Supporting Information

tert-Butanol as isobutene equivalent in IED-HDA reaction of *in situ* generated oxindole-embedded *o*-QMs

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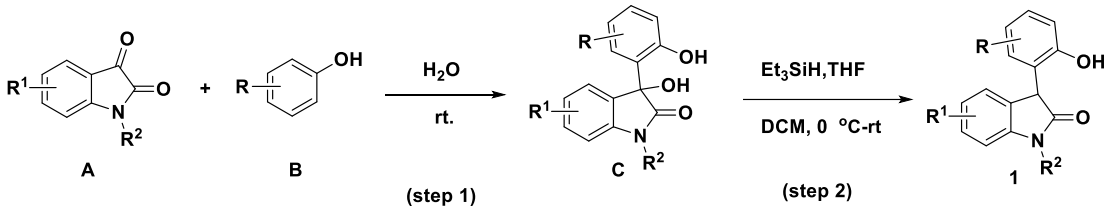
1. General Information

Unless otherwise noted, all reagents were purchased from the commercial sources and used as received. All the solvents used in the reaction were distilled prior to use. 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 or 300-400 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 400 or 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 isatins and alcohols were purchased from adamas-beta. 3-(2-hydroxyphenyl)indolin-2-ones were prepared according to literature.[1, 2]

2. General Procedure

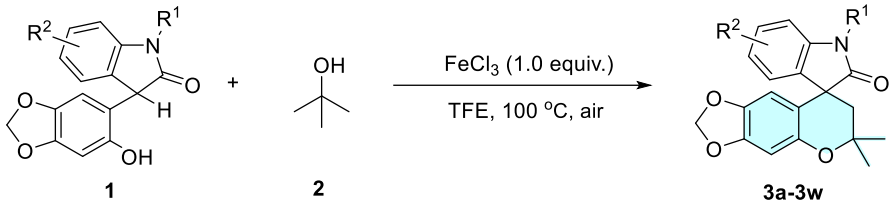
2.1 General Procedure for the Synthesis of 1[1, 2]



Step 1: A round-bottom flask was charged with isatin **A** (5.0 mmol, 1.0 equiv.), phenol **B** (15.0 mmol, 3.0 equiv.) and H_2O (30.0 mL). The reaction mixture was stirred vigorously at room temperature and monitored by TLC. After the consumption of isatin **A**, the reaction mixture was extracted with ethyl acetate, and the combined organic layers were dried over anhydrous sodium sulfate. The solvent was concentrated in vacuo, and the residue was purified by flash column chromatography (column chromatography eluent: petroleum ether/ethyl acetate = 5/1) to afford products **C**.

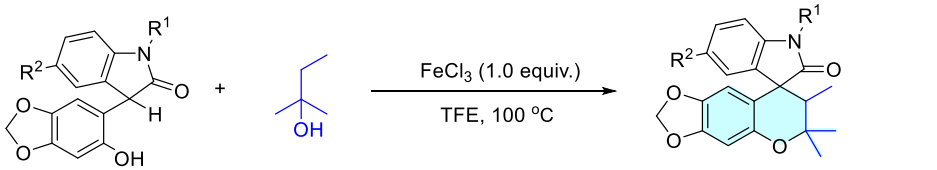
Step 2: A round-bottom flask was charged with products **C** (4.0 mmol, 1.0 equiv.), Et_3SiH (5.2 mmol, 1.3equiv.) and DCM (20.0 mL). The reaction mixture was stirred vigorously at 0 °C, then TFA (24.0 mmol, 6.0 equiv.) was dropwise added to the reaction system slowly. The reaction mixture was stirred vigorously at room temperature and monitored by TLC. After the consumption of **C**, the reaction mixture was extracted with methylene chloride, and the combined organic layers were dried over anhydrous sodium sulfate. The solvent was concentrated in vacuo, and the residue was purified by flash column chromatography (column chromatography eluent, petroleum ether/ethyl acetate =6/1) to afford products **1**.

2.2 General Procedure for the Synthesis of 3a-3w



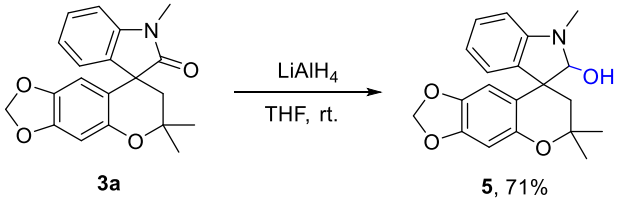
A reaction tube was charged with 3-(2-hydroxyphenyl)indolin-2-one **1** (0.1 mmol, 1.0 equiv.), $FeCl_3$ (0.1 mmol, 1.0 equiv., 16.2 mg), and alcohol **2** (2.10 mmol, 21.0 equiv., 0.2 mL) in 1.0 mL of TFE. The mixture was stirred at 100 ℃ for 3 h. Upon reaction completion (as indicated by thin-layer chromatography (TLC)), residue was purified by silica-gel column chromatography using petroleum ether/ethyl acetate (10:1, v:v) to obtain the desired products **3a-3w.**

2.3 General Procedure for the Synthesis of 3x and 3y



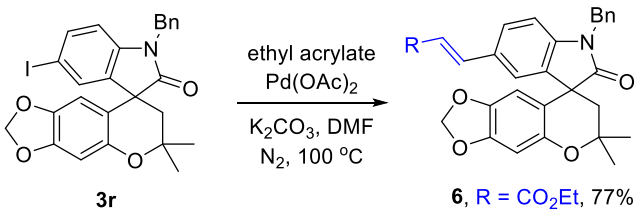
A reaction tube was charged with 3-(2-hydroxyphenyl)indolin-2-one **1** (0.1 mmol, 1.0 equiv.), $FeCl_3$ (0.1 mmol, 1.0 equiv., 16.2 mg), and alcohol **4** (2.10 mmol, 21.0 equiv., 0.2 mL) in 1.0 mL of TFE. The mixture was stirred at 100 ℃ for 3 h. Upon reaction completion (as indicated by thin-layer chromatography (TLC)), residue was purified by silica-gel column chromatography using petroleum ether/ethyl acetate (10:1, v:v) to obtain the desired products **3x** and **3y.**

2.4 General Procedure for the Synthesis of 5



A sealed tube was charged with product **3a** (0.1 mmol, 1.0 equiv., 33.7 mg) and THF (1.0 mL). The reaction mixture was stirred vigorously at ice-water bath, $LiAlH_4$ (0.3 mmol, 3 equiv., 11.4 mg) was added to reaction system. Then, the ice-bath was removed, and the reaction was stirred for 2 h at room temperature which point TLC analysis indicated consumption of the starting material. Then poured into aqueous NaOH (10%), and extracted with ethyl acetate (10 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 (ethyl acetate/petroleum ether, 1:10) to afford the desired product **5** in 71% yield.

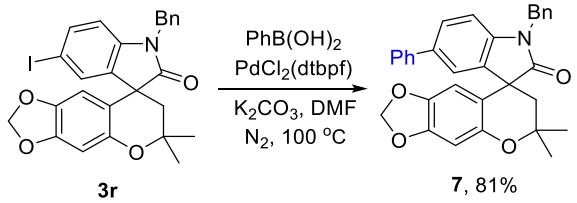
2.5 General Procedure for the Synthesis of 6



3r **6**, R = CO_2Et, 77%

A sealed tube was charged with **3r** (0.1 mmol, 1.0 equiv., 53.9 mg), ethyl acrylate (0.15 mmol, 1.5 equiv., 15.0 mg), $Pd(PPh_3)_2Cl_2$ (5 mol%, 3.5 mg), K_2CO_3 (0.25 mmol, 2.5 equiv., 34.5 mg), and DMF (1 mL). The mixture was stirred at 100 °C under N_2 atmosphere. Upon completion of the reaction as indicated 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 (ethyl acetate/petroleum ether, 1:8) to afford the desired product **6** in 77% yield.

2.6 General Procedure for the Synthesis of 7

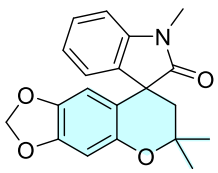


3r **7**, 81%

A sealed tube was charged with **3r** (0.1 mmol, 1.0 equiv., 53.9 mg), phenylboronic acid (0.1 mmol, 1.5 equiv.18.3 mg), $PdCl_2$(dtbpf) (10 mol%, 6.5 mg), K_2CO_3 (0.25 mmol, 2.5 equiv., 34.5 mg), and DMF (1 mL). The mixture was stirred at 100 °C under N_2 atmosphere. Upon completion of the reaction as indicated 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 (ethyl acetate/petroleum ether, 1:10) to afford the desired product **7** in 81% yield.

3. Characterization of Products

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

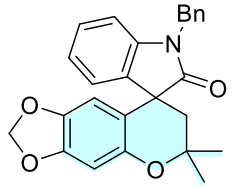


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (22 mg, 65% yield), as a yellow solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.20 (td, *J* = 7.7, 1.2 Hz, 1H), 7.08 (dd, *J* = 7.4, 1.3 Hz, 1H), 6.94 (td, *J* = 7.6, 1.0 Hz, 1H), 6.83 – 6.76 (m, 1H), 6.36 (s, 1H), 5.82 (s, 1H), 5.72 (dd, *J* = 8.6, 1.4

Hz, 2H), 3.18 (s, 3H), 2.31 (d, *J* = 14.3 Hz, 1H), 2.08 (d, *J* = 14.3 Hz, 1H), 1.47 (s, 3H), 1.41 (s, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 179.6, 149.2, 147.7, 143.2, 142.1, 136.6, 128.2, 124.2, 123.2, 114.3, 108.1, 106.0, 101.0, 100.4, 74.4, 49.3, 43.9, 28.9, 27.5, 26.6. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{20}H_{20}NO_4^+$ 338.1386; found: 338.1384.

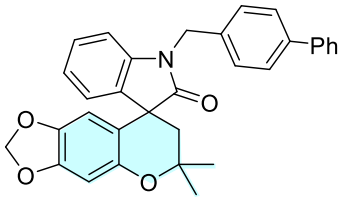
1-benzyl-6',6'-dimethyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3b)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (23 mg, 55% yield), as a yellow solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 4.4 Hz, 4H), 7.32 (dq, *J* = 8.5, 4.1 Hz, 1H), 7.19 (dt, *J* = 7.6, 3.9 Hz, 2H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.51 (s, 1H), 5.97 (s, 1H), 5.84 (s, 2H), 5.02 (d, *J* = 15.5 Hz, 1H), 4.95 (d, *J* = 15.5 Hz, 1H), 2.49 (d, *J* = 14.3 Hz, 1H), 2.25 (d, *J* = 14.3 Hz, 1H), 1.63 (s, 3H), 1.55 (s, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 179.8, 149.2, 147.8, 142.3, 142.2, 136.7, 136.0, 128.9, 128.1, 127.8, 127.4, 124.3, 123.3, 114.3, 109.2, 106.0, 101.1, 100.5, 74.5, 49.3, 44.2, 44.1, 29.0, 27.5. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{26}H_{24}NO_4^+$ 414.1700; found: 414.1696.

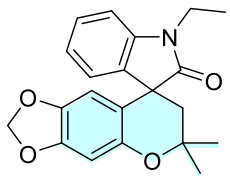
1-([1,1'-biphenyl]-4-ylmethyl)-6',6'-dimethyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3c)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (23 mg, 47% yield), as a yellow solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 7.7 Hz, 4H), 7.47 (d, *J* = 7.6 Hz, 4H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 7.9 Hz, 2H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 6.53 (s, 1H), 6.01 (s, 1H), 5.86 (s, 2H), 5.08 (d, *J* = 15.6 Hz, 1H), 5.00 (d, *J* = 15.5 Hz, 1H), 2.52 (d, *J* = 14.3 Hz, 1H), 2.28 (d, *J* = 14.3 Hz, 1H), 1.65 (s, 3H), 1.57 (s, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 179.8, 149.3, 147.8, 142.3, 142.2, 140.8, 140.6, 136.7, 135.1, 128.8, 128.2, 127.9, 127.7, 127.4, 127.1, 124.4, 123.4, 114.3, 109.2, 106.1, 101.1, 100.5, 74.5, 49.4, 44.2, 43.8, 29.0, 27.5. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{32}H_{28}NO_4^+$ 490.2012; found: 490.2010.

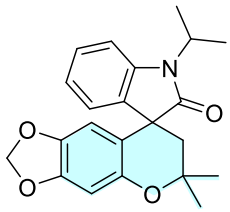
1-ethyl-6',6'-dimethyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3d)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (22 mg, 63% yield), as a yellow solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.29 (t, *J* = 7.7 Hz, 1H), 7.19 (d, *J* = 7.4 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 6.47 (s, 1H), 5.92 (s, 1H), 5.83 (d, *J* = 8.6 Hz, 2H), 3.83 (m, 2H), 2.40 (d, *J* = 14.4 Hz, 1H), 2.18 (d, *J* = 14.4 Hz, 1H), 1.58 (s, 3H), 1.51 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 179.2, 149.1, 147.6, 142.2, 142.1, 137.0, 128.2, 124.4, 123.0, 114.4, 108.3, 105.9, 101.0, 100.4, 74.4, 49.2, 43.8, 35.0, 29.0, 27.4, 12.7. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{21}H_{22}NO_4^+$ 352.1543; found: 352.1541.

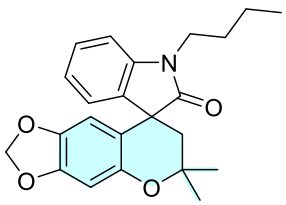
1-isopropyl-6',6'-dimethyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3e)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (17 mg, 47% yield), as a yellow solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.24 (dd, *J* = 14.5, 6.8 Hz, 1H), 7.15 (d, *J* = 7.4 Hz, 1H), 7.04 (d, *J* = 7.9 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.44 (d, *J* = 1.1 Hz, 1H), 5.89 (d, *J* = 1.2 Hz, 1H), 5.80 (dd, *J* = 9.3, 1.6 Hz, 2H), 4.65 (hept, *J* = 7.0 Hz, 1H), 2.37 (d, *J* = 14.4 Hz, 1H), 2.15 (d, *J* = 14.4 Hz, 1H), 1.54 (s, 3H), 1.52 (d, *J* = 6.3 Hz, 6H), 1.48 (s, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 179.3, 149.1, 147.6, 142.1, 141.8, 137.3, 127.9, 124.5, 122.7, 114.8, 109.8, 105.8, 101.0, 100.4, 74.5, 49.0, 44.04, 44.00, 29.1, 27.4, 19.5, 19.4. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{22}H_{24}NO_4^+$ 366.1700; found: 366.1710.

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

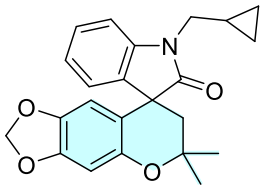


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (15 mg, 39% yield), as a yellow solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.21 – 7.16 (m, 1H), 7.07 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.92 (td, *J* = 7.6, 1.0 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.36 (s, 1H), 5.82 (s, 1H), 5.76 – 5.70 (m, 2H), 3.73 – 3.60 (m, 2H), 2.29 (d, *J* = 14.4 Hz, 1H), 2.08 (d, *J* = 14.4 Hz, 1H), 1.63 (dt, *J* = 15.0, 7.6 Hz, 2H), 1.47 (s, 3H), 1.41 (s, 3H), 1.37 – 1.31 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (125 MHz,

Chloroform-d) δ 179.5, 149.2, 147.6, 142.6, 142.1, 136.9, 128.1, 124.3, 123.0, 114.5, 108.4, 105.9, 101.0, 100.4, 74.5, 49.2, 44.0, 40.0, 29.5, 29.1, 27.4, 20.2, 13.8. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{23}H_{26}NO_4^+$ 380.1856; found: 380.1855.

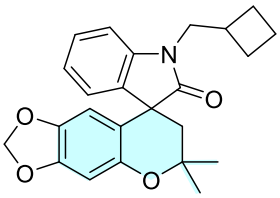
1-(cyclopropylmethyl)-6',6'-dimethyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3g)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (17 mg, 44% yield), as a yellow solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.21 – 7.16 (m, 1H), 7.08 (dd, *J* = 7.5, 1.2 Hz, 1H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 7.9 Hz, 1H), 6.36 (s, 1H), 5.89 (s, 1H), 5.75 – 5.68 (m, 2H), 3.56 (d, *J* = 7.0 Hz, 2H), 2.29 (d, *J* = 14.4 Hz, 1H), 2.09 (d, *J* = 14.4 Hz, 1H), 1.47 (s, 3H), 1.41 (s, 3H), 1.21 – 1.12 (m, 1H), 0.47 (dt, *J* = 8.2, 3.2 Hz, 2H), 0.33 (ddt, *J* = 6.2, 4.2, 2.4 Hz, 2H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 179.7, 149.1, 147.6, 142.8, 142.2, 136.9, 128.1, 124.3, 123.0, 114.6, 108.6, 105.9, 101.0, 100.4, 74.5, 49.2, 44.4, 43.9, 29.1, 27.3, 9.7, 3.8. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{23}H_{24}NO_4^+$ 378.1700; found: 378.1711.

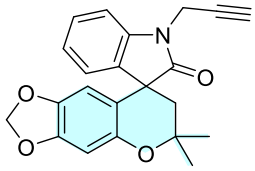
1-(cyclobutylmethyl)-6',6'-dimethyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3h)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (16 mg, 41% yield), as a yellow solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.24 (td, *J* = 7.7, 1.3 Hz, 1H), 7.13 (dd, *J* = 7.5, 1.2 Hz, 1H), 6.99 (td, *J* = 7.6, 1.0 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 6.43 (s, 1H), 5.89 (s, 1H), 5.84 – 5.79 (m, 2H), 3.86 (dd, *J* = 14.0, 7.8 Hz, 1H), 3.71 (dd, *J* = 14.0, 7.0 Hz, 1H), 2.83 (dt, *J* = 15.8, 7.7 Hz, 1H), 2.35 (d, *J* = 14.4 Hz, 1H), 2.15 (d, *J* = 14.3 Hz, 1H), 2.05 (dtd, *J* = 11.7, 4.4, 2.2 Hz, 2H), 1.88 (tdd, *J* = 12.9, 6.7, 3.0 Hz, 4H), 1.55 (s, 3H), 1.48 (s, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 179.8, 149.1, 147.6, 142.8, 142.1, 136.8, 128.0, 124.2, 122.9, 114.5, 108.5, 105.9, 101.0, 100.38, 74.5, 49.2, 45.2, 44.0, 33.9, 29.1, 27.3, 26.3, 26.1, 18.3. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{24}H_{26}NO_4^+$ 392.1856; found: 392.1867.

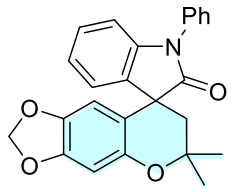
6',6'-dimethyl-1-(prop-2-yn-1-yl)-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3i)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (14 mg, 38% yield), as a yellow solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.22 (td, *J* = 7.7, 1.3 Hz, 1H), 7.09 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.03 – 6.96 (m, 2H), 6.36 (s, 1H), 5.84 (s, 1H), 5.72 (dd, *J* = 8.1, 1.5 Hz, 2H), 4.48 (dd, *J* = 17.6, 2.5 Hz, 1H), 4.44 (dd, *J* = 17.6, 2.5 Hz, 1H), 2.30 (d, *J* = 14.5 Hz, 1H), 2.19 (t, *J* = 2.5 Hz, 1H), 2.10 (d, *J* = 14.4 Hz, 1H), 1.47 (s, 3H), 1.41 (s, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 178.7, 149.1, 147.8, 142.2, 141.2, 136.5, 128.2, 124.3, 123.7, 114.0, 109.2, 106.0, 101.0, 100.4, 74.4, 72.5, 49.2, 43.8, 29.6, 29.0, 27.3. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{22}H_{20}NO_4^+$ 362.1387; found: 362.1384.

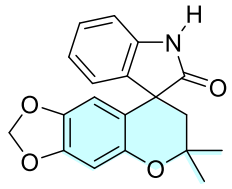
6',6'-dimethyl-1-phenyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3j)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (12 mg, 31% yield), as a white solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.53 (t, *J* = 7.7 Hz, 2H), 7.47 – 7.40 (m, 3H), 7.19 (t, *J* = 7.6 Hz, 2H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.46 (s, 1H), 6.10 (s, 1H), 5.87 – 5.80 (m, 2H), 2.51 (d, *J* = 14.4 Hz, 1H), 2.30 (d, *J* = 14.4 Hz, 1H), 1.56 (s, 3H), 1.52 (s, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 178.9, 149.2, 147.8, 143.0, 142.2, 136.5, 134.5, 129.6, 128.14, 128.11, 126.6, 124.5, 123.8, 114.5, 109.5, 106.0, 101.1, 100.5, 74.8, 49.3, 44.2, 29.3, 27.1. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{25}H_{22}NO_4^+$ 400.1543; found:400.1557.

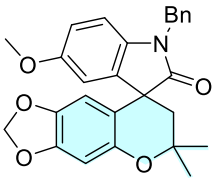
6',6'-dimethyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3k)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (18 mg, 51% yield), as a yellow solid.

^{1}H NMR (500 MHz, DMSO-d_6) δ 10.54 (s, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 1H), 6.99 – 6.89 (m, 2H), 6.48 (s, 1H), 5.89 (s, 1H), 5.87 (d, *J* = 6.1 Hz, 2H), 2.32 (d, *J* = 14.4 Hz, 1H), 2.09 (d, *J* = 14.4 Hz, 1H), 1.46 (s, 3H), 1.43 (s, 3H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 181.0, 149.0, 147.6, 142.2, 142.0, 137.4, 128.6, 124.6, 122.7, 114.8, 110.1, 106.0, 101.5, 100.2, 74.5, 49.5, 43.4, 28.5, 28.0. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{19}H_{18}NO_4^+$ 324.1230; found: 324.1229.

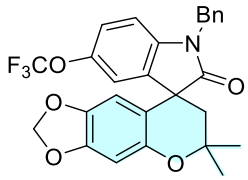
1-benzyl-5-methoxy-6',6'-dimethyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3l)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (27 mg, 61% yield), as a yellow solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.27 – 7.22 (m, 4H), 7.20 (ddd, *J* = 8.7, 3.8, 2.4 Hz, 1H), 6.67 (dd, *J* = 1.9, 1.0 Hz, 1H), 6.63 – 6.57 (m, 2H), 6.38 (s, 1H), 5.86 (s, 1H), 5.79 – 5.71 (m, 2H), 4.87 (d, *J* = 15.5 Hz, 1H), 4.80 (d, *J* = 15.5 Hz, 1H), 3.61 (s, 3H), 2.37 (d, *J* = 14.3 Hz, 1H), 2.12 (d, *J* = 14.3 Hz, 1H), 1.50 (s, 3H), 1.43 (s, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 179.5, 156.4, 149.2, 147.8, 142.2, 137.9, 136.1, 135.6 128.9, 127.8, 127.4, 114.4, 112.5, 111.5, 109.6, 106.1, 101.1, 100.4, 74.5, 55.7, 49.7, 44.2, 44.1, 29.1, 27.4. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{27}H_{26}NO_5^+$ 444.1805; found: 444.1801.

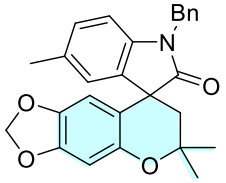
1-benzyl-6',6'-dimethyl-5-(trifluoromethoxy)-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3m)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (27 mg, 54% yield), as a yellow solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.39 – 7.29 (m, 5H), 7.08 – 6.99 (m, 2H), 6.75 (d, *J* = 8.5 Hz, 1H), 6.47 (s, 1H), 5.91 (s, 1H), 5.87 – 5.80 (m, 2H), 4.97 (d, *J* = 15.6 Hz, 1H), 4.91 (d, *J* = 15.5 Hz, 1H), 2.45 (d, *J* = 14.3 Hz, 1H), 2.17 (d, *J* = 14.3 Hz, 1H), 1.57 (s, 3H), 1.50 (s, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 179.4, 149.3, 148.1, 142.4, 140.8, 137.9, 135.5, 129.0, 128.0, 127.4, 121.2, 120.4 (q, *J* = 255.5 Hz), 118.4, 113.5, 109.6, 105.7, 101.2, 100.7, 74.5, 49.7, 44.3, 44.2, 28.9, 27.6. **^{19}F NMR** (470 MHz, Chloroform-*d*) δ -58.23. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{27}H_{23}F_3NO_5^+$ 498.1523; found: 498.1515.

