Palladium-catalysed Ring-opening [3+2]-Annulation of Spirovinylcyclopropyl Oxindole to Diastereoselectively Access Spirooxindoles

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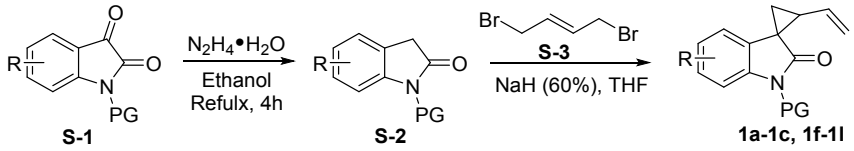
1. General Information

Unless otherwise noted, all the reagents were purchased from commercial suppliers and used without further purification. ^{1}H NMR spectra were recorded at 300 MHz. The chemical shifts were recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration. ^{13}C NMR data were collected at 75 MHz with complete proton decoupling. Chemical shifts were reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. Infrared spectra (IR) were measured by FT-IR apparatus. High resolution mass spectroscopy (HRMS) was recorded on TOF MS mass spectrometer and acetonitrile was used to dissolve the sample. Column chromatography was carried out on silica gel (200-300 mesh). All solvents and commercially available reagents were either purified via literature procedures or used without further purification. The N-protected isatin derivatives **S-1** and Spirovinylcyclopropane **5** were synthesized according to the refrences.[1-3]

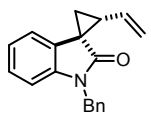
2. Experimental Procedures and Characterization Data

2.1 General procedure for the synthesis of spirovinylcyclopropanyl oxindole 1a-1c, 1g-1i.

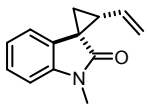


To a solution of N-protected isatin derivative **S-1** in ethanol (0.1 M) was added hydrazine hydrate (40% aqueous, 3.0 equiv.). The mixture was refluxed for 4 h, then ethanol was removed and extracted twice with EtOAc and washed with brine. The combined organic phases was dried and concentrated to afford the crude product 2-oxindole derivative **S-2**, which was used in the next step without further purification. To a solution of 2-oxindole derivative **S-2** in anhydrous THF was added NaH (3.0 equiv., 60% dispersion in mineral oil). The mixture was stirred at room temperature for 5 min and then 1,4-dibromo-2-butene **S-3** (1.0 equiv.) was added to it. The reaction mixture was stirred at room temperature for 10 min before then water (10 mL) was added to quench the excess NaH. The residue was extracted with twice with EtOAc and washed with brine. The organic phase was dried and concentrated in *vacuo*. The resulting residue was purified by flash column

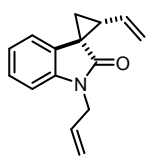
chromatography with PE:EtOAc = 19:1-9:1 to afford spirovinylcyclopropyl oxindole **1** as a white solid.



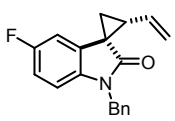
1′-Benzyl-2-vinylspiro[cyclopropane-1,3′-indolin]-2′-one (**1a**): White solid (2.6 g, 9.4 mmol, 47% yield over two steps); m.p. 97-99 °C; **IR (KBr)** ν 3080, 2935, 1794, 1696, 1612, 1465, 1365, 1173, 971, 904 cm^{-1}; IR (KBr) ν 3078, 2928, 1691, 1617, 1460, 1367, 1178, 906, 754cm^{-1}; **^{1}H NMR (DMSO-d_6, 300 MHz)** δ 7.23-7.35 (m, 5H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.06-7.08 (m, 1H), 6.94-6.99 (m, 2H), 6.11-6.23 (m, 1H), 5.30 (d, *J* = 17.1 Hz, 1H), 5.10 (d, *J* = 11.4 Hz, 1H), 2.68 (q, *J* = 8.7 Hz, 1H), 4.96 (s, 2H), 2 .12 (dd, *J* = 4.5, 8.7 Hz, 1H), 1.87 (dd, *J* = 4.5, 7.8 Hz,1H); **^{13}C NMR ($CDCl_3$, 75 MHz)** δ 174.8, 142.4, 136.2, 134.0, 130.4, 128.7, 127.5, 127.3, 126.7, 122.0, 118.0, 116.9, 108.9, 44.0, 37.5, 33.7, 24.9; **HRMS (TOF-ES+) m/z**: calcd for $C_{19}H_{17}NNaO$ $[M+Na]^+$ 298.1208, found 298.1193.



1′-Methyl-2-vinylspiro[cyclopropane-1,3′-indolin]-2′-one (**1b**): White solid (1.5 g, 7.6 mmol, 38% yield over two steps); m.p. 78-80 °C; **IR (KBr)** ν 3089, 2935, 1694, 1617, 1494, 1425, 1335, 1253, 1133, 906, 814 cm^{-1}; **^{1}H NMR ($CDCl_3$, 300 MHz)** δ 7.27 (t, *J* = 7.5 Hz, 1H), 7.06 (t, *J* = 9.0 Hz, 1H), 6.88 (t, *J* = 8.4 Hz, 2H), 6.21-6.34 (m, 1H), 5.26 (dd, *J* = 1.2, 17.1 Hz, 1H), 5.14 (dd, *J* = 1.5, 10.2 Hz, 1H), 3.29 (s, 3H), 2.51 (q, *J* = 8.7 Hz, 1H), 1.92-2.01 (m, 2H); **^{13}C NMR ($CDCl_3$, 75 MHz)** δ 174.6, 143.0, 134.1, 130.4, 126.8, 122.0, 117.9, 116.7, 37.1, 33.7, 26.5, 24.6; **HRMS (TOF-ES+) m/z**: $[M+Na]^+$ calcd for $C_{13}H_{13}NONa$ 222.0895, found 222.0885.

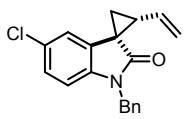


1′-Allyl-2-vinylspiro[cyclopropane-1,3′-indolin]-2′-one (**1c**): White solid (1.3 g, 5.8 mmol, 29% yield over two steps); m.p. 54-58 °C; **IR (KBr)** ν 2990, 1701, 1611, 1481, 1462, 1362, 1187, 993, 811, 749cm^{-1}; **^{1}H NMR ($CDCl_3$, 300 MHz)** δ 7.24 (td, *J* = 0.9, 7.5 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.86-6.91 (m, 2H), 6.27 (dt, *J* = 9.9, 17.1 Hz, 1H), 5.52-5.94 (m, 1H), 5.22-5.53(m, 3H), 5.14 (dd, *J* = 1.5, 10.2 Hz, 1H), 4.42-4.44 (m, 2H), 2.53 (q, *J* = 8.4 Hz, 1H), 1.94-2.03 (m, 2H); **^{13}C NMR ($CDCl_3$, 75 MHz)** δ 174.5, 142.5, 134.0, 131.9, 130.4, 126.7, 122.0, 118.0, 117.5, 116.8, 108.8, 42.7, 37.4, 33.6, 24.8; **HRMS (TOF-ES+) m/z**: $[M+Na]^+$ calcd for $C_{15}H_{15}NONa$ 248.1051, found 248.1041.

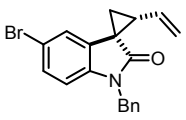


1′-Benzyl--5′-fluoro-2-vinylspiro[cyclopropane-1,3′-indolin]-2′-one (**1f**): White solid (1.8 g, 6.0 mmol, 30% yield over two steps); m.p. 79-81 °C; **IR (KBr)** ν 3071, 2993, 1699, 1602, 1484, 1362, 1160, 1008, 923,774 cm^{-1}; **^{1}H NMR ($CDCl_3$, 300 MHz)** δ 7.25-7.37 (m, 5H), 6.83 (td, *J* = 2.7, 8.7 Hz, 1H), 6.64 (ddd, *J* = 4.2, 8.4, 12.6 Hz, 1H), 6.24-6.36 (m, 1H), 5.31(dd, *J* = 1.5, 17.1

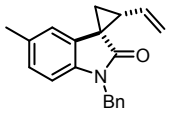
Hz, 1H), 5.20 (dd, *J* = 1.5, 10.5 Hz, 1H), 4.98 (s, 2H), 2.54 (dd, *J* = 8.7 Hz, 1H), 2 .10 (dd, *J* = 4.8, 7.8 Hz, 1H), 1.99 (dd, *J* = 4.8, 9 Hz, 1H); **^{13}C NMR ($CDCl_3$, 75 MHz)** δ 174.5, 160.8, 157.6, 138.2 (d, $J_{C\text{-}F}$ = 1.9 Hz), 135.9, 133.6, 132.2 (d, $J_{C\text{-}F}$ = 8.8 Hz), 128.8, 127.6, 127.3, 117.3, 113.0, 112.7, 109.3 (d, $J_{C\text{-}F}$ = 8.3 Hz), 106.3 (d, $J_{C\text{-}F}$ = 25.5 Hz), 44.2, 37.9, 34.1 (d, $J_{C\text{-}F}$ = 2.2 Hz), 25.1; **HRMS (TOF-ES+) m/z**: $[M+Na]^+$ calcd for $C_{19}H_{16}NOFNa$ 316.1114, found 316.1110.



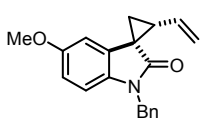
1′-Benzyl-5′-chloro-2-vinylspiro[cyclopropane-1,3′-indolin]-2′-one (**1g**): Colorless oil (1.7 g, 5 mmol, 27% yield over two steps); IR (KBr) ν 3053, 2918, 1701, 1485, 1367, 1280, 1178, 1006, 799, 744cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.30-7.33 (m, 1H), 7.23-7.25 (m, 2H), 6.97 (t, *J* = 4.2 Hz, 1H), 6.68 (s, 1H), 2.41-2.46 (m, 4H), 2.11 (s, 3H), 1.97-2.04 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 196.8, 169.4, 146.4, 141.0, 138.4, 129.7, 128.1, 127.0, 125.6, 70.9, 38.2, 25.8, 22.4, 21.2, 21.1; HRMS (TOF-ES+) m/z: calcd for $C_{19}H_{16}ClNONa$ $[M+Na]^+$ 332.0818, found 332.0809.



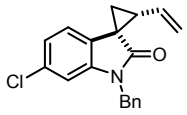
1′-Benzyl--5′-bromo-2-vinylspiro[cyclopropane-1,3′-indolin]-2′-one (**1h**): White solid (1.3 g, 3.6 mmol, 18% yield over two steps); m.p. 89-91 °C; **IR (KBr)** ν 3077, 2940, 1691, 1604, 1482, 1367, 1073, 986, 754 cm^{-1}; **^{1}H NMR ($CDCl_3$, 300 MHz)** δ 7.23-7.33 (m, 6H), 6.98 (d, *J* = 1.8 Hz, 1H), 6.63 (d, *J* = 8.4 Hz, 1H), 6.22-6.34 (m, 1H), 5.31(dd, *J* = 1.2, 17.1 Hz, 1H), 5.20 (dd, *J* = 1.5, 10.5 Hz, 1H), 4.97 (dd, *J* = 15.9, 18.0 Hz, 2H), 2.56 (q, *J* = 8.7 Hz, 1H), 2 .09 (dd, *J* = 4.9, 7.9 Hz, 1H), 2.01 (dd, *J* = 4.8, 8.8 Hz, 1H); **^{13}C NMR ($CDCl_3$, 75 MHz)** δ 174.2, 141.3, 135.7, 133.5, 132.6, 129.4, 128.8, 127.7, 127.2, 121.3, 117.5, 114.8, 110.2, 44.1, 37.9, 33.6, 25.1; **HRMS (TOF-ES+) m/z**: $[M+Na]^+$ calcd for $C_{19}H_{16}NOBrNa$ 376.0313, found 376.0312.



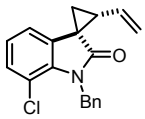
1′-Benzyl--5′-methyl-2-vinylspiro[cyclopropane-1,3′-indolin]-2′-one (**1i**): White solid (2.2 g, 7.6 mmol, 38% yield over two steps); m.p. 76-78 °C; **IR (KBr)** ν 3097, 2983, 1676, 1597, 1494, 1372, 1178, 991, 879, 752 cm^{-1}; **^{1}H NMR ($CDCl_3$, 300 MHz)** δ 7.25-7.36 (m, 5H), 6.96 (d, *J* = 7.5 Hz, 1H), 6.66-6.70 (m, 2H), 6.27-6.39 (m, 1H), 5.29 (dd, *J* = 1.5, 17.1 Hz, 1H), 5.17 (dd, *J* = 1.5, 10.2 Hz, 1H), 4.99 (s, 2H), 2.54 (dd, *J* = 8.7, 17.1 Hz, 1H), 2.33 (s, 3H), 2.06 (dd, *J* = 4.7, 7.8 Hz, 1H), 1.98 (dd, *J* = 4.7, 8.7 Hz,1H); **^{13}C NMR ($CDCl_3$,75 MHz)** δ 174.8, 140.1, 136.3, 134.2, 131.7, 130.5, 128.7, 127.5, 127.3, 127.0, 118.9, 116.8, 108.6, 44.0, 37.4, 33.7, 24.8, 21.1; **HRMS (TOF-ES+) m/z**: $[M+Na]^+$ calcd for $C_{20}H_{19}NONa$ 312.1364, found 312.1360.



1′-Benzyl--5′-methoxyl-2-vinylspiro[cyclopropane-1,3′-indolin]-2′-one (**1j**): White solid (1.3 g, 4.3 mmol, 22% yield over two steps); m.p. 99-101 °C; **IR (KBr)** ν 2920, 2828, 1694, 1494, 1372, 1233, 1170, 1028, 919, 757 cm^{-1}; **^{1}H NMR ($CDCl_3$, 300 MHz)** δ 7.27-7.34 (m, 5H), 6.65-6.71 (m, 2H), 6.49-6.50 (m, 1H), 6.28-6.40 (m, 1H), 5.31 (dd, *J* = 1.2, 17.1, 1H), 5.19 (dd, *J* = 1.5, 10.2, 1H), 4.98 (s, 2H), 3.78 (s, 3H), 2.54 (q, *J* = 8.7 Hz, 1H), 2.08 (dd, *J* = 4.5, 7.5, 1H), 1.98 (dd, *J* = 4.8, 8.7, 1H); **^{13}C NMR ($CDCl_3$, 75 MHz)** δ 174.6, 155.9, 136.3, 136.0, 134.1, 131.8, 128.7, 127.5, 127.3, 116.9, 110.9,109.2, 105.7, 55.8, 44.1, 37.7, 34.0, 24.9; **HRMS (TOF-ES+) m/z**: $[M+Na]^+$ calcd for $C_{20}H_{19}NO_2Na$ 328.1313, found 328.1299.

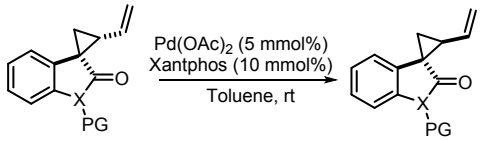


1′-Benzyl-6′-chloro-2-vinylspiro[cyclopropane-1,3′-indolin]-2′-one (**1k**): White solid (1.5 g, 4.9 mmol, 24% yield over two steps); m.p. 90-92 °C; **IR (KBr)** ν 3027, 2928, 1701, 1614, 1370, 1253, 1175, 1121, 1068, 998 cm^{-1}; **^{1}H NMR ($CDCl_3$, 300 MHz)** δ 7.26-7.38 (m, 5H), 6.99 (dd, *J* = 1.5, 7.8 Hz, 1H), 6.75-6.78 (m, 2H), 6.28 (m, 1H), 5.30 (dd, *J* = 1.5, 17.1 Hz, 1H), 5.19 (dd, *J* = 1.5, 10.2 Hz, 1H), 4.96 (s, 2H), 2.54 (q, *J* = 8.7 Hz, 1H), 2.08 (dd, *J* = 4.8, 7.8 Hz, 1H), 2.00 (dd, *J* = 4.8, 8.7 Hz, 1H); **^{13}C NMR ($CDCl_3$, 75 MHz)** δ 174.7, 143.5, 135.7, 133.6, 132.4, 128.9, 127.7, 127.3, 121.9, 118.9, 117.3, 109.4, 44.1, 37.7, 33.5, 25.0; **HRMS (TOF-ES+) m/z**: $[M+Na]^+$ calcd for $C_{19}H_{16}NOClNa$ 332.0818, found 332.0812.



1′-Benzyl-7′-chloro-2-vinylspiro[cyclopropane-1,3′-indolin]-2′-one (**1l**): White solid (1.1 g, 3.7 mmol, 18% yield over two steps); m.p. 101-103 °C; **IR (KBr)** ν 3077, 3029, 2958, 1701, 1609, 1455, 1360, 1168, 1013, 909, 732 cm^{-1}; **^{1}H NMR ($CDCl_3$, 300 MHz)** δ 7.12-7.35 (m, 5H), 7.13 (dd, *J* = 1.2, 8.1 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.75 (dd, *J* = 1.2, 7.5 Hz, 1H), 6.22-6.34 (m, 1H), 5.44 (dd, *J* = 16.2, 19.8 Hz, 2H), 5.31 (dd, *J* = 1.5, 17.4 Hz, 1H), 5.20 (dd, *J* = 1.5, 10.2 Hz, 1H), 2.56 (q, *J* = 8.7 Hz, 1H), 2.12 (dd, *J* = 4.8, 8.1 Hz, 1H), 2.03 (dd, *J* = 4.8, 8.7 Hz, 1H); **^{13}C NMR ($CDCl_3$, 75 MHz)** δ 175.2, 138.3, 137.9, 133.6, 129.2, 128.5, 127.1, 126.6, 122.9, 117.5, 116.4, 115.3, 45.0, 38.6, 33.6, 25.5; **HRMS (TOF-ES+) m/z**: $[M+Na]^+$ calcd for $C_{19}H_{16}NOClNa$ 332.0818, found 332.0811.

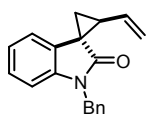
2.2 General procedure for the synthesis of diasteriomer SVCPs 1a' and 1b'



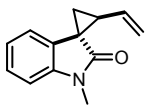
1a, PG = Bn
1b, PG = Me

1a′, PG = Bn
1b′, PG = Me

To a solution of SVCP (0.2 mmol) in toluene (2 mL) were added $Pd(OAc)_2$ (2.2 mg, 0.01 mmol) and Xantphos (11.5 mg, 0.02 mmol). The mixture was stirred at room temperature for 12 h. Then the solvent was removed and purified by column chromatography to afford diasteriomer **1a'** or **1b'** as a white solid.

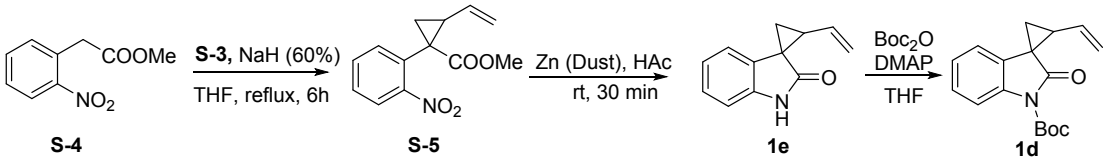


1′-Benzyl-2-vinylspiro[cyclopropane-1,3′-indolin]-2′-one (**1a**'): White solid (42.9 mg, 0.16 mmol, 74% yield); m.p. 95-96 °C; **IR (KBr)** ν 3075, 2944, 1781, 1660,, 1443, 1380, 1133, 964cm^{-1}; **^{1}H NMR ($CDCl_3$, 300 MHz)** δ 7.28-7.35 (m, 5H), 7.17 (dt, *J* = 1.8, 7.5 Hz, 1H), 6.95-7.04 (m, 2H), 6.83 (d, *J* = 7.8 Hz, 1H), 5.82-5.94 (m, 1H), 5.40 (d, *J* = 17.1 Hz, 1H), 5.28 (d, *J* = 10.5 Hz, 1H), 5.01 (dd, *J* = 15.6, 23.7 Hz, 2H), 2.73 (dd, *J* = 8.1, 16.5 Hz, 1H), 2.15 (dd, *J* = 4.8, 9.0 Hz, 1H), 1.73 (dd, *J* = 4.5, 7.8 Hz, 1H); **^{13}C NMR ($CDCl_3$, 75 MHz)** δ 176.3, 143.2, 135.2, 128.8, 127.6, 127.4, 126.7, 121.7, 121.0, 118.9, 109.1, 44.2, 35.6, 33.3, 23.3; **HRMS (TOF-ES+) m/z**: calcd for $C_{19}H_{17}NNaO$ $[M+Na]^+$ 298.1208, found 298.1211.



1′-Methyl-2-vinylspiro[cyclopropane-1,3′-indolin]-2′-one (**1b**'): White solid (26.3 mg, 13.2 mmol, 66% yield); m.p. 76-78 °C; **IR (KBr)** ν 3088, 2992, 1733, 1662, 1490, 1356, 1278, 1108, 975cm^{-1}; **^{1}H NMR ($CDCl_3$, 300 MHz)** δ 7.26-7.31 (m, 1H), 7.04 (dt, *J* = 0.9, 7.5 Hz, 1H), 6.94 (t, *J* = 8.1 Hz, 2H), 5.79-5.39 (m, 1H), 5.33-5.39 (m, 1H), 5.23-5.27 (m, 1H), 3.31 (s, 3H), 2.64 (dd, *J* = 7.8, 16.5 Hz, 1H), 2.08 (dd, *J* = 4.5, 8.7 Hz, 1H), 1.68 (dd, *J* = 4.5, 7.5 Hz, 1H); **^{13}C NMR ($CDCl_3$, 75 MHz)** δ 176.1, 144.1, 133.5, 127.5, 126.8, 121.6, 120.9, 118.7, 108.1, 35.4, 33.3, 26.6, 23.0; **HRMS (TOF-ES+) m/z**: $[M+Na]^+$ calcd for $C_{13}H_{13}NONa$ 222.0895, found 222.0893.

2.3 Experimental procedure for the synthesis of 1′-*t*-Butyloxycarbonyl-2-vinylspiro[cyclopropane-1,3′-indolin]-2′-one (1d) and 1′-H-2-vinylspiro[cyclopropane-1,3′-indolin]-2′-one (1e).

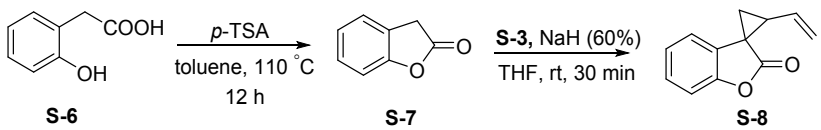


To a solution of 2-nitro benzoic methylester **S-4** (3.0 g, 15.4 mmol) in anhydours THF was add NaH (1.8 g, 46.2 mmol, 3.0 equiv., 60% dispersion in mineral oil) in small portions. The mixture was stirred at room temperature for 10 min, then 1,4-dibromo-2-butene **S-3** (1.0 equiv.) was added. The reaction mixture was refluxed for 6 h and water (10 mL) was added. The resulting mixture was extracted with EA (100 mL×2) and washed with brine (100 mL×2). The combined organic layers was dried, concentrated to yield the vinyl cyclopropane **S-5**. The vinyl cyclopropane **S-5** was then

used in the next step without further purification. To the solution of crude product vinyl cyclopropane **S-5** in AcOH (30 mL) was added Zn dust (5.0 g, 77 mmol, 5 equiv.) in small portions. The reaction mixture was stirred at room temperature for 30 minutes and EA (100 mL) was added. The mixture was extracted with EA (100 mL×2) and washed with saturated $NaHCO_3$. The combined organic layer was dried, concentrated and purified by flash column chromatography with PE:EtOAc = 9:1-5:1 to afford spirovinylcyclopropyl oxindole **1e** as white solid (1.1 g, 6.2 mmol, 40% yield over two steps). m.p. 132-134 °C; **IR (KBr)** ν 3084, 2851, 1798, 1619, 1474, 1357, 1310, 1196, 1195, 990, 742 cm^{-1}; **^{1}H NMR ($CDCl_3$, 300 MHz)** δ 8.98 (s, 1H), 7.21 (t, *J* = 7.8 Hz,1H), 6.96-7.06 (m, 2H), 6.85 (d, *J* = 7.5 Hz,1H), 6.26 (dt, *J* = 9.9, 17.2 Hz, 1H), 5.28 (d, *J* = 17.1 Hz, 3H), 5.16 (d, *J* = 10.2 Hz,1H), 2.53 (dd, *J* = 8.7, 17.1 Hz, 1H), 1.95-2.03 (m, 2H); **^{13}C NMR ($CDCl_3$, 75 MHz)** δ 176.4, 140.2, 133.8, 130.9, 126.8, 122.0, 118.3, 116.9, 109.4, 37.6, 33.9, 24.8; **HRMS (TOF-ES+) m/z**: $[M+Na]^+$ calcd for $C_{12}H_{11}NONa$ 208.0738, found 208.0731.

To a solution of spirovinylcyclopropyl oxindole **1d** (1.0 g, 5.4 mmol) in THF was added DMAP (65.9 mg, 0.54 mmol, 0.1 equiv.) and Boc_2O (1.4 g, 6.5 mmol, 1.2 equiv.) respectively. The reaction mixture was stirred at room temperature for 12 h and the solvent was removed. Then, 3N HCl (10 mL) was added and the mixture was extracted with EA (50 mL×2) and washed with brine (100 mL). the combined organic layers was dried, concentrated and purified by flash column chromatography with PE:EtOAc = 19:1-9:1 to afford spirovinylcyclopropyl oxindole **1d** as white solid (1.1 g, 3.8 mmol, 61% yield). m.p. 113-115 °C; **IR (KBr)** ν 3073, 2983, 1759, 1718, 1465, 1367, 1153, 1016, 914, 744cm^{-1}; **^{1}H NMR ($CDCl_3$, 300 MHz)** δ 7.88 (d, *J* = 8.1 Hz, 1H), 7.26-7.28 (m, 1H), 7.15-7.18 (m, 1H), 6.84 (dd, *J* = 0.9, 7.5 Hz, 1H), 6.15-6.27 (m, 1H), 5.28 (dd, *J* = 1.5, 17.1 Hz, 1H), 5.17 (dd, *J* = 1.5, 10.2 Hz, 1H), 2.50 (q, *J* = 8.7 Hz, 1H), 2.02-2.07 (m, 1H), 1.94-1.96 (m, 1H), 1.68 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)** δ173.0, 149.4, 139.2, 133.3, 127.0, 124.2, 117.7, 114.9, 84.2, 39.5, 34.1, 28.1, 26.3; **HRMS (TOF-ES+) m/z**: calcd for $C_{17}H_{19}NNaO_3$ $[M+Na]^+$ 308.1263, found 308.1255.

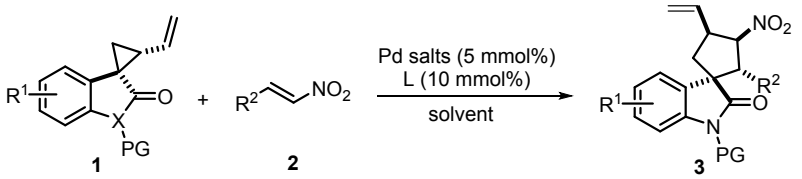
2.4 Experimental proceduce for the synthesis of 2'-vinylspiro[benzofunan-3(*2H*), 1'-cyclopropane]-2-one (1f).



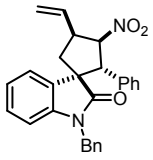
To a solution of 2-hydroxyphenylacetic acid (3.0 g, 19.7 mmol) in toluene (50 mL) was added *p*-TSA (0.68 g, 3.9 mmol, 0.2 equiv.). the reaction mixture was refluxed at 110 ℃ for 12 h. Then, the solvent was removed and the residue was extracted with EA (100 mL ×2) and washed with brine. The combined organic layers was dried, concentrated and purif

ied by flash column chromatography with PE:EtOAc = 19:1-9:1 to afford 2(3H)-benzofuranon e **S-8** as white solid (1.7 g, 6.1 mmol, 41% yield over two steps). m.p. 172-174 °C; **IR (KBr)** ν 2921, 2859, 1794, 1706, 1496, 1363, 928, 725cm^{-1}; **^{1}H NMR ($CDCl_3$, 300 MHz)** δ 7.26-7.31 (m, 1H), 7.12-7.17 (m, 2H), 6.88-6.91 (m, 1H), 6.04-6.16 (m, 1H), 5.33 (d, *J* = 17.1 Hz, 1H), 5.23 (d, *J* = 10.8 Hz, 1H), 2.58 (dd, *J* = 8.7, 17.4 Hz, 1H), 2.06 (d, *J* = 8.4 Hz, 2H); **^{13}C NMR ($CDCl_3$, 75 MHz)** δ 174.7, 153.3, 132.6, 128.9, 127.6, 124.0, 118.5, 118.4, 110.6, 38.6, 31.5, 26.1; **HRMS (TOF-ES+) m/z**: calcd for $C_{12}H_{10}NaO_2$ $[M+Na]^+$ 209.0578, found 209.0573.

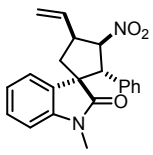
2.5 General Experimental procedure for the synthesis of spirooxindole 3.



To a solution of SVCP 1 (0.2 mmol) and α,β-unsaturated nitroalkene 2 (0.3 mmol, 1.5 equiv.) in toluene was added palladium salt (5 mol%) and ligand (10 mol%). The mixture was stirred at room temperature for the given time. Then the solvent was removed and purified by flash column chromatography with PE:EtOAc = 19:1-9:1 to afford spirooxindole **3** as white solid.

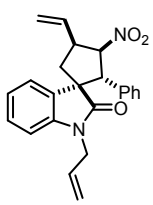


1'-Benzyl-2'-oxo-2-phenyl-3-nitro-4-vinylspiro[cyclopentane-1,3'-indoline] (**3a**): White solid (75.5 mg, 0.18 mmol, 89% yield, 86:14 *dr,* major diastereomer); m.p. 153-155 °C; **IR (KBr)** ν 3456, 3048, 2952, 1740, 1373, 1232, 1021, 893, 758cm^{-1}; **^{1}H NMR (DMSO-d_6, 300 MHz)** δ 7.77 (d, *J* = 7.5 Hz, 1H), 6.88-7.21 (m, 12H), 6.63-6.68 (m, 1H), 6.34 (t, *J* = 10.5 Hz, 1H), 5.84-5.96 (m, 1H), 5.34 (d, *J* = 16.8 Hz, 1H), 5.23 (d, *J* = 10.2 Hz, 1H), 5.00 (d, *J* = 15.9 Hz, 1H), 4.68 (d, *J* = 15.9 Hz, 1H), 4.55 (d, *J* = 11.1 Hz, 1H), 3.90-4.02 (m, 1H), 2.40-2.44 (m, 1H), 2.20-2.27 (m, 1H); **^{13}C NMR (DMSO-d_6, 75 MHz)** δ 177.3, 142.2, 136.1, 135.3, 134.5, 130.0, 129.0, 128.9, 128.7(4),128.7(1), 128.2, 127.6, 127.3, 125.5, 122.7, 120.0, 109.6, 92.0, 58.3, 57.2, 44.5, 43.3, 41.8; **HRMS (TOF-ES+) m/z**: calcd for $C_{27}H_{24}N_2NaO_3$ $[M+Na]^+$ 447.1685, found 447.1669.

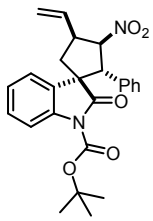


1'-Methyl-2'-oxo-2-phenyl-3-nitro-4-vinylspiro[cyclopentane-1,3'-indoline] (**3b)**: White solid (42.5 mg, 0.12 mmol, 61% yield, 83:17 *dr,* major diastereomer); m.p. 155-157 °C; **IR (KBr)** ν 3056, 2938, 1708, 1649, 1610, 1492, 1462, 997, 750cm^{-1}; **^{1}H NMR (DMSO-d_6, 300 MHz)**

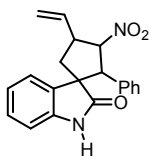
δ 7.70 (d, *J* = 7.5 Hz, 1H), 7.16 (t, *J* = 7.8 Hz, 1H), 6.90-7.08 (m, 6H), 6.80 (d, *J* = 7.8 Hz, 1H), 6.33 (t, *J* = 10.5 Hz, 1H), 5.83-5.95 (m, 1H), 5.34 (d, *J* = 16.8 Hz, 1H), 5.21 (d, *J* = 10.2 Hz, 1H), 4.69 (d, *J* = 10.8 Hz, 1H), 3.88-3.93 (m, 1H), 3.05 (s, 3H), 2.33-2.41 (m, 1H)， 2.14-2.21 (m, 1H); **^{13}C NMR (DMSO-d_6, 75 MHz)** δ 177.3, 143.1, 135.4, 134.7, 130.1, 128.7, 128.6, 128.0, 127.7, 125.2, 122.6, 119.9, 108.9, 91.6, 58.2, 56.9, 44.6, 41.4, 26.7; **HRMS (TOF-ES+) m/z**: calcd for $C_{21}H_{20}N_2NaO_3$ $[M+Na]^+$ 371.1372, found 371.1375.



