Supporting Information

Switchable construction of oxa-heterocycles with divergent ring sizes via dibrominated compounds-controlled chemoselective cyclization

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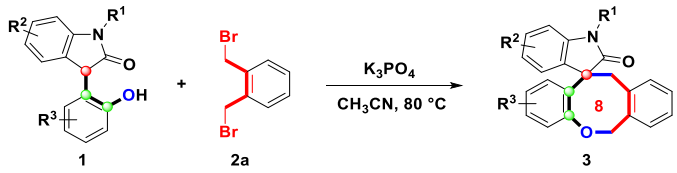
1. General Information

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 (^{1}H NMR) were recorded on a Bruker 500 MHz NMR spectrometer ($CDCl_3$ or DMSO-d_6 solvent). The chemical shifts were reported in parts per million (ppm), downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 7.26, singlet) or dimethyl sulfoxide-d_6 (δ 2.54, singlet). Multiplicities were afforded as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublets of doublet) or m (multiplets). The number of protons for a given resonance is indicated by nH. Coupling constants were reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) was referenced to the appropriate residual solvent peak. High resolution mass spectral analysis (HRMS) was performed on Waters XEVO G2 Q-TOF. All 3-(2-hydroxyphenyl)indolin-2-ones were prepared according to literature.[1]

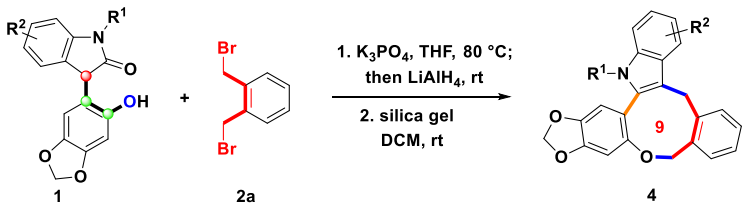
2. General Procedure

2.1 General Procedure for Synthesis of Spirooxindole-fused Dibenzo[*b*,*f*]oxocines 3



A sealed tube was charged with 3-(2-hydroxyphenyl)indolin-2-one **1** (0.1 mmol), 1,2-bis(bromomethyl)benzene **2a** (1.1 equiv.), K_3PO_4 (3 equiv.), and CH_3CN (1 mL). The mixture was stirred at 80 °C. 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 spirooxindole-fused dibenzo[*b*,*f*]oxocines **3a-m**.

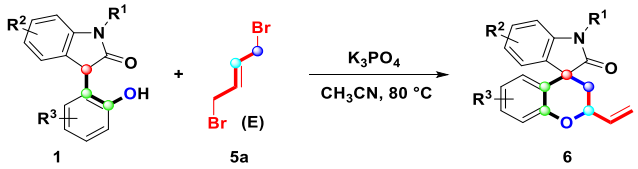
2.2 General Procedure for Synthesis of Indole Fused Nine-membered Oxa-heterocycles 4



A sealed tube was charged with 3-(2-hydroxyphenyl)indolin-2-one **1** (0.3 mmol), 1,2-bis(bromomethyl)benzene **2a** (1.1 equiv.), K_3PO_4 (3 equiv.), and THF (3 mL). The mixture was stirred at 80 °C. Upon completion of the reaction as indicated by TLC analysis, $LiAlH_4$ (6 equiv.) was added to the mixture and stirred at room temperature. When product **3** was consumed up by TLC analysis, H_2O (5 mL) was added dropwise to the system at 0 °C and the resulting solution was extracted with

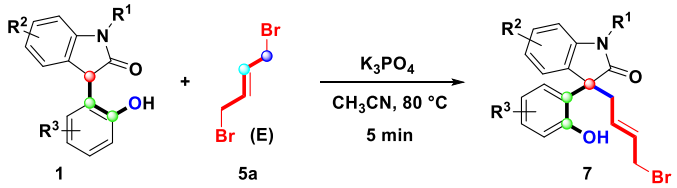
EtOAc (5 mL×3). The combined organic extracts were dried with anhydrous Na_2SO_4 and concentrated in vacuo. The residue could be used in next step without needing to purify. Then silica gel (200 mg) was added in the residue, and the mixture was stirred in DCM (3 mL) at room temperature for 5 h. Upon completion of the reaction, 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 indole fused nine-membered oxa-heterocycles **4a-e**.

2.3 General Procedure for Synthesis of Spirooxindole-fused Chromans 6



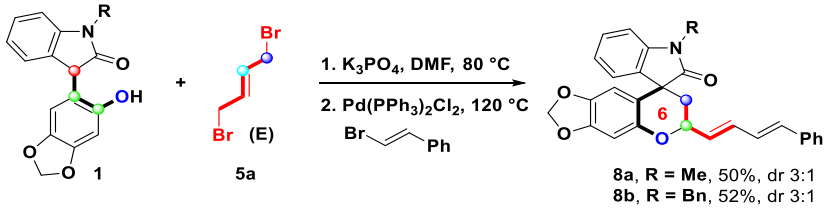
A sealed tube was charged with 3-(2-hydroxyphenyl)indolin-2-one **1** (0.1 mmol), (*E*)-1,4-dibromobut-2-ene **5a** (1.1 equiv.), K_3PO_4 (3 equiv.), and CH_3CN (1 mL). The mixture was stirred at 80 °C. Upon completion of the reaction as indicated by TLC analysis, the mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether, 1:20) to afford the desired spirooxindole-fused chromans **6a-l**.

2.4 General Procedure for Synthesis of Allylated Oxindoles 7



A sealed tube was charged with 3-(2-hydroxyphenyl)indolin-2-one **1** (0.1 mmol), (*E*)-1,4-dibromobut-2-ene **5a** (1.1 equiv.), K_3PO_4 (3 equiv.), and CH_3CN (1 mL). The mixture was stirred at 80 °C for 5 minute. 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 allylated oxindoles **7a-c**.

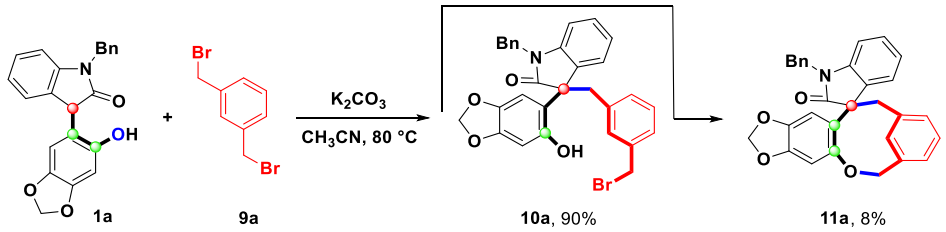
2.5 General Procedure for "One-pot" Synthesis of Conjugated Alkene Substituted Chromans 8



A sealed tube was charged with 3-(2-hydroxyphenyl)indolin-2-one **1** (0.1 mmol), (*E*)-1,4-dibromobut-2-ene **5a** (1.1 equiv.), K_3PO_4 (3 equiv.), and DMF (1 mL). The mixture was stirred at 80 °C. Upon completion of the reaction as indicated by TLC analysis, $Pd(PPh_3)_2Cl_2$ (15 mol%) and β-bromostyrene (1 equiv.) were added to the mixture and stirred at 120 °C. When product **6** was consumed up by TLC analysis, H_2O (3 mL) was added dropwise to the system at 0 °C and the resulting solution was extracted with EtOAc (5 mL×3). The combined organic extracts were dried with

anhydrous Na_2SO_4 and concentrated in vacuo. The residue was directly purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether, 1:20) to afford the desired conjugated alkene substituted chromans **8a** and **8b**.

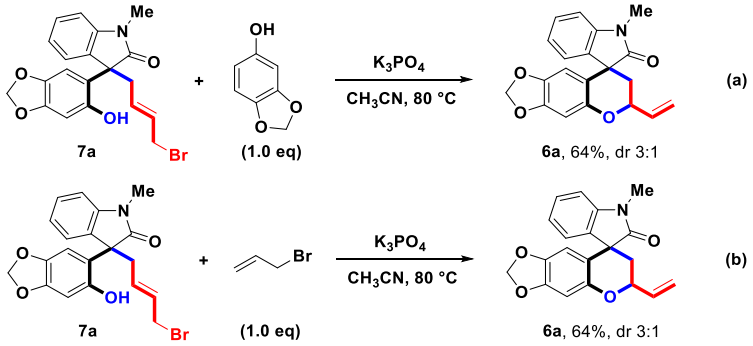
2.6 General Procedure for Synthesis of Benzylated Product 10a and Oxa-heterocycle 11a



A sealed tube was charged with 3-(2-hydroxyphenyl)indolin-2-one **1** (0.1 mmol), 1,3-bis(bromomethyl)benzene **9a** (1.1 equiv.), K_3PO_4 (3 equiv.), and CH_3CN (1 mL). The mixture was stirred at 80 °C 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 benzylated product **10a** in 90% yield.

A sealed tube was charged with 3-(2-hydroxyphenyl)indolin-2-one **1** (0.1 mmol), 1,3-bis(bromomethyl)benzene **9a** (1.1 equiv.), K_3PO_4 (3 equiv.), and CH_3CN (1 mL). The mixture was stirred at 80 °C for 6 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 oxa-heterocycle **11a** in 8% yield.

3. Control Experiments



(a) A sealed tube was charged with allylated oxindole **7a** (0.1 mmol), sesamol (1 equiv.), K_3PO_4 (3 equiv.), and CH_3CN (1 mL). The mixture was stirred at 80 °C. 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). The spirooxindole-fused chroman **6a** was obtained in 64% yield.

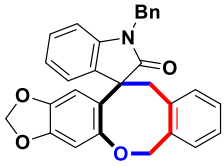
(b) A sealed tube was charged with allylated oxindole **7a** (0.1 mmol), allyl bromide (1 equiv.), K_3PO_4 (3 equiv.), and CH_3CN (1 mL). The mixture was stirred at 80 °C. Upon completion of the reaction as indicated by TLC analysis, the mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether, 1:20). The spirooxindole-fused chroman **6a** was obtained in 64% yield.

The control experiments between **7a** and sesamol/allyl bromide demonstrated that intramolecular

nucleophilic substitution completely surpassed intermolecular reaction.

4. Characterization of Products

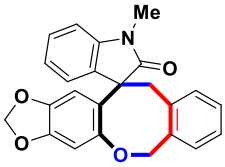
1-benzyl-6',11'-dihydrospiro[indoline-3,12'-[1,3]dioxolo[4',5':4,5]benzo[1,2-b]benzo[f]oxocin]-2-one (3a)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (36.2 mg, 75% yield, ar 1:1) as a faint yellow solid. (atropisomer ratio = ar)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.3 Hz, 1H), 7.42 (d, *J* = 7.2 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 3H), 7.29 (s, 5H), 7.23 (s, 3H), 7.19 – 7.09 (m, 4H), 7.05 – 6.90 (m, 5H), 6.86 – 6.75 (m, 3H), 6.75 – 6.64 (m, 2H), 6.20 (s, 1H), 5.82 – 5.60 (m, 7H), 5.11 – 4.95 (m, 5H), 4.88 (t, *J* = 13.6 Hz, 2H), 4.28 (d, *J* = 13.5 Hz, 1H), 2.94 (d, *J* = 13.5 Hz, 1H), 2.62 (d, *J* = 12.7 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 179.1, 178.5, 152.8, 150.5, 147.8, 147.5, 144.4, 144.2, 142.4, 140.9, 136.8, 136.2, 136.1, 135.9, 135.7, 135.6, 135.5, 134.1, 133.1, 132.9, 128.9, 128.9, 128.3, 127.9, 127.8, 127.7, 127.7, 127.5, 127.3, 127.3, 127.2, 127.1, 127.0, 126.7, 126.2, 124.5, 124.3, 123.4, 122.2, 109.5, 108.9, 108.5, 107.8, 104.7, 103.9, 101.5, 57.9, 57.0, 53.5, 43.9, 43.8, 42.3, 41.9. **HRMS (ESI) m/z:** $[M+Na]^+$ calcd for $C_{30}H_{23}NaNO_4$ 484.1525; found: 484.1527.

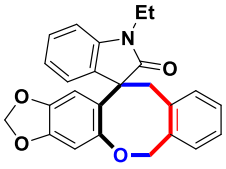
1-methyl-6',11'-dihydrospiro[indoline-3,12'-[1,3]dioxolo[4',5':4,5]benzo[1,2-b]benzo[f]oxocin]-2-one (3b)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (23.1 mg, 60% yield, ar 1:1) as a faint yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.3 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 7.4 Hz, 1H), 7.18 – 7.13 (m, 2H), 7.11 (s, 2H), 7.07 – 7.02 (m, 1H), 6.95 (d, *J* = 5.5 Hz, 3H), 6.88 (d, *J* = 7.1 Hz, 3H), 6.78 (d, *J* = 7.6 Hz, 1H), 6.67 (d, *J* = 7.6 Hz, 2H), 6.59 (s, 1H), 6.11 (s, 1H), 5.69 (dd, *J* = 10.0, 5.2 Hz, 5H), 5.58 (dd, *J* = 22.2, 14.0 Hz, 2H), 4.97 (d, *J* = 13.9 Hz, 2H), 4.74 (d, *J* = 12.8 Hz, 1H), 4.17 (d, *J* = 13.5 Hz, 1H), 3.28 (s, 3H), 3.17 (s, 3H), 2.83 (d, *J* = 13.5 Hz, 1H), 2.50 (d, *J* = 12.8 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 179.1, 178.3, 152.7, 150.5, 147.7, 147.4, 144.3, 144.0, 143.4, 141.9, 136.7, 136.0, 135.7, 135.4, 134.1, 133.0, 132.9, 128.3, 128.0, 127.7, 127.3, 127.2, 127.1, 127.0, 127.0, 126.7, 126.1, 124.3, 124.2, 123.3, 122.2, 108.6, 108.4, 107.9, 104.6, 103.8, 101.5, 57.9, 57.0, 41.9, 41.7, 26.6, 26.4. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{24}H_{20}NO_4$ 386.1387; found: 386.1371.

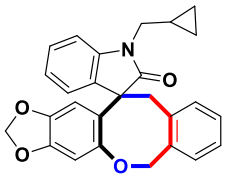
1-methyl-6',11'-dihydrospiro[indoline-3,12'-[1,3]dioxolo[4',5':4,5]benzo[1,2-b]benzo[f]oxocin]-2-one (3c)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (32.3 mg, 81% yield, ar 1:1) as a faint yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 6.1 Hz, 1H), 7.41 – 7.28 (m, 2H), 7.25 – 7.15 (m, 4H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.08 – 6.90 (m, 6H), 6.87 (d, *J* = 7.5 Hz, 1H), 6.80-6.67 (m, 3H), 6.18 (s, 1H), 5.77 (s, 5H), 5.65 (dd, *J* = 20.1, 14.2 Hz, 2H), 5.04 (d, *J* = 13.8 Hz, 2H), 4.82 (d, *J* = 12.4 Hz, 1H), 4.25 (d, *J* = 13.4 Hz, 1H), 4.00 – 3.85 (m, 2H), 3.85-3.71 (m, 2H), 2.87 (d, *J* = 13.4 Hz, 1H), 2.55 (d, *J* = 12.6 Hz, 1H), 1.38 (t, *J* = 6.7 Hz, 3H), 1.28 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 178.6, 177.8, 152.7, 150.5, 147.6, 147.3, 144.3, 144.0, 142.4, 140.9, 136.7, 135.9, 135.9, 135.7, 135.4, 134.3, 133.1, 132.9, 128.2, 127.9, 127.6, 127.2, 127.2, 127.1, 126.9, 126.9, 126.8, 126.3, 124.5, 124.3, 123.1, 121.9, 108.5, 108.0, 107.7, 104.6, 103.8, 101.4, 57.8, 56.8, 41.9, 41.6, 34.9, 34.7, 12.9, 12.7. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{25}H_{22}NO_4$ 400.1543; found: 400.1520.

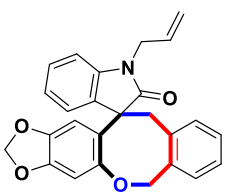
1-(cyclopropylmethyl)-6',11'-dihydrospiro[indoline-3,12'-[1,3]dioxolo[4',5':4,5]benzo[1,2-b]benzo[f]oxocin]-2-one (3d)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (28.0 mg, 66% yield, ar 1.3:1) as a faint yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.3 Hz, 1H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.29 (d, *J* = 7.3 Hz, 1H), 7.21 (dd, *J* = 17.3, 11.3 Hz, 4H), 7.12 (t, *J* = 7.2 Hz, 1H), 7.04 (d, *J* = 7.6 Hz, 4H), 6.98 – 6.88 (m, 3H), 6.79 – 6.64 (m, 3H), 6.24 (s, 1H), 5.77 (t, *J* = 10.0 Hz, 5H), 5.71 – 5.58 (m, 2H), 5.04 (d, *J* = 13.8 Hz, 2H), 4.83 (d, *J* = 12.8 Hz, 1H), 4.27 (d, *J* = 13.5 Hz, 1H), 3.74 (t, *J* = 6.8 Hz, 3H), 3.63 (d, *J* = 6.3 Hz, 2H), 2.88 (d, *J* = 13.5 Hz, 1H), 2.56 (d, *J* = 12.7 Hz, 1H), 1.25 (dd, *J* = 25.1, 16.7 Hz, 4H), 0.65 – 0.47 (m, 7H), 0.44 – 0.29 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 179.2, 178.4, 152.7, 150.5, 147.6, 147.4, 144.4, 144.1, 143.1, 141.4, 136.8, 135.9, 135.8, 135.7, 135.4, 134.2, 133.1, 132.9, 128.2, 127.9, 127.6, 127.2, 127.1, 127.0, 126.9, 126.8, 126.2, 124.5, 124.4, 123.1, 121.9, 108.8, 108.5, 108.3, 107.8, 104.6, 103.8, 101.4, 57.9, 56.9, 44.4, 44.2, 41.9, 41.8, 9.9, 9.7, 4.0, 3.9, 3.8, 3.7. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{27}H_{24}NO_4$ 426.1700; found: 426.1681.

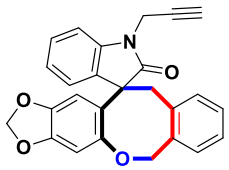
1-allyl-6',11'-dihydrospiro[indoline-3,12'-[1,3]dioxolo[4',5':4,5]benzo[1,2-b]benzo[f]oxocin]-2-one (3e)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (28.8 mg, 70% yield, ar 1:1) as a faint yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 6.8 Hz, 1H), 7.30 (d, *J* = 5.7 Hz, 2H), 7.19 (s, 4H), 7.13 (d, *J* = 6.7 Hz, 1H), 7.02 (d, *J* = 5.4 Hz, 3H), 6.94 (d, *J* = 6.1 Hz, 3H), 6.85 (d, *J* = 7.2 Hz, 1H), 6.74 (d, *J* = 12.7 Hz, 2H), 6.67 (s, 1H), 6.19 (s, 1H), 5.95 (d, *J* = 4.7 Hz, 1H), 5.90 – 5.72 (m, 6H), 5.72 – 5.58 (m, 2H), 5.39 – 5.14 (m, 4H), 5.04 (d, *J* = 13.8 Hz, 2H), 4.84 (d, *J* = 12.7 Hz, 1H), 4.48 (s, 2H), 4.37 (s, 2H), 4.27 (d, *J* = 13.4 Hz, 1H), 2.90 (d, *J* = 13.5 Hz, 1H), 2.59 (d, *J* = 12.7 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 178.7, 177.9, 152.7, 150.5, 147.7, 147.4, 144.2, 144.1, 142.5, 140.9, 136.7, 135.9, 135.6, 135.4, 134.0, 133.0, 132.9, 131.5, 128.2, 127.9, 127.6, 127.3, 127.2, 127.2, 126.9, 126.7, 126.1, 124.4, 124.2, 123.3, 122.1, 117.6, 117.5, 109.3, 108.8, 108.4, 107.7, 104.6, 103.8, 101.4, 57.8, 56.9, 42.5, 42.2, 41.8. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{26}H_{22}NO_4$ 412.1543; found: 412.1545.

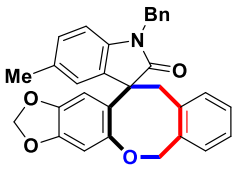
1-(prop-2-yn-1-yl)-6',11'-dihydrospiro[indoline-3,12'-[1,3]dioxolo[4',5':4,5]benzo[1,2-b]benzo[f]oxocin]-2-one (3f)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (28.2 mg, 69% yield, ar 1:1) as a faint yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.3 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.34 – 7.26 (m, 2H), 7.20 (dd, *J* = 18.9, 6.9 Hz, 4H), 7.13 (t, *J* = 7.3 Hz, 1H), 7.07 (t, *J* = 8.5 Hz, 3H), 7.02 (s, 1H), 6.95 (dd, *J* = 12.7, 6.0 Hz, 2H), 6.75 (d, *J* = 6.0 Hz, 2H), 6.67 (s, 1H), 6.17 (s, 1H), 5.77 (t, *J* = 8.3 Hz, 5H), 5.65 (dd, *J* = 19.5, 14.1 Hz, 2H), 5.04 (d, *J* = 14.0 Hz, 2H), 4.81 (d, *J* = 12.8 Hz, 1H), 4.65 (s, 2H), 4.59 (d, *J* = 17.9 Hz, 1H), 4.48 (d, *J* = 18.8 Hz, 1H), 4.25 (d, *J* = 13.6 Hz, 1H), 2.89 (d, *J* = 13.6 Hz, 1H), 2.60 (d, *J* = 12.8 Hz, 1H), 2.26 (d, *J* = 13.1 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 178.1, 177.3, 152.6, 150.4, 147.8, 147.5, 144.4, 144.1, 141.4, 139.9, 136.7, 135.8, 135.5, 135.5, 133.9, 133.0, 132.9, 128.4, 127.9, 127.7, 127.3, 127.2, 127.1, 127.0, 126.4, 126.2, 124.5, 123.9, 123.7, 122.6, 109.5, 108.9, 108.6, 107.7, 104.6, 103.8, 101.5, 72.5, 72.4, 57.8, 56.9, 41.9, 41.6, 29.6, 29.3. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{26}H_{20}NO_4$ 410.1387; found: 410.1376.

1-benzyl-5-methyl-6',11'-dihydrospiro[indoline-3,12'-[1,3]dioxolo[4',5':4,5]benzo[1,2-b]benzo[f]oxocin]-2-one (3g)

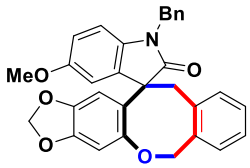


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (32.3 mg, 68% yield, ar 5:4) as a faint yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.41 (d, *J* = 7.4 Hz, 2H), 7.38 – 7.32 (m, 3H), 7.32 – 7.26 (m, 5H), 7.25 – 7.16 (m, 3H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.07 – 7.00 (m, 2H), 6.97 (d, *J* = 7.4 Hz, 1H), 6.93 (d, *J* = 6.6 Hz, 2H), 6.77 (s, 1H), 6.68 (dd, *J* = 14.0, 10.0 Hz, 3H), 6.52 (s, 1H), 6.20 (s, 1H), 5.83 (s, 1H), 5.81

(s, 2H), 5.77 (d, *J* = 6.2 Hz, 2H), 5.67 (dd, *J* = 20.0, 14.1 Hz, 2H), 5.05 (dd, *J* = 17.3, 4.1 Hz, 4H), 5.01 – 4.94 (m, 1H), 4.88 (t, *J* = 15.3 Hz, 2H), 4.28 (d, *J* = 13.5 Hz, 1H), 2.92 (d, *J* = 13.6 Hz, 1H), 2.59 (d, *J* = 12.7 Hz, 1H), 2.28 (s, 3H), 2.23 (s, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 179.0, 178.4, 152.7, 150.5, 147.7, 147.4, 144.4, 144.1, 139.9, 138.5, 136.8, 136.3, 136.2, 135.9, 135.6, 135.4, 134.1, 133.1, 133.0, 132.9, 131.6, 128.9, 128.8, 128.5, 128.3, 127.7, 127.6, 127.6, 127.5, 127.3, 127.2, 127.2, 127.0, 126.9, 126.8, 126.7, 125.1, 124.4, 109.2, 108.7, 108.6, 107.9, 104.6, 103.8, 101.5, 57.9, 57.1, 43.9, 43.7, 42.4, 41.8, 29.7, 21.2. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{31}H_{26}NO_4$ 476.1856; found: 476.1838.

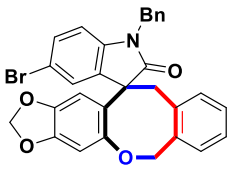
1-benzyl-5-methoxy-6',11'-dihydrospiro[indoline-3,12'-[1,3]dioxolo[4',5':4,5]benzo[1,2-b]benzo[f]oxocin]-2-one (3h)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (34.4 mg, 70% yield, ar 1:1) as a faint yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.4 Hz, 2H), 7.32 (m, 9H), 7.24 – 7.16 (m, 3H), 7.14 (d, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 5.0 Hz, 1H), 6.96 (d, *J* = 6.2 Hz, 2H), 6.83 – 6.74 (m, 2H), 6.68 (dd, *J* = 20.5, 6.7 Hz, 4H), 6.30 (d, *J* = 1.7 Hz, 1H), 6.22 (s, 1H), 5.79 (dd, *J* = 25.3, 7.9 Hz, 5H), 5.69 (d, *J* = 14.3 Hz, 1H), 5.63 (d, *J* = 13.7 Hz, 1H), 5.11 – 5.00 (m, 4H), 4.92 (dt, *J* = 30.7, 15.7 Hz, 3H), 4.26 (d, *J* = 13.5 Hz, 1H), 3.74 (s, 3H), 3.65 (s, 3H), 2.95 (d, *J* = 13.5 Hz, 1H), 2.61 (d, *J* = 12.8 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 178.9, 178.2, 156.5, 155.4, 152.7, 150.5, 147.8, 147.4, 144.4, 144.2, 136.9, 136.8, 136.3, 136.2, 135.9, 135.8, 135.5, 135.2, 134.4, 133.1, 133.1, 128.9, 128.8, 127.7, 127.7, 127.6, 127.5, 127.4, 127.3, 127.3, 127.2, 127.1, 126.8, 126.6, 124.2, 113.5, 112.8, 112.4, 111.7, 109.9, 109.3, 108.5, 107.8, 104.6, 103.9, 101.5, 101.5, 58.3, 57.4, 55.8, 55.7, 44.0, 43.8, 42.4, 41.7, 29.8. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{31}H_{26}NO_5$ 492.1805; found: 492.1781.

1-benzyl-5-bromo-6',11'-dihydrospiro[indoline-3,12'-[1,3]dioxolo[4',5':4,5]benzo[1,2-b]benzo[f]oxocin]-2-one (3i)

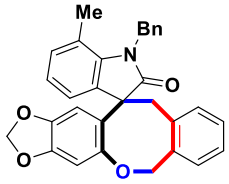


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (37.2 mg, 69% yield, ar 4:3) as a faint yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.45 – 7.34 (m, 6H), 7.33-7.29 (m, 4H), 7.28-7.26 (m, 2H), 7.25 – 7.21 (m, 3H), 7.14 (t, *J* = 7.3 Hz, 1H), 7.08-7.02 (m, 1H), 6.97 (d, *J* = 7.3 Hz, 1H), 6.95-6.88 (s, 1H), 6.79 (m, *J* = 12.6 Hz, 2H), 6.69 (s, 2H), 6.63 (d, *J* = 8.2 Hz, 1H), 6.18 (s, 1H), 5.90-5.75 (m, 5H), 5.74-5.55 (m, 2H), 5.10-5.00 (m, 4H), 5.00-4.85 (m, 3H), 4.23 (d, *J* = 13.5 Hz, 1H), 2.93 (d, *J* = 13.5 Hz, 1H), 2.57 (d, *J* = 12.8 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 178.5, 177.8, 152.7, 150.5, 147.9, 147.6, 144.4, 144.3, 139.9, 137.5, 136.6, 135.9, 135.7, 135.6, 135.5, 134.9, 132.9, 132.8, 131.1, 130.8, 129.1, 128.9, 128.9, 127.9, 127.8, 127.7, 127.6, 127.3, 127.2, 127.1, 125.9, 123.3, 116.0, 114.9, 110.9, 110.4, 108.2, 107.6,

104.7, 103.9, 101.6, 101.5, 44.0, 43.7, 42.2, 41.7. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{30}H_{23}BrNO_4$ 540.0805; found: 540.0778.

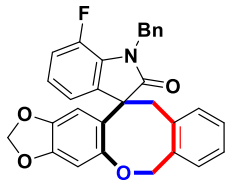
1-benzyl-7-methyl-6',11'-dihydrospiro[indoline-3,12'-[1,3]dioxolo[4',5':4,5]benzo[1,2-b]benzo[f]oxocin]-2-one (3j)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (30.9 mg, 65% yield, ar 1:1) as a faint yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.1 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 6H), 7.23 (d, *J* = 7.5 Hz, 1H), 7.22 – 7.09 (m, 6H), 7.06 – 6.99 (m, 2H), 6.93 (m, 5H), 6.77 (s, 1H), 6.68 (s, 1H), 6.56 (d, *J* = 7.3 Hz, 1H), 6.21 (s, 1H), 5.89 (s, 1H), 5.81 (s, 2H), 5.77 (d, *J* = 14.1 Hz, 2H), 5.66 (dd, *J* = 18.8, 14.1 Hz, 2H), 5.43 (d, *J* = 16.8 Hz, 1H), 5.30 – 5.18 (m, 3H), 5.06 (dd, *J* = 14.0, 4.2 Hz, 2H), 4.90 (d, *J* = 12.7 Hz, 1H), 4.33 (d, *J* = 13.5 Hz, 1H), 2.95 (d, *J* = 13.6 Hz, 1H), 2.66 (d, *J* = 12.7 Hz, 1H), 2.36 (s, 3H), 2.32 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 179.9, 179.5, 152.7, 150.4, 147.7, 147.4, 144.4, 144.1, 140.5, 139.1, 138.1, 137.9, 136.8, 136.3, 135.8, 135.5, 135.4, 134.7, 133.1, 132.1, 131.9, 128.9, 128.8, 127.5, 127.2, 127.1, 126.9, 126.9, 126.8, 125.8, 125.7, 124.6, 124.3, 123.4, 122.5, 122.1, 120.0, 119.5, 108.6, 107.9, 104.6, 103.8, 101.4, 57.2, 56.6, 45.2, 44.9, 42.9, 42.4, 19.1, 18.9. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{31}H_{26}NO_4$ 476.1856; found: 476.1841.

1-benzyl-7-fluoro-6',11'-dihydrospiro[indoline-3,12'-[1,3]dioxolo[4',5':4,5]benzo[1,2-b]benzo[f]oxocin]-2-one (3k)

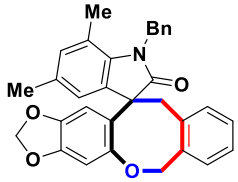


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (28.7 mg, 60% yield, ar 5:4) as a faint yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.1 Hz, 3H), 7.39 – 7.32 (m, 4H), 7.29 (d, *J* = 6.6 Hz, 4H), 7.20 – 7.11 (m, 3H), 7.05 – 6.98 (m, 2H), 6.97 – 6.89 (m, 4H), 6.86 (d, *J* = 6.9 Hz, 1H), 6.77 (s, 1H), 6.65 (s, 1H), 6.48 (d, *J* = 7.3 Hz, 1H), 6.12 (s, 1H), 5.85 – 5.72 (m, 5H), 5.72-5.55 (m, 2H), 5.19 (dd, *J* = 38.0, 15.1 Hz, 2H), 5.13 – 4.99 (m, 4H), 4.88 (d, *J* = 12.8 Hz, 1H), 4.24 (d, *J* = 13.5 Hz, 1H), 2.89 (d, *J* = 13.5 Hz, 1H), 2.58 (d, *J* = 12.8 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 178.8, 178.2, 151.5 (d, *J* = 242.5 Hz), 148.7, 147.9, 147.6, 147.2 (d, *J* = 243.7 Hz), 144.5, 144.2, 138.5, 137.4, 137.4, 136.9, 136.8, 135.4, 135.1, 133.1, 132.9, 129.3, 128.8, 128.6, 127.8, 127.7 (d, *J* = 1.1 Hz), 127.6, 127.4, 127.3, 127.3, 127.1 (d, *J* = 1.2 Hz), 126.2, 123.9 (d, *J* = 0.6 Hz), 123.7, 122.7 (d, *J* = 0.6 Hz), 122.1, 120.4, 116.3 (d, *J* = 20.0 Hz), 115.1 (d, *J* = 20.0 Hz), 108.3, 107.8, 104.7, 103.9, 101.6, 101.5, 58.2, 57.2, 45.5, 45.5, 45.3, 45.3, 42.3, 42.0. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{30}H_{23}FNO_4$ 480.1606; found: 480.1583.

1-benzyl-5,7-dimethyl-6',11'-dihydrospiro[indoline-3,12'-[1,3]dioxolo[4',5':4,5]benzo[1,2-

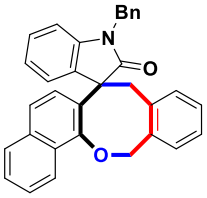
b]benzo[f]oxocin]-2-one (3l)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (27.8 mg, 57% yield, ar 5:4) as a faint yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.31 – 7.25 (m, 6H), 7.22 (d, *J* = 7.4 Hz, 1H), 7.18 (t, *J* = 6.7 Hz, 3H), 7.14 (d, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 7.3 Hz, 1H), 7.04 (d, *J* = 6.6 Hz, 1H), 6.94 (dd, *J* = 14.5, 7.2 Hz, 2H), 6.81 (s, 1H), 6.77 (s, 1H), 6.72 (s, 1H), 6.69 (s, 1H), 6.35 (s, 1H), 6.21 (s, 1H), 5.92 (s, 1H), 5.81 (s, 2H), 5.77 (d, *J* = 14.4 Hz, 2H), 5.67 (t, *J* = 13.2 Hz, 2H), 5.41 (d, *J* = 16.8 Hz, 1H), 5.23 (d, *J* = 16.9 Hz, 1H), 5.19 (s, 2H), 5.07 (s, 1H), 5.04 (s, 1H), 4.91 (d, *J* = 12.7 Hz, 1H), 4.33 (d, *J* = 13.5 Hz, 1H), 2.93 (d, *J* = 13.5 Hz, 1H), 2.63 (d, *J* = 12.7 Hz, 1H), 2.30 (s, 2H), 2.27 (s, 3H), 2.26 (s, 3H), 2.20 (s, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 179.9, 179.4, 152.8, 150.5, 147.7, 147.4, 144.5, 144.1, 138.2, 138.0, 138.0, 136.8, 136.6, 136.4, 135.8, 135.5, 135.4, 134.8, 133.3, 133.2, 132.9, 132.6, 132.4, 131.5, 128.9, 128.8, 127.5, 127.3, 127.2, 127.2, 127.1, 127.1, 126.9, 126.9, 126.7, 125.8, 125.7, 125.0, 124.8, 123.1, 119.7, 119.3, 108.8, 108.0, 104.6, 103.8, 101.5, 57.3, 56.7, 45.1, 44.8, 42.9, 42.4, 20.9, 20.8, 18.9, 18.8. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{32}H_{28}NO_4$ 490.2013; found: 490.2000.

