Supporting information

for

Stereoselective Construction of α-Tetralone-Fused Spirooxindoles via Pd-Catalyzed Domino Carbene Migratory Insertion/Conjugate Addition Sequence

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1. General information

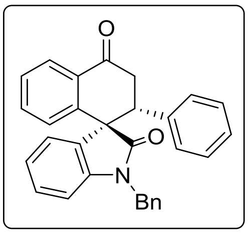
All reactions were carried out in oven-dried reaction tubes. Reactions were monitored by thin-layer chromatography (TLC) using Merck silica gel 60 F_{254} precoated plates (0.25 mm) and visualized by UV fluorescence quenching using appropriate mixture of ethyl acetate and hexanes. Silica gel (particle size: 100-200 mesh) was purchased from Avra Synthesis Pvt. Ltd and used for column chromatography using hexanes and ethyl acetate mixture as eluent. All the reactions were carried out in temperature controlled IKA magnetic stirrers. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz and 500 MHz (100 MHz and 125 MHz for ^{13}C) instrument. ^{1}H NMR spectra were reported relative to residual $CDCl_3$ (δ 7.26 ppm) and DMSO-d_6 (δ 2.50 ppm) or residual TMS. ^{13}C NMR were reported relative to $CDCl_3$ (δ 77.16 ppm) and DMSO-d_6 (δ 39.51 ppm). Chemical shifts were reported in parts per million and multiplicities are as indicated: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), m (multiplet), and br (broad). Coupling constants, *J*, are reported in Hertz. Melting points were recorded on a Guna capillary melting point apparatus and are corrected with benzoic acid as reference. Infrared spectra were recorded on a FTIR 4000 Series Spectrometer using dry KBr pellet. The wave numbers of recorded IR signals are quoted in cm^{-1}. High resolution mass spectra (HRMS) were recorded on Q-Tof Micro mass spectrometer.

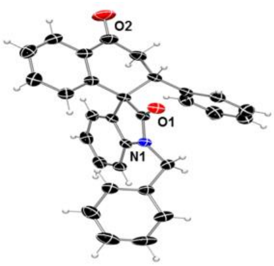
Solvents used for extraction and column chromatography were laboratory grade and used as received. Reaction solvents used were obtained from Fischer Scientific, India Pvt. Ltd. Allylpalladium chloride dimer and PPh_3 were obtained from Sigma-Aldrich and used directly as received.

2. Experimental data

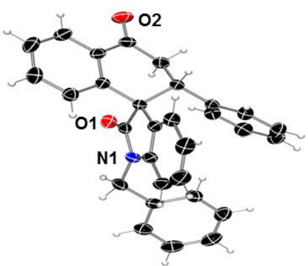
2.1. General procedure for the synthesis of α-tetralone-fused spirooxindoles 3

Under open atmosphere, *E*-2'-iodochalcone **1** (167 mg, 0.5 mmol), isatin-derived *N*-tosylhydrazone **2** (304 mg, 0.75 mmol), $[Pd(allyl)Cl]_2$ (18.5 mg, 0.05 mmol), PPh_3 (39.5 mg, 0.15 mmol), TBAB (40 mg, 0.125 mmol) and DIPEA (262 μL, 1.5 mmol) were successively added to oven-dried reaction tube. CH_3CN (3 mL) was added and closed with a glass-stopper. The reaction tube was then immersed in a 50 ºC pre-heated oil bath with stirring (500 rpm) till complete consumption of 2'-iodochalcone. Upon cooling down to room temperature, the solvent was removed under reduced pressure. Water (approx.10 mL) was added to the reaction mixture and extracted with dichloromethane (3×5 mL). Brine wash (1×5 mL) was given to the combined organic extractions and dried over anhydrous Na_2SO_4. The dr was determined by ^{1}H NMR analysis of the crude reaction mixture and was subsequently purified by silica gel column separation using hexanes and ethylacetate mixture (8:2, v/v) as mobile phase afforded the corresponding spirooxindoles **3**.

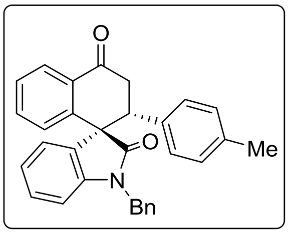




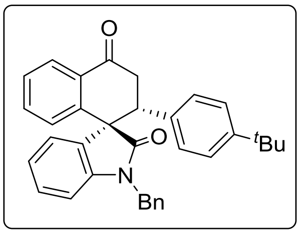
1-Benzyl-2'-phenyl-2',3'-dihydro-4'*H*-spiro[indoline-3,1'-naphthalene]-2,4'-dione (3b): 189 mg, 88% yield; 91:09 dr (*anti:syn*); **Major**: white solid; mp 164-166 ^{o}C; R_f 0.42 (20% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.01 (dd, *J* = 18.2, 4.4 Hz, 1H), 3.54 (dd, *J* = 18.2, 14.4 Hz, 1H), 4.23 (dd, *J* = 14.4, 4.4 Hz, 1H), 4.58 (d, *J* = 15.8 Hz, 1H), 4.90 (d, *J* = 15.8 Hz, 1H), 6.44-6.51 (m, 1H), 6.64 (d, *J* = 6.4 Hz, 2H), 6.85 (d, *J* = 7.2 Hz, 2H), 6.89-7.02 (m, 2H), 7.06-7.28 (m, 8H), 7.44 (td, *J* = 7.4, 1.4 Hz, 1H), 7.49 (td, *J* = 7.4, 1.4 Hz, 1H), 8.23 (dd, *J* = 8.0, 1.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 40.7, 44.0, 47.5, 58.8, 110.2, 122.7, 125.1, 126.8, 127.4, 127.5, 128.0 (2C), 128.3, 128.4, 128.6, 128.8, 128.9, 130.1, 131.9, 135.0, 135.1, 137.7, 142.6, 143.5, 177.9, 196.9; FTIR (KBr) 3059, 3032, 2920, 1714, 1685, 1608, 1466, 1359, 1294, 758, 700 cm^{-1}; HRMS (*m*/*z*): $[M+Na]^+$ calcd for $C_{30}H_{23}NO_2Na$: 452.1626; found: 452.1607.



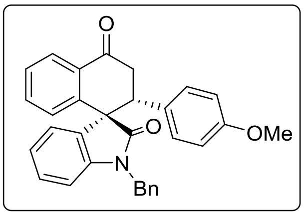
Minor (3b') : white solid; mp 191-193 ^{o}C; R_f 0.45 (20% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.86 (dd, *J* = 16.6, 3.8 Hz, 1H), 4.05 (dd, *J* = 14.6, 3.8 Hz, 1H), 4.37 (dd, *J* = 16.6, 14.6 Hz, 1H), 4.65 (d, *J* = 15.8 Hz, 1H), 4.71 (d, *J* = 15.8 Hz, 1H), 6.43-6.49 (m, 1H), 6.61 (dd, *J* = 7.8, 1.0 Hz, 1H), 6.81-6.89 (m, 2H), 6.97-7.26 (m, 11H), 7.39 (td, *J* = 7.4, 1.6 Hz, 1H), 7.44 (td, *J* = 7.4, 1.6 Hz, 1H), 8.25 (dd, *J* = 7.8, 1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 39.4, 43.9, 48.6, 57.4, 109.4, 123.2, 124.5, 127.1, 127.5, 127.6, 127.9, 128.0, 128.1, 128.4, 128.6, 128.7, 128.8, 132.6, 133.0, 134.1, 135.3, 137.7, 142.6, 143.5, 176.0, 197.5; FTIR (KBr) 3060, 3032, 1704, 1610, 1492, 1359, 1297, 751, 700 cm^{-1}; HRMS (*m*/*z*): $[M+Na]^+$ calcd for $C_{30}H_{24}Na$: 430.1807; found: 430.1836.



1-Benzyl-2'-(*p*-tolyl)-2',3'-dihydro-4'*H*-spiro[indoline-3,1'-naphthalene]-2,4'-dione (3c): 186 mg, 84% yield; 91:09 dr (*anti:syn*); Major: white solid; mp 101-103 ^{o}C; R_f 0.41 (20% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.31 (s, 3H), 2.97 (dd, *J* = 18.2, 4.5 Hz, 1H), 3.52 (dd, *J* = 18.2, 14.5 Hz, 1H), 4.20 (dd, *J* = 14.5, 4.5 Hz, 1H), 4.55 (d, *J* = 16.0 Hz, 1H), 5.00 (d, *J* = 16.0 Hz, 1H), 6.47-6.51 (m, 1H), 6.66 (d, *J* = 7.5 Hz, 2H), 6.73 (d, *J* = 8.0 Hz, 2H), 6.87-7.01 (m, 4H), 7.09-7.23 (m, 5H), 7.43 (td, *J* = 7.5, 1.8 Hz, 1H), 7.48 (td, *J* = 7.5, 1.8 Hz, 1H), 8.22 (dd, *J* = 7.7, 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.4, 40.9, 44.1, 47.1, 58.9, 110.2, 122.7, 125.2, 126.9, 127.3, 127.4, 128.0, 128.3, 128.5, 128.7, 128.8, 129.1, 130.3, 131.9, 134.8, 135.0, 135.1, 137.5, 142.6, 143.7, 178.0, 197.1; FTIR (KBr) 3060, 3030, 1714, 1685, 1606, 1462, 1359, 1294, 736 cm^{-1}; HRMS (*m*/*z*): $[M+H]^+$ calcd for $C_{31}H_{26}NO_2$: 444.1964; found: 444.1993.

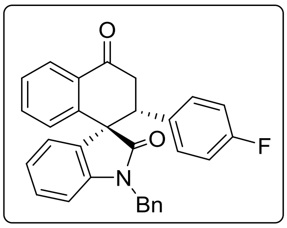


1-Benzyl-2'-(4-(*tert*-butyl)phenyl)-2',3'-dihydro-4'*H*-spiro[indoline-3,1'-naphthalene]-2,4'-dione (3d): 209 mg, 86% yield; 91:09 dr (*anti:syn*); Major: white solid; mp 120-122 ^{o}C; R_f 0.51 (20% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.26 (s, 9H), 3.00 (dd, *J* = 18.0, 4.4 Hz, 1H), 3.51 (dd, *J* = 18.0, 14.4 Hz, 1H), 4.19 (dd, *J* = 14.4, 4.4 Hz, 1H), 4.57 (d, *J* = 15.8 Hz, 1H), 4.74 (d, *J* = 15.8 Hz, 1H), 6.48 (d, *J* = 7.6 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 2H), 6.88-7.01 (m, 4H), 7.05-7.15 (m, 4H), 7.19-7.25 (m, 3H), 7.43 (td, *J* = 7.4, 1.4 Hz, 1H), 7.48 (td, *J* = 7.4, 1.4 Hz, 1H), 8.22 (dd, *J* = 7.8, 1.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.5, 34.6, 40.7, 44.2, 47.1, 58.8, 110.0, 122.6, 124.9, 125.1, 127.1, 127.4, 127.6, 127.9, 128.2, 128.3, 128.8, 128.9, 130.3, 132.1, 134.6, 134.9, 135.4, 142.7, 143.4, 150.7, 178.0, 197.1; FTIR (KBr) 3058, 2959, 2926, 1713, 1685, 1608, 1465, 1361, 1294, 833, 753 cm^{-1}; HRMS (*m*/*z*): $[M+H]^+$ calcd for $C_{34}H_{32}NO_2$: 486.2433; found: 486.2415.

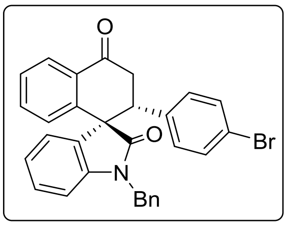


1-Benzyl-2'-(4-methoxyphenyl)-2',3'-dihydro-4'*H*-spiro[indoline-3,1'-naphthalene]-2,4'-dione (3e): 211 mg, 92% yield; 89:11 dr (*anti:syn*); Major: white solid; mp 196-198 ^{o}C; R_f 0.38 (20% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.97 (dd, *J* = 18.0, 4.4 Hz, 1H), 3.50 (dd, *J* = 18.0, 14.4 Hz, 1H), 3.75 (s, 3H), 4.19 (dd, *J* = 14.4, 4.4 Hz, 1H), 4.55 (d, *J* = 16.0 Hz, 1H), 5.03 (d, *J* = 16.0 Hz, 1H), 6.50 (d, *J* = 7.6 Hz, 1H), 6.63 (d, *J* = 8.4 Hz, 4H), 6.76 (d, *J* = 8.8 Hz, 2H), 6.89-7.02 (m, 2H), 7.08-7.23 (m, 5H), 7.43 (td, *J* = 7.6, 1.4 Hz, 1H), 7.48 (td, *J* = 7.6, 1.4 Hz, 1H), 8.22 (dd, *J* = 7.6, 1.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ

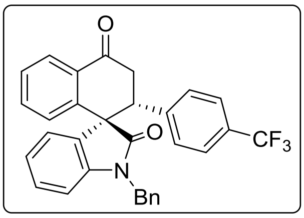
41.1, 44.0, 46.7, 55.2, 59.0, 110.2, 113.7, 122.7, 125.1, 126.8, 127.3, 127.5, 128.0, 128.3, 128.7, 128.8, 129.7, 129.9 (2C), 130.2, 131.9, 135.0, 142.6, 143.7, 159.3, 178.0, 197.0; FTIR (KBr) 3060, 2952, 1714, 1685, 1608, 1512, 1465, 1359, 1250, 832, 735 cm^{-1}; HRMS (*m*/*z*): $[M+Na]^+$ calcd for $C_{31}H_{25}NO_3Na$: 482.1732; found: 482.1708.



1-Benzyl-2'-(4-fluorophenyl)-2',3'-dihydro-4'*H*-spiro[indoline-3,1'-naphthalene]-2,4'-dione (3f): 190 mg, 85% yield; 91:09 dr (*anti:syn*); Major: white solid; mp 163-165 °C; R_f 0.44 (20% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) 2.97 (dd, *J* = 18.0, 4.2 Hz, 1H), 3.48 (dd, *J* = 18.0, 14.4 Hz, 1H), 4.22 (dd, *J* = 14.4, 4.2 Hz, 1H), 4.58 (d, *J* = 15.8 Hz, 1H), 4.95 (d, *J* = 15.8 Hz, 1H), 6.54 (d, *J* = 8.0 Hz, 2H), 6.65-6.84 (m, 6H), 6.92 (dd, *J* = 7.6, 0.8 Hz, 1H), 6.99 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.09-7.25 (m, 5H), 7.44 (td, *J* = 7.6, 1.6 Hz, 1H), 7.49 (td, *J* = 7.6, 1.6 Hz, 1H), 8.22 (dd, *J* = 7.8, 1.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 40.8, 44.1, 46.7, 58.8, 110.2, 115.2 (d, *J* = 21 Hz), 122.8, 125.2, 126.9, 127.4, 127.7, 128.0, 128.4, 128.8, 129.1, 129.9, 130.2 (d, *J* = 8 Hz), 131.9, 133.5 (d, *J* = 4 Hz), 135.0, 135.1, 142.6, 143.4, 162.5 (d, *J* = 245 Hz), 177.8, 196.5; FTIR (KBr) 3060, 2910, 1714, 1686, 1604, 1487, 1362, 1295, 839, 735 cm^{-1}; HRMS (*m*/*z*): $[M+H]^+$ calcd for $C_{30}H_{23}NO_2F$: 448.1713; found: 448.1700.

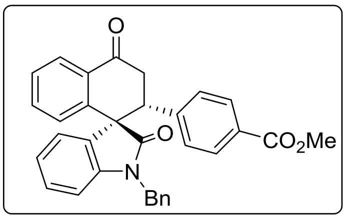


1-Benzyl-2'-(4-bromophenyl)-2',3'-dihydro-4'*H*-spiro[indoline-3,1'-naphthalene]-2,4'-dione (3g): 216 mg, 85% yield; 89:11 dr (*anti:syn*); Major: white solid; mp 167-169 °C; R_f 0.38 (20% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.96 (dd, *J* = 18.0, 4.2 Hz, 1H), 3.48 (dd, *J* = 18.0, 14.5 Hz, 1H), 4.20 (dd, *J* = 14.5, 4.2 Hz, 1H), 4.54 (d, *J* = 15.7 Hz, 1H), 5.04 (d, *J* = 15.7 Hz, 1H), 6.56 (d, *J* = 8.0 Hz, 1H), 6.64-6.69 (m, 2H), 6.71 (d, *J* = 8.5 Hz, 2H), 6.91 (dd, *J* = 7.8, 0.8 Hz, 1H), 6.99 (td, *J* = 7.5, 1.0 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 1H), 7.16 (td, *J* = 7.5, 1.3 Hz, 1H), 7.21 (d, *J* = 8.5 Hz, 2H), 7.22-7.29 (m, 3H), 7.44 (td, *J* = 7.5, 1.5 Hz, 1H), 7.49 (td, *J* = 7.5, 1.5 Hz, 1H), 8.22 (dd, *J* = 8.0, 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 40.6, 44.2, 46.8, 58.5, 110.3, 122.1, 122.9, 125.1, 126.8, 127.3, 127.7, 128.0, 128.4, 128.9, 129.1, 129.8, 130.3, 131.5, 131.8, 134.8, 135.1, 136.7, 142.6, 143.4, 177.7, 196.4; FTIR (KBr) 3025, 2957, 1706, 1690, 1598, 1457, 1352, 1244, 773, 730 cm^{-1}; HRMS (*m*/*z*): $[M+Na]^+$ calcd for $C_{30}H_{22}NO_2NaBr$: 530.0732; found: 530.0719.

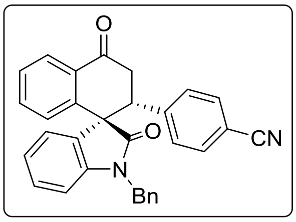


1-Benzyl-2'-(4-(trifluoromethyl)phenyl)-2',3'-dihydro-4'*H*-spiro[indoline-3,1'-naphthalene]-2,4'-dione (3h): 201 mg, 81% yield; 88:12 dr (*anti:syn*); Major: white solid; mp 167-169 °C; R_f 0.42 (20% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.98 (dd, *J* = 18.0, 4.0 Hz, 1H), 3.53 (dd, *J* = 18.0, 14.8 Hz, 1H), 4.30 (dd, *J* = 14.8, 4.0 Hz, 1H), 4.58 (d, *J* = 15.6 Hz, 1H), 4.91 (d, *J* = 15.6 Hz, 1H), 6.56 (d, *J* = 7.6 Hz, 1H), 6.74 (d, *J* =

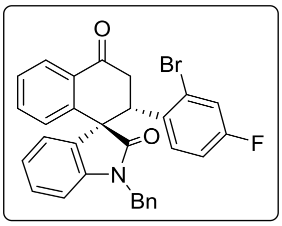
6.8 Hz, 2H), 6.91 (dd, J = 7.6, 0.8 Hz, 1H), 6.96 (d, J = 8.0 Hz, 2H), 7.01 (t, J = 7.6 Hz, 1H), 7.10-7.25 (m, 5H), 7.33 (d, J = 8.0 Hz, 2H), 7.45 (td, J = 7.2, 1.4 Hz, 1H), 7.50 (td, J = 7.2, 1.4 Hz, 1H), 8.23 (dd, J = 7.6, 1.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 40.4, 44.2, 47.0, 58.4, 110.3, 123.0, 124.2 (q, J = 270 Hz), 125.1, 125.2 (q, J = 4 Hz), 126.9, 127.3, 127.8, 128.1, 128.5, 128.8, 129.1, 129.3, 129.7, 130.1 (q, J = 32 Hz), 131.8, 134.9, 135.2, 141.7, 142.5, 143.2, 177.6, 196.1; FTIR (KBr) 3056, 3034, 2993, 1714, 1688, 1607, 1485, 1325, 1295, 1124, 849, 755 cm^{-1}; HRMS (*m*/*z*): $[M+Na]^+$ calcd for $C_{31}H_{22}NO_2F_3Na$: 520.1500; found: 520.1526.



Methyl-4-(1-benzyl-2,4'-dioxo-3',4'-dihydro-2'*H*-spiro-[indoline-3,1'-naphthalen]-2'-yl)benzoate (3i): 197 mg, 81% yield; 89:11 dr (*anti:syn*); Major: white solid; mp 156-158 ^{o}C; R_f 0.32 (20% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.99 (dd, J = 18.0, 4.2 Hz, 1H), 3.53 (dd, J = 18.0, 14.4 Hz, 1H), 3.91 (s, 3H), 4.28 (dd, J = 14.4, 4.2 Hz, 1H), 4.50 (d, J = 15.6 Hz, 1H), 4.81 (d, J = 15.6 Hz, 1H), 6.54 (d, J = 8.0 Hz, 1H), 6.75 (d, J = 7.2 Hz, 2H), 6.85-6.93 (m, 3H), 7.00 (t, J = 7.6 Hz, 1H), 7.07-7.22 (m, 5H), 7.40-7.54 (m, 2H), 7.73 (d, J = 8.4 Hz, 2H), 8.23 (d, J = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 40.3, 44.1, 47.3, 52.3, 58.5, 110.2, 122.9, 125.2, 127.0, 127.4, 127.7, 128.0, 128.5, 128.6, 128.8, 129.2, 129.5, 129.7, 129.8, 131.9, 135.0, 135.1, 142.5, 142.7, 143.2, 166.9, 177.6, 196.2; FTIR (KBr) 3055, 2952, 1718, 1610, 1486, 1364, 1266, 753, 700 cm^{-1}; HRMS (*m*/*z*): $[M+Na]^+$ calcd for $C_{32}H_{25}NO_4Na$: 510.1681; found: 510.1693.

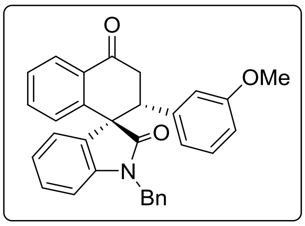


1-Benzyl-2,4'-dioxo-3',4'-dihydro-2'*H*-spiro[indoline-3,1'-naphthalen]-2'-yl)benzonitrile (3j): 134 mg, 59% yield; 87:13 dr (*anti:syn*); Major: white solid; mp 189-191 ^{o}C; R_f 0.30 (20% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.96 (dd, J = 18.0, 4.4 Hz, 1H), 3.49 (dd, J = 18.0, 14.6 Hz, 1H), 4.26 (dd, J = 14.6, 4.4 Hz, 1H), 4.58 (d, J = 15.6 Hz, 1H), 4.87 (d, J = 15.6 Hz, 1H), 6.63 (d, J = 7.6 Hz, 1H), 6.74-6.81 (m, 2H), 6.87-6.94 (m, 3H), 7.02 (td, J = 7.6, 0.8 Hz, 1H), 7.09-7.34 (m, 7H), 7.45 (td, J = 7.6, 1.4 Hz, 1H), 7.50 (td, J = 7.6, 1.4 Hz, 1H), 8.19-8.25 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 39.9, 44.2, 47.3, 58.3, 110.2, 111.9, 118.6, 123.1, 125.2, 127.1, 127.3, 128.0, 128.1, 128.6, 128.9, 129.3, 129.4, 131.7, 132.0, 134.9, 135.2, 142.5, 142.7 (2C), 142.9, 177.4, 195.7; FTIR (KBr) 3056, 2899, 2228, 1713, 1686, 1607, 1484, 1363, 1294, 847, 756 cm^{-1}; HRMS (*m*/*z*): $[M+Na]^+$ calcd for $C_{31}H_{22}N_2O_2Na$: 477.1579; found: 477.1579.

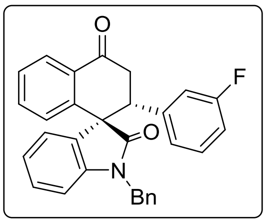


1-Benzyl-2'-(2-bromo-4-fluorophenyl)-2',3'-dihydro-4'*H*-spiro [indoline-3,1'-naphthalene]-2,4'-dione (3k): 197 mg, 75% yield; 88:12 dr (*anti:syn*); Major: white solid; mp 207-209 ^{o}C; R_f 0.38 (20% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.06-3.25 (m, 2H), 4.51 (d, J =

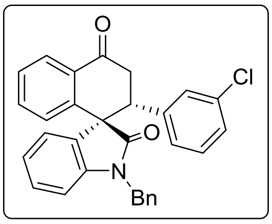
15.6 Hz, 1H), 4.90 (dd, J = 12.0, 5.6 Hz, 1H), 5.16 (d, J = 15.6 Hz, 1H), 6.32 (dd, J = 8.8, 6.0 Hz, 1H), 6.51-6.59 (m, 1H), 6.70 (d, J = 7.6 Hz, 1H), 6.78-6.94 (m, 4H), 6.98 (td, J = 7.6, 0.8 Hz, 1H), 7.16-7.30 (m, 5H), 7.42-7.53 (m, 2H), 8.20-8.27 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 41.2, 43.8, 44.1, 57.3, 110.1, 114.5 (d, J = 20 Hz), 120.6 (d, J = 24 Hz), 122.9, 125.6, 126.1 (d, J = 9 Hz), 127.1, 127.2, 127.7, 128.1, 128.5, 128.8, 128.9, 129.0, 129.3, 129.7, 132.0, 134.0 (d, J = 3 Hz), 135.1, 135.2, 143.0 (d, J = 11 Hz), 161.4 (d, J = 250 Hz), 177.1, 196.2; FTIR (KBr) 3059, 2919, 1718, 1685, 1599, 1485, 1361, 1293, 751, 701 cm^{-1}; HRMS (m/z): $[M+H]^+$ calcd for $C_{30}H_{22}NO_2FBr$: 526.0818; found: 526.0828.



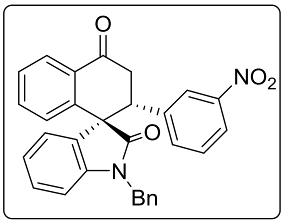
1-Benzyl-2'-(3-methoxyphenyl)-2',3'-dihydro-4'*H*-spiro[indoline-3,1'-naphthalene]-2,4'-dione (3l): 211 mg, 92% yield; 88:12 dr (*anti:syn*); Major: white solid; mp 71-73 °C; R_f 0.38 (20% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.01 (dd, J = 18.0, 4.2 Hz, 1H), 3.45 (s, 3H), 3.50 (dd, J = 18.0, 14.4 Hz, 1H), 4.21 (dd, J = 14.4, 4.2 Hz, 1H), 4.57 (d, J = 16.0 Hz, 1H), 4.97 (d, J = 16.0 Hz, 1H), 6.27 (t, J = 2.0 Hz, 1H), 6.48-6.56 (m, 2H), 6.62-6.69 (m, 2H), 6.75-6.81 (m, 1H), 6.93 (dd, J = 7.6, 0.8 Hz, 1H), 6.96-7.07 (m, 2H), 7.09-7.24 (m, 5H), 7.44 (td, J = 7.6, 1.4 Hz, 1H), 7.49 (td, J = 7.6, 1.4 Hz, 1H), 8.18-8.25 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 40.9, 44.1, 47.5, 55.1, 58.7, 110.2, 112.9, 114.7, 121.3, 122.7, 125.1, 126.8, 127.4, 127.5, 128.0, 128.3, 128.9 (2C), 129.4, 130.4, 132.0, 135.0, 135.1, 139.2, 142.8, 143.6, 159.4, 177.8, 196.8; FTIR (KBr) 3060, 2953, 1685, 1603, 1715, 1363, 1295, 789 cm^{-1}; HRMS (m/z): $[M+Na]^+$ calcd for $C_{31}H_{25}NO_3Na$: 482.1732; found: 482.1712.



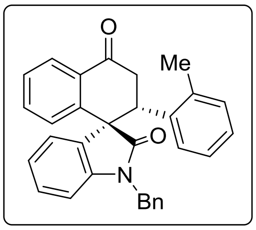
1-Benzyl-2'-(3-fluorophenyl)-2',3'-dihydro-4'*H*-spiro[indoline-3,1'-naphthalene]-2,4'-dione (3m): 177 mg, 79% yield; 90:10 dr (*anti:syn*); Major: white solid; mp 118-120 °C; R_f 0.39 (20% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.00 (dd, J = 18.0, 4.4 Hz, 1H), 3.48 (dd, J = 18.0, 14.4 Hz, 1H), 4.23 (dd, J = 14.4, 4.4 Hz, 1H), 4.63 (d, J = 15.8 Hz, 1H), 4.88 (d, J = 15.8 Hz, 1H), 6.46-6.53 (m, 1H), 6.55 (d, J = 7.6 Hz, 1H), 6.68 (d, J = 7.6 Hz, 1H), 6.73-6.80 (m, 2H), 6.86-6.95 (m, 2H), 7.00 (td, J = 7.6, 0.8 Hz, 1H), 7.02-7.25 (m, 6H), 7.45 (td, J = 7.4, 1.6 Hz, 1H), 7.50 (td, J = 7.4, 1.6 Hz, 1H), 8.22 (dd, J = 7.6, 1.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 40.5, 44.1, 47.1, 58.5, 110.2, 115.0 (d, J = 21 Hz), 115.4 (d, J = 22 Hz), 122.9, 124.5 (d, J = 2 Hz), 125.1, 126.9, 127.4, 127.6, 128.0, 128.4, 128.9, 129.2, 129.7 (d, J = 9 Hz), 129.8, 131.8, 135.1, 140.1, 140.2, 142.6, 143.3, 162.5 (d, J = 245 Hz), 177.7, 196.3; FTIR (KBr) 3060, 2921, 1714, 1687, 1608, 1485, 1364, 1295, 733, 699 cm^{-1}; HRMS (m/z): $[M+Na]^+$ calcd for $C_{30}H_{22}NO_2FNa$: 470.1532; found: 470.1507.



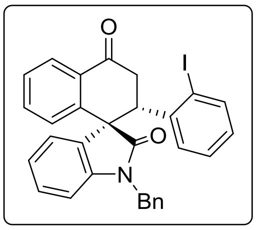
1-Benzyl-2'-(3-chlorophenyl)-2',3'-dihydro-4'*H*-spiro[indoline-3,1'-naphthalene]-2,4'-dione (3n): 174 mg, 75% yield; 90:10 dr (*anti:syn*); Major: white solid; mp 81-83 ^{o}C; R_f 0.38 (20% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.98 (dd, *J* = 18.0, 4.0 Hz, 1H), 3.48 (dd, *J* = 18.0, 14.6 Hz, 1H), 4.19 (dd, *J* = 14.6, 4.0 Hz, 1H), 4.62 (d, *J* = 15.8 Hz, 1H), 4.89 (d, *J* = 15.8 Hz, 1H), 6.56 (d, *J* = 8.0 Hz, 1H), 6.69-6.82 (m, 4H), 6.92 (d, *J* = 7.2 Hz, 1H), 6.96-7.05 (m, 2H), 7.08-7.25 (m, 6H), 7.44 (td, *J* = 7.4, 1.2 Hz, 1H), 7.50 (td, *J* = 7.4, 1.2 Hz, 1H), 8.22 (dd, *J* = 7.6, 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 40.5, 44.1, 47.1, 58.5, 110.3, 122.9, 125.1, 126.8 (2C), 127.4, 127.6, 128.0, 128.2, 128.5, 128.7, 128.9, 129.2, 129.6, 129.7, 131.8, 134.1, 135.0, 135.1, 139.7, 142.5, 143.2, 177.6, 196.3; FTIR (KBr) 3062, 2978, 1714, 1686, 1607, 1485, 1363, 1295, 754, 699 cm^{-1}; HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{30}H_{22}NO_2NaCl$: 486.1237; found: 486.1268.



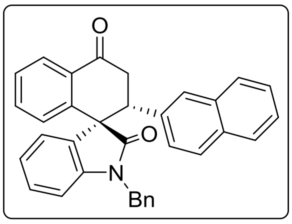
1-Benzyl-2'-(3-nitrophenyl)-2',3'-dihydro-4'*H*-spiro[indoline-3,1'-naphthalene]-2,4'-dione (3o): 183 mg, 77% yield; 90:10 dr (*anti:syn*); Major: white solid; mp 162-164 ^{o}C; R_f 0.32 (20% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.00 (dd, *J* = 18.0, 3.8 Hz, 1H), 3.46-3.61 (m, 1H), 4.33 (dd, *J* = 14.4, 3.8 Hz, 1H), 4.61 (d, *J* = 15.6 Hz, 1H), 4.77 (d, *J* = 15.6 Hz, 1H), 6.61 (d, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 7.2 Hz, 2H), 6.92 (t, *J* = 7.6 Hz, 1H), 7.06 (t, *J* = 7.4 Hz, 1H), 7.12-7.28 (m, 7H), 7.43-7.59 (m, 3H), 7.96-8.04 (m, 1H), 8.23 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 40.2, 44.1, 46.9, 58.2, 110.2, 123.0, 123.1, 123.3, 125.2, 127.2, 127.4, 128.0, 128.1, 128.6, 128.9 (2C), 129.2, 129.6, 131.8, 135.0, 135.1, 135.2, 139.5, 142.3, 142.8, 147.8, 177.4, 195.6; FTIR (KBr) 3066, 2941, 1712, 1686, 1607, 1529, 1467, 1349, 1295, 754, 694 cm^{-1}; HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{30}H_{22}N_2O_4Na$: 497.1477; found: 497.1468.



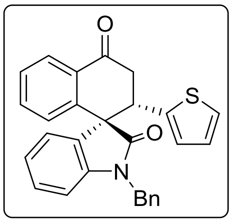
1-Benzyl-2'-(*o*-tolyl)-2',3'-dihydro-4'*H*-spiro[indoline-3,1'-naphthalene]-2,4'-dione (3p): 155 mg, 70% yield; 95:05 dr (*anti:syn*); Major: white solid; mp 137-139 ^{o}C; R_f 0.44 (20% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.39 (s, 3H), 2.98 (dd, *J* = 18.4, 4.4 Hz, 1H), 3.40 (dd, *J* = 18.4, 13.6 Hz, 1H), 4.44 (d, *J* = 16.0 Hz, 1H), 4.64 (dd, *J* = 13.6, 4.4 Hz, 1H), 5.16 (d, *J* = 16.0 Hz, 1H), 6.32 (d, *J* = 7.6 Hz, 1H), 6.49-6.57 (m, 3H), 6.70-6.79 (m, 1H), 6.90-6.95 (m, 1H), 6.99 (td, *J* = 7.4, 0.8 Hz, 1H), 7.03-7.22 (m, 7H), 7.45 (td, *J* = 7.6, 1.6Hz, 1H), 7.50 (td, *J* = 7.6, 1.6 Hz, 1H), 8.21-8.28 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.4, 41.3, 41.8, 44.0, 58.2, 110.2, 122.8, 125.4, 125.8, 126.6, 126.7, 127.1, 127.4, 127.5, 128.1, 128.3, 128.9, 129.0, 130.5, 131.0, 132.0, 135.0 (2C), 136.8, 137.4, 142.8, 144.1, 178.2, 197.2; FTIR (KBr) 3056, 2924, 2853, 1714, 1684, 1608, 1466, 1363, 1294, 756, 736 cm^{-1}; HRMS (*m*/*z*): $[M+Na]^+$ calcd for $C_{31}H_{25}NO_2Na$: 466.1783; found: 466.1773.



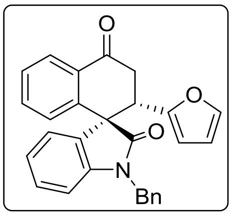
1-Benzyl-2'-(2-iodophenyl)-2',3'-dihydro-4'*H*-spiro[indoline-3,1'-naphthalene]-2,4'-dione (3q): 178 mg, 64% yield; 89:11 dr (*anti:syn*); Major: white solid; mp 99-101 °C; R_f 0.39 (20% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 500 MHz) δ 3.15 (dd, *J* = 18.5, 11.0 Hz, 1H), 3.30 (dd, *J* = 18.5, 5.2 Hz, 1H), 4.56 (d, *J* = 15.5 Hz, 1H), 4.69 (dd, *J* = 11.0, 5.2 Hz, 1H), 5.11 (d, *J* = 15.5 Hz, 1H), 6.42 (dd, *J* = 7.5, 2.0 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 6.71 (d, *J* = 7.5 Hz, 1H), 6.82-6.97 (m, 6H), 7.13-7.23 (m, 4H), 7.41-7.50 (m, 2H), 7.83 (dd, *J* = 7.5, 1.5 Hz, 1H), 8.23-8.29 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 41.1, 44.1, 50.0, 57.3, 103.6, 110.1, 122.8, 125.7, 127.1, 127.3, 127.6, 128.1, 128.3, 128.4, 128.9 (2C), 129.1, 129.4, 129.9, 132.3, 134.9, 135.4, 140.4, 141.6, 142.8, 143.2, 177.0, 196.4; FTIR (KBr) 3061, 2904, 1718, 1683, 1608, 1467, 1361, 1294, 755, 735 cm^{-1}; HRMS (*m*/*z*): $[M+H]^+$ calcd for $C_{30}H_{23}NO_2I$: 556.0774; found: 556.0760.



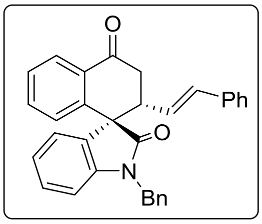
1-Benzyl-2'-(naphthalen-2-yl)-2',3'-dihydro-4'*H*-spiro-[indoline-3,1'-naphthalene]-2,4'-dione (3r): 201 mg, 84% yield; 88:12 dr (*anti:syn*); Major: white solid; mp 159-161 °C; R_f 0.39 (20% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 3.06 (dd, *J* = 18.0, 4.2 Hz, 1H), 3.66 (dd, *J* = 18.0, 14.4 Hz, 1H), 4.41 (d, *J* = 16.0 Hz, 1H), 4.43 (dd, *J* = 14.4, 4.2 Hz, 1H), 5.00 (d, *J* = 16.0 Hz, 1H), 6.31 (d, *J* = 7.2 Hz, 2H), 6.41 (d, *J* = 7.6 Hz, 1H), 6.56 (t, *J* = 7.8 Hz, 2H), 6.87 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.89-6.98 (m, 2H), 7.03 (td, *J* = 7.6, 1.2 Hz, 1H), 7.13 (td, *J* = 7.6, 1.2 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.39-7.56 (m, 6H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 8.26 (dd, *J* = 7.8, 1.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 41.0, 44.0, 47.6, 58.8, 110.3, 122.8, 125.2, 126.0, 126.2, 126.3, 126.4, 127.2, 127.4, 127.7, 127.9, 128.0, 128.2, 128.3, 128.4 (2C), 129.0, 130.2, 131.9, 133.1, 133.3, 134.6, 135.1, 135.3, 142.6, 143.7, 177.9, 196.8; FTIR (KBr) 3058, 2910, 1715, 1685, 1606, 1486, 1362, 1294, 751, 736 cm^{-1}; HRMS (*m*/*z*): $[M+H]^+$ calcd for $C_{34}H_{26}NO_2$: 480.1964; found: 480.1963.



