Highly Stereoselective Brønsted Acid-Catalyzed Synthesis of Spirooxindole Pyrans

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Supporting Information

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General Information

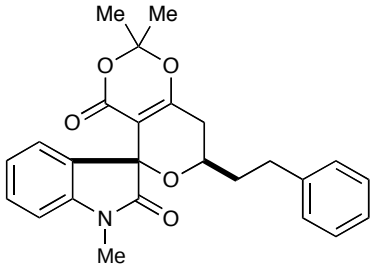
All reactions were carried out under a nitrogen atmosphere in oven-dried glassware with magnetic stirring. THF, toluene, and DMF were purified by passage through a bed of activated alumina.[1] Reagents were purified prior to use unless otherwise stated following the guidelines of Perrin and Armarego.[2] Purification of reaction products was carried out by flash chromatography using EM Reagent silica gel 60 (230-400 mesh). Analytical thin layer chromatography was performed on EM Reagent 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light and ceric ammonium nitrate stain or potassium permangenate stain followed by heating. Infrared spectra were recorded on a Brucker Tensor 37 FT-IR spectrometer. ^{1}H-NMR spectra were recorded on a Bruker Avance 500 (500 MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 7.26 ppm). Data are reported as (ap = apparent, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad; coupling constant(s) in Hz; integration. Proton-decoupled ^{13}C-NMR spectra were recorded on a Brucker Avance 500 (125 MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 77.1 ppm). Mass spectra data were obtained on a Varian 1200 Quadrupole Mass Spectrometer and Micromass Quadro II Spectrometer. The microwave reaction was carried with a single mode microwave reactor from Biotage.

All β-hydroxy-dioxinones were prepared in the same manner as described in former paper published from our group.[3] All isatin dimethyl acetals were prepared by the method reported by Butenschön.[4]

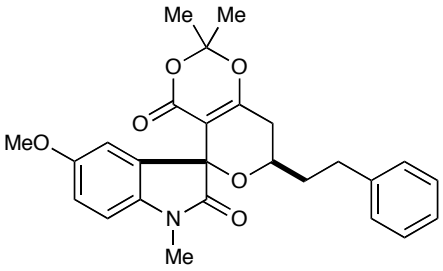
General Procedure for the Synthesis of Spiro-oxindoles

A 10 mL round bottom flask was charged with powdered 5 Å molecular sieves (250 mg) and flame-dried prior to use. A solution of is the isatin dimethyl acetal (0.12 mmol, 1 equiv.) and hydroxy dioxinone (0.18 mmol, 1.5 equiv.) in CH_2Cl_2 (2.5 mL) was added to the flask and cooled to 0 °C, then trifluorosulfonic acid (0.024 mmol, 0.2 equiv.) in CH_2Cl_2 was added dropwise. The resulted reaction mixture was stirred for 30 min at 0 °C before warming up to 20 °C (room temperature) over 2 hours and then quenched by the addition of saturated sodium bicarbonate (3 mL). The layers were separated and aqueous layer was extracted with CH_2Cl_2 (3 x 2 mL). The combined organic layers were dried over Na_2SO_4, filtered, concentrated in vacuo. The crude product was purified by flash chromatography with EtOAc/hexanes to afford the corresponding spiro-oxindole products.

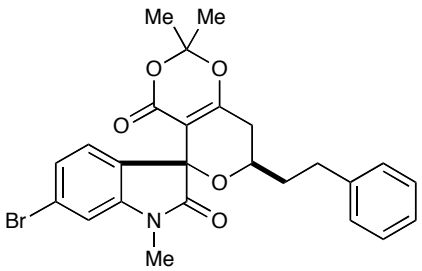
[1] A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics* **1996**, *15*, 1518.
[2] D. D. Perrin, W. L. Armarego, *Purification of Laboratory Chemicals;* 3rd Ed., Pergamon Press, Oxford. 1988.
[3] W. J. Morris, D. W. Custar, K. A. Scheidt, *Org. Lett.* **2005**, *7*, 1113.
[4] B. Muschalek, I. Weidner, H. Butenschön, *J. Organomet. Chem.* **2007**, *692*, 2415.



Spiro-oxindole 4a: Purified by flash chromatography using 20% ethyl acetate/hexanes to afford 35 mg (93% yield) of **4a** (20:1 dr) as a light yellowish solid. R_f = 0.24 (33% ethyl acetate/hexanes; Analytical data for **4a**: FTIR (film) $\tilde{\nu}$ = 2938, 1722, 1650, 1614, 1416, 1203, 1091, 733 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$): δ 7.44 (td, *J* = 7.7, 1.1 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.29-7.25 (m, 4H), 7.15 (t, *J* = 7.2 Hz, 1H), 6.96 (d, *J* = 7.8 Hz, 1H), 5.02 (tt, *J* = 8.4, 4.2 Hz, 1H), 3.35 (s, 3H), 2.88 (ddd, *J* = 14.3, 10.0, 4.8 Hz, 1H), 2.76-2.70 (m, 1H), 2.51-2.49 (m, 2H), 2.06-2.04 (m, 1H), 1.95-1.92 (m, 1H), 1.81 (d, *J* = 12.7 Hz, 6H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 174.7, 165.6, 157.8, 144.6, 141.3, 130.2, 128.9, 128.2, 128.2, 125.8, 123.2, 122.7, 108.5, 106.4, 102.1, 75.5, 68.6, 36.7, 32.8, 31.2, 27.0, 26.2, 22.7. LRMS (ESI): Mass calcd for $C_{25}H_{25}NO_5$ $[M+H]^+$: 420; found 420.

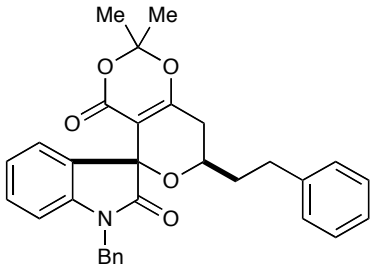


Spiro-oxindole 4b: Purified by flash chromatography using 20% ethyl acetate/hexanes to afford 48 mg (89% yield) of **4b** (20:1 dr) as a light reddish solid. R_f = 0.21 (33% ethyl acetate/hexanes); Analytical data for **4b**: FTIR (film) $\tilde{\nu}$ = 2940, 1719, 1649, 1495, 1416, 1287, 1037, 702 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$): δ 7.38-7.35 (m, 2H), 7.26 (dd, *J* = 10.2, 3.4 Hz, 3H), 6.95 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.88-6.86 (m, 2H), 5.02 (tt, *J* = 7.9, 5.1 Hz, 1H), 3.87 (s, 3H), 3.33 (s, 3H), 2.87 (ddd, *J* = 14.0, 10.5, 5.3 Hz, 1H), 2.75-2.69 (m, 1H), 2.50-2.49 (m, 2H), 2.07-2.01 (m, 1H), 1.96-1.90 (m, 1H), 1.81 (d, *J* = 13.4 Hz, 6H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 174.7, 165.9, 158.0, 156.2, 141.6, 138.3, 130.4, 128.5, 128.5, 126.0, 124.8, 113.9, 111.6, 109.0, 106.7, 76.1, 69.0, 55.9, 37.0, 33.1, 31.4, 27.3, 26.6, 23.0.; LRMS (ESI): Mass calcd for $C_{26}H_{27}NO_6$ $[M+H]^+$: 450, found $[M+H]^+$: 450.

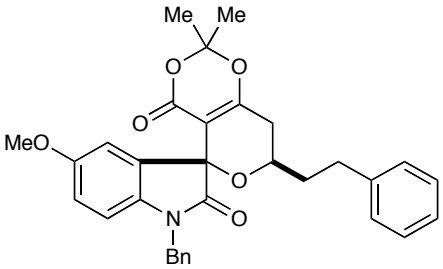


Spiro-oxindole 4c: Purified by flash chromatography using 20% ethyl acetate/hexanes to afford 48 mg (80% yield) of **4c** (20:1 dr) as a yellowish solid. R_f = 0.55 (33% ethyl

acetate/hexanes); Analytical data for **4c**: FTIR (film) $\tilde{\nu}$ = 2940, 1726, 1649, 1607, 1416, 1367, 1096, 708 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$): δ 7.39-7.36 (m, 2H), 7.30-7.25 (m, 4H), 7.12-7.11 (m, 2H), 5.00-4.95 (m, 1H), 3.34 (s, 3H), 2.86 (ddd, *J* = 14.0, 10.3, 5.2 Hz, 1H), 2.75-2.69 (m, 1H), 2.50-2.49 (m, 2H), 2.03 (dddd, *J* = 13.6, 10.4, 8.2, 5.4 Hz, 1H), 1.93 (dddd, *J* = 13.8, 10.5, 6.1, 4.7 Hz, 1H), 1.81 (d, *J* = 3.5 Hz, 6H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 174.8, 166.1, 158.0, 146.2, 141.5, 128.5, 128.5, 128.1, 126.1, 125.7, 124.8, 124.1, 112.4, 106.8, 101.8, 75.4, 67.0, 38.0, 33.0, 31.4, 27.3, 26.6, 23.0; LRMS (ESI): Mass calcd for $C_{25}H_{24}BrNO_5$ $[M+H]^+$: 498; found 498.

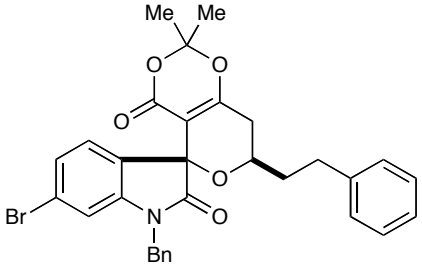


Spiro-oxindole 4d: Purified by flash chromatography using 20% ethyl acetate/hexanes to afford 42 mg (71% yield) of **4d** (20:1 dr) as a light yellowish solid. R_f = 0.22 (33% ethyl acetate/hexanes); Analytical data for **4d**: FTIR (film) $\tilde{\nu}$ = 2941, 1725, 1649, 1608, 1418, 1202, 921, 702 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$): δ 7.41 (d, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.28-7.25 (m, 4H), 7.20-7.14 (m, 4H), 7.02 (d, *J* = 7.8 Hz, 1H), 6.80 (d, *J* = 1.7 Hz, 1H), 5.01 (d, *J* = 16.1 Hz, 1H), 4.92-4.86 (m, 2H), 2.79 (ddd, *J* = 14.2, 9.9, 4.8 Hz, 1H), 2.63 (ddd, *J* = 13.8, 10.1, 6.4 Hz, 1H), 2.42-2.40 (m, 2H), 1.97-1.89 (m, 1H), 1.84 (dddd, *J* = 14.0, 10.2, 6.3, 4.0 Hz, 1H), 1.73 (d, *J* = 4.5 Hz, 6H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 174.9, 166.4, 158.2, 145.3, 141.5, 135.0, 129.0, 128.6, 128.5, 128.2, 127.8, 127.1, 126.1, 125.9, 124.9, 124.1, 113.3, 106.9, 101.6, 75.5, 69.0, 44.0, 37.1, 33.1, 31.5, 27.3, 23.0; LRMS (ESI): Mass calcd for $C_{31}H_{29}NO_5$ $[M+H]^+$: 496, found $[M+H]^+$: 496.

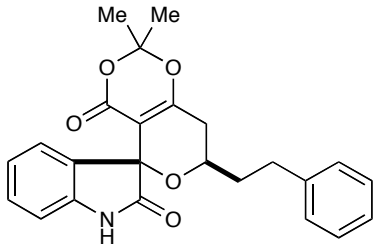


Spiro-oxindole 4e: Purified by flash chromatography using 20% ethyl acetate/hexanes to afford 58 mg (94% yield) of **4e** (20:1 dr) as a light yellowish solid. R_f = 0.40 (33% ethyl acetate/hexanes); Analytical data for **4e**: FTIR (film) $\tilde{\nu}$ = 2939, 1718, 1648, 1495, 1417, 1272, 1179, 1018, 700 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$): δ 7.42 (d, *J* = 7.6 Hz, 2H), 7.33-7.30 (m, 2H), 7.28-7.24 (m, 3H), 7.18-7.15 (m, 3H), 6.77 (d, *J* = 2.6 Hz, 1H), 6.71-6.69 (m, 1H), 6.54 (d, *J* = 8.5 Hz, 1H), 5.05 (d, *J* = 16.0 Hz, 1H), 4.96 (tt, *J* = 8.6, 4.3 Hz, 1H), 4.87 (d, *J* = 16.0 Hz, 1H), 3.72 (s, 3H), 2.81 (ddd, *J* = 14.0, 10.3, 5.1 Hz, 1H), 2.65 (ddd, *J* = 13.9, 10.2, 6.2 Hz, 1H), 2.43-2.41 (m, 2H), 1.96 (dddd, *J* = 13.7, 10.3, 8.4, 5.3 Hz, 1H), 1.88-1.81 (m, 1H), 1.73 (d, *J* = 14.4 Hz, 6H); ^{13}C NMR (125 MHz; $CDCl_3$): δ

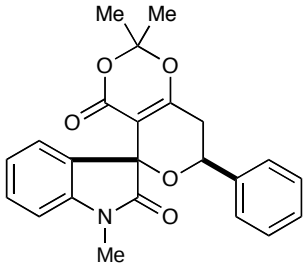
174.8, 166.2, 158.2, 156.2, 141.6, 137.2, 135.7, 130.4, 128.8, 128.5, 128.5, 127.5, 127.2, 126.0, 113.9, 111.5, 110.3, 106.8, 102.1, 76.2, 68.9, 55.8, 44.0, 37.1, 33.2, 31.5, 27.3, 23.0; LRMS (ESI): Mass calcd for $C_{32}H_{31}NO_6$ $[M+H]^+$: 526, found $[M+H]^+$: 526.



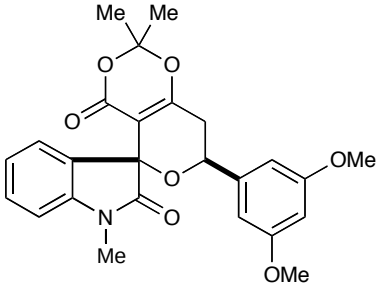
Spiro-oxindole 4f: Purified by flash chromatography using 20% ethyl acetate/hexanes to afford 56 mg (81% yield) of **4f** (20:1 dr) as a yellowish solid. R_f = 0.35 (33% ethyl acetate/hexanes); Analytical data for **4f**: FTIR (film) $\tilde{\nu}$ = 2940, 1724, 1649, 1613, 1468, 1351, 1170, 752, 698 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$): δ 7.44 (d, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.26 (qd, *J* = 7.4, 6.2 Hz, 3H), 7.22-7.16 (m, 4H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.66 (d, *J* = 7.8 Hz, 1H), 5.07 (d, *J* = 16.1 Hz, 1H), 4.96 (dt, *J* = 8.6, 4.3 Hz, 1H), 4.91 (d, *J* = 16.1 Hz, 1H), 2.82 (ddd, *J* = 14.3, 10.0, 4.8 Hz, 1H), 2.68-2.62 (m, 1H), 2.44-2.42 (m, 2H), 2.00-1.93 (m, 1H), 1.89-1.82 (m, 1H), 1.74 (d, *J* = 14.0 Hz, 6H). ^{13}C NMR (125 MHz; $CDCl_3$): δ 175.1, 166.1, 158.2, 143.9, 141.6, 135.6, 130.3, 129.2, 128.8, 128.5, 128.5, 127.5, 127.2, 126.0, 123.5, 123.0, 110.0, 106.8, 102.1, 75.9, 68.9, 43.9, 37.1, 33.2, 31.5, 27.4, 22.9; LRMS (ESI): Mass calcd for $C_{31}H_{28}BrNO_5$ $[M+H]^+$: 574, found $[M+H]^+$: 574.



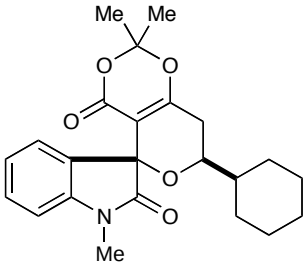
Spiro-oxindole 4g: Purified by flash chromatography using 20% ethyl acetate/hexanes to afford 35 mg (72% yield) of **4g** (20:1 dr) as a light yellowish solid. R_f = 0.18 (33% ethyl acetate/hexanes); Analytical data for **4g**: IR (film) $\tilde{\nu}$ = 3272, 2940, 1727, 1647, 1620, 1418, 1204, 752 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$): δ 7.88 (s, 1H), 7.28-7.24 (m, 3H), 7.17-7.13 (m, 4H), 7.02 (td, *J* = 7.5, 0.9 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 4.85 (tt, *J* = 8.6, 4.3 Hz, 1H), 2.78 (ddd, *J* = 14.3, 9.6, 5.1 Hz, 1H), 2.64 (ddd, *J* = 13.9, 9.8, 6.5 Hz, 1H), 2.41-2.38 (m, 2H), 1.98-1.91 (m, 1H), 1.87-1.81 (m, 1H), 1.72 (d, *J* = 16.2 Hz, 6H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 176.5, 166.2, 158.4, 141.9, 141.5, 130.4, 129.6, 128.5, 128.5, 126.0, 124.0, 123.0, 110.7, 106.8, 102.1, 76.0, 68.8, 37.0, 33.1, 31.4, 27.4, 22.9; LRMS (ESI): Mass calcd for $C_{24}H_{23}NO_5$ $[M+H]^+$: 406, found $[M+H]^+$: 406.



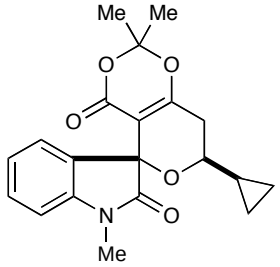
Spiro-oxindole 4h: Purified by flash chromatography using 20% ethyl acetate/hexanes to afford 38 mg (81% yield) of **4h** (20:1 d.r.) as a yellowish solid. R_f = 0.21 (33% ethyl acetate/hexanes); Analytical data for **4h**: mp = 120-150 °C (decomp.); FTIR (film) $\tilde{\nu}$ = 2939, 1720, 1650, 1613, 1416, 1274, 1091, 736 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$): δ 7.37 (d, *J* = 7.2 Hz, 2H), 7.34-7.28 (m, 4H), 7.21 (d, *J* = 6.9 Hz, 1H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 5.92 (dd, *J* = 10.5, 3.1 Hz, 1H), 3.21 (s, 3H), 2.75 (dd, *J* = 18.0, 10.5 Hz, 1H), 2.64 (dd, *J* = 18.0, 3.2 Hz, 1H), 1.73 (d, *J* = 16.1 Hz, 6H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 174.9, 165.7, 158.0, 145.0, 139.7, 130.5, 128.9, 128.7, 128.5, 123.6, 123.0, 108.9, 106.9, 102.3, 77.4, 77.2, 76.9, 34.7, 27.4, 26.5, 23.0; LRMS (ESI): Mass calcd for $C_{23}H_{21}NO_5$ $[M+H]^+$: 392; found 392.