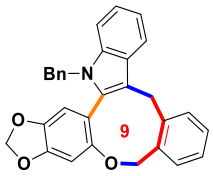
1'-benzyl-8,13-dihydrospiro[benzo[f]naphtho[1,2-b]oxocine-7,3'-indolin]-2'-one (3m)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (33.6 mg, 72% yield, ar 5:4) as a faint yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.3 Hz, 1H), 8.27 (d, *J* = 8.3 Hz, 1H), 7.75 (d, *J* = 7.3 Hz, 1H), 7.73 – 7.64 (m, 2H), 7.55 (dd, *J* = 17.1, 9.0 Hz, 2H), 7.44 (dd, *J* = 20.1, 7.0 Hz, 4H), 7.40 – 7.29 (m, 6H), 7.25 (d, *J* = 11.6 Hz, 4H), 7.19 (t, *J* = 7.3 Hz, 1H), 7.16 – 7.05 (m, 3H), 6.98 (dt, *J* = 22.8, 7.3 Hz, 3H), 6.91 (t, *J* = 6.3 Hz, 2H), 6.87 (d, *J* = 7.4 Hz, 2H), 6.80 (dd, *J* = 13.7, 7.7 Hz, 2H), 6.60 (d, *J* = 7.2 Hz, 1H), 6.41 (d, *J* = 8.6 Hz, 1H), 5.93 (d, *J* = 14.4 Hz, 1H), 5.84 (d, *J* = 13.5 Hz, 1H), 5.46 (t, *J* = 13.0 Hz, 2H), 5.19 (d, *J* = 12.8 Hz, 1H), 5.15 – 5.05 (m, 2H), 5.00 – 4.91 (m, 2H), 4.54 (d, *J* = 13.5 Hz, 1H), 3.06 (d, *J* = 13.6 Hz, 1H), 2.72 (d, *J* = 12.8 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 179.1, 178.4, 153.4, 150.9, 142.6, 141.1, 136.8, 136.3, 136.1, 135.6, 135.4, 135.3, 135.1, 134.7, 134.3, 134.1, 133.2, 132.9, 130.2, 129.0, 128.9, 128.8, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.7, 127.5, 127.4, 127.3, 127.2, 127.1, 126.9, 126.9, 126.8, 126.5, 126.4, 126.1, 126.0, 125.2, 124.7, 124.4, 123.3, 122.7, 122.1, 121.9, 109.5, 108.9, 76.7, 76.3, 58.8, 57.8, 44.0, 43.8, 42.6, 42.1. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{33}H_{26}NO_2$ 468.1958; found: 468.1937.

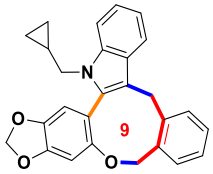
17-benzyl-5,17-dihydro-10H-[1,3]dioxolo[4'',5'':4',5']benzo[1',2':2,3]benzo[7,8]oxonino[4,5-b]indole (4a)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (30.3 mg, 68% yield) as a faint yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.4 Hz, 1H), 7.84 (d, *J* = 5.5 Hz, 1H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.23 – 7.15 (m, 5H), 7.15 – 7.11 (m, 1H), 7.10 – 7.05 (m, 2H), 6.98 (d, *J* = 7.4 Hz, 2H), 6.79 (s, 1H), 6.60 (s, 1H), 5.96 (s, 2H), 5.33 – 5.18 (m, 3H), 5.06 (d, *J* = 11.1 Hz, 1H), 4.15 (d, *J* = 14.1 Hz, 1H), 3.76 (d, *J* = 11.6 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 154.4, 148.8, 143.1, 140.9, 138.2, 137.4, 136.3, 133.4, 131.4, 129.4, 128.9, 128.7, 127.8, 127.0, 126.2, 125.9, 121.5, 119.5, 119.3, 115.4, 112.3, 110.5, 109.2, 102.2, 101.6, 47.9, 31.2. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{30}H_{24}NO_3$ 446.1751; found: 446.1738.

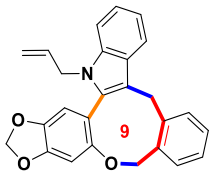
17-(cyclopropylmethyl)-5,17-dihydro-10H-[1,3]dioxolo[4'',5'':4',5']benzo[1',2':2,3]benzo[7,8]oxonino[4,5-b]indole (4b)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (23.7 mg, 58% yield) as a faint yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.83 (s, 1H), 7.40 (t, *J* = 10.1 Hz, 2H), 7.17 (dd, *J* = 17.3, 8.2 Hz, 4H), 6.84 (s, 1H), 6.76 (s, 1H), 6.06 (d, *J* = 11.8 Hz, 2H), 5.34 (d, *J* = 11.0 Hz, 1H), 5.07 (d, *J* = 10.8 Hz, 1H), 4.19 (dd, *J* = 14.6, 3.8 Hz, 1H), 4.11 (d, *J* = 14.1 Hz, 1H), 3.88 – 3.62 (m, 2H), 0.97 (s, 1H), 0.41 (s, 1H), 0.29 (s, 1H), 0.16 (d, *J* = 3.8 Hz, 1H), -0.08 (d, *J* = 3.6 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 154.6, 148.6, 143.2, 141.2, 137.4, 136.4, 133.0, 131.3, 129.5, 128.9, 127.7, 126.2, 121.2, 119.3, 119.2, 116.1, 112.4, 110.2, 109.6, 102.4, 101.8, 48.3, 31.1, 11.5, 4.2. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{27}H_{24}NO_3$ 410.1751; found: 410.1735.

17-allyl-5,17-dihydro-10H-[1,3]dioxolo[4'',5'':4',5']benzo[1',2':2,3]benzo[7,8]oxonino[4,5-b]indole (4c)

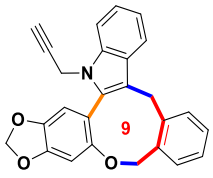


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (24.9 mg, 63% yield) as a faint yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.82 (d, *J* = 5.7 Hz, 1H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.26 – 7.22 (m, 1H), 7.20 – 7.11 (m, 4H), 6.81 (d, *J* = 9.5 Hz, 2H), 6.01 (d, *J* = 3.7 Hz, 2H), 5.97 – 5.86 (m, 1H), 5.29 (d, *J* = 11.2 Hz, 1H), 5.14 (d, *J* = 10.4 Hz, 1H), 5.05 (d, *J* = 11.2 Hz, 1H), 4.94 (d, *J* = 17.2 Hz, 1H), 4.60 (s, 2H), 4.11 (d, *J* = 14.1 Hz, 1H), 3.72 (d, *J* = 11.1 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 154.3, 148.8,

143.2, 140.9, 137.4, 136.3, 134.1, 133.2, 131.4, 129.5, 129.0, 127.7, 126.2, 121.4, 119.5, 119.3, 116.4, 115.6, 112.1, 110.4, 109.2, 102.2, 101.8, 46.8, 31.2. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{26}H_{21}NO_3$ 396.1594; found: 396.1571.

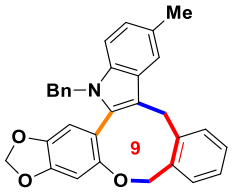
17-(prop-2-yn-1-yl)-5,17-dihydro-10H-[1,3]dioxolo[4'',5'':4',5']benzo[1',2':2,3]benzo[7,8]oxonino[4,5-b]indole (4d)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:15) afforded the product (24.3 mg, 62% yield) as a faint yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 5.6 Hz, 1H), 7.81 (s, 1H), 7.43 (d, *J* = 7.7 Hz, 1H), 7.36 (d, *J* = 6.5 Hz, 1H), 7.24 – 7.11 (m, 4H), 7.01 (s, 1H), 6.83 (s, 1H), 6.06 (s, 2H), 5.31 (d, *J* = 11.0 Hz, 1H), 5.07 (d, *J* = 10.9 Hz, 1H), 4.80 – 4.62 (m, 2H), 4.11 (d, *J* = 14.1 Hz, 1H), 3.72 (s, 1H), 2.35 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 154.3, 148.9, 143.4, 140.7, 137.0, 136.1, 132.7, 131.4, 129.5, 129.1, 127.8, 126.3, 121.8, 119.9, 119.4, 115.0, 112.4, 109.9, 109.5, 102.3, 101.8, 79.2, 72.8, 34.3, 31.0. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{26}H_{20}NO_3$ 394.1438; found: 394.1420.

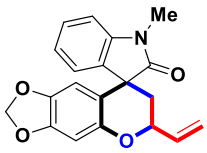
17-benzyl-3-methyl-5,17-dihydro-10H-[1,3]dioxolo[4'',5'':4',5']benzo[1',2':2,3]benzo[7,8]oxonino[4,5-b]indole (4e)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:15) afforded the product (28.5 mg, 62% yield) as a faint yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.70 (s, 1H), 7.39 (t, *J* = 7.0 Hz, 1H), 7.20 (dt, *J* = 6.8, 5.8 Hz, 5H), 6.97 (t, *J* = 5.9 Hz, 3H), 6.89 (d, *J* = 8.2 Hz, 1H), 6.78 (s, 1H), 6.60 (s, 1H), 5.96 (s, 2H), 5.26 (dd, *J* = 37.0, 18.2 Hz, 3H), 5.05 (d, *J* = 10.9 Hz, 1H), 4.11 (d, *J* = 14.0 Hz, 1H), 3.75 (s, 1H), 2.48 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 154.3, 148.7, 143.1, 141.0, 138.4, 136.4, 135.8, 133.5, 131.4, 129.4, 128.9, 128.7, 128.0, 127.0, 126.1, 125.9, 123.1, 119.0, 115.6, 111.8, 110.3, 109.2, 102.2, 101.7, 47.9, 31.3, 21.8. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{31}H_{26}NO_3$ 460.1907; found: 460.1880.

1-methyl-6'-vinyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (6a)

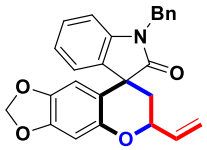


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:15) afforded the product (18.8 mg, 56% yield, dr 3:1) as a faint yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (t, *J* = 7.7 Hz, 1H), 7.15 (d, *J* = 7.4 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H),

6.87 (d, *J* = 7.8 Hz, 1H), 6.42 (s, 1H), 5.97 – 5.88 (m, 1H), 5.86 (s, 1H), 5.74 (s, 2H), 5.37 (d, *J* = 17.3 Hz, 1H), 5.21 (d, *J* = 10.6 Hz, 1H), 4.74 (dd, *J* = 11.8, 5.7 Hz, 1H), 3.25 (s, 3H), 2.39 – 2.27 (m, 1H), 1.79 (dd, *J* = 13.5, 1.9 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 179.3, 150.3, 147.9, 142.5, 142.4, 136.7, 136.4, 128.4, 124.2, 123.0, 117.3, 111.8, 108.5, 106.0, 101.1, 99.1, 72.9, 49.9, 37.9, 26.8. **HRMS (ESI) m/z:** $[M+H]^+$ calcd. for $C_{20}H_{18}NO_4$: 336.1230, found: 336.1212.

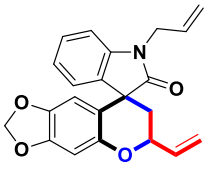
1-benzyl-6'-vinyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (6b)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (23.8 mg, 58% yield, dr 3:1) as a faint yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 4.3 Hz, 4H), 7.29 (dd, *J* = 8.5, 4.3 Hz, 1H), 7.20 (dd, *J* = 10.1, 7.7 Hz, 2H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.51 (s, 1H), 6.06 – 5.97 (m, 1H), 5.96 (s, 1H), 5.82 (d, *J* = 3.7 Hz, 2H), 5.46 (d, *J* = 17.2 Hz, 1H), 5.29 (d, *J* = 10.6 Hz, 1H), 5.00 (q, *J* = 15.5 Hz, 2H), 4.82 (dd, *J* = 11.9, 5.8 Hz, 1H), 2.48 (t, *J* = 12.8 Hz, 1H), 1.91 (d, *J* = 13.5 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 179.4, 150.3, 148.0, 142.4, 141.5, 136.6, 136.4, 135.8, 128.9, 128.3, 127.8, 127.4, 124.3, 122.9, 117.4, 111.8, 109.5, 106.1, 101.1, 99.2, 72.9, 49.8, 44.2, 38.1. **HRMS (ESI) m/z:** $[M+H]^+$ calcd. for $C_{26}H_{22}NO_4$: 412.1543, found: 412.1539.

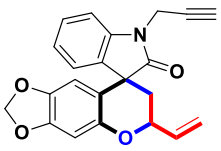
1-allyl-6'-vinyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (6c)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (19.9 mg, 55% yield, dr 2.5:1) as a faint yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, *J* = 7.7 Hz, 1H), 7.15 (d, *J* = 7.4 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.42 (s, 1H), 5.98 – 5.88 (m, 1H), 5.88 (s, 1H), 5.86 – 5.78 (m, 1H), 5.75 (s, 2H), 5.38 (d, *J* = 17.2 Hz, 1H), 5.29 – 5.12 (m, 3H), 4.75 (dd, *J* = 11.7, 5.7 Hz, 1H), 4.36 (d, *J* = 15.9 Hz, 2H), 2.35 (t, *J* = 12.8 Hz, 1H), 1.80 (dd, *J* = 13.5, 1.7 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 178.9, 150.3, 147.9, 142.4, 141.6, 136.6, 136.4, 131.3, 128.3, 124.3, 122.9, 117.9, 117.4, 111.8, 109.4, 106.0, 101.2, 99.2, 72.9, 49.8, 42.7, 38.1. **HRMS (ESI) m/z:** $[M+H]^+$ calcd. for $C_{22}H_{20}NO_4$: 362.1387, found: 362.1370.

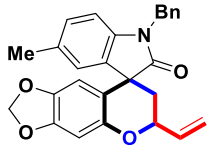
1-(prop-2-yn-1-yl)-6'-vinyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (6d)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (19.4 mg, 54% yield, dr 3:1) a faint yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 11.1, 4.3 Hz, 1H), 7.20 – 7.15 (m, 1H), 7.08 (d, *J* = 7.8 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.42 (s, 1H), 5.96 – 5.89 (m, 1H), 5.88 (d, *J* = 5.7 Hz, 1H), 5.74 (s, 2H), 5.37 (d, *J* = 17.3 Hz, 1H), 5.21 (d, *J* = 10.6 Hz, 1H), 4.74 (dd, *J* = 11.5, 5.8 Hz, 1H), 4.53 (m, 2H), 2.33 (dd, *J* = 13.4, 12.4 Hz, 1H), 2.2 (s, 1H), 1.83 (dd, *J* = 13.6, 2.0 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 178.4, 150.2, 148.1, 142.4, 140.5, 136.6, 136.2, 128.4, 124.4, 123.4, 117.4, 111.6, 109.6, 105.9, 101.2, 99.2, 72.9, 72.6, 49.7, 37.8, 29.7. **HRMS (ESI) m/z:** $[M+H]^+$ calcd. for $C_{22}H_{18}NO_4$: 360.1230, found: 360.1211.

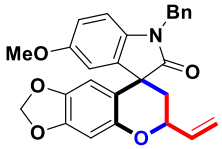
1-benzyl-5-methyl-6'-vinyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (6e)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (22.9 mg, 54% yield, dr 2.5:1) a faint yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (dd, *J* = 10.1, 2.9 Hz, 4H), 7.21 (m, 1H), 6.94 (s, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.64 (d, *J* = 7.9 Hz, 1H), 6.43 (s, 1H), 5.94 (m, 1H), 5.89 (s, 1H), 5.75 (dd, *J* = 2.4, 1.4 Hz, 2H), 5.40 (m, 1H), 5.23 (m, 1H), 4.91 (q, *J* = 15.5 Hz, 2H), 4.79 – 4.71 (m, 1H), 2.39 (dd, *J* = 13.4, 12.3 Hz, 1H), 2.19 (s, 3H), 1.83 (dd, *J* = 13.5, 2.0 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 179.4, 150.3, 147.9, 142.4, 139.1, 136.7, 136.5, 135.9, 132.6, 128.9, 128.6, 127.8, 127.4, 125.2, 117.3, 112.0, 109.3, 106.2, 101.2, 99.1, 72.9, 49.9, 44.2, 38.1, 21.1. **HRMS (ESI) m/z:** $[M+H]^+$ calcd. for $C_{27}H_{24}NO_4$: 426.1700, found: 426.1680.

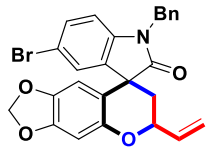
1-benzyl-5-methoxy-6'-vinyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (6f)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (26.9 mg, 61% yield, dr 3:1) a faint yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 4H), 7.32 – 7.27 (m, 1H), 6.81 (d, *J* = 1.9 Hz, 1H), 6.72 (t, *J* = 6.0 Hz, 2H), 6.50 (s, 1H), 6.06 – 5.98 (m, 1H), 5.97 (s, 1H), 5.83 (d, *J* = 1.2 Hz, 2H), 5.46 (d, *J* = 17.3 Hz, 1H), 5.30 (d, *J* = 10.6 Hz, 1H), 4.98 (q, *J* = 15.5 Hz, 2H), 4.80 (dd, *J* = 11.5, 5.8 Hz, 1H), 3.71 (s, 3H), 2.55 – 2.42 (m, 1H), 1.91 (dd, *J* = 13.5, 2.0 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 179.1, 156.2, 150.3, 148.0, 142.4, 137.7, 136.6, 135.9, 134.9, 128.9, 127.8, 127.4, 117.4, 112.2, 112.1, 111.8, 109.8, 106.1, 101.1, 99.2, 72.9, 55.8, 50.2, 44.3, 38.1. **HRMS (ESI) m/z:** $[M+H]^+$ calcd. for $C_{27}H_{24}NO_5$: 442.1649, found: 442.1622.

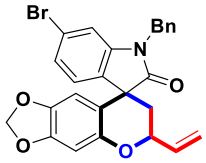
1-benzyl-5-bromo-6'-vinyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (6g)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (29.5 mg, 60% yield, dr 2:1) a faint yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 5H), 6.70 (d, *J* = 8.1 Hz, 1H), 6.52 (d, *J* = 9.3 Hz, 1H), 6.01 (m, 1H), 5.93 (s, 1H), 5.86 (d, *J* = 10.1 Hz, 2H), 5.49 (d, *J* = 17.2 Hz, 1H), 5.32 (d, *J* = 10.4 Hz, 1H), 4.98 (q, *J* = 15.5 Hz, 2H), 4.75 (dd, *J* = 11.9, 5.6 Hz, 1H), 2.47 (t, *J* = 12.9 Hz, 1H), 1.91 (d, *J* = 13.4 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 178.8, 150.4, 148.3, 142.5, 140.6, 138.3, 136.4, 135.4, 131.2, 129.0, 128.0, 127.5, 127.3, 117.5, 115.8, 111.0, 110.9, 105.9, 101.2, 99.3, 72.7, 49.9, 44.3, 38.0. **HRMS (ESI) m/z:** $[M+H]^+$ calcd. for $C_{26}H_{21}BrNO_4$: 492.0628, found: 492.0626.

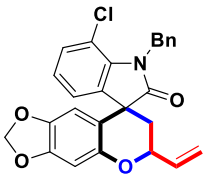
1-benzyl-6-bromo-6'-vinyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (6h)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (25.0 mg, 51% yield, dr 2:1, mixture) a faint yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 7H), 7.19 – 7.13 (m, 1H), 7.07 (d, *J* = 7.9 Hz, 1H), 6.93 (dd, *J* = 22.9, 15.8 Hz, 2H), 6.51 (d, *J* = 12.4 Hz, 1H), 5.99 (m, 1H), 5.92 (s, 1H), 5.88 – 5.78 (m, 3H), 5.48 (dd, *J* = 24.2, 17.3 Hz, 1H), 5.40 (dd, *J* = 10.0, 6.1 Hz, 1H), 5.30 (d, *J* = 10.5 Hz, 1H), 4.97 (q, *J* = 15.6 Hz, 2H), 4.83 (d, *J* = 15.6 Hz, 1H), 4.75 (dd, *J* = 11.8, 5.8 Hz, 1H), 2.45 (t, *J* = 12.8 Hz, 1H), 2.15 – 2.02 (m, 1H), 1.88 (d, *J* = 13.4 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 179.2, 179.1, 151.0, 150.3, 148.2, 148.1, 144.0, 142.9, 142.5, 142.1, 136.6, 136.4, 135.3, 135.2, 133.0, 129.1, 129.1, 128.1, 127.9, 127.3, 127.2, 126.3, 125.8, 125.6, 125.1, 122.0, 121.9, 117.6, 117.3, 112.8, 112.5, 111.2, 111.1, 105.9, 105.9, 101.2, 101.2, 99.4, 99.2, 72.9, 71.9, 49.6, 48.3, 44.3, 43.9, 38.1, 37.2. **HRMS (ESI) m/z:** $[M+H]^+$ calcd. for $C_{26}H_{21}BrNO_4$: 492.0628, found: 492.0626.

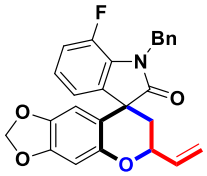
1-benzyl-7-chloro-6'-vinyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (6i)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (25.8 mg, 58% yield, dr 2:1) a faint yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, *J* = 7.7 Hz, 1H), 7.25 – 7.17 (m, 4H), 7.12 (d, *J* = 8.2 Hz, 1H), 7.05 (d, *J* = 7.4 Hz, 1H), 6.89 (t, *J* = 7.8 Hz, 1H), 6.43 (s, 1H), 5.98 – 5.90 (m, 1H), 5.89 (d, *J* = 4.0 Hz, 1H), 5.76 (s, 2H), 5.40 (t, *J* = 15.4 Hz, 2H), 5.33 (d, *J* = 16.0 Hz, 1H), 5.23 (d, *J* = 10.5 Hz, 1H), 4.71 (dd, *J* = 11.6, 5.8 Hz, 1H), 2.39 (t, *J* = 12.9 Hz, 1H), 1.84 (dd, *J* = 13.5, 1.7 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 180.1, 150.4, 148.2, 142.5, 139.2, 137.8, 137.6, 136.4, 130.9, 128.7, 127.4, 126.7, 123.9, 123.1, 117.6, 115.8, 111.3, 106.0, 101.3, 99.2, 72.7, 49.6, 45.3, 38.6. **HRMS (ESI) m/z:** $[M+H]^+$ calcd. for $C_{26}H_{21}ClNO_4$: 446.1154, found: 446.1131.

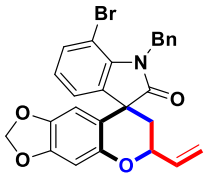
1-benzyl-7-fluoro-6'-vinyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (6j)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (25.7 mg, 60% yield, dr 2.5:1) a faint yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.6 Hz, 2H), 7.27 (t, *J* = 7.4 Hz, 2H), 7.21 (dd, *J* = 13.9, 6.6 Hz, 1H), 6.95 – 6.83 (m, 3H), 6.42 (s, 1H), 5.98 – 5.88 (m, 1H), 5.84 (s, 1H), 5.76 (dd, *J* = 5.4, 1.1 Hz, 2H), 5.38 (d, *J* = 17.2 Hz, 1H), 5.23 (d, *J* = 10.6 Hz, 1H), 5.12 – 5.02 (m, 2H), 4.70 (dd, *J* = 11.9, 5.7 Hz, 1H), 2.42 – 2.30 (m, 1H), 1.82 (dd, *J* = 13.5, 2.0 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 179.2, 150.3, 148.2, 147.6 (d, *J* = 245.0 Hz), 142.3, 139.2, 137.2, 136.5, 128.7, 128.4 (d, *J* = 7.5 Hz), 127.8, 127.7, 123.7 (d, *J* = 6.3 Hz), 120.3, 117.5, 116.5 (d, *J* = 20.0 Hz), 111.4, 105.9, 101.2, 99.2, 72.8, 50.1, 45.8, 45.7, 38.2. **HRMS (ESI) m/z:** $[M+H]^+$ calcd. for $C_{26}H_{21}FNO_4$: 430.1449, found: 430.1422.

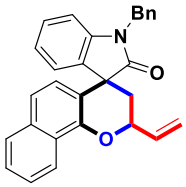
1-benzyl-7-bromo-6'-vinyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (6k)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (28.5 mg, 58% yield, dr 3:1) a faint yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.29 – 7.24 (m, 2H), 7.22 – 7.17 (m, 3H), 7.12 – 7.07 (m, 1H), 6.83 (t, *J* = 7.8 Hz, 1H), 6.43 (s, 1H), 5.98 – 5.90 (m, 1H), 5.89 (s, 1H), 5.76 (d, *J* = 1.5 Hz, 2H), 5.47 (d, *J* = 16.3 Hz, 1H), 5.43 – 5.34 (m, 2H), 5.23 (d, *J* = 10.5 Hz, 1H), 4.71 (dd, *J* = 11.5, 5.9 Hz, 1H), 2.38 (dd, *J* = 13.4, 12.4 Hz, 1H), 1.84 (dd, *J* = 13.5, 2.0 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 180.3, 150.4, 148.2, 142.5, 139.5, 139.3, 137.5, 136.4, 134.3, 128.7, 127.3, 126.5, 124.2, 123.7, 117.6, 111.2, 106.1, 102.9, 101.3, 99.2, 72.6, 49.5, 44.9, 38.7. **HRMS (ESI) m/z:** $[M+H]^+$ calcd. for $C_{26}H_{21}BrNO_4$: 492.0628, found: 492.0615.

1'-benzyl-2-vinyl-2,3-dihydrospiro[benzo[h]chromene-4,3'-indolin]-2'-one (6l)

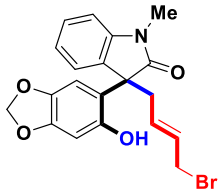


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (25.4 mg, 61% yield, dr 2.5:1) a faint yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.42 (m, 2H), 7.35 – 7.27 (m, 4H), 7.24 (d, *J* = 6.8 Hz, 1H), 7.18 (s, 1H), 7.17 – 7.09 (m, 2H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.80 (d, *J* = 7.8 Hz, 1H), 6.54 (d, *J* = 8.5 Hz, 1H), 6.17 – 5.99 (m, 1H), 5.55 (d, *J* = 17.3 Hz, 1H), 5.31 (d, *J* = 10.6 Hz, 1H), 5.06 – 4.90 (m, 3H), 2.64 – 2.49 (m, 1H), 2.00 (dd, *J* = 13.4, 2.0 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 179.4, 150.5, 141.8, 136.7, 136.3, 135.9, 133.9, 128.9, 128.4, 127.8, 127.5, 127.5, 126.6, 125.7, 125.5,

124.9, 124.6, 122.9, 121.9, 121.1, 117.2, 114.0, 109.5, 73.0, 50.1, 44.3, 38.3. **HRMS (ESI) m/z:** $[M+H]^+$ calcd. for $C_{29}H_{24}NO_2$: 418.1802, found: 418.1786.

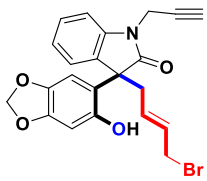
3-(4-bromobut-2-en-1-yl)-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)-1-methylindolin-2-one (7a)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:15) afforded the product (38.2 mg, 92% yield) a faint yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.44 (s, 1H), 7.37 – 7.29 (m, 2H), 7.20 – 7.17 (m, 1H), 6.87 (d, *J* = 7.7 Hz, 1H), 6.53 (s, 1H), 6.42 (s, 1H), 5.81 (d, *J* = 1.3 Hz, 1H), 5.75 (d, *J* = 1.3 Hz, 1H), 5.58 (m, 1H), 5.25 – 5.16 (m, 1H), 3.70 – 3.60 (m, 2H), 3.26 – 3.19 (m, 1H), 3.16 (s, 3H), 2.93 (dd, *J* = 13.7, 6.3 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 180.9, 152.5, 147.9, 142.9, 141.1, 131.2, 129.8, 129.5, 128.9, 126.5, 123.4, 114.9, 109.4, 107.9, 102.2, 101.3, 57.4, 36.9, 32.2, 26.6. **HRMS (ESI) m/z:** $[M+H]^+$ calcd. for $C_{20}H_{19}BrNO_4$: 416.0492, found: 416.0477.

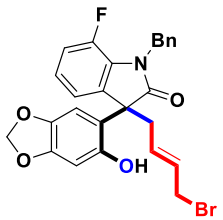
3-(4-bromobut-2-en-1-yl)-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)-1-(prop-2-yn-1-yl)indolin-2-one (7b)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:15) afforded the product (39.5 mg, 90% yield) a faint yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.95 (s, 1H), 7.34 (dd, *J* = 17.6, 8.1 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 1H), 7.08 (d, *J* = 7.8 Hz, 1H), 6.48 (dd, *J* = 34.0, 1.0 Hz, 2H), 5.79 (d, *J* = 29.4 Hz, 2H), 5.56 (dd, *J* = 15.0, 7.5 Hz, 1H), 5.19 (dt, *J* = 14.8, 7.3 Hz, 1H), 4.43 (q, *J* = 17.7 Hz, 2H), 3.63 (p, *J* = 9.8 Hz, 2H), 3.27 (dd, *J* = 13.5, 8.7 Hz, 1H), 2.90 (dd, *J* = 13.6, 6.2 Hz, 1H), 2.18 (d, *J* = 1.7 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 179.0, 151.2, 147.0, 140.2, 140.1, 130.3, 128.7, 128.0, 127.8, 125.4, 122.6, 113.7, 109.2, 106.8, 101.1, 100.3, 75.2, 71.9, 56.2, 36.4, 31.1, 28.7. **HRMS (ESI) m/z:** $[M+H]^+$ calcd. for $C_{22}H_{19}BrNO_4$: 440.0492, found: 440.0473.

1-benzyl-3-(4-bromobut-2-en-1-yl)-7-fluoro-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl) indolin-2-one (7c)

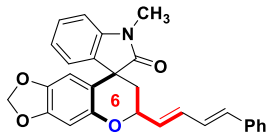


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:15) afforded the product (47.3 mg, 93% yield) a faint yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.25 – 7.21 (m, 4H), 7.19 (m, 1H), 7.08 (m, 2H), 6.99 (m, 1H),

6.51 (s, 1H), 6.37 (s, 1H), 5.81 (d, *J* = 1.1 Hz, 1H), 5.76 (d, *J* = 1.1 Hz, 1H), 5.52 (m, 1H), 5.13 (m, 1H), 5.00 (d, *J* = 15.3 Hz, 1H), 4.91 (d, *J* = 15.4 Hz, 1H), 3.52 (m, 2H), 3.36 (dd, *J* = 13.8, 8.2 Hz, 1H), 2.85 (dd, *J* = 13.8, 6.7 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 179.8, 151.2, 147.1 (d, *J* = 245.0 Hz), 147.1, 140.2, 135.2, 131.9 (d, *J* = 2.5 Hz), 130.6, 127.7, 127.7, 126.8, 126.5 (d, *J* = 1.3 Hz), 122.9 (d, *J* = 6.3 Hz), 121.2 (d, *J* = 3.8 Hz), 115.9 (d, *J* = 20 Hz), 113.7, 106.5, 101.1, 100.3, 56.4, 44.9, 36.5, 30.8. **HRMS (ESI) m/z:** $[M+H]^+$ calcd. for $C_{26}H_{22}BrFNO_4$: 510.0711, found: 510.0690.

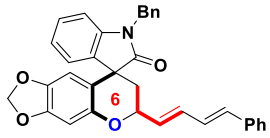
1-methyl-6'-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (8a)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (21.9 mg, 50% yield, dr 3:1) as a faint yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.5 Hz, 2H), 7.37 – 7.33 (m, 3H), 7.28 (d, *J* = 4.7 Hz, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.98 (d, *J* = 7.8 Hz, 1H), 6.85 – 6.78 (m, 1H), 6.66 – 6.57 (m, 2H), 6.53 (s, 1H), 6.02 – 5.91 (m, 2H), 5.87 – 5.82 (m, 2H), 4.94 (dd, *J* = 11.6, 6.6 Hz, 1H), 3.35 (d, *J* = 4.8 Hz, 3H), 2.53 – 2.44 (m, 1H), 1.92 (dd, *J* = 13.6, 1.8 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 179.3, 150.3, 147.9, 142.5, 142.4, 136.9, 136.4, 133.9, 132.9, 131.2, 128.7, 128.4, 127.8, 127.8, 126.5, 124.2, 123.0, 111.8, 108.5, 106.1, 101.2, 99.1, 72.8, 49.9, 38.1, 26.8. **HRMS (ESI) m/z:** $[M+H]^+$ calcd. for $C_{28}H_{24}NO_4$: 438.1700, found: 438.1683.

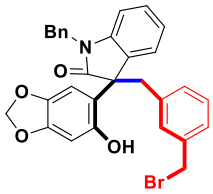
1-benzyl-6'-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (8b)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (26.7 mg, 52% yield, dr 3:1) a faint yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.6 Hz, 2H), 7.37 – 7.29 (m, 8H), 7.25 – 7.19 (m, 3H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.88 – 6.82 (m, 1H), 6.82 – 6.77 (m, 1H), 6.60 (dd, *J* = 15.5, 4.4 Hz, 1H), 6.53 (s, 1H), 6.04 – 5.91 (m, 2H), 5.83 (t, *J* = 6.1 Hz, 2H), 5.08 – 4.91 (m, 3H), 2.58 – 2.50 (m, 1H), 1.95 (dd, *J* = 13.5, 1.6 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 179.4, 150.4, 148.0, 142.4, 141.6, 136.9, 136.4, 135.9, 134.0, 133.0, 131.2, 128.9, 128.7, 128.3, 127.8, 127.8, 127.7, 127.4, 126.6, 124.3, 123.0, 111.8, 109.6, 106.1, 101.2, 99.2, 72.7, 49.9, 44.2, 38.5. **HRMS (ESI) m/z:** $[M+H]^+$ calcd. for $C_{34}H_{28}NO_4$: 514.2013, found: 514.1994.

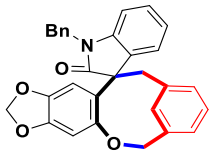
1-benzyl-3-(3-(bromomethyl)benzyl)-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)indolin-2-one (10a)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (48.7 mg, 90% yield) a faint yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.71 (s, 1H), 7.31 – 7.27 (m, 1H), 7.17 – 7.12 (m, 2H), 7.12 – 7.05 (m, 4H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.78 – 6.70 (m, 2H), 6.61 (d, *J* = 6.5 Hz, 3H), 6.50 (dd, *J* = 10.2, 2.9 Hz, 2H), 5.80 (dd, *J* = 23.9, 1.2 Hz, 2H), 4.77 (d, *J* = 16.0 Hz, 1H), 4.48 (d, *J* = 16.0 Hz, 1H), 4.15 (q, *J* = 10.2 Hz, 2H), 4.05 (d, *J* = 13.4 Hz, 1H), 3.33 (d, *J* = 13.3 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 180.9, 152.7, 148.1, 142.3, 141.2, 137.4, 136.2, 134.4, 131.1, 130.6, 129.4, 128.9, 128.8, 128.4, 127.6, 127.5, 127.1, 126.6, 123.1, 115.5, 110.5, 108.1, 102.4, 101.3, 59.0, 44.1, 40.4, 33.3. **HRMS (ESI) m/z:** $[M+H]^+$ calcd. for $C_{30}H_{25}BrNO_4$: 542.0961, found: 542.0940.

