

Supporting Information

Redox-Triggered Cascade Dearomative Cyclizations Enabled by Hexafluoroisopropanol

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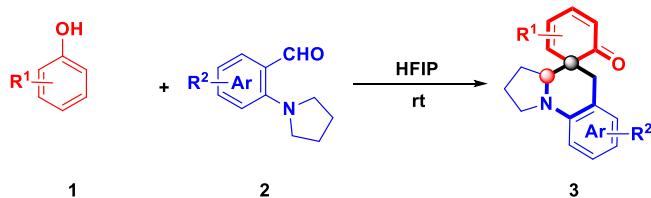
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1. General Information

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 (¹H NMR) were recorded on a Bruker 500 MHz NMR spectrometer (CDCl₃ or DMSO-d₆ solvent). The chemical shifts were reported in parts per million (ppm), downfield from SiMe₄ (δ 0.0) and relative to the signal of chloroform-d (δ 7.26, singlet) or dimethyl sulfoxide-d₆ (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 (¹³C 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, phenols, and naphthols were purchased from adamas-beta. All *o*-aminobenzaldehydes were prepared according to literature.¹

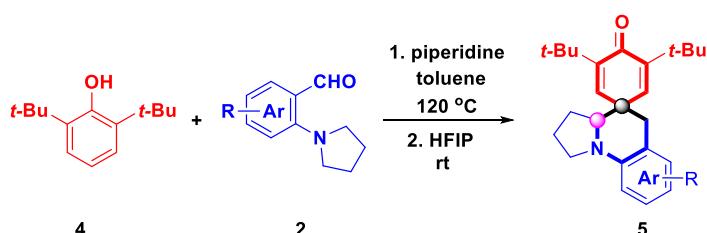
2. General Procedure

2.1 General Procedure for the Synthesis of *Ortho*-Spiro Cyclohexaketenes



A reaction tube was charged with phenol **1** (0.13 mmol), *o*-aminobenzaldehyde **2** (0.1 mmol), and HFIP (2.0 mL). The mixture was stirred at room temperature 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 *ortho*-spiro cyclohexaketene **3**.

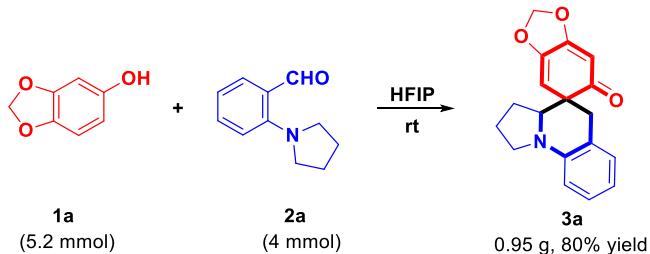
2.2 General Procedure for the Synthesis of *Para*-Spiro Cyclohexaketenes



A sealed tube was charged with 2,6-di-*tert*-butylphenol **4** (0.13 mmol), *o*-aminobenzaldehyde **2** (0.1 mmol), piperidine (0.2 mmol), and toluene (1.0 mL). The mixture was stirred at 120 °C under an air atmosphere for 12 h. Then the reaction system cooled to room temperature and HFIP (1.0 mL) was added stirring for another 10 min. The mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography on neutral alumina (eluent: ethyl

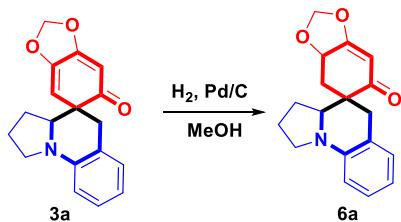
acetate/petroleum ether, 1:200) to afford the desired *para*-spiro cyclohexaketene **5**.

2.3 Gram-scale synthesis of **3a**



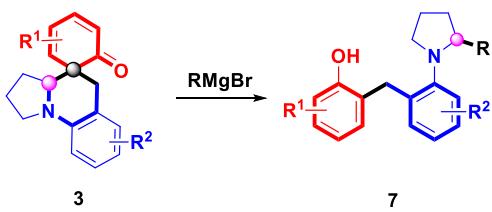
A round-bottomed flask was charged with sesamol **1a** (5.2 mmol), 2-(pyrrolidin-1-yl)benzaldehyde **2a** (4 mmol), and HFIP (80.0 mL). The mixture was stirred at room temperature under an air atmosphere. Upon completion of the reaction as indicated by TLC analysis, the mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether, 1:20) to afford the desired **3a** in 80% yield (0.95 g).

2.4 General Procedure for the Partial Hydrogenation of *Ortho*-Spiro Cyclohexaketene



To a solution of **3a** (0.1 mmol) in MeOH (1.0 mL) was added 5% by wt Pd/C (20% by wt relative to **3a**). The tube was equipped with a magnetic stir bar, and the suspension was sealed with a septum under an atmosphere of H₂ supplied via a balloon. Upon completion of the reaction as indicated by TLC analysis, the suspension was filtered through a pad of Celite. The filtrate was concentrated in vacuum. The residue was directly purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether, 1:100) to afford the partially hydrogenated product **6a** in 60% yield.

2.5 General Procedure for the Direct C-H Functionalization of Amines



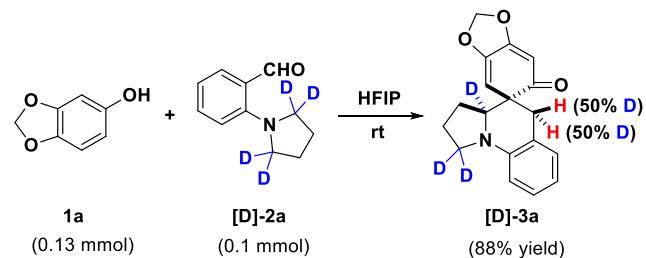
To a cold solution (0 °C) of *ortho*-spiro cyclohexaketene **3** (0.1 mmol) in anhydrous THF (1.0 mL) under an atmosphere of nitrogen was added Grignard reagents (0.4 mmol) dropwise. The mixture was stirred for 10 minutes at 0 °C, then stirred at room temperature. Upon completion, the saturated NaCl (10 mL) was added dropwise to the system at 0 °C and the resulting solution was extracted with EtOAc (10 mL×3). The combined organic extracts were dried with anhydrous

Na_2SO_4 and concentrated in vacuum. The residue was directly purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether, 1:10) to afford the desired amines **7**.

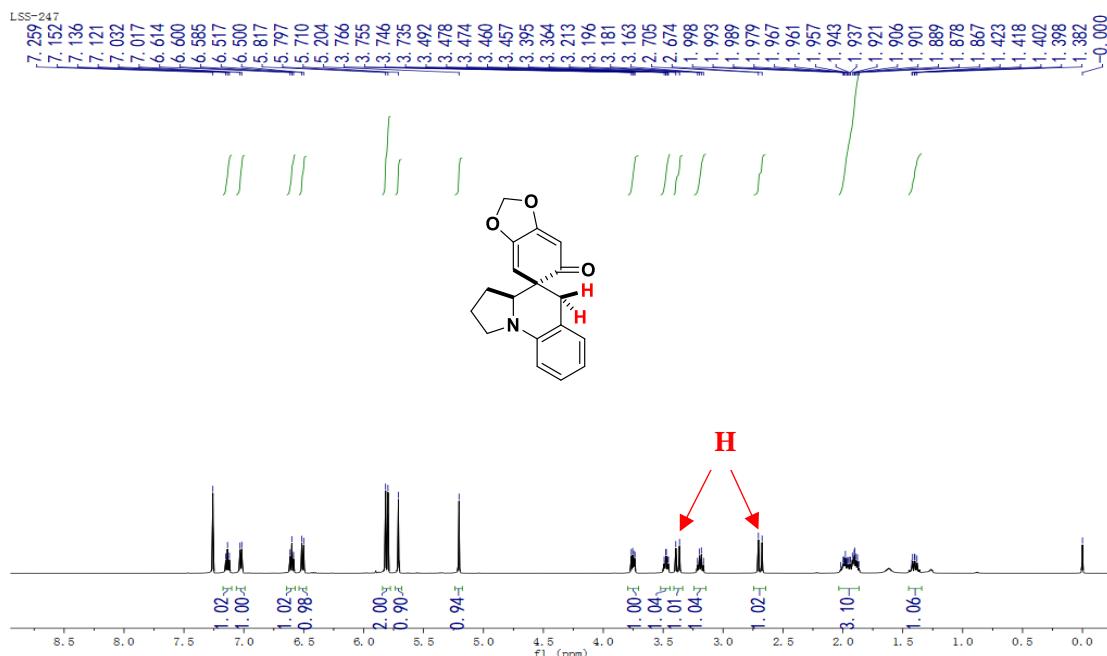
3. Mechanistic Experiments

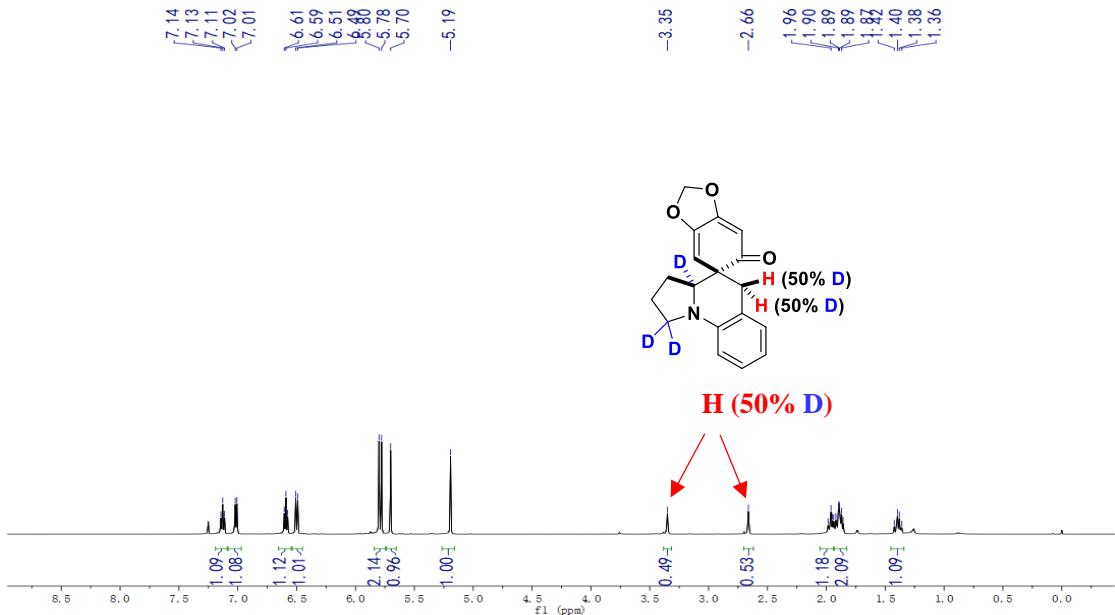
3.1 Deuterium labeling experiments

(1)

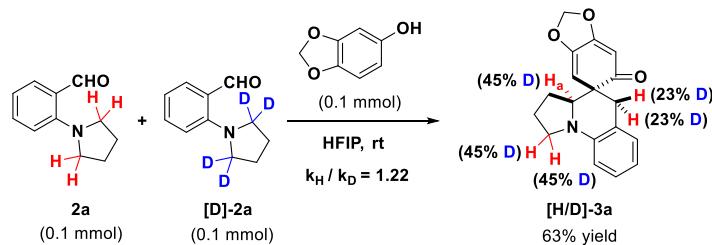


A reaction tube was charged with sesamol **1a** (0.13 mmol), *o*-aminobenzaldehyde **[D]-2a** (0.1 mmol), and HFIP (2.0 mL). The mixture was stirred at room temperature under an air atmosphere. Upon completion of the reaction as indicated by TLC analysis, the mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether, 1:20) to afford the desired *ortho*-spiro cyclohexaketene **[D]-3a** in 88% yield. The deuterated ratio was measured by ¹H NMR.

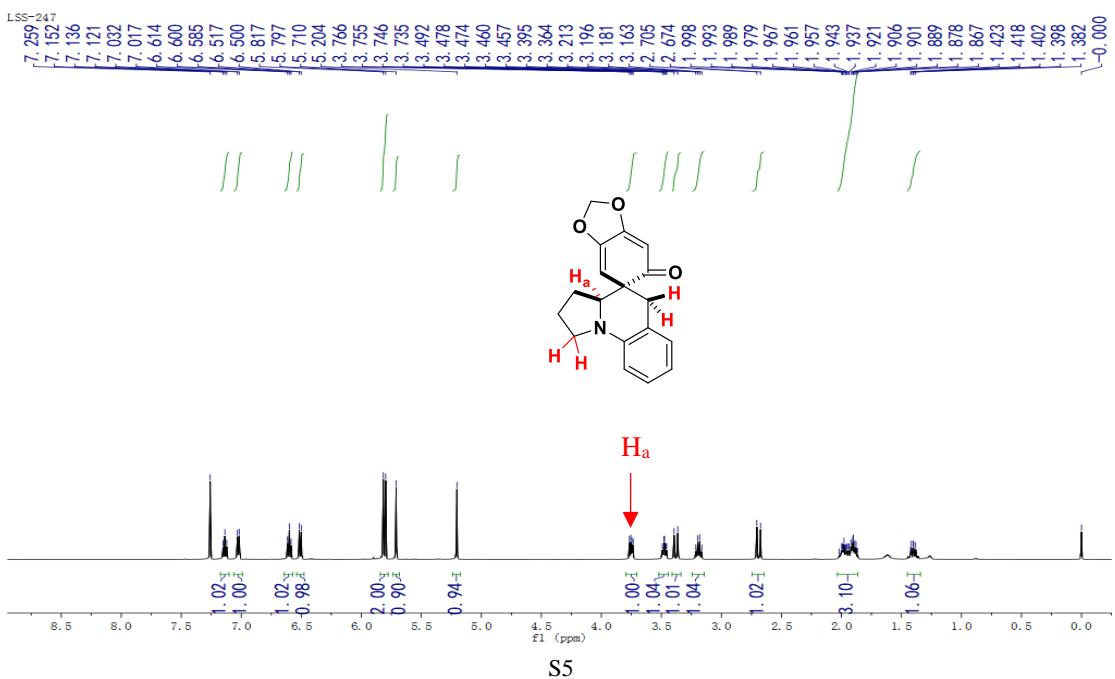


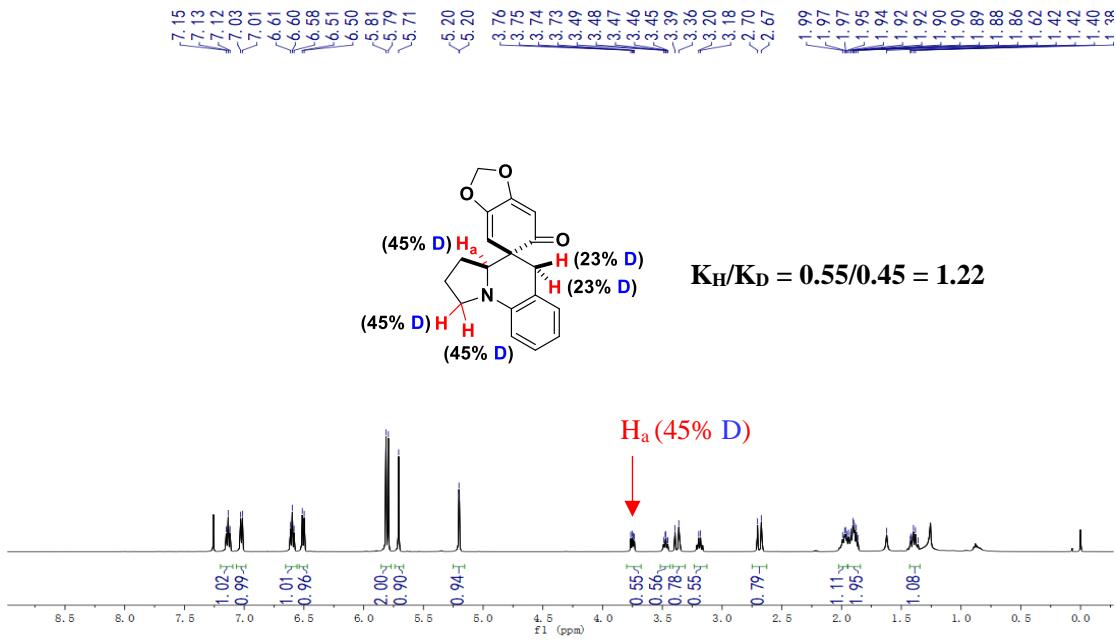


(2)

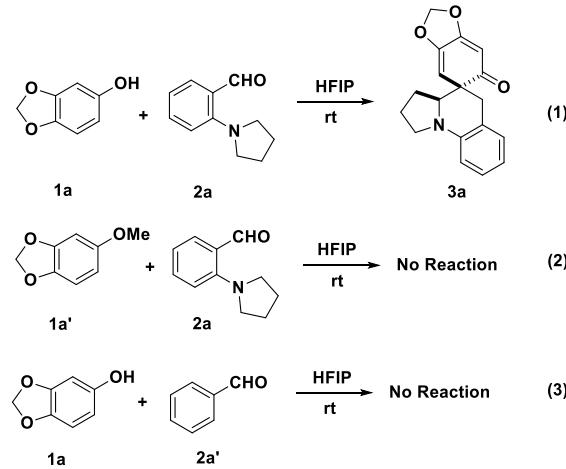


A reaction tube was charged with sesamol **1a** (0.1 mmol), *o*-aminobenzaldehyde **2a** (0.1 mmol), *o*-aminobenzaldehyde **[D]-2a** (0.1 mmol), and HFIP (2.0 mL). The mixture was stirred at room temperature under an air atmosphere for 1 h. Then the mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether, 1:20) to afford the desired *ortho*-spiro cyclohexaketene **3a** and **[D]-3a**. The ratio of **3a** and **[D]-3a** was measured by ¹H NMR.





3.2 Controlled experiments



A reaction tube was charged with 5-methoxybenzo[*d*][1,3]dioxole **1a'** (0.13 mmol), *o*-aminobenzaldehyde **2a** (0.1 mmol), and HFIP (2.0 mL). The mixture was stirred at room temperature under an air atmosphere. The reaction was monitored by TLC. However, the two substrates were intact without any product was observed. This result elucidated the indispensability of the hydrogen bonding interaction between free hydroxyl group and HFIP in facilitating this reaction.

Besides, a reaction tube was charged with sesamol **1a** (0.13 mmol), benzaldehyde **2a'** (0.1 mmol), and HFIP (2.0 mL). The mixture was stirred at room temperature under an air atmosphere. The reaction was monitored by TLC. However, the two substrates were intact without any product was observed. The absence of hydride donor rendered this reaction unproductive, implying the significance of hydride transfer in triggering the whole sequential process.

4. Characterization of Starting Materials and Products

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



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (26.0 mg, 88% yield) as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 7.14 (t, *J* = 7.7 Hz, 1H), 7.02 (d, *J* = 7.3 Hz, 1H), 6.60 (t, *J* = 7.3 Hz, 1H), 6.51 (d, *J* = 8.1 Hz, 1H), 5.82 (s, 1H), 5.80 (s, 1H), 5.71 (s, 1H), 5.20 (s, 1H), 3.75 (dd, *J* = 9.8, 5.4 Hz, 1H), 3.52 – 3.44 (m, 1H), 3.38 (d, *J* = 15.5 Hz, 1H), 3.19 (dd, *J* = 16.3, 8.7 Hz, 1H), 2.69 (d, *J* = 15.6 Hz, 1H), 1.99 (dd, *J* = 5.8, 3.7 Hz, 1H), 1.96 – 1.85 (m, 2H), 1.46 – 1.35 (m, 1H); **¹³C NMR** (126 MHz, CDCl₃) δ 201.2, 163.8, 145.18, 142.9, 129.3, 127.6, 119.2, 115.36, 110.4, 104.6, 101.5, 99.3, 65.43, 48.4, 47.11, 41.1, 27.5, 23.5. **HRMS (ESI)**: calcd. for C₁₈H₁₈NO₃ [M+H]⁺: 296.1287, found: 296.1295.

8'-methyl-1',2',3',3a'-tetrahydro-5'H,6H-spiro[benzo[d][1,3]dioxole-5,4'-pyrrolo[1,2-a]quinolin]-6-one (3b)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (21.9 mg, 71% yield) as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 6.91 (d, *J* = 7.5 Hz, 1H), 6.43 (d, *J* = 7.4 Hz, 1H), 6.33 (s, 1H), 5.80 (d, *J* = 9.4 Hz, 2H), 5.70 (s, 1H), 5.22 (s, 1H), 3.73 (dd, *J* = 9.8, 5.4 Hz, 1H), 3.52 – 3.43 (m, 1H), 3.33 (d, *J* = 15.4 Hz, 1H), 3.18 (dd, *J* = 16.2, 8.8 Hz, 1H), 2.66 (d, *J* = 15.5 Hz, 1H), 2.31 (s, 3H), 1.98 (dt, *J* = 10.6, 4.2 Hz, 1H), 1.95 – 1.81 (m, 2H), 1.39 (dd, *J* = 9.9, 8.0 Hz, 1H); **¹³C NMR** (126 MHz, CDCl₃) δ 201.3, 163.8, 145.1, 142.7, 137.3, 129.1, 116.3, 116.2, 111.1, 104.7, 101.5, 99.3, 65.4, 48.6, 47.1, 40.8, 27.5, 23.5, 21.6. **HRMS (ESI)**: calcd. for C₁₉H₂₀NO₃ [M+H]⁺: 310.1443, found: 310.1445.

8'-(trifluoromethyl)-1',2',3',3a'-tetrahydro-5'H,6H-spiro[benzo[d][1,3]dioxole-5,4'-pyrrolo[1,2-a]quinolin]-6-one (3c)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (30.5 mg, 84% yield) as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 7.09 (d, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 7.5 Hz, 1H), 6.68 (s, 1H), 5.82 (d, *J* = 10.7 Hz, 2H), 5.73 (s, 1H), 5.11 (s, 1H), 3.76 (dd, *J* = 9.6, 5.1 Hz, 1H), 3.51 (t, *J* = 8.3 Hz, 1H), 3.37 (d, *J* = 15.8 Hz, 1H), 3.21 (d, *J* = 8.0 Hz, 1H), 2.72 (d, *J* = 15.8 Hz, 1H), 2.02 (t, *J* = 6.4 Hz, 1H), 1.99 – 1.84 (m, 2H), 1.51 – 1.37 (m, 1H); **¹³C NMR** (126 MHz, CDCl₃) δ 200.7, 163.9, 145.5, 142.8, 130.3, 130.0, 129.7, 129.5 (d, *J* = 12.1 Hz), 125.7, 123.5, 122.8, 111.7 (q, *J* = 3.9 Hz), 106.5 (q, *J* = 3.8 Hz), 103.7, 101.6, 99.4, 65.4, 53.5, 47.6, 47.2, 40.8, 27.5, 23.4. **HRMS (ESI)**: calcd. for C₁₉H₁₇F₃NO₃ [M+H]⁺: 364.1161, found: 364.1157.

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



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (27.0 mg, 82% yield) as a red solid.

¹H NMR (500 MHz, CDCl₃) δ 6.91 (d, *J* = 7.9 Hz, 1H), 6.55 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.46 (d, *J* = 1.7 Hz, 1H), 5.81 (d, *J* = 10.2 Hz, 2H), 5.71 (s, 1H), 5.12 (s, 1H), 3.73 (dd, *J* = 10.0, 5.4 Hz, 1H), 3.50 – 3.39 (m, 1H), 3.29 (d, *J* = 15.5 Hz, 1H), 3.15 (dd, *J* = 16.3, 8.9 Hz, 1H), 2.64 (d, *J* = 15.6 Hz, 1H), 2.07 – 1.97 (m, 1H), 1.92 (ddd, *J* = 15.1, 11.9, 7.9 Hz, 2H), 1.39 (dd, *J* = 10.1, 7.9 Hz, 1H); **¹³C NMR** (126 MHz, CDCl₃) δ 200.8, 163.9, 145.4, 143.7, 133.01, 130.1, 117.6, 115.1, 110.0, 103.9, 101.6, 99.3, 65.3, 47.9, 47.2, 40.6, 27.5, 23.4. **HRMS (ESI)**: calcd. for C₁₈H₁₇ClNO₃ [M+H]⁺: 330.0897, found: 330.0899.

8'-bromo-1',2',3',3a'-tetrahydro-5'H,6H-spiro[benzo[d][1,3]dioxole-5,4'-pyrrolo[1,2-a]quinolin]-6-one (3e)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (31.4 mg, 84% yield) as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 6.86 (d, *J* = 7.9 Hz, 1H), 6.70 (dd, *J* = 7.9, 1.6 Hz, 1H), 6.61 (d, *J* = 1.4 Hz, 1H), 5.82 (d, *J* = 9.6 Hz, 2H), 5.71 (s, 1H), 5.13 (s, 1H), 3.73 (dd, *J* = 10.0, 5.4 Hz, 1H), 3.50 – 3.40 (m, 1H), 3.27 (d, *J* = 15.5 Hz, 1H), 3.15 (dd, *J* = 16.3, 9.0 Hz, 1H), 2.64 (d, *J* = 15.6 Hz, 1H), 2.00 (dd, *J* = 11.4, 4.2 Hz, 1H), 1.92 (ddd, *J* = 15.3, 11.9, 7.9 Hz, 2H), 1.39 (dd, *J* = 10.1, 7.9 Hz, 1H); **¹³C NMR** (126 MHz, CDCl₃) δ 200.8, 163.9, 145.4, 143.9, 130.4, 121.2, 118.1, 117.9, 112.9, 103.9, 101.6, 99.3, 65.3, 47.9, 47.2, 40.6, 27.5, 23.4. **HRMS (ESI)**: calcd. for C₁₈H₁₇BrNO₃ [M+H]⁺: 374.0397,

found: 374.0399.

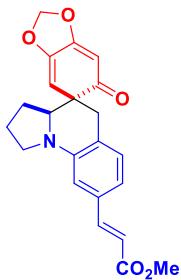
8'-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)-1',2',3',3a'-tetrahydro-5'H,6H-spiro[benzo[d][1,3]dioxole-5,4'-pyrrolo[1,2-a]quinolin]-6-one (3f)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (29.5 mg, 70% yield) as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 7.11 – 6.99 (m, 2H), 6.95 (s, 1H), 5.80 (d, *J* = 9.6 Hz, 2H), 5.70 (s, 1H), 5.18 (s, 1H), 3.79 – 3.69 (m, 1H), 3.57 (s, 1H), 3.39 (d, *J* = 15.8 Hz, 1H), 3.26 (d, *J* = 7.8 Hz, 1H), 2.70 (d, *J* = 15.8 Hz, 1H), 1.96 (d, *J* = 10.3 Hz, 1H), 1.90 (dd, *J* = 15.9, 10.1 Hz, 2H), 1.40 (d, *J* = 8.9 Hz, 1H), 1.34 (s, 12H); **¹³C NMR** (126 MHz, CDCl₃) δ 201.2, 163.9, 145.2, 142.4, 128.8, 122.6, 122.0, 116.3, 104.6, 101.5, 99.3, 83.6, 65.6, 48.3, 47.3, 41.3, 27.5, 24.9, 24.8, 23.5. **HRMS (ESI)**: calcd. for C₂₄H₂₉BNO₅ [M+H]⁺: 422.2139, found: 422.2143.

methyl(*E*)-3-(6-oxo-1',2',3',3a'-tetrahydro-5'H,6H-spiro[benzo[d][1,3]dioxole-5,4'-pyrrolo[1,2-a]quinolin]-8'-yl)acrylate (3g)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (35.2 mg, 93% yield) as a brown solid.

¹H NMR (500 MHz, CDCl₃) δ 7.65 (d, *J* = 16.0 Hz, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.79 (d, *J* = 7.5 Hz, 1H), 6.62 (s, 1H), 6.40 (d, *J* = 16.0 Hz, 1H), 5.82 (d, *J* = 10.3 Hz, 2H), 5.72 (s, 1H), 5.15 (s, 1H), 3.80 (s, 3H), 3.75 (dd, *J* = 9.9, 5.3 Hz, 1H), 3.50 (t, *J* = 7.9 Hz, 1H), 3.37 (d, *J* = 15.9 Hz, 1H), 3.21 (dd, *J* = 16.3, 8.8 Hz, 1H), 2.70 (d, *J* = 16.0 Hz, 1H), 2.09 – 1.99 (m, 1H), 1.99 – 1.81 (m, 2H), 1.48 – 1.34 (m, 1H); **¹³C NMR** (126 MHz, CDCl₃) δ 200.8, 167.7, 163.9, 145.8, 145.4, 143.1, 133.7, 129.7, 122.2, 116.6, 115.6, 109.3, 104.1, 101.6, 99.3, 65.4, 51.6, 48.1, 47.1, 41.0, 27.5, 23.5. **HRMS (ESI)**: calcd. for C₂₂H₂₂NO₅ [M+H]⁺: 380.1498, found: 380.1494.

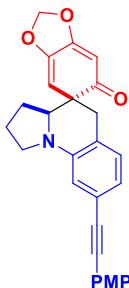
6-oxo-1',2',3',3a'-tetrahydro-5'H,6H-spiro[benzo[d][1,3]dioxole-5,4'-pyrrolo[1,2-a]quinoline]-8'-carbonitrile (3h)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (24.0 mg, 75% yield) as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 7.07 (d, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 6.69 (s, 1H), 5.84 (d, *J* = 10.8 Hz, 2H), 5.73 (s, 1H), 5.05 (s, 1H), 3.74 (dd, *J* = 10.0, 5.3 Hz, 1H), 3.47 (t, *J* = 8.3 Hz, 1H), 3.36 (d, *J* = 16.1 Hz, 1H), 3.17 (dd, *J* = 16.6, 8.7 Hz, 1H), 2.71 (d, *J* = 16.1 Hz, 1H), 2.11 – 2.00 (m, 1H), 2.00 – 1.84 (m, 2H), 1.42 (dd, *J* = 10.0, 8.3 Hz, 1H); **¹³C NMR** (126 MHz, CDCl₃) δ 200.2, 163.9, 145.7, 143.0, 129.7, 124.6, 119.8, 118.8, 112.7, 111.1, 103.2, 101.7, 99.4, 65.34, 47.3, 47.2, 40.9, 27.4, 23.4. **HRMS (ESI)**: calcd. for C₁₉H₁₇N₂O₃ [M+H]⁺: 321.1239, found: 321.1240.

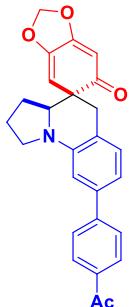
8'-(4-methoxyphenyl)-1',2',3',3a'-tetrahydro-5'H,6H-spiro[benzo[d][1,3]dioxole-5,4'-pyrrolo[1,2-a]quinolin]-6-one (3i)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (34.1 mg, 81% yield) as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 7.47 (d, *J* = 8.6 Hz, 2H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.77 (d, *J* = 7.6 Hz, 1H), 6.65 (s, 1H), 5.81 (d, *J* = 9.6 Hz, 2H), 5.71 (s, 1H), 5.16 (s, 1H), 3.83 (s, 3H), 3.76 (dd, *J* = 9.8, 5.3 Hz, 1H), 3.49 (t, *J* = 8.0 Hz, 1H), 3.37 (d, *J* = 15.7 Hz, 1H), 3.20 (d, *J* = 7.7 Hz, 1H), 2.69 (d, *J* = 15.8 Hz, 1H), 2.02 (dd, *J* = 13.0, 3.2 Hz, 1H), 1.93 (ddd, *J* = 15.5, 11.4, 7.1 Hz, 2H), 1.47 – 1.34 (m, 1H); **¹³C NMR** (126 MHz, CDCl₃) δ 201.0, 163.9, 159.5, 145.3, 142.6, 133.0, 129.2, 122.4, 119.7, 118.8, 115.7, 113.9, 112.9, 104.3, 101.5, 99.3, 88.9, 88.1, 65.4, 55.3, 48.2, 47.2, 41.0, 27.5, 23.5. **HRMS (ESI)**: calcd. for C₂₇H₂₄NO₄ [M+H]⁺: 426.1705, found: 426.1694.

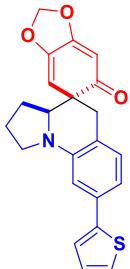
8'-(4-acetylphenyl)-1',2',3',3a'-tetrahydro-5'H,6H-spiro[benzo[d][1,3]dioxole-5,4'-pyrrolo[1,2-a]quinolin]-6-one (3j)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (34.7 mg, 84% yield) as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 8.02 (d, *J* = 8.2 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 7.7 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 6.72 (s, 1H), 5.82 (d, *J* = 9.6 Hz, 2H), 5.73 (s, 1H), 5.24 (s, 1H), 3.80 (dd, *J* = 9.8, 5.3 Hz, 1H), 3.57 (t, *J* = 8.0 Hz, 1H), 3.41 (d, *J* = 15.6 Hz, 1H), 3.27 (d, *J* = 7.8 Hz, 1H), 2.75 (d, *J* = 15.7 Hz, 1H), 2.64 (s, 3H), 2.03 (d, *J* = 7.3 Hz, 1H), 1.95 (ddd, *J* = 15.5, 11.5, 7.1 Hz, 2H), 1.50 – 1.37 (m, 1H); **¹³C NMR** (126 MHz, CDCl₃) δ 201.0, 197.8, 163.9, 146.6, 145.4, 143.2, 139.4, 135.6, 129.8, 128.8, 127.2, 119.6, 114.5, 108.9, 104.3, 101.6, 99.4, 65.5, 48.3, 47.2, 40.8, 27.5, 26.7, 23.5. **HRMS (ESI):** calcd. for C₂₆H₂₄NO₄ [M+H]⁺: 414.1705, found: 414.1707.

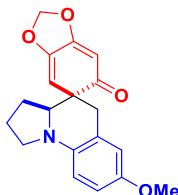
8'-(thiophen-2-yl)-1',2',3',3a'-tetrahydro-5'H,6H-spiro[benzo[d][1,3]dioxole-5,4'-pyrrolo[1,2-a]quinolin]-6-one (3k)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (33.2 mg, 88% yield) as a brown solid.

