Supporting Information for

Domino Prins/Pinacol reaction for the stereoselective synthesis of spiro[pyran-4,4'-quinoline]-2',3'-dione derivatives

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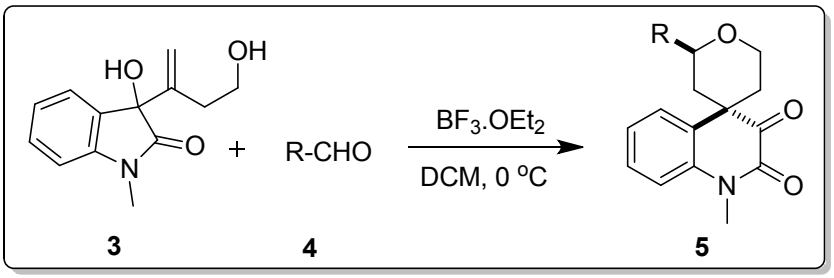

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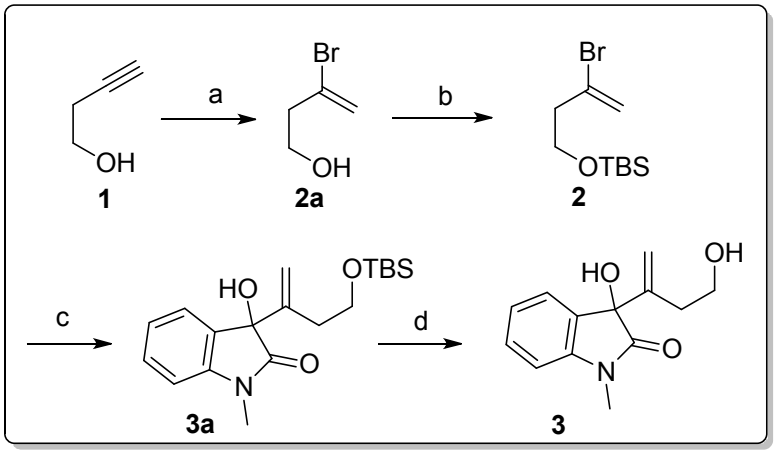
Experimental

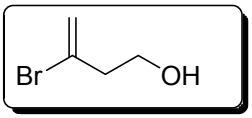
1. General. All solvents were dried according to standard literature procedures. Reactions were performed in oven-dried round bottom flasks, and the flasks were fitted with rubber septa and the reactions were conducted under a nitrogen atmosphere. Glass syringes were used to transfer solvents. Crude 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 vapors and/or by exposure to methanolic acidic solution of *p*-anisaldehyde followed by heating (<1 min) on a hot plate (~250°C). Organic solutions were concentrated on rotary evaporator at 35–40 °C.
^{1}H and ^{13}C NMR (proton-decoupled) spectra were recorded in $CDCl_3$ solvent on 200, 300, 400 or 500 MHz NMR spectrometer. Chemical shifts (δ) were reported in parts per million (ppm) with respect to TMS as an internal standard. Coupling constants (*J*) are quoted in hertz (Hz). Mass spectra were recorded on mass spectrometer by Electrospray ionization (ESI) or Atmospheric pressure chemical ionization (APCI) technique.

Scheme 1. Synthetic procedure for **3**



Reagents & conditions: (a) PBr_3, H_2O, TEAB, DCM, -40 ^{o}C (b) TBSCl, imidazole, DCM, 0 ^{o}C to rt (c) *n*-BuLi, THF, *N*-methylisatin, -78^{o}C (d) TBAF,THF.

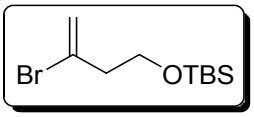
General Procedure for 3-bromobut-3-en-1-ol (2a)



HBr gas was produced by adding PBr_3 (1.46 mL, 11 mmol) dropwise to water (0.59 mL, 33 mmol). Thus produced HBr gas was bubbled through tetraethylammonium bromide (6.3 g) in 40 mL of dichloromethane at 0 °C, after which the weight of dichloromethane solution of TEAB.HBr was found to be 2.25g. To this solution, 3-butyn-1-ol (1.89 mL, 12 mmol) was added and the resulting mixture was heated at 40 °C for 5 h. After completion, the mixture

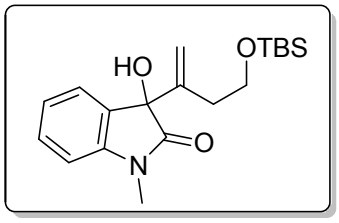
was cooled to 0 °C and diluted with water and then extracted with ether, dried over Na_2SO_4 and the solvent was removed in *vacuo*. The crude product was used as such for further step.

General Procedure for (3-bromobut-3-enyloxy)(*tert*-butyl)dimethylsilane (2)



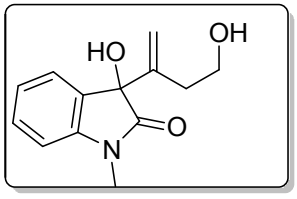
3-Bromobut-3-en-1-ol **2a** (5.0 g, 33.3 mmol) was taken in to dry DCM and imidazole (2.49 g, 36.6 mmol) was added at 0 °C. After few min, *tert*-butyldimethylsilyl chloride (5.0g, 33.3 mmol) was added and the mixture was stirred at room temperature for 30 min. The reaction was quenched with cold water and extracted with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The crude residue was then purified by flash chromatography on silica gel column with hexane-ethyl acetate to give the compound **2** as a liquid.

General Procedure for 1-(4-(*tert*-butyldimethylsilyloxy)but-1-en-2-yl)cyclobutanol (3a)



A solution of *n*-BuLi (1.9 M solution in pentane, 2.0 equiv.) was slowly added to a solution of **2** (1.040 g, 4.0 equiv) in anhydrous THF at -78 °C over a period of 10 min. The resulting solution was stirred at -78 °C for 0.5 h and then *N*-methylisatin (644 mg, 4.0 equiv.) was added and the resulting mixture was stirred at -78 °C for 0.5 h and then at 25 °C for 1h. Up on completion, the mixture was quenched with sat. solution of NH_4Cl and the aqueous layer was extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was then purified by flash chromatography on silica gel column with hexane-ethyl acetate to give the compound **3a** as a semi solid.

General Procedure for 1-(4-hydroxybut-1-en-2-yl)cyclobutanol (3)



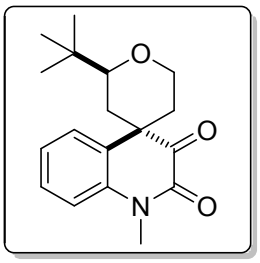
To a solution of **3a** (1.0 g, 4.3 mmol) in THF (15 mL) at 0 °C was added TBAF (1.0 N in THF, 4.3 mL,4.3 mmol). After stirring for 10 min, the reaction mixture was quenched with sat. NH_4Cl solution and extracted thrice with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, and then filtered and evaporated in vacuo. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc) to afford the required alcohol **3** (90%) as a solid.

Solid, m.p. 150-152 °C. Purified by column chromatography ethyl acetate/hexane (50:50) ^{1}H NMR (300 MHz, $CDCl_3$+DMSO) δ 7.38 – 7.28 (m, 2H), 7.15 – 7.04 (m, 1H), 6.83 (d, *J* = 7.5 Hz, 1H), 5.23 (s, 1H), 5.11 (s, 1H), 3.70 (t, *J* = 6.2 Hz, 2H), 3.20 (s, 3H), 2.59 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$+DMSO): δ 176.5, 144.3, 142.9, 130.5, 128.6, 123.5, 12.10, 112.4, 107.3, 60.5, 33.1, 25.4 ppm; MS (ESI): *m/z* 256 $(M+Na)^+$; HRMS (ESI) calcd for $C_{13}H_{15}O_3NNa$: 256.09441 $(M+Na)^+$,Found 256.09465

Procedure for large scale synthesis: To a stirred solution of **3** (4.29 mmol) and benzaldehyde (5.15 mmol) in dry dichloromethane (30 mL) was added 10 mol% $BF_3.OEt_2$ at 0 °C. The resulting mixture was stirred at the same temperature under nitrogen atmosphere for 35 min. After completion, as indicated by TLC, the reaction mixture was quenched with sat. $NaHCO_3$ (1.0 mL) and extracted with dichloromethane (10x5 mL). The combined organic layers were washed with brine (20 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The resulting crude product was purified by silica gel column chromatography (60–120 mesh) using ethyl acetate/hexane (1:9) as eluent to afford the product **5h** in 80% yield.

2. Characterization data of products 5(a-p) & 3:

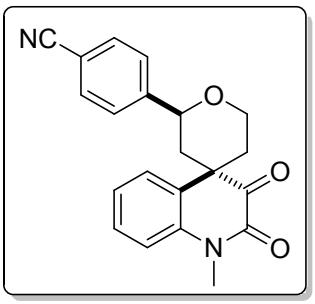
2-(*tert*-Butyl)-1'-methyl-2,3,5,6-tetrahydro-1'*H*-spiro[pyran-4,4'-quinoline]-2',3'-dione (5a):



Solid, m.p. 147-149 °C. Purified by column chromatography (10% ethyl acetate/hexane);^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43-7.32 (m, 2H), 7.20 (t, *J* = 7.7 Hz, 1H), 7.10 (d *J* = 8.1

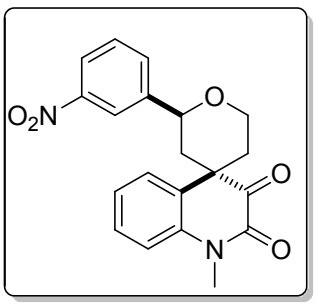
Hz,1H), 4.09 – 3.97 (m, 1H), 3.77 (td, *J* = 11.8, 3.1 Hz, 1H), 3.48 (s, 3H), 3.14 (d, *J* = 11.6 Hz, 1H), 2.33 – 2.05 (m, 3H), 1.80 – 1.67 (m, 1H), 0.89 (s, 9H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.2, 158.6, 137.3, 129.6, 128.9, 125.0, 124.9, 116.1, 81.3, 64.9, 50.8, 34.0, 32.2, 30.4, 29.8, 25.7 ppm; MS (ESI): *m/z* 302 $(M+H)^+$; HRMS (ESI) calcd for $C_{18}H_{24}O_3N$: 302.17522 $(M+H)^+$, Found 302.17507

4-(1'-Methyl-2',3'-dioxo-2,2',3,3',5,6-hexahydro-1'*H*-spiro[pyran-4,4'-quinolin]-2-yl)benzonitrile (5b):



Solid, m.p. 180-182 °C. Purified by column chromatography (13% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.62 (m, 2H), 7.56 – 7.48 (m, 2H), 7.39 (td, *J* = 8.1, 1.4 Hz, 1H), 7.31 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.18 (td, *J* = 7.7, 1.1 Hz, 1H), 7.12 (dd, *J* = 8.2, 0.9 Hz, 1H), 4.82 (dd, *J* = 11.5, 1.9 Hz, 1H), 4.16 (ddd, *J* = 12.3, 4.8, 1.4 Hz, 1H), 3.86 (td, *J* = 12.5, 2.1 Hz, 1H), 3.51 (s, 3H), 2.47 – 2.30 (m, 2H), 2.18 (ddd, *J* = 14.1, 12.8, 4.9 Hz, 1H), 2.07-1.95 (m, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.5, 158.0, 147.2, 137.1, 132.3, 129.2, 128.3, 126.3, 125.1, 124.8, 118.7, 116.2, 111.4, 75.0, 64.8, 50.6, 38.2, 31.5, 29.9 ppm; MS (ESI): *m/z* 347 $(M+H)^+$; HRMS (ESI) calcd for $C_{21}H_{19}O_3N_2$ = 347.13902 $(M+H)^+$, Found 347.13938

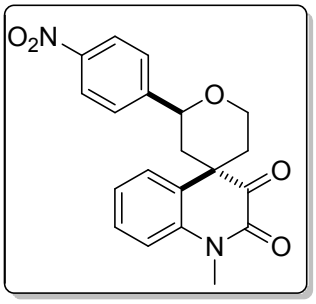
1'-Methyl-2-(3-nitrophenyl)-2,3,5,6-tetrahydro-1'*H*-spiro[pyran-4,4'-quinoline]-2',3'-dione (5c):



Solid, m.p. 220-222 °C. Purified by column chromatography (14% ethyl acetate/hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.15 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.71 (d, *J* = 7.7 Hz, 1H), 7.53 (t, *J* = 7.9 Hz, 1H), 7.40 (dt, *J* = 8.2, 6.1 Hz, 1H), 7.33 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.24 – 7.16 (m, 1H), 7.12 (d, *J* = 8.1 Hz, 1H), 4.89 (dd, *J* = 11.5, 1.7 Hz, 1H), 4.25 – 4.12 (m, 1H), 3.88 (td, *J* = 12.5, 2.0 Hz, 1H), 3.51(s, 3H), 2.47 (dt, *J* = 13.6, 2.1 Hz, 1H), 2.36

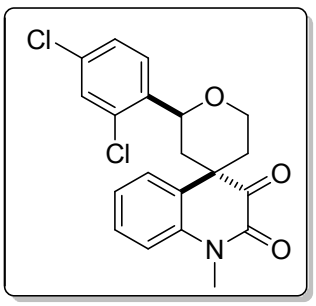
(dd, *J* = 14.2, 1.9 Hz, 1H), 2.27 – 2.15 (m, 1H), 2.07 (dd, *J* = 13.6, 11.6 Hz, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ (101 MHz, $CDCl_3$) δ 196.5, 158.0, 148.4, 144.1, 137.1, 132.0, 129.3, 129.2, 128.3, 125.1, 124.8, 122.6, 120.6, 116.2, 74.6, 64.8, 50.6, 38.10, 31.6, 29.9 ppm; MS (ESI): *m/z* 367 $(M+H)^+$; HRMS (ESI) calcd for $C_{20}H_{19}O_5N_2$ = 367.12885 $(M+H)^+$, Found 367.12942.

1'-Methyl-2-(4-nitrophenyl)-2,3,5,6-tetrahydro-1'*H*-spiro[pyran-4,4'-quinoline]-2',3'-dione (5d):



Solid, m.p. 223-225 °C. Purified by column chromatography (14% ethyl acetate/hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 8.8, 2.0 Hz, 2H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 7.7 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 8.1 Hz, 1H), 4.89 (d, *J* = 11.4 Hz, 1H), 4.16 (dt, *J* = 18.5, 9.2 Hz, 1H), 3.86 (t, *J* = 12.5 Hz, 1H), 3.52 (s, 3H), 2.44 (d, *J* = 13.7 Hz, 1H), 2.36 (d, *J* = 14.0 Hz, 1H), 2.19 (td, *J* = 13.4, 4.9 Hz, 1H), 2.07 – 1.98 (m, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.8, 158.1, 149.2, 147.4, 137.2, 129.3, 128.3, 126.4, 125.1, 124.8, 123.7, 116.3, 74.9, 64.8, 50.7, 38.2, 31.7, 30.0 ppm; MS (ESI) *m/z* 367 $(M+H)^+$; HRMS (ESI) calcd for $C_{20}H_{19}O_5N_2$:367.12885 $(M+H)^+$, Found 367.12942

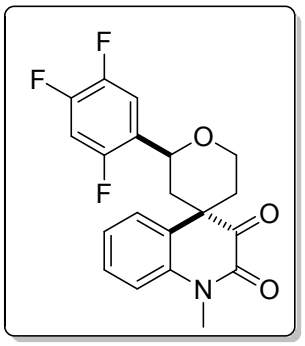
2-(2,4-Dichlorophenyl)-1'-methyl-2,3,5,6-tetrahydro-1'*H*-spiro[pyran-4,4'-quinoline]-2',3'-dione (5e):



Solid, m.p. 165-167 °C. Purified by column chromatography (10% ethyl acetate/hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.4 Hz, 1H), 7.41 – 7.29 (m, 3H), 7.28 – 7.23 (m, 1H), 7.20 – 7.14 (m, 1H), 7.09 (d, *J* = 7.5 Hz, 1H), 4.98 (dd, *J* = 11.3, 1.6 Hz, 1H), 4.30 – 4.12 (m, 1H), 3.99 (td, *J* = 12.1, 2.6 Hz, 1H), 3.49 (s, 3H), 2.67 (dt, *J* = 13.8, 2.0 Hz, 1H),

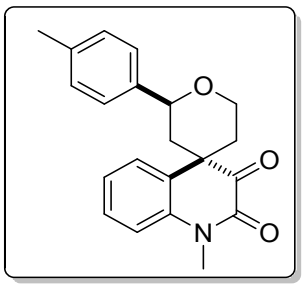
2.41 – 2.16 (m, 2H), 1.76 (dd, *J* = 13.9, 11.4 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.2, 157.9, 138.2, 137.2, 133.6, 132.1, 129.1, 129.0, 128.5, 127.6, 127.3, 124.9, 124.7, 116.1,72.5, 65.0, 50.7, 37.6, 3.48, 29.9 ppm MS (ESI): *m/z* 390.4 $(M+H)^+$; HRMS (ESI) calcd for $C_{20}H_{18}O_3NCl_2$: 390.06583 $(M+H)^+$, Found 390.06673

1'-Methyl-2-(2,4,5-trifluorophenyl)-2,3,5,6-tetrahydro-1'*H*-spiro[pyran-4,4'-quinoline]-2',3'-dione (5f):