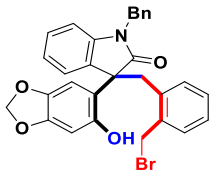
1-benzyl-6'H,12'H-spiro[indoline-3,13'-[7,11](metheno)[1,3]dioxolo[4',5':4,5]benzo[1,2-b][1]oxacycloundecin]-2-one (11a)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (3.7 mg, 8% yield) a faint yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.33 (d, *J* = 7.7 Hz, 1H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.17 – 7.08 (m, 6H), 7.03 (dd, *J* = 7.3, 0.8 Hz, 1H), 6.96 – 6.84 (m, 3H), 6.48 (d, *J* = 7.8 Hz, 1H), 6.38 (d, *J* = 2.5 Hz, 1H), 5.88 (dd, *J* = 4.0, 1.4 Hz, 2H), 4.72 (d, *J* = 15.8 Hz, 1H), 4.52 (q, *J* = 11.3 Hz, 2H), 4.38 (dd, *J* = 22.3, 10.3 Hz, 2H), 3.65 (d, *J* = 15.8 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 177.6, 149.9, 148.1, 143.4, 141.8, 138.1, 136.7, 135.8, 130.8, 129.4, 129.1, 129.0, 128.7, 128.4, 128.2, 127.5, 127.3, 124.1, 122.9, 121.6, 109.5, 107.2, 101.5, 95.9, 75.9, 70.7, 43.1, 33.1. **HRMS (ESI) m/z:** $[M+H]^+$ calcd. for $C_{30}H_{24}NO_4$: 462.1700, found: 462.1677.

1-benzyl-3-(2-(bromomethyl)benzyl)-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)indolin-2-one (12a)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (49.8 mg, 92% yield) a faint yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.64 (s, 1H), 7.28 (d, *J* = 3.6 Hz, 1H), 7.27 – 7.25 (m, 1H), 7.25 – 7.22 (m, 3H), 7.21 – 7.17 (m, 1H), 7.15 (td, *J* = 7.6, 0.9 Hz, 1H), 7.04 (dd, *J* = 7.5, 0.7 Hz, 1H), 6.96 (td, *J* = 7.6, 1.4 Hz, 1H), 6.82 (dd, *J* = 7.3, 1.9 Hz, 2H), 6.75 (s, 1H), 6.69 (d, *J* = 7.8 Hz, 1H), 6.59 (d, *J* = 6.1 Hz, 2H), 5.91 (dd, *J* = 29.7, 1.4 Hz, 2H), 5.05 (d, *J* = 15.9 Hz, 1H), 4.60 (d, *J* = 15.9 Hz, 1H), 4.34 (d, *J* = 10.5 Hz, 1H), 4.21 (d, *J* = 10.5 Hz, 1H), 4.05 (d, *J* = 14.2 Hz, 1H), 3.86 (d, *J* = 14.2 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$)

δ 181.3, 152.7, 148.2, 142.2, 141.3, 137.5, 134.8, 134.4, 131.2, 130.7, 129.4, 129.0, 128.9, 128.5, 127.7, 127.6, 127.2, 126.6, 122.9, 115.3, 110.5, 108.3, 102.5, 101.3, 58.3, 44.1, 35.9, 32.1. **HRMS (ESI) m/z:** $[M+H]^+$ calcd. for $C_{30}H_{25}BrNO_4$: 542.0961, found: 542.0940.

Reference: Shi, H.; Wang, L.; Li, S.-S.; Liu, Y.; Xu, L. *Org. Chem. Front.* **2020**, *7*, 747.

5. Crystal Structures and Data

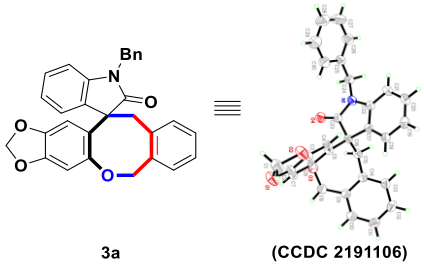
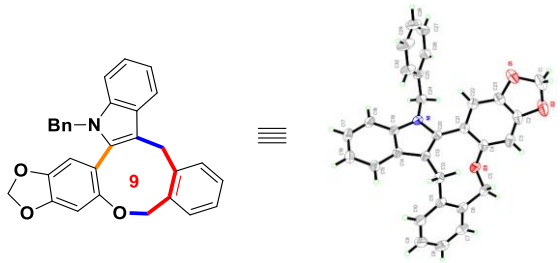


Table S1. Crystal data and structure refinement for **3a**.

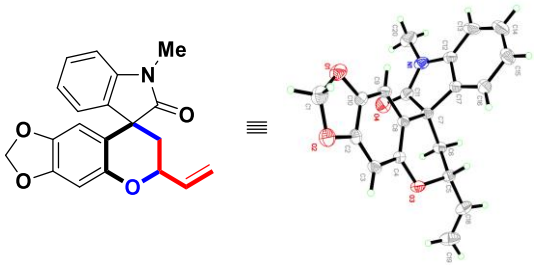
Identification code	**3a**
Empirical formula	$C_{30}H_{23}NO_4$
Formula weight	461.49
Temperature	293(2) K
Wavelength	1.54184 A
Crystal system, space group	monoclinic, P21/c
Unit cell dimensions	a = 8.1555(5) A alpha = 90 deg.
	b = 27.2024(14) A beta = 108.457(6) deg.
	c = 10.8788(6) A gamma = 90 deg.
Volume	2289.3(2) A^3
Z, Calculated density	4, 1.339 Mg/m^3
Absorption coefficient	0.717 mm^-1
F(000)	968
Crystal size	0.14 x 0.12 x 0.12 mm
Theta range for data collection	4.58 to 67.24 deg.
Limiting indices	-9<=h<=9, -32<=k<=27, -12<=l<=13
Reflections collected / unique	8125 / 4101 [R(int) = 0.0429]
Completeness to theta = 67.24	99.9 %
Max. and min. transmission	0.9189 and 0.9063
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4101 / 0 / 316
Goodness-of-fit on F^2	1.039
Final R indices [I>2sigma(I)]	R1 = 0.0616, wR2 = 0.1411
R indices (all data)	R1 = 0.1037, wR2 = 0.1717
Largest diff. peak and hole	0.254 and -0.201 e.A^-3



4a (CCDC 2192548)

Table S2. Crystal data and structure refinement for **4a**.

Identification code	**4a**
Empirical formula	$C_{30}H_{23}NO_3$
Formula weight	445.49
Temperature	293(2) K
Wavelength	1.54184 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 10.0716(8) A alpha = 78.010(8) deg.
	b = 11.1150(10) A beta = 73.634(8) deg.
	c = 11.1165(12) A gamma = 71.600(8) deg.
Volume	1123.3(2) A^3
Z, Calculated density	2, 1.317 Mg/m^3
Absorption coefficient	0.676 mm^-1
F(000)	468
Crystal size	0.140 x 0.120 x 0.120 mm
Theta range for data collection	4.181 to 67.243 deg.
Limiting indices	-12<=h<=8, -13<=k<=11, -13<=l<=12
Reflections collected / unique	6993 / 4012 [R(int) = 0.0302]
Completeness to theta = 67.243	99.7 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4012 / 0 / 308
Goodness-of-fit on F^2	1.052
Final R indices [I>2sigma(I)]	R1 = 0.0446, wR2 = 0.1004
R indices (all data)	R1 = 0.0714, wR2 = 0.1196
Extinction coefficient	0.0083(5)
Largest diff. peak and hole	0.145 and -0.135 e.A^-3



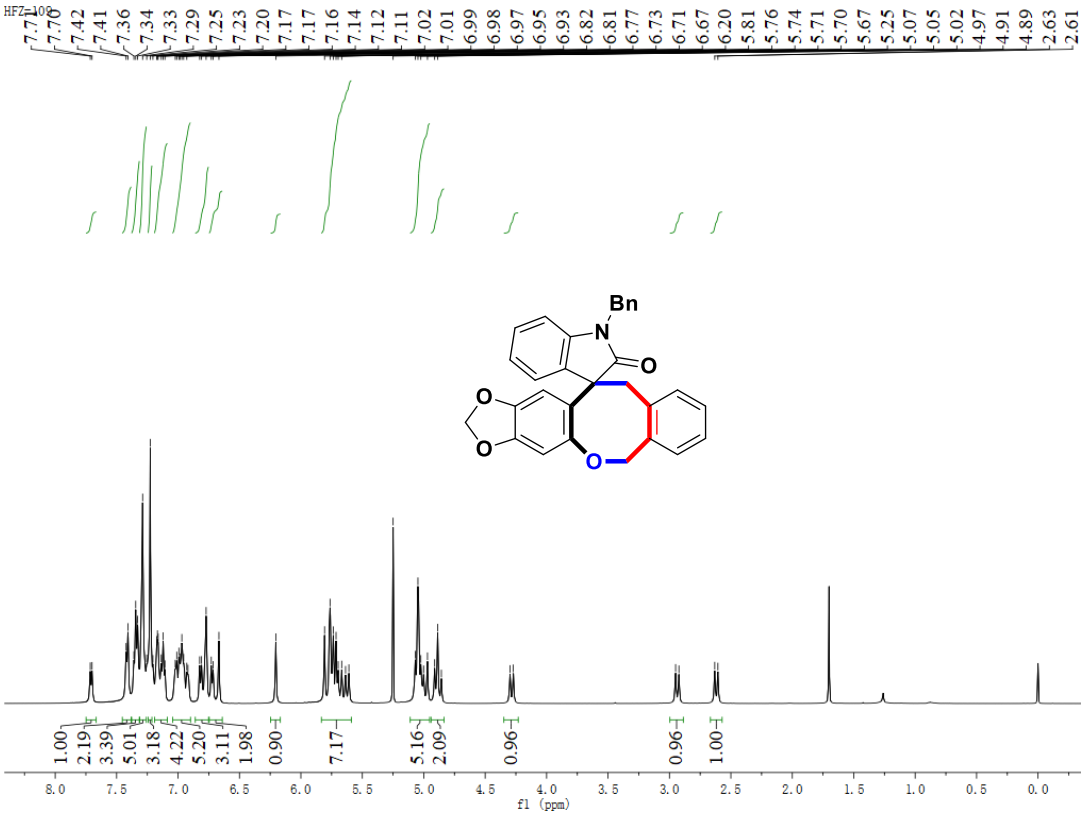
6a (CCDC 2190999)

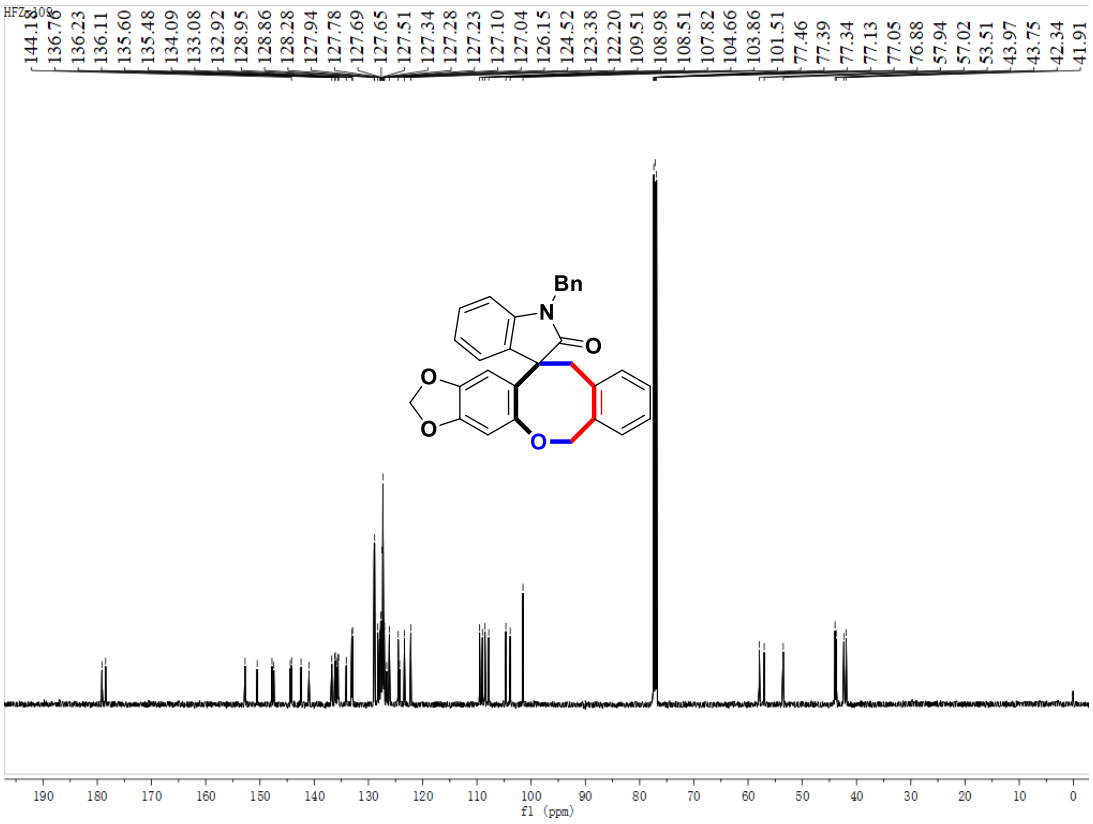
Table S3. Crystal data and structure refinement for **6a**.

Identification code	**6a**
Empirical formula	$C_{20}H_{17}NO_4$
Formula weight	335.35
Temperature	293(2) K
Wavelength	1.54184 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 8.1822(3) A alpha = 90 deg.
	b = 23.2770(6) A beta = 109.551(3) deg.
	c = 9.2073(3) A gamma = 90 deg.
Volume	1652.49(9) A^3
Z, Calculated density	4, 1.348 Mg/m^3
Absorption coefficient	0.774 mm^-1
F(000)	704
Crystal size	0.080 x 0.080 x 0.070 mm
Theta range for data collection	5.441 to 67.222 deg.
Limiting indices	-9<=h<=8, -27<=k<=27, -7<=l<=11
Reflections collected / unique	6202 / 2941 [R(int) = 0.0233]
Completeness to theta = 67.222	99.7 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2941 / 0 / 227
Goodness-of-fit on F^2	1.056
Final R indices [I>2sigma(I)]	R1 = 0.0443, wR2 = 0.1159
R indices (all data)	R1 = 0.0529, wR2 = 0.1227
Extinction coefficient	n/a
Largest diff. peak and hole	0.203 and -0.206 e.A^-3

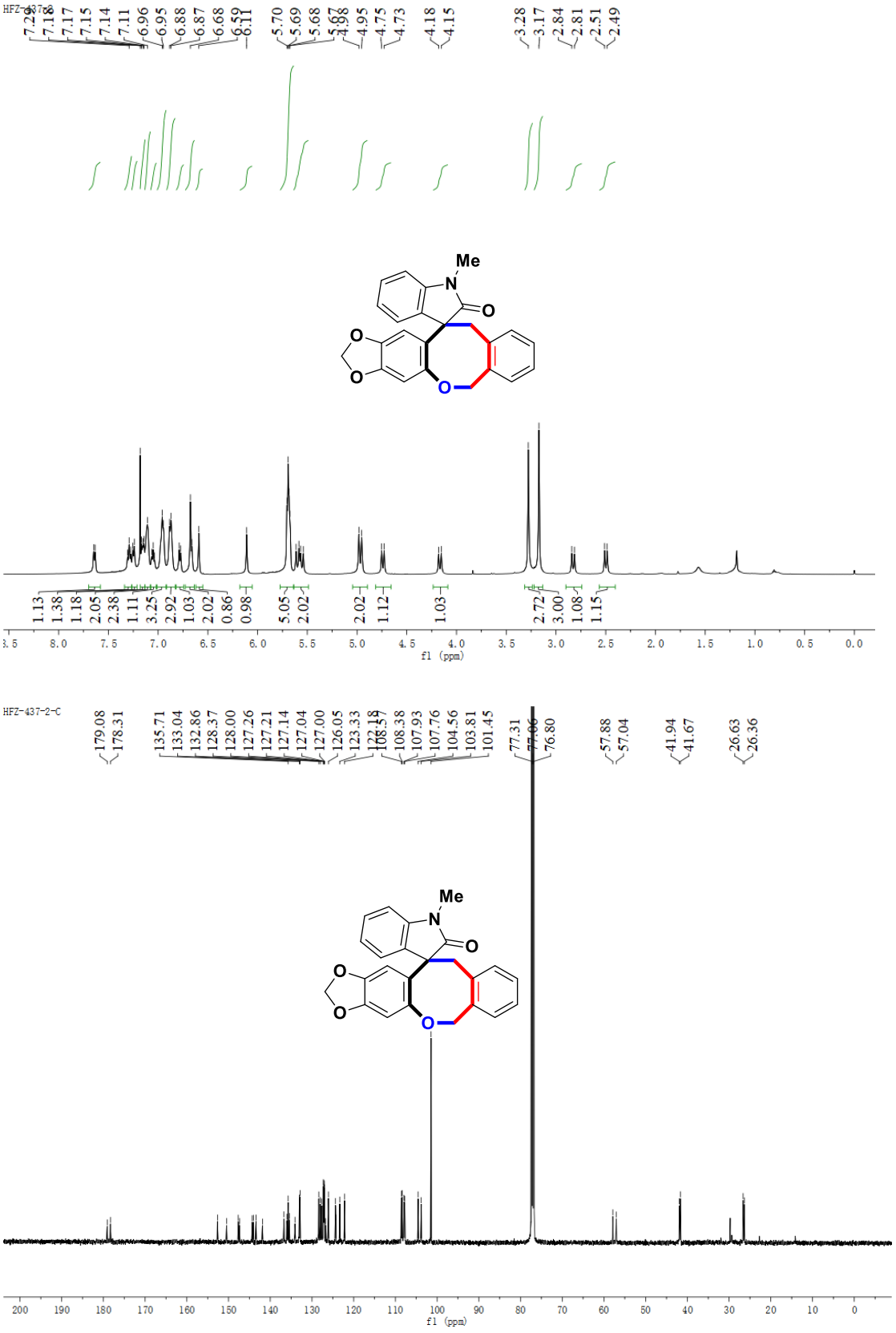
6. ^{1}H and ^{13}C NMR Spectra

1-benzyl-6',11'-dihydrospiro[indoline-3,12'-[1,3]dioxolo[4',5':4,5]benzo[1,2-b]benzo[f]oxocin]-2-one (3a)

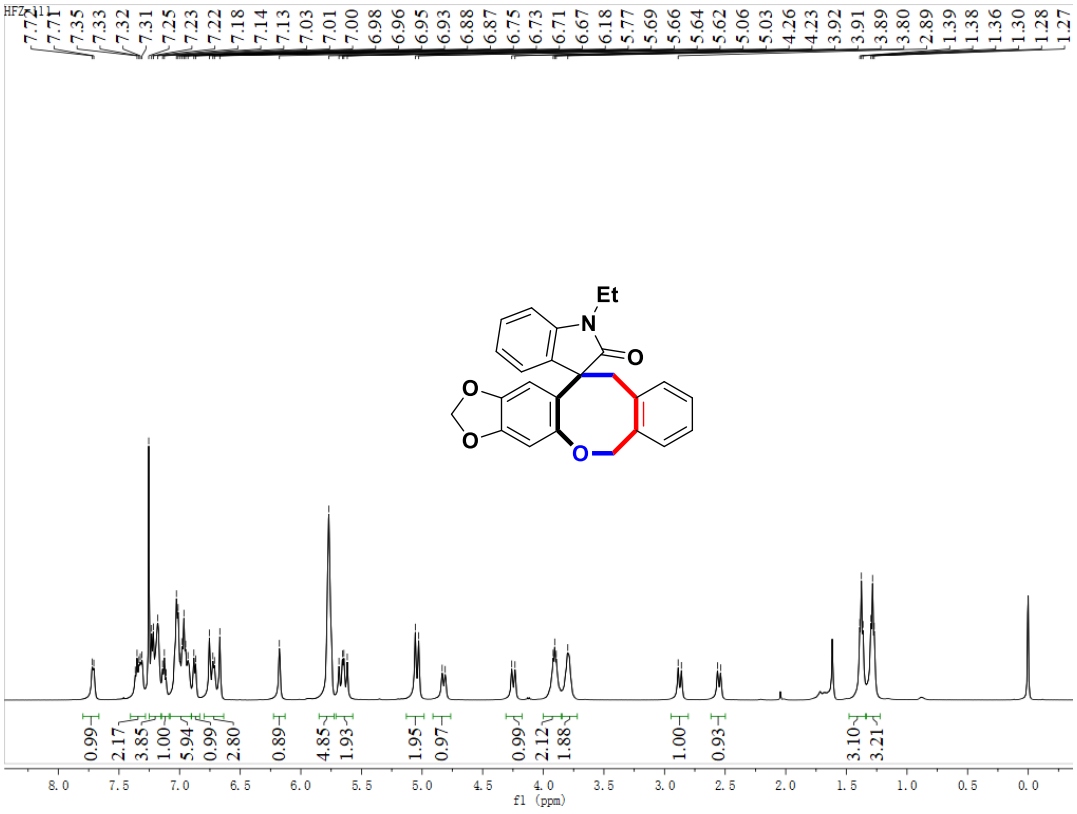


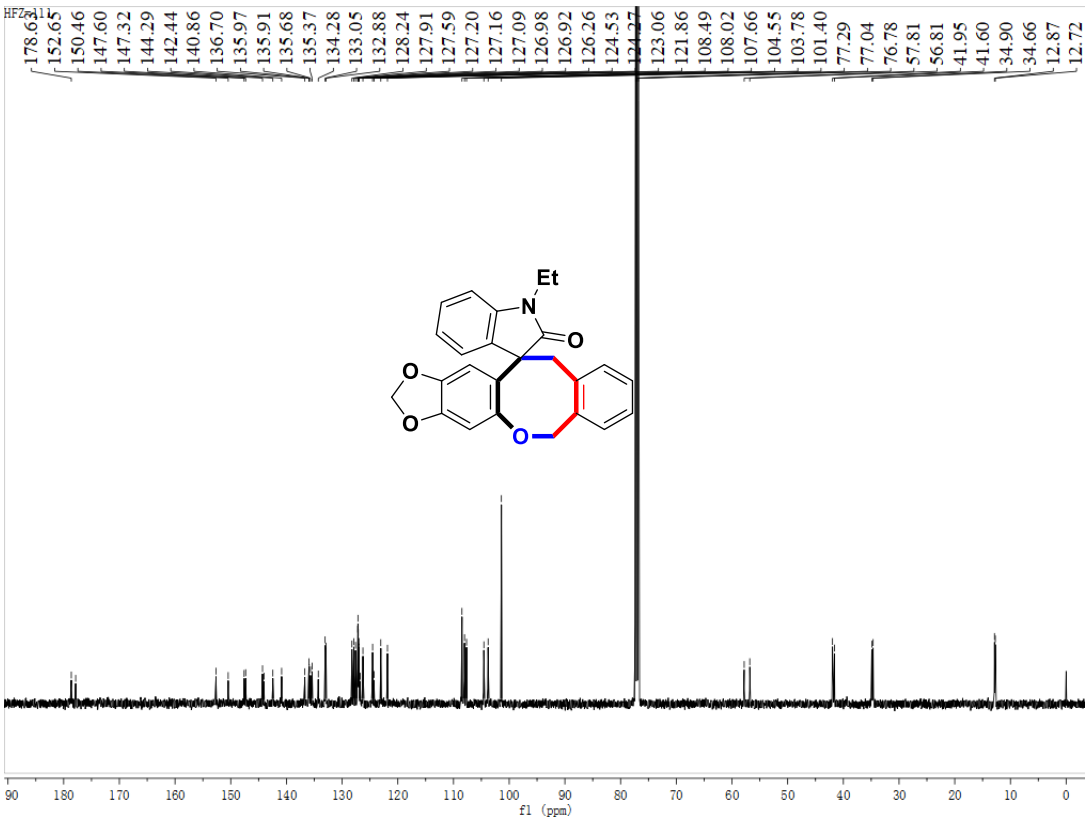


1-methyl-6',11'-dihydrospiro[indoline-3,12'-[1,3]dioxolo[4',5':4,5]benzo[1,2-b]benzo[f]oxocin]-2-one (3b)

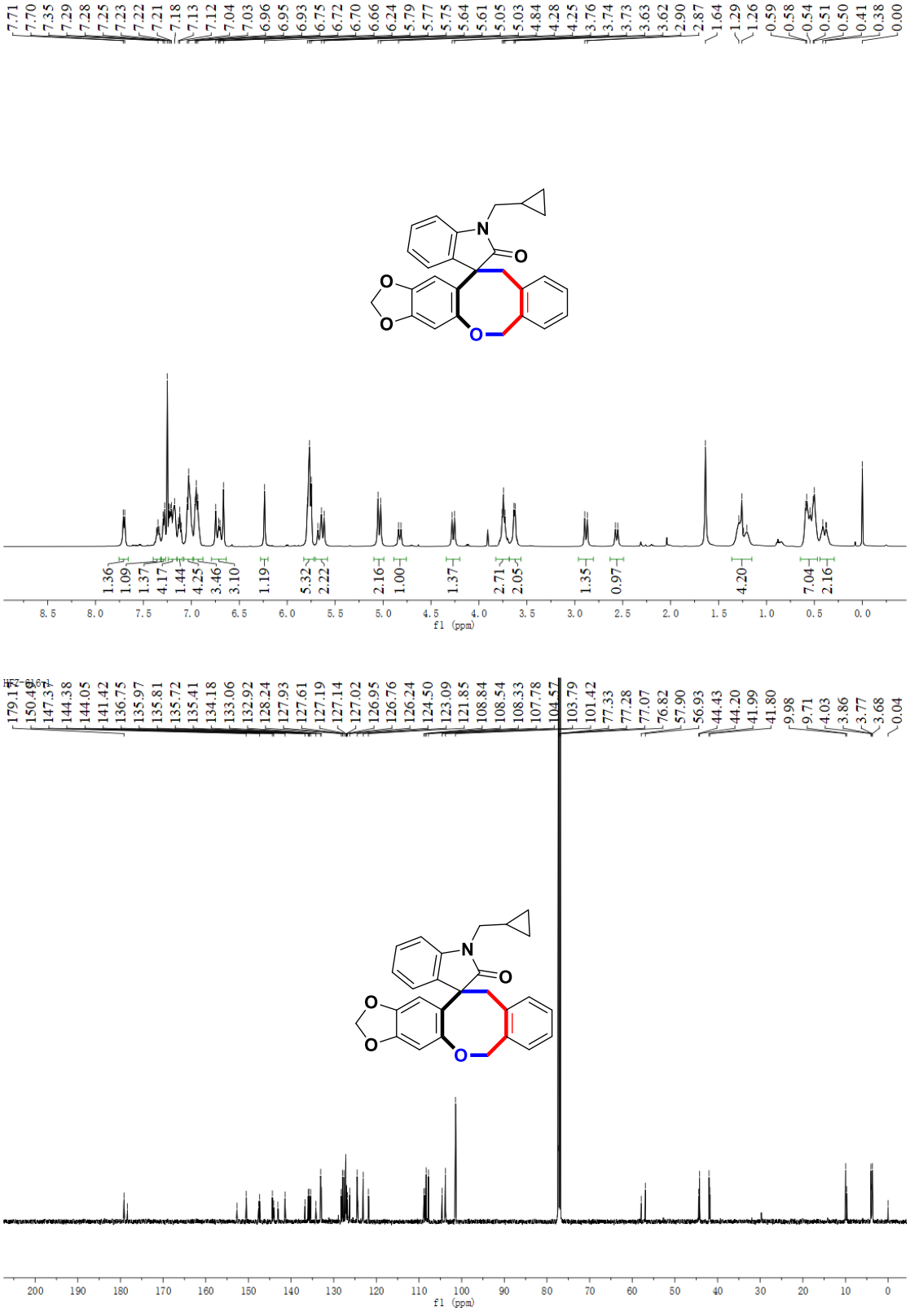


1-methyl-6',11'-dihydrospiro[indoline-3,12'-[1,3]dioxolo[4',5':4,5]benzo[1,2-b]benzo[f]oxocin]-2-one (3c)

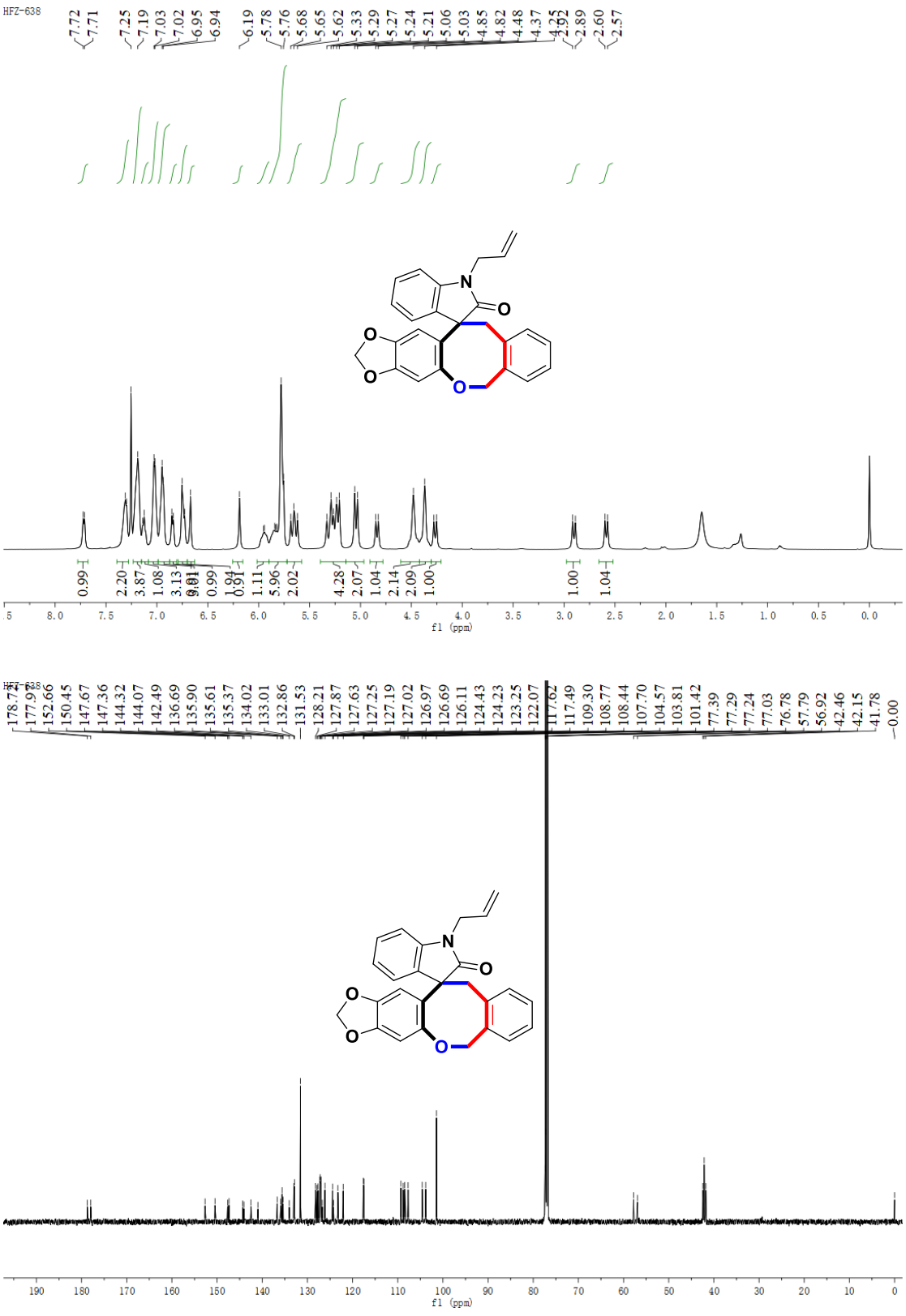




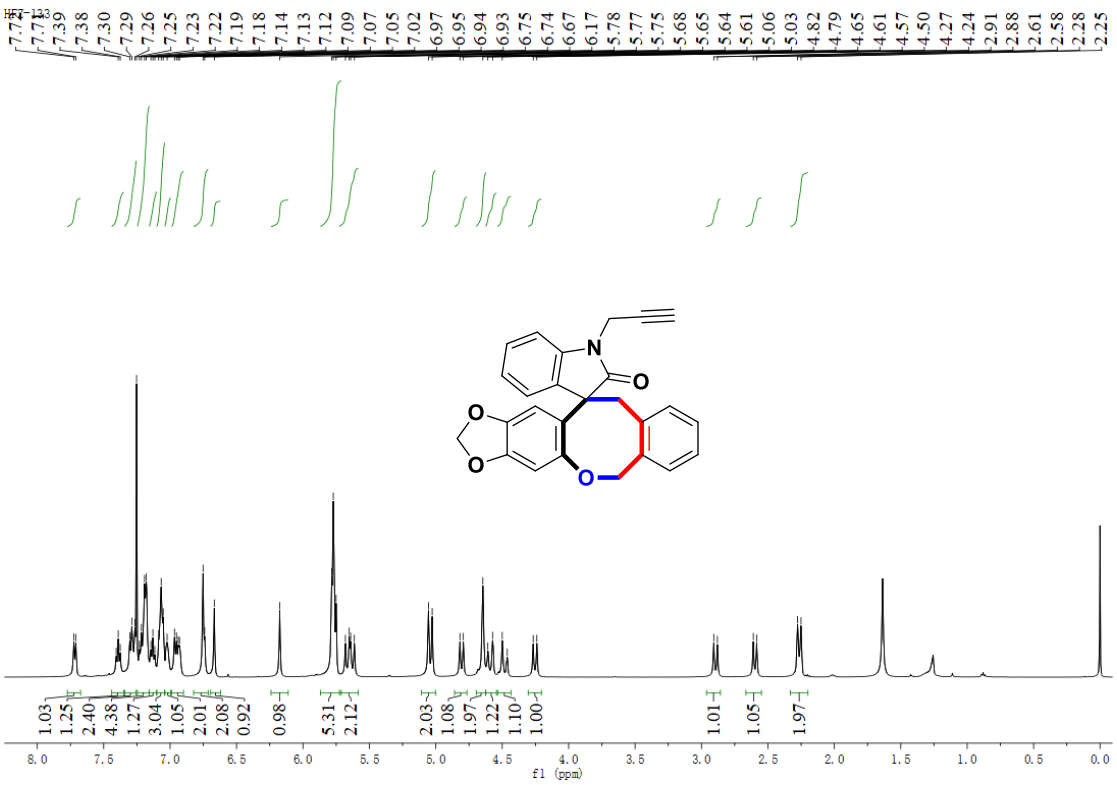
1-(cyclopropylmethyl)-6',11'-dihydrospiro[indoline-3,12'-[1,3]dioxolo[4',5':4,5]benzo[1,2-b]benzo[f]oxocin]-2-one (3d)

