Electronic Supplementary Material (ESI) for Chemical Communications.

Supplementary Information

Quaternary Carbon Construction through Piancatelli Rearrangement: Easy Access to Spirocyclopentenones

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1. General Information

All chemicals have been purchased from commercial sources and were used without further purification unless otherwise noted. All solvents are reagent grade or HPLC grade. The synthetic transformations have been monitored by thin layer chromatography (TLC). TLC was performed on silica gel 60 F_{254} plates (glass plates). Concentration under reduced pressure was performed by rotary evaporation below 45 °C. Column chromatography was performed using silica gel (100-200 mesh) packed in glass columns. Yields refer to spectroscopically pure compounds after isolation. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded in $CDCl_3$ or DMSO-*d6* using 400 or 500 MHz (^{1}H), 100 or 125 MHz (^{13}C) and 377 MHz (^{19}F). Chemical shifts (δ-values) are reported in ppm, spectra were calibrated related to solvents' residual proton chemical shifts ($CDCl_3$, δ = 7.26) or (DMSO-*d6*, 2.5) and solvents' residual carbon chemical shifts ($CDCl_3$, δ = 77.16 ppm) or (DMSO-*d6*, δ = 49.0), multiplicity is reported as follows: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, ddd= doublet of doublet of doublet, td = triplet of doublet, m = multiplet or unresolved and coupling constant *J* in Hz. Melting points (mp) were determined in open capillaries and are uncorrected. Infrared spectra (IR) were recorded on a 0.1 mm KBr demountable cell. High-resolution mass spectra (HRMS) were obtained by electrospray ionization using a Q-TOF mass spectrometer in positive ion mode (M, M+H or M+Na) as indicated.

2. Experimental and Characterization of Compounds

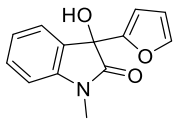
2.1. Synthesis of Furfuryl Alcohol Substrates

2.1.1. General Preparation of Furfuryl Alcohols 1 and 3[1]

To a solution of furan (1.4 mmol, 1.4 equiv) in anhydrous THF (20 mL) at -78 °C was added *n*-BuLi (1.2 mmol, 1.2 equiv). After, the resulting light yellow coloured solution was stirred for 1 h, then corresponding isatin/fluorenone/xanthane/thioxanthane (1.0 mmol, 1.0 equiv) in anhydrous THF (20 mL) was added to the reaction mixture in dropwise and the stirring was continued for 0.5 h to 4 h at the same temperature. The reaction was then quenched by saturated aqueous NH_4Cl (10 mL) and was allowed to warm to room temperature. The reaction mixture was extracted with EtOAc (2 x 50 mL), and the organic layer was separated and washed with water (10 mL) followed by brine solution (10 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by chromatography on silica gel to afford the furfuryl alcohols **1a-f** and **3a-c**.

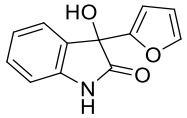
2.1.2. Experimental and Characterization of Furfuryl Alcohols 1a-f and 3a-c

3-(Furan-2-yl)-3-hydroxy-1-methylindolin-2-one (1a)



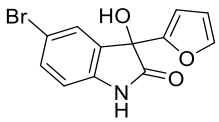
By following the general procedure, the reaction was performed with *N*-methylisatin (500 mg, 3.1 mmol) using furan (0.32 ml, 4.3 mmol) and *n*-BuLi (1.5 mL, 3.7 mmol) in THF at given conditions for 1 h. The residue was purified by silica gel column chromatography (20% EtOAc/hexanes) to afford **1a** (512 mg, 72%) as a white solid. mp 184-185 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (ddd, *J* = 7.4, 1.2, 0.4 Hz, 1H), 7.43 (t, *J* = 1.3 Hz, 1H), 7.37 (td, *J* = 7.8, 1.3 Hz, 1H), 7.14 (td, *J* = 7.6, 0.9 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 6.31 (d, *J* = 1.3 Hz, 2H), 3.78 (s, 1H), 3.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 151.4, 144.1, 143.6, 130.4, 128.3, 125.5, 123.5, 110.5, 109.1, 108.8, 73.6, 26.6. IR (thin film): ν_{max}/cm^{-1} 3386, 3208, 1715, 1616, 1477, 1371, 1099, 1022, 754. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{13}H_{12}NO_3$ 230.0817, found 230.0813.

3-(Furan-2-yl)-3-hydroxyindolin-2-one (1b)



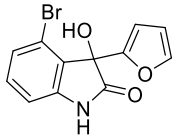
By following the general procedure, the reaction was performed with isatin (500 mg, 3.4 mmol) using furan (0.3 ml, 4.7 mmol) and *n*-BuLi (1.6 mL, 4.1 mmol) in THF at given conditions for 3 h. The residue was purified by silica gel column chromatography (20% EtOAc/hexanes) to afford **1b** (468 mg, 64%) as a white solid. mp 170-172 °C. ^{1}H NMR (500 MHz, DMSO-*d6*) δ 10.45 (s, 1H), 7.59 (dd, *J* = 1.8, 0.9 Hz, 1H), 7.30 (d, *J* = 7.3 Hz, 1H), 7.24 (td, *J* = 7.7, 1.3 Hz, 1H), 6.98 (td, *J* = 7.5, 0.9 Hz, 1H), 6.85 (d, *J* = 7.7 Hz, 1H), 6.73 (s, 1H), 6.40 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.31 (dd, *J* = 3.3, 0.8 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-*d6*) δ 176.2, 153.0, 143.2, 141.7, 130.9, 129.6, 125.0, 121.9, 110.3, 109.9, 107.7, 73.5. IR (thin film): ν_{max}/cm^{-1} 3638, 3407, 3378, 3204, 2924, 2859, 1739, 1469, 1214, 1098, 770, 673. HRMS (EI): *m/z* calculated for $[M]^+$ $C_{12}H_9NO_3$ 215.0582, found 215.0592.

5-Bromo-3-(furan-2-yl)-3-hydroxyindolin-2-one (1c)



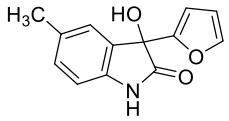
By following the general procedure, the reaction was performed with 5-bromoisatin (400 mg, 1.8 mmol) using furan (1.8 ml, 2.5 mmol) and *n*-BuLi (0.8 mL, 2.1 mmol) in THF at given conditions for 2 h. The residue was purified by silica gel column chromatography (30% EtOAc/hexanes) to afford **1c** (479 mg, 91%) as an off-white solid. mp 219-220 °C. ^{1}H NMR (400 MHz, DMSO-*d6*) δ 11.06 (s, 1H), 8.34 (d, *J* = 2.4 Hz, 1H), 8.23 (d, *J* = 7.8 Hz, 1H), 8.08 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.52 (dd, *J* = 5.9, 1.1 Hz, 1H), 7.16 (dd, *J* = 5.9, 1.3 Hz, 1H), 6.99 (d, *J* = 8.6 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-*d6*) δ 175.7, 152.2, 143.5, 141.0, 133.1, 132.3, 127.7, 113.5, 112.1, 110.5, 108.1, 73.4. IR (thin film): ν_{max}/cm^{-1} 3401, 3293, 2928, 1728, 1472, 1071, 745, 627. HRMS (ESI): *m/z* calculated for $[M+Na]^+$ $C_{12}H_8NNaBrO_3$ 315.9585, found 315.9584.

4-Bromo-3-(furan-2-yl)-3-hydroxyindolin-2-one (1d)



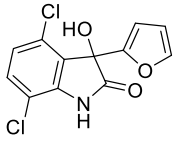
By following the general procedure, the reaction was performed with 4-bromoisatin (400 mg, 1.8mmol) using furan (1.8 ml, 2.5 mmol) and *n*-BuLi (0.8 mL, 2.1 mmol) in THF at given conditions for 4 h. The residue was purified by silica gel column chromatography (30% EtOAc/hexanes) to afford **1d** (452 mg, 86%) as a peach solid. mp 206°C. ^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.67 (s, 1H), 7.51 (d, *J* = 0.8 Hz, 1H), 7.21 (dd, *J* = 11.1, 4.7 Hz, 1H), 7.12 – 7.08 (m, 1H), 6.88 (d, *J* = 7.1 Hz, 1H), 6.81 (s, 1H), 6.46 (ddd, *J* = 5.0, 3.2, 1.3 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-*d6*) δ 175.7, 151.3, 144.2, 142.5, 131.7, 129.0, 125.9, 119.6, 110.5, 109.4, 108.5, 75.9. IR (thin film): ν_{max}/cm^{-1} 3410, 3291, 2900, 1680, 1470, 1050, 740, 630. HRMS (ESI): *m/z* calculated for $[M]^+$ $C_{12}H_8BrNO_3$ 292.9688, found 292.9685.

3-(Furan-2-yl)-3-hydroxy-5-methylindolin-2-one (1e)



By following the general procedure, the reaction was performed with 5-methylisatin (450 mg, 2.7mmol) using furan (0.3 ml, 3.8 mmol) and *n*-BuLi (1.5 mL, 3.9 mmol) in THF at given conditions for 2.5 h. The residue was purified by silica gel column chromatography (15% EtOAc/hexanes) to afford **1e** (482 mg, 75%) as a pale-yellow solid. mp 201-203 °C. ^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.36 (s, 1H), 7.58 (s, 1H), 7.11 (s, 1H), 7.05 (d, *J* = 7.8 Hz, 1H), 6.74 (d, *J* = 7.8 Hz, 1H), 6.70 (s, 1H), 6.40 (dd, *J* = 3.0, 1.8 Hz, 1H), 6.32 (d, *J* = 3.0 Hz, 1H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, DMSO-*d6*) δ 176.3, 153.2, 143.2, 139.3, 130.9, 130.8, 129.8, 125.6, 110.3, 109.7, 107.6, 73.7, 20.6. IR (thin film): ν_{max}/cm^{-1} 3510, 3022, 2218, 1707, 1215, 749, 671. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{13}H_{11}NO_3$ 230.20, found 230.0813.

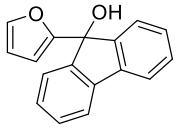
4,7-Dichloro-3-(furan-2-yl)-3-hydroxyindolin-2-one (1f)



By following the general procedure, the reaction was performed with 4,7-dichloroisatin (450 mg, 2.1mmol) using furan (0.2 ml, 2.9 mmol) and *n*-BuLi (1.0 mL, 2.5 mmol) in THF at given conditions for 2 h. The residue was purified by silica gel column chromatography (30% EtOAc/hexanes) to afford **1f (**460 mg, 78%) as an off-white solid. mp 196 °C. ^{1}H NMR (400 MHz,

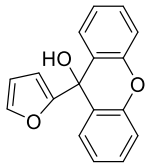
DMSO-*d6*) δ 11.14 (s, 1H), 7.54 (dd, *J* = 1.7, 0.9 Hz, 1H), 7.39 (d, *J* = 8.7 Hz, 1H), 7.00 (t, *J* = 4.4 Hz, 2H), 6.50 (dd, *J* = 3.3, 0.8 Hz, 1H), 6.44 (dd, *J* = 3.3, 1.8 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-*d6*) δ 175.8, 150.9, 143.1, 141.7, 131.3, 129.8, 128.8, 124.3, 113.4, 110.7, 108.7, 75.7. IR (thin film): ν_{max}/cm^{-1} 3280, 2470, 1735, 1618, 1470, 1162, 810, 751. HRMS (ESI): *m/z* calculated for $[M+Na]^+$ $C_{12}H_7Cl_2NNaO_3$ 305.9700, found 305.0357.

9-(Furan-2-yl)-9*H*-fluoren-9-ol (3a)



By following the general procedure, the reaction was performed with fluorenone (450 mg, 2.5 mmol) using furan (0.4 ml, 3.5 mmol) and *n*-BuLi (1.0 mL, 3 mmol) in THF at given conditions for 0.5 h. The residue was purified by silica gel column chromatography (12% EtOAc/hexanes) to afford **3a** (539 mg, 87%) as an off-white solid. mp 108 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.5 Hz, 2H), 7.66 (d, *J* = 7.5 Hz, 2H), 7.43 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.41 (td, *J* = 7.5, 1.1 Hz, 2H), 6.28 – 6.25 (m, 2H), 6.12 (dd, *J* = 3.3, 0.7 Hz, 2H), 2.73 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.6, 163.3, 144.8, 142.6, 142.0, 141.4, 136.0, 128.7, 128.6, 128.0, 127.4, 125.4, 122.9, 120.8, 120.5, 77.8, 69.3. IR (thin film): ν_{max}/cm^{-1} 3478, 3340, 2820, 1609, 1462, 1312, 1249, 1009, 880, 756. HRMS (ESI): *m/z* calculated for $[M]^+$ $C_{17}H_{12}O_2$ 248.0837, found 248.0836.

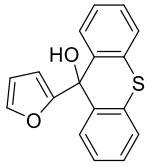
9-(Furan-2-yl)-9*H*-xanthen-9-ol (3b)



By following the general procedure, the reaction was performed with xanthone (500 mg, 2.5 mmol) using furan (0.27 ml, 3.6 mmol) and *n*-BuLi (1.2 mL, 3.1 mmol) in THF at given conditions for 0.5 h. The residue was purified by silica gel column chromatography (15% EtOAc/hexanes) to afford **3b** (579 mg, 86%) as an off-white solid. mp 91 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 1.6 Hz, 1H), 7.58 (d, *J* = 1.6 Hz, 1H), 7.36 (ddd, *J* = 8.6, 7.2, 1.6 Hz, 2H), 7.30 (dd, *J* = 1.8, 0.9 Hz, 1H), 7.21 (d, *J* = 1.1 Hz, 1H), 7.19 (d, *J* = 1.1 Hz, 1H), 7.18 – 7.13 (m, 2H), 6.31 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.25 (dd, *J* = 3.2, 0.8 Hz, 1H), 2.82 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6,

150.1, 142.9, 129.8, 128.5, 124.3, 123.6, 116.7, 110.2, 107.5, 68.0. IR (thin film): ν_{max}/cm^{-1} 3473, 2930, 2430, 1739, 1611, 1483, 1310, 1250, 1110, 808, 759. HRMS (EI): *m/z* calculated for $[M]^+$ $C_{17}H_{12}O_3$ 264.0786, found 264.0790.

9-(Furan-2-yl)-9*H*-thioxanthen-9-ol (3c)



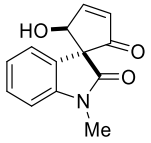
By following the general procedure, the reaction was performed with thioxanthone (500 mg, 2.4 mmol) using furan (0.25mL, 3.3 mmol) and *n*-BuLi (1.1 mL, 2.8 mmol) in THF at given conditions for 0.5 h. The residue was purified by silica gel column chromatography (15% EtOAc/hexanes) to afford **3c** (528 mg, 89%) as an off-white solid. mp 117 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 7.8, 1.3 Hz, 2H), 7.46 – 7.35 (m, 4H), 7.33 – 7.25 (m, 3H), 6.18 (dd, *J* = 3.3, 1.8 Hz, 1H), 5.70 (dd, *J* = 3.3, 0.8 Hz, 1H), 3.08 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 143.5, 137.9, 131.7, 128.2, 127.0, 126.9, 126.5, 110.5, 109.6, 73.4. IR (thin film): ν_{max}/cm^{-1} 3518, 3409, 1455, 1191, 1150, 1027, 751. HRMS (ESI): *m/z* calculated for $[M]^+$ $C_{17}H_{12}O_2S$ 280.0558, found 280.0559.

2.2. General Procedure for Hydroxy Spirocyclopentenones 2 and 4

To a solution of furfuyl alcohol **1a-f/3a-c** (1.0 equiv) in HFIP/H_2O (2:1), was added *R*-(-)-1,1′-binaphthyl-2,2′-diyl hydrogenphosphate, (*R*)-BINOL.PA (2.5 mol%). Then the reaction mixture was stirred at 90 °C temperature for 0.5-1.0 h (the reaction was monitored by TLC). Upon completion, the solvent was removed under vacuum and the residue was purified by silica gel column chromatography using hexanes/EtOAc to obtain spirocyclopentenone derivatives **2a-f** and **4a-c**.

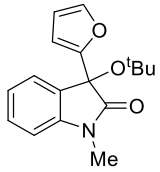
2.3. Experimental and Characterization of Hydroxy Spirocyclopentenones 2a-2f

2-Hydroxy-1'-methylspiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione (2a)



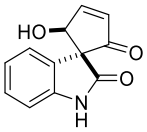
By following the general procedure, the reaction was performed with 3-(furan-2-yl)-3-hydroxy-1-methylindolin-2-one **la** (100 mg, 0.43mmol, 1.0 equiv) and (*R*)-BINOL.PA (3.8 mg, 2.5 mol%) for 1 h, the product **2a** (62 mg, 62%) was isolated as white solid after silica gel column chromatography (hexanes/EtOAc 6:4). mp 104 °C. ^{1}H NMR (400 MHz, DMSO-*d6*) δ 8.08 (dd, *J* = 5.5, 1.3 Hz, 1H), 7.37 – 7.28 (m, 1H), 7.06 (d, *J* = 7.9 Hz, 1H), 7.01 (d, *J* = 5.5 Hz, 2H), 6.51 (d, *J* = 5.6 Hz, 1H), 5.85 (d, *J* = 6.3 Hz, 1H), 5.06 (d, *J* = 6.2 Hz, 1H), 3.16 (s, 3H). ^{13}C NMR (125 MHz, DMSO-*d6*) δ 201.8, 174.1, 168.4, 145.5, 133.5, 128.9, 126.3, 125.6, 122.4, 109.2, 75.3, 67.5, 26.8. IR (thin film): ν_{max}/cm^{-1} 3557, 3479, 3399, 1710, 1612, 1481, 1369, 1124, 761. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{13}H_{12}NO_3$ 230.0817, found 230.0811.

3-(*tert*-Butoxy)-3-(furan-2-yl)-1-methylindolin-2-one (2a′)



To a solution of furfuyl alcohol **1a** (100 mg, 0.43mol, 1.0 equiv) in ^{t}BuOH/water (7:3, 1.0 mL), was added $B(C_6F_5)_3$ (5 mol%). Then the reaction mixture was stirred at 90°C temperature for 3 h (the reaction was monitored by TLC). Upon completion, the crude product extracted with ethyl acetate (2 x 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography using (hexanes/EtOAc 6:4) to obtain product **2a′** (79 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 5.8, 1.3 Hz, 1H), 7.69 (d, *J* = 7.5 Hz, 1H), 7.19 (td, *J* = 7.7, 1.2 Hz, 1H), 7.02 (td, *J* = 7.6, 1.0 Hz, 1H), 6.81 (d, *J* = 7.7 Hz, 1H), 6.57 (dd, *J* = 5.8, 1.5 Hz, 1H), 6.52 (s, 1H), 3.26 (s, 3H), 1.45 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 165.7, 141.3, 139.6, 127.0, 126.8, 122.7, 121.9, 107.5, 105.5, 28.8, 25.9. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{17}H_{20}NO_3$ 286.1443, found 286.1430.

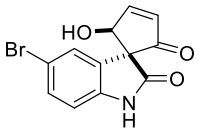
2-Hydroxyspiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione (2b)



By following the general procedure, the reaction was performed with 3-(furan-2-yl)-3-hydroxyindolin-2-one **1b** (100 mg, 0.46 mmol, 1.0 equiv) and (*R*)-BINOL.PA (4 mg, 2.5 mol%)

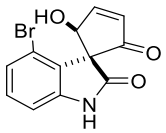
for 1 h, the product **2b** (64 mg, 64%) was isolated as pale-yellow powder after silica gel column chromatography (hexanes/EtOAc 6: 4). mp 171 °C. ^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.61 (s, 1H), 8.06 (dd, *J* = 5.6, 2.3 Hz, 1H), 7.20 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.04 – 6.82 (m, 3H), 6.47 (dd, *J* = 5.6, 1.4 Hz, 1H), 5.85 (d, *J* = 6.4 Hz, 1H), 5.03 (ddd, *J* = 6.4, 2.3, 1.5 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-*d6*) δ 213.2, 187.0, 179.4, 155.2, 144.6, 140.0, 138.4, 137.1, 132.8, 121.1, 86.2, 79.1. IR (thin film): ν_{max}/cm^{-1} 3397, 3227, 229, 2928, 1713, 1628, 1470, 1212, 761. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{12}H_{10}NO_3$ 216.0661, found 216.0653.

5'-Bromo-2-hydroxyspiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione (2c)



By following the general procedure, the reaction was performed with 5-bromo-3-(furan-2-yl)-3-hydroxyindolin-2-one **1c** (100 mg, 0.34 mmol, 1.0 equiv) and (*R*)-BINOL.PA (4 mg, 2.5 mol%) for 1 h, the product **2c** (55 mg, 55%) was isolated as pale-yellow solid after silica gel column chromatography (hexanes/EtOAc 7:3). mp 220 °C. ^{1}H NMR (400 MHz, DMSO-*d6*) δ (*dr* 5.5:1) 10.77 (s, 1H), 8.08 (dd, *J* = 5.6, 2.4 Hz, 1H), 7.42 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.11 (d, *J* = 2.0 Hz, 1H), 6.86 (d, *J* = 8.3 Hz, 1H), 6.50 (dd, *J* = 5.6, 1.4 Hz, 1H), 5.95 (d, *J* = 6.6 Hz, 1H), 5.02 (ddd, *J* = 6.6, 2.3, 1.5 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-*d6*) δ 200.9, 174.8, 167.9, 143.1, 133.1, 131.1, 128.0, 128.2, 112.9, 111.5, 74.7, 67.5. IR (thin film): ν_{max}/cm^{-1} 3411, 3372, 1703, 1605, 1452, 1309, 1149, 1129, 765. HRMS (EI): *m/z* calculated for $[M+H]^+$ $C_{12}H_9BrNO_3$ 293.9766, found 292.9774.

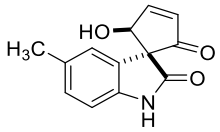
4'-Bromo-2-hydroxyspiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione (2d)



By following the general procedure, the reaction was performed with 4-bromo-3-(furan-2-yl)-3-hydroxyindolin-2-one **1d** (100 mg, 0.34mmol, 1.0 equiv) and (*R*)-BINOL.PA (4 mg, 2.5 mol%) for 30 min, the product **2d** (80 mg, 80%) was isolated as white solid after silica gel column chromatography (hexanes/EtOAC 7:3). mp 197 °C. ^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.72 (s, 1H), 7.93 (dd, *J* = 5.7, 1.9 Hz, 1H), 7.33 – 7.05 (m, 2H), 6.87 (dd, *J* = 7.6, 0.8 Hz, 1H), 6.53 (dd,

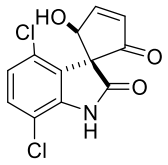
J = 5.7, 1.7 Hz, 1H), 6.12 (d, *J* = 6.9 Hz, 1H), 5.45 (dt, *J* = 6.9, 1.8 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-*d6*) δ 198.3, 170.6, 166.1, 145.6, 134.1, 131.0, 127.3, 124.8, 118.0, 108.8, 74.8, 70.4. IR (thin film): ν_{max}/cm^{-1} 3405, 3381, 1713, 1617, 1454, 1303, 1153, 1127, 769. HRMS (EI): *m/z* calculated for $[M]^+$ $C_{12}H_8BrNO_3$ 292.9688, found 292.9679.

2-Hydroxy-5'-methylspiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione (2e)



By following the general procedure, the reaction was performed with 3-(furan-2-yl)-3-hydroxy-5-methylindolin-2-one **1e** (100 mg, 0.43 mmol, 1.0 equiv) and (*R*)-BINOL.PA (4 mg, 2.5 mol%) for 45 min, the product **2e** (64 mg, 64%) was isolated as pale-yellow powder after silica gel column chromatography (hexanes/EtOAc 7:3). mp 186 °C. ^{1}H NMR (400 MHz, DMSO-*d6*) δ (*dr* 1.5:1) 10.50 (s, 1H), 8.05 (dd, *J* = 5.6, 2.3 Hz, 1H), 7.02 (d, *J* = 7.9 Hz, 1H), 6.79 (s, 1H), 6.76 (d, *J* = 7.9 Hz, 1H), 6.46 (dd, *J* = 5.6, 1.4 Hz, 1H), 5.82 (d, *J* = 6.4 Hz, 1H), 5.02 (dt, 1H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, DMSO-*d6*) δ (minor diastereomer peak in parenthesis) 201.6(200.6), 175.3(171.7), 167.8(167.0), 141.2(141.0), 133.0(132.9), 129.9(130.6), 128.5(128.8), 126.1(126.9), 124.3, 109.3(108.9), 74.7(78.1), 67.6(69.4), 20.7. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{13}H_{12}NO_3$ 230.0817, found 230.0813.

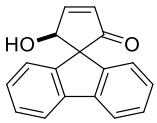
4',7'-Dichloro-2-hydroxyspiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione (2f)



By following the general procedure, the reaction was performed with 4,7-dichloro-3-(furan-2-yl)-3-hydroxyindolin-2-one **1f** (100 mg, 0.35 mmol, 1.0 equiv) and (*R*)-BINOL.PA (4 mg, 2.5 mol%) for 45 min, the product **2f** (85 mg, 85%) was isolated as olive green powder after silica gel column chromatography (hexanes/EtOAc 7:3). mp 228 °C. ^{1}H NMR (500 MHz, DMSO-*d6*) δ 11.22 (s, 1H), 7.97 (dd, *J* = 5.7, 1.9 Hz, 1H), 7.40 (d, *J* = 8.8 Hz, 1H), 7.08 (d, *J* = 8.8 Hz, 1H), 6.56 (dd, *J* = 5.7, 1.6 Hz, 1H), 6.22 (d, *J* = 6.7 Hz, 1H), 5.42 (dt, *J* = 6.7, 1.8 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-*d6*) δ 197.7, 170.5, 166.5, 143.0, 133.8, 130.6, 127.5, 126.7, 123.0, 112.7, 75.0, 70.4. IR

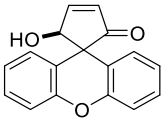
(thin film): ν_{max}/cm^{-1} 3532, 3307, 3185, 1720, 1624, 1495, 1154, 1182, 851, 767. HRMS (EI): *m/z* calculated for $[M]^+$ $C_{12}H_7Cl_2NO_3$ 282.9803, found 282.9812.

2-Hydroxyspiro[cyclopentane-1,9'-fluoren]-3-en-5-one (4a)



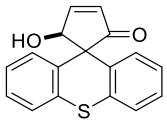
By following the general procedure, the reaction was performed with 9-(furan-2-yl)-9*H*-fluoren-9-ol **3a** (100 mg, 0.4 mmol, 1.0 equiv) and (*R*)-BINOL.PA (3.5 mg, 2.5 mol%) for 30 min, the product **4a** (80 mg, 80%) was isolated as off-white sticky solid after silica gel column chromatography (hexanes/EtOAC 8:2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 5.8, 2.2 Hz, 1H), 7.78 – 7.70 (m, 2H), 7.40 (ddd, *J* = 7.3, 4.1, 1.1 Hz, 2H), 7.26 (dt, *J* = 6.6, 1.8 Hz, 3H), 7.16 (d, *J* = 7.6 Hz, 1H), 6.57 (dd, *J* = 5.8, 1.3 Hz, 1H), 5.21 (s, 1H), 2.12 (dd, *J* = 2.4, 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.6, 163.3, 144.8, 142.6, 141.9, 141.4, 136.0, 128.7, 128.6, 128.0, 127.4, 125.4, 122.9, 120.8, 120.5, 77.8, 69.3. IR (thin film): ν_{max}/cm^{-1} 3478, 3340, 2820, 1609, 1462, 1312, 1249, 1009, 880, 756. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{17}H_{13}O_2$ 249.0916, found 248.0919.

2-Hydroxyspiro[cyclopentane-1,9'-xanthen]-3-en-5-one (4b)



By following the general procedure, the reaction was performed with 9-(furan-2-yl)-9*H*-xanthen-9-ol **3b** (100 mg, 0.38 mmol, 1.0 equiv) and (*R*)-BINOL.PA (3.3 mg, 2.5 mol%) for 30 min, the product **4b** (80 mg, 80%) was isolated as white solid after silica gel column chromatography (hexanes/EtOAc 8:2). mp 142 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 6.0, 2.2 Hz, 1H), 7.33 – 7.26 (m, 2H), 7.18 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.14 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.08 – 7.03 (m, 2H), 6.91 (dd, *J* = 7.8, 1.5 Hz, 1H), 6.86 (dd, *J* = 7.8, 1.5 Hz, 1H), 6.72 (dd, *J* = 6.0, 1.5 Hz, 1H), 4.83 (d, *J* = 7.0 Hz, 1H), 1.79 (d, *J* = 7.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.7, 164.3, 152.2, 151.3, 136.6, 129.6, 129.0, 128.1, 126.7, 124.1, 123.4, 122.7, 118.1, 117.6, 117.0, 84.2, 56.5. IR (thin film): ν_{max}/cm^{-1} 3766, 3475, 3421, 2924, 1715, 1498, 1451, 1309, 1257, 1116, 764. HRMS (EI): *m/z* calculated for $[M]^+$ $C_{17}H_{12}O_3$ 264.0786, found 264.0791.

2-Hydroxyspiro[cyclopentane-1,9'-thioxanthen]-3-en-5-one (4c)



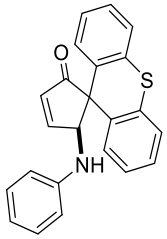
By following the general procedure, the reaction was performed with 9-(furan-2-yl)-9*H*-thioxanthen-9-ol **3c** (100 mg, 0.36 mmol, 1.0 equiv) and (*R*)-BINOL.PA (3.1 mg, 2.5 mol%) for 30 min, the product **4c** (82 mg, 82%) was isolated as light orange powder after silica gel column chromatography (hexanes/EtOAc 8:2). mp 126 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 6.0, 2.2 Hz, 1H), 7.34 – 7.26 (m, 2H), 7.16 (ddd, *J* = 21.3, 8.2, 1.2 Hz, 2H), 7.06 (ddd, *J* = 15.1, 7.7, 1.3 Hz, 2H), 6.90 (dd, *J* = 7.8, 1.5 Hz, 1H), 6.85 (dd, *J* = 7.8, 1.5 Hz, 1H), 6.70 (dd, *J* = 6.0, 1.4 Hz, 1H), 4.81 (d, *J* = 6.7 Hz, 1H), 1.85 (d, *J* = 7.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.7, 164.3, 152.2, 151.3, 136.6, 129.6, 129.0, 128.2, 126.7, 124.1, 123.3, 122.7, 118.2, 117.6, 117.0, 84.2, 56.5. IR (thin film) ν_{max}/cm^{-1} 3708, 3479, 1570, 1230, 1198, 1055, 762. HRMS (EI): *m/z* calculated for $[M]^+$ $C_{17}H_{12}O_2S$ 280.0558, found 280.0552.

2.4. General Procedure for Amino Spirocyclopentenones 6

To a solution of furfuyl alcohol **3a-c** (100-200 mg, 1.0equiv) and aromatic amines (1.0 equiv) in HFIP (2-4 mL) under nitrogen atmosphere, was added (±)-BINOL.PA (2.5 mol%). Then the reaction mixture was stirred at room temperature for 5-20 min (the reaction was monitored by TLC). Upon completion, the reaction solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography using hexanes/EtOAc to obtain spiro cyclopentenone derivatives **6b-t**.

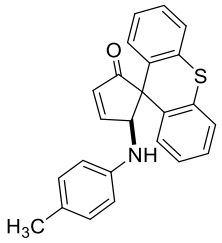
2.5. Experimental and Characterization of Amino Spirocyclopentenones 6b-t

5-(Phenylamino)spiro[cyclopentane-1,9'-thioxanthen]-3-en-2-one (6b)



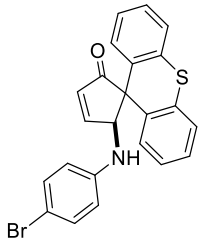
By following the general procedure, the reaction was performed with 9-(furan-2-yl)-9H-thioxanthen-9-ol **3c** (100 mg, 0.36 mmol, 1.0 equiv), aniline (33 mg, 0.35 mmol, 1.0 equiv), (±)-BINOL.PA (3.1 mg, 2.5 mol%) for 5 min, the product **6b** (103 mg, 82%) was isolated as pale-brown powder after silica gel column chromatography (hexanes/EtOAc 7:3). R_f = 0.3 (30% EtOAc in hexanes). mp 151 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 5.8, 2.6 Hz, 1H), 7.37 – 7.31 (m, 1H), 7.26 – 7.22 (m, 1H), 7.21 – 7.19 (m, 2H), 7.19 – 7.14 (m, 2H), 7.11 – 7.08 (m, 1H), 7.07 – 6.95 (m, 3H), 6.72 – 6.60 (m, 2H), 6.20 (dd, *J* = 8.6, 0.9 Hz, 2H), 4.72 (d, *J* = 9.0 Hz, 1H), 2.93 (d, *J* = 9.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.0, 163.0, 145.8, 137.4, 135.1, 134.8, 132.7, 132.2, 129.1, 128.6, 127.7, 127.3, 126.9, 126.8, 126.7, 126.3, 118.6, 114.0, 68.1, 62.0. IR (thin film) ν_{max}/cm^{-1} 3399, 3058, 2927, 1713, 1601, 1509, 1258, 756. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{23}H_{18}NOS$ 356.1124, found 356.1109.

5-(*p*-Tolylamino)spiro[cyclopentane-1,9'-thioxanthen]-3-en-2-one (6c)



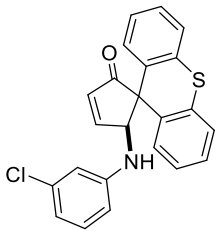
By following the general procedure, the reaction was performed with 9-(furan-2-yl)-9H-thioxanthen-9-ol **3c** (100 mg, 0.36 mmol, 1.0 equiv), *p*-toluidine (38 mg, 0.36 mmol, 1.0 equiv), (±)-BINOL.PA (3.1 mg, 2.5 mol%) for 10 min, the product **6c** (121 mg, 92%) was isolated as shiny gray colour powder after silica gel column chromatography (hexanes/EtOAc 7:3). R_f = 0.3 (30% EtOAc in hexanes). mp 158 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 5.8, 2.5 Hz, 1H), 7.42 – 7.30 (m, 1H), 7.30 – 7.14 (m, 5H), 7.14 – 7.08 (m, 1H), 7.08 – 6.98 (m, 1H), 6.82 (d, *J* = 8.2 Hz, 2H), 6.66 (dd, *J* = 5.8, 1.3 Hz, 1H), 6.12 (d, *J* = 8.4 Hz, 2H), 4.68 (d, *J* = 8.2 Hz, 1H), 2.80 (d, *J* = 9.4 Hz, 1H), 2.20 (d, *J* = 21.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.8, 162.9, 143.3, 137.3, 134.6, 132.6, 132.1, 129.3, 128.3, 127.5, 127.4, 126.9, 126.6, 126.5, 126.4, 126.4, 126.1, 113.8, 68.1, 61.7, 20.2.IR (thin film) ν_{max}/cm^{-1} 3395, 3058, 3019, 1713, 1613, 1520, 1473, 1295, 815, 758. HRMS (ESI) : *m/z* calculated for $[M+H]^+$ $C_{24}H_{20}NOS$ 370.1266, found 370.1284.

2-((4-Bromophenyl)amino)spiro[cyclopentane-1,9'-thioxanthen]-3-en-5-one (6d)



By following the general procedure, the reaction was performed with 9-(furan-2-yl)-9H-thioxanthen-9-ol **3c** (100 mg, 0.37 mmol, 1.0 equiv), 4-bromoaniline (60 mg, 0.37 mmol, 1.0 equiv), (±)-BINOL.PA (3.1 mg, 2.5 mol%) for 5 min, the product **6d** (139 mg, 90%) was isolated as shiny gray colour powder after silica gel column chromatography (hexanes/EtOAc 7:3). R_f = 0.3 (30% EtOAc in hexanes). mp 189 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 5.8, 2.6 Hz, 1H), 7.41 – 7.29 (m, 1H), 7.25 – 7.15 (m, 5H), 7.11 – 7.08 (m, 3H), 7.06 – 7.00 (m, 1H), 6.70 (dd, *J* = 5.8, 1.5 Hz, 1H), 6.15 – 6.02 (m, 2H), 4.66 (d, *J* = 9.1 Hz, 1H), 2.95 (d, *J* = 9.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.7, 162.4, 144.9, 137.2, 135.5, 134.8, 132.6, 132.1, 131.8, 128.6, 127.8, 127.4, 126.9, 126.8, 126.5, 115.6, 110.4, 68.1, 62.1. IR (thin film) ν_{max}/cm^{-1} 3791, 3837, 3349, 1716, 1598, 1508, 1071, 764. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{23}H_{17}BrNOS$ 434.0219, found 434.0214.

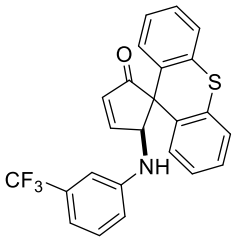
2-((3-Chlorophenyl)amino)spiro[cyclopentane-1,9'-thioxanthen]-3-en-5-one (6e)



By following the general procedure, the reaction was performed with 9-(furan-2-yl)-9H-thioxanthen-9-ol **3c** (100 mg, 0.37 mmol, 1.0 equiv), 3-chloroaniline (45 mg, 0.37 mmol, 1.0 equiv), (±)-BINOL.PA (3.1 mg, 2.5 mol%) for 5 min, the product **6e** (122 mg, 88%) was isolated as off-white powder after silica gel column chromatography (hexanes/EtOAc 7:3). R_f = 0.3 (30% EtOAc in hexanes). mp 137 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 5.8, 2.5 Hz, 1H), 7.39 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.29 – 7.26 (m, 1H), 7.23 (ddd, *J* = 8.9, 6.2, 1.6 Hz, 4H), 7.15 – 7.09 (m,

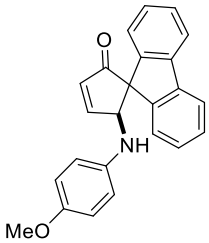
1H), 7.07 (dd, *J* = 7.7, 1.4 Hz, 1H), 6.94 (t, *J* = 8.0 Hz, 1H), 6.73 (dd, *J* = 5.8, 1.3 Hz, 1H), 6.66 (dd, *J* = 7.9, 1.1 Hz, 1H), 6.20 (t, *J* = 2.1 Hz, 1H), 6.09 (dd, *J* = 8.1, 2.0 Hz, 1H), 4.70 (dd, *J* = 10.1, 1.6 Hz, 1H), 3.04 (d, *J* = 10.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.6, 162.2, 146.9, 137.1, 135.5, 134.8, 132.4, 132.2, 130.1, 128.6, 127.9, 127.4, 126.9, 126.8, 126.5, 118.6, 113.9, 112.4, 67.9, 62.0. IR (thin film) ν_{max}/cm^{-1} 3979, 3811, 3563, 3379, 1713, 1597, 1512, 769. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{23}H_{17}ClNOS$ 390.0719, found 390.0738.

5-((3-(Trifluoromethyl)phenyl)amino)spiro[cyclopentane-1,9'-thioxanthen]-3-en-2-one (6f)



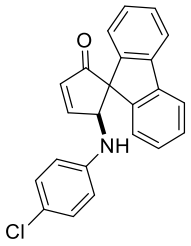
By following the general procedure, the reaction was performed with 9-(furan-2-yl)-9H-thioxanthen-9-ol **3c** (100 mg, 0.37 mmol, 1.0 equiv), 3-(trifluoromethyl)aniline (58 mg, 0.37 mmol, 1.0 equiv), (±)-BINOL.PA (3.1 mg, 2.5 mol%) for 5 min, the product **6f** (121 mg, 80%) was isolated as off-white powder after silica gel column chromatography (hexanes/EtOAC 7:3). R_f = 0.3 (30% EtOAc in hexanes). mp 158 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 5.8, 2.6 Hz, 1H), 7.35 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.28 – 7.16 (m, 5H), 7.10 (t, *J* = 6.8 Hz, 2H), 7.04 (dd, *J* = 7.6, 1.4 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 6.73 (dd, *J* = 5.8, 1.3 Hz, 1H), 6.35 (d, *J* = 7.4 Hz, 2H), 4.77 – 4.70 (m, 1H), 3.14 (d, *J* = 10.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.6, 162.1, 146.0, 136.9, 135.8, 134.6, 132.2(q, *J* = 40 Hz), 129.5, 128.6, 127.9, 127.5, 127.0, 126.8, 126.8, 126.5, 117.3, 115.3 (d, *J* =4 Hz), 110.7 (d, J =4 Hz), 68.1, 62.1. ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.11. IR (thin film) ν_{max}/cm^{-1} 3391, 3064, 1712, 1607, 1481, 1340, 1282, 1166, 1125, 755, 659. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{24}H_{17}F_3NOS$ 424.0098, found 424.1001.

2-((4-Methoxyphenyl)amino)spiro[cyclopentane-1,9'-fluoren]-3-en-5-one (6g)



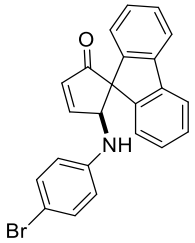
By following the general procedure, the reaction was performed with 9-(furan-2-yl)-9H-fluoren-9-ol **3a** (100 mg, 0.40 mmol, 1.0 equiv), 4-methoxyaniline (50 mg, 0.40 mmol, 1.0 equiv), (±)-BINOL.PA (3.5 mg, 2.5 mol%) for 20 min, the product **6g** (122 mg, 86%) was isolated as off-white powder after silica gel column chromatography (hexanes/EtOAc 7:3). R_f = 0.2 (30% EtOAc in hexanes). mp 122°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 5.8, 2.1 Hz, 1H), 7.70 – 7.64 (m, 2H), 7.41 – 7.32 (m, 4H), 7.24 (ddd, *J* = 7.9, 4.2, 0.8 Hz, 2H), 6.66 (dd, *J* = 5.8, 1.9 Hz, 1H), 6.50 – 6.41 (m, 2H), 6.14 – 6.05 (m, 2H), 5.20 (t, *J* = 1.9 Hz, 1H), 3.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.0, 162.4, 152.4, 145.1, 142.4, 141.7, 141.6, 139.4, 135.4, 128.3, 128.1, 127.8, 127.0, 123.4, 122.4, 120.7, 120.3, 115.0, 114.2, 68.7, 64.1, 55.4. IR (thin film) ν_{max}/cm^{-1} 3394, 3059, 3017, 2832, 1711, 1515, 1241, 1161, 1037, 757. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{24}H_{20}NO_2$ 354.1494, found 354.1509.

2-((4-Chlorophenyl)amino)spiro[cyclopentane-1,9'-fluoren]-3-en-5-one (6h)



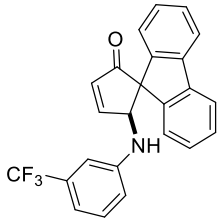
By following the general procedure, the reaction was performed with 9-(furan-2-yl)-9*H*-fluoren-9-ol **3a** (100 mg, 0.40 mmol, 1.0 equiv), aniline (38 mg, 0.40 mmol, 1.0 equiv), (±)-BINOL.PA (3.5 mg, 2.5 mol%) for 10 min, the product **6h** (123 mg, 82%) was isolated as off-white powder after silica gel column chromatography (hexanes/EtOAc 7:3). R_f = 0.3 (30% EtOAc in hexanes). mp 122 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.92 (m, 1H), 7.69 (dd, *J* = 7.1, 6.3 Hz, 2H), 7.42 (ddd, *J* = 7.6, 6.8, 3.8 Hz, 1H), 7.37 – 7.31 (m, 3H), 7.23 – 7.17 (m, 2H), 6.84 – 6.77 (m, 2H), 6.68 (dd, *J* = 5.8, 1.8 Hz, 1H), 6.09 – 5.96 (m, 2H), 5.19 (d, *J* = 7.2 Hz, 1H), 3.90 (d, *J* = 7.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.0, 161.9, 145.3, 144.3, 142.7, 141.9, 141.6, 136.1, 129.0, 128.8, 128.6, 128.2, 127.3, 123.9, 123.1, 122.7, 121.1, 120.7, 114.8, 68.7, 63.3. IR (thin film) ν_{max}/cm^{-1} 3388, 3062, 2924, 1709, 1599, 1501, 1445, 1324, 1161, 814, 754. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{23}H_{17}ClNO$ 358.0999, found 358.1011.

2-((4-Bromophenyl)amino)spiro[cyclopentane-1,9'-fluoren]-3-en-5-one (6i)



By following the general procedure, the reaction was performed with 9-(furan-2-yl)-9*H*-fluoren-9-ol **3a** (100 mg, 0.40 mmol, 1.0 equiv), 4-bromoaniline (68 mg, 0.40 mmol, 1.0 equiv), (±)-BINOL.PA (3.5 mg, 2.5 mol%) for 10 min, the product **6i** (142 mg, 88%) was isolated as off-white powder after silica gel column chromatography (hexanes/EtOAc 7:3). R_f = 0.3 (30% EtOAc in hexanes). mp 122 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 5.8, 2.2 Hz, 1H), 7.73 – 7.62 (m, 2H), 7.46 – 7.37 (m, 1H), 7.39 – 7.28 (m, 3H), 7.22 – 7.16 (m, 2H), 6.99 – 6.89 (m, 2H), 6.66 (dd, *J* = 5.8, 1.9 Hz, 1H), 6.07 – 5.92 (m, 2H), 5.16 (s, 1H), 3.92 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.3, 162.2, 145.5, 145.1, 143.0, 142.2, 141.9, 136.4, 132.0, 129.1, 129.0, 128.5, 127.6, 124.2, 123.0, 121.4, 121.0, 115.5, 110.4, 69.0, 63.5. IR (thin film) ν_{max}/cm^{-1} 3390, 3060, 3020, 1710, 1594, 1498, 1309, 1161, 754. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{23}H_{17}BrNO$ 402.0494, found 402.0507.

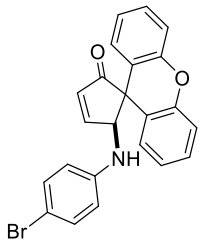
5-((3-(Trifluoromethyl)phenyl)amino)spiro[cyclopentane-1,9'-fluoren]-3-en-2-one (6j)



By following the general procedure, the reaction was performed with 9-(furan-2-yl)-9*H*-fluoren-9-ol **3a** (100 mg, 0.40 mmol, 1.0 equiv), 3-(trifluoromethyl)aniline (65 mg, 0.40 mmol, 1.0 equiv), (±)-BINOL.PA (3.5 mg, 2.5 mol%) for 5 min, the product **6j** (140 mg, 89%) was isolated as off-white powder after silica gel column chromatography (hexanes/EtOAC 7:3). R_f = 0.3 (30% EtOAc in hexanes). mp 122°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 5.8, 2.2 Hz, 1H), 7.67 (dd, *J* = 14.9, 7.6 Hz, 2H), 7.49 – 7.39 (m, 1H), 7.39 – 7.30 (m, 3H), 7.22 – 7.15 (m, 2H), 6.93 (t, *J* = 8.2 Hz, 1H), 6.76 (d, *J* = 7.7 Hz, 1H), 6.70 (dd, *J* = 5.8, 2.0 Hz, 1H), 6.25 (d, *J* = 6.8 Hz, 2H), 5.32 –

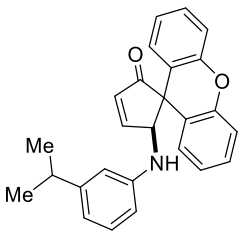
5.19 (m, 1H), 4.13 (d, *J* = 8.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.0, 161.6, 146.0, 145.2, 142.7, 141.8, 141.6, 136.3, 131.1 (q, *J* = 31.25), 129.2, 128.7 (d, *J* = 3.75), 128.2, 127.2, 124.1 (q, *J* = 271 Hz), 123.9, 122.6, 121.0, 116.8, 114.8 (d, *J* = 3.78 Hz), 110.5 (d, *J* = 3.78 Hz), 68.6, 63.2. ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.04. IR (thin film) ν_{max}/cm^{-1} 3389, 3062, 1712, 1609, 1489, 1447, 1344, 1165, 1125, 758. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{24}H_{17}F_3NO$ 392.1262, found 392.1277.