1'-Allyl-2'-oxo-2-phenyl-3-nitro-4-vinylspiro[cyclopentane-1,3'-indoline] (**3c**): White solid 61.3 mg, 0.16 mmol, 82% yield, 86:14 *dr,* major diastereomer); m.p. 110-113 °C; **IR (KBr)** ν 3058, 2922, 1716, 1549, 1462, 1364, 986, 744cm^{-1}; **^{1}H NMR (DMSO-d_6, 300 MHz)** δ 7.75 (d, *J* = 7.5 Hz, 1H), 6.99-7.09 (m, 7H), 6.71 (d, *J* = 7.8 Hz, 1H), 6.34 (t, *J* = 10.5 Hz, 1H), 5.38-5.94 (m, 1H), 5.58-5.71 (m, 1H), 5.34 (d, *J* = 16.8 Hz, 1H), 5.22 (d, *J* = 10.2 Hz, 1H), 4.93 (d, *J* = 13.5 Hz, 1H), 4.58 (d, *J* = 17.1 Hz, 1H), 4.50 (d, *J* = 11.1 Hz, 1H), 4.33-4.40 (m, 1H), 4.09-4.16 (m, 1H), 3.91-4.00 (m, 1H), 2.36-2.43 (m, 1H), 2.17-2.24 (m, 1H); **^{13}C NMR (DMSO-d_6, 75 MHz)** δ 177.0, 142.2, 135.4, 134.5, 131.7, 130.0, 128.7, 128.6, 128.1, 128.0, 125.4, 122.6, 120.0, 116.7, 109.5, 91.8, 58.2, 57.2, 44.5, 42.1, 41.5; **HRMS (TOF-ES+) m/z**: calcd for $C_{23}H_{22}N_2NaO_3$ $[M+Na]^+$ 397.1528, found 397.1534.

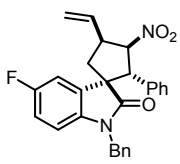


1'-*t*-Butyl**o**xy **c**arbonyl-2'-oxo-2-phenyl-3-nitro-4-vinylspiro[cyclopentane-1,3'-indoline] (**3d**): Wax-like solid (48.6 mg, 0.11 mmol, 56% yield, 88:12 *dr,* major diastereomer); **IR (KBr)** ν 3456, 3048, 2952, 1740, 1373, 1232, 1021, 893, 758cm^{-1}; **^{1}H NMR ($CDCl_3$, 300 MHz)** δ 7.63-7.65 (m, 1H), 7.27-7.30 (m, 2H), 7.17-7.24 (m, 2H), 7.03-7.08 (m, 2H), 6.89-6.92 (m, 2H), 5.91-6.02 (m, 1H), 5.77-5.84 (m, 1H), 5.24-5.35 (m, 2H), 4.68 (d, *J* = 11.7 Hz, 1H), 3.72-3.84 (m, 1H), 2.67 (dd, *J* = 8.7, 13.5 Hz,1H), 2.35 (dd, *J* = 7.8, 13.5 Hz, 1H), 1.62 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)** δ 176.3, 148.6, 139.1, 135.3, 134.3, 132.8, 129.0, 128.9, 128.3, 128.1, 127.3, 124.3, 123.4, 120.0, 118.9, 115.3, 114.9, 91.2, 84.6, 59.7, 58.5, 57.7, 56.9, 44.5, 41.2, 28.0; **HRMS (TOF-ES+) m/z**: calcd for $C_{25}H_{26}N_2NaO_5$ $[M+Na]^+$ 457.1739, found 457.1753.

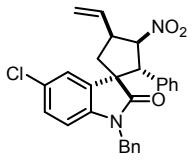


1'-H-2'-oxo-2-phenyl-3-nitro-4-vinylspiro[cyclopentane-1,3'-indoline] (**3e**): White solid (44.8 mg, 0.13 mmol, 67% yield, mixture of two diastereomers, 51:49 *dr,* mixture of two diastereomers); m.p. 189-191 °C; **IR (KBr)** ν 3081, 2957, 1792, 1708, 1616, 1465, 952, 869cm^{-1}; **^{1}H NMR (DMSO-d_6, 300 MHz)** δ 10.48-10.50 (m, 1.4H), 7.65 (d, *J* = 7.5 Hz, 1.0H), 7.46 (d, *J* = 7.5 Hz, 0.5H), 7.00-7.11 (m, 8.2H), 6.92 (t, *J* = 7.8 Hz, 1.2H), 6.81 (t, *J* = 7.5 Hz,

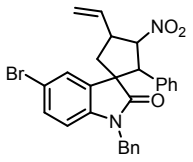
0.5H), 6.63 (d, *J* = 7.5 Hz, 0.9H), 6.58 (d, *J* = 7.5 Hz, 0.5H), 6.30 (t, *J* = 10.2 Hz, 1.0H), 6.01-6.12 (m, 1.0H), 5.80-5.92 (m, 1.0H), 5.26-5.34 (m, 1.5H), 5.21 (d, *J* = 10.2 Hz, 1.4H), 4.14 (d, *J* = 10.8 Hz, 1.0H), 4.28 (d, *J* = 12.0 Hz, 0.5H), 3.82-3.94 (m, 1.0H), 3.45-3.51 (m, 0.5H), 2.30-2.37 (m, 1.0H), 2.12-2.19 (m, 1.0H), 1.93-2.01 (m, 0.6H); **^{13}C NMR (DMSO-d_6, 75 MHz)** δ 181.1, 179.0, 141.6, 136.8, 135.4, 134.9, 134.5, 132.1, 128.6(4), 128.5(7), 128.0(0), 127.8(8), 126.0, 125.6, 121.9, 119.9, 118.9, 109.9, 109.5, 91.9, 91.3, 58.6, 56.8, 56.1, 49.1, 44.6, 41.7; **HRMS (TOF-ES+) m/z**: calcd for $C_{20}H_{18}N_2NaO_3$ $[M+Na]^+$ 357.1215, found 357.1224.



1'-Benzyl-2'-oxo-2-phenyl-3-nitro-4-vinylspiro[cyclopentane-1,3'-(5'-flouro-indoline)] (**3f**): White solid 66.3 mg, 0.15 mmol, 75% yield, 83:17 *dr*, major diastereomer); m.p. 161-163 °C; **IR (KBr)** ν 3087, 2921, 1710, 1652, 1559, 1490, 978, 817cm^{-1}; **^{1}H NMR ($CDCl_3$, 300 MHz)** δ 7.10-7.24 (m, 8H), 7.05-7.08 (m, 2H), 6.79-6.82 (m, 1H), 6.74 (d, *J* = 7.2 Hz, 1H), 6.37-6.41 (m, 1H), 5.90-6.02 (m, 1H), 5.81 (t, *J* = 10.8 Hz, 1H), 5.36 (d, *J* = 16.8 Hz, 1H), 5.28 (d, *J* = 9.9 Hz, 1H), 5.14 (d, *J* = 16.2 Hz, 1H), 4.74 (d, *J* = 11.4 Hz, 1H), 4.51 (d, *J* = 15.9 Hz, 1H), 3.73-3.87 (m, 1H), 2.66-2.73 (m, 1H), 2.29-2.36 (m, 1H); **^{13}C NMR ($CDCl_3$, 75 MHz)** δ 176.7, 160.5, 157.3, 138.3 (d, $J_{C\text{-}F}$ = 1.5 Hz), 134.5, 134.2, 133.0, 131.5 (d, $J_{C\text{-}F}$ = 7.5 Hz), 128.7, 128.6, 128.2, 127.9, 127.5, 126.6, 120.1, 115.0 (d, $J_{C\text{-}F}$ = 22.5 Hz), 112.0 (d, $J_{C\text{-}F}$ = 24.8 Hz), 110.3 (d, $J_{C\text{-}F}$ = 7.5 Hz), 91.7, 58.7, 57.1, 44.5, 44.0, 40.9; **HRMS (TOF-ES+) m/z**: calcd for $C_{27}H_{23}FN_2NaO_3$ $[M+Na]^+$ 465.1590, found 465.1592.

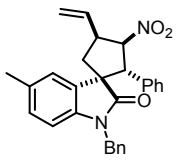


1'-Benzyl-2'-oxo-2-phenyl-3-nitro-4-vinylspiro[cyclopentane-1,3'-(5'-chloro-indoline)] (**3g**): White solid (75.1 mg, 0.16 mmol, 82% yield, 79:21 *dr,* major diastereomer); m.p. 167-169 °C; **IR (KBr)** ν 3033, 2980, 1714, 1548, 1488, 1356, 1190, 928, 819cm^{-1}; **^{1}H NMR (DMSO-d_6, 300 MHz)** δ 7.93 (d, *J* = 1.5 Hz, 1H), 7.20-7.22 (m, 4H), 7.07-7.13 (m, 4H), 7.01-7.03 (m, 2H), 6.93-6.95 (m, 2H), 6.66 (d, *J* = 8.4 Hz, 1H), 6.44 (t, *J* = 10.5 Hz, 1H), 5.85-5.96 (m, 1H), 5.34 (d, *J* = 16.8 Hz, 1H), 5.22 (d, *J* = 10.2 Hz, 1H), 5.00 (d, *J* = 15.9 Hz, 1H), 4.69 (d, *J* = 15.9 Hz, 1H), 4.54 (d, *J* = 10.8 Hz, 1H), 3.87-3.97 (m, 1H), 2.38-2.45 (m, 1H), 2.26-2.33 (m, 1H); **^{13}C NMR (DMSO-d_6, 75 MHz)** δ 177.3, 141.1, 135.8, 135.2, 134.3, 132.1, 129.0, 128.9, 128.7, 128.3, 128.1, 127.8, 127.3, 125.8, 120.1, 110.9, 91.5, 58.5, 57.1, 55.7, 44.5, 43.5, 41.5; **HRMS (TOF-ES+) m/z**: calcd for $C_{27}H_{23}ClN_2NaO_3$ $[M+Na]^+$ 481.1295, found 481.1281.

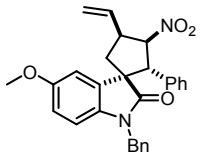


1'-Benzyl-2'-oxo-2-phenyl-3-nitro-4-vinylspiro[cyclopentane-1,3'-(5'-bromo-indoline)] (**3h**): White solid (84.3 mg, 0.17 mmol, 84% yield, 57:43 *dr*, mixture of two diasteriomers); m.p. 164-167 °C; **IR**

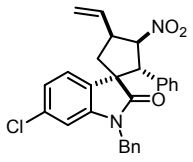
(KBr) ν 3153, 2925, 1714, 1549, 1484, 1350, 926, 871cm^{-1}; **^{1}H NMR (DMSO-d_6, 300 MHz)** δ 8.03 (s, 1.0H), 7.86 (s, 0.7H), 7.27-7.34 (m, 3.4H), 7.19-7.22 (m, 5.5H), 7.01-7.13 (m, 8.8H), 6.93-6.95 (m, 2.2H), 6.60-6.67 (m, 1.8H), 6.45 (t, *J* = 10.5 Hz, 1.0H), 6.23 (t, *J* = 11.1 Hz, 0.7H), 6.02-6.13 (m, 0.8H), 5.85-5.97 (m, 1.1H), 5.28-5.37 (m, 1.8H), 5.21 (d, *J* = 10.2 Hz, 1.0H), 5.02 (d, *J* = 7.8 Hz, 0.7H), 4.97 (d, *J* = 7.2 Hz, 1.1H), 4.66-4.79 (m, 1.8H), 4.54 (d, *J* = 11.1 Hz, 1.0H), 4.37 (d, *J* = 12.0 Hz, 0.8H), 3.87-3.98 (m, 1.0H), 3.46-3.58 (m, 0.8H), 2.54-2.61 (m, 0.7H), 2.38-2.45 (m, 1.1H), 2.26-2.33 (m, 1.0H), 2.05-2.13 (m, 0.8H); **^{13}C NMR (DMSO-d_6, 75 MHz)** δ 179.4, 177.2, 141.6, 141.5, 136.4, 136.2, 135.6, 135.3, 134.3, 134.0, 133.6, 132.5, 131.5, 131.2, 129.0, 128.9, 128.8, 128.6, 128.3, 128.1, 127.8, 127.3, 120.0, 119.2, 115.0, 114.8, 111.4, 111.0. 91.5, 90.8, 58.9, 58.5, 57.1, 55.7, 49.4, 44.6, 43.5(4), 43.4(4), 41.5; **HRMS (TOF-ES+) m/z:** calcd for $C_{27}H_{23}BrKN_2O_3$ $[M+K]^+$ 541.0529, found 541.0503.



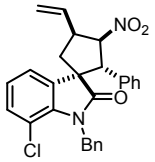
1'-Benzyl-2'-oxo-2-phenyl-3-nitro-4-vinylspiro[cyclopentane-1,3'-(5'-methyl-indoline)] (**3i**): White solid (56.1g, 0.13 mmol, 64% yield, 95:5 *dr*, major diastereomer); m.p. 171-173 °C; **IR (KBr)** ν 3456, 3048, 2952, 1740, 1373, 1232, 1021, 893, 758cm^{-1}; **^{1}H NMR ($CDCl_3$, 300 MHz)** δ 7.06-7.18 (m, 7H), 6.91-6.98 (m, 3H), 6.70 (d, *J* = 7.2 Hz, 2H), 6.37 (d, *J* = 7.8 Hz, 1H), 5.92-6.03 (m, 1H), 5.85 (t, *J* =11.1 Hz, 1H), 5.34 (d, *J* = 16.8 Hz, 1H), 5.27 (d, *J* = 9.9 Hz, 1H), 5.13 (d, *J* = 16.2 Hz, 1H), 4.69 (d, *J* = 11.7 Hz, 1H), 4.48 (d, *J* = 15.9 Hz, 1H), 3.79-3.88 (m, 1H), 2.63-2.71 (m, 1H), 2.40 (s, 3H), 2.29-2.36 (m, 1H); **^{13}C NMR ($CDCl_3$, 75 MHz)** δ 172.0, 135.2, 130.2, 129.8, 128.6, 127.3, 125.3, 123.8, 123.3, 122.5, 121.8, 119.8, 115.1, 104.8, 87.3, 53.5, 52.3, 39.7, 39.1, 36.3, 16.5; **HRMS (TOF-ES+) m/z**: calcd for $C_{28}H_{26}N_2NaO_3$ $[M+Na]^+$ 461.1841, found 461.1833.



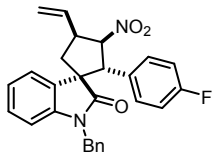
1'-Benzyl-2'-oxo-2-phenyl-3-nitro-4-vinylspiro[cyclopentane-1,3'-(5'-methoxyl-indoline)] (**3j**): White solid (55.4 mg, 0.12 mmol, 61% yield, 90:10 *dr*, major diastereomer); m.p. 147-150 °C; **IR (KBr)** ν 3035, 2913, 1714, 1547, 1487, 1350, 1178, 939, 809cm^{-1}; **^{1}H NMR ($CDCl_3$, 300 MHz)** δ 7.07-7.28 (m, 6H), 6.97-7.04 (m, 3H), 6.71-6.73 (m, 2H), 6.61-6.64 (m, 1H), 6.37 (d, *J* = 8.4 Hz, 1H), 5.90-6.02 (m, 1H), 5.82 (t, *J* = 11.1 Hz, 1H), 5.34 (d, *J* = 16.8 Hz, 1H), 5.26 (d, *J* = 9.9 Hz, 1H), 5.13 (d, *J* = 15.9 Hz, 1H), 4.71 (d, *J* = 11.4 Hz, 1H), 4.48 (d, *J* = 15.9 Hz, 1H), 3.80 (s, 3H), 2.63-2.71 (m, 1H), 2.28-2.35 (m, 1H); **^{13}C NMR ($CDCl_3$, 75 MHz)** δ 176.5, 155.7, 135.9, 134.9, 134.4, 133.2, 131.5, 128.6, 128.5, 128.0, 127.3, 126.6, 119.9, 112.5, 111.0, 109.9, 91.9, 58.5, 57.0, 55.9, 44.4, 43.9, 41.0; **HRMS (TOF-ES+) m/z**: calcd for $C_{28}H_{26}N_2NaO_4$ $[M+Na]^+$ 477.1790, found 477.1781.



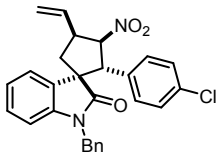
1'-Benzyl-2'-oxo-2-phenyl-3-nitro-4-vinylspiro[cyclopentane-1,3'-(6'-chloro-indoline)] (**3k**): White solid (63.2 mg, 0.14 mmol, 69% yield, 76:24 *dr*, major diastereomer); m.p. 180-183 °C; **IR (KBr)** ν 2933, 2855, 1714, 1557, 1484, 1362, 1192, 989, 871cm^{-1}; **^{1}H NMR (DMSO-d_6, 300 MHz)** δ 7.81 (d, *J* = 7.8 Hz, 1H), 7.21-7.23 (m, 3H), 7.07-7.17 (m, 3H), 7.00-7.02 (m, 3H), 6.95-6.96 (m, 2H), 6.80 (s, 1H), 6.36 (t, *J* = 10.5 Hz, 1H), 5.83-5.95 (m, 1H), 5.34 (d, *J* = 17.1 Hz, 1H), 5.23 (d, *J* = 9.9 Hz, 1H), 5.01 (d, *J* = 16.2 Hz, 1H), 4.73 (d, *J* = 15.9 Hz, 1H), 4.54 (d, *J* = 11.1 Hz, 1H), 3.87-3.98 (m, 1H), 2.39-2.46 (m, 1H), 2.23-2.29 (m, 1H); **^{13}C NMR (DMSO-d_6, 75 MHz)** δ 177.6, 143.8, 135.8, 135.2, 134.3, 133.2, 129.0, 128.8, 128.4, 128.1, 127.8, 127.7, 127.3, 122.3, 120.1, 109.9, 91.7, 58.1, 57.2, 55.5, 44.5, 43.4, 41.6; **HRMS (TOF-ES+) m/z**: calcd for $C_{27}H_{23}ClN_2NaO_3$ $[M+Na]^+$ 481.1295, found 481.1292.



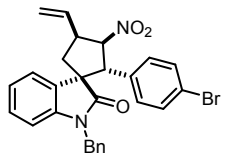
1'-Benzyl-2'-oxo-2-phenyl-3-nitro-4-vinylspiro[cyclopentane-1,3'-(7'-chloro-indoline)] (**3l**): White solid (61.4 g, 0.13 mmol, 67% yield, 91:9 *dr*, major diastereomer); m.p. 193-195 °C; **IR (KBr)** ν 3083, 2965, 1709, 1557, 1452, 1352, 1131, 996, 883cm^{-1}; **^{1}H NMR (DMSO-d_6, 300 MHz)** δ 7.82 (d, *J* = 7.2 Hz, 1H), 7.13-7.18 (m, 7H), 7.01-7.09 (m, 3H), 6.72-6.75 (m, 2H), 6.38 (t, *J* = 10.5 Hz, 1H), 5.84-5.96 (m, 1H), 5.34 (d, *J* = 17.1 Hz, 1H), 5.18-5.29 (m, 3H), 4.57 (d, *J* = 11.4 Hz, 1H), 3.90-4.01 (m, 1H), 2.40-2.48 (m, 1H), 2.29-2.36 (m, 1H); **^{13}C NMR (DMSO-d_6, 75 MHz)** δ 178.2, 138.3, 137.5, 135.2, 134.1, 133.3, 131.1, 128.9, 128.8, 128.5, 128.3, 127.2, 126.0, 124.8, 124.2, 120.2, 114.6, 91.9, 58.1, 57.5, 45.1, 44.4, 42.2; **HRMS (TOF-ES+) m/z**: calcd for $C_{27}H_{23}ClN_2NaO_3$ $[M+Na]^+$ 481.1295, found 481.1251.



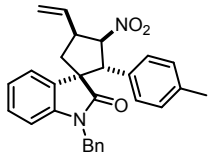
1'-Benzyl-2'-oxo-2-(4-flouro-phenyl)-3-nitro-4-vinylspiro[cyclo-pentane-1,3'-indoline] (**3m**): White solid (72.5 mg, 0.16 mmol, 82% yield, 94:6 *dr*, major diastereomer); m.p. 179-181 °C; **IR (KBr)** ν 3068, 2921, 1709, 1549, 1364, 1223, 996, 754cm^{-1}; **^{1}H NMR ($CDCl_3$, 300 MHz)** δ 7.37 (d, *J* = 7.2 Hz, 1H), 7.16-7.24 (m, 5H), 6.86-6.94 (m, 2H), 6.72-6.77 (m, 4H), 6.53 (d, *J* = 7.5 Hz, 1H), 5.89-6.01 (m, 1H), 5.76 (t, *J* = 11.1 Hz, 1H), 5.34 (d, *J* = 17.1 Hz, 1H), 5.27 (d, *J* = 10.2 Hz, 1H), 5.14 (d, *J* = 15.9 Hz, 1H), 4.67 (d, *J* = 11.7 Hz, 1H), 4.51 (d, *J* = 15.9 Hz, 1H), 3.77-3.89 (m, 1H), 2.62-2.70 (m, 1H), 2.33 (dd, *J* = 7.8, 13.2 Hz, 1H); **^{13}C NMR ($CDCl_3$, 75 MHz)** δ 176.7, 142.4, 134.8, 134.4, 129.8, 129.7, 128.9, 128.6, 127.5, 126.6, 123.7, 122.6, 120.0, 115.5, 115.2, 109.9, 92.1, 58.0, 56.5, 44.3, 43.8, 40.7; **HRMS (TOF-ES+) m/z**: calcd for $C_{27}H_{23}FKN_2O_3$ $[M+K]^+$ 481.1330, found 481.1331.



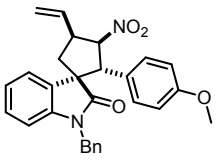
1'-Benzyl-2'-oxo-2-(4-chloro-phenyl)-3-nitro-4-vinylspiro[cyclopentane-1,3'-indoline] (**3n**): White solid (77.9 g, 0.17 mmol, 85% yield, 94:6 *dr*, major diastereomer); m.p. 163-165 °C; **IR (KBr)** ν 3065, 2982, 1711, 1619, 1554, 1365, 1190, 929, 753cm^{-1}; **^{1}H NMR (DMSO-d_6, 300 MHz)** δ 7.78 (d, *J* = 7.5 Hz, 1H), 7.11-7.21 (m, 6H), 7.00-7.05 (m, 3H), 6.90-6.93 (m, 2H), 6.69 (d, *J* = 7.8 Hz, 1H), 6.34 (t, *J* = 10.5 Hz, 1H), 5.83-5.94 (m, 1H), 5.34 (d, *J* = 17.1 Hz, 1H), 5.23 (d, *J* = 9.9 Hz, 1H), 5.02 (d, *J* = 16.2 Hz, 1H), 4.68 (d, *J* = 15.9 Hz, 1H), 4.52 (d, *J* = 11.1 Hz, 1H), 3.90-4.02 (m, 1H), 2.39-2.46 (m, 1H), 2.21-2.28 (m, 1H); **^{13}C NMR (DMSO-d_6, 75 MHz)** δ 177.1, 142.2, 136.1, 135.2, 133.4, 130.1, 129.7, 128.9, 128.8, 127.7, 127.3, 125.5, 122.8, 120.2, 109.8, 91.7, 58.2, 56.7, 44.5, 43.3, 41.5; **HRMS (TOF-ES+) m/z**: calcd for $C_{27}H_{23}ClN_2NaO_3$ $[M+Na]^+$ 481.1295, found 481.1294.



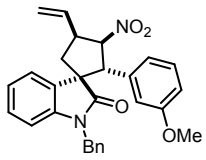
1'-Benzyl-2'-oxo-2-(4-bromo-phenyl)-3-nitro-4-vinylspiro[cyclopentane-1,3'-indoline] (**3o**): White solid (80.3 mg, 0.16 mmol, 80% yield, 91:9 *dr*, major diastereomer); m.p. 167-170 °C; **IR (KBr)** ν 3065, 2983, 1711, 1557, 1367, 1190, 934, 752cm^{-1}; **^{1}H NMR ($CDCl_3$, 300 MHz)** δ 7.36 (d, *J* = 7.2 Hz, 1H), 7.08-7.26 (m, 7H), 6.81 (d, *J* = 8.4 Hz, 2H), 6.69-6.72 (m, 2H), 6.53 (d, *J* = 7.5 Hz, 1H), 5.88-6.00 (m, 1H), 5.75 (t, *J* = 11.1 Hz, 1H), 5.26-5.38 (m, 2H), 5.16 (d, *J* = 15.9 Hz, 1H), 4.62 (d, *J* = 11.7 Hz, 1H), 4.50 (d, *J* = 15.9 Hz, 1H), 3.78-3.90 (m, 1H), 2.62-2.90 (m, 1H), 2.30-2.38 (m, 1H); **^{13}C NMR (DMSO-d_6, 75 MHz)** δ 177.1, 142.2, 136.1, 135.2, 133.8, 131.7, 130.4, 129.7, 129.0, 128.8, 127.7, 127.3, 125.5, 122.8, 121.6, 120.2, 109.8, 91.7, 58.2, 56.7, 55.4, 44.4, 43.3, 26.8; **HRMS (TOF-ES+) m/z**: calcd for $C_{27}H_{23}BrKN_2O_3$ $[M+K]^+$ 541.0529, found 541.0563.



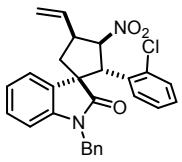
1'-Benzyl-2'-oxo-2-(4-methyl-phenyl)-3-nitro-4-vinylspiro[cyclopentane-1,3'-indoline] (**3p**): White solid (76.2 mg, 0.17 mmol, 87% yield, 81:19 *dr*, major diastereomer); m.p. 166-169 °C; IR (KBr) ν 3456, 3048, 2952, 1740, 1373, 1232, 1021, 893, 758cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.36-7.39 (m, 1H), 7.09-7.24 (m, 5H), 6.81-6.90 (m, 4H), 6.72 (d, *J* = 7.5 Hz, 1H), 6.48 (d, *J* = 7.2 Hz, 1H), 5.90-6.02 (m, 1H), 5.80 (t, *J* = 11.1 Hz, 1H), 5.34 (d, *J* = 16.8 Hz, 1H), 5.27 (d, *J* = 9.9 Hz, 1H), 5.17 (d, *J* = 15.9 Hz, 1H), 4.66 (d, *J* = 11.7 Hz, 1H), 4.79 (d, *J* = 15.9 Hz, 1H), 3.77-3.86 (m, 1H), 2.63-2.71 (m, 1H), 2.31 (dd, *J* = 7.8, 13.2 Hz, 1H), 2.24 (s, 3H); **^{13}C NMR ($CDCl_3$, 75 MHz)** δ 176.9, 142.4, 137.7, 134.8, 134.6, 130.1(4), 130.1(1), 129.1, 128.7, 128.5, 128.0, 127.3, 126.6, 123.7, 122.4, 119.8, 109.8, 92.2, 58.2, 57.0, 44.4, 43.8, 41.0, 21.1; **HRMS (TOF-ES+) m/z**: calcd for $C_{28}H_{26}KN_2O_3$ $[M+K]^+$ 477.1580, found 477.1568.



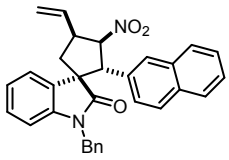
1'-Benzyl-2'-oxo-2-(4-methoxyl-phenyl)-3-nitro-4-vinylspiro-[cyclopentane-1,3'-indoline] (**3q**): White solid (70.8 mg, 0.16 mmol, 78% yield, 76:24 *dr*, major diastereomer); m.p. 162-165 °C; **IR (KBr)** ν 3058, 2960, 1714, 1609, 1552, 1360, 1250, 923, 834cm^{-1}; **^{1}H NMR (DMSO-d_6, 300 MHz)** δ 7.79 (d, *J* = 7.5 Hz, 1H), 7.09-7.21 (m, 4H), 7.00-7.05 (m, 1H), 6.90-6.92 (m, 4H), 6.59-6.68 (m, 3H), 6.25 (t, *J* = 10.5 Hz, 1H), 5.81-5.92 (m, 1H), 5.34 (d, *J* = 16.8 Hz, 1H), 5.22 (d, *J* = 10.2 Hz, 1H), 5.02 (d, *J* = 15.9 Hz, 1H), 4.67 (d, *J* = 16.2 Hz, 1H), 4.47 (d, *J* = 11.1 Hz, 1H), 3.92-3.98 (m, 1H), 3.63 (s, 3H), 2.37-2.45 (m, 1H), 2.18-2.24 (m, 1H); **^{13}C NMR (DMSO-d_6, 75 MHz)** δ 177.3, 159.2, 142.2, 136.1, 135.4, 130.1, 129.5, 128.8, 127.7, 126.2, 125.5, 122.7, 120.0, 114.1, 109.7, 92.4, 58.3, 56.9, 55.4, 44.2, 43.3, 41.7; **HRMS (TOF-ES+) m/z**: calcd for $C_{28}H_{26}N_2NaO_4$ $[M+Na]^+$ 477.1790, found 477.1784.



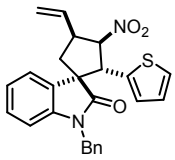
1'-Benzyl-2'-oxo-2-(3-methoxyl-phenyl)-3-nitro-4-vinylspiro-[cyclopentane-1,3'-indoline] (**3r**): White solid (69.9 mg, 0.15 mmol, 77% yield, 76:24 *dr*, major diastereomer); m.p. 144-146 °C; **IR (KBr)** ν 3085, 2985, 1711, 1552, 1489, 1362, 1051, 988, 757cm^{-1}; **^{1}H NMR (DMSO-d_6, 100 MHz)** δ 7.81 (d, *J* = 7.2 Hz, 1H), 7.08-7.19 (m, 4H), 6.98-7.08 (m, 2H), 6.89-6.94 (m, 2H), 6.57-6.69 (m, 4H), 6.34 (t, *J* = 10.5 Hz, 1H), 5.82-5.93 (m, 1H), 5.34 (d, *J* = 17.1 Hz, 1H), 5.23 (d, *J* = 10.2 Hz, 1H), 5.03 (d, *J* = 16.2 Hz, 1H), 4.68 (d, *J* = 16.2 Hz, 1H), 4.52 (d, *J* = 10.8 Hz, 1H), 3.93-3.96 (m, 1H), 3.52 (s, 3H), 2.39-2.46 (m, 1H), 2.19-2.26 (m, 1H); **^{13}C NMR (DMSO-d_6, 75 MHz)** δ 177.3, 159.4, 142.2, 136.0(4), 136.0(0), 135.3, 130.0, 129.8, 128.9, 127.6, 127.1, 125.6, 122.7, 120.7, 120.1, 113.9, 113.7, 109.7, 92.1, 58.4, 57.3, 55.3, 44.5, 43.3, 41.9; **HRMS (TOF-ES+) m/z**: calcd for $C_{28}H_{26}N_2NaO_4$ $[M+Na]^+$ 477.1790, found 477.1760.



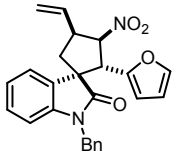
1'-Benzyl-2'-oxo-2-(2-chloro-phenyl)-3-nitro-4-vinylspiro[cyclo-pentane-1,3'-indoline] (**3s**): White solid (39.4 mg, 0.086 mmol, 43% yield, 91:9 *dr*, major diastereomer); m.p. 199-202 °C; **IR (KBr)** ν 3065, 2923, 1709, 1609, 1552, 1355, 1033, 931, 744cm^{-1}; **^{1}H NMR (DMSO-d_6, 300 MHz)** δ 7.72 (d, *J* = 7.5 Hz, 1H), 7.28-7.36 (m, 2H), 7.20-7.22 (m, 3H), 6.93-7.13 (m, 6H), 6.62 (d, *J* = 7.8 Hz, 1H), 6.35 (t, *J* = 9.9 Hz, 1H), 6.14-6.26 (m, 1H), 5.32 (d, *J* = 16.8 Hz, 1H), 5.17-5.25 (m, 2H), 4.92 (d, *J* = 15.9 Hz, 1H), 4.73 (d, *J* = 15.9 Hz, 1H), 3.82-3.92 (m, 1H), 2.36-2.47 (m, 1H); **^{13}C NMR (DMSO-d_6, 75 MHz)** δ 177.9, 142.4, 136.3, 135.4, 134.3, 132.9, 130.2, 130.0, 129.9, 129.6, 128.9, 128.8, 127.7, 127.3, 127.0, 126.1, 122.4, 119.8, 109.4, 92.9, 56.5, 51.8, 45.8, 43.4; **HRMS (TOF-ES+) m/z**: calcd for $C_{27}H_{23}ClN_2NaO_3$ $[M+Na]^+$ 481.1295, found 481.1302.



