Supporting Information

Access to Densely Functionalized Spirocyclopentenonyl Oxindole Frameworks *via* Aza- and Carbo-Piancatelli Rearrangement

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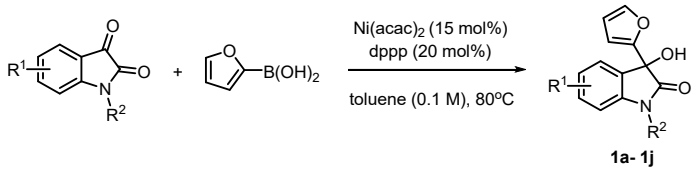
1. **General Information.** Unless otherwise mentioned, all reactions in the current study were performed under nitrogen or argon atmosphere. Standard protocols were followed for drying the laboratory solvents. All reagents/catalysts were purchased commercially and used without any further purification. 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) was purchased from Spectrochem, India and used directly in the reaction. Reactions were monitored by TLC, using Merck silica gel 60 F 254 plates. TLC plates were visualized using either with UV light (254 nm) or using stains such as 10% ethanolic phosphomolybdic acid (PMA) or 1% aqueous $KMnO_4$ or iodine. Flash column chromatography was performed using silica gel (230-400 mesh). ^1H and ^{13}C NMR spectra were recorded on Avance III, Bruker 400 MHz and 100 MHz spectrometers respectively using $CDCl_3$ or DMSO-d_6. ^1H NMR chemicals shift are expressed in ppm (δ) relative to δ = 7.26 for $CDCl_3$ and δ = 2.50 for DMSO-d_6. ^{13}C NMR chemical shift are expressed in ppm (δ) relative to δ = 77.16 for $CDCl_3$ and δ = 39.51 for DMSO-d_6 resonance. HRMS and Electron Spray Ionization (ESI) (m/z) spectra were recorded on Agilent Technologies 6530 Accurate- Mass Q-TOF LC/MS. Compound **1a** is known in the literature.[10] Compounds **1b**-**1i** were prepared following the same procedure.

2. List of the starting materials.

Following furan-2-yl-3-hydroxyindolin-2-one starting materials were prepared from isatin derivatives as illustrated in Scheme S1 and structure of the products are provided in Figure S1.



Scheme S1. Ni-catalyzed method for the preparation of furanyl-3-hydroxyindolinones

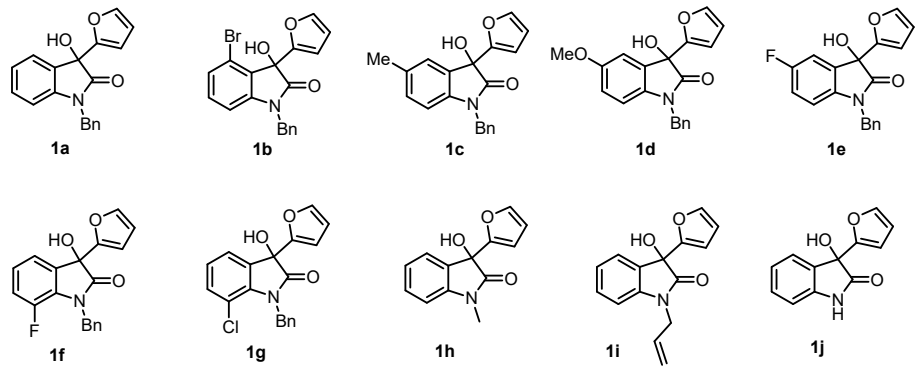


Figure S1. List of furanyl-3-hydroxyindolinones prepared in the study.

Anilines:

Following commercially available anilines (**2a**-**2y**) were used in the present study.

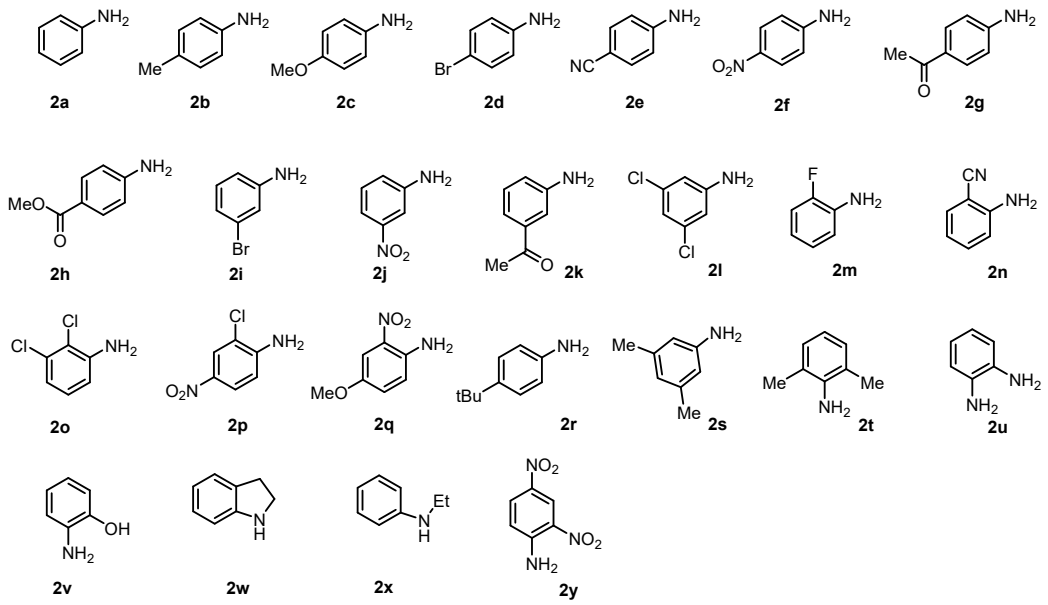


Figure S2. List of anilines.

Indoles: Following indole derivatives were used (**29a**-**29f**) were used in the present study.

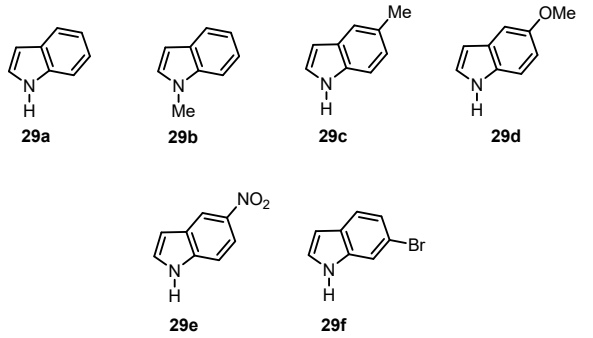


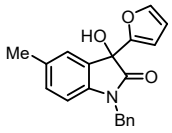
Figure S3. List of indoles.

General procedure for the preparation of furan-2-yl-3-hydroxyindolin-2-ones (1).[1] N-protected isatin derivatives (0.2 mmol) and furylboronic acid (0.4 mmol) were taken in dry toluene (2.0 mL) and were successively added $Ni(acac)_2$ (15 mol%) and 1,3-bis(diphenylphosphino)propane [dppp] (20 mol%) under N_2 atmosphere. The reaction was heated at 80 °C. After completion of the reaction (TLC monitored), solvent was removed under reduced pressure and the crude residue was purified by silica gel column chromatography (EtOAc-Hex as eluent) to afford the desired product**.**

1-Benzyl-4-bromo-3-(furan-2-yl)-3-hydroxyindolin-2-one (1b).

Following the general procedure, N-benzyl-4-bromoisatin (0.79 g, 2.50 mmol) was transformed into compound **1b** which was isolated as brown solid in 76% (0.73 g) yield. R_f 0.3 (EtOAc: Hexane 4:6); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.32 - 7.26 (m, 6H), 7.18 (d, J = 8.2 Hz, 1H), 7.10 (t, J = 7.8 Hz, 1H), 6.67 (d, J = 7.7 Hz, 1H), 6.52 (s, 1H), 6.40 (s, 1H), 5.00 (d, J = 15.9 Hz, 1H), 4.81 (d, J = 15.9 Hz, 1H), 3.80 (s, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 174.3,149.9, 144.9, 143.5, 134.8, 131.7, 129.1, 128.0, 127.6, 127.3, 127.1, 120.4, 110.8, 109.5, 109.0, 75.8, 44.2; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{19}H_{14}BrNNaO_3$ calcd. 406.0055, found, 406.0061.

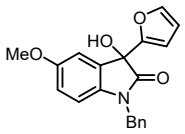
1-Benzyl-3-(furan-2-yl)-3-hydroxy-5-methylindolin-2-one (1c).



Following the general procedure, N-benzyl-5-methylisatin (0.17 g, 0.68 mmol) was transformed into compound **1c** which was isolated as white solid in 64% (0.14 g) yield. R_f 0.35 (EtOAc: Hexane 3:7); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 - 7.32 (m, 2H), 7.25 - 7.17 (m, 5H), 6.95 (d, J = 7.8 Hz, 1H), 6.53 (d, J = 8.0 Hz, 1H), 6.35 - 6.35 (m, 1H), 6.27-6.25 (m, 1H), 4.92 (d, J = 15.8 Hz, 1H), 4.72 (d, J = 15.8 Hz, 1H), 4.44 (s, 1H), 2.23 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 175.5, 151.8, 143.8, 140.1, 135.3, 133.1, 130.4, 128.8, 128.6, 127.7, 127.1, 126.2, 110.4, 109.6, 108.8,

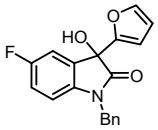
73.9, 43.9, 21.1; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{20}H_{17}NNaO_3$ calcd. 342.1106, found, 342.1146.

1-Benzyl-3-(furan-2-yl)-3-hydroxy-5-methoxyindolin-2-one (1d).



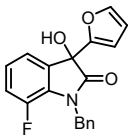
Following the general procedure N-benzyl-5-methoxyisatin (0.25g, 0.94 mmol) was transformed into compound **1d** which was isolated as brown solid in 60% (0.19 g) yield. R_f 0.35 (EtOAc: Hexane 3:7); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41-7.10 (m, 1H), 7.28 - 7.19 (m, 5H), 7.16 (d, J = 2.6 Hz, 1H), 6.72-6.70 (m, 1H), 6.57 (d, J = 8.6 Hz, 1H), 6.36 - 6.35 (m, 1H), 6.30 - 6.29 (m, 1H), 4.95 (d, J = 15.8 Hz, 1H), 4.76 (d, J = 15.8 Hz, 1H), 4.11 (s, 1H), 3.72 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 175.3, 156.6, 151.5, 144.0, 135.9, 135.3, 129.6, 129.0, 127.8, 127.2, 115.2, 112.3, 110.5, 110.5, 109.0, 74.1, 55.9, 44.1; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{20}H_{17}NNaO_4$ calcd. 358.1055, found, 358.1086.

1-Benzyl-5-fluoro-3-(furan-2-yl)-3-hydroxyindolin-2-one (1e).



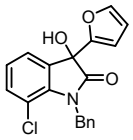
Following the general procedure N-benzyl-5-fluoroisatin (0.17 g, 0.67mmol) was transformed into compound **1e** which was isolated as red solid in 61% (0.13 g) yield. R_f 0.5 (EtOAc: Hexane 3:7); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 - 7.26 (m, 7H), 6.91 (s, 1H), 6.62 (s, 1H), 6.38 (d, J = 28.5 Hz, 2H), 5.01- 4.79 (m, 2H), 4.27 (s, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 175.4, 160.8, 158.4, 150.9, 144.2, 138.4, 134.9, 130.1, 130.0, 129.1, 128.0, 127.2, 116.7, 116.4, 113.9, 113.7, 110.6, 110.6, 109.2, 73.8, 44.2; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{19}H_{14}FNNaO_3$ calcd. 346.0855, found, 346.0903.

1-Benzyl-7-fluoro-3-(furan-2-yl)-3-hydroxyindolin-2-one (1f).



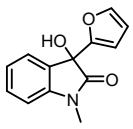
Following the general procedure N-benzyl-7-fluoroisatin (0.17g, 0.67mmol) was transformed into compound **1f** which was isolated as brown solid in 66% (0.143g) yield. R_f 0.4 (EtOAc: Hexane 3:7); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 -7.39 (m, 1H), 7.33 (dd, *J* = 6.9, 1.4 Hz, 1H), 7.26 - 7.20 (m, 5H), 7.02 - 6.93 (m, 2H), 6.32-6.32 (m, 1H), 6.29-6.27 (m, 1H), 5.06 - 4.96 (m, 2H), 4.18 (s, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 175.2, 151.0, 148.86, 146.4, 144.2, 136.4, 131.2, 128.8, 127.8, 127.4, 124.4, 124.3, 121.5, 118.5, 118.3, 110.6, 109.2, 73.7, 45.7; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{19}H_{14}FNNaO_3$ calcd. 346.0855, found, 346.0891.

1-Benzyl-7-chloro-3-(furan-2-yl)-3-hydroxyindolin-2-one (1g).



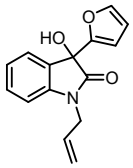
Following the general procedure N-benzyl-7-chloroisatin (0.170g, 0.63 mmol) was transformed into compound **1g** which was isolated as red solid in 68% (0.14g) yield. R_f 0.35 (EtOAc: Hexane 3:7); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47-7.45 (m, 1H), 7.37-7.37 (m, 1H), 7.26 - 7.14 (m, 6H), 6.97 (t, *J* = 7.8 Hz, 1H), 6.34 - 6.34(m, 1H), 6.27-6.26 (m, 1H), 5.30 (s, 2H), 4.72 (s, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 176.2, 151.0, 144.0, 138.6, 136.9, 132.6, 131.5, 128.7, 127.3, 126.3, 124.5, 124.3, 116.0, 110.5, 109.2, 73.2, 45.1; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{19}H_{14}ClNNaO_3$ calcd. 362.0560, found, 362.0564.

3-(Furan-2-yl)-3-hydroxy-1-methylindolin-2-one (1h).



Following the general procedure N-methylisatin (0.08 g, 0.49 mmol) was transformed into compound **1h** which was isolated as brown solid in 48% (0.055g) yield. R_f 0.35 (EtOAc: Hexane 3:7); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.3 Hz, 1H), 7.42 (s, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.31 (s, 2H), 3.96 (s, 1H), 3.21 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 175.3, 151.4, 144.0, 143.6, 130.4, 128.4, 125.5, 123.5, 110.5, 109.1, 108.8, 73.6, 26.6; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{13}H_{11}NNaO_3$ calcd. 252.0637, found, 252.0666.

1-Allyl-3-(furan-2-yl)-3-hydroxyindolin-2-one (1i).

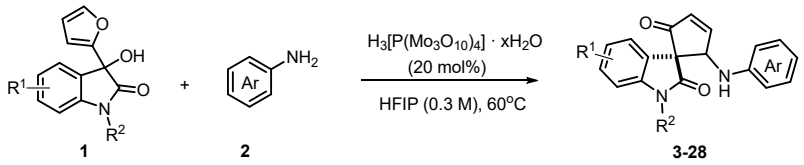


Following the general procedure N-allyl isatin (0.20g, 1.07 mmol) was transformed into compound **1i** which was isolated as yellow solid in 59% (0.16g) yield. R_f 0.4 (EtOAc: Hexane 3:7); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.4 Hz, 1H), 7.35 (s, 1H), 7.26 (t, *J* = 7.7 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 7.8 Hz, 1H), 6.29 (m, 1H), 6.25-6.24 (m, 1H), 5.81- 5.72 (m, 1H), 5.18 - 5.13 (m, 2H), 4.41 (s, 1H), 4.35 (dd, *J* = 16.4, 4.9 Hz, 1H), 4.19 (dd, *J* = 16.4, 4.9 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 175.1, 151.5, 143.8, 142.6, 130.8, 130.1, 128.6, 125.5, 123.4, 117.7, 110.4, 109.6, 108.8, 73.6, 42.5; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{15}H_{13}NNaO_3$ calcd. 278.0793, found, 278.0832.

Reference:

1. Y. -Y. Zhang, H. Chen, X. Jiang, H. Liang, X. He, Y. Zhang, X. Chen, W. He, Y. Li and L. Qiu, *Tetrahedron,* 2018, **74**, 2245-2250

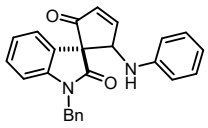
3. General procedure for *aza*-Piancatelli rearrangement.



To a solution of compound **1** (1.0 equiv) and aniline (**2**, 2.0 equiv) in HFIP (0.3M), was added phosphomolybdic acid (20 mol%). The reaction mixture was stirred at 60 °C (sealed tube was used) and the progress of the reaction was monitored by TLC. After completion of the reaction (*ca*. 24 h), HFIP was removed under the reduced pressure. The crude was diluted with ethyl acetate and washed with water and brine (10 mL x 3). The combined organic layer was then dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under *vacuo* and crude residue was purified by silica gel column chromatography to obtain spirocyclic oxindoles **3, 5-28**.

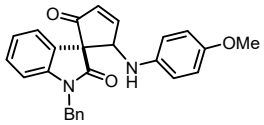
4. Characterization data of the compounds (3-28)

1'-Benzyl-5-(phenylamino)spiro[cyclopentane-1,3'-indolin]-3-ene-2,2'-dione (3).



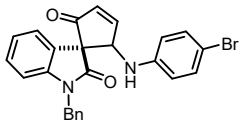
Following the general procedure, reaction of compound **1a** (0.035g, 0.11 mmol ,1.0 equiv) and aniline (0.022g, 0.23 mmol, 2.0 equiv) in presence of PMA (0.04 g, 0.02 mmol) delivered compound **3**, which was purified by silica gel chromatography (7:3 Hexane: EtOAc) to furnish the title compound in 71% (0.031g) yield as an inseparable mixture of diastereomers (1:1). R_f 0.4 (EtOAC: Hexane 3:7); **^{1}H NMR** (800 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 5.4, 1.5 Hz, 1H), 7.51 (s, 1H), 7.43 (t, *J* = 7.7 Hz, 1.67H), 7.30 - 7.22 (m, 8H), 7.16 -7.13 (m, 4H), 7.11 -7.07 (m, 4H), 7.04 -7.00 (m, 3H), 6.98 - 6.93 (m, 3H), 6.78 (d, *J* = 7.2 Hz, 0.72H), 6.76 (d, *J* = 7.4 Hz, 1.79H), 6.66 (t, *J* = 7.1 Hz, 0.86H), 6.56-6.53 (m, 3.57H), 6.50 (d, *J* = 7.7 Hz, 0.86H), 6.38 (d, *J* = 7.9 Hz, 1.71H), 5.94 (s, 0.62H), 5.46 (s, 1H), 5.38 (d, *J* = 11.3 Hz, 1H), 5.09 (d, *J* = 12.0 Hz, 0.83H), 4.99 (d, *J* = 16.2 Hz, 1H), 4.89 (d, *J* = 15.9 Hz, 1.26H), 4.84 (d, *J* = 15.9 Hz, 1.1H), 4.59 (d, *J* = 16.2 Hz, 1H); **^{13}C{^{1}H} NMR** (200 MHz, $CDCl_3$) δ 200.2, 194.9, 174.4, 172.6, 169.7, 164.1, 145,6, 145.4, 144.5, 143.7, 138.8, 135.1, 135.0, 134.6, 129.8, 129.6, 129.4, 129.2, 129.0, 128.9, 127.6, 127.3, 127.1, 126.6, 125.6, 125.3, 123.4, 123.1, 122.7, 122.0, 121.1, 120.3, 119.2, 115.1, 114.2, 110.3, 110.1, 101.8, 66.8, 65.7 61.8, 61.1, 44.2, 44.1. **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{25}H_{20}N_2NaO_2$ calcd. 403.1422, found, 403.1419.

1'-Benzyl-2-((4-methoxyphenyl)amino)spiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione (5).



Following the general procedure, reaction of compound **1a** (0.04 g, 0.13 mmol, 1.0 equiv) and 4-methoxyaniline **2c** (0.033 g, 0.26 mmol, 2.0 equiv) in presence of PMA (0.048 g, 0.03 mmol) delivered compound **5**, which was purified by silica gel column chromatography (7:3 Hexane: EtOAc) to furnish the title compound (brown semi solid) in 52% (0.028 g) yield as an inseparable mixture of diastereomers (2:1 *dr*). R_f 0.3 (EtOAc: Hexane 3:7); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 54.1 Hz, 1H), 7.26 - 7.21 (m, 4H), 7.18-7.17 (m, 2H), 7.13 - 7.08 (m, 3H), 7.02-6.88 (m, 4H), 6.75 (d, *J* = 7.2 Hz, 1H), 6.56 (t, *J* = 8.0 Hz, 2H), 6.50 (d, *J* = 7.6 Hz, 1H), 6.44 (d, *J* = 8.6 Hz, 0.86H), 6.38 (d, *J* = 8.5 Hz, 1H), 5.71 (d, *J* = 24.1 Hz, 1H), 5.47 (brs, 0.52H), 5.25 (d, *J* = 11.7 Hz, 0.43H), 4.97 (d, *J* = 16.2 Hz, 1H), 4.89 (d, *J* = 12.5 Hz, 0.51H), 4.60 (dd, *J* = 26.2, 16.1 Hz, 1H), 3.84 (s, 3H), 3.69 (s, 1.37H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 194.9, 194.6, 175.7, 172.7, 171.0, 170.6, 157.6, 154.0, 153.7, 144.6, 143.7, 139.3, 139.0, 135.2, 131.8, 131.7, 129.1, 128.8, 128.7, 127.4, 127.3, 126.7(2), 125.9, 123.2, 123.0, 122.6, 117.3, 116.5, 115.0, 114.9(2), 110.3, 110.0, 100.6, 99.8, 66.1, 65.6, 62.4, 61.9, 55.7, 55.6, 44.1, 44.0; **HRMS(ESI-TOF)** m/z: $[M + H]^+$ $C_{26}H_{23}N_2O_3$ calcd. 411.1709, found, 411.1692.

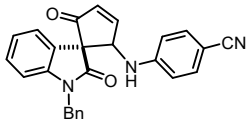
1'-Benzyl-2-((4-bromophenyl)amino)spiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione (6).



Following the general procedure, reaction of compound **1a** (0.04 g, 0.13 mmol, 1.0 equiv) and 4-bromoaniline **2d** (0.045 g, 0.26 mmol, 2.0 equiv) furnished spirooxindole **6**, which was purified by silica gel column chromatography (7:3 Hex: EtOAc) to afford the title compound (brown solid) in 53% (0.032 g) yield as inseparable mixture of diastereomers (*dr n.d*). R_f 0.4 (EtOAc: Hexane 3:7); mp. 117-120 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (m, 1H), 7.47 (d, *J* = 9.5 Hz, 0.53H), 7.26 -7.23 (m, 2.50H), 7.15 (d, *J* = 7.0 Hz, 5H), 7.08 -7.04 (m, 3H), 6.98-6.96 (m, 1.52H), 6.81 (d, *J* = 5.4 Hz, 1.33H), 6.57 (d, *J* = 6.9 Hz, 1H), 6.50-6.49 (m, 1.32H), 6.26 (d, *J* = 7.8 Hz, 1.44H), 6.20 (d, *J* = 7.8 Hz, 0.72H), 5.33 (d, *J* = 5.7 Hz, 0.34 H), 5.20 (d, *J* = 10.7 Hz, 0.72H), 4.89 (dt, *J* = 31.8, 14.5 Hz, 2.74H), 4.55 (d, *J* = 16.1 Hz, 0.84H), 4.11 (d, *J* = 9.2 Hz, 0.56H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 200.3, 200.0, 174.3, 171.4, 163.6, 144.8, 144.5, 144.4, 143.7, 135.0, 134.7(2), 132.2, 132.1, 129.3(2), 129.0, 128.9, 128.8, 127.8, 127.6, 127.1, 126.6, 123.6, 123.2, 122.7, 122.0,

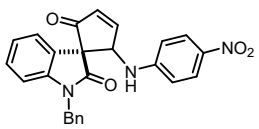
115.8, 115.5,110.9, 110.3, 110.2, 66.6, 66.3, 62.5, 61.6, 44.2, 44.1; **HRMS (ESI-TOF)** m/z: $[M + H]^+$ $C_{25}H_{20}BrN_2O_2$ calcd. 459.0708, found, 459.0698.

4-((1'-Benzyl-2,2'-dioxospiro[cyclopentane-1,3'-indolin]-3-en-5-yl)amino)benzonitrile(7).



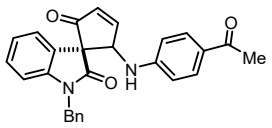
Following the general procedure, reaction of compound **1a** (0.05 g, 0.16 mmol, 1.0 equiv) and 4-aminobenzonitrile **2e** (0.039 g, 0.33 mmol, 2.0 equiv) in presence of PMA (0.06 g, 0.033 mmol) delivered spirooxindole **7**, which was purified by silica gel column chromatography (Hexane/EtOAc6:4) to furnish the title compound (red solid) in 65% (0.043 g) yield as inseparable mixture of diastereomers (2.1:1 *dr*). R_f 0.4 (EtOAc: Hexane 4:6); mp. 203-205 °C; **FT-IR** (ν cm^{-1}): 3355, 2926, 2215, 1726, 1695, 1604, 1528, 1491, 1468, 1345, 1174; **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 8.26 (dd, *J* = 5.2, 1.6 Hz, 0.47H), 8.13 (d, *J* = 4.1 Hz, 1H), 7.52 (d, *J* = 8.8 Hz, 1H), 7.42 (d, *J* = 7.3 Hz, 1H), 7.36 (d, *J* = 3.8 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 3H), 7.14 (m, *J* = 13.1, 7.1 Hz, 3H), 7.07 (t, *J* = 7.7 Hz, 2H), 6.91 (d, *J* = 7.4 Hz, 2H), 6.85 (t, *J* = 7.7 Hz, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 6.71-6.67(m,1H), 6.37 (d, *J* = 7.7 Hz, 2H), 6.28 (d, *J* = 8.3 Hz, 1H), 5.49 (d, *J* = 8.7 Hz, 1H), 5.21 (d, *J* = 8.7 Hz, 0.46H), 4.94-4.90 (m, 2H), 4.63 (d, *J* = 16.0 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-*d6*) δ 201.1, 200.9, 173.8, 170.4, 165.9, 165.5, 150.5, 150.2, 143.8, 143.3, 135.9, 135.5, 133.4, 133.3, 133.2, 128.9, 128.6 (2), 128.4, 128.3, 127.5, 127.1, 126.7, 125.0, 124.6, 123.0 (2), 122.2, 120.1, 120.0, 113.4, 112.4, 109.4, 97.2, 97.1, 66.7, 65.6, 61.6, 60.0, 43.0, 42.7; **HRMS(ESI-TOF)** m/z: $[M+ Na]^+$ $C_{26}H_{19}N_3NaO_2$ calcd. 428.1375, found, 428.1370.

1'-Benzyl-2-((4-nitrophenyl)amino)spiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione(8).



Following the general procedure, reaction of compound **1a** (0.05 g, 0.16 mmol, 1.0 equiv) and 4-nitroaniline **2f** (0.045 g, 0.32 mmol, 2.0 equiv) in presence of PMA (0.06 g, 0.032 mmol) delivered spirooxindole **8**, which was purified by silica gel column chromatography (Hexane: EtOAc 5:5) to furnish the title compound (yellow solid) in 69% (0.048 g) yield as inseparable mixture of diastereomers (2.5:1 *dr*). R_f 0.35 (EtOAc: Hexane 6:4); mp. 175-177 °C; **FT-IR** (ν cm^{-1}): 3341, 2928, 1726, 1695, 1599,1505, 1485, 1467, 1321, 1112; **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 8.28 - 7.94 (m, 4H), 7.75 - 7.65 (m, 3H), 7.44 - 7.28 (m, 4H), 7.13 - 7.09 (m, 3H), 6.99-6.92(m, 5H), 6.82 (d, *J* = 5.9 Hz, 1H), 6.72 (s, 1H), 6.35-6.29(m, 3H), 5.55 (d, *J* = 5.5 Hz, 1H), 5.27 (d, *J* = 6.3 Hz, 0.41H), 4.92 (d, *J* = 15.3 Hz, 2H), 4.62 (d, *J* = 15.6 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-*d6*) δ 201.0, 200.8, 173.6, 170.3, 165.5, 165.1, 152.9, 143.4, 136.7, 136.0, 135.5, 133.7, 129.1, 128.6, 128.3, 128.2, 127.6, 127.1, 126.7, 125.8, 123.1, 112.4, 109.5, 66.7, 65.5, 61.8, 60.1, 43.1, 42.8; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{25}H_{19}N_3NaO_4$ calcd. 448.1273, found, 448.1279.

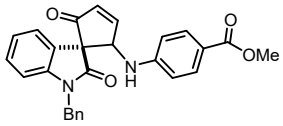
2-((4-Acetylphenyl)amino)-1'-benzylspiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione(9).



Following the general procedure, reaction of compound **1a** (0.050 g, 0.16 mmol, 1.0 equiv) and 1-(4-aminophenyl)ethan-1-one **2g** (0.045 g, 0.33 mmol, 2.0 equiv) in presence of PMA (0.06 g, 0.033 mmol) delivered spirooxindole **9**, which was purified by silica gel column chromatography (Hexane: EtOAc 5:5) to furnish the title compound as (red solid) in 78% (0.054 g) yield as inseparable mixture of diastereomers (1.4:1 *dr*). R_f 0.3 (EtOAc: Hexane 5:5); mp. 174-176 °C; **FT-IR** (ν cm^{-1}): 3354, 2924, 2852, 1728, 1699, 1597, 1523, 1488, 1468, 1358, 1274, 1181; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (ddd, *J* = 10.7, 5.6, 1.9 Hz, 2H), 7.65 (d, *J* = 8.6 Hz, 2H), 7.55 (d, *J* = 8.6 Hz, 1.5H), 7.28 - 7.22 (m, 4.41H), 7.19 (d, *J* = 8.0 Hz, 1.8H), 7.14-7.04 (m, 4.9H), 6.98 (d, *J* = 7.3 Hz, 0.8H), 6.92-6.88 (m, 2.70H), 6.63 (dd, *J* = 7.7, 3.4 Hz, 1.82H), 6.58 - 6.54 (m, 1.74H), 6.41 (d, *J* = 8.6 Hz, 2H), 6.35 (d, *J* = 8.6 Hz, 1.44H), 5.46 - 5.29 (m, 2.94H), 4.95-4.90 (m, 2.39H), 4.65-4.60 (m, 1.65H), 2.45 (s, 3H), 2.41 (s, 2.23 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 200.0, 199.9, 196.5(2), 174.1, 171.3, 162.9(2), 150.0, 149.7, 144.3, 143.7, 135.1, 135.0, 134.9, 134.6, 130.9, 130.8, 130.7, 129.5, 129.4, 129.0, 128.8, 128.5, 128.3,128.1, 127.8, 127.6, 127.3,126.7,

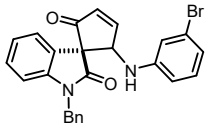
124.9,123.7, 123.6,122.8, 122.2, 113.8, 112.8, 112.4, 110.3, 66.5, 66.4, 61.8, 60.6, 44.2, 44.1, 26.2(2).; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{27}H_{22}N_2NaO_3$ calcd. 445.1528, found, 445.1546.

Methyl 4-((1'-benzyl-2,2'-dioxospiro[cyclopentane-1,3'-indolin]-3-en-5-yl)amino)benzoate(10).



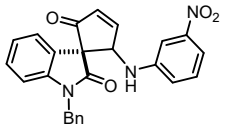
Following the general procedure, reaction of compound **1a** (0.050 g, 0.16 mmol, 1.0 equiv) and methyl 4-aminobenzoate **2h** (0.05 g, 0.33 mmol, 2.0 equiv) in presence of PMA (0.06 g, 0.033 mmol) delivered spirooxindole **10**, which was purified by silica gel column chromatography (Hexane: EtOAc 6:4) to furnish the title compound as (red solid) in 80% (0.058 g) yield as inseparable mixture of diastereomers (1:1 *dr*). R_f 0.35 (EtOAc: Hexane 6:4); mp. 169-171 °C; **FT-IR** (ν cm^{-1}): 3364, 2919, 1701, 1604, 1528, 1488, 1468, 1432, 1347, 1281, 1177, 1109; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (m, 1.92H), 7.67 (d, *J* = 8.6 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.26 - 7.24 (m, 3H), 7.21-7.14(m, 4H), 7.12-7.04 (m, 5H), 6.95 (d, *J* = 7.3 Hz, 1H), 6.88-6.85 (m, 3H), 6.58 (d, *J* = 7.5 Hz, 2H), 6.53 - 6.48 (m, 2H), 6.37 (d, *J* = 8.6 Hz, 2H), 6.31 (d, *J* = 8.6 Hz, 1.42H), 5.40 (d, *J* = 9.7 Hz, 0.84H), 5.32 (q, *J* = 10.8 Hz, 2H), 4.90-4.87 (m, 2H), 4.62 - 4.56 (m, 2H), 3.81 (s, 3H), 3.79 (s, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 200.0, 199.9, 174.1, 171.4, 167.0(2), 163.0, 149.7, 149.4, 144.4, 143.7, 135.0(2), 134.9, 134.6, 131.7, 131.5, 129.5, 129.4, 129.0, 128.8, 127.8, 127.6, 127.2, 126.6, 124.9, 123.7, 123.5, 122.8, 122.2, 120.3, 120.2, 112.9, 112.5, 110.3, 110.2, 66.5, 64.4, 61.9, 60.7, 51.8, 51.7, 44.3, 44.1; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{27}H_{22}N_2NaO_4$ calcd. 461.1477, found, 461.1491.

1'-Benzyl-2-((3-bromophenyl)amino)spiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione(11).



Following the general procedure, reaction of compound **1a** (0.050 g, 0.16 mmol, 1.0 equiv) and 3-bromoaniline **2i** (0.057 g, 0.33 mmol, 2.0 equiv) in presence of PMA (0.06 g, 0.033 mmol) delivered spirooxindole **11**, which was purified by silica gel column chromatography (Hexane/EtOAc 7:3) to furnish the title compound as (brown solid) in 49% (0.037 g) yield as inseparable mixture of diastereomers (1.8:1 *dr*). R_f 0.3 (EtOAc: Hexane 3:7); mp. 105-107 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 - 7.86 (m, 1.47H), 7.29-7.26 (m, 2.37 H), 7.23 -7.16 (m, 6.29H), 7.11 (t, *J* = 7.5 Hz, 2H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.92 (d, *J* = 7.2 Hz, 2.37H), 6.85 - 6.82 (m, 1.87H), 6.81 - 6.77 (m, 1.41H), 6.63 - 6.58 (m, 1.77 H), 6.56- 6.50 (m, 3.2H), 6.35 (d, *J* = 7.5 Hz, 1H), 6.30 (dd, *J* = 7.1, 1.9 Hz, 0.52 H), 5.36 (d, *J* = 10.1 Hz, 0.55H), 5.22 (d, *J* = 11.1 Hz, 1H), 5.04-4.98 (m, 1.60 H), 4.91 (d, *J* = 16.0 Hz, 1H), 4.80 (d, *J* = 15.9 Hz, 0.62H), 4.66 (d, *J* = 16.0 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 200.2, 199.9, 174.3, 171.4, 163.3(2), 147.1, 146.8, 144.5, 143.8, 135.1, 134.8(2), 130.7, 130.6, 129.4(2), 129.0, 128.9, 128.7, 127.7, 127.6, 127.0, 126.7, 125.0, 123.7, 123.3, 123.2, 123.1, 122.8(2), 122.2, 122.0, 117.0 (2), 112.9, 112.4, 110.3(2), 66.6, 66.5, 62.5, 61.5, 44.3, 44.1; **HRMS (ESI-TOF)** m/z: $[M + H]^+$ $C_{25}H_{20}BrN_2O_2$ calcd. 459.0708, found, 459.0700.

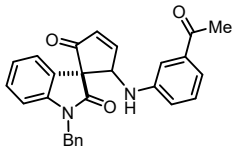
1'-Benzyl-2-((3-nitrophenyl)amino)spiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione (12).



Following the general procedure, reaction of 1-benzyl-3-(furan-2-yl)-3-hydroxyindolin-2-one **1a** (0.050 g, 0.1637 mmol, 1.0 equiv) and 3-nitroaniline **2j** (0.045 g, 0.3275 mmol, 2.0 equiv) in presence of PMA (0.060 g, 0.033 mmol) delivered spirooxindole **12**, which was purified by silica gel column chromatography (Hexane:EtOAc 5:5) to furnish the title compound as (red solid) in 79% (0.055 g) yield as inseparable mixture of diastereomers (1.6:1 *dr*). R_f 0.3 (EtOAc: Hexane 5:5); mp. 121-123 °C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 8.31 - 8.27 (m, 0.63H), 8.14 (d, *J* = 4.3 Hz, 1H), 7.46 (d, *J* = 7.2 Hz, 1H), 7.31 - 7.23 (m, 6.67H), 7.19 - 7.09 (m, 4.2H), 7.05-7.00 (m, 3.63H), 6.88 (d, *J* = 7.6 Hz, 2.65H), 6.80 - 6.75 (m, 2.40H), 6.72 - 6.63 (m, 1.67H), 5.48 (d, *J* =

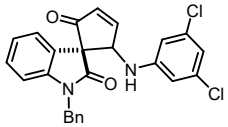
8.8 Hz, 1H), 5.26 (d, *J* = 8.8 Hz, 0.43H), 5.01 (d, *J* = 15.9 Hz, 0.50H), 4.85 (t, *J* = 16.0 Hz, 1.50H), 4.62 (d, *J* = 16.0 Hz, 0.95H); **$^{13}C\{^{1}H\}$ NMR** (100 MHz, DMSO-*d6*) δ 201.2, 201.0, 173.9, 170.4, 166.1, 165.6, 148.6, 148.4, 148.0, 147.8, 143.8, 143.3, 135.9, 135.5, 133.4, 133.2, 129.9, 129.8, 128.9, 128.6, 128.5, 128.3, 127.5, 127.1(2), 126.5, 125.1, 124.6, 123.0(2), 122.2, 119.2, 118.4, 111.0 (2), 109.4, 109.3, 105.8, 105.6, 66.7, 65.7, 62.4, 60.6, 42.9, 42.8; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{25}H_{19}N_3NaO_4$ calcd. 448.1273, found, 448.1285.

2-((3-Acetylphenyl)amino)-1'-benzylspiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione(13).



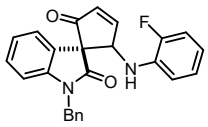
Following the general procedure, reaction of 1-benzyl-3-(furan-2-yl)-3-hydroxyindolin-2-one **1a** (0.050 g, 0.164 mmol, 1.0 equiv) and 1-(3-aminophenyl)ethan-1-one **2k** (0.045 g, 0.33 mmol, 2.0 equiv) in presence of PMA (0.06 g, 0.033 mmol) delivered spirooxindole **13**, which was purified by silica gel column chromatography (Hexane: EtOAc 5:5) to furnish the title compound as (red solid) in 75% (0.052 g) yield as inseparable mixture of diastereomers (2:1 *dr*). R_f 0.3 (EtOAc: Hexane 5:5); mp. 121-123 °C; **FT-IR** (ν cm^{-1}): 3363, 2927, 1722, 1693, 1601, 1488, 1468, 1436, 1361, 1268, 1240, 1159; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 - 7.94 (m, 0.47H), 7.92 (dd, *J* = 5.7, 2.2 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 1.2H), 7.23 (d, 2.12H), 7.21(s,1.31H), 7.19-7.16 (m, 2H), 7.13 (d, *J* = 7.7 Hz, 2H), 7.09 (d, *J* = 7.6 Hz, 2.31H), 7.07 - 7.05 (m, 0.87H), 7.03 -7.00 (m, 1H), 6.93 (d, *J* = 10.7 Hz, 2H), 6.85 (d, *J* = 7.3 Hz, 2H), 6.71 (dd, *J* = 8.0, 2.1 Hz, 1H), 6.62- 6.52 (m, 3.80H), 5.46 (d, *J* = 7.6 Hz, 0.60H), 5.35 (d, *J* = 11.2 Hz, 1H), 5.10 (d, *J* = 11.3 Hz, 1H), 4.99 (d, *J* = 15.9 Hz, 0.68H), 4.89 (d, *J* = 16.0 Hz, 1H), 4.76 (d, *J* = 16.0 Hz, 0.65H), 4.63 (d, *J* = 16.0 Hz, 1H), 2.43 (s, 1.77H), 2.21 (s, 3H); **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$) δ 200.2, 199.9, 198.1, 198.0, 174.25, 171.4, 163.5, 163.4, 146.0, 145.8, 144.5, 143.8, 138.3, 138.1, 135.1, 134.8(2), 129.7, 129.6, 129.3(2) 129.0, 128.9, 128.9, 127.7, 127.6, 127.0, 126.7, 125.0, 123.7, 123.3, 122.8, 122.3, 119.6, 119.3, 119.2, 118.2, 113.7, 112.7, 110.3, 110.2, 66.6, 66.4, 62.5, 61.6, 44.2, 26.7, 26.5; **HRMS (ESI-TOF)** m/z: $[M + Na]^+$ $C_{27}H_{22}N_2NaO_3$ calcd. 445.1528, found, 445.1542.

1'-Benzyl-2-((3,5-dichlorophenyl)amino)spiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione(14).



