Supporting Information for

Rhodium-catalyzed cycloaddition of carbonyl ylides for the synthesis of spiro [furo[2,3-a]xanthene-2,3'-indolin]-2'-one scaffolds

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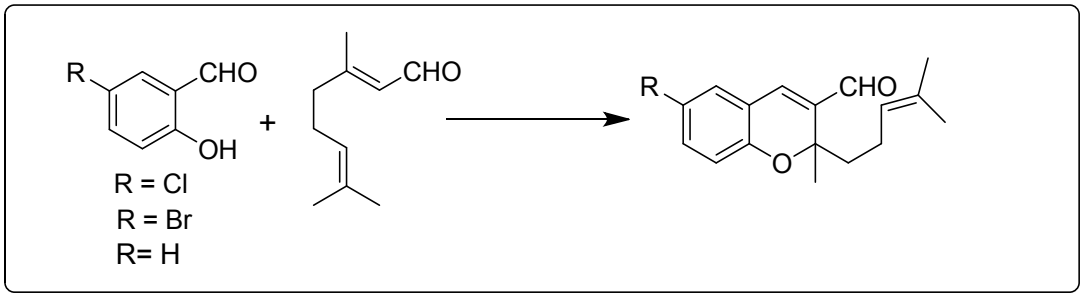
Table of Contents

General methods. All solvents were dried according to standard literature procedures. Unless otherwise noted, reactions were performed in flame-dried glassware under an atmosphere of dry argon. Dichloroethane was dried over Calcium hydride prior to use. ^{1}H NMR spectra were recorded at 500 MHz, 300 MHz and 400 MHz and ^{13}C NMR at 125 MHz, 100 MHz and 75MHz. For ^{1}H NMR, tetramethylsilane (TMS) was used as internal standard ($\delta = 0$) and the values are reported as follows: chemical shift, multiplicity, integration (s = singlet, d = doublet, t= triplet, q = quartet, m = multiplet, dd = doublet of doublet), and the coupling constants in Hz. For ^{13}C NMR, CDCl3 ($\delta = 77.00$) was used as internal standard and spectra were obtained with complete proton decoupling. Low-resolution MS and HRMS data were obtained using ESI ionization. IR spectra were recorded on FT-IR spectrometer (KBr) and reported in reciprocal centimeters (cm^{-1}). Melting points were measured on micro melting point apparatus. Glass syringes were used to transfer solvents. Crude products were purified by column chromatography on silica gel of 60–120 or 100-200 mesh. Thin layer chromatography plates were visualized by exposure to ultraviolet light and/or by exposure to iodine vapours and/or by exposure to methanolic acidic solution of 2-napthol followed by heating (<1 min) on a hot plate (~250°C). 3-Diazooxidole, 3-arylidene oxindole and were prepared according to the literature procedure

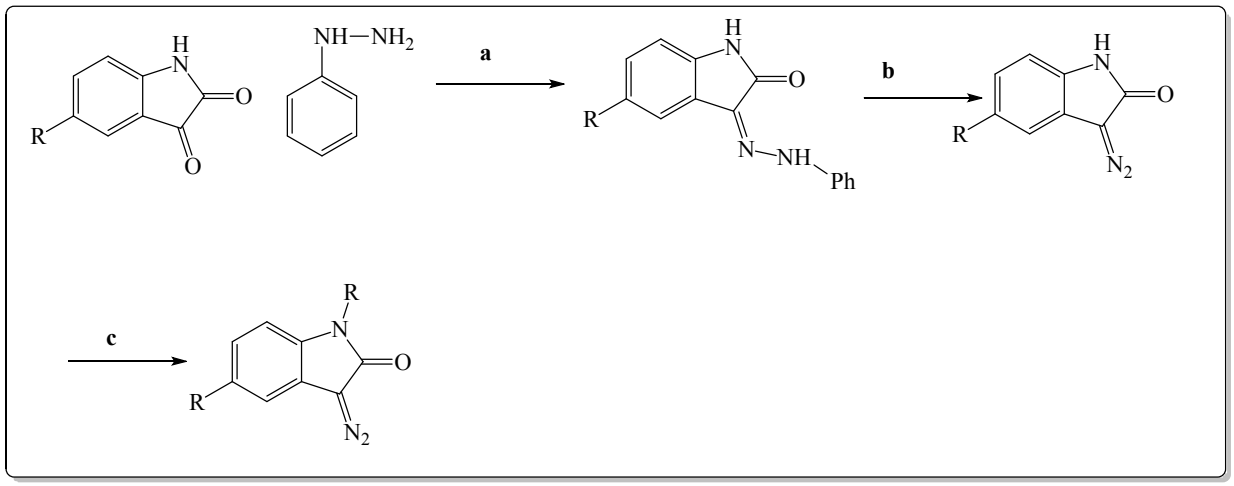
2. Experimental procedures

a) Preparation of 2-methyl-2-(4-methylpent-3-en-1-yl)-2*H*-chromene-3-carbaldehyde:



Reagents & conditions: K_2CO_3, 1, 4-dioxane, 3 days.

b) Preparation of 3-diazo-1-methylindolin-2-one:



Reagents & conditions: (a) MeOH, 0 °C, 12h (b) 4N NaOH, 45 °C,4h; (c) R-Br, K_2CO_3, DMF, 25 °C, 15h.

c)Preparation of the 2-methyl-2-(4-methylpent-3-en-1-yl)-2H-chromene-3-carbaldehyde:

A solution of sodium carbonate (14.08 mmol, 1.4 g) in water (5 mL) was stirred at 25 ^oC. After complete dissolution of sodium carbonate, a solution of salicylaldehyde (12.8 mmol, 2 g) in 1, 4-dioxane (15 mL) was added at 0 ^oC. After 15 min, citral (38.4 mmol, 6.61 mL) was added at room temperature. The resulting mixture was stirred at 55 ^oC for 72 h. After completion, as monitored by TLC, the reaction mixture was extracted with ethyl acetate and washed with brine solution. Removal of the solvent followed by purification on silica gel

column chromatography using a gradient mixture of EtOAc/hexane (1:9) afforded the 2-methyl-2-(4-methylpent-3-enyl)-2*H*-chromene-3-carbaldehyde in 60% yield.

d) Preparation of the 3-diazooxindoles:

A mixture of isatin (2.0 g, 13.6 mmol) and $TsNHNH_2$ (2.66 g, 14.3 mmol) in MeOH (20 mL) was stirred at 25 ºC for 1 h and then the mixture was cooled and filtered. The filtrate was treated with 4N aq. NaOH solution and stirred at 45 ºC for 4 h. After being cooled to ambient temperature, the reaction mixture was neutralized with dry ice. The red solid was filtered off and dried under air to give the 3- diazooxindole (1.8 g, 83% over two steps), which was used in the next step without further purification.

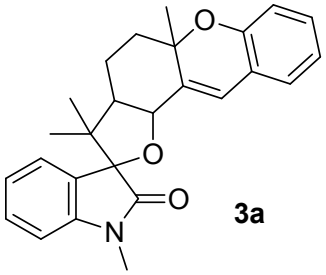
A mixture of 3-diazooxindole (1.0 g, 6.3 mmol), K_2CO_3 (1.0 g, 7.5 mmol) and CH_3I (0.82 mL, 6.9 mmol) was stirred in DMF (6 mL) at room temperature for 15 h. Then the mixture was diluted with ether and washed with water (60 mL× 3). The combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The resulting residue was purified by flash chromatography to give the *N*-methyl-3-diazooxindole **1a** (1.4 g, 89%) as an orange solid. The NMR spectral data was consistent with the data reported in literature. Other 3-diazooxindoles were prepared following a similar method.

e) Typical experimental procedure:

To a solution of 2-methyl-2-(4-methylpent-3-enyl)-2*H*-chromene-3-carbaldehyde **2** (1.1 equiv) and $Rh_2(OAc)_4$ (5 mol-%) in dry dichloroethane under argon at room temperature was added slowly a solution of diazooxindole **1** (1 equiv.) through a syringe pump over 20 min. After addition, the mixture was stirred for another 10 min. The progress of the reaction was monitored by TLC; upon completion, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (EtOAc/hexane) to give the pure product.

3. Characterization data of compounds 3(a-p)

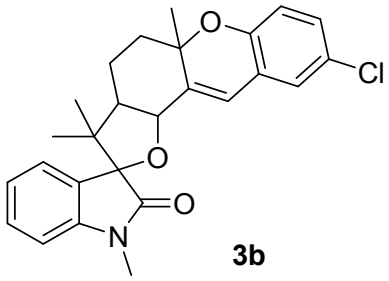
1',3,3,5*a*-Tetramethyl-3,3*a*,4,5,5a,11*b*-hexahydrospiro[furo[2,3-*a*]xanthene-2,3'-indolin]-2'-one (3a):



3a

Colorless solid. m.p: 210-211 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 7.4 Hz, 1H), 7.28 – 7.23 (m, 1H), 7.14 – 7.09 (m, 1H), 7.05 – 6.98 (m, 2H), 6.87 – 6.72 (m, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.74 (d, *J* = 7.7 Hz, 1H), 6.63 (s, 1H), 5.37 – 5.34 (m, 1H), 3.09 (s, 3H), 2.21 – 2.16 (m, 1H), 2.05 – 1.85 (m, 4H), 1.52 (s, 3H), 1.38 (s, 3H), 0.88 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.0, 152.9, 144.9, 134.0, 129.5, 129.4, 128.8, 126.8, 126.1, 126.1, 122.1, 122.0, 121.1, 116. 2, 108.2, 88.6, 80.7, 77.4, 50.9, 47.9, 38.1, 29.5, 26.2, 24.5, 24.4, 21.9; IR (KBr): ν_{max} 3426, 2923, 2851, 1688, 1488, 1457, 1244, 1117, 1039, 753 cm^{-1}; MS (EI): *m/z* ([M+H]$^{+}$): 402; HRMS (EI): *m/z* calcd $C_{26}H_{28}NO_3$: 402.20637; found: 402.20804.

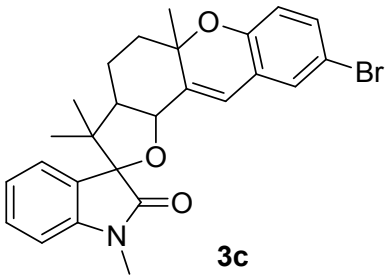
9-Chloro-1',3,3,5*a*-tetramethyl-3,3*a*,4,5,5*a*,11-hexahydrospiro[furo[2,3-*a*]xanthene-2,3'-indolin]-2'-one (3b):



3b

Colorless solid. m.p:180-181 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 2H), 7.08 – 7.00 (m, 2H), 6.97 – 6.95 (m, 1H), 6.73 (dd, *J* = 13.3, 8.2 Hz, 2H), 6.55 (s, 1H), 5.35 – 5.32 (m, 1H), 3.10 (s, 3H), 2.20 – 2.14 (m, 1H), 2.02 – 1.85 (m, 4H), 1.51 (s, 3H), 1.38 (s, 3H), 0.88 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.9, 151.5, 144.5, 135.5, 129.5, 129.1, 128.6, 126.2, 126.1, 125.8, 125.0, 123.4, 122.0, 117.5, 108.3, 88.9, 80.4, 77.9, 50.9, 47.9, 38.0, 29.4, 26.2, 24.5, 24.4, 21.9; IR (KBr): ν_{max} 3435, 2932, 2862, 1656, 1484, 1455, 1243, 1127, 1049, 763 cm^{-1}; MS (EI): *m/z* ([M+H]$^{+}$): 436; HRMS (EI): *m/z* calcd for $C_{26}H_{27}ClNO_3$: 436.16740; found: 436.16953.

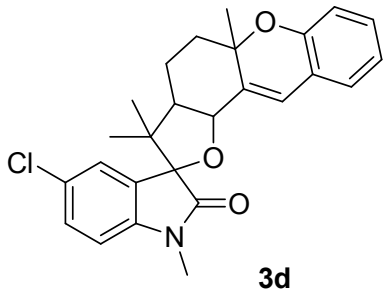
9-Bromo-1',3,3,5*a*-tetramethyl-3,3*a*,4,5,5*a*,11*b*-hexahydrospiro[furo[2,3-*a*]xanthene-2,3'-indolin]-2'-one (3c) :



3c

Colorless solid. m.p: 220-221 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 2H), 7.21 – 7.18 (m, 1H), 7.11 – 7.08 (m, 1H), 7.05 – 6.98 (m, 1H), 6.75 (d, *J* = 7.7 Hz, 1H), 6.67 (d, *J* = 8.6 Hz, 1H), 6.54 (s, 1H), 5.35 – 5.32 (m, 1H), 3.10 (s, 3H), 2.19 – 2.15 (m, 1H), 2.02 – 1.84 (m, 4H), 1.51 (s, 3H), 1.38 (s, 3H), 0.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.8, 152.0, 144.5, 135.5, 132.0, 129.5, 129.0, 128.6, 126.1, 124.8, 123.9, 122.0, 118.0, 113.0, 108.3, 88.7, 80.4, 77.9, 50.9, 47.9, 47.9, 38.0, 29.4, 26.2, 24.1, 21.9; IR (KBr): ν_{max} 3447, 3060, 2971, 1740, 1375, 1286, 1008, 981, 872, 781 cm^{-1}; MS (EI): *m/z* ($[M+H]^+$): 480; HRMS (EI): *m/z* calcd for $C_{26}H_{27}BrNO_3$: 480.39354; found: 480.39344.

5'-Chloro-1',3,3,5*a*-tetramethyl-3,3*a*,4,5,5*a*,11-hexahydrospiro[furo[2,3-*a*]xanthene-2,3'-indolin]-2'-one (3d):

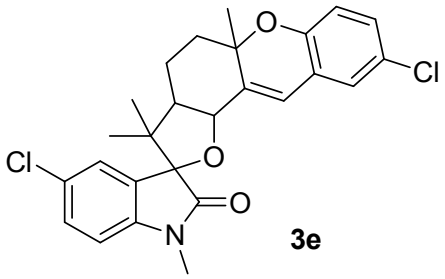


3d

Colorless solid. m.p: 215-216 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 2H), 7.15 – 7.10 (m, 1H), 7.02 – 6.99 (m, 1H), 6.88 – 6.78 (m, 2H), 6.63 (d, *J* = 7.9 Hz, 2H), 5.36 – 5.33 (m, 1H), 3.08 (s, 3H), 2.20 – (m, 1H), 2.05 – 1.79 (m, 4H), 1.51 (s, 3H), 1.37 (s, 3H), 0.90 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.4, 152.9, 143.6, 133.7, 132.3, 130.8, 129.6, 129.1, 126.8, 126.3, 122.0, 121.2, 116.3, 114.7, 109.7, 88.5, 80.9, 80.7, 50.8, 48.2, 37.9, 29.4, 26.3, 24.6, 24.4, 22.1; IR (KBr): ν_{max} 3441, 3056, 2964, 1593, 1512, 1459, 1299, 1246, 1173, 1112,

1031, 754 cm^{-1}; MS (EI): *m/z* ($[M+H]^+$): 436; HRMS (EI): *m/z* calcd for $C_{26}H_{27}ClNO_3$; 436.16740; found: 436.16952.

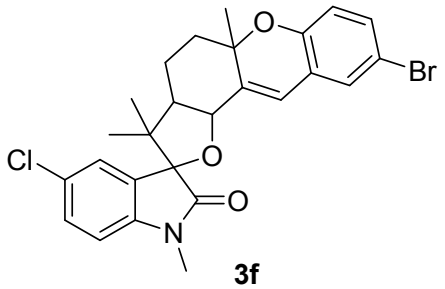
5',9-Dichloro-1',3,3,5*a*-tetramethyl-3,3*a*,4,5,5*a*,11*b*-hexahydrospiro[furo[2,3-*a*]xanthene-2, 3'-indolin]-2'-one (3e):



3e

Colorless solid. m.p: 239-240 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 1H), 7.37 – 7.34 (m, 1H), 7.10 – 7.04 (m, 1H), 6.99 – 6.95 (m, 1H), 6.73 (d, *J* = 8.6 Hz, 1H), 6.63 (d, *J* = 8.3 Hz, 1H), 6.55 (s, 1H), 5.35 – 5.31 (m, 1H), 3.08 (s, 3H), 2.24 – 2.15 (m, 1H), 2.03 – 1.79 (m, 4H), 1.50 (s, 3H), 1.36 (s, 3H), 0.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.3, 151.5, 143.6, 135.2, 132. 3, 130.6, 129.2, 129.1, 126.2, 125.2, 123.3, 117.6, 114.7, 109.8, 88.5, 80.7, 50.8, 48.2, 37.8, 29.3, 26.4, 24.6, 24.4, 22.0; IR (KBr): ν_{max} 3412, 3059, 2856, 1712, 1388, 1260, 1242, 1030, 881, 744 cm^{-1}; MS (EI): *m/z* ($[M+H]^+$): 470; HRMS (EI): *m/z* calcd for $C_{26}H_{26}Cl_2NO_3$: 470.38760; found: 470.38732.

9-Bromo-5'-chloro-1',3,3,5*a*-tetramethyl-3,3*a*,4,5,5*a*,11b-hexahydrospiro[furo[2,3-*a*]xant henes-2, 3'-indolin]-2'-one (3f):

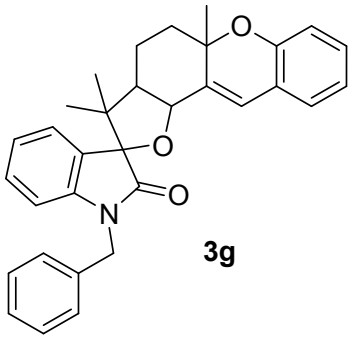


3f

Colourless solid. m.p. 256-257 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43-7.33 (m, 2H), 7.24 – 7.18 (m, 1H), 7.12 – 7.08 (m, 1H), 6.66 (dd, *J*=14.2,8.4Hz, 2H), 6.54 (s, 1H), 5.35 – 5.29 (m, 1H), 3.08 (s, 3H), 2.25 – 2.13 (m, 1H), 2.05 – 1.77 (m, 4H), 1.50 (s, 3H), 1.36 (s, 3H), 0.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.2, 152.0, 143.5, 135.1, 132.3, 132.1, 130.6, 129.1, 129.0, 125.1, 123.8, 118.1, 114.7, 113.0, 109.7, 80.5, 80.6, 77.7, 50.7, 48.2, 37.8, 29.7, 29.3,

26.3, 24.6, 24.4, 21.9; IR (KBr): ν_{max} 3425, 3056, 2996, 1721, 1606, 1331, 1299, 1246, 1159, 1016, 804, 702 cm^{-1}; MS (EI): *m/z* ($[M+H]^+$): 514; HRMS (EI): *m/z* calcd for $C_{26}H_{26}BrClNO_3$: 514.83860; found: 514.83845.

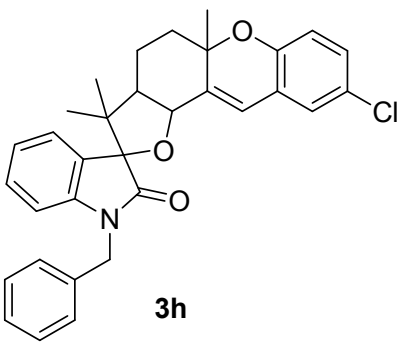
1'-Benzyl-3,3,5*a*-trimethyl-3,3*a*,4,5,5*a*,11*b*-hexahydrospiro[furo[2,3-*a*]xanthene-2,3'-indolin]-2'-one(3g):



3g

Colorless solid. m.p: 205-206 °C; ^{1}H NMR (500 MHz, $CDCl_3$) 7.38 – 7.22 (m, 7H), 7.16 – 7.09 (m, 1H), 7.06 – 6.95 (m, 2H), 6.90 – 6.82 (m, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.66 (s, 1H), 6.62 (d, *J* = 7.8 Hz, 1H), 5.39 – (m, 1H), 5.12 (d, *J* = 15.8 Hz, 1H), 4.46 (d, *J* = 15.8 Hz, 1H), 2.30 – 2.13 (m, 1H), 2.10 – 1.77 (m, 4H), 1.53 (s, 3H), 1.43 (s, 3H), 0.90 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.9, 152.9, 143.6, 135.9, 134.0, 129.5, 129.3, 128.8, 127.6, 127.2, 126.8, 126.2, 126.1, 122.0, 121.2, 116.2, 109.2, 88.7, 80.8, 50.9, 48.2, 43.8, 38.1, 29.7, 24.62, 24.4, 21.9; IR (KBr): ν_{max} 3423, 3059 , 2963, 2788, 1755, 1482, 1370, 1123, 873, 720 cm^{-1}; MS (EI): *m/z* ($[M+H]^+$): 478; HRMS (EI): *m/z* calcd for $C_{32}H_{32}NO_3$: 478.23767; found: 478.23999.

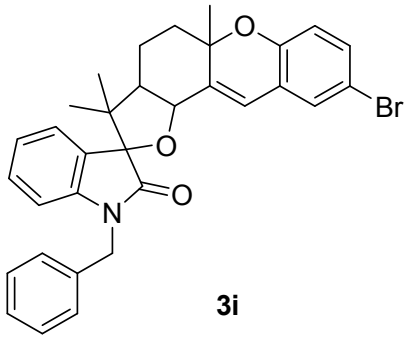
1'-Benzyl-9-chloro-3,3,5*a*-trimethyl-3,3*a*,4,5,5*a*,11*b*-hexahydrospiro[furo[2,3*a*]xanthene-2,3'-indolin]-2'-one(3h):



3h

Colorless solid. m.p: 220-221 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 6H), 7.17 – 7.11 (m, 1H), 7.09 – 7.04 (m, 1H), 7.02 – 6.97 (m, 2H), 6.73 (d, *J* = 8.6 Hz, 1H), 6.62 (d, *J* = 7.6 Hz, 1H), 6.58 (s, 1H), 5.40 – 5.35 (m, 1H), 5.13 (d, *J* = 15.8 Hz, 1H), 4.46 (d, *J* = 15.8 Hz, 1H), 2.22 – 2.15 (m, 1H), 2.07 – 1.85 (m, 4H), 1.53 (s, 3H), 1.43 (s, 3H), 0.90 (s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.8, 151.5, 143.6, 135.9, 135.5, 129.4, 129.1, 128.9, 128.6, 127.6, 127.2, 126.2, 126.1, 125.8, 125.1, 123.4, 122.1, 117.6, 109.2, 88.8, 80.6, 77.8, 50.9, 48.2, 43.8, 38.0, 29.9, 24.6, 24.4, 21.9; IR (KBr): ν_{max} 3425, 3065, 2926, 2856, 1726, 1479, 1259, 1176, 1071, 702 cm^{-1}; MS (EI): *m/z* ([M+H]$^+$): 512; HRMS (EI): *m/z* calcd for $C_{32}H_{31}ClNO_3$: 512.19897; found: 512.20099.

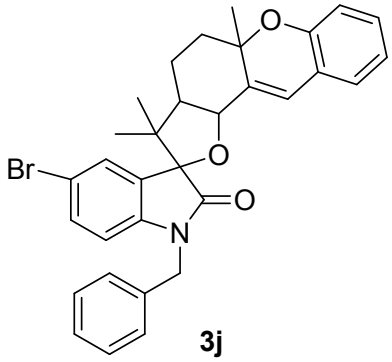
1'-Benzyl-9-bromo-3,3,5*a*-trimethyl-3,3*a*,4,5,5*a*,11*b*-hexahydrospiro[furo[2,3*a*]xanthene-2,3'-indolin]-2'-one(3i):



3i

Colorless solid. m.p. 225-226 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 6H), 7.23 – 7.17 (m, 1H), 7.16 – 7.14 (m, 1H), 7.13 – 7.11 (m, 1H), 7.03 – 6.98 (m, 1H), 6.68 (d, *J* = 8.5 Hz, 1H), 6.62 (d, *J* = 7.7 Hz, 1H), 6.57 (s, 1H), 5.40 – 5.35 (m, 1H), 5.13 (d, *J* = 15.8 Hz, 1H), 4.46 (d, *J* = 15.8 Hz, 1H), 2.23 – 2.14 (m, 1H), 2.04 – 1.83 (m, 4H), 1.53 (s, 3H), 1.43 (s, 3H), 0.90 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.8, 152.0, 146.1, 143.6, 135.9, 135.5, 132.1, 129.4, 129.1, 128.9, 128.6, 127.6, 127.2, 126.2, 124.9, 124.0, 122.1, 118.0, 113.1, 109.2, 88.8, 80.6, 77.9, 50.9, 48.2, 43.8, 38.0, 29.9, 24.6, 24.5, 21.9; IR (KBr): ν_{max} 3445, 3056 , 2929, 2862, 1745, 1482, 1276, 1125, 1068, 757 cm^{-1}; MS (EI): *m/z* ([M+H]$^+$): 556; HRMS (EI): *m/z* calcd for $C_{32}H_{31}BrNO_3$: 556.13026; found: 556.13033.

