Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.
This journal is © The Royal Society of Chemistry 2018

Supporting Information

Efficient Construction of Tetrahydroquinoline-fused Spirooxindoles via Fluorinated Alcohol Mediated Cascade [1,5]-Hydride Transfer/Cyclization

Chunqi Chen,† Lubin Xu,† Liang Wang* and Shuai-Shuai Li*

†College of Chemistry and Pharmaceutical Sciences, Shandong Province Key Laboratory of Applied Mycology, Qingdao Agricultural University, Qingdao 266109, China

Table of Contents

1. General Information…….....S2

2. General Procedure……S2

3. Characterization of Starting Materials and Products..……S3

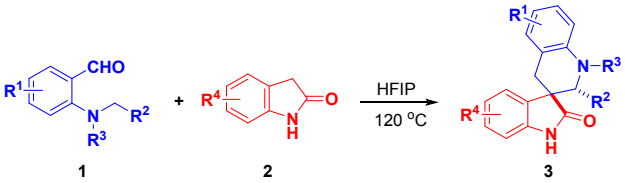
4. ^{1}H and ^{13}C NMR Spectra……..…….....S15

1. General Information

Unless otherwise noted, all reagents and solvents were purchased from the commercial sources and used as received. Thin layer chromatography (TLC) was used to monitor the reaction on Merck 60 F254 precoated silica gel plate (0.2 mm thickness). TLC spots were visualized by UV-light irradiation on Spectroline Model ENF-24061/F 254 nm. The products were purified by flash column chromatography (200-300 mesh silica gel) eluted with the gradient of petroleum ether and ethyl acetate. Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on a Bruker 500 MHz NMR spectrometer ($CDCl_3$ or DMSO-d_6 solvent). The chemical shifts were reported in parts per million (ppm), downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 7.26, singlet) or dimethyl sulfoxide-d_6 (δ 2.54, singlet). Multiplicities were afforded as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublets of doublet) or m (multiplets). The number of protons for a given resonance is indicated by nH. Coupling constants were reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) was referenced to the appropriate residual solvent peak. High resolution mass spectral analysis (HRMS) was performed on Waters XEVO G2 Q-TOF. All substituted 2-fluorobenzaldehydes, oxindoles, and 1,3-dicarbonyl compounds were purchased from adamas-beta. All *o*-aminobenzaldehydes were prepared according to literature.[1]

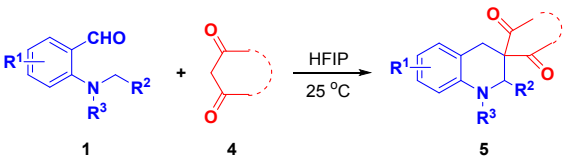
2. General Procedure

2.1 General Procedure for the Synthesis of Tetrahydroquinoline-fused Spirooxindoles



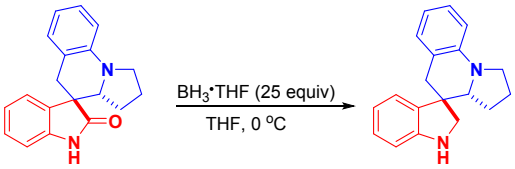
A sealed tube was charged with *o*-aminobenzaldehyde **1** (0.15 mmol), oxindole **2** (0.10 mmol), and HFIP (1.0 mL). The mixture was stirred at 120 °C under an air atmosphere. Upon completion of the reaction as indicated by TLC analysis, the mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether, 1:20) to afford the desired tetrahydroquinoline-fused spirooxindoles **3**.

2.2 General Procedure for the Synthesis of Tetrahydroquinoline-fused Spirocycles



A sealed tube was charged with *o*-aminobenzaldehyde **1** (0.15 mmol), 1,3-dicarbonyl compounds **4** (0.10 mmol), and HFIP (1.0 mL). The mixture was stirred at 25 °C under an air atmosphere. Upon completion of the reaction as indicated by TLC analysis, the mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether, 1:50) to afford the desired tetrahydroquinoline-fused Spirocycles **3**.

2.2 General Procedure for the Reduction of Tetrahydroquinoline-fused Spirooxindoles

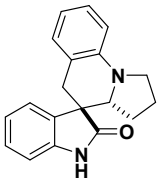


3a **8a**, 50% yield

To a vial equipped with a stir bar was added **3a** (29 mg, 0.1 mmol) and THF (1 mL). To this mixture was added BH_3/THF (2.5 mL, 2.5 mmol, 1M) in ten portions (every five minutes) at 0 °C. After that, the reaction was allowed to stir at 0 °C for 1 h and stir at room temperature for another 3 h. Then the reaction was quenched with MeOH (2 mL) and the mixture was concentrated in vacuum. The residue was directly purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether, 1:20) to afford the desired spiroindoline-fused tetrahydroquinoline **6a**.

3. Characterization of Products

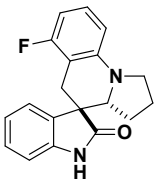
1',2',3',3a'-tetrahydro-5'H-spiro[indoline-3,4'-pyrrolo[1,2-a]quinolin]-2-one (3a)



Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:20) afforded the product (25.6 mg, 89% yield) as a pale yellow solid and the diastereoselectivity was 90:10.

^{1}H NMR (500 MHz, DMSO) δ 10.62 (s, 1H), 7.13 (q, *J* = 7.3 Hz, 2H), 6.98 (d, *J* = 7.2 Hz, 1H), 6.89 (d, *J* = 7.7 Hz, 1H), 6.70 (t, *J* = 7.5 Hz, 1H), 6.55 (t, *J* = 8.5 Hz, 2H), 6.20 (d, *J* = 7.5 Hz, 1H), 3.70 (dd, *J* = 9.6, 5.7 Hz, 1H), 3.47 (t, *J* = 8.7 Hz, 1H), 3.22 – 3.03 (m, 2H), 2.58 (d, *J* = 15.6 Hz, 1H), 1.95 – 1.66 (m, 3H), 0.84 – 0.67 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 183.9, 148.1, 146.5, 133.9, 133.7, 132.2, 132.2, 128.4, 125.8, 122.1, 119.7, 119.6, 114.4, 113.8, 66.4, 51.6, 50.1, 41.1, 31.4, 27.4 ppm. **HRMS (ESI):** calcd. for $C_{19}H_{19}N_2O$ $[M+H]^+$: 291.1497, found: 291.1498.

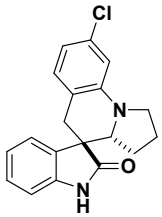
6'-fluoro-1',2',3',3a'-tetrahydro-5'H-spiro[indoline-3,4'-pyrrolo[1,2-a]quinolin]-2-one (3b)



Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:20) afforded the product (43.3 mg, 47% yield) as a pale yellow solid and the diastereoselectivity was 80:20.

^{1}H NMR (500 MHz, DMSO) δ 10.68 (s, 1H), 7.21 – 7.12 (m, 2H), 6.91 (t, *J* = 7.0 Hz, 1H), 6.75 (t, *J* = 7.5 Hz, 1H), 6.41 (dd, *J* = 17.1, 8.4 Hz, 2H), 6.25 (d, *J* = 7.4 Hz, 1H), 3.67 (dd, *J* = 9.2, 5.9 Hz, 1H), 3.50 (t, *J* = 8.7 Hz, 1H), 3.12 (q, *J* = 8.5 Hz, 1H), 2.91 (d, *J* = 16.1 Hz, 1H), 2.73 (d, *J* = 16.0 Hz, 1H), 1.96 – 1.66 (m, 3H), 0.83 – 0.68 (m, 1H); **^{13}C NMR** (126 MHz, DMSO) δ 179.5, 161.5, 145.6, 145.6, 142.5, 129.7, 129.0, 128.5, 124.1, 122.1, 110.0, 106.7, 105.2, 102.1, 61.9, 47.9, 45.4, 29.8, 29.7, 27.2, 23.2 ppm. **HRMS (ESI):** calcd. for $C_{19}H_{18}FN_2O$ $[M+H]^+$: 308.1403, found: 308.1401.

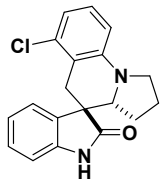
8'-chloro-1',2',3',3a'-tetrahydro-5'H-spiro[indoline-3,4'-pyrrolo[1,2-a]quinolin]-2-one (3c)



Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:20) afforded the product (47.1 mg, 74% yield) as a pale yellow solid and the diastereoselectivity was >20:1.

^{1}H NMR (500 MHz, DMSO) δ 10.65 (s, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 8.1 Hz, 1H), 6.89 (d, *J* = 7.7 Hz, 1H), 6.76 (t, *J* = 7.5 Hz, 1H), 6.56 (d, *J* = 6.5 Hz, 2H), 6.20 (d, *J* = 7.4 Hz, 1H), 3.70 (dd, *J* = 9.8, 5.6 Hz, 1H), 3.48 (dd, *J* = 18.3, 9.6 Hz, 1H), 3.09 (d, *J* = 15.1 Hz, 2H), 2.61 (d, *J* = 15.8 Hz, 1H), 1.94 – 1.68 (m, 3H), 0.83 – 0.67 (m, 1H); **^{13}C NMR** (126 MHz, DMSO) δ 183.5, 149.2, 146.5, 136.7, 135.0, 133.6, 132.3, 128.3, 126.0, 121.5, 119.0 , 113.9 , 113.6, 66.3, 51.6, 49.9, 40.5, 31.2, 27.3 ppm. **HRMS (ESI):** calcd. for $C_{19}H_{18}ClN_2O$ $[M+H]^+$: 325.1108, found: 325.1109

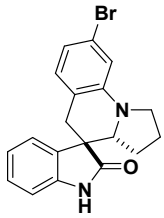
6'-chloro-1',2',3',3a'-tetrahydro-5'H-spiro[indoline-3,4'-pyrrolo[1,2-a]quinolin]-2-one (3d)



Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:20) afforded the product (27.3 mg, 71% yield) as a pale yellow solid and the diastereoselectivity was 88:12.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (s, 1H), 7.15 (dt, *J* = 27.5, 7.7 Hz, 2H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.82 (t, *J* = 7.4 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 6.49 (d, *J* = 7.7 Hz, 2H), 3.89 – 3.75 (m, 1H), 3.50 (t, *J* = 8.0 Hz, 1H), 3.25 (dd, *J* = 21.9, 12.5 Hz, 2H), 3.09 (d, *J* = 16.5 Hz, 1H), 1.98 – 1.76 (m, 3H), 0.98 (dd, *J* = 18.9, 10.5 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 180.7, 145.0, 140.7, 135.1, 129.8, 128.1, 128.0, 124.8, 122.8, 116.5, 116.5, 109.6, 108.7, 77.3, 77.0, 76.8, 61.8, 47.5, 47.1, 34.4, 27.1, 23.4 ppm. **HRMS (ESI):** calcd. for $C_{19}H_{18}ClN_2O$ $[M+H]^+$: 325.1108, found: 325.1106.

8'-bromo-1',2',3',3a'-tetrahydro-5'H-spiro[indoline-3,4'-pyrrolo[1,2-a]quinolin]-2-one (3e)

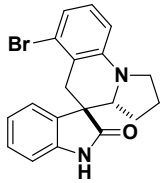


Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:20) afforded the product (36.3 mg, 56% yield) as a pale yellow solid and the diastereoselectivity was 73:27.

^{1}H NMR (500 MHz, DMSO) δ 10.79 (s, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.93 (t, *J* = 8.4 Hz, 2H), 6.75 (t, *J* = 7.4 Hz, 1H), 6.68 (s, 2H), 6.20 (d, *J* = 7.3 Hz, 1H), 3.74 – 3.64 (m, 1H), 3.51 – 3.45 (m, 1H), 3.07 (dd, *J* = 18.2, 11.9 Hz, 2H), 2.59 (d, *J* = 15.8 Hz, 1H), 1.94 – 1.75 (m, 2H), 1.75 – 1.68 (m, 1H), 0.81 – 0.66 (m, 1H); **^{13}C NMR** (126 MHz, DMSO) δ 183.5, 149.4, 146.6, 135.4, 133.6, 132.3, 128.2, 126.0,

125.2, 122.0, 121.9, 116.4, 114.0, 66.3, 51.6, 49.8, 40.6, 31.1, 27.3 ppm. **HRMS (ESI):** calcd. for $C_{19}H_{18}BrN_2O$ $[M+H]^+$: 369.0603, found: 369.0604.

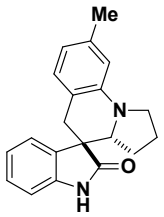
6'-bromo-1',2',3',3a'-tetrahydro-5'H-spiro[indoline-3,4'-pyrrolo[1,2-a]quinolin]-2-one (3f)



Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:20) afforded the product (31.2 mg, 78% yield) as a pale yellow solid and the diastereoselectivity was >20:1.

^{1}H NMR (500 MHz, DMSO) δ 10.71 (s, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.08 (t, *J* = 7.9 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.60 (d, *J* = 8.0 Hz, 1H), 6.29 (d, *J* = 7.2 Hz, 1H), 3.67 (d, *J* = 7.4 Hz, 1H), 3.47 (t, *J* = 8.8 Hz, 1H), 3.14 (q, *J* = 8.3 Hz, 1H), 2.99 (d, *J* = 16.3 Hz, 1H), 2.78 (d, *J* = 16.3 Hz, 1H), 1.94 – 1.67 (m, 3H), 0.86 – 0.69 (m, 1H); **^{13}C NMR** (126 MHz, DMSO) δ 183.3, 149.6, 146.5, 133.8, 133.6, 132.6, 129.4, 128.2, 126.2, 123.3, 121.6, 114.2, 114.0, 65.9, 51.8, 50.4, 41.7, 31.1, 27.4 ppm. **HRMS (ESI):** calcd. for $C_{19}H_{18}BrN_2O$ $[M+H]^+$: 369.0603, found: 369.0604.

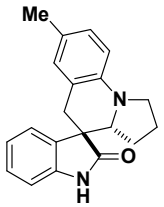
8'-methyl-1',2',3',3a'-tetrahydro-5'H-spiro[indoline-3,4'-pyrrolo[1,2-a]quinolin]-2-one (3g)



Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:20) afforded the product (25.8 mg, 76% yield) as a white solid and the diastereoselectivity was >20:1.

^{1}H NMR (500 MHz, DMSO) δ 10.71 (s, 1H), 7.11 (t, *J* = 7.7 Hz, 1H), 6.90 (d, *J* = 7.7 Hz, 1H), 6.86 (d, *J* = 7.3 Hz, 1H), 6.71 (t, *J* = 7.5 Hz, 1H), 6.37 (d, *J* = 11.0 Hz, 2H), 6.21 (d, *J* = 7.4 Hz, 1H), 3.66 (dd, *J* = 9.5, 5.6 Hz, 1H), 3.46 (t, *J* = 8.7 Hz, 1H), 3.08 (dd, *J* = 16.1, 7.1 Hz, 2H), 2.53 (d, *J* = 15.9 Hz, 1H), 2.27 (s, 3H), 1.91 – 1.81 (m, 1H), 1.81 – 1.75 (m, 1H), 1.74 – 1.66 (m, 1H), 0.80 – 0.67 (m, 1H); **^{13}C NMR** (126 MHz, DMSO) δ 179.9, 144.0, 142.6, 137.1, 130.0, 129.6, 128.1, 124.4, 121.8, 116.5, 115.6, 111.0, 109.8, 62.4, 47.5, 46.3, 36.8, 27.2, 23.4, 21.8 ppm. **HRMS (ESI):** calcd. for $C_{20}H_{21}N_2O$ $[M+H]^+$: 305.1654, found: 305.1652.

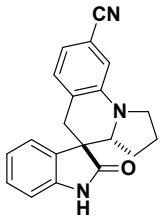
7'-methyl-1',2',3',3a'-tetrahydro-5'H-spiro[indoline-3,4'-pyrrolo[1,2-a]quinolin]-2-one (3h)



Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:20) afforded the product (58.8 mg, 68% yield) as a white solid and the diastereoselectivity was >20:1.

^{1}H NMR (500 MHz, DMSO) δ 10.67 (s, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.88 (dd, *J* = 15.5, 7.5 Hz, 2H), 6.72 (t, *J* = 7.5 Hz, 1H), 6.38 (d, *J* = 11.2 Hz, 2H), 6.21 (d, *J* = 7.4 Hz, 1H), 3.67 (dd, *J* = 9.1, 6.0 Hz, 1H), 3.47 (t, *J* = 8.6 Hz, 1H), 3.10 (d, *J* = 14.5 Hz, 2H), 2.54 (d, *J* = 15.6 Hz, 1H), 2.27 (s, 3H), 1.94 – 1.63 (m, 3H), 0.82 – 0.68 (m, 1H); **^{13}C NMR** (126 MHz, DMSO) δ 179.9, 144.0, 142.5, 137.1, 130.0, 129.6, 128.1, 124.5, 121.8, 116.5, 115.6, 111.0, 109.8, 62.4, 47.5, 46.3, 36.8, 27.2, 23.4, 21.8 ppm. **HRMS (ESI):** calcd. for $C_{20}H_{21}N_2O$ $[M+H]^+$: 305.1654, found: 305.1654.

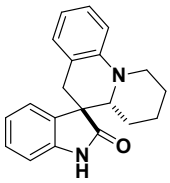
2-oxo-1',2',3',3a'-tetrahydro-5'H-spiro[indoline-3,4'-pyrrolo[1,2-a]quinoline]-8'-carbonitrile (3i)



Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:20) afforded the product (24.1 mg, 61% yield) as a white solid and the diastereoselectivity was 72:28.

^{1}H NMR (500 MHz, DMSO) δ 10.69 (s, 1H), 7.21 – 7.16 (m, 1H), 7.15 – 7.10 (m, 1H), 6.93 (dd, *J* = 22.1, 9.5 Hz, 3H), 6.74 (t, *J* = 7.4 Hz, 1H), 6.17 (d, *J* = 7.3 Hz, 1H), 3.73 (dd, *J* = 9.2, 5.8 Hz, 1H), 3.53 (t, *J* = 9.1 Hz, 1H), 3.20 – 3.07 (m, 2H), 2.72 (d, *J* = 16.3 Hz, 1H), 1.95 – 1.80 (m, 2H), 1.77 – 1.69 (m, 1H), 0.82 – 0.68 (m, 1H); **^{13}C NMR** (126 MHz, DMSO) δ 179.3, 144.4, 142.5, 130.6, 129.4, 128.5, 124.5, 124.2, 122.1, 120.1, 118.9, 112.6, 110.7, 110.0, 62.3, 47.6, 45.4, 37.0, 27.1, 23.3 ppm. **HRMS (ESI):** calcd. for $C_{20}H_{18}N_3O$ $[M+H]^+$: 316.1450, found: 316.1451.

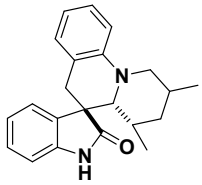
2',3',4',4a'-tetrahydro-1'H,6'H-spiro[indoline-3,5'-pyrido[1,2-a]quinolin]-2-one (3k)



Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:20) afforded the product (20.7 mg, 85% yield) as a pale yellow solid and the diastereoselectivity was 81:19.

^{1}H NMR (500 MHz, DMSO) δ 10.63 (s, 1H), 7.13 (d, *J* = 7.1 Hz, 2H), 7.05 (d, *J* = 7.6 Hz, 1H), 6.96 – 6.82 (m, 2H), 6.75 (d, *J* = 6.5 Hz, 1H), 6.59 (dd, *J* = 26.8, 12.3 Hz, 2H), 4.11 (d, *J* = 11.0 Hz, 1H), 3.21 (d, *J* = 15.5 Hz, 1H), 3.13 (t, *J* = 12.4 Hz, 1H), 2.68 (t, *J* = 11.0 Hz, 1H), 2.45 (d, *J* = 15.5 Hz, 1H), 1.86 – 1.52 (m, 2H), 1.34 (dt, *J* = 21.8, 20.9 Hz, 3H), 0.59 (d, *J* = 10.9 Hz, 1H); **^{13}C NMR** (126 MHz, DMSO) δ 179.6, 146.7, 142.3, 131.0, 130.1, 128.2, 128.0, 125.2, 121.8, 120.9, 118.1, 113.9, 109.7, 60.2, 50.0, 48.5, 37.2, 27.1, 25.9, 23.4 ppm. **HRMS (ESI):** calcd. for $C_{20}H_{21}N_2O$ $[M+H]^+$: 305.1654, found: 305.1451.

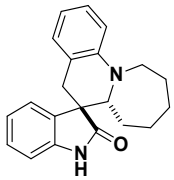
2',4'-dimethyl-2',3',4',4a'-tetrahydro-1'H,6'H-spiro[indoline-3,5'-pyrido[1,2-a]quinolin]-2-one (3l)



Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:20) afforded the product (30.8 mg, 72% yield) as a pale yellow solid and the diastereoselectivity was 87:13.

^{1}H NMR (500 MHz, DMSO) δ 10.60 (s, 1H), 7.11 (t, *J* = 7.6 Hz, 2H), 6.89 (t, *J* = 6.8 Hz, 2H), 6.71 (d, *J* = 7.2 Hz, 1H), 6.65 (t, *J* = 7.4 Hz, 1H), 6.52 (t, *J* = 7.2 Hz, 1H), 6.09 (d, *J* = 7.4 Hz, 1H), 3.97 (d, *J* = 13.0 Hz, 1H), 3.24 (d, *J* = 9.9 Hz, 1H), 2.92 (d, *J* = 14.0 Hz, 1H), 2.68 (t, *J* = 12.2 Hz, 1H), 2.24 (d, *J* = 14.0 Hz, 1H), 1.61 (dd, *J* = 28.1, 8.8 Hz, 2H), 1.07 (dd, *J* = 24.0, 5.2 Hz, 1H), 0.85 (dd, *J* = 25.0, 9.2 Hz, 4H), 0.40 (d, *J* = 6.3 Hz, 3H); **^{13}C NMR** (126 MHz, DMSO) δ 180.2, 146.5, 141.7, 130.6, 129.0, 128.3, 128.1, 125.1, 122.4, 121.2, 116.9, 113.1, 110.1, 66.4, 56.5, 52.5, 43.9, 39.2, 34.9, 30.4, 19.0, 18.5 ppm. **HRMS (ESI):** calcd. for $C_{22}H_{25}N_2O$ $[M+H]^+$: 333.1967, found: 333.1967.

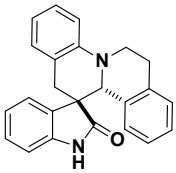
6a,7,8,9,10,11-hexahydro-5H-spiro[azepino[1,2-a]quinoline-6,3'-indolin]-2'-one (3m)



Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:20) afforded the product (30.8 mg, 32% yield) as a pale yellow solid and the diastereoselectivity was 61:39.

^{1}H NMR (500 MHz, DMSO) δ 10.60 (s, 1H), 7.16 – 7.09 (m, 2H), 6.93 (d, *J* = 7.3 Hz, 1H), 6.88 (d, *J* = 7.7 Hz, 1H), 6.81 – 6.72 (m, 2H), 6.58 (t, *J* = 7.3 Hz, 1H), 6.52 (d, *J* = 7.5 Hz, 1H), 3.60 – 3.44 (m, 2H), 3.15 (d, *J* = 15.9 Hz, 1H), 2.52 (d, *J* = 15.3 Hz, 2H), 1.71 (d, *J* = 6.0 Hz, 1H), 1.66 – 1.54 (m, 2H), 1.52 – 1.44 (m, 2H), 1.20 (ddd, *J* = 23.7, 18.2, 9.5 Hz, 3H); **^{13}C NMR** (126 MHz, DMSO) δ 180.1, 147.4, 142.4, 130.6, 129.8, 128.2, 127.8, 125.1, 121.6, 119.9, 116.6, 112.7, 109.8, 62.6, 50.1, 49.5, 37.2, 29.8, 29.4, 29.0, 26.0 ppm. **HRMS (ESI):** calcd. for $C_{22}H_{23}N_2O$ $[M+H]^+$: 319.1810, found: 319.1811.

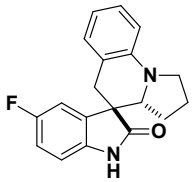
7',11b'-dihydro-6'H,13'H-spiro[indoline-3,12'-isoquinolino[2,1-a]quinolin]-2-one (3n)



Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:20) afforded the product (26.4 mg,82% yield) as a pale yellow solid and the diastereoselectivity was >20:1.

^{1}H NMR (500 MHz, DMSO) δ 10.48 (s, 1H), 7.25 (d, *J* = 5.8 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.01 (dd, *J* = 18.1, 10.6 Hz, 4H), 6.94 (d, *J* = 9.9 Hz, 2H), 6.72 – 6.57 (m, 4H), 4.78 (s, 1H), 4.06 (d, *J* = 11.0 Hz, 1H), 3.49 (d, *J* = 16.3 Hz, 1H), 3.14 (t, *J* = 10.9 Hz, 1H), 2.61 (d, *J* = 16.2 Hz, 1H), 2.55 (d, *J* = 14.3 Hz, 2H); **^{13}C NMR** (126 MHz, DMSO) δ 180.2, 145.9, 141.9, 136.5, 133.6, 131.0, 129.8, 128.3, 128.2, 127.7, 127.6, 127.0, 125.9, 125.3, 121.3, 120.0, 117.2, 112.0, 109.3, 61.8, 51.8, 43.2, 37.7, 29.5 ppm. **HRMS (ESI):** calcd. for $C_{24}H_{21}N_2O$ $[M+H]^+$: 353.1654, found: 353.1656.

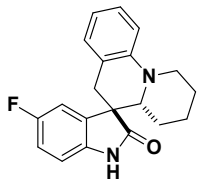
5-fluoro-1',2',3',3a'-tetrahydro-5'H-spiro[indoline-3,4'-pyrrolo[1,2-a]quinolin]-2-one (3o)



Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:20) afforded the product (30.8 mg, 68% yield) as a white solid and the diastereoselectivity was >20:1.

^{1}H NMR (500 MHz, DMSO) δ 10.66 (s, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 6.99 (dd, *J* = 18.3, 8.3 Hz, 2H), 6.93 – 6.83 (m, 1H), 6.58 (t, *J* = 7.2 Hz, 2H), 5.91 (d, *J* = 8.6 Hz, 1H), 3.70 (dd, *J* = 8.6, 6.3 Hz, 1H), 3.48 (t, *J* = 8.5 Hz, 1H), 3.13 (dd, *J* = 25.1, 12.0 Hz, 2H), 2.62 (d, *J* = 15.6 Hz, 1H), 1.96 – 1.68 (m, 3H), 0.81 – 0.65 (m, 1H); **^{13}C NMR** (126 MHz, DMSO) δ 179.5, 158.8, 156.9, 143.7, 138.7, 131.4, 129.7, 128.3, 117.8, 115.7, 114.4, 111.7, 110.3, 62.2, 47.4, 46.5, 46.5, 36.7, 27.0, 23.1 ppm. **HRMS (ESI):** calcd. for $C_{19}H_{18}FN_2O$ $[M+H]^+$: 308.1403, found: 308.1401.

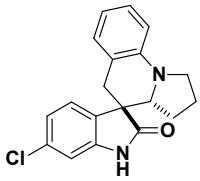
5-fluoro-2',3',4',4a'-tetrahydro-1'H,6'H-spiro[indoline-3,5'-pyrido[1,2-a]quinolin]-2-one (3p)



Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:20) afforded the product (28.2 mg, 79% yield) as a pale yellow solid and the diastereoselectivity was >20:1.

^{1}H NMR (500 MHz, DMSO) δ 10.71 (s, 1H), 7.16 (t, *J* = 7.3 Hz, 1H), 7.09 (d, *J* = 8.1 Hz, 1H), 7.01 (t, *J* = 8.8 Hz, 1H), 6.91 (dd, *J* = 14.7, 6.4 Hz, 2H), 6.68 (t, *J* = 6.8 Hz, 1H), 6.31 (d, *J* = 8.5 Hz, 1H), 4.14 (d, *J* = 11.8 Hz, 1H), 3.21 (dd, *J* = 37.1, 13.4 Hz, 2H), 2.70 (t, *J* = 11.8 Hz, 1H), 2.50 (d, *J* = 16.7 Hz, 1H), 1.71 (d, *J* = 11.6 Hz, 1H), 1.60 (d, *J* = 10.9 Hz, 1H), 1.50 – 1.21 (m, 3H), 0.60 (q, *J* = 11.9 Hz, 1H); **^{13}C NMR** (126 MHz, DMSO) δ 179.3, 158.0, 146.4, 138.6, 138.6, 132.5, 132.5, 130.2, 128.1, 120.4, 118.3, 114.4, 113.9, 112.6, 110.3, 59.9, 50.4, 50.4, 48.3, 36.9, 27.0, 25.8, 23.2 ppm. **HRMS (ESI):** calcd. for $C_{20}H_{20}FN_2O$ $[M+H]^+$: 323.1560, found: 323.1561.

6-chloro-1',2',3',3a'-tetrahydro-5'H-spiro[indoline-3,4'-pyrrolo[1,2-a]quinolin]-2-one (3q)

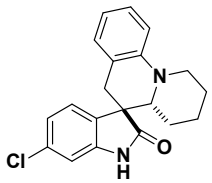


Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:20) afforded the product (33.2 mg, 76% yield) as a white solid and the diastereoselectivity was 72:28.

^{1}H NMR (500 MHz, DMSO) δ 10.78 (s, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 7.2 Hz, 1H), 6.90 (s, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.56 (t, *J* = 7.6 Hz, 2H), 6.16 (d, *J* = 8.0 Hz, 1H), 3.75 – 3.63 (m, 1H), 3.47 (t, *J* = 8.6 Hz, 1H), 3.20 – 3.02 (m, 2H), 2.61 (d, *J* = 15.7 Hz, 1H), 1.94 – 1.67 (m, 3H), 0.82 – 0.67 (m, 1H); **^{13}C NMR** (126 MHz, DMSO) δ 179.8, 144.1, 143.9, 132.7, 129.8, 128.8, 128.3, 125.7, 121.6, 118.2,

115.8, 110.5, 109.9, 62.3, 47.5, 46.1, 36.8, 27.2, 23.3 ppm. **HRMS (ESI):** calcd. for $C_{20}H_{19}ClN_2O$ $[M+H]^+$: 325.1108, found: 316.1109.

