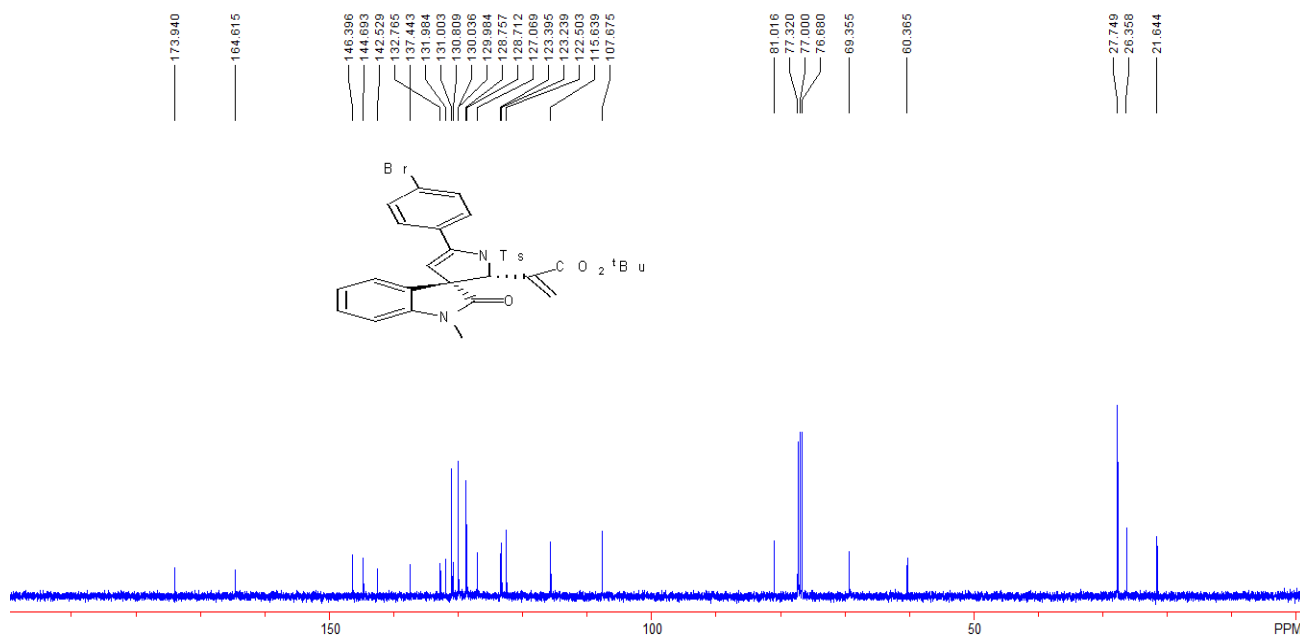


Compound 3c: A pale yellow solid, 99 mg, 84% yield; m.p. 113-114 °C; ^1H NMR (CDCl_3 , 400 MHz, TMS): δ 1.31 (s, 9H, 3 CH_3), 2.54 (s, 3H, CH_3), 3.05 (s, 3H, CH_3), 4.83 (s, 1H, CH), 5.24 (s, 1H, =CH), 5.47 (d, $J = 7.6$ Hz, 1H, Ar), 6.43 (s, 1H, = CH_2), 6.62 (s, 1H, = CH_2), 6.67-6.74 (m, 2H, Ar), 7.21 (t, $J = 8.0$ Hz, 1H, Ar), 7.33 (d, $J = 8.4$ Hz, 2H, Ar), 7.39 (d, $J = 8.4$ Hz, 2H, Ar), 7.49 (d, $J = 8.4$ Hz, 2H, Ar), 7.54 (d, $J = 8.4$ Hz, 2H, Ar); ^{13}C NMR (CDCl_3 , 100 MHz, TMS): δ 21.6, 26.3, 27.7, 60.3, 69.3, 81.0, 107.6, 115.6, 122.5, 123.2, 127.0, 128.0, 128.68, 128.71, 129.7, 130.0, 130.3, 132.0, 132.7, 135.1, 137.4, 142.5, 144.7, 146.3, 164.6, 173.9; HRMS (ESI) Calcd. For $\text{C}_{32}\text{H}_{32}\text{ClN}_2\text{O}_5\text{S}^+$ ($\text{M}+\text{H}$) $^+$ requires 591.1715, Found: 591.1727; IR (CH_2Cl_2): ν 663, 677, 750, 814, 1014, 1088, 1149, 1170, 1491, 1610, 1716, 2930, 3054 cm^{-1} .

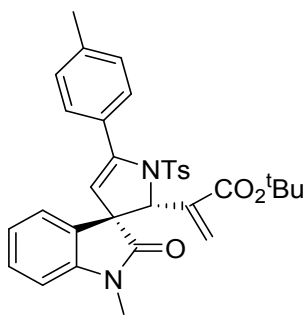
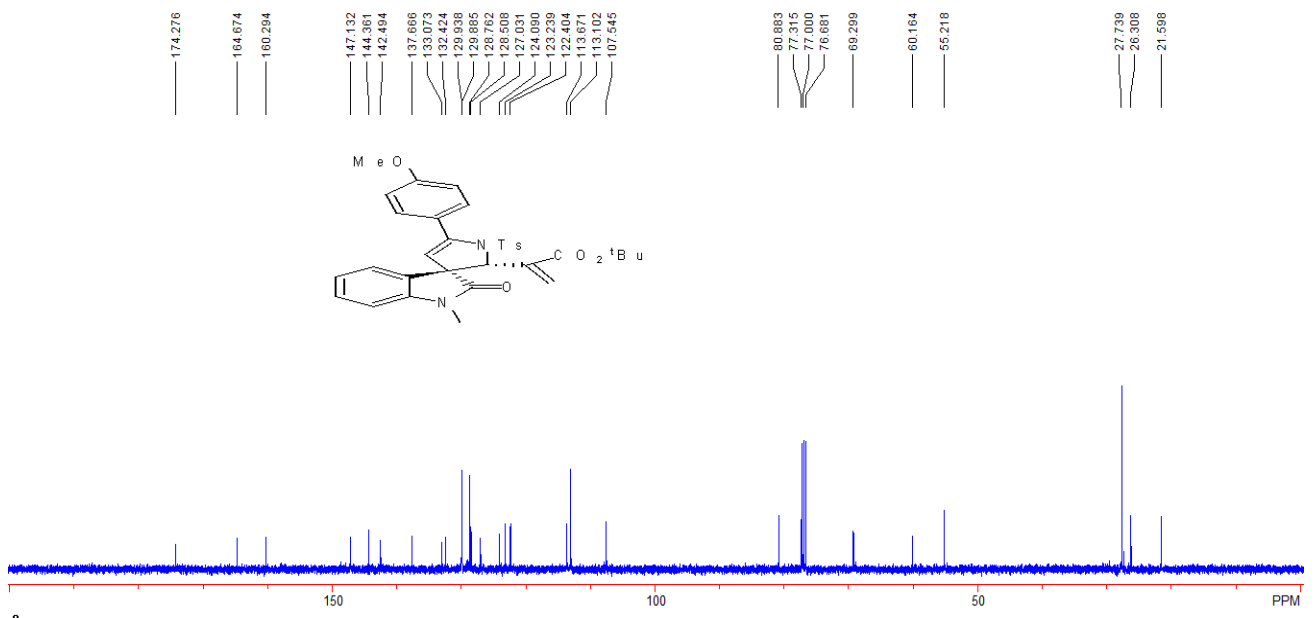
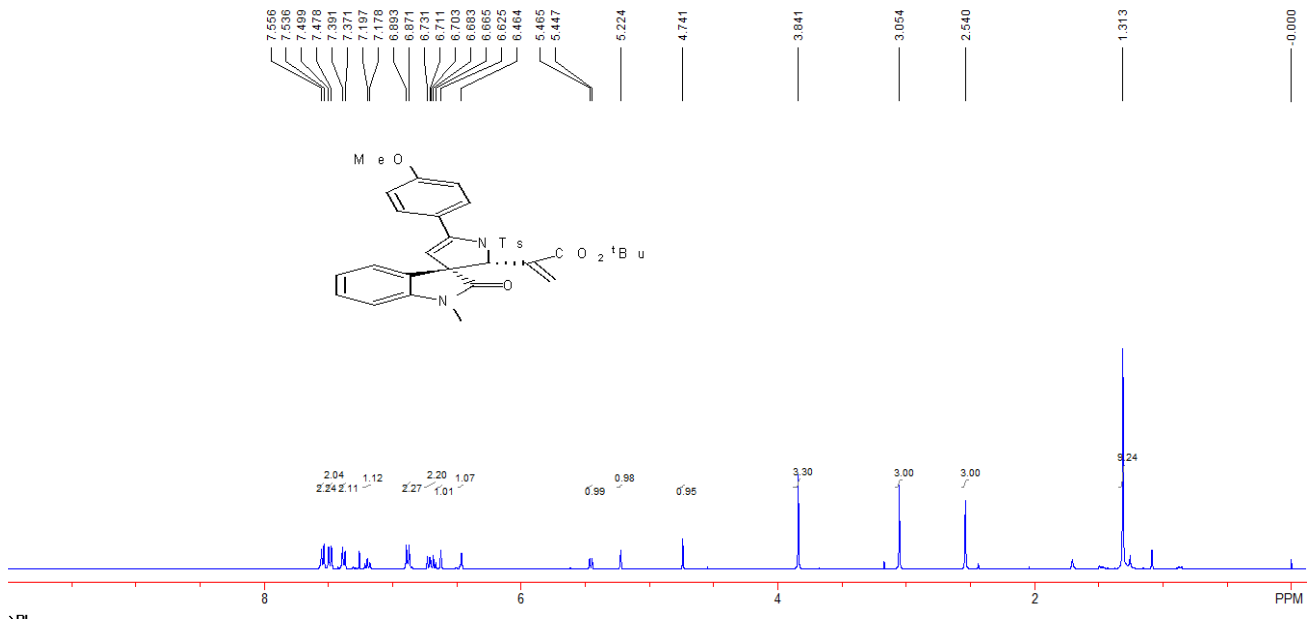


Compound 3d: A pale yellow solid, 99 mg, 78% yield; m.p. 129-130 °C; ^1H NMR (CDCl_3 , 400 MHz, TMS): δ 1.31 (s, 9H, 3 CH_3), 2.55 (s, 3H, CH_3), 3.06 (s, 3H, CH_3), 4.84 (s, 1H, CH), 5.23 (s, 1H, =CH), 5.46 (d, $J = 7.2$ Hz, 1H, Ar), 6.43 (s, 1H, = CH_2), 6.62 (s, 1H, = CH_2), 6.67-6.74 (m, 2H, Ar), 7.21 (t, $J = 8.0$ Hz, 1H, Ar), 7.40 (d, $J = 8.0$ Hz, 2H, Ar), 7.43 (d, $J = 8.4$ Hz, 2H, Ar), 7.50 (d, $J = 8.4$ Hz, 2H, Ar), 7.54 (d, $J = 8.0$ Hz, 2H, Ar); ^{13}C NMR (CDCl_3 , 100 MHz, TMS): δ 21.6, 26.4, 27.7, 60.4, 69.4, 81.0, 107.7, 115.6, 122.5, 123.2, 123.4, 127.1, 128.71, 128.76, 129.98, 130.04, 130.8, 131.0, 132.0, 132.8, 137.4, 142.5, 144.7, 146.4, 164.6, 173.9; HRMS (ESI) Calcd. For $\text{C}_{32}\text{H}_{32}\text{BrN}_2\text{O}_5\text{S}^+$ ($\text{M}+\text{H}$) $^+$ requires 635.1210, Found: 635.1224; IR (CH_2Cl_2): ν 663, 705, 764, 814, 1010, 1085, 1150, 1170, 1365, 1393, 1491, 1611, 1717, 2930, 2976 cm^{-1} .

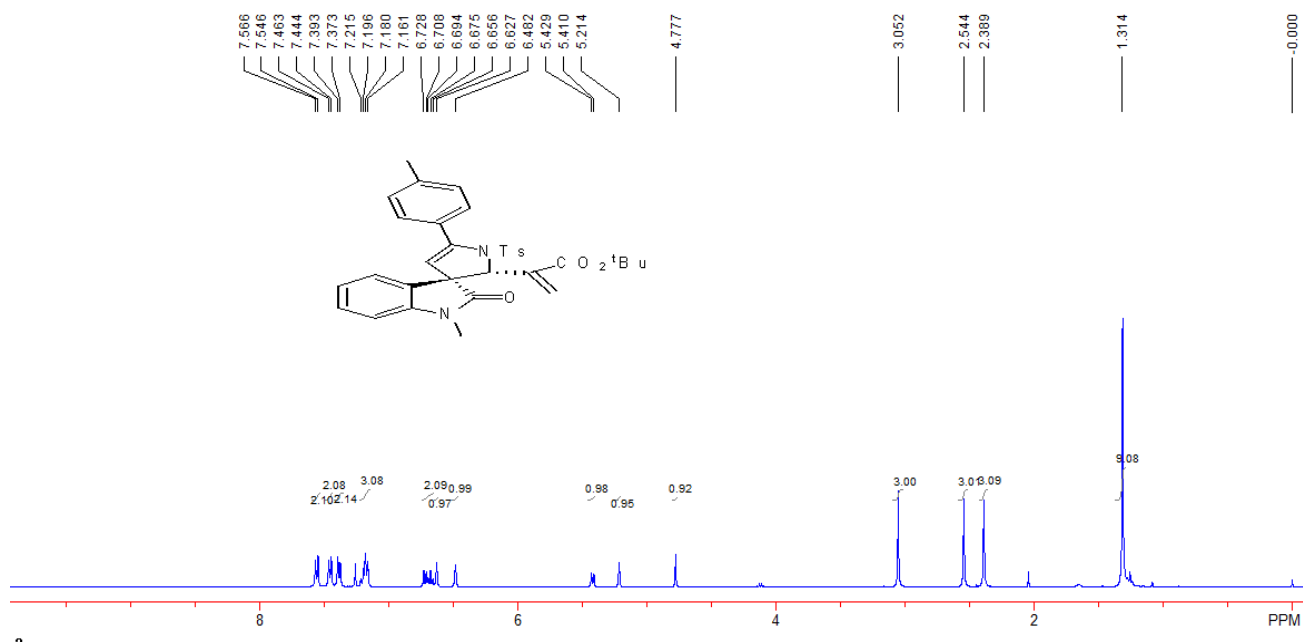


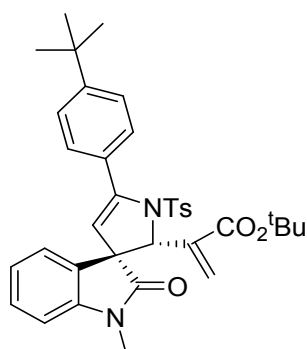
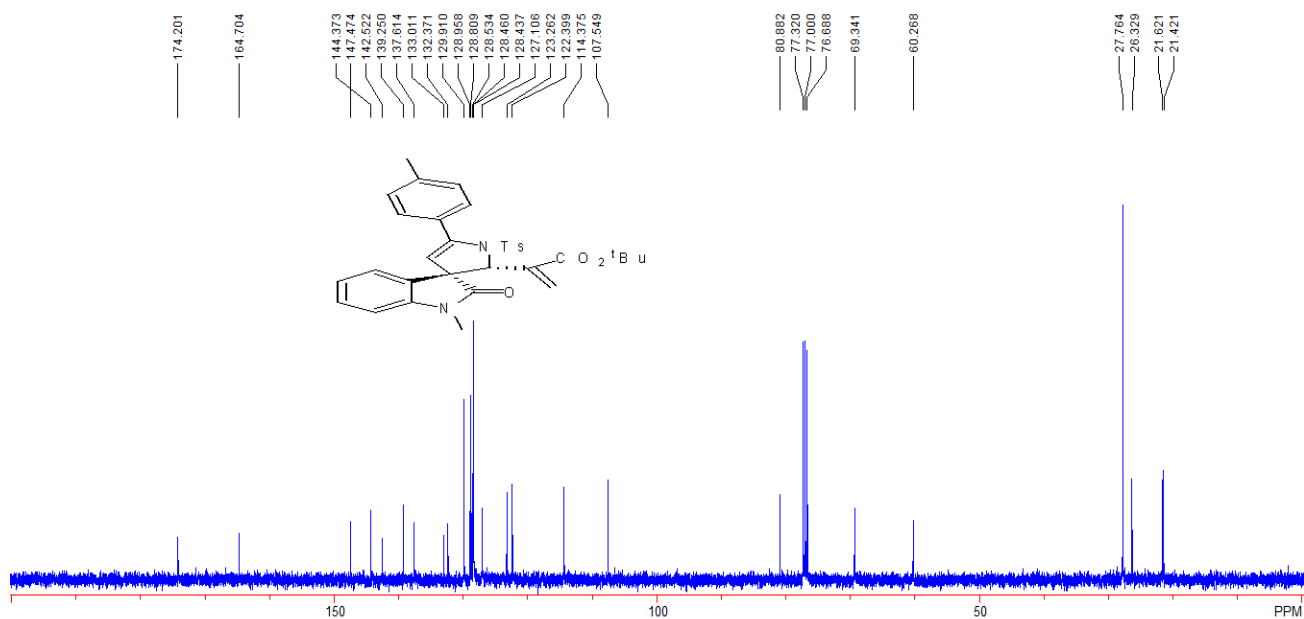


Compound 3e: A pale yellow solid, 111 mg, 95% yield; m.p. 167-168 °C; ^1H NMR (CDCl_3 , 400 MHz, TMS): δ 1.31 (s, 9H, 3 CH_3), 2.54 (s, 3H, CH_3), 3.05 (s, 3H, CH_3), 3.84 (s, 3H, CH_3), 4.74 (s, 1H, CH), 5.22 (s, 1H, =CH), 5.46 (d, $J = 7.2$ Hz, 1H, Ar), 6.46 (s, 1H, = CH_2), 6.63 (s, 1H, = CH_2), 6.66-6.73 (m, 2H, Ar), 6.88 (d, $J = 8.8$ Hz, 2H, Ar), 7.20 (t, $J = 7.6$ Hz, 1H, Ar), 7.38 (d, $J = 8.0$ Hz, 2H, Ar), 7.49 (d, $J = 8.4$ Hz, 2H, Ar), 7.55 (d, $J = 8.0$ Hz, 2H, Ar); ^{13}C NMR (CDCl_3 , 100 MHz, TMS): δ 21.6, 26.3, 27.7, 55.2, 60.2, 69.3, 80.9, 107.5, 113.1, 113.7, 122.4, 123.2, 124.1, 127.0, 128.5, 128.8, 129.89, 129.94, 132.4, 133.1, 137.7, 142.5, 144.4, 147.1, 160.3, 164.7, 174.3; HRMS (ESI) Calcd. For $\text{C}_{33}\text{H}_{35}\text{N}_2\text{O}_6\text{S}^+$ ($\text{M}+\text{H}$) $^+$ requires 587.2210, Found: 587.2225; IR (CH_2Cl_2): ν 663, 679, 706, 815, 837, 1031, 1086, 1149, 1169, 1250, 1364, 1510, 1609, 1716, 2931, 2975 cm^{-1} .