2-((4-Bromophenyl)amino)spiro[cyclopentane-1,9'-xanthen]-3-en-5-one (6k)



By following the general procedure, the reaction was performed with 9-(furan-2-yl)-9*H*-xanthen-9-ol **3b** (100 mg, 0.38 mmol, 1.0 equiv), 4-bromo aniline (65 mg, 0.38 mmol, 1.0 equiv), (±)-BINOL.PA (3.3 mg, 2.5 mol%) for 10 min, the product **6k** (147 mg, 93%) was isolated as pale-yellow powder after silica gel column chromatography (hexanes/EtOAc 7:3). R_f = 0.3 (30% EtOAc in hexanes). mp 209.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dd, J = 5.9, 2.4 Hz, 1H), 7.40 – 7.29 (m, 1H), 7.18 – 7.12 (m, 2H), 7.12 – 7.07 (m, 1H), 6.99 (dd, J = 8.0, 1.5 Hz, 1H), 6.91 (dd, J = 7.2, 1.2 Hz, 1H), 6.90 – 6.84 (m, 3H), 6.82 (dd, *J* = 5.8, 1.9 Hz, 2H), 6.45 (d, *J* = 8.9 Hz, 1H), 5.92 (d, *J* = 8.9 Hz, 2H), 4.67 (dt, J = 8.9, 2.2 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-*d6*) δ 207.7, 166.1, 150.6, 149.8, 145.8, 134.7, 130.8, 129.0, 128.8, 128.5, 126.4, 123.9, 122.1, 118.6, 116.1, 115.4, 113.9, 106.8, 70.6, 54.7. IR (thin film) ν_{max}/cm^{-1} 3392, 3060, 3025, 1710, 1594, 1496, 1312, 1159, 751. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{23}H_{17}BrNO_2$ 418.0443, found 418.0452.

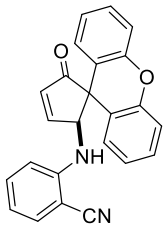
2-((2-Isopropylphenyl)amino)spiro[cyclopentane-1,9'-xanthen]-3-en-5-one (6l)



By following the general procedure, the reaction was performed with 9-(furan-2-yl)-9H-xanthen-9-ol **3b** (100 mg, 0.38 mmol, 1.0 equiv), 2-isopropylaniline (51 mg, 0.38 mmol, 1.0 equiv), (±)-

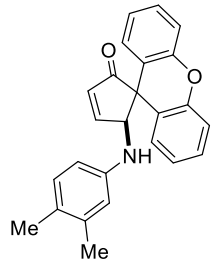
BINOL.PA (3.3 mg, 2.5 mol%) for 5 min, the product **6l (**140 mg, 97%) was isolated as yellow solid after silica gel column chromatography (hexanes/EtOAc 3:2). R_f= 0.3 (50% EtOAc in hexanes). mp 117.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 5.9, 2.1 Hz, 1H), 7.29-7.24 (m, 1H), 7.17-7.05 (m, 2H), 7.02 (d, *J* = 8.2 Hz, 1H), 6.99-6.92 (m, 2H), 6.84-6.76 (m, 3H), 6.74 (dd, *J* = 5.9,1.9 Hz, 1H), 6.48 (d, *J* = 7.6 Hz, 1H), 5.93 – 5.87 (m, 2H), 4.87 (d, *J* = 6.5 Hz, 1H), 3.61 (d, *J* = 8.4 Hz, 1H), 2.58-2.48 (m, 1H), 1.03 (dd, *J* = 6.9,3.0 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.2, 164.2, 152.0, 150.9, 149.8, 145.4, 136.4, 129.0, 128.8, 128.7, 126.9, 126.2, 124.0, 123.9, 122.7, 119.0, 117.0, 116.8, 116.8, 111.7, 111.5, 71.3, 55.8, 34.1, 23.8, 23.7 ppm. IR (thin film) ν_{max}/cm^{-1} 3721, 3621, 3401, 3214, 3121, 3014, 2922, 2885, 1709, 771, 648. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $C_{26}H_{24}NO_2$ 382.1801, found 382.1805.

2-((2-Oxospiro[cyclopentane-1,9'-xanthen]-3-en-5-yl)amino)benzonitrile (6m)



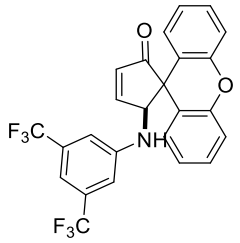
By following the general procedure, the reaction was performed with 9-(furan-2-yl)-9*H*-xanthen-9-ol **3b** (100 mg, 0.38 mmol, 1.0 equiv), 2-aminobenzonitrile (45 mg, 0.38 mmol, 1.0 equiv), (±)-BINOL.PA (3.3 mg, 2.5 mol%) for 10 min, the product **6m** (62 mg, 45% yield) was isolated as brown solid after silica gel column chromatography (hexanes/EtOAc 4:1). R_f = 0.3 (30% EtOAc in hexanes). mp 197.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 5.9, 2.4 Hz, 1H), 7.35 – 7.28 (m, 1H), 7.19 – 7.01 (m, 6H), 6.98 – 6.95 (m, 1H), 6.86 - 6.82 (m, 2H), 6.78 (dd, *J* = 8.2, 1.1 Hz, 1H), 6.60 (td, *J* = 7.7, 0.6 Hz, 1H), 6.15 (d, *J* = 8.5 Hz, 1H), 4.87 (dt, *J* = 10.2, 2.0 Hz, 1H), 4.51 (d, *J* = 10.2 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.3, 162.0, 151.6, 150.8, 147.9, 137.6, 133.7, 132.5, 129.4, 129.1, 127.3, 126.1, 124.1, 123.8, 123.6, 118.3, 118.0, 116.9, 116.8, 116.6, 112.0, 96.6, 70.0, 55.4 ppm. IR (thin film) ν_{max}/cm^{-1} 3363, 2217, 1718, 1592, 1516, 1478, 1451, 1313, 1258, 1162, 915, 887, 801, 749. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $C_{24}H_{17}N_2O_2$ 365.1284, found 365.1268.

2-((3,4-Dimethylphenyl)amino)spiro[cyclopentane-1,9'-xanthen]-3-en-5-one (6n)



By following the general procedure, the reaction was performed with 9-(furan-2-yl)-9*H*-xanthen-9-ol **3b** (100 mg, 0.38 mmol, 1.0 equiv), 3,4-dimethyl aniline (46 mg, 0.38 mmol, 1.0 equiv), (±)-BINOL.PA (3.3 mg, 2.5 mol%) for 5 min, the product **6n** (133 mg, 96%) was isolated as pale-yellow crystalline solid after silica gel column chromatography (hexanes/EtOAc 7:3). R_f = 0.3 (30% EtOAc in hexanes). mp 209.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 5.9, 2.3 Hz, 1H), 7.29-7.24 (m, 1H), 7.19-7.12 (m, 1H), 7.09 (td, *J* = 7.5, 1.3 Hz, 1H), 7.05-6.99 (m, 1H), 6.98-6.93 (m, 2H), 6.85-6.78 (m, 2H), 6.73 (dd, *J* = 5.9,2.1 Hz, 1H), 6.66 – 6.62 (m, 1H), 5.88 – 5.83 (m, 2H), 4.81 (dt, *J* = 11.1, 2.1 Hz, 1H), 3.45 (d, *J* = 11.1 Hz, 1H), 2.05 (s, 3H), 1.94 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.2, 164.3, 152.0, 151.1, 143.4, 137.0, 136.2, 129.9, 128.9, 128.6, 126.8, 126.6, 126.3, 124.0, 123.9, 122.7, 119.1, 116.9, 116.7, 115.3,111.2, 71.4, 55.9, 19.7, 18.7. IR (thin film) ν_{max}/cm^{-1} 3569, 3506, 3409, 3020, 2924, 1720, 1459, 770, 652. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $C_{25}H_{21}NO_2$ 368.1645, found 368.1642.

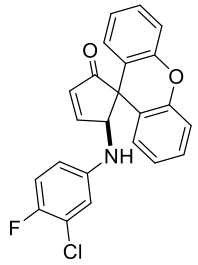
2-((3,5-Bis(trifluoromethyl)phenyl)amino)spiro[cyclopentane-1,9'-xanthen]-3-en-5-one (6o)



By following the general procedure, the reaction was performed with 9-(furan-2-yl)-9*H*-xanthen-9-ol **3b** (100 mg, 0.38 mmol, 1.0 equiv), 3,5 bis(trifluoromethyl)aniline (86 mg, 0.38 mmol), (±)-BINOL.PA (3.3 mg, 2.5 mol%) for 10 min, the product **6o (**153 mg, 85%) was isolated as brown solid after silica gel column chromatography (hexanes/EtOAc 3:2),). R_f = 0.3 (50% EtOAc in hexanes). mp 219.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 5.9, 2.4 Hz, 1H), 7.33 – 7.28 (m, 1H), 7.15 – 7.09 (m, 2H), 7.09 – 7.03 (m, 2H), 6.99 (td, *J* = 7.6, 1.3 Hz, 1H), 6.95 – 6.93 (m, 1H), 6.85 (dd, *J* = 5.9, 2.1 Hz, 1H), 6.74 (ddd, *J* = 11.3, 8.0, 1.4 Hz, 2H), 6.40 (s, 2H), 4.88 (dt, *J*

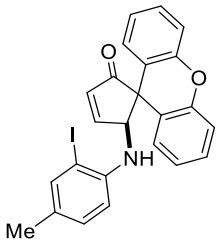
= 11.1, 2.3 Hz, 1H), 3.96 (d, *J* = 11.1 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.4, 161.9, 151.9, 150.4, 146.5, 137.6, 132.5, 132.05 (q, *J* = 33.0 Hz), 129.4, 129.2, 126.8, 125.8, 124.2, 123.5, 123.1 (q, *J* = 272.9 Hz), 123.0, 118.6, 117.2, 116.7, 113.2, 111.9, 71.0, 55.5. ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.45. IR (thin film) ν_{max}/cm^{-1} 3378, 1711, 1621, 1480, 1467, 1394, 1307, 1279, 1175, 1132, 872, 758. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $C_{25}H_{16}F_6NO_2$ 476.1087, found 476.1086.

2-((3-Chloro-4-fluorophenyl)amino)spiro[cyclopentane-1,9'-xanthen]-3-en-5-one (6p)



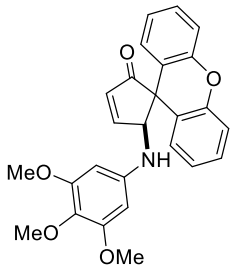
By following the general procedure, the reaction was performed with 9-(furan-2-yl)-9*H*-xanthen-9-ol **3b** (100 mg, 0.38 mmol), 3-chloro-4-fluoroaniline (55 mg, 0.38 mmol), (±)-BINOL.PA (3.3 mg, 2.5 mol%) for 5 min, the product **6p (**144 mg, 98%) was isolated as yellow solid after silica gel column chromatography (hexanes/EtOAc 3:2). R_f = 0.3 (50% EtOAc in hexanes). mp 210 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 5.8, 2.1 Hz, 1H), 7.33-7.23 (m, 1H), 7.19-7.14 (m, 1H), 7.12-7.03 (m, 2H), 6.99 (t, *J* = 7.1 Hz, 1H), 6.95-6.89 (m, 1H), 6.84 (d, *J* = 8.2 Hz, 1H), 6.81-6.73 (m, 2H), 6.65 (t, *J* = 8.8 Hz, 1H), 6.02 (dd, *J* = 5.9, 2.8 Hz, 1H), 5.91-5.85 (m, 1H), 4.74 (d, *J* = 11.4 Hz, 1H), 3.55 (d, *J* = 11.3 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.7, 163.1, 152.8, 152.1,150.8, 150.4,142.3, 137.0, 129.2, 129.0, 126.7, 126.1, 124.1, 123.8, 122.9, 120.9, 120.7, 118.9, 116.9, 116.6, 116.4, 115.1, 113.0 (d, *J* = 6.4 Hz), 71.6, 55.7. ^{19}F NMR (377 MHz, $CDCl_3$) *δ* -129.08. IR (thin film) ν_{max}/cm^{-1} 3843, 3794, 3720, 3651, 3408, 2925, 1710, 1510, 1258, 1224, 770, 654. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $C_{23}H_{16}NO_2FCl$ 392.0848; found 392.0857.

2-((2-Iodo-4-methylphenyl)amino)spiro[cyclopentane-1,9'-xanthen]-3-en-5-one (6q)



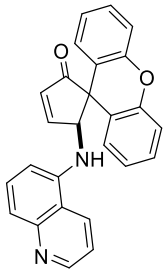
By following the general procedure, the reaction was performed with 9-(furan-2-yl)-9*H*-xanthen-9-ol **3b** (100 mg, 0.38 mmol), 2-iodo-4-methylaniline (88 mg, 0.38 mmol), (±)-BINOL.PA (3.3 mg, 2.5 mol%) for 10 min, the product **6q** (62 mg, 34%) was isolated as white solid after silica gel column chromatography (hexanes/EtOAc 3:2). R_f = 0.7 (30% EtOAc in hexanes). mp 292 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 5.9, 2.2 Hz, 1H), 7.31 – 7.27 (m, 2H), 7.20 – 7.16 (m, 1H), 7.12 – 7.06 (m, 2H), 7.02 (td, *J* = 7.6, 1.3 Hz, 1H), 6.98-6.26 (m, 1H), 6.90 (ddd, *J* = 13.0, 8.0, 1.3 Hz, 2H), 6.80 (dd, *J* = 5.9, 2.0 Hz, 1H), 6.75 (dd, *J* = 8.3, 1.8 Hz, 1H), 6.02 (d, *J* = 8.3 Hz, 1H), 4.79 (dt, *J* = 10.1, 1.8 Hz, 1H), 4.11 (d, *J* = 10.1 Hz, 1H), 2.11 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.8, 163.3, 151.9, 151.1, 142.4, 139.3, 136.5, 129.6, 129.3, 128.9, 127.2, 126.4, 124.0, 117.0, 116.8, 111.2, 85.3, 70.6, 55.6, 19.8 ppm. IR (thin film) ν_{max}/cm^{-1} 3464, 3248, 2548, 2099, 1728, 1591, 1220, 771. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $C_{24}H_{19}NO_2I$ 480.0455, found 480.0470.

5-((3, 4, 5-Trimethoxyphenyl)amino)spiro[cyclopentane-1,9'-xanthen]-3-en-2-one (6r)



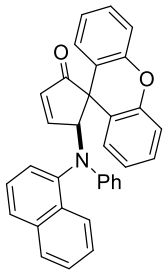
By following the general procedure, the reaction was performed with 9-(furan-2-yl)-9*H*-xanthen-9-ol **3b** (100 mg, 0.38 mmol), 3,4,5-trimethoxyaniline (69 mg, 0.38 mmol), (±)-BINOL.PA (3.3 mg, 2.5 mol%) for 5 min, the product **6r (**153 mg, 95%) was isolated as pale-yellow solid after silica gel column chromatography (hexanes/EtOAc 3:2). R_f = 0.3 (50% EtOAc in hexanes). mp 195 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 5.9, 2.3 Hz, 1H), 7.24 (dd, *J* = 11.2, 4.2 Hz, 1H),7.16 – 7.12 (m, 1H), 7.10 – 7.06 (m, 1H), 7.02 (d, *J* = 8.2 Hz, 1H), 6.99 – 6.93 (m, 2H), 6.85 – 6.81 (m, 1H), 6.79 (dd, *J* = 7.7, 1.3 Hz, 1H), 6.75 (dd, *J* = 5.9, 2.1 Hz, 1H), 5.25 (s, 2H), 4.83 (d, *J* = 9.4 Hz, 1H), 3.68 (s, 3H), 3.64-3.59 (m,1H), 3.45 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.9, 163.9, 153.4, 152.0, 150.8, 142.0, 136.6, 130.9, 129.0, 128.7, 126.9, 126.2, 124.2, 123.9, 122.7, 118.9, 116.8,116.8, 91.5, 72.2, 61.1, 55.8, 55.0. IR (thin film) ν_{max}/cm^{-1} 3845, 3652,3514, 3428, 2929, 1714, 1611, 1515, 1452, 1310, 1255, 1131, 765, 658, 633. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $C_{26}H_{24}NO_5$ 430.1649, found 430.1659.

5-(Quinolin-4-ylamino)spiro[cyclopentane-1,9'-xanthen]-3-en-2-one (6s)



By following the general procedure, the reaction was performed with 9-(furan-2-yl)-9*H*-xanthen-9-ol **3b** (100 mg, 0.38 mmol), 4-amino quinoline (54 mg, 0.38 mmol), (±)-BINOL.PA (3.3 mg, 2.5 mol%) for 15 min, the product **6s** (139 mg, 94% yield) was isolated as brown sticky solid after silica gel column chromatography (hexanes/EtOAc 3:2). R_f = 0.3 (50% EtOAc in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (d, *J* = 2.8 Hz, 1H),8.07 (dd, *J* = 5.8, 2.0 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.30 (t, *J*= 7.2 Hz, 1H), 7.27-7.21 (m, 1H), 7.14 -7.05 (m, 3H), 7.04-7.00 (m, 1H), 6.99-6.96 (m, 1H), 6.91-6.87 (m, 1H), 6.84 (dd, *J* = 5.7, 1.6 Hz, 1H), 6.75 – 6.71 (m, 2H), 6.53-6.49 (m, 1H), 6.34 (d, *J* = 10.4 Hz, 1H), 6.20 (d, *J* = 7.5 Hz, 1H), 5.04 (d, *J* = 10.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.4, 164.0, 151.5, 150.9, 146.7, 142.2, 137.8, 136.7, 135.7, 128.8, 128.3, 128.1, 127.6, 126.1, 126.2, 124.4, 123.8, 122.9, 121.2, 118.8, 116.7, 115.7, 107.2, 70.95, 55.7. IR (thin film) ν_{max}/cm^{-1} 3485, 2925, 1716, 1588, 1456, 1220, 771, 683, 643. HRMS (ESI): m/z $[M+H]^+$ calculated for $C_{26}H_{19}N_2O_2$ 391.1441, found 391.1437.

2-(Naphthalen-1-yl(phenyl)amino)spiro[cyclopentane-1,9'-xanthen]-3-en-5-one (6t)



By following the general procedure, the reaction was performed with 9-(furan-2-yl)-9*H*-xanthen-9-ol **3b** (100 mg, 0.38 mmol), *N*-phenylnaphthalen-1-amine (83 mg, 0.38 mmol), (±)-BINOL.PA (3.3 mg, 2.5 mol%) for 15 min, the product **6t (**81 mg, 55%) was isolated as brown semisolid after silica gel column chromatography (hexanes/EtOAc 3:2). R_f = 0.3 (50% EtOAc in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 – 8.26 (m, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.42 – 7.30 (m, 3H), 7.24-7.17 (m, 6H), 7.11 (d, *J* = 8.3 Hz, 2H), 6.94-6.92 (m 2H), 6.88 (t, *J* = 7.3 Hz, 2H), 6.74 (d, *J*

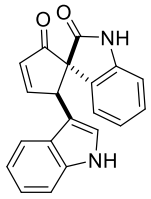
= 8.1 Hz, 2H), 6.56 – 6.44 (m, 2H), 5.76 (s, 1H), 5.10 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.4, 164.0, 151.5, 150.9, 146.7, 142.2, 137.8, 136.7, 135.7, 128.8, 128.3, 128.1, 127.6, 126.1, 126.2, 124.4, 123.8, 122.9, 121.2, 118.8, 116.7, 115.7, 107.2, 70.95, 55.7. IR (thin film) ν_{max}/cm^{-1} 3767, 3651, 3518, 3409, 2918, 2357, 1601, 1449, 1305, 1259, 955, 765, 658. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $C_{33}H_{24}NO_2$ 466.1801, found 466.1807.

2.6. General Procedure for Indolyl Spirocyclopentenones 8

To a solution of furfuyl alcohol **1a,b/3a,c** (100 mg, 1.0 equiv) and substituted indole(1.0 equiv) in HFIP (2-4 mL) under nitrogen atmosphere, was added (*R*)-BINOL.PA (2.5 mol%). Then the reaction mixture was stirred at room temperature for 10-15 min (the reaction was monitored by TLC). Upon completion, the reaction was quenched with water (10 mL) and extracted with ethyl acetate (2 x 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography using hexanes/EtOAc to obtain spirocyclopentenone derivatives **8a-e**.

2.7. Experimental and Characterization of Indolyl Spirocyclopentenones 8a-e

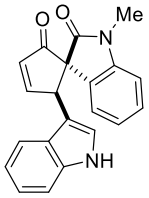
2-(1*H*-Indol-3-yl)spiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione (8a)



By following the general procedure, the reaction was performed with 3-(furan-2-yl)-3-hydroxyindolin-2-one **1b** (100 mg, 0.46 mmol, 1.0 equiv), indole (54 mg, 0.46 mmol, 1.0 equiv), (*R*)-BINOL.PA (4 mg, 2.5 mol%) for 15 min at 90 °C, the product **8a** (90 mg, 62%) was isolated as light brown colour powder after silica gel column chromatography (hexanes/EtOAc 7:3). R_f = 0.3 (40% EtOAc in hexanes). mp 231 °C. ^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.99 (s, 1H), 10.11 (s, 1H), 8.37 (d, *J* = 4.1 Hz, 1H), 7.44 (d, *J* = 7.3 Hz, 1H), 7.27 (t, *J* = 7.1 Hz, 2H), 7.16 – 7.03 (m, 2H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.72 (d, *J* = 7.6 Hz, 1H), 6.65 (t, *J* = 7.4 Hz, 1H), 6.58 – 6.46 (m, 2H), 4.99 (s, 1H). ^{13}C NMR (100 MHz, DMSO-*d6*) δ 203.8, 172.5, 168.6, 143.4, 135.8, 132.2, 129.8, 128.8, 126.6, 124.3, 123.6, 121.8, 120.9, 118.3, 117.7, 111.3, 110.1, 109.3, 67.6, 48.9. IR

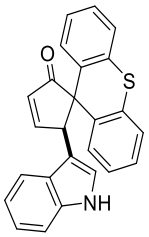
(thin film) ν_{max}/cm^{-1} 3758, 3530, 3398, 3249, 3200, 2761, 1710, 1694, 1550, 1209, 740, 656. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $C_{20}H_{15}N_2O_2$ 315.1134, found 315.1142.

2-(1*H*-Indol-3-yl)-1'-methylspiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione (8b)



By following the general procedure, the reaction was performed with 3-(furan-2-yl)-3-hydroxy-1-methylindolin-2-one **1a** (100 mg, 0.44 mmol, 1.0 equiv), indole (51 mg, 0.44mmol, 1.0 equiv), (*R*)-BINOL.PA (3.8 mg, 2.5 mol%) for 15 min at 90 °C, the product **8b** (86 mg, 60%) was isolated as brown colour powder after silica gel column chromatography (hexanes/EtOAc 7:3). R_f = 0.3 (40% EtOAc in hexanes). mp 162 °C. ^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.70 (s, 1H), 8.46 (dd, *J* = 5.5, 2.3 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 1H), 7.23 (s, 1H), 7.09 (d, *J* = 7.9 Hz, 1H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.88 (dt, *J* = 21.6, 7.5 Hz, 2H), 6.68 (d, *J* = 7.7 Hz, 1H), 6.60 (dd, *J* = 5.5, 2.3 Hz, 1H), 6.49 (t, *J* = 7.5 Hz, 1H), 6.40 (d, *J* = 7.2 Hz, 1H), 4.89 (s, 1H), 3.70 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 203.8, 176.2, 169.6, 143.6, 137.0, 132.3, 128.7, 128.4, 128.1, 127.6, 124.5, 121.7, 121.4, 119.3, 118.3, 110.4, 110.2, 109.9, 67.1, 47.4, 32.9. IR (thin film) ν_{max}/cm^{-1} 3781, 3529, 3417, 3246, 3204, 2899, 2330, 1722, 1689, 1556, 1473, 1209, 744, 659. HRMS (ESI): *m*/*z* $[M]^+$ calculated for $C_{21}H_{17}N_2O_2$ 329.1290, found 329.1299.

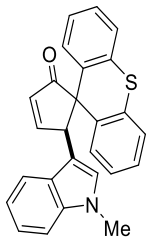
2-(1*H*-Indol-3-yl)spiro[cyclopentane-1,9'-thioxanthen]-3-en-5-one (8c)



By following the general procedure, the reaction was performed with 9-(furan-2-yl)-9*H*-thioxanthen-9-ol **3c** (100 mg, 0.35 mmol, 1.0 equiv), indole (42 mg, 0.35 mmol, 1.0 equiv), (*R*)-BINOL.PA (3.1 mg, 2.5 mol%) for 10 min at room temperature, the product **8c** (119 mg, 88%) was isolated as shiny gray colour powder after silica gel column chromatography (hexanes/EtOAc 7:3). R_f = 0.3 (30% EtOAc in hexanes). mp 198 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (s, 1H),

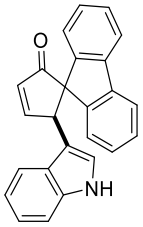
7.75 (dd, *J*= 5.7, 2.9 Hz, 1H), 7.48 (d, *J* = 8.1 Hz, 1H), 7.46 – 7.43 (m, 1H), 7.25 – 7.18 (m, 3H), 7.17 – 7.12 (m, 2H), 7.10 – 7.04 (m, 1H), 7.02 – 6.93 (m, 2H), 6.88 (td, *J* = 7.6, 1.4 Hz, 1H), 6.81 (td, *J* = 7.5, 1.3 Hz, 1H), 6.77 (dd, *J* = 5.7, 2.0 Hz, 1H), 6.60 (d, *J* = 2.5 Hz, 1H), 4.69 (d, *J* = 4.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.0, 166.2, 139.8, 135.8, 135.1, 133.9, 133.4, 133.2, 129.3, 127.0, 126.9, 126.8, 126.6, 126.4, 126.2, 125.5, 124.3, 121.9, 119.8, 119.2, 112.1, 110.9, 63.3, 54.9.IR (thin film) ν_{max}/cm^{-1} 3399, 3057, 2927, 1701, 1680, 1467, 1345, 1219, 1094, 753. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $C_{25}H_{18}NOS$ 380.1109, found 380.1117.

2-(1-Methyl-1*H*-indol-3-yl)spiro[cyclopentane-1,9'-thioxanthen]-3-en-5-one (8d)



By following the general procedure, the reaction was performed with 9-(furan-2-yl)-9*H*-thioxanthen-9-ol **3c** (100 mg, 0.35 mmol, 1.0 equiv), 1-methyl-1*H*-indole (47 mg, 0.35 mmol, 1.0 equiv), (*R*)-BINOL.PA (3.1 mg, 2.5 mol%) for 10 min at room temperature, the product **8d** (119 mg, 85%) was isolated as shiny gray colour powder after silica gel column chromatography (hexanes/EtOAc 7:3). R_f = 0.4 (30% EtOAc in hexanes). mp 210 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 5.7, 2.9 Hz, 1H), 7.50 – 7.42 (m, 2H), 7.25 – 7.18 (m, 3H), 7.15 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.10 – 7.04 (m, 2H), 7.00 – 6.86 (m, 3H), 6.81 (td, *J* = 7.5, 1.4 Hz, 1H), 6.74 (dd, *J* = 5.7, 2.0 Hz, 1H), 6.39 (s, 1H), 4.73 – 4.60 (m, 1H), 3.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.0, 166.2, 139.8, 136.6, 135.2, 133.9, 133.1, 129.3, 129.0, 127.3, 127.0, 126.9, 126.7, 126.6, 126.4, 126.2, 125.4, 121.4, 119.8, 118.7, 110.3, 108.0, 63.3, 54.8, 32.6. IR (thin film) ν_{max}/cm^{-1} 3690, 3021, 2408, 2342, 1708, 1533,1477, 1216, 749, 617. HRMS (ESI): *m*/*z* $[M]^+$ calculated for $C_{26}H_{19}NOS$ 393.1187, found 393.1200.

2-(1*H*-Indol-3-yl)spiro[cyclopentane-1,9'-fluoren]-3-en-5-one (8e)



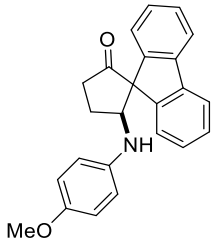
By following the general procedure, the reaction was performed with 9-(furan-2-yl)-9*H*-fluoren-9-ol **3a** (100 mg, 0.40 mmol, 1.0 equiv), indole (47 mg, 0.40 mmol, 1.0 equiv), (*R*)-BINOL.PA (3.5 mg, 2.5 mol%) for 10 min, the product **8e** (120 mg, 86%) was isolated as shiny gray colour powder after silica gel column chromatography (hexanes/EtOAc 7:3). R_f = 0.4 (30% EtOAc in hexanes). mp 94 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (dd, *J* = 5.7, 2.5 Hz, 1H), 8.02 (s, 1H), 7.73 (d, *J* = 7.3 Hz, 1H), 7.56 – 7.36 (m, 4H), 7.12 (d, *J* = 8.2 Hz, 1H), 7.04 (td, *J* = 7.5, 1.0 Hz, 1H), 6.99 – 6.93 (m, 1H), 6.80 (d, *J* = 1.9 Hz, 1H), 6.77 – 6.67 (m, 3H), 6.56 (dd, *J* = 12.7, 7.9 Hz, 2H), 5.03 (dd, *J* = 2.2, 1.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.1, 165.8, 146.8, 143.6, 142.0, 141.9, 136.0, 134.6, 128.3, 127.8, 127.6, 127.1, 126.4, 125.0, 122.4, 122.1, 121.7, 120.5, 119.9, 119.5, 119.0, 114.3, 110.9, 68.4, 50.2. IR (thin film) ν_{max}/cm^{-1} 3812, 3426, 3379, 3047, 3016, 1702, 1449, 1160, 745, 662. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $C_{25}H_{18}NO$ 348.1388, found 348.1398.

2.8. Gram Scale Synthesis of Hydroxy Spirocyclopentenone Oxindole 2b

To a solution of furfuyl alcohol **1b** (1 g, 4.6 mmol, 1.0 equiv) in HFIP/H_2O (3:1, 9 mL), was added (*R*)-BINOL.PA catalyst (40 mg, 0.12 mmol, 2.5 mol%). Then the reaction mixture was stirred at 90 °C temperature for 1.5 h (the reaction was monitored by TLC). Upon completion, the reaction was quenched with water (5 mL) and extracted with ethyl acetate (2 x 15 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography using hexanes/EtOAc (hexanes/EtOAc 6: 4) to obtain spirocyclopentenoneoxindole **2b** (0.665 g, 62%) as a pale yellow solid.

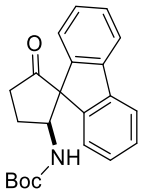
2.9. Product Derivatization

2-((4-Methoxyphenyl)amino)spiro[cyclopentane-1,9'-fluoren]-5-one (9)[2]



To a flask charged with a solution of compound **6g** (200 mg, 0.56 mmol) in EtOAc (6 mL) was added Pd/C (50 mg, 10 wt%) in one portion. The flask was evacuated and refilled with H_2 with a balloon. The reaction mixture was stirred under H_2 atmosphere for 3 h before it was filtered through a pad of celite, which was washed with EtOAc (10 mL x 3). The filtrate was concentrated, and the crude mixture was purified by silica gel column chromatography (hexanes/EtOAc 7:3) to give product **9** (179 mg, 89%) as white solid. mp 144 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.67 – 7.60 (m, 1H), 7.43 (ddd, *J* = 7.6, 6.1, 2.4 Hz, 2H), 7.37 – 7.30 (m, 4H), 6.55 – 6.48 (m, 2H), 6.21 (d, *J* = 9.0 Hz, 2H), 4.70 (dd, *J* = 10.8, 6.7 Hz, 1H), 3.64 (s, 3H), 3.13 (s, 1H), 3.01 – 2.85 (m, 2H), 2.80 – 2.63 (m, 1H), 2.37 – 2.19 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.21, 152.52, 146.24, 142.81, 142.02, 141.41, 140.51, 128.76, 128.34, 128.12, 127.45, 124.30, 123.06, 121.21, 120.36, 115.82, 114.54, 69.89, 62.48, 55.82, 38.18, 28.78. IR (thin film) ν_{max}/cm^{-1} 3733, 3662, 3527, 3116, 2013, 1872, 1748, 1514, 1238, 758, 667. HRMS (ESI): *m*/*z* $[M+H]^+$ calculated for $C_{24}H_{22}NO_2$ 356.1651, found 356.1668.

tert-Butyl-(2-oxospiro[cyclopentane-1,9'-fluoren]-5-yl)carbamate (10)

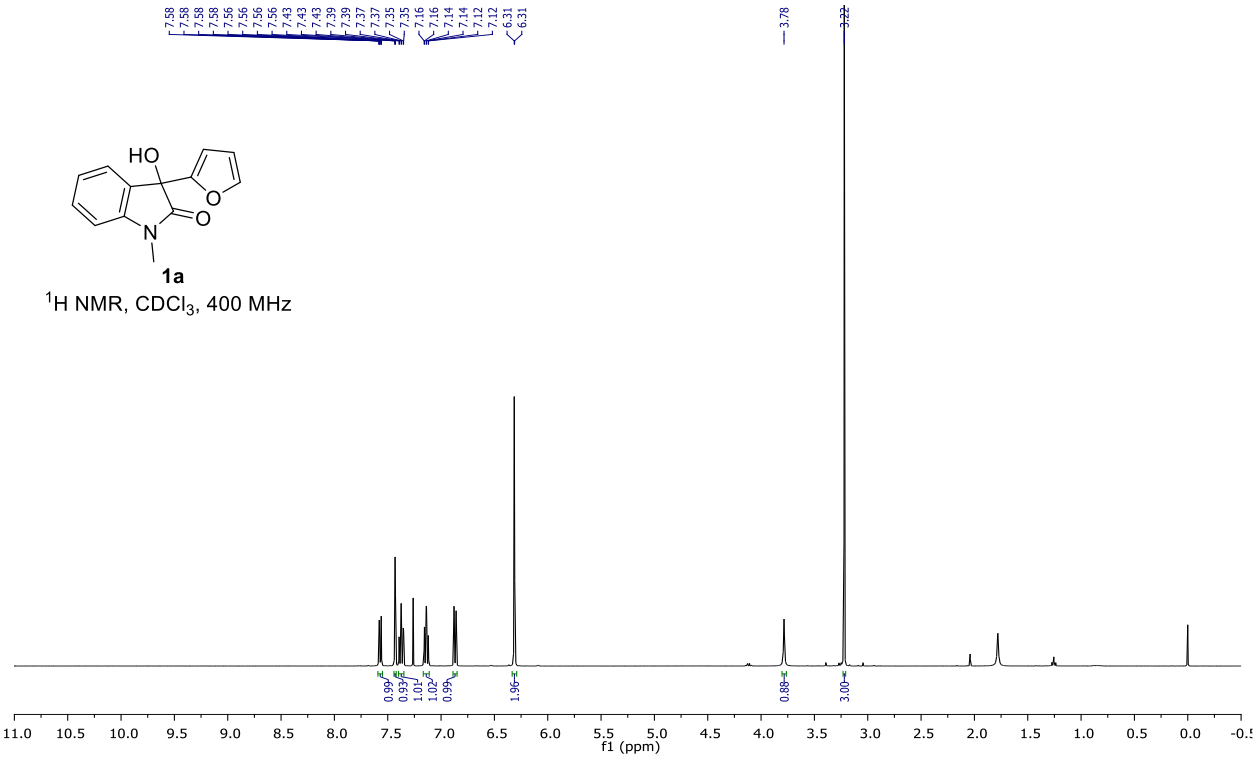


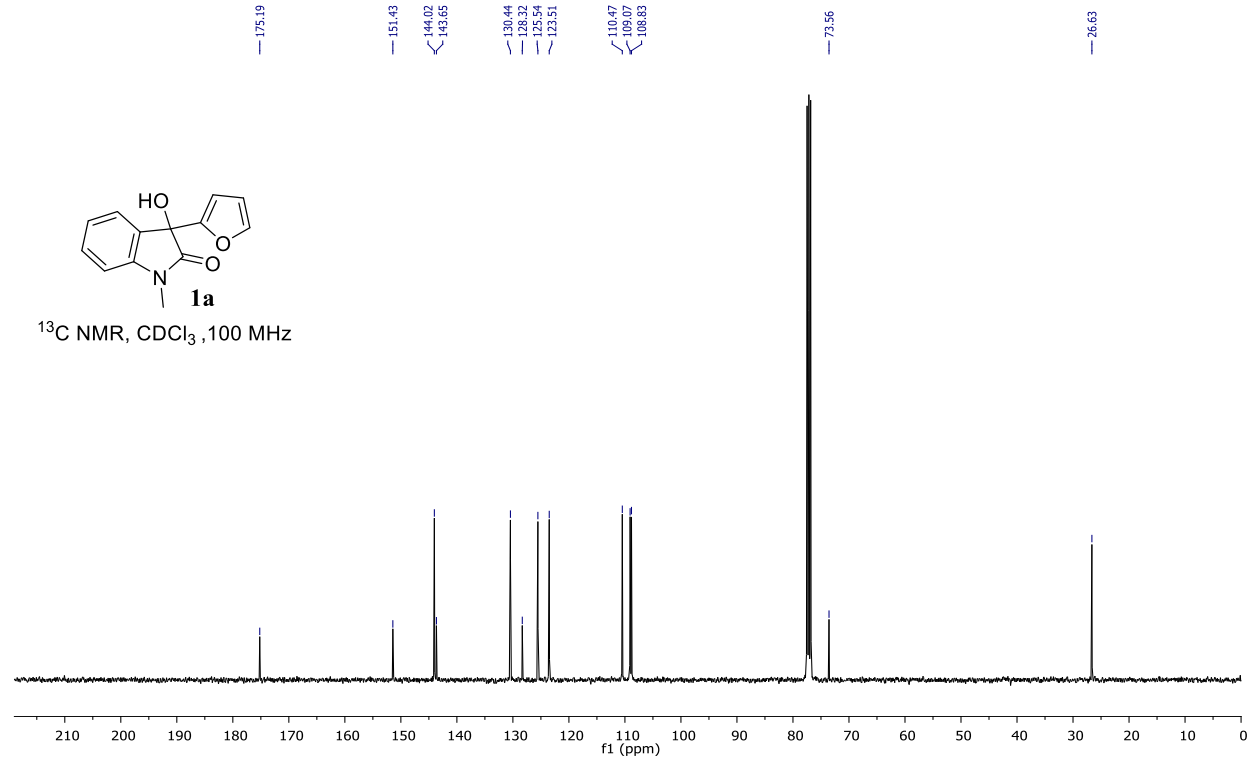
To a solution of compound **9** (100 mg, 0.282 mmol, 1.0 equiv) in CH_3CN (6 mL) at 0 °C, was added an aqueous 1 M solution of H_2SO_4 (3 mL). Next, a solution of aqueous ceric ammonium nitrate (2 mL, 0.912 mmol, 0.25 g/mL concentration) was added dropwise. The mixture was stirred at 0 °C for 2 h. The mixture was extracted with DCM (20 mL×3). The combined organic layers were washed with a saturated aqueous Na_2SO_3 solution (5 mL) and a saturated aqueous K_2CO_3

solution (5 mL) and dried over anhydrous Na_2SO_4 and concentrated. The crude residue was dissolved in DCM (2 mL), was added DIPEA (1.1equiv) and Boc anhydride (1.1 equiv) at room temperature and maintained for 8 h. The mixture was extracted with DCM (3 x 10 mL) and dried over anhydrous Na_2SO_4 and concentrated. The filtrate was concentrated, and the crude mixture was purified by silica gel column chromatography (hexanes/EtOAc 8:2) to give product **10** (71 mg, 73%) as white solid. mp 153 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.5 Hz, 1H), 7.76 – 7.69 (m, 1H), 7.41 (ddd, *J* = 21.6, 14.2, 6.6 Hz, 4H), 7.34 – 7.26 (m, 2H), 4.95 (s, 1H), 4.15 (d, *J* = 26.2 Hz, 1H), 2.91 (dd, *J* = 18.8, 9.3 Hz, 2H), 2.79 – 2.62 (m, 1H), 2.40 – 2.16 (m, 1H), 1.24 (d, *J* = 7.6 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.0, 155.1, 144.9, 142.6, 141.8, 140.8, 128.9, 128.4, 128.3, 127.5, 124.0, 123.7, 121.2, 120.1, 79.8, 77.2, 68.5, 57.1, 37.8, 28.14. IR (thin film) ν_{max}/cm^{-1} 3619, 3569, 3238, 2990, 1746, 1721, 1503, 1490, 1375, 1248, 1165, 1132, 75. HRMS (EI): *m*/*z* $[M]^+$ calculated for $C_{22}H_{23}N_1O_3$ 349.1678, found 349.1692.

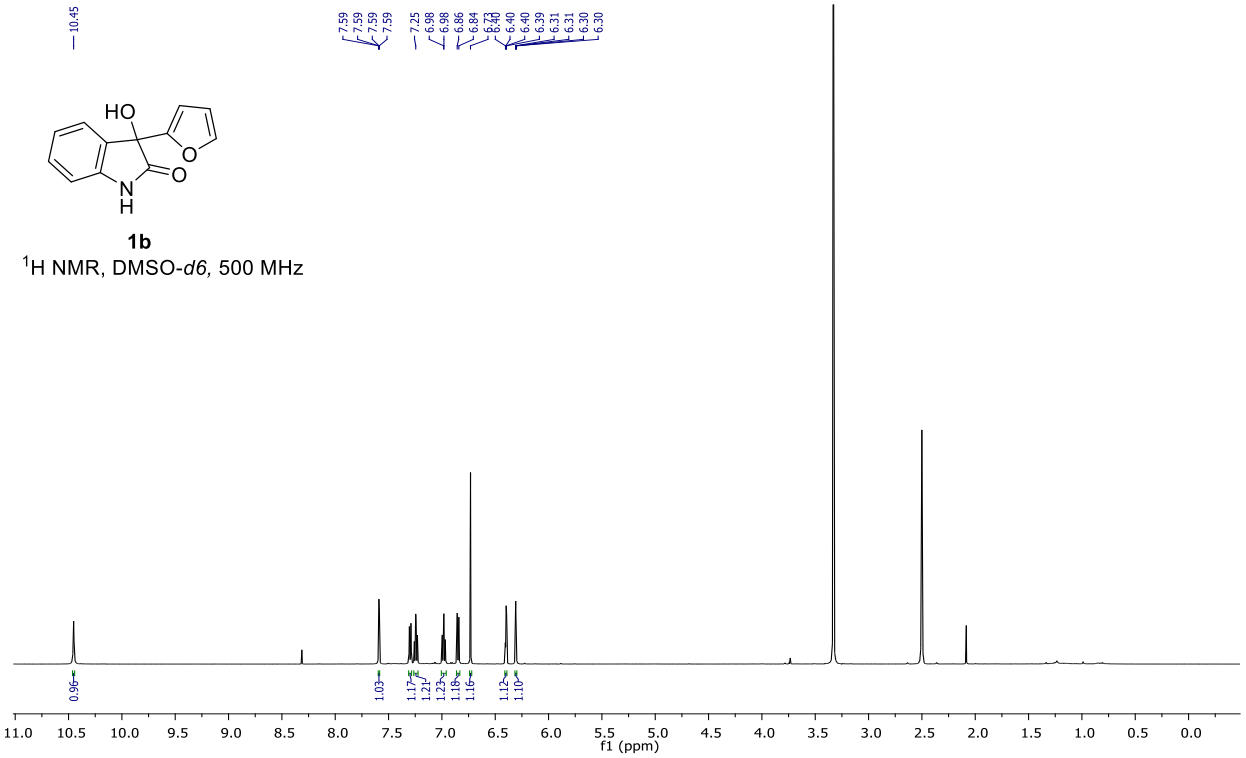
3. ^{1}H, ^{13}C and ^{19}F NMR Spectra of Compounds

3-(Furan-2-yl)-3-hydroxy-1-methylindolin-2-one (1a)



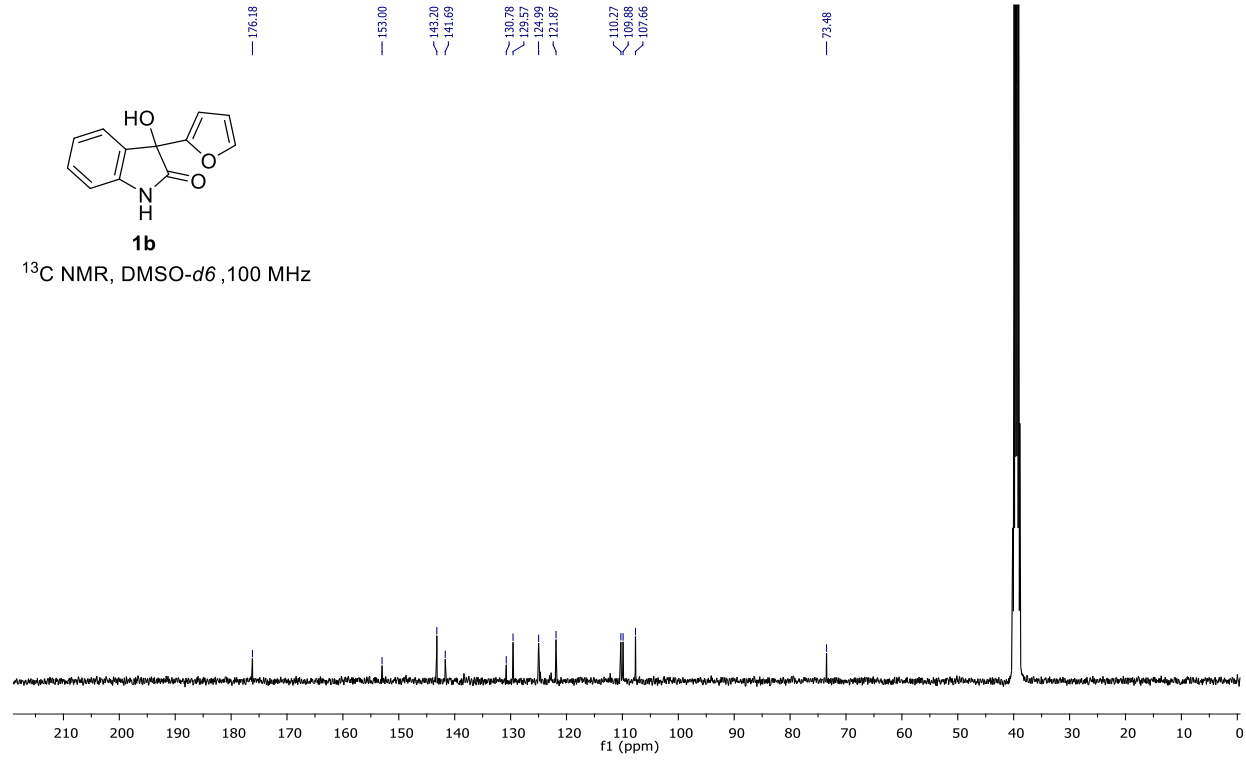


3-(Furan-2-yl)-3-hydroxy-1-methylindolin-2-one (1b)



