Construction of the tetrahydroquinoline spiro skeleton via cascade [1,5]-hydride transfer-involved C(sp^3)-H functionalization "on water"

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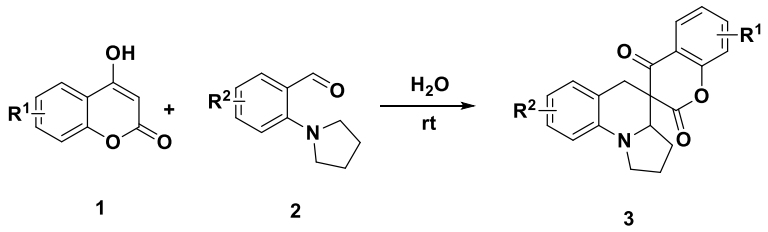
1. General Information

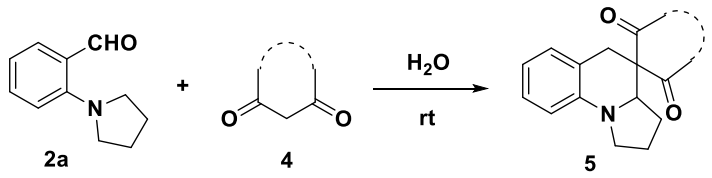
Reagents were purchased from chemical companies. All the reactions were performed in sealed tube and monitored by TLC (0.2 mm silica gel-coated HSGF 254 plates). The products were purified by flash column chromatography (200-300 mesh silica gel) eluted with the gradient of petroleum ether and ethyl acetate. 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 given 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) were reported in ppm using solvent $CDCl_3$ (δ (ppm) = 77.16 ppm) as an internal standard. HRMS analyses were performed on a Waters XEVO QTOF mass spectrometer.

2. Experimental Procedures



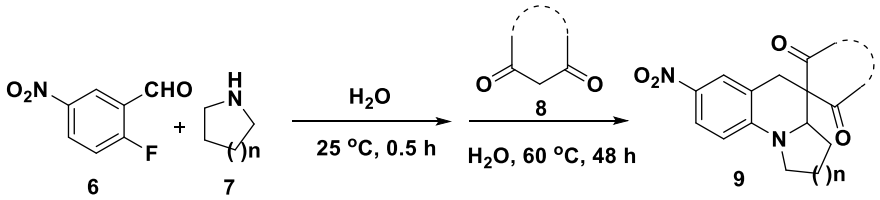
1 2 3

To a 15 mL pressure tube equipped with a magnetic stirrer bar were added water (1 mL), 4-hydroxycoumarin **1** (0.15 mmol), 2-(pyrrolidin-1-yl)benzaldehyde **2** (0.1 mmol)[1]. The resulting mixture was then stirred at room temperature (25 ℃). Reaction was monitored by TLC till 2-(pyrrolidin-1-yl)benzaldehyde **2** was consumed up. Afterwards the mixture was extracted thrice with ethyl acetate (3×5 mL), and the combined organic phases were washed with brine, dried over $MgSO_4$, and filtered. The volatile was removed in vacuo and the residue was purified on silica gel column, eluated with the gradient of petroleum ether and ethyl acetate to afford the desired product **3**.



2a 4 5

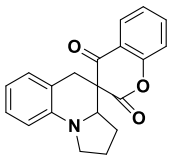
To a 15 mL pressure tube equipped with a magnetic stirrer bar were added water (1 mL), 1,3-carbonyl **4** (0.15 mmol), 2-(pyrrolidin-1-yl)benzaldehyde **2a** (0.1 mmol). The resulting mixture was then stirred at room temperature (25 ℃). Reaction was monitored by TLC till 2-(pyrrolidin-1-yl)benzaldehyde **2a** was consumed up. Afterwards the mixture was extracted thrice with ethyl acetate (3×5 mL), and the combined organic phases were washed with brine, dried over $MgSO_4$, and filtered. The volatile was removed in vacuo and the residue was purified on silica gel column, eluated with the gradient of petroleum ether and ethyl acetate to afford the desired product **5**.



To a 15 mL pressure tube equipped with a magnetic stirrer bar were added water (1 mL), 2-fluorobenzaldehyde **6** (0.1 mmol), pyrrolidine **7** (0.15 mmol). The resulting mixture was then stirred at room temperature (25 ℃). Reaction was monitored by TLC till 2-fluorobenzaldehyde **6** was consumed up. Then **8** (0.15 mmol) was added to the mixture, and it was heated to 60 ℃ for 48 h. Afterwards the mixture was extracted thrice with ethyl acetate (3×5 mL), and the combined organic phases were washed with brine, dried over $MgSO_4$, and filtered. The volatile was removed in vacuo and the residue was purified on silica gel column, eluated with the gradient of petroleum ether and ethyl acetate to afford the desired product **9**.

3. Characterization of Products

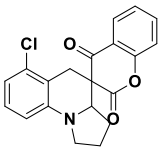
1',2',3',3a'-tetrahydro-5'H-spiro[chromane-3,4'-pyrrolo[1,2-a]quinoline]-2,4-dione (3a).



Via flash chromatography with a gradient of petroleum ether/EtOAc from 50/1 to 10/1, 26.2 mg yellow was funrished. The isolated yield was 82% and the diastereoselectivity was 70:30.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.69 (td, *J* = 8.4, 1.6 Hz, 1H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.21 (d, *J* = 8.2 Hz, 1H), 7.17 (dd, *J* = 9.3, 6.0 Hz, 1H), 7.07 (d, *J* = 7.4 Hz, 1H), 6.68 (t, *J* = 7.4 Hz, 1H), 6.62 (d, *J* = 8.2 Hz, 1H), 3.88 (dd, *J* = 9.4, 5.6 Hz, 1H), 3.62 – 3.56 (m, 2H), 3.40 – 3.35 (m, 1H), 3.08 (d, *J* = 16.4 Hz, 1H), 2.08 – 2.00 (m, 1H), 1.97 (ddd, *J* = 11.7, 8.8, 4.9 Hz, 2H), 1.68 – 1.61 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 192.66, 164.82, 155.19, 143.17, 137.28, 128.31, 127.53, 127.12, 124.90, 118.34, 117.63, 117.26, 116.22, 111.27, 63.82, 55.12, 47.47, 36.24, 28.02, 23.38.; **HRMS (ESI):** calcd. for $C_{20}H_{18}NO_3$ $[M+H]^+$: 320.1287, found: 320.1286.

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

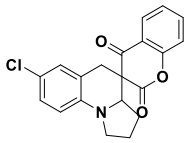


Via flash chromatography with a gradient of petroleum ether/EtOAc from 50/1 to 10/1, 26.5 mg yellow was funrished. The isolated yield was 75% and the diastereoselectivity was 71:29.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 – 7.99 (m, 1H), 7.70 (dd, *J* = 11.3, 4.3 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 8.3 Hz, 1H), 7.12 – 7.06 (m, 1H), 6.76 (d, *J* = 8.2 Hz, 1H), 6.53 (d, *J* = 8.2 Hz, 1H), 3.75 (dd, *J* = 8.9, 5.7 Hz, 1H), 3.56 (t, *J* = 7.8 Hz, 1H), 3.43 (s, 1H), 3.39 (d, *J* = 8.8 Hz, 2H), 2.10 – 2.00 (m, 1H), 2.00 – 1.91 (m, 2H), 1.68 – 1.60 (m, 1H); **^{13}C NMR** (125MHz, $CDCl_3$) δ 191.12, 164.05, 154.18, 143.33, 136.48, 132.90, 126.64, 126.25, 124.07, 117.40, 116.70, 116.09, 116.02, 108.78, 62.90,

54.41, 46.63, 32.09, 27.08, 22.33; **HRMS (ESI):** calcd. for $C_{20}H_{17}ClNO_3$ $[M+H]^+$: 354.0897, found: 354.0891.

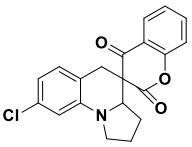
7'-chloro-1',2',3',3a'-tetrahydro-5'H-spiro[chromane-3,4'-pyrrolo[1,2-a]quinoline]-2,4-dione (3c).



Via flash chromatography with a gradient of petroleum ether/EtOAc from 50/1 to 10/1, 27.5 mg yellow was funrished. The isolated yield was 78% and the diastereoselectivity was 71:29.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.74 – 7.68 (m, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 8.3 Hz, 1H), 7.14 – 7.09 (m, 1H), 7.05 (s, 1H), 6.52 (d, *J* = 8.7 Hz, 1H), 3.83 (dd, *J* = 9.4, 5.6 Hz, 1H), 3.59 – 3.52 (m, 2H), 3.37 – 3.30 (m, 1H), 3.02 (d, *J* = 16.6 Hz, 1H), 2.04 (ddd, *J* = 9.4, 8.6, 3.3 Hz, 1H), 1.95 (ddd, *J* = 13.9, 8.2, 4.7 Hz, 2H), 1.67 – 1.60 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 191.27, 163.83, 154.12, 140.75, 136.47, 126.97, 126.29, 126.18, 124.06, 119.86, 119.10, 117.29, 116.68, 111.29, 63.06, 53.79, 46.61, 34.59, 27.02, 22.32; **HRMS (ESI):** calcd. for $C_{20}H_{17}ClNO_3$ $[M+H]^+$: 354.0897, found: 354.0899.

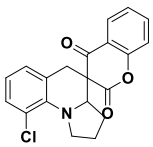
8'-chloro-1',2',3',3a'-tetrahydro-5'H-spiro[chromane-3,4'-pyrrolo[1,2-a]quinoline]-2,4-dione (3d).



Via flash chromatography with a gradient of petroleum ether/EtOAc from 50/1 to 10/1, 27.5 mg yellow was funrished. The isolated yield was 78% and the diastereoselectivity was 70:30.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.8 Hz, 1H), 7.70 (t, *J* = 8.4 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.25 – 7.19 (m, 1H), 6.96 (d, *J* = 7.9 Hz, 1H), 6.63 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.57 (s, 1H), 3.88 (dd, *J* = 9.6, 5.4 Hz, 1H), 3.59 – 3.51 (m, 2H), 3.33 (dd, *J* = 15.8, 8.7 Hz, 1H), 3.05 (d, *J* = 16.4 Hz, 1H), 2.11 – 2.01 (m, 1H), 2.00 – 1.95 (m, 2H), 1.68 – 1.62 (m, 1H); **^{13}C NMR** (125MHz, $CDCl_3$) δ 192.47, 164.70, 155.15, 144.06, 137.49, 133.15, 129.20, 127.22, 125.07, 118.25, 117.71, 116.69, 115.97, 111.05, 63.42, 54.66, 47.53, 36.03, 28.00, 23.41; **HRMS (ESI):** calcd. for $C_{20}H_{17}ClNO_3$ $[M+H]^+$: 354.0897, found: 354.0895.

9'-chloro-1',2',3',3a'-tetrahydro-5'H-spiro[chromane-3,4'-pyrrolo[1,2-a]quinoline]-2,4-dione (3e).

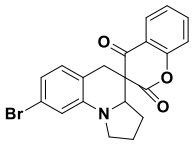


Via flash chromatography with a gradient of petroleum ether/EtOAc from 50/1 to 10/1, 25.7 mg yellow was funrished. The isolated yield was 73% and the diastereoselectivity was 65:35.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.6 Hz, 1H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.5 Hz,

1H), 7.27 (t, *J* = 10.2 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 1H), 7.06 (d, *J* = 7.2 Hz, 1H), 6.81 (t, *J* = 7.7 Hz, 1H), 4.32 (dd, *J* = 17.5, 8.7 Hz, 1H), 3.75 (t, *J* = 11.6 Hz, 2H), 3.41 (t, *J* = 10.2 Hz, 1H), 3.09 (d, *J* = 16.9 Hz, 1H), 2.15 (dt, *J* = 20.9, 10.6 Hz, 1H), 1.93 (d, *J* = 18.8 Hz, 2H), 1.82 – 1.74 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 192.50, 167.75, 155.55, 140.87, 137.56, 129.03, 127.26, 127.11, 125.47, 125.27, 122.49, 120.44, 119.02, 117.83, 69.26, 54.43, 53.21, 35.18, 28.30, 23.60; **HRMS (ESI):** calcd. for $C_{20}H_{17}ClNO_3$ $[M+H]^+$: 354.0897, found: 354.0896.

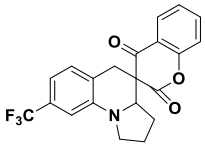
8'-bromo-1',2',3',3a'-tetrahydro-5'H-spiro[chromane-3,4'-pyrrolo[1,2-a]quinoline]-2,4-dione (3f).



Via flash chromatography with a gradient of petroleum ether/EtOAc from 50/1 to 10/1, 29.7 mg yellow was funrished. The isolated yield was 75% and the diastereoselectivity was 68:32.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.73 – 7.67 (m, 1H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.22 (d, *J* = 8.2 Hz, 1H), 6.91 (d, *J* = 7.9 Hz, 1H), 6.77 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.72 (d, *J* = 1.6 Hz, 1H), 3.87 (dd, *J* = 9.7, 5.5 Hz, 1H), 3.58 – 3.52 (m, 1H), 3.50 (d, *J* = 16.4 Hz, 1H), 3.36 – 3.29 (m, 1H), 3.03 (d, *J* = 16.4 Hz, 1H), 2.09 – 2.01 (m, 1H), 2.01 – 1.94 (m, 2H), 1.68 – 1.60 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 191.37, 163.68, 154.11, 143.25, 136.48, 128.48, 126.18, 124.05, 120.21, 117.81, 117.22, 116.67, 116.33, 112.85, 62.42, 53.59, 46.48, 34.90, 26.96, 22.36; **HRMS (ESI):** calcd. for $C_{20}H_{17}BrNO_3$ $[M+H]^+$: 398.0392, found: 398.0396.

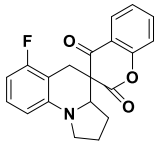
8'-(trifluoromethyl)-1',2',3',3a'-tetrahydro-5'H-spiro[chromane-3,4'-pyrrolo[1,2-a]quinoline]-2,4-dione (3g).



Via flash chromatography with a gradient of petroleum ether/EtOAc from 50/1 to 10/1, 32.1 mg yellow was funrished. The isolated yield was 83% and the diastereoselectivity was 69:31.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.73 – 7.68 (m, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 8.3 Hz, 1H), 7.15 (d, *J* = 7.8 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.79 (s, 1H), 3.85 (dd, *J* = 9.5, 5.5 Hz, 1H), 3.61 (td, *J* = 10.9, 5.9 Hz, 2H), 3.41 – 3.36 (m, 1H), 3.10 (d, *J* = 16.7 Hz, 1H), 2.06 (dt, *J* = 7.9, 6.6 Hz, 1H), 2.02 – 1.96 (m, 2H), 1.66 (ddd, *J* = 20.4, 11.0, 5.1 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 192.24, 164.86, 155.16, 143.13, 137.60, 129.85, 128.55, 127.26, 125.17, 122.24, 118.31, 117.76, 112.66, 107.61, 63.99, 54.63, 47.46, 35.67, 28.08, 23.33; **HRMS (ESI):** calcd. for $C_{21}H_{17}F_3NO_3$ $[M+H]^+$: 388.1161, found: 388.1163.

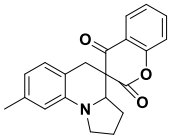
6'-fluoro-1',2',3',3a'-tetrahydro-5'H-spiro[chromane-3,4'-pyrrolo[1,2-a]quinoline]-2,4-dione (3h).



Via flash chromatography with a gradient of petroleum ether/EtOAc from 50/1 to 10/1, 27.9 mg yellow was funrished. The isolated yield was 83% and the diastereoselectivity was 70:30.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.72 – 7.68 (m, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 8.3 Hz, 1H), 7.11 (dt, *J* = 14.7, 6.7 Hz, 1H), 6.43 (t, *J* = 6.4 Hz, 1H), 6.40 (d, *J* = 8.3 Hz, 1H), 3.80 (dd, *J* = 9.2, 5.7 Hz, 1H), 3.59 (dt, *J* = 8.7, 5.4 Hz, 1H), 3.40 – 3.34 (m, 2H), 3.30 (d, *J* = 4.2 Hz, 1H), 2.08 – 2.00 (m, 1H), 2.00 – 1.92 (m, 2H), 1.68 – 1.59 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 192.40, 164.87, 162.00, 160.08, 155.18, 137.47, 127.84, 127.76, 127.23, 125.07, 118.37, 117.71, 106.94, 106.93, 102.93, 102.75, 63.61, 54.41, 47.74, 28.92, 28.91, 28.88, 28.87, 28.11, 23.33; **HRMS (ESI)**: calcd for $C_{20}H_{18}FNO_3[M+H]^+$:338.1192, found:338.1190.

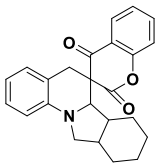
8'-methyl-1',2',3',3a'-tetrahydro-5'H-spiro[chromane-3,4'-pyrrolo[1,2-a]quinoline]-2,4-dione (3i).



Via flash chromatography with a gradient of petroleum ether/EtOAc from 50/1 to 10/1, 26.6 mg yellow was funrished. The isolated yield was 80% and the diastereoselectivity was 69:31.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.70 – 7.66 (m, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.20 (d, *J* = 8.3 Hz, 1H), 6.95 (d, *J* = 7.5 Hz, 1H), 6.50 (d, *J* = 7.5 Hz, 1H), 6.44 (s, 1H), 3.87 (dd, *J* = 9.3, 5.5 Hz, 1H), 3.63 – 3.56 (m, 2H), 3.38 – 3.32 (m, 1H), 3.05 (d, *J* = 16.2 Hz, 1H), 2.32 (s, 3H), 2.07 – 1.99 (m, 1H), 1.96 (dd, *J* = 15.1, 6.8 Hz, 2H), 1.68 – 1.61 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 192.81, 164.87, 155.24, 143.07, 137.26, 136.51, 128.19, 127.15, 124.90, 118.40, 117.66, 117.26, 115.39, 112.06, 63.78, 55.34, 47.49, 36.22, 28.05, 23.44, 21.65; **HRMS (ESI):** calcd. for $C_{21}H_{20}NO_3$ $[M+H]^+$: 344.1443, found: 344.1447.

6a',6b',7',8',9',10',10a',11'-octahydro-5'H-spiro[chromane-3,6'-isoindolo[2,1-a]quinoline]-2,4-dione (3k).

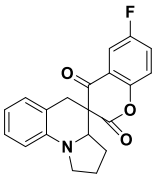


Via flash chromatography with a gradient of petroleum ether/EtOAc from 50/1 to 10/1, 32.8 mg yellow was funrished. The isolated yield was 88% and the diastereoselectivity was 70:30.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 – 7.96 (m, 1H), 7.71 – 7.66 (m, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.19 (dd, *J* = 18.5, 8.0 Hz, 2H), 6.98 (d, *J* = 7.3 Hz, 1H), 6.60 (dd, *J* = 12.4, 5.3 Hz, 2H), 3.98 – 3.95 (m, 1H), 3.73 – 3.65 (m, 1H), 3.40 (t, *J* = 11.9 Hz, 1H), 3.11 (dt, *J* = 16.2, 12.5 Hz, 1H), 2.91 (dt, *J* = 10.4, 8.2 Hz, 1H), 2.00 – 1.92 (m, 1H), 1.81 (dtd, *J* = 18.4, 7.1, 3.6 Hz, 1H), 1.77 – 1.67 (m, 2H), 1.63 (t, *J* = 16.1 Hz, 1H), 1.25 (ddt, *J* = 16.1, 6.7, 6.0 Hz, 3H), 1.13 (dtd, *J* = 24.1, 11.8, 3.0 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 193.21, 164.11, 155.28, 143.61, 137.32, 128.29, 128.13, 127.17, 125.01, 117.97, 117.71, 116.39, 115.25, 110.17, 67.55, 53.14, 52.08, 46.71, 43.21, 39.23, 29.15, 28.59, 25.54, 25.48; **HRMS (ESI):** calcd. for $C_{24}H_{24}NO_3$ $[M+H]^+$:374.1756, found: 374.1761.

6-fluoro-1',2',3',3a'-tetrahydro-5'H-spiro[chromane-3,4'-pyrrolo[1,2-a]quinoline]-2,4-dione

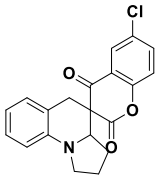
(3l).



Via flash chromatography with a gradient of petroleum ether/EtOAc from 50/1 to 10/1, 28.3 mg yellow was funrished. The isolated yield was 84% and the diastereoselectivity was 68:32.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 7.7, 3.0 Hz, 1H), 7.44 – 7.37 (m, 1H), 7.21 (dd, *J* = 9.0, 4.0 Hz, 1H), 7.17 (t, *J* = 7.3 Hz, 1H), 7.07 (d, *J* = 7.4 Hz, 1H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 8.1 Hz, 1H), 3.85 (dd, *J* = 9.2, 5.5 Hz, 1H), 3.58 (dd, *J* = 12.6, 9.0 Hz, 2H), 3.39 – 3.34 (m, 1H), 3.07 (d, *J* = 16.4 Hz, 1H), 2.03 (ddd, *J* = 9.2, 8.7, 3.2 Hz, 1H), 2.00 – 1.94 (m, 2H), 1.66 – 1.59 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 192.07, 164.40, 160.08, 158.12, 151.36, 143.09, 128.36, 127.66, 124.75, 123.97, 119.68, 118.16, 116.39, 111.40, 64.07, 54.90, 47.52, 36.32, 28.06, 23.39; **HRMS (ESI):** calcd. for $C_{20}H_{17}FNO_3$ $[M+H]^+$:338.1192, found: 338.1190.

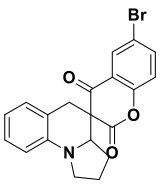
6-chloro-1',2',3',3a'-tetrahydro-5'H-spiro[chromane-3,4'-pyrrolo[1,2-a]quinoline]-2,4-dione (3m).



Via flash chromatography with a gradient of petroleum ether/EtOAc from 50/1 to 10/1, 28.2 mg yellow was funrished. The isolated yield was 80% and the diastereoselectivity was 70:30.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 2.1 Hz, 1H), 7.61 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.17 (dd, *J* = 10.2, 6.1 Hz, 2H), 7.06 (d, *J* = 7.3 Hz, 1H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.61 (d, *J* = 8.1 Hz, 1H), 3.85 (dd, *J* = 9.1, 5.4 Hz, 1H), 3.58 (dd, *J* = 13.0, 8.5 Hz, 2H), 3.39 – 3.31 (m, 1H), 3.06 (d, *J* = 16.4 Hz, 1H), 2.02 (dd, *J* = 14.8, 5.8 Hz, 1H), 1.95 (dt, *J* = 14.6, 7.3 Hz, 2H), 1.64 – 1.57 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 191.73, 164.17, 153.59, 143.04, 137.06, 130.61, 128.35, 127.66, 126.51, 119.39, 119.23, 118.09, 116.39, 111.38, 64.03, 55.14, 47.50, 36.29, 28.05, 23.38; **HRMS (ESI):** calcd. for $C_{20}H_{17}ClNO_3$ $[M+H]^+$:354.0897, found: 354.0895.

6-bromo-1',2',3',3a'-tetrahydro-5'H-spiro[chromane-3,4'-pyrrolo[1,2-a]quinoline]-2,4-dione (3n).

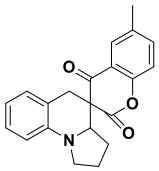


Via flash chromatography with a gradient of petroleum ether/EtOAc from 50/1 to 10/1, 30.9 mg yellow was funrished. The isolated yield was 78% and the diastereoselectivity was 68:32.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 2.4 Hz, 1H), 7.75 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.16 (dd, *J* = 12.6, 4.8 Hz, 1H), 7.10 (d, *J* = 8.7 Hz, 1H), 7.06 (d, *J* = 7.4 Hz, 1H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.61 (d, *J*

= 8.1 Hz, 1H), 3.84 (dd, *J* = 9.2, 5.5 Hz, 1H), 3.62 – 3.55 (m, 2H), 3.35 (dd, *J* = 13.6, 6.4 Hz, 1H), 3.06 (d, *J* = 16.4 Hz, 1H), 2.03 (td, *J* = 9.3, 3.4 Hz, 1H), 2.00 – 1.95 (m, 2H), 1.65 – 1.57 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 191.59, 164.11, 154.07, 143.03, 139.88, 129.59, 128.34, 127.65, 119.65, 118.08, 116.38, 111.37, 64.02, 55.17, 47.49, 36.28, 28.05, 23.37; **HRMS (ESI):** calcd. for $C_{20}H_{17}BrNO_3$ $[M+H]^+$:398.0392, found: 398.0394.

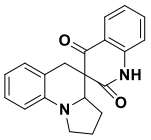
6-methyl-1',2',3',3a'-tetrahydro-5'H-spiro[chromane-3,4'-pyrrolo[1,2-a]quinoline]-2,4-dione (3o).



Via flash chromatography with a gradient of petroleum ether/EtOAc from 50/1 to 10/1, 26.9 mg yellow was funrished. The isolated yield was 81% and the diastereoselectivity was 70:30.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.54 – 7.50 (m, 1H), 7.24 – 7.14 (m, 2H), 7.11 (d, *J* = 7.4 Hz, 1H), 6.71 (t, *J* = 7.4 Hz, 1H), 6.65 (d, *J* = 8.1 Hz, 1H), 3.90 (dd, *J* = 9.3, 5.6 Hz, 1H), 3.63 (dd, *J* = 15.6, 5.3 Hz, 2H), 3.43 – 3.40 (m, 1H), 3.10 (d, *J* = 16.4 Hz, 1H), 2.45 (s, 3H), 2.05 (dd, *J* = 13.5, 6.9 Hz, 1H), 2.02 – 1.97 (m, 2H), 1.69 (dd, *J* = 13.7, 6.4 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 192.84, 165.11, 153.30, 143.20, 138.21, 134.81, 128.32, 127.50, 126.74, 118.48, 117.44, 117.06, 116.20, 111.26, 63.84, 54.99, 47.49, 36.18, 28.05, 23.40, 20.61; **HRMS (ESI):** calcd. for $C_{21}H_{20}NO_3$ $[M+H]^+$: 344.1443, found: 344.1438.

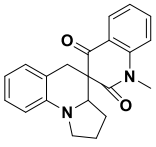
1,2,3,3a-tetrahydro-2'H,5H-spiro[pyrrolo[1,2-a]quinoline-4,3'-quinoline]-2',4'(1'H)-dione (5a).



Via flash chromatography with a gradient of petroleum ether/EtOAc from 50/1 to 10/1, 27.9 mg yellow was funrished. The isolated yield was 88% and the diastereoselectivity was 57:43.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.00 (s, 1H), 7.95 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.53 – 7.48 (m, 1H), 7.22 – 7.18 (m, 1H), 7.13 (d, *J* = 7.3 Hz, 1H), 7.03 (d, *J* = 7.3 Hz, 1H), 6.62 (dd, *J* = 8.6, 3.3 Hz, 3H), 3.97 (dd, *J* = 9.4, 5.4 Hz, 1H), 3.65 – 3.59 (m, 1H), 3.49 (d, *J* = 16.1 Hz, 1H), 3.27 (dd, *J* = 15.9, 8.7 Hz, 1H), 3.01 (d, *J* = 8.1 Hz, 1H), 1.97 (t, *J* = 6.5 Hz, 2H), 1.89 (td, *J* = 7.7, 3.7 Hz, 1H), 1.62 (dd, *J* = 14.7, 9.7 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 195.92, 171.11, 144.17, 141.22, 136.35, 128.18, 127.43, 127.18, 123.39, 119.25, 118.55, 116.30, 115.91, 110.85, 64.07, 54.36, 47.93, 37.32, 27.71, 23.71; **HRMS (ESI)**: calcd for $C_{20}H_{19}N_2O_2$ $[M+H]^+$:319.1447, found: 319.1442.

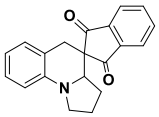
1'-methyl-1,2,3,3a-tetrahydro-2'H,5H-spiro[pyrrolo[1,2-a]quinoline-4,3'-quinoline]-2',4'(1'H)-dione (5b).



Via flash chromatography with a gradient of petroleum ether/EtOAc from 50/1 to 10/1, 29.5 mg yellow was funrished. The isolated yield was 89% and the diastereoselectivity was 52:48.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.68 – 7.64 (m, 1H), 7.18 (d, *J* = 4.8 Hz, 1H), 7.15 (d, *J* = 3.3 Hz, 1H), 6.96 (d, *J* = 7.3 Hz, 1H), 6.64 (t, *J* = 7.7 Hz, 1H), 6.60 (d, *J* = 8.3 Hz, 2H), 4.10 (dd, *J* = 9.3, 6.3 Hz, 1H), 3.58 (dd, *J* = 8.2, 3.5 Hz, 1H), 3.55 (s, 3H), 3.52 (s, 1H), 3.36 – 3.32 (m, 1H), 2.99 (d, *J* = 8.0 Hz, 1H), 1.94 (ddd, *J* = 11.5, 9.8, 6.1 Hz, 3H), 1.60 – 1.55 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 192.75, 168.66, 143.75, 142.47, 135.51, 127.99, 127.77, 127.15, 122.85, 119.97, 118.28, 115.64, 114.61, 110.84, 63.71, 54.16, 47.62, 36.91, 29.28, 27.37, 23.51; **HRMS (ESI)**: calcd for $C_{21}H_{21}N_2O_2$ $[M+H]^+$:333.1603, found: 333.1602.

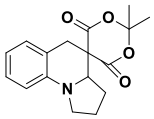
1',2',3',3a'-tetrahydro-5'H-spiro[indene-2,4'-pyrrolo[1,2-a]quinoline]-1,3-dione (5c).



Via flash chromatography with a gradient of petroleum ether/EtOAc from 50/1 to 10/1, 26.6 mg white was funrished. The isolated yield was 88%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 – 7.98 (m, 1H), 7.89 – 7.79 (m, 3H), 7.18 (t, *J* = 7.7 Hz, 1H), 7.00 (d, *J* = 7.3 Hz, 1H), 6.65 – 6.57 (m, 2H), 3.88 (dd, *J* = 10.2, 5.6 Hz, 1H), 3.61 – 3.56 (m, 1H), 3.33 – 3.27 (m, 2H), 2.81 (d, *J* = 16.1 Hz, 1H), 2.00 – 1.89 (m, 2H), 1.88 – 1.81 (m, 1H), 1.34 – 1.24 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 202.70, 199.68, 143.86, 142.49, 141.34, 135.90, 135.39, 128.54, 127.75, 123.11, 123.00, 117.90, 115.59, 110.70, 61.12, 51.43, 47.41, 34.25, 28.08, 23.77; **HRMS (ESI)**: calcd for $C_{20}H_{18}NO_2$[M+H]$^+$:304.1338, found: 304.1339.

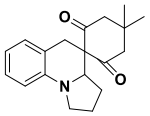
2',2'-dimethyl-1,2,3,3a-tetrahydro-5H-spiro[pyrrolo[1,2-a]quinoline-4,5'-[1,3]dioxane]-4',6'-dione (5d).



Via flash chromatography with a gradient of petroleum ether/EtOAc from 50/1 to 10/1, 28.0 mg white was funrished. The isolated yield was 93%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (t, *J* = 7.7 Hz, 1H), 7.04 (d, *J* = 7.4 Hz, 1H), 6.66 (t, *J* = 7.4 Hz, 1H), 6.61 (d, *J* = 8.1 Hz, 1H), 3.96 (dd, *J* = 8.8, 6.3 Hz, 1H), 3.62 (td, *J* = 8.5, 2.6 Hz, 1H), 3.55 (d, *J* = 16.2 Hz, 1H), 3.30 (dd, *J* = 16.0, 8.7 Hz, 1H), 3.13 (d, *J* = 16.3 Hz, 1H), 2.19 (dtd, *J* = 9.3, 6.7, 2.8 Hz, 1H), 2.08 – 1.90 (m, 2H), 1.78 (s, 3H), 1.75 (s, 3H), 1.67 (dt, *J* = 19.7, 8.9 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.10, 164.11, 143.16, 128.25, 127.81, 116.97, 116.11, 111.52, 104.73, 64.68, 47.89, 47.30, 36.52, 30.01, 28.48, 28.15, 23.17 ; **HRMS (ESI)**: calcd for $C_{17}H_{20}NO_4$[M+H]$^+$:302.1392, found: 302.1387.

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

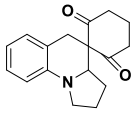


Via flash chromatography with a gradient of petroleum ether/EtOAc from 50/1 to 10/1, 24.0 mg white

was funrished. The isolated yield was 81%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (t, *J* = 7.7 Hz, 1H), 6.90 (d, *J* = 7.3 Hz, 1H), 6.51 (t, *J* = 7.3 Hz, 1H), 6.47 (d, *J* = 8.1 Hz, 1H), 4.02 (dd, *J* = 10.3, 5.9 Hz, 1H), 3.53 (t, *J* = 8.2 Hz, 1H), 3.27 – 3.19 (m, 1H), 3.12 (q, *J* = 15.4 Hz, 2H), 2.89 (d, *J* = 15.1 Hz, 1H), 2.76 (d, *J* = 14.6 Hz, 1H), 2.48 (dd, *J* = 15.1, 2.6 Hz, 1H), 2.19 (dd, *J* = 14.6, 2.6 Hz, 1H), 2.10 – 2.04 (m, 2H), 2.03 – 1.93 (m, 1H), 1.73 (qd, *J* = 10.9, 7.3 Hz, 1H), 1.15 (s, 3H), 0.90 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 209.44, 205.07, 144.40, 128.45, 127.94, 115.84, 114.69, 110.70, 59.93, 59.85, 52.38, 52.16, 47.86, 40.78, 30.63, 30.35, 27.25, 26.70, 24.34; **HRMS (ESI)**: calcd for $C_{19}H_{24}NO_4[M+H]^+$:298.1807, found: 298.1803.

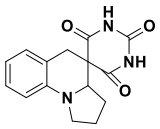
1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,6-dione (5f).