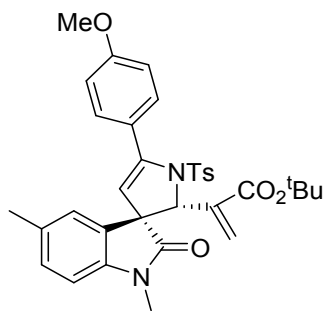
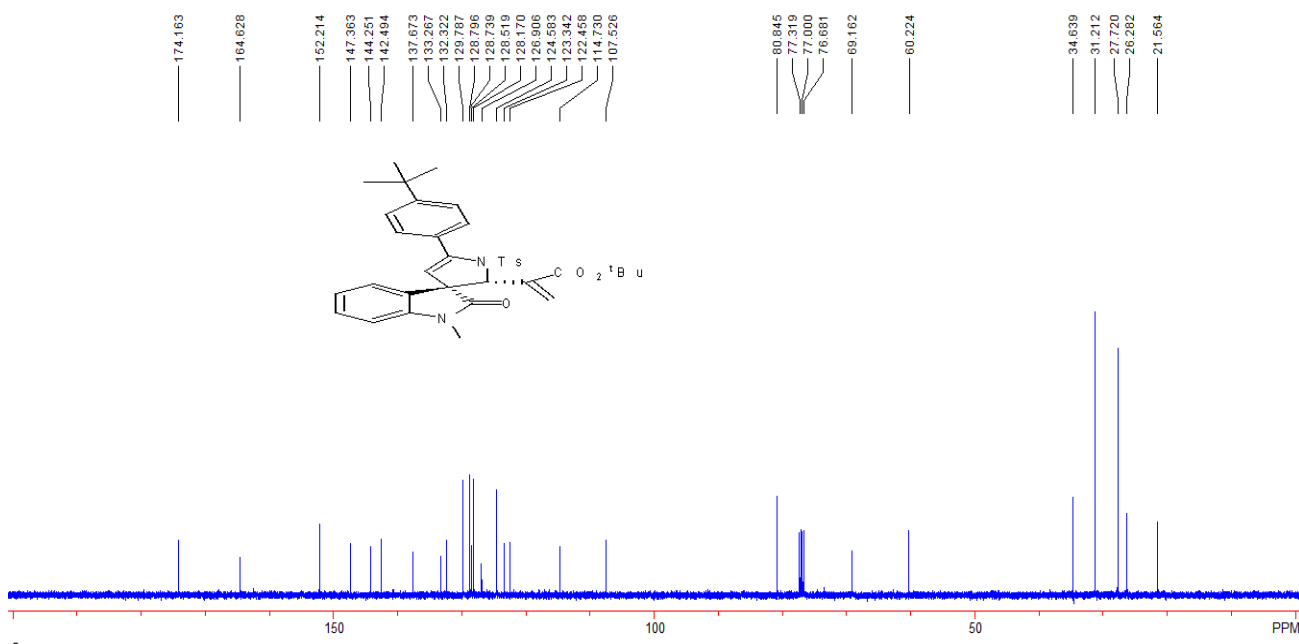
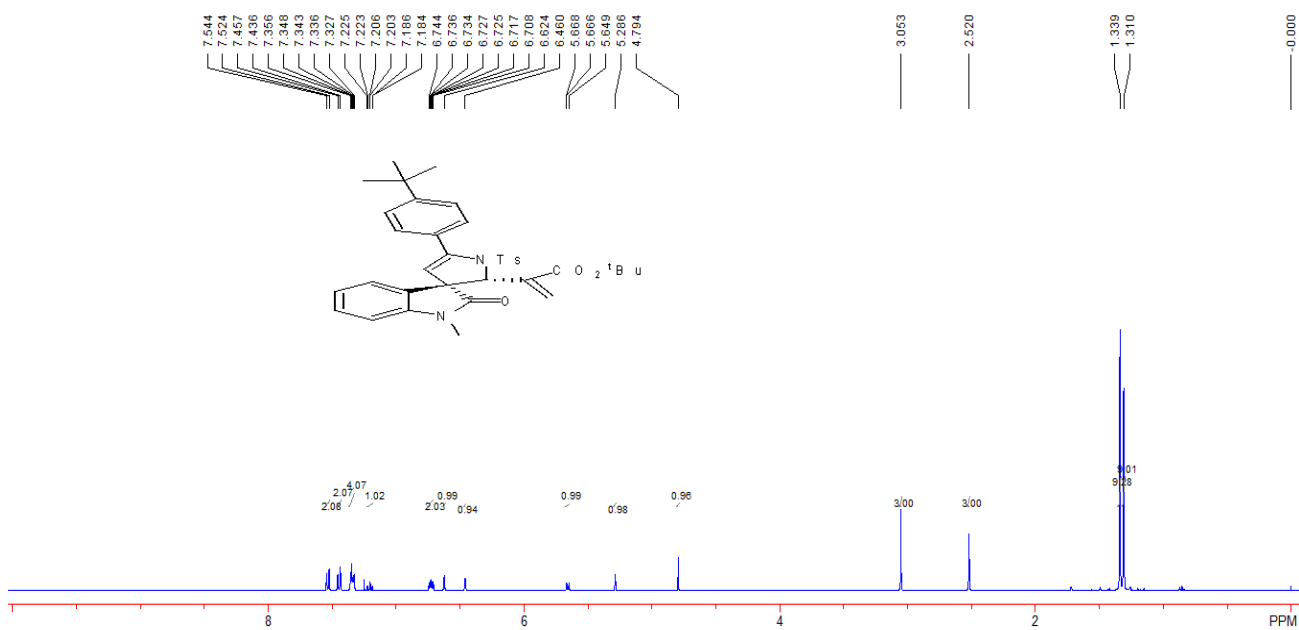


Compound 3f: A pale yellow solid, 98 mg, 86% yield; m.p. 126-127 °C; ¹H NMR (CDCl₃, 400 MHz, TMS): δ 1.31 (s, 9H, 3CH₃), 2.39 (s, 3H, CH₃), 2.54 (s, 3H, CH₃), 3.05 (s, 3H, CH₃), 4.78 (s, 1H, CH), 5.21 (s, 1H, =CH), 5.42 (d, *J* = 7.6 Hz, 1H, Ar), 6.48 (s, 1H, =CH₂), 6.63 (s, 1H, =CH₂), 6.65-6.73 (m, 2H, Ar), 7.16-7.22 (m, 3H, Ar), 7.38 (d, *J* = 8.0 Hz, 2H, Ar), 7.45 (d, *J* = 7.6 Hz, 2H, Ar), 7.56 (d, *J* = 8.0 Hz, 2H, Ar); ¹³C NMR (CDCl₃, 100 MHz, TMS): δ 21.4, 21.6, 26.3, 27.8, 60.3, 69.3, 80.9, 107.5, 114.4, 122.4, 123.3, 127.1, 128.40, 128.46, 128.53, 128.8, 129.0, 129.9, 132.4, 133.0, 137.6, 139.3, 142.5, 144.4, 147.5, 164.7, 174.2; HRMS (ESI) Calcd. For C₃₃H₃₅N₂O₅S⁺ (M+H)⁺ requires 571.2261, Found: 571.2260; IR (CH₂Cl₂): ν 663, 679, 750, 813, 1034, 1086, 1148, 1170, 1364, 1491, 1610, 1716, 2927, 2976 cm⁻¹.

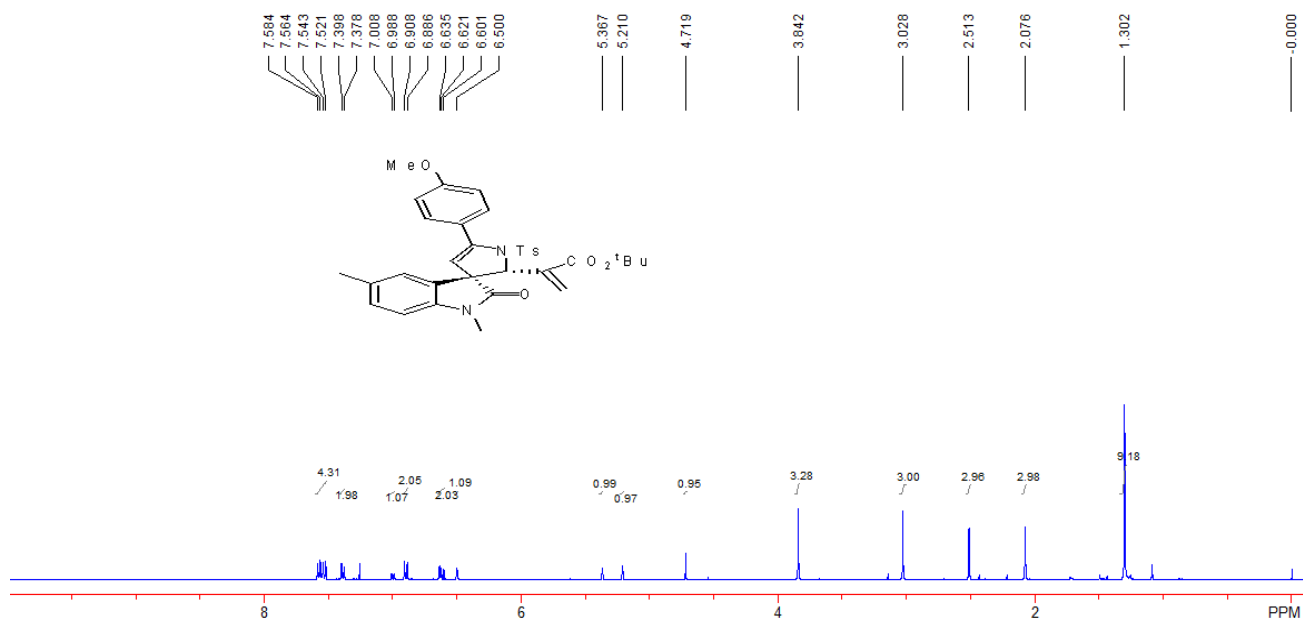


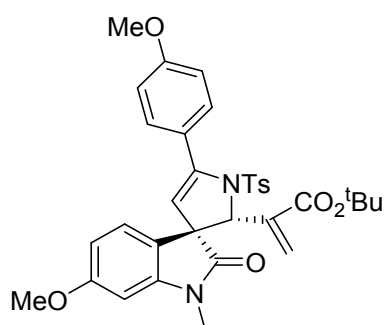
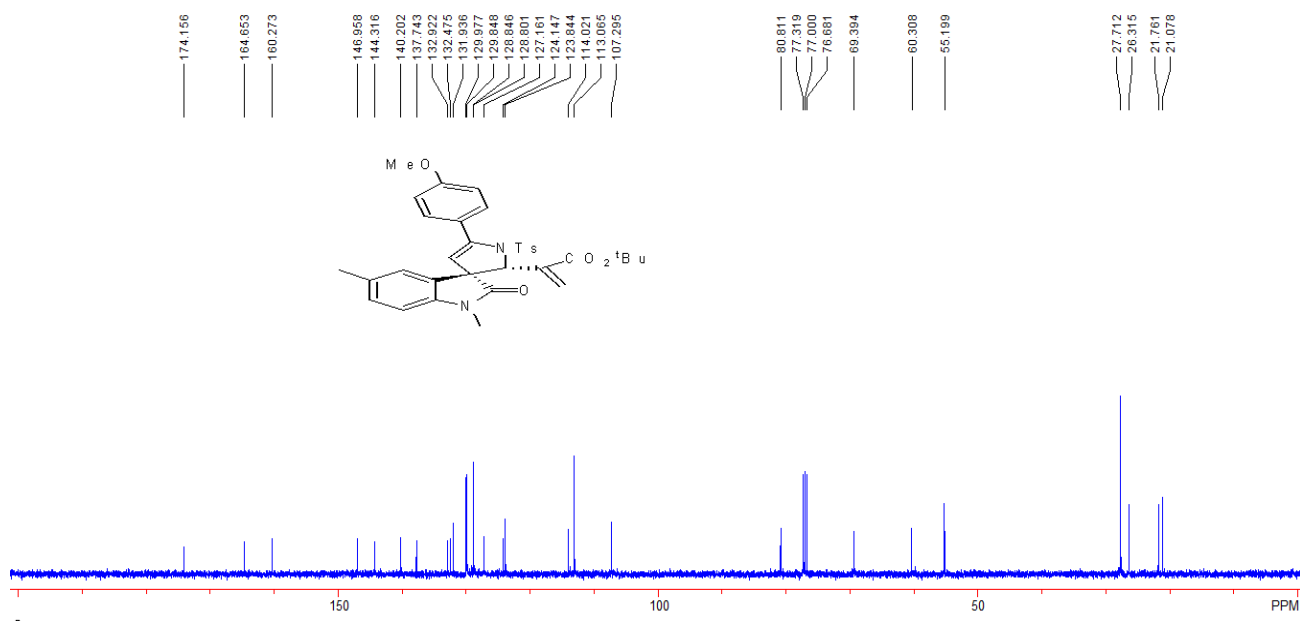


Compound 3g: A pale yellow solid, 107 mg, 88% yield; m.p. 116-117 °C; ^1H NMR (CDCl_3 , 400 MHz, TMS): δ 1.31 (s, 9H, 3CH₃), 1.34 (s, 9H, 3CH₃), 2.52 (s, 3H, CH₃), 3.05 (s, 3H, CH₃), 4.79 (s, 1H, CH), 5.29 (s, 1H, =CH), 5.66 (dd, $J_1 = 7.6$ Hz, $J_2 = 0.8$ Hz, 1H, Ar), 6.46 (s, 1H, =CH₂), 6.62 (s, 1H, =CH₂), 6.70-6.75 (m, 2H, Ar), 7.20 (dt, $J_1 = 8.0$ Hz, $J_2 = 0.8$ Hz, 1H, Ar), 7.32-7.36 (m, 4H, Ar), 7.45 (d, $J = 8.4$ Hz, 2H, Ar), 7.53 (d, $J = 8.0$ Hz, 2H, Ar); ^{13}C NMR (CDCl_3 , 100 MHz, TMS): δ 21.6, 26.3, 27.7, 31.2, 34.6, 60.2, 69.2, 80.8, 107.5, 114.7, 122.5, 123.3, 124.6, 126.9, 128.2, 128.5, 128.7, 128.8, 129.8, 132.3, 133.3, 137.7, 142.5, 144.3, 147.4, 152.2, 164.6, 174.2; HRMS (ESI) Calcd. For $\text{C}_{36}\text{H}_{41}\text{N}_2\text{O}_5\text{S}^+$ ($\text{M}+\text{H}$)⁺ requires 613.2731, Found: 613.2751; IR (CH_2Cl_2): ν 663, 678, 750, 814, 1018, 1086, 1150, 1171, 1365, 1470, 1492, 1611, 1718, 2930, 2963 cm^{-1} .