Following the general procedure, reaction of 1-benzyl-3-(furan-2-yl)-3-hydroxyindolin-2-one **1a** (0.050 g, 0.164 mmol, 1.0 equiv) and 3,5-dichloroaniline **2l** (0.053 g, 0.33 mmol, 2.0 equiv) in presence of PMA (0.06 g, 0.033 mmol) delivered compound **14**, which was purified by silica gel column chromatography (Hexane: EtOAc 8:2) to furnish the title compound as (brown solid) in 76% (0.056 g) yield as inseparable mixture of diastereomers (>20:1 *dr*). R_f 0.4 (EtOAc: Hexane 2:8); mp. 229-230 °C; **FT-IR** (ν cm^{-1}): 3359, 2927, 2855, 1725, 1693, 1592, 1488, 1466, 1453, 1361, 1162; **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 8.10 (d, *J* = 4.6 Hz, 1H), 7.44 (d, *J* = 7.3 Hz, 1H), 7.27 (t, *J* = 7.6 Hz, 1H), 7.19-7.14 (m, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 7.3 Hz, 2H), 6.78 (d, *J* = 7.7 Hz, 1H), 6.66 (d, *J* = 4.5 Hz, 1H), 6.57 (s, 1H), 6.24 (s, 2H), 5.41 (s, 1H), 4.92 (d, *J* = 16.1 Hz, 1H), 4.66 (d, *J* = 16.1 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-*d6*) δ 200.9, 170.4, 165.5, 149.1, 149.0, 143.4, 135.6, 134.3, 133.4, 128.9, 128.5, 128.4, 127.1, 126.5, 123.1, 123.0, 122.9, 115.5, 110.8, 109.5, 67.0, 62.1, 42.8; **HRMS (ESI-TOF)** m/z: $[M + Na]^+$ $C_{25}H_{18}Cl_2N_2NaO_2$ calcd. 471.0643, found, 471.0652.

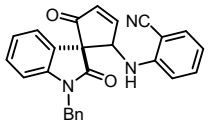
1'-Benzyl-2-((2-fluorophenyl)amino)spiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione(15).



Following the general procedure, reaction of 1-benzyl-3-(furan-2-yl)-3-hydroxyindolin-2-one **1a** (0.050 g, 0.16 mmol, 1.0 equiv) and 2-fluoroaniline **2m** (0.037 g, 0.33 mmol, 2.0 equiv) in presence of PMA (0.06 g, 0.033 mmol) delivered compound **15**, which was purified by silica gel column chromatography (Hexane: EtOAc 9:1) to furnish the title compound (yellow solid) in 74% (0.048 g) yield as inseparable mixture of diastereomers (1.1:1 *dr*). R_f 0.35 (EtOAc: Hexane 1:9); mp. 137-139 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 5.6, 2.3 Hz, 0.89H), 8.00 (dd, *J* = 5.7, 2.2 Hz, 1H), 7.38-7.33(m, 3H), 7.29 (dd, *J* = 7.5, 1.5 Hz, 2H), 7.24 - 7.22 (m, 3.48H), 7.19-7.13 (m, 2H), 7.09 (d, *J* = 6.8 Hz, 0.90H), 7.06 - 6.98 (m, 4H), 6.85 -6.71 (m, 3.82H), 6.68-6.60 (m,

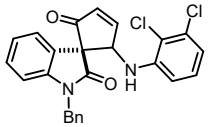
5.62H), 6.40- 6.36 (m, 1H), 5.52 (d, *J* = 10.7 Hz, 0.89H), 5.37 (d, *J* = 11.3 Hz, 1H), 5.18 (dd, *J* = 11.3, 2.2 Hz, 1H), 4.99 (dd, *J* = 15.9, 7.4 Hz, 2H), 4.91 (d, *J* = 15.9 Hz, 0.92H), 4.74 (d, *J* = 16.0 Hz, 1H), 4.41 (dd, *J* = 10.7, 3.1 Hz, 0.84H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 200.1, 200.0, 174.4, 171.2, 163.5, 163.4, 144.3, 143.9, 135.2, 134.9, 134.8, 134.3, 134.2, 134.0, 133.9, 129.3, 129.2, 129.0, 128.9, 128.7, 127.7, 127.5, 127.2, 126.8, 125.0, 124.6 (2), 124.5(2), 123.5, 123.2, 122.8, 122.2, 118.8(2), 118.7, 118.6, 115.3, 115.2, 114.8, 114.6, 113.3(2), 110.1, 110.0, 66.7, 66.5, 62.2, 61.1, 44.2, 44.1; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{25}H_{19}FN_2NaO_2$ calcd. 421.1328, found, 421.1323.

2-((1'-Benzyl-2,2'-dioxospiro[cyclopentane-1,3'-indolin]-3-en-5-yl)amino)benzonitrile(16).



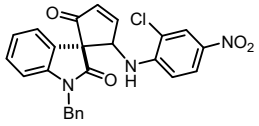
Following the general procedure, reaction of 1-benzyl-3-(furan-2-yl)-3-hydroxyindolin-2-one **1a** (0.050 g, 0.164 mmol, 1.0 equiv) and 2-aminobenzonitrile **2n** (0.039 g, 0.33 mmol, 2.0 equiv) in presence of PMA (0.06 g, 0.033 mmol) delivered compound **16**, which was purified by silica gel column chromatography (Hexane: EtOAc 6:4) to furnish the title compound as (red solid) in 81% (0.054 g) yield as inseparable mixture of diastereomers (1:1 *dr*). R_f 0.4 (EtOAc: Hexane 4:6); mp. 152-154 °C; **FT-IR** (ν cm^{-1}): 3364, 3027, 2215, 1726, 1698, 1604, 1582, 1519, 1485, 1466, 1451, 1366, 1162; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 16.1, 4.1 Hz, 2H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.28 - 7.26 (m, 6.31H), 7.21 - 7.07 (m, 10H), 7.01-6.96 (m, 3.88H), 6.72-6.59 (m, 6.21H), 6.46 (d, *J* = 8.4 Hz, 1H), 6.24 (d, *J* = 8.4 Hz, 1H), 5.66 (d, *J* = 10.2 Hz, 0.94H), 5.46 (d, *J* = 9.6 Hz, 1H), 5.31 (d, *J* = 10.3 Hz, 1H), 4.97-4.90 (m, 4H), 4.65 (d, *J* = 15.8 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 199.5, 174.1, 170.9, 162.3, 148.1, 148.0, 147.8, 144.1, 144.0, 143.9, 135.3, 135.2, 135.1, 134.9, 134.5, 134.3, 134.1, 133.4, 132.8, 129.5, 129.4, 128.9, 128.8, 128.3, 127.8, 127.5, 127.4, 127.0, 124.6, 123.7, 123.5, 123.3, 122.3, 118.5, 118.3, 117.0, 111.9, 111.5, 110.1, 110.0, 98.3, 97.1, 66.3, 66.0, 61.7, 60.4, 44.2(2); **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{26}H_{19}N_3NaO_2$ calcd. 428.1375, found, 428.1372.

1'-Benzyl-2-((2,3-dichlorophenyl)amino)spiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione(17).



Following the general procedure, reaction of 1-benzyl-3-(furan-2-yl)-3-hydroxyindolin-2-one **1a** (0.050 g, 0.164 mmol, 1.0 equiv) and 2,3-dichloroaniline **2o** (0.053 g, 0.33 mmol, 2.0 equiv) in presence of PMA (0.060 g, 0.033 mmol) delivered compound **17**, which was purified by silica gel column chromatography (Hexane: EtOAc 8:2) to furnish the title compound (brown solid) in 76% (0.056 g) yield as inseparable mixture of diastereomers (1.5:1 *dr*). R_f 0.4 (EtOAc: Hexane 2:8); mp. 154-156 °C **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 5.6, 2.2 Hz, 0.66H), 7.87 (dd, *J* = 5.7, 2.1 Hz, 1H), 7.24 -7.19 (m, 4H), 7.17 - 7.11 (m, 4.70H), 7.06 (t, *J* = 7.6 Hz, 1.73H), 6.98 (d, *J* = 7.2 Hz, 0.69H), 6.92-6.87 (m, 2.84H), 6.74 (dd, *J* = 8.0, 1.1 Hz, 1H), 6.70-6.66(m, 2.36H), 6.63-6.57 (m, 1.80H), 6.55 -6.52 (m, 1.72H), 6.35 -6.33(m, 0.68H), 6.12 (d, *J* = 8.0 Hz, 1H), 5.61 (d, *J* = 10.7 Hz, 1H), 5.38 (d, *J* = 9.9 Hz, 0.70H), 5.24 (d, *J* = 10.7 Hz, 1H), 4.96 (d, *J* = 15.8 Hz, 1H), 4.87-4.81 (m, 2H), 4.56 (d, *J* = 15.8 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 199.8, 199.7, 174.2, 171.0, 162.8, 162.7, 144.1, 143.9, 143.4, 143.1, 135.1(2), 135.0, 134.8, 133.6, 133.1, 129.4(2), 129.0, 128.8, 128.5, 127.8, 127.7, 127.6(2), 127.3, 126.9, 124.7, 123.5(2), 123.0, 122.3, 119.7, 119.6, 118.7, 117.7, 110.1(2), 110.0, 109.8, 66.7, 66.2, 62.0, 61.0, 44.2(2); **HRMS (ESI-TOF)** m/z: $[M + Na]^+$ $C_{25}H_{18}Cl_2N_2NaO_2$ calcd. 471.0643, found, 471.0649.

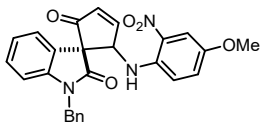
1'-Benzyl-2-((2-chloro-4-nitrophenyl)amino)spiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione(18).



Following the general procedure, reaction of 1-benzyl-3-(furan-2-yl)-3-hydroxyindolin-2-one **1a** (0.050 g, 0.164 mmol, 1.0 equiv) and 2-chloro-4-nitroaniline **2p** (0.056 g, 0.33 mmol, 2.0 equiv) in presence of PMA (0.060 g, 0.033 mmol) delivered spirooxindole **18**, which was purified by silica gel column chromatography (Hexane:EtOAc 6:4) to furnish the title compound (red solid) in 73% (0.055g) yield as inseparable mixture of diastereomers (>20:1 *dr*). R_f 0.4 (EtOAc: Hexane

5:5); mp. 182-184 °C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 8.28 (dd, *J* = 5.2, 1.9 Hz, 0.26H), 8.24 (dd, *J* = 5.4, 1.5 Hz, 1H), 8.17 (d, *J* = 2.3 Hz, 1H), 7.94 (d, *J* = 2.3 Hz, 0.21H), 7.66 (dd, *J* = 9.2, 2.2 Hz, 1H), 7.50-7.48(m, 0.30 H), 7.44 (d, *J* = 7.4 Hz, 1H), 7.40-7.35 (m, 1H), 7.30 (t, *J* = 7.7 Hz, 1.74H), 7.15-7.03(m, 4.33H), 6.93 (d, *J* = 7.8 Hz, 2H), 6.85 (d, *J* = 9.2 Hz, 1H), 6.72 (dd, *J* = 5.4Hz, 1.24H), 6.45 (d, *J* = 9.3 Hz, 1H), 6.71(m, 1H), 6.4 (d, *J* = 9.1 Hz, 0.22H), 5.81 (d, *J* = 8.8 Hz, 1H), 4.93 (d, *J* = 15.6 Hz, 1.33H), 4.70 (d, *J* = 15.8 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-*d6*) δ 200.7, 200.0, 173.8, 170.6, 165.9, 165.3, 148.0, 147.7, 143.8, 143.2, 137.2, 136.7, 135.9, 135.5, 133.4, 132.8, 129.2, 128.6, 128.3, 128.0, 127.7,127.6, 127.3, 126.9, 125.4, 125.0, 124.7, 124.6, 124.2, 123.2, 123.2, 122.2, 117.7, 117.1, 110.4, 109.9, 109.7, 109.4, 66.1, 65.1, 60.6, 60.3, 43.1, 42.9; **HRMS (ESI-TOF)** m/z: $[M + Na]^+$ $C_{25}H_{18}ClN_3NaO_4$ calcd. 482.0884, found, 482.0896.

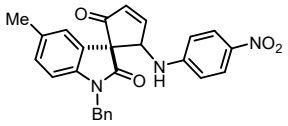
1'-Benzyl-2-((4-methoxy-2-nitrophenyl)amino)spiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione (19).



Following the general procedure, reaction of 1-benzyl-3-(furan-2-yl)-3-hydroxyindolin-2-one **1a** (0.050 g, 0.16 mmol, 1.0 equiv) and 4-methoxy-2-nitroaniline **2q** (0.055 g, 0.33 mmol, 2.0 equiv) in presence of PMA (0.060 g, 0.033 mmol) delivered spirooxindole **19**, which was purified by silica gel column chromatography (Hexane: EtOAc 6:4) to furnish the title compound as (red solid) in 73% (0.054 g) yield as inseparable mixture of diastereomers (1.7:1 *dr*). R_f 0.4 (EtOAc: Hexane 5:5); mp. 168-170 °C; **FT-IR** (ν cm^{-1}): 3360, 3065, 3028, 2936, 1725, 1696, 1610, 1572, 1517, 1468, 1347, 1292, 1234, 1153, 1063, 1037; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 7.2 Hz, 1.16H), 8.20 (d, *J* = 6.1 Hz, 0.63H), 8.08-8.01 (m, 1.92H), 7.68 (s, 1H), 7.50 (s, 0.72H), 7.39 (s, 2.49H), 7.33 (d, *J* = 7.7 Hz, 1.90H), 7.29 - 7.24 (m, 1.76H), 7.20-7.19 (m, 5.25H), 7.05 (m, 3H), 6.96 (d, 1H), 6.83- 6.70 (m, 5H), 6.60 (d, *J* = 8.9 Hz, 0.63H), 6.39 (d, *J* = 8.0 Hz, 1.15H), 5.58 (d, *J* = 7.3 Hz, 0.53H), 5.41 (d, *J* = 7.3 Hz, 1.1H), 5.03-5.01 (m, 2.23H), 4.69 (d, *J* = 15.4 Hz, 1H), 3.83 (s, 3H), 3.77 (s, 1.75H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 199.6, 199.5, 174.0, 170.5, 162.2, 162.0, 150.7, 144.0, 138.5, 138.2, 135.4, 135.3, 135.0, 133.1, 132.3, 129.6, 129.5, 129.0, 128.7, 128.2, 128.0, 127.6, 127.5, 127.2, 126.4, 125.9, 124.6, 123.8, 123.5, 123.1,122.4,

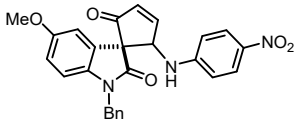
115.4,115.3, 110.1, 110.0, 108.4, 107.9, 66.8, 66.2, 62.1, 60.5, 55.9, 44.3, 44.2; **HRMS (ESI-TOF)** m/z: $[M + Na]^+$ $C_{26}H_{21}N_3NaO_5$ calcd. 478.1379, found, 478.1391.

1'-Benzyl-5'-methyl-2-((4-nitrophenyl)amino)spiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione (21).



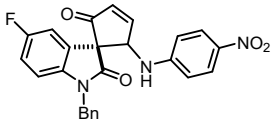
Following the general procedure, reaction of 1-benzyl-3-(furan-2-yl)-3-hydroxy-5-methylindolin-2-one **1c** (0.050 g, 0.157 mmol, 1.0 equiv) and 4-nitroaniline **2f** (0.058 g, 0.313 mmol, 2.0 equiv) in presence of PMA (0.058 g, 0.031 mmol) delivered compound **21**, which was purified by silica gel column chromatography (Hexane: EtOAc6:4) to furnish the title compound (red solid) in 79% (0.055 g) yield as inseparable mixture of diastereomers (>20:1 *dr*). R_f 0.35 (EtOAc: Hexane 4:6); mp. 180-182 °C; **FT-IR** (ν cm^{-1}): 3343, 2925, 1726, 1695, 1602, 1496, 1321, 1264, 1273, 1191, 1112; **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 8.15 - 8.14 (m, 1H), 8.04 (d, *J* = 8.6 Hz, 0.94H), 7.76 (d, *J* = 8.7 Hz, 2H), 7.24 (s, 1H), 7.08 (d, *J* = 6.7 Hz, 2H), 6.99 (t, *J* = 7.4 Hz, 2H), 6.91 (d, *J* = 7.5 Hz, 1.87H), 6.70 (d, *J* = 7.6 Hz, 2H), 6.35-6.29 (m, 1.80H), 5.49 (d, *J* = 8.6 Hz, 1H), 4.88 (d, *J* = 15.9 Hz, 1H), 4.59 (d, *J* = 15.9 Hz, 1H), 2.31 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-*d6*) δ 200.9, 170.2, 165.0, 152.9, 140.9, 136.7, 135.6, 133.7, 132.2, 129.2, 128.4, 128.1, 127.0, 126.7, 125.8, 123.6, 109.2, 63.4, 61.8, 42.8, 20.7; **HRMS (ESI-TOF)** m/z: $[M + Na]^+$ $C_{26}H_{21}N_3NaO_4$ calcd. 462.1430, found, 462.1444.

1'-Benzyl-5'-methoxy-2-((4-nitrophenyl)amino)spiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione(22).



Following the general procedure, reaction of 1-benzyl-3-(furan-2-yl)-3-hydroxy-5-methoxyindolin-2-one **1d** (0.050 g, 0.15 mmol, 1.0 equiv) and 4-nitroaniline **2f** (0.055g, 0.298 mmol, 2.0 equiv) in presence of PMA (0.055 g, 0.03 mmol) delivered spirooxindole **22**, which was purified by silica gel column chromatography (Hexane: EtOAc 7:3) to furnish the title compound as (brown solid) in 80% (0.054 g) yield as inseparable mixture of diastereomers (5:1 *dr*). R_f 0.4 (EtOAc: Hexane 4:6); mp. 170-172 °C; **FT-IR** (ν cm^{-1}): 3334, 2927, 2854, 1715, 1694, 1607, 1494, 1454, 1436, 1338, 1200, 1182; **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 8.31-8.28 (m, 0.30H), 8.14 (dd, *J* = 5.6, 2.0 Hz, 1H), 8.03 (d, *J* = 8.7 Hz, 1H), 7.77 (d, *J* = 8.9 Hz, 1.9H), 7.67 (d, *J* = 8.8 Hz, 0.45H), 7.38-7.30 (m,1.20H), 7.14 (d, *J* = 2.4 Hz, 1H), 7.09 (t, *J* = 7.3 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1.92H), 6.91-6.89 (m, 1.91H), 6.85 - 6.81 (m, 1.22H), 6.77 (d, *J* = 8.6 Hz, 0.26H), 6.72-6.68 (m, 2H), 6.64 (dd, *J* = 8.5, 2.4 Hz, 0.31H), 6.37 - 6.29 (m, 2H), 5.56 (d, *J* = 8.7 Hz, 1H), 5.27 (d, *J* = 8.8 Hz, 0.24 H), 4.96(d, *J* = 8.8 Hz ,0.27H), 4.90-4.84 (m,1.2H), 4.58 (d, *J* = 15.9 Hz, 1H), 3.75 (s, 3H), 3.60 (s, 0.68H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-*d6*) δ 200.9, 200.7, 173.2, 169.9, 165.5, 165.0, 155.8, 155.1, 152.9, 152.6, 137.1, 136.7(2), 136.6, 136.0, 135.6, 133.6, 133.5, 129.4, 128.6, 128.1, 127.6, 127.0, 126.7, 125.8, 113.6, 113.5, 111.7, 110.3, 110.0, 109.9, 67.0, 65.7, 61.7, 59.9, 55.6(2), 43.1, 42.8; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{26}H_{21}N_3NaO_5$ calcd. 478.1379, found, 478.1373.

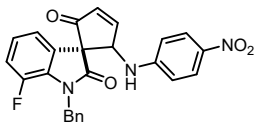
1'-Benzyl-5'-fluoro-2-((4-nitrophenyl)amino)spiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione (23).



Following the general procedure, reaction of 1-benzyl-5-fluoro-3-(furan-2-yl)-3-hydroxyindolin-2-one **1e** (0.050 g, 0.155 mmol, 1.0 equiv) and 4-nitroaniline **2f** (0.057g, 0.31 mmol, 2.0 equiv) in presence of PMA (0.057 g, 0.03 mmol) delivered spirooxindole **23**, which was purified by silica gel column chromatography (Hexane/EtOAc 7:3) to furnish the title compound as (red solid) in 75% (0.056 g) yield as inseparable mixture of diastereomers (5:1 *dr*). R_f 0.3 (EtOAc: Hexane 3:7);

mp. 170-172 °C; **FT-IR** (ν cm^{-1}): 3350, 2930, 1726, 1694, 1596, 1502, 1488, 1454, 1314, 1276, 1171, 1114; **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 8.29 (d, *J* = 3.4 Hz, 0.22H), 8.16 (d, *J* = 4.2 Hz, 1H), 8.06 (d, *J* = 8.6 Hz, 1H), 7.96-7.93 (m, 0.38H), 7.79 (d, *J* = 8.7 Hz, 2H), 7.68 (d, *J* = 8.6 Hz,0.37H), 7.49-7.47 (m, 1H), 7.37 - 7.33 (m, 1H), 7.15 -7.07 (m, 2.3H), 6.99 (t, *J* = 7.4 Hz, 2.1H), 6.90-6.88 (m, 2.1H), 6.82-6.79 (m, 1H), 6.71 (d, *J* = 3.8 Hz, 1.25H), 6.60 (d, *J* = 8.9 Hz, 0.23H), 6.38 - 6.29 (m, 2.1H), 5.61 (d, *J* = 8.6 Hz, 1H), 5.30 (d, *J* = 9.0 Hz, 0.21H), 4.92 (d, *J* = 15.9 Hz, 1.2H), 4.62 (d, *J* = 15.9 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-*d6*) δ 200.4, 200.0, 173.3, 170.0, 165.6, 165.1, 159.8, 157.4, 152.8, 152.4, 139.6, 139.6, 136.8, 135.7, 135.3, 133.5, 129.8, 129.7, 128.6, 128.2, 127.7, 127.6, 127.1, 126.6, 126.4, 125.9, 125.8, 115.4, 115.1, 112.4, 111.7, 111.4, 110.4, 110.3, 67.1, 65.6, 61.4, 60.0, 43.2, 42.9; **HRMS(ESI-TOF)** m/z: $[M + Na]^{+}$ $C_{25}H_{18}FN_3NaO_4$ calcd. 466.1179, found, 466.1195.

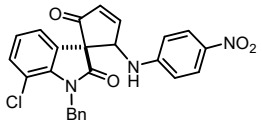
1'-Benzyl-7'-fluoro-2-((4-nitrophenyl)amino)spiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione(24).



Following the general procedure, reaction of 1-benzyl-7-fluoro-3-(furan-2-yl)-3-hydroxyindolin-2-one **1f** (0.055 g, 0.17 mmol, 1.0 equiv) and 4-nitroaniline **2f** (0.063g, 0.340 mmol, 2.0 equiv) in presence of PMA (0.063 g, 0.034 mmol) delivered spirooxindole **24**, which was purified by silica gel column chromatography (Hexane:EtOAc 6:4) to furnish the title compound (red solid) in 76% (0.057 g) yield as inseparable mixture of diastereomers (5:1 *dr*). R_f 0.3 (EtOAc: Hexane 5:5); mp. 162-164 °C; **FT-IR** (ν cm^{-1}): 3350, 2929, 2854, 1728, 1696, 1601, 1505, 1485, 1315, 1191, 1153, 1113; **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 8.31 (dd, *J* = 5.5, 2.2 Hz, 0.26H), 8.18 (dd, *J* = 5.6, 1.8 Hz, 1.15H), 8.11 (d, *J* = 8.7 Hz, 1H), 7.99 (d, *J* = 8.8 Hz, 0.27H), 7.81 (d, *J* = 8.9 Hz, 2.15H), 7.69 (d, *J* = 8.9 Hz, 0.39H), 7.35-7.32 (m, 2.30H), 7.22-7.17 (m, 2.21H), 7.09 (t, *J* = 7.3 Hz, 1H), 6.98 (t, *J* = 7.6 Hz, 2.32H), 6.84 (d, *J* = 7.5 Hz, 2H), 6.73 (dd, *J* = 5.6, 1.8 Hz, 1.3H), 6.38 - 6.29 (m, 2H), 5.61 (d, *J* = 8.6 Hz, 1H), 5.31(d, *J* = 8.6 Hz ,0.20H), 5.04 - 4.95 (m, 1.36H), 4.73 (d, *J* = 16.2 Hz, 1H); **^{13}C{^{1}H}** NMR (100 MHz, DMSO-*d6*) δ 200.2, 199.8, 173.3, 169.9, 165.7, 165.3, 152.8, 152.4, 147.6, 145.1, 136.9, 136.9, 136.6, 136.3, 133.4, 131.0(2), 129.8, 129.7, 128.6, 128.1, 127.6, 127.0(2), 126.4, 126.0, 125.9, 125.8, 124.4, 124.3, 119.6(2), 117.3, 117.1, 112.4, 66.9, 65.6, 61.8,

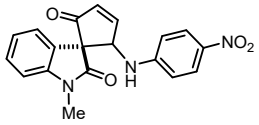
60.3, 44.6(2); **HRMS (ESI-TOF)** m/z: $[M + Na]^+$ $C_{25}H_{18}FN_3NaO_4$ calcd. 466.1179, found, 466.1192.

1'-Benzyl-7'-chloro-2-((4-nitrophenyl)amino)spiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione (25).



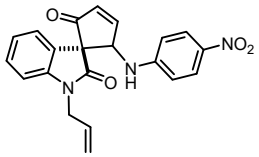
Following the general procedure, reaction of 1-benzyl-7-chloro-3-(furan-2-yl)-3-hydroxyindolin-2-one **1g** (0.050 g, 0.148 mmol, 1.0 equiv) and 4-nitroaniline **2f** (0.054 g, 0.29 mmol, 2.0 equiv) in presence of PMA (0.054 g, 0.03 mmol) delivered spirooxindole **25**, which was purified by silica gel column chromatography (Hexane: EtOAc 6:4) to furnish the title compound (red semi solid) in 75% (0.051g) yield as inseparable mixture of diastereomers (2:1 *dr*). R_f 0.3 (EtOAc: Hexane 5:5); **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 8.32 (dd, *J* = 5.5, 2.3 Hz, 0.52H), 8.18 (dd, *J* = 5.6, 2.0 Hz, 1H), 8.09 (d, *J* = 8.8 Hz, 1H), 8.02 (d, *J* = 8.6 Hz, 0.54H), 7.86 (d, *J* = 9.1 Hz, 2H), 7.80 (d, *J* = 9.1 Hz, 1H), 7.50 (d, *J* = 7.1 Hz, 1H), 7.34-2.29 (m, 2.63H), 7.24 (d, *J* = 7.4 Hz, 0.83H), 7.20 (d, *J* = 7.7 Hz, 1.1H), 7.17-7.14 (m, 1.4H), 7.10 (t, *J* = 7.4 Hz, 0.6H), 6.98 (t, *J* = 7.6 Hz, 1.16H), 6.92 (t, *J* = 7.6 Hz, 0.54H), 6.81 (d, *J* = 7.6 Hz, 1.87H), 6.76 (dd, *J* = 5.6, 1.9 Hz, 1.85H), 6.73 (dd, *J* = 5.6, 1.9 Hz, 1H), 6.42-6.35 (m, 2.57H), 5.65 (d, *J* = 8.7 Hz, 1H), 5.37 -5.32 (m, 1H), 5.24 (d, *J* = 16.6 Hz, 0.65H), 5.15-5.05 (m, 2H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-D6-*d6*) δ 200.2, 199.7, 174.2, 170.7, 165.9, 165.5, 152.8, 152.4, 139.7, 139.1, 137.2, 137.0, 136.9(2), 133.3, 133.2, 131.3, 131.1, 131.0, 128.5, 128.1, 127.7, 127.2, 126.8, 126.2, 126.0, 125.9, 125.5, 124.6, 123.9, 123.8, 122.4, 114.2, 114.1, 66.7, 65.2, 61.8, 60.3, 44.6, 44.3; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{25}H_{18}ClN_3NaO_4$ calcd. 482.0884, found, 482.0844.

1'-Methyl-2-((4-nitrophenyl)amino)spiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione(26).



Following the general procedure, reaction of 3-(furan-2-yl)-3-hydroxy-1-methylindolin-2-one **1h** (0.050 g, 0.22 mmol, 1.0 equiv) and 4-nitroaniline **2f** (0.060 g, 0.44 mmol, 2.0 equiv) in presence of PMA (0.08 g, 0.043 mmol) delivered spirooxindole **26**, which was purified by silica gel column chromatography (Hexane:EtOAc 8:2) to furnish the title compound (brown solid) in 69% (0.053g) yield as inseparable mixture of diastereomers (1.6:1 *dr*). R_f 0.3 (EtOAc: Hexane 2:8); mp. 164-166 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 - 7.86 (m, 5H), 7.40 - 7.36 (m, 1.87H), 7.25 - 7.21 (m, 0.8 H), 7.16 (d, *J* = 4.3 Hz, 2H), 6.96 - 6.95 (m, 1.1H), 6.84 (d, *J* = 7.8 Hz, 1.1H), 6.76 (d, *J* = 7.9 Hz, 0.68H), 6.57 (dd, *J* = 5.6, 1.8 Hz, 1.57H), 6.40 (d, *J* = 9.1 Hz, 2H), 6.35 (d, *J* = 9.1 Hz, 1.1H), 5.68 (d, *J* = 10.3 Hz, 0.89H), 5.37 (d, *J* = 9.5 Hz, 0.68 H), 5.25 (d, *J* = 10.3 Hz, 1H), 4.81 (d, *J* = 9.6 Hz, 0.65H), 3.20 (s, 2.33H), 3.06 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 199.6, 199.5, 173.8, 171.2, 162.0, 151.3, 151.1, 145.1, 144.4, 139.2, 135.3, 129.8, 129.7, 128.1, 126.4, 126.0(2), 124.4, 123.8, 123.5, 122.9, 122.2, 113.4, 112.6, 112.5, 112.2, 109.3(2), 66.1, 66.0, 61.8, 60.6, 26.9, 26.6; **HRMS (ESI-TOF)** m/z: $[M + Na]^+$ $C_{19}H_{15}N_3NaO_4$ calcd. 372.0960, found, 372.0971.

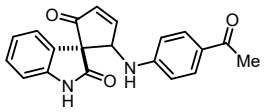
1'-Allyl-2-((4-nitrophenyl)amino)spiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione(27).



Following the general procedure, reaction of 1-allyl-3-(furan-2-yl)-3-hydroxyindolin-2-one **1i** (0.050 g, 0.196 mmol, 1.0 equiv) and 4-nitroaniline **2f** (0.05 g, 0.39 mmol, 2.0 equiv) in presence of PMA (0.072g, 0.039 mmol) delivered spirooxindole **27**, which was purified by silica gel column chromatography (Hexane: EtOAc 8:2) to furnish the title compound (yellow solid) in 59% (0.044g) yield as inseparable mixture of diastereomers (>20:1 *dr*). R_f 0.3 (EtOAc: Hexane 2:8); mp. 174-176 °C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 8.12 (dd, *J* = 5.6, 1.9 Hz, 1H), 7.93 (d, *J* = 8.7 Hz, 1H), 7.75 (d, *J* = 8.9 Hz, 2H), 7.41 (d, *J* = 7.3 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.68 (dd, *J* = 5.6, 1.8 Hz, 1H), 6.34 (s, 2H), 5.51 (d, *J* = 8.7 Hz, 1H), 5.39 (ddd, *J* = 15.3, 9.9, 4.7 Hz, 1H), 4.77 (dd, *J* = 20.6, 14.0 Hz, 2H), 4.24 - 4.16 (m, 1H), 4.06 (dd, *J* = 16.7, 4.9 Hz, 1H); **^{113}C{^{1}H} NMR** (100 MHz, DMSO-*d6*) δ 200.8, 169.8, 164.9,

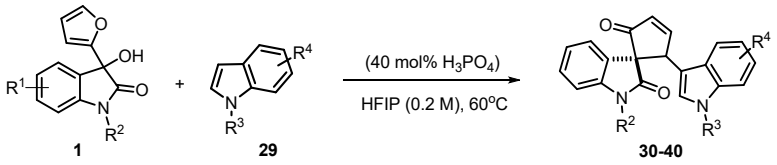
153.0, 143.4, 136.7, 133.8, 130.9, 129.0, 128.3, 125.6, 123.0, 122.9, 116.1, 109.4, 66.6, 61.8, 41.4; **HRMS (ESI-TOF)** m/z: $[M + Na]^+$ $C_{21}H_{17}N_3NaO_4$ calcd. 398.1117, found, 398.1112.

2-((4-acetylphenyl)amino)spiro[cyclopent[3]ene-1,3'-indoline]-2',5-dione(28):



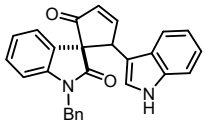
Following the general procedure, reaction of compound **1j** (0.05 g, 0.23 mmol, 1.0 equiv) and1-(4-aminophenyl)ethan-1-one **2g** (0.063 g, 0.46 mmol, 2.0 equiv) in presence of PMA (0.084 g, 0.046 mmol) delivered spirooxindole **28**, which was purified by silica gel column chromatography (Hexane: EtOAc 5:5) to furnish the title compound (red semi solid) in 51% (0.042 g) yield as inseparable mixture of diastereomers (3:1 *dr*). R_f 0.25 (EtOAc: Hexane 6:4); **^{1}H NMR** (800 MHz, DMSO-*d6*) δ 10.71 (s, 0.37H), 10.53 (s, 1H), 8.21 (d, *J* = 3.1 Hz, 0.32H), 8.06 (d, *J* = 3.8 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 0.72H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.6 Hz, 0.38H), 7.33 (d, *J* = 6.9 Hz, 1H), 7.27 (m, 2H), 7.09 - 7.05 (m, 1.62H), 6.80 (d, *J* = 7.5 Hz, 1H)6.74 (d, *J* = 7.3 Hz, 0.32H), 6.63 - 6.61 (m, 1H), 6.34 - 6.32 (m, 2.41H), 5.35 (d, *J* = 8.1 Hz, 1H), 5.13 (d, *J* = 8.0 Hz, 0.32H), 2.33 (s, 4H).**^{13}C{^{1}H} NMR** (200 MHz, DMSO-*d6*) δ 201.6, 201.5, 195.3, 175.6, 172.0, 166.0, 165.5, 151.3, 151.1, 143.5, 143.1, 133.5, 133.2, 130.3, 130.1, 129.5, 129.0, 128.5, 126.1, 125.9, 125.8, 124.8, 123.2, 122.2, 121.4, 109.7(2), 67.1, 66.3, 62.1, 60.0, 26.0 (2); **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{20}H_{16}N_2NaO_3$ calcd. 355.1035, found, 355.1059.

General procedure for *carbo*-Piancatelli rearrangement: synthesis of compounds 30-40.



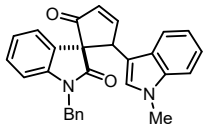
To a solution of compound **1** (1.0 equiv) and indole derivative (**29** 2.0 equiv) in HFIP (0.2 M), was added H_3PO_4 (40 mol%). The reaction mixture was stirred at 60 °C (sealed tube was used) and the progress of the reaction was monitored by TLC analysis. After completion of the reaction (1-3 h), HFIP was removed under the reduced pressure. The crude residue was diluted in ethyl acetate and washed with water (three times) and brine. Combined organic layer dried over anhydrous Na_2SO_4 and filtered. Solvent was removed under vacuo and the crude residue was purified by silica gel column chromatography using Hex-EtOAc as eluent to obtain the desired indolo-spirooxindole derivative **30-40**.

1'-Benzyl-2-(1H-indol-3-yl)spiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione (30).



Following the general procedure, reaction of 1-benzyl-3-(furan-2-yl)-3-hydroxyindolin-2-one **1a** (0.030 g, 0.098 mmol, 1.0 equiv) and 1H-indole **29a** (0.023 g, 0.196 mmol, 2.0 equiv) in presence of H_3PO_4 (0.004 g, 0.041 mmol) delivered compound **30**, which was purified by silica gel column chromatography (Hexane: EtOAc 6:4) to furnish the title compound as brown solid in 74% (0.030g) yield. R_f 0.3 (EtOAc: Hexane 4:6); mp. 155-157 °C; **FT-IR** (ν cm^{-1}): 3363, 2927, 2854, 1717, 1694, 1613, 1488, 1468, 1454, 1356, 1159, 1101; **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 11.06 (s, 1H), 8.42 (d, *J* = 5.0 Hz, 1H), 7.58 (d, *J* = 7.1 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.23 (t, 1H), 7.17 - 7.13 (m, 2H), 7.05-6.99 (m, 2H), 6.88 (t, *J* = 7.3 Hz, 2H), 6.68 - 6.59 (m, 4H), 6.40 (d, *J* = 7.3 Hz, 2H), 5.15 (s, 1H), 4.71 (d, *J* = 16.3 Hz, 1H), 4.42 (d, *J* = 16.3 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-*d6*) δ 203.4, 171.1, 169.0, 143.8, 135.8, 135.2, 132.2, 128.8, 128.7, 128.1 , 126.7(2), 126.0, 124.6, 123.6, 122.7, 121.0, 118.6, 117.8, 111.4, 109.7, 109.0, 67.6, 48.8, 42.3; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{27}H_{20}N_2NaO_2$ calcd. 427.1422, found, 427.1429.

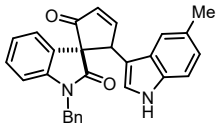
1'-Benzyl-2-(1-methyl-1H-indol-3-yl)spiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione (31).



Following the general procedure, reaction of 1-benzyl-3-(furan-2-yl)-3-hydroxyindolin-2-one **1a** (0.050 g, 0.163 mmol, 1.0 equiv) and 1-methyl-1H-indole **29b** (0.044 g, 0.33 mmol, 2.0 equiv) in

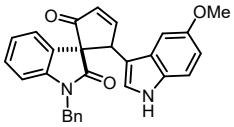
presence of H_3PO_4 (0.007 g, 0.07 mmol) delivered compound **31**, which was purified by silica gel column chromatography (Hexane:EtOAc 7:3) to furnish the title compound as brown semi solid in 61% (0.042 g) yield. R_f 0.25 (EtOAc: Hexane 3:7); mp. 163-165 °C; **FT-IR** (ν cm^{-1}): 3057, 3016, 2926, 1725, 1696, 1613, 1491, 1468, 1358, 1231, 1159; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 5.6, 1.8 Hz, 1H), 7.37 (d, *J* = 6.7 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 1H), 7.21-7.14 (m, 3H), 7.07 (s, 1H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.88 - 6.81 (m, 3H), 6.68 (d, *J* = 8.0 Hz, 1H), 6.60 (dd, *J* = 5.6, 2.5 Hz, 1H), 6.47 (d, *J* = 7.6 Hz, 1H), 6.33 (d, *J* = 7.6 Hz, 2H), 5.02 (s, 1H), 4.91 (d, *J* = 16.2 Hz, 1H), 4.29 (d, *J* = 16.2 Hz, 1H), 3.73 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 203.4, 171.6, 166.4, 144.3, 136.7, 135.0, 133.5, 129.2, 128.8, 128.6,128.5, 127.5, 127.0 ,126.2, 123.2, 123.1, 121.9, 119.6, 118.5, 109.7,109.5, 109.4, 68.0, 49.7, 43.7, 33.0; **HRMS (ESI-TOF)** m/z: $[M + Na]^+$ $C_{28}H_{22}N_2NaO_2$ calcd. 441.1579, found, 441.1594.

1'-Benzyl-2-(5-methyl-1H-indol-3-yl)spiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione(32).



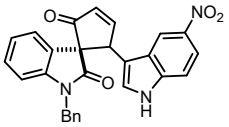
Following the general procedure, reaction of 1-benzyl-3-(furan-2-yl)-3-hydroxyindolin-2-one **1a** (0.050 g, 0.163 mmol, 1.0 equiv) and 5-methyl-1H-indole **29c** (0.044 g, 0.3275 mmol, 2.0 equiv) in presence of H_3PO_4 (0.007 g, 0.07 mmol) delivered compound **32**, which was purified by silica gel column chromatography (Hexane:EtOAc 6:4) to furnish the title compound as brown solid in 60% (0.041g) yield. R_f 0.3 (EtOAc: Hexane 4:6); mp. 232-234 °C; **FT-IR** (ν cm^{-1}): 3328, 2922, 1717,1687, 1610, 1491, 1466, 1362, 1160; **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 10.89 (s, 1H), 8.44-8.43 (m, 1H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.26 - 7.22 (m, 2H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.12 (s, 1H), 7.05 (t, *J* = 7.2 Hz, 1H), 6.91 (t, *J* = 7.5 Hz, 2H), 6.83 (d, *J* = 8.1 Hz, 1H), 6.62-6.60 (m, 2H), 6.41 (d, *J* = 7.4 Hz, 2H), 6.25 (s, 1H), 5.09 (s, 1H), 4.70 (d, *J* = 16.3 Hz, 1H), 4.41 (d, *J* = 16.3 Hz, 1H), 1.99 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-*d6*) δ 203.4, 171.1, 168.8, 144.0, 135.3, 134.2, 132.2, 128.9, 128.6, 128.2, 126.8(2), 126.7, 126.0, 124.3, 123.7, 122.6(2), 117.9, 111.0, 109.4, 109.0, 67.6, 49.1, 42.4, 21.1; **HRMS (ESI-TOF)** m/z: $[M + Na]^+$ $C_{28}H_{22}N_2NaO_2$ calcd. 441.1579, found, 441.1603.

1'-Benzyl-2-(5-methoxy-1H-indol-3-yl)spiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione (33).



Following the general procedure, reaction of 1-benzyl-3-(furan-2-yl)-3-hydroxyindolin-2-one **1a** (0.050 g, 0.163 mmol, 1.0 equiv) and 5-methoxy-1H-indole **29d** (0.048 g, 0.33 mmol, 2.0 equiv) in presence of H_3PO_4 (0.007 g, 0.07 mmol) delivered compound **33**, which was purified by silica gel column chromatography (Hexane:EtOAc 6:4) to furnish the title compound as brown solid in 67% (0.048g) yield. R_f 0.3 (EtOAc: Hexane 4:6); mp. 185-187 °C; **FT-IR** (ν cm^{-1}): 3328, 2953, 2927, 2855, 1719,1693,1609, 1488,1468,1358,1211; **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 10.87 (s, 1H), 8.45 (dd, *J* = 5.5, 1.6 Hz, 1H), 7.62 (d, *J* = 7.2 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 2H), 7.18-7.14 (m, 2H), 7.04 (t, *J* = 7.3 Hz, 1H), 6.89 (t, *J* = 7.6 Hz, 2H), 6.64-6.60 (m, 3H), 6.38 (d, *J* = 7.5 Hz, 2H), 5.93 (d, *J* = 1.6 Hz, 1H), 5.12 (s, 1H), 4.74 (d, *J* = 16.3 Hz, 1H), 4.42 (d, *J* = 16.3 Hz, 1H), 3.17 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-*d6*) δ 203.3, 170.9, 168.8, 153.0, 144.0, 135.2, 132.2, 130.8, 128.9, 128.6, 128.1, 126.8, 126.7, 125.9, 124.7, 123.7, 122.5, 112.1, 111.7, 109.8, 109.2, 99.1, 67.6, 54.4, 48.9, 42.4; **HRMS (ESI-TOF)** m/z: $[M + Na]^+$ $C_{28}H_{22}N_2NaO_3$ calcd. 457.1528, found, 457.1550.