Semi solid; Purified by column chromatography (12% ethyl acetate/hexane);^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 – 7.28 (m,3H), 7.24 – 7.06 (m, 2H), 6.90 (dd, *J* = 16.1, 9.6 Hz, 1H), 4.97 (d, *J* = 11.2 Hz, 1H), 4.15 (dd, *J* = 12.2, 3.4 Hz, 1H), 3.90 (dd, *J* = 12.2, 10.2 Hz, 1H), 3.50 (s, 3H), 2.50 (d, *J* = 13.8 Hz, 1H), 2.23 (ddd, *J* = 20.4, 18.6, 8.6 Hz, 2H), 2.06 – 1.85 (m, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.2, 157.9, 137.2, 129.2, 128.4, 125.6, 125.0, 124.2, 116.1, 115.0(dd), 105.4(q), 69.4, 64.9, 50.6, 37.3, 31.2, 29.9 ppm; MS (ESI): *m/z* 376 $(M+H)^+$; HRMS (ESI) calcd for $C_{20}H_{17}O_3NF_3$:376.11550 $(M+H)^+$, Found 376.11653

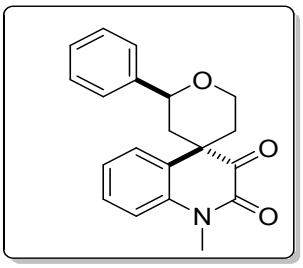
1'-Methyl-2-(p-tolyl)-2,3,5,6-tetrahydro-1'*H*-spiro[pyran-4,4'-quinoline]-2',3'-dione (5g):



Solid, m.p. 145-147°C. Purified by column chromatography (10% ethyl acetate/hexane);^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 –7.32 (m, 2H), 7.29 – 7.24 (m, 2H), 7.21 – 7.12 (m, 3H), 7.09 (d, *J* = 8.1 Hz, 1H), 4.65 (dd, *J* = 11.5, 1.7 Hz, 1H), 4.14 (ddd, *J* = 12.1, 4.7, 1.5 Hz, 1H), 3.91 (td, *J* = 12.2, 2.4 Hz, 1H), 3.48 (s, 3H), 2.41 (dt, *J* = 13.7, 2.1 Hz, 1H), 2.36 – 2.27 (m, 4H), 2.27 – 2.18 (m, 1H), 2.11 – 2.03 (m, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.7, 158.2, 138.7, 137.5, 137.1, 129.0, 129.0, 128.9, 125.7, 125.0, 124.8, 116.0,75.8, 64.9, 50.9,

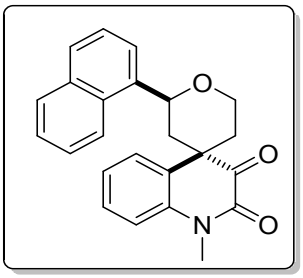
38.9, 30.9, 29.8, 21.1 ppm; MS (ESI): *m/z* 336 $(M+H)^+$; HRMS (ESI) calcd for $C_{21}H_{22}O_3N$:336.15942 $(M+H)^+$, Found 336.15967

1'-Methyl-2-phenyl-2,3,5,6-tetrahydro-1'*H*-spiro[pyran-4,4'-quinoline]-2',3'-dione (5h):



Solid. m.p. 135-137 °C. Purified by column chromatography (10% ethyl acetate/hexane);^{1}H 145-147NMR (500 MHz, $CDCl_3$) δ 7.36 (dt, *J* = 11.4, 7.7 Hz, 6H), 7.29 (d, *J* = 7.1 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 4.70 (dd, *J* = 11.5, 1.6 Hz, 1H), 4.16 (dd, *J* = 12.2, 3.4 Hz, 1H), 3.92 (td, *J* = 12.3, 2.3 Hz, 1H), 3.49 (s, 3H), 2.44 (dd, *J* = 11.7, 2.2 Hz, 1H), 2.32 (dd, *J* = 13.9, 1.9 Hz, 1H), 2.30 – 2.18 (m, 1H), 2.07 (dd, *J* = 13.8, 11.7 Hz, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.7, 158.2, 141.7, 137.1, 129.0, 128.8, 128.4, 127.8, 125.7, 125.0, 124.8, 116.1,75.9, 64.9, 50.8, 38.8, 31.0, 29.8 ppm; MS (ESI): *m/z* 322 $(M+H)^+$; HRMS (ESI) calcd for $C_{20}H_{20}O_3N$ = 322.14377 $(M+H)^+$, Found 322.14393

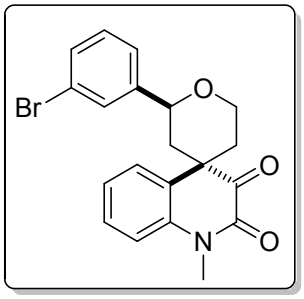
1'-Methyl-2-(naphthalen-1-yl)-2,3,5,6-tetrahydro-1'*H*-spiro[pyran-4,4'-quinoline]-2',3'-dione (5i):



Semi solid; Purified by column chromatography (12% ethyl acetate/hexane);^{1}H NMR (500 MHz, CDCl3) δ 8.28 (d, J = 8.5 Hz, 1H), 7.86 (d, J = 8.1 Hz, 1H), 7.79 (d, J = 8.2 Hz, 1H), 7.70 (d, J = 7.1 Hz, 1H), 7.60 – 7.54 (m, 1H), 7.52 – 7.45 (m, 2H), 7.38 – 7.32 (m, 1H), 7.29 (dd, J = 7.9, 1.3 Hz, 1H), 7.18 – 7.06 (m, 2H), 5.57 (d, J = 10.3 Hz, 1H), 4.30 – 4.21 (m, 1H), 3.99 (td, J = 12.6, 2.0 Hz, 1H), 3.50 (s, 3H), 2.70 (d, J = 13.9 Hz, 1H), 2.47 – 2.40 (m, 1H), 2.25 (td, J = 13.5, 4.8 Hz, 1H), 2.17 (dd, J = 13.8, 11.4 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.3, 158.4, 138.1, 137.2, 135.5, 133.5, 129.9, 129.0, 128.8, 128.7, 127.9, 126.3, 125.6, 125.4, 125.0, 124.8, 123.1, 122.2, 116.1, 73.0, 65.3, 51.2, 37.8, 32.41, 29.9 ppm. MS

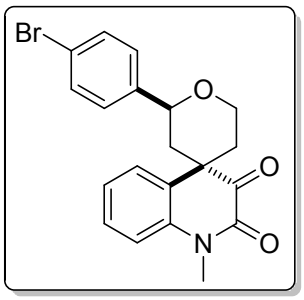
(ESI): *m/z* 372 $(M+H)^+$; HRMS (ESI) calcd for $C_{24}H_{22}O_3N$: 372.15942 $(M+H)^+$, Found 372.16003

2-(3-Bromophenyl)-1'-methyl-2,3,5,6-tetrahydro-1'*H*-spiro[pyran-4,4'-quinoline]-2',3'-dione (3j):



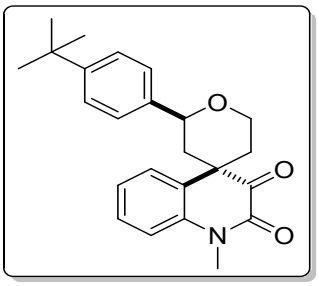
Solid, m.p.159-160 °C. Purified by column chromatography (10% ethyl acetate/hexane);^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.44 – 7.27 (m, 4H), 7.24 – 7.15 (m, 2H), 7.10 (d, *J* = 8.1 Hz, 1H), 4.69 (dd, *J* = 20.6, 10.6 Hz, 1H), 4.14 (dd, *J* = 12.2, 3.6 Hz, 1H), 3.87 (td, *J* = 12.4, 1.9 Hz, 1H), 3.49 (s, 3H), 2.41 (d, *J* = 13.8 Hz, 1H), 2.37 – 2.27 (m, 1H), 2.26 – 2.14 (m, 1H), 2.03 (dd, *J* = 13.7, 11.7 Hz, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.6, 158.1, 144.2, 137.2, 130.8, 130.0, 129.2, 128.8, 128.6, 125.1, 124.9, 124.5, 122.6, 116.2,75.1, 64.9,50.8, 38.6, 31.3, 29.9 ppm; MS (ESI): *m/z* 302 $(M+H)^+$; HRMS (ESI) calcd for $C_{20}H_{19}O_3NBr$: 400.05428 $(M+H)^+$, Found 400.05490

2-(4-Bromophenyl)-1'-methyl-2,3,5,6-tetrahydro-1'*H*-spiro[pyran-4,4'-quinoline]-2',3'-dione (3k):



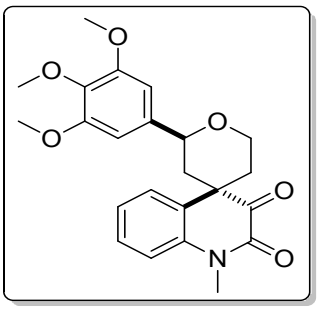
Solid, m.p. 160-162 °C. Purified by column chromatography (10% ethyl acetate/hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 (dd, *J* = 6.7, 1.8 Hz, 2H), 7.41 – 7.31 (m, 2H), 7.29 – 7.23 (m, 2H), 7.21 – 7.14 (m, 1H), 7.10 (d, *J* = 8.1 Hz, 1H), 4.68 (d, *J* = 11.5 Hz, 1H), 4.23 – 4.05 (m, 1H), 3.88 (m, 1H), 3.49 (s, 3H), 2.39 (dd, *J* = 13.8, 2.0 Hz, 1H), 2.31 (dd, *J* = 14.0, 1.8 Hz, 1H), 2.19 (m, 1H), 2.01 (dd, *J* = 13.7, 11.7 Hz, 1H) ppm;^{13}C NMR (126 MHz, $CDCl_3$): δ 196.6, 158.1, 144.2, 137.2, 130.8, 130.0, 129.2, 128.8, 128.6, 125.1, 124.9, 124.5, 122.6, 116.2, 75.1, 64.9, 50.8, 38.6, 31.3, 29.9 ppm; MS (ESI): *m/z* 302 $(M+H)^+$; HRMS (ESI) calcd for $C_{20}H_{19}O_3NBr$ = 400.05428 $(M+H)^+$, Found 400.05472

2-(4-(*tert*-Butyl)phenyl)-1'-methyl-2,3,5,6-tetrahydro-1'*H*-spiro[pyran-4,4'-quinoline]-2',3'-dione (5l):



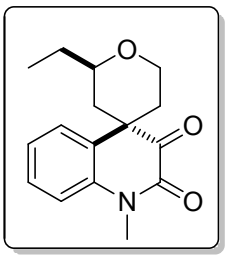
Solid, m.p.150-152°C. Purified by column chromatography (12% ethyl acetate/hexane); ^{1}H NMR (500 MHz, CDCl3): δ 7.40 – 7.33 (m, 4H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.17 (m, 1H), 7.11 – 7.07 (m, 1H), 4.65 (dd, *J* = 11.6, 1.7 Hz, 1H), 4.20 – 4.11 (m, 1H), 3.93 (m, 1H), 3.48 (s, 3H), 2.44 (m, 1H), 2.34 – 2.20 (m, 2H), 2.08 (dt, *J* = 18.5, 9.2 Hz, 1H), 1.30 (s, 9H) ppm; 13C NMR (125 MHz, CDCl3): δ 196.7, 158.2, 138.6, 137.2, 129.0, 125.5, 125.3, 125.0, 124.8, 116.0, 75.1, 64.9, 5.9, 38.8, 34.5, 31.3, 30.8, 29.8 ppm; MS (ESI): *m/z* 302 $(M+H)^+$; HRMS (ESI) calcd for $C_{24}H_{28}O_3N$: 378.20637 $(M+H)^+$, Found 378.20717.

1'-Methyl-2-(3,4,5-trimethoxyphenyl)-2,3,5,6-tetrahydro-1'*H*-spiro[pyran-4,4'-quinoline]-2',3'-dione (5m):



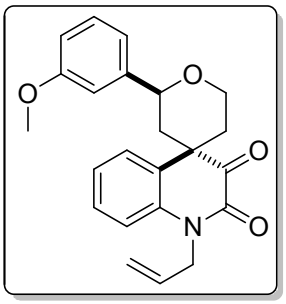
Semi-solid; Purified by column chromatography (15% ethyl acetate/hexane);^{1}H NMR (500 MHz, CDCl3): δ 1H NMR (500 MHz, CDCl3) δ) δ 7.38 (t, J = 8.3 Hz, 2H), 7.20 (t, J = 7.5 Hz, 1H), 7.11 (d, J = 7.9 Hz, 1H), 6.60 (s, 2H), 4.62 (d, J = 11.1 Hz, 1H), 4.25 – 4.12 (m, 1H), 4.00 – 3.74 (m, 13H), 3.48 (s, 3H), δ 2.43 (d, J = 13.7 Hz, 1H), 2.36 – 2.18 (m, 2H), 2.12 – 2.02 (m, 1H). ppm; 13C NMR (125 MHz, CDCl3): δ 196.7, 158.1, 153.3, 137.4, 137.2, 129.1, 128.7, 125.0, 124.9, 116.1, 102.8, 77.2, 77.0, 76.7, 76.1, 64.9, 60.7, 56.1, 50.9, 38.8, 31.0, 29.9.ppm; MS (ESI): *m/z* 302 $(M+H)^+$; HRMS (ESI) calcd for $C_{23}H_{26}O_6N$:412.17546 $(M+H)^+$, Found 412.17629.

2-Ethyl-1'-methyl-2,3,5,6-tetrahydro-1'*H*-spiro[pyran-4,4'-quinoline]-2',3'-dione (5n):



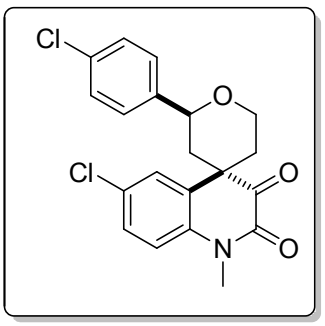
Semi-solid; Purified by column chromatography (10% ethyl acetate/hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.32 (m, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.10 (d, *J* = 8.2 Hz, 1H), 4.00 (dd, *J* = 11.9, 3.4 Hz, 1H), 3.75 (dd, *J* = 12.1, 9.7 Hz, 1H), 3.48 (m, 4H), 2.30 – 2.19 (m, 2H), 2.17 – 2.05 (m, 1H), 1.73 (dd, *J* = 13.9, 11.5 Hz, 1H), 1.55 – 1.44 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.9, 158.2, 137.1, 129.2, 128.9, 125.0, 124.8, 116.0, 75.0, 64.5, 50.5, 36.7, 30.9, 29.8, 29.2, 9.7 ppm; MS (ESI): *m/z* 274 $(M+H)^+$; HRMS (ESI) calcd for $C_{16}H_{19}O_3N$: 274.14377 $(M+H)^+$, Found 274.14395

1'-Allyl-2-(3-methoxyphenyl)-2,3,5,6-tetrahydro-1'*H*-spiro[pyran-4,4'-quinoline]-2',3'-dione(5p)



Semi-solid: Purified by column chromatography (12% ethyl acetate/hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 – 7.22 (m, 3H), 7.14 (m, 2H), 6.96 (m, 2H), 6.83 (m, 1H), 5.91 (m, 1H), 5.37 – 5.20 (m, 2H), 4.82 – 4.58 (m, 3H), 4.16 (dd, *J* = 12.2, 3.0 Hz, 1H), 4.01 – 3.75 (m, 4H), 2.45 (m, 1H), 2.40 – 2.15 (m, 2H), 2.08 (dd, *J* = 13.8, 11.6 Hz, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.8, 159.7, 158.0, 143.4, 136.4, 130.9, 129.5, 128.9, 128.9, 125.0, 124.9, 118.3, 118.0, 116.8, 113.4, 111.1,75.8, 64.9, 55.2, 51.0, 45.5, 38.7, 31.1 ppm. MS (ESI): *m/z* 378 $(M+H)^+$; HRMS (ESI) calcd for $C_{23}H_{24}O_4N$: 378.16998 $(M+H)^+$, Found 378.17092

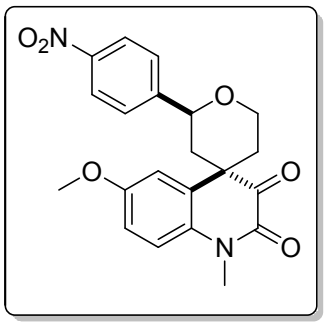
6'-Chloro-2-(3-chlorophenyl)-1'-methyl-2,3,5,6-tetrahydro-1'*H*-spiro[pyran-4,4'-quinoline]-2',3'-dione



Semi-solid; Purified by column chromatography (10% ethyl acetate/hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 6H), 7.03 (d, *J* = 8.7 Hz, 1H), 4.68 (dd, *J* = 11.5, 2.0 Hz, 1H),

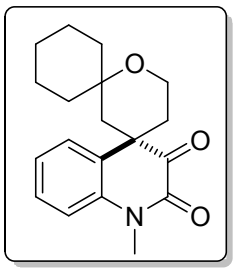
4.14 (m, 1H), 3.45 (s, 3H), 3.86 (td, *J* = 12.4, 2.1 Hz, 1H), 2.38 (dt, *J* = 13.7, 2.2 Hz, 1H), 2.30 (m, 1H), 2.21 – 2.13 (m, 1H), 1.97 (dd, *J* = 13.7, 11.5 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.7, 157.7, 140.1, 135.8, 133.5, 130.6, 130.4, 129.0, 129.0, 128.6, 127.1, 125.7, 125.2, 117.4, 75.3, 64.7, 50.8, 38.5, 31.2, 30.1. MS (ESI): *m/z* 413 $(M+Na)^+$; HRMS (ESI) calcd for $C_{20}H_{17}O_2NCl_2Na$: 413.26961,$(M+Na)^+$, Found 413.26645