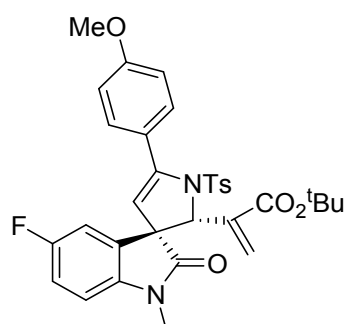
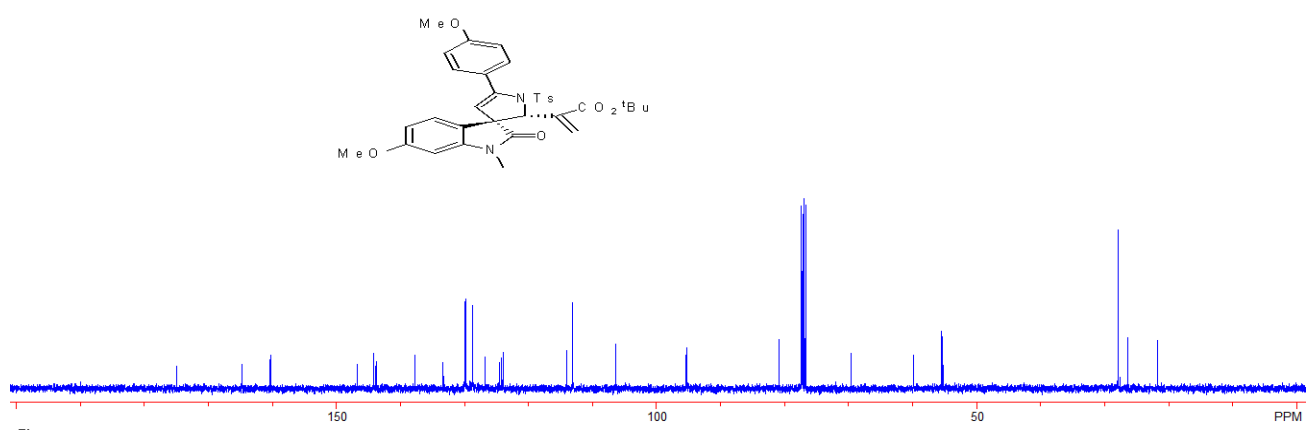
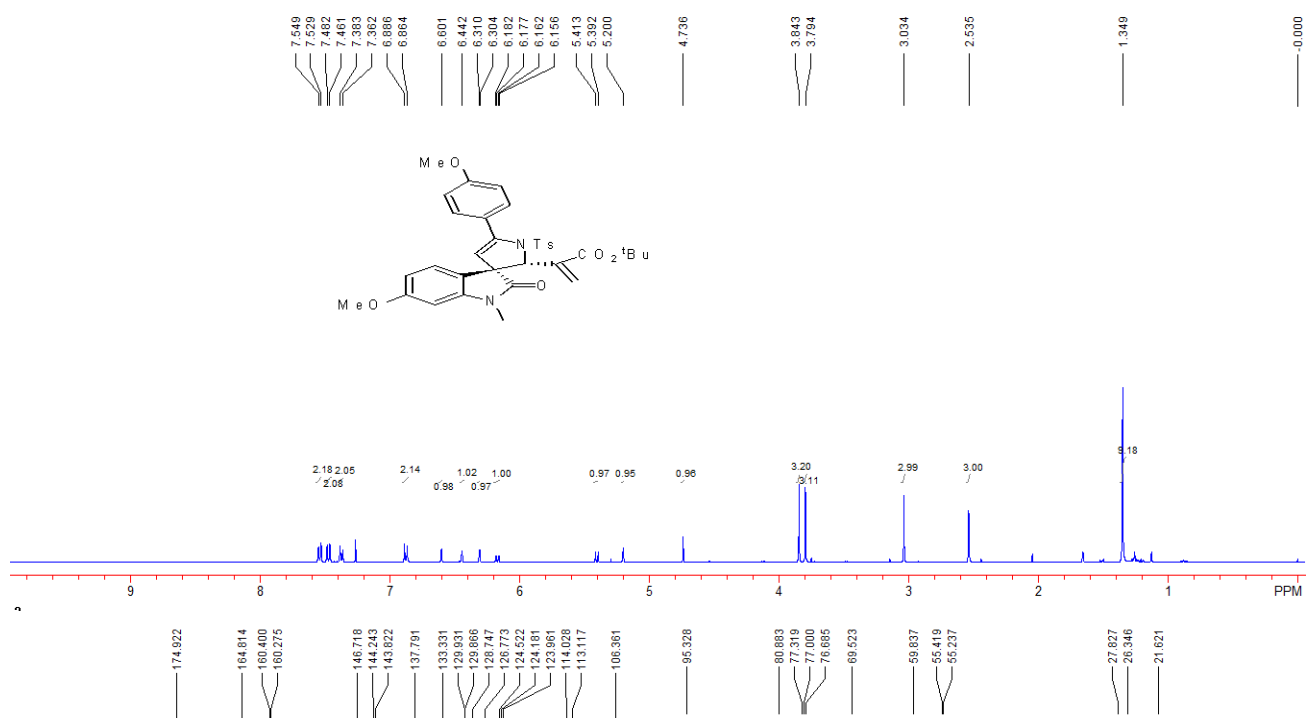


Compound 3h: A pale yellow solid, 105 mg, 88% yield; m.p. 158-159 °C; ¹H NMR (CDCl₃, 400 MHz, TMS): δ 1.30 (s, 9H, 3CH₃), 2.08 (s, 3H, CH₃), 2.51 (s, 3H, CH₃), 3.03 (s, 3H, CH₃), 3.84 (s, 3H, CH₃), 4.72 (s, 1H, CH), 5.21 (s, 1H, =CH), 5.37 (s, 1H, Ar), 6.50 (s, 1H, =CH₂), 6.61 (d, *J* = 8.0 Hz, 1H, Ar), 6.64 (s, 1H, =CH₂), 6.90 (d, *J* = 8.8 Hz, 2H, Ar), 7.00 (d, *J* = 8.0 Hz, 1H, Ar), 7.39 (d, *J* = 8.0 Hz, 2H, Ar), 7.53 (d, *J* = 8.8 Hz, 2H, Ar), 7.57 (d, *J* = 8.0 Hz, 2H, Ar); ¹³C NMR (CDCl₃, 100 MHz, TMS): δ 21.1, 21.8, 26.3, 27.7, 55.2, 60.3, 69.4, 80.8, 107.3, 113.1, 114.0, 123.8, 124.1, 127.2, 128.80, 128.85, 129.8, 130.0, 131.9, 132.5, 132.9, 137.7, 140.2, 144.3, 147.0, 160.3, 164.7, 174.2; HRMS (ESI) Calcd. For C₃₄H₃₇N₂O₆S⁺ (M+H)⁺ requires 601.2367, Found: 601.2364; IR (CH₂Cl₂): ν 662, 705, 763, 809, 835, 1031, 1088, 1149, 1169, 1250, 1362, 1499, 1510, 1606, 1713, 2926, 2974 cm⁻¹.



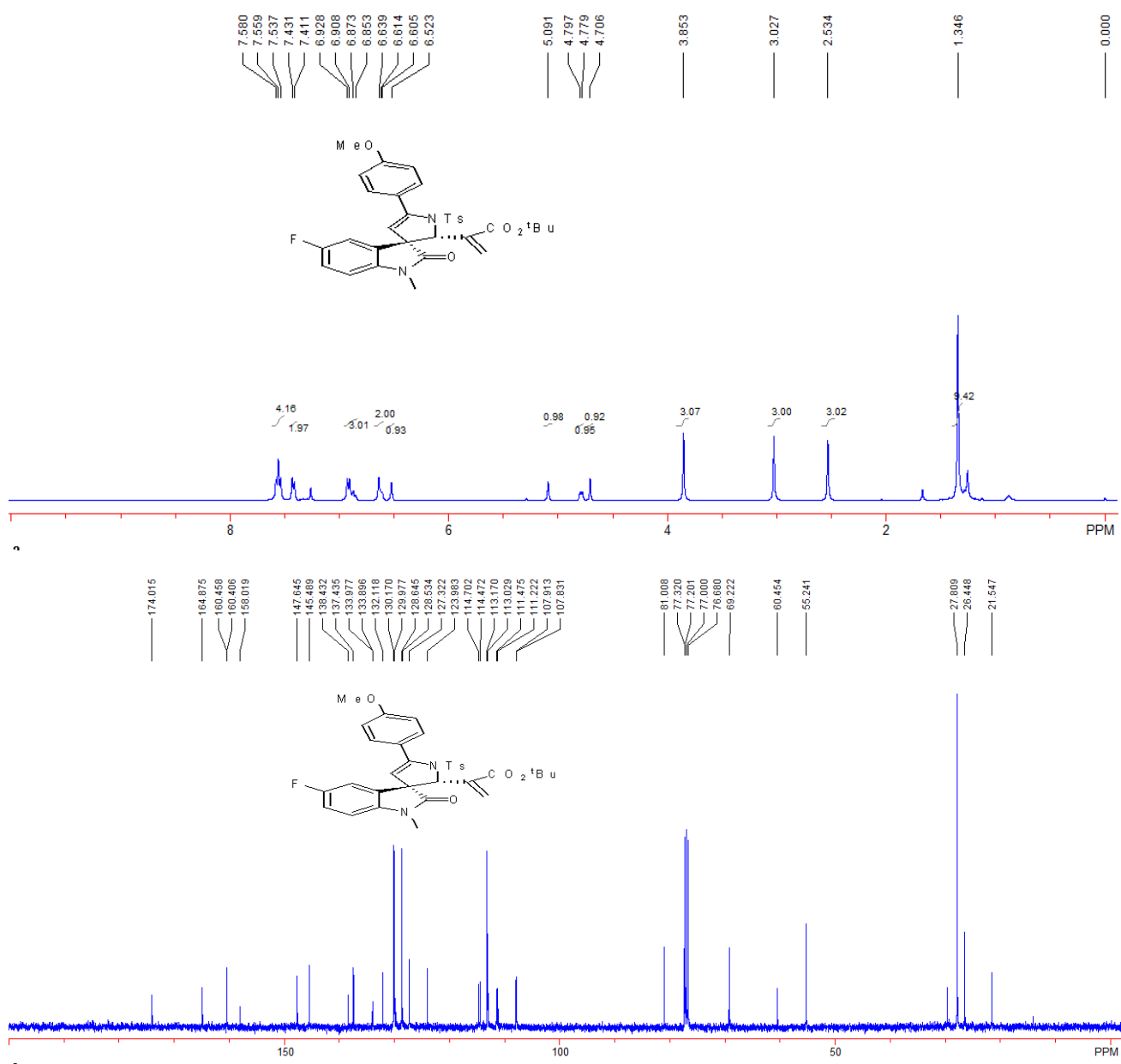


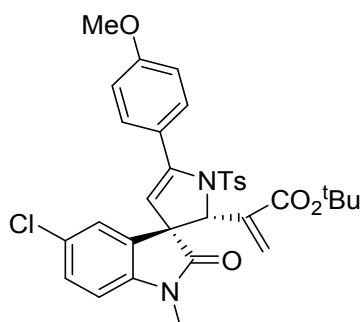
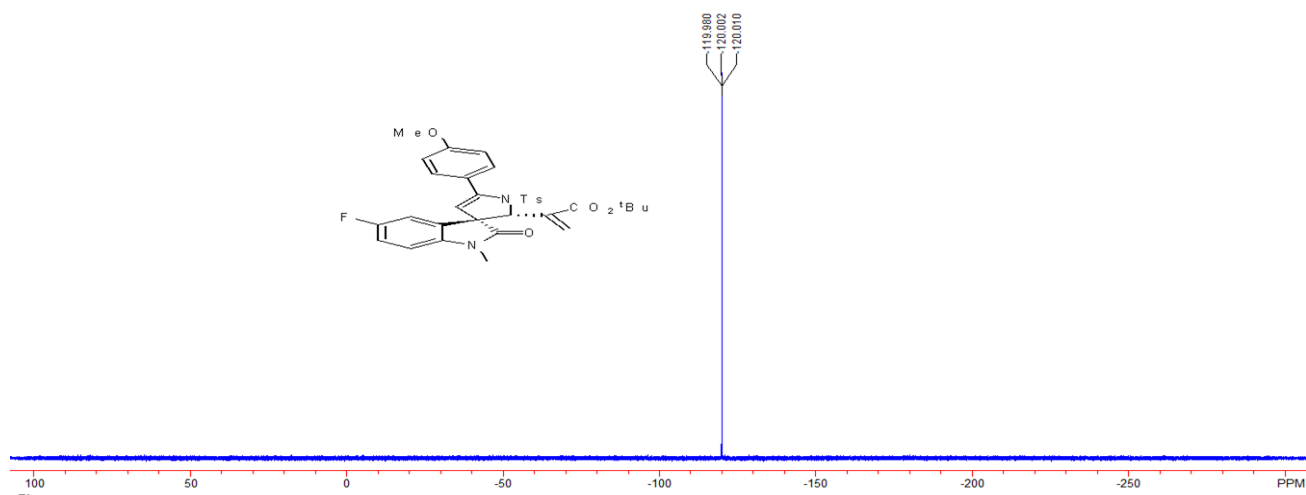
Compound 3i: A pale yellow solid, 103 mg, 84% yield; m.p. 188-189 °C; ^1H NMR (CDCl_3 , 400 MHz, TMS): δ 1.35 (s, 9H, 3 CH_3), 2.54 (s, 3H, CH_3), 3.03 (s, 3H, CH_3), 3.79 (s, 3H, CH_3), 3.84 (s, 3H, CH_3), 4.74 (s, 1H, CH), 5.20 (s, 1H, =CH), 5.40 (d, $J = 8.4$ Hz, 1H, Ar), 6.17 (dd, $J_1 = 8.0$ Hz, $J_2 = 2.0$ Hz, 1H, Ar), 6.31 (d, $J = 2.4$ Hz, 1H, Ar), 6.44 (s, 1H, = CH_2), 6.60 (s, 1H, = CH_2), 6.88 (d, $J = 8.8$ Hz, 2H, Ar), 7.37 (d, $J = 8.4$ Hz, 2H, Ar), 7.47 (d, $J = 8.4$ Hz, 2H, Ar), 7.54 (d, $J = 8.0$ Hz, 2H, Ar); ^{13}C NMR (CDCl_3 , 100 MHz, TMS): δ 21.6, 26.3, 27.8, 55.2, 55.4, 59.8, 69.5, 80.9, 95.3, 106.4, 113.1, 114.0, 124.0, 124.2, 124.5, 126.8, 128.7, 129.87, 129.93, 133.3, 137.8, 143.8, 144.2, 146.7, 160.3, 160.4, 164.8, 174.9; HRMS (ESI) Calcd. For $\text{C}_{34}\text{H}_{37}\text{N}_2\text{O}_7\text{S}^+$ ($\text{M}+\text{H}$) $^+$ requires 617.2316, Found: 617.2314; IR (CH_2Cl_2): ν 663, 677, 815, 834, 1032, 1087, 1150, 1171, 1251, 1366, 1459, 1508, 1624, 1719, 2926, 2951 cm^{-1} .



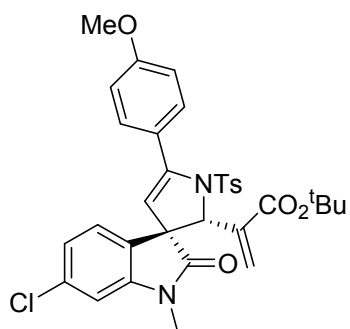
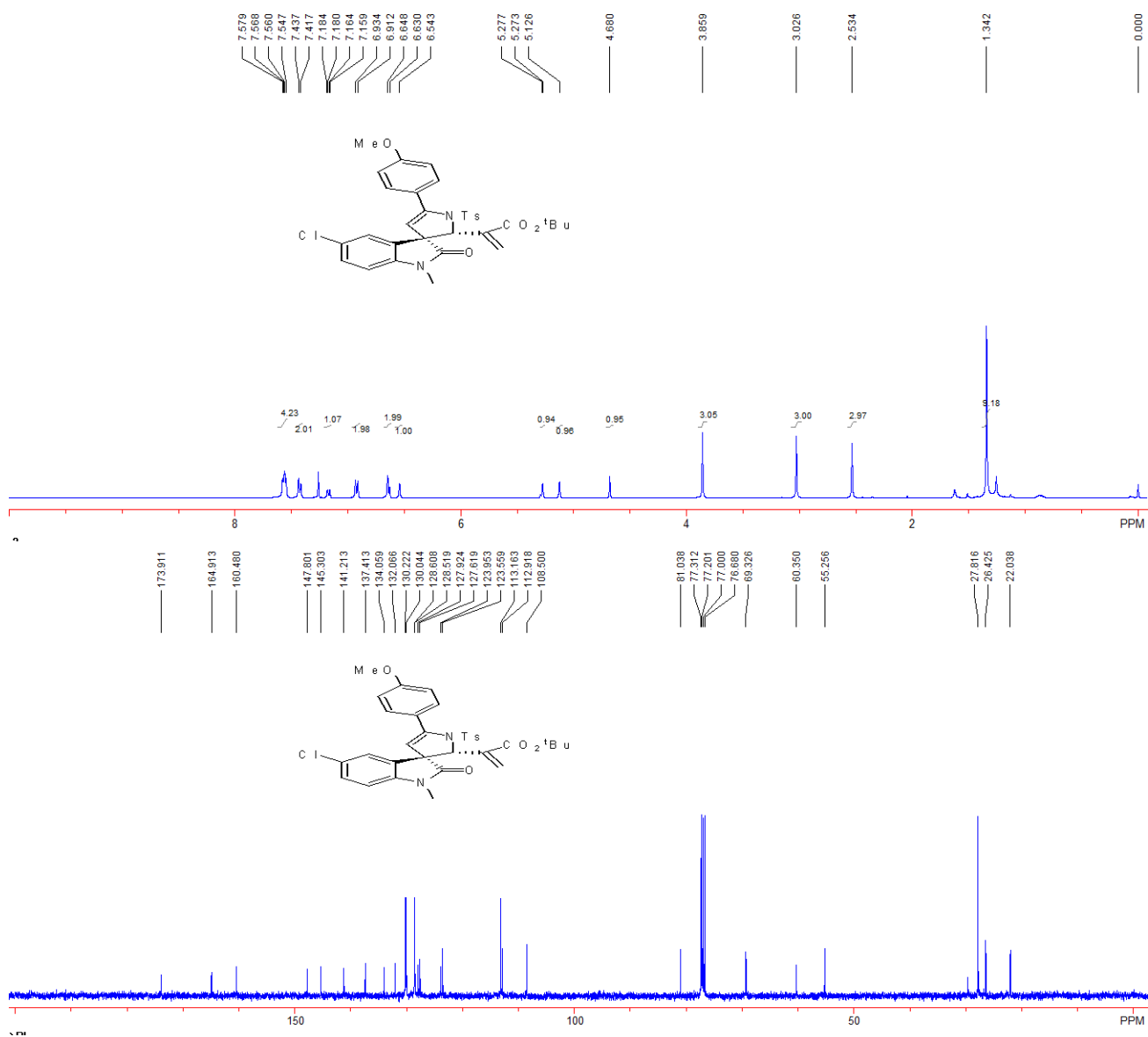
Compound 3j: A pale yellow solid, 76 mg, 63% yield; m.p. 173-174 °C; ¹H NMR (CDCl₃, 400 MHz, TMS): δ 1.35 (s, 9H, 3CH₃), 2.53 (s, 3H, CH₃), 3.03 (s, 3H, CH₃), 3.85 (s, 3H, CH₃), 4.71 (s, 1H, CH), 4.79 (d, *J* = 7.2 Hz, 1H, Ar), 5.09 (s, 1H, =CH), 6.52 (s, 1H, =CH₂), 6.60-6.64 (m, 2H, =CH₂,

Ar), 6.87 (d, $J = 8.0$ Hz, 1H, Ar), 6.92 (d, $J = 8.0$ Hz, 2H, Ar), 7.42 (d, $J = 8.0$ Hz, 2H, Ar), 7.55 (d, $J = 8.8$ Hz, 2H, Ar), 7.57 (d, $J = 8.4$ Hz, 2H, Ar); ^{13}C NMR (CDCl_3 , 100 MHz, TMS): δ 21.5, 26.4, 27.8, 55.2, 60.5, 69.2, 81.0, 107.9 (d, $J = 8.2$ Hz), 111.3 (d, $J = 25.3$ Hz), 113.0, 113.2, 114.6 (d, $J = 23.0$ Hz), 124.0, 127.3, 128.6, 130.0, 130.2, 132.1, 133.9 (d, $J = 8.1$ Hz), 137.4, 138.4, 145.5, 147.6, 159.2 (d, $J = 238.7$ Hz), 160.5, 164.9, 174.0; ^{19}F NMR (CDCl_3 , 376 MHz, CFCl_3): δ -120.01 - 119.98 (m); HRMS (ESI) Calcd. For $\text{C}_{33}\text{H}_{34}\text{FN}_2\text{O}_6\text{S}^+$ ($\text{M}+\text{H}$) $^+$ requires 605.2116, Found: 605.2115. IR (CH_2Cl_2): ν 662, 706, 812, 836, 1032, 1087, 1149, 1171, 1251, 1365, 1494, 1510, 1608, 1719, 2926, 2977 cm^{-1} .