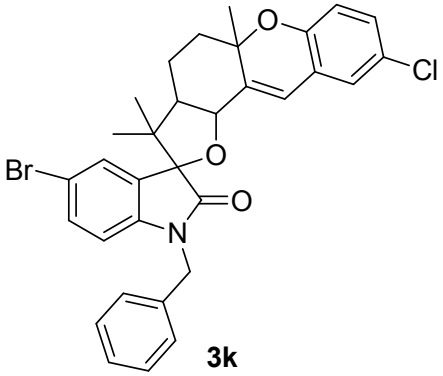
1'-Benzyl-5'-bromo-3,3,5*a*-trimethyl-3,3*a*,4,5,5*a*,11*b*-hexahydrospiro[furo[2,3-*a*]xanthene-2,3'-indolin]-2'-one (3j):



3j

Colorless solid. m.p. 238-240 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.36 (m, 1H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.28 – 7.24 (m, 4H), 7.16 – 7.10 (m, 1H), 7.05 – 6.90 (m, 1H), 6.89 – 6.83 (m, 2H), 6.66 (s, 1H), 6.49 (d, *J* = 8.3 Hz, 1H), 5.41 – 5.36 (m, 1H), 5.08 (d, *J* = 15.8 Hz, 1H), 4.48 (d, *J* = 15.8 Hz, 1H), 2.24 – 2.17 (m, 1H), 2.05 – 1.95 (m, 2H), 1.87 – (m, 2H), 1.53 (s, 3H), 1.42 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.3, 153.0, 142.6, 135.4, 133.6, 132.1, 130.8, 129.6, 129.1, 128.9, 127.8, 127.2, 126.9, 126.5, 122.0, 121.2, 116.3, 114.8, 110.6, 88.6, 81.1, 50.8\, 48.5, 43.9, 38.0, 29.6, 24.7, 24.5, 22.1; IR (KBr): ν_{max} 3421, 3059, 2925, 2856, 1721, 1606, 1259, 933, 804 cm^{-1}; MS (EI): *m/z* ([M+H]$^+$): 556; HRMS (EI): *m/z* calcd for $C_{32}H_{31}BrNO_3$: 556.13026; found: 556.13033.

1'-Benzyl-5'-bromo-9-chloro-3,3,5*a*-trimethyl-3,3*a*,4,5,5*a*,11b-hexahydrospiro[furo[2,3-*a*] xanthene-2, 3'-indolin]-2'-one) (3k):

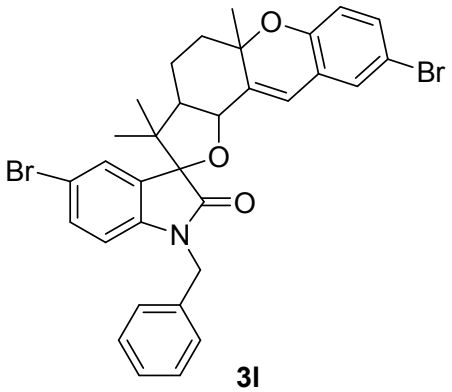


3k

Colorless solid. m.p. 215-216 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.23 (m, 7H), 7.10 – 7.05 (m, 1H), 7.01 – 6.97 (m, 1H), 6.74 (d, *J* = 8.6 Hz, 1H), 6.58 (s, 1H), 6.49 (d, *J* = 8.3 Hz, 1H), 5.40 – 5.35 (m, 1H), 5.08 (d, *J* = 15.8 Hz, 1H), 4.48 (d, *J* = 15.8 Hz, 1H), 2.22 (s, 1H), 2.04 – 1.95 (m, 2H), 1.92 – 1.80 (m, 2H), 1.52 (s, 3H), 1.42 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.2, 151.5, 142.6, 135.3, 135.1, 132.2, 130.7, 129.3, 129.1, 129.0, 127.8, 127.1, 126.2, 125.8, 125.4, 123.3, 117.6, 114.8, 110.7, 88.7, 80.8, 77.7, 50.8, 48.5,

43.9, 37.9, 29.6, 24.7, 24.4, 22.0; IR (KBr): ν_{max} 3425, 3065, 2925, 1741, 1612, 1495, 1245, 1176, 1113, 770 cm^{-1}; MS (EI):*m/z* ($[M+H]^+$):590; HRMS (EI): *m/z* calcd for $C_{32}H_{30}BrClNO_3$: 590.10921; found: 590.11166.

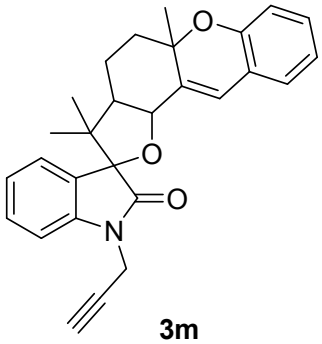
1'-Benzyl-5',9-dibromo-3,3,5*a*-trimethyl-3,3*a*,4,5,5*a*,11b-hexahydrospiro[furo[2,3-*a*]xanthene-2,3'-indolin]-2'-one (3l) :



3l

Colorless solid. m.p. 245-250 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 5H), 7.26 – 7.20 (m, 3H), 7.14 – 7.10 (m, 1H), 6.69 (d, *J* = 8.6 Hz, 1H), 6.57 (s, 1H), 6.49 (d, *J* = 8.3 Hz, 1H), 5.39 – 5.34 (m, 1H), 5.08 (d, *J* = 15.8 Hz, 1H), 4.48 (d, *J* = 15.8 Hz, 1H), 2.22 – 2.17 (m, 1H), 2.03 – 1.95 (m, 2H), 1.91 – 1.81 (m, 2H), 1.52 (s, 3H), 1.42 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.2, 152.0, 142.8, 142.7, 142.6, 135.3, 135.1, 132.2, 130.7, 129.1, 129.0, 127.8, 127.1, 125.2, 123.9, 118.1, 114.8, 113.1, 110.7, 88.7, 80.8, 77.7, 50.8, 48.5, 43.9, 37.9, 29.6, 24.7, 24.5, 22.0; IR (KBr): ν_{max} 3431, 2915, 2839, 1607, 1489, 1453, 1244, 1109, 1033, 824 cm^{-1}; MS (EI): *m/z* ($[M+H]^+$): 634; HRMS (EI): *m/z* calcd for $C_{32}H_{30}Br_2NO_3$: 634.16740; found: 634.16990.

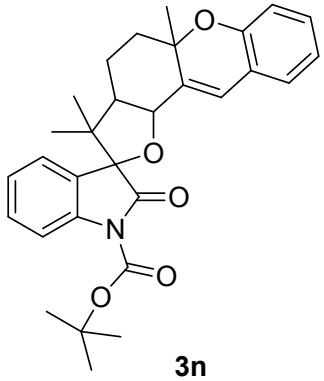
3,3,5*a*-Trimethyl-1'-(prop-2-yn-1-yl)-3,3*a*,4,5,5*a*,11*b*-hexahydrospiro[furo[2,3-*a*]xanthene-2,3'-indolin]-2'-one (3m):



3m

Colorless solid. m.p. 225-226 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.4 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.16 – 7.09 (m, 1H), 7.08 – 7.04 (m, 1H), 7.02 – 6.95 (m, 2H), 6.88 – 6.83 (m, 1H), 6.79 (d, *J* = 8.1 Hz, 1H), 6.63 (s, 1H), 5.37 – 5.32 (m, 1H), 4.61 – 4.54 (m, 1H), 4.25 – 4.15 (m, 1H), 2.22 – 2.16 (m, 2H), 2.05 – 1.84 (m, 4H), 1.53 (s, 3H), 1.38 (s, 3H), 0.88 (s, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.1, 152.9, 142.5, 133.9, 129.5, 129.3, 128.7, 126.8, 126.2, 126.1, 122.4, 122.1, 121.2, 116.2, 109.2, 88.8, 80.9, 72.3, 50.9, 48.3, 38.1, 29.4, 29.2, 24.5, 24.4, 21.9; IR (KBr): ν_{max} 3445, 3056 , 2929, 2862, 1745, 1482, 1276, 1125, 1068, 757 cm^{-1}; MS (EI): *m/z* ([M+H]$^+$): 425; HRMS (EI): *m/z* calcd for $C_{28}H_{28}NO_3$: 425.11688; found: 425.12110.

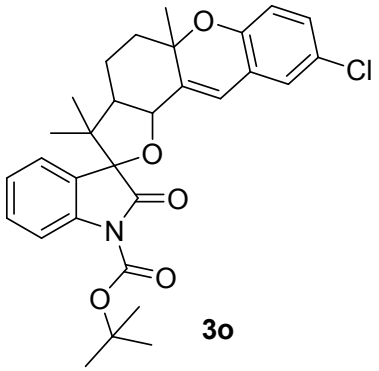
tert-Butyl 3,3,5*a*-trimethyl-2'-oxo-3,3*a*,4,5,5*a*,11b-hexahydrospiro[furo[2,3-*a*]xanthene-2,3'-indoline]-1'-carboxylate (3n):



3n

Colorless solid. m.p. 180-181 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (t, *J* = 6.0 Hz, 1H), 7.35 – 7.25 (m, 2H), 7.16 – 7.10 (m, 2H), 7.03 – 6.99 (m, 1H), 6.88 – 6.78 (m, 2H), 6.63 (s, 1H), 5.35 – 5.30 (m, 1H), 2.21 – 2.15 (m, 1H), 2.05 – 1.81 (m, 4H), 1.62 (s, 9H), 1.37 (s, 3H), 1.26 (s, 3H), 0.82 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.0, 152.9, 149.2, 139.9, 133.7, 129.6, 129.5, 127.6, 126.8, 126.3, 125.7, 123.8, 122.1, 121.2, 116.3, 114.9, 88.6, 84.1, 81.1, 51.0, 49.1, 38.0, 32.0, 29.7, 29.3, 28.2, 24.4, 23.9, 21.9; IR (KBr): ν_{max} 3421, 3059 , 2925, 2856, 1721, 1475, 1259, 1176, 1113, 720 cm^{-1}; MS (EI): *m/z* ([M+1]$^+$): 488; HRMS (EI): *m/z* calcd for $C_{30}H_{34}NO_5$: 488.08032; found: 488.08041.

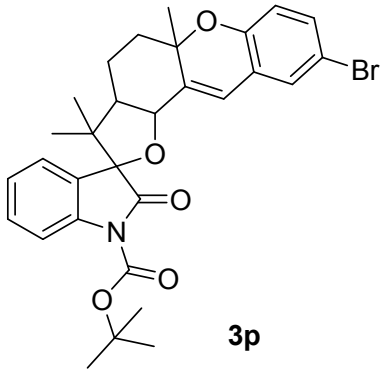
tert-Butyl 9-chloro-3,3,5*a*-trimethyl-2'-oxo-3,3*a*,4,5,5*a*,11*b*-hexahydrospiro[furo[2,3-*a*]xanthene-2,3'-indoline]-1'-carboxylate (3o):



3o

Colorless solid. m.p. 187-188 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.1 Hz,1H), 7.33-7.30 (m, 2H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.09 – 7.04 (m, 1H), 6.99 – 6.96 (m, 1H), 6.73 (d, *J* = 8.6, 1H), 6.55 (s, 1H), 5.33 – 5.28 (m, 1H), 2.20 – 2.13 (m, 1H), 1.98 – 1.94 (m, 4H), 1.62 (s, 9H), 1.53 (s, 3H), 1.36 (s, 3H*)*, 0.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.9, 151.4, 149.1, 139.9, 135.2, 129.5, 129.2, 126.2, 125.8, 125.6, 125.2, 123.8, 117.5, 114.9, 88.5, 84.5, 84.1, 80.8, 77.7, 62.1, 50.9, 49.1, 37.9, 29.7, 29.2, 28.1, 24.3, 23.9, 22.7, 21.8, 14.1; IR (KBr): ν_{max} 3426, 2853, 1714, 1612, 1495, 1460, 1245, 1176, 1113, 770, 699 cm^{-1}; MS (EI): *m/z* ($[M+H]^+$): 522; HRMS (EI): *m/z* calcd for $C_{30}H_{33}ClNO_5$: 522.19690; found: 522.19723.

***tert*-Butyl 9-bromo-3,3,5*a*-trimethyl-2'-oxo-3,3*a*,4,5,5*a*,11*b*-hexahydrospiro[furo[2,3-*a*]xanthene-2,3'-indoline]-1'-carboxylate) (3p):**

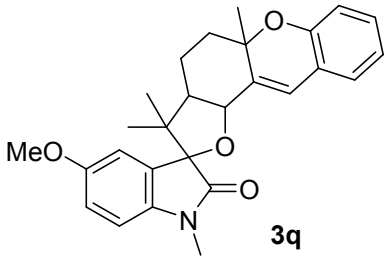


3p

Colorless solid. m.p. 179-180 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.1 Hz,1H), 7.33-7.28 (m, 2H), 7.23 – 7.18 (m, 1H), 7.16 – 7.12 (m, 1H), 7.12 – 7.10 (m, 1H), 6.71 – 6.66 (m,1H), 6.54 (s, 1H), 5.34 – 5.27 (m, 1H), 2.20 – 2.14 (m, 1H), 2.01 – 1.83 (m, 4H), 1.62 (s, 9H), 1.53 (s, 3H), 1.36 (s, 3H), 0.83 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 177.1, 152.5, 149.1, 139.8, 133.7, 129.7, 127.6, 126.3, 125.7, 123.8, 122.0, 121.1, 116.2, 114.8, 114.8, 88.5, 84.0, 81.1, 51.0, 49.1, 38.0, 29.7, 29.2, 28.1, 24.4, 23.9, 22.7, 21.9, 14.1; IR (KBr): ν_{max}

3428, 2830, 1874, 1623, 1564, 1474, 1228, 1133, 1021, 789 cm^{-1}; MS (EI): *m/z* ($[M+H]^+$): 566; HRMS (EI): *m/z* calcd for $C_{30}H_{33}BrNO_5$: 566.15366; found: 566.15608.

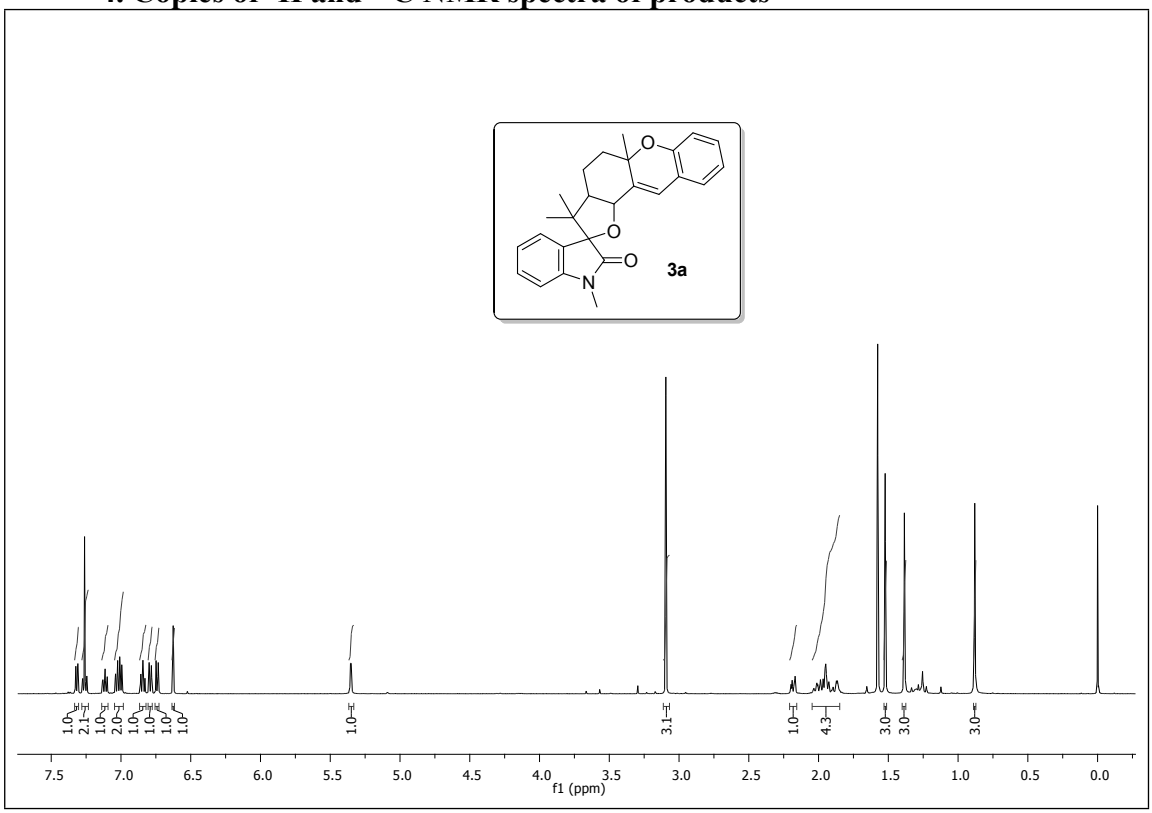
5'-Methoxy-1',3,3,5a-tetramethyl-3a,5,5a,11b-tetrahydro-3*H*,4*H*-spiro[furo[2,3-a]xanthene-2,3'-indolin]-2'-one (5q):



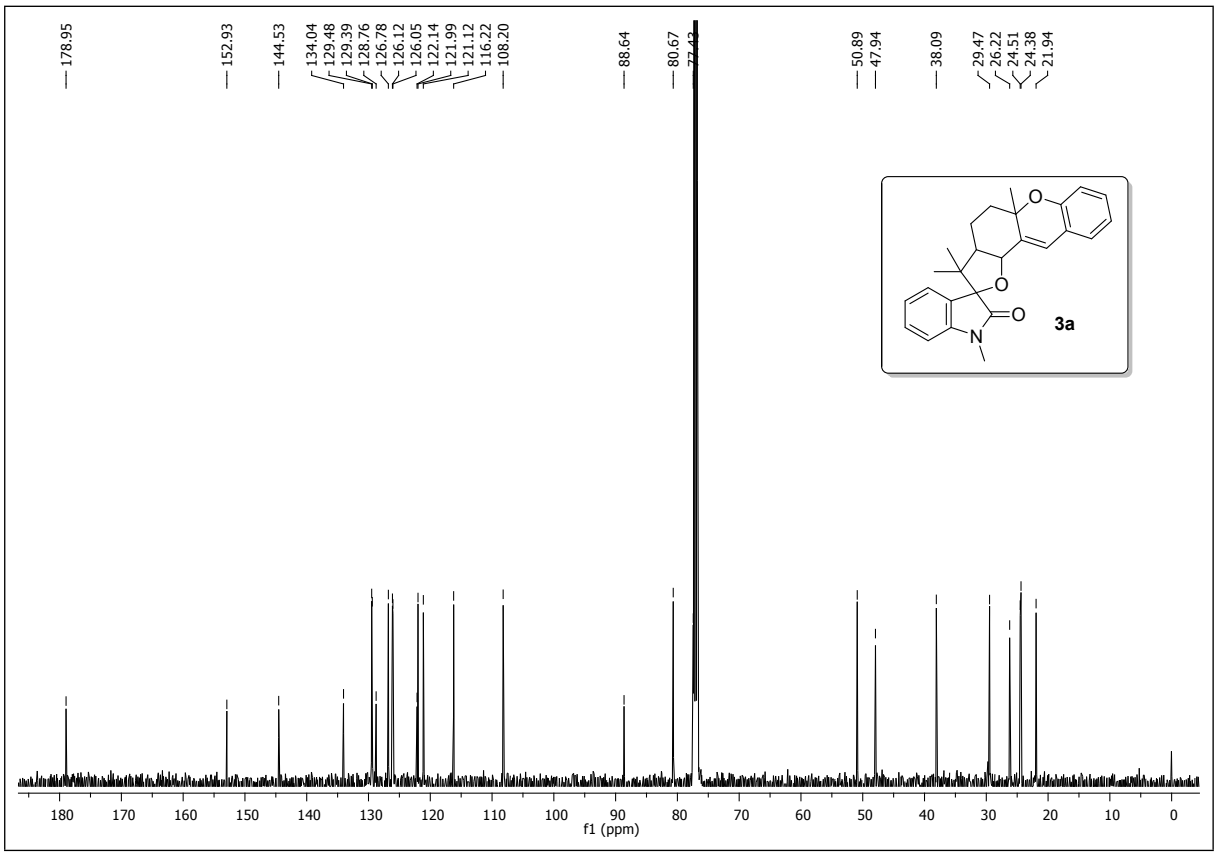
3q

Colorless solid. m.p: 214-215 °C; ^1H NMR (500 MHz, CDCl3) δ 7.12 (t, *J* = 7.8, 1.6 Hz, 1H), 7.00 (dd, *J* = 7.4, 1.5 Hz, 1H), 6.93 (d, *J* = 2.5 Hz, 1H), 6.84 (dd, *J* = 7.4, 6.6 Hz, 1H), 6.81 – 6.75 (m, 2H), 6.67 – 6.58 (m, 2H), 5.35 (d, *J* = 3.4 Hz, 1H), 3.79 (s, 3H), 3.07 (s, 3H), 2.22 – 2.13 (m, 1H), 2.05 – 1.83 (m, 4H), 1.52 (s, 3H), 1.38 (s, 3H), 0.90 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.6, 155.3, 152.9, 138.1, 133.9, 130.2, 129.4, 126.7, 126.0, 122.1, 121.1, 116.2, 114.7, 112.5, 108.2, 88.9, 80.7, 55.8, 50.8, 48.0, 38.0, 29.4, 26.3, 24.4, 21.9; IR (KBr): ν_{max} 3425, 2926, 2857, 1687, 1488, 1456, 1264, 1127, 1029, 743 cm^{-1}; MS (EI): *m/z* ($[M+H]^+$): 432; HRMS (EI): *m/z* calcd $C_{26}H_{28}NO_3$: 432.20636; found: 432.20805.