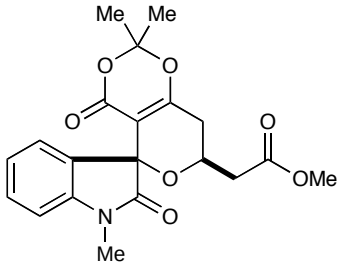
Spiro-oxindole 4i: Purified by flash chromatography using 20% ethyl acetate/hexanes to afford 34 mg (63% yield) of **4i** (20:1 dr) as a light yellowish solid. R_f = 0.25 (33% ethyl acetate/hexanes); Analytical data for **4i**: FTIR (film) $\tilde{\nu}$ = 2940, 1720, 1650, 1612, 1471, 1405, 1276, 1204, 1156, 923, 730 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$): δ 7.32 (td, *J* = 7.8, 1.2 Hz, 1H), 7.20 (dd, *J* = 7.3, 0.9 Hz, 1H), 7.04 (td, *J* = 7.5, 0.7 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.51 (d, *J* = 2.3 Hz, 2H), 6.37 (t, *J* = 2.3 Hz, 1H), 5.84 (dd, *J* = 10.4, 3.2 Hz, 1H), 3.75 (s, 6H), 3.21 (s, 3H), 2.72 (dd, *J* = 18.0, 10.5 Hz, 1H), 2.61 (dd, *J* = 18.0, 3.3 Hz, 1H), 1.74 (d, *J* = 13.8 Hz, 6H). ^{13}C NMR (125 MHz; $CDCl_3$): δ 174.8, 165.6, 161.0, 158.0, 145.0, 142.1, 130.5, 128.8, 123.6, 123.0, 108.8, 106.9, 104.5, 102.2, 100.1, 76.2, 70.8, 55.5, 34.7, 27.3, 26.5, 23.0; LRMS (ESI): Mass calcd for $C_{25}H_{25}NO_7$ $[M+H]^+$: 452, found $[M+H]^+$: 452.



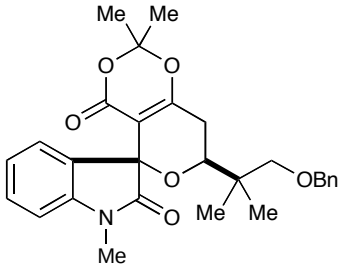
Spiro-oxindole 4j: Purified by flash chromatography using 20% ethyl acetate/hexanes to afford 42 mg (88% yield) of **4j** (20:1 dr) as a light yellowish oil. R_f = 0.50 (33% ethyl acetate/hexanes); Analytical data for **4j**: FTIR (film) $\tilde{\nu}$ = 2927, 2853, 1722, 1651, 1614, 1471, 1405, 1275, 1092, 732 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$): δ 7.31 (td, *J* = 7.7, 1.3 Hz, 1H), 7.10 (dt, *J* = 7.3, 0.6 Hz, 1H), 7.01 (td, *J* = 7.5, 0.8 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 4.61 (ddd, *J* = 9.4, 7.2, 4.0 Hz, 1H), 3.22 (s, 3H), 2.42-2.33 (m, 2H), 1.85 (bd, *J* = 13.0 Hz, 1H), 1.73-1.62 (m, 10H), 1.46 (tdt, *J* = 11.3, 7.5, 3.7 Hz, 1H), 1.22-1.10 (m, 3H), 1.06-0.93 (m, 2H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 175.2, 166.5, 158.1, 144.8, 130.3, 129.3, 123.4, 122.9, 108.7, 106.6, 102.4, 75.7, 73.1, 41.8, 30.4, 28.9, 27.9, 27.3, 26.5, 26.4, 26.0, 25.8, 23.0. LRMS (ESI): Mass calcd for $C_{23}H_{27}NO_5$ $[M+H]^+$: 398, found $[M+H]^+$: 398.



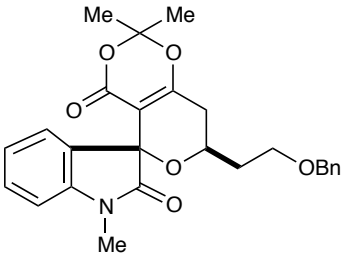
Spiro-oxindole 4k: Purified by flash chromatography using 20% ethyl acetate/hexanes to afford 28 mg (66% yield) of **4k** (20:1 dr) as a light yellowish oil. R_f = 0.45 (33% ethyl acetate/hexanes); Analytical data for **4k**: FTIR (film) $\tilde{\nu}$ = 3001, 2940, 1719, 1651, 1614, 1417, 1276, 1091, 753 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$): δ 7.30 (td, *J* = 7.7, 1.3 Hz, 1H), 7.15-7.14 (m, 1H), 7.02 (td, *J* = 7.7, 1.3 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 4.11 (ddd, *J* = 10.1, 9.0, 3.1 Hz, 1H), 3.21 (s, 3H), 2.57 (dd, *J* = 18.0, 10.2 Hz, 1H), 2.48 (dd, *J* = 18.0, 3.2 Hz, 2H), 1.70 (d, *J* = 14.3 Hz, 6H), 0.96-0.91 (m, 1H), 0.57-0.54 (m, 2H), 0.43-0.40 (m, 1H), 0.27 (m, 1H). ^{13}C NMR (125 MHz; $CDCl_3$): δ 175.0, 166.0, 158.1, 144.9, 130.4, 129.0, 123.5, 123.0, 108.8, 106.7, 102.2, 76.0, 74.3, 33.0, 27.3, 26.5, 23.0, 15.2, 4.0, 2.3. LRMS (ESI): Mass calcd for $C_{20}H_{21}NO_5$ $[M+H]^+$: 356, found $[M+H]^+$: 356.



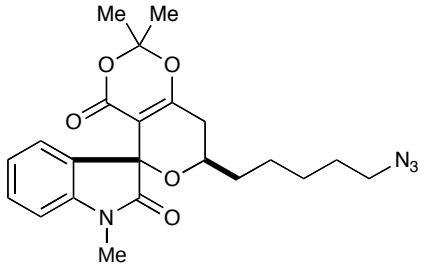
Spiro-oxindole 4l: Purified by flash chromatography using 20% ethyl acetate/hexanes to afford 32 mg (69% yield) of **4l** (20:1 dr) as a light yellowish oil. R_f = 0.15 (33% ethyl acetate/hexanes); Analytical data for **4l**: FTIR (film) $\tilde{\nu}$ = 2950, 1722, 1650, 1614, 1411, 1276, 1204, 1091, 755 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$): δ 7.32 (td, *J* = 7.7, 1.3 Hz, 1H), 7.11 (dt, *J* = 7.4, 0.6 Hz, 1H), 7.02 (td, *J* = 7.5, 0.8 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 5.29-5.24 (m, 1H), 3.65 (s, 3H), 3.22 (s, 3H), 2.69 (dd, *J* = 15.9, 5.7 Hz, 1H), 2.61-2.49 (m, 3H), 1.70 (d, *J* = 6.5 Hz, 6H). ^{13}C NMR (125 MHz; $CDCl_3$): δ 174.6, 170.2, 165.3, 157.9, 144.9, 130.6, 128.7, 123.5, 123.0, 108.8, 106.8, 102.0, 75.7, 65.7, 52.0, 39.8, 32.5, 27.3, 26.5, 23.0; LRMS (ESI): Mass calcd for $C_{20}H_{21}NO_7$ $[M+H]^+$: 388, found 388.



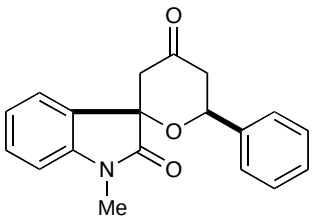
Spiro-oxindole 4m: Purified by flash chromatography using 20% ethyl acetate/hexanes to afford 38 mg (66% yield) of **4m** (20:1 dr) as a light yellowish oil. R_f = 0.48 (33% ethyl acetate/hexanes); Analytical data for **4m**: FTIR (film) $\tilde{\nu}$ = 2963, 2936, 2875, 1722, 1650, 1614, 1404, 1276, 1202, 1092, 751 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$): δ 7.34-7.31 (m, 5H), 7.28 (dd, *J* = 6.2, 2.4 Hz, 1H), 7.07 (dd, *J* = 7.1, 1.2 Hz, 1H), 7.01 (td, *J* = 7.4, 0.9 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 4.73 (dd, *J* = 10.8, 2.9 Hz, 1H), 4.49 (d, *J* = 12.2 Hz, 1H), 4.41 (d, *J* = 12.2 Hz, 1H), 3.31 (d, *J* = 9.0 Hz, 1H), 3.21 (s, 3H), 3.18 (d, *J* = 9.0 Hz, 1H), 2.65 (dd, *J* = 17.9, 12.0 Hz, 1H), 2.32 (dd, *J* = 17.9, 2.9 Hz, 1H), 1.69 (d, *J* = 5.2 Hz, 6H), 0.96 (s, 3H), 0.90 (s, 3H).^{13}C NMR (125 MHz; $CDCl_3$): δ 175.0, 167.0, 158.2, 144.9, 138.9, 130.2, 129.5, 128.4, 127.5, 127.5, 123.5, 122.7, 108.6, 106.6, 102.2, 76.3, 75.6, 73.5, 73.4, 38.0, 28.5, 27.3, 26.4, 23.0, 21.1, 21.0; LRMS (ESI): Mass calcd for $C_{28}H_{31}NO_6$ $[M+H]^+$: 478; found 478.



Spiro-oxindole 4n: Purified by flash chromatography using 20% ethyl acetate/hexanes to afford 20 mg (51% yield) of **4n** (20:1 dr) as a light yellowish oil. R_f = 0.31 (33% ethyl acetate/hexanes); Analytical data for **4n**: FTIR (film) $\tilde{\nu}$ = 2941, 2963, 1721, 1650, 1613, 1408, 1375, 1204, 1091, 752 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$): δ 7.34-7.31 (m, 5H), 7.29-7.26 (m, 1H), 7.12 (dd, *J* = 7.3, 1.1 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 5.02-4.99 (m, 1H), 4.46 (q, *J* = 9.6 Hz, 2H), 3.59-3.51 (m, 2H), 3.22 (s, 3H), 2.46-2.44 (m, 2H), 1.96-1.83 (m, 2H), 1.70 (d, *J* = 7.6 Hz, 6H).^{13}C NMR (125 MHz; $CDCl_3$): δ 174.9, 165.6, 157.8, 144.7, 138.4, 130.5, 129.1, 128.5, 127.7, 127.2, 123.1, 122.8, 109.0, 106.5, 102.2, 75.4, 73.1, 67.2, 66.8, 35.1, 33.0, 27.3, 26.1, 23.0; LRMS (ESI): Mass calcd for $C_{26}H_{27}NO_6$ $[M+H]^+$: 450; found 450.

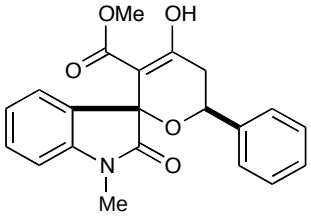


Spiro-oxindole 4o: Purified by flash chromatography using 20% ethyl acetate/hexanes to afford 29 mg (57% yield) of **4n** (20:1 dr) as a light yellowish oil. R_f = 0.45 (33% ethyl acetate/hexanes); Analytical data for **4n**: FTIR (film) $\tilde{\nu}$ = 2939, 2862, 2095, 1719, 1650, 1613, 1406, 1275, 1091, 753 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$): δ 7.32 (td, *J* = 7.7, 1.3 Hz, 1H), 7.12 (dd, *J* = 7.2, 1.0 Hz, 1H), 7.03 (td, *J* = 7.5, 0.9 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 4.84 (td, *J* = 6.5, 2.6 Hz, 1H), 3.26-3.21 (m, 5H), 2.38-2.36 (m, 2H), 1.70 (d, *J* = 9.4 Hz, 6H), 1.61-1.52 (m, 4H), 1.39-1.33 (m, 4H). ^{13}C NMR (125 MHz; $CDCl_3$): δ 175.1, 165.9, 158.1, 144.8, 130.4, 129.1, 123.4, 123.0, 108.8, 106.7, 102.3, 75.8, 69.1, 51.4, 35.0, 33.1, 28.8, 27.3, 26.6, 26.5, 24.7, 22.9; LRMS (ESI): Mass calcd for $C_{22}H_{26}N_4O_5$ $[M+H]^+$: 427; found 427.

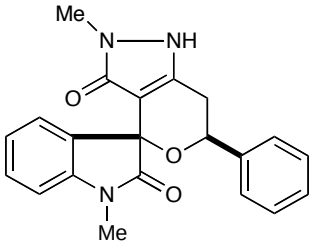


Pyranone 5: A solution of **4h** (30 mg, 0.08 mmol) in DMSO (4 mL) and H_2O (0.5 mL) was heated to 120 °C (bath temperature) for 24 hours. The mixture was then cooled to room temperature and diluted with brine (10 mL) and extracted with EtOAc (3 x 3mL).

The combined organic layers were filtered, concentrated and purified by flash chromatography (15% ethyl acetate/hexanes) to yield 22 mg (93%) of **5** as a yellowish oil. R_f = 0.18 (20% ethyl acetate/hexanes); Analytical data for **5**: FTIR (film) $\tilde{\nu}$ = 2922, 1722, 1615, 1471, 1375, 1094, 752 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$): δ 7.47 (dd, *J* = 7.4, 0.8 Hz, 1H), 7.42-7.40 (m, 2H), 7.38-7.29 (m, 3H), 7.15 (d, *J* = 0.8 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 5.97 (dd, *J* = 11.1, 3.2 Hz, 1H), 3.17 (s, 3H), 2.95 (dd, *J* = 14.9, 0.8 Hz, 1H), 2.86 (ddd, *J* = 14.9, 3.2, 1.9 Hz, 1H), 2.74 (ddd, *J* = 14.9, 11.1, 0.8 Hz, 1H), 2.54 (dd, *J* = 14.9, 1.9 Hz, 1H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 203.6, 174.5, 143.4, 140.8, 130.7, 128.8, 128.4, 127.8, 126.2, 124.1, 123.6, 108.9, 78.2, 73.7, 49.0, 45.8, 26.1. LRMS (ESI): Mass calcd for $C_{19}H_{17}NO_3$ $[M+H]^+$: 308; found 308.

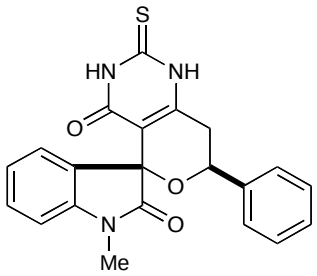


Ketoester 6: A septum-sealed microwave tube charged with spiro-oxindole **4h** (50 mg, 0.128 mmol) and MeOH (0.05 mL, 1.28 mmol) in toluene (2 mL) was irradiated in a monomode microwave cavity at 160 °C for 2 h. The solvent was removed in vacuo and the crude product was purified by flash chromatography (30% ethyl acetate/hexanes) to yield 38 mg (81%) of **6** as a light yellowish solid. R_f = 0.25 (33% ethyl acetate/hexanes); Analytical data for **6**: FTIR (film) $\tilde{\nu}$ = 3059, 3033, 2921, 1719, 1660, 1615, 1471, 1220, 1092, 752 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$): δ 12.37 (s, 1H), 7.36 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.33-7.30 (m, 2H), 7.29-7.26 (m, 2H), 7.20 (dd, *J* = 7.3, 0.8 Hz, 1H), 7.03 (td, *J* = 7.5, 0.9 Hz, 1H), 6.77 (d, *J* = 7.7 Hz, 1H), 5.77 (dd, *J* = 10.9, 2.9 Hz, 1H), 3.40 (s, 3H), 3.19 (s, 3H), 2.86 (dd, *J* = 17.6, 10.9 Hz, 1H), 2.68 (dd, *J* = 17.6, 3.0 Hz, 1H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 175.9, 173.5, 170.0, 144.5, 140.1, 130.7, 129.9, 128.6, 128.3, 126.6, 123.7, 123.0, 108.1, 97.5, 76.8, 70.7, 51.7, 36.4, 26.3; LRMS (ESI): Mass calcd for $C_{21}H_{19}NO_5$ $[M+H]^+$: 366; found 366.

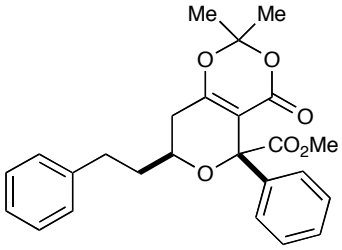


Pyrazolone 7: A septum-sealed microwave tube charged with spiro-oxindole **4h** (25 mg, 0.064 mmol) and MeOH (0.05 mL, 1.28 mmol) in toluene (2 mL) was irradiated in a monomode microwave cavity at 160 °C for 2 h. Then methyl hydrazine (0.02 mL, 0.41 mmol) was added and the reaction mixture was irradiated at 90 °C for an extra 30 min. The solvent was removed in vacuo and **7** (18 mg, 81%) was obtained as white prisms after washing with diethyl ether. Analytical data for **7**: IR (film) $\tilde{\nu}$ = 3399, 2923, 2129, 1717, 1603, 1011, 750 cm^{-1}; ^1H NMR (500 MHz; CD_3OD): δ 7.42-7.40 (m, 2H), 7.38-

7.33 (m, 3H), 7.30-7.27 (m, 1H), 7.21 (dd, *J* = 7.4, 0.8 Hz, 1H), 7.08 (td, *J* = 7.5, 0.9 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 1H), 5.80 (dd, *J* = 9.3, 4.8 Hz, 1H), 3.39 (s, 3H), 3.22 (s, 3H), 2.94-2.92 (m, 2H); ^{13}C NMR (125 MHz; CD_3OD): δ 177.4, 147.2, 142.0, 131.3, 130.2, 129.6, 129.5, 129.1, 127.4, 125.7, 124.3, 110.0, 77.4, 73.5, 49.6, 30.9, 26.4; LRMS (ESI): Mass calcd for $C_{21}H_{19}N_3O_3$ $[M+H]^+$: 362; found 362.