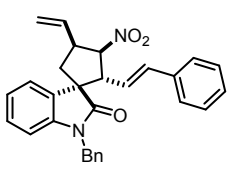
1'-Benzyl-2'-oxo-2-(2-napthyl)-3-nitro-4-vinylspiro[cyclopentane-1,3'-indoline] (**3t**): White solid (75.8 mg, 0.16 mmol, 80% yield, 94:6 *dr*, major diastereomer); m.p. 160-163 °C; **IR (KBr)** ν 3075, 2913, 1704, 1609, 1467, 1362, 921, 746cm^{-1}; **^{1}H NMR (DMSO-d_6, 300 MHz)** δ 7.87-7.89 (m, 1H), 7.72-7.79 (m, 2H), 7.59-7.62 (m, 2H), 7.45-7.48 (m, 2H), 7.14-7.19 (m, 1H), 7.03-7.12 (m, 3H), 6.75-6.88 (m, 4H), 6.45-6.55 (m, 2H), 5.88-6.00 (m, 1H), 5.38 (d, *J* = 16.8 Hz, 1H), 5.26 (d, *J* = 10.2 Hz, 1H), 5.03 (d, *J* = 16.2 Hz, 1H), 4.73 (d, *J* = 10.8 Hz, 1H), 4.61 (d, *J* = 16.2 Hz, 1H), 3.97-4.09 (m, 1H), 2.25-2.32 (m, 1H); **^{13}C NMR (DMSO-d_6, 75 MHz)** δ 177.3, 142.2, 135.9, 132.9, 132.7, 132.1, 130.0, 128.8, 128.6, 128.2, 127.8, 127.7, 127.5, 127.0, 126.8, 126.7, 125.7(1), 125.6(6), 122.7, 120.2, 109.7, 92.2, 58.5, 57.6, 44.7, 43.3, 41.8; **HRMS (TOF-ES+) m/z**: calcd for $C_{31}H_{26}N_2NaO_3$ $[M+Na]^+$ 497.1841, found 497.1827.



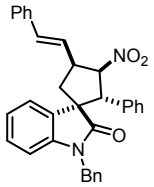
1'-Benzyl-2'-oxo-2-(2-thienyl)-3-nitro-4-vinylspiro[cyclopentane-1,3'-indoline] (**3u**): White solid (57.6 mg, 0.13 mmol, 67% yield, 80:20 *dr*, major diastereomer); m.p. 132-135 °C; **IR (KBr)** ν 3083, 2918, 1709, 1609, 1547, 1365, 1198, 996, 757cm^{-1}; **^{1}H NMR (DMSO-d_6, 300 MHz)** δ 7.76 (d, *J* = 7.2 Hz, 1H), 7.19-7.27 (m, 5H), 7.03-7.08 (m, 1H), 6.95-6.96 (m, 2H), 6.79-6.82 (m, 1H), 6.71-6.75 (m, 2H), 6.06 (t, *J* = 10.5 Hz, 1H), 5.77-5.91 (m, 1H), 5.32 (d, *J* = 16.8 Hz, 1H), 5.23 (d, *J* = 10.2 Hz, 1H), 5.00 (d, *J* = 16.2 Hz, 1H), 4.74-4.82 (m, 2H), 3.93-4.05 (m, 1H), 2.36-2.43 (m, 1H), 2.20-2.27 (m, 1H); **^{13}C NMR (DMSO-d_6, 75 MHz)** δ 176.8, 142.6, 136.5, 136.1, 135.1, 129.7, 129.2, 128.9, 127.7, 127.2, 126.5, 125.5, 122.9, 120.3, 109.8, 94.2, 58.0, 55.7, 53.2, 44.0, 43.4, 41.4; **HRMS (TOF-ES+) m/z**: calcd for $C_{25}H_{22}N_2NaO_3S$ $[M+Na]^+$ 453.1249, found 453.1227.



1'-Benzyl-2'-oxo-2-(2-furanyl)-3-nitro-4-vinylspiro[cyclopentane-1,3'-indoline] (**3v**): White solid (50.5 mg, 0.12 mmol, 61% yield, 89:11 *dr*, major diastereomer); m.p. 138-141 °C; **IR (KBr)** ν 3055, 2926, 1719, 1607, 1557, 1365, 1190, 941, 757cm^{-1}; **^{1}H NMR (DMSO-d_6, 300 MHz)** δ 7.54 (d, *J* = 7.2 Hz, 1H), 7.20-7.39 (m, 8H), 7.10-7.15 (m, 1H), 6.89-6.98 (m, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 6.12-6.17 (m, 2H), 5.99-6.01 (m, 1H), 5.83-5.92 (m, 1H), 5.33 (d, *J* = 16.8 Hz, 1H), 5.26-5.27 (m, 1H), 5.09 (d, *J* = 15.9 Hz , 1H), 4.81 (d, *J* = 15.9 Hz, 1H), 4.65 (d, *J* = 10.2 Hz, 1H), 3.83-3.95 (m, 1H), 2.36-2.40 (m, 1H), 2.13-2.22 (m, 1H); **^{13}C NMR (DMSO-d_6, 75 MHz)** δ 177.3, 149.5, 143.1, 142.3, 136.4, 134.7, 130.1, 129.0, 128.8, 127.8, 127.4, 125.1, 122.7, 120.3, 110.7, 109.6, 107.5, 91.6, 56.8, 54.4, 50.8, 44.8, 43.4, 41.9; **HRMS (TOF-ES+) m/z**: calcd for $C_{25}H_{22}N_2NaO_4$ $[M+Na]^+$ 437.1477, found 437.1485.



1'-Benzyl-2'-oxo-2-((1*E*)-2-phenylethenyl)-3-nitro-4-vinylspiro[cyclopentane-1,3'-indoline] (**3w**): White solid (78.3 mg, 0.17 mmol, 87% yield, 70:30 *dr*, major diastereomer); m.p. 154-157 °C; **IR (KBr)** ν 3083, 2913, 1706, 1544, 1362, 1192, 963, 749cm^{-1}; **^{1}H NMR ($CDCl_3$, 300 MHz)** δ 7.21-7.29 (m, 5H), 7.05-7.16 (m, 5H), 6.86-6.94 (m, 2H), 6.68 (d, *J* = 7.8 Hz, 1H), 6.59 (d, *J* = 15.9 Hz , 1H), 5.87-5.99 (m, 1H), 5.44-5.56 (m, 1H), 5.37 (d, *J* = 18.0 Hz , 1H), 5.24-5.29 (m, 2H), 4.61 (d, *J* = 15.9 Hz, 1H), 4.26 (t, *J* = 9.9 Hz , 1H), 3.69-3.78 (m, 1H), 2.59-2.66 (m, 1H), 2.25 (dd, *J* = 7.8, 13.2 Hz, 1H); **^{13}C NMR ($CDCl_3$, 75 MHz)** δ 177.0, 142.4, 136.1, 135.8, 134.9, 134.3, 130.0, 128.9, 128.7, 128.5, 128.1, 127.4, 126.7, 126.6, 123.2, 122.8, 122.0, 119.8, 110.0, 93.1, 57.6, 56.2, 45.3, 44.0, 40.6; **HRMS (TOF-ES+) m/z**: calcd for $C_{29}H_{26}N_2NaO_3$ $[M+Na]^+$ 473.1841, found 473.1845.



1'-Benzyl-2'-oxo-2-phenyl-3-nitro-4-((1*E*)-2-phenylethenyl)-spiro[cyclopentane-1,3'-indoline] (**6**): White solid (78.3 mg, 0.17 mmol, 92% yield, 84:16 *dr*, major diastereomer); m.p. 181-183 °C; **IR (KBr)** ν 3026, 2982, 2817, 1724, 1554, 1481, 1376, 1131, 974, 764; **^{1}H NMR (DMSO-d_6, 300 MHz)** δ 7.82 (d, *J* = 7.2 Hz, 1H), 7.47-7.50 (m, 2H), 7.35-7.40 (m, 2H), 7.27-7.29 (m, 4H), 7.16 (d, *J* = 6.6 Hz, 2H), 7.03-7.05 (m, 6H), 6.94 (t, *J* = 7.4 Hz, 1H), 6.65-6.73 (m, 2H), 6.59 (d, *J* = 8.1 Hz, 1H), 6.19 (t, *J* = 11.0 Hz, 1H), 5.00 (d, *J* = 15.6 Hz, 1H), 4.76 (d, *J* = 15.9 Hz, 1H), 4.42 (d, *J* = 12.0 Hz, 1H), 3.67-3.79 (m, 1H), 2.72 (dd, *J* = 13.5, 9.6 Hz, 1H), 2.16 (dd, *J* = 13.5, 10.5 Hz, 1H); **^{13}C NMR (DMSO-d_6, 75 MHz)** δ 179.4, 142.2, 136.7, 136.4, 134.0, 133.1, 131.4, 129.2, 129.0, 128.6, 128.3, 128.2, 127.8, 127.7, 127.3, 126.8, 126.0, 122.7, 109.3, 91.3, 59.0, 55.9, 48.6, 43.5; **HRMS (TOF-ES+) m/z**: $[M+Na]^+$ calcd for $C_{33}H_{28}N_2NaO_3$ 523.1998, found 523.2025.

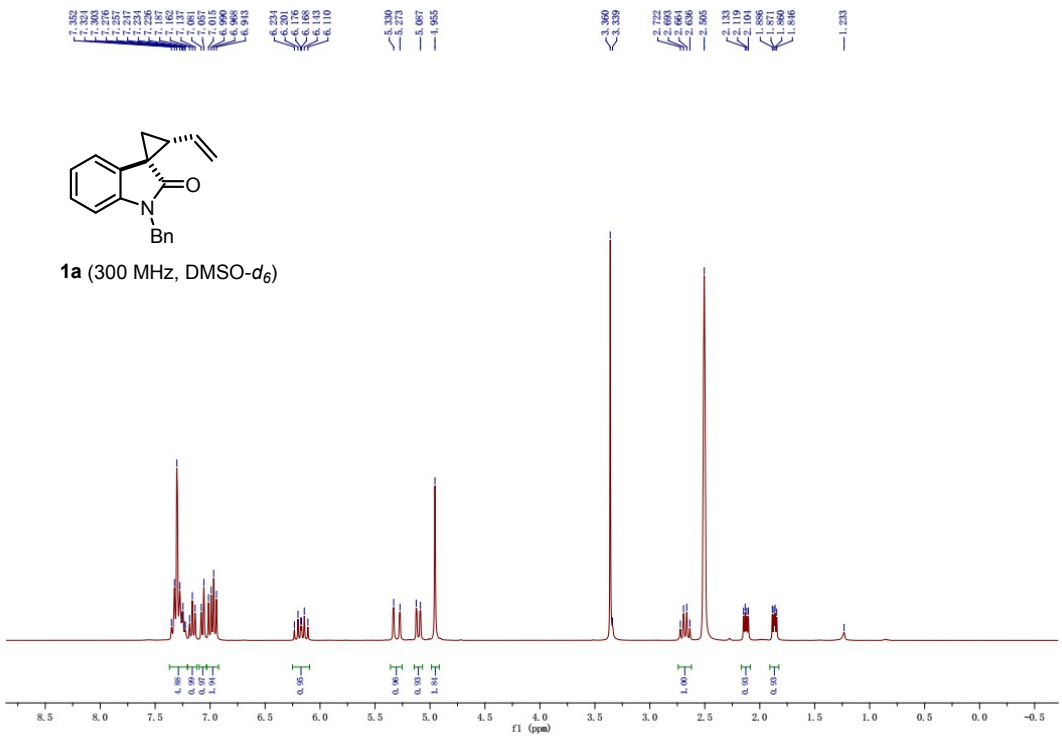
3. Refrences

[1] Buxton, C. S.; Blakemore, D. C.; Bower, J. F. *Angew. Chem. Int. Ed.* **2017**, *56*, 13824-13828.

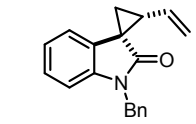
[2] Zhang, J.-Y.; Cheng, C.; Wang, D.; Miao, Z.-W. *J. Org. Chem.* **2017**, *82*, 10121-10128.

[3] Ivanova, O. A.; Chagarovskiy, A. O.; Shumsky, A. N.; Krasnobrov, V. D.; Levina, I. I.; Trushkov, I. V. *J. Org. Chem.* **2018**, *83*, 543-560.

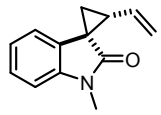
4. ^{1}H and ^{13}C NMR Spectra



1a (300 MHz, DMSO-d_6)



1a (75 MHz, $CDCl_3$)



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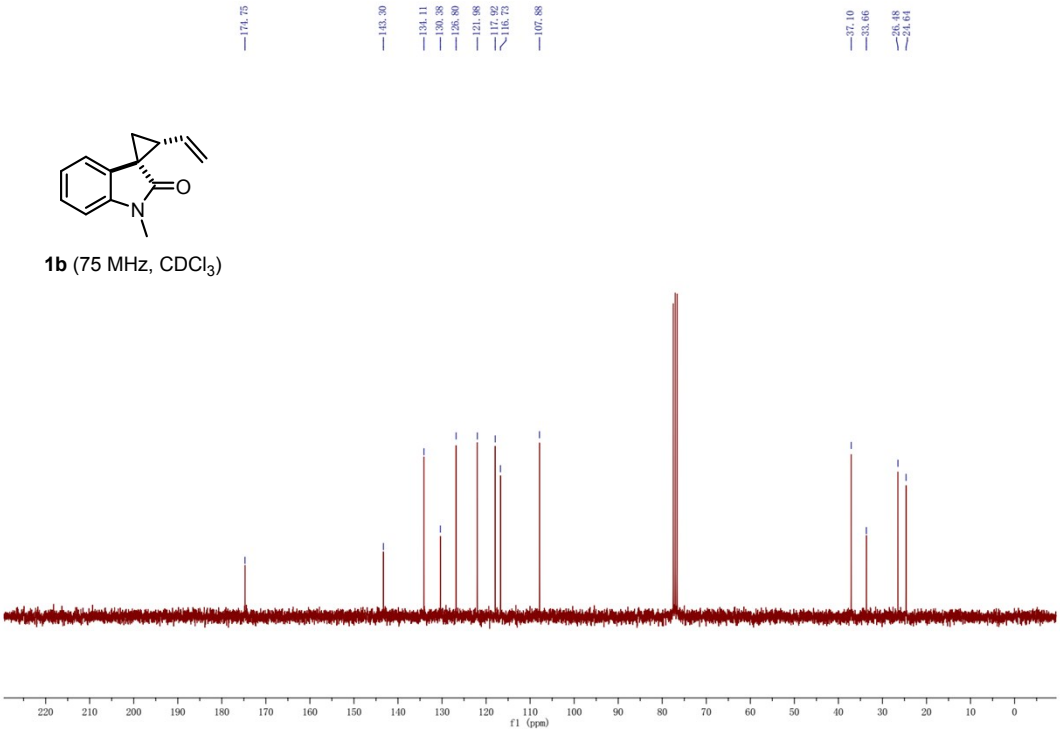

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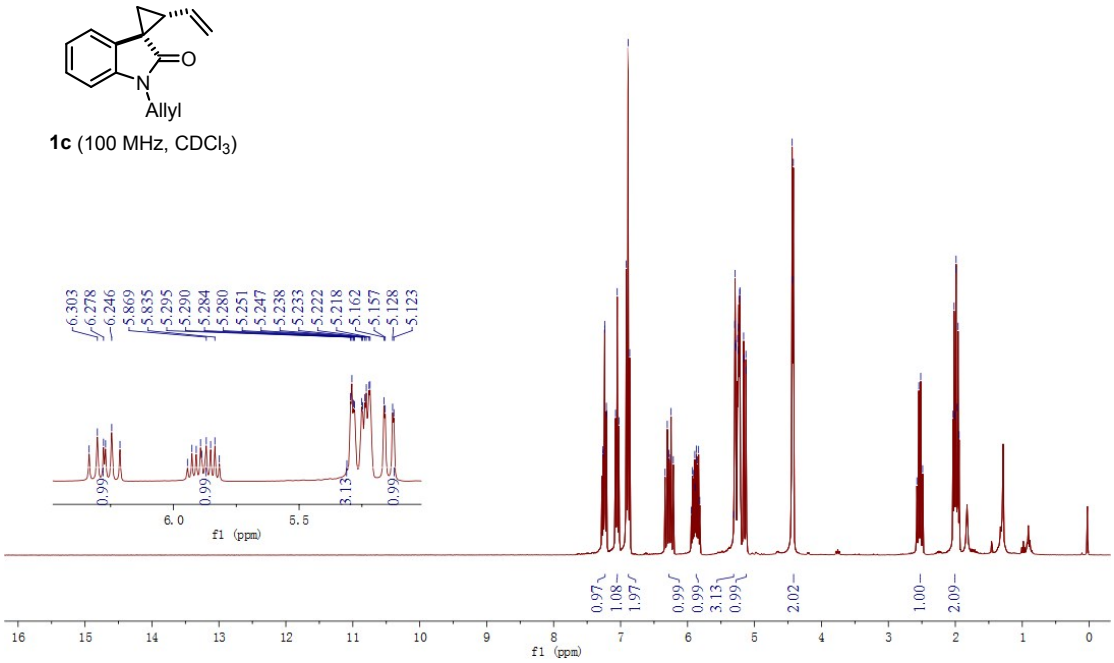

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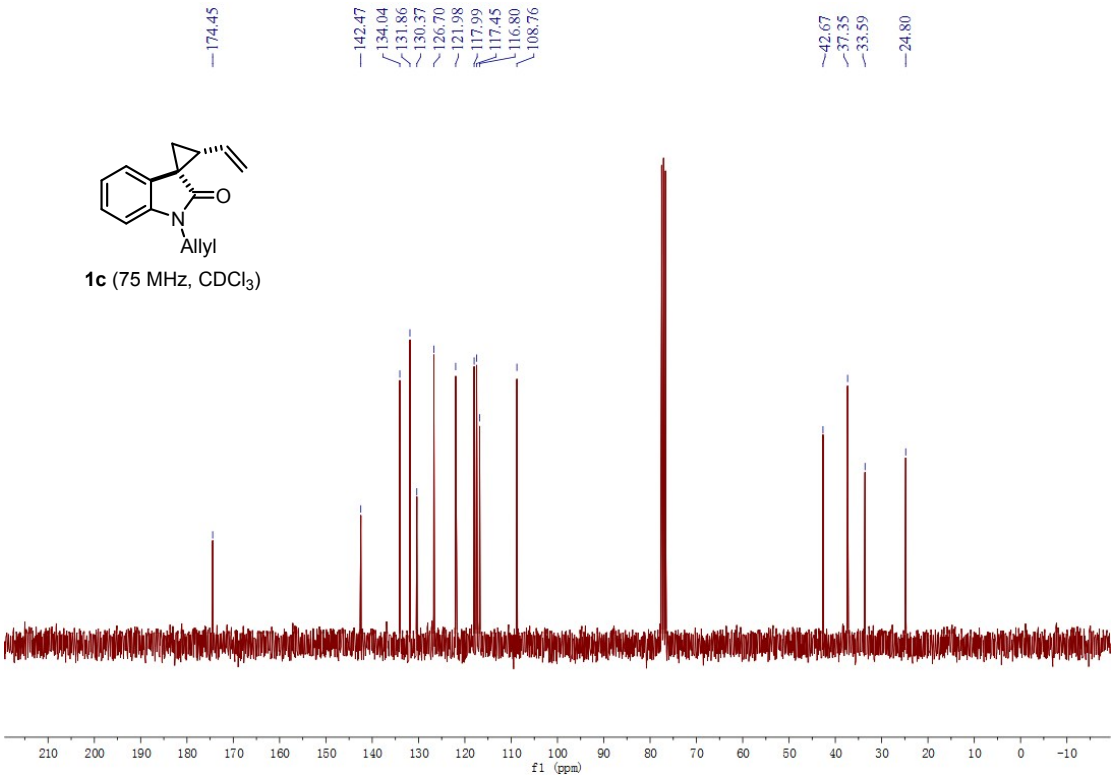

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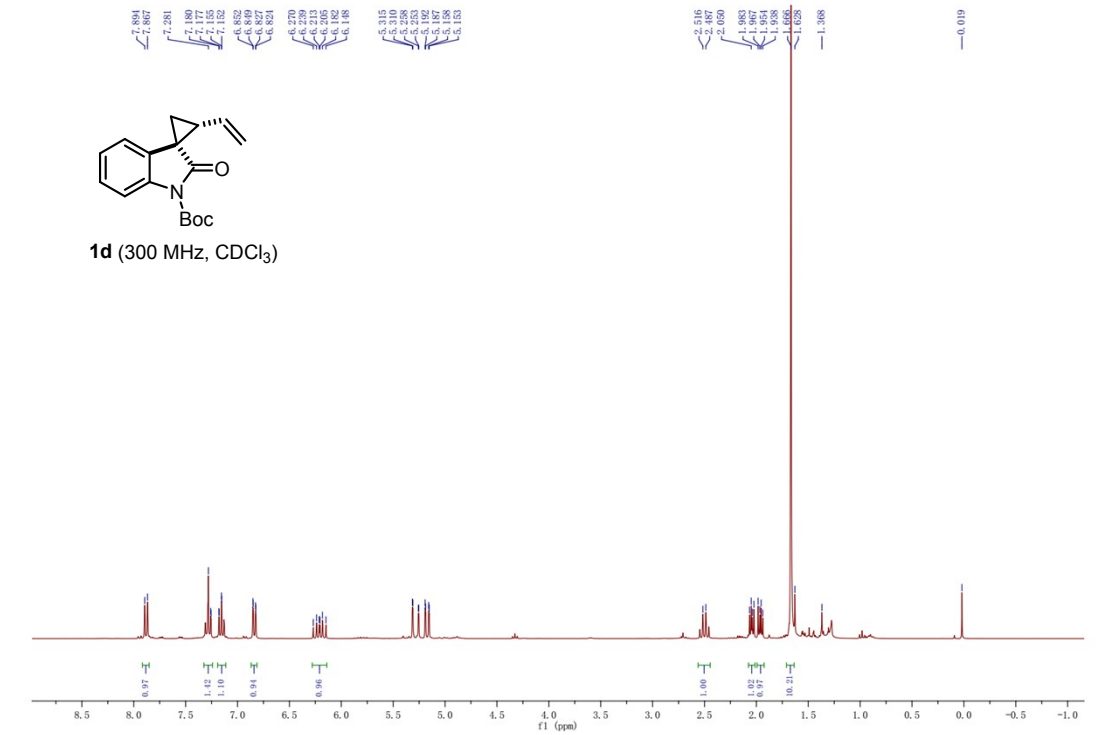

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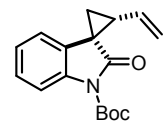

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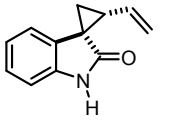

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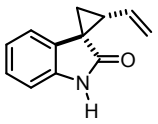

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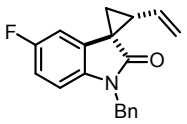

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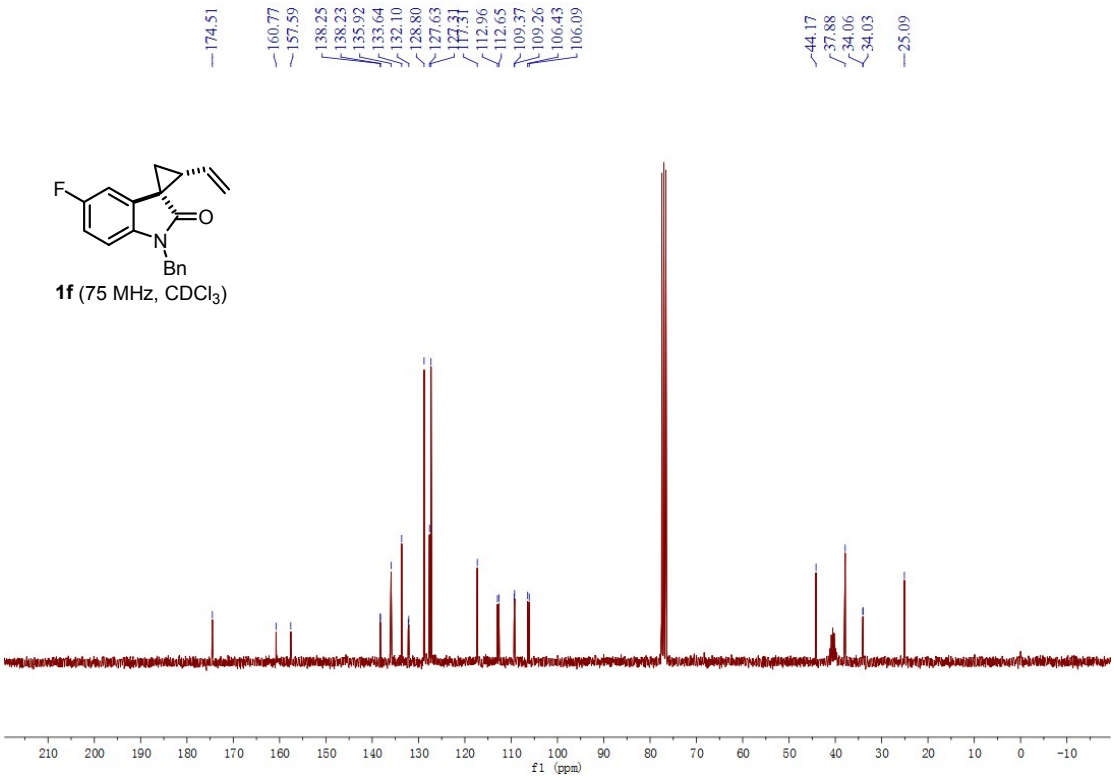

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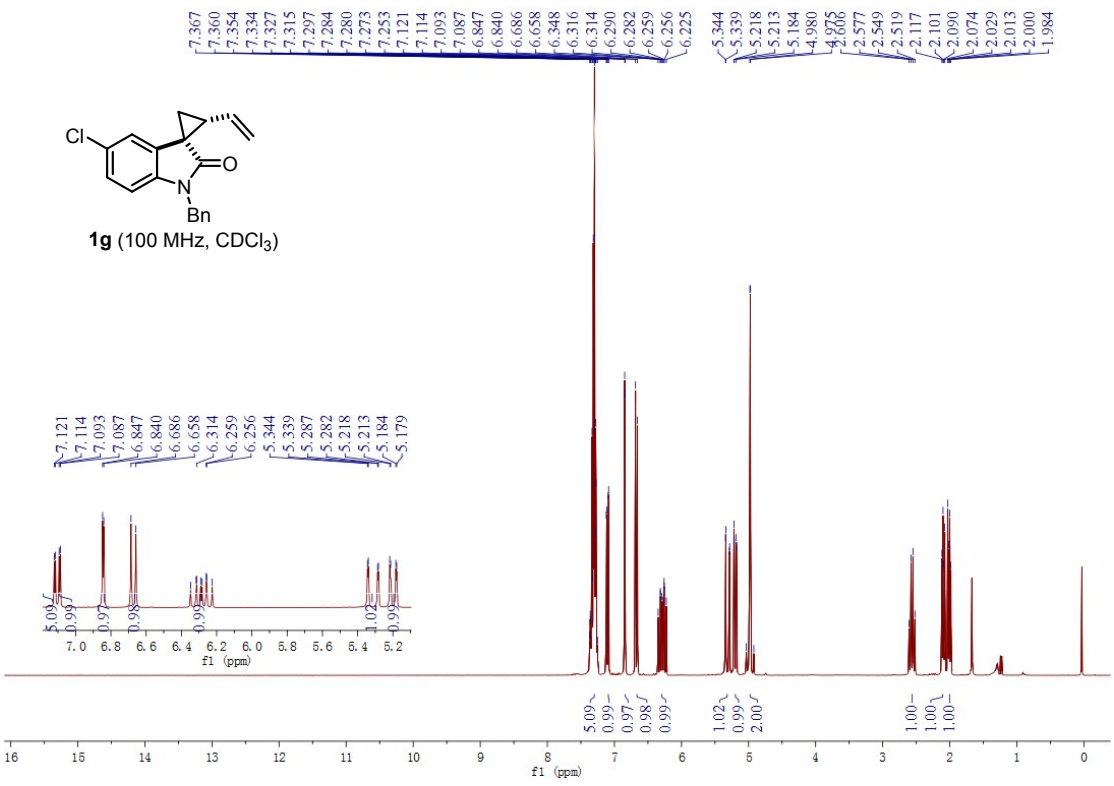

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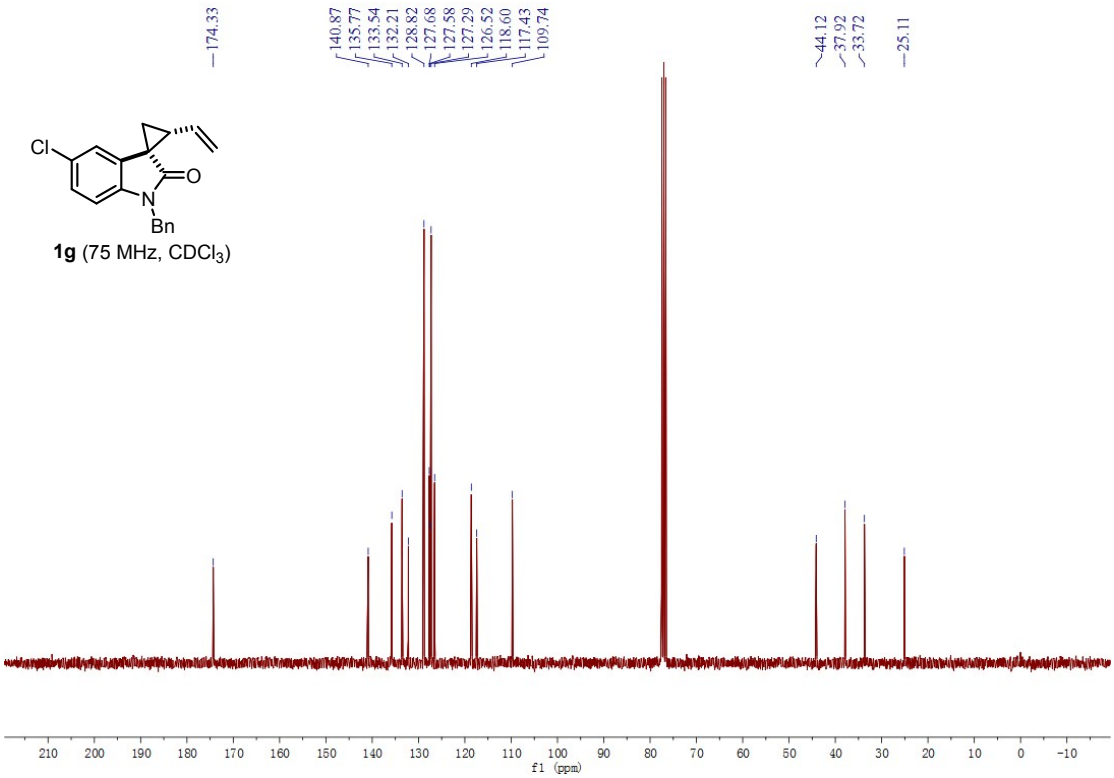