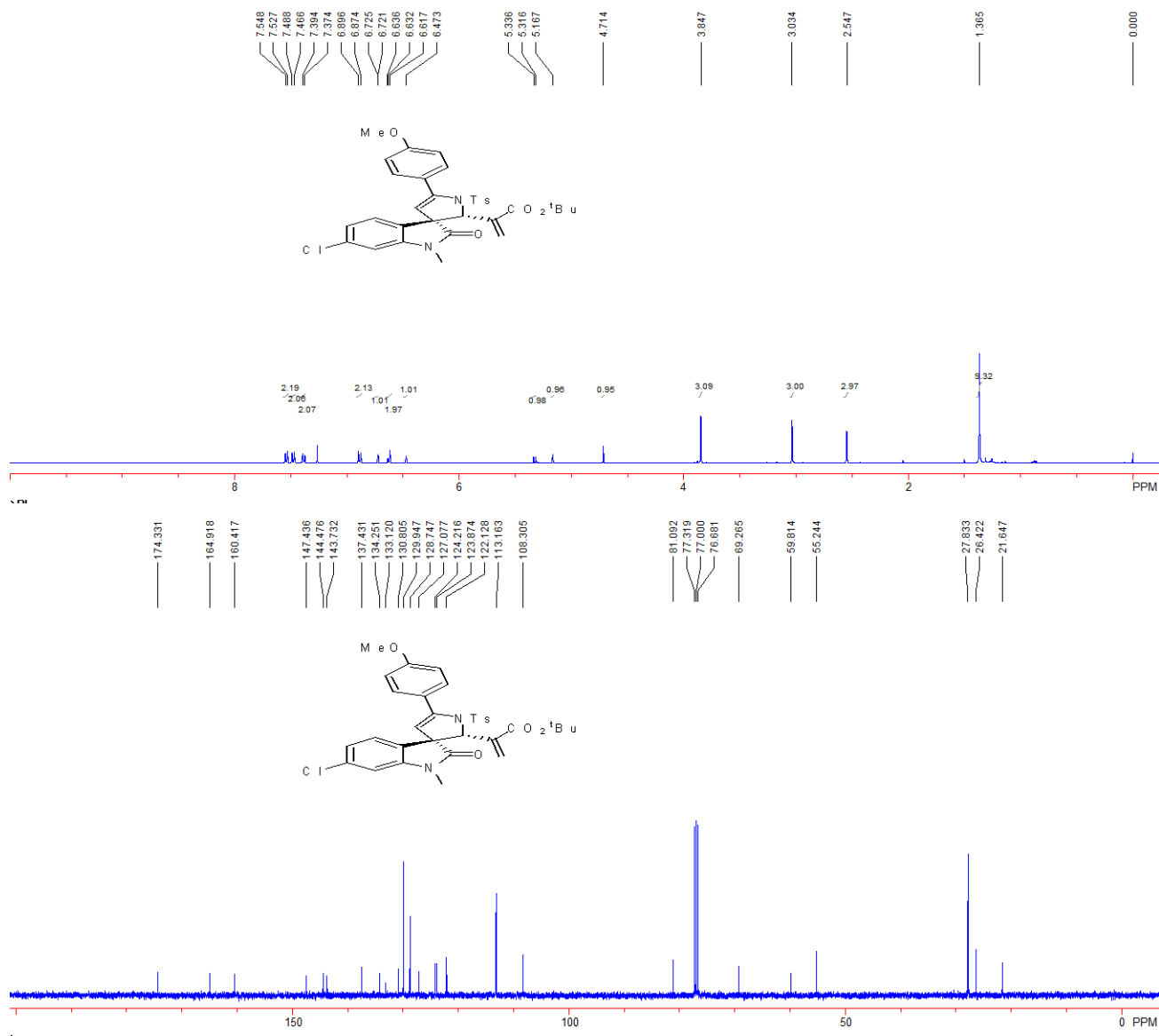


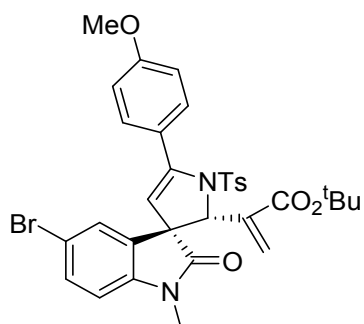
Compound 3k: A pale yellow solid, 80 mg, 65% yield; m.p. 168-169 °C; ^1H NMR (CDCl_3 , 400 MHz, TMS): δ 1.34 (s, 9H, 3 CH_3), 2.53 (s, 3H, CH_3), 3.03 (s, 3H, CH_3), 3.86 (s, 3H, CH_3), 4.68 (s, 1H, CH), 5.13 (s, 1H, =CH), 5.28 (d, $J = 1.6$ Hz, 1H, Ar), 6.54 (s, 1H, = CH_2), 6.63-6.65 (m, 2H, = CH_2 , Ar), 6.92 (d, $J = 8.8$ Hz, 2H, Ar), 7.17 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.6$ Hz, 1H, Ar), 7.43 (d, $J = 8.0$ Hz, 2H, Ar), 7.56 (d, $J = 8.4$ Hz, 2H, Ar), 7.57 (d, $J = 7.6$ Hz, 2H, Ar); ^{13}C NMR (CDCl_3 , 100 MHz, TMS): δ 22.0, 26.4, 27.8, 55.3, 60.4, 69.3, 81.0, 108.5, 112.9, 113.2, 123.6, 124.0, 127.6, 127.9, 128.5, 128.6, 130.0, 130.2, 132.1, 134.1, 137.4, 141.2, 145.3, 147.8, 160.5, 164.9, 173.9; HRMS (ESI) Calcd. For $\text{C}_{33}\text{H}_{34}\text{ClN}_2\text{O}_6\text{S}^+$ ($\text{M}+\text{H}$) $^+$ requires 621.1821, Found: 621.1820; IR (CH_2Cl_2): ν 661, 728, 814, 836, 1032, 1097, 1150, 1171, 1251, 1365, 1490, 1510, 1608, 1722, 2925, 2955 cm^{-1} .



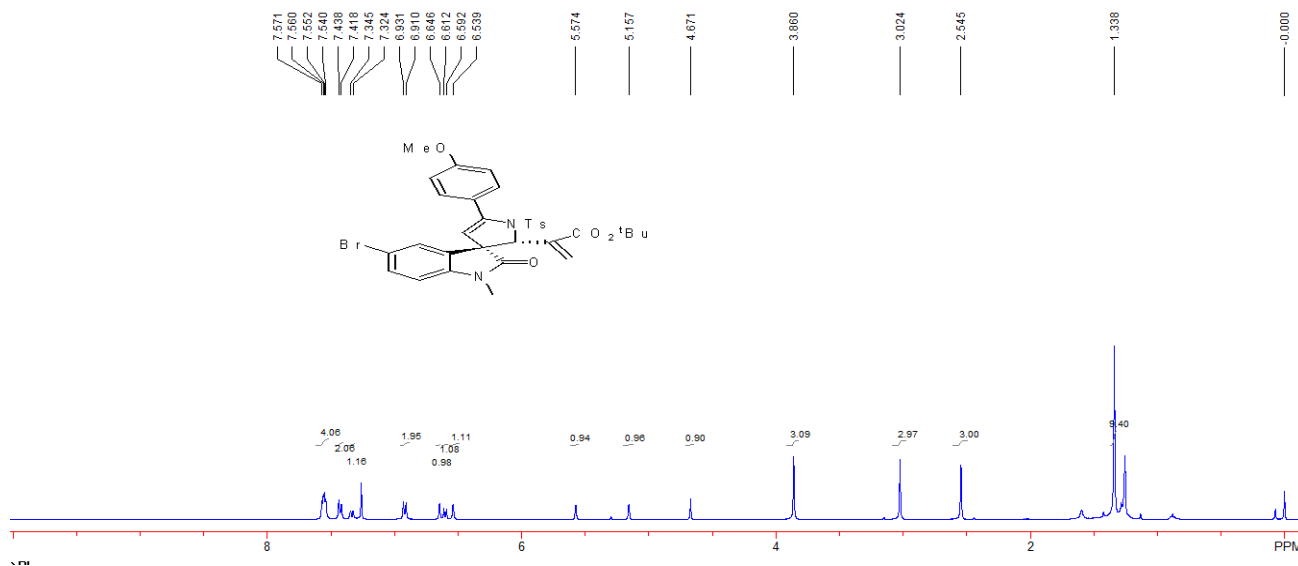
Compound 3I: A pale yellow solid, 67 mg, 54% yield; m.p. 186-187 °C; ¹H NMR (CDCl₃, 400 MHz, TMS): δ 1.37 (s, 9H, 3CH₃), 2.55 (s, 3H, CH₃), 3.03 (s, 3H, CH₃), 3.85 (s, 3H, CH₃), 4.71 (s, 1H, CH), 5.17 (s, 1H, =CH), 5.33 (d, *J* = 8.0 Hz, 1H, Ar), 6.47 (s, 1H, =CH₂), 6.62 (s, 1H, =CH₂), 6.63 (d,

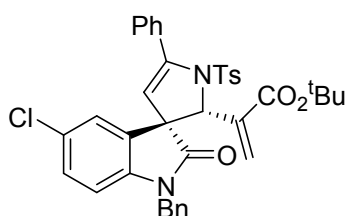
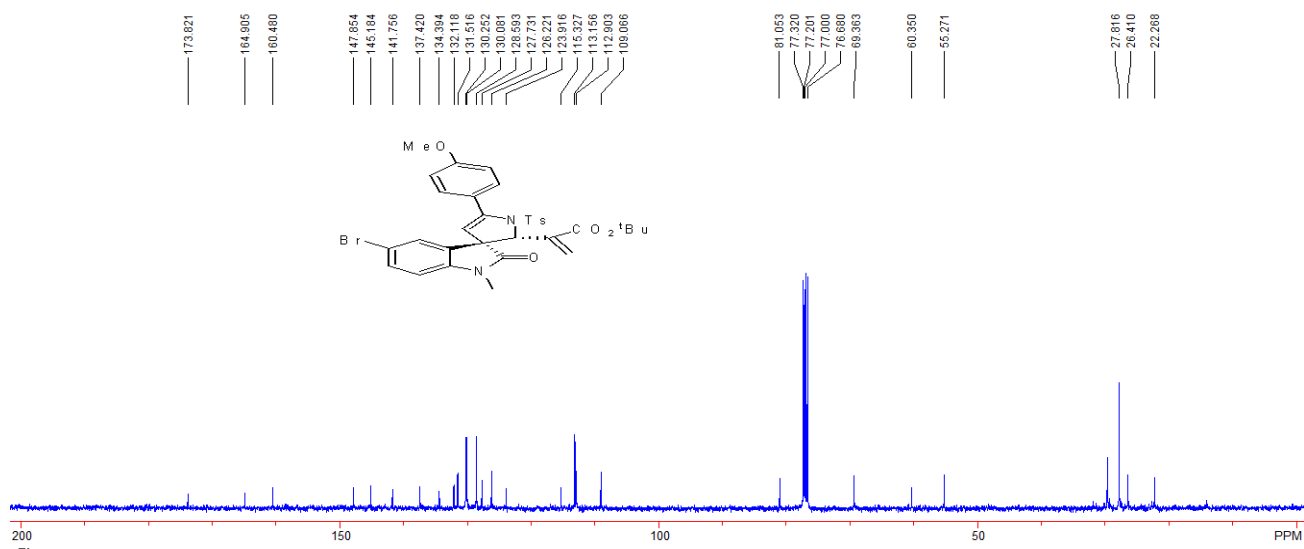
$J = 1.6$ Hz, 1H, Ar), 6.72 (d, $J = 1.6$ Hz, 1H, Ar), 6.89 (d, $J = 8.8$ Hz, 2H, Ar), 7.38 (d, $J = 8.0$ Hz, 2H, Ar), 7.48 (d, $J = 8.8$ Hz, 2H, Ar), 7.54 (d, $J = 8.4$ Hz, 2H, Ar); ^{13}C NMR (CDCl_3 , 100 MHz, TMS): δ 21.6, 26.4, 27.8, 55.2, 59.8, 69.3, 81.1, 108.3, 113.2, 122.1, 123.9, 124.2, 127.1, 128.7, 129.9, 130.8, 133.1, 134.3, 137.4, 143.7, 144.5, 147.4, 160.4, 164.9, 174.3; HRMS (ESI) Calcd. For $\text{C}_{33}\text{H}_{34}\text{ClN}_2\text{O}_6\text{S}^+$ ($\text{M}+\text{H}$) $^+$ requires 621.1821, Found: 621.1817; IR (CH_2Cl_2): ν 661, 672, 735, 813, 1031, 1087, 1150, 1170, 1249, 1365, 1510, 1606, 1722, 2923, 2954 cm^{-1} .



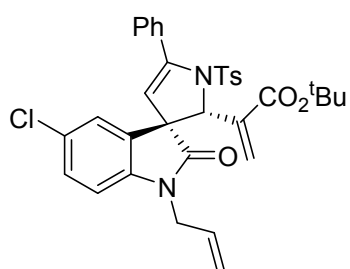
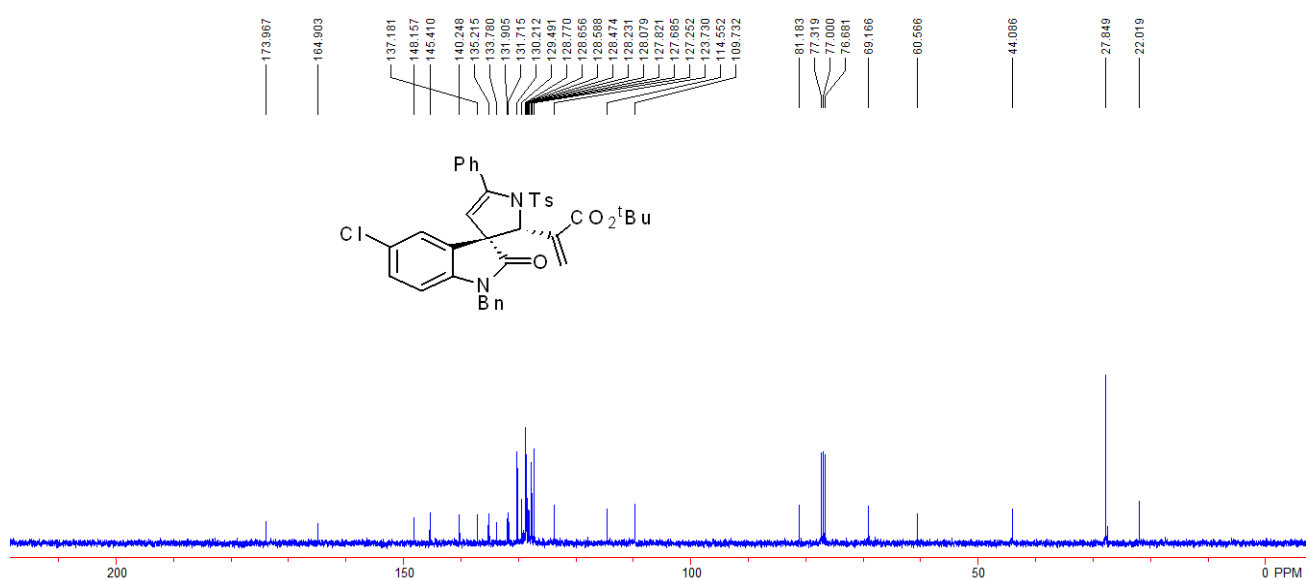
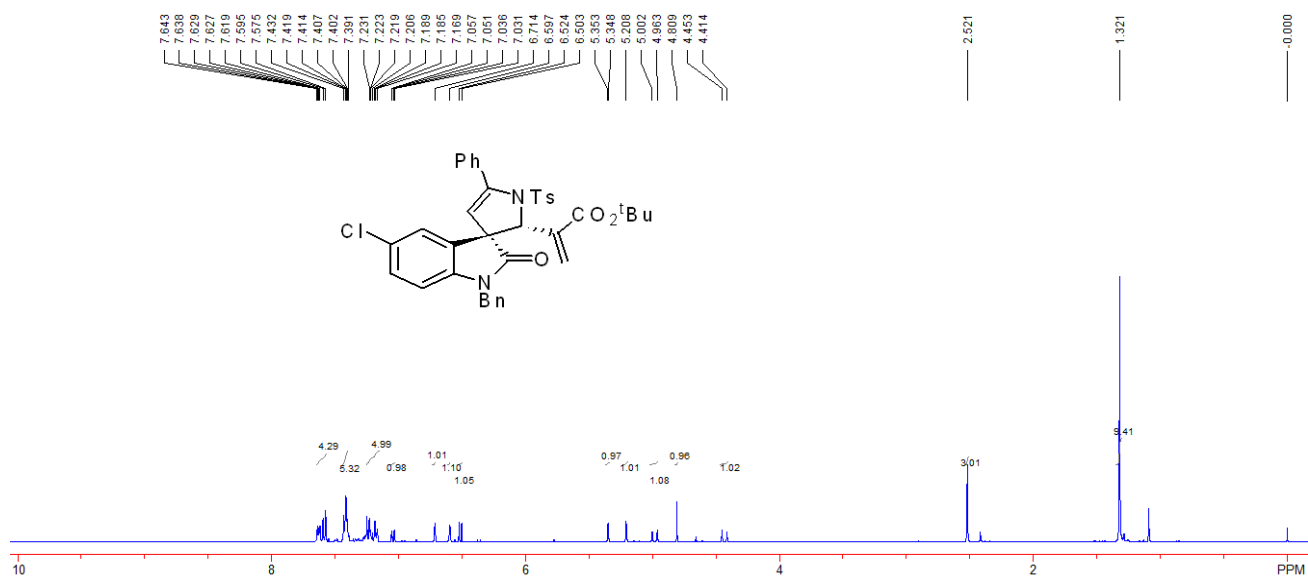