Via flash chromatography with a gradient of petroleum ether/EtOAc from 50/1 to 10/1, 15.6 mg white was funrished. The isolated yield was 58%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (t, *J* = 7.7 Hz, 1H), 6.92 (d, *J* = 7.3 Hz, 1H), 6.53 (t, *J* = 7.4 Hz, 1H), 6.49 (d, *J* = 8.2 Hz, 1H), 3.97 (dd, *J* = 10.1, 6.0 Hz, 1H), 3.54 (dd, *J* = 10.2, 6.1 Hz, 1H), 3.24 (ddd, *J* = 15.3, 8.9, 6.8 Hz, 1H), 3.12 (s, 2H), 2.85 (ddd, *J* = 16.1, 10.4, 5.7 Hz, 1H), 2.72 (ddd, *J* = 16.2, 10.4, 6.1 Hz, 1H), 2.61 (ddd, *J* = 16.2, 8.2, 3.0 Hz, 1H), 2.39 (dt, *J* = 15.8, 5.4 Hz, 1H), 2.18 – 2.09 (m, 1H), 2.01 (qdd, *J* = 12.1, 9.6, 5.2 Hz, 3H), 1.91 – 1.81 (m, 1H), 1.75 – 1.63 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 209.97, 205.26, 144.36, 128.32, 128.04, 116.10, 114.82, 110.75, 60.86, 60.61, 47.88, 39.88, 38.98, 38.81, 27.37, 24.25, 17.45; **HRMS (ESI)**: calcd for $C_{17}H_{20}NO_2[M+H]^+$:270.1494, found: 270.1498.

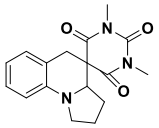
1',2',3',3a'-tetrahydro-2H,5'H-spiro[pyrimidine-5,4'-pyrrolo[1,2-a]quinoline]-2,4,6(1H,3H)-trione (5g).



Via flash chromatography with a gradient of petroleum ether/EtOAc from 50/1 to 10/1, 27.1 mg white was funrished. The isolated yield was 95%.

^{1}H NMR (500 MHz, DMSO) δ 11.47 (s, 1H), 11.19 (s, 1H), 7.06 – 6.94 (m, 2H), 6.56 – 6.47 (m, 2H), 3.60 (dd, *J* = 8.6, 6.4 Hz, 1H), 3.50 – 3.43 (m, 1H), 3.24 (d, *J* = 16.6 Hz, 1H), 3.17 – 3.05 (m, 2H), 2.08 – 2.00 (m, 1H), 1.93 (dd, *J* = 15.5, 7.9 Hz, 2H), 1.55 (dt, *J* = 18.0, 9.0 Hz, 1H); **^{13}C NMR** (125 MHz, DMSO) δ 172.64, 169.27, 150.73, 143.85, 128.27, 126.99, 120.04,115.79, 111.45, 63.30, 48.49, 47.88, 34.97, 27.88, 23.20; **HRMS (ESI)**: calcd for $C_{15}H_{16}N_3O_3[M+H]^+$:286.1192, found: 286.1197.

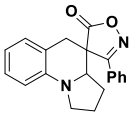
1,3-dimethyl-1',2',3',3a'-tetrahydro-2H,5'H-spiro[pyrimidine-5,4'-pyrrolo[1,2-a]quinoline]-2,4,6(1H,3H)-trione (5h).



Via flash chromatography with a gradient of petroleum ether/EtOAc from 50/1 to 10/1, 27.5 mg white was funrished. The isolated yield was 88%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (t, *J* = 7.7 Hz, 1H), 7.02 (d, *J* = 7.4 Hz, 1H), 6.66 (t, *J* = 7.4 Hz, 1H), 6.60 (d, *J* = 8.1 Hz, 1H), 3.91 (dd, *J* = 9.1, 6.0 Hz, 1H), 3.62 – 3.54 (m, 2H), 3.38 (s, 3H), 3.33 (dd, *J* = 16.6, 8.1 Hz, 1H), 3.22 (s, 3H), 3.01 (d, *J* = 16.3 Hz, 1H), 2.06 (dt, *J* = 17.3, 5.7 Hz, 1H), 2.01 – 1.94 (m, 2H), 1.52 – 1.42 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.83, 166.86, 151.23, 143.27, 128.10, 127.56, 118.21, 116.22, 111.18, 63.98, 49.04, 47.76, 37.20, 29.07, 28.35, 28.01, 23.26; **HRMS (ESI)**: calcd for $C_{17}H_{20}N_3O_3[M+H]^+$:314.1505, found:314.1506.

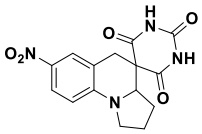
3-phenyl-1',2',3',3a'-tetrahydro-5H,5'H-spiro[isoxazole-4,4'-pyrrolo[1,2-a]quinolin]-5-one (5i).



Via flash chromatography with a gradient of petroleum ether/EtOAc from 50/1 to 10/1, 14.9 mg white was funrished. The isolated yield was 47% and the diastereoselectivity was 69:31.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 5.3, 3.3 Hz, 1H), 7.51 – 7.47 (m, 1H), 7.11 (d, *J* = 7.9 Hz, 1H), 7.08 (d, *J* = 0.7 Hz, 1H), 7.07 (s, 2H), 7.04 (d, *J* = 7.9 Hz, 1H), 6.69 (q, *J* = 8.0 Hz, 1H), 6.21 (d, *J* = 8.1 Hz, 1H), 3.72 (dd, *J* = 9.3, 6.3 Hz, 1H), 3.67 – 3.53 (m, 2H), 3.31 – 3.22 (m, 2H), 2.60 (dd, *J* = 16.7, 8.0 Hz, 1H), 2.18 – 2.10 (m, 1H), 1.94 – 1.88 (m, 2H), 1.61 (dd, *J* = 10.8, 7.8 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 179.37, 169.58, 143.01, 130.66, 129.34, 128.25, 128.00, 127.64, 127.25, 116.83, 116.68, 111.32, 62.40, 50.62, 46.33, 34.76, 27.52, 22.89; **HRMS (ESI)**: calcd for $C_{20}H_{19}N_2O_2[M+H]^+$:319.1447, found:319.1443.

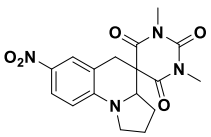
7'-nitro-1',2',3',3a'-tetrahydro-2H,5'H-spiro[pyrimidine-5,4'-pyrrolo[1,2-a]quinoline]-2,4,6(1H,3H)-trione (9b).



Via flash chromatography with a gradient of petroleum ether/EtOAc from 50/1 to 10/1, 31.3 mg yellow was funrished. The isolated yield was 95%.

^{1}H NMR (500 MHz, DMSO) δ 11.63 (s, 1H), 11.36 (s, 1H), 7.98 (dd, J = 9.1, 2.6 Hz, 1H), 7.91 (s, 1H), 6.60 (d, J = 9.1 Hz, 1H), 3.85 (dd, J = 10.3, 5.8 Hz, 1H), 3.68 (t, J = 8.9 Hz, 1H), 3.39 (s, 1H), 3.29 – 3.16 (m, 2H), 2.13 – 1.92 (m, 3H), 1.53 (qd, J = 11.3, 7.5 Hz, 1H).**^{13}C NMR** (125 MHz, DMSO) δ 171.98, 168.94, 150.48, 149.17, 135.77, 124.60, 124.30, 120.04, 110.09, 63.08, 48.22, 47.25, 35.14, 27.71, 23.06; **HRMS (ESI)**: calcd for $C_{15}H_{15}N_4O_5[M+H]^+$:331.1042, found: 331.1041.

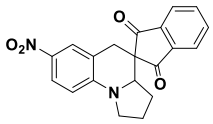
1,3-dimethyl-7'-nitro-1',2',3',3a'-tetrahydro-2H,5'H-spiro[pyrimidine-5,4'-pyrrolo[1,2-a]quinoline]-2,4,6(1H,3H)-trione (9c).



Via flash chromatography with a gradient of petroleum ether/EtOAc from 50/1 to 10/1, 32.2 mg yellow was funrished. The isolated yield was 90%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 – 8.08 (m, 1H), 7.96 (s, 1H), 6.54 (d, J = 9.1 Hz, 1H), 4.07 (dd, J = 10.2, 5.4 Hz, 1H), 3.72 (t, J = 8.8 Hz, 1H), 3.53 (d, J = 16.3 Hz, 1H), 3.41 (s, 3H), 3.37 (d, J = 9.4 Hz, 1H), 3.23 (s, 3H), 3.09 (d, J = 16.3 Hz, 1H), 2.11 (dd, J = 11.1, 5.9 Hz, 2H), 2.04 (dd, J = 21.9, 16.8 Hz, 1H), 1.52 – 1.43 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.00, 166.46, 150.68, 148.25, 136.93, 125.04, 124.59, 117.53, 109.70, 63.48, 47.99, 47.83, 37.43, 29.30, 28.47, 27.78, 23.19; **HRMS (ESI)**: calcd for $C_{17}H_{19}N_4O_5[M+H]^+$:359,1355, found: 359,1354.

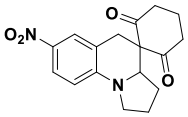
7'-nitro-1',2',3',3a'-tetrahydro-5'H-spiro[indene-2,4'-pyrrolo[1,2-a]quinoline]-1,3-dione (9d).



Via flash chromatography with a gradient of petroleum ether/EtOAc from 50/1 to 10/1, 31.3 mg yellow was funrished. The isolated yield was 90%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 9.1, 2.4 Hz, 1H), 8.06 – 8.01 (m, 1H), 7.94 (s, 1H), 7.92 – 7.85 (m, 3H), 6.54 (d, *J* = 9.1 Hz, 1H), 3.97 (dd, *J* = 10.9, 5.5 Hz, 1H), 3.69 (t, *J* = 9.1 Hz, 1H), 3.38 (td, *J* = 10.1, 7.2 Hz, 1H), 3.28 (d, *J* = 16.2 Hz, 1H), 2.87 (d, *J* = 16.3 Hz, 1H), 2.07 (dt, *J* = 12.9, 6.6 Hz, 1H), 2.00 (ddd, *J* = 18.7, 7.8, 4.4 Hz, 1H), 1.89 (dd, *J* = 11.8, 5.9 Hz, 1H), 1.37 – 1.27 (m, 1H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 201.12, 199.09, 148.79, 142.10, 141.10, 136.65, 136.44, 136.03, 125.21, 125.06, 123.55, 123.31, 117.69, 109.43, 61.32, 50.36, 47.74, 33.87, 27.85, 23.57; **HRMS (ESI)**: calcd for $C_{20}H_{17}N_2O_4[M+H]^+$:349.1188, found: 349.1186.

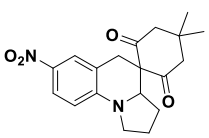
7'-nitro-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,6-dione (9e).



Via flash chromatography with a gradient of petroleum ether/EtOAc from 50/1 to 10/1, 27.3 mg yellow was funrished. The isolated yield was 87%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 9.1, 2.5 Hz, 1H), 7.90 (s, 1H), 6.42 (d, *J* = 9.2 Hz, 1H), 4.04 (dd, *J* = 10.8, 5.8 Hz, 1H), 3.63 (t, *J* = 9.0 Hz, 1H), 3.41 – 3.30 (m, 1H), 3.21 (d, *J* = 15.7 Hz, 1H), 3.09 (d, *J* = 15.7 Hz, 1H), 2.90 (ddd, *J* = 16.4, 10.8, 5.7 Hz, 1H), 2.77 (ddd, *J* = 16.5, 10.8, 6.0 Hz, 1H), 2.71 – 2.64 (m, 1H), 2.45 (dt, *J* = 16.1, 5.2 Hz, 1H), 2.18 (ddt, *J* = 19.2, 13.5, 6.4 Hz, 2H), 2.03 (qdd, *J* = 12.2, 10.5, 6.8 Hz, 2H), 1.93 – 1.82 (m, 1H), 1.70 (qd, *J* = 11.1, 7.1 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 208.58, 205.08, 148.93, 135.92, 125.76, 124.85, 115.75, 109.48, 60.99, 60.19, 48.03, 39.04, 38.76, 38.73, 27.05, 23.88, 17.32; **HRMS (ESI)**: calcd for $C_{17}H_{19}N_2O_4[M+H]^+$:315.1345, found: 315.1346.

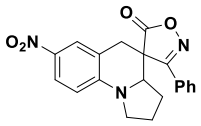
4,4-dimethyl-7'-nitro-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,6-dione (9f).



Via flash chromatography with a gradient of petroleum ether/EtOAc from 50/1 to 10/1, 29.8 mg yellow was funrished. The isolated yield was 87%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 9.1, 2.4 Hz, 1H), 7.90 (s, 1H), 6.40 (d, *J* = 9.2 Hz, 1H), 4.09 (dd, *J* = 10.7, 5.9 Hz, 1H), 3.62 (t, *J* = 9.1 Hz, 1H), 3.36 (td, *J* = 10.4, 6.9 Hz, 1H), 3.28 (d, *J* = 15.6 Hz, 1H), 3.04 (d, *J* = 15.5 Hz, 1H), 2.94 (d, *J* = 15.1 Hz, 1H), 2.83 (d, *J* = 14.8 Hz, 1H), 2.53 (dd, *J* = 15.1, 2.6 Hz, 1H), 2.24 (dd, *J* = 14.8, 2.5 Hz, 1H), 2.14 (ddd, *J* = 17.4, 12.6, 6.6 Hz, 2H), 2.09 – 1.97 (m, 1H), 1.76 (qd, *J* = 11.4, 7.3 Hz, 1H), 1.19 (s, 3H), 0.90 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 208.15, 204.99, 148.96, 135.78, 125.94, 124.81, 115.44, 109.44, 60.35, 59.36, 52.06, 51.89, 48.05, 39.87, 30.75, 30.37, 26.86, 26.51, 23.97; **HRMS (ESI)**: calcd for $C_{19}H_{22}N_2O_4[M+H]^+$:343.1658, found:343.1655.

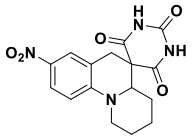
7'-nitro-3-phenyl-1',2',3',3a'-tetrahydro-5H,5'H-spiro[isoxazole-4,4'-pyrrolo[1,2-a]quinolin]-5-one (9g).



Via flash chromatography with a gradient of petroleum ether/EtOAc from 50/1 to 10/1, 31.9 mg yellow was funrished. The isolated yield was 88% and the diastereoselectivity was 19:1.

^{1}H NMR (500 MHz, DMSO) δ 8.06 (dd, *J* = 9.1, 2.6 Hz, 1H), 7.97 (d, *J* = 2.2 Hz, 1H), 7.86 (d, *J* = 7.4 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 2H), 6.71 (d, *J* = 9.2 Hz, 1H), 4.33 (dd, *J* = 10.5, 5.6 Hz, 1H), 3.74 (t, *J* = 9.1 Hz, 1H), 3.66 (d, *J* = 16.3 Hz, 1H), 3.53 – 3.46 (m, 1H), 3.28 (td, *J* = 10.1, 7.2 Hz, 1H), 2.12 – 2.03 (m, 2H), 1.97 (dt, *J* = 22.0, 9.5 Hz, 1H), 1.42 – 1.26 (m, 1H); **^{13}C NMR** (125 MHz, DMSO) δ 175.36, 167.40, 149.12, 136.32, 132.45, 129.97, 127.95, 127.02, 125.42, 125.19, 116.48, 110.49, 60.15, 48.61, 48.25, 32.57, 28.41, 22.91; **HRMS (ESI)**: calcd for $C_{20}H_{18}N_3O_4[M+H]^+$:364.1297, found: 364.1299.

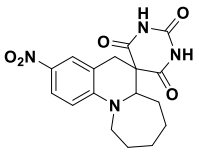
8-nitro-2,3,4,4a-tetrahydro-1H,2'H,6H-spiro[pyrido[1,2-a]quinoline-5,5'-pyrimidine]-2',4',6'(1'H,3'H)-trione (9h).



Via flash chromatography with a gradient of petroleum ether/EtOAc from 50/1 to 10/1, 31.3 mg yellow was funrished. The isolated yield was 91%.

^{1}H NMR (500 MHz, DMSO) δ 7.99 – 7.76 (m, 2H), 6.99 (d, *J* = 9.4 Hz, 1H), 4.21 (d, *J* = 13.5 Hz, 1H), 3.76 (d, *J* = 11.5 Hz, 1H), 3.37 (d, *J* = 17.0 Hz, 1H), 3.06 (dd, *J* = 33.2, 14.9 Hz, 2H), 1.78 (d, *J* = 12.2 Hz, 1H), 1.66 – 1.54 (m, 2H), 1.51 (d, *J* = 12.5 Hz, 1H), 1.45 – 1.33 (m, 1H), 1.23 (tt, *J* = 12.3, 6.0 Hz, 1H); **^{13}C NMR** (125 MHz, DMSO) δ 171.72, 169.76, 150.96, 150.12, 136.82, 124.59, 123.88, 122.13, 111.93, 60.95, 51.93, 48.93, 29.45, 27.25, 24.23, 23.74; **HRMS (ESI)**: calcd for $C_{16}H_{17}N_4O_5[M+H]^+$:345.1199, found: 345.1198.

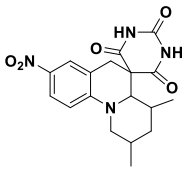
3-nitro-6a,7,8,9,10,11-hexahydro-2'H,5H-spiro[azepino[1,2-a]quinoline-6,5'-pyrimidine]-2',4',6'(1'H,3'H)-trione (9i).



Via flash chromatography with a gradient of petroleum ether/EtOAc from 50/1 to 10/1, 32.6 mg yellow was funrished. The isolated yield was 91%.

^{1}H NMR (500 MHz, DMSO) δ 7.95 (s, 1H), 7.91 (dd, *J* = 9.2, 2.5 Hz, 1H), 6.73 (d, *J* = 9.3 Hz, 1H), 3.97 (dd, *J* = 10.9, 4.0 Hz, 1H), 3.88 (dd, *J* = 14.8, 4.8 Hz, 1H), 3.46 (d, *J* = 17.8 Hz, 1H), 3.32 – 3.23 (m, 1H), 2.93 (d, *J* = 17.8 Hz, 1H), 1.92 (dd, *J* = 10.2, 4.6 Hz, 1H), 1.66 – 1.57 (m, 2H), 1.57 – 1.48 (m, 2H), 1.44 – 1.36 (m, 1H), 1.36 – 1.28 (m, 1H), 1.24 (d, *J* = 4.8 Hz, 1H); **^{13}C NMR** (125 MHz, DMSO) δ 171.80, 170.71, 151.54, 149.23, 136.46, 124.76, 123.87, 120.97, 110.38, 63.62, 51.74, 50.80, 30.75, 26.93, 25.68, 25.33, 25.10; **HRMS (ESI)**: calcd for $C_{17}H_{19}N_4O_5[M+H]^+$:359.1355, found: 359.1357.

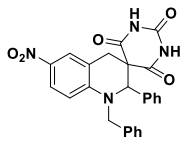
2,4-dimethyl-8-nitro-2,3,4,4a-tetrahydro-1H,2'H,6H-spiro[pyrido[1,2-a]quinoline-5,5'-pyrimidine]-2',4',6'(1'H,3'H)-trione (9j).



Via flash chromatography with a gradient of petroleum ether/EtOAc from 50/1 to 10/1, 32.7 mg yellow was funrished. The isolated yield was 88% and the diastereoselectivity was 90:8:2.

^{1}H NMR (500 MHz, DMSO) δ 11.77 (s, 1H), 11.50 (s, 1H), 7.96 (dd, *J* = 9.2, 2.7 Hz, 1H), 7.81 (d, *J* = 2.5 Hz, 1H), 6.91 (d, *J* = 9.3 Hz, 1H), 4.11 (d, *J* = 12.9 Hz, 1H), 3.82 (d, *J* = 10.1 Hz, 1H), 3.53 (d, *J* = 14.8 Hz, 1H), 3.37 (d, *J* = 2.7 Hz, 3H), 2.87 – 2.77 (m, 2H), 2.54 – 2.48 (m, 1H), 1.79 – 1.69 (m, 2H), 1.69 – 1.61 (m, 1H), 0.93 (d, *J* = 6.5 Hz, 3H), 0.69 (d, *J* = 6.4 Hz, 3H);**^{13}C NMR** (125MHz, DMSO) δ 172.02, 168.57, 152.10, 150.11, 135.96, 125.38, 124.23, 120.58, 111.41, 65.14, 55.82, 53.64, 37.43, 33.09, 30.54, 19.26, 18.78; **HRMS (ESI)**: calcd for $C_{18}H_{21}N_4O_5[M+H]^+$:373.1512, found: 373.1512.

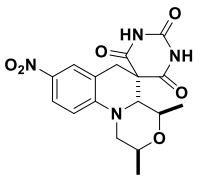
1',2'-dibenzyl-6'-nitro-1',4'-dihydro-2H,2'H-spiro[pyrimidine-5,3'-quinoline]-2,4,6(1H,3H)-trione (9k).



Via flash chromatography with a gradient of petroleum ether/EtOAc from 50/1 to 10/1, 42.4 mg yellow was funrished. The isolated yield was 93%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (s, 1H), 8.03 (dd, *J* = 9.2, 2.4 Hz, 1H), 7.98 (s, 1H), 7.87 (s, 1H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.33 – 7.27 (m, 5H), 7.06 (t, *J* = 6.2 Hz, 4H), 6.74 (d, *J* = 9.2 Hz, 1H), 4.88 (s, 1H), 4.76 (d, *J* = 16.9 Hz, 1H), 4.22 (d, *J* = 17.0 Hz, 1H), 3.45 (d, *J* = 17.0 Hz, 1H), 3.32 (d, *J* = 17.0 Hz, 1H); **^{13}C NMR** (125 MHz, DMSO) δ 171.72, 169.01, 150.72, 150.02, 137.75, 137.48, 137.32, 129.05, 128.95, 128.86, 127.92, 127.45, 126.57, 124.27, 123.88, 122.42, 110.86, 66.91, 54.09, 53.07, 26.02; **HRMS (ESI)**: calcd for $C_{26}H_{23}N_4O_5[M+H]^+$:457.1512, found: 457.1512.

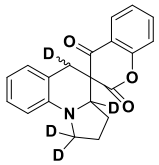
2',4'-dimethyl-8'-nitro-1',2',4',4a'-tetrahydro-2H,6'H-spiro[pyrimidine-5,5'-[1,4]oxazino[4,3-a]quinoline]-2,4,6(1H,3H)-trione(11).



Via flash chromatography with a gradient of petroleum ether/EtOAc from 50/1 to 10/1, 34.8 mg yellow was funrished. The isolated yield was 93%.

^{1}H NMR (500 MHz, DMSO) δ 11.89 (s, 1H), 11.58 (s, 1H), 7.98 (dd, *J* = 9.2, 2.6 Hz, 1H), 7.84 (d, *J* = 2.1 Hz, 1H), 7.04 (d, *J* = 9.4 Hz, 1H), 4.30 (d, *J* = 12.3 Hz, 1H), 3.93 (d, *J* = 9.0 Hz, 1H), 3.66 – 3.57 (m, 2H), 3.54 (dt, *J* = 12.8, 6.4 Hz, 1H), 2.99 (dd, *J* = 13.6, 10.8 Hz, 1H), 2.88 (d, *J* = 14.9 Hz, 1H), 1.17 (d, *J* = 6.1 Hz, 3H), 0.95 (d, *J* = 6.3 Hz, 3H); **^{13}C NMR** (125 MHz, DMSO) δ 171.60, 168.19, 150.94, 149.92, 136.21, 125.18, 124.52, 119.58, 111.19, 72.60, 71.57, 62.95, 55.37, 53.22, 51.55, 37.48, 18.96, 18.65; **HRMS (ESI)**: calcd for $C_{17}H_{19}N_4O_6[M+H]^+$:375.1305, found: 375.1306.

1',2',3',3a'-tetrahydro-5'H-spiro[chromane-3,4'-pyrrolo[1,2-a]quinoline]-2,4-dione-1',1',3a',5'-d4(13)



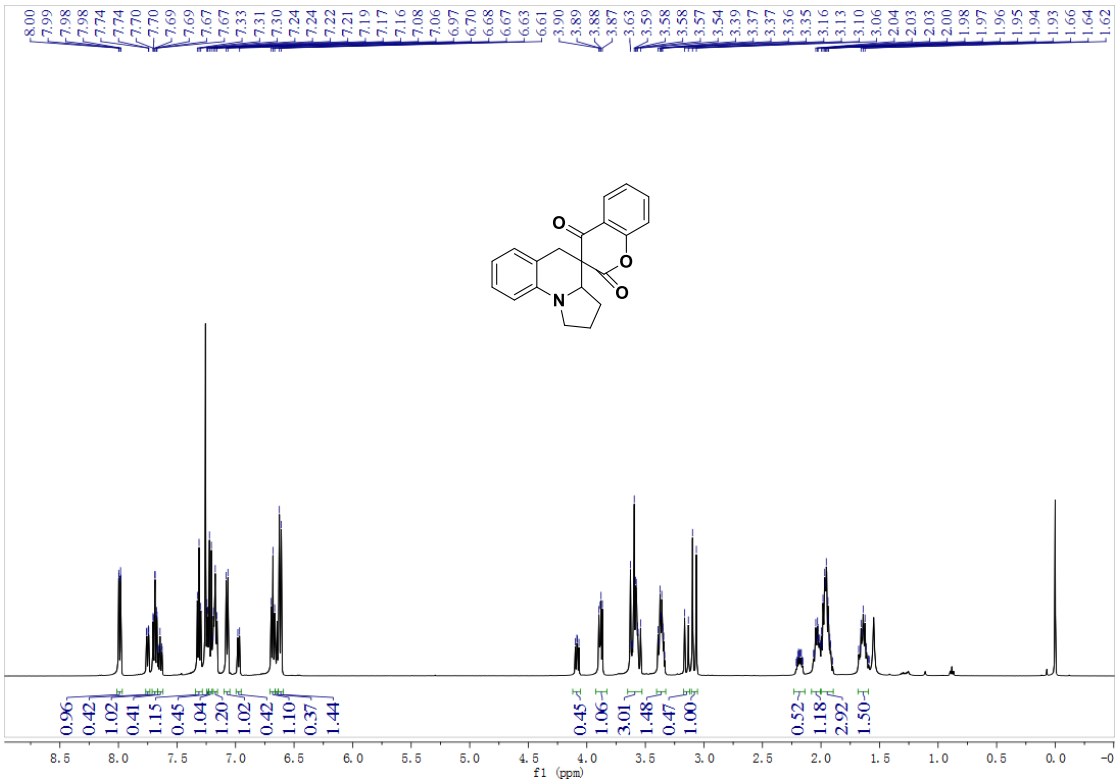
The deuterated substrate was synthesized according to the reference 1. The deuterated substrate (0.05 mmol) was subjected to the optimal condition and the product was purified via flash chromatography with a gradient of petroleum ether/EtOAc from 50/1 to 10/1, 7.1 mg yellow was funrished. The isolated yield was 44% and the diastereoselectivity was 70:30.

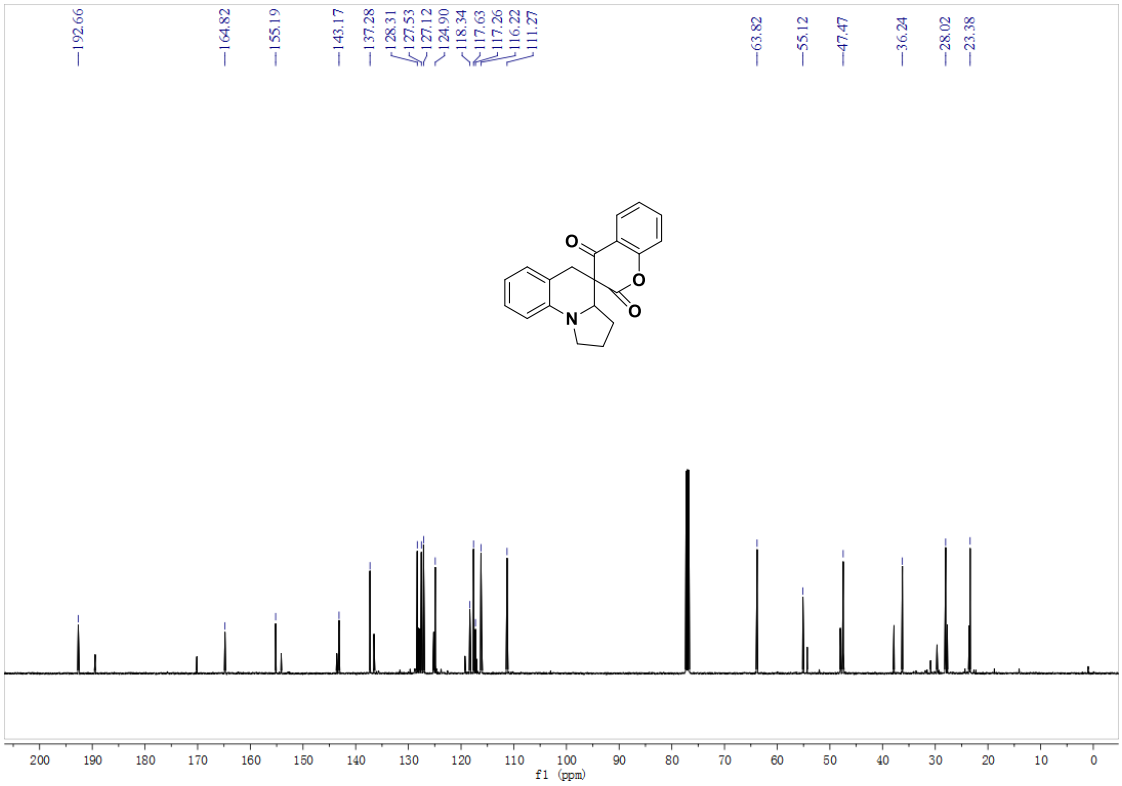
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.75 – 7.70 (m, 1H), 7.37 – 7.32 (m, 1H), 7.24 (d, *J* = 8.3 Hz, 1H), 7.23 – 7.17 (m, 1H), 7.10 (dd, *J* = 7.4, 0.8 Hz, 1H), 6.71 (t, *J* = 7.4 Hz, 1H), 6.64 (d, *J* = 8.2 Hz, 1H), 3.61 (s, 0.5H), 3.09 (s, 0.5H), 2.08 – 2.02 (m, 1H), 2.01 – 1.96 (m, 2H), 1.69 – 1.66 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 192.79, 164.90, 155.24, 143.29, 137.33, 128.40, 128.33, 127.62, 127.17, 124.95, 118.39, 117.70, 116.24, 111.31, 54.97(t, $J_{C\text{-}D}$=21.0Hz), 47.01(m), 35.92(t, $J_{C\text{-}D}$=21.0Hz), 27.95, 23.24. **HRMS (ESI):** calcd. for $C_{20}H_{18}NO_3$ $[M+H]^+$: 324.1538, found: 324.1535.