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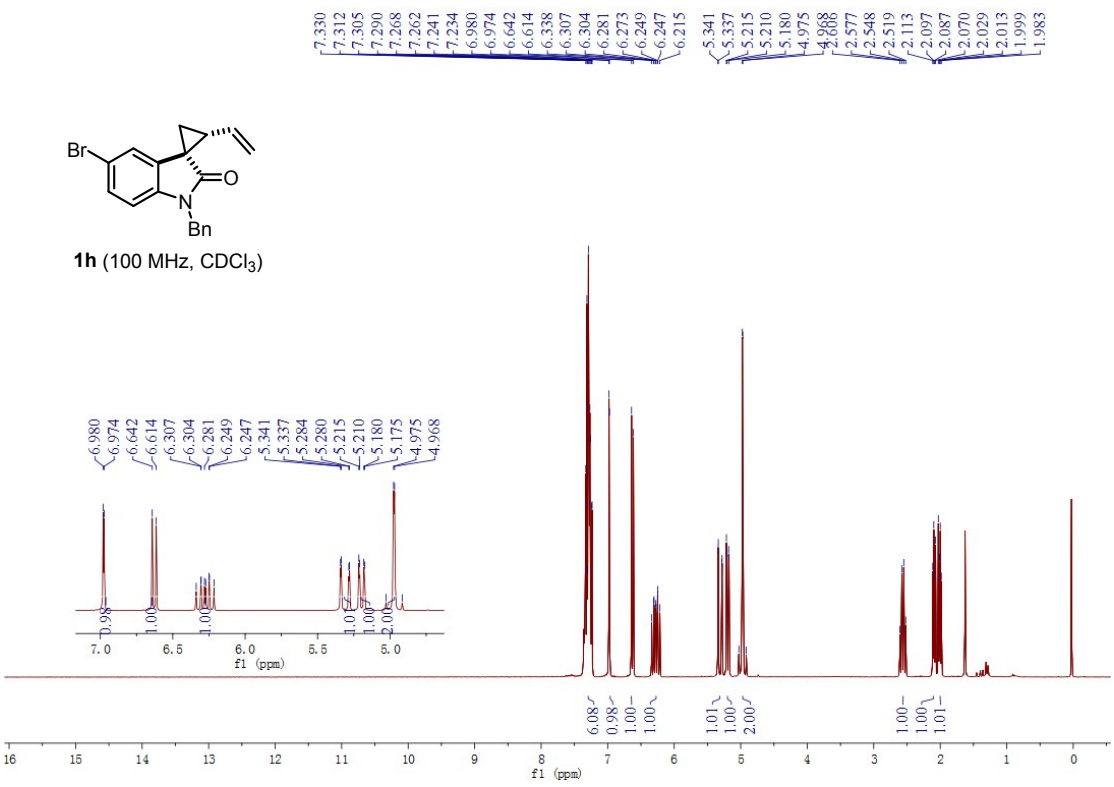

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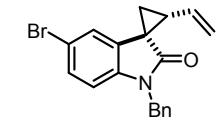
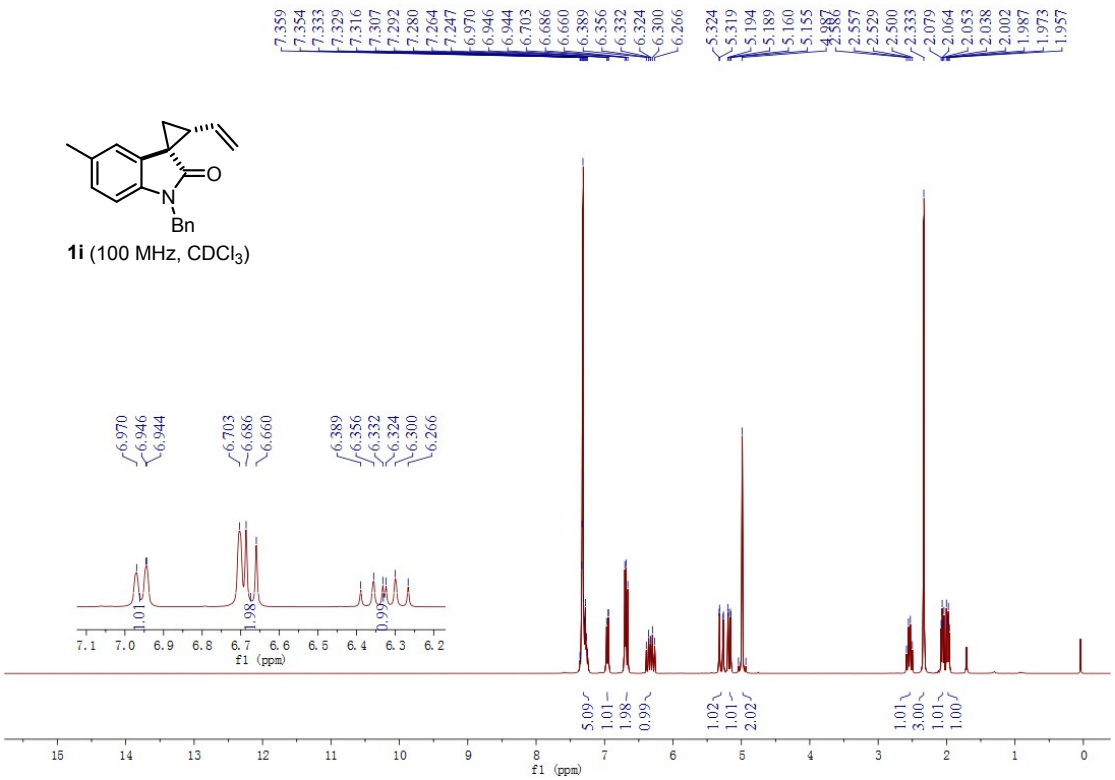
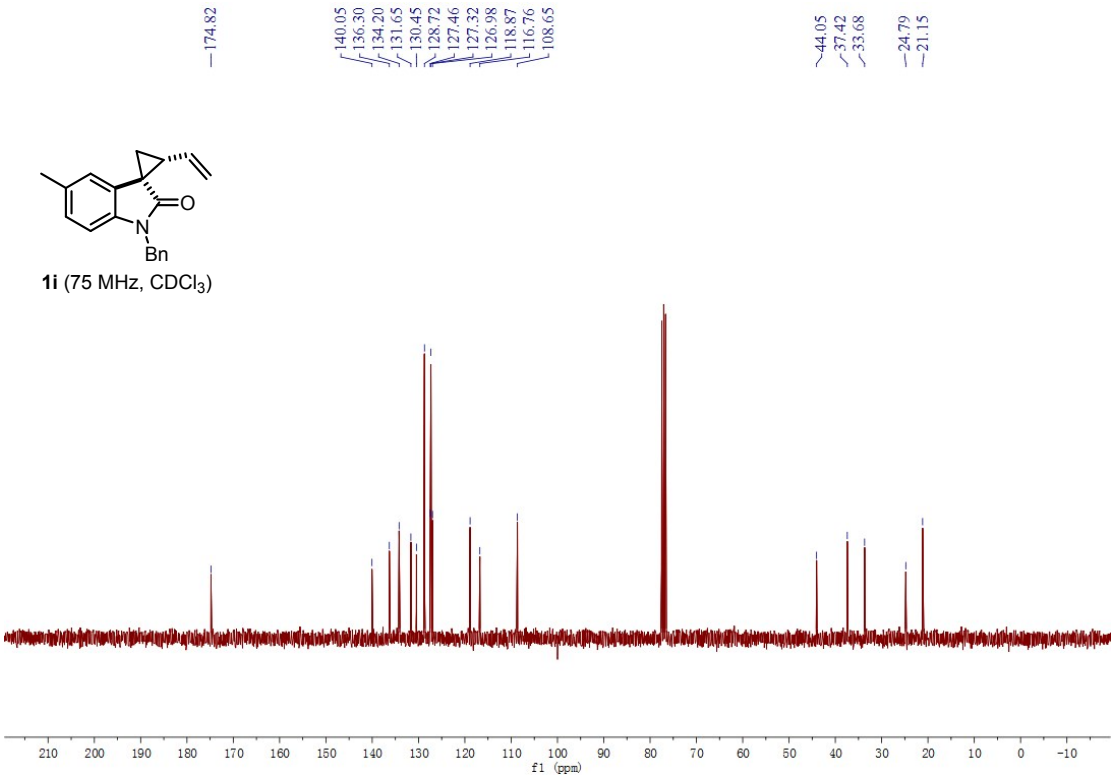


1h (75 MHz, $CDCl_3$)

1i (100 MHz, $CDCl_3$)





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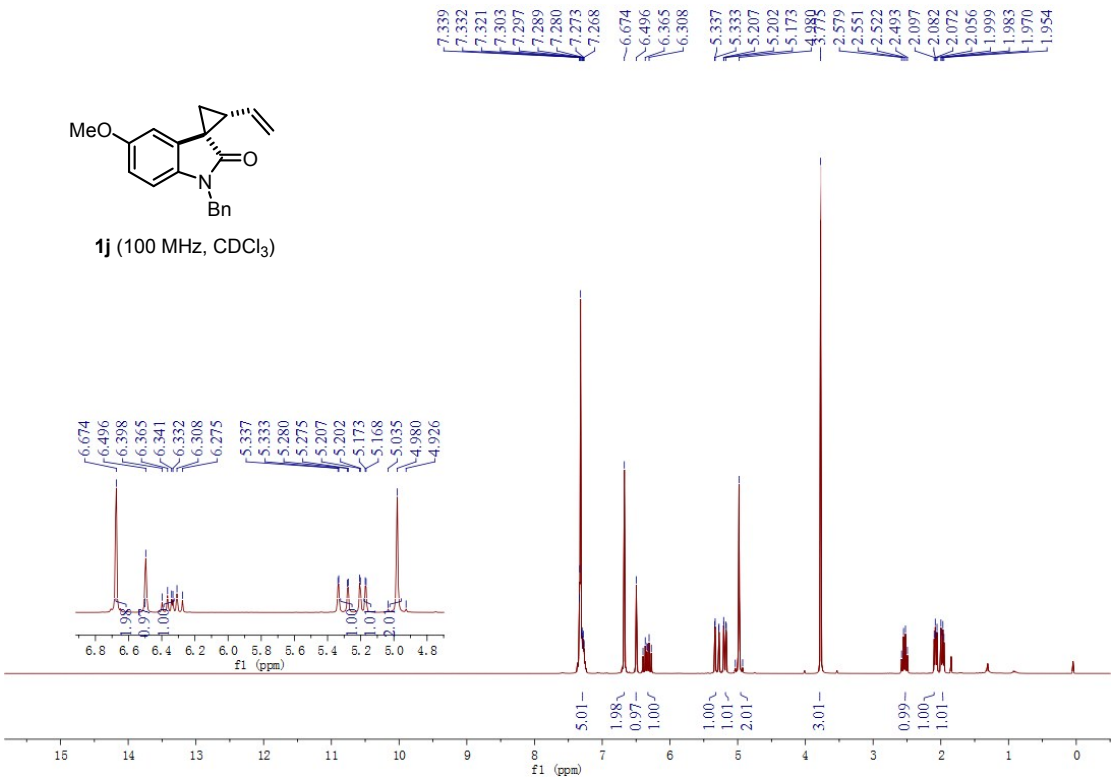

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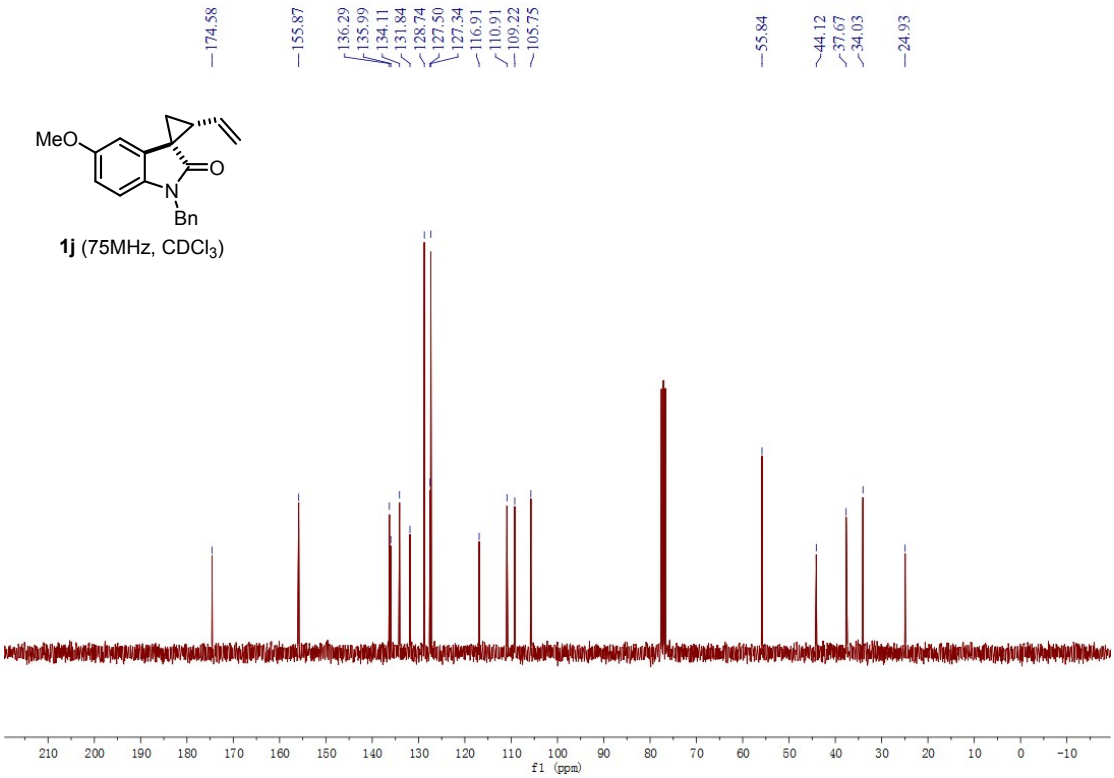

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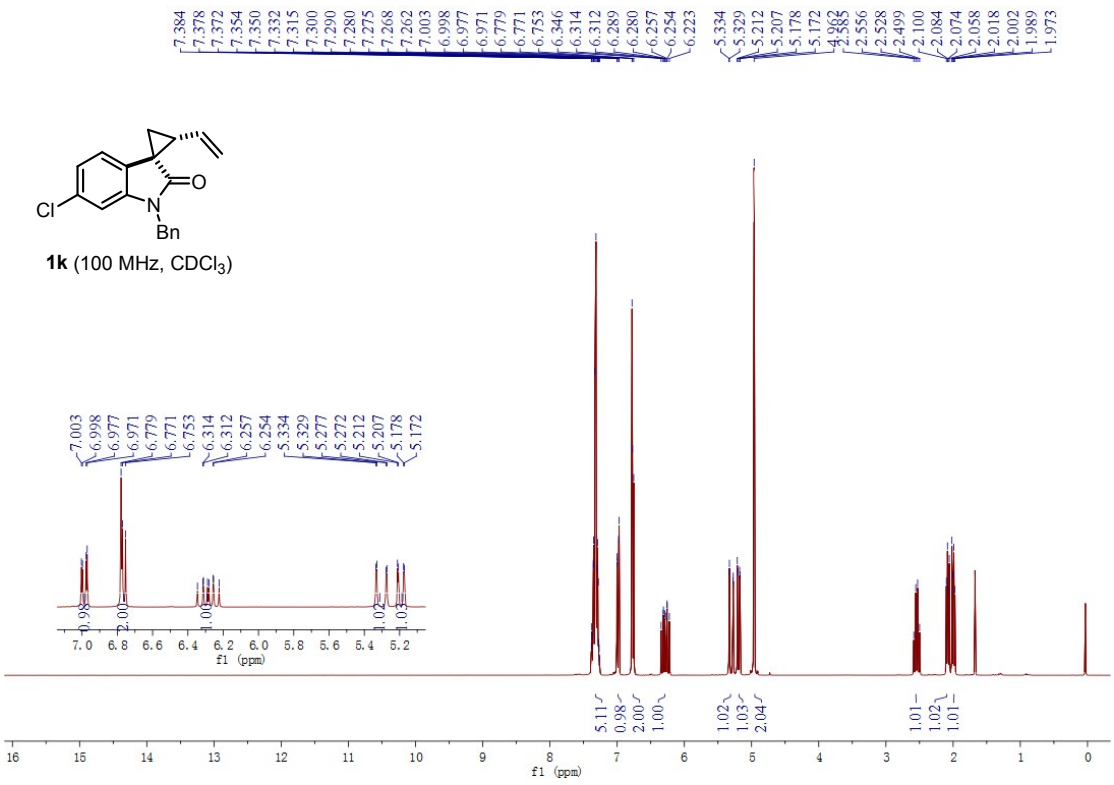

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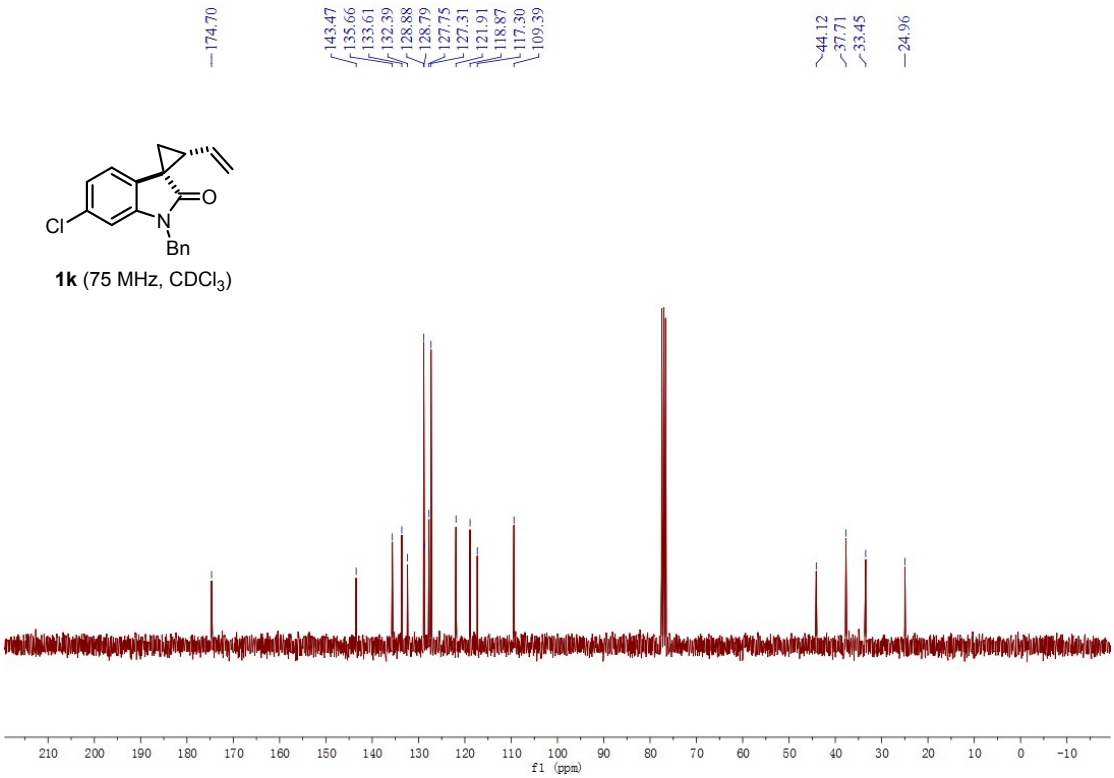
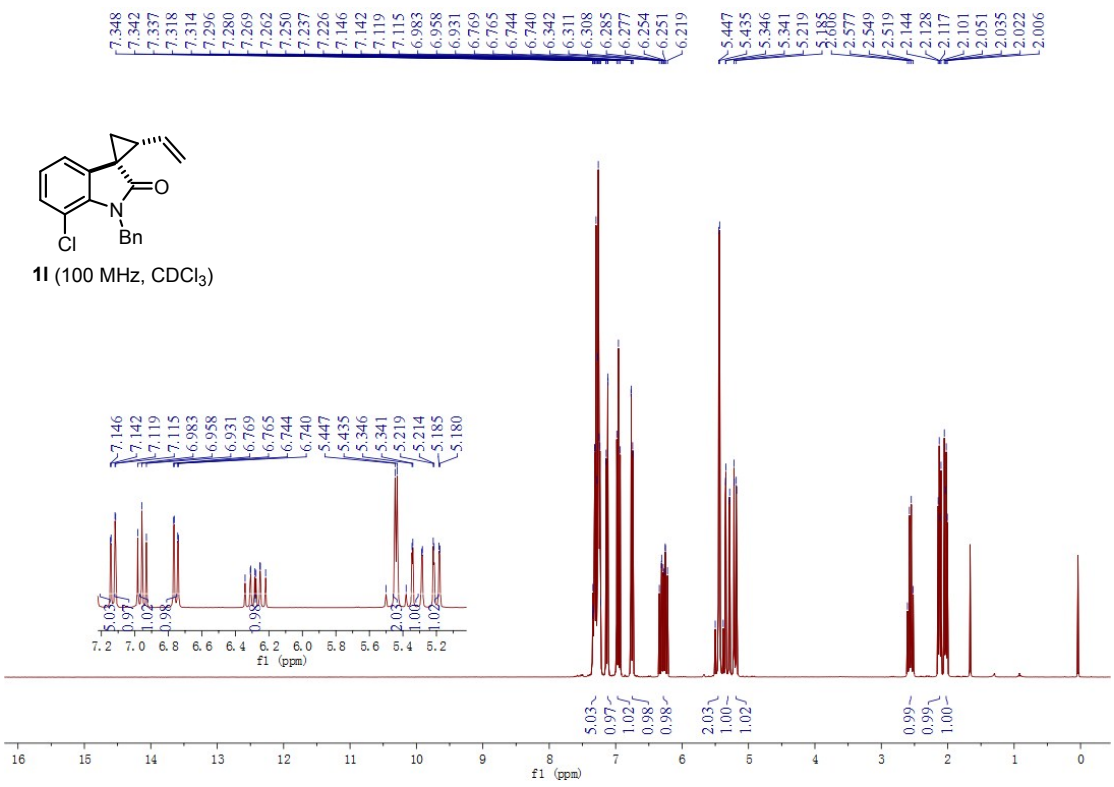


1k (75 MHz, $CDCl_3$)



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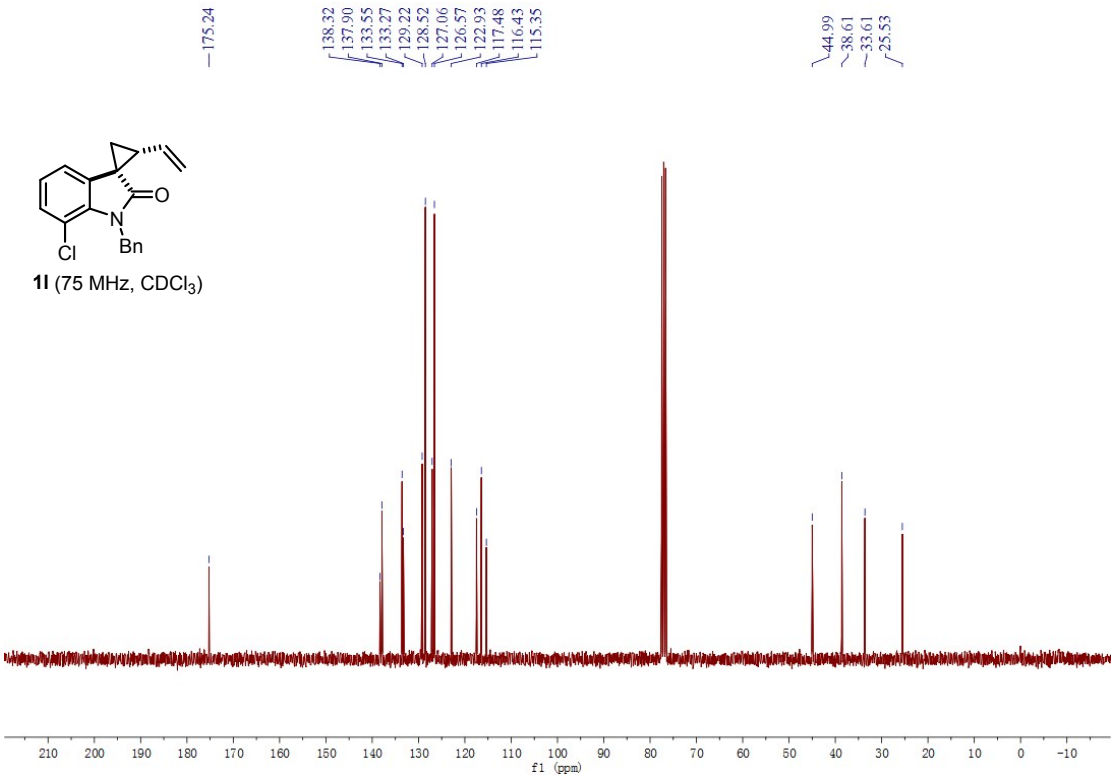
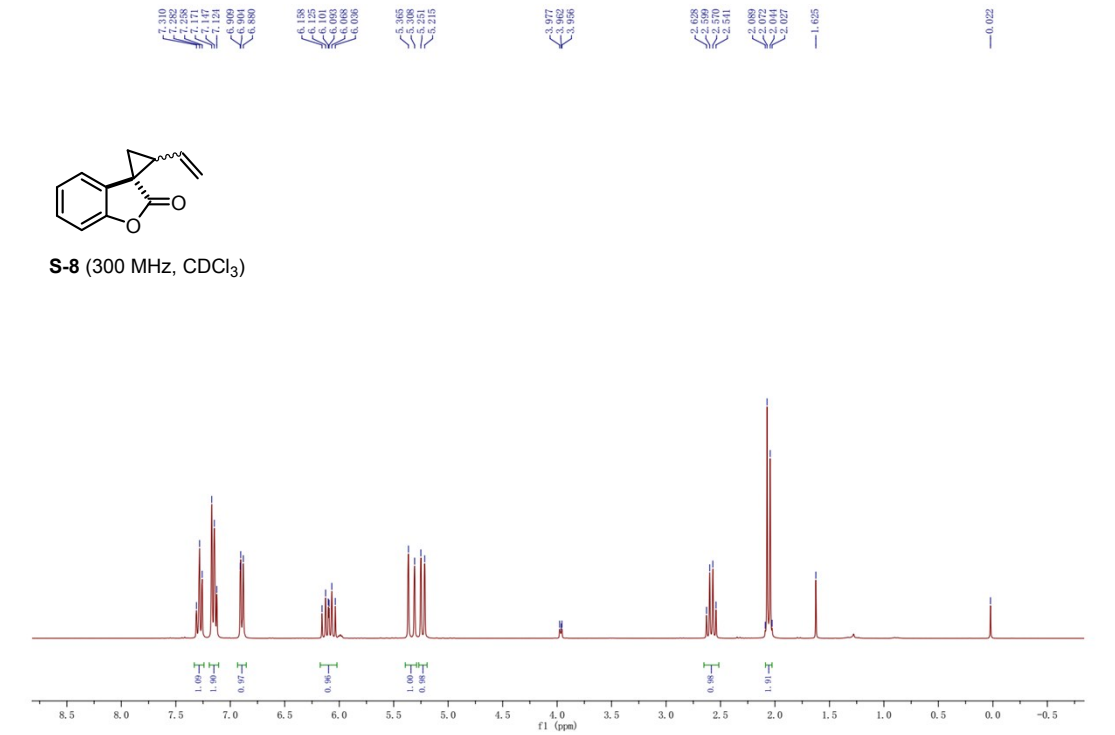
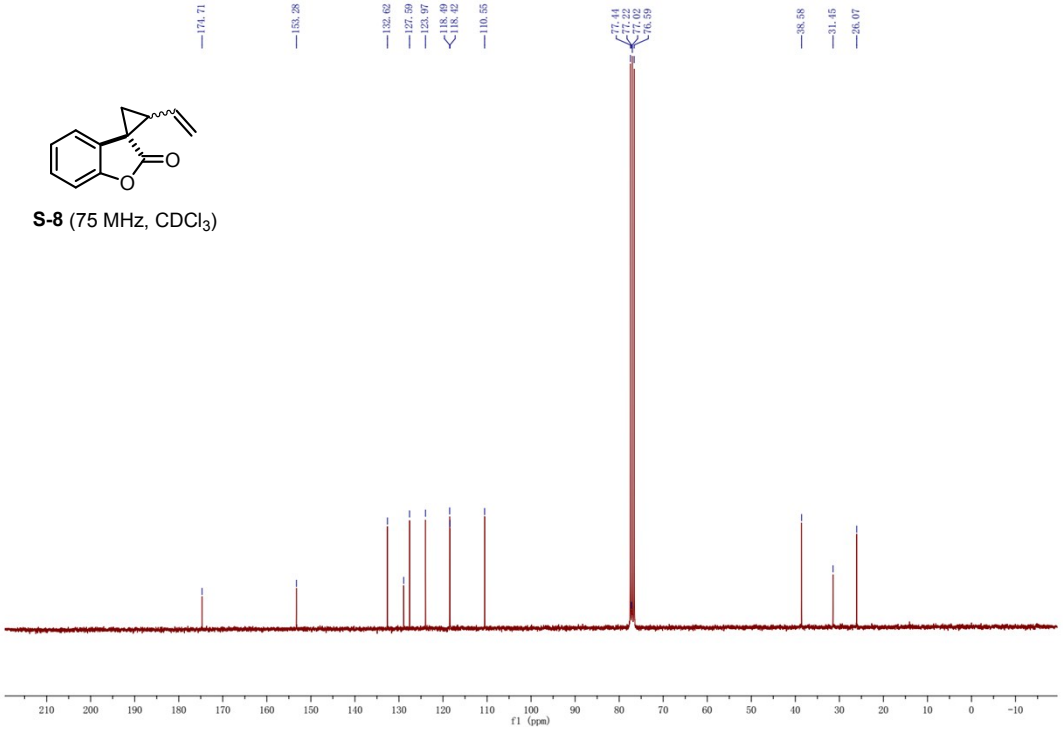


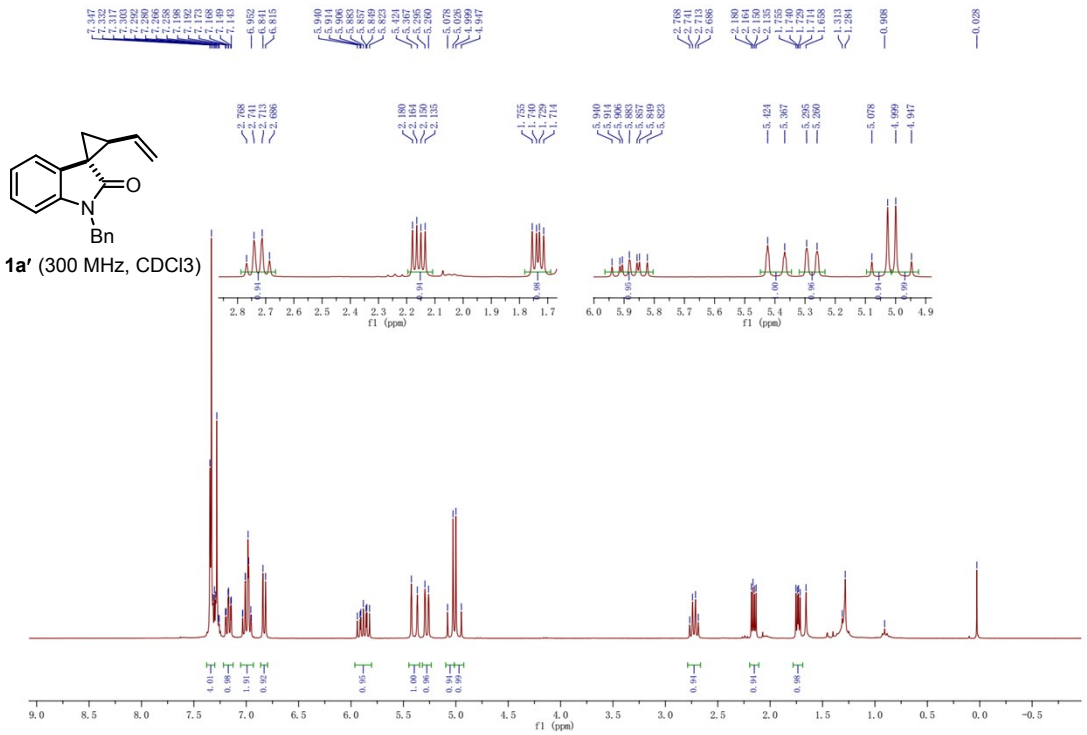
1l (75 MHz, $CDCl_3$)