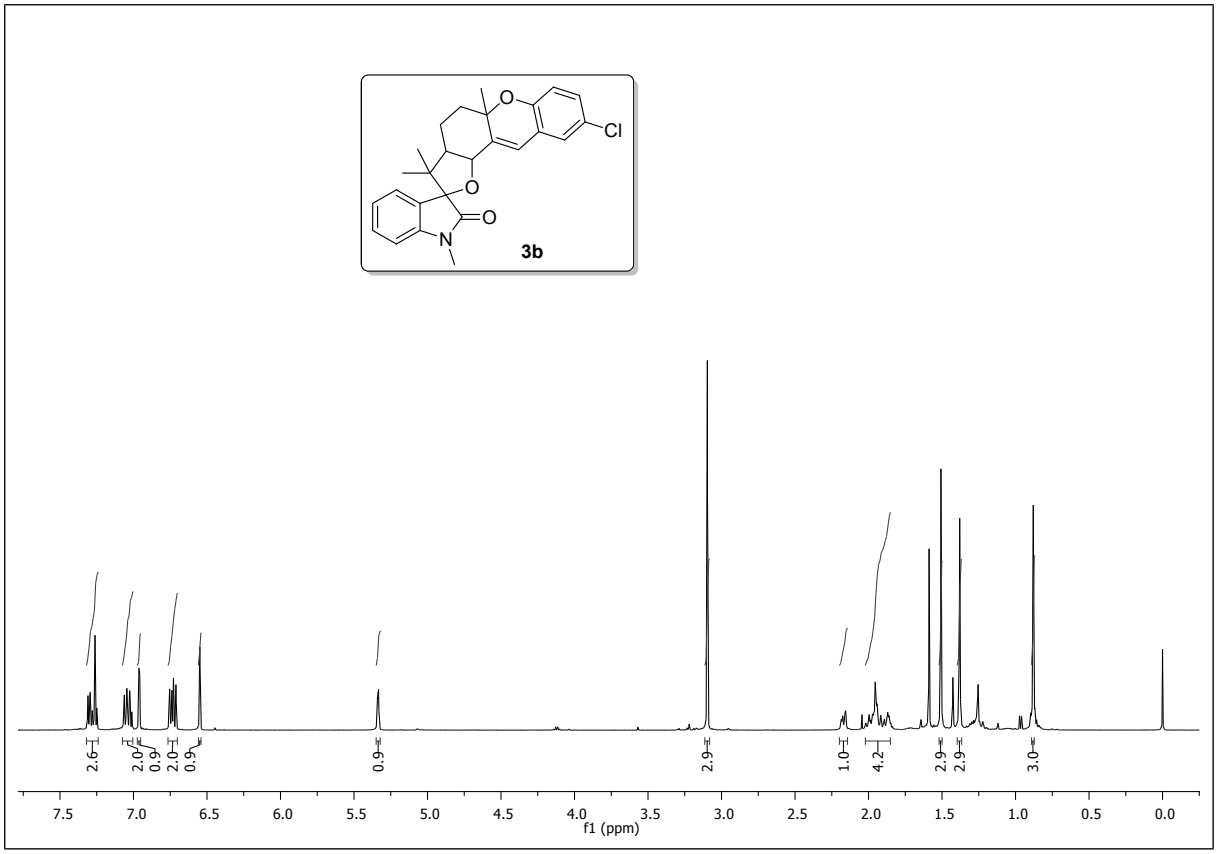
4. Copies of ^{1}H and ^{13}C NMR spectra of products



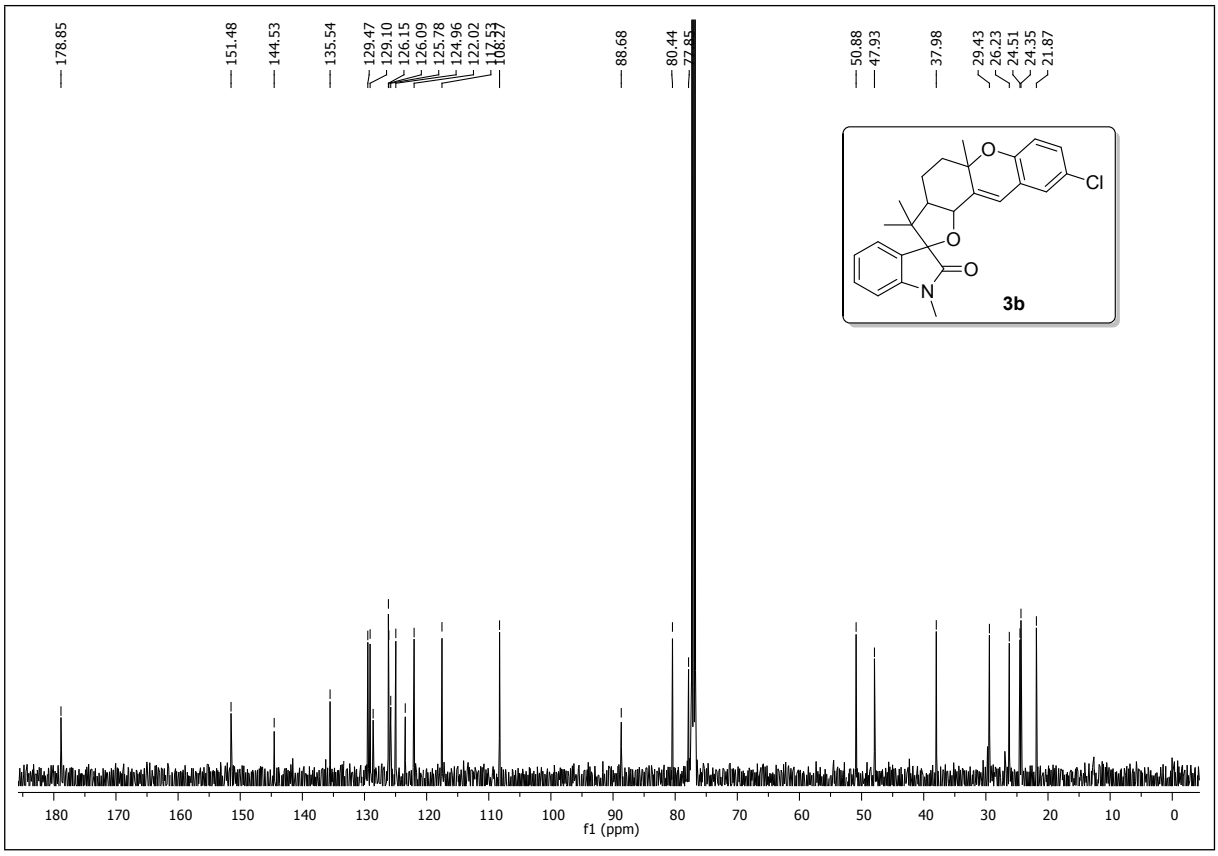
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 3a



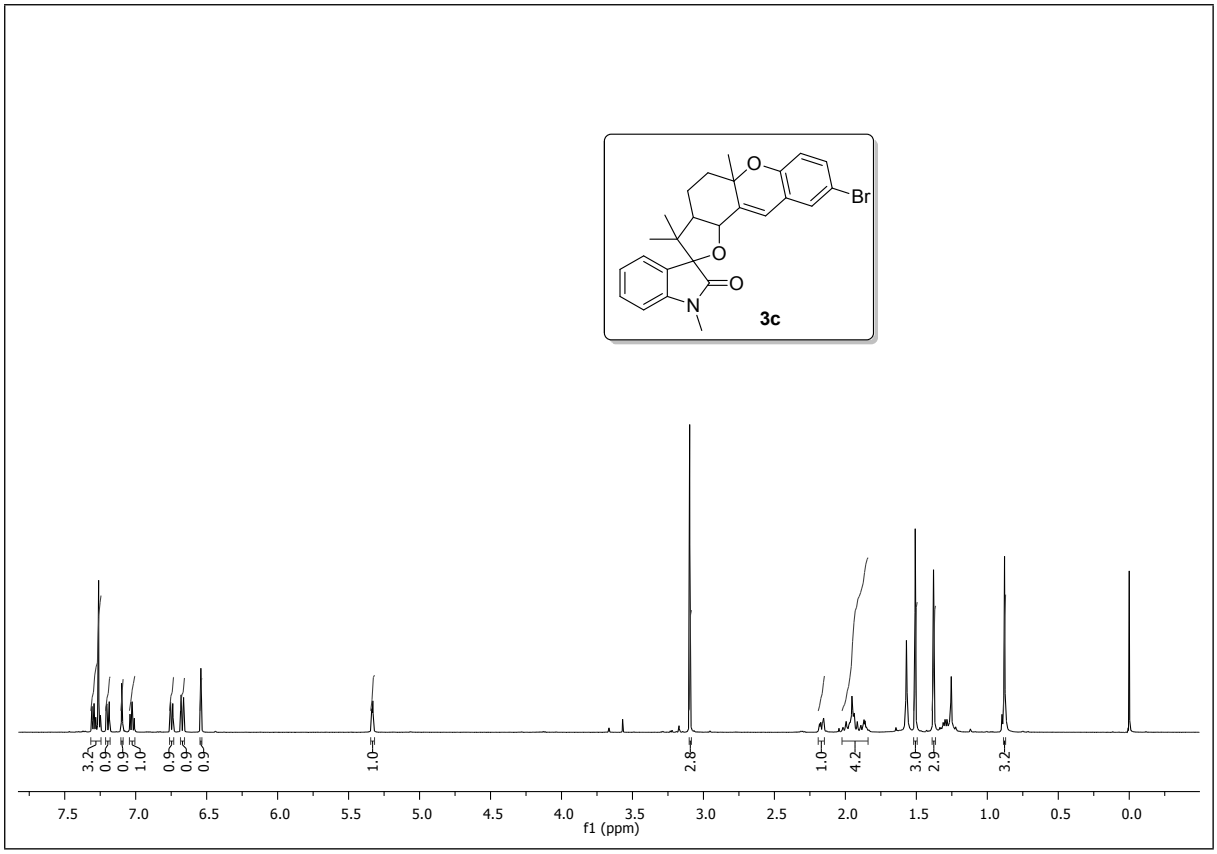
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 3a



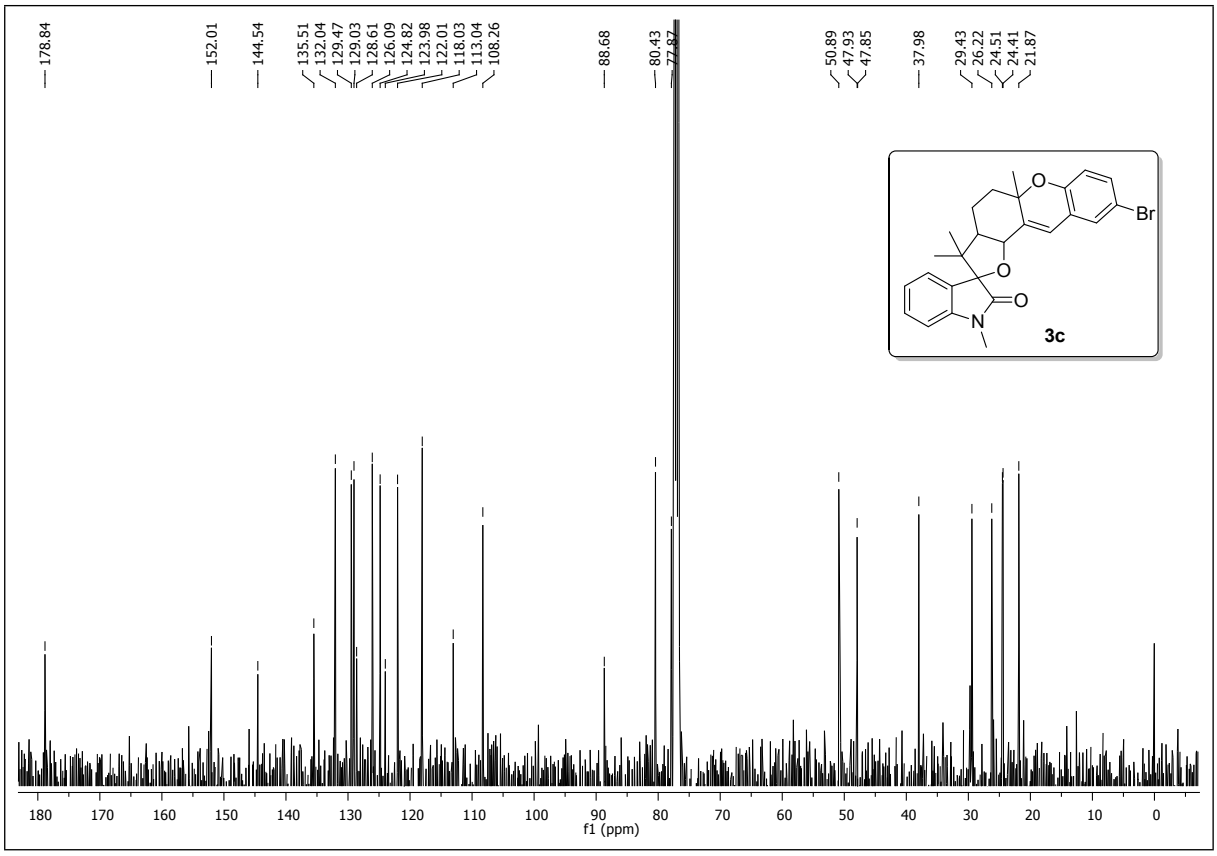
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 3b



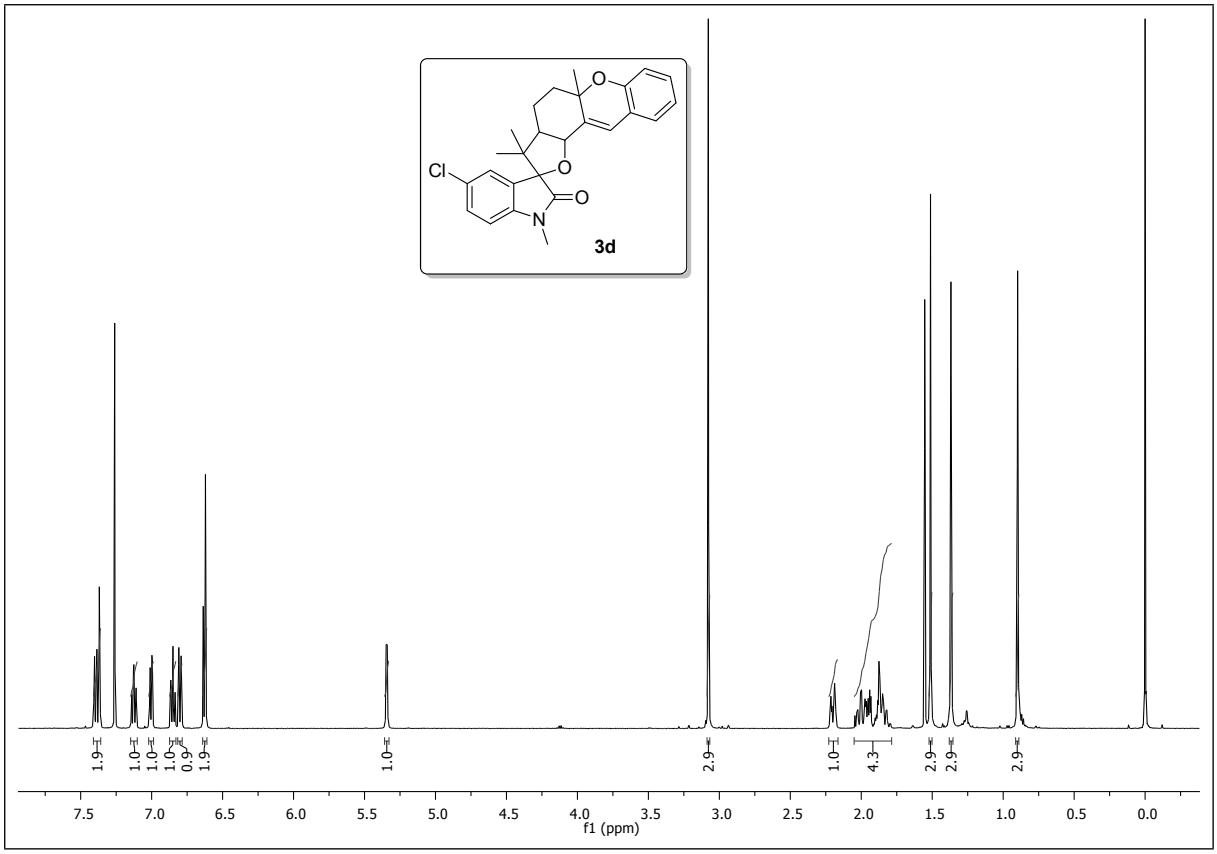
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 3b



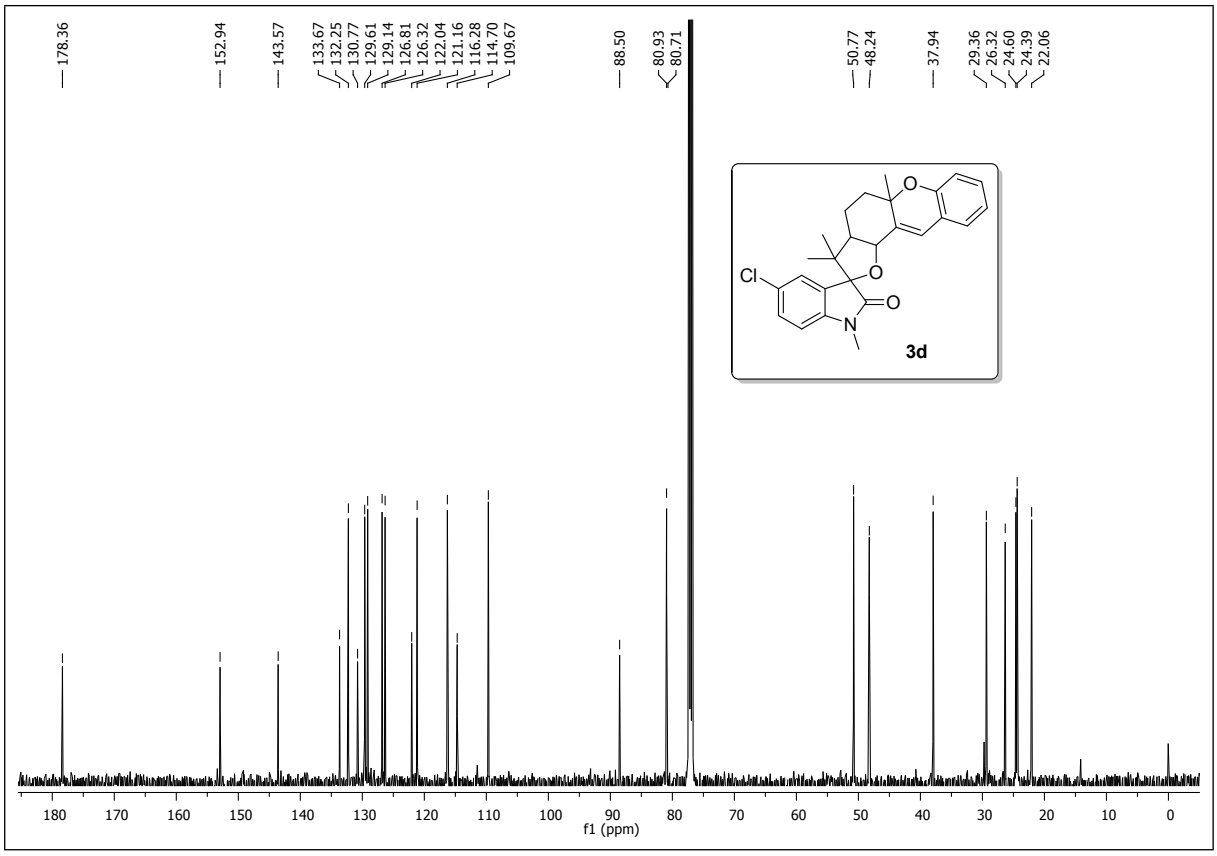
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 3c



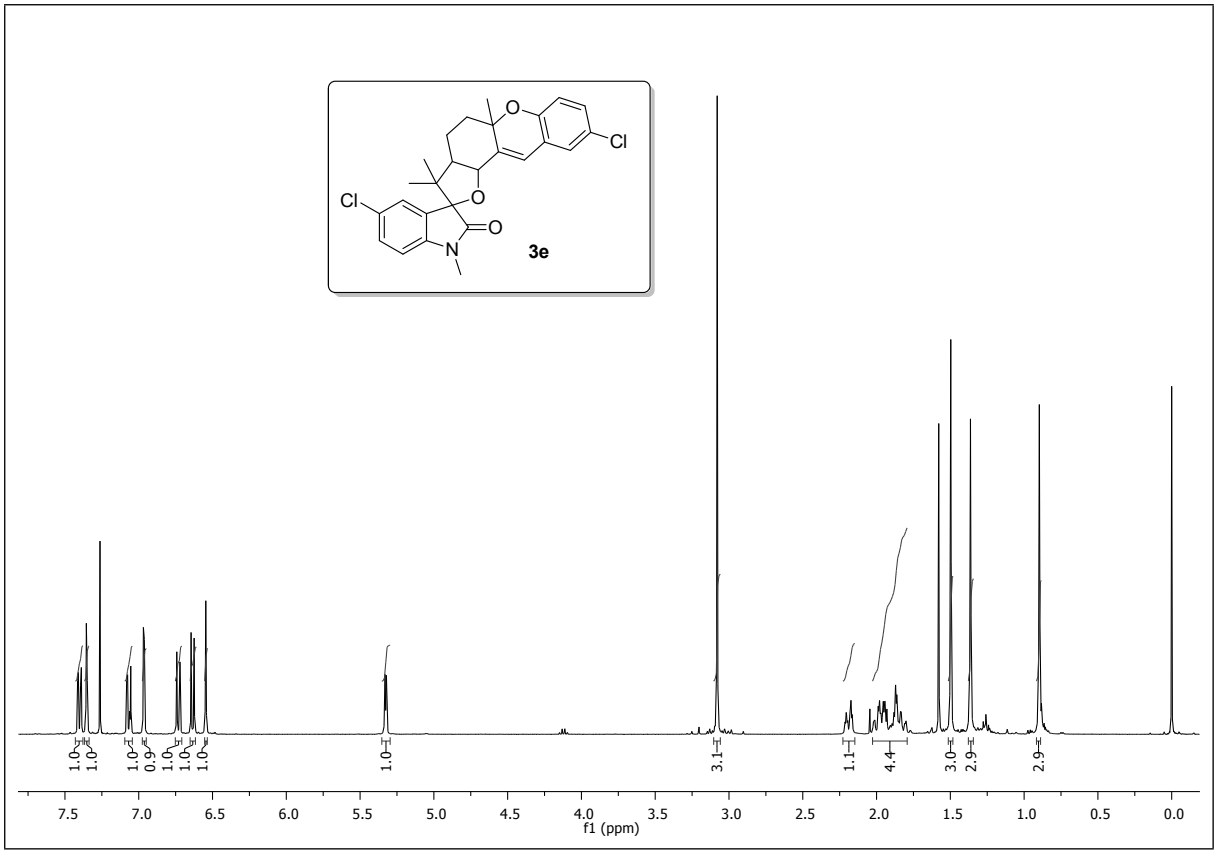
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 3c



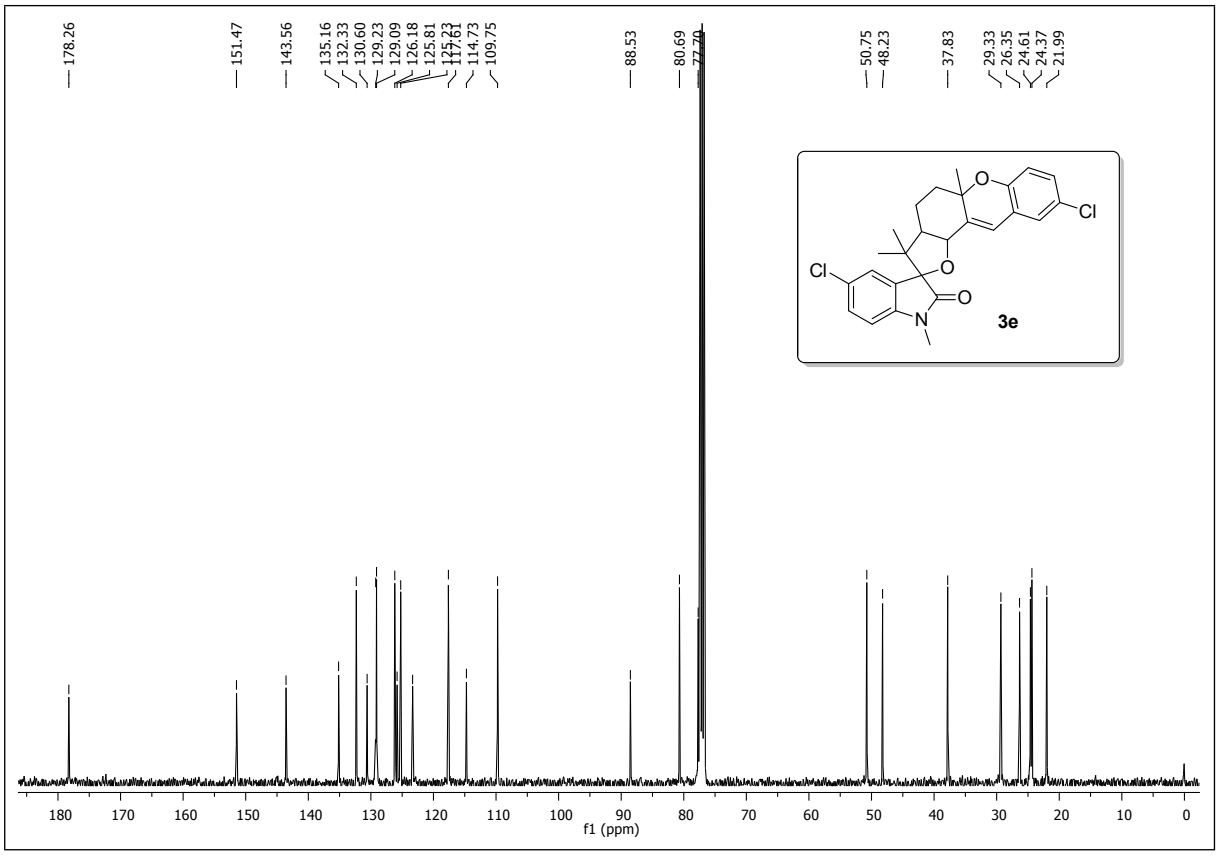
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 3d