1b

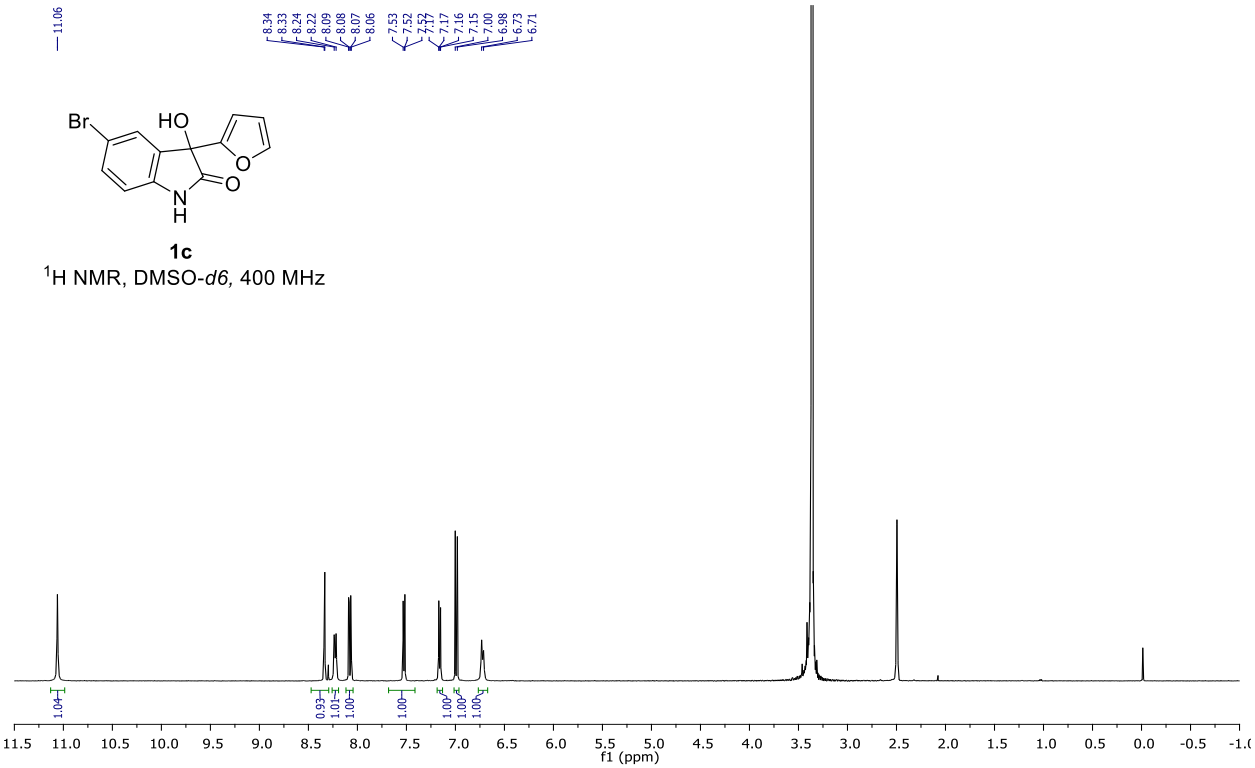
^{1}H NMR, DMSO-*d6,* 500 MHz



1b

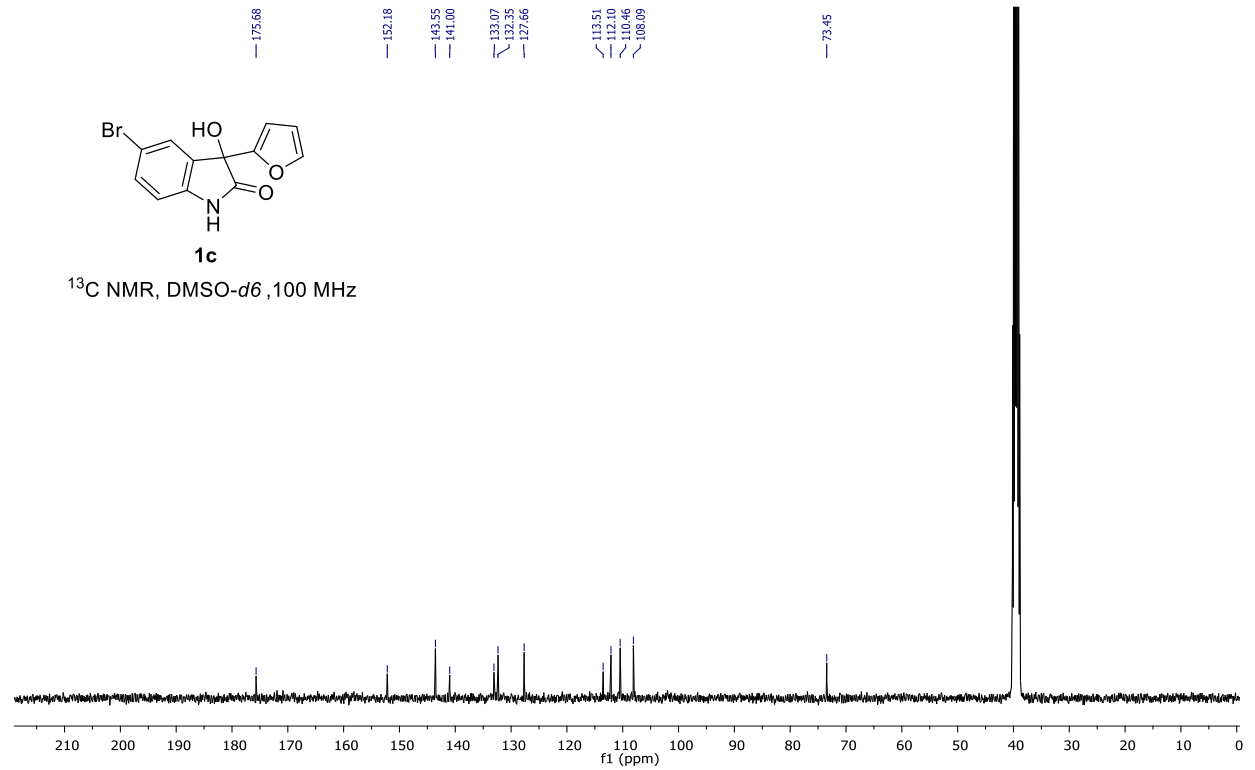
^{13}C NMR, DMSO-*d6* ,100 MHz

5-Bromo-3-(furan-2-yl)-3-hydroxyindolin-2-one (1c)



1c

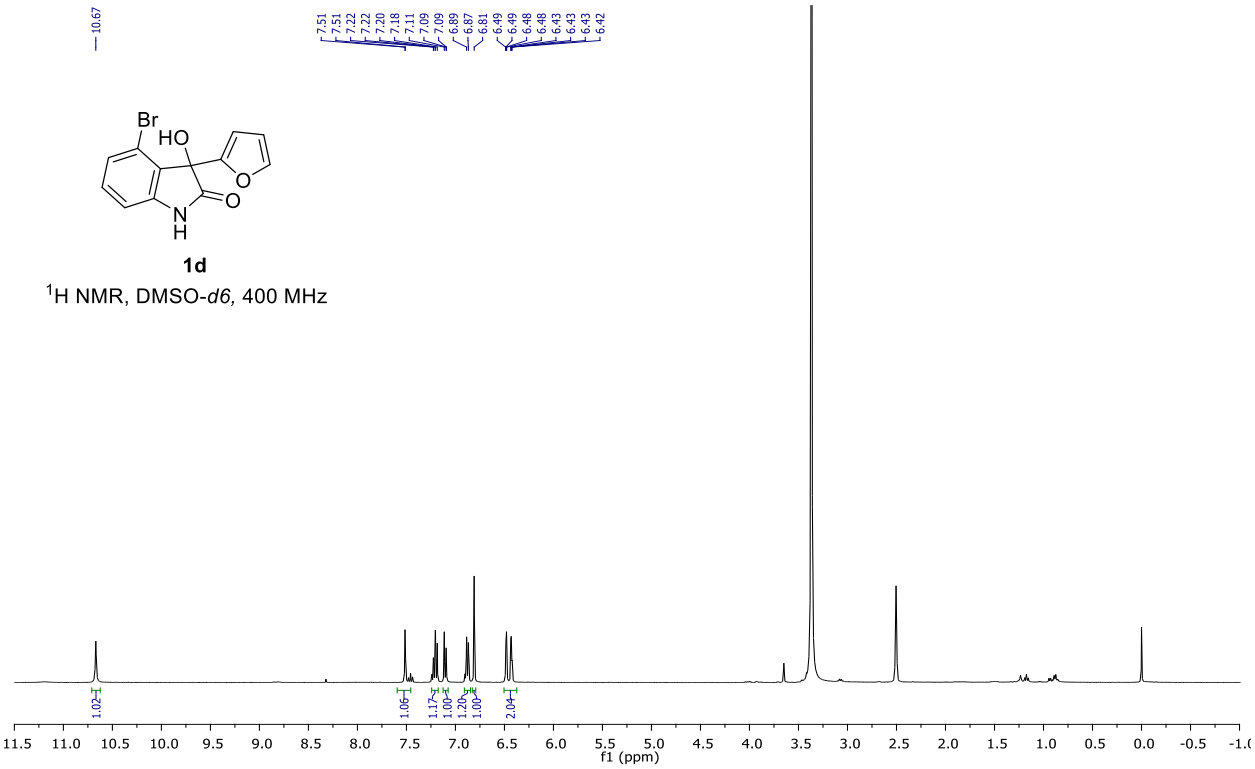
^{1}H NMR, DMSO-*d6,* 400 MHz



1c

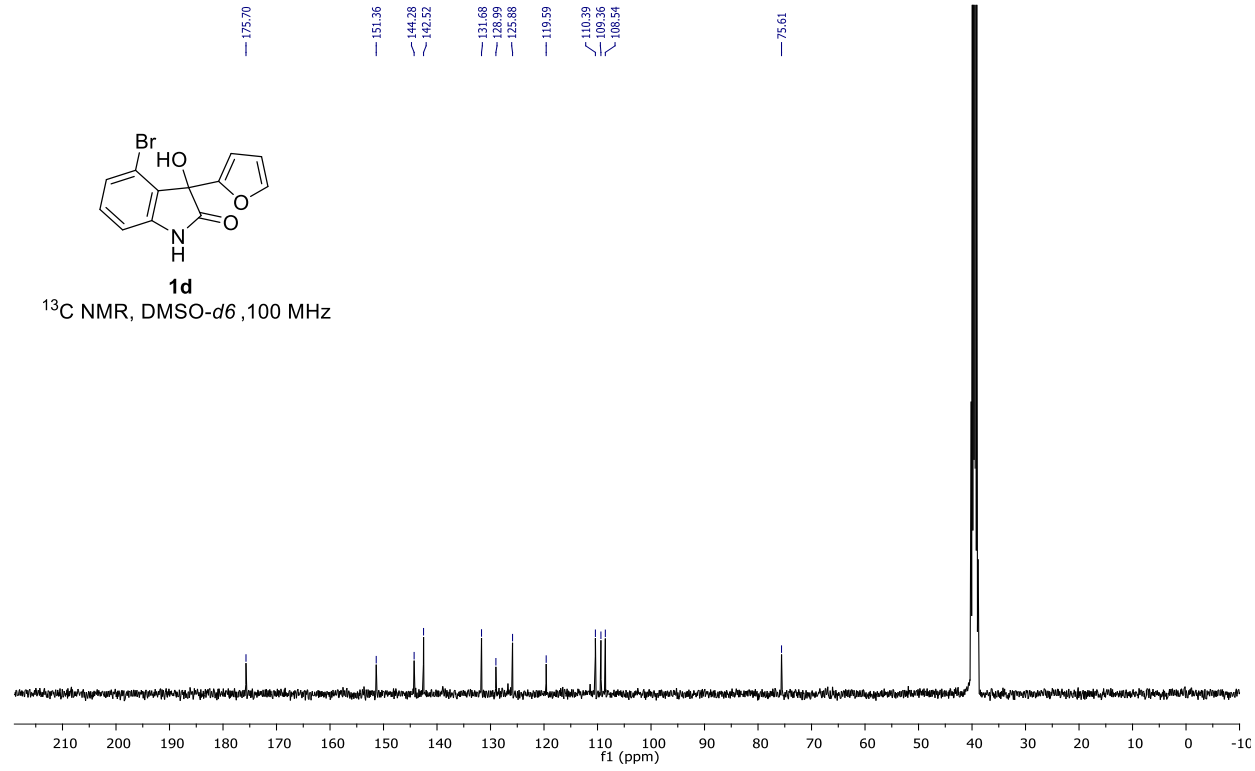
^{13}C NMR, DMSO-*d6* ,100 MHz

4-Bromo-3-(furan-2-yl)-3-hydroxyindolin-2-one (1d)



1d

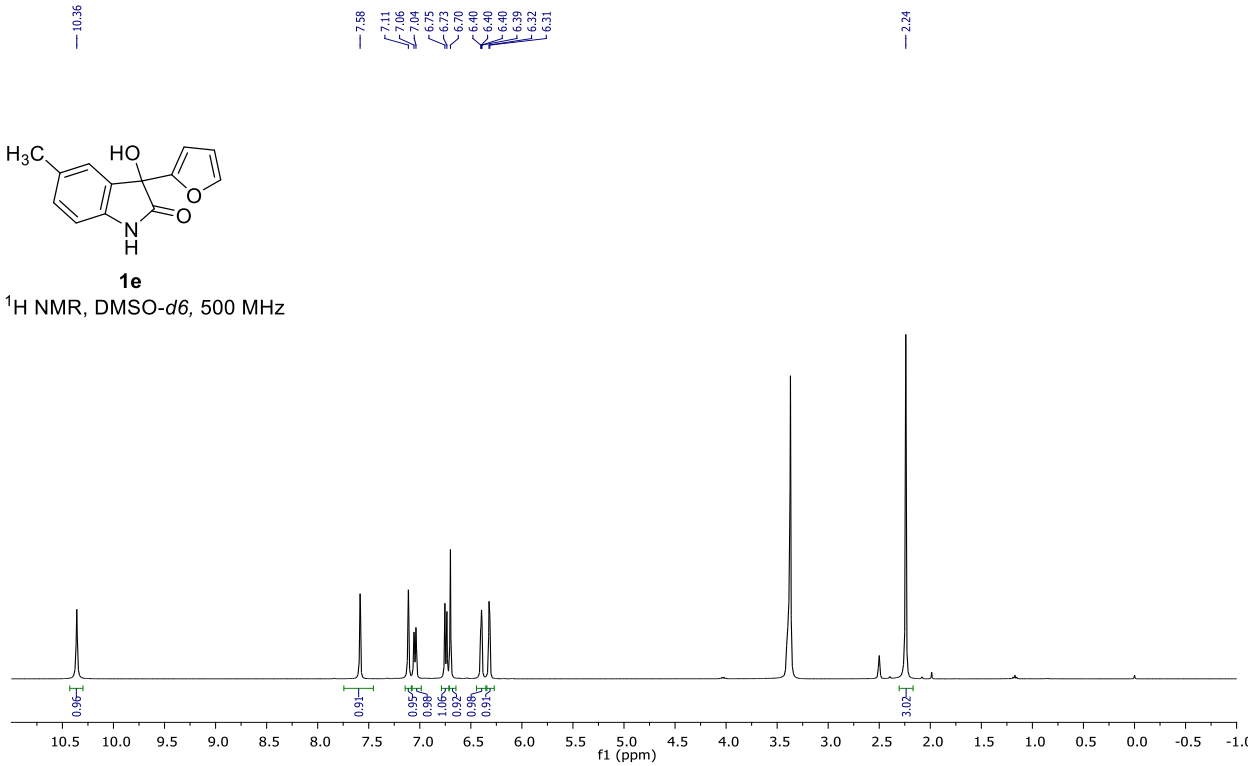
^{1}H NMR, DMSO-*d6,* 400 MHz



1d

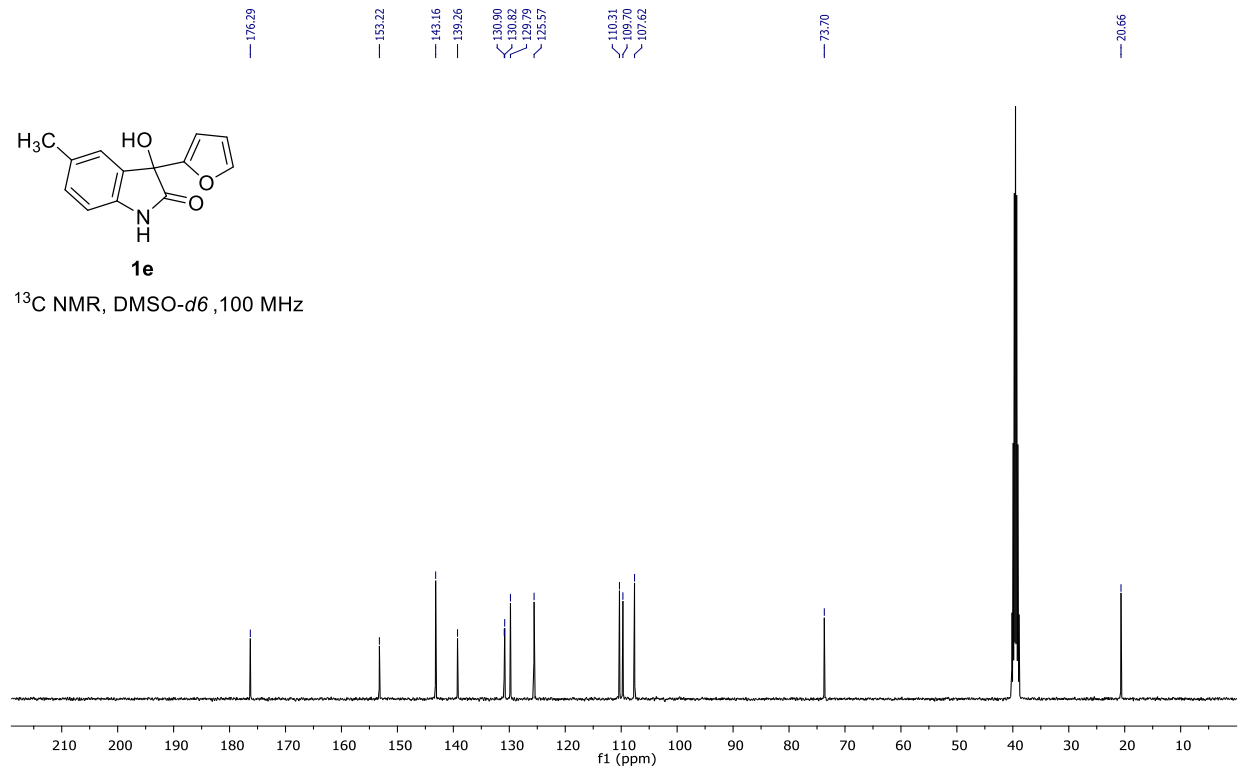
^{13}C NMR, DMSO-*d6* ,100 MHz

3-(Furan-2-yl)-3-hydroxy-5-methylindolin-2-one (1e)



1e

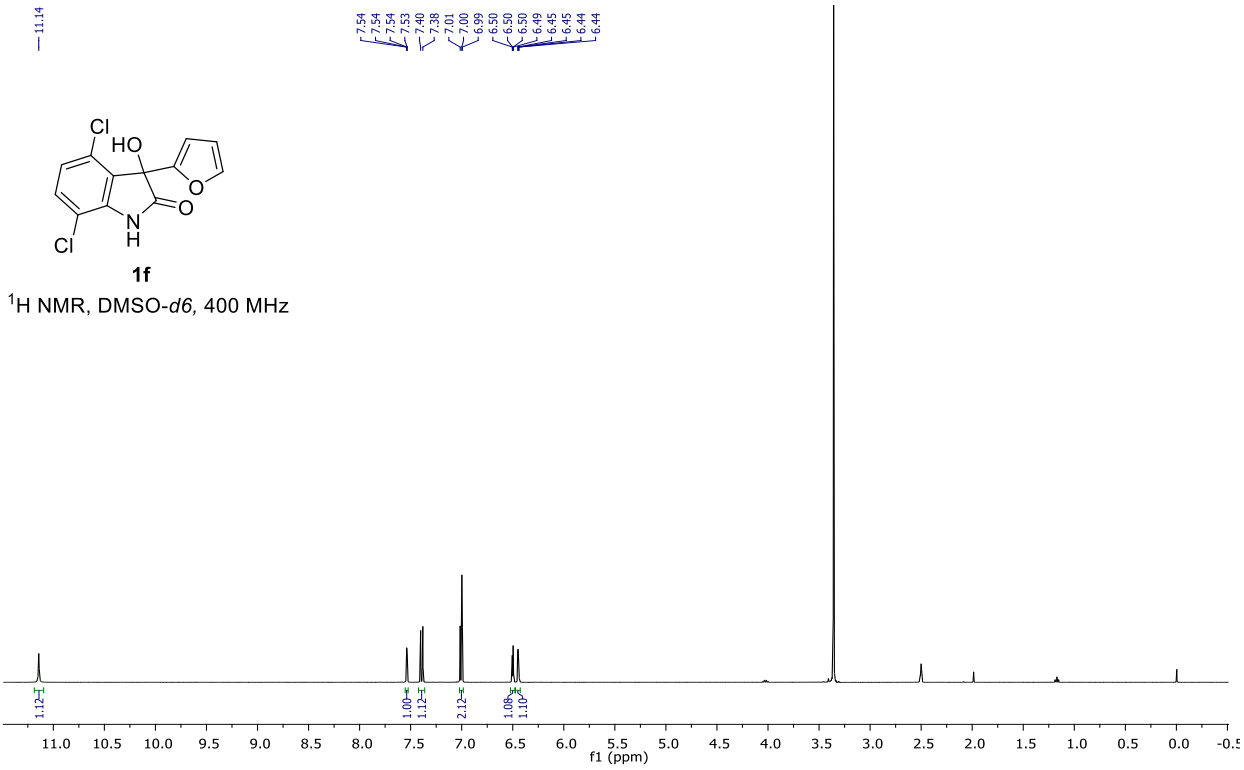
^{1}H NMR, DMSO-*d6,* 500 MHz



1e

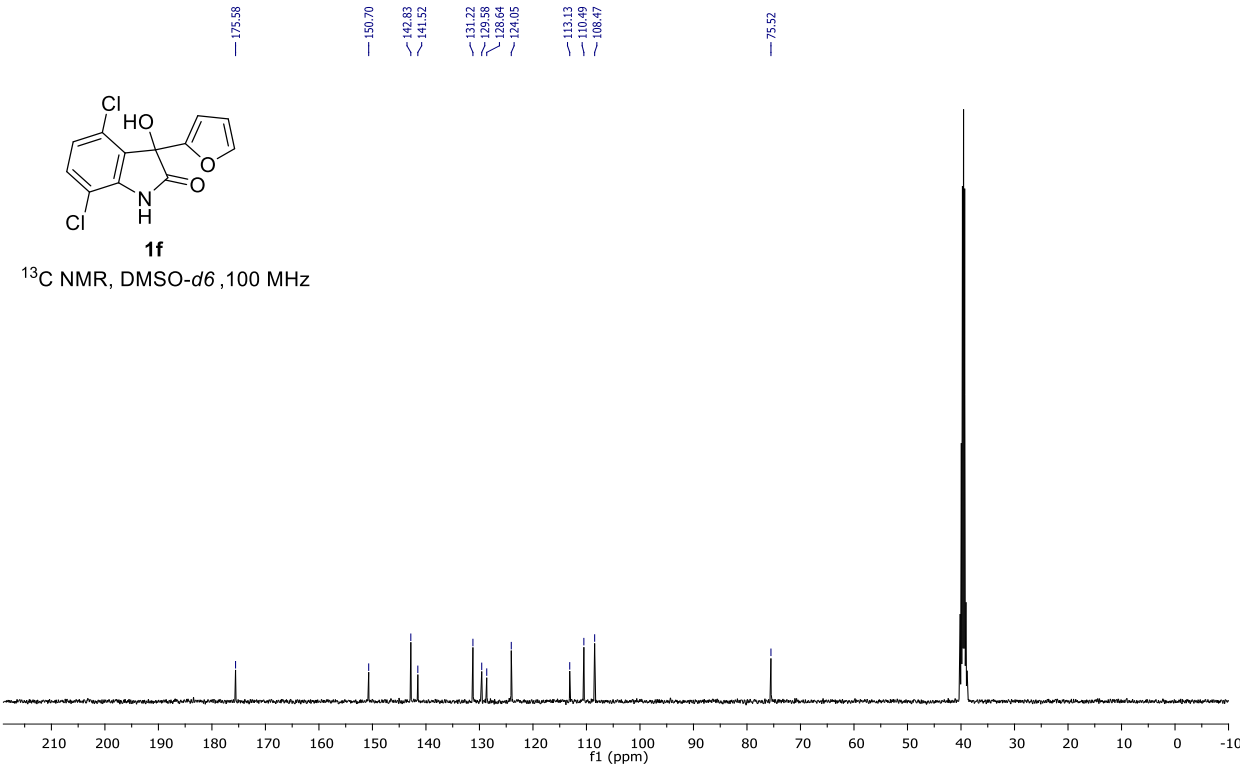
^{13}C NMR, DMSO-*d6* ,100 MHz

4,7-Dichloro-3-(furan-2-yl)-3-hydroxyindolin-2-one (1f)



1f

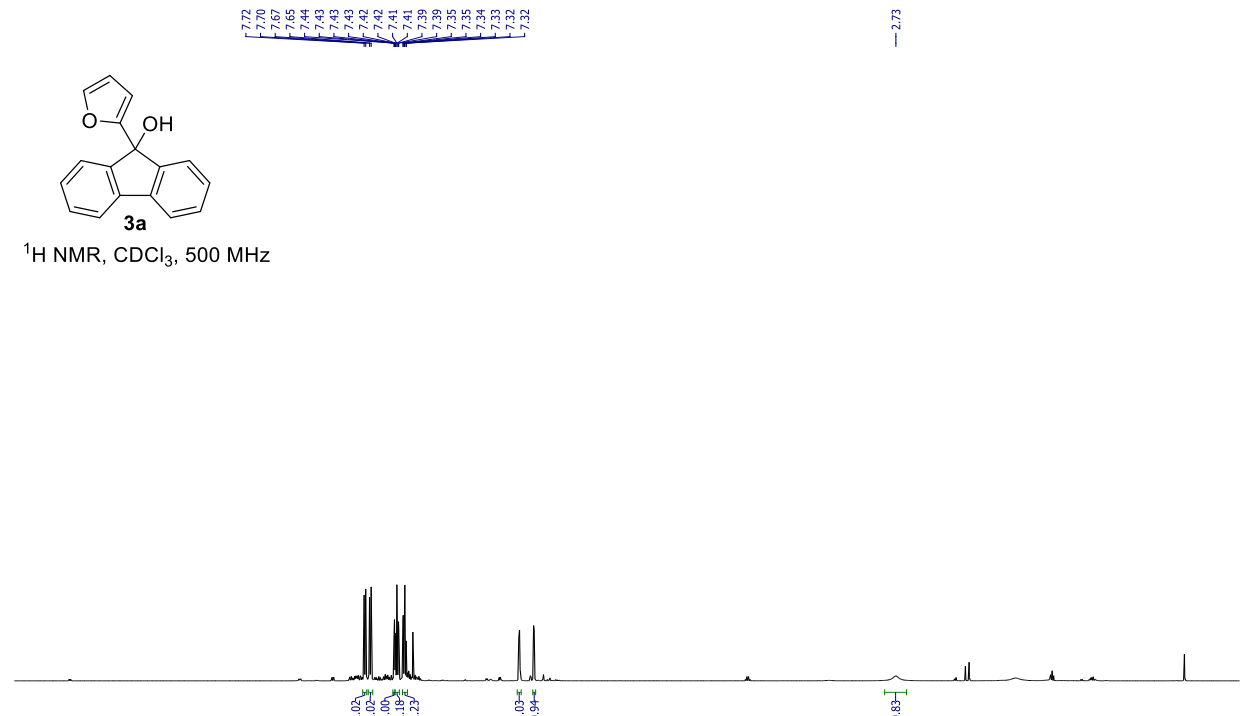
^{1}H NMR, DMSO-*d6,* 400 MHz



1f

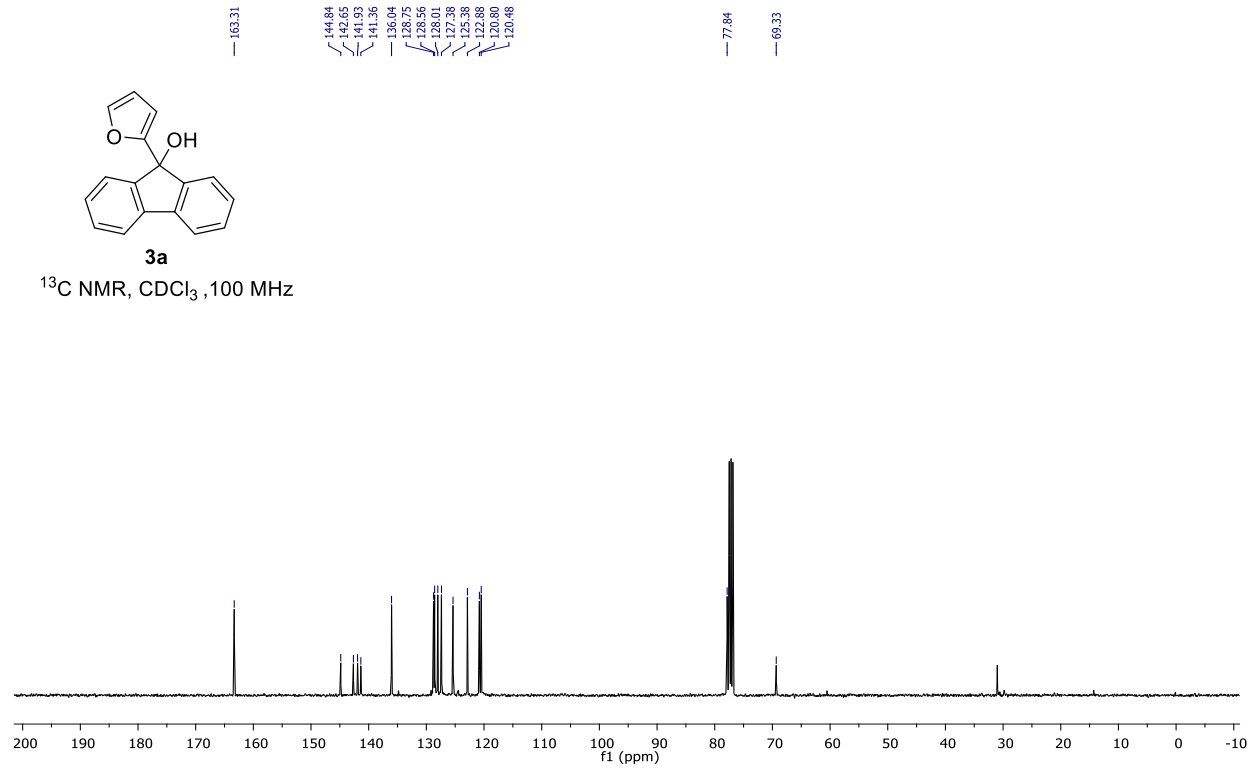
^{13}C NMR, DMSO-*d6* ,100 MHz

9-(Furan-2-yl)-9*H*-fluoren-9-ol (3a)



3a

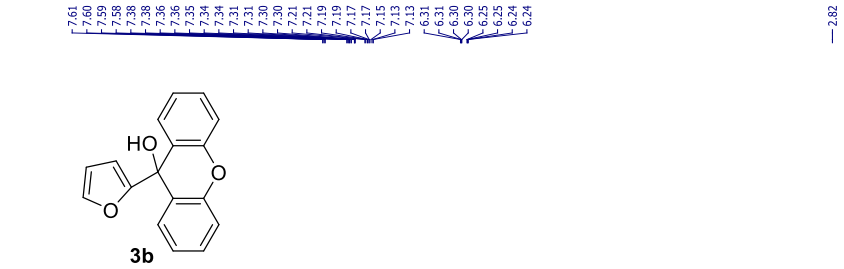
^{1}H NMR, $CDCl_3$, 500 MHz



3a

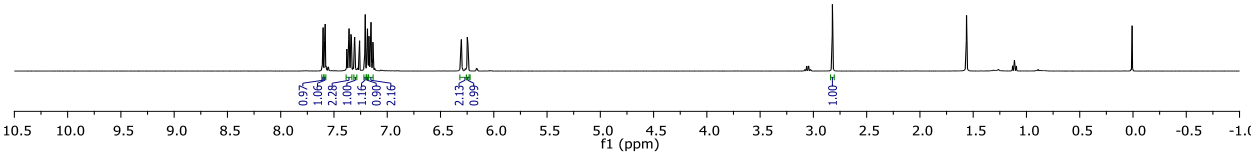
^{13}C NMR, $CDCl_3$,100 MHz

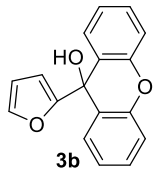
9-(Furan-2-yl)-9*H*-xanthen-9-ol (3b)



3b

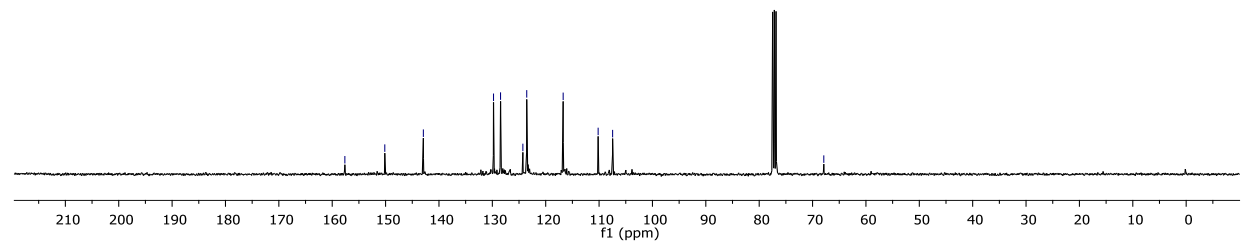
^{1}H NMR, $CDCl_3$, 500 MHz



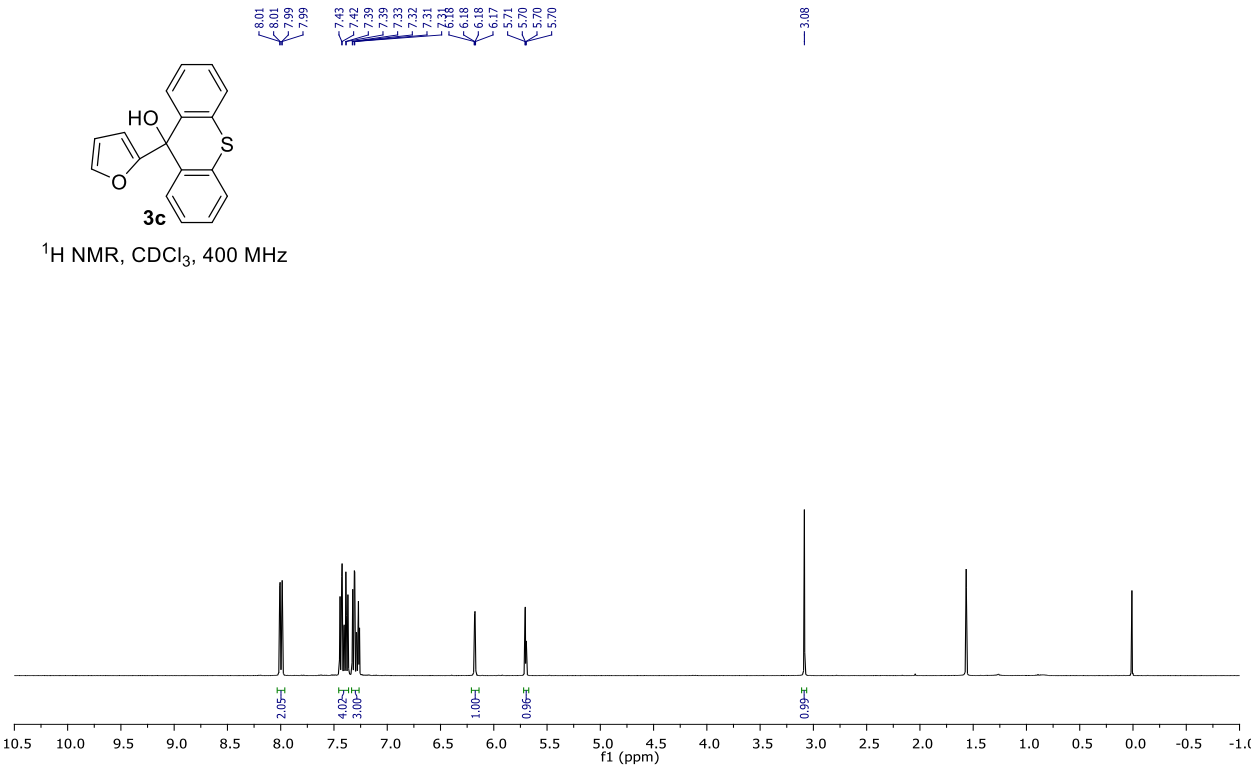


3b

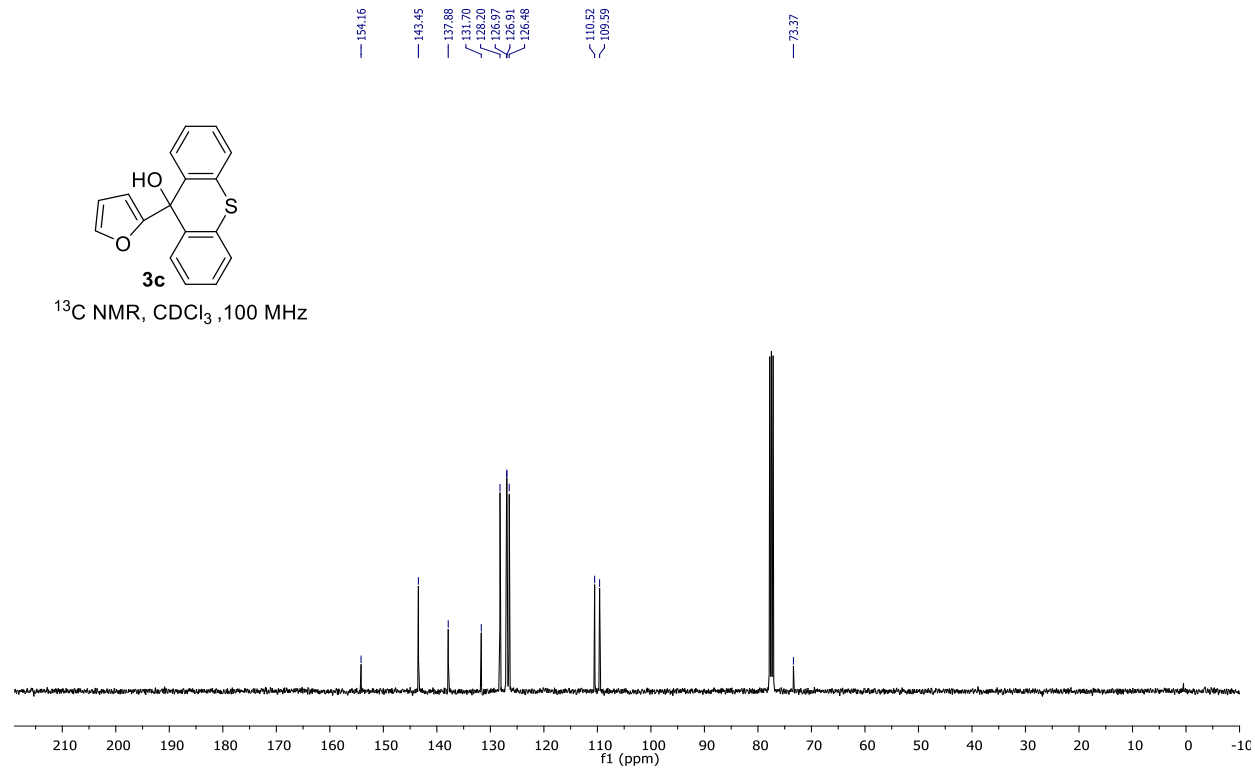
^{13}C NMR, $CDCl_3$,100 MHz



9-(Furan-2-yl)-9*H*-thioxanthen-9-ol (3c)

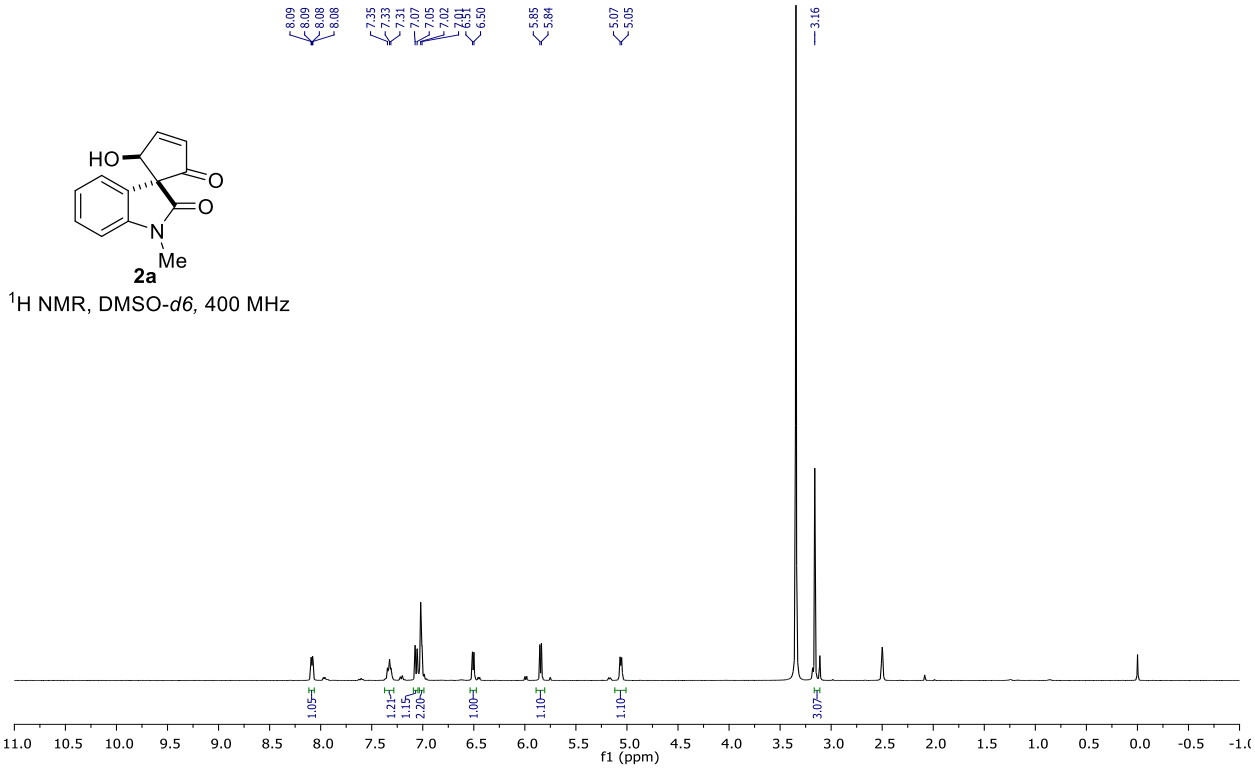


^{1}H NMR, $CDCl_3$, 400 MHz

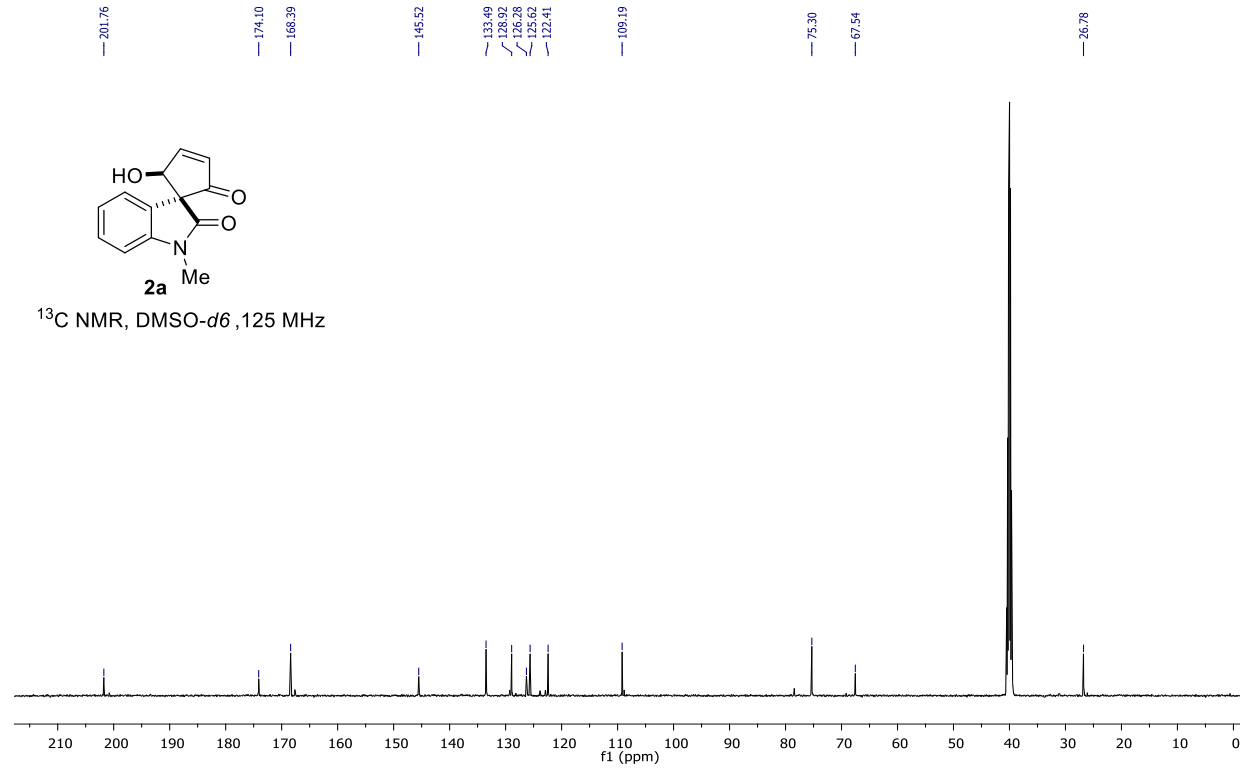


^{13}C NMR, $CDCl_3$,100 MHz

2-Hydroxy-1'-methylspiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione (2a)

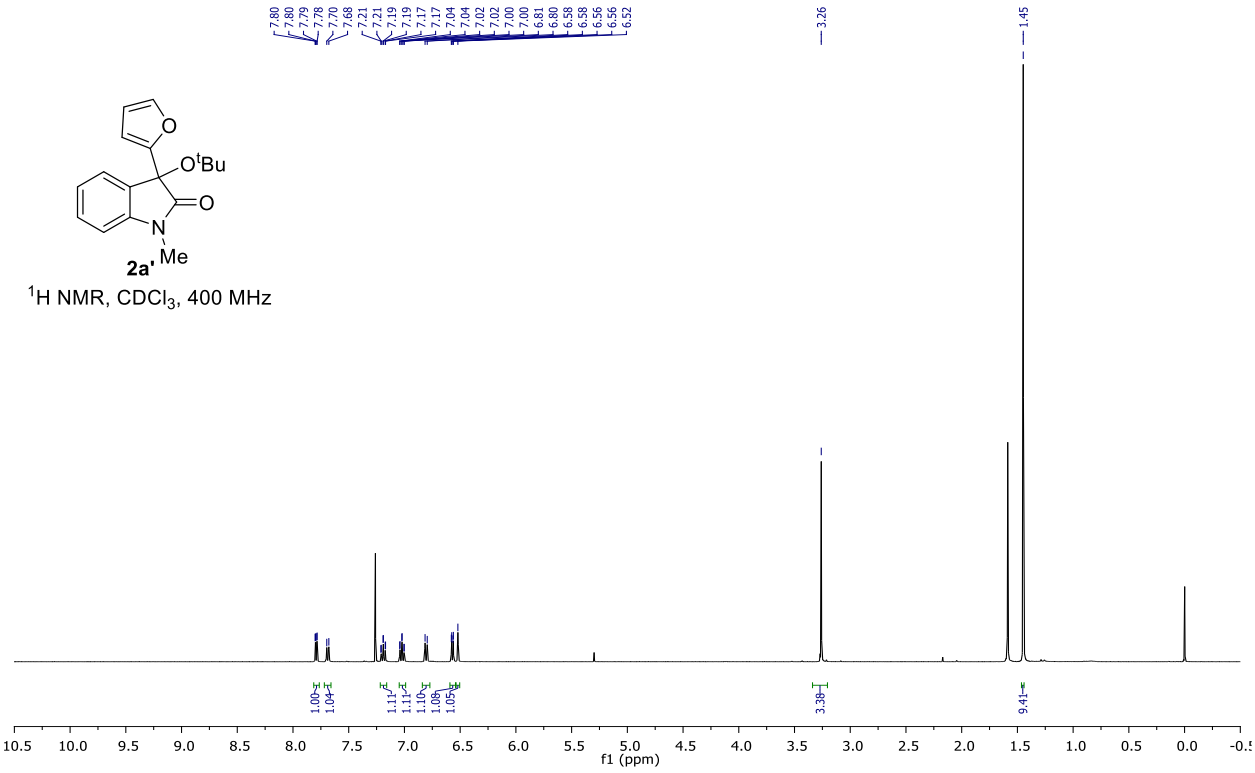


^{1}H NMR, DMSO-*d6,* 400 MHz

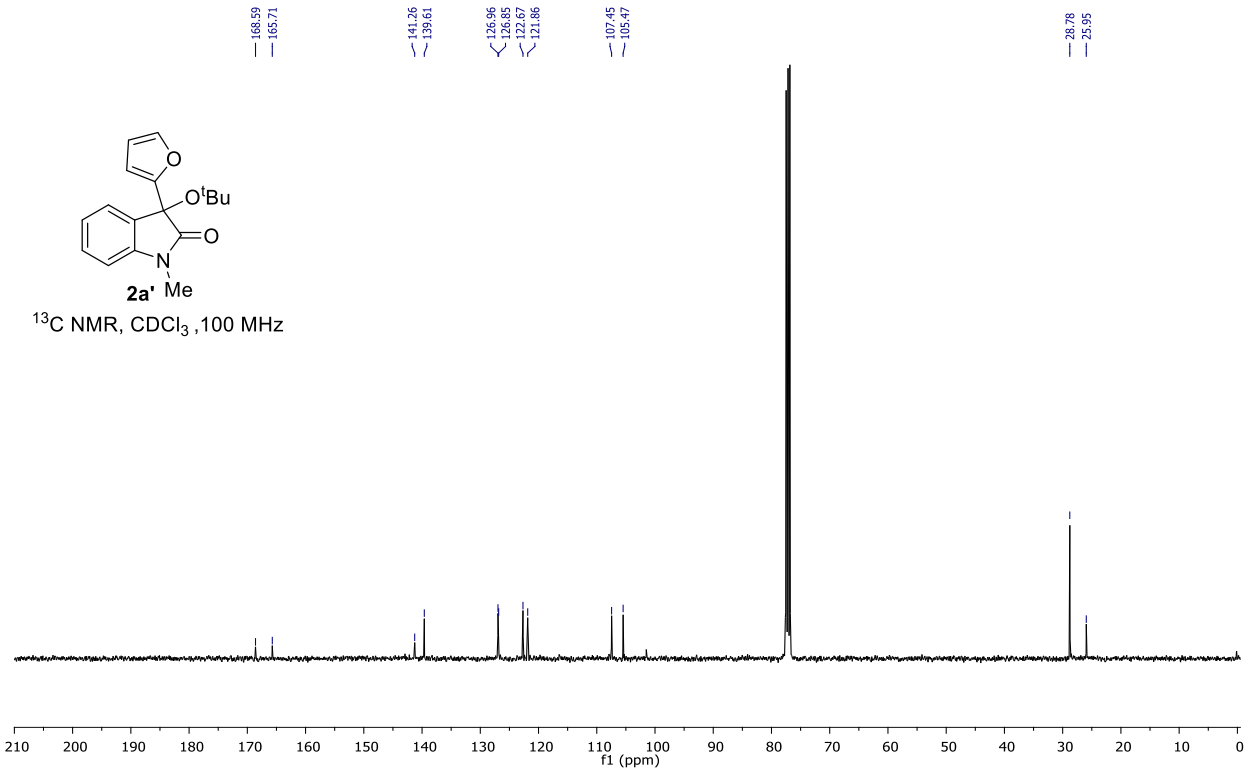


^{13}C NMR, DMSO-*d6* ,125 MHz

3-(*tert*-Butoxy)-3-(furan-2-yl)-1-methylindolin-2-one (2a′)