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

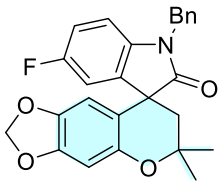


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (30 mg, 69% yield), as a yellow solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.37 (d, *J* = 4.4 Hz, 4H), 7.34 – 7.29 (m, 1H), 6.99 (t, *J* = 3.6

Hz, 2H), 6.70 (d, *J* = 8.3 Hz, 1H), 6.50 (s, 1H), 5.97 (s, 1H), 5.89 – 5.82 (m, 2H), 5.00 (d, *J* = 15.4 Hz, 1H), 4.92 (d, *J* = 15.5 Hz, 1H), 2.46 (d, *J* = 14.4 Hz, 1H), 2.27 (s, 3H), 2.25 (d, *J* = 14.4 Hz, 1H), 1.62 (s, 3H), 1.54 (s, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 179.7, 149.2, 147.7, 142.2, 139.8, 136.7, 136.2, 132.9, 128.9, 128.4, 127.7, 127.4, 125.0, 114.5, 108.9, 106.1, 101.1, 100.4, 74.5, 49.3, 44.2, 44.0, 29.2, 27.3, 21.2. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{27}H_{26}NO_4^+$ 428.1856; found: 428.1853.

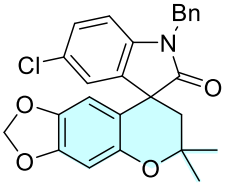
1-benzyl-5-fluoro-6',6'-dimethyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3o)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (25 mg, 58% yield), as a yellow solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.37 – 7.29 (m, 5H), 6.91 (dd, *J* = 8.2, 2.6 Hz, 1H), 6.84 (td, *J* = 8.8, 2.6 Hz, 1H), 6.68 (dd, *J* = 8.6, 4.2 Hz, 1H), 6.46 (s, 1H), 5.91 (s, 1H), 5.83 (t, *J* = 1.2 Hz, 2H), 4.96 (d, *J* = 15.5 Hz, 1H), 4.89 (d, *J* = 15.5 Hz, 1H), 2.45 (d, *J* = 14.3 Hz, 1H), 2.17 (d, *J* = 14.3 Hz, 1H), 1.57 (s, 3H), 1.50 (s, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 179.4, 159.6 (d, *J* = 240.0 Hz),149.2, 148.0, 142.3, 138.2, 138.1, 135.7, 129.0 (d, *J* = 10.0 Hz), 127.9, 127.4, 127.3, 114.5 (d, *J* = 23.7 Hz), 113.8, 112.4 (d, *J* = 25.0 Hz), 109.7 (d, *J* = 7.5 Hz), 105.8, 101.1, 100.6, 74.5, 49.7, 44.2, 44.1, 29.0, 27.5. **^{19}F NMR** (470 MHz, Chloroform-*d*) δ -119.34. **RMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{26}H_{23}FNO_4^+$ 432.1606; found: 432.1602.

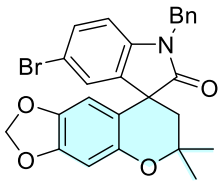
1-benzyl-5-chloro-6',6'-dimethyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3p)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (24 mg, 54% yield), as a yellow solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.35 – 7.29 (m, 5H), 7.11 (dd, *J* = 6.2, 2.2 Hz, 2H), 6.70 – 6.66 (m, 1H), 6.46 (s, 1H), 5.90 (s, 1H), 5.83 (q, *J* = 1.5 Hz, 2H), 4.95 (d, *J* = 15.5 Hz, 1H), 4.88 (d, *J* = 15.6 Hz, 1H), 2.43 (d, *J* = 14.3 Hz, 1H), 2.18 (d, *J* = 14.4 Hz, 1H), 1.57 (s, 3H), 1.50 (s, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 179.2, 149.3, 148.0, 142.3, 140.8, 138.2, 135.6, 129.0, 128.6, 128.1, 128.0, 127.4, 124.8, 113.6, 110.1, 105.8, 101.2, 100.6, 74.5, 49.5, 44.2, 44.1, 29.1, 27.3. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{26}H_{23}ClNO_4^+$ 448.1310; found: 448.1324.

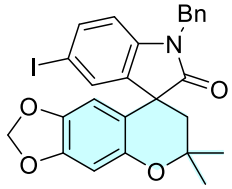
1-benzyl-5-bromo-6',6'-dimethyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3q)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (30 mg, 61% yield), as a yellow solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.40 – 7.35 (m, 2H), 7.35 – 7.28 (m, 5H), 6.68 (d, *J* = 8.2 Hz, 1H), 6.50 (s, 1H), 5.94 (s, 1H), 5.86 (q, *J* = 1.5 Hz, 2H), 4.99 (d, *J* = 15.6 Hz, 1H), 4.92 (d, *J* = 15.5 Hz, 1H), 2.46 (d, *J* = 14.3 Hz, 1H), 2.22 (d, *J* = 14.4 Hz, 1H), 1.61 (s, 3H), 1.53 (s, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 179.1, 149.2, 148.0, 142.3, 141.2, 138.6, 135.6, 131.0, 129.0, 128.0, 127.5, 127.4, 115.9, 113.5, 110.7, 105.8, 101.2, 100.6, 74.5, 49.4, 44.13, 44.08, 29.1, 27.3. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{26}H_{23}BrNO_4^+$ 492.0805; found: 492.0798.

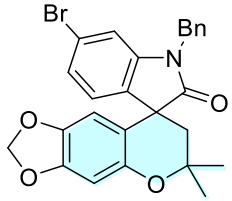
1-benzyl-5-iodo-6',6'-dimethyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3r)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (20 mg, 36% yield), as a yellow solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.46 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.43 – 7.38 (m, 1H), 7.37 – 7.32 (m, 2H), 7.29 (dd, *J* = 7.6, 2.1 Hz, 3H), 6.57 – 6.49 (m, 1H), 6.46 (d, *J* = 1.9 Hz, 1H), 5.90 (d, *J* = 3.5 Hz, 1H), 5.87 – 5.81 (m, 2H), 4.95 (d, *J* = 15.5 Hz, 1H), 4.87 (d, *J* = 15.5 Hz, 1H), 2.40 (dd, *J* = 14.3, 2.4 Hz, 1H), 2.18 (dd, *J* = 14.3, 2.1 Hz, 1H), 1.57 (d, *J* = 2.1 Hz, 3H), 1.49 (s, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 178.9, 149.2, 148.0, 142.3, 141.9, 138.9, 137.0, 135.5, 133.0, 129.0, 128.0, 127.4, 113.5, 111.2, 105.9, 101.1, 100.6, 74.5, 49.2, 44.1, 43.9, 29.2, 27.2. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{26}H_{23}INO_4^+$ 540.0666; found: 540.0658.

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

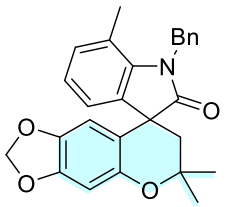


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (31 mg, 64% yield), as a yellow solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.30 – 7.21 (m, 5H), 7.03 (dd, *J* = 8.1, 1.7 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.84 (d, *J* = 1.7 Hz, 1H), 6.37 (s, 1H), 5.81 (s, 1H), 5.74 (s, 2H), 4.85 (d, *J* = 15.6 Hz, 1H), 4.79 (d, *J* = 15.5 Hz, 1H), 2.33 (d, *J* = 14.3 Hz, 1H), 2.07 (d, *J* = 14.4 Hz, 1H), 1.48 (s,

3H), 1.40 (s, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 179.5, 149.2, 148.0, 143.6, 142.3, 135.52, 135.48, 129.1, 128.0, 127.4, 126.1, 125.7, 121.6, 113.6, 112.4, 105.8, 101.2, 100.6, 74.5, 49.1, 44.14, 44.09, 29.0, 27.4. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{26}H_{23}BrNO_4^+$ 492.0805; found: 492.0798.

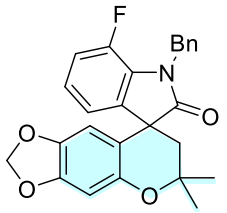
1-benzyl-6',6',7-trimethyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3t)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (19 mg, 45% yield), as a yellow solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.38 (t, *J* = 7.5 Hz, 2H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 2H), 7.03 (dd, *J* = 6.7, 2.1 Hz, 1H), 6.99 – 6.92 (m, 2H), 6.50 (s, 1H), 6.08 (s, 1H), 5.85 (dd, *J* = 9.2, 1.4 Hz, 2H), 5.31 (d, *J* = 16.6 Hz, 1H), 5.21 (d, *J* = 16.7 Hz, 1H), 2.46 (d, *J* = 14.3 Hz, 1H), 2.38 (s, 3H), 2.30 (d, *J* = 14.5 Hz, 1H), 1.62 (s, 3H), 1.54 (s, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 180.8, 149.2, 147.7, 142.2, 140.3, 137.9, 137.6, 132.1, 129.0, 127.3, 125.8, 123.4, 122.3, 119.7, 114.7, 106.2, 101.1, 100.4, 74.7, 48.7, 45.3, 44.9, 29.6, 27.0, 19.0. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{27}H_{26}NO_4^+$ 428.1856; found: 428.1870.

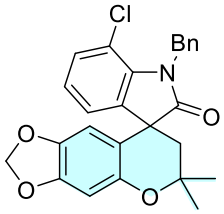
1-benzyl-7-fluoro-6',6'-dimethyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3u)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (27 mg, 62% yield), as a yellow solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 7.7 Hz, 2H), 7.33 (dd, *J* = 8.3, 6.5 Hz, 2H), 7.30 – 7.26 (m, 1H), 6.94 – 6.88 (m, 3H), 6.45 (s, 1H), 5.87 (s, 1H), 5.81 (s, 2H), 5.11 (d, *J* = 15.1 Hz, 1H), 5.05 (d, *J* = 15.7 Hz, 1H), 2.39 (d, *J* = 14.3 Hz, 1H), 2.18 (d, *J* = 14.4 Hz, 1H), 1.57 (s, 3H), 1.48 (s, 3H).**^{13}C NMR** (125 MHz, Chloroform-*d*) δ 179.4, 149.1, 147.9, 147.2 (d, *J* = 243.2 Hz), 142.3, 139.6 (d, *J* = 2.8 Hz), 137.3, 128.7, 127.73, 127.71, 123.9 (d, *J* = 6.2 Hz), 120.11, 120.09, 116.2 (d, *J* = 20.0 Hz), 113.9, 105.9, 101.1, 100.5, 74.5, 45.6, 45.5, 44.3, 29.3, 27.1. **^{19}F NMR** (470 MHz, Chloroform-*d*) δ -133.44. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{26}H_{23}FNO_4^+$ 432.1606; found: 432.1602.

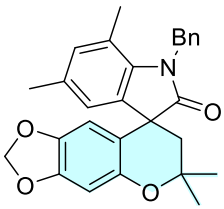
1-benzyl-7-chloro-6',6'-dimethyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3v)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (28 mg, 62% yield), as a yellow solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.35 – 7.24 (m, 5H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 7.4 Hz, 1H), 6.91 (t, *J* = 7.8 Hz, 1H), 6.45 (s, 1H), 5.93 (s, 1H), 5.86 – 5.77 (m, 2H), 5.41 (d, *J* = 16.0 Hz, 1H), 5.36 (d, *J* = 16.0 Hz, 1H), 2.37 (d, *J* = 14.4 Hz, 1H), 2.20 (d, *J* = 14.4 Hz, 1H), 1.56 (s, 3H), 1.48 (s, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 180.2, 149.2, 148.0, 142.3, 139.7, 138.4, 137.7, 130.7, 128.7, 127.3, 126.8, 124.2, 123.0, 115.2, 114.0, 106.0, 101.2, 100.5, 74.7, 49.0, 45.1, 44.6, 29.7, 26.8. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{26}H_{23}ClNO_4^+$ 448.1309; found: 448.1308.

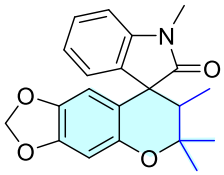
1-benzyl-5,6',6',7-tetramethyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3w)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (26 mg, 51% yield), as a yellow solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.32 (t, *J* = 7.5 Hz, 2H), 7.25 (d, *J* = 6.7 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 2H), 6.76 (d, *J* = 26.1 Hz, 2H), 6.46 (d, *J* = 1.2 Hz, 1H), 6.04 (d, *J* = 1.2 Hz, 1H), 5.82 (dt, *J* = 13.7, 1.5 Hz, 2H), 5.24 (d, *J* = 16.7 Hz, 1H), 5.14 (d, *J* = 16.7 Hz, 1H), 2.39 (d, *J* = 14.4, 1.2 Hz, 1H), 2.28 (s, 3H), 2.25 (d, *J* = 14.4 Hz, 1H), 2.20 (s, 3H), 1.57 (s, 3H), 1.50 (s, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 180.7, 149.2, 147.6, 142.2, 138.0, 137.8, 137.7, 132.9, 132.5, 128.9, 127.2, 125.8, 122.9, 119.4, 114.9, 106.3, 101.0, 100.4, 74.7, 48.8, 45.2, 44.9, 29.8, 26.8, 20.8, 18.8. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{28}H_{28}NO_4^+$ 442.2013; found: 442.2023.

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

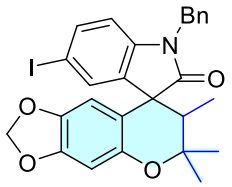


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (14 mg, 41% yield, dr>20:1), as a yellow solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.19 (td, *J* = 7.6, 1.5 Hz, 2H), 6.97 – 6.88 (m, 2H), 6.78 (d, *J* = 7.8 Hz, 1H), 6.33 (s, 1H), 5.72 (d, *J* = 1.8 Hz, 2H), 5.70 (d, *J* = 1.4 Hz, 1H), 3.19 (s, 3H), 2.36 (q, *J* = 7.2 Hz, 1H), 1.48 (s, 3H), 1.38 (s, 3H), 0.71 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (125 MHz,

Chloroform-*d*) δ 176.4, 147.7, 146.6, 142.6, 140.9, 135.5, 127.2, 122.4, 122.3, 113.5, 106.6, 105.4, 99.9, 98.8, 77.4, 53.3, 45.6, 28.2, 25.2, 19.5, 10.3. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{21}H_{22}NO_4^+$ 352.1543; found: 352.1553.

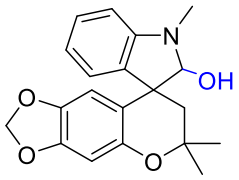
1-benzyl-5-iodo-6',6',7'-trimethyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3y)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (18 mg, 32% yield, dr>20:1), as a yellow solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 8.3 Hz, 1H), 7.34 – 7.09 (m, 7H), 6.49 (d, *J* = 8.4 Hz, 1H), 6.35 (s, 1H), 5.76 (d, *J* = 12.8 Hz, 2H), 4.84 (q, *J* = 15.4 Hz, 2H), 2.33 (q, *J* = 7.1 Hz, 1H), 1.49 (s, 3H), 1.39 (s, 3H), 0.77 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 142.6, 138.8, 137.0, 135.8, 132.4, 129.0, 128.0, 127.7, 113.9, 110.9, 106.2, 101.2, 100.1, 78.4, 54.2, 46.8, 44.2, 29.2, 20.6, 11.7. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{27}H_{25}INO_4^+$ 554.0823; found: 554.0836.

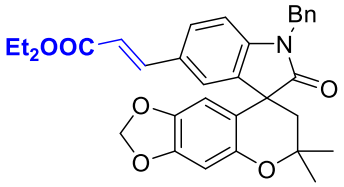
1,6',6'-trimethyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-ol (5)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (28 mg, 71% yield, dr = 1.5:1), as a yellow solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.08 (dtd, *J* = 11.6, 7.6, 1.3 Hz, 2H), 6.85 (dd, *J* = 7.3, 1.2 Hz, 1H), 6.78 – 6.71 (m, 1H), 6.67 – 6.57 (m, 2H), 6.45 (dd, *J* = 18.7, 7.8 Hz, 2H), 6.35 (s, 1H), 6.26 (s, 1H), 6.20 (s, 1H), 6.16 (s, 1H), 5.75 (s, 2H), 5.69 (dd, *J* = 12.0, 1.4 Hz, 2H), 4.88 (dd, *J* = 10.3, 3.4 Hz, 2H), 2.88 (s, 2H), 2.81 (s, 3H), 2.43 (d, *J* = 14.3 Hz, 1H), 2.21 (d, *J* = 14.5 Hz, 1H), 2.15 – 1.98 (m, 3H), 1.94 (d, *J* = 10.9 Hz, 1H), 1.40 (s, 5H), 1.35 (s, 3H), 1.29 (s, 2H). **^{13}C NMR** (125 MHz, Chloroform-d) δ 149.5, 149.4, 148.8, 147.8, 147.5, 141.6, 135.9, 135.4, 128.8, 128.6, 123.8, 123.6, 118.8, 118.6, 117.3, 112.6, 107.9, 106.9, 106.7, 106.6, 101.0, 100.8, 99.8, 99.2, 97.5, 97.0, 74.6, 74.0, 49.3, 49.1, 46.5, 37.6, 31.9, 30.6, 30.5, 30.3, 26.0, 25.2. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{20}H_{22}NO_4^+$ 340.1543; found: 340.1556.

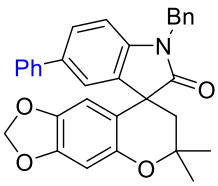
ethyl (E)-3-(1-benzyl-6',6'-dimethyl-2-oxo-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-5-yl)acrylate (6)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (39 mg, 77% yield), as a yellow solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 15.9 Hz, 1H), 7.36 – 7.29 (m, 7H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.48 (s, 1H), 6.24 (d, *J* = 16.0 Hz, 1H), 5.90 (s, 1H), 5.83 (s, 2H), 4.98 (d, *J* = 15.6 Hz, 1H), 4.92 (d, *J* = 15.5 Hz, 1H), 4.26 – 4.17 (m, 2H), 2.43 (d, *J* = 14.3 Hz, 1H), 2.21 (d, *J* = 14.4 Hz, 1H), 1.58 (s, 3H), 1.52 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 179.6, 167.0, 149.3, 148.0, 144.1, 144.0, 142.3, 137.4, 135.6, 130.0, 129.3, 129.0, 128.0, 127.4, 123.3, 116.5, 113.7, 109.4, 105.8, 101.1, 100.6, 74.5, 60.4, 49.2, 44.2, 44.2, 29.2, 27.2, 14.3. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{31}H_{30}NO_6^+$ 512.2068; found: 512.2077.

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



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (40 mg, 81% yield), as a yellow solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.45 – 7.42 (m, 2H), 7.40 – 7.34 (m, 8H), 7.28 (dddd, *J* = 11.0, 7.4, 5.2, 2.1 Hz, 2H), 6.84 (d, *J* = 8.1 Hz, 1H), 6.47 (s, 1H), 5.97 (s, 1H), 5.81 (s, 2H), 5.00 (d, *J* = 15.5 Hz, 1H), 4.94 (d, *J* = 15.5 Hz, 1H), 2.47 (d, *J* = 14.4 Hz, 1H), 2.28 (d, *J* = 14.4 Hz, 1H), 1.60 (s, 3H), 1.53 (s, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 179.8, 149.3, 147.8, 142.3, 141.6, 140.7, 137.3, 136.8, 136.0, 129.0, 128.8, 127.9, 127.5, 127.1, 127.0, 126.8, 123.2, 114.2, 109.4, 106.1, 101.1, 100.5, 74.6, 49.5, 44.3, 44.2, 29.2, 27.3. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{32}H_{28}NO_4^+$ 490.2013; found: 490.2026.

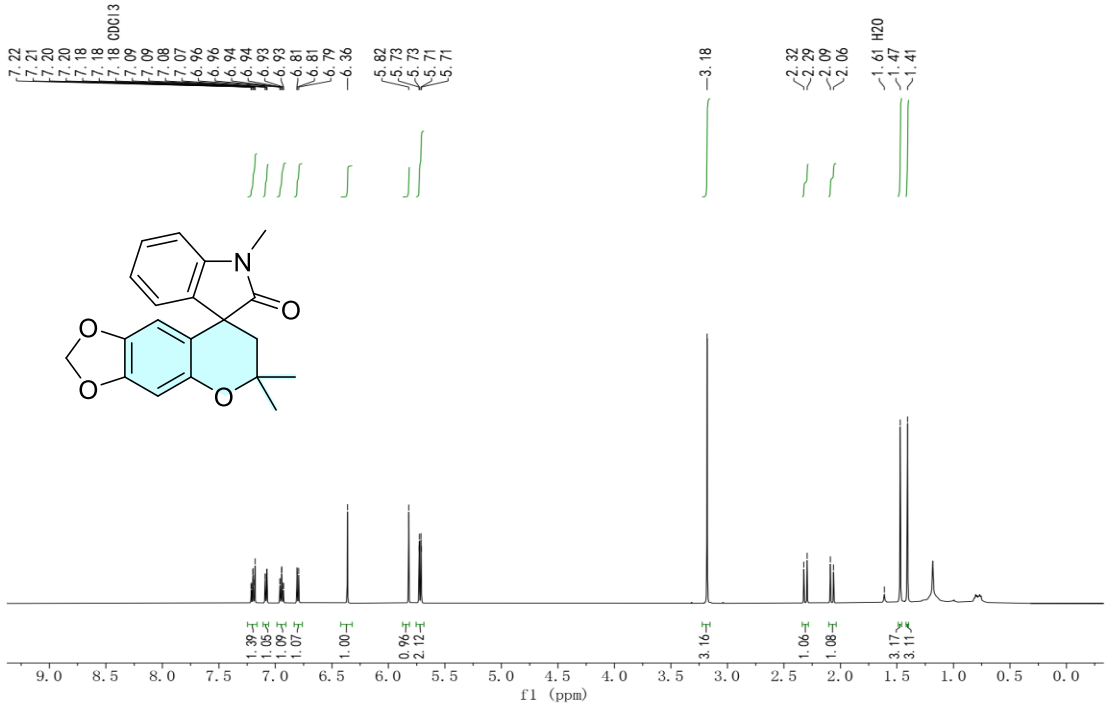
Reference:

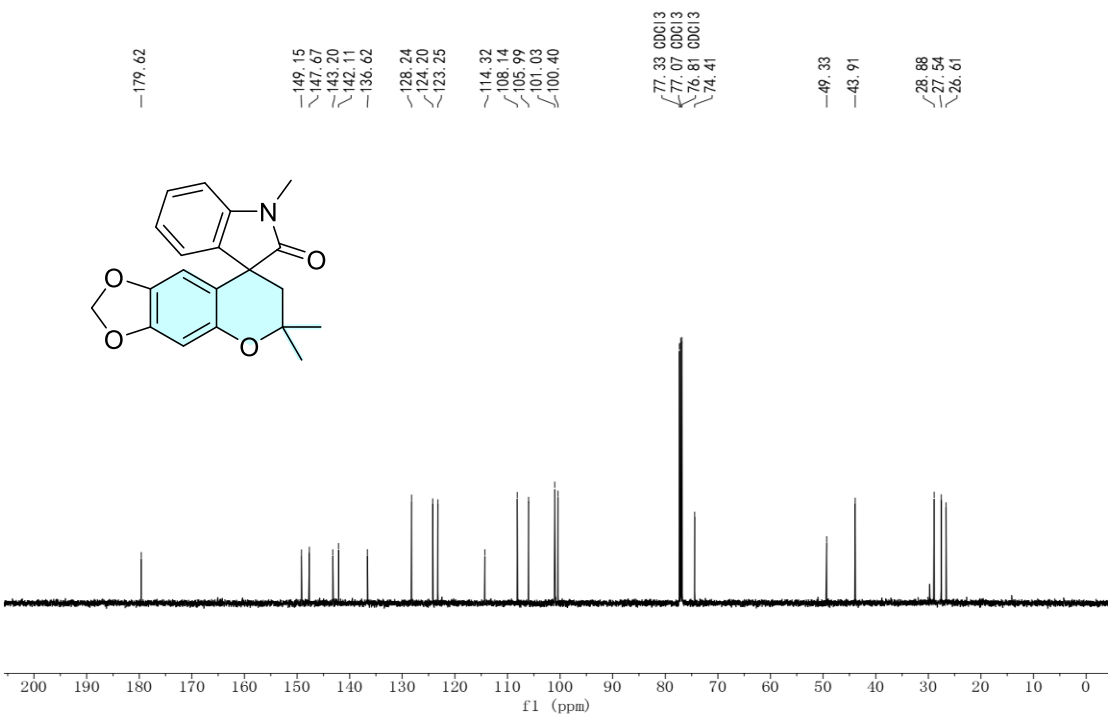
1. H. Shi, L. Wang, S.-S. Li, Y. Liu and L. Xu, *Org. Chem. Front.*, 2020, **7**, 747.