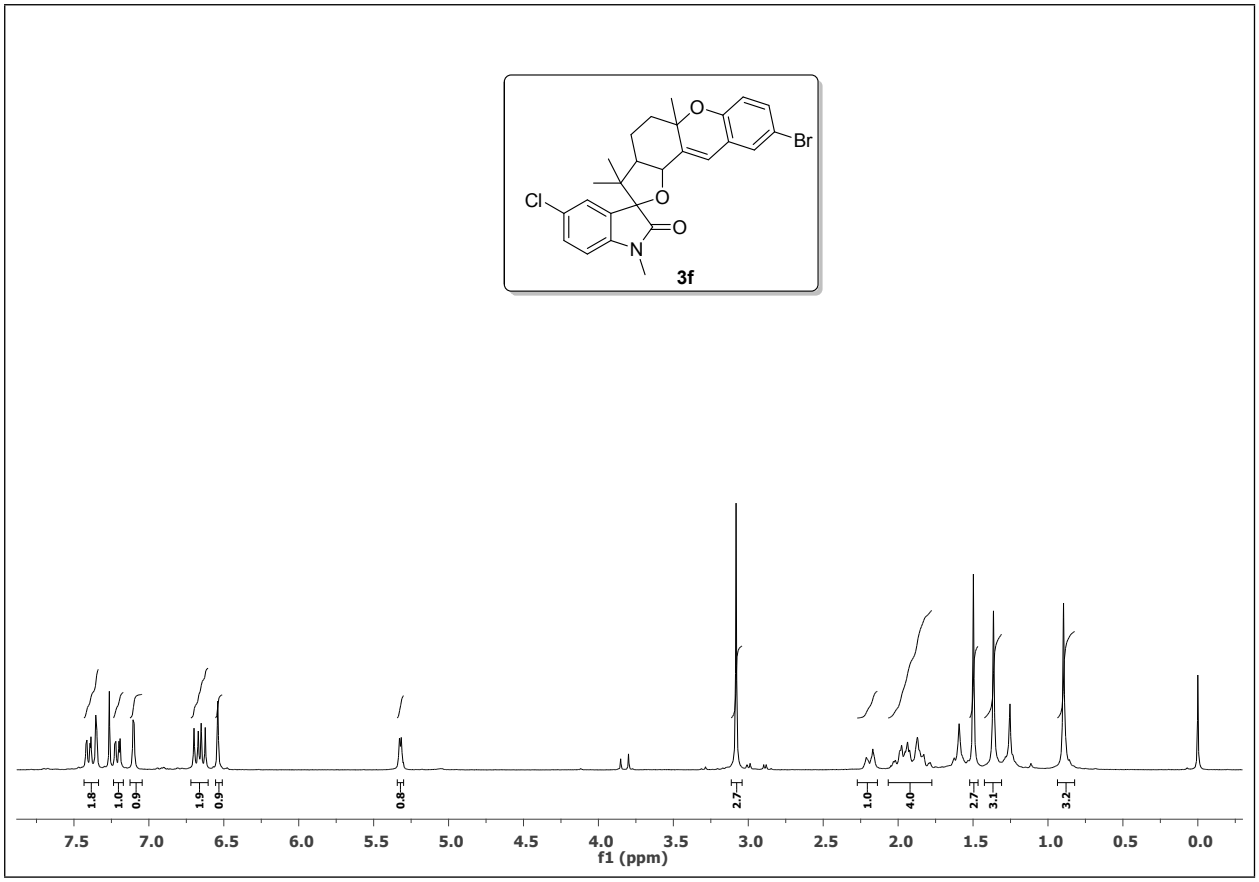
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound 3d



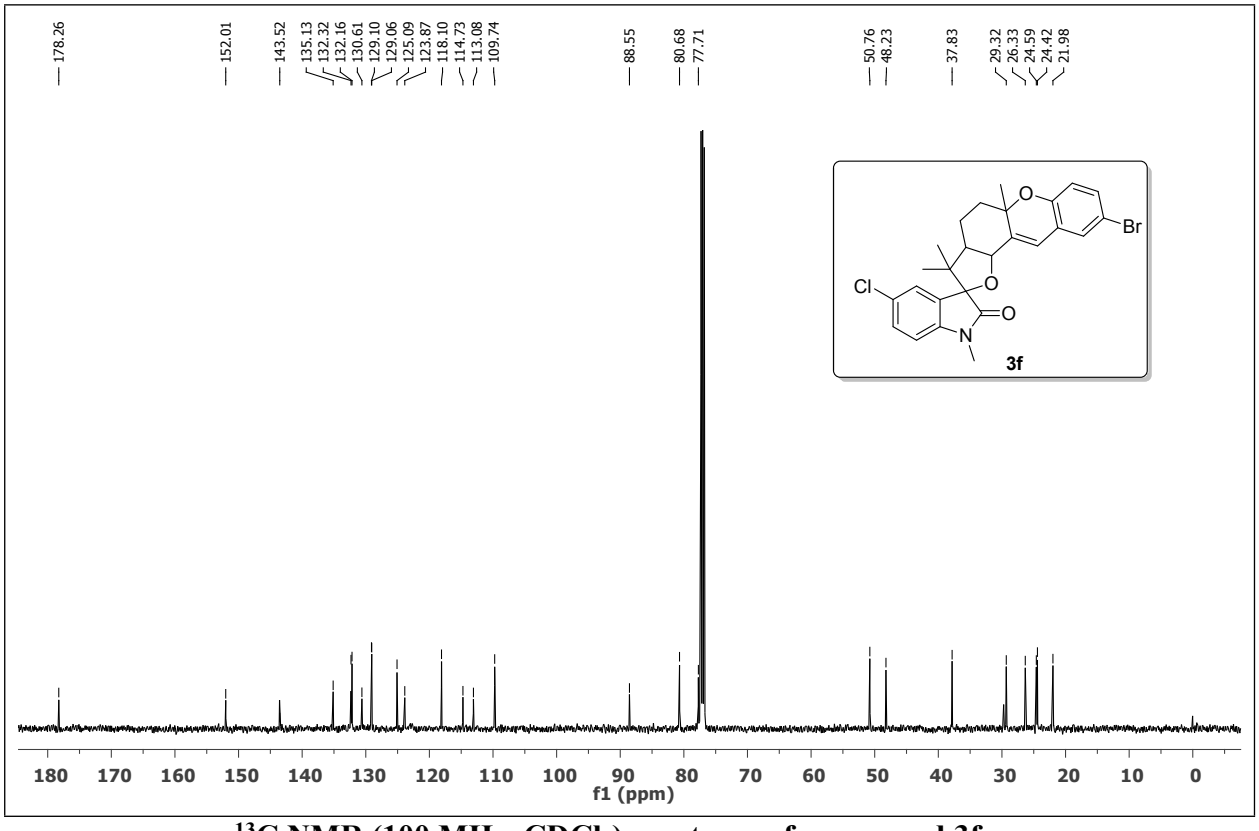
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3e



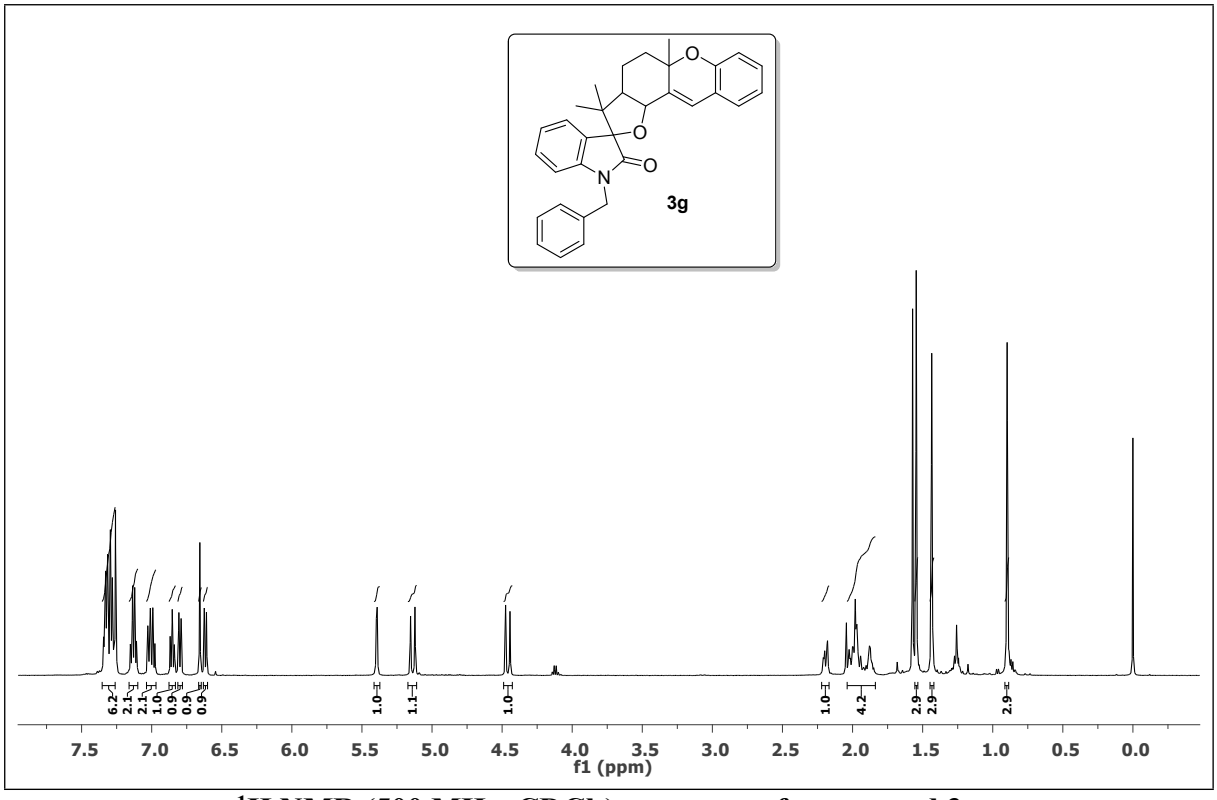
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 3e



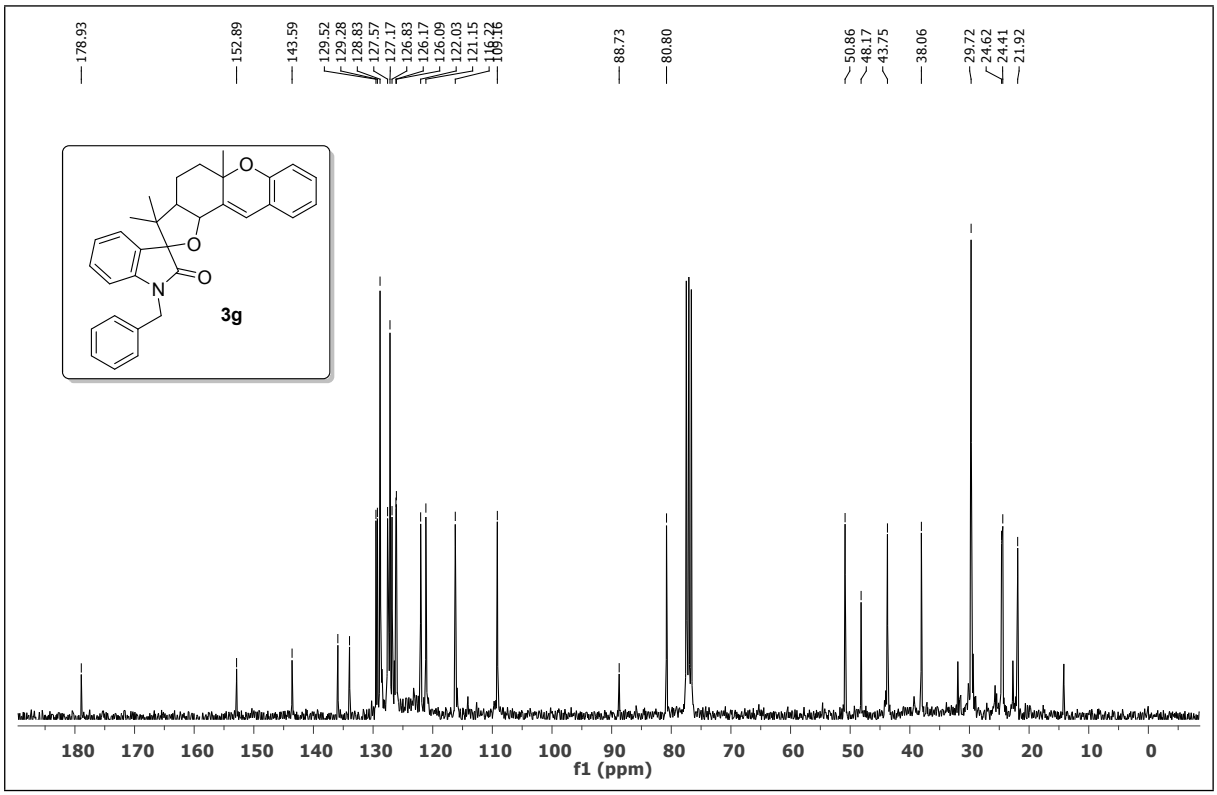
^{1}H NMR (300 MHz, $CDCl_3$) spectrum of compound 3f



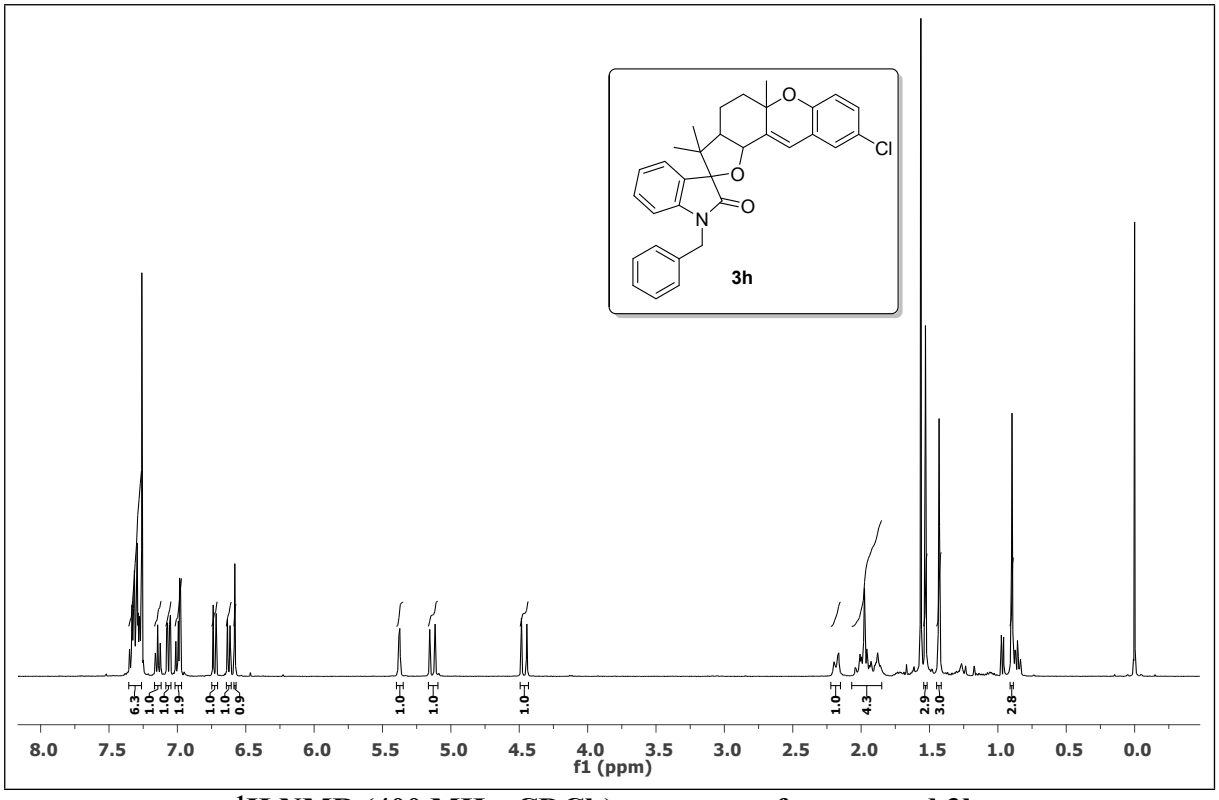
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 3f



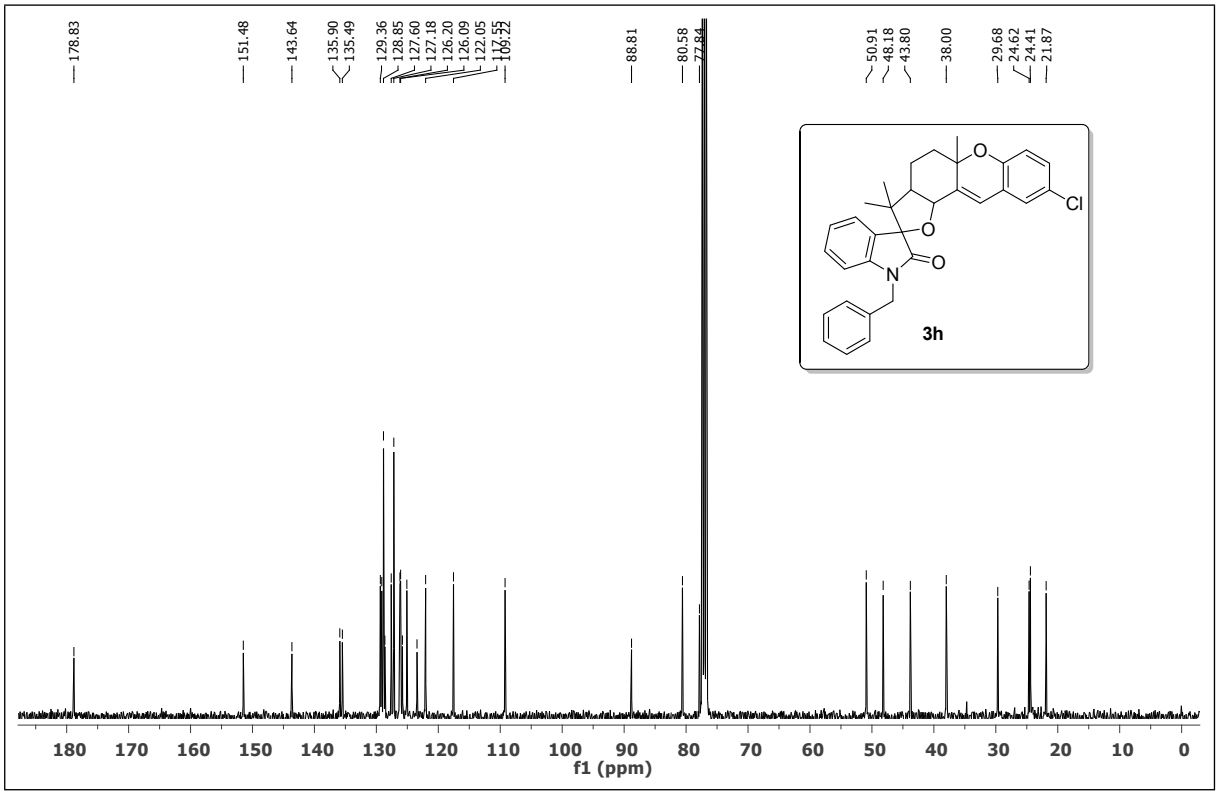
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 3g



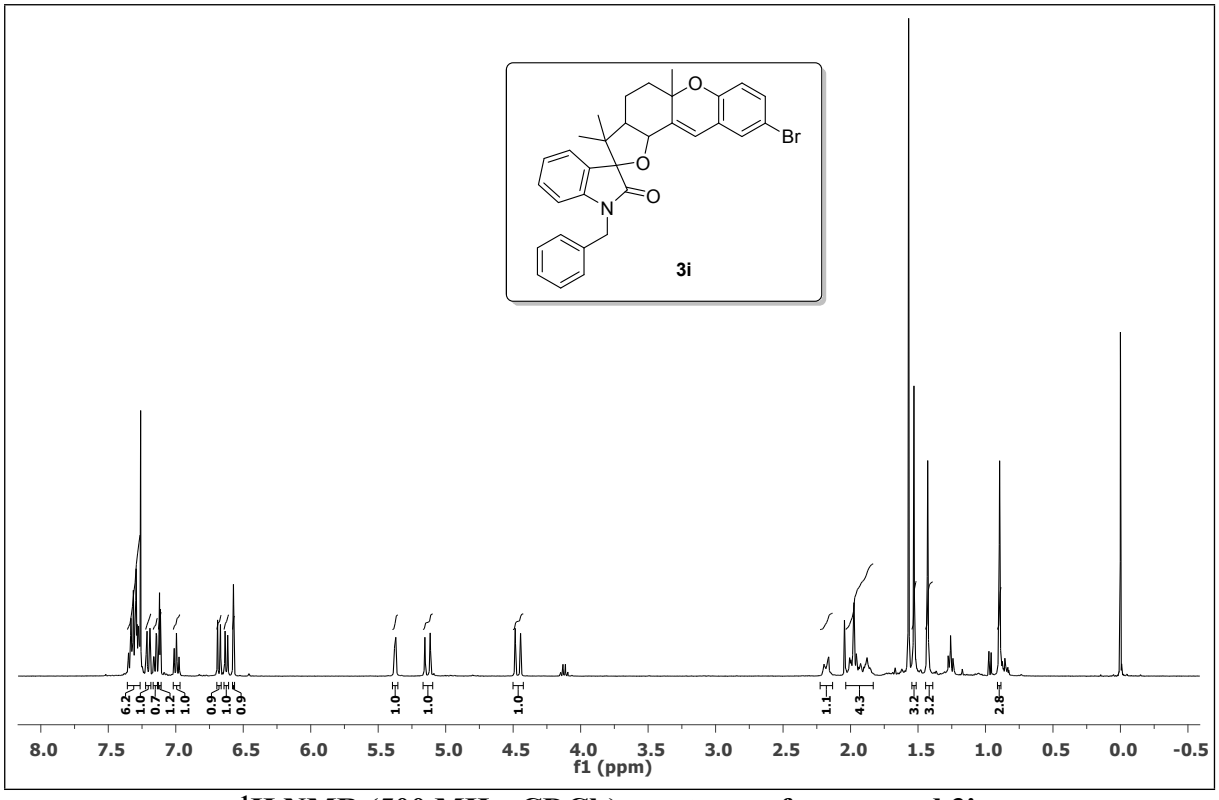
^{13}C NMR (75 MHz, $CDCl_3$) spectrum of compound 3g