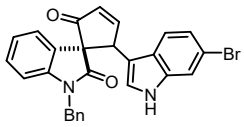
1'-Benzyl-2-(5-nitro-1H-indol-3-yl)spiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione (34).



Following the general procedure, reaction of 1-benzyl-3-(furan-2-yl)-3-hydroxyindolin-2-one **1a** (0.050 g, 0.163 mmol, 1.0 equiv) and 5-nitro-1H-indole **29e** (0.053 g, 0.33 mmol, 2.0 equiv) in presence of H_3PO_4 (0.007 g, 0.07 mmol) delivered compound **34**, which was purified by silica gel column chromatography (Hexane/EtOAc 6:4) to furnish the title compound as brown solid in 71% (0.052g) yield. R_f 0.3 (EtOAc: Hexane 4:6); mp. 215-217 °C; **FT-IR** (ν cm^{-1}): 3353, 2925, 1697,1613, 1517, 1466, 1335; **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 11.81 (s, 1H), 8.49 (dd, *J* = 5.6, 1.9 Hz, 1H), 7.90 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.63 (d, *J* = 7.2 Hz, 1H), 7.54-7.52 (m, 2H), 7.46 (d, *J* = 1.8 Hz, 1H), 7.27 (t, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.88 (t, *J* = 7.6 Hz, 2H), 6.70-6.67 (m, 2H), 6.39 (d, *J* = 7.5 Hz, 2H), 5.26 (s, 1H), 4.69 (d, *J* = 16.1 Hz, 1H), 4.40 (d, *J* = 16.1 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-*d6*) δ 202.9, 171.0, 168.0, 143.7,

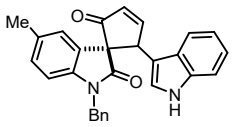
140.3, 139.1, 135.3, 132.6, 129.0, 128.3, 128.2, 128.1, 126.9, 126.1, 125.8, 123.8, 122.9, 116.5, 115.6, 112.8, 112.0, 109.2, 67.3, 48.4, 42.5; **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{27}H_{19}N_3NaO_4$ calcd. 472.1273, found, 472.1298.

1'-Benzyl-2-(6-bromo-1H-indol-3-yl)spiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione(35).



Following the general procedure, reaction of 1-benzyl-3-(furan-2-yl)-3-hydroxyindolin-2-one **1a** (0.050 g, 0.163 mmol, 1.0 equiv) and 5-bromo-1H-indole **29f** (0.065g, 0.33 mmol, 2.0 equiv) in presence of H_3PO_4 (0.007 g, 0.07 mmol) delivered compound **35**, which was purified by silica gel column chromatography (Hexane/EtOAc 6:4) to furnish the title compound as brown solid in 71% (0.056g) yield. R_f 0.25 (EtOAc: Hexane 3:7); mp. 181-182 °C; **FT-IR** (ν cm^{-1}): 3335, 2925, 1718, 1695,1613, 1491, 1466, 1454, 1355, 1222, 1157; **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 11.21 (s, 1H), 8.42 (dd, *J* = 5.6, 1.6 Hz, 1H), 7.57-7.55 (m, 2H), 7.27-7.21 (m, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.08 (t, *J* = 7.3 Hz, 1H), 6.93 (t, *J* = 7.6 Hz, 2H), 6.77 (d, *J* = 8.4 Hz, 1H), 6.65-6.62 (m, 2H), 6.47 (d, *J* = 8.4 Hz, 1H), 6.38 (d, *J* = 7.5 Hz, 2H), 5.13 (s, 1H), 4.73 (d, *J* = 16.2 Hz, 1H), 4.41 (d, *J* = 16.2 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-*d6*) δ 203.2, 171.0, 168.5, 143.7, 136.7, 135.3, 132.4, 128.8, 128.6, 128.1, 126.8, 126.0, 125.6, 123.6, 122.7, 121.4, 119.6, 114.1, 113.9, 110.1, 109.1, 67.4, 48.6, 42.4; **HRMS (ESI-TOF)** m/z: $[M + Na]^+$ $C_{27}H_{19}BrN_2NaO_2$ calcd. 505.0528, found, 505.0557

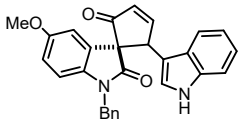
1'-Benzyl-2-(1H-indol-3-yl)-5'-methylspiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione (36).



Following the general procedure, reaction of 1-benzyl-3-(furan-2-yl)-3-hydroxy-5-methylindolin-2-one **1c** (0.032 g, 0.10 mmol, 1.0 equiv) and 1H-indole **29a** (0.024 g, 0.20 mmol, 2.0 equiv) in presence of H_3PO_4 (0.004 g, 0.04 mmol) delivered compound **36** (reaction time: 3h), which was purified by silica gel column chromatography (Hexane: EtOAc 6:4) to furnish the title compound

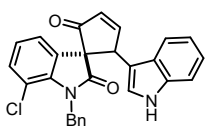
as brown solid in 75% (0.031g) yield. R_f 0.3 (EtOAc: Hexane 4:6); mp. 222-223 °C; **FT-IR** (ν cm^{-1}): 3330, 2925, 1721,1689, 1621, 1602, 1497, 1457, 1437, 1344, 1191, 1143; **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 11.04 (s, 1H), 8.41 (d, *J* = 3.8 Hz, 1H), 7.37-7.35 (m, 2H), 7.16 (s, 1H), 7.03 (s, 3H), 6.88 (t, *J* = 6.5 Hz, 2H), 6.71 - 6.62 (m, 3H), 6.46 (dd, *J* = 26.5, 7.1 Hz, 3H), 5.10 (s, 1H), 4.67 (d, *J* = 16.1 Hz, 1H), 4.39 (d, *J* = 16.3 Hz, 1H), 2.34 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-*d6*) δ 203.7, 171.1, 169.0, 141.4, 135.8, 135.3,132.1, 131.7, 128.9, 128.8, 128.1, 126.7,126.0, 124.5, 124.0, 121.0, 118.6, 117.9, 111.4, 109.8, 108.8, 67.4, 48.9, 42.3, 20.8; **HRMS(ESI-TOF)** m/z: [M + Na]$^+$ $C_{28}H_{22}N_2NaO_2$ calcd. 441.1579, found, 441.1577.

1'-Benzyl-2-(1H-indol-3-yl)-5'-methoxyspiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione (37).



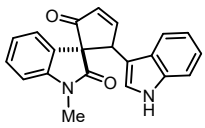
Following the general procedure, reaction of 1-benzyl-3-(furan-2-yl)-3-hydroxy-5-methoxyindolin-2-one **1d** (0.040 g, 0.12 mmol, 1.0 equiv) and 1H-indole **29a** (0.028g, 0.24 mmol, 2.0 equiv) in presence of H_3PO_4 (0.005 g, 0.05 mmol) delivered compound **37** (reaction time: 3h), which was purified by silica gel column chromatography (Hexane: EtOAc 6:4) to furnish the title compound as brown solid in 64% (0.033g) yield. R_f 0.3 (EtOAc: Hexane 4:6); mp. 185-186 °C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 11.05 (s, 1H), 8.41-8.40 (m, 1H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.29 (s, 1H), 7.17 (s, 1H), 7.03-7.00 (m, 2H), 6.87 (t, *J* = 7.4 Hz, 2H), 6.80-6.78 (m, 1H), 6.72-6.66 (m, 2H), 6.62-6.61 (m, 1H), 6.49 (d, *J* = 8.5 Hz, 1H), 6.39 (d, *J* = 7.5 Hz, 2H), 5.17 (s, 1H), 4.68 (d, *J* = 16.3 Hz, 1H), 4.38 (d, *J* = 16.3 Hz, 1H), 3.77 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-*d6*) δ 203.5, 170.9, 169.0, 155.7, 137.1, 135.8, 135.4, 132.1, 130.0, 128.1, 126.7(2), 126.0, 124.6, 121.0, 118.6, 117.9, 113.3, 111.4, 110.7, 109.8, 109.4, 68.0, 55.7, 48.8, 42.4; **HRMS(ESI-TOF)** m/z: [M + Na]$^+$ $C_{28}H_{22}N_2NaO_3$ calcd. 457.1528, found, 457.1551.

1'-Benzyl-7'-chloro-2-(1H-indol-3-yl)spiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione(38).



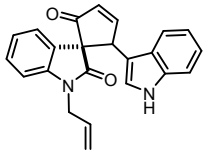
Following the general procedure, reaction of 1-benzyl-7-chloro-3-(furan-2-yl)-3-hydroxyindolin-2-one **1g** (0.055 g, 0.16 mmol, 1.0 equiv) and 1H-indole **29a** (0.038g, 0.32 mmol, 2.0 equiv) in presence of H_3PO_4 (0.007 g, 0.06 mmol) delivered compound **38** (reaction time: 3h), which was purified by silica gel column chromatography (Hexane:EtOAc 6:4) to furnish the title compound as brown solid in 58% (0.041g) yield. R_f 0.3 (EtOAc: Hexane 4:6); mp. 204-205 °C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 11.09 (s, 1H), 8.44 (d, *J* = 4.8 Hz, 1H), 7.65 (d, *J* = 7.0 Hz, 1H), 7.39 (d, *J* = 7.9 Hz, 1H), 7.28 (d, *J* = 7.8 Hz, 1H), 7.22 -7.18(m, 2H), 7.06 - 6.98 (m, 2H), 6.84 -6.74 (m, 3H), 6.67 (d, *J* = 11.0 Hz, 2H), 6.25 (d, *J* = 7.0 Hz, 2H), 5.23 (s, 1H), 4.90-4.89 (m, 2H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-*d6*) δ 202.4, 171.5, 169.3, 139.6, 136.7, 135.8, 131.8, 131.65, 130.9, 128.0, 126.6, 126.3, 125.0, 124.8, 124.2, 122.9, 121.1, 118.7, 117.7, 113.8, 111.6, 109.3, 67.6, 49.0, 43.9; **HRMS (ESI-TOF)** m/z: $[M + Na]^+$ $C_{27}H_{19}ClN_2NaO_2$ calcd. 461.1033, found, 461.0994.

2-(1H-indol-3-yl)-1'-methylspiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione (39).



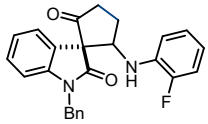
Following the general procedure, reaction of 3-(furan-2-yl)-3-hydroxy-1-methylindolin-2-one **1h** (0.050 g, 0.22 mmol, 1.0 equiv) and 1H-indole **29a** (0.051g, 0.44 mmol, 2.0 equiv) in presence of H_3PO_4 (0.009 g, 0.09 mmol) delivered compound **39**, which was purified by silica gel column chromatography (Hexane:EtOAc 6:4) to furnish the title compound as brown solid in 58% (0.042g) yield. R_f 0.3 (EtOAc: Hexane 4:6); mp. 168-169 °C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 10.99 (s, 1.6H), 8.41 (dd, *J* = 5.6, 1.9 Hz, 1H), 7.49 (d, *J* = 7.3 Hz, 1H), 7.40-7.34 (m, 2H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.19 - 7.15 (m, 3H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.97-6.92 (m, 2H), 6.86 (d, *J* = 2.2 Hz, 0.69H), 6.80 (t, *J* = 7.4 Hz, 0.78H), 6.67 (t, *J* = 7.5 Hz, 1H), 6.59 (dd, *J* = 5.6, 2.4 Hz, 1H), 6.52 (d, *J* = 7.9 Hz, 1H), 5.03 (s, 1H), 3.26 (s, 0.85H), 2.72 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ 203.5,176.9, 171.0, 168.9, 144.8, 142.8, 136.9, 135.8, 133.7, 132.0, 129.1, 128.9, 128.0, 126.6, 125.6, 124.6, 124.3(2), 123.2, 122.6, 122.2, 121.0(2), 120.7, 118.3, 117.6, 114.1, 111.6, 111.4, 110.0, 108.7, 108.5, 66.9, 52.2, 49.0, 26.3, 25.9; **HRMS (ESI-TOF)** m/z: $[M + Na]^+$ $C_{21}H_{16}N_2NaO_2$ calcd. 351.1109, found, 351.1107.

1'-Allyl-2-(1H-indol-3-yl)spiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione(40).



Following the general procedure, reaction of 1-allyl-3-(furan-2-yl)-3-hydroxyindolin-2-one **1i** (0.036 g, 0.1411 mmol, 1.0 equiv) and 1H-indole **29a** (0.034g, 0.28 mmol, 2.0 equiv) in presence of H_3PO_4 (0.006 g, 0.06 mmol) delivered compound **40**, which was purified by silica gel column chromatography (Hexane:EtOAc 6:4) to furnish the title compound as brown solid in 69% (0.035g) yield. R_f 0.3 (EtOAc: Hexane 4:6); mp. 209-210 °C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 10.97 (s, 1H), 8.41 (dd, *J* = 5.6, 1.8 Hz, 1H), 7.53 (d, *J* = 7.3 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.28 (d, *J* = 8.1 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.13 (d, *J* = 1.9 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 7.8 Hz, 1H), 6.64 (t, *J* = 7.5 Hz, 1H), 6.60 (dd, *J* = 5.6, 2.5 Hz, 1H), 6.49 (d, *J* = 7.9 Hz, 1H), 5.20-5.11(m, *J* = 15.0, 9.8, 4.5 Hz, 1H), 5.07 (s, 1H), 4.60 (d, *J* = 10.5 Hz, 1H), 4.33 (d, *J* = 17.3 Hz, 1H), 4.00 - 3.95 (m, 1H), 3.83 (dd, *J* = 16.9, 4.7 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-*d6*) δ 203.5, 170.7, 168.7, 143.9, 135.8, 132.2, 130.8, 128.9, 128.7, 126.6, 124.3, 123.4, 122.5, 120.9, 118.3, 117.7, 115.6, 111.3, 109.8, 109.0, 67.2, 49.0, 41.1; **HRMS (ESI-TOF)** m/z: $[M + Na]^+$ $C_{23}H_{18}N_2NaO_2$ calcd. 377.1266, found, 377.1261.

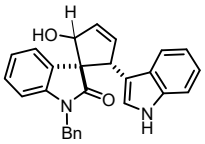
1'-Benzyl-2-((2-fluorophenyl)amino)spiro[cyclopentane-1,3'-indoline]-2',5-dione (41).



To a solution of compound **15** (0.070 g, 0.176 mmol, 1.0 equiv; used as diastereomeric mixture) in EtOAc (2.0 mL), was added 10% Pd/C (0.006 g) and the reaction flask was evacuated and backfilled with argon (three times). Next the same operation was performed with H_2 gas fitted with a balloon and left for 2 h. Upon completion of the reaction (TLC monitored), the mixture was passed through a pad of celite and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (2:8 EtOAc:hexane) to afford compound **41** as colourless oil in 51% (0.036 g) yield as mixture of diastereomer. R_f 0.5 (2:8 EtOAc:Hexane);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 - 7.11 (m, 10H), 7.09- 7.00 (m, 6H), 6.91-6.86 (m, 2H), 6.83 - 6.77 (m, 2H), 6.66 (t, *J* = 7.7 Hz, 1H), 6.62- 6.59 (m, 1H), 6.56 - 6.50 (m, 3H), 6.29 (t, *J* = 8.4 Hz, 1H), 5.07-5.00 (m, 1H), 4.94 (d, *J* = 16.0 Hz, 1H), 4.84 (d, *J* = 16.0 Hz, 1H), 4.77- 4.70 (m, 3H),

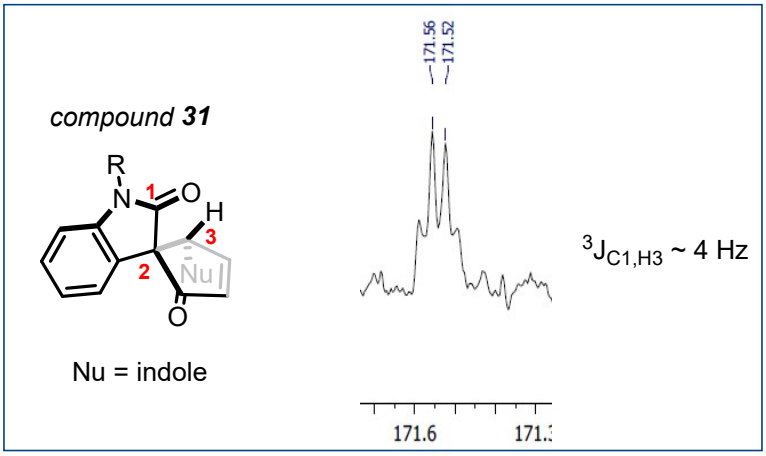
4.58 (dd, J = 9.0, 2.3 Hz, 1H), 3.98 (d, J = 10.6 Hz, 1H), 2.97 - 2.85 (m, 2H), 2.81 - 2.76 (m, 2H), 2.71 - 2.60 (m, 3H), 2.22- 2.13 (m, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 210.1, 209.6, 175.1, 171.7, 144.2, 135.0(2),134.7, 134.6(2), 134.4, 129.4, 129.2, 128.9(2), 127.6,126.9, 126.8, 124.9, 124.8(2), 124.3(2), 123.4, 124.3, 123.4, 123.3, 123.0, 122.8, 118.3, 118.2, 118.0, 117.9, 114.9, 114.7(2), 114.5, 114.3(2), 113.8, 113.7, 110.4, 109.9, 68.3, 67.8, 60.6, 58.7, 44.2, 43.8, 38.4, 38.0, 29.5, 28.1. **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{25}H_{21}FN_2NaO_2$ calcd. 423.1485, found, 423.1501.

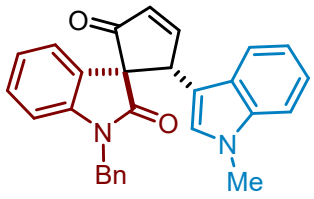
1'-Benzyl-2-hydroxy-5-(1H-indol-3-yl)spiro[cyclopentane-1,3'-indolin]-3-en-2'-one (42).



To a solution of compound **30** (0.040 g, 0.09 mmol, 1.0 equiv) in dry MeOH (1.0 mL, 0.1 M), was added $CeCl_3.7H_2O$ (0.018 g, 0.04 mmol, 0.5 equiv) at room temperature and the reaction was stirred at room temperature for 30 min. After that the reaction mixture was transferred to a chiller with set temperature of -20 ^{o}C and $NaBH_4$ (0.004g, 0.09 mmol) was added. The reaction mixture was stirred for 4h at the same temperature and then quenched with saturated aqueous solution of NH_4Cl. It was diluted EtOAc (10 mL) and washed with water and brine (10 mL x3). Combined organic layer was dried with anhydrous Na_2SO_4 and concentrated in vacuo. Crude residue was purified by silica gel column chromatography (4:6 EtOAc/hexane) to afford compound **42** as colorless oil in 55 % (0.022 g) yield as a single detectable diastereomer. R_f 0.25 (4:6 EtOAc:Hexane);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.56 (d, J = 6.9 Hz, 1H), 7.33 (d, J = 8.2 Hz, 1H), 7.20 (t, J = 7.1 Hz, 1H), 7.14 (td, J = 7.7, 1.0 Hz, 1H), 7.08 (t, J = 7.7 Hz, 1H), 7.04 (t, J = 7.4 Hz, 1H), 7.00 (d, J = 2.3 Hz, 1H), 6.89 (t, J = 7.7 Hz, 2H), 6.75 (t, J = 7.5 Hz, 1H), 6.53 (d, J = 8.0 Hz, 1H), 6.35 (d, J = 7.6 Hz, 1H), 6.26 (d, J = 7.5 Hz, 2H), 6.15 (s, 2H), 5.35 (d, J = 11.3 Hz, 1H), 4.90 (d, J = 16.2 Hz, 1H), 4.71 (s, 1H), 4.20 (d, J = 16.2 Hz, 1H), 3.08 (d, J = 11.7 Hz, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 176.2, 143.5, 136.9, 135.1, 135.0, 133.9, 133.0, 128.6, 128.3, 126.9(2), 126.1, 123.7, 123.2, 122.4, 121.9, 119.6, 118.6, 113.8, 111.2, 109.5, 84.8, 66.3, 52.7, 52.3, 43.4. **HRMS(ESI-TOF)** m/z: $[M + Na]^+$ $C_{27}H_{22}N_2NaO_2$ calcd. 429.1579, found, 429.1586.

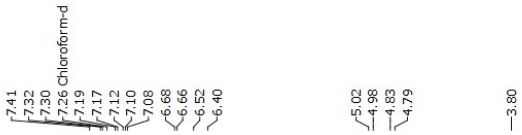
5. Stereochemical analysis of compound 31 by heteronuclear coupling constant between the C1-carbon and the proton at C3 *via* non-decoupling ^{13}CNMR.