2. N. Kumar, J. Kaur, A. Kumar, N. Islam and S.S. Chimni, *Asian J. Org. Chem.*, 2016, **5**, 1334.

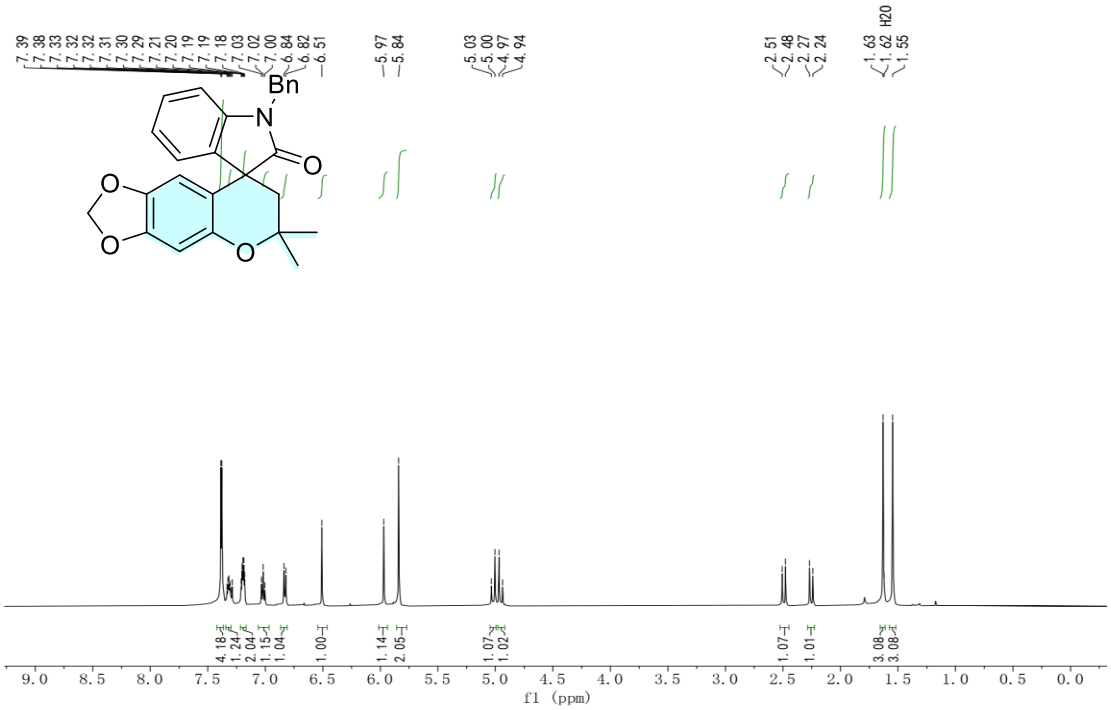
4. NMR Spectra

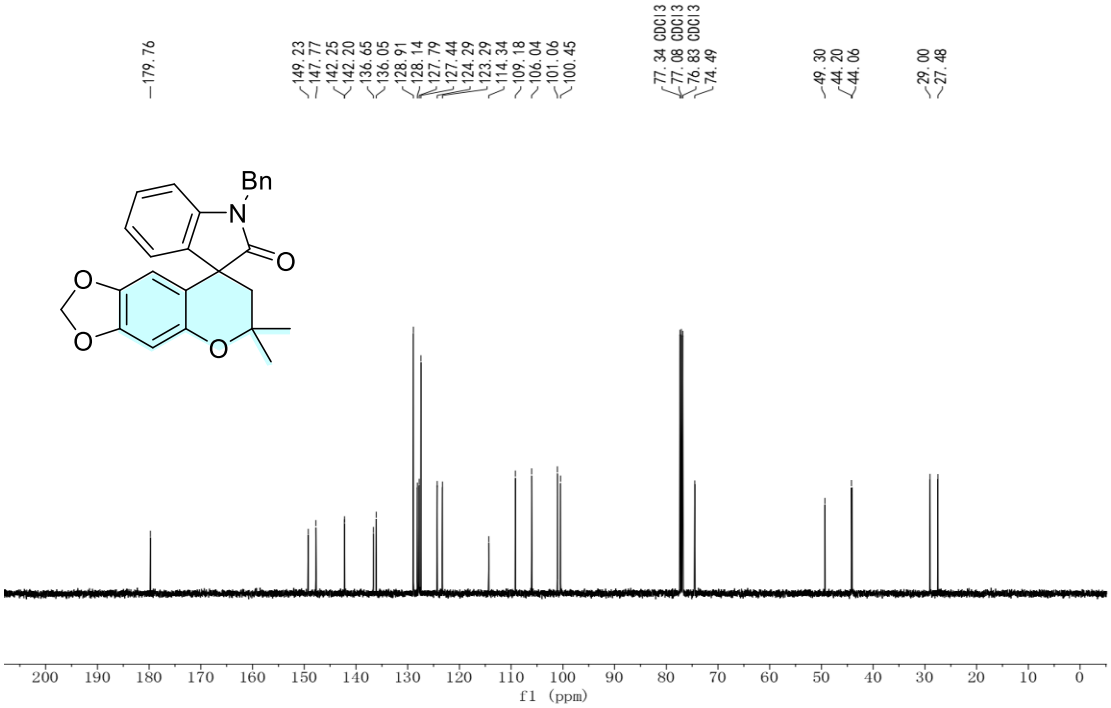
1,6',6'-trimethyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3a)



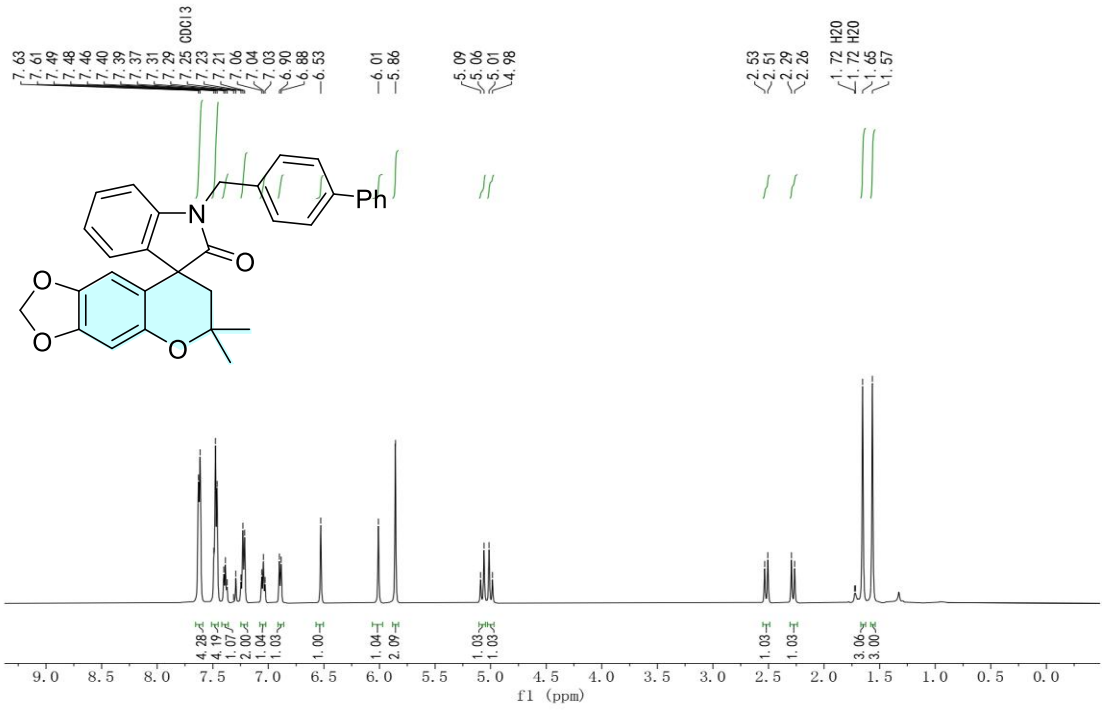


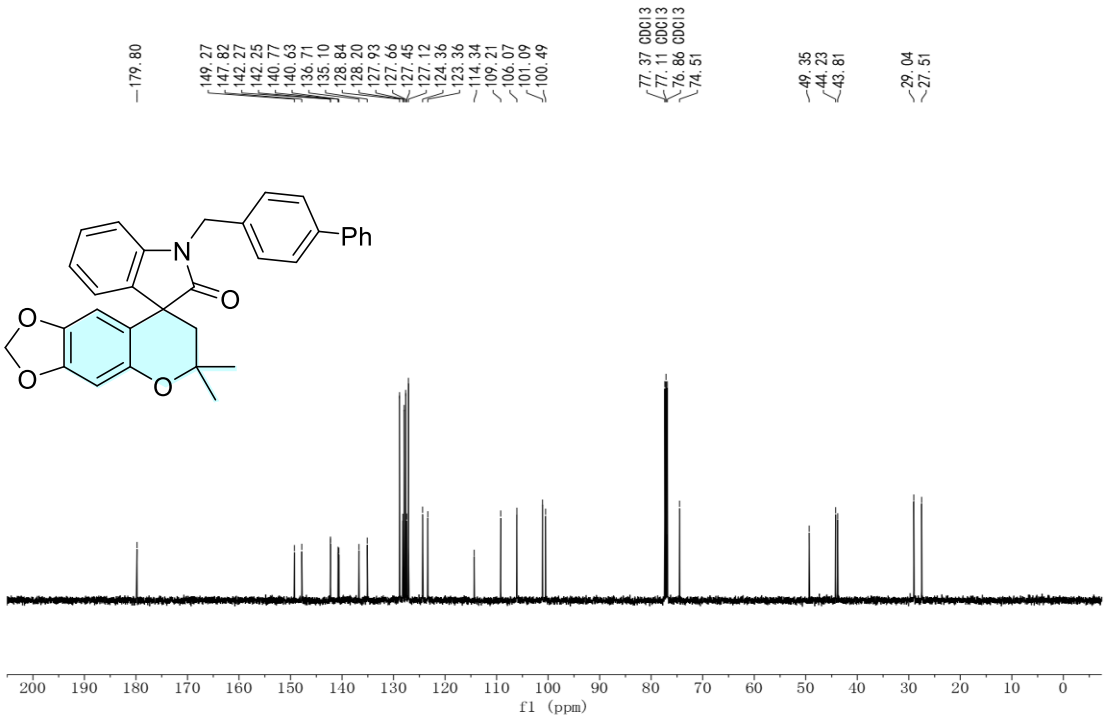
1-benzyl-6',6'-dimethyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3b)



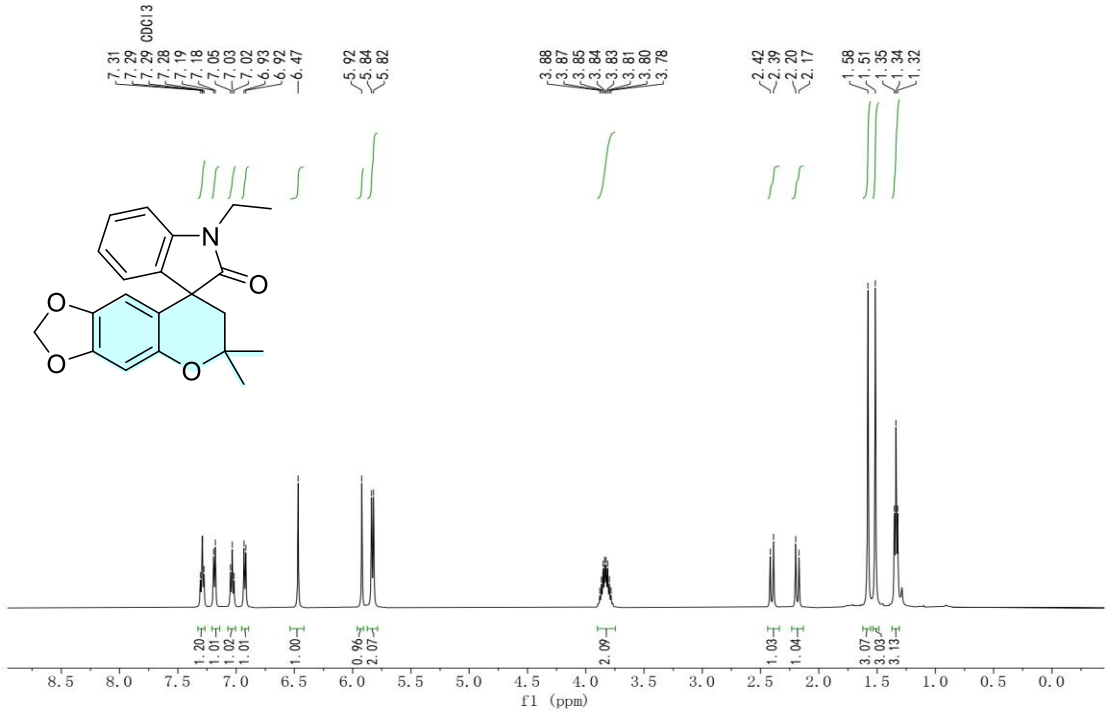


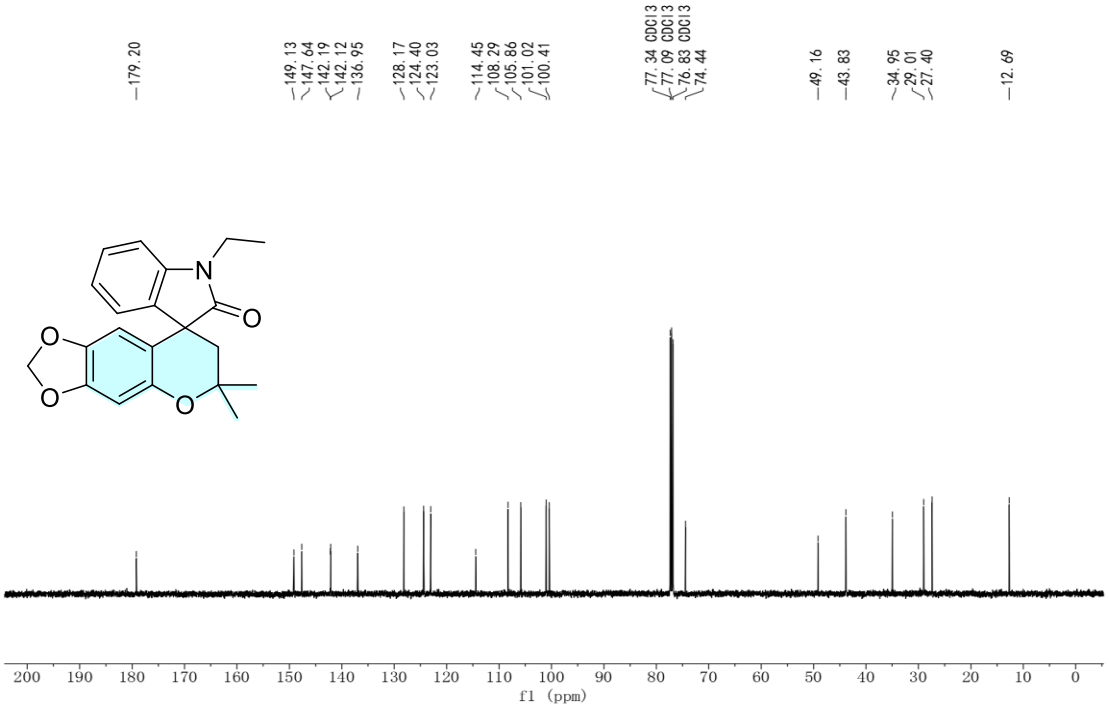
1-([1,1'-biphenyl]-4-ylmethyl)-6',6'-dimethyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3c)



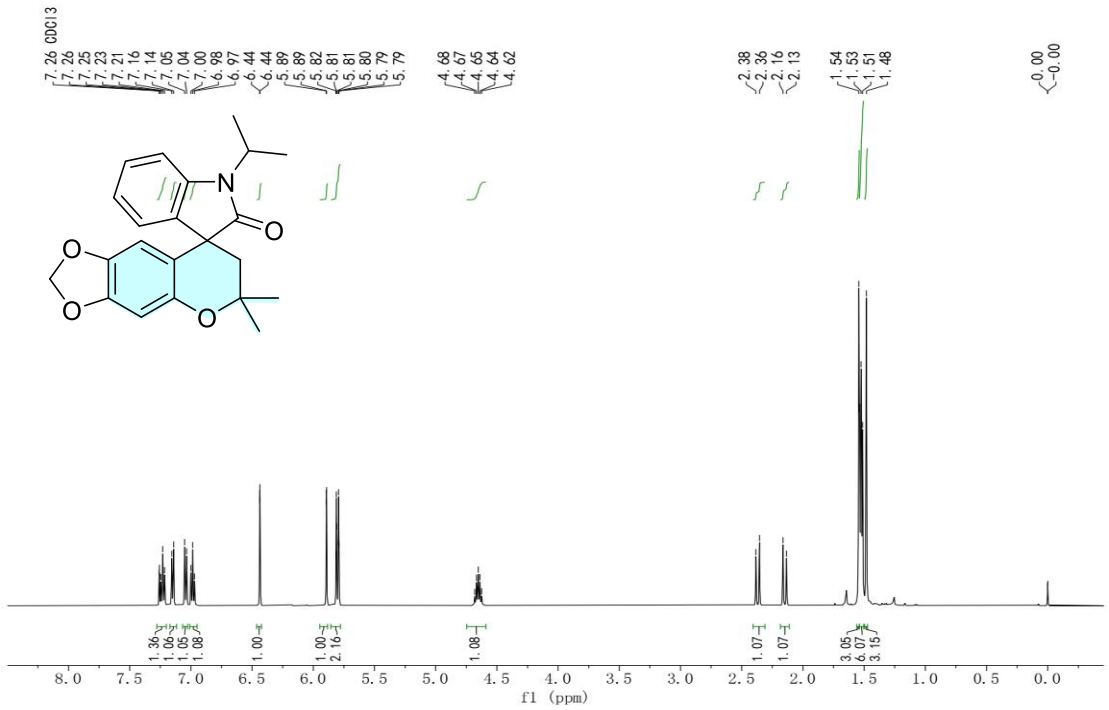


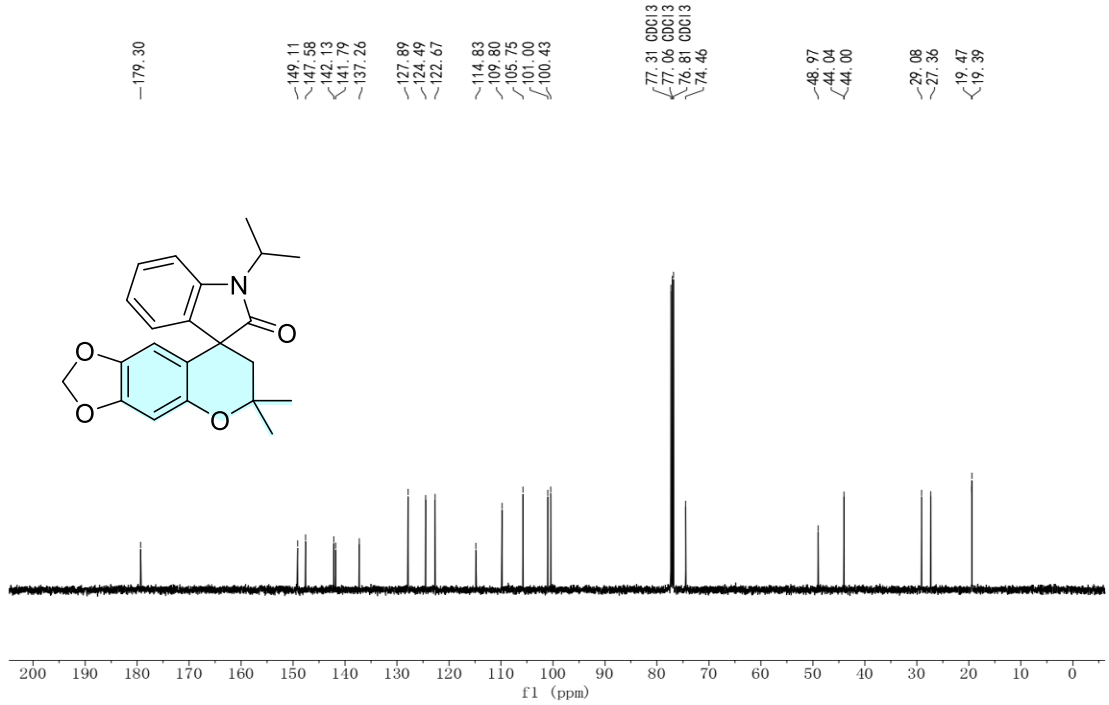
1-ethyl-6',6'-dimethyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3d)