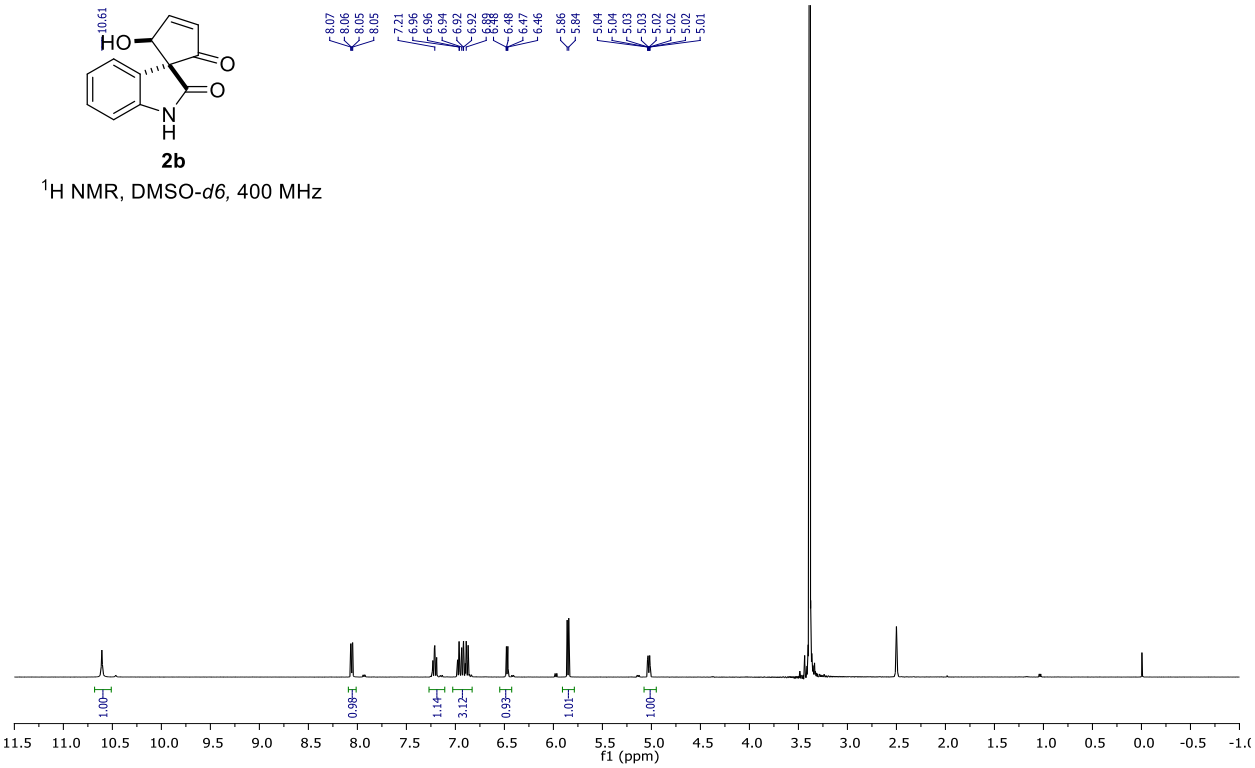


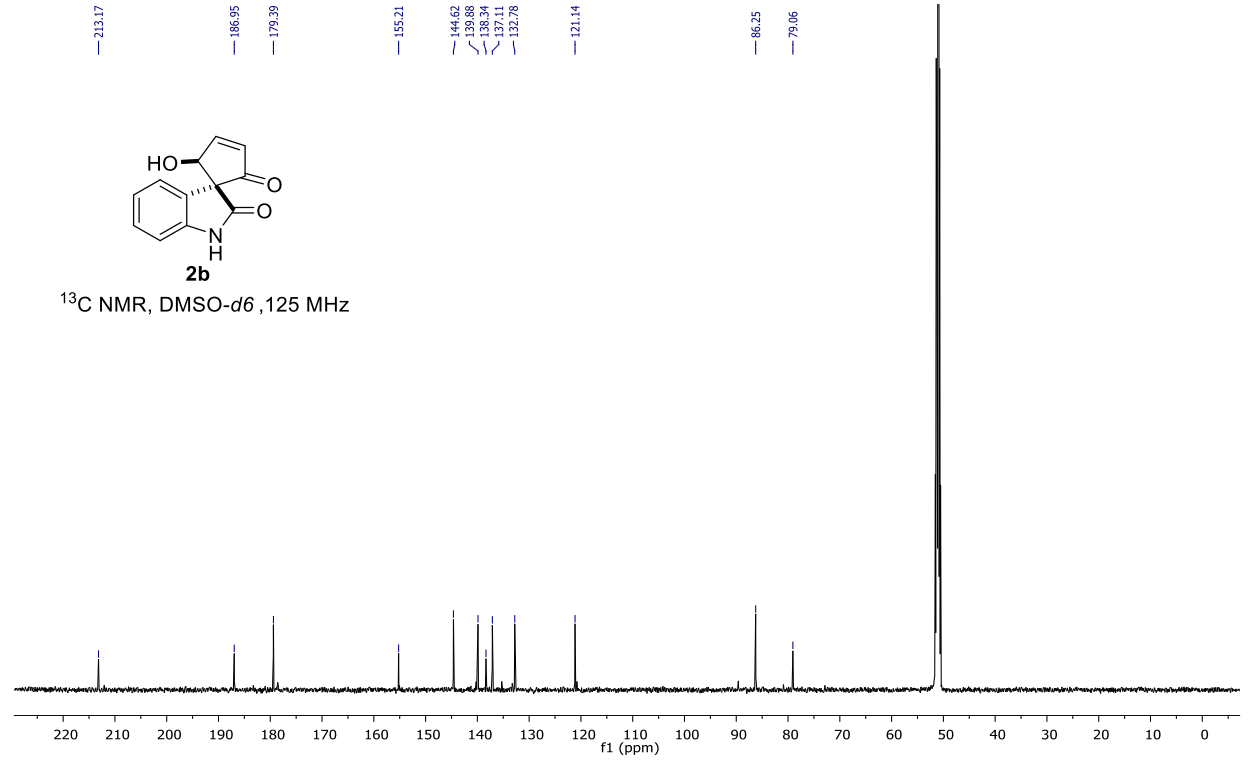
^{1}H NMR, $CDCl_3$, 400 MHz



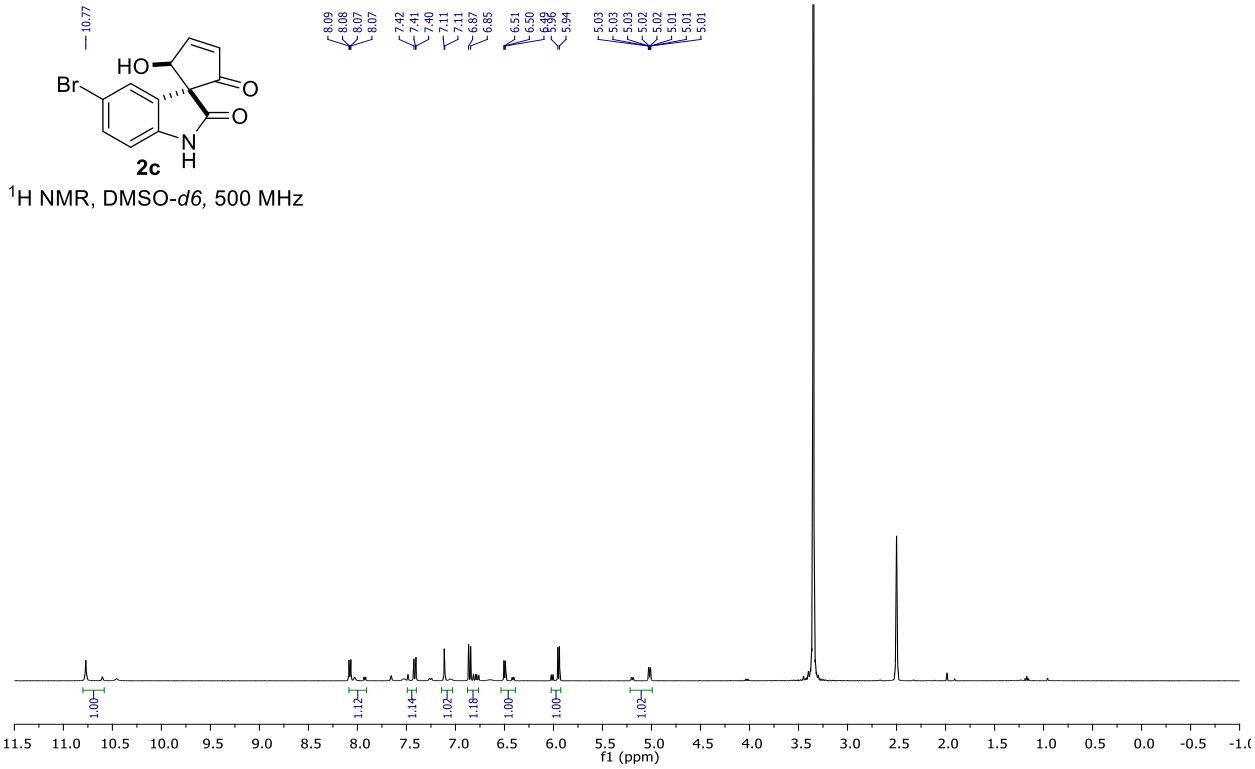
^{13}C NMR, $CDCl_3$,100 MHz

2-Hydroxyspiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione (2b)

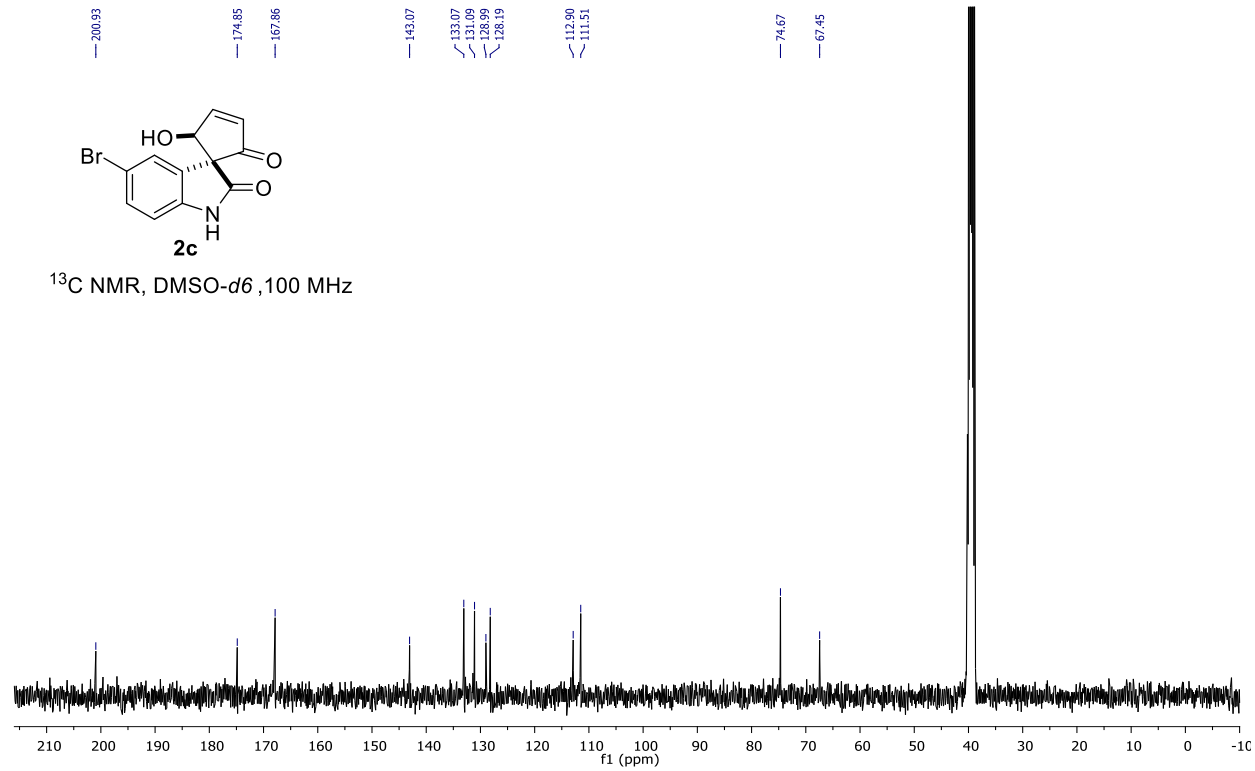




5'-Bromo-2-hydroxyspiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione (2c)

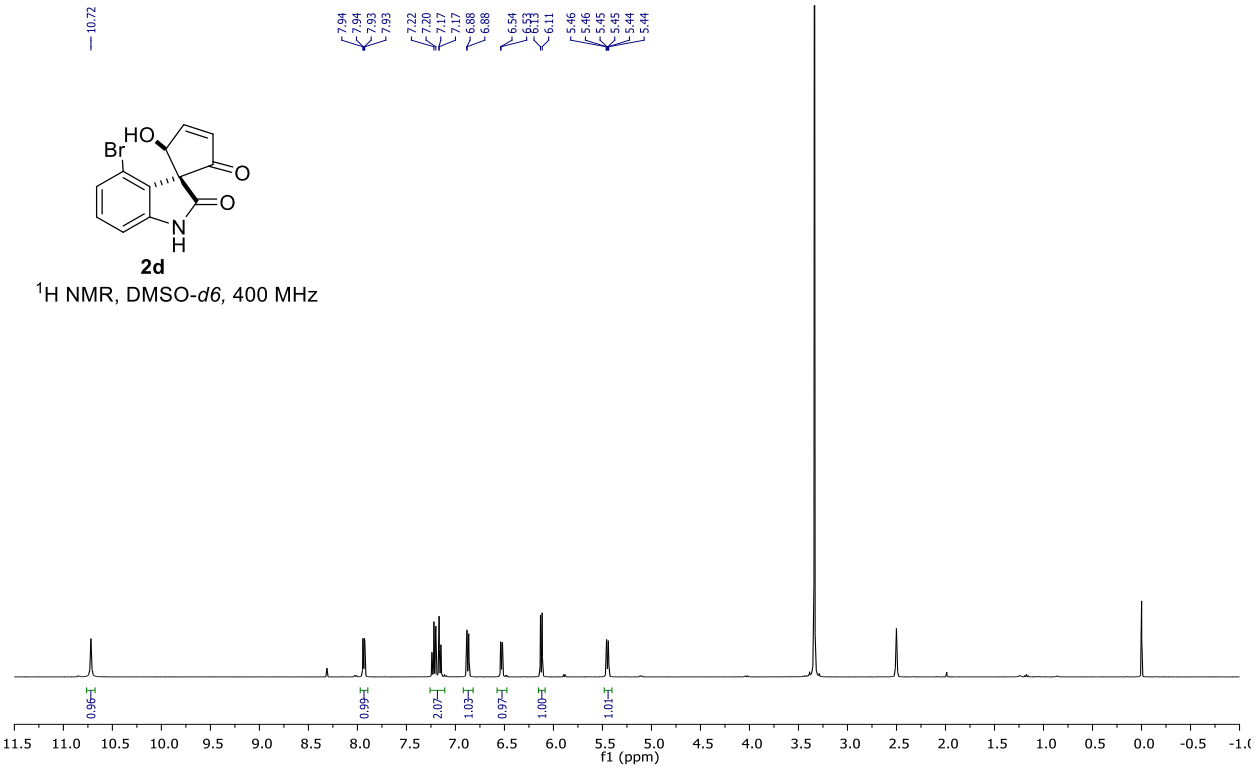


^{1}H NMR, DMSO-*d6,* 500 MHz



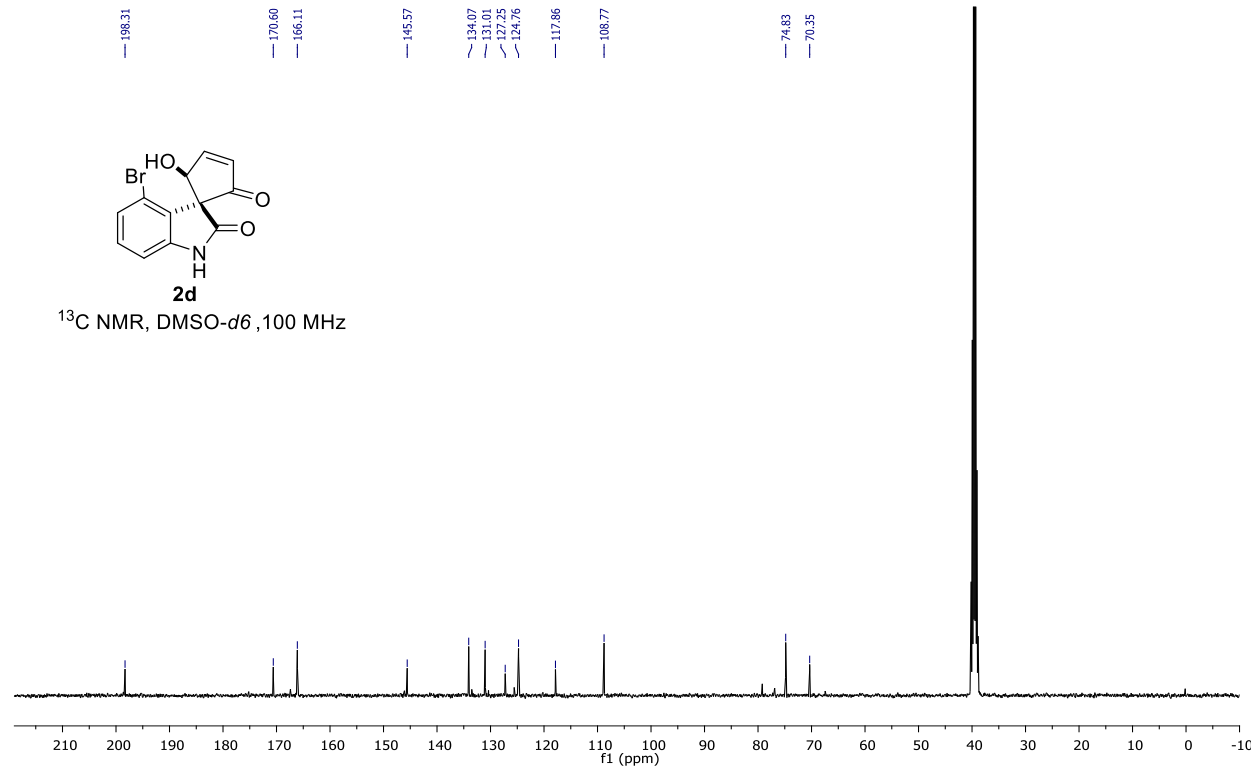
^{13}C NMR, DMSO-*d6* ,100 MHz

4'-Bromo-2-hydroxyspiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione (2d)



2d

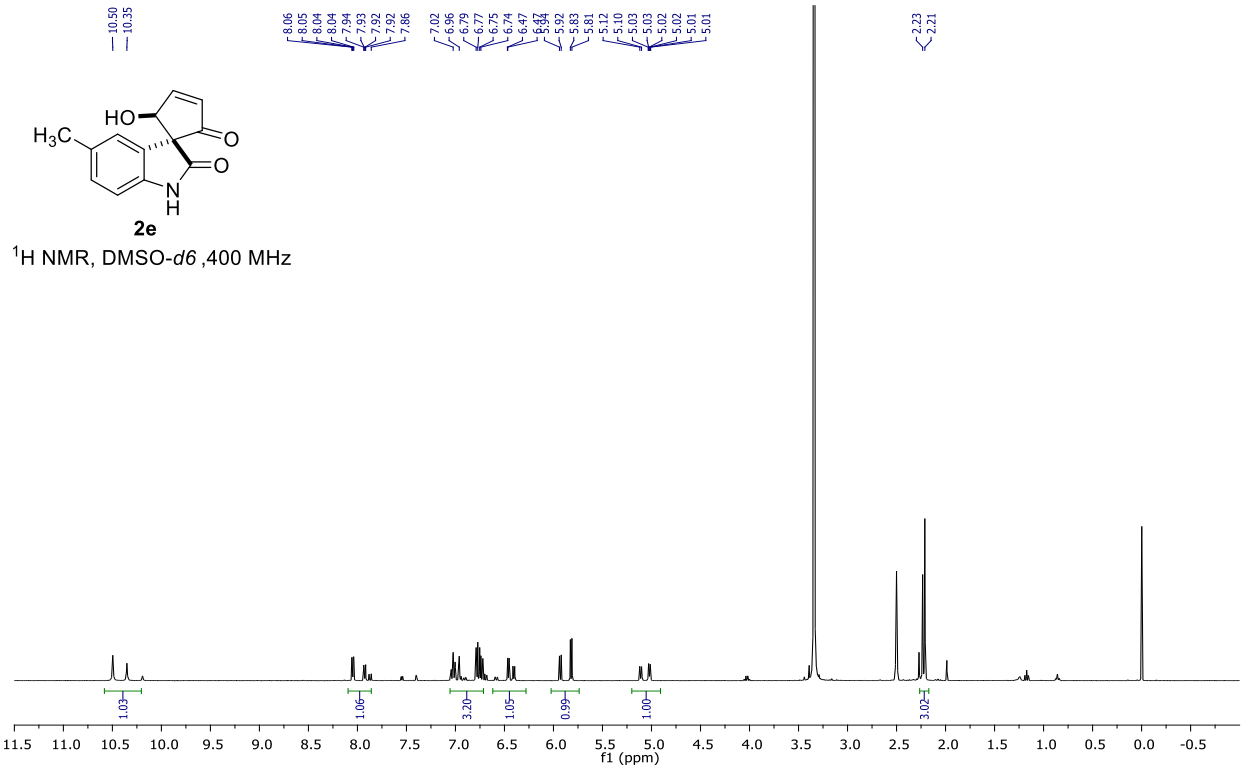
^{1}H NMR, DMSO-*d6*, 400 MHz

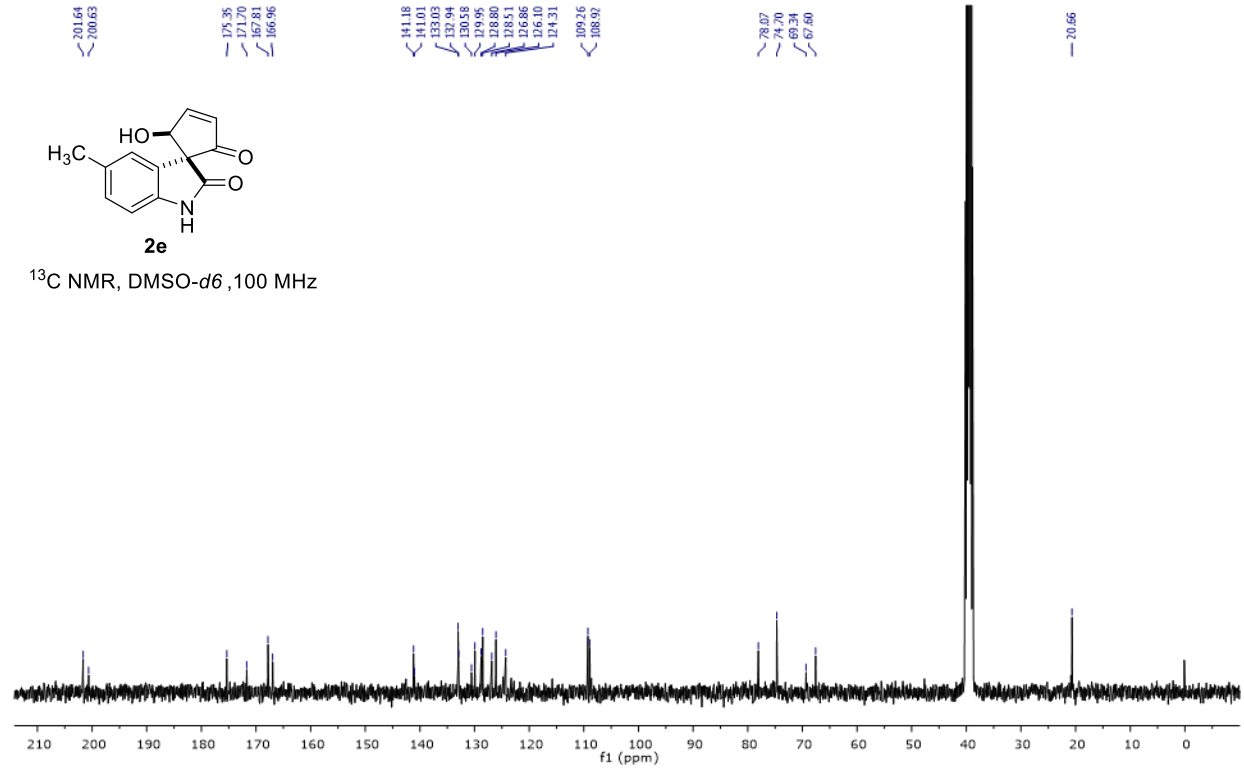


2d

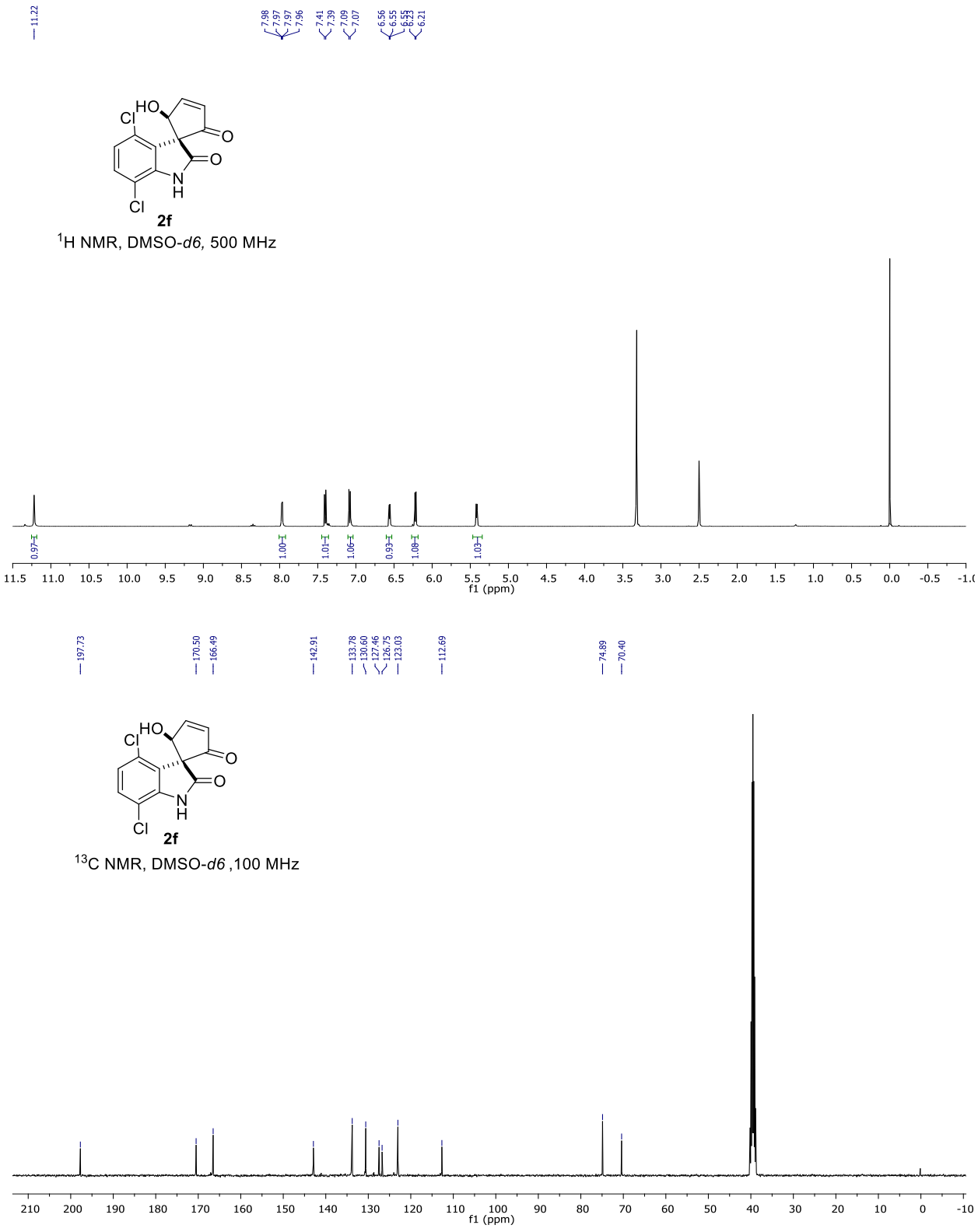
^{13}C NMR, DMSO-*d6* ,100 MHz

2-Hydroxy-5'-methylspiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione (2e)

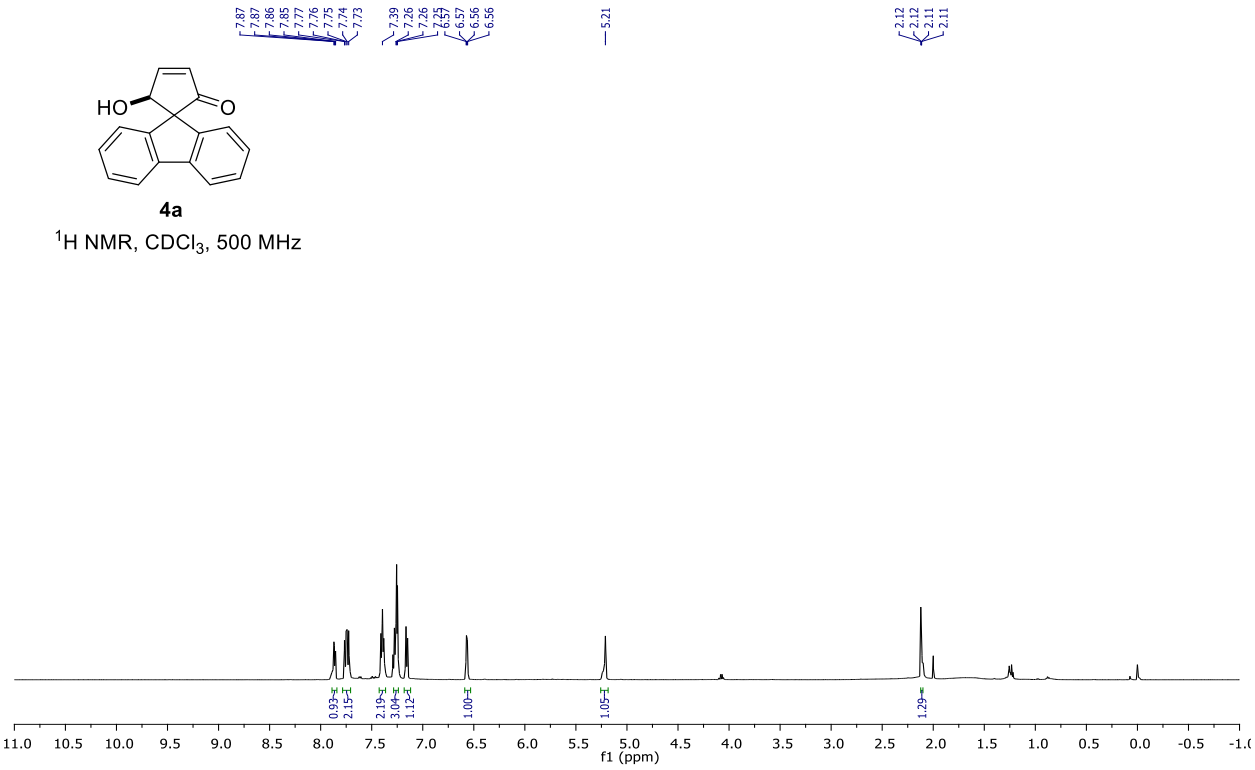




4',7'-Dichloro-2-hydroxyspiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione (2f)

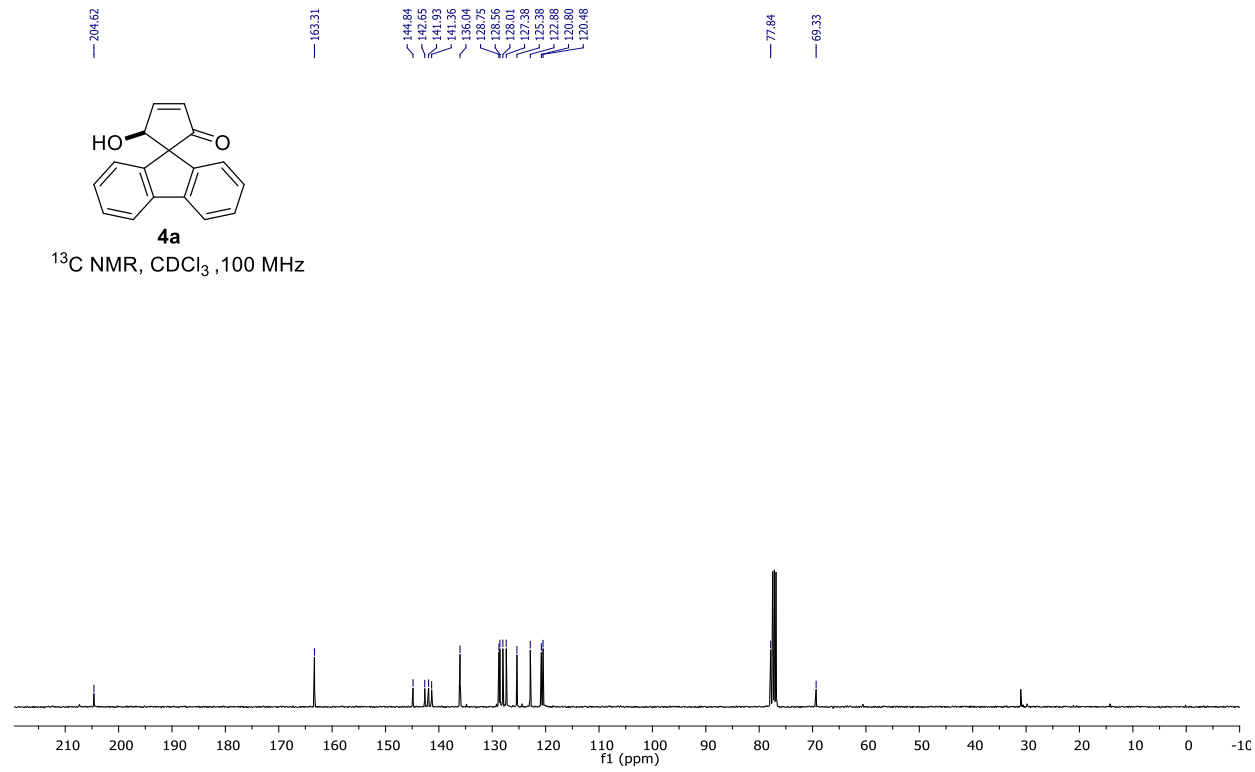


2-Hydroxyspiro[cyclopentane-1,9'-fluoren]-3-en-5-one (4a)



4a

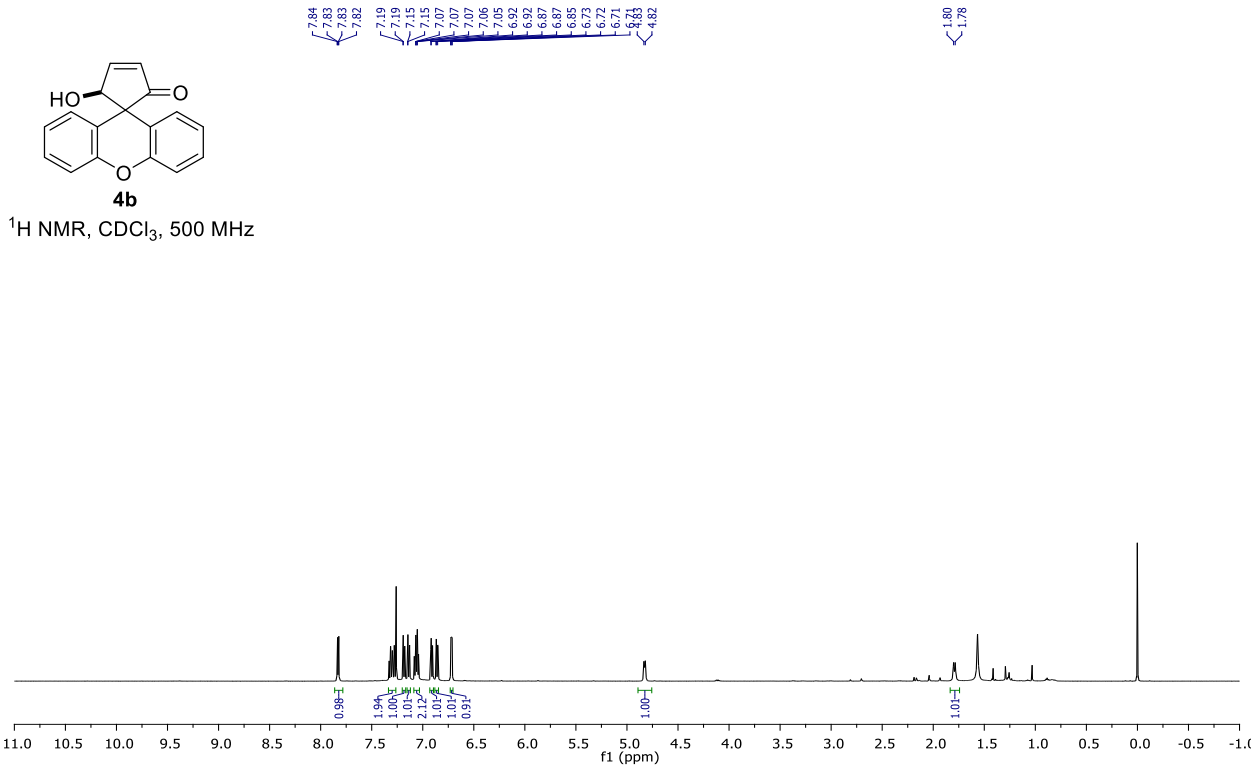
^{1}H NMR, $CDCl_3$, 500 MHz

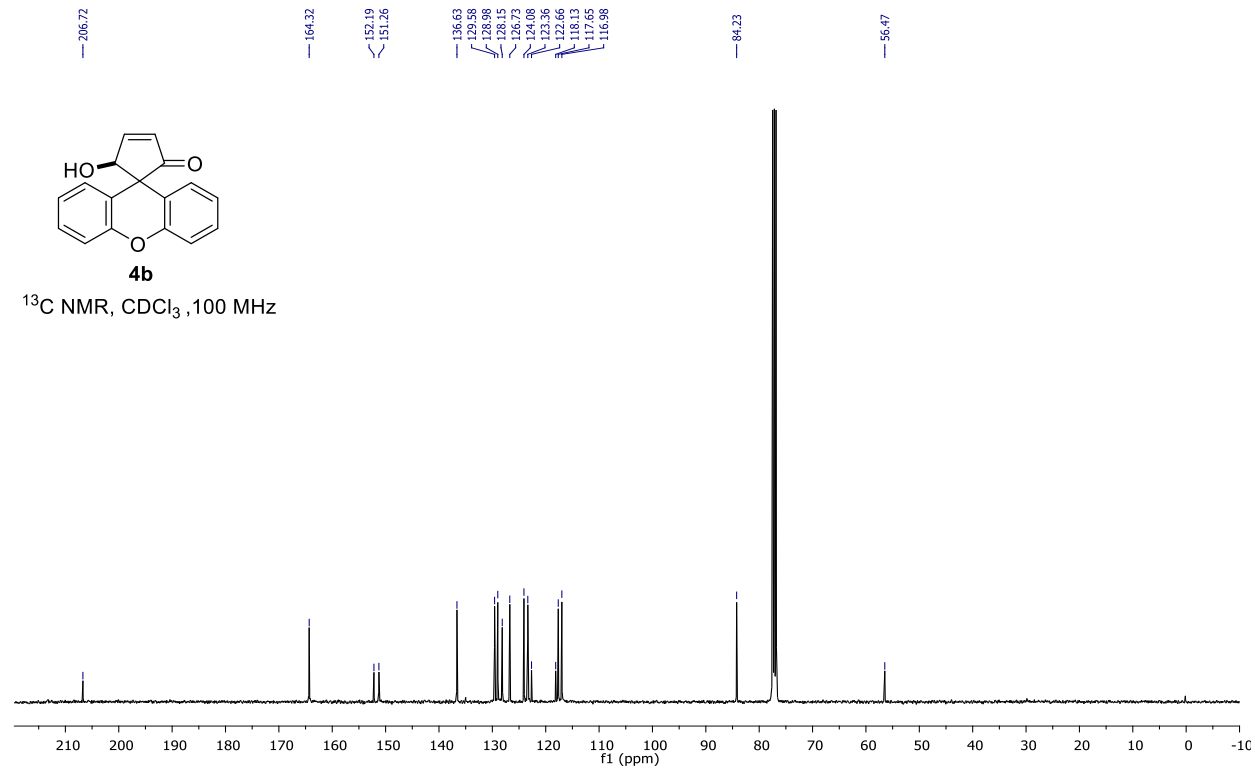


4a

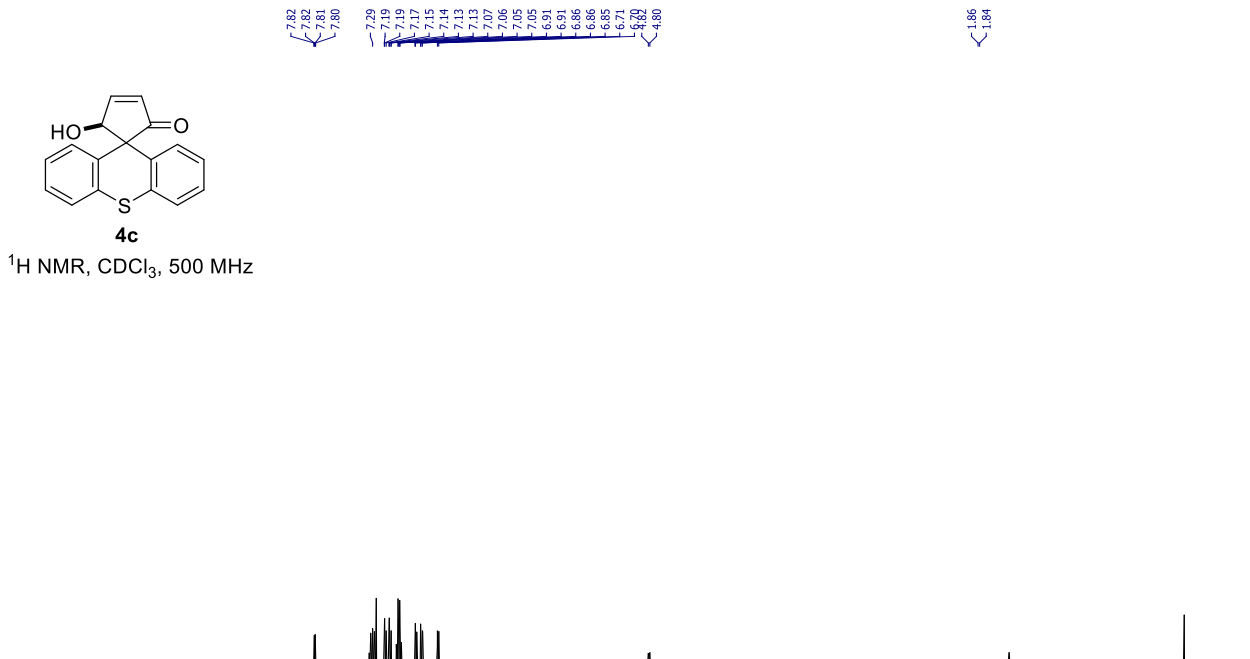
^{13}C NMR, $CDCl_3$,100 MHz

2-Hydroxyspiro[cyclopentane-1,9'-xanthen]-3-en-5-one (4b)

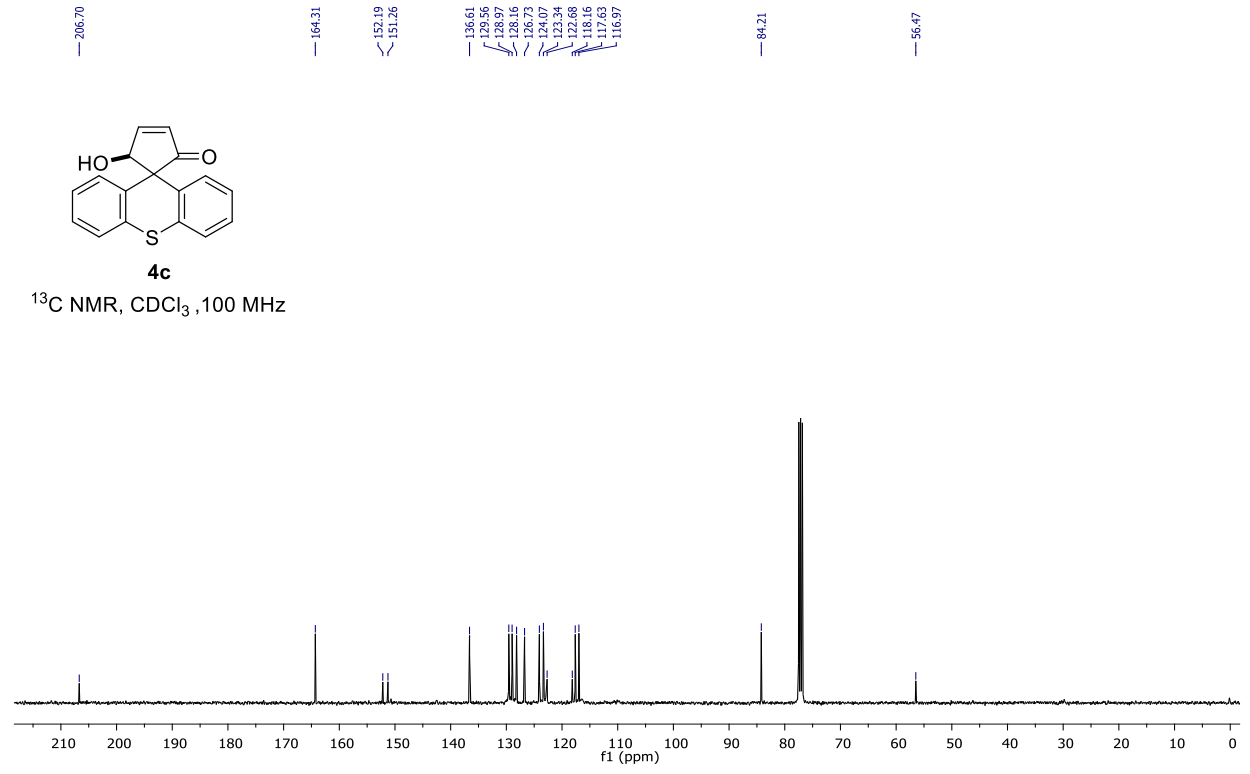




2-Hydroxyspiro[cyclopentane-1,9'-thioxanthen]-3-en-5-one (4c)