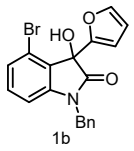




31

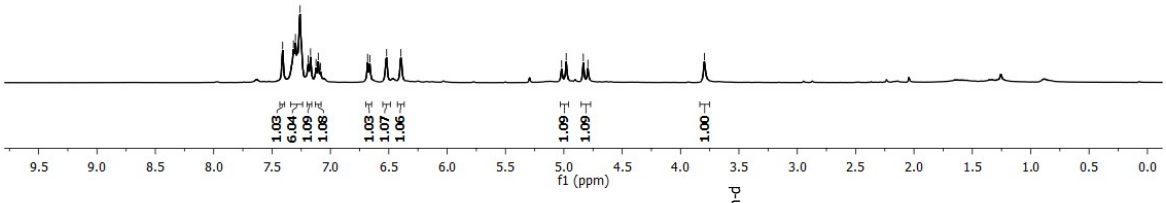
6. NMR spectra of new compound

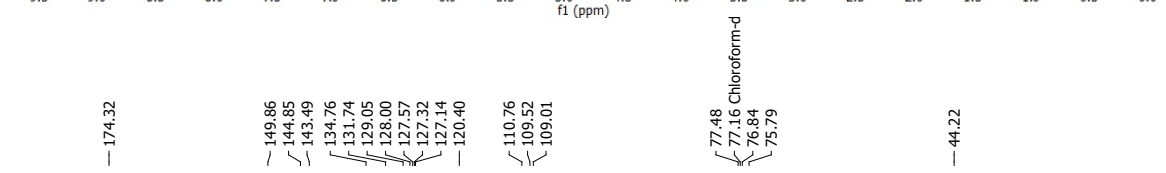


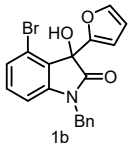


1b

^{1}H NMR, $CDCl_3$, 400 MHz

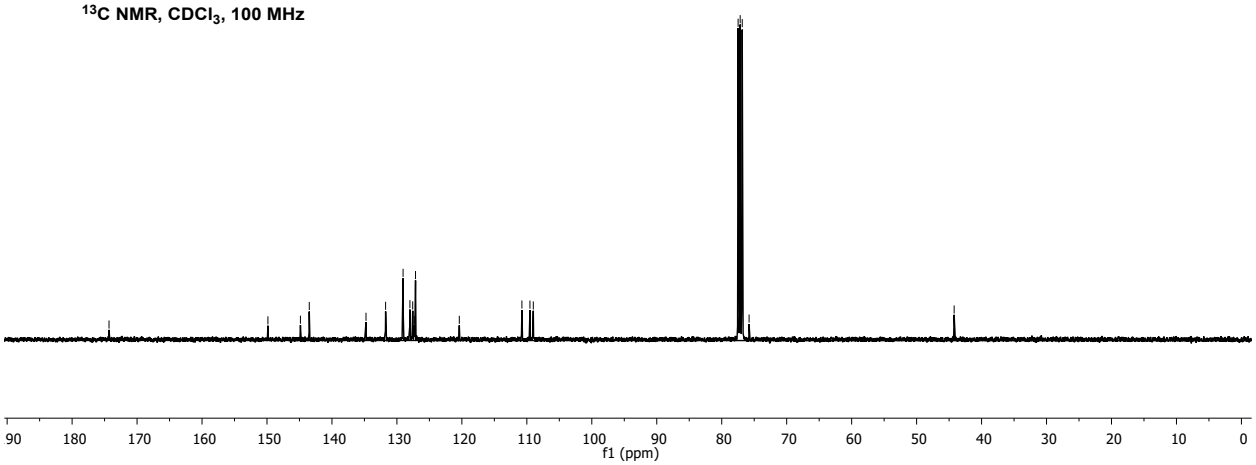


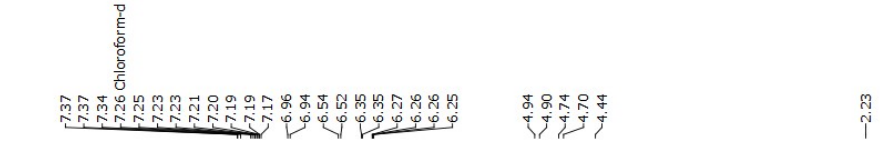


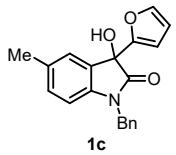


1b

^{13}C NMR, $CDCl_3$, 100 MHz

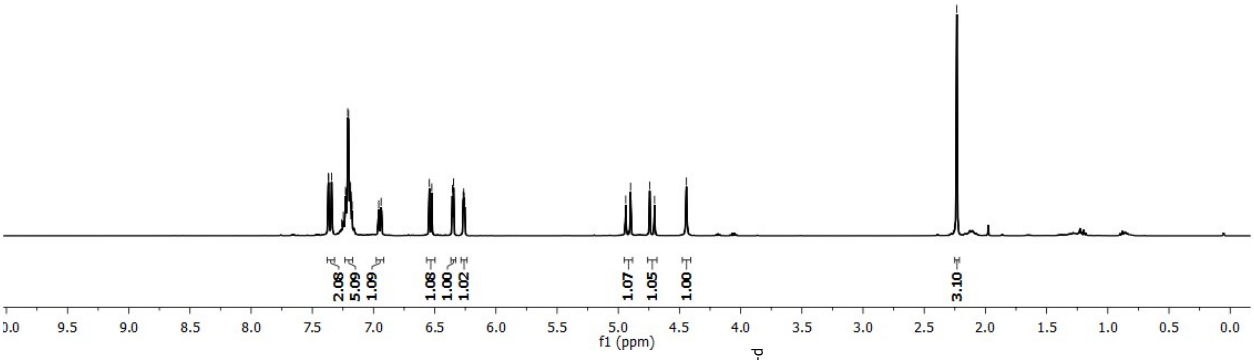


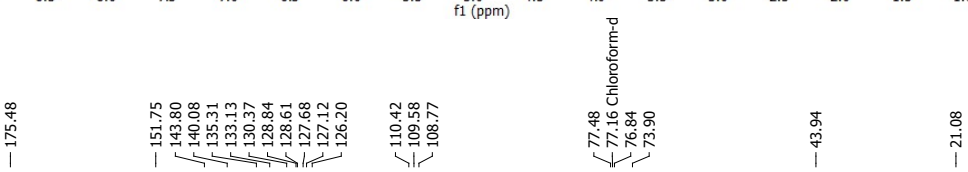


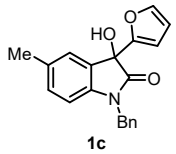


1c

^{1}H NMR, $CDCl_3$, 400 MHz

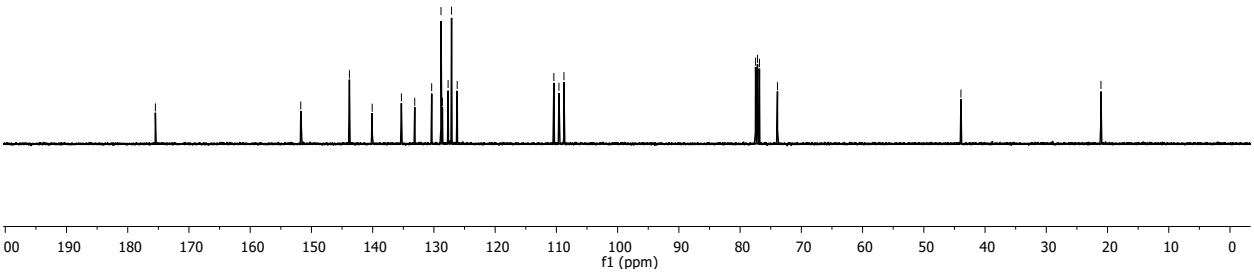


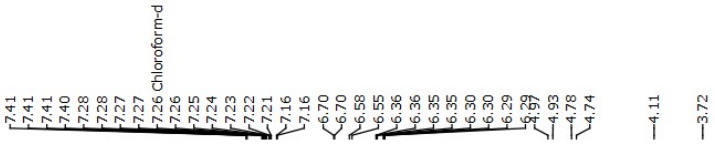


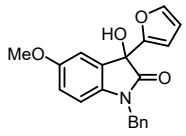


1c

^{13}C NMR, $CDCl_3$, 100 MHz

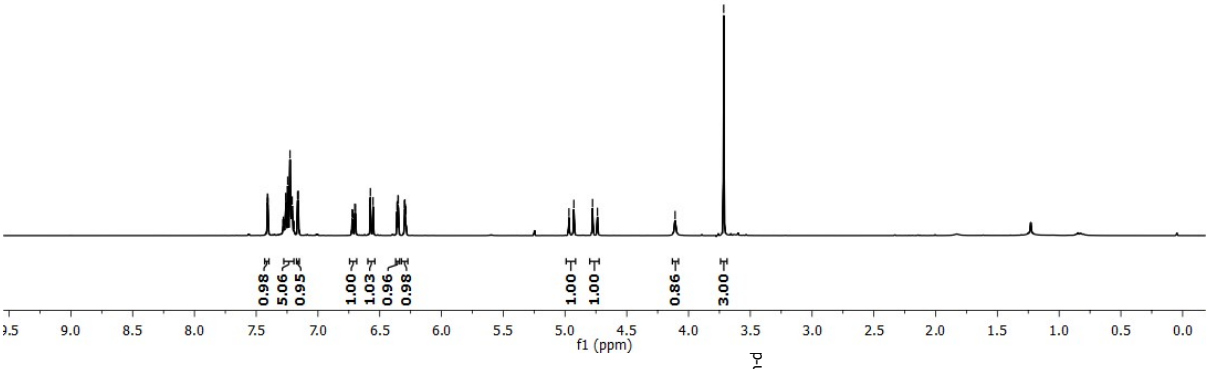


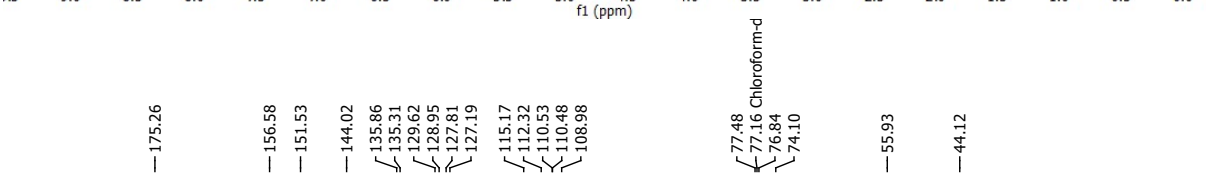


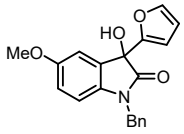


1d

^{1}H NMR, $CDCl_3$, 400 MHz

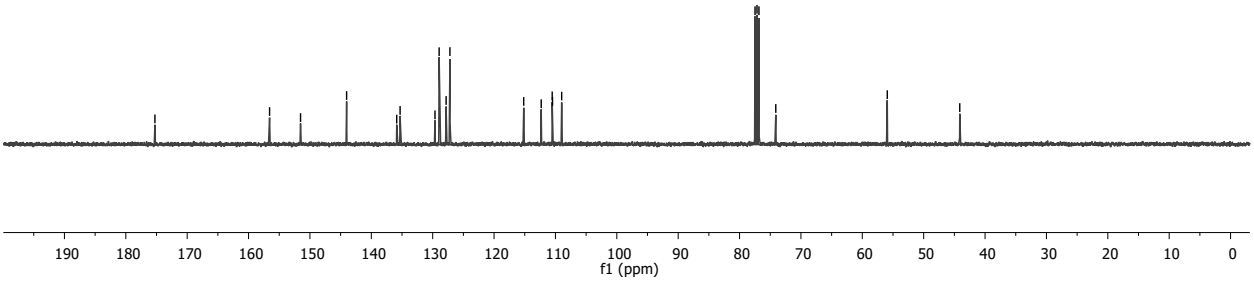


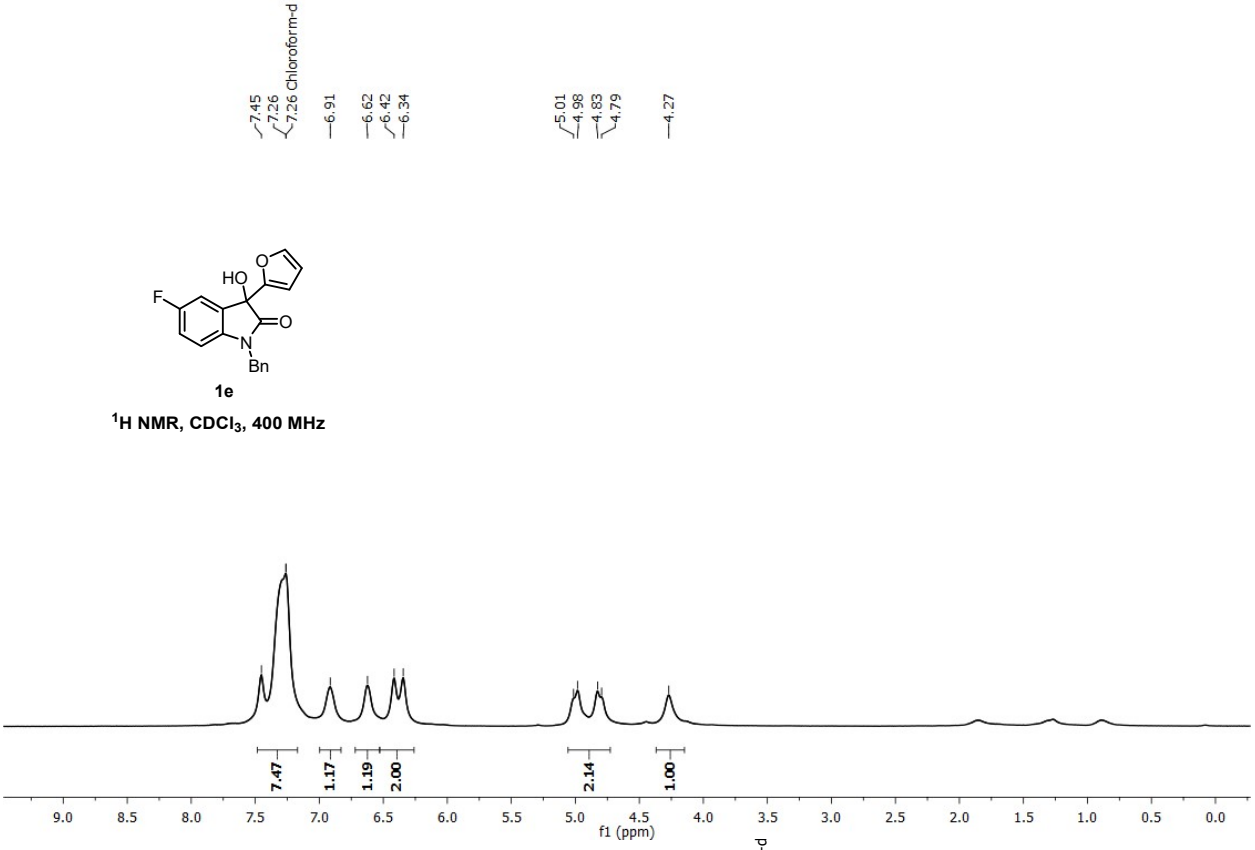




1d

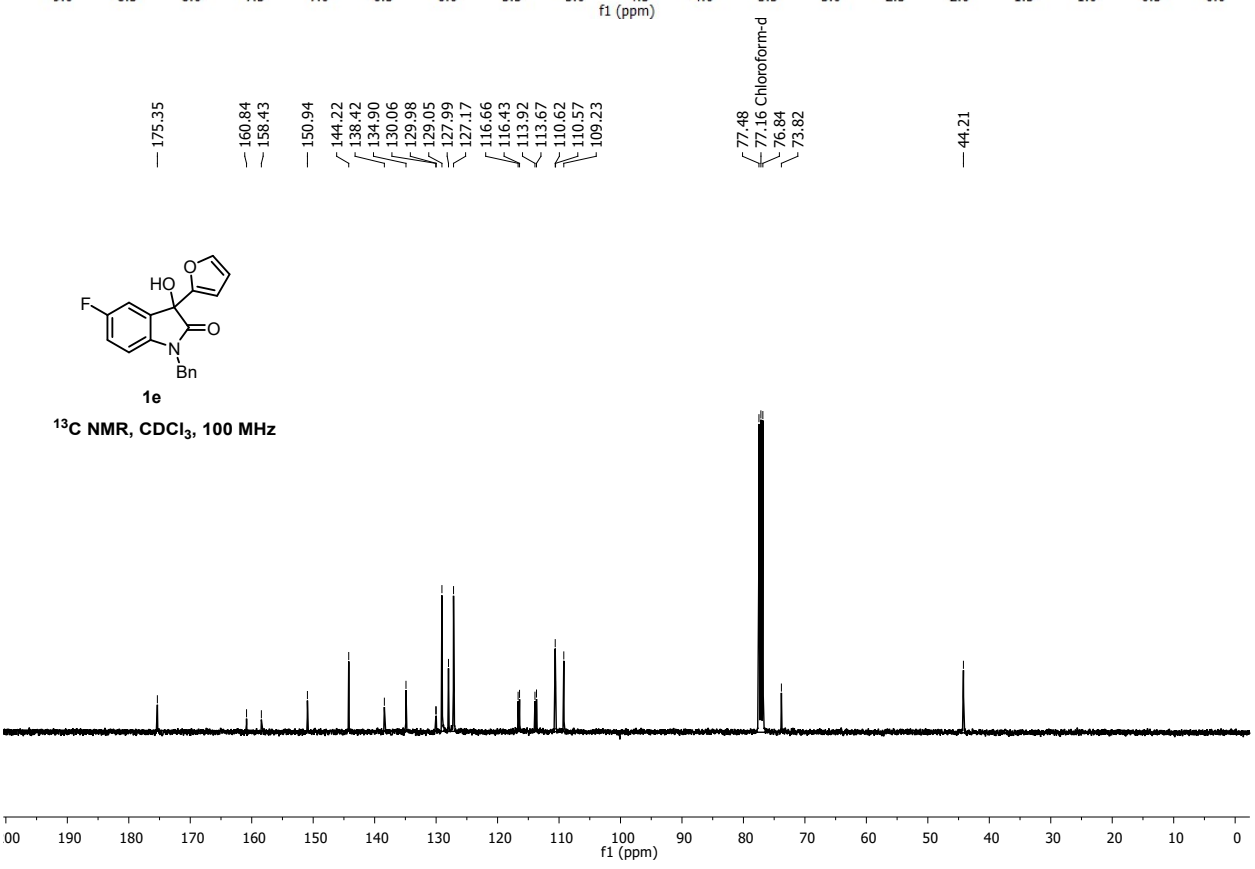
^{13}C NMR, $CDCl_3$, 100 MHz





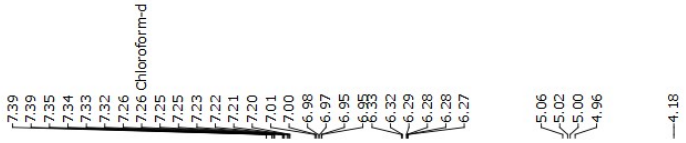
1e

^{1}H NMR, $CDCl_3$, 400 MHz



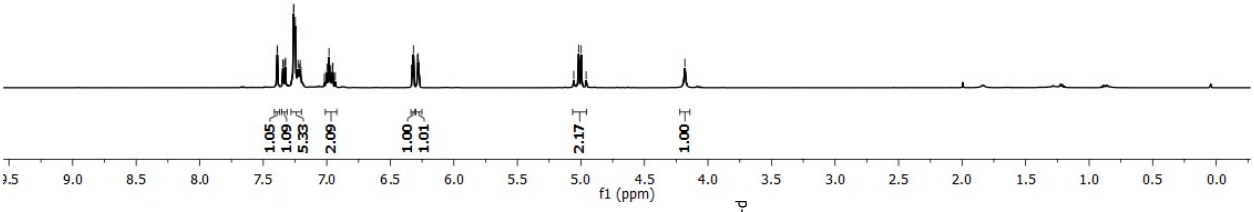
1e

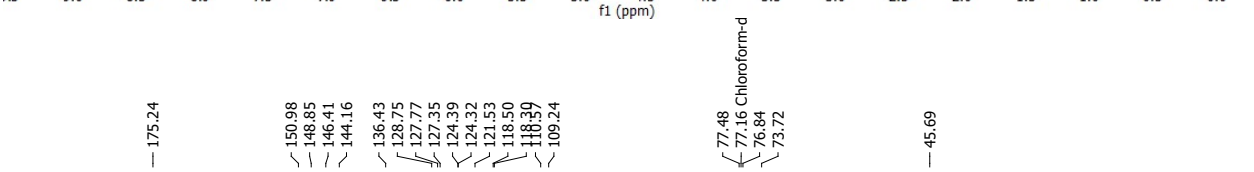
^{13}C NMR, $CDCl_3$, 100 MHz



1f

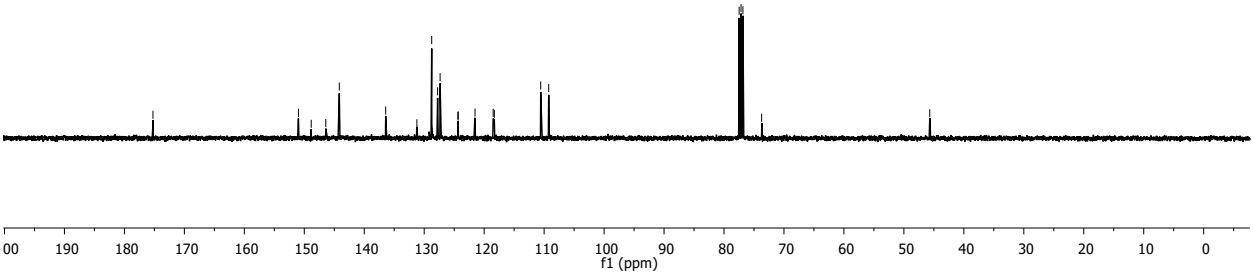
^{1}H NMR, $CDCl_3$, 400 MHz

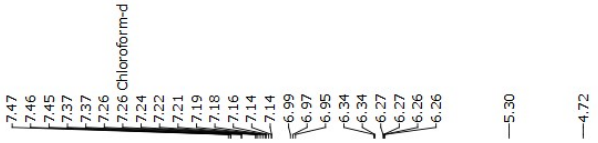


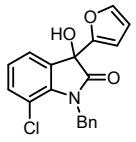


1f

^{13}C NMR, $CDCl_3$, 100 MHz

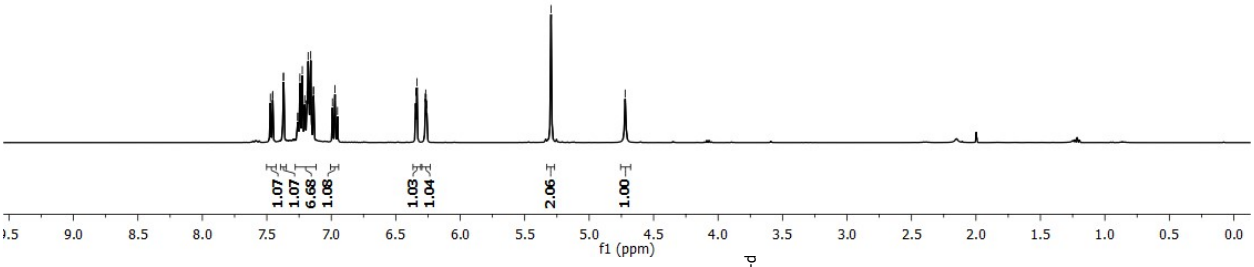


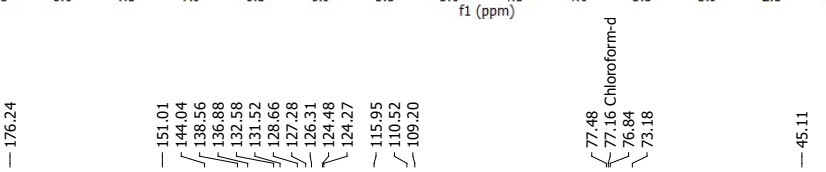


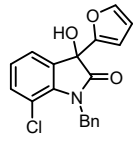


1g

^{1}H NMR, $CDCl_3$, 400 MHz

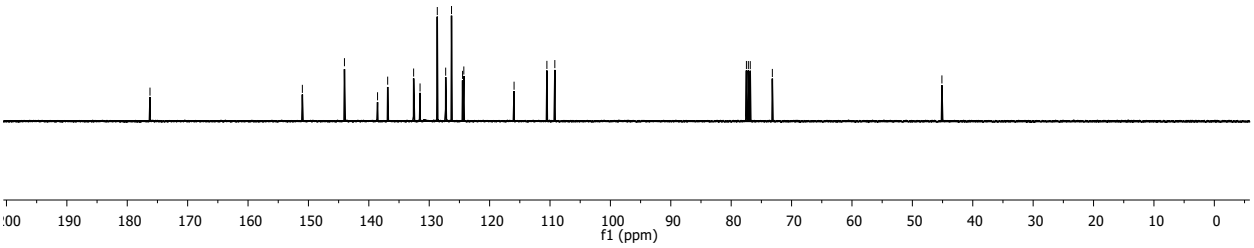


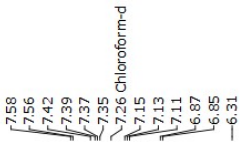


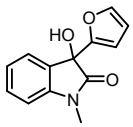


1g

^{13}C NMR, $CDCl_3$, 100 MHz

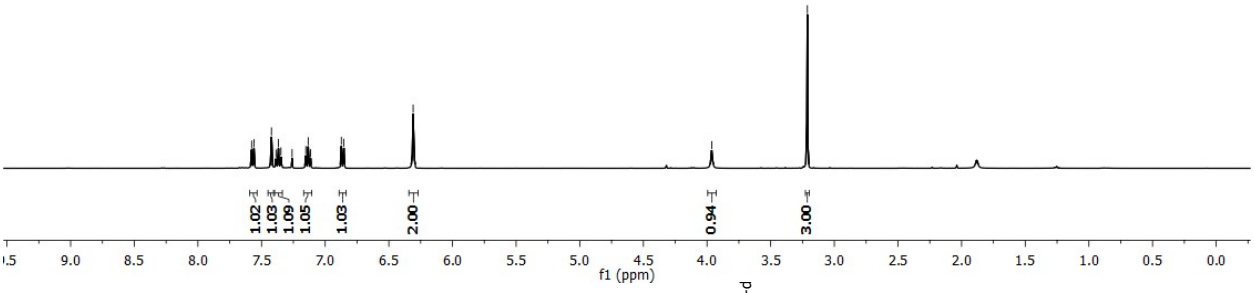


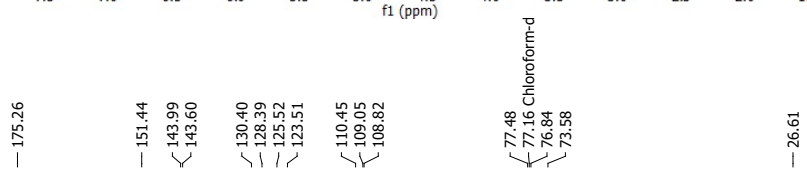


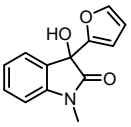


1h

^{1}H NMR, $CDCl_3$, 400 MHz

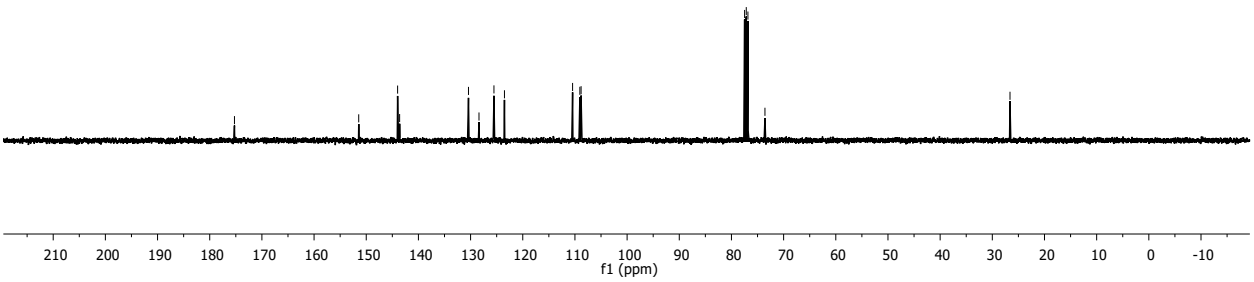


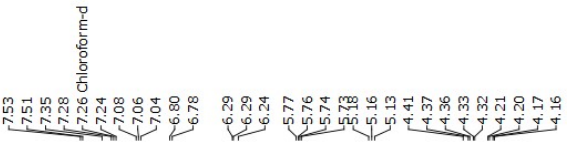


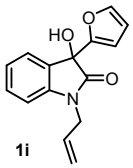


1h

^{13}C NMR, $CDCl_3$, 100 MHz

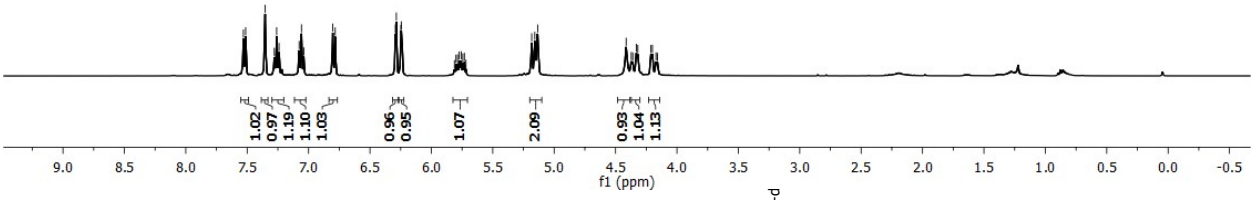


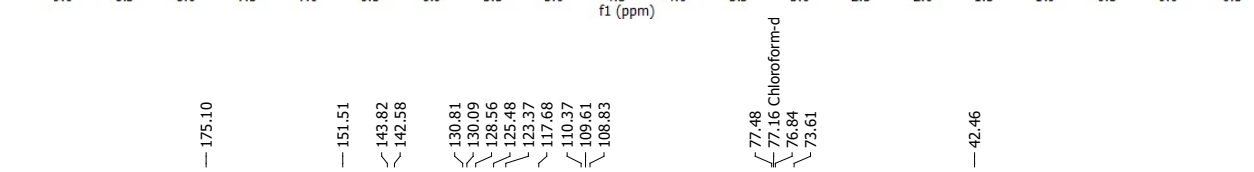


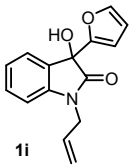