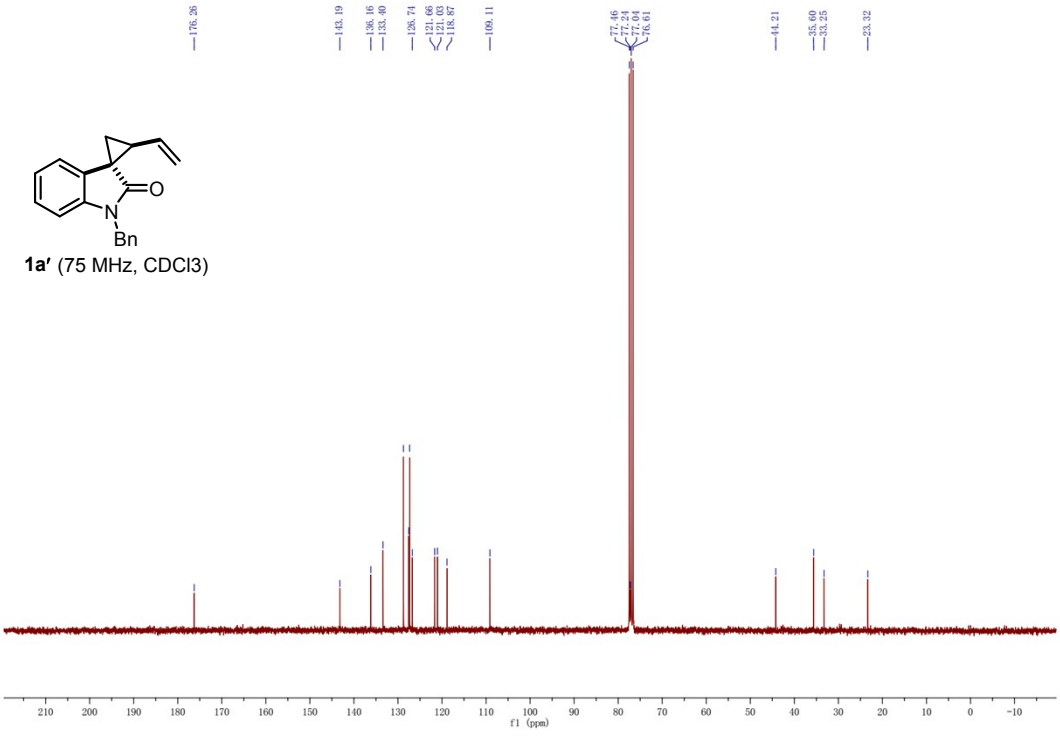
S-8 (300 MHz, $CDCl_3$)



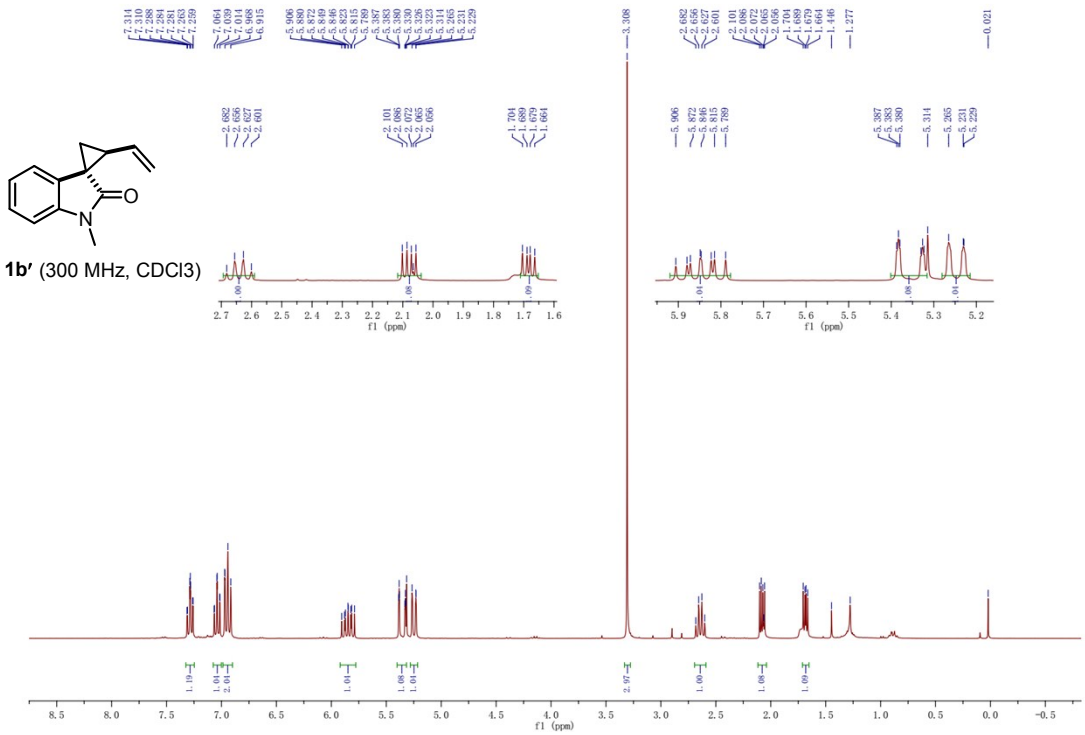
S-8 (75 MHz, $CDCl_3$)



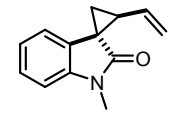
1a′ (300 MHz, CDCl3)



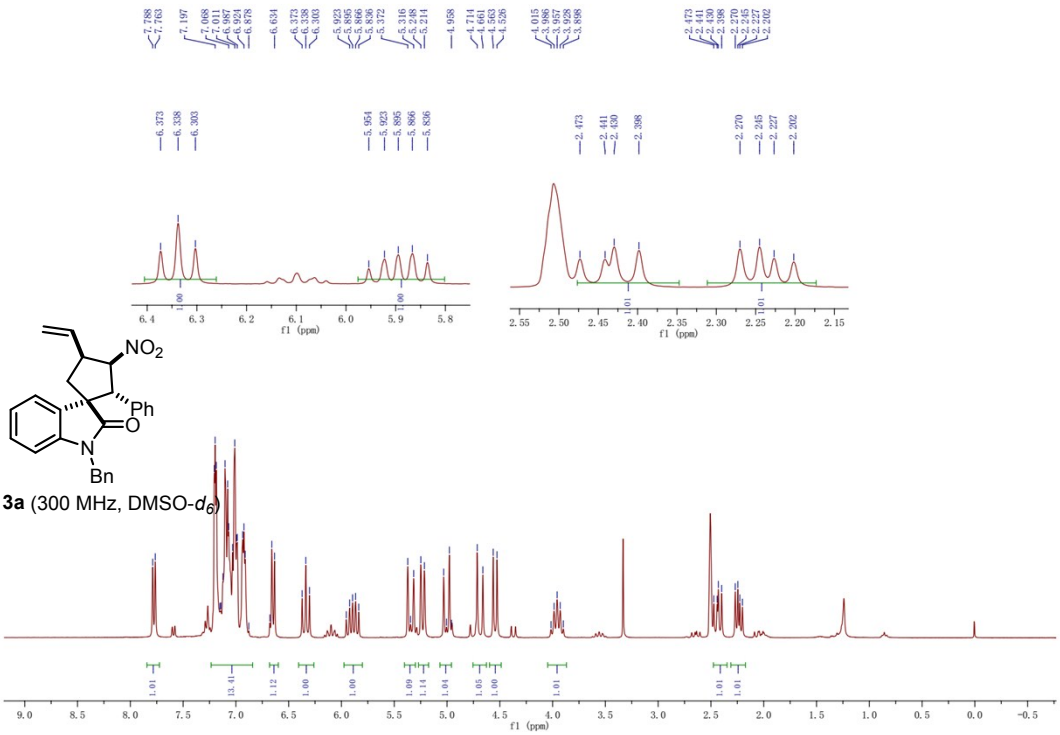
1a′ (75 MHz, CDCl3)



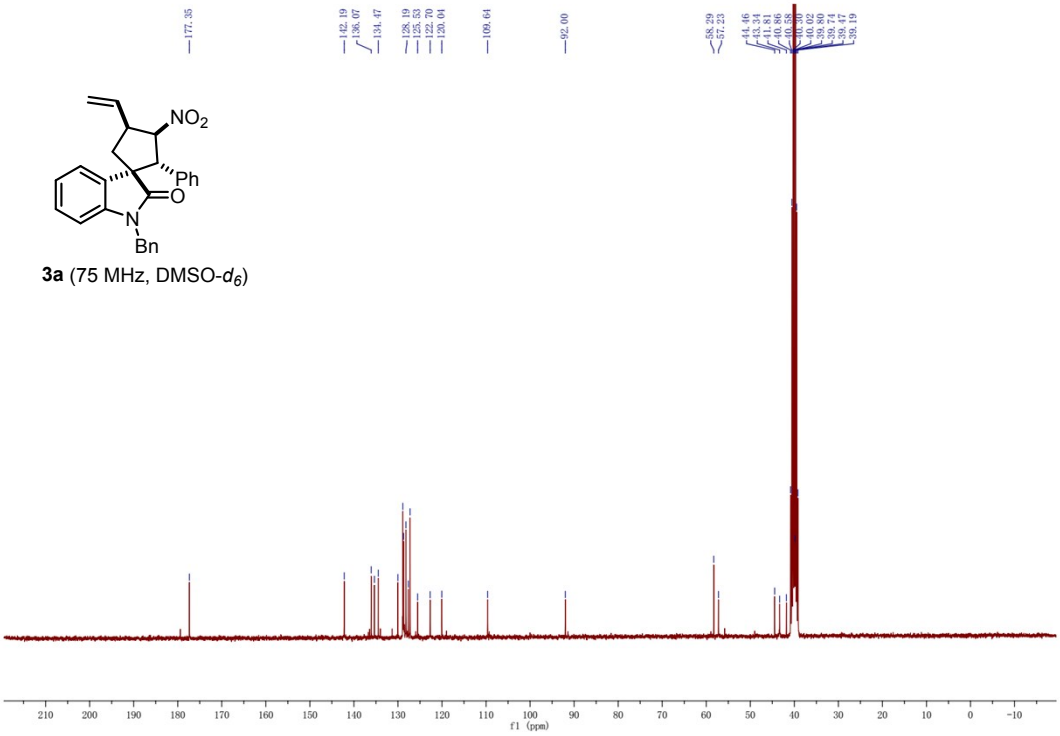
1b′ (300 MHz, CDCl3)



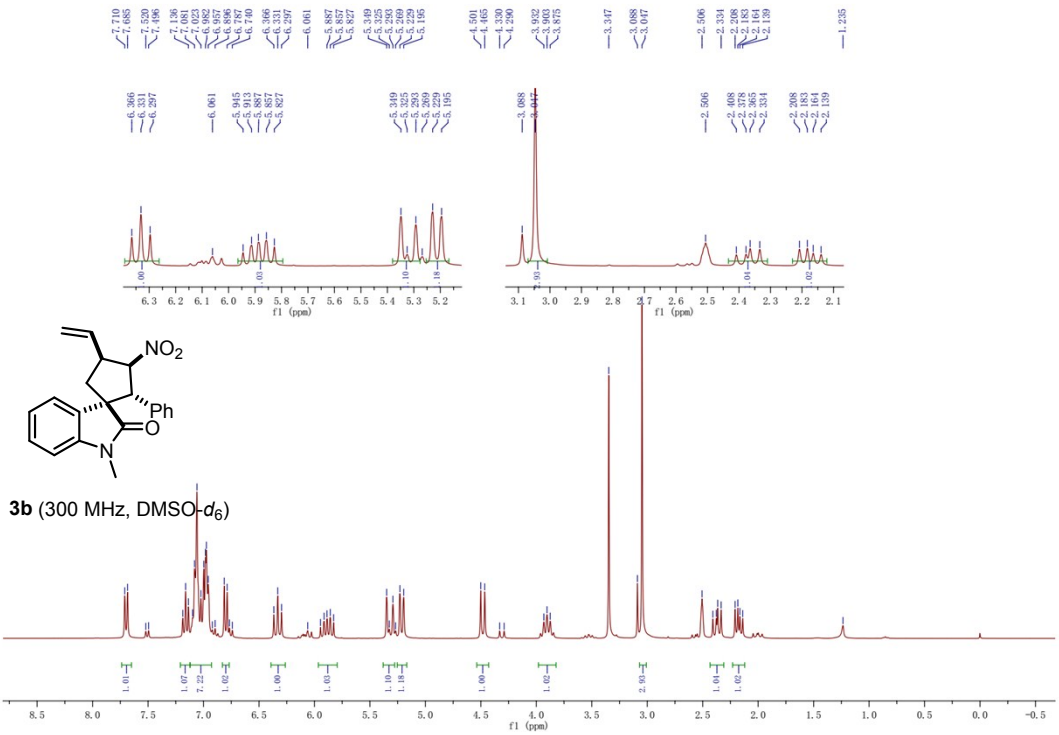
1b′ (75 MHz, CDCl3)



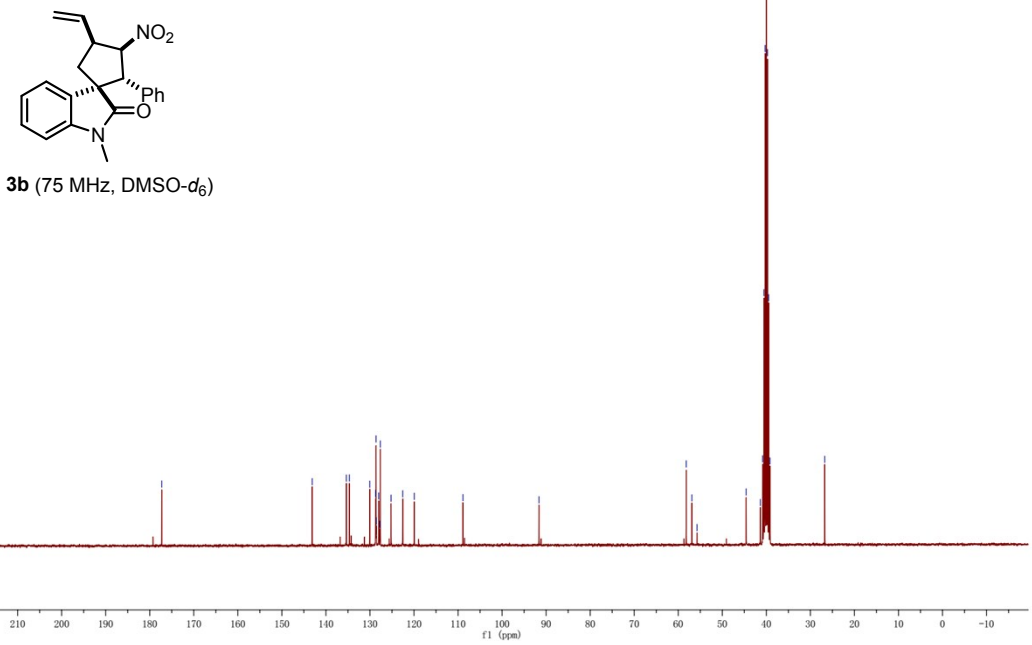
3a (300 MHz, DMSO-d_6)



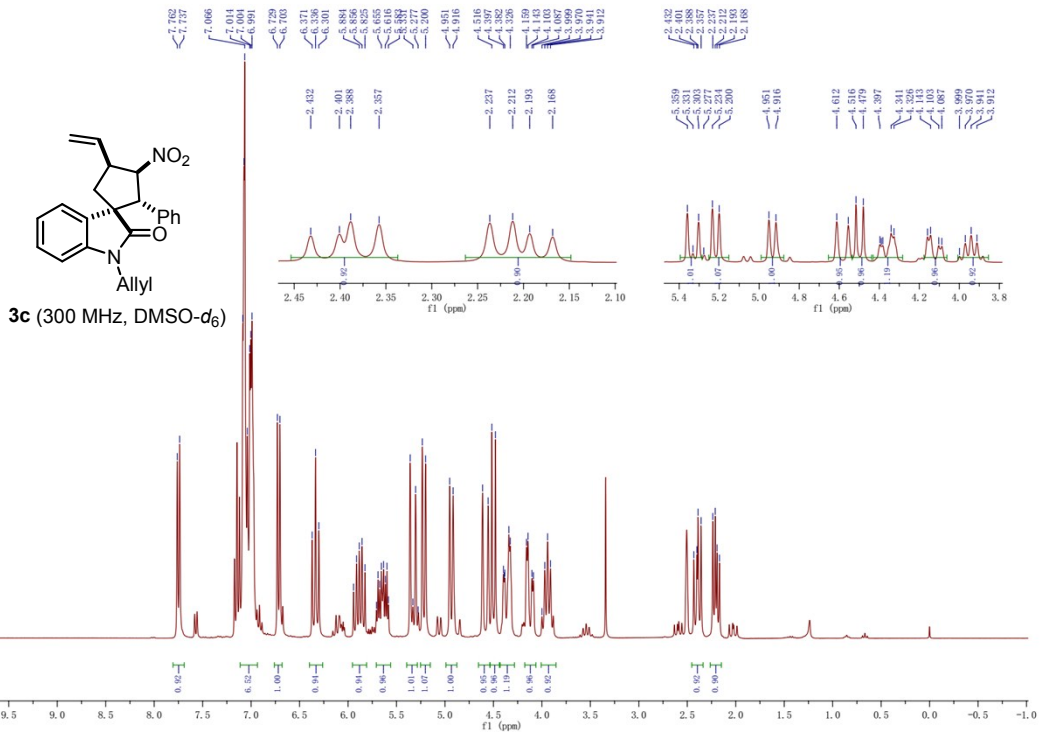
3a (75 MHz, DMSO-d_6)



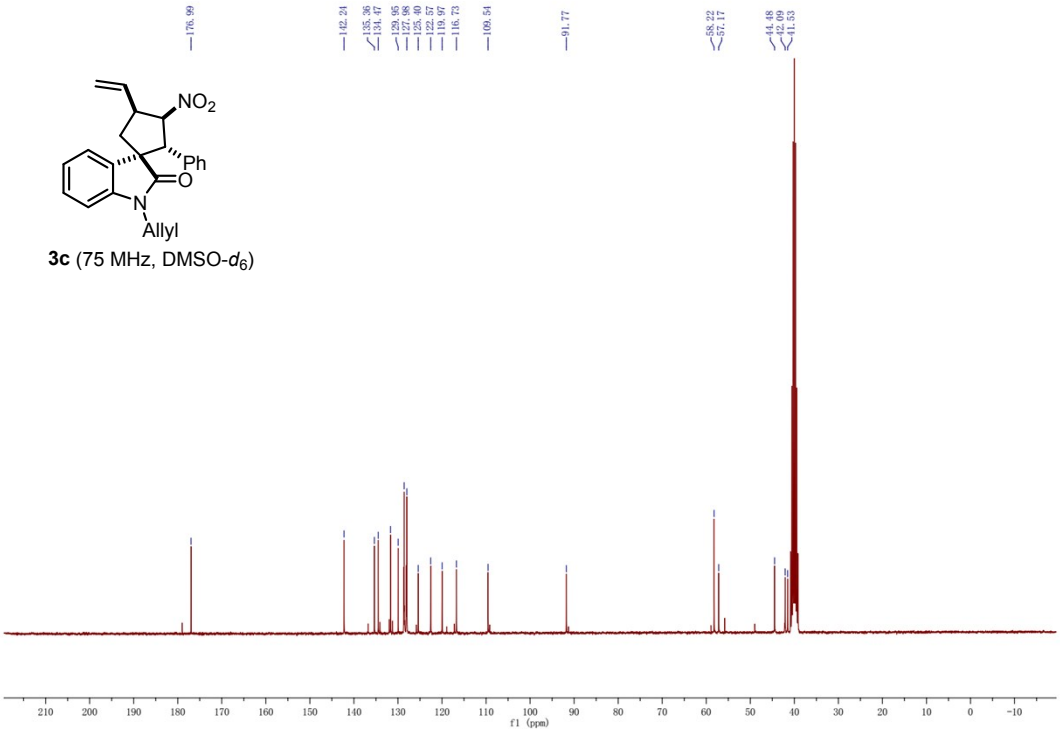
3b (300 MHz, DMSO-d_6)



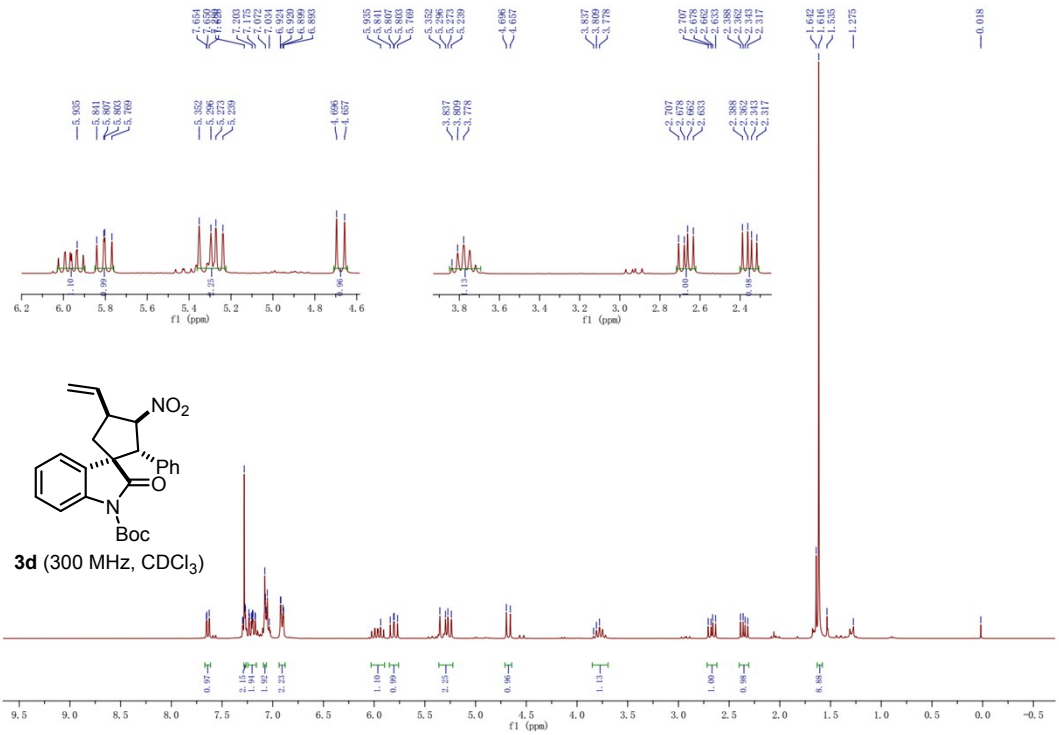
3b (75 MHz, DMSO-d_6)



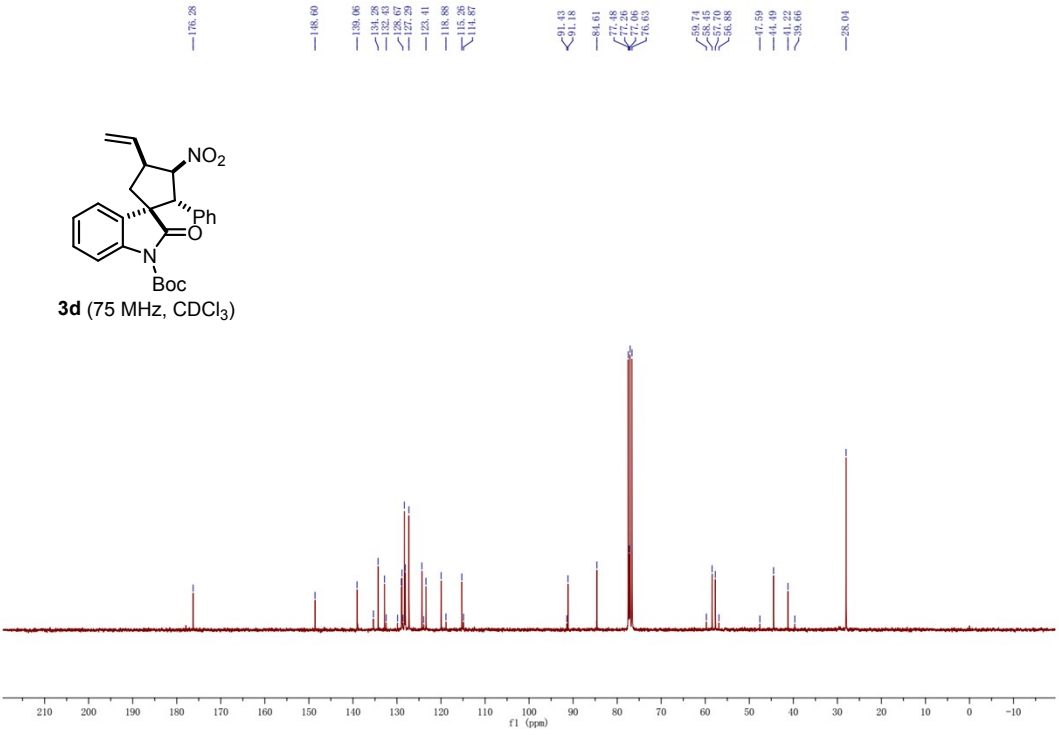
3c (300 MHz, DMSO-d_6)



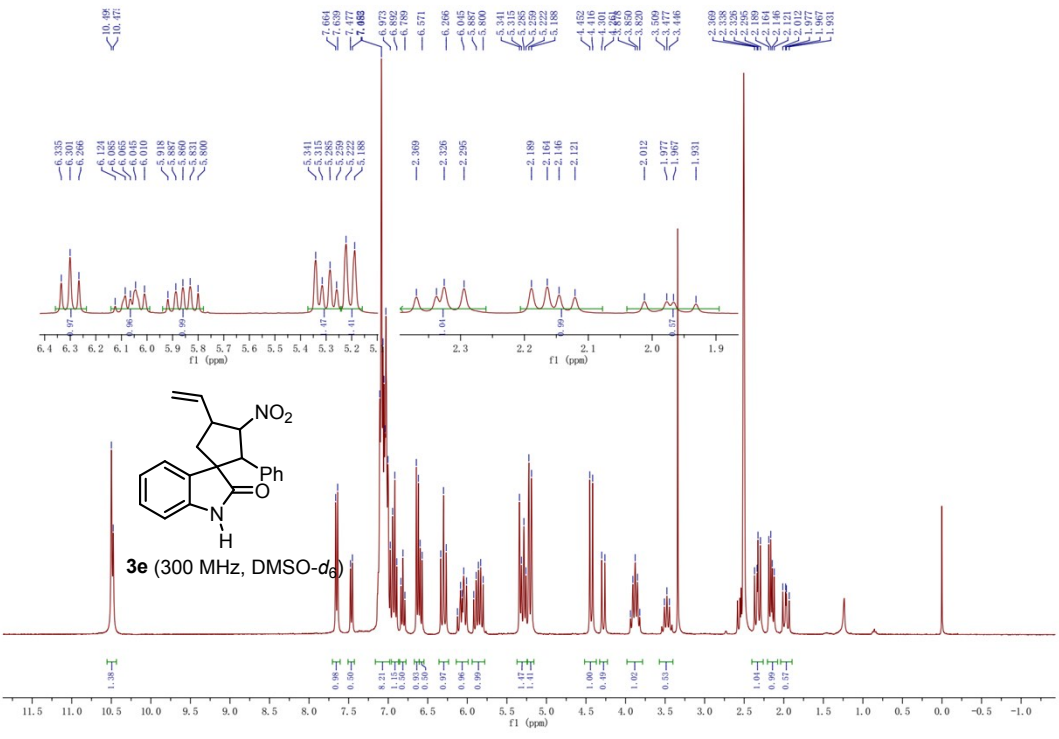
3c (75 MHz, DMSO-d_6)



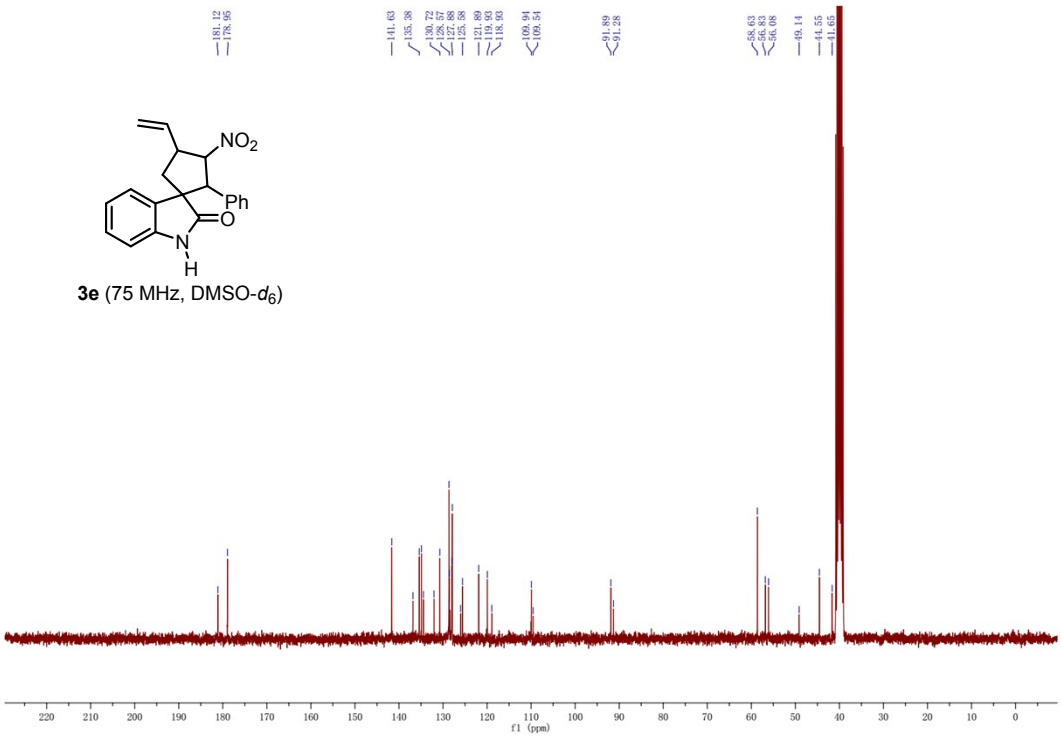
3d (300 MHz, $CDCl_3$)



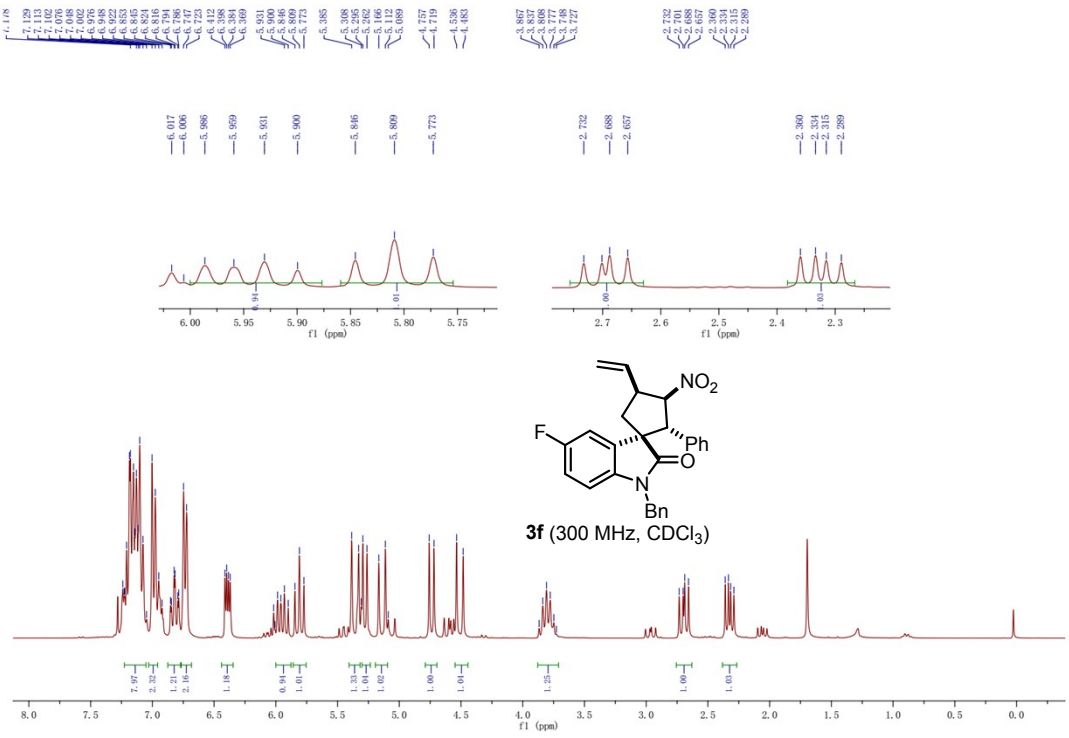
3d (75 MHz, $CDCl_3$)