1. D. F. Chen, Z. Y. Han, Y. P. He, J. Yu and L. Z. Gong, *Angew. Chem. Int. Ed.*, 2012, **51**, 12307.

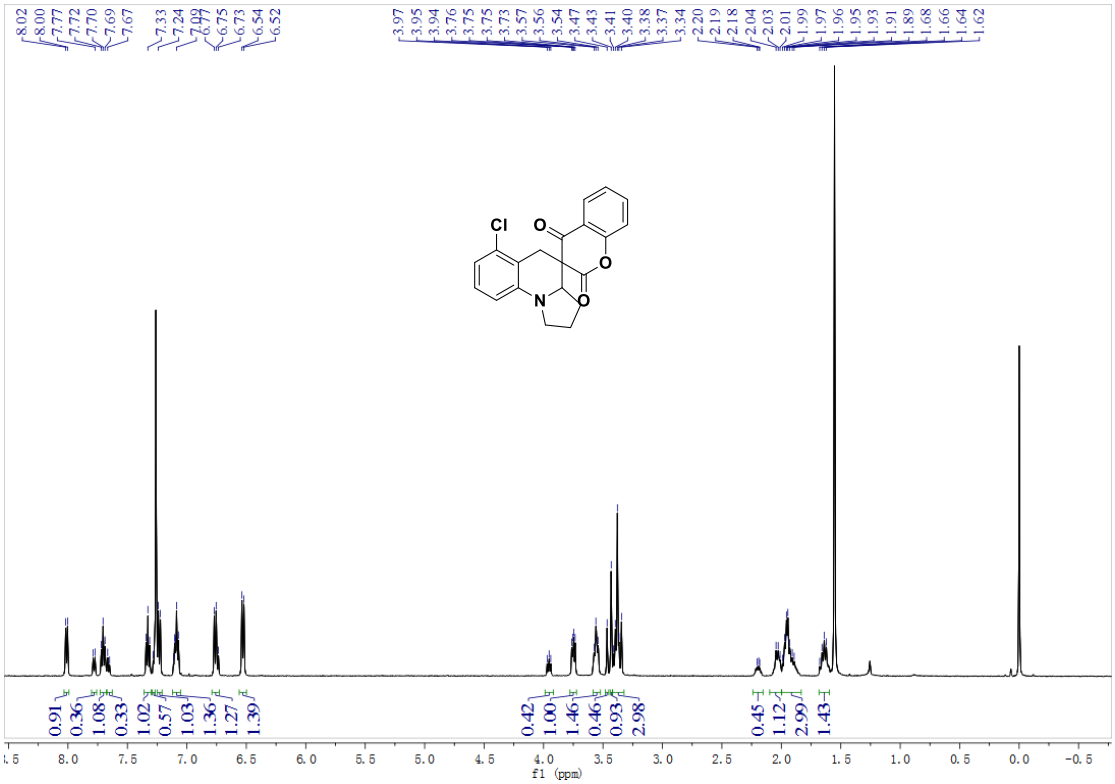
^{1}H and ^{13}C Spectra

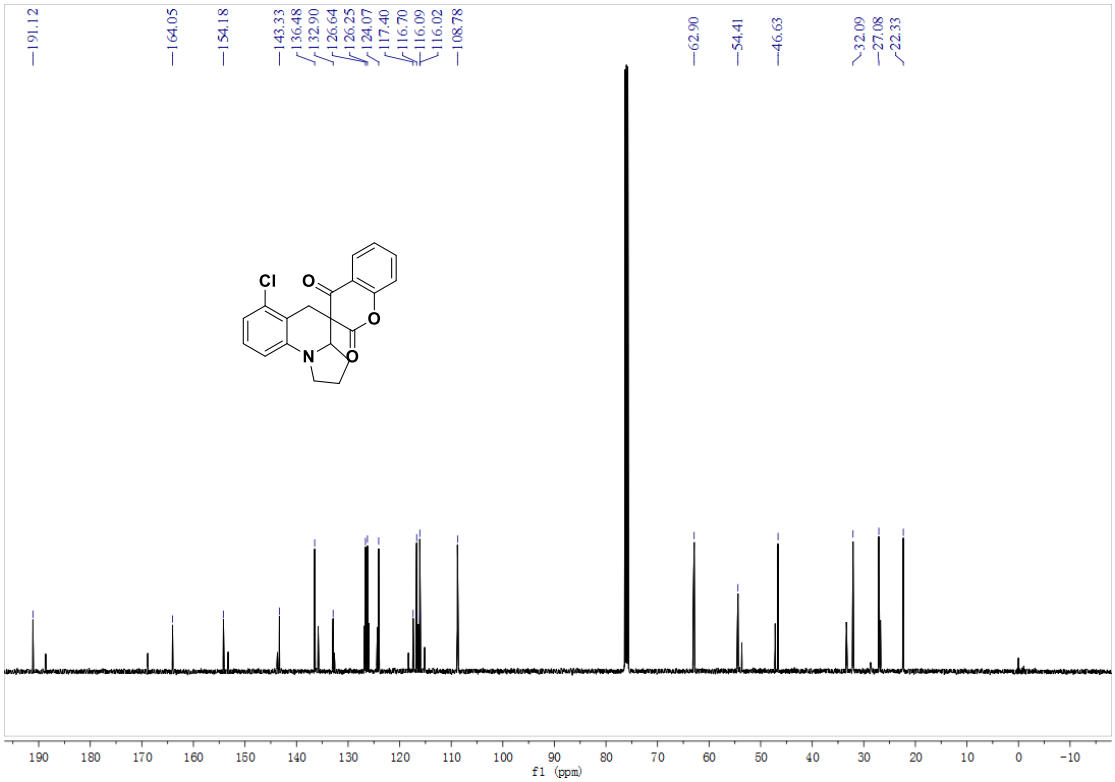
1',2',3',3a'-tetrahydro-5'H-spiro[chromane-3,4'-pyrrolo[1,2-a]quinoline]-2,4-dione **3a**



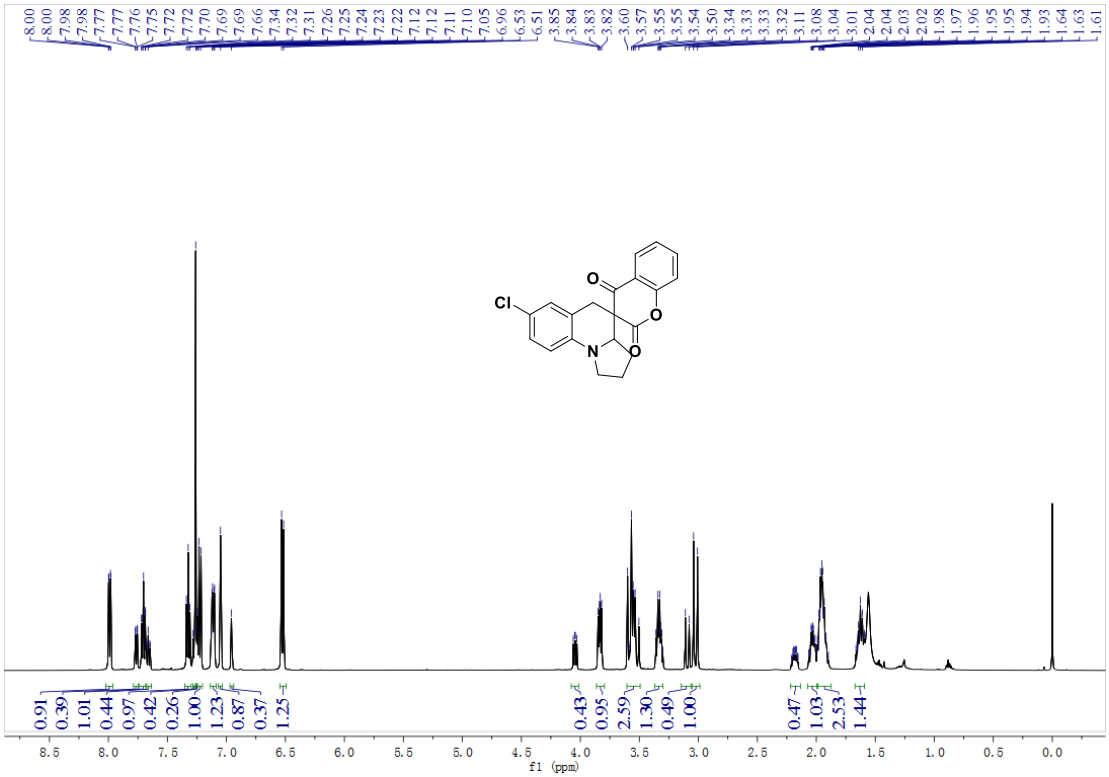


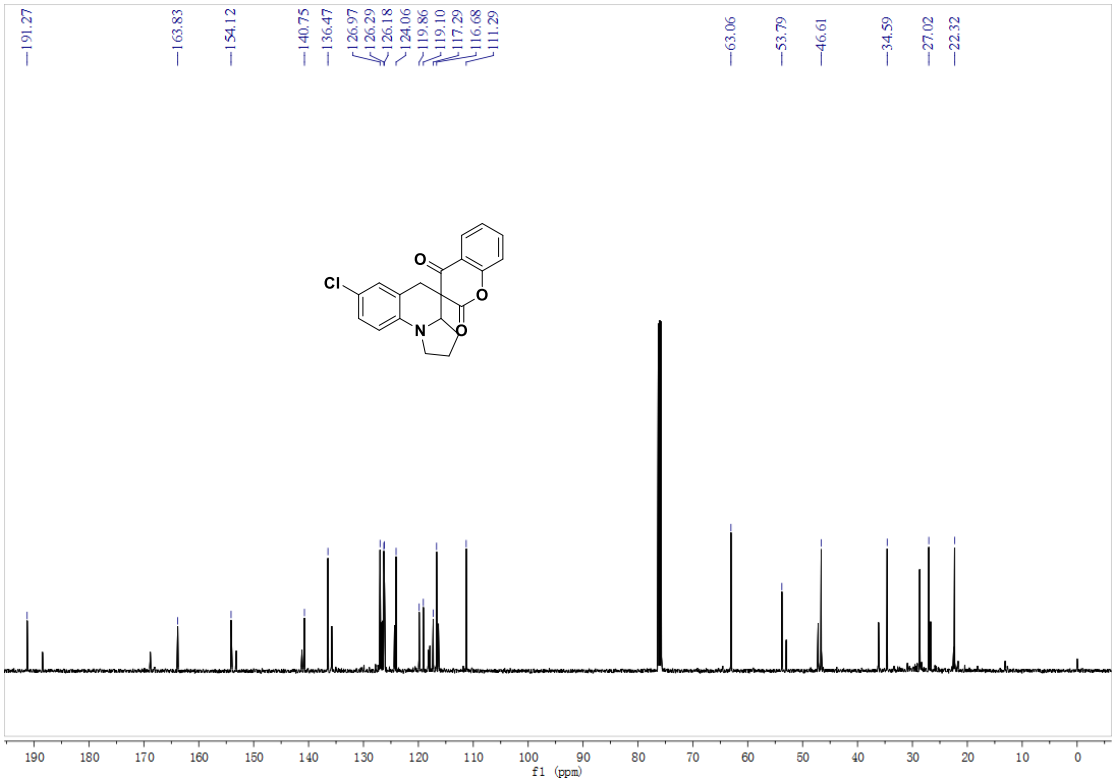
6'-chloro-1',2',3',3a'-tetrahydro-5'H-spiro[chromane-3,4'-pyrrolo[1,2-a]quinoline]-2,4-dione **3b**



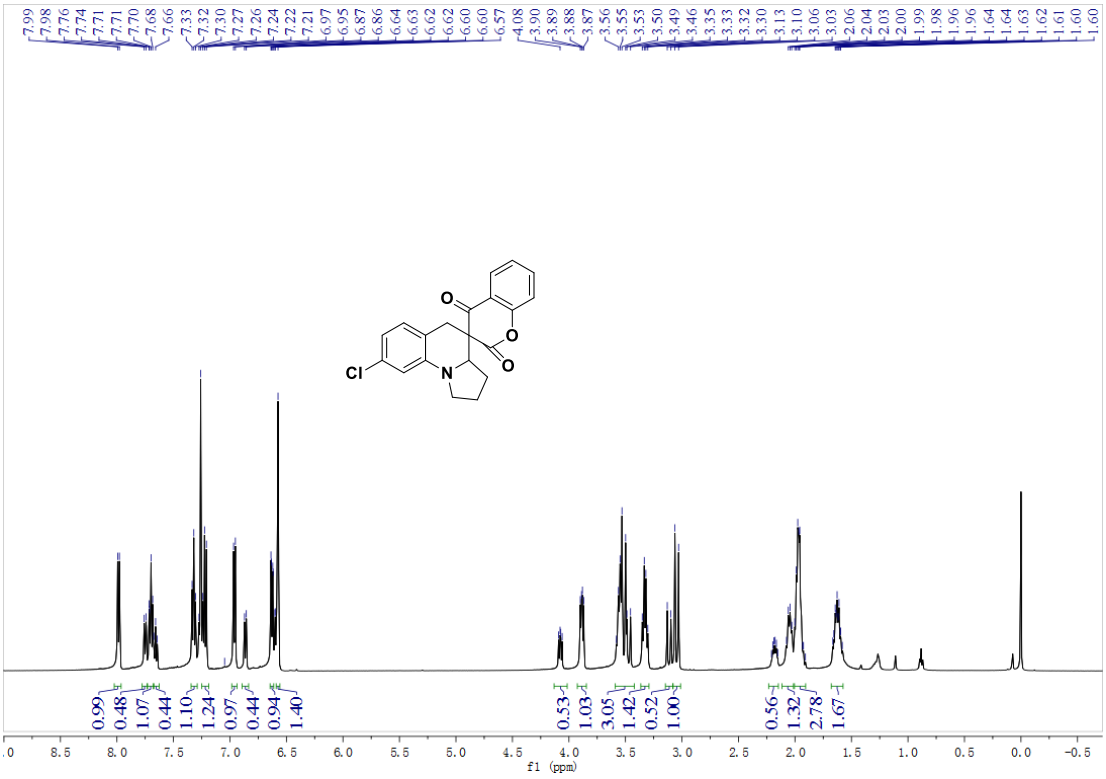


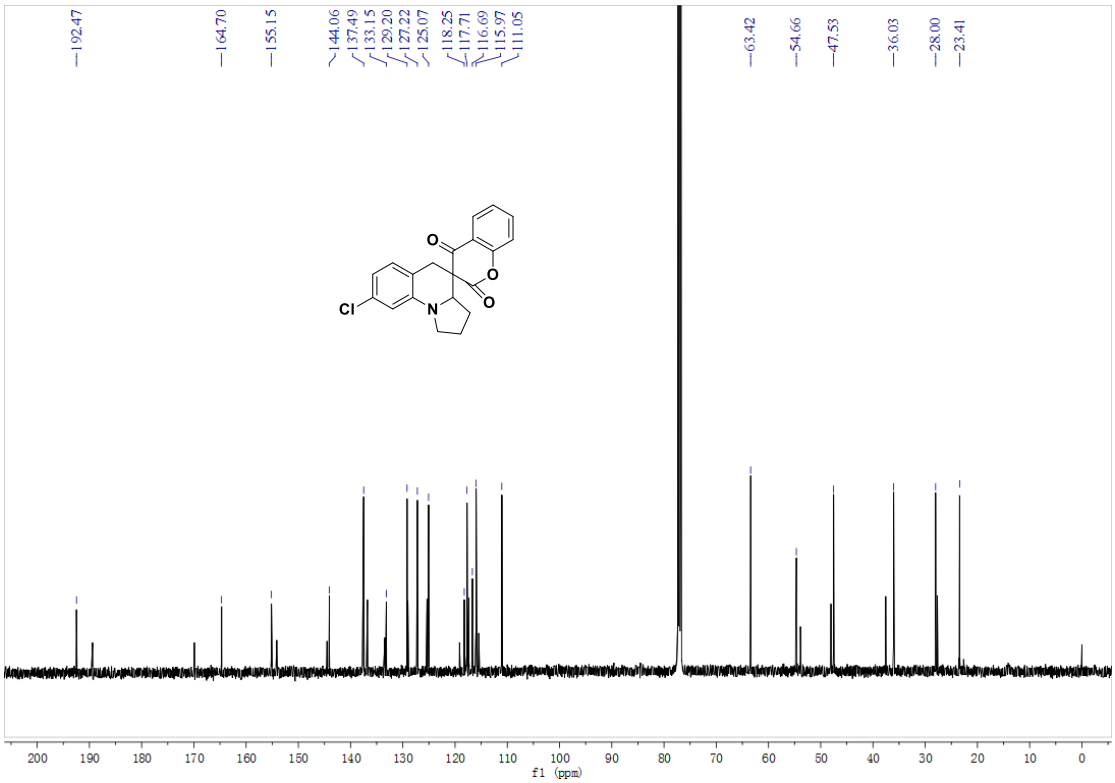
7'-chloro-1',2',3',3a'-tetrahydro-5'H-spiro[chromane-3,4'-pyrrolo[1,2-a]quinoline]-2,4-dione **3c**



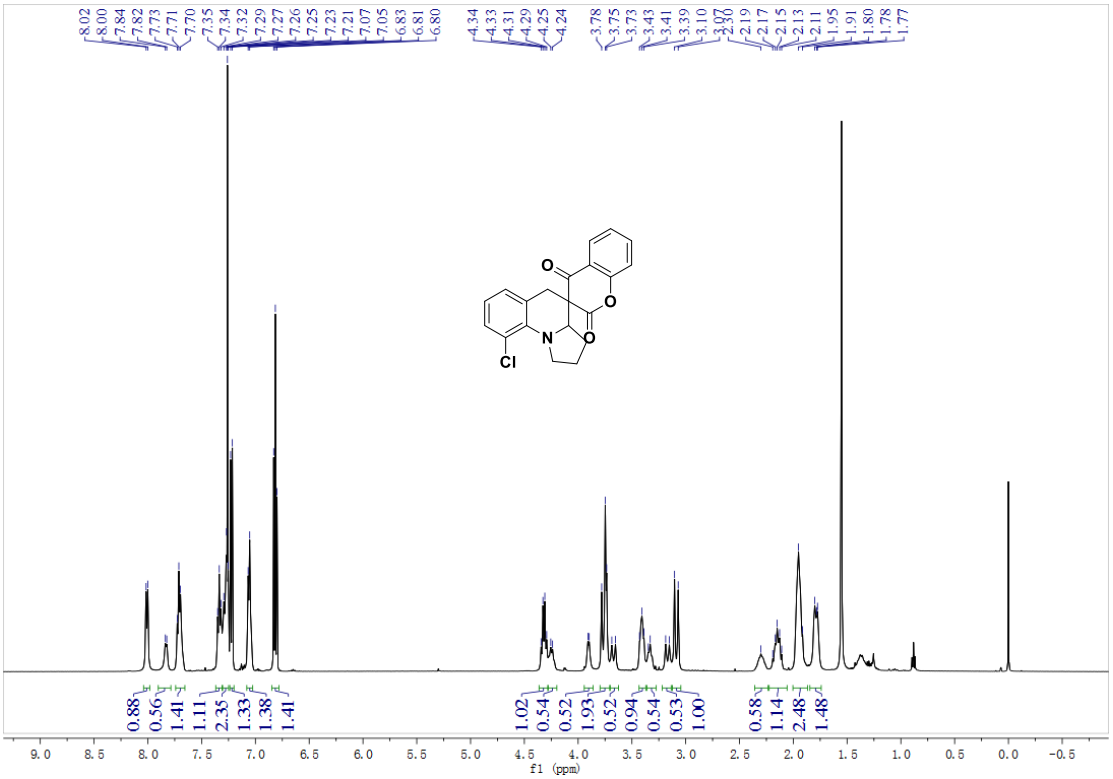


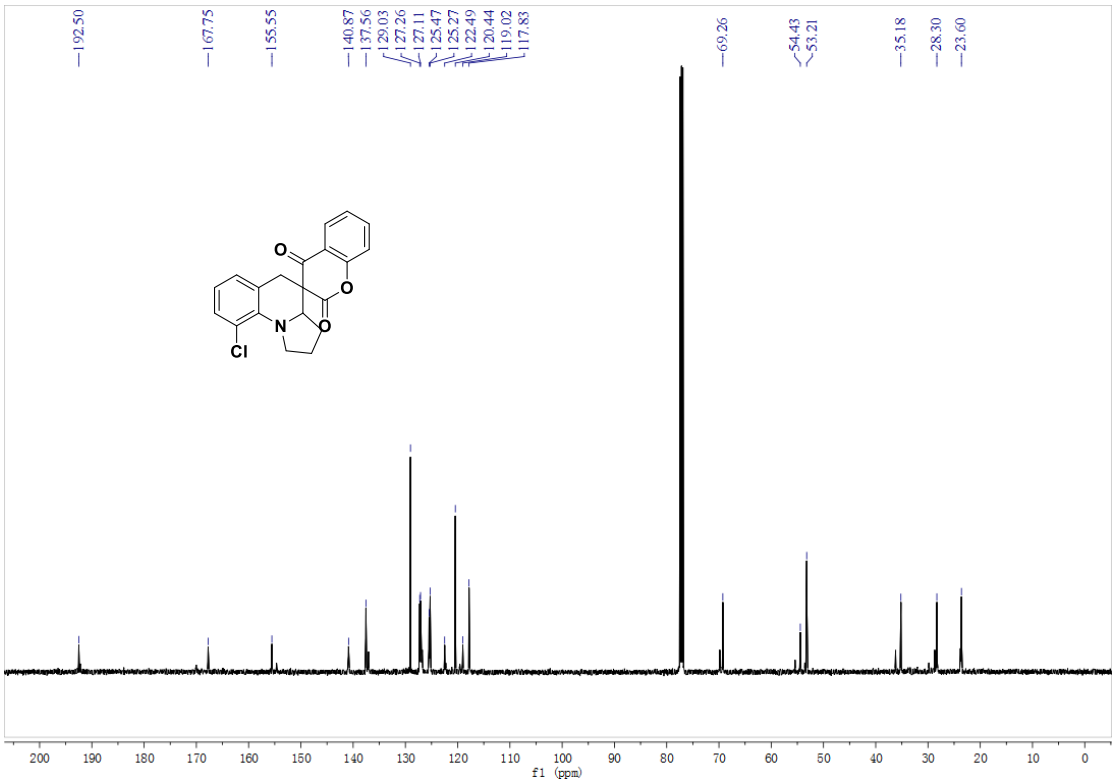
8'-chloro-1',2',3',3a'-tetrahydro-5'H-spiro[chromane-3,4'-pyrrolo[1,2-a]quinoline]-2,4-dione **3d**



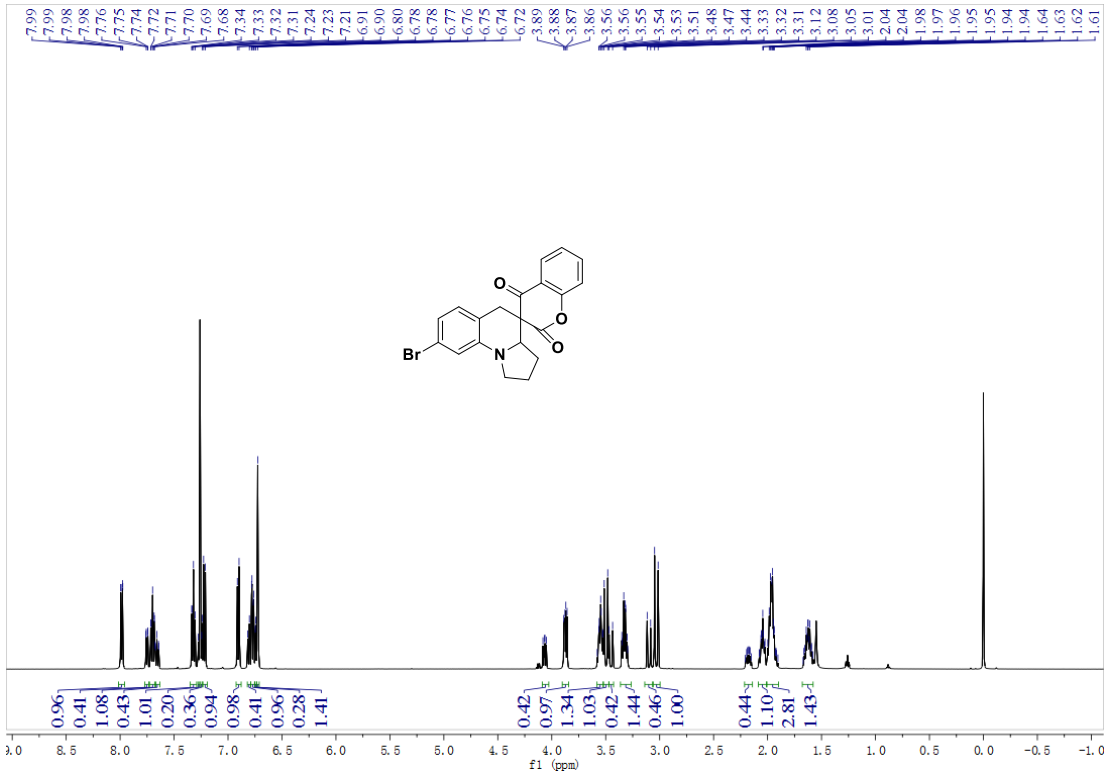


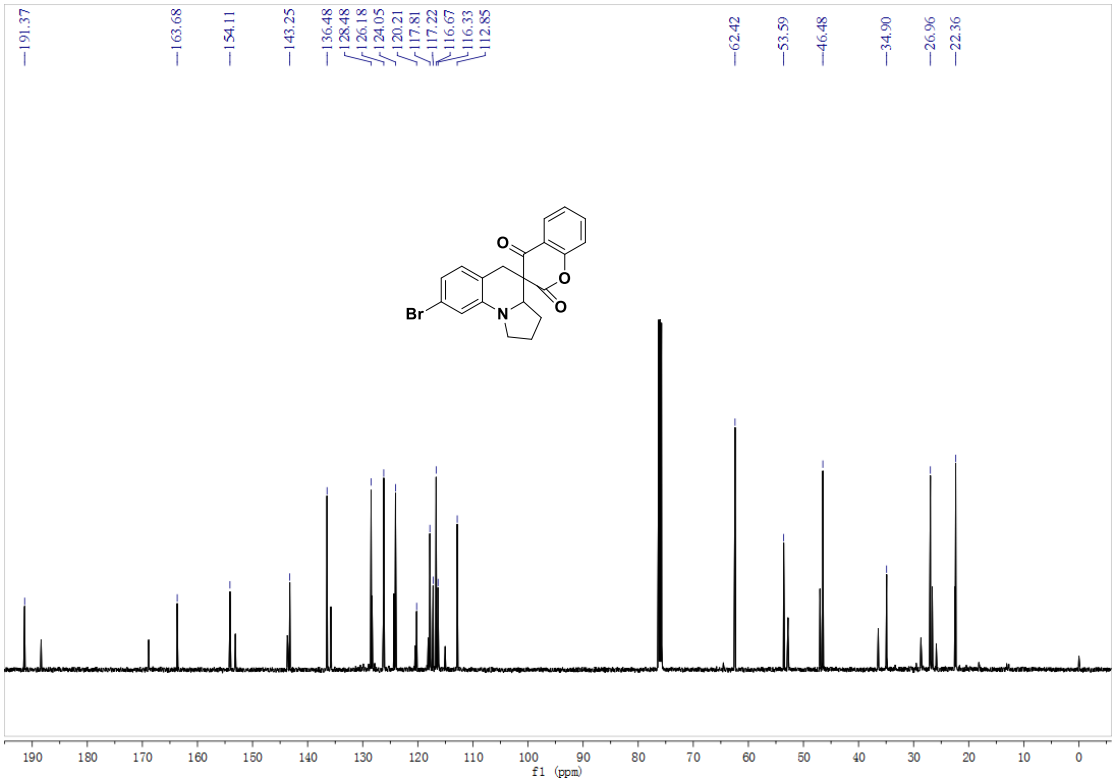
9'-chloro-1',2',3',3a'-tetrahydro-5'H-spiro[chromane-3,4'-pyrrolo[1,2-a]quinoline]-2,4-dione **3e**



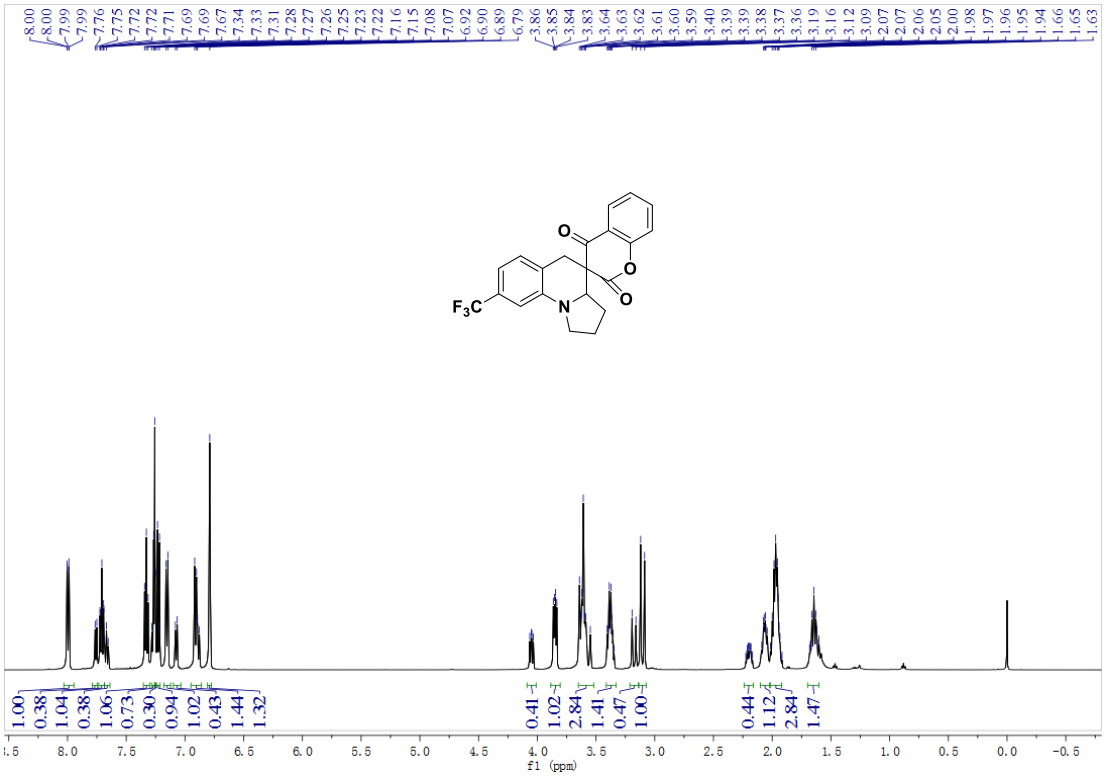


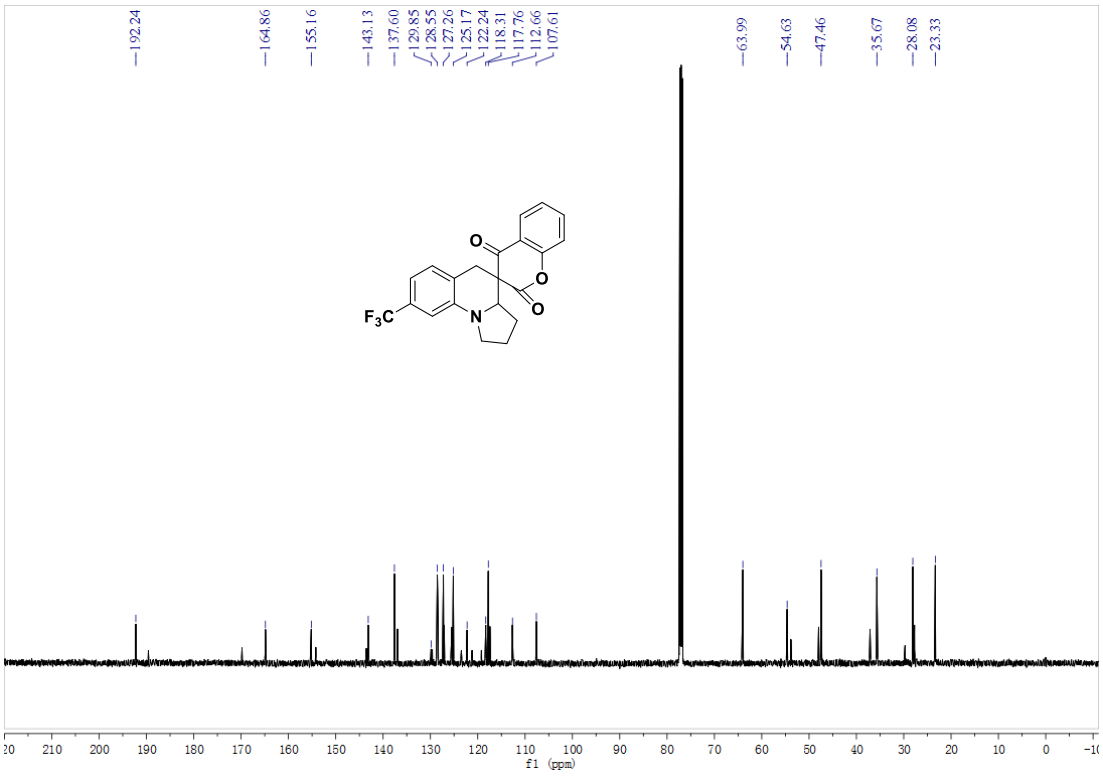
8'-bromo-1',2',3',3a'-tetrahydro-5'H-spiro[chromane-3,4'-pyrrolo[1,2-a]quinoline]-2,4-dione **3f**



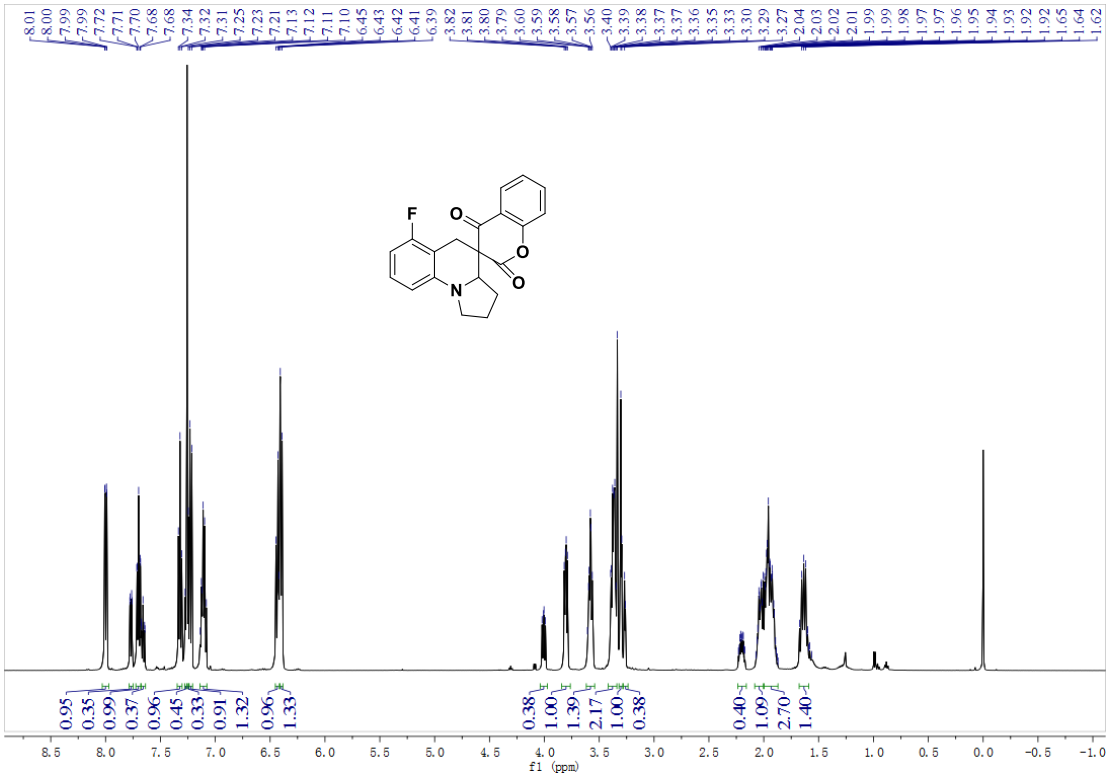


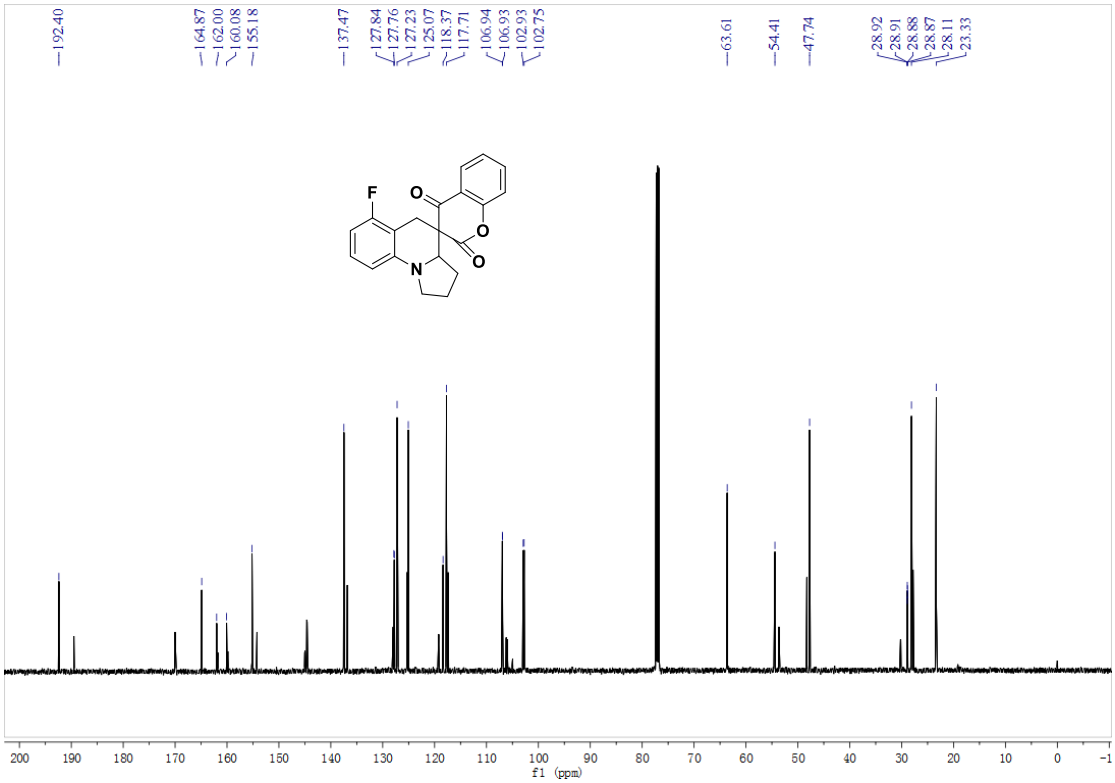
8'-(trifluoromethyl)-1',2',3',3a'-tetrahydro-5'H-spiro[chromane-3,4'-pyrrolo[1,2-a]quinoline]-2,4-dione **3g**