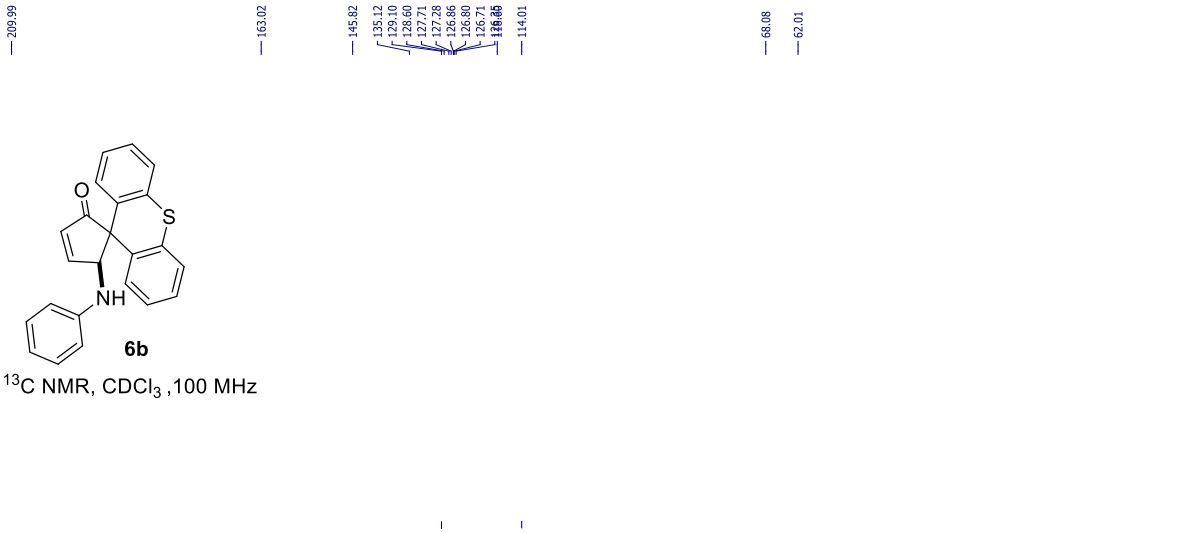


^{1}H NMR, $CDCl_3$, 500 MHz

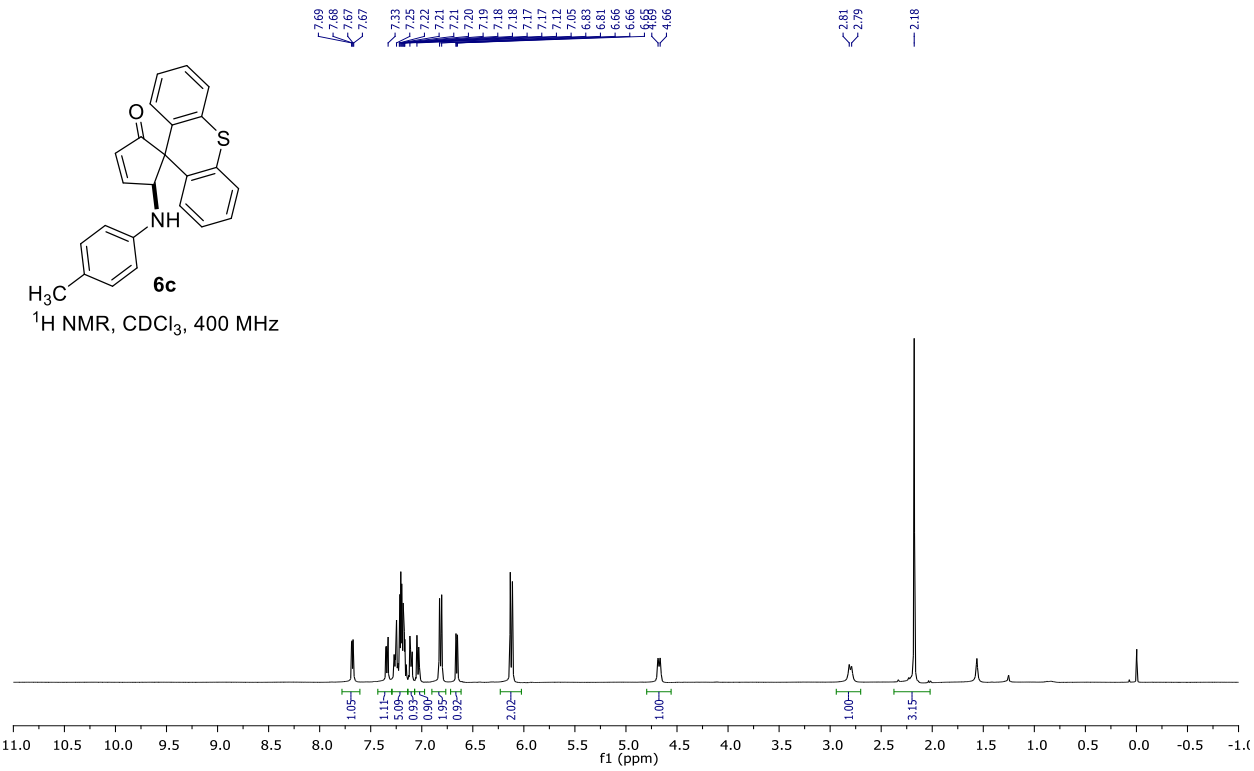


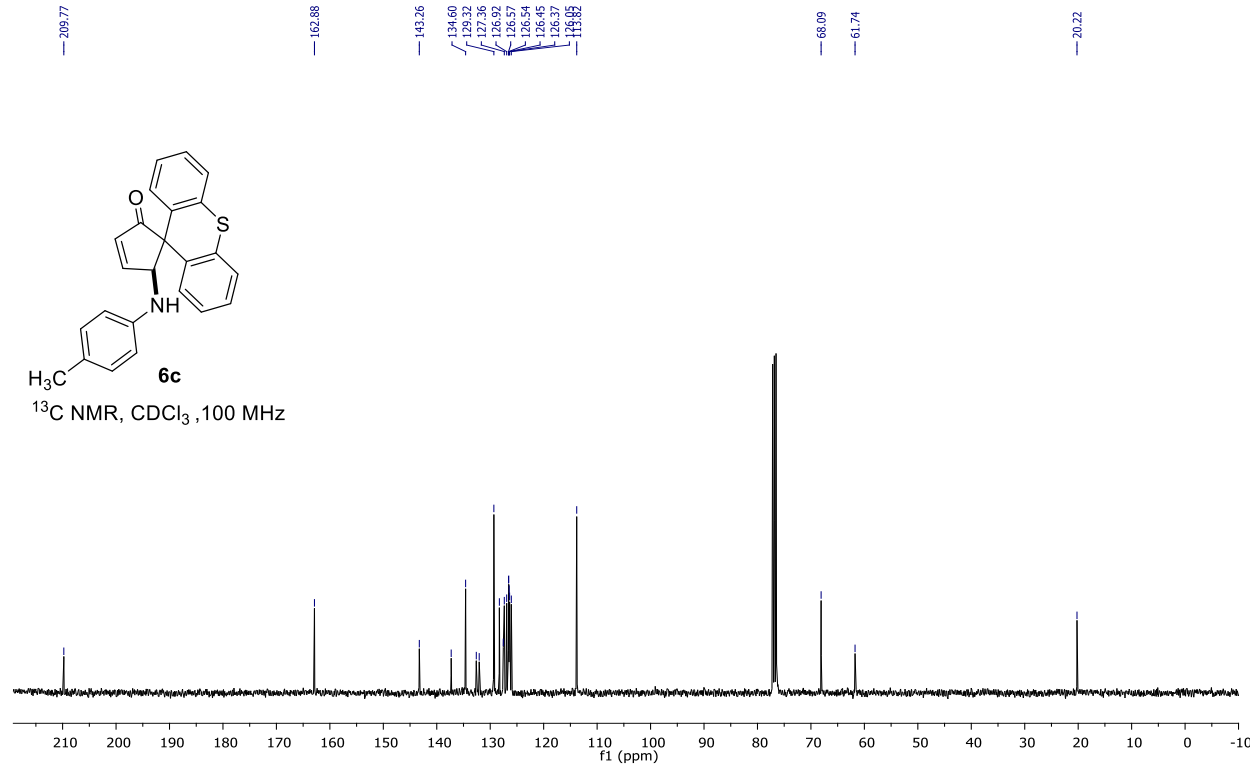
^{13}C NMR, $CDCl_3$,100 MHz

5-(Phenylamino)spiro[cyclopentane-1,9'-thioxanthen]-3-en-2-one (6b)

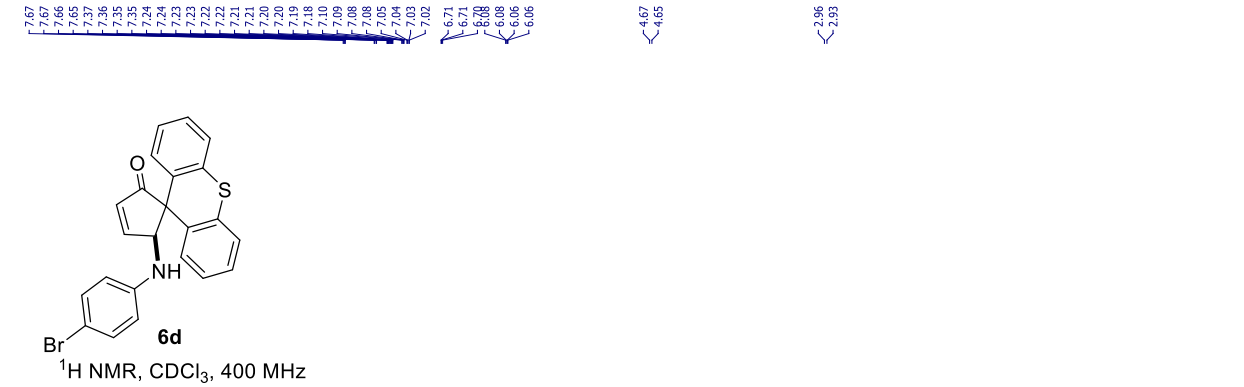


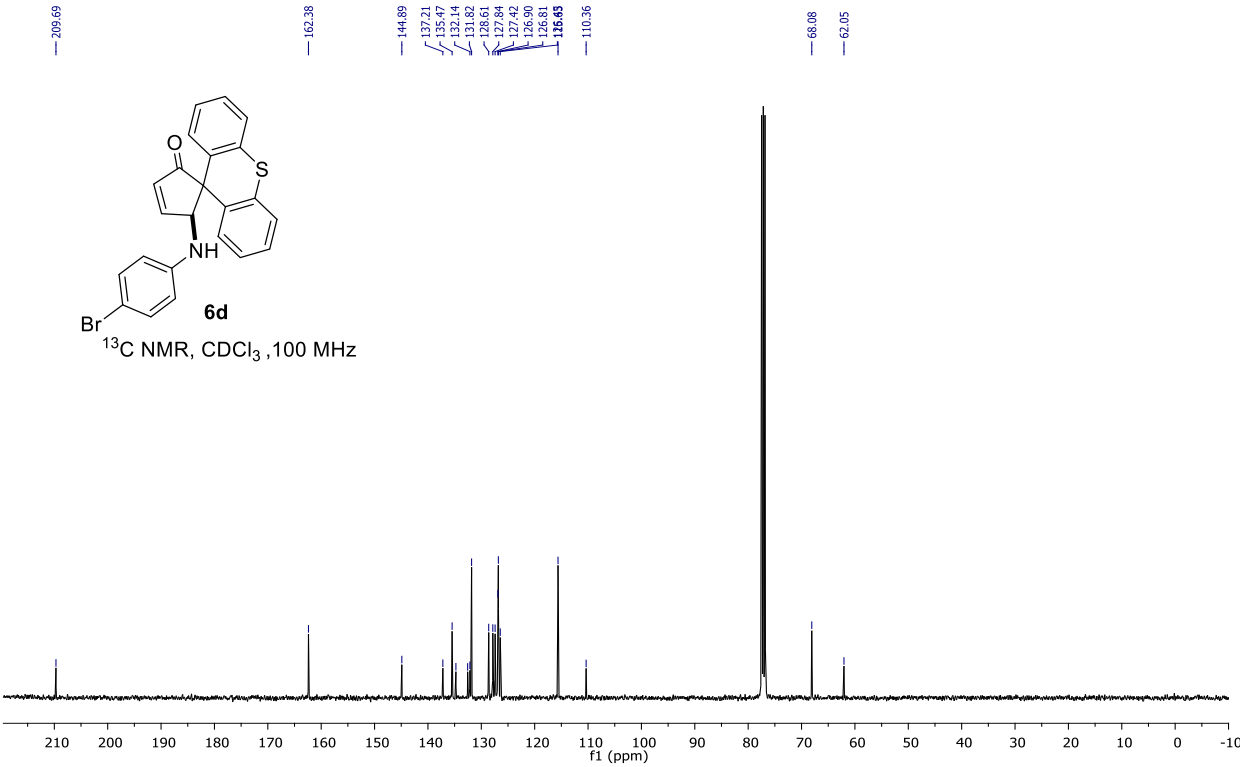
5-(*p*-Tolylamino)spiro[cyclopentane-1,9'-thioxanthen]-3-en-2-one (6c)



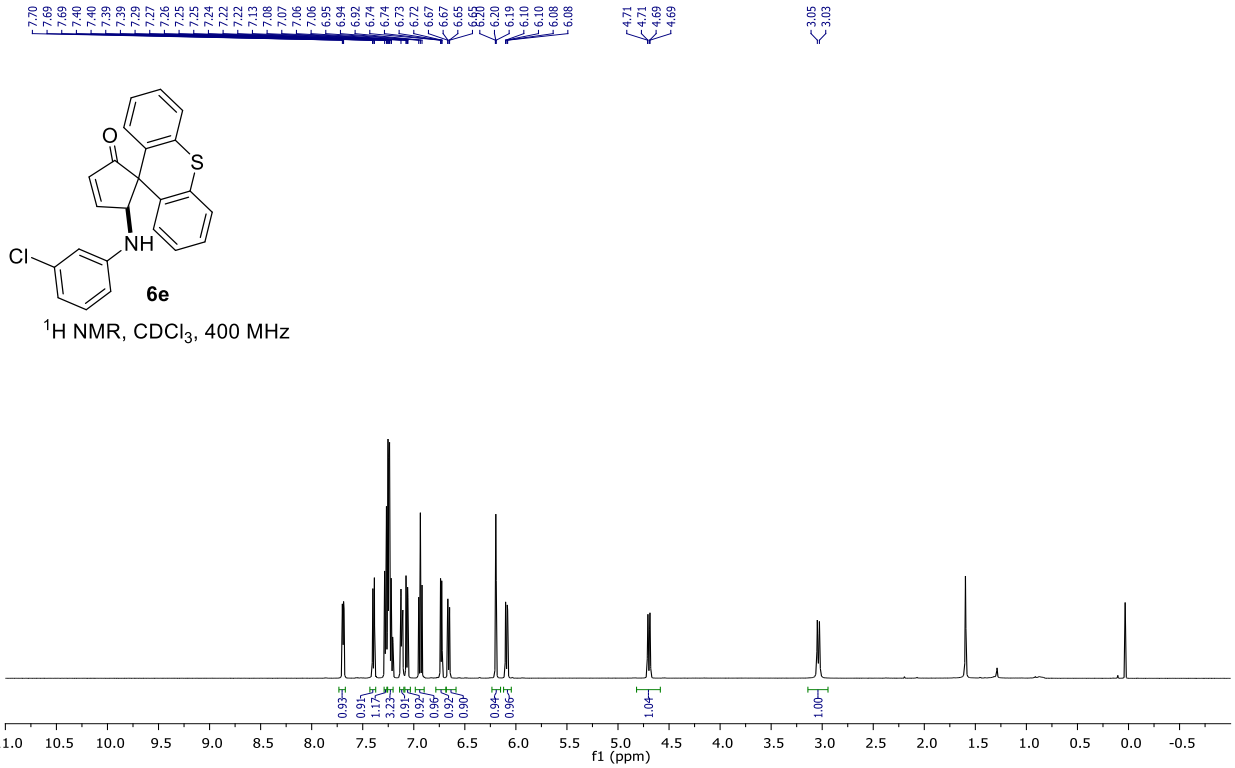


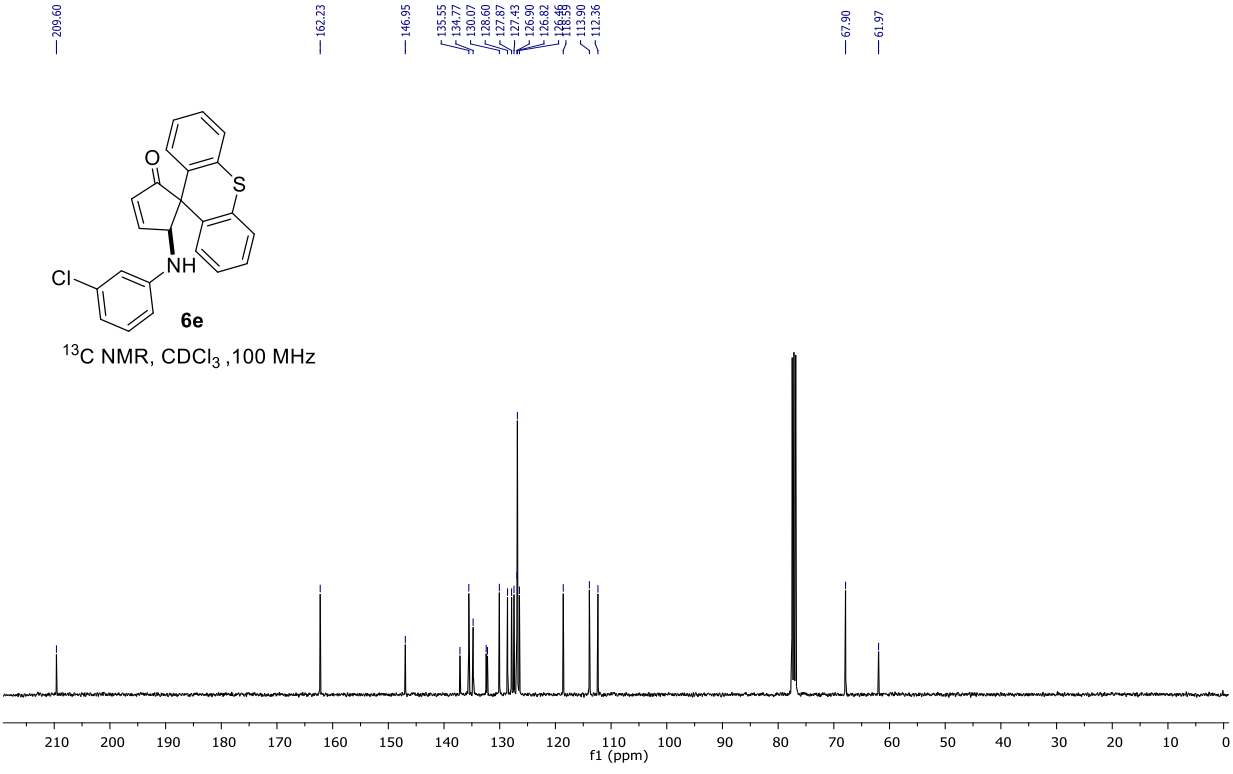
2-((4-Bromophenyl)amino)spiro[cyclopentane-1,9'-thioxanthen]-3-en-5-one (6d)



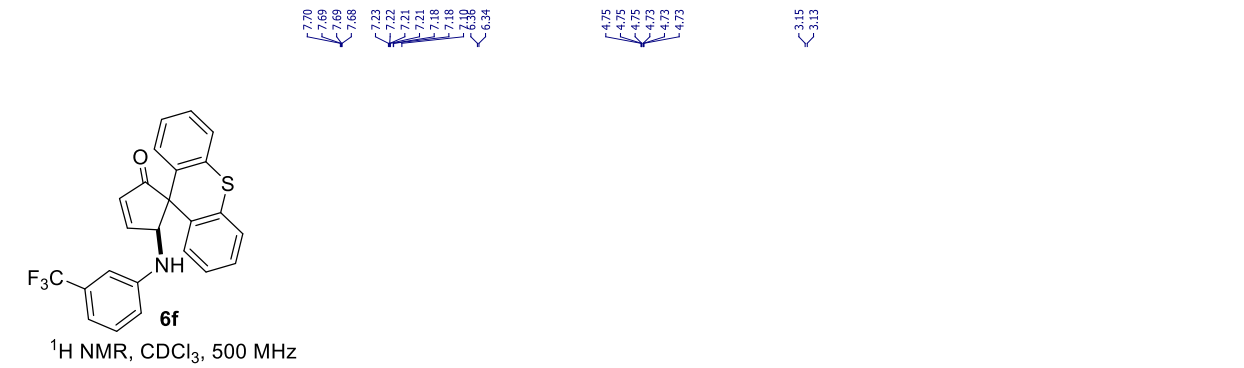


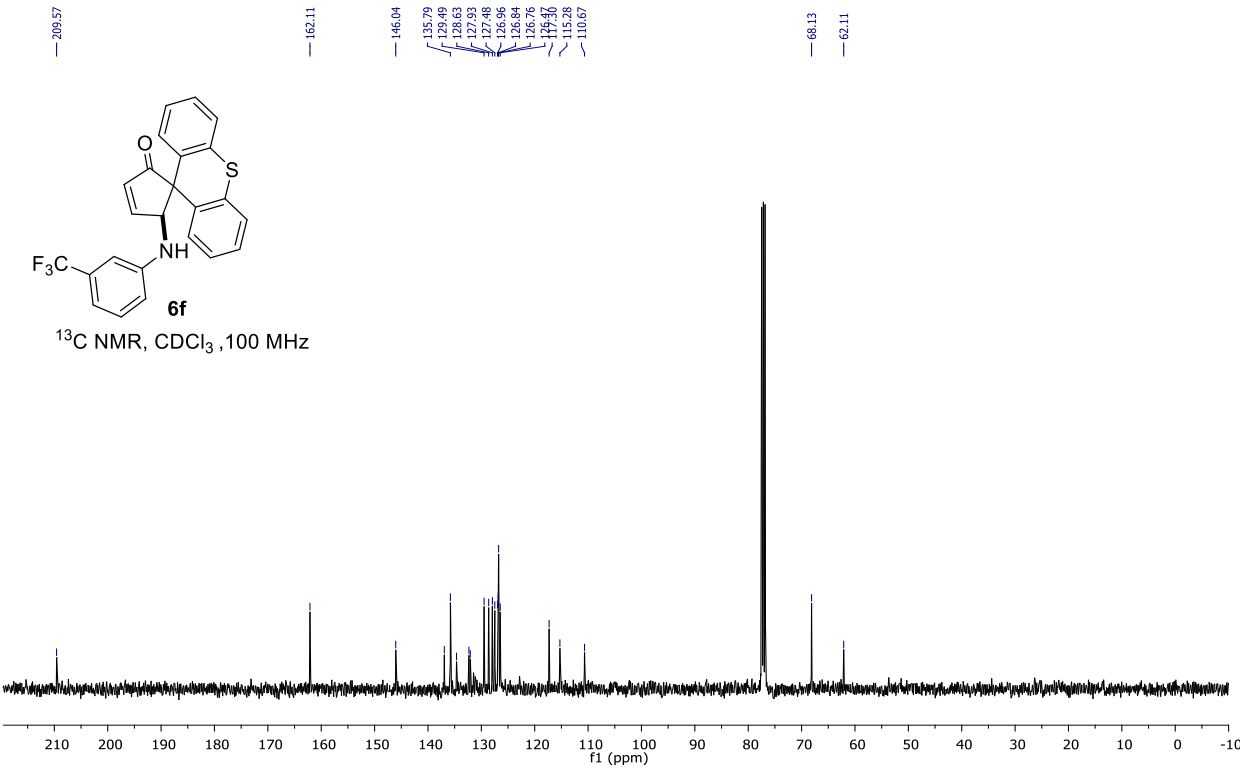
2-((3-Chlorophenyl)amino)spiro[cyclopentane-1,9'-thioxanthen]-3-en-5-one (6e)



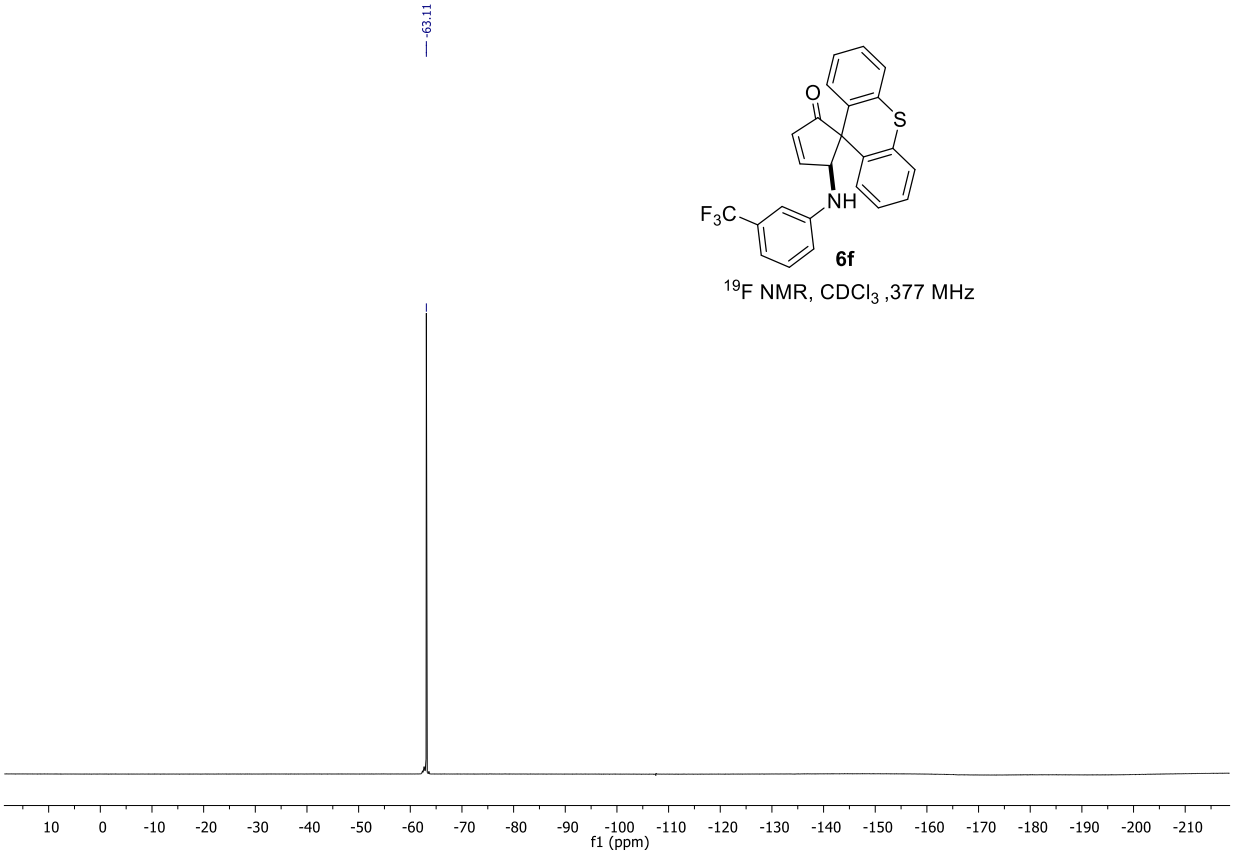


5-((3-(Trifluoromethyl)phenyl)amino)spiro[cyclopentane-1,9'-thioxanthen]-3-en-2-one (6f)

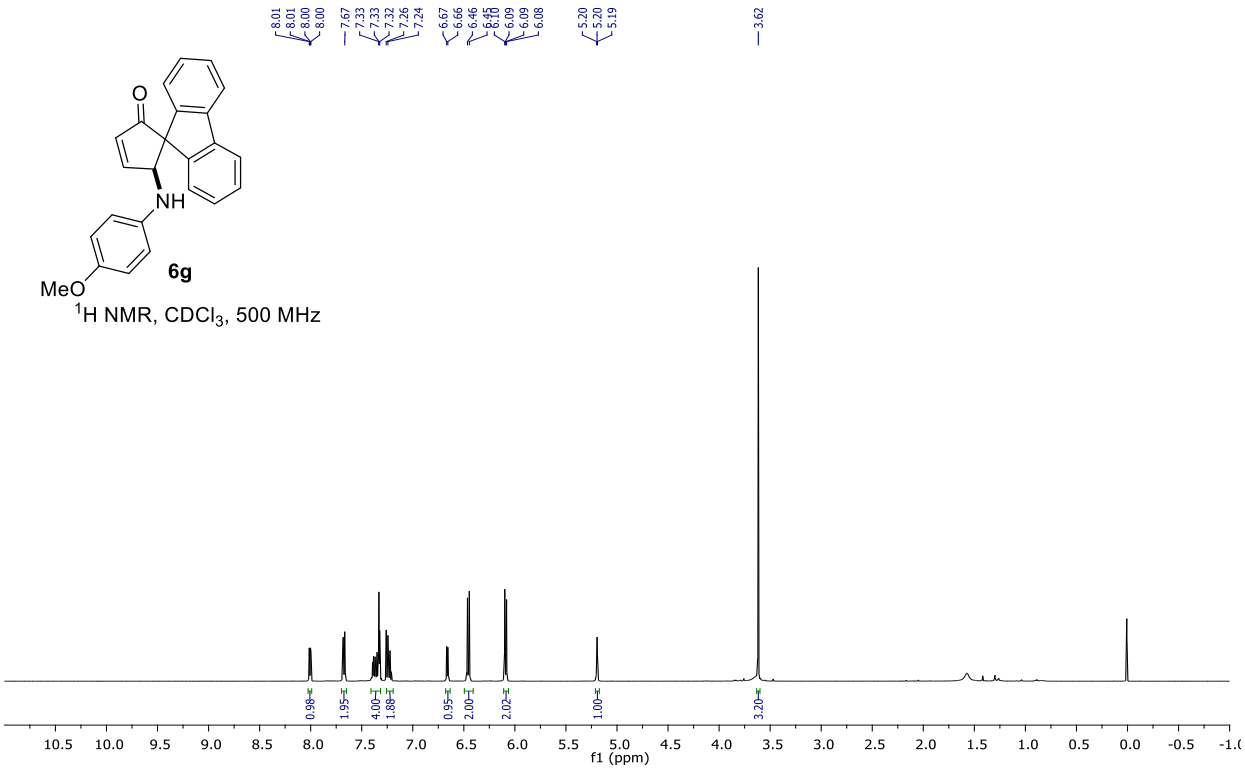


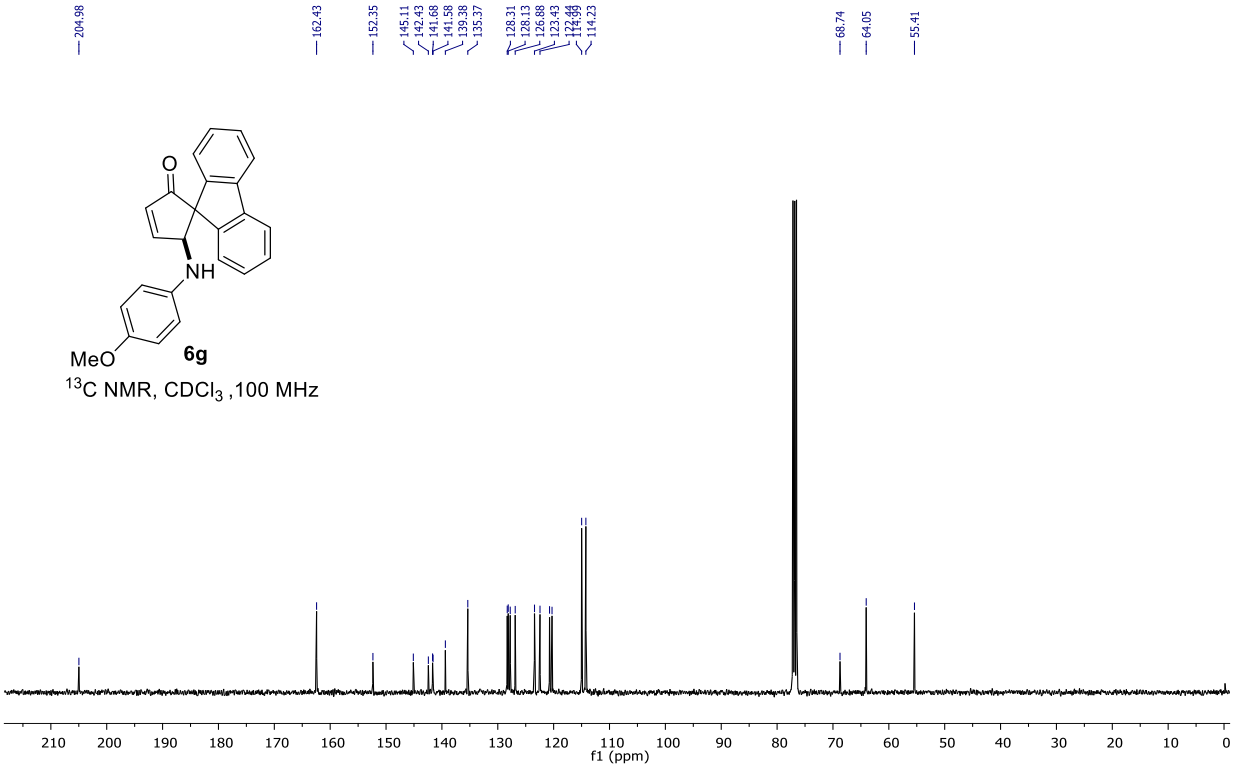


^{19}F Spectrum of compound 6f

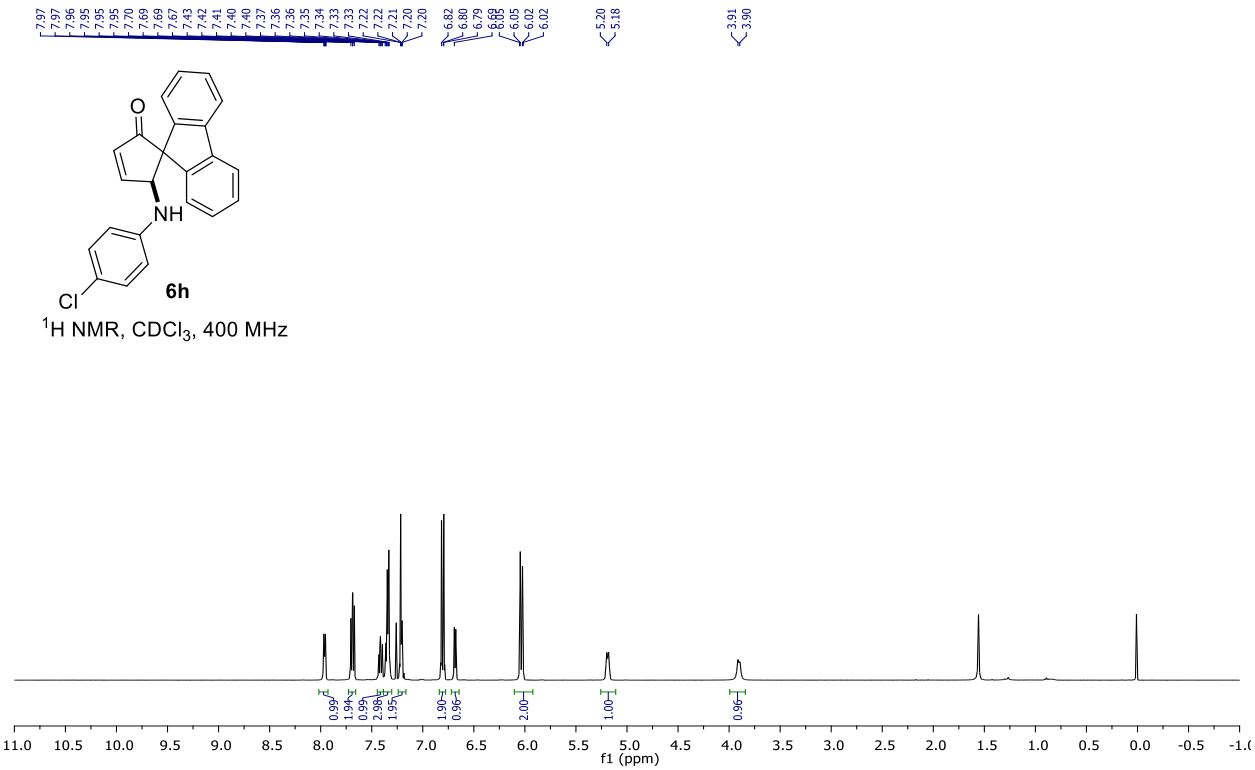


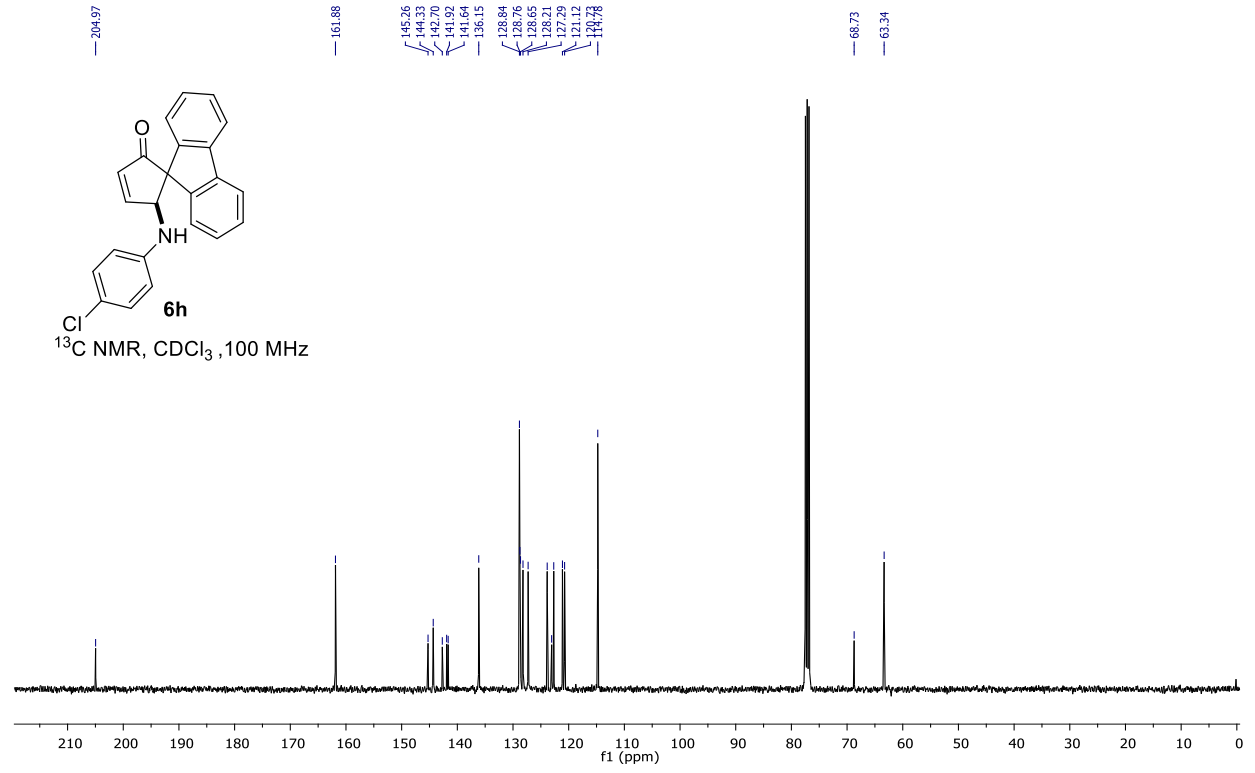
2-((4-Methoxyphenyl)amino)spiro[cyclopentane-1,9'-fluoren]-3-en-5-one (6g)



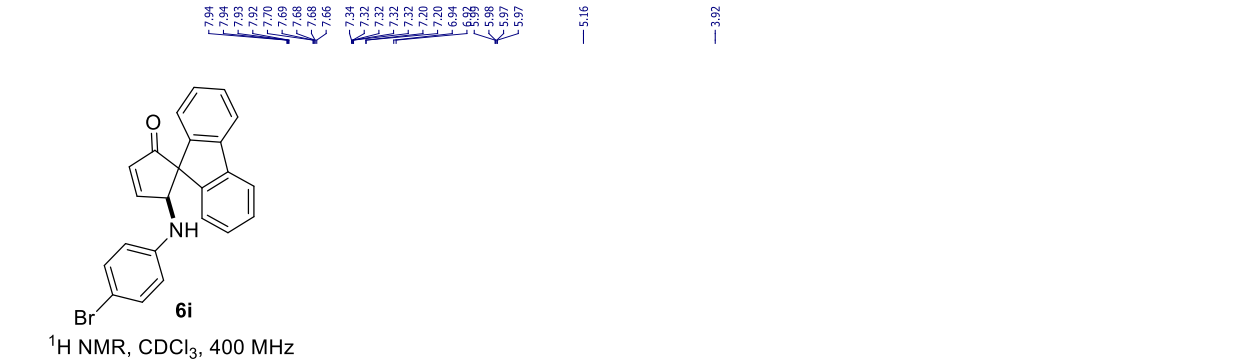


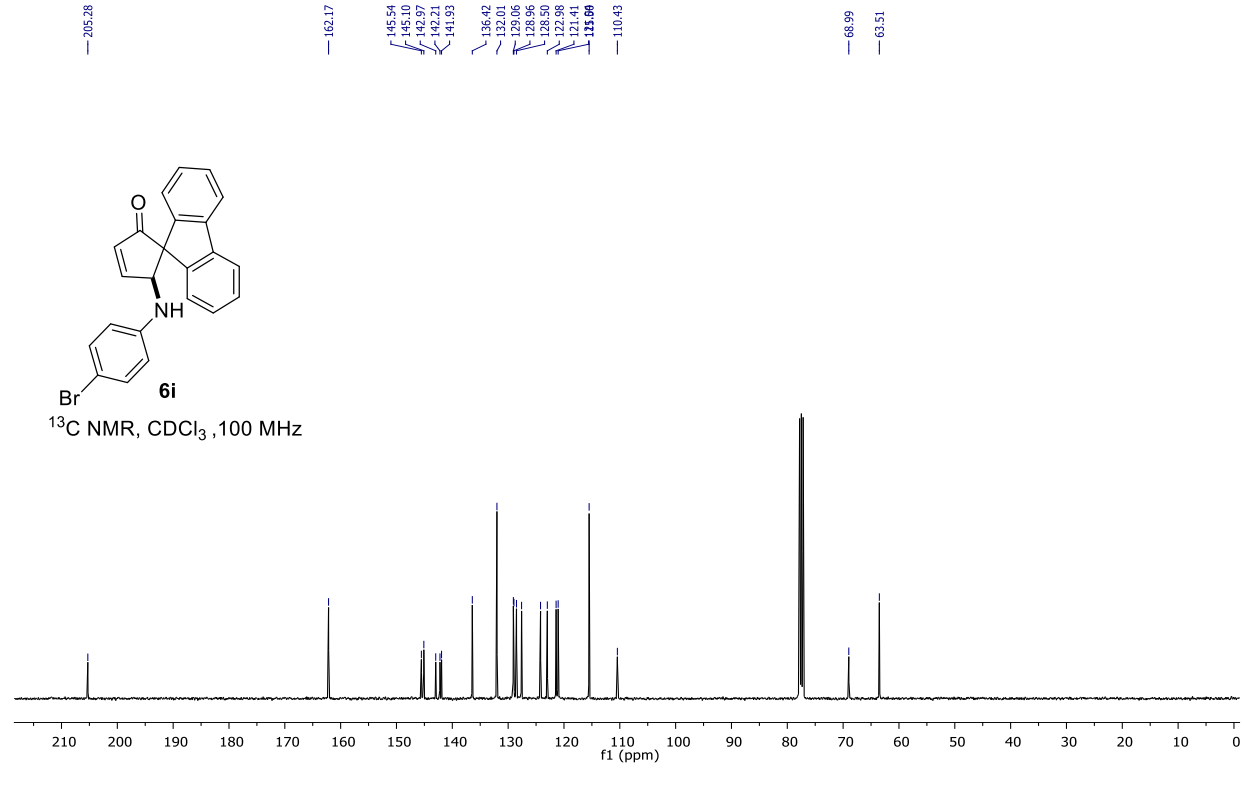
2-((4-Chlorophenyl)amino)spiro[cyclopentane-1,9'-fluoren]-3-en-5-one (6h)



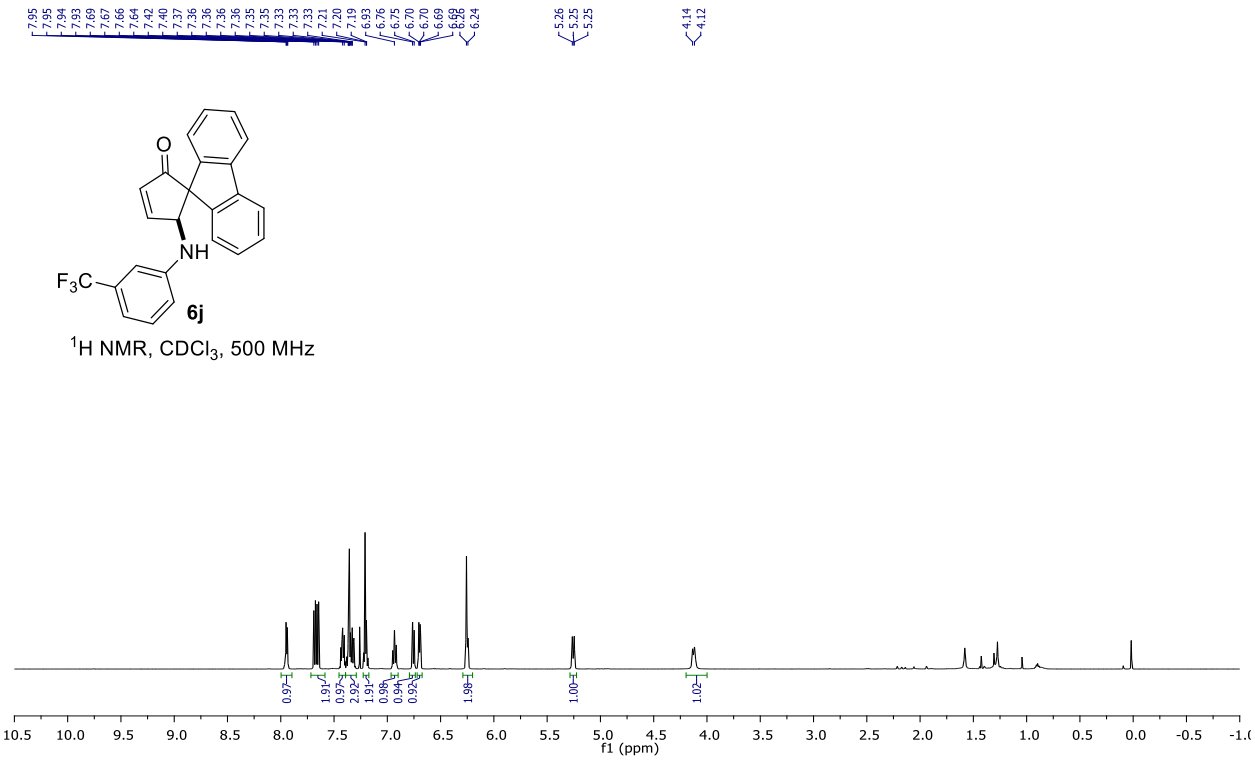


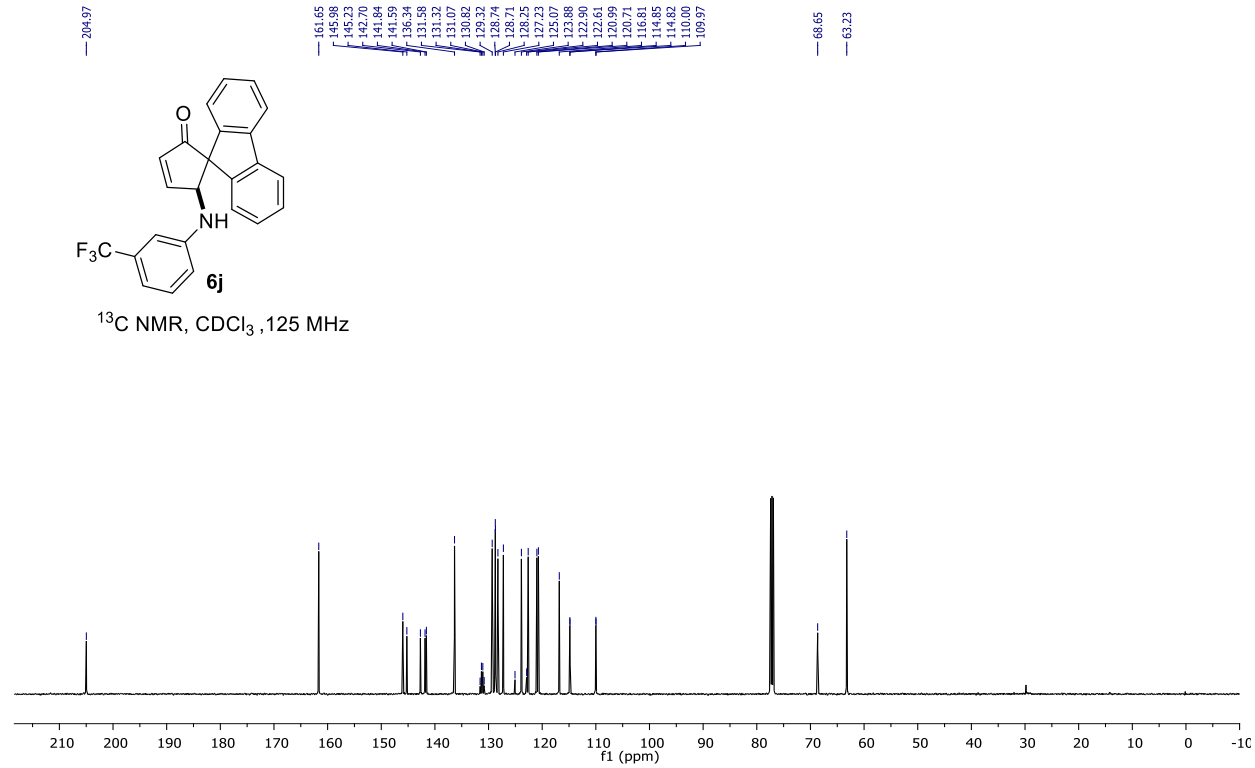
2-((4-Bromophenyl)amino)spiro[cyclopentane-1,9'-fluoren]-3-en-5-one (6i)