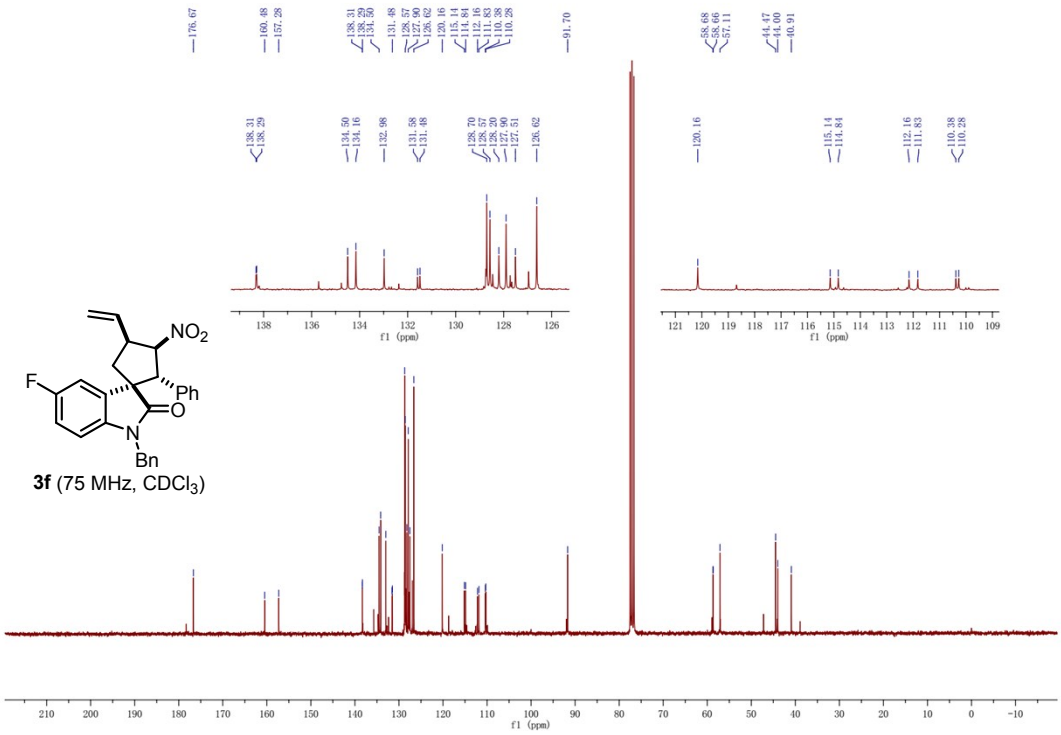
3e (300 MHz, DMSO-d_6)



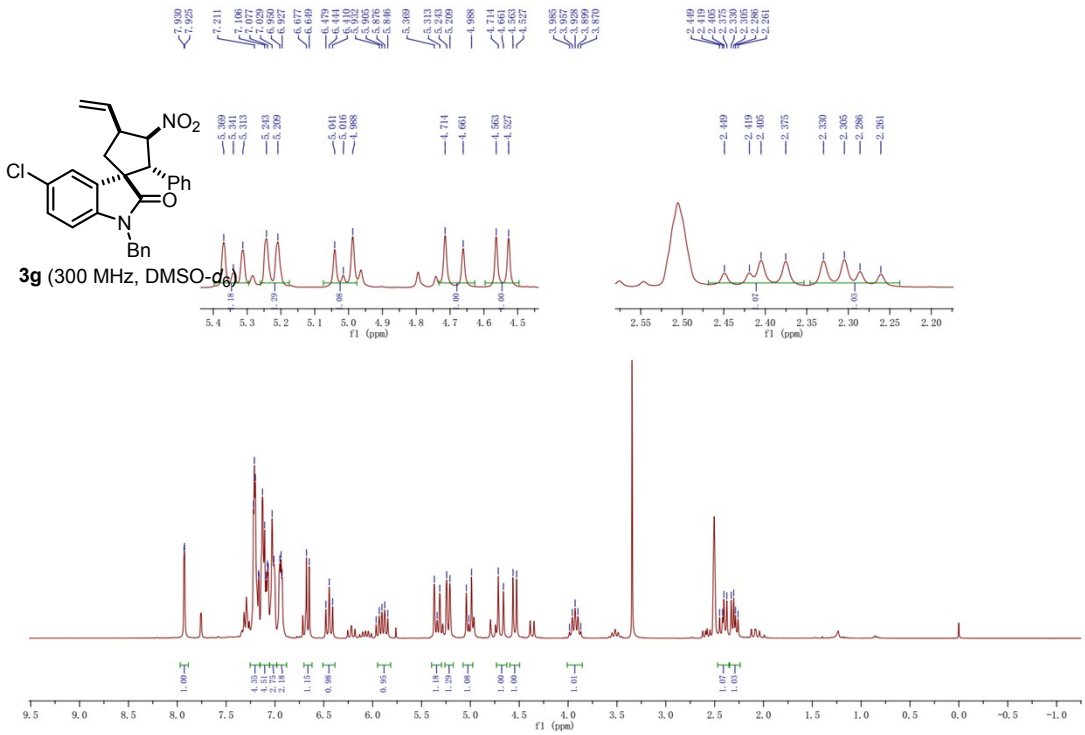
3e (75 MHz, DMSO-d_6)



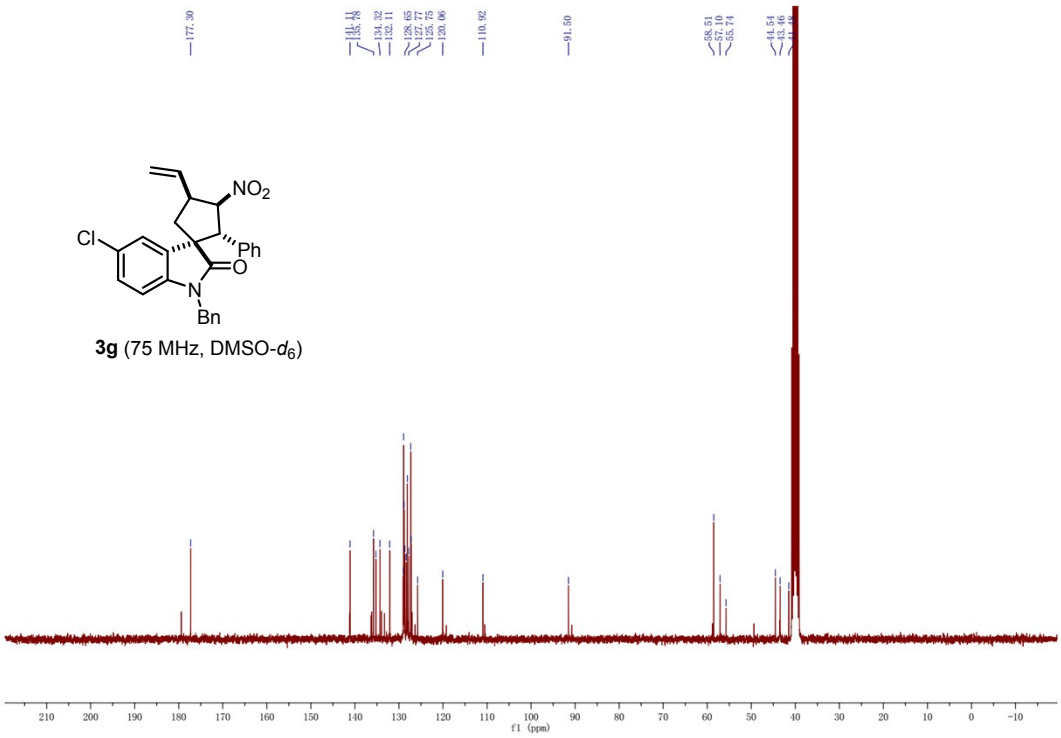
3f (300 MHz, $CDCl_3$)



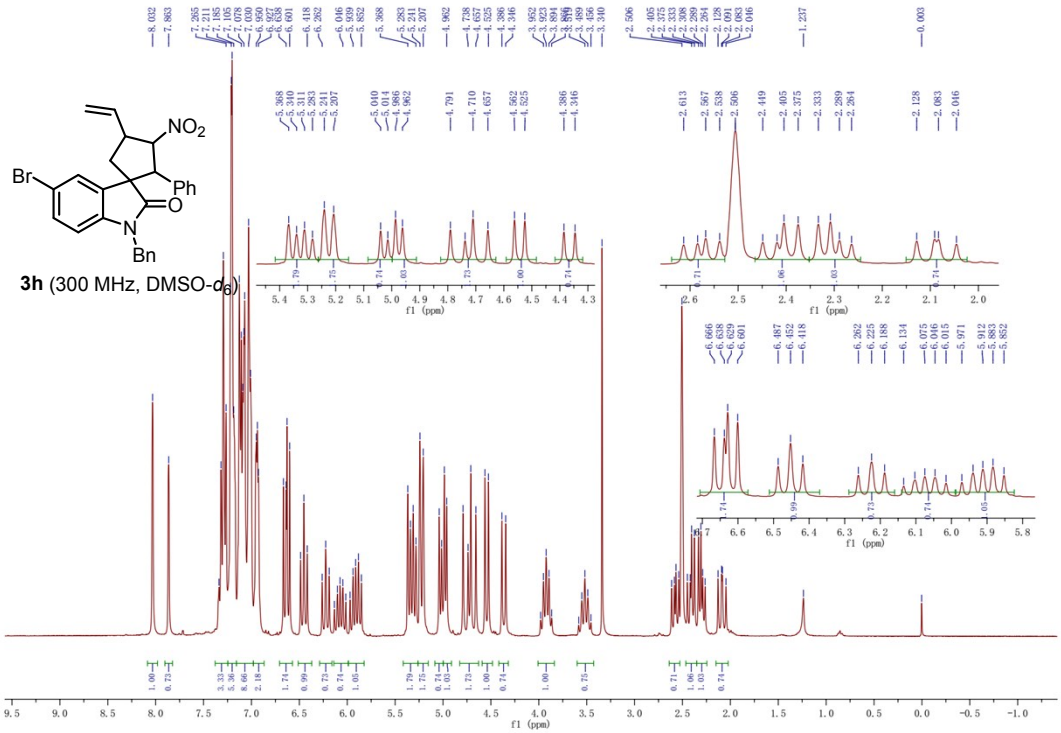
3f (75 MHz, $CDCl_3$)



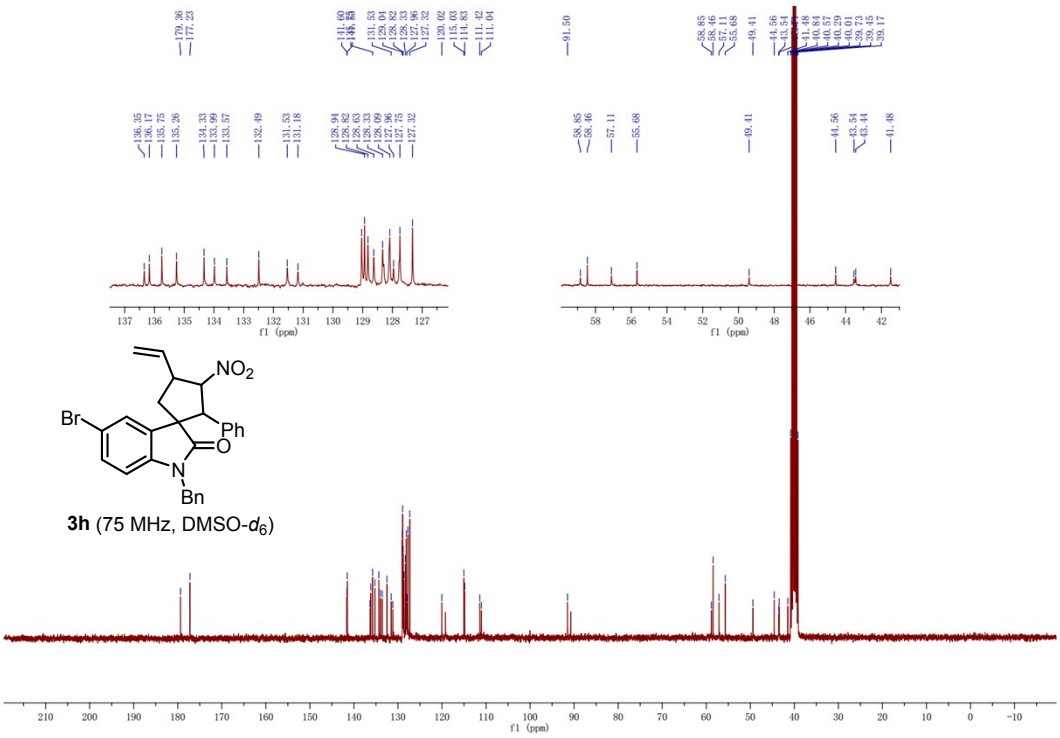
3g (300 MHz, DMSO-d_6)



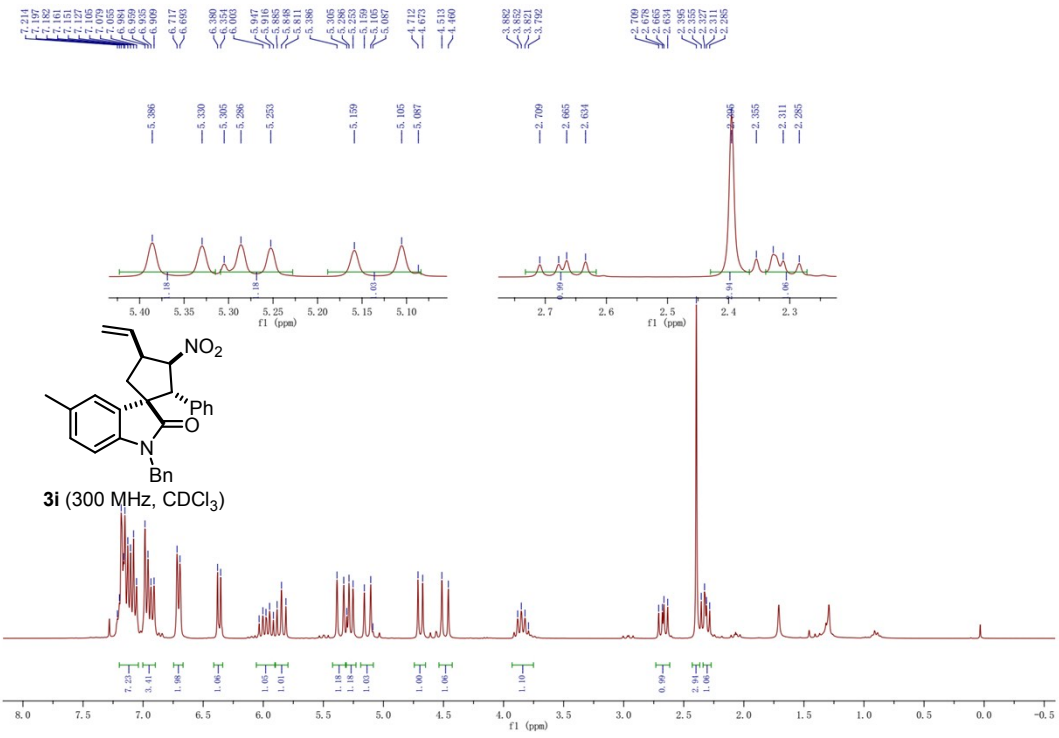
3g (75 MHz, DMSO-d_6)



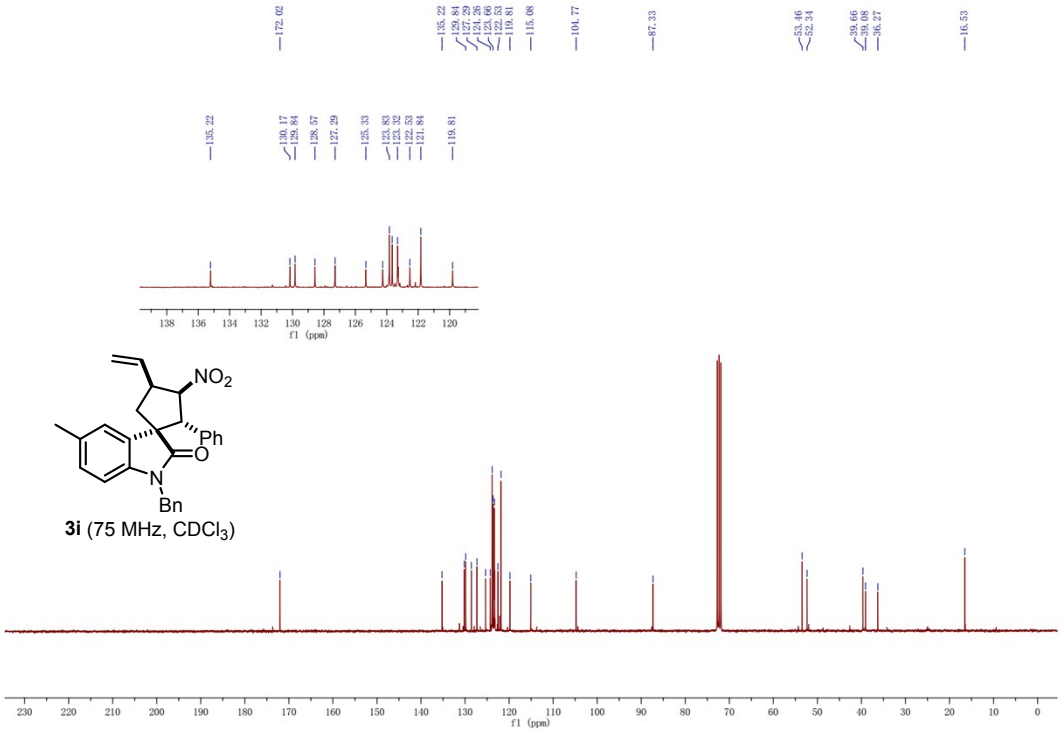
3h (300 MHz, DMSO-d_6)



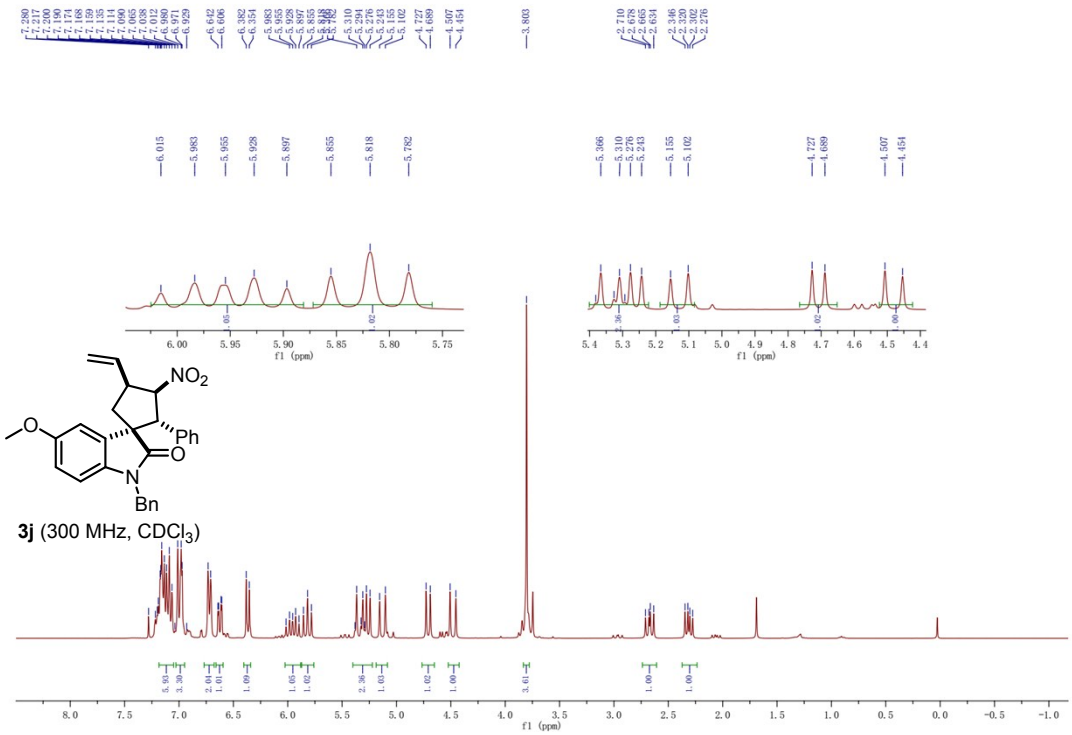
3h (75 MHz, DMSO-d_6)



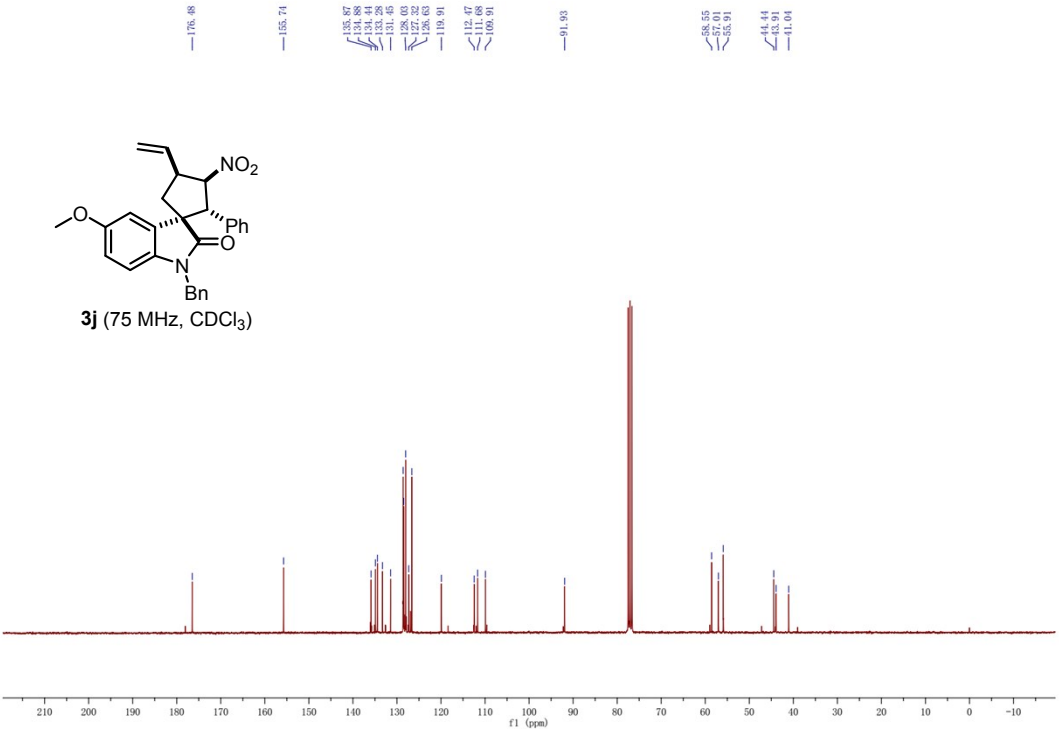
3i (300 MHz, $CDCl_3$)



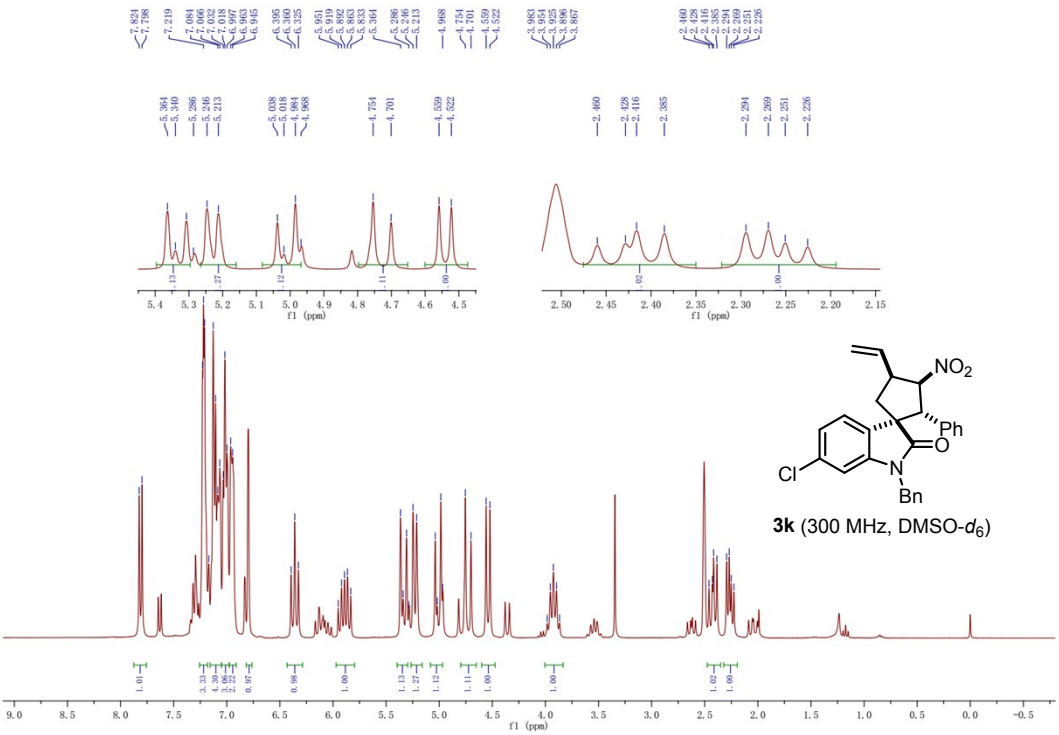
3i (75 MHz, $CDCl_3$)



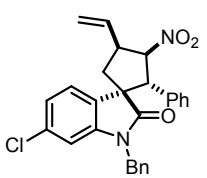
3j (300 MHz, $CDCl_3$)



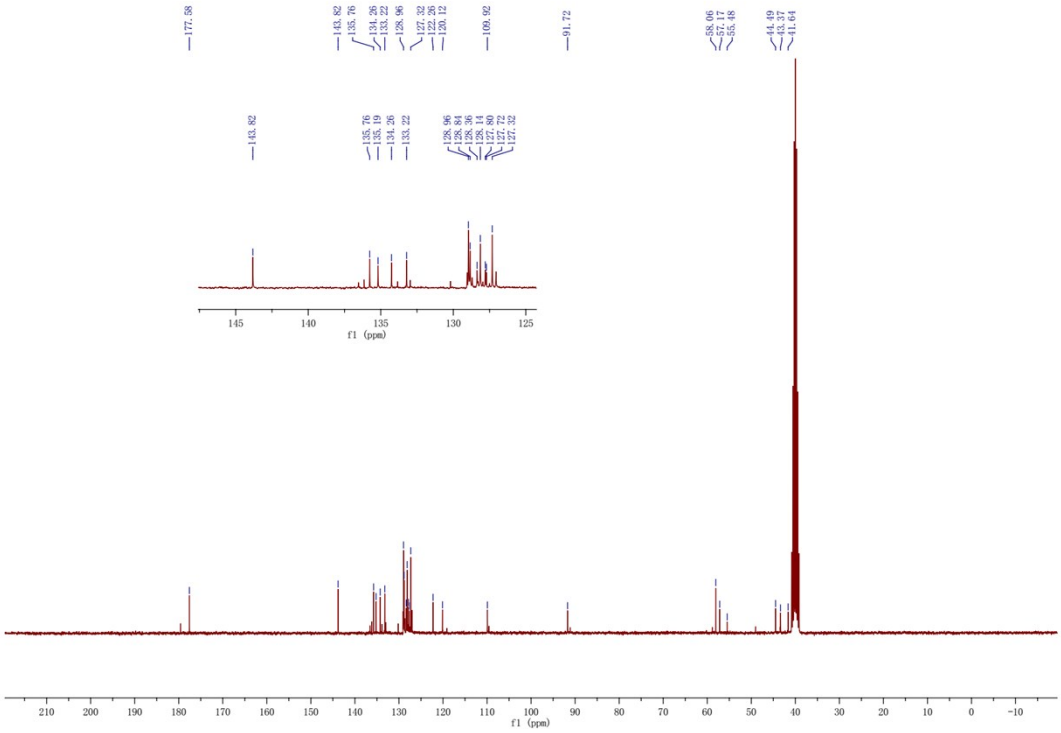
3j (75 MHz, $CDCl_3$)

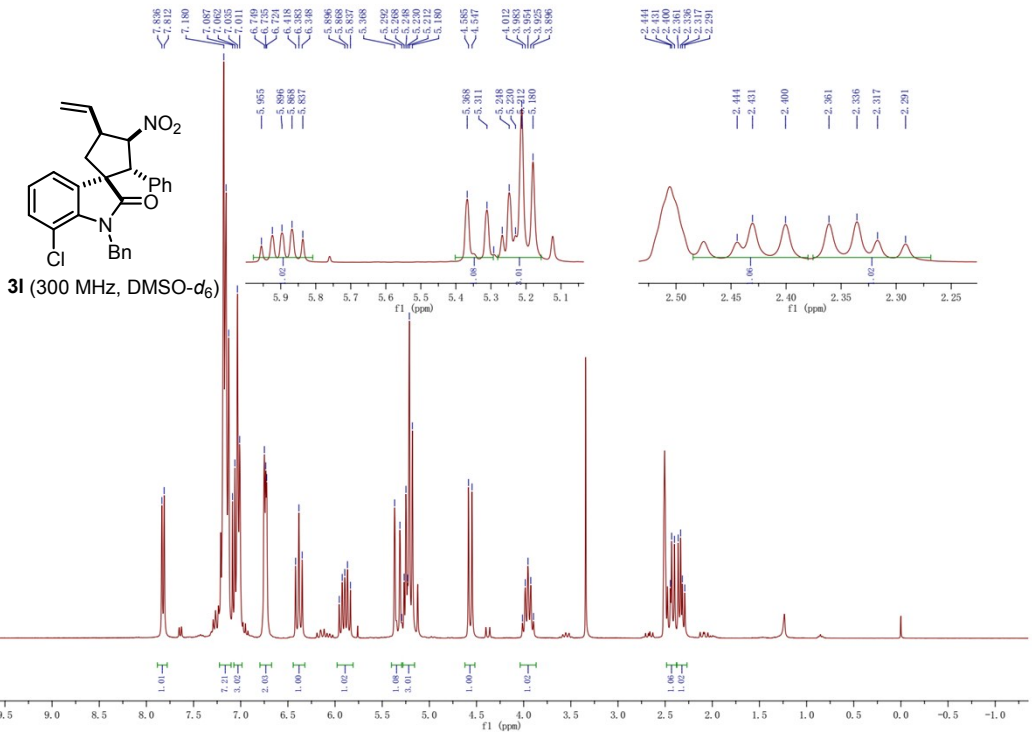


3k (300 MHz, DMSO-d_6)

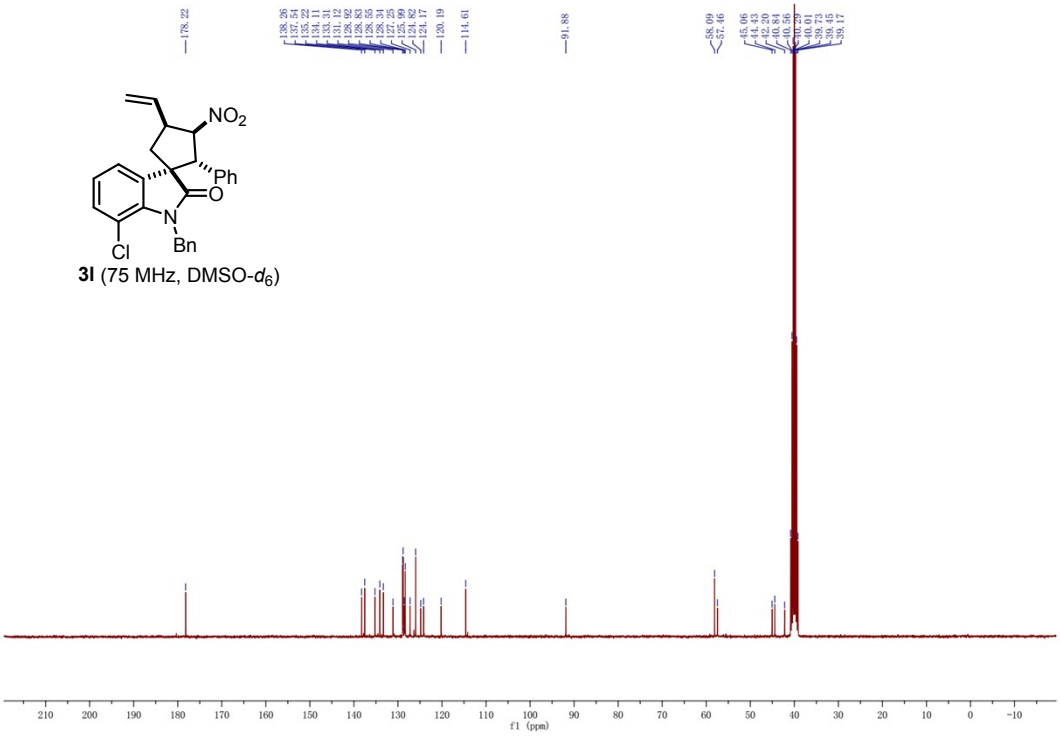


3k (75 MHz, DMSO-d_6)