6'-Methoxy-1'-methyl-2-(4-nitrophenyl)-2,3,5,6-tetrahydro-1'*H*-spiro[pyran-4,4'-quinoline]-2',3'-dione (5q)



Semi-solid; Purified by column chromatography (15% ethyl acetate/hexane);^{1}H NMR (500 MHz, CDCl3) δ 8.22 (d, J = 8.7 Hz, 2H), 7.57 (d, J = 8.7 Hz, 2H), 7.04 (d, J = 8.8 Hz, 1H), 6.91 – 6.82 (m, 2H), 4.87 (dd, J = 11.5, 1.8 Hz, 1H), 4.20 – 4.12 (m, 1H), 3.92 – 3.82 (m, 1H), 3.80 (s, 3H), 3.48 (s, 3H), 2.42 (dt, J = 13.6, 2.2 Hz, 1H), 2.33 (dd, J = 14.2, 2.0 Hz, 1H), 2.20 – 2.12 (m, 1H), 1.97 (dd, J = 13.7, 11.6 Hz, 1H); ^{13}C NMR (126 MHz, CDCl3) δ 196.7, 157.6, 156.9, 149.1, 147.3, 130.5, 129.8, 126.4, 123.7, 117.3, 112.8, 111.9, 74.8, 64.8, 55.6, 50.6, 38.2, 31.6, 30.1. MS (ESI): *m/z* 336 $((M+Na))^+$; HRMS (ESI) calcd for $C_{20}H_{17}O_2NCl_2Na$: 413.26961,$(M+Na)^+$, Found 413.26645

Dispiro compound (5r)

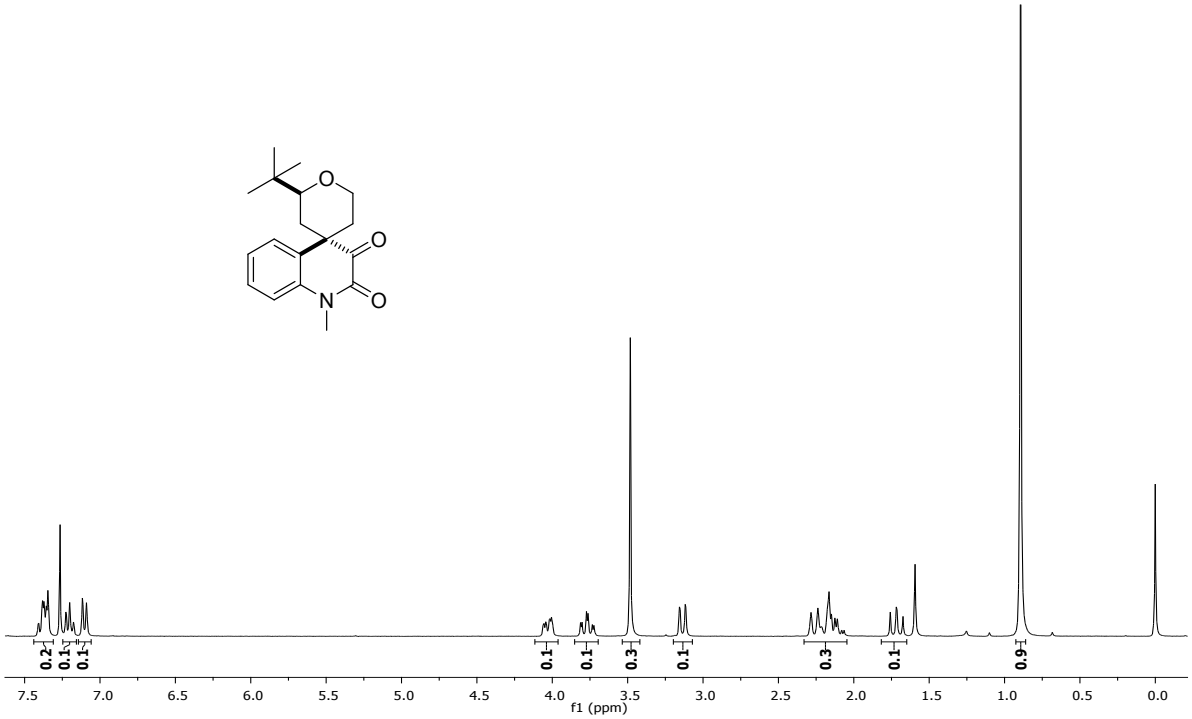


Semi-solid; Purified by column chromatography (12% ethyl acetate/hexane);^{1}H NMR (500 MHz, CDCl3) δ 7.40 – 7.28 (m, 2H), 7.17 (td, J = 7.7, 1.0 Hz, 1H), 7.07 (dd, J = 8.1, 0.8 Hz, 1H), 4.06 – 3.98 (m, 1H), 3.93-3.85 (m, 1H), 3.48 (s, 3H), 2.36 (dd, J = 14.5, 2.0 Hz, 1H), 2.31 – 2.19 (m, 2H), 1.92 (m, 1H), 1.62 – 1.57 (m, 2H), 1.55 – 1.49 (m, 1H), 1.48 – 1.35 (m, 4H), 1.31-1.24 (m, 1H), 1.23 – 1.08 (m, 2H). ^{13}C NMR (101 MHz, CDCl3) δ 199.3, 159.3,

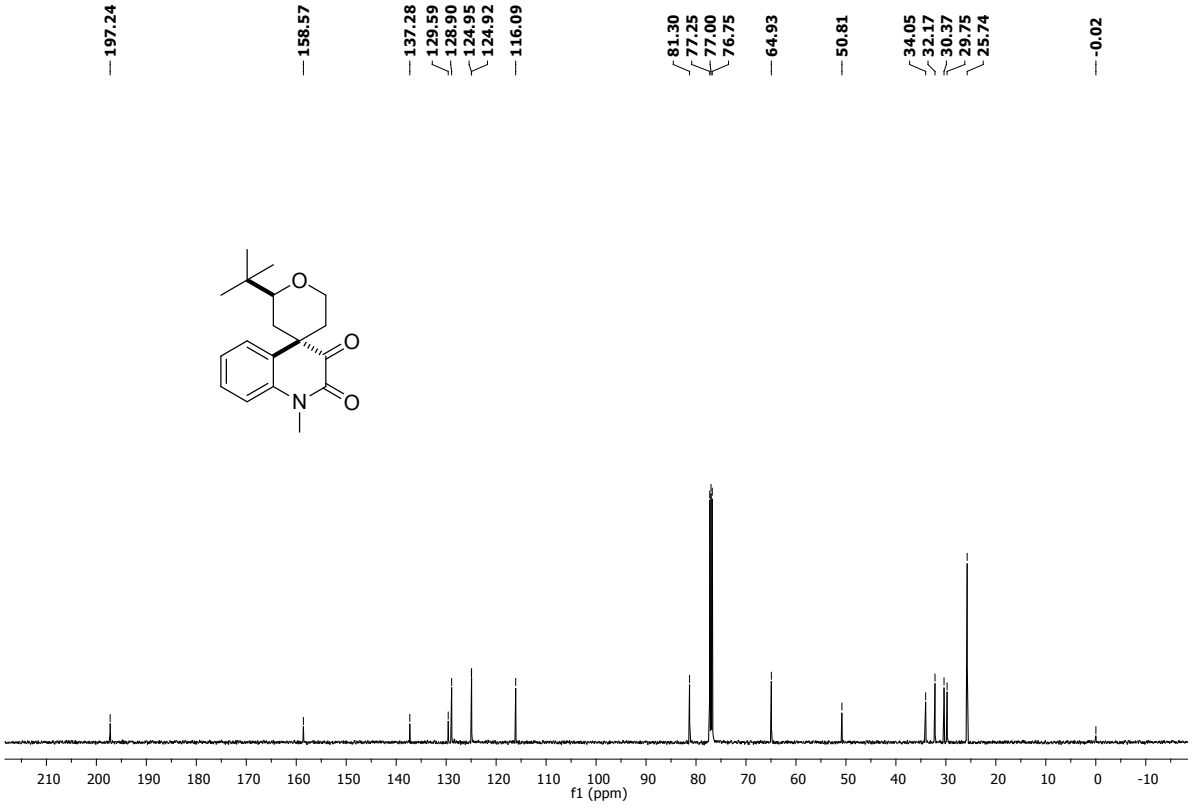
137.3, 129.9, 128.9, 125.0, 124.7, 116.0, 77.3, 77.0, 76.6, 72.5, 57.8, 49.5, 44.9, 40.1, 30.4, 29.6, 26.9, 25.6, 21.5, 21.3. MS (ESI): *m/z* 413 $(M+Na)^+$; HRMS (ESI) calcd for $C_{19}H_{24}O_3N$: 314.17454, $(M+H)^+$, Found: 314.17504

3. Copies of ^1H & ^{13}C NMR spectra of 5(a-p) & 3

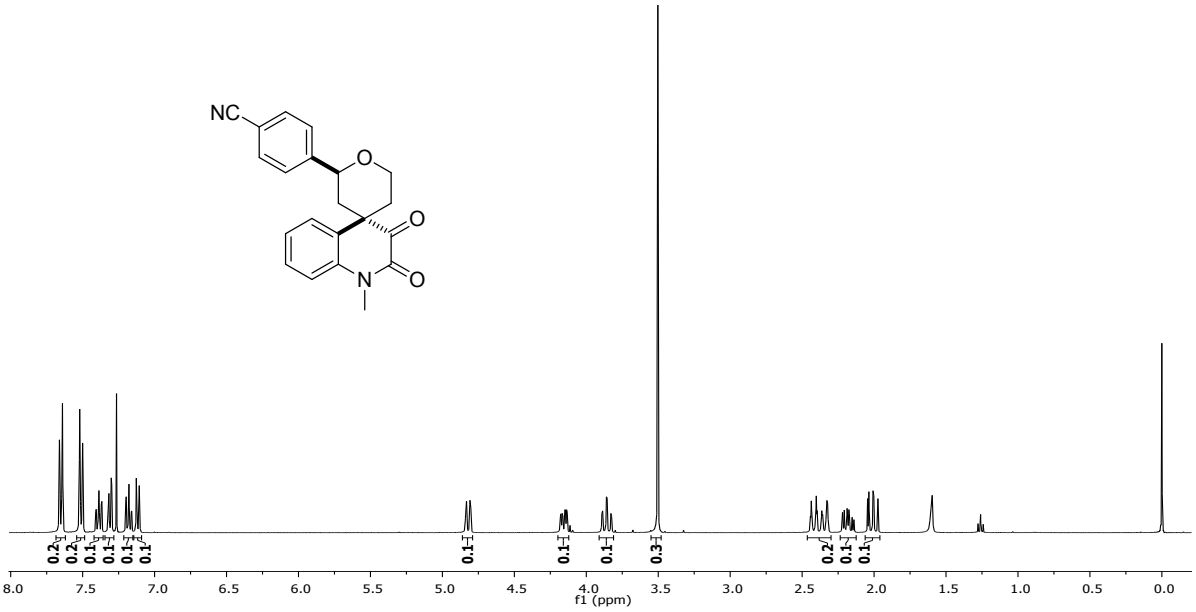
^1H NMR of 2-(*tert*-butyl)-1'-methyl-2,3,5,6-tetrahydro-1'*H*-spiro[pyran-4,4'-quinoline]-2',3'-dione (5a):



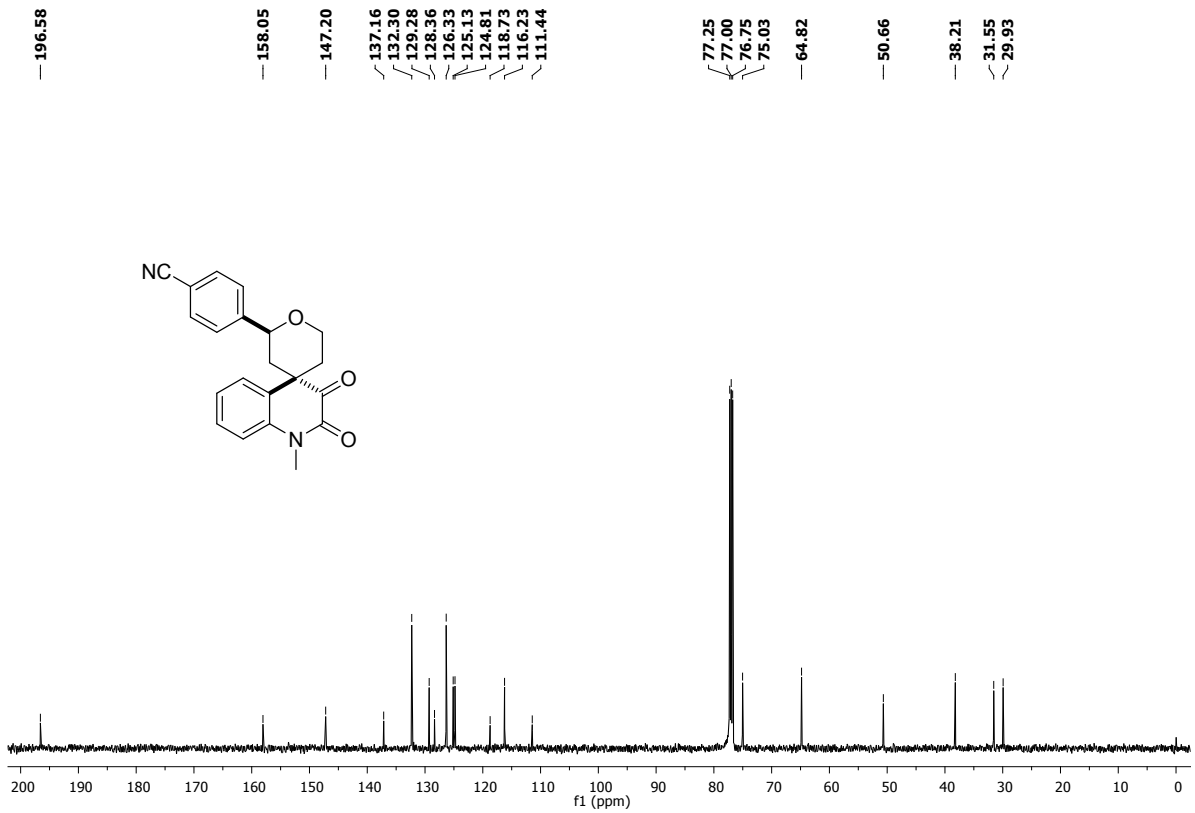
^{13}C NMR of 2-(tert-butyl)-1'-methyl-2,3,5,6-tetrahydro-1'*H*-spiro[pyran-4,4'-quinoline]-2',3'-dione (5a)).



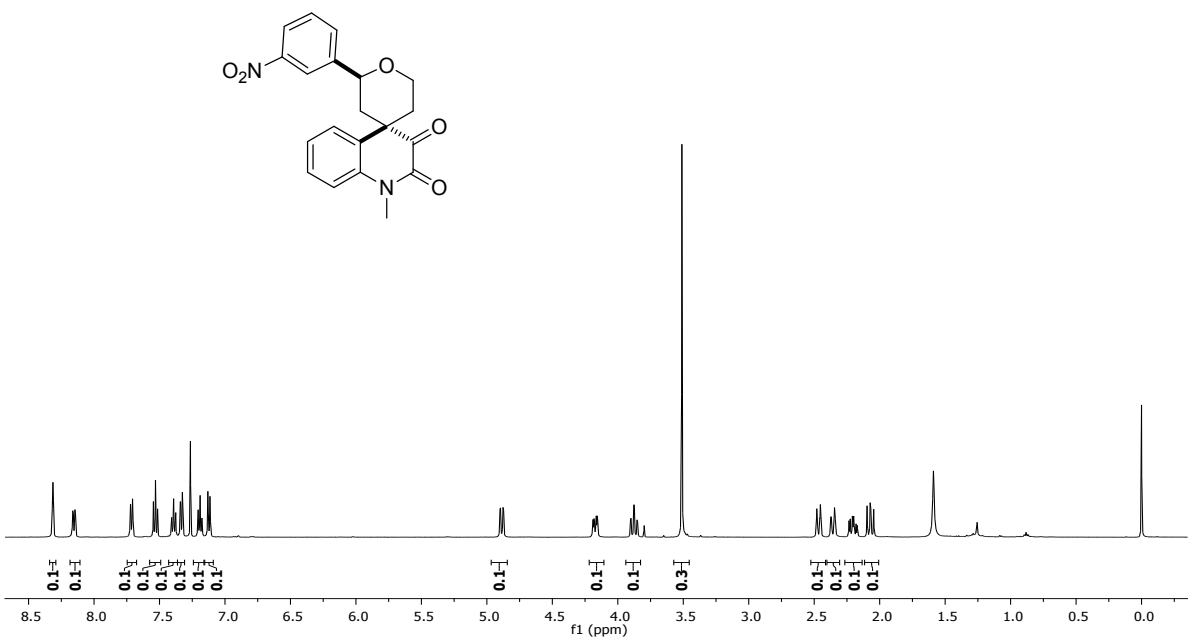
^{1}H NMR of 4-1'-methyl-2',3'-dioxo-2,2',3,3',5,6-hexahydro-1'*H*-spiro[pyran-4,4'-quinolin]-2-yl)benzonitrile (5b):