1-Benzyl-2'-(thiophen-2-yl)-2',3'-dihydro-4'*H*-spiro[indoline-3,1'-naphthalene]-2,4'-dione (3s): 187 mg, 86% yield; 92:08 dr (*anti:syn*); Major: white solid; mp 215-217 °C; R_f 0.43 (20% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 500 MHz) δ 3.16 (dd, *J* = 18.2, 4.5 Hz, 1H), 3.44 (dd, *J* = 18.2, 13.5 Hz, 1H), 4.56 (dd, *J* = 13.5, 4.5 Hz, 1H), 4.67 (d, *J* = 15.7 Hz, 1H), 5.04 (d, *J* = 15.7 Hz, 1H), 6.60 (d, *J* = 8.0 Hz, 1H), 6.73 (dd, *J* = 8.5, 1.0 Hz, 1H), 6.78-6.84 (m, 3H), 6.92-6.96 (m, 1H), 6.99 (td, *J* = 7.5, 1.0 Hz, 1H), 7.03-7.09 (m, 2H), 7.17 (td, *J* = 7.7, 1.2 Hz, 1H), 7.19-7.25 (m, 3H), 7.44 (td, *J* = 7.5, 1.5 Hz, 1H), 7.49 (td, *J* = 7.5, 1.5 Hz, 1H), 8.18-8.24 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 42.7, 43.4, 44.1, 58.6, 110.2, 122.9, 125.0, 125.4, 126.3, 126.8, 126.9, 127.4, 127.5, 128.0, 128.4, 128.9, 129.1, 129.9, 131.8, 135.0, 135.1, 140.9, 143.0, 143.2, 177.7, 195.8; FTIR (KBr) 3066, 2952, 1715, 1684, 1606, 1465, 1295, 761 cm^{-1}; HRMS (*m*/*z*): $[M+H]^+$ calcd for $C_{28}H_{22}NO_2S$: 436.1371; found: 436.1393.

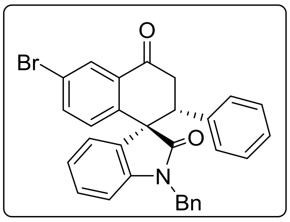


1-Benzyl-2'-(furan-2-yl)-2',3'-dihydro-4'*H*-spiro[indoline-3,1'-naphthalene]-2,4'-dione (3t): 109 mg, 52% yield; 85:15 dr (*anti:syn*) (93:07 dr from the ^1H NMR of purified compound); Major: white solid; mp 173-175 ^oC; R_f 0.41 (20% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 500 MHz) δ 3.28 (dd, *J* = 18.0, 5.0 Hz, 1H), 3.39 (dd, *J* = 18.0, 12.0 Hz, 1H), 4.26 (dd, *J* = 12.0, 5.0 Hz, 1H), 4.88-4.98 (m, 2H), 5.79 (d, *J* = 3.5 Hz, 1H), 6.11 (dd, *J* = 3.5, 1.8 Hz, 1H), 6.70 (d, *J* = 7.5 Hz, 1H), 6.85 (dd, *J* = 7.5, 1.2 Hz, 2H), 6.92 (td, *J* = 7.5, 1.0 Hz, 1H), 7.05 (dd, *J* = 2.0, 0.5 Hz, 1H), 7.15 (td, *J* = 7.5, 1.0 Hz, 1H), 7.16-7.20 (m, 2H), 7.24-7.34 (m, 3H), 7.40-7.48 (m, 2H), 8.19-8.28 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 38.4, 41.2, 44.3, 57.2, 107.7, 109.8, 110.2, 125.2, 127.4, 127.5, 127.8, 127.9, 128.4, 128.8, 129.0 (2C), 130.7, 132.1, 134.9, 135.5, 141.8, 142.5, 142.6, 152.5, 177.8, 196.0; FTIR (KBr) 3060, 2915, 1714, 1687, 1608, 1485, 1363, 1295, 739, 700 cm^{-1}; $[M+Na]^+$ calcd for $C_{28}H_{21}NO_3Na$: 442.1419; found: 442.1449.

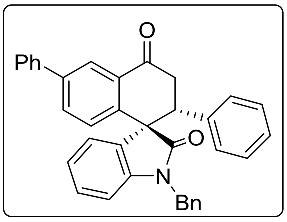


1-Benzyl-2',6'-diphenyl-2',3'-dihydro-4'*H*-spiro[indoline-3,1'-naphthalene]-2,4'-dione (3u): 173 mg, 76% yield; 65:35 dr (*anti:syn*); **Major**: white solid; mp 91-93 ^oC; R_f 0.42 (20% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 2.99 (dd, *J* = 18.0, 4.8 Hz, 1H), 3.19 (dd, *J* = 18.0, 13.2 Hz, 1H), 3.75-3.85 (m, 1H), 4.72 (d, *J* = 15.6 Hz, 1H), 5.27 (d, *J* = 15.6 Hz, 1H), 5.59 (dd, *J* = 15.6, 9.2 Hz, 1H), 6.57 (d, *J* = 15.6 Hz, 1H), 6.76 (d, *J* = 7.6 Hz, 1H), 6.87-6.94 (m, 3H), 6.98 (td, *J* = 7.6, 0.8 Hz, 1H), 7.03-7.15 (m, 4H), 7.17-7.27 (m, 6H), 7.42 (td, *J* = 7.4, 1.6 Hz, 1H), 7.47 (td, *J* = 7.4, 1.6 Hz, 1H), 8.17-8.22 (m, 1H);^{13}C NMR ($CDCl_3$, 100 MHz) δ 40.2, 44.5, 45.8, 110.2, 122.9, 125.1, 126.1, 126.7, 127.3, 127.4, 127.7, 127.8, 128.0, 128.1, 128.7 (2C), 128.8, 128.9, 130.2, 132.0, 134.1, 134.9, 135.2, 136.4, 142.6, 143.3, 178.3, 196.3; FTIR (KBr) 3030, 2925, 1715, 1687, 1605, 1461, 1357, 1295, 969, 752, 697 cm^{-1}; HRMS (*m*/*z*): $[M+Na]^+$ calcd for $C_{32}H_{25}NO_2Na$: 478.1782; found: 478.1773.

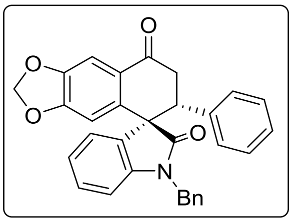
Minor (**3u'**): white solid; mp 147-149 ^oC; R_f 0.46 (20% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 2.85 (dd, *J* = 17.0, 4.2 Hz, 1H), 3.64 (dddd, *J* = 13.8, 7.2, 4.2, 1.0 Hz, 1H), 3.95 (dd, *J* = 17.0, 13.8 Hz, 1H), 4.66 (d, *J* = 16.0 Hz, 1H), 5.09 (d, *J* = 16.0 Hz, 1H), 5.83 (dd, *J* = 15.6, 7.4 Hz, 1H), 6.26 (d, *J* = 15.6 Hz, 1H), 6.61-6.67 (m, 1H), 6.74 (d, *J* = 7.6 Hz, 1H), 6.95-7.06 (m, 4H), 7.10-7.28 (m, 9H), 7.36-7.47 (m, 2H), 8.20-8.25 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 38.8, 44.2, 46.2, 56.2, 109.5, 123.6, 124.1, 126.1, 126.5, 127.2, 127.6, 127.8, 128.0, 128.4, 128.7, 128.9, 129.0, 132.6, 133.0, 133.5, 134.0, 135.5, 136.5, 142.4, 143.8, 175.7, 196.9; FTIR (KBr) 3029, 2929, 1706, 1689, 1609, 1490, 1357, 1295, 694 cm^{-1}; HRMS (*m*/*z*): $[M+H]^+$ calcd for $C_{32}H_{26}NO_2$: 456.1963; found: 456.1968.



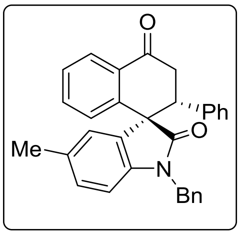
1-Benzyl-6'-bromo-2'-phenyl-2',3'-dihydro-4'*H*-spiro[indoline-3,1'-naphthalene]-2,4'-dione (3v): 198 mg, 78% yield; 90:10 dr (*anti:syn*); Major: white solid; mp 168-170 °C; R_f 0.54 (20% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 3.01 (dd, *J* = 18.0, 4.2 Hz, 1H), 3.51 (dd, *J* = 18.0, 14.4 Hz, 1H), 4.19 (dd, *J* = 14.4, 4.2 Hz, 1H), 4.57 (d, *J* = 15.8 Hz, 1H), 4.88 (d, *J* = 15.8 Hz, 1H), 6.49 (d, *J* = 8.0 Hz, 1H), 6.64 (d, *J* = 6.8 Hz, 2H), 6.76-6.87 (m, 3H), 7.00 (t, *J* = 7.6 Hz, 1H), 7.05-7.28 (m, 8H), 7.59 (dd, *J* = 8.4, 2.0 Hz, 1H), 8.34 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 40.5, 44.1, 47.3, 58.4, 110.3, 122.7, 122.9, 125.1, 126.8, 127.5, 128.1, 128.4, 128.6, 128.9, 129.2, 129.3, 129.6, 130.8, 133.5, 135.0, 137.3, 137.7, 142.3, 142.6, 177.5, 195.6; FTIR (KBr) 3060, 2946, 1713, 1689, 1608, 1468, 1353, 1293, 736, 701 cm^{-1}; HRMS (*m*/*z*): $[M+Na]^+$ calcd for $C_{30}H_{22}NO_2NaBr$: 530.0732; found: 530.0726.



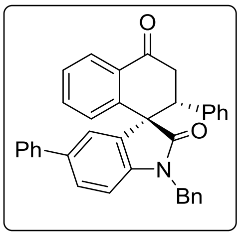
1-Benzyl-2',6'-diphenyl-2',3'-dihydro-4'*H*-spiro[indoline-3,1'-naphthalene]-2,4'-dione (3w): 210 mg, 83% yield; 90:10 dr (*anti:syn*); Major: white solid; mp 196-198 °C; R_f 0.48 (20% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 3.05 (dd, *J* = 18.0, 4.4 Hz, 1H), 3.59 (dd, *J* = 18.0, 14.4 Hz, 1H), 4.27 (dd, *J* = 14.4, 4.4 Hz, 1H), 4.61 (d, *J* = 15.8 Hz, 1H), 4.93 (d, *J* = 15.8 Hz, 1H), 6.50 (d, *J* = 8.0 Hz, 1H), 6.63-6.70 (m, 2H), 6.88 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 7.08-7.29 (m, 8H), 7.35-7.52 (m, 3H), 7.58-7.66 (m, 2H), 7.73 (dd, *J* = 8.0, 2.0 Hz, 1H), 8.46 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 40.8, 44.1, 47.5, 58.6, 110.2, 122.8, 125.2, 126.3, 126.8, 127.2, 127.5, 128.0, 128.1, 128.4, 128.7, 128.9, 129.0, 129.1, 130.1, 132.3, 133.5, 135.0, 137.6, 139.6, 141.3, 142.3, 142.6, 177.9, 196.9; FTIR (KBr) 3057, 2894, 1715, 1685, 1608, 1486, 1359, 1266, 756, 701 cm^{-1}; HRMS (*m*/*z*): $[M+H]^+$ calcd for $C_{36}H_{28}NO_2$: 506.2120; found: 506.2137.



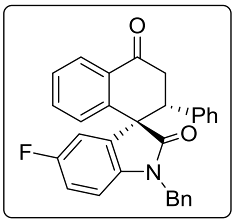
1-Benzyl-6'-phenyl-6',7'-dihydro-8'*H*-spiro[indoline-3,5'-naphtho[2,3-*d*][1,3]dioxole]-2,8'-dione (3x): 147 mg, 62% yield; 88:12 dr (*anti:syn*); Major: white solid; mp 223-225 °C; R_f 0.35 (20% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 500 MHz) δ 2.93 (dd, *J* = 18.0, 4.2 Hz, 1H), 3.46 (dd, *J* = 18.0, 14.2 Hz, 1H), 4.18 (dd, *J* = 14.4, 4.2 Hz, 1H), 4.55 (d, *J* = 16.0 Hz, 1H), 4.88 (d, *J* = 16.0 Hz, 1H), 5.98 (d, *J* = 14.2 Hz, 1H), 5.99 (d, *J* = 14.2 Hz, 1H), 6.28 (s, 1H), 6.46 (d, *J* = 8.0 Hz, 1H), 6.62 (d, *J* = 6.5 Hz, 2H), 6.83 (d, *J* = 7.5 Hz, 2H), 7.00 (td, *J* = 7.5, 1.0 Hz, 1H), 7.05-7.27 (m, 8H) 7.63 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 40.3, 44.0, 47.6, 58.9, 102.2, 106.6, 106.7, 110.2, 122.8, 125.1, 126.7, 127.4, 127.5, 127.9, 128.3, 128.6, 128.8, 129.0, 129.9, 135.0, 137.6, 140.2, 142.5, 148.3, 153.2, 177.8, 195.1; FTIR (KBr) 3059, 2904, 1713, 1674, 1611, 1483, 1363, 1295, 1268, 1038, 736, 701 cm^{-1}; HRMS (*m*/*z*): $[M+H]^+$ calcd for $C_{31}H_{24}NO_4$: 474.1705; found: 474.1724.



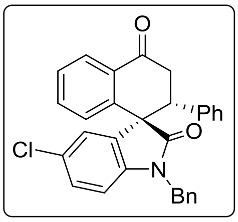
1-Benzyl-5-methyl-2'-phenyl-2',3'-dihydro-4'*H*-spiro[indoline-3,1'-naphthalene]-2,4'-dione (3y): 160 mg, 72% yield; 91:09 dr (*anti:syn*); Major: white solid; mp 194-196 °C; R_f 0.43 (20% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.25 (s, 3H), 3.00 (dd, *J* = 18.0, 4.2 Hz, 1H), 3.55 (dd, *J* = 18.0, 14.4 Hz, 1H), 4.22 (dd, *J* = 14.4, 4.2 Hz, 1H), 4.55 (d, *J* = 16.0 Hz, 1H), 4.88 (d, *J* = 16.0 Hz, 1H), 6.36 (d, *J* = 8.4 Hz, 1H), 6.62 (d, *J* = 6.4 Hz, 2H), 6.86 (d, *J* = 7.2 Hz, 2H), 6.89-6.96 (m, 3H), 7.09-7.28 (m, 6H), 7.44 (td, *J* = 7.6, 1.4 Hz, 1H), 7.50 (td, *J* = 7.6, 1.4 Hz, 1H), 8.23 (dd, *J* = 7.8, 1.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.3, 40.7, 44.0, 47.4, 58.9, 109.9, 125.8, 126.7, 127.4 (2C), 127.9, 128.0, 128.3, 128.4, 128.7, 128.8, 129.3, 130.1, 131.9, 132.3, 135.0, 135.2, 137.8, 140.2, 143.8, 177.8, 197.1; FTIR (KBr) 3060, 3032, 2915, 1712, 1685, 1495, 1349, 1294, 736, 700 cm^{-1}; HRMS (*m*/*z*): $[M+Na]^+$ calcd for $C_{31}H_{25}NO_2Na$: 466.1783; found: 466.1763.



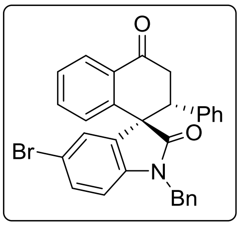
1-Benzyl-2',5-diphenyl-2',3'-dihydro-4'*H*-spiro[indoline-3,1'-naphthalene]-2,4'-dione (3z): 200 mg, 79% yield; 90:10 dr (*anti:syn*); Major: white solid; mp 169-171 °C; R_f 0.44 (20% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.07 (dd, *J* = 18.0, 4.5 Hz, 1H), 3.60 (dd, *J* = 18.0, 14.0 Hz, 1H), 4.26 (dd, *J* = 14.0, 4.5 Hz, 1H), 4.64 (d, *J* = 16.0 Hz, 1H), 4.91 (d, *J* = 16.0 Hz, 1H), 6.55 (d, *J* = 8.5 Hz, 1H), 6.69 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 7.5 Hz, 2H), 6.95 (dd, *J* = 7.2, 0.8 Hz, 1H), 7.12 (t, *J* = 7.7 Hz, 2H), 7.15-7.33 (m, 6H), 7.35-7.44 (m, 5H), 7.46 (td, *J* = 7.5, 1.2 Hz, 1H), 7.51 (td, *J* = 7.5, 1.2 Hz, 1H), 8.25 (dd, *J* = 8.0, 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 40.7, 44.2, 47.5, 58.9, 110.4, 123.9, 126.8, 126.9, 127.4, 127.5, 127.6, 127.8, 128.0, 128.1, 128.5 (2C), 128.7, 128.9, 129.0, 130.8, 132.0, 135.0, 135.1, 136.2, 137.7, 140.3, 142.0, 143.3, 177.9, 196.8; FTIR (KBr) 3028, 2904, 1714, 1685, 1612, 1482, 1294, 1348, 736, 699 cm^{-1}; HRMS (*m*/*z*): $[M+H]^+$ calcd for $C_{36}H_{28}NO_2$: 506.2120; found: 506.2100.



1-Benzyl-5-fluoro-2'-phenyl-2',3'-dihydro-4'*H*-spiro[indoline-3,1'-naphthalene]-2,4'-dione (3aa) 141 mg, 63% yield; 89:11 dr (*anti:syn*); Major: white solid; mp 166-168 °C; R_f 0.43 (20% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.03 (dd, *J* = 18.0, 4.5 Hz, 1H), 3.49 (dd, *J* = 18.0, 14.5 Hz, 1H), 4.24 (dd, *J* = 14.5, 4.5 Hz, 1H), 4.57 (d, *J* = 16.0 Hz, 1H), 4.88 (d, *J* = 16.0 Hz, 1H), 6.35-6.41 (m, 1H), 6.62 (d, *J* = 7.0 Hz, 2H), 6.82 (td, *J* = 8.7, 2.7 Hz, 1H), 6.86 (dd, *J* = 8.0, 2.5 Hz, 1H), 6.88-6.93 (m, 3H), 7.09-7.29 (m, 6H), 7.47 (td, *J* = 7.5, 1.5 Hz, 1H), 7.51 (td, *J* = 7.5, 1.5 Hz, 1H), 8.24 (dd, *J* = 7.5, 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 40.5, 44.2, 47.4, 59.2, 110.8 (d, *J* = 9 Hz), 113.2 (d, *J* = 25 Hz), 115.3 (d, *J* = 24 Hz), 126.7 (2C), 127.5 (d, *J* = 30 Hz), 128.1, 128.2, 128.5, 128.6, 128.7, 128.9, 131.7 (d, *J* = 8 Hz), 131.9, 134.7, 135.1, 137.4, 138.5, 142.8, 159.0 (d, J = 241 Hz), 177.7, 196.4; FTIR (KBr) 3057, 2926, 1715, 1688, 1601, 1489, 1345, 1294, 737, 702 cm^{-1}; HRMS (m/z): $[M+H]^+$ calcd for $C_{30}H_{23}NO_2F$: 448.1713; found: 448.1692.



1-Benzyl-5-chloro-2'-phenyl-2',3'-dihydro-4'*H*-spiro[indoline-3,1'-naphthalene]-2,4'-dione (3ab) 162 mg, 70% yield; 92:08 dr (*anti:syn*); Major: white solid; mp 189-191 °C; R_f 0.47 (20% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 3.03 (dd, J = 18.0, 4.0 Hz, 1H), 3.50 (dd, J = 18.0, 14.4 Hz, 1H), 4.22 (dd, J = 14.4, 4.0 Hz, 1H), 4.57 (d, J = 15.6 Hz, 1H), 4.86 (d, J = 15.6 Hz, 1H), 6.38 (d, J = 8.5 Hz, 1H), 6.62 (d, J = 7.2 Hz, 2H), 6.85-6.92 (m, 3H), 7.04-7.30 (m, 8H), 7.44-7.55 (m, 2H), 8.24 (dd, J = 7.6, 1.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 40.5, 44.2, 47.4, 59.0, 111.1, 125.4, 126.7 (2C), 127.3, 127.7, 128.1, 128.2, 128.5 (2C), 128.6, 128.7, 129.0 (2C), 131.9, 134.6, 135.1, 137.3, 141.2, 142.7, 177.5, 196.4; FTIR (KBr) 3066, 2956, 1717, 1687, 1604, 1483, 1343, 1294, 738, 698 cm^{-1}; HRMS (m/z): $[M+Na]^+$ calcd for $C_{30}H_{22}NO_2NaCl$: 486.1237; found: 486.1225.



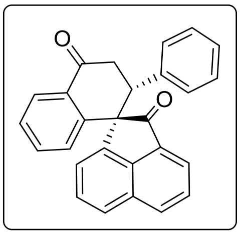
1-Benzyl-5-bromo-2'-phenyl-2',3'-dihydro-4'*H*-spiro[indoline-3,1'-naphthalene]-2,4'-dione (3ac): 188 mg, 74% yield; 88:12 dr (*anti:syn*); Major: white solid; mp 196-198 °C; R_f 0.47 (20% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 3.03 (dd, J = 18.0, 4.4 Hz, 1H), 3.50 (dd, J = 18.0, 14.4 Hz, 1H), 4.22 (dd, J = 14.4, 4.4 Hz, 1H), 4.57 (d, J = 16.0 Hz, 1H), 4.85 (d, J = 16.0 Hz, 1H), 6.33 (d, J = 8.4 Hz, 1H), 6.62 (d, J = 6.8 Hz, 2H), 6.84-6.92 (m, 3H), 7.10-7.29 (m, 8H), 7.44-7.55 (m, 2H), 8.22-8.28 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 40.5, 44.1, 47.5, 58.9, 111.6, 115.4, 126.7, 127.4, 127.7, 128.0, 128.1, 128.2, 128.5, 128.6, 128.7, 129.0, 131.8, 131.9, 132.2, 134.5, 135.1, 137.3, 141.7, 142.7, 177.4, 196.4; FTIR (KBr) 3058, 2911, 1718, 1686, 1602, 1480, 1344, 1295, 741, 699 cm^{-1}; HRMS (m/z): $[M+Na]^+$ calcd for $C_{30}H_{22}NO_2NaBr$: 530.0732; found: 530.0745.

2.2. Procedure for one-synthesis of α-tetralone-fused spirooxindoles 3 from isatin

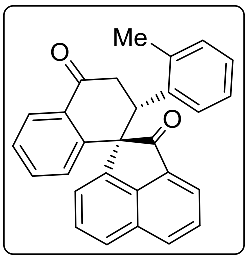
To a rapidly stirred suspension of tosylhydrazide (0.3 mmol) in CH_3CN (1 mL), *N*-benzylisatin (0.3 mmol) was added and the mixture was stirred at 60 °C for 1 h. After brought into room temperature, *E*-2'-iodochalcone **1** (0.2 mmol), $[Pd(allyl)Cl]_2$ (0.02 mmol), PPh_3 (0.06 mmol), TBAB 0.05 mmol) , DIPEA (0.6 mmol) and CH_3CN (1 mL) were successively added. The reaction tube was then immersed in a 50 ºC pre-heated oil bath with stirring (500 rpm) till complete consumption of 2'-iodochalcone. Upon cooling down to room temperature, the solvent was removed under reduced pressure. Water (approx.10 mL) was added to the reaction mixture and extracted with dichloromethane (3×5 mL). Brine wash (1×5 mL) was given to the combined organic extractions and dried over anhydrous Na_2SO_4. The dr was determined by ^1H NMR analysis of the crude reaction mixture and was subsequently purified by silica gel column separation using hexanes and ethylacetate mixture (8:2, v/v) as mobile phase afforded the corresponding spirooxindoles **3**.

3. General procedure for the synthesis of spiroacenaphthylenes 7

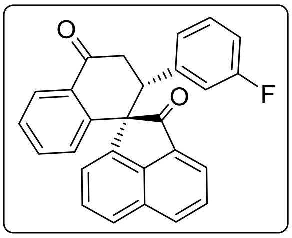
Under open atmosphere, *E*-2'-iodochalcone **1** (167 mg, 0.5 mmol), acenaphthenequinone-derived tosylhydrazones **6** (263 mg, 0.75 mmol), $[Pd(allyl)Cl]_2$ (18.5 mg, 0.05 mmol), PPh_3 (39.5 mg, 0.15 mmol), TBAB (40 mg, 0.125 mmol) and DIPEA (262 µL, 1.5 mmol) were successively added to oven-dried reaction tube. CH_3CN (3 mL) was added and closed with a glass-stopper. The reaction tube was then immersed in a 50 ºC pre-heated oil bath with stirring (500 rpm) till complete consumption of 2'-iodochalcone. Upon cooling down to room temperature, the solvent was removed under reduced pressure. Water (approx.10 mL) was added to the reaction mixture and extracted with dichloromethane (3×5 mL). Brine wash (1×5 mL) was given to the combined organic extractions and dried over anhydrous Na_2SO_4. The dr was determined by ^{1}H NMR analysis of the crude reaction mixture and was subsequently purified by silica gel column separation using hexanes and ethylacetate mixture (8:2, v/v) as mobile phase afforded the corresponding spiroacenaphthylenes **7**.



2'-Phenyl-2',3'-dihydro-2*H*,4'*H*-spiro[acenaphthylene-1,1'-naphthalene]-2,4'-dione (7a): 135 mg, 72% yield; 80:20 dr (*anti:syn*) (80:20 dr from the ^{1}H NMR of purified compound); Major: white solid; mp 186-188 ^{o}C; R_f 0.46 (20% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.10 (dd, *J* = 18.0, 4.2 Hz, 1H), 3.60 (dd, *J* = 18.0, 13.0 Hz, 1H), 4.24 (dd, *J* = 13.0, 4.2 Hz, 1H), 6.63-6.69 (m, 2H), 6.73 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.78-6.90 (m, 3H), 7.23 (d, *J* = 7.0 Hz, 1H), 7.37 (td, *J* = 7.5, 1.5 Hz, 1H), 7.42 (td, *J* = 7.5, 1.5 Hz, 1H), 7.52-7.63 (m, 2H), 7.79-7.83 (m, 2H), 7.99 (d, *J* = 8.0 Hz, 1H), 8.24-8.29 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 41.1, 47.7, 63.1, 122.2, 122.4, 125.0, 127.4, 127.6, 127.8, 128.0, 128.1, 128.2, 128.3, 128.4, 130.9, 131.9, 132.5, 133.4, 134.6, 138.1, 139.9, 142.1, 144.4, 197.2, 205.8; FTIR (KBr) 3060, 2952, 1719, 1686, 1451, 1598, 1294, 764, 702 cm^{-1}; HRMS (*m*/*z*): $[M+H]^+$ calcd for $C_{27}H_{19}O_2$: 375.1385; found: 375.1380.



2'-(*o*-tolyl)-2',3'-dihydro-2*H*,4'*H*-spiro[acenaph-thylene-1,1'-naphthalene]-2,4'-dione (7b): 115 mg, 59% yield; 85:15 dr (*anti:syn*) (93:07 dr from the ^{1}H NMR of purified compound); Major: white solid; mp 143-145 ^{o}C; R_f 0.49 (20% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.16 (s, 3H), 2.81 (dd, *J* = 17.6, 4.0 Hz, 1H), 4.01 (dd, *J* = 17.6, 14.4 Hz, 1H), 4.57 (dd, *J* = 14.4, 4.0 Hz, 1H), 6.45 (d, *J* = 8.0 Hz, 1H), 6.64-6.76 (m, 3H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.26-7.32 (m, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 7.2 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 6.8 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 8.29 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.0, 41.6, 41.9, 62.5, 122.5, 122.8, 125.0, 125.4, 126.4, 127.1, 127.8, 127.9, 128.1, 128.4, 128.5, 130.6, 130.9, 132.0, 132.7 (2C), 134.5, 136.6, 137.8, 140.1, 142.3, 144.1, 197.5, 204.6; FTIR (KBr) 3018, 2923, 1713, 1682, 1598, 1462, 1341, 1294, 785, 726 cm^{-1}; HRMS (*m*/*z*): $[M+Na]^+$ calcd for $C_{28}H_{20}O_2Na$: 411.1361; found: 411.1359.

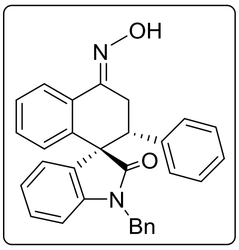


2'-(3-Fluorophenyl)-2',3'-dihydro-2*H*,4'*H*-spiro[acenaph-thylene-1,1'-naphthalene]-2,4'-dione (7c): 122 mg, 62% yield; 87:13 dr (*anti:syn*); Major: white solid; mp 208-210 °C; R_f 0.41 (20% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.09 (dd, *J* = 17.6, 3.8 Hz, 1H), 3.55 (dd, *J* = 17.6, 13.6 Hz, 1H), 4.23 (dd, *J* = 13.6, 3.8 Hz, 1H), 6.28-6.36 (m, 1H), 6.50 (d, *J* = 7.6 Hz, 1H), 6.57 (t, *J* = 8.2 Hz, 1H), 6.73 (d, *J* = 7.6 Hz, 1H), 6.76-6.86 (m, 1H), 7.22-7.28 (m, 1H), 7.34-7.46 (m, 2H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.78-7.89 (m, 2H), 8.03 (d, *J* = 8.4 Hz, 1H), 8.25 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 40.9, 47.3, 62.9, 114.4 (d, *J* = 21 Hz), 115.2 (d, *J* = 22 Hz), 122.3, 122.4, 124.3 (d, *J* = 3 Hz), 125.2, 127.8, 128.0, 128.2, 128.5(2C), 129.3 (d, *J* = 8 Hz), 130.9, 132.2, 132.4, 133.2, 134.7, 139.5, 140.7 (d, *J* = 7 Hz), 142.1, 144.2, 162.0 (d, *J* = 245 Hz), 196.7, 205.5; FTIR (KBr) 3029, 2968, 1718, 1688, 1591, 1488, 1342, 1294, 782 cm^{-1}; HRMS (*m*/*z*): $[M+Na]^+$ calcd for $C_{27}H_{17}O_2FNa$: 415.1110; found: 415.1108.

4.0 Synthetic transformations of product 3b

4.1 Procedure for synthesis of 8:

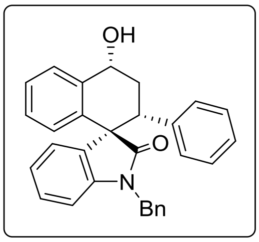
The compound **3b** (43 mg, 0.1 mmol) was taken in oven dried 10 mL RB flask and dissolved in 1 mL of EtOH. $NH_2OH.HCl$ (0.5 mmol) and sodium acetate (0.4 mmol) were added successively and stirred at rt till complete consumption of **3b** as monitored by TLC. After 2 h, solvent was removed under vaccum and the resulting crude product was purified by silica gel column chromatography using hexanes and ethylacetate mixture (7:3, v/v) afforded pure oxime **8**.



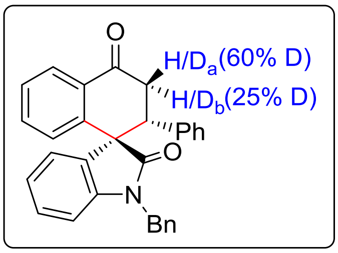
1-benzyl-4'-(hydroxyimino)-2'-phenyl-3',4'-dihydro-2'*H*-spiro[indoline-3,1'-naphthalen]-2-one (8): 43 mg, 96% yield; white solid; mp 159-161 °C; R_f 0.61 (30% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.32 (dd, *J* = 18.8, 14.0 Hz, 1H), 3.49 (dd, *J* = 18.8, 5.2 Hz, 1H), 3.89 (dd, *J* = 14.0, 5.2 Hz, 1H), 4.51 (d, *J* = 16.0 Hz, 1H), 4.96 (d, *J* = 16.0 Hz, 1H), 6.45 (d, *J* = 8.0 Hz, 1H), 6.56 (d, *J* = 6.8 Hz, 2H), 6.84-6.92 (m, 3H), 6.98 (td, *J* = 7.6, 1.0 Hz, 1H), 7.05-7.19 (m, 7H), 7.21-7.35 (m, 3H), 8.05-8.12 (m, 1H), 8.55 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 27.1, 43.9, 45.9, 58.8, 109.9, 122.8, 124.8, 125.1, 126.7, 127.1, 127.3, 127.8, 128.0, 128.3, 128.6, 128.8 (2C), 130.0, 130.5, 130.7, 135.2, 138.6, 139.3, 142.4, 154.7, 178.2; FTIR (KBr) 3483, 3014, 2883, 1605, 1702, 1455, 1352, 959, 756 cm^{-1}; HRMS (*m*/*z*): $[M+H]^+$ calcd for $C_{30}H_{25}N_2O_2$: 445.1916; found: 445.1910.

4.2 Procedure for synthesis of 9:

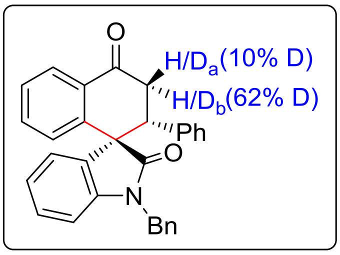
The compound **3b** (43 mg, 0.1 mmol) was taken in oven dried 10 mL RB flask and dissolved in 1 mL of MeOH. The solution was brought to 0 °C by means of ice-bath, then $NaBH_4$ (0.15 mmol) was added in two portions and stirred at same temperature for 10 mins led to the completion of reaction (TLC). Water was added slowly to quench the reaction and extracted with dichloromethane (3×5 mL). Brine wash (1×5 mL) was given to the combined organic extractions and dried over anhydrous Na_2SO_4. The dr was determined by ^{1}H NMR analysis of the crude reaction mixture, and was subsequently purified by silica gel column separation using hexanes and ethylacetate mixture (7:3, v/v) as mobile phase afforded the corresponding alcohol **9**.



1-Benzyl-4'-hydroxy-2'-phenyl-3',4'-dihydro-2'*H*-spiro[indoline-3,1'-naphthalen]-2-one (9): 42 mg, 97% yield; ≥95:05 dr; white solid; mp 165-167 °C; R_f 0.36 (30% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.38-2.50 (m, 2H), 2.65-2.78 (m, 1H), 3.81 (dd, *J* = 13.6, 2.0 Hz, 1H), 4.69 (d, *J* = 15.8 Hz, 1H), 4.79 (d, *J* = 15.8 Hz, 1H), 5.22 (dd, *J* = 10.4, 6.4 Hz, 1H), 6.39 (d, *J* = 7.6 Hz, 1H), 6.61 (dd, *J* = 7.6, 0.8 Hz, 1H), 6.73-6.80 (m, 2H), 6.86 (d, *J* = 7.2 Hz, 2H), 6.94 (td, *J* = 7.6, 0.8 Hz, 1H), 7.00-7.07 (m, 3H), 7.09-7.21 (m, 5H), 7.24-7.34 (m, 2H), 7.73 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 35.6, 44.0, 46.5, 59.4, 69.2, 109.5, 122.6, 125.7, 127.0, 127.2, 127.4, 127.8, 127.9, 128.0 (2C), 128.2, 128.4, 128.6, 128.8, 133.5, 135.4, 136.5, 139.3, 1397, 142.3, 179.6; FTIR (KBr) 3404, 3057, 2945, 1696, 1609, 1488, 1364, 1267, 734, 700 cm^{-1}; $[M+H]^+$ calcd for $C_{30}H_{26}NO_2$: 432.1964; found: 432.1948. Relative configuration was determined by NOE and 2D NMR.

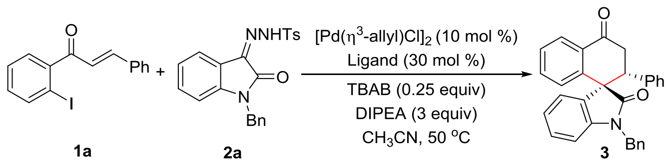


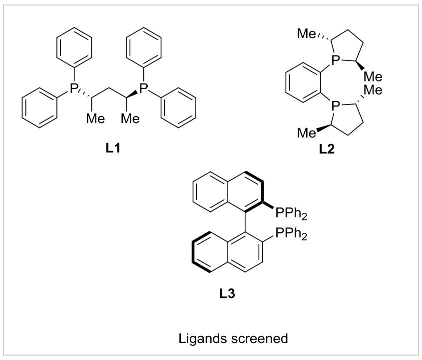
Compound **10**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.01 (dd, *J* = 18.0, 4.4 Hz, **0.4H**), 3.48-3.60 (m, **0.75H**), 4.18-4.28 (m, 1H), 4.58 (d, *J* = 15.8 Hz, 1H), 4.90 (d, *J* = 15.8 Hz, 1H), 6.43-6.50 (m, 1H), 6.60-6.67 (m, 2H), 6.85 (d, *J* = 7.6 Hz, 2H), 6.89-6.95 (m, 1H), 6.99 (td, J = 7.6, 0.8 Hz, 1H), 7.06-7.26 (m, 8H), 7.44 (td, *J* = 7.6, 1.6 Hz, 1H), 7.49 (td, *J* = 7.6, 1.6 Hz, 1H), 8.19-8.25 (m, 1H).



Compound **11**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.01 (dd, *J* = 18.0, 4.5 Hz, **0.9H**), 3.54 (dd, *J* = 18.0, 14.5 Hz, **0.38H**), 4.18-4.28 (m, 1H), 4.59 (d, *J* = 16.0 Hz, 1H), 4.89 (d, *J* = 16.0 Hz, 1H), 6.45-6.50 (m, 1H), 6.62-6.68 (m, 2H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.90-6.94 (m, 1H), 6.98 (td, *J* = 7.5, 1.0 Hz, 1H), 7.07-7.26 (m, 8H), 7.44 (td, *J* = 7.5, 1.3 Hz, 1H), 7.49 (td, *J* = 7.5, 1.3 Hz, 1H), 8.23 (dd, *J* = 7.8, 1.8 Hz, 1H).