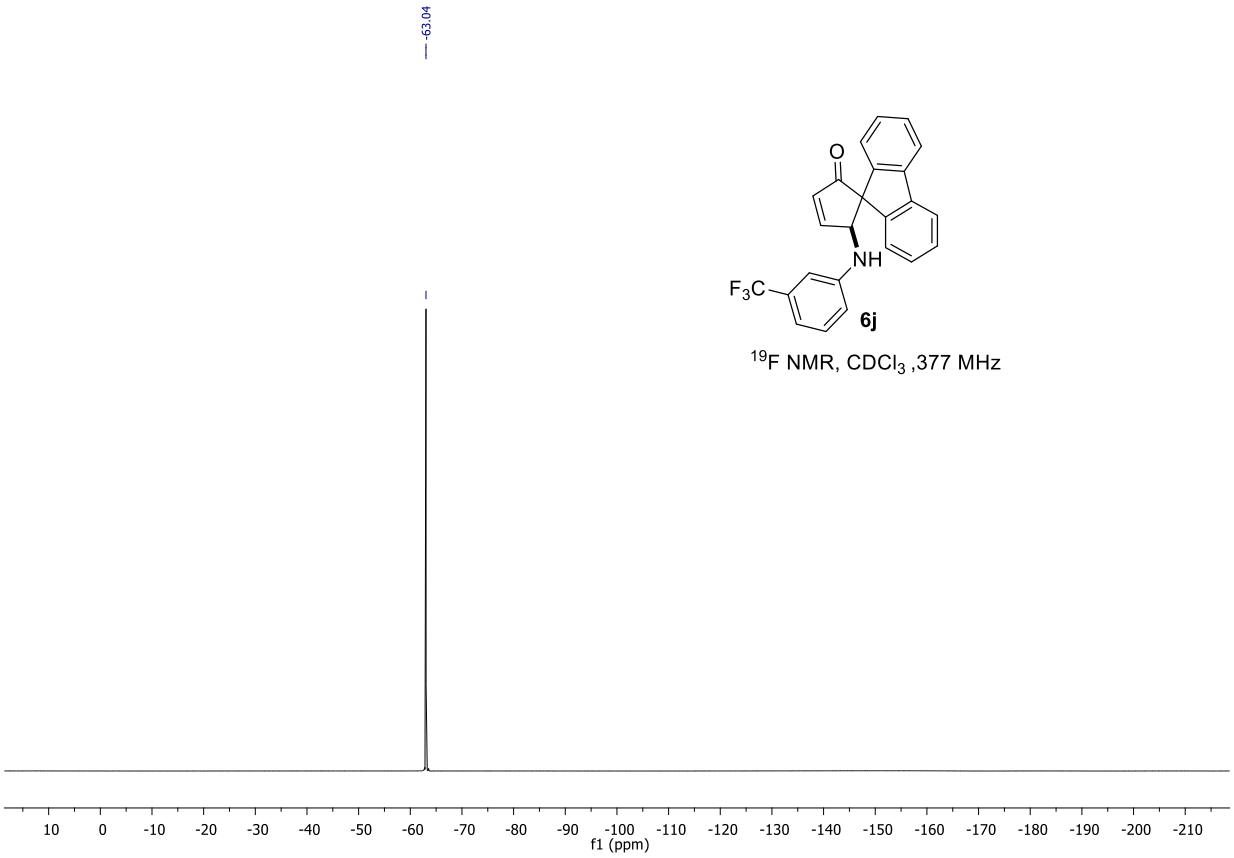


5-((3-(Trifluoromethyl)phenyl)amino)spiro[cyclopentane-1,9'-fluoren]-3-en-2-one (6j)

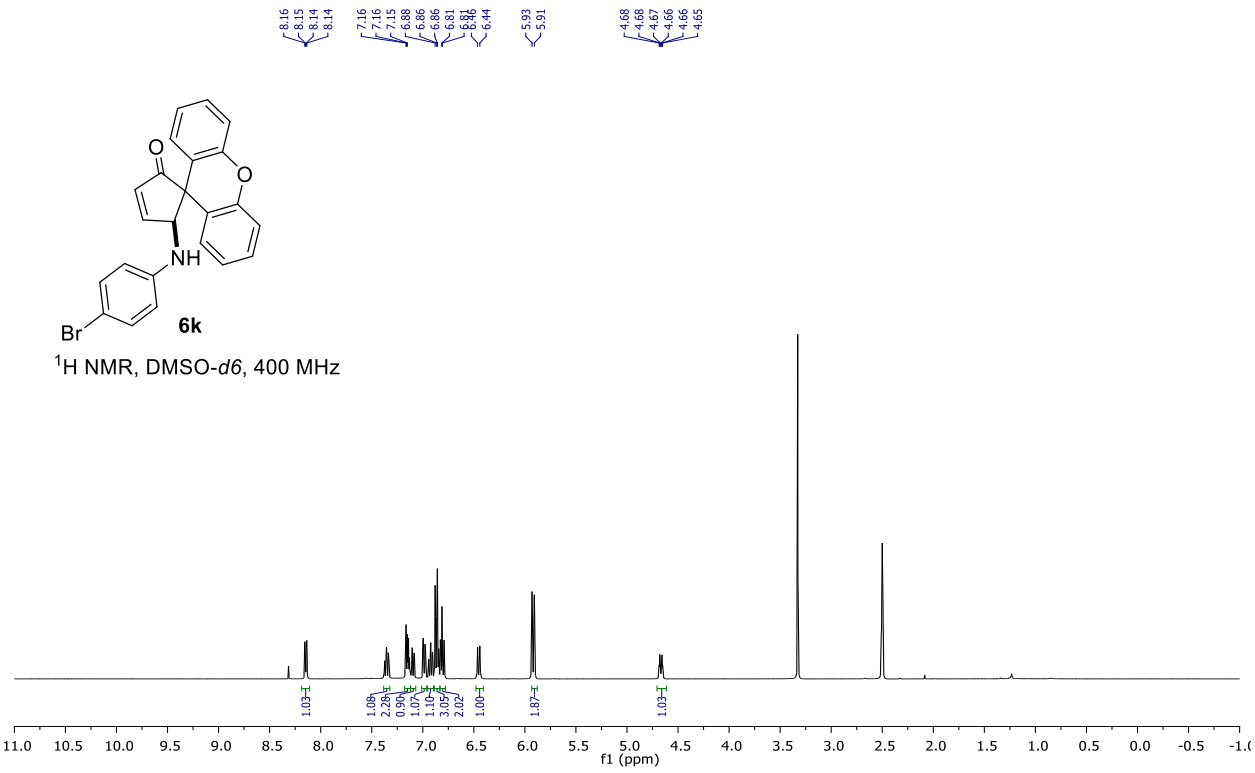


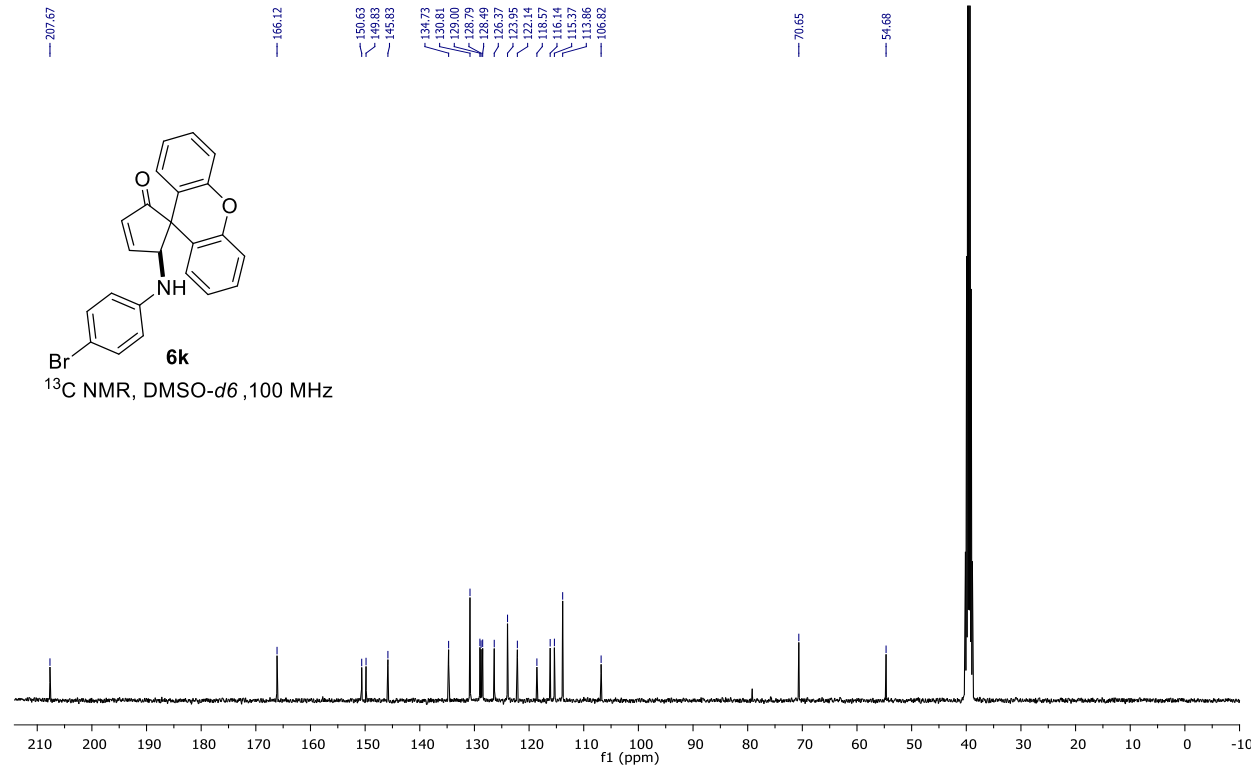


^{19}F Spectrum of compound 6j

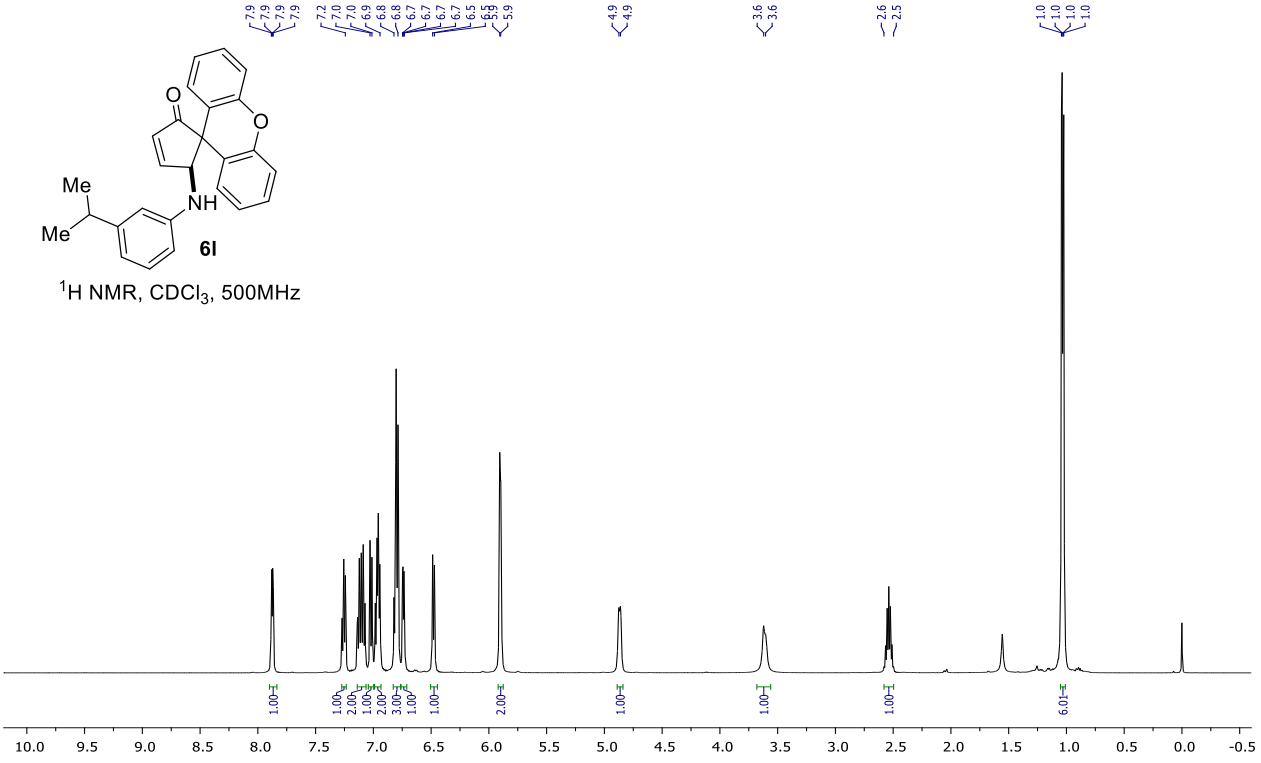


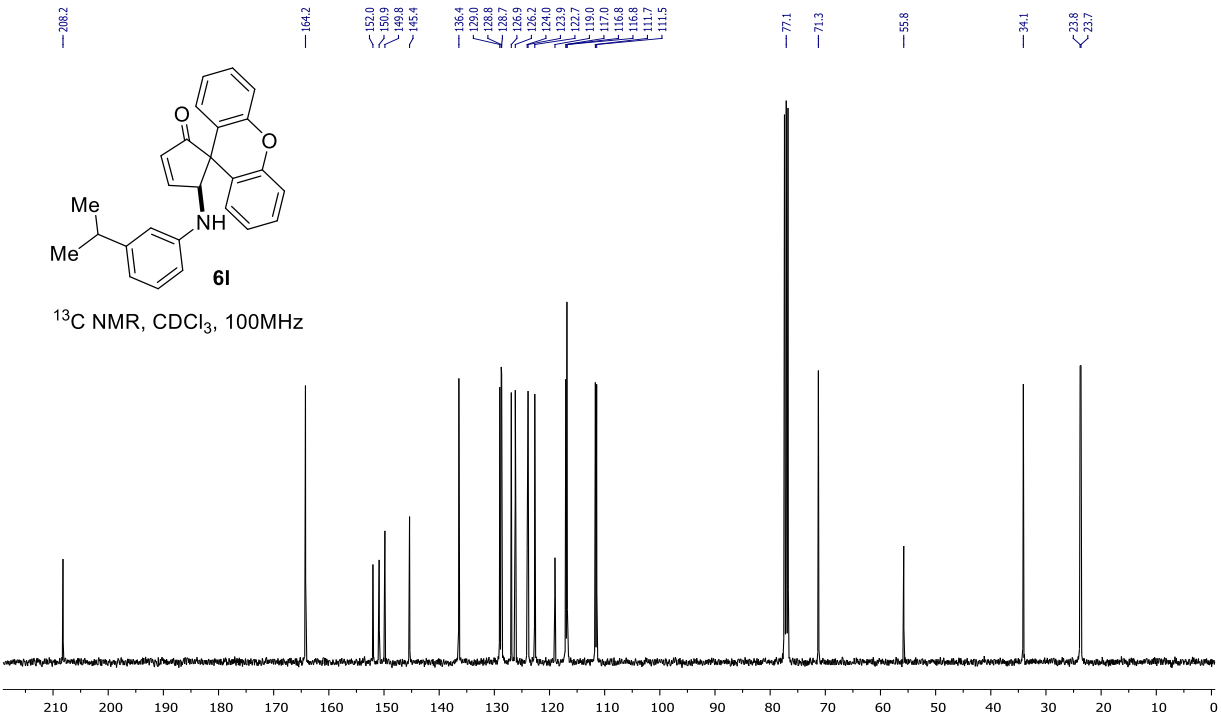
2-((4-Bromophenyl)amino)spiro[cyclopentane-1,9'-xanthen]-3-en-5-one (6k)



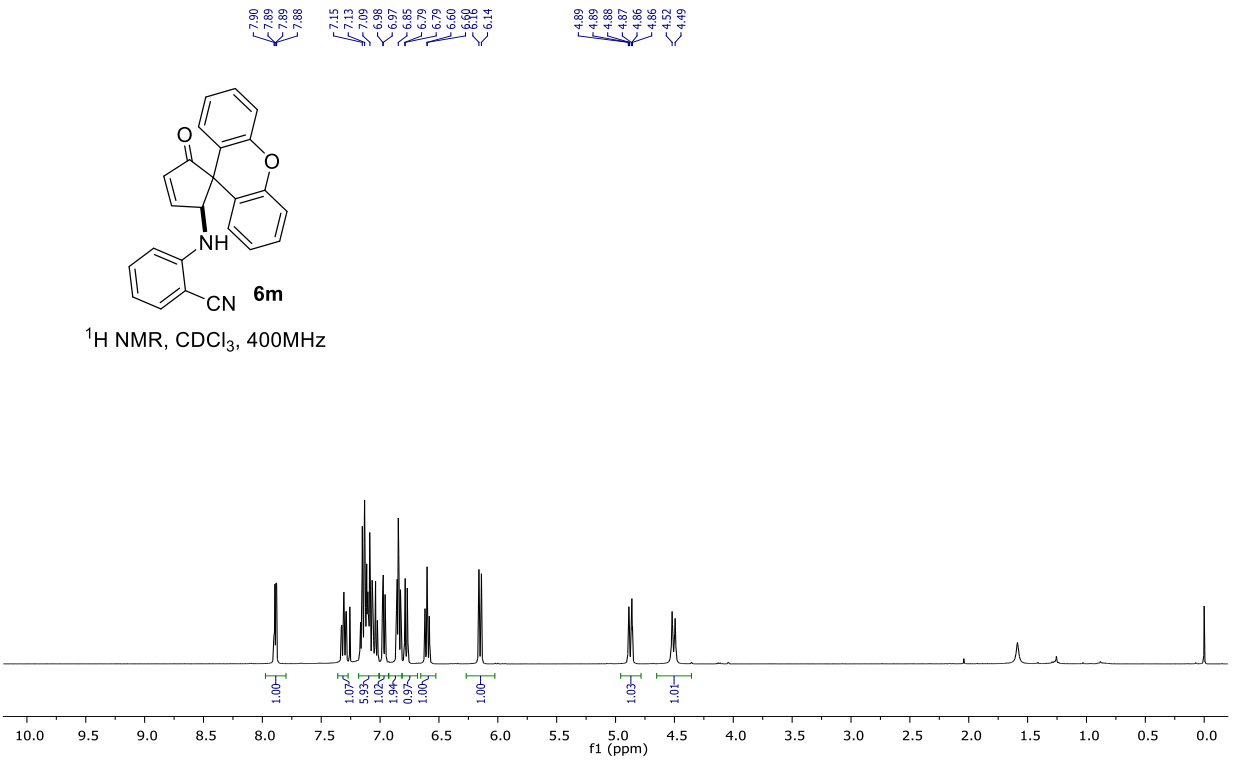


2-((2-Isopropylphenyl)amino)spiro[cyclopentane-1,9'-xanthen]-3-en-5-one (6l)

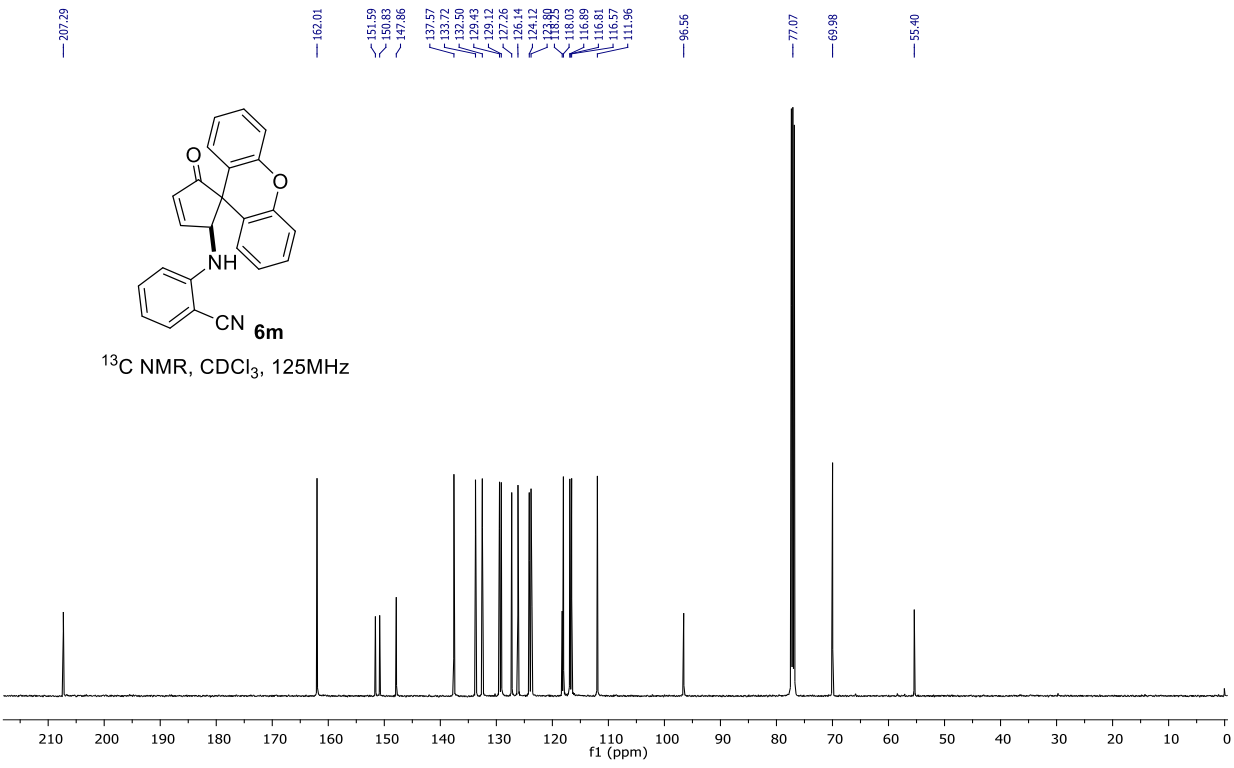




2-((2-Oxospiro[cyclopentane-1,9'-xanthen]-3-en-5-yl)amino)benzonitrile (6m)

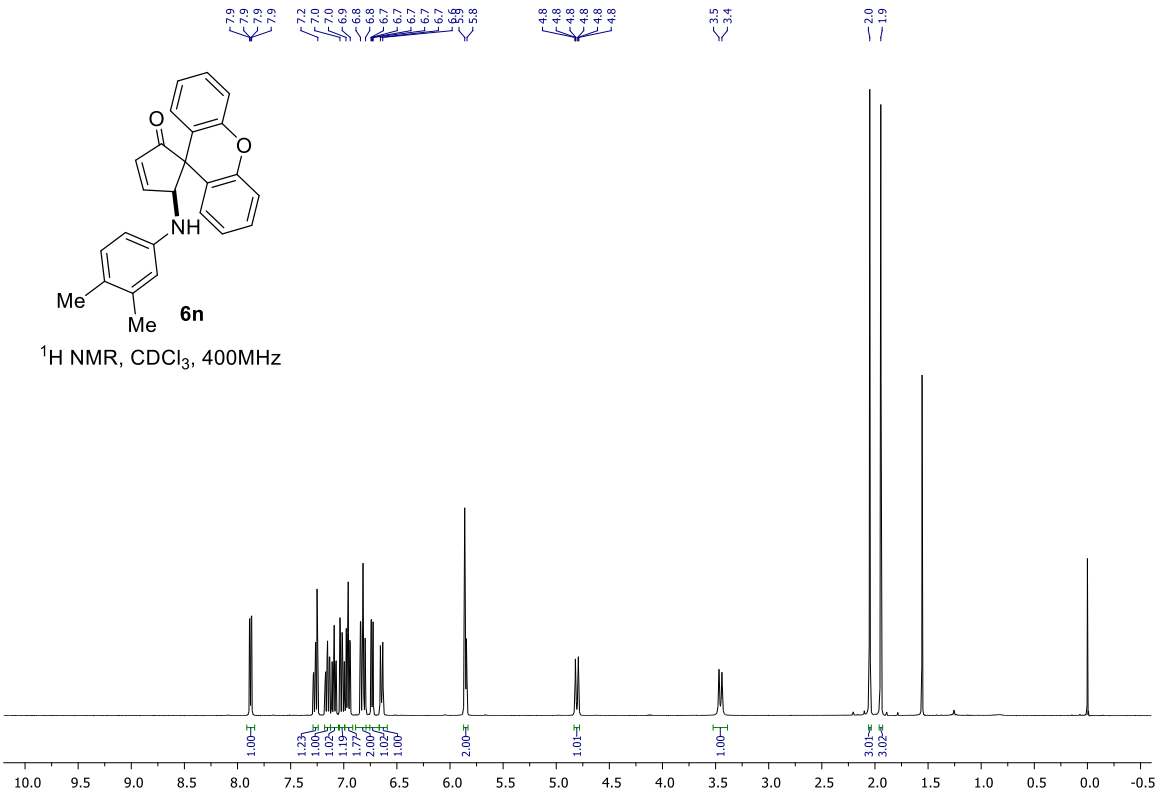


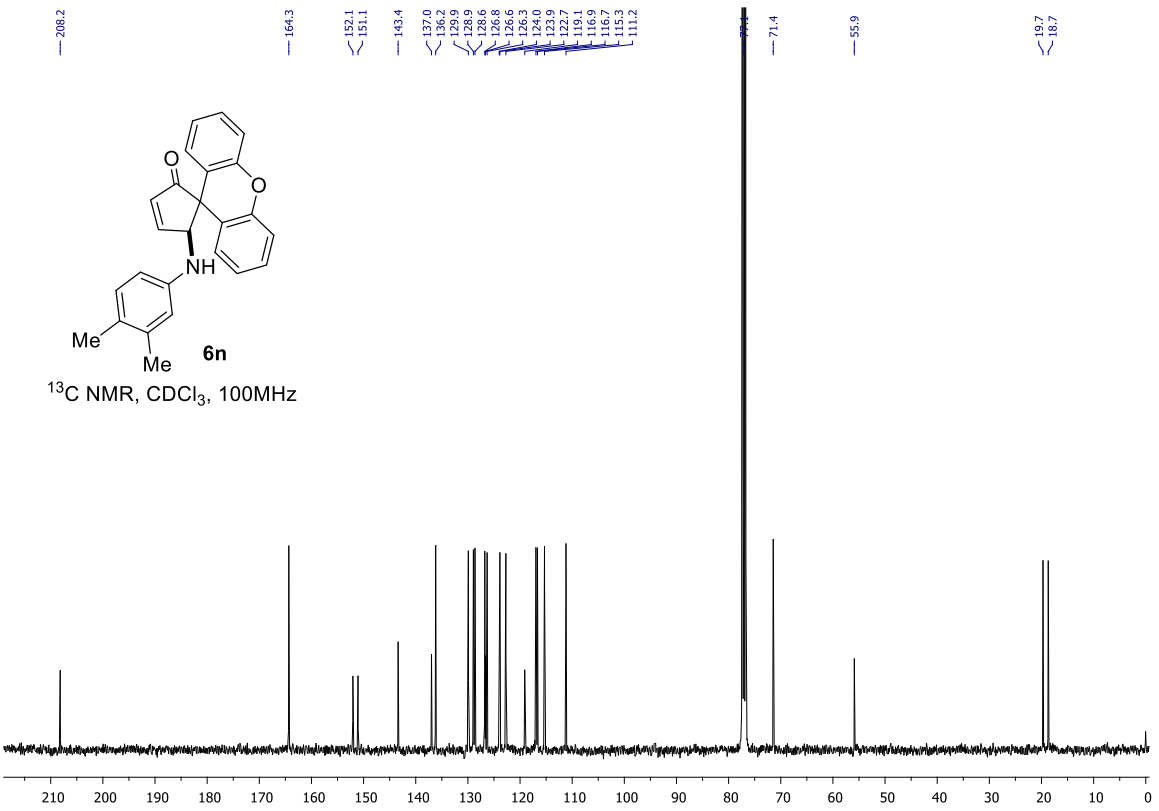
^{1}H NMR, $CDCl_3$, 400MHz



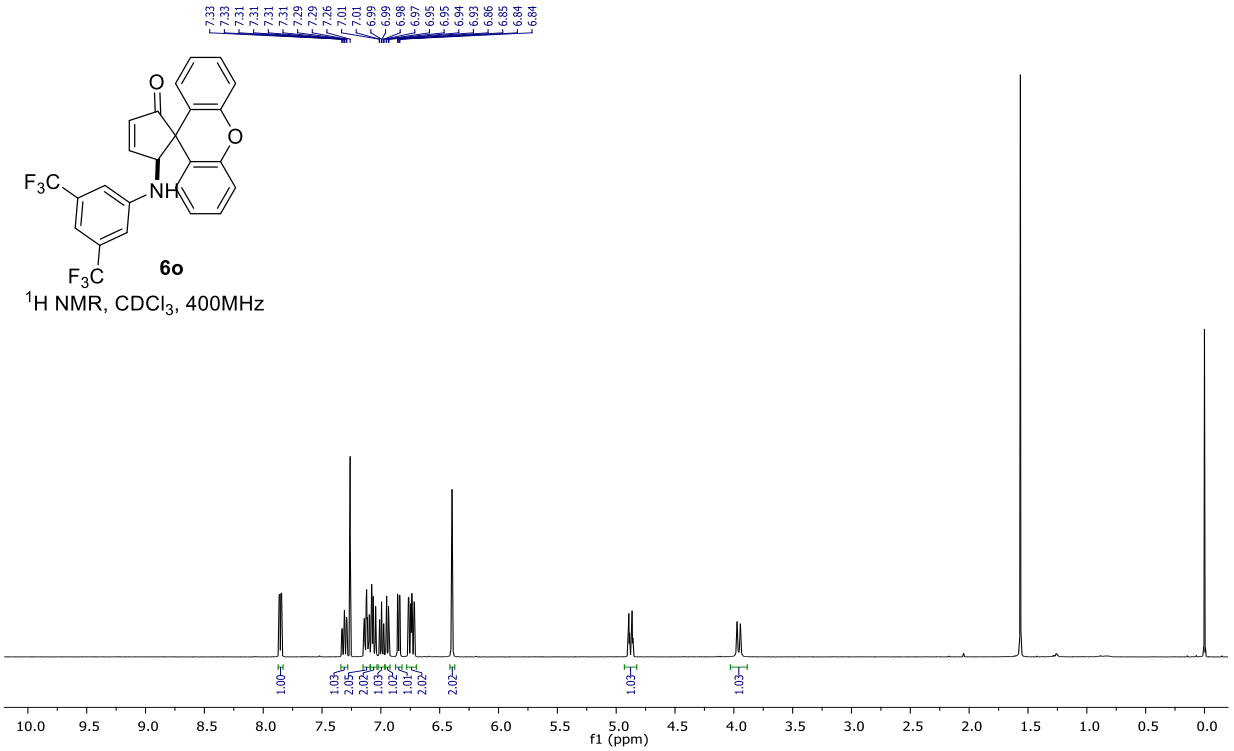
^{13}C NMR, $CDCl_3$, 125MHz

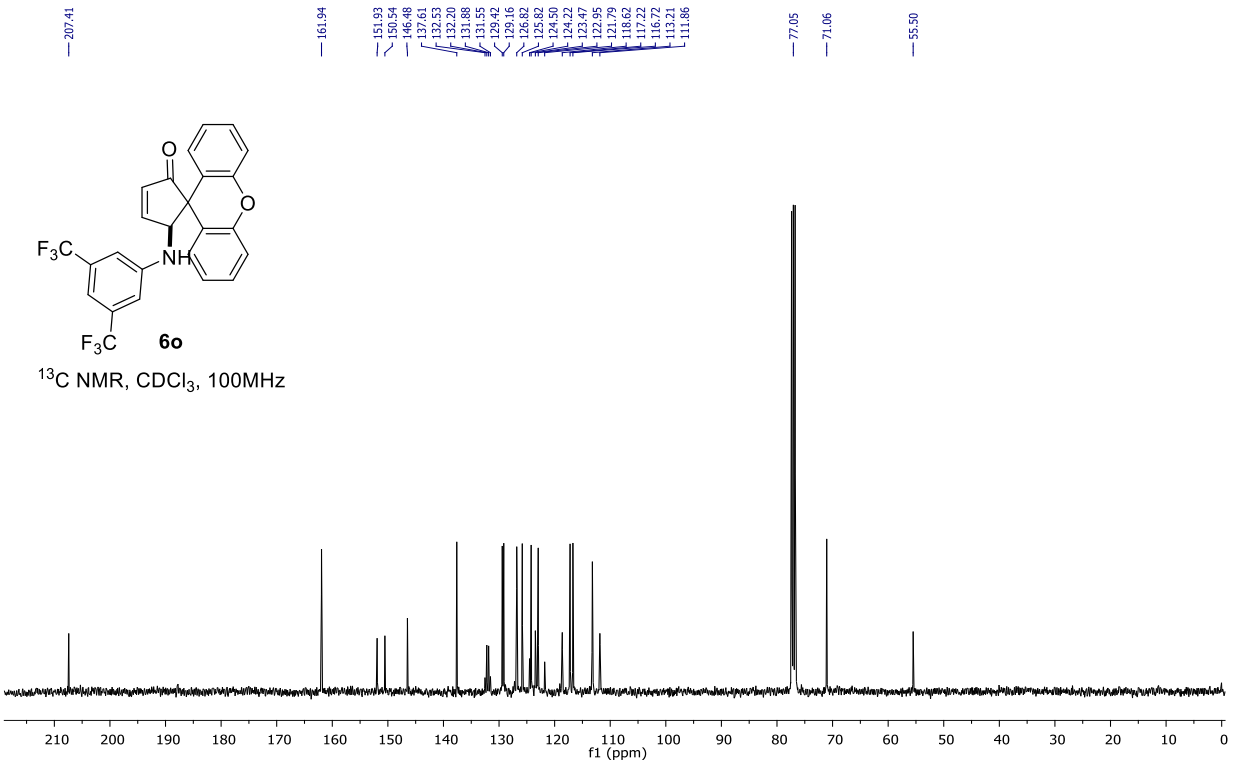
2-((3,4-Dimethylphenyl)amino)spiro[cyclopentane-1,9'-xanthen]-3-en-5-one (6n)



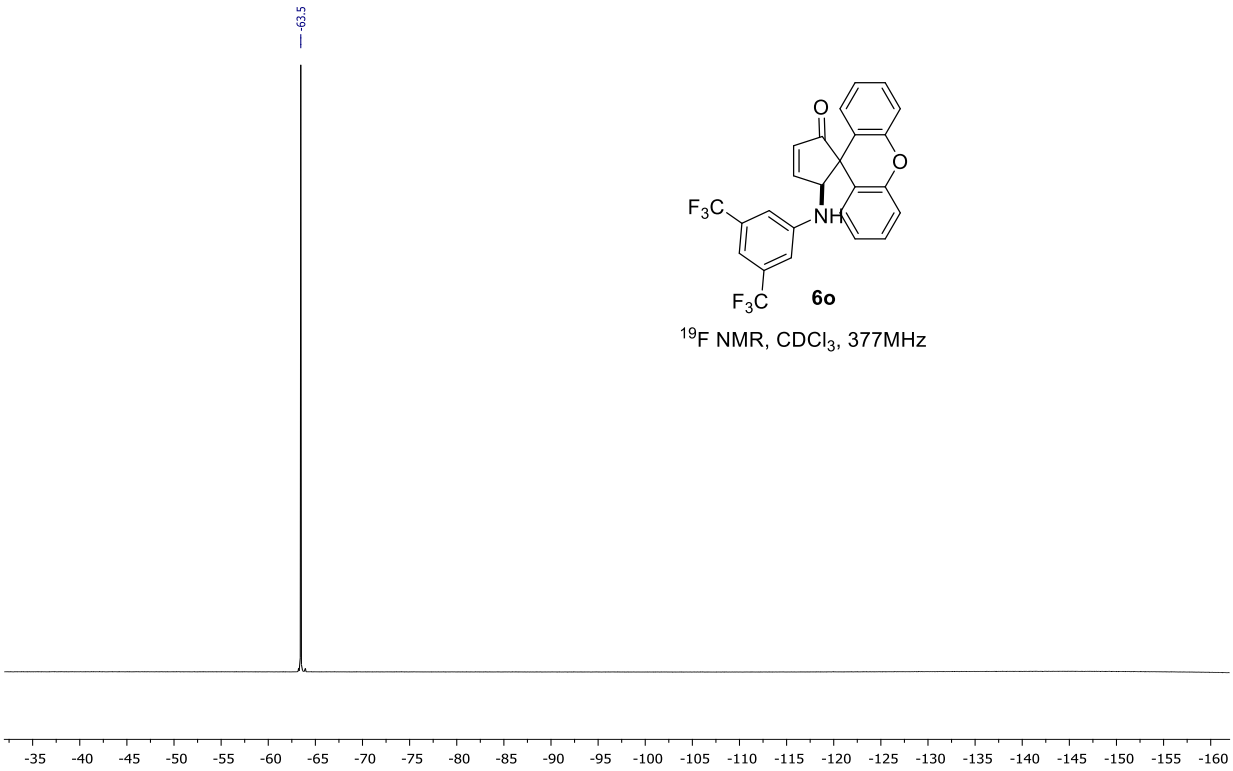


2-((3, 5-Bis(trifluoromethyl)phenyl)amino)spiro[cyclopentane-1,9'-xanthen]-3-en-5-one (6o)

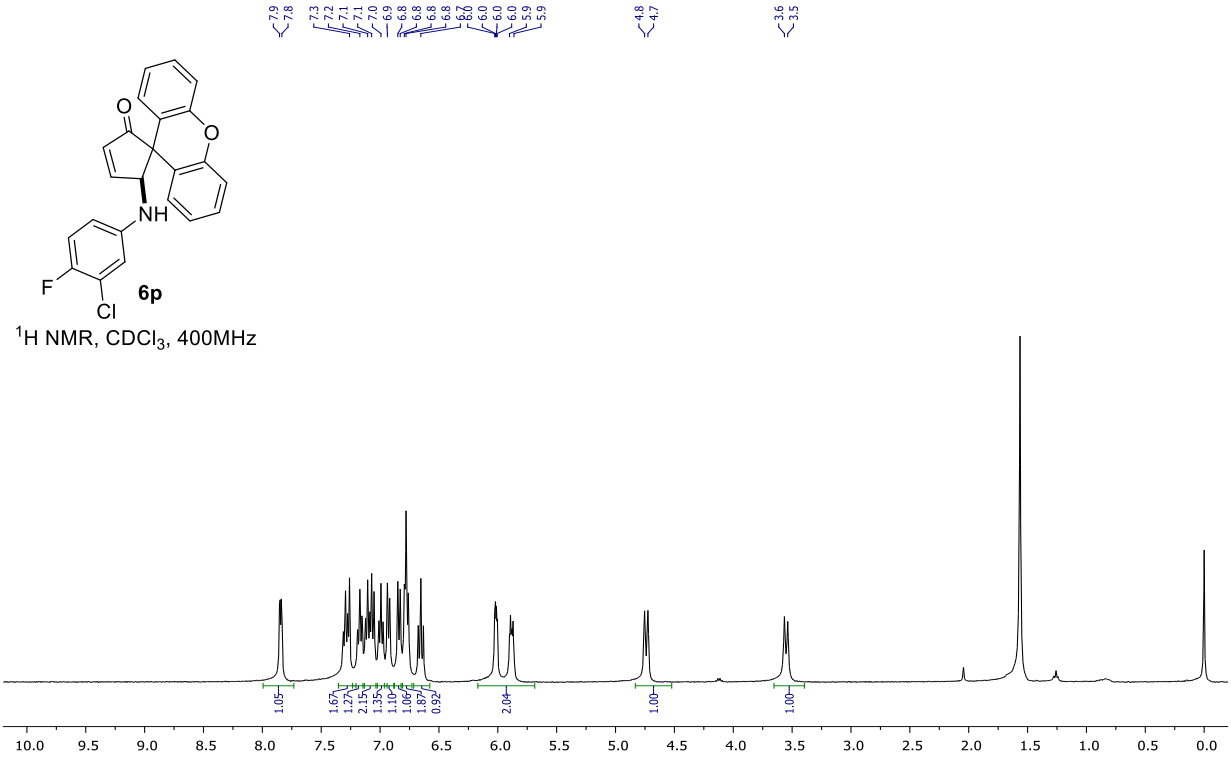


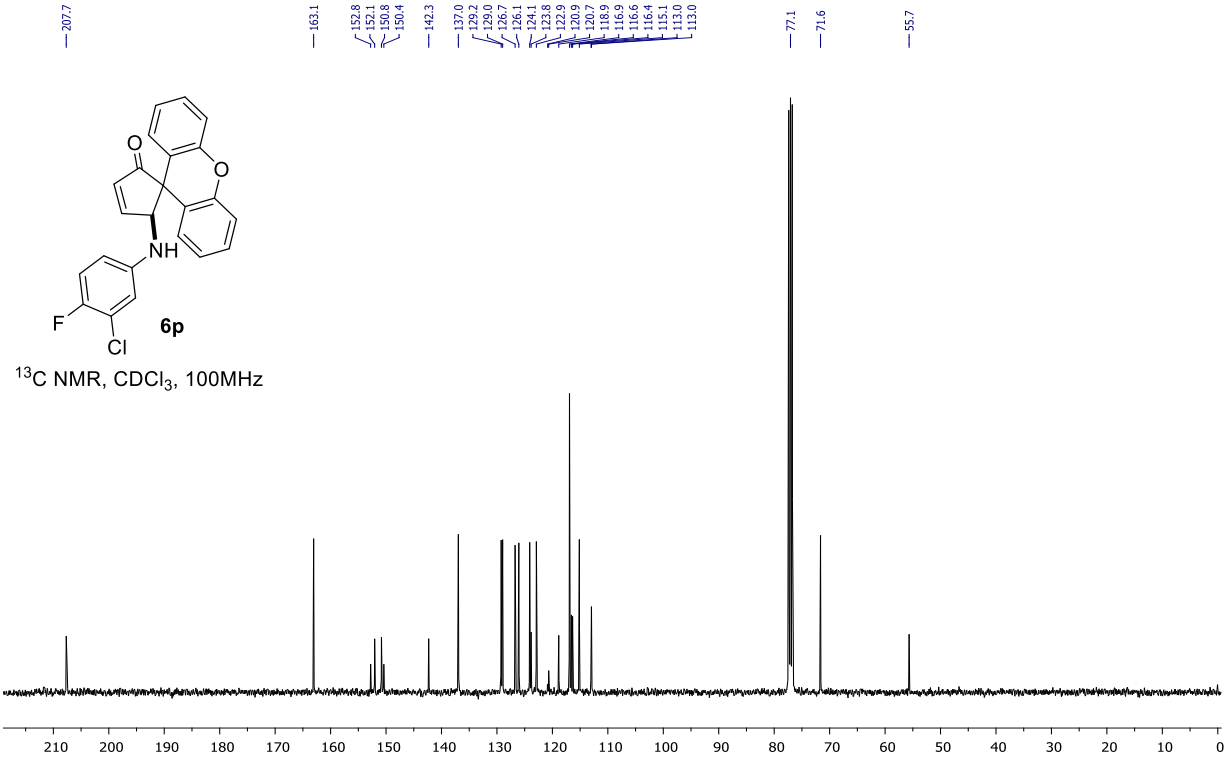


^{19}F Spectrum of compound 6o

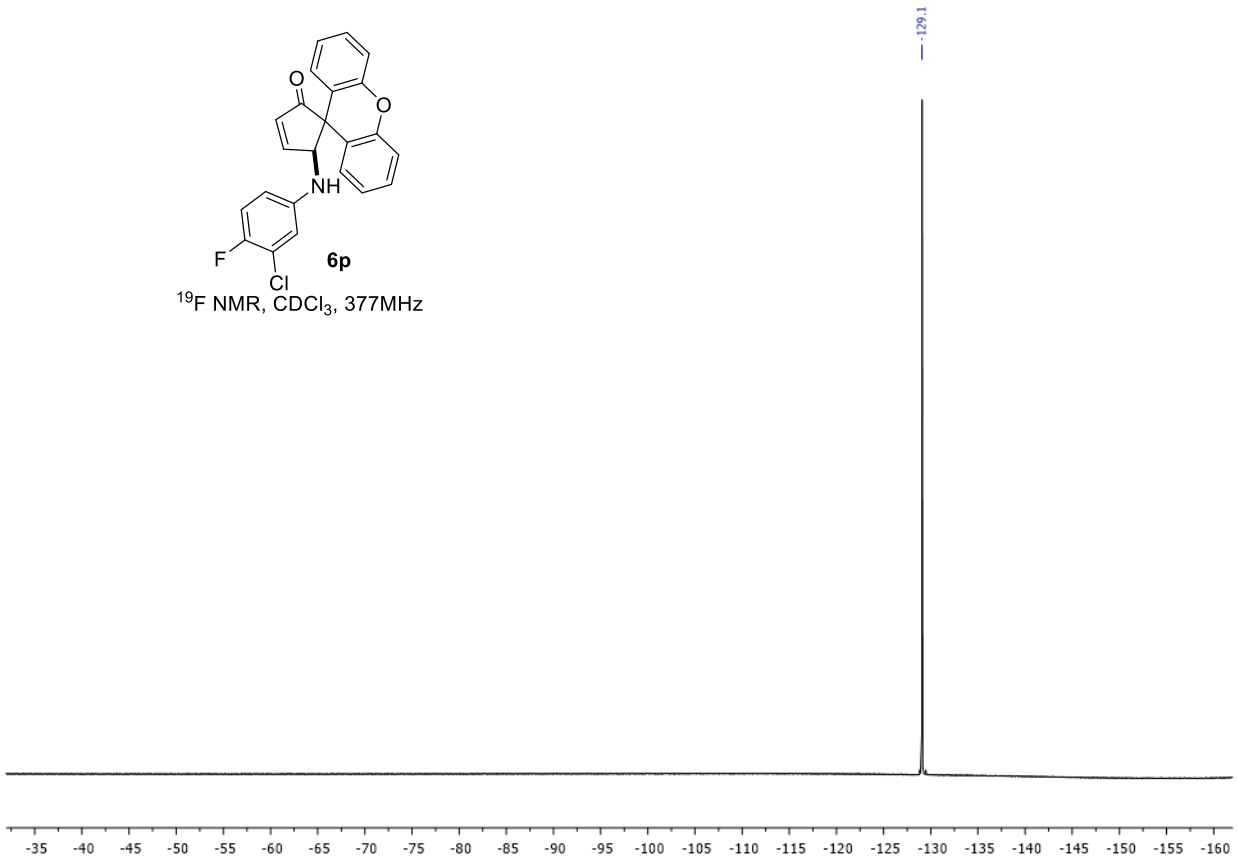


2-((3-Chloro-4-fluorophenyl)amino)spiro[cyclopentane-1,9'-xanthen]-3-en-5-one (6p)