¹H NMR (500 MHz, CDCl₃) δ 7.28 (d, *J* = 3.4 Hz, 1H), 7.24 (d, *J* = 5.0 Hz, 1H), 7.13 – 7.05 (m, 1H), 7.03 (d, *J* = 7.7 Hz, 1H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.72 (s, 1H), 5.81 (d, *J* = 9.7 Hz, 2H), 5.72 (s, 1H), 5.22 (s, 1H), 3.78 (dd, *J* = 9.8, 5.4 Hz, 1H), 3.55 (dd, *J* = 12.1, 4.9 Hz, 1H), 3.37 (d, *J* = 15.6 Hz, 1H), 3.25 (t, *J* = 8.3 Hz, 1H), 2.71 (d, *J* = 15.7 Hz, 1H), 2.01 (dd, *J* = 11.0, 3.9 Hz, 1H), 1.93 (ddd, *J* = 16.1, 11.5, 4.4 Hz, 2H), 1.50 – 1.35 (m, 1H); **¹³C NMR** (126 MHz, CDCl₃) δ 201.1, 163.9, 145.3, 145.3, 143.1, 133.8, 129.7, 127.8, 124.2, 122.7, 118.9, 113.5, 107.8, 104.4, 101.5, 99.3, 65.5, 48.4, 47.2, 40.9, 27.5, 23.5. **HRMS (ESI):** calcd. for C₂₂H₂₀NO₃S [M+H]⁺: 378.1164, found: 378.1160.

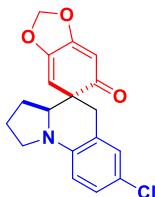
7'-methoxy-1',2',3',3a'-tetrahydro-5'H,6H-spiro[benzo[d][1,3]dioxole-5,4'-pyrrolo[1,2-a]quinolin]-6-one (3l)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (26.0 mg, 80% yield) as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 6.75 (d, *J* = 8.6 Hz, 1H), 6.66 (s, 1H), 6.46 (d, *J* = 8.7 Hz, 1H), 5.81 (d, *J* = 10.3 Hz, 2H), 5.70 (s, 1H), 5.21 (s, 1H), 3.74 (s, 3H), 3.69 (dd, *J* = 9.4, 5.3 Hz, 1H), 3.41 (dd, *J* = 16.3, 12.4 Hz, 2H), 3.25 – 3.09 (m, 1H), 2.65 (d, *J* = 15.7 Hz, 1H), 1.92 (ddd, *J* = 20.3, 12.0, 6.5 Hz, 3H), 1.50 – 1.33 (m, 1H); **¹³C NMR** (126 MHz, CDCl₃) δ 201.2, 163.8, 150.5, 145.2, 137.7, 120.3, 115.5, 113.2, 111.3, 104.7, 101.5, 99.3, 65.7, 55.9, 48.8, 47.6, 41.1, 27.4, 23.5. **HRMS (ESI)**: calcd. for C₁₉H₂₀NO₄ [M+H]⁺: 326.1392, found: 326.1390.

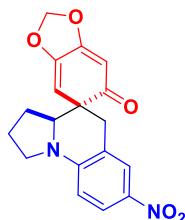
7'-chloro-1',2',3',3a'-tetrahydro-5'H,6H-spiro[benzo[d][1,3]dioxole-5,4'-pyrrolo[1,2-a]quinolin]-6-one (3m)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (25.3 mg, 77% yield) as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 7.07 (d, *J* = 8.5 Hz, 1H), 6.99 (s, 1H), 6.41 (d, *J* = 8.6 Hz, 1H), 5.82 (d, *J* = 8.8 Hz, 2H), 5.71 (s, 1H), 5.12 (s, 1H), 3.72 (dd, *J* = 9.5, 5.1 Hz, 1H), 3.45 (t, *J* = 8.4 Hz, 1H), 3.33 (d, *J* = 15.7 Hz, 1H), 3.15 (dd, *J* = 16.2, 8.3 Hz, 1H), 2.63 (d, *J* = 15.7 Hz, 1H), 2.07 – 1.82 (m, 3H), 1.47 – 1.33 (m, 1H); **¹³C NMR** (126 MHz, CDCl₃) δ 200.8, 163.9, 145.4, 141.4, 128.8, 127.3, 120.7, 119.9, 111.3, 103.9, 101.6, 99.3, 65.5, 47.9, 47.3, 40.8, 27.5, 23.5. **HRMS (ESI)**: calcd. for C₁₈H₁₆ClNaNO₃ [M+Na]⁺: 352.0716, found: 352.0714.

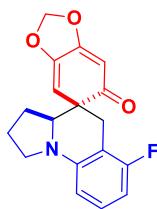
7'-nitro-1',2',3',3a'-tetrahydro-5'H,6H-spiro[benzo[d][1,3]dioxole-5,4'-pyrrolo[1,2-a]quinolin]-6-one (3n)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (23.1 mg, 68% yield) as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 8.07 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.97 (s, 1H), 6.46 (d, *J* = 9.1 Hz, 1H), 5.85 (d, *J* = 6.2 Hz, 2H), 5.75 (s, 1H), 5.03 (s, 1H), 3.87 (dd, *J* = 10.5, 5.2 Hz, 1H), 3.62 (t, *J* = 9.1 Hz, 1H), 3.35 (d, *J* = 15.6 Hz, 1H), 3.29 (dd, *J* = 17.1, 9.7 Hz, 1H), 2.75 (d, *J* = 15.6 Hz, 1H), 2.13 – 2.05 (m, 1H), 1.98 (ddd, *J* = 13.7, 10.2, 6.2 Hz, 2H), 1.45 (dd, *J* = 10.7, 7.4 Hz, 1H); **¹³C NMR** (126 MHz, CDCl₃) δ 199.8, 163.9, 147.7, 145.9, 136.6, 125.6, 125.1, 118.8, 109.1, 102.6, 101.8, 99.4, 65.6, 47.6, 47.3, 40.7, 27.5, 23.2. **HRMS (ESI)**: calcd. for C₁₈H₁₇N₂O₅ [M+H]⁺: 341.1137, found: 341.1139.

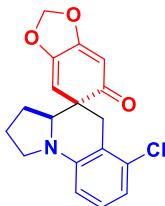
6'-fluoro-1',2',3',3a'-tetrahydro-5'H,6H-spiro[benzo[d][1,3]dioxole-5,4'-pyrrolo[1,2-a]quinolin]-6-one (3o)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (30.7 mg, 98% yield) as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 7.06 (dd, *J* = 15.0, 7.9 Hz, 1H), 6.35 (t, *J* = 8.7 Hz, 1H), 6.29 (d, *J* = 8.2 Hz, 1H), 5.81 (d, *J* = 9.5 Hz, 2H), 5.72 (s, 1H), 5.16 (s, 1H), 3.70 (dd, *J* = 9.9, 5.3 Hz, 1H), 3.47 (td, *J* = 9.1, 2.2 Hz, 1H), 3.20 (dd, *J* = 16.3, 8.7 Hz, 1H), 3.07 (d, *J* = 16.1 Hz, 1H), 2.94 (d, *J* = 16.0 Hz, 1H), 2.06 – 1.96 (m, 1H), 1.96 – 1.86 (m, 2H), 1.41 (dd, *J* = 9.6, 8.2 Hz, 1H); **¹³C NMR** (126 MHz, CDCl₃) δ 200.9, 163.9, 162.5, 160.6, 145.4, 144.3 (d, *J* = 7.7 Hz), 127.9 (d, *J* = 10.8 Hz), 106.4, 104.1, 102.2, 102.1, 101.6, 99.4, 64.8, 47.5 (d, *J* = 11.8 Hz), 33.5 (d, *J* = 4.3 Hz), 27.5, 23.4. **HRMS (ESI)**: calcd. for C₁₈H₁₇FNO₃ [M+H]⁺: 314.1192, found: 314.1193.

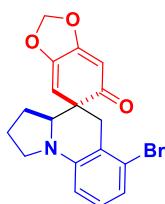
6'-chloro-1',2',3',3a'-tetrahydro-5'H,6H-spiro[benzo[d][1,3]dioxole-5,4'-pyrrolo[1,2-a]quinolin]-6-one (3p)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (27.0 mg, 82% yield) as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 7.04 (t, *J* = 8.0 Hz, 1H), 6.67 (d, *J* = 7.9 Hz, 1H), 6.41 (d, *J* = 8.2 Hz, 1H), 5.82 (d, *J* = 7.8 Hz, 2H), 5.73 (s, 1H), 5.16 (s, 1H), 3.70 (dd, *J* = 9.8, 5.3 Hz, 1H), 3.46 (td, *J* = 8.6, 2.0 Hz, 1H), 3.21 (dd, *J* = 16.3, 8.5 Hz, 1H), 3.15 (d, *J* = 16.4 Hz, 1H), 3.06 (d, *J* = 16.4 Hz, 1H), 2.07 – 1.97 (m, 1H), 1.97 – 1.84 (m, 2H), 1.42 (dd, *J* = 9.7, 8.2 Hz, 1H); **¹³C NMR** (126 MHz, CDCl₃) δ 200.8, 163.9, 145.4, 144.1, 134.7, 127.8, 117.1, 116.2, 108.9, 104.2, 101.6, 99.4, 64.8, 48.3, 47.4, 38.4, 27.5, 23.5. **HRMS (ESI)**: calcd. for C₁₈H₁₇BrNO₃ [M+H]⁺: 330.0897, found: 330.0893.

6'-bromo-1',2',3',3a'-tetrahydro-5'H,6H-spiro[benzo[d][1,3]dioxole-5,4'-pyrrolo[1,2-a]quinolin]-6-one (3q)

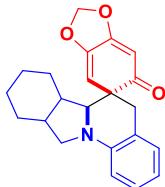


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (33.9 mg, 91% yield) as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 6.97 (t, *J* = 8.0 Hz, 1H), 6.86 (d, *J* = 7.9 Hz, 1H), 6.45 (d, *J* = 8.1 Hz, 1H), 5.83 (d, *J* = 6.8 Hz, 2H), 5.73 (s, 1H), 5.17 (s, 1H), 3.70 (dd, *J* = 9.7, 5.3 Hz, 1H), 3.45 (t, *J* = 8.9

Hz, 1H), 3.21 (d, J = 8.0 Hz, 1H), 3.16 (d, J = 16.5 Hz, 1H), 3.03 (d, J = 16.4 Hz, 1H), 2.07 – 1.98 (m, 1H), 1.97 – 1.85 (m, 2H), 1.49 – 1.36 (m, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 200.7, 164.0, 145.4, 144.2, 128.3, 125.65, 119.5, 118.7, 109.5, 104.1, 101.6, 99.4, 64.9, 48.5, 47.3, 41.4, 27.4, 23.6. HRMS (ESI): calcd. for $\text{C}_{18}\text{H}_{17}\text{BrNO}_3$ [M+H] $^+$: 374.0392, found: 374.0393.

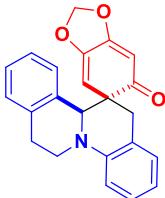
6a',6b',7',8',9',10',10a',11'-octahydro-5'H,6H-spiro[benzo[d][1,3]dioxole-5,6'-isoindolo[2,1-a]quinolin]-6-one (3r)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (18.1 mg, 52% yield, 1.7:1 dr) as a yellow solid.

^1H NMR (500 MHz, CDCl_3) δ 7.13 (t, J = 7.6 Hz, 1H), 6.99 (t, J = 7.3 Hz, 1H), 6.56 (dt, J = 14.4, 7.3 Hz, 1H), 6.46 (d, J = 8.1 Hz, 1H), 5.84 (s, 1H), 5.79 (s, 1H), 5.71 (s, 1H), 5.16 (s, 1H), 3.68 (d, J = 8.8 Hz, 1H), 3.58 (t, J = 7.9 Hz, 1H), 3.35 (d, J = 15.4 Hz, 1H), 3.27 (d, J = 15.3 Hz, 1H), 3.22 (d, J = 3.3 Hz, 1H), 2.4 (t, J = 7.9 Hz, 1H), 2.67 (d, J = 20 Hz, 1H), 1.99 – 1.88 (m, 1H), 1.80 – 1.64 (m, 2H), 1.58 (d, J = 4.7 Hz, 1H), 1.48 (dt, J = 7.9, 4.1 Hz, 1H), 1.38 (dd, J = 23.2, 10.9 Hz, 1H), 1.25 (t, J = 11.9 Hz, 1H), 1.18 – 1.09 (m, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 201.9, 201.5, 163.94, 163.7, 151.3, 148.2, 144.8, 144.6, 143.3, 142.7, 141.2, 129.0, 127.7, 127.6, 118.8, 118.6, 114.9, 114.6, 110.0, 109.3, 108.1, 106.7, 105.4, 105.1, 101.5, 101.5, 101.1, 99.3, 99.1, 98.3, 70.3, 65.5, 53.8, 51.8, 47.8, 47.6, 43.2, 42.4, 42.4, 40.8, 37.3, 29.6, 28.9, 28.6, 26.7, 25.7, 25.2, 21.6. HRMS (ESI): calcd. for $\text{C}_{22}\text{H}_{24}\text{NO}_3$ [M+H] $^+$: 350.1756, found: 350.1754.

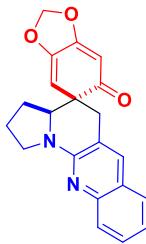
7',11b'-dihydro-6H,6'H,13'H-spiro[benzo[d][1,3]dioxole-5,12'-isoquinolino[2,1-a]quinolin]-6-one (3s)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (25.0 mg, 70% yield) as a reddish brown solid.

^1H NMR (500 MHz, CDCl_3) δ 7.16 (dd, J = 17.0, 8.9 Hz, 2H), 7.07 (s, 4H), 6.79 (d, J = 7.9 Hz, 1H), 6.71 (t, J = 6.6 Hz, 1H), 5.65 (s, 1H), 5.57 (s, 1H), 5.54 (s, 2H), 4.88 (s, 1H), 3.94 (d, J = 9.8 Hz, 1H), 3.71 (d, J = 16.1 Hz, 1H), 3.32 (t, J = 11.1 Hz, 1H), 3.03 (t, J = 11.1 Hz, 1H), 2.84 – 2.65 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 201.7, 163.5, 144.9, 144.1, 136.5, 133.9, 129.4, 128.3, 127.9, 127.2, 126.9, 125.9, 120.7, 116.8, 112.2, 105.4, 101.2, 99.6, 65.0, 53.6, 44.4, 40.9, 30.0. HRMS (ESI): calcd. for $\text{C}_{23}\text{H}_{20}\text{NO}_3$ [M+H] $^+$: 358.1443, found: 358.1441.

1',2',3',3a'-tetrahydro-5'H,6H-spiro[benzo[d][1,3]dioxole-5,4'-benzo[g]pyrrolo[1,2-a][1,8]naphthyridin]-6-one (3t)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (30.1 mg, 87% yield) as a reddish brown solid.

¹H NMR (500 MHz, CDCl₃) δ 7.71 (d, *J* = 8.4 Hz, 1H), 7.60 (s, 1H), 7.56 – 7.46 (m, 2H), 7.17 (t, *J* = 7.4 Hz, 1H), 5.84 (s, 1H), 5.81 (s, 1H), 5.75 (s, 1H), 5.19 (s, 1H), 4.00 (dd, *J* = 10.2, 5.1 Hz, 1H), 3.96 (t, *J* = 9.5 Hz, 1H), 3.64 (dd, *J* = 13.9, 5.1 Hz, 1H), 3.47 (d, *J* = 15.7 Hz, 1H), 2.84 (d, *J* = 15.5 Hz, 1H), 2.03 – 1.98 (m, 1H), 1.94 (dd, *J* = 16.8, 8.4 Hz, 2H), 1.52 – 1.43 (m, 1H); **¹³C NMR** (126 MHz, CDCl₃) δ 200.1, 163.9, 152.4, 145.7, 135.1, 129.0, 127.0, 125.8, 122.9, 121.8, 118.0, 103.2, 101.7, 99.3, 65.4, 48.5, 46.7, 40.9, 28.1, 23.2. **HRMS (ESI)**: calcd. for C₂₁H₁₉N₂O₃ [M+H]⁺: 347.1396, found: 347.1399.

1',2',3',12a'-tetrahydro-6H,11'H-spiro[benzo[d][1,3]dioxole-5,12'-naphtho[1,8-ef]pyrrolo[1,2-a]azepin]-6-one (3u)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (19.3 mg, 56% yield, 1.7:1 dr) as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 7.62 (d, *J* = 7.9 Hz, 1H), 7.29 (dd, *J* = 13.4, 6.8 Hz, 3H), 6.93 (d, *J* = 6.8 Hz, 1H), 6.72 (d, *J* = 6.9 Hz, 1H), 5.89 (s, 1H), 5.87 (s, 1H), 5.85 (s, 1H), 5.65 (s, 1H), 4.17 (d, *J* = 9.4 Hz, 1H), 3.57-3.54 (m, 1H), 3.45 (d, *J* = 13.7 Hz, 1H), 3.10 (dd, *J* = 17.2, 9.3 Hz, 1H), 2.55 (d, *J* = 14 Hz, 1H), 2.10-2.07 (m, 1H), 2.03 – 1.96 (m, 1H), 1.80 – 1.74 (m, 1H), 1.39 (dd, *J* = 12.7, 6.9 Hz, 1H); **¹³C NMR** (126 MHz, CDCl₃) δ 200.7, 199.5, 163.4, 162.7, 150.3, 149.9, 144.3, 143.9, 135.5, 134.7, 133.6, 127.1, 126.9, 126.8, 126.6, 126.5, 126.1, 126.0, 125.5, 125.4, 125.1, 119.4, 118.7, 107.6, 107.5, 107.5, 107.2, 101.5, 99.9, 98.3, 72.5, 71.1, 60.0, 58.5, 51.3, 51.1, 44.5, 43.7, 28.5, 28.1, 25.4, 23.7. **HRMS (ESI)**: calcd. for C₂₂H₂₀NO₃ [M+H]⁺: 346.1443, found: 346.1446.

4-methoxy-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (3v)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:15) afforded the product (14.9 mg, 53% yield) as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 7.15 (t, *J* = 7.7 Hz, 1H), 7.03 (d, *J* = 7.4 Hz, 1H), 6.63 (t, *J* = 7.4 Hz, 1H), 6.52 (d, *J* = 8.1 Hz, 1H), 6.44 (d, *J* = 10.2 Hz, 1H), 6.24 (d, *J* = 10.2 Hz, 1H), 5.69 (s, 1H), 3.90

(dd, $J = 9.5, 6.1$ Hz, 1H), 3.78 (s, 3H), 3.58 (d, $J = 15.7$ Hz, 1H), 3.47 (t, $J = 8.1$ Hz, 1H), 3.25 (q, $J = 8.2$ Hz, 1H), 2.65 (d, $J = 15.8$ Hz, 1H), 2.05 – 1.95 (m, 1H), 1.96 – 1.88 (m, 1H), 1.84 (dt, $J = 12.7, 6.5$ Hz, 1H), 1.47 – 1.34 (m, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 187.9, 177.4, 145.1, 142.94, 129., 129.2, 127.8, 118.5, 115.8, 110.8, 103.5, 62.5, 56.1, 47.3, 42.6, 38.2, 27.6, 23.2. HRMS (ESI): calcd. for $\text{C}_{18}\text{H}_{20}\text{NO}_2$ [M+H] $^+$: 282.1494, found: 282.1499.

3,4-dimethoxy-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (3w)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:6) afforded the product (20.8 mg, 67% yield) as a yellow solid.

^1H NMR (500 MHz, CDCl_3) δ 7.14 (t, $J = 7.7$ Hz, 1H), 7.05 (d, $J = 7.4$ Hz, 1H), 6.61 (t, $J = 7.3$ Hz, 1H), 6.53 (d, $J = 8.1$ Hz, 1H), 5.58 (s, 1H), 4.92 (s, 1H), 3.85 (s, 3H), 3.72 (dd, $J = 9.6, 5.5$ Hz, 1H), 3.50 (s, 3H), 3.47 (dd, $J = 8.6, 2.7$ Hz, 1H), 3.40 (d, $J = 15.6$ Hz, 1H), 3.20 (dd, $J = 16.3, 8.6$ Hz, 1H), 2.66 (d, $J = 15.7$ Hz, 1H), 2.01 – 1.91 (m, 2H), 1.90 – 1.85 (m, 1H), 1.38 (dd, $J = 15.1, 5.7$ Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 201.3, 166.6, 147.8, 142.9, 129.4, 127.4, 119.5, 115.4, 110.5, 107.1, 101.9, 65.4, 56.6, 55.5, 47.7, 47.2, 40.5, 27.3, 23.5. HRMS (ESI): calcd. for $\text{C}_{19}\text{H}_{22}\text{NO}_3$ [M+H] $^+$: 312.1600, found: 312.1602.

2,4-dimethoxy-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (3x)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:15) afforded the product (18.0 mg, 58% yield) as a red solid.

^1H NMR (500 MHz, CDCl_3) δ 7.09 (t, $J = 7.6$ Hz, 1H), 6.97 (d, $J = 7.4$ Hz, 1H), 6.60 (t, $J = 7.3$ Hz, 1H), 6.50 (d, $J = 8.0$ Hz, 1H), 5.63 (s, 1H), 5.51 (s, 1H), 4.03 – 3.91 (m, 1H), 3.76 (s, 3H), 3.60 (d, $J = 16.3$ Hz, 2H), 3.35 (s, 3H), 3.12 (dd, $J = 15.7, 7.8$ Hz, 1H), 2.74 (d, $J = 16.6$ Hz, 1H), 1.95 – 1.80 (m, 3H), 1.46 (td, $J = 7.9, 2.3$ Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 188.1, 175.0, 173.1, 144.1, 127.7, 126.7, 120.4, 115.4, 111.0, 102.4, 101.9, 61.6, 56.5, 55.8, 48.4, 45.2, 35.7, 27.4, 23.5. HRMS (ESI): calcd. for $\text{C}_{19}\text{H}_{22}\text{NO}_3$ [M+H] $^+$: 312.1600, found: 312.1602.

4-(diethylamino)-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (3y)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:80) afforded the product (31.2 mg, 97% yield) as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 7.12 (t, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 7.3 Hz, 1H), 6.58 (t, *J* = 7.3 Hz, 1H), 6.50 (d, *J* = 8.1 Hz, 1H), 6.39 (dd, *J* = 10.5, 2.2 Hz, 1H), 6.16 (d, *J* = 10.5 Hz, 1H), 5.33 (d, *J* = 2.1 Hz, 1H), 3.86 (dd, *J* = 9.9, 5.1 Hz, 1H), 3.54 – 3.43 (m, 2H), 3.37 (q, *J* = 7.1 Hz, 4H), 3.18 (d, *J* = 7.5 Hz, 1H), 2.62 (d, *J* = 15.8 Hz, 1H), 1.99 – 1.87 (m, 3H), 1.34 – 1.28 (m, 1H), 1.22 (t, *J* = 7.1 Hz, 6H); ¹³C NMR (126 MHz, CDCl₃) δ 197.4, 156.5, 143.9, 143.2, 129.1, 127.3, 119.9, 118.5, 114.9, 110.1, 96.6, 64.4, 47.2, 45.7, 44.9, 39.7, 27.8, 23.5. HRMS (ESI): calcd. for C₂₁H₂₇N₂O [M+H]⁺: 323.2123, found: 323.2125.

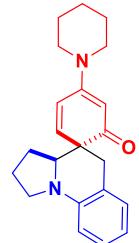
4-(pyrrolidin-1-yl)-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (3z)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product (41.7 mg, 96% yield) as a reddish brown solid.

¹H NMR (500 MHz, CDCl₃) δ 7.12 (t, *J* = 7.7 Hz, 1H), 7.02 (d, *J* = 7.3 Hz, 1H), 6.57 (t, *J* = 7.3 Hz, 1H), 6.49 (d, *J* = 8.1 Hz, 1H), 6.37 (d, *J* = 10.3 Hz, 1H), 6.14 (d, *J* = 10.3 Hz, 1H), 5.21 (s, 1H), 3.87 (dd, *J* = 9.9, 5.0 Hz, 1H), 3.54 (s, 2H), 3.50 – 3.41 (m, 2H), 3.32 (s, 2H), 3.18 (d, *J* = 8.0 Hz, 1H), 2.60 (d, *J* = 15.8 Hz, 1H), 2.00 (s, 4H), 1.95 (dd, *J* = 10.7, 5.4 Hz, 3H), 1.35 – 1.28 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 197.0, 155.9, 144.0, 143.2, 129.1, 127.3, 119.9, 119.9, 115.0, 110.1, 96.9, 64.3, 48.2, 47.9, 47.2, 46.2, 39.9, 27.9, 25.4, 24.8, 23.6. HRMS (ESI): calcd. for C₂₁H₂₅N₂O [M+H]⁺: 321.1967, found: 321.1969.

4-(piperidin-1-yl)-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (3za)

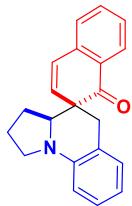


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the

product (29.1 mg, 87% yield) as a red solid.

¹H NMR (500 MHz, CDCl₃) δ 7.12 (t, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 7.3 Hz, 1H), 6.59 (d, *J* = 7.2 Hz, 1H), 6.50 (d, *J* = 8.0 Hz, 1H), 6.46 (d, *J* = 10.5 Hz, 1H), 6.12 (d, *J* = 10.5 Hz, 1H), 5.45 (s, 1H), 3.84 (dd, *J* = 9.8, 4.7 Hz, 1H), 3.53 – 3.36 (m, 6H), 3.18 (d, *J* = 7.8 Hz, 1H), 2.62 (d, *J* = 15.8 Hz, 1H), 2.00 – 1.85 (m, 3H), 1.67 (dd, *J* = 25.1, 4.2 Hz, 6H), 1.32 (d, *J* = 10.2 Hz, 1H); **¹³C NMR** (126 MHz, CDCl₃) δ 198.3, 157.9, 143.3, 143.2, 129.2, 127.3, 119.8, 118.8, 115.0, 110.2, 98.5, 64.4, 48.1, 47.2, 45.9, 39.7, 27.8, 25.6, 24.4, 23.5. **HRMS (ESI)**: calcd. for C₂₂H₂₇N₂O [M+H]⁺: 335.2123, found: 335.2115.

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



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:150) afforded the product (21.4 mg, 71% yield) as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 7.59 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 3.2 Hz, 1H), 7.16 (t, *J* = 7.7 Hz, 1H), 7.05 (d, *J* = 7.3 Hz, 1H), 6.67 (d, *J* = 10.0 Hz, 1H), 6.62 (t, *J* = 7.3 Hz, 1H), 6.55 (d, *J* = 8.1 Hz, 1H), 5.82 (d, *J* = 10.0 Hz, 1H), 3.85 (dd, *J* = 9.8, 5.7 Hz, 1H), 3.51 (t, *J* = 8.6 Hz, 1H), 3.46 (d, *J* = 15.5 Hz, 1H), 3.21 (dd, *J* = 16.7, 8.6 Hz, 1H), 2.73 (d, *J* = 15.5 Hz, 1H), 1.93 (dt, *J* = 17.1, 7.4 Hz, 2H), 1.80 (dt, *J* = 11.9, 6.0 Hz, 1H), 1.46 – 1.33 (m, 1H); **¹³C NMR** (126 MHz, CDCl₃) δ 201.9, 143.0, 138.3, 134.6, 133.2, 129.4, 128.0, 127.6, 127.6, 126.7, 126.4, 119.2, 115.4, 110.4, 65.2, 47.7, 47.2, 39.7, 27.6, 23.6. **HRMS (ESI)**: calcd. for C₂₁H₂₀NO [M+H]⁺: 302.1545, found: 302.1543.

4-chloro-1',2',3',3a'-tetrahydro-1*H*,5'*H*-spiro[naphthalene-2,4'-pyrrolo[1,2-*a*]quinolin]-1-one (3zc)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (27.6 mg, 75% yield,) as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 8.12 (d, *J* = 7.5 Hz, 1H), 7.81 (d, *J* = 7.7 Hz, 1H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 7.1 Hz, 1H), 6.65 (t, *J* = 7.1 Hz, 1H), 6.57 (d, *J* = 7.9 Hz, 1H), 5.99 (s, 1H), 3.90 – 3.74 (m, 1H), 3.49 (t, *J* = 10.9 Hz, 2H), 3.26 (q, *J* = 8.0 Hz, 1H), 2.80 (d, *J* = 15.6 Hz, 1H), 2.03 – 1.95 (m, 1H), 1.91 (d, *J* = 8.8 Hz, 1H), 1.85 – 1.77 (m, 1H), 1.46 – 1.33 (m, 1H); **¹³C NMR** (126 MHz, CDCl₃) δ 199.8, 142.7, 135.8, 134.8, 130.2, 129.9, 129.5, 129.5, 129.2, 127.8, 127.0, 125.6, 118.5, 115.7, 110.7, 65.5, 49.7, 47.0, 39.5, 27.7, 23.5. **HRMS (ESI)**: calcd. for C₂₁H₁₉ClNO [M+H]⁺: 336.1155, found: 336.1158.

3-hydroxy-1',2',3',3a'-tetrahydro-2*H*,5'*H*-spiro[naphthalene-1,4'-pyrrolo[1,2-*a*]quinolin]-2-o

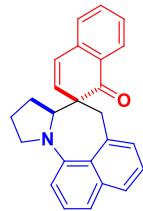
ne (3zd)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (24.7 mg, 78% yield, 4:1 dr) as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 7.26 – 7.18 (m, 3H), 7.15 (d, J = 5 Hz, 1H), 7.0 (t, J = 10 Hz, 1H), 6.92 (s, 1H), 6.76 (d, J = 8.0 Hz, 1H), 6.71 (t, J = 10 Hz, 1H), 6.63 (d, J = 10 Hz, 1H), 6.43 (s, 1H), 3.81 (d, J = 16.8 Hz, 1H), 3.57 (dd, J = 8.4, 5.9 Hz, 1H), 3.48 – 3.41 (m, 1H), 3.17 (dd, J = 15.9, 7.4 Hz, 1H), 2.83 (d, J = 16.8 Hz, 1H), 1.79 – 1.66 (m, 2H), 1.52 – 1.43 (m, 1H), 1.11 – 0.98 (m, 1H); **¹³C NMR** (126 MHz, CDCl₃) δ 197.7, 145.8, 143.5, 139.3, 137.9, 130.8, 129.0, 128.4, 128.1, 127.4, 127.2, 127.1, 126.7, 121.3, 118.5, 116.4, 115.9, 111.2, 110.8, 110.6, 67.5, 67.4, 51.2, 48.4, 48.1, 46.9, 39.6, 37.7, 29.3, 27.3, 27.2, 26.4, 23.1, 22.9. **HRMS (ESI)**: calcd. for C₂₁H₂₀NO₂ [M+H]⁺: 318.1494, found: 318.1496.

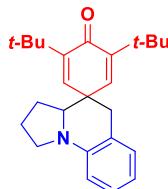
9',10',10a',12'-tetrahydro-1H,8'H-spiro[naphthalene-2,11'-naphtho[1,8-ef]pyrrolo[1,2-a]azepin]-1-one (3ze)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (18.6 mg, 53% yield, 1.5:1 dr) as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 8.11 (t, J = 9.2 Hz, 1H), 7.64 (d, J = 8.1 Hz, 1H), 7.59 (q, J = 6.8 Hz, 1H), 7.43 – 7.35 (m, 1H), 7.29 (dd, J = 14.7, 8.1 Hz, 4H), 6.92 (d, J = 6.7 Hz, 1H), 6.81 (d, J = 9.8 Hz, 1H), 6.74 (t, J = 7.1 Hz, 1H), 6.55 (d, J = 9.8 Hz, 1H), 4.27 (d, J = 9.4 Hz, 1H), 3.56 (dd, J = 21.3, 11.7 Hz, 2H), 3.11 (dd, J = 16.2, 10.2 Hz, 1H), 2.54 – 2.51 (m, 1H), 2.19 – 2.14 (m, 1H), 1.99 – 1.95 (m, 1H), 1.69 – 1.67 (m, 1H), 1.38-1.34 (m, 1H); **¹³C NMR** (126 MHz, CDCl₃) δ 201.3, 199.8, 150.5, 149.8, 138.1, 137.6, 136.6, 136.5, 135.6, 134.9, 134.5, 134.4, 133.8, 130.9, 128.8, 128.2, 128.1, 127.4, 127.4, 127.2, 126.9, 126.9, 126.8, 126.7, 126.6, 126.4, 126.4, 126.0, 125.6, 125.6, 125.5, 125.2, 124.8, 119.4, 118.8, 107.6, 107.4, 72.2, 70.4, 59.7, 57.9, 51.2, 50.7, 42.6, 42.4, 31.6, 28.9, 27.7, 25.5, 23.6, 22.7, 14.2. **HRMS (ESI)**: calcd. for C₂₅H₂₂NO [M+H]⁺: 352.1701, found: 352.1708.

3,5-di-tert-butyl-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,5-dien-4-one (5a)

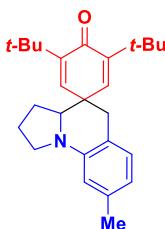


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:200) afforded the

product (21.8 mg, 60% yield) as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 7.14 (t, *J* = 7.7 Hz, 1H), 6.99 (d, *J* = 7.4 Hz, 1H), 6.62 (t, *J* = 7.3 Hz, 1H), 6.51 (d, *J* = 8.1 Hz, 1H), 6.35 (d, *J* = 2.9 Hz, 1H), 6.33 (d, *J* = 2.8 Hz, 1H), 3.63 (dd, *J* = 9.2, 6.2 Hz, 1H), 3.45 (td, *J* = 8.6, 3.6 Hz, 1H), 3.24 (dd, *J* = 16.5, 8.2 Hz, 1H), 3.18 (d, *J* = 15.8 Hz, 1H), 2.55 (d, *J* = 15.8 Hz, 1H), 1.91 (ddd, *J* = 15.2, 9.0, 5.7 Hz, 2H), 1.79 (ddd, *J* = 12.5, 6.3, 3.0 Hz, 1H), 1.27 (s, 9H), 1.13 (s, 9H); **¹³C NMR** (126 MHz, CDCl₃) δ 186.8, 149.1, 148.2, 144.3, 143.5, 139.5, 129.0, 127.7, 118.6, 115.9, 110.6, 64.3, 47.5, 39.9, 38.4, 34.9, 34.9, 30.4, 29.5, 27.7, 23.3. **HRMS (ESI):** calcd. for C₂₅H₃₄NO [M+H]⁺: 364.2640, found: 364.2642.