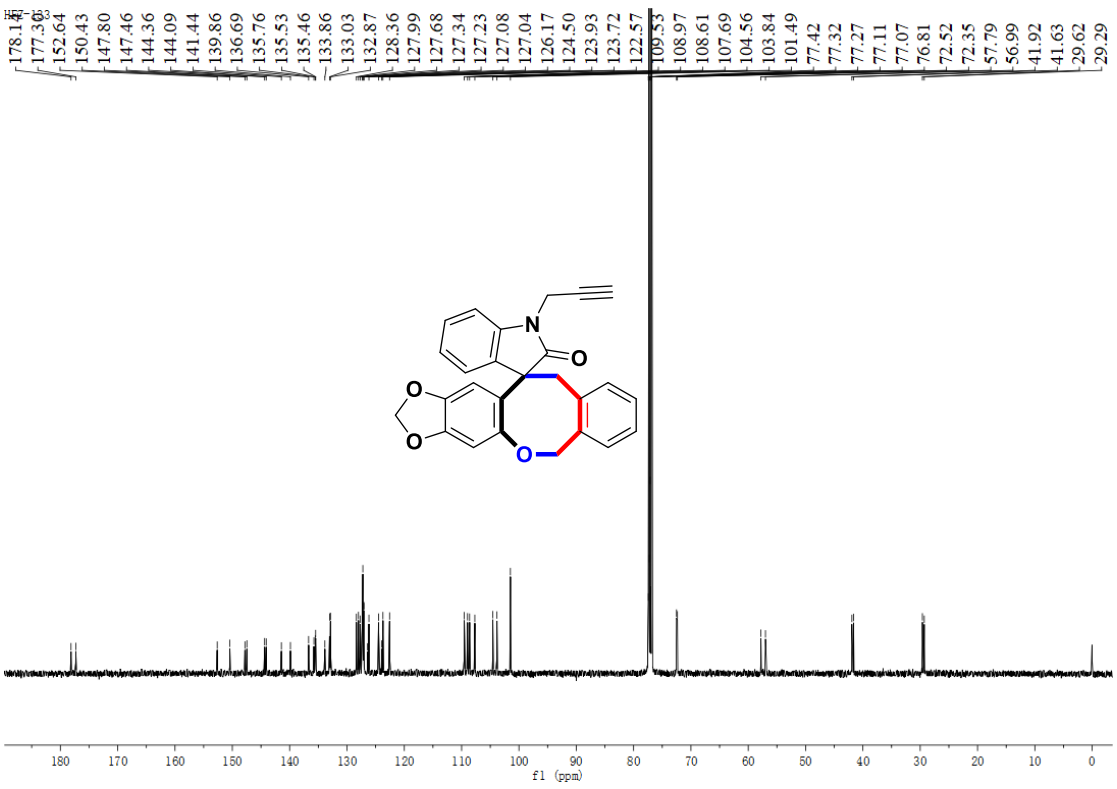


1-allyl-6',11'-dihydrospiro[indoline-3,12'-[1,3]dioxolo[4',5':4,5]benzo[1,2-b]benzo[f]oxocin]-2-one (3e)

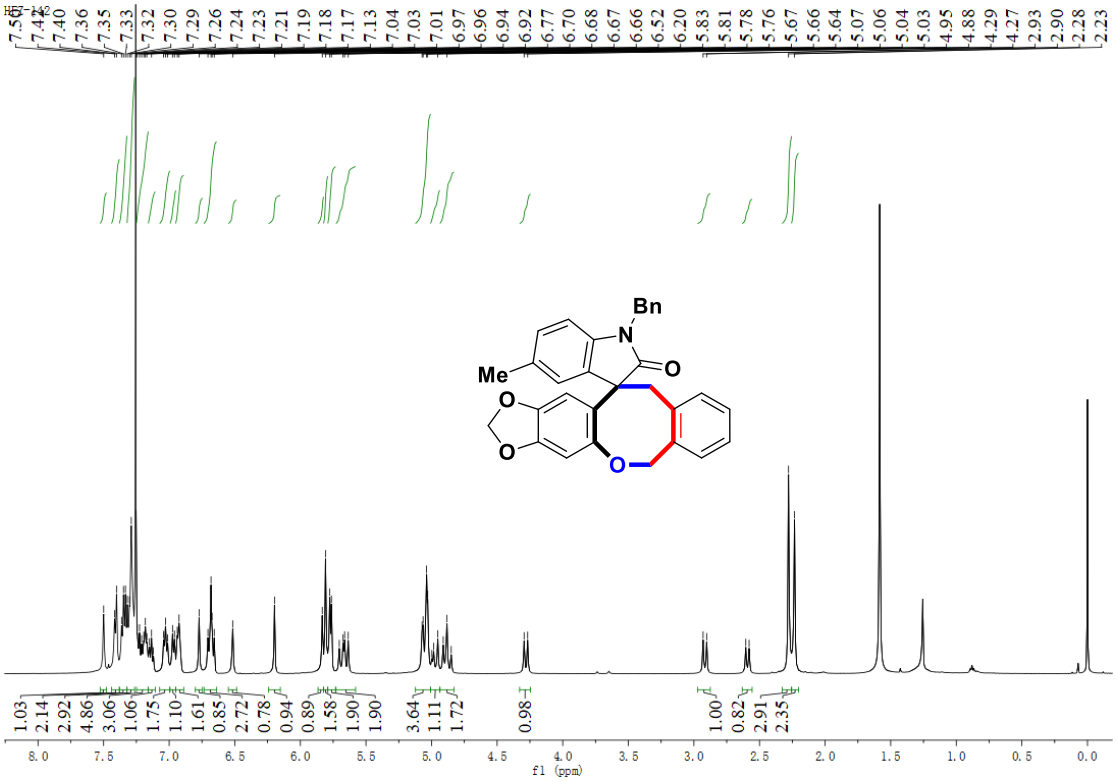


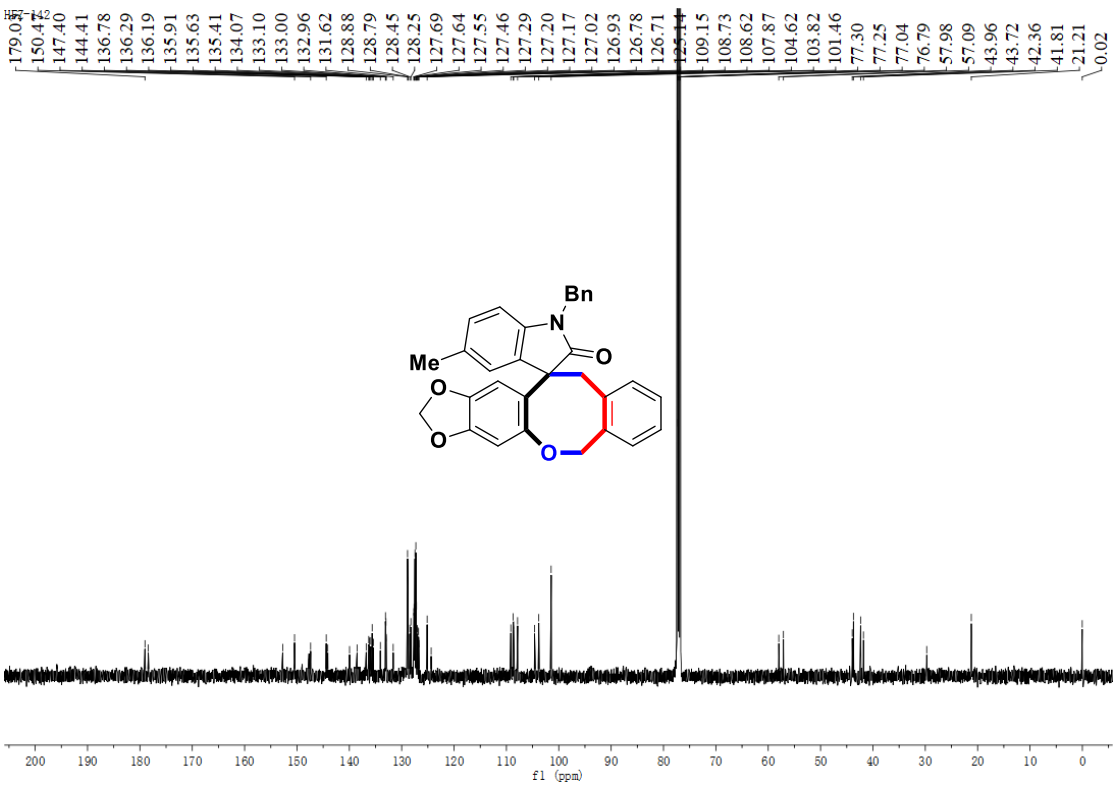
1-(prop-2-yn-1-yl)-6',11'-dihydrospiro[indoline-3,12'-[1,3]dioxolo[4',5':4,5]benzo[1,2-b]benzo[f]oxocin]-2-one (3f)



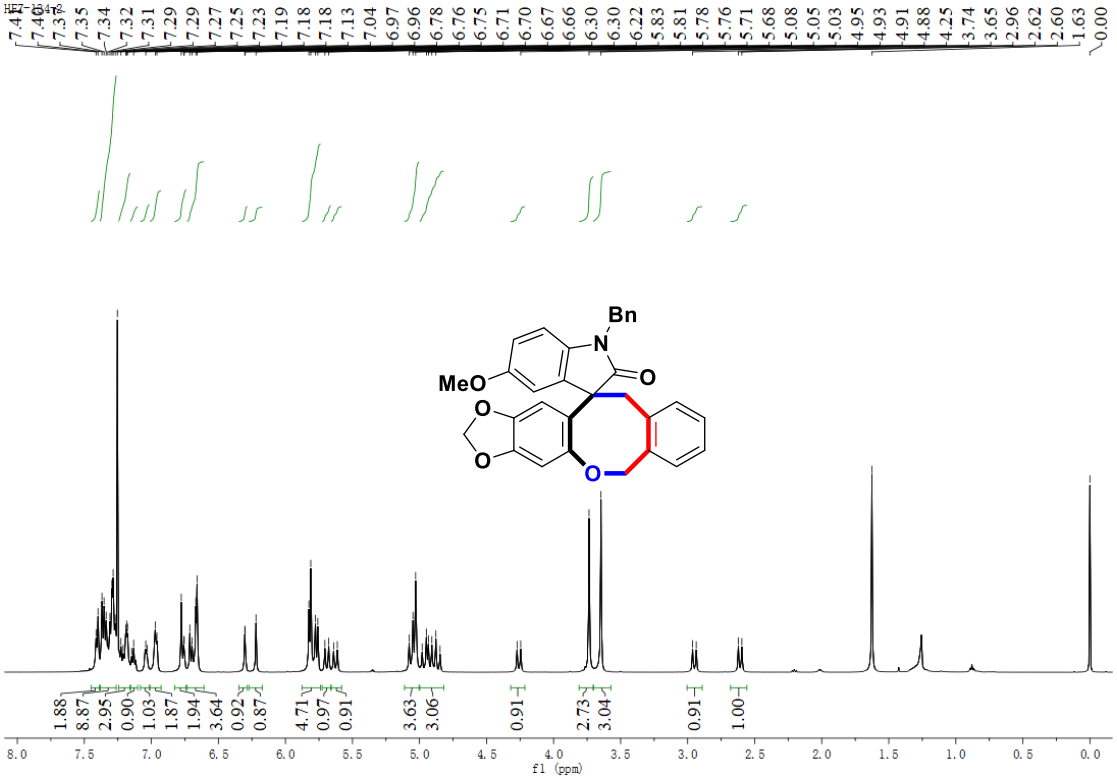


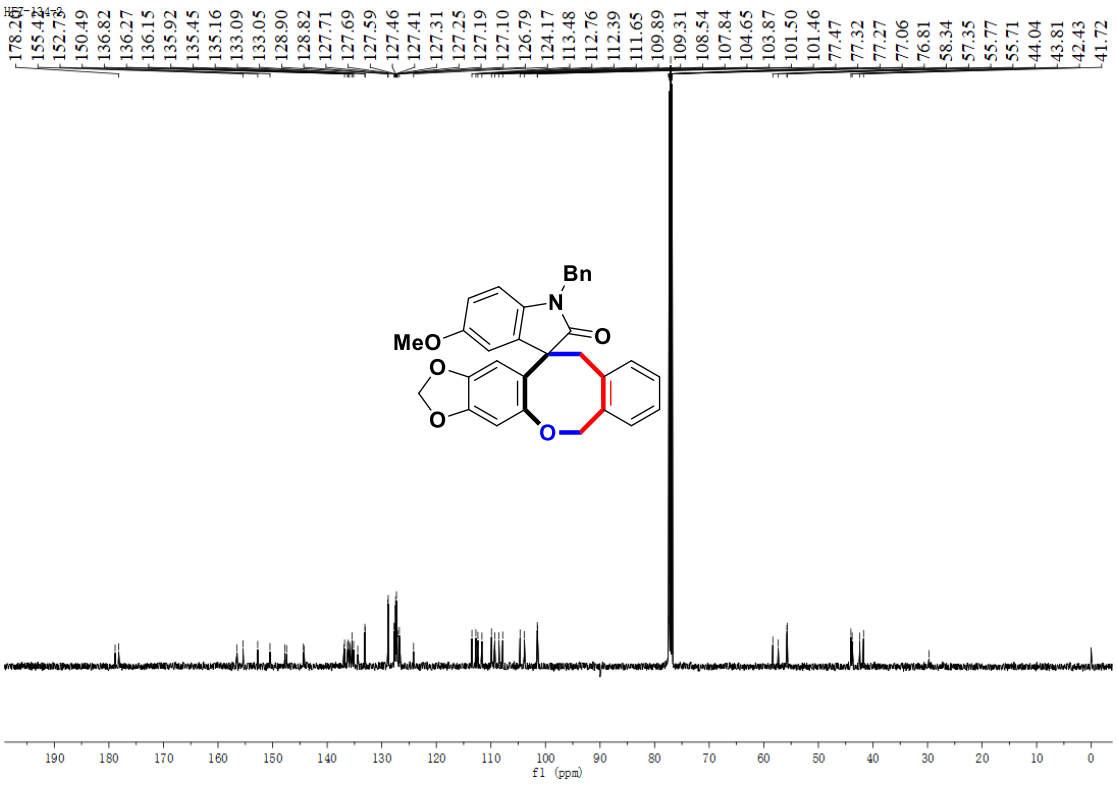
1-benzyl-5-methyl-6',11'-dihydrospiro[indoline-3,12'-[1,3]dioxolo[4',5':4,5]benzo[1,2-b]benzo[f]oxocin]-2-one (3g)



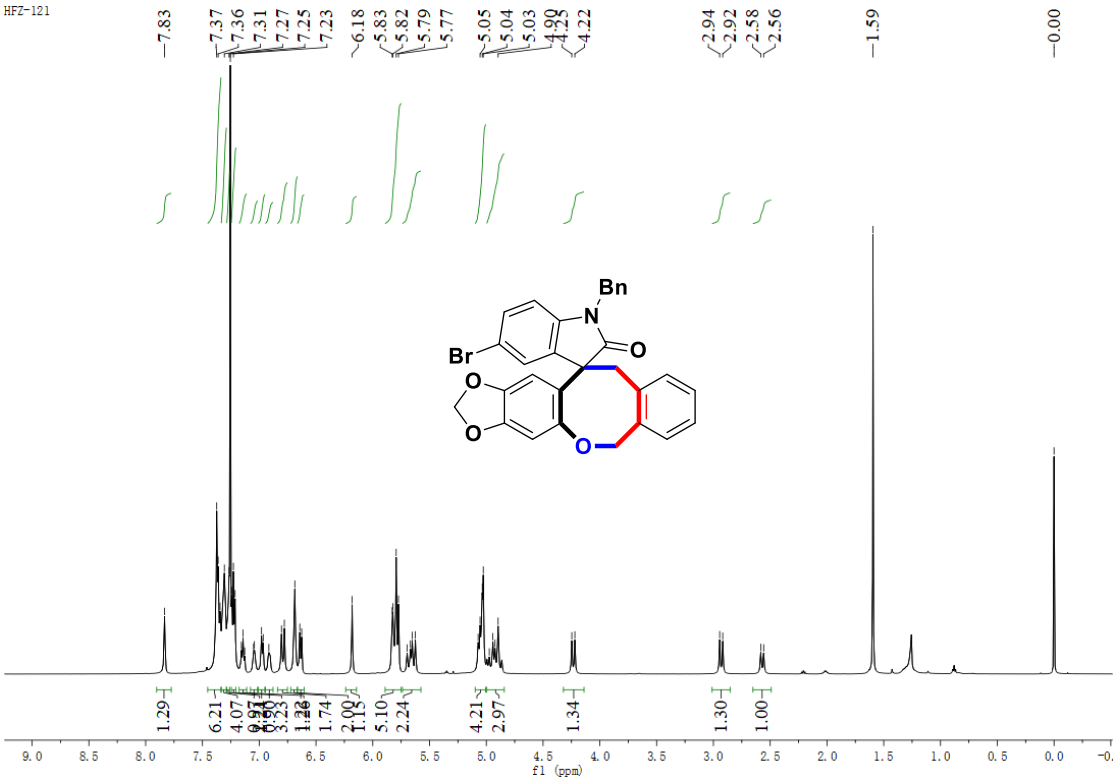


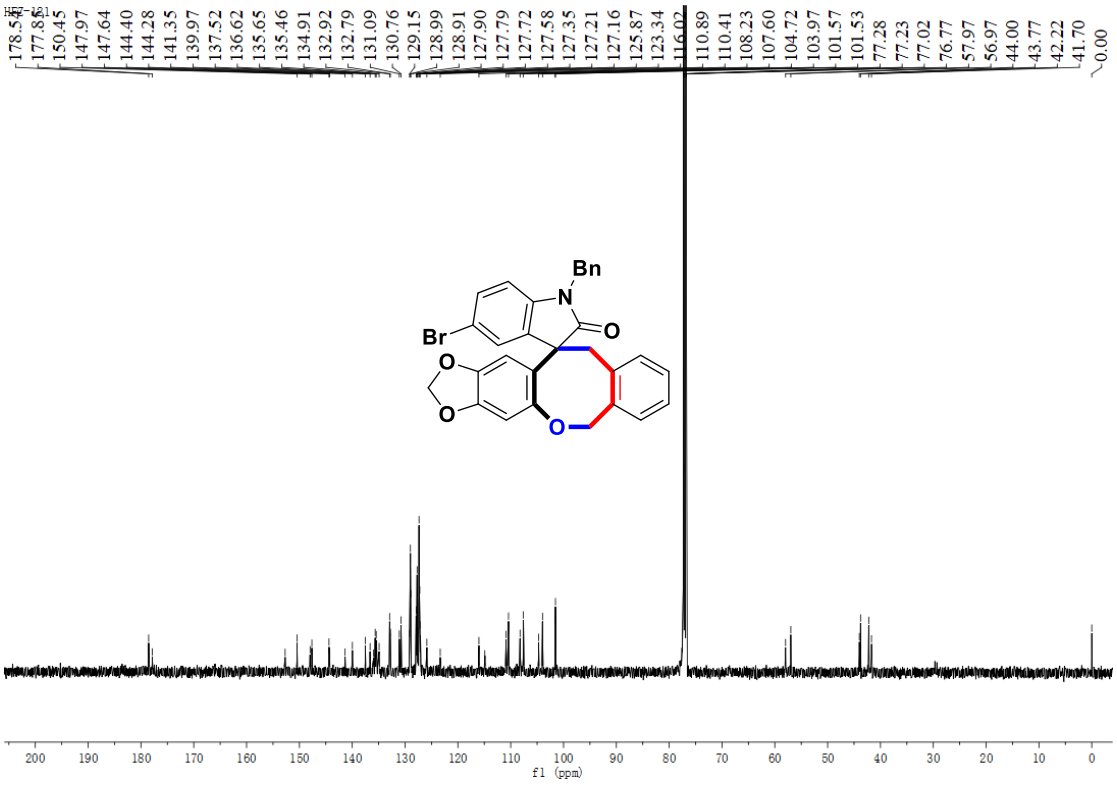
1-benzyl-5-methoxy-6',11'-dihydrospiro[indoline-3,12'-[1,3]dioxolo[4',5':4,5]benzo[1,2-b]benzo[f]oxocin]-2-one (3h)



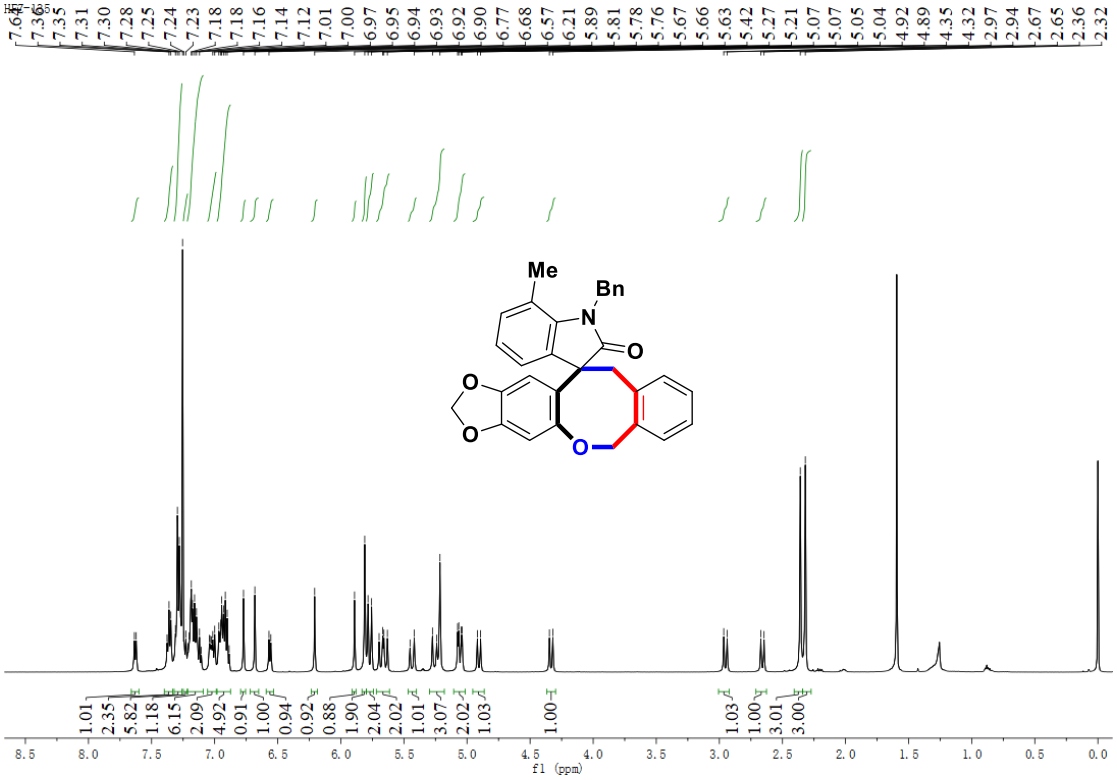


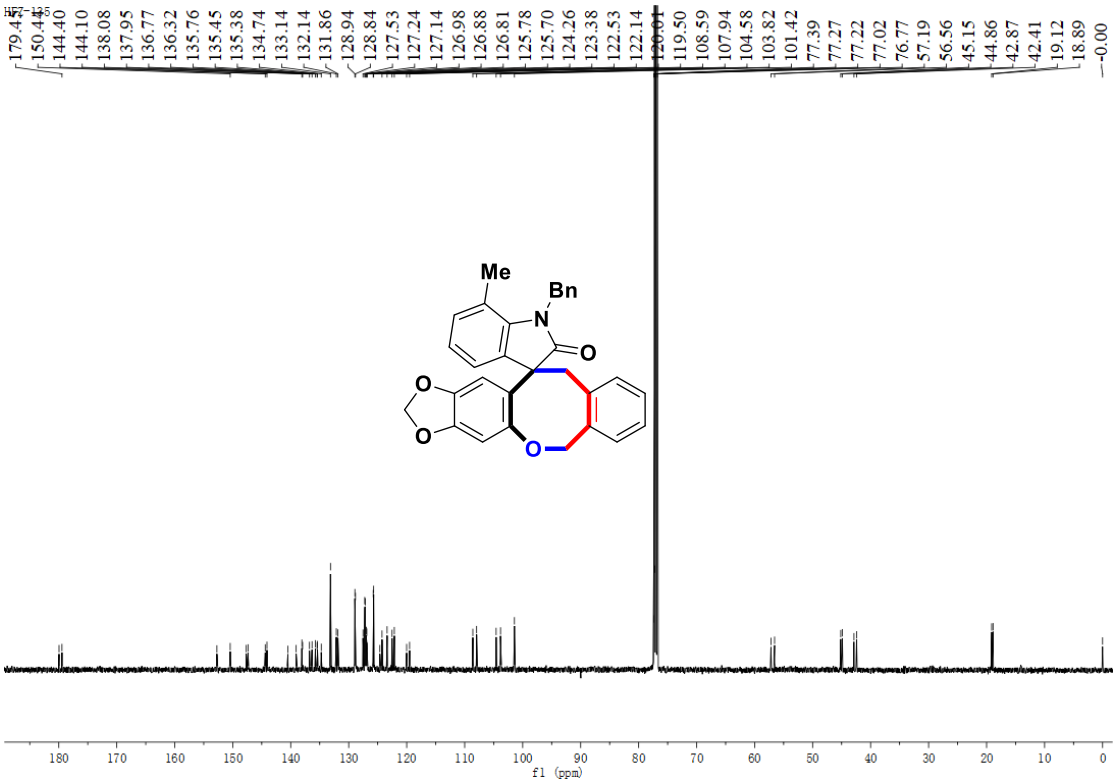
1-benzyl-5-bromo-6',11'-dihydrospiro[indoline-3,12'-[1,3]dioxolo[4',5':4,5]benzo[1,2-b]benzo[f]oxocin]-2-one (3i)



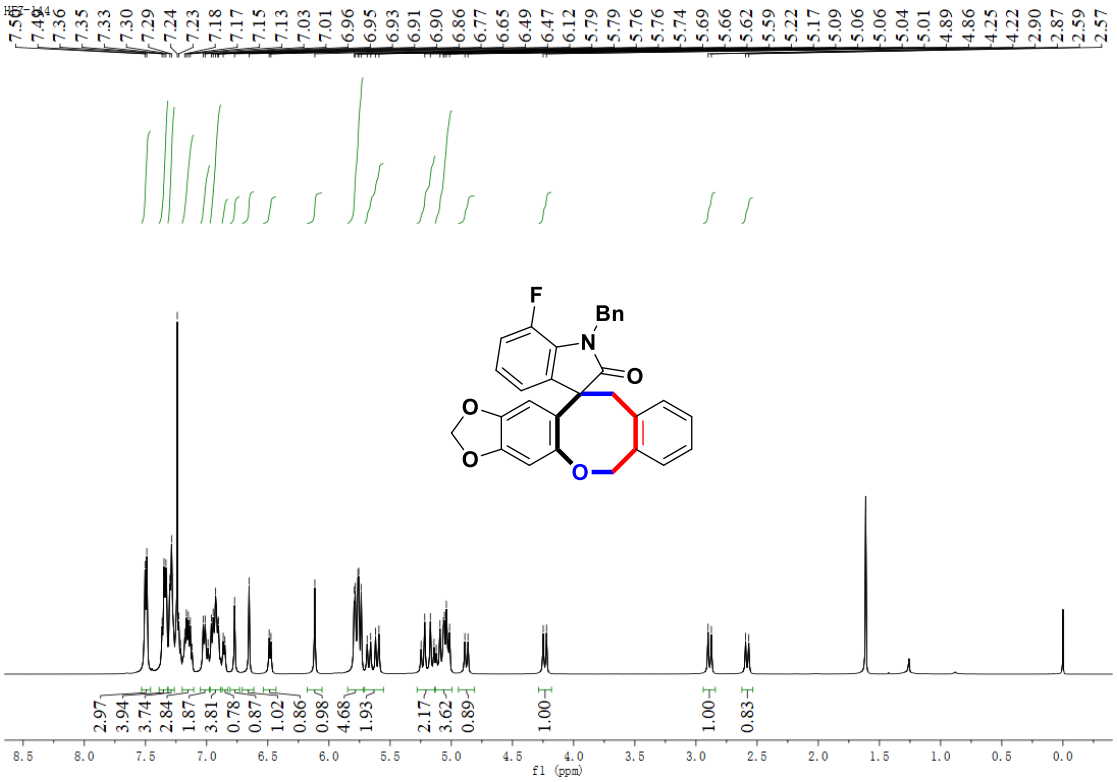


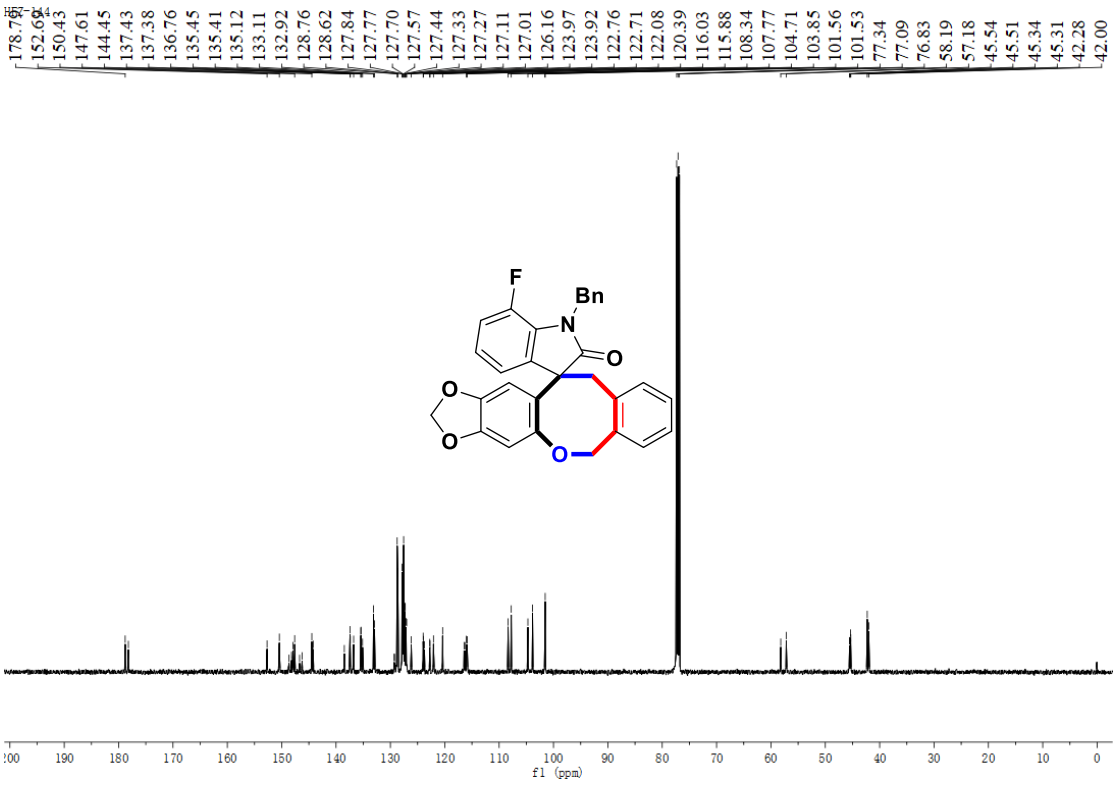
1-benzyl-7-methyl-6',11'-dihydrospiro[indoline-3,12'-[1,3]dioxolo[4',5':4,5]benzo[1,2-b]benzo[f]oxocin]-2-one (3j)



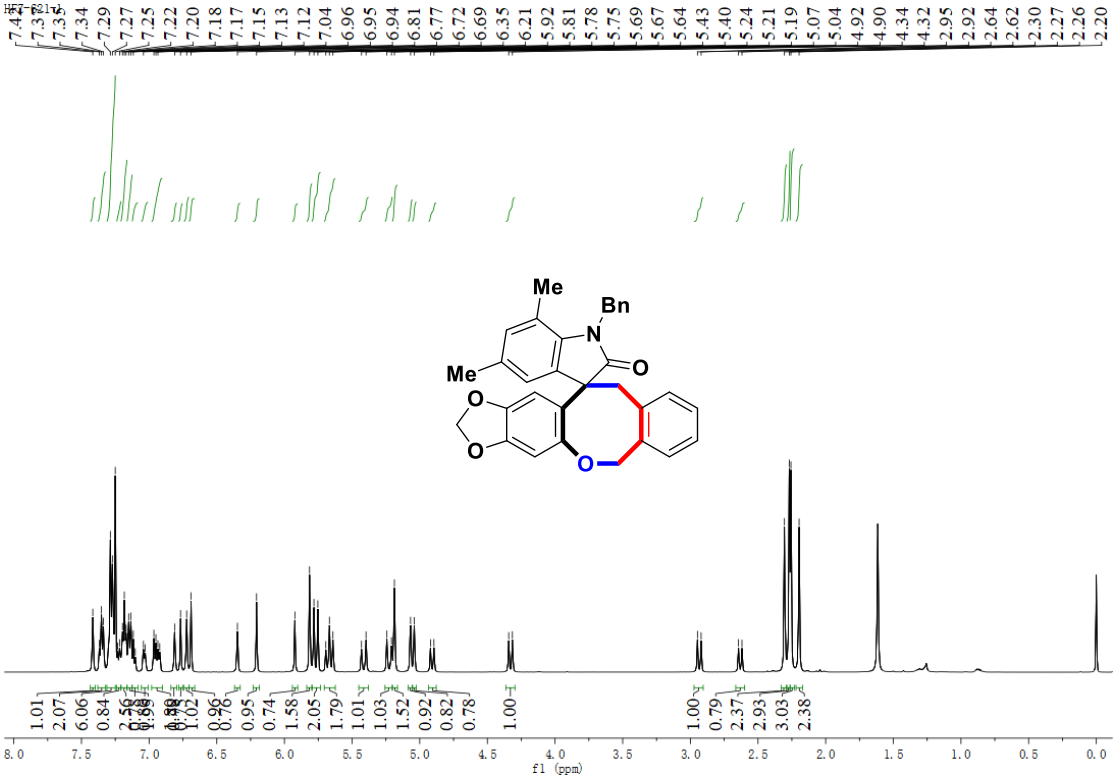


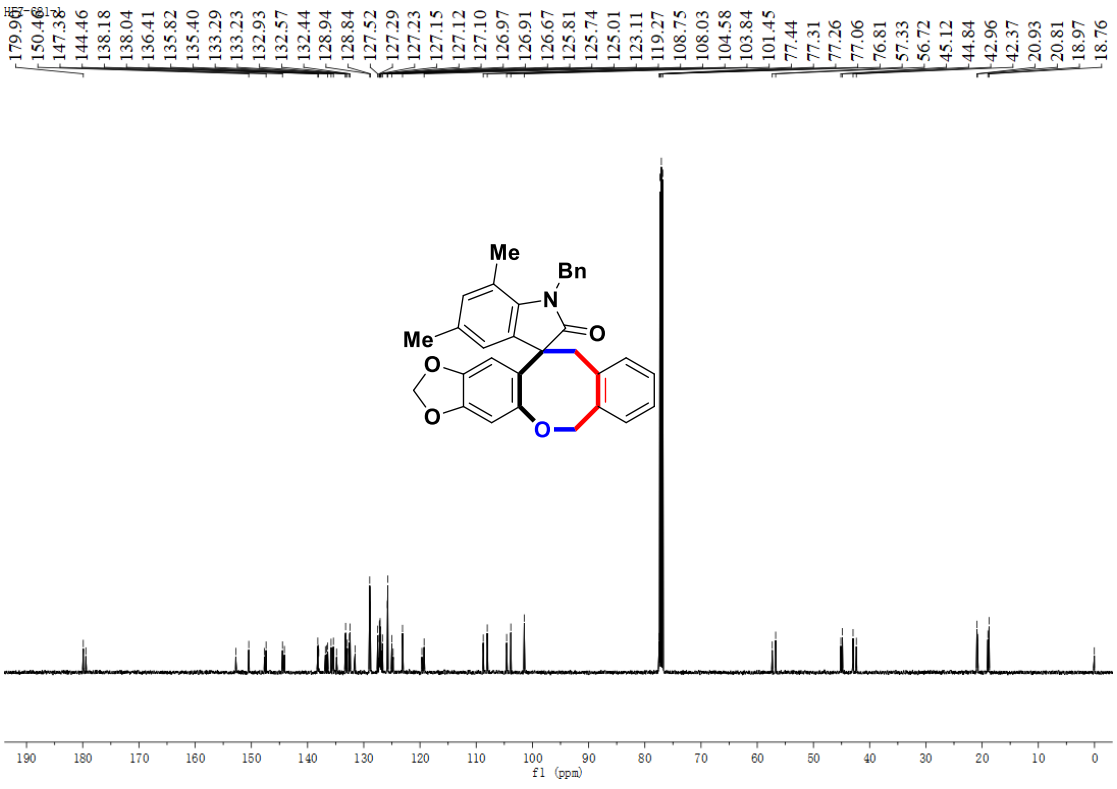
1-benzyl-7-fluoro-6',11'-dihydrospiro[indoline-3,12'-[1,3]dioxolo[4',5':4,5]benzo[1,2-b]benzo[f]oxocin]-2-one (3k)