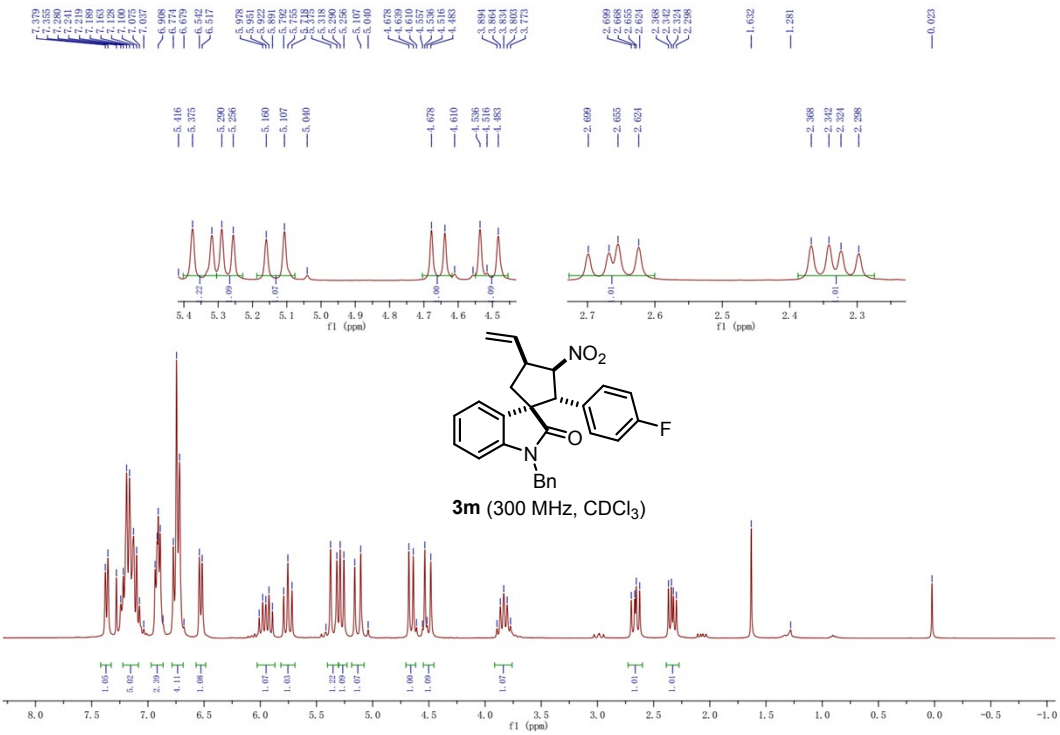




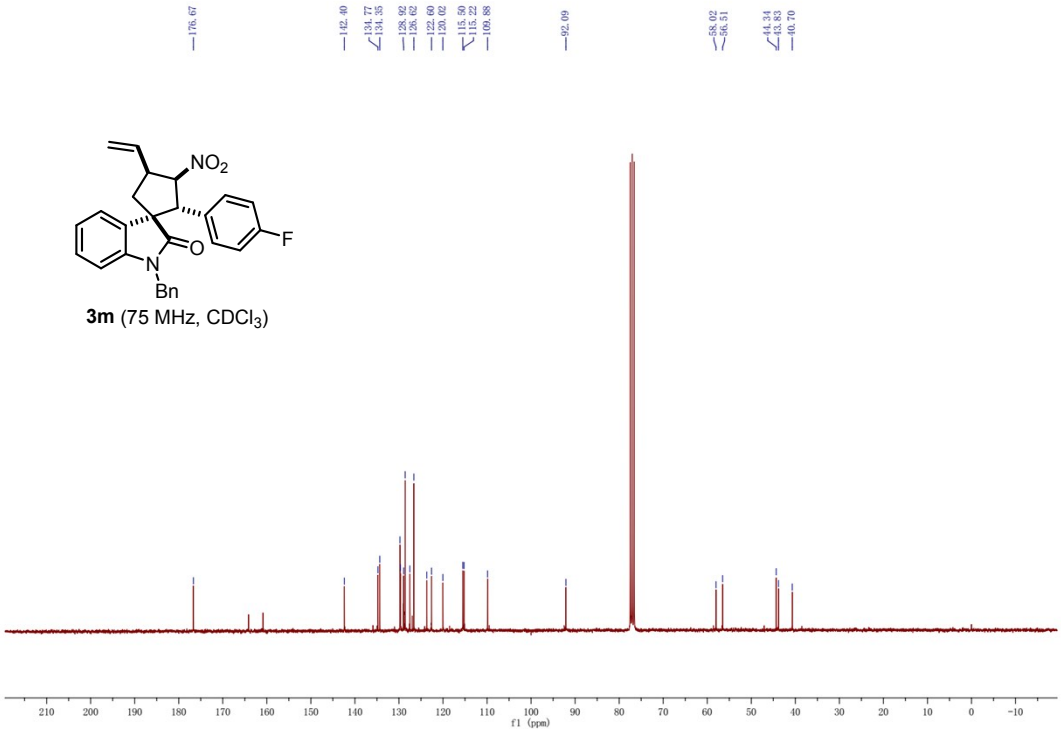
3l (300 MHz, DMSO-d_6)



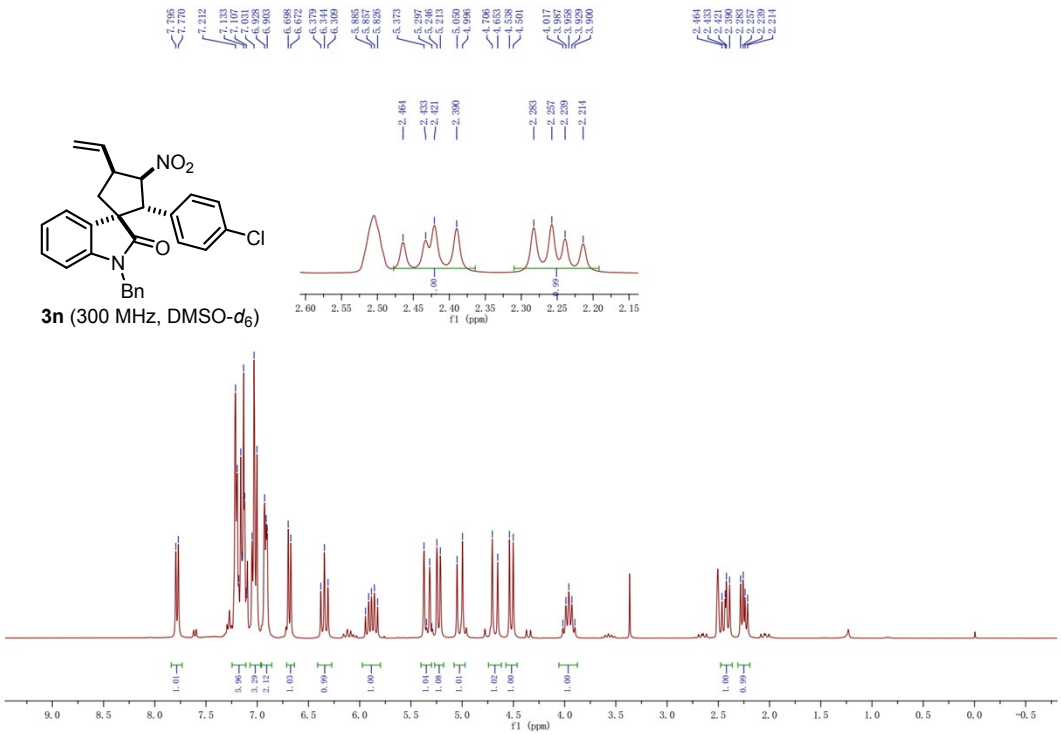
3l (75 MHz, DMSO-d_6)



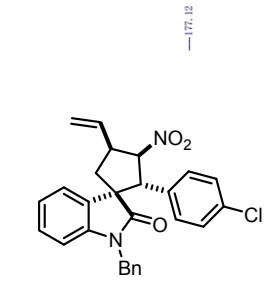
3m (300 MHz, $CDCl_3$)



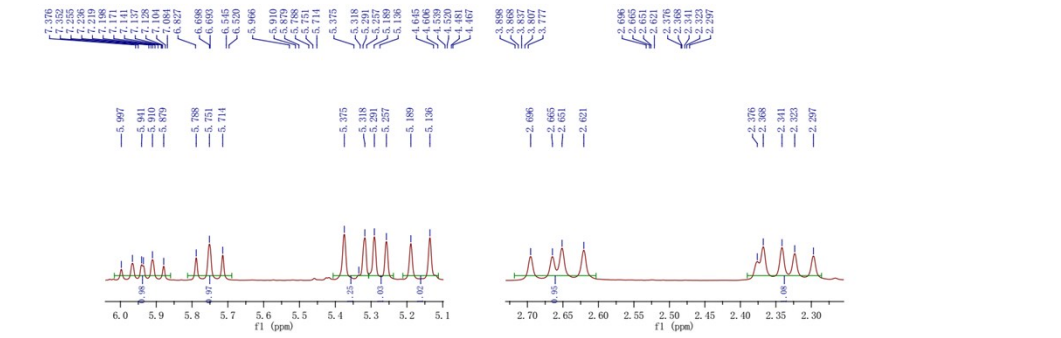
3m (75 MHz, $CDCl_3$)

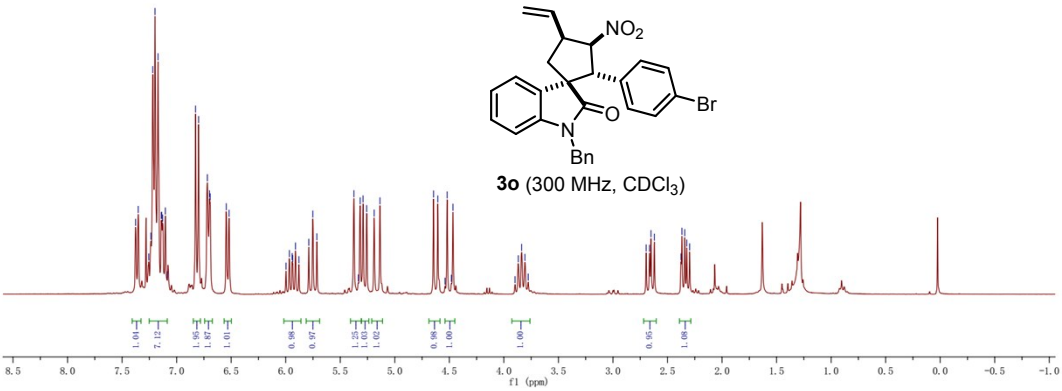


3n (300 MHz, DMSO-d_6)

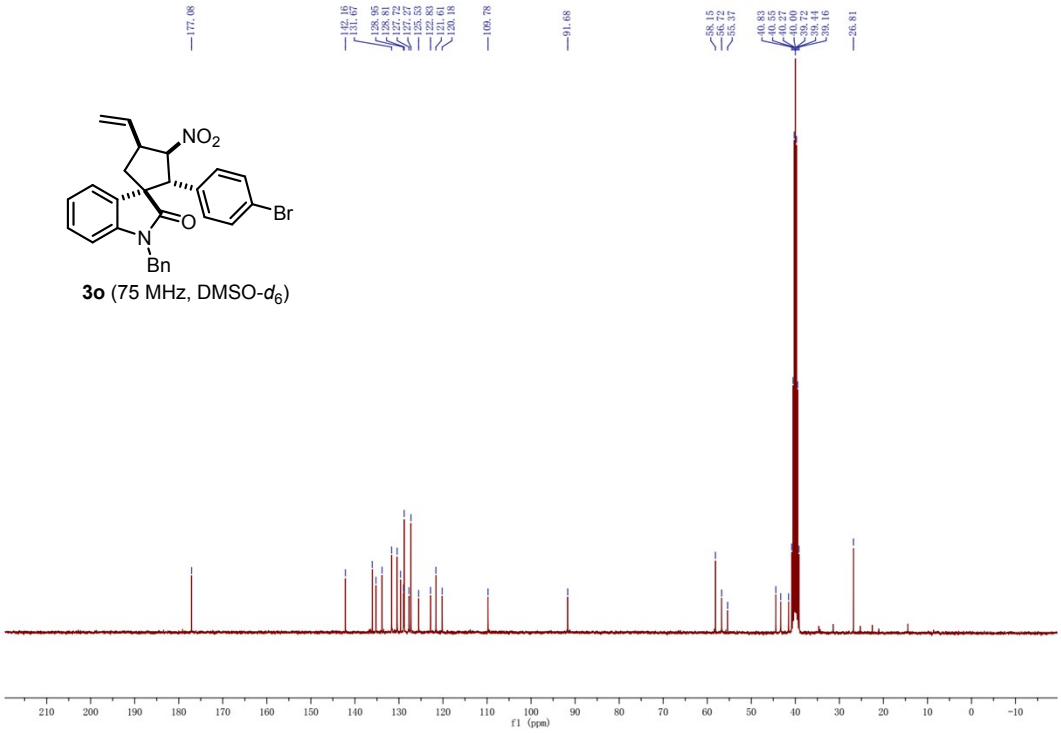


3n (75 MHz, DMSO-d_6)

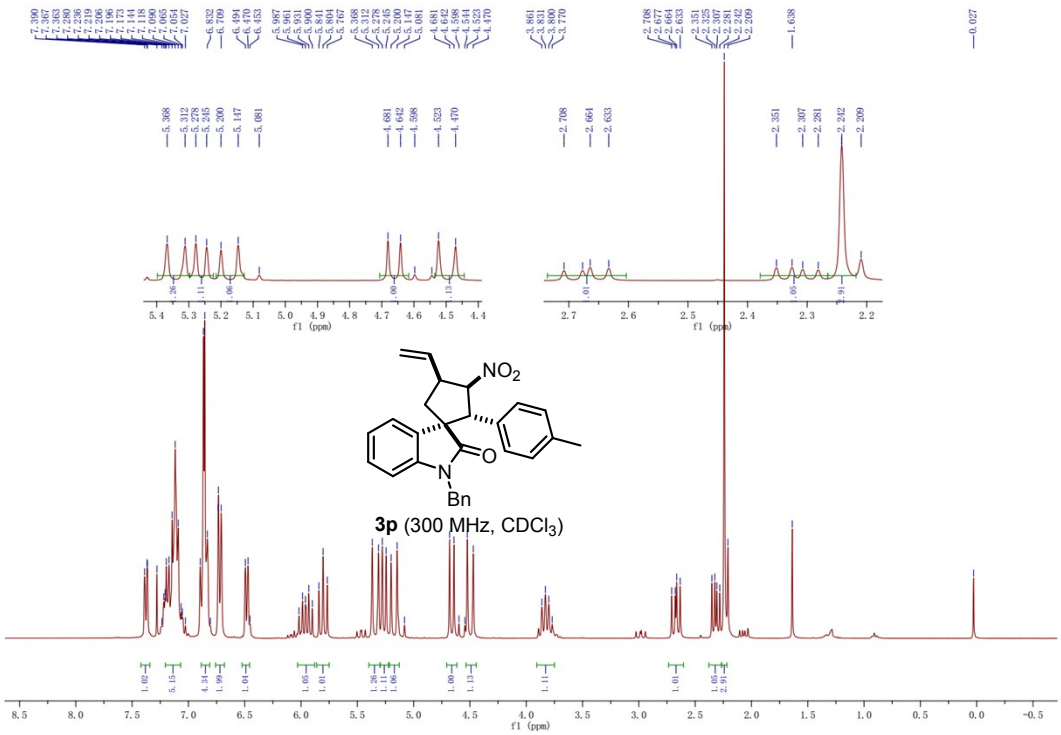




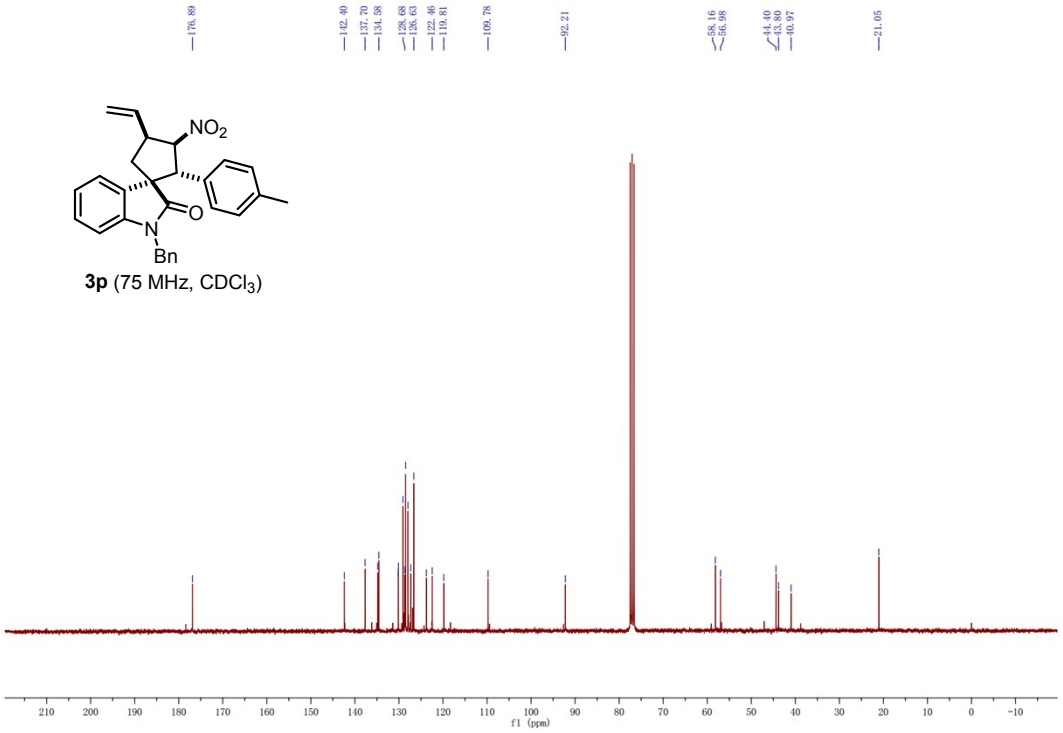
3o (300 MHz, $CDCl_3$)



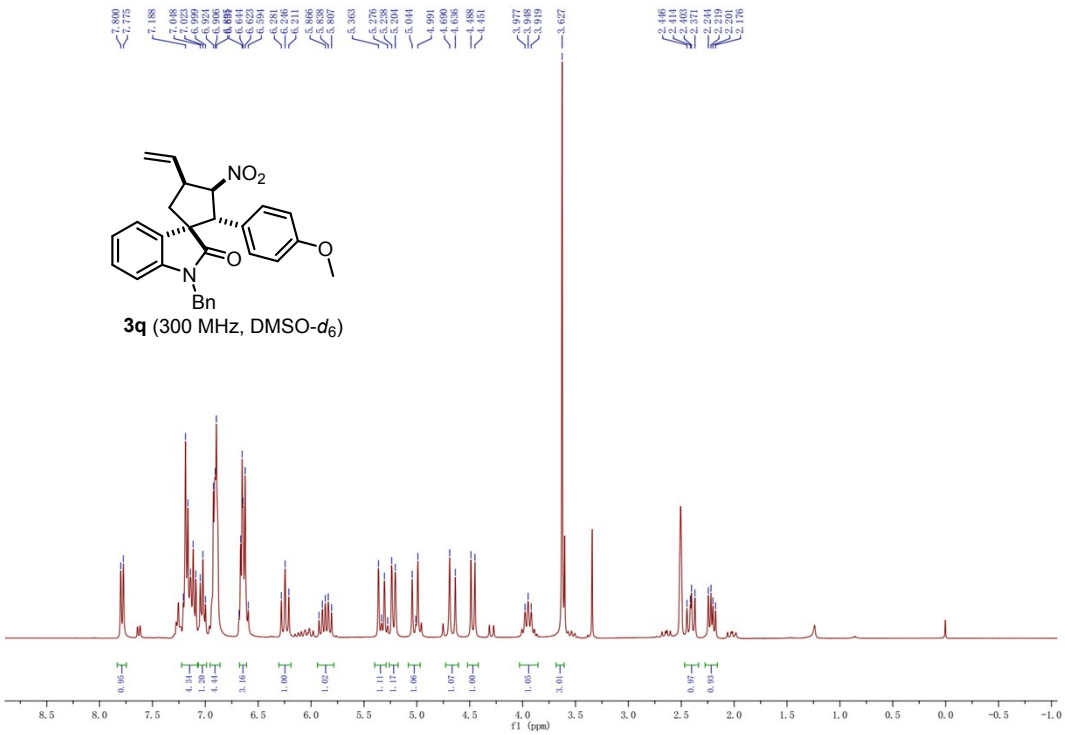
3o (75 MHz, DMSO-d_6)



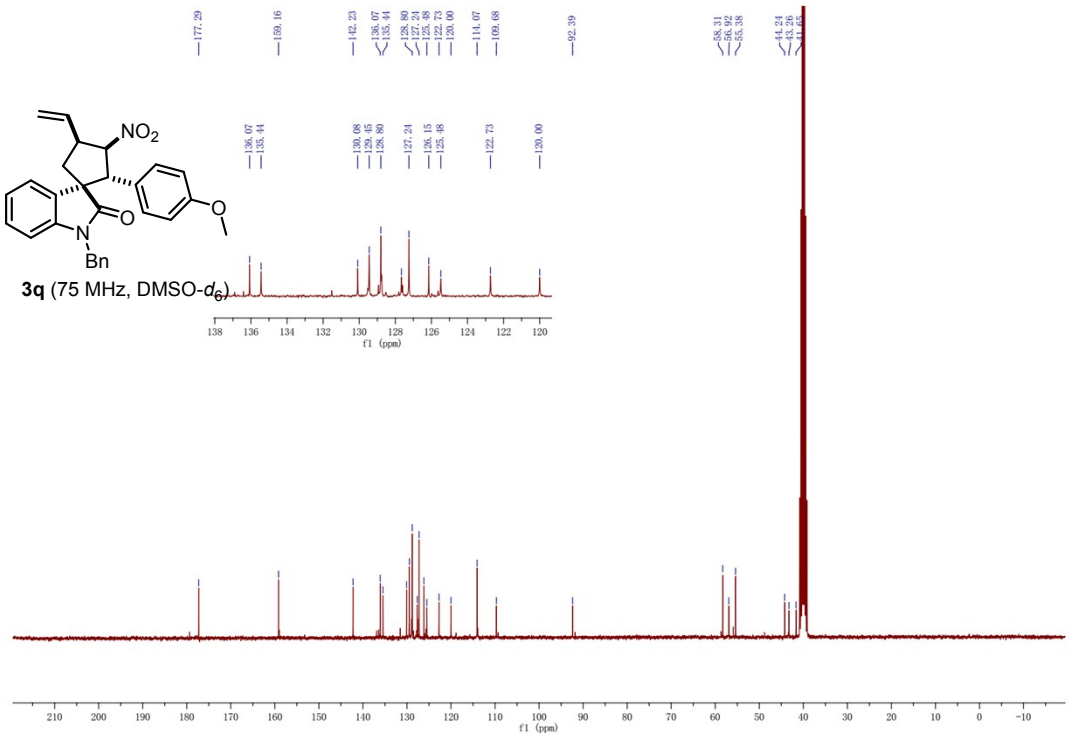
3p (300 MHz, $CDCl_3$)



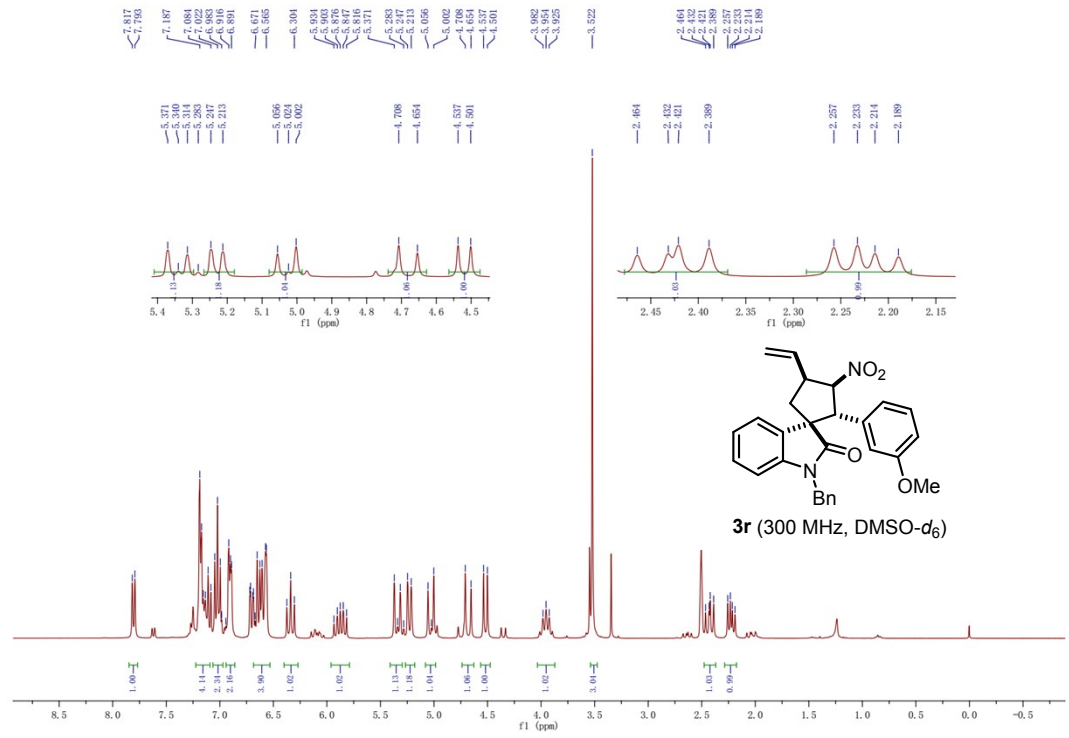
3p (75 MHz, $CDCl_3$)



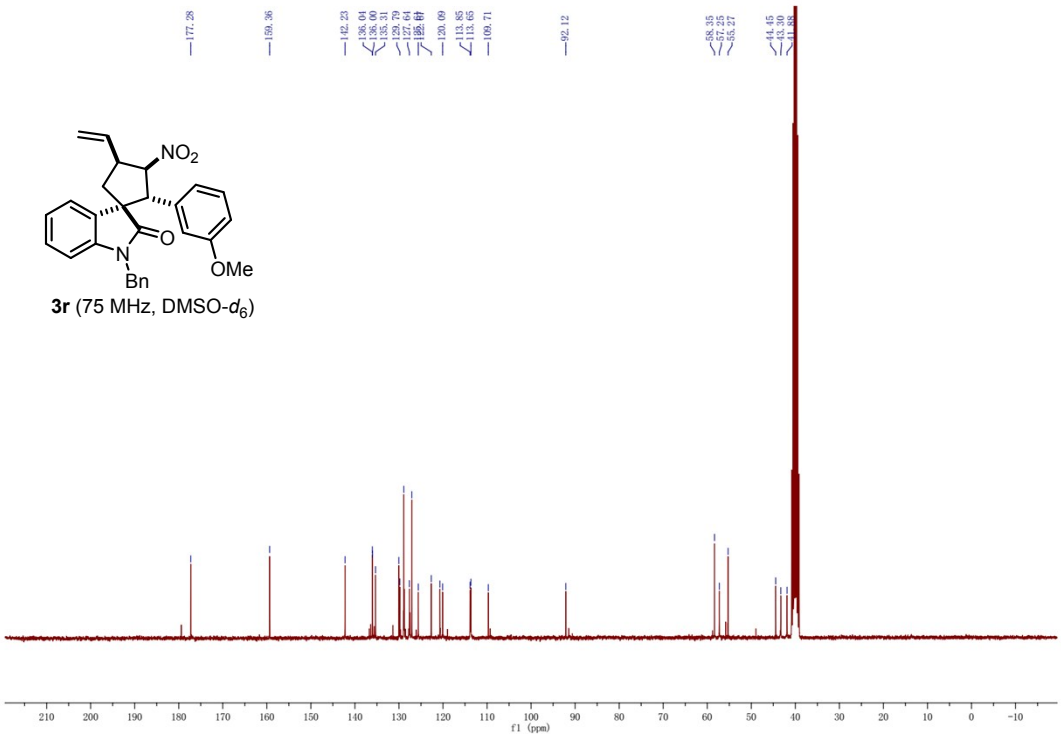
3q (300 MHz, DMSO-d_6)



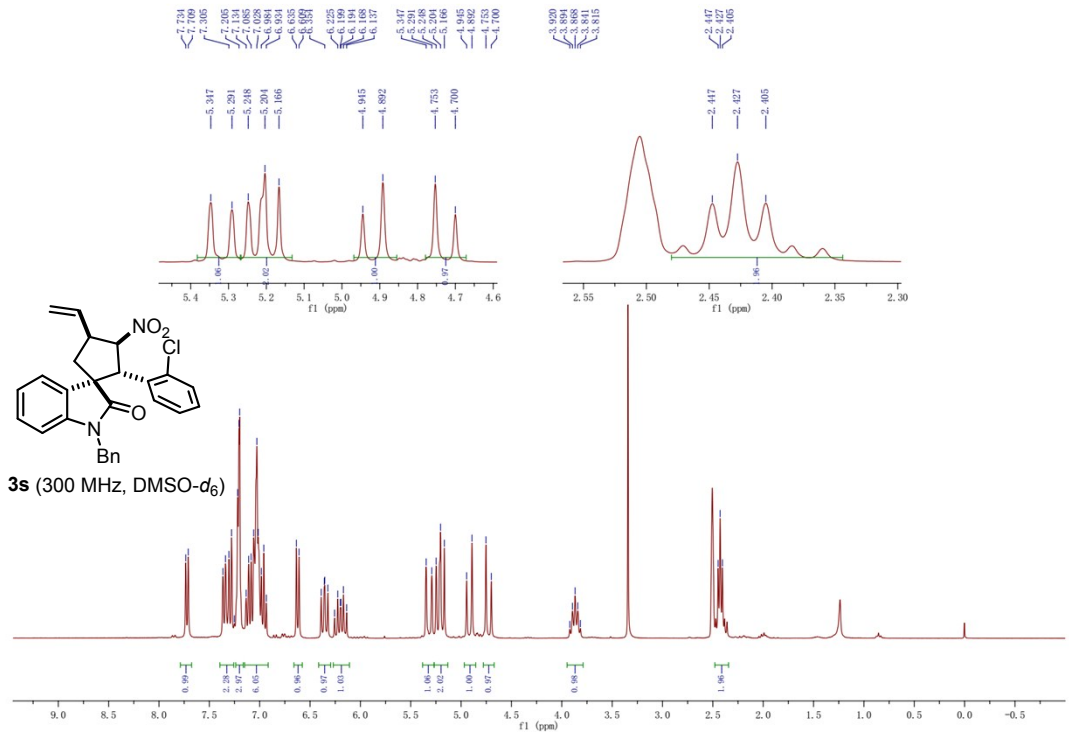
3q (75 MHz, DMSO-d_6)