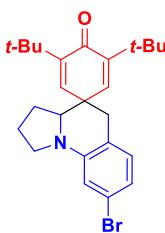
3,5-di-*tert*-butyl-8'-methyl-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,5-dien-4-one (5b)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:200) afforded the product (32.1 mg, 85% yield) as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 6.88 (d, *J* = 7.5 Hz, 1H), 6.45 (d, *J* = 7.4 Hz, 1H), 6.34 (d, *J* = 11.1 Hz, 3H), 3.59 (dd, *J* = 9.0, 6.3 Hz, 1H), 3.43 (td, *J* = 8.7, 3.5 Hz, 1H), 3.24 (q, *J* = 8.1 Hz, 1H), 3.13 (d, *J* = 15.7 Hz, 1H), 2.52 (d, *J* = 15.7 Hz, 1H), 2.31 (s, 3H), 1.95 – 1.83 (m, 2H), 1.77 (dtd, *J* = 9.6, 6.5, 3.0 Hz, 1H), 1.31 – 1.21 (m, 10H), 1.13 (s, 9H); **¹³C NMR** (126 MHz, CDCl₃) δ 186.9, 148.9, 148.1, 144.4, 143.3, 139.7, 137.3, 128.8, 116.7, 115.7, 111.4, 77.3, 77.0, 76.8, 64.3, 47.4, 39.6, 38.7, 34.9, 34.8, 29.6, 29.5, 27.7, 23.3, 21.6. **HRMS (ESI):** calcd. for C₂₆H₃₆NO [M+H]⁺: 378.2797, found: 378.2792.

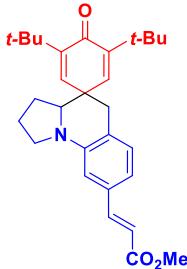
8'-bromo-3,5-di-*tert*-butyl-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,5-dien-4-one (5c)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:200) afforded the product (22.1 mg, 50% yield) as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 6.83 (d, *J* = 7.8 Hz, 1H), 6.72 (dd, *J* = 7.9, 1.9 Hz, 1H), 6.61 (d, *J* = 1.9 Hz, 1H), 6.33 (d, *J* = 2.9 Hz, 1H), 6.24 (d, *J* = 2.9 Hz, 1H), 3.61 (dd, *J* = 9.5, 6.0 Hz, 1H), 3.43 (td, *J* = 8.8, 3.2 Hz, 1H), 3.20 (dd, *J* = 16.4, 8.7 Hz, 1H), 3.08 (dd, *J* = 15.8, 0.8 Hz, 1H), 2.51 (d, *J* = 15.8 Hz, 1H), 1.98 – 1.84 (m, 2H), 1.79 (dtd, *J* = 10.0, 6.4, 3.2 Hz, 1H), 1.29 – 1.23 (m, 11H), 1.13 (s, 10H); **¹³C NMR** (126 MHz, CDCl₃) δ 186.7, 149.4, 148.5, 144.5, 143.7, 138.7, 130.2, 121.3, 118.5, 117.5, 113.1, 77.3, 77.0, 76.8, 64.1, 47.5, 39.5, 38.0, 35.0, 34.9, 29.5, 29.5, 27.7, 23.3. **HRMS (ESI):** calcd. for C₂₅H₃₃BrNO [M+H]⁺: 442.1746, found: 442.1746.

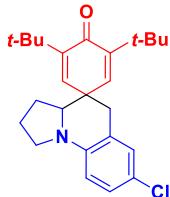
methyl(*E*)-3-(3,5-di-*tert*-butyl-4-oxo-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-*a*]quinoline]-2,5-dien-8'-yl)acrylate (5d)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:200) afforded the product (35.8 mg, 80% yield) as a yellow solid.

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.66 (d, $J = 16.0$ Hz, 1H), 7.00 (d, $J = 7.5$ Hz, 1H), 6.81 (d, $J = 7.5$ Hz, 1H), 6.62 (s, 1H), 6.41 (d, $J = 15.9$ Hz, 1H), 6.34 (s, 1H), 6.27 (s, 1H), 3.81 (s, 3H), 3.68 – 3.59 (m, 1H), 3.48 (t, $J = 8.5$ Hz, 1H), 3.26 (d, $J = 8.2$ Hz, 1H), 3.16 (d, $J = 16.1$ Hz, 1H), 2.58 (d, $J = 16.1$ Hz, 1H), 1.93 (dd, $J = 16.7, 7.8$ Hz, 2H), 1.80 (dd, $J = 7.7, 4.4$ Hz, 1H), 1.31 (s, 1H), 1.26 (s, 9H), 1.12 (s, 9H); **$^{13}\text{C NMR}$** (126 MHz, CDCl_3) δ 186.7, 167.7, 149.4, 148.5, 145.8, 143.7, 143.7, 138.9, 133.8, 129.4, 121.6, 116.6, 116.3, 109.5, 64.3, 51.6, 47.5, 40.0, 38.2, 35.0, 34.9, 29.5, 27.8, 23.3. **HRMS (ESI)**: calcd. for $\text{C}_{29}\text{H}_{38}\text{NO}_3$ [$\text{M}+\text{H}]^+$: 448.2852, found: 448.2856.

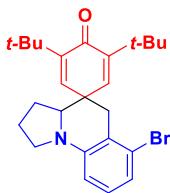
3,5-di-*tert*-butyl-7'-chloro-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-*a*]quinoline]-2,5-dien-4-one (5e)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:200) afforded the product (24.6 mg, 62% yield) as a white solid.

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.08 (d, $J = 8.6$ Hz, 1H), 6.95 (s, 1H), 6.41 (d, $J = 8.6$ Hz, 1H), 6.32 (d, $J = 1.7$ Hz, 1H), 6.25 (s, 1H), 3.60 (dd, $J = 9.0, 6.3$ Hz, 1H), 3.50 – 3.39 (m, 1H), 3.20 (d, $J = 8.2$ Hz, 1H), 3.12 (d, $J = 15.9$ Hz, 1H), 2.51 (d, $J = 15.9$ Hz, 1H), 1.90 (dd, $J = 17.2, 9.0$ Hz, 2H), 1.79 (dd, $J = 7.4, 4.5$ Hz, 1H), 1.34 – 1.23 (m, 10H), 1.13 (s, 9H); **$^{13}\text{C NMR}$** (126 MHz, CDCl_3) δ 186.7, 149.4, 148.5, 143.7, 142.1, 138.8, 128.6, 127.5, 120.3, 120.1, 111.6, 64.3, 47.6, 39.7, 38.1, 35.0, 34.9, 29.5, 27.7, 23.3. **HRMS (ESI)**: calcd. for $\text{C}_{25}\text{H}_{33}\text{ClNO}$ [$\text{M}+\text{H}]^+$: 398.2251, found: 398.2253.

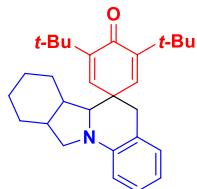
6'-bromo-3,5-di-*tert*-butyl-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-*a*]quinoline]-2,5-dien-4-one (5f)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:200) afforded the product (22.9 mg, 52% yield) as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 6.99 (t, *J* = 7.9 Hz, 1H), 6.89 (d, *J* = 7.9 Hz, 1H), 6.46 (d, *J* = 8.1 Hz, 1H), 6.35 (s, 1H), 6.27 (s, 1H), 3.61 – 3.50 (m, 1H), 3.43 (d, *J* = 3.0 Hz, 1H), 3.27 (d, *J* = 8.2 Hz, 1H), 2.92 (d, *J* = 16.7 Hz, 1H), 2.84 (d, *J* = 16.7 Hz, 1H), 1.98 – 1.84 (m, 2H), 1.81 (dd, *J* = 9.8, 6.3 Hz, 1H), 1.31 (d, *J* = 11.7 Hz, 1H), 1.28 (s, 9H), 1.15 (s, 9H); **¹³C NMR** (126 MHz, CDCl₃) δ 186.7, 149.3, 148.6, 144.9, 143.6, 138.8, 128.4, 125.5, 119.9, 118.2, 109.9, 63.7, 47.7, 40.2, 38.9, 35.0, 34.9, 29.5, 29.5, 27.5, 23.4. **HRMS (ESI)**: calcd. for C₂₅H₃₃BrNO [M+H]⁺: 442.1746, found: 442.1749.

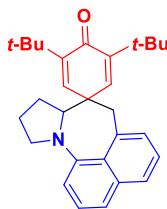
3,5-di-*tert*-butyl-6a',6b',7',8',9',10',10a',11'-octahydro-5'H-spiro[cyclohexane-1,6'-isoindolo[2,1-a]quinoline]-2,5-dien-4-one (5g)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:200) afforded the product (31.3 mg, 75% yield) as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 7.13 (t, *J* = 7.3 Hz, 1H), 6.93 (d, *J* = 7.0 Hz, 1H), 6.57 (t, *J* = 6.9 Hz, 1H), 6.46 (d, *J* = 7.8 Hz, 1H), 6.40 (s, 1H), 6.31 (s, 1H), 3.58 (t, *J* = 7.5 Hz, 1H), 3.39 (d, *J* = 7.2 Hz, 1H), 3.14 (d, *J* = 15.3 Hz, 1H), 2.72 (t, *J* = 9.4 Hz, 1H), 2.40 (d, *J* = 15.4 Hz, 1H), 1.97 (d, *J* = 12.0 Hz, 1H), 1.81 – 1.61 (m, 4H), 1.26 (s, 10H), 1.11 (s, 10H), 1.08 – 0.94 (m, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 186.7, 148.4, 147.0, 144.8, 143.2, 140.2, 128.7, 127.8, 117.8, 115.2, 109.4, 68.8, 51.7, 48.3, 43.4, 40.8, 37.9, 34.9, 34.9, 29.8, 29.5, 29.3, 29.2, 25.7. **HRMS (ESI)**: calcd. for C₂₉H₄₀NO [M+H]⁺: 418.3110, found: 418.3105.

3,5-di-*tert*-butyl-8a',9',10',11'-tetrahydro-7'H-spiro[cyclohexane-1,8'-naphtho[1,8-ef]pyrrolo[1,2-a]azepine]-2,5-dien-4-one (5h)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:200) afforded the product (37.8 mg, 91% yield) as a brown solid.

¹H NMR (500 MHz, CDCl₃) δ 7.65 (d, *J* = 8.2 Hz, 1H), 7.31 (s, 3H), 7.05 (d, *J* = 6.6 Hz, 1H), 6.86 (s, 1H), 6.71 (s, 2H), 3.78 (d, *J* = 13.0 Hz, 1H), 3.66 (d, *J* = 9.3 Hz, 1H), 3.56 (d, *J* = 6.4 Hz, 1H), 3.07 (d, *J* = 8.7 Hz, 1H), 2.48 (d, *J* = 13.0 Hz, 1H), 1.92 (d, *J* = 6.8 Hz, 2H), 1.67 – 1.59 (m, 1H), 1.33 (s, 9H), 1.24 (s, 10H); **¹³C NMR** (126 MHz, CDCl₃) δ 186.7, 150.5, 148.5, 147.5, 142.9, 142.9, 135.5, 134.7, 127.3, 126.8, 125.9, 125.8, 125.5, 119.1, 107.6, 70.8, 51.7, 49.4, 44.3, 35.1, 34.9, 29.6, 26.9, 25.3. **HRMS (ESI)**: calcd. for C₂₉H₃₆NO [M+H]⁺: 414.2797, found: 414.2790.

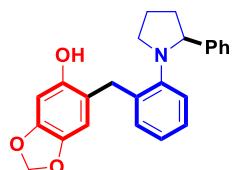
1',2',3a,3',3a',4-hexahydro-5'H,6H-spiro[benzo[d][1,3]dioxole-5,4'-pyrrolo[1,2-a]quinolin]-6-one (6a)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (17.8 mg, 60% yield) as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 7.12 (t, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 7.2 Hz, 1H), 6.46 (d, *J* = 7.9 Hz, 1H), 5.62 (s, 1H), 5.52 (s, 1H), 5.31 (s, 1H), 4.68 (dd, *J* = 10.9, 5.4 Hz, 1H), 3.99 (d, *J* = 6.4 Hz, 1H), 3.32 (dd, *J* = 15.2, 7.6 Hz, 2H), 2.98 (d, *J* = 15.9 Hz, 1H), 2.80 (d, *J* = 15.9 Hz, 1H), 2.09 – 1.88 (m, 4H), 1.81 (t, *J* = 11.8 Hz, 1H), 1.54 (d, *J* = 8.3 Hz, 1H); **¹³C NMR** (126 MHz, CDCl₃) δ 197.8, 186.8, 149.3, 148.4, 146.5, 143.9, 143.8, 139.4, 139.2, 135.7, 129.6, 128.8, 127.1, 119.0, 115.0, 109.2, 64.4, 47.5, 39.7, 38.4, 35.0, 34.9, 30.3, 29.6, 29.6, 27.8, 26.7, 23.3. **HRMS (ESI)**: calcd. for C₁₈H₂₀NO₃ [M+H]⁺: 298.1443, found: 298.1445.

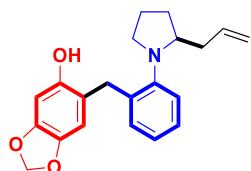
6-(2-(2-phenylpyrrolidin-1-yl)benzyl)benzo[d][1,3]dioxol-5-ol (7a)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (24.6 mg, 66% yield) as a red solid.

¹H NMR (500 MHz, CDCl₃) δ 10.00 (s, 1H), 7.11 (d, *J* = 22.5 Hz, 7H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.92 (t, *J* = 7.1 Hz, 1H), 6.51 (s, 1H), 6.38 (s, 1H), 5.70 (d, *J* = 7.0 Hz, 2H), 4.21 (t, *J* = 7.2 Hz, 1H), 3.45 (s, 1H), 3.36 (q, *J* = 14.2 Hz, 2H), 2.99 (dd, *J* = 15.7, 8.5 Hz, 1H), 2.37 (dd, *J* = 16.6, 9.2 Hz, 1H), 2.20 (s, 2H), 2.03 (d, *J* = 3.8 Hz, 1H); **¹³C NMR** (126 MHz, CDCl₃) δ 149.2, 146.8, 146.1, 140.9, 139.7, 138.6, 130.6, 128.4, 128.1, 127.6, 127.5, 125.9, 122.4, 119.9, 108.8, 100.8, 99.4, 70.4, 56.1, 33.5, 32.9, 23.2. **HRMS (ESI)**: calcd. for C₂₄H₂₄NO₃ [M+H]⁺: 374.1756, found: 374.1758.

6-(2-(2-allylpyrrolidin-1-yl)benzyl)benzo[d][1,3]dioxol-5-ol (7b)



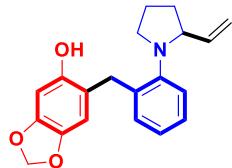
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (25.3 mg, 75% yield) as a red solid.

¹H NMR (500 MHz, CDCl₃) δ 7.08 (t, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 7.2 Hz, 1H), 6.54 (t, *J* = 7.2 Hz, 1H), 6.39 (d, *J* = 8.0 Hz, 1H), 5.98 (td, *J* = 16.6, 7.9 Hz, 1H), 5.49 (d, *J* = 9.9 Hz, 2H), 5.19 (dd, *J* = 18.4, 14.1 Hz, 2H), 5.01 (s, 1H), 4.61 (s, 1H), 3.77 (dd, *J* = 10.4, 4.4 Hz, 1H), 3.29 (t, *J* = 9.1 Hz, 1H), 3.20 (q, *J* = 8.6 Hz, 1H), 3.02 (d, *J* = 14.9 Hz, 1H), 2.70 (d, *J* = 14.9 Hz, 1H), 2.55 (dd, *J* = 13.2, 7.2 Hz, 1H), 2.47 (dd, *J* = 13.2, 7.3 Hz, 1H), 2.34 (dd, *J* = 11.6, 5.7 Hz, 1H), 2.06 – 1.96 (m, 1H), 1.94 – 1.79 (m, 1H), 1.65 (dd, *J* = 20.1, 10.8 Hz, 1H); **¹³C NMR** (126 MHz, CDCl₃) δ 145.9, 145.6, 143.7, 133.7,

129.3, 127.3, 120.0, 119.5, 114.9, 109.4, 99.4, 99.3, 96.1, 62.1, 46.2, 42.9, 41.7, 36.4, 30.1, 23.7.

HRMS (ESI): calcd. for $C_{21}H_{24}NO_3$ [M+H]⁺: 338.1756, found: 338.1753.

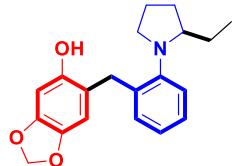
6-(2-(2-vinylpyrrolidin-1-yl)benzyl)benzo[d][1,3]dioxol-5-ol (7c)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (24.2 mg, 75% yield) as a red solid.

¹H NMR (500 MHz, CDCl₃) δ 10.40 (s, 1H), 7.32 (d, *J* = 7.4 Hz, 1H), 7.21 – 7.11 (m, 2H), 7.08 (t, *J* = 7.1 Hz, 1H), 6.70 (s, 1H), 6.43 (s, 1H), 5.80 (d, *J* = 15.5 Hz, 2H), 5.74 (dd, *J* = 17.5, 8.9 Hz, 1H), 5.07 (d, *J* = 17.1 Hz, 1H), 5.00 (d, *J* = 10.2 Hz, 1H), 3.92 (d, *J* = 14.0 Hz, 1H), 3.89 – 3.79 (m, 1H), 3.66 (d, *J* = 14.0 Hz, 1H), 3.58 (t, *J* = 8.8 Hz, 1H), 2.90 – 2.79 (m, 1H), 2.20 (dd, *J* = 9.5, 6.5 Hz, 1H), 2.17 – 2.07 (m, 1H), 2.05 – 1.92 (m, 2H); **¹³C NMR** (126 MHz, CDCl₃) δ 149.6, 146.9, 145.0, 140.7, 138.5, 137.1, 130.7, 127.4, 125.9, 121.8, 119.7, 118.3, 108.7, 100.7, 99.4, 67.1, 55.9, 33.8, 30.9, 22.3. **HRMS (ESI):** calcd. for $C_{20}H_{22}NO_3$ [M+H]⁺: 324.1600, found: 324.1601.

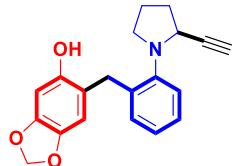
6-(2-(2-ethylpyrrolidin-1-yl)benzyl)benzo[d][1,3]dioxol-5-ol (7d)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (21.1 mg, 65% yield) as a red solid.

¹H NMR (500 MHz, CDCl₃) δ 10.57 (s, 1H), 7.35 (d, *J* = 7.4 Hz, 1H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 1H), 7.11 (t, *J* = 7.1 Hz, 1H), 6.70 (s, 1H), 6.42 (s, 1H), 5.81 (d, *J* = 12.5 Hz, 2H), 3.91 (d, *J* = 13.9 Hz, 1H), 3.69 (d, *J* = 13.9 Hz, 1H), 3.50 (t, *J* = 8.8 Hz, 1H), 3.28 – 3.12 (m, 1H), 2.78 (q, *J* = 8.7 Hz, 1H), 2.31 – 2.19 (m, 1H), 2.17 – 2.04 (m, 1H), 1.95 (d, *J* = 8.7 Hz, 1H), 1.74 (dd, *J* = 19.1, 9.4 Hz, 1H), 1.51 (dd, *J* = 11.1, 9.0 Hz, 1H), 1.33 (dt, *J* = 20.2, 8.4 Hz, 1H), 0.85 (t, *J* = 7.3 Hz, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 149.5, 146.8, 145.7, 140.7, 139.1, 130.8, 127.6, 126.0, 121.4, 119.9, 108.7, 100.7, 99.5, 65.8, 56.4, 33.8, 29.3, 24.9, 21.8, 11.5. **HRMS (ESI):** calcd. for $C_{20}H_{24}NO_3$ [M+H]⁺: 326.1756, found: 326.1759.

6-(2-(2-ethynylpyrrolidin-1-yl)benzyl)benzo[d][1,3]dioxol-5-ol (7e)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (26.3 mg, 82% yield) as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 9.86 (s, 1H), 7.34 (d, *J* = 7.4 Hz, 1H), 7.25 (d, *J* = 6.8 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 7.2 Hz, 1H), 6.72 (s, 1H), 6.41 (s, 1H), 5.81 (d, *J* = 14.0 Hz, 2H), 4.21 (s, 1H), 3.87 (d, *J* = 14.1 Hz, 1H), 3.79 (d, *J* = 14.1 Hz, 1H), 3.53 (dd, *J* = 15.4, 7.5 Hz, 1H), 3.02 (t, *J* = 9.9 Hz, 1H), 2.53 – 2.38 (m, 1H), 2.27 – 2.12 (m, 3H), 2.12 – 1.98 (m, 1H); **¹³C NMR** (126 MHz, CDCl₃) δ 149.8, 146.9, 143.7, 140.6, 137.9, 130.7, 127.3, 126.5, 122.2, 119.1, 108.7, 100.8, 99.0, 81.8, 73.7, 55.8, 51.7, 33.5, 31.8, 22.2. **HRMS (ESI)**: calcd. for C₂₀H₂₀NO₃ [M+H]⁺: 322.1443, found: 322.1444.

Reference

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

5. Crystal Structures and Data

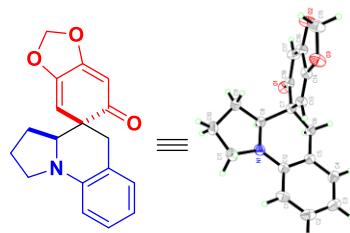


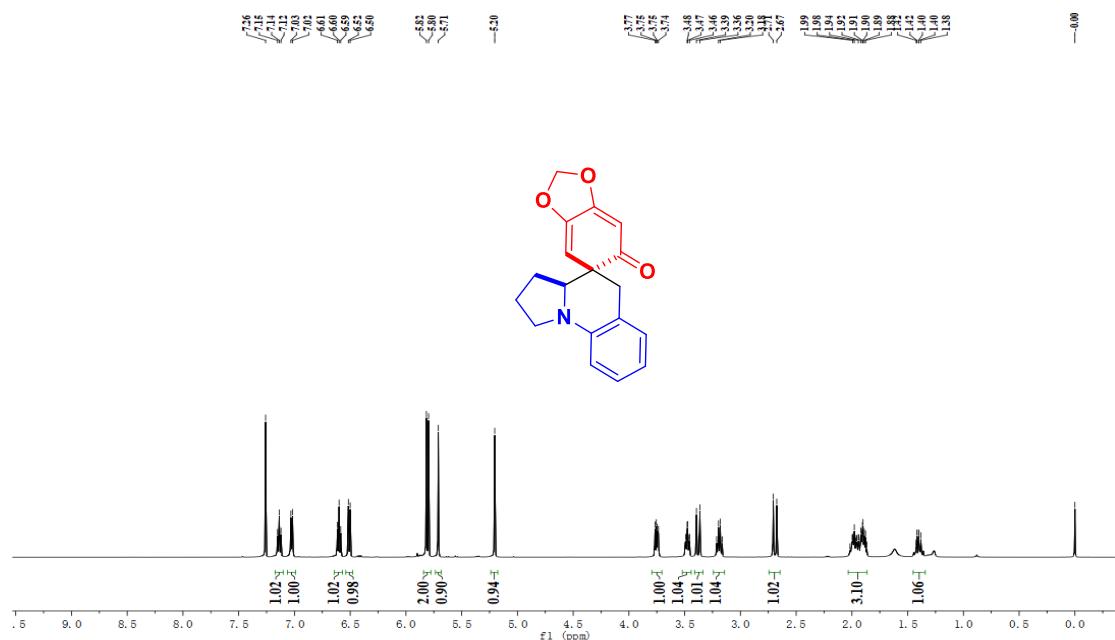
Table 1. Crystal data and structure refinement for 3a.

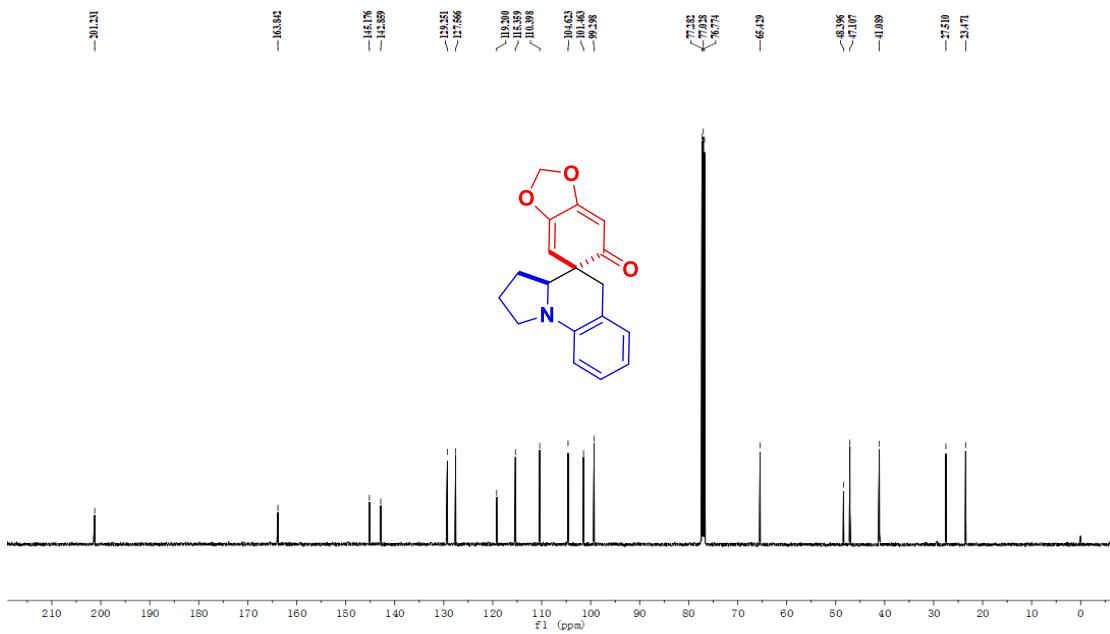
Identification code	3a	
Empirical formula	C ₁₈ H ₁₇ NO ₃	
Formula weight	295.33	
Temperature	293(2) K	
Wavelength	1.54184 Å	
Crystal system, space group	triclinic, P-1	
Unit cell dimensions	a = 8.5960(6) Å	alpha = 101.132(7) deg.
	b = 9.3242(8) Å	beta = 103.244(6) deg.
	c = 9.5215(7) Å	gamma = 96.071(6) deg.
Volume	719.84(10) Å ³	
Z, Calculated density	2, 1.363 Mg/m ³	
Absorption coefficient	0.754 mm ⁻¹	
F(000)	312	
Crystal size	0.08 x 0.07 x 0.07 mm	
Theta range for data collection	4.89 to 67.23 deg.	
Limiting indices	-10<=h<=6, -10<=k<=11, -11<=l<=11	
Reflections collected / unique	4109 / 2581 [R(int) = 0.0241]	
Completeness to theta = 67.23	99.9 %	
Max. and min. transmission	0.9491 and 0.9421	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2581 / 0 / 200	

Goodness-of-fit on F^2	1.111
Final R indices [I>2sigma(I)]	R1 = 0.0510, wR2 = 0.1461
R indices (all data)	R1 = 0.0547, wR2 = 0.1520
Extinction coefficient	0.039(4)
Largest diff. peak and hole	0.380 and -0.241 e.A^-3

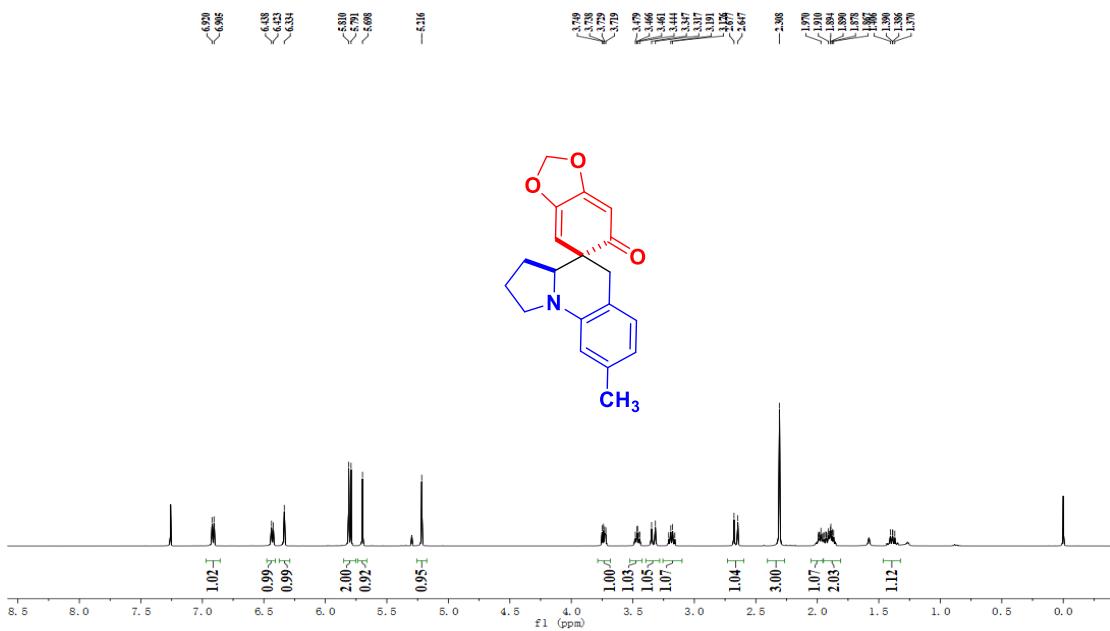
6. ^1H and ^{13}C NMR Spectra

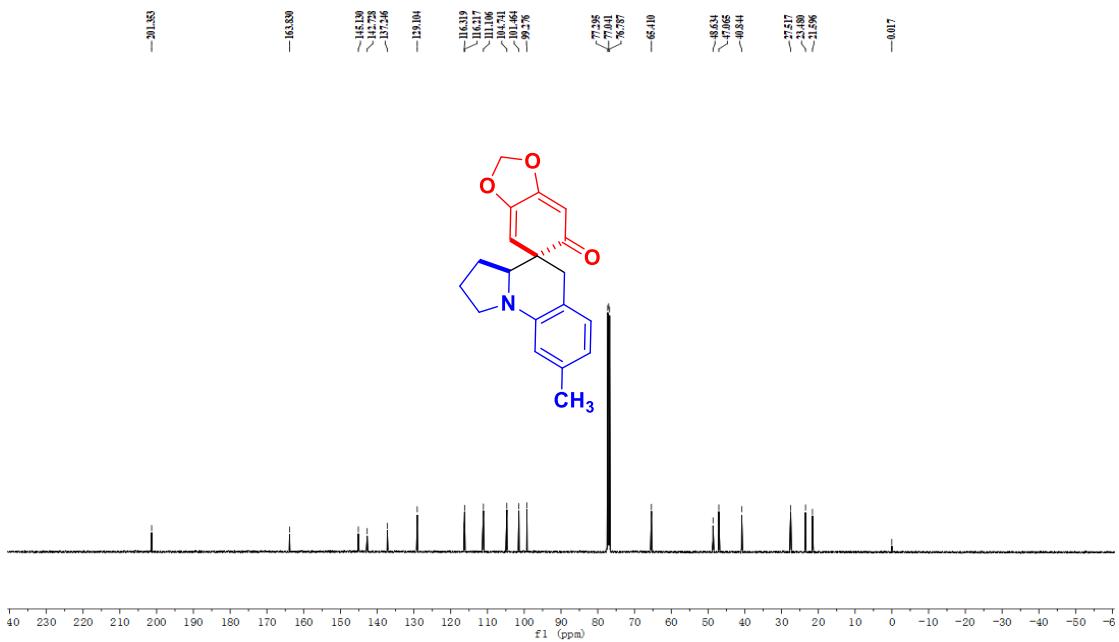
1',2',3',3a'-tetrahydro-5'H,6H-spiro[benzo[d][1,3]dioxole-5,4'-pyrrolo[1,2-a]quinolin]-6-one (3a)