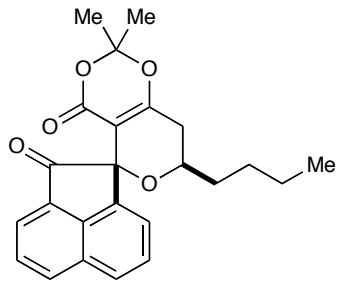


Thio-pyrimidine-one 8: A septum-sealed microwave tube charged with spiro-oxindole **4h** (50 mg, 0.128 mmol) and thiourea (97 mg, 1.28 mmol) in toluene (2 mL) was irradiated in a monomode microwave cavity at 160 °C for 4 h. The solvent was removed in vacuo and the crude product was purified by flash chromatography (30% ethyl acetate/hexanes) to yield 21 mg (42%) of **8** as a brownish solid. R_f = 0.21 (33% ethyl acetate/hexanes); Analytical data for **8**: FTIR (film) $\tilde{\nu}$ = 3218, 3159, 3059, 2932, 1724, 1653, 1614, 1569, 1470, 1374, 1200, 1129, 1024, 731 cm^{-1}; ^{1}H NMR (500 MHz; $CDCl_3$): δ 11.74 (bs, 1H), 7.45-7.39 (m, 6H), 7.14 (d, *J* = 7.2 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 5.97 (bs, 1H), 5.73 (d, *J* = 9.2 Hz, 1H), 2.77 (s, 3H), 2.66-2.59 (m, 1H), 2.43-2.38 (m, 1H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 174.9, 174.3, 159.4, 151.9, 144.6, 139.7, 130.4, 129.1, 128.9, 128.1, 127.1, 123.8, 123.3, 109.9, 108.3, 76.4, 70.9, 33.2, 26.1; LRMS (ESI): Mass calcd for $C_{21}H_{17}N_3O_3S$ $[M+H]^+$: 392; found 392.



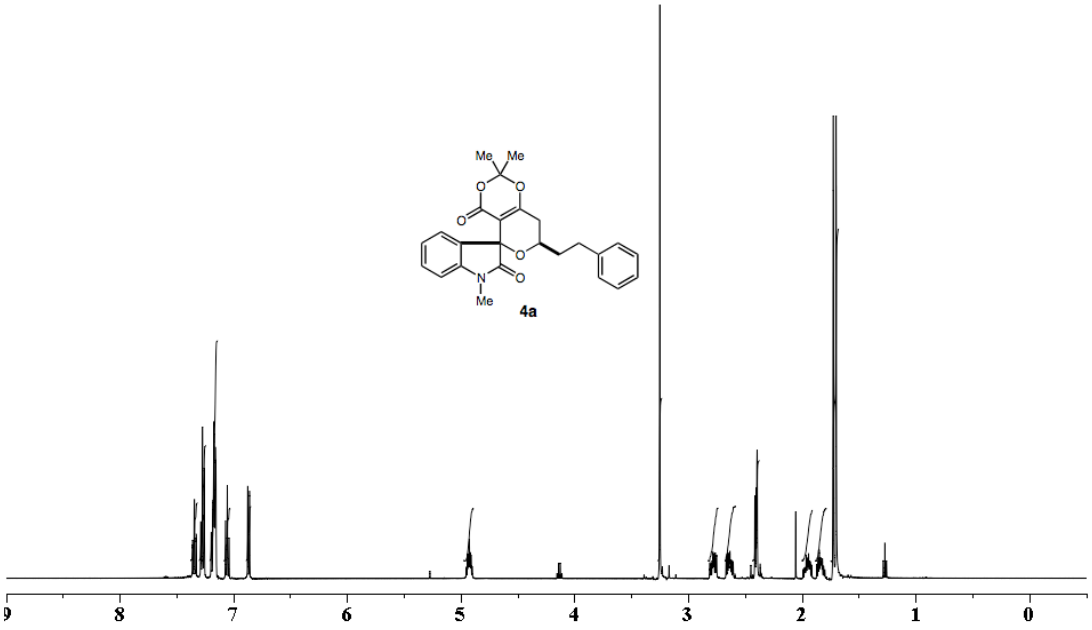
Bicyclic dioxinone 10a: Prepared according to the general procedure using 6-(2-hydroxy-4-phenylbutyl)-2,2-dimethyl-4*H*-1,3-dioxin-4-one (50 mg, 0.18 mmol) and methyl 2,2-dimethoxy-2-phenylethanoate (25 mg, 0.12 mmol) and purified by flash chromatography using 30% EtOAc/hexanes to afford 40 mg (79% yield) of **10a** (20:1 dr) as a yellow oil. R_f = 0.45 (33% ethyl acetate/hexanes); Analytical data for **10a**: FTIR (film) $\tilde{\nu}$ = 2924, 2853, 1730, 1644, 1404, 1273, 1205, 1011, 751 cm^{-1}; ^{1}H NMR (500 MHz; $CDCl_3$): δ 7.56-7.54 (m, 2H), 7.35-7.27 (m, 5H), 7.21-7.17 (m, 3H), 3.97 (tdd, *J* = 7.5, 7.2, 4.0 Hz, 1H), 3.81 (s, 3H), 2.86 (ddd, *J* = 14.1, 8.9, 5.3 Hz, 1H), 2.71 (dt, *J* = 14.1, 8.1 Hz, 1H), 2.42 (dd, *J* = 17.9, 10.6 Hz, 1H), 2.30 (dd, *J* = 17.8, 3.2 Hz, 1H), 2.07-2.01 (m, 1H), 1.97-1.90 (m, 1H), 1.66 (s, 3H), 1.50 (s, 3H); ^{13}C NMR (125 MHz; $CDCl_3$): δ 170.8, 163.4, 158.5, 141.4, 139.7, 128.6, 128.3, 127.8, 127.5, 126.1, 106.2,

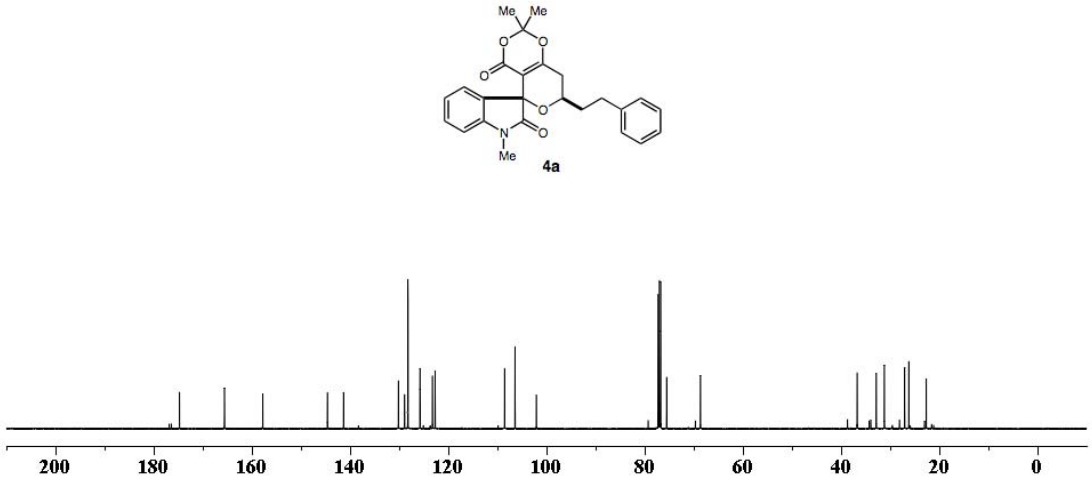
106.1, 81.2, 70.1, 52.9, 36.9, 33.5, 31.2, 29.8, 27.1, 23.4; LRMS (ESI): Mass calcd for $C_{25}H_{26}O_6$ $[M+H]^+$: 423; found 423.

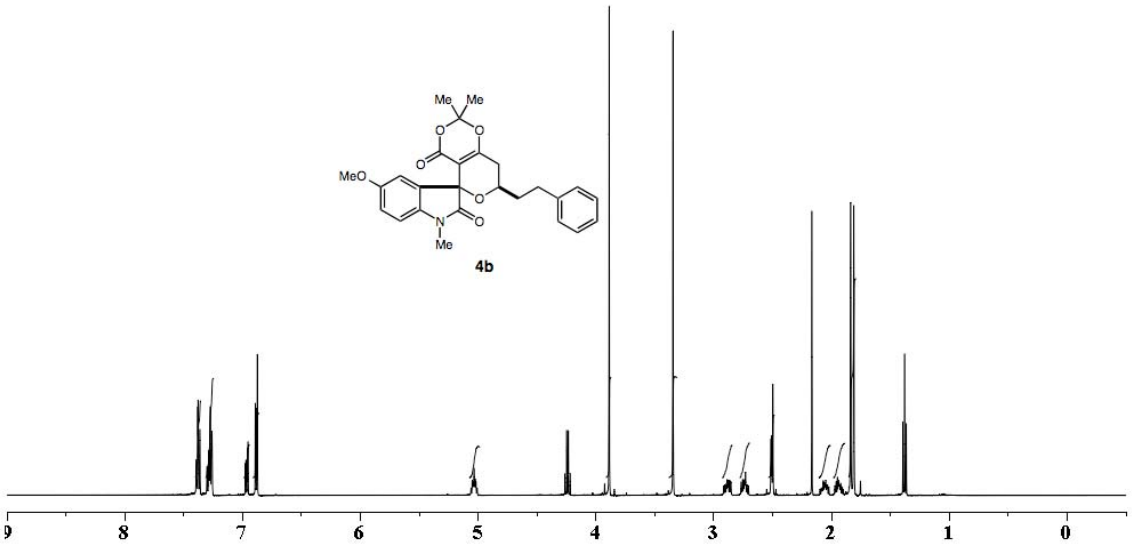


Bicyclic dioxinone 10b: Prepared according to the general procedure using 2,2-dimethoxyacenaphthylen-1-(2*H*)-one (50 mg, 0.22 mmol) and 6-(2-hydroxyhexyl)-2,2-dimethyl-4*H*-1,3-dioxin-4-one (75 mg, 0.33 mmol) and purified by flash chromatography using 30% EtOAc/hexanes to afford 71 mg (82% yield) of **10b** (20:1 dr) as a white solid. R_f = 0.77 (33% ethyl acetate/hexanes); Analytical data for **10b**: mp = 120-150 °C (decomp.); FTIR (film) $\tilde{\nu}$ = 2955, 2934, 2870, 1723, 1650, 1406, 1276, 1202, 1009, 786 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$): δ 8.09 (d, *J* = 8.2 Hz, 1H), 7.99 (d, *J* = 7.0 Hz, 1H), 7.89 (d, *J* = 8.3 Hz, 1H), 7.73 (dd, *J* = 8.1, 7.0 Hz, 1H), 7.63 (dd, *J* = 8.3, 6.9 Hz, 1H), 7.44 (d, *J* = 6.9 Hz, 1H), 4.79-4.74 (m, 1H), 2.46-2.44 (m, 2H), 1.78 (s, 3H), 1.72 (s, 3H), 1.61-1.55 (m, 1H), 1.53-1.47 (m, 1H), 1.31-1.23 (m, 4H), 0.83 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz; $CDCl_3$): δ 201.7, 166.1, 158.5, 142.5, 139.4, 131.6, 131.5, 130.9, 128.6, 128.4, 126.0, 122.3, 119.9, 106.6, 102.9, 79.1, 70.1, 34.9, 33.3, 27.3, 27.2, 22.9, 22.6, 14.0. LRMS (ESI): Mass calcd for $C_{24}H_{24}O_5$ $[M+H]^+$: 393; found 393.