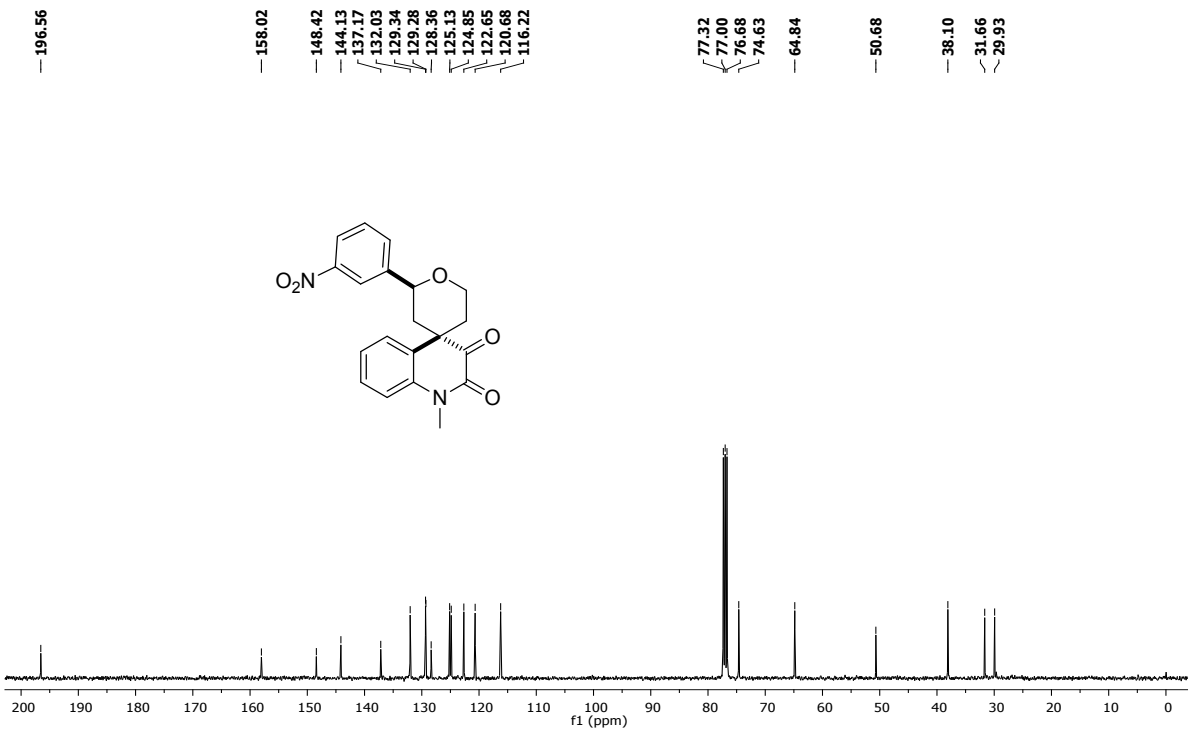
^{13}C NMR of 4-1'-methyl-2',3'-dioxo-2,2',3,3',5,6-hexahydro-1'*H*-spiro[pyran-4,4'-quinolin]-2-yl)benzonitrile (5b):



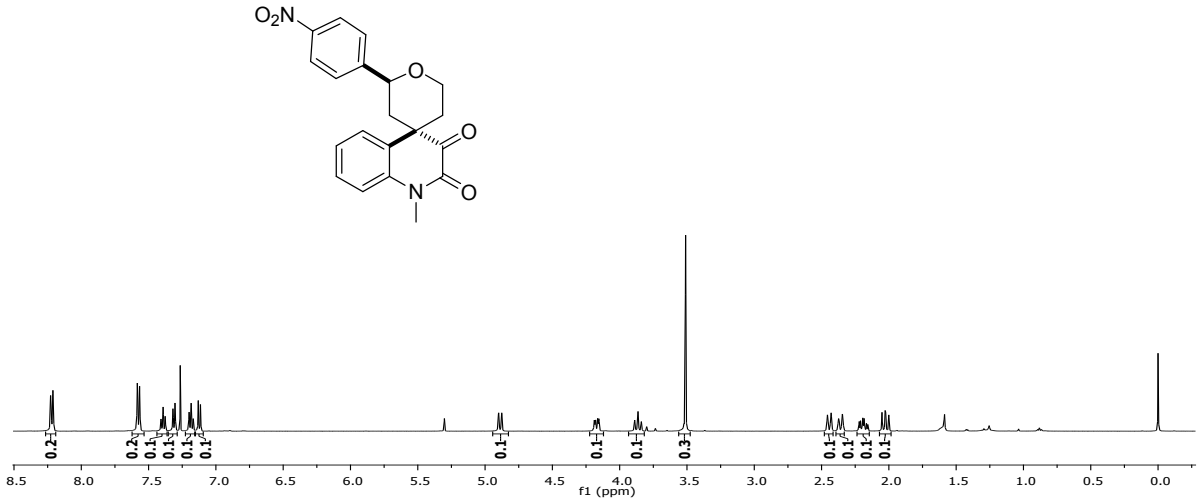
^{1}H NMR of 1'-methyl-2-(3-nitrophenyl)-2,3,5,6-tetrahydro-1'*H*-spiro[pyran-4,4'-quinoline]-2',3'-dione (5c):



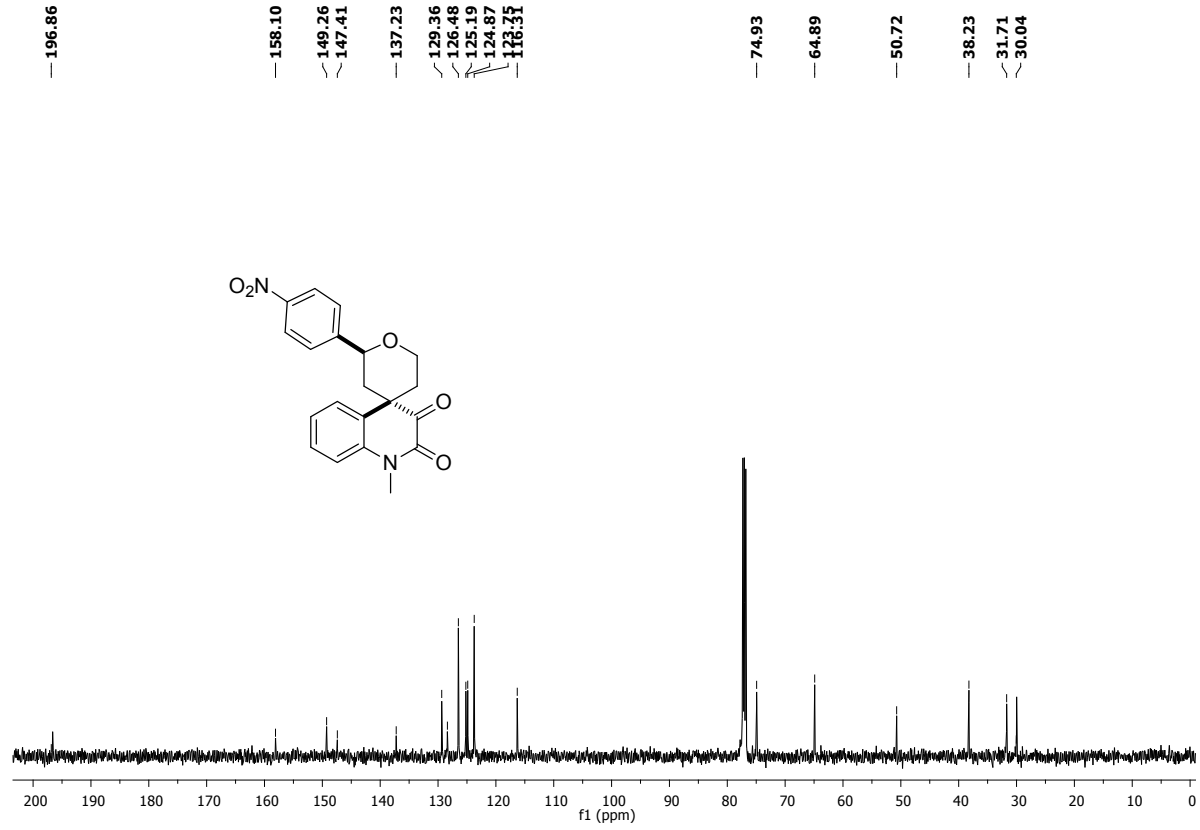
^{13}C NMR of 1'-methyl-2-(3-nitrophenyl)-2,3,5,6-tetrahydro-1'H-spiro[pyran-4,4'-quinoline]-2',3'-dione (5c):



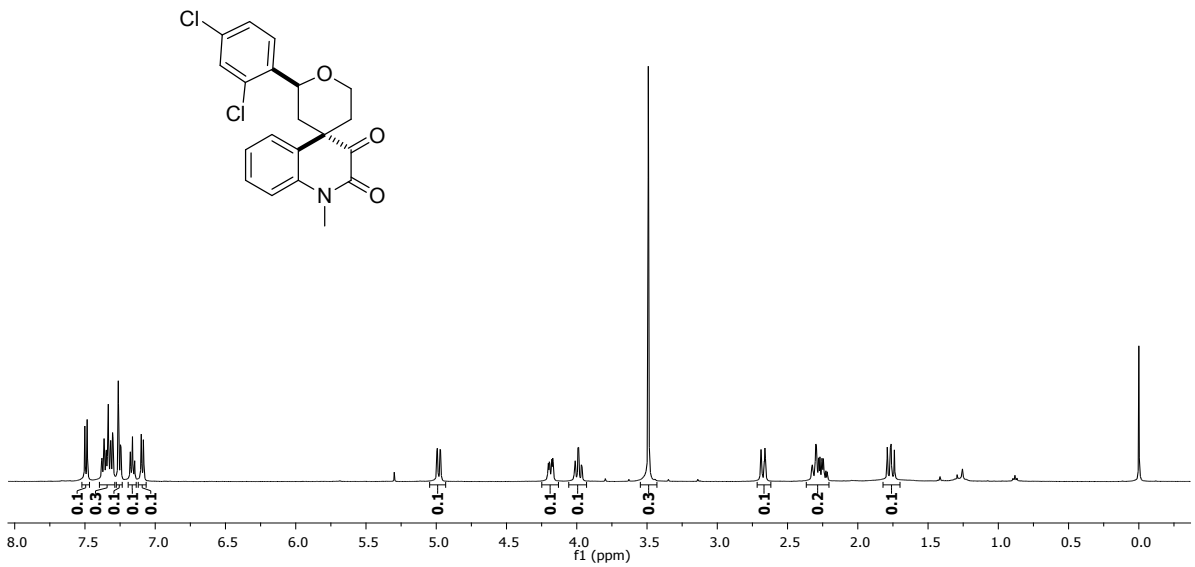
^{1}H NMR of 1'-methyl-2-(4-nitrophenyl)-2,3,5,6-tetrahydro-1'*H*-spiro[pyran-4,4'-quinoline]-2',3'-dione (5d):



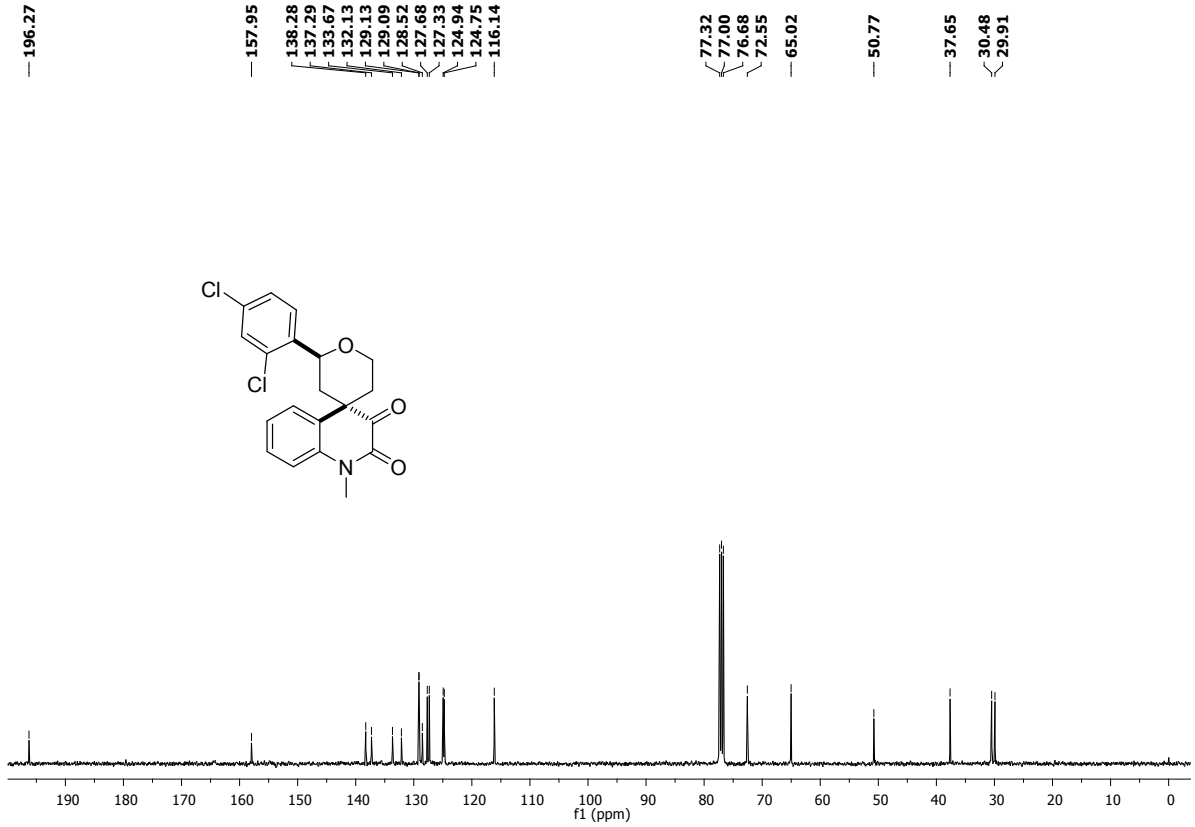
^{13}C NMR of 1'-methyl-2-(4-nitrophenyl)-2,3,5,6-tetrahydro-1'H-spiro[pyran-4,4'-quinoline]-2',3'-dione (5d):



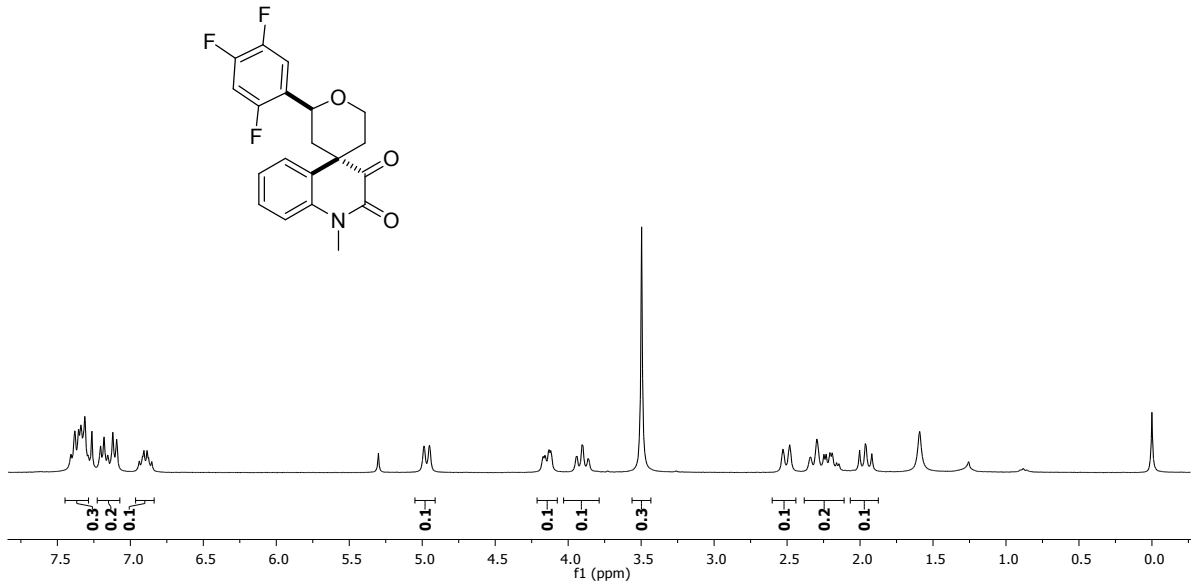
^{1}H NMR of 2-(2,4-dichlorophenyl)-1'-methyl-2,3,5,6-tetrahydro-1'*H*-spiro[pyran-4,4'-quinoline]-2',3'-dione (5e):