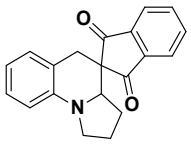
6-chloro-2',3',4',4a'-tetrahydro-1'H,6'H-spiro[indoline-3,5'-pyrido[1,2-a]quinolin]-2-one (3r)



Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:20) afforded the product (27.4 mg, 81% yield) as a pale yellow solid and the diastereoselectivity was >20:1.

^{1}H NMR (500 MHz, DMSO) δ 10.80 (s, 1H), 7.10 (d, *J* = 7.1 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.92 – 6.86 (m, 2H), 6.84 – 6.79 (m, 1H), 6.63 (t, *J* = 6.7 Hz, 1H), 6.51 (d, *J* = 7.9 Hz, 1H), 4.08 (d, *J* = 11.8 Hz, 1H), 3.21 (d, *J* = 15.6 Hz, 1H), 3.13 (d, *J* = 11.1 Hz, 1H), 2.66 (t, *J* = 11.6 Hz, 1H), 2.45 (d, *J* = 15.6 Hz, 1H), 1.68 (d, *J* = 9.9 Hz, 1H), 1.56 (d, *J* = 8.9 Hz, 1H), 1.39 (d, *J* = 12.2 Hz, 1H), 1.34 – 1.18 (m, 2H), 0.57 (q, *J* = 11.3 Hz, 1H); **^{13}C NMR** (126 MHz, DMSO) δ 179.5, 146.6, 143.9, 132.8, 130.2, 129.8, 128.1, 126.5, 121.5, 120.6, 118.3, 113.9, 109.9, 60.1, 49.9, 48.4, 37.0, 27.1, 25.8, 23.3 ppm. **HRMS (ESI):** calcd. for $C_{20}H_{20}ClN_2O$ $[M+H]^+$: 339.1264, found: 339.1266.

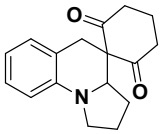
1',2',3',3a'-tetrahydro-5'H-spiro[indene-2,4'-pyrrolo[1,2-a]quinoline]-1,3-dione (5a)



Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:50) afforded the product (19.3 mg, 87% yield) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 5.8, 2.0 Hz, 1H), 7.88 – 7.79 (m, 3H), 7.18 (t, *J* = 7.7 Hz, 1H), 7.00 (d, *J* = 7.3 Hz, 1H), 6.62 (dd, *J* = 12.1, 7.8 Hz, 2H), 3.88 (dd, *J* = 10.2, 5.6 Hz, 1H), 3.62 – 3.54 (m, 1H), 3.35 – 3.24 (m, 2H), 2.81 (d, *J* = 16.1 Hz, 1H), 1.95 (tdd, *J* = 8.1, 4.4, 2.0 Hz, 2H), 1.85 (dtd, *J* = 8.5, 5.7, 2.4 Hz, 1H), 1.39 – 1.19 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 202.7, 199.6, 143.8, 142.4, 141.3, 135.9, 135.3, 128.5, 127.7, 123.1, 123.0, 117.9, 115.5, 110.7, 61.1, 51.4, 47.4, 34.2, 28.0, 23.7 ppm. **HRMS (ESI):** calcd. for $C_{20}H_{18}NO_2$ $[M+H]^+$: 304.1338, found: 304.1335.

1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,6-dione (5b)

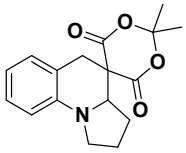


Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:30) afforded the product (16.0 mg, 79% yield) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (dd, *J* = 13.7, 6.6 Hz, 1H), 6.93 (t, *J* = 6.4 Hz, 1H), 6.52 (dt, *J* = 20.3, 6.9 Hz, 2H), 3.97 (dt, *J* = 12.0, 5.9 Hz, 1H), 3.55 (d, *J* = 7.3 Hz, 1H), 3.33 – 3.20 (m, 1H), 3.12 (d, *J* = 5.9 Hz, 2H), 2.86 (ddd, *J* = 16.2, 11.5, 5.9 Hz, 1H), 2.73 (dt, *J* = 16.2, 6.0 Hz, 1H), 2.62 (dd, *J* = 16.0, 5.7 Hz, 1H), 2.40 (dd, *J* = 15.7, 5.5 Hz, 1H), 2.14 (dt, *J* = 18.5, 6.1 Hz, 1H), 2.10 – 1.95 (m, 3H), 1.93 –

1.80 (m, 1H), 1.77 – 1.64 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 209.9, 205.2, 144.3, 128.3, 128.0, 116.0, 114.8, 110.7, 60.8, 60.5, 47.8, 39.8, 38.9, 38.7, 27.3, 24.2, 17.4 ppm. **HRMS (ESI):** calcd. for $C_{17}H_{20}NO_2$ $[M+H]^+$: 270.1494, found: 270.1494.

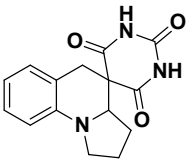
2',2'-dimethyl-1,2,3,3a-tetrahydro-5H-spiro[pyrrolo[1,2-a]quinoline-4,5'-[1,3]dioxane]-4',6'-dione (5c)



Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:20) afforded the product (10.8 mg, 52% yield) as a pale yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (t, *J* = 7.7 Hz, 1H), 7.07 (d, *J* = 7.4 Hz, 1H), 6.73 – 6.61 (m, 2H), 4.00 (dd, *J* = 8.8, 6.3 Hz, 1H), 3.64 (ddd, *J* = 35.6, 20.8, 9.4 Hz, 2H), 3.34 (dd, *J* = 16.0, 8.7 Hz, 1H), 3.17 (d, *J* = 16.3 Hz, 1H), 2.23 (dtd, *J* = 9.3, 6.7, 2.8 Hz, 1H), 2.11 – 1.95 (m, 2H), 1.80 (d, *J* = 14.3 Hz, 6H), 1.71 (dt, *J* = 19.7, 8.9 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.0, 170.0, 164.0, 164.0, 143.1, 143.1, 128.2, 128.2, 127.7, 127.7, 116.9, 116.9, 116.0, 116.0, 111.4, 111.4, 104.6, 104.6, 64.6, 64.6, 47.8, 47.8, 47.2, 47.2, 36.4, 36.4, 29.9, 29.9, 28.4, 28.4, 28.1, 28.1, 23.1, 23.1 ppm. **HRMS (ESI):** calcd. for $C_{17}H_{20}NO_4$ $[M+H]^+$: 302.1392, found: 270.1394.

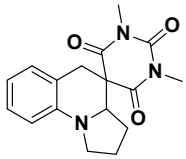
1',2',3',3a'-tetrahydro-2H,5'H-spiro[pyrimidine-5,4'-pyrrolo[1,2-a]quinoline]-2,4,6(1H,3H)-trione (5d)



Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:20) afforded the product (15.4 mg, 72% yield) as a pale yellow solid.

^{1}H NMR (500 MHz, DMSO) δ 11.48 (s, 1H), 11.20 (s, 1H), 7.04 – 6.95 (m, 2H), 6.56 – 6.47 (m, 2H), 3.60 (dd, *J* = 8.9, 6.2 Hz, 1H), 3.46 (td, *J* = 8.4, 4.0 Hz, 1H), 3.24 (d, *J* = 16.6 Hz, 1H), 3.15 – 3.06 (m, 2H), 2.04 (dtd, *J* = 10.2, 6.4, 3.7 Hz, 1H), 1.97 – 1.85 (m, 2H), 1.55 (dq, *J* = 11.8, 9.0 Hz, 1H); **^{13}C NMR** (126 MHz, DMSO) δ 172.6, 169.2, 150.7, 143.8, 128.2, 126.9, 120.0, 115.7, 111.4, 63.3, 48.4, 47.8, 34.9, 27.8, 23.2 ppm. **HRMS (ESI):** calcd. for $C_{15}H_{16}N_3O_3$ $[M+H]^+$: 286.1192, found: 286.1195.

1,3-dimethyl-1',2',3',3a'-tetrahydro-2H,5'H-spiro[pyrimidine-5,4'-pyrrolo[1,2-a]quinoline]-2,4,6(1H,3H)-trione (5e)

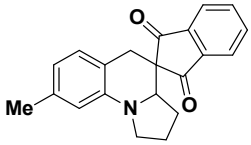


Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:20) afforded the product (57.2 mg, 76% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (t, *J* = 7.7 Hz, 1H), 7.02 (d, *J* = 7.4 Hz, 1H), 6.71 – 6.54 (m, 2H), 3.91 (dd, *J* = 9.1, 6.0 Hz, 1H), 3.63 – 3.53 (m, 2H), 3.41 – 3.28 (m, 4H), 3.22 (s, 3H), 3.01 (d, *J* = 16.3

Hz, 1H), 2.06 (dt, *J* = 17.3, 5.7 Hz, 1H), 2.02 – 1.94 (m, 2H), 1.52 – 1.42 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.7, 166.8, 151.1, 143.2, 128.0, 127.5, 118.1, 116.1, 111.1, 63.9, 48.9, 47.7, 37.1, 29.0, 28.3, 27.9, 23.2 ppm. **HRMS (ESI):** calcd. for $C_{17}H_{20}N_3O_3$ $[M+H]^+$: 314.1505, found: 314.1504.

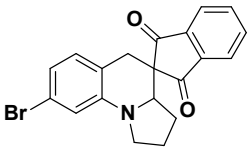
8'-methyl-1',2',3',3a'-tetrahydro-5'H-spiro[indene-2,4'-pyrrolo[1,2-a]quinoline]-1,3-dione (5f)



Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:50) afforded the product (27.4 mg, 63% yield) as a pale yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 6.3 Hz, 1H), 7.83 (d, *J* = 12.3 Hz, 3H), 6.89 (d, *J* = 7.1 Hz, 1H), 6.44 (d, *J* = 11.4 Hz, 2H), 3.87 (dd, *J* = 8.9, 4.1 Hz, 1H), 3.57 (t, *J* = 8.1 Hz, 1H), 3.37 – 3.17 (m, 2H), 2.78 (d, *J* = 16.0 Hz, 1H), 2.33 (s, 3H), 2.03 – 1.76 (m, 3H), 1.36 – 1.20 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 202.7, 199.6, 143.6, 142.4, 141.2, 137.2, 135.8, 135.3, 128.3, 123.0, 122.9, 116.5, 114.9, 111.4, 61.0, 51.6, 47.3, 34.0, 28.0, 23.7, 21.6 ppm. **HRMS (ESI):** calcd. for $C_{21}H_{20}NO_2$ $[M+H]^+$: 318.1494, found: 318.1492.

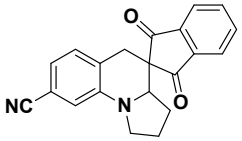
8'-bromo-1',2',3',3a'-tetrahydro-5'H-spiro[indene-2,4'-pyrrolo[1,2-a]quinoline]-1,3-dione (5g)



Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:50) afforded the product (33.6 mg, 62% yield) as a pale yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 4.8 Hz, 1H), 7.85 (d, *J* = 5.0 Hz, 3H), 6.84 (d, *J* = 7.5 Hz, 1H), 6.72 (d, *J* = 7.5 Hz, 2H), 3.92 – 3.80 (m, 1H), 3.54 (t, *J* = 8.3 Hz, 1H), 3.34 – 3.13 (m, 2H), 2.76 (d, *J* = 16.2 Hz, 1H), 2.05 – 1.78 (m, 3H), 1.35 – 1.20 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 202.2, 199.4, 144.8, 142.3, 141.2, 136.0, 135.5, 129.6, 123.2, 123.0, 121.4, 118.2, 116.8, 113.2, 60.9, 50.9, 47.3, 33.7, 27.9, 23.7 ppm. **HRMS (ESI):** calcd. for $C_{20}H_{17}BrNO_2$ $[M+H]^+$: 382.0443, found: 382.0442.

1,3-dioxo-1,1',2',3,3',3a'-hexahydro-5'H-spiro[indene-2,4'-pyrrolo[1,2-a]quinoline]-8'-carbonitrile (5h)

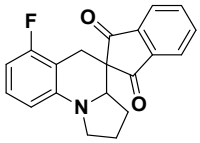


Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:50) afforded the product (33.6 mg, 62% yield) as a pale yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 4.6 Hz, 1H), 7.87 (s, 3H), 7.05 (d, *J* = 7.3 Hz, 1H), 6.89 (d, *J* = 7.3 Hz, 1H), 6.78 (s, 1H), 3.88 (dd, *J* = 9.2, 4.1 Hz, 1H), 3.57 (t, *J* = 8.4 Hz, 1H), 3.26 (t, *J* = 13.4 Hz, 2H), 2.83 (d, *J* = 16.6 Hz, 1H), 2.09 – 1.82 (m, 3H), 1.37 – 1.20 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 201.6, 199.3, 143.9, 142.2, 141.2, 136.2, 135.7, 129.0, 123.3, 123.2, 123.1, 119.9, 118.9, 113.0,

111.1, 61.0, 50.3, 47.3, 33.9, 27.9, 23.6 ppm. **HRMS (ESI):** calcd. for $C_{20}H_{17}BrNO_2$ $[M+H]^+$: 382.0443, found: 382.0442.

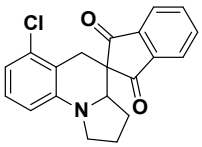
6'-fluoro-1',2',3',3a'-tetrahydro-5'H-spiro[indene-2,4'-pyrrolo[1,2-a]quinoline]-1,3-dione (5i)



Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:50) afforded the product (31.5 mg, 81% yield) as a pale yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 6.0 Hz, 1H), 7.94 – 7.77 (m, 3H), 7.11 (q, *J* = 7.1 Hz, 1H), 6.37 (t, *J* = 9.5 Hz, 2H), 3.91 – 3.76 (m, 1H), 3.57 (t, *J* = 7.9 Hz, 1H), 3.40 – 3.24 (m, 1H), 3.02 (dd, *J* = 38.5, 16.7 Hz, 2H), 2.09 – 1.77 (m, 3H), 1.28 (dd, *J* = 19.4, 9.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.3, 199.4, 162.0, 160.1, 145.2, 145.2, 142.3, 141.3, 136.0, 135.5, 128.0, 127.9, 123.1, 123.0, 106.3, 106.3, 105.3, 105.1, 102.2, 102.0, 60.5, 53.4, 50.5, 47.6, 28.0, 26.6, 26.6, 23.6 ppm. **HRMS (ESI):** calcd. for $C_{20}H_{17}FNO_2$ $[M+H]^+$: 322.1243, found: 322.1242.

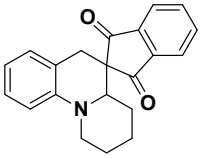
6'-chloro-1',2',3',3a'-tetrahydro-5'H-spiro[indene-2,4'-pyrrolo[1,2-a]quinoline]-1,3-dione (5j)



Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:50) afforded the product (20.9 mg, 79% yield) as a pale yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.86 (d, *J* = 12.0 Hz, 3H), 7.08 (d, *J* = 7.0 Hz, 1H), 6.69 (d, *J* = 7.1 Hz, 1H), 6.51 (d, *J* = 7.5 Hz, 1H), 3.81 (s, 1H), 3.55 (s, 1H), 3.32 (d, *J* = 7.9 Hz, 1H), 3.15 (d, *J* = 16.9 Hz, 1H), 3.05 (d, *J* = 17.0 Hz, 1H), 1.95 (s, 2H), 1.86 (d, *J* = 8.9 Hz, 1H), 1.36 – 1.23 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 202.1, 199.6, 145.0, 142.4, 141.4, 136.1, 135.6, 134.0, 127.9, 123.2, 123.1, 116.3, 116.1, 109.2, 60.6, 51.3, 47.5, 31.2, 28.1, 23.7 ppm. **HRMS (ESI):** calcd. for $C_{20}H_{17}ClNO_2$ $[M+H]^+$: 338.0948, found: 338.0949.

2',3',4',4a'-tetrahydro-1'H,6'H-spiro[indene-2,5'-pyrido[1,2-a]quinoline]-1,3-dione (5k)

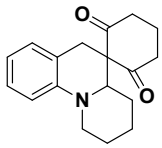


Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:50) afforded the product (20.9 mg, 82% yield) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 25.6, 2.7 Hz, 2H), 7.84 (d, *J* = 2.8 Hz, 2H), 7.17 (t, *J* = 7.3 Hz, 1H), 6.95 (dd, *J* = 25.3, 7.5 Hz, 2H), 6.69 (t, *J* = 6.8 Hz, 1H), 4.14 (d, *J* = 12.3 Hz, 1H), 3.36 (d, *J* = 11.6 Hz, 1H), 3.24 (d, *J* = 16.1 Hz, 1H), 2.78 (dd, *J* = 27.1, 14.4 Hz, 2H), 1.70 (s, 2H), 1.60 (dd, *J* = 15.1, 10.0 Hz, 1H), 1.45 (d, *J* = 12.3 Hz, 1H), 1.34 (dd, *J* = 24.2, 11.4 Hz, 1H), 1.15 (q, *J* = 12.2 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 202.2, 199.6, 145.7, 142.1, 141.2, 135.9, 135.4, 129.0, 127.5, 123.2, 123.1,

120.2, 117.6, 113.2, 59.5, 55.0, 48.8, 32.9, 28.5, 24.9, 24.1 ppm. **HRMS (ESI):** calcd. for $C_{21}H_{20}NO_2$ $[M+H]^+$: 318.1494, found: 318.1494.

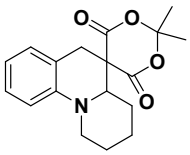
2',3',4',4a'-tetrahydro-1'H,6'H-spiro[cyclohexane-1,5'-pyrido[1,2-a]quinoline]-2,6-dione (5l)



Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:50) afforded the product (26.9 mg, 78% yield) as a pale yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (d, *J* = 6.2 Hz, 1H), 7.06 (s, 1H), 6.77 (d, *J* = 7.6 Hz, 2H), 4.08 (dd, *J* = 29.7, 12.9 Hz, 2H), 3.25 (d, *J* = 17.0 Hz, 1H), 3.13 (dd, *J* = 15.8, 10.4 Hz, 1H), 3.00 (t, *J* = 13.0 Hz, 1H), 2.95 – 2.76 (m, 2H), 2.59 (dd, *J* = 45.8, 13.9 Hz, 2H), 2.19 (s, 1H), 1.86 (d, *J* = 10.1 Hz, 1H), 1.61 (dd, *J* = 25.8, 13.7 Hz, 3H), 1.37 (d, *J* = 11.9 Hz, 2H), 1.21 (d, *J* = 12.8 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 205.4, 204.4, 141.6, 129.6, 126.7, 122.3, 118.4, 113.43, 77.2, 77.0, 76.7, 70.1, 63.3, 50.3, 37.7, 35.9, 25.9, 24.1, 23.8, 20.8, 18.6 ppm. **HRMS (ESI):** calcd. for $C_{18}H_{22}NO_2$ $[M+H]^+$: 284.1651, found: 284.1654.

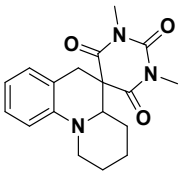
2',2'-dimethyl-2,3,4,4a-tetrahydro-1H,6H-spiro[pyrido[1,2-a]quinoline-5,5'-[1,3]dioxane]-4',6'-dione (5m)



Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:50) afforded the product (21.4 mg, 71% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (t, *J* = 7.4 Hz, 1H), 6.97 (dd, *J* = 15.9, 7.7 Hz, 2H), 6.74 (t, *J* = 6.8 Hz, 1H), 4.11 (d, *J* = 12.2 Hz, 1H), 3.53 (d, *J* = 16.3 Hz, 1H), 3.45 (d, *J* = 10.1 Hz, 1H), 3.13 (d, *J* = 16.3 Hz, 1H), 2.79 (t, *J* = 12.4 Hz, 1H), 1.88 (d, *J* = 10.1 Hz, 1H), 1.76 (d, *J* = 10.8 Hz, 8H), 1.64 (dd, *J* = 21.8, 12.3 Hz, 1H), 1.49 – 1.33 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.3, 164.8, 144.8, 128.6, 127.5, 119.3, 118.2, 113.3, 105.0, 61.6, 52.1, 48.6, 34.3, 30.2, 28.0, 28.0, 24.5, 23.8 ppm. **HRMS (ESI):** calcd. for $C_{18}H_{22}NO_4$ $[M+H]^+$: 316.1549, found: 316.1547.

1',3'-dimethyl-2,3,4,4a-tetrahydro-1H,2'H,6H-spiro[pyrido[1,2-a]quinoline-5,5'-pyrimidine]-2',4',6'(1'H,3'H)-trione (5n)

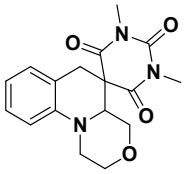


Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:50) afforded the product (31.2 mg, 75% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 – 7.10 (m, 1H), 7.02 (d, *J* = 7.4 Hz, 1H), 6.92 (d, *J* = 8.3 Hz, 1H), 6.75 (td, *J* = 7.4, 0.8 Hz, 1H), 4.12 (d, *J* = 12.7 Hz, 1H), 3.41 (dd, *J* = 11.7, 2.2 Hz, 1H), 3.38 – 3.32 (m,

4H), 3.30 (s, 3H), 3.20 (d, J = 16.6 Hz, 1H), 2.81 (ddd, J = 15.5, 8.5, 4.5 Hz, 1H), 1.82 (dd, J = 9.3, 6.9 Hz, 1H), 1.67 – 1.58 (m, 2H), 1.50 – 1.40 (m, 2H), 1.36 – 1.24 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.4, 167.9, 151.3, 143.8, 128.6, 127.1, 120.8, 118.2, 113.2, 62.6, 53.5, 49.0, 32.2, 29.0, 28.7, 26.5, 24.3, 23.3 ppm. **HRMS (ESI):** calcd. for $C_{18}H_{22}N_3O_3$ $[M+H]^+$: 238.1661, found: 238.1663.

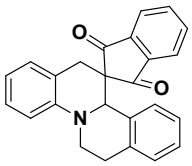
1,3-dimethyl-1',2',4',4a'-tetrahydro-2H,6'H-spiro[pyrimidine-5,5'-[1,4]oxazino[4,3-a]quinoline]-2,4,6(1H,3H)-trione (5o)



Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:50) afforded the product (20.5 mg, 82% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (t, J = 7.6 Hz, 1H), 7.02 (d, J = 7.4 Hz, 1H), 6.90 (d, J = 8.3 Hz, 1H), 6.81 (td, J = 7.4, 0.8 Hz, 1H), 3.98 – 3.92 (m, 1H), 3.82 (dt, J = 12.3, 2.4 Hz, 1H), 3.70 (t, J = 2.4 Hz, 1H), 3.68 (t, J = 2.7 Hz, 1H), 3.60 (d, J = 2.9 Hz, 1H), 3.59 – 3.56 (m, 1H), 3.36 (s, 3H), 3.30 – 3.26 (m, 4H), 3.10 – 3.02 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.6, 167.0, 150.6, 143.9, 128.6, 127.2, 120.5, 119.2, 112.7, 66.5, 66.4, 59.8, 49.8, 46.8, 35.1, 29.0, 28.5 ppm. **HRMS (ESI):** calcd. for $C_{17}H_{20}N_3O_4$ $[M+H]^+$: 330.1454, found: 330.1451.

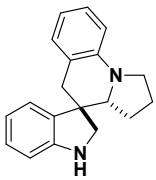
7',11b'-dihydro-6'H,13'H-spiro[indene-2,12'-isoquinolino[2,1-a]quinoline]-1,3-dione (5p)



Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:50) afforded the product (17.4 mg, 69% yield) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, J = 6.9 Hz, 1H), 7.61 (dd, J = 22.1, 6.8 Hz, 3H), 7.21 (t, J = 7.1 Hz, 1H), 7.13 (d, J = 6.7 Hz, 1H), 6.89 (dd, J = 19.7, 9.7 Hz, 4H), 6.79 (dd, J = 17.6, 9.9 Hz, 2H), 4.84 (s, 1H), 3.98 (d, J = 10.2 Hz, 1H), 3.54 (d, J = 16.8 Hz, 1H), 3.33 (t, J = 11.4 Hz, 1H), 2.99 (t, J = 13.3 Hz, 1H), 2.88 (d, J = 16.8 Hz, 1H), 2.59 (d, J = 15.2 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 202.5, 200.5, 146.2, 142.6, 142.0, 135.9, 135.1, 134.8, 132.3, 128.8, 128.5, 127.7, 127.1, 126.9, 125.7, 122.7, 122.2, 120.6, 117.6, 112.8, 62.6, 58.3, 44.0, 32.2, 29.6 ppm. **HRMS (ESI):** calcd. for $C_{25}H_{20}NO_2$ $[M+H]^+$: 366.1494, found: 366.1497.

1',2',3',3a'-tetrahydro-5'H-spiro[indoline-3,4'-pyrrolo[1,2-a]quinoline] (6a)



Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:20) afforded the product (13.8 mg, 50% yield) as a yellow solid.

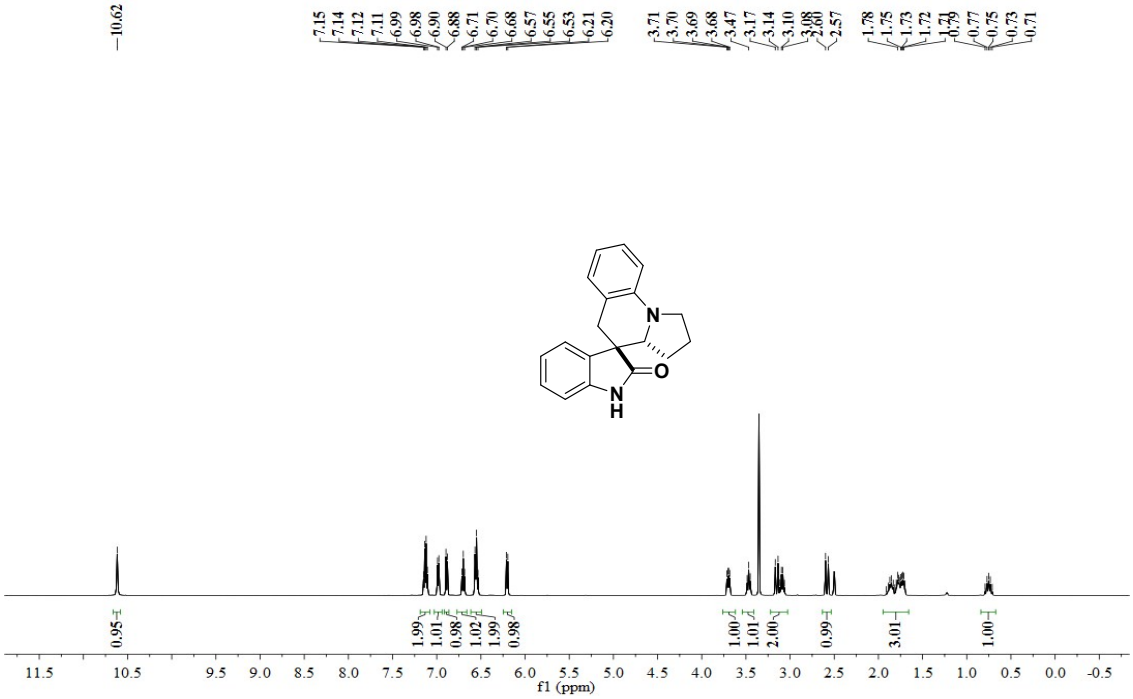
^{1}H NMR (500 MHz, DMSO) δ 7.05 (t, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 7.2 Hz, 1H), 6.85 (t, *J* = 7.6 Hz, 1H), 6.48 (t, *J* = 8.0 Hz, 2H), 6.42 (d, *J* = 8.0 Hz, 1H), 6.26 (t, *J* = 7.4 Hz, 1H), 6.11 (d, *J* = 7.3 Hz, 1H), 3.50 (dd, *J* = 10.2, 5.4 Hz, 1H), 3.39 – 3.32 (m, 2H), 3.25 (d, *J* = 9.5 Hz, 1H), 3.05 (q, *J* = 8.6 Hz, 1H), 2.95 (d, *J* = 15.7 Hz, 1H), 2.75 (d, *J* = 15.8 Hz, 1H), 1.99 – 1.91 (m, 1H), 1.87 – 1.78 (m, 2H), 1.11 – 0.97 (m, 1H); **^{13}C NMR** (126 MHz, DMSO) δ 153.3, 144.7, 131.0, 129.2, 127.9, 127.8, 124.7, 120.2, 117.1, 115.2, 109.6, 108.7, 64.8, 58.0, 47.3, 43.6, 41.0, 28.1, 23.5 ppm. **HRMS (ESI):** calcd. for $C_{19}H_{21}N$ $[M+H]^+$: 277.1699, found: 277.1705.