1i

^{1}H NMR, $CDCl_3$, 400 MHz

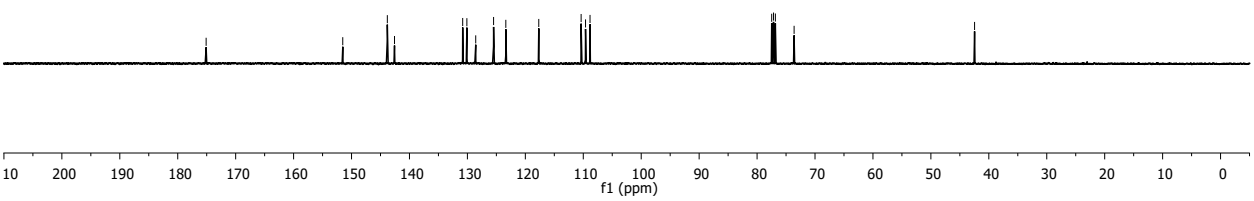


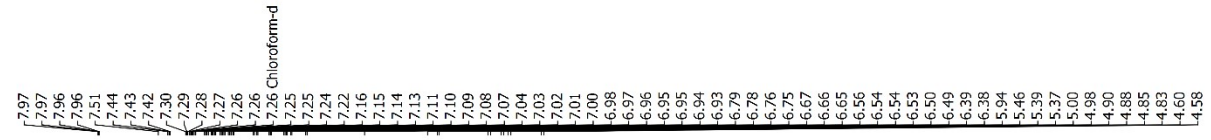


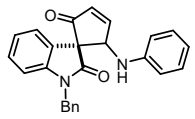


1i

^{13}C NMR, $CDCl_3$, 100 MHz

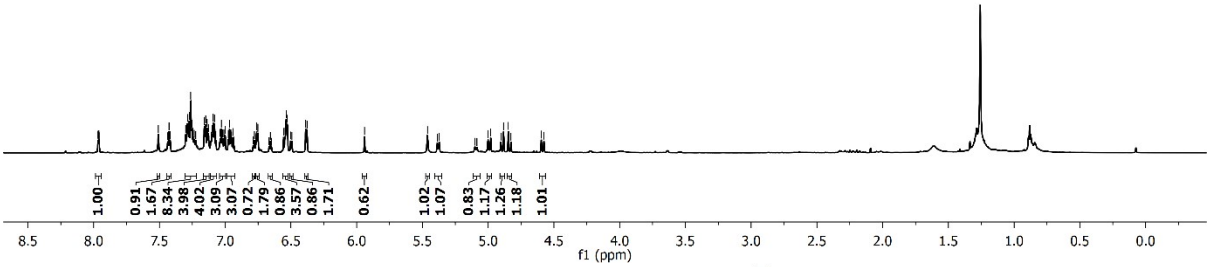


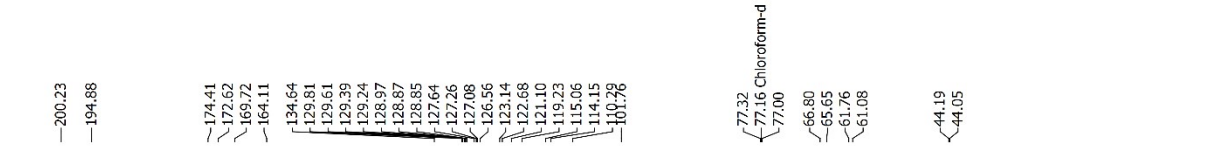


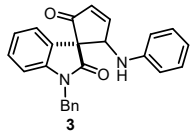


3

^{1}H NMR, $CDCl_3$, 800 MHz

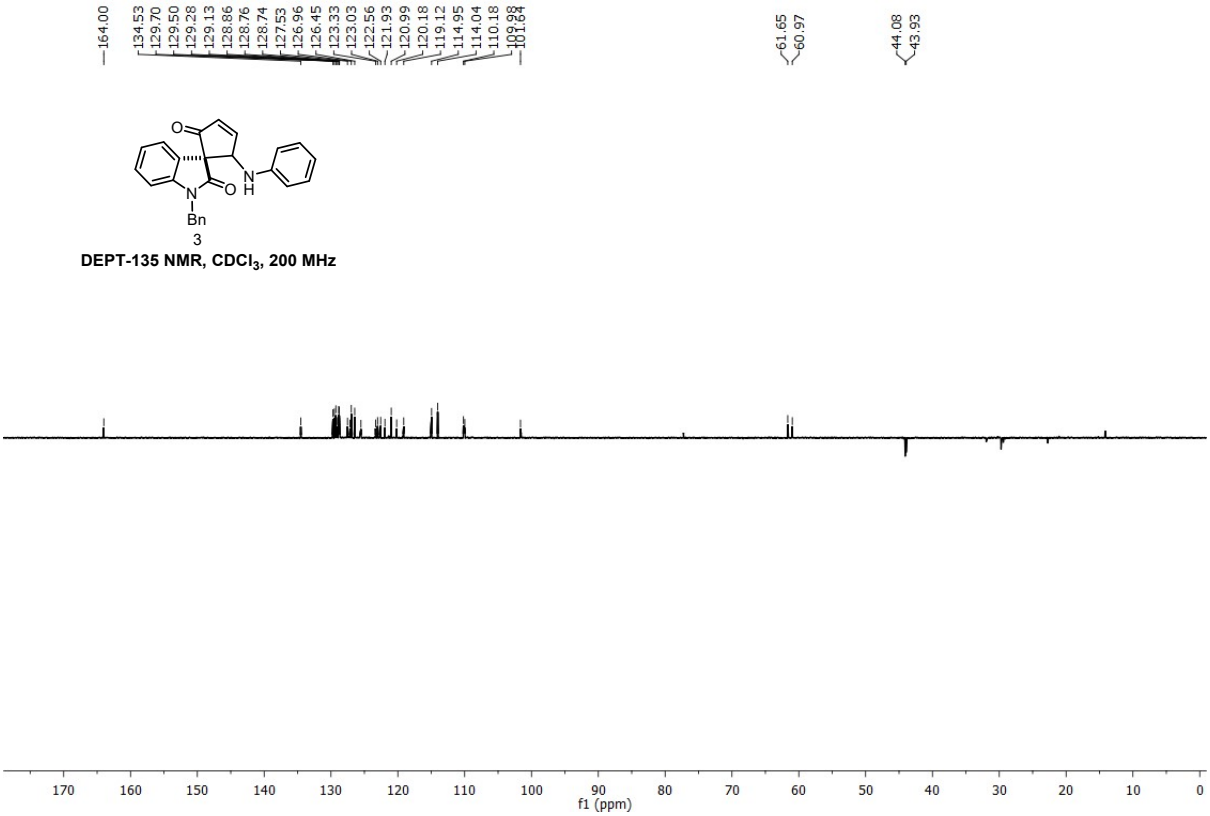






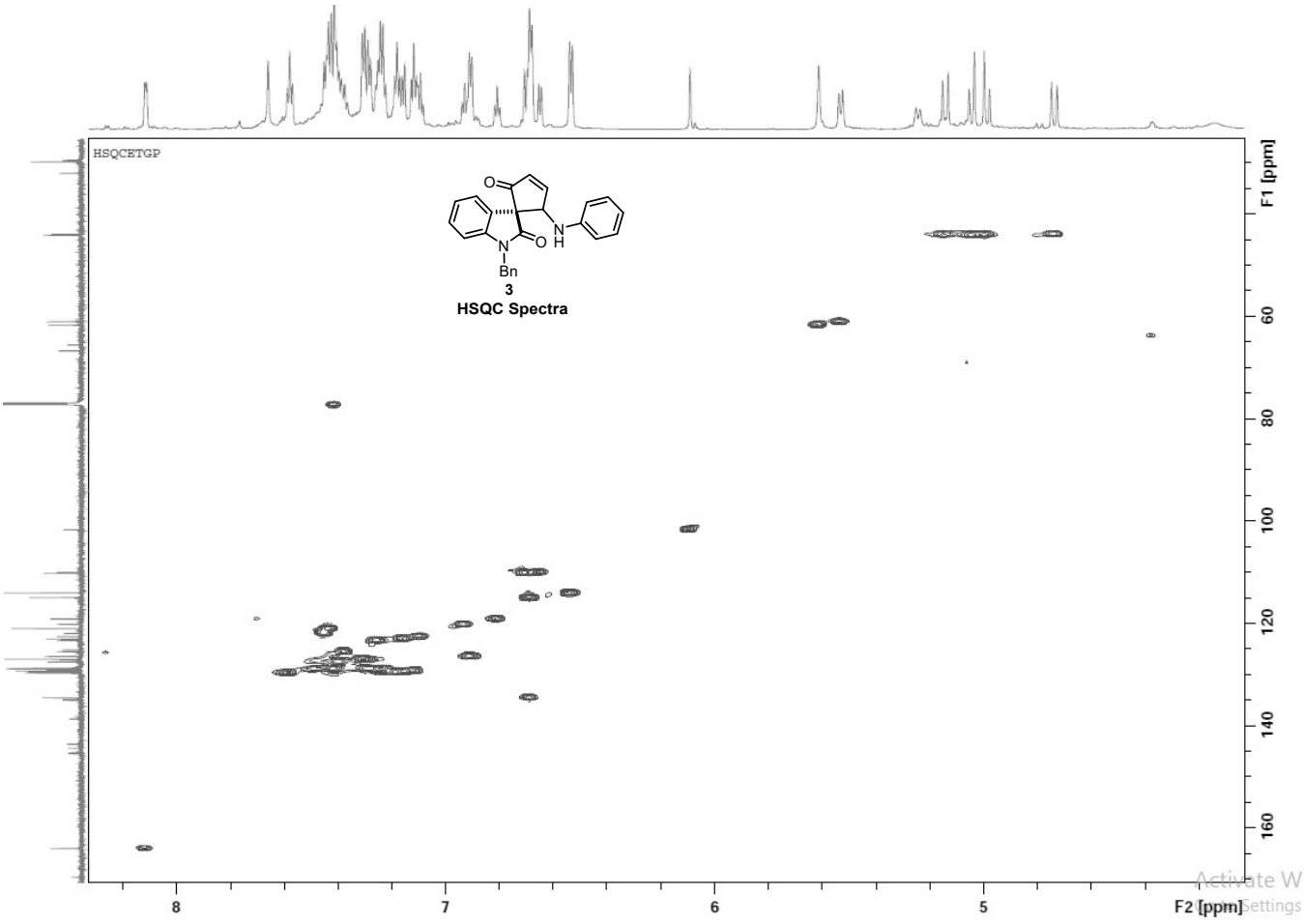
3

^{13}C NMR, $CDCl_3$, 200 MHz



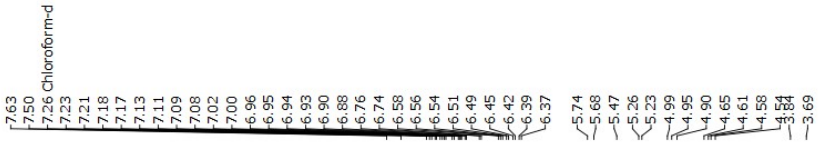
3

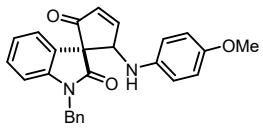
DEPT-135 NMR, $CDCl_3$, 200 MHz



3

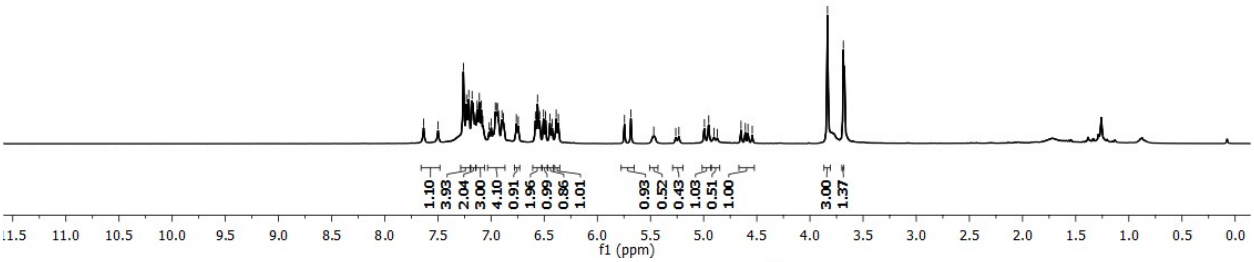
HSQC Spectra

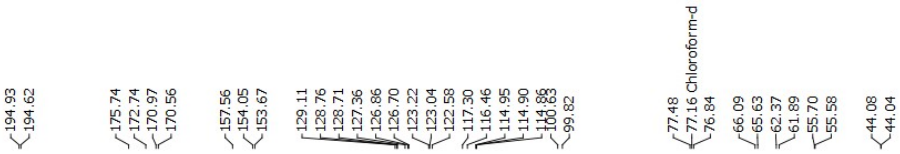


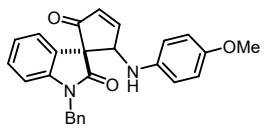


5

^{1}H NMR, $CDCl_3$, 400 MHz

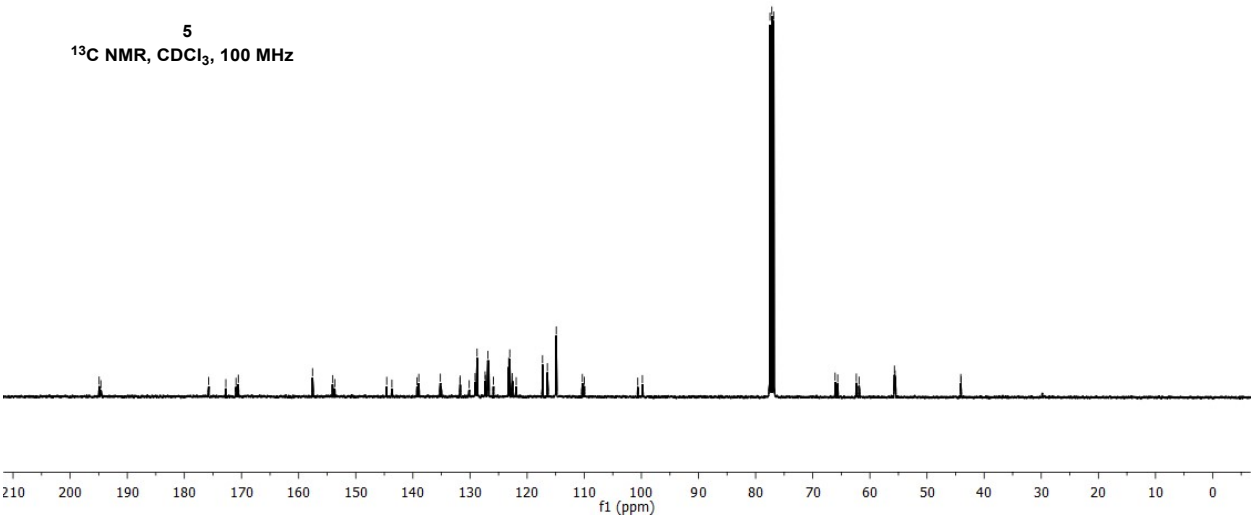


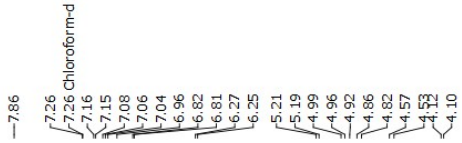


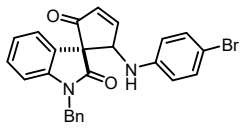


5

^{13}C NMR, $CDCl_3$, 100 MHz

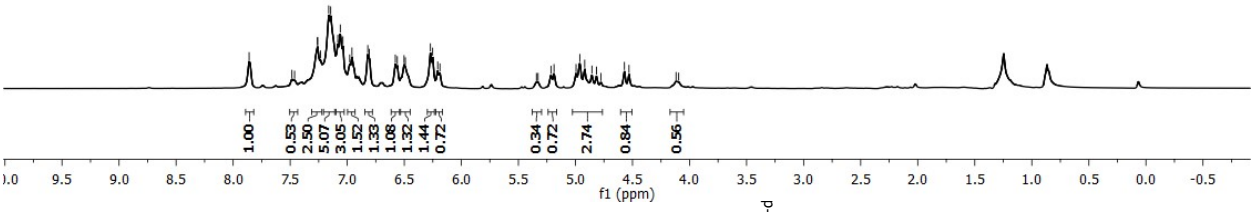


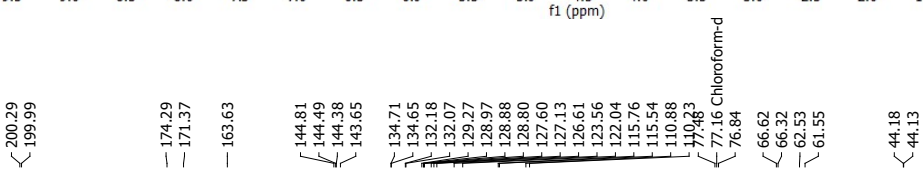


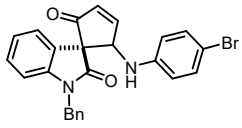


6

^{1}H NMR, $CDCl_3$, 400 MHz

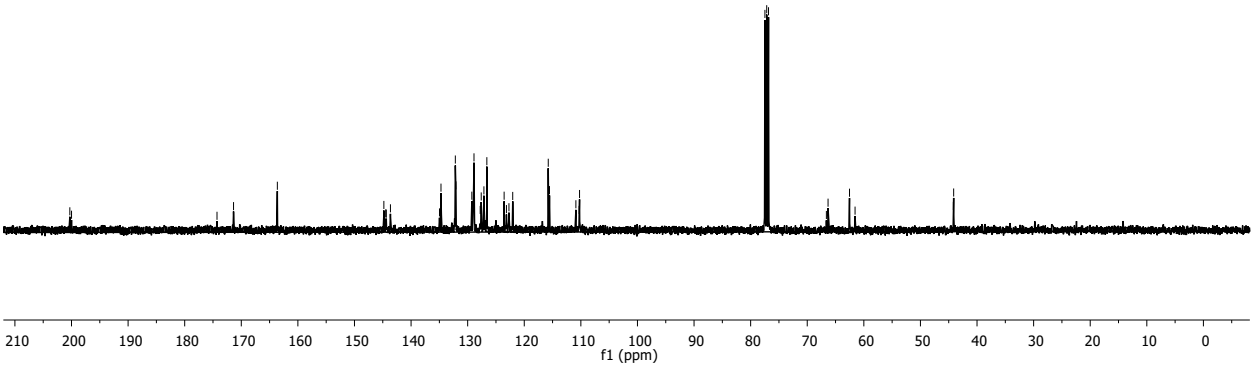


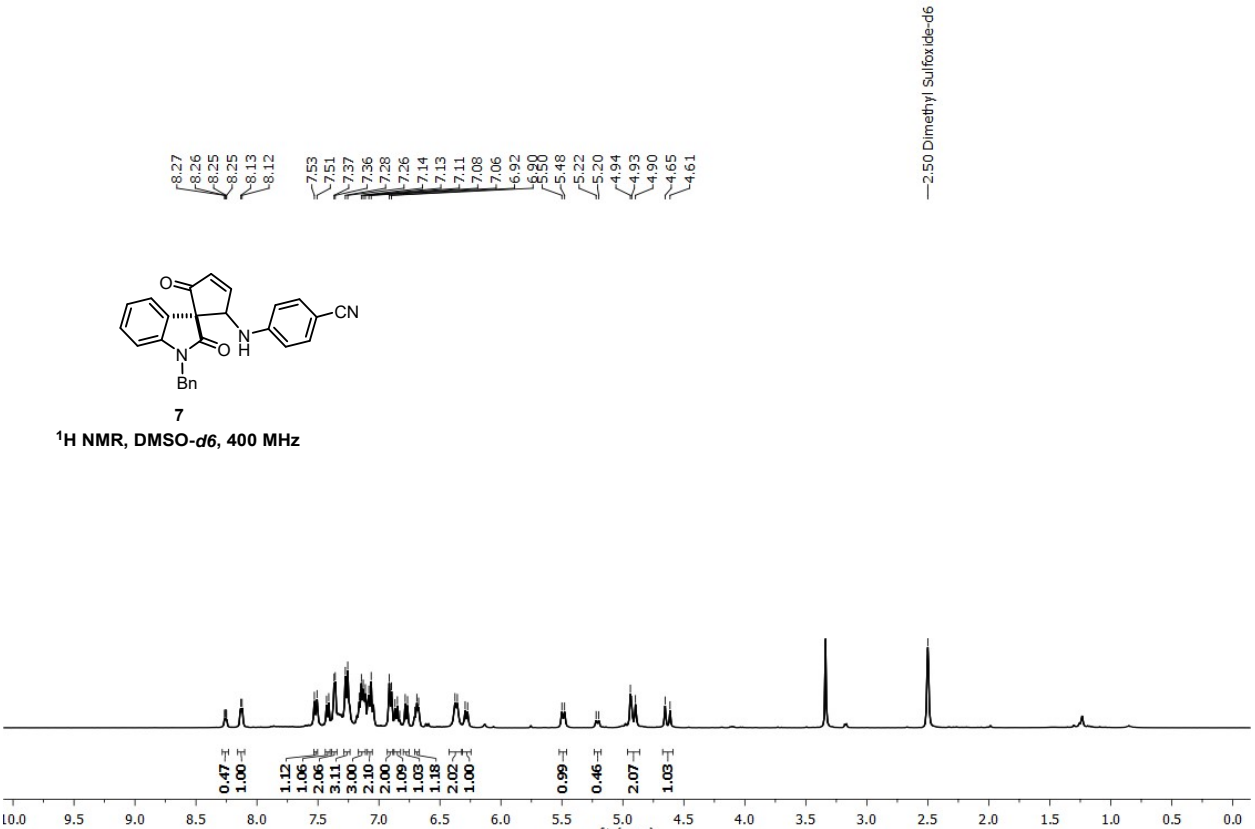




6

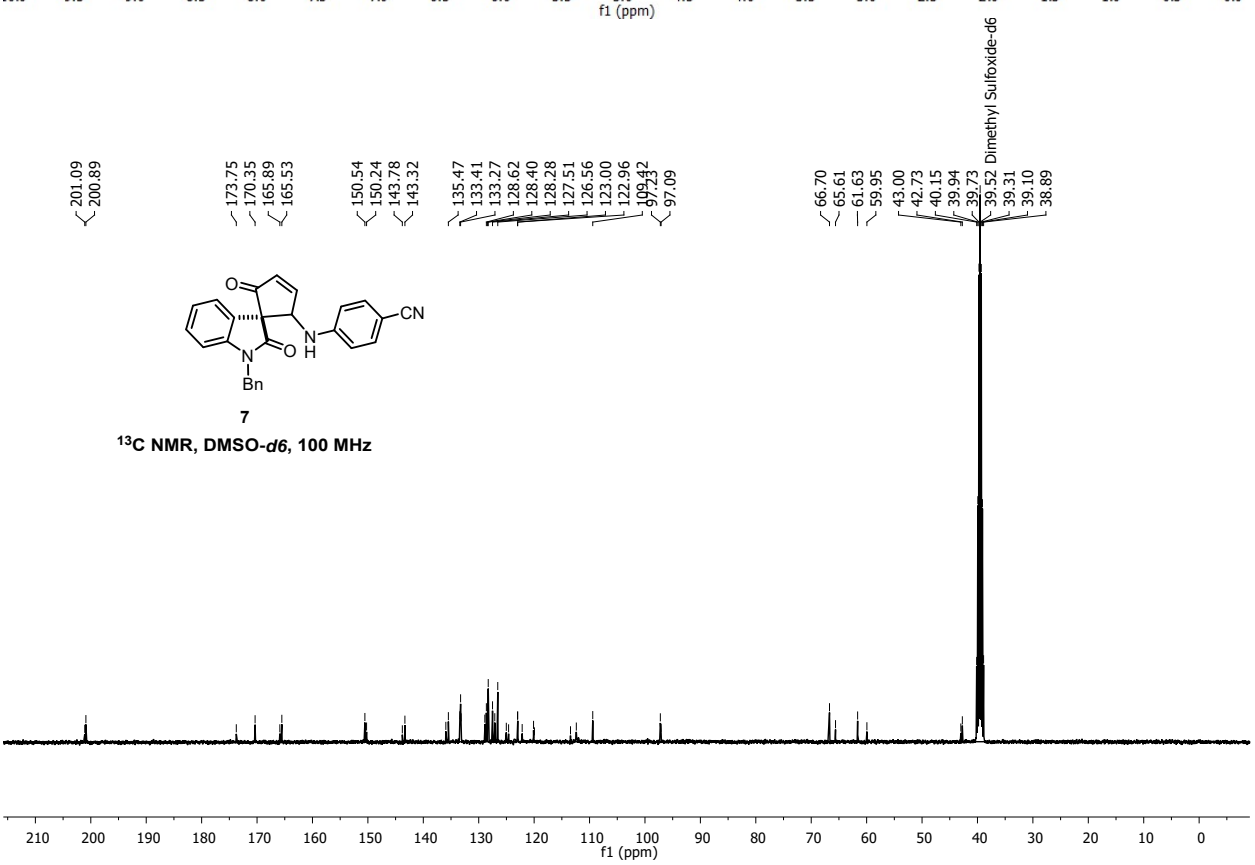
^{13}C NMR, $CDCl_3$, 100 MHz





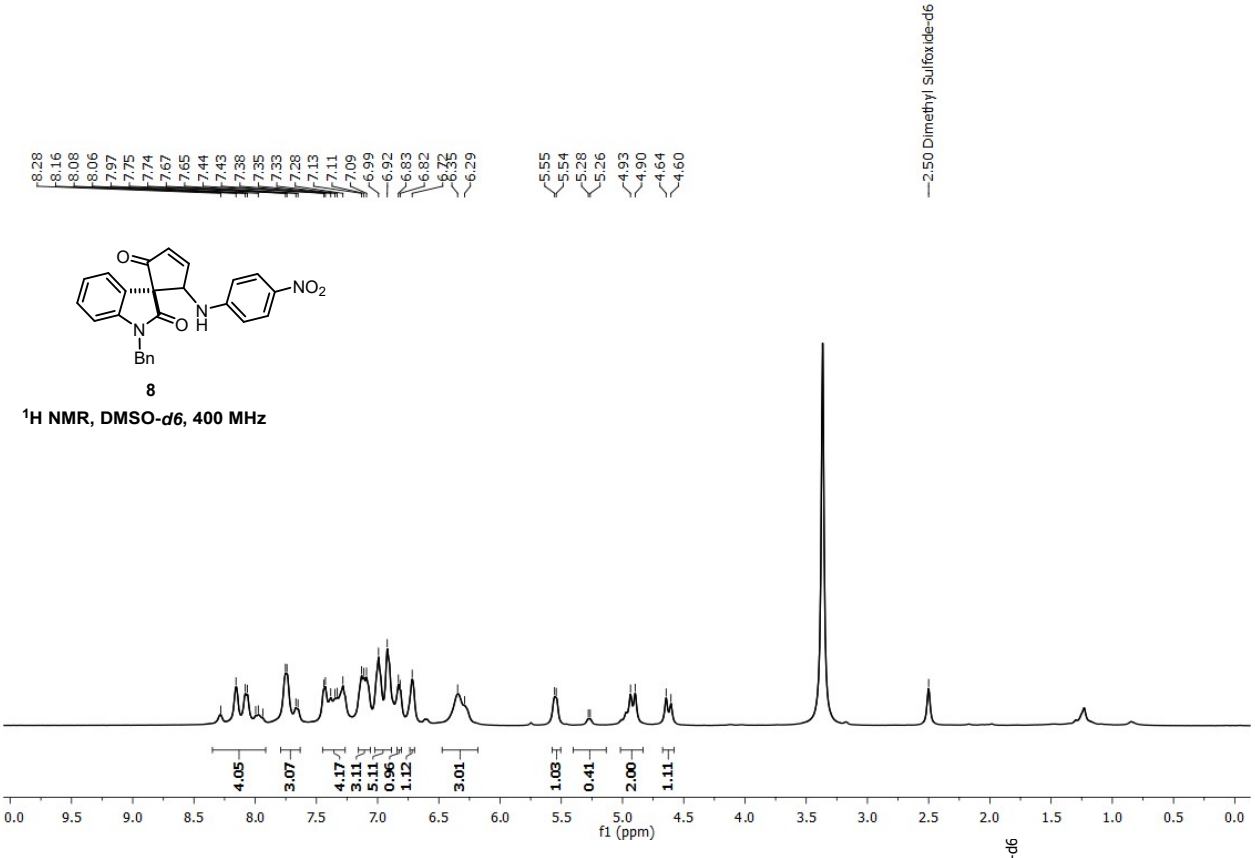
7

^{1}H NMR, DMSO-*d6*, 400 MHz



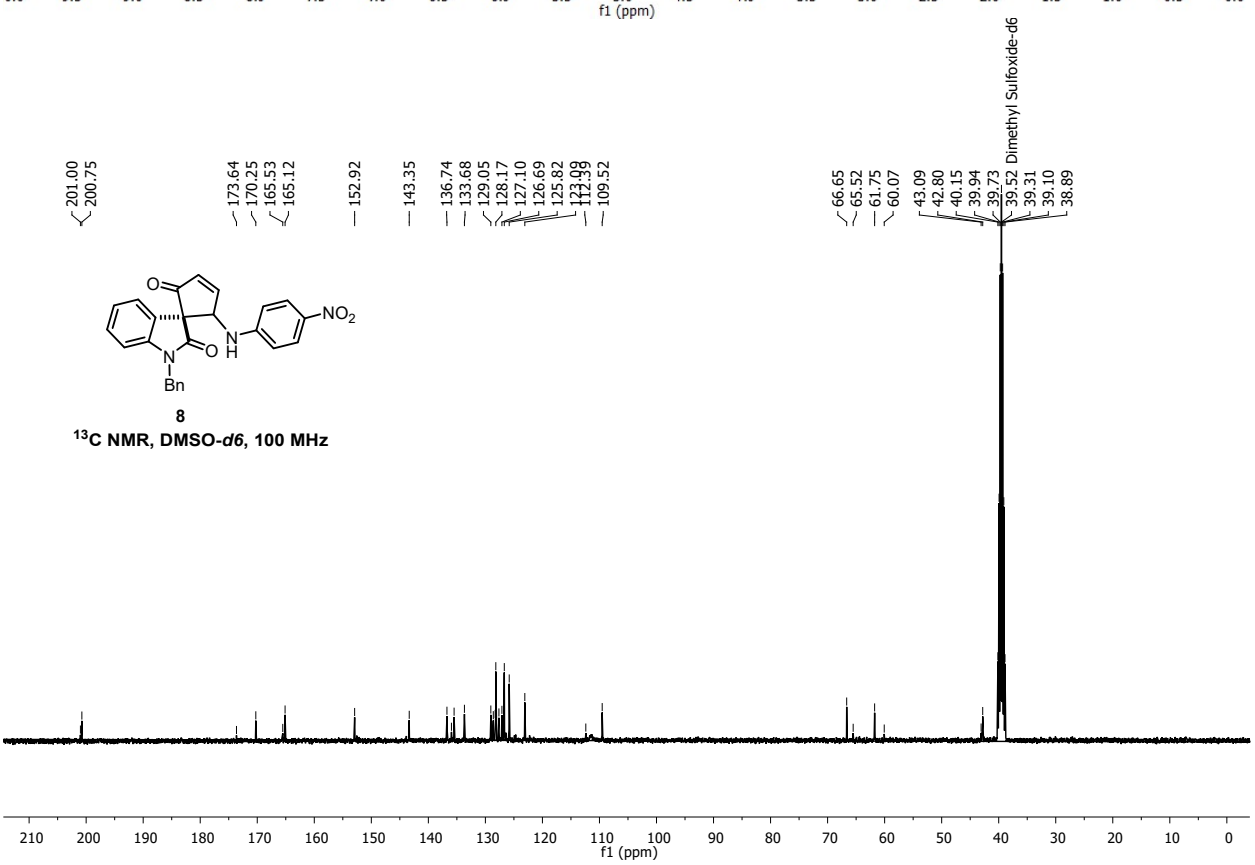
7

^{13}C NMR, DMSO-*d6*, 100 MHz



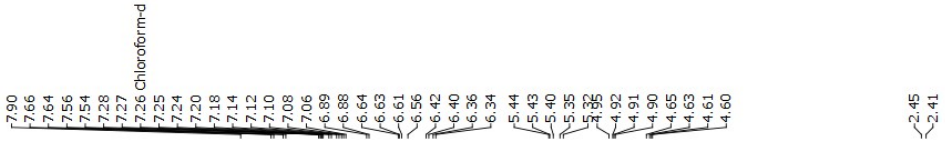
8

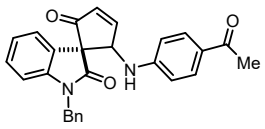
^{1}H NMR, DMSO-*d6*, 400 MHz



8

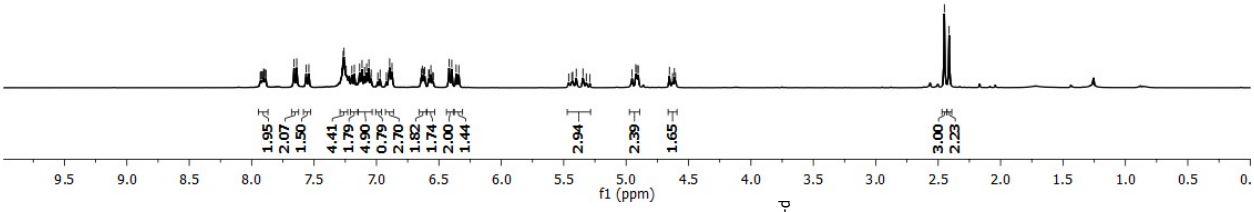
^{13}C NMR, DMSO-*d6*, 100 MHz

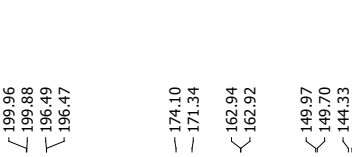


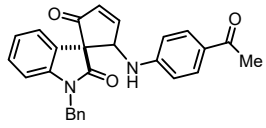


9

^{1}H NMR, $CDCl_3$, 400 MHz

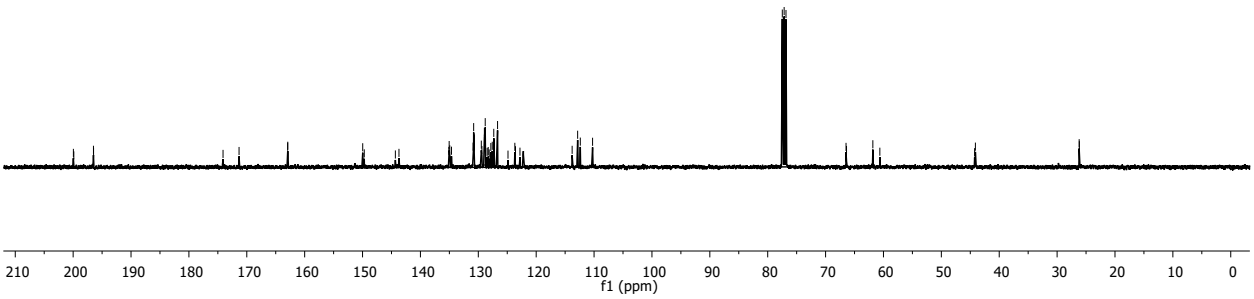


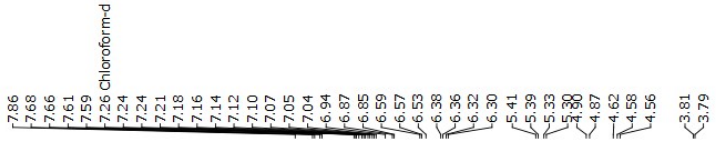


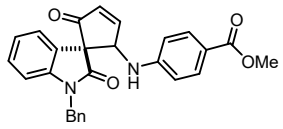


9

^{13}C NMR, $CDCl_3$, 100 MHz

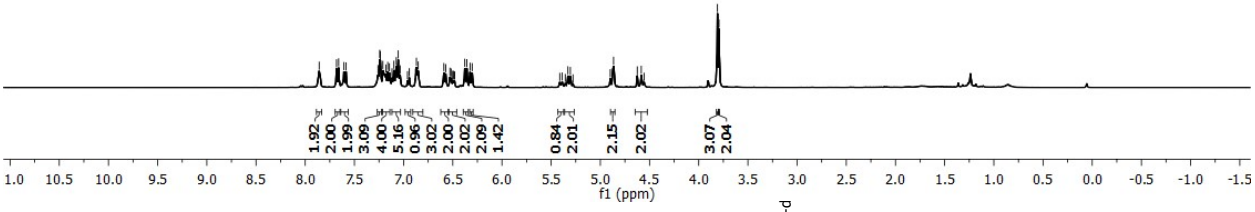


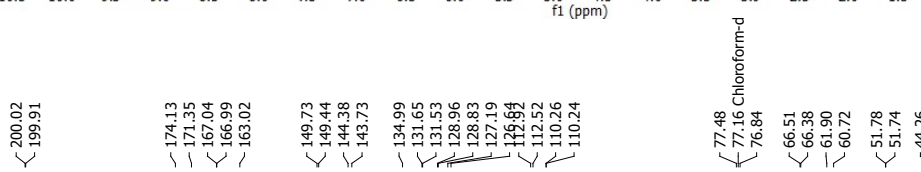


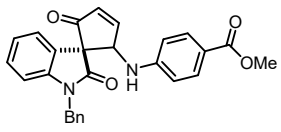


10

^{1}H NMR, $CDCl_3$, 400 MHz

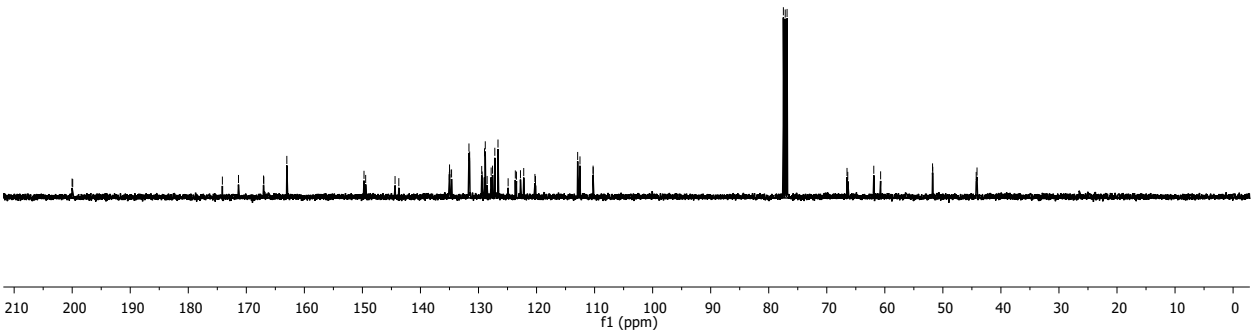


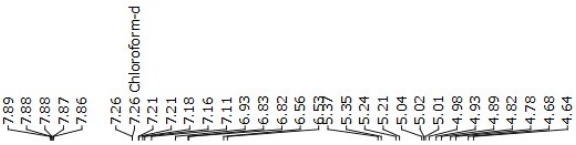


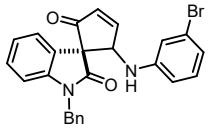


10

^{13}C NMR, $CDCl_3$, 100 MHz