Selected NMR Spectra



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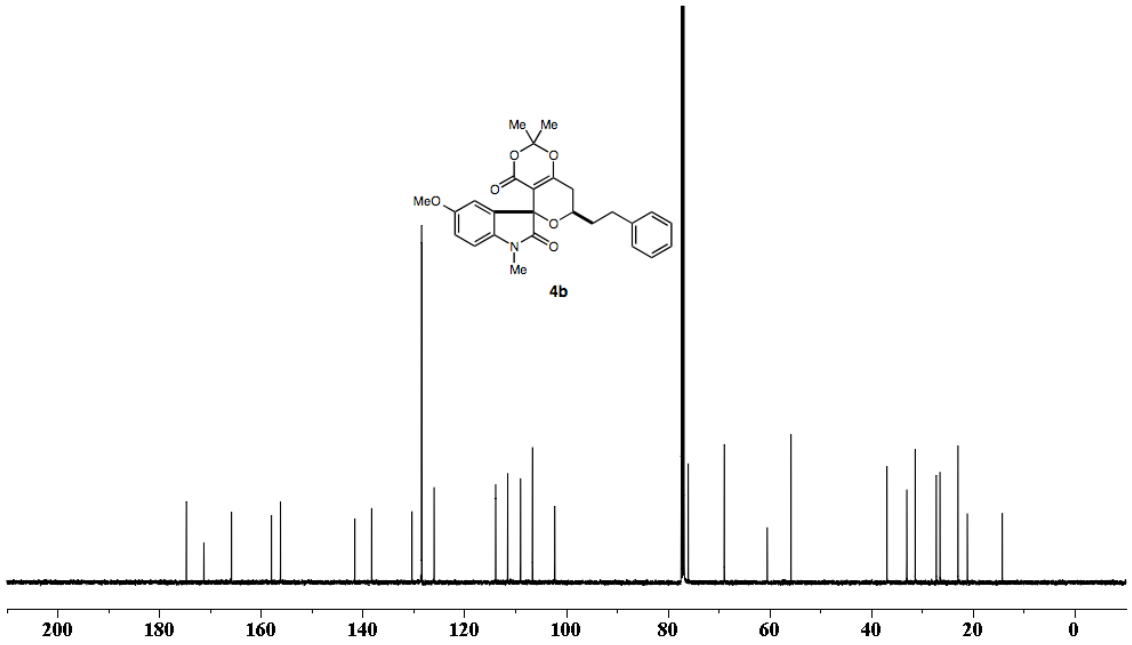
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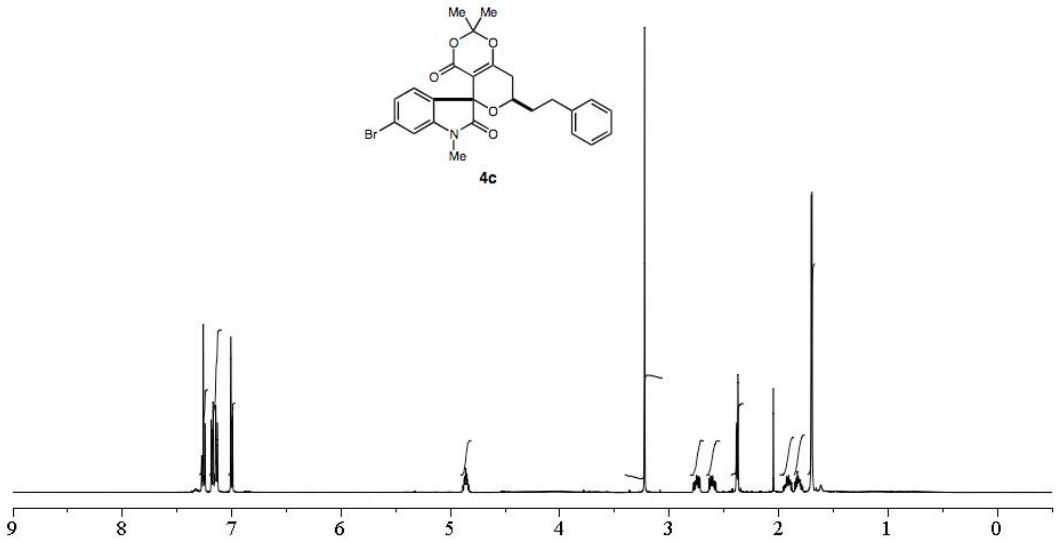
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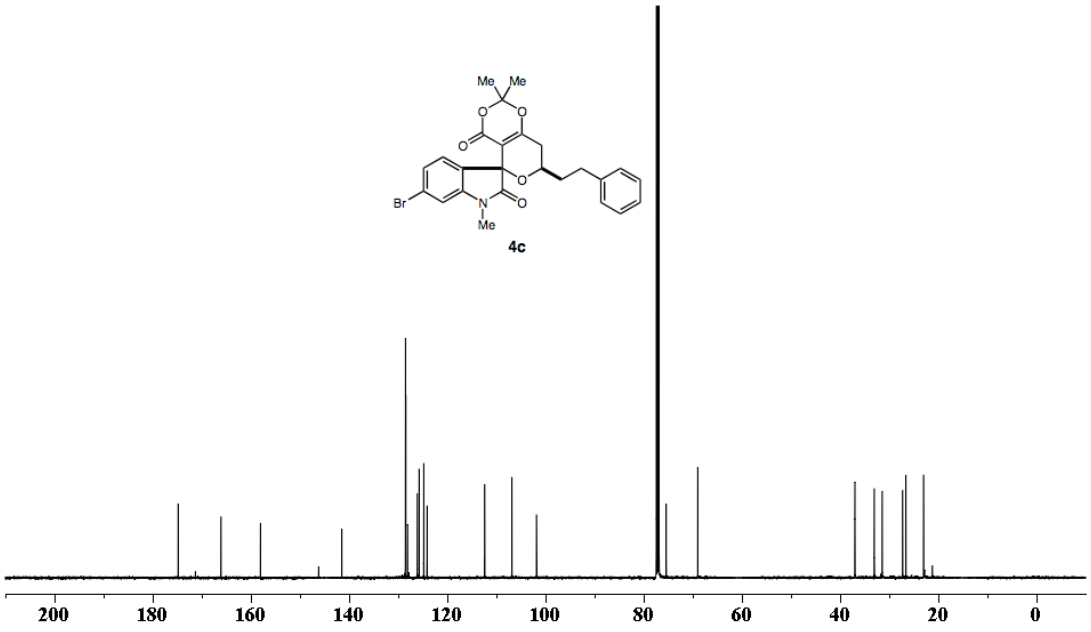
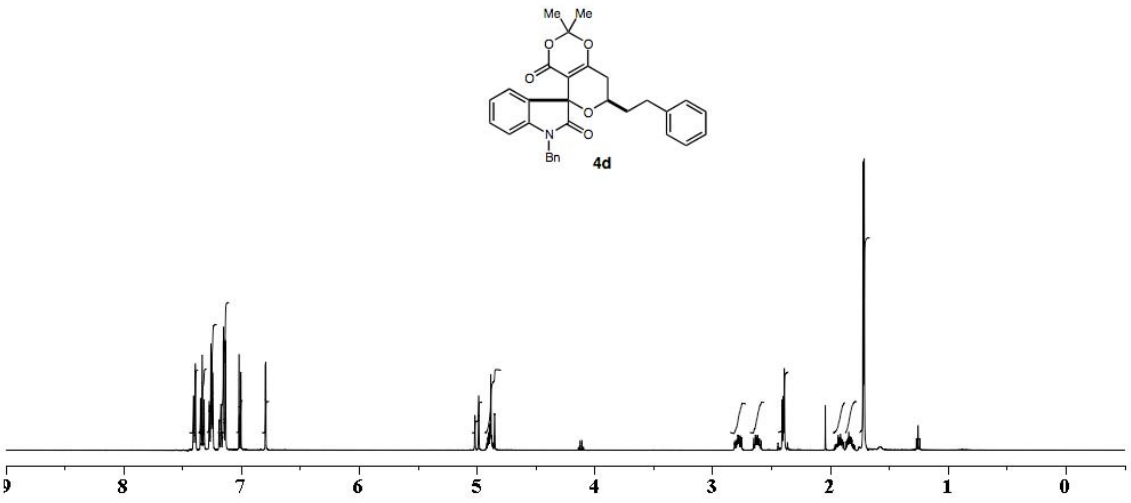
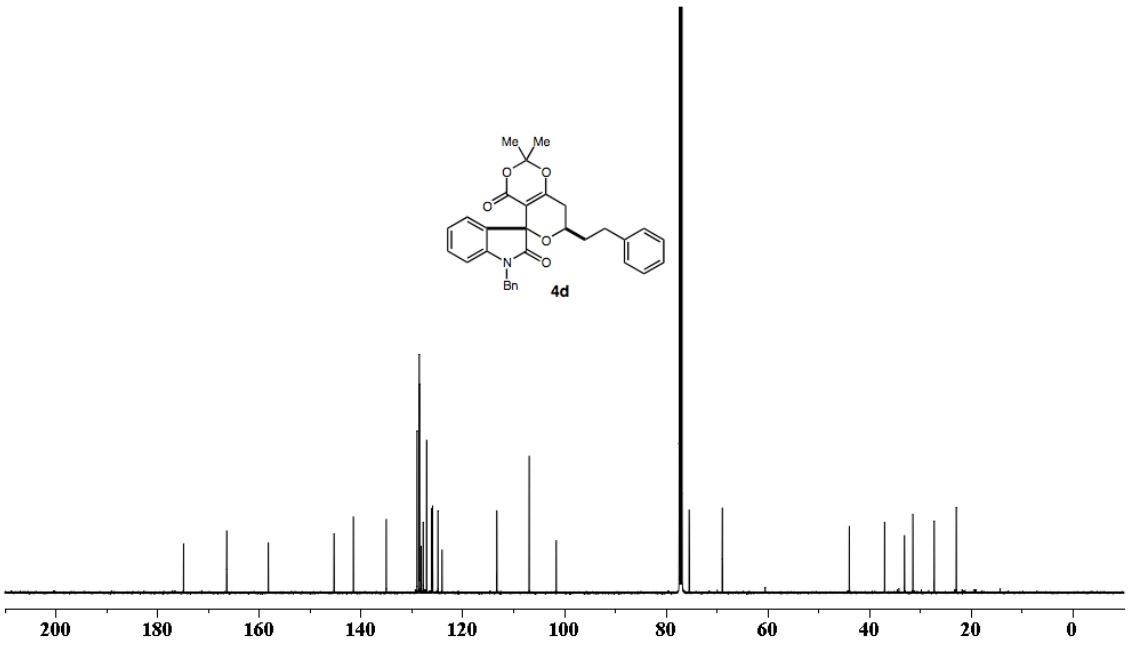
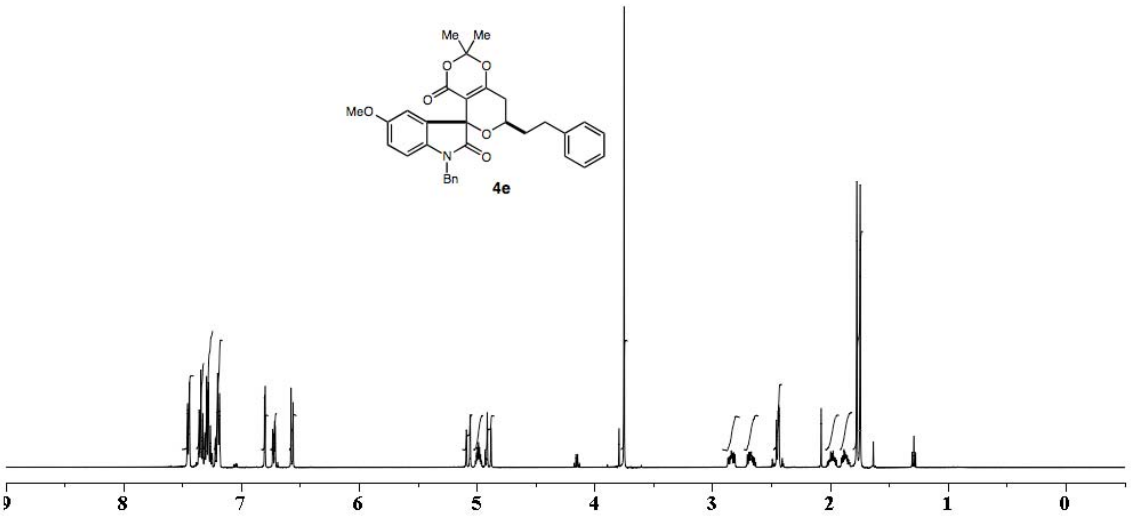
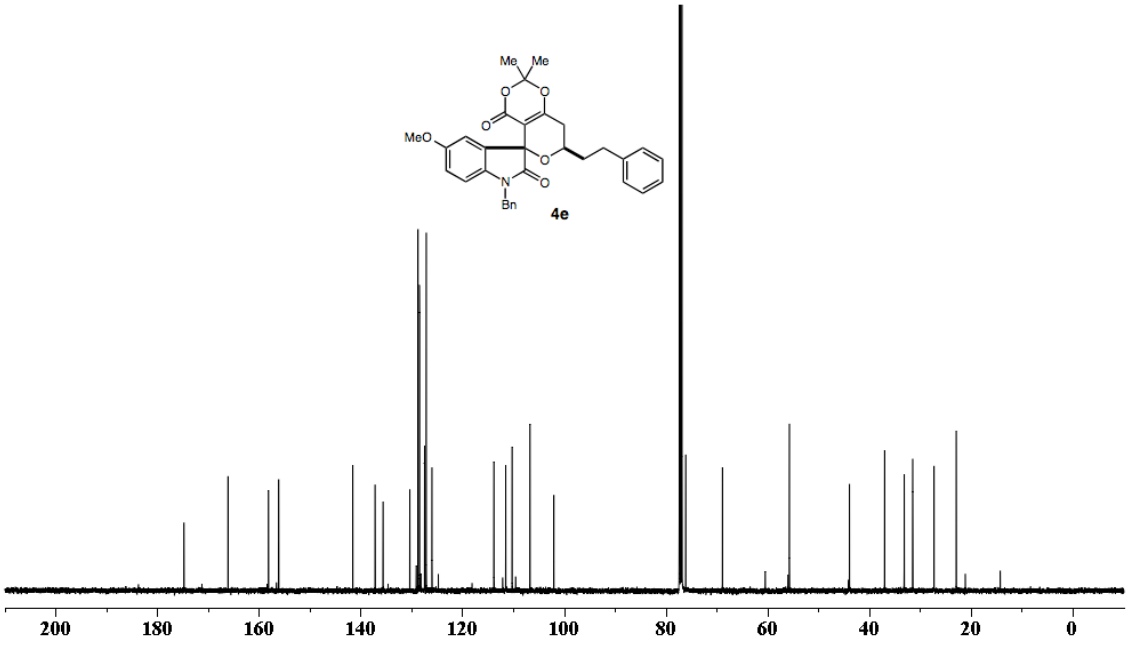
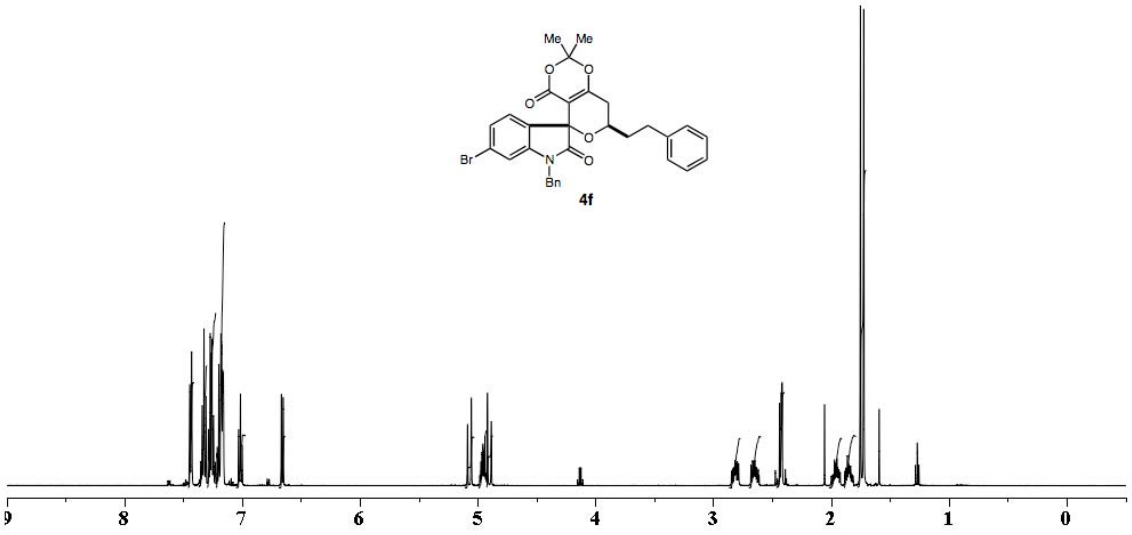