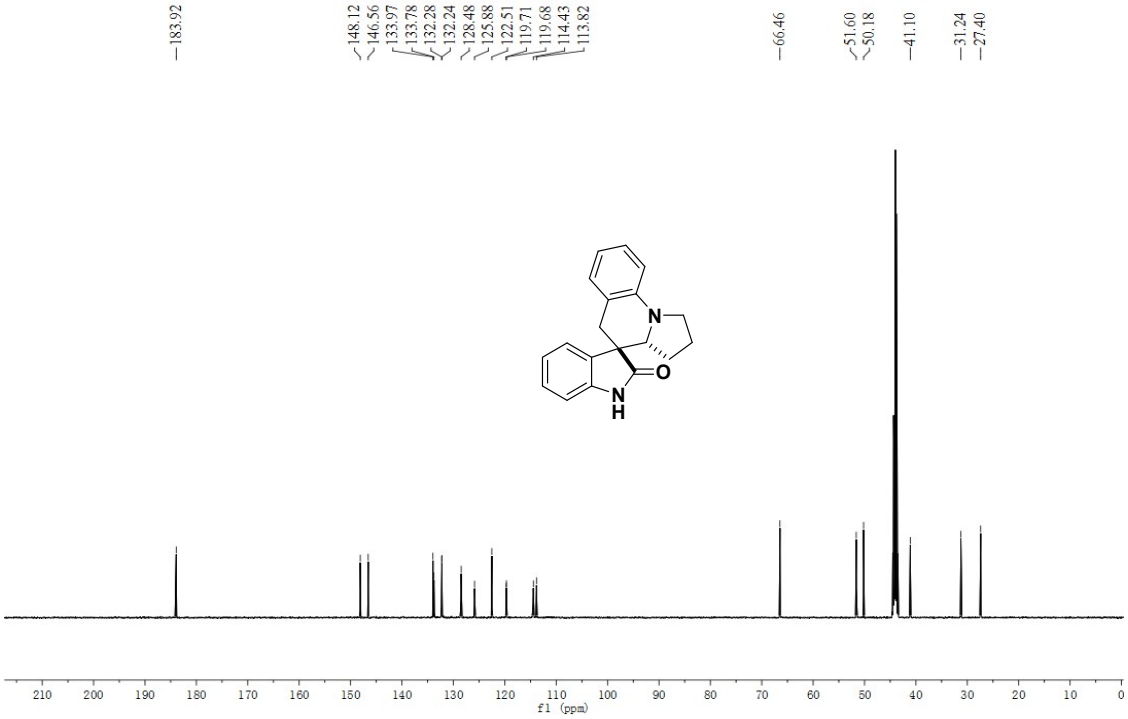
Reference

1. I. D. Jurberg, B. Peng, E. Wçstefeld, M. Wasserloos, N. Maulide, *Angew. Chem. Int. Ed.* **2012**, *51*, 1950.

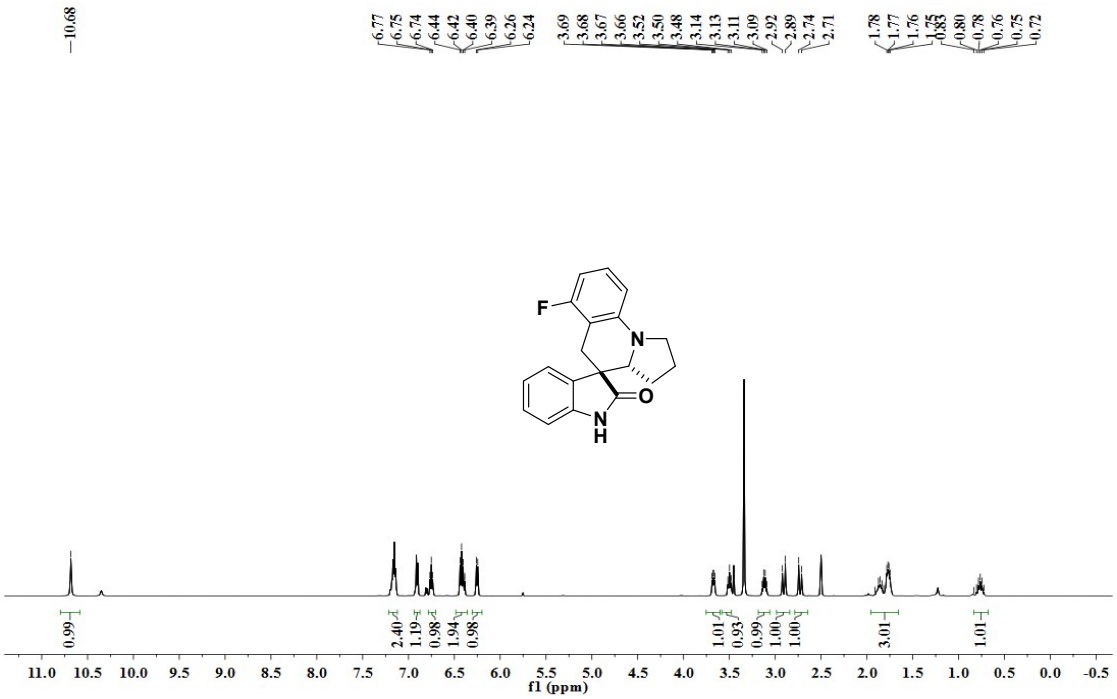
4. ^{1}H and ^{13}C NMR Spectra

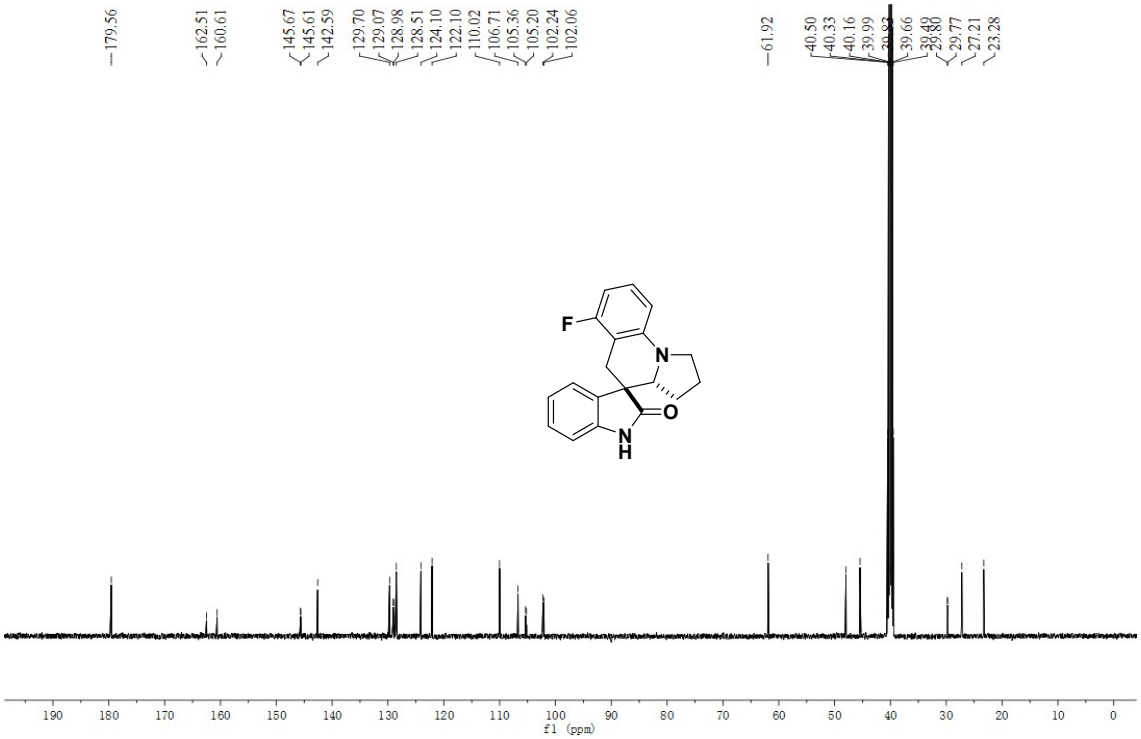
1',2',3',3a'-tetrahydro-5'H-spiro[indoline-3,4'-pyrrolo[1,2-a]quinolin]-2-one (3a)



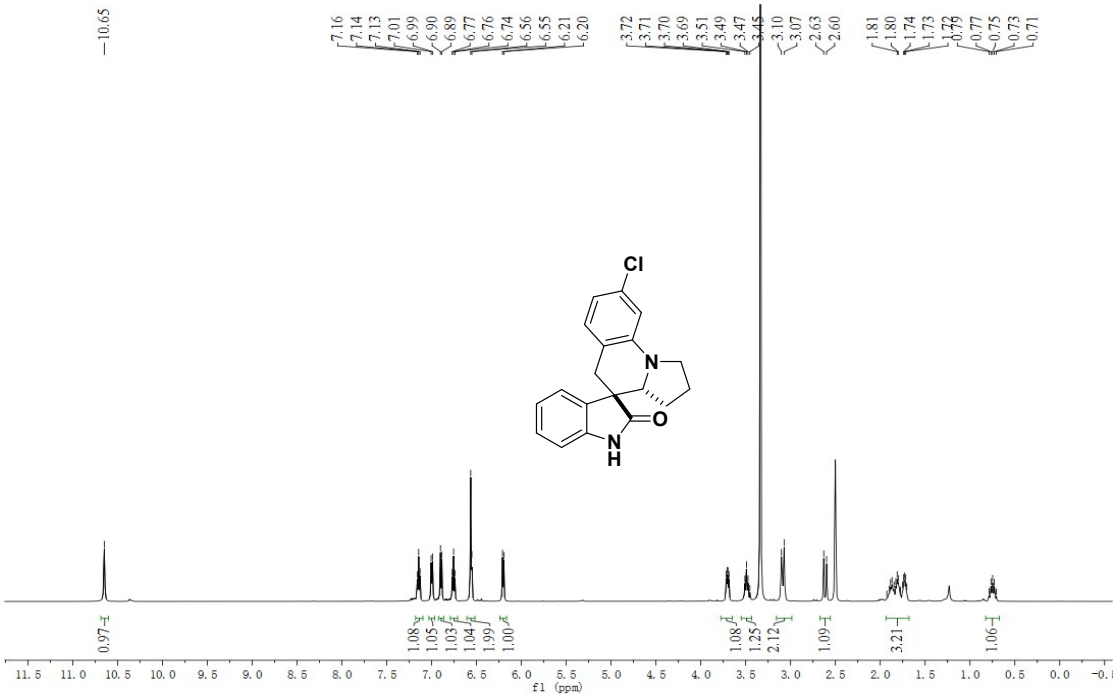


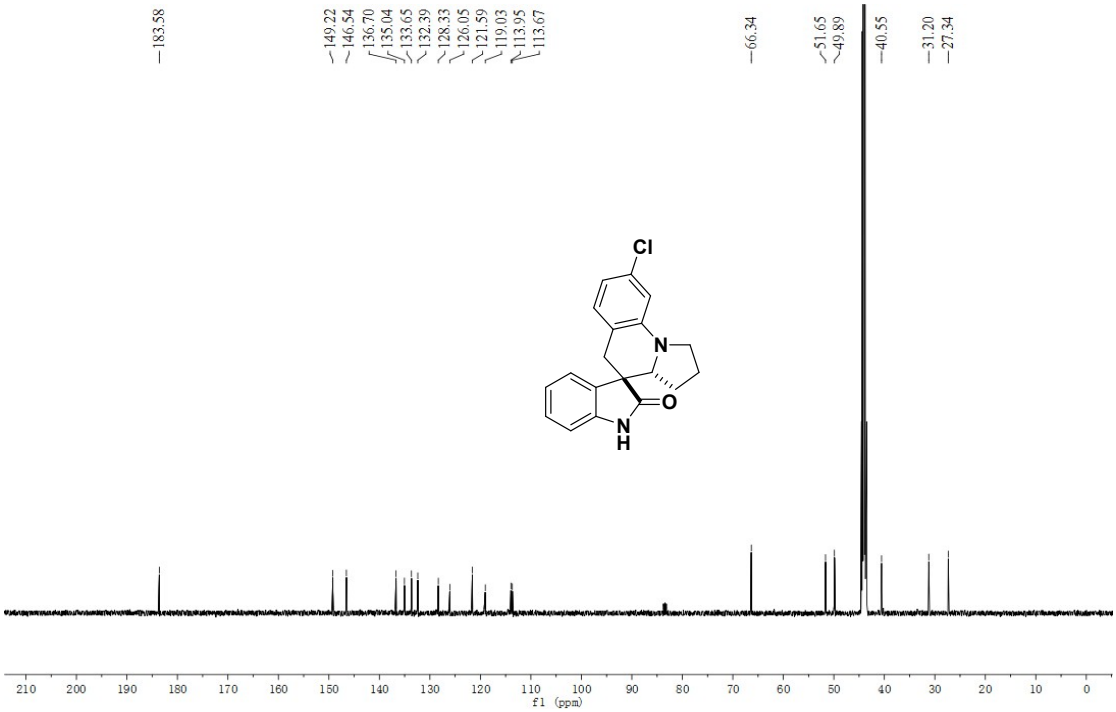
6'-fluoro-1',2',3',3a'-tetrahydro-5'H-spiro[indoline-3,4'-pyrrolo[1,2-a]quinolin]-2-one (3b)



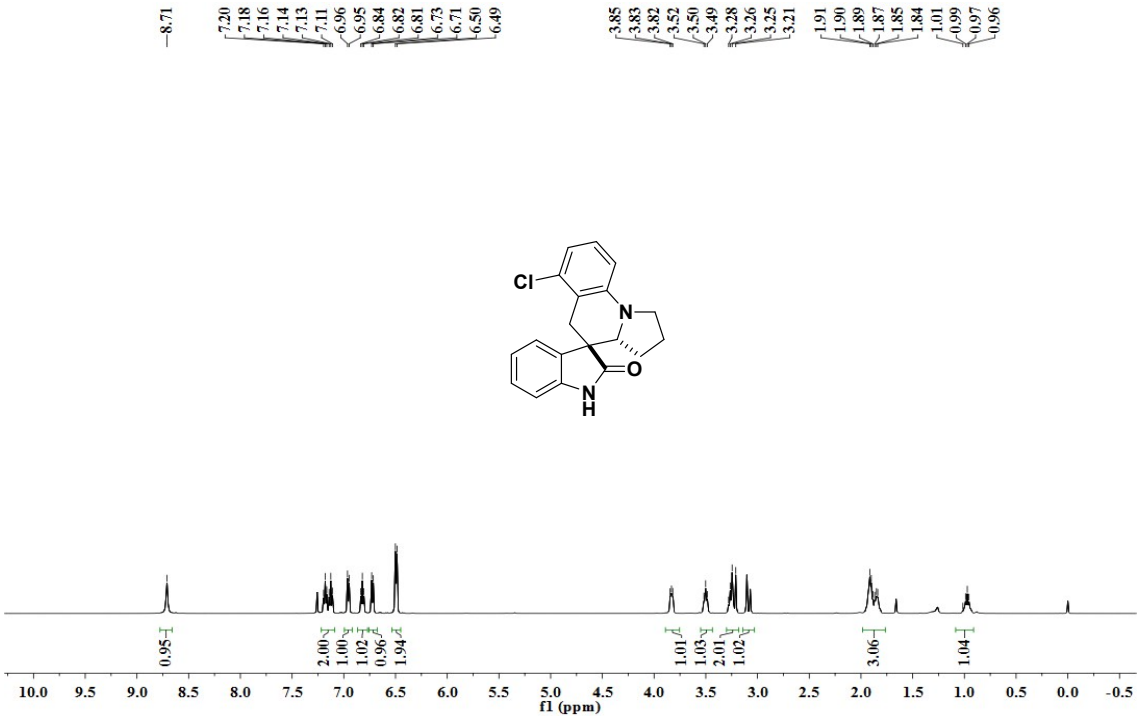


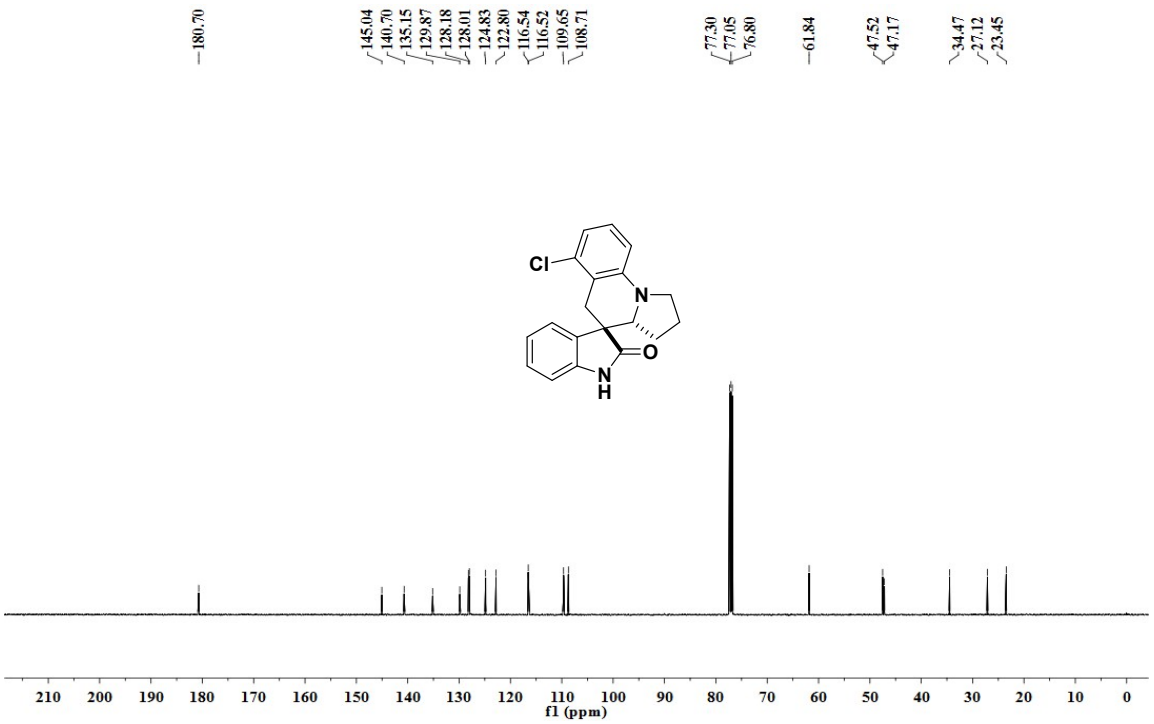
8'-chloro-1',2',3',3a'-tetrahydro-5'H-spiro[indoline-3,4'-pyrrolo[1,2-a]quinolin]-2-one (3c)



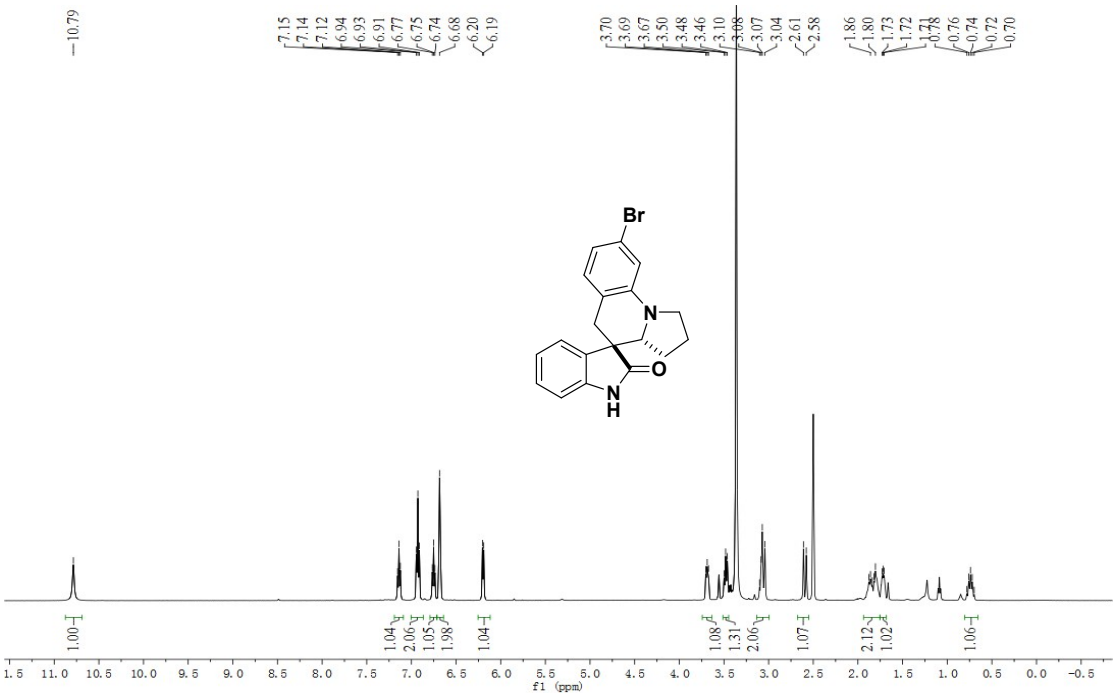


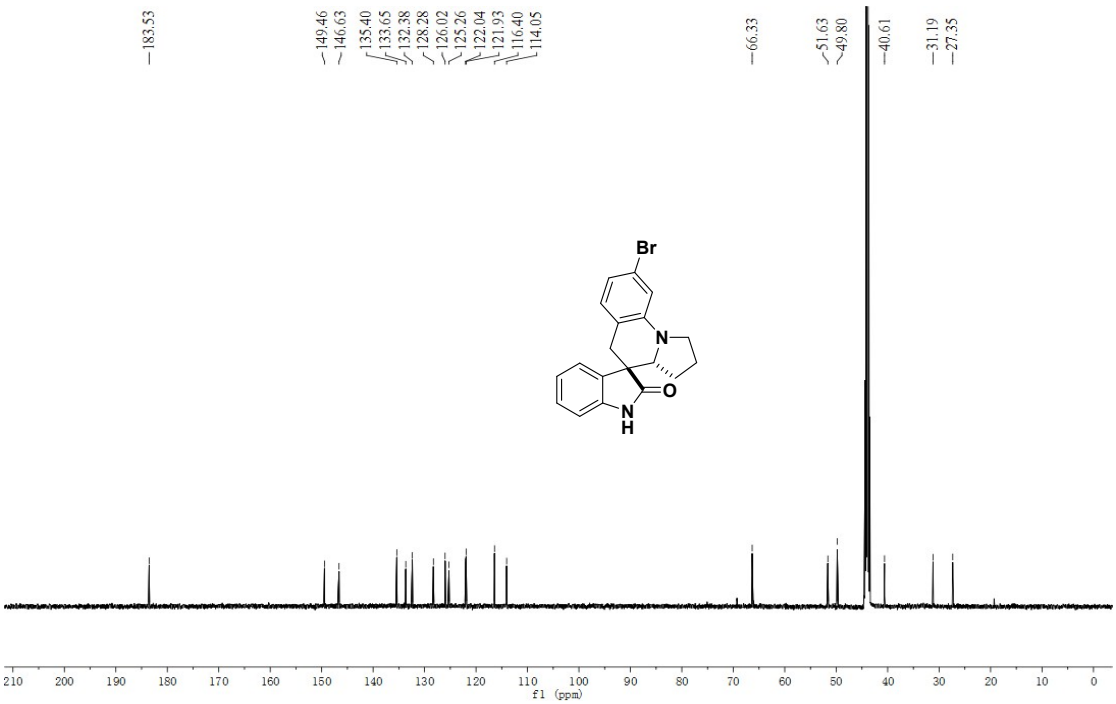
6'-chloro-1',2',3',3a'-tetrahydro-5'H-spiro[indoline-3,4'-pyrrolo[1,2-a]quinolin]-2-one (3d)



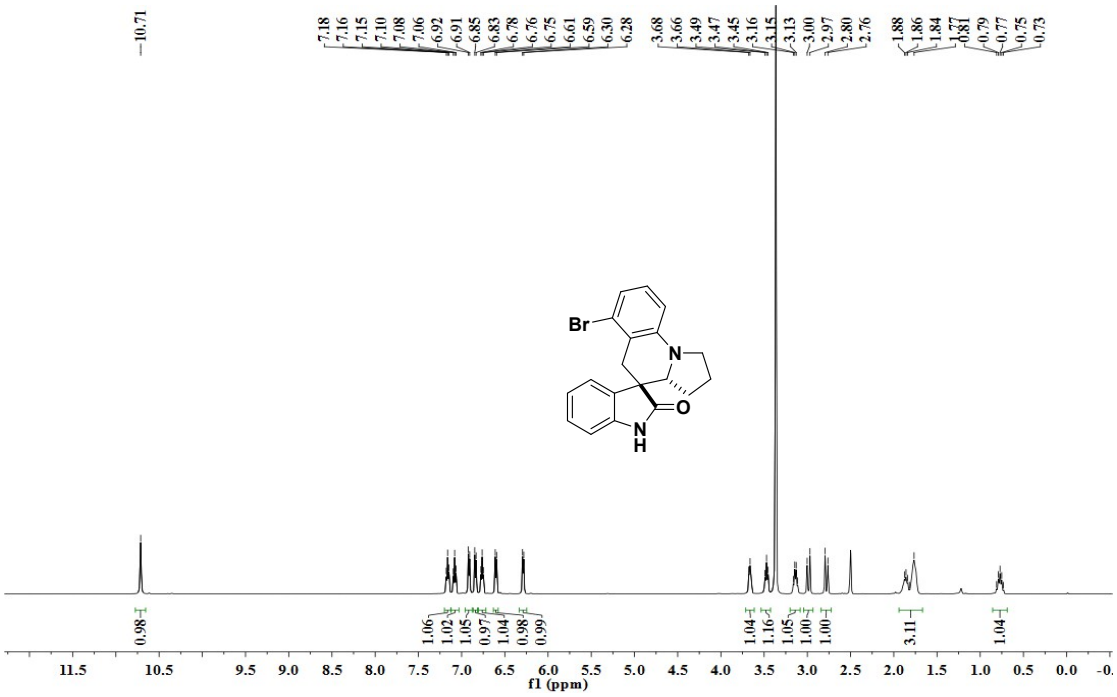


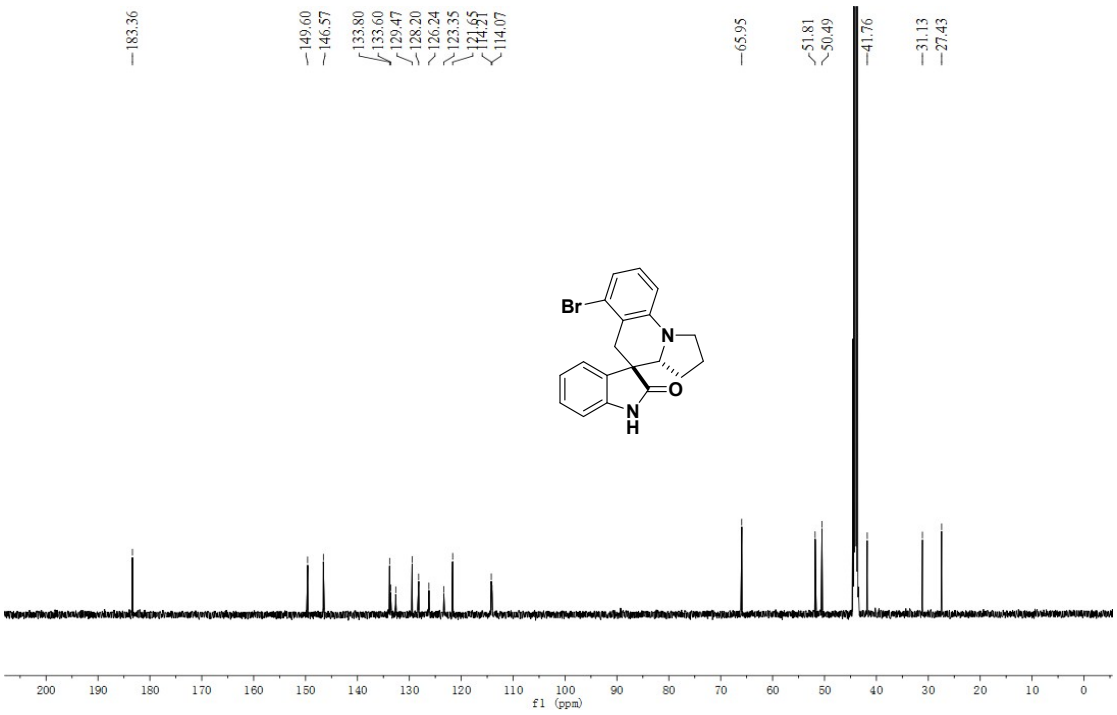
8'-bromo-1',2',3',3a'-tetrahydro-5'H-spiro[indoline-3,4'-pyrrolo[1,2-a]quinolin]-2-one (3e)