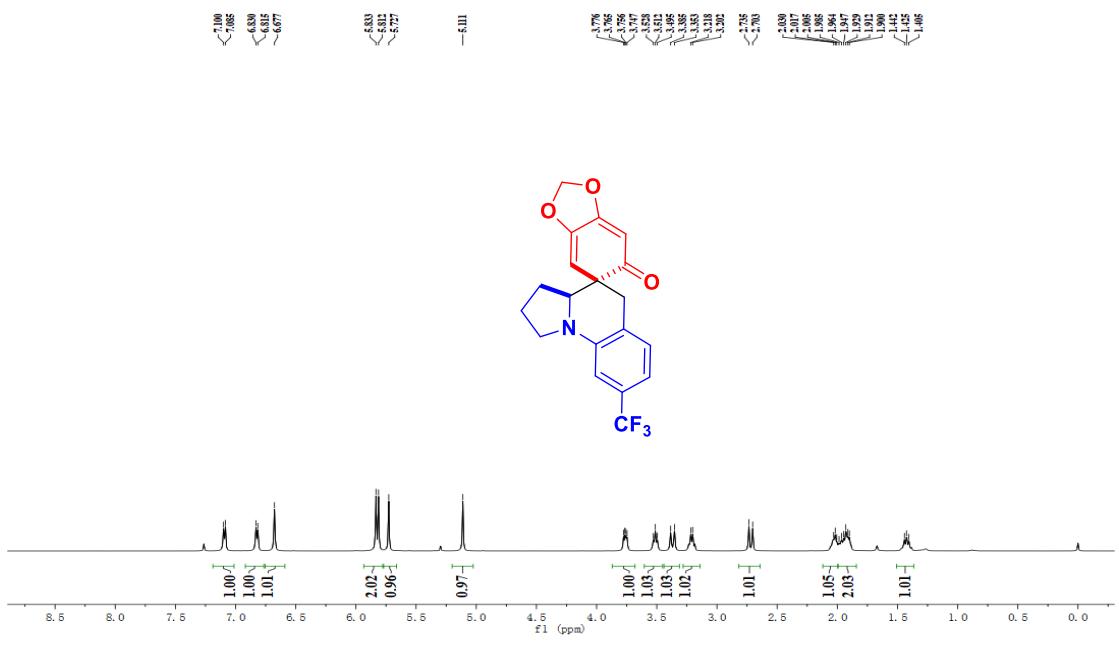


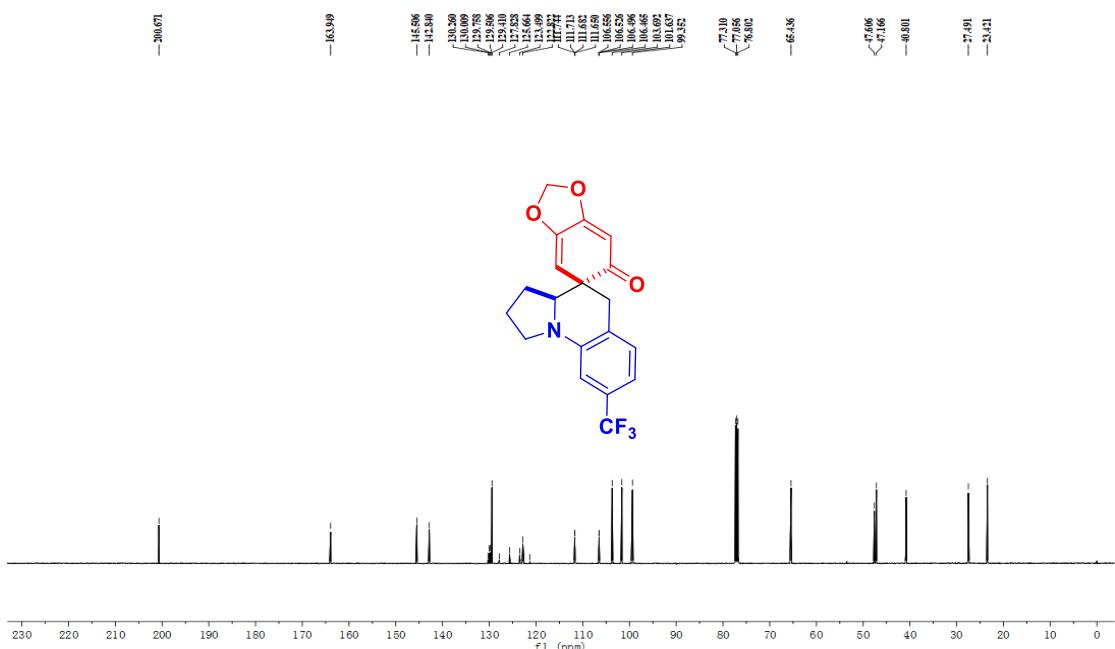
8'-methyl-1',2',3',3a'-tetrahydro-5'H,6H-spiro[benzo[d][1,3]dioxole-5,4'-pyrrolo[1,2-a]quinolin]-6-one (3b)



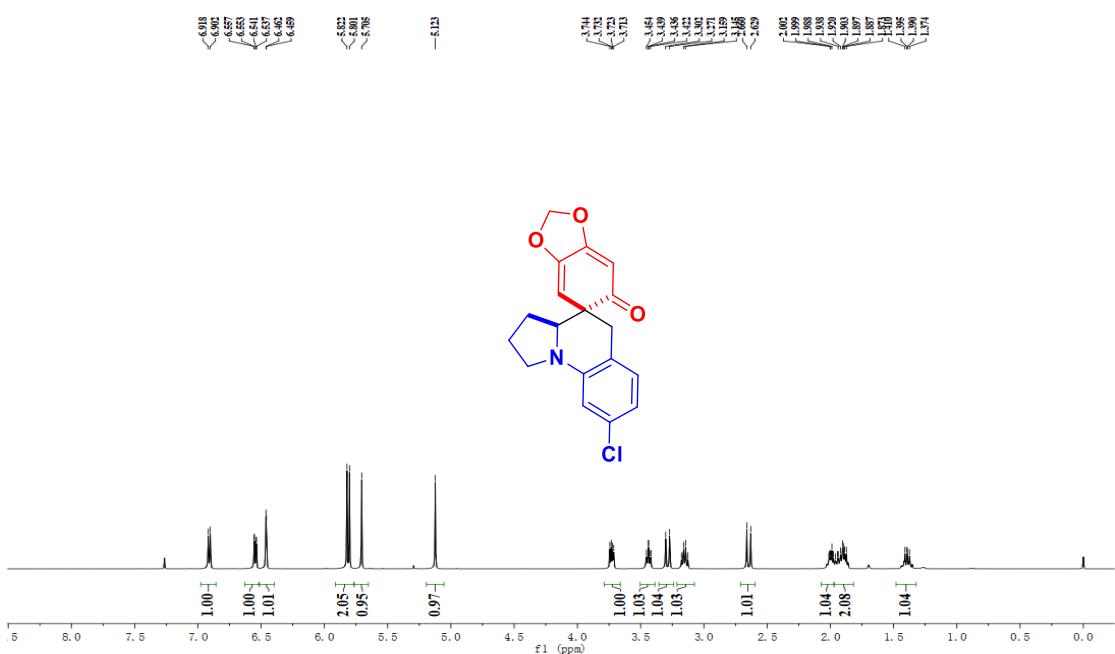


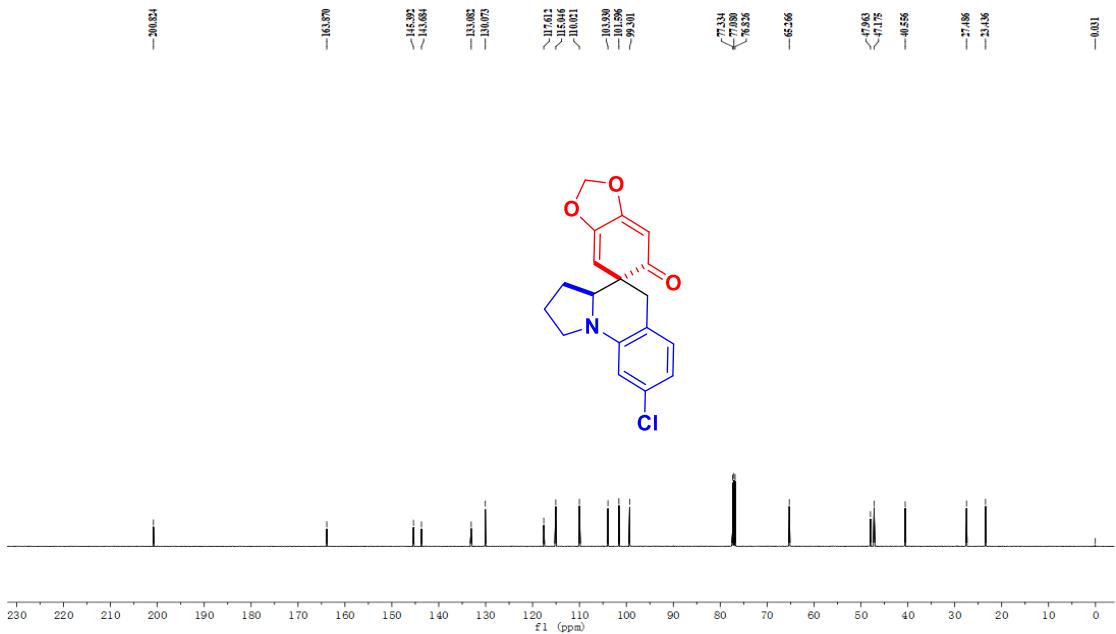
8'-(trifluoromethyl)-1',2',3',3a'-tetrahydro-5'H,6H-spiro[benzo[d][1,3]dioxole-5,4'-pyrrolo[1,2-a]quinolin]-6-one (3c)



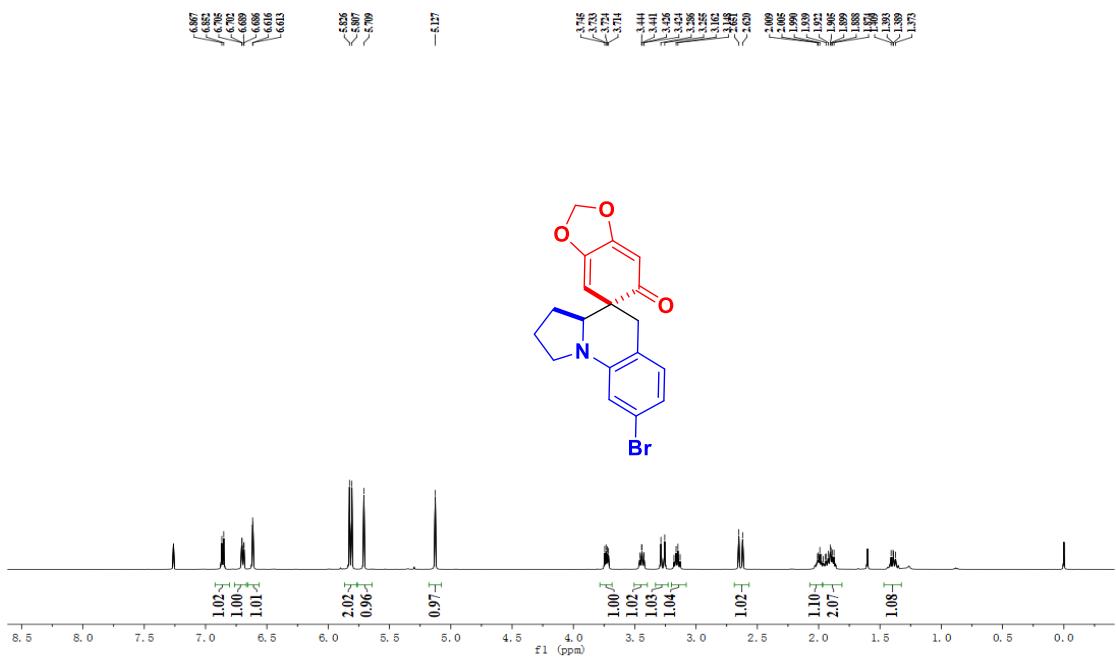


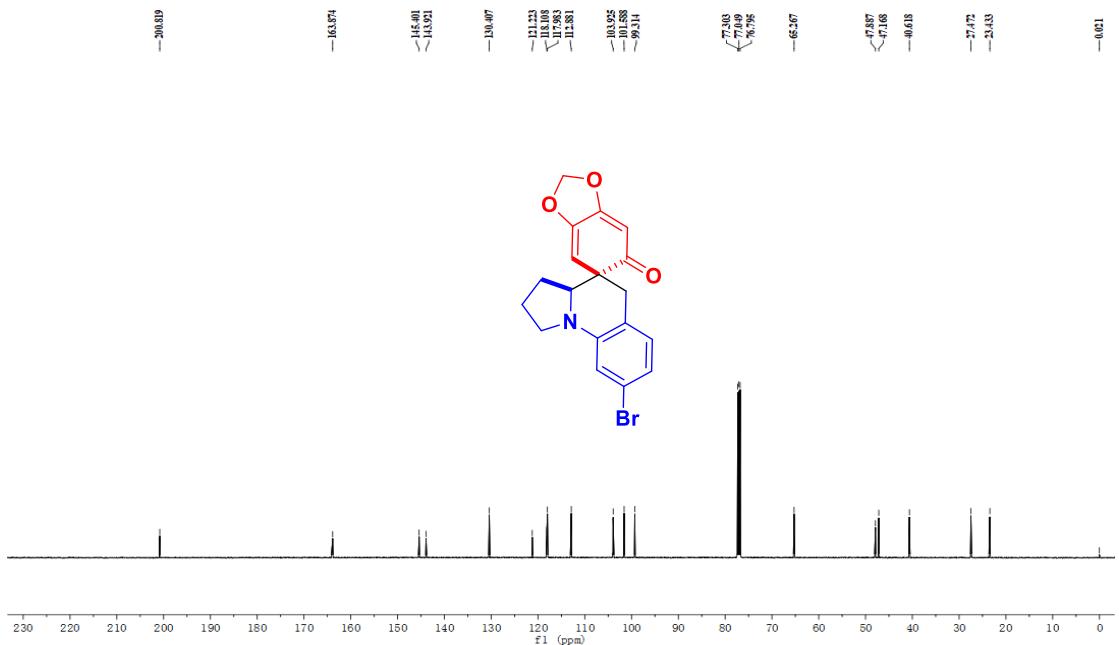
8'-chloro-1',2',3',3a'-tetrahydro-5'H,6H-spiro[benzo[d][1,3]dioxole-5,4'-pyrrolo[1,2-a]quinolin-6-one (3d)



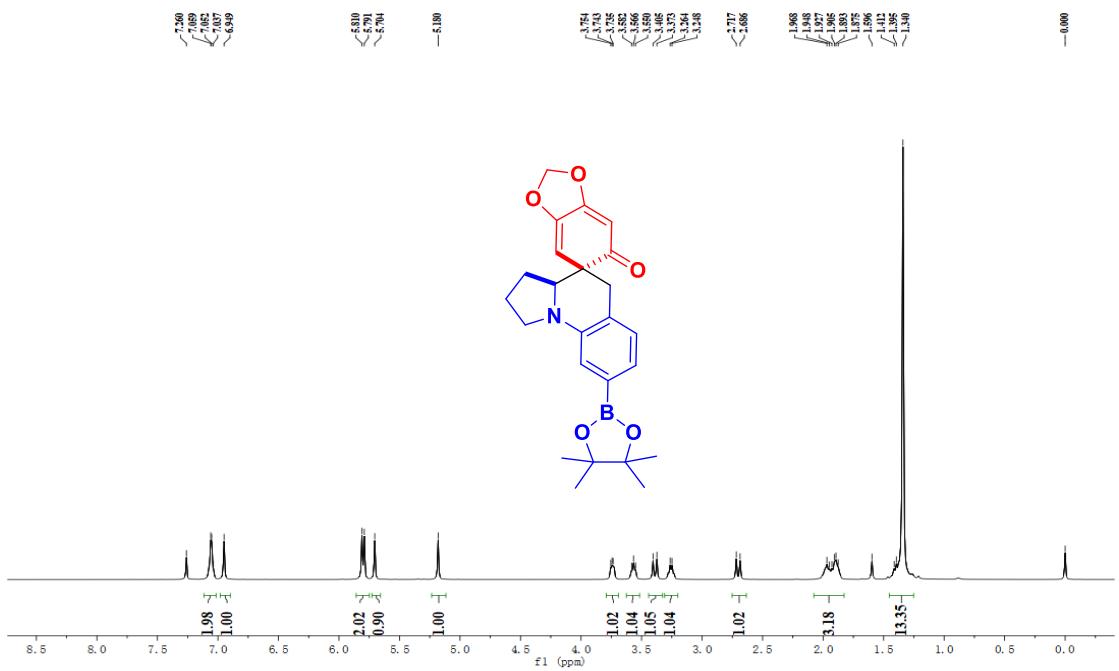


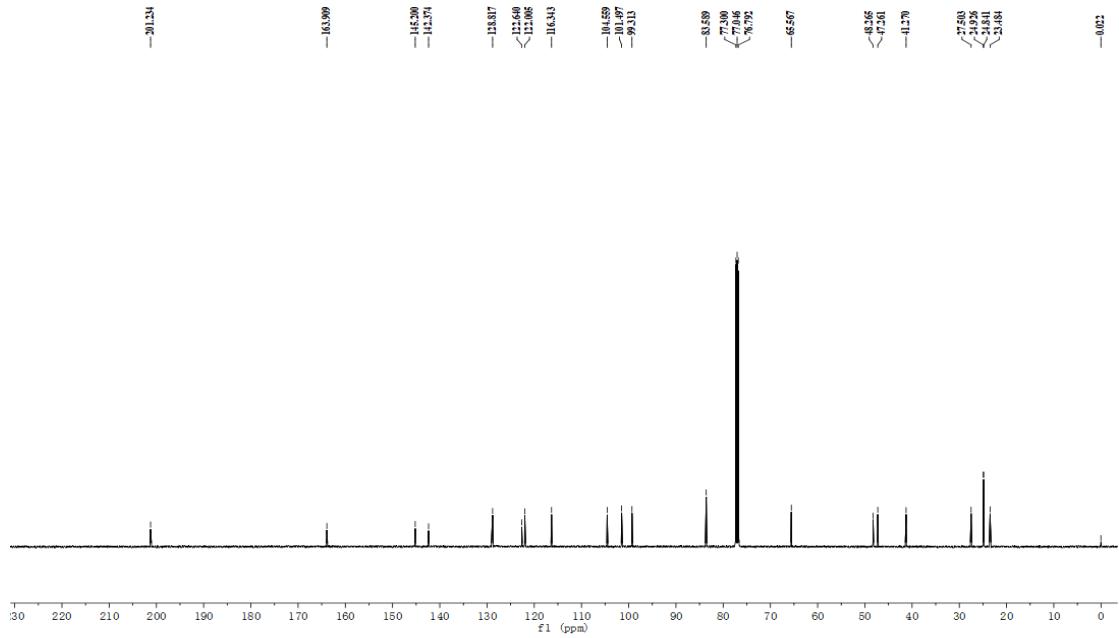
8'-bromo-1',2',3',3a'-tetrahydro-5'H,6H-spiro[benzo[d][1,3]dioxole-5,4'-pyrrolo[1,2-a]quinolin-6-one (3e)



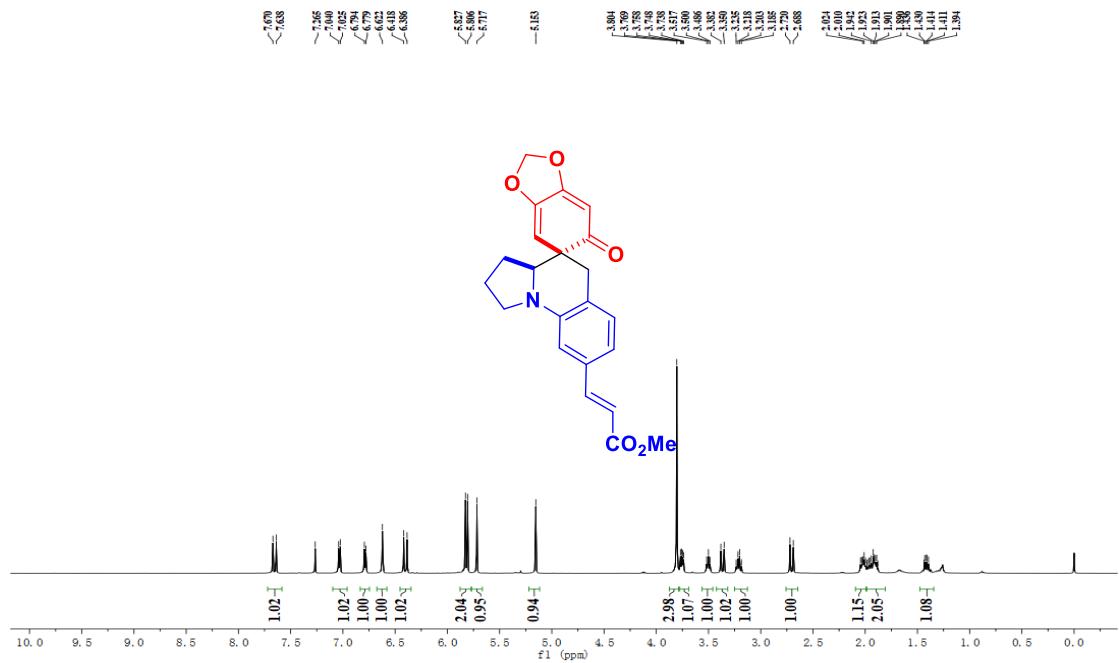


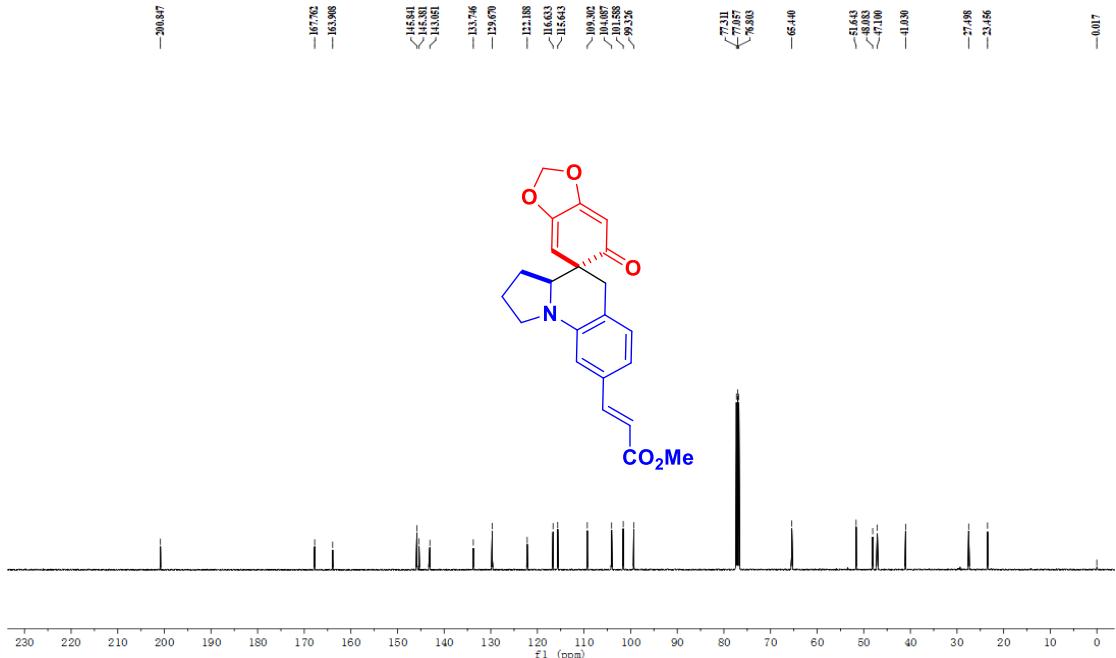
8'-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)-1',2',3',3a'-tetrahydro-5'H,6H-spiro[benzo[d][1,3]dioxole-5,4'-pyrrolo[1,2-a]quinolin]-6-one (3f)



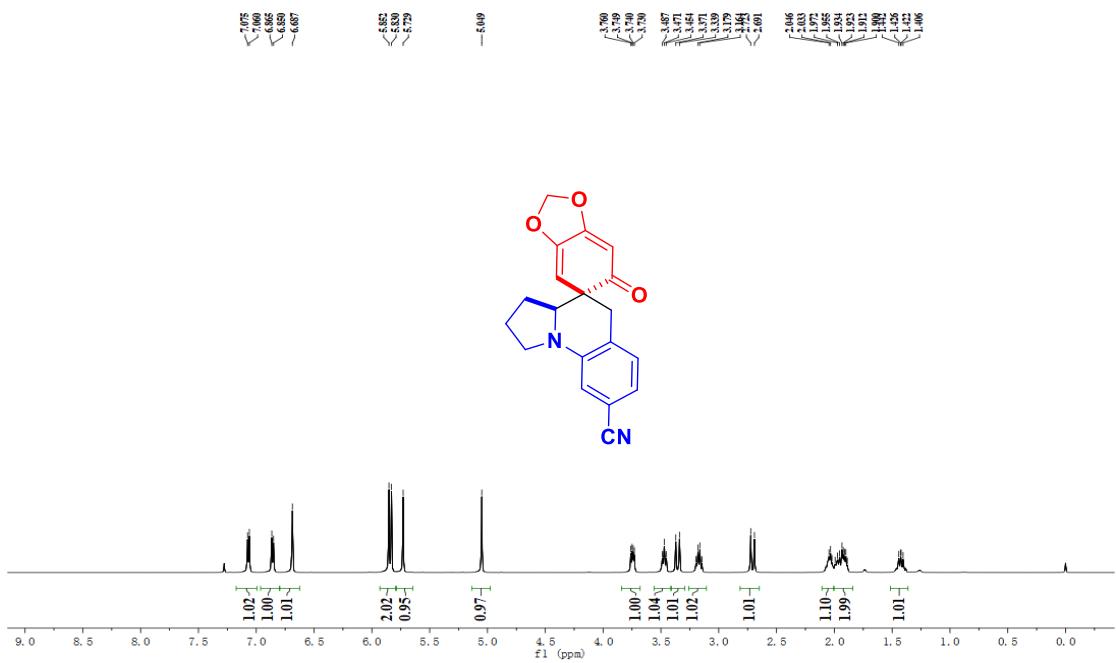


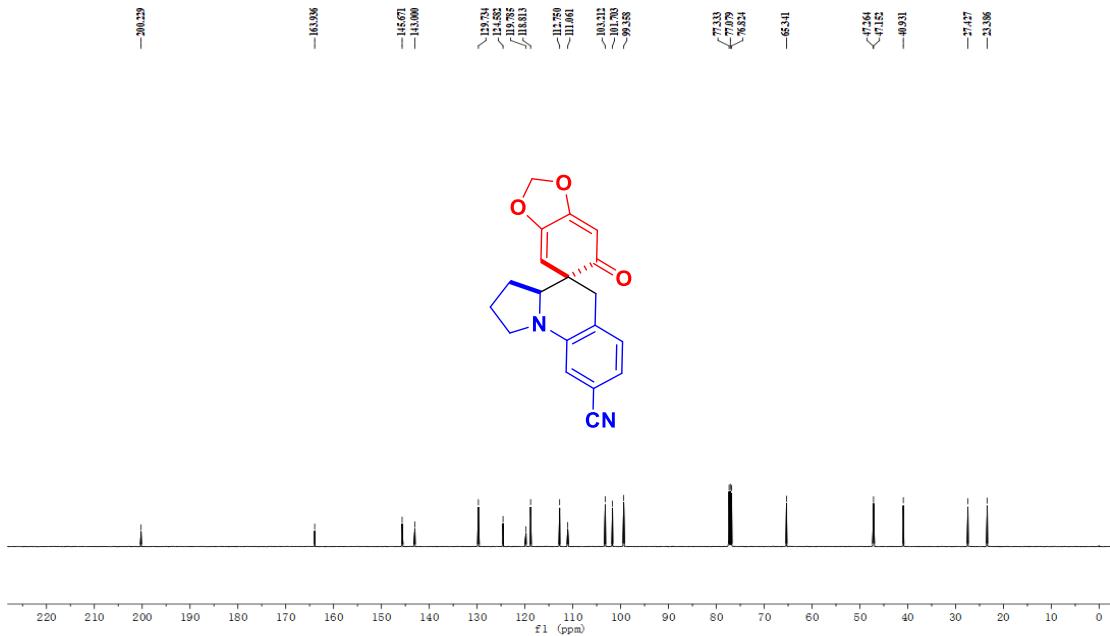
methyl(*E*)-3-(6-oxo-1',2',3',3a'-tetrahydro-5'H,6H-spiro[benzo[d][1,3]dioxole-5,4'-pyrrolo[1,2-a]quinolin]-8'-yl)acrylate (3g)



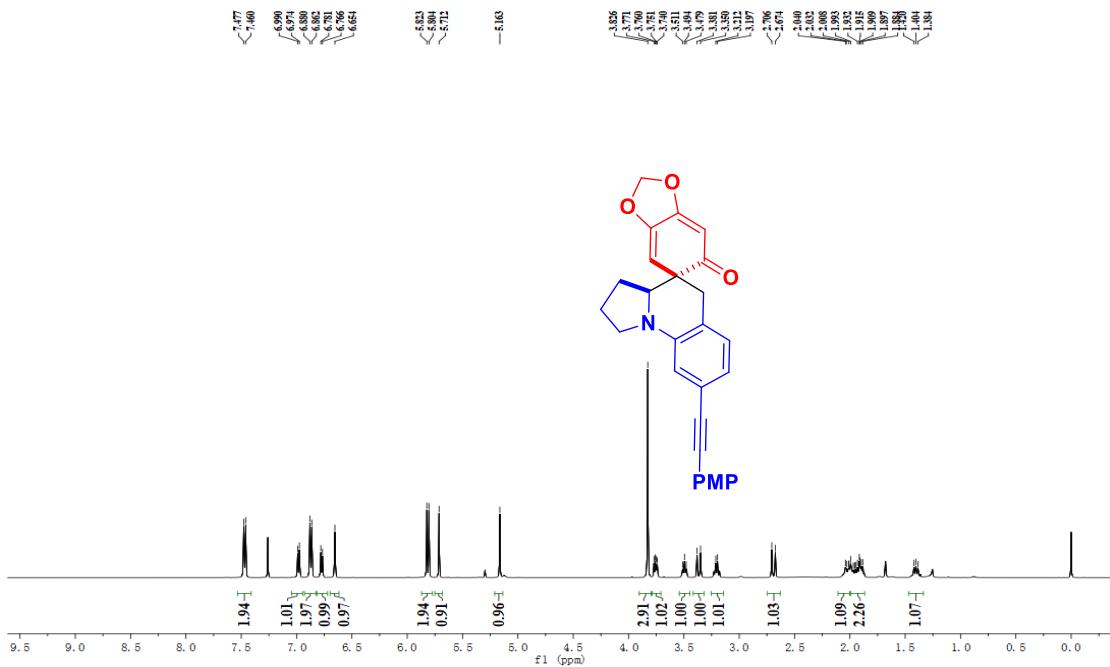


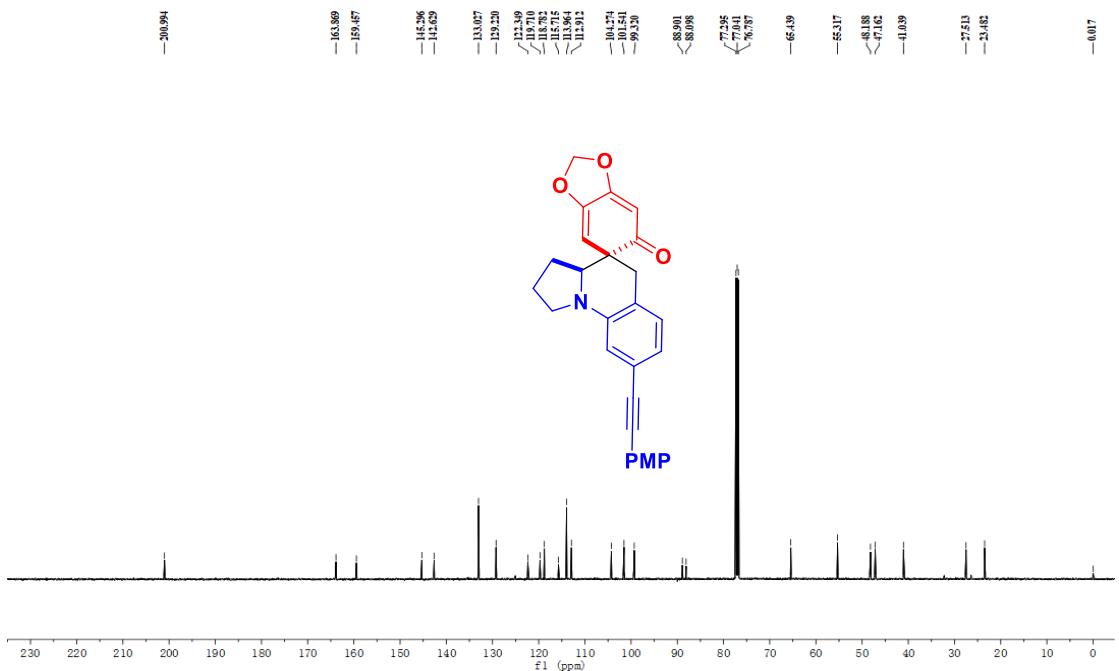
6-oxo-1',2',3',3a'-tetrahydro-5'H,6H-spiro[benzo[d][1,3]dioxole-5,4'-pyrrolo[1,2-a]quinoline]-8'-carbonitrile (3h)