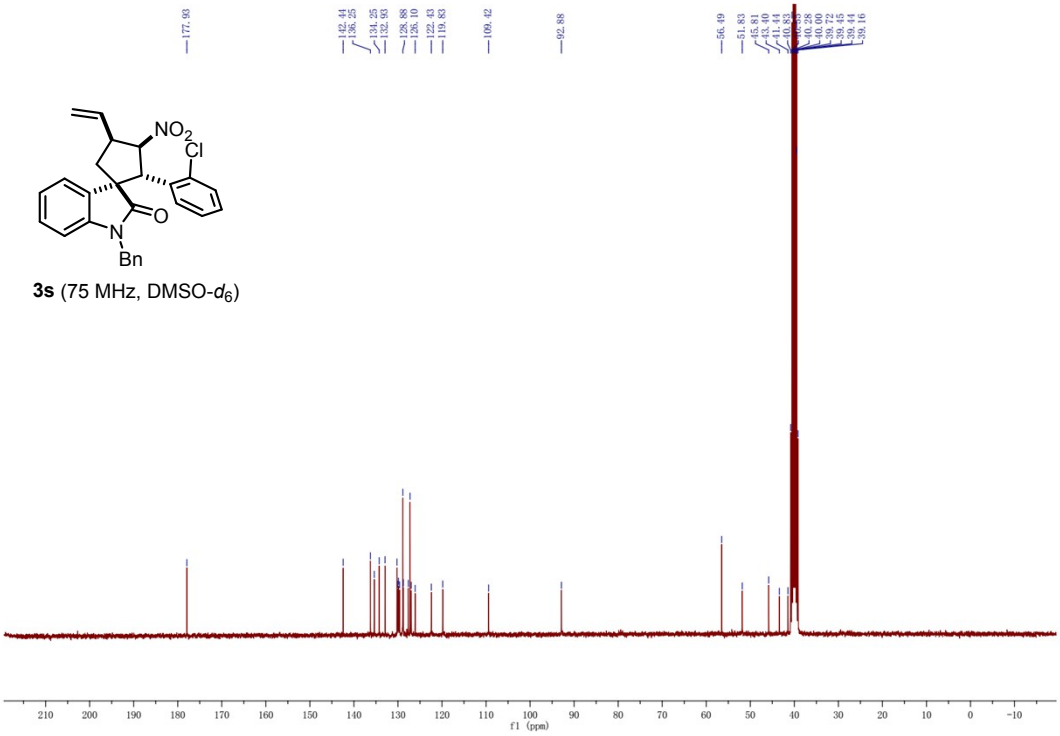
3r (300 MHz, DMSO-d_6)



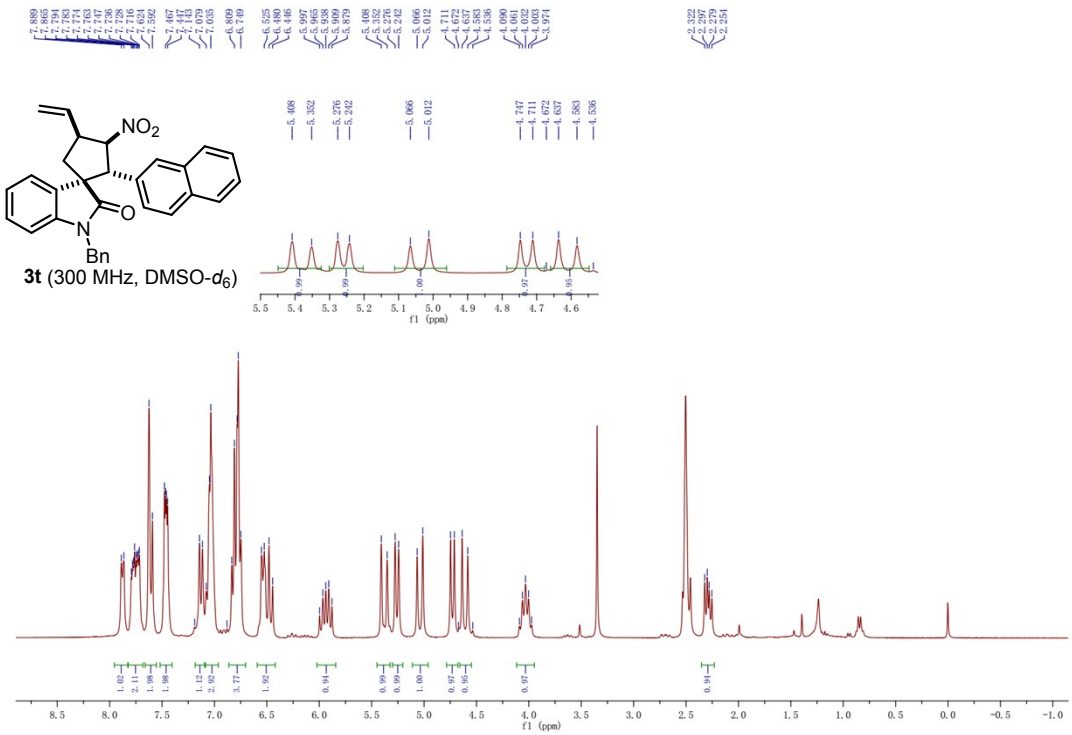
3r (75 MHz, DMSO-d_6)



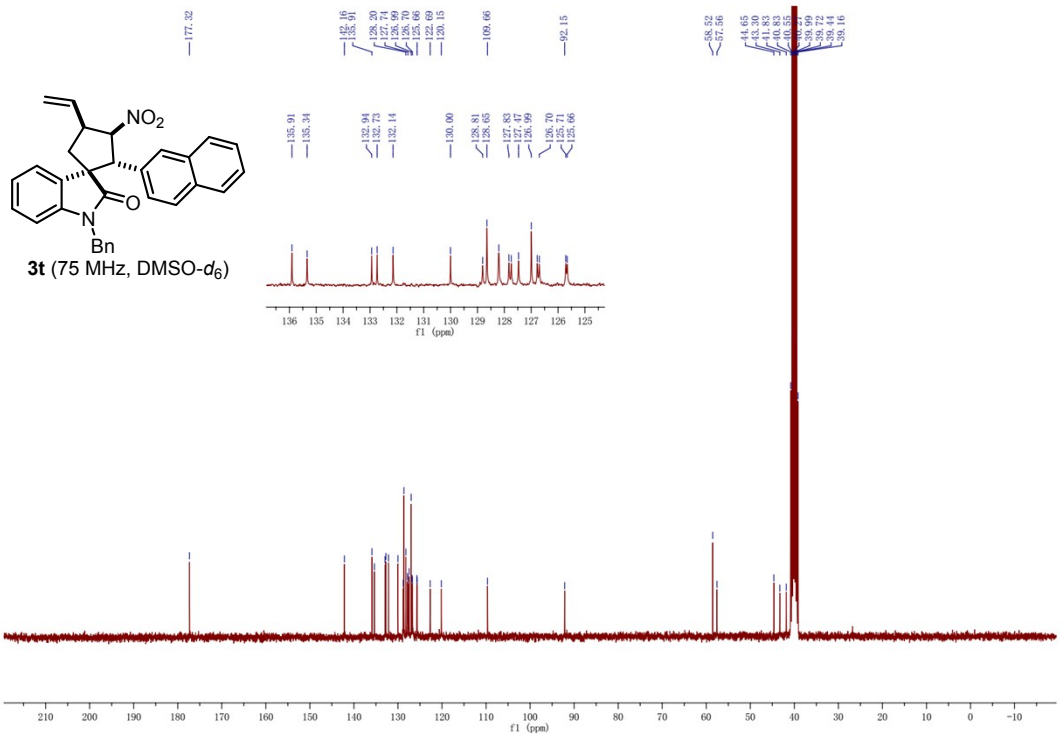
3s (300 MHz, DMSO-d_6)



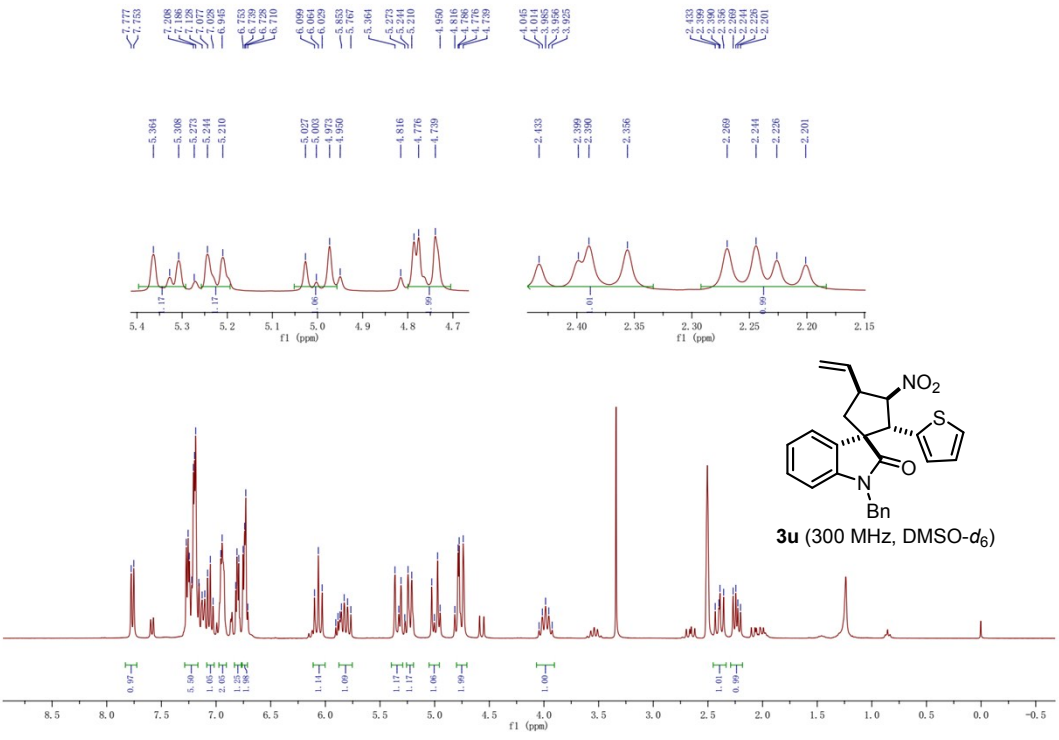
3s (75 MHz, DMSO-d_6)



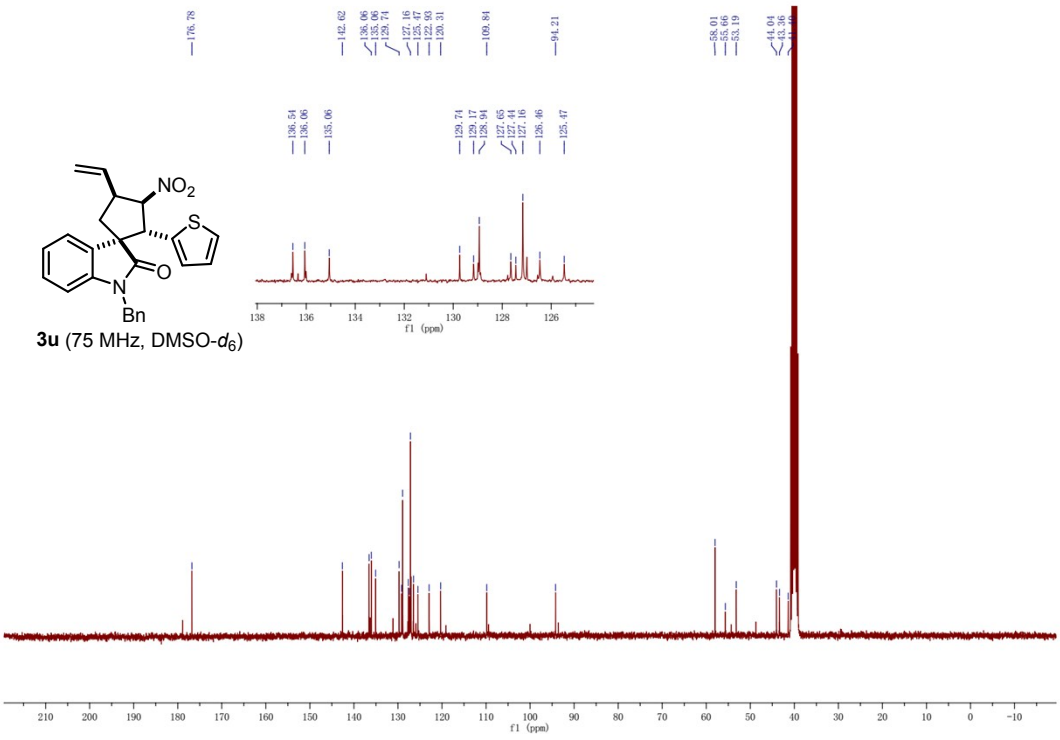
3t (300 MHz, DMSO-d_6)



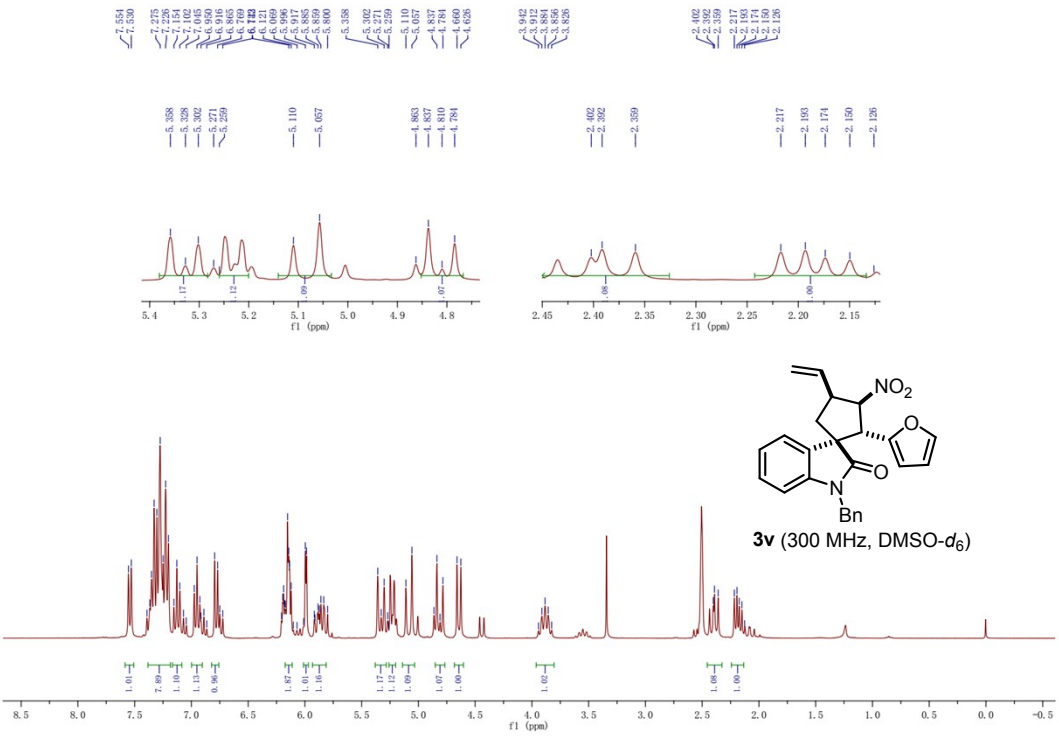
3t (75 MHz, DMSO-d_6)



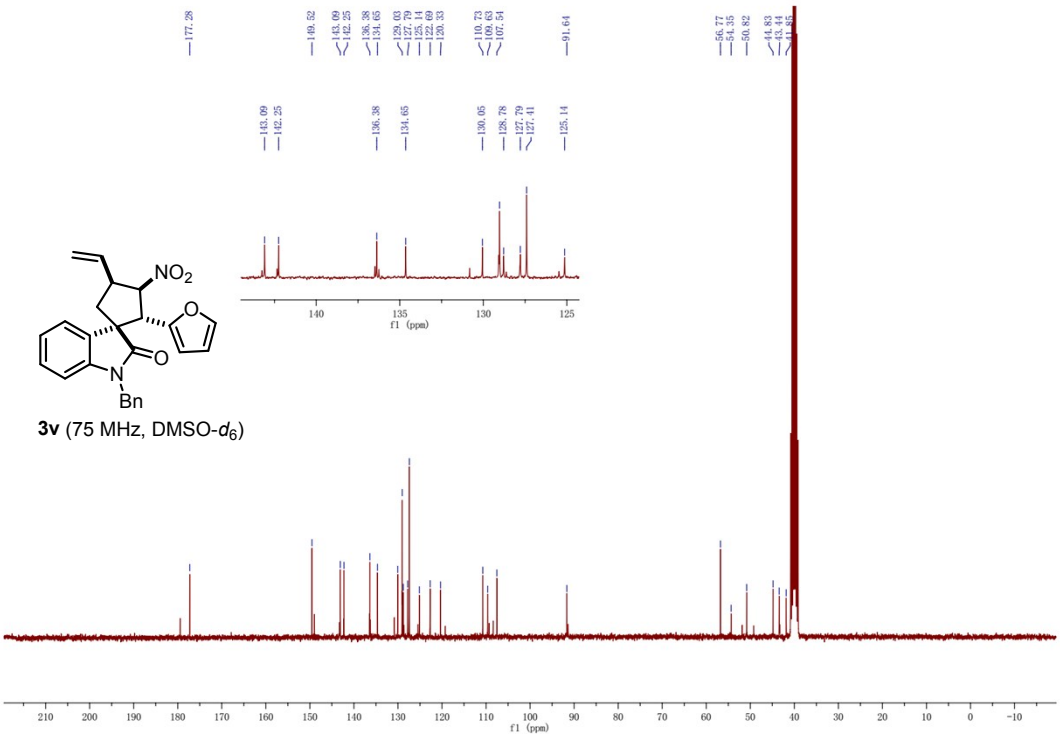
3u (300 MHz, DMSO-d_6)



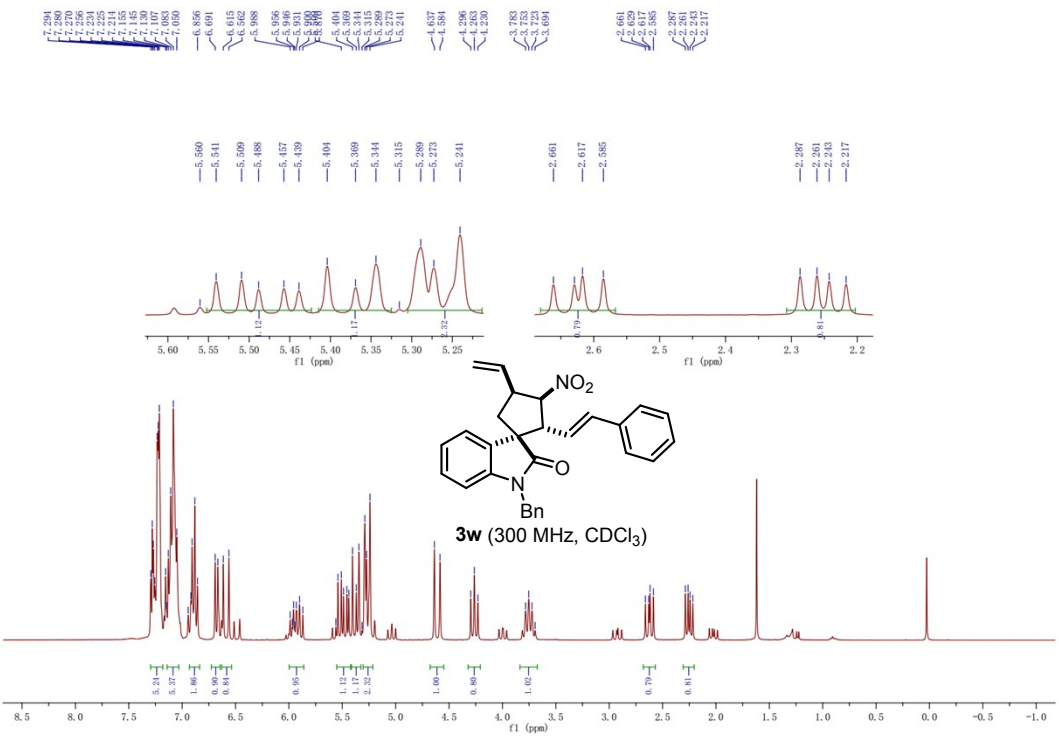
3u (75 MHz, DMSO-d_6)



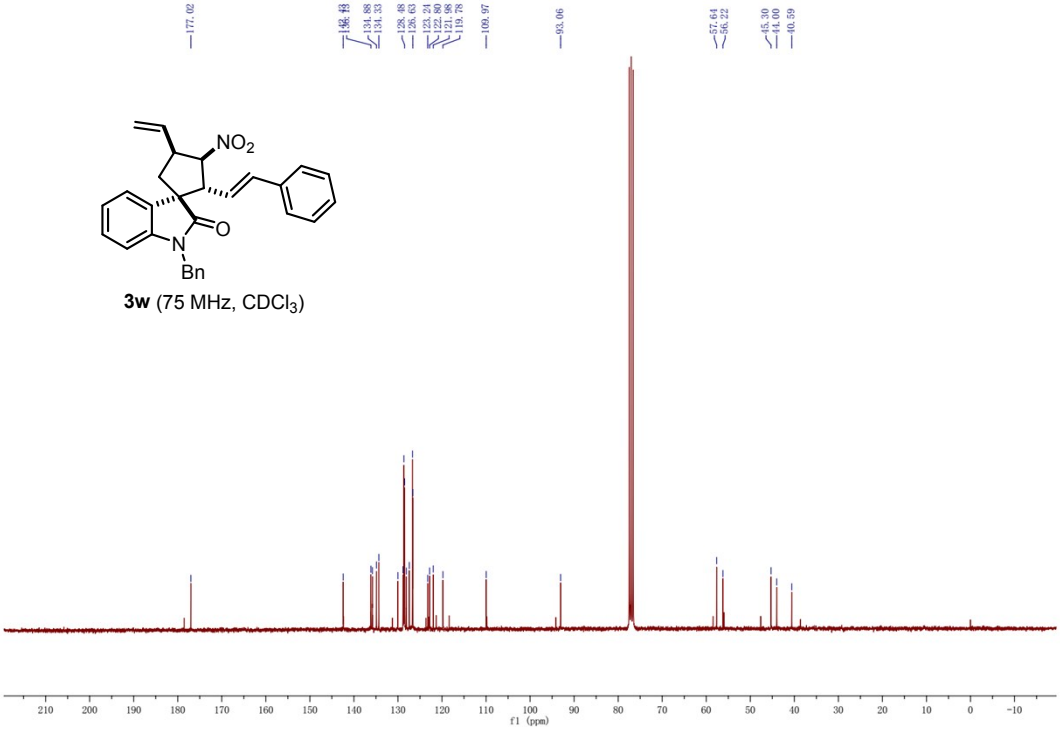
3v (300 MHz, DMSO-d_6)



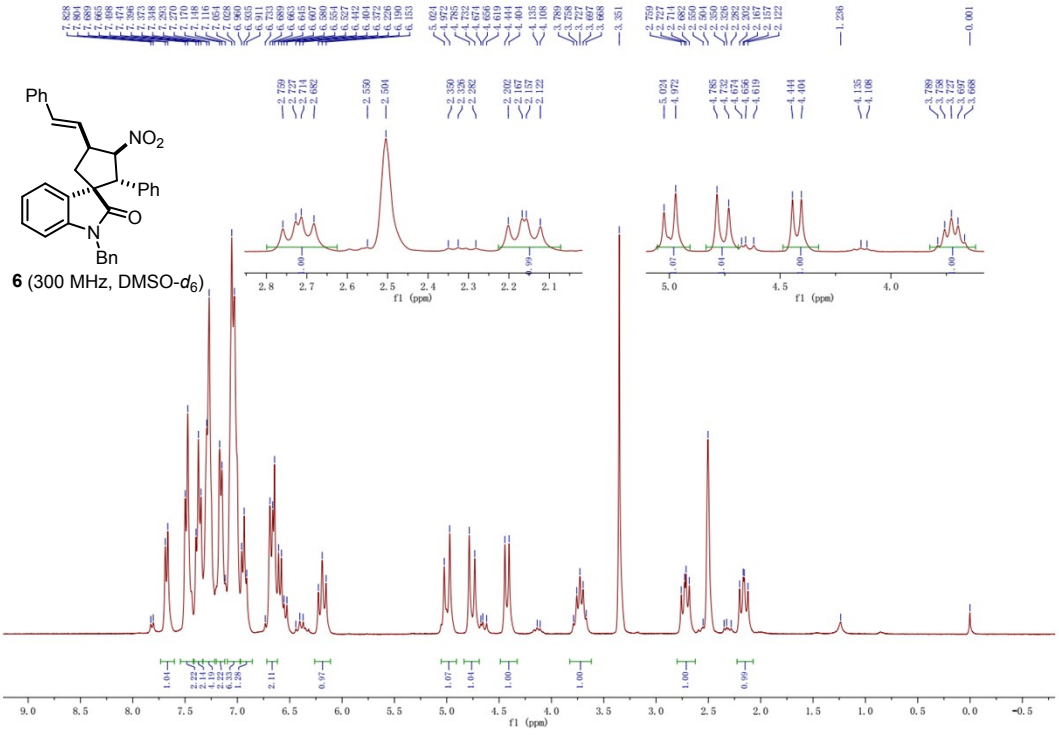
3v (75 MHz, DMSO-d_6)



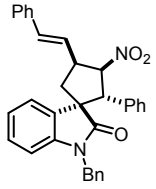
3w (300 MHz, $CDCl_3$)



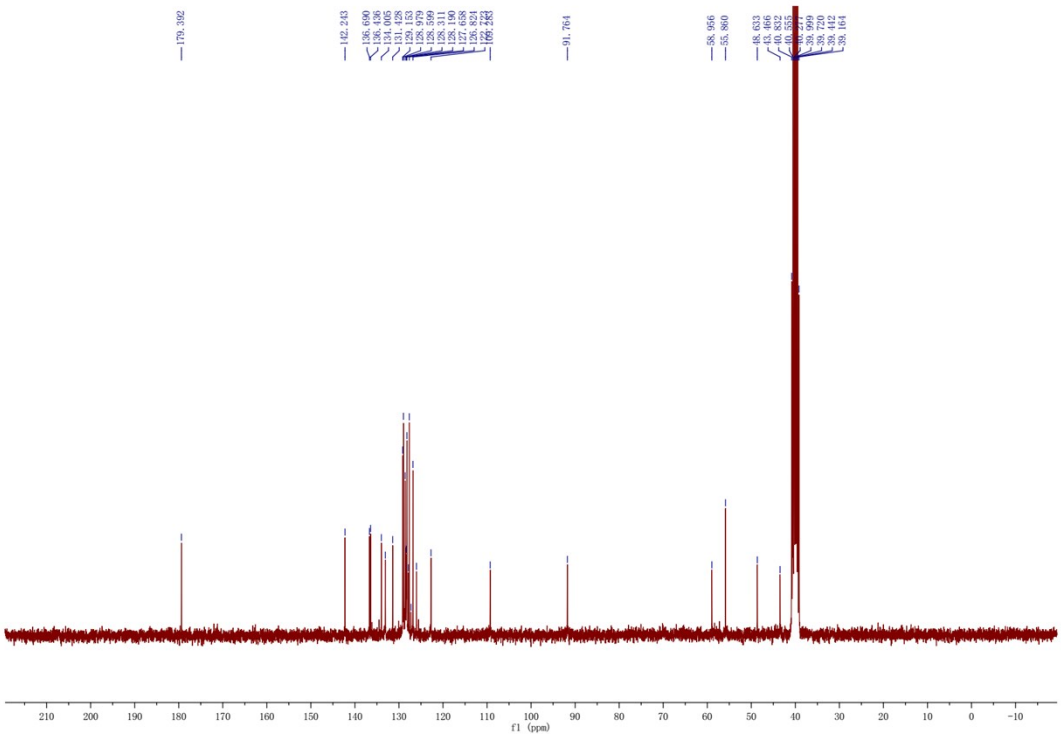
3w (75 MHz, $CDCl_3$)



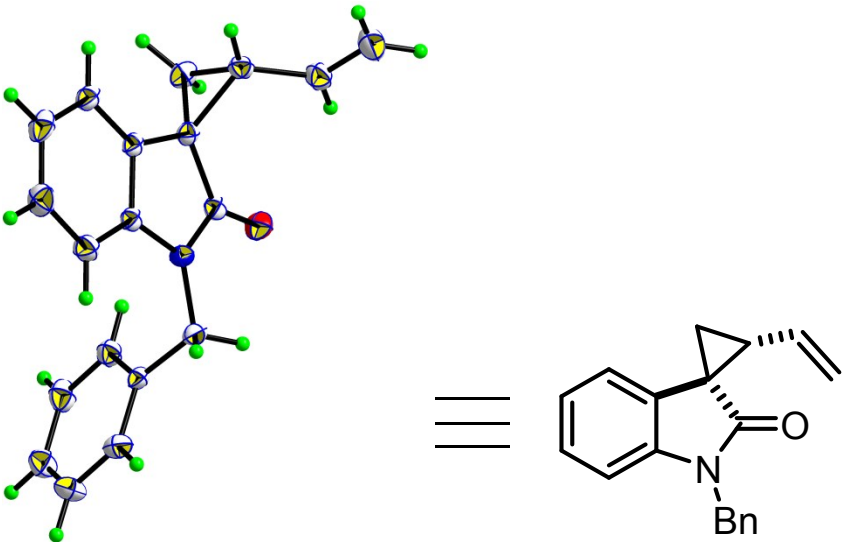
6 (300 MHz, DMSO-d_6)



6 (75 MHz, DMSO-d_6)

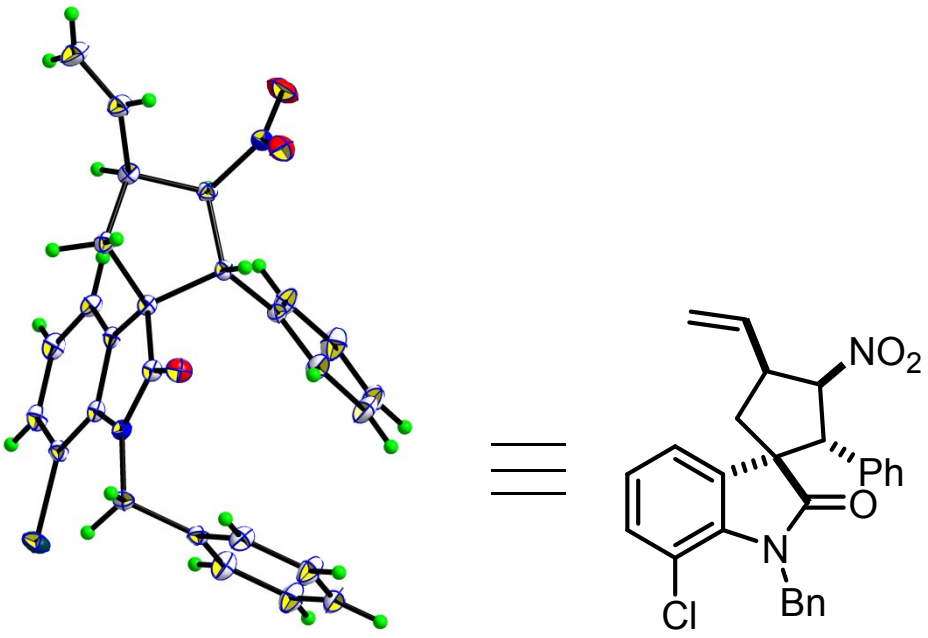


5. X-Ray Crystal Structures



X-ray structures of **1a** (with 20% probability level):

Compound 1a		**CCDC: 1857257**
Bond precision: C-C = 0.0023 Å		Wavelength = 0.71073
a = 16.7527(11)	b = 9.2802(6)	c = 19.4280(11)
alpha = 90.00	beta = 90.00	gamma = 90.00
Cell setting: Orthorhombic		Moiety formula: $C_{19}H_{17}NO$
Cell volume = 3020.4(3)		Space group: Pbca
Data completeness = 0.997		Theta(max) = 27.530
R(reflections) = 0.0534(2552)		WR2(reflections) = 0.1428(3460)
S = 1.007		Radiation type: MoK\a
Measurement device type: CCD area detector		Measurement method: phi and omega scans
Structure solution: SHELXS-97		Structure refinement: SHELXL-97
Solution primary: direct		Solution secondary: difmap
Solution hydrogens: geom		Hydrogen treatment: mixed



X-ray structures of **3l** (with 20% probability level):

Compound 31		**CCDC: 1857258**
Bond precision: C-C = 0.0025 Å		Wavelength = 0.71076
a = 8.9496(3)	b = 9.6224(3)	c = 14.1054(5)
alpha = 100.8225(11)	beta = 90.1216(11)	gamma = 110.2565(10)
Cell setting: Triclinic		Moiety formula: $C_{27}H_{23}ClN_2O_3$
Cell volume = 1116.34(6)		Space group: P-1
Data completeness = 0.994		Theta(max) = 27.520
R(reflections) = 0.0446(4153)		WR2(reflections) = 0.1210(5119)
S = 1.025		Radiation type: MoK\a
Measurement device type: CCD area detector		Measurement method: phi and omega scans
Structure solution: SHELXS-97		Structure refinement: SHELXL-97
Solution primary: direct		Solution secondary: difmap
Solution hydrogens: geom		Hydrogen treatment: mixed