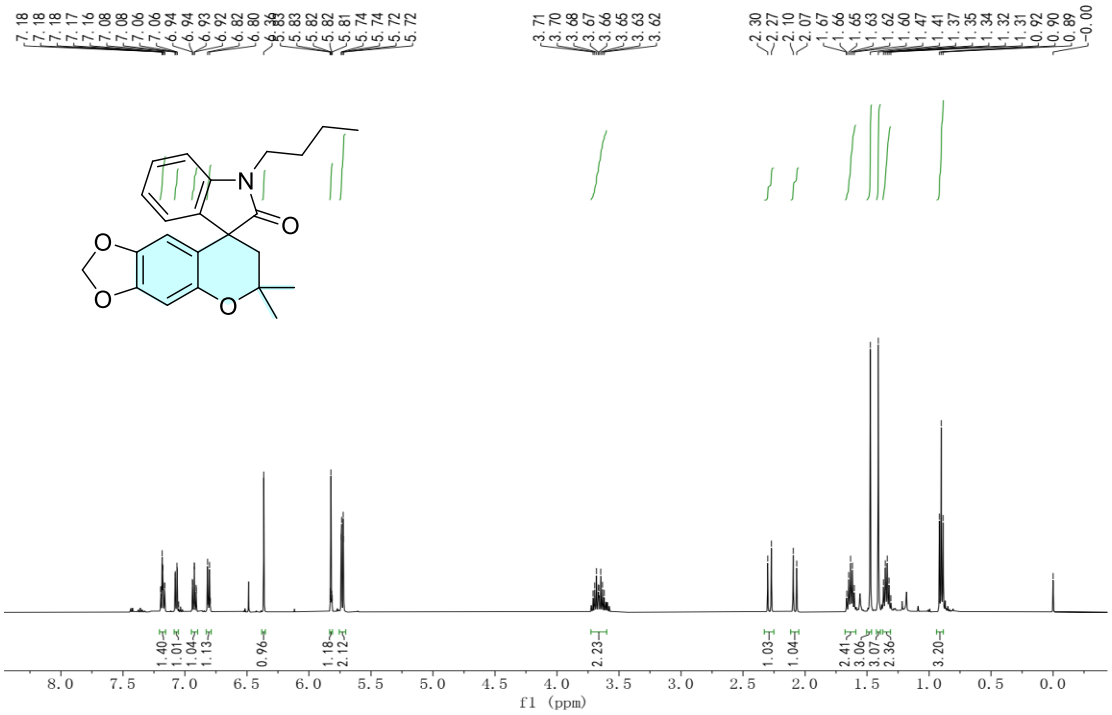


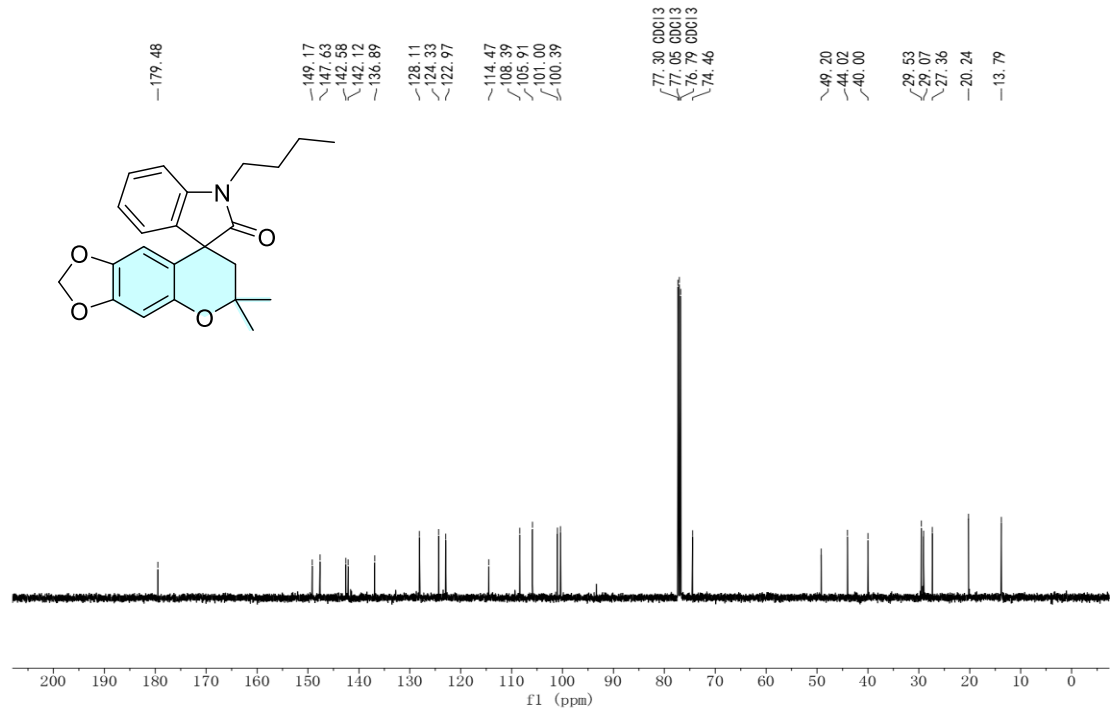
1-isopropyl-6',6'-dimethyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3e)



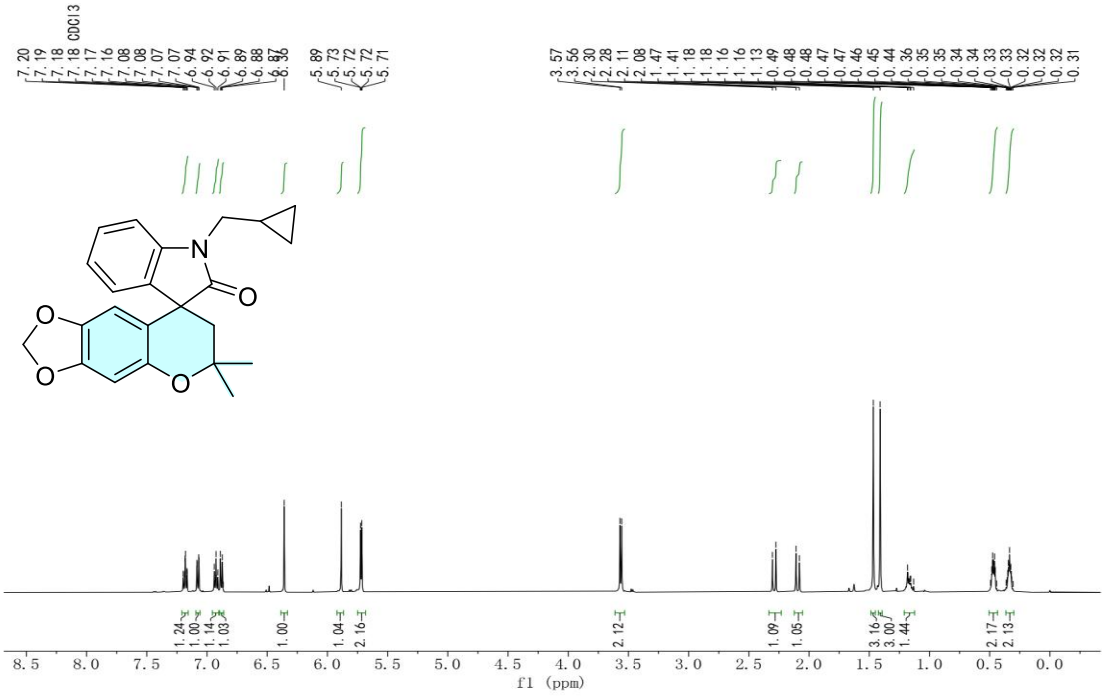


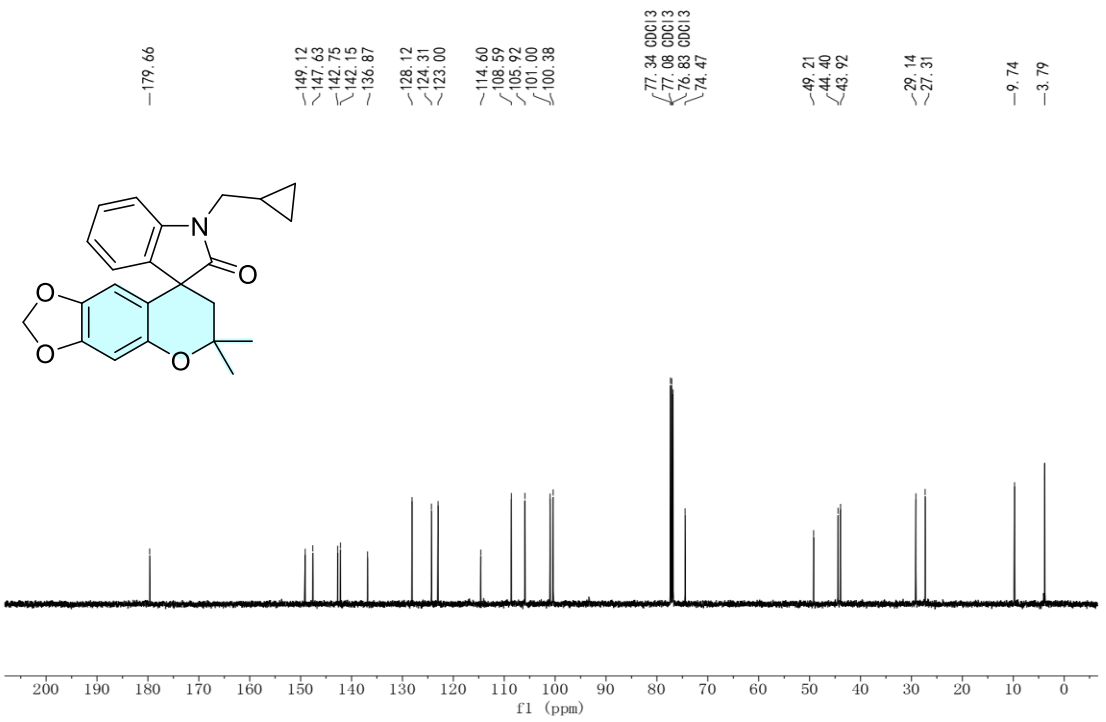
1-butyl-6',6'-dimethyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3f)



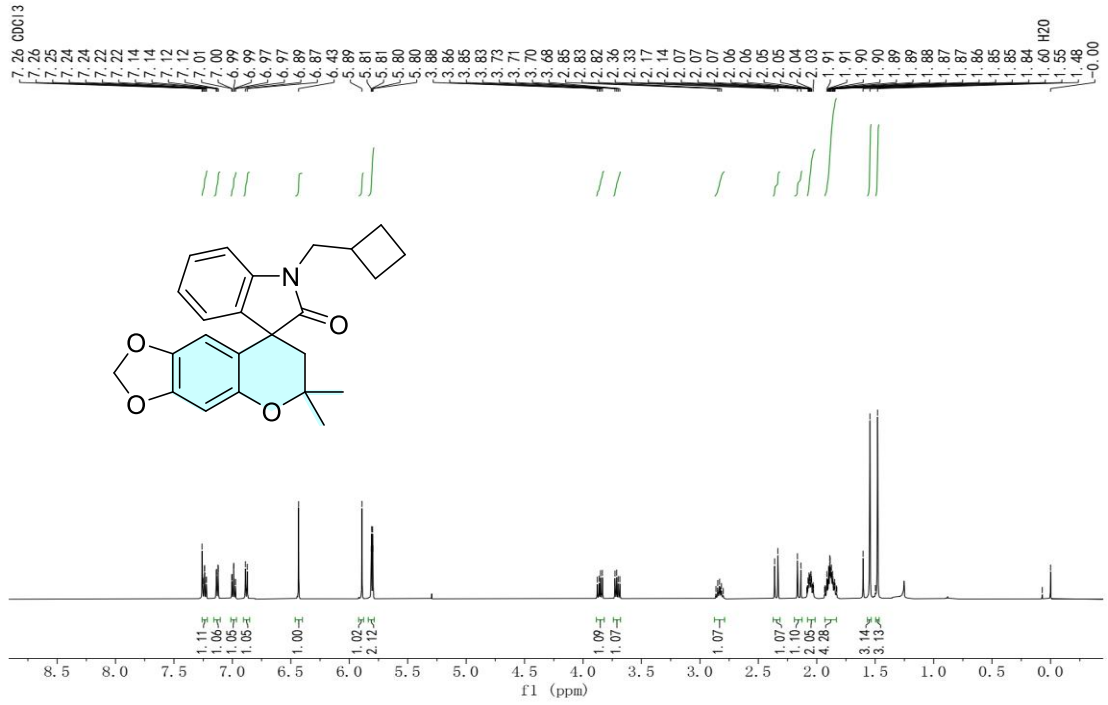


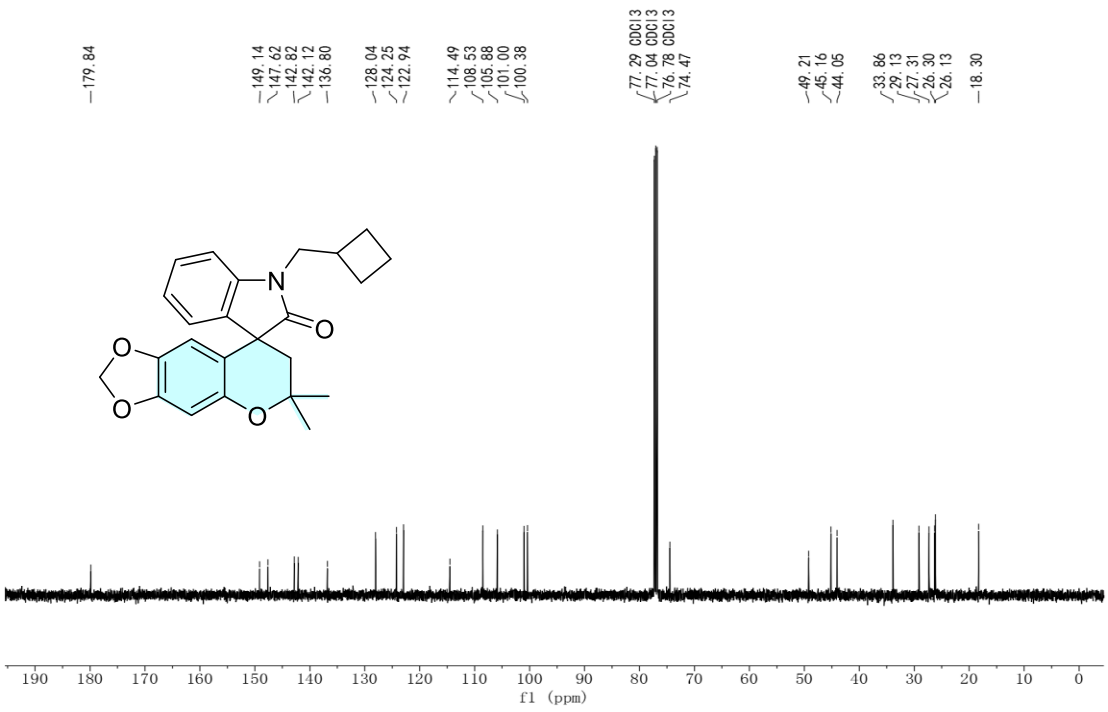
1-(cyclopropylmethyl)-6',6'-dimethyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3g)



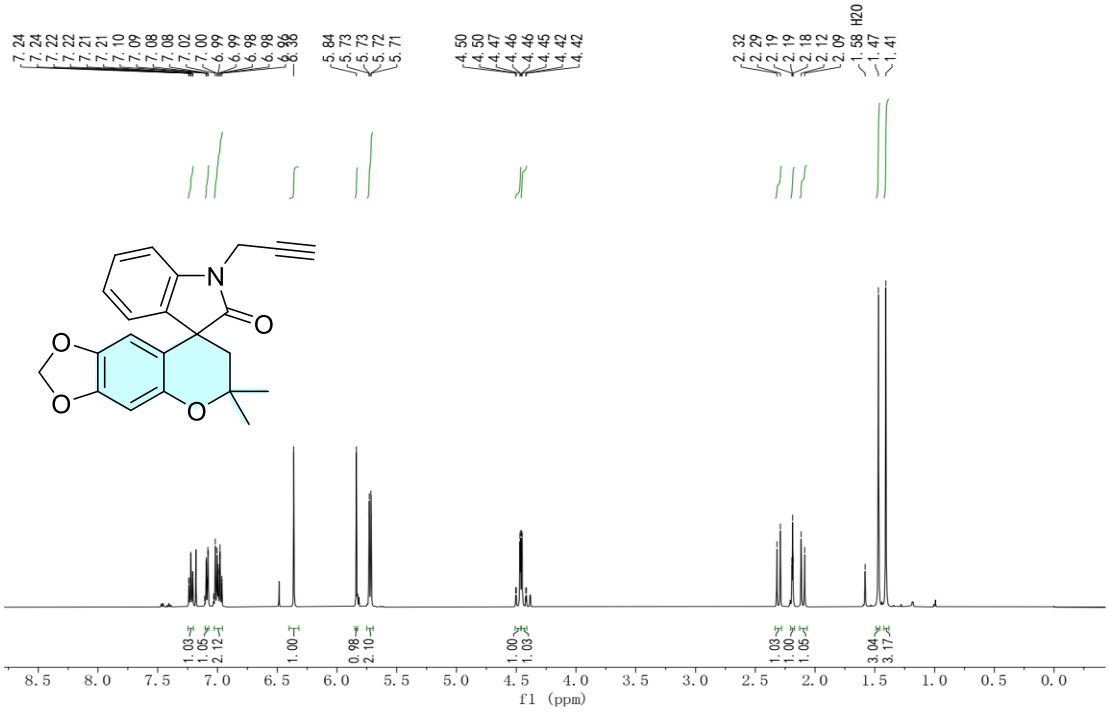


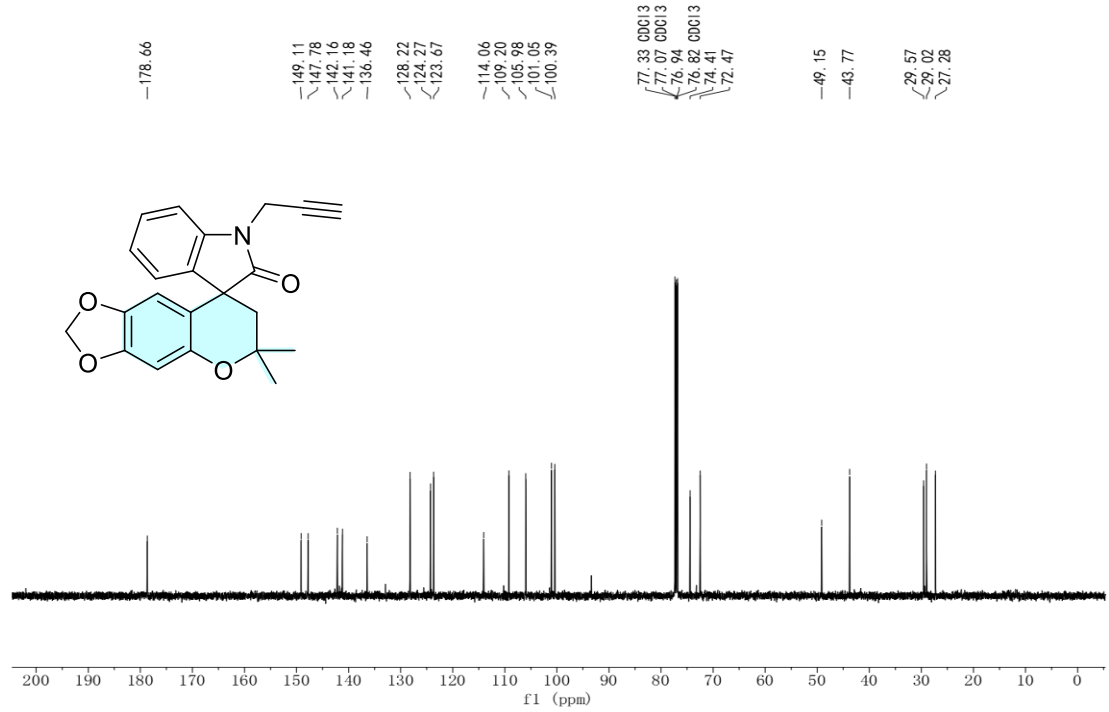
1-(cyclobutylmethyl)-6',6'-dimethyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3h)



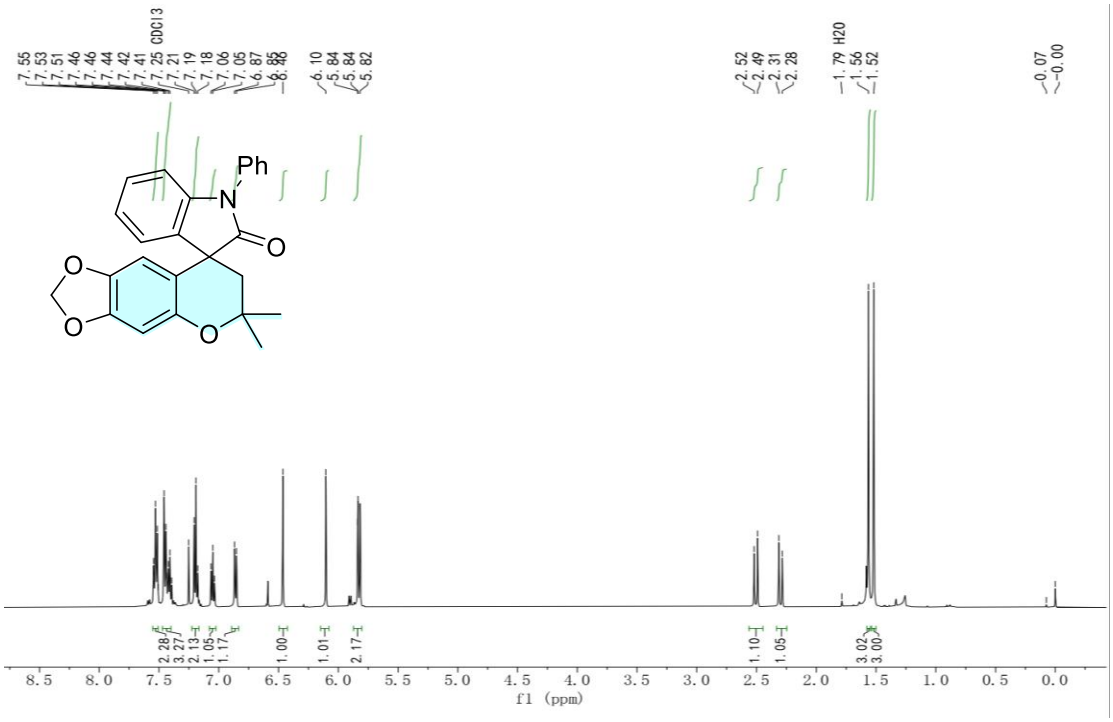


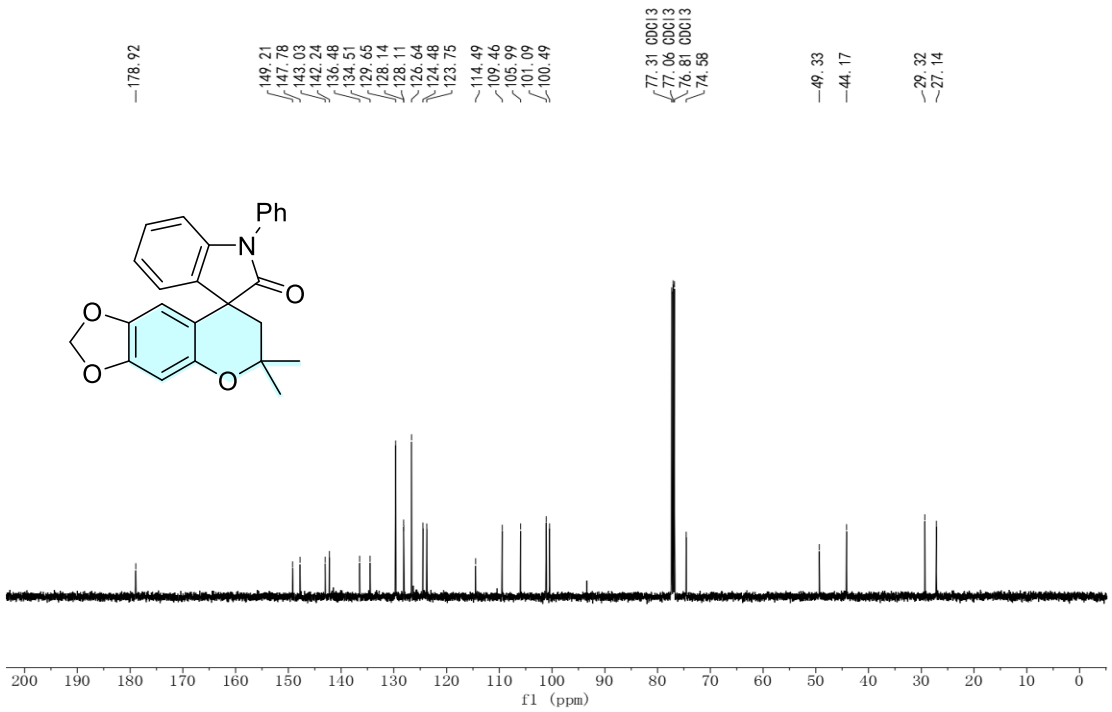
6',6'-dimethyl-1-(prop-2-yn-1-yl)-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3i)