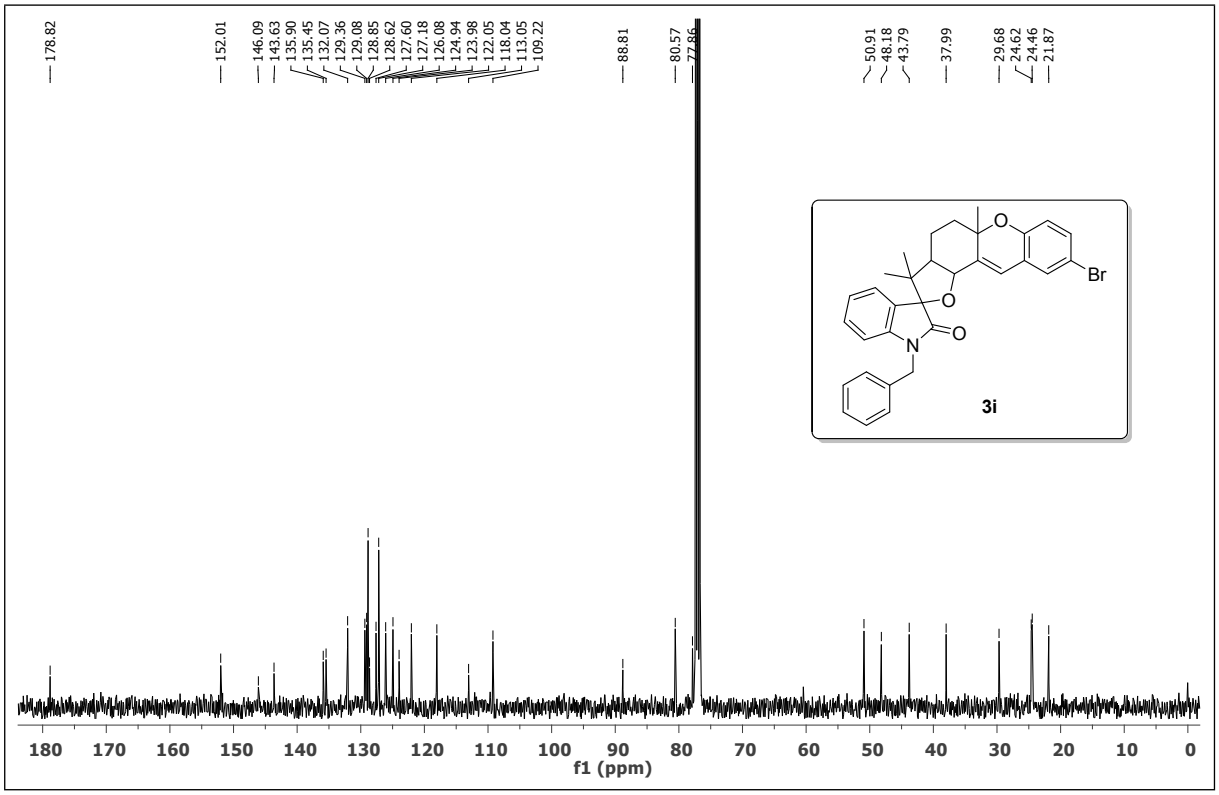
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3h



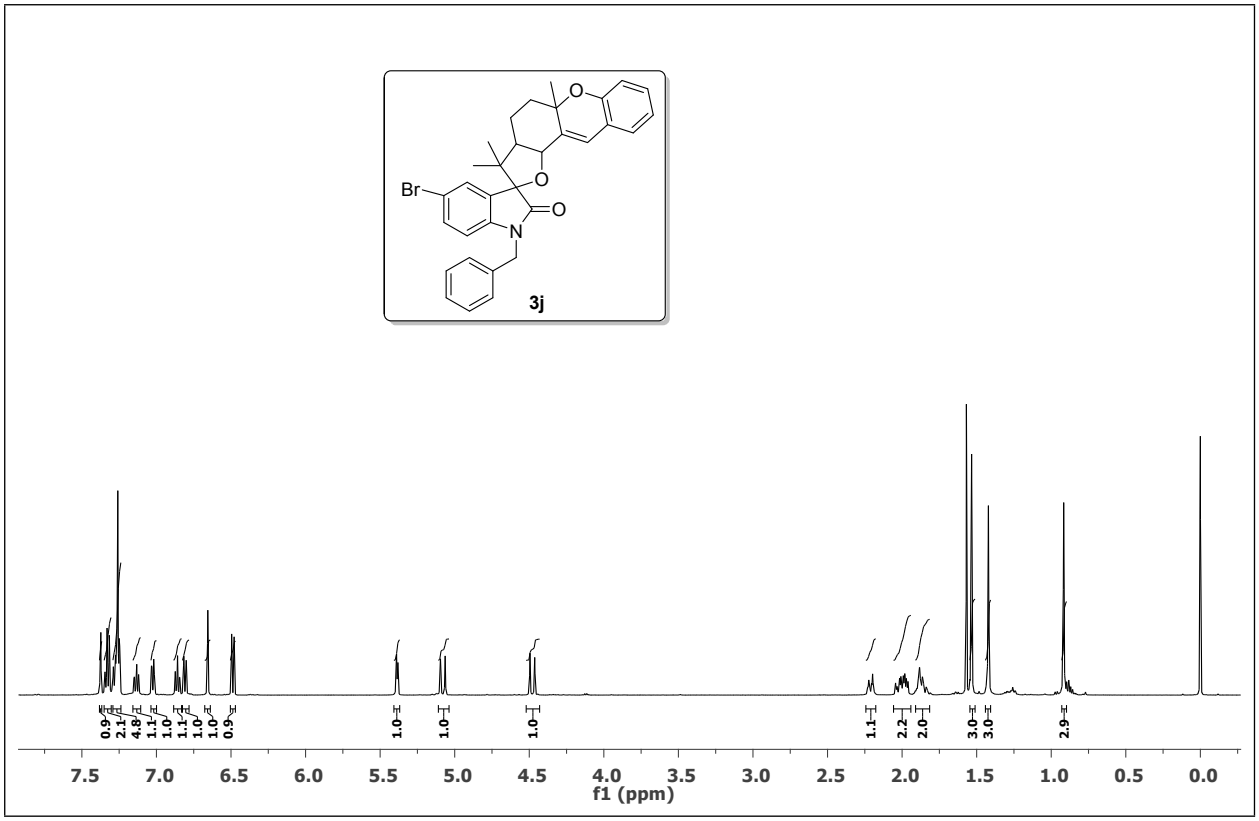
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 3h



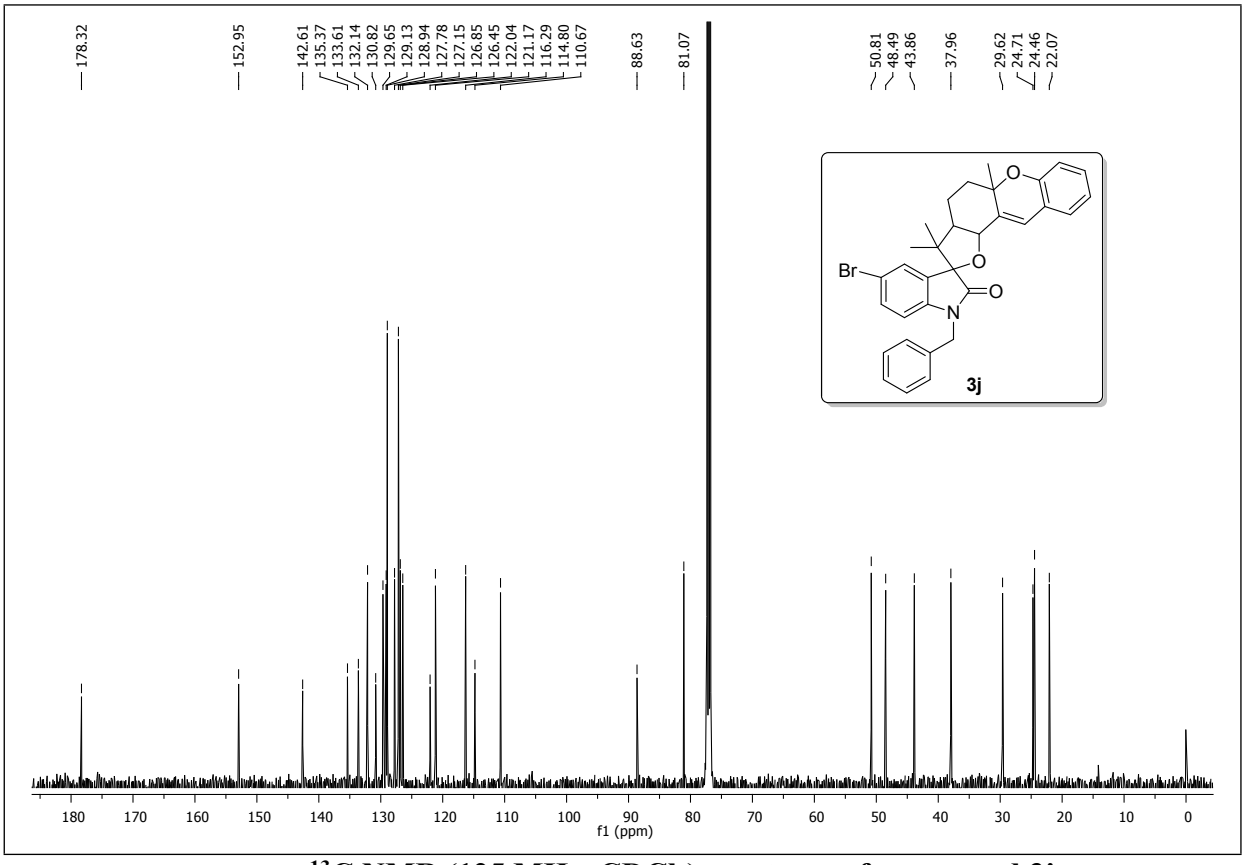
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 3i



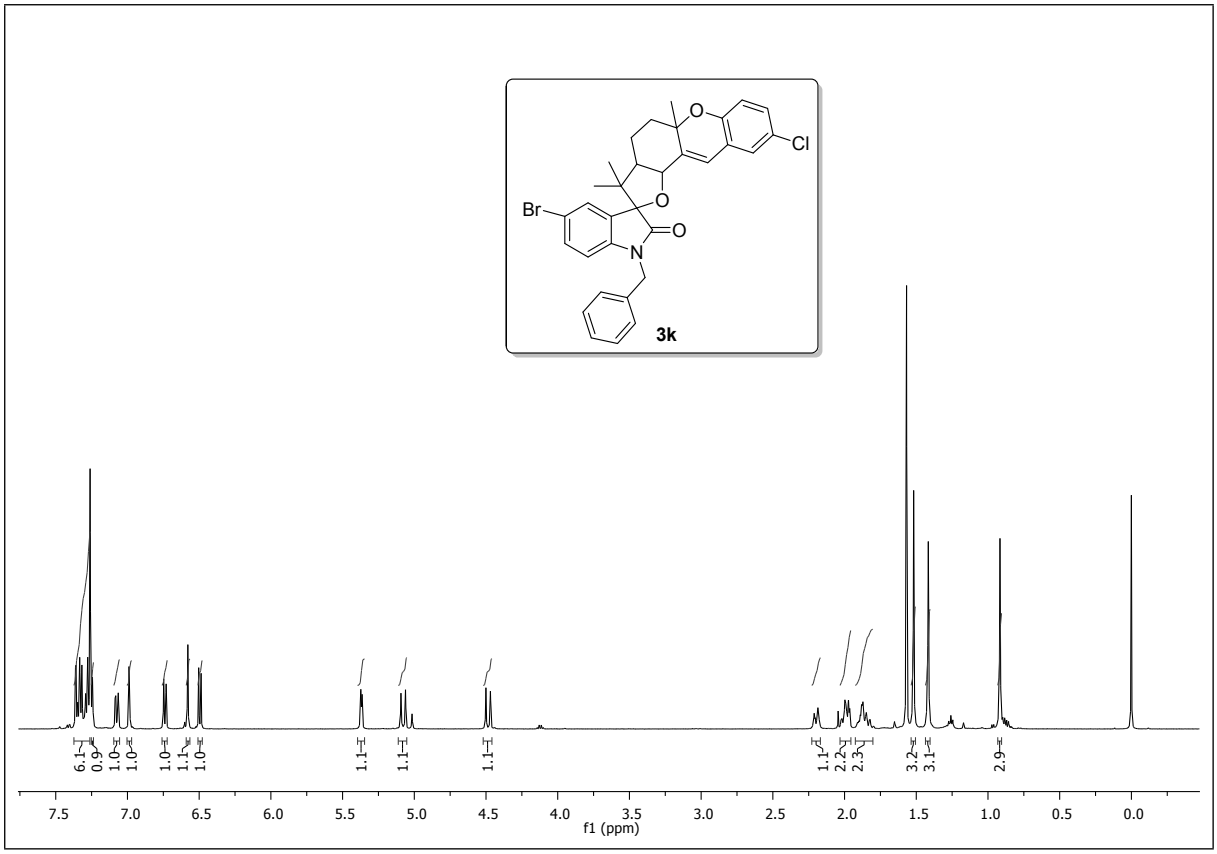
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 3i



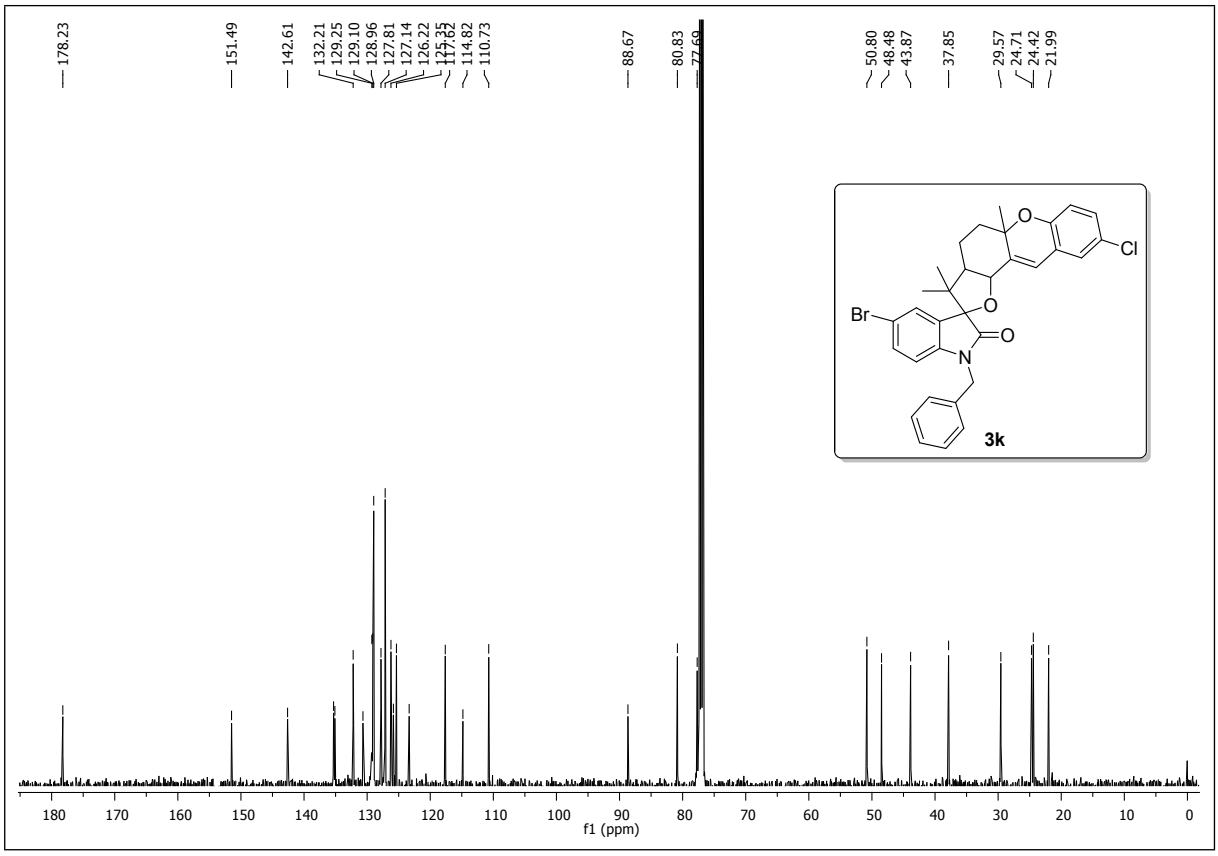
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 3j



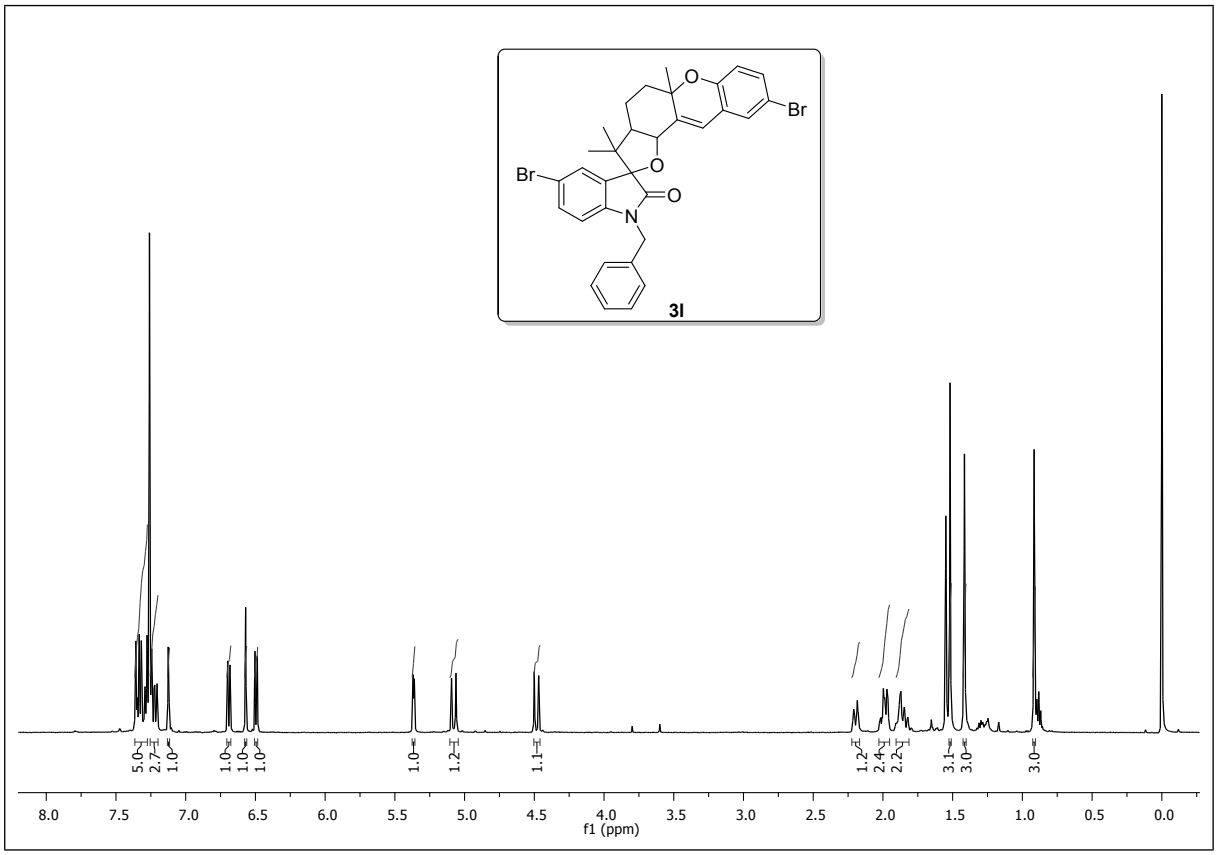
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 3j



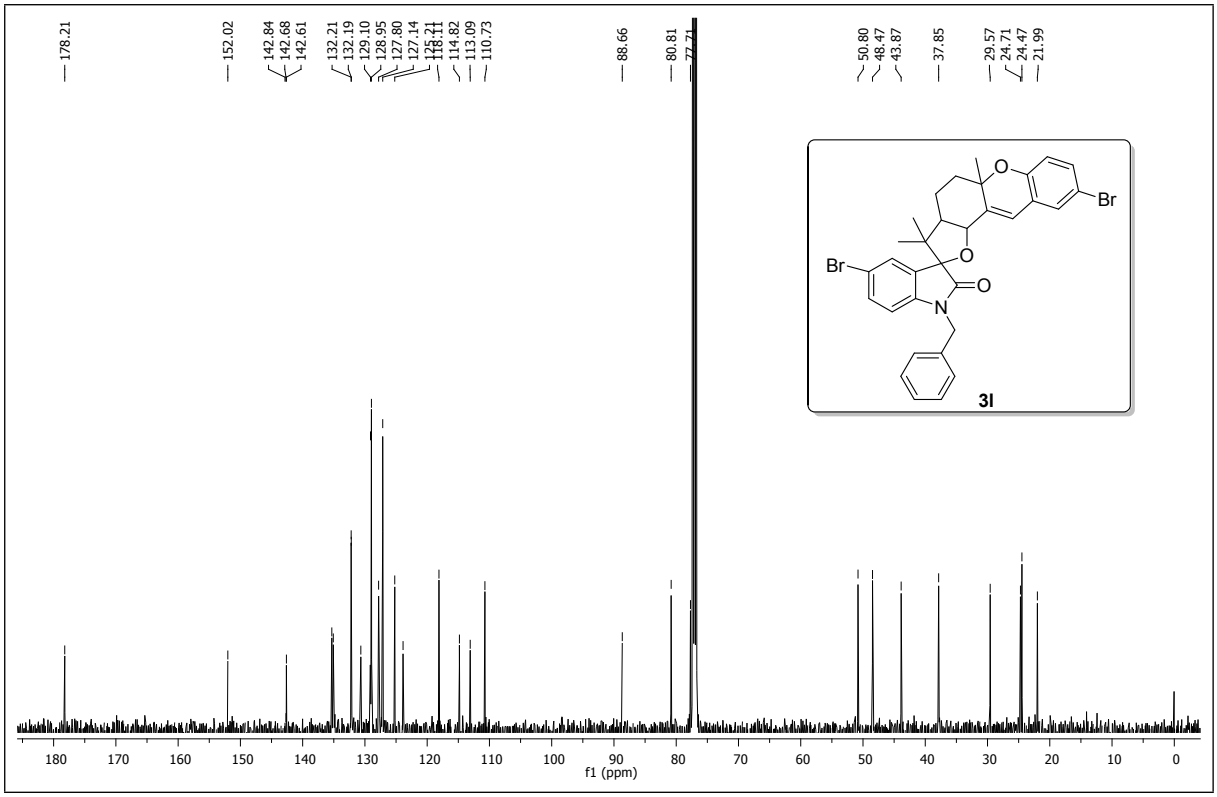
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 3k



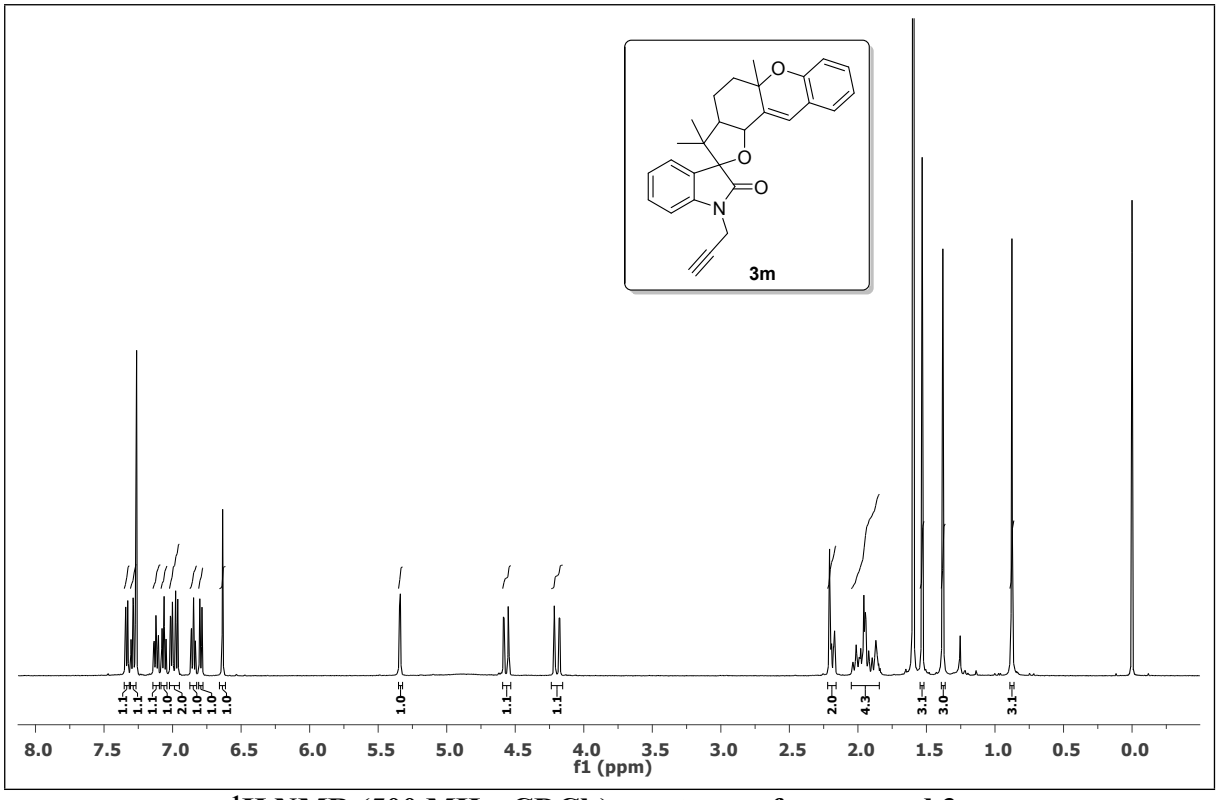
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 3k