5.0 Preliminary asymmetric results[a]

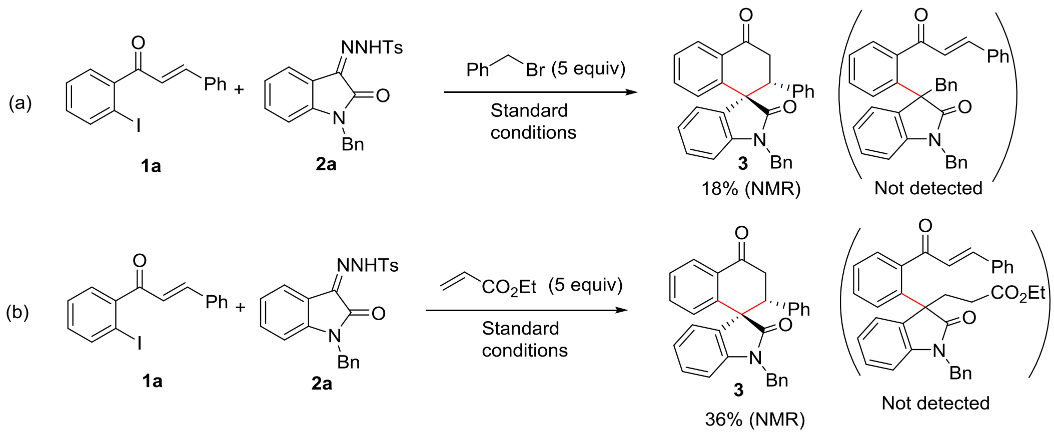




Entry	Ligand	Yield (%)	dr *anti:syn*	ee
1	**L1**	NR	-	-
2	**L2**	trace	-	-
3	**L3**	NR	-	-

[a]Reaction condition: 0.2 mmol of **1a**.

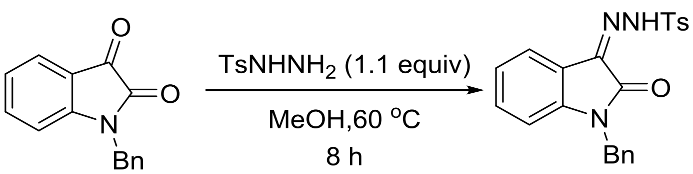
6.0 Control experiments



7.0 General procedure for the preparation of 2'-iodochalcone

2'-Iodochalcones **1** were prepared according to our previous reported procedure.[1]

7.1. General procedure for the synthesis of isatin-derived *N*-tosylhydrazone



Isatin-derived *N*-tosylhydrazone **2** were prepared according to slightly modified reported procedure.[2]

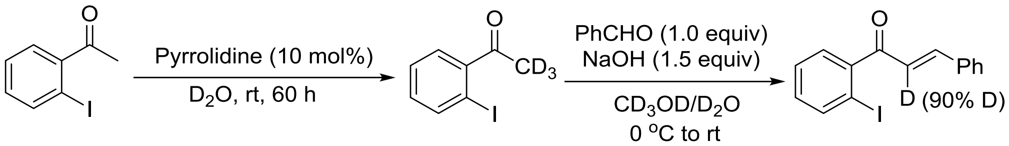
A solution of $TsNHNH_2$ (1.02 g, 5.5 mmol) in methanol (5 mL) was stirred at 60 °C until the $TsNHNH_2$ was completely dissolved. The mixture was cooled to room temperature and then *N*-benzyl isatin was added in small portions. After 5-10 minutes, a yellow precipitation was observed. Then the reaction was stirred at 60 °C for about 8 h. The mixture was cooled to 0 °C, and the precipitates was filtered out and washed with cold methanol to afford the pure *N*-tosylhydrazones.

***N'*-(1-Benzyl-2-oxoindolin-3-ylidene)-4-methylbenzenesulfonohydrazide (2a)**: Yellow solid; yield 89 %; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.41 (s, 3H), 4.88 (s, 2H), 6.73 (d, *J* = 8.0 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 7.19-7.36 (m, 8H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 2H), 12.5 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 43.4, 110.0, 119.6, 121.4, 123.5, 127.5, 128.0, 128.2, 129.1, 129.9, 131.3, 134.9, 135.2, 135.6, 142.6, 144.7, 161.2.

Compound **6a** was prepared according to the above mentioned procedure and data was in good agreement with the reported literature.[3]

8.0 Procedure for the synthesis of α-deuterated 2'-iodochalcone

A reported literature procedure was followed to synthesize **1a-(D$_1$)**[4]



A solution of 2'-iodoacetophenone (1.0 mmol), pyrrolidine (0.1 mmol) and D_2O (99% D, 1.5 mL) was stirred at room temperature for 60 h under nitrogen. The reaction mixture was concentrated under vacuum to get crude D_3-2'-iodoacetophenone which was taken to next step without further purifications.

D_3-2'-Iodoacetophenone (230 mg, 0.93 mmol) was dissolved in CD_3OD (1.5 mL) which was cooled to 0 °C. A solution of NaOH (55 mg, 1.39 mmol) in D_2O (0.2 mL) was added followed by the slow addition of benzaldehyde (94 μL, 0.93 mmol). The reaction mixture was then allowed to warm to room temperature. After 30 min, solvents were removed under vacuum and the crude material was purified by short pad of silica gel column chromatography (hexane/EtOAc 9:1 v/v) to yield the desired product D_1-2'-iodochalcone (90% D-atom) as yellow semi-solid (78% yield).

9. References:

1. Arunprasath, D.; Muthupandi, P.; Sekar, G. *Org. Lett.* **2015,** *17*, 5448-5451.
2. Marti, C.; Carreira, E. M. *J. Am. Chem. Soc.* **2005,** *127*, 11505-11515.
3. McMahon, R. J.; Chapman, O. L.; Hayes, R. A.; Hess, T. C.; Krimmer, H. P. *J. Am. Chem. Soc.* **1985,** *107*, 7597-606.