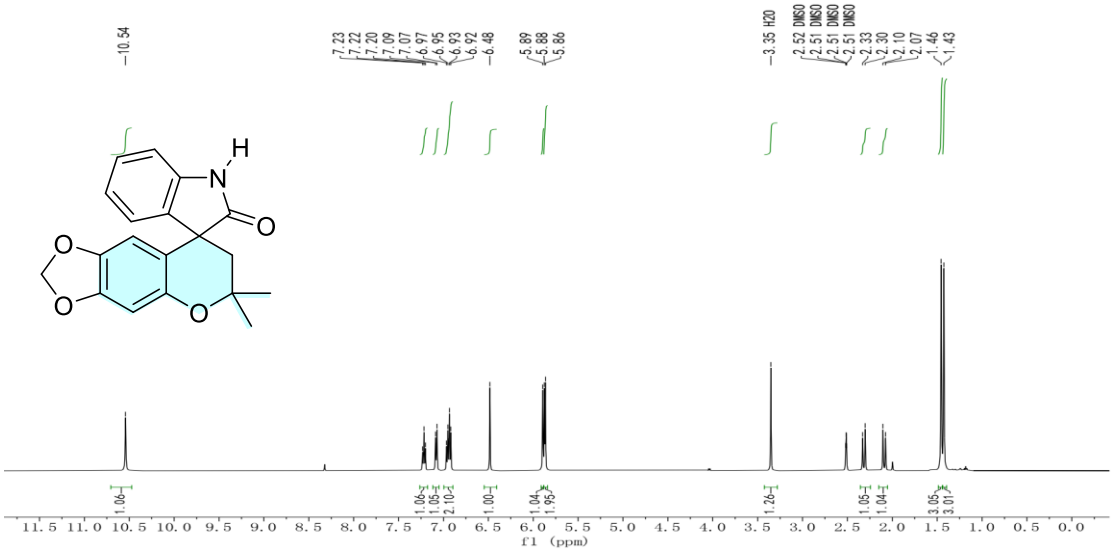


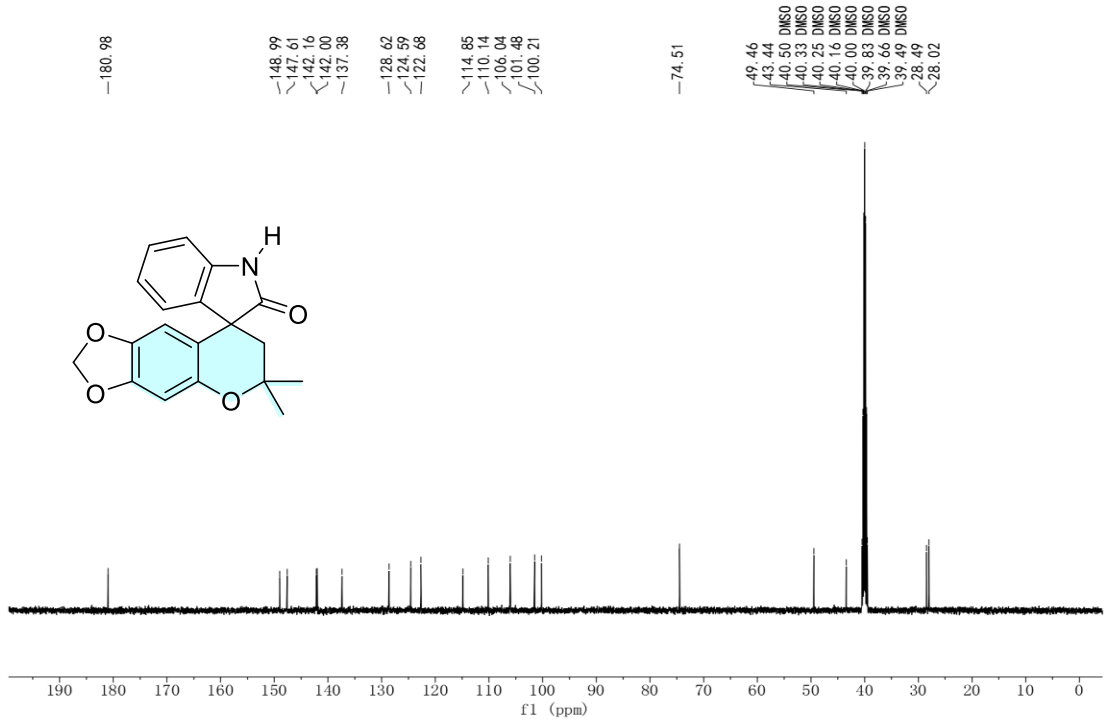
6',6'-dimethyl-1-phenyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3j)



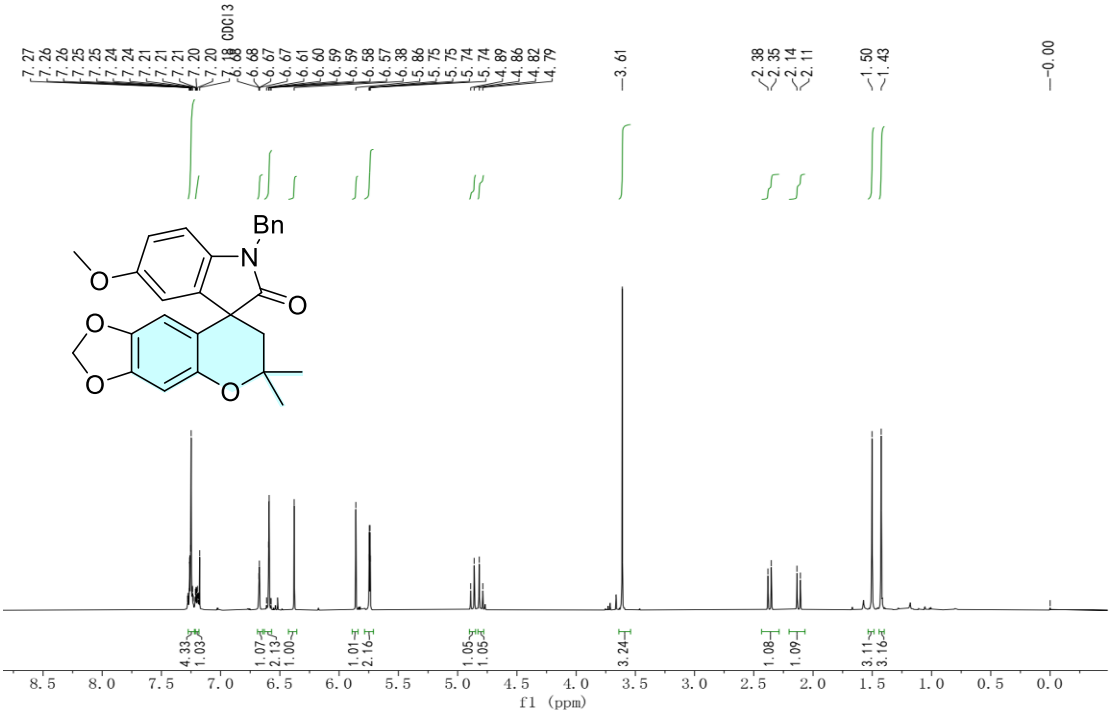


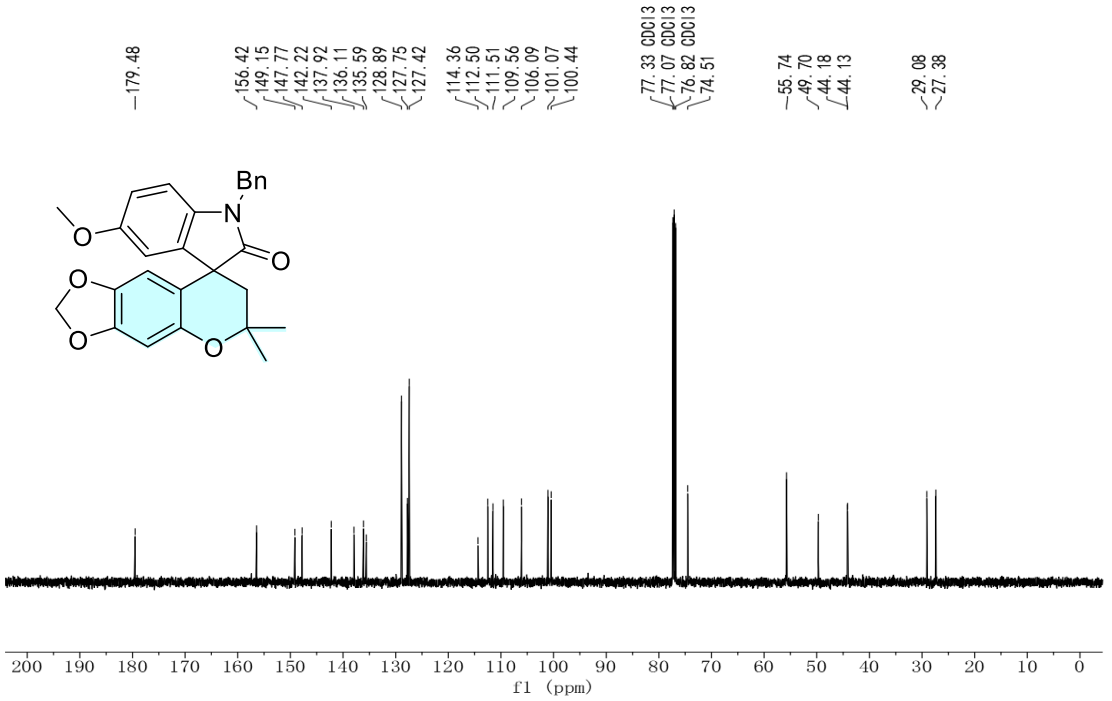
6',6'-dimethyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3k)



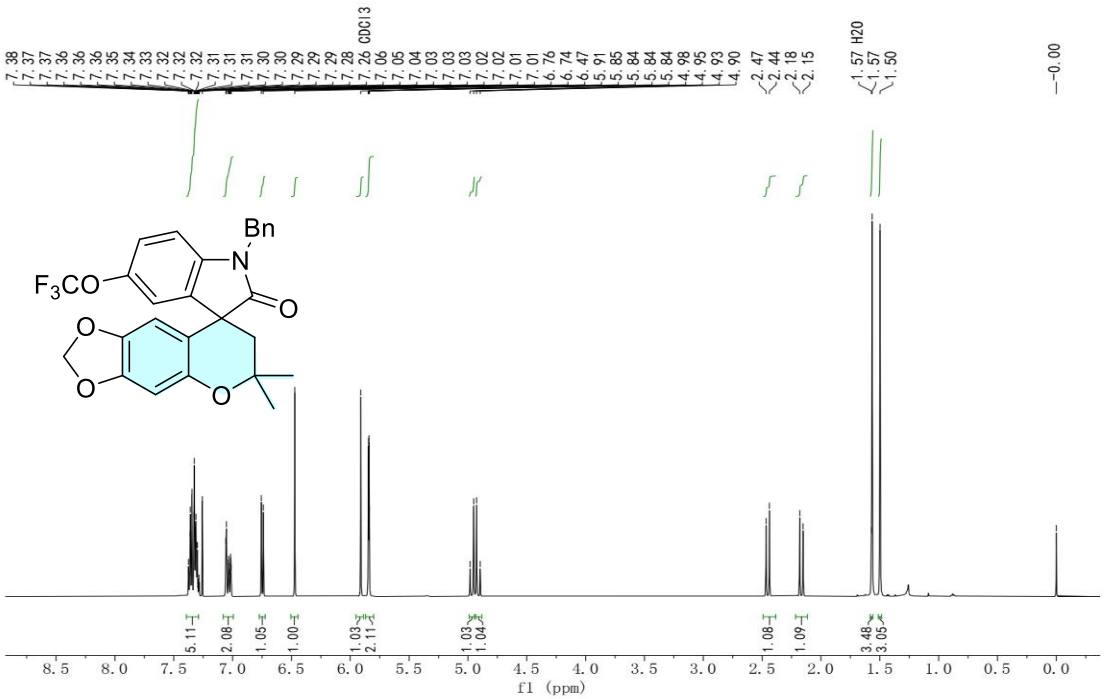


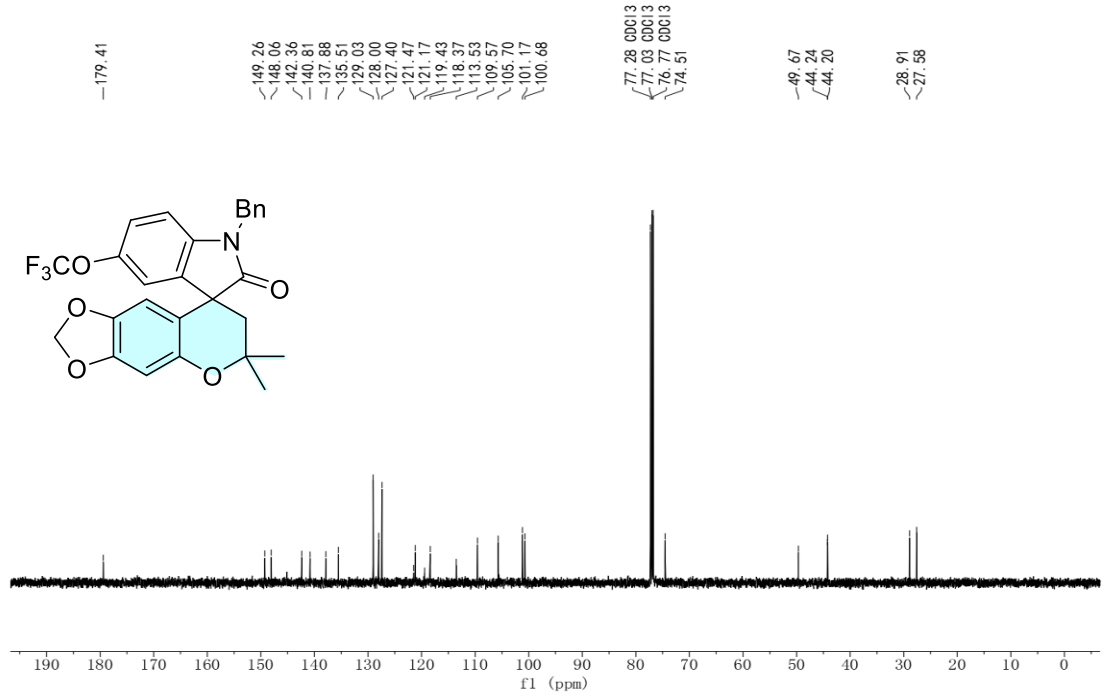
1-benzyl-5-methoxy-6',6'-dimethyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3l)

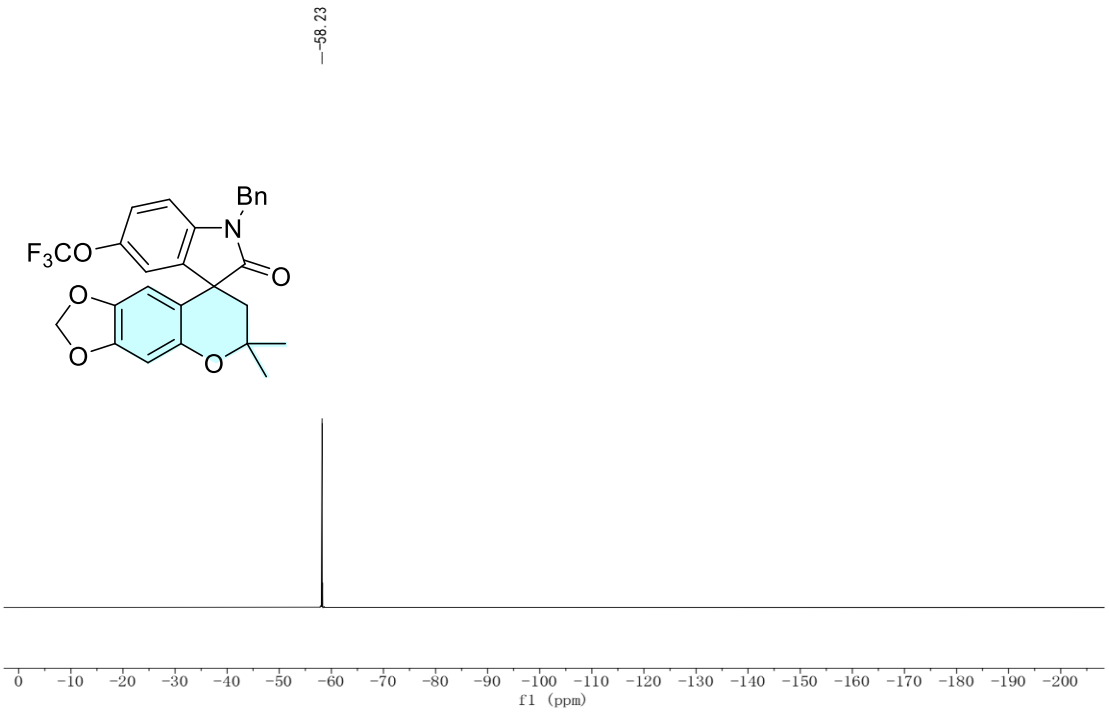




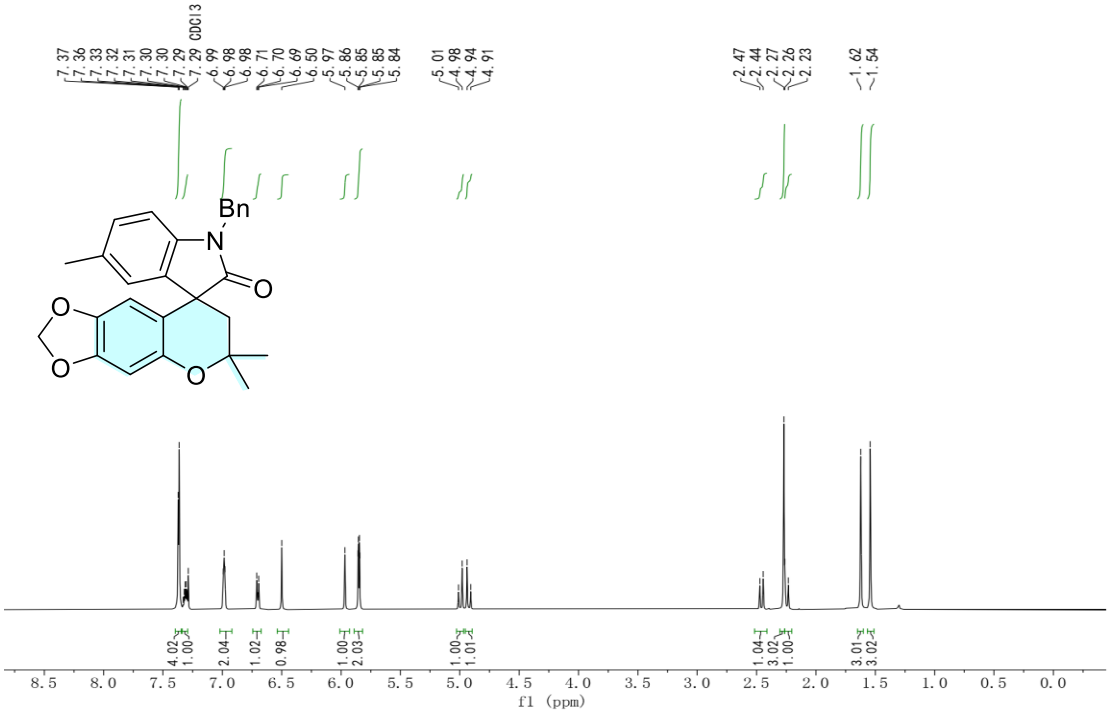
1-benzyl-6',6'-dimethyl-5-(trifluoromethoxy)-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3m)

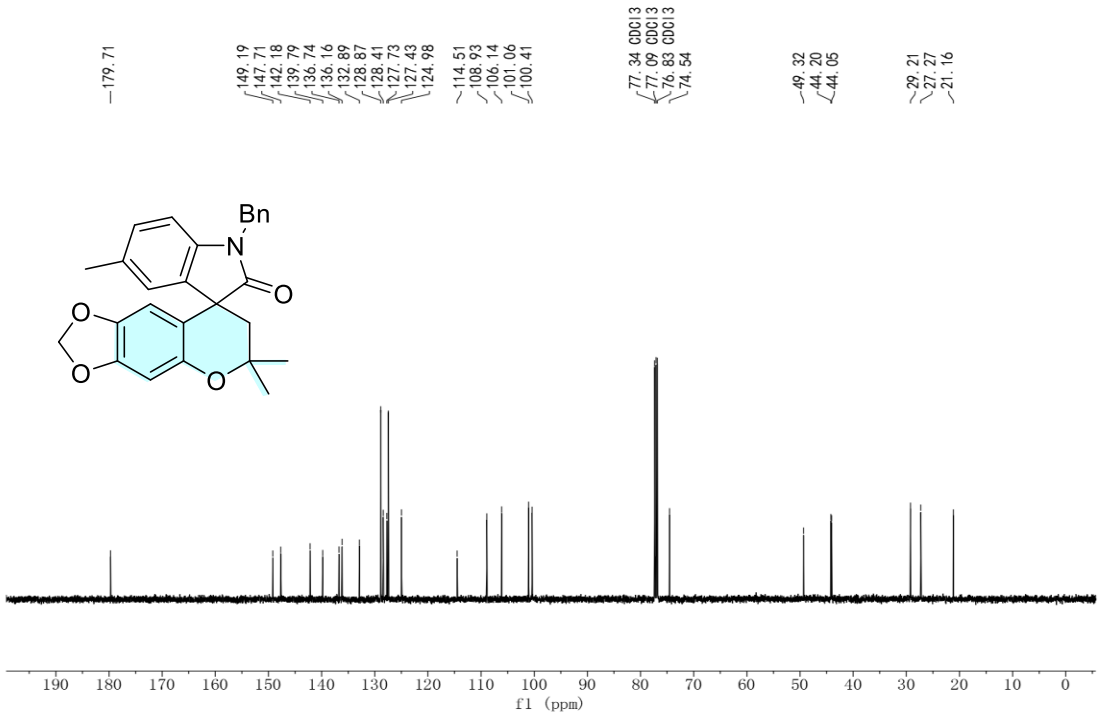




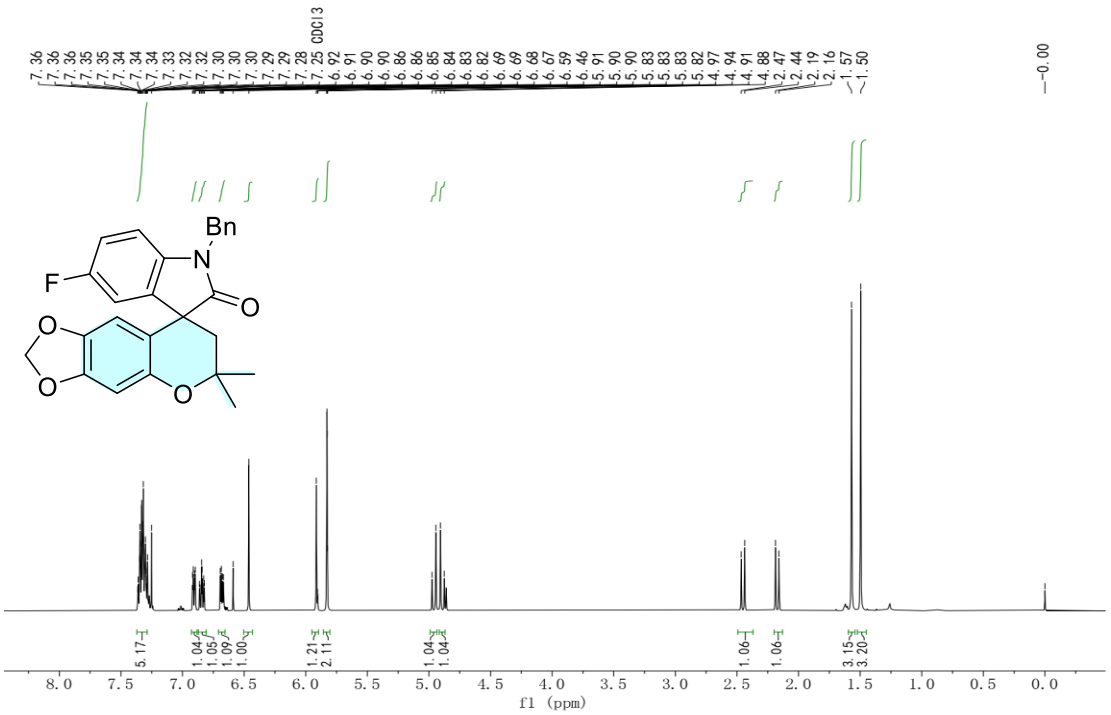

-58.23
Bn
N
F3CO
O
O
O
O
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

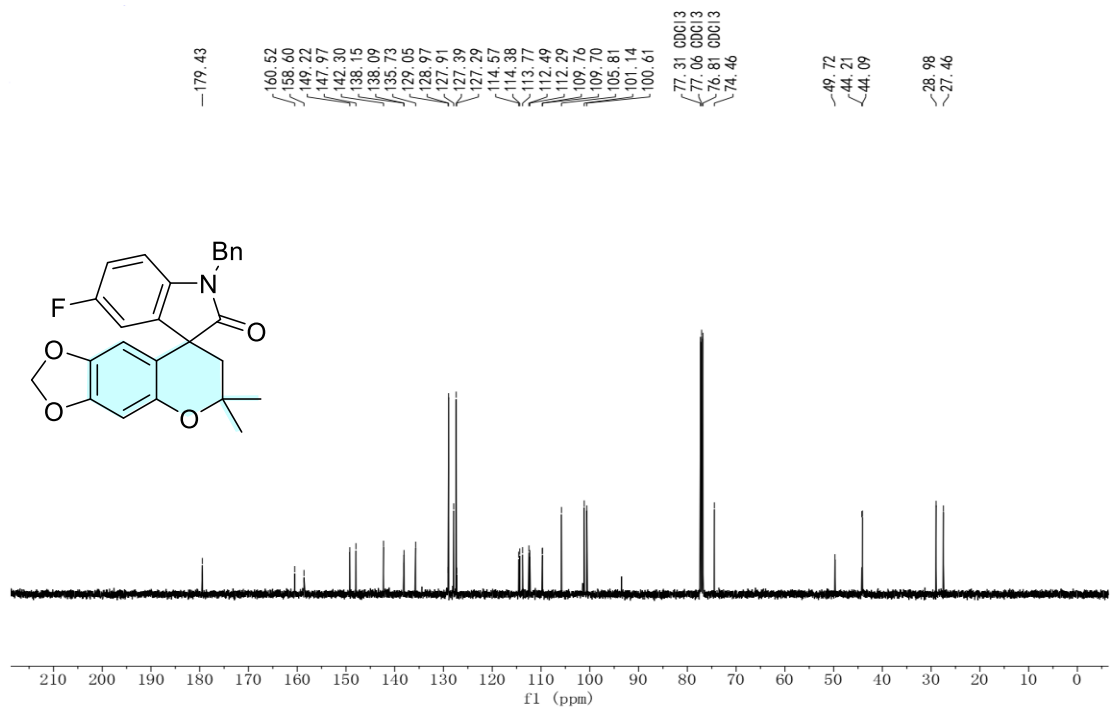
1-benzyl-5,6',6'-trimethyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3n)