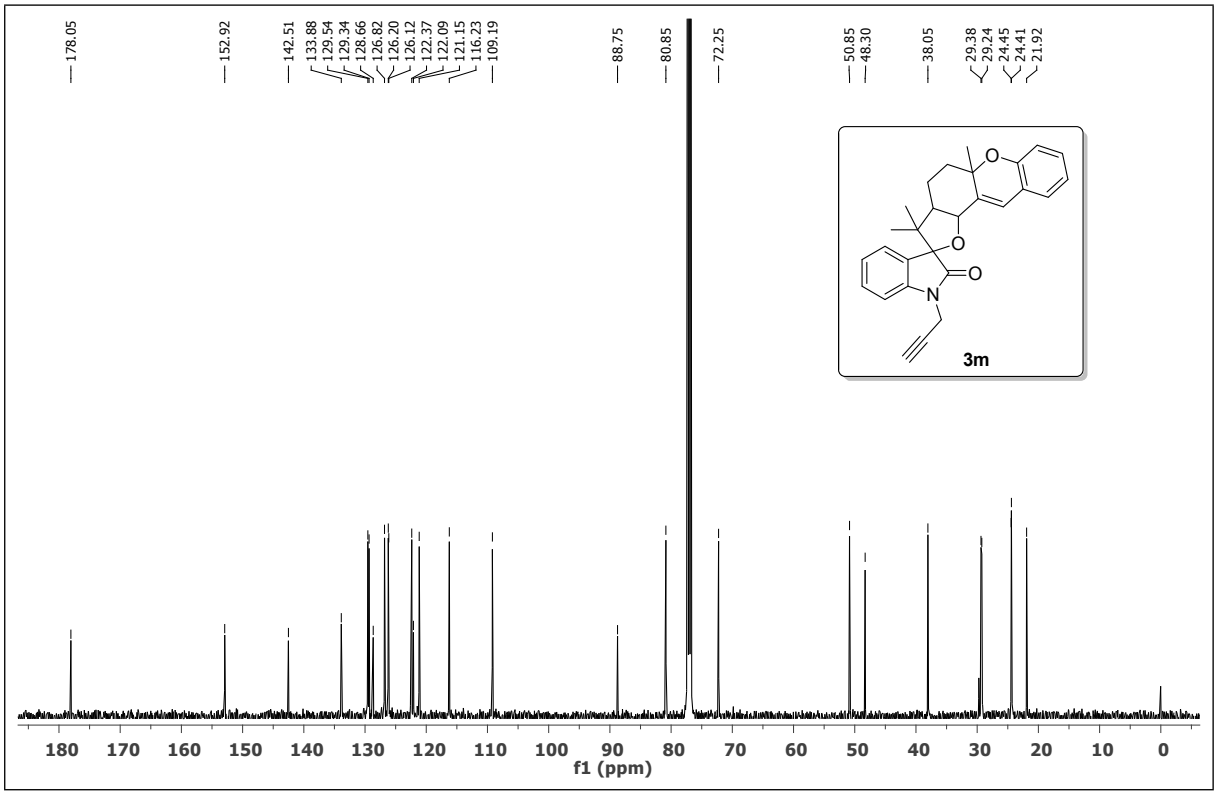
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 3l



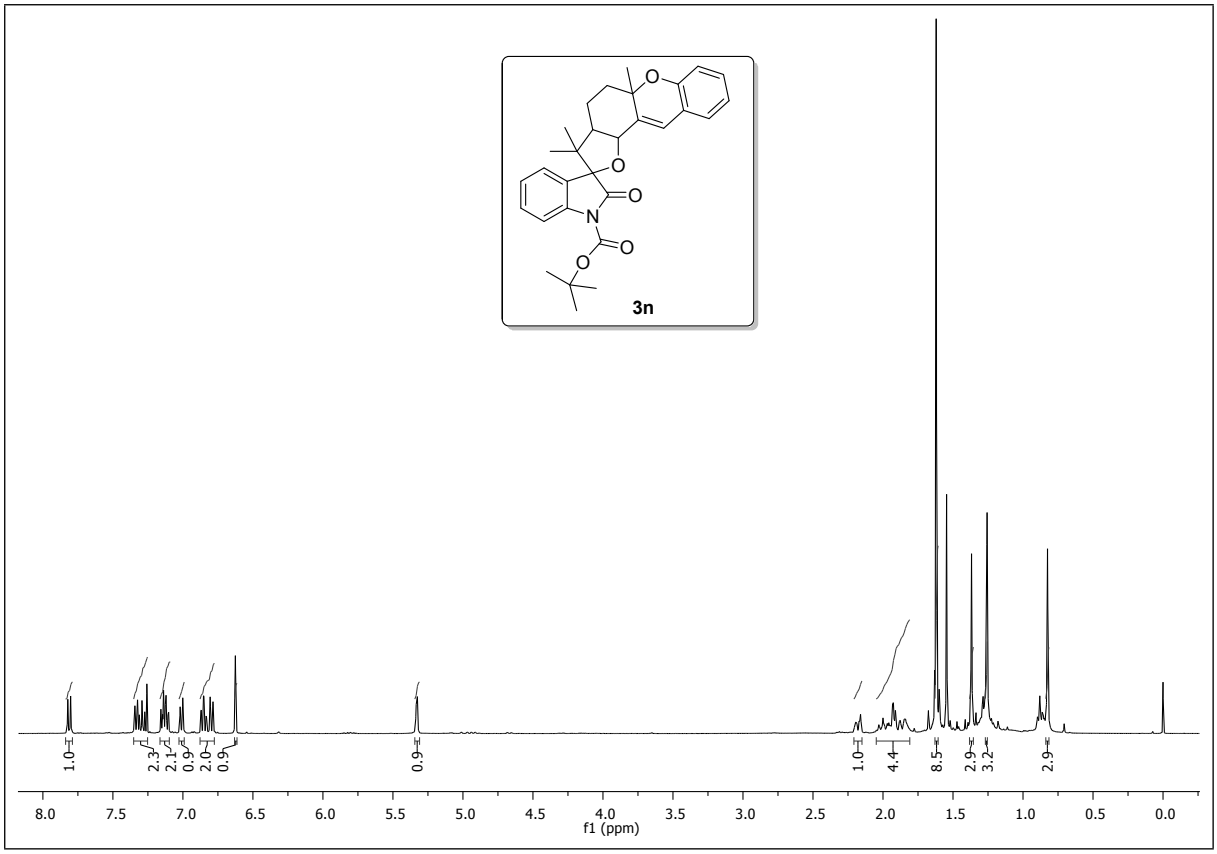
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 3l



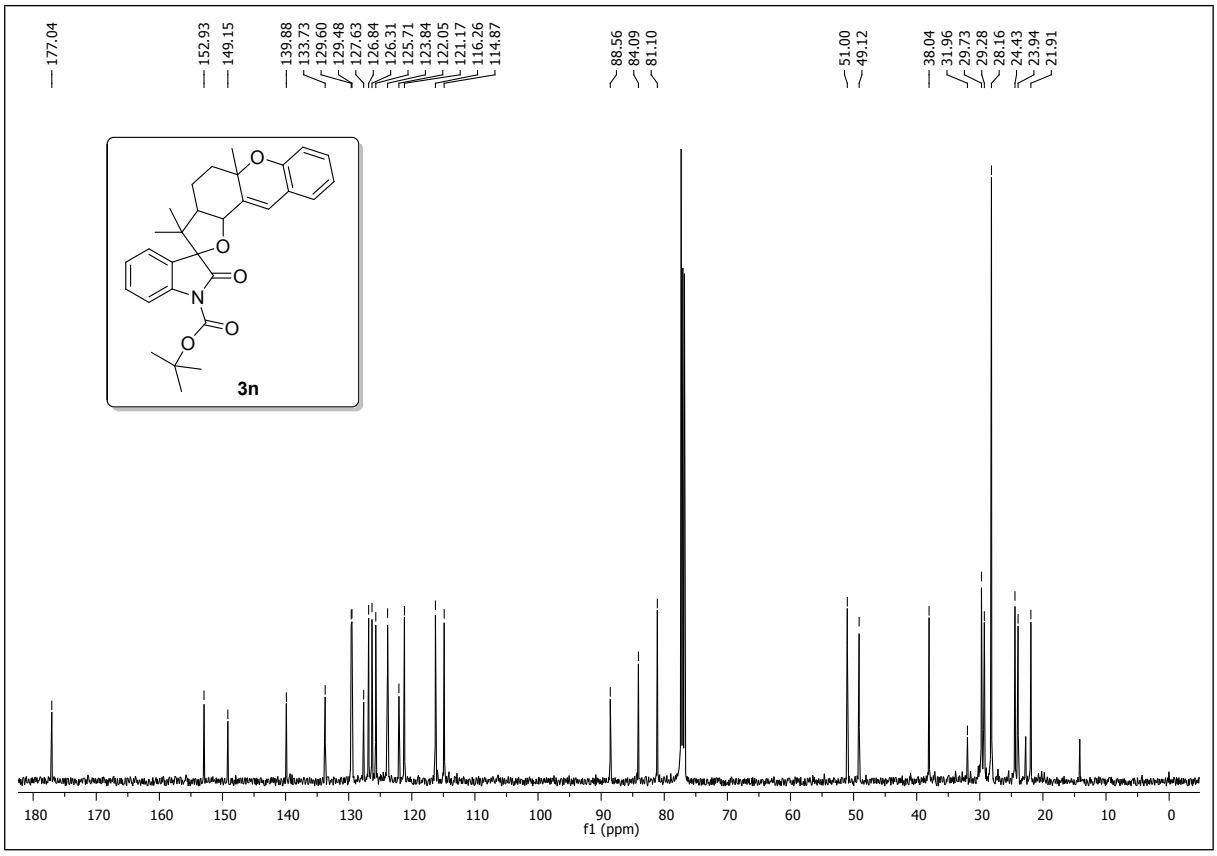
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 3m



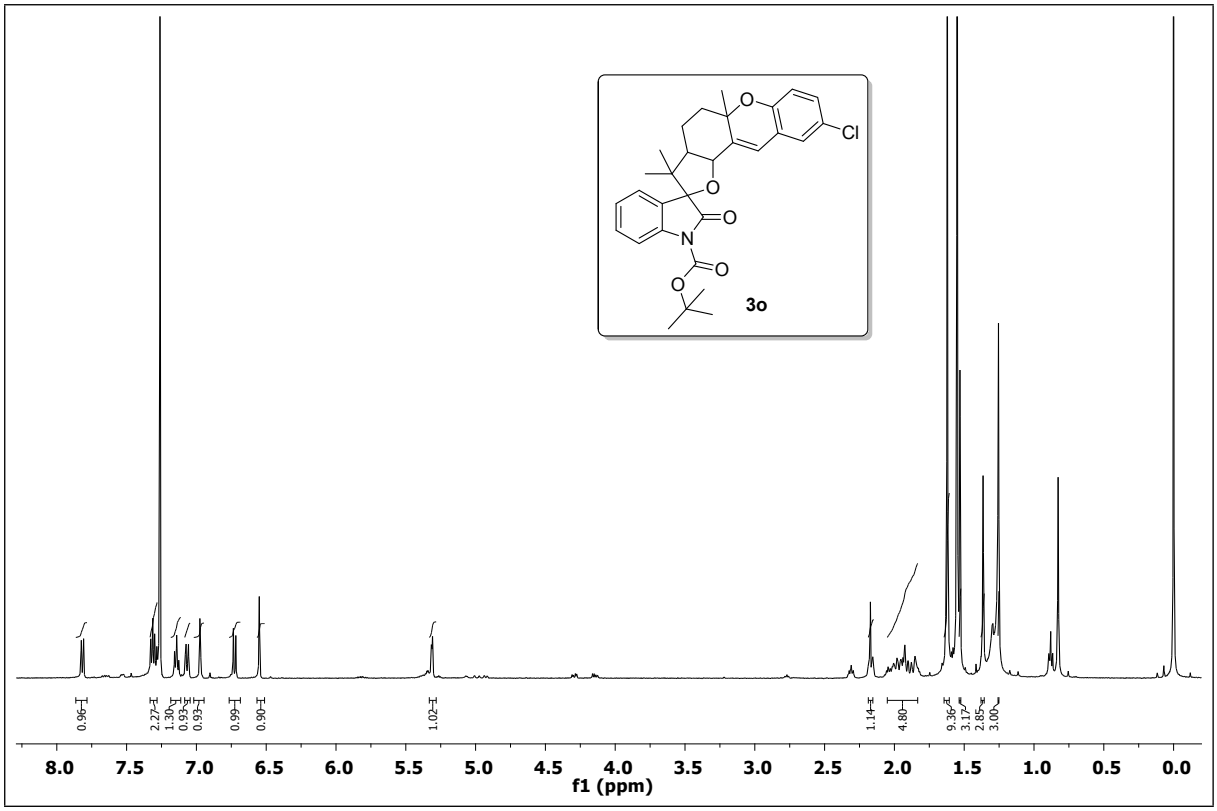
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 3m



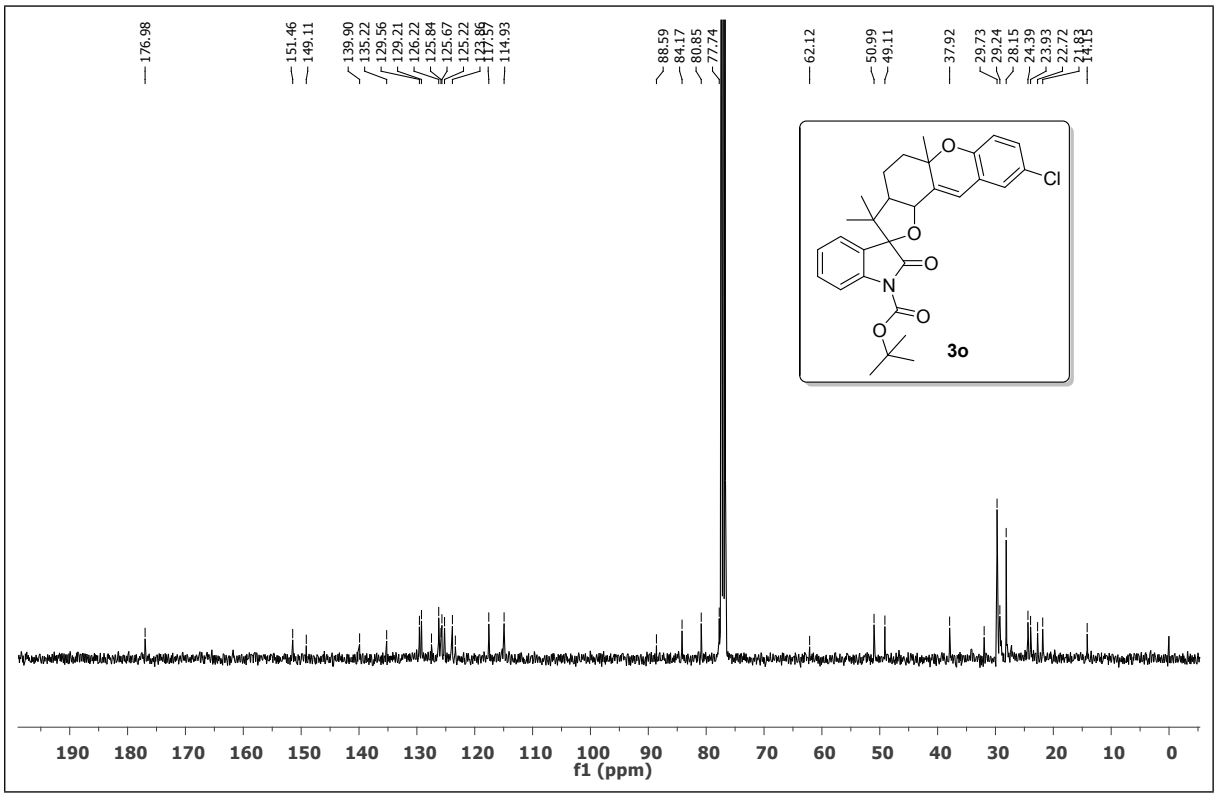
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3n



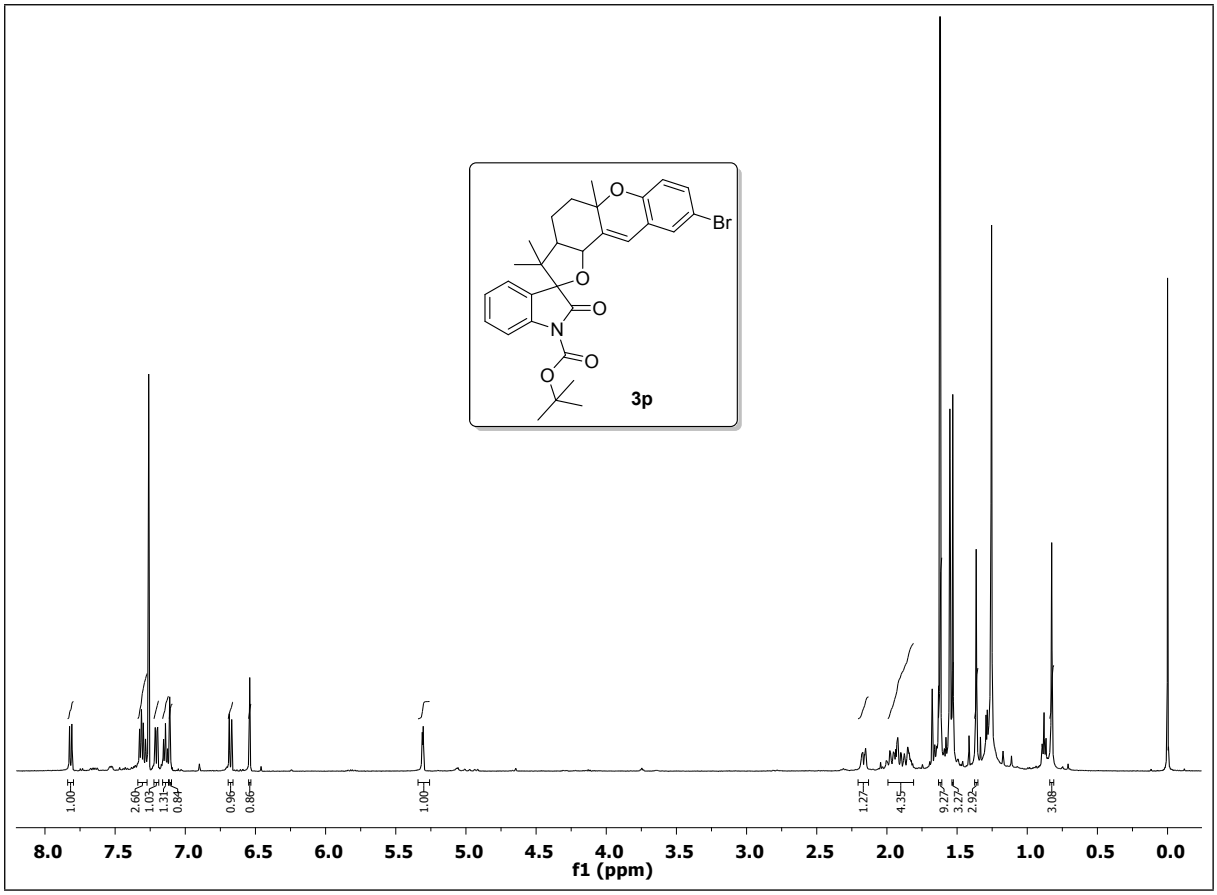
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 3n



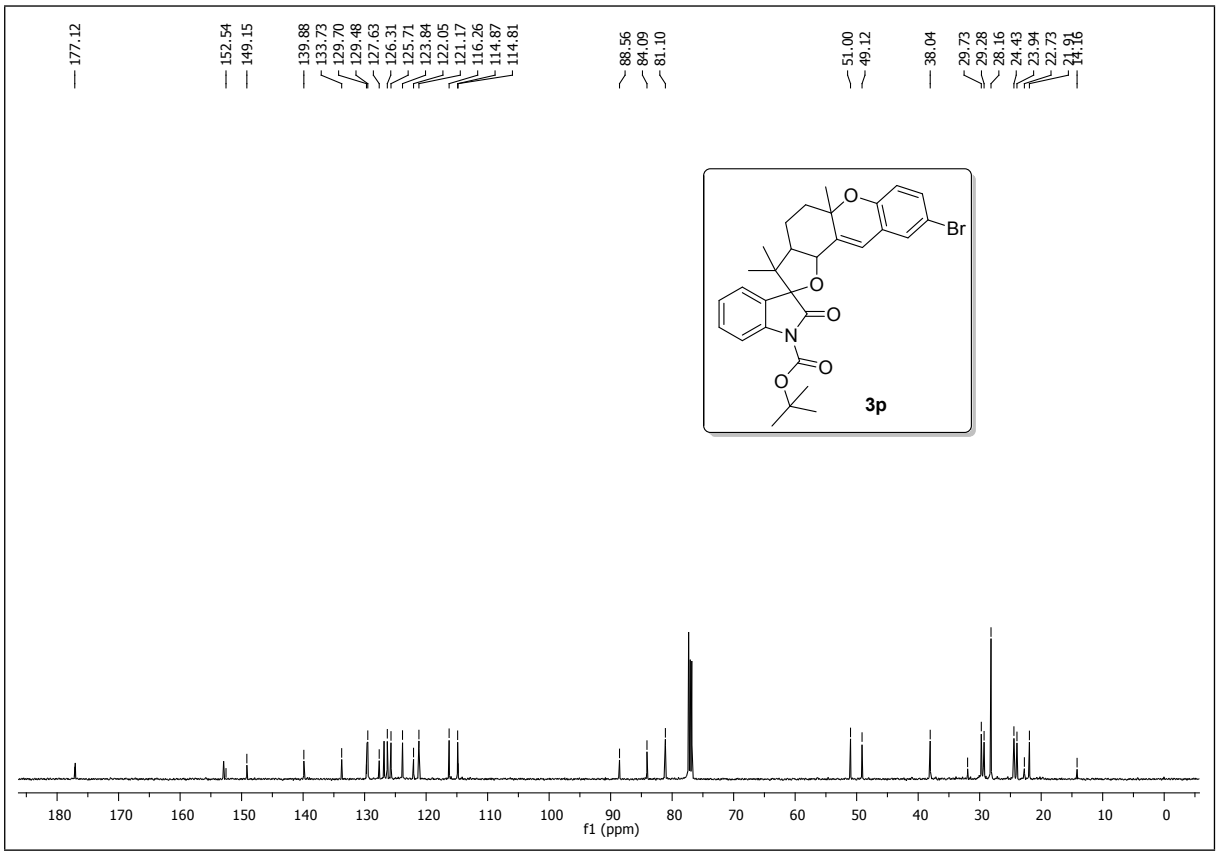
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3o