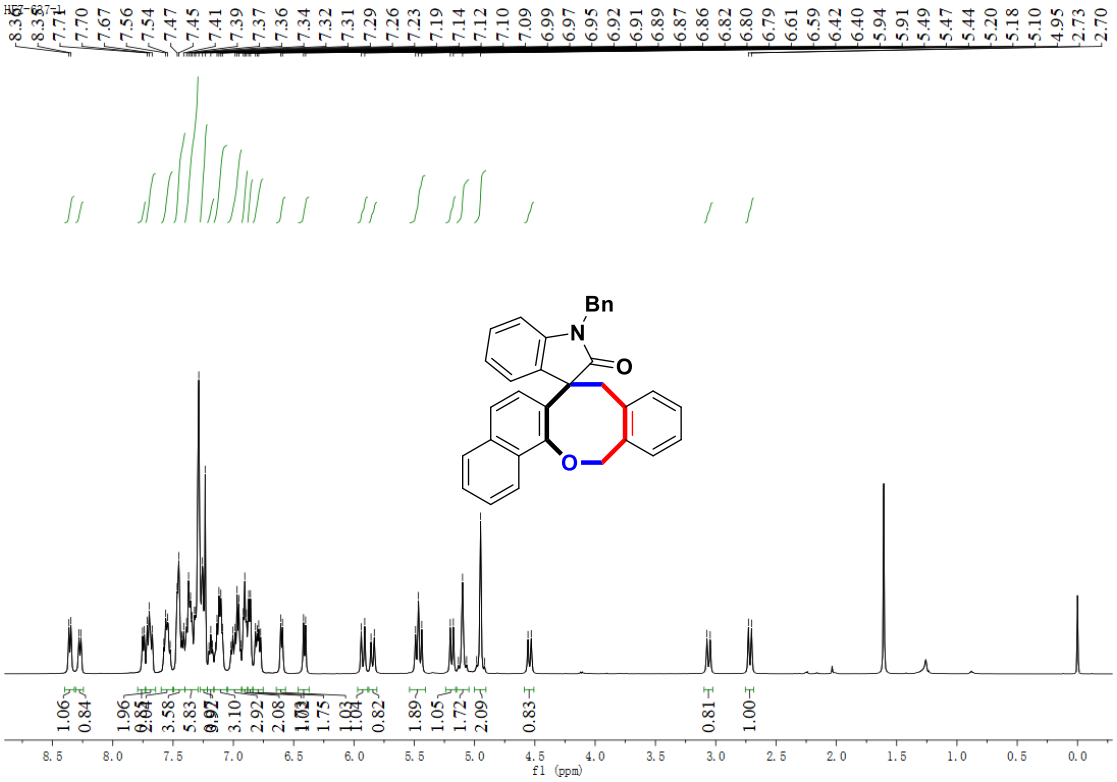


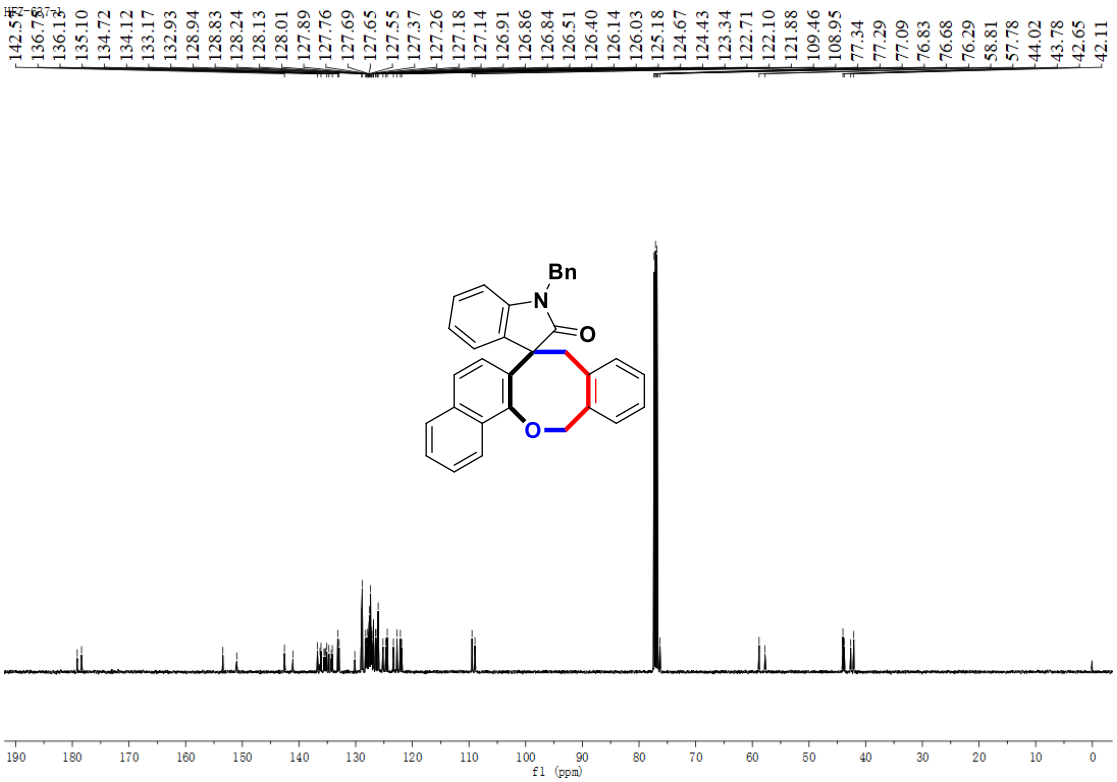
1-benzyl-5,7-dimethyl-6',11'-dihydrospiro[indoline-3,12'-[1,3]dioxolo[4',5':4,5]benzo[1,2-b]benzo[f]oxocin]-2-one (3l)



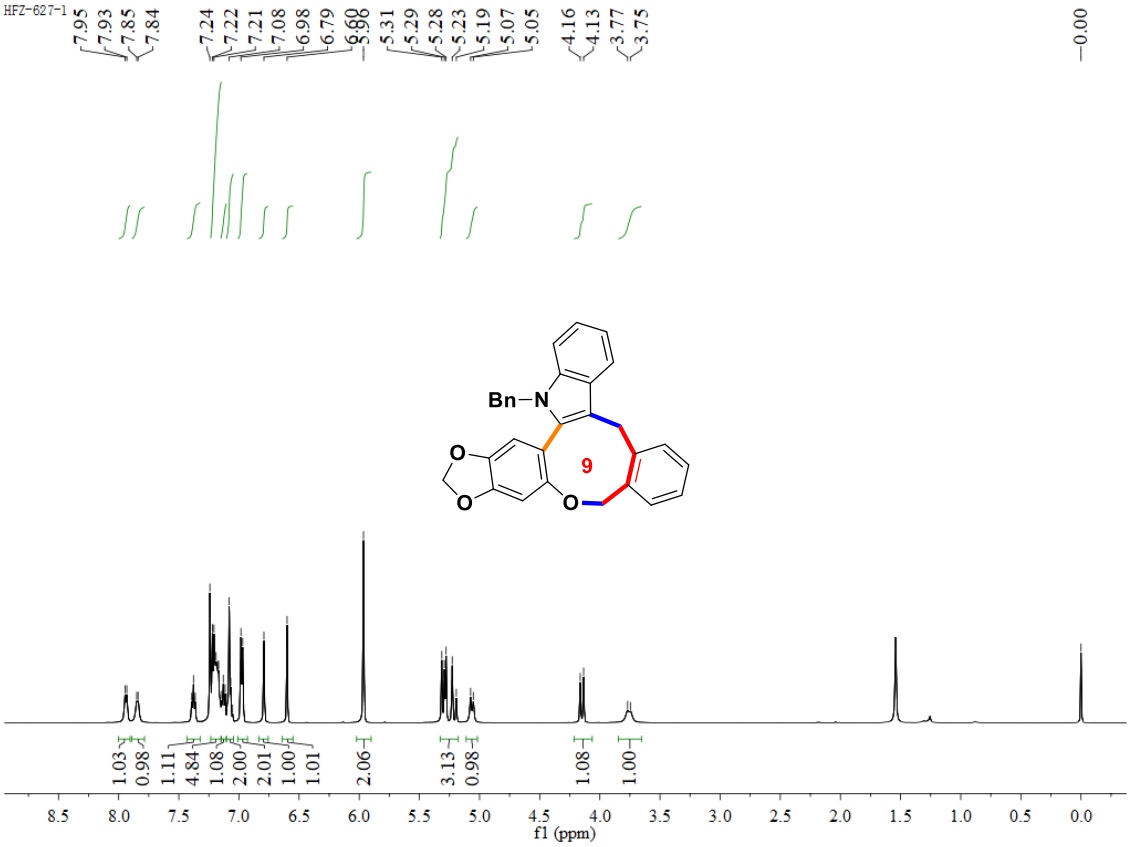


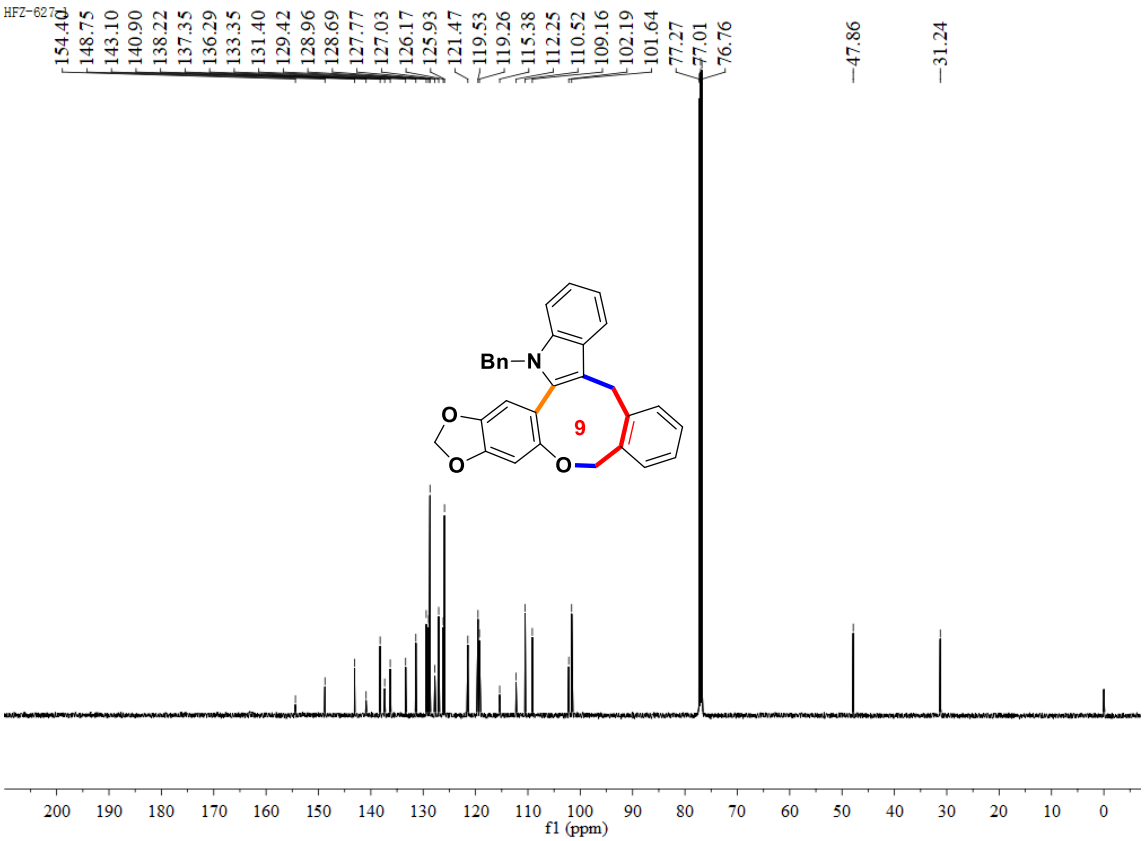
1'-benzyl-8,13-dihydrospiro[benzo[f]naphtho[1,2-b]oxocine-7,3'-indolin]-2'-one (3m)



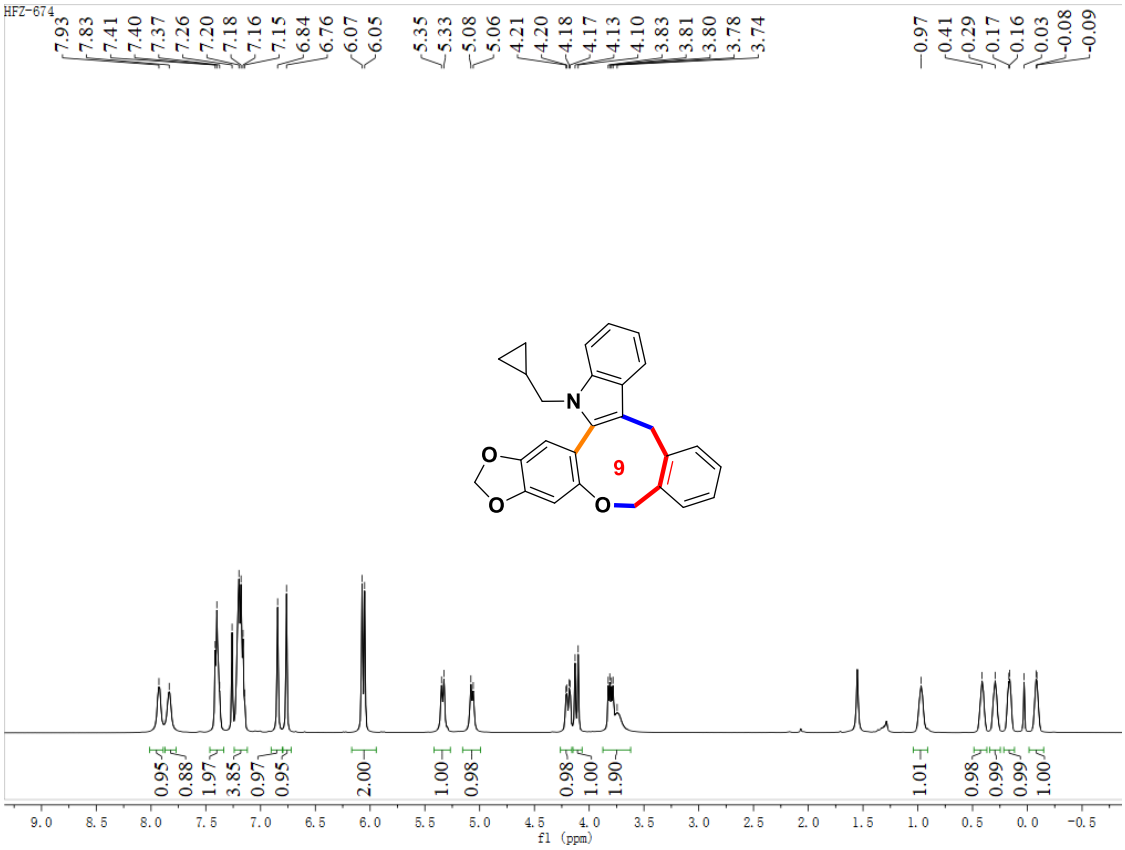


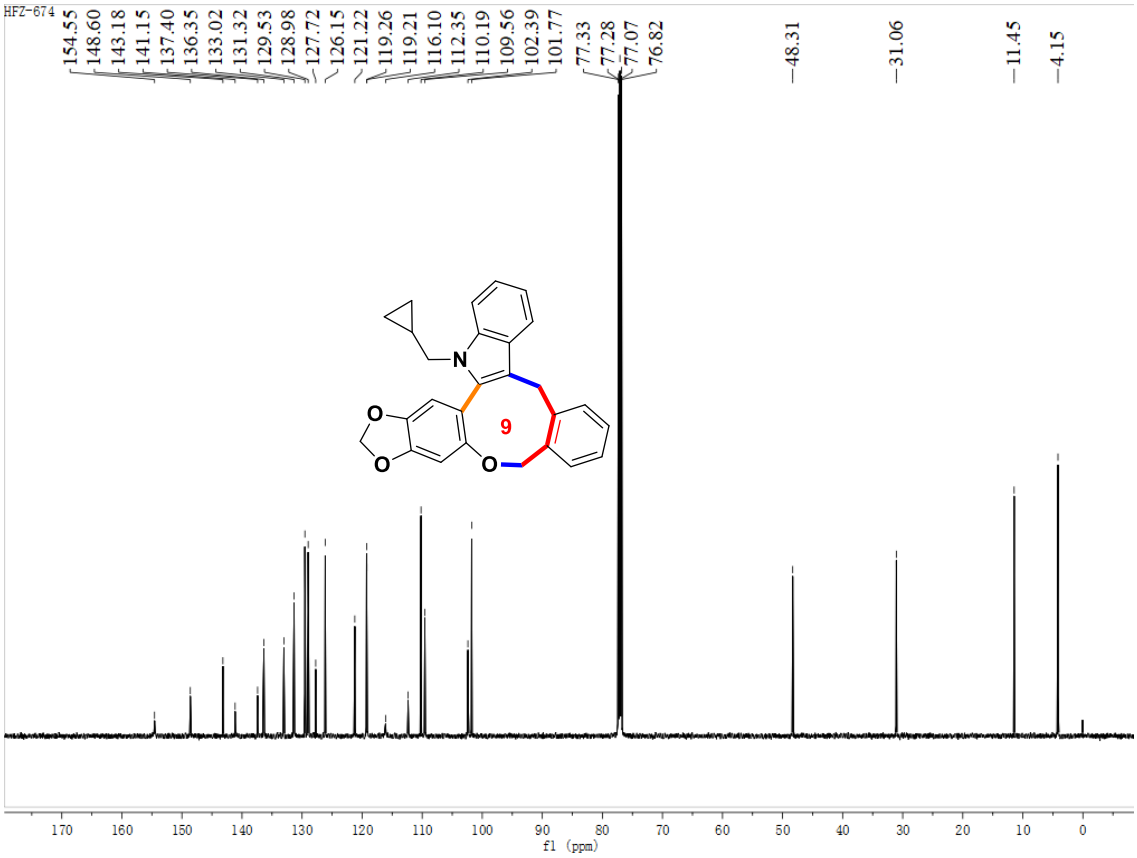
17-benzyl-5,17-dihydro-10H-[1,3]dioxolo[4'',5'':4',5']benzo[1',2':2,3]benzo[7,8]oxonino[4,5-b]indole (4a)



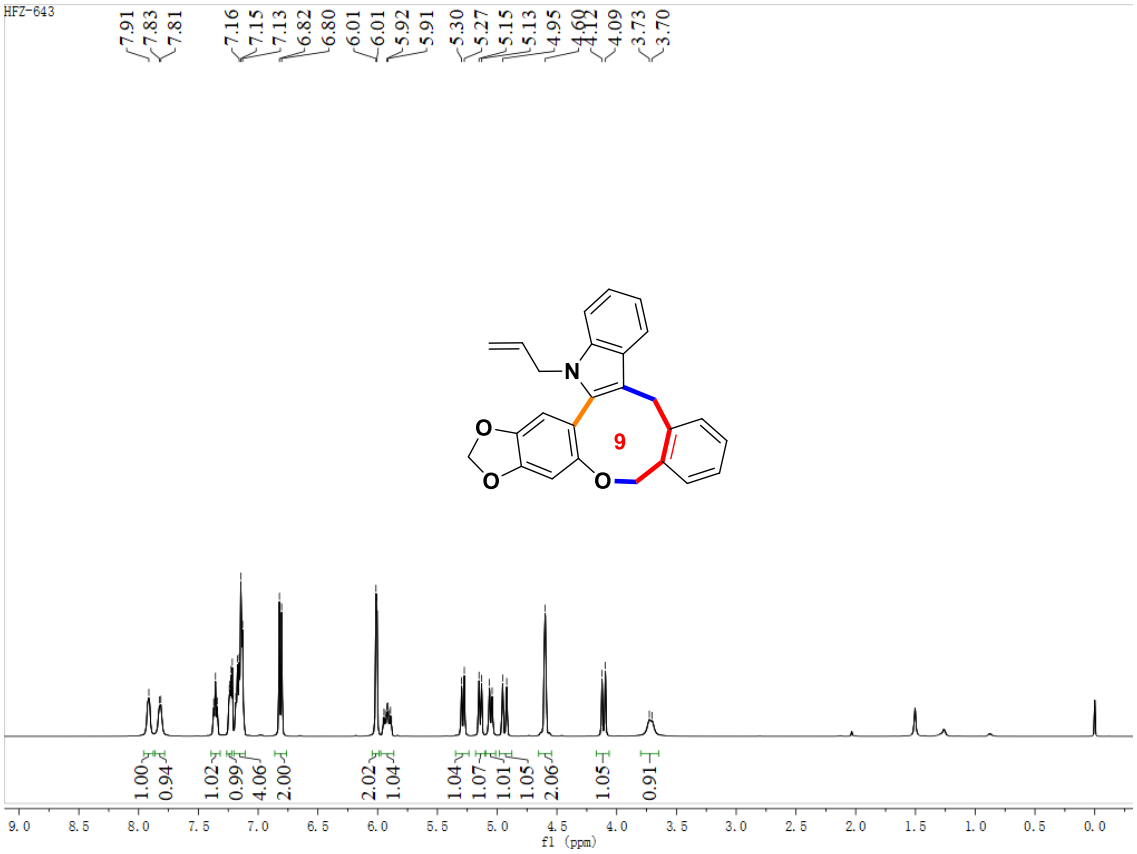


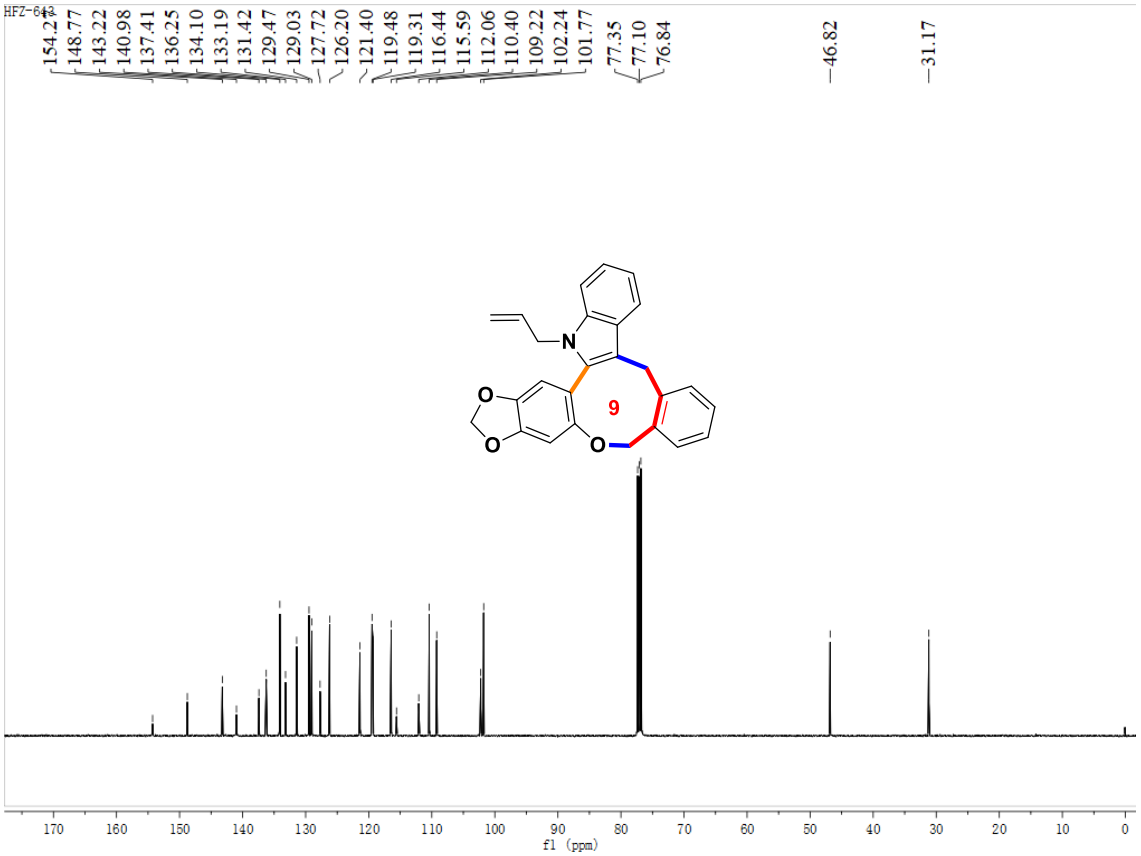
17-(cyclopropylmethyl)-5,17-dihydro-10H-[1,3]dioxolo[4'',5'':4',5']benzo[1',2':2,3]benzo[7,8]oxonino[4,5-b]indole (4b)



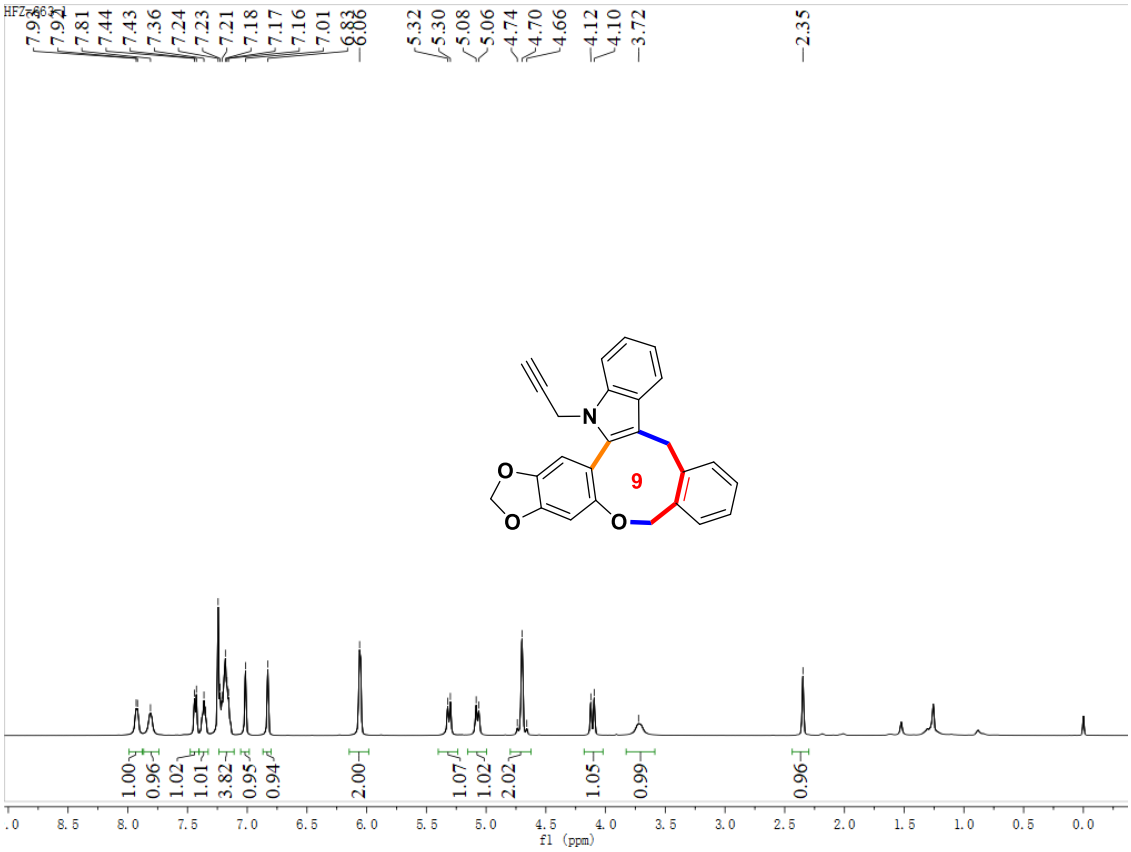


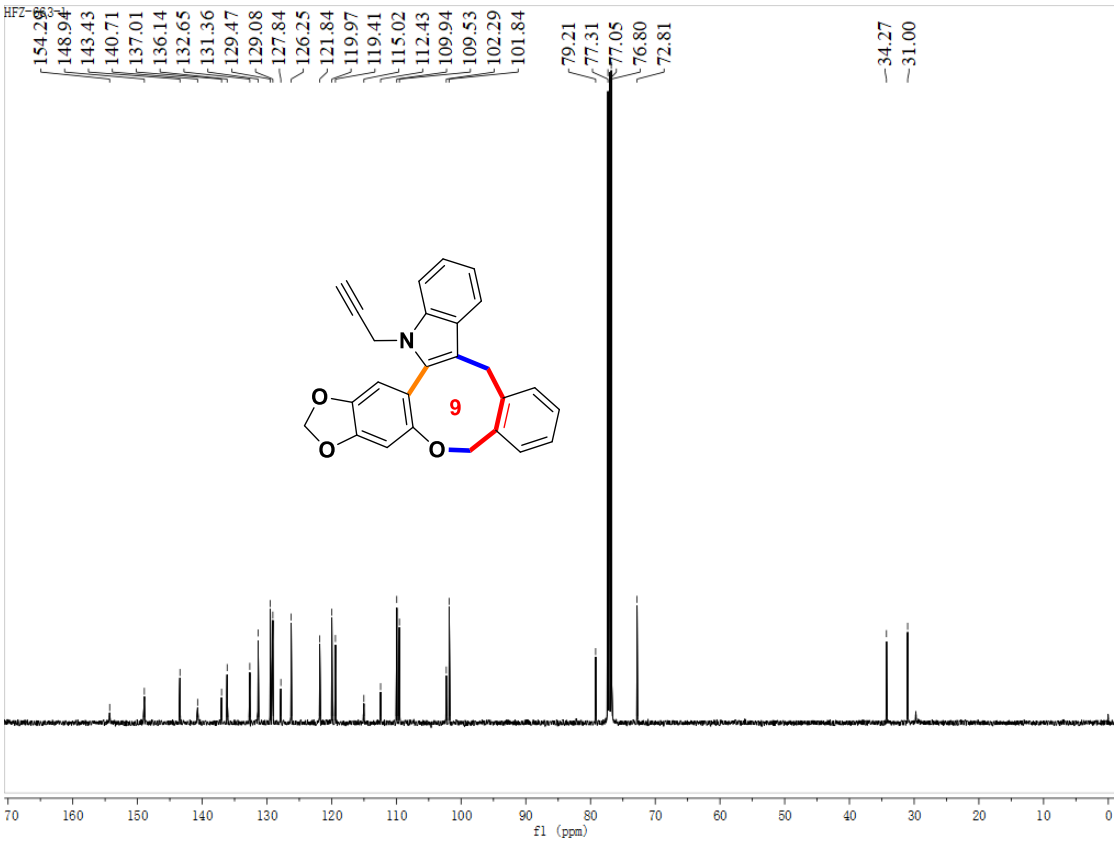
17-allyl-5,17-dihydro-10H-[1,3]dioxolo[4'',5'':4',5']benzo[1',2':2,3]benzo[7,8]oxonino[4,5-b]indole (4c)