4. Zhan, M.; Zhang, T.; Huang, H.; Xie, Y.; Chen, Y. *J. Labelled Compd. Radiopharm.* **2014,** *57*, 533-539.

10. ^{1}H and ^{13}C spectra for all compounds

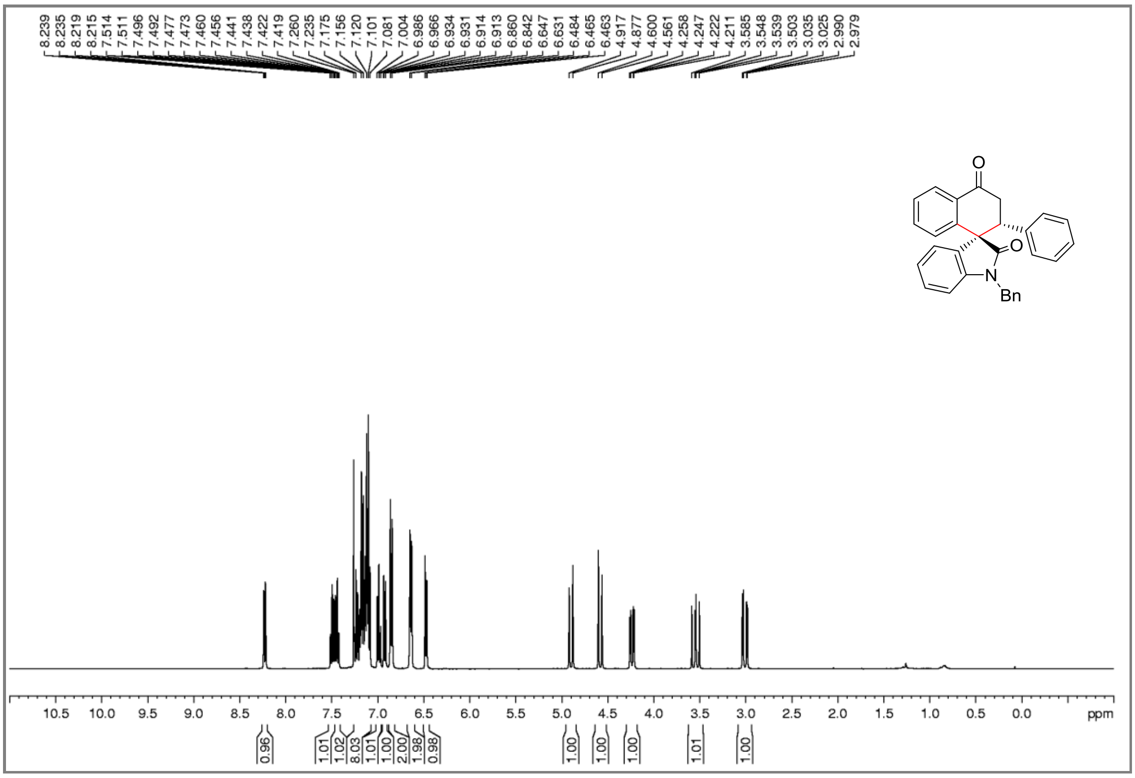


Figure 1: 400 MHz ^{1}H-NMR spectrum of **3b** in $CDCl_3$

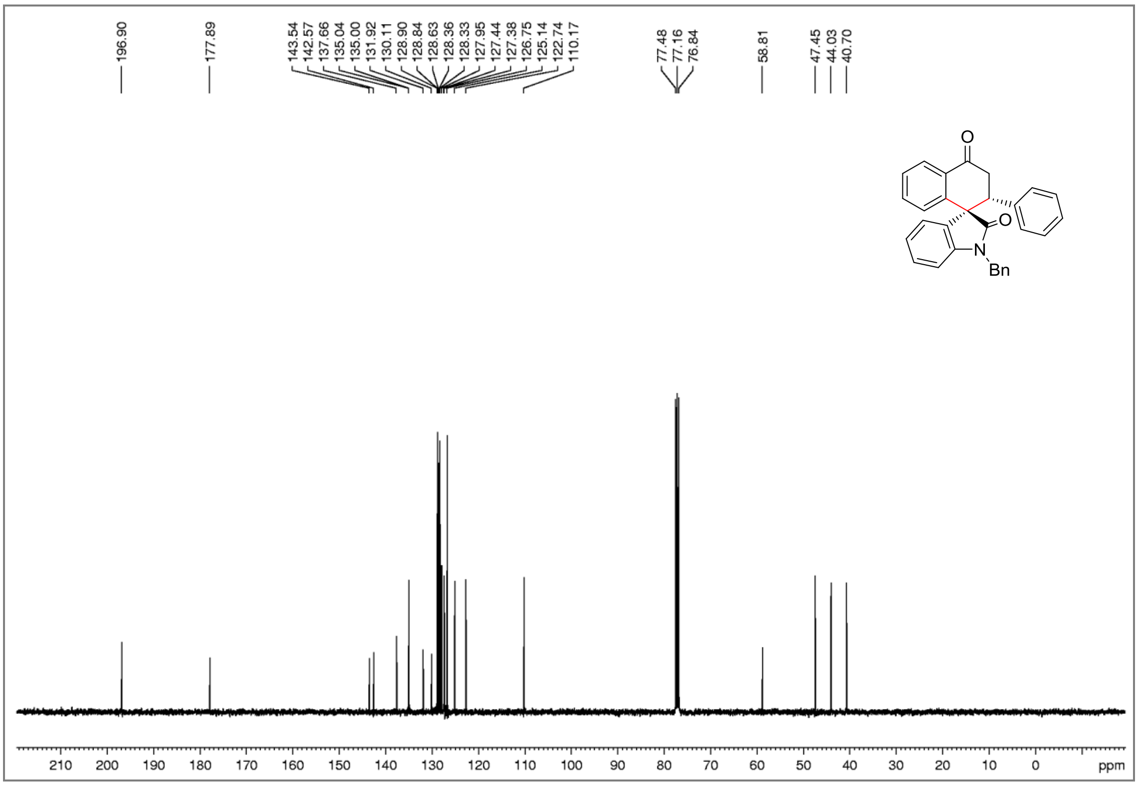


Figure 2: 100 MHz ^{13}C-NMR spectrum of **3b** in $CDCl_3$

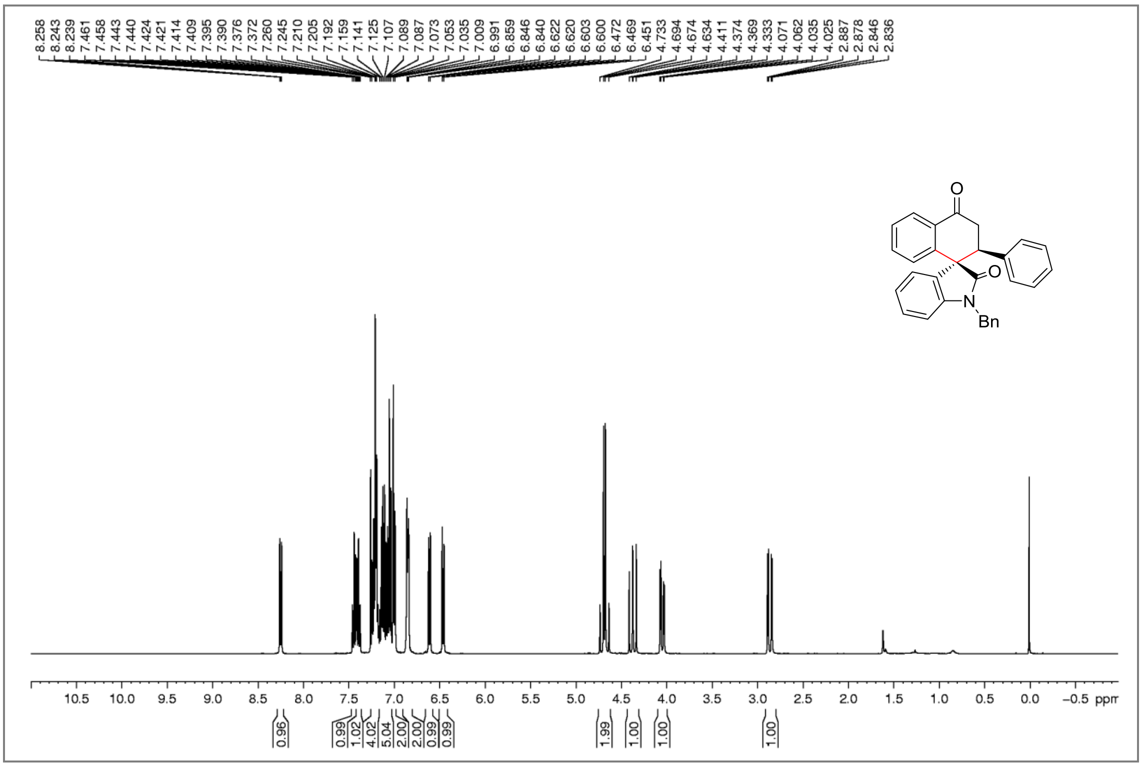


Figure 3: 400 MHz ^{1}H-NMR spectrum of **3b'** in $CDCl_3$

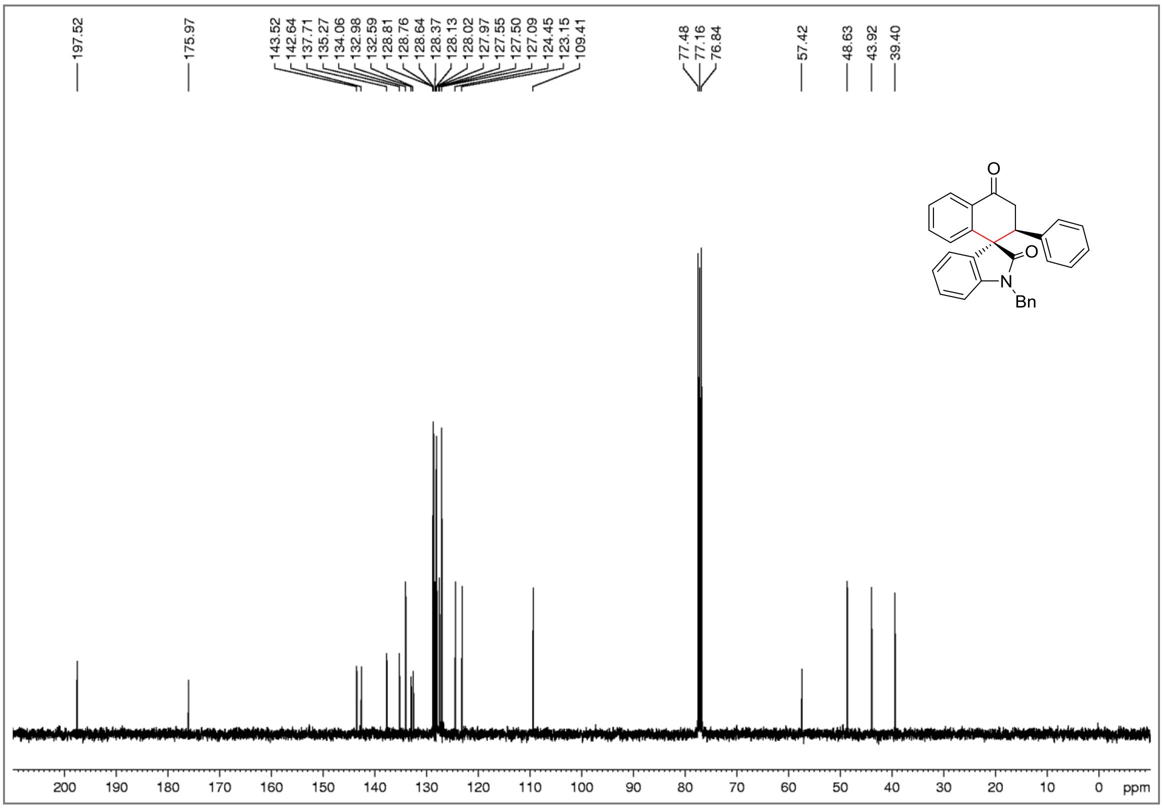


Figure 4: 100 MHz ^{13}C-NMR spectrum of **3b'** in $CDCl_3$

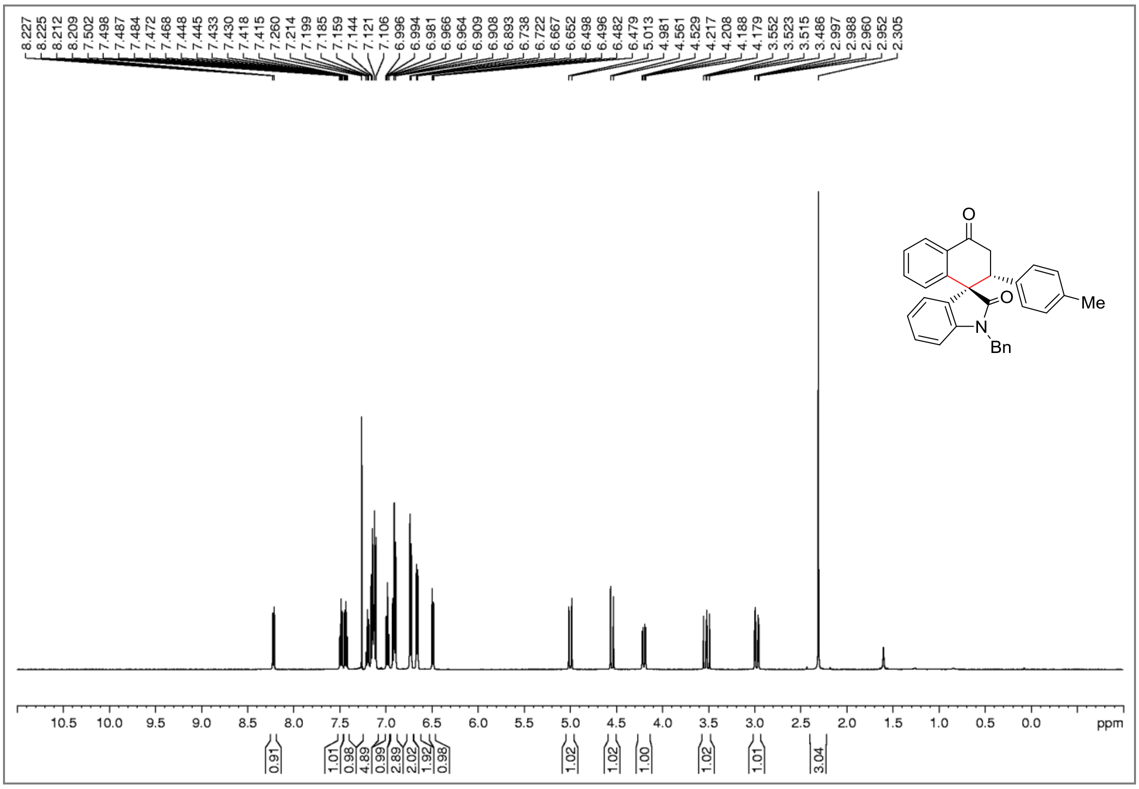


Figure 5: 500 MHz ^{1}H-NMR spectrum of **3c** in $CDCl_3$

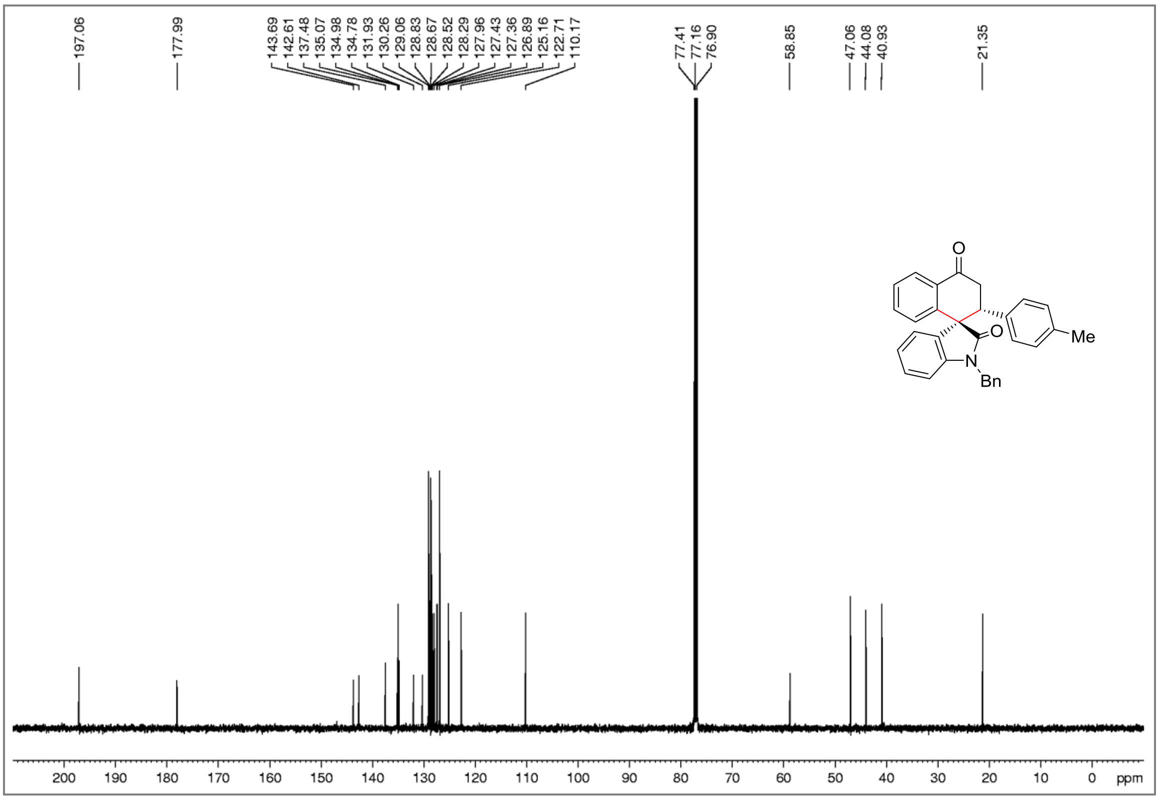


Figure 6: 125 MHz ^{13}C-NMR spectrum of **3c** in $CDCl_3$

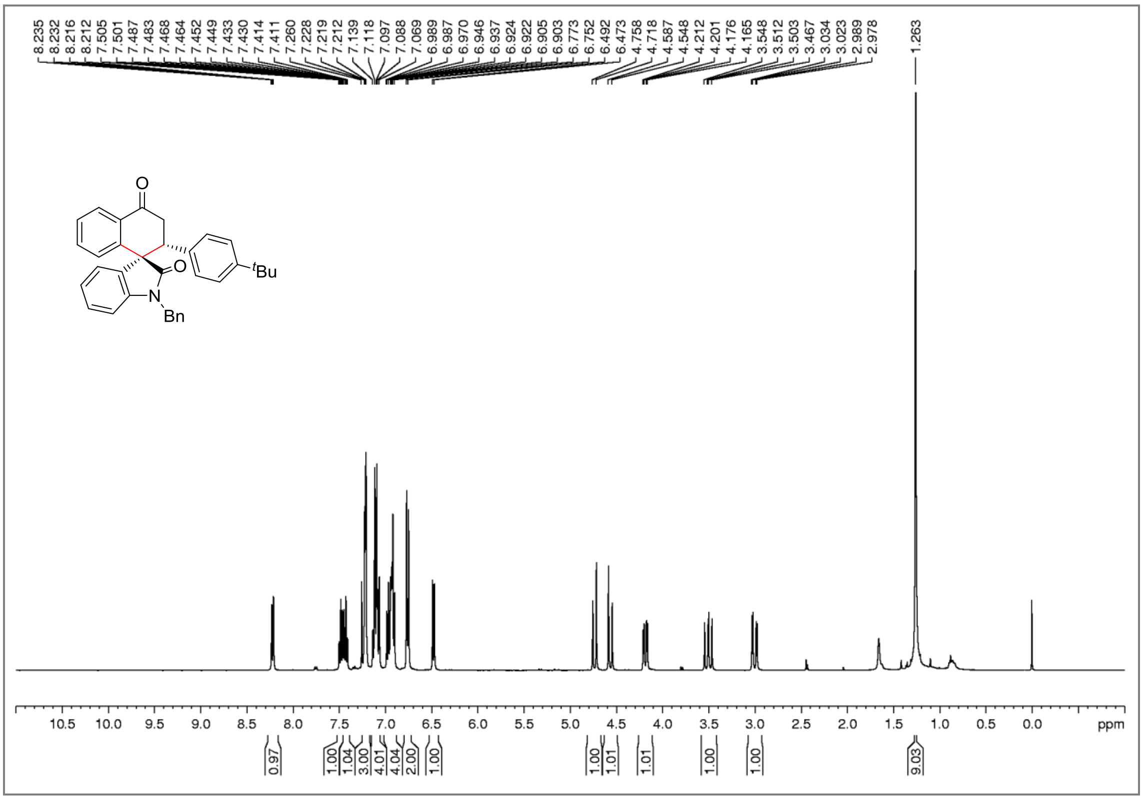


Figure 7: 400 MHz ^{1}H-NMR spectrum of **3d** in $CDCl_3$

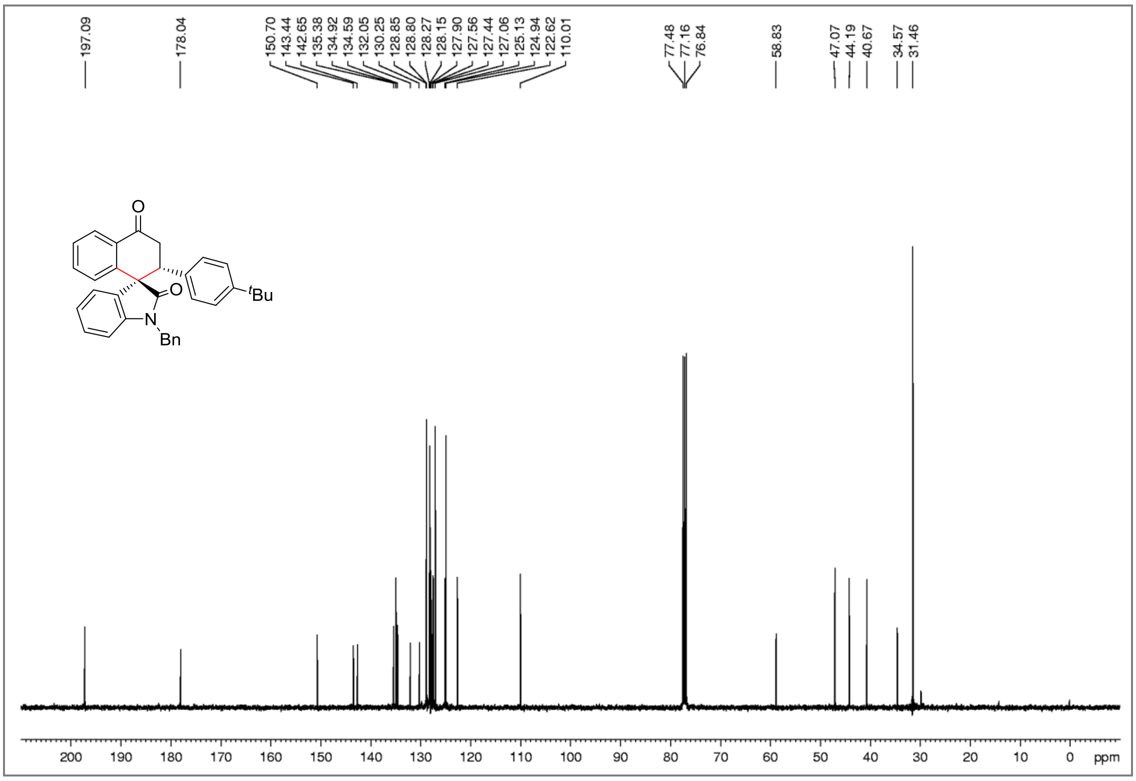


Figure 8: 100 MHz ^{13}C-NMR spectrum of **3d** in $CDCl_3$

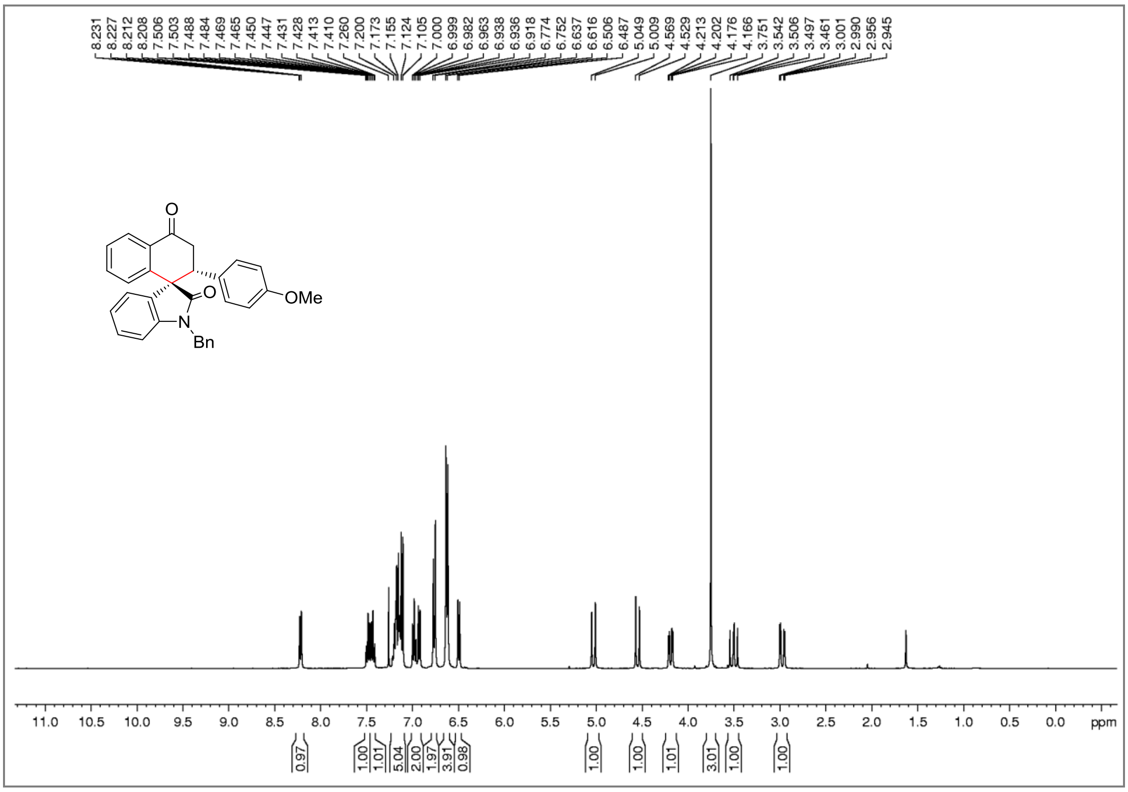


Figure 9: 400 MHz ^{1}H-NMR spectrum of **3e** in $CDCl_3$

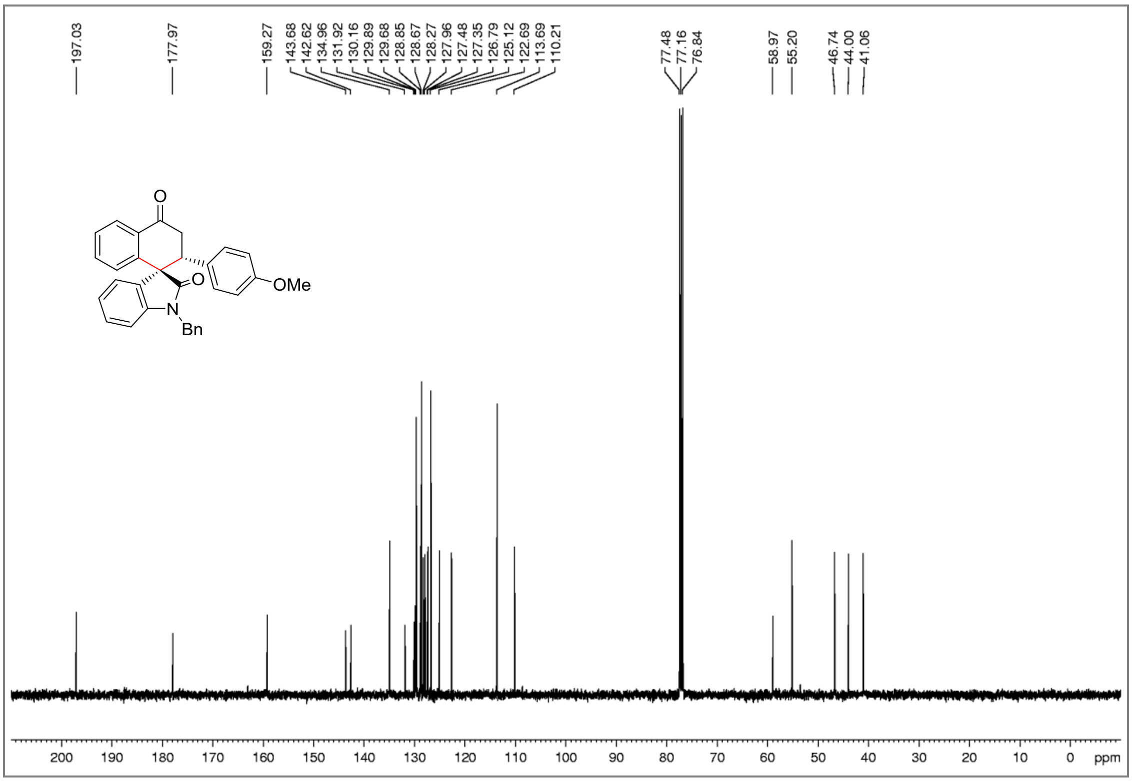


Figure 10: 100 MHz ^{13}C-NMR spectrum of **3e** in $CDCl_3$

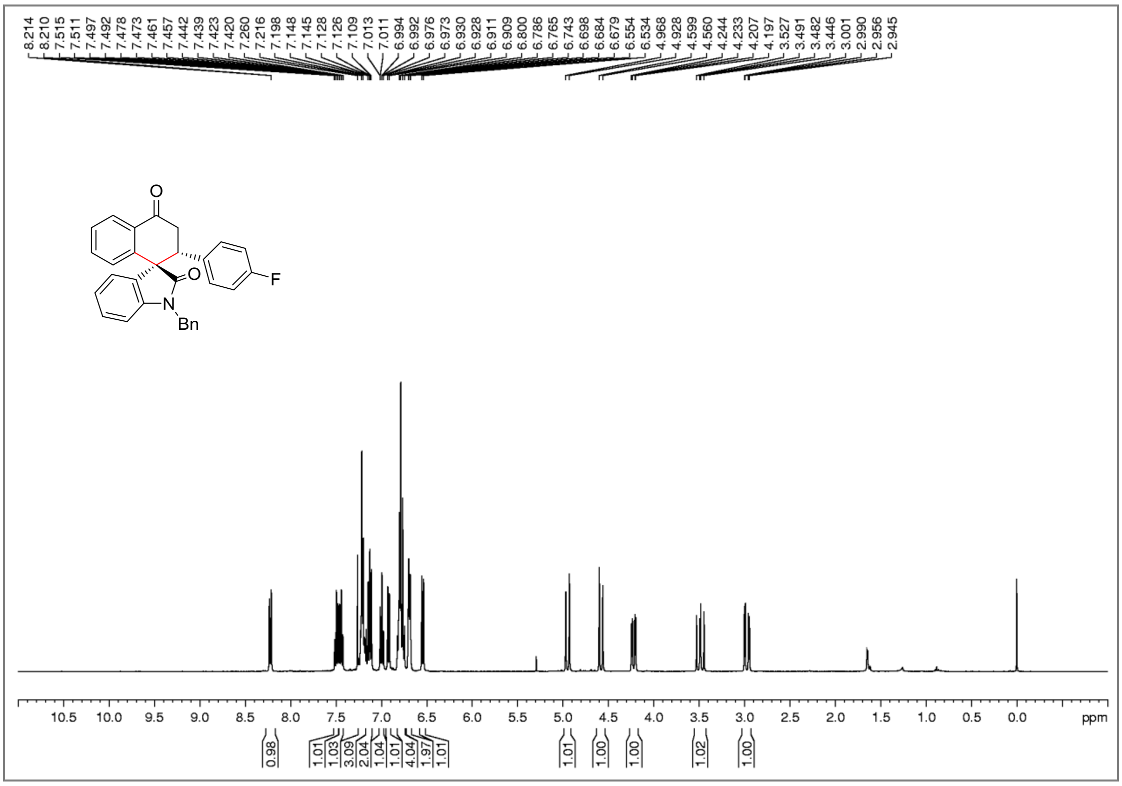


Figure 11: 400 MHz ^{1}H-NMR spectrum of **3f** in $CDCl_3$

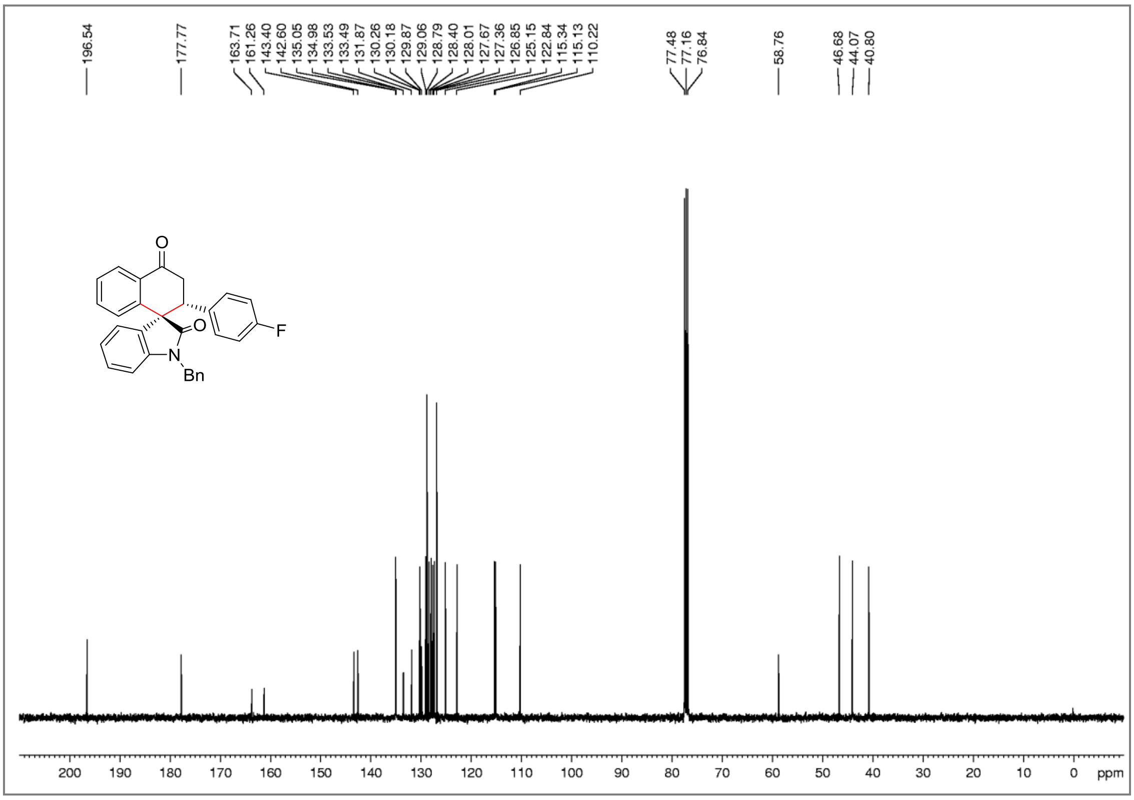


Figure 12: 100 MHz ^{13}C-NMR spectrum of **3f** in $CDCl_3$

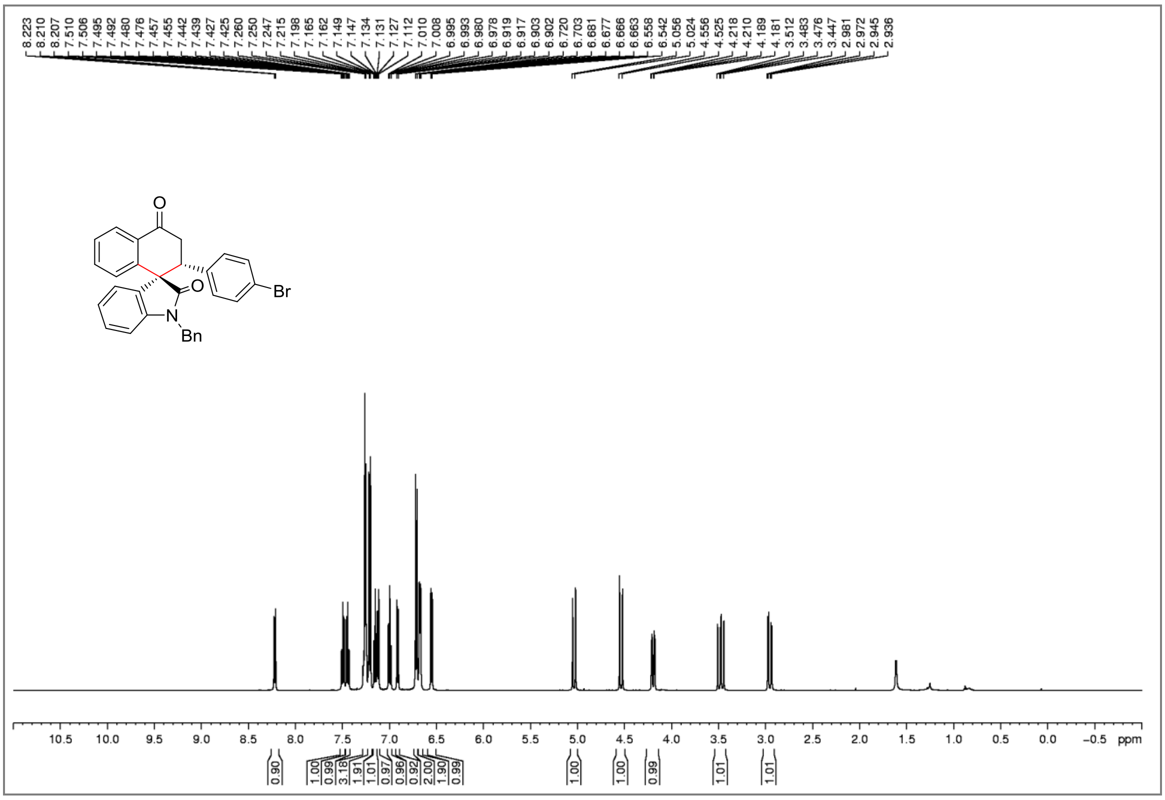


Figure 13: 500 MHz ^{1}H-NMR spectrum of **3g** in $CDCl_3$

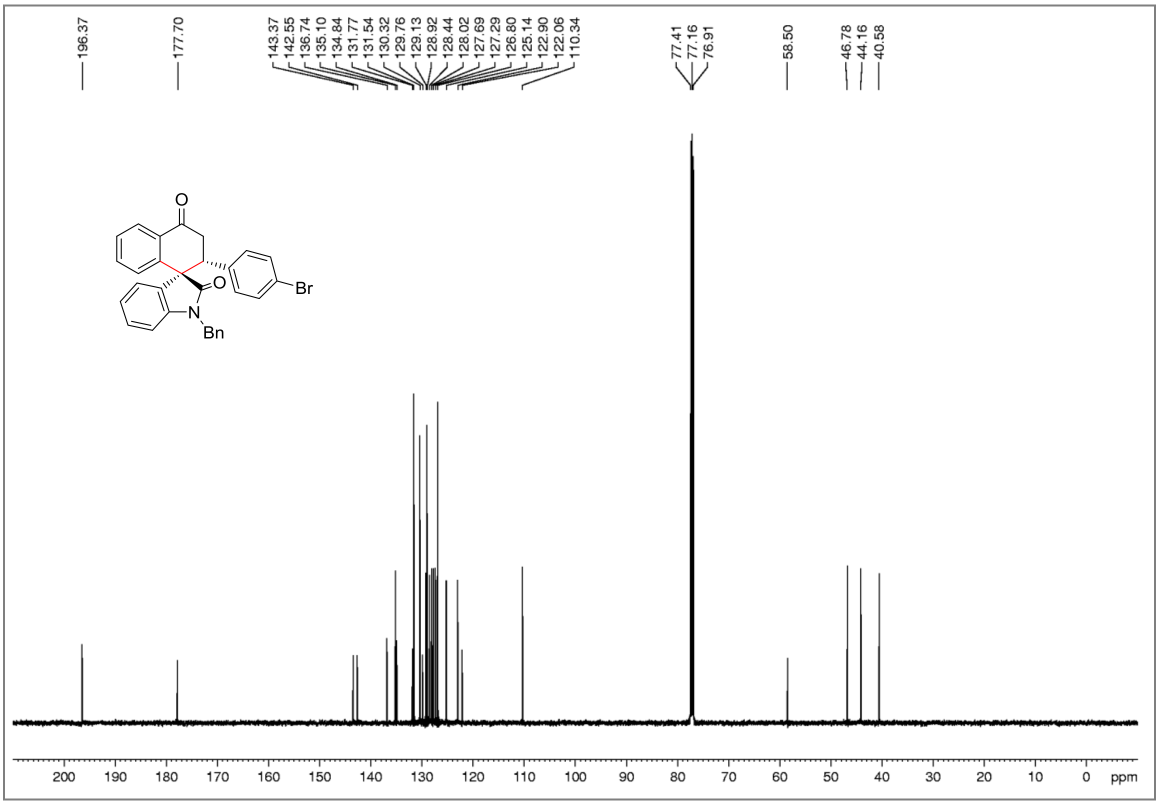


Figure 14: 125 MHz ^{13}C-NMR spectrum of **3g** in $CDCl_3$

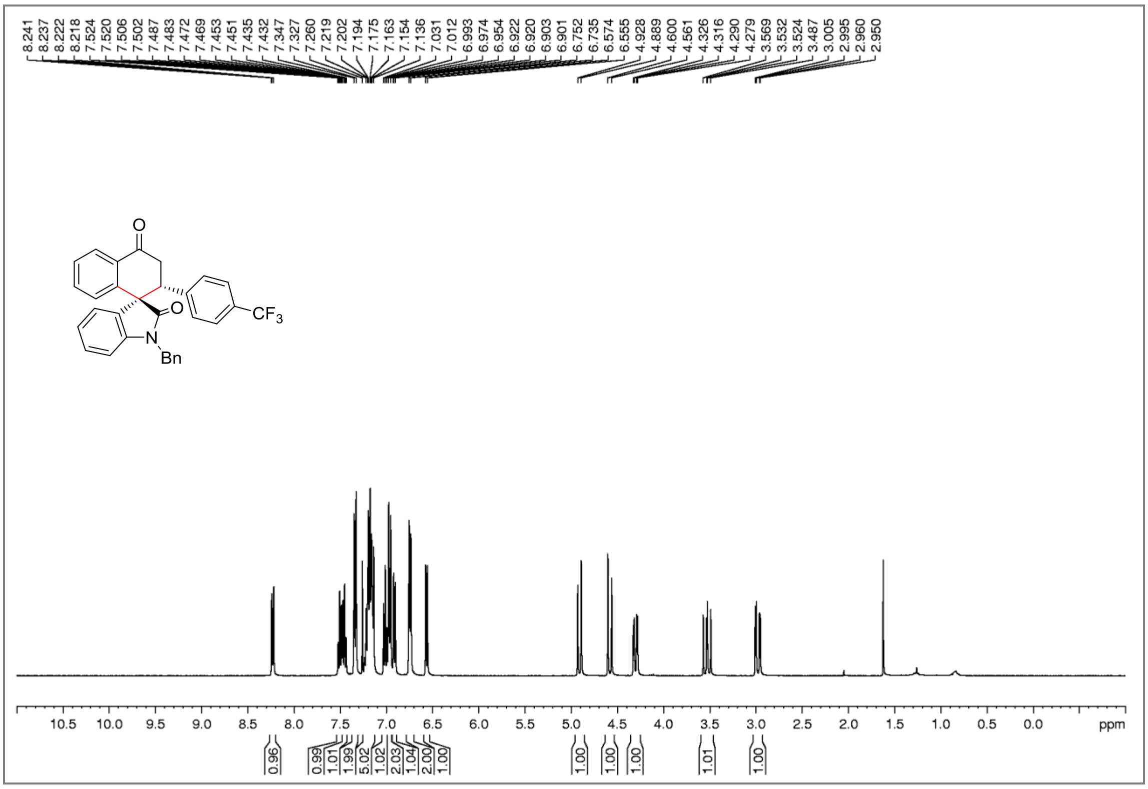


Figure 15: 400 MHz ^{1}H-NMR spectrum of **3h** in $CDCl_3$

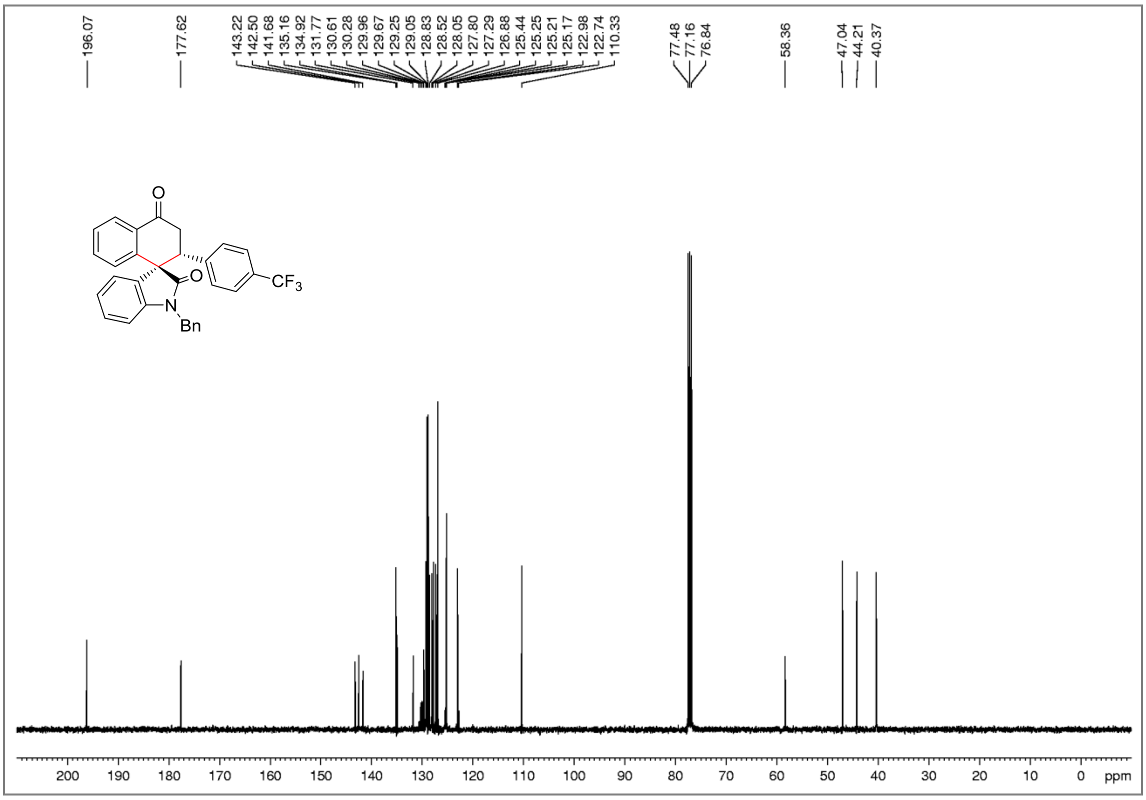


Figure 16: 100 MHz ^{13}C-NMR spectrum of **3h** in $CDCl_3$

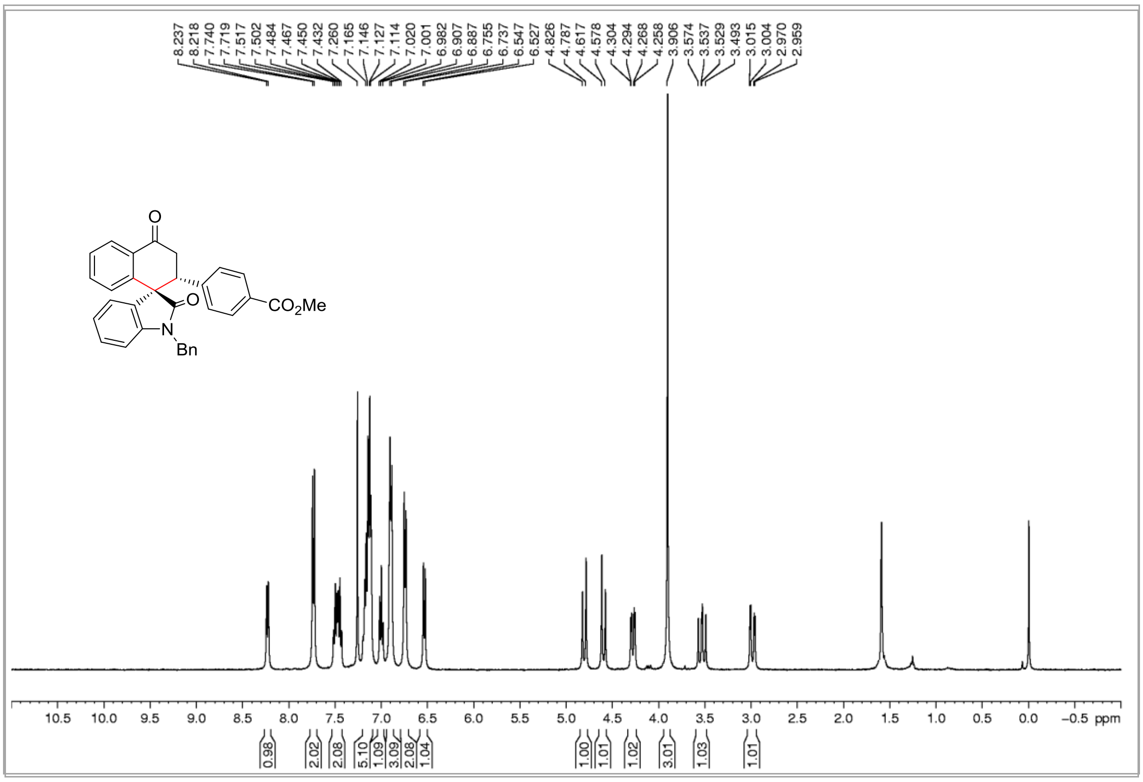


Figure 17: 400 MHz ^{1}H-NMR spectrum of **3i** in $CDCl_3$

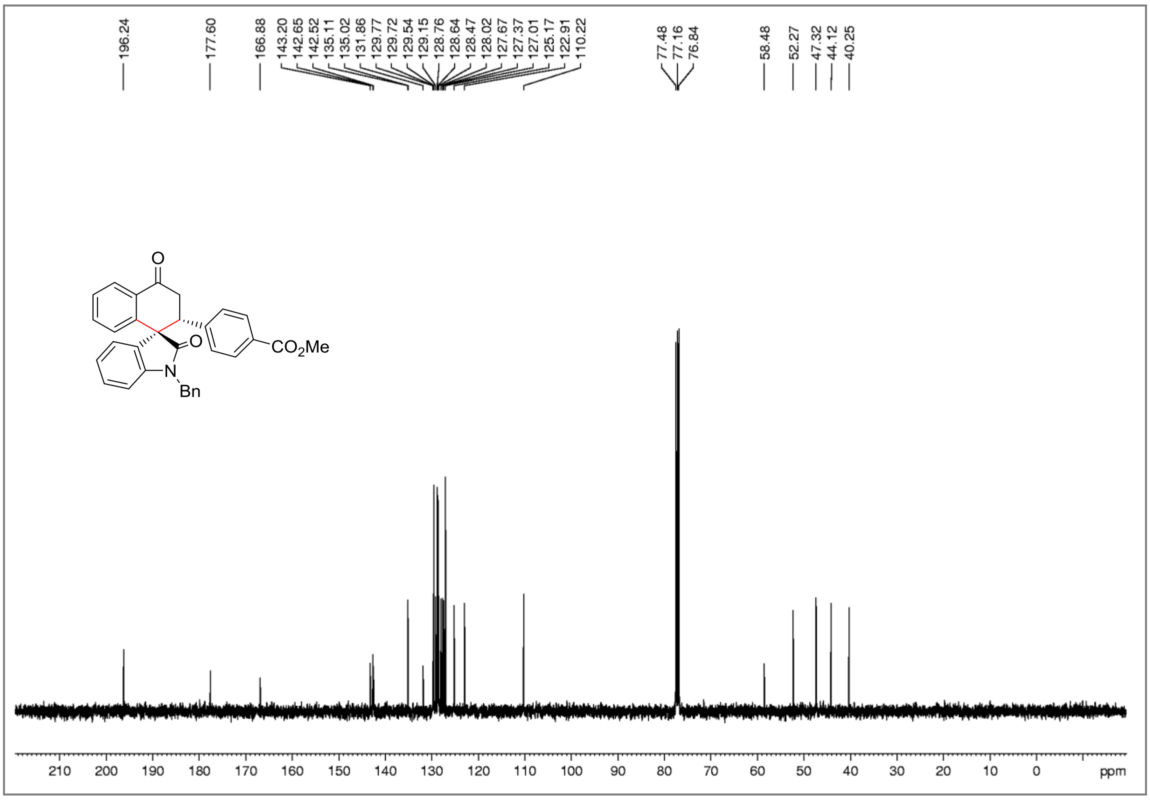


Figure 18: 100 MHz ^{13}C-NMR spectrum of **3i** in $CDCl_3$

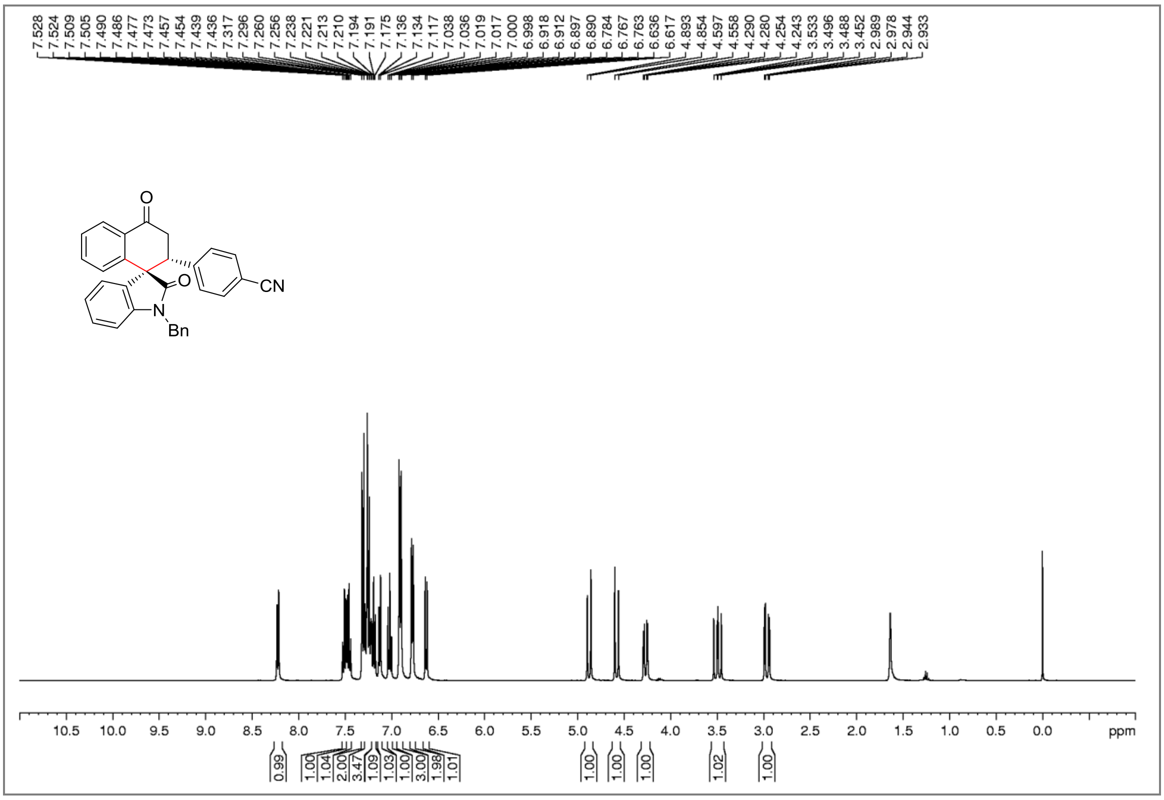


Figure 19: 400 MHz ^{1}H-NMR spectrum of **3j** in $CDCl_3$

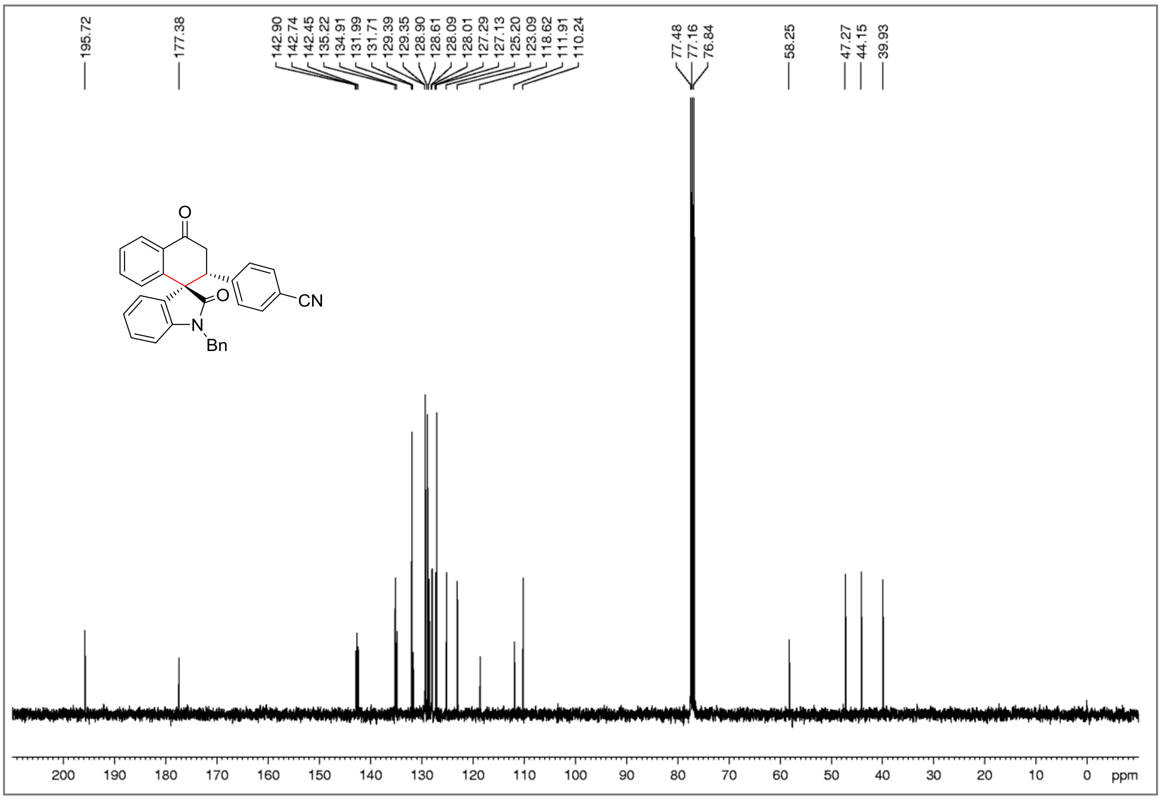


Figure 20: 100 MHz ^{13}C-NMR spectrum of **3j** in $CDCl_3$

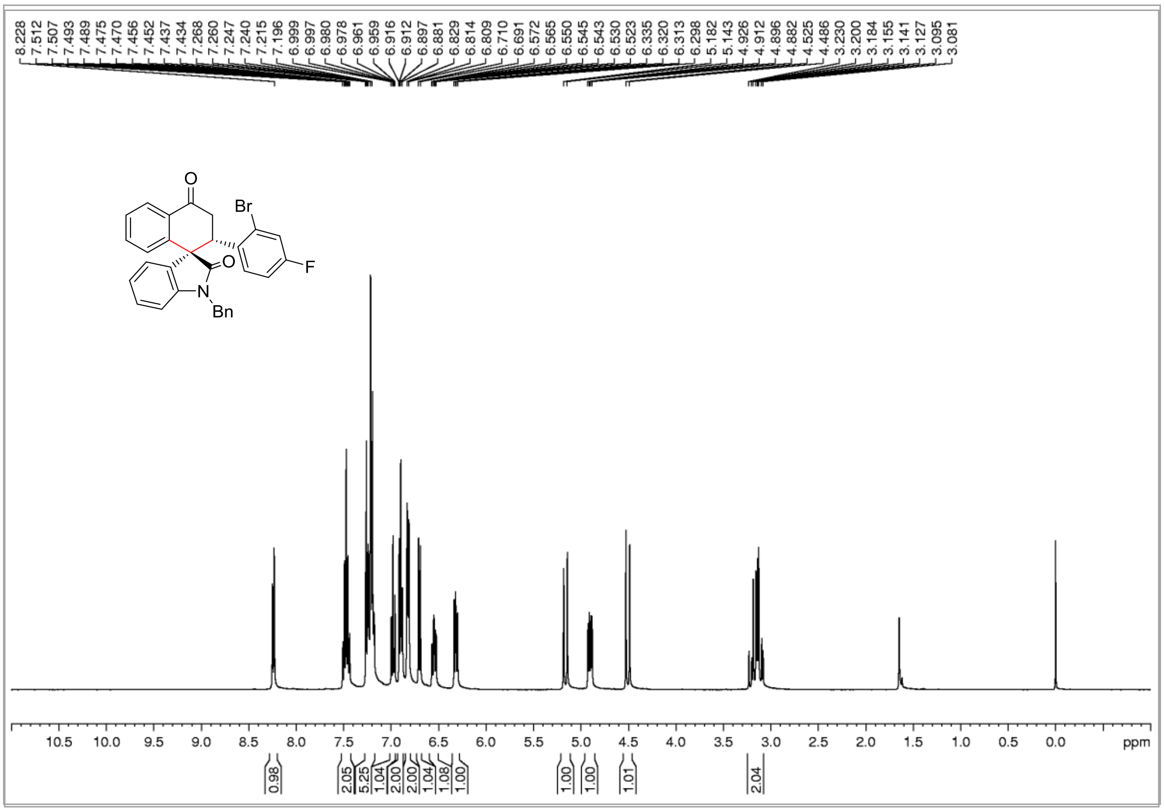


Figure 21: 400 MHz ^{1}H-NMR spectrum of **3k** in $CDCl_3$

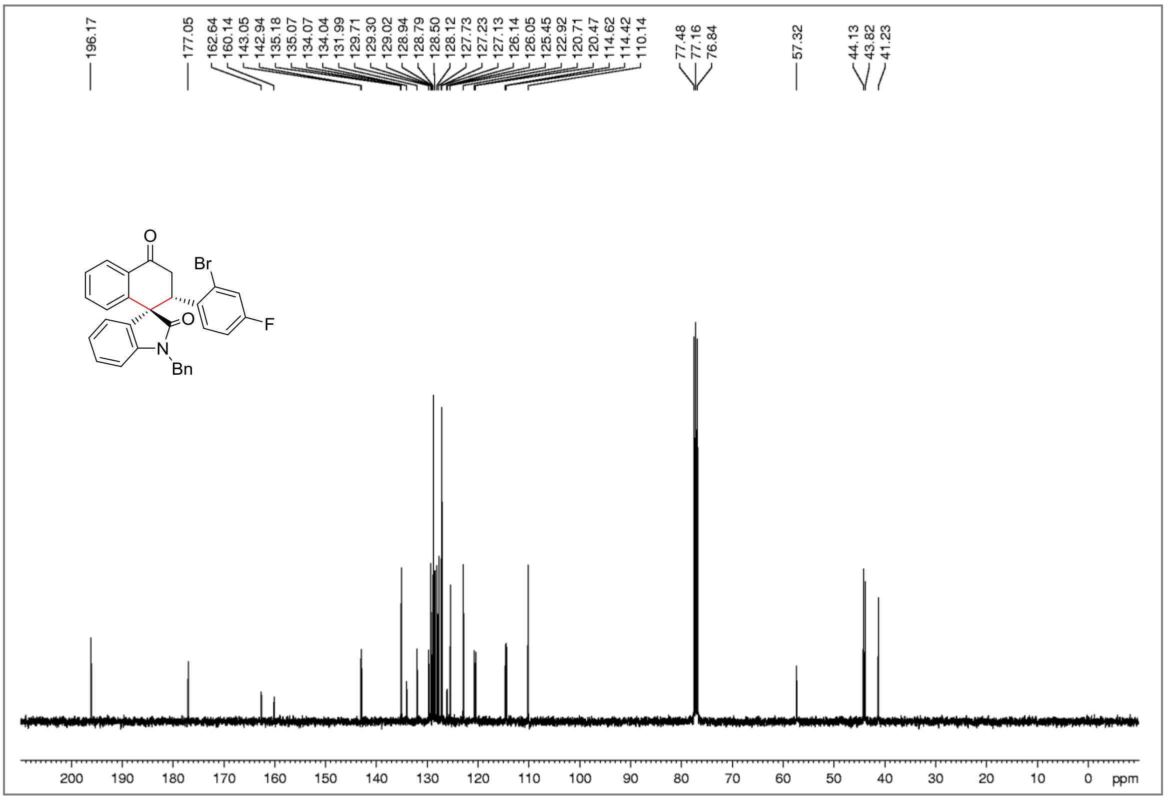


Figure 22: 100 MHz ^{13}C-NMR spectrum of **3k** in $CDCl_3$

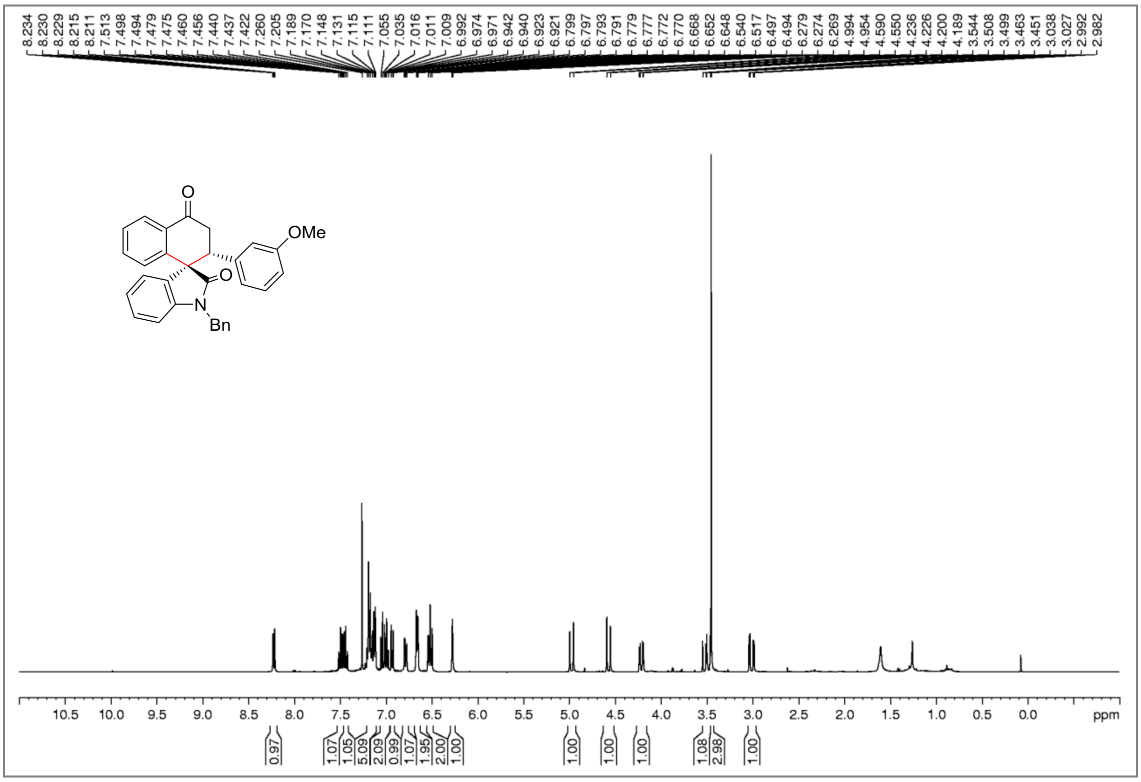


Figure 23: 400 MHz ^{1}H-NMR spectrum of **3l** in $CDCl_3$

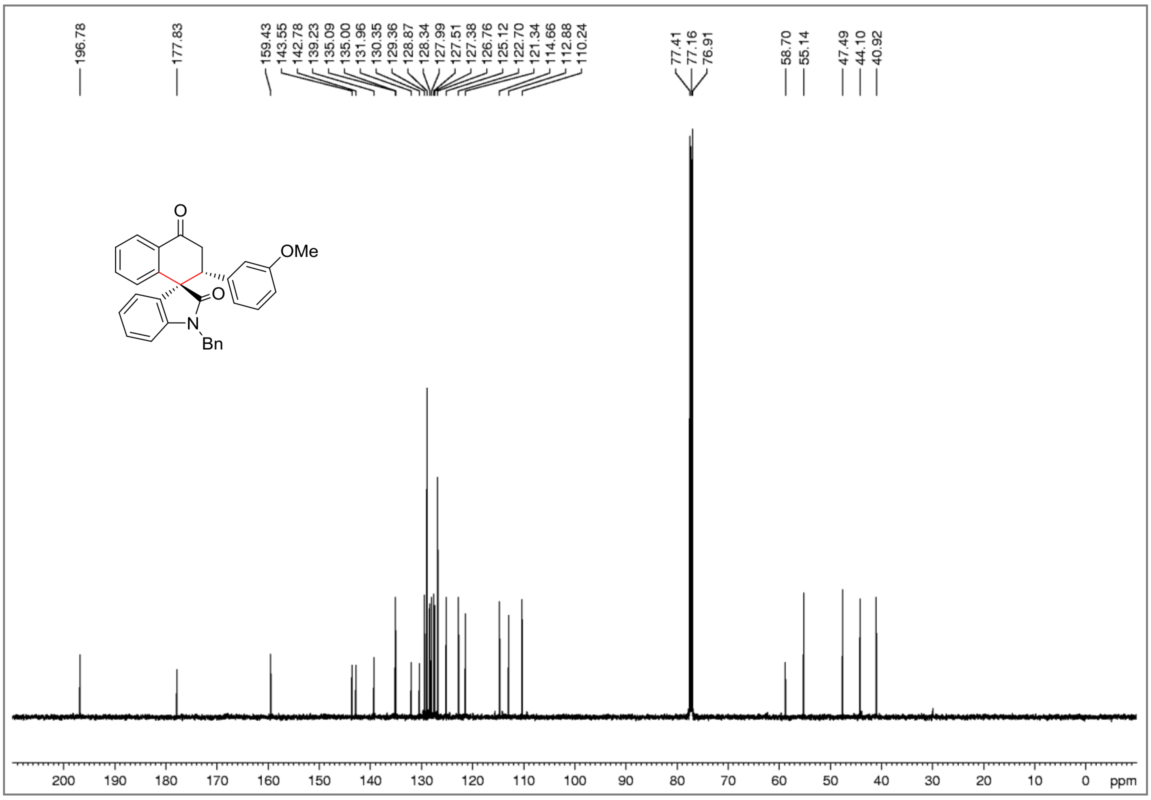


Figure 24: 125 MHz ^{13}C-NMR spectrum of **3l** in $CDCl_3$

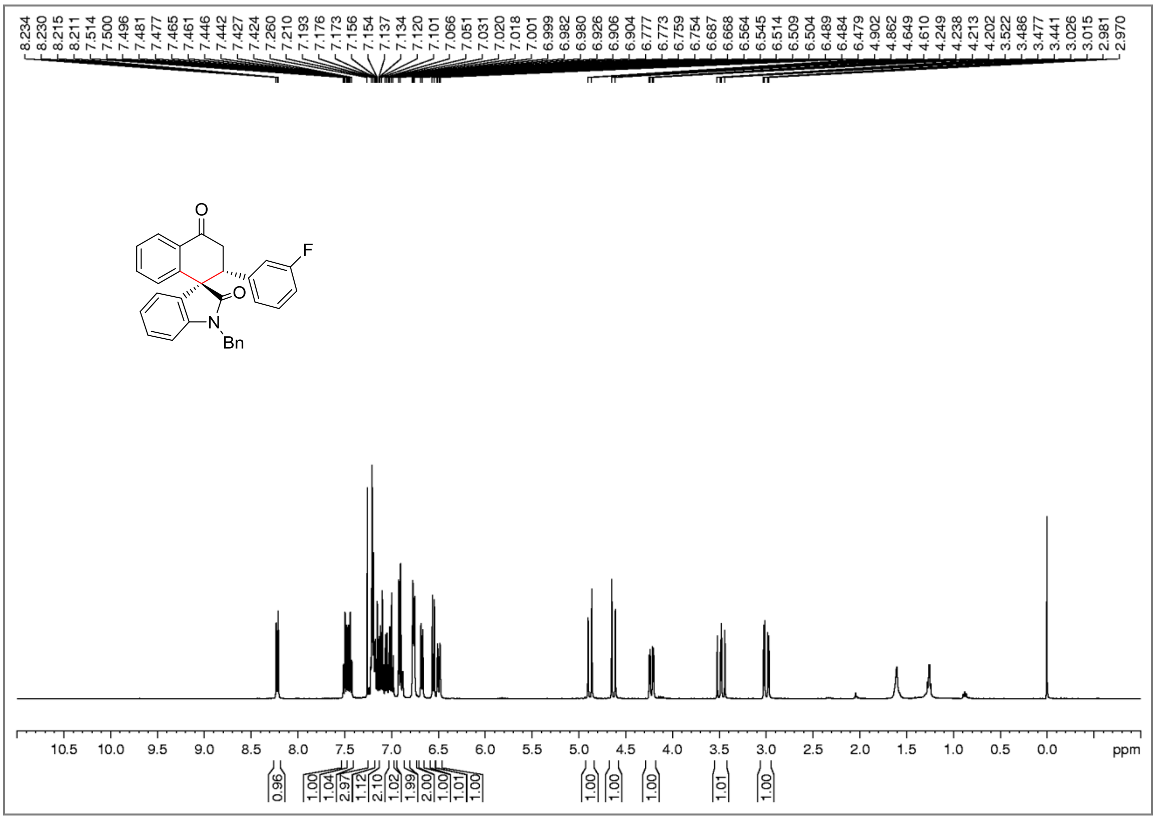


Figure 25: 400 MHz ^{1}H-NMR spectrum of **3m** in $CDCl_3$

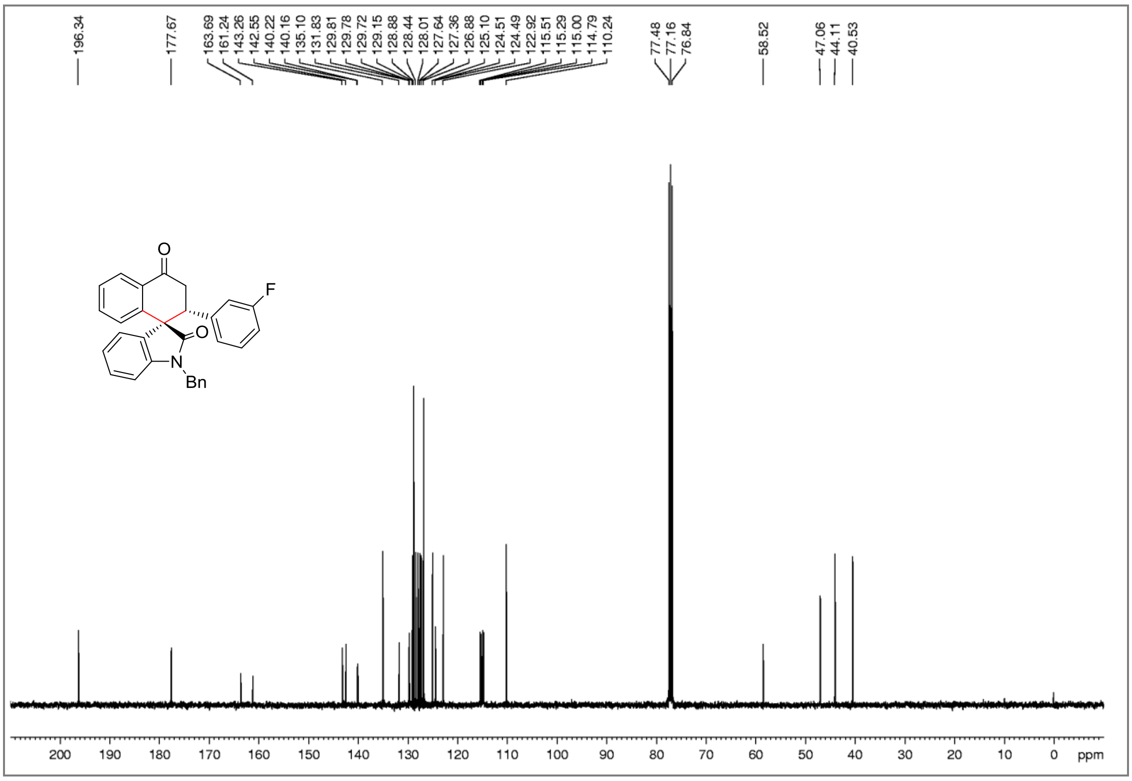


Figure 26: 100 MHz ^{13}C-NMR spectrum of **3m** in $CDCl_3$

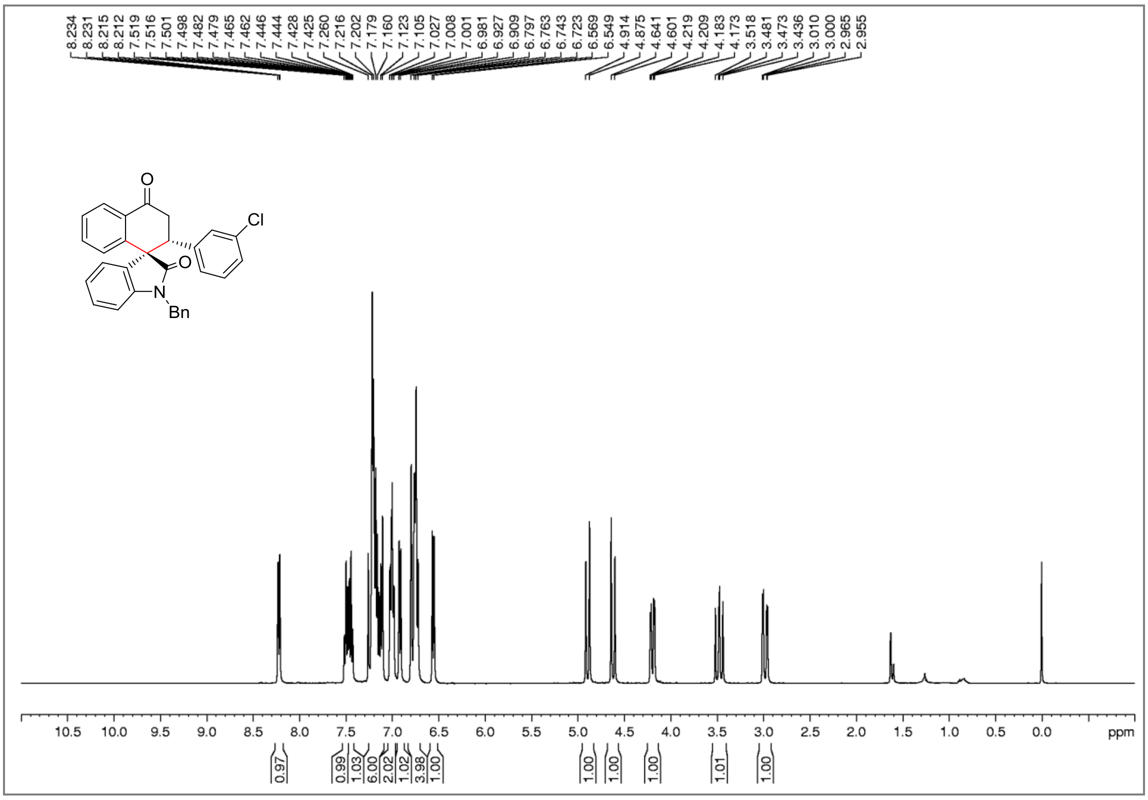


Figure 27: 400 MHz ^{1}H-NMR spectrum of **3n** in $CDCl_3$

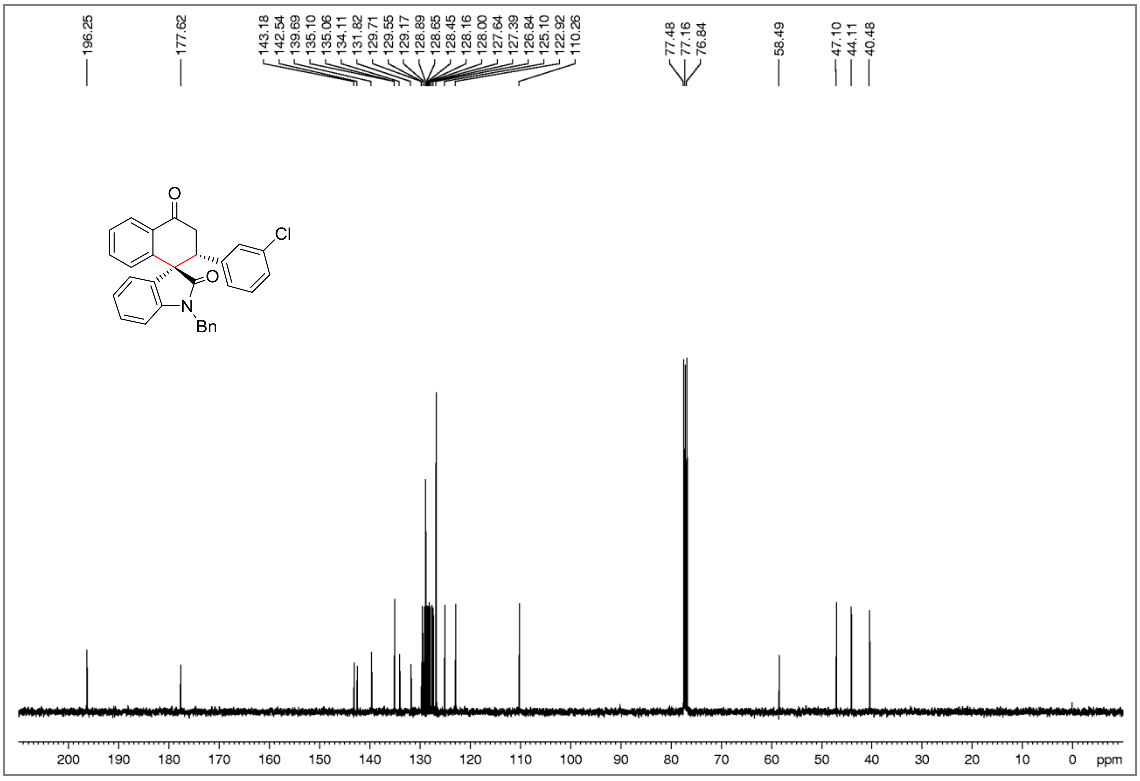


Figure 28: 100 MHz ^{13}C-NMR spectrum of **3n** in $CDCl_3$

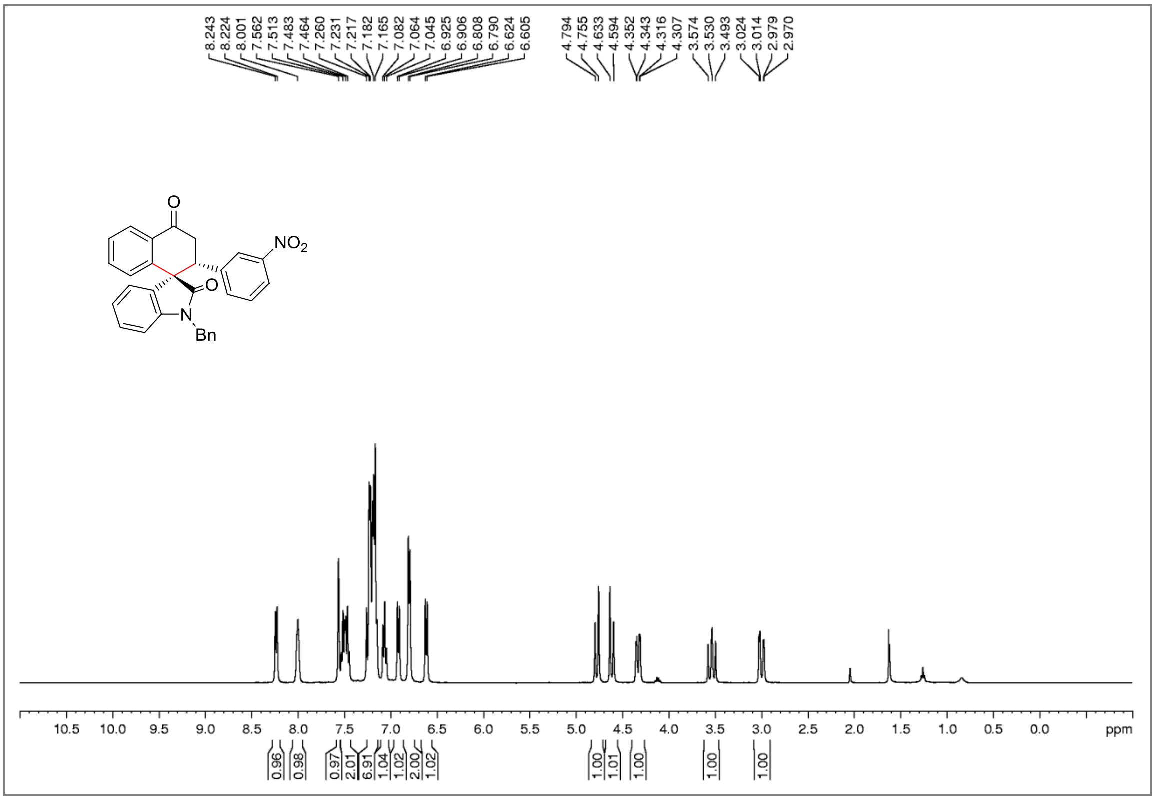


Figure 29: 400 MHz ^{1}H-NMR spectrum of **3o** in $CDCl_3$

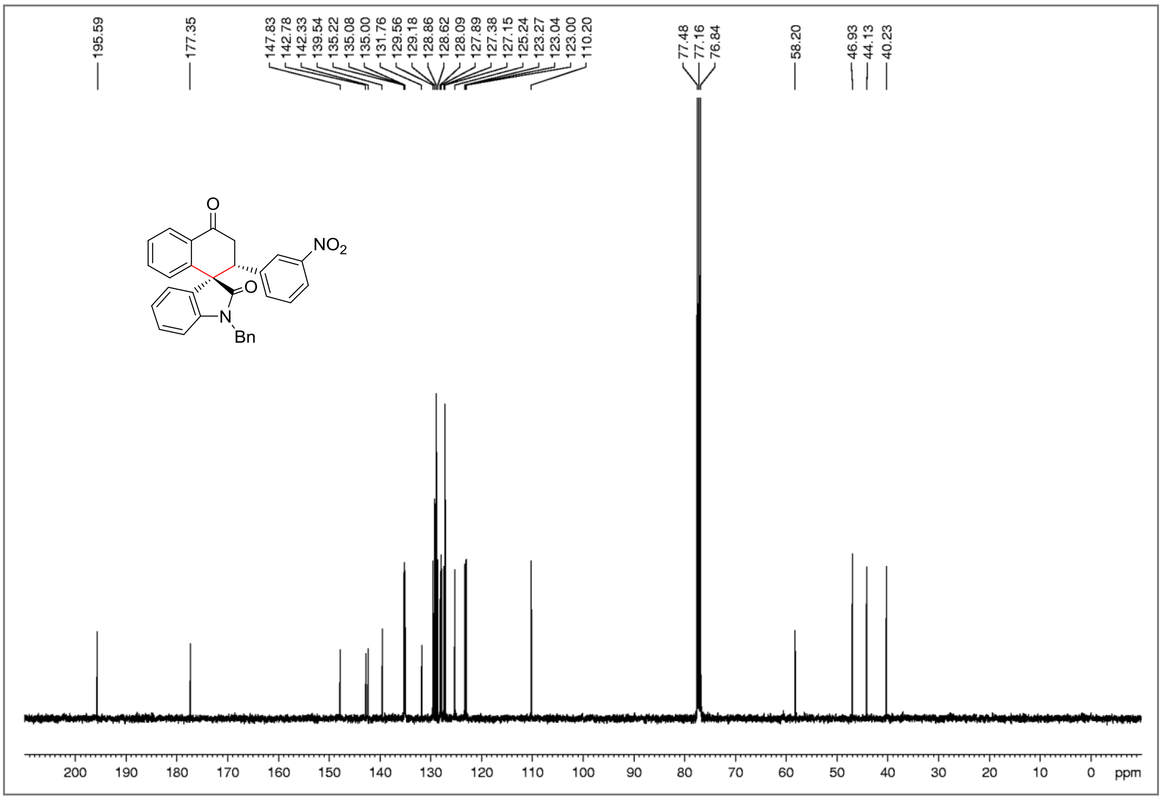


Figure 30: 100 MHz ^{13}C-NMR spectrum of **3o** in $CDCl_3$

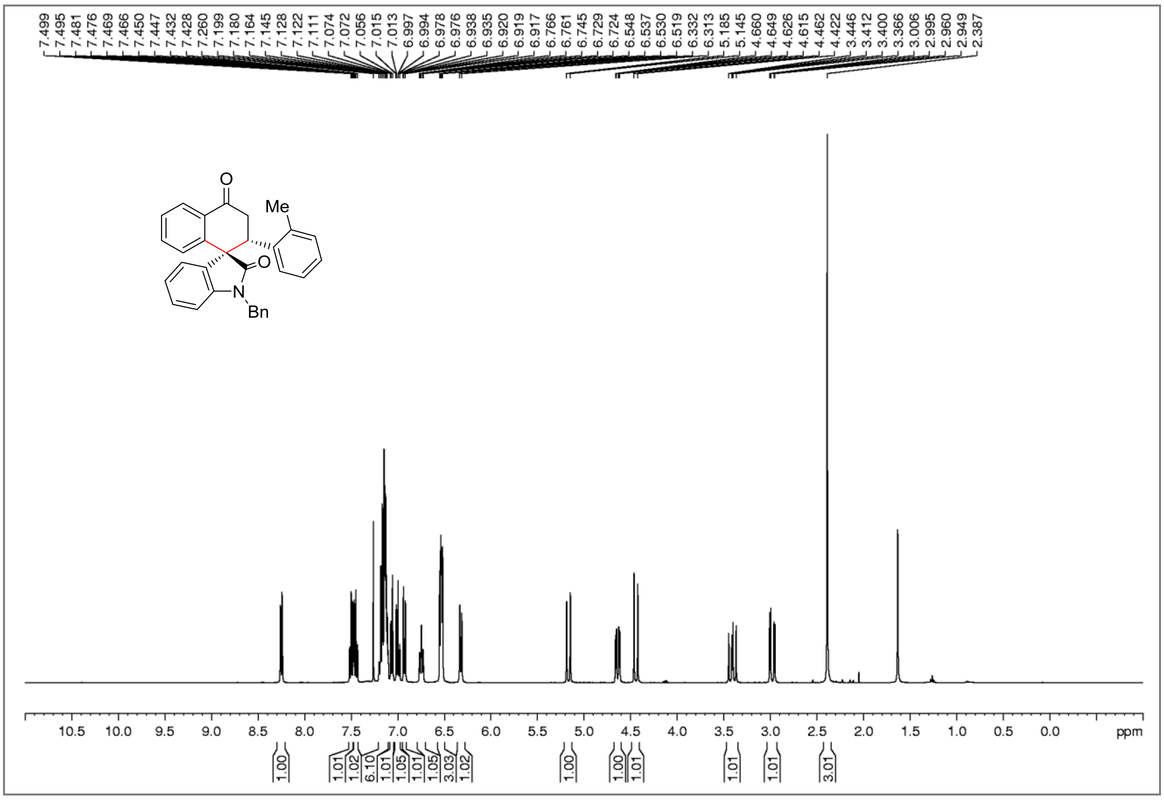


Figure 31: 400 MHz ^{1}H-NMR spectrum of **3p** in $CDCl_3$

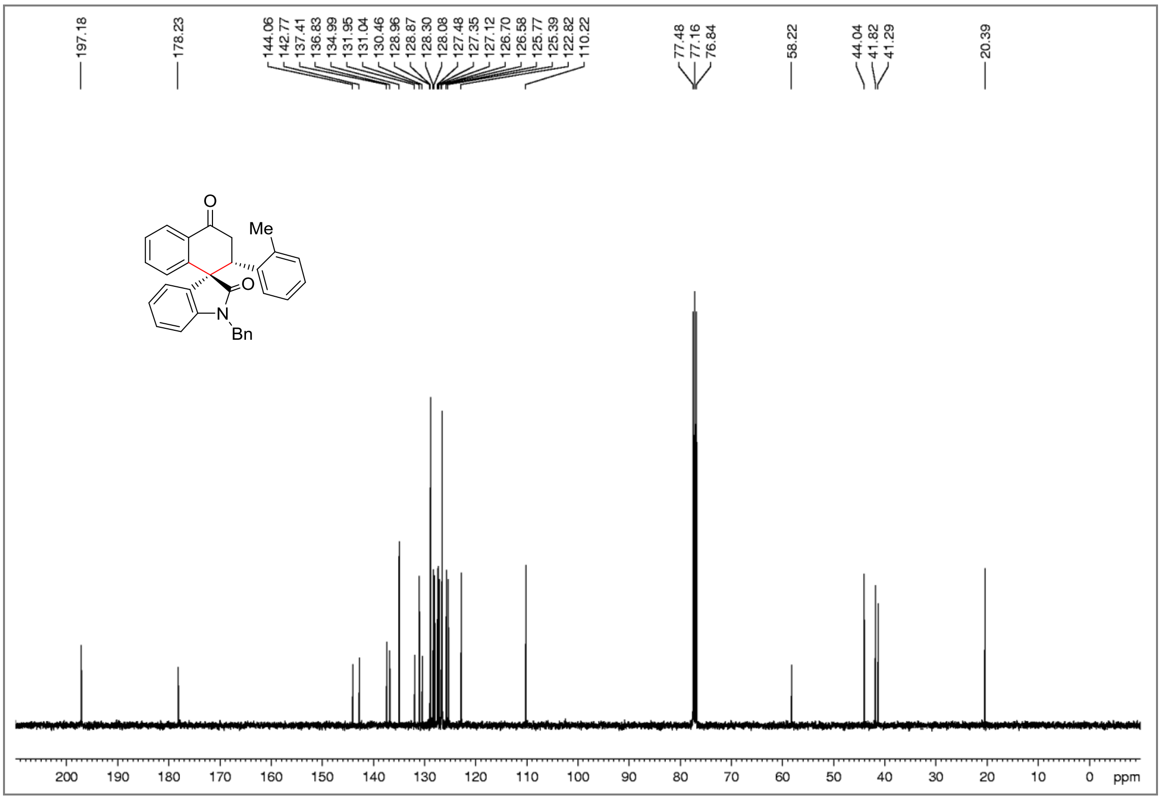


Figure 32: 100 MHz ^{13}C-NMR spectrum of **3p** in $CDCl_3$

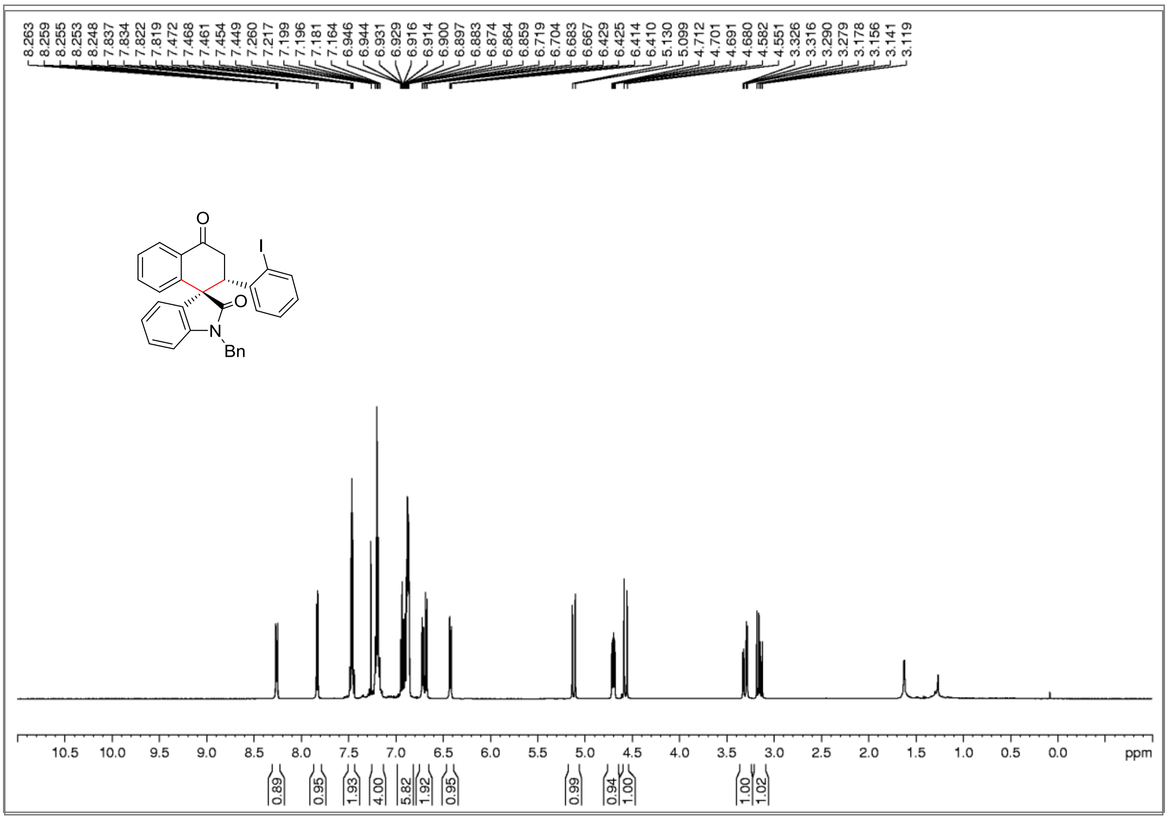


Figure 33: 500 MHz ^{1}H-NMR spectrum of **3q** in $CDCl_3$

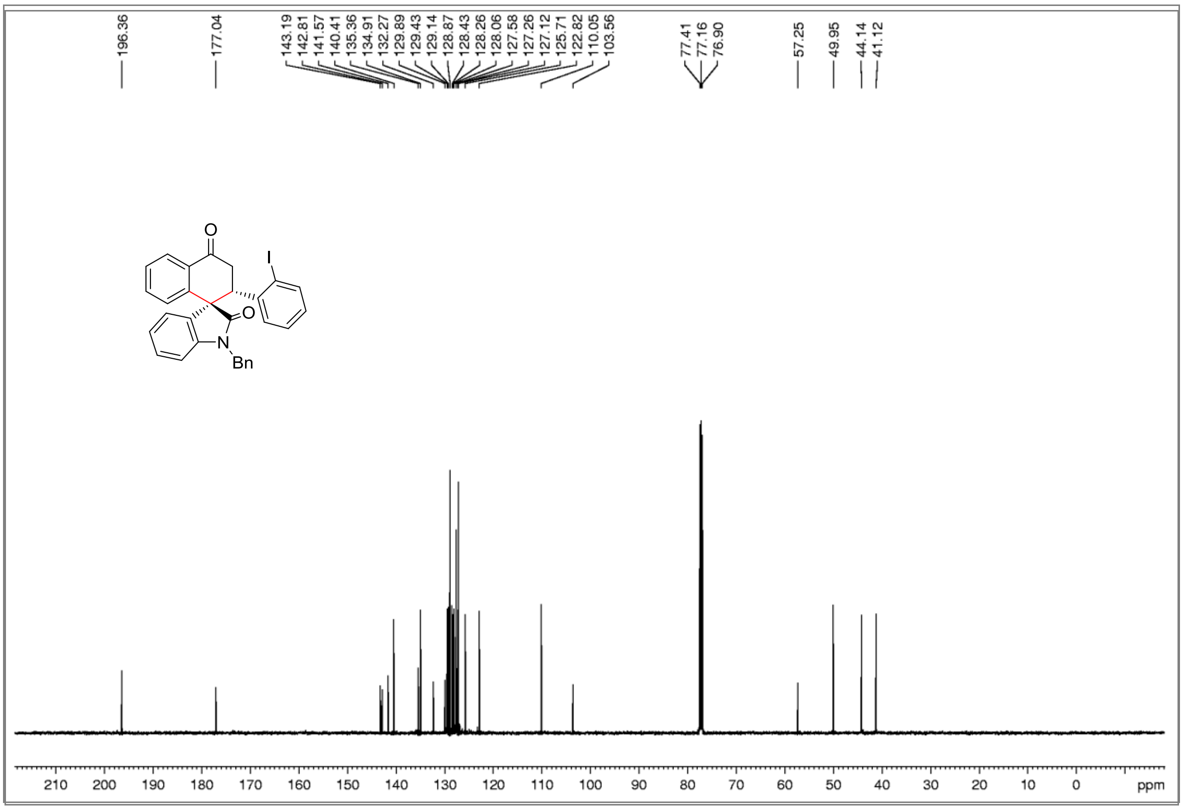


Figure 34: 125 MHz ^{13}C-NMR spectrum of **3q** in $CDCl_3$

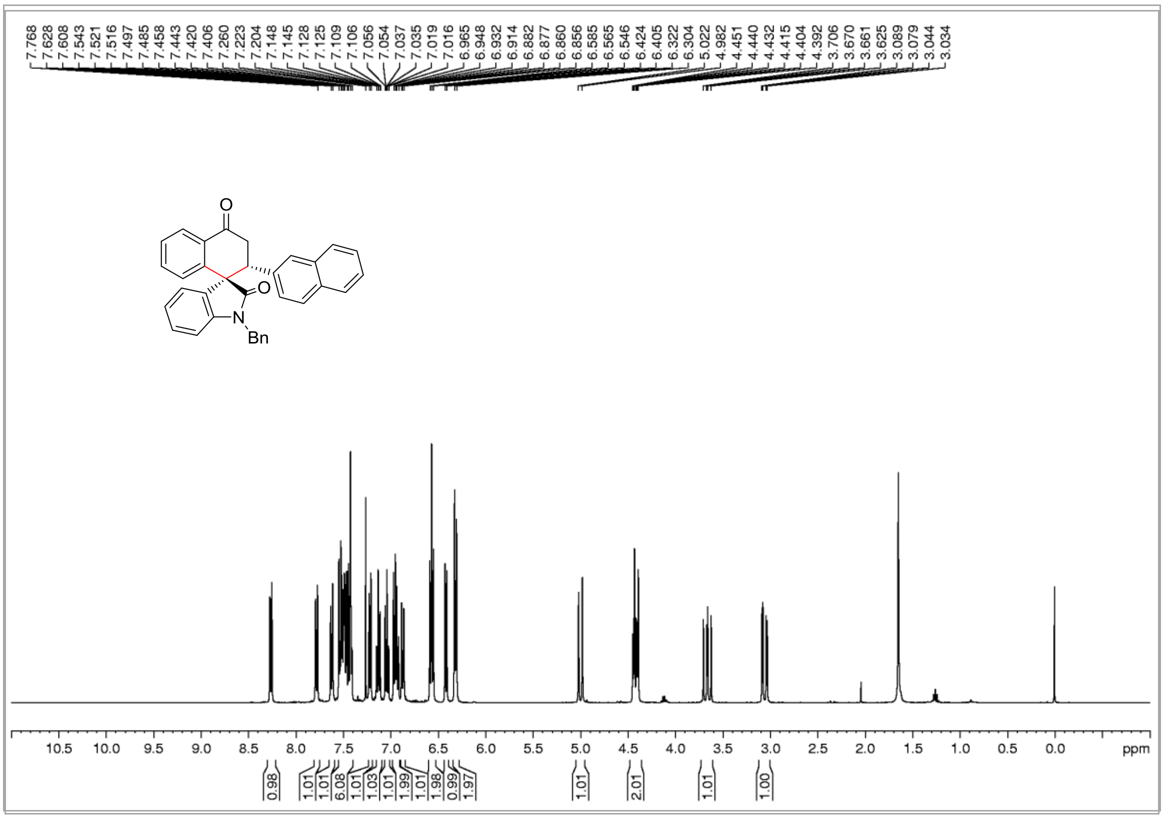


Figure 35: 400 MHz ^{1}H-NMR spectrum of **3r** in $CDCl_3$

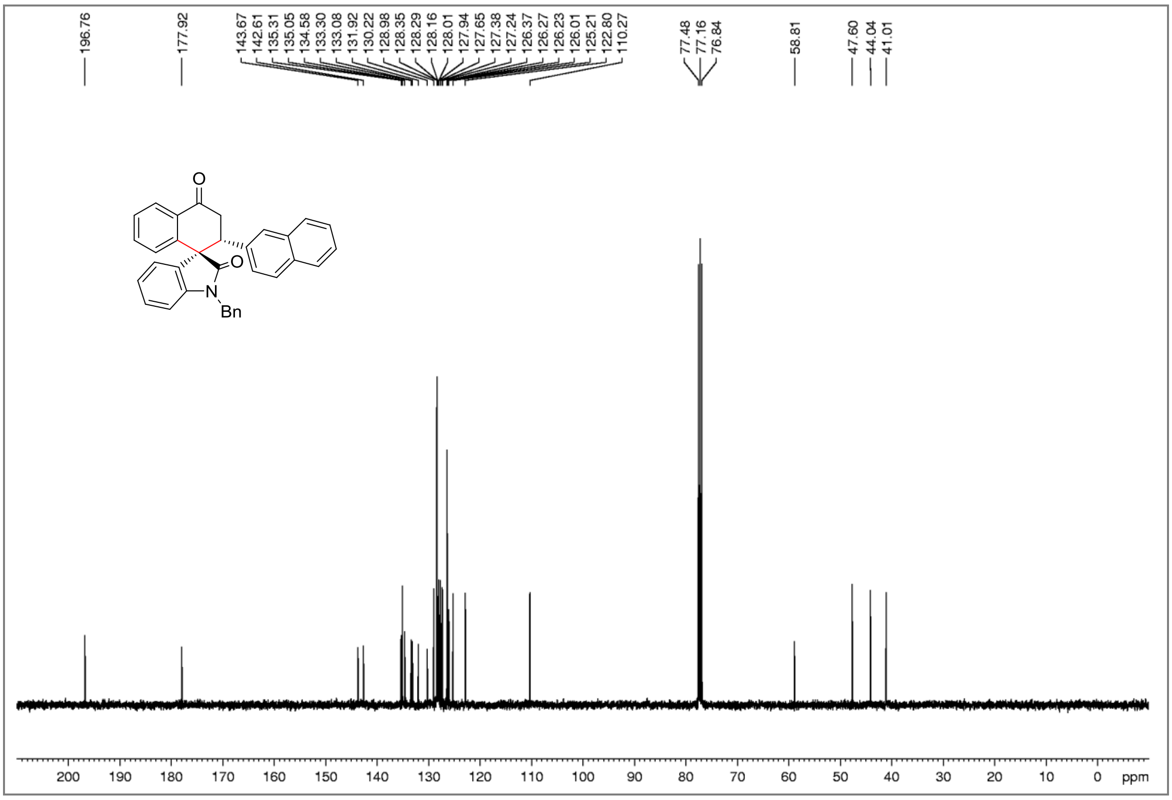


Figure 36: 100 MHz ^{13}C-NMR spectrum of **3r** in $CDCl_3$