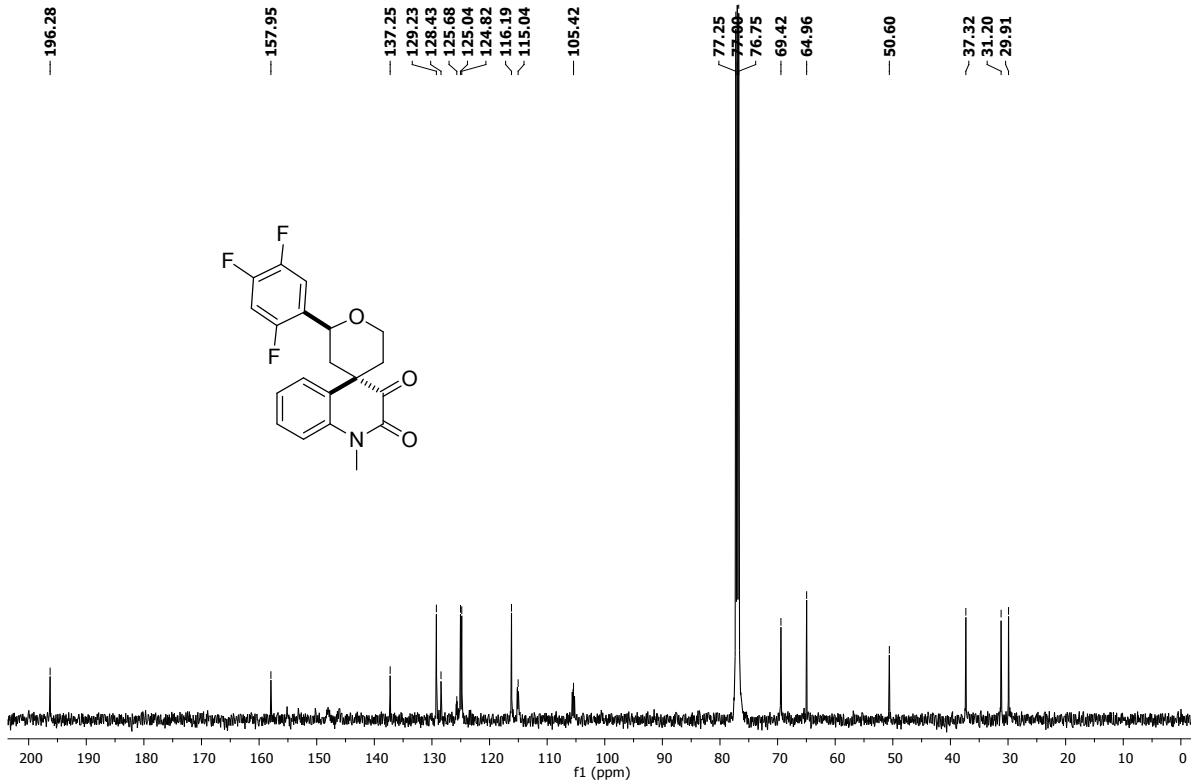
[13] C NMR of 2-(2,4-dichlorophenyl)-1'-methyl-2,3,5,6-tetrahydro-1'H-spiro[pyran-4,4'-quinoline]-2',3'-dione (5e):



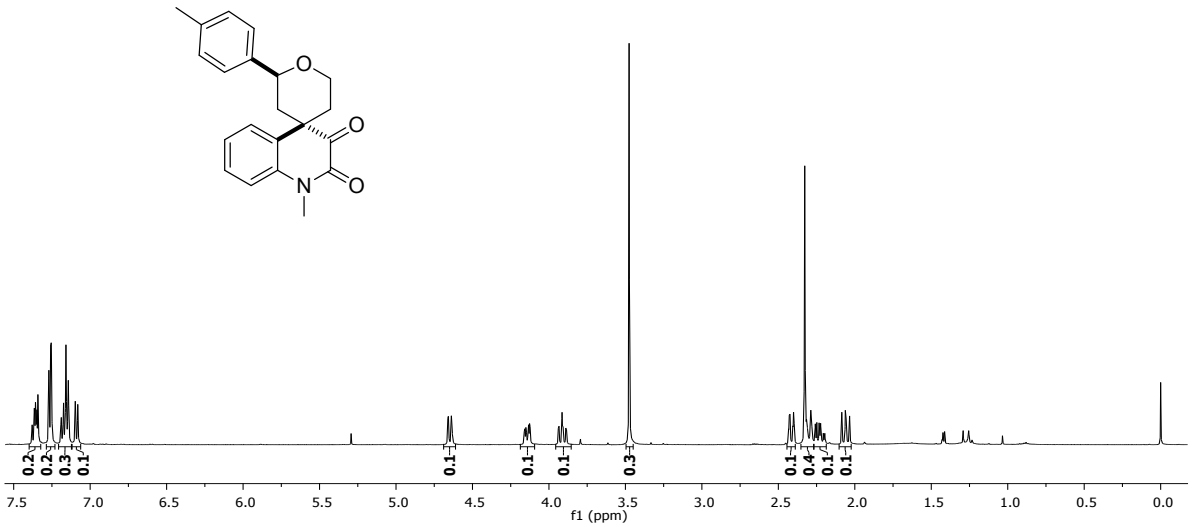
^{1}H NMR of 1'-methyl-2-(2,4,5-trifluorophenyl)-2,3,5,6-tetrahydro-1'*H*-spiro[pyran-4,4'-quinoline]-2',3'-dione (5f):



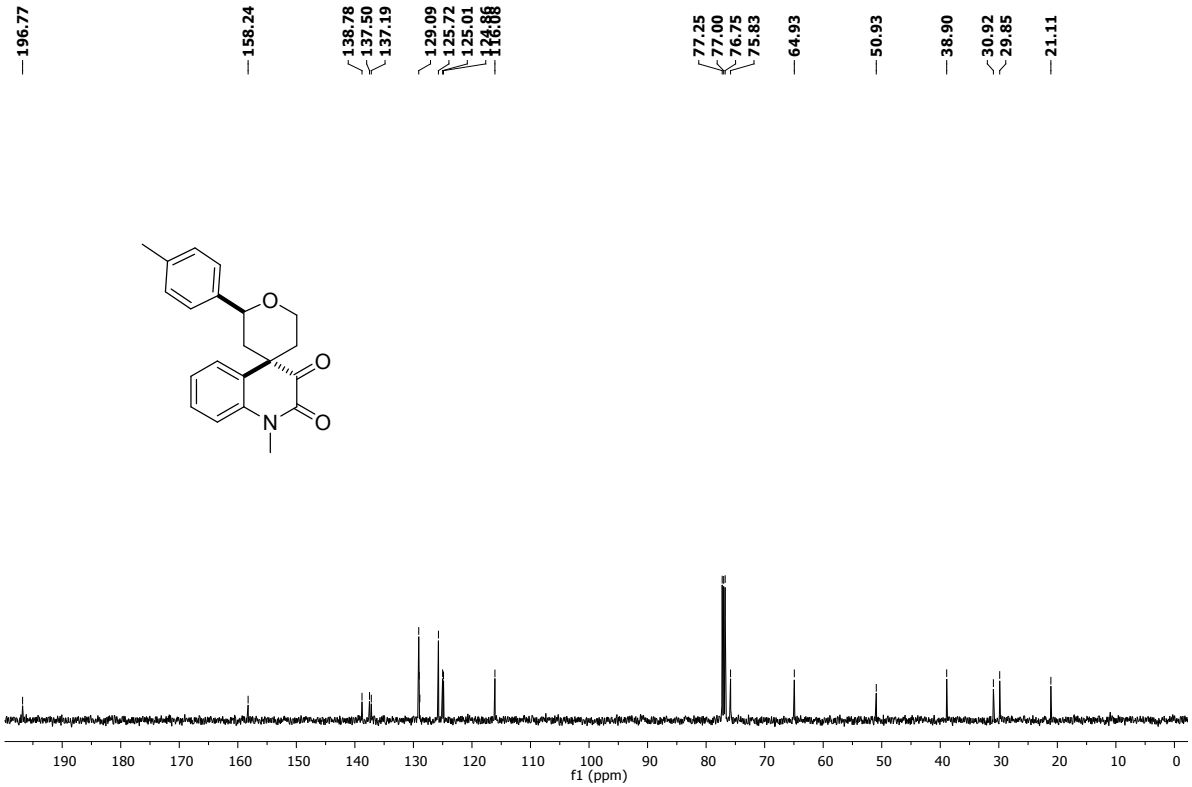
^{13}C NMR of 1'-methyl-2-(2,4,5-trifluorophenyl)-2,3,5,6-tetrahydro-1'H-spiro[pyran-4,4'-quinoline]-2',3'-dione (5f):



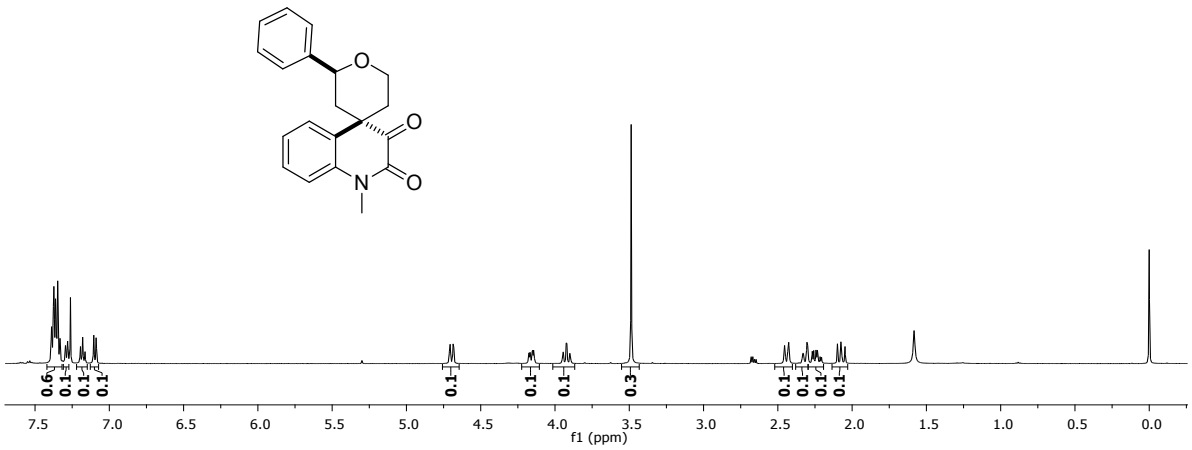
^{1}H NMR of 1'-methyl-2-(p-tolyl)-2,3,5,6-tetrahydro-1'*H*-spiro[pyran-4,4'-quinoline]-2',3'-dione (5g):



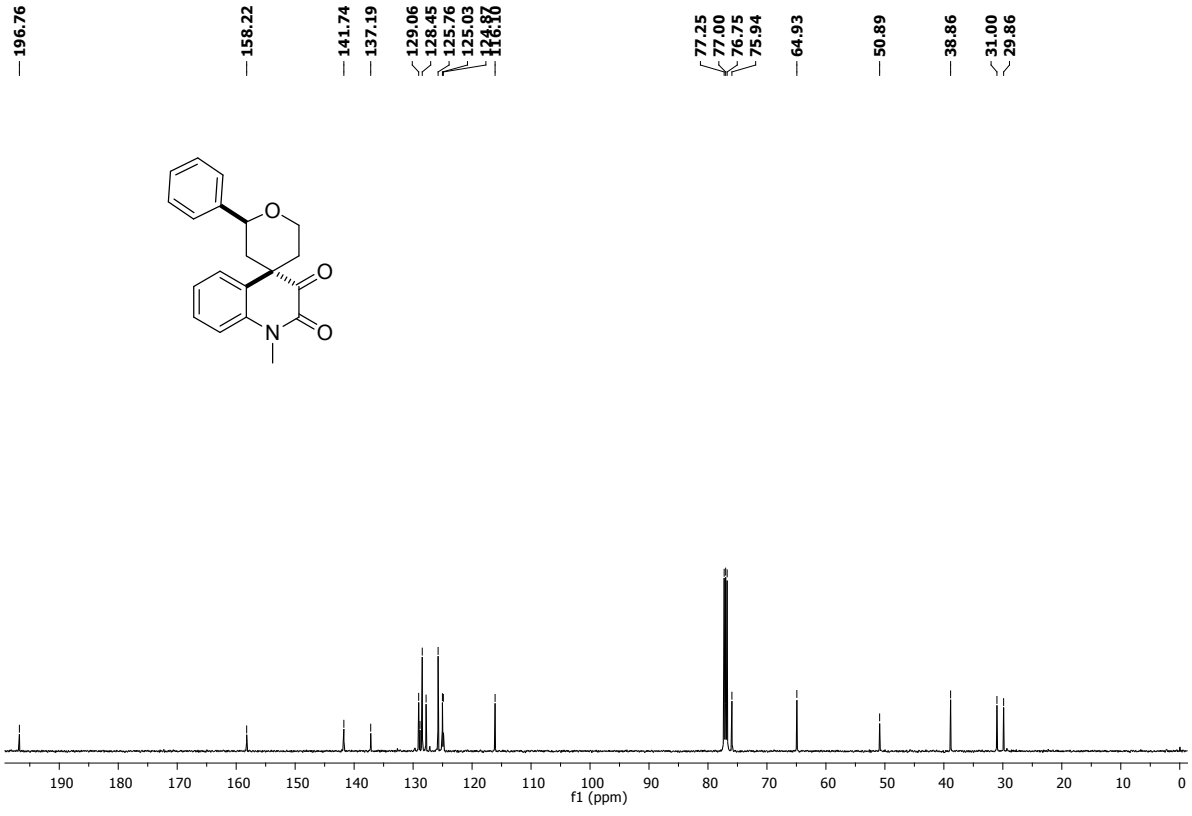
^{13}C NMR of 1'-methyl-2-(p-tolyl)-2,3,5,6-tetrahydro-1'H-spiro[pyran-4,4'-quinoline]-2',3'-dione (5g):



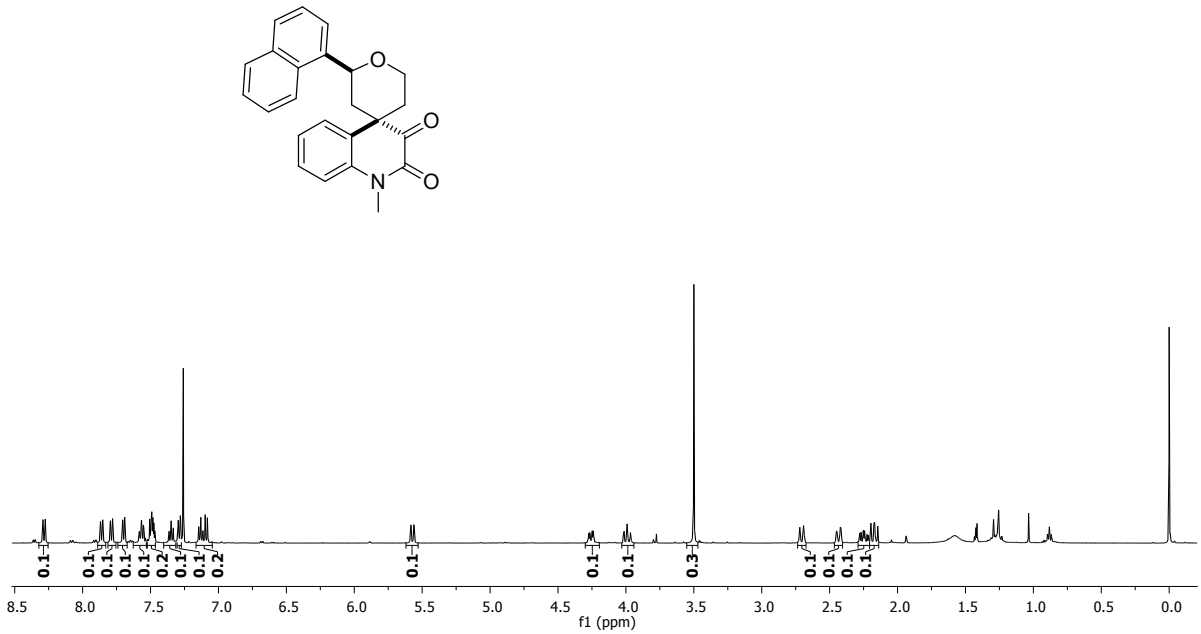
^{1}H NMR of 1'-methyl-2-phenyl-2,3,5,6-tetrahydro-1'*H*-spiro[pyran-4,4'-quinoline]-2',3'-dione (5h):



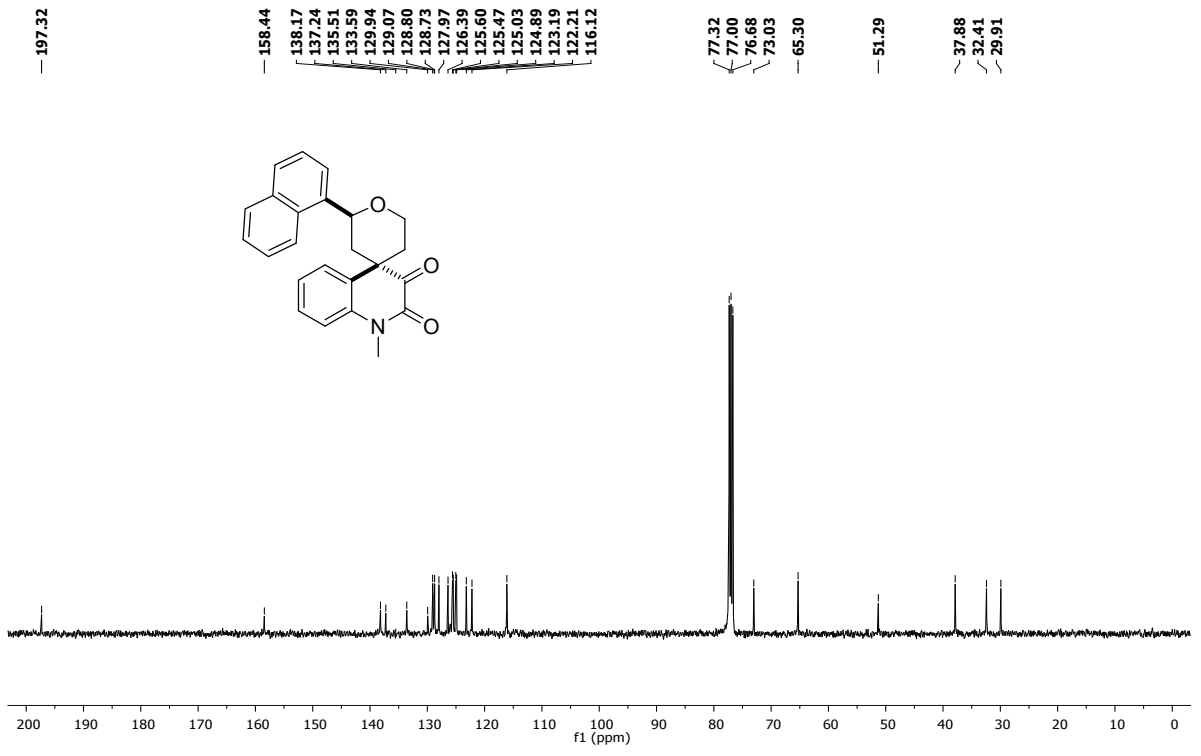
^{13}C NMR of 1'-methyl-2-phenyl-2,3,5,6-tetrahydro-1'H-spiro[pyran-4,4'-quinoline]-2',3'-dione (5h):