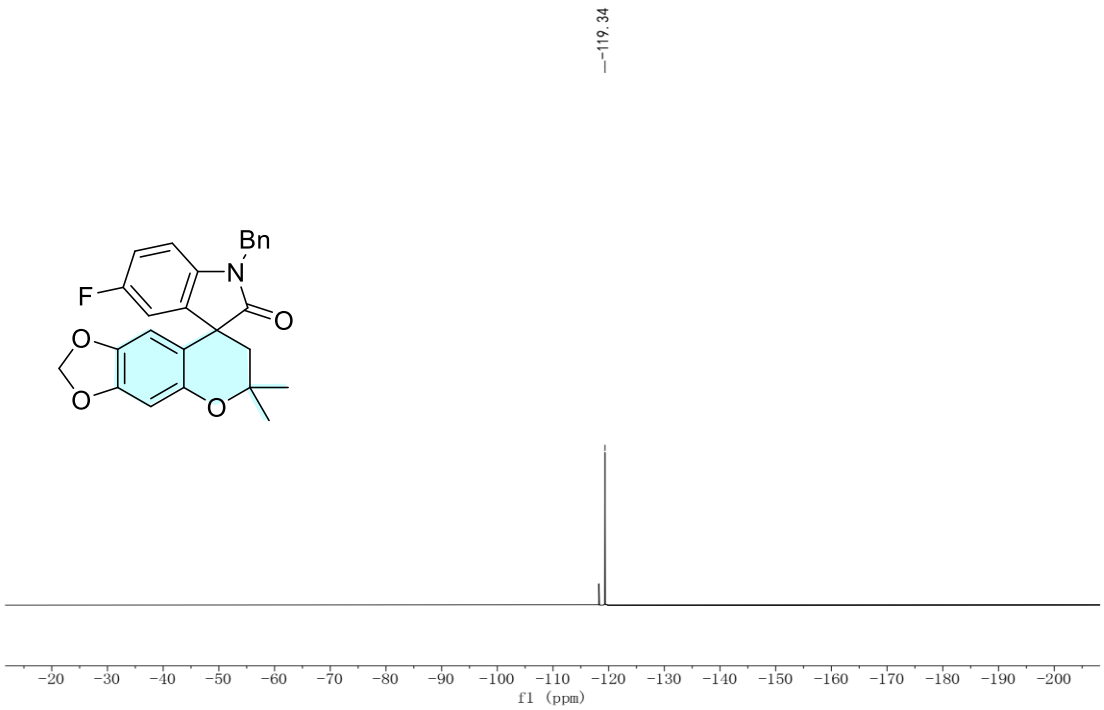




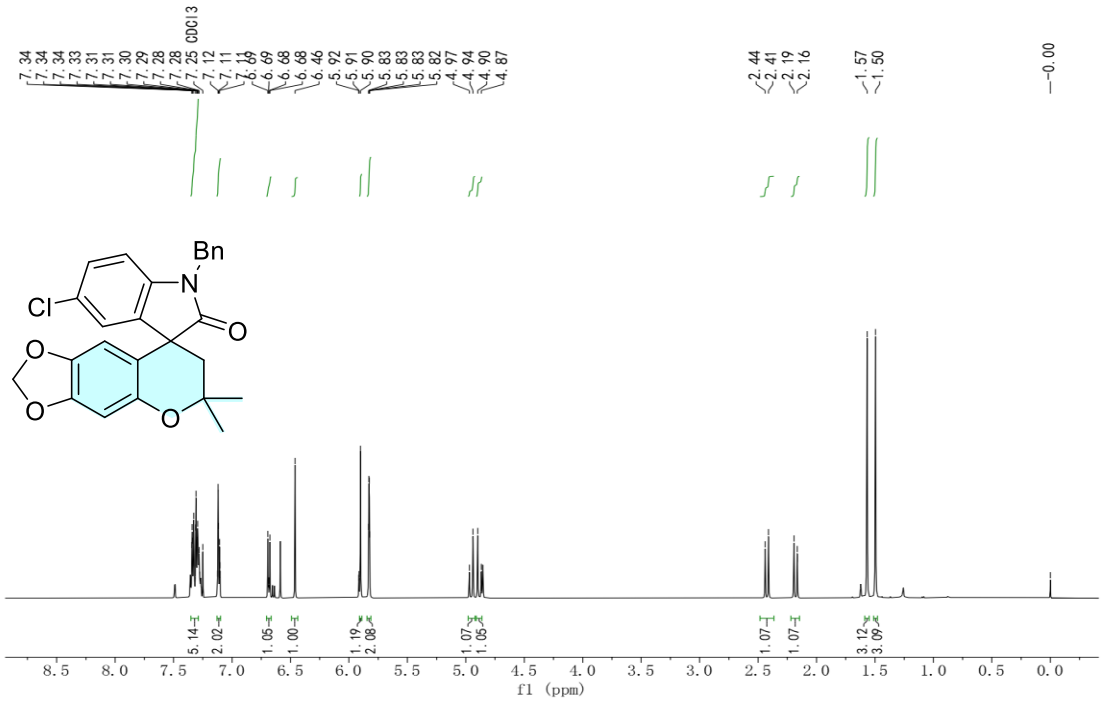
1-benzyl-5-fluoro-6',6'-dimethyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3o)

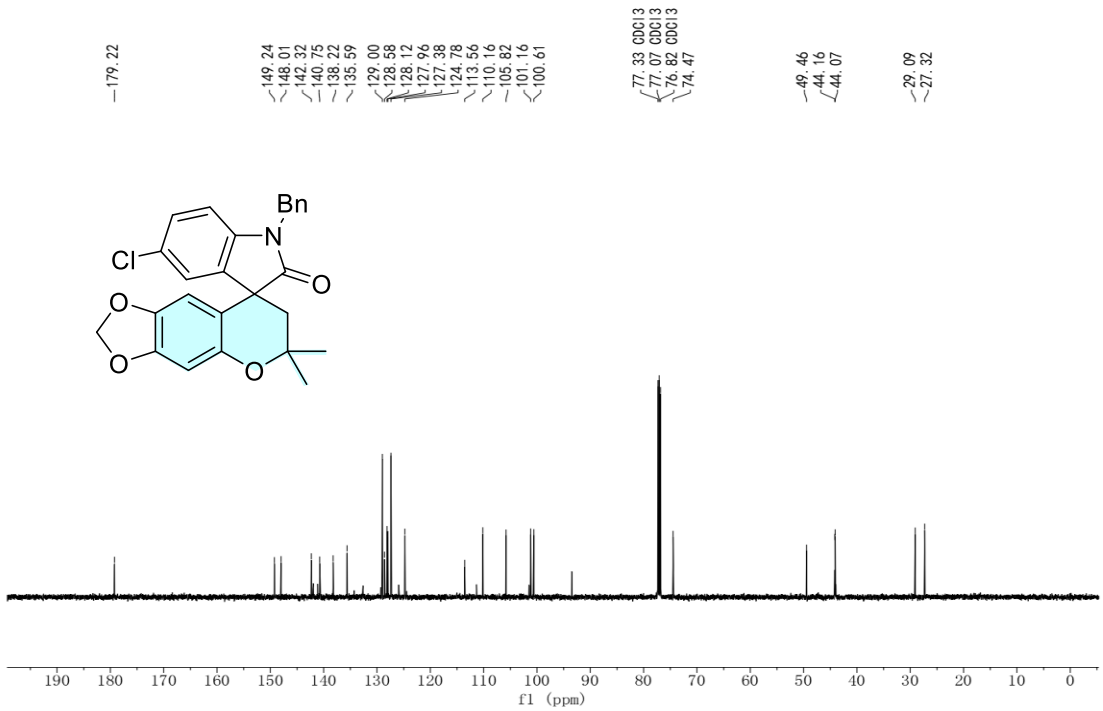




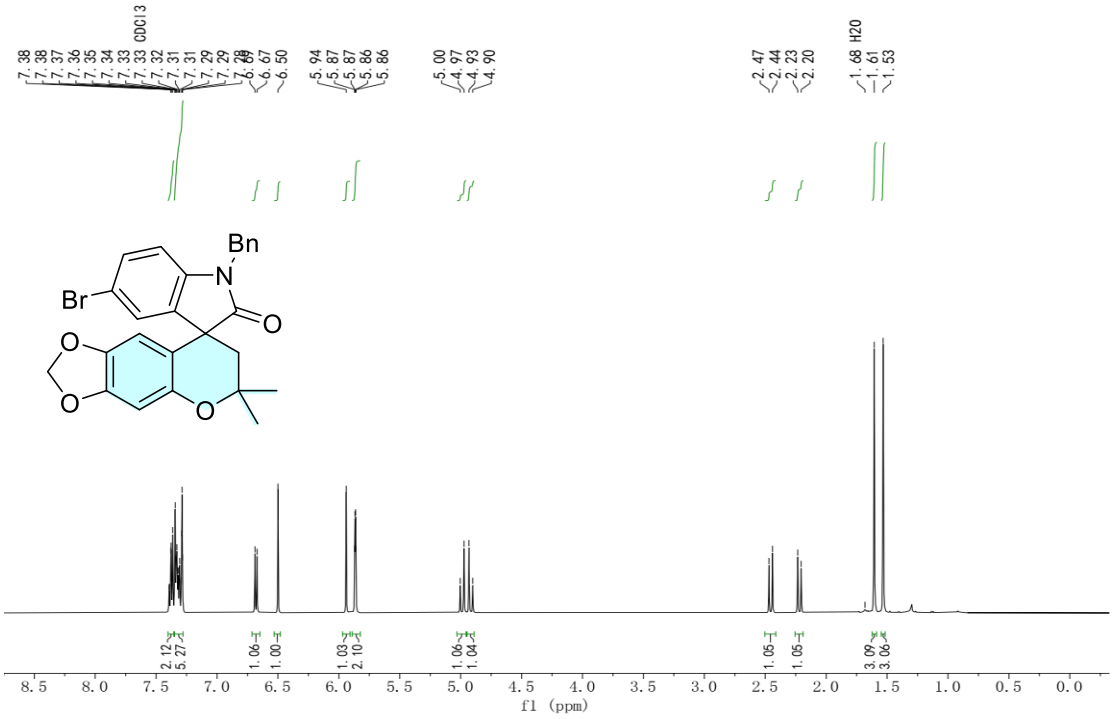

−119.34
Bn
N
F
O
O
O
O
−20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200
f1 (ppm)

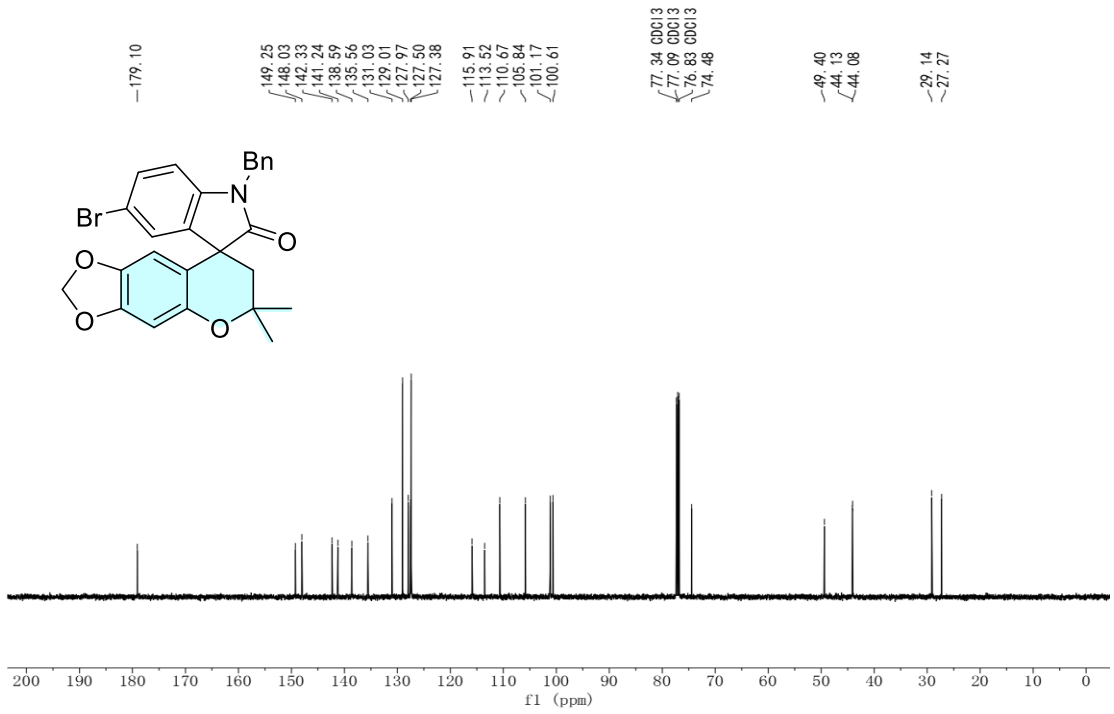
1-benzyl-5-chloro-6',6'-dimethyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3p)



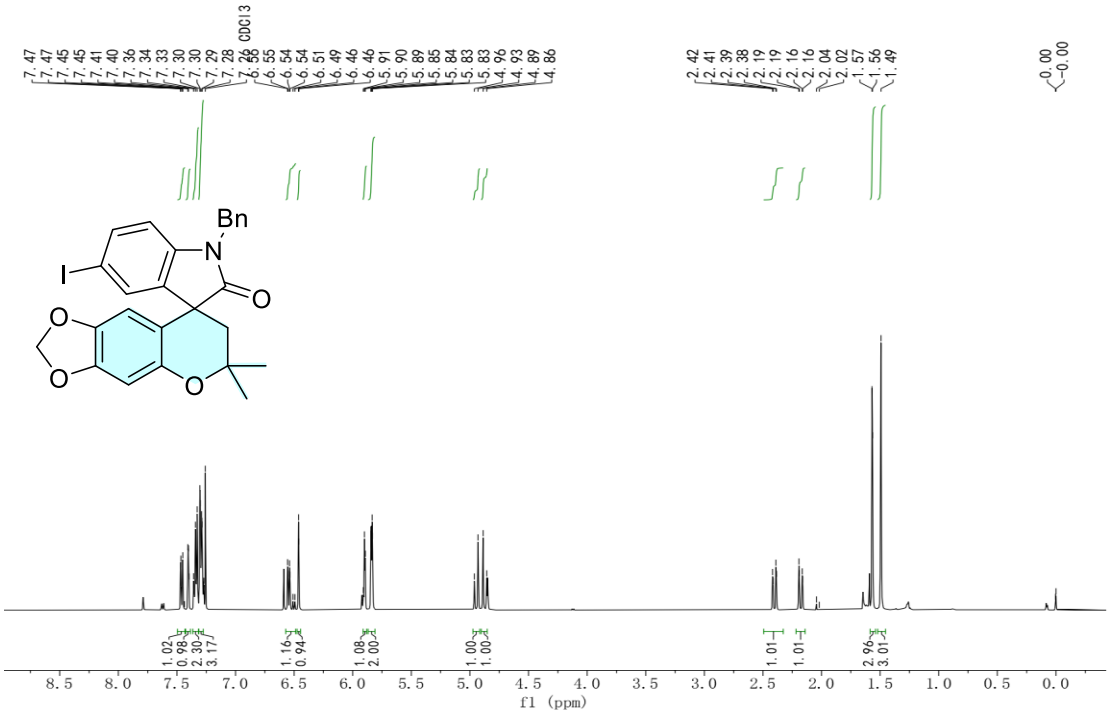


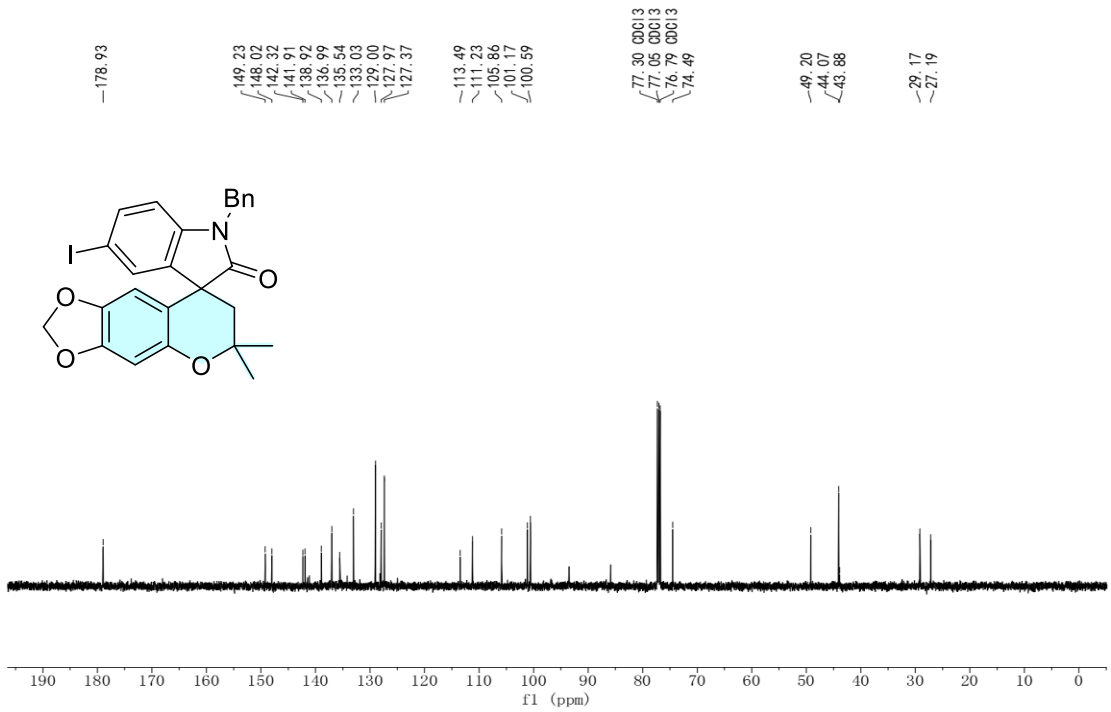
1-benzyl-5-bromo-6',6'-dimethyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3q)



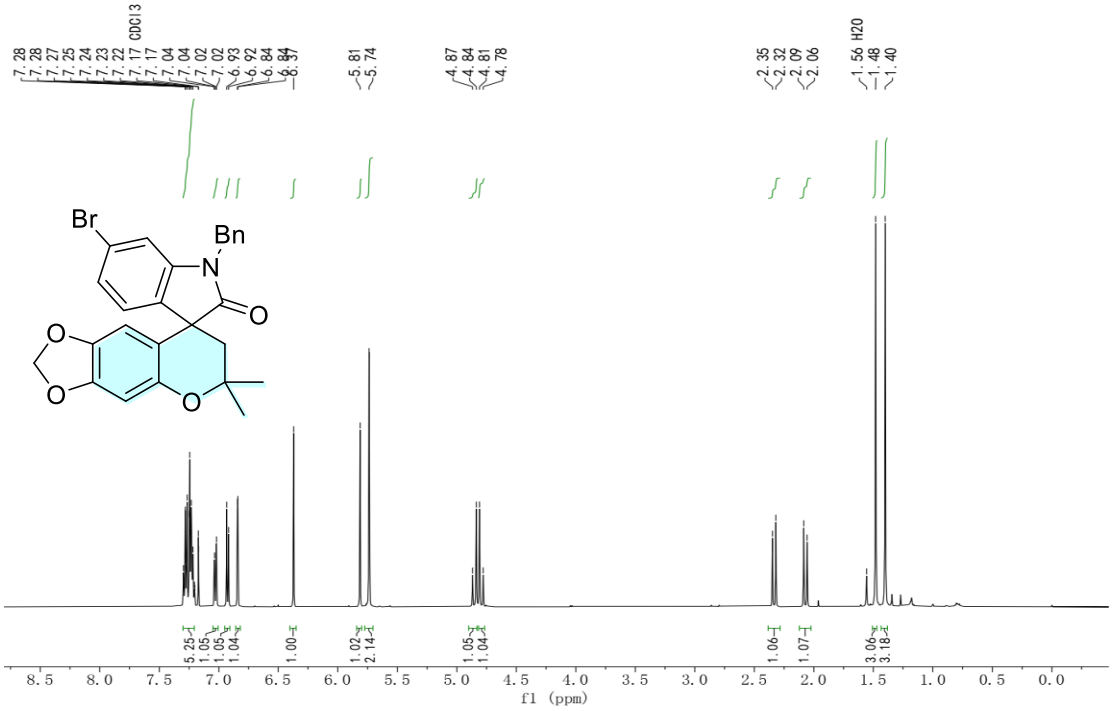


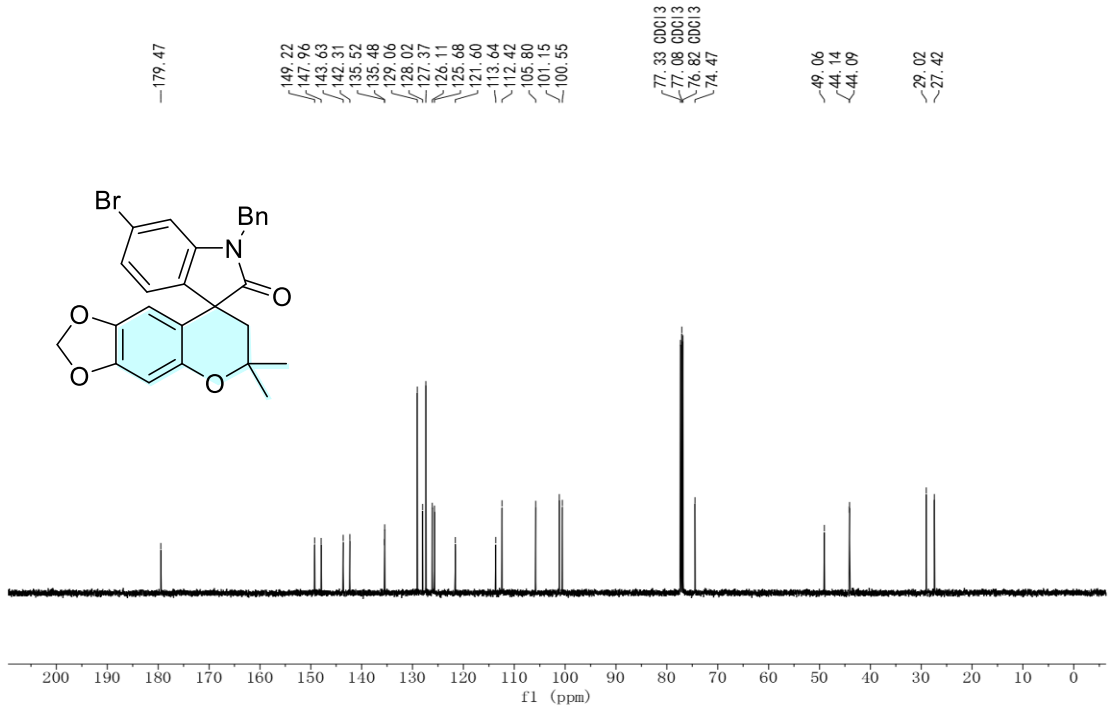
1-benzyl-5-iodo-6',6'-dimethyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3r)