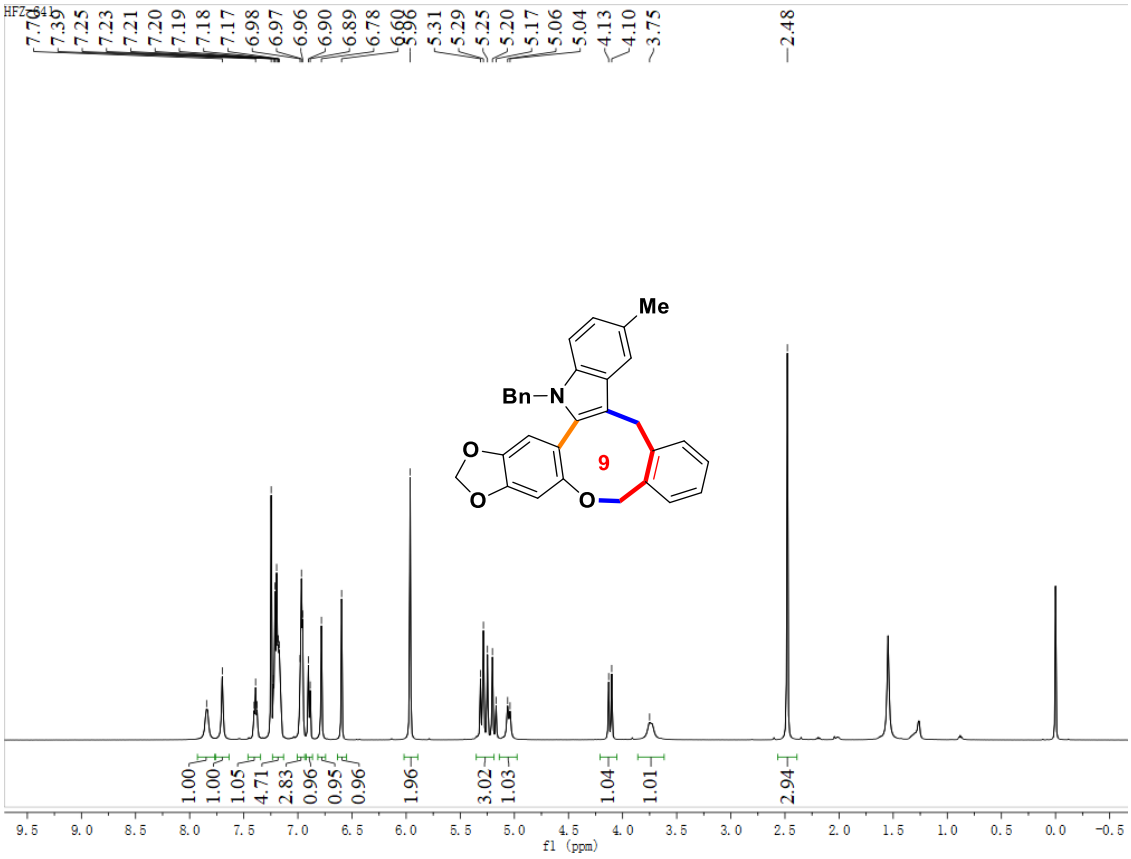


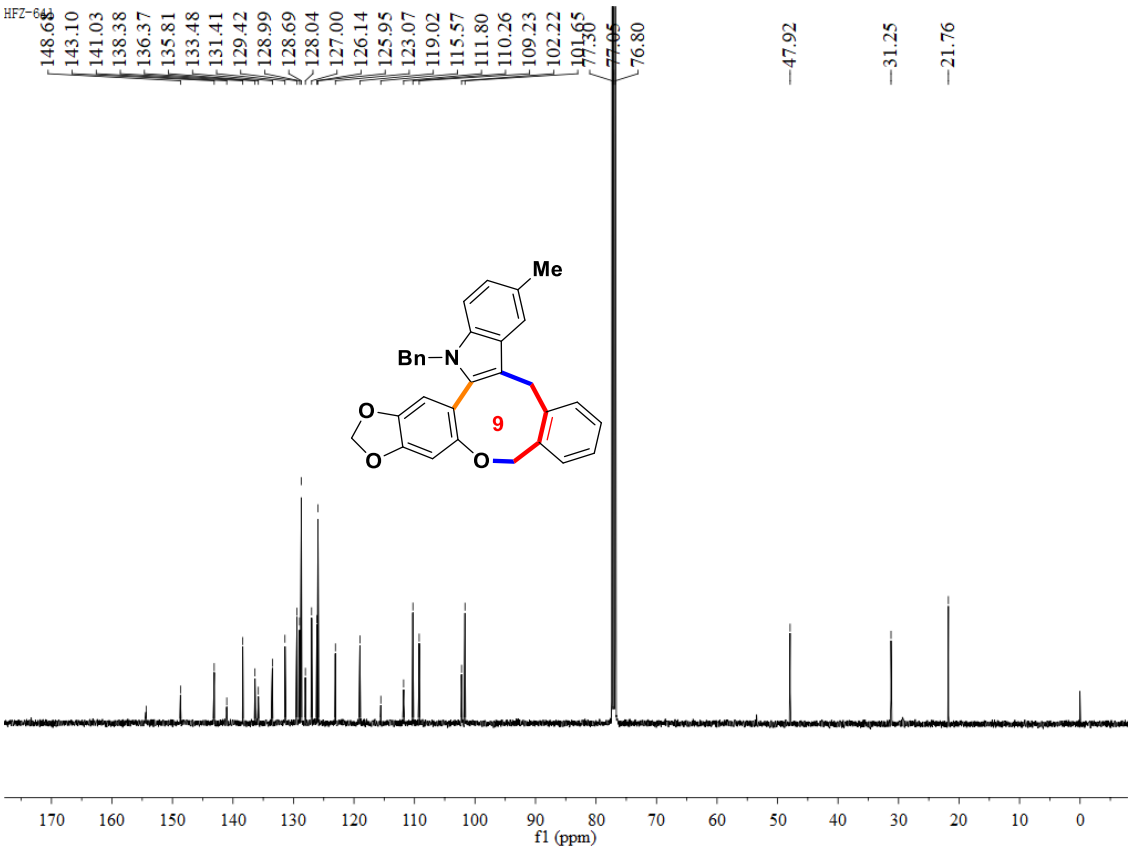
17-(prop-2-yn-1-yl)-5,17-dihydro-10H-[1,3]dioxolo[4'',5'':4',5']benzo[1',2':2,3]benzo[7,8]oxonino[4,5-b]indole (4d)



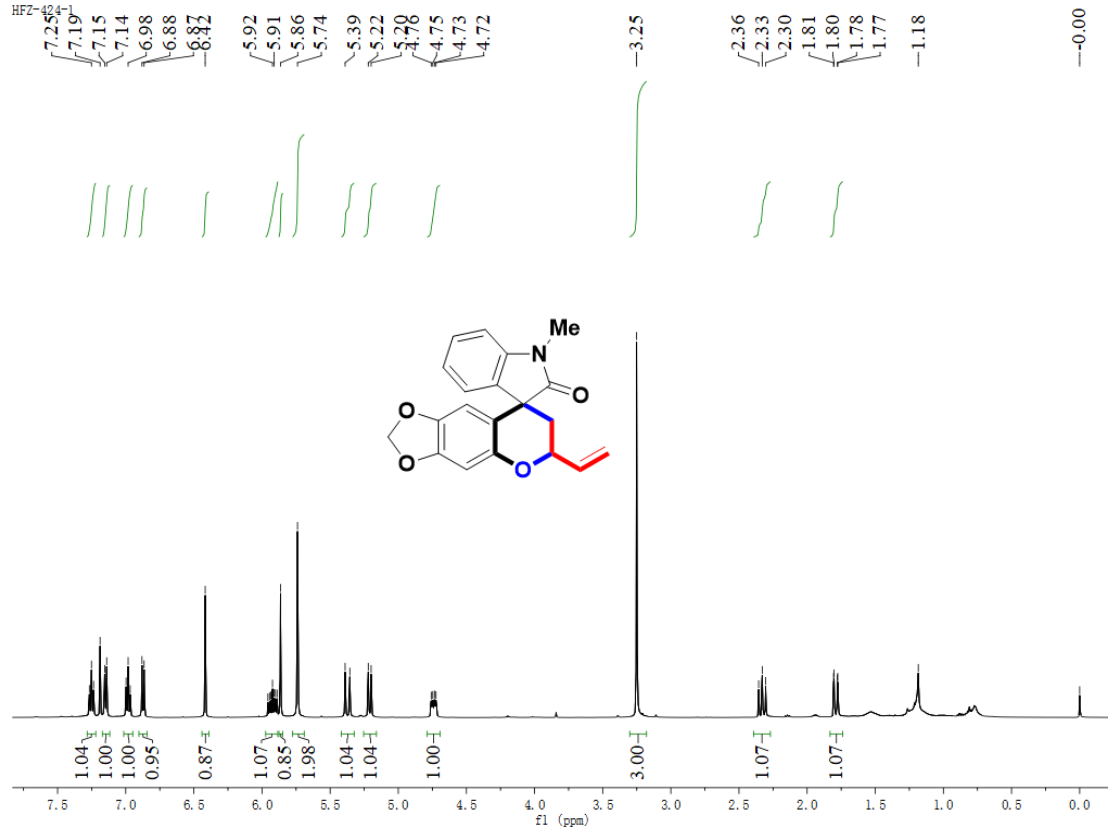


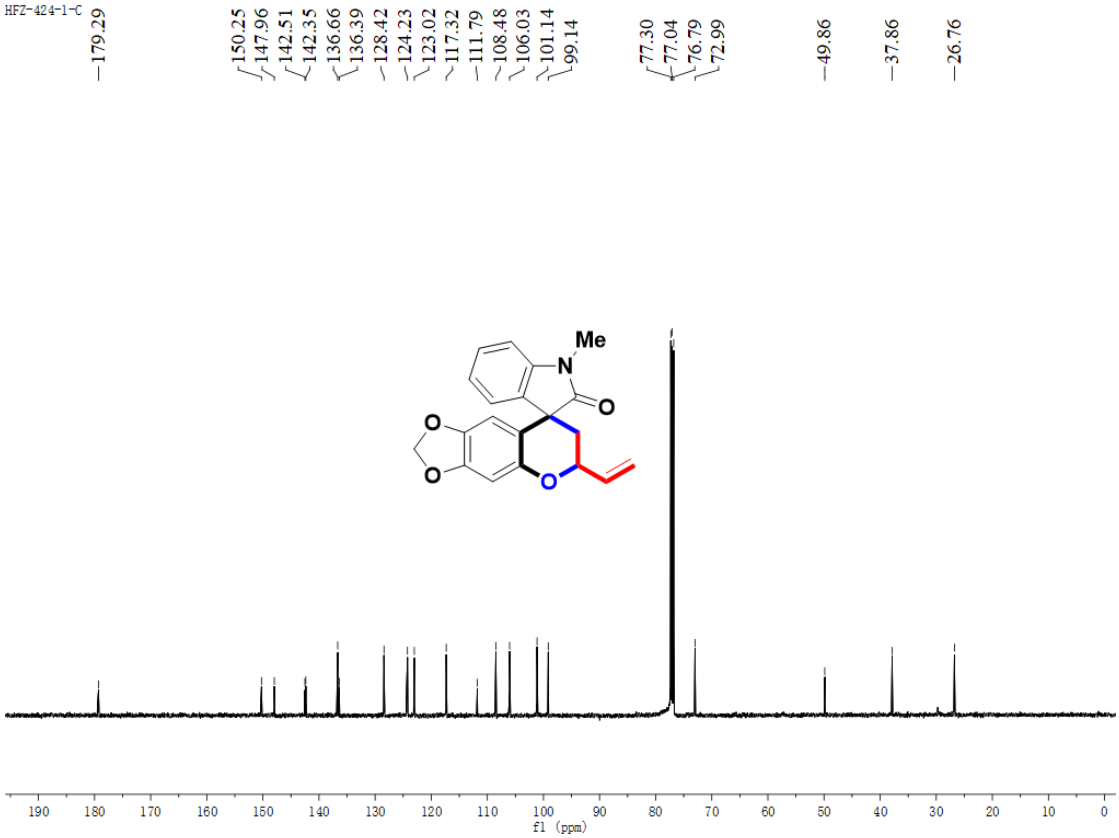
17-benzyl-3-methyl-5,17-dihydro-10H-[1,3]dioxolo[4'',5'':4',5']benzo[1',2':2,3]benzo[7,8]oxonino[4,5-b]indole (4e)



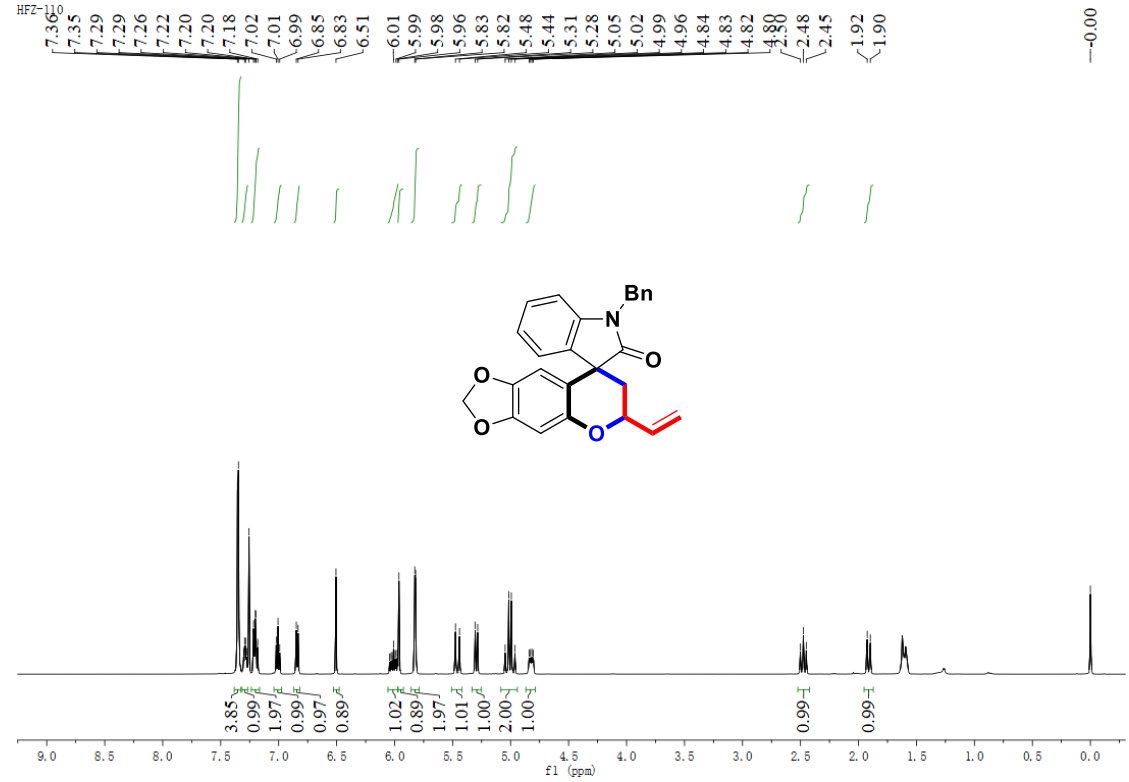


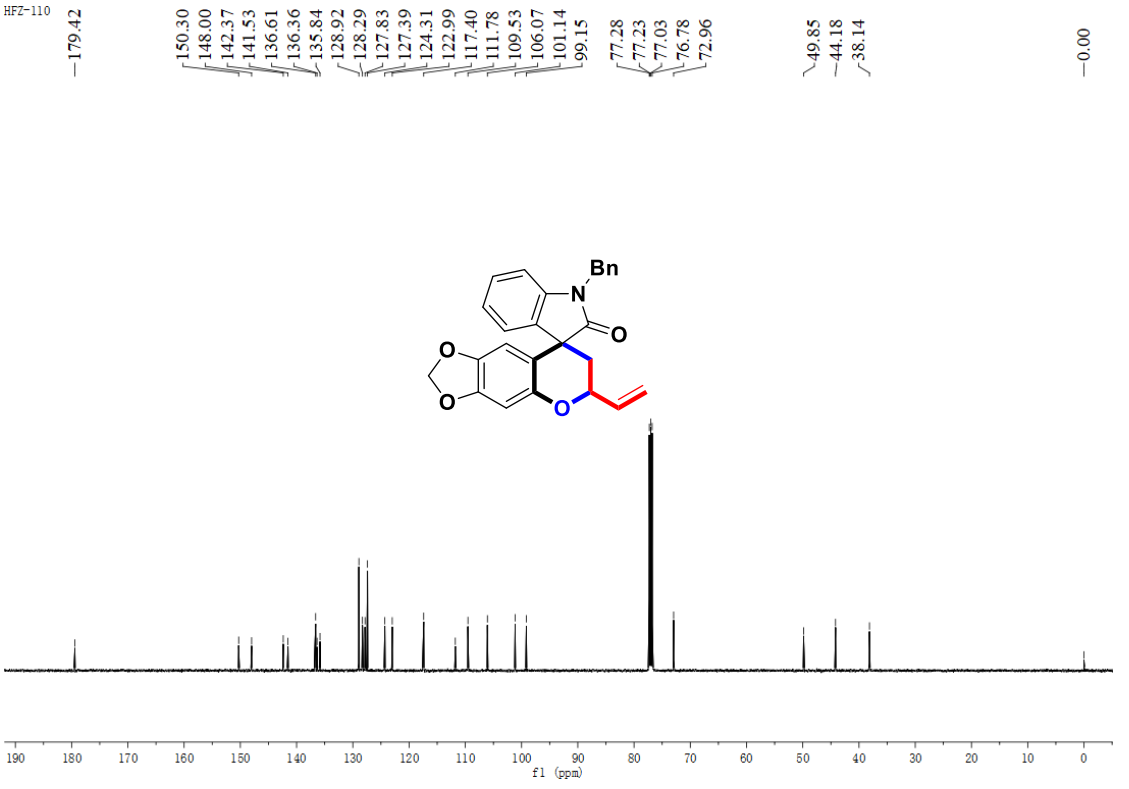
1-methyl-6'-vinyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (6a)



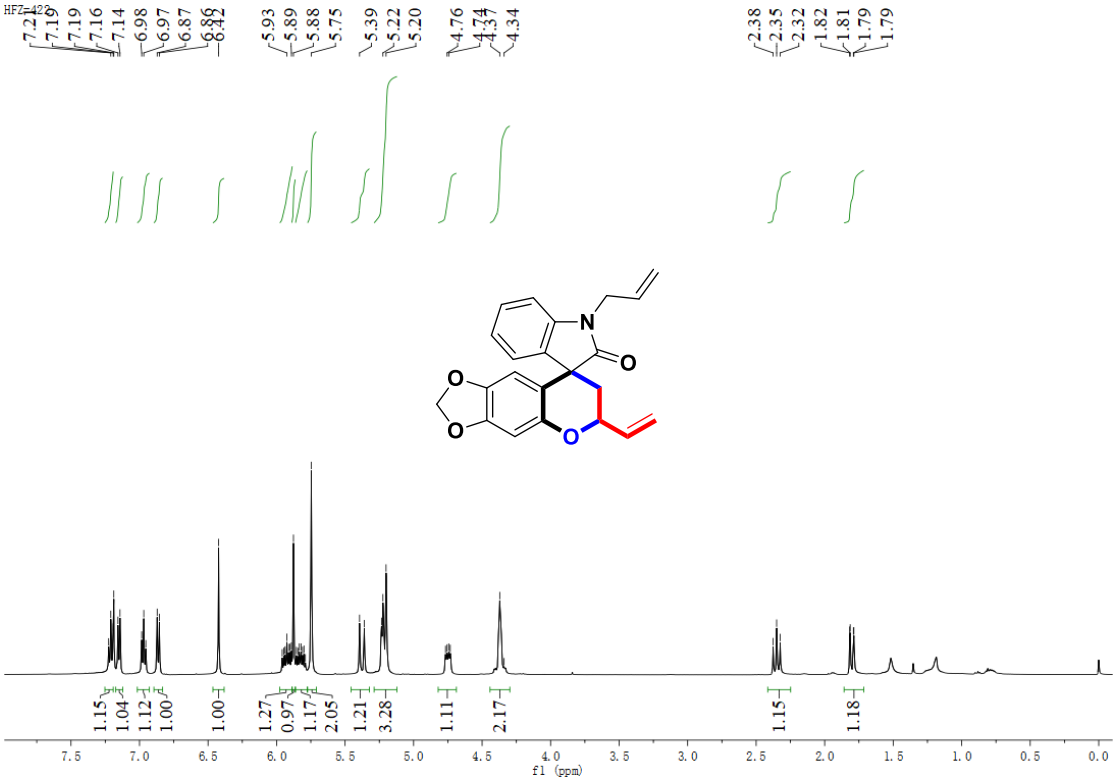


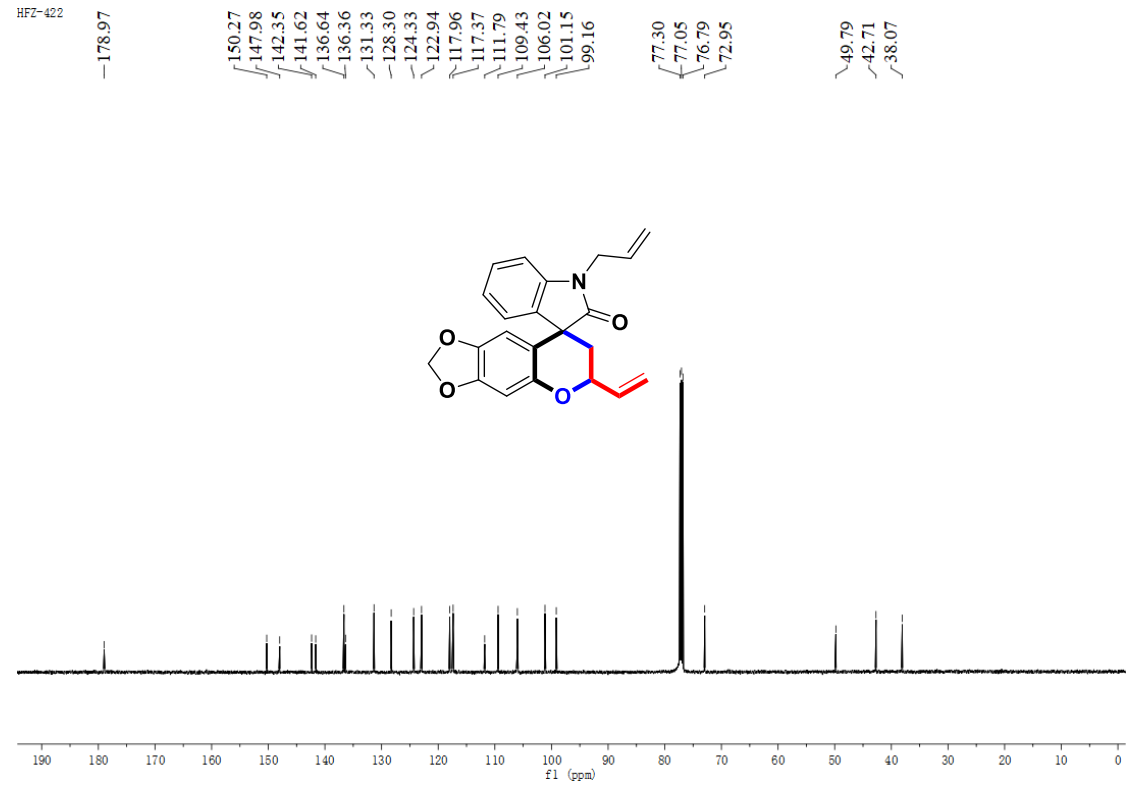
1-benzyl-6'-vinyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (6b)



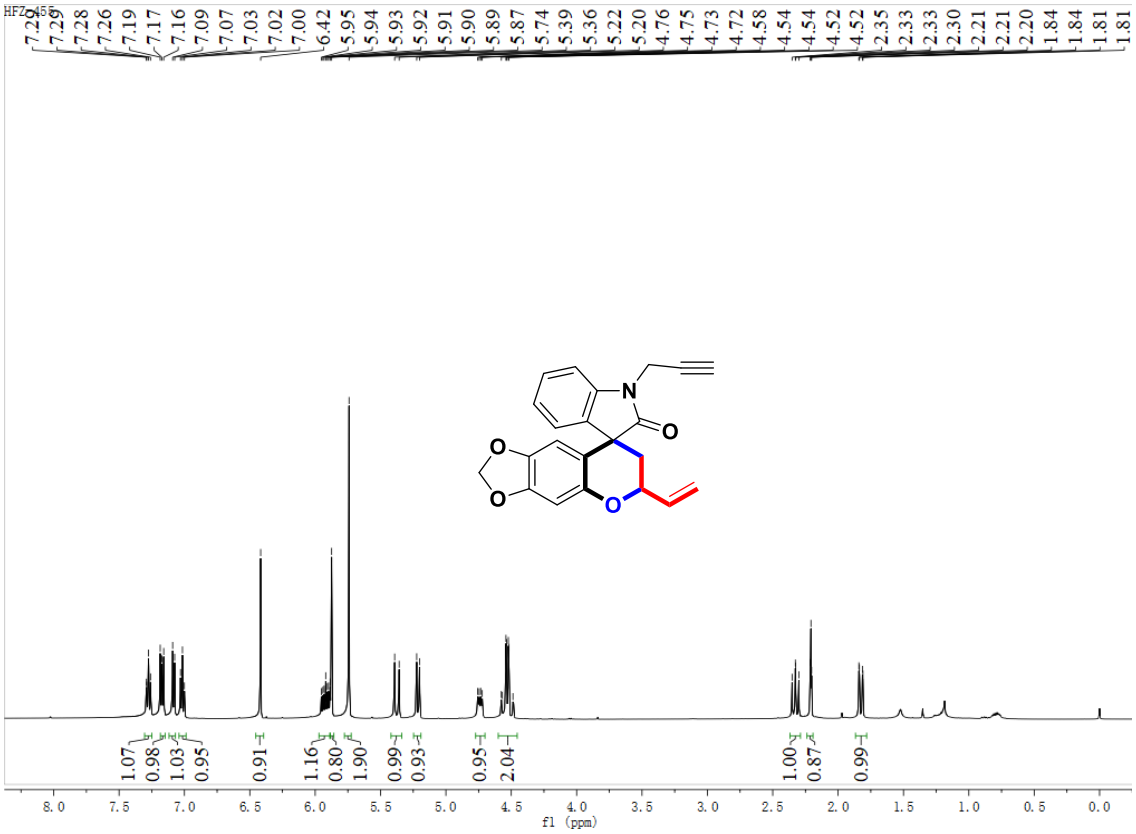


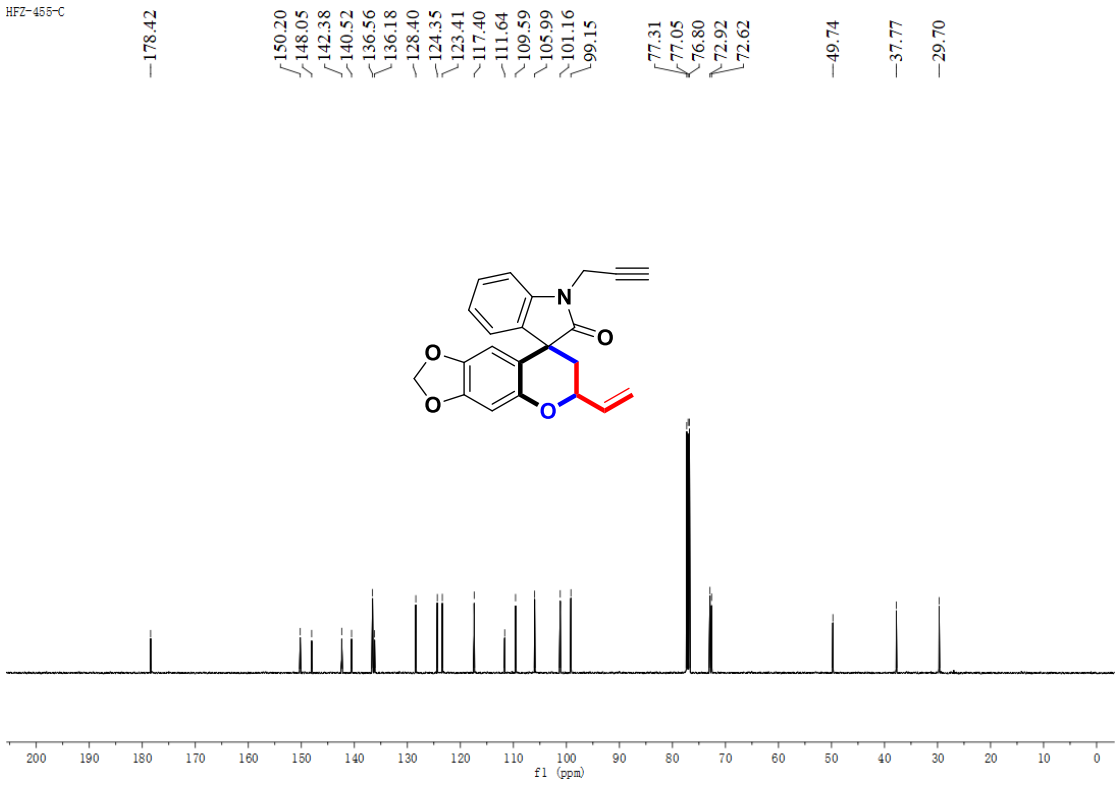
1-allyl-6'-vinyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (6c)



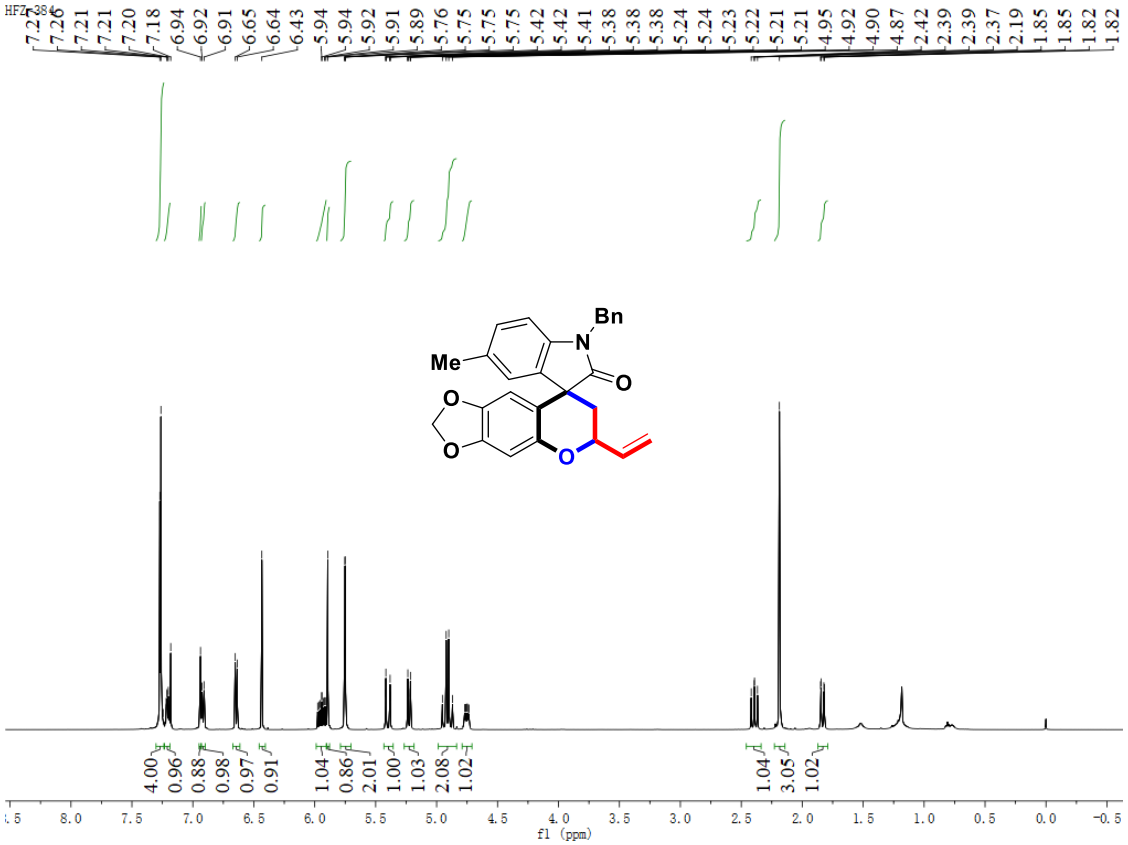


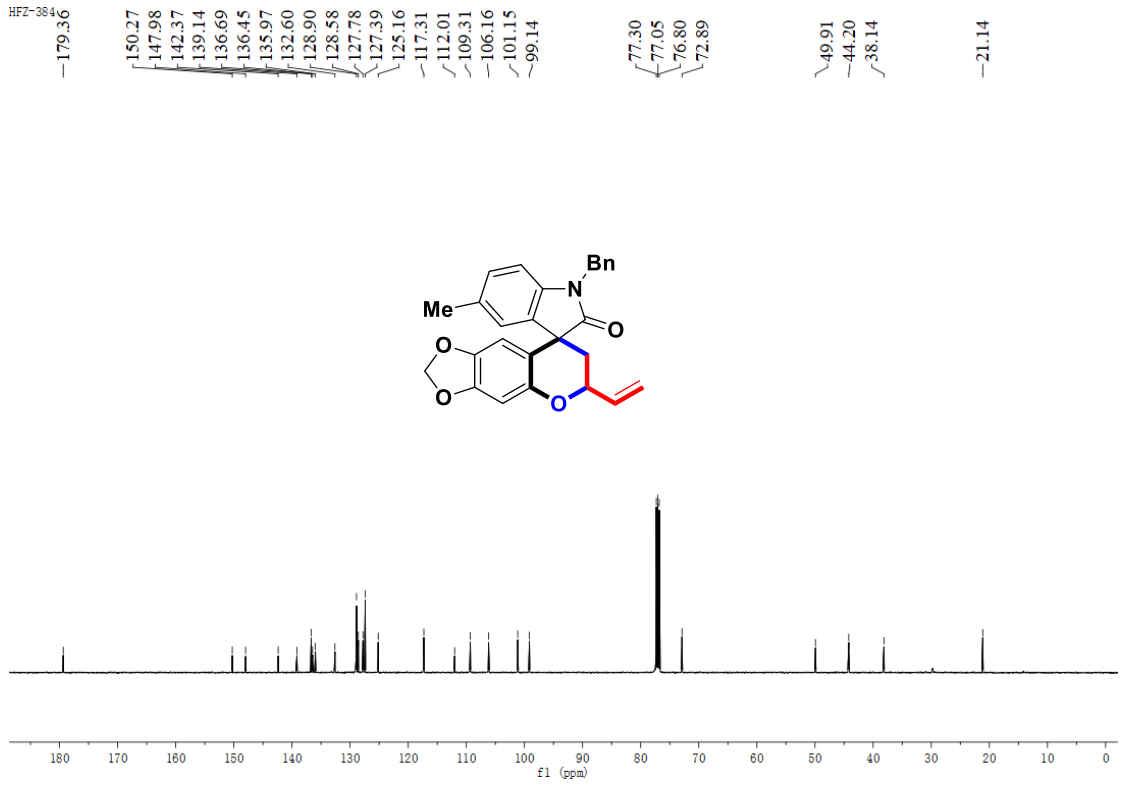
1-(prop-2-yn-1-yl)-6'-vinyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (6d)