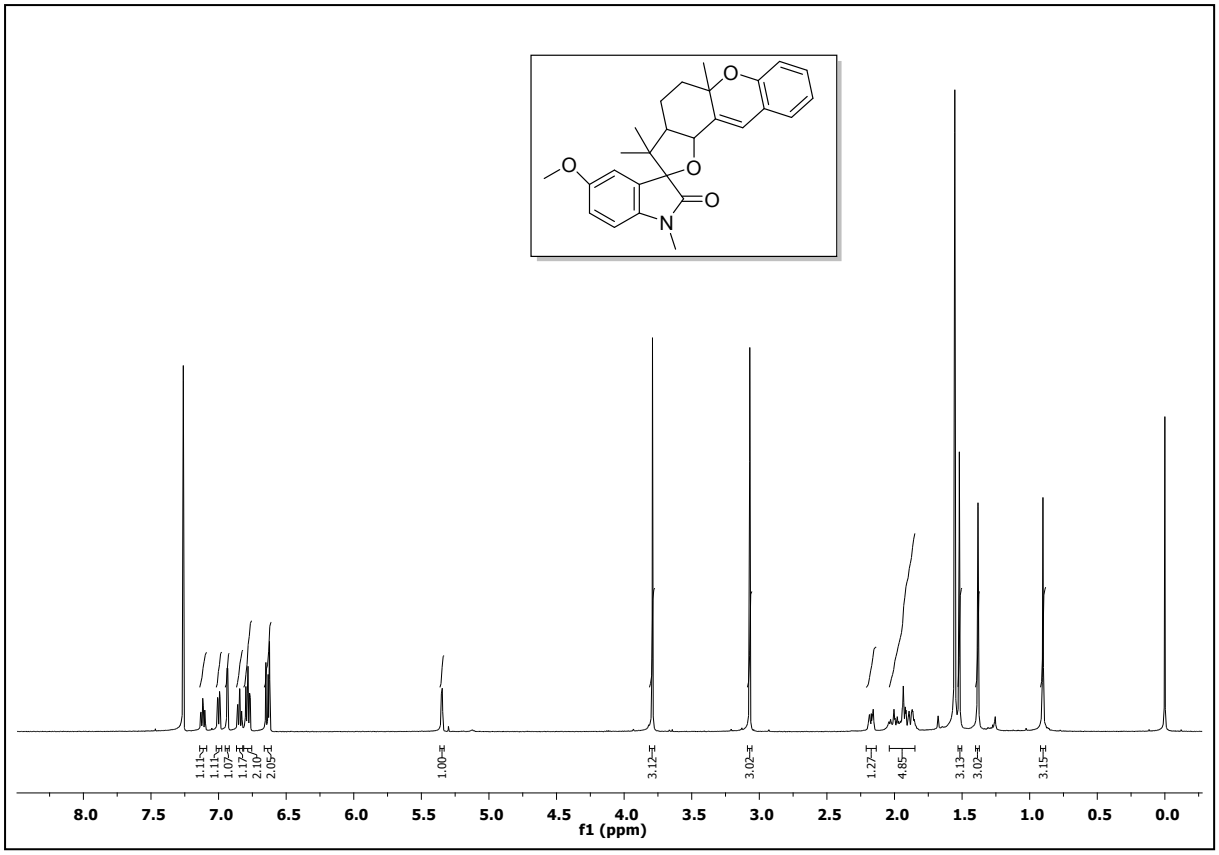
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 3o



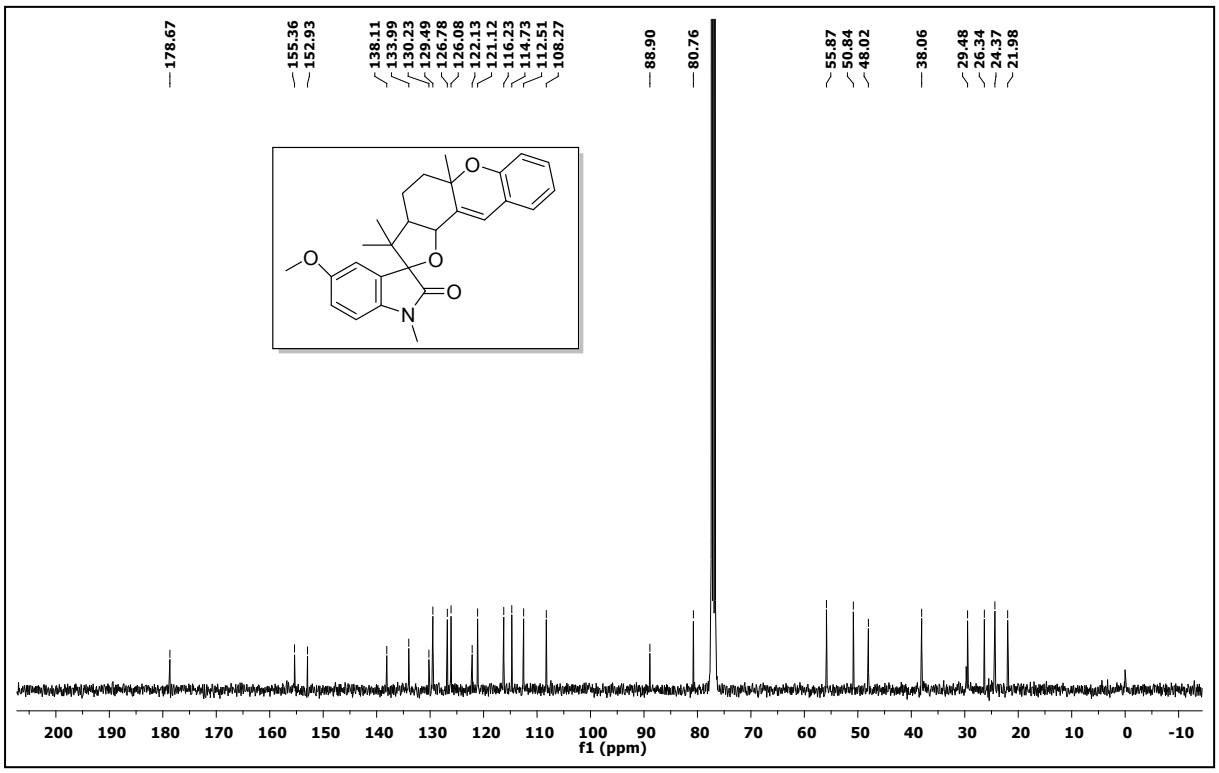
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 3p



^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound 3p



^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 3q



^{13}C NMR (500 MHz, $CDCl_3$) spectrum of compound 3q

5. X-ray Crystallography

X-ray data for the compounds were collected at room temperature using a Bruker Smart Apex CCD diffractometer with graphite monochromated MoKα radiation (λ=0.71073Å) with ω-scan method [1]. Preliminary lattice parameters and orientation matrices were obtained from four sets of frames.

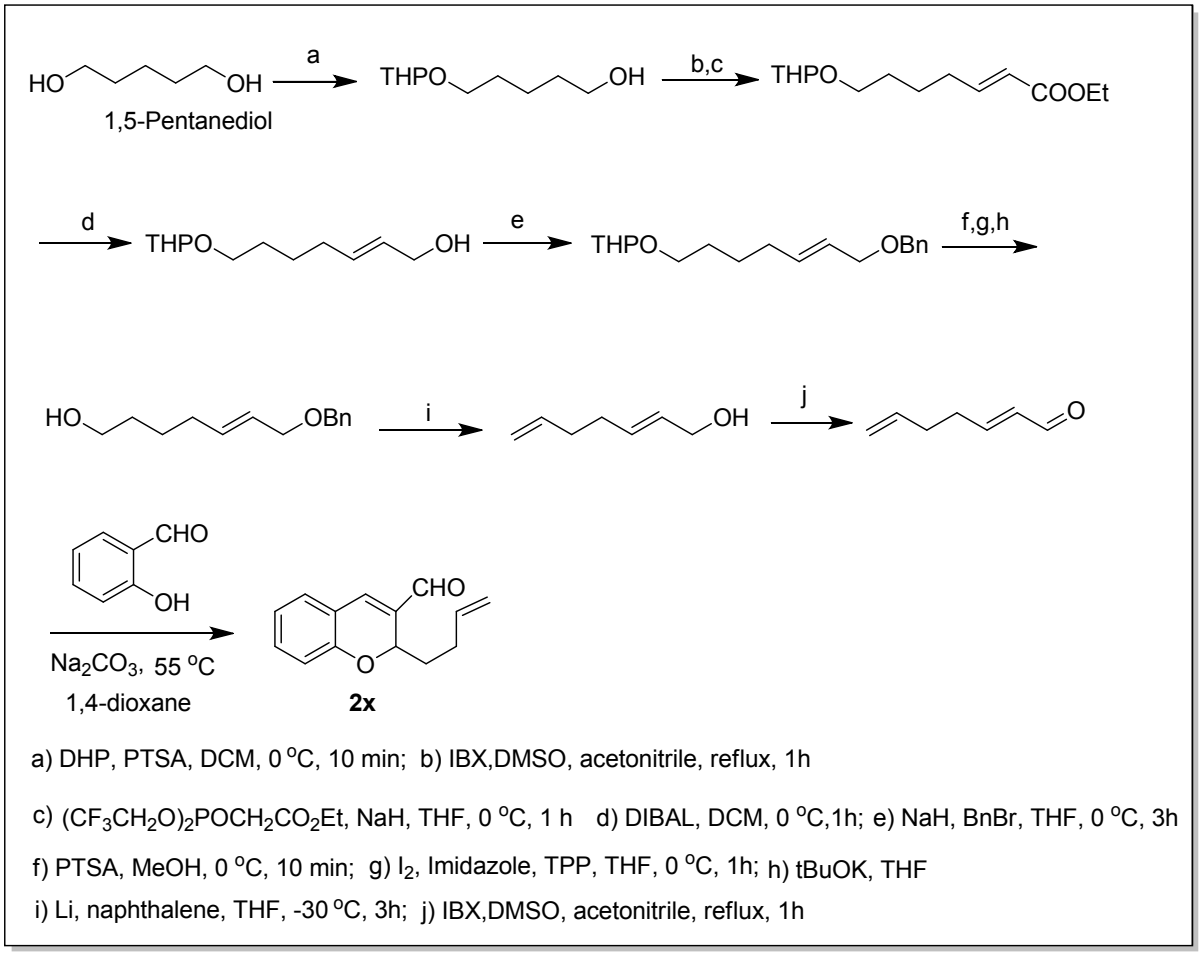
Integration and scaling of intensity data were accomplished using SAINT program [1]. The structure was solved by direct methods using SHELXS [2] and refinement was carried out by full-matrix least-squares technique using SHELXL [2]. Anisotropic displacement parameters were included for all non-hydrogen atoms. All H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H or $1.2U_{eq}(c)$ for other H atoms]. The methyl groups were allowed to rotate but not to tip.

Crystal Data for 3j: $C_{32}H_{30}NO_3Br$ (M =556.48): monoclinic, space group $P2_1/n$ (no. 14), a = 12.0331(11) Å, b =13.3098(13) Å, c = 17.0383(16) Å, β = 103.742(2)°, V = 2650.7(4) Å^3, Z = 4, T = 294.15 K, μ(MoKα) = 1.585 mm^{-1}, *Dcalc* = 1.394 g/mm^3, 30408 reflections measured ($3.758 \leq 2\Theta \leq 56.578$), 6390 unique ($R_{int}$ = 0.0360) which were used in all calculations. The final R_1 was 0.0444 ($I > 2\sigma(I)$) and wR_2 was 0.1176 (all data).CCDC 1451304 contains supplementary Crystallographic data for the structure. These data can be obtained free of charge at www.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 (2001). SAINT (Version 6.28a) & SMART (Version 5.625). Bruker AXS Inc., Madison, Wisconsin, USA.
2. Sheldrick G. M. (2015**)** Acta Crystallography C71: 3-8.

Figure 2. A view of **3j**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by circles of arbitrary radii.

6. Preparation of starting material 2x



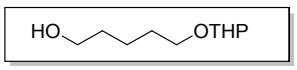
a) DHP, PTSA, DCM, 0 °C, 10 min; b) IBX,DMSO, acetonitrile, reflux, 1h

c) $(CF_3CH_2O)_2POCH_2CO_2Et$, NaH, THF, 0 °C, 1 h d) DIBAL, DCM, 0 °C,1h; e) NaH, BnBr, THF, 0 °C, 3h

f) PTSA, MeOH, 0 °C, 10 min; g) I_2, Imidazole, TPP, THF, 0 °C, 1h; h) tBuOK, THF

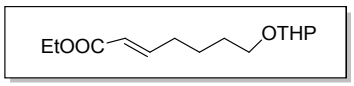
i) Li, naphthalene, THF, -30 °C, 3h; j) IBX,DMSO, acetonitrile, reflux, 1h

5-((Tetrahydro-2*H*-pyran-2-yl) oxy) pentan-1-ol



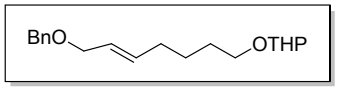
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.57 (d, *J* = 3.2 Hz, 1H), 3.85 (dt, *J* = 11.8, 8.0 Hz, 1H), 3.80 – 3.71 (m, 1H), 3.69 – 3.60 (m, 2H), 3.55 – 3.46 (m, 1H), 3.45 – 3.35 (m, 1H), 2.03 (dd, *J* = 14.7, 9.3 Hz, 1H), 1.83 (dt, *J* = 9.7, 6.2 Hz, 1H), 1.75 – 1.66 (m, 1H), 1.66 – 1.42 (m, 10H).^{13}C NMR (101 MHz, $CDCl_3$) δ 98.80, 67.54, 62.39, 32.26, 30.74, 29.44, 25.48, 22.49, 21.99, 19.67.

(*E*)-Ethyl 7-((tetrahydro-2*H*-pyran-2-yl)oxy)hept-2-enoate



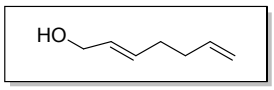
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (dt, *J* = 15.6, 6.9 Hz, 1H), 5.83 (dt, *J* = 15.6, 1.5 Hz, 1H), 4.57 (t, *J* = 3.5 Hz, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 3.86 (ddd, *J* = 11.1, 7.6, 3.4 Hz, 1H), 3.75 (dt, *J* = 9.8, 6.4 Hz, 1H), 3.54 – 3.47 (m, 1H), 3.44 – 3.35 (m, 1H), 2.24 (qd, *J* = 7.2, 1.5 Hz, 2H), 1.82 (ddd, *J* = 10.2, 8.0, 4.4 Hz, 1H), 1.75 – 1.52 (m, 9H), 1.31 – 1.27 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.69, 148.97, 121.50, 98.85, 67.11, 62.31, 60.13, 31.96, 30.73, 29.22, 25.48, 24.81, 19.63, 14.27.

(*E*)-2-((7-(Benzyloxy)hept-5-en-1-yl)oxy)tetrahydro-2*H*-pyran



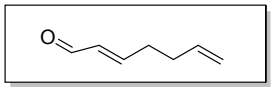
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 4H), 7.30 – 7.25 (m, 1H), 5.78 – 5.54 (m, 2H), 4.57 (dd, *J* = 4.2, 3.0 Hz, 1H), 4.50 (d, *J* = 5.7 Hz, 2H), 3.97 (dd, *J* = 6.1, 0.9 Hz, 2H), 3.89 – 3.81 (m, 1H), 3.77 – 3.69 (m, 1H), 3.52 – 3.46 (m, 1H), 3.38 (dq, *J* = 9.7, 6.3 Hz, 1H), 2.13 – 2.06 (m, 2H), 1.87 – 1.77 (m, 1H), 1.73 – 1.68 (m, 1H), 1.64 – 1.45 (m, 9H).

(*E*)-Hepta-2,6-dien-1-ol



^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88 – 5.73 (m, 1H), 5.72 – 5.61 (m, 2H), 5.05 – 4.95 (m, 2H), 4.09 (d, *J* = 4.6 Hz, 2H), 2.17 – 2.13 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.07, 132.43, 129.41, 114.87, 63.75, 33.28, 31.56.

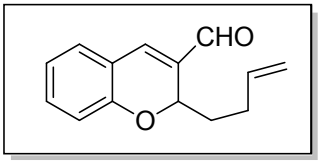
(*E*)-Hepta-2,6-dienal



^{1}H NMR (400 MHz, $CDCl_3$) δ 9.50 (d, *J* = 7.9 Hz, 1H), 6.86 (dt, *J* = 15.6, 6.7 Hz, 1H), 6.15 (ddt, *J* = 15.6, 7.9, 1.5 Hz, 1H), 5.81 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.10 – 5.02 (m, 2H),

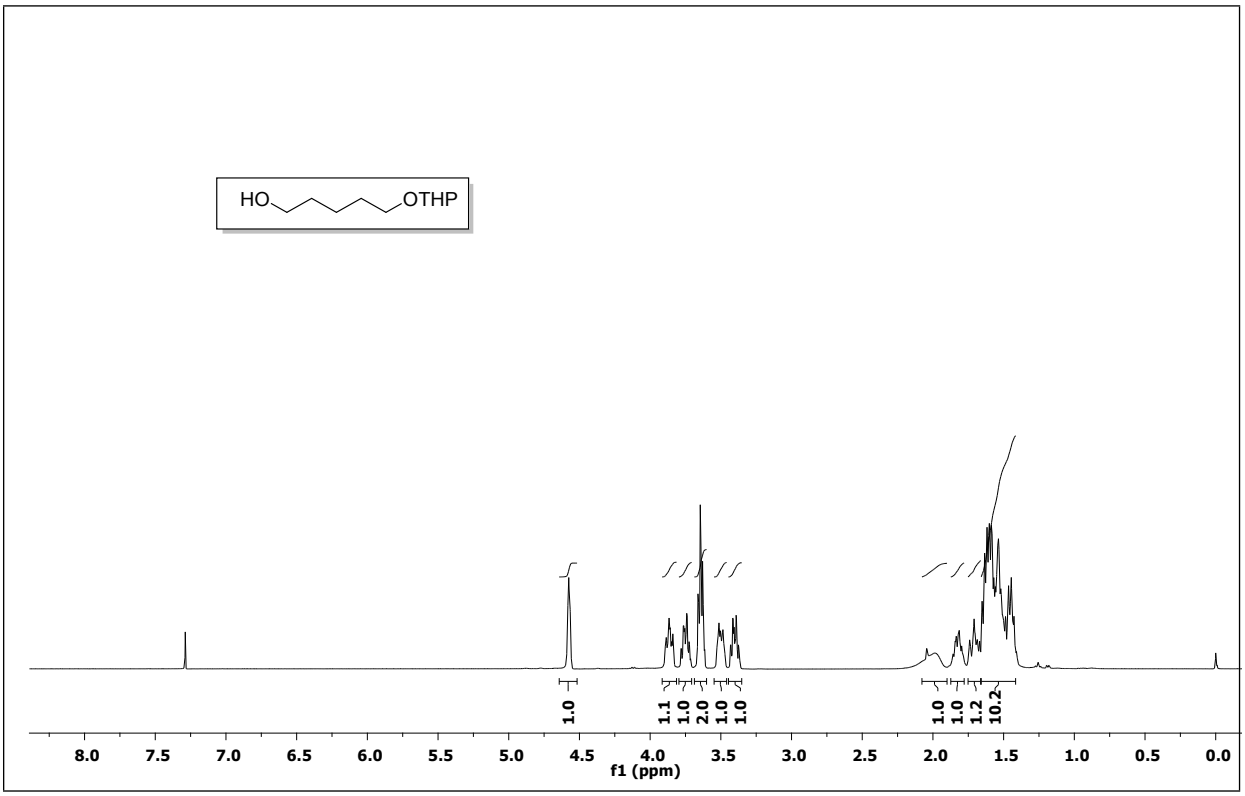
2.49 – 2.40 (m, 2H), 2.28 (dd, *J* = 13.6, 7.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.32, 157.81, 136.62, 133.31, 116.00, 31.82, 20.71.

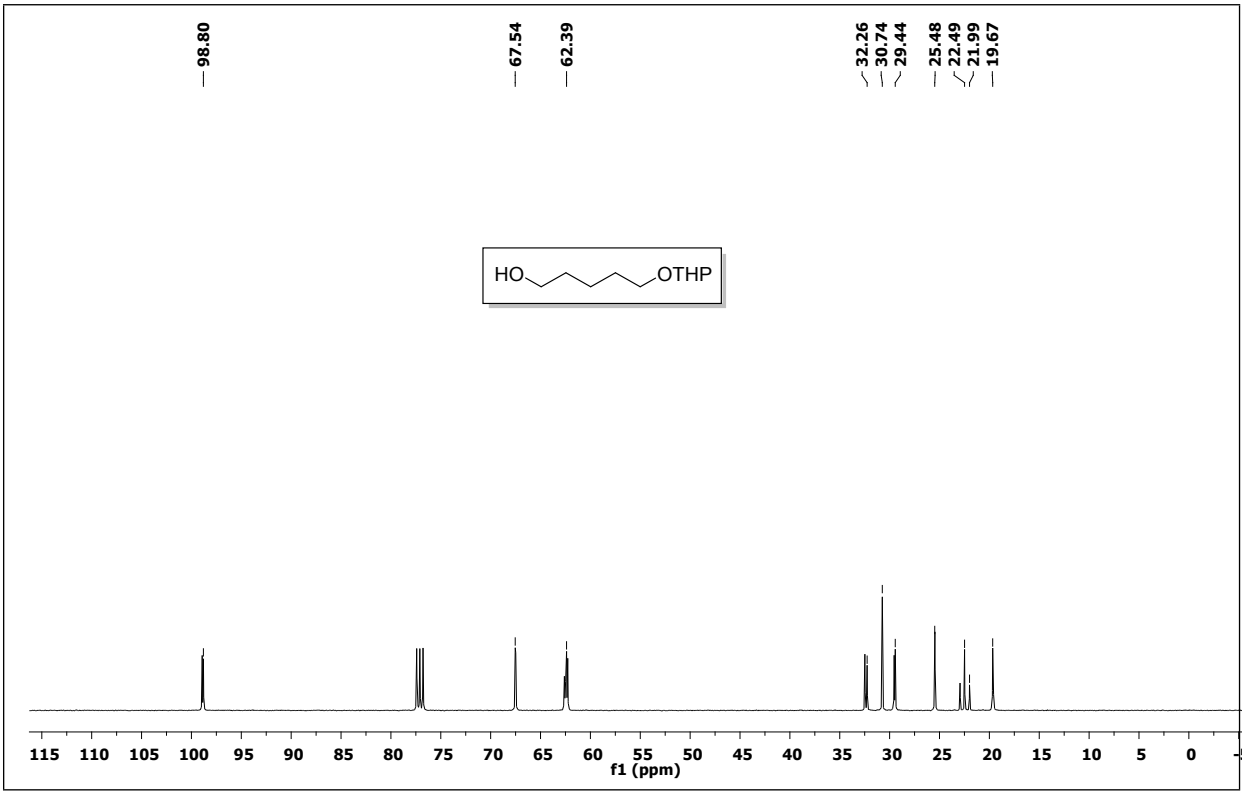
2-(But-3-en-1-yl)-2*H*-chromene-3-carbaldehyde