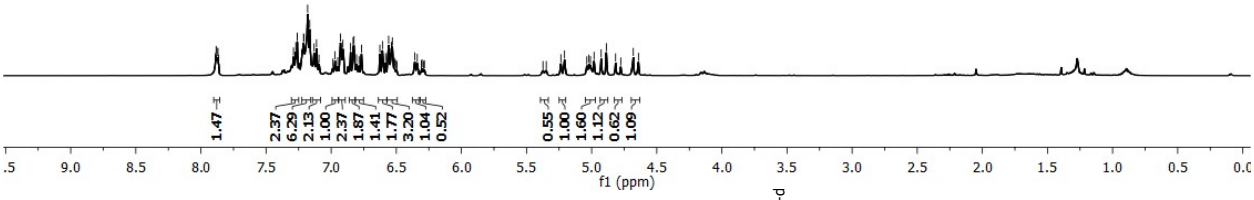


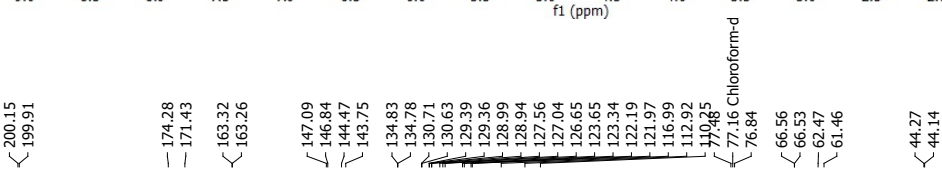


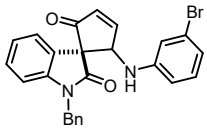


11

^{1}H NMR, $CDCl_3$, 400 MHz

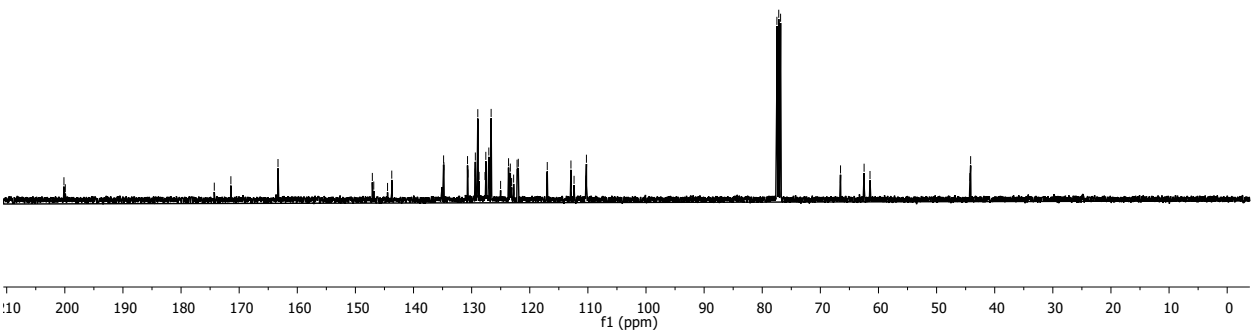


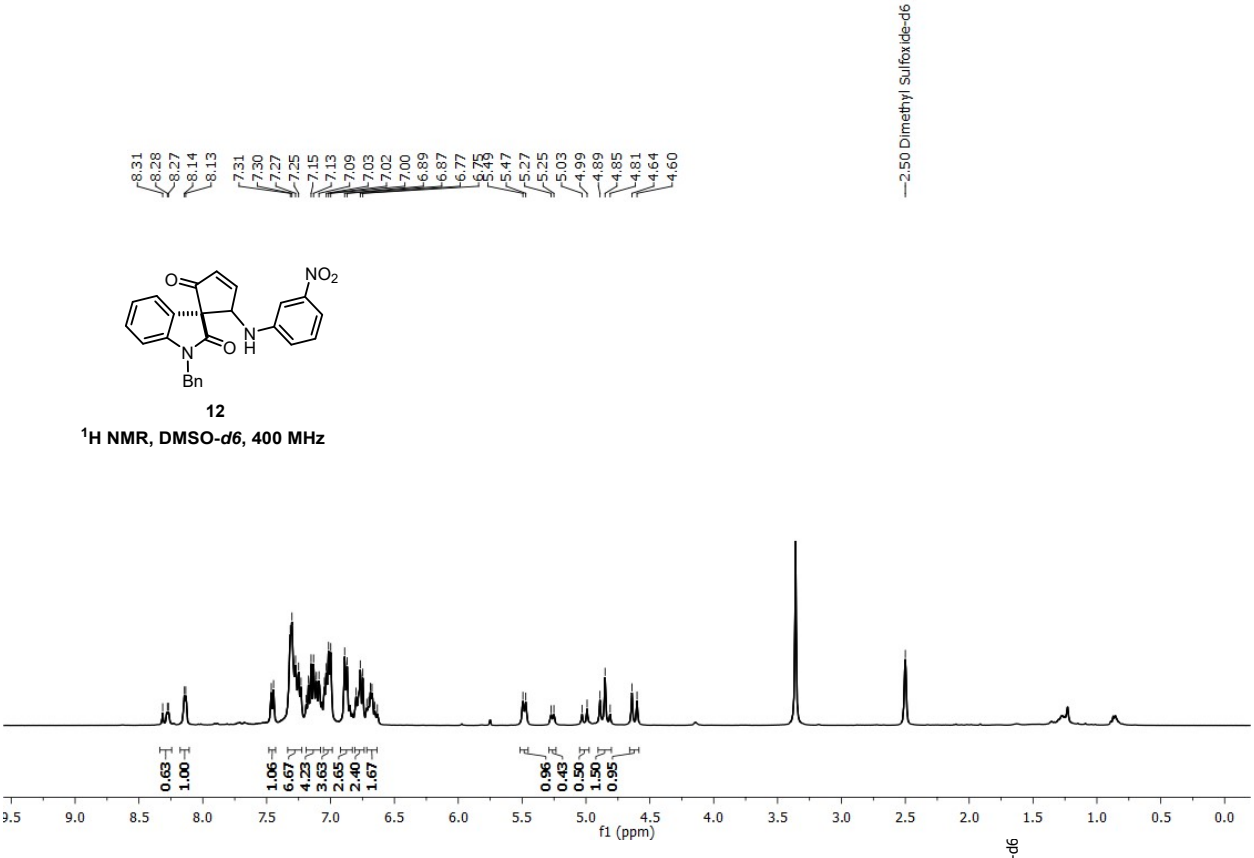




11

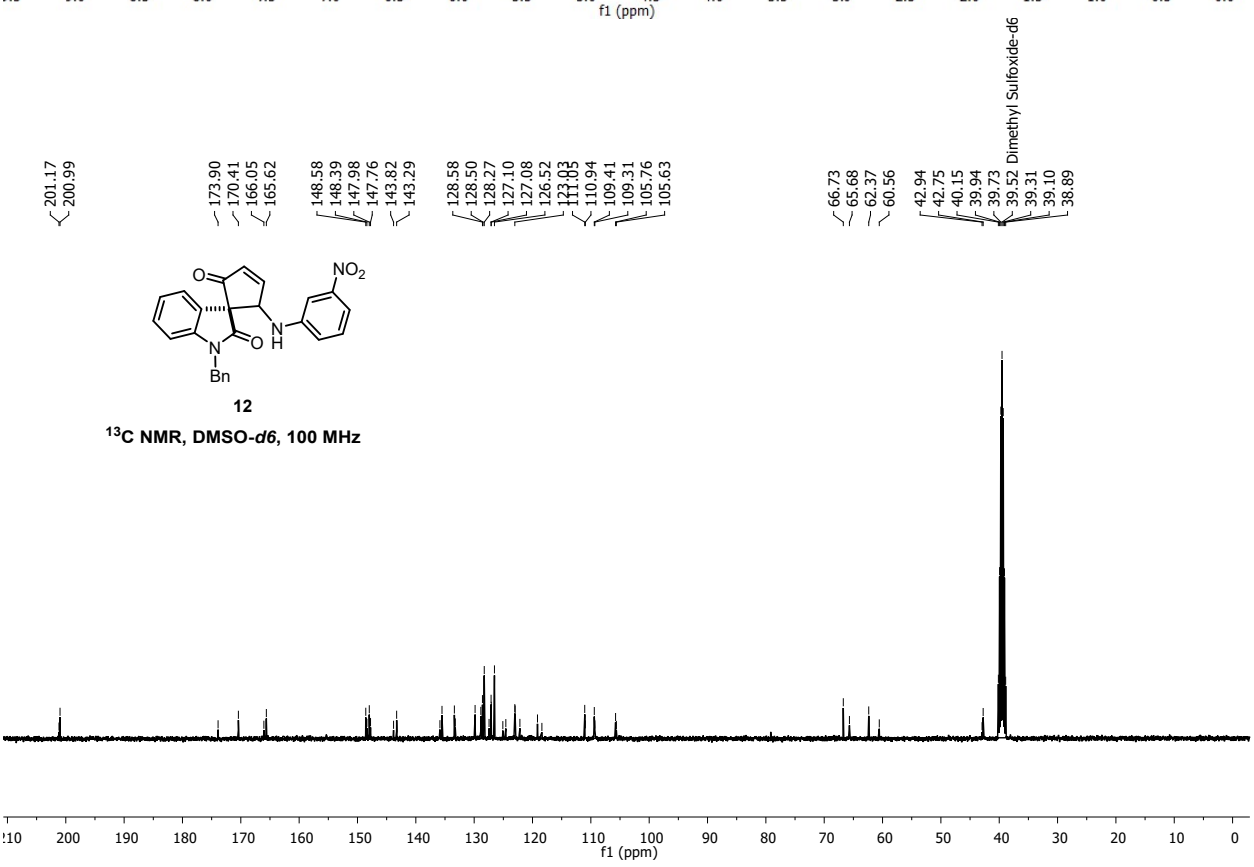
^{13}C NMR, $CDCl_3$, 100 MHz





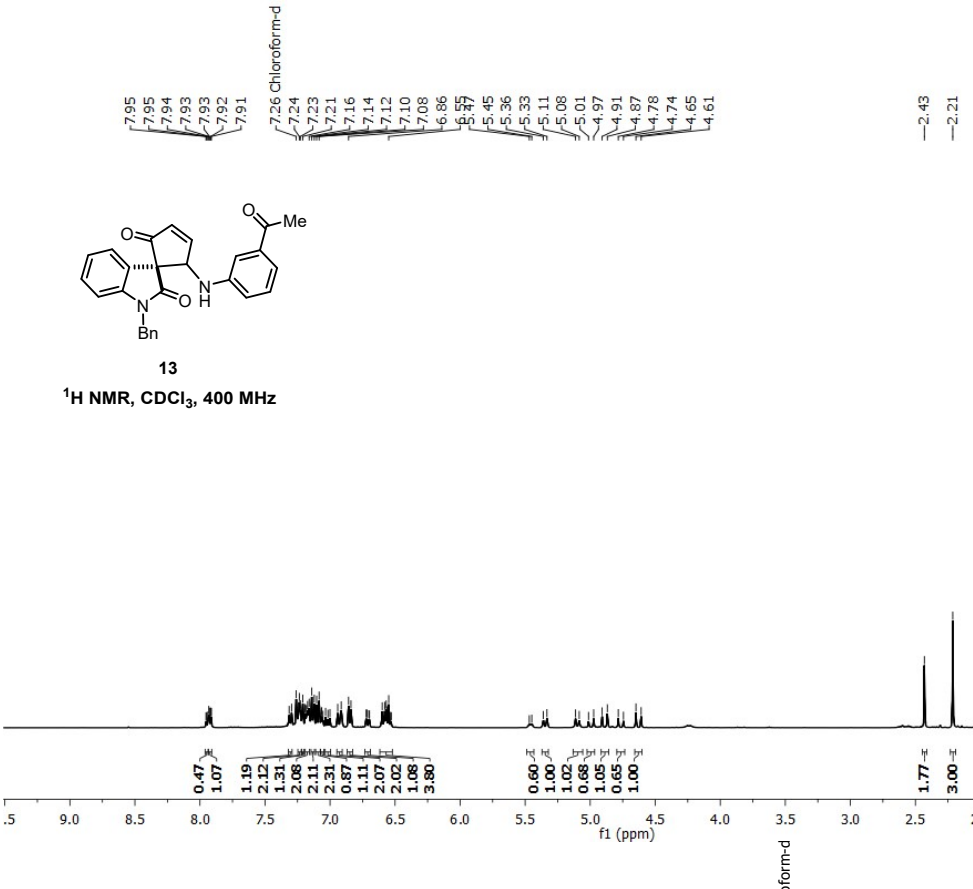
12

^{1}H NMR, DMSO-*d6*, 400 MHz



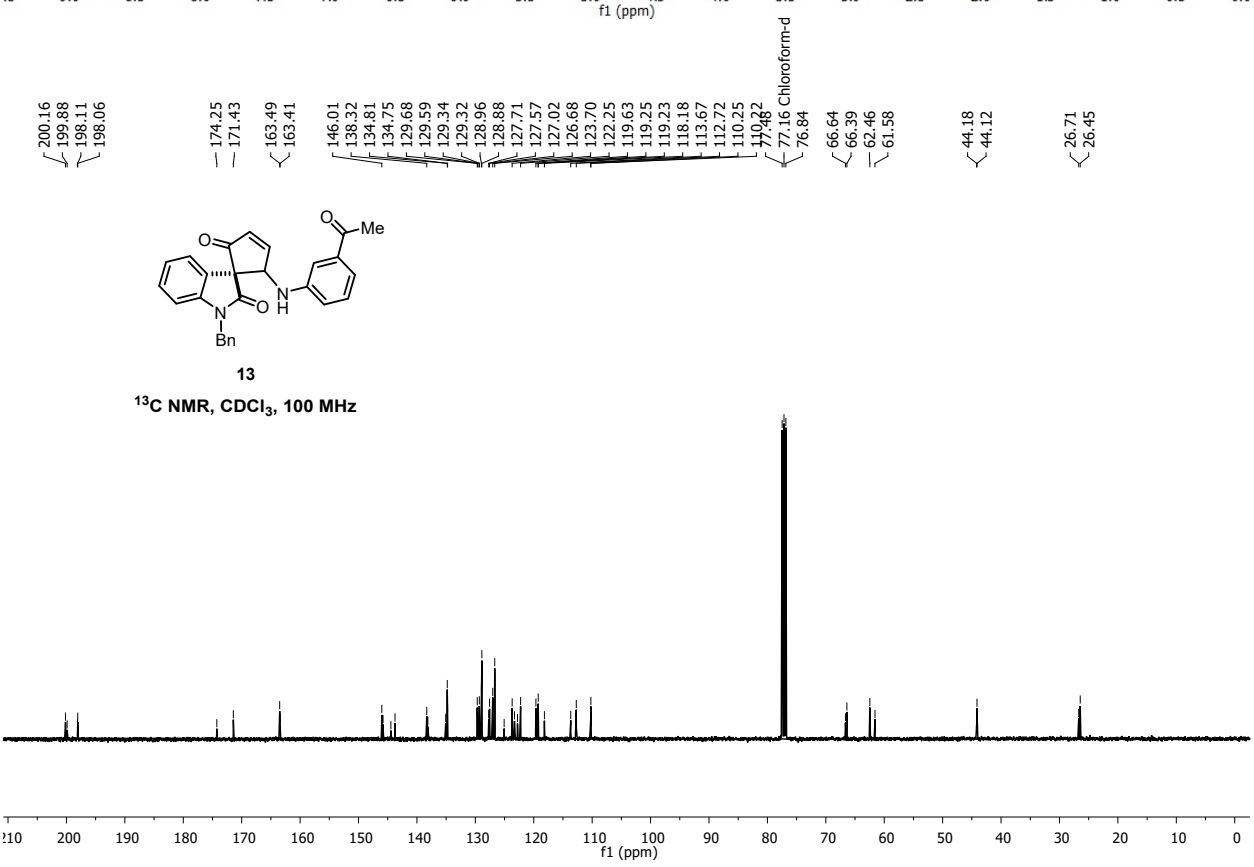
12

^{13}C NMR, DMSO-*d6*, 100 MHz



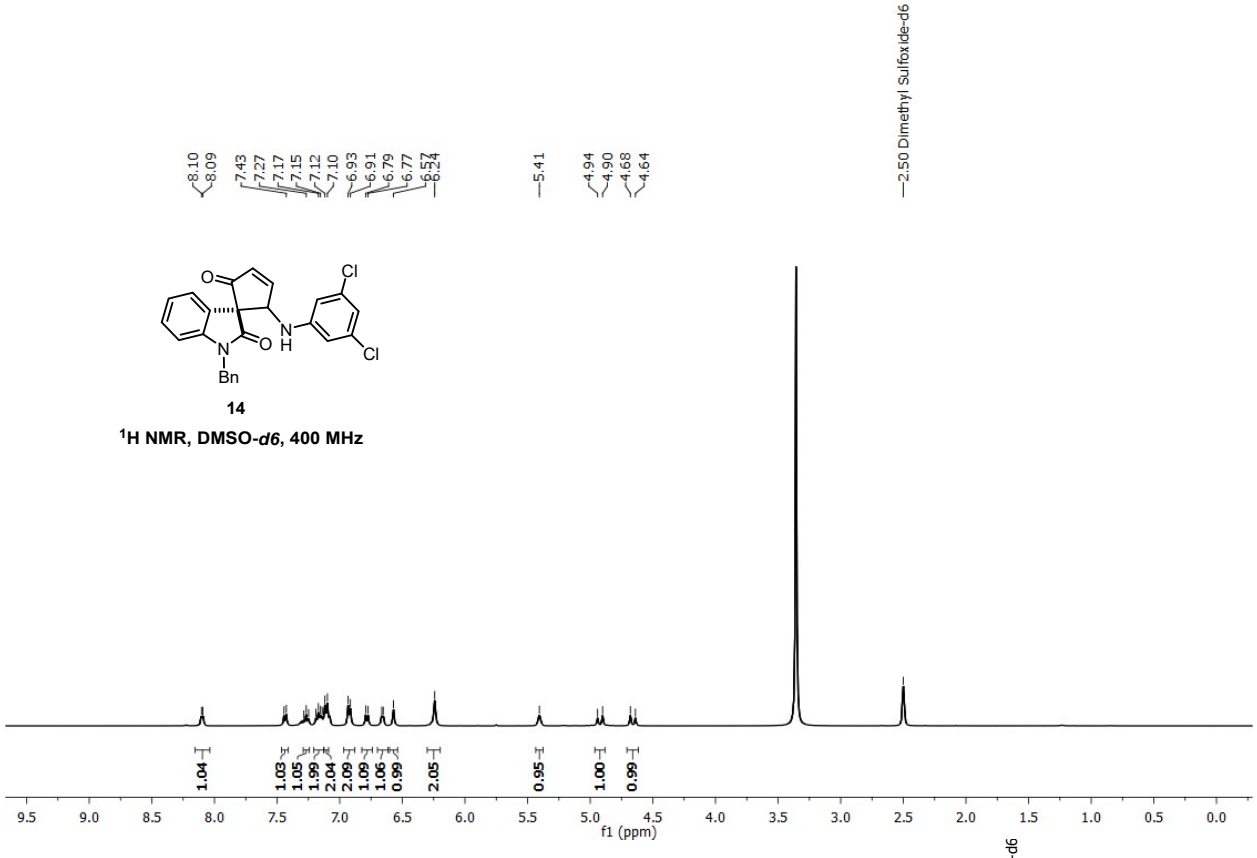
13

^{1}H NMR, $CDCl_3$, 400 MHz



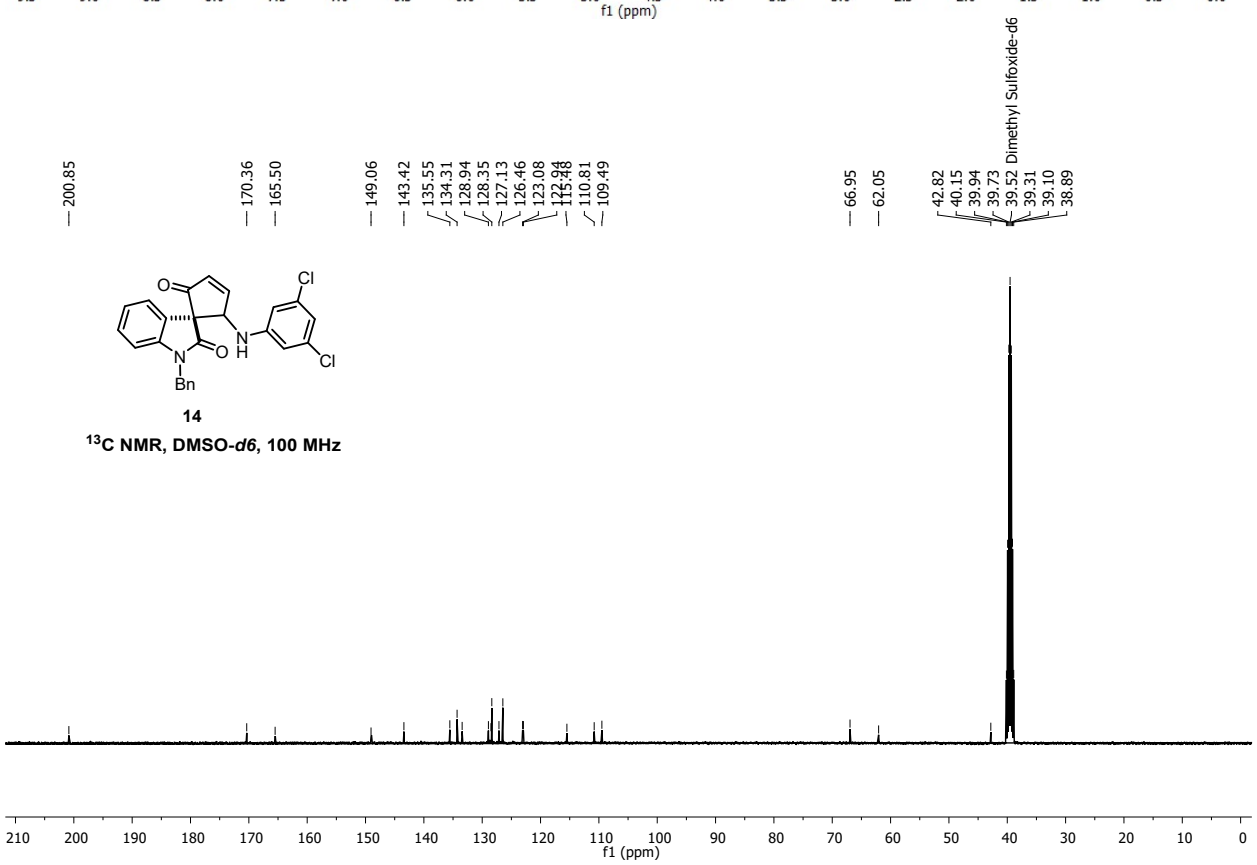
13

^{13}C NMR, $CDCl_3$, 100 MHz



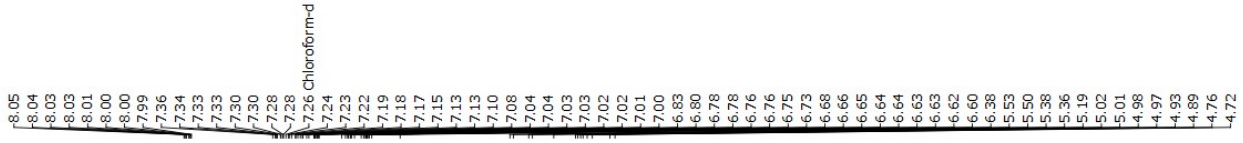
14

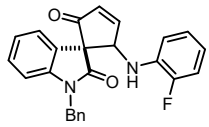
^{1}H NMR, DMSO-*d6*, 400 MHz



14

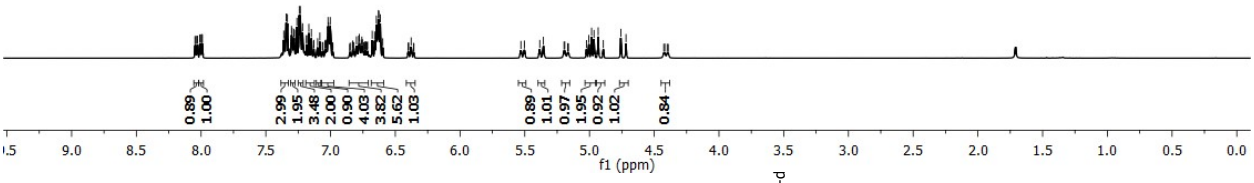
^{13}C NMR, DMSO-*d6*, 100 MHz

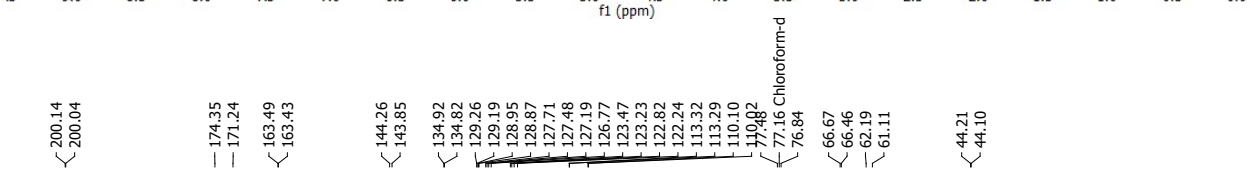


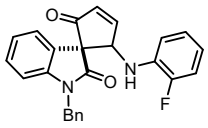


15

^{1}H NMR, $CDCl_3$, 400 MHz

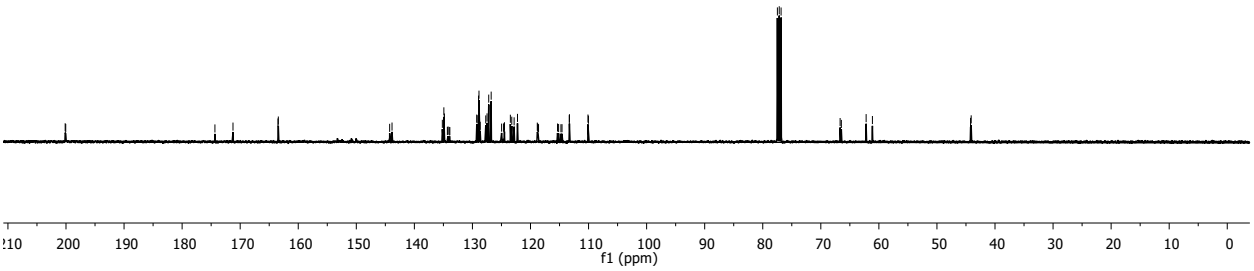


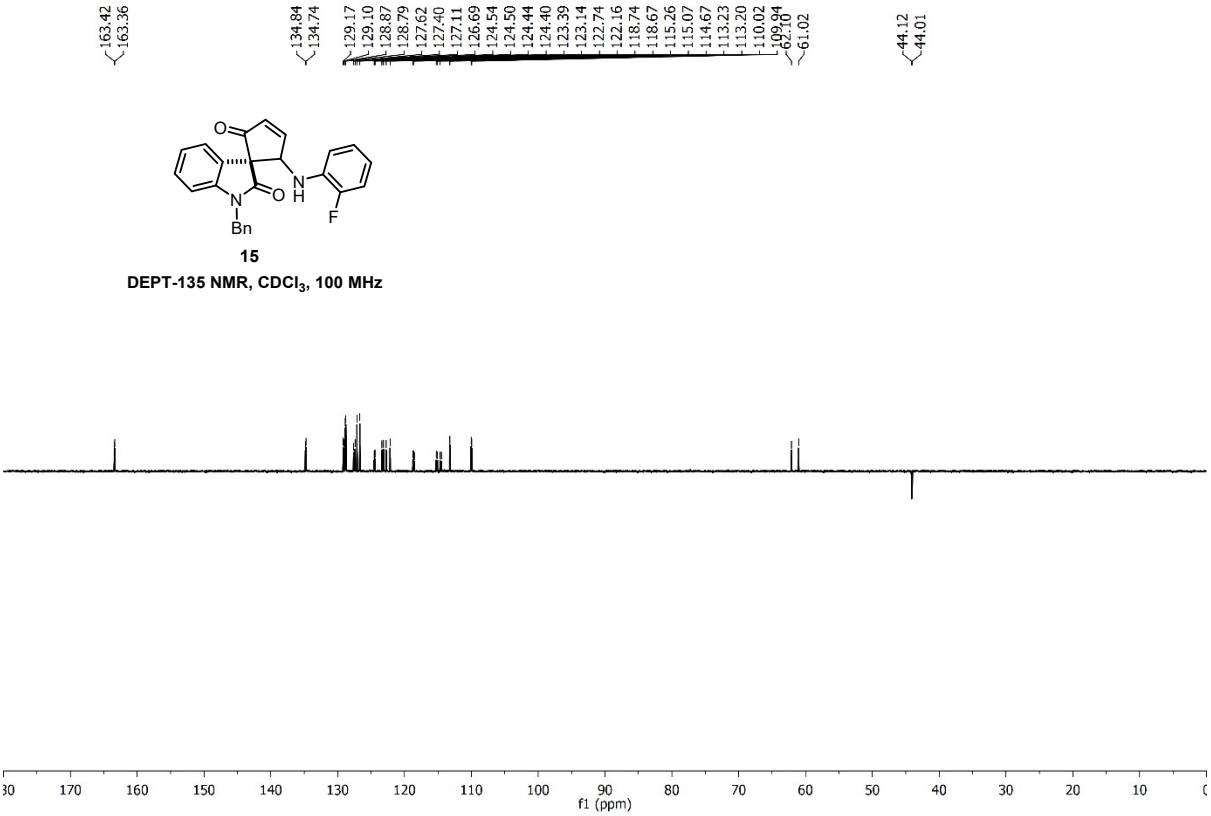




15

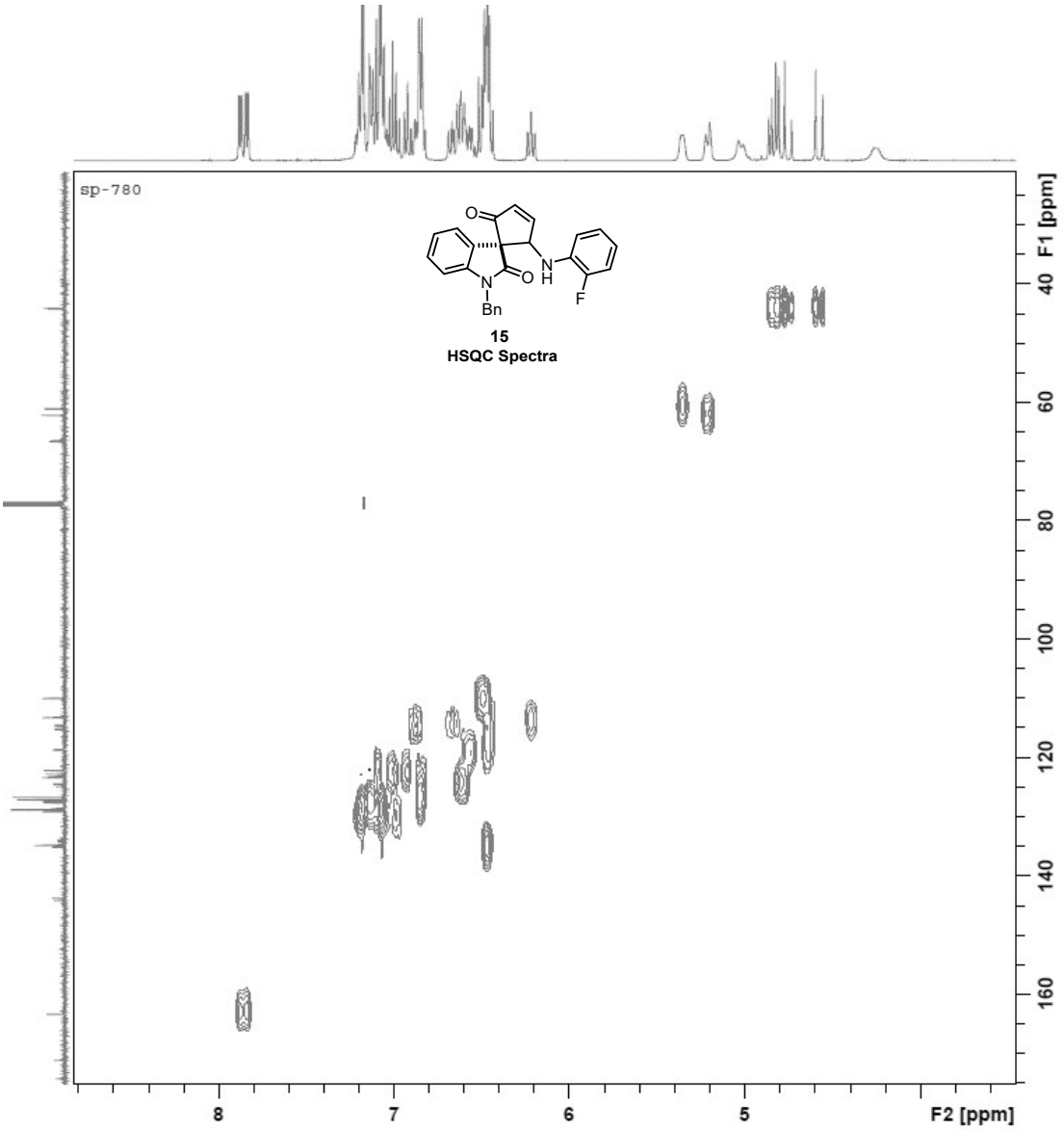
^{13}C NMR, $CDCl_3$, 100 MHz



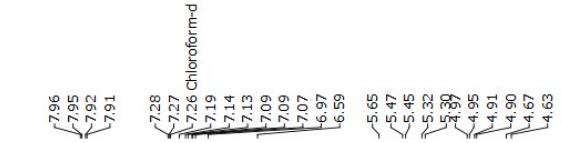


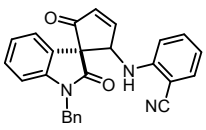
15

DEPT-135 NMR, $CDCl_3$, 100 MHz



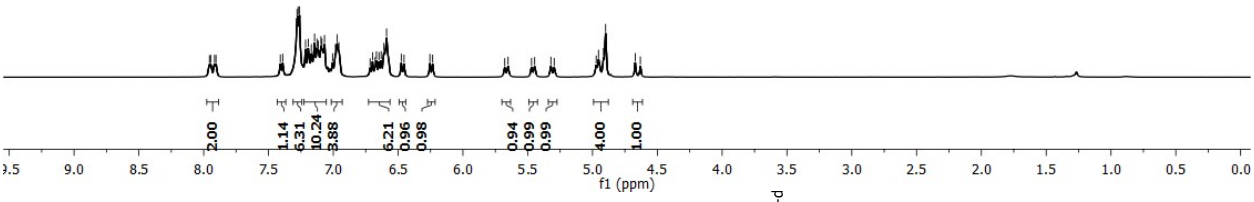
15
HSQC Spectra

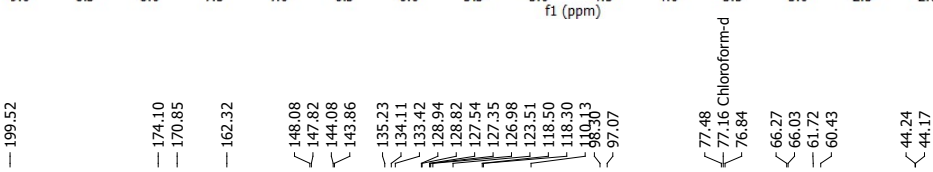


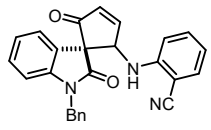


16

^{1}H NMR, $CDCl_3$, 400 MHz

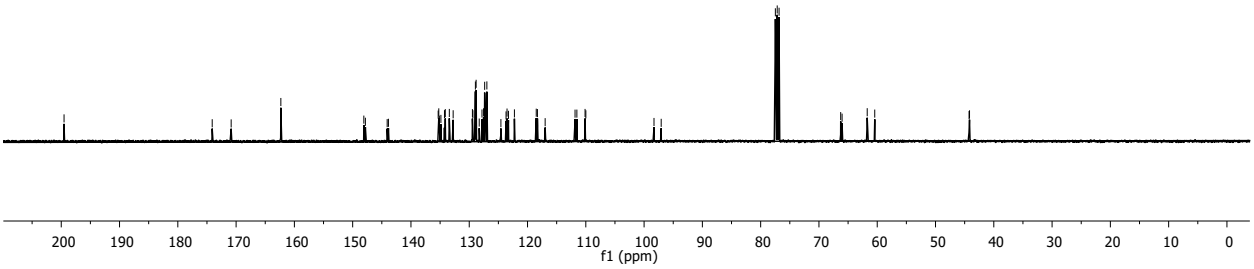


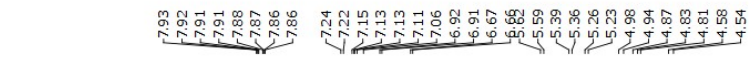


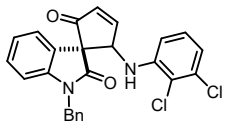


16

^{13}C NMR, $CDCl_3$, 100 MHz

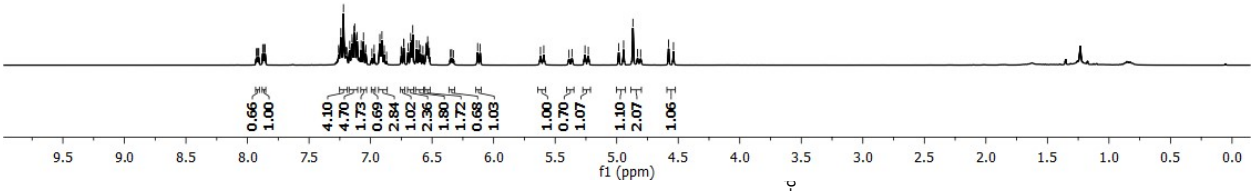


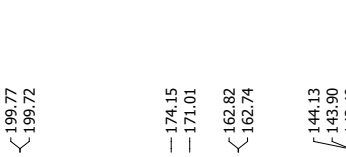


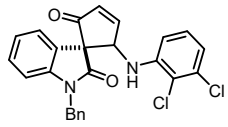


17

^{1}H NMR, $CDCl_3$, 400 MHz

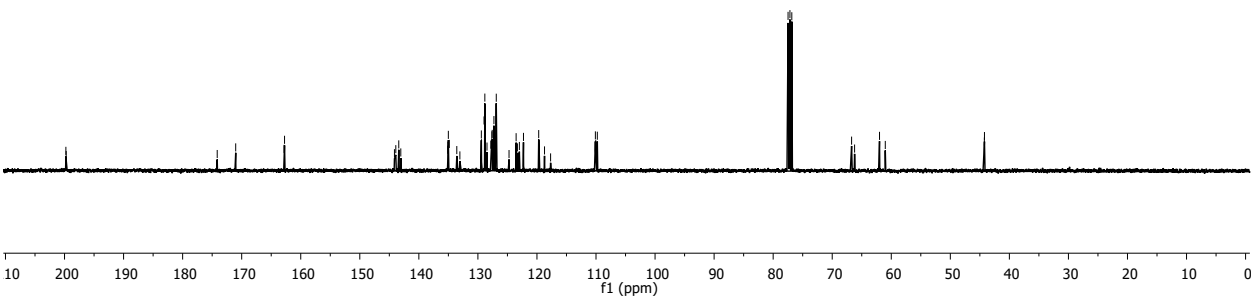


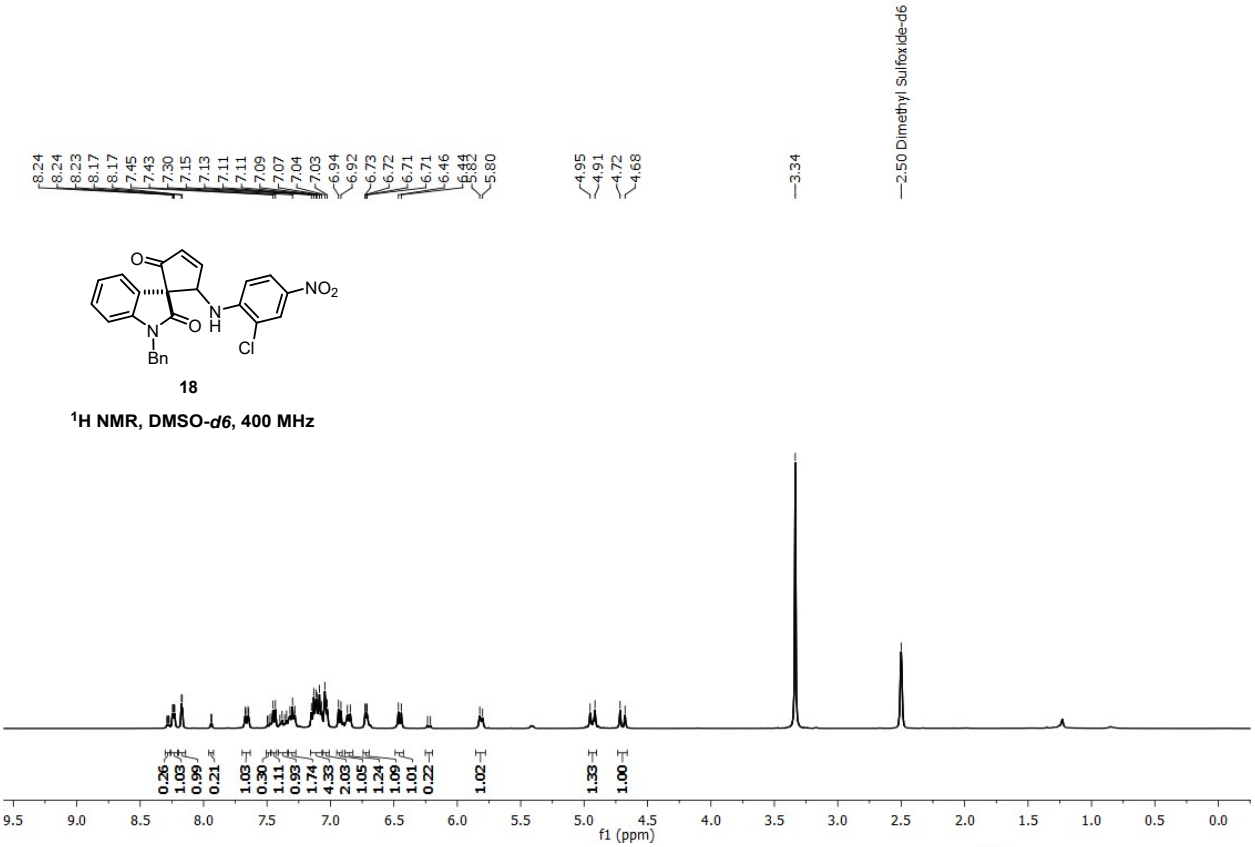




17

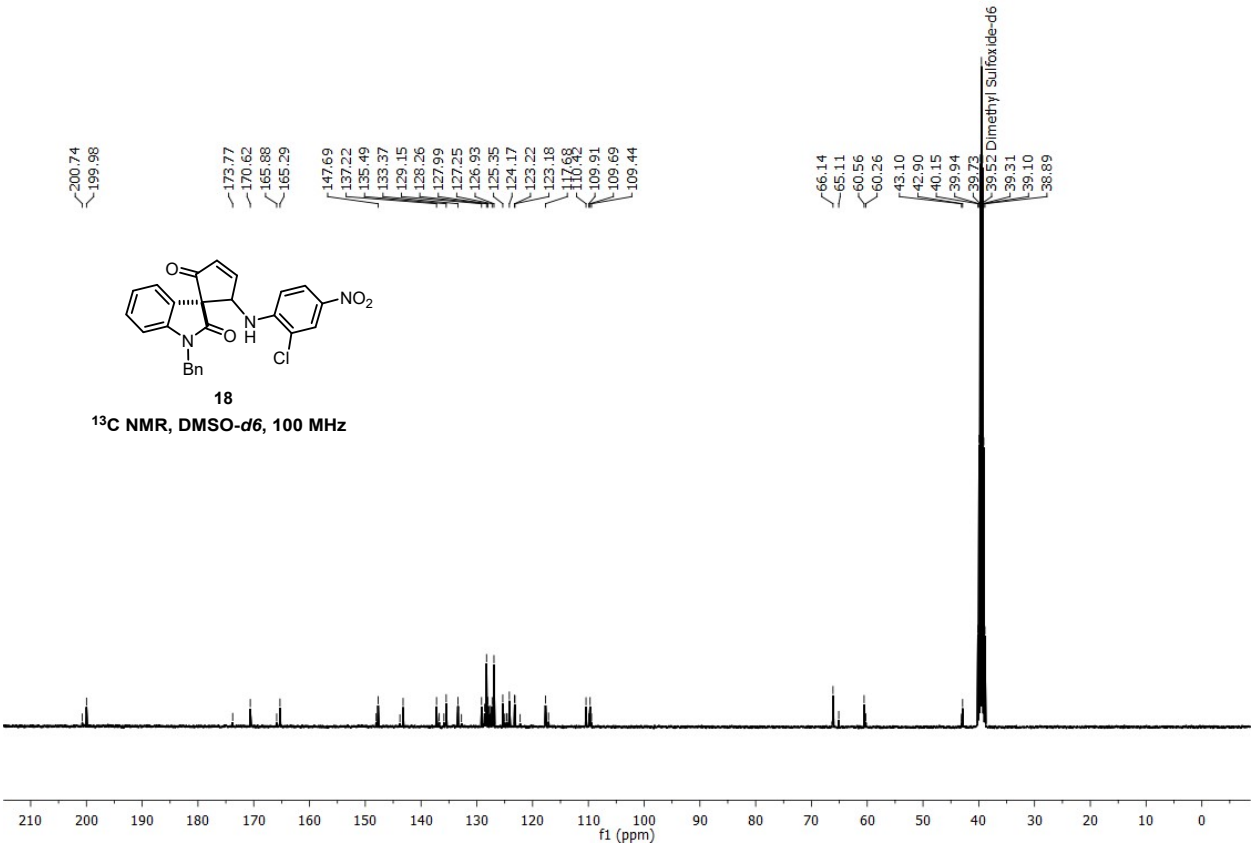
^{13}C NMR, $CDCl_3$, 100 MHz





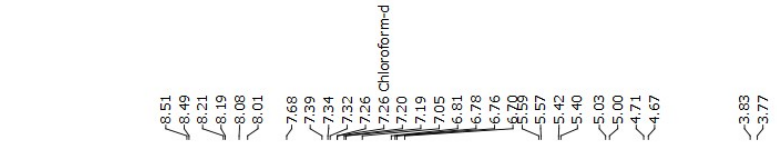
18

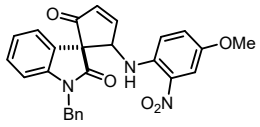
^{1}H NMR, DMSO-*d6*, 400 MHz



18

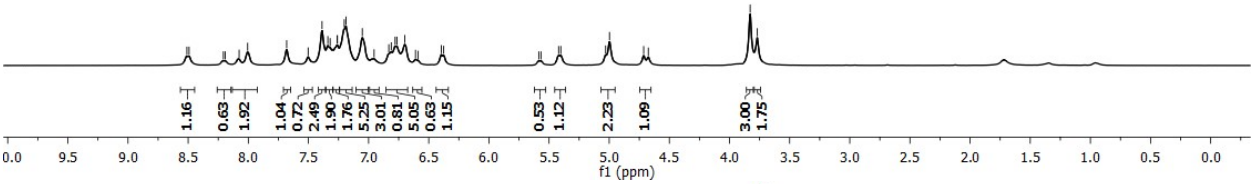
^{13}C NMR, DMSO-*d6*, 100 MHz

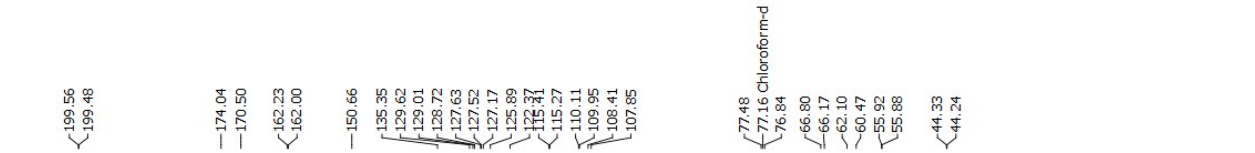


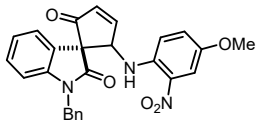


19