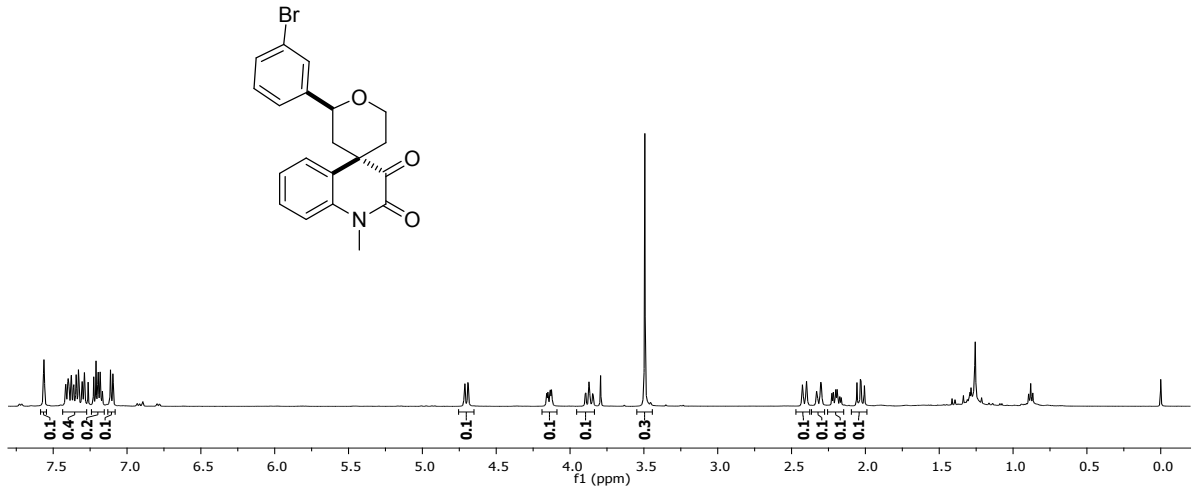
^{1}H NMR of 1'-methyl-2-(naphthalen-1-yl)-2,3,5,6-tetrahydro-1'*H*-spiro[pyran-4,4'-quinoline]-2',3'-dione (5i):



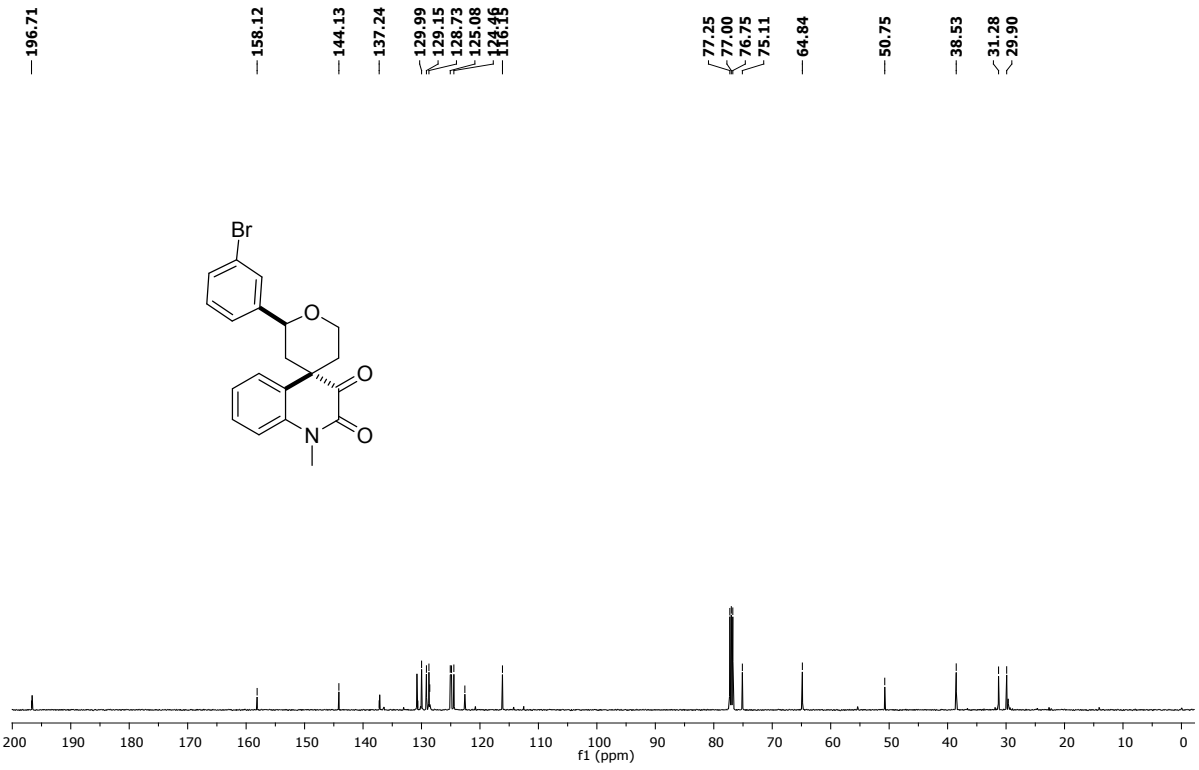
^{13}C NMR of 1'-methyl-2-(naphthalen-1-yl)-2,3,5,6-tetrahydro-1'H-spiro[pyran-4,4'-quinoline]-2',3'-dione (5i):



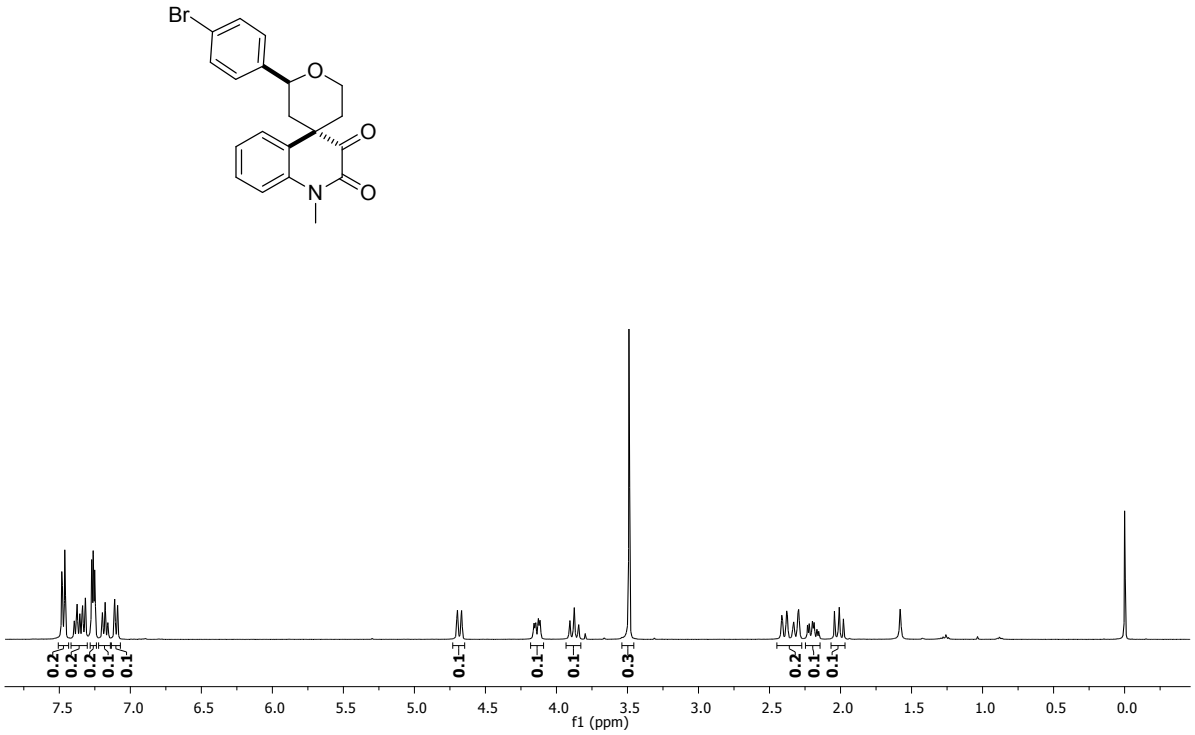
^{1}H NMR of 2-(3-bromophenyl)-1'-methyl-2,3,5,6-tetrahydro-1'*H*-spiro[pyran-4,4'-quinoline]-2',3'-dione (5j):



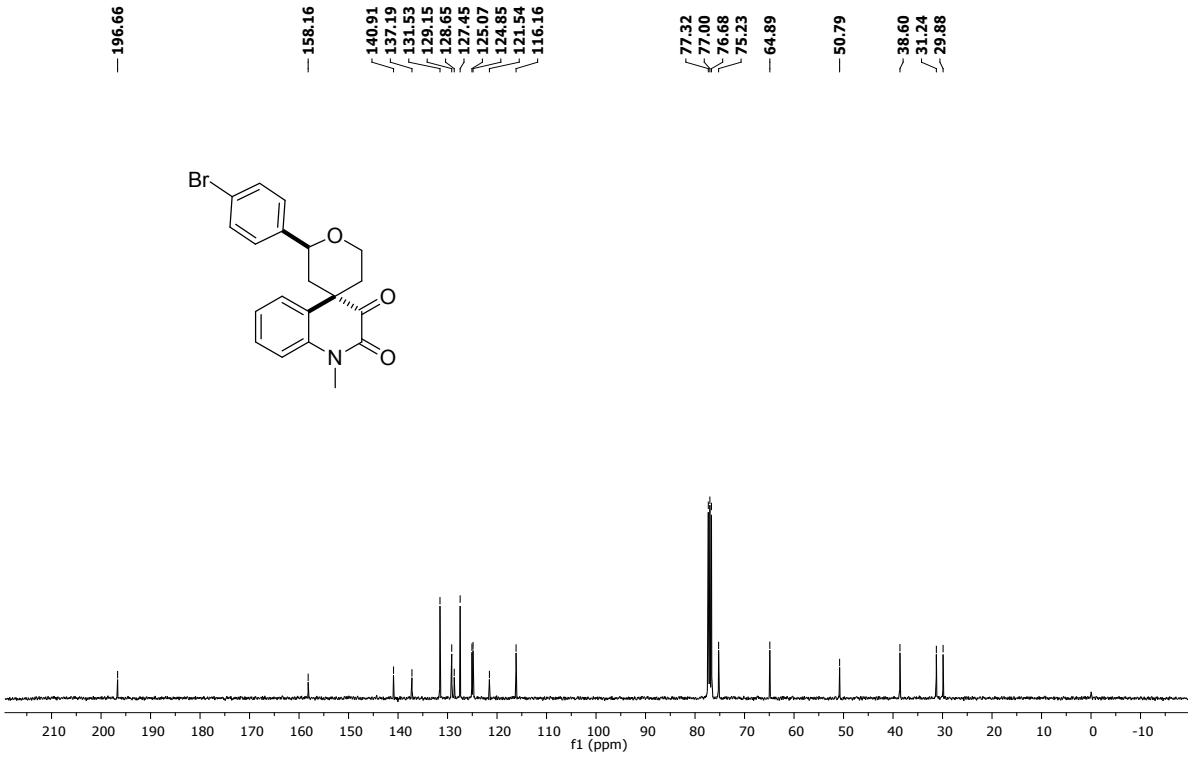
^{13}C NMR of 2-(3-bromophenyl)-1'-methyl-2,3,5,6-tetrahydro-1'H-spiro[pyran-4,4'-quinoline]-2',3'-dione (5j):



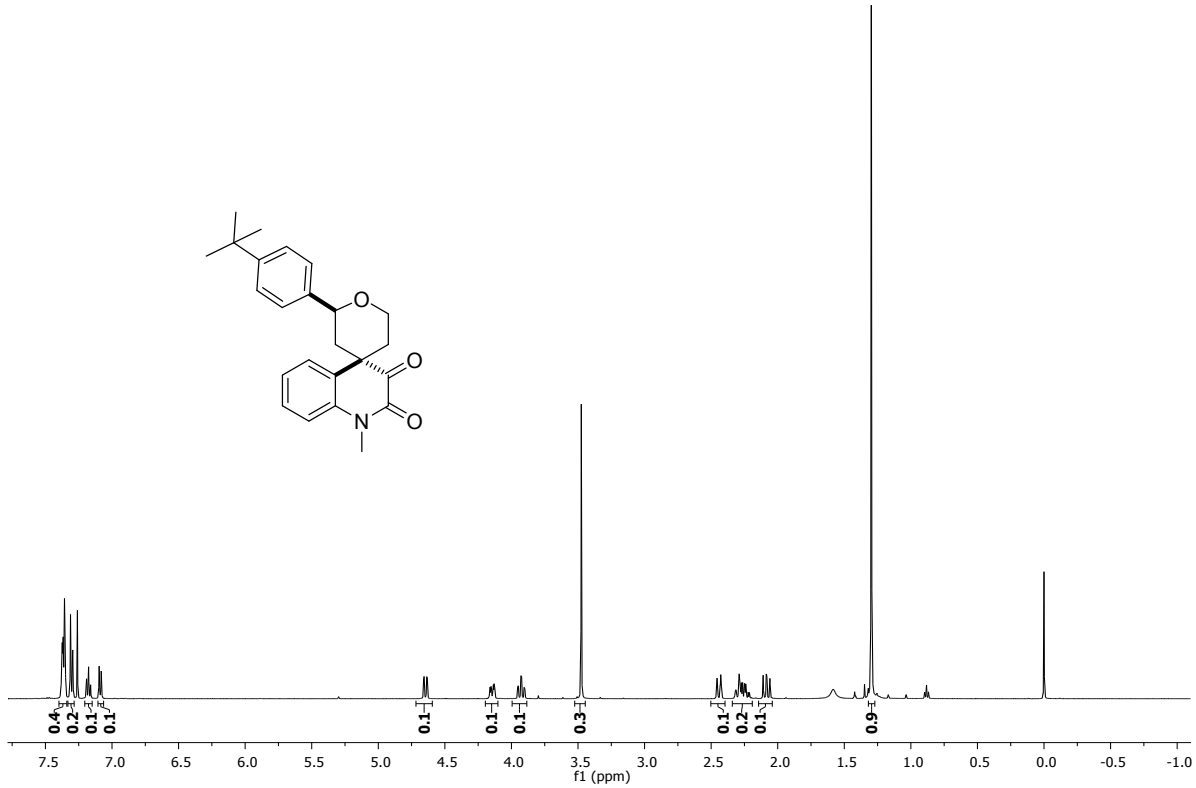
^{1}H NMR of 2-(4-bromophenyl)-1'-methyl-2,3,5,6-tetrahydro-1'*H*-spiro[pyran-4,4'-quinoline]-2',3'-dione (5k):



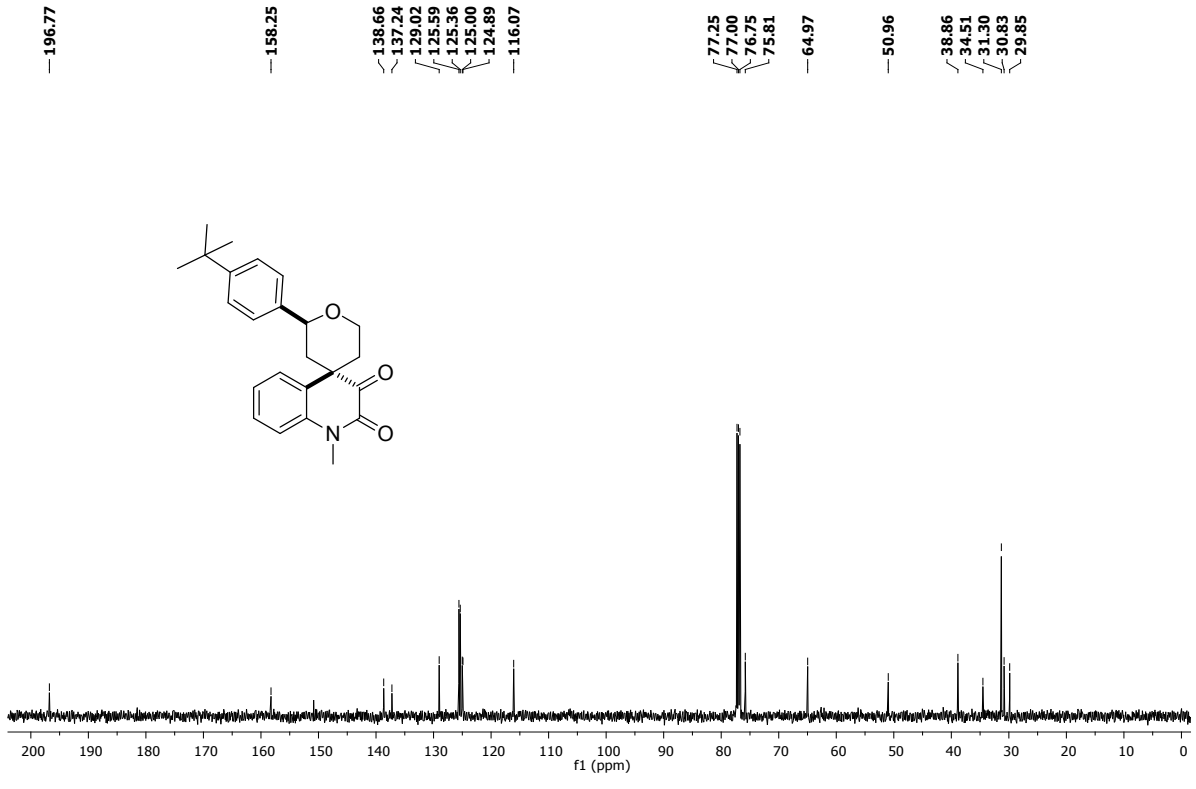
^{13}C NMR of 2-(4-bromophenyl)-1'-methyl-2,3,5,6-tetrahydro-1'*H*-spiro[pyran-4,4'-quinoline]-2',3'-dione (5k):