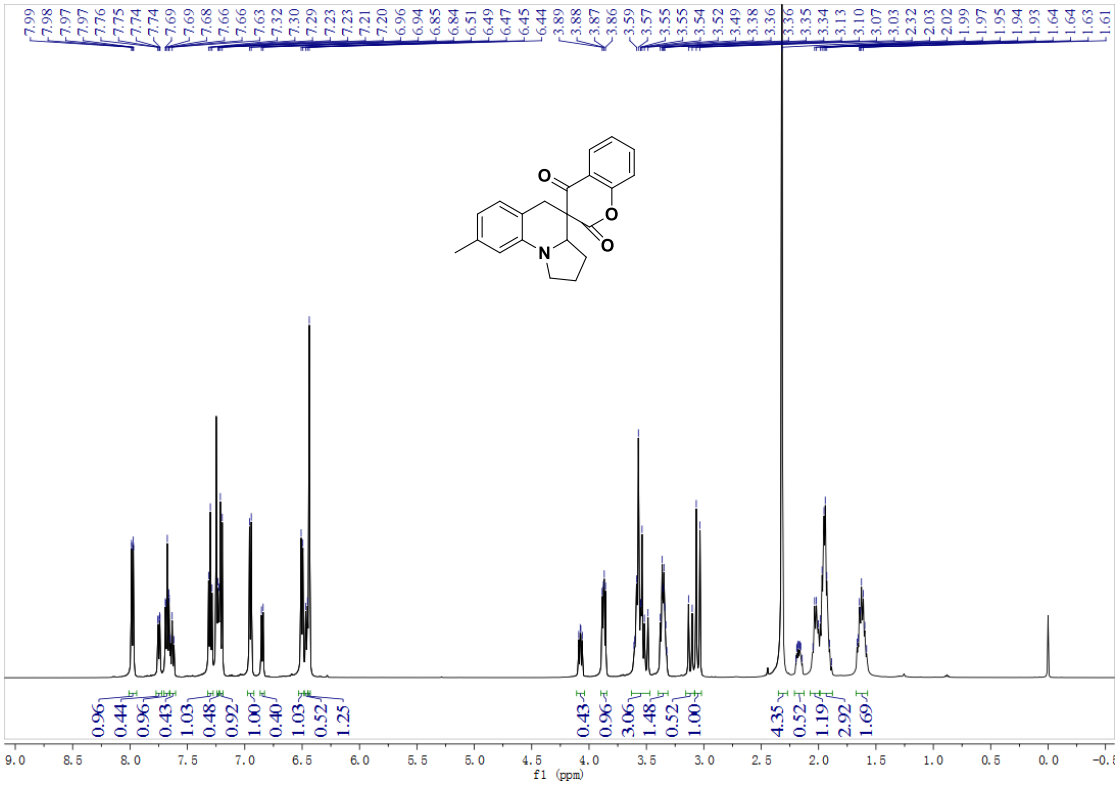


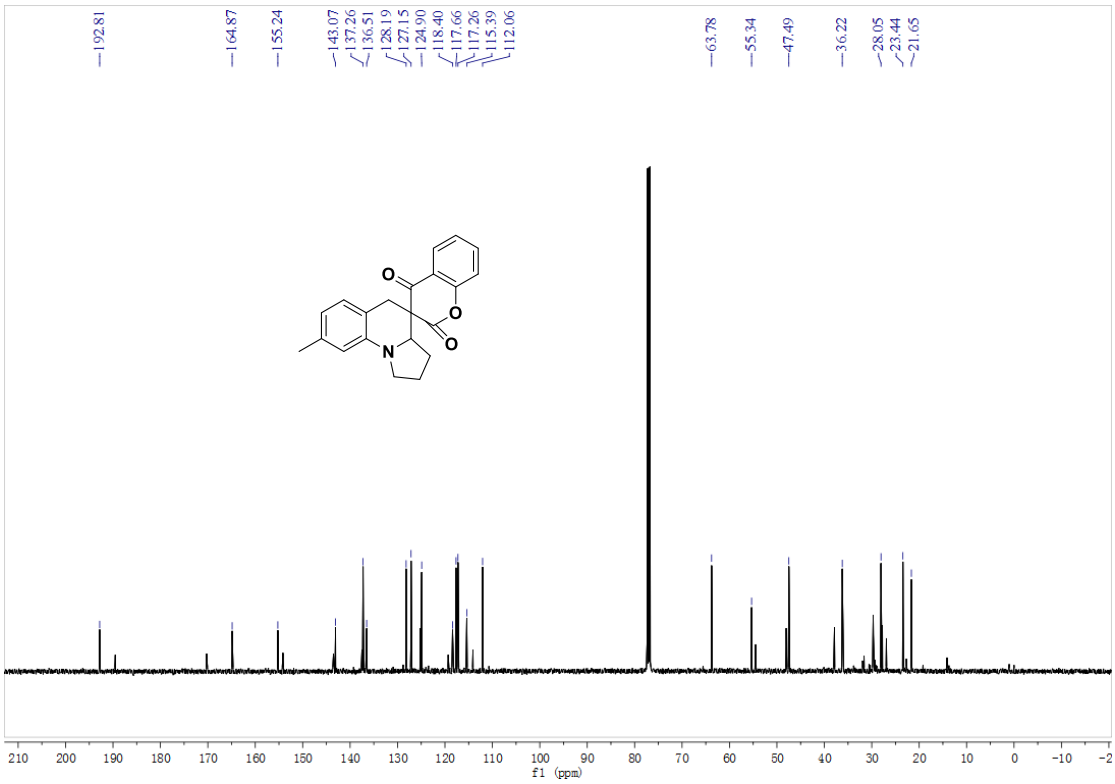
6'-fluoro-1',2',3',3a'-tetrahydro-5'H-spiro[chromane-3,4'-pyrrolo[1,2-a]quinoline]-2,4-dione **3h**





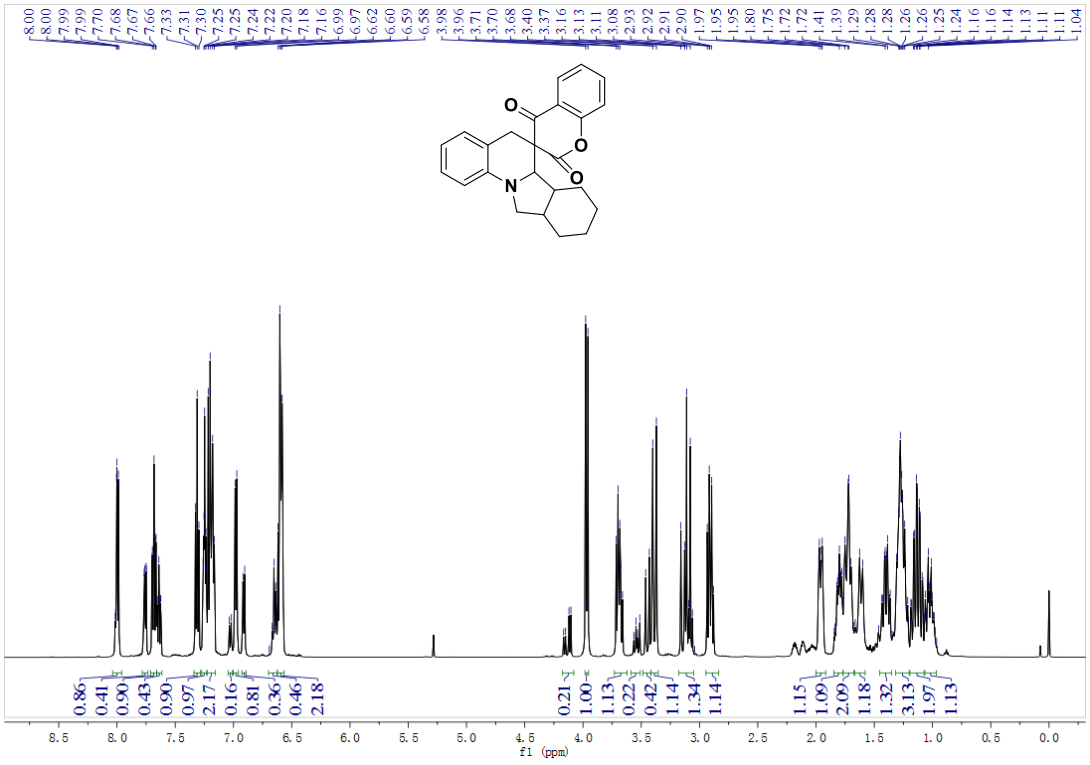
8'-methyl-1',2',3',3a'-tetrahydro-5'H-spiro[chromane-3,4'-pyrrolo[1,2-a]quinoline]-2,4-dione **3i**

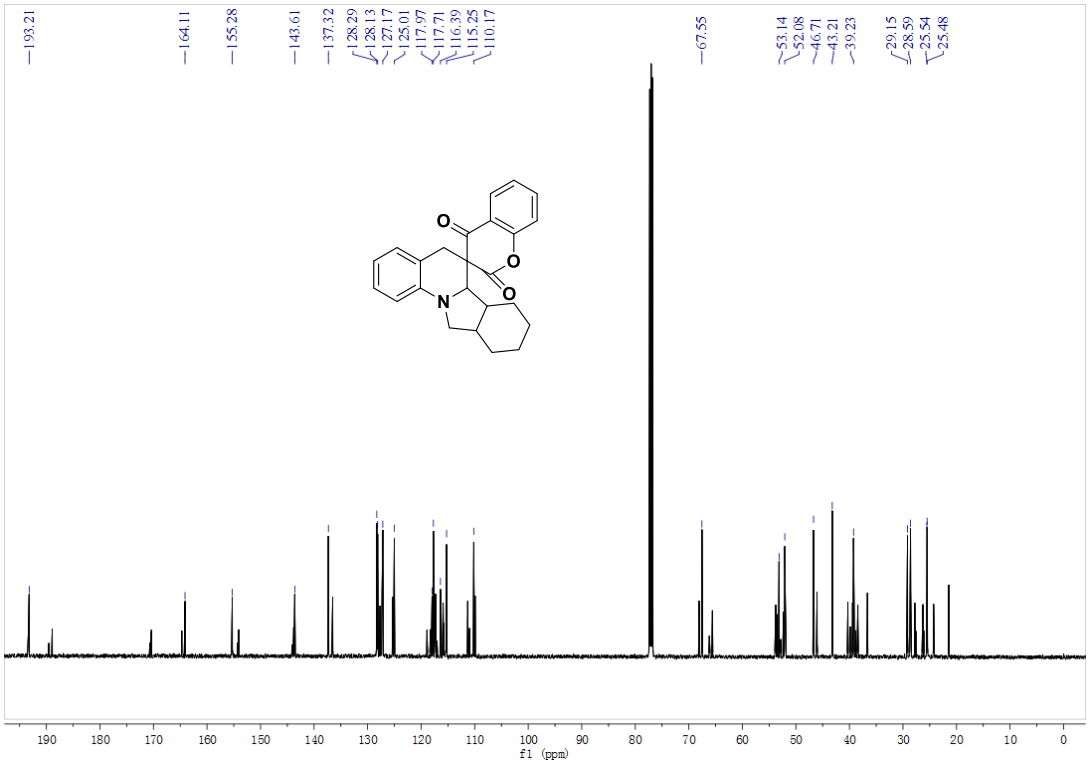




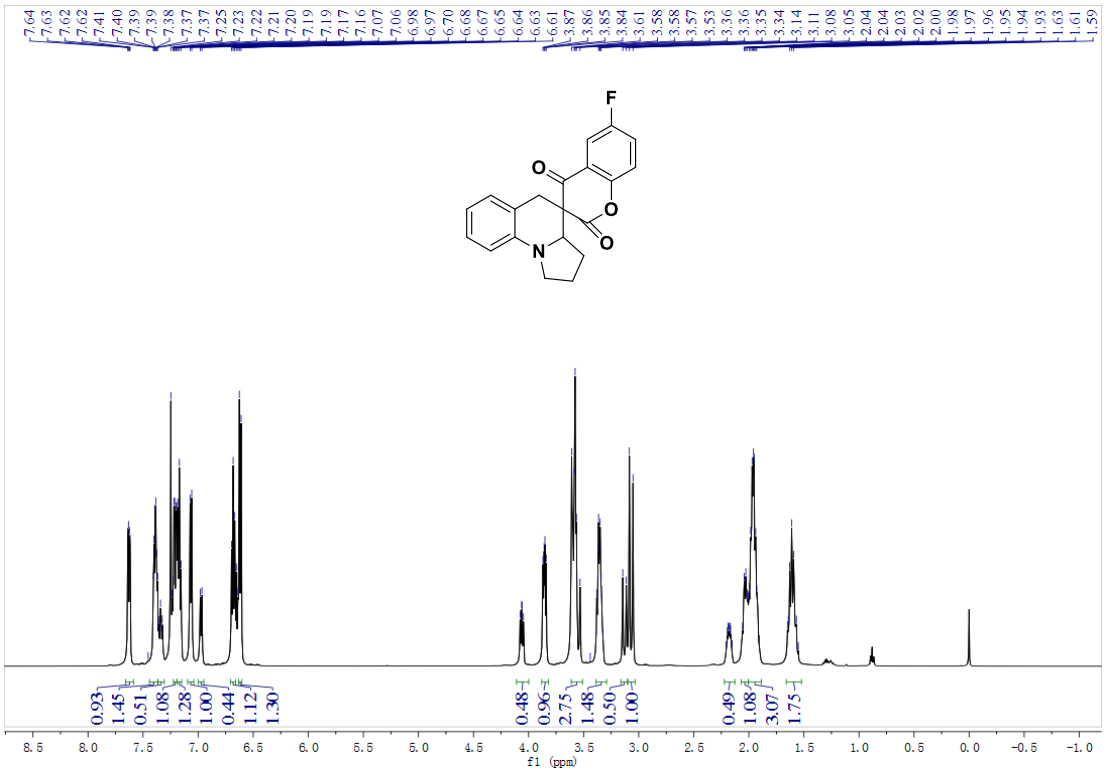
6a',6b',7',8',9',10',10a',11'-octahydro-5'H-spiro[chromane-3,6'-isoindolo[2,1-a]quinoline]-2,4-dione

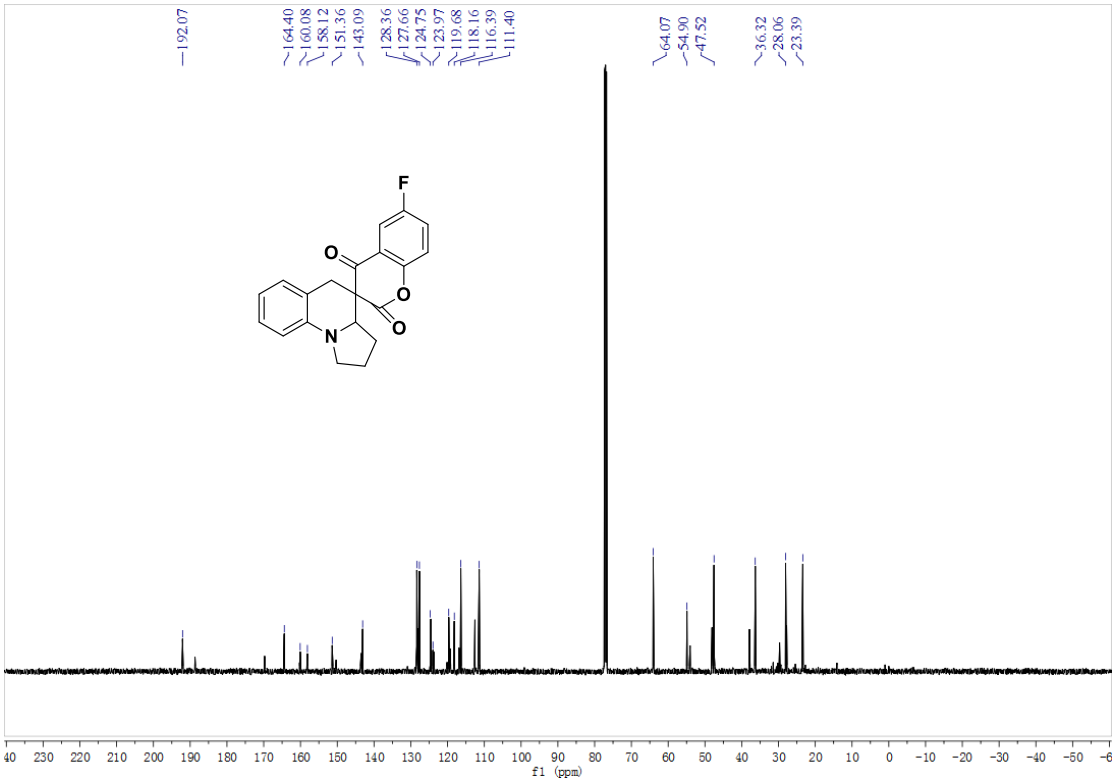
3k



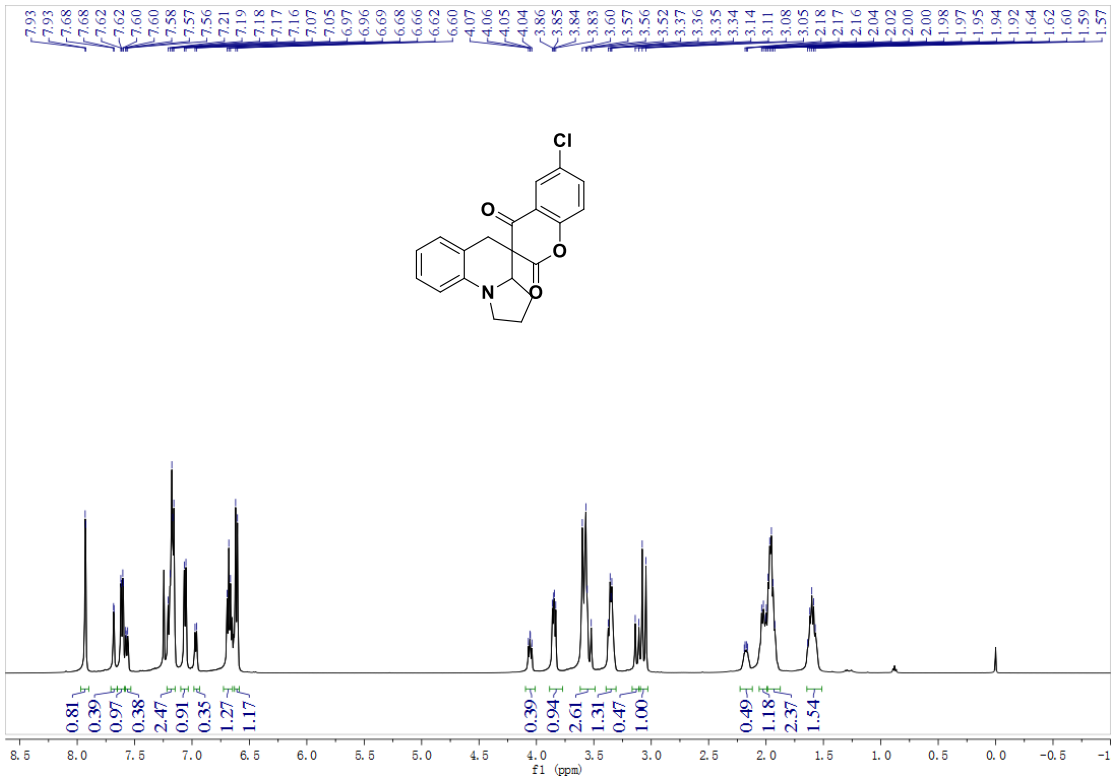


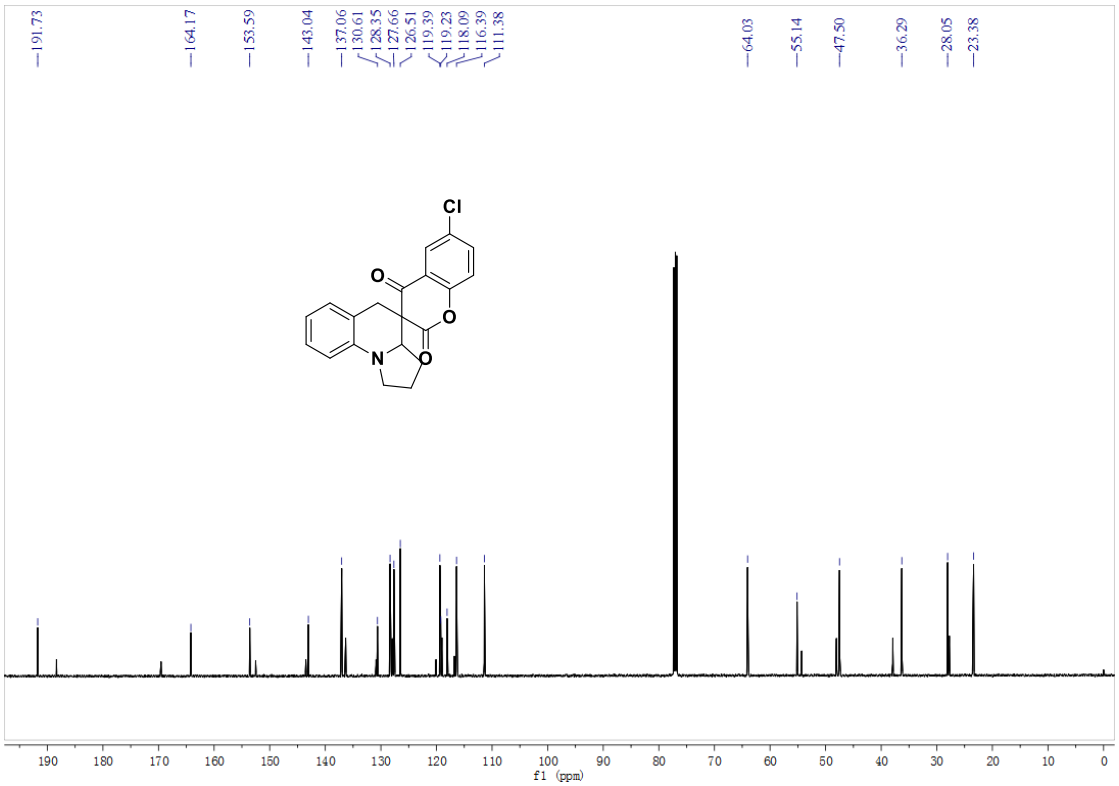
6-fluoro-1',2',3',3a'-tetrahydro-5'H-spiro[chromane-3,4'-pyrrolo[1,2-a]quinoline]-2,4-dione **3l**



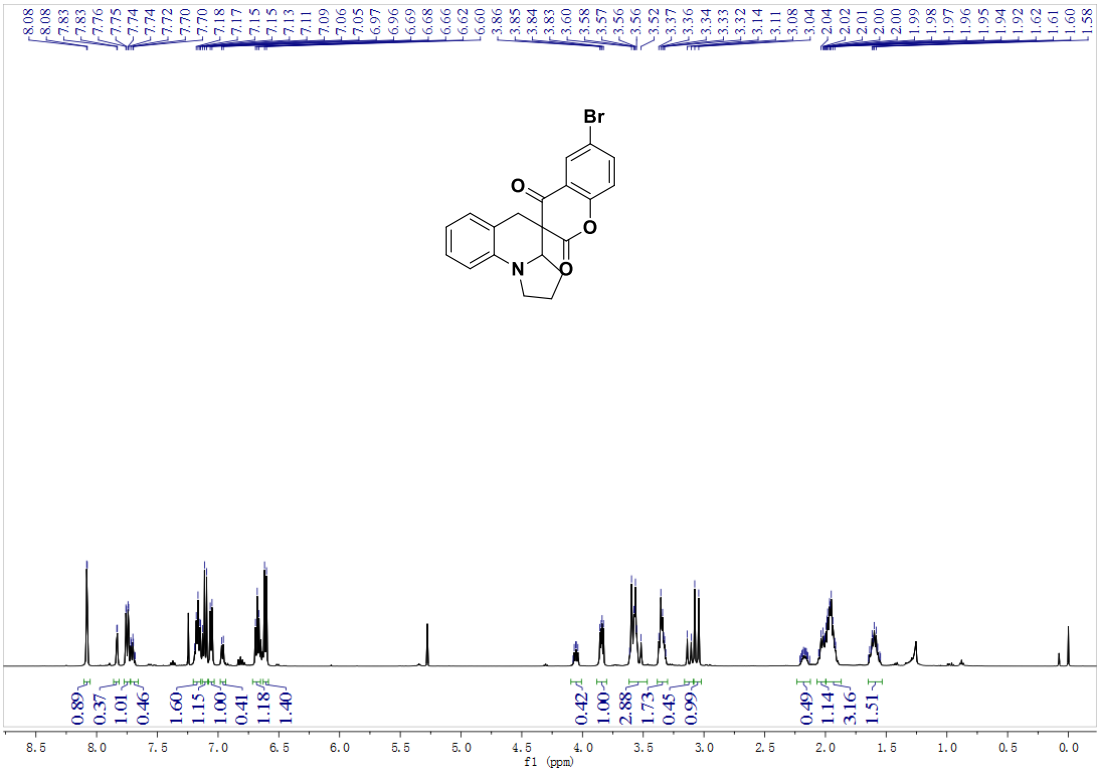


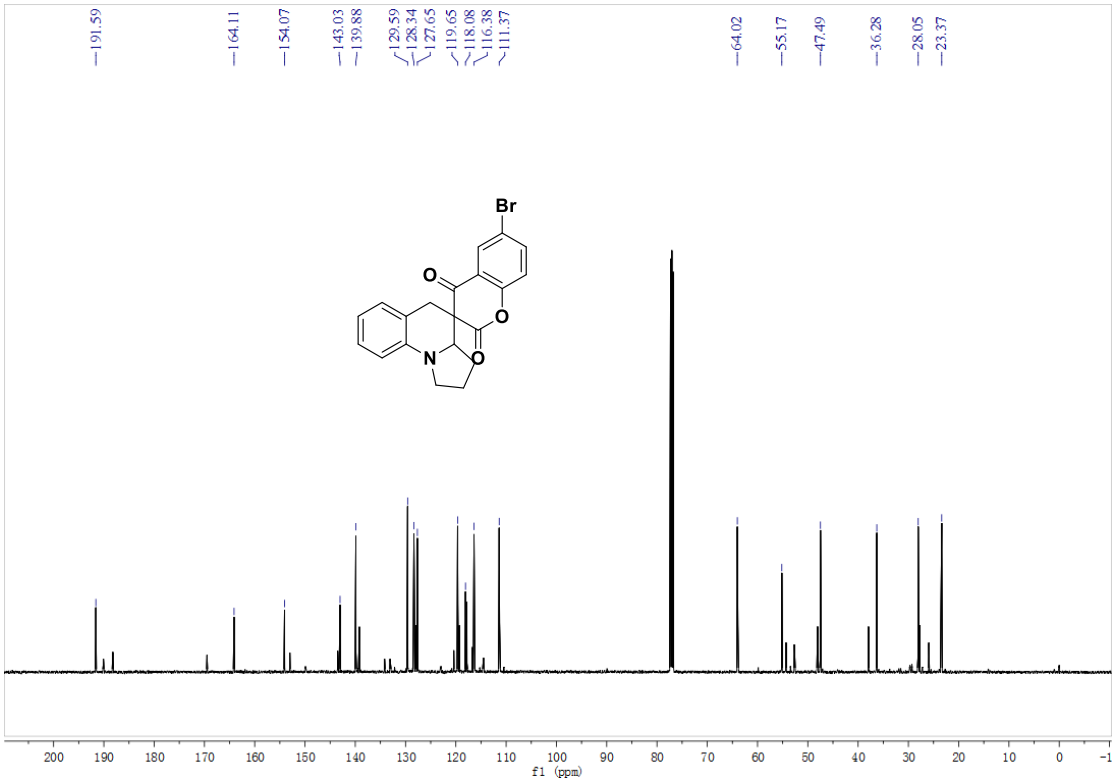
6-chloro-1',2',3',3a'-tetrahydro-5'H-spiro[chromane-3,4'-pyrrolo[1,2-a]quinoline]-2,4-dione **3m**



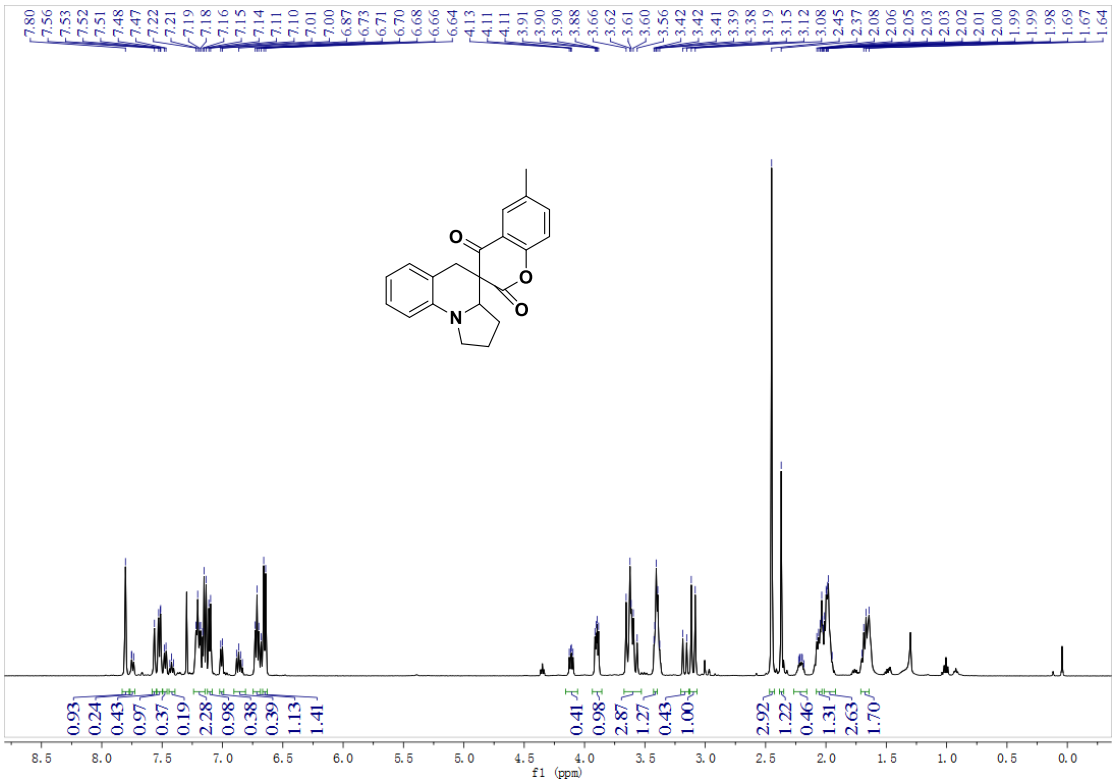


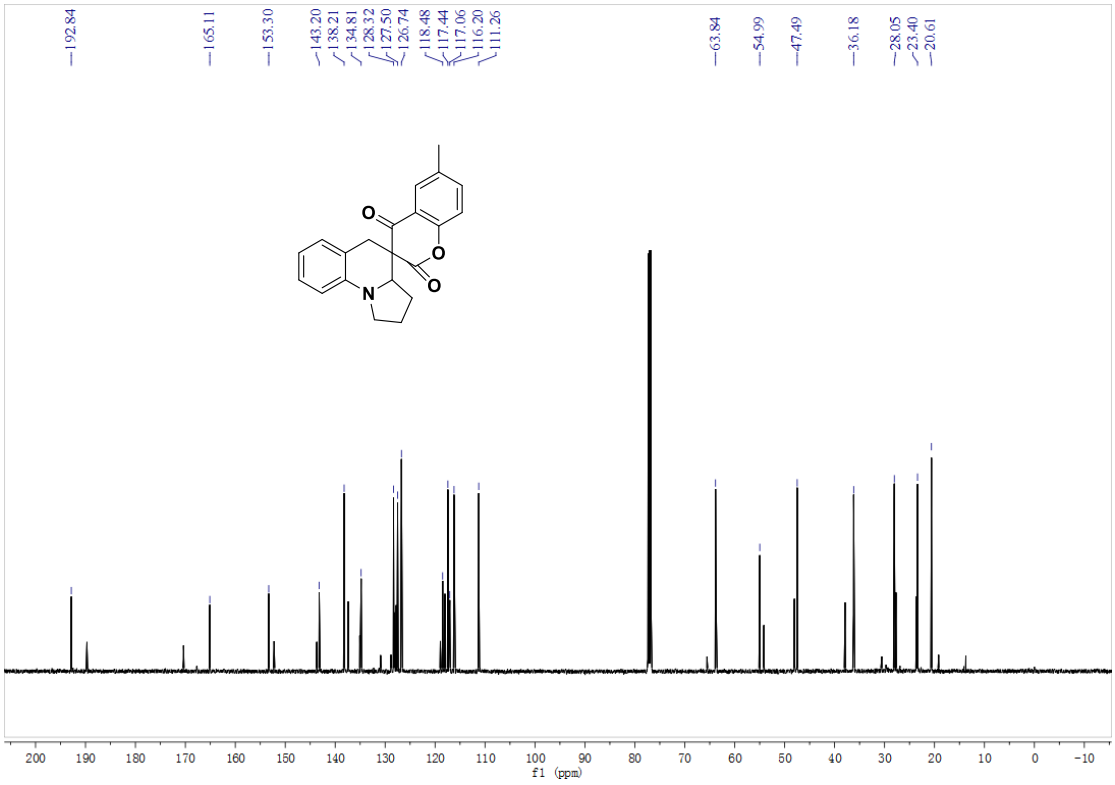
6-bromo-1',2',3',3a'-tetrahydro-5'H-spiro[chromane-3,4'-pyrrolo[1,2-a]quinoline]-2,4-dione **3n**