^{1}H NMR, $CDCl_3$, 400 MHz

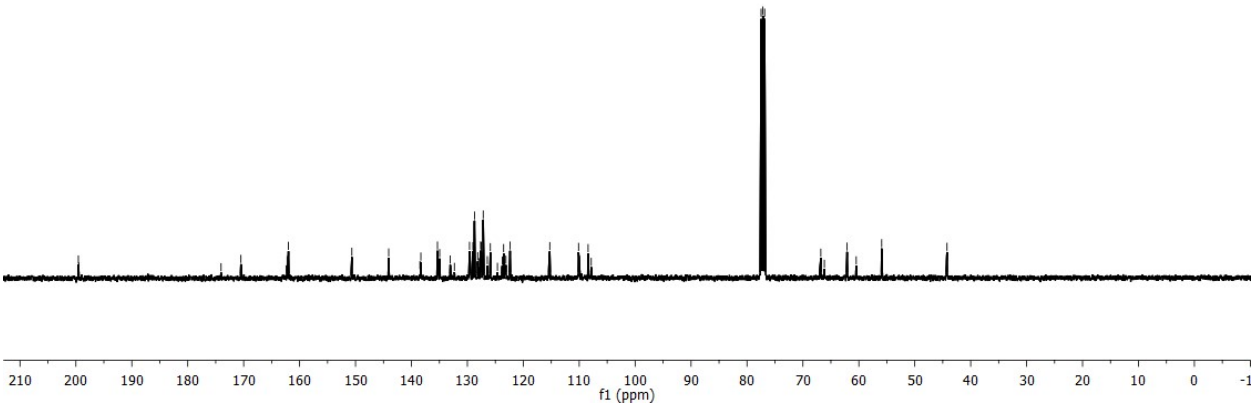


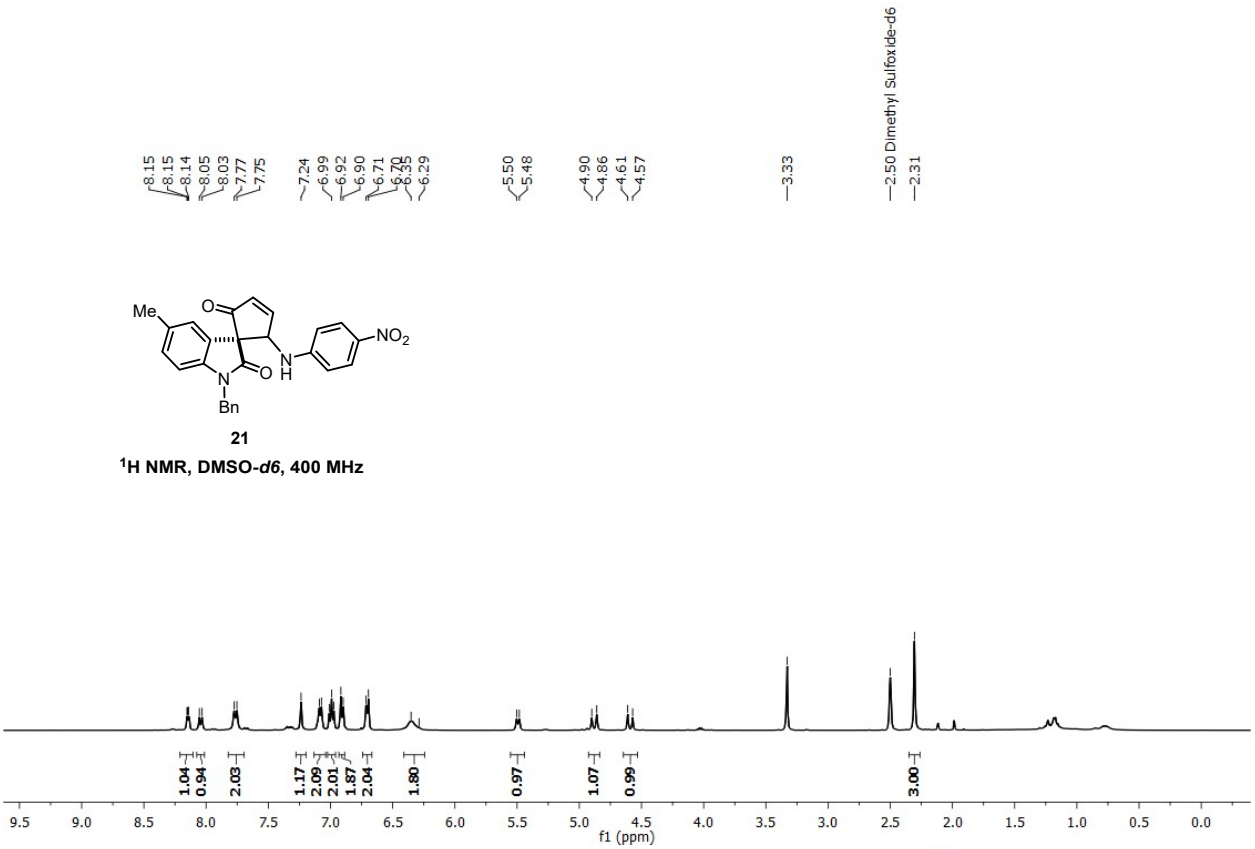




19

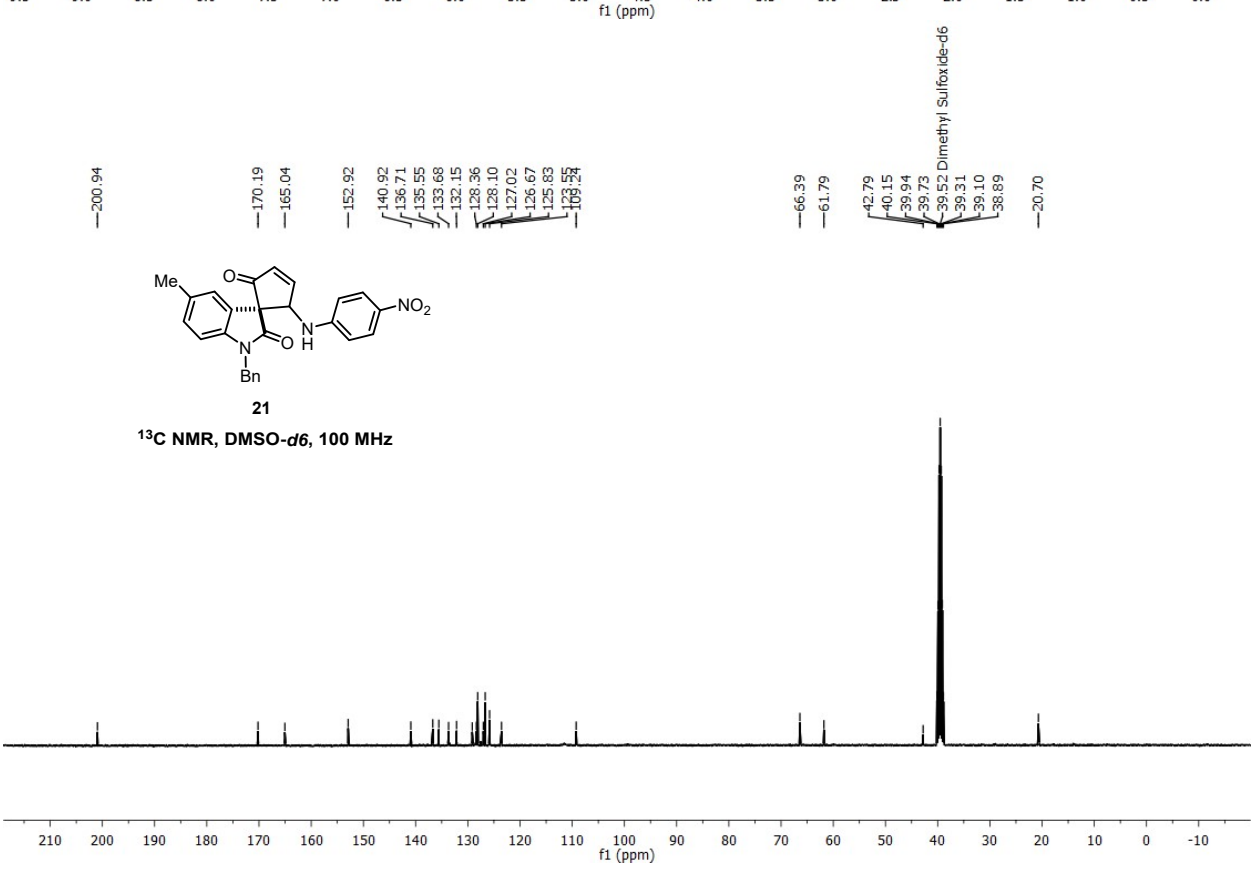
^{13}C NMR, $CDCl_3$, 100 MHz





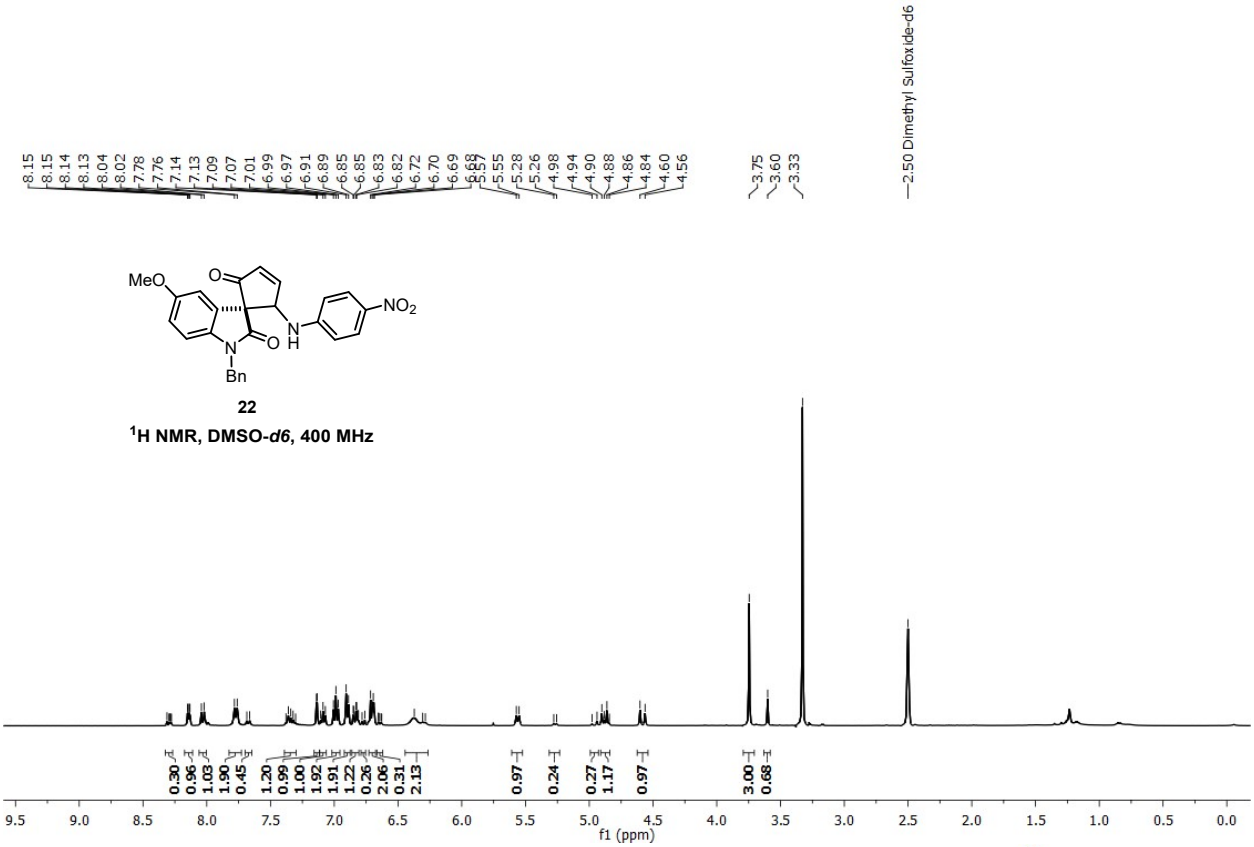
21

^{1}H NMR, DMSO-*d6*, 400 MHz



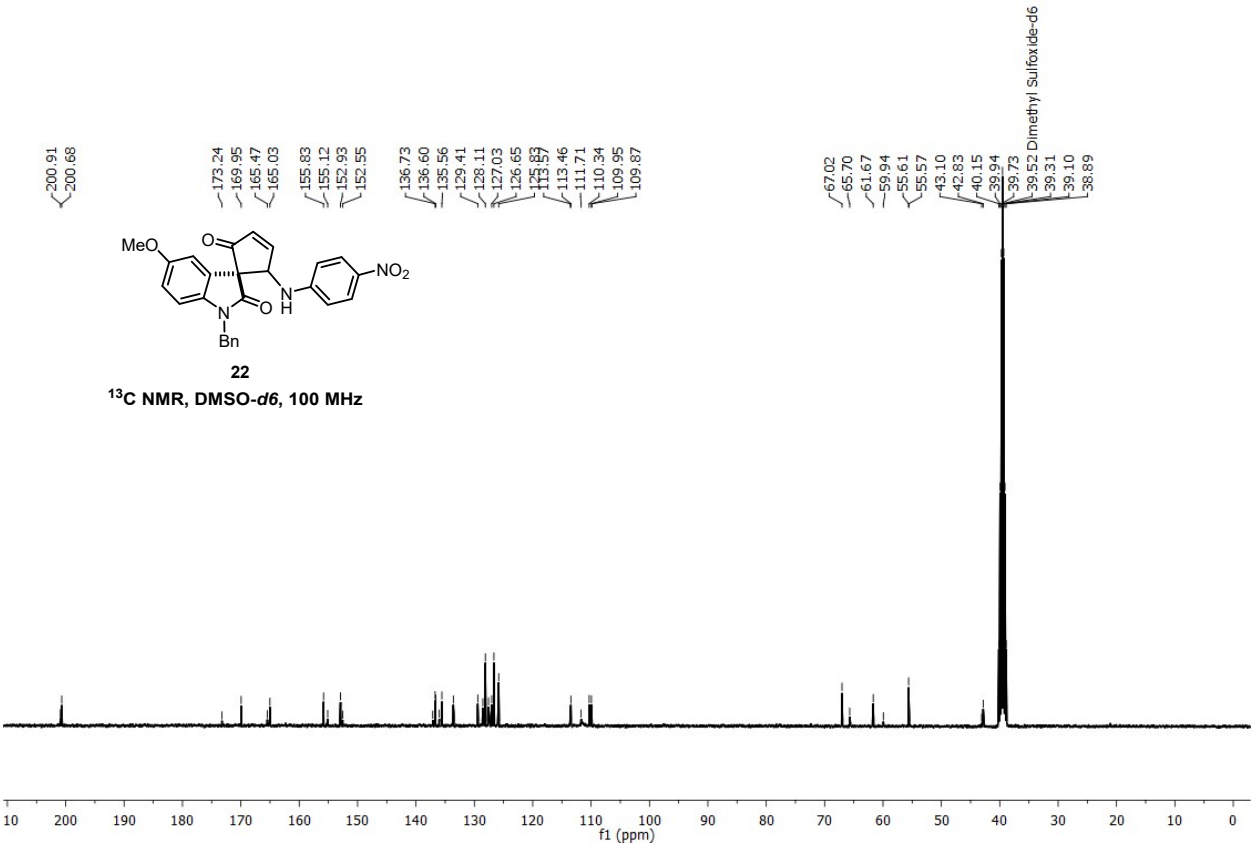
21

^{13}C NMR, DMSO-*d6*, 100 MHz



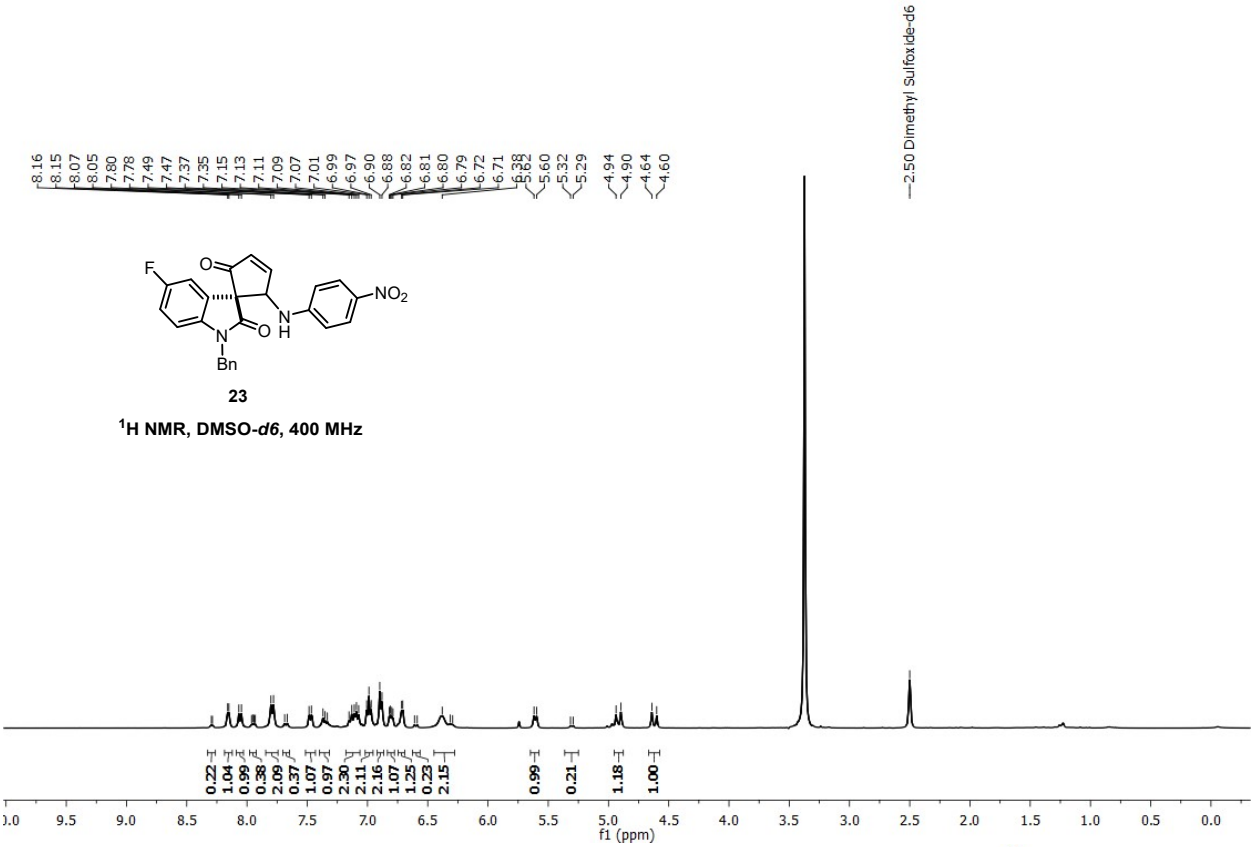
22

^{1}H NMR, DMSO-*d6*, 400 MHz



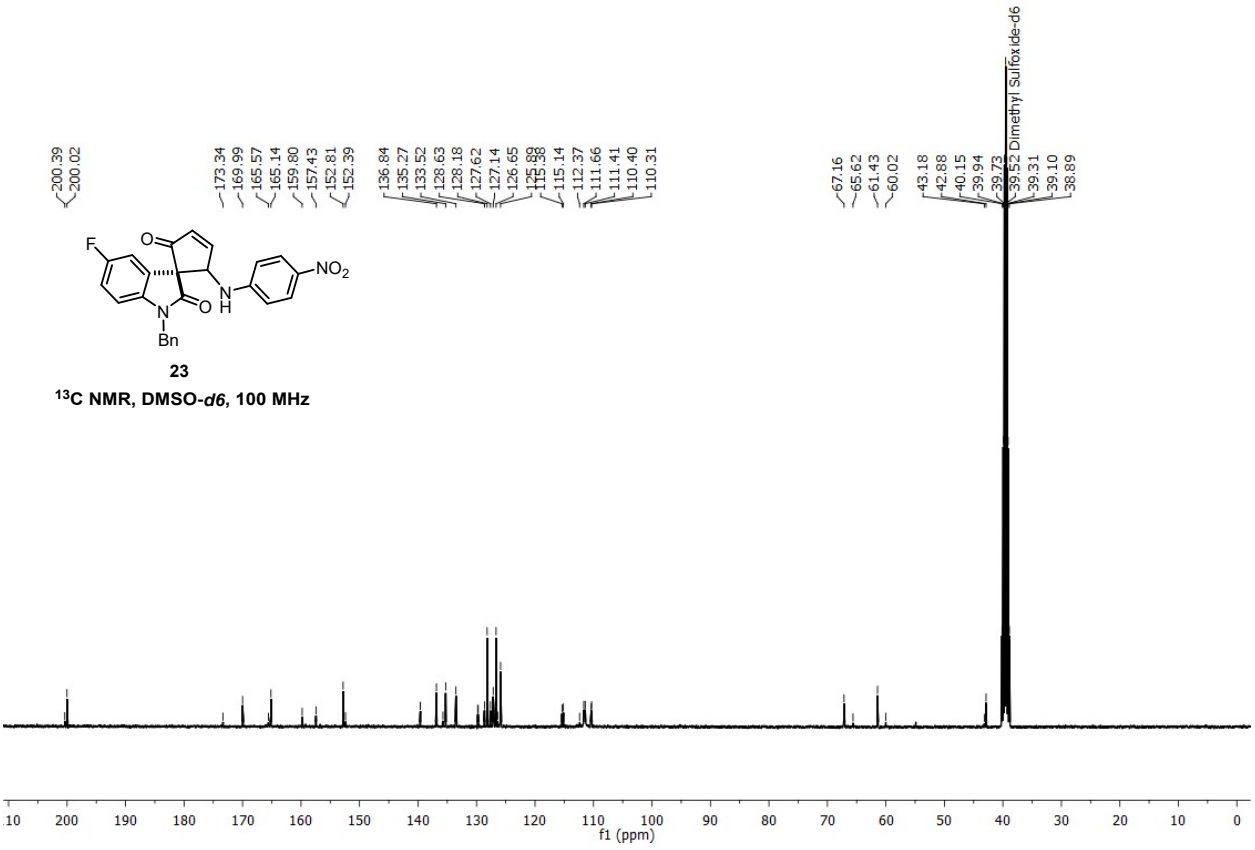
22

^{13}C NMR, DMSO-*d6*, 100 MHz



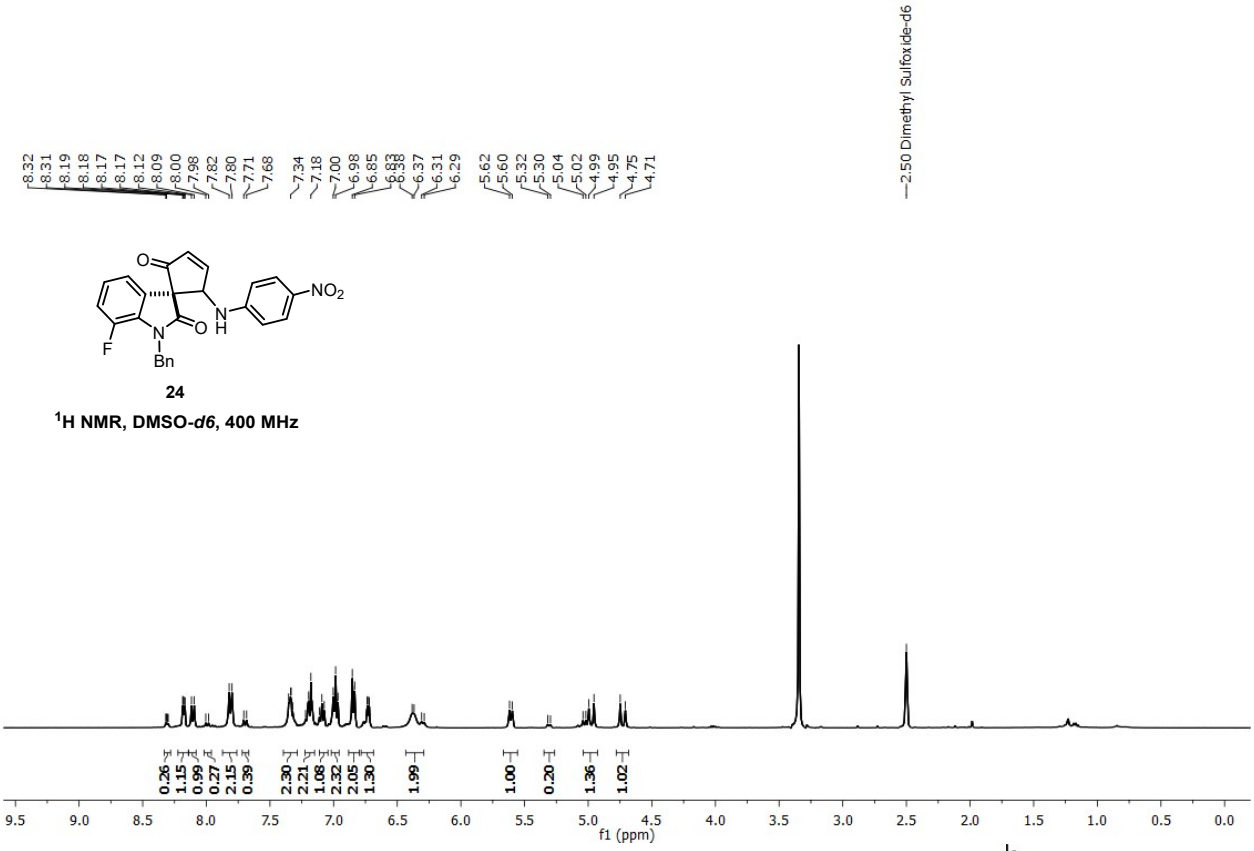
23

^{1}H NMR, DMSO-*d6*, 400 MHz



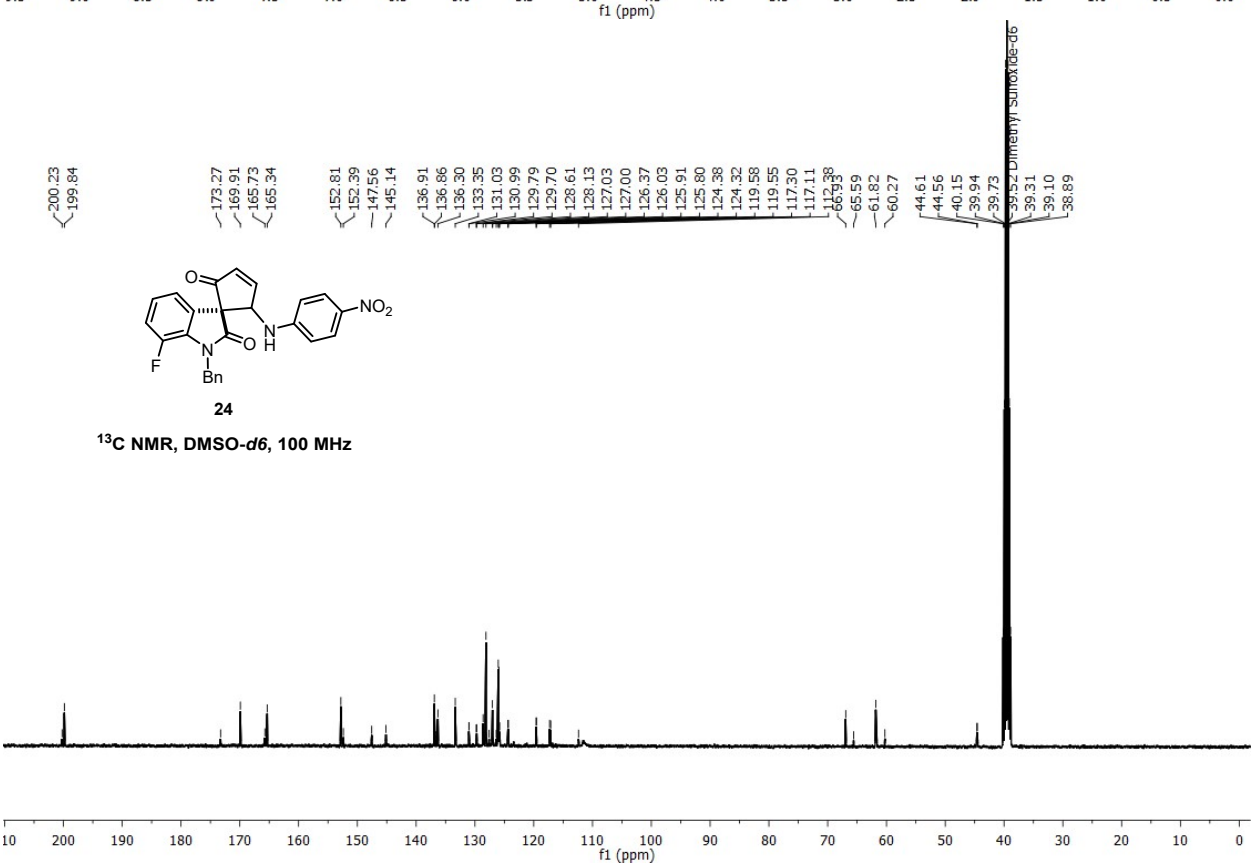
23

^{13}C NMR, DMSO-*d6*, 100 MHz



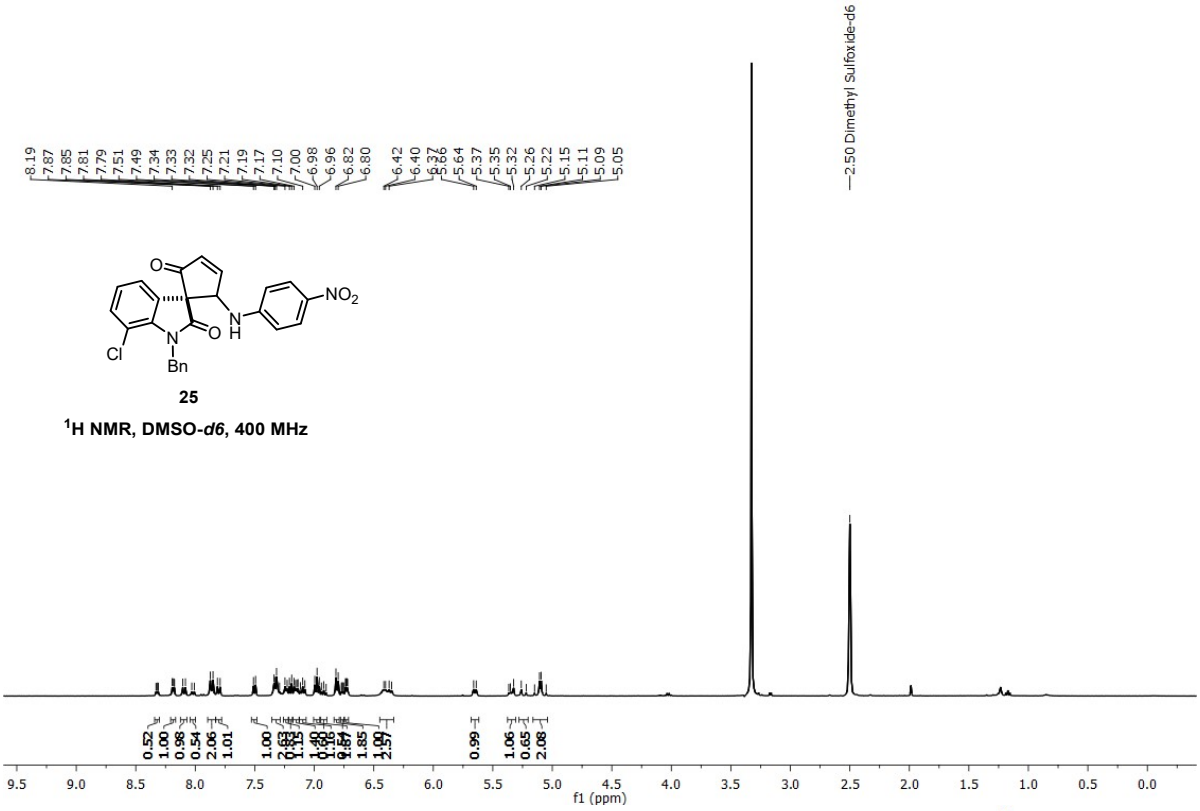
24

^{1}H NMR, DMSO-*d6*, 400 MHz



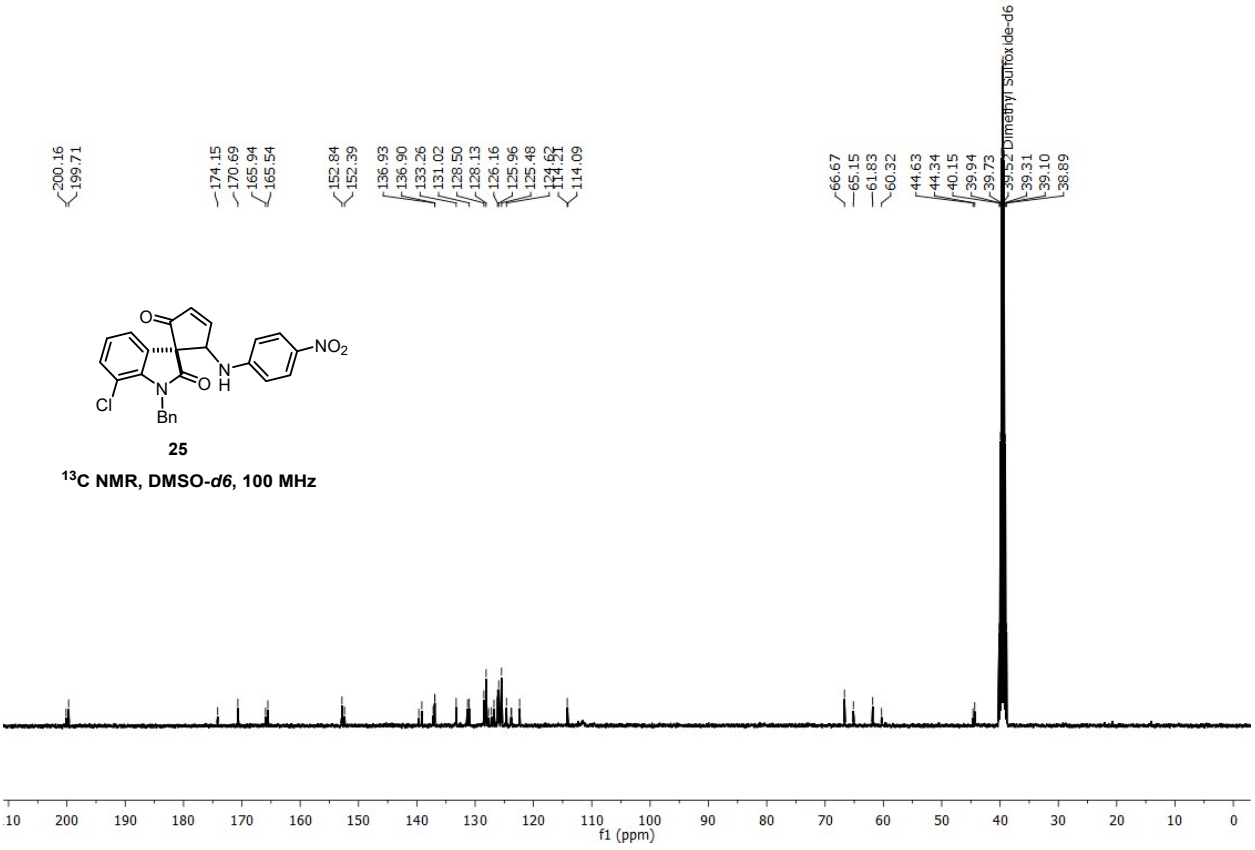
24

^{13}C NMR, DMSO-*d6*, 100 MHz



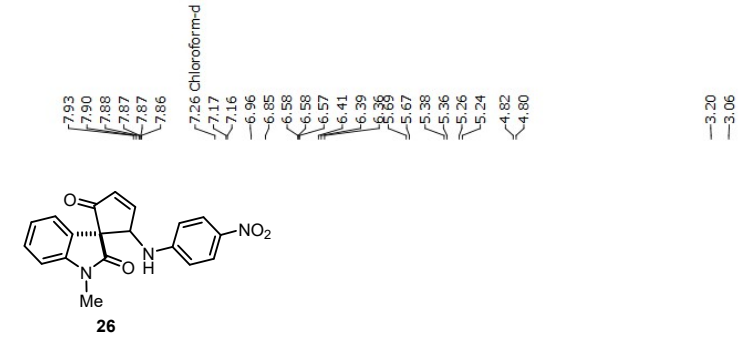
25

^{1}H NMR, DMSO-*d6*, 400 MHz



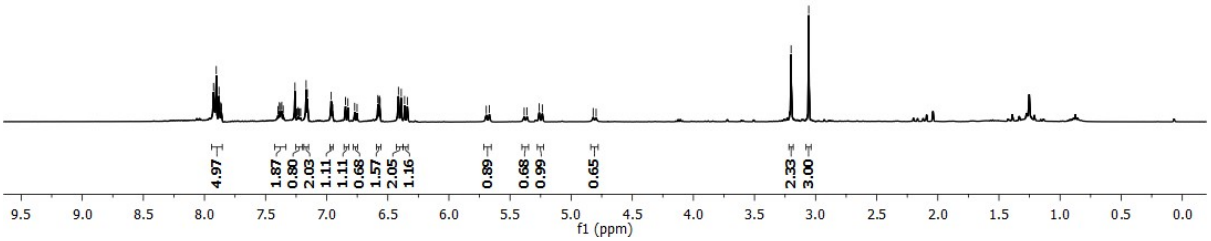
25

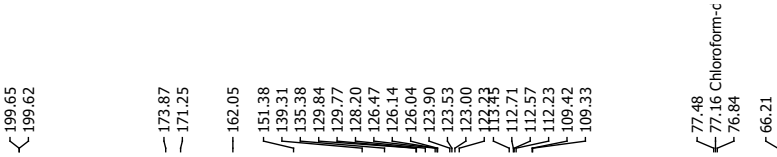
^{13}C NMR, DMSO-*d6*, 100 MHz

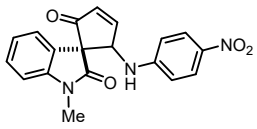


26

^{1}H NMR, $CDCl_3$, 400 MHz

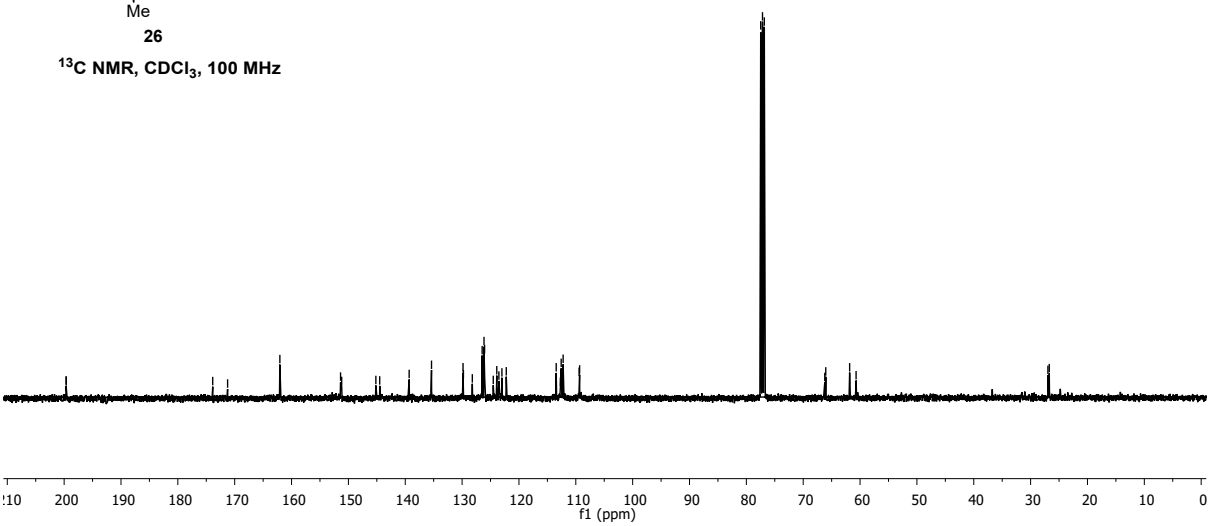


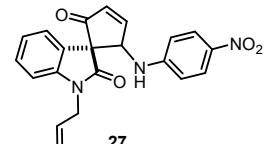




26

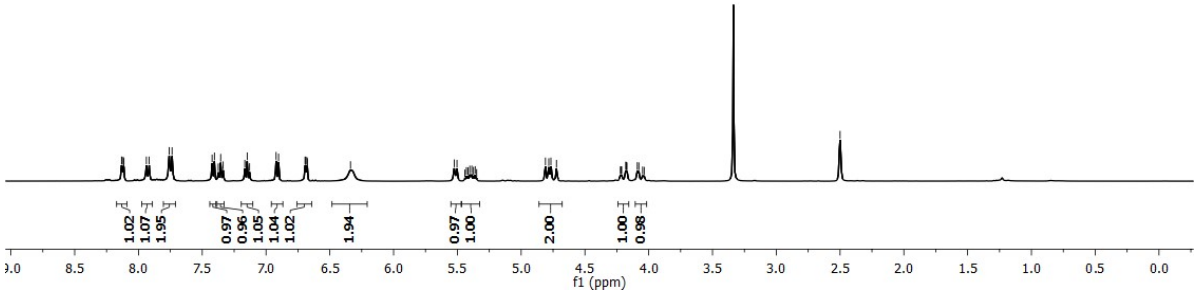
^{13}C NMR, $CDCl_3$, 100 MHz

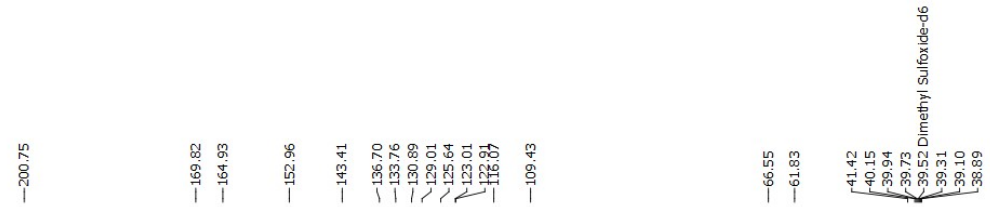


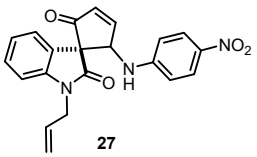


27

^{1}H NMR, DMSO-*d6*, 400 MHz

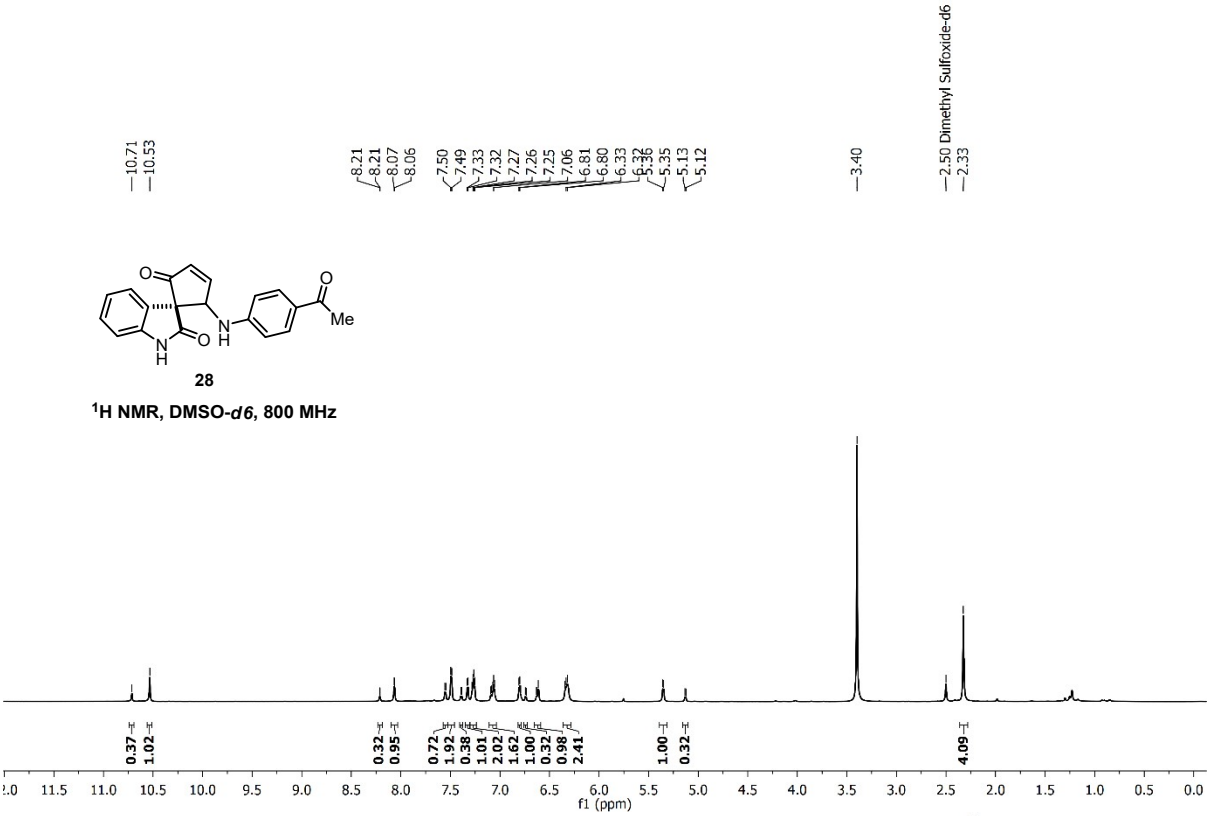






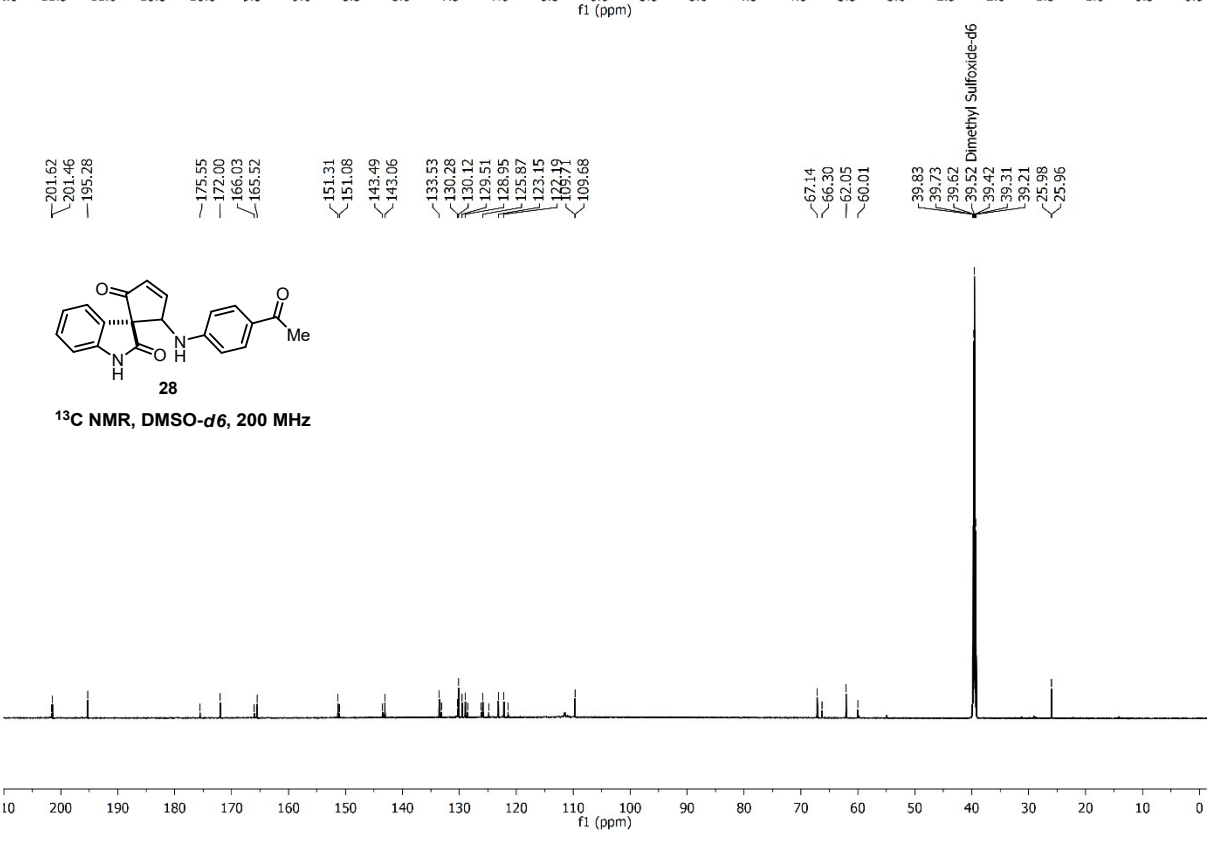
27

^{13}C NMR, DMSO-*d6*, 100 MHz



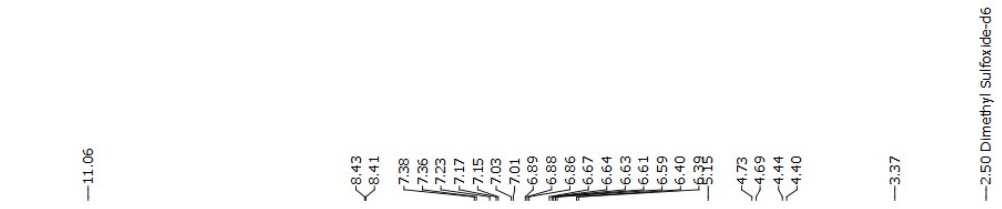
28

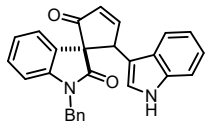
^{1}H NMR, DMSO-*d6*, 800 MHz



28

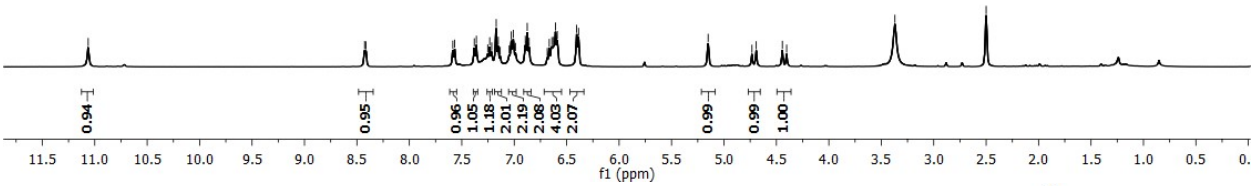
^{13}C NMR, DMSO-*d6*, 200 MHz

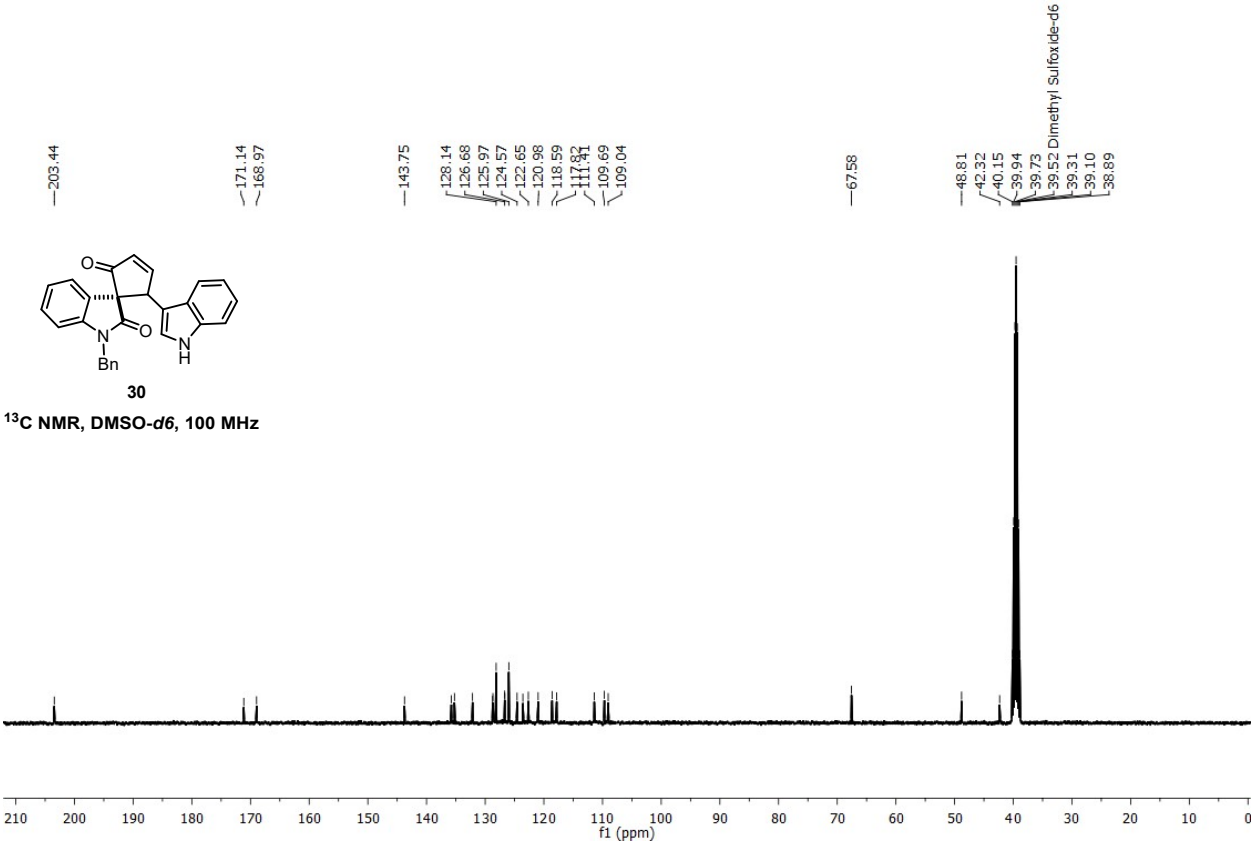




30

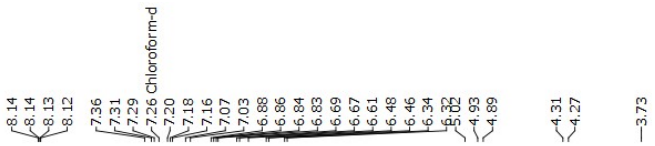
^{1}H NMR, DMSO-*d6*, 400 MHz

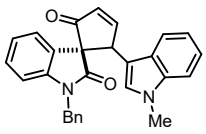




30

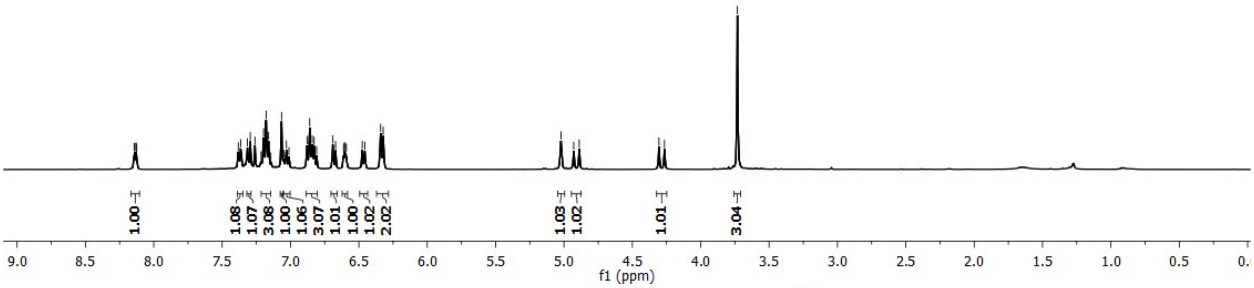
^{13}C NMR, DMSO-*d6*, 100 MHz

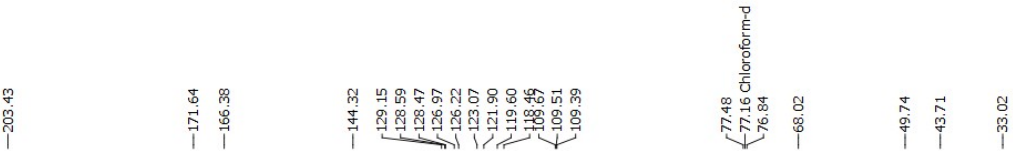


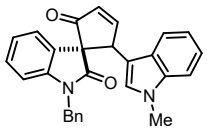


31

^{1}H NMR, $CDCl_3$, 400 MHz

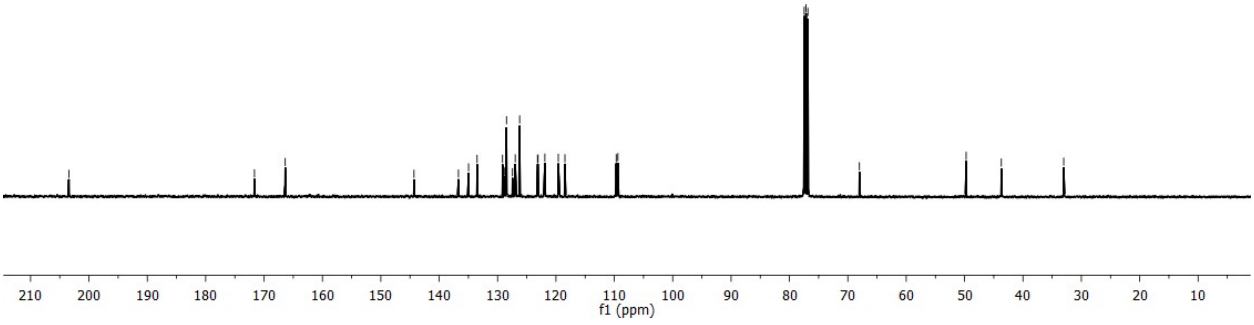


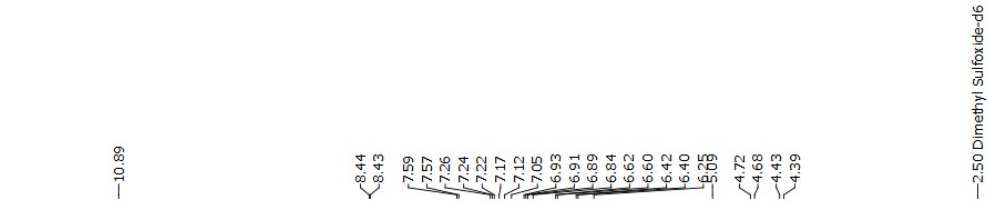


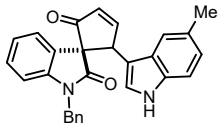


31

^{13}C NMR, $CDCl_3$, 100 MHz