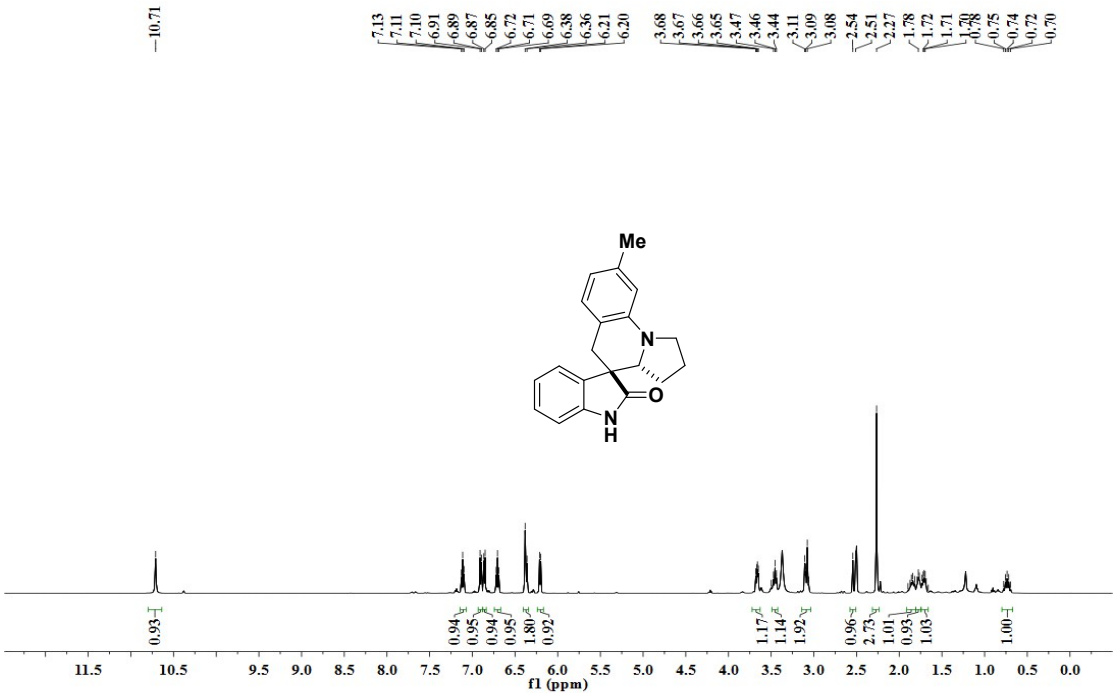


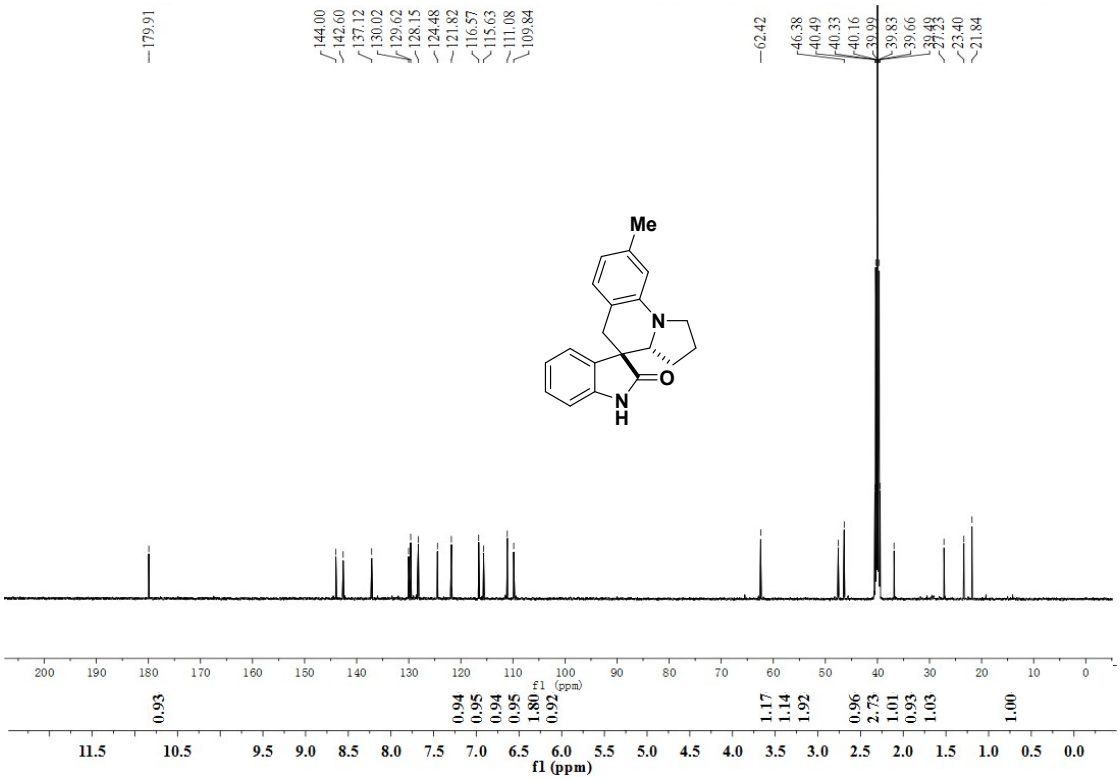
6'-bromo-1',2',3',3a'-tetrahydro-5'H-spiro[indoline-3,4'-pyrrolo[1,2-a]quinolin]-2-one (3f)



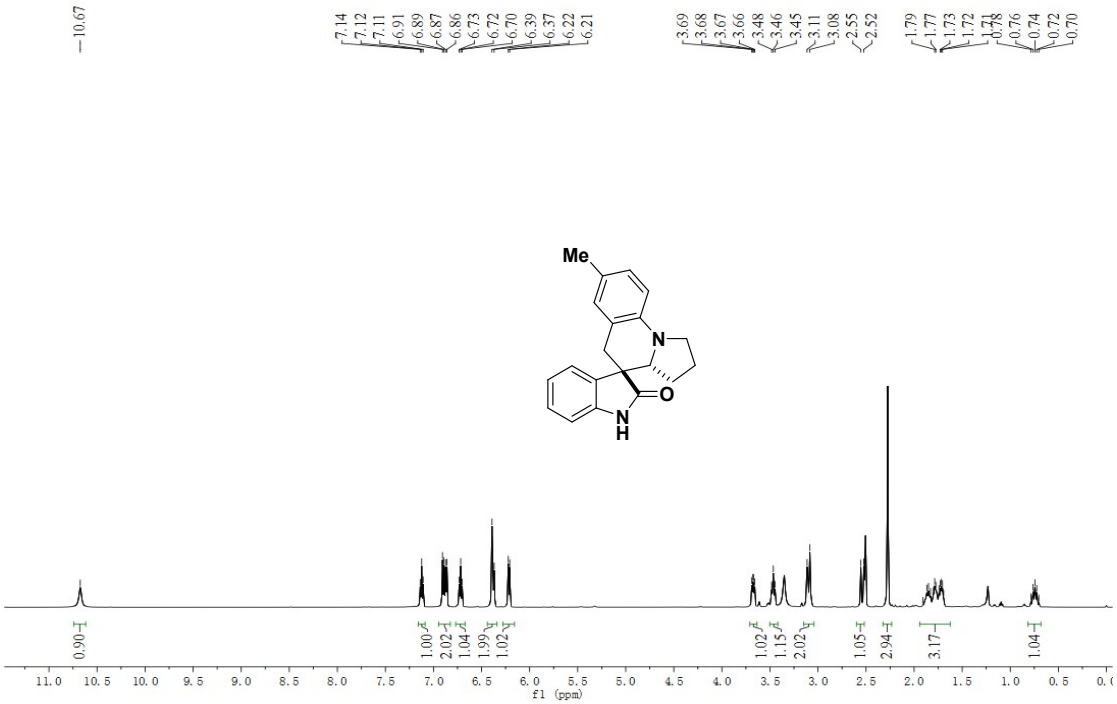


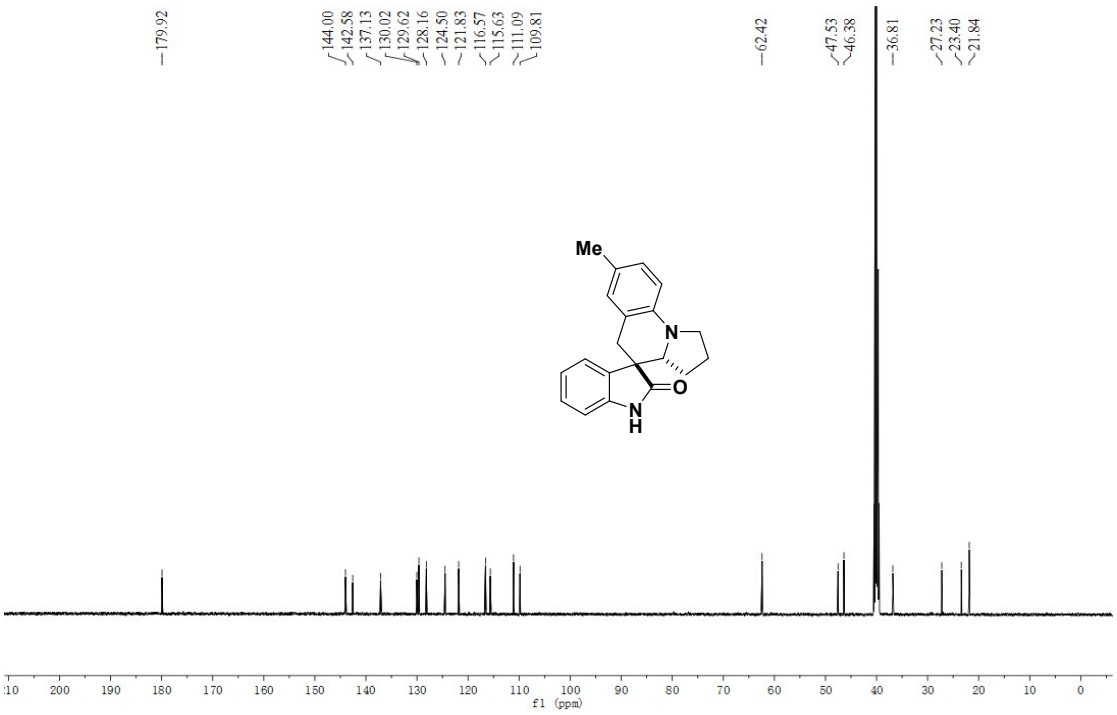
8'-methyl-1',2',3',3a'-tetrahydro-5'H-spiro[indoline-3,4'-pyrrolo[1,2-a]quinolin]-2-one (3g)



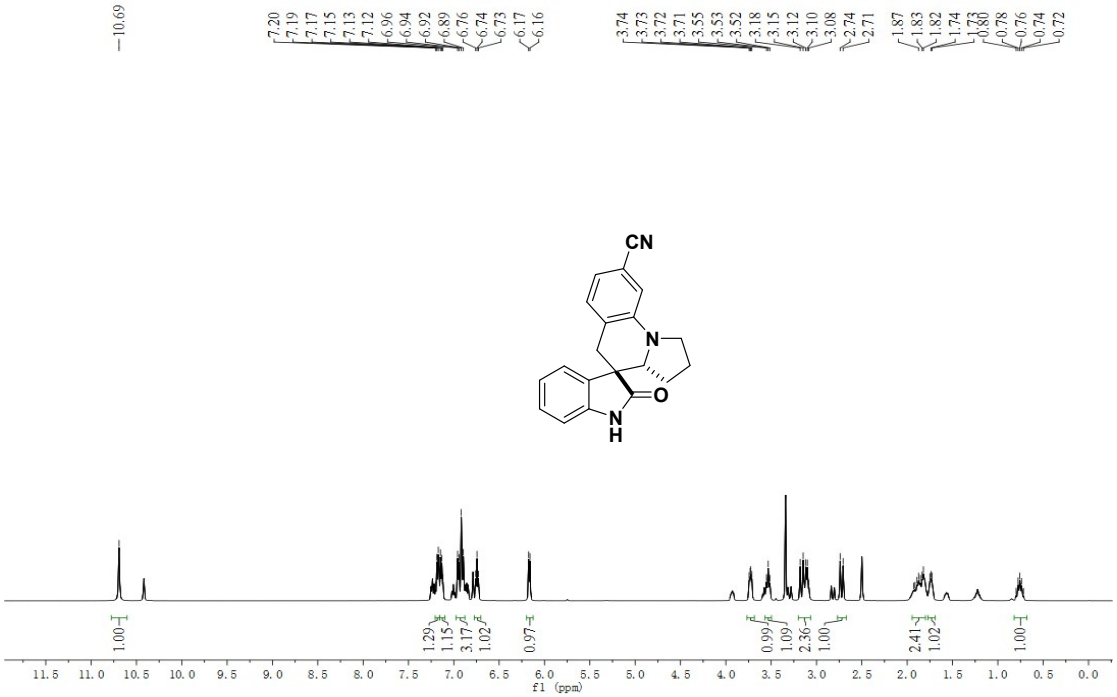


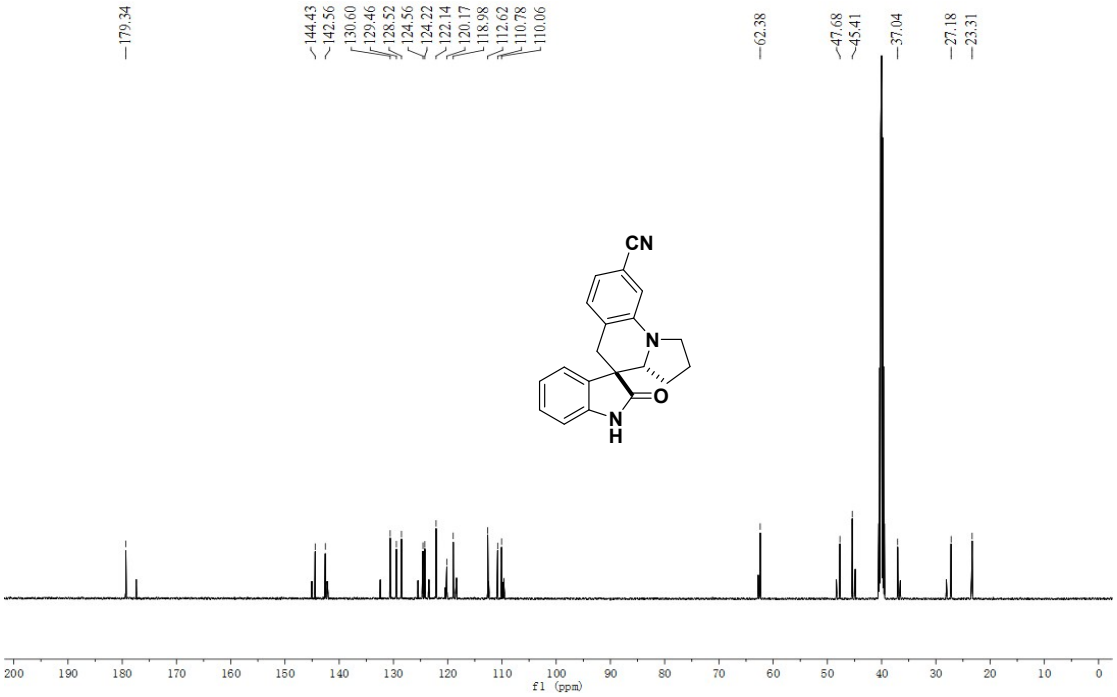
7'-methyl-1',2',3',3a'-tetrahydro-5'H-spiro[indoline-3,4'-pyrrolo[1,2-a]quinolin]-2-one (3h)



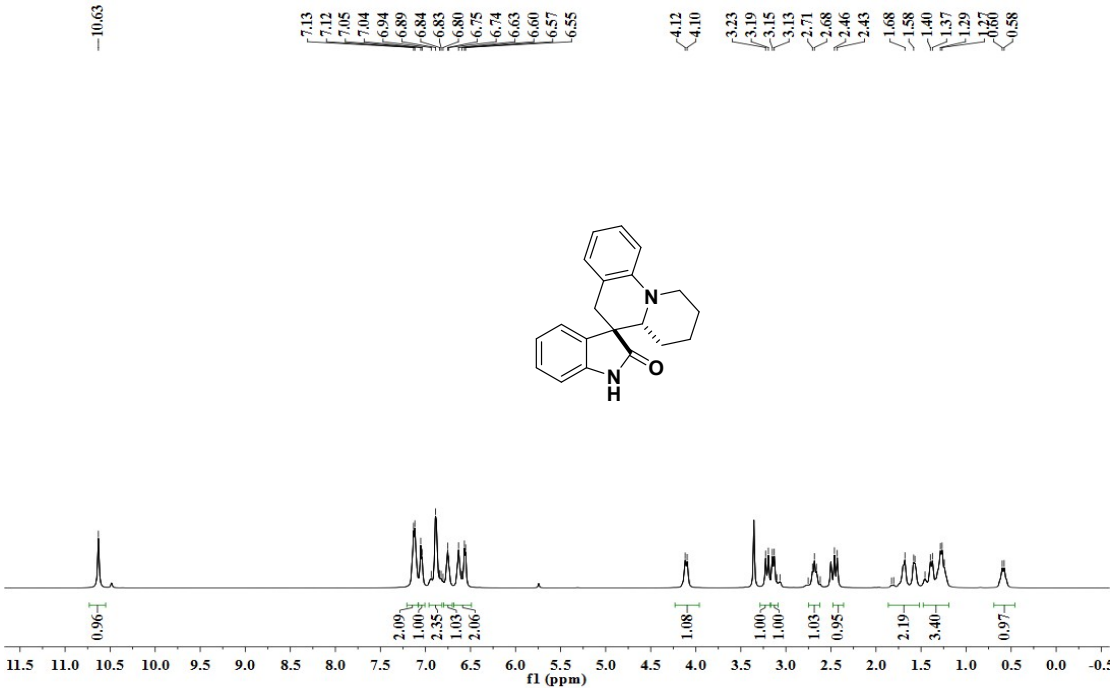


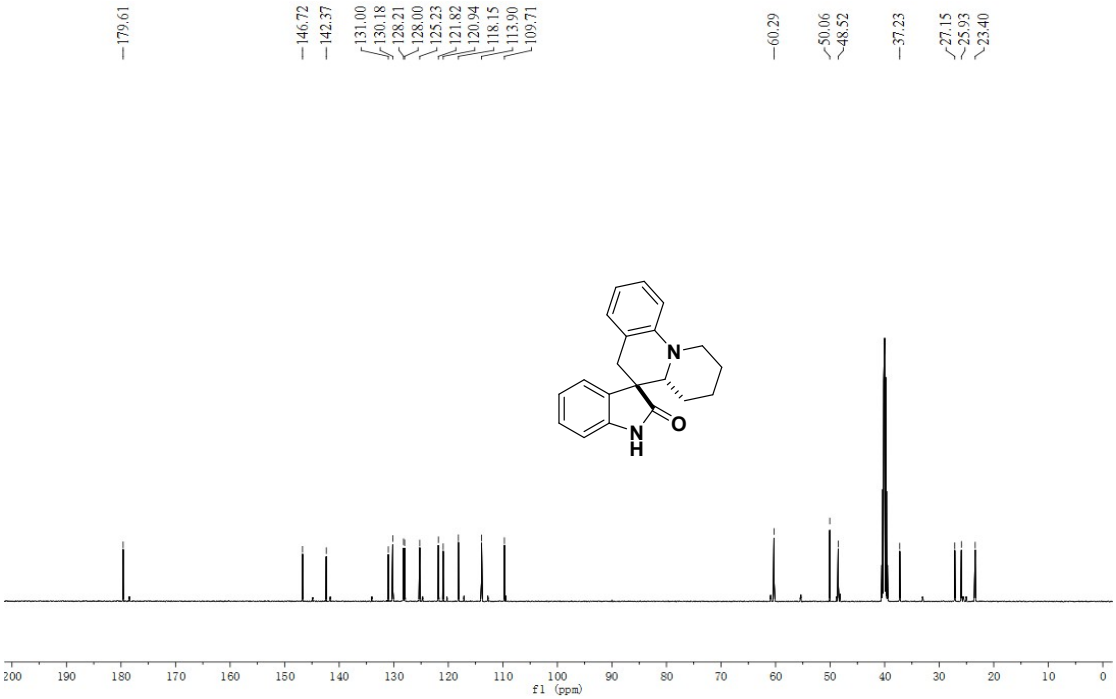
2-oxo-1',2',3',3a'-tetrahydro-5'H-spiro[indoline-3,4'-pyrrolo[1,2-a]quinoline]-8'-carbonitrile (3i)



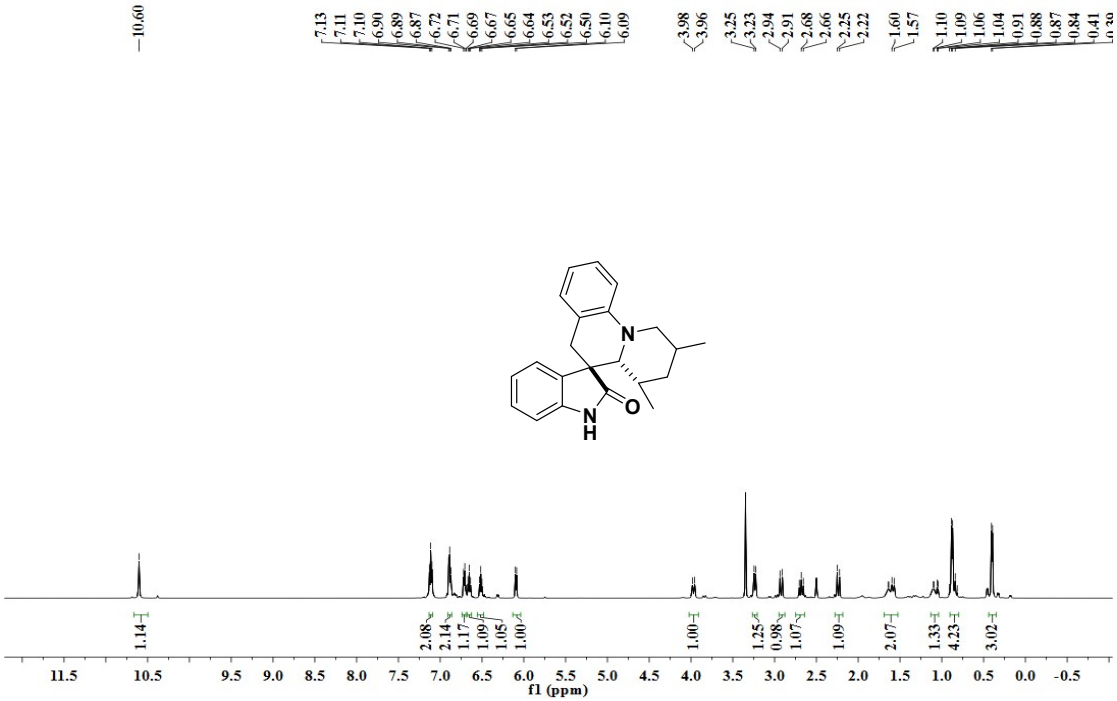


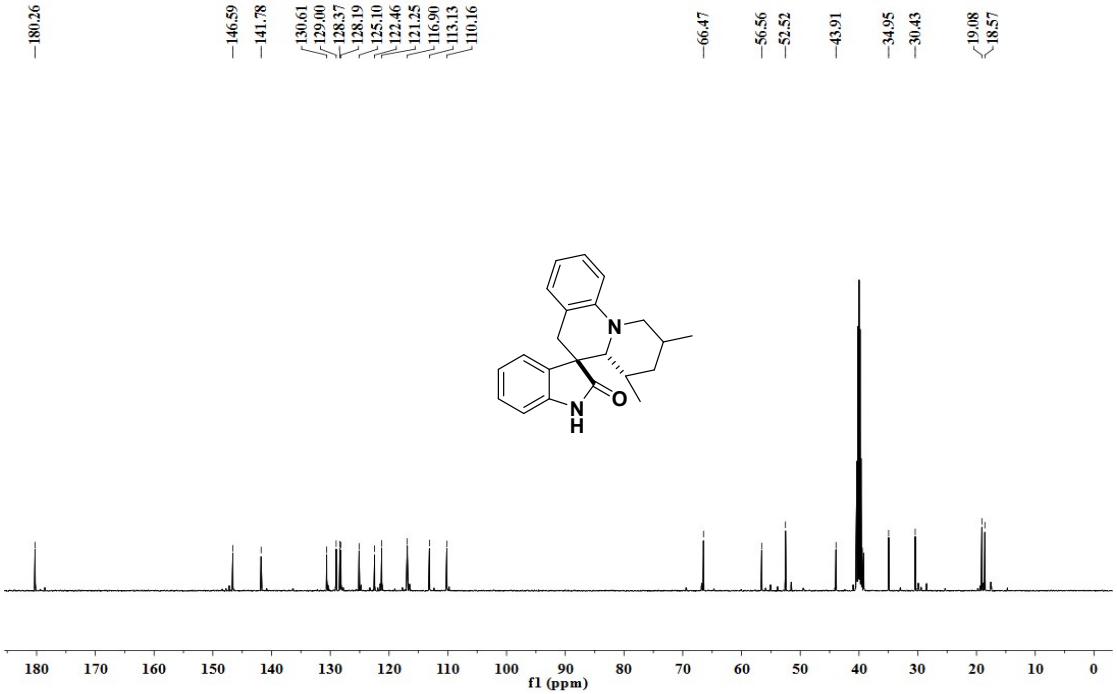
2',3',4',4a'-tetrahydro-1'H,6'H-spiro[indoline-3,5'-pyrido[1,2-a]quinolin]-2-one (3k)



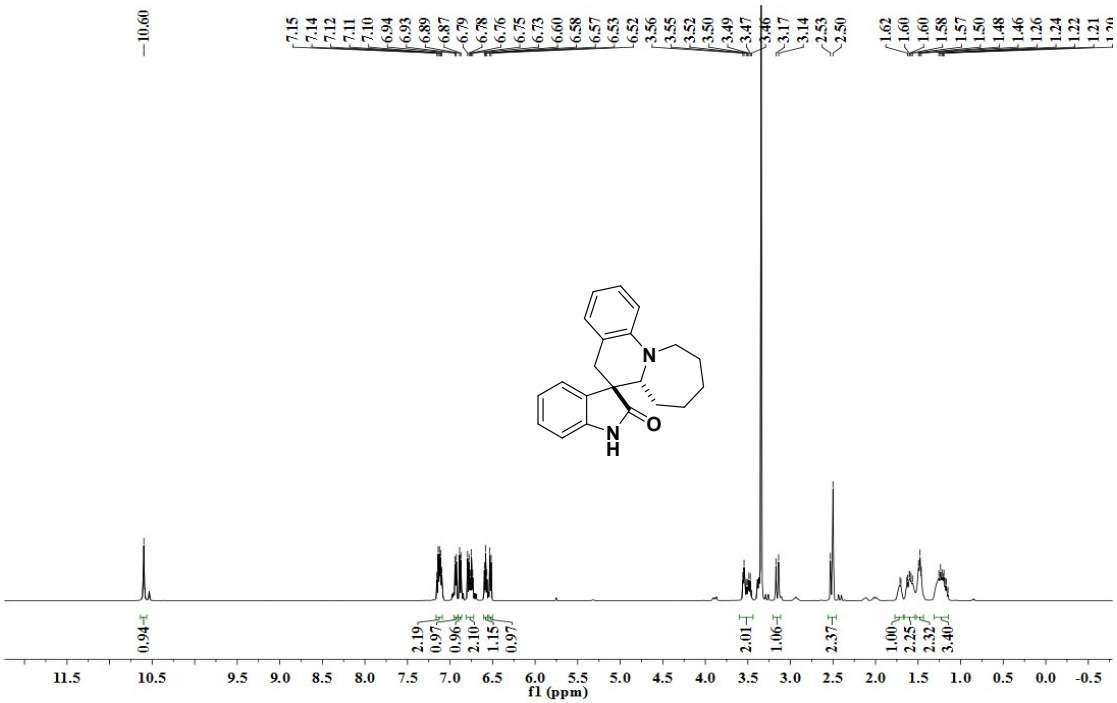


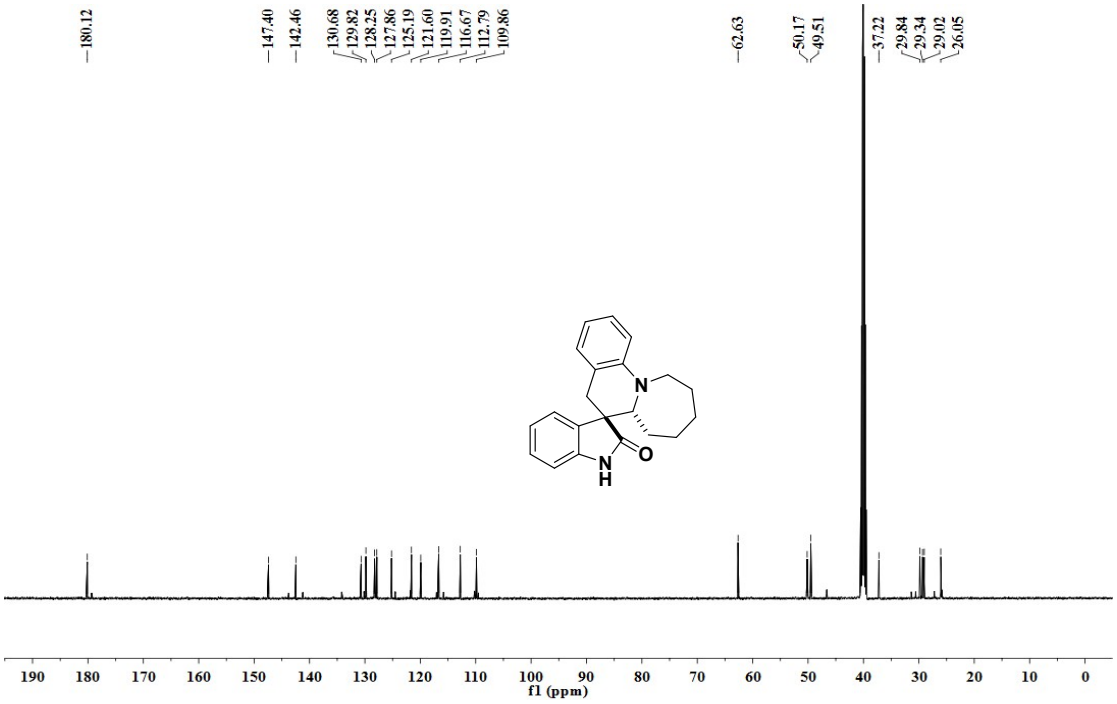
2',4'-dimethyl-2',3',4',4a'-tetrahydro-1'H,6'H-spiro[indoline-3,5'-pyrido[1,2-a]quinolin]-2-one (3l)