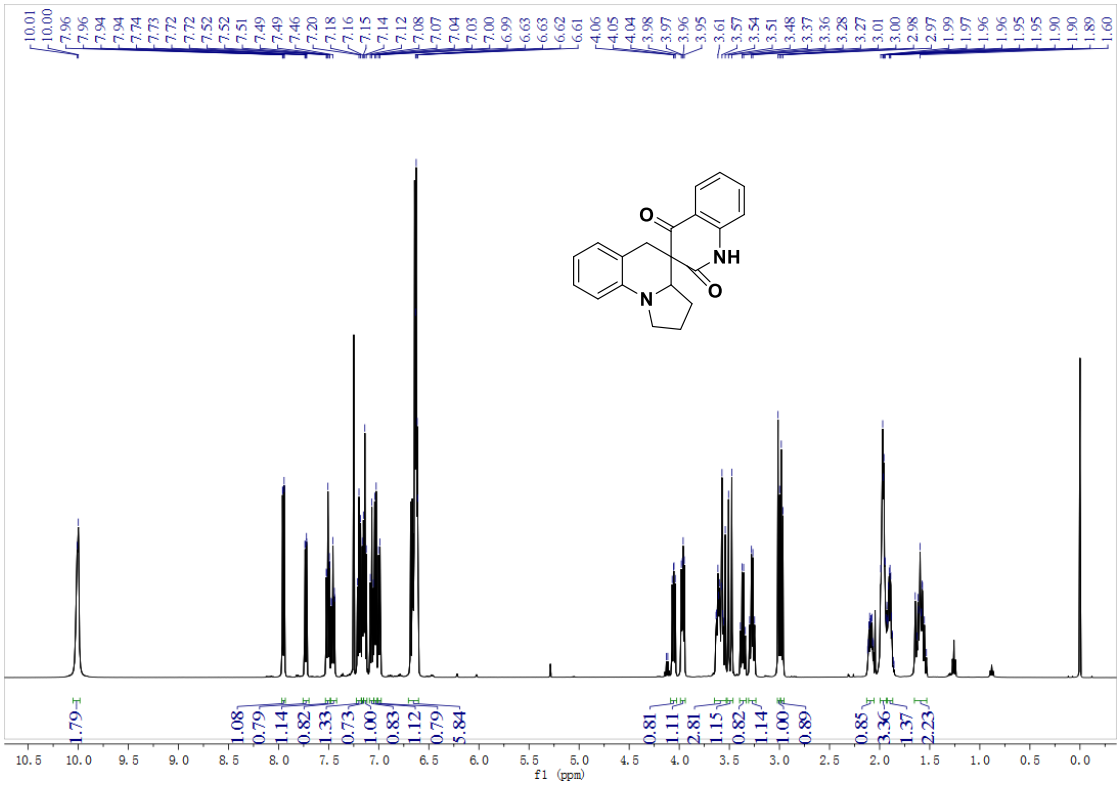


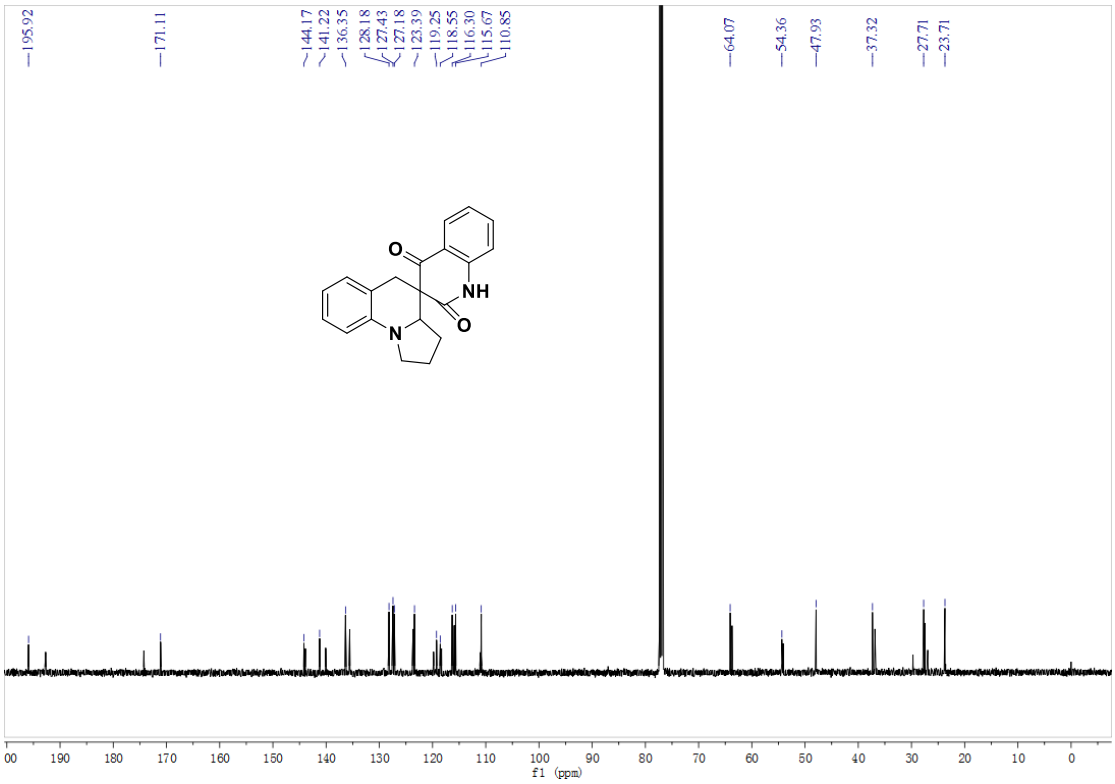
6-methyl-1',2',3',3a'-tetrahydro-5'H-spiro[chromane-3,4'-pyrrolo[1,2-a]quinoline]-2,4-dione **3o**



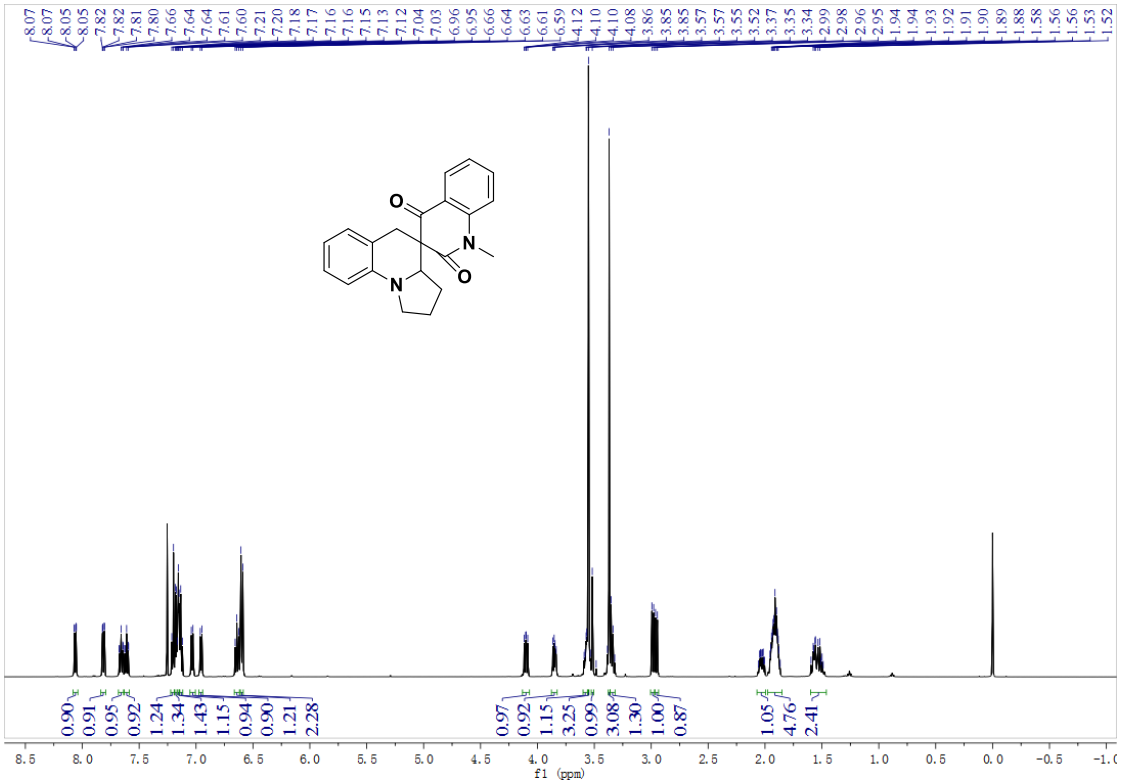


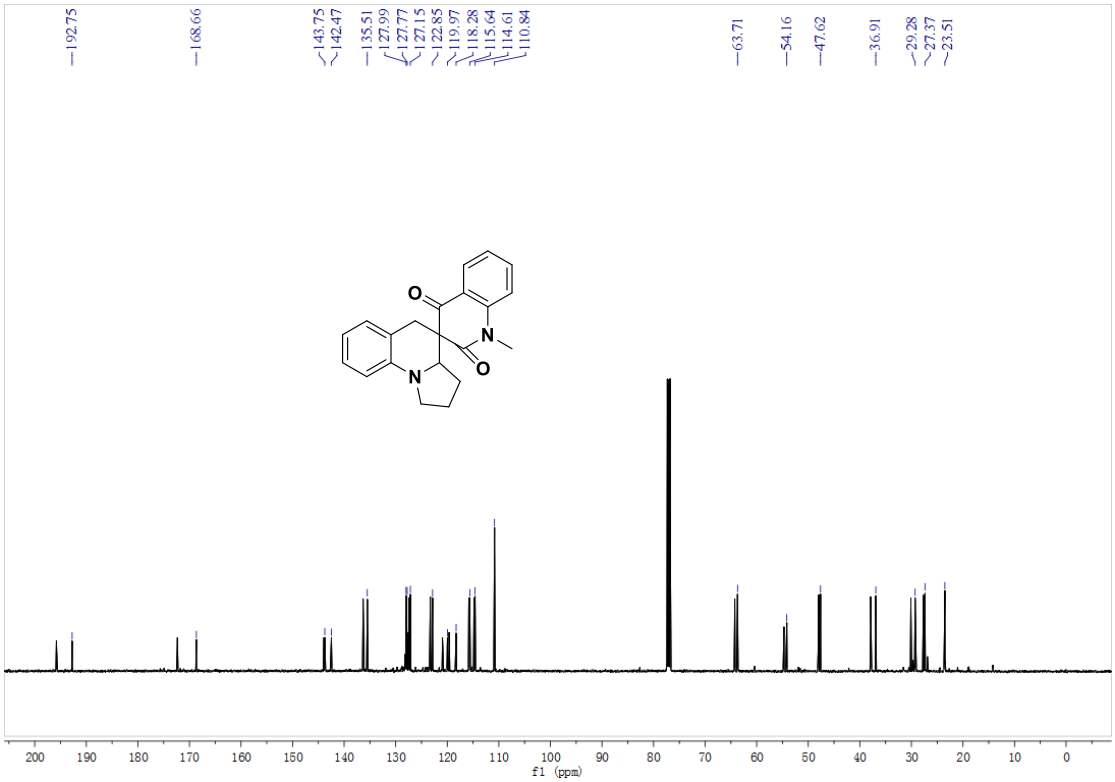
1,2,3,3a-tetrahydro-2'H,5H-spiro[pyrrolo[1,2-a]quinoline-4,3'-quinoline]-2',4'(1'H)-dione **5a**



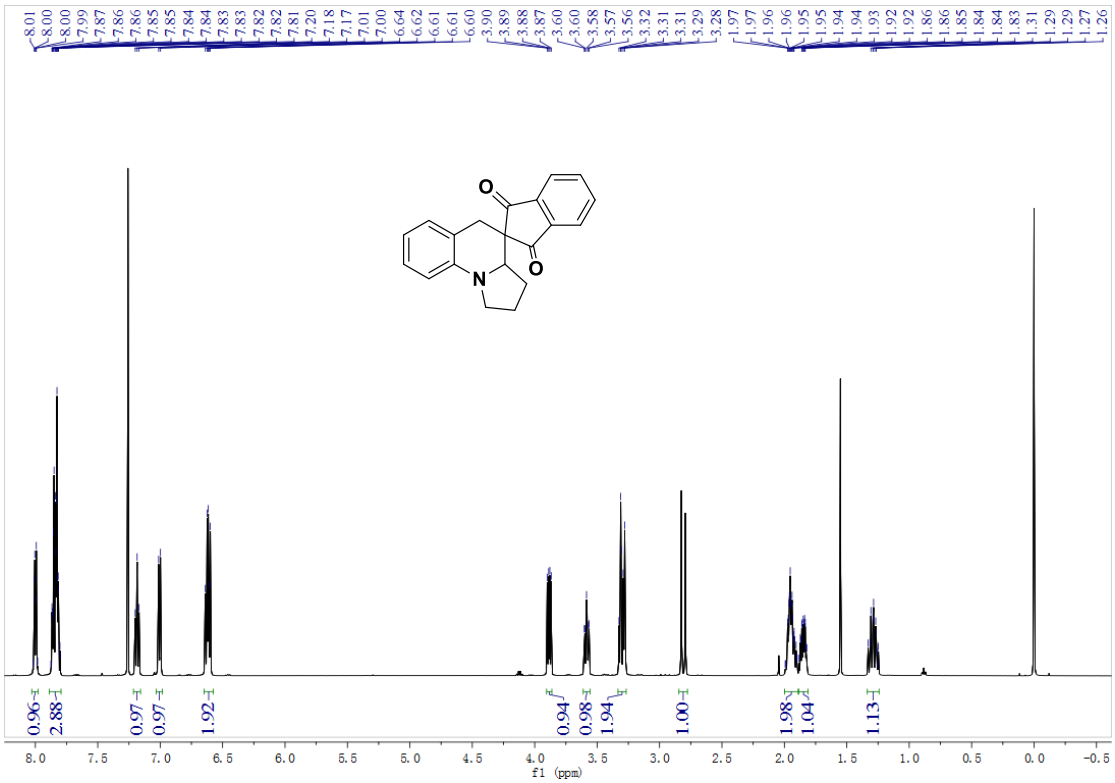


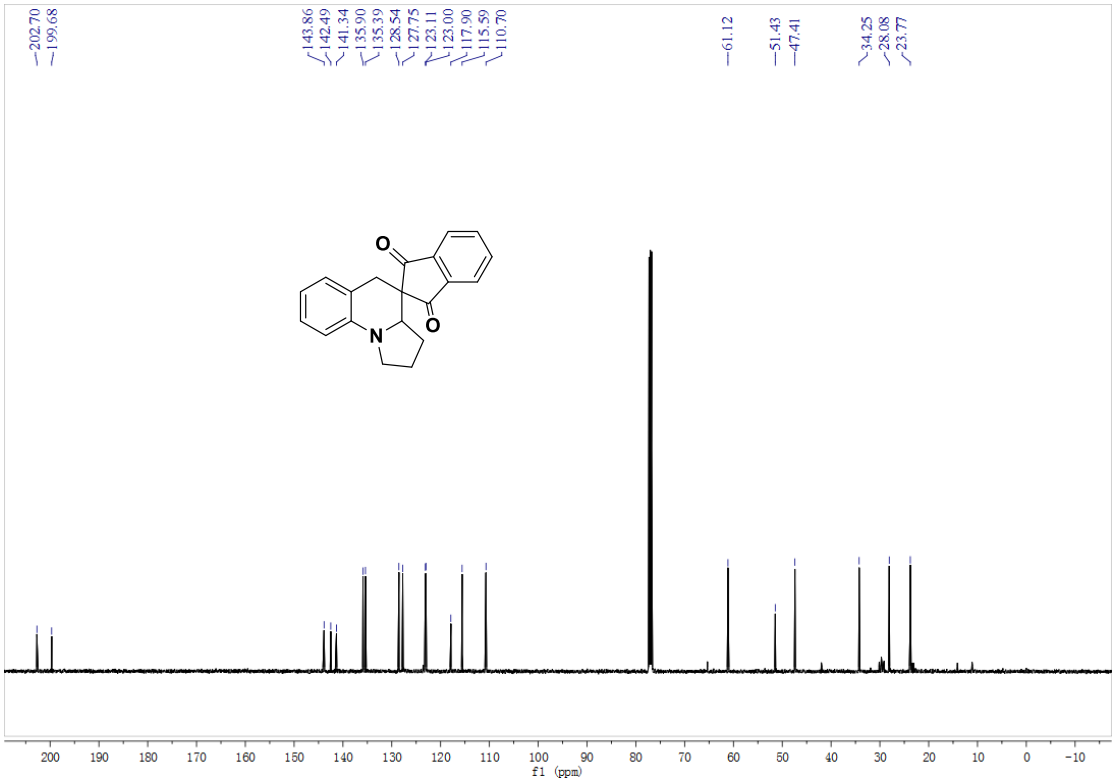
1'-methyl-1,2,3,3a-tetrahydro-2'H,5H-spiro[pyrrolo[1,2-a]quinoline-4,3'-quinoline]-2',4'(1'H)-dion e **5b**





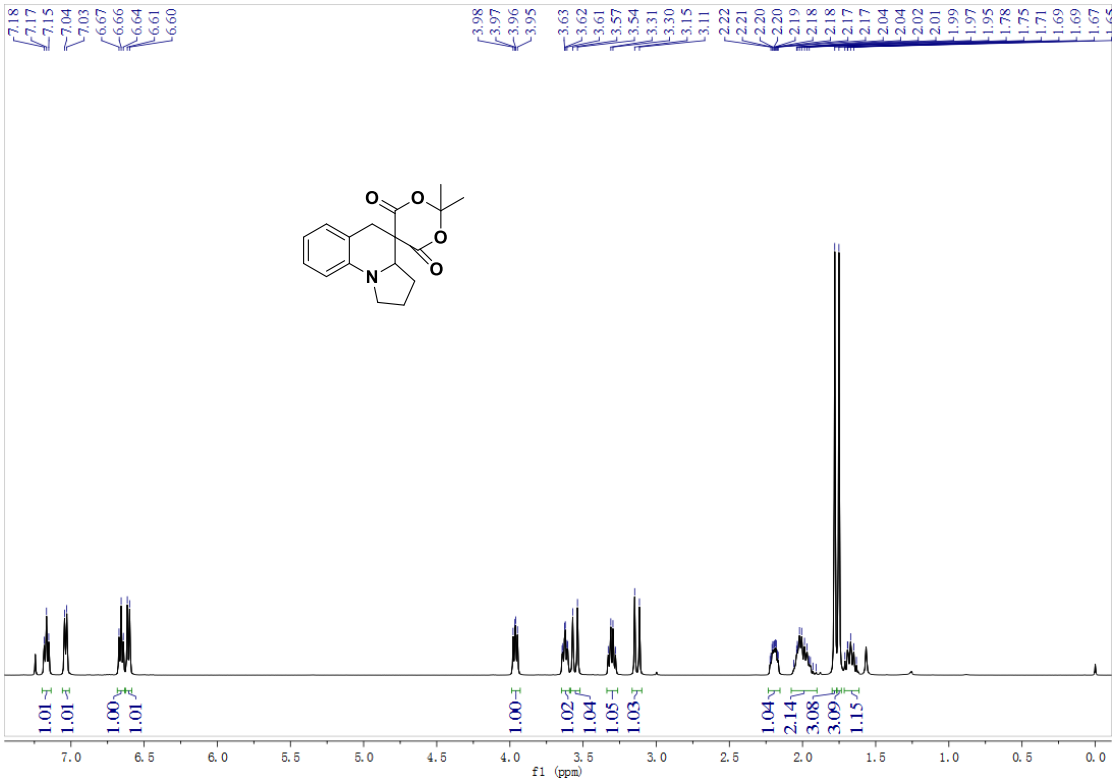
1',2',3',3a'-tetrahydro-5'H-spiro[indene-2,4'-pyrrolo[1,2-a]quinoline]-1,3-dione **5c**

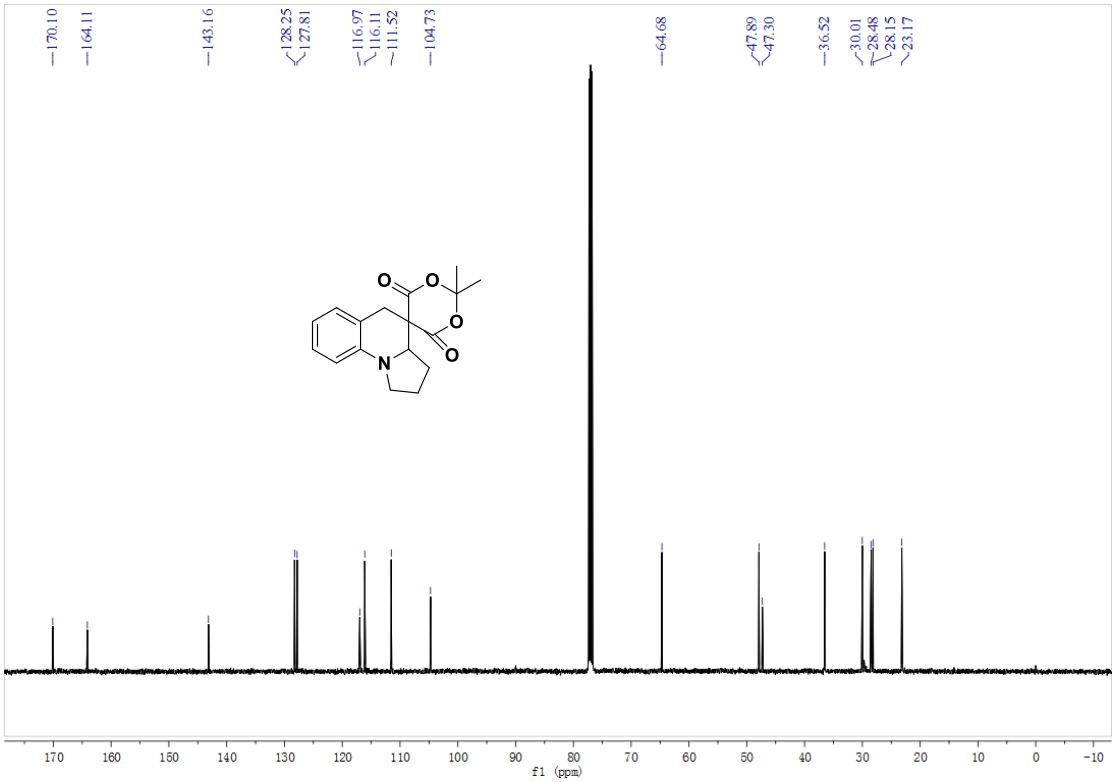




2',2'-dimethyl-1,2,3,3a-tetrahydro-5H-spiro[pyrrolo[1,2-a]quinoline-4,5'-[1,3]dioxane]-4',6'-dione

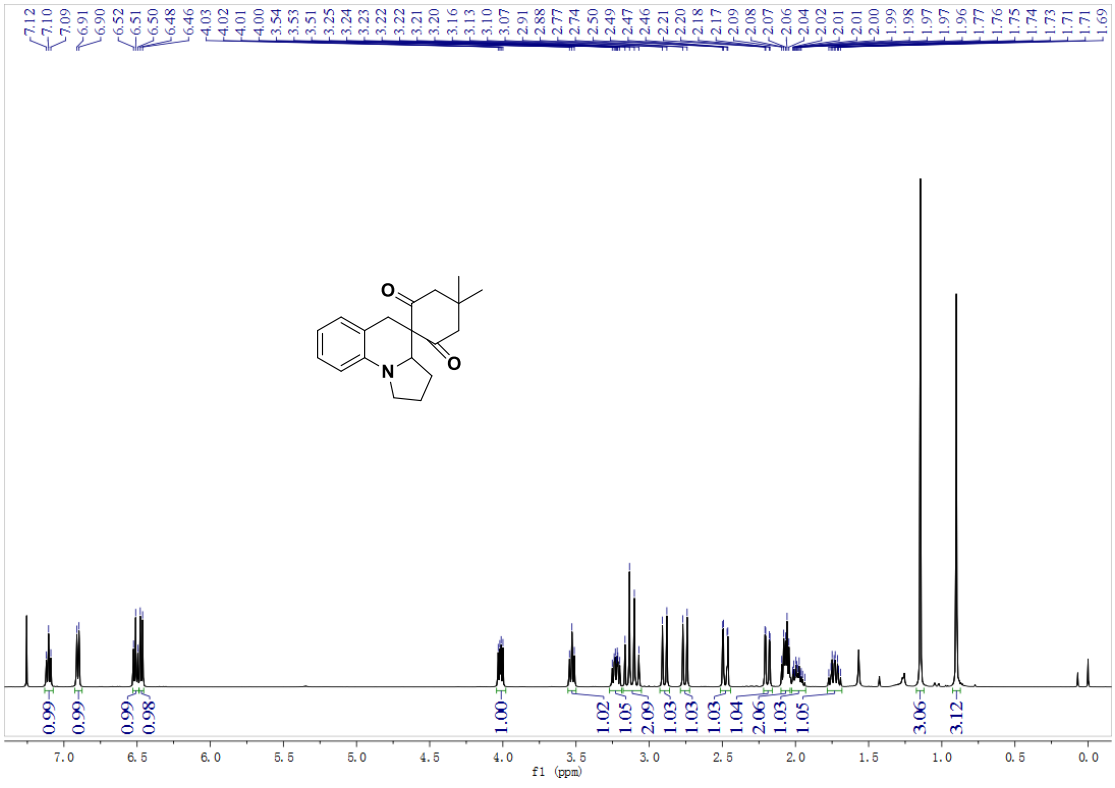
5d

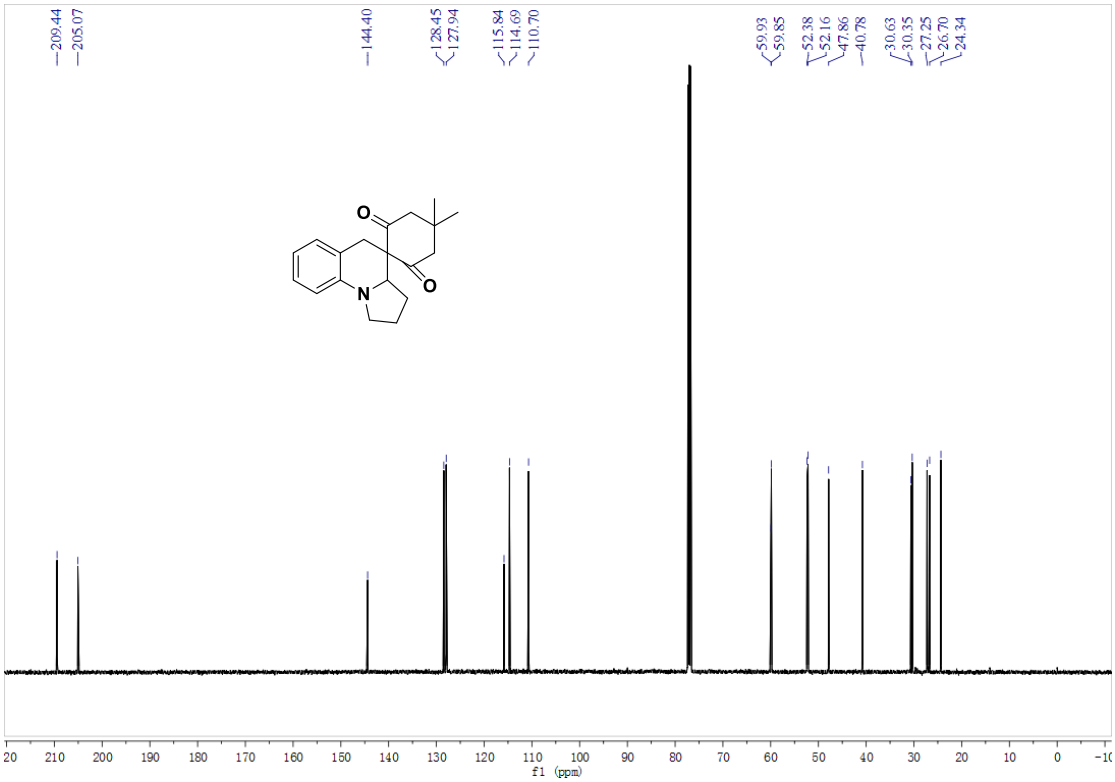




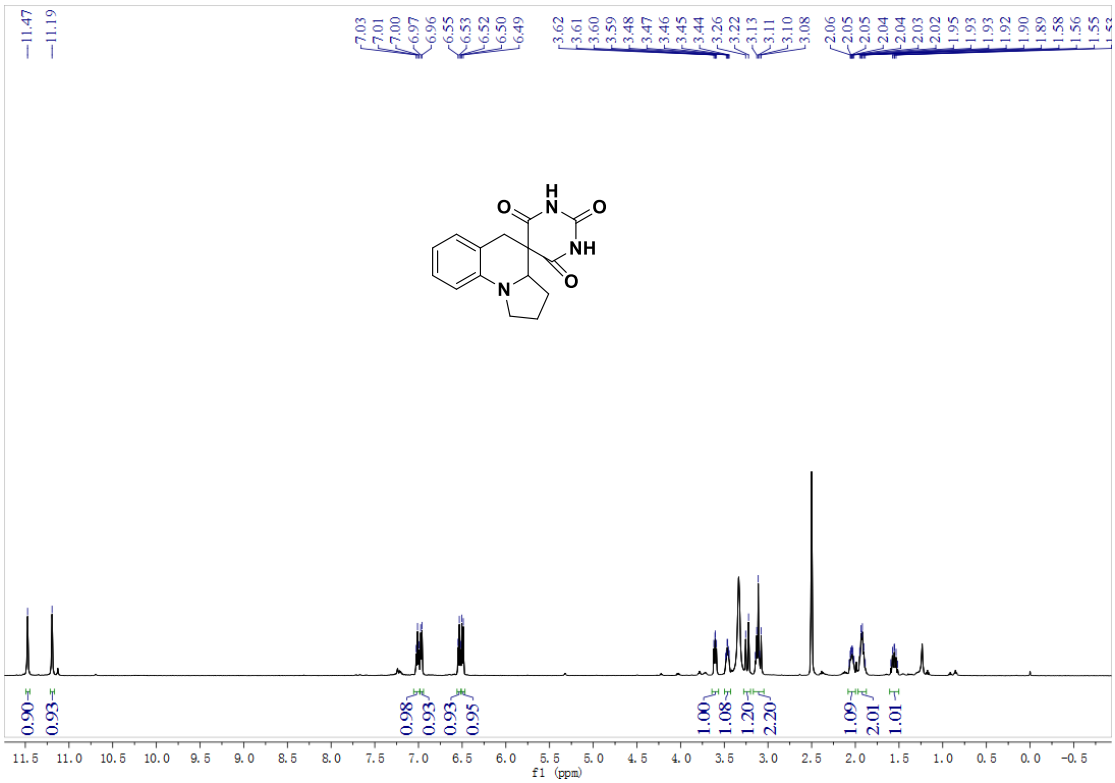
4,4-dimethyl-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,6-dione