Compound 3m: A pale yellow solid, 90 mg, 68% yield; m.p. 192-193 °C; ^1H NMR (CDCl_3 , 400 MHz, TMS): δ 1.34 (s, 9H, 3CH₃), 2.55 (s, 3H, CH₃), 3.02 (s, 3H, CH₃), 3.86 (s, 3H, CH₃), 4.67 (s, 1H, CH), 5.16 (s, 1H, =CH), 5.57 (s, 1H, Ar), 6.54 (s, 1H, =CH₂), 6.60 (d, J = 8.0 Hz, 1H, Ar), 6.65 (s, 1H, =CH₂), 6.92 (d, J = 8.4 Hz, 2H, Ar), 7.33 (d, J = 8.4 Hz, 1H, Ar), 7.43 (d, J = 8.0 Hz, 2H, Ar), 7.54-7.57 (m, 4H, Ar); ^{13}C NMR (CDCl_3 , 100 MHz, TMS): δ 22.3, 26.4, 27.8, 55.3, 60.4, 69.4, 81.1, 109.1, 112.9, 113.2, 115.3, 123.9, 126.2, 127.7, 128.6, 130.1, 130.3, 131.5, 132.1, 134.4, 137.4, 141.8, 145.2, 147.9, 160.5, 164.9, 173.8; HRMS (ESI) Calcd. For $\text{C}_{33}\text{H}_{34}\text{BrN}_2\text{O}_6\text{S}^+$ ($\text{M}+\text{H}$)⁺ requires 665.1315, Found: 665.1312; IR (CH_2Cl_2): ν 661, 728, 814, 1032, 1093, 1151, 1171, 1251, 1365, 1461, 1510, 1607, 1723, 2922, 2954 cm^{-1} .



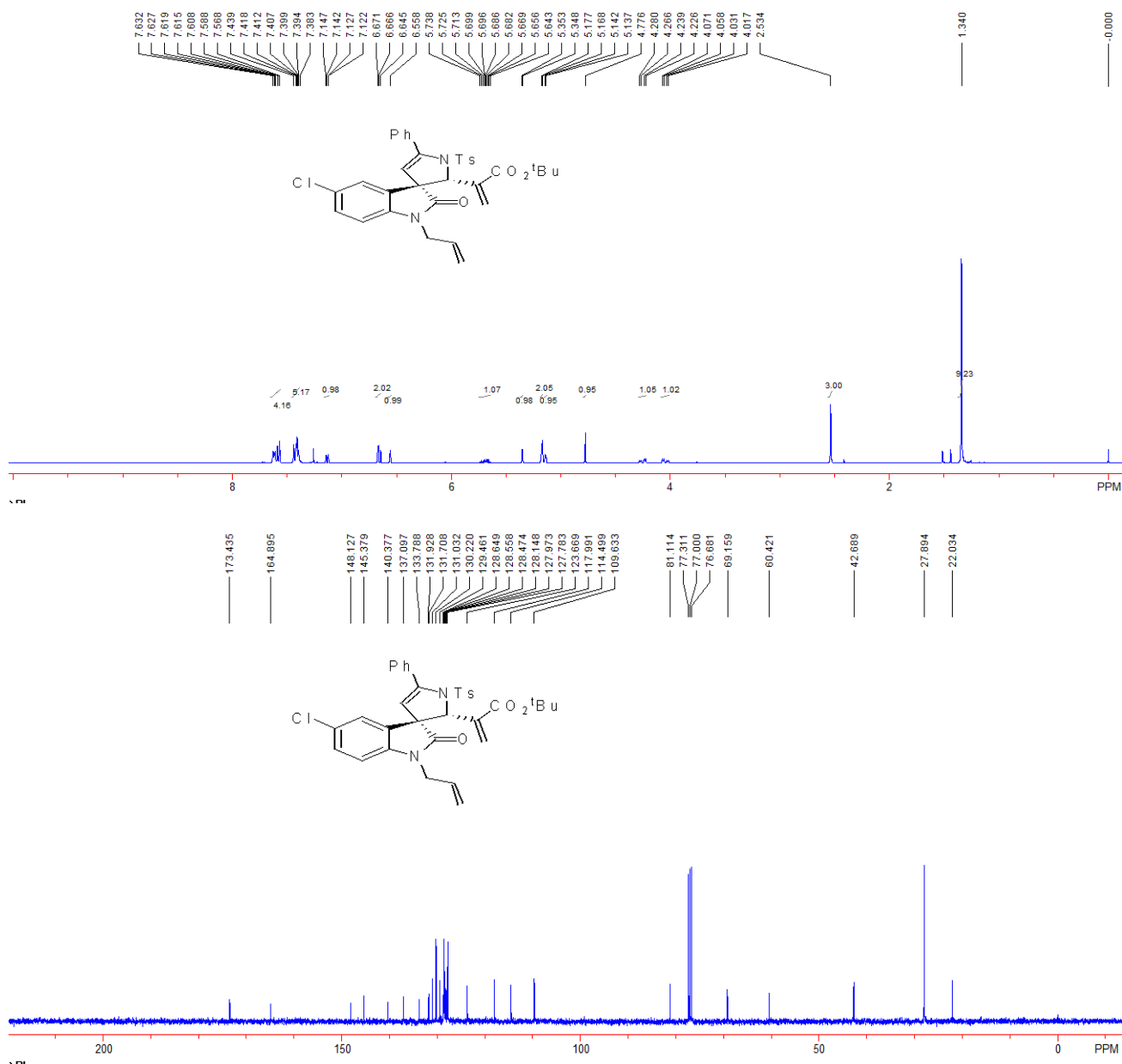


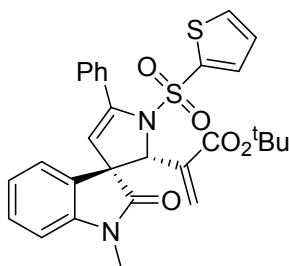
Compound 3n: A pale yellow solid, 83 mg, 62% yield; m.p. 177-178 °C; ^1H NMR (CDCl_3 , 400 MHz, TMS): δ 1.32 (s, 9H, 3 CH_3), 2.52 (s, 3H, CH_3), 4.43 (d, $J = 15.6$ Hz, 1H, CH_2), 4.81 (s, 1H, CH), 4.98 (d, $J = 15.6$ Hz, 1H, CH_2), 5.21 (s, 1H, =CH), 5.35 (d, $J = 2.0$ Hz, 1H, Ar), 6.51 (d, $J = 8.4$ Hz, 1H, Ar), 6.60 (s, 1H, = CH_2), 6.71 (s, 1H, = CH_2), 7.04 (dd, $J_1 = 8.4$ Hz, $J_2 = 2.0$ Hz, 1H, Ar), 7.17-7.23 (m, 5H, Ar), 7.39-7.44 (m, 5H, Ar), 7.57-7.65 (m, 4H, Ar); ^{13}C NMR (CDCl_3 , 100 MHz, TMS): δ 22.0, 27.8, 44.1, 60.6, 69.2, 81.2, 109.7, 114.6, 123.7, 127.3, 127.7, 127.8, 128.1, 128.2, 128.5, 128.6, 128.7, 128.8, 129.5, 130.2, 131.7, 131.9, 133.8, 135.2, 137.2, 140.2, 145.4, 148.2, 164.9, 174.0; HRMS (ESI) Calcd. For $\text{C}_{38}\text{H}_{36}\text{ClN}_2\text{O}_5\text{S}^+$ ($\text{M}+\text{H}$) $^+$ requires 667.2028, Found: 667.2023; IR (CH_2Cl_2): ν 685, 758, 815, 1089, 1158, 1327, 1445, 1475, 1548, 1607, 1716, 2920, 2954 cm^{-1} .



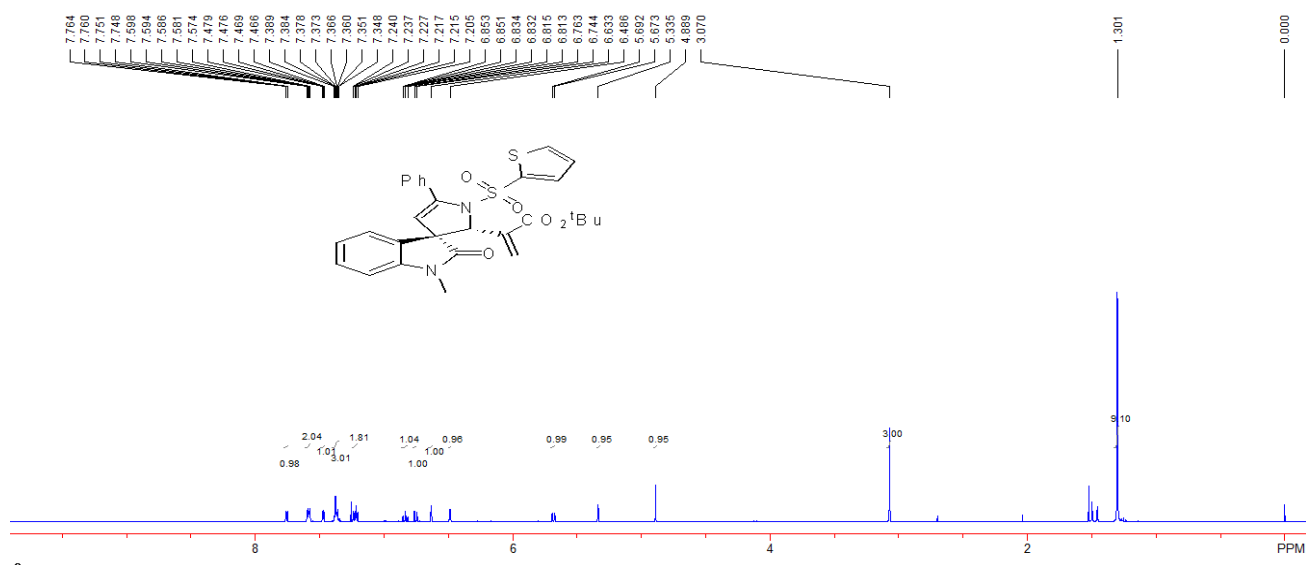
Compound 30: A pale yellow solid, 84 mg, 68% yield; m.p. 103-104 °C; ¹H NMR (CDCl₃, 400 MHz, TMS): δ 1.34 (s, 9H, 3CH₃), 2.53 (s, 3H, CH₃), 4.04 (dd, *J*₁ = 16.0 Hz, *J*₂ = 5.2 Hz, 1H, CH₂), 4.25 (dd, *J*₁ = 16.4 Hz, *J*₂ = 5.2 Hz, 1H, CH₂), 4.78 (s, 1H, CH), 5.14 (d, *J* = 2.0 Hz, 1H, =CH), 5.17

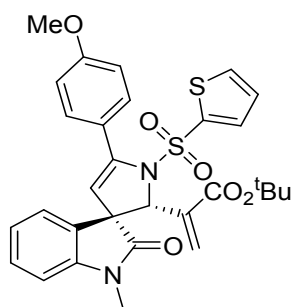
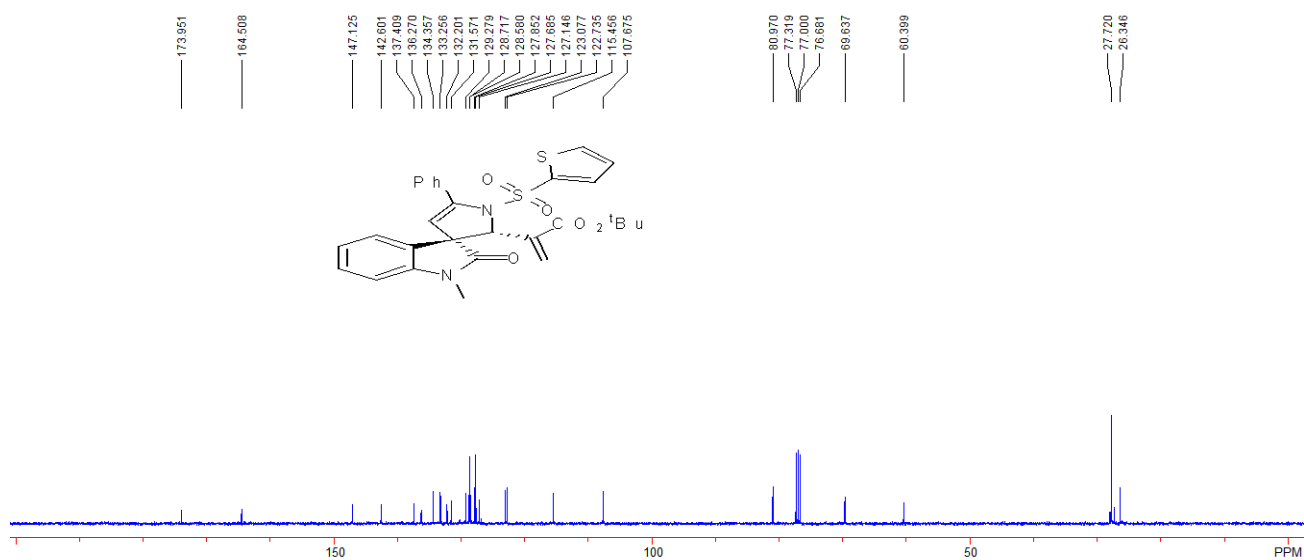
(d, $J = 3.6$ Hz, 2H, =CH₂), 5.35 (d, $J = 2.0$ Hz, 1H, Ar), 5.64-5.74 (m, 1H, =CH), 6.56 (s, 1H, =CH₂), 6.66 (d, $J = 8.4$ Hz, 1H, Ar), 6.67 (s, 1H, =CH₂), 7.13 (dd, $J_1 = 8.0$ Hz, $J_2 = 2.0$ Hz, 1H, Ar), 7.39-7.44 (m, 5H, Ar), 7.56-7.64 (m, 4H, Ar); ¹³C NMR (CDCl₃, 100 MHz, TMS): δ 22.0, 27.9, 42.7, 60.4, 69.2, 81.1, 109.6, 114.5, 118.0, 123.7, 127.8, 128.0, 128.1, 128.50, 128.56, 128.65, 129.5, 130.2, 131.0, 131.7, 131.9, 133.8, 137.1, 140.4, 145.4, 148.1, 164.9, 173.4; HRMS (ESI) Calcd. For C₃₄H₃₄ClN₂O₅S⁺ (M+H)⁺ requires 617.1871, Found: 617.1868; IR (CH₂Cl₂): ν 659, 695, 736, 753, 814, 1149, 1170, 1346, 1365, 1484, 1718, 2971 cm⁻¹.