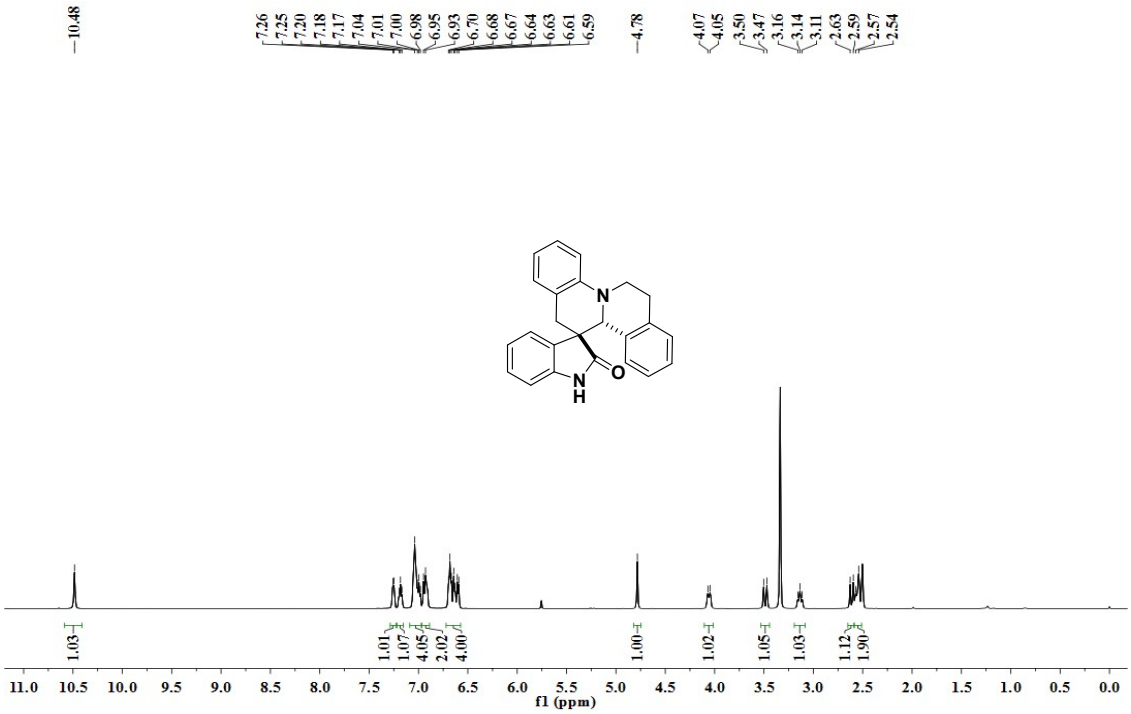


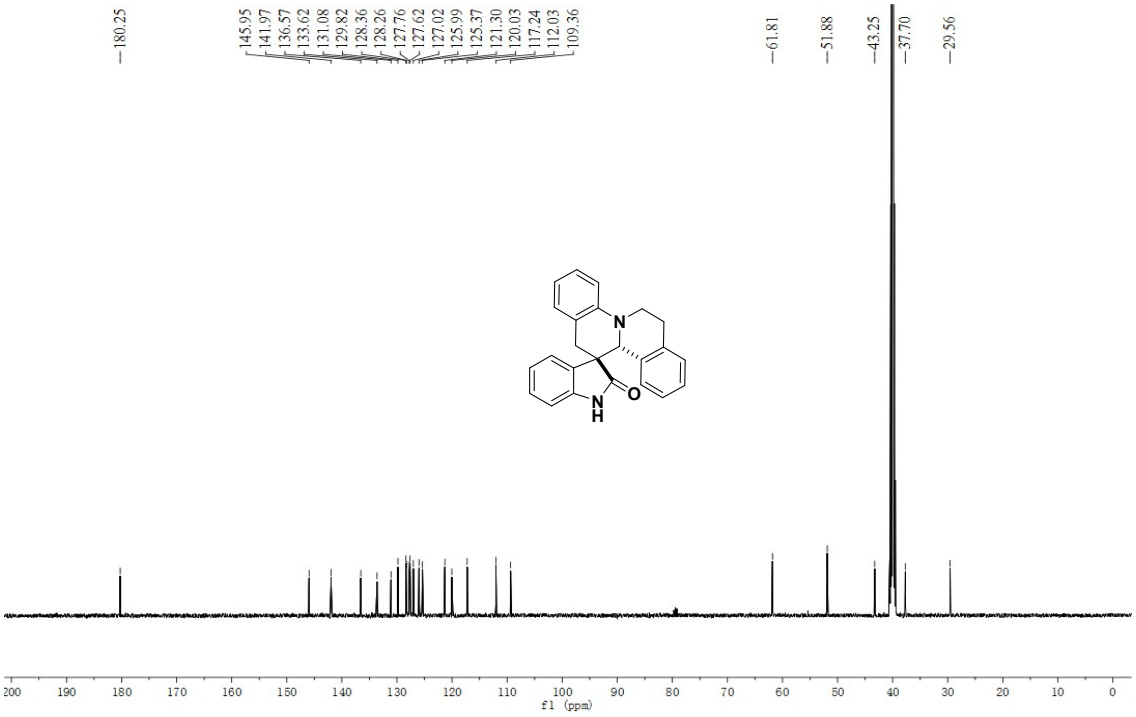
6a,7,8,9,10,11-hexahydro-5H-spiro[azepino[1,2-a]quinoline-6,3'-indolin]-2'-one (3m)



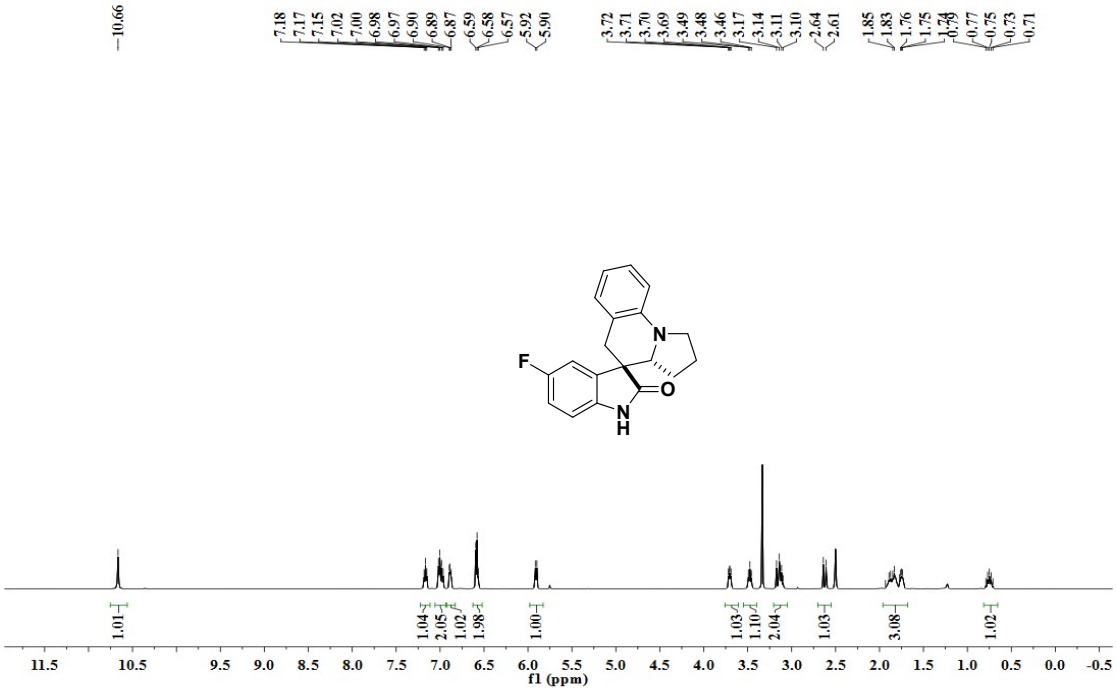


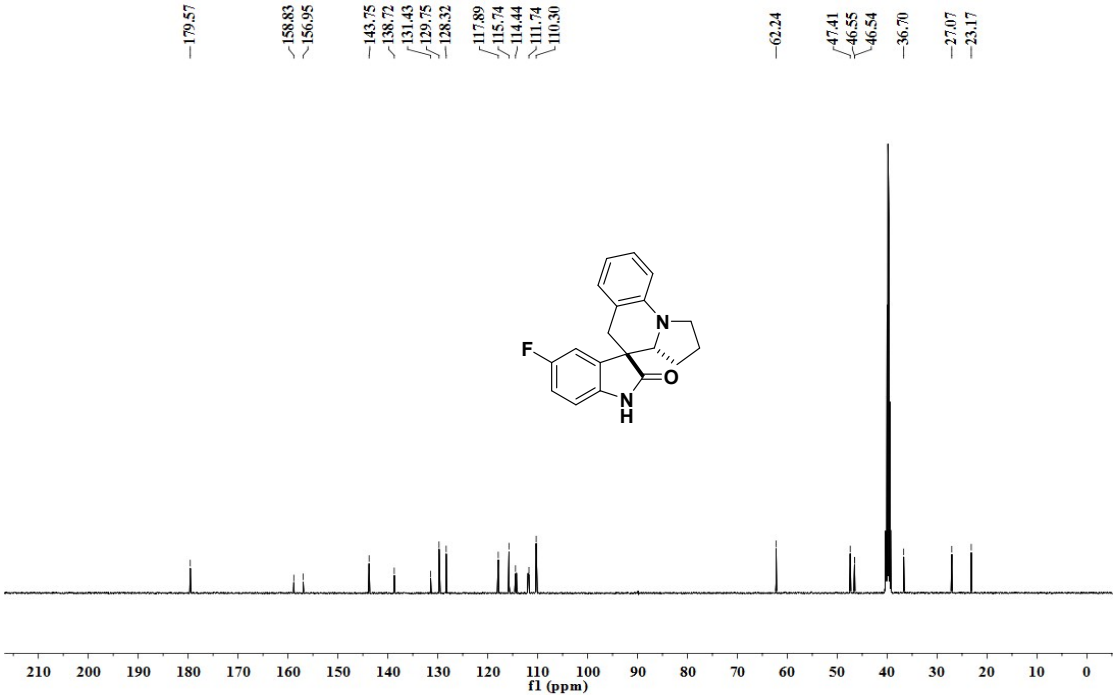
7',11b'-dihydro-6'H,13'H-spiro[indoline-3,12'-isoquinolino[2,1-a]quinolin]-2-one (3n)



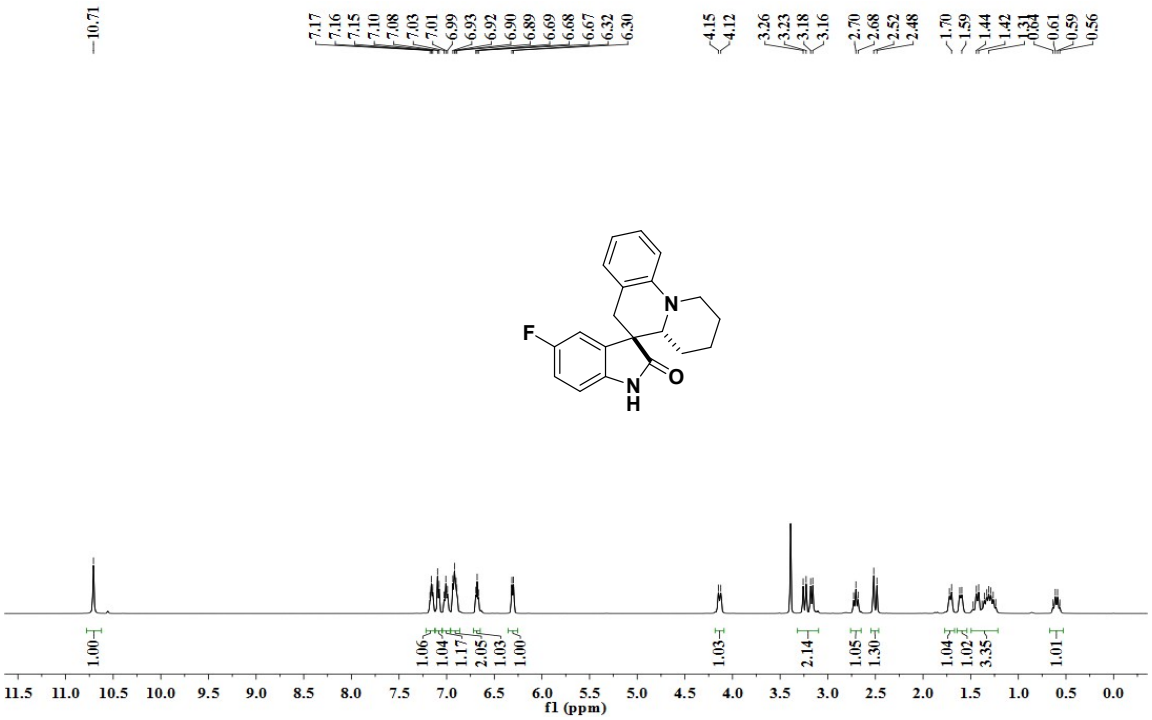


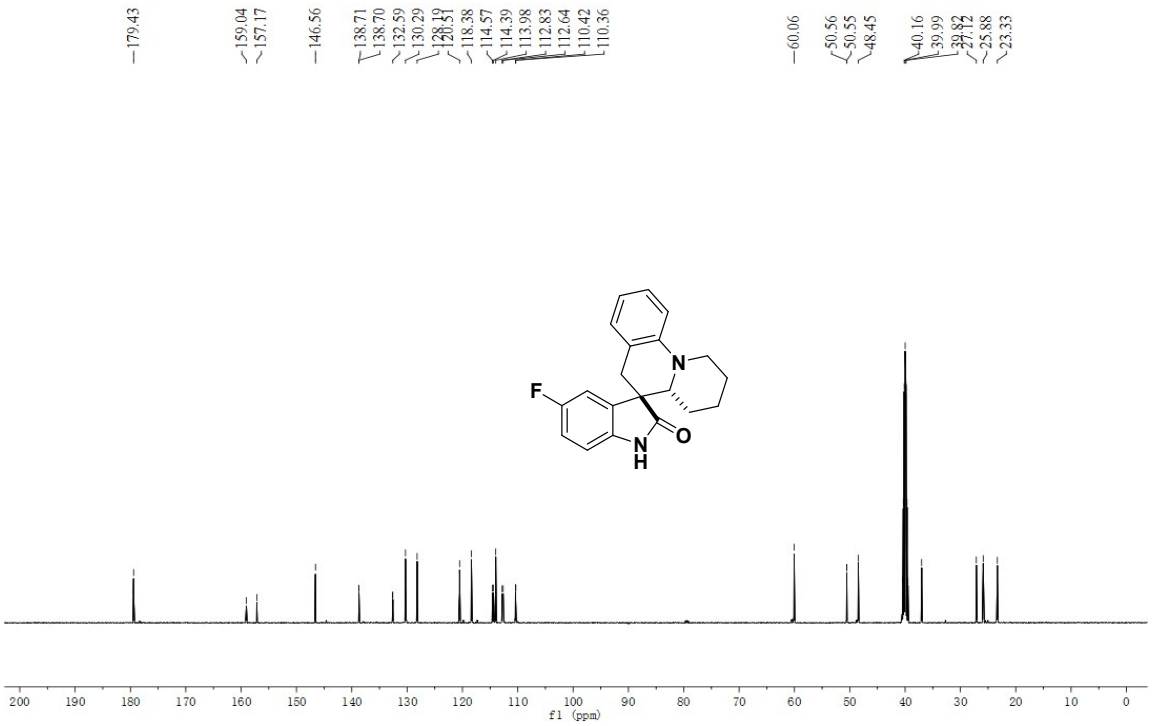
5-fluoro-1',2',3',3a'-tetrahydro-5'H-spiro[indoline-3,4'-pyrrolo[1,2-a]quinolin]-2-one (3o)



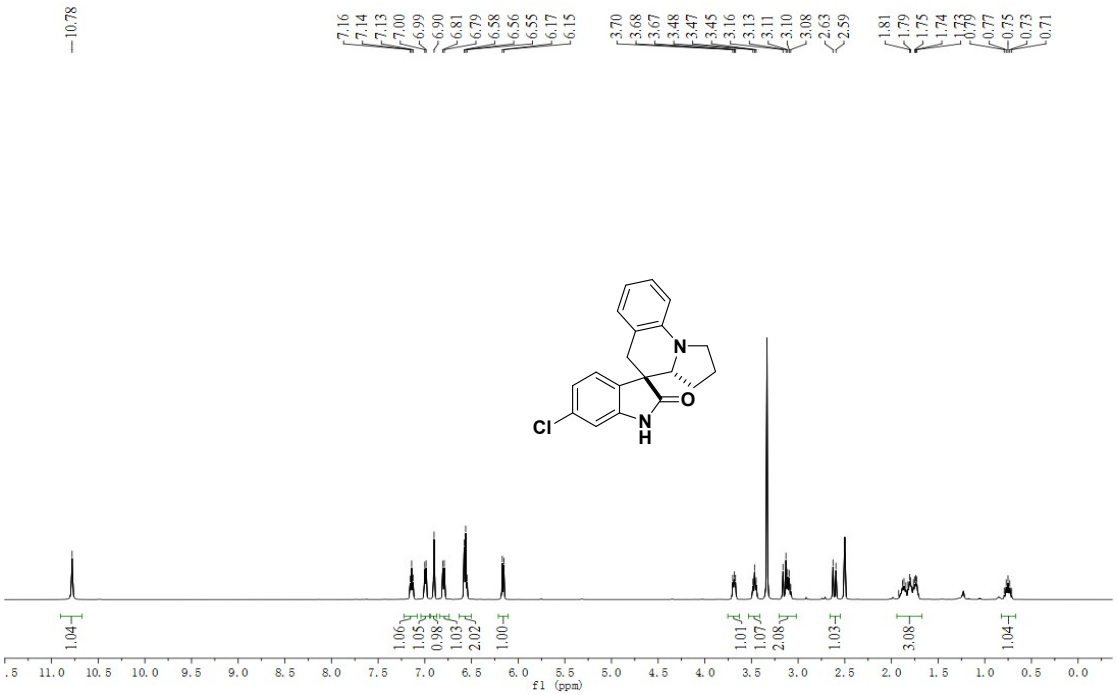


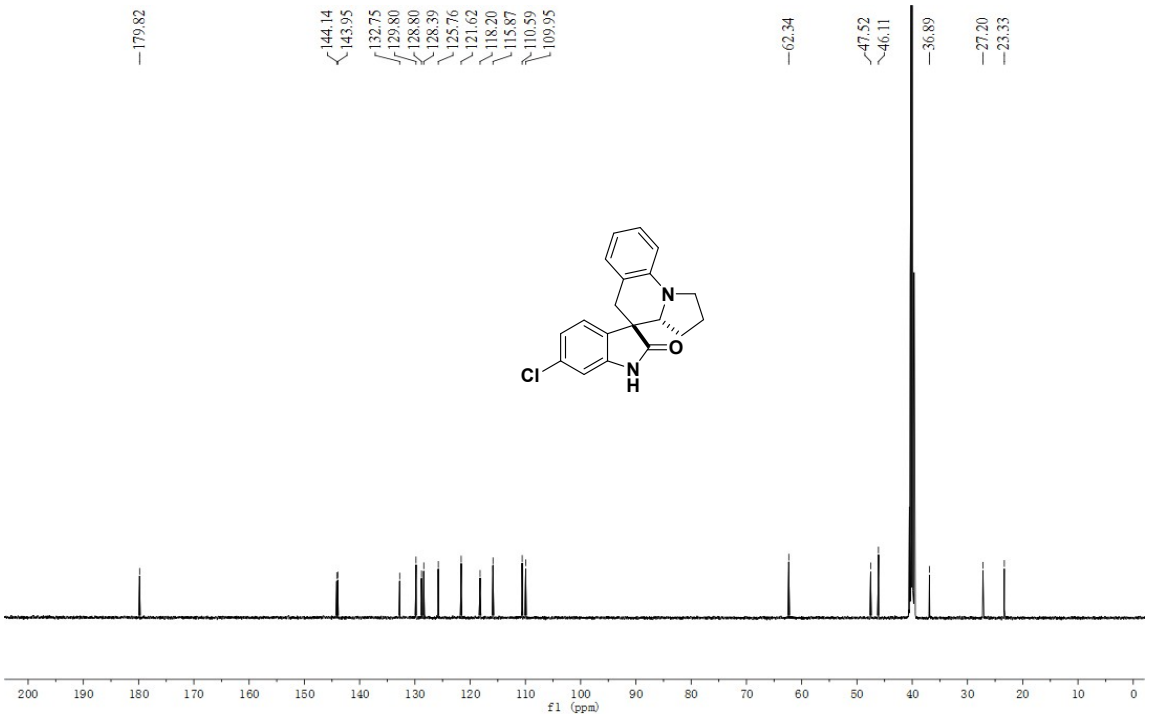
5-fluoro-2',3',4',4a'-tetrahydro-1'H,6'H-spiro[indoline-3,5'-pyrido[1,2-a]quinolin]-2-one (3p)



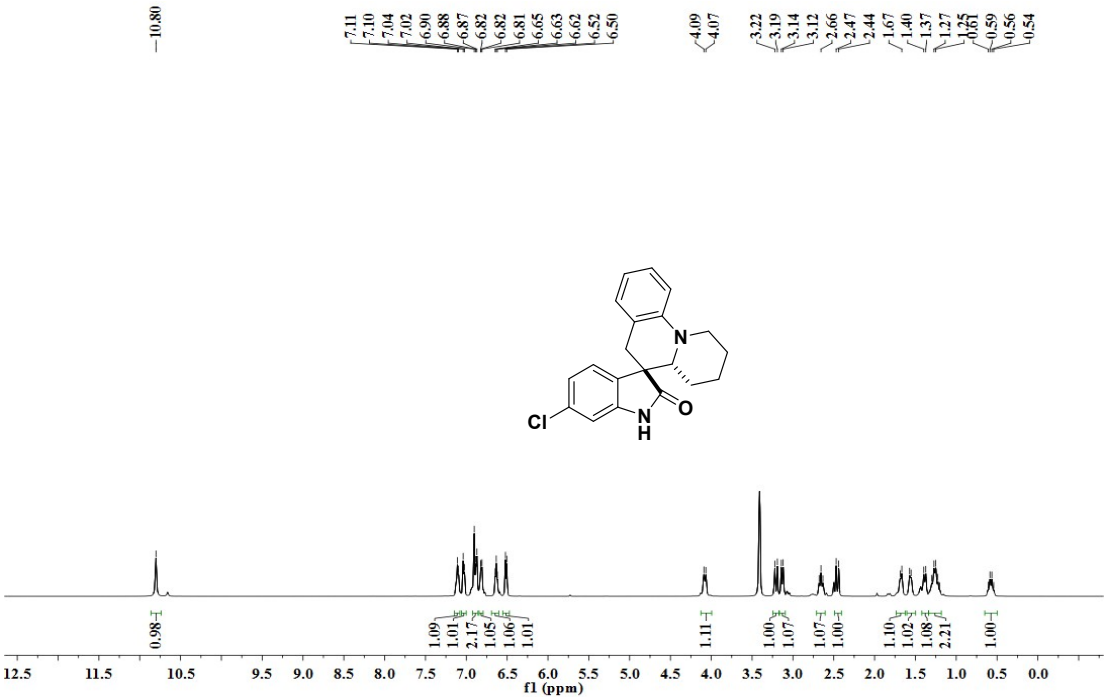


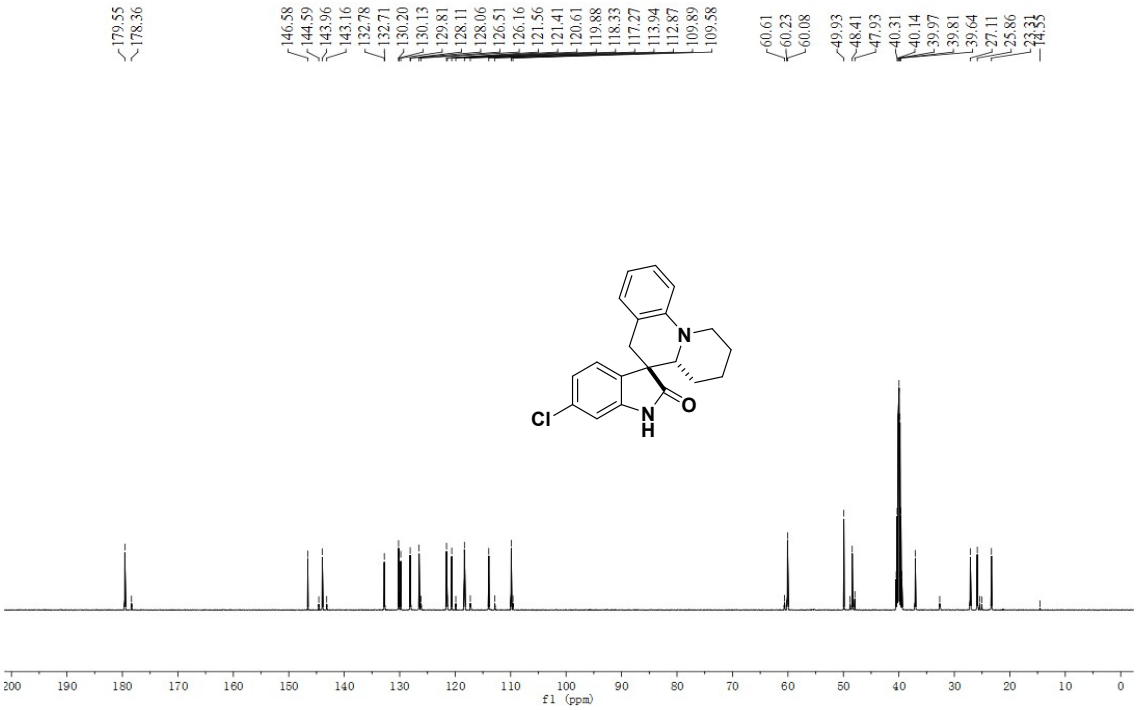
6-chloro-1',2',3',3a'-tetrahydro-5'H-spiro[indoline-3,4'-pyrrolo[1,2-a]quinolin]-2-one (3q)



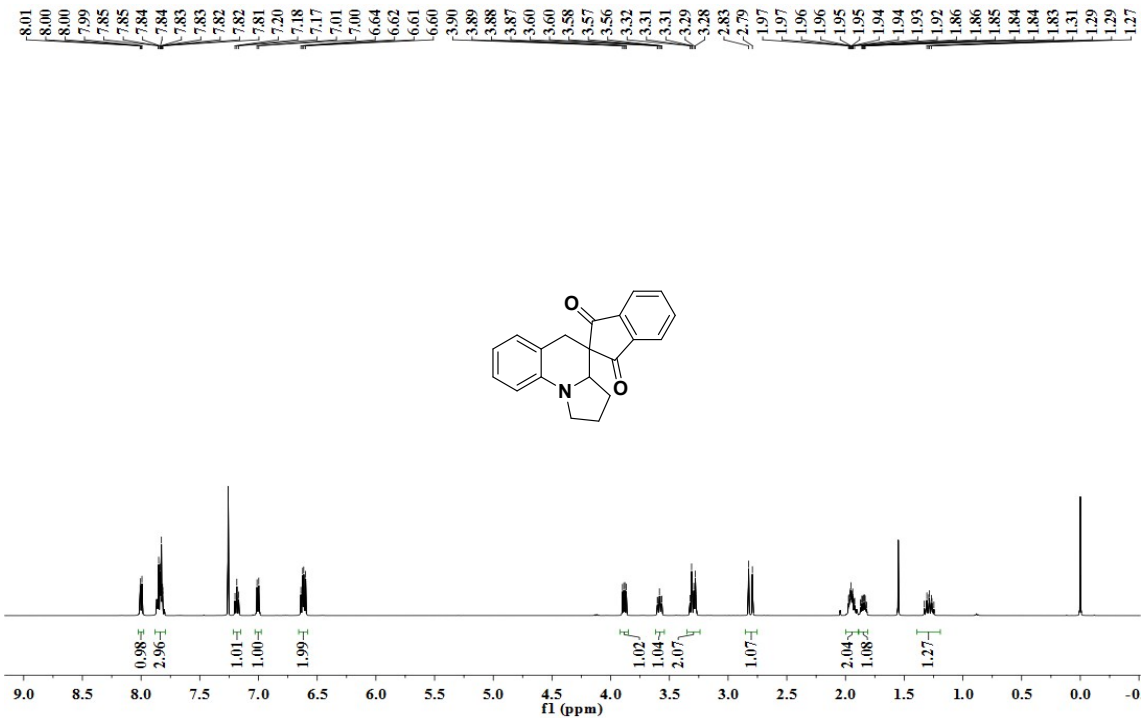


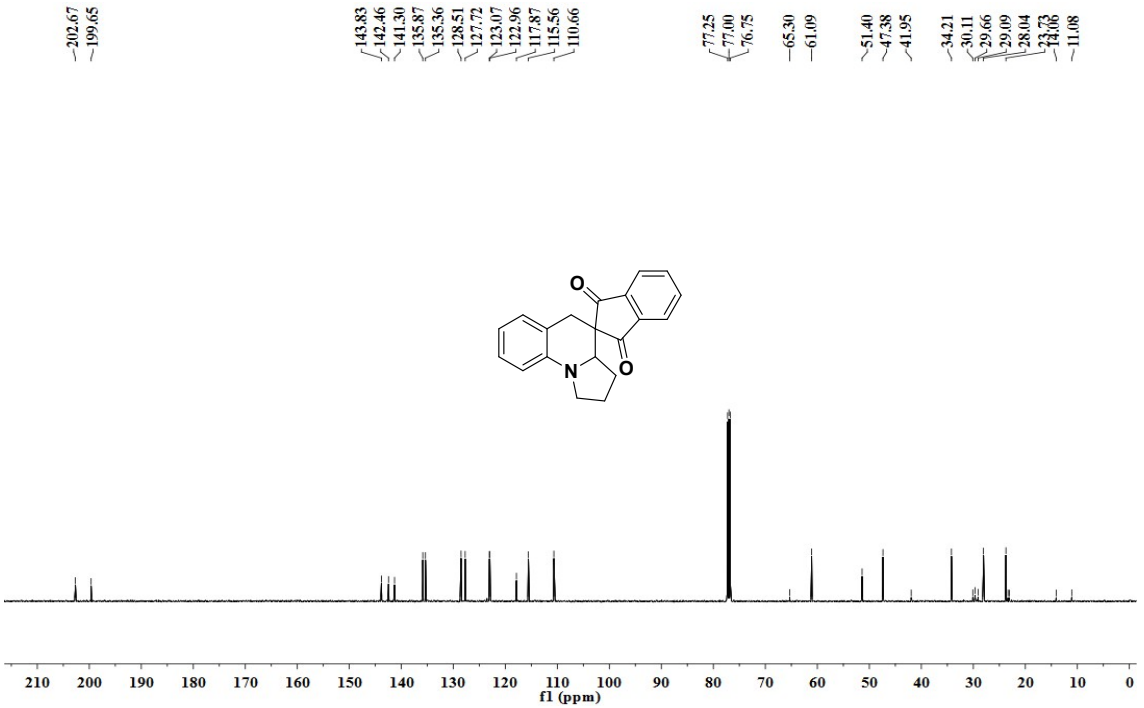
6-chloro-2',3',4',4a'-tetrahydro-1'H,6'H-spiro[indoline-3,5'-pyrido[1,2-a]quinolin]-2-one (3r)