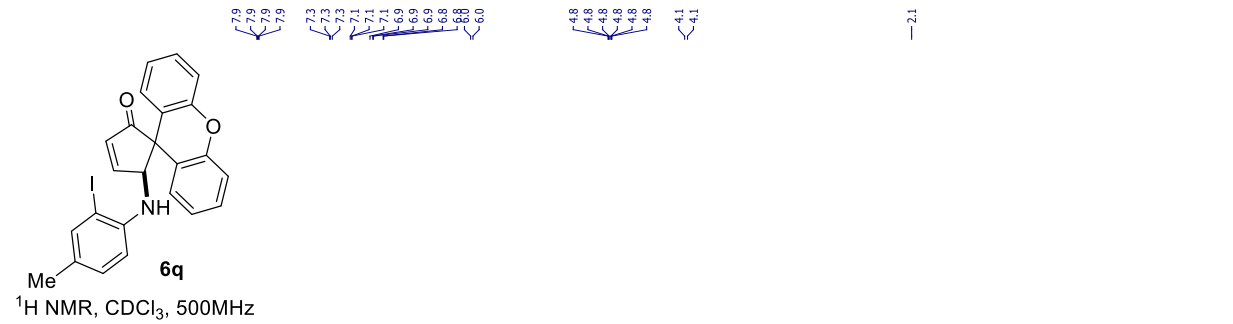




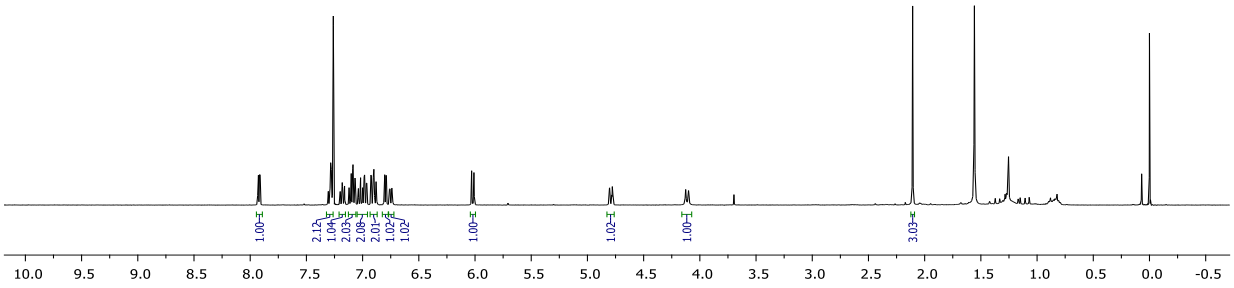
^{19}F Spectrum of compound 6p

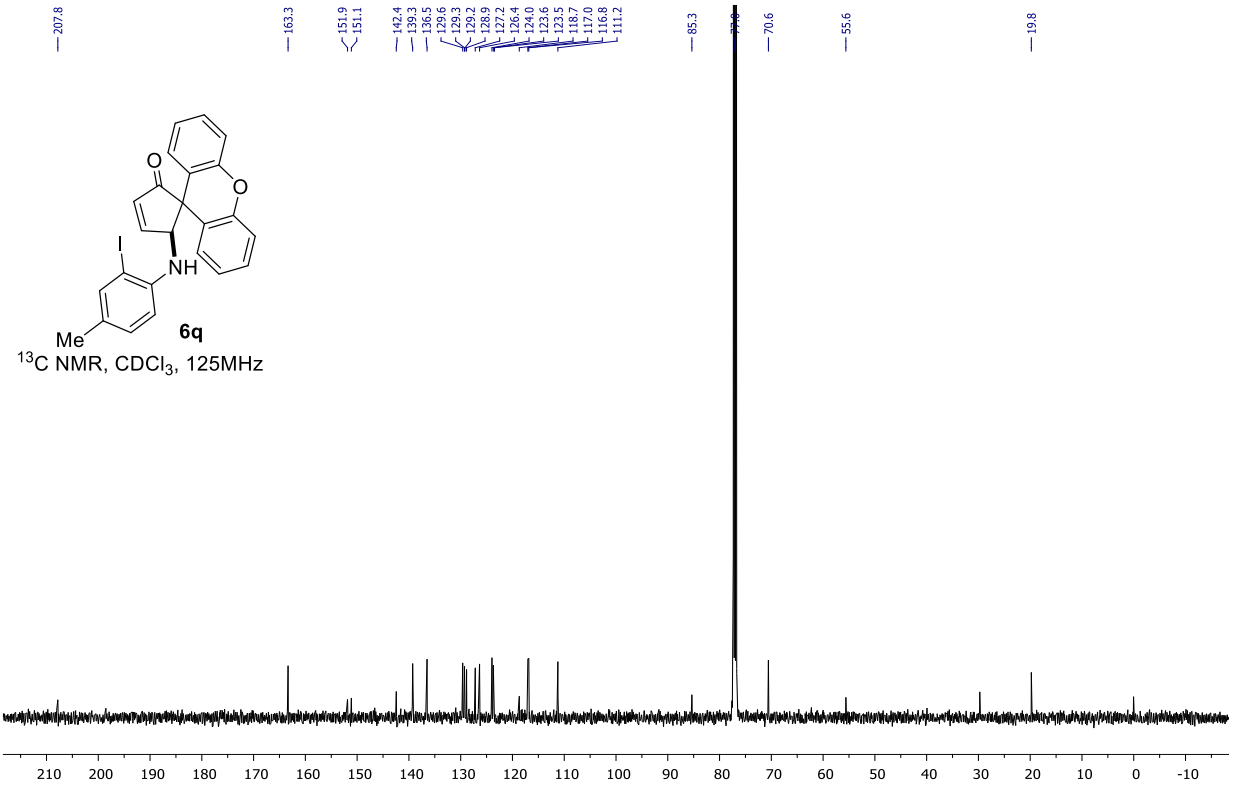


2-((2-Iodo-4-methylphenyl)amino)spiro[cyclopentane-1,9'-xanthen]-3-en-5-one (6q)



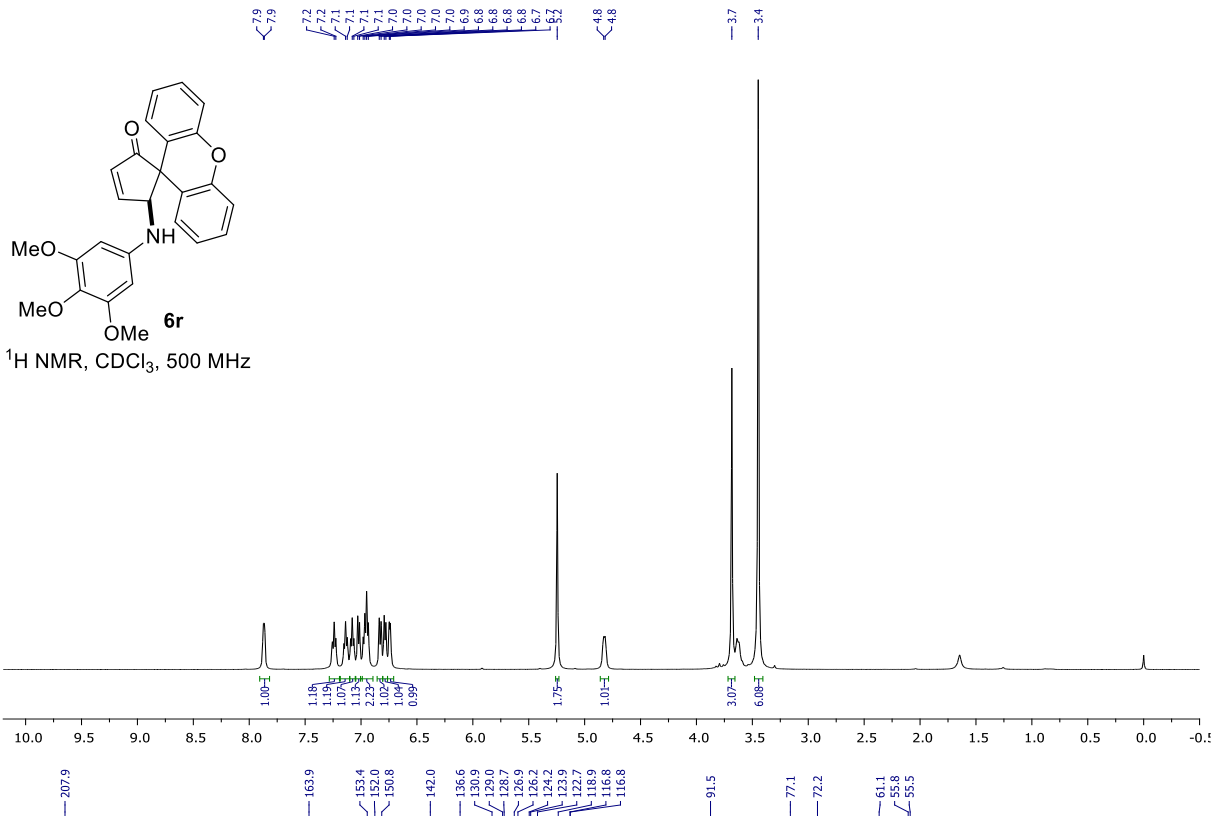
^{1}H NMR, $CDCl_3$, 500MHz

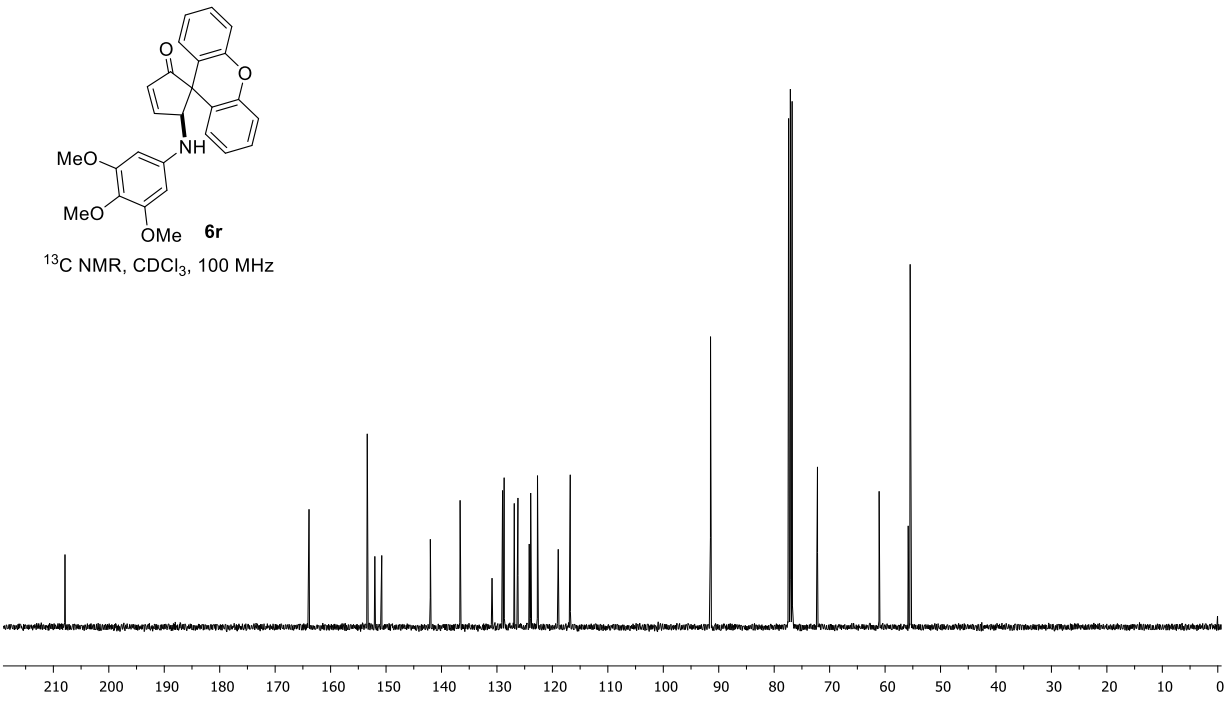




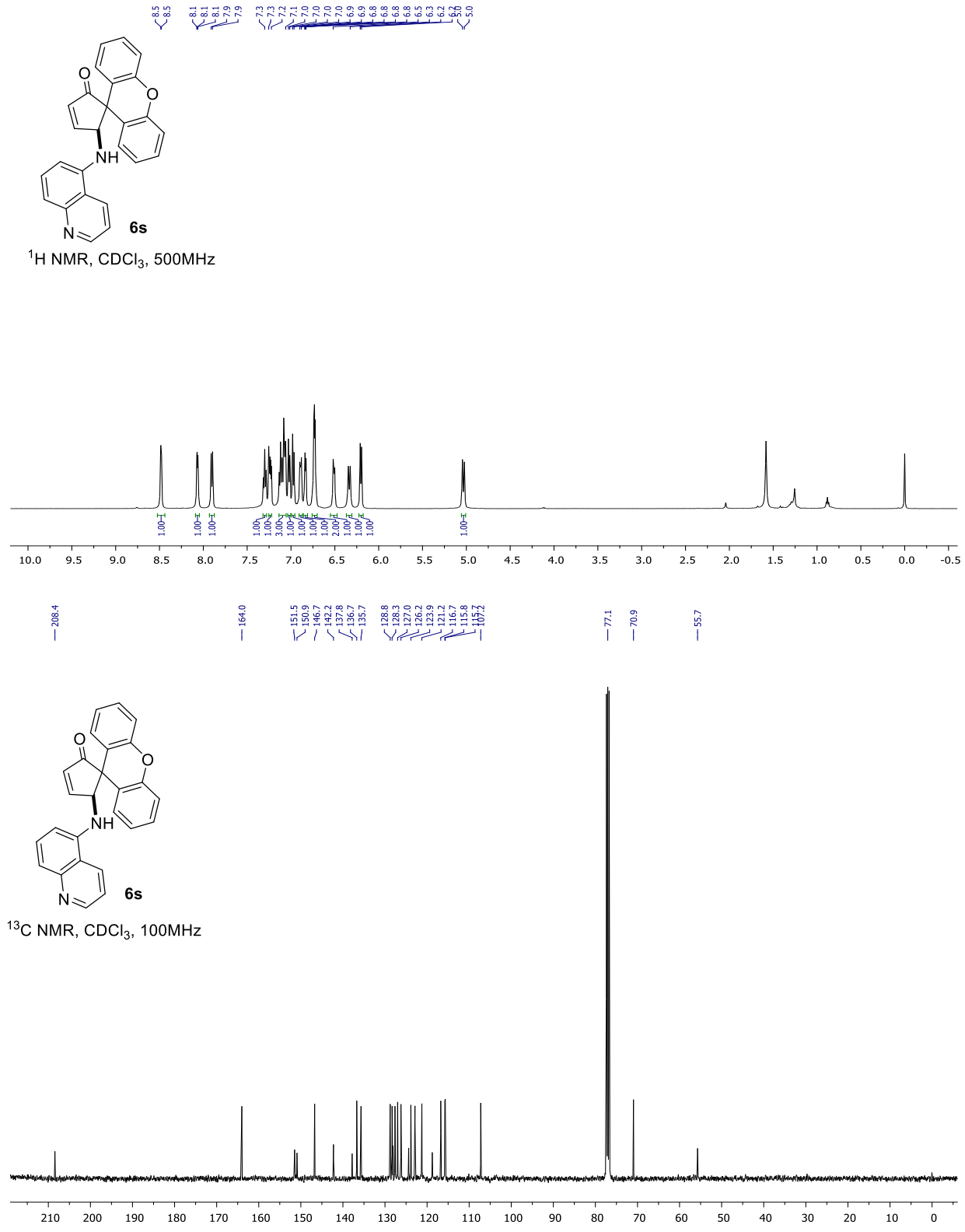
^{13}C NMR, $CDCl_3$, 125MHz

5-((3,4,5-Trimethoxyphenyl)amino)spiro[cyclopentane-1,9'-xanthen]-3-en-2-one (6r)

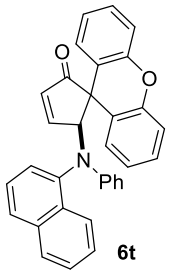




5-(Quinolin-4-ylamino)spiro[cyclopentane-1,9'-xanthen]-3-en-2-one (6s)

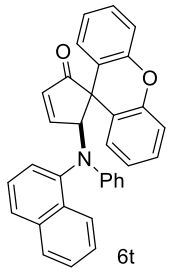


2-(Naphthalen-1-yl(phenyl)amino)spiro[cyclopentane-1,9'-xanthen]-3-en-5-one (6t)



6t

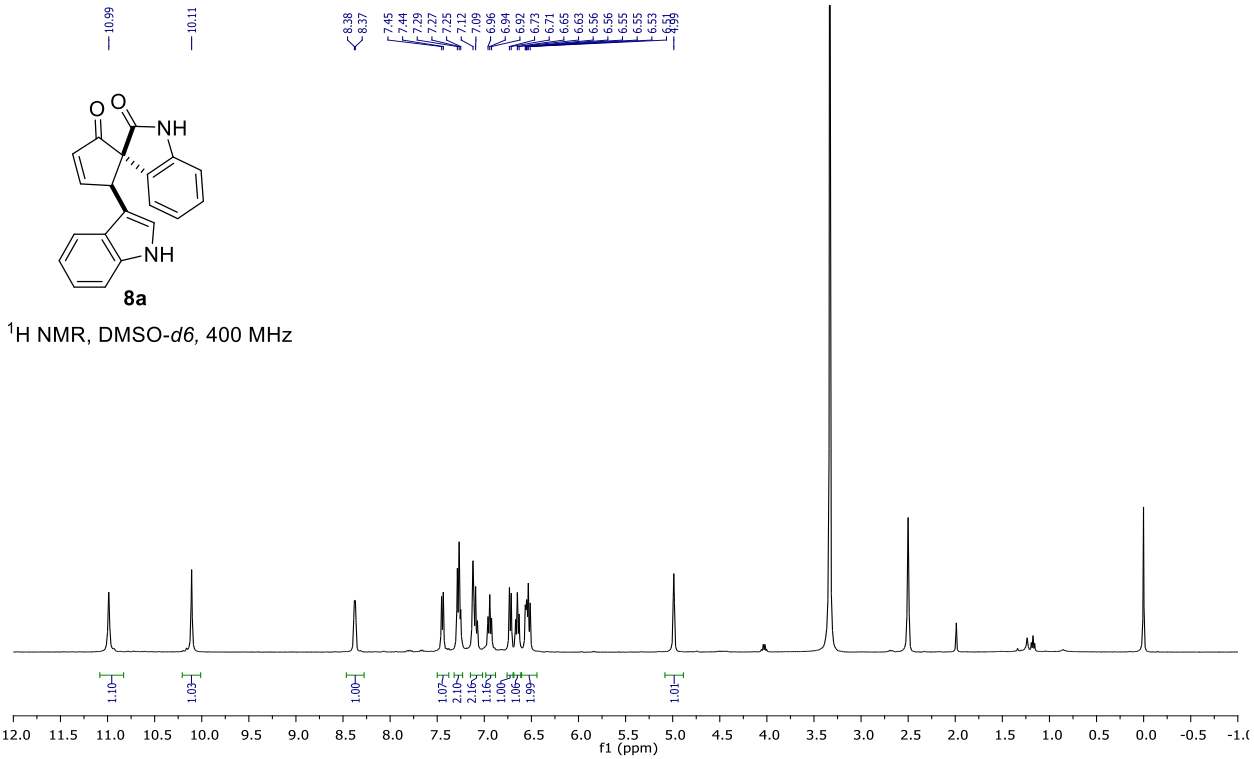
^{1}H NMR, $CDCl_3$, 500MHz



6t

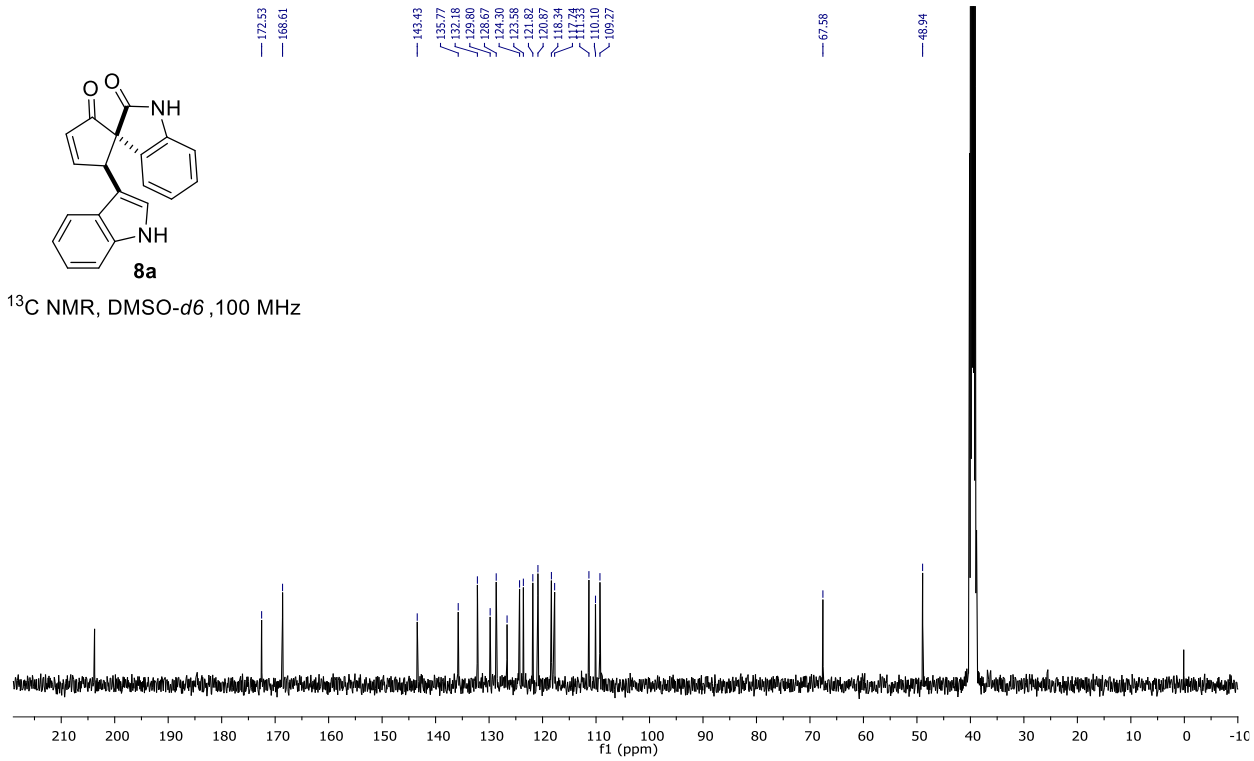
^{13}C NMR, $CDCl_3$, 100MHz

2-(1*H*-Indol-3-yl)spiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione (8a)



8a

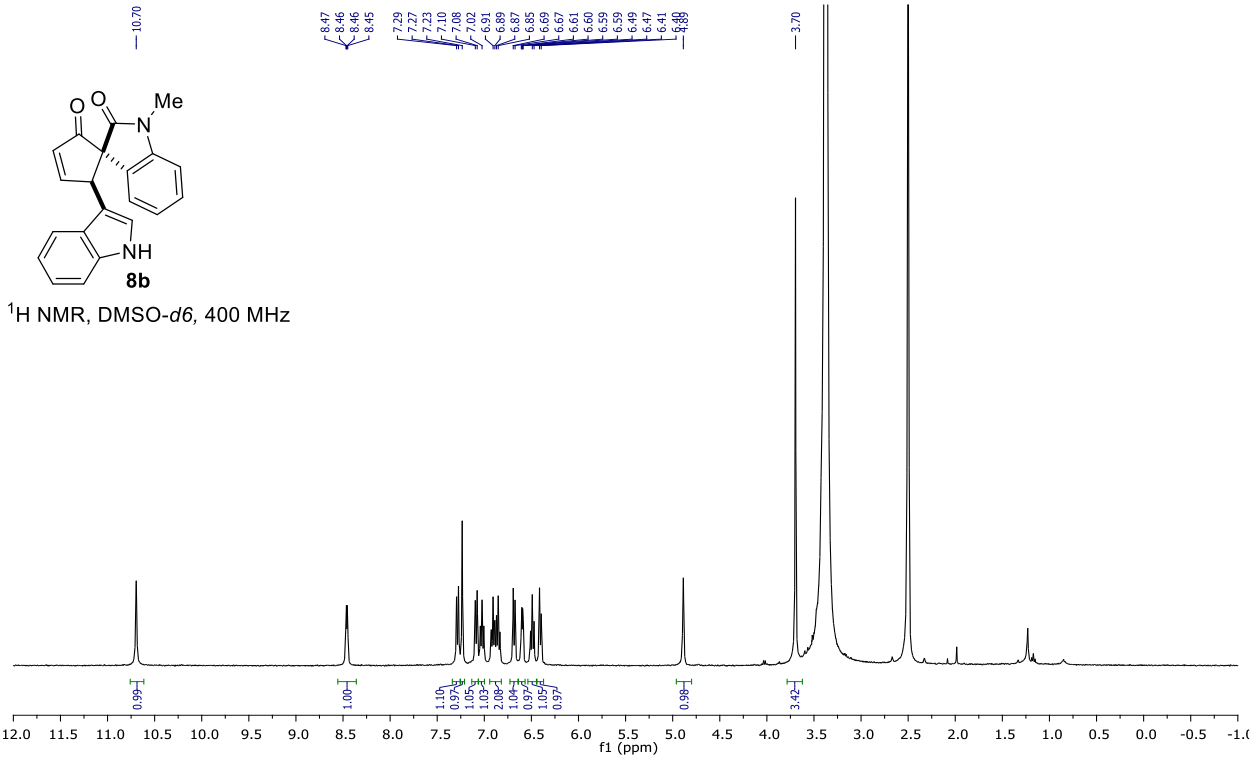
^{1}H NMR, DMSO-*d6,* 400 MHz



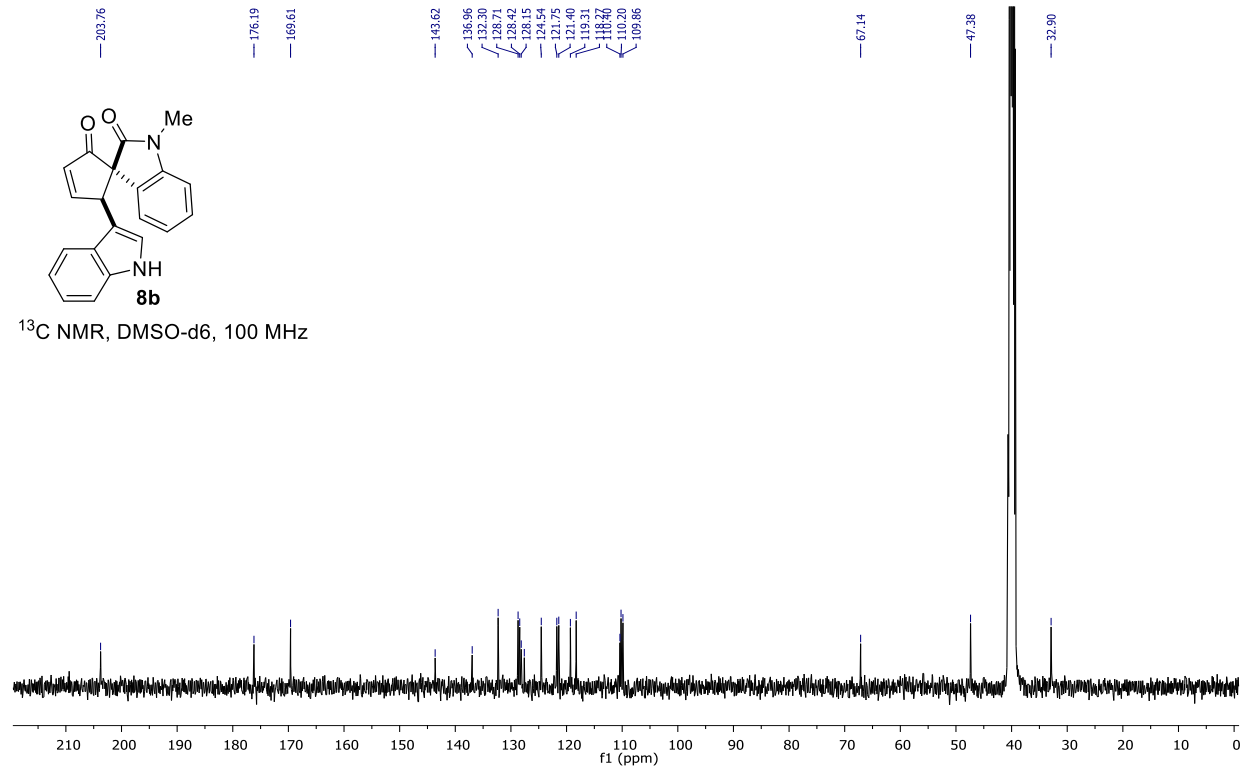
8a

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

2-(1*H*-Indol-3-yl)-1'-methylspiro[cyclopentane-1,3'-indolin]-3-ene-2',5-dione (8b)

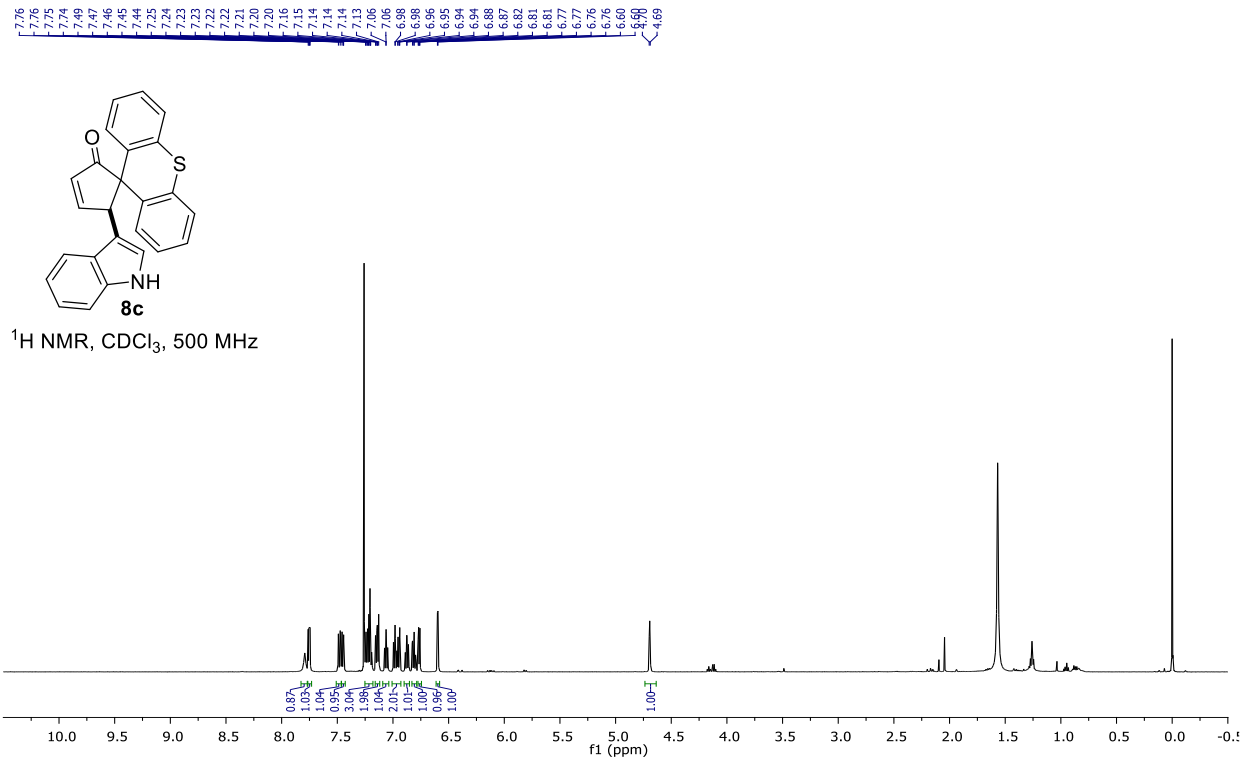


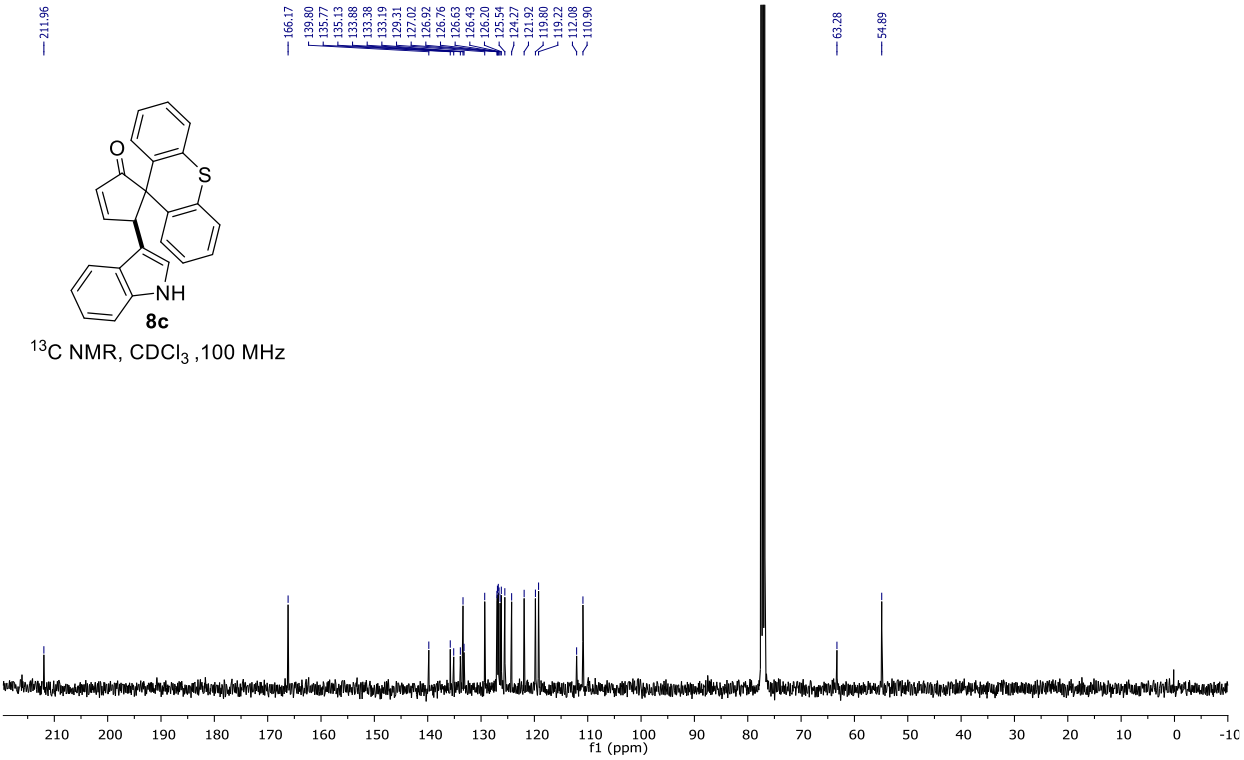
^{1}H NMR, DMSO-*d6,* 400 MHz



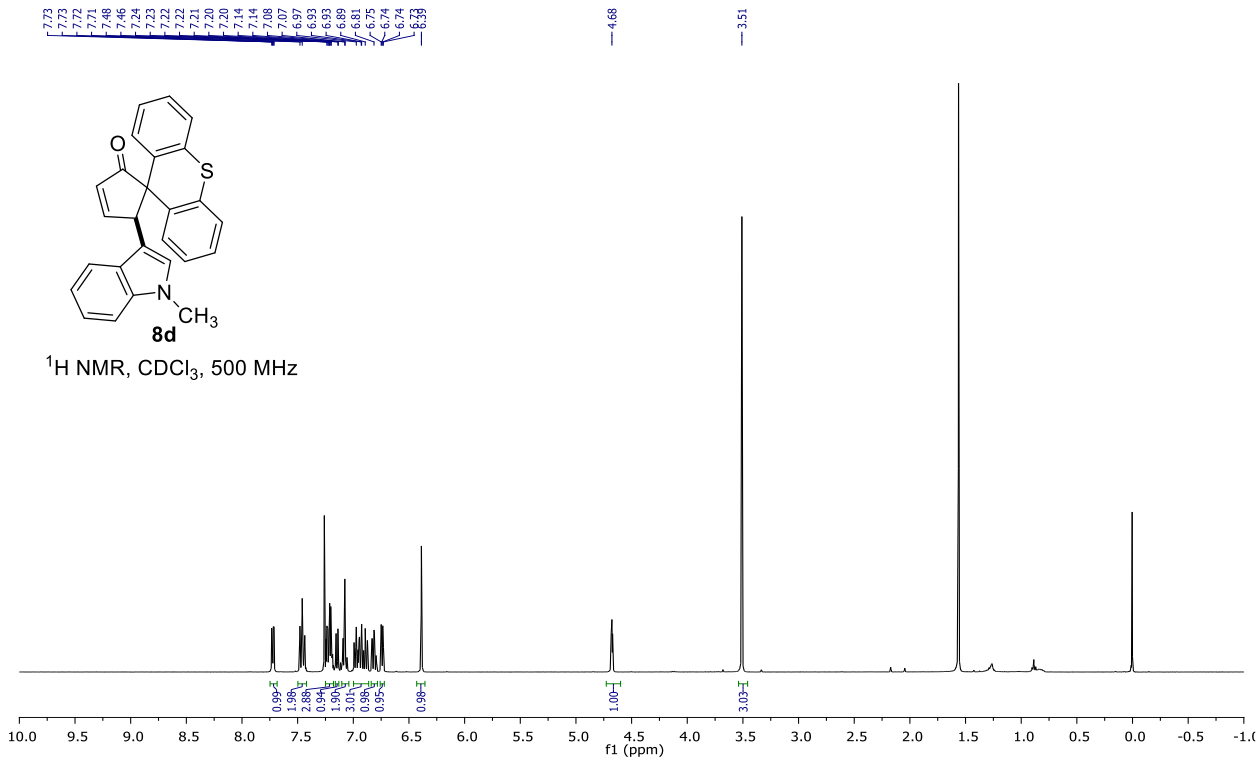
^{13}C NMR, DMSO-d6, 100 MHz

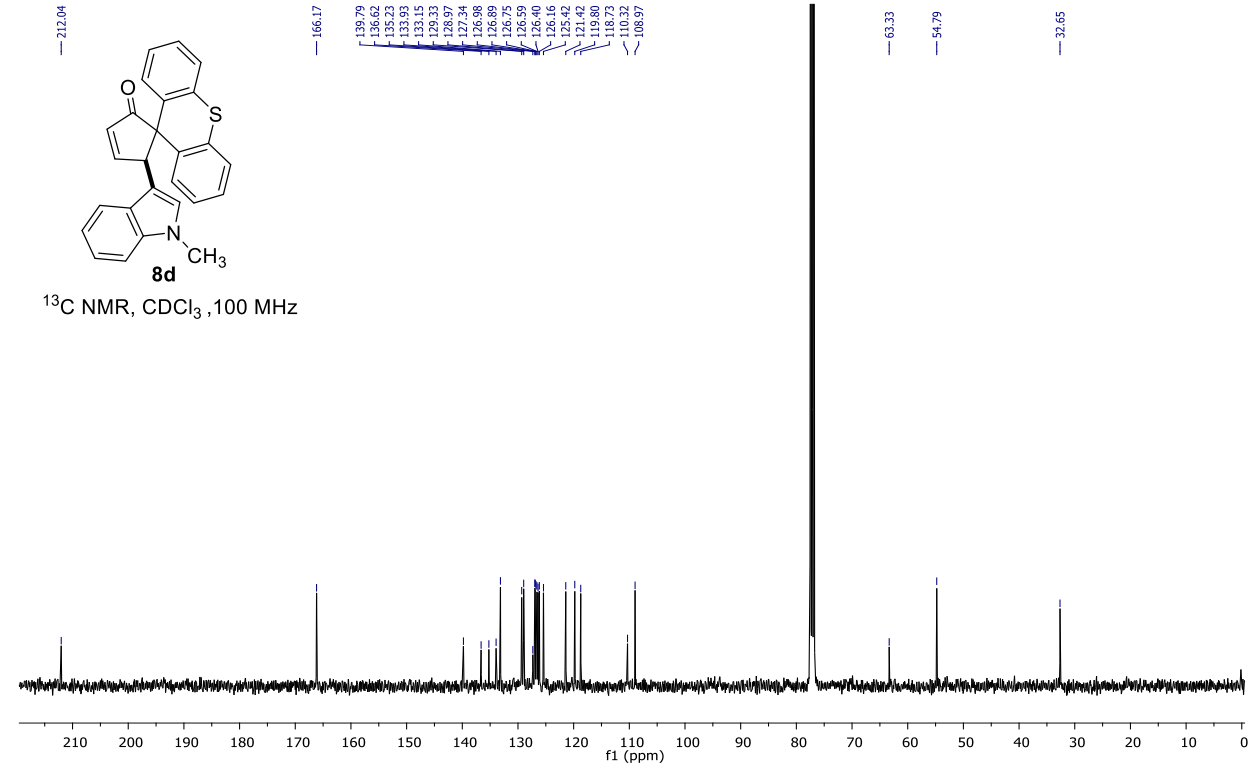
2-(1*H*-Indol-3-yl)spiro[cyclopentane-1,9'-thioxanthen]-3-en-5-one (8c)



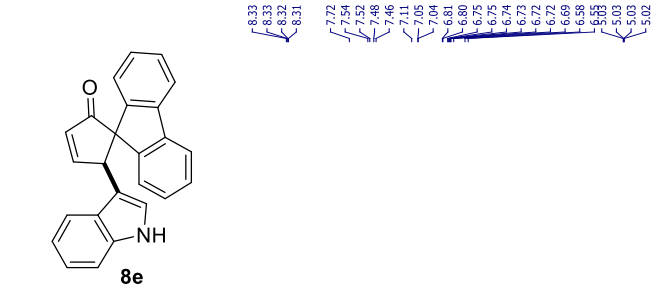


2-(1-Methyl-1*H*-indol-3-yl)spiro[cyclopentane-1,9'-thioxanthen]-3-en-5-one (8d)



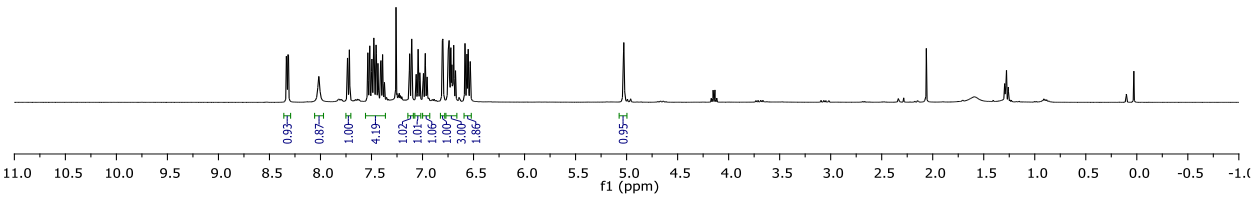


2-(1*H*-Indol-3-yl)spiro[cyclopentane-1,9'-fluoren]-3-en-5-one (8e)



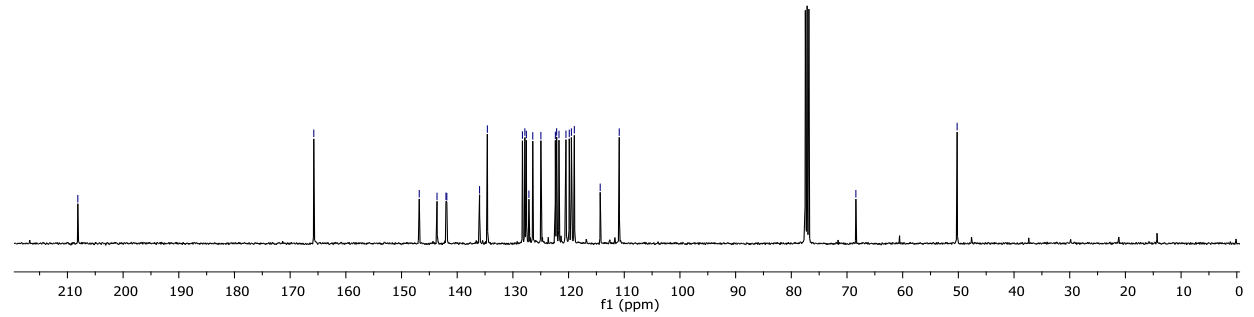
8e

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

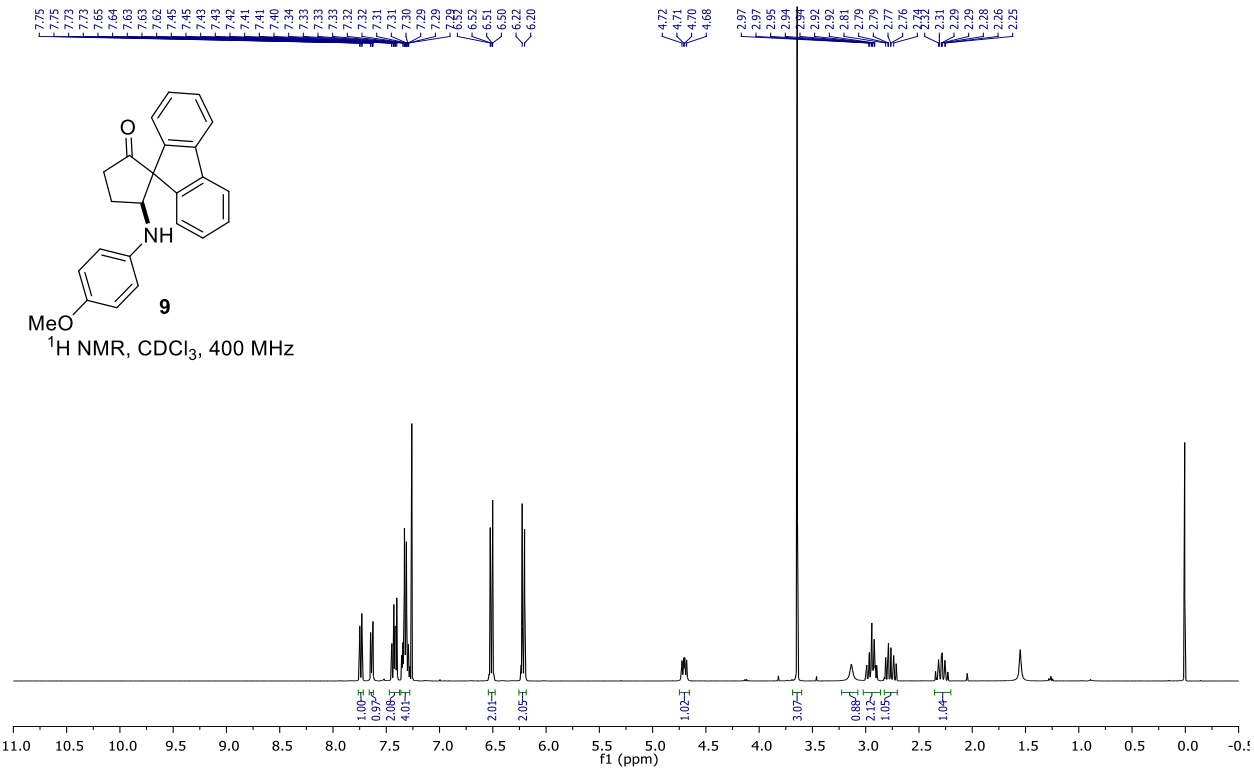


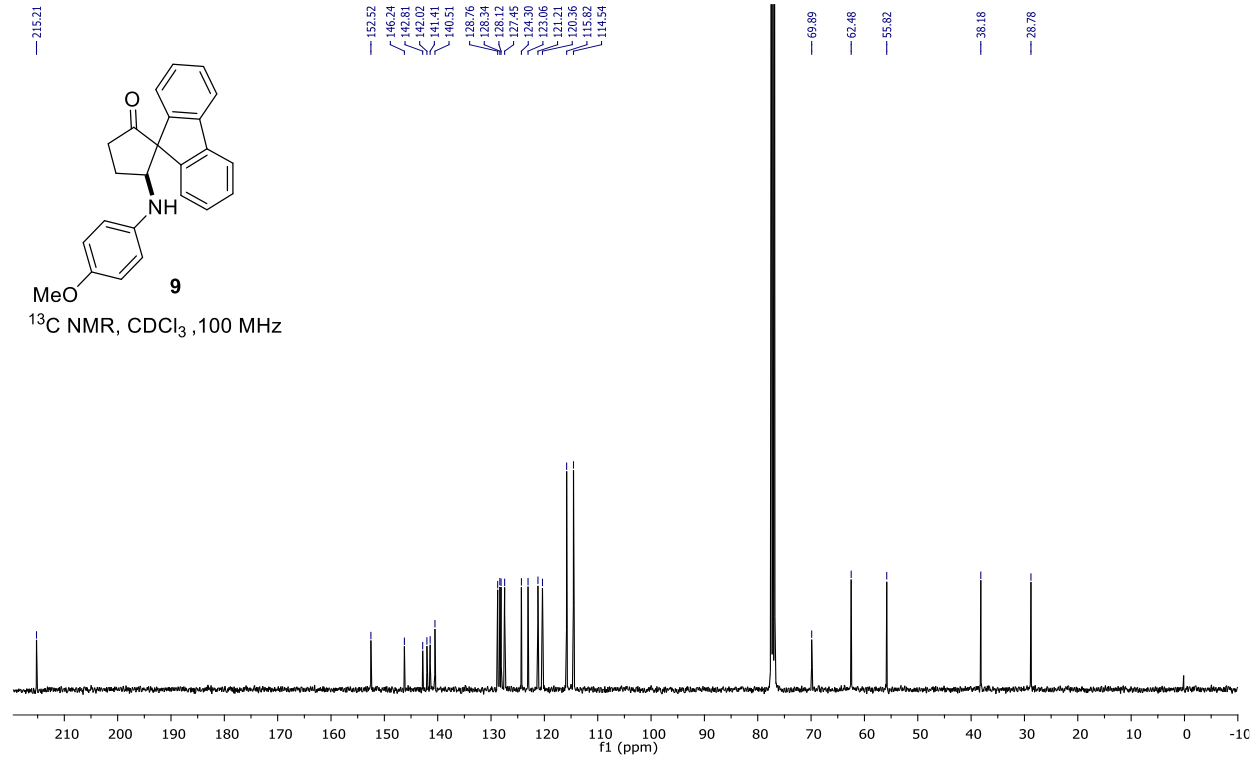
8e

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

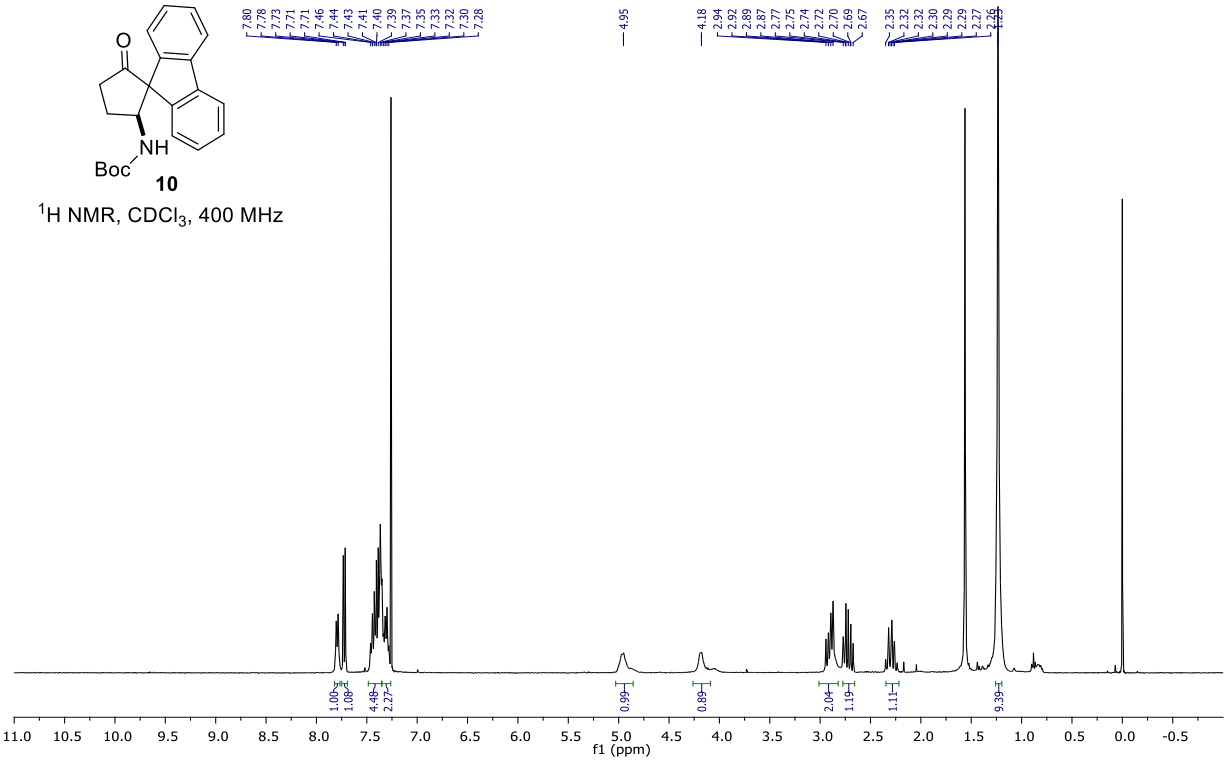


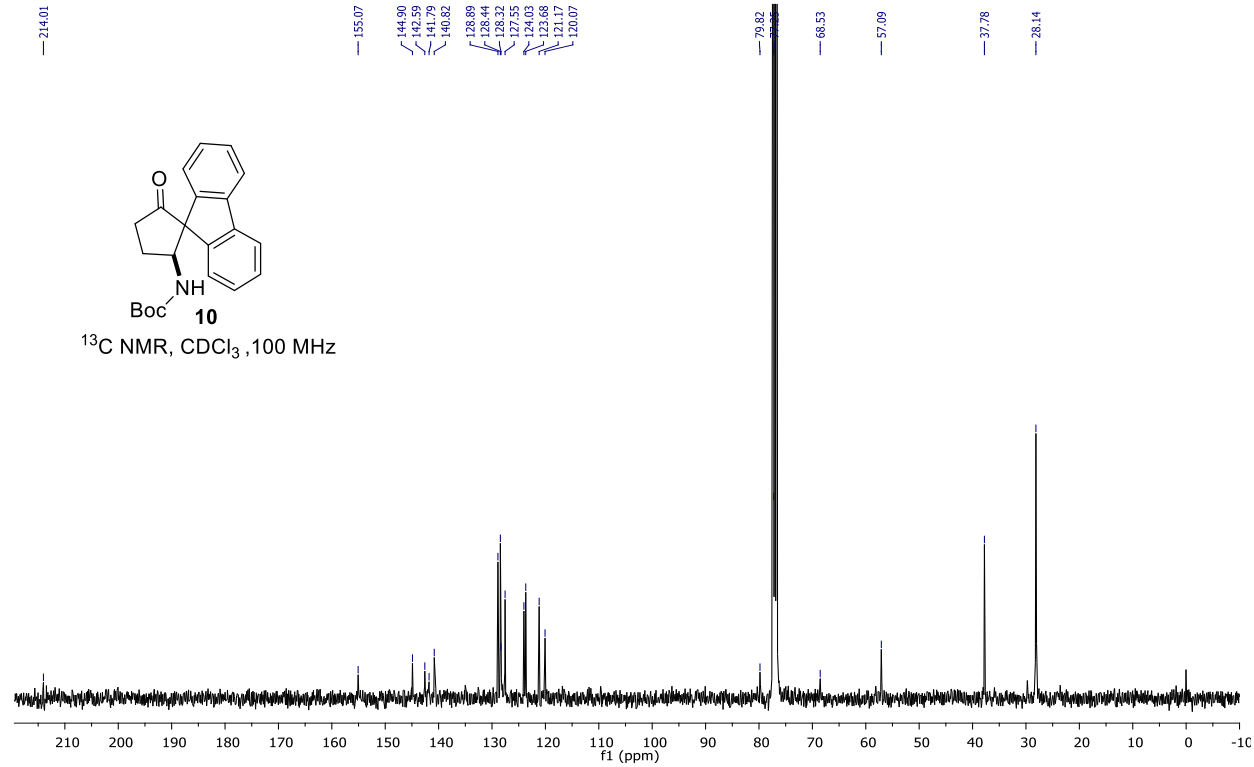
2-((4-Methoxyphenyl)amino)spiro[cyclopentane-1,9'-fluoren]-5-one (9)





tert-Butyl -(2-oxospiro[cyclopentane-1,9'-fluoren]-5-yl)carbamate (10)