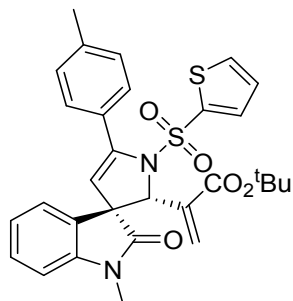
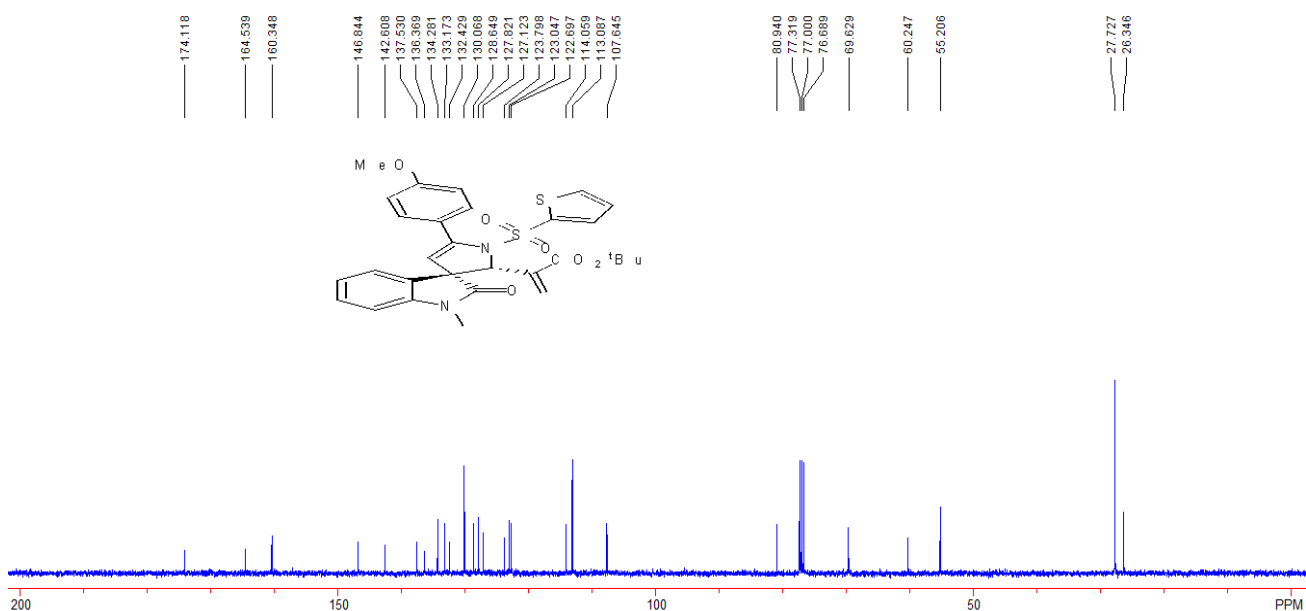
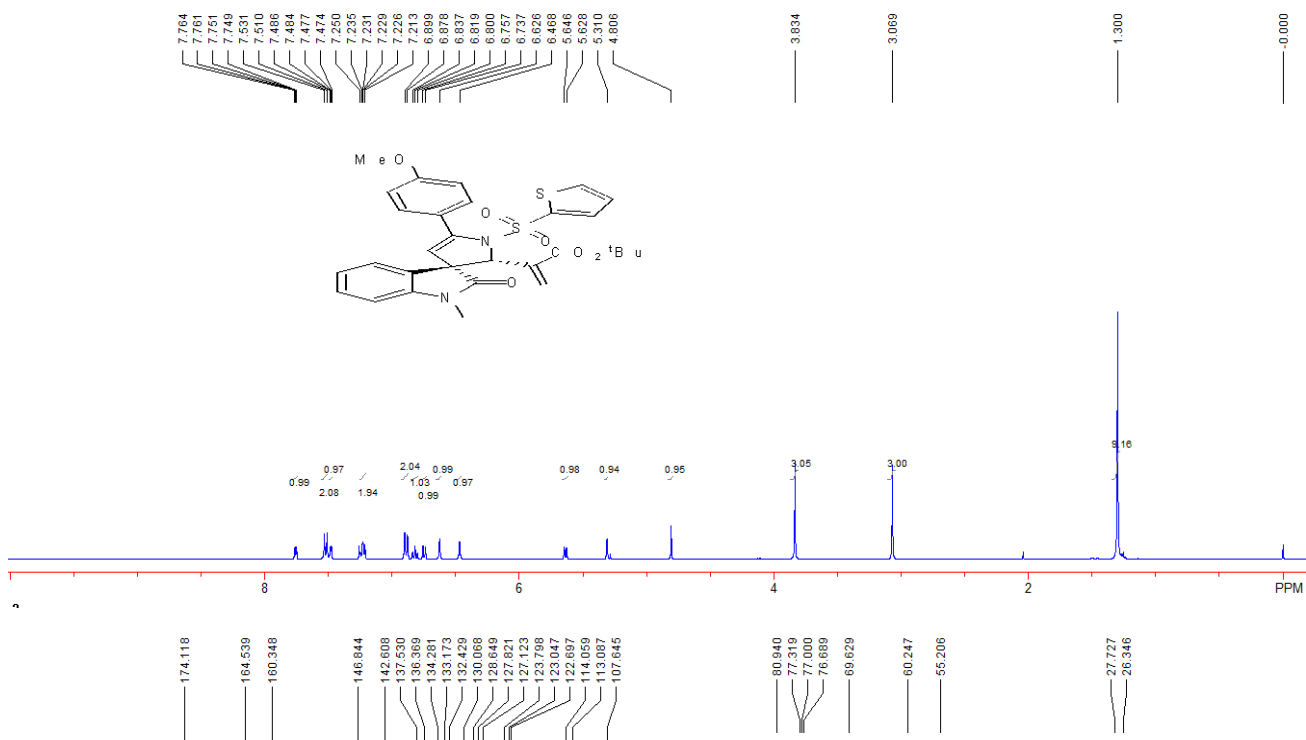


Compound 3p: A pale yellow solid, 92 mg, 84 yield; m.p. 152-153 °C; ^1H NMR (CDCl_3 , 400 MHz, TMS): δ 1.30 (s, 9H, 3CH_3), 3.07 (s, 3H, CH_3), 4.89 (s, 1H, CH), 5.34 (s, 1H, =CH), 5.68 (d, $J = 7.6$ Hz, 1H, Ar), 6.49 (s, 1H, = CH_2), 6.63 (s, 1H, = CH_2), 6.75 (d, $J = 7.6$ Hz, 1H, Ar), 6.83 (dt, $J_1 = 7.6$ Hz, $J_2 = 0.8$ Hz, 1H, Ar), 7.20-7.24 (m, 2H, Ar), 7.36-7.39 (m, 3H, Ar), 7.47 (dd, $J_1 = 4.0$ Hz, $J_2 = 0.8$ Hz, 1H, Ar), 7.57-7.60 (m, 2H, Ar), 7.76 (dd, $J_1 = 5.2$ Hz, $J_2 = 1.6$ Hz, 1H, Ar); ^{13}C NMR (CDCl_3 , 100 MHz, TMS): δ 26.3, 27.7, 60.4, 69.6, 81.0, 107.7, 115.5, 122.7, 123.1, 127.1, 127.7, 127.9, 128.6, 128.7, 129.3, 131.6, 132.2, 133.3, 134.4, 136.3, 137.4, 142.6, 147.1, 164.5, 174.0; HRMS (ESI) Calcd. For $\text{C}_{29}\text{H}_{29}\text{N}_2\text{O}_5\text{S}_2^+$ ($\text{M}+\text{H}$) $^+$ requires 549.1512, Found: 549.1509; IR (CH_2Cl_2): ν 668, 698, 732, 751, 849, 1149, 1169, 1368, 1467, 1489, 1610, 1712, 2971 cm^{-1} .



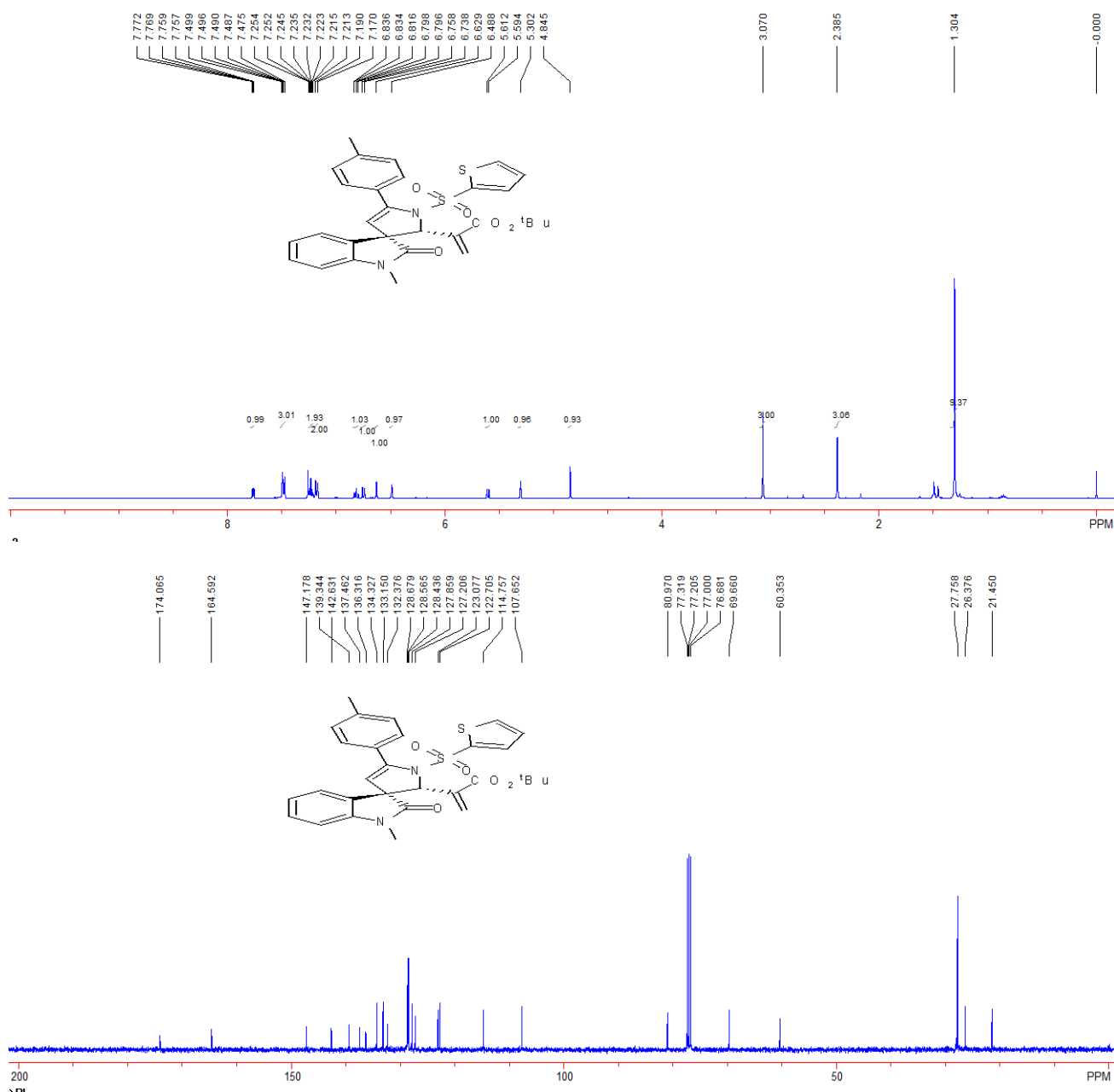


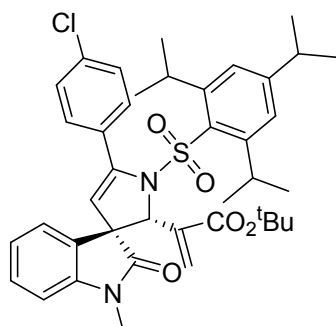
Compound 3q: A pale yellow solid, 93 mg, 80% yield; m.p. 196-197 °C; ^1H NMR (CDCl_3 , 400 MHz, TMS): δ 1.30 (s, 9H, 3 CH_3), 3.07 (s, 3H, CH_3), 3.83 (s, 3H, CH_3), 4.81 (s, 1H, CH), 5.31 (s, 1H, =CH), 5.64 (d, $J = 8.8$ Hz, 1H, Ar), 6.47 (s, 1H, = CH_2), 6.63 (s, 1H, = CH_2), 6.75 (d, $J = 8.0$ Hz, 1H, Ar), 6.82 (t, $J = 7.2$ Hz, 1H, Ar), 6.89 (d, $J = 8.4$ Hz, 2H, Ar), 7.21-7.25 (m, 2H, Ar), 7.48 (dd, $J_1 = 4.0$ Hz, $J_2 = 1.2$ Hz, 1H, Ar), 7.52 (d, $J = 8.4$ Hz, 2H, Ar), 7.76 (dd, $J_1 = 4.8$ Hz, $J_2 = 1.2$ Hz, 1H, Ar); ^{13}C NMR (CDCl_3 , 100 MHz, TMS): δ 26.3, 27.7, 55.2, 60.2, 69.6, 80.9, 107.6, 113.1, 114.1, 122.7, 123.0, 123.8, 127.1, 127.8, 128.6, 130.1, 132.4, 133.2, 134.3, 136.4, 137.5, 142.6, 146.8, 160.3, 164.5, 174.1; HRMS (ESI) Calcd. For $\text{C}_{30}\text{H}_{31}\text{N}_2\text{O}_6\text{S}_2^+$ ($\text{M}+\text{H}$) $^+$ requires 579.1618, Found: 579.1615; IR (CH_2Cl_2): ν 668, 680, 732, 837, 1030, 1082, 1148, 1168, 1250, 1366, 1467, 1510, 1609, 1714, 2924, 2954 cm^{-1} .



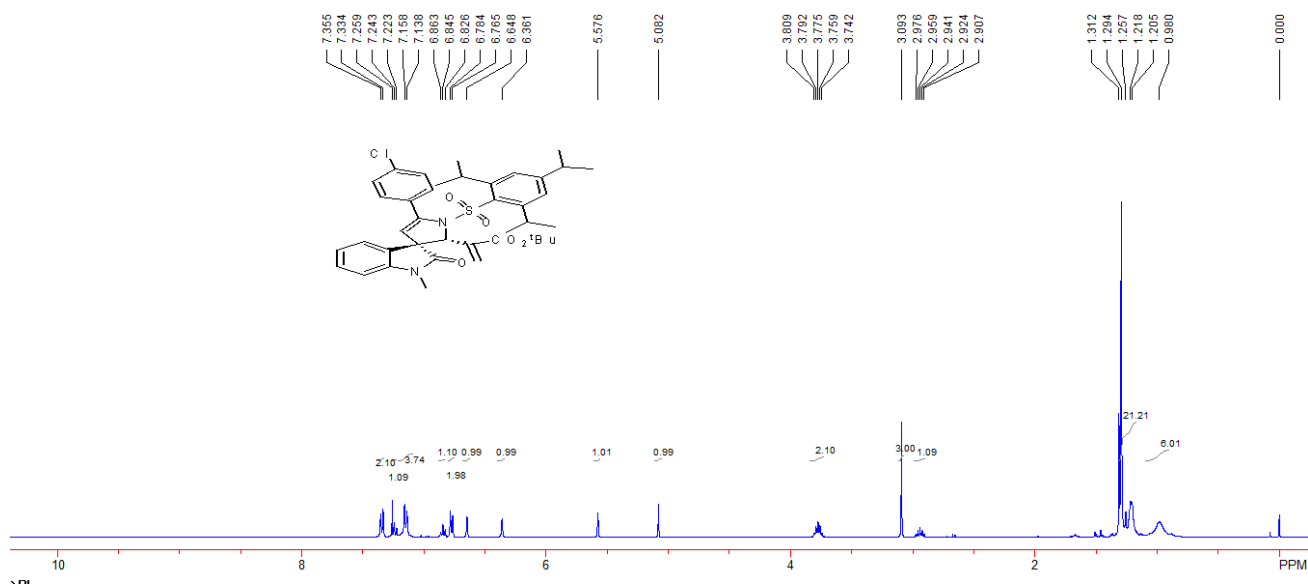
Compound 3r: A pale yellow solid, 85 mg, 76% yield; m.p. 117-118 °C; ¹H NMR (CDCl₃, 400 MHz, TMS): δ 1.30 (s, 9H, 3CH₃), 2.39 (s, 3H, CH₃), 3.07 (s, 3H, CH₃), 4.85 (s, 1H, CH), 5.30 (s,

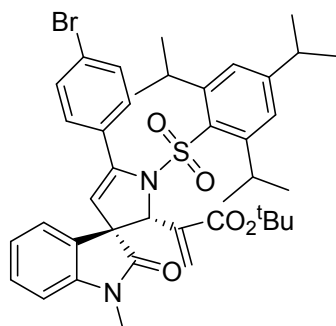
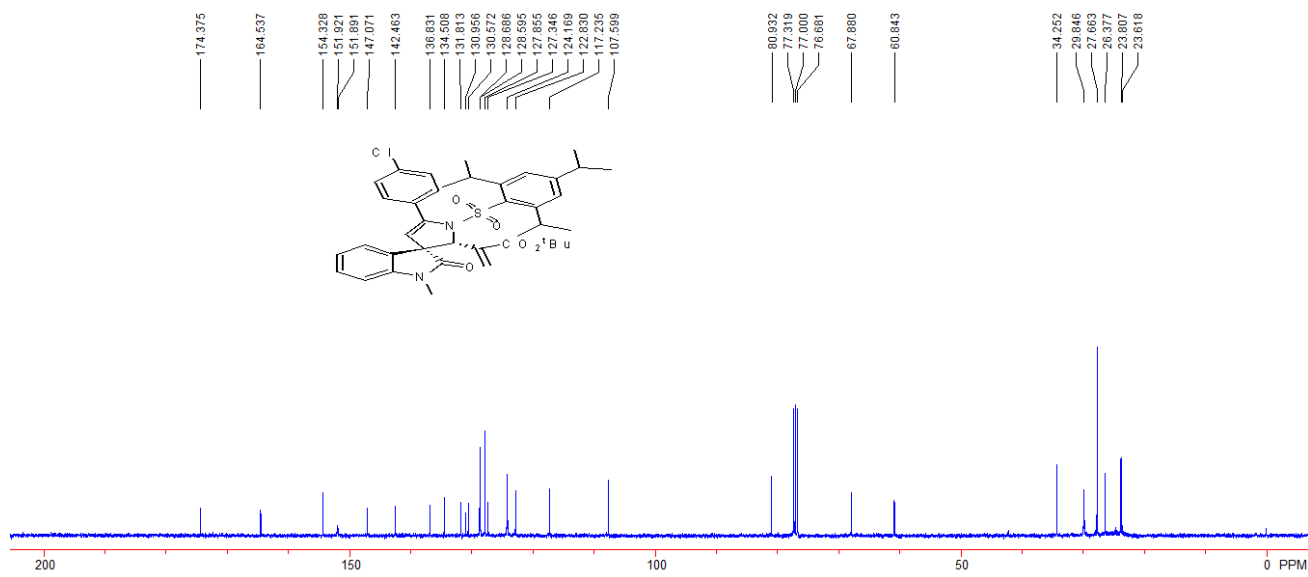
1H, =CH), 5.60 (d, $J = 7.2$ Hz, 1H, Ar), 6.49 (s, 1H, =CH₂), 6.63 (s, 1H, =CH₂), 6.75 (d, $J = 8.0$ Hz, 1H, Ar), 6.82 (dt, $J_1 = 8.0$ Hz, $J_2 = 0.8$ Hz, 1H, Ar), 7.18 (d, $J = 8.0$ Hz, 2H, Ar), 7.21-7.26 (m, 2H, Ar), 7.47-7.50 (m, 3H, Ar), 7.77 (dd, $J_1 = 5.2$ Hz, $J_2 = 1.2$ Hz, 1H, Ar); ¹³C NMR (CDCl₃, 100 MHz, TMS): δ 21.5, 26.4, 27.8, 60.4, 69.7, 81.0, 107.7, 114.8, 122.7, 123.1, 127.2, 127.9, 128.4, 128.6, 128.7, 132.4, 133.2, 134.3, 136.3, 137.5, 139.3, 142.6, 147.2, 164.6, 174.1; HRMS (ESI) Calcd. For C₃₀H₃₁N₂O₅S₂⁺ (M+H)⁺ requires 563.1669, Found: 563.1664; IR (CH₂Cl₂): ν 668, 680, 734, 814, 1020, 1035, 1083, 1149, 1169, 1256, 1367, 1470, 1491, 1610, 1715, 2971 cm⁻¹.