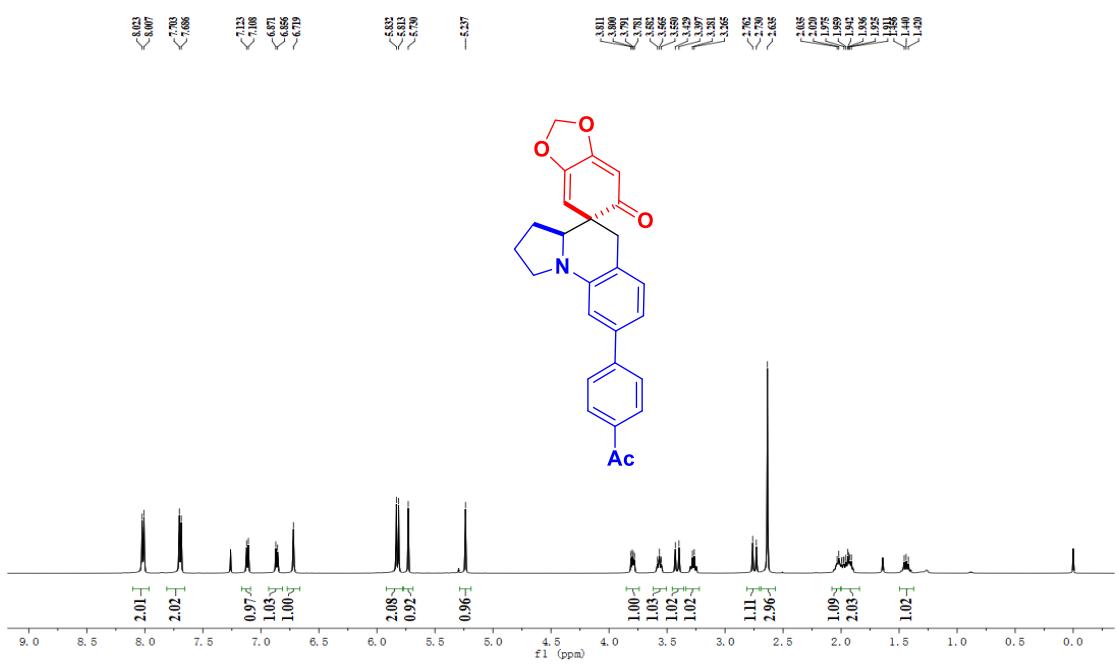


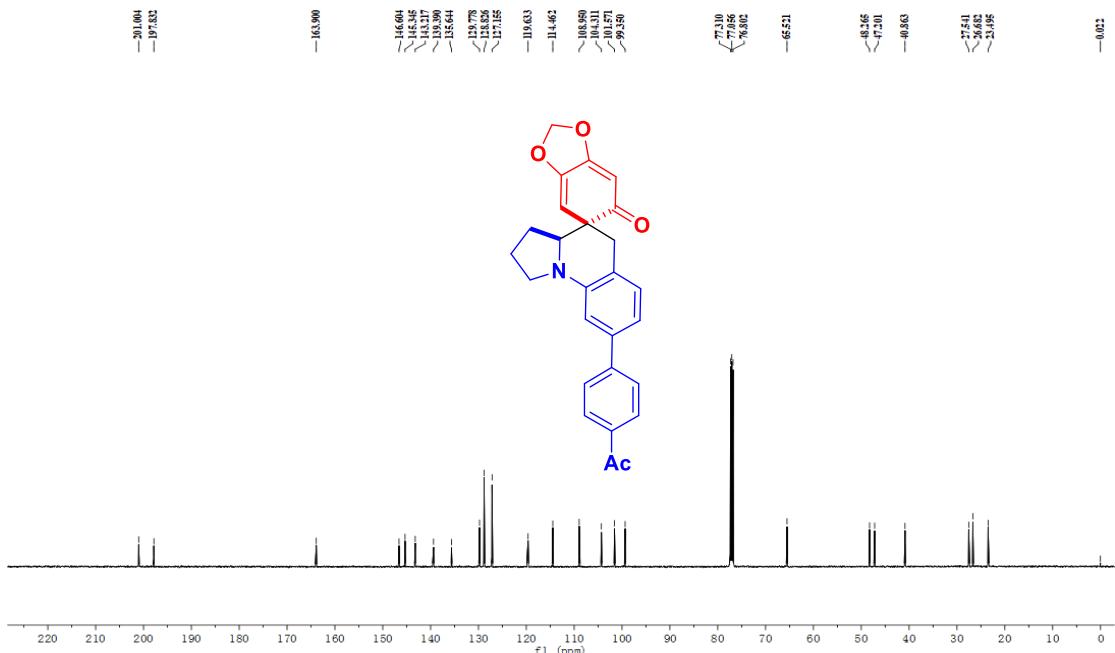
8'-(4-methoxyphenyl)ethynyl)-1',2',3',3a'-tetrahydro-5'H,6H-spiro[benzo[d][1,3]dioxole-5,4'-pyrrolo[1,2-a]quinolin]-6-one (3i)



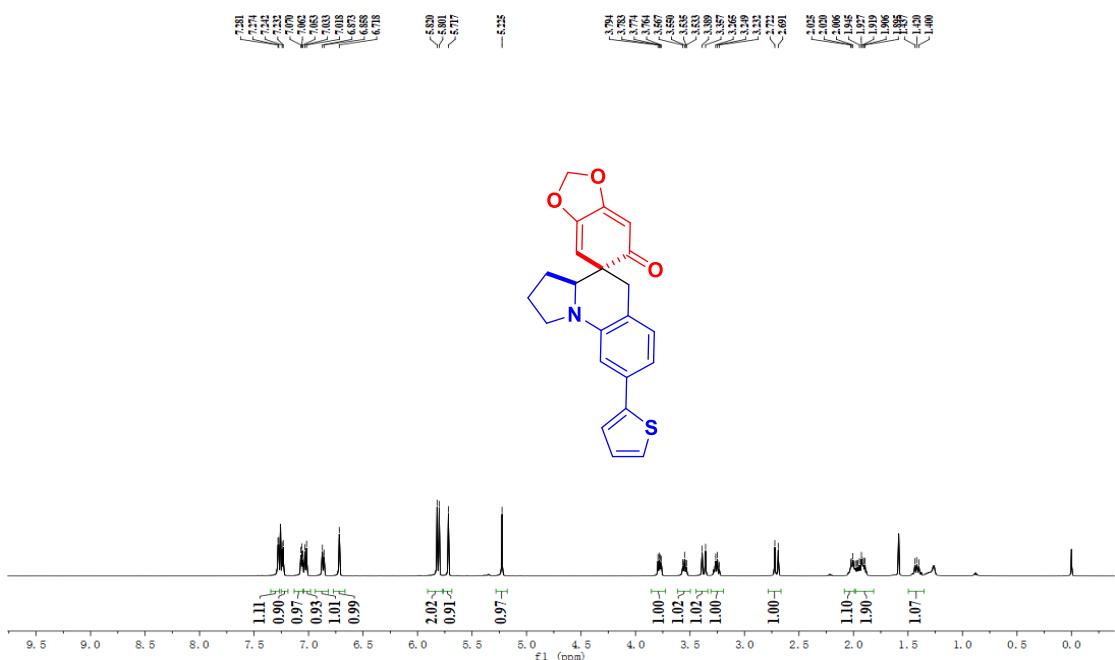


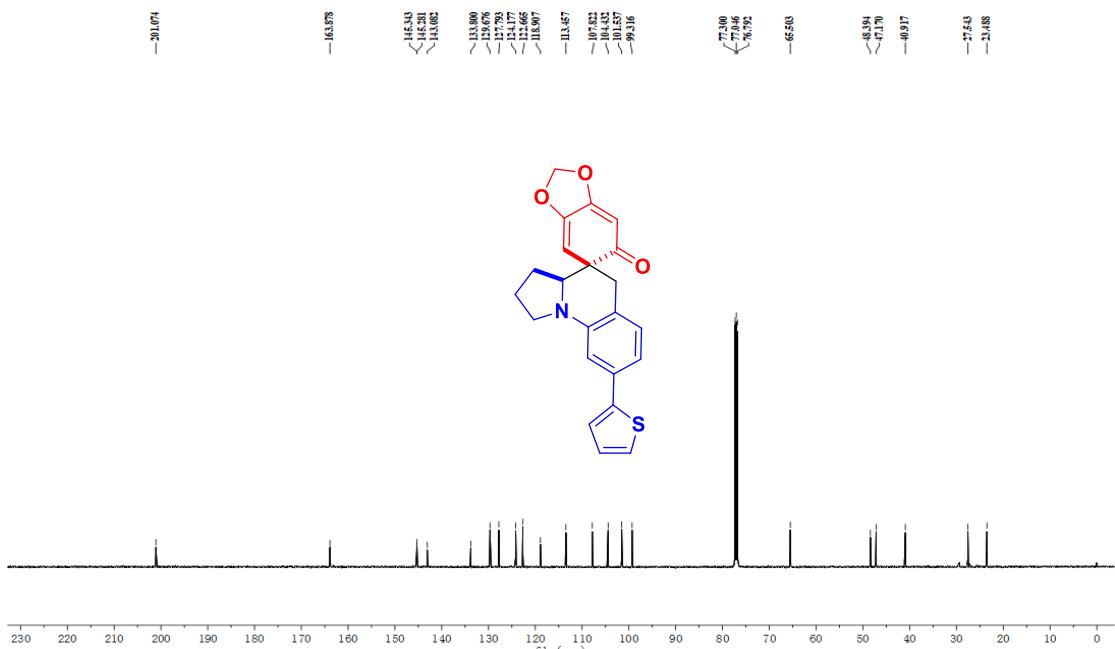
8'-(4-acetylphenyl)-1',2',3',3a'-tetrahydro-5'H,6H-spiro[benzo[d][1,3]dioxole-5,4'-pyrrolo[1,2-a]quinolin]-6-one (3j)



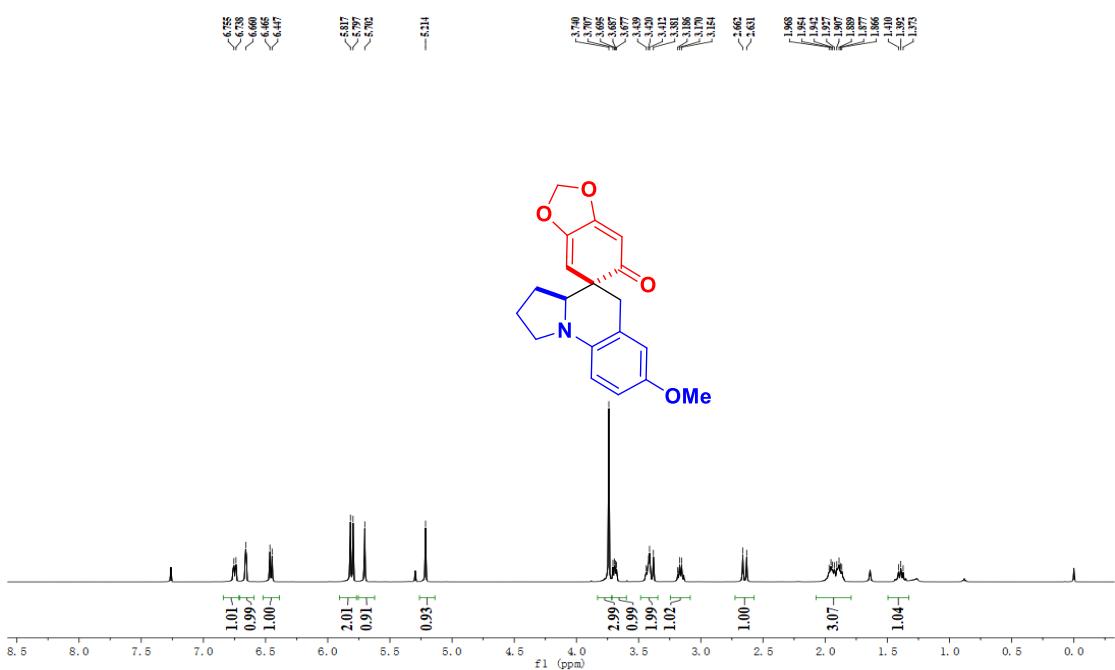


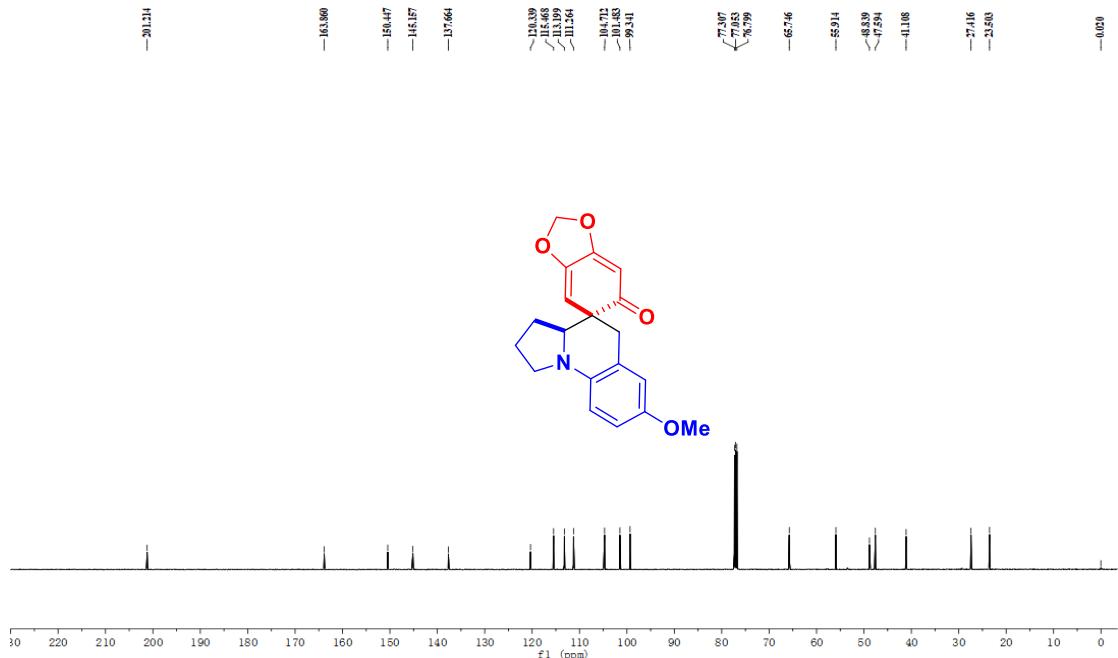
8'-(thiophen-2-yl)-1',2',3',3a'-tetrahydro-5'H,6H-spiro[benzo[d][1,3]dioxole-5,4'-pyrrolo[1,2-a]quinolin]-6-one (3k)



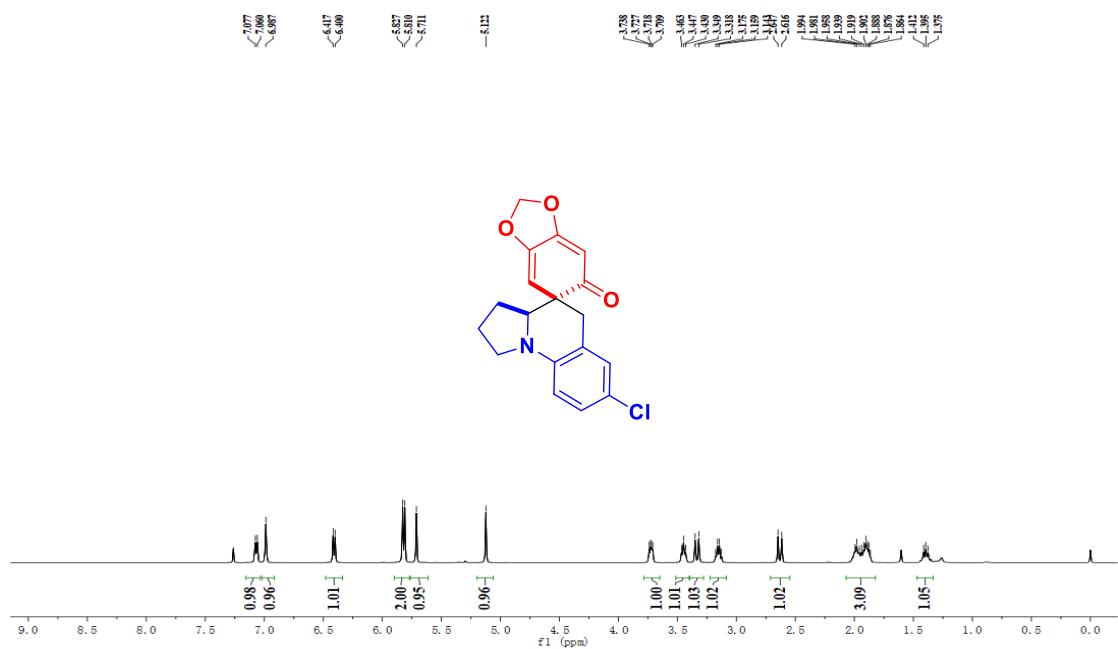


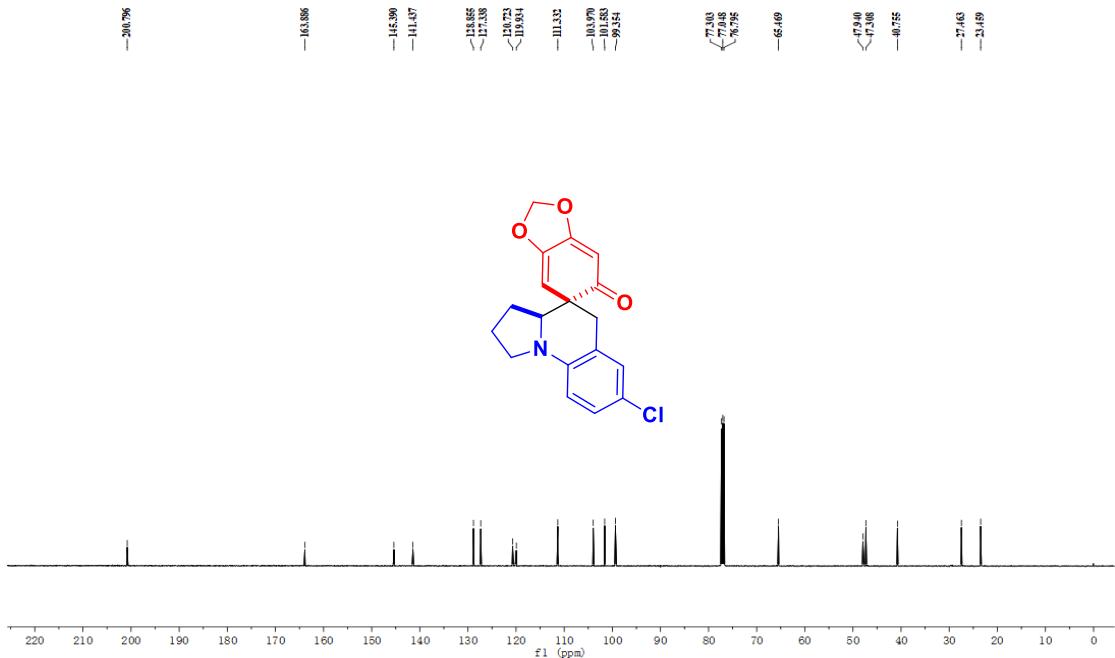
7'-methoxy-1',2',3',3a'-tetrahydro-5'H,6H-spiro[benzo[d][1,3]dioxole-5,4'-pyrrolo[1,2-a]quinolin]-6-one (3l)



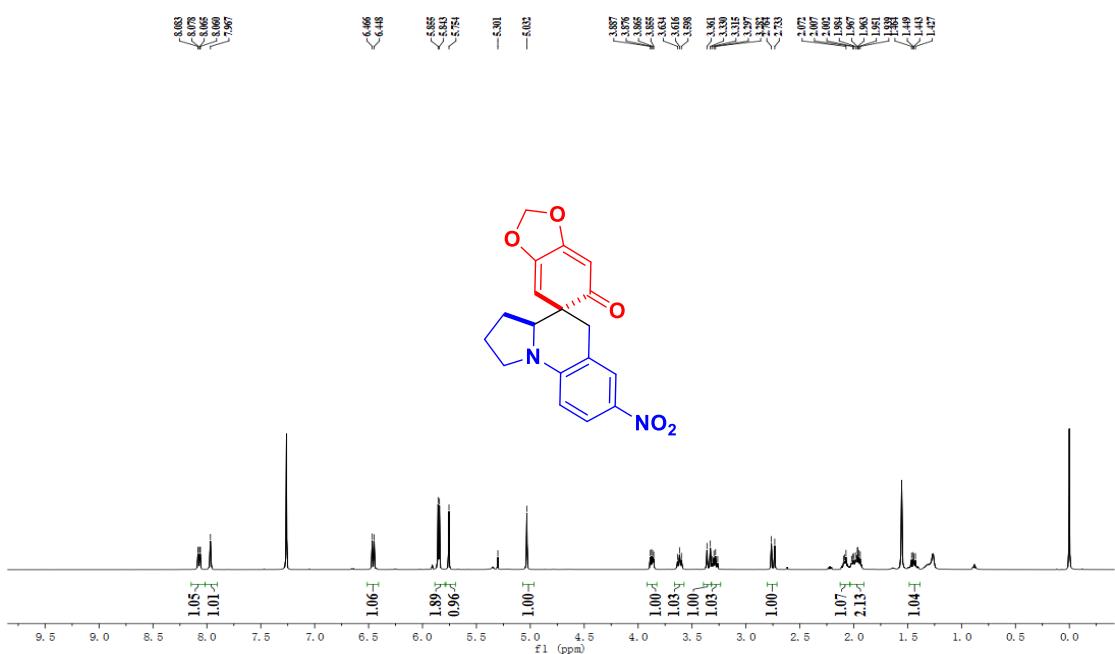


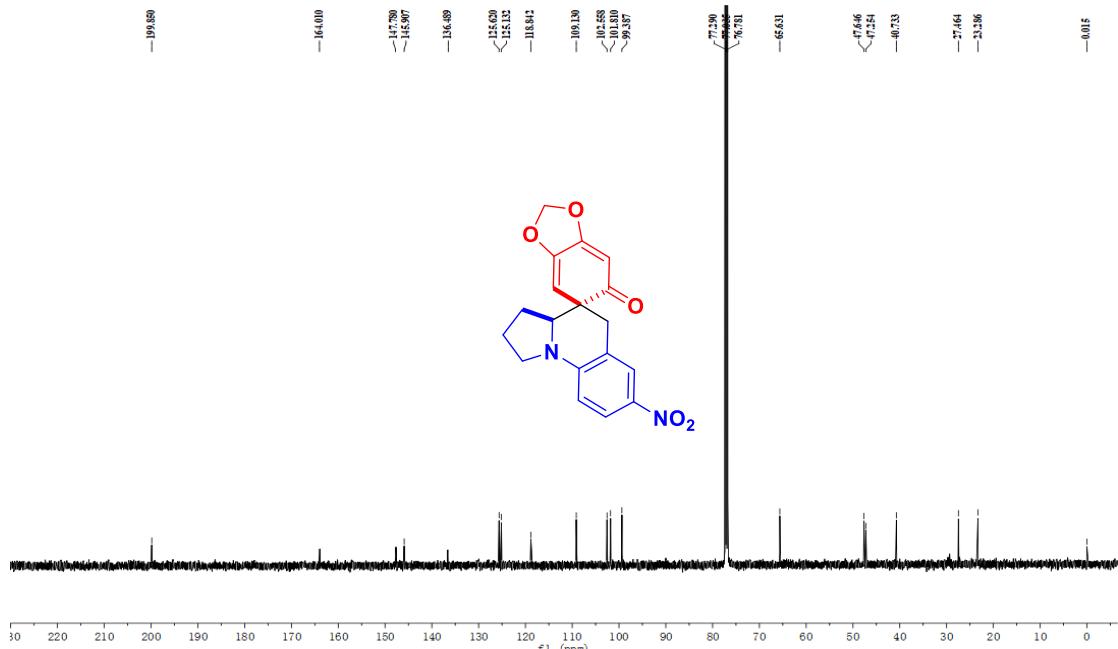
7'-chloro-1',2',3',3a'-tetrahydro-5'H,6H-spiro[benzo[d][1,3]dioxole-5,4'-pyrrolo[1,2-a]quinolin]-6-one (3m)



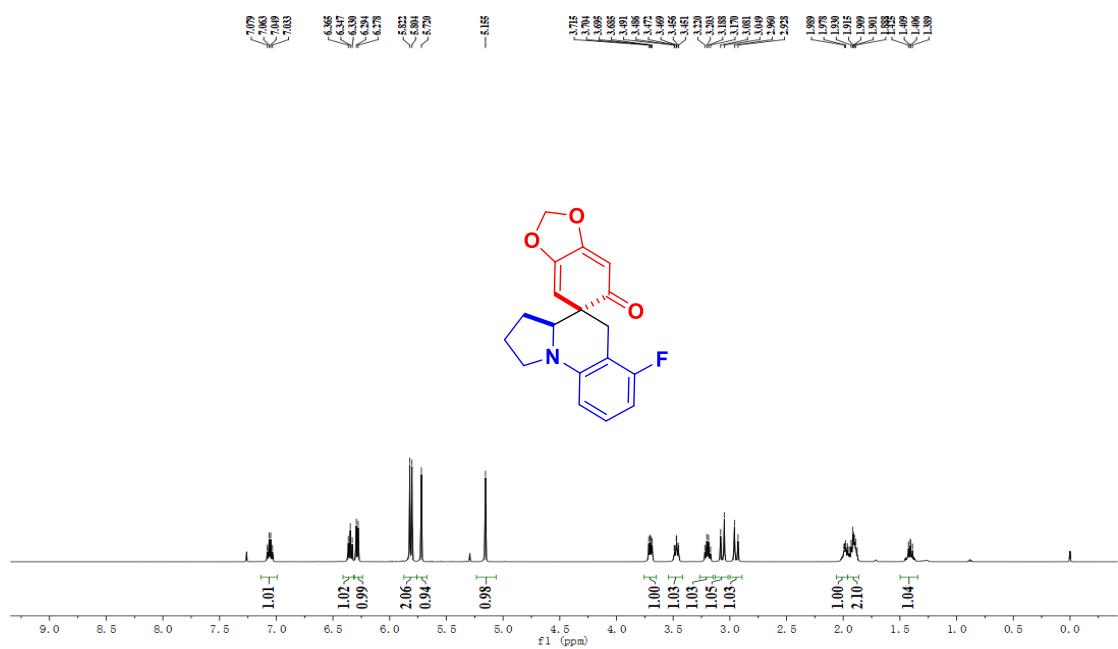


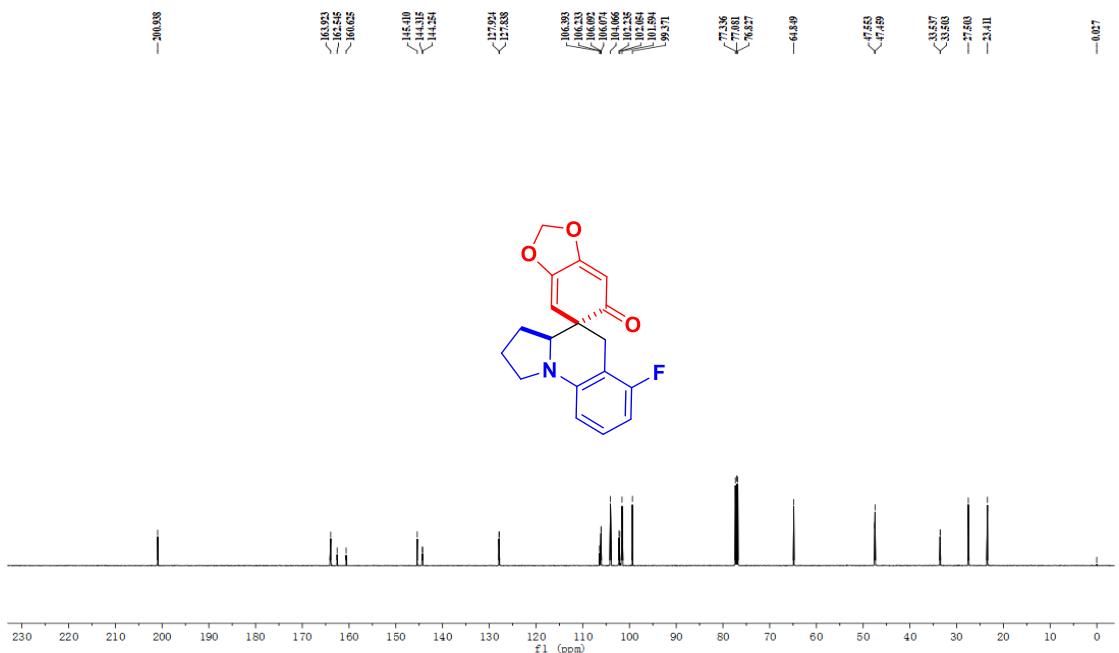
7'-nitro-1',2',3',3a'-tetrahydro-5'H,6H-spiro[benzo[d][1,3]dioxole-5,4'-pyrrolo[1,2-a]quinolin]-6-one (3n)



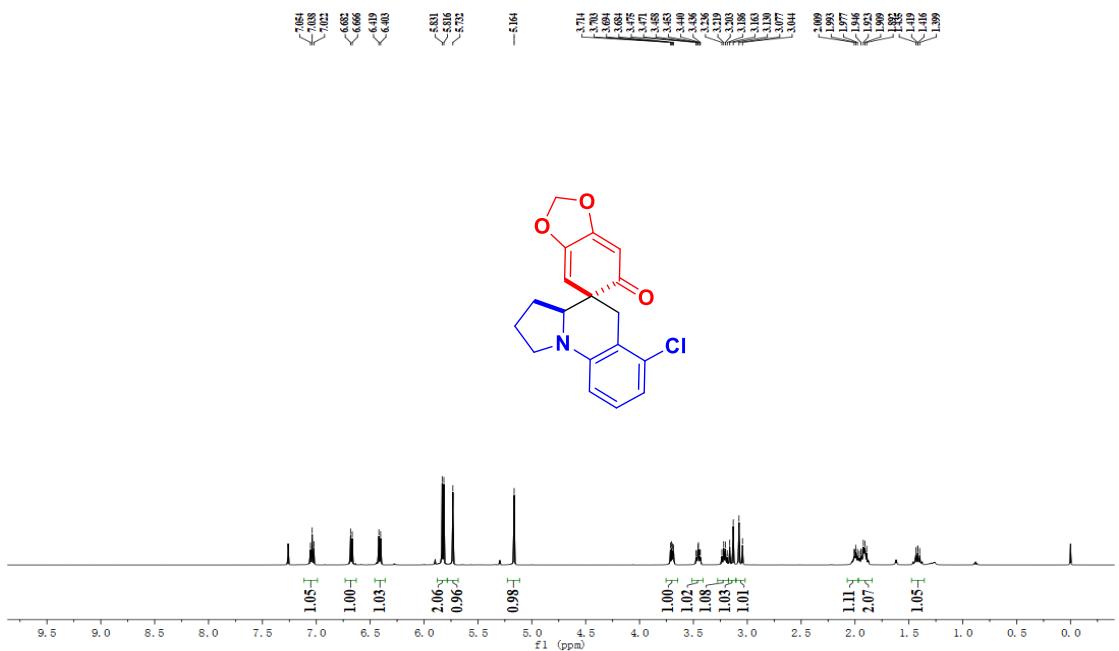


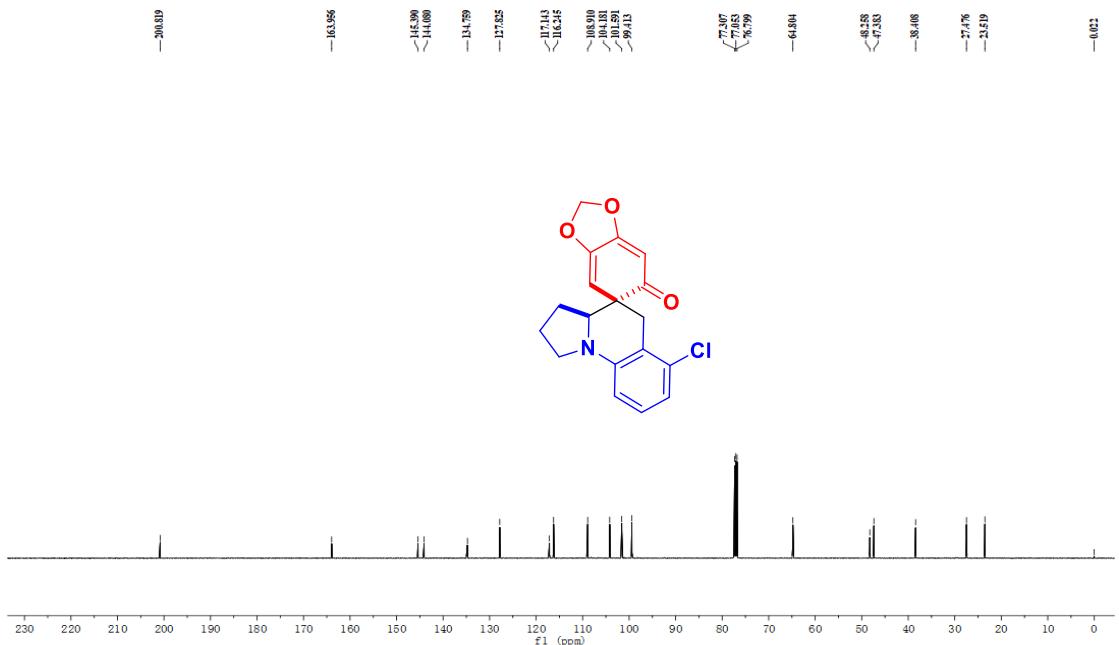
6'-fluoro-1',2',3',3a'-tetrahydro-5'H,6H-spiro[benzo[d][1,3]dioxole-5,4'-pyrrolo[1,2-a]quinolin]-6-one (3o)