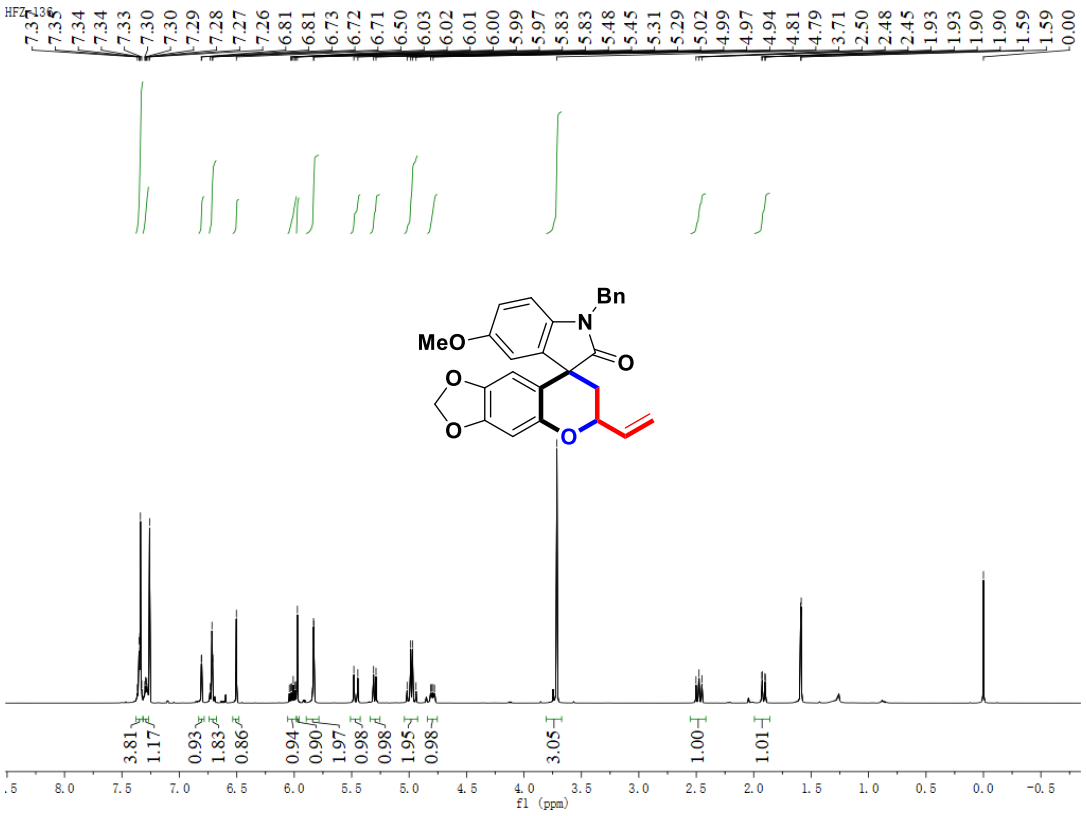


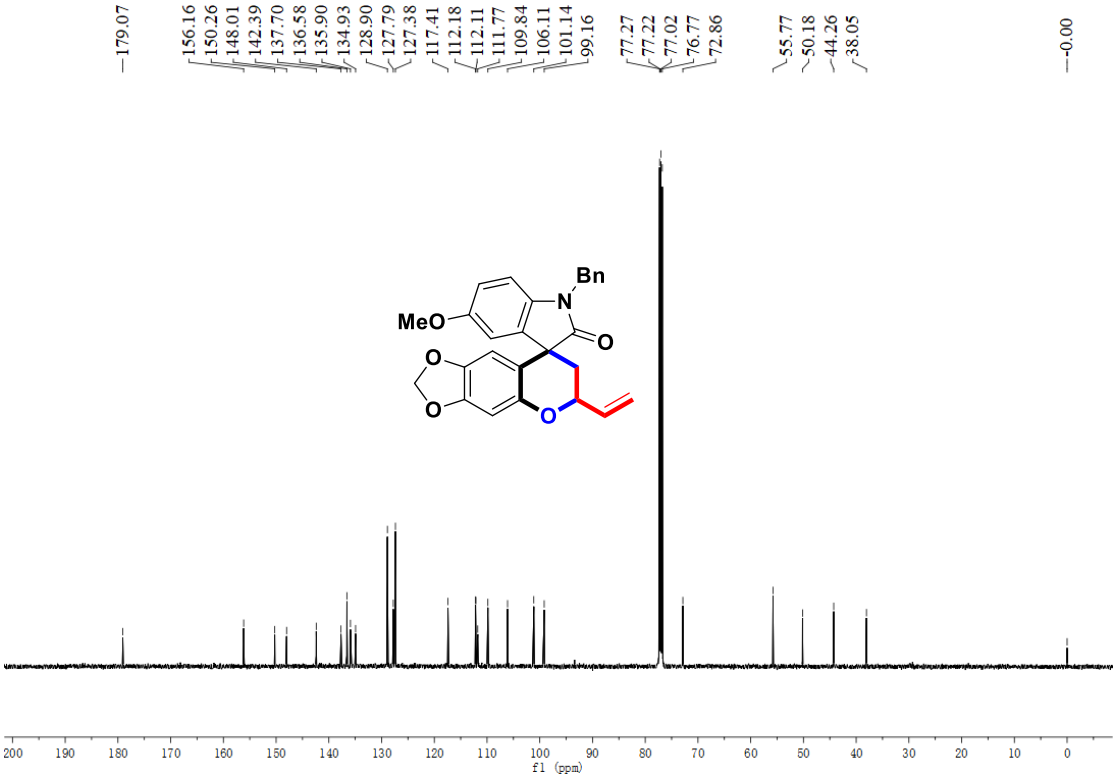
1-benzyl-5-methyl-6'-vinyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (6e)



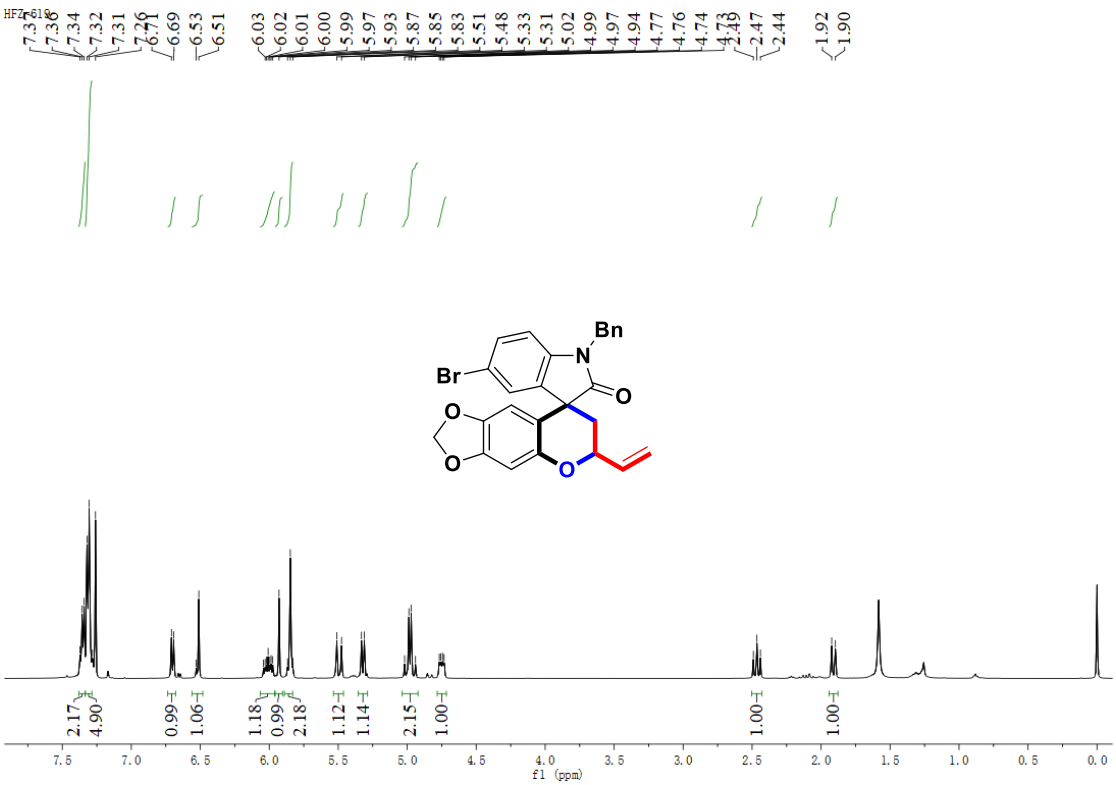


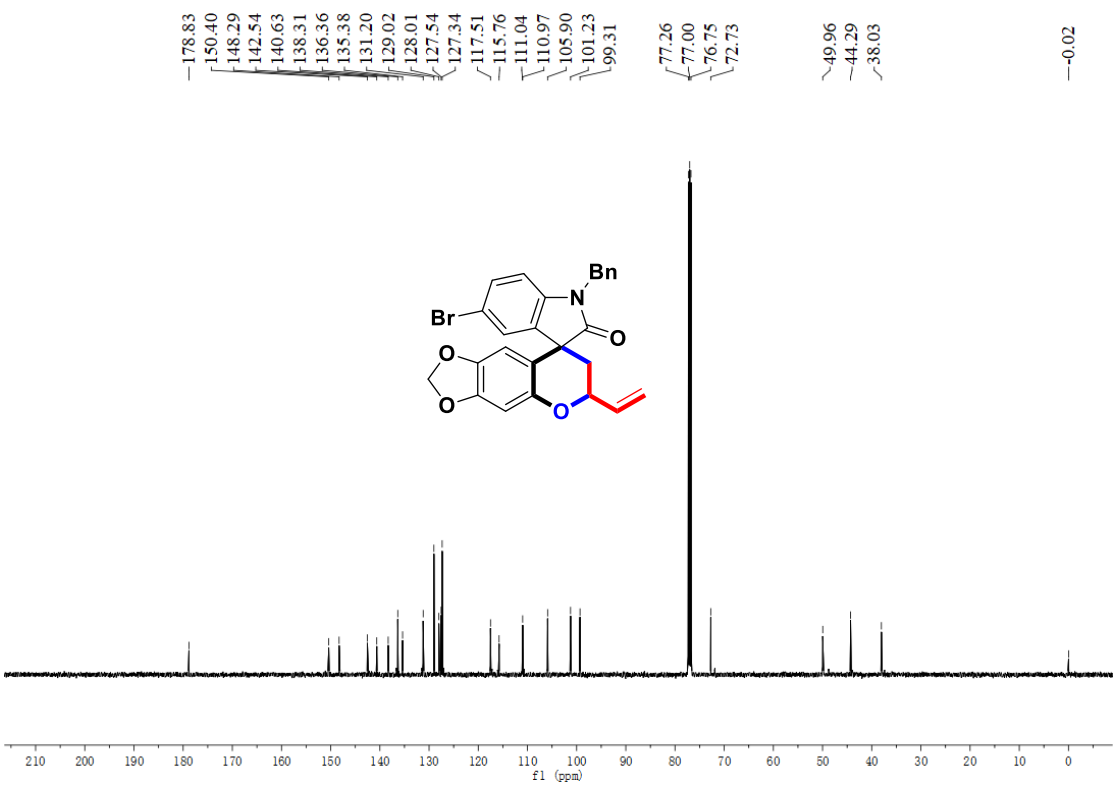
1-benzyl-5-methoxy-6'-vinyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (6f)



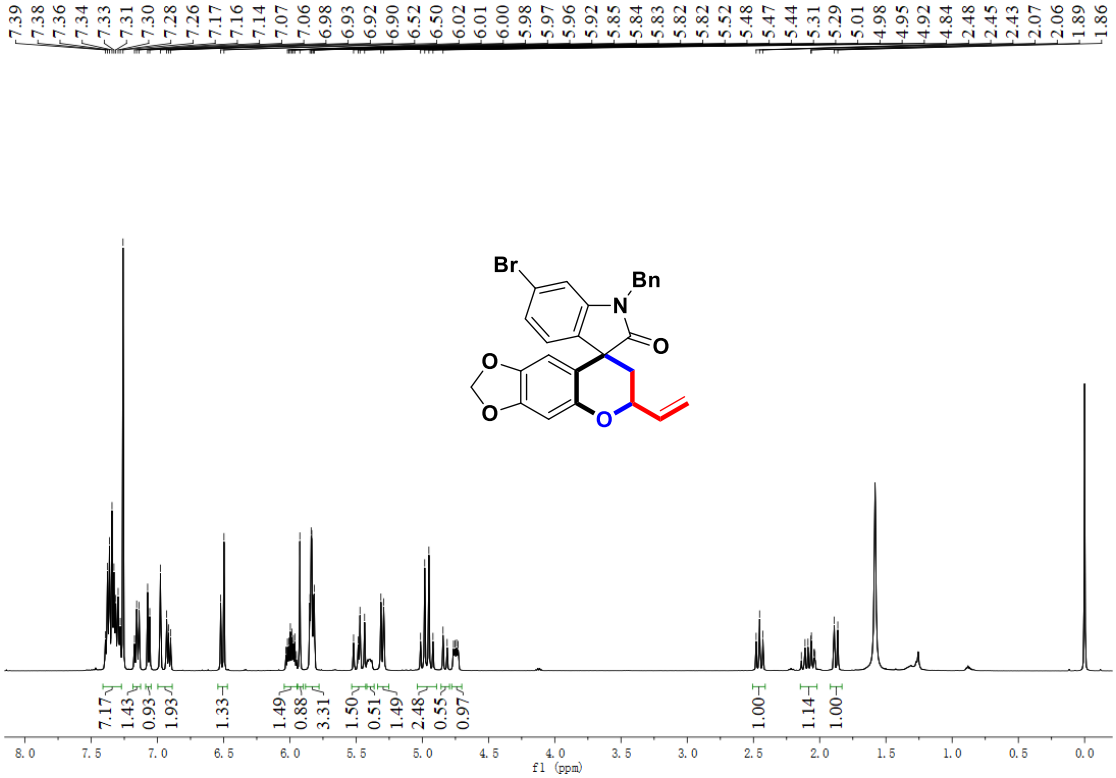


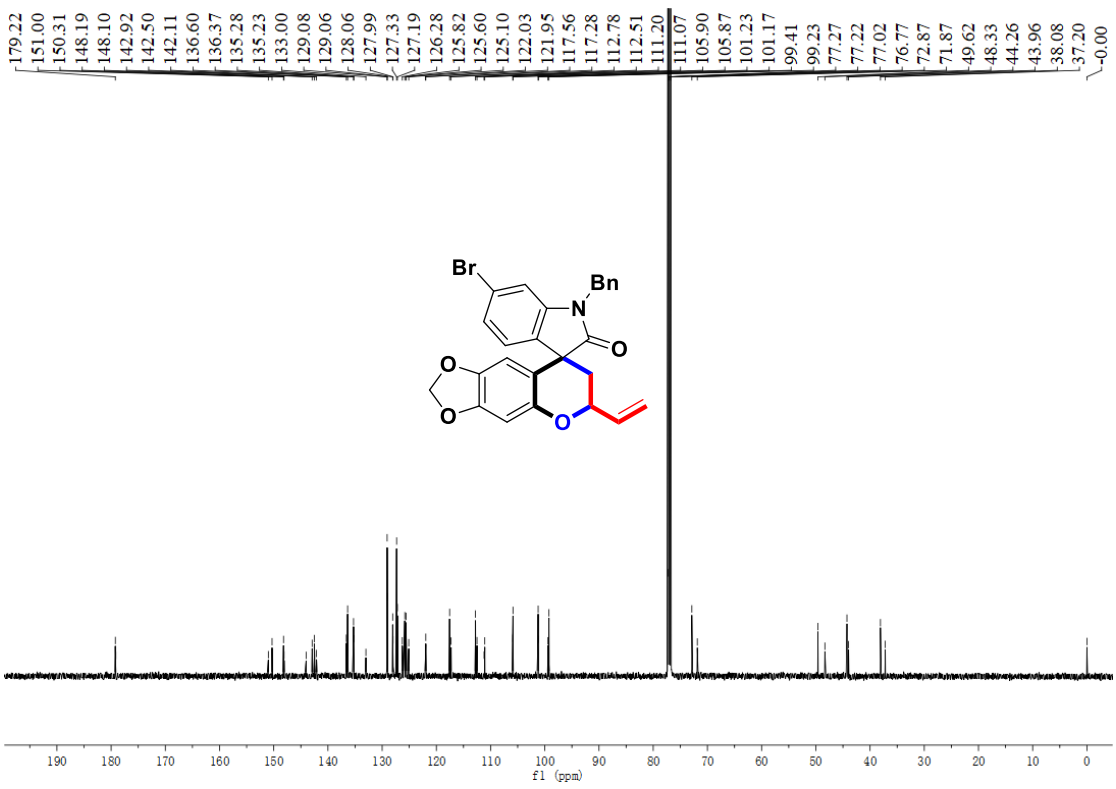
1-benzyl-5-bromo-6'-vinyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (6g)



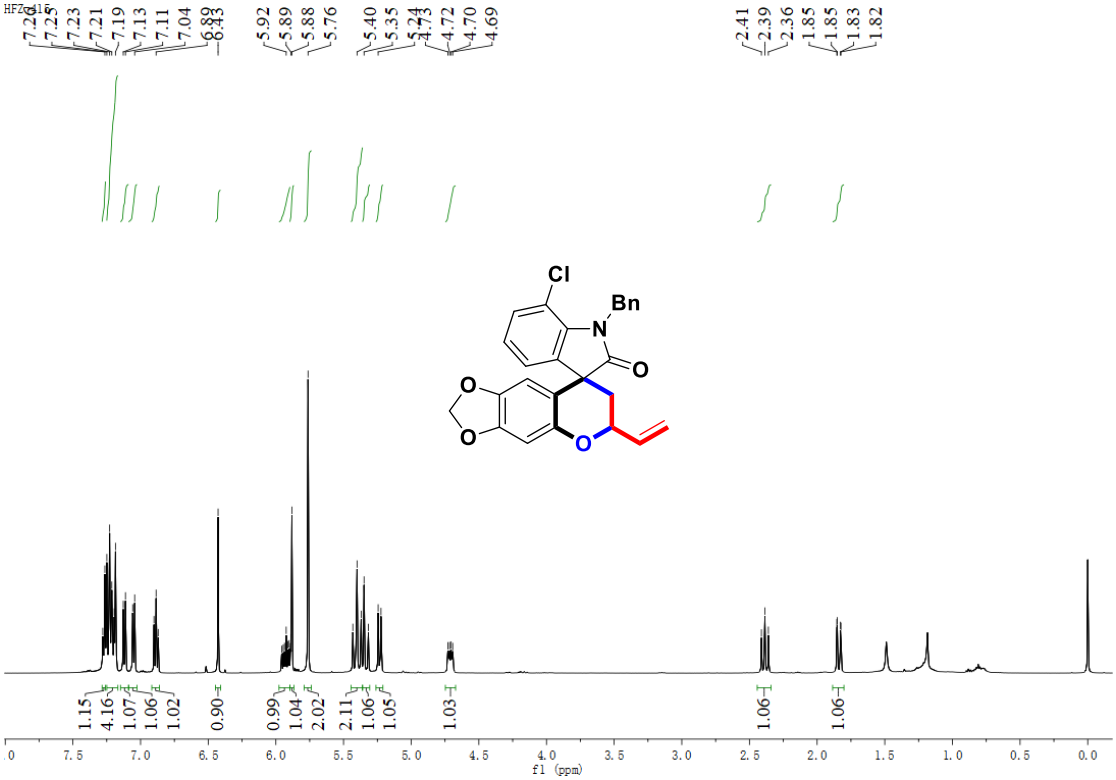


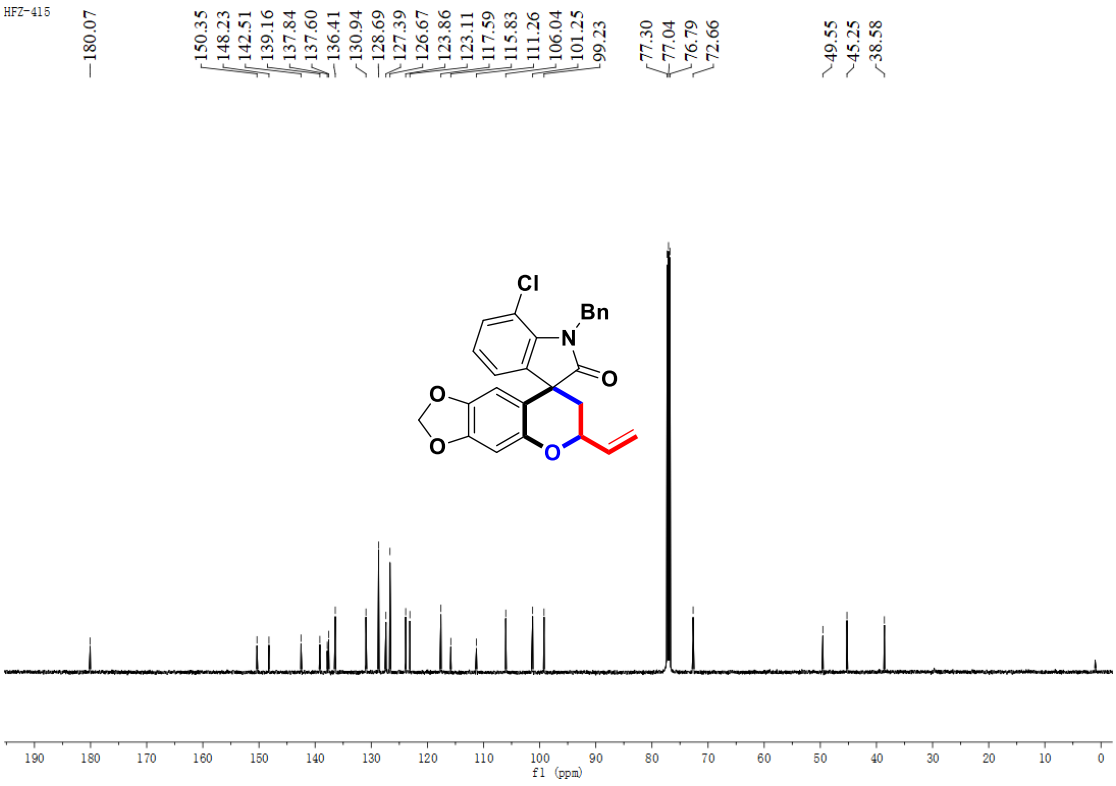
1-benzyl-6-bromo-6'-vinyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (6h)



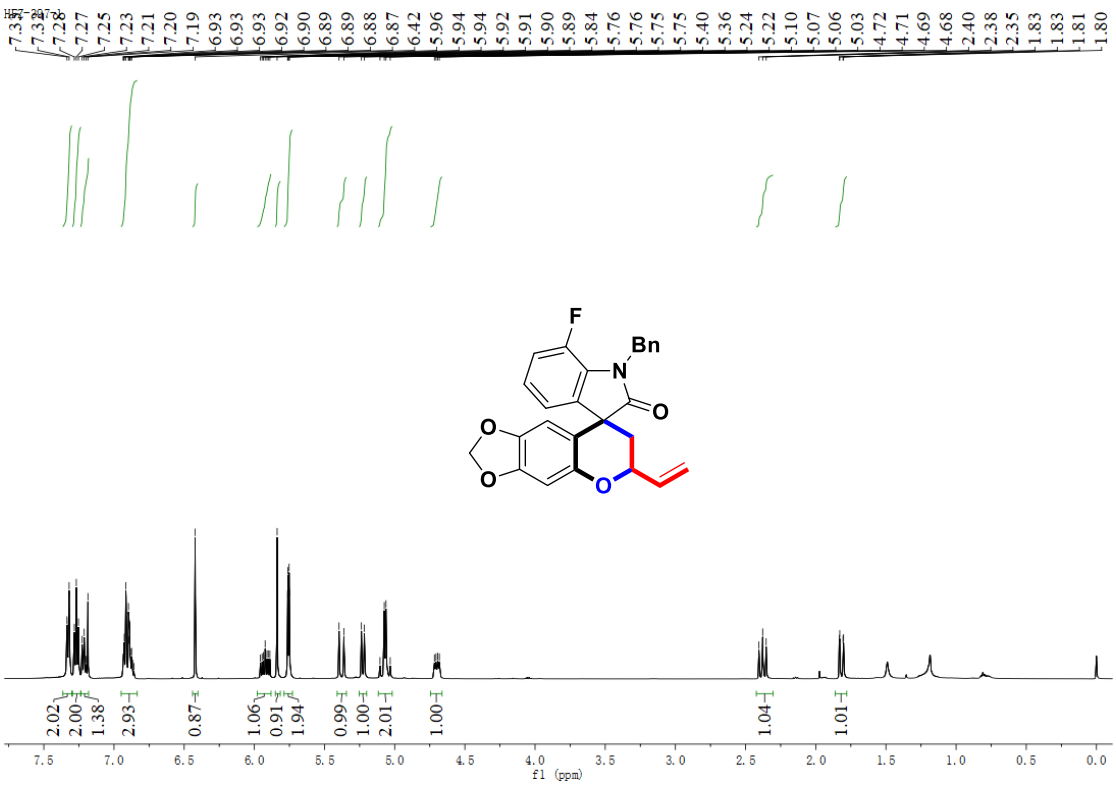


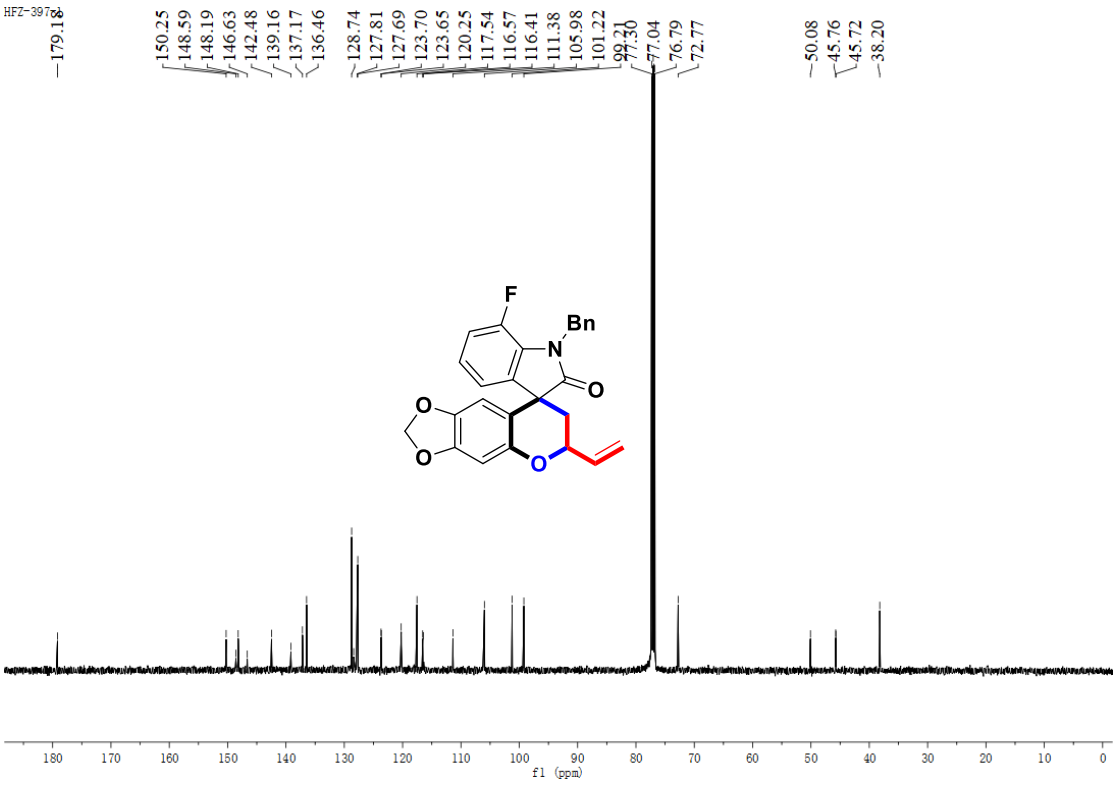
1-benzyl-7-chloro-6'-vinyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (6i)



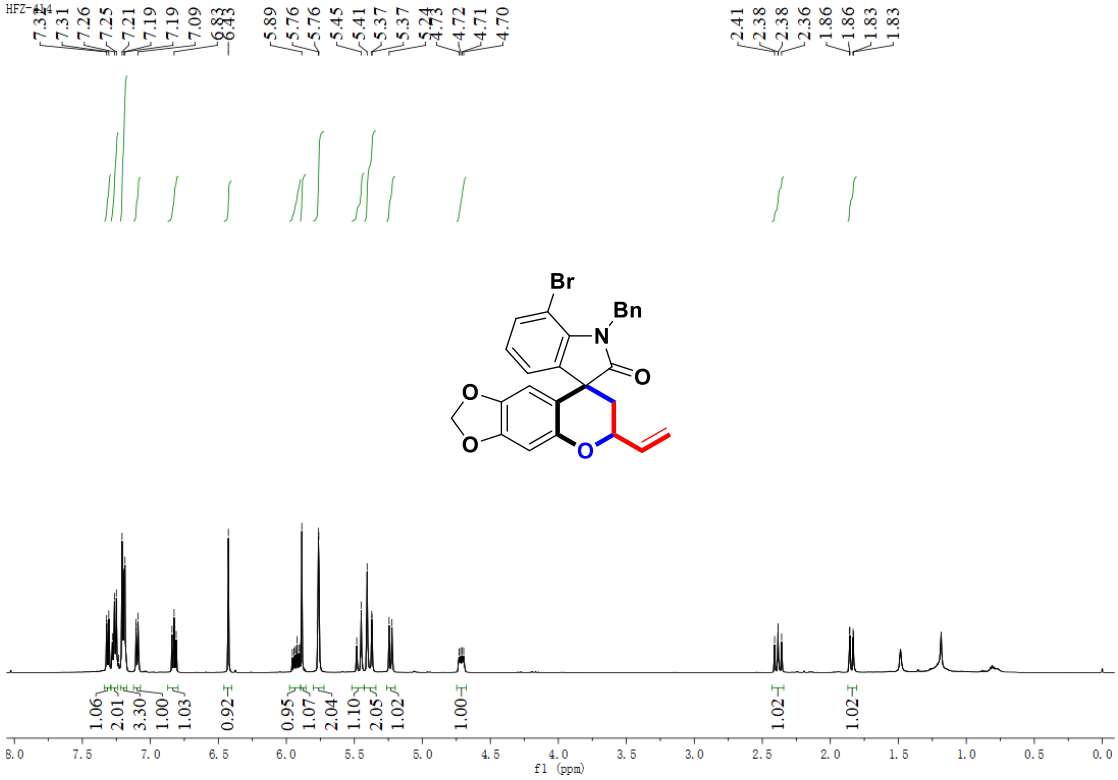


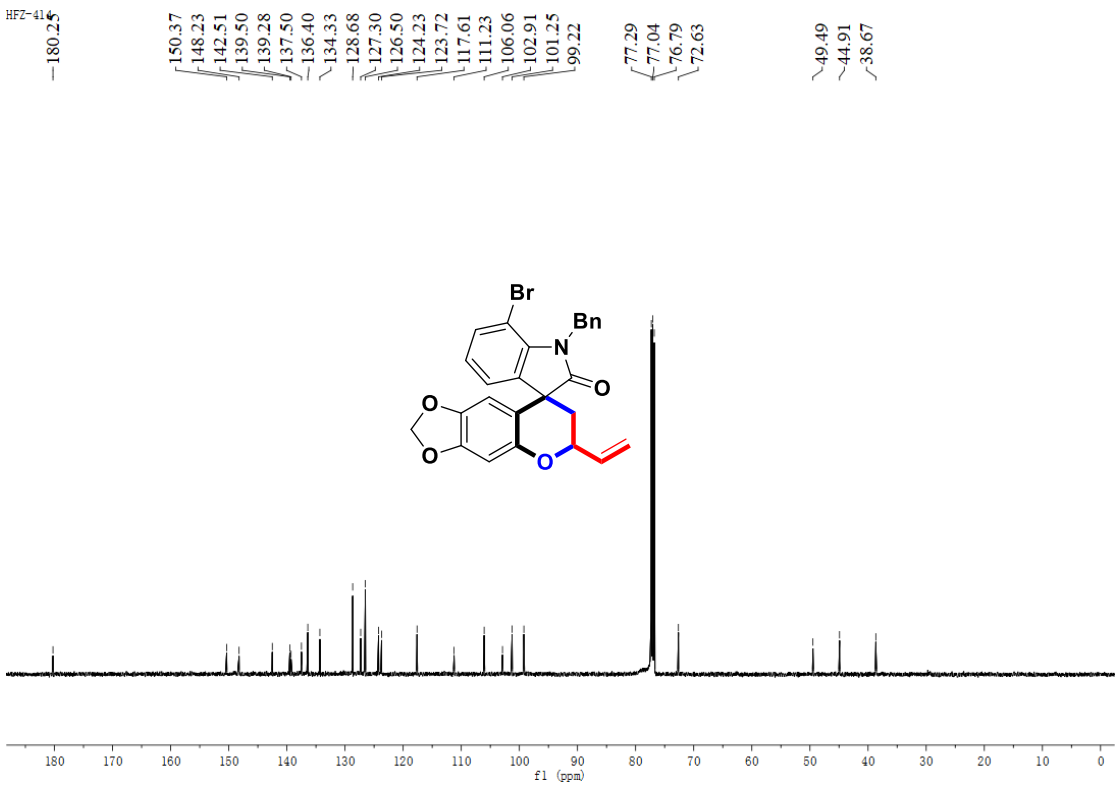
1-benzyl-7-fluoro-6'-vinyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (6j)



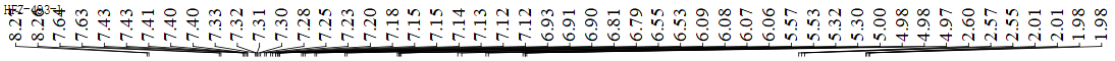


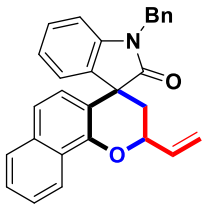
1-benzyl-7-bromo-6'-vinyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (6k)

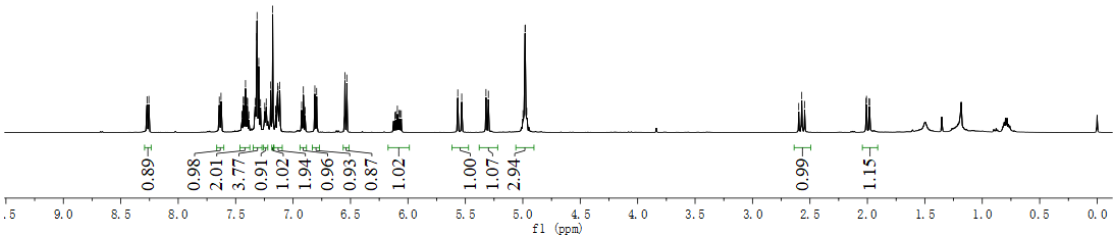


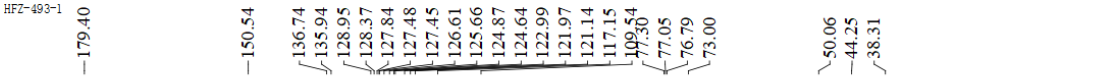


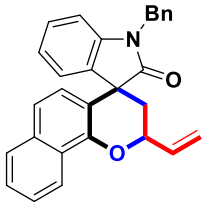
1'-benzyl-2-vinyl-2,3-dihydrospiro[benzo[h]chromene-4,3'-indolin]-2'-one (6l)