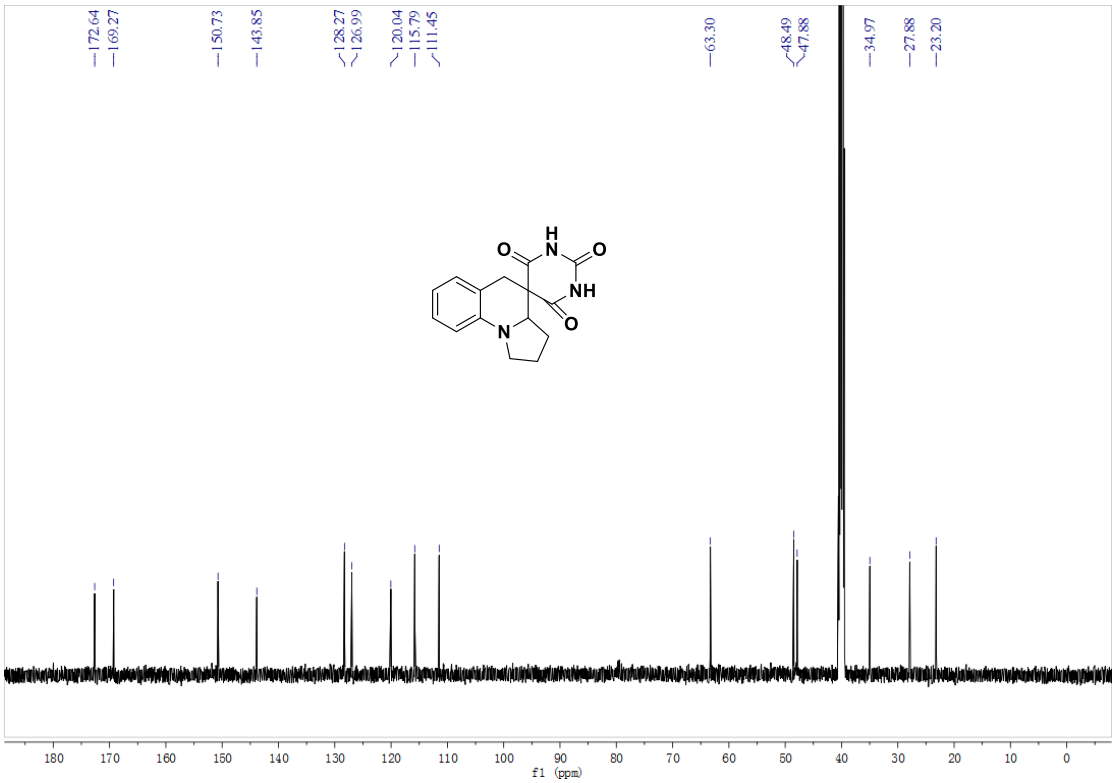
5e



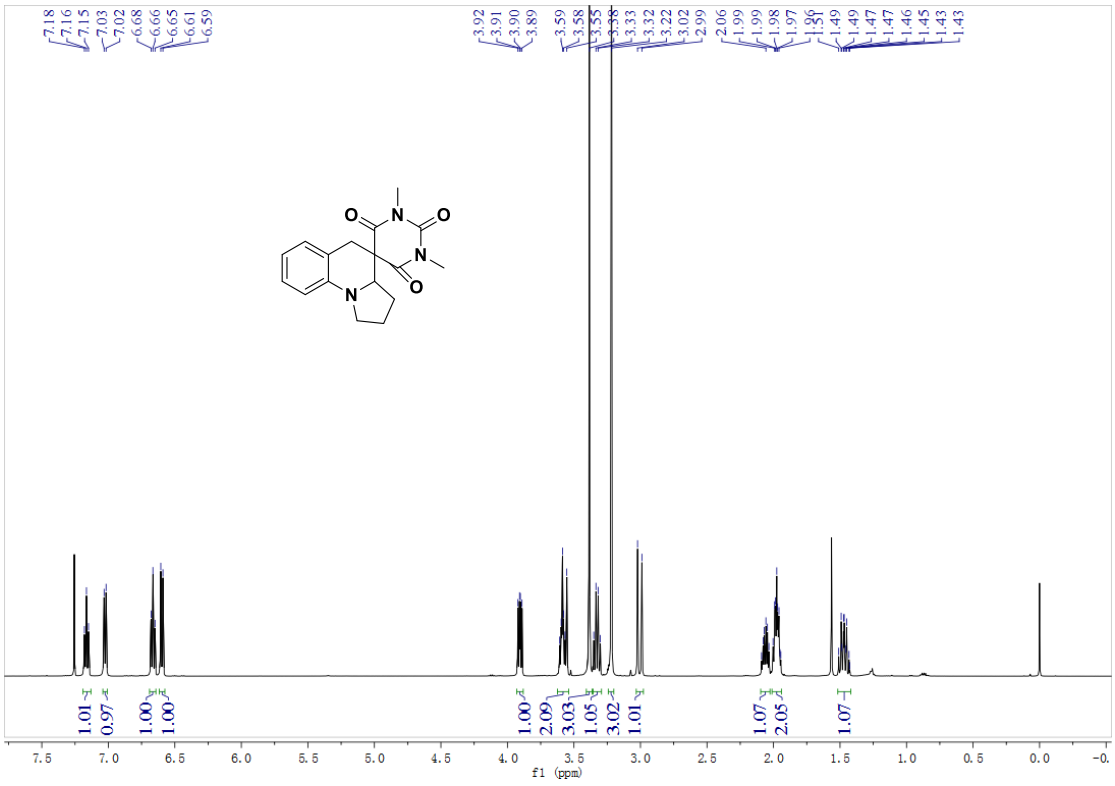


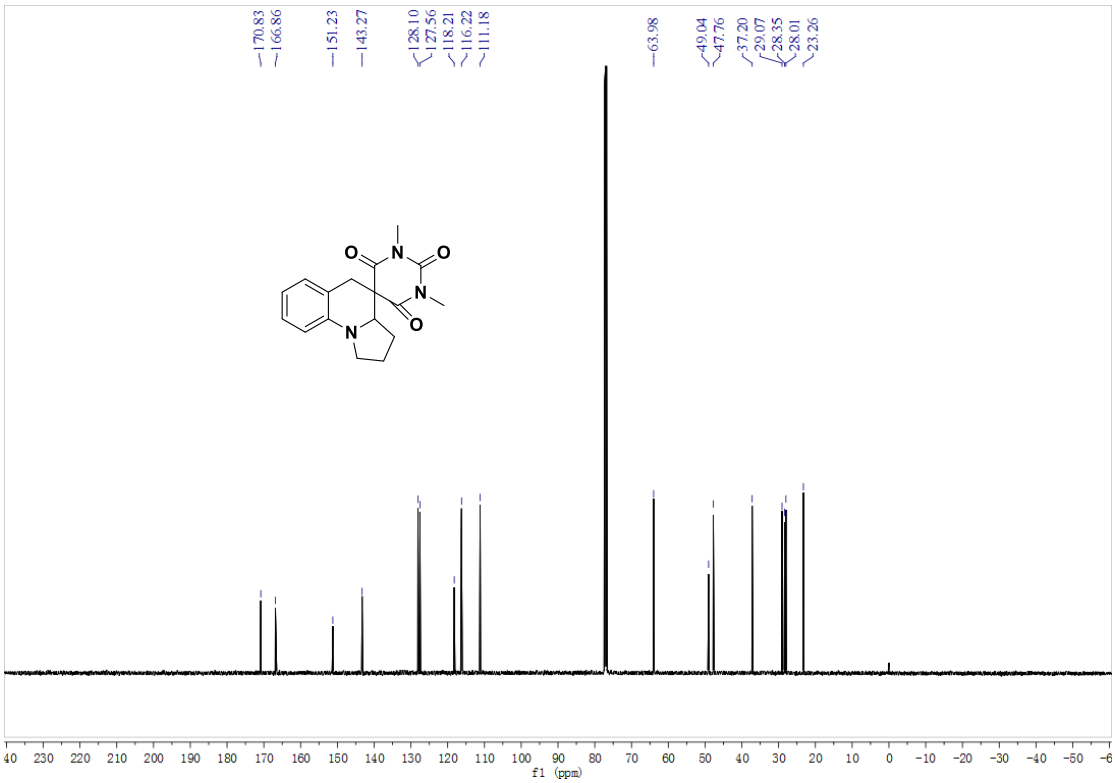
1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,6-dione **5f**



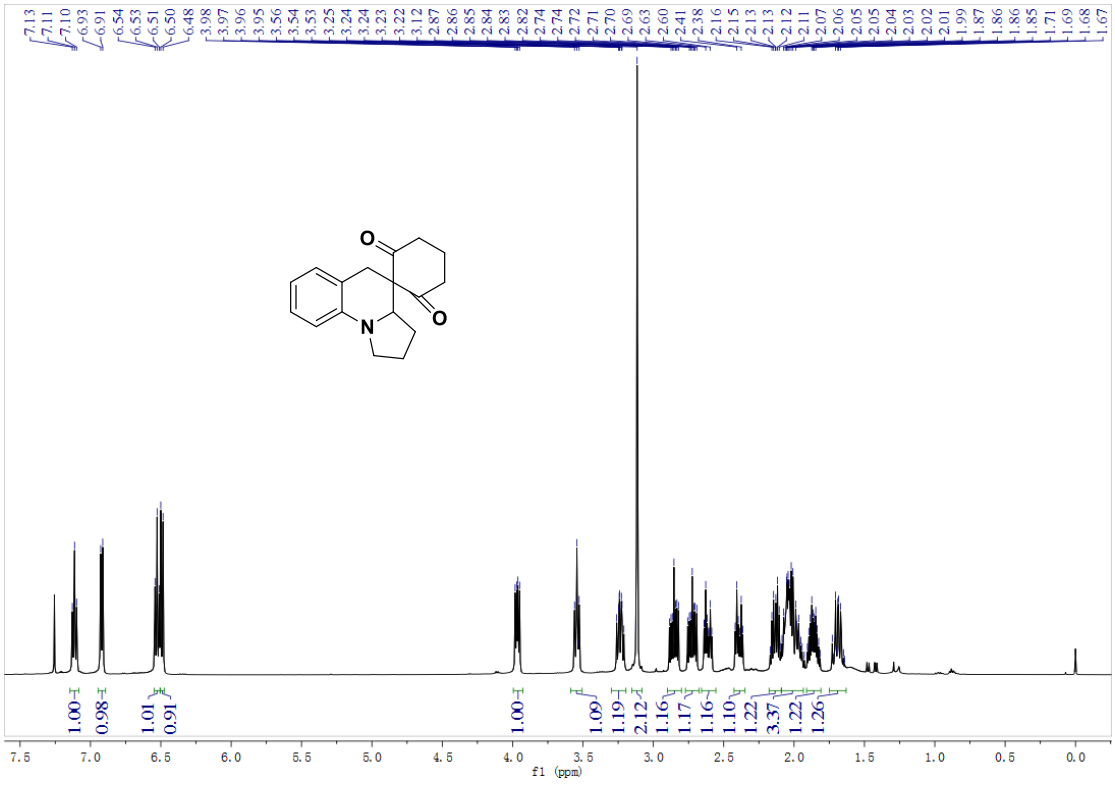


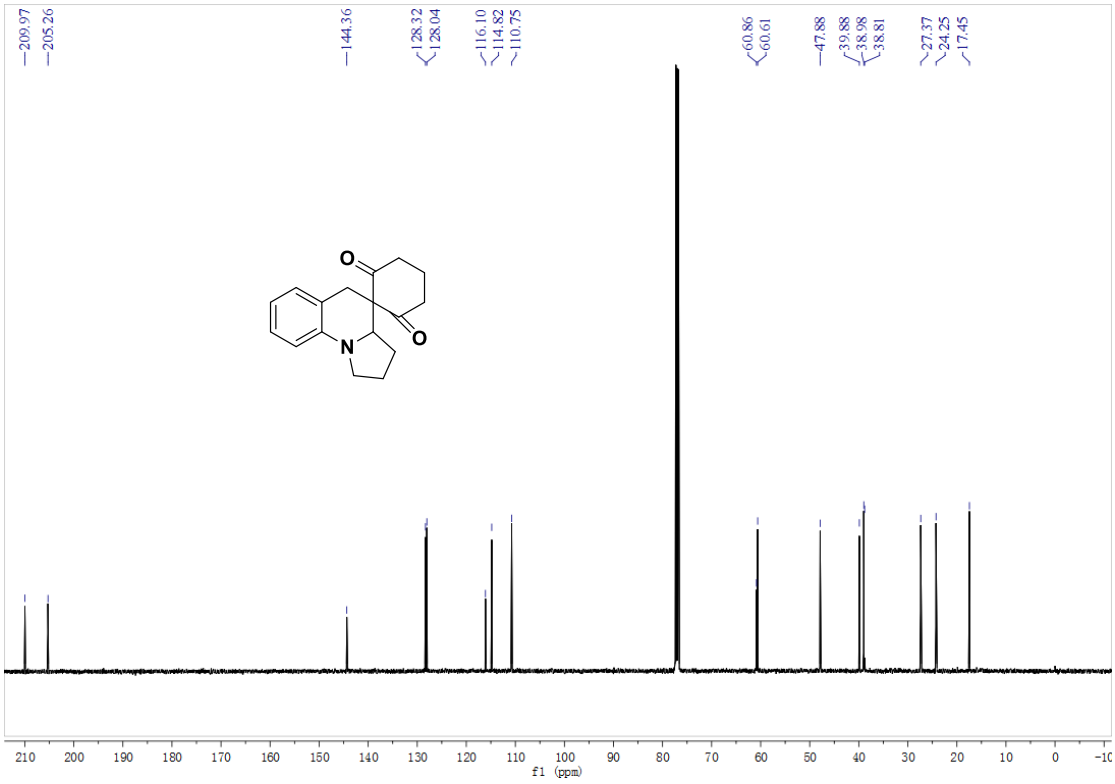
1,3-dimethyl-1',2',3',3a'-tetrahydro-2H,5'H-spiro[pyrimidine-5,4'-pyrrolo[1,2-a]quinoline]-2,4,6(1H,3H)-trione **5g**



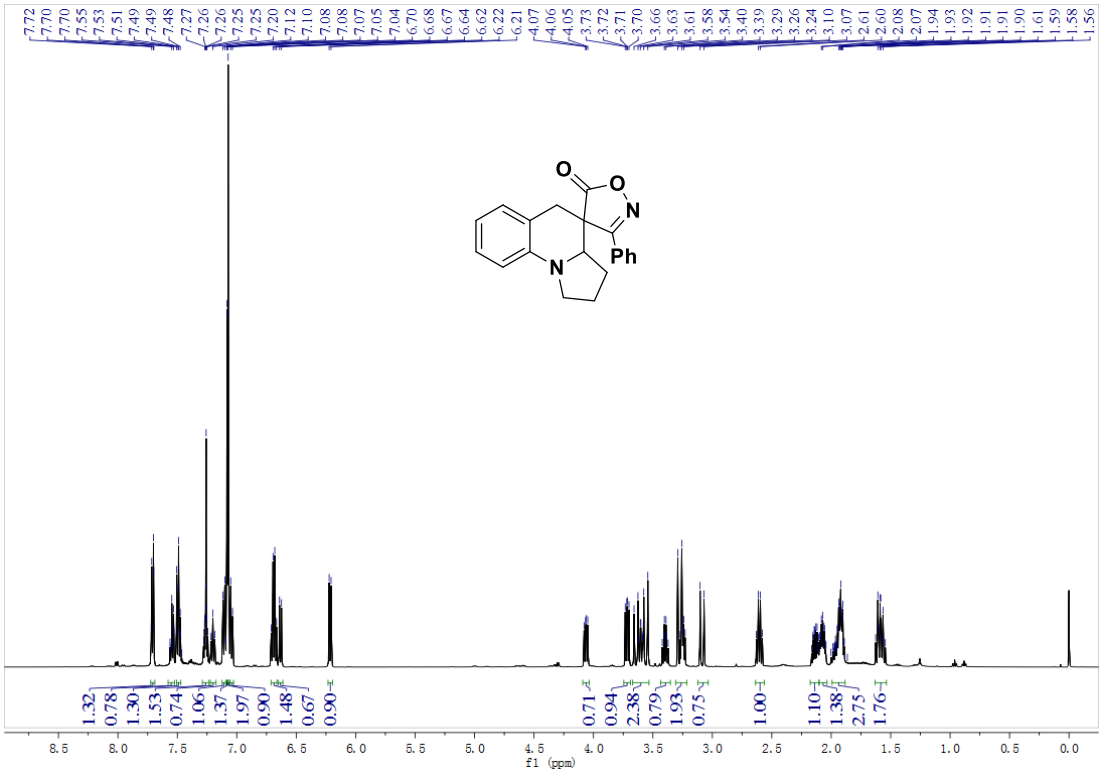


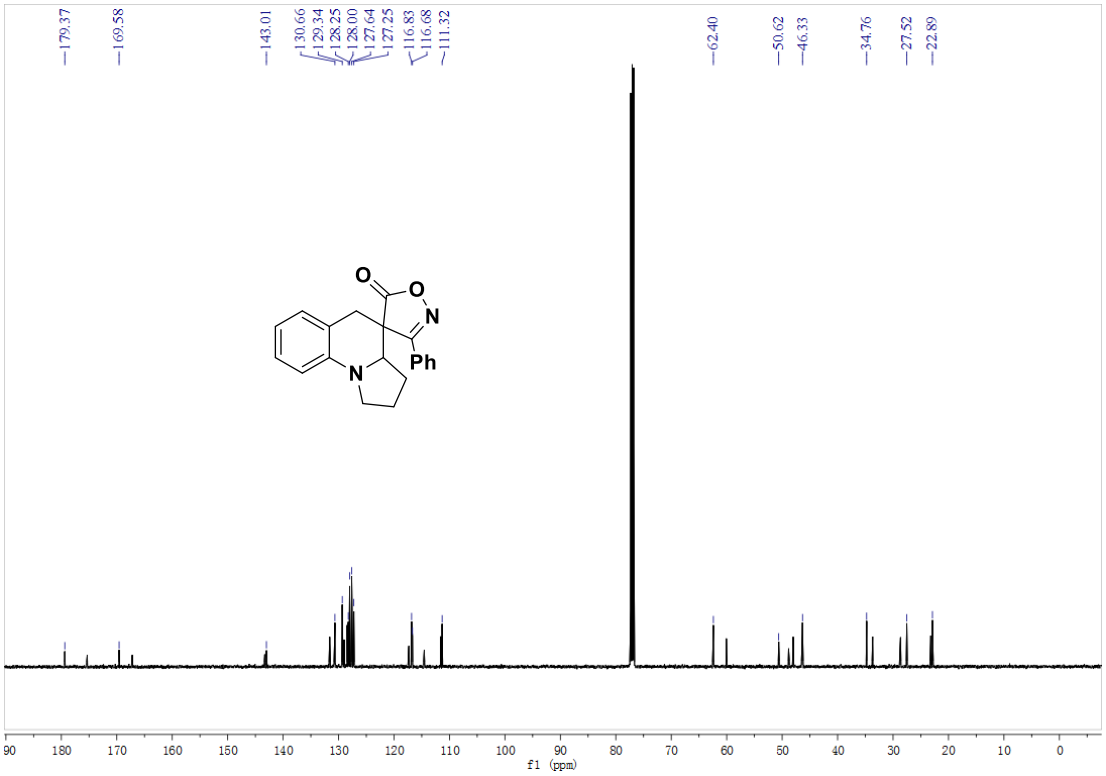
1,3-dimethyl-1',2',3',3a'-tetrahydro-2H,5'H-spiro[pyrimidine-5,4'-pyrrolo[1,2-a]quinoline]-2,4,6(1H,3H)-trione **5h**



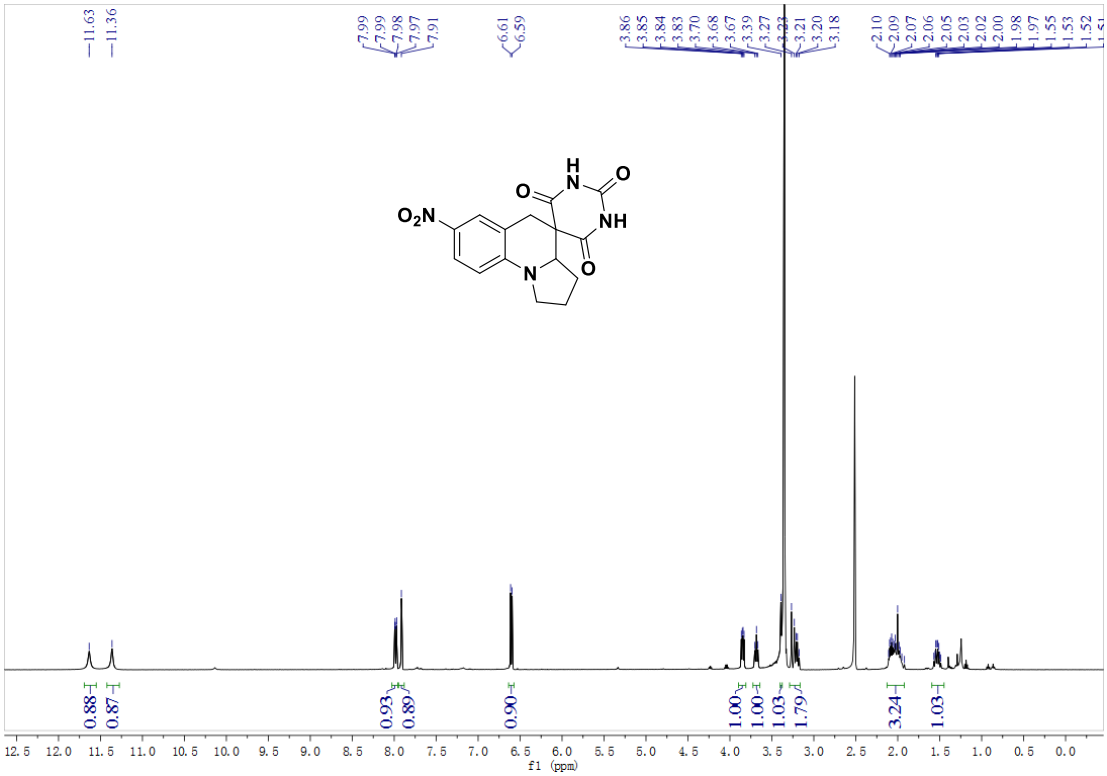


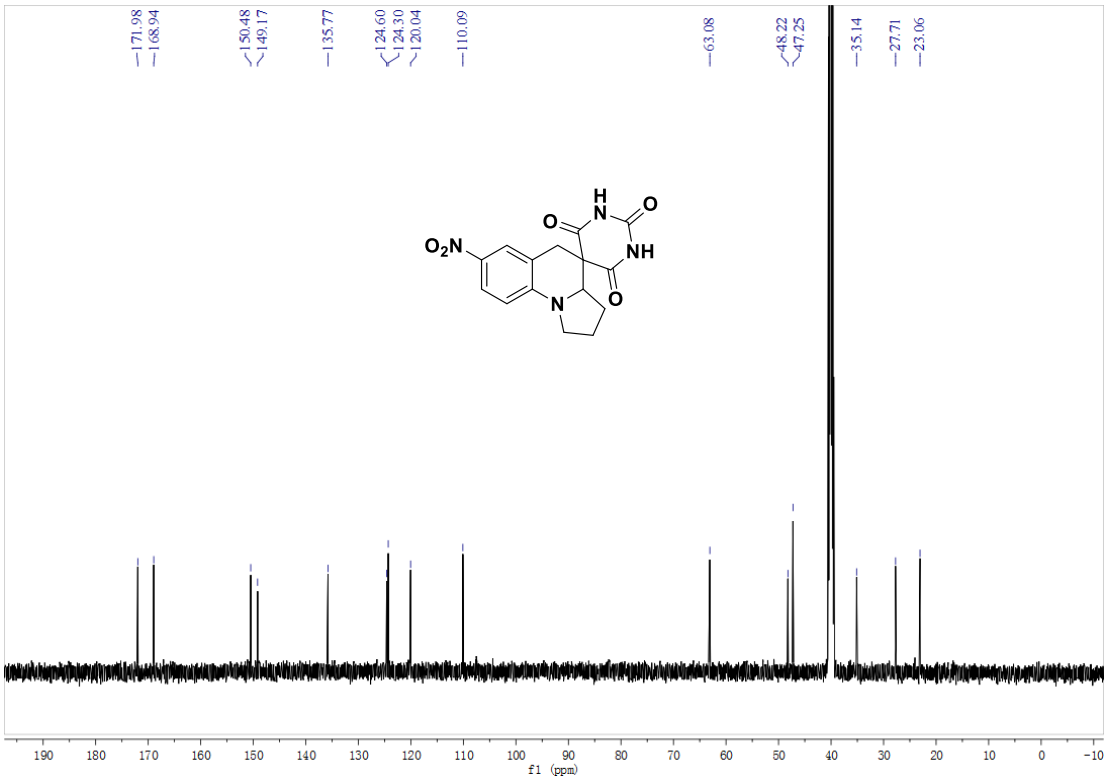
3-phenyl-1',2',3',3a'-tetrahydro-5H,5'H-spiro[isoxazole-4,4'-pyrrolo[1,2-a]quinolin]-5-one **5i**



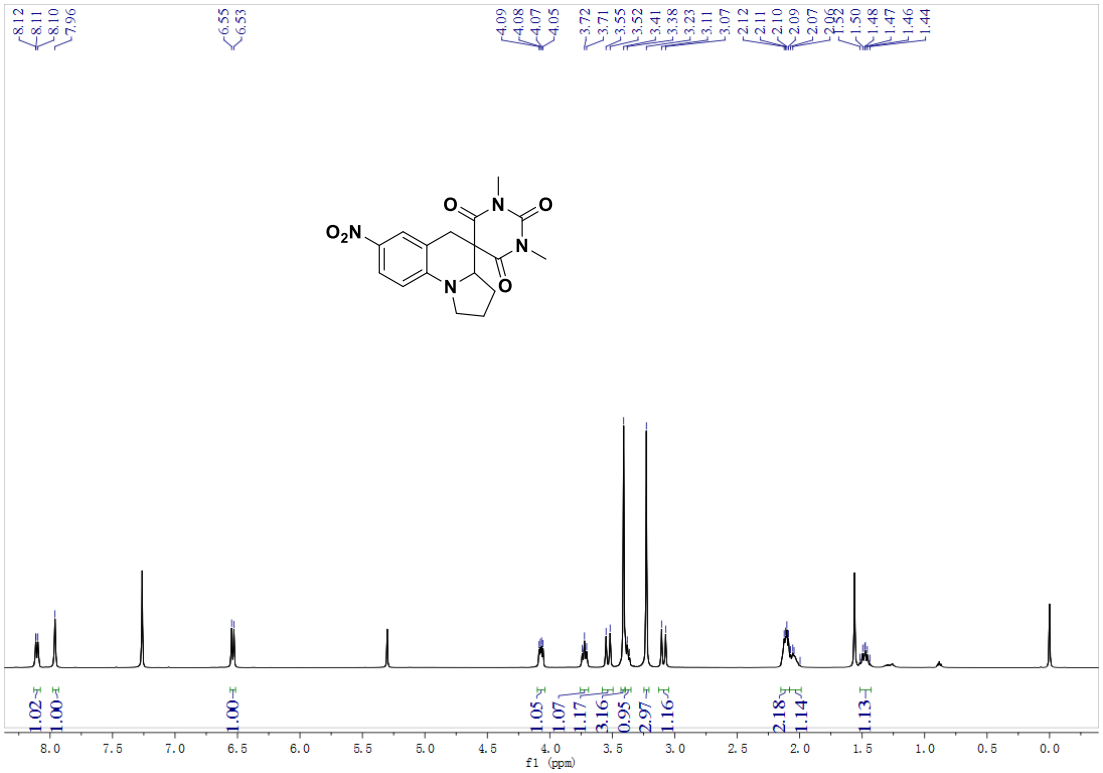


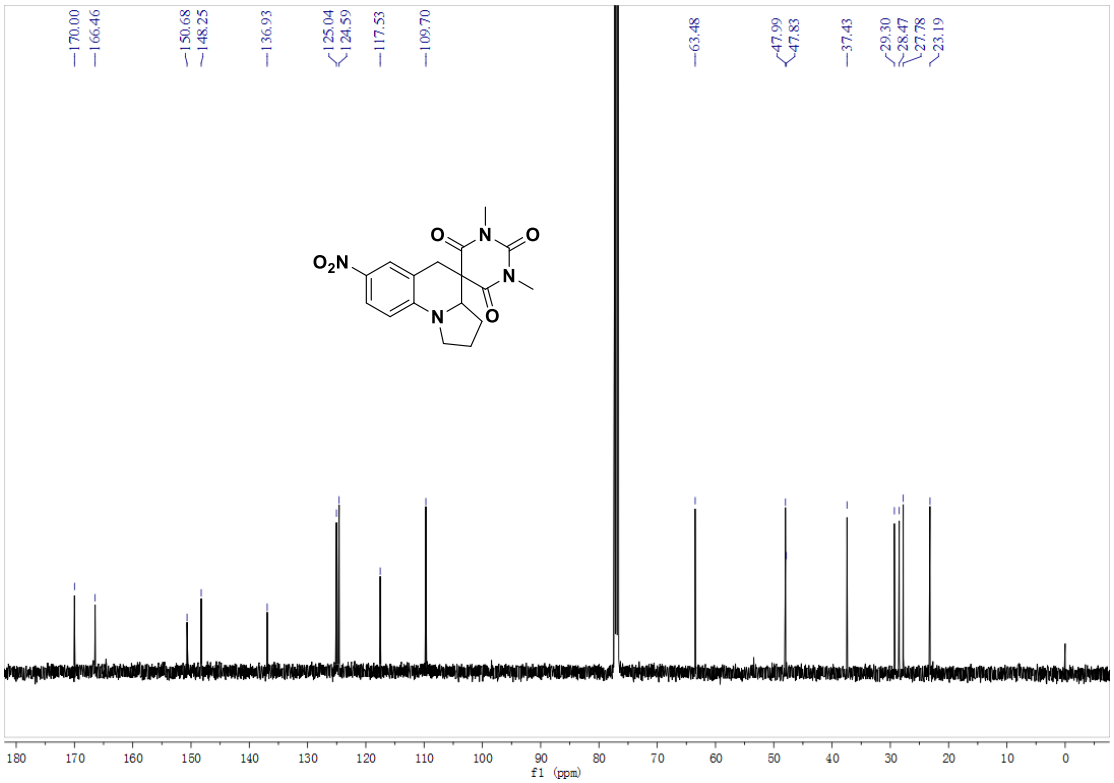
7'-nitro-1',2',3',3a'-tetrahydro-2H,5'H-spiro[pyrimidine-5,4'-pyrrolo[1,2-a]quinoline]-2,4,6(1H,3H)-trione **9b**



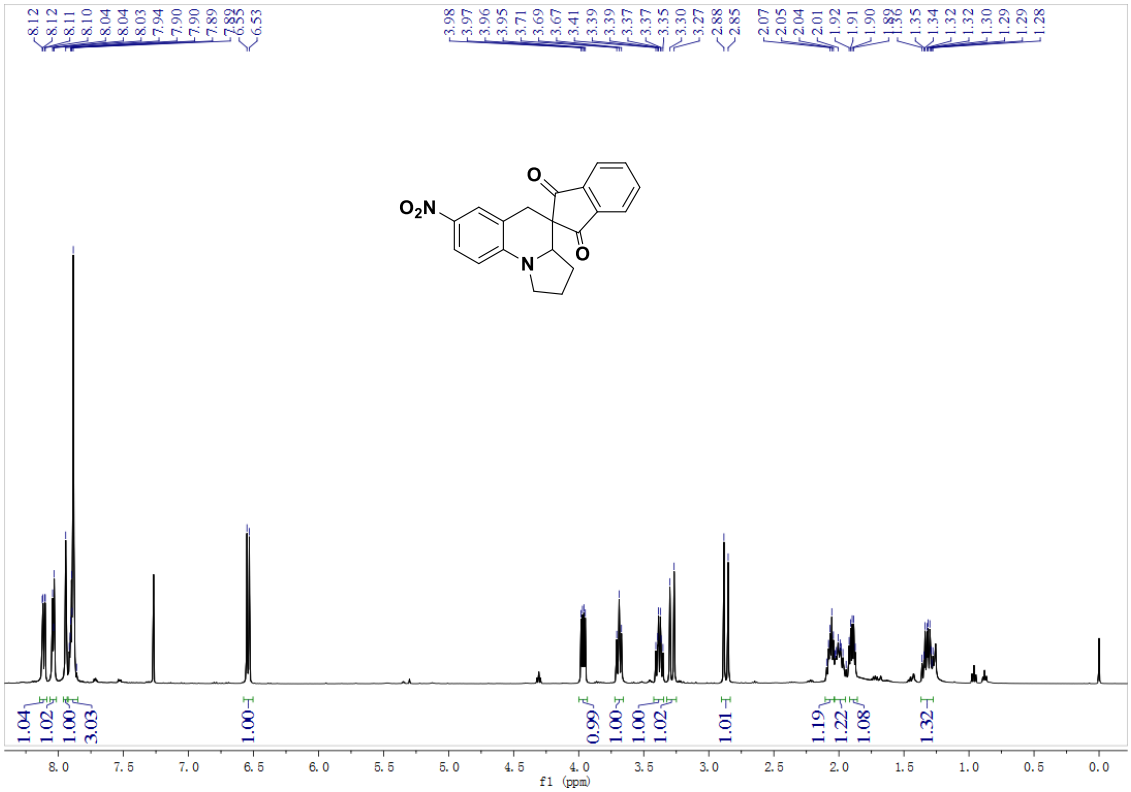


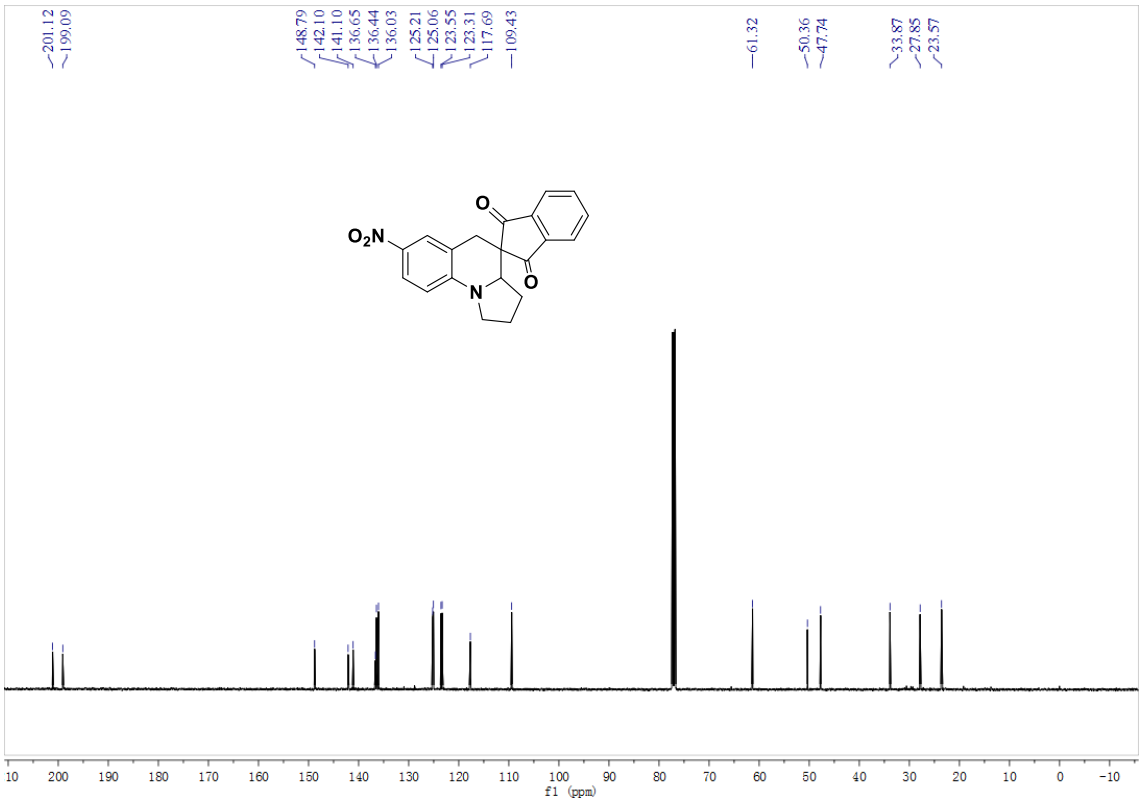
1,3-dimethyl-7'-nitro-1',2',3',3a'-tetrahydro-2H,5'H-spiro[pyrimidine-5,4'-pyrrolo[1,2-a]quinoline]-2,4,6(1H,3H)-trione **9c**