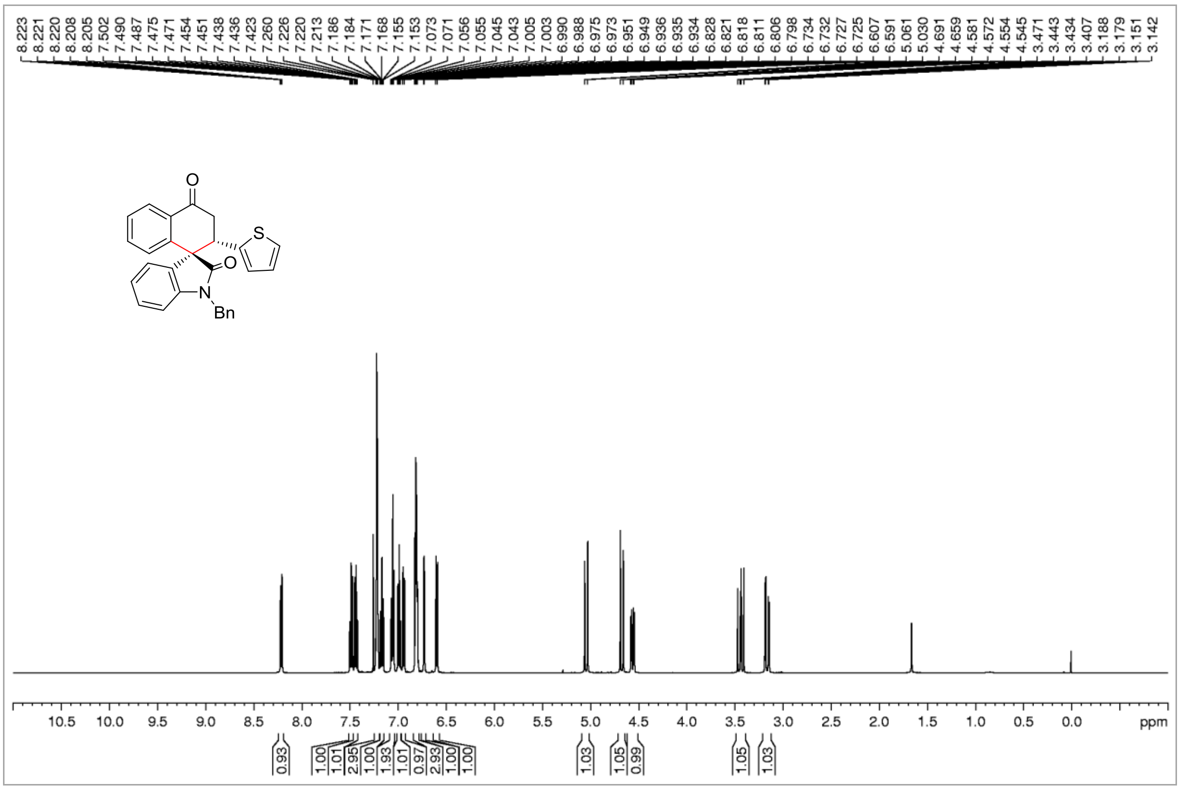


Figure 37: 500 MHz ^{1}H-NMR spectrum of **3s** in $CDCl_3$

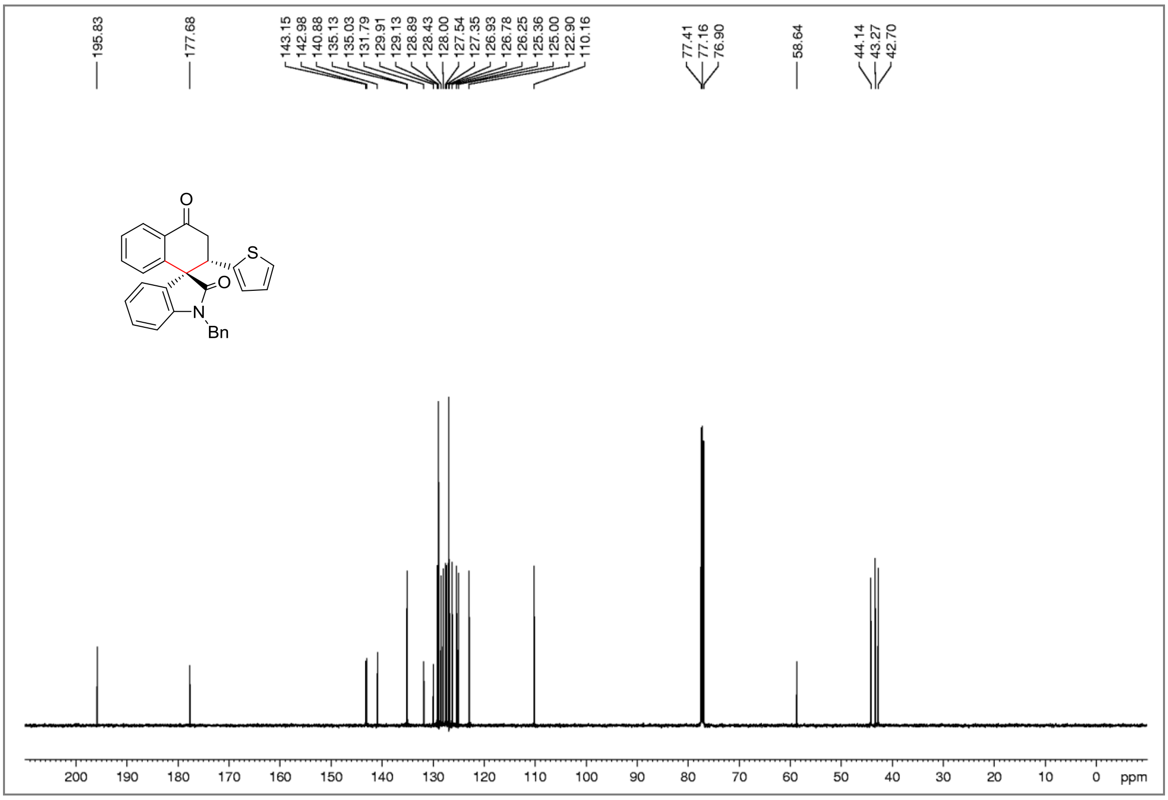


Figure 38: 125 MHz ^{13}C-NMR spectrum of **3s** in $CDCl_3$

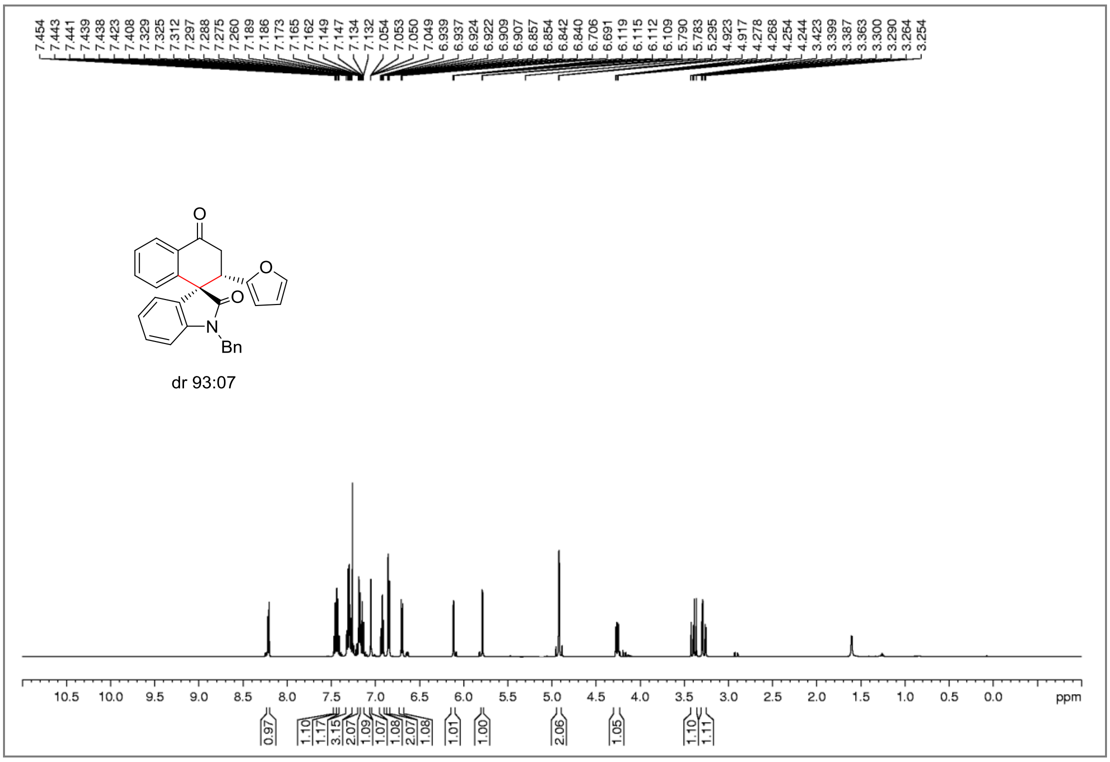


Figure 39: 500 MHz ^{1}H-NMR spectrum of **3t** in $CDCl_3$

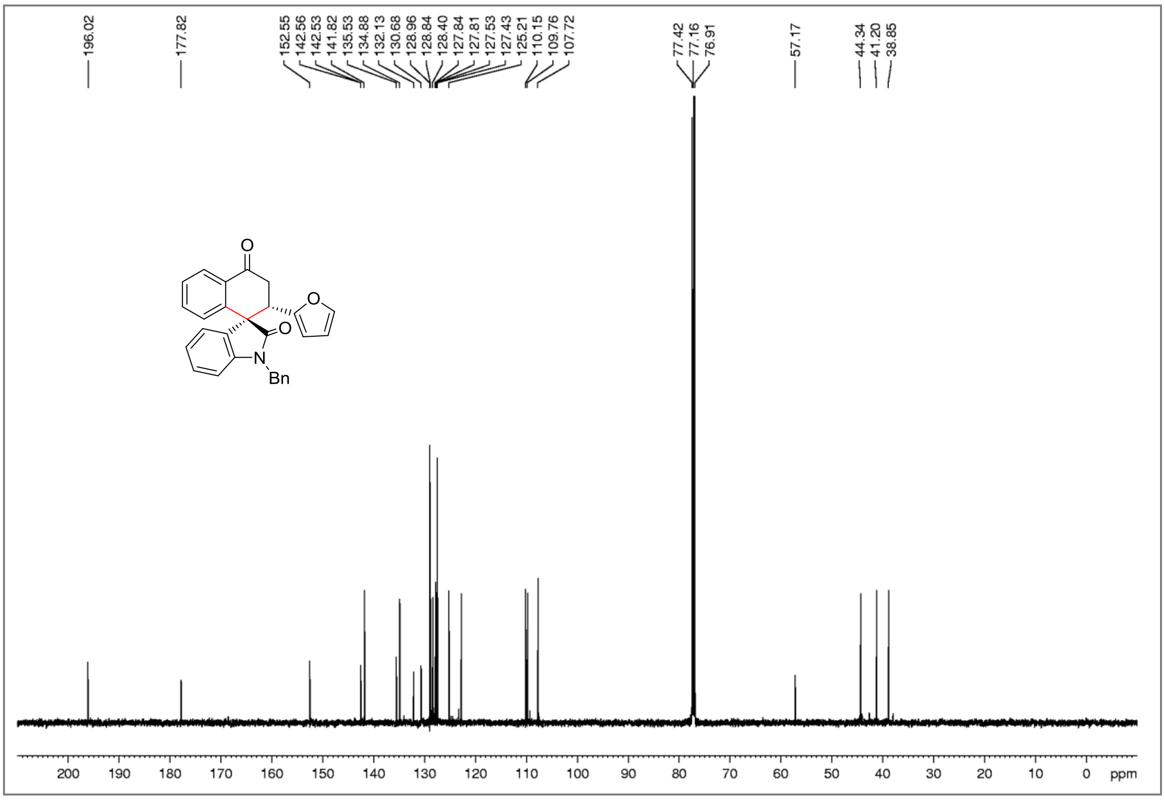


Figure 40: 125 MHz ^{13}C-NMR spectrum of **3t** in $CDCl_3$

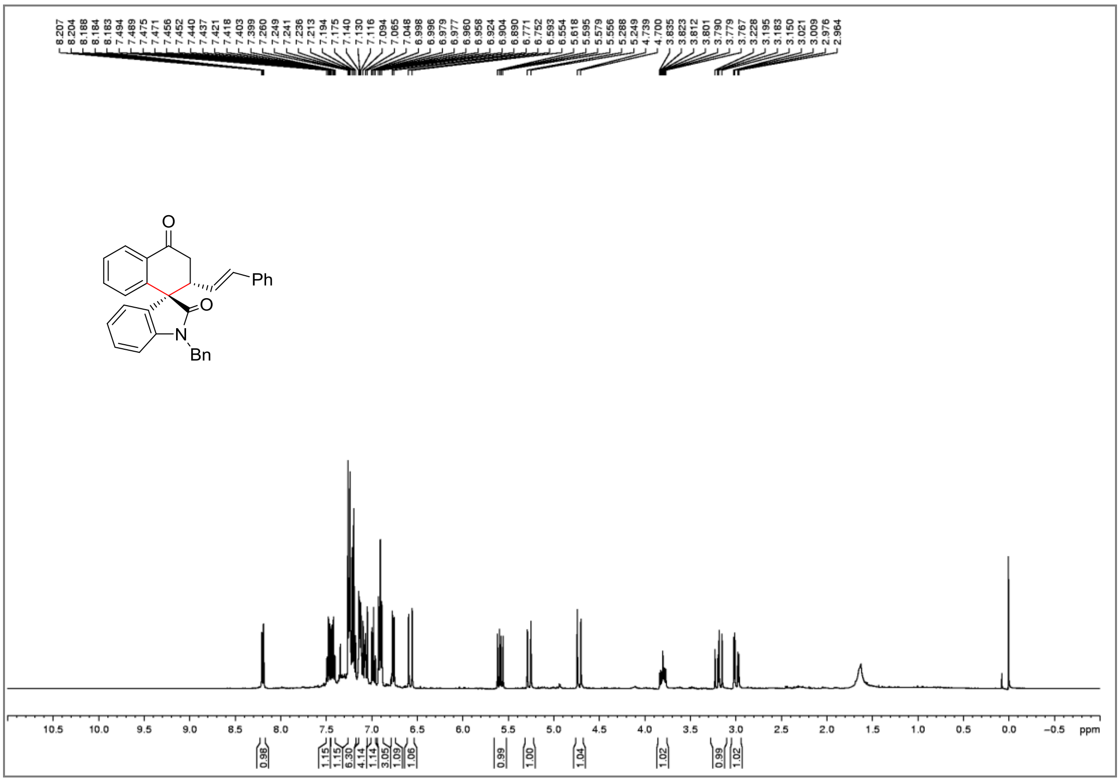


Figure 41: 400 MHz ^{1}H-NMR spectrum of **3u** in $CDCl_3$

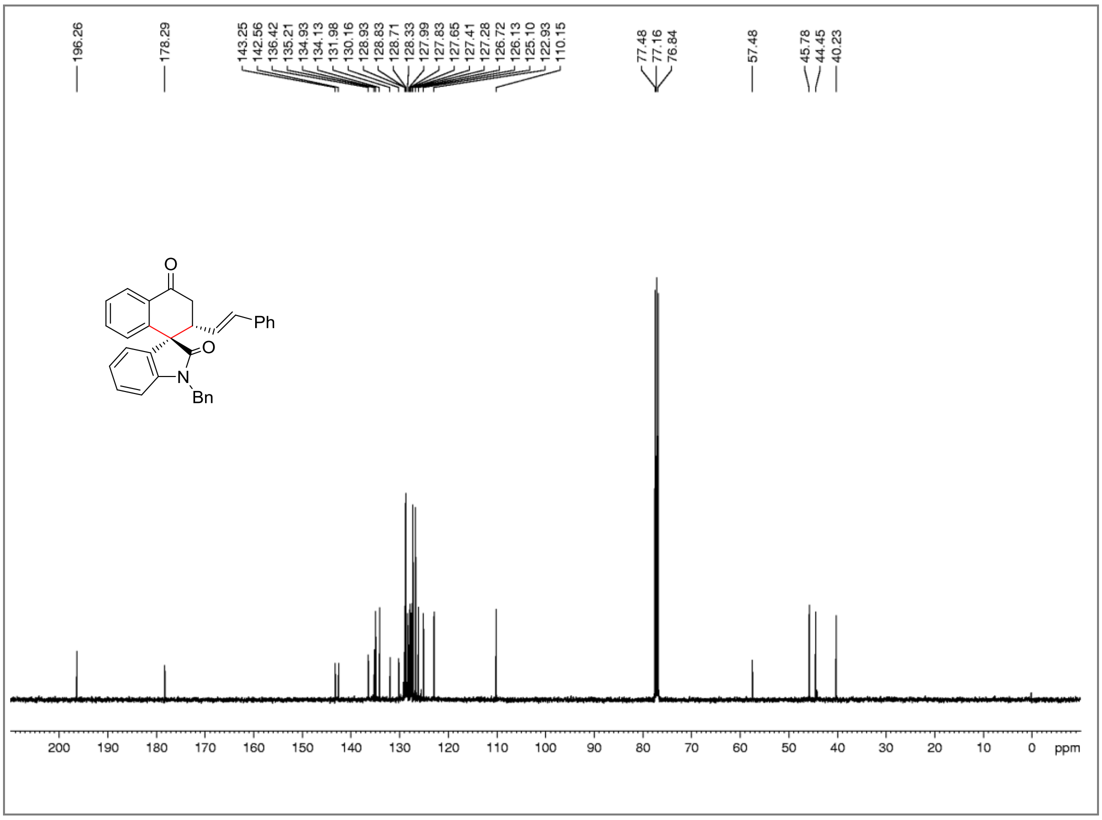


Figure 42: 100 MHz ^{13}C-NMR spectrum of **3u** in $CDCl_3$

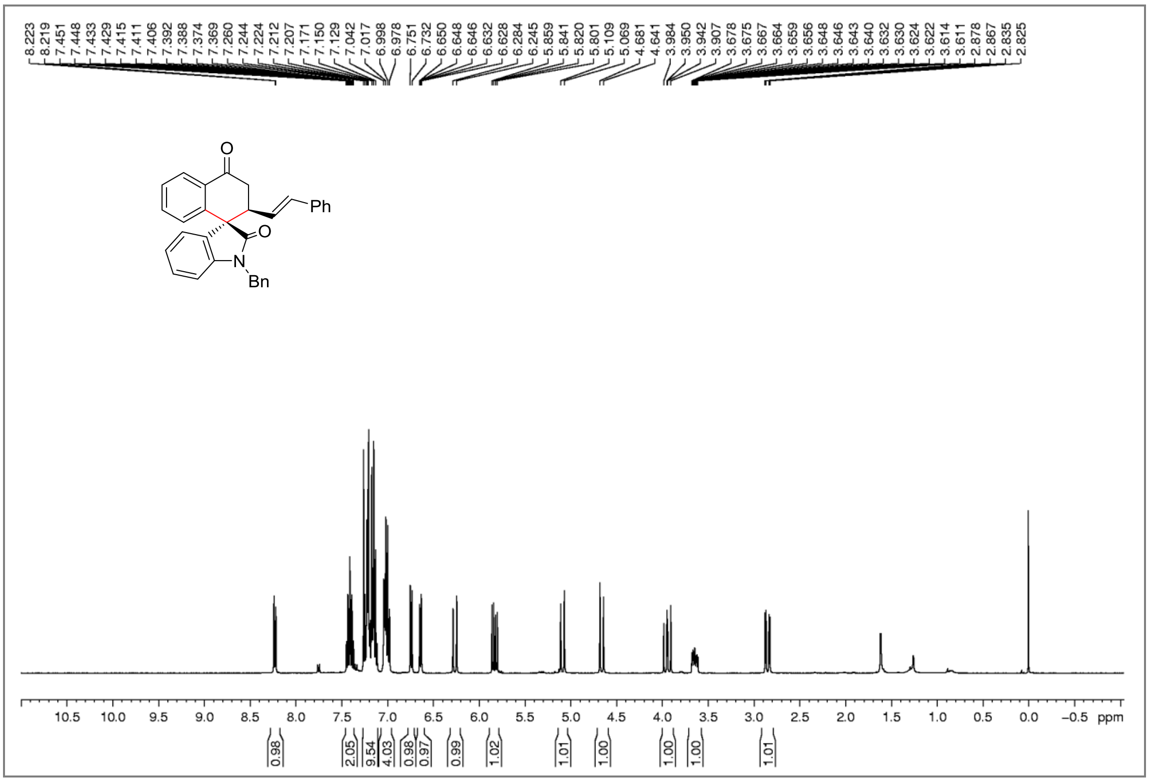


Figure 43: 400 MHz ^{1}H-NMR spectrum of **3u'** in $CDCl_3$

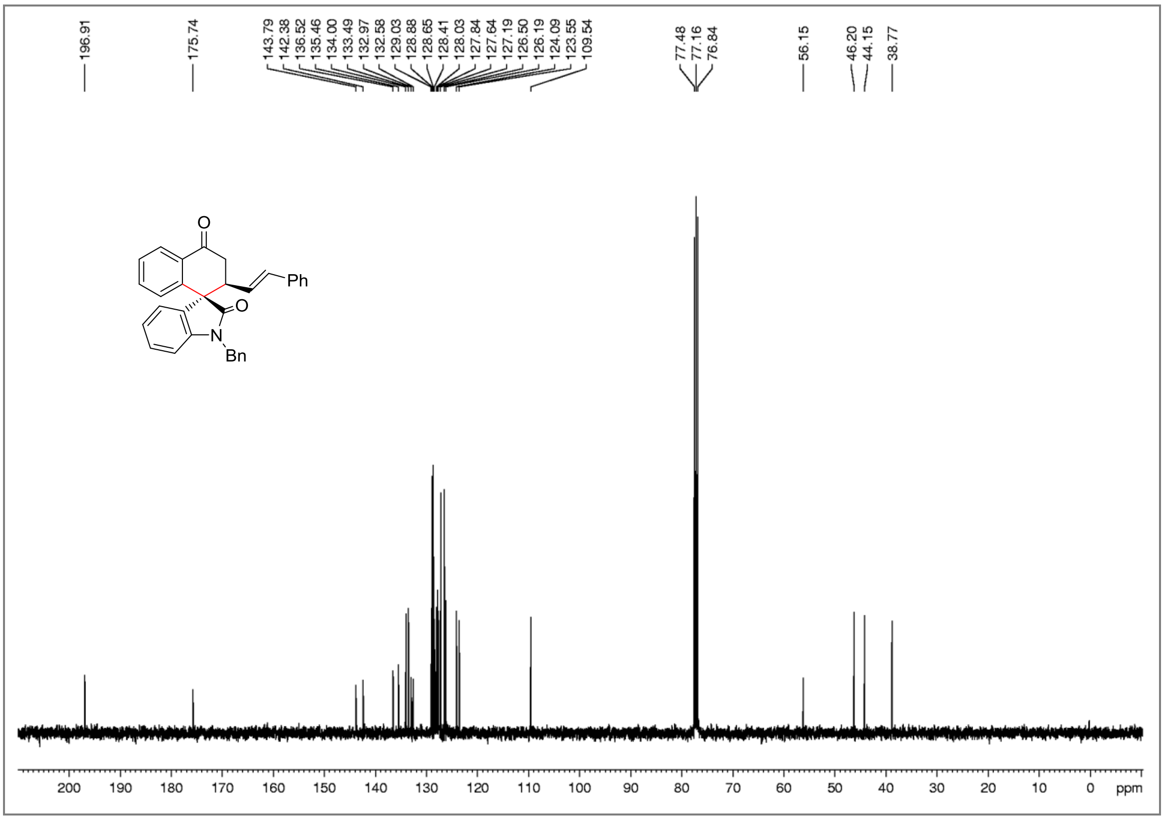


Figure 44: 100 MHz ^{13}C-NMR spectrum of **3u'** in $CDCl_3$

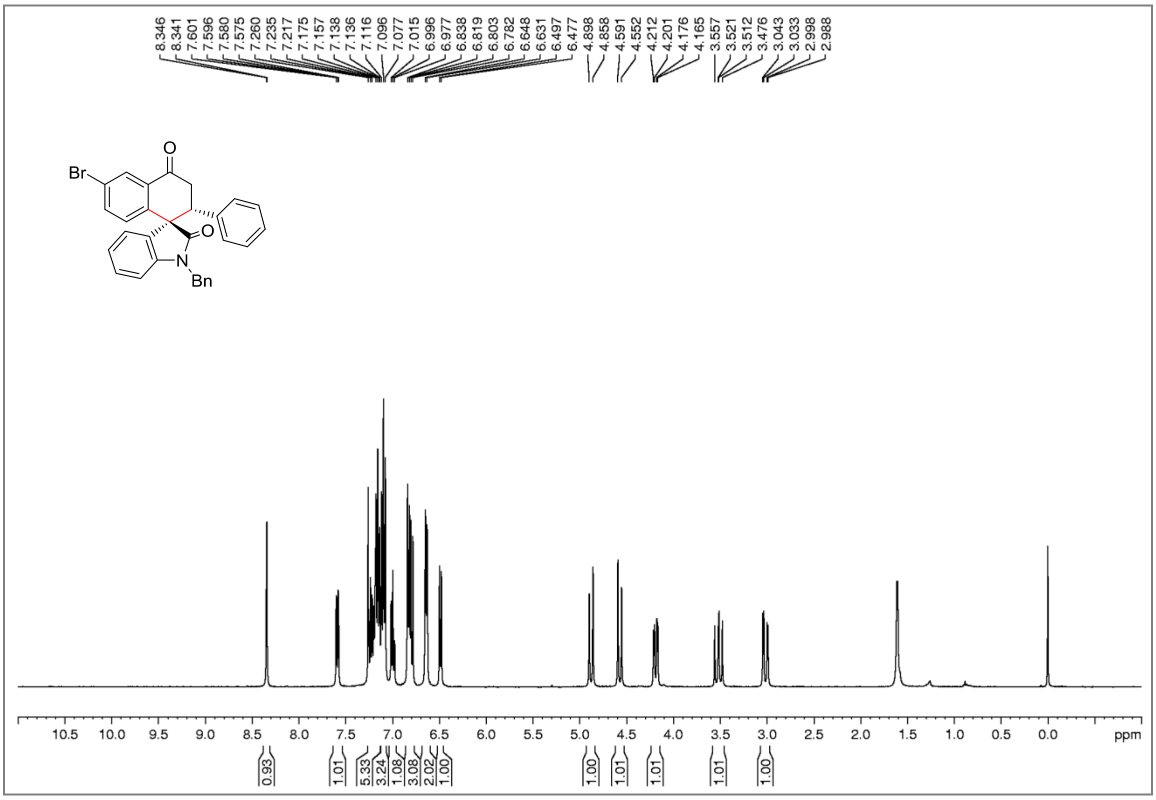


Figure 45: 400 MHz ^{1}H-NMR spectrum of **3v** in $CDCl_3$

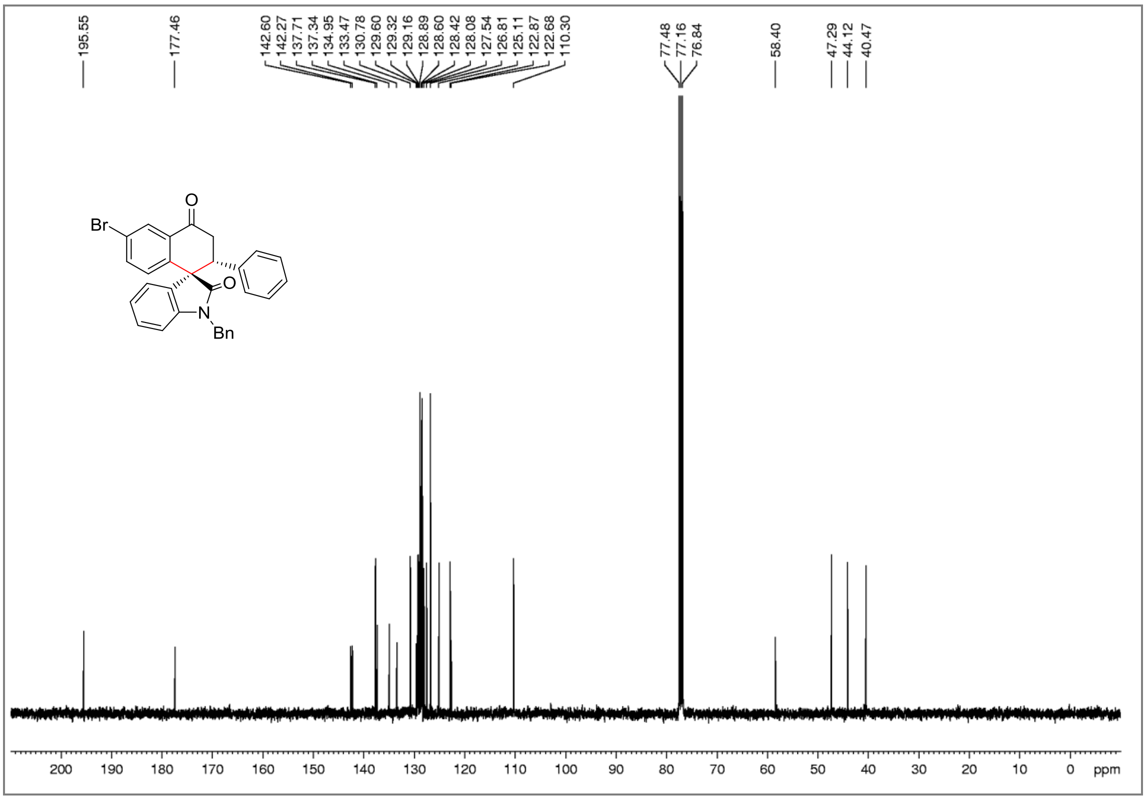


Figure 46: 100 MHz ^{13}C-NMR spectrum of **3v** in $CDCl_3$

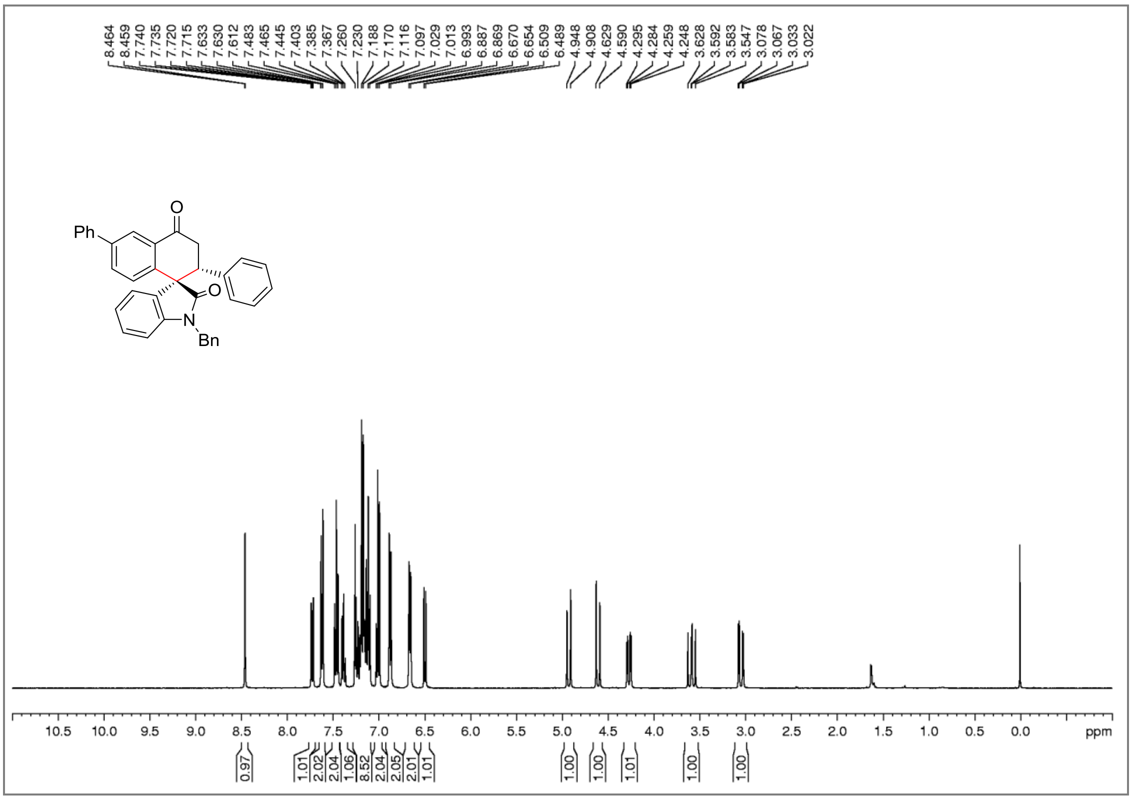


Figure 47: 400 MHz ^{1}H-NMR spectrum of **3w** in $CDCl_3$

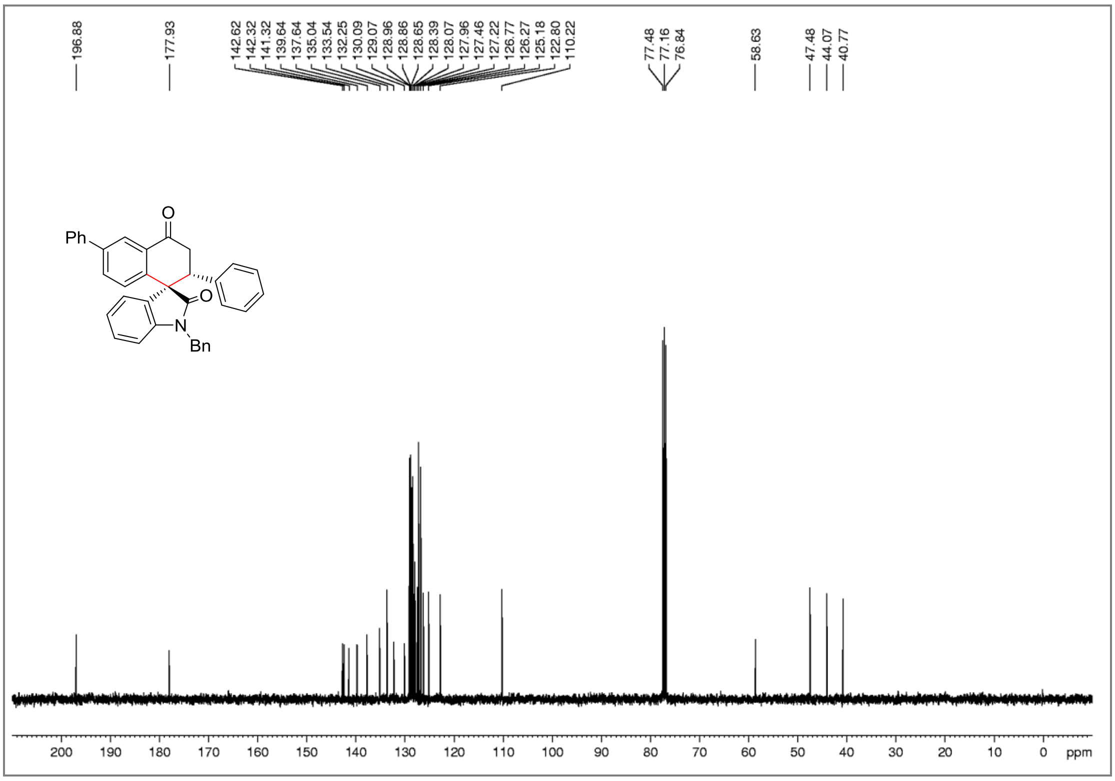


Figure 48: 100 MHz ^{13}C-NMR spectrum of **3w** in $CDCl_3$

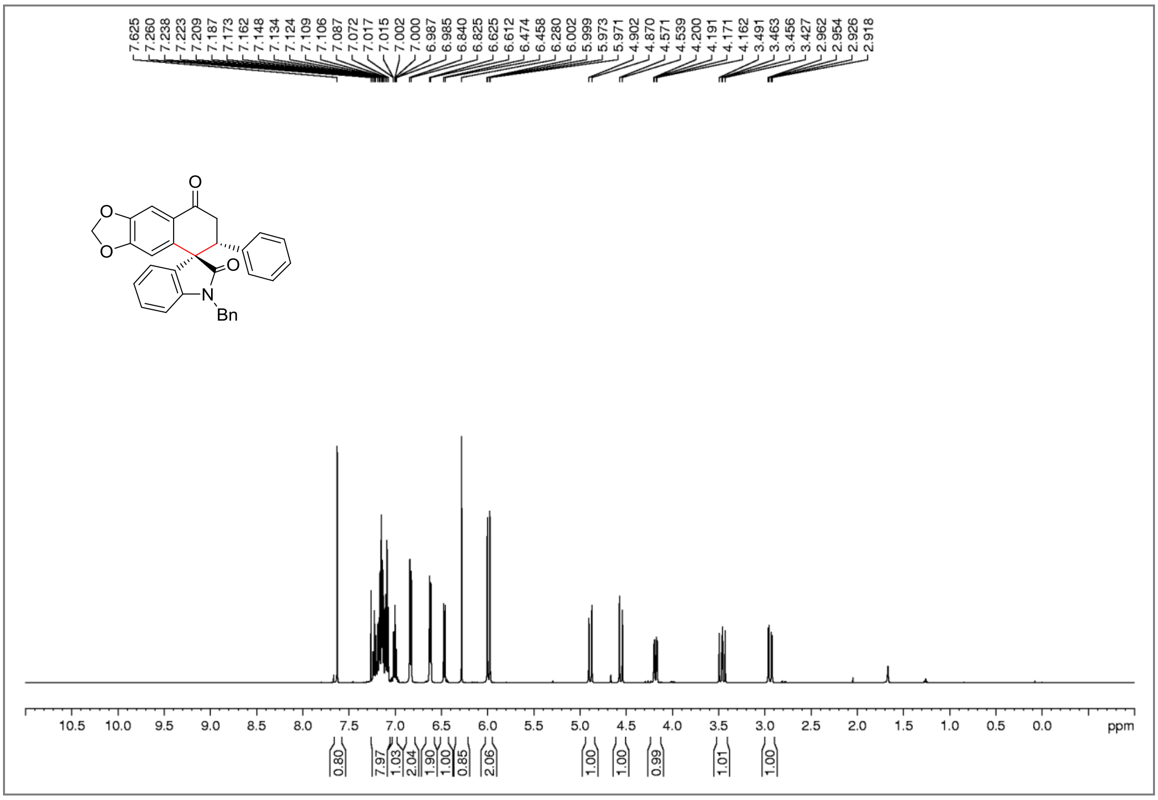


Figure 49: 500 MHz ^{1}H-NMR spectrum of **3x** in $CDCl_3$

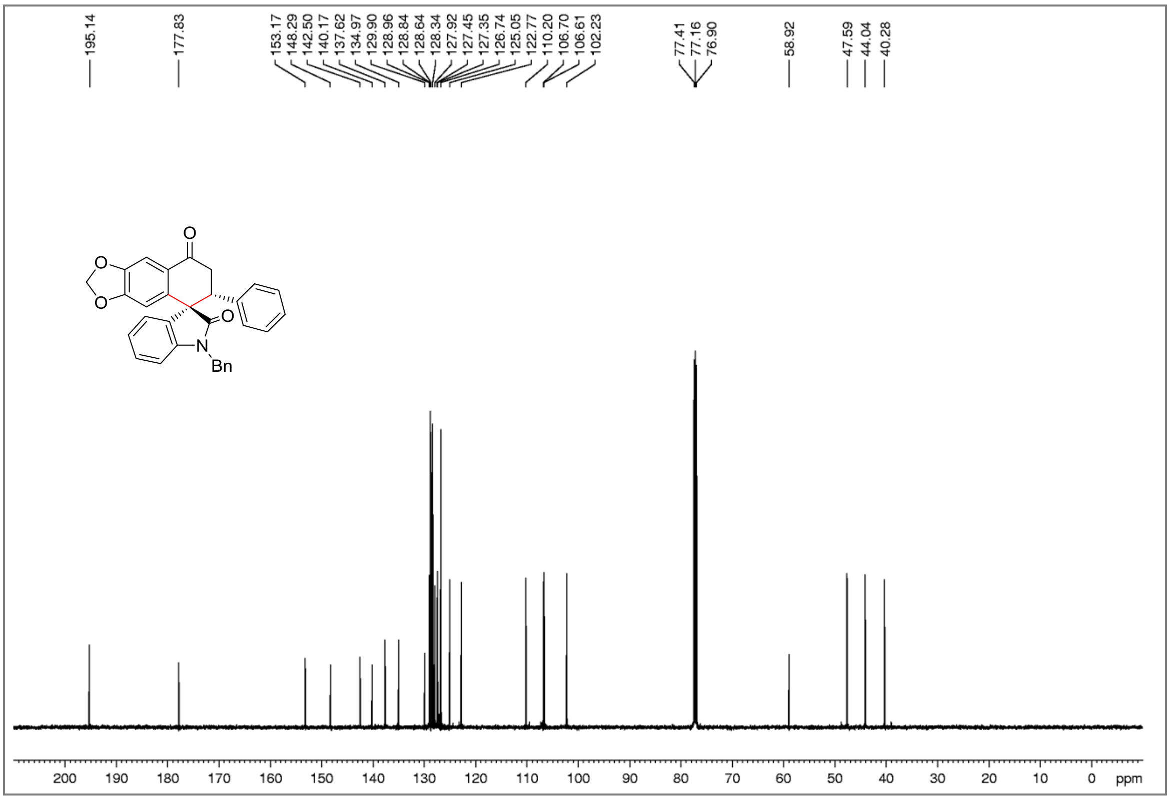


Figure 50: 125 MHz ^{13}C-NMR spectrum of **3x** in $CDCl_3$

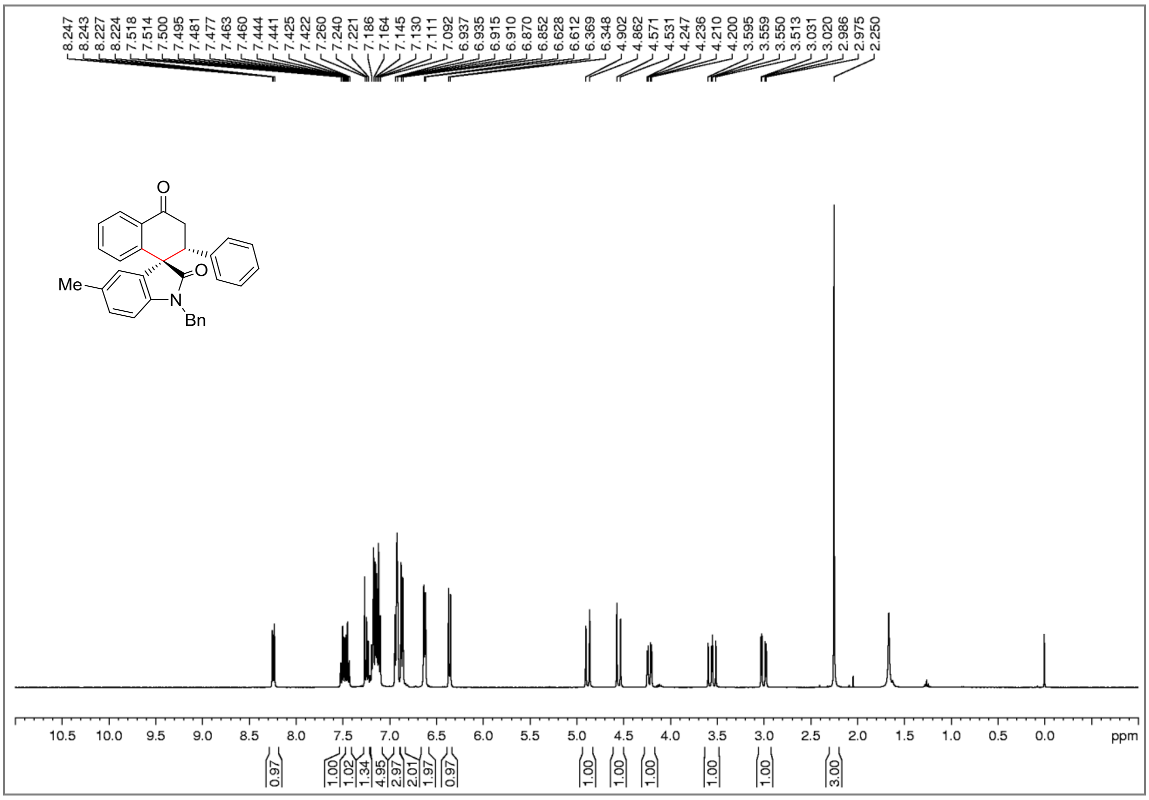


Figure 51: 400 MHz ^{1}H-NMR spectrum of **3y** in $CDCl_3$

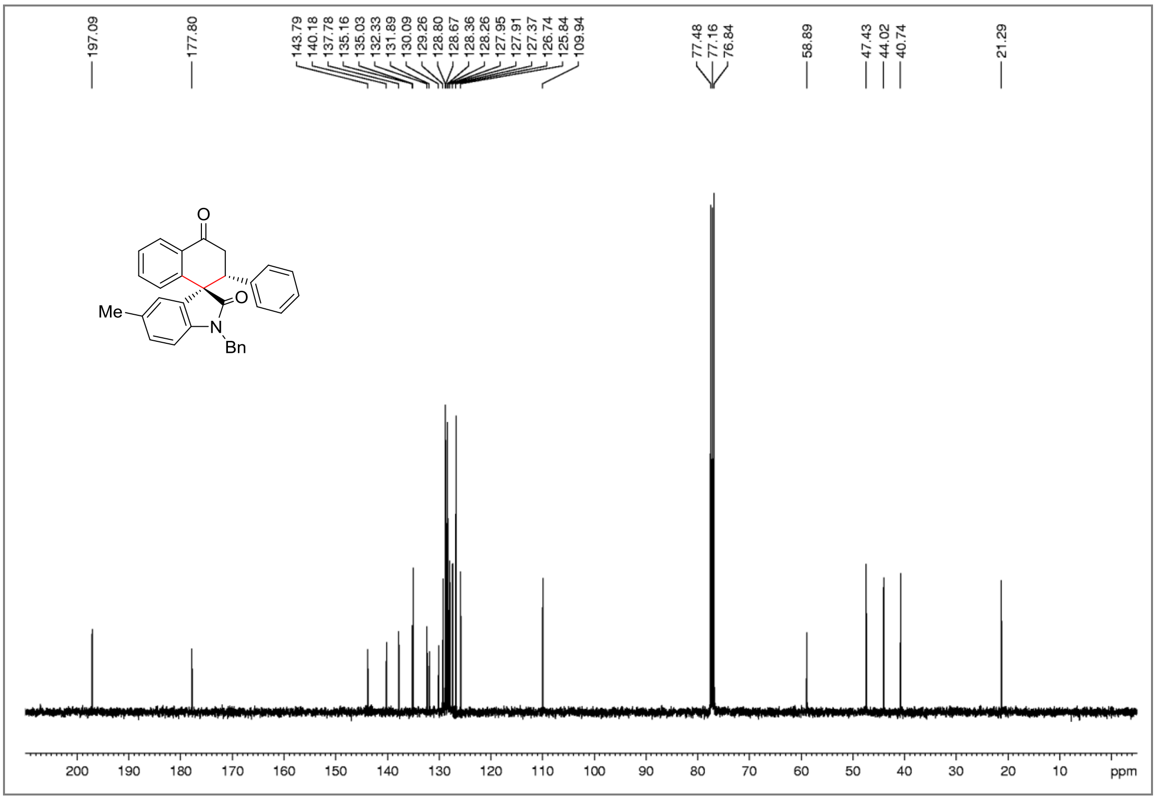


Figure 52: 100 MHz ^{13}C-NMR spectrum of **3y** in $CDCl_3$

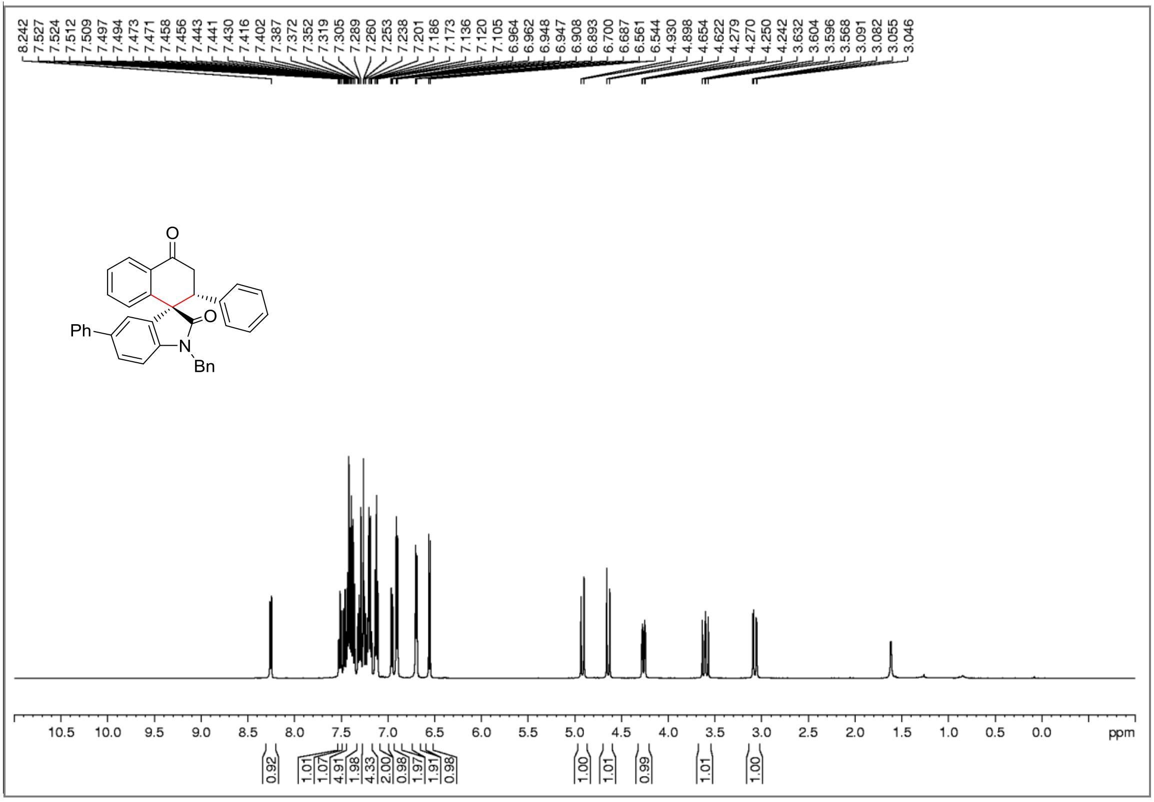


Figure 53: 500 MHz ^{1}H-NMR spectrum of **3z** in $CDCl_3$

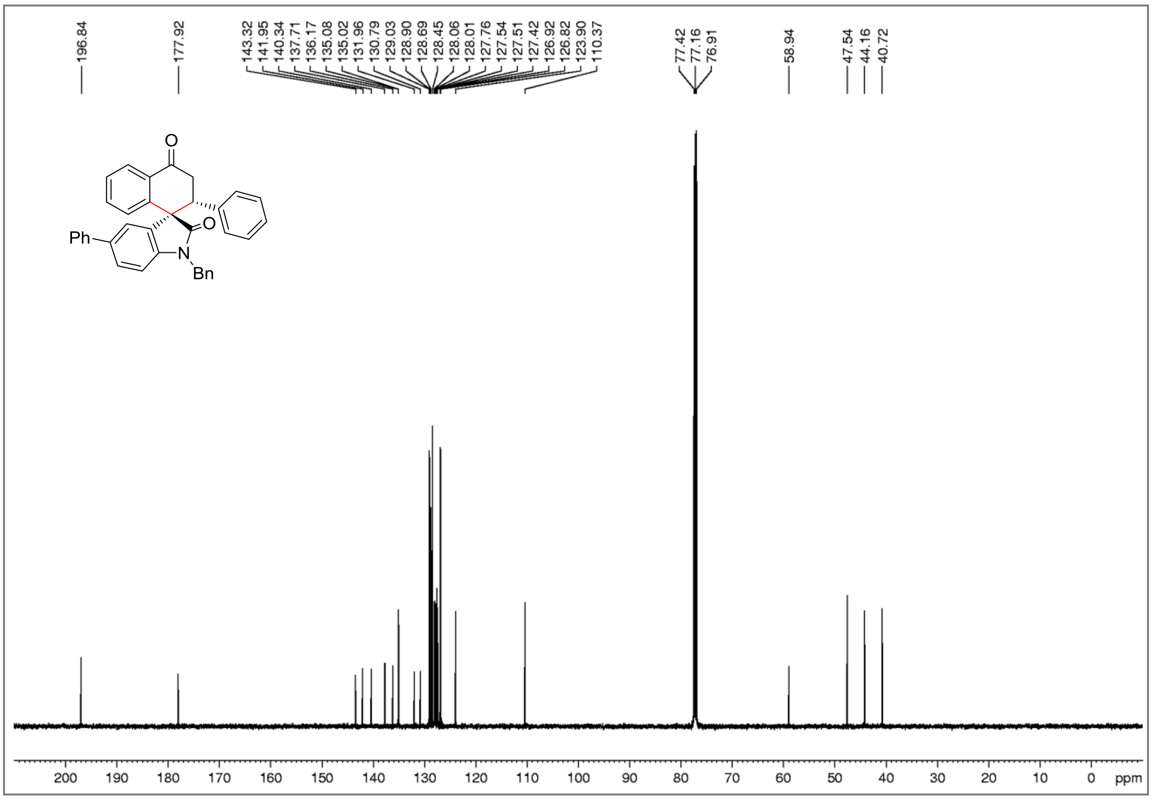


Figure 54: 125 MHz ^{13}C-NMR spectrum of **3z** in $CDCl_3$

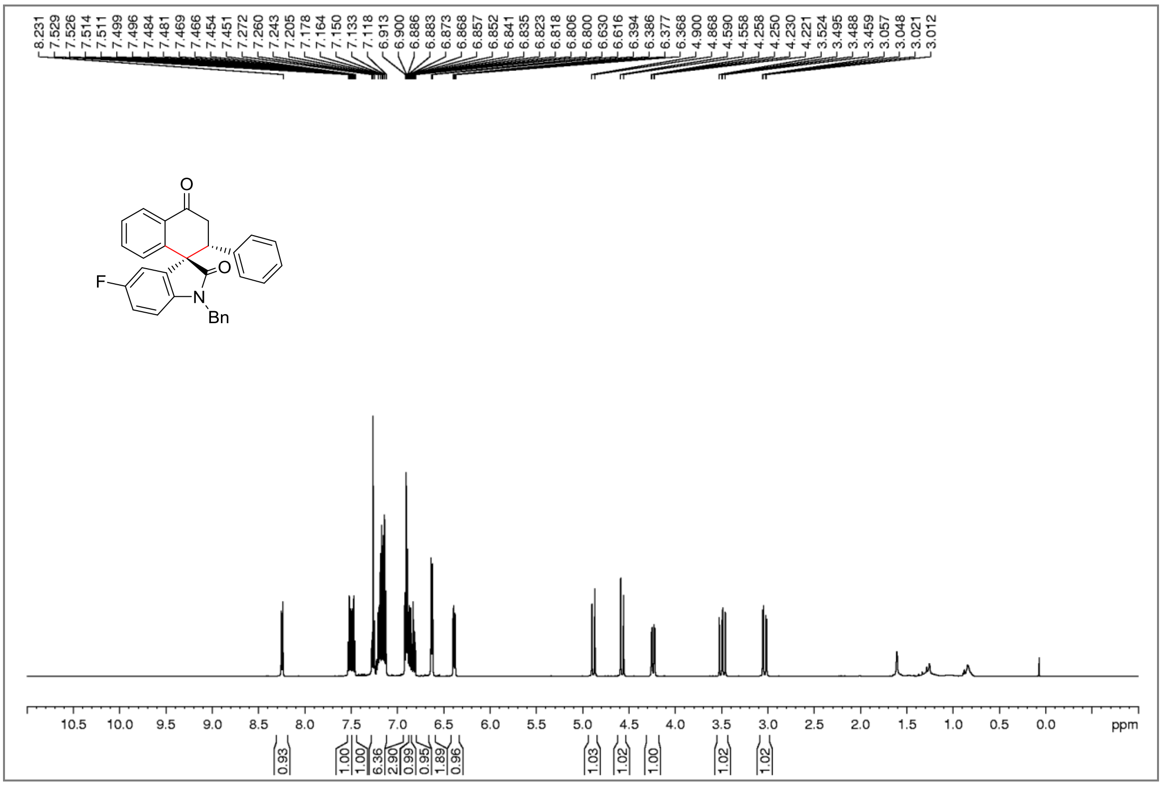


Figure 55: 500 MHz ^{1}H-NMR spectrum of **3aa** in $CDCl_3$

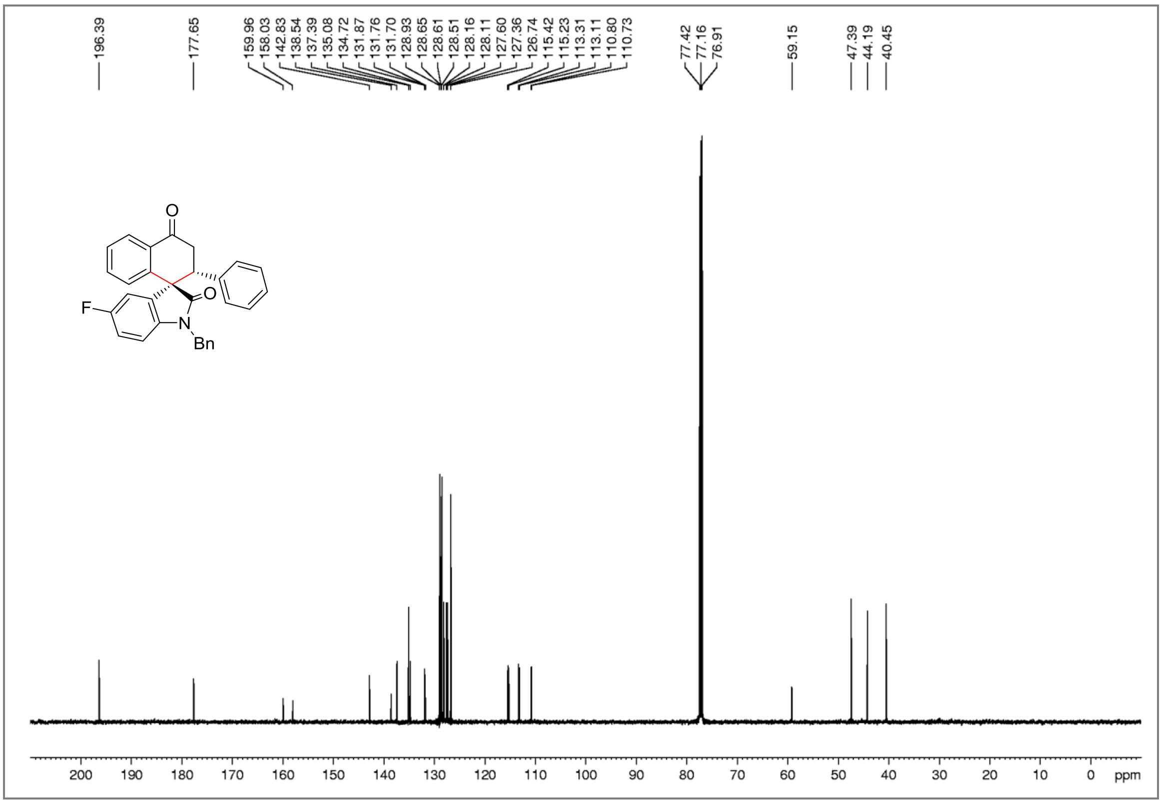


Figure 56: 125 MHz ^{13}C-NMR spectrum of **3aa** in $CDCl_3$

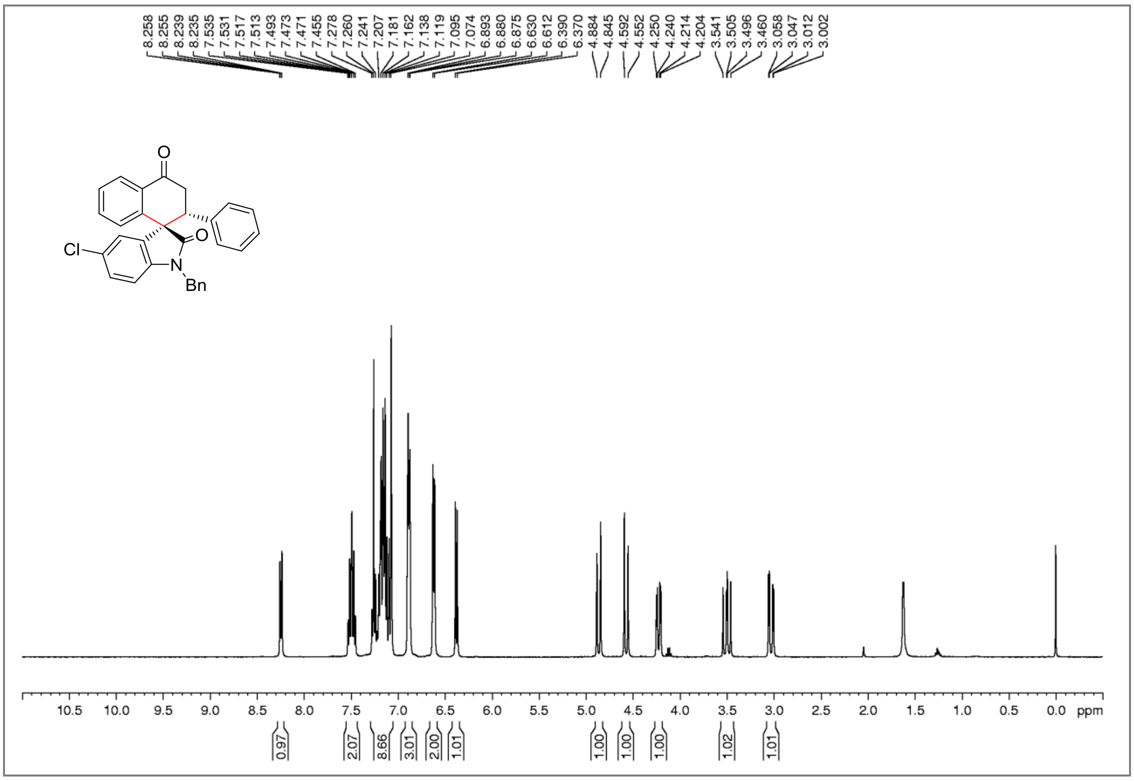


Figure 57: 400 MHz ^{1}H-NMR spectrum of **3ab** in $CDCl_3$

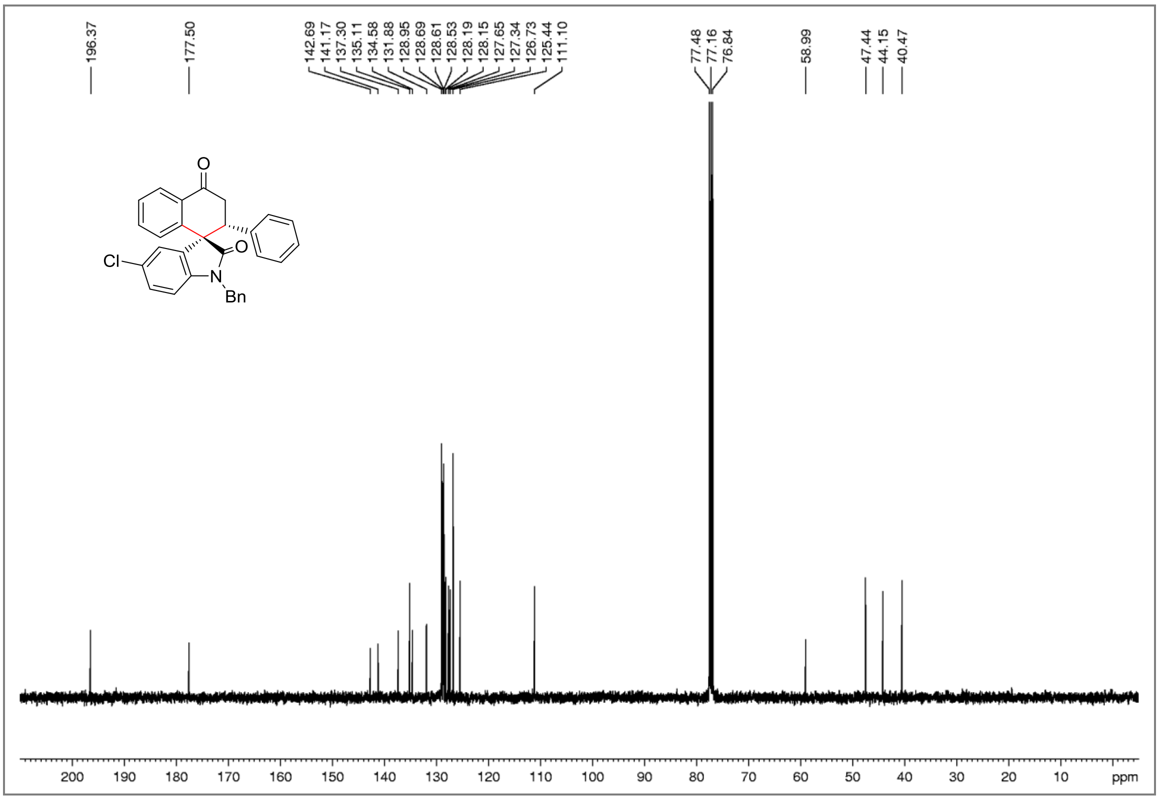


Figure 58: 100 MHz ^{13}C-NMR spectrum of **3ab** in $CDCl_3$

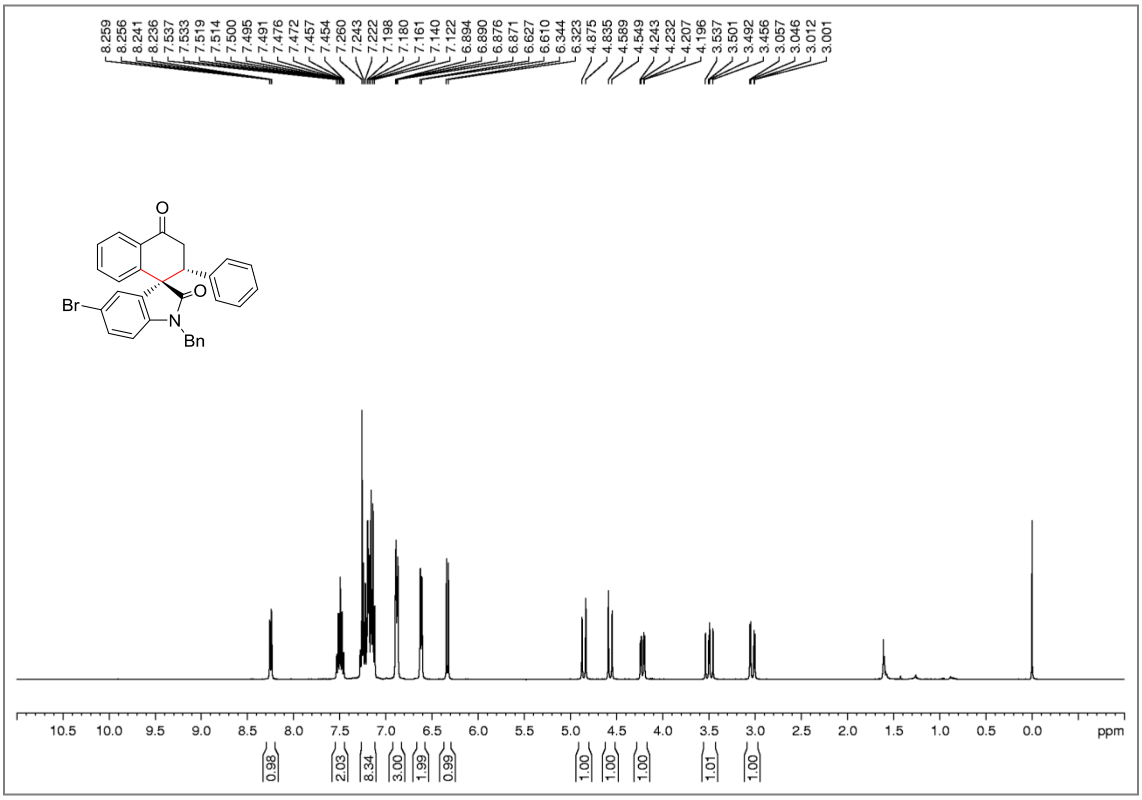


Figure 59: 400 MHz ^{1}H-NMR spectrum of **3ac** in $CDCl_3$

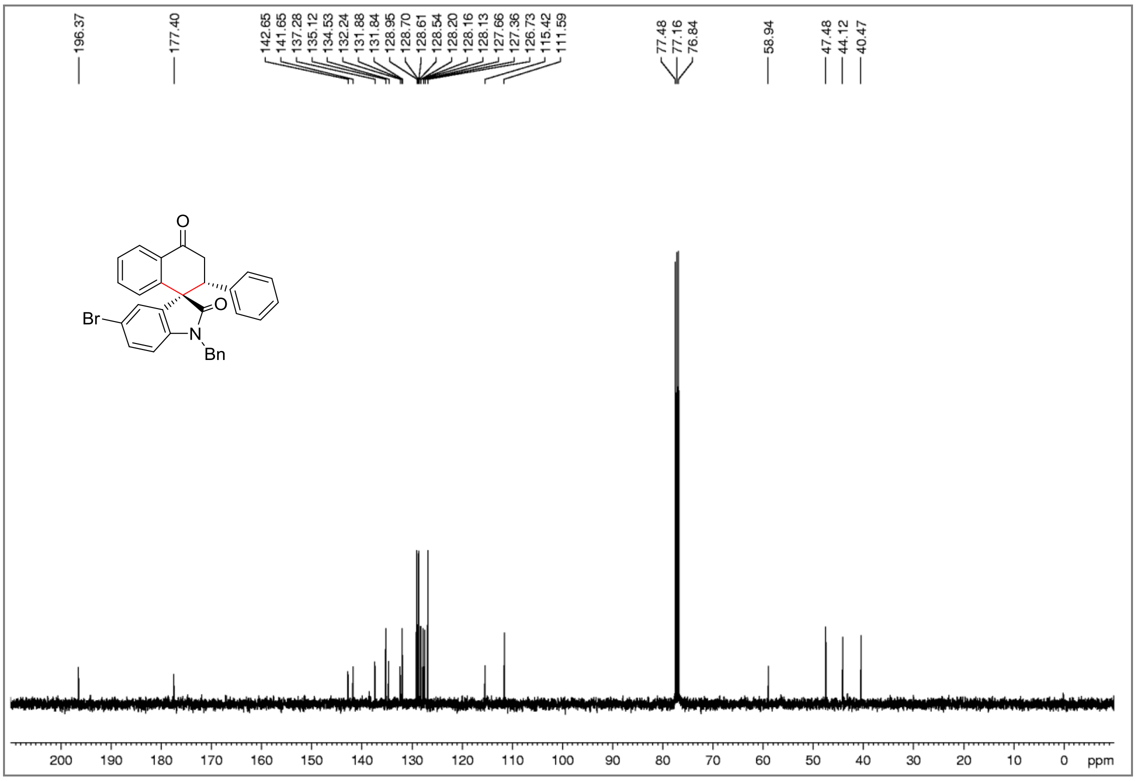


Figure 60: 100 MHz ^{13}C-NMR spectrum of **3ac** in $CDCl_3$

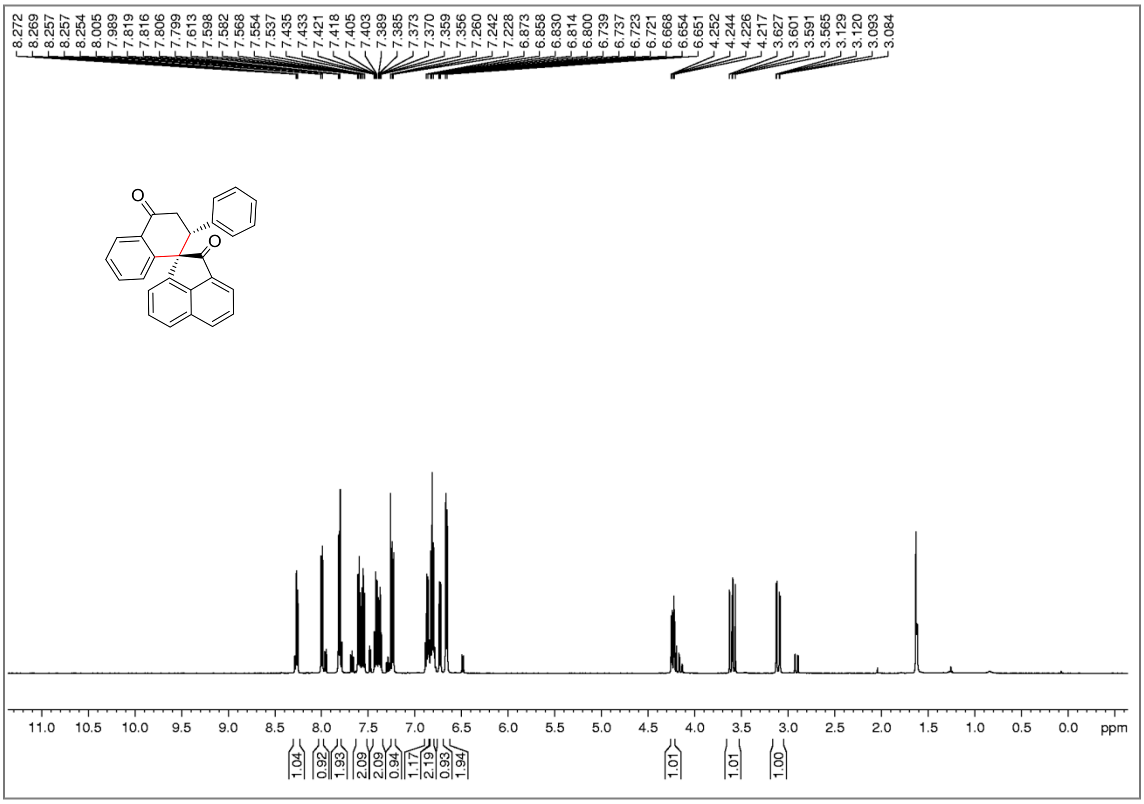


Figure 61: 500 MHz ^{1}H-NMR spectrum of **7a** in $CDCl_3$

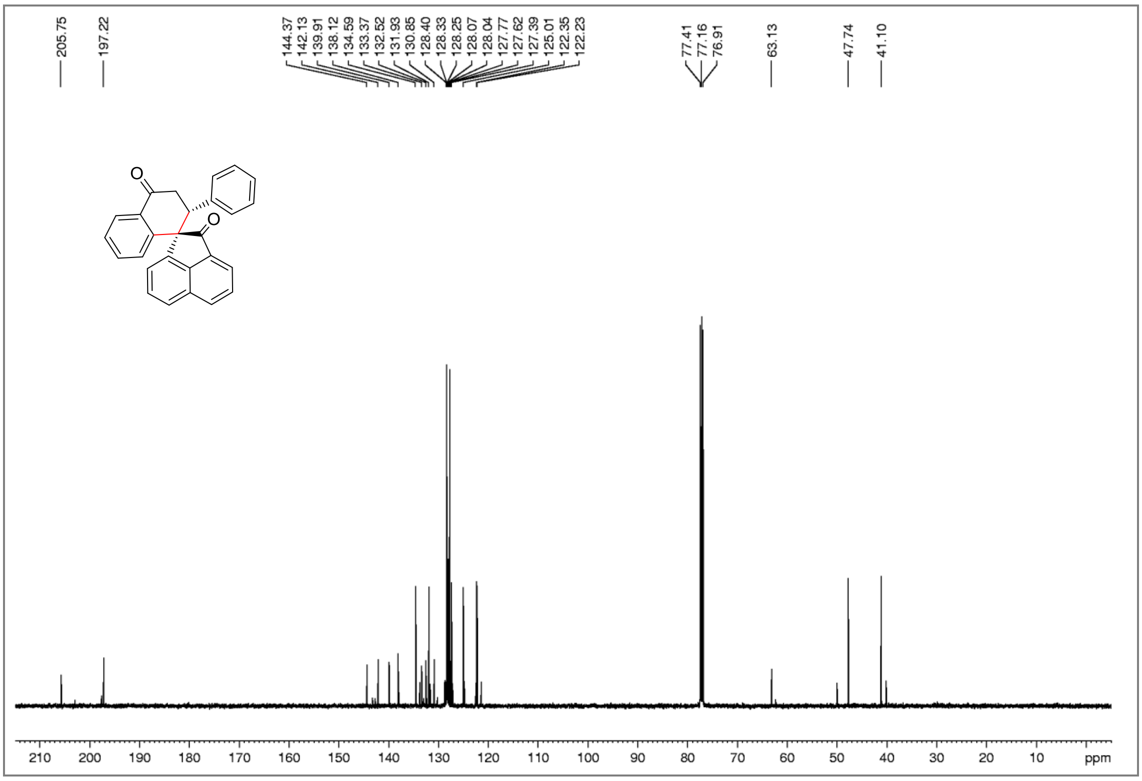


Figure 62: 125 MHz ^{13}C-NMR spectrum of **7a** in $CDCl_3$

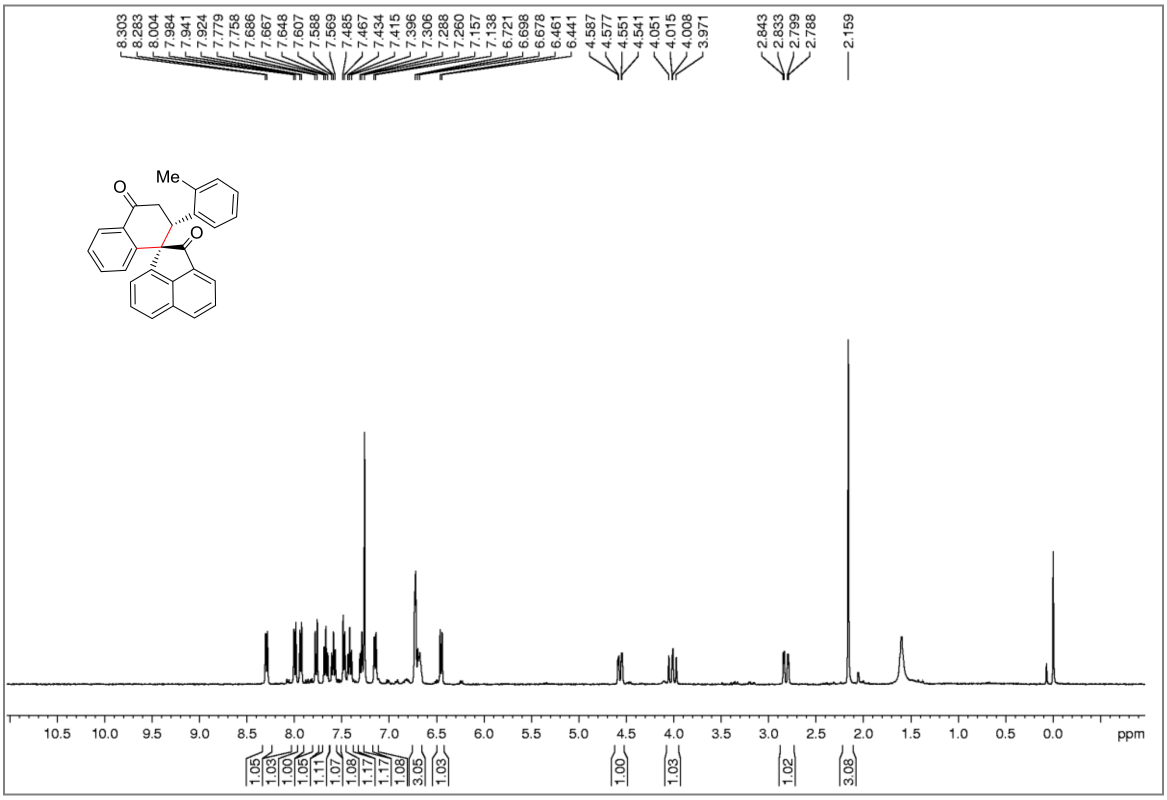


Figure 63: 400 MHz ^{1}H-NMR spectrum of **7b** in $CDCl_3$

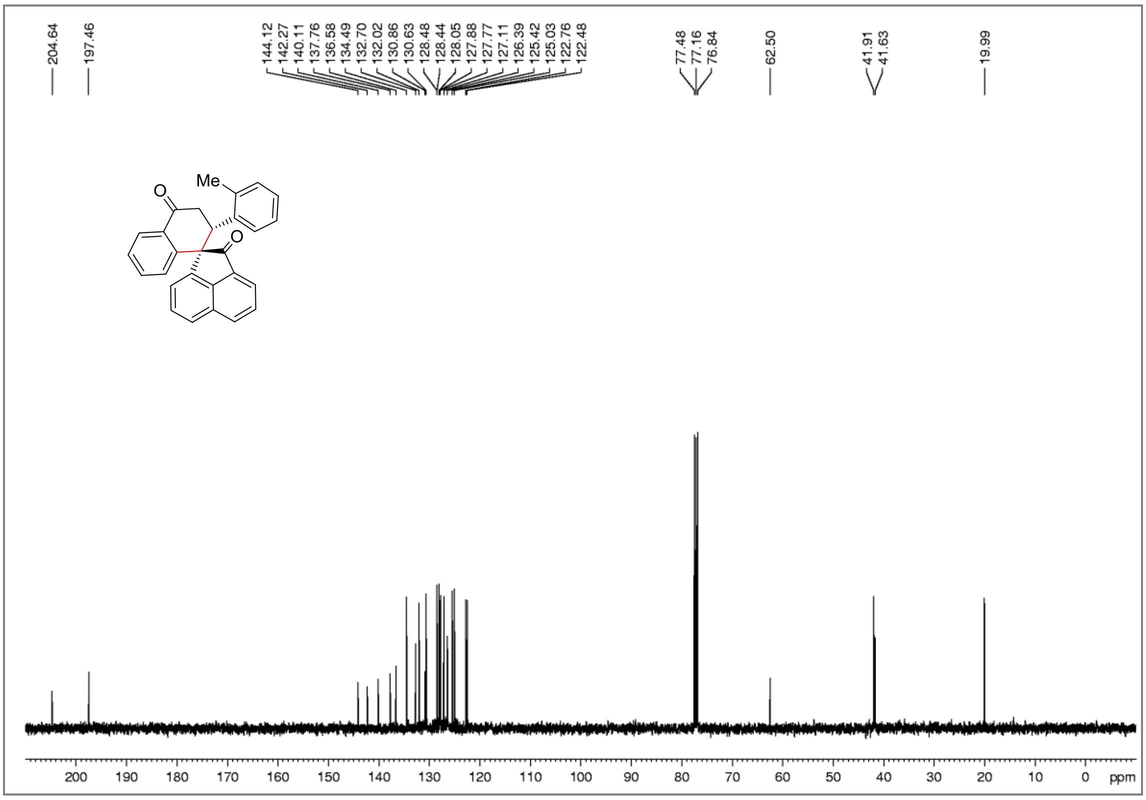


Figure 64: 100 MHz ^{13}C-NMR spectrum of **7b** in $CDCl_3$

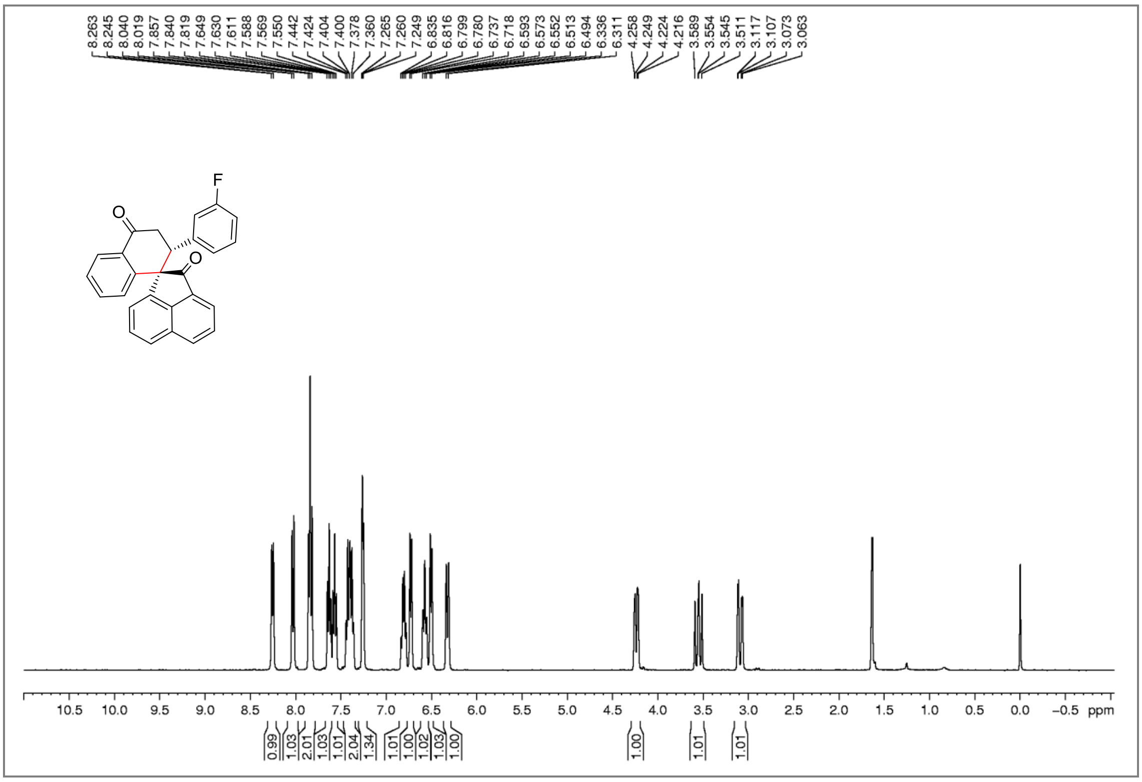


Figure 65: 400 MHz ^{1}H-NMR spectrum of **7c** in $CDCl_3$

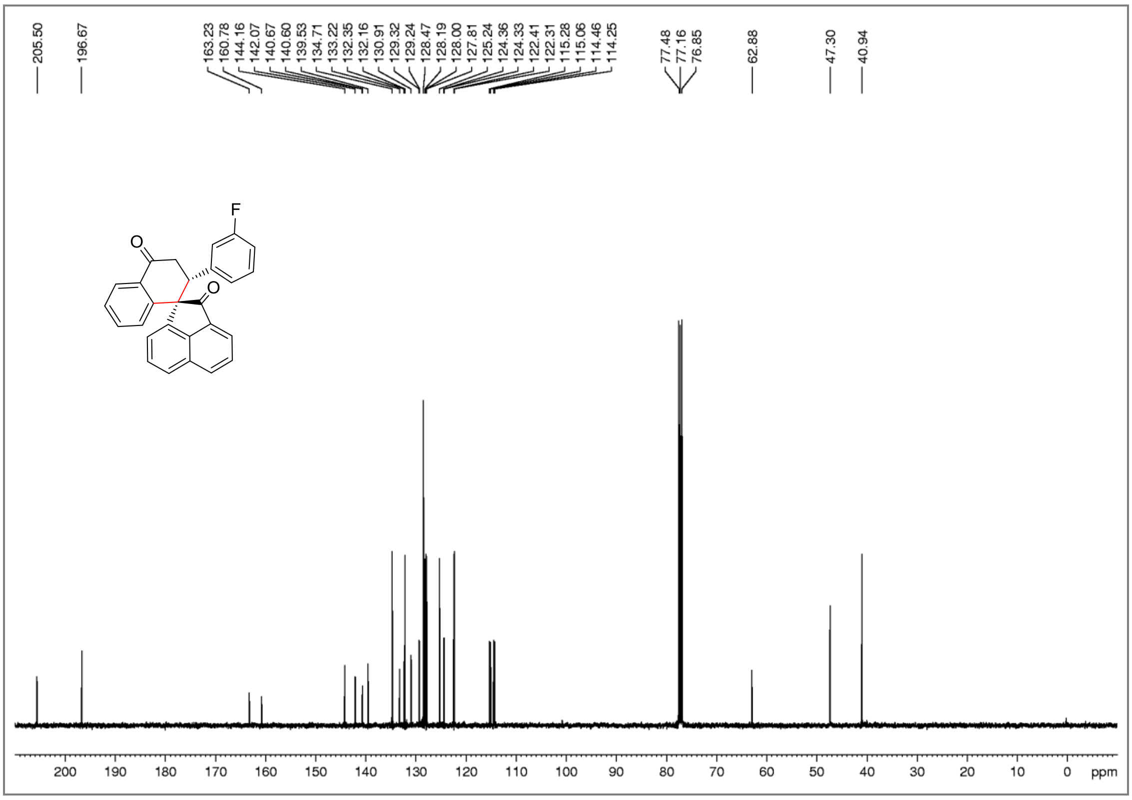


Figure 66: 100 MHz ^{13}C-NMR spectrum of **7c** in $CDCl_3$

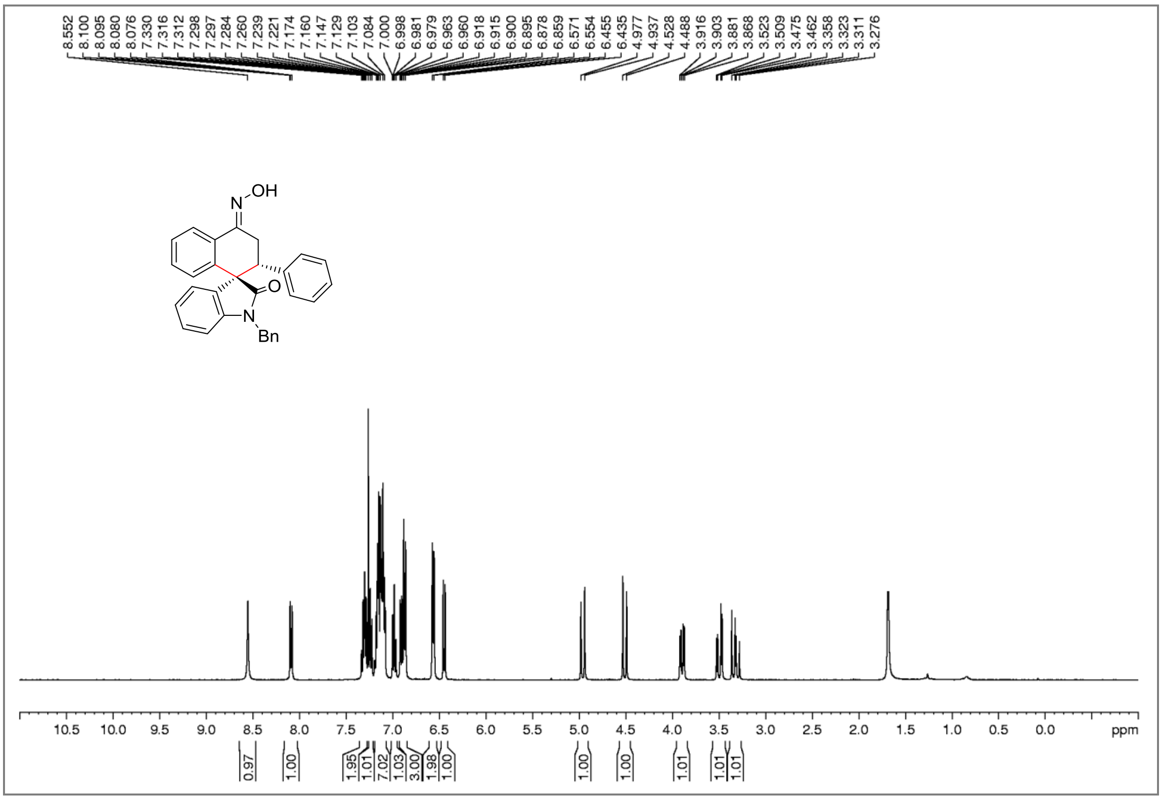


Figure 67: 400 MHz ^{1}H-NMR spectrum of **8** in $CDCl_3$

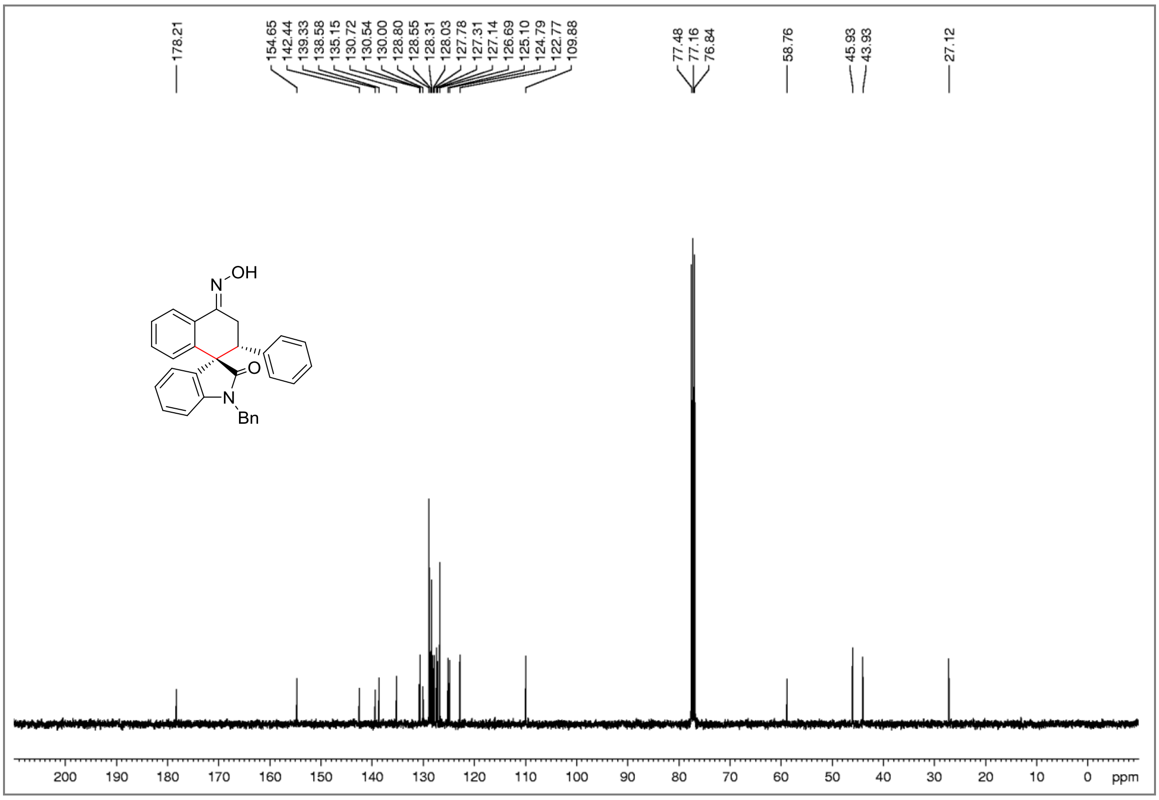


Figure 68: 100 MHz ^{13}C-NMR spectrum of **8** in $CDCl_3$

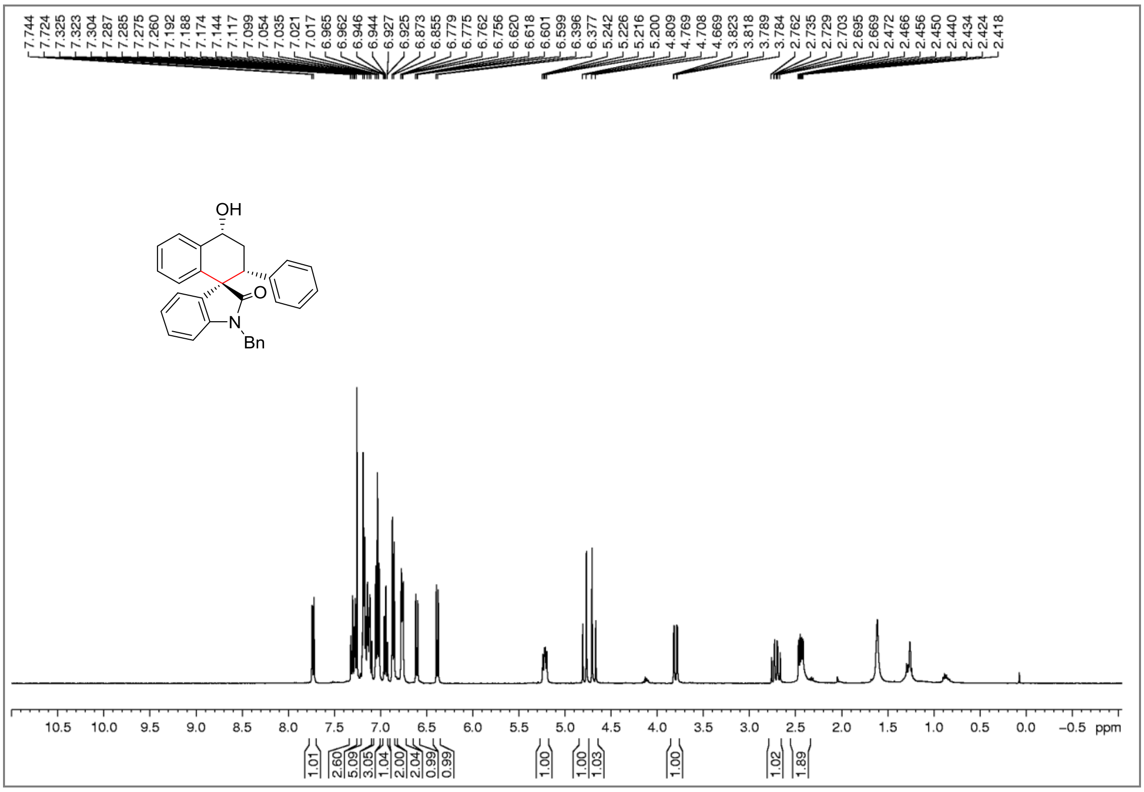


Figure 69: 400 MHz ^{1}H-NMR spectrum of **9** in $CDCl_3$

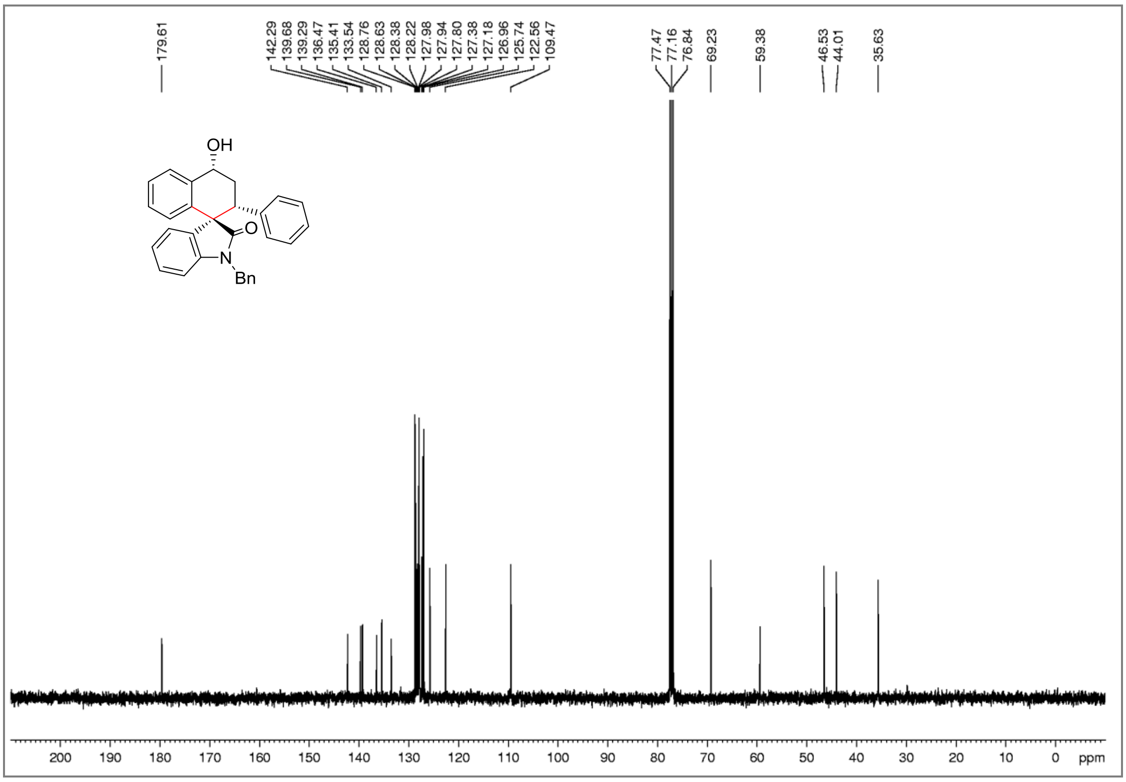


Figure 70: 100 MHz ^{13}C-NMR spectrum of **9** in $CDCl_3$

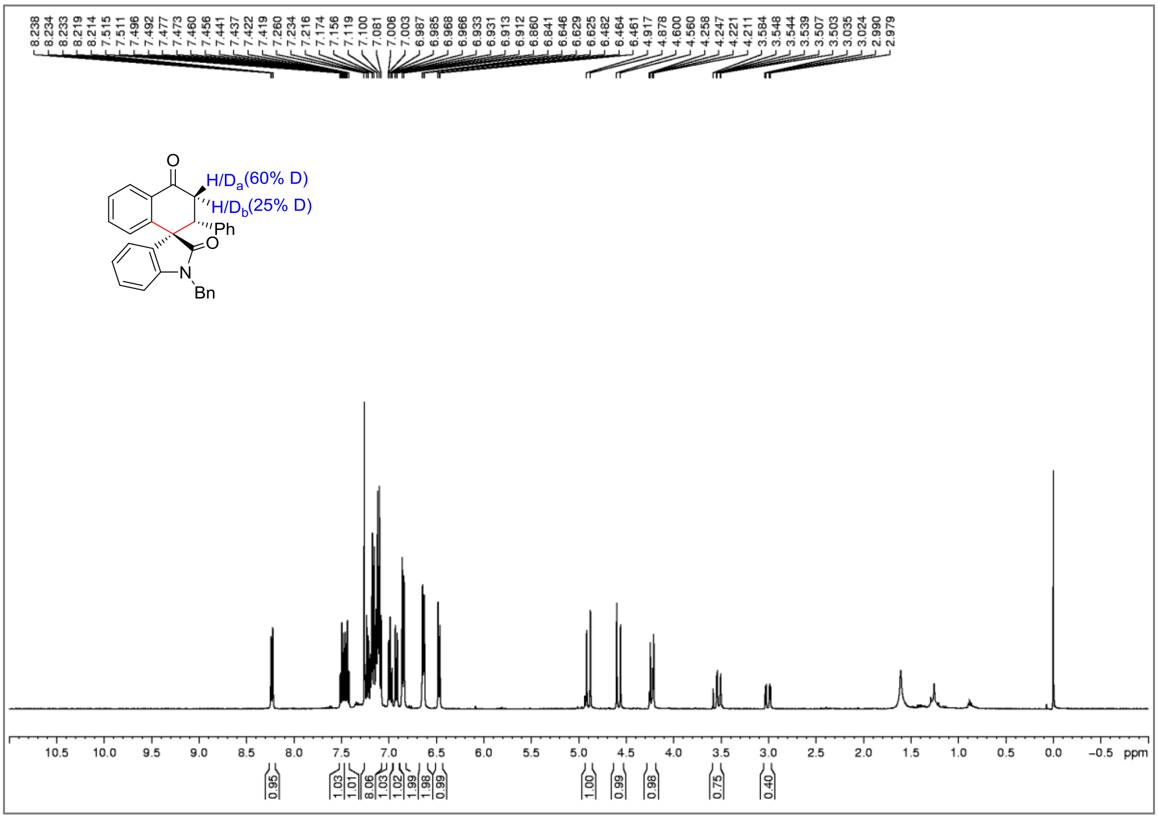


Figure 71: 400 MHz ^{1}H-NMR spectrum of **10** in $CDCl_3$

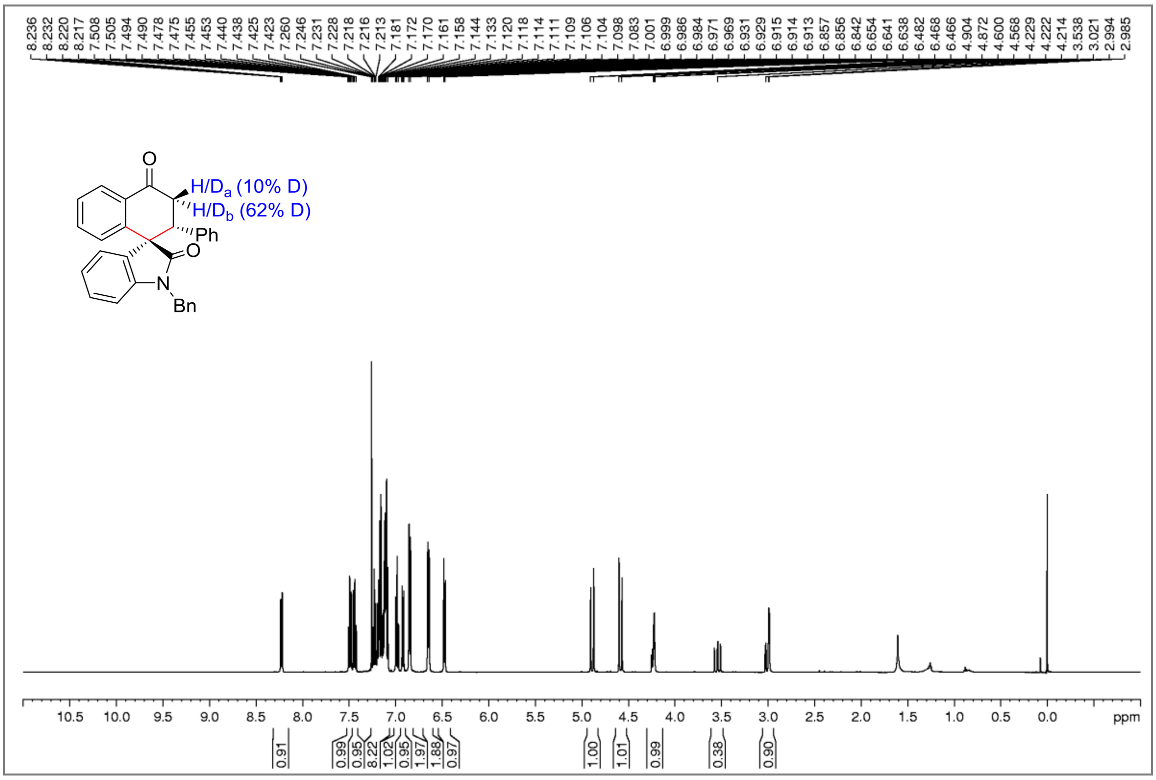


Figure 72: 500 MHz ^{1}H-NMR spectrum of **11** in $CDCl_3$

11. Single crystal XRD data

XRD Data for Compound 3b (CCDC No. 1558658)