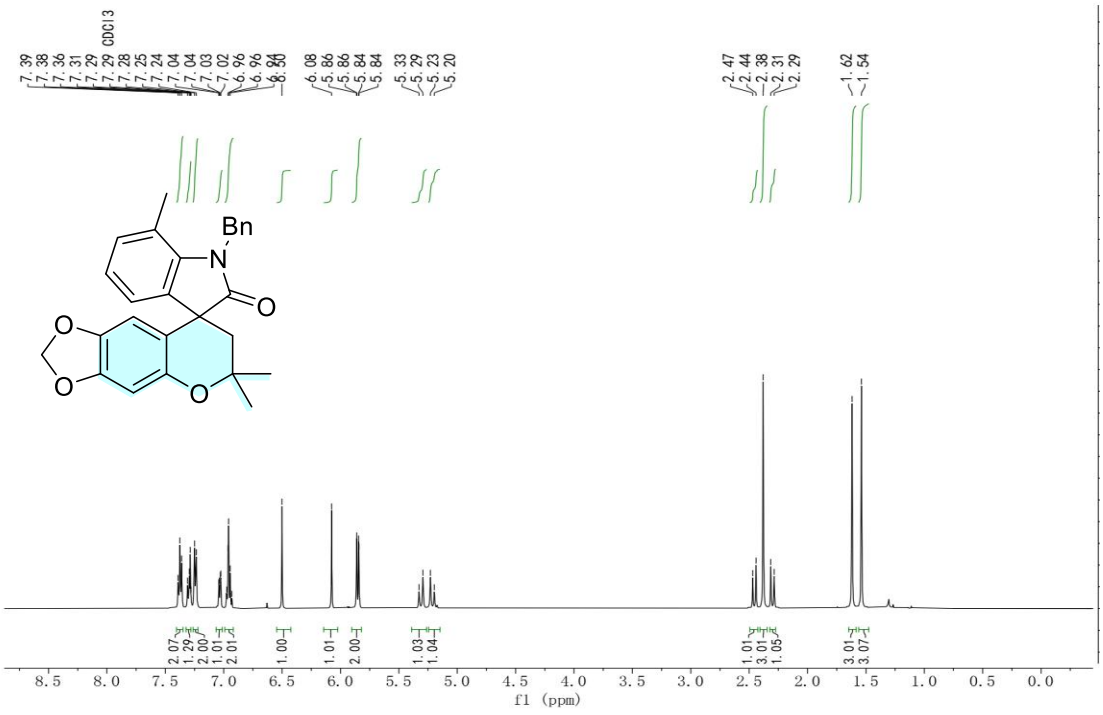


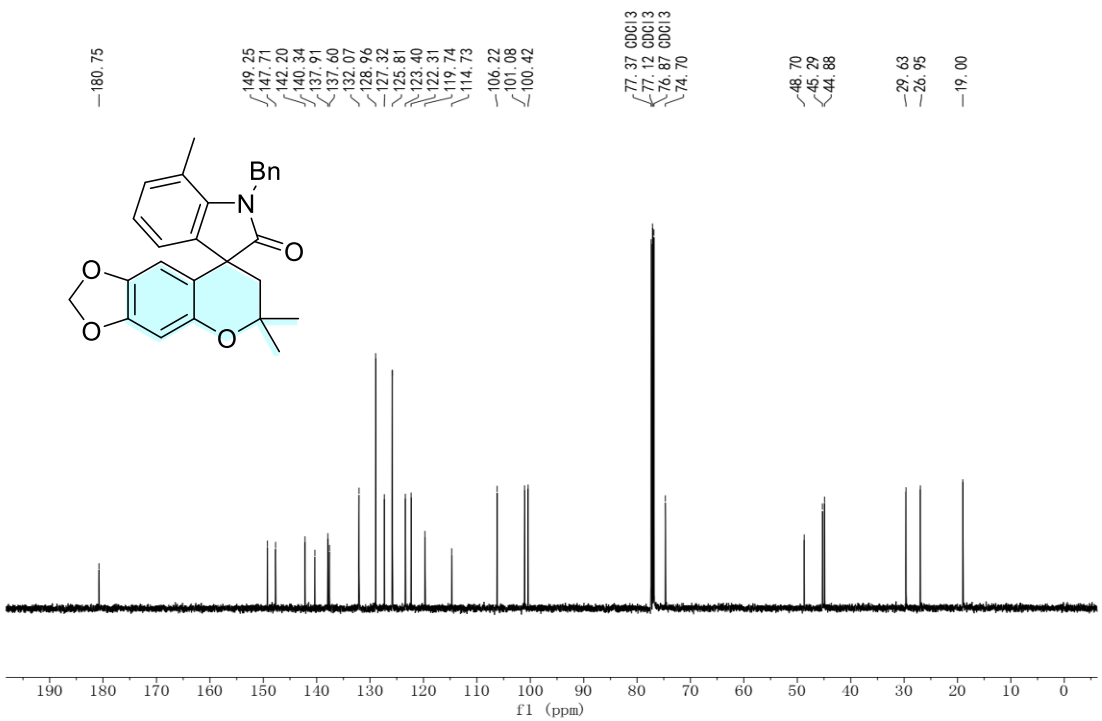
1-benzyl-6-bromo-6',6'-dimethyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3s)



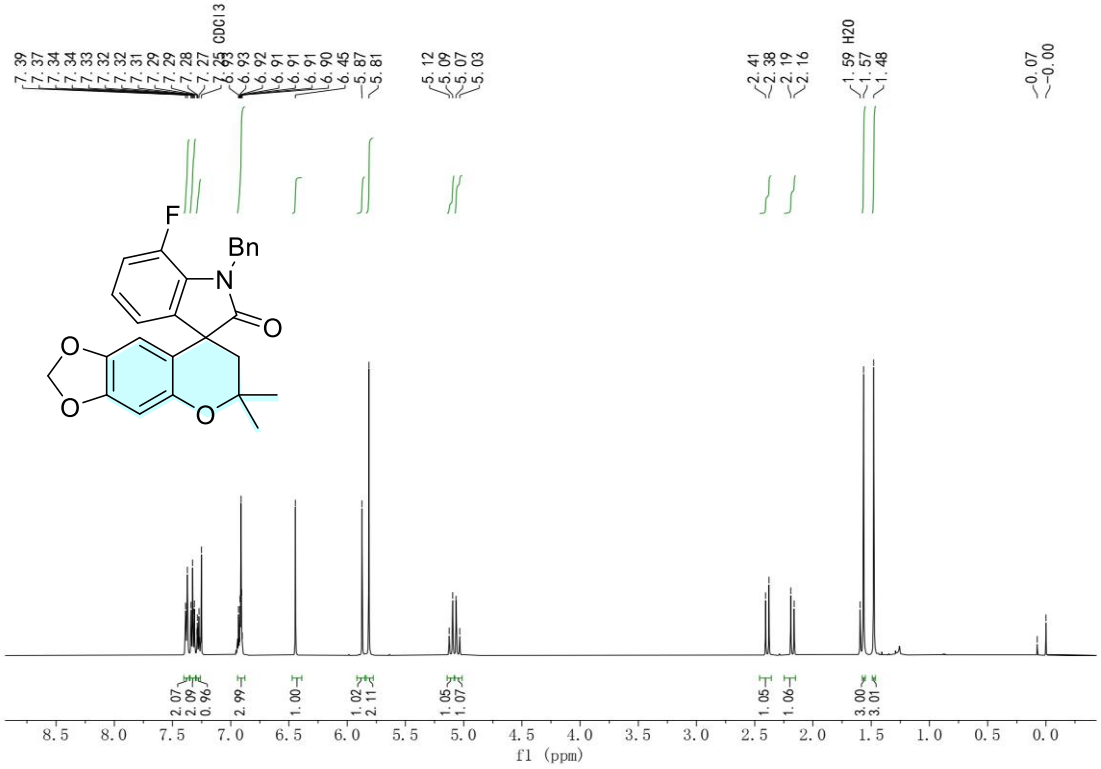


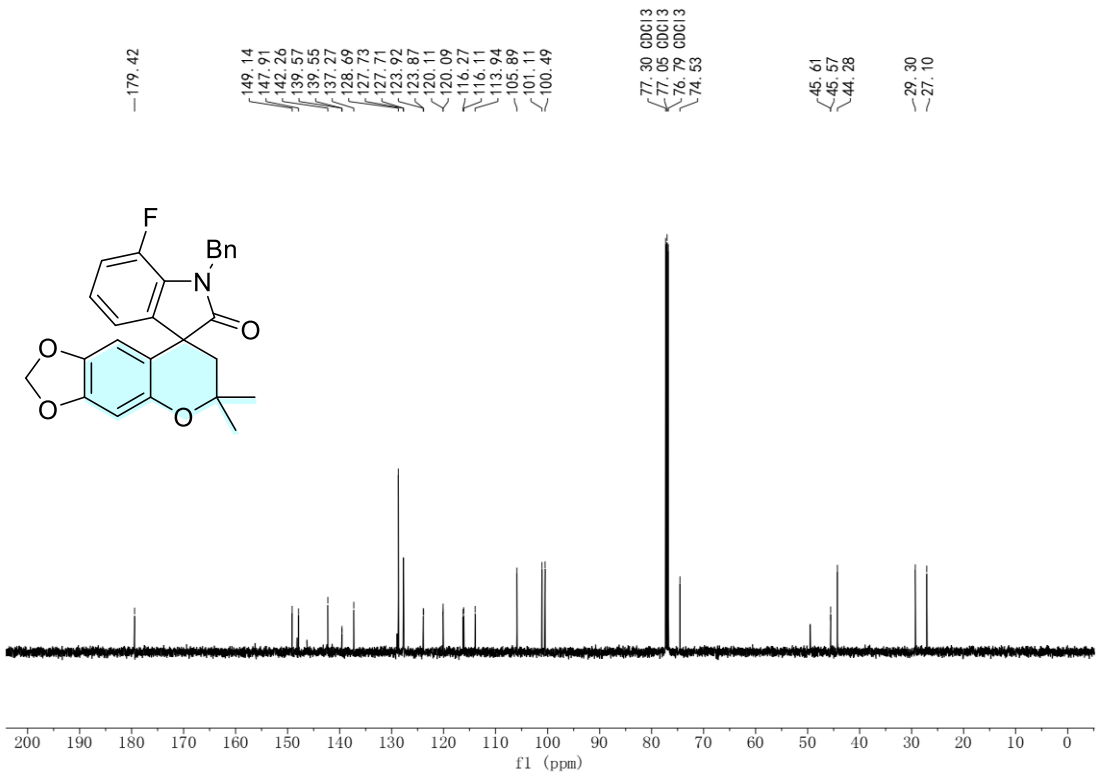
1-benzyl-6',6',7-trimethyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3t)

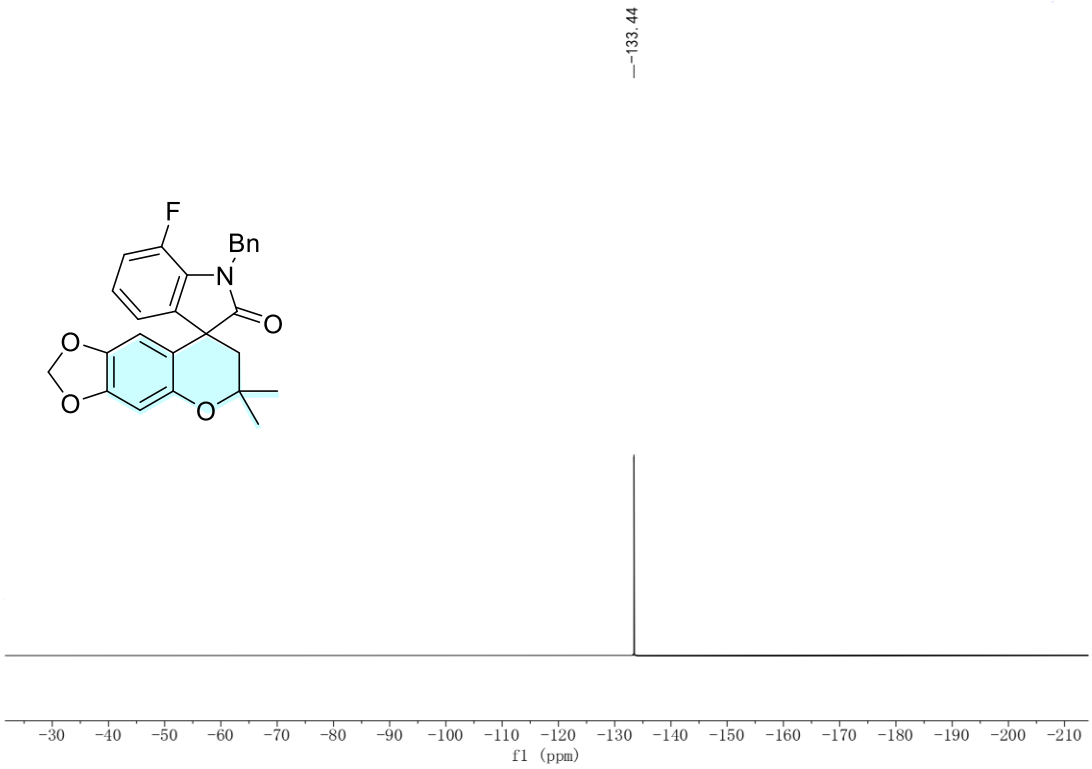




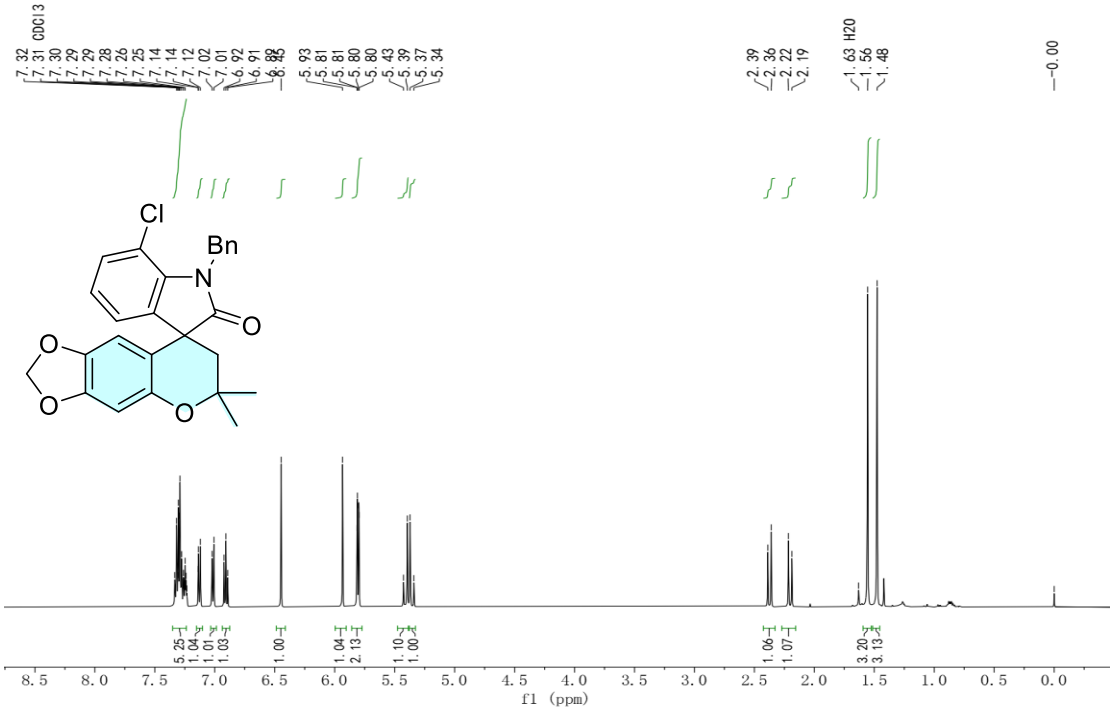
1-benzyl-7-fluoro-6',6'-dimethyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3u)

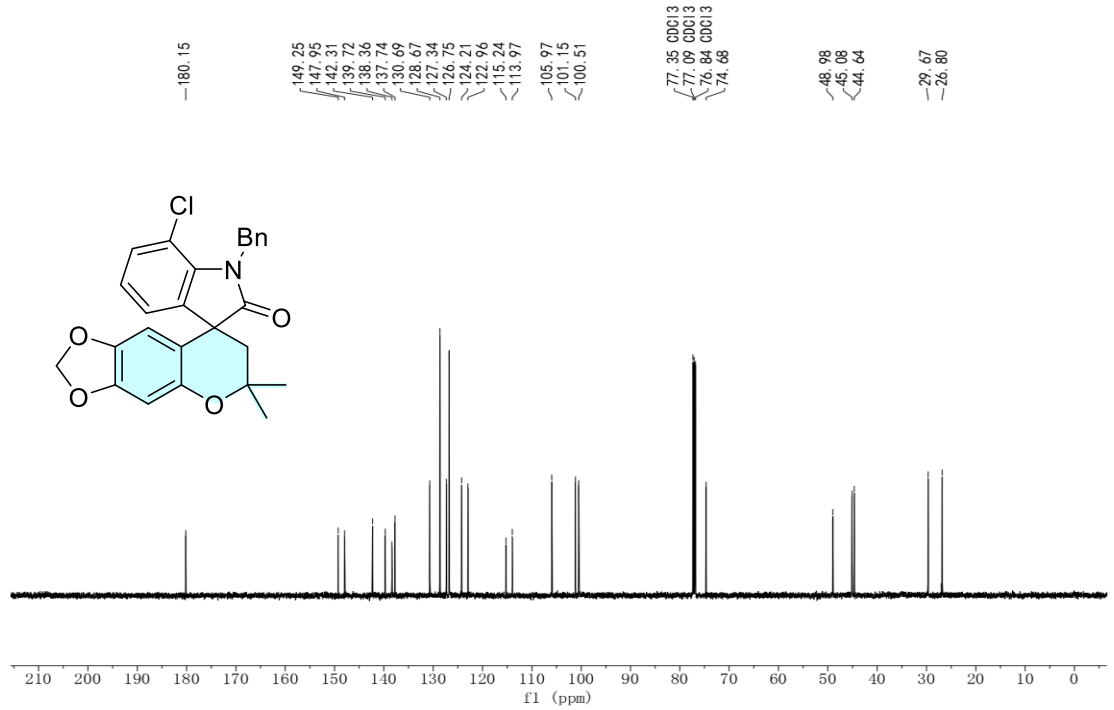




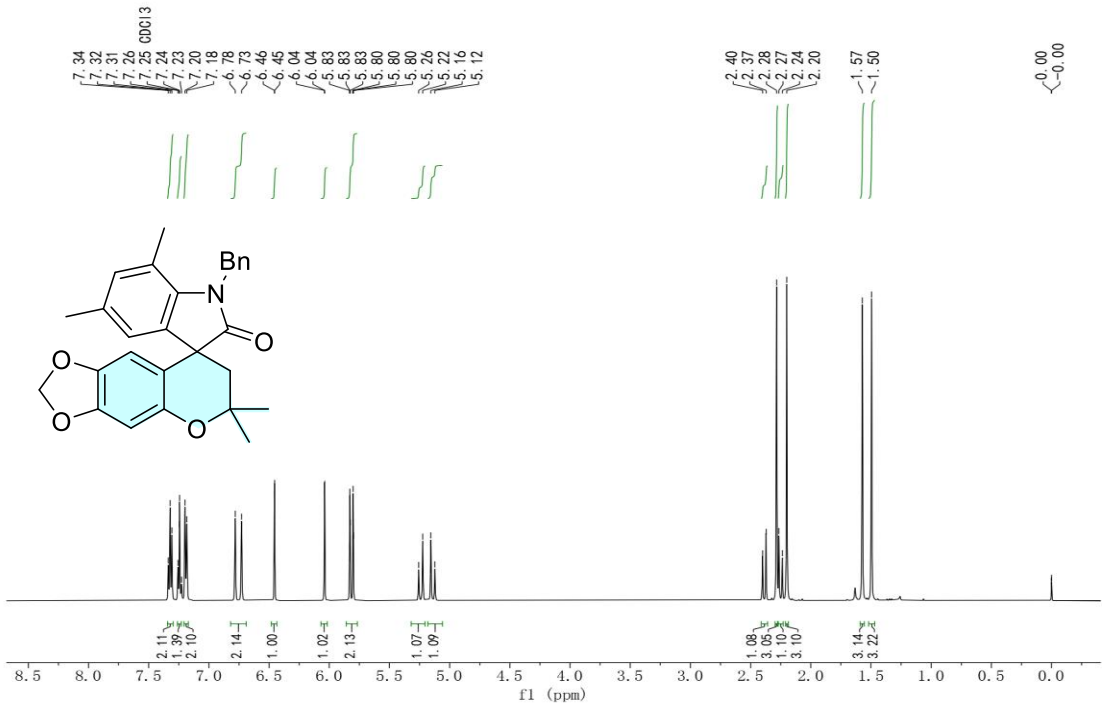

−133.44
F
Bn
N
O
O
O
O
−30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

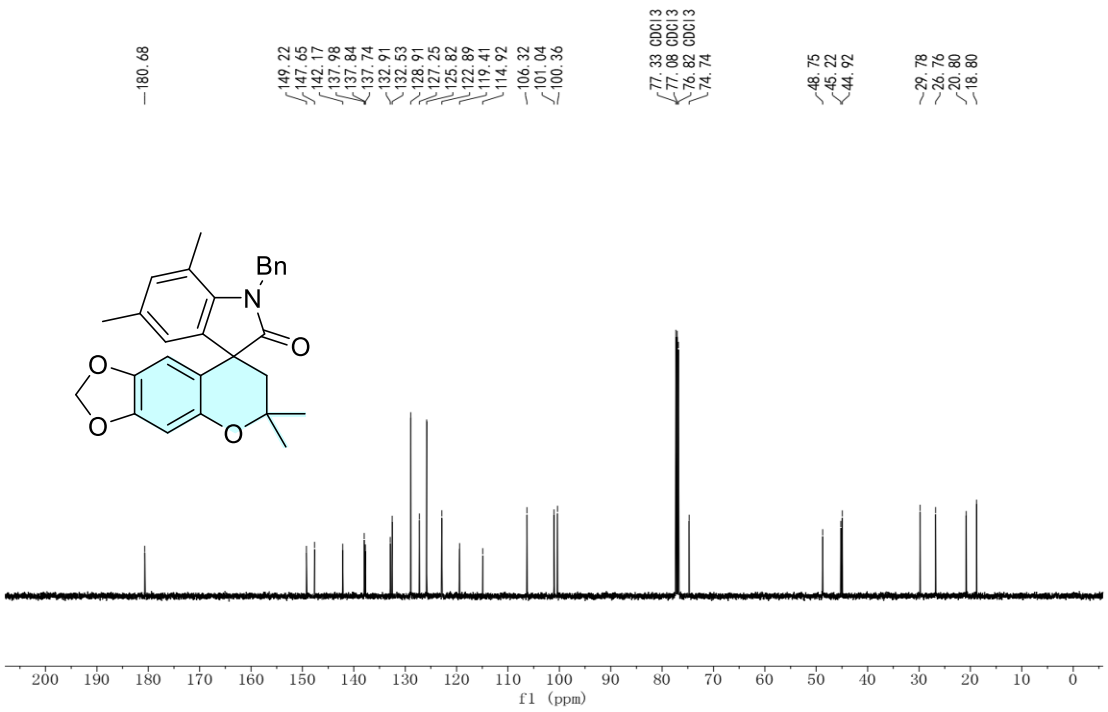
1-benzyl-7-chloro-6',6'-dimethyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3v)