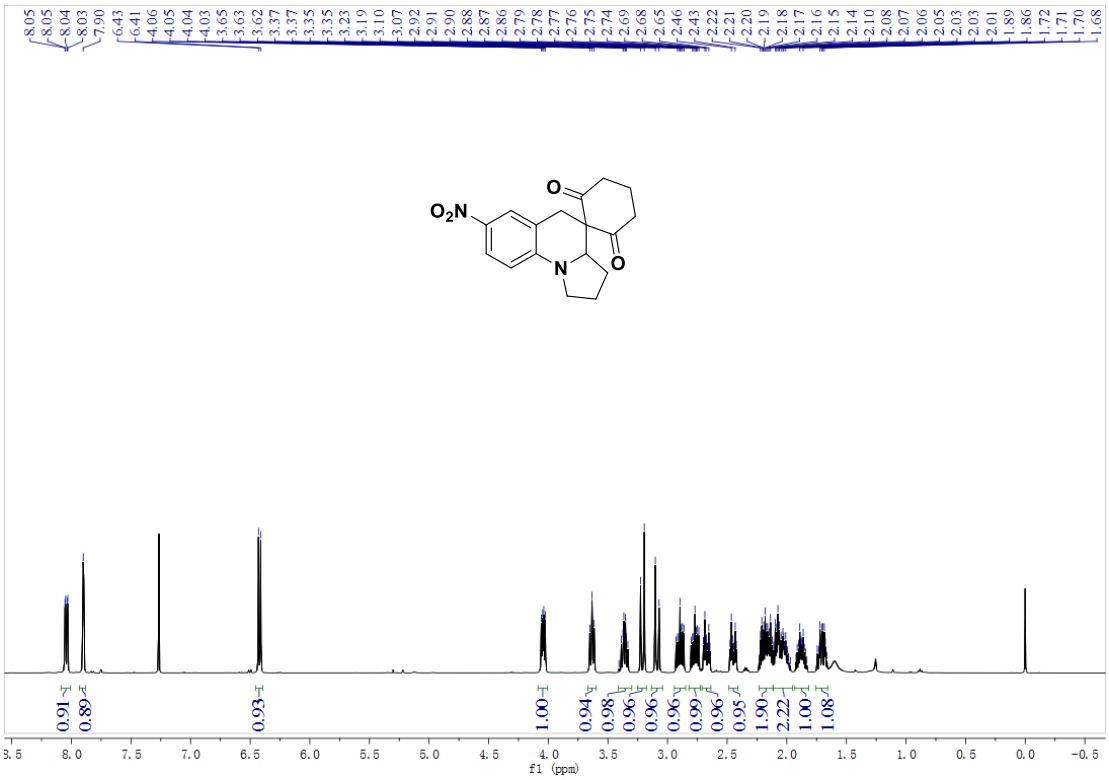


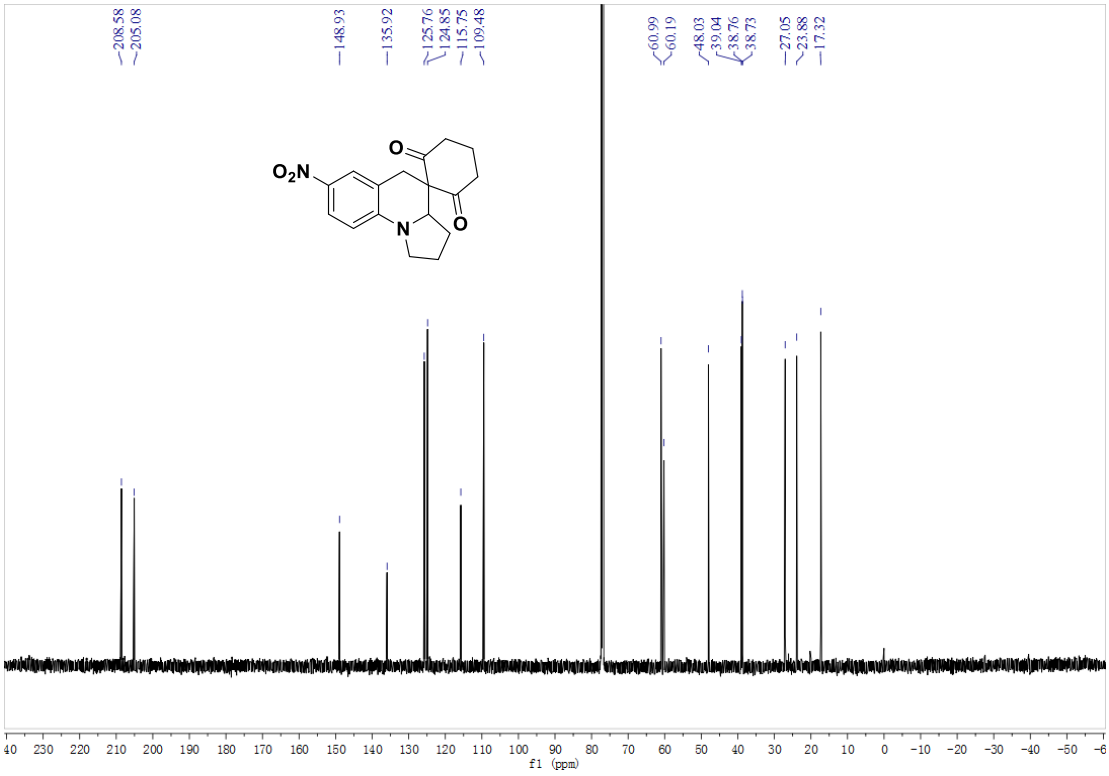
7'-nitro-1',2',3',3a'-tetrahydro-5'H-spiro[indene-2,4'-pyrrolo[1,2-a]quinoline]-1,3-dione **9d**



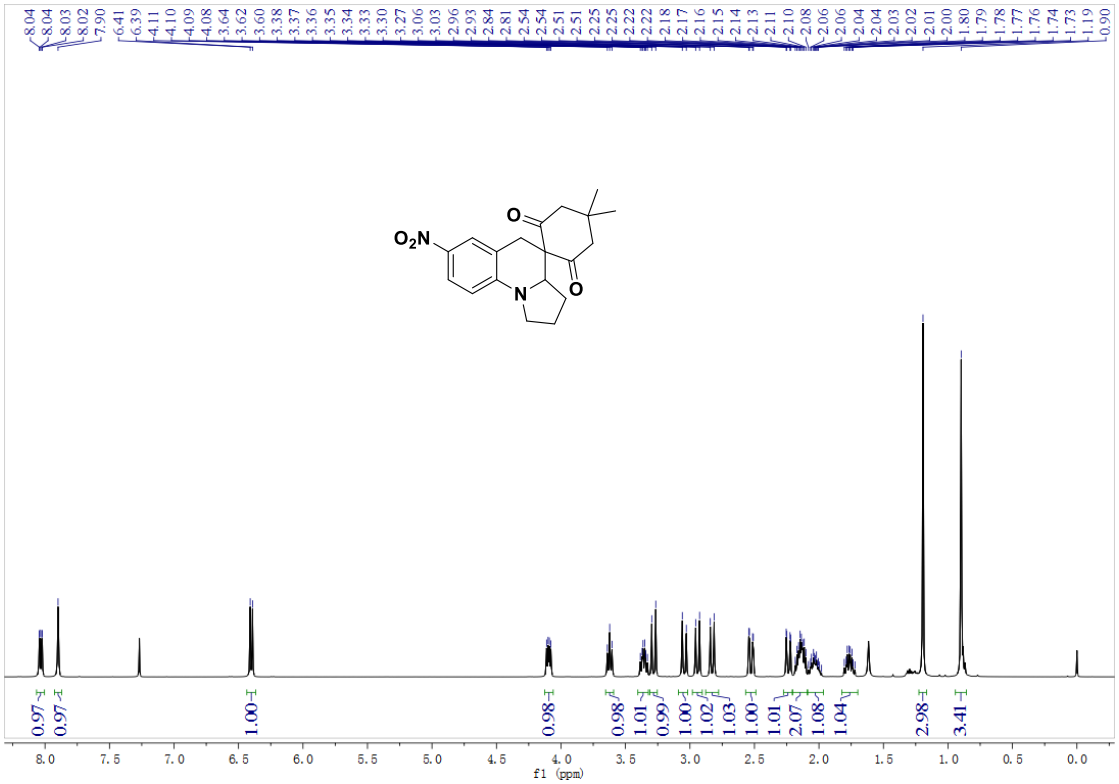


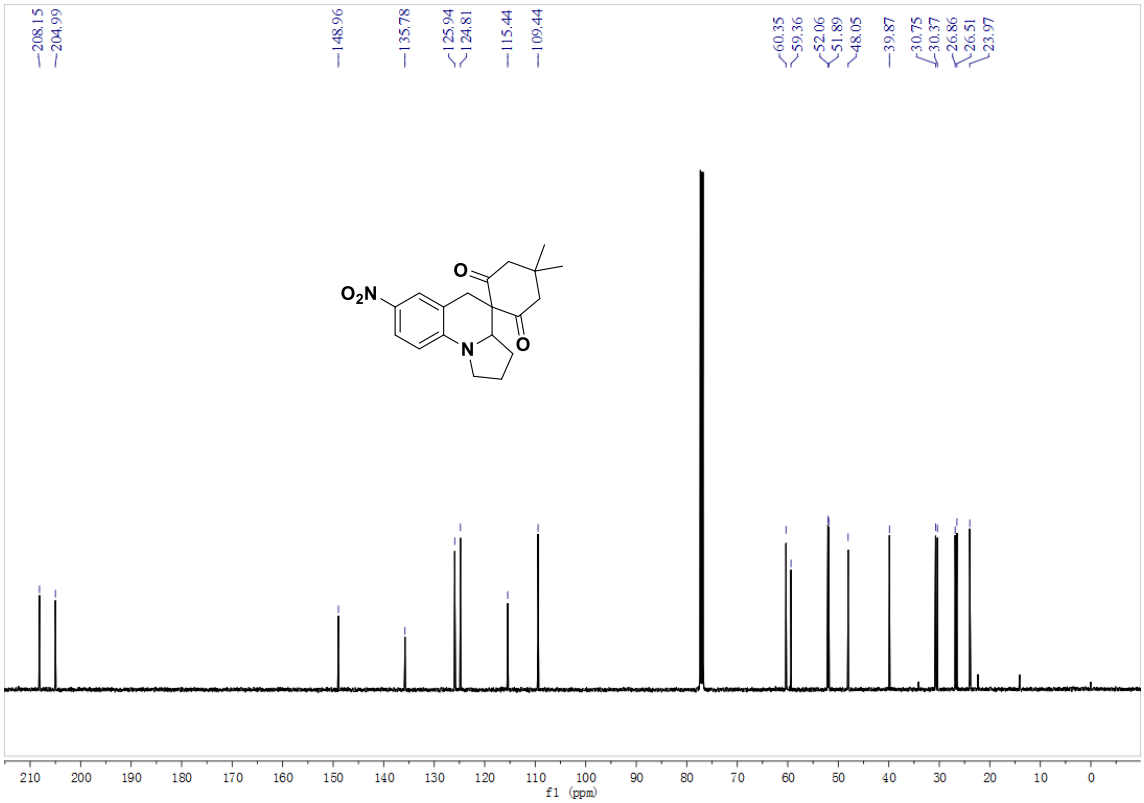
7'-nitro-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,6-dione **9e**





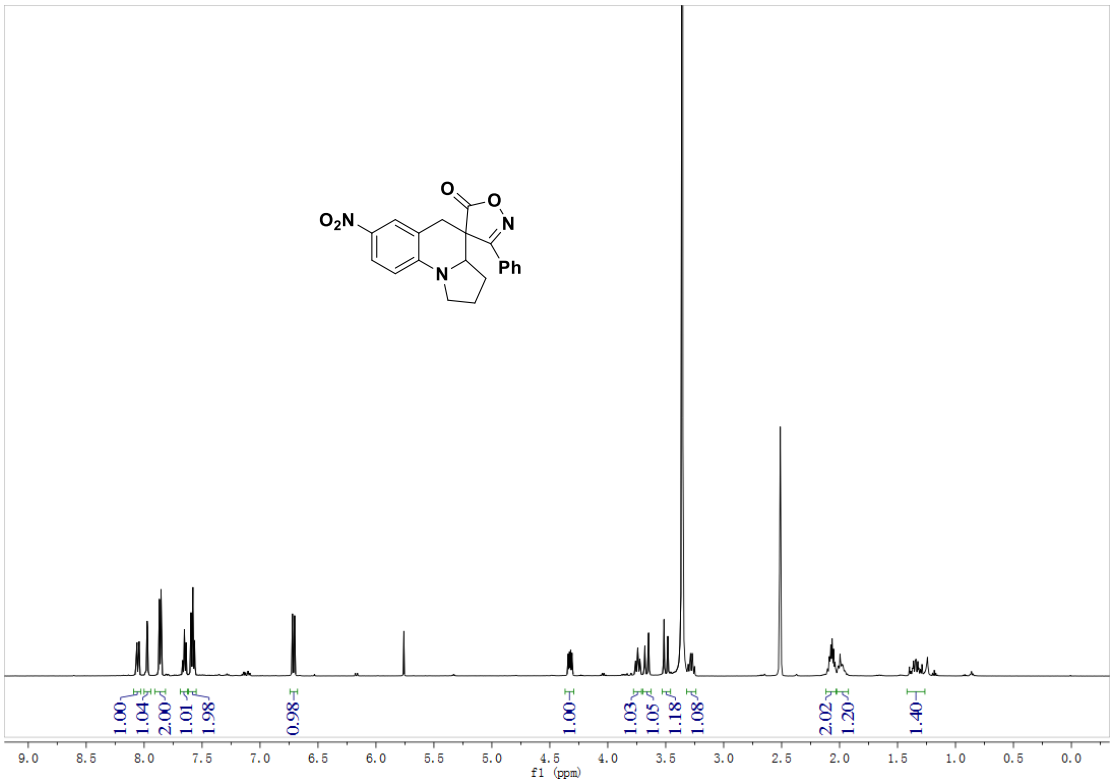
4,4-dimethyl-7'-nitro-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,6-dione **9f**

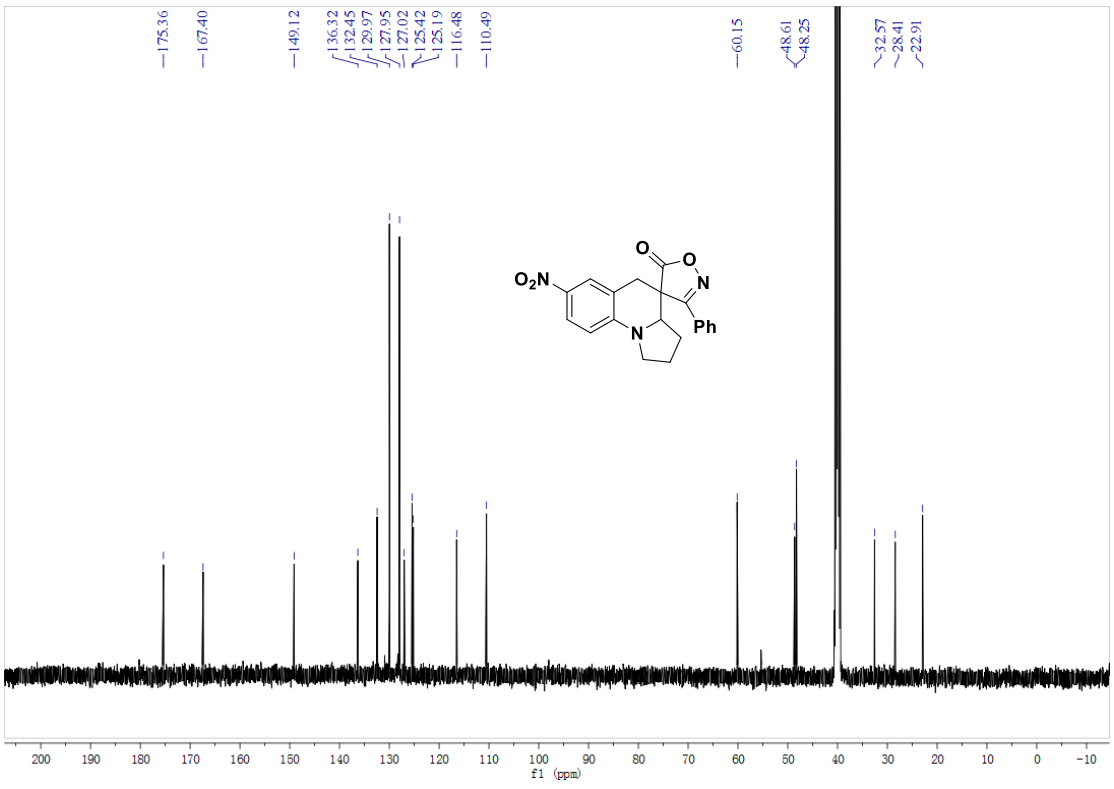




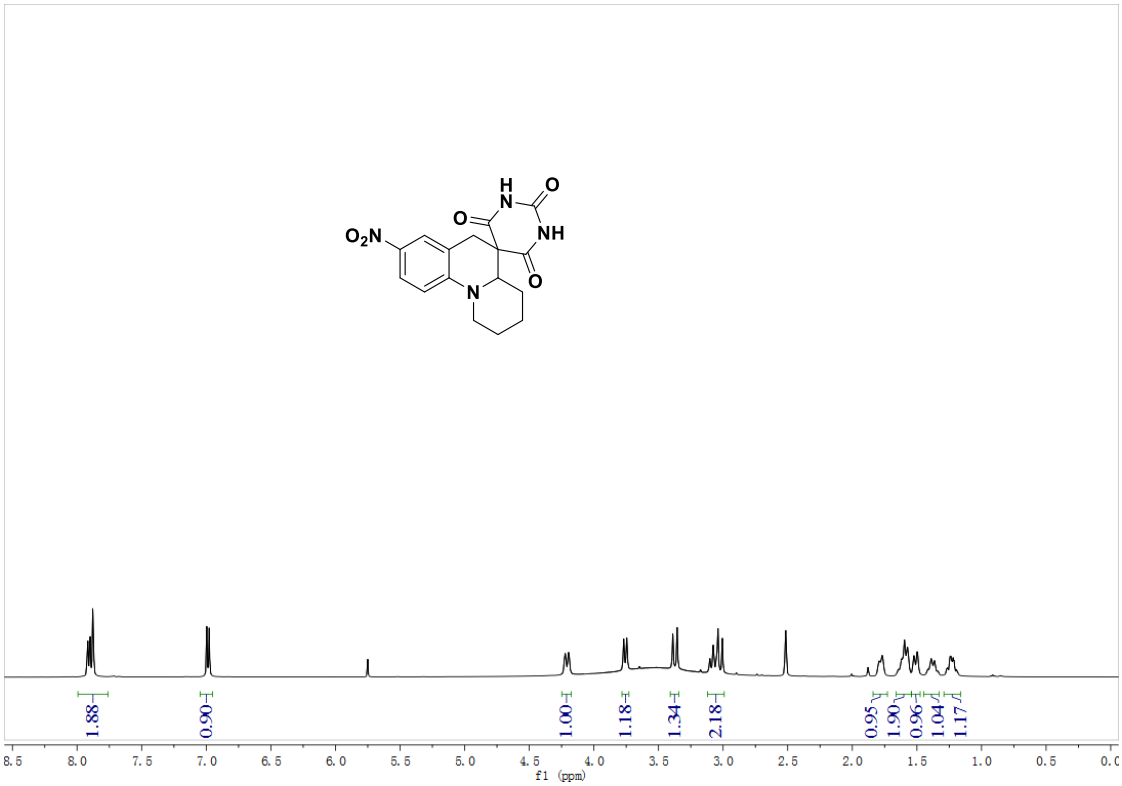
7'-nitro-3-phenyl-1',2',3',3a'-tetrahydro-5H,5'H-spiro[isoxazole-4,4'-pyrrolo[1,2-a]quinolin]-5-one

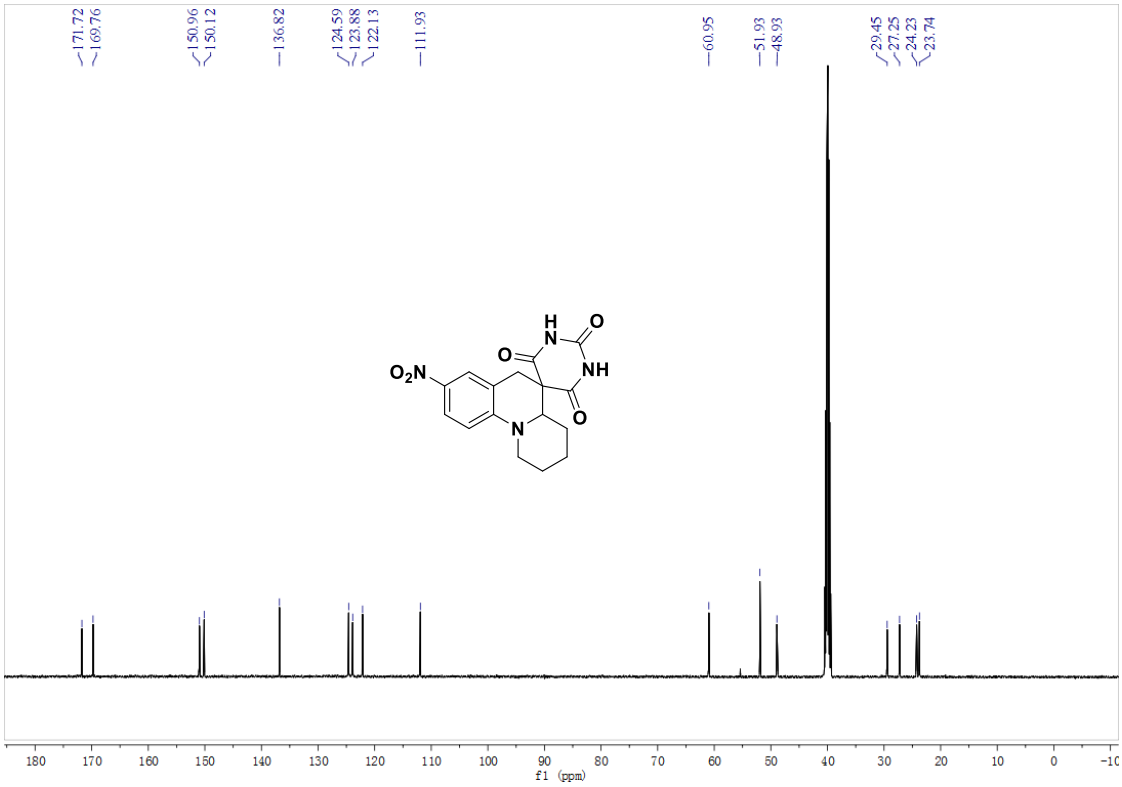
9g



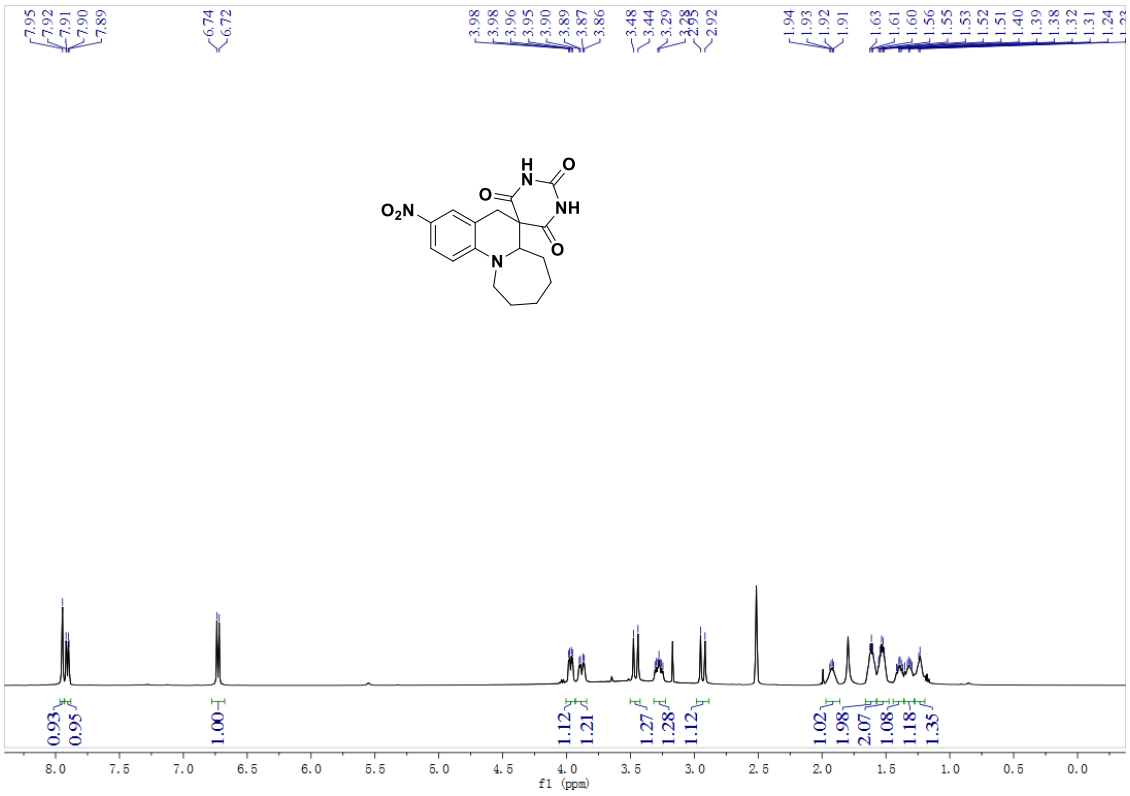


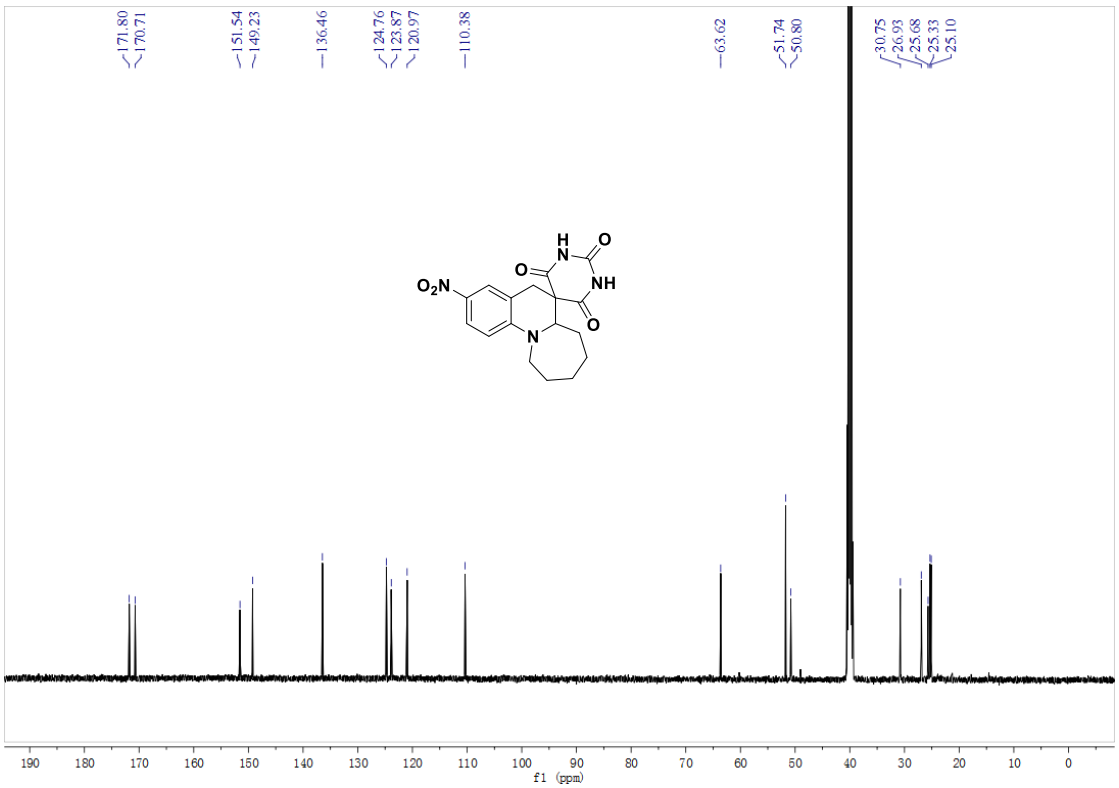
8-nitro-2,3,4,4a-tetrahydro-1H,2'H,6H-spiro[pyrido[1,2-a]quinoline-5,5'-pyrimidine]-2',4',6'(1'H,3'H)-trione **9h**


1.88
0.90
1.00
1.18
1.34
2.18
0.95
1.90
0.96
1.04
1.17
f1 (ppm)

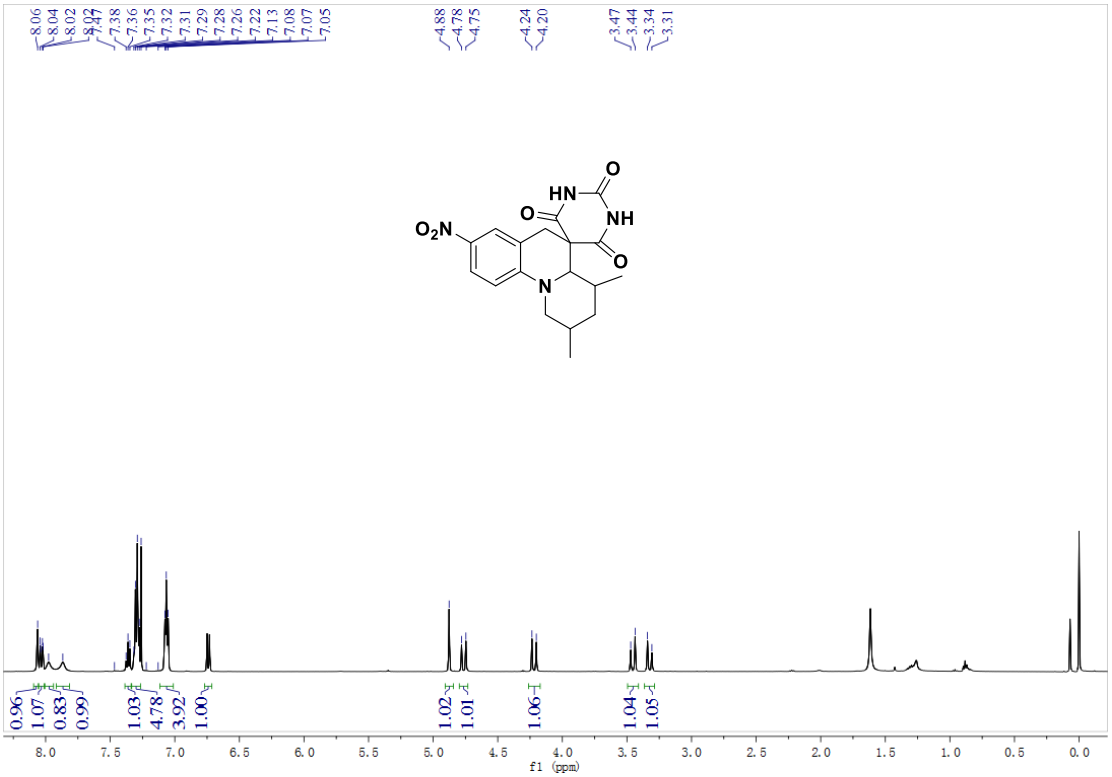

171.72
169.76
150.96
150.12
136.82
124.59
123.88
122.13
111.93
60.95
51.93
48.93
29.45
27.25
24.23
23.74
f1 (ppm)

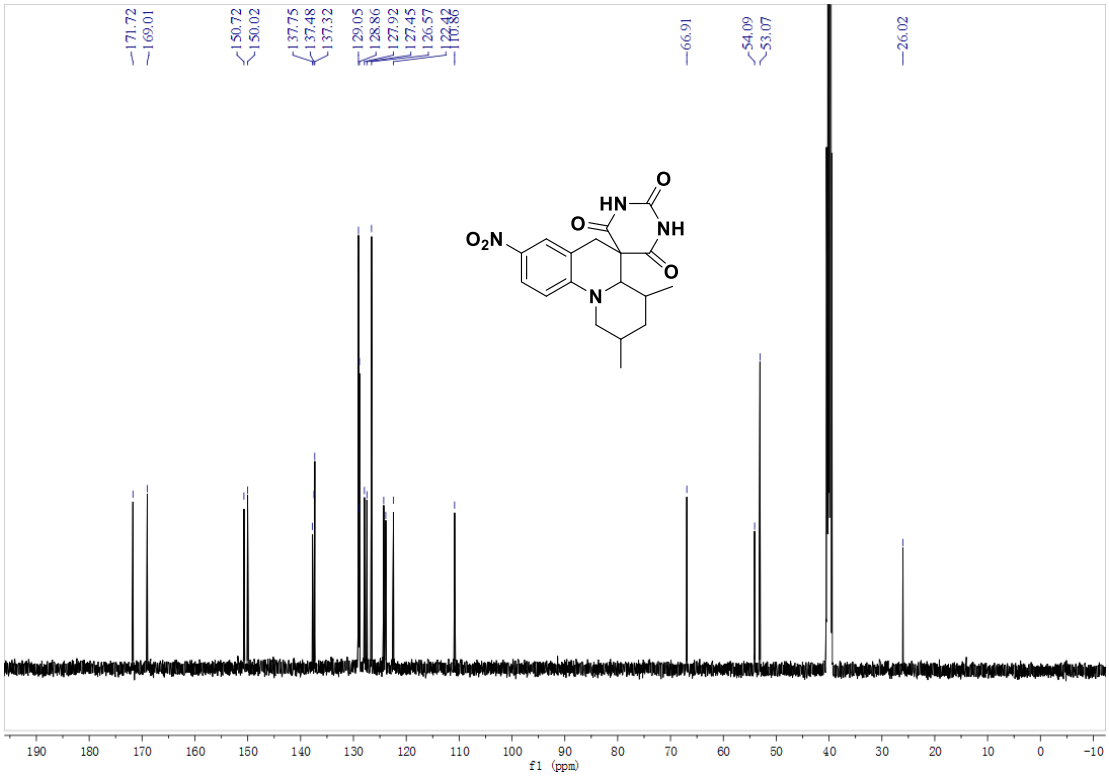
3-nitro-6a,7,8,9,10,11-hexahydro-2'H,5H-spiro[azepino[1,2-a]quinoline-6,5'-pyrimidine]-2',4',6'(1'H,3'H)-trione **9i**