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) spiro

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: spiro

```
Bond precision:  C-C = 0.0067 A          Wavelength=0.71073

Cell:         a=10.9070(3)       b=11.8602(3)      c=12.5989(3)
              alpha=114.5329(10) beta=105.8396(10) gamma=100.6194(10)
Temperature: 296 K

                Calculated                 Reported
Volume          1341.35(6)                 1341.35(6)
Space group     P -1                       P -1
Hall group      -P 1                       -P 1
Moiety formula  C30 H23 N O2, C H Cl3      ?
Sum formula     C31 H24 Cl3 N O2           C31 H24 Cl3 N O2
Mr              548.86                     548.86
Dx,g cm-3       1.359                      1.359
Z               2                          2
Mu (mm-1)       0.371                      0.371
F000            568.0                      568.0
F000'           569.09
h,k,lmax        12,14,14                   12,14,14
Nref            4716                       4715
Tmin,Tmax       0.911,0.942                0.913,0.943
Tmin'           0.911

Correction method= # Reported T Limits: Tmin=0.913 Tmax=0.943
AbsCorr = MULTI-SCAN

Data completeness= 1.000          Theta(max)= 24.998

R(reflections)= 0.0801( 3627)     wR2(reflections)= 0.2135( 4715)

S = 0.941                  Npar= 334
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT244_ALERT_4_C Low    'Solvent' Ueq as Compared to Neighbors of        C31 Check
PLAT340_ALERT_3_C Low Bond Precision on  C-C Bonds ...............    0.00673 Ang.
PLAT906_ALERT_3_C Large K value in the Analysis of Variance ......      2.244 Check
PLAT911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L=  0.595          2 Report
```

Alert level G

```
PLAT066_ALERT_1_G Predicted and Reported Tmin&Tmax Range Identical          ? Check
PLAT154_ALERT_1_G The s.u.'s on the Cell Angles are Equal ..(Note)      0.001 Degree
PLAT793_ALERT_4_G The Model has Chirality at C14      (Centro SPGR)         R Verify
PLAT793_ALERT_4_G The Model has Chirality at C15      (Centro SPGR)         R Verify
PLAT909_ALERT_3_G Percentage of Observed Data at Theta(Max) Still          51 % Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.         11 Note
```

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
4 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
6 **ALERT level G** = General information/check it is not something unexpected

2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
1 ALERT type 2 Indicator that the structure model may be wrong or deficient
4 ALERT type 3 Indicator that the structure quality may be low
3 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

XRD Data for Compound 3b' (CCDC No. 1558659)

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) spiro

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: spiro

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Bond precision:   C-C = 0.0023 A          Wavelength=0.71073

Cell:             a=9.0802(3)    b=9.9498(4)          c=24.9306(9)
                  alpha=90       beta=98.8194(13)     gamma=90
Temperature:      296 K

                 Calculated                  Reported
Volume           2225.75(14)                 2225.75(14)
Space group      P 21/n                      P 21/n
Hall group       -P 2yn                      -P 2yn
Moiety formula   C30 H23 N O2                ?
Sum formula      C30 H23 N O2                C30 H23 N O2
Mr               429.49                      429.49
Dx,g cm-3        1.282                       1.282
Z                4                           4
Mu (mm-1)        0.080                       0.080
F000             904.0                       904.0
F000'            904.38
h,k,lmax         10,11,29                    10,11,29
Nref             3900                        3899
Tmin,Tmax        0.980,0.992
Tmin'            0.980

Correction method= Not given