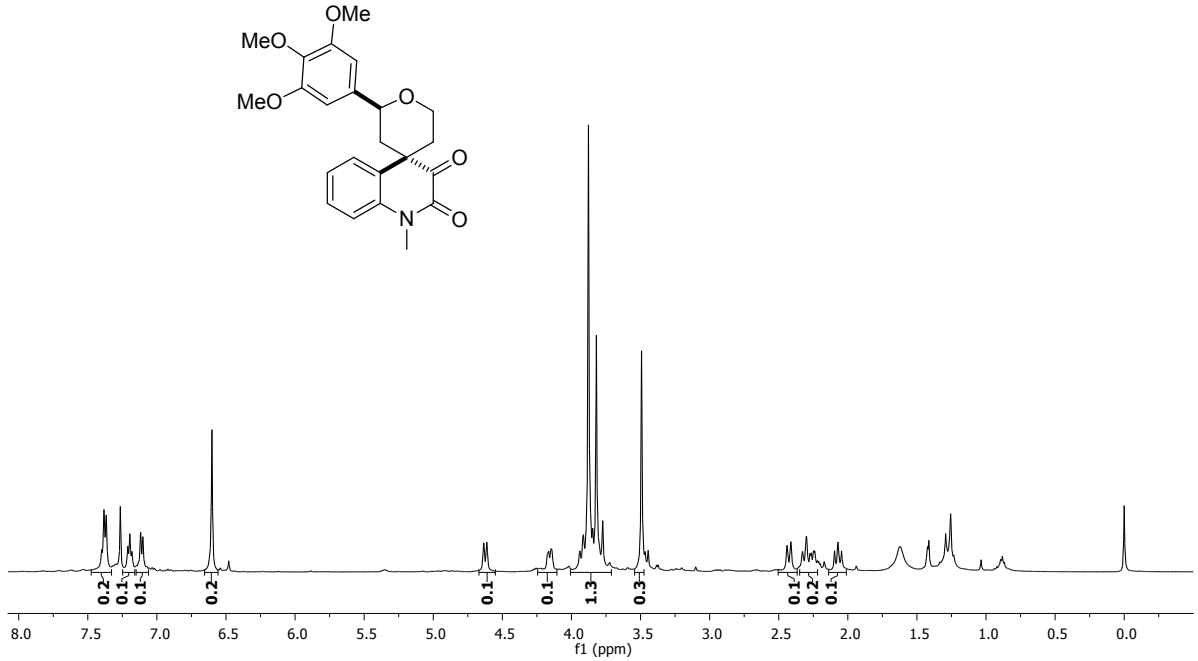
^{1}H NMR of 2-(4-(tert-butyl)phenyl)-1'-methyl-2,3,5,6-tetrahydro-1'*H*-spiro[pyran-4,4'-quinoline]-2',3'-dione (5l):



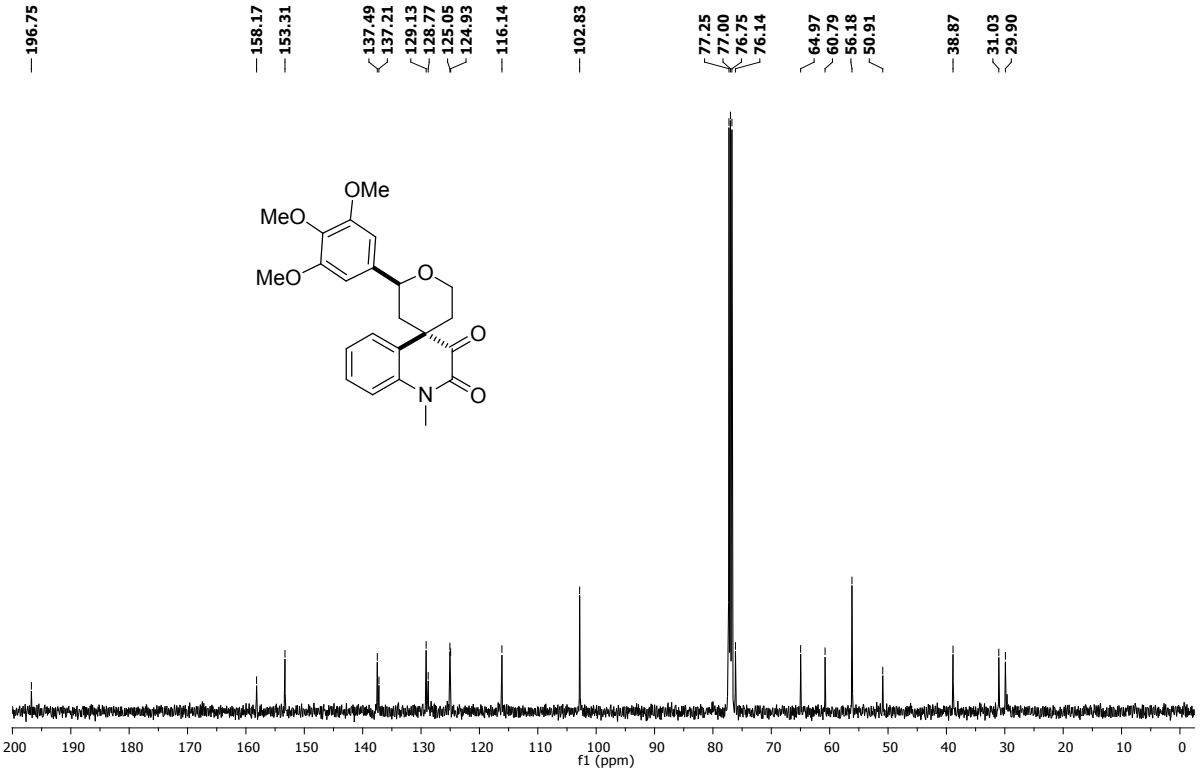
^{13}C NMR of 2-(4-(tert-butyl)phenyl)-1'-methyl-2,3,5,6-tetrahydro-1'*H*-spiro[pyran-4,4'-quinoline]-2',3'-dione (5l):



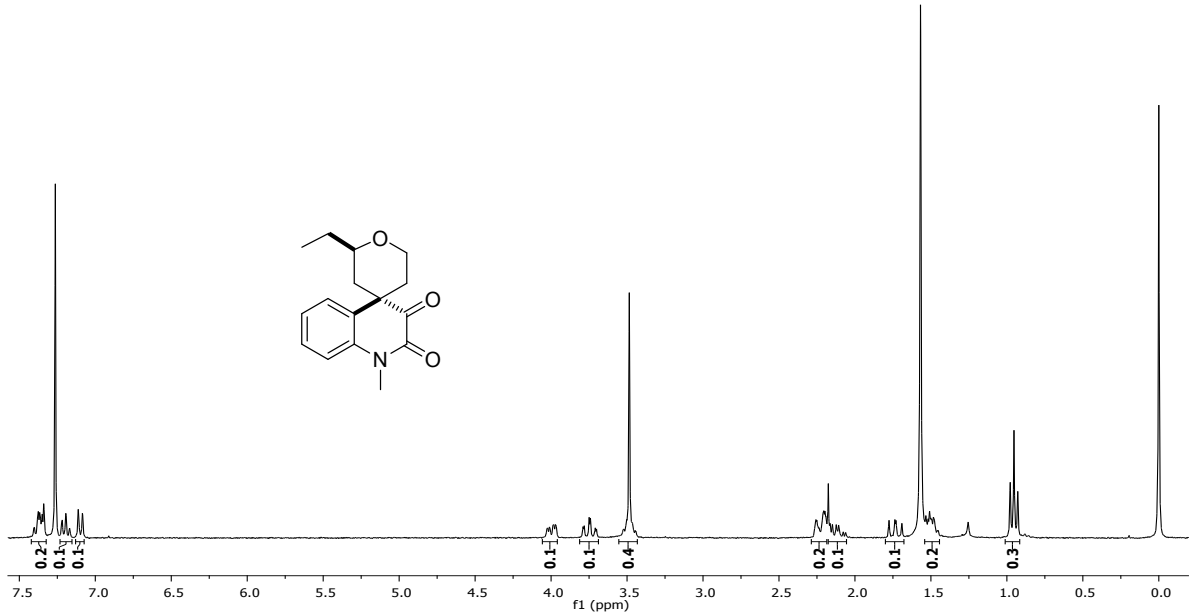
^{1}H NMR of 1'-methyl-2-(3,4,5-trimethoxyphenyl)-2,3,5,6-tetrahydro-1'*H*-spiro[pyran-4,4'-quinoline]-2',3'-dione (5m):



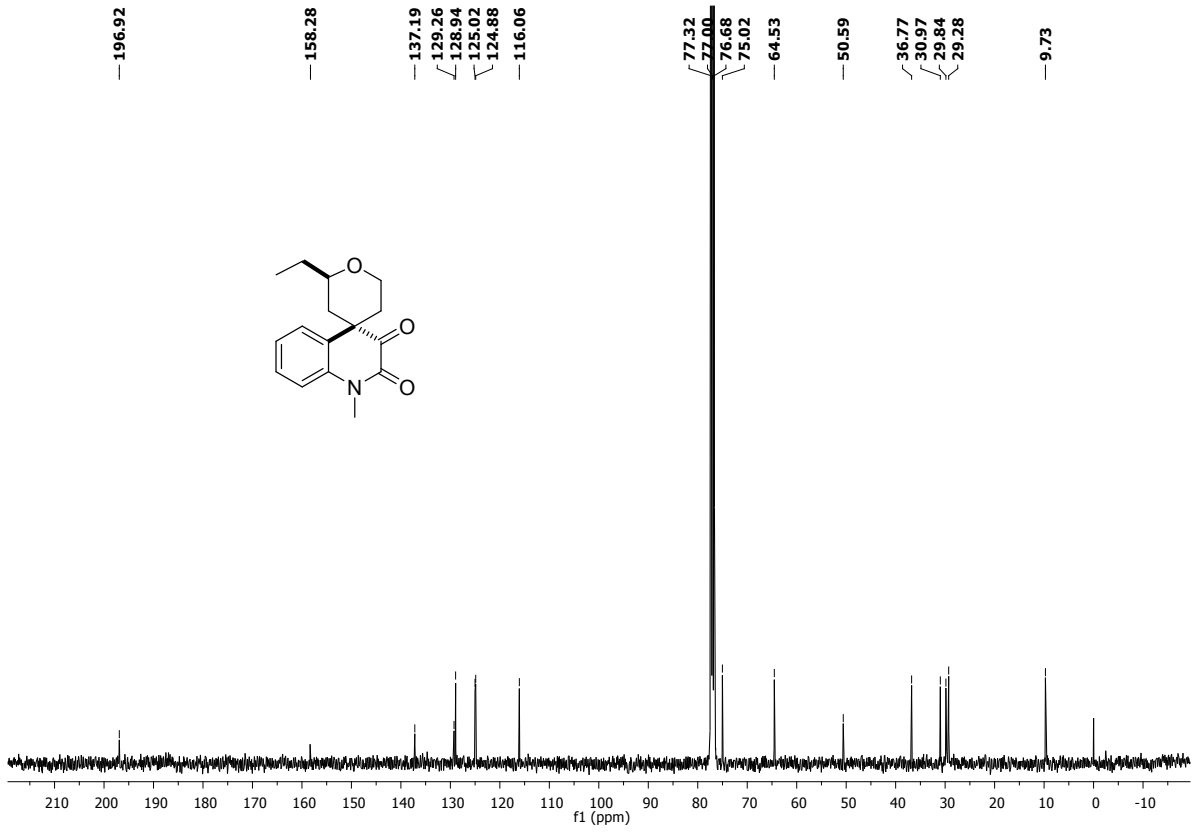
^{13}C NMR of 1'-methyl-2-(3,4,5-trimethoxyphenyl)-2,3,5,6-tetrahydro-1'*H*-spiro[pyran-4,4'-quinoline]-2',3'-dione (5m):



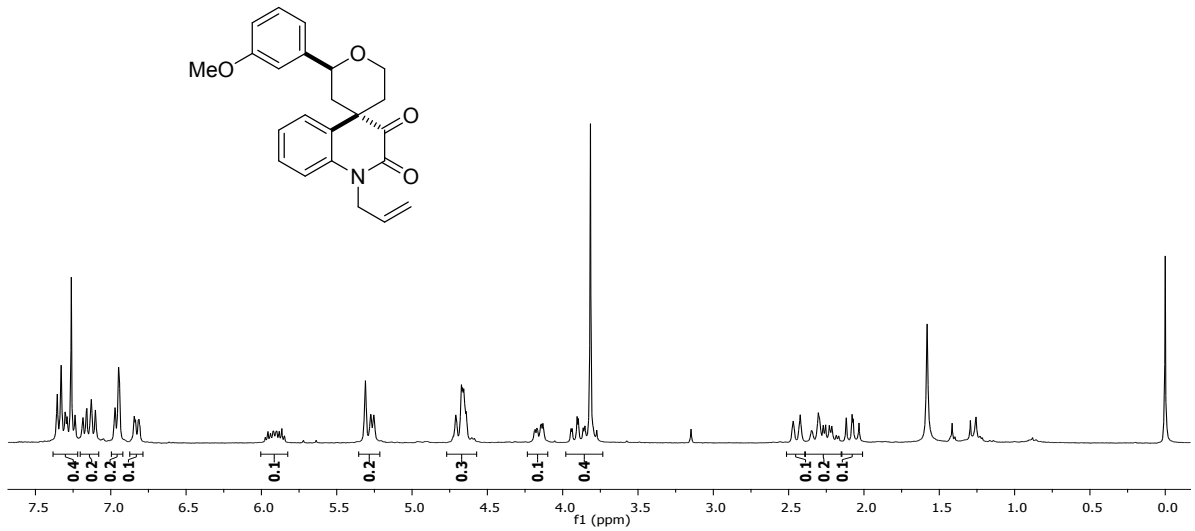
^{1}H NMR of 2-ethyl-1'-methyl-2,3,5,6-tetrahydro-1'*H*-spiro[pyran-4,4'-quinoline]-2',3'-dione(5n):



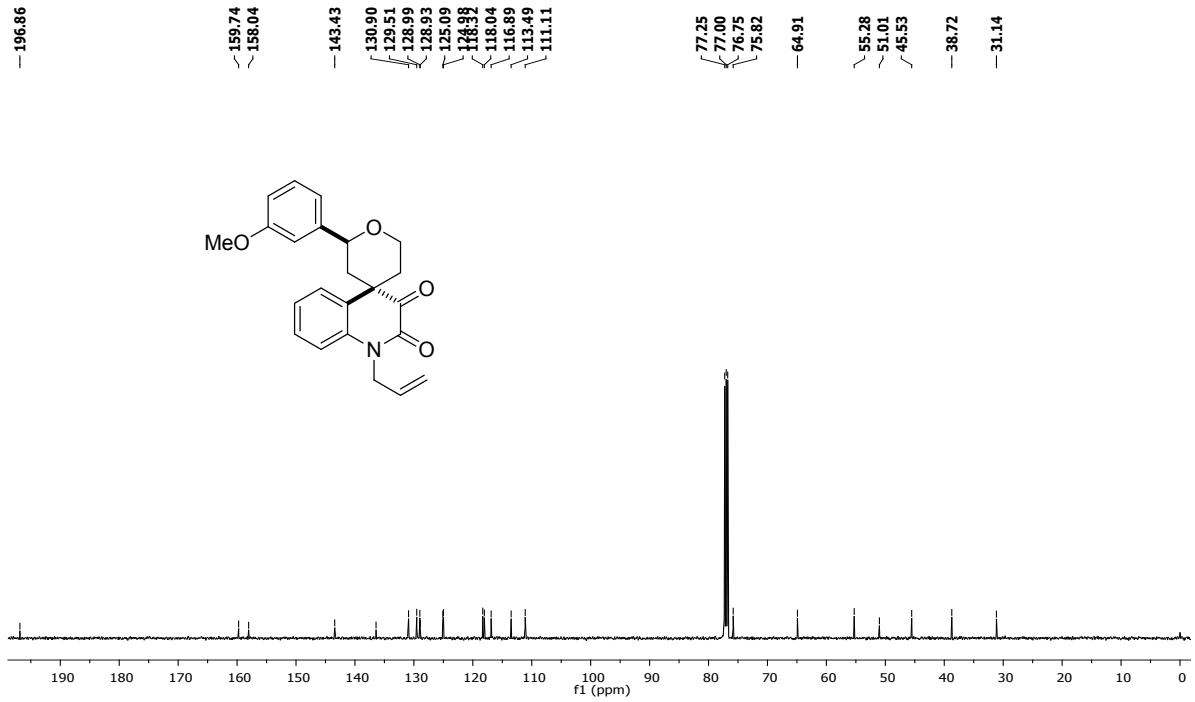
^{13}C NMR of 2-ethyl-1'-methyl-2,3,5,6-tetrahydro-1'*H*-spiro[pyran-4,4'-quinoline]-2',3'-dione(5n):