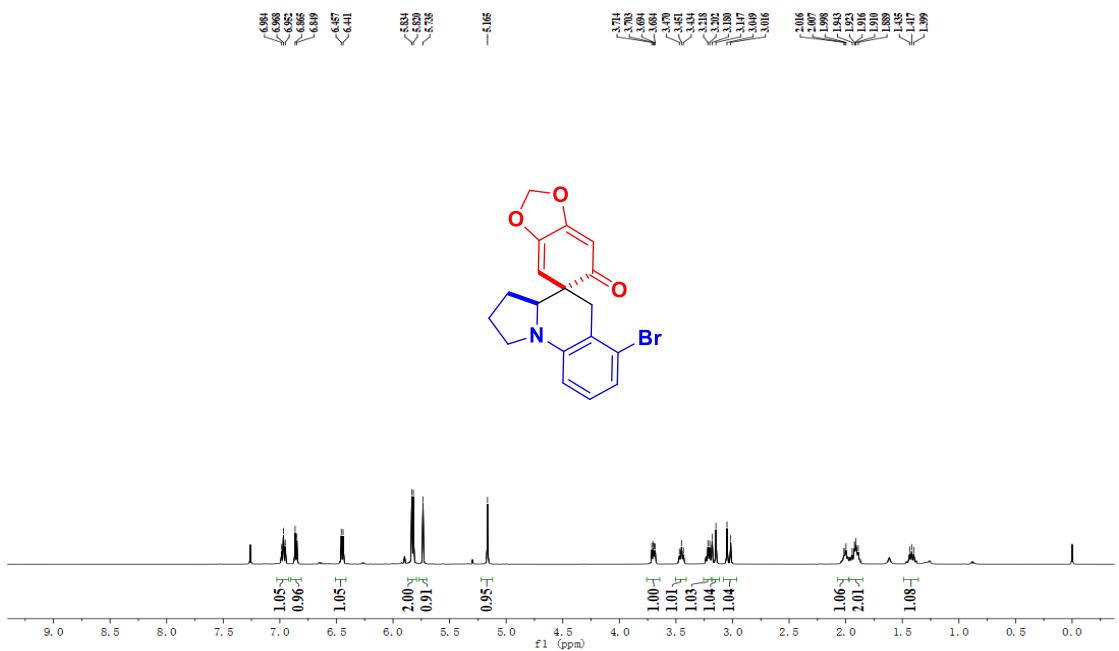


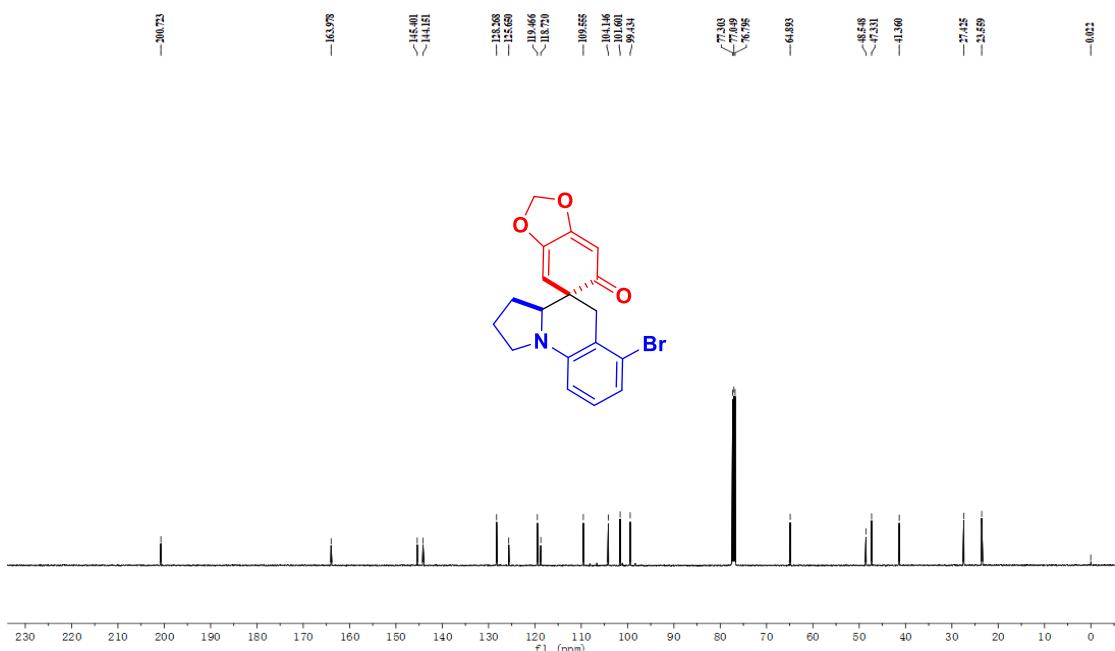
6'-chloro-1',2',3',3a'-tetrahydro-5'H,6H-spiro[benzo[d][1,3]dioxole-5,4'-pyrrolo[1,2-a]quinolin-6-one (3p)



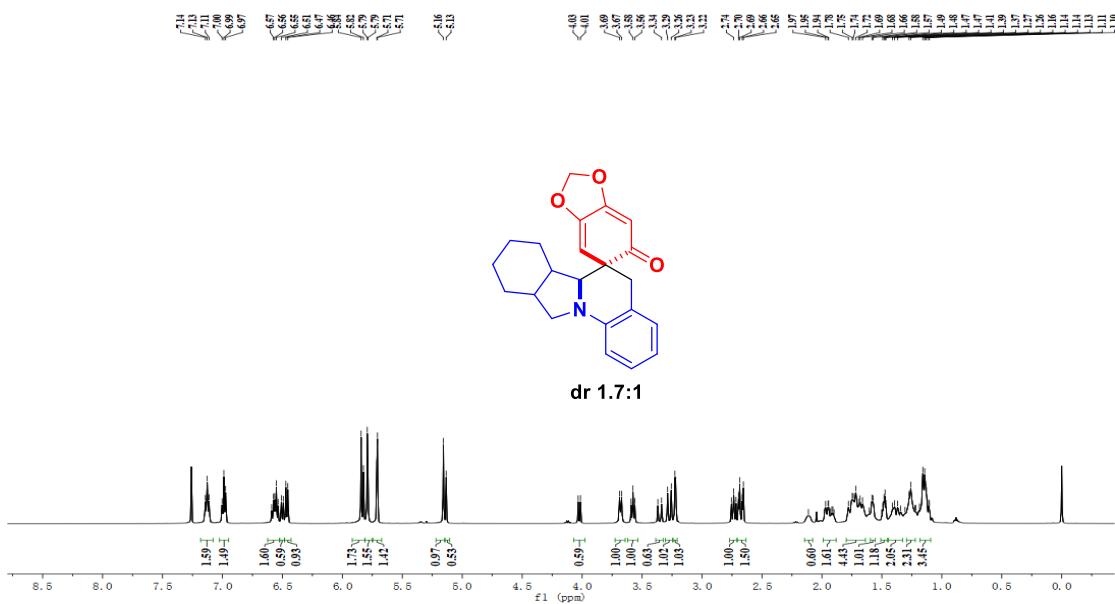


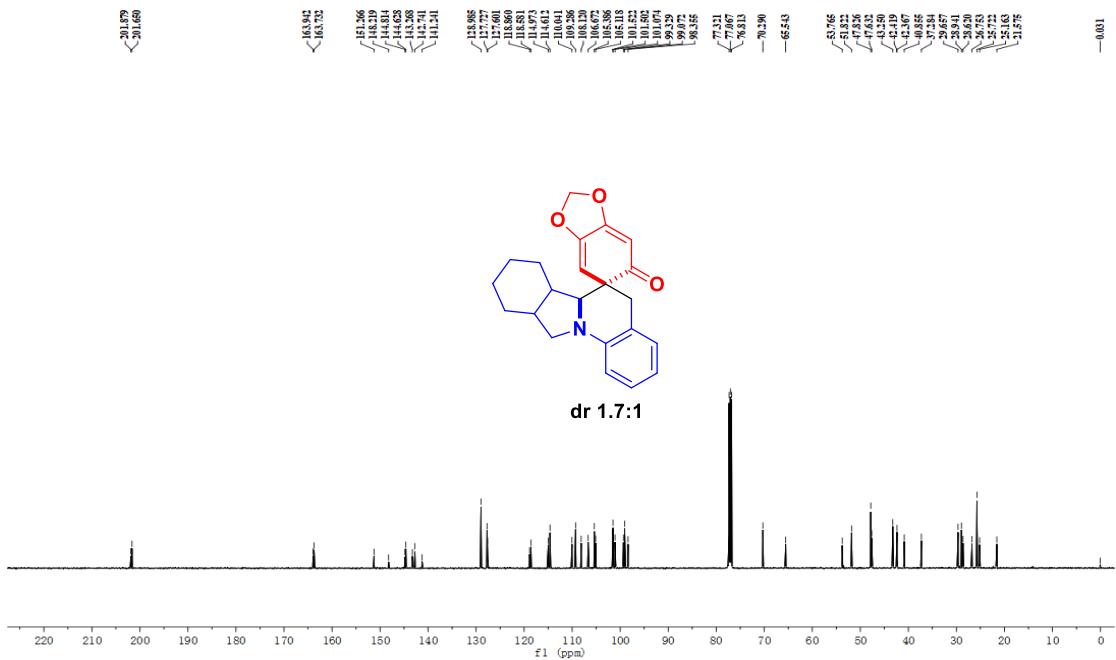
6'-bromo-1',2',3',3a'-tetrahydro-5'H,6H-spiro[benzo[d][1,3]dioxole-5,4'-pyrrolo[1,2-a]quinolin]-6-one (3q)



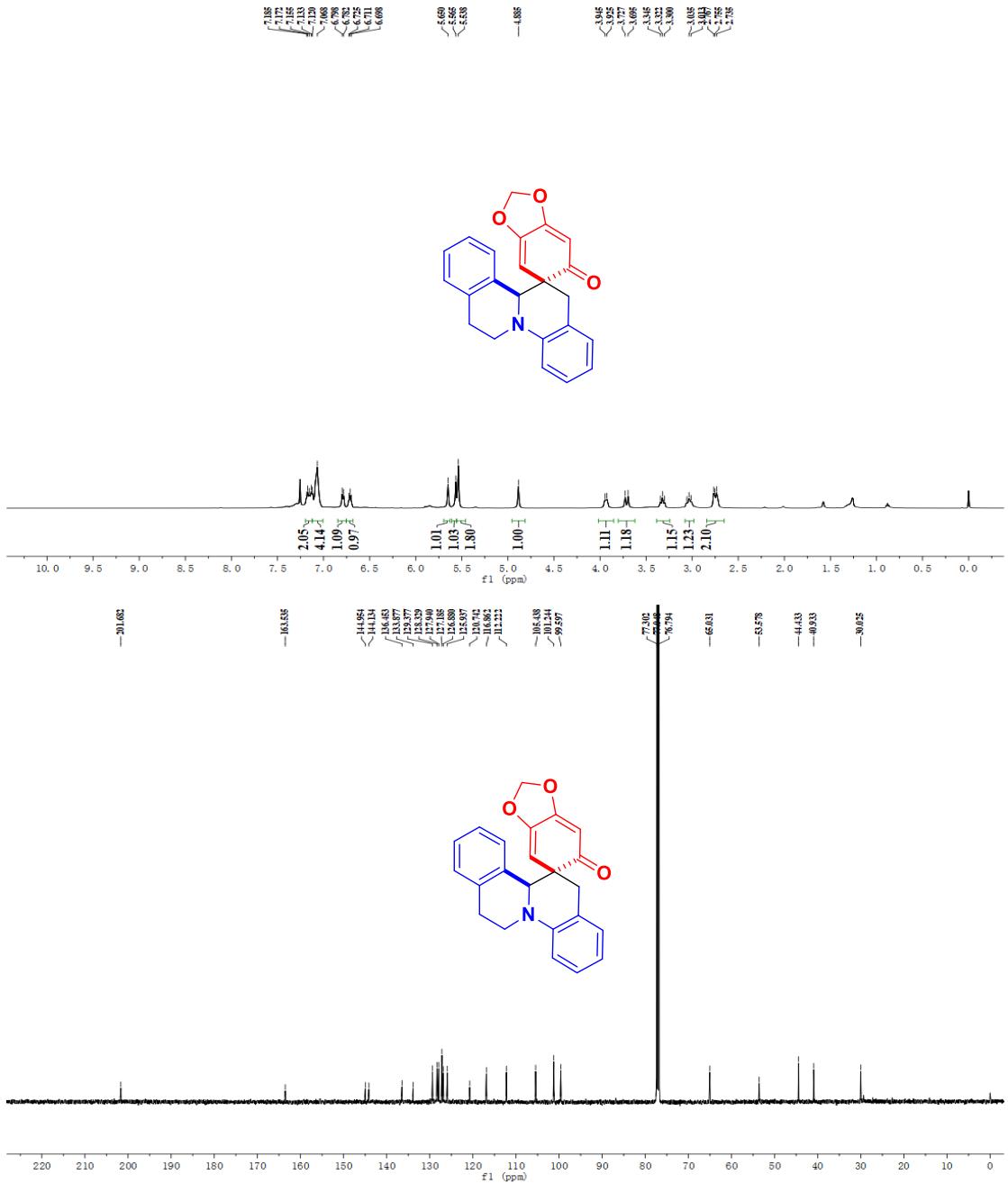


6a',6b',7',8',9',10',10a',11'-octahydro-5'H,6H-spiro[benzo[d][1,3]dioxole-5,6'-isoindolo[2,1-a]quinolin]-6-one (3r)

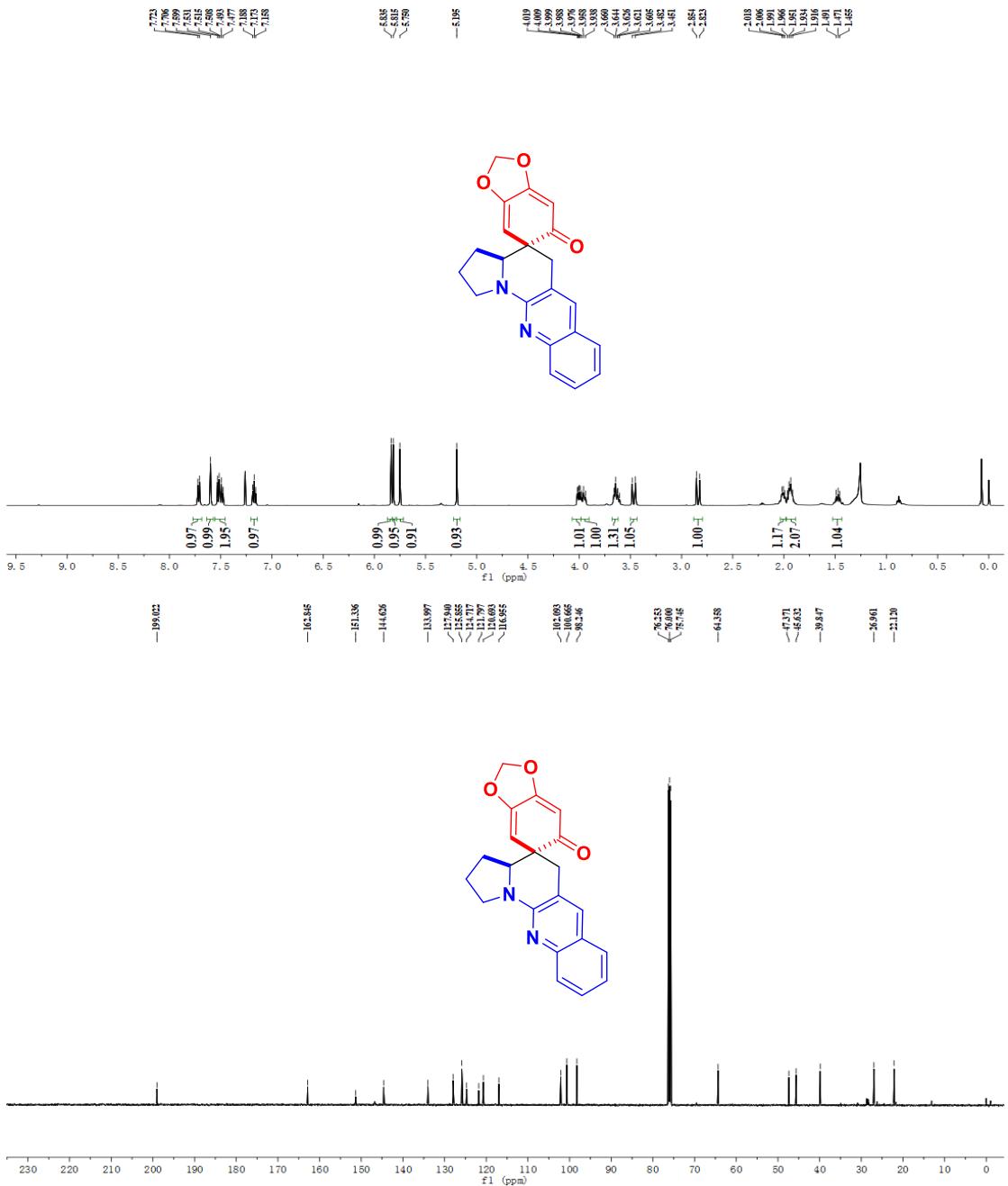




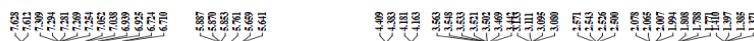
7',11b'-dihydro-6*H*,6'*H*,13'*H*-spiro[benzo[*d*][1,3]dioxole-5,12'-isoquinolino[2,1-*a*]quinolin]-6-one (3s)



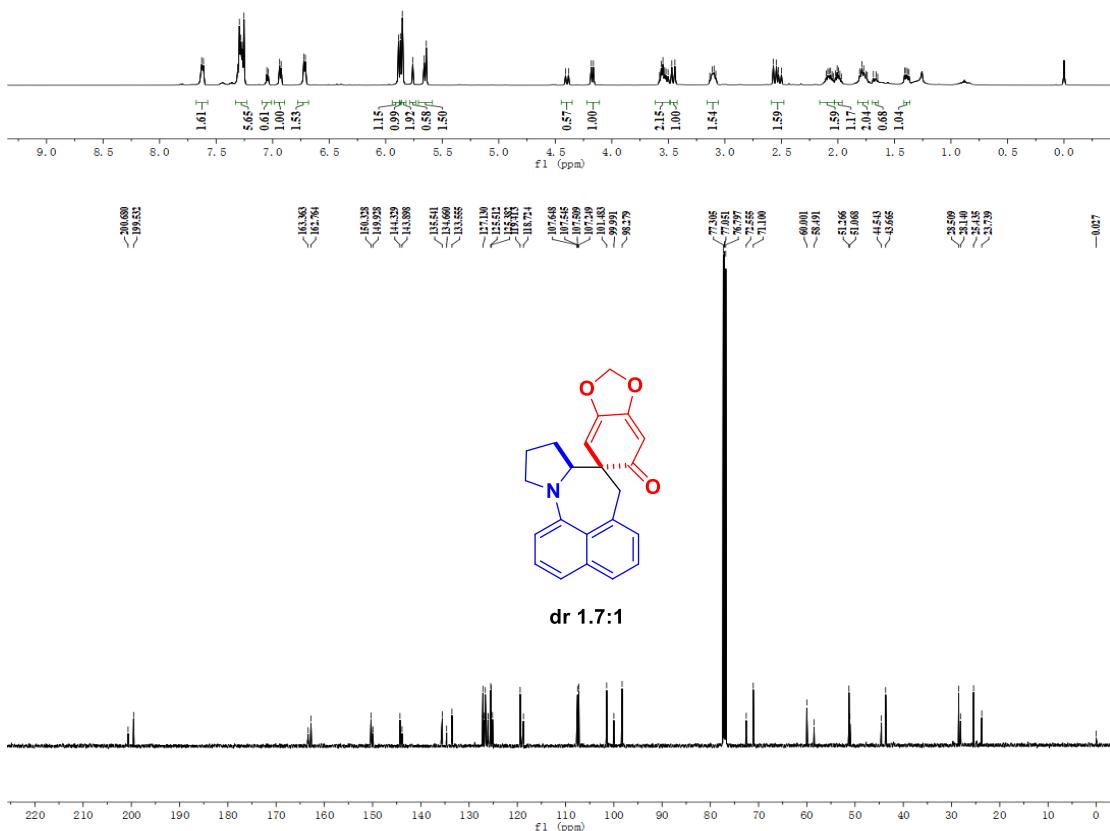
1',2',3',3a'-tetrahydro-5'H,6H-spiro[benzo[d][1,3]dioxole-5,4'-benzo[g]pyrrolo[1,2-a][1,8]naphthyridin]-6-one (3t)



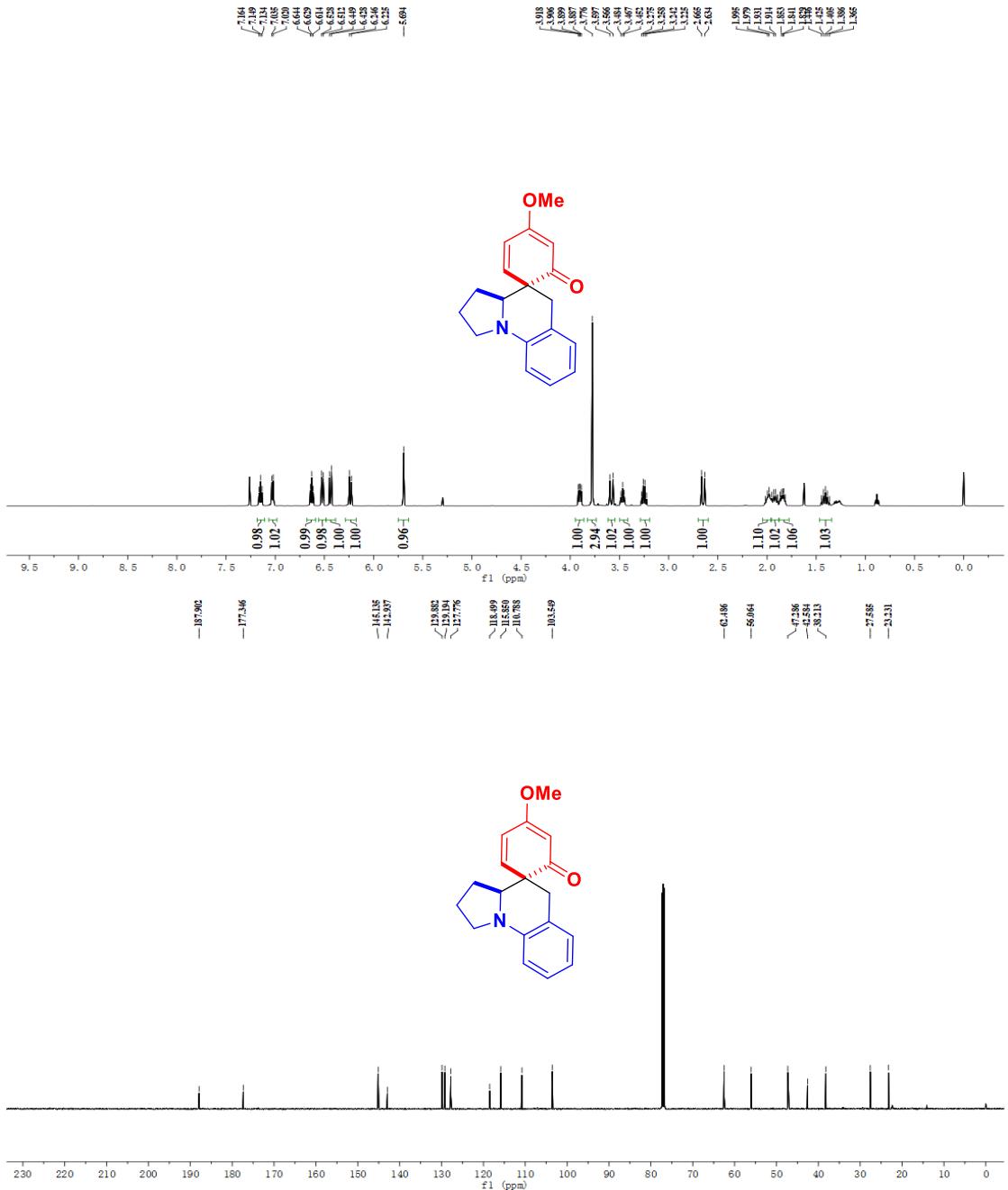
1',2',3',12a'-tetrahydro-6*H*,11'*H*-spiro[benzo[*d*][1,3]dioxole-5,12'-naphtho[1,8-*ef*]pyrrolo[1,2-*a*]azepin]-6-one (3u)



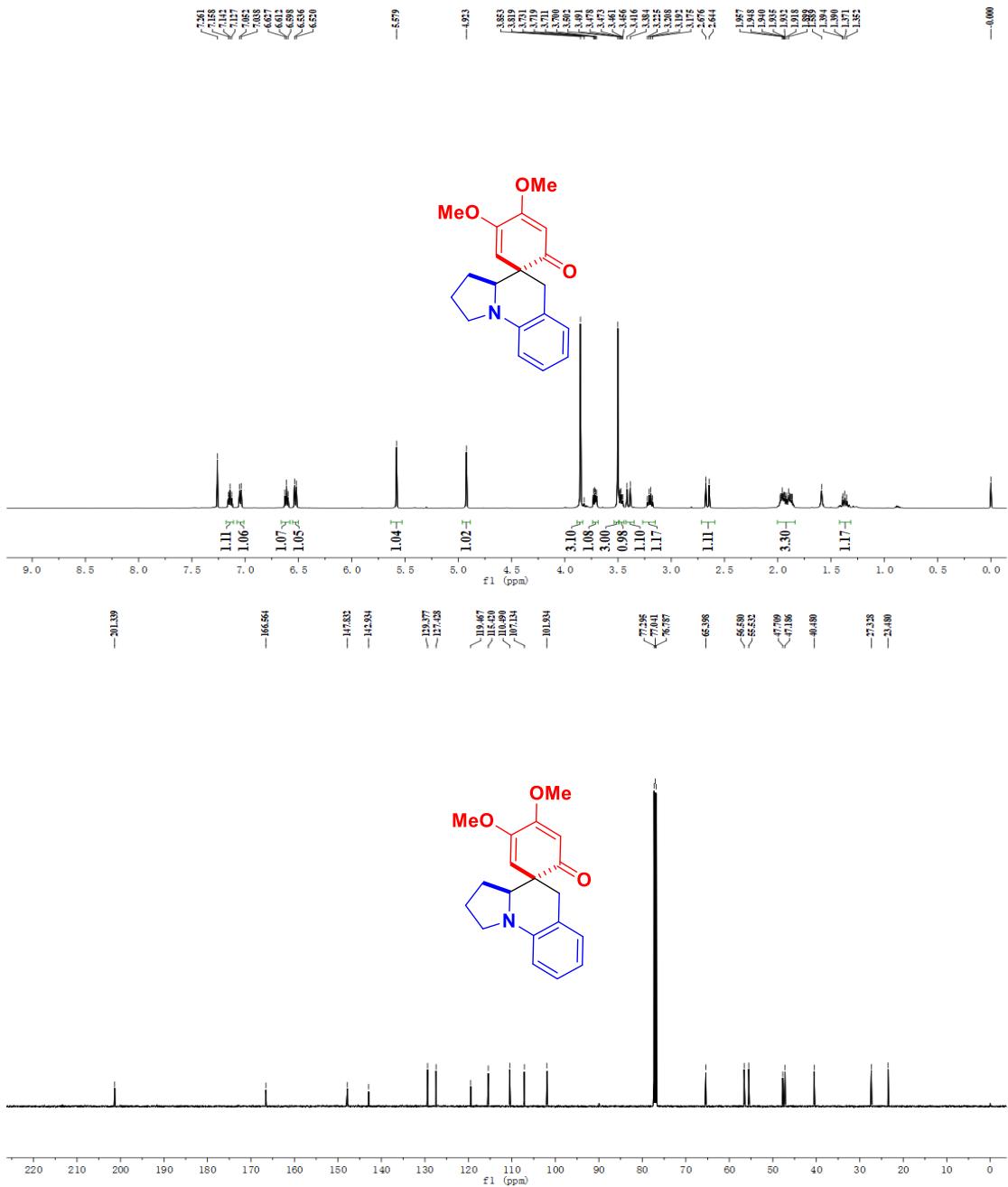
dr 1.7:1



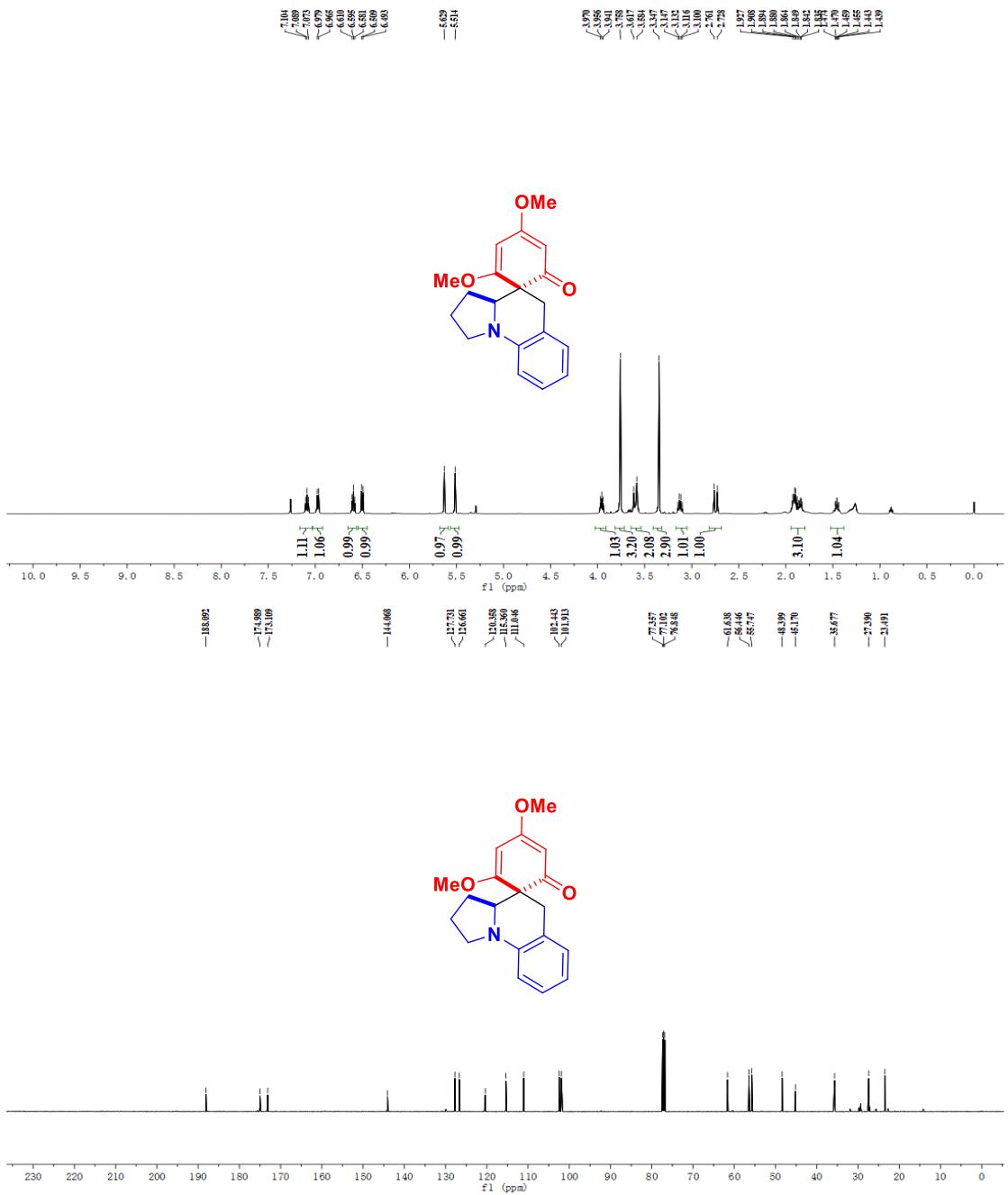
4-methoxy-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (3v)



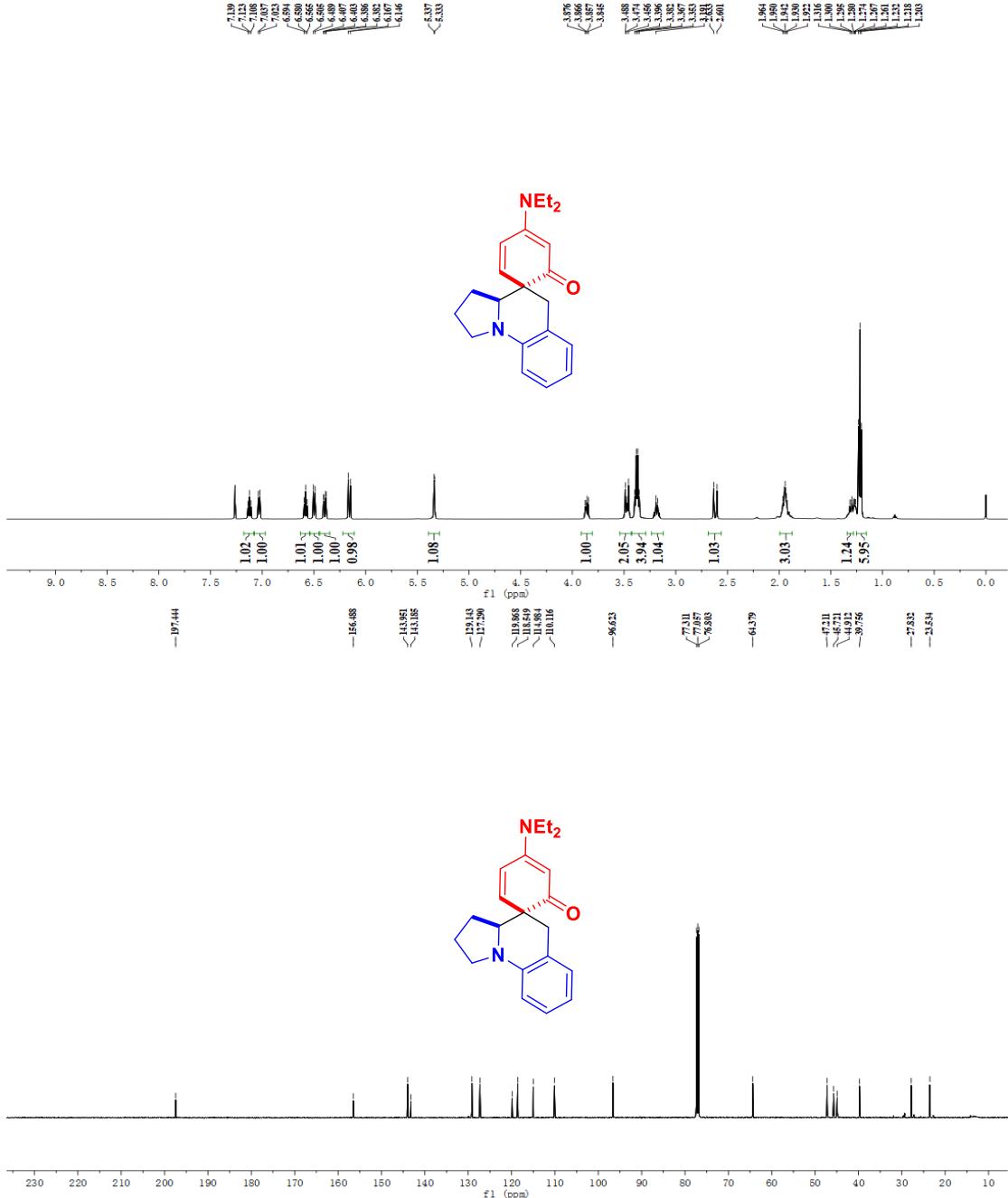
3,4-dimethoxy-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (3w)