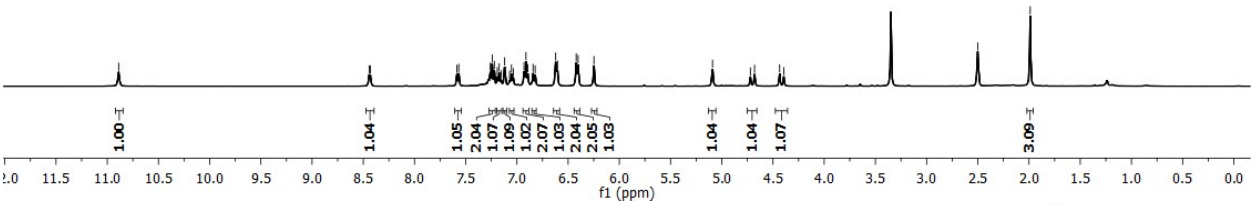


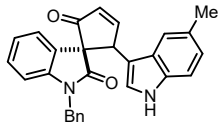




32

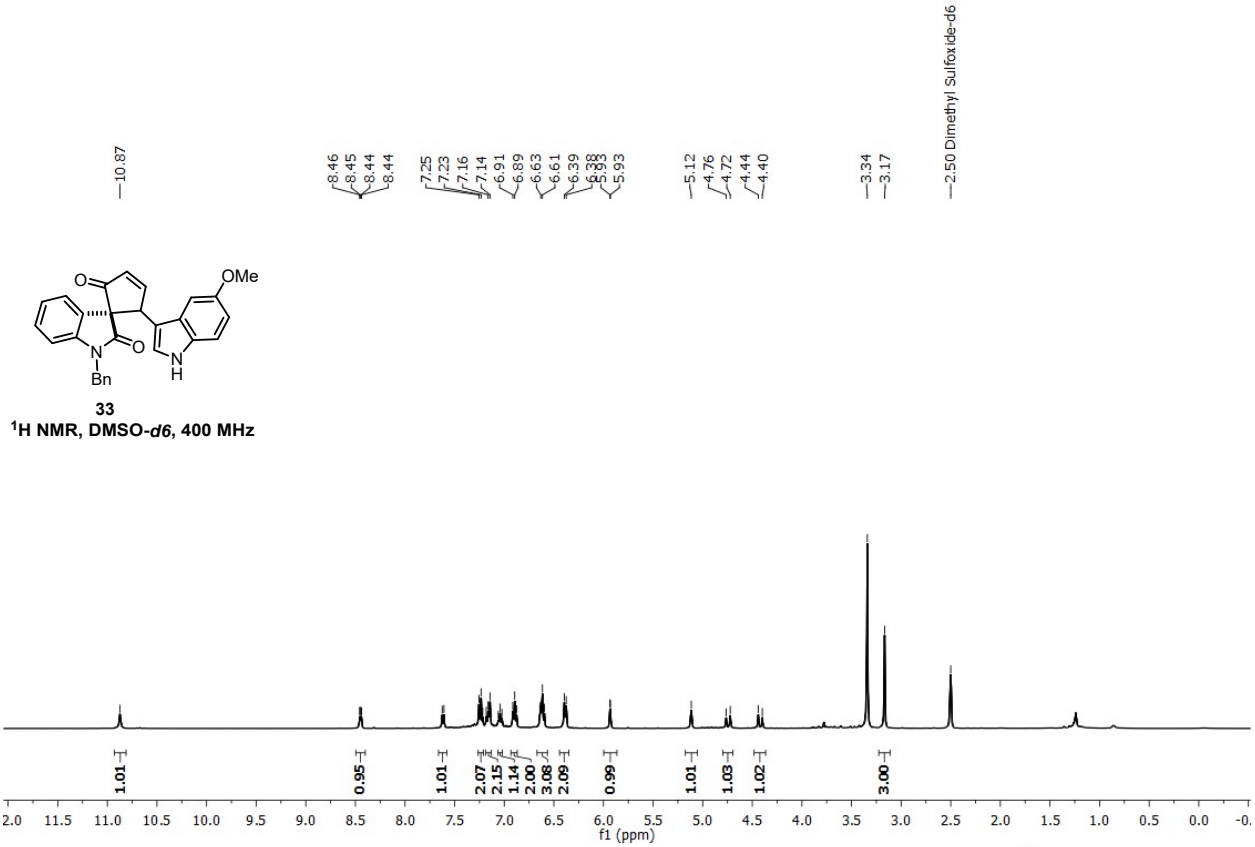
^{1}H NMR, DMSO-*d6*, 400 MHz





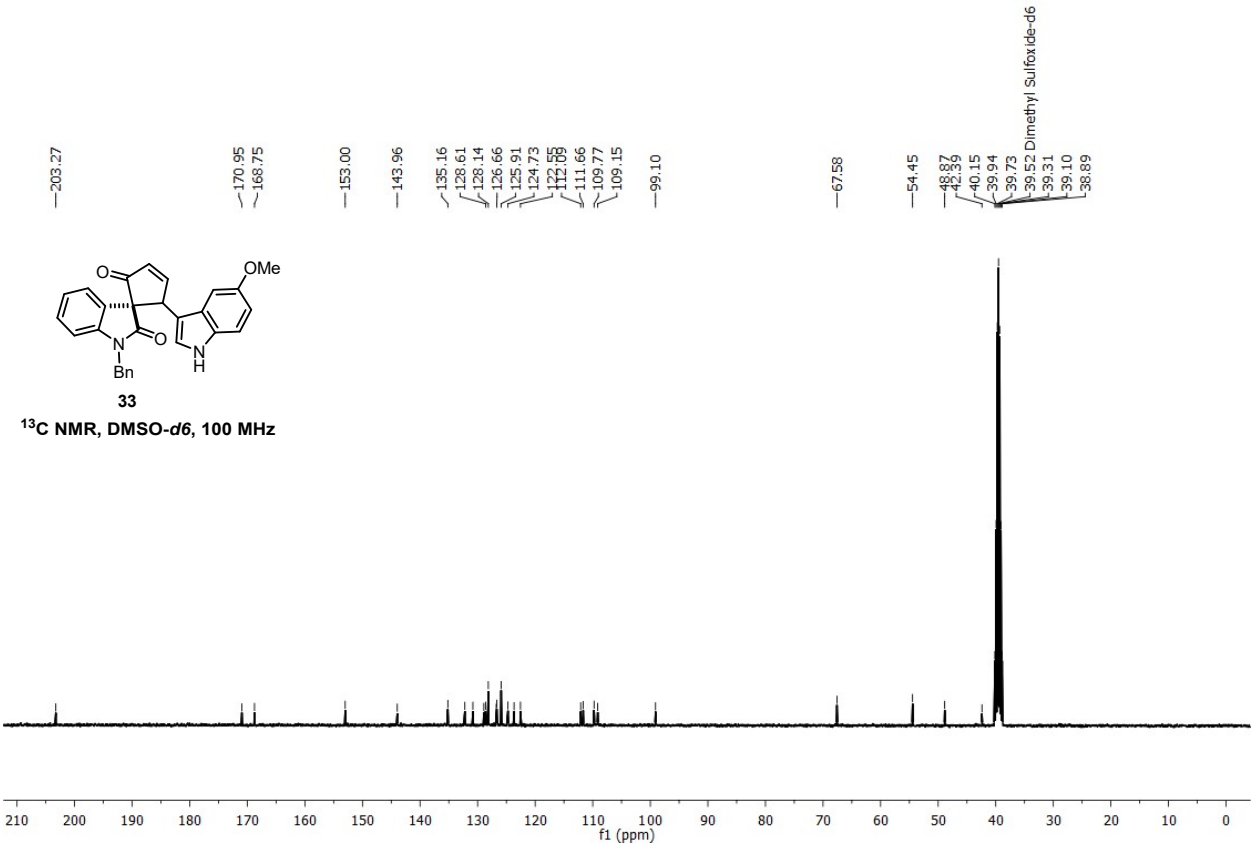
32

^{13}C NMR, DMSO-*d6*, 100 MHz



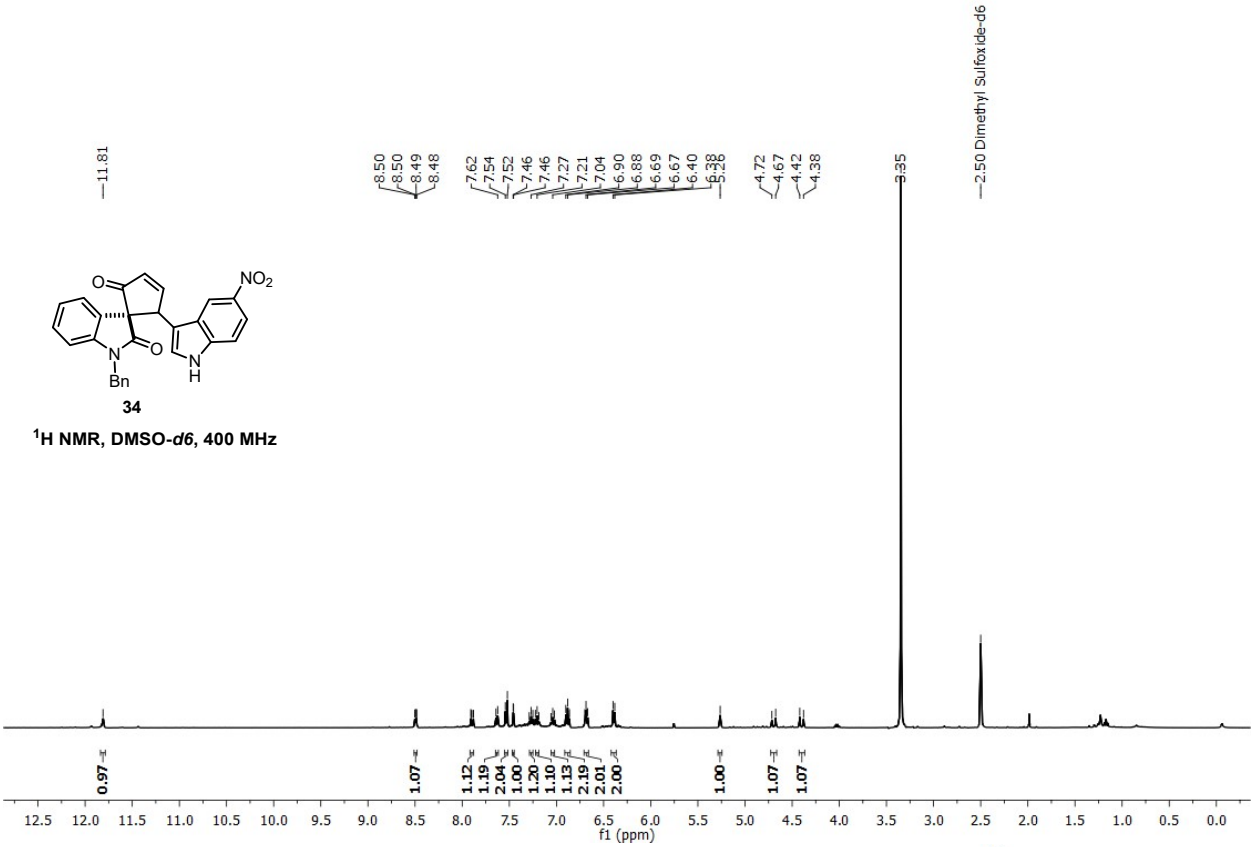
33

^{1}H NMR, DMSO-*d6*, 400 MHz



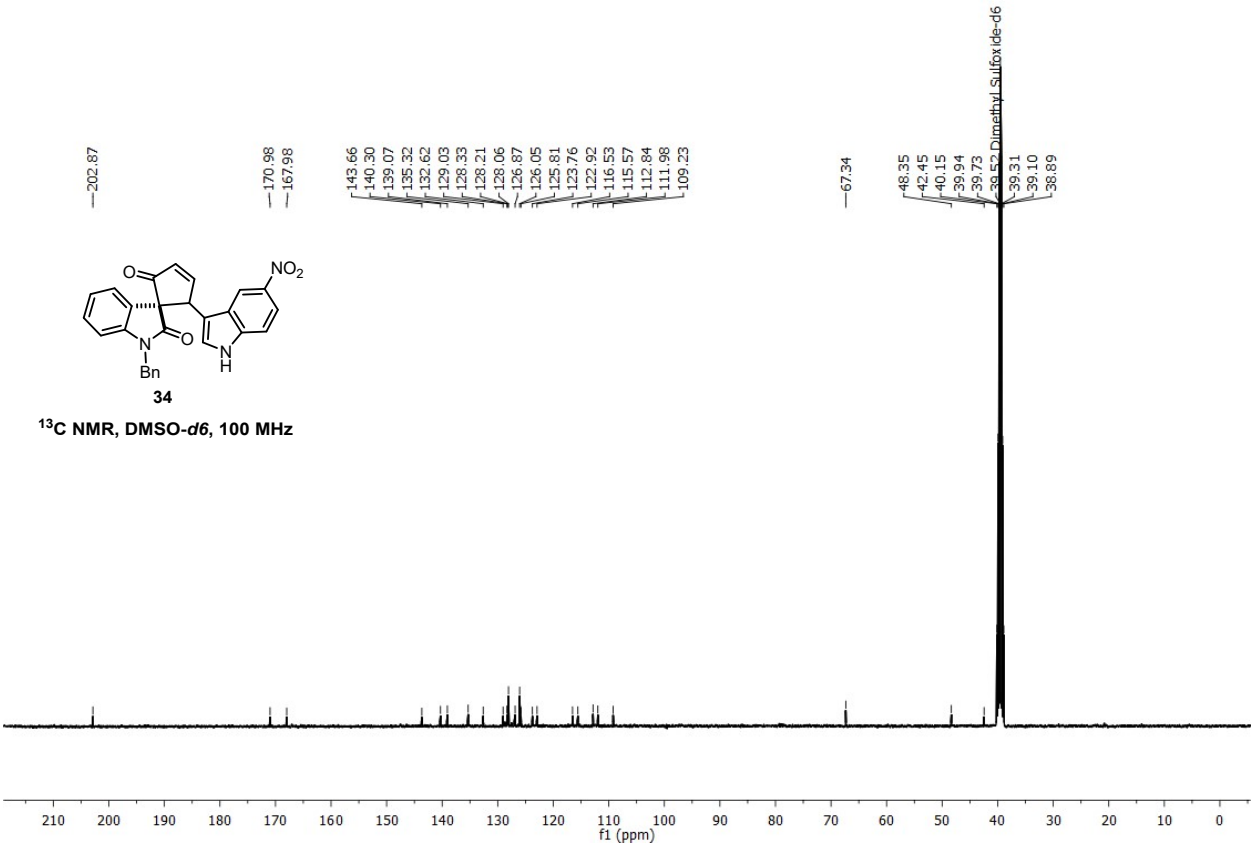
33

^{13}C NMR, DMSO-*d6*, 100 MHz



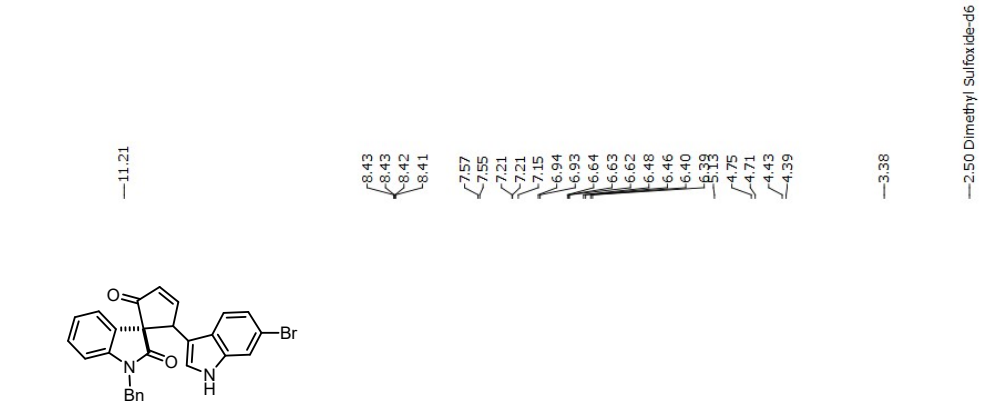
34

^{1}H NMR, DMSO-*d6*, 400 MHz



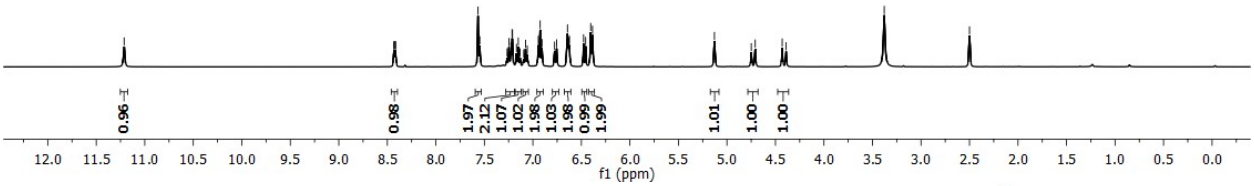
34

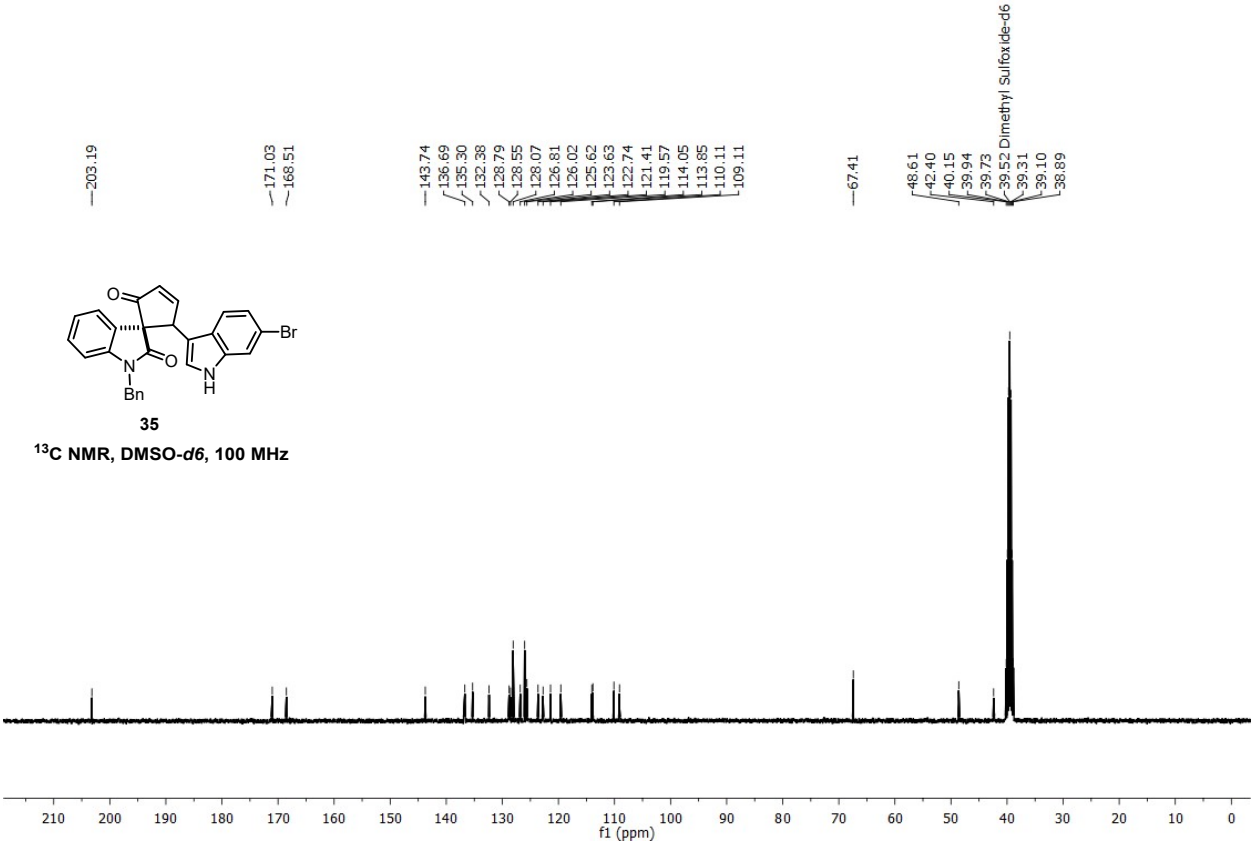
^{13}C NMR, DMSO-*d6*, 100 MHz



35

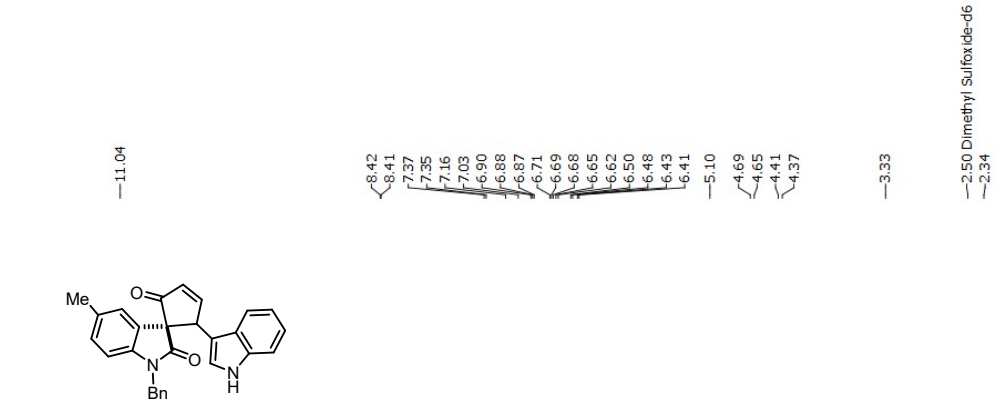
^{1}H NMR, DMSO-*d6*, 400 MHz





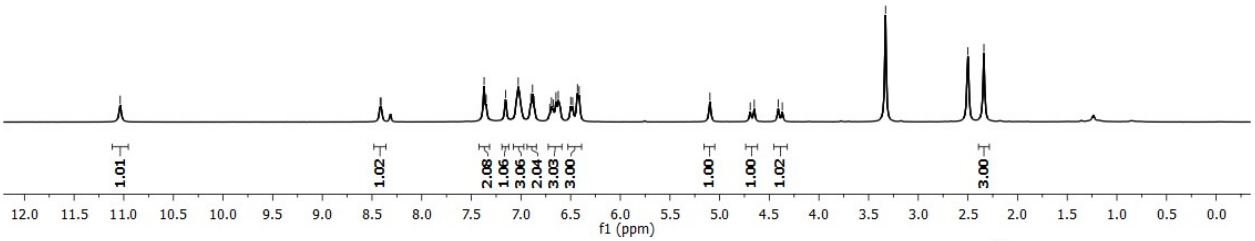
35

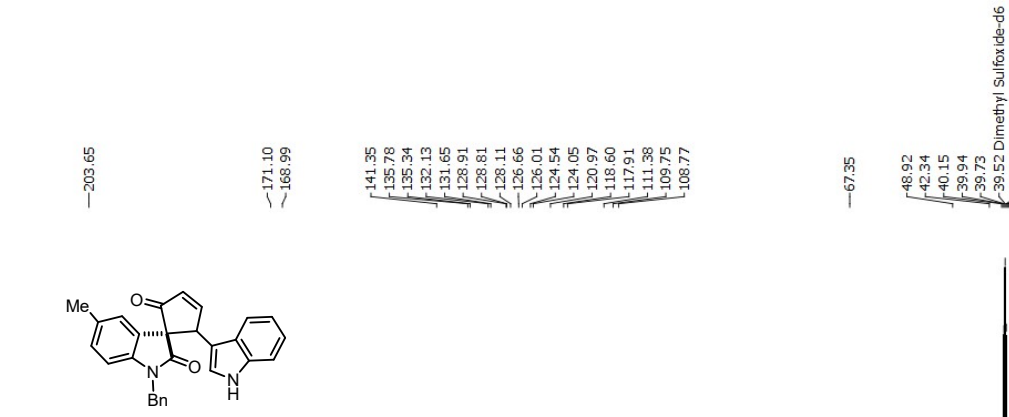
^{13}C NMR, DMSO-*d6*, 100 MHz



36

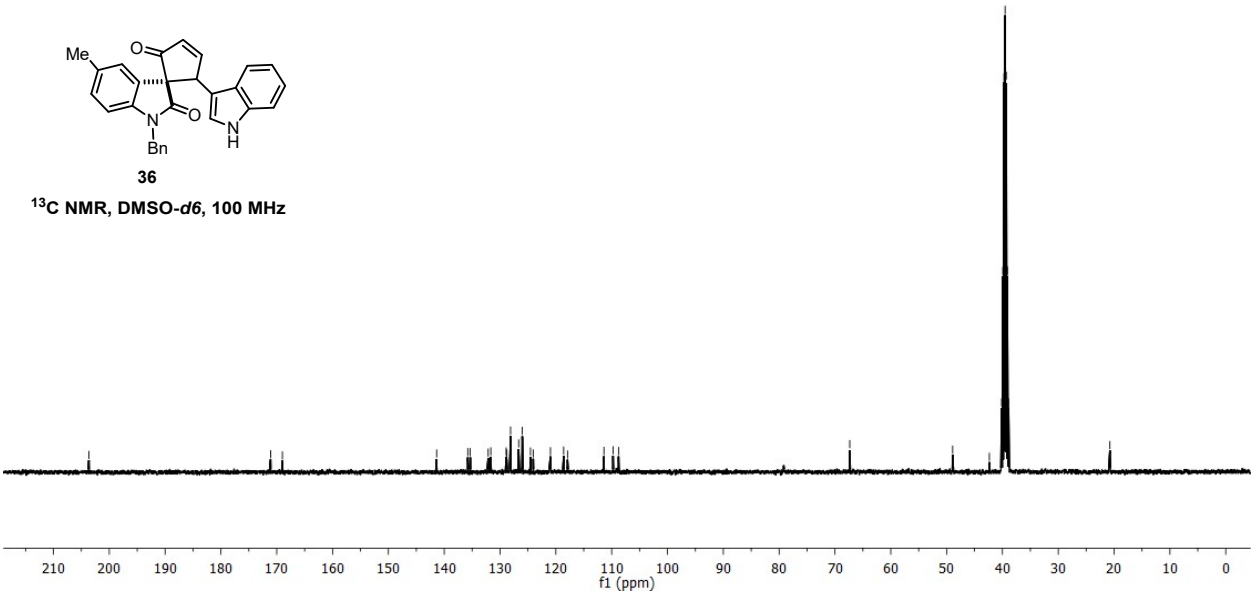
^{1}H NMR, DMSO-*d6*, 400 MHz

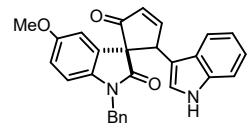




36

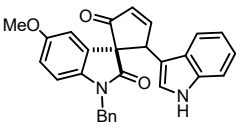
^{13}C NMR, DMSO-*d6*, 100 MHz





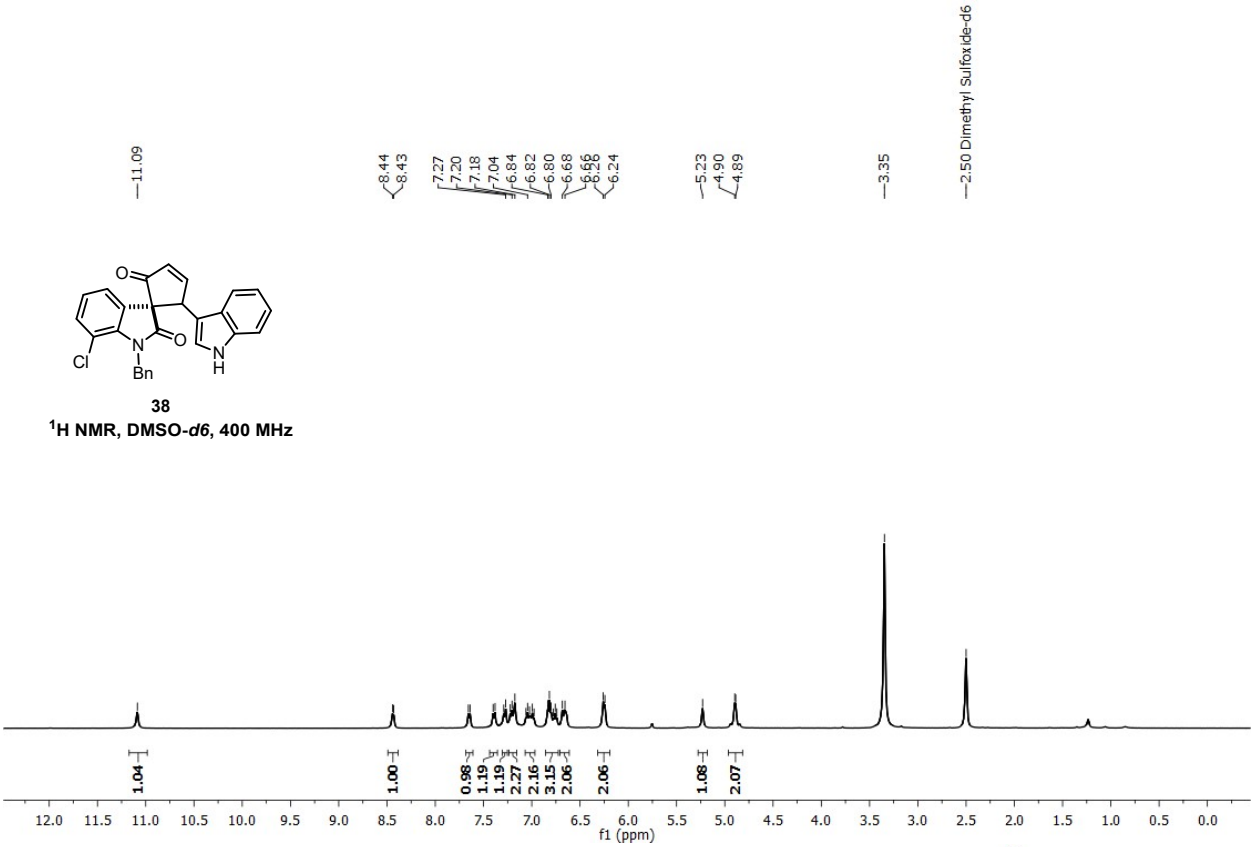
37

^{1}H NMR, DMSO-*d6*, 400 MHz



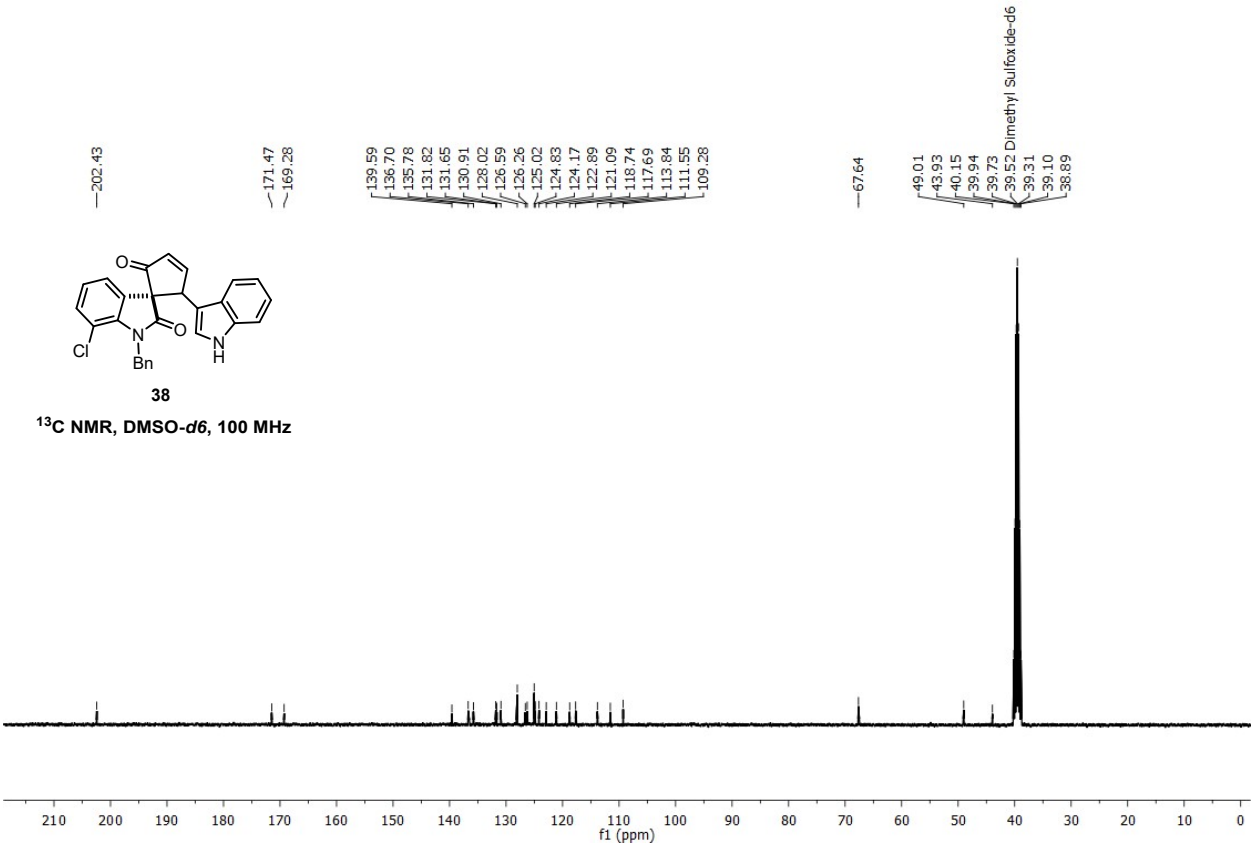
37

^{13}C NMR, DMSO-*d6*, 100 MHz



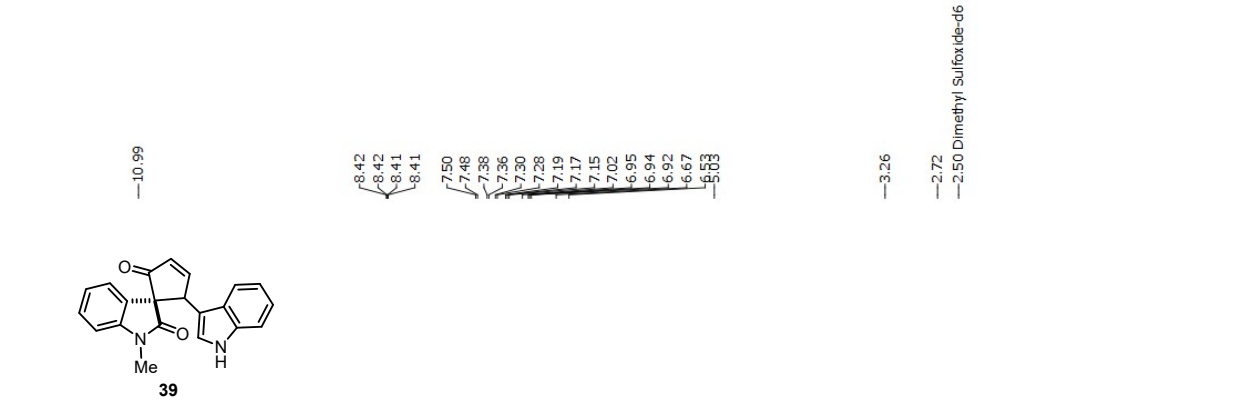
38

^{1}H NMR, DMSO-*d6*, 400 MHz



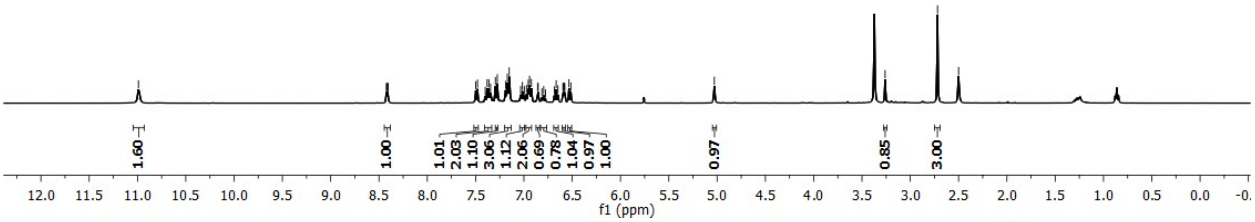
38

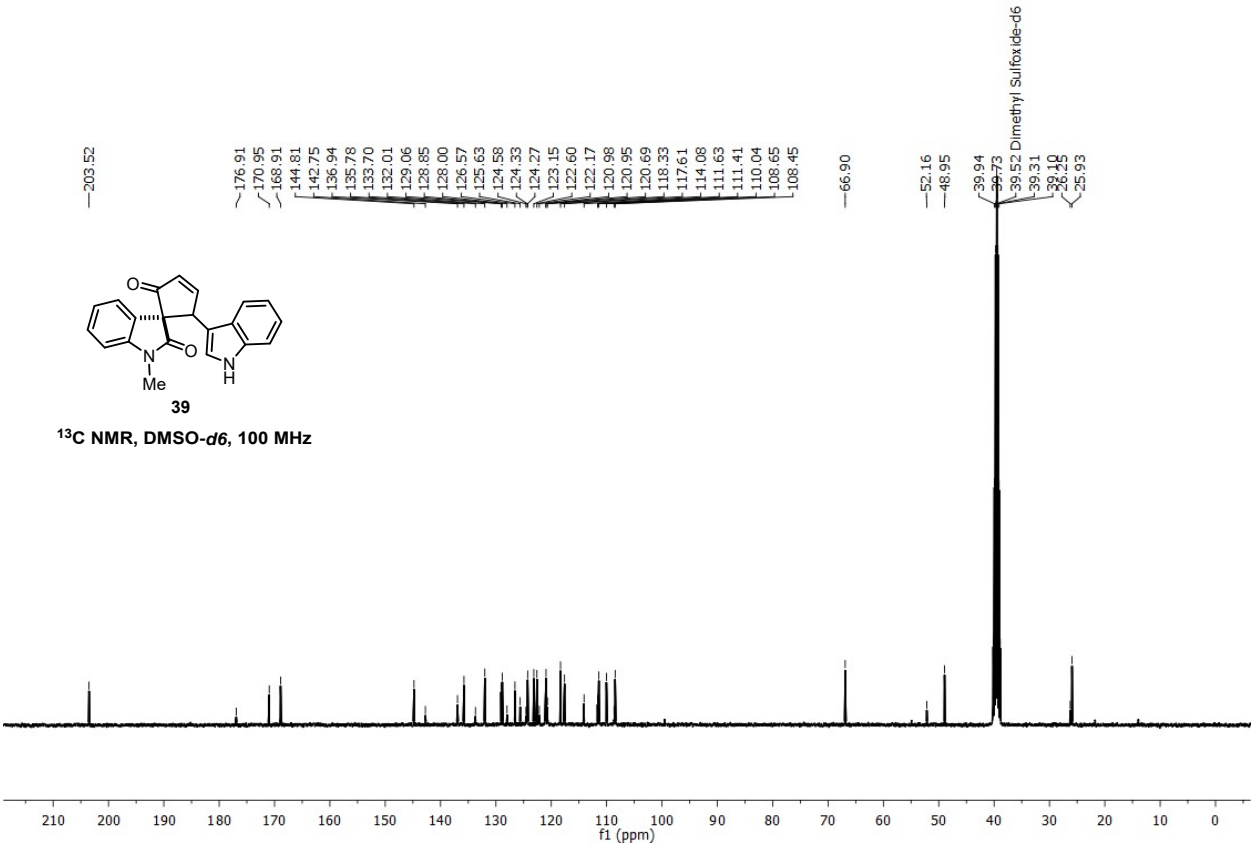
^{13}C NMR, DMSO-*d6*, 100 MHz



39

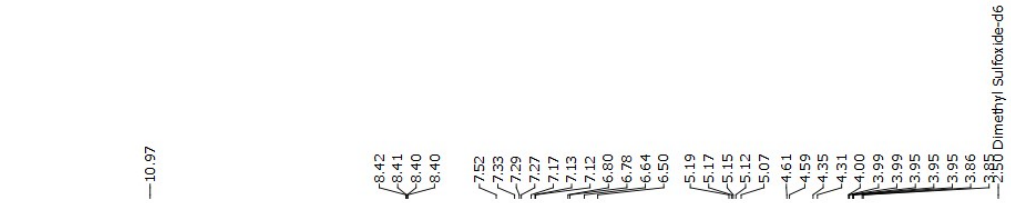
^{1}H NMR, DMSO-*d6*, 400 MHz

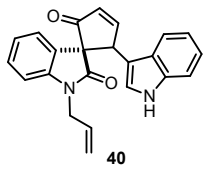




39

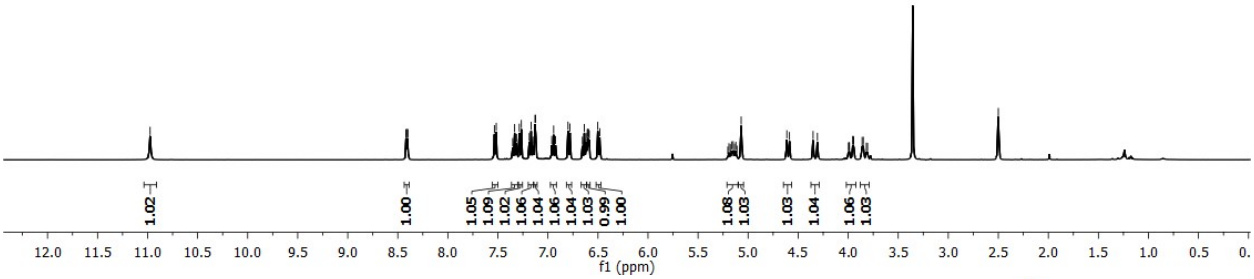
^{13}C NMR, DMSO-*d6*, 100 MHz

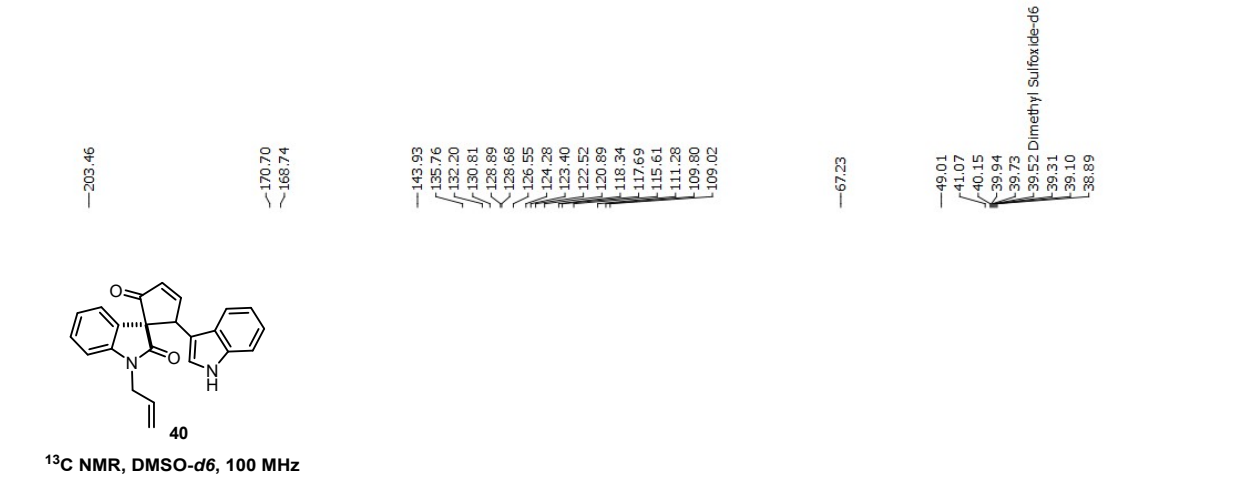




40

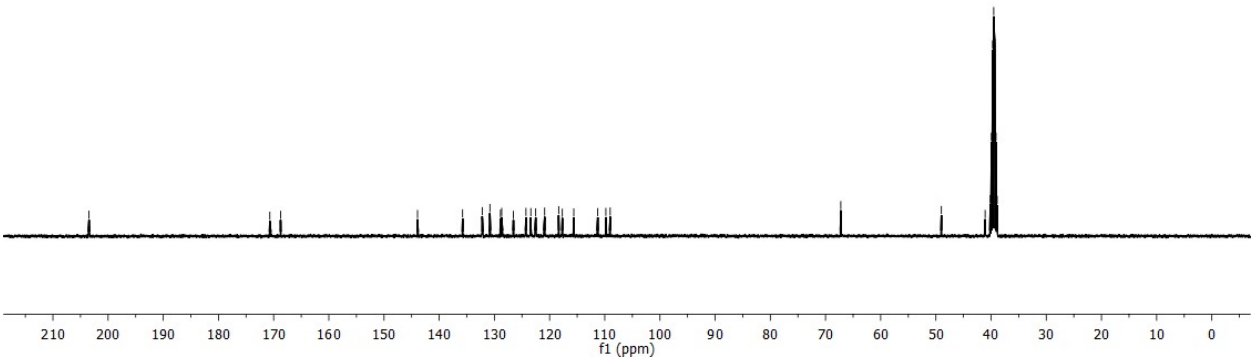
^{1}H NMR, DMSO-*d6*, 400 MHz

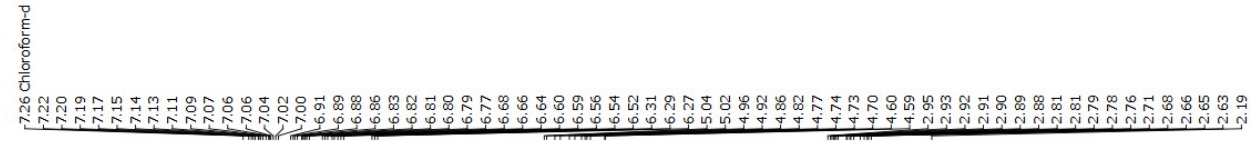


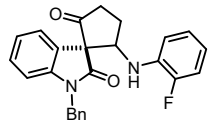


40

^{13}C NMR, DMSO-*d6*, 100 MHz

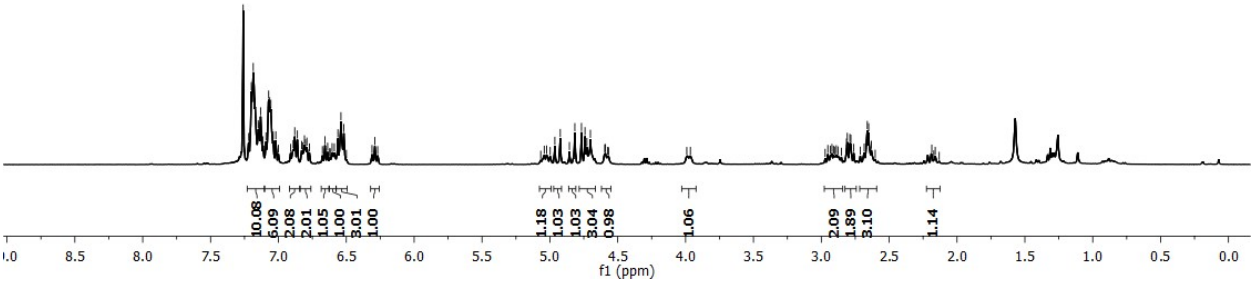


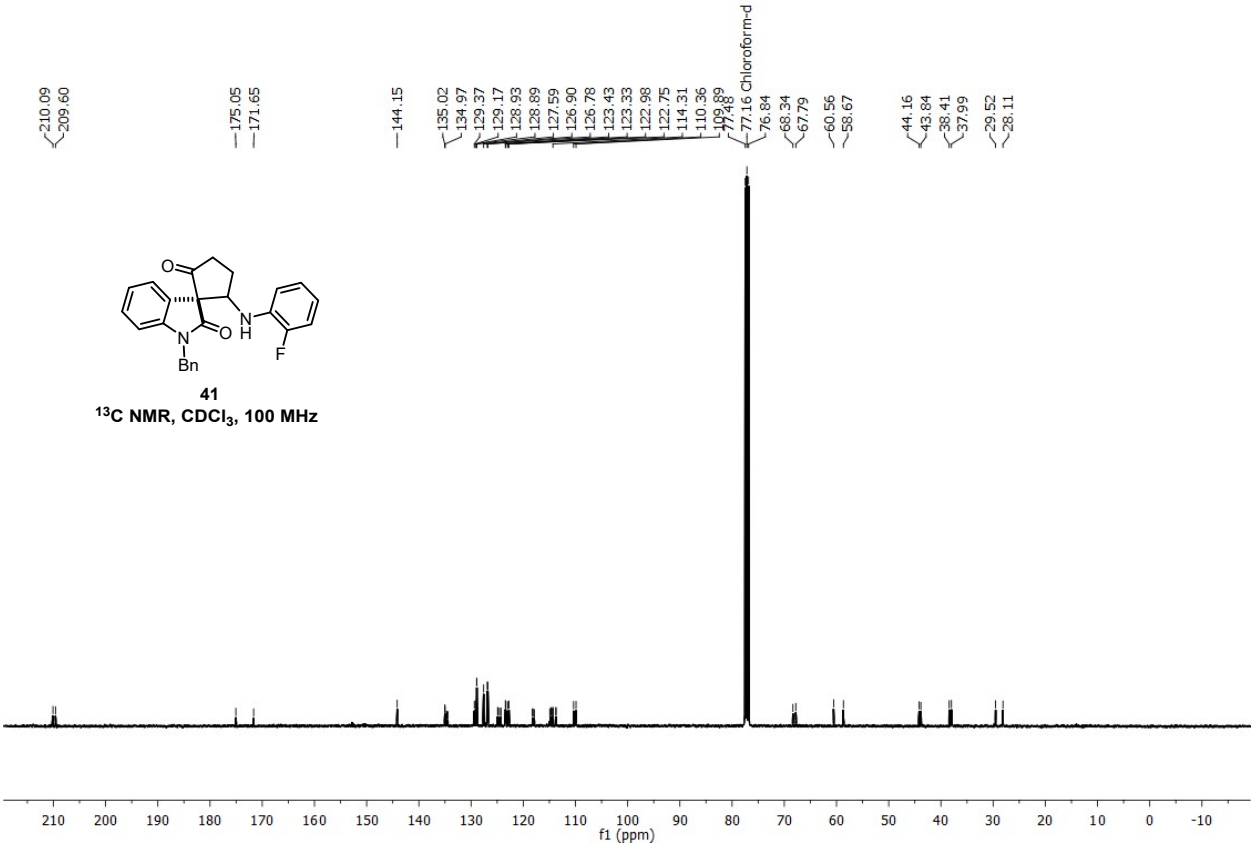




41

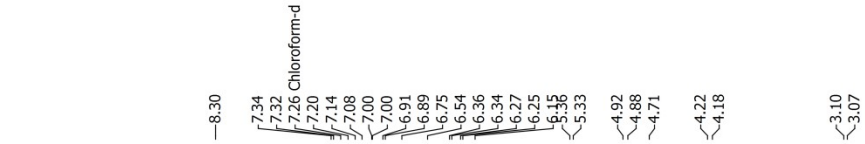
^{1}H NMR, $CDCl_3$, 400 MHz

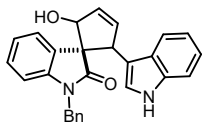




41

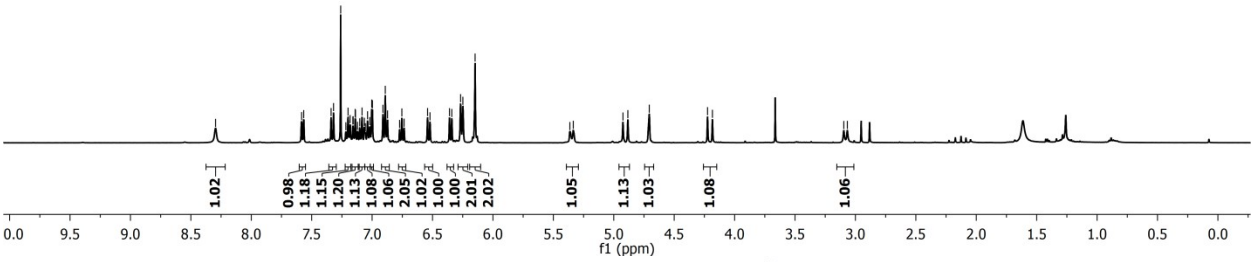
^{13}C NMR, $CDCl_3$, 100 MHz

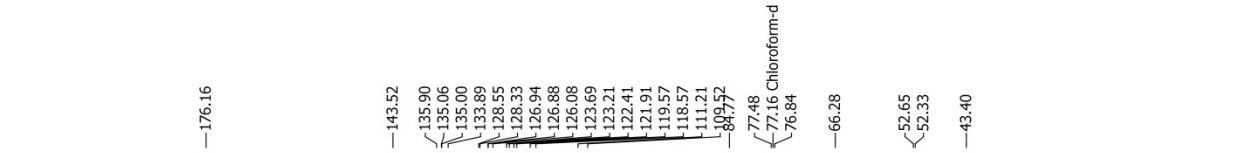


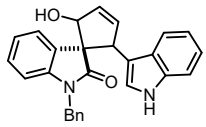


42

^{1}H NMR, $CDCl_3$, 400 MHz







42

^{13}C NMR, $CDCl_3$, 100 MHz