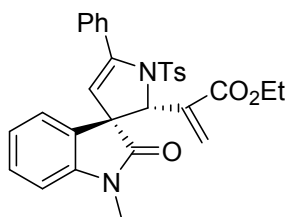
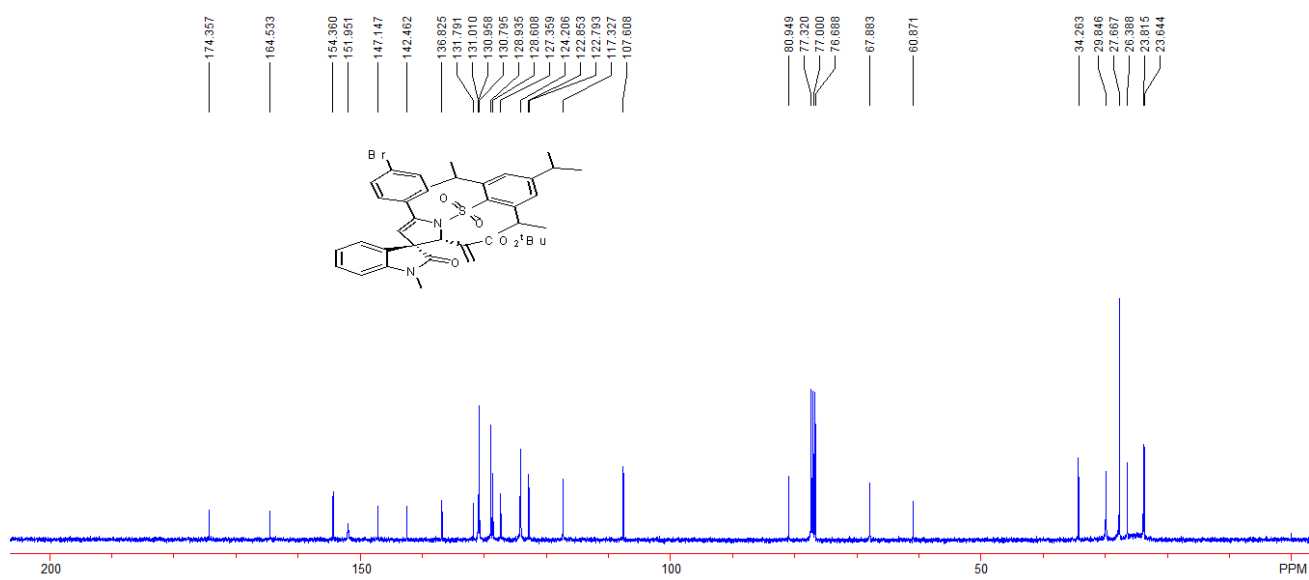
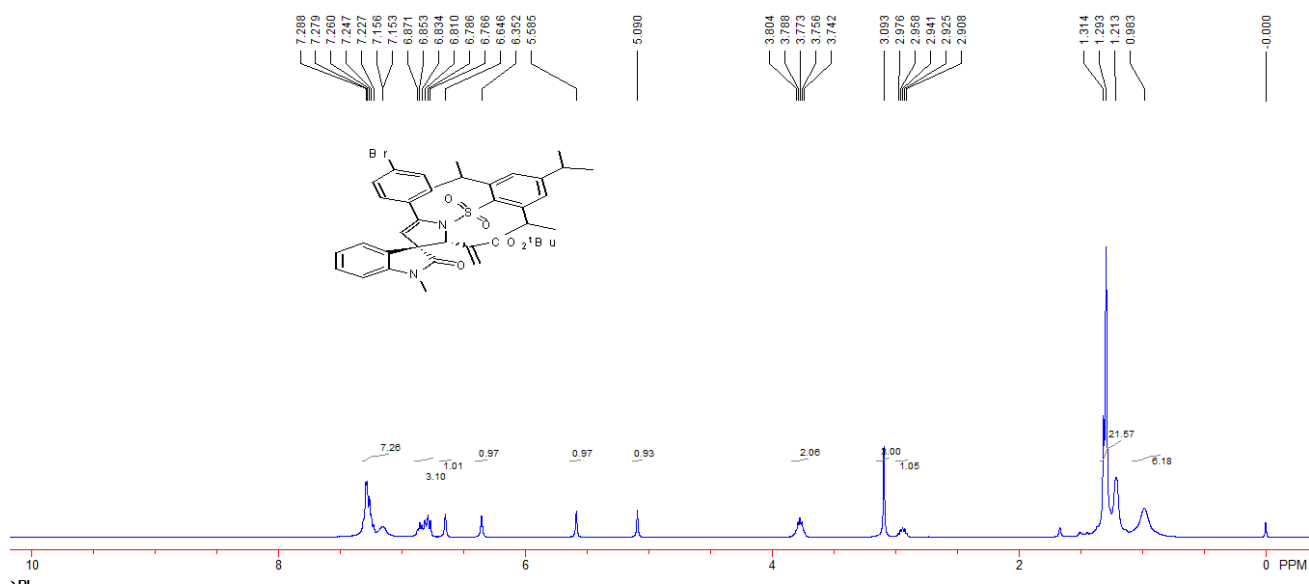


Compound 3s: A pale yellow solid, 116 mg, 83% yield; m.p. 124-125 °C; ^1H NMR (CDCl_3 , 400 MHz, TMS): δ 0.98 (s, 6H, 2 CH_3), 1.21-1.31 (m, 21H, 7 CH_3), 2.91-2.98 (m, 1H, CH), 3.09 (s, 3H, CH_3), 3.74-3.81 (m, 2H, 2CH), 5.08 (s, 1H, CH), 5.58 (s, 1H, =CH), 6.36 (s, 1H, = CH_2), 6.65 (s, 1H, = CH_2), 6.77 (d, $J = 7.6$ Hz, 2H, Ar), 6.85 (t, $J = 7.6$ Hz, 1H, Ar), 7.15 (d, $J = 8.0$ Hz, 4H, Ar), 7.24 (t, $J = 8.0$ Hz, 1H, Ar), 7.34 (d, $J = 8.4$ Hz, 2H, Ar); ^{13}C NMR (CDCl_3 , 100 MHz, TMS): δ 23.6, 23.8, 26.4, 27.7, 29.8, 34.3, 60.8, 67.9, 80.9, 107.6, 117.2, 122.8, 124.2, 127.3, 127.9, 128.6, 128.7, 130.6, 131.0, 131.8, 134.5, 136.8, 142.5, 147.1, 151.89, 151.92, 154.3, 164.5, 174.4; HRMS (ESI) Calcd. For $\text{C}_{40}\text{H}_{48}\text{ClN}_2\text{O}_5\text{S}^+$ ($\text{M}+\text{H}$) $^+$ requires 703.2967, Found: 703.2956; IR (CH_2Cl_2): ν 660, 672, 736, 750, 1088, 1150, 1257, 1315, 1345, 1370, 1491, 1610, 1715, 2959 cm^{-1} .



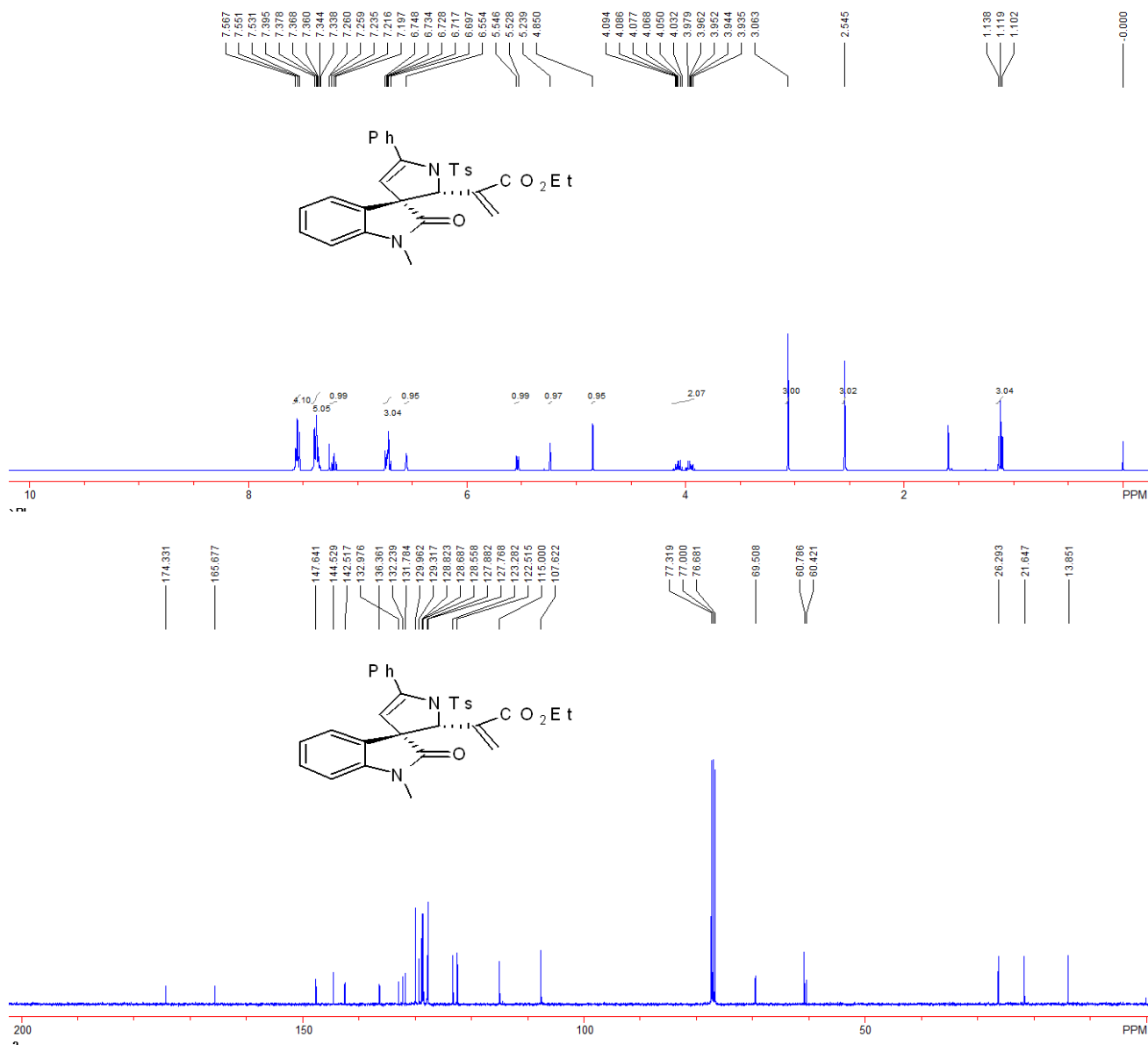


Compound 3t: A pale yellow solid, 122 mg, 82% yield; m.p. 130-131 °C; ^1H NMR (CDCl_3 , 400 MHz, TMS): δ 0.98 (s, 6H, 2 CH_3), 1.21-1.31 (m, 21H, 7 CH_3), 2.90-2.98 (m, 1H, CH), 3.09 (s, 3H, CH_3), 3.74-3.81 (m, 2H, 2CH), 5.09 (s, 1H, CH), 5.59 (s, 1H, =CH), 6.35 (s, 1H, = CH_2), 6.65 (s, 1H, = CH_2), 6.76-6.88 (m, 3H, Ar), 7.22-7.29 (m, 7H, Ar); ^{13}C NMR (CDCl_3 , 100 MHz, TMS): δ 23.6, 23.8, 26.4, 27.7, 29.8, 34.3, 60.9, 67.9, 80.9, 107.6, 117.3, 122.8, 122.9, 124.2, 127.4, 128.6, 128.9, 130.8, 130.96, 131.01, 131.8, 136.8, 142.5, 147.1, 152.0, 154.4, 164.5, 174.4; HRMS (ESI) Calcd. For $\text{C}_{40}\text{H}_{48}\text{BrN}_2\text{O}_5\text{S}^+$ ($\text{M}+\text{H}$) $^+$ requires 747.2462, Found: 747.2453; IR (CH_2Cl_2): ν 660, 735, 750, 818, 1009, 1150, 1171, 1370, 1610, 1715, 2951 cm^{-1} .



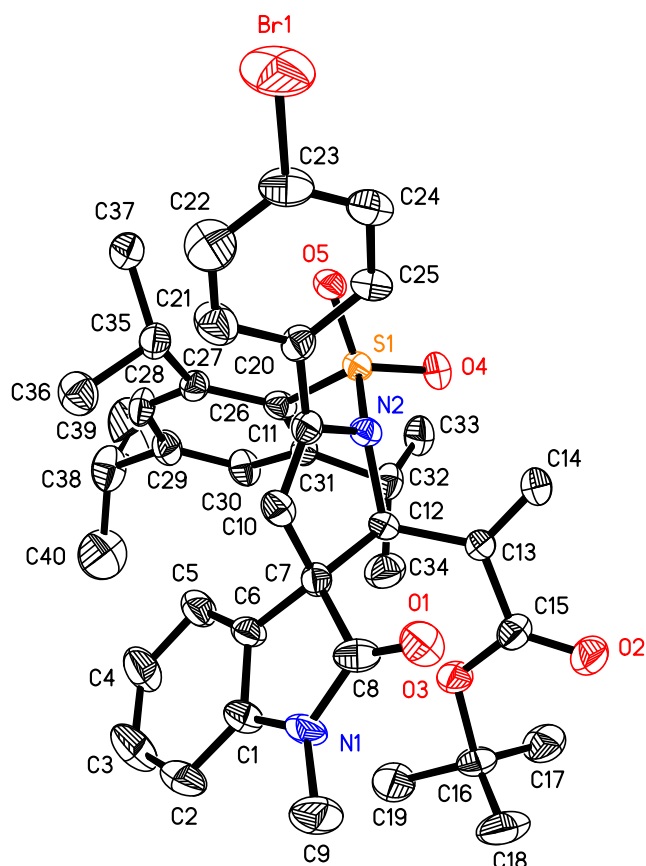
Compound 3u: A pale yellow solid, 88 mg, 85% yield; m.p. 98-99 °C; ^1H NMR (CDCl_3 , 400 MHz, TMS): δ 1.12 (t, $J = 7.6$ Hz, 3H, CH_3), 2.55 (s, 3H, CH_3), 3.06 (s, 3H, CH_3), 3.93-4.10 (m, 2H, CH_2), 4.85 (s, 1H, CH), 5.24 (s, 1H, =CH), 5.54 (d, $J = 7.2$ Hz, 1H, Ar), 6.55 (s, 1H, = CH_2), 6.69-6.75 (m, 3H, = CH_2 , Ar), 7.22 (t, $J = 7.6$ Hz, 1H, Ar), 7.34-7.40 (m, 5H, Ar), 7.53-7.57 (m, 4H, Ar); ^{13}C NMR

(CDCl₃, 100 MHz, TMS): δ 13.9, 21.7, 26.3, 60.4, 60.8, 69.5, 107.4, 115.0, 122.5, 123.3, 127.8, 127.9, 128.6, 128.7, 128.8, 129.3, 130.0, 131.8, 132.3, 133.0, 136.4, 142.5, 144.6, 147.7, 165.7, 174.4; HRMS (ESI) Calcd. For C₃₀H₂₉N₂O₅S⁺ (M+H)⁺ requires 529.1792, Found: 529.1791; IR (CH₂Cl₂): ν 662, 735, 752, 816, 1031, 1086, 1170, 1261, 1304, 1349, 1364, 1470, 1491, 1610, 1716, 2923 cm⁻¹.