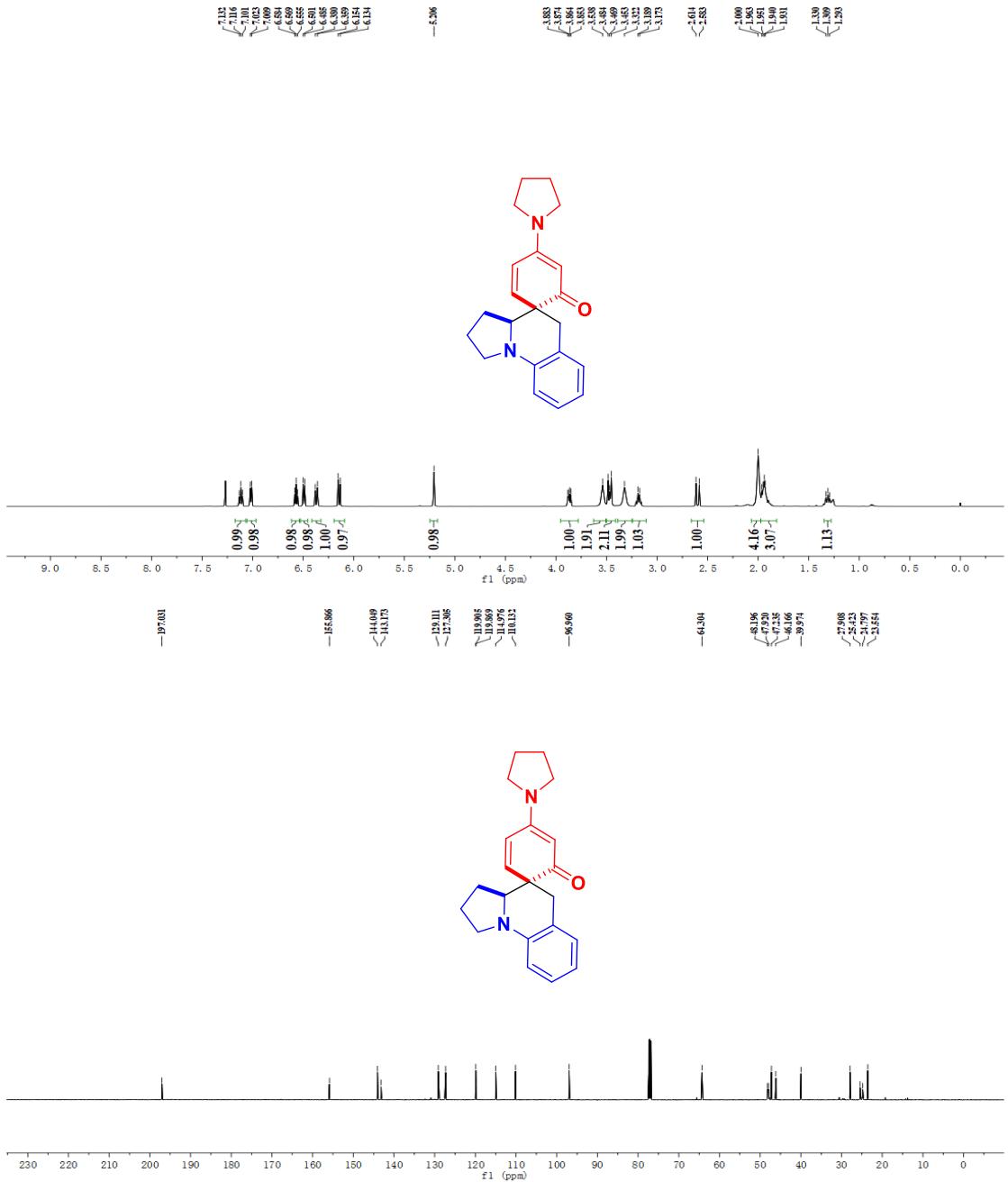
2,4-dimethoxy-1',2',3',3a'-tetrahydro-5'*H*-spiro[cyclohexane-1,4'-pyrrolo[1,2-*a*]quinoline]-2,4-dien-6-one (3x)



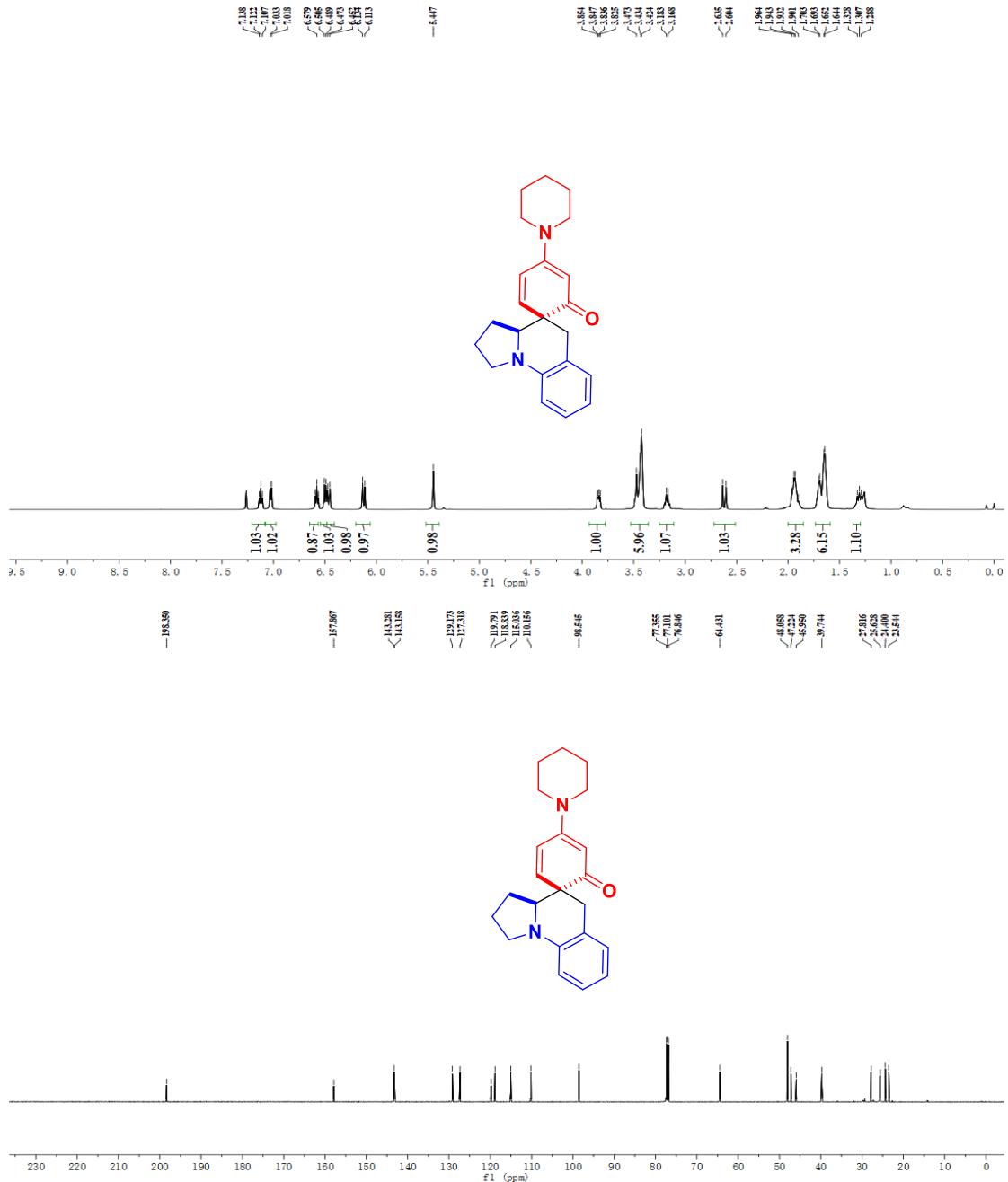
4-(diethylamino)-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (3y)



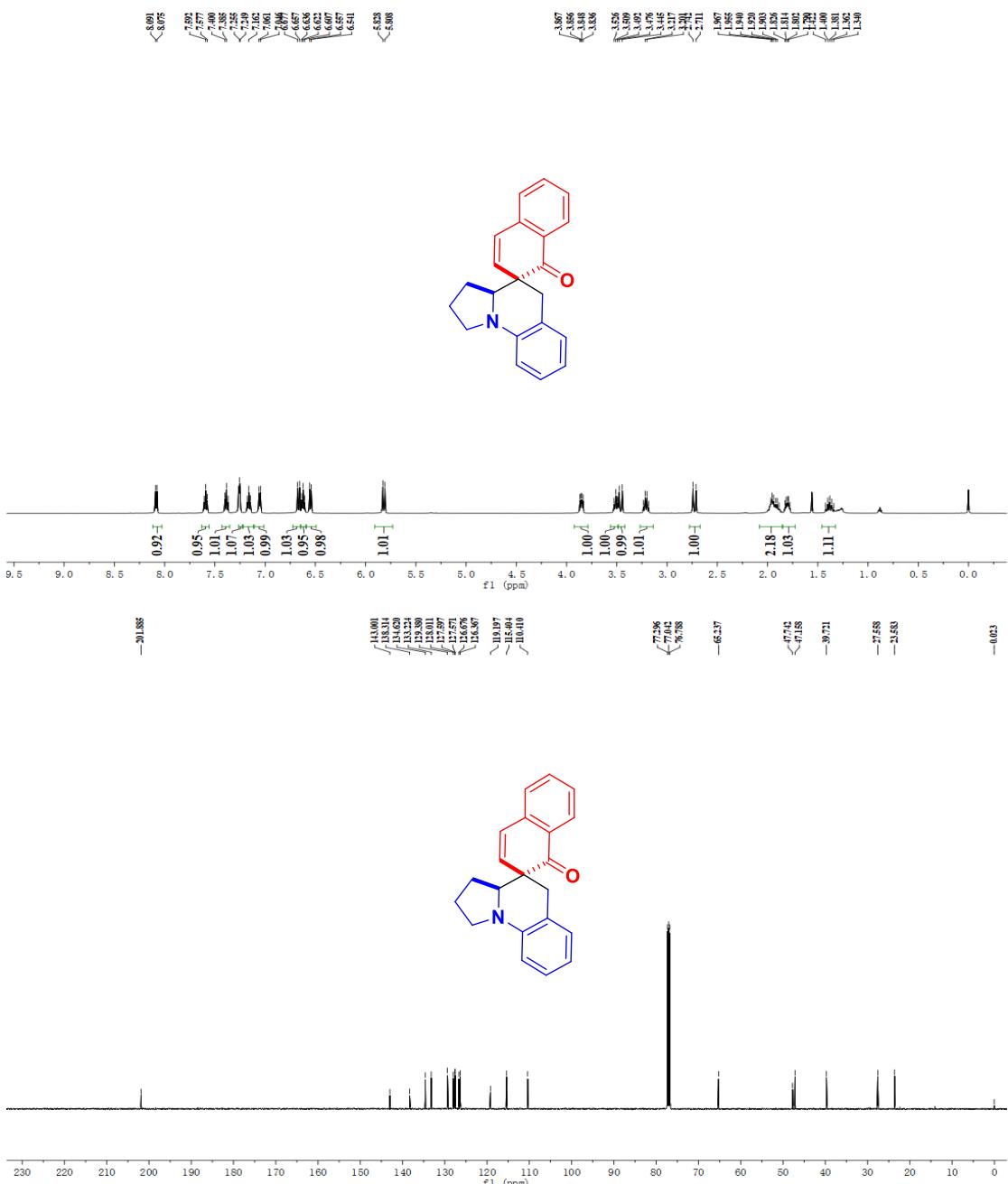
4-(pyrrolidin-1-yl)-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (3z)



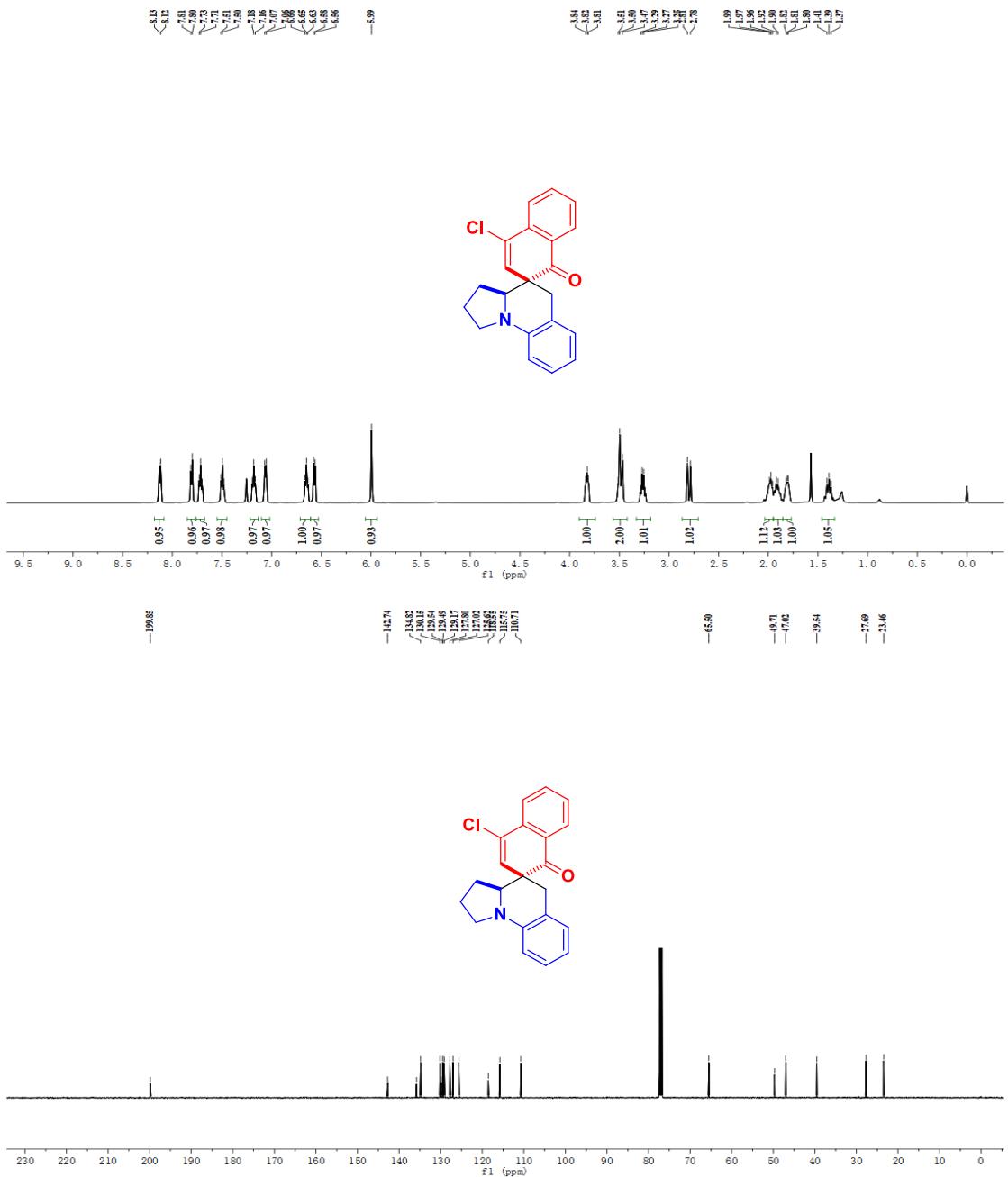
4-(piperidin-1-yl)-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,4-dien-6-one (3za)



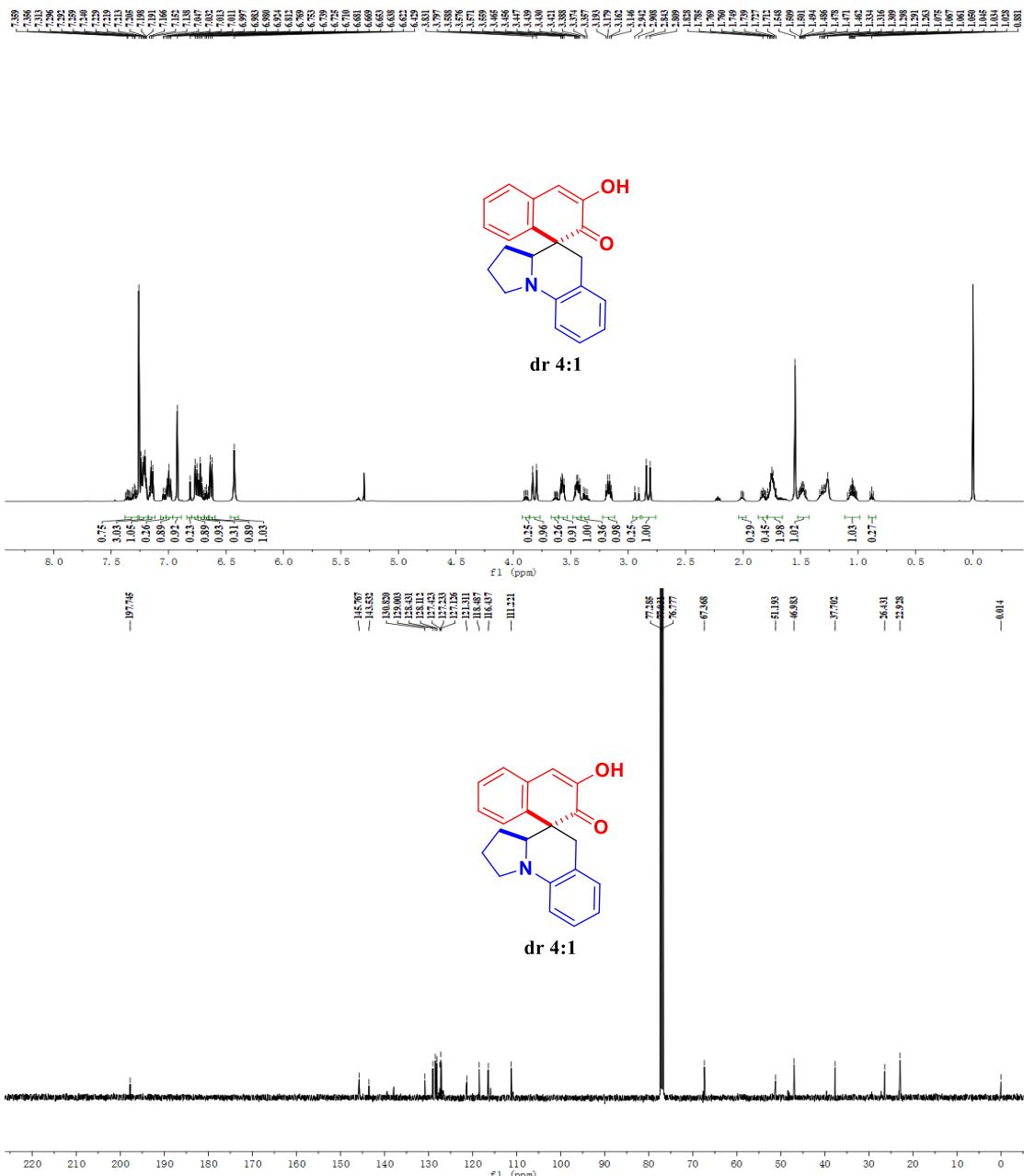
1',2',3',3a'-tetrahydro-1*H*,5'*H*-spiro[naphthalene-2,4'-pyrrolo[1,2-*a*]quinolin]-1-one (3zb)

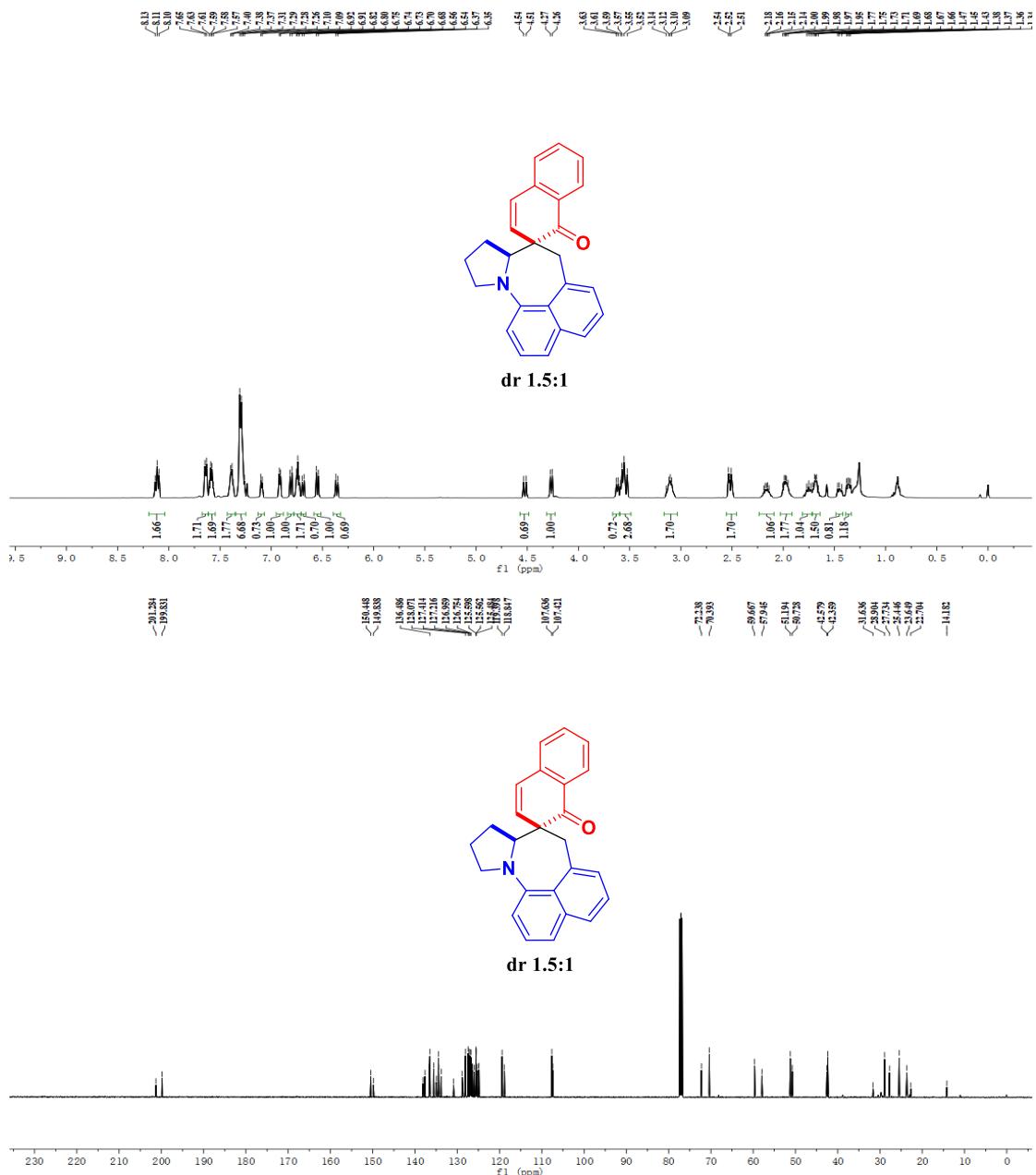


4-chloro-2',3',3a',5'-tetrahydro-1H,1'H-spiro[naphthalene-2,4'-pyrrolo[1,2-a]quinolin]-1-one (3zc)

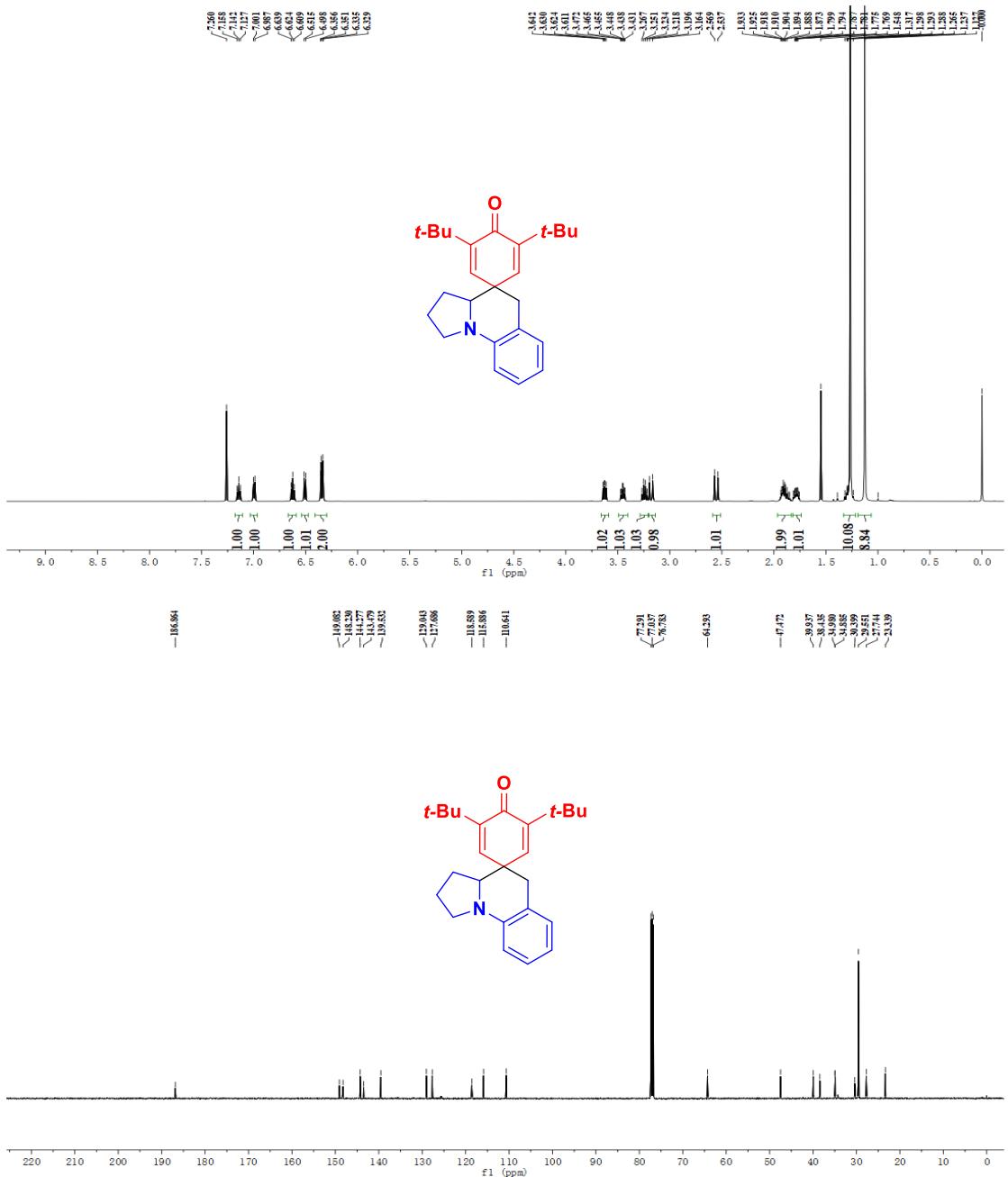


3-hydroxy-1',2',3',3a'-tetrahydro-2H,5'H-spiro[naphthalene-1,4'-pyrrolo[1,2-a]quinolin]-2-one (3zd)

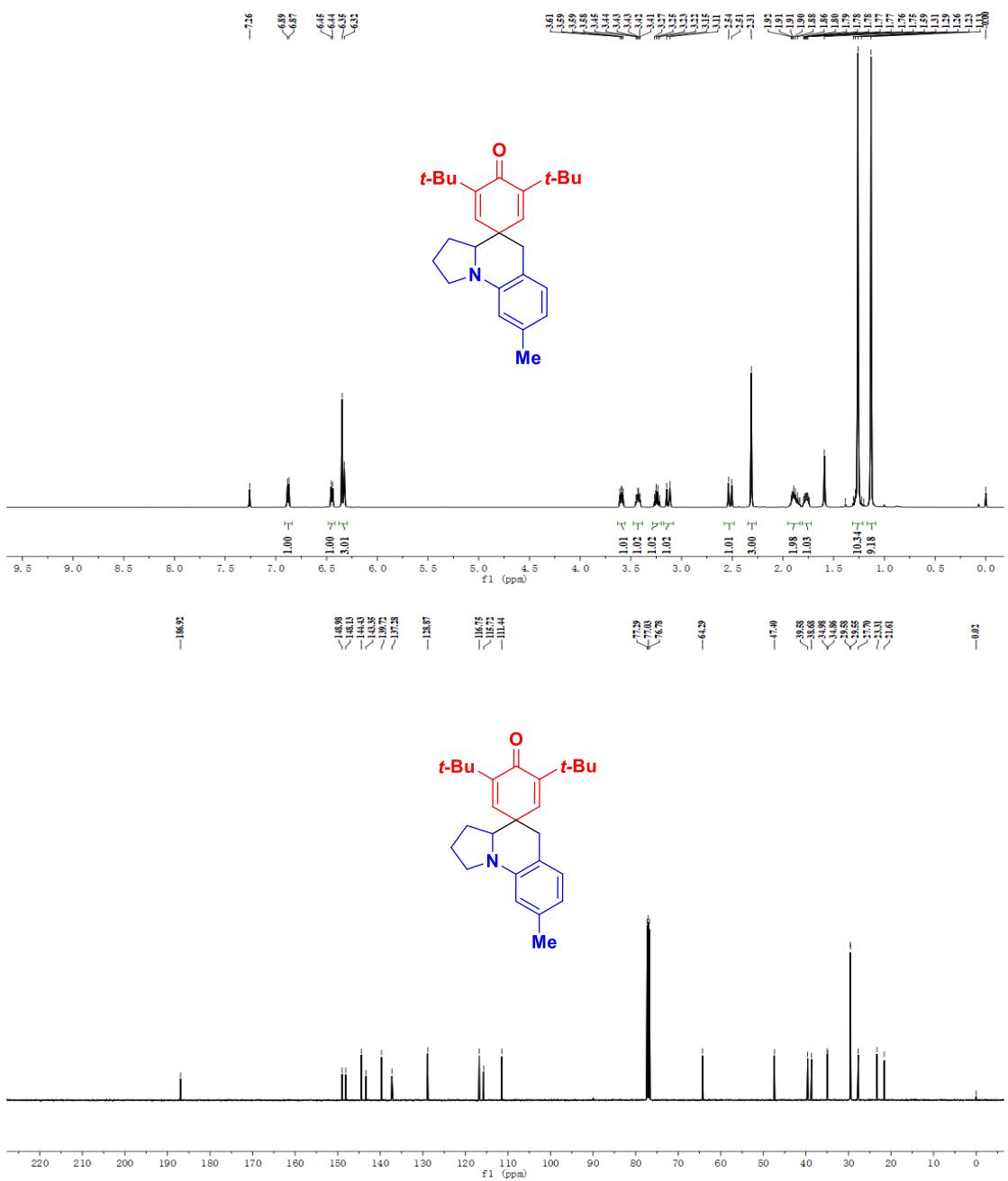




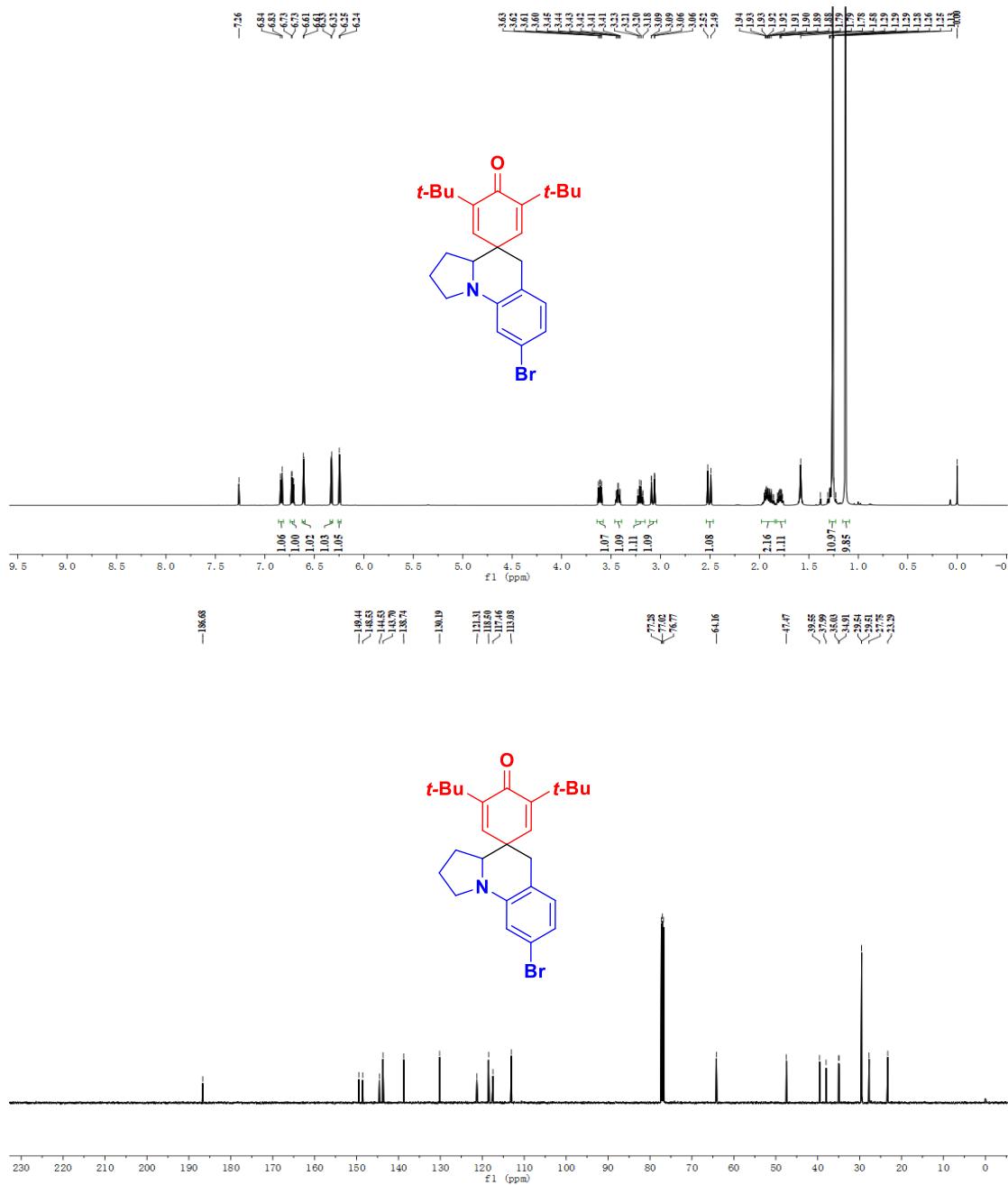
3,5-di-*tert*-butyl-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2-5-dien-4-one (5a)