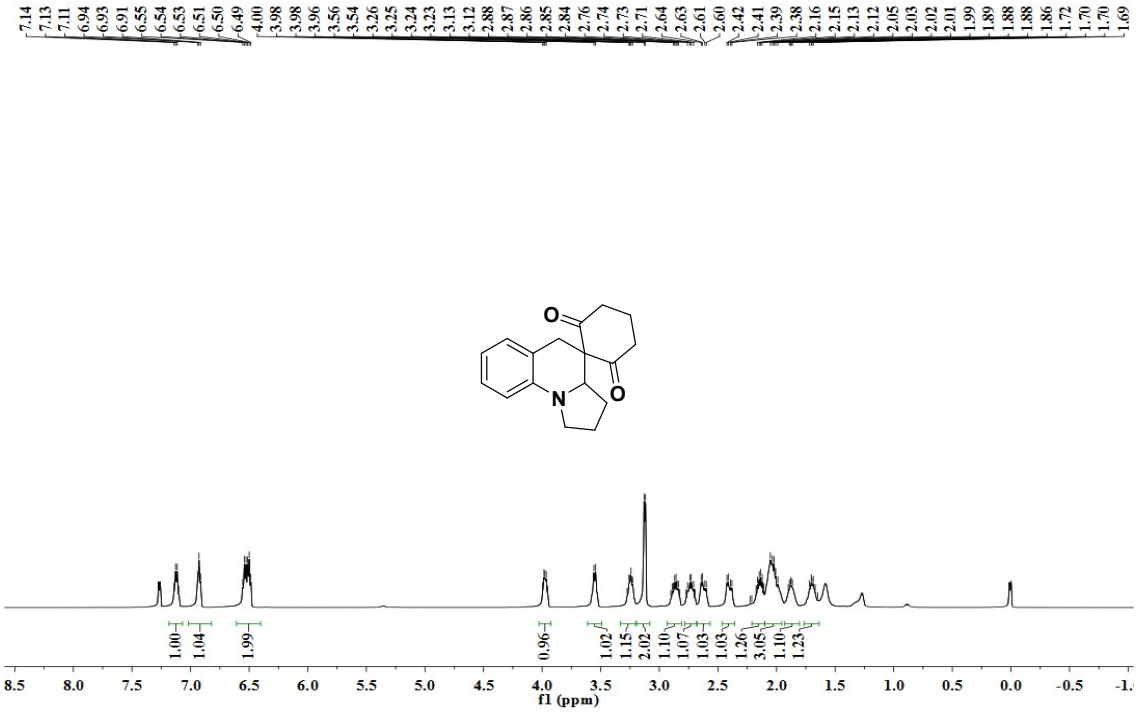


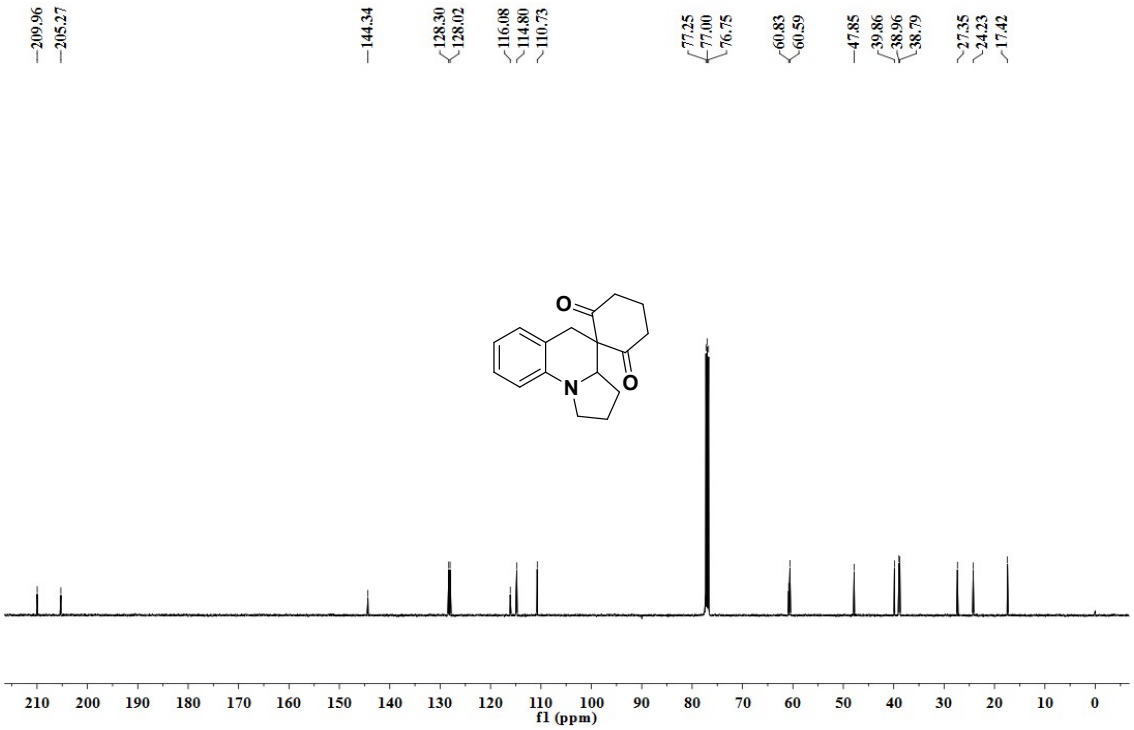
1',2',3',3a'-tetrahydro-5'H-spiro[indene-2,4'-pyrrolo[1,2-a]quinoline]-1,3-dione (5a)



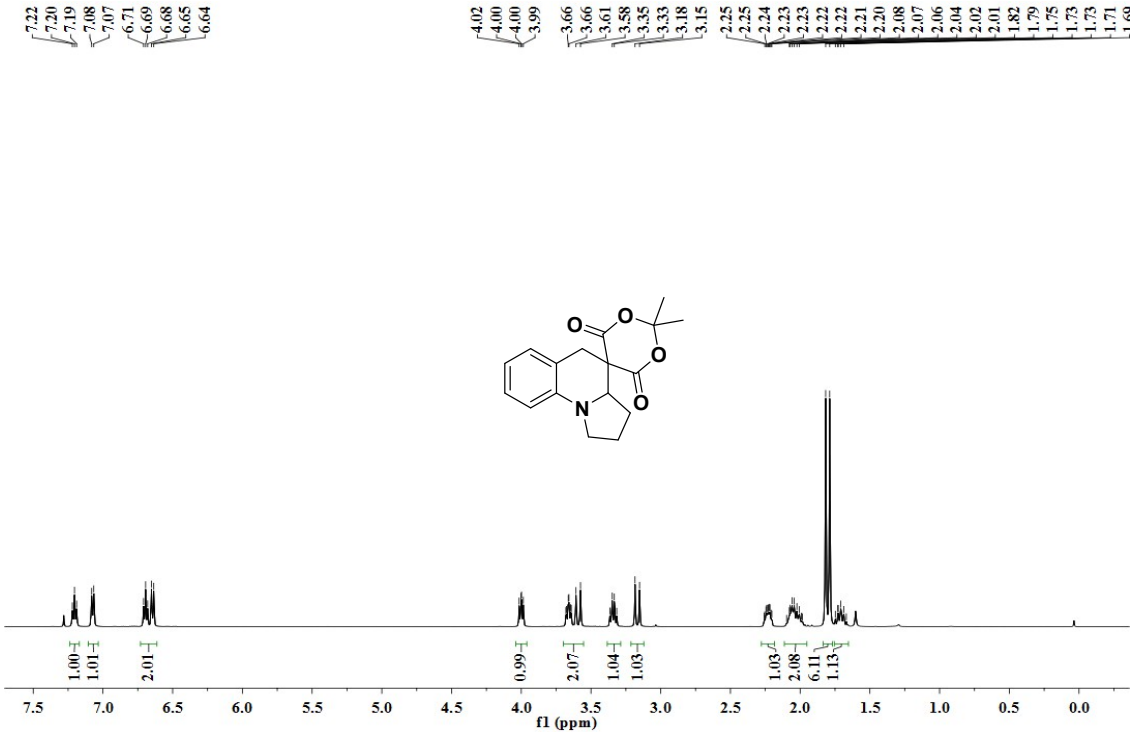


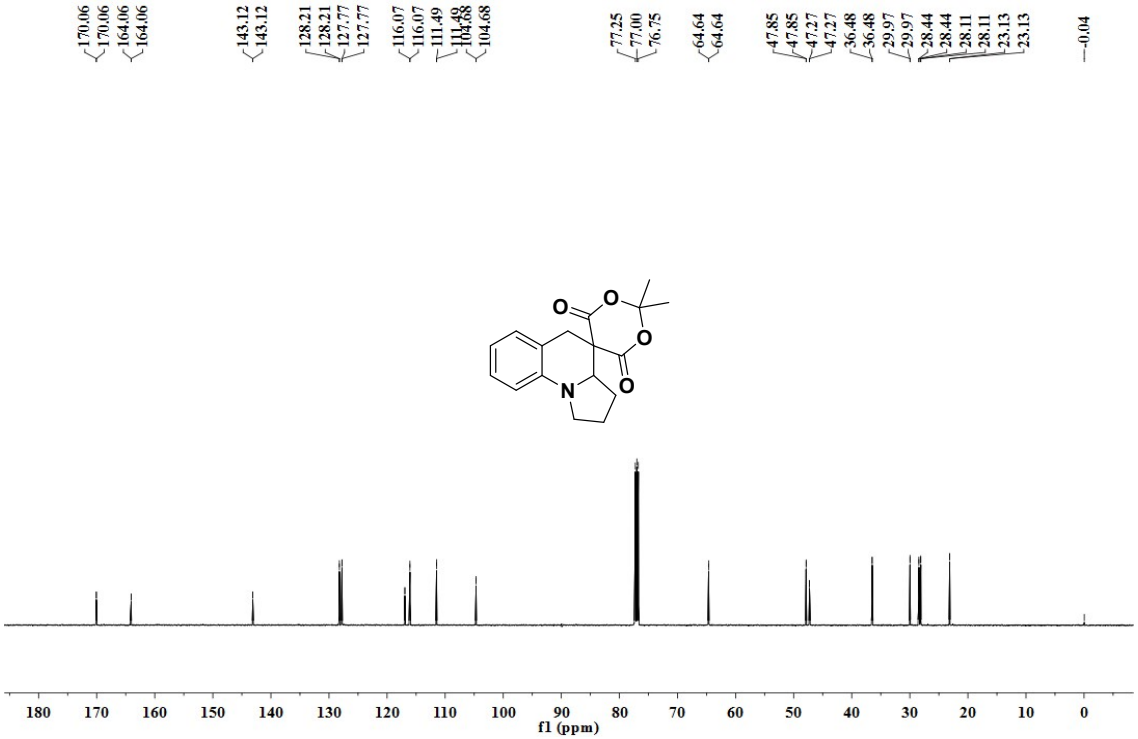
1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,6-dione (5b)



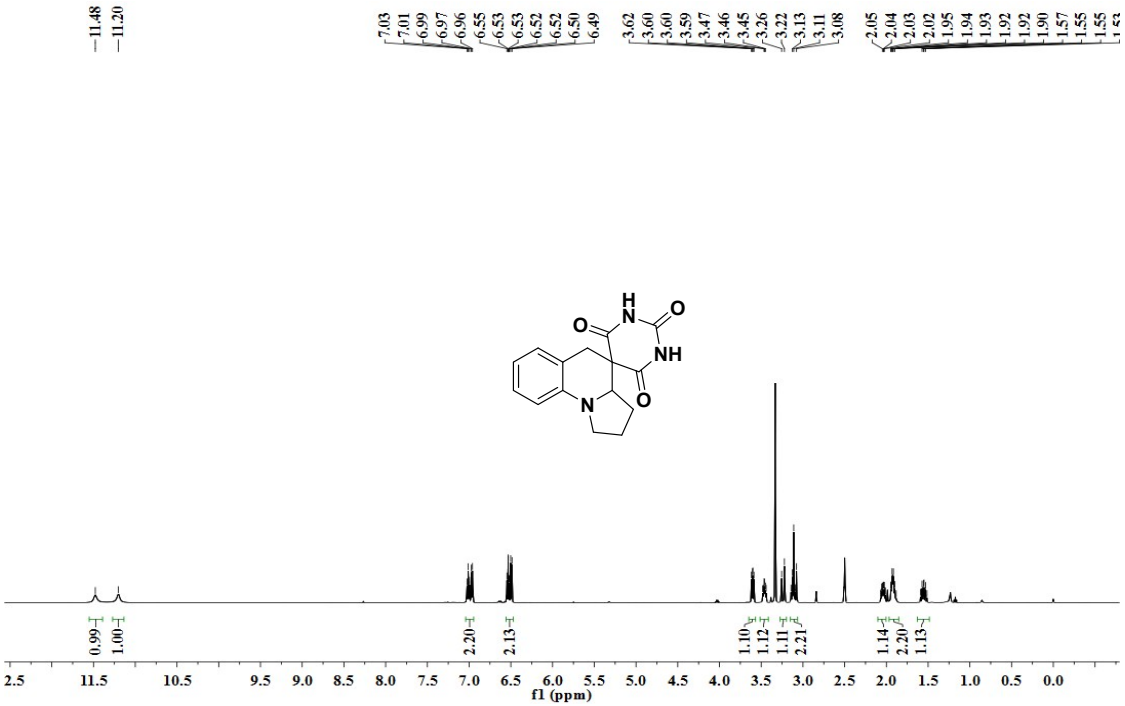


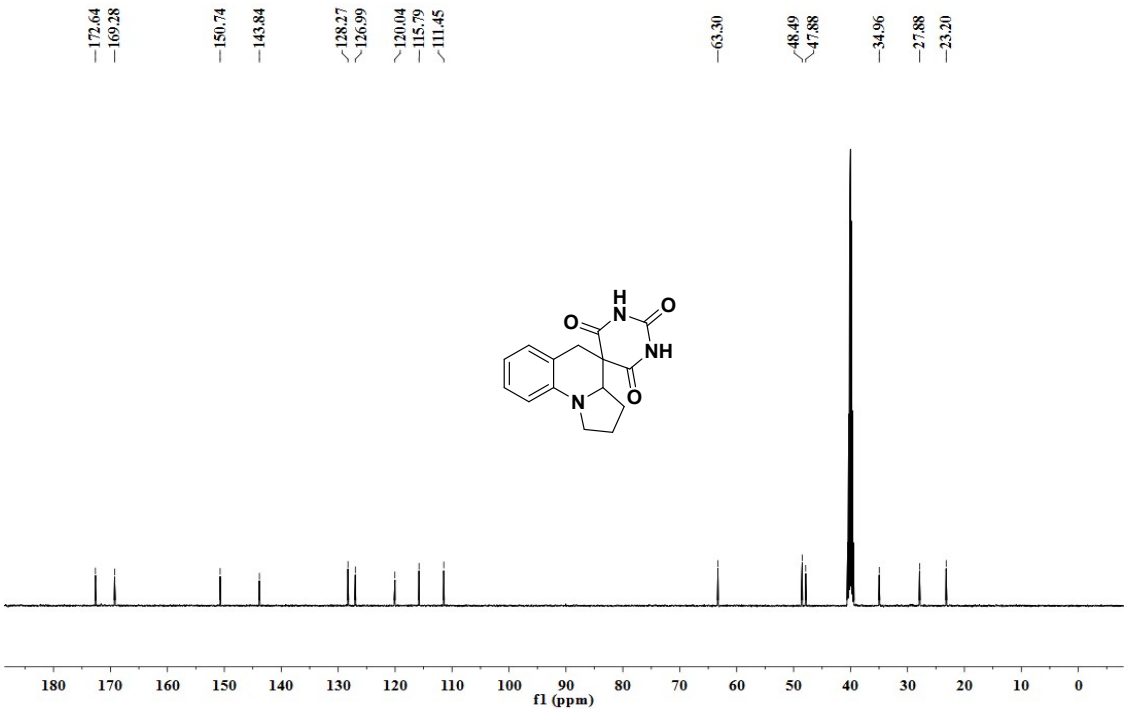
2',2'-dimethyl-1,2,3,3a-tetrahydro-5H-spiro[pyrrolo[1,2-a]quinoline-4,5'-[1,3]dioxane]-4',6'-dione (5c)



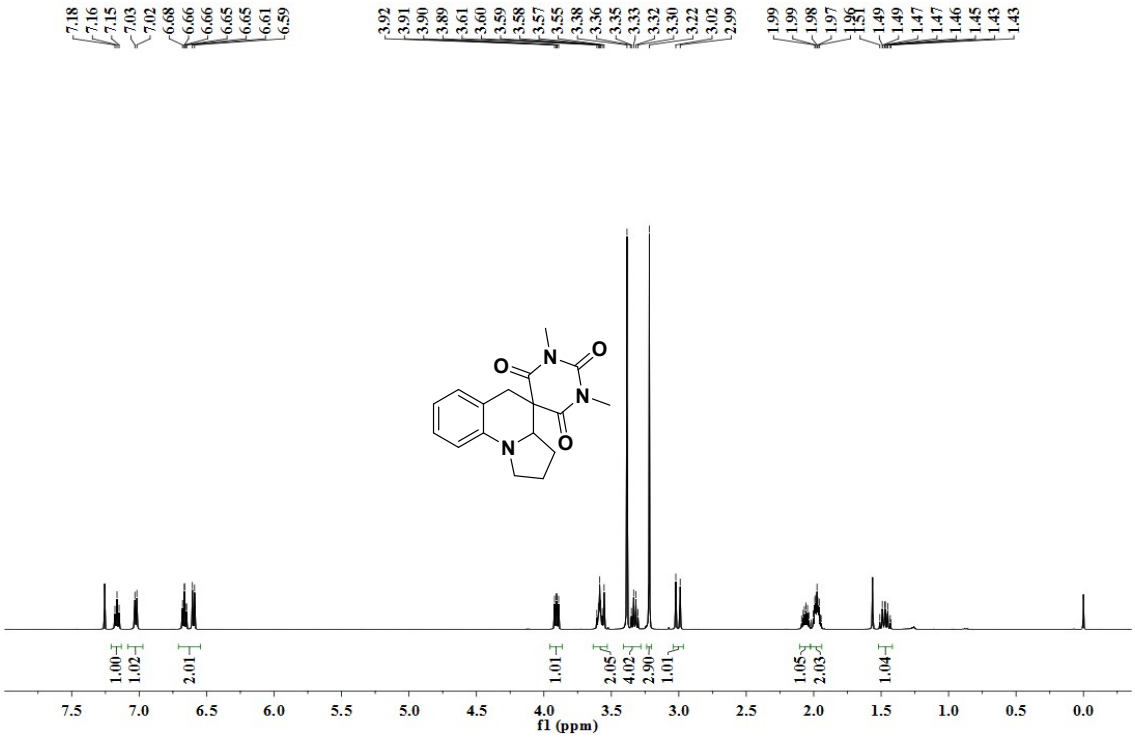


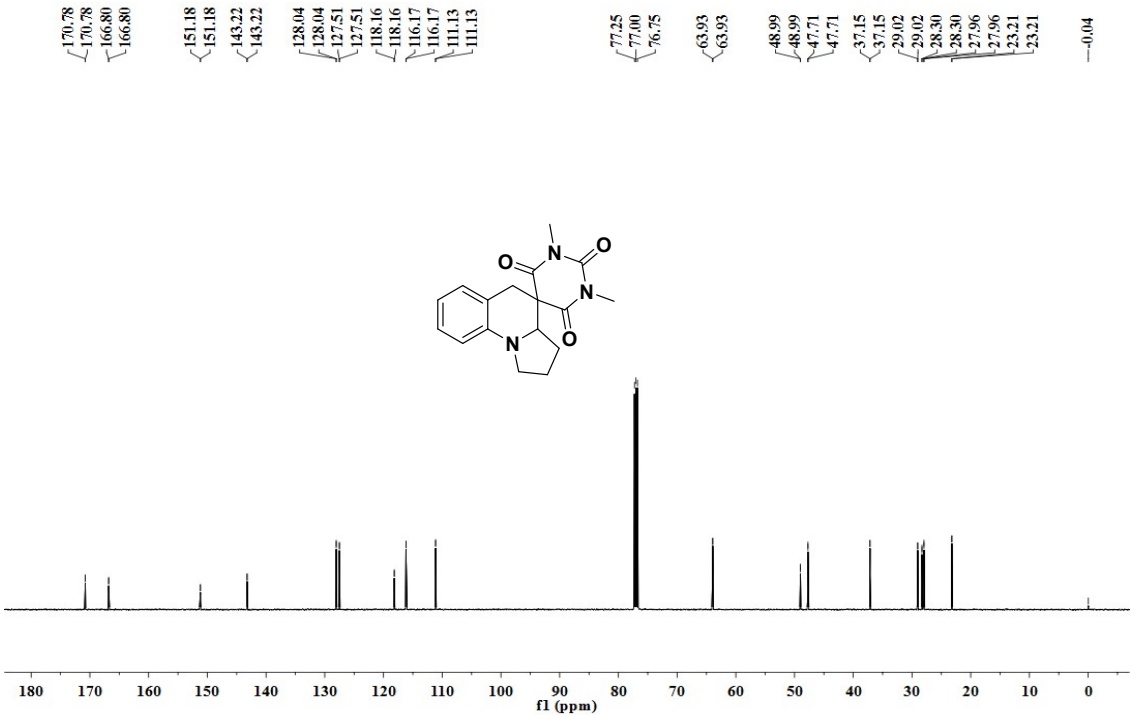
1',2',3',3a'-tetrahydro-2H,5'H-spiro[pyrimidine-5,4'-pyrrolo[1,2-a]quinoline]-2,4,6(1H,3H)-trione (5d)



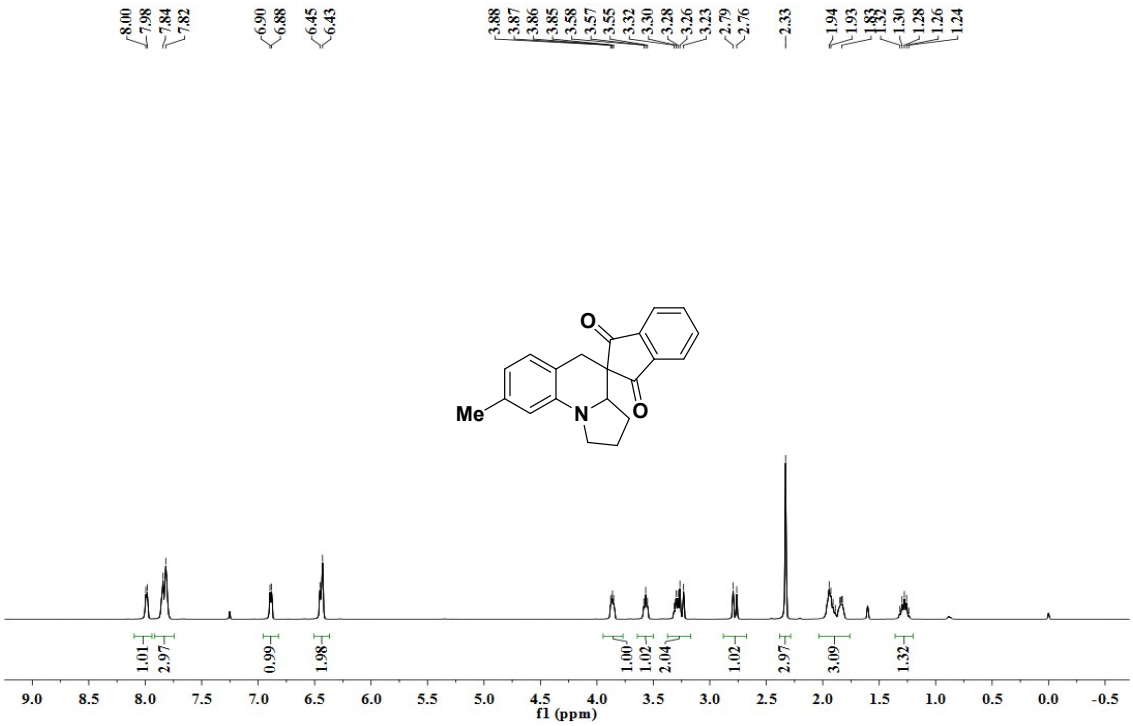


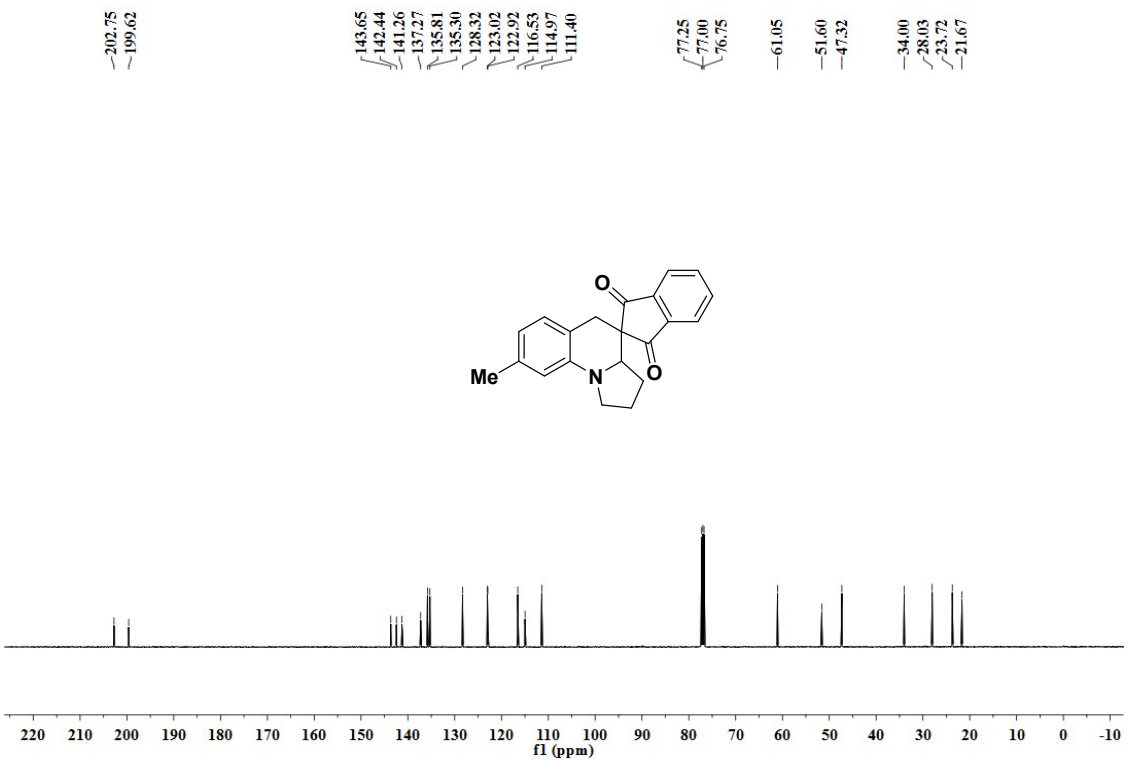
1,3-dimethyl-1',2',3',3a'-tetrahydro-2H,5'H-spiro[pyrimidine-5,4'-pyrrolo[1,2-a]quinoline]-2,4,6(1H,3H)-trione (5e)



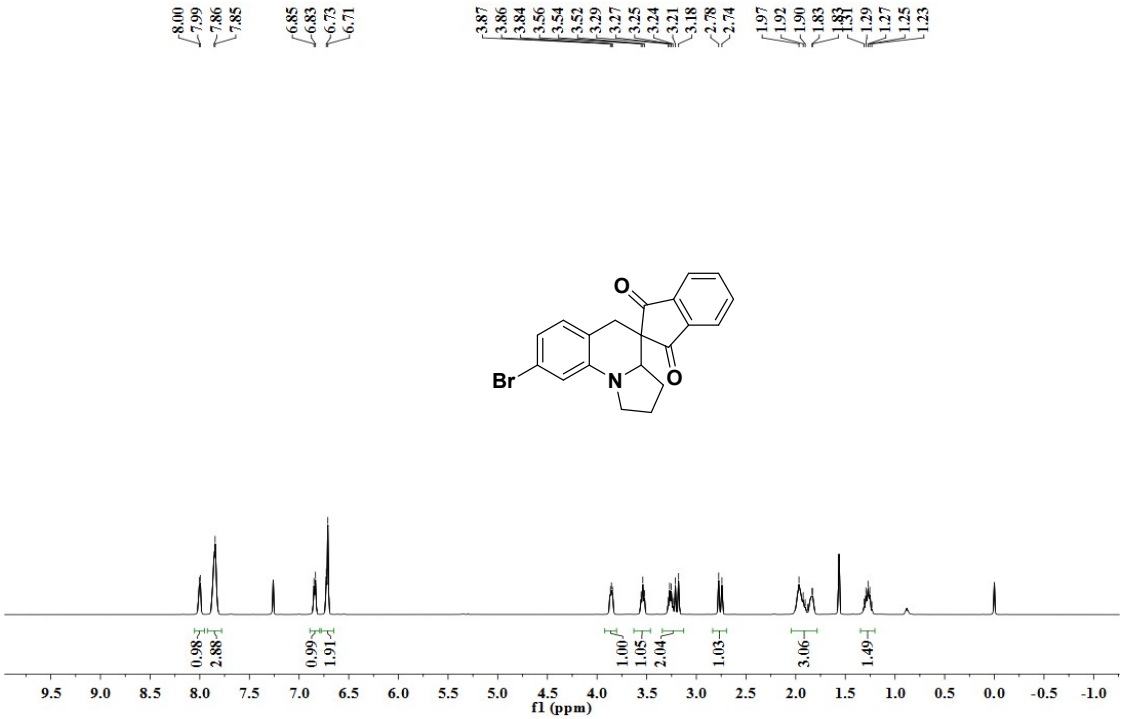


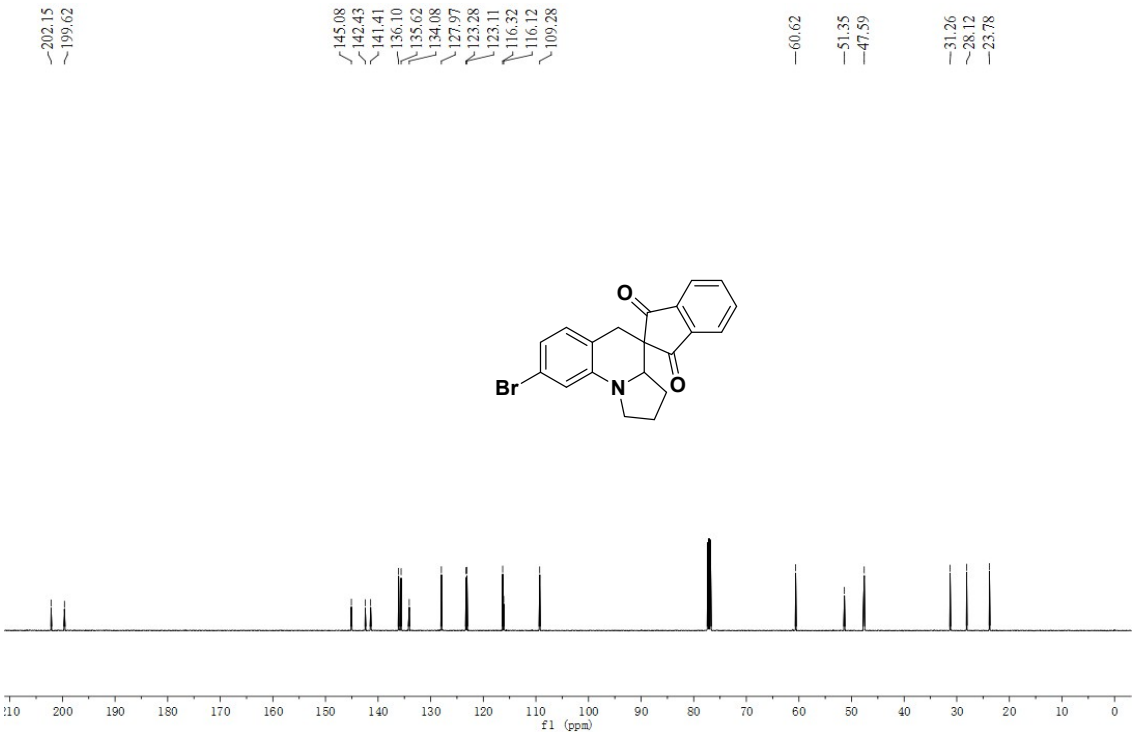
8'-methyl-1',2',3',3a'-tetrahydro-5'H-spiro[indene-2,4'-pyrrolo[1,2-a]quinoline]-1,3-dione (5f)