Me
Me
O
O
O
O
O
Br
N
O
Me
4c
200
180
160
140
120
100
80
60
40
20
0

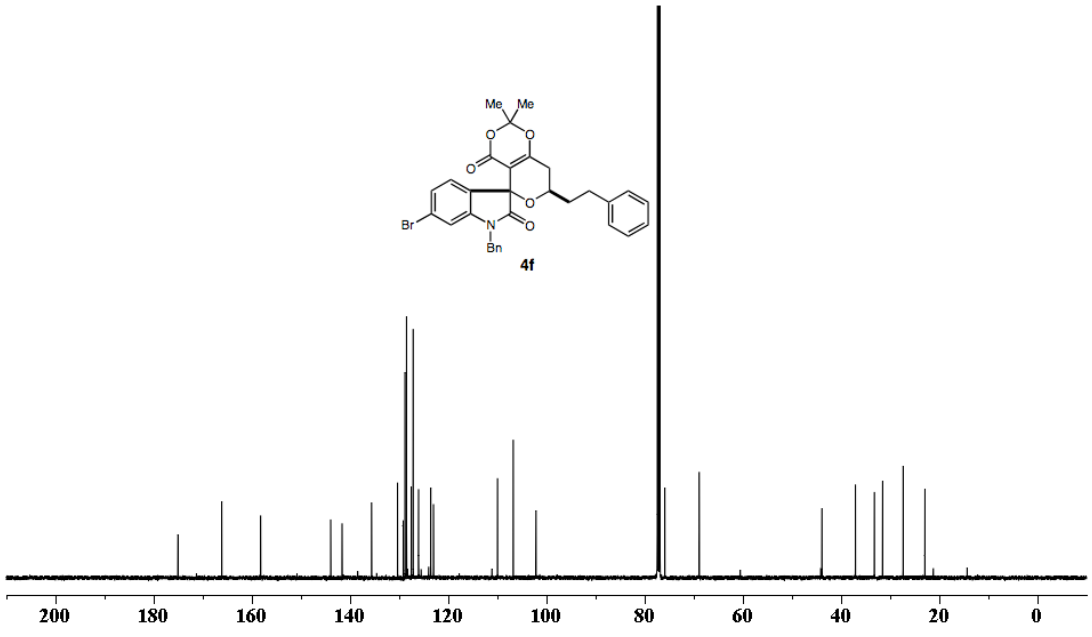

Me
Me
O
O
O
O
O
N
Bn
O
4d
9
8
7
6
5
4
3
2
1
0

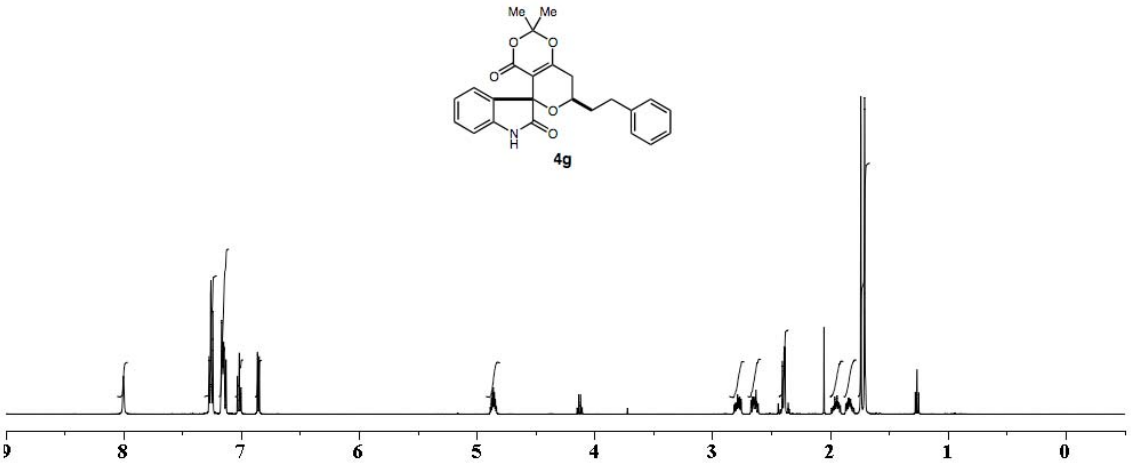

Me
Me
O
O
O
O
O
N
Bn
O
4d
200
180
160
140
120
100
80
60
40
20
0

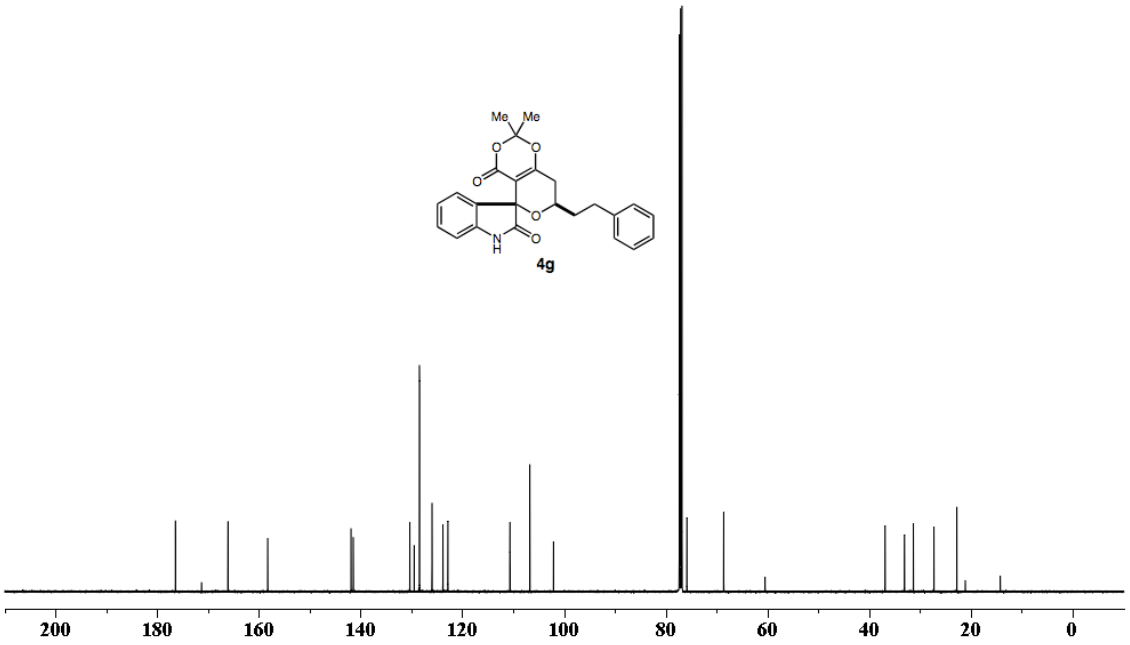

Me
Me
O
O
O
MeO
O
N
Bn
O
4e
9
8
7
6
5
4
3
2
1
0

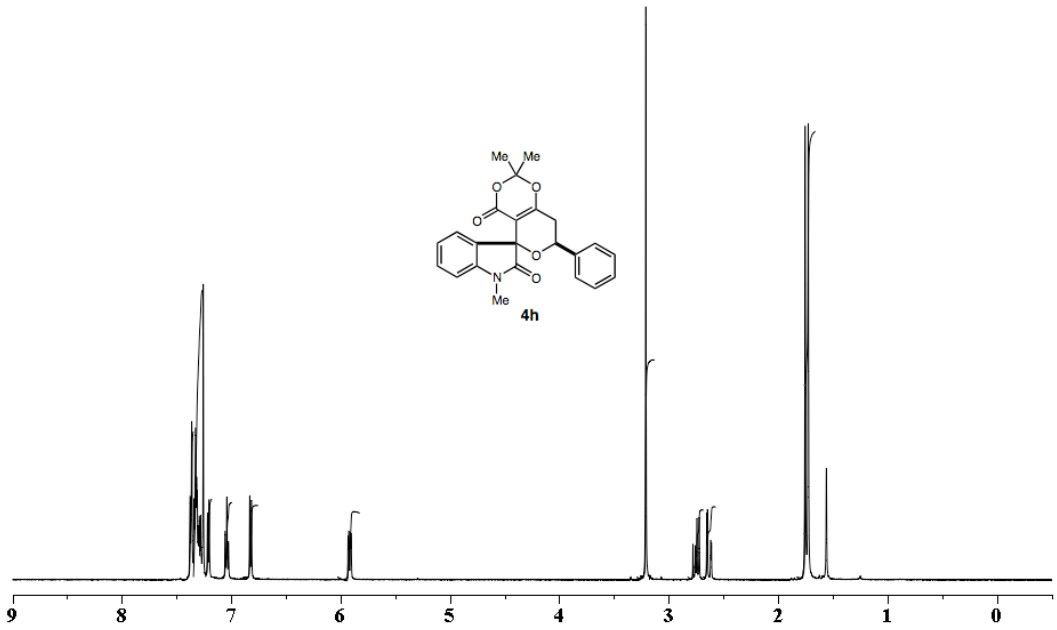

Me
Me
O
O
O
MeO
O
N
Bn
O
4e
200
180
160
140
120
100
80
60
40
20
0

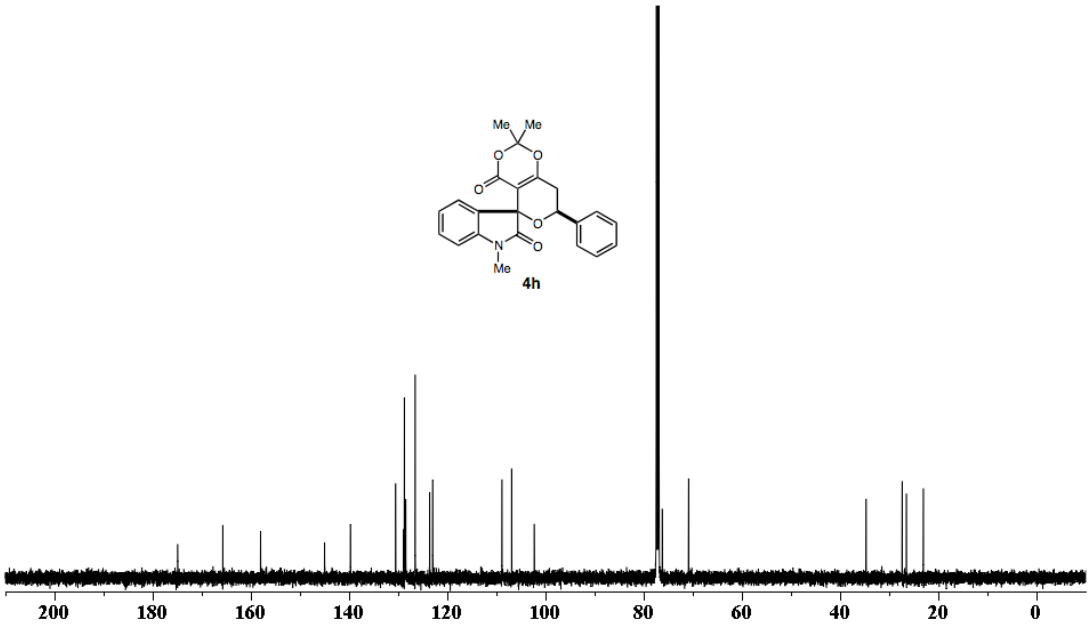

Me
Me
O
O
O
O
Br
N
O
Bn
4f
9
8
7
6
5
4
3
2
1
0

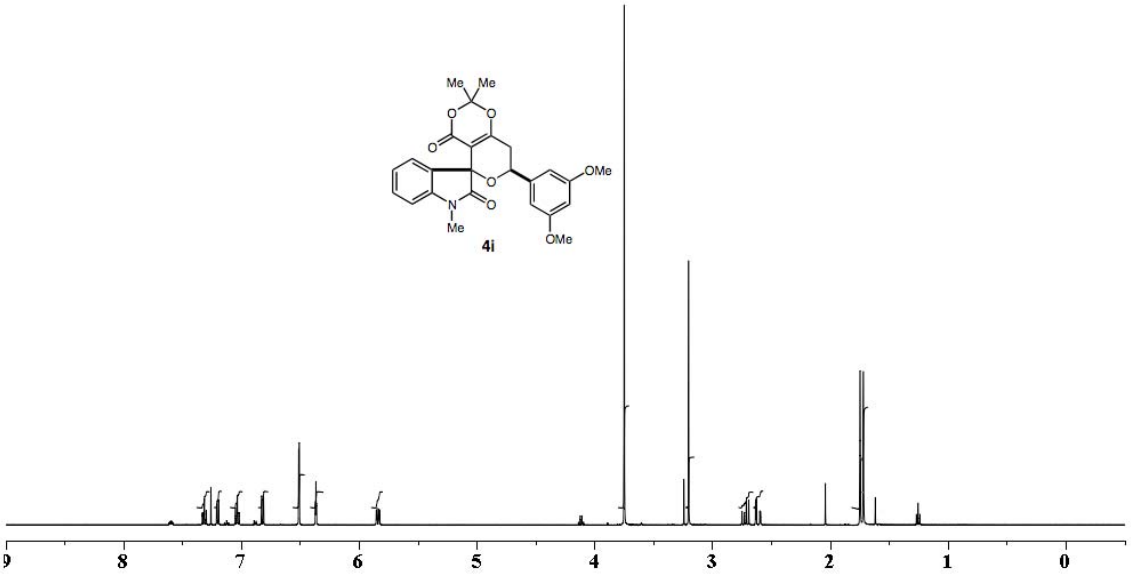

Me
Me
O
O
O
O
Br
N
O
Bn
4f
200
180
160
140
120
100
80
60
40
20
0

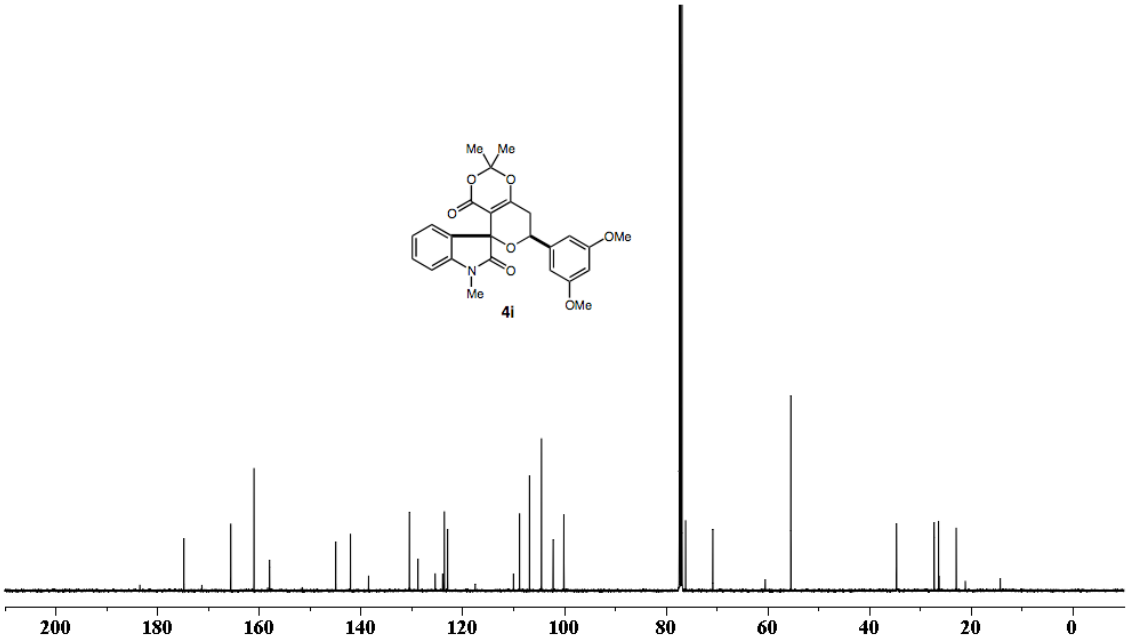

Me
Me
O
O
O
O
O
N
H
O
4g
9
8
7
6
5
4
3
2
1
0

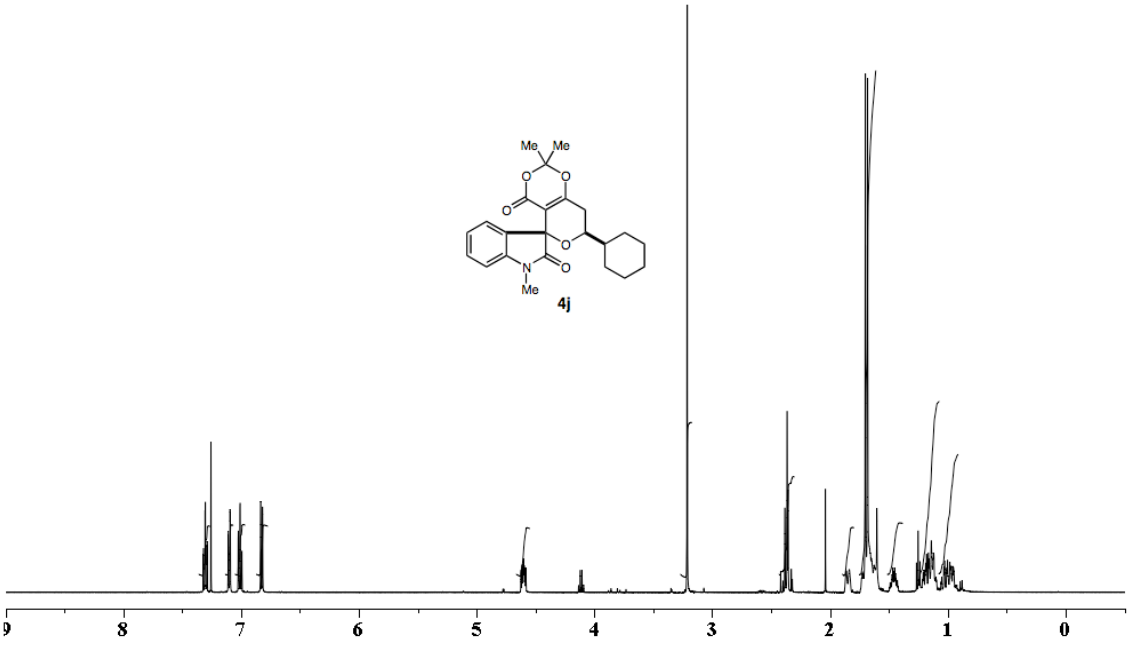

Me
Me
O
O
O
O
O
N
H
O
4g
200
180
160
140
120
100
80
60
40
20
0

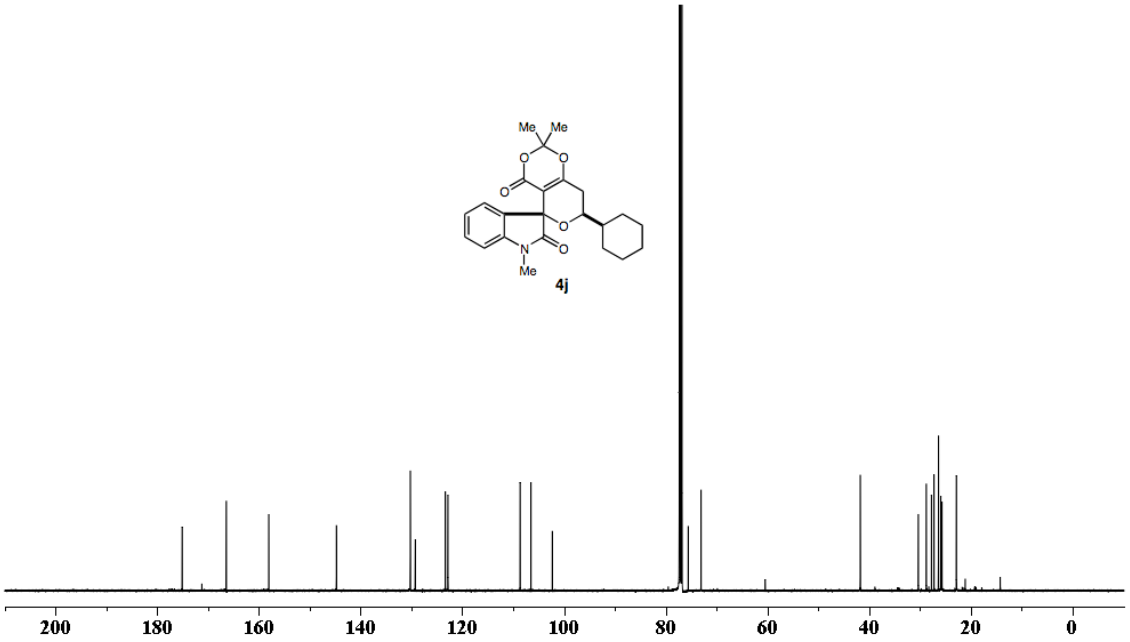

Me
Me
O
O
O
O
O
N
Me
O
4h
9
8
7
6
5
4
3
2
1
0

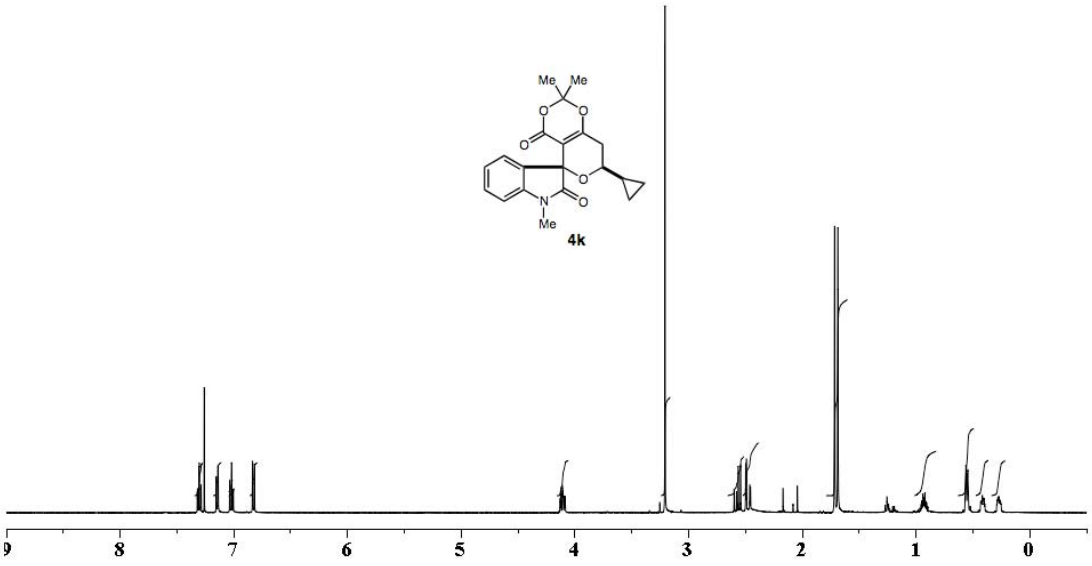

Me
Me
O
O
O
O
O
N
Me
O
4h
200
180
160
140
120
100
80
60
40
20
0

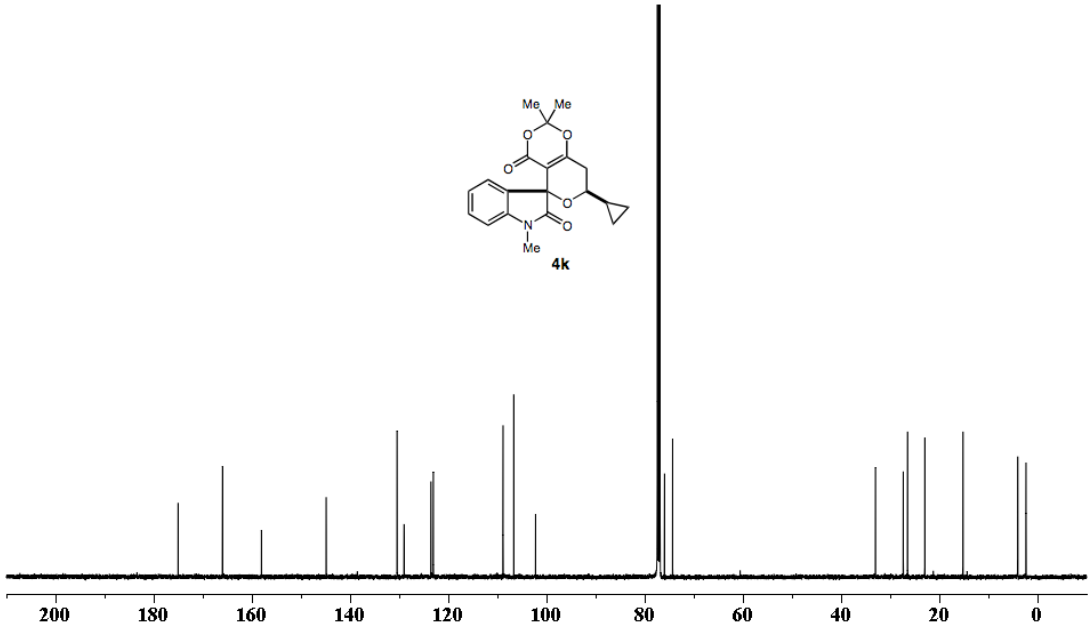

Me
Me
O
O
O
O
O
N
Me
OMe
OMe
4i
9
8
7
6
5
4
3
2
1
0

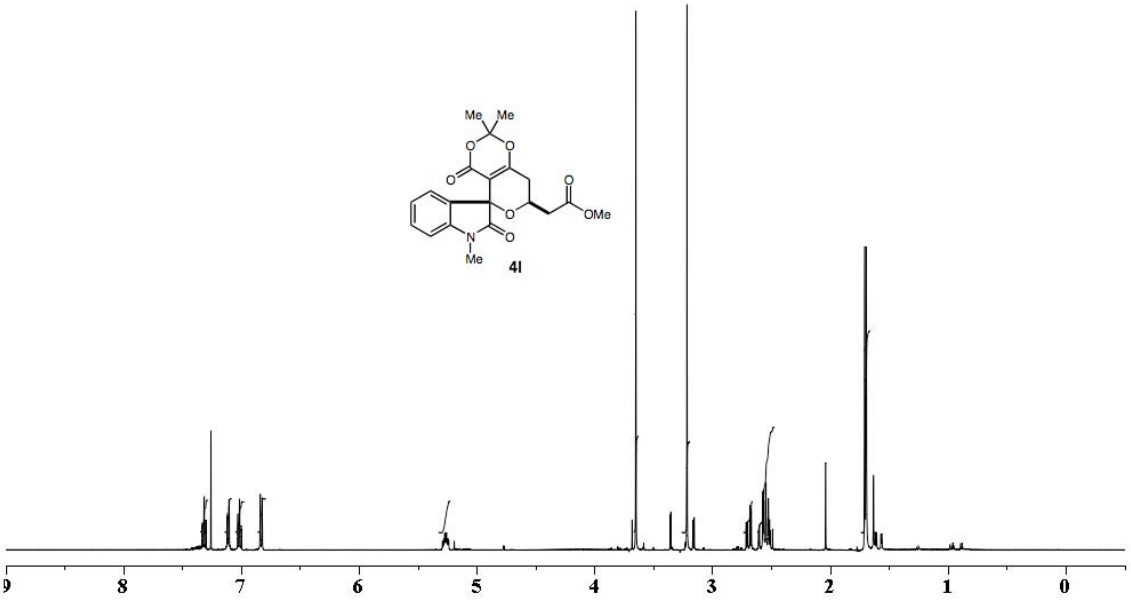

Me
Me
O
O
O
O
O
N
Me
OMe
OMe
4i
200
180
160
140
120
100
80
60
40
20
0

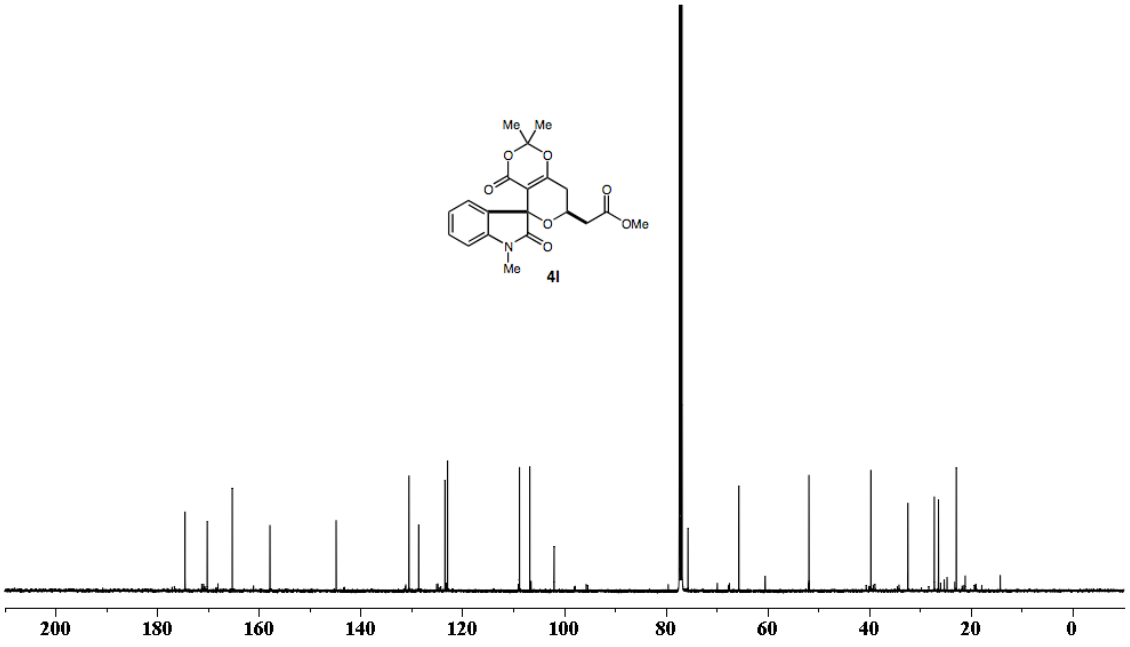

Me
Me
O
O
O
O
O
N
Me
O
4j
9
8
7
6
5
4
3
2
1
0

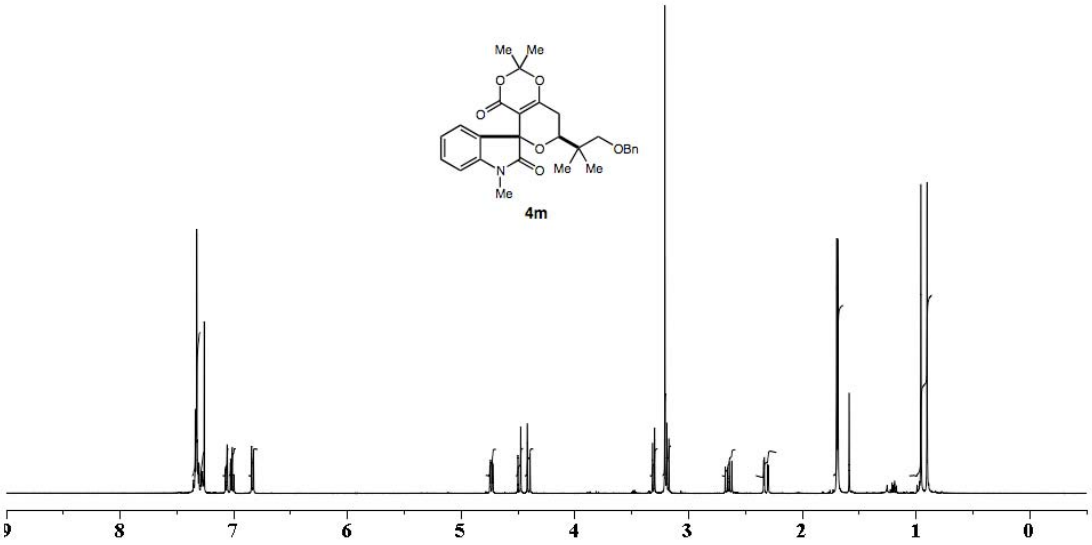

Me
Me
O
O
O
O
O
N
Me
O
4j
200
180
160
140
120
100
80
60
40
20
0

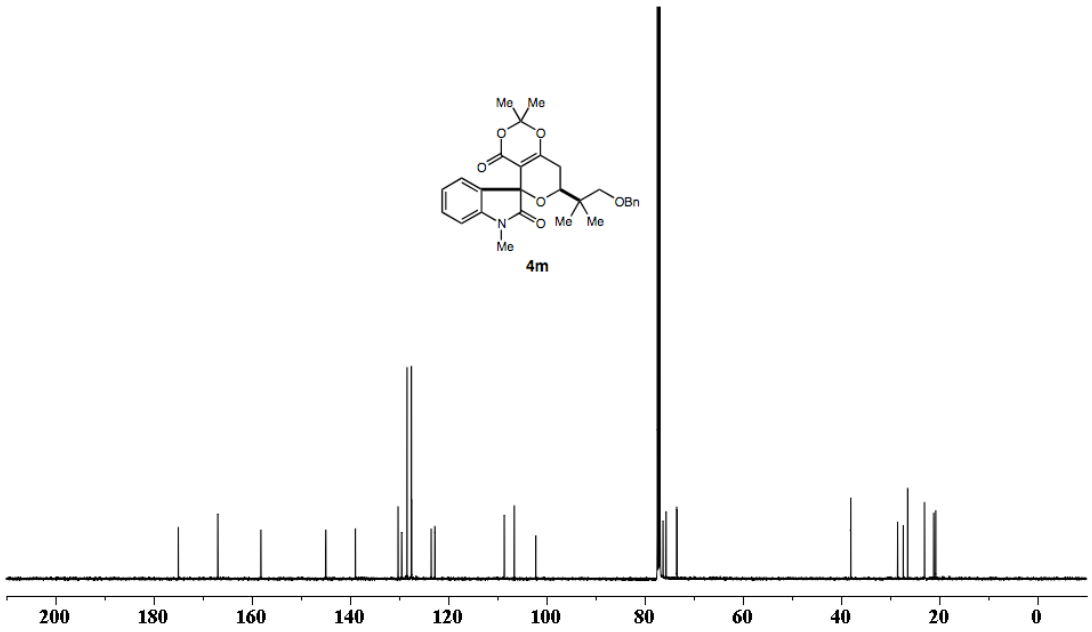

Me
Me
O
O
O
O
N
Me
O
4k
9
8
7
6
5
4
3
2
1
0

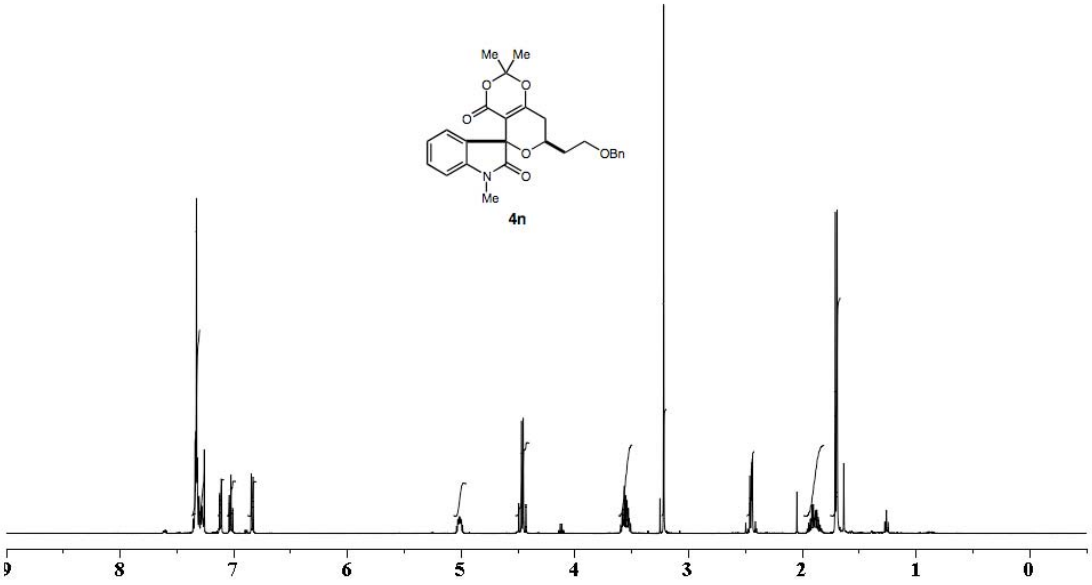