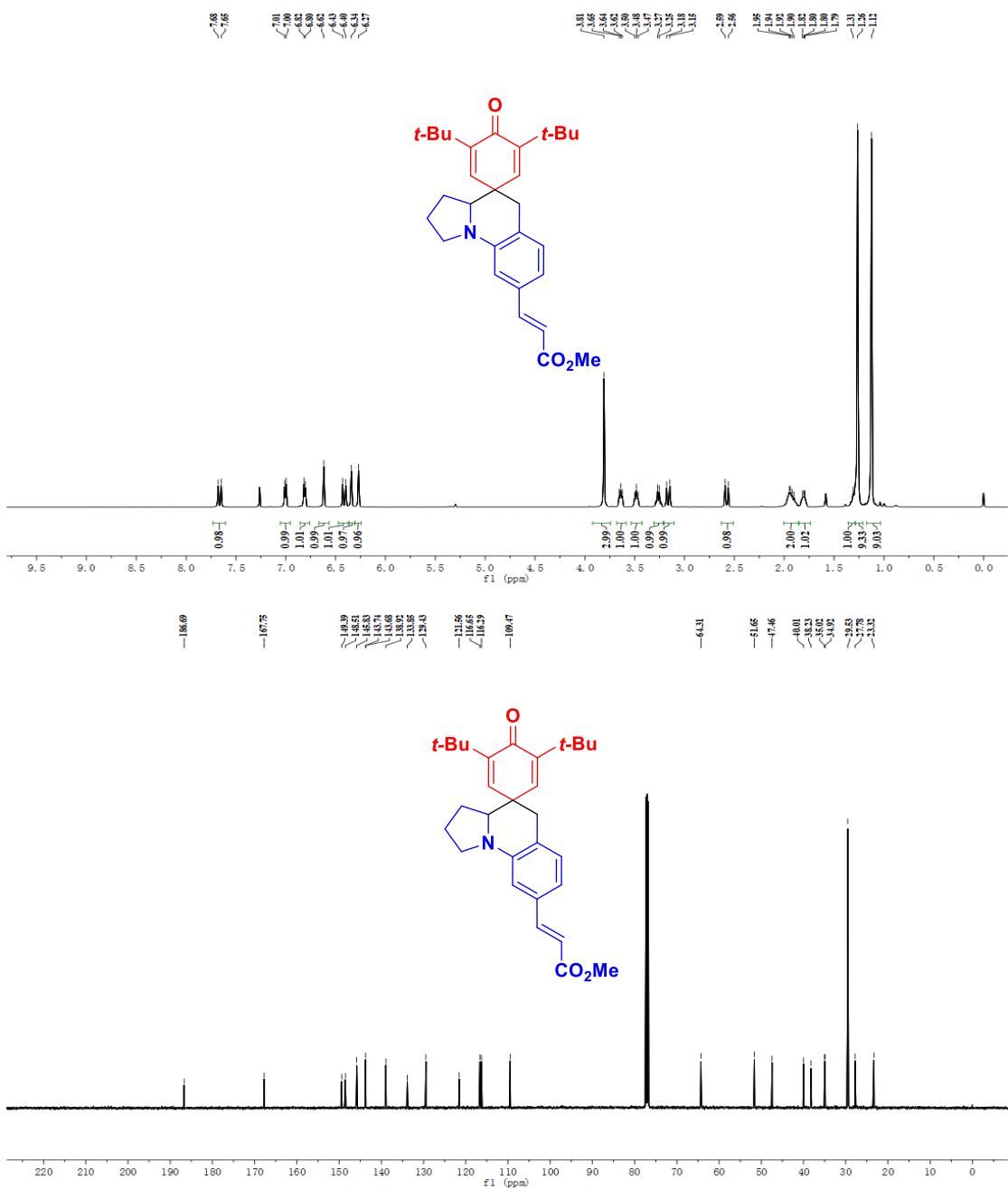
(R)-3,5-di-tert-butyl-8'-methyl-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,5-dien-4-one (5b)



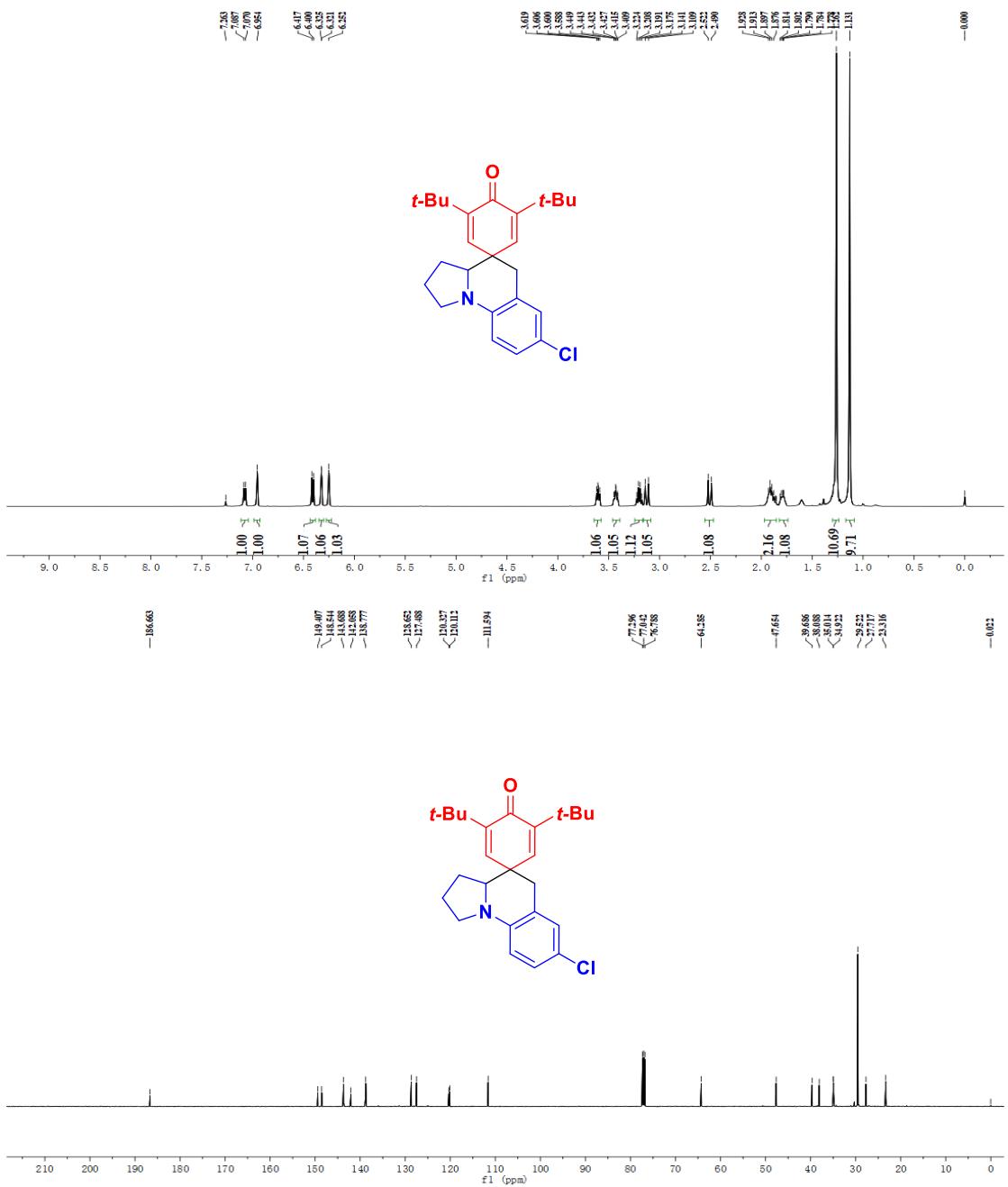
8'-bromo-3,5-di-*tert*-butyl-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,5-dien-4-one (5c)



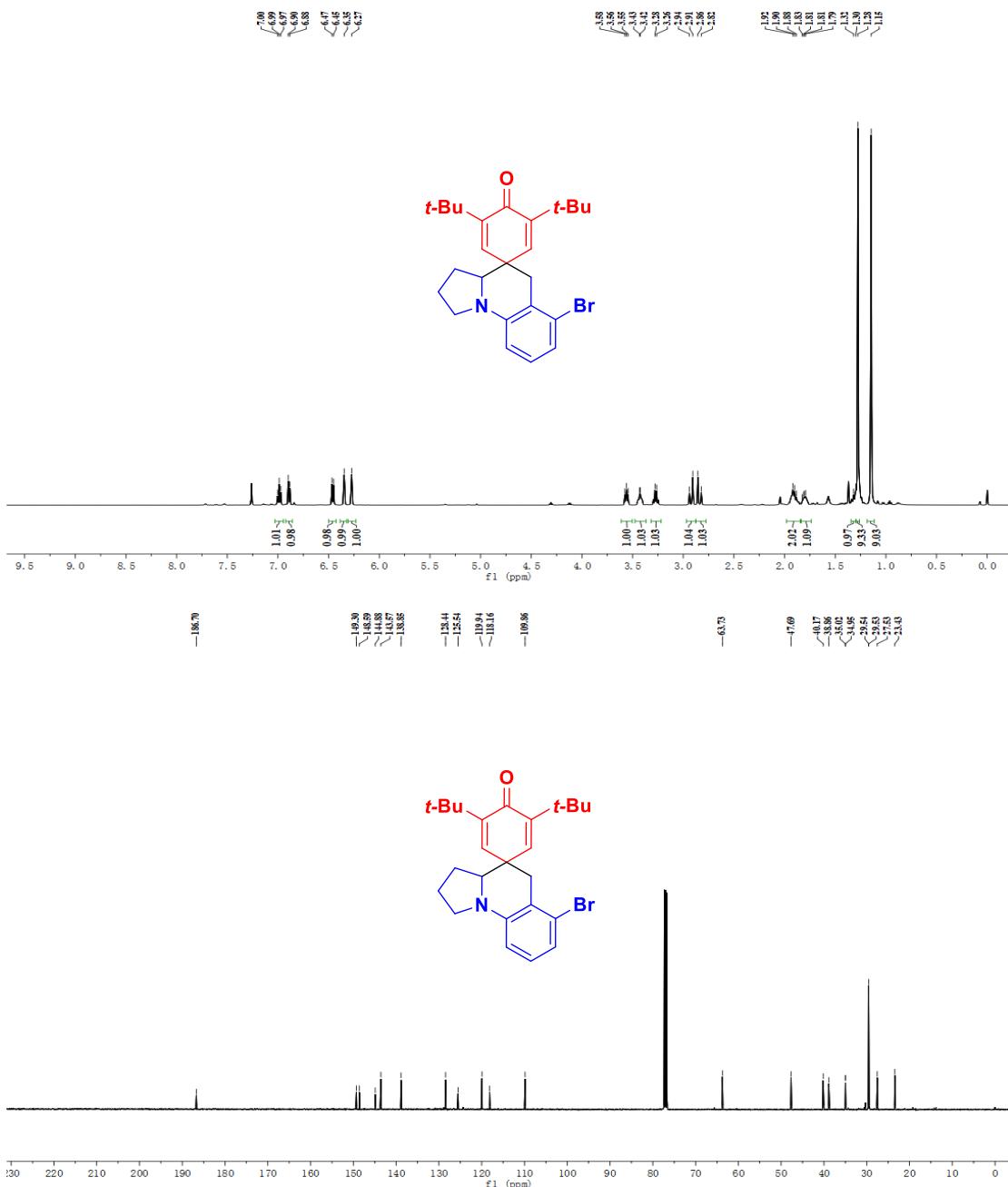
methyl(*E*)-3-(3,5-di-*tert*-butyl-4-oxo-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrol-*o*[1,2-*a*]quinoline]-2,5-dien-8'-yl)acrylate (5d)



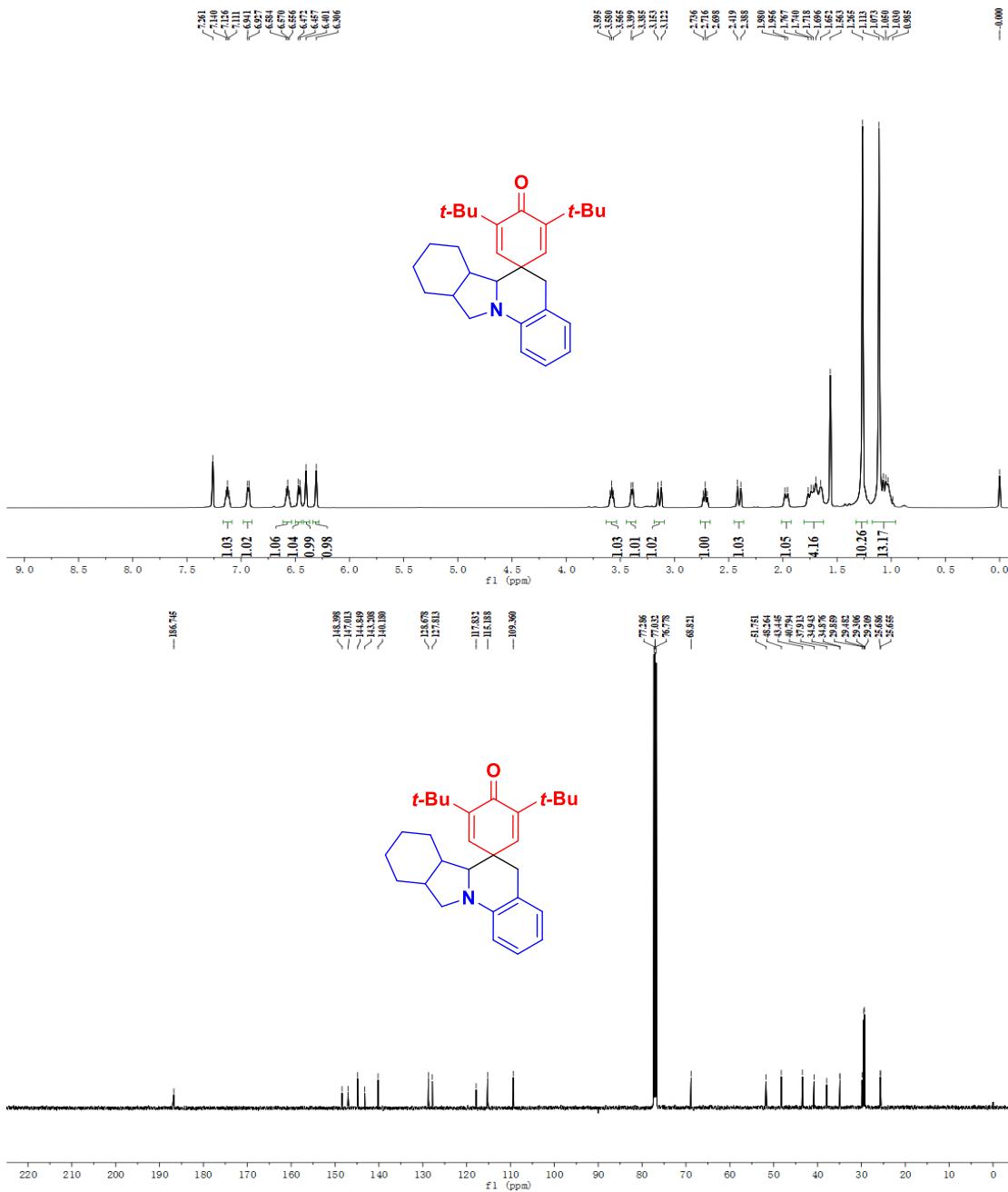
3,5-di-*tert*-butyl-7'-chloro-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-*a*]quinoline]-2,5-dien-4-one (5e)



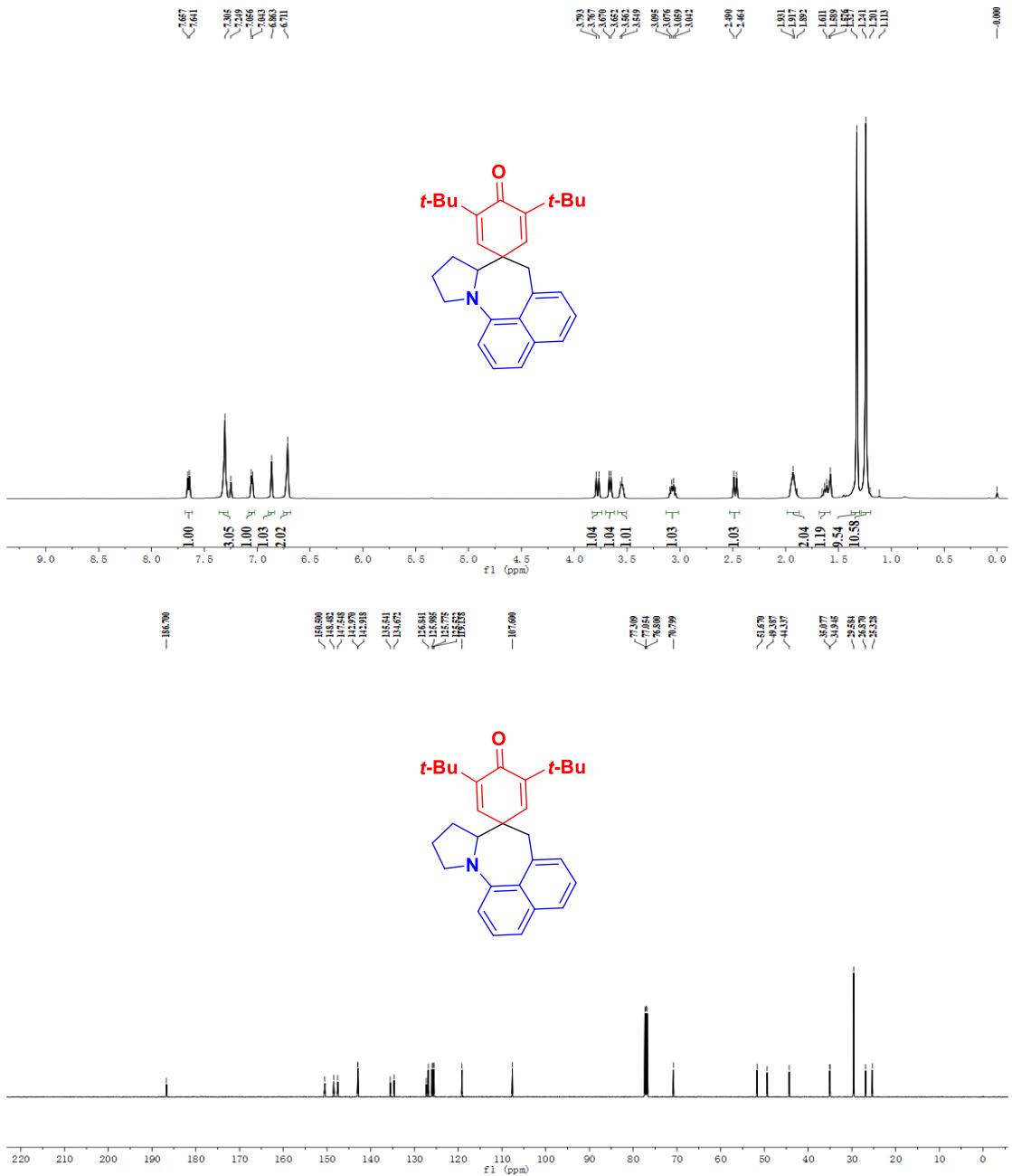
6'-bromo-3,5-di-*tert*-butyl-1',2',3',3a'-tetrahydro-5'H-spiro[cyclohexane-1,4'-pyrrolo[1,2-a]quinoline]-2,5-dien-4-one (5f)



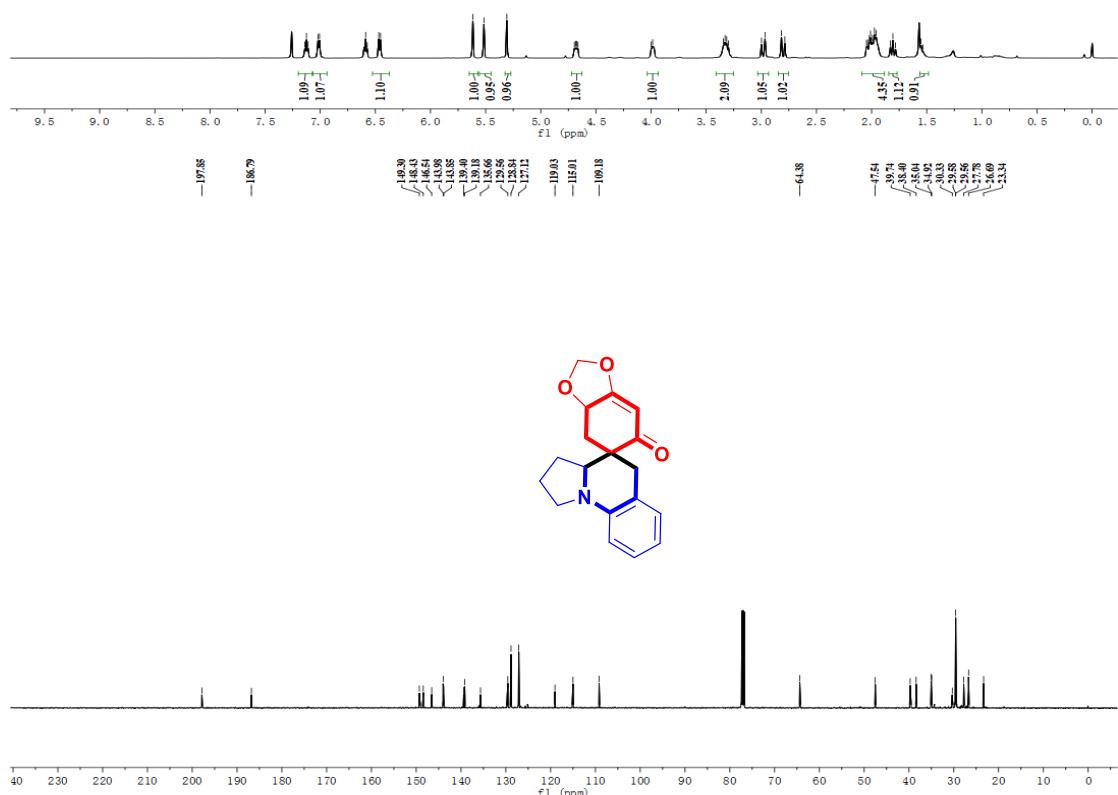
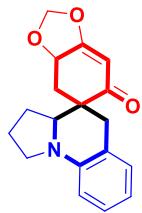
3,5-di-*tert*-butyl-6*a'*,6*b'*,7',8',9',10',10*a'*,11'-octahydro-5'*H*-spiro[cyclohexane-1,6'-isoindolo[2,1-*a*]quinoline]-2,5-dien-4-one (5g)



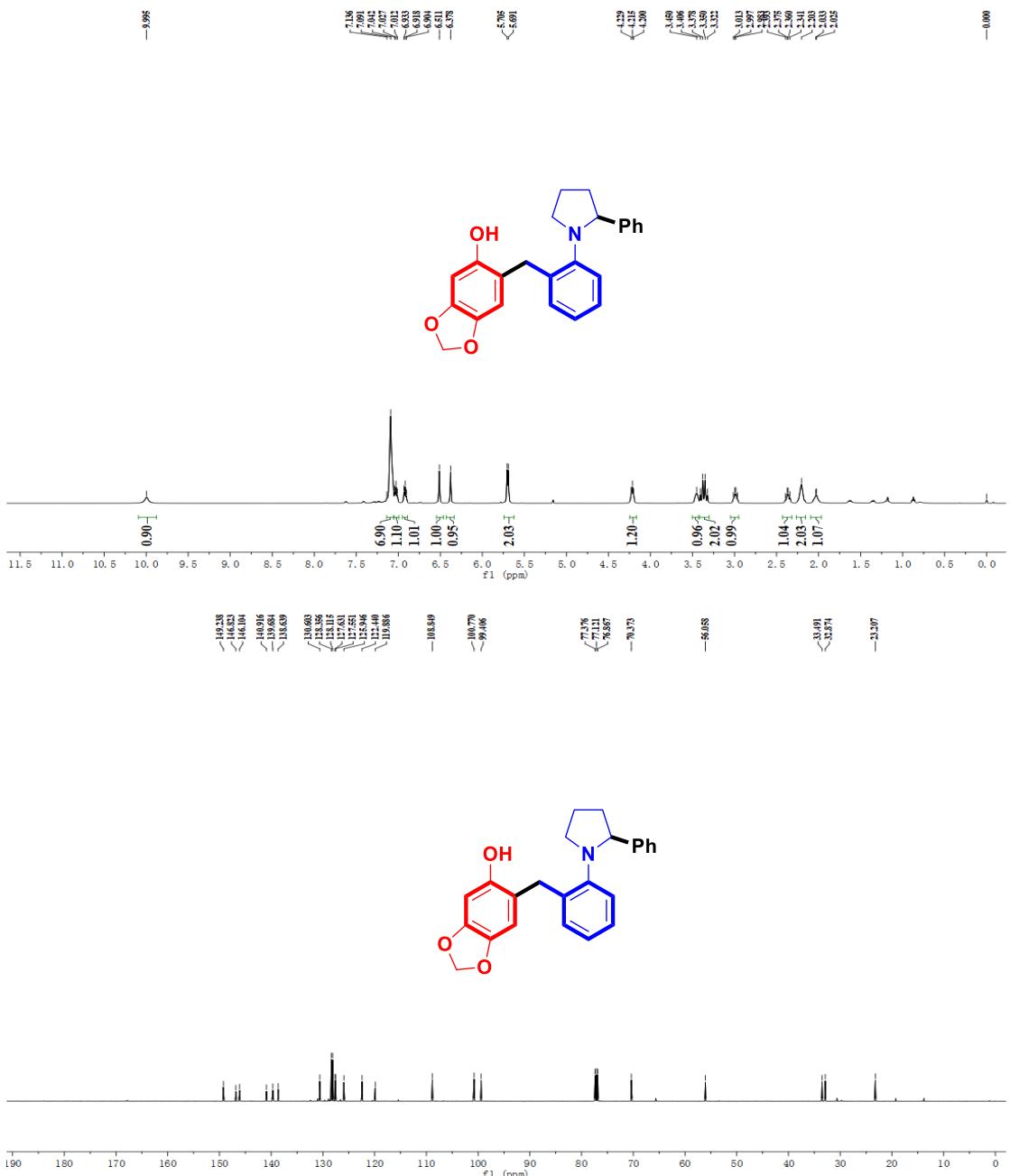
3,5-di-*tert*-butyl-8*a*',9',10',11'-tetrahydro-7*H*-spiro[cyclohexane-1,8'-naphtho[1,8-*ef*]pyrrolo[1,2-*a*]azepine]-2,5-dien-4-one (5h)



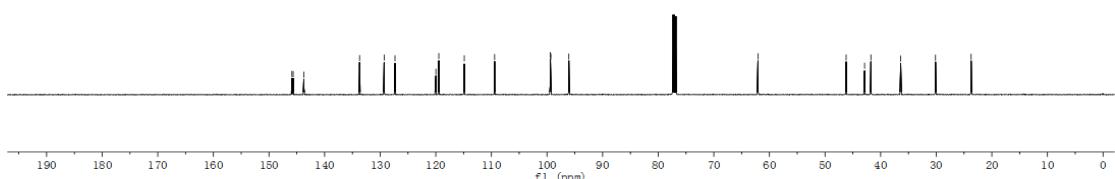
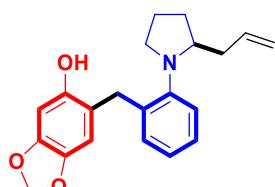
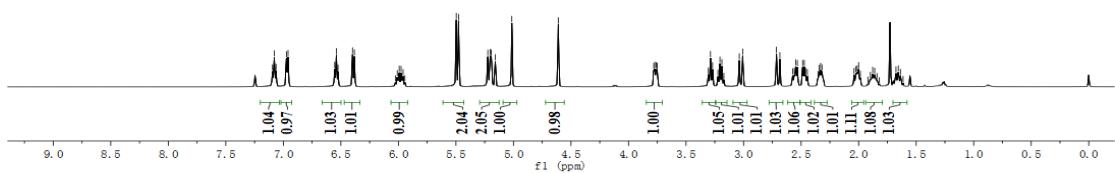
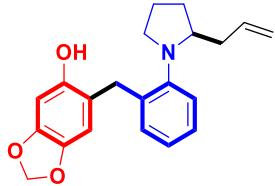
1',2',3a,3a',4-hexahydro-5'H,6H-spiro[benzo[d][1,3]dioxole-5,4'-pyrrolo[1,2-a]quinolin]-6-one (6a)



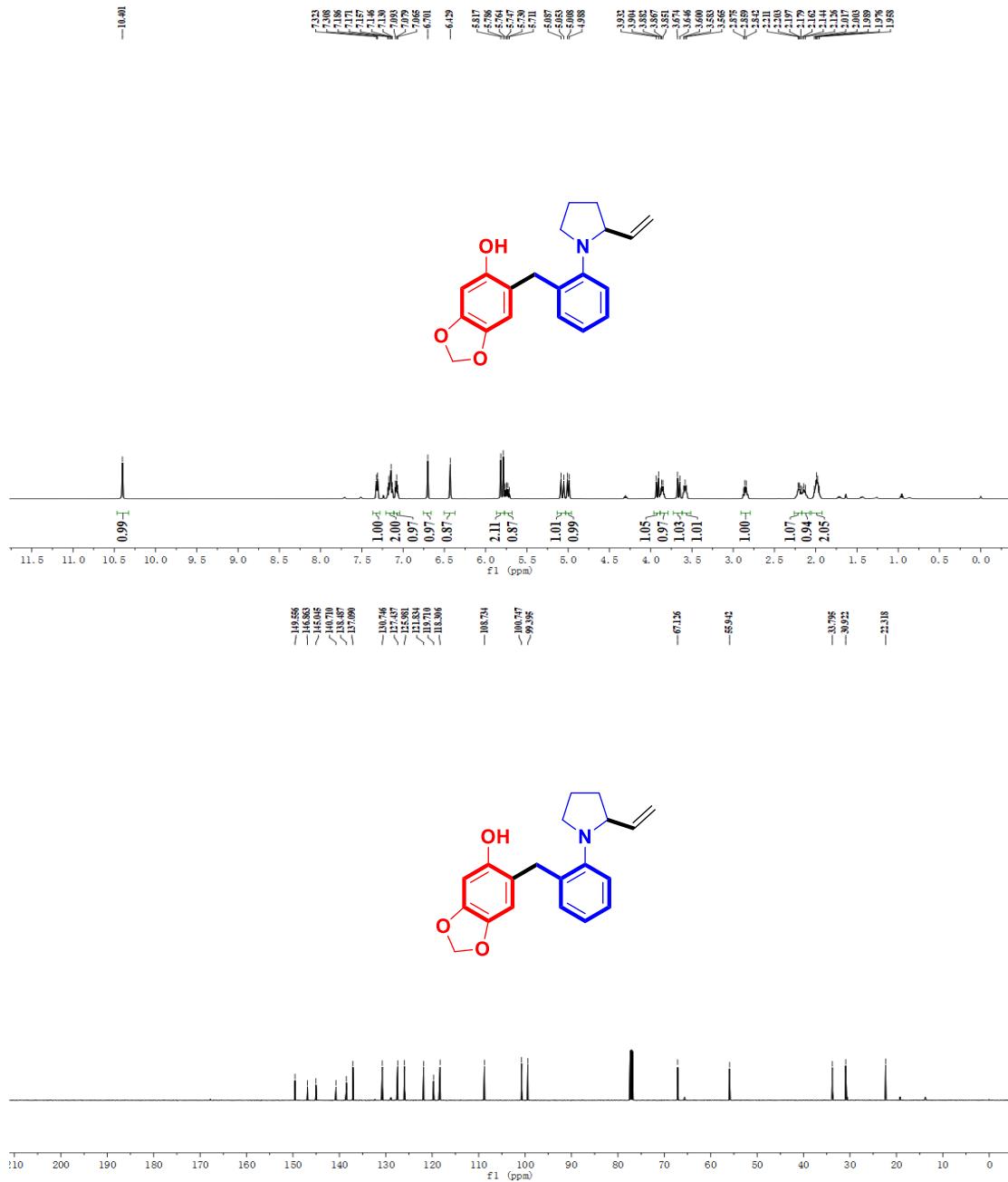
6-(2-(2-phenylpyrrolidin-1-yl)benzyl)benzo[d][1,3]dioxol-5-ol (7a)



6-(2-(2-allylpyrrolidin-1-yl)benzyl)benzo[d][1,3]dioxol-5-ol (7b)



6-(2-(2-vinylpyrrolidin-1-yl)benzyl)benzo[d][1,3]dioxol-5-ol (7c)



6-(2-(2-ethylpyrrolidin-1-yl)benzyl)benzo[d][1,3]dioxol-5-ol (7d)