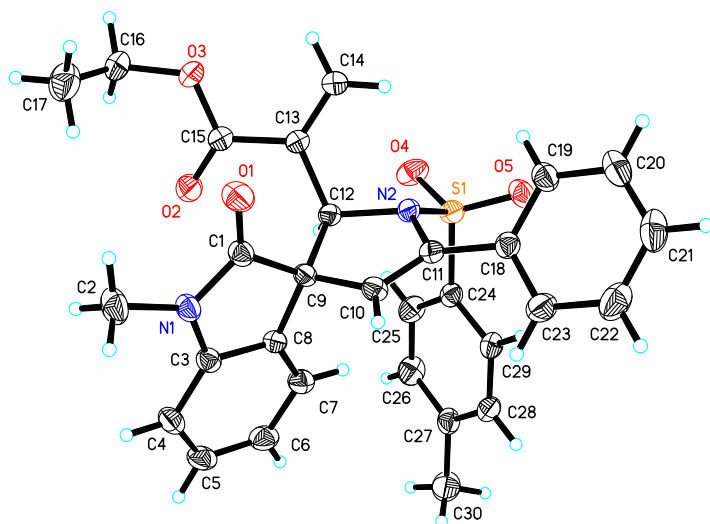
4. X-ray Data of 3t and 3u

X-ray Data of 3t



The crystal data of **3t** have been deposited in CCDC with number 1024783. Empirical Formula: $C_{41}H_{49}BrCl_2N_2O_5S$; Formula Weight: 832.69; Crystal Color, Habit: colorless; Crystal Dimensions: 0.211 x 0.123 x 0.106 mm³; Crystal System: Orthorhombic; Lattice Parameters: $a = 29.462(4)$ Å, $\alpha = 90$ deg. $b = 12.7234(15)$ Å, $\beta = 90$ deg. $c = 11.2553(14)$ Å, $\gamma = 90$ deg; $V = 4219.2(9)$ Å³; Space group: $Pca2_1$; $Z = 4$; $D_{calc} = 1.311$ g/cm³; $F_{000} = 1736$; Diffractometer: Rigaku AFC7R; Residuals: $R; R_w$: 0.0662, 0.1523.

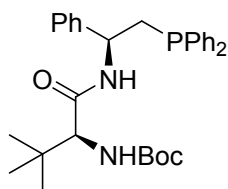
X-ray Data of **3u**



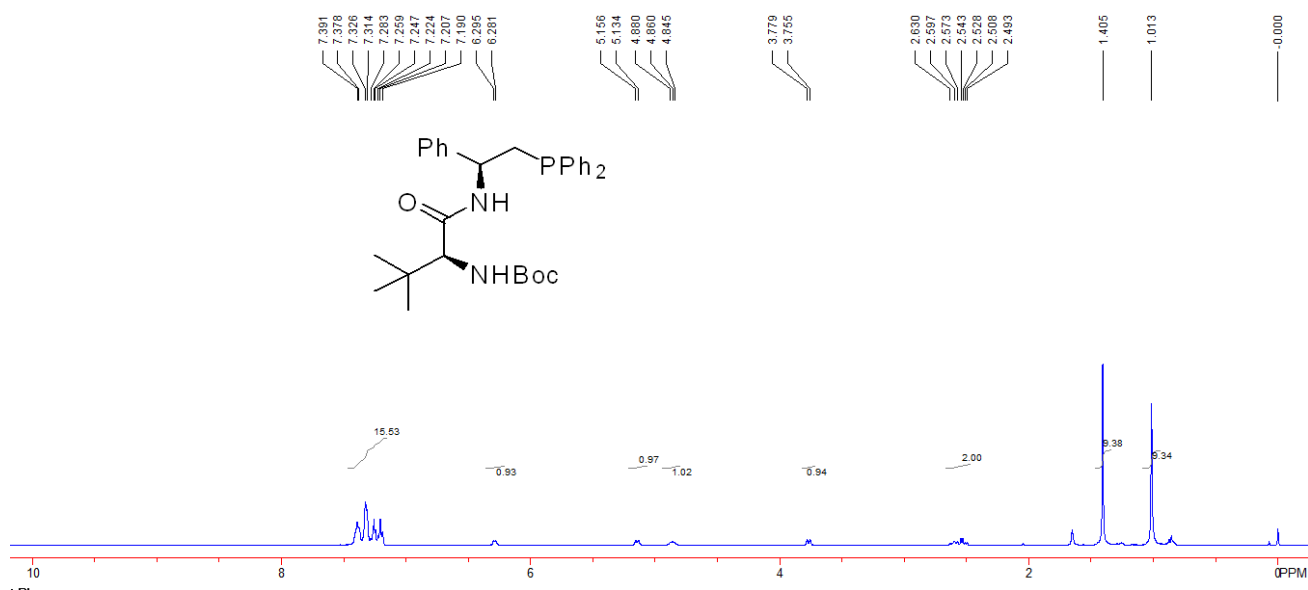
The crystal data of **3u** have been deposited in CCDC with number 1019412. Empirical Formula: $C_{30}H_{28}N_2O_4S$; Formula Weight: 528.60; Crystal Color, Habit: colorless; Crystal Dimensions: 0.320 x 0.220 x 0.20 mm³; Crystal System: Monoclinic; Lattice Parameters: $a = 13.2726(8)$ Å, $\alpha = 90$ deg. $b = 14.2499(8)$ Å, $\beta = 98.9150(10)$ deg. $c = 13.8765(8)$ Å, $\gamma = 90$ deg; $V = 2592.8(3)$ Å³; Space group: P 21/n; $Z = 4$; $D_{calc} = 1.354$ g/cm³; $F_{000} = 1112$; Diffractometer: Rigaku AFC7R; Residuals: $R; R_w: 0.0480, 0.1222$.

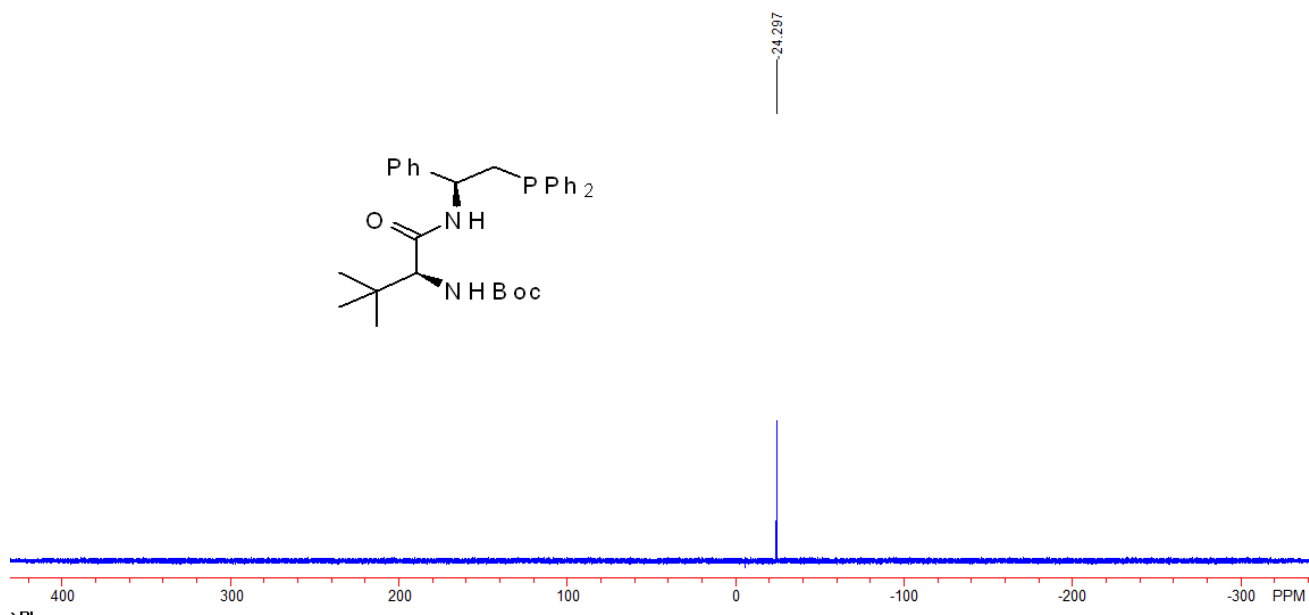
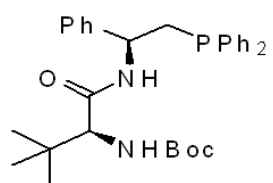
5. Synthesis of Chiral Organophosphane Catalyst CP.

Chiral organophosphane catalyst **CP** were prepared according to a procedure in the previous literature.²

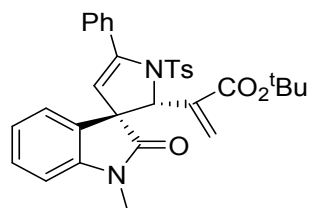


Chiral Organophosphane Catalyst CP: A white solid; m. p. 65-67 °C; ¹H NMR (CDCl₃, 400 MHz, TMS): δ 1.01 (s, 9H, 3CH₃), 1.41 (s, 9H, 3CH₃), 2.49-2.63 (m, 2H, CH₂), 3.77 (br, 1H, NH), 4.84-4.88 (m, 1H, CH), 5.15 (br, 1H, NH), 6.29 (br, 1H, CH), 7.19-7.40 (m, 15H, Ar); ³¹P NMR (CDCl₃, 161.94 MHz, 85% H₃PO₄): δ -24.30; IR (CH₂Cl₂) ν 696, 739, 802, 1013, 1048, 1067, 1170, 1245, 1366, 1391, 1434, 1455, 1495, 1652, 1699, 2964, 3053, 3324 cm⁻¹. HRMS (ESI) calcd. for C₃₁H₄₀N₂O₃P⁺ (M+H)⁺ requires: 519.2771, Found: 519.2784; [α]_D²⁰ = +12.8 (c 1.0, CH₂Cl₂).

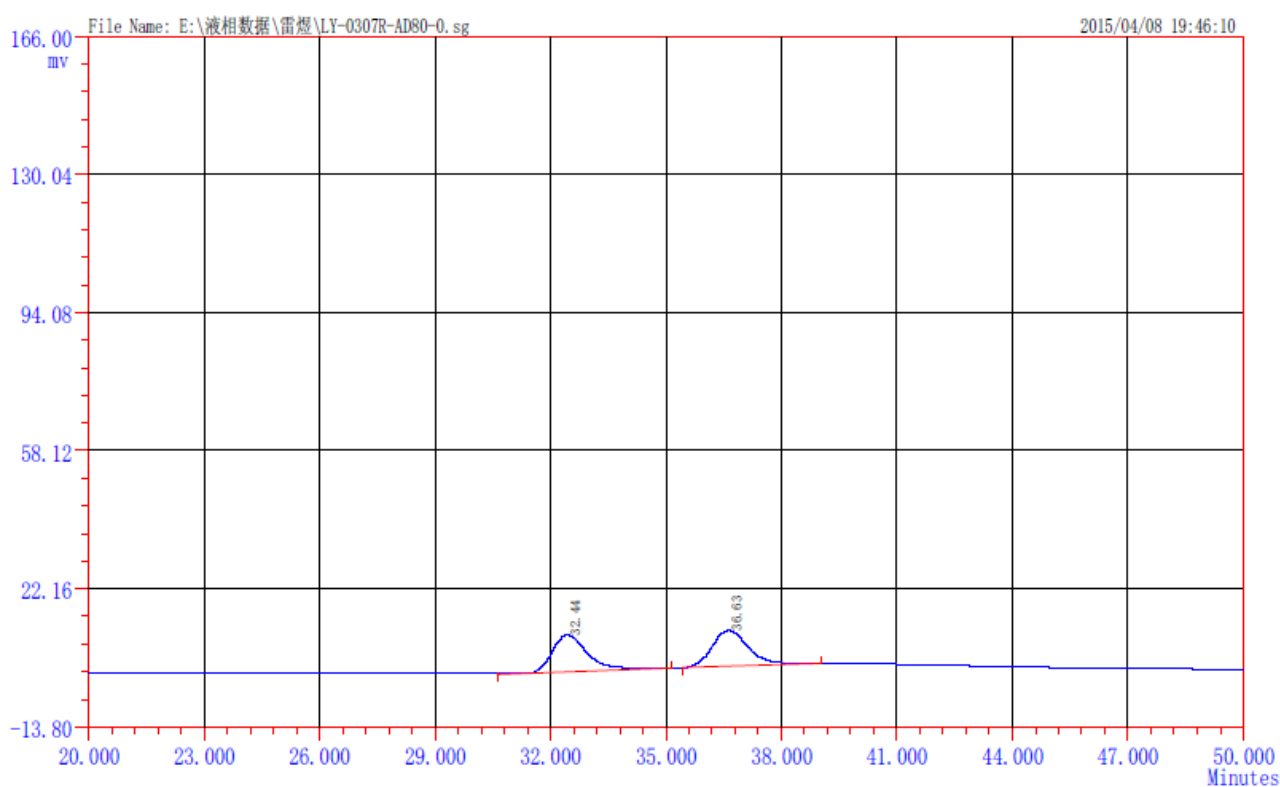




6. Copies of Chiral HPLC Data of Product 3a.

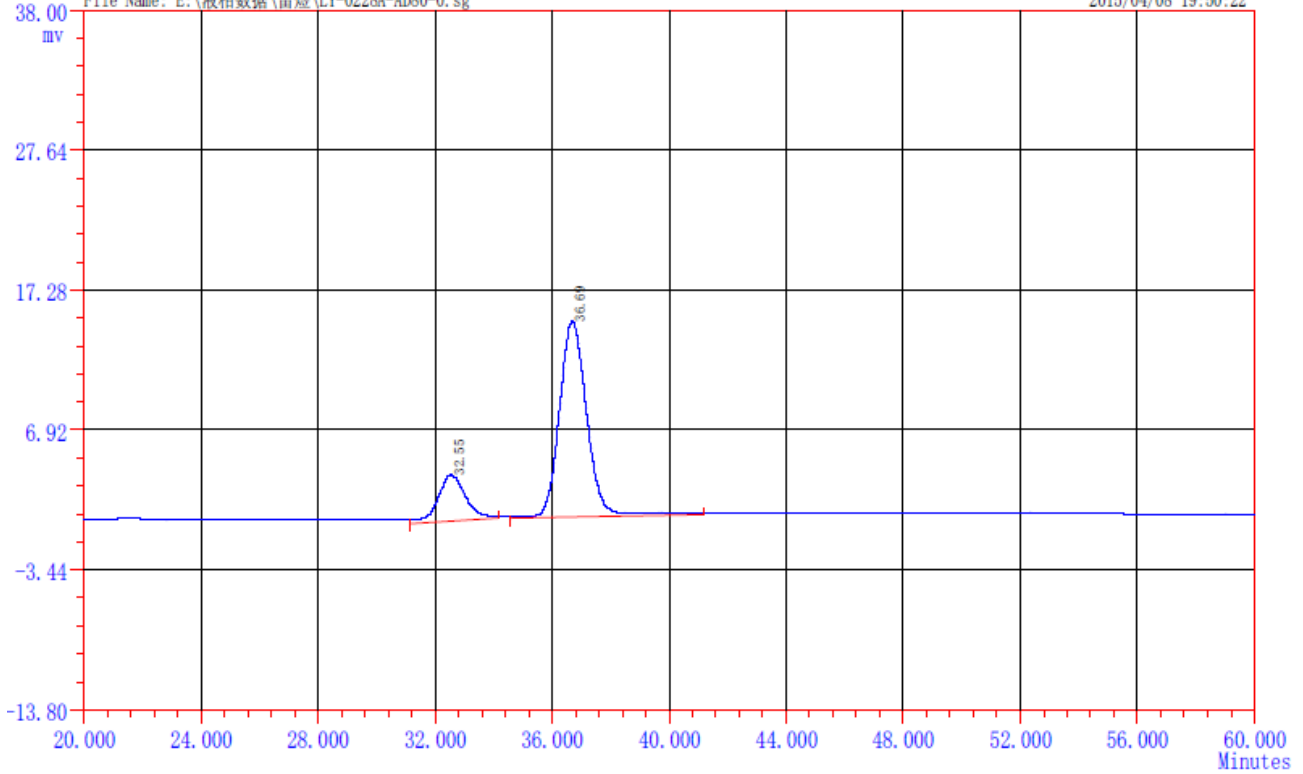


Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [$\lambda = 254 \text{ nm}$; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.60 mL/min; $t_{minor} = 32.55 \text{ min}$, $t_{major} = 36.69 \text{ min}$; $ee\% = 61\%$; $[\alpha]_D^{20} = +63.6$ (c 1.0, CH_2Cl_2)].



ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		32.443	9549	609980.4	49.7186	2.28	5141
2		36.632	9359	616886.2	50.2814	1.91	6156
Σ :			18908	1226866.6	100.0000		

NO.	R. Time	Peak Height	Pead Area	Percent
1	32.443	9549	609980.4	49.7186
2	36.632	9359	616886.2	50.2814
Total		18908	1226866.6	100.0000



ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		32.550	3435	229096.1	19.2840	1.33	4747
2		36.693	14474	958913.4	80.7160	1.13	6114
Σ:			17909	1188009.5	100.0000		

NO.	R. Time	Peak Height	Pead Area	Percent
1	32.550	3435	229096.1	19.2840
2	36.693	14474	958913.4	80.7160
Total		17909	1188009.5	100.0000

7. Reference

1. a) Z. Shi, Q. Tong, W. W. Y. Leong, G. Zhong, *Chem.-Eur. J.* 2012, **18**, 9802; b) K. Jiang, B. Tiwari, Y. R. Chi, *Org. Lett.* 2012, **14**, 2382; c) C. Sima, T. Lebl, A. M. Z. Slawin, A. D. Smith, *Angew. Chem. Int. Ed.* 2012, **51**, 3653.
2. H.-P. Deng, Y. Wei, M. Shi, *Adv. Synth. Catal.* 2012, **354**, 783.