Me
Me
O
O
O
O
N
Me
O
4k
200
180
160
140
120
100
80
60
40
20
0

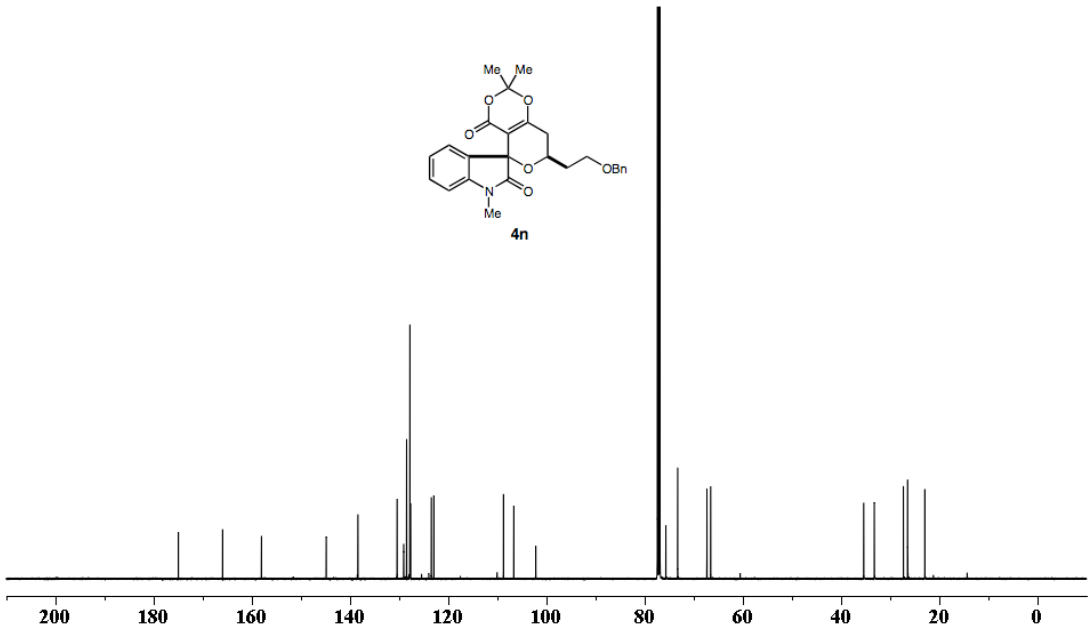

Me
Me
O
O
O
O
O
O
OMe
N
Me
4l
9
8
7
6
5
4
3
2
1
0

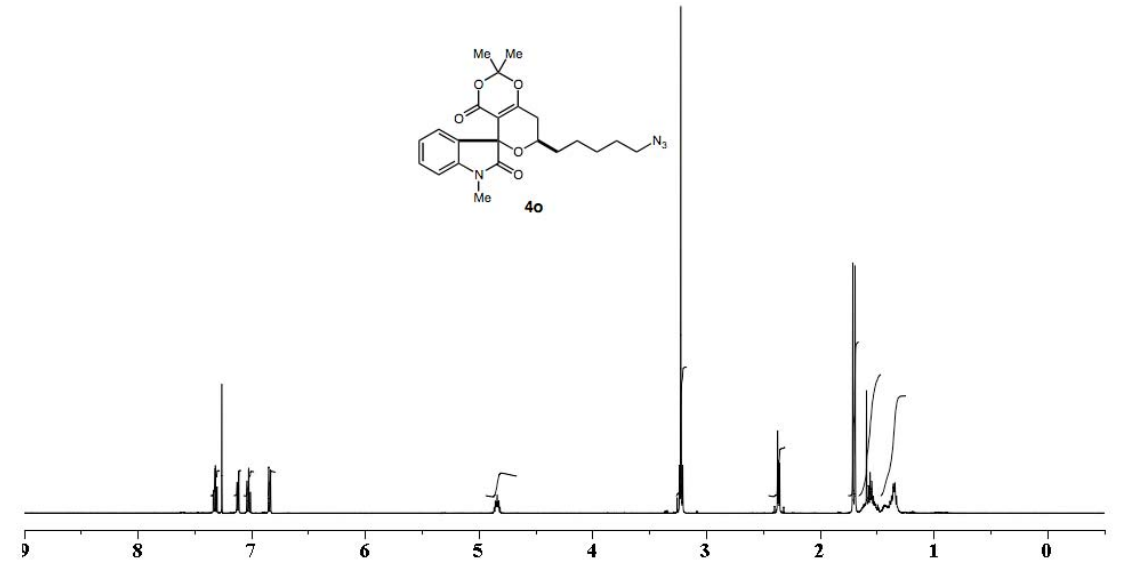

Me
Me
O
O
O
O
O
O
OMe
N
Me
4l
200
180
160
140
120
100
80
60
40
20
0

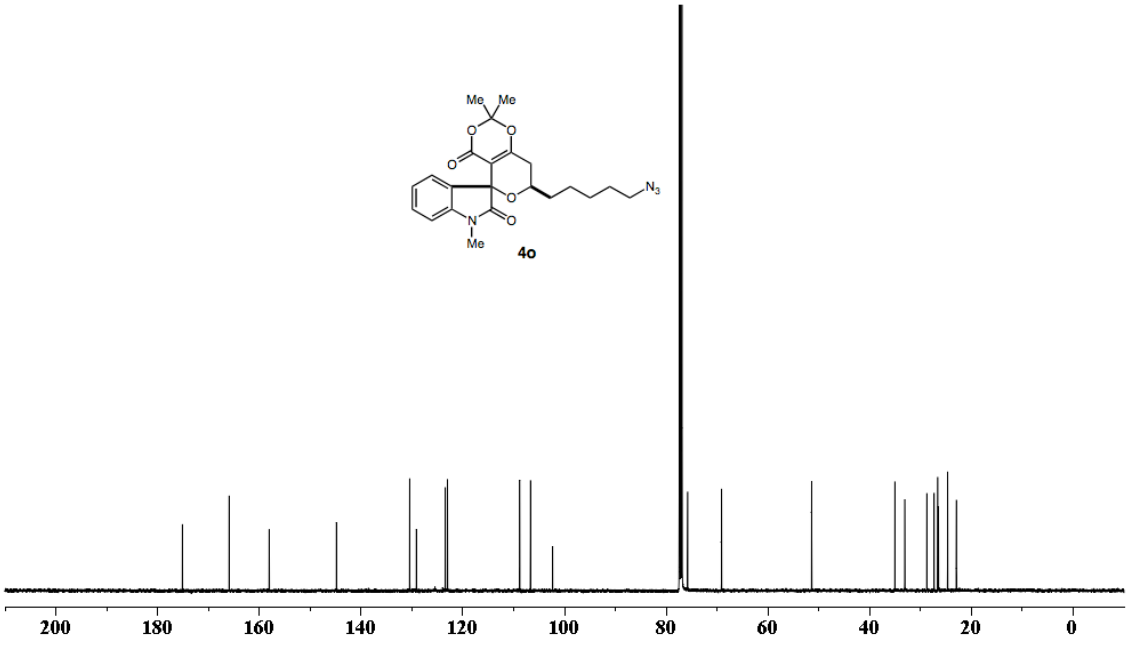

Me
Me
O
O
O
O
O
N
Me
O
Me
Me
OBn
Me
4m
9
8
7
6
5
4
3
2
1
0

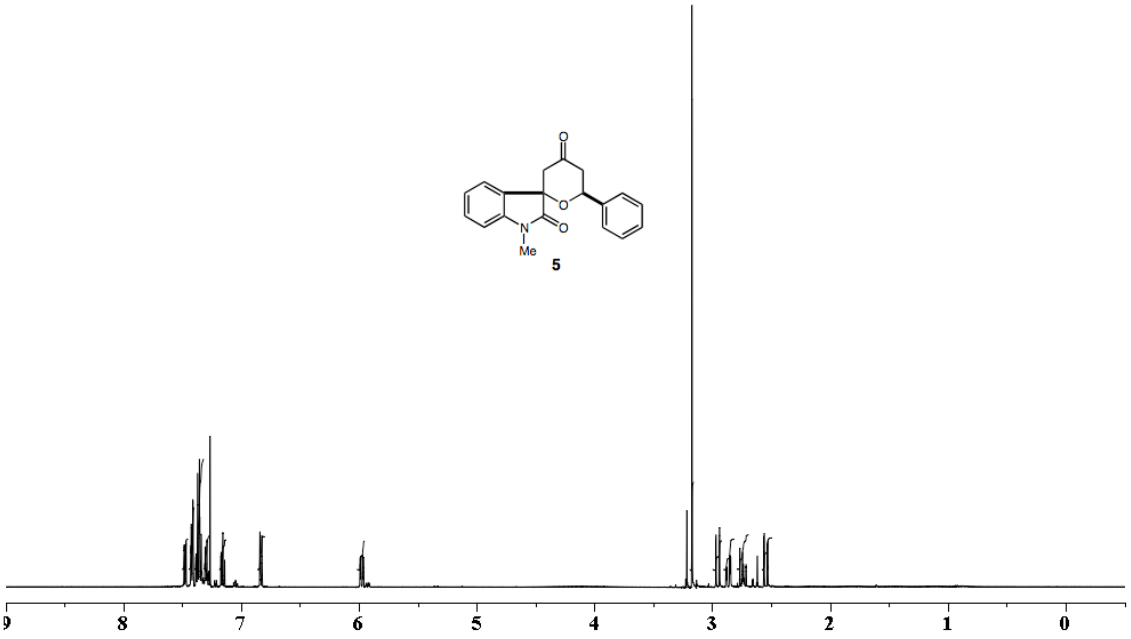

Me
Me
O
O
O
O
O
N
Me
O
Me
Me
OBn
Me
4m
200
180
160
140
120
100
80
60
40
20
0

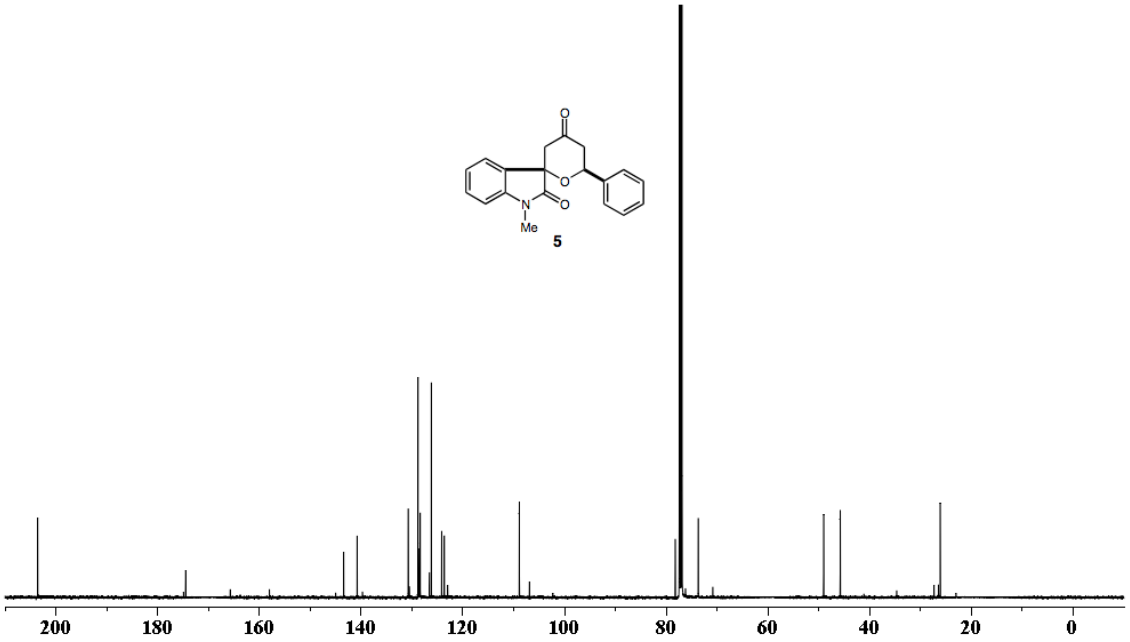

Me
Me
O
O
O
O
O
N
Me
O
OBn
4n
9
8
7
6
5
4
3
2
1
0

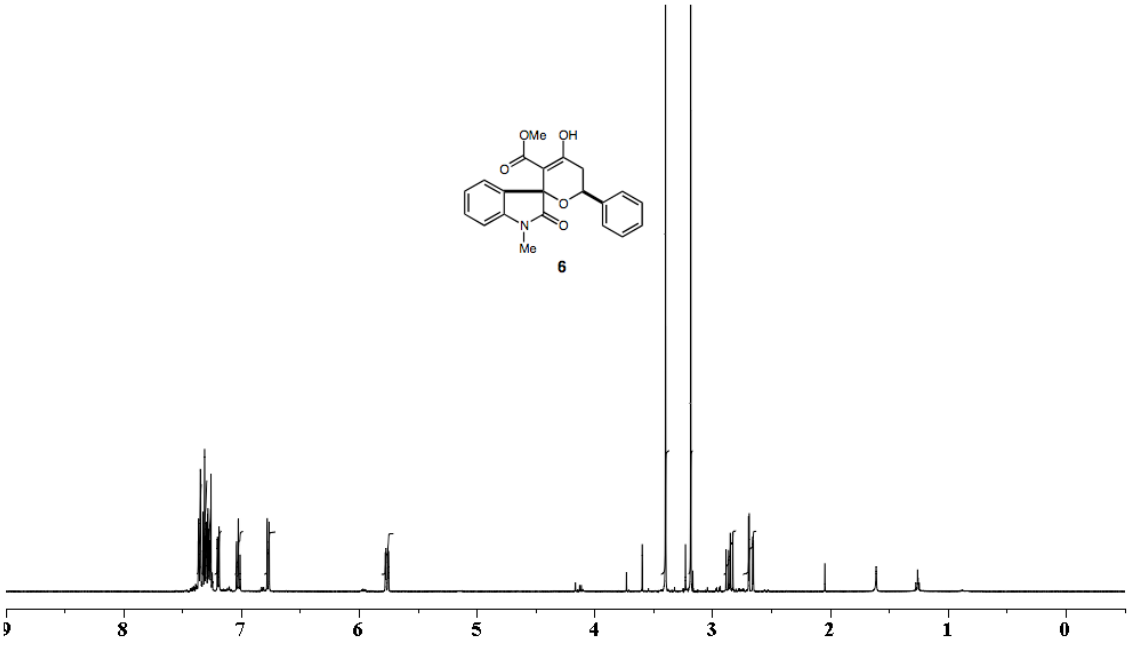

Me
Me
O
O
O
O
O
N
Me
O
OBn
4n
200
180
160
140
120
100
80
60
40
20
0

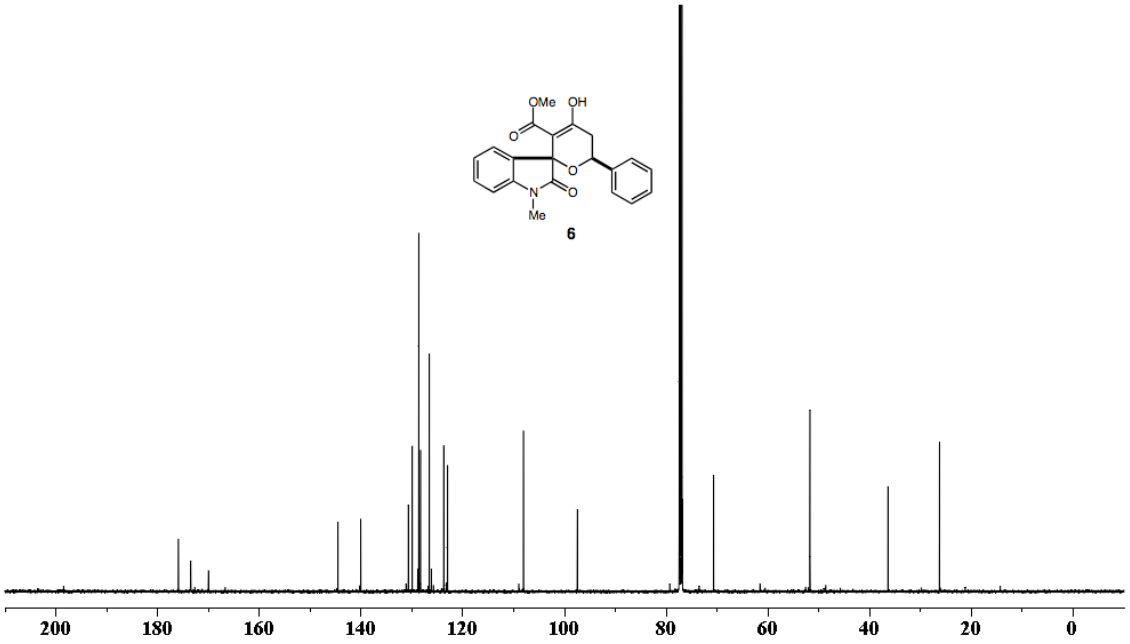

Me
Me
O
O
O
O
N
Me
N3
4o
9
8
7
6
5
4
3
2
1
0

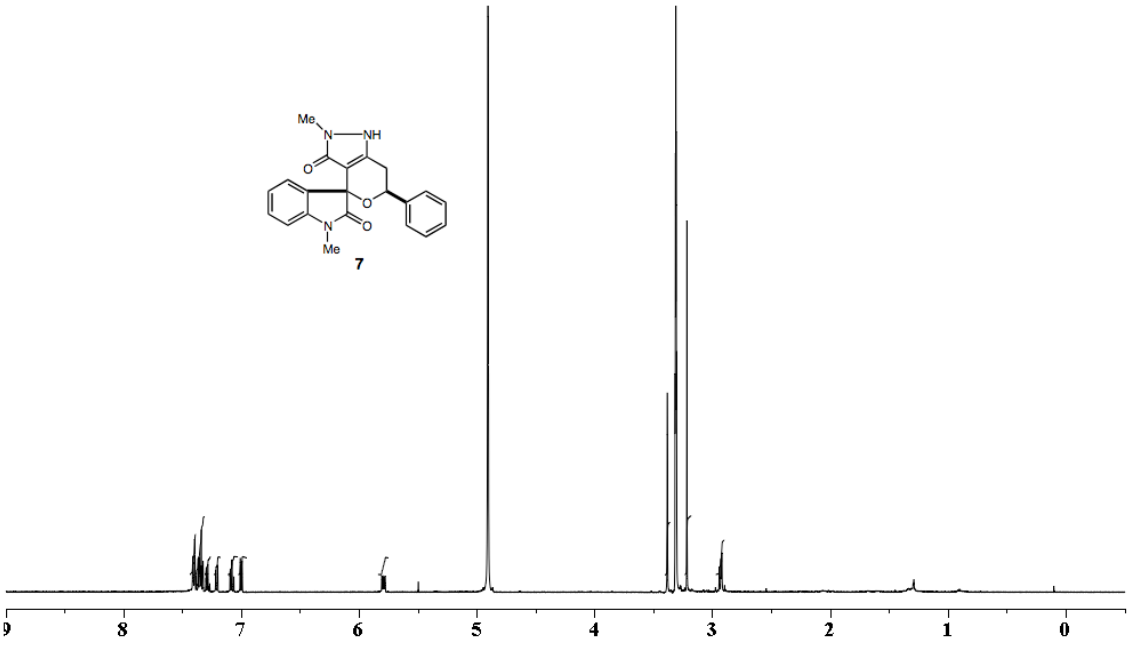

Me
Me
O
O
O
O
N
Me
N3
4o
200
180
160
140
120
100
80
60
40
20
0

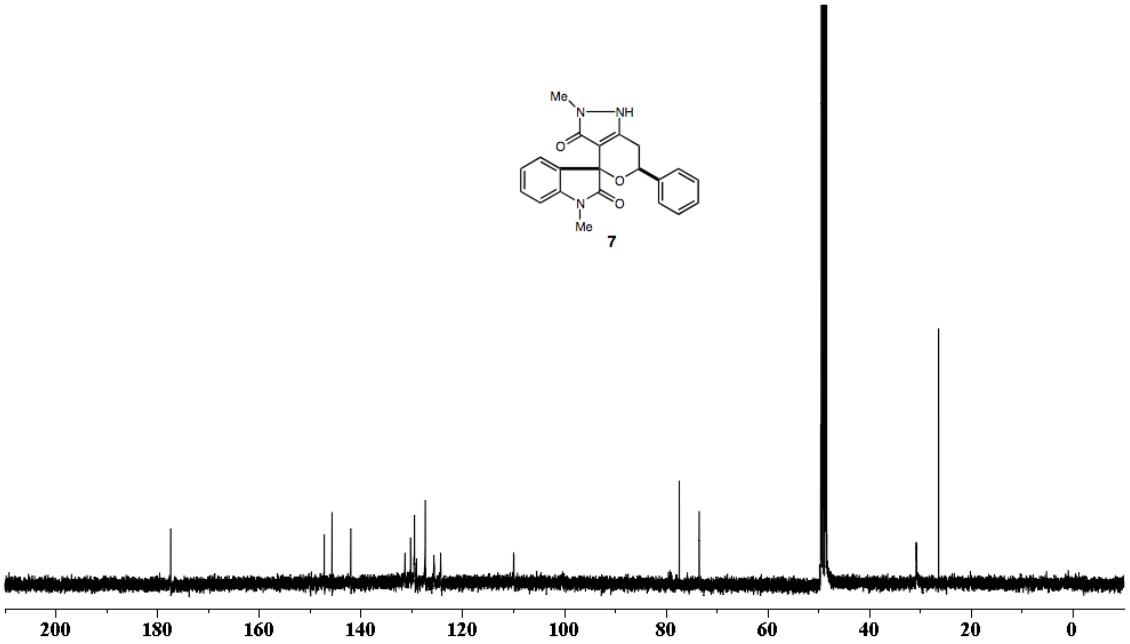

O
O
O
N
Me
O
5
9
8
7
6
5
4
3
2
1
0

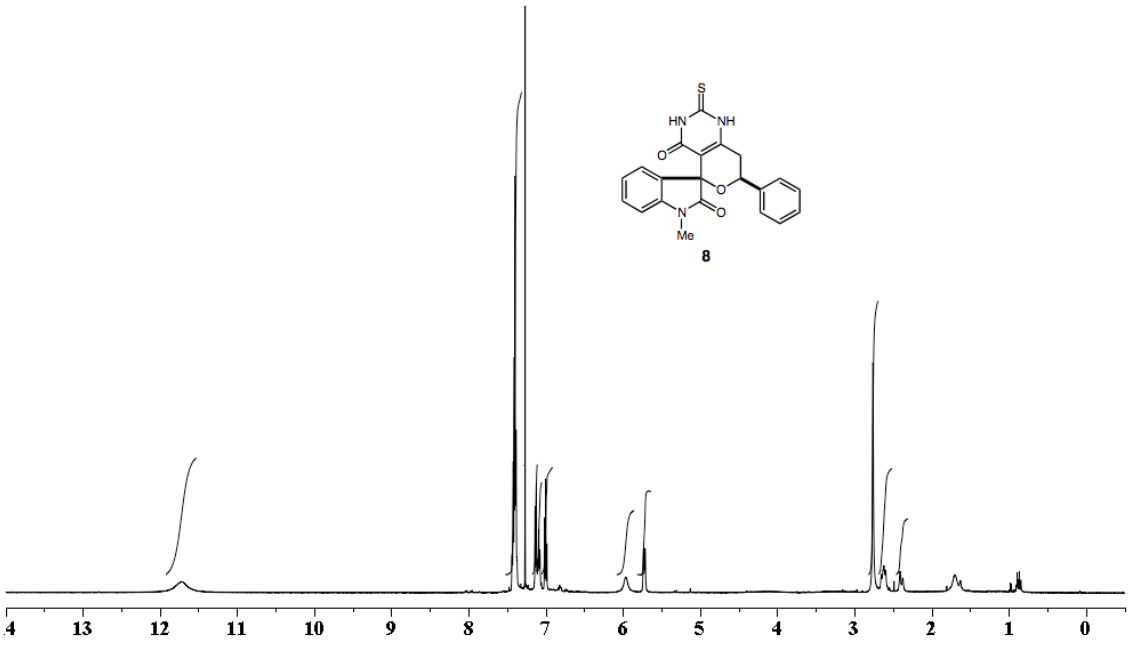

O
O
O
N
Me
O
5
200
180
160
140
120
100
80
60
40
20
0

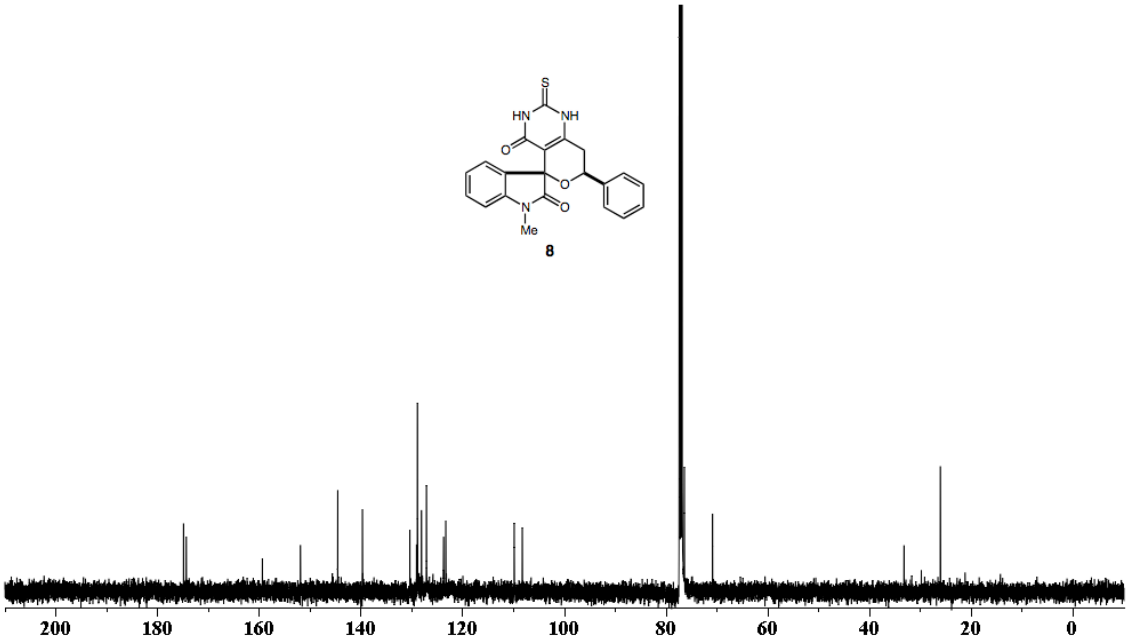

OMe
OH
O
O
N
Me
O
6
9
8
7
6
5
4
3
2
1
0

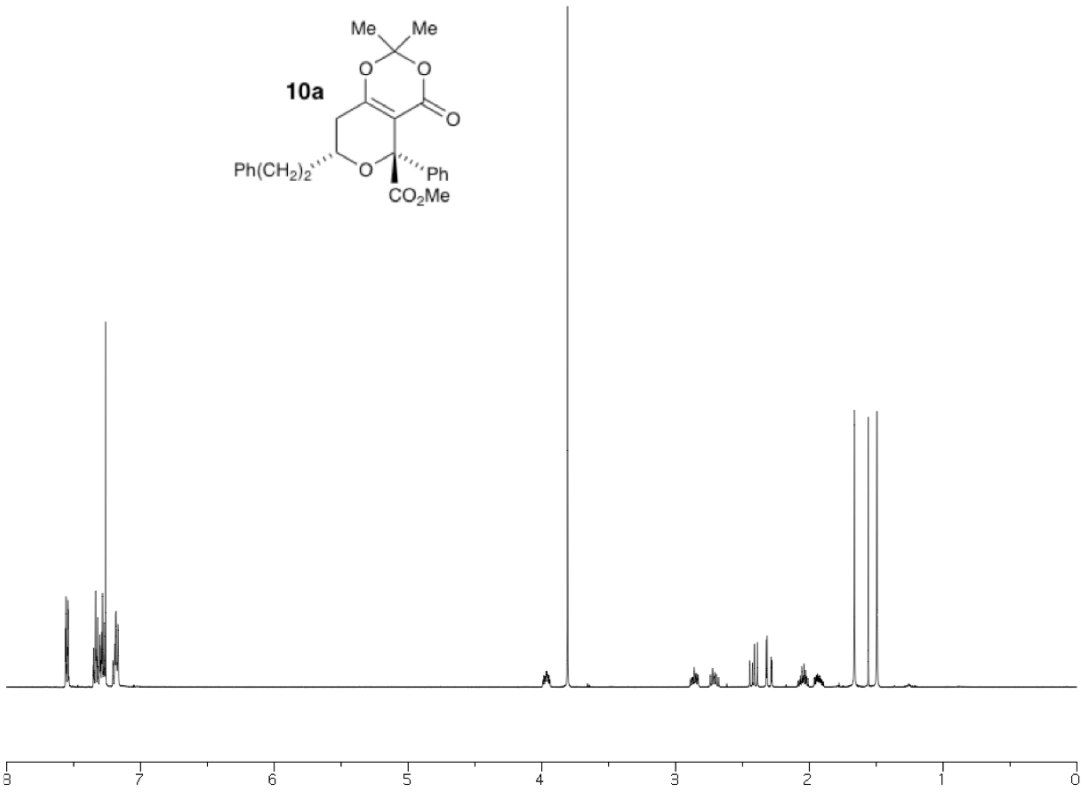

OMe
OH
O
O
N
Me
O
6
200
180
160
140
120
100
80
60
40
20
0

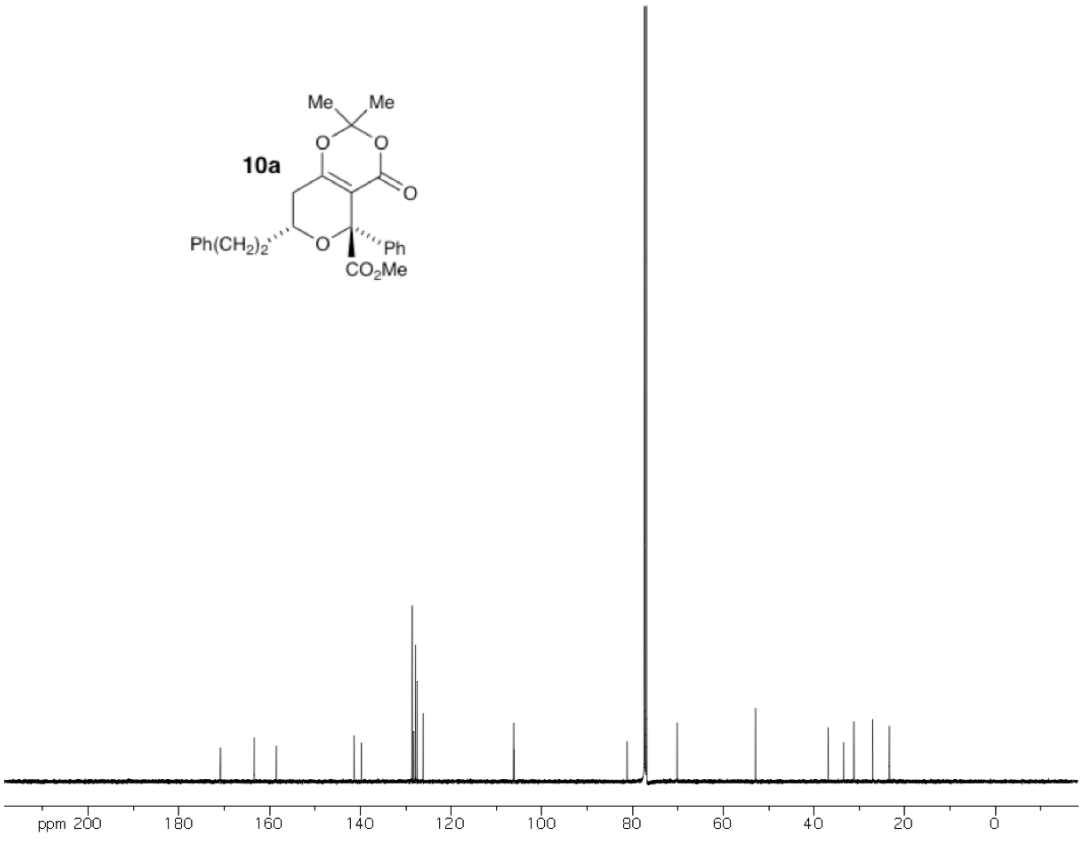

Me
N
NH
O
O
N
Me
7
9
8
7
6
5
4
3
2
1
0

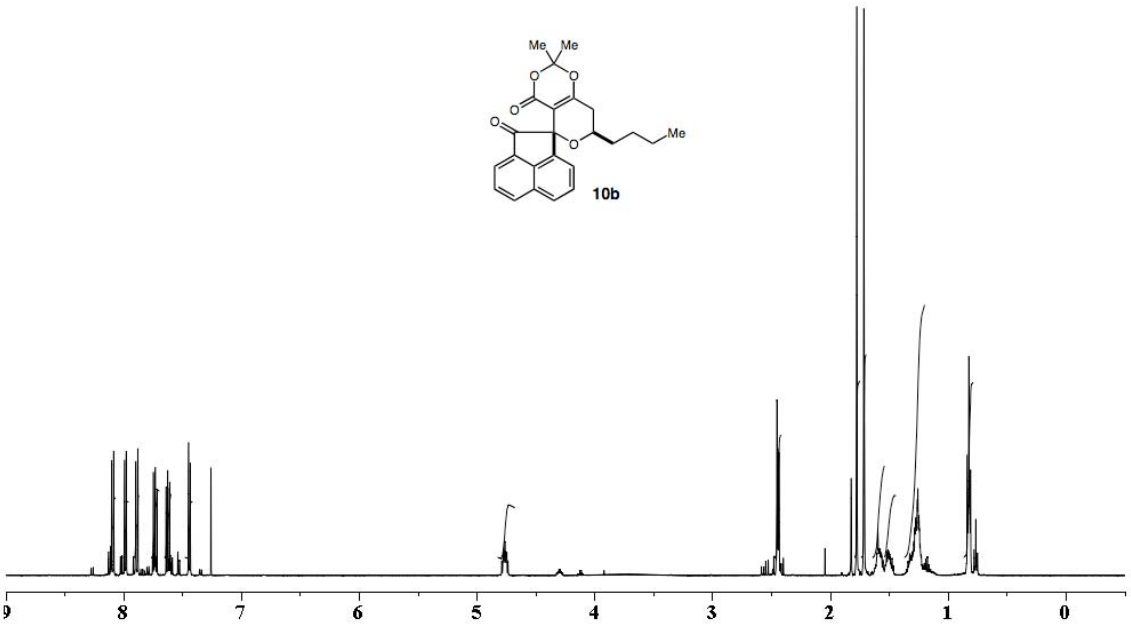

Me
N
NH
O
O
N
Me
7
200
180
160
140
120
100
80
60
40
20
0

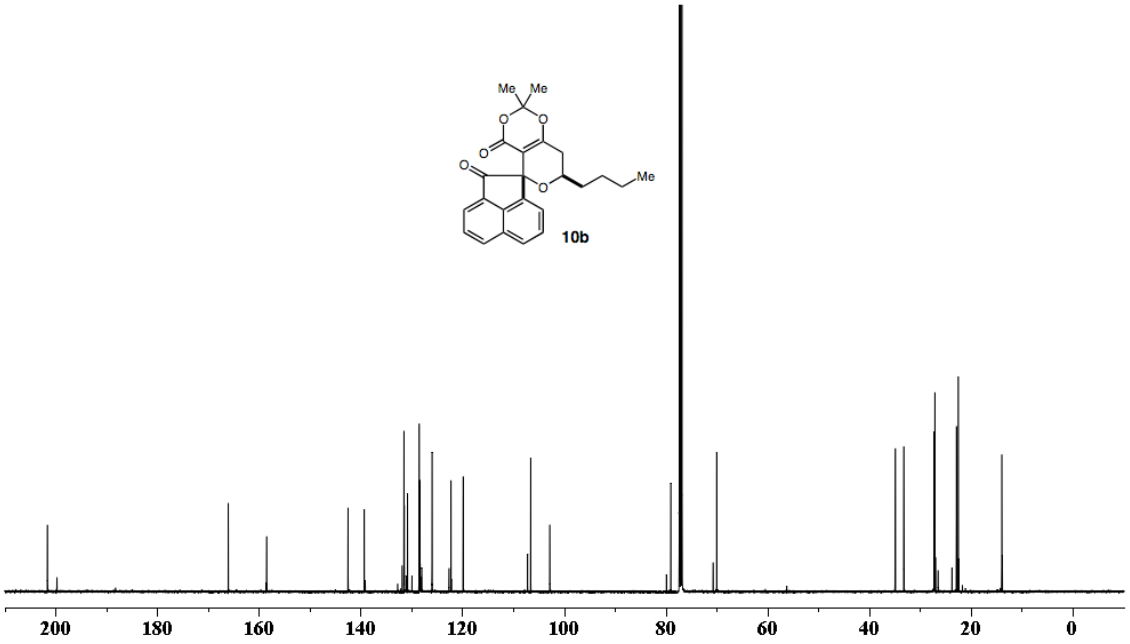

S
HN
NH
O
O
N
Me
8
4
13
12
11
10
9
8
7
6
5
4
3
2
1
0


S
HN
NH
O
O
N
Me
8
200
180
160
140
120
100
80