Data completeness= 1.000          Theta(max)= 24.998

R(reflections)= 0.0360( 2979)     wR2(reflections)= 0.0997( 3899)

S = 1.006                 Npar= 299
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level G

```
PLAT793_ALERT_4_G The Model has Chirality at C9      (Centro SPGR)          R Verify
PLAT793_ALERT_4_G The Model has Chirality at C10     (Centro SPGR)          S Verify
PLAT909_ALERT_3_G Percentage of Observed Data at Theta(Max) Still          50 % Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          3 Note
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   0 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   4 ALERT level G = General information/check it is not something unexpected

   0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   1 ALERT type 2 Indicator that the structure model may be wrong or deficient
   1 ALERT type 3 Indicator that the structure quality may be low
   2 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

XRD Data for Compound 3x (CCDC No. 1558660)

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) dioxy

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: dioxy

```
Bond precision:  C-C = 0.0030 A          Wavelength=0.71073

Cell:            a=9.3618(4)    b=10.5515(5)        c=24.1467(11)
                 alpha=90       beta=96.2562(19)    gamma=90
Temperature:     296 K

                 Calculated                 Reported
Volume           2371.03(19)                2371.03(19)
Space group      P 21/c                     P 21/c
Hall group       -P 2ybc                    -P 2ybc
Moiety formula   C31 H23 N O4               C31 H23 N O4
Sum formula      C31 H23 N O4               C31 H23 N O4
Mr               473.50                     473.50
Dx,g cm-3        1.327                      1.326
Z                4                          4
Mu (mm-1)        0.088                      0.088
F000             992.0                      992.0
F000'            992.47
h,k,lmax         11,12,28                   11,12,28
Nref             4184                       4181
Tmin,Tmax        0.976,0.986                0.976,0.986
Tmin'            0.976

Correction method= # Reported T Limits: Tmin=0.976 Tmax=0.986
AbsCorr = MULTI-SCAN

Data completeness= 0.999           Theta(max)= 24.999

R(reflections)= 0.0454( 3397)      wR2(reflections)= 0.1175( 4181)

S = 1.073                  Npar= 325
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT220_ALERT_2_C Non-Solvent Resd 1   C   Ueq(max)/Ueq(min) Range        3.6 Ratio
PLAT241_ALERT_2_C High   'MainMol' Ueq as Compared to Neighbors of        O1 Check
PLAT241_ALERT_2_C High   'MainMol' Ueq as Compared to Neighbors of       C28 Check
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of       C26 Check
PLAT906_ALERT_3_C Large K value in the Analysis of Variance ......     3.150 Check
PLAT911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L=  0.595         3 Report
```

Alert level G

```
PLAT066_ALERT_1_G Predicted and Reported Tmin&Tmax Range Identical         ? Check
PLAT398_ALERT_2_G Deviating  C-O-C  Angle from 120 Deg for O1          106.8 Degree
PLAT398_ALERT_2_G Deviating  C-O-C  Angle from 120 Deg for O2          105.9 Degree
PLAT793_ALERT_4_G The Model has Chirality at C10      (Centro SPGR)        R Verify
PLAT793_ALERT_4_G The Model has Chirality at C11      (Centro SPGR)        R Verify
PLAT909_ALERT_3_G Percentage of Observed Data at Theta(Max) Still         56 % Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.         9 Note
```

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
6 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
7 **ALERT level G** = General information/check it is not something unexpected

1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
7 ALERT type 2 Indicator that the structure model may be wrong or deficient