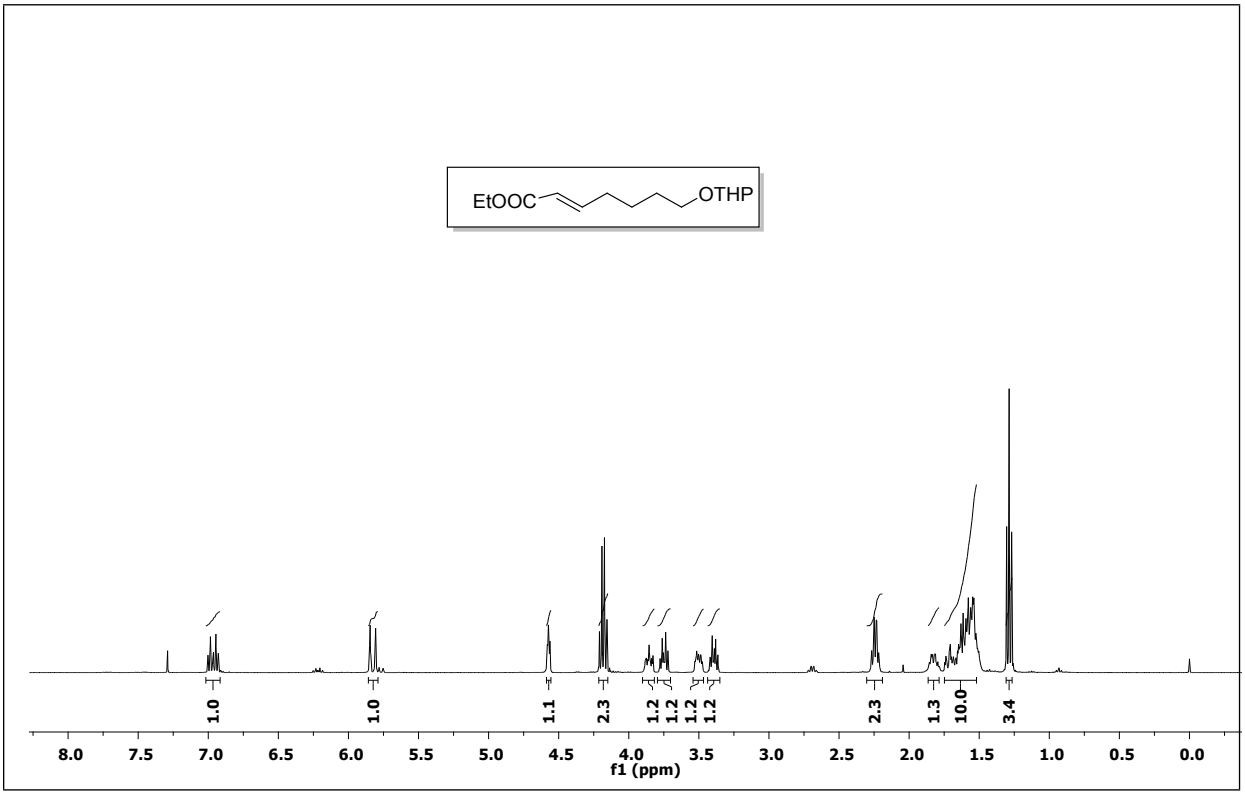


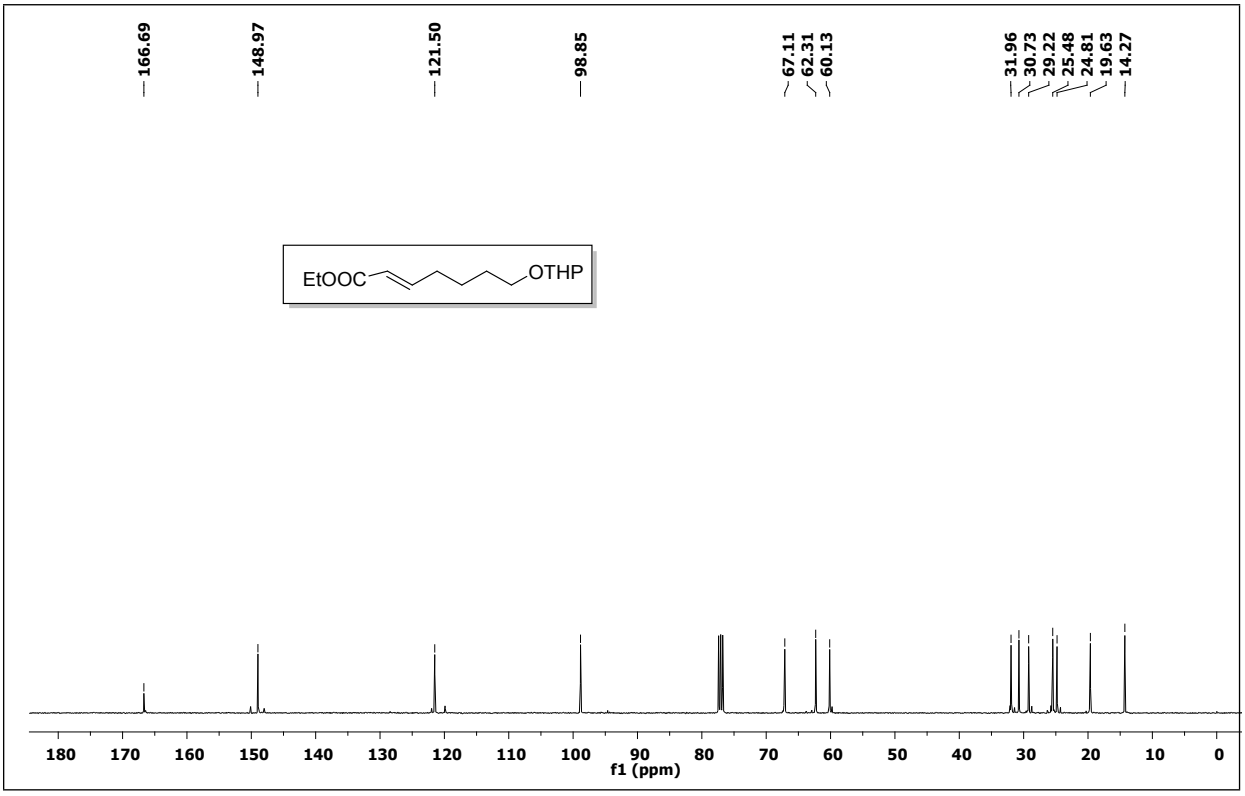
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.50 (S, 1H), 7.59 – 7.50 (m, 1H), 7.34 – 7.26 (m, 1H), 7.25 – 7.19 (m, 1H), 7.05 – 6.97 (m, 1H), 6.84 (dt, *J* = 15.6, 6.7 Hz, 1H), 6.17 – 6.10 (m, 1H), 5.85 – 5.76 (m, 1H), 5.10 – 5.03 (m, 2H), 2.49 – 2.40 (m, 2H), 2.28 (dt, *J* = 13.5, 6.7 Hz, 2H).

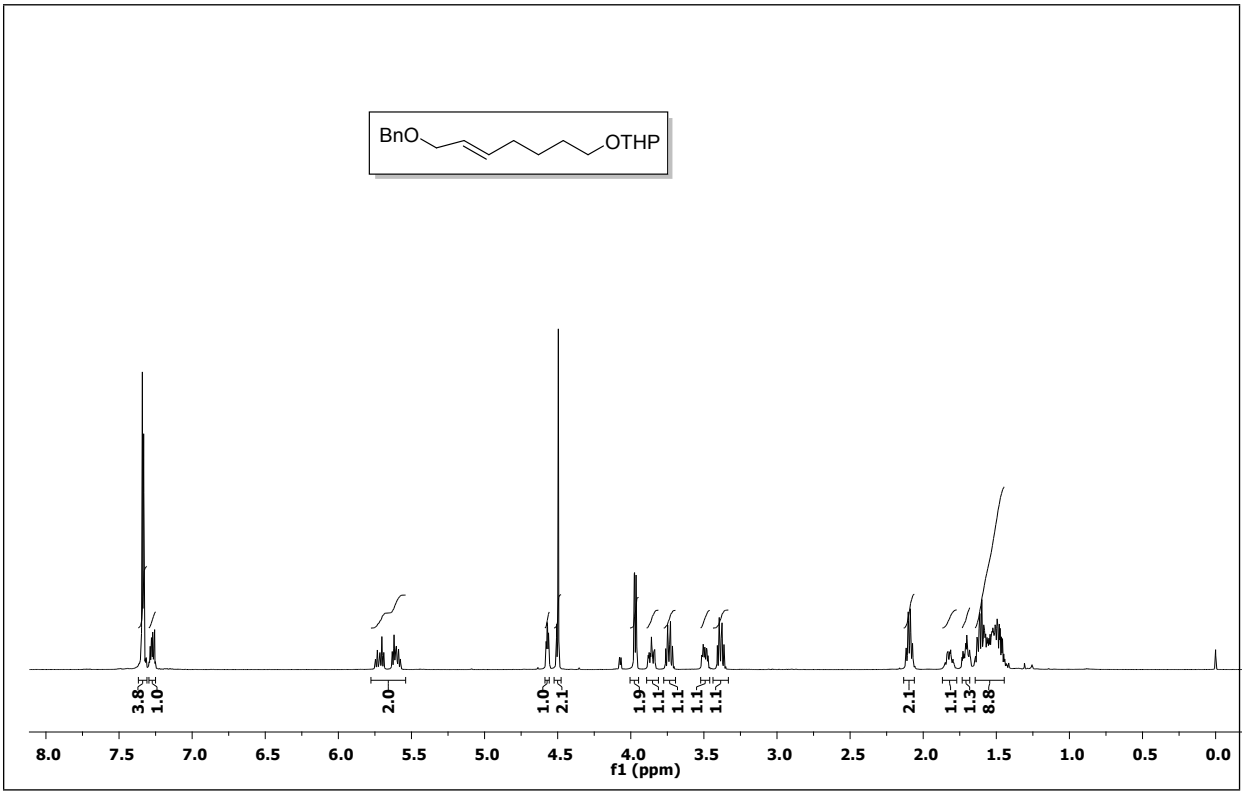
NMR spectra

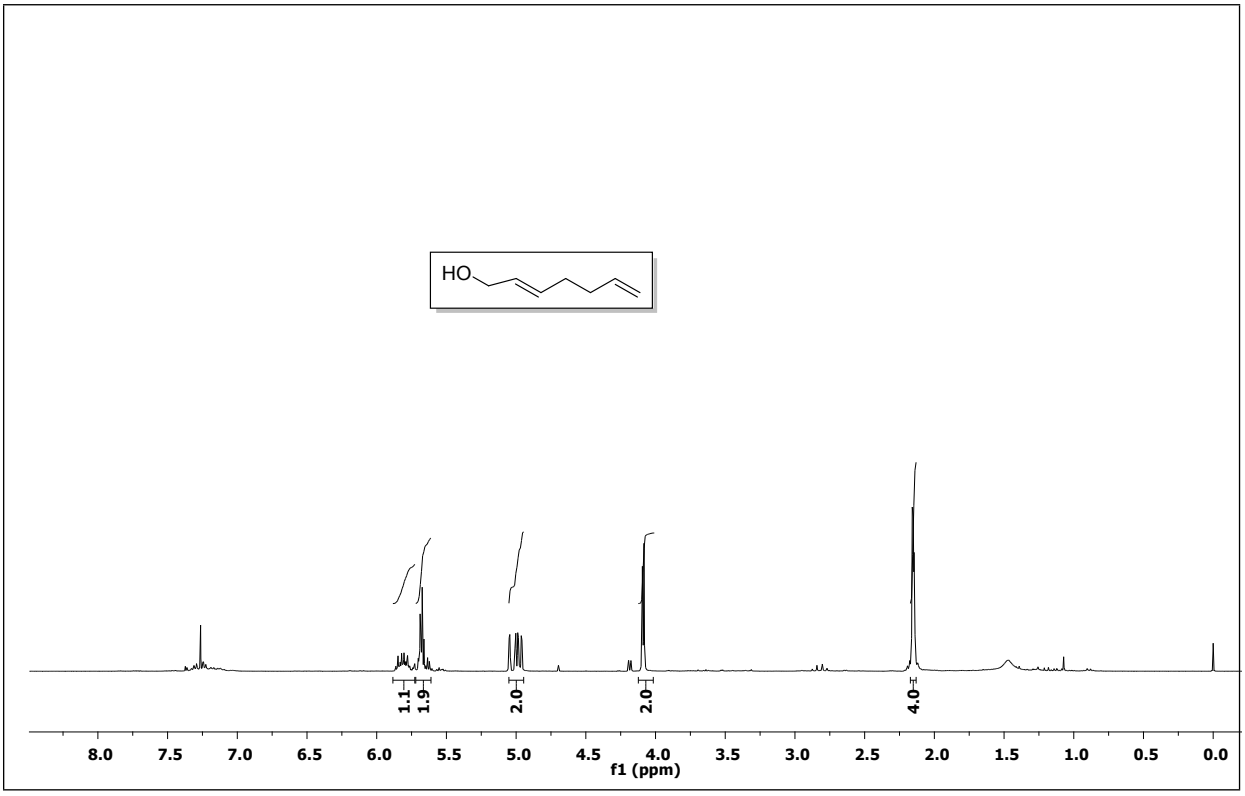


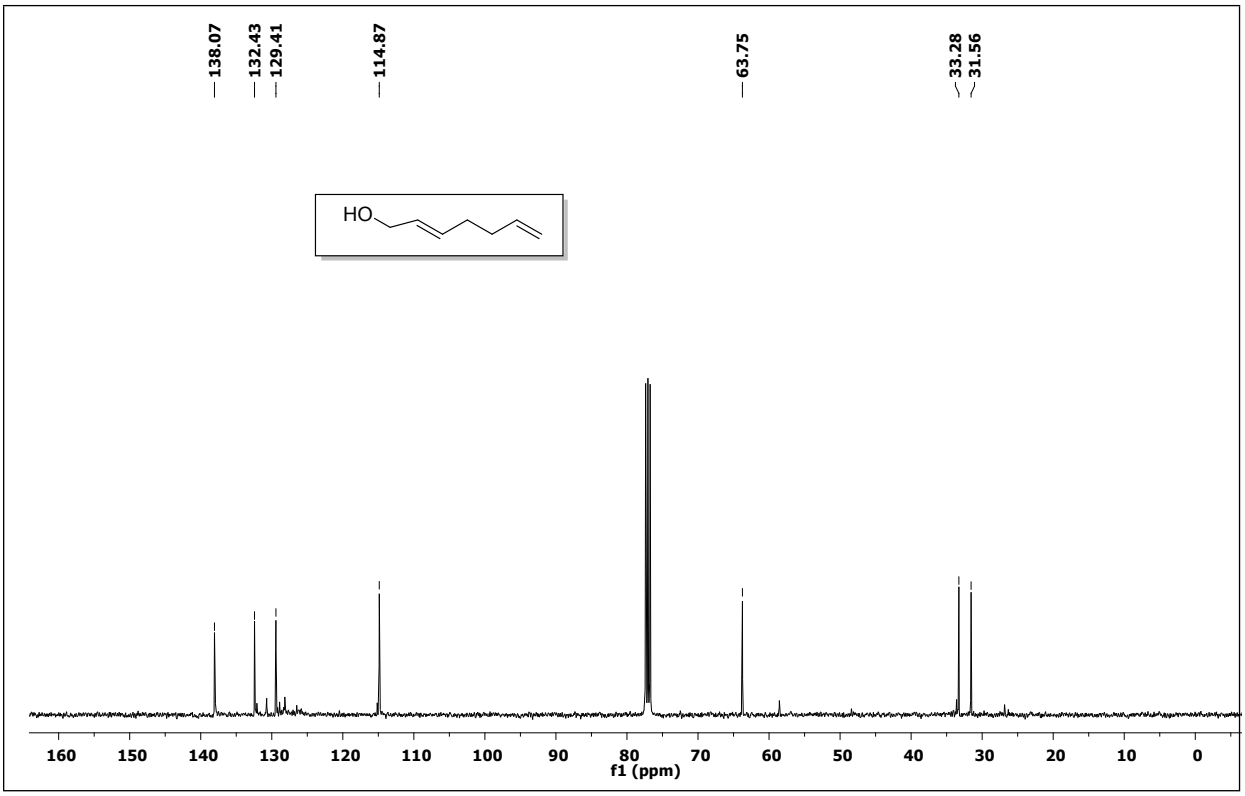

98.80
67.54
62.39
32.26
30.74
29.44
25.48
22.49
21.99
19.67
HO
OTHP
f1 (ppm)

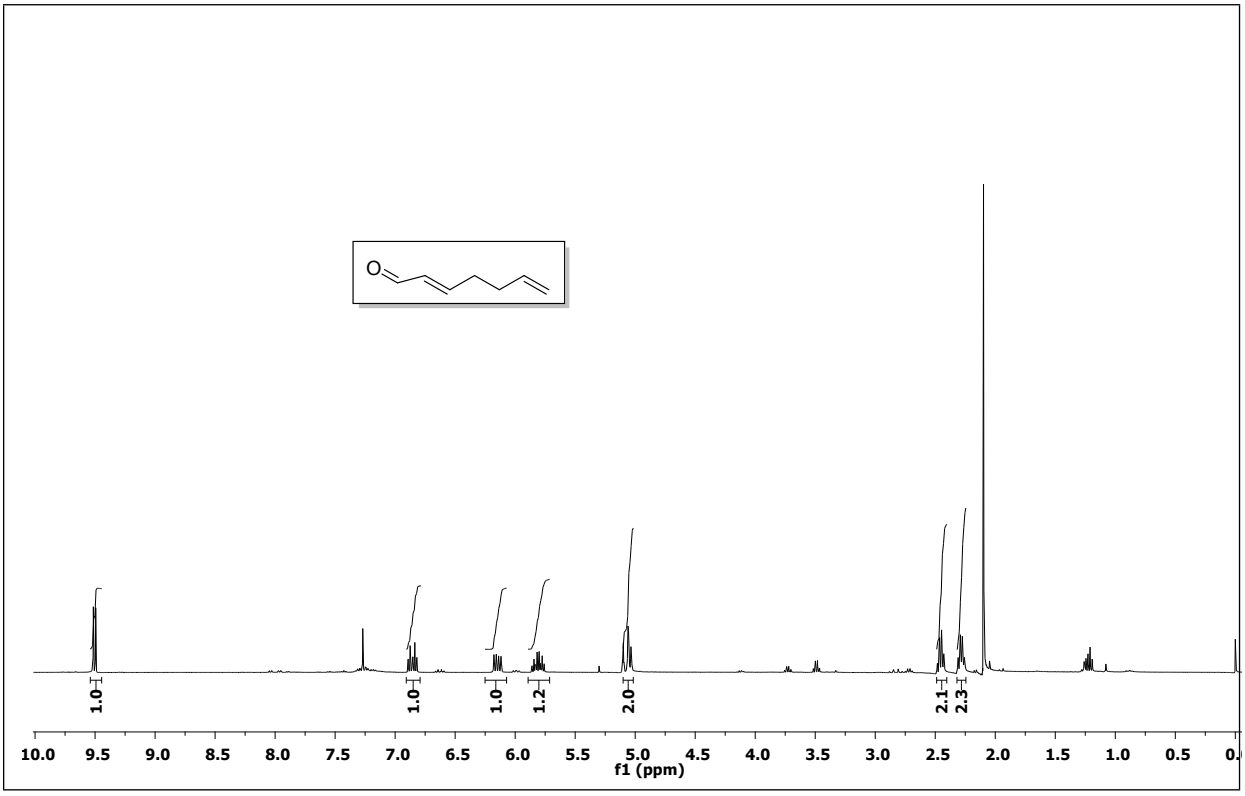

EtOOC
OTHP
1.0
1.0
1.1
2.3
1.2
1.2
1.2
2.3
1.3
10.0
3.4
f1 (ppm)

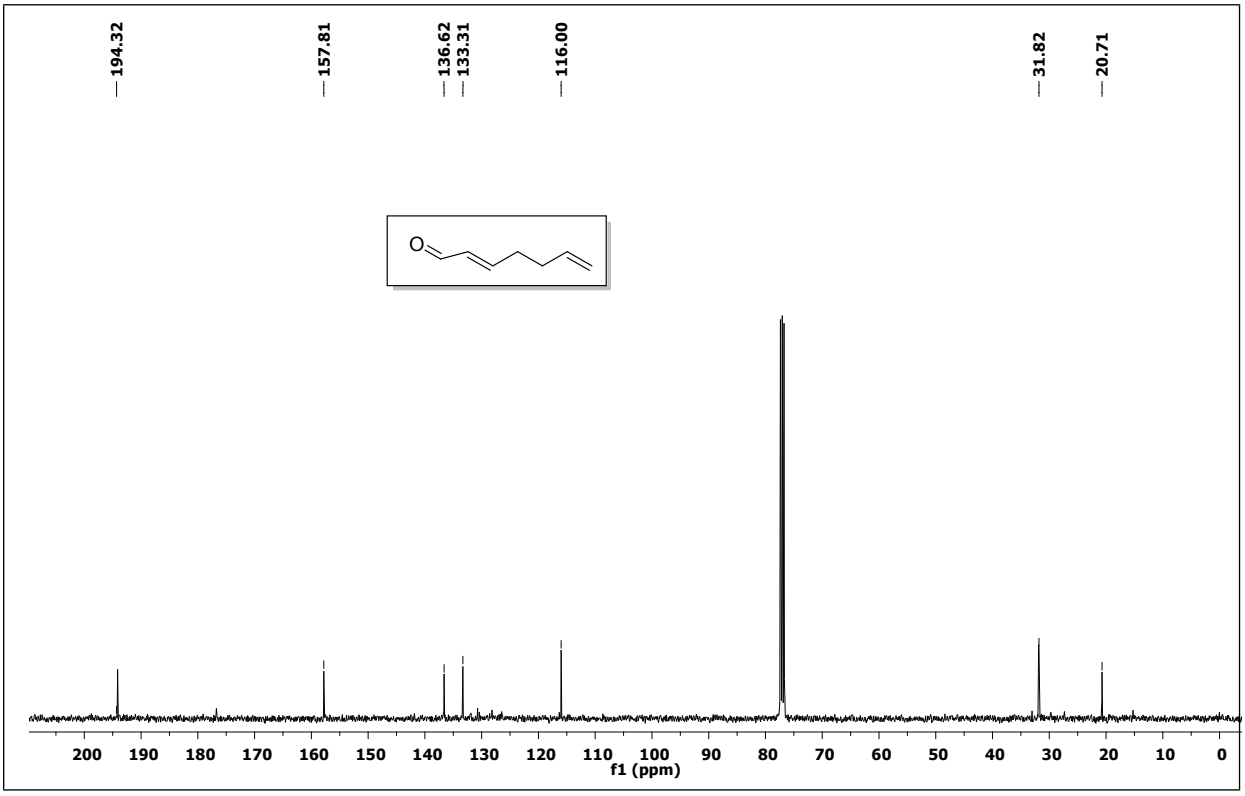

166.69
148.97
121.50
98.85
67.11
62.31
60.13
31.96
30.73
29.22
25.48
24.81
19.63
14.27
EtOOC
OTHP
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

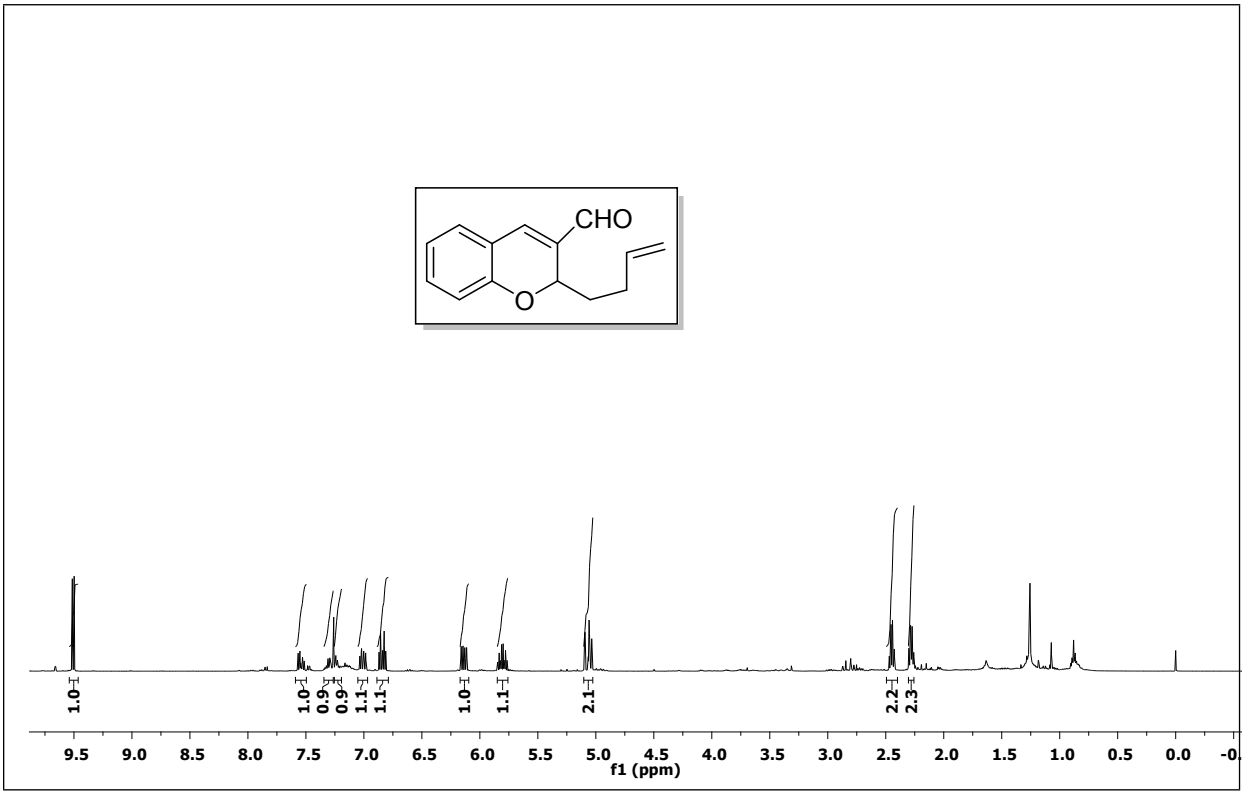

BnO
OTHP
3.8
1.0
2.0
1.0
2.1
1.9
1.1
1.1
1.1
1.1
2.1
1.1
1.3
8.8
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


HO
1.1
1.9
2.0
2.0
4.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


138.07
132.43
129.41
114.87
63.75
33.28
31.56
HO
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
1.0
1.0
1.0
1.2
2.0
2.1
2.3
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


194.32
157.81
136.62
133.31
116.00
31.82
20.71
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


CHO
O
1.0
1.0
0.9
0.9
1.1
1.1
1.0
1.1
2.1
2.2
2.3
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)