60
40
20
0


Me
Me
O
O
10a
O
Ph(CH2)2
O
Ph
CO2Me
8
7
6
5
4
3
2
1
0

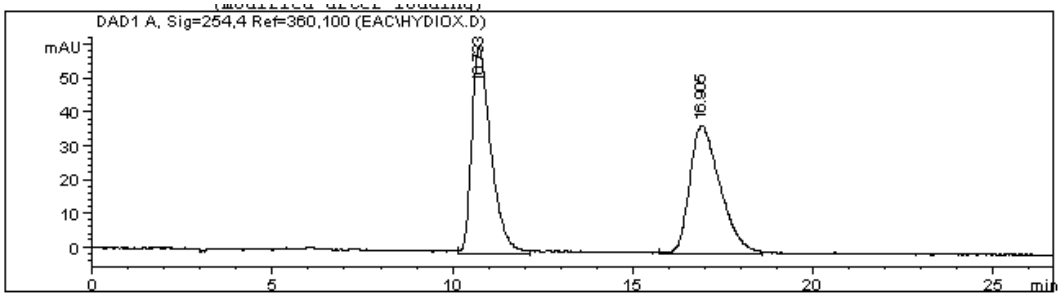

Me
Me
O
O
10a
O
Ph(CH2)2
O
Ph
CO2Me
ppm 200
180
160
140
120
100
80
60
40
20
0


Me
Me
O
O
O
O
O
Me
10b
9
8
7
6
5
4
3
2
1
0


Me
Me
O
O
O
O
O
Me
10b
200
180
160
140
120
100
80
60
40
20
0

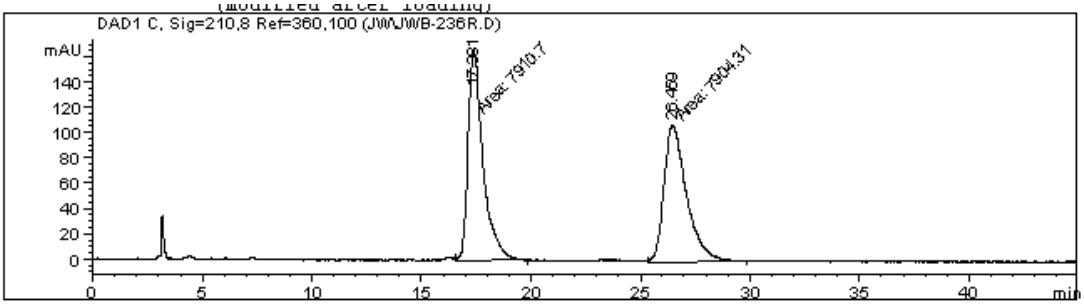
HPLC Traces of Racemic and Enantioenriched Compounds

Racemic 1a:



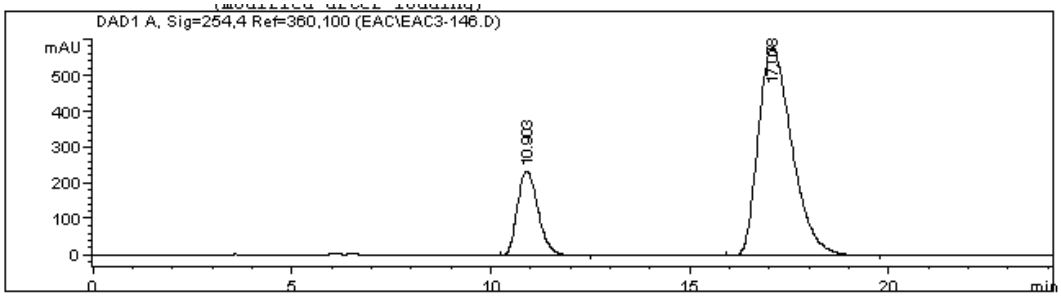

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.733 VV    0.5353 2257.78271   61.07483  49.9406
   2  16.905 VV    0.7104 2263.14990   38.13558  50.0594

Totals :                  4520.93262   99.21040
```

Racemic 4a:



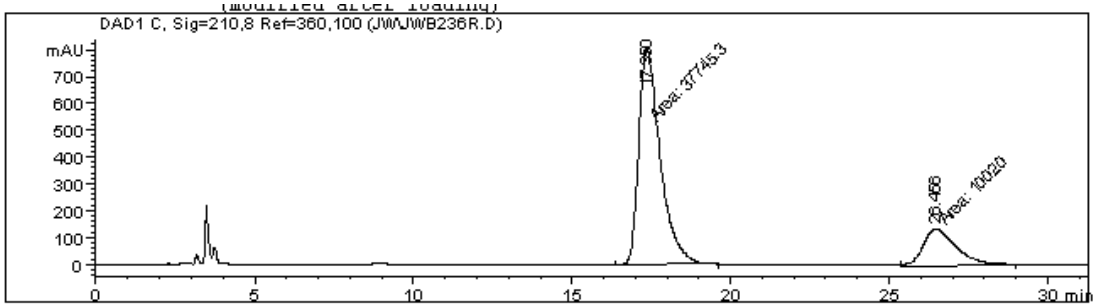

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  17.381 MM    0.7904 7910.69678  166.81557  50.0202
   2  26.459 MM    1.2115 7904.31299  108.74008  49.9798

Totals :                  1.58150e4   275.55565
```

Enatioenriched 1a:




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.903 VB    0.5817 8595.79297  235.55894  20.0497
   2  17.078 VB    0.9036 3.42767e4   579.93500  79.9503

Totals :                  4.28725e4   815.49394
```

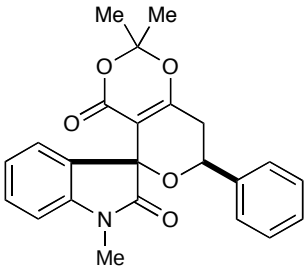
Enatioenriched 4a




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  17.350 MM    0.7889 3.77453e4   797.42822  79.0225
   2  26.456 MM    1.2182 1.00200e4   137.09073  20.9775

Totals :                  4.77653e4   934.51895
```

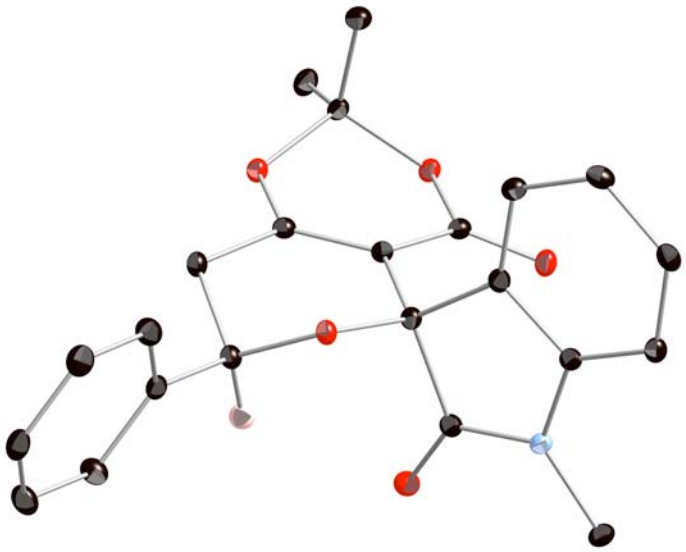
Determination of Absolute Stereochemistry of 4h