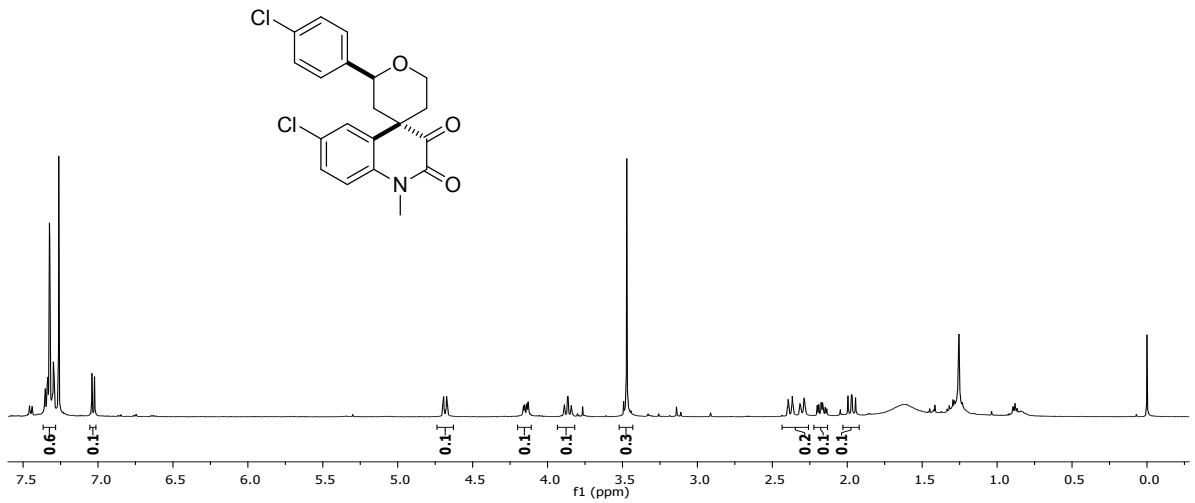
^{1}H NMR of 1'-allyl-2-(3-methoxyphenyl)-2,3,5,6-tetrahydro-1'*H*-spiro[pyran-4,4'-quinoline]-2',3'-dione(5o)



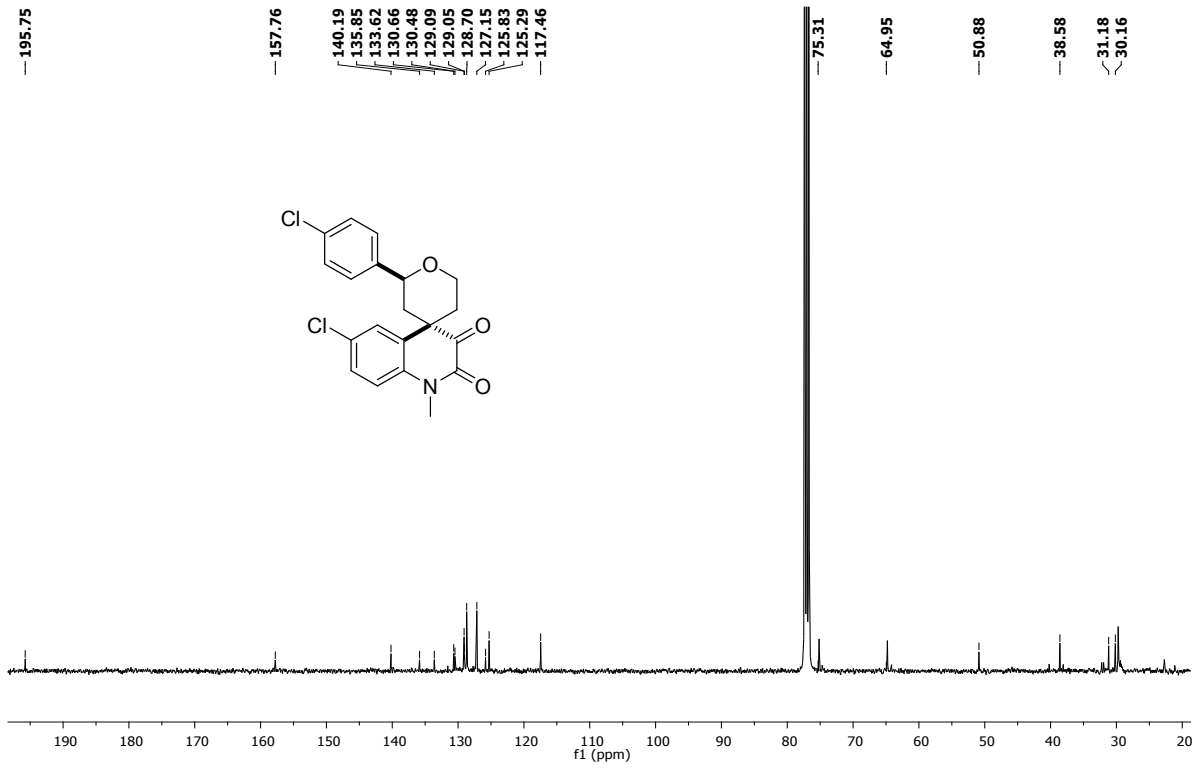
^{13}C NMR of 1'-allyl-2-(3-methoxyphenyl)-2,3,5,6-tetrahydro-1'*H*-spiro[pyran-4,4'-quinoline]-2',3'-dione(5o)



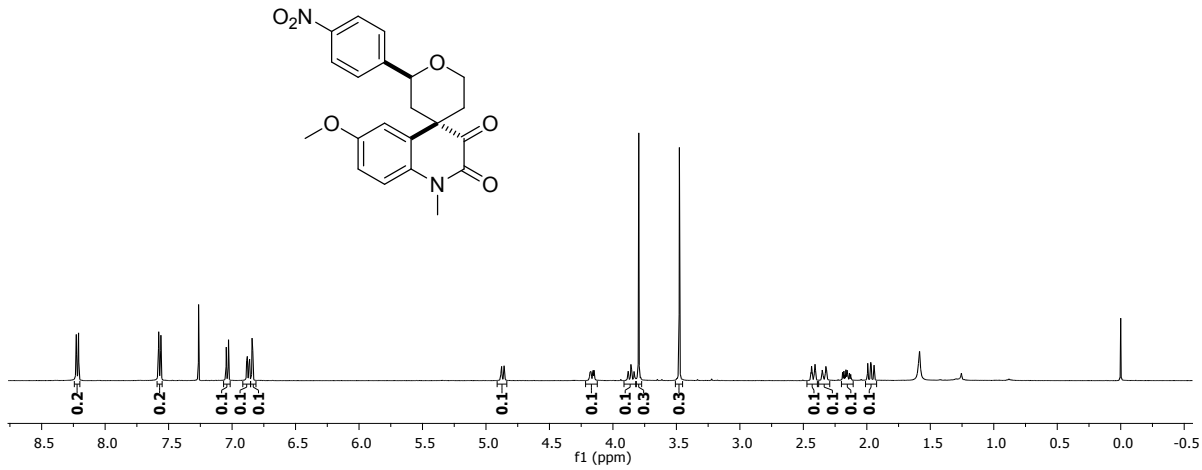
^{1}H NMR of 6'-chloro-2-(3-chlorophenyl)-1'-methyl-2,3,5,6-tetrahydro-1'*H*-spiro[pyran-4,4'-quinoline]-2',3'-dione (5p)



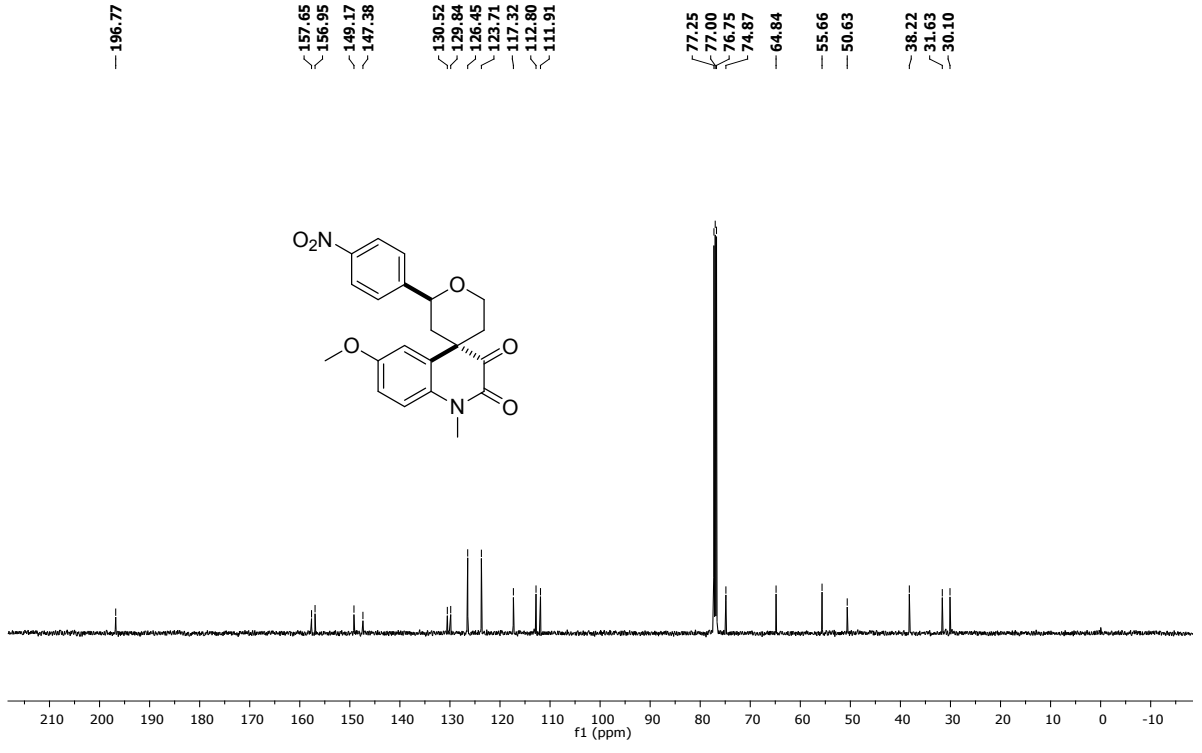
^{13}C NMR of 6'-chloro-2-(3-chlorophenyl)-1'-methyl-2,3,5,6-tetrahydro-1'*H*-spiro[pyran-4,4'-quinoline]-2',3'-dione (5p)



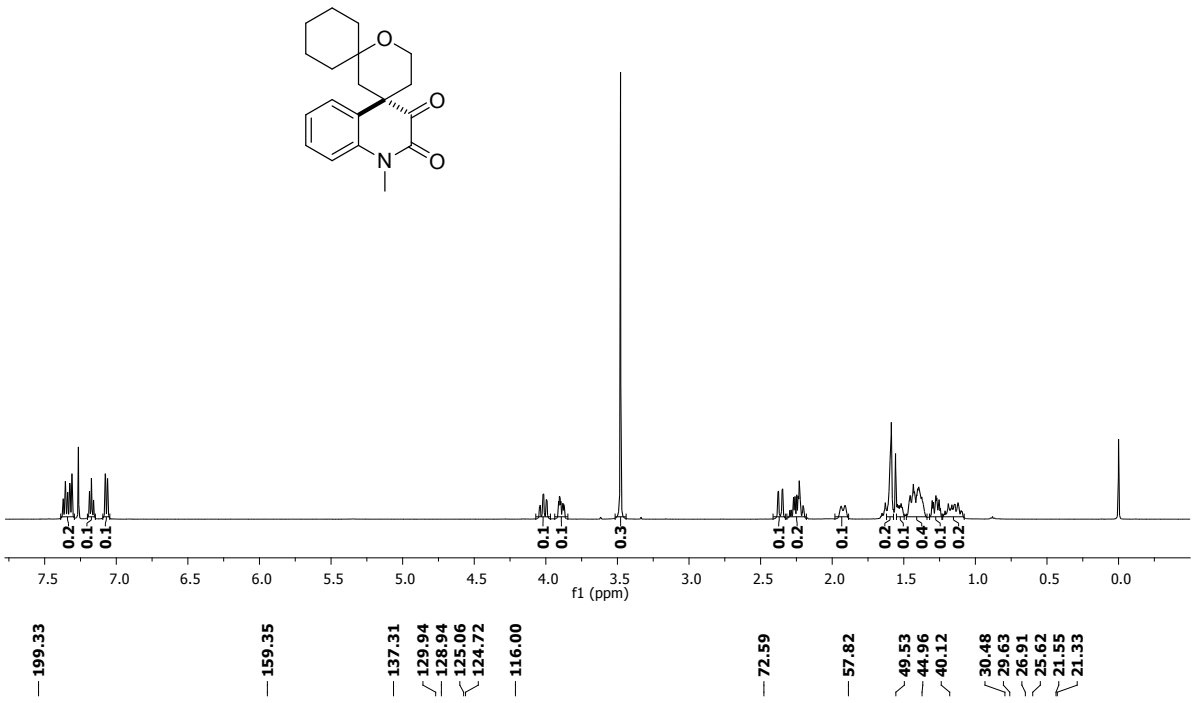
^{1}H NMR of 6'-methoxy-1'-methyl-2-(4-nitrophenyl)-2,3,5,6-tetrahydro-1'H-spiro[pyran-4,4'-quinoline]-2',3'-dione (5q)



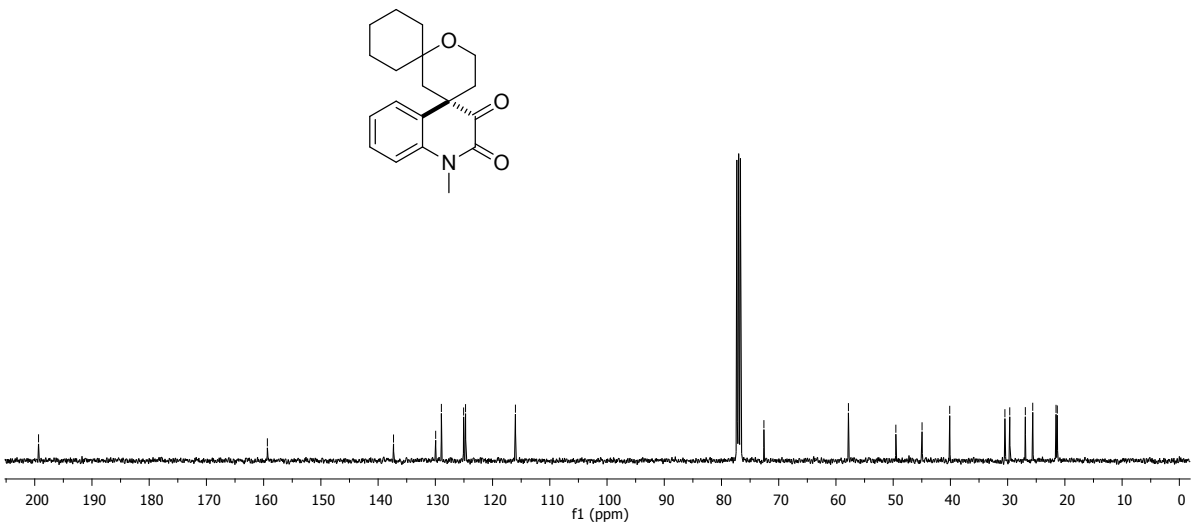
^{13}C NMR of 6'-methoxy-1'-methyl-2-(4-nitrophenyl)-2,3,5,6-tetrahydro-1'H-spiro[pyran-4,4'-quinoline]-2',3'-dione (5q)



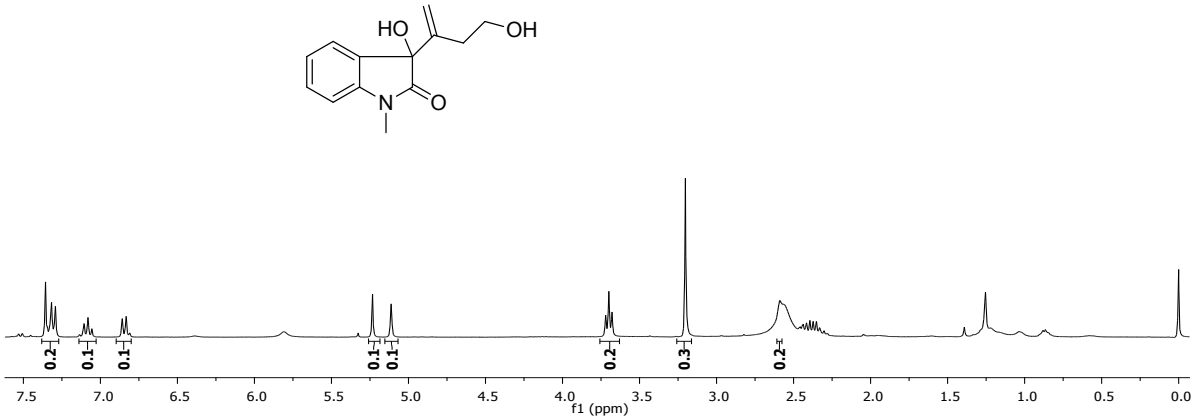
^{1}H &^{13}C NMR spectra of (5r)



199.33 159.35 137.31 129.94 128.94 125.06 124.72 116.00 72.59 57.82 49.53 44.96 40.12 30.48 29.63 26.91 25.62 21.55 21.33



^{1}H NMR of 3-hydroxy-3-(4-hydroxybut-1-en-2-yl)-1-methylindolin-2-one (3)



^{13}C NMR of 3-hydroxy-3-(4-hydroxybut-1-en-2-yl)-1-methylindolin-2-one (3)