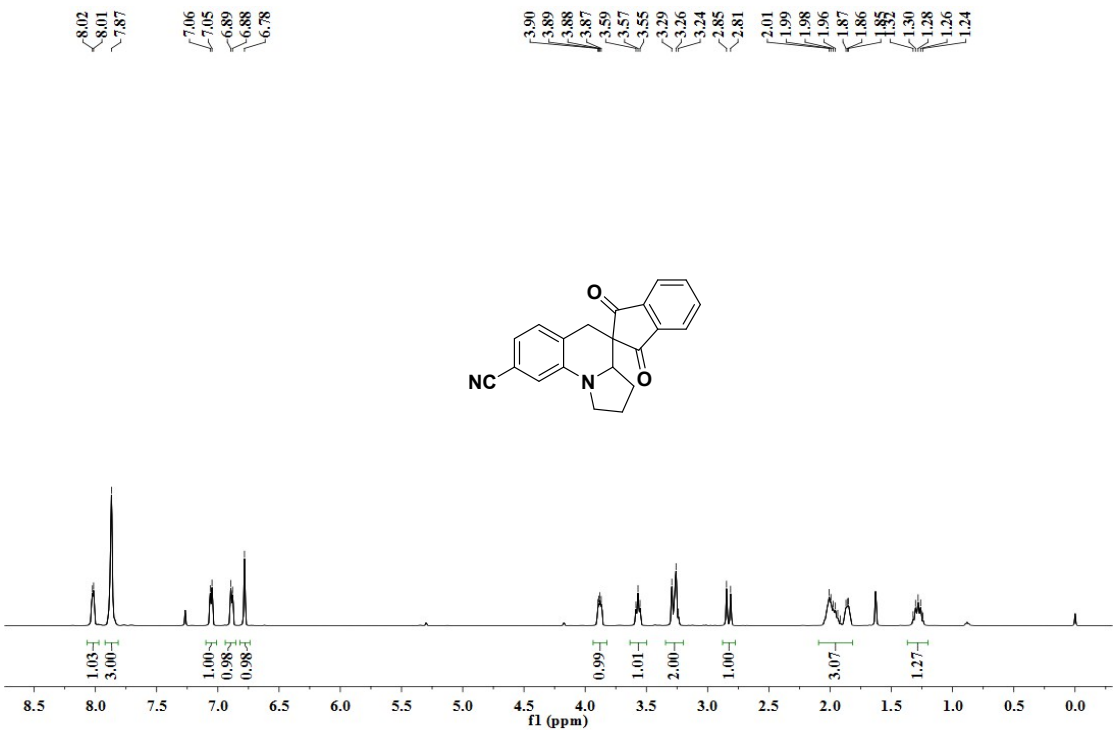


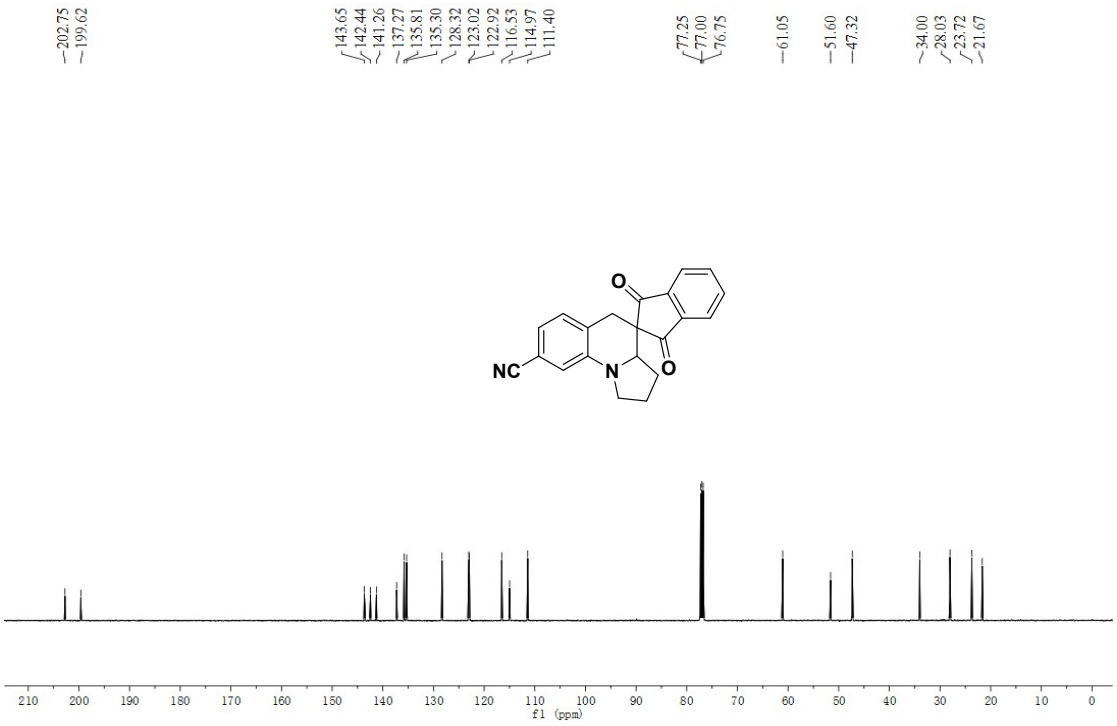
8'-bromo-1',2',3',3a'-tetrahydro-5'H-spiro[indene-2,4'-pyrrolo[1,2-a]quinoline]-1,3-dione (5g)



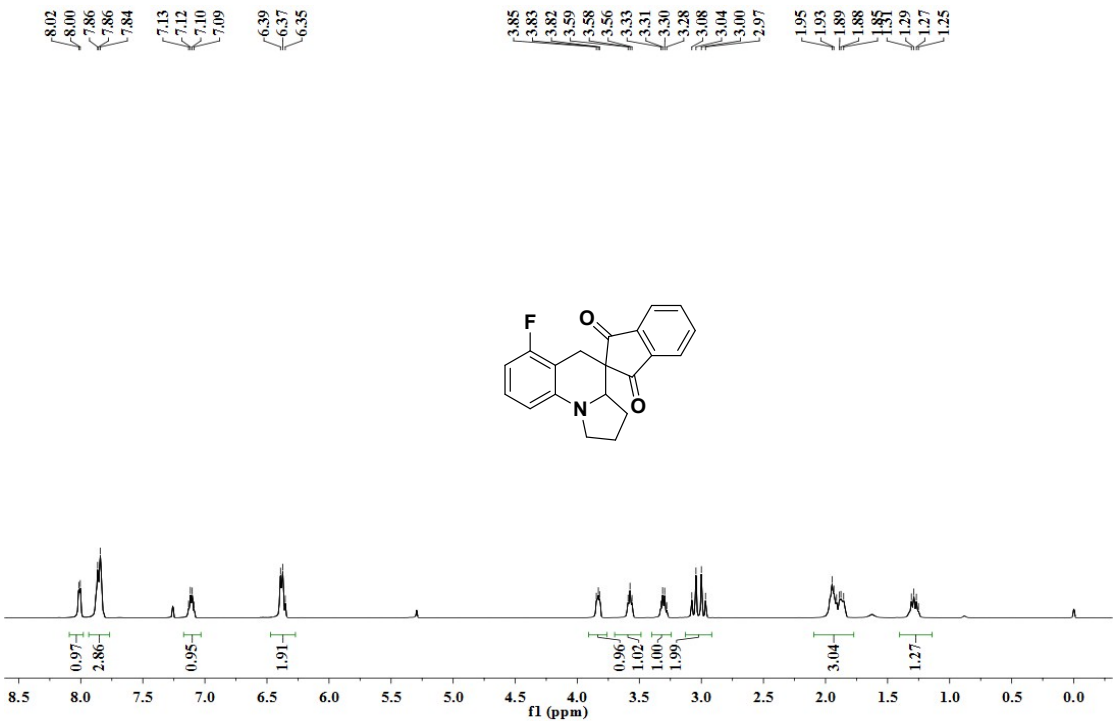


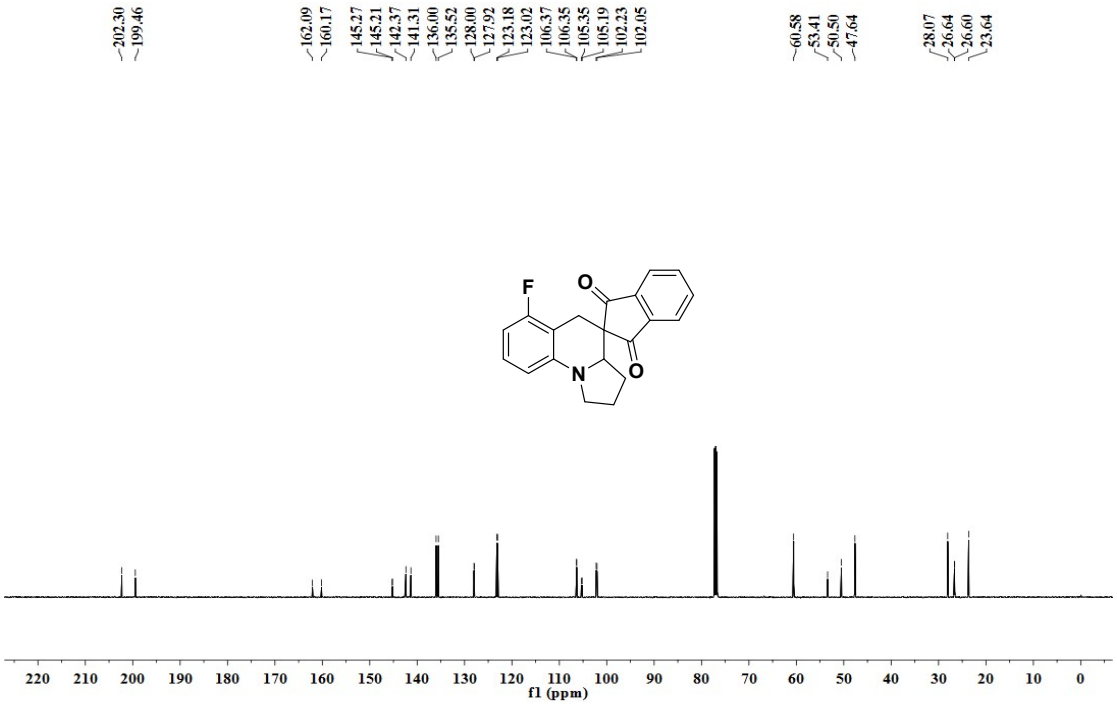
1,3-dioxo-1,1',2',3,3',3a'-hexahydro-5'H-spiro[indene-2,4'-pyrrolo[1,2-a]quinoline]-8'-carbonitrile (5h)



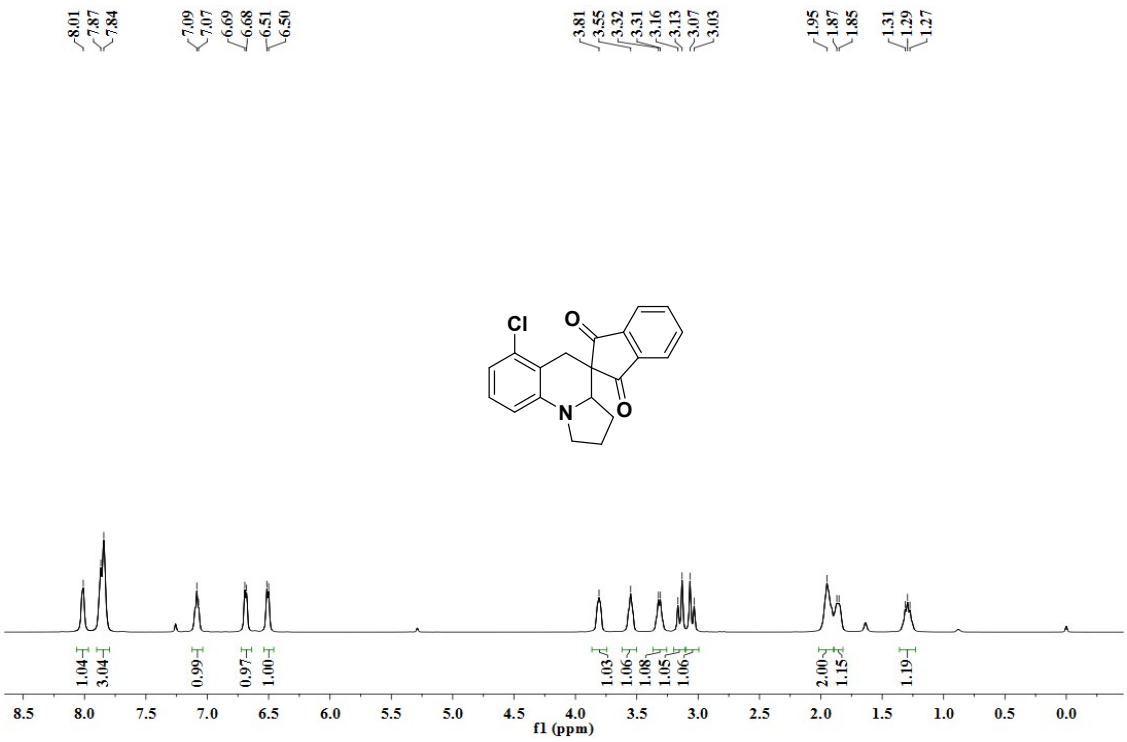


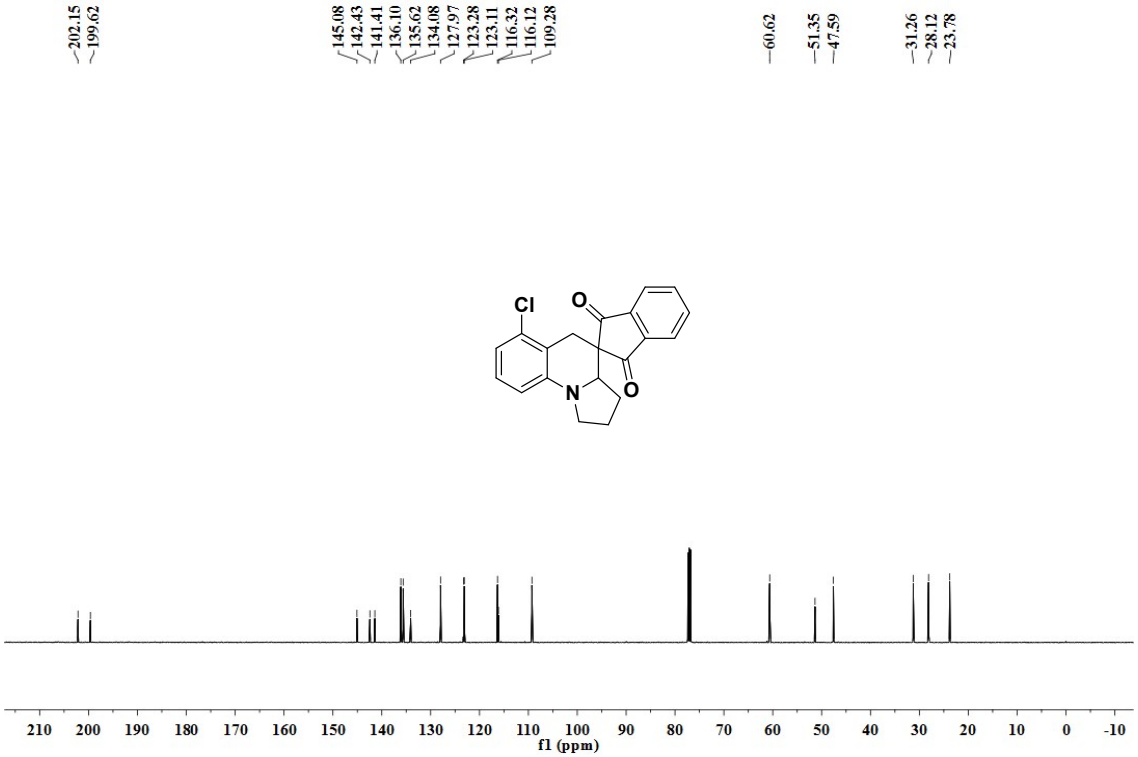
6'-fluoro-1',2',3',3a'-tetrahydro-5'H-spiro[indene-2,4'-pyrrolo[1,2-a]quinoline]-1,3-dione (5i)



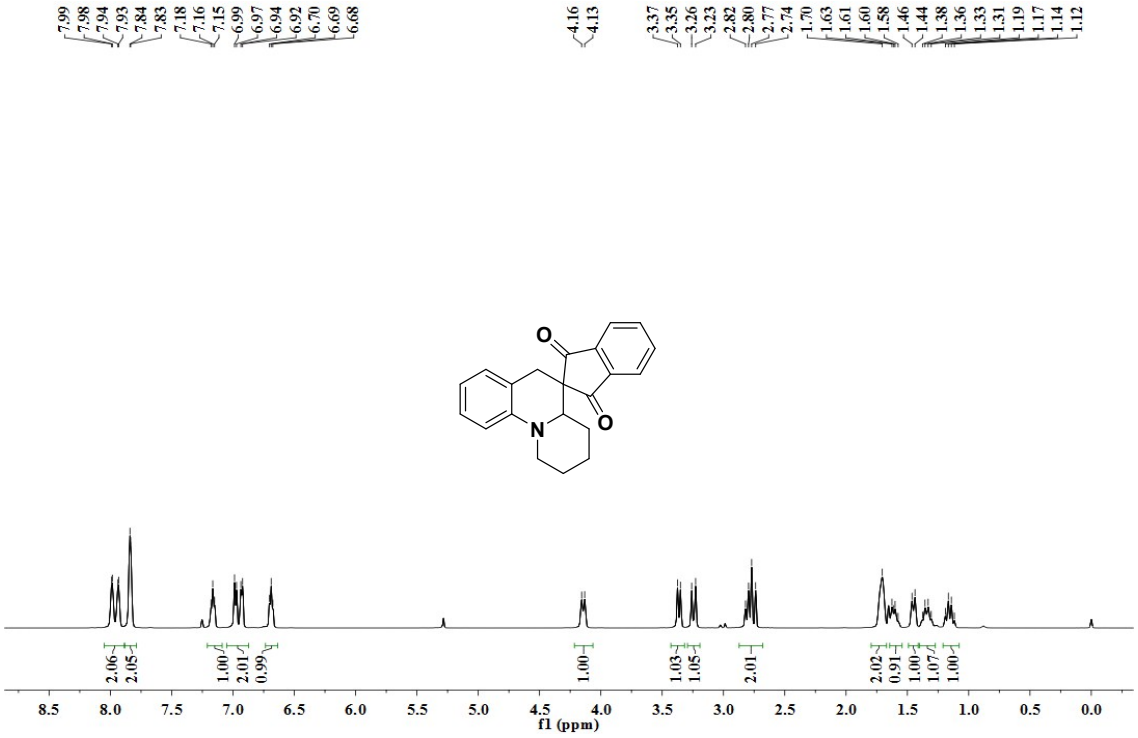


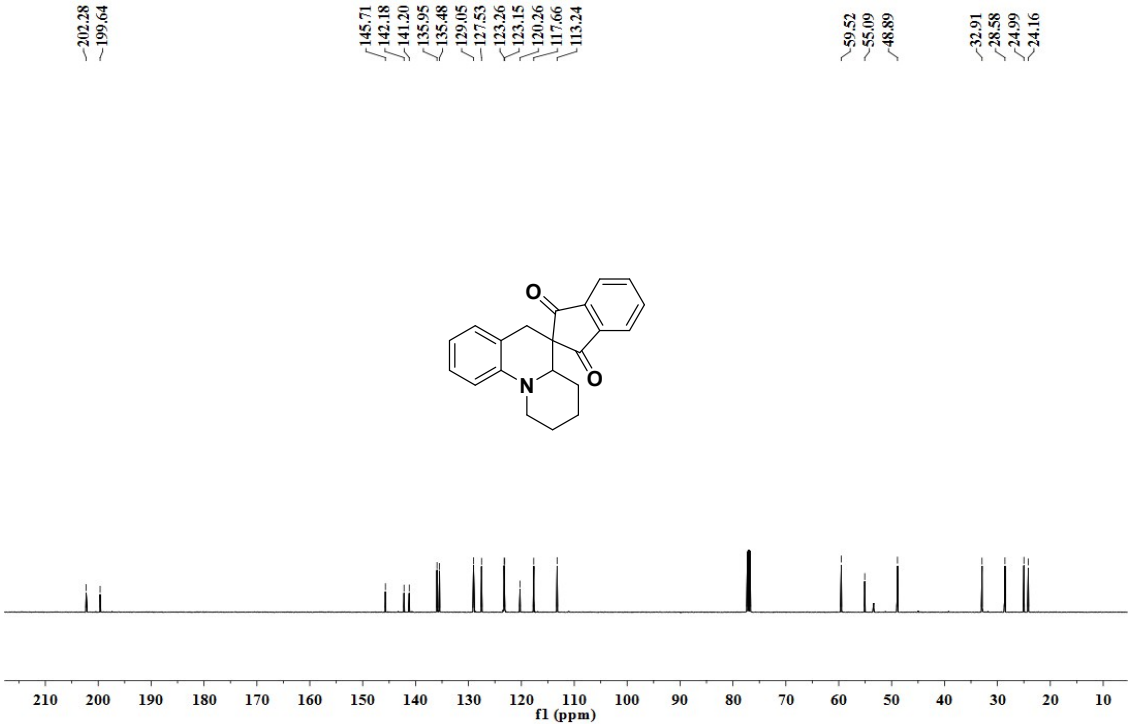
6'-chloro-1',2',3',3a'-tetrahydro-5'H-spiro[indene-2,4'-pyrrolo[1,2-a]quinoline]-1,3-dione (5j)



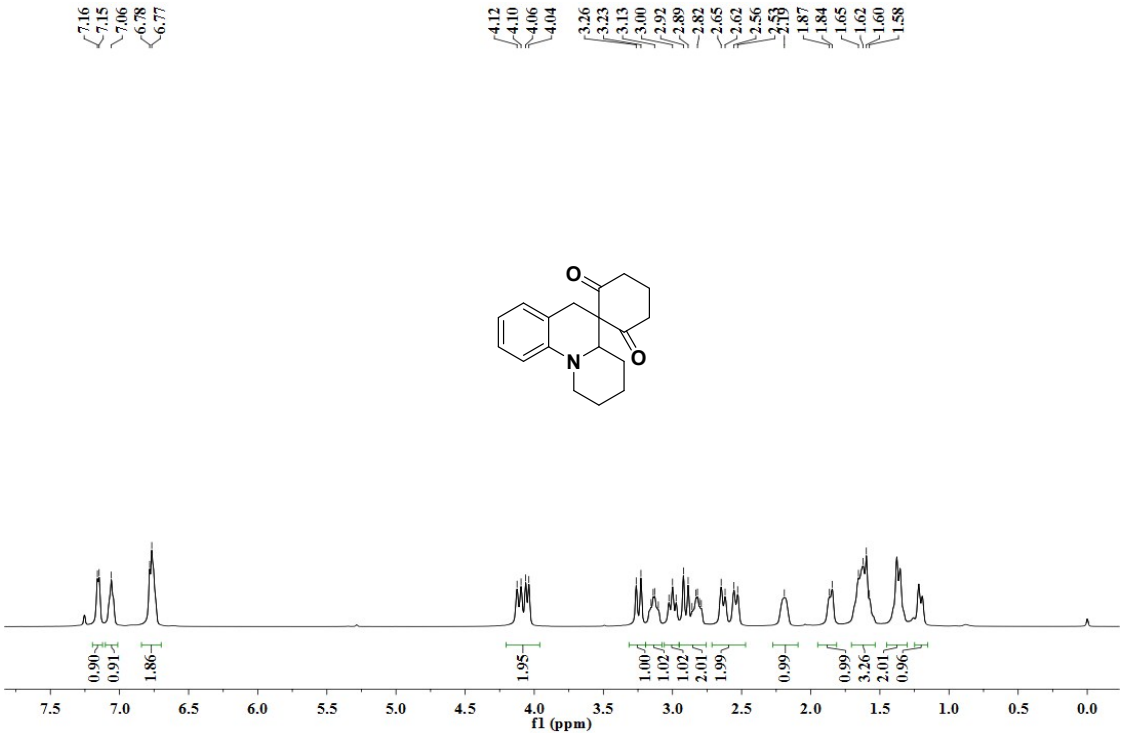


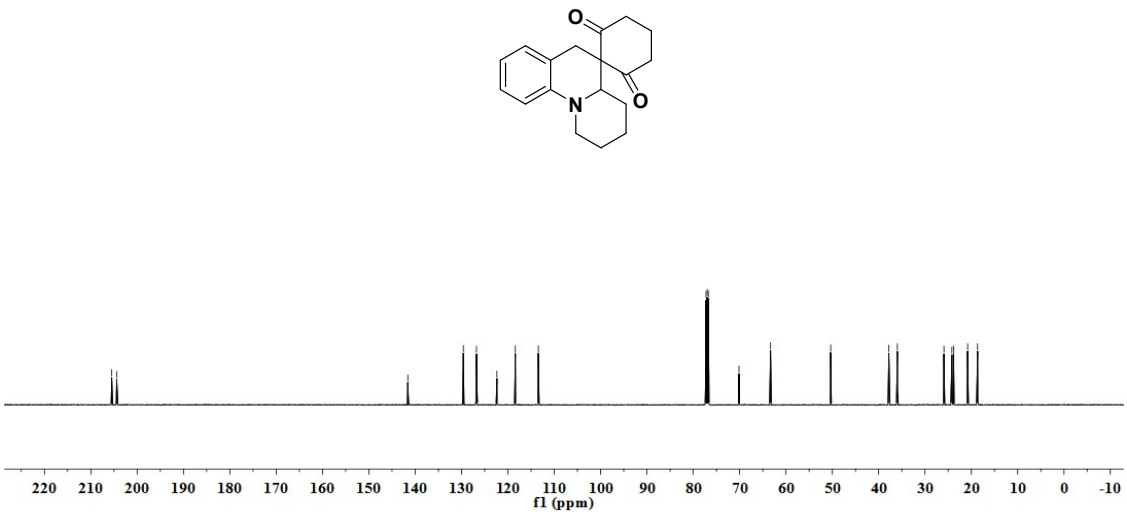
2',3',4',4a'-tetrahydro-1'H,6'H-spiro[indene-2,5'-pyrido[1,2-a]quinoline]-1,3-dione (5k)