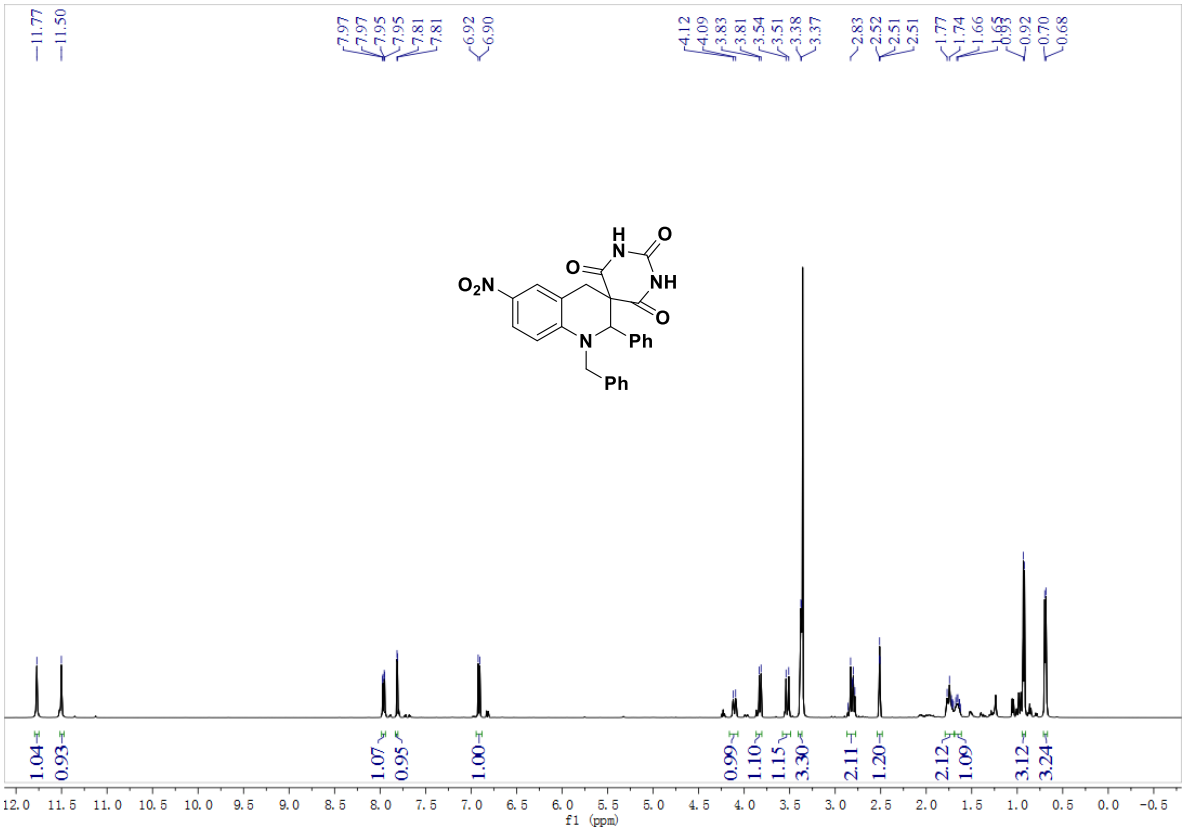
2,4-dimethyl-8-nitro-2,3,4,4a-tetrahydro-1H,2'H,6H-spiro[pyrido[1,2-a]quinoline-5,5'-pyrimidine]-2',4',6'(1'H,3'H)-trione **9j**

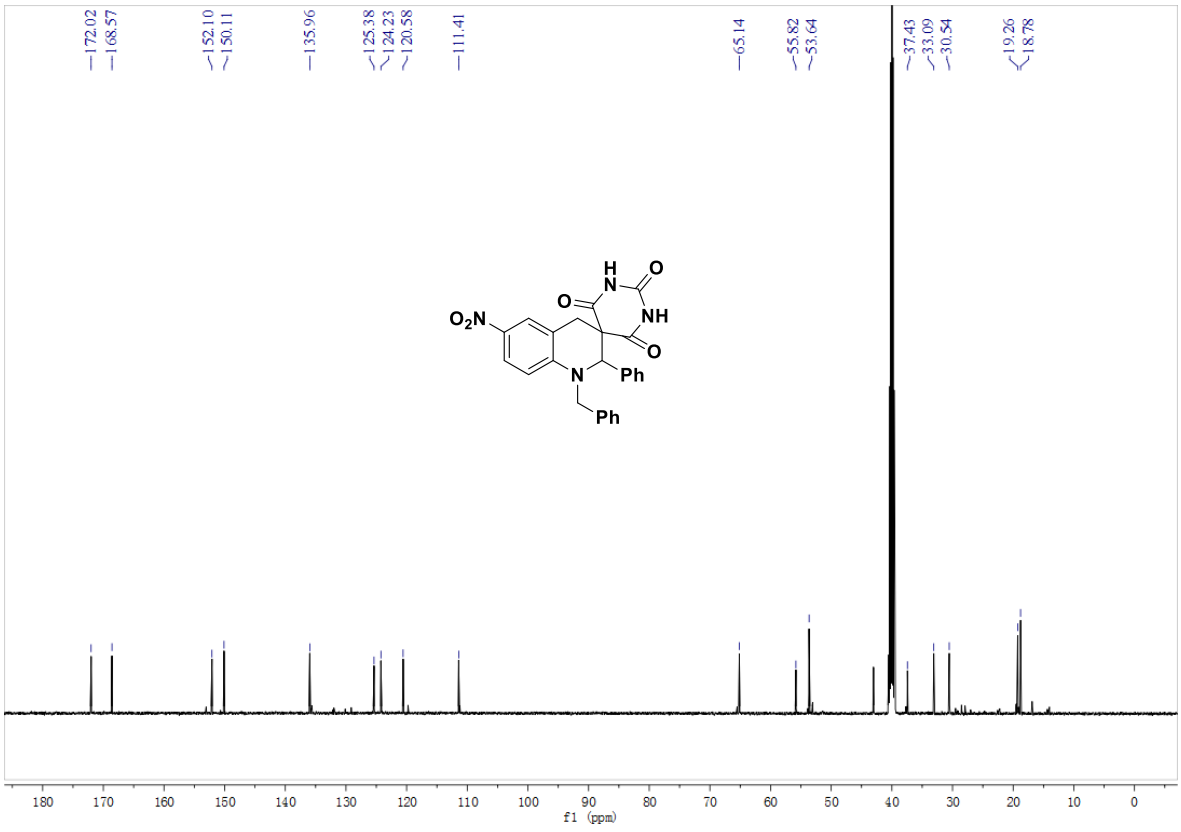




1',2'-dibenzyl-6'-nitro-1',4'-dihydro-2H,2'H-spiro[pyrimidine-5,3'-quinoline]-2,4,6(1H,3H)-trione

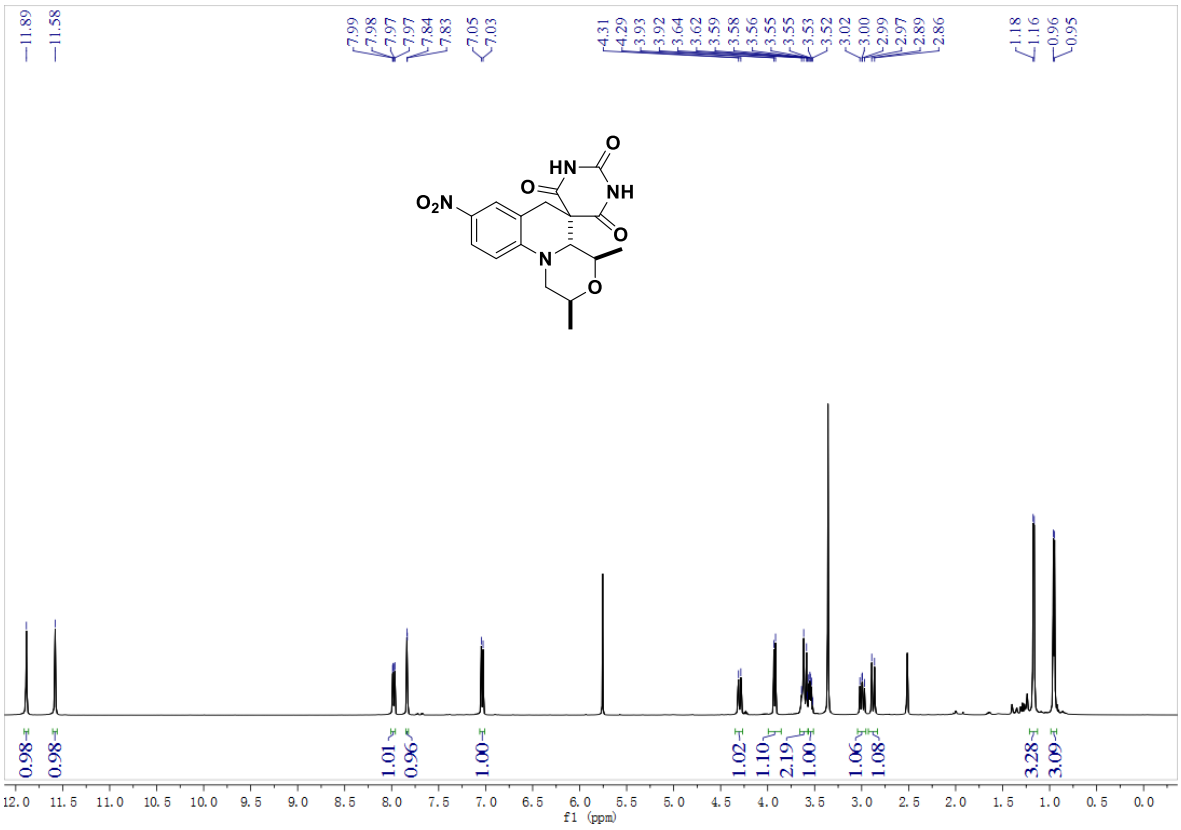
9k

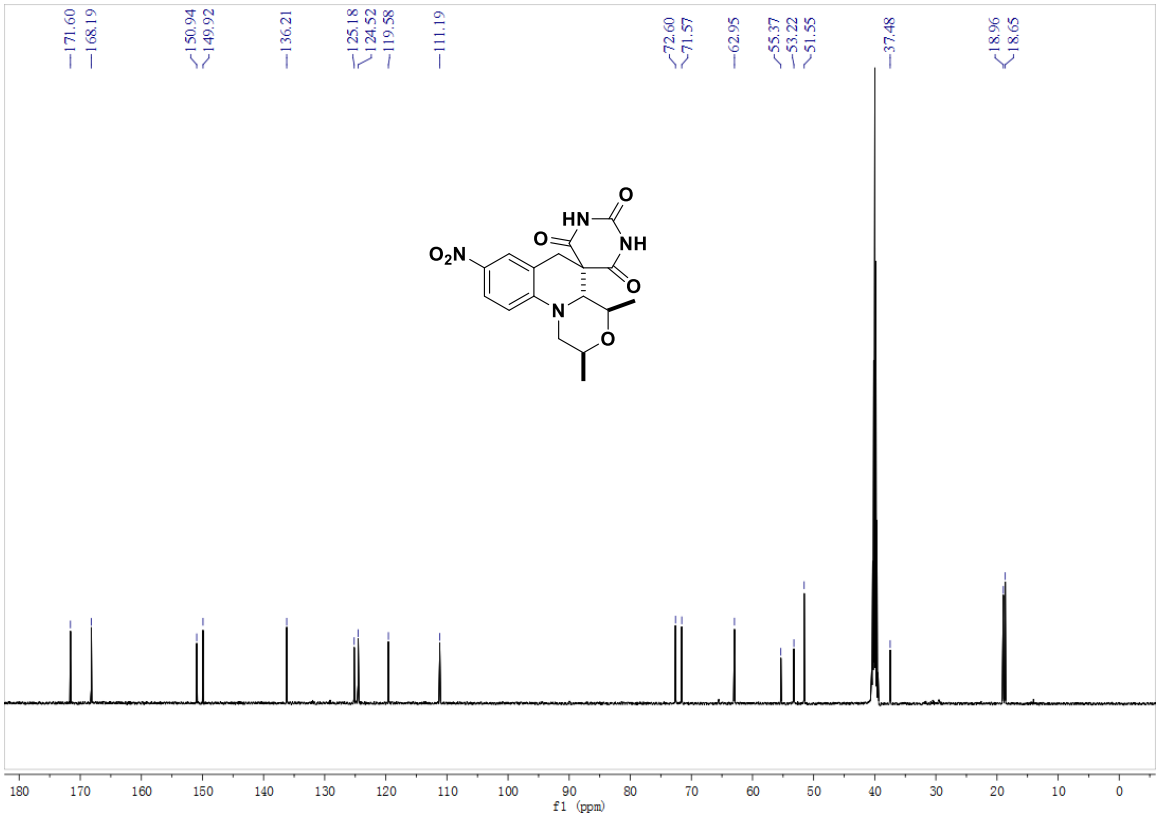




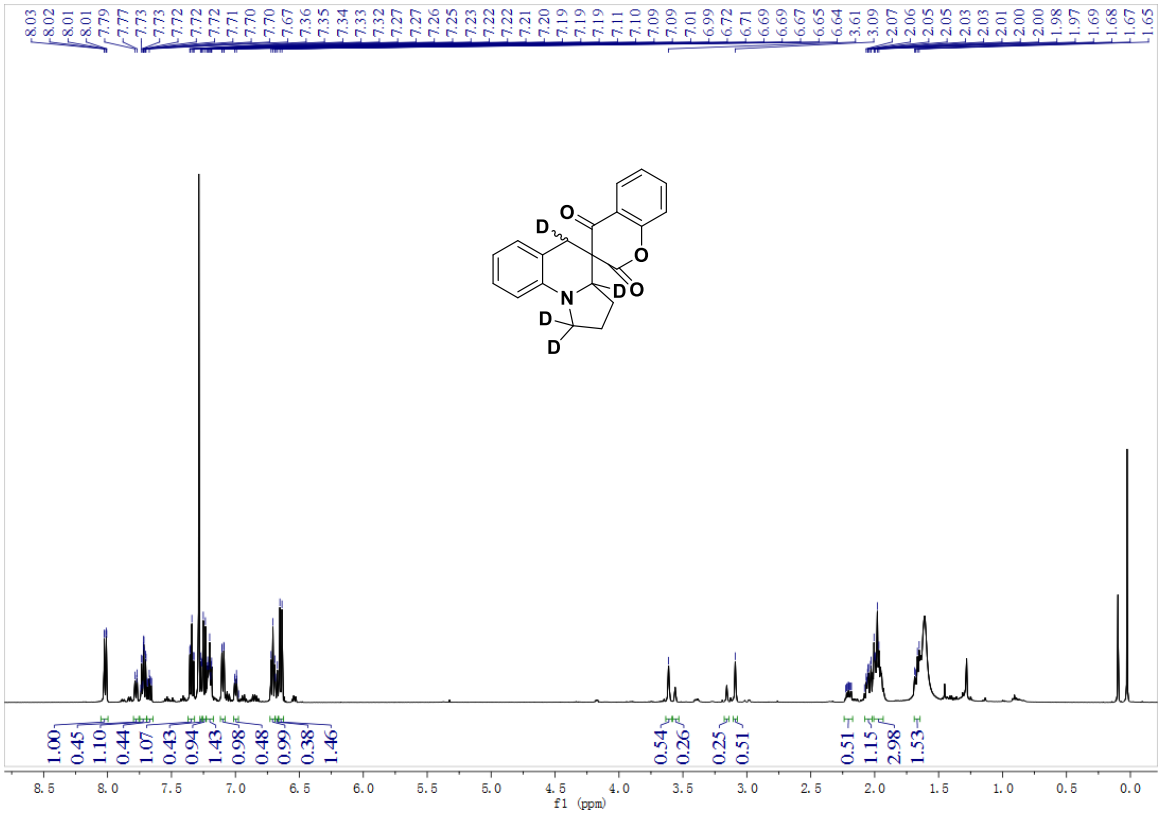
2',4'-dimethyl-8'-nitro-1',2',4',4a'-tetrahydro-2H,6'H-spiro[pyrimidine-5,5'-[1,4]oxazino[4,3-a]quin

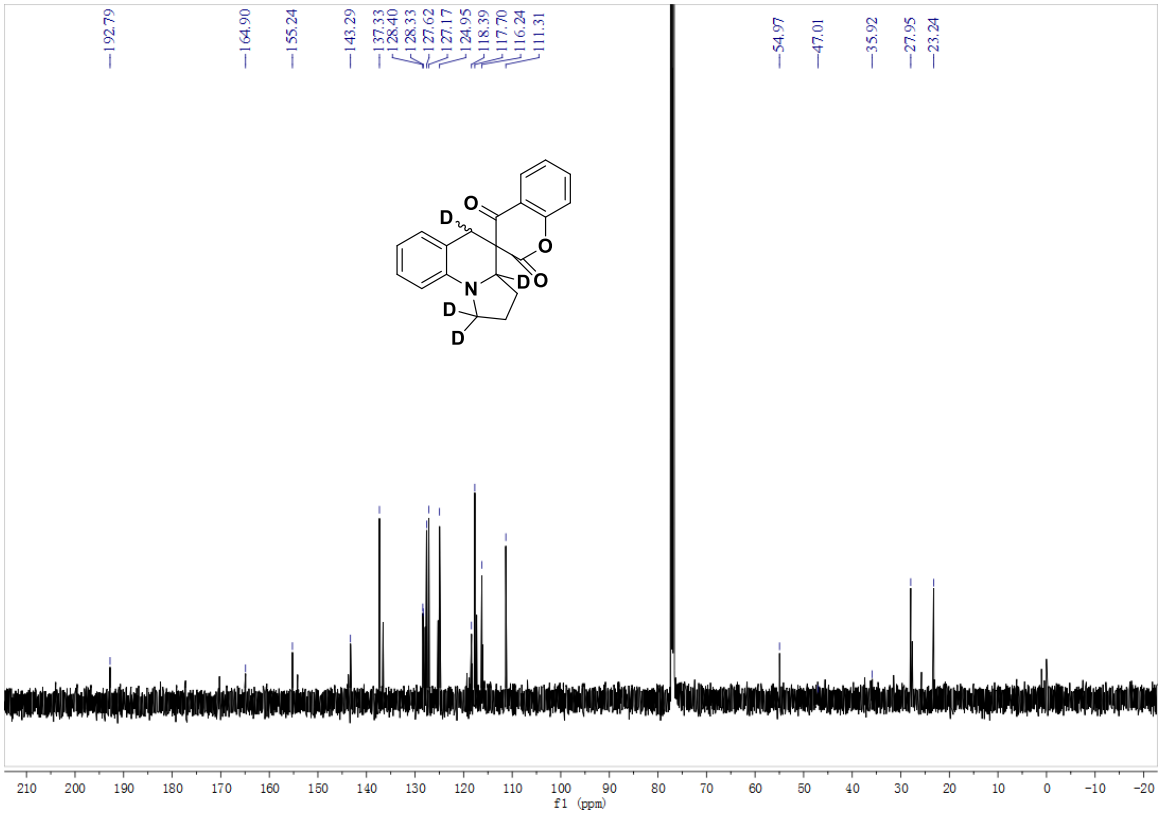
oline]-2,4,6(1H,3H)-trione **11**





1',2',3',3a'-tetrahydro-5'H-spiro[chromane-3,4'-pyrrolo[1,2-a]quinoline]-2,4-dione-1',1',3a',5'-d4 **13**


8.03 8.02 8.01 8.01 7.79 7.77 7.73 7.73 7.72 7.72 7.72 7.71 7.70 7.70 7.67 7.36 7.35 7.34 7.33 7.32 7.27 7.27 7.26 7.25 7.23 7.22 7.22 7.21 7.20 7.19 7.19 7.19 7.11 7.10 7.09 7.09 7.01 6.99 6.72 6.71 6.69 6.69 6.67 6.65 6.64 3.61 3.09 2.07 2.06 2.05 2.05 2.03 2.03 2.01 2.00 2.00 1.98 1.97 1.69 1.68 1.67 1.65
O
D
O
N
D O
D
D
1.00 0.45 1.10 0.44 1.07 0.43 0.94 1.43 0.98 0.48 0.99 0.38 1.46 0.54 0.26 0.25 0.51 0.51 1.15 2.98 1.53
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


192.79 164.90 155.24 143.29 137.33 128.40 128.33 127.62 127.17 124.95 118.39 117.70 116.24 111.31 54.97 47.01 35.92 27.95 23.24
O
D
O
N
D O
D
D
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

Crystallographic data of compound 3f (CCDC No. 1545490)

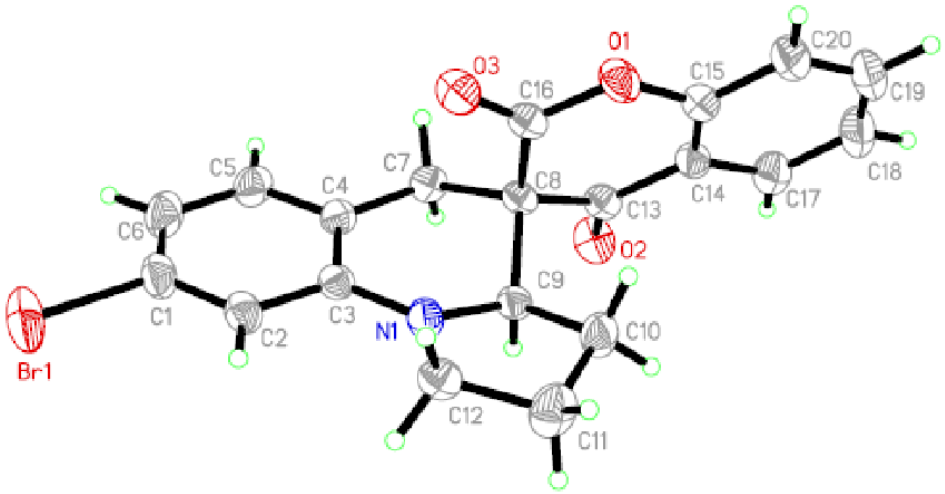


Table 1. Crystal data and structure refinement for 3f.

Identification code	3f
Empirical formula	C20 H16 Br N O3
Formula weight	398.25
Temperature	293(2) K
Wavelength	1.54184 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 8.2200(12) A alpha = 71.212(7) deg. b = 8.7275(7) A beta = 72.443(10) deg. c = 13.0899(9) A gamma = 79.120(10) deg.
Volume	843.24(15) A^3
Z, Calculated density	2, 1.568 Mg/m^3
Absorption coefficient	3.485 mm^-1
F(000)	404
Crystal size	0.12 x 0.11 x 0.11 mm
Theta range for data collection	3.69 to 67.25 deg.

Limiting indices	-9<=h<=9, -10<=k<=8, -15<=l<=13
Reflections collected / unique	4724 / 2991 [R(int) = 0.0233]
Completeness to theta = 67.25	98.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7004 and 0.6798
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2991 / 0 / 226
Goodness-of-fit on F^2	1.069
Final R indices [I>2sigma(I)]	R1 = 0.0520, wR2 = 0.1421
R indices (all data)	R1 = 0.0576, wR2 = 0.1484
Largest diff. peak and hole	0.529 and -0.484 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 3f.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Br(1)	2148(1)	-53(1)	13885(1)	89(1)
N(1)	5308(3)	2779(3)	9746(2)	47(1)
O(1)	9953(3)	1376(3)	7857(2)	59(1)
O(2)	9484(3)	5754(3)	8459(2)	61(1)
O(3)	8440(3)	294(3)	9533(2)	58(1)
C(1)	4069(5)	928(4)	12762(3)	58(1)
C(2)	3969(4)	1450(4)	11671(3)	50(1)
C(3)	5358(4)	2182(3)	10844(2)	42(1)
C(4)	6821(4)	2323(3)	11140(2)	43(1)
C(5)	6832(5)	1756(4)	12260(3)	57(1)
C(6)	5450(6)	1084(5)	13084(3)	66(1)

C(7)	8360(4)	3051(4)	10283(3)	46(1)
C(8)	8424(3)	3170(3)	9068(2)	39(1)
C(9)	6560(3)	3792(4)	8922(2)	41(1)
C(10)	6256(4)	3848(5)	7817(3)	60(1)
C(11)	4436(6)	3518(6)	8099(3)	74(1)
C(12)	4027(4)	2477(4)	9291(3)	50(1)
C(13)	9528(4)	4491(4)	8253(3)	44(1)
C(14)	10556(4)	4198(4)	7185(3)	47(1)
C(15)	10701(4)	2674(4)	7035(3)	53(1)
C(16)	8931(4)	1509(4)	8871(3)	43(1)
C(17)	11397(5)	5418(5)	6314(3)	65(1)
C(18)	12377(7)	5108(6)	5332(4)	86(1)
C(19)	12489(7)	3572(6)	5208(4)	97(2)
C(20)	11666(6)	2356(5)	6044(3)	77(1)

Table 3. Bond lengths [A] and angles [deg] for 3f.

Br(1)-C(1)	1.920(4)
N(1)-C(3)	1.374(4)
N(1)-C(9)	1.437(4)
N(1)-C(12)	1.455(4)
O(1)-C(16)	1.368(4)
O(1)-C(15)	1.378(4)
O(2)-C(13)	1.208(4)
O(3)-C(16)	1.182(4)
C(1)-C(6)	1.367(6)
C(1)-C(2)	1.376(5)
C(2)-C(3)	1.403(4)
C(3)-C(4)	1.407(4)
C(4)-C(5)	1.390(4)
C(4)-C(7)	1.501(5)
C(5)-C(6)	1.379(6)
C(7)-C(8)	1.547(4)
C(8)-C(16)	1.513(4)
C(8)-C(13)	1.520(4)
C(8)-C(9)	1.573(4)
C(9)-C(10)	1.525(4)
C(10)-C(11)	1.489(5)
C(11)-C(12)	1.503(5)
C(13)-C(14)	1.473(4)
C(14)-C(15)	1.385(5)
C(14)-C(17)	1.389(5)

C(15)-C(20)	1.385(5)
C(17)-C(18)	1.375(6)
C(18)-C(19)	1.384(7)
C(19)-C(20)	1.363(7)

C(3)-N(1)-C(9)	121.8(2)
C(3)-N(1)-C(12)	125.0(3)
C(9)-N(1)-C(12)	113.2(2)
C(16)-O(1)-C(15)	122.6(2)
C(6)-C(1)-C(2)	123.5(3)
C(6)-C(1)-Br(1)	118.8(3)
C(2)-C(1)-Br(1)	117.7(3)
C(1)-C(2)-C(3)	118.2(3)
N(1)-C(3)-C(2)	120.9(3)
N(1)-C(3)-C(4)	119.3(3)
C(2)-C(3)-C(4)	119.8(3)
C(5)-C(4)-C(3)	118.6(3)
C(5)-C(4)-C(7)	119.5(3)
C(3)-C(4)-C(7)	121.9(3)
C(6)-C(5)-C(4)	122.1(3)
C(1)-C(6)-C(5)	117.7(3)
C(4)-C(7)-C(8)	114.4(2)
C(16)-C(8)-C(13)	115.2(2)
C(16)-C(8)-C(7)	110.2(2)
C(13)-C(8)-C(7)	110.2(2)
C(16)-C(8)-C(9)	109.0(2)
C(13)-C(8)-C(9)	105.0(2)
C(7)-C(8)-C(9)	106.8(2)
N(1)-C(9)-C(10)	103.6(2)
N(1)-C(9)-C(8)	112.0(2)
C(10)-C(9)-C(8)	116.6(2)
C(11)-C(10)-C(9)	105.1(3)
C(10)-C(11)-C(12)	106.1(3)
N(1)-C(12)-C(11)	104.1(3)
O(2)-C(13)-C(14)	122.1(3)
O(2)-C(13)-C(8)	120.7(3)
C(14)-C(13)-C(8)	117.0(2)
C(15)-C(14)-C(17)	118.6(3)
C(15)-C(14)-C(13)	119.8(3)
C(17)-C(14)-C(13)	121.7(3)
O(1)-C(15)-C(14)	122.9(3)
O(1)-C(15)-C(20)	115.9(3)
C(14)-C(15)-C(20)	121.2(4)
O(3)-C(16)-O(1)	116.6(3)

O(3)-C(16)-C(8)	123.9(3)
O(1)-C(16)-C(8)	119.5(3)
C(18)-C(17)-C(14)	120.6(4)
C(17)-C(18)-C(19)	119.3(4)
C(20)-C(19)-C(18)	121.4(4)
C(19)-C(20)-C(15)	118.9(4)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for 3f.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Br(1)	103(1)	94(1)	53(1)	-20(1)	18(1)	-34(1)
N(1)	39(1)	63(2)	40(1)	-13(1)	-12(1)	-11(1)
O(1)	66(1)	51(1)	57(1)	-26(1)	-1(1)	-2(1)
O(2)	69(2)	58(1)	66(2)	-27(1)	-8(1)	-25(1)
O(3)	56(1)	48(1)	67(2)	-20(1)	-5(1)	-13(1)
C(1)	67(2)	54(2)	42(2)	-17(1)	4(2)	-7(2)
C(2)	51(2)	49(2)	47(2)	-18(1)	-4(1)	-6(1)
C(3)	44(2)	42(1)	41(2)	-17(1)	-10(1)	1(1)
C(4)	49(2)	45(1)	41(2)	-19(1)	-14(1)	2(1)
C(5)	69(2)	61(2)	45(2)	-17(1)	-23(2)	0(2)
C(6)	86(3)	70(2)	38(2)	-15(2)	-14(2)	-3(2)
C(7)	48(2)	54(2)	47(2)	-20(1)	-20(1)	-6(1)
C(8)	33(1)	45(1)	43(2)	-19(1)	-10(1)	-4(1)
C(9)	37(1)	47(1)	41(2)	-13(1)	-11(1)	-3(1)
C(10)	50(2)	90(2)	42(2)	-12(2)	-17(1)	-12(2)
C(11)	74(2)	97(3)	62(2)	-14(2)	-32(2)	-24(2)
C(12)	43(2)	57(2)	57(2)	-20(1)	-16(1)	-8(1)
C(13)	37(1)	51(2)	51(2)	-19(1)	-14(1)	-8(1)
C(14)	41(2)	56(2)	44(2)	-14(1)	-11(1)	-3(1)
C(15)	52(2)	56(2)	46(2)	-16(1)	-10(1)	4(1)
C(16)	37(1)	48(2)	51(2)	-21(1)	-12(1)	-5(1)
C(17)	69(2)	63(2)	55(2)	-10(2)	-11(2)	-10(2)
C(18)	97(3)	88(3)	47(2)	-5(2)	3(2)	-9(2)
C(19)	113(4)	96(3)	47(2)	-17(2)	9(2)	18(3)
C(20)	95(3)	70(2)	52(2)	-23(2)	-5(2)	15(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 3f.

	x	y	z	U(eq)
H(2)	3006	1321	11486	60
H(5)	7802	1831	12460	68
H(6)	5457	749	13833	79
H(7A)	9386	2401	10463	55
H(7B)	8376	4134	10332	55
H(9)	6273	4891	9013	49
H(10A)	6439	4908	7281	72
H(10B)	7022	3027	7504	72
H(11A)	4291	2952	7610	89
H(11B)	3687	4528	8021	89
H(12A)	2878	2792	9694	60
H(12B)	4120	1337	9328	60
H(17)	11296	6454	6396	78
H(18)	12959	5921	4758	103
H(19)	13139	3366	4541	116
H(20)	11752	1330	5950	93

Table 6. Torsion angles [deg] for 3f.

C(6)-C(1)-C(2)-C(3)	0.0(5)
Br(1)-C(1)-C(2)-C(3)	179.4(2)
C(9)-N(1)-C(3)-C(2)	168.3(3)
C(12)-N(1)-C(3)-C(2)	-11.6(4)
C(9)-N(1)-C(3)-C(4)	-11.2(4)
C(12)-N(1)-C(3)-C(4)	168.9(3)
C(1)-C(2)-C(3)-N(1)	-177.7(3)
C(1)-C(2)-C(3)-C(4)	1.8(4)
N(1)-C(3)-C(4)-C(5)	178.1(3)
C(2)-C(3)-C(4)-C(5)	-1.3(4)
N(1)-C(3)-C(4)-C(7)	-2.3(4)
C(2)-C(3)-C(4)-C(7)	178.2(3)
C(3)-C(4)-C(5)-C(6)	-0.9(5)
C(7)-C(4)-C(5)-C(6)	179.6(3)
C(2)-C(1)-C(6)-C(5)	-2.1(5)

Br(1)-C(1)-C(6)-C(5)	178.4(3)
C(4)-C(5)-C(6)-C(1)	2.6(5)
C(5)-C(4)-C(7)-C(8)	163.0(3)
C(3)-C(4)-C(7)-C(8)	-16.5(4)
C(4)-C(7)-C(8)-C(16)	-75.2(3)
C(4)-C(7)-C(8)-C(13)	156.5(2)
C(4)-C(7)-C(8)-C(9)	43.0(3)
C(3)-N(1)-C(9)-C(10)	168.0(3)
C(12)-N(1)-C(9)-C(10)	-12.2(3)
C(3)-N(1)-C(9)-C(8)	41.6(4)
C(12)-N(1)-C(9)-C(8)	-138.6(2)
C(16)-C(8)-C(9)-N(1)	63.9(3)
C(13)-C(8)-C(9)-N(1)	-172.1(2)
C(7)-C(8)-C(9)-N(1)	-55.1(3)
C(16)-C(8)-C(9)-C(10)	-55.1(3)
C(13)-C(8)-C(9)-C(10)	68.8(3)
C(7)-C(8)-C(9)-C(10)	-174.1(3)
N(1)-C(9)-C(10)-C(11)	24.8(4)
C(8)-C(9)-C(10)-C(11)	148.2(3)
C(9)-C(10)-C(11)-C(12)	-28.7(4)
C(3)-N(1)-C(12)-C(11)	174.6(3)
C(9)-N(1)-C(12)-C(11)	-5.3(4)
C(10)-C(11)-C(12)-N(1)	21.1(4)
C(16)-C(8)-C(13)-O(2)	-164.4(3)
C(7)-C(8)-C(13)-O(2)	-38.9(4)
C(9)-C(8)-C(13)-O(2)	75.7(3)
C(16)-C(8)-C(13)-C(14)	19.3(3)
C(7)-C(8)-C(13)-C(14)	144.8(2)
C(9)-C(8)-C(13)-C(14)	-100.6(3)
O(2)-C(13)-C(14)-C(15)	173.5(3)
C(8)-C(13)-C(14)-C(15)	-10.3(4)
O(2)-C(13)-C(14)-C(17)	-6.4(5)
C(8)-C(13)-C(14)-C(17)	169.8(3)
C(16)-O(1)-C(15)-C(14)	3.5(5)
C(16)-O(1)-C(15)-C(20)	-178.5(3)
C(17)-C(14)-C(15)-O(1)	178.3(3)
C(13)-C(14)-C(15)-O(1)	-1.6(5)
C(17)-C(14)-C(15)-C(20)	0.3(5)
C(13)-C(14)-C(15)-C(20)	-179.6(3)
C(15)-O(1)-C(16)-O(3)	-175.8(3)
C(15)-O(1)-C(16)-C(8)	7.1(4)
C(13)-C(8)-C(16)-O(3)	164.9(3)
C(7)-C(8)-C(16)-O(3)	39.5(4)
C(9)-C(8)-C(16)-O(3)	-77.4(4)

C(13)-C(8)-C(16)-O(1)	-18.2(4)
C(7)-C(8)-C(16)-O(1)	-143.6(3)
C(9)-C(8)-C(16)-O(1)	99.5(3)
C(15)-C(14)-C(17)-C(18)	-1.2(6)
C(13)-C(14)-C(17)-C(18)	178.7(4)
C(14)-C(17)-C(18)-C(19)	1.5(7)
C(17)-C(18)-C(19)-C(20)	-0.9(8)
C(18)-C(19)-C(20)-C(15)	0.0(8)
O(1)-C(15)-C(20)-C(19)	-177.8(4)
C(14)-C(15)-C(20)-C(19)	0.3(6)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for 3f [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)