The absolute stereochemistry of **4h** was determined by the X-ray diffraction. Pure material was obtained by recrystallization from dichloromethane.



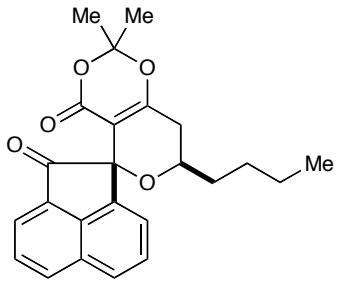
X-ray crystal structure of (3,7'-*cis*)-1,2',2'-trimethyl-7'-phenyl-7',8'-dihydro-4'*H*-spiro[indoline-3,5'-pyrano[4,3-*d*][1,3]dioxine]-2,4'-dione **4h:**

X-ray diffraction was performed at –120 ^{o}C and raw frame data were processed using SAINT. Molecular structure was solved using direct methods and refined by F2 by full-matrix least-squares techniques. The GOF = 1.06 for 265 variables refined to R1 = 0.032 for 3371 reflections with I>2α(I). There was no absorption correction. The flack parameter was 0.0. Further information is contained in the CCDC file 803846.



Determination of Absolute Stereochemistry of 10b

The relative stereochemistry of **10b** (the minor diastereomer from the reaction) was determined by the X-ray diffraction. Pure material was obtained by recrystallization from diethyl ether/ethyl acetate.



X-ray crystal structure of (1,7'-*cis*)-7'-butyl-2',2'-dimethyl-7',8'-dihydro-2*H*,4'*H*-spiro[acenaphthylene-1,5'-pyrano[4,3-*d*][1,3]dioxine]-2,4'-dione **10b:**

X-ray diffraction was performed at –120 ^{o}C and raw frame data were processed using SAINT. Molecular structure was solved using direct methods and refined by F2 by full-matrix least-squares techniques. The GOF = 1.03 for 265 variables refined to R1 = 0.042 for 2521 reflections with I>2α(I). There was no absorption correction. The flack parameter was 0.0. Further information is contained in the CCDC file 803480.