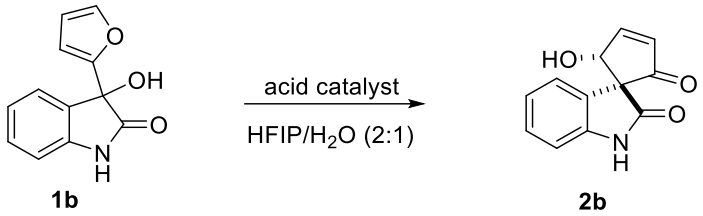




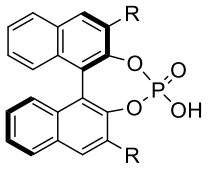
4. Study of Stereoselectivity of Hydroxy Spirocyclopentenoneoxindole 2b

The stereoselectivity of spirocycle **2b** was checked by reaction with different BINOL-derived phosphoric acid, BINOL.PA catalysts and compared the results by chiral HPLC for crude reaction mixture before silica gel column purification (Table S1). All reactions were monitored by TLC (completion of starting material) and crude reaction mixture after work up was taken for HPLC analysis to check the ratio of 4 stereoisomers. The reaction with the Lewis acid $B(C_6F_5)_3$ catalyst gave *trans/cis* ratio 1.0:1.8. Reaction with racemic BINOL-derived phosphoric acid [(±)-BINOL.PA-**1**] gave stereoselectivity (*trans/cis* ratio 2:1). (*R*)-BINOL derived phosphoric acid [(*R*)-BINOL.PA-**2**] gave stereoselectivity (*trans/cis* ratio 3.5:1) at 90 °C and there is no change in the stereoselectivity (*trans/cis* ratio 3.5:1) when the reaction was carried out at room temperature. Low catalyst loading (1 mol%) has not improved but decreased the stereoselectivity (*trans/cis* ratio 1.9:1). (*R*)-BINOL.PA-**3** and (*R*)-BINOL.PA-**4** catalysts gave stereoselectivity 2.5:1 and 1.1:1 respectively. A combination of Lewis acid and Brønsted acid catalysts was checked to see the effect of cooperative catalysis. Reaction with $Ln(OTf)_3$ (1 mol%) and (*R*)-BINOL.PA-**3** (1 mol%) gave better stereoselectivity (*trans/cis* ratio 1:4.9) with *cis*-isomer as major product. The above results indicate that stereoselectivity is depending on the structure of the catalyst but not on the catalyst loading, reaction temperature and time (entries 2-7).

Table S1. Study of stereoselectivity of hydroxy-spirocyclopentenone 2b[a]



(±)-BINOL.PA-**1** = R = H; 1,1′-Binaphthyl-2,2′-diyl hydrogenphosphate (racemic)
(R)-BINOL.PA-**2** = R = H;
(*R*)-BINOL.PA-**3** = R = 9-anthracenyl;
(*R*)-BINOL.PA-**4** = R = 2,4,6-(^{i}Pr)$_3$-C$_6$H$_2$;



entry	catalyst	catalyst loading (mol%)	temp (°C)	time (h)	*trans/cis* ratio[b]
1	$B(C_6F_5)_3$	2.5	rt	48	35:65
2	(±)-BINOL.PA-**1**	2.5	rt	6	67:33
3	**(*R*)-BINOL.PA-2**	**2.5**	**90**	**0.5**	**78:22**
4	(*R*)- BINOL.PA-**2**	2.5	rt	5	77:23
5	(*R*)- BINOL.PA-**2**	1.0	rt	12	65:35
6	(*R*)- BINOL.PA-**3**	2.5	rt	18	71:29
7	(*R*)- BINOL.PA-**4**	2.5	rt	24	53:47
8	**Ln(OTf)$_3$ & (*R*)-BINOL.PA-3**	**1.0 (each)**	**rt**	**18**	**17:83**

[a]Reaction completion was monitored by TLC (consumption of starting material). [b]Chiral HPLC of crude product after workup (without purification) as mentioned in the above conditions. rt = room temperature (25 °C).

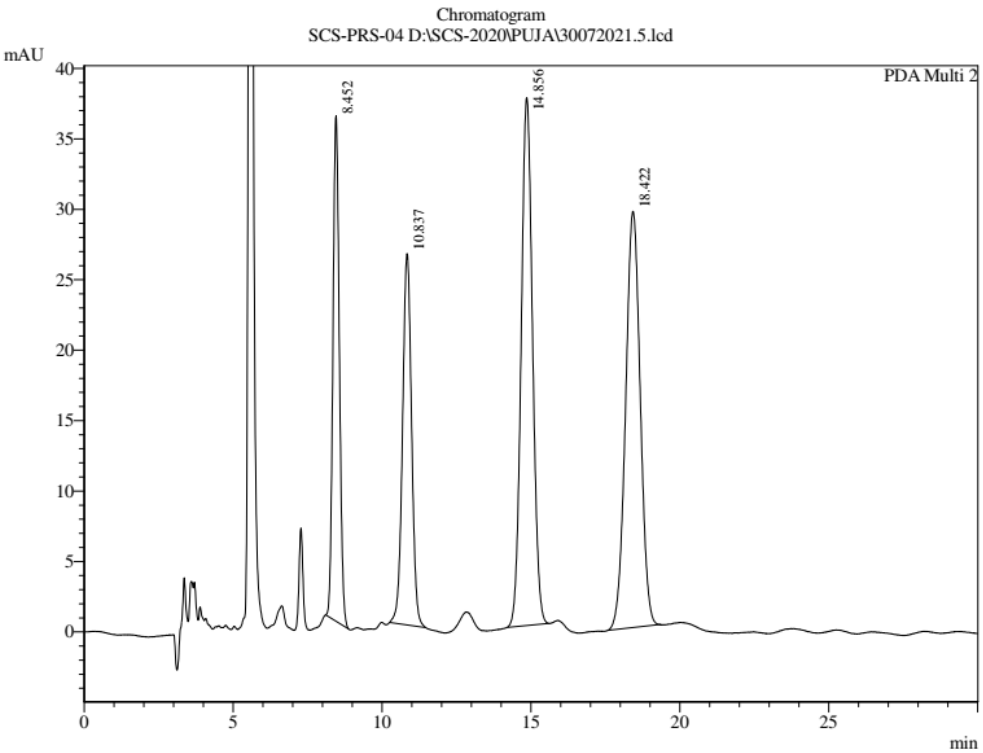
4.1. HPLC chromatogram of the compound 2b obtained by $B(C_6F_5)_3$ catalyst

HPLC analysis conditions: CHIRALPAK IC column, 30% ^{i}PrOH in hexanes, flow rate 1.0 mL/min, λ = 225 nm, t_r (diastereomer 1) = 8.452 min, t_r (diastereomer 2) = 10.837 min, t_r (diastereomer 3) = 14.856 min and t_r (diastereomer 4) = 18.422 min. The *trans/cis* ratio was determined by HPLC analysis of crude product obtained by using 2.5 mol% of $B(C_6F_5)_3$ catalyst at room temperature (25 °C) for 48 h.

HPLC Analysis Report

Sample Name : SCS-PRS-04
Sample ID : SCS-PRS-04
Vail # : 66
Injection Volume : 10 uL
Data File Name : 30072021.5.lcd
Method File Name : 30072021.lcm
Report File Name : HPLC Report.lcr
Data Acquired : 7/30/2021 2:02:39 PM
Data Processed : 7/30/2021 5:02:53 PM
Chromatographic Conditions: COLUMN : CHIRALPAK IC 250X4.6mm 5u
MOBILE PHASE : 30% IPA IN HEXANE
FLOW RATE : 1ml/min

<Chromatogram>



1 PDA Multi 2 / 225nm 4nm

PeakTable

PDA Ch2 225nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.452	536991	35878	17.344	27.756
2	10.837	556292	26370	17.967	20.401
3	14.856	994832	37475	32.132	28.992
4	18.422	1008006	29537	32.557	22.851
Total		3096121	129260	100.000	100.000

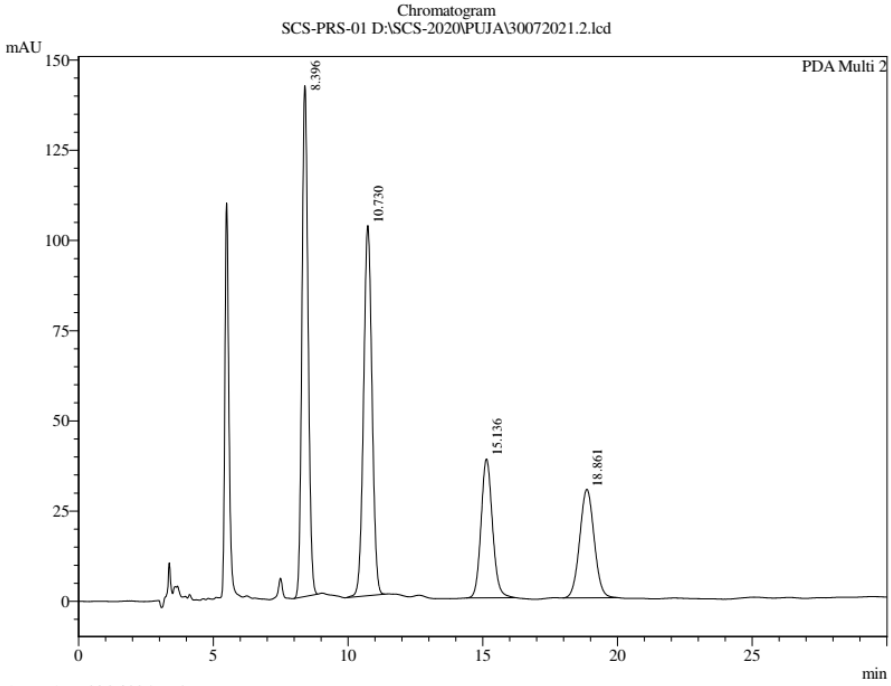
4.2. HPLC chromatogram of the compound 2b obtained by racemic BINOL-derived phosphoric acid catalyst [(±)-BINOL.PA-1]

HPLC analysis conditions: CHIRALPAK IC column, 30% ^{i}PrOH in hexanes, flow rate 1.0 mL/min, λ = 225 nm, t_r (diastereomer 1) = 8.396 min, t_r (diastereomer 2) = 10.73 min, t_r (diastereomer 3) = 15.136 min and t_r (diastereomer 4) = 18.861 min. The *trans/cis* ratio was determined by HPLC analysis of crude product obtained by using 2.5 mol% of **[(±)-BINOL.PA-1]** catalyst at room temperature (25 °C) for 6 h.

HPLC Analysis Report

Sample Name : SCS-PRS-01
Sample ID : SCS-PRS-01
Vail # : 63
Injection Volume : 10 uL
Data File Name : 30072021.2.lcd
Method File Name : 30072021.lcm
Report File Name : HPLC Report.lcr
Data Acquired : 7/30/2021 12:31:01 PM
Data Processed : 7/30/2021 4:15:40 PM
Chromatographic Conditions: COLUMN : CHIRALPAK IC 250X4.6mm 5u
MOBILE PHASE : 30% IPA IN HEXANE
FLOW RATE : 1ml/min

<Chromatogram>



1 PDA Multi 2 / 225nm 4nm

PeakTable

PDA Ch2 225nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.396	2256243	141598	33.398	45.269
2	10.730	2240123	102606	33.159	32.803
3	15.136	1137119	38512	16.832	12.312
4	18.861	1122126	30076	16.610	9.615
Total		6755611	312792	100.000	100.000

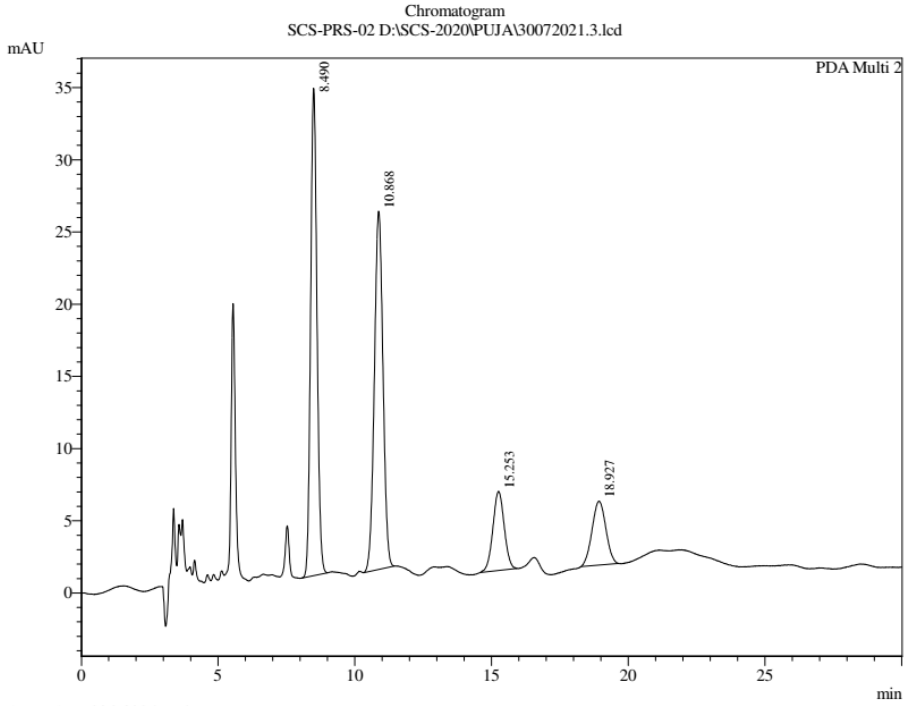
4.3. HPLC chromatogram of the compound 2b obtained by (*R*)-BINOL-derived phosphoric acid [(*R*)-BINOL.PA-2] at 90 °C

HPLC analysis conditions: CHIRALPAK IC column, 30% ^{i}PrOH in hexanes, flow rate 1.0 mL/min, λ = 225 nm, t_r (diastereomer 1) = 8.49 min, t_r (diastereomer 2) = 10.868 min, t_r (diastereomer 3) = 15.253 min and t_r (diastereomer 4) = 18.927 min. The *trans/cis* ratio was determined by HPLC analysis of crude product obtained by using 2.5 mol% of **[(*R*)-BINOL.PA-2]** catalyst at 90 °C for 30 min.

HPLC Analysis Report

Sample Name : SCS-PRS-02
Sample ID : SCS-PRS-02
Vail # : 64
Injection Volume : 10 uL
Data File Name : 30072021.3.lcd
Method File Name : 30072021.lcm
Report File Name : HPLC Report.lcr
Data Acquired : 7/30/2021 1:01:33 PM
Data Processed : 7/30/2021 4:18:51 PM
Chromatographic Conditions: COLUMN : CHIRALPAK IC 250X4.6mm 5u
MOBILE PHASE : 30% IPA IN HEXANE
FLOW RATE : 1ml/min

<Chromatogram>



1 PDA Multi 2 / 225nm 4nm

PeakTable

PDA Ch2 225nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.490	544921	33763	38.869	49.294
2	10.868	543443	24812	38.764	36.225
3	15.253	157845	5476	11.259	7.996
4	18.927	155735	4442	11.109	6.486
Total		1401944	68494	100.000	100.000

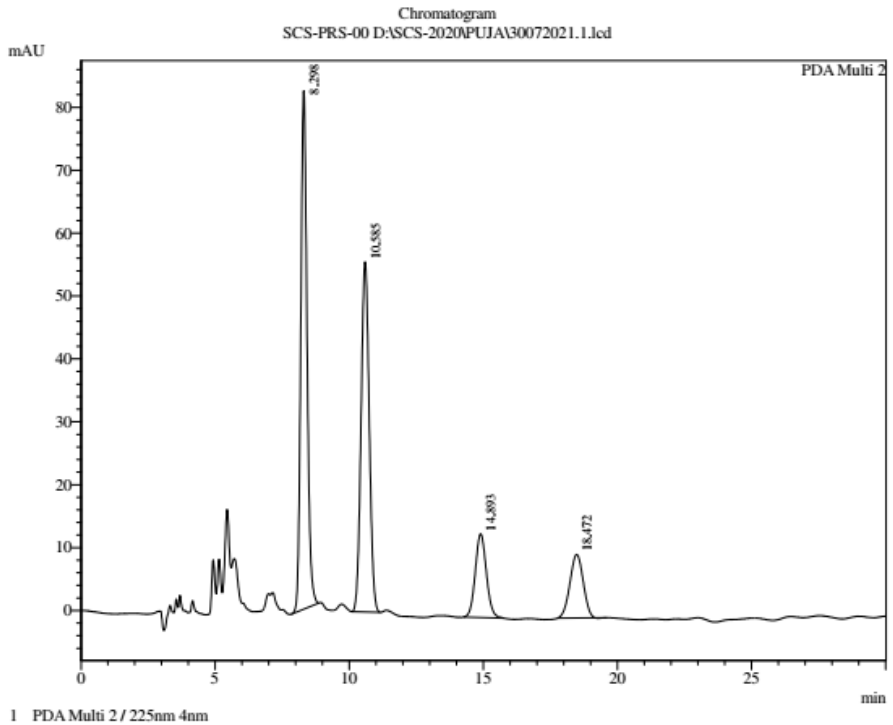
4.4. HPLC chromatogram of the compound 2b obtained by (*R*)-BINOL-derived phosphoric acid catalyst [(*R*)-BINOL.PA-2] at 25 °C

HPLC analysis conditions: CHIRALPAK IC column, 30% ^{i}PrOH in hexanes, flow rate 1.0 mL/min, λ = 225 nm, t_r (diastereomer 1) = 8.49 min, t_r (diastereomer 2) = 10.868 min, t_r (diastereomer 3) = 15.253 min and t_r (diastereomer 4) = 18.927 min. The *trans/cis* ratio was determined by HPLC analysis of crude product obtained by using 2.5 mol% of **[(*R*)-BINOL.PA-2]** catalyst at room temperature (25 °C) for 5 h.

HPLC Analysis Report

Sample Name : SCS-PRS-00
Sample ID : SCS-PRS-00
Vail # : 62
Injection Volume : 10 uL
Data File Name : 30072021.1.lcd
Method File Name : 30072021.lcm
Report File Name : HPLC Report.lcr
Data Acquired : 7/30/2021 12:00:27 PM
Data Processed : 7/30/2021 4:13:32 PM
Chromatographic Conditions: COLUMN : CHIRALPAK IC 250X4.6mm 5u
MOBILE PHASE : 30% IPA IN HEXANE
FLOW RATE : 1ml/min

<Chromatogram>



1 PDA Multi 2 / 225nm 4nm

PeakTable

PDA Ch2 225nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.298	1334034	82437	41.133	51.025
2	10.585	1177053	55695	36.292	34.473
3	14.893	383617	13319	11.828	8.244
4	18.472	348555	10110	10.747	6.258
Total		3243259	161561	100.000	100.000

4.5. HPLC chromatogram of the compound 2b obtained by (*R*)-BINOL-derived phosphoric acid [(*R*)-BINOL.PA-2] (1 mol% at 25 °C)

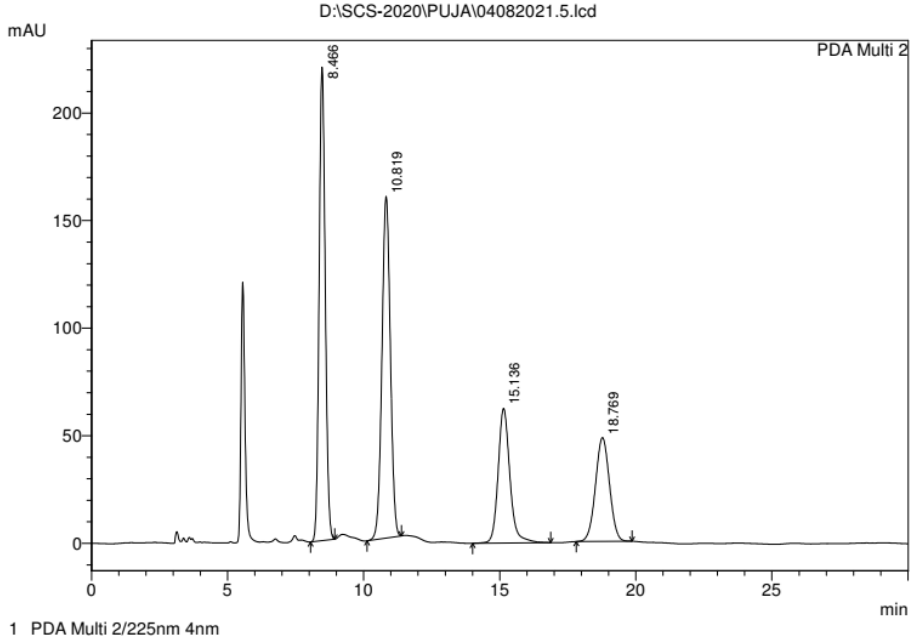
HPLC analysis conditions: CHIRALPAK IC column, 30% ^{i}PrOH in hexanes, flow rate 1.0 mL/min, λ = 225 nm, t_r (diastereomer 1) = 8.466 min, t_r (diastereomer 2) = 10.819 min, t_r (diastereomer 3) = 15.136 min and t_r (diastereomer 4) = 18.769 min. The *trans/cis* ratio was determined by HPLC analysis of crude product obtained by using 1.0 mol% of **[(*R*)-BINOL.PA-2]** catalyst at room temperature (25 °C) for 12 h.

HPLC Analysis Report

Acquired by	: Manjula
Sample Name	: SCS-PRS-08
Sample ID	: SCS-PRS-08
Tray#	: 1
Vail #	: 34
Injection Volume	: 10 uL
Data File Name	: 04082021.5.lcd
Method File Name	: 04082021.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 8/4/2021 5:06:29 PM
Data Processed	: 8/4/2021 5:36:33 PM

COLUMN: CHIRALPAK IC 250X4.6mm 5u
MOBILE PHASE: 30% IPA IN HEXANE
FLOW RATE : 1ml/min

<Chromatogram>



1 PDA Multi 2/225nm 4nm

PeakTable

PDA Ch2 225nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.466	3437236	220128	32.916	44.943
2	10.819	3399020	158845	32.550	32.431
3	15.136	1882061	62571	18.023	12.775
4	18.769	1724210	48248	16.511	9.851
Total		10442527	489792	100.000	100.000

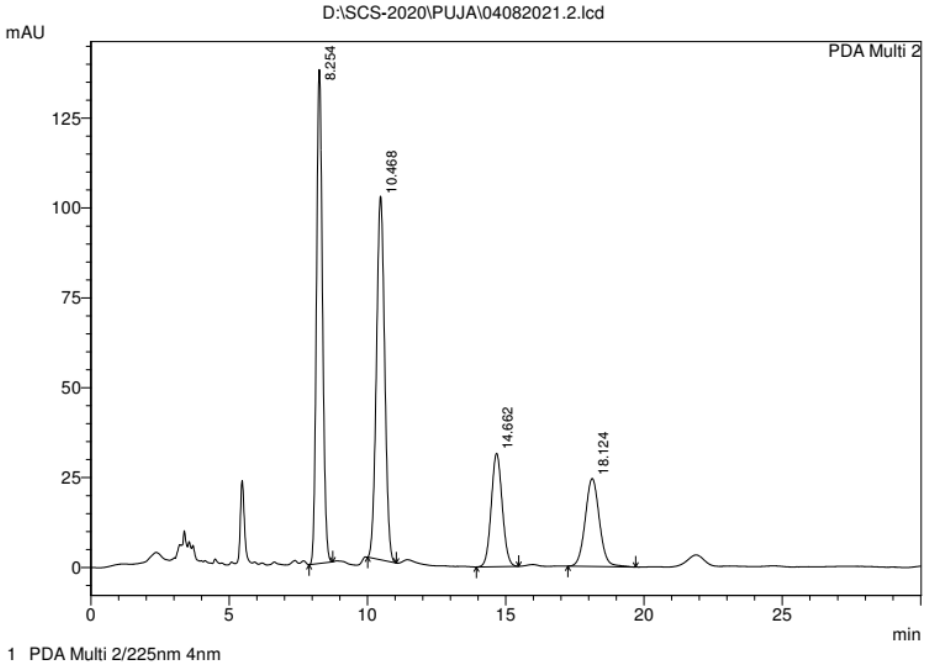
4.6. HPLC chromatogram of the compound 2b obtained by (*R*)-BINOL-derived phosphoric acid [(*R*)-BINOL.PA-3] at room temperature (25 °C)

HPLC analysis conditions: CHIRALPAK IC column, 30% ^{i}PrOH in hexanes, flow rate 1.0 mL/min, λ = 225 nm, t_r (diastereomer 1) = 8.254 min, t_r (diastereomer 2) = 10.468 min, t_r (diastereomer 3) = 14.662 min and t_r (diastereomer 4) = 18.124 min. The *trans/cis* ratio was determined by HPLC analysis of crude product obtained by using 2.5 mol% of **[(*R*)-BINOL.PA-3]** catalyst at room temperature (25 °C) for 18 h.

HPLC Analysis Report

Acquired by : Manjula
Sample Name : SCS-PRS-05
Sample ID : SCS-PRS-05
Tray# : 1
Vail # : 31
Injection Volume : 10 uL
Data File Name : 04082021.2.lcd
Method File Name : 04082021.lcm
Batch File Name :
Report File Name : Default.lcr
Data Acquired : 8/4/2021 3:32:28 PM
Data Processed : 8/4/2021 4:02:32 PM
COLUMN: CHIRALPAK IC 250X4.6mm 5u
MOBILE PHASE: 30% IPA IN HEXANE
FLOW RATE : 1ml/min

<Chromatogram>



1 PDA Multi 2/225nm 4nm

PeakTable

PDA Ch2 225nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.254	2094499	137462	35.292	46.650
2	10.468	2094850	101168	35.298	34.333
3	14.662	870885	31545	14.674	10.705
4	18.124	874503	24492	14.735	8.312
Total		5934737	294667	100.000	100.000

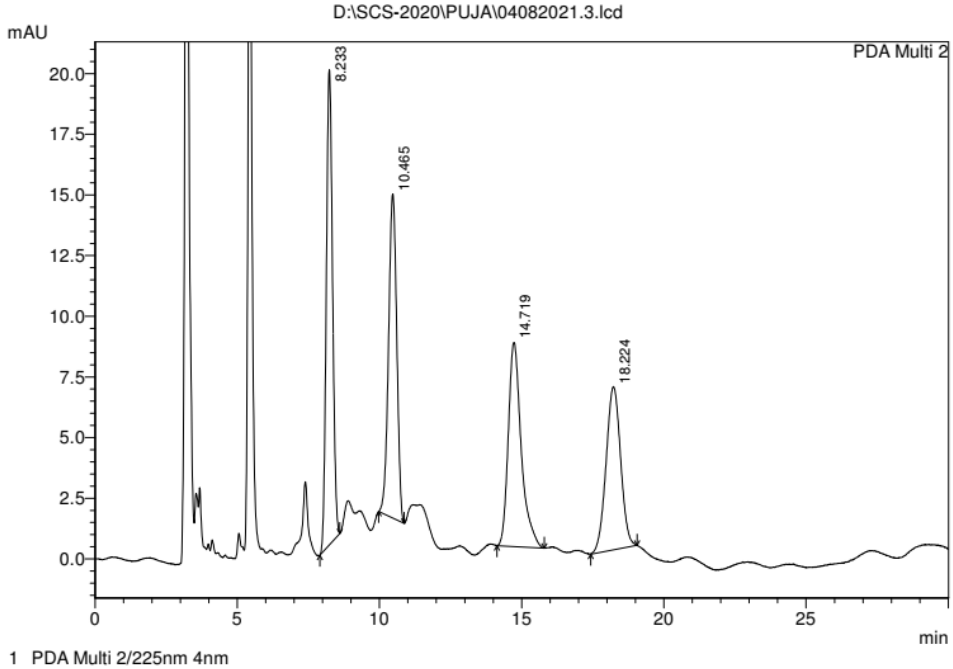
4.7. HPLC chromatogram of the compound 2b obtained by (*R*)-BINOL-derived phosphoric acid [(*R*)-BINOL.PA-4] at room temperature (25 °C)

HPLC analysis conditions: CHIRALPAK IC column, 30% ^{i}PrOH in hexanes, flow rate 1.0 mL/min, λ = 225 nm, t_r (diastereomer 1) = 8.233 min, t_r (diastereomer 2) = 10.465 min, t_r (diastereomer 3) = 14.719 min and t_r (diastereomer 4) = 18.224 min. The *trans/cis* ratio was determined by HPLC analysis of crude product obtained by using 2.5 mol% of **[(*R*)-BINOL.PA-4]** catalyst at room temperature (25 °C) for 24 h.

HPLC Analysis Report

Acquired by : Manjula
Sample Name : SCS-PRS-06
Sample ID : SCS-PRS-06
Tray# : 1
Vail # : 32
Injection Volume : 10 uL
Data File Name : 04082021.3.lcd
Method File Name : 04082021.lcm
Batch File Name :
Report File Name : Default.lcr
Data Acquired : 8/4/2021 4:03:20 PM
Data Processed : 8/4/2021 4:33:24 PM
COLUMN: CHIRALPAK IC 250X4.6mm 5u
MOBILE PHASE: 30% IPA IN HEXANE
FLOW RATE : 1ml/min

<Chromatogram>



1 PDA Multi 2/225nm 4nm

PeakTable

PDA Ch2 225nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.233	298205	19592	27.880	40.734
2	10.465	266069	13358	24.875	27.772
3	14.719	266237	8416	24.891	17.499
4	18.224	239110	6732	22.355	13.996
Total		1069621	48097	100.000	100.000

4.8. HPLC chromatogram of the compound 2b obtained by $Ln(OTf)_3$ and (*R*)-BINOL-derived phosphoric acid [(*R*)-BINOL.PA-3] at room temperature (25 °C)

HPLC analysis conditions: CHIRALPAK IC column, 30% ^{i}PrOH in hexanes, flow rate 1.0 mL/min, λ = 225 nm, t_r (diastereomer 1) = 8.393 min, t_r (diastereomer 2) = 10.48 min, t_r (diastereomer 3) = 14.741 min and t_r (diastereomer 4) = 17.895 min. The *trans/cis* ratio was determined by HPLC analysis of crude product obtained by using a combination of $Ln(OTf)_3$ (1.0 mol%) and [(*R*)-BINOL.PA-**3**] catalyst (1 mol%) at room temperature (25 °C) for 18 h.

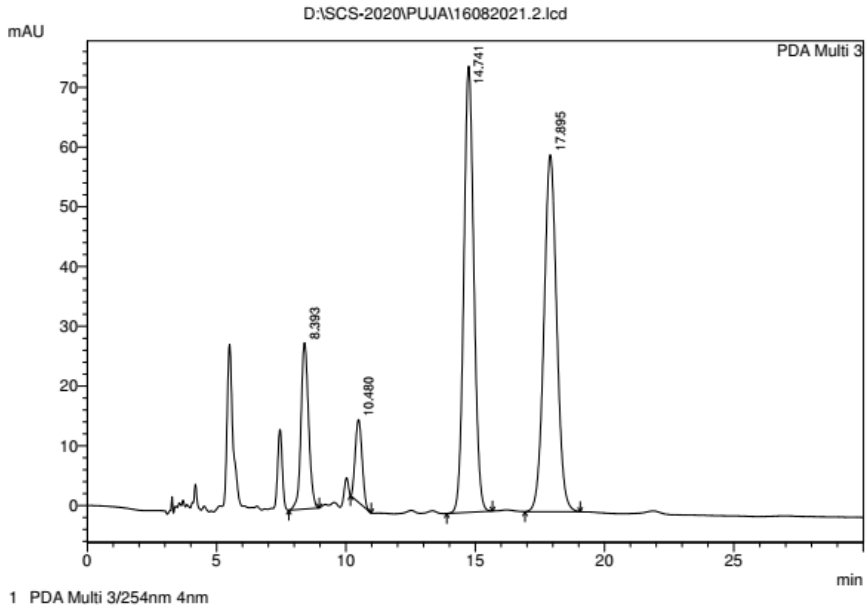
HPLC Analysis Report

D:\SCS-2020\PUJA\16082021.2.lcd

Acquired by	: Manjula
Sample Name	: SCS-PRS-09
Sample ID	: SCS-PRS-09
Tray#	: 1
Vail #	: 3
Injection Volume	: 5 uL
Data File Name	: 16082021.2.lcd
Method File Name	: 16082021.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 8/16/2021 2:45:58 PM
Data Processed	: 8/16/2021 4:37:21 PM

COLUMN:CHIRALPAK IC 250X4.6mm 5u
MOBILE PHASE: 30%IPA IN HEXANE
FLOW RATE : 1ml/min

<Chromatogram>



1 PDA Multi 3/254nm 4nm

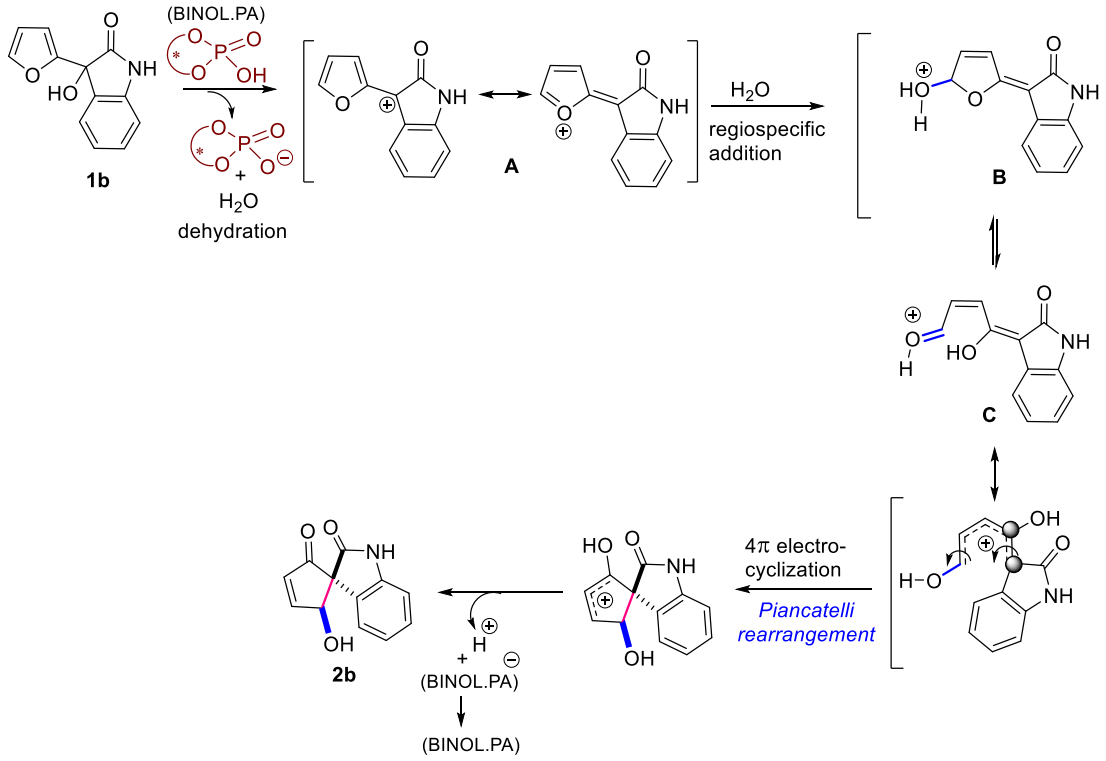
PeakTable

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.393	566325	27802	11.610	15.794
2	10.480	252861	13838	5.184	7.861
3	14.741	2011638	74678	41.240	42.424
4	17.895	2047097	59709	41.967	33.920
Total		4877920	176027	100.000	100.000

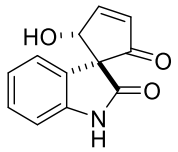
5. Plausible mechanism for the formation of Spirocyclopentenoneoxindole 2b

Based on the previous literature and present experimental results, we envisioned a plausible mechanistic pathway shown in Scheme S1. Hypothesized that, in the presence of acidic media the furanoxindolyl alcohol **1b** forms a highly reactive oxocarbenium ion **A** that facilitates the regiospecific addition of nucleophile to give intermediate **B** which further rearranges to intermediate **C**. Once intermediate **C** is formed, the remaining process would rely on the same principles as Piancatelli rearrangement to govern the generation of spirocyclopentenone oxindole **2b** through a Nazarov-type 4π electrocyclization.



Scheme S1 Plausible reaction pathway

6. X-ray Crystallographic Data of Compounds 2b, 6n and 8a



Structure of compound 2b

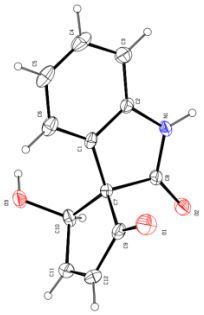
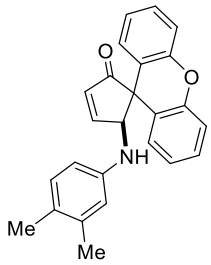


Figure S1. A view of **2b**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by circles of arbitrary radii.



Structure of compound 6n

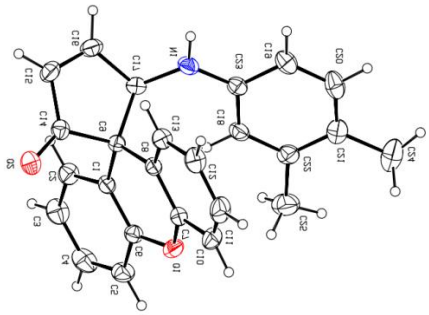
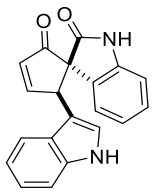


Figure S2. A view of **6n**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by circles of arbitrary radii.



Structure of compound 8a

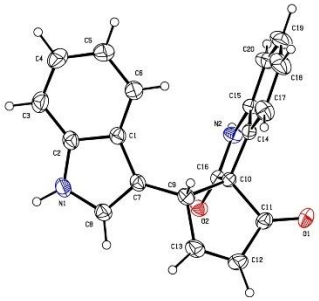


Figure S3. A view of **8a**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by circles of arbitrary radii.

Crystallization of 2b: To a mixture ofcompound **2b** (15 mg) and dichloromethane (3 mL) in a culture vial and added five drops of hexanes and two drops of methanol. The vial was covered with perforated aluminium foil and left aside for 2 days at 25 °C for crystal growth. After slow evaporation of the solvent, pale orange crystals were obtained.

Crystallization of 6n: During the purification of crude compound **6n** by silica gel column chromatography using hexanes and EtOAc, compound **6n** was isolated as pale yellow crystals after the removal of solvent from the collected fractions by rotary evaporator. These crystals were directly used for X-ray structure determination.

Crystallization of 8a: To a mixture ofcompound **8a** (10 mg) and methanol (2 mL) in a culture vial. The vial was covered with perforated aluminium foil and left aside for 3 days at 25 °C for crystal growth. After slow evaporation of the solvent, brown crystals were obtained.

X-ray data for the compounds **2b**, **6n** and **8a** were collected at room temperatureon a Bruker D8 QUEST instrument with an IμS Mo micro source (λ = 0.7107 A) and a PHOTON-100 detector. The raw data frames were reduced and corrected for absorption effects using the Bruker Apex 3 software suite programs.[1]The structure was solved using intrinsic phasing method[2] and further refined with the SHELXL[2] program and expanded using Fourier techniques. Anisotropic displacement parameters were included for all non-hydrogen atoms. The N bound H atoms and O-

bound H atoms were located in the difference Fourier map and the positional parameters of H atoms were refined. All H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å, and U_{iso}(H) = 1.5Ueq(C) for methyl H or 1.2Ueq(C) for other H atoms].

Crystal structure determination of 2b

Crystal Data for 2b: $C_{12}H_9NO_3$ (M =215.20 g/mol): orthorhombic, space group P212121 (no. 19), a = 7.0423(14) Å, b = 8.8382(13) Å, c = 17.048(3) Å, V = 1061.1(3) Å3, Z = 4, T = 294.15 K, μ(MoKα) = 0.098 mm-1, D*calc* = 1.347 g/cm3, 10127 reflections measured (5.192° ≤ 2Θ ≤ 53.186°), 2198 unique (R_{int} = 0.0780, R_{sigma} = 0.0675) which were used in all calculations. The final R1 was 0.0636 (I > 2σ(I)) and wR2 was 0.1375 (all data). CCDC **2104599** contains supplementary Crystallographic data for the structure.

Crystal structure determination of 6n

Crystal Data for 6n: $C_{25}H_{21}NO_2$ (M =367.43 g/mol): monoclinic, space group P21/n (no. 14), a = 12.2675(6) Å, b = 11.9199(7) Å, c = 12.9994(7) Å, β = 94.172(3)°, V = 1895.83(18) Å3, Z = 4, T = 294.15 K, μ(MoKα) = 0.081 mm-1, D*calc* = 1.287 g/cm3, 40343 reflections measured (4.408° ≤ 2Θ ≤ 56.656°), 4669 unique (R_{int} = 0.0724, R_{sigma} = 0.0384) which were used in all calculations. The final R1 was 0.0532 (I > 2σ(I)) and wR2 was 0.1453 (all data). CCDC **2104600** contains supplementary Crystallographic data for the structure.

Crystal structure determination of 8a

Crystal Data for 8a: $C_{20}H_{14}N_2O_2$ (M =314.33 g/mol): triclinic, space group P-1 (no. 2), a = 6.5740(7) Å, b = 8.6042(6) Å, c = 14.8471(8) Å, α = 102.836(3)°, β = 101.585(8)°, γ = 99.182(9)°, V = 783.60(11) Å3, Z = 2, T = 294.15 K, μ(MoKα) = 0.088 mm-1, D*calc* = 1.332 g/cm3, 10367 reflections measured (4.97° ≤ 2Θ ≤ 52.776°), 3214 unique (R_{int} = 0.0797, R_{sigma} = 0.0750) which were used in all calculations. The final R1 was 0.0451 (I > 2σ(I)) and wR2 was 0.1393 (all data). CCDC **2104601** contains supplementary Crystallographic data for the structure. These data can be obtained free of charge at ww.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: deposit@ccdc.cam.ac.uk].

1. Bruker (2016). APEX3, SAINT and SADABS. Bruker AXS, Inc., Madison, Wisconsin, USA.
2. Sheldrick G. M. (2015) ActaCrystallogrC71:3-8.

7. References

1. Liu, Y.; Sun, Z.; Li, S.; Xiang, K.; Zhang, Y.; Li, Y. *RSC Adv*. **2016**, *6*, 26954–26958.

2. Li, H.; Tong, R.; Sun, J. *Angew. Chem., Int. Ed*. **2016**, *55*, 15125 –15128.