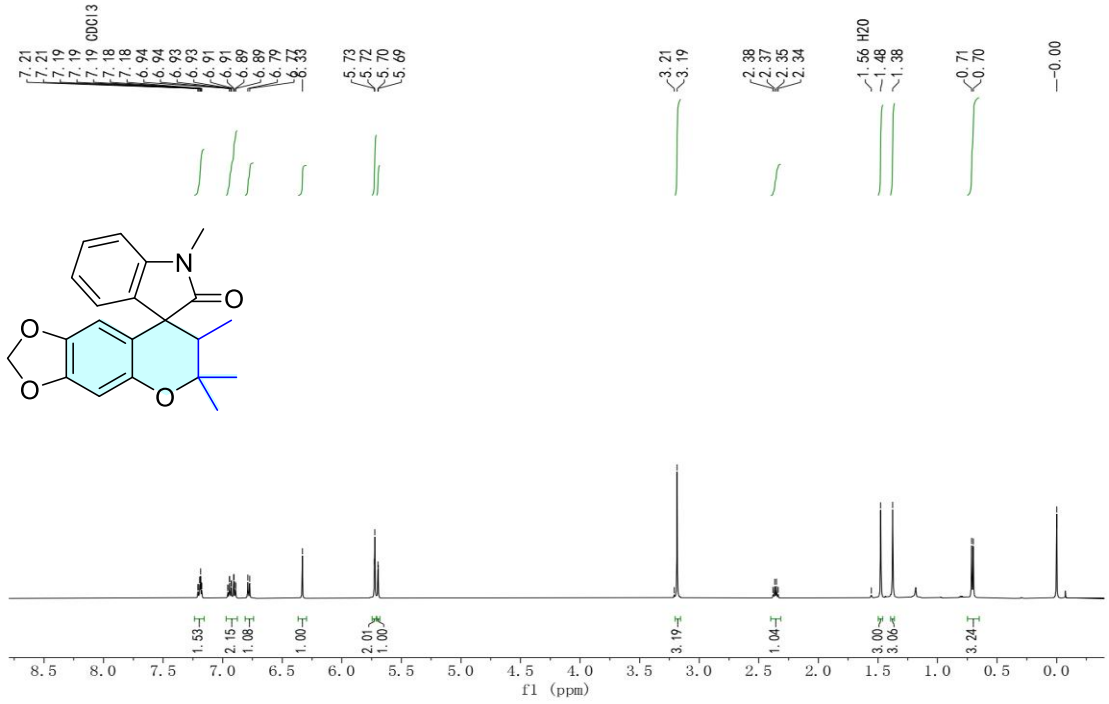


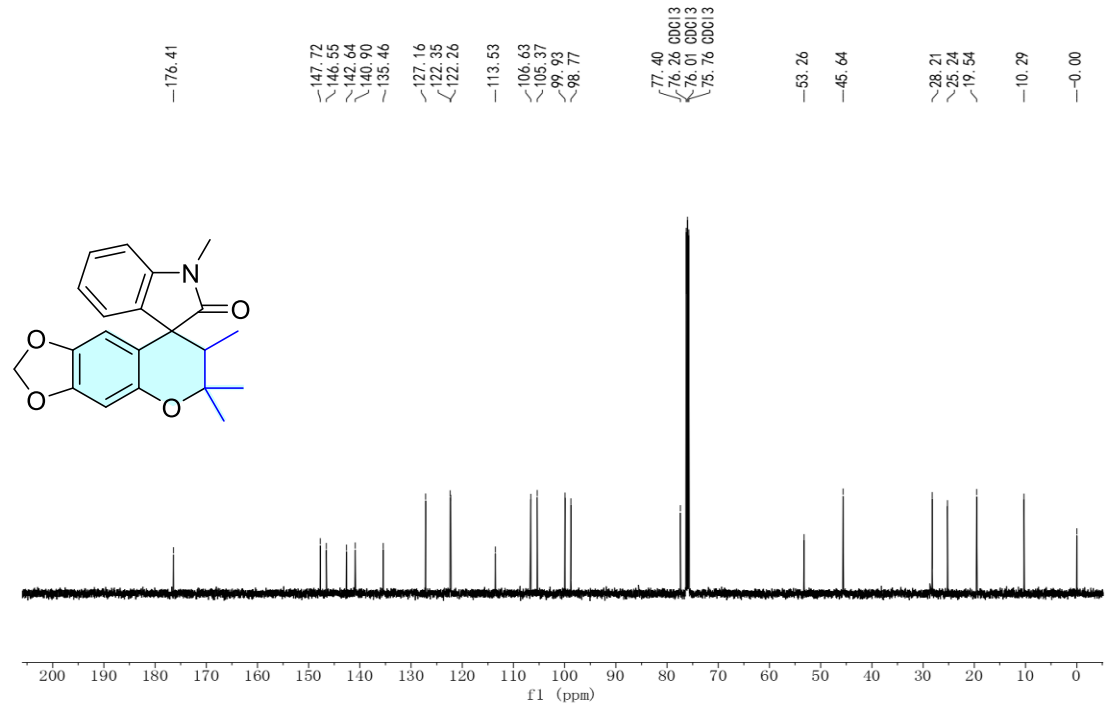
1-benzyl-5,6',6',7-tetramethyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3w)



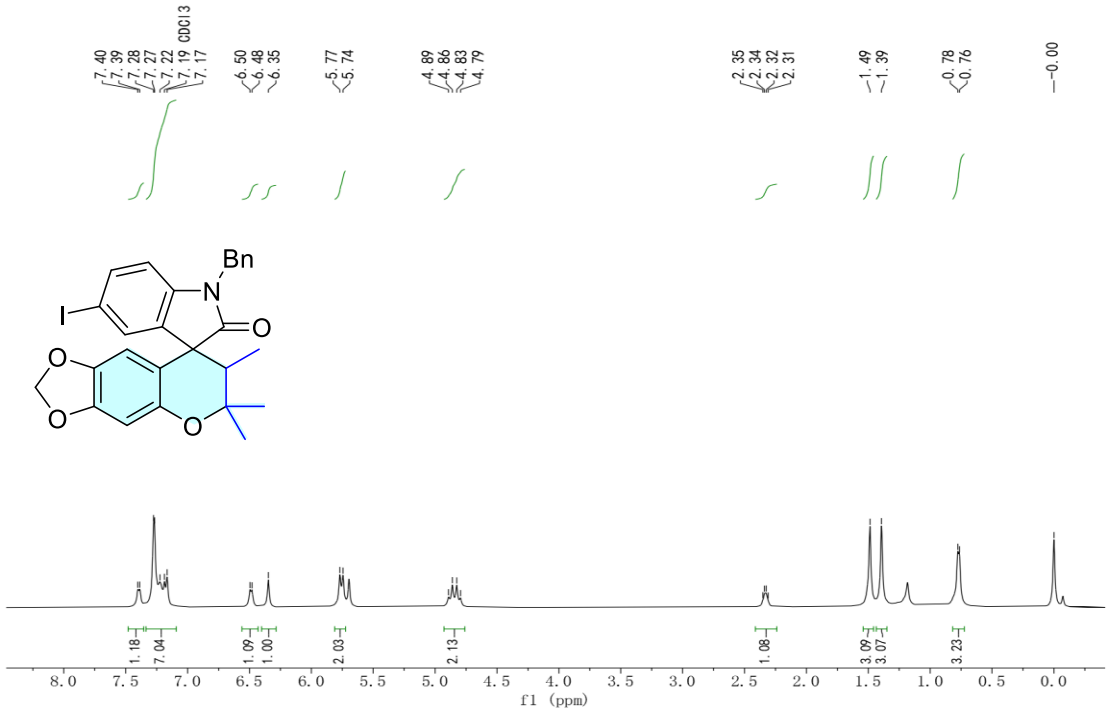


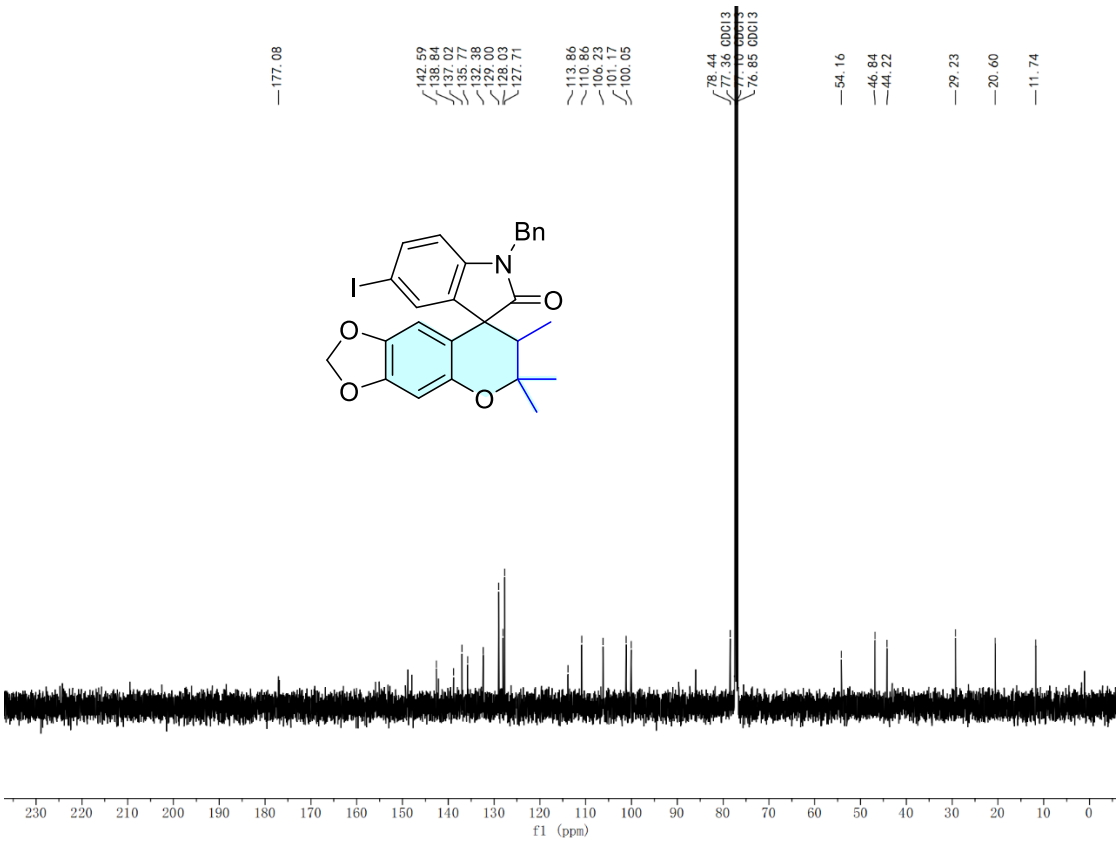
1,6',6',7'-tetramethyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3x)



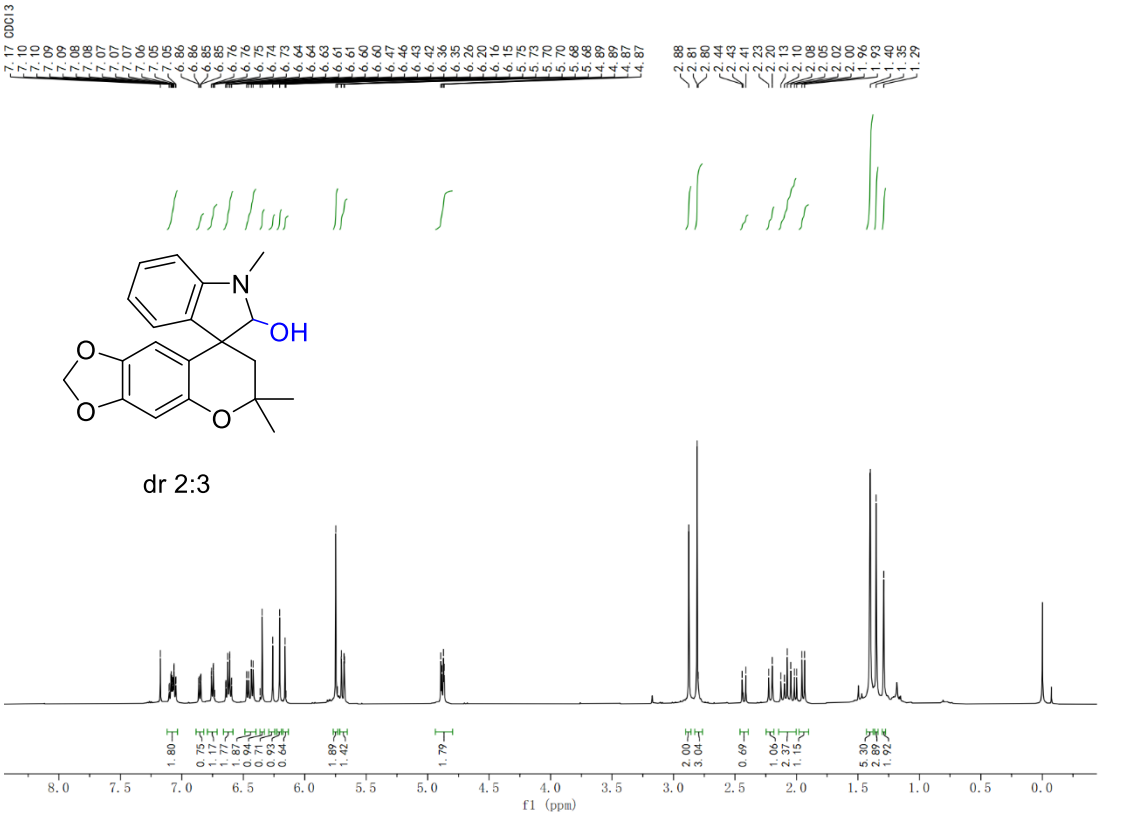


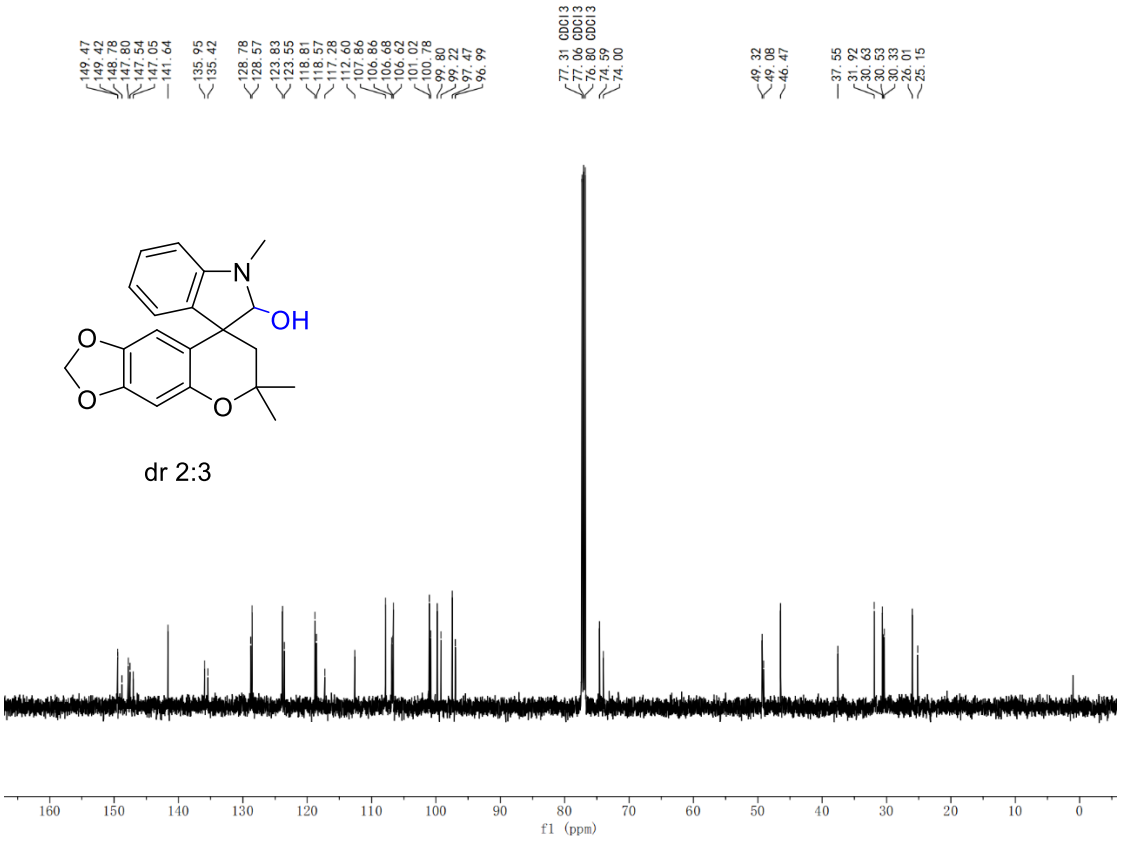
1-benzyl-5-iodo-6',6',7'-trimethyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-one (3y)



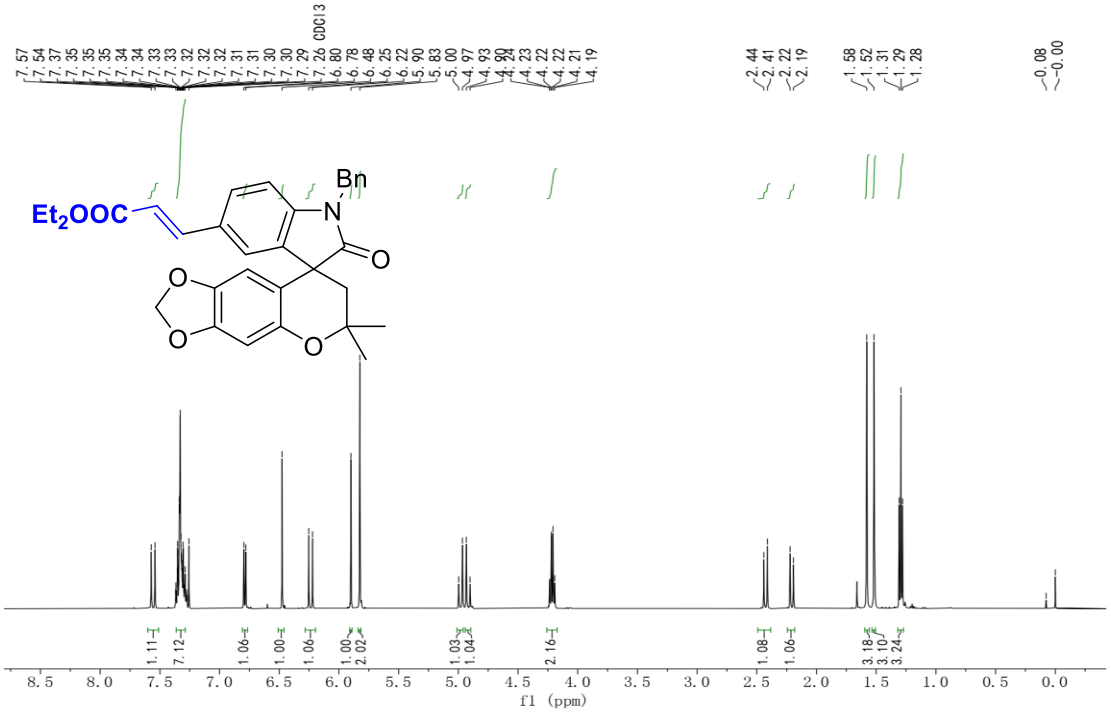


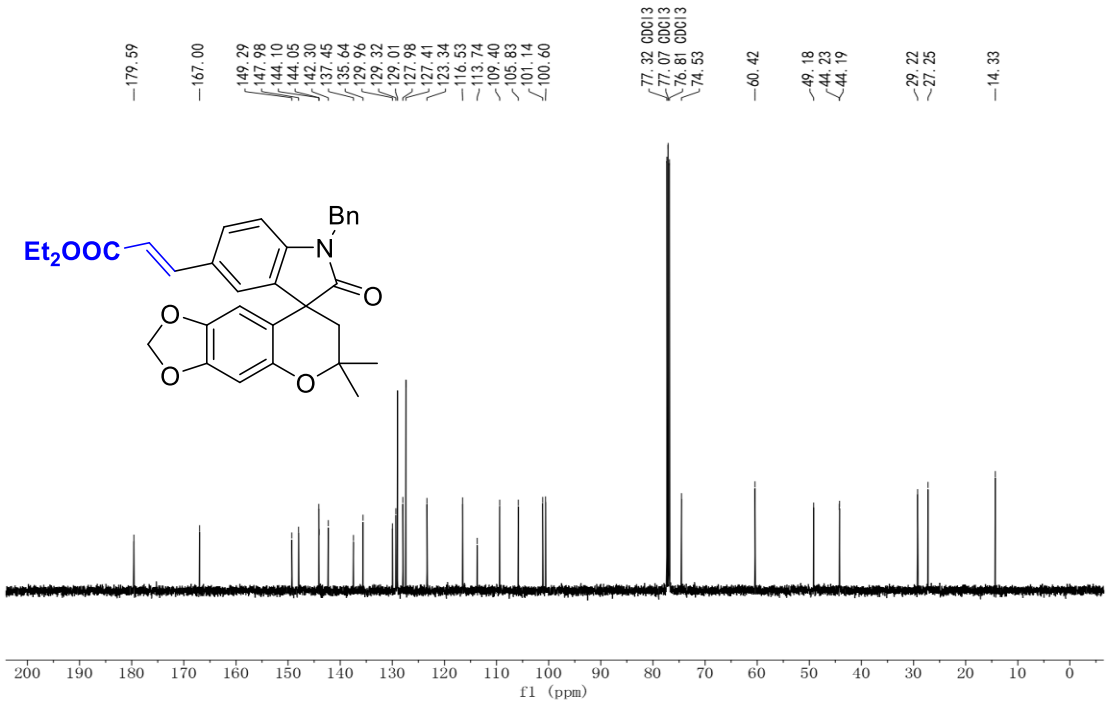
1,6',6'-trimethyl-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-2-ol (5)





ethyl (E)-3-(1-benzyl-6',6'-dimethyl-2-oxo-6',7'-dihydrospiro[indoline-3,8'-[1,3]dioxolo[4,5-g]chromen]-5-yl)acrylate (6)





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