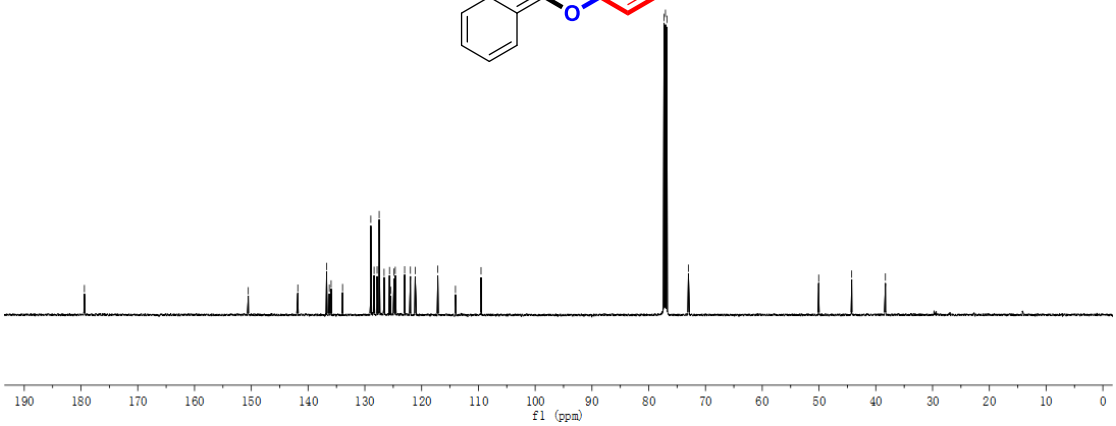




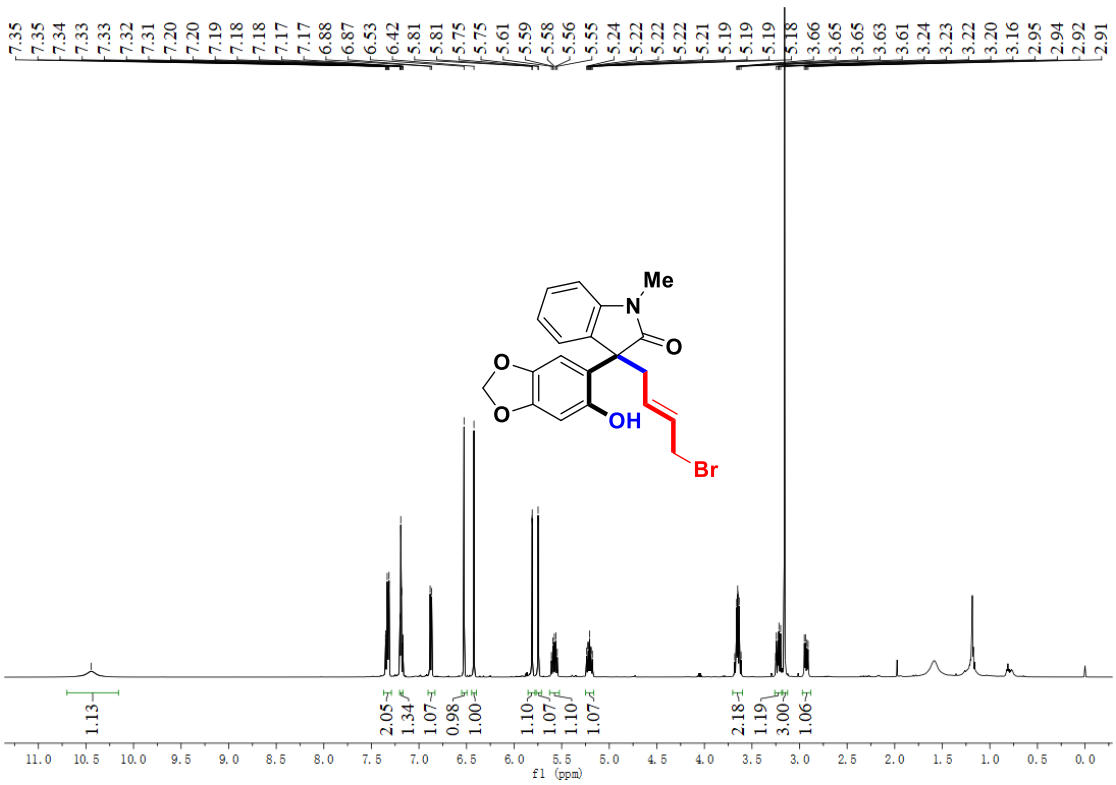


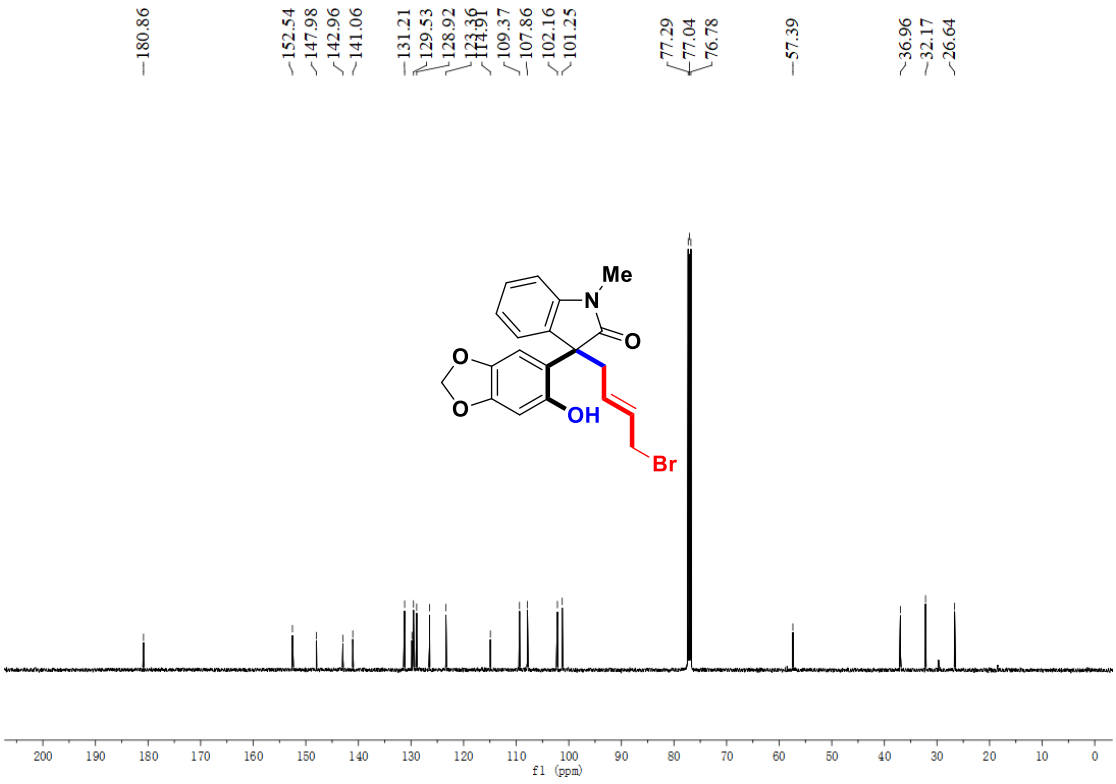




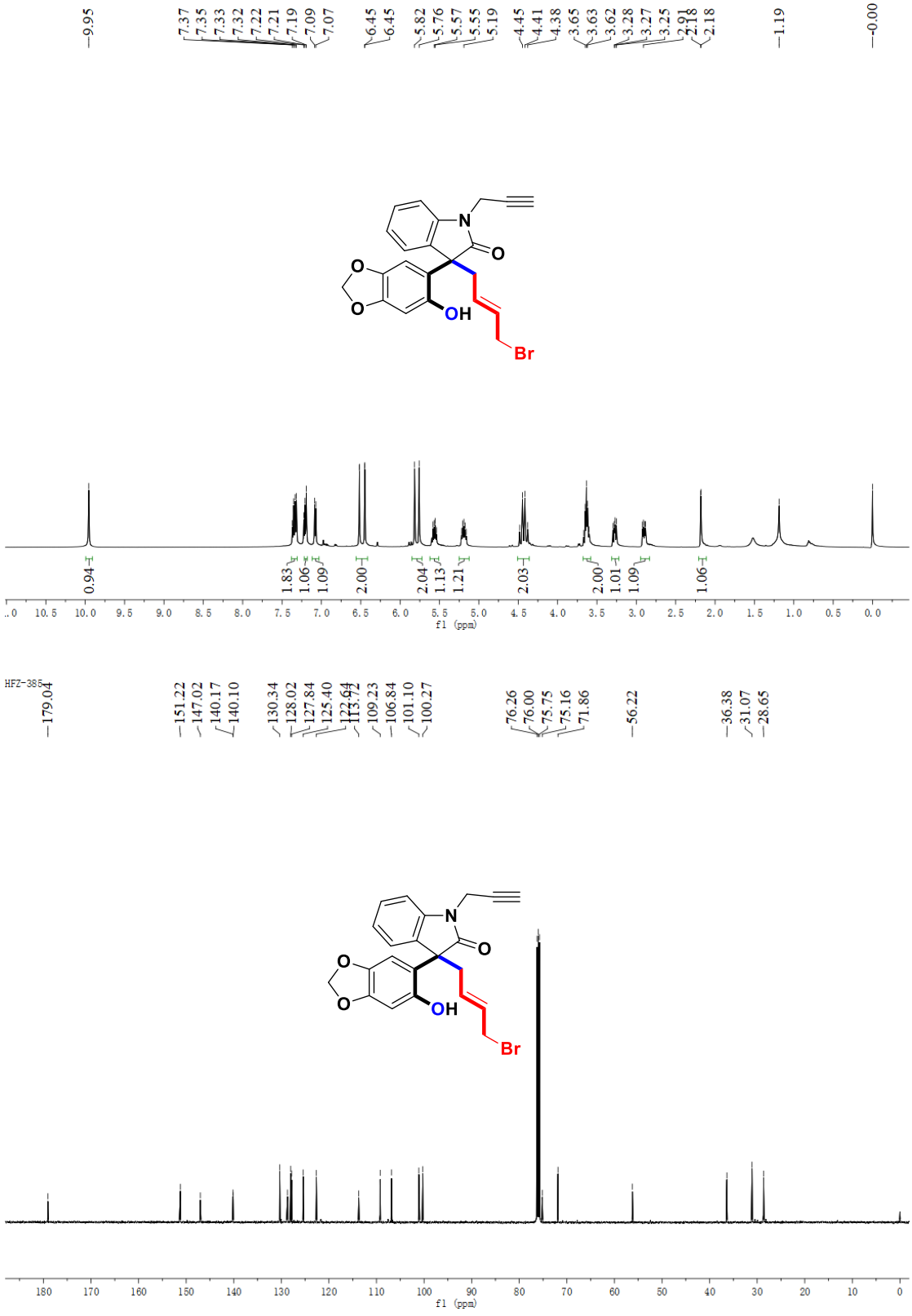


(E)-3-(4-bromobut-2-en-1-yl)-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)-1-methylindolin-2-one (7a)

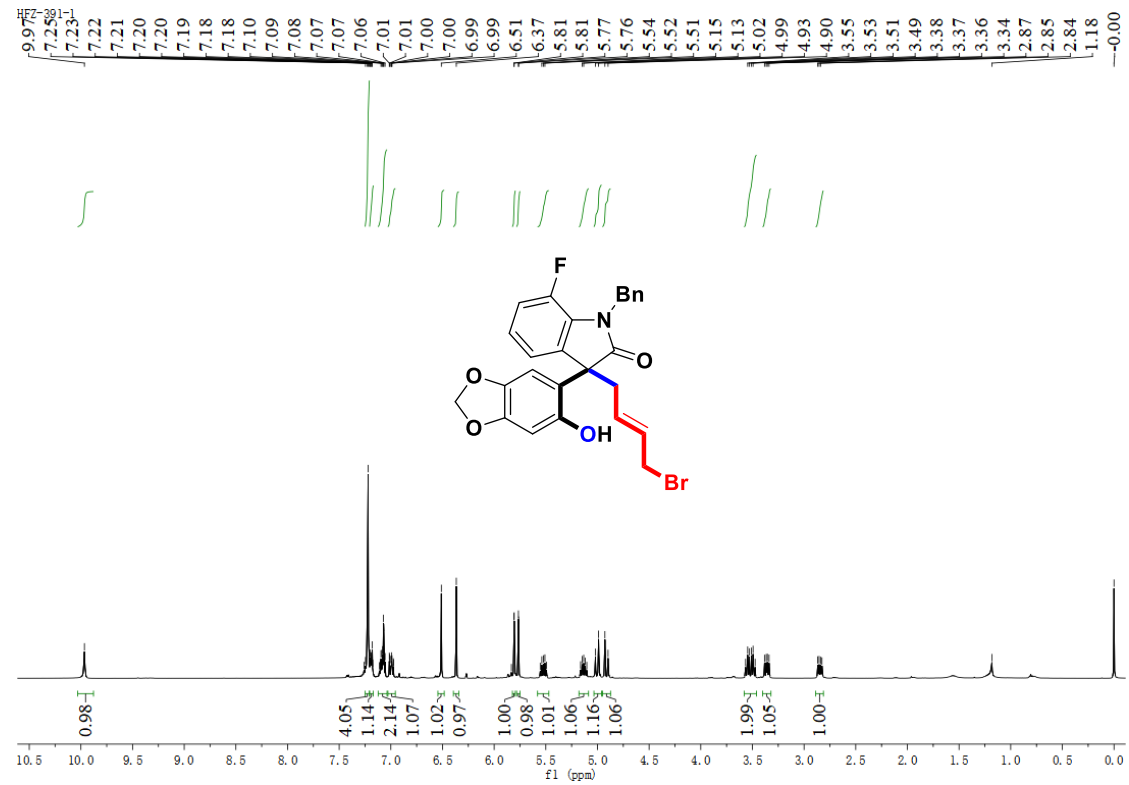


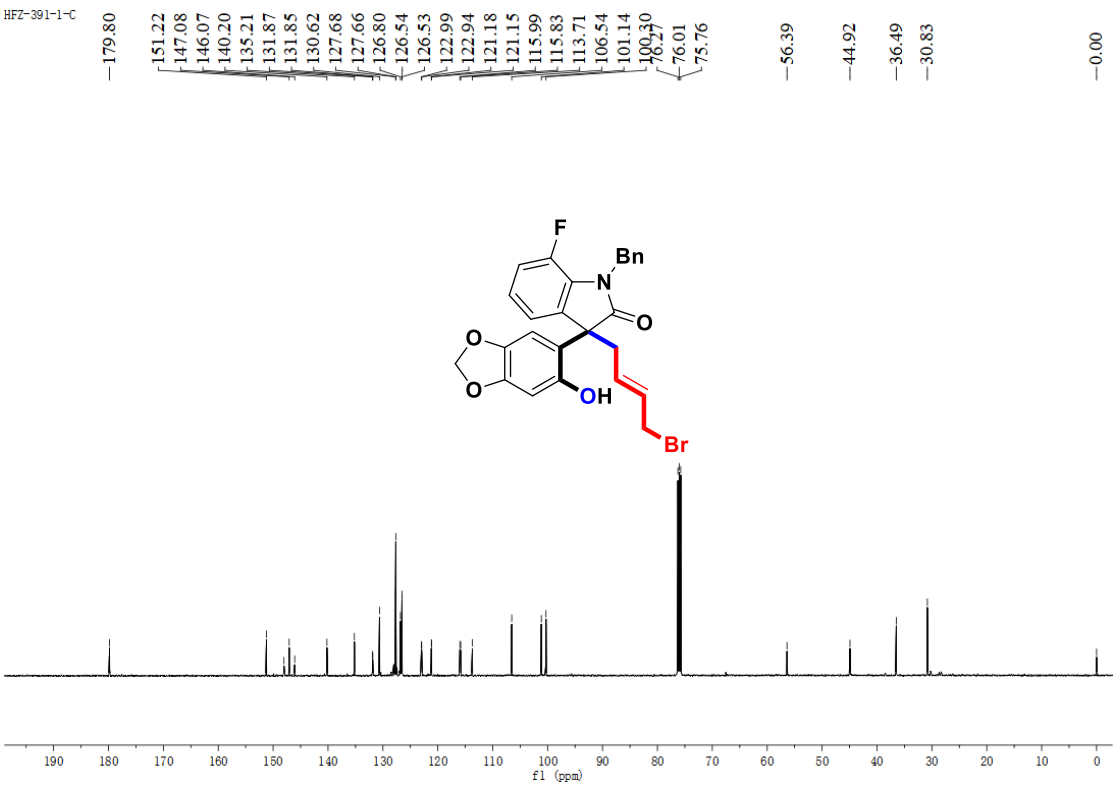


(E)-3-(4-bromobut-2-en-1-yl)-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)-1-(prop-2-yn-1-yl)indolin-2-one (7b)

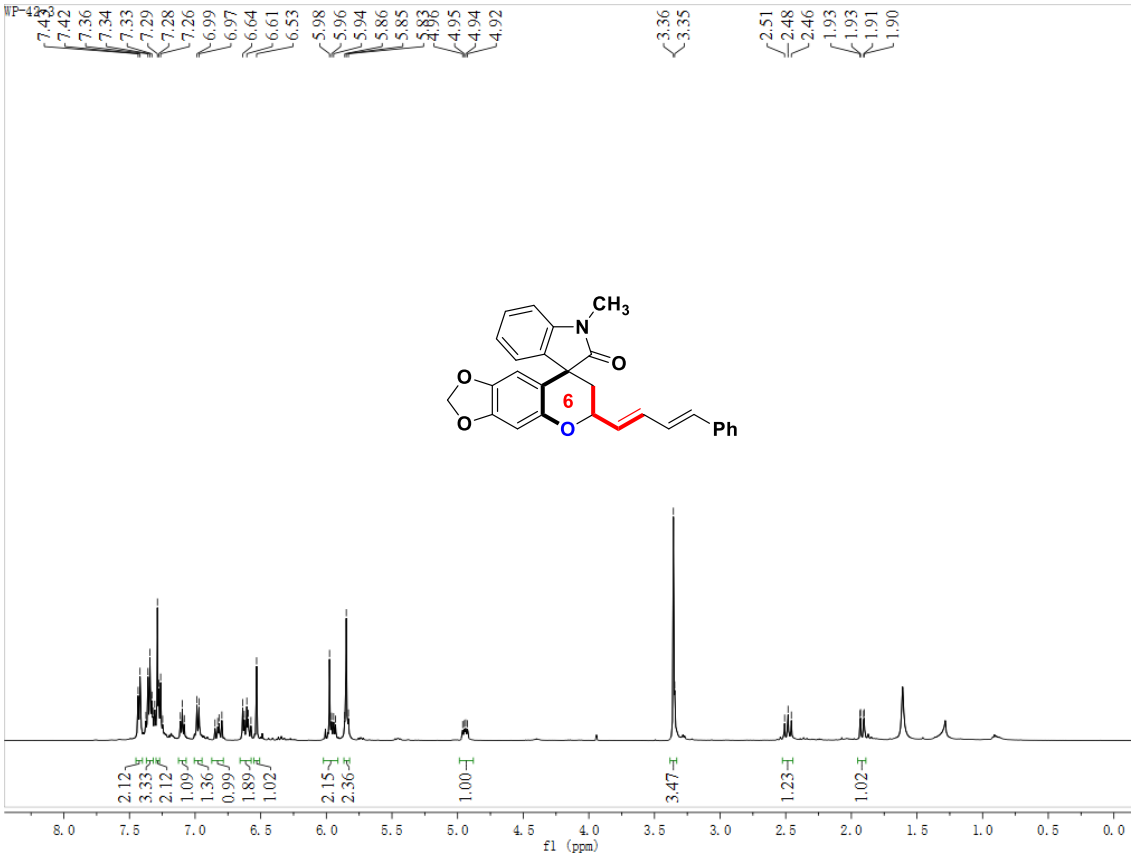


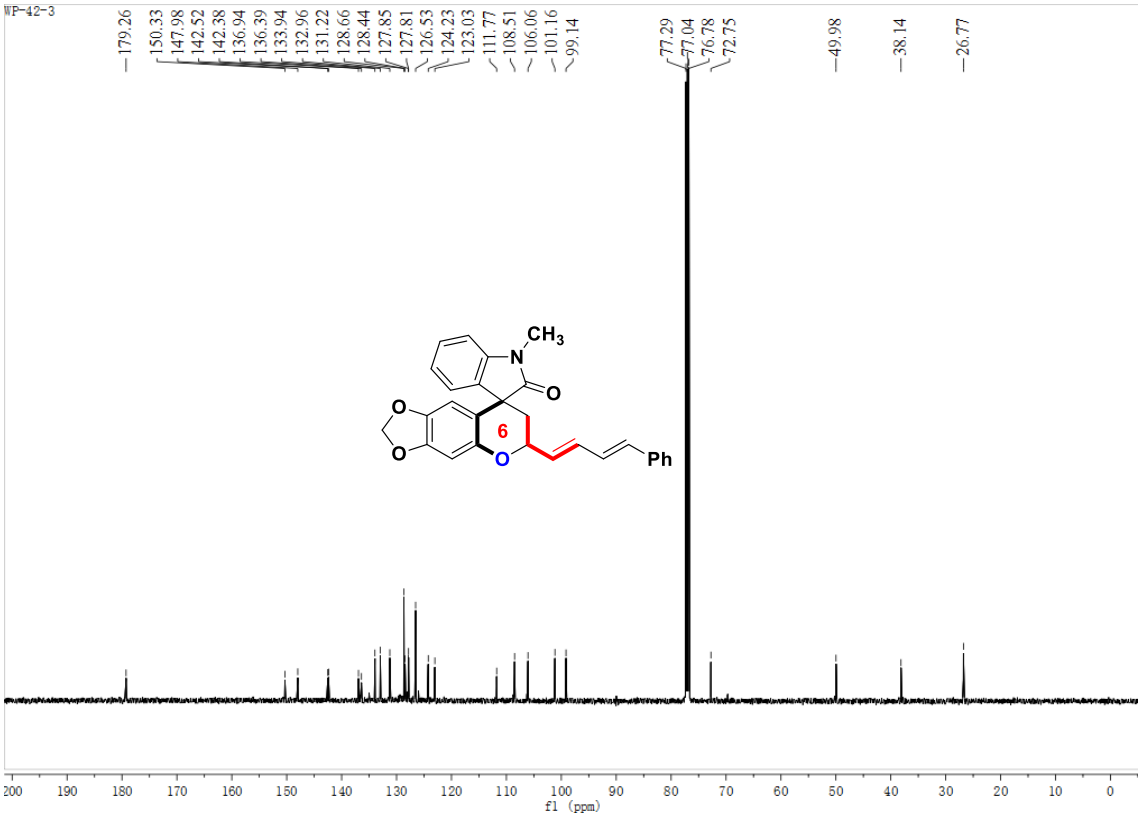
(E)-1-benzyl-3-(4-bromobut-2-en-1-yl)-7-fluoro-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl) indolin-2-one (7c)



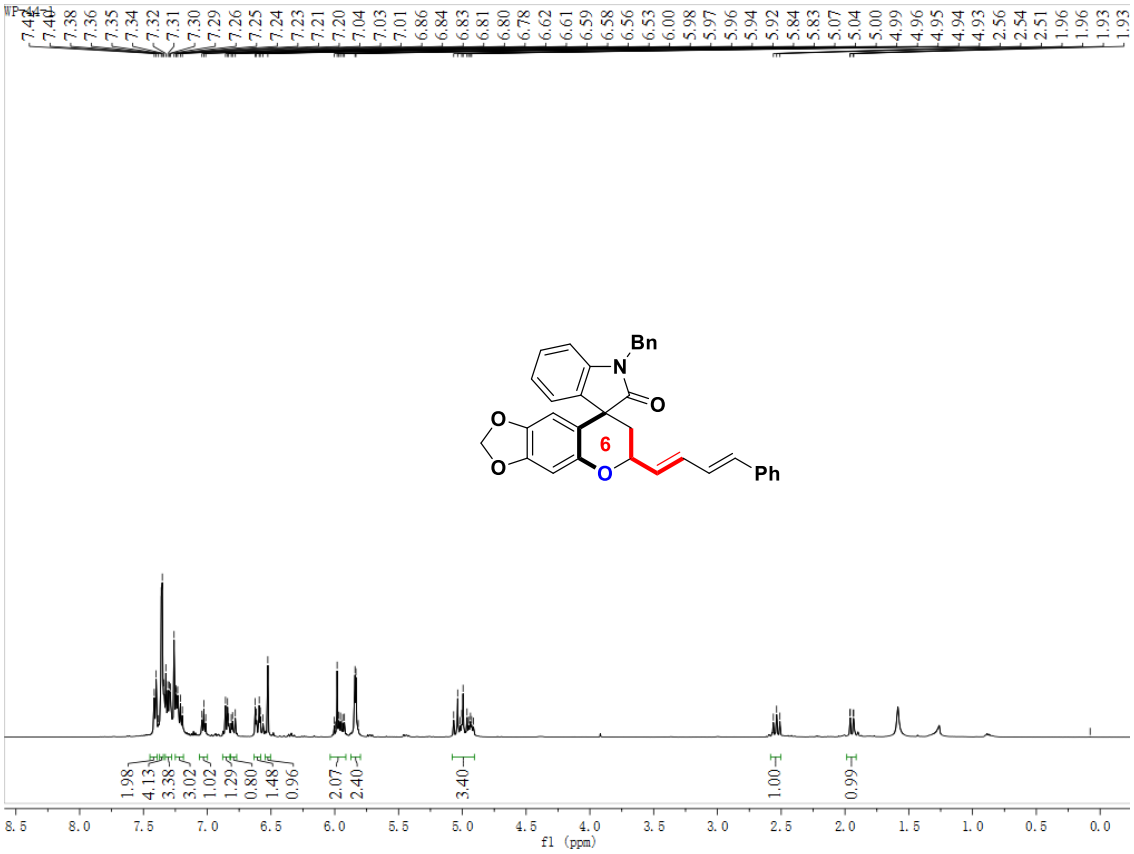


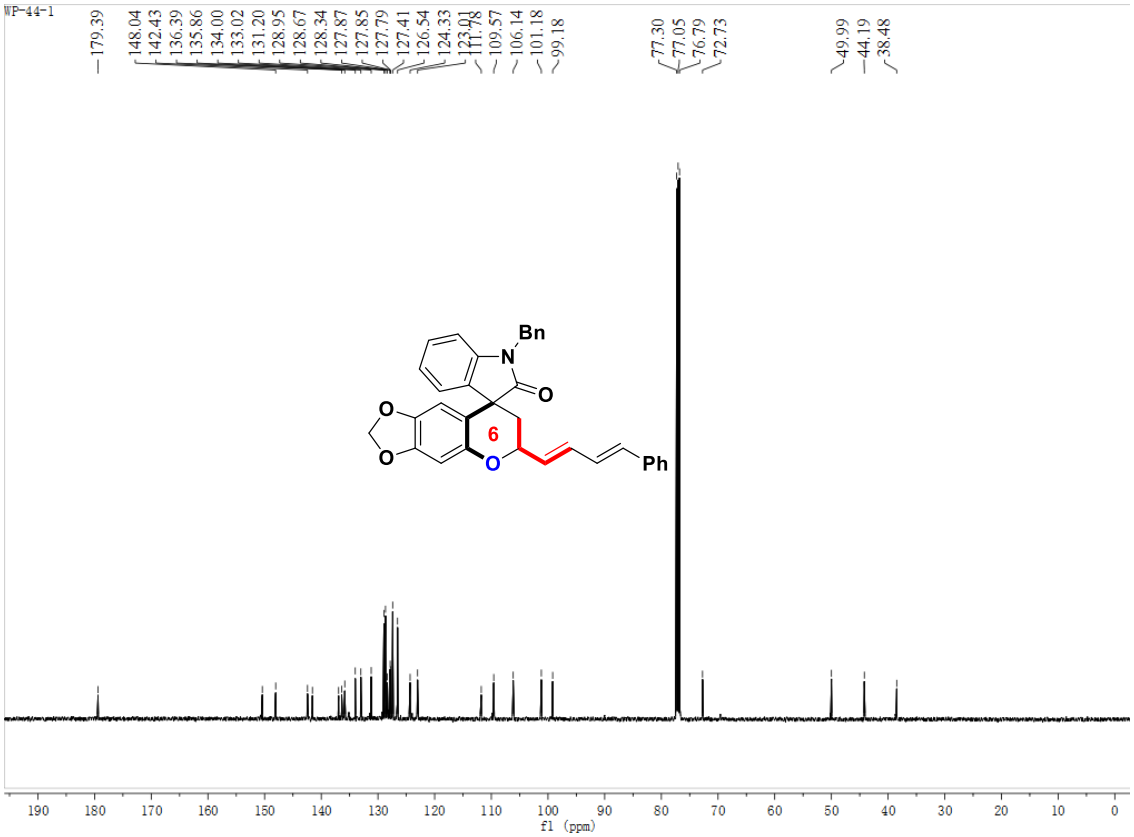
1-methyl-6'-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (8a)



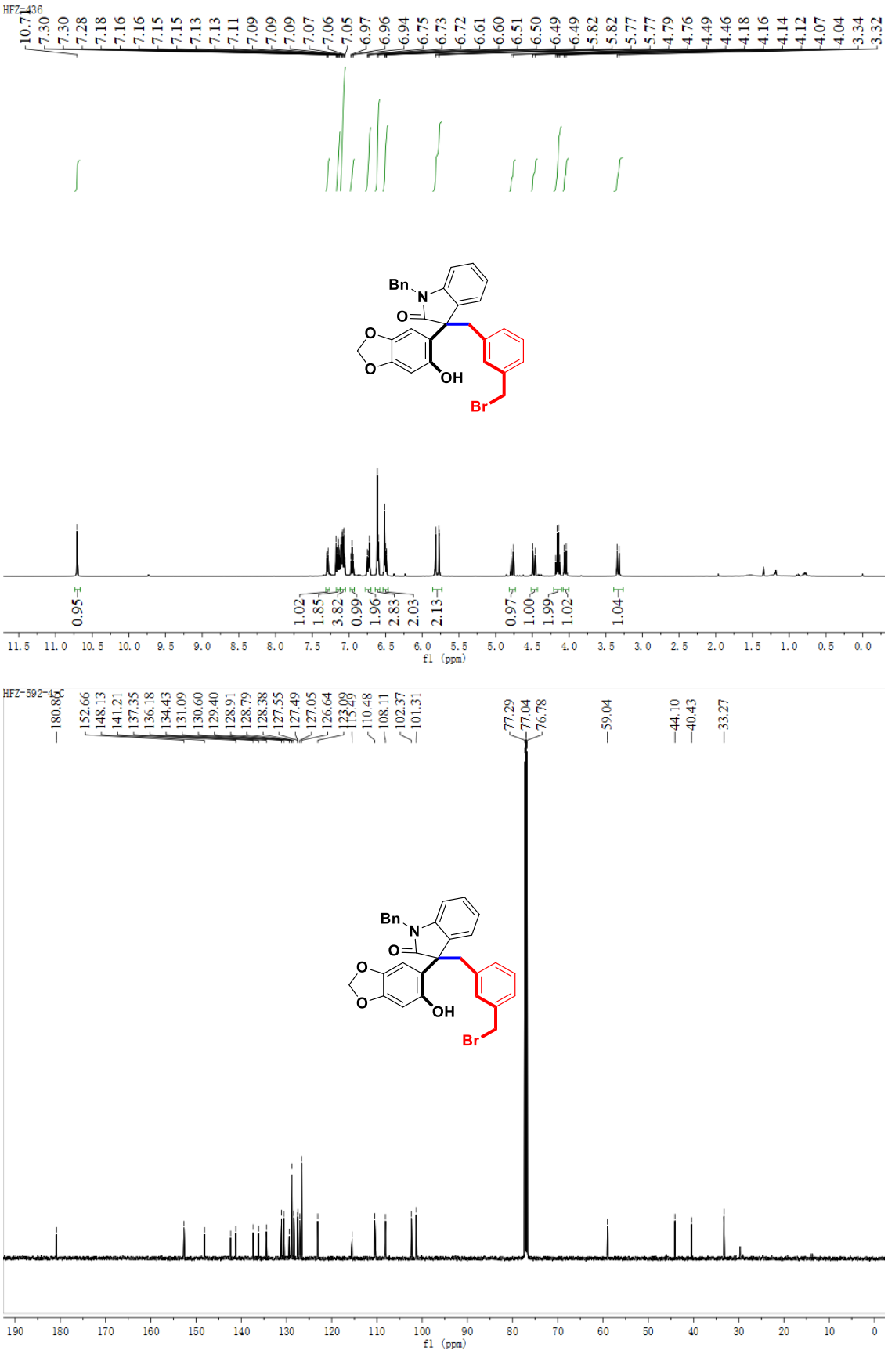


1-benzyl-6'-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (8b)

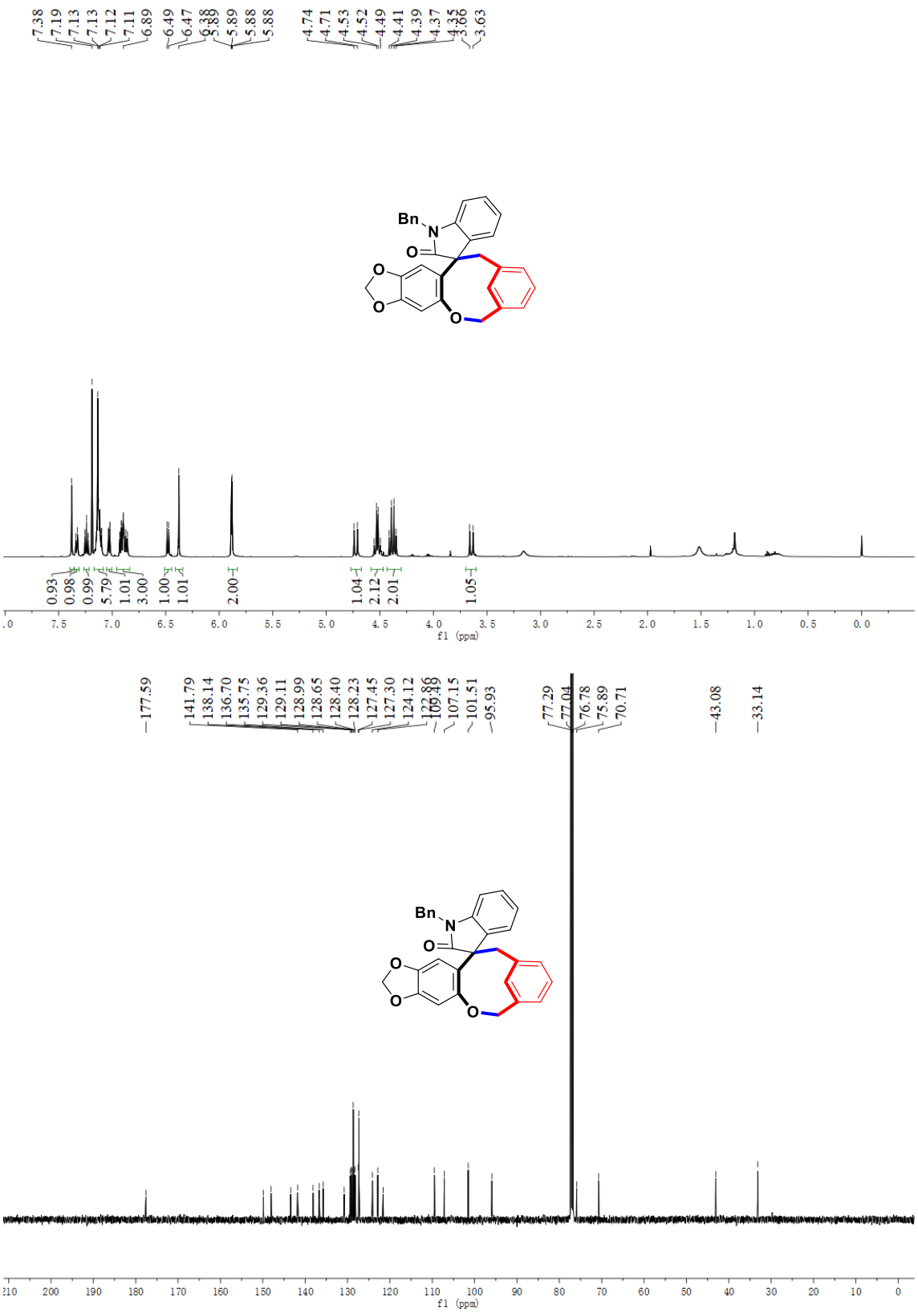




1-benzyl-3-(3-(bromomethyl)benzyl)-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)indolin-2-one (10a)



1-benzyl-6'H,12'H-spiro[indoline-3,13'-[7,11](metheno)[1,3]dioxolo[4',5':4,5]benzo[1,2-b][1]oxacycloundecin]-2-one (11a)



1-benzyl-3-(2-(bromomethyl)benzyl)-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)indolin-2-one (12a)