3 ALERT type 3 Indicator that the structure quality may be low
2 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

XRD Data for Compound 7a (CCDC No. 1558661)

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) acenap

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: acenap

```
Bond precision:   C-C = 0.0049 A          Wavelength=0.71073

Cell:          a=8.7392(3)         b=10.6106(3)      c=11.8953(4)
               alpha=73.1183(16)   beta=78.1739(17)  gamma=66.4494(15)
Temperature:   296 K

                  Calculated                 Reported
Volume            962.60(6)                  962.60(6)
Space group       P -1                       P -1
Hall group        -P 1                       -P 1
Moiety formula    C27 H18 O2                 ?
Sum formula       C27 H18 O2                 C27 H18 O2
Mr                374.41                     374.41
Dx,g cm-3         1.292                      1.292
Z                 2                          2
Mu (mm-1)         0.080                      0.080
F000              392.0                      392.0
F000'             392.17
h,k,lmax          10,12,14                   10,12,14
Nref              3394                       3281
Tmin,Tmax         0.977,0.987                0.975,0.987
Tmin'             0.975

Correction method= # Reported T Limits: Tmin=0.975 Tmax=0.987
AbsCorr = MULTI-SCAN

Data completeness= 0.967          Theta(max)= 24.996

R(reflections)= 0.0706( 2529)     wR2(reflections)= 0.2232( 3281)

S = 1.071                    Npar= 262
```

```
The following ALERTS were generated. Each ALERT has the format
       test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.
```

Alert level B

```
PLAT230_ALERT_2_B Hirshfeld Test Diff for    C6     --  C7      ..         7.3 s.u.
```

Author Response: This alarm is due to the elongated ADPs of carbon atoms which suggest that these are having high thermal motion. In particular, carbon atoms C6,C7,C8,C10 and C11 in the acenapthylene moiety may be disordered. The crystal data was collected in room temp.

Alert level C

```
DIFMX02_ALERT_1_C  The maximum difference density is > 0.1*ZMAX*0.75
            The relevant atom site should be identified.
PLAT029_ALERT_3_C _diffrn_measured_fraction_theta_full value Low .      0.967 Note
PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density ....       2.91 Report
PLAT097_ALERT_2_C Large Reported Max.  (Positive) Residual Density       0.73 eA-3
PLAT230_ALERT_2_C Hirshfeld Test Diff for    O1     --  C1      ..         5.5 s.u.
```

Author Response: This alarm is due to the elongated ADPs of carbon atoms which suggest that these are having high thermal motion. In particular, carbon atoms C6,C7,C8,C10 and C11 in the acenapthylene moiety may be disordered. The crystal data was collected in room temp.

```
PLAT230_ALERT_2_C Hirshfeld Test Diff for    C7     --  C8      ..         6.0 s.u.
```

Author Response: This alarm is due to the elongated ADPs of carbon atoms which suggest that these are having high thermal motion. In particular, carbon atoms C6,C7,C8,C10 and C11 in the acenapthylene moiety may be disordered. The crystal data was collected in room temp.

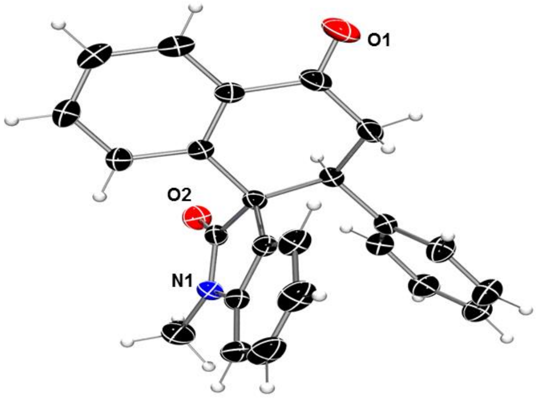
```
PLAT230_ALERT_2_C Hirshfeld Test Diff for    C10    --  C11     ..         7.0 s.u.
```

Author Response: This alarm is due to the elongated ADPs of carbon atoms which suggest that these are having high thermal motion. In particular, carbon atoms C6,C7,C8,C10 and C11 in the acenapthylene moiety may be disordered. The crystal data was collected in room temp.

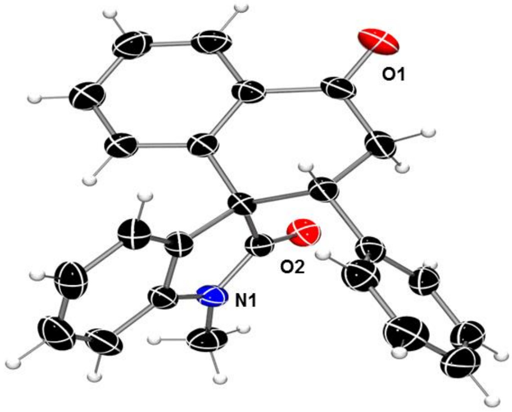
```
PLAT340_ALERT_3_C Low Bond Precision on  C-C Bonds ...............     0.00487 Ang.
PLAT911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L=  0.595       113 Report
```

---

12. Crystal structures of 3a and 3a'



3a (*anti*)
CCDC 1561150



3a' (*syn*)
CCDC 1561151