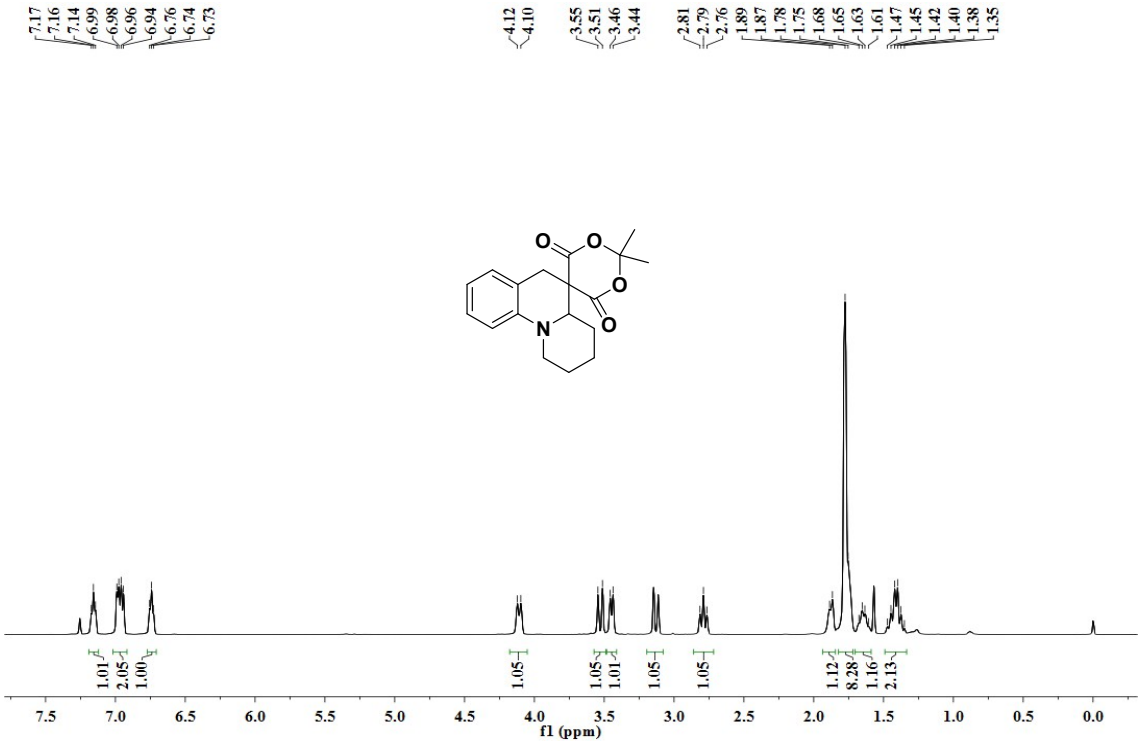


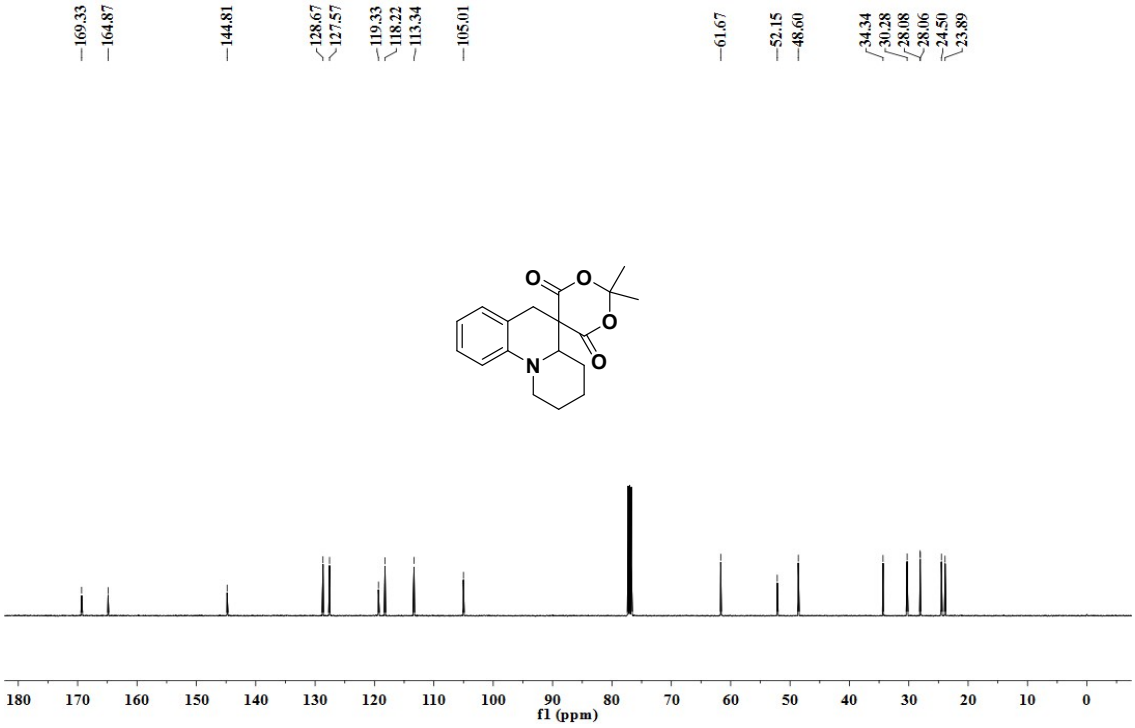
2',3',4',4a'-tetrahydro-1'H,6'H-spiro[cyclohexane-1,5'-pyrido[1,2-a]quinoline]-2,6-dione (5l)



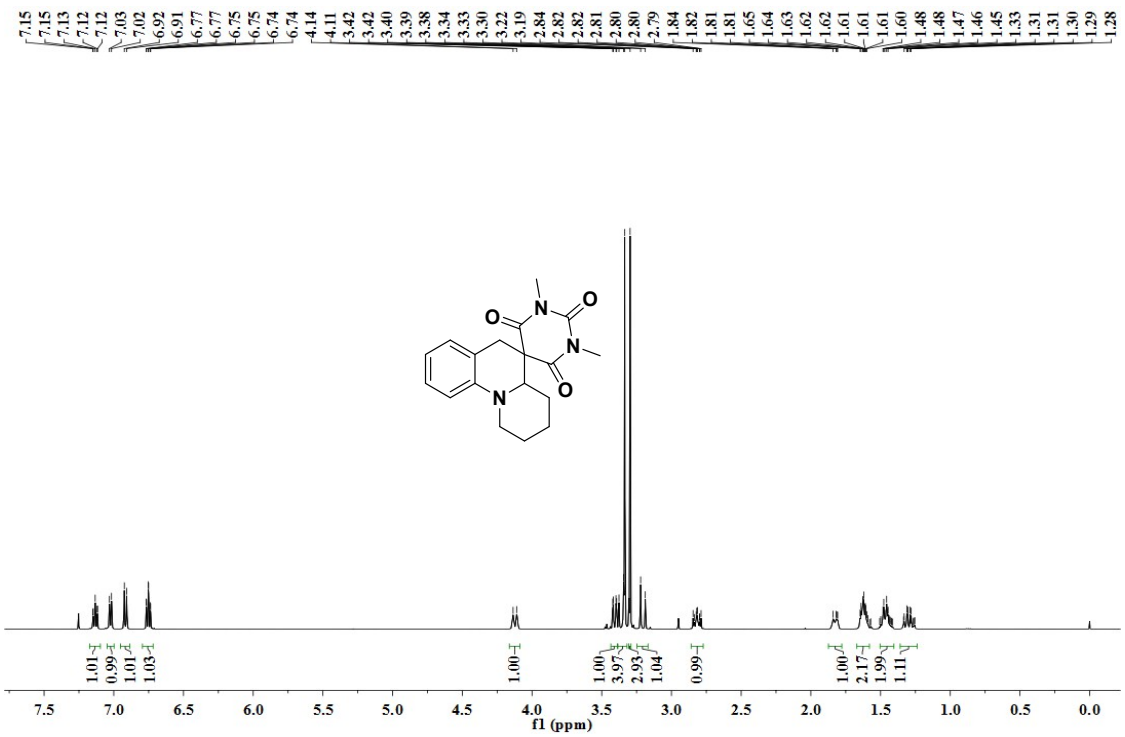


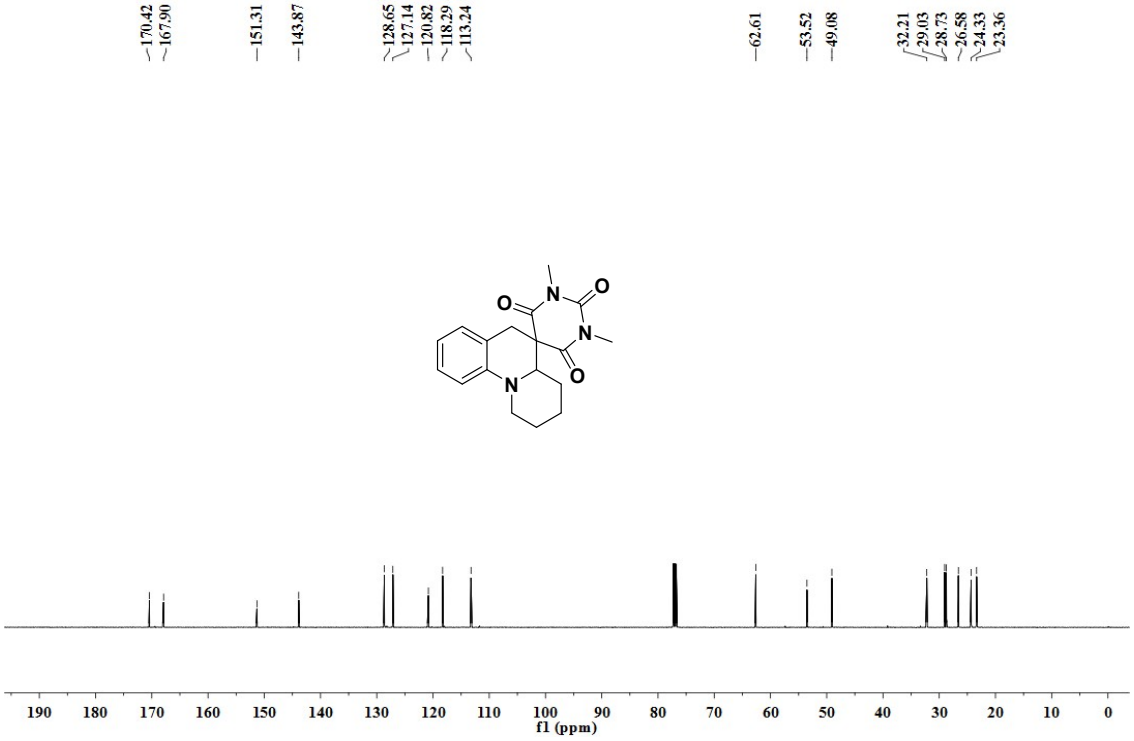
2',2'-dimethyl-2,3,4,4a-tetrahydro-1H,6H-spiro[pyrido[1,2-a]quinoline-5,5'-[1,3]dioxane]-4',6'-dione (5m)



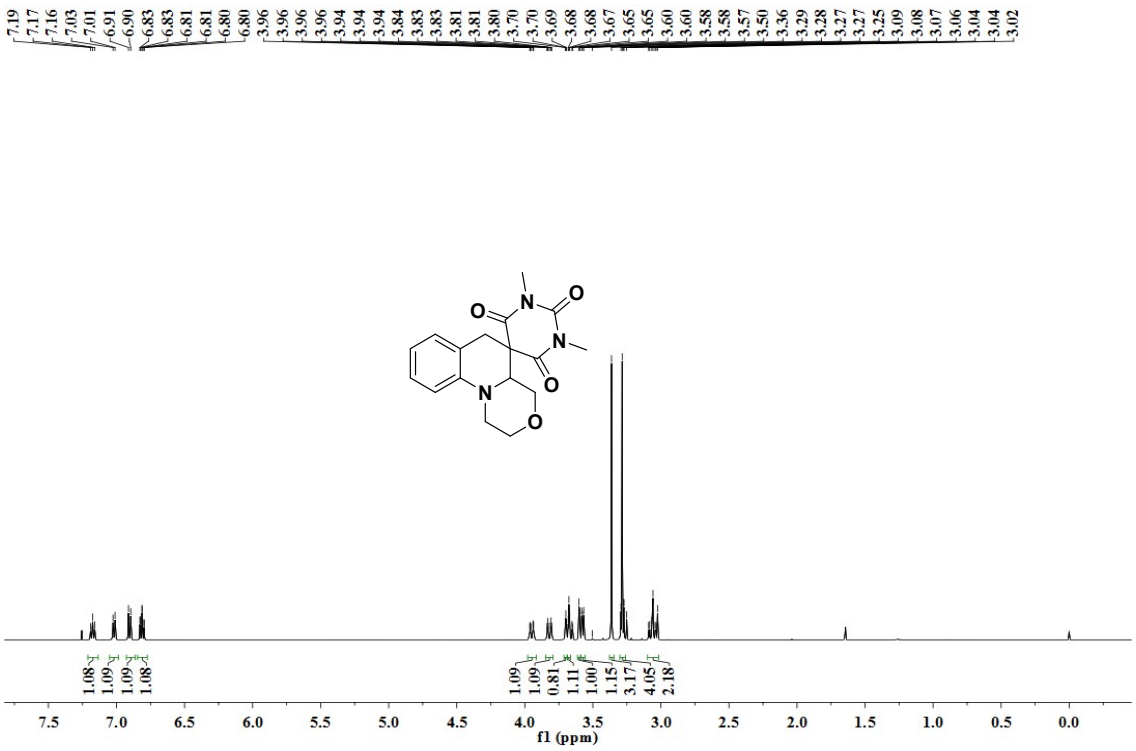


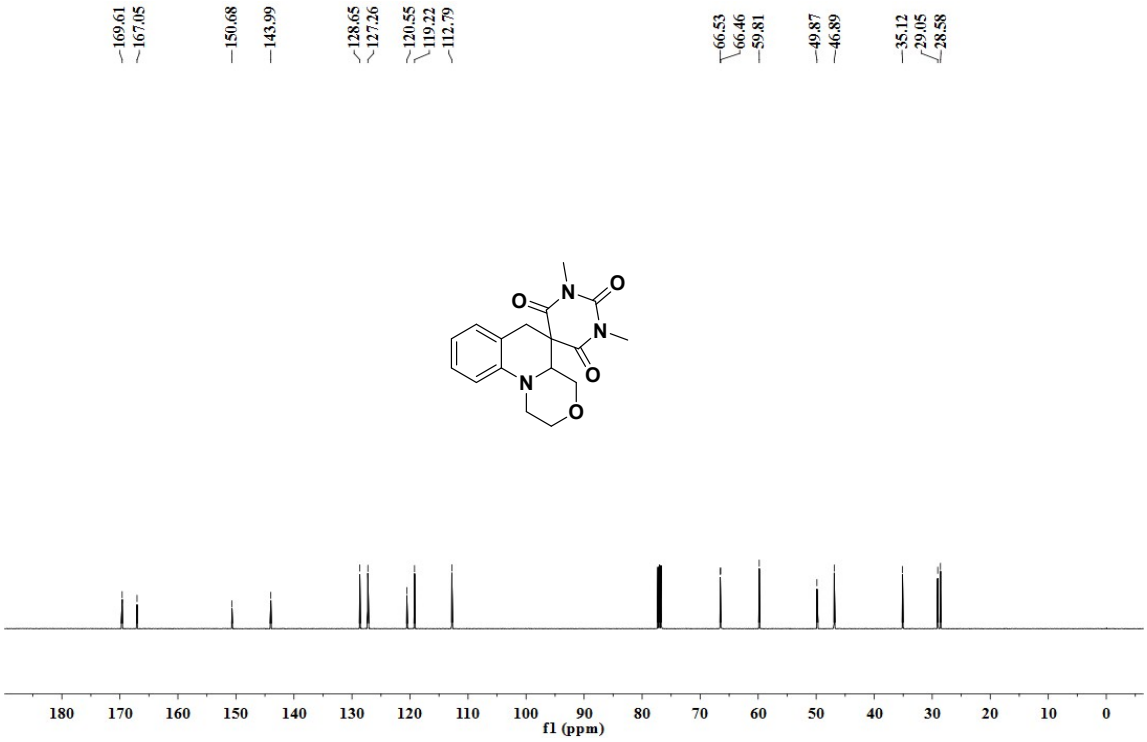
1',3'-dimethyl-2,3,4,4a-tetrahydro-1H,2'H,6H-spiro[pyrido[1,2-a]quinoline-5,5'-pyrimidine]-2',4',6'(1'H,3'H)-trione (5n)



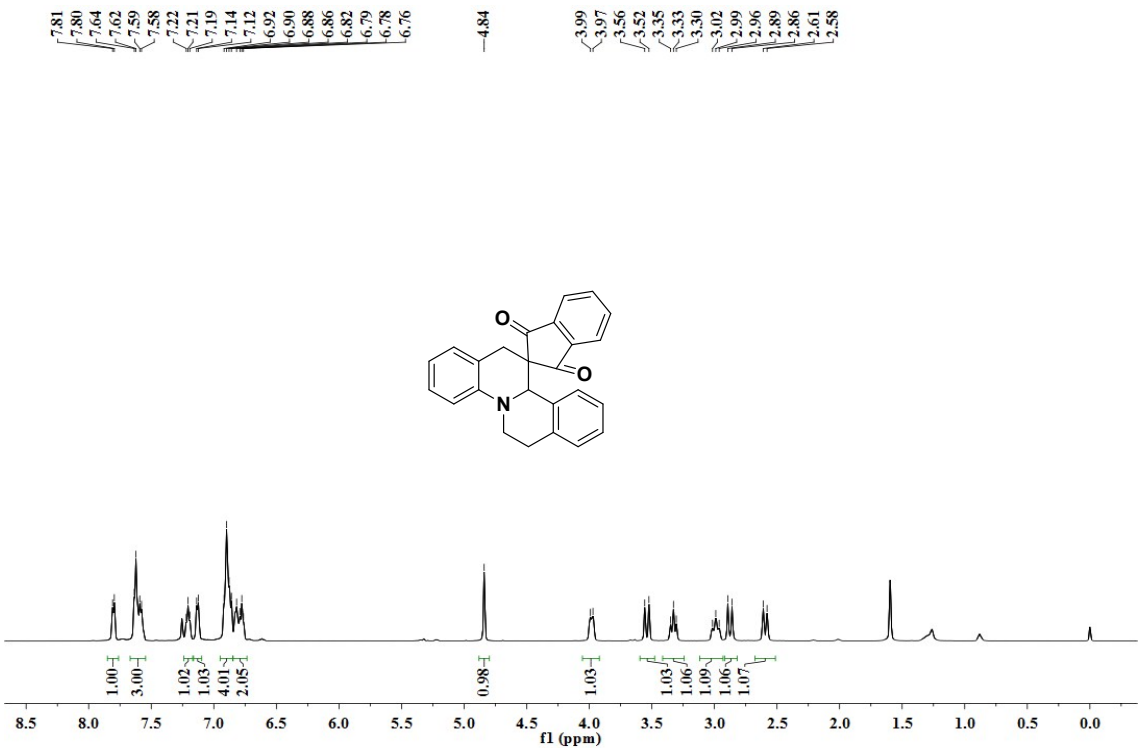


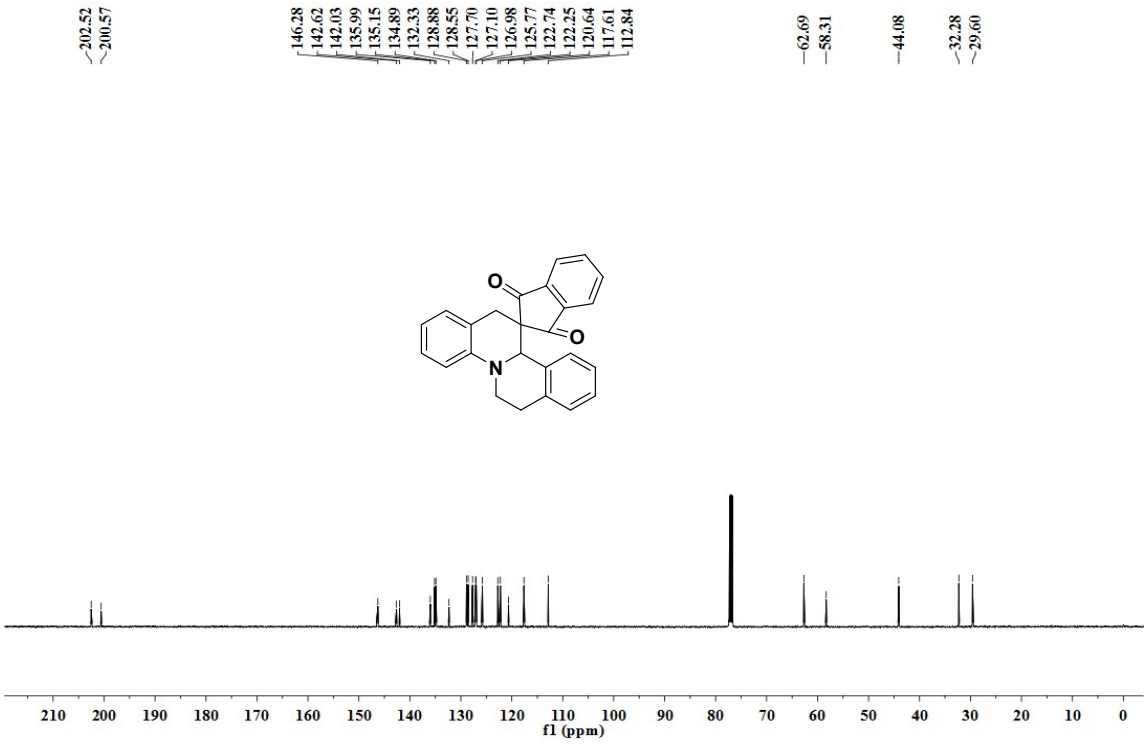
1,3-dimethyl-1',2',4',4a'-tetrahydro-2H,6'H-spiro[pyrimidine-5,5'-[1,4]oxazino[4,3-a]quinoline]-2,4,6(1H,3H)-trione (5o)



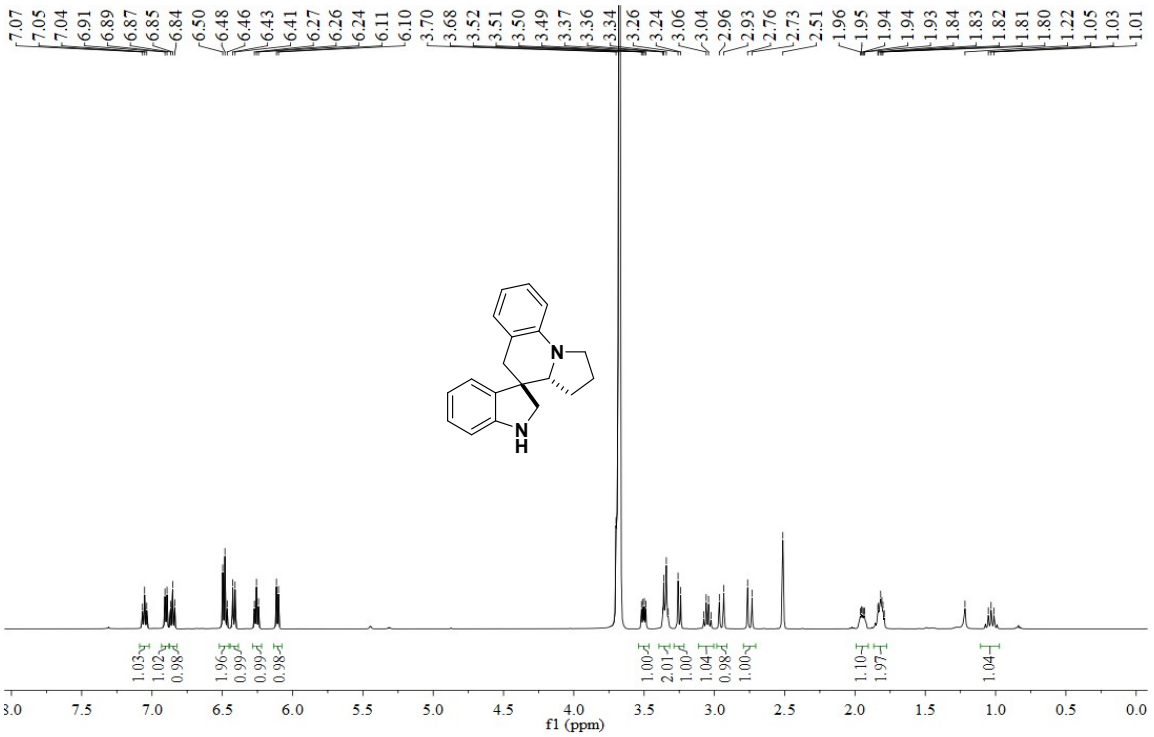


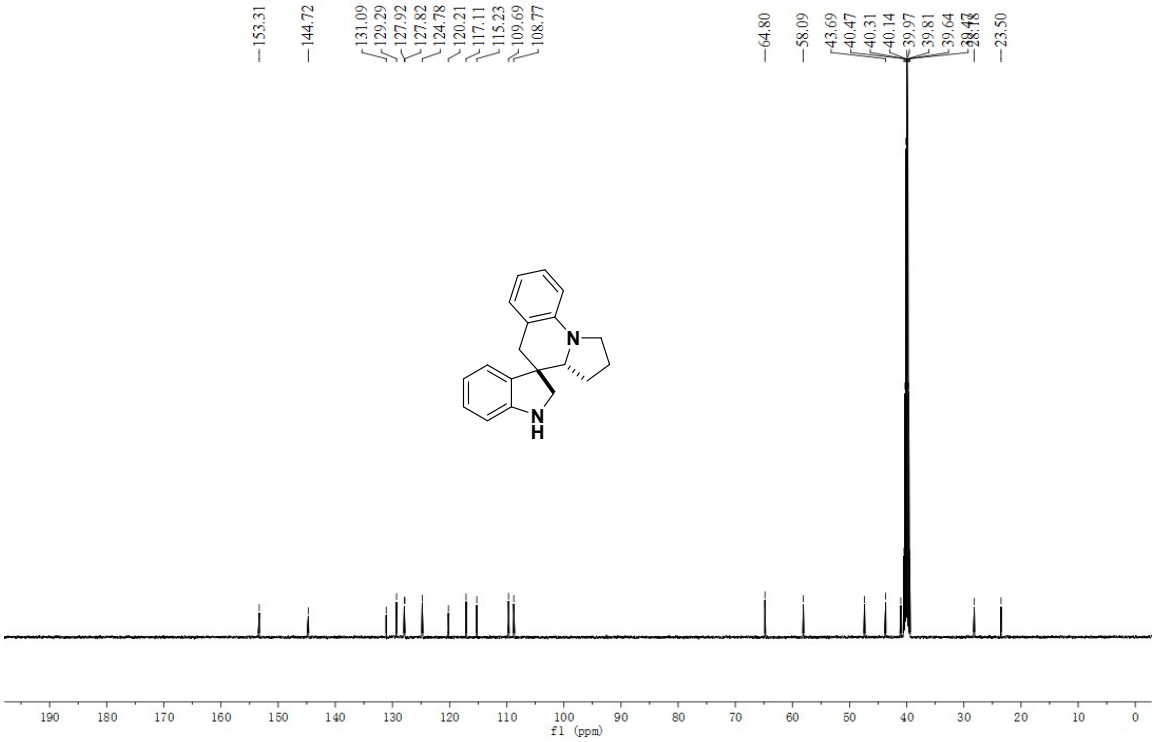
7',11b'-dihydro-6'H,13'H-spiro[indene-2,12'-isoquinolino[2,1-a]quinoline]-1,3-dione (5p)



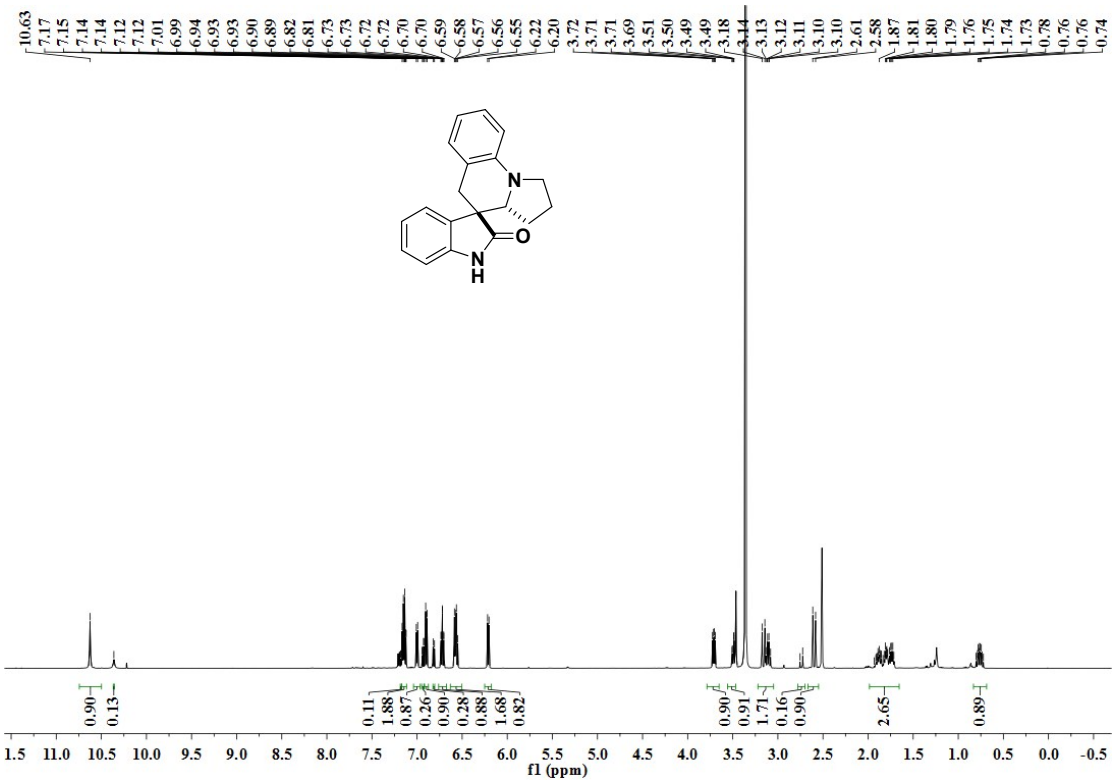


1',2',3',3a'-tetrahydro-5'H-spiro[indoline-3,4'-pyrrolo[1,2-a]quinoline] (6a)





The measurement of dr value to the crude product of 1',2',3',3a'-tetrahydro-5'H- spiro[indoline-3,4'-pyrrolo[1,2-a]quinolin]-2-one (**3a**)


10.63
7.17
7.15
7.14
7.14
7.12
7.12
7.01
6.99
6.94
6.93
6.93
6.90
6.89
6.82
6.81
6.73
6.73
6.72
6.72
6.70
6.70
6.59
6.58
6.57
6.56
6.55
6.22
6.20
3.72
3.71
3.71
3.69
3.51
3.50
3.49
3.49
3.18
3.14
3.13
3.12
3.11
3.10
3.10
2.61
2.58
1.87
1.81
1.80
1.79
1.76
1.75
1.74
1.73
0.78
0.76
0.76
0.74
N
O
N
H
0.90
0.13
0.11
1.88
0.87
0.26
0.90
0.28
0.88
1.68
0.82
0.90
0.91
1.71
0.16
0.90
2.65
0.89
1.5 11.0 10.5 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 0.0 -0.5
f1 (ppm)