

Supporting Information

Modular Dehydrogenative Cross-nucleophile Coupling for Direct Construction of Tetrasubstituted Carbons

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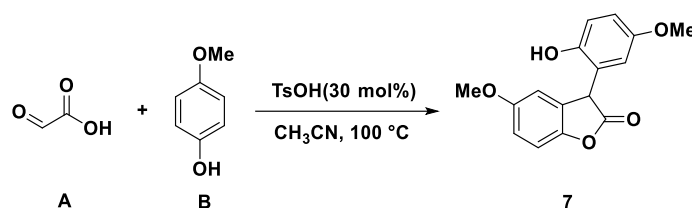
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1. General Information

Unless otherwise noted, all reagents and solvents were purchased from the commercial sources (from Adamas-beta) and used as received. Thin layer chromatography (TLC) was used to monitor the reaction on Merck 60 F254 precoated silica gel plate (0.2 mm thickness). TLC spots were visualized by UV-light irradiation on Spectroline Model ENF-24061/F 254 nm. The products were purified by flash column chromatography (200-300 mesh silica gel) eluted with the gradient of petroleum ether and ethyl acetate. Proton nuclear magnetic resonance spectra (^1H NMR) were recorded on a Bruker 500 MHz or 400 MHz NMR spectrometer (CDCl_3 or $\text{DMSO}-d_6$ 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. 3-(2-hydroxyphenyl)indolin-2-ones were prepared according to literature.¹

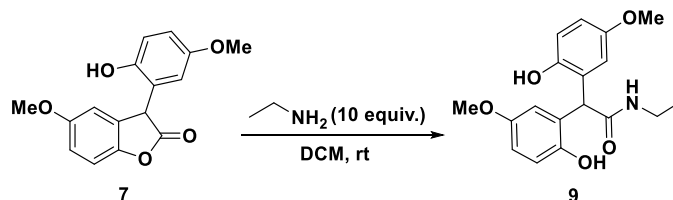
2. General Procedure

2.1 General Procedure for Construction of 3-(2-Hydroxyphenyl)benzofuran-2(3H)-one **7**



A round-bottom flask was charged with glyoxylic acid **A** (5 mmol), 4-methoxyphenol **B** (10 mmol), *p*-toluenesulfonic acid (30 mol%), and CH_3CN (20 mL). The mixture was stirred at $100\text{ }^\circ\text{C}$ for 12 h. Upon completion of the reaction as indicated by TLC analysis, H_2O (20 mL) was added dropwise to the system and the resulting solution was extracted with EtOAc (20 mL \times 3). The combined organic extracts were dried with anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate, 5:1) to afford the desired 3-(2-hydroxyphenyl)benzofuran-2(3H)-one **7**.

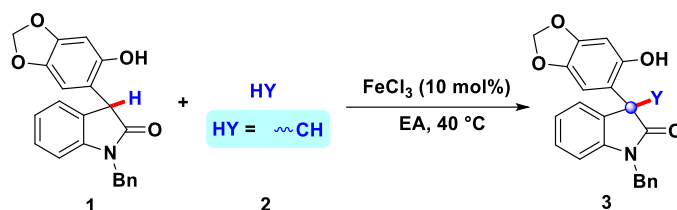
2.2 General Procedure for Construction of *N*-ethyl-2,2-bis(2-hydroxyphenyl)acetamide **9**



A round-bottom flask was charged with 3-(2-hydroxyphenyl)benzofuran-2(3H)-one **7** (1 mmol), ethylamine (10 mmol), and DCM (10 mL). The mixture was stirred at room temperature for 10 h. Upon completion of the reaction as indicated by TLC analysis, H_2O (10 mL) was added dropwise to the system and the resulting solution was extracted with DCM (10 mL \times 3). The combined organic extracts were dried with anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by flash

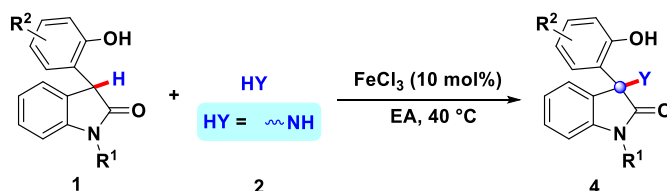
column chromatography on silica gel (petroleum ether: ethyl acetate, 2:1) to afford the desired *N*-ethyl-2,2-bis(2-hydroxyphenyl)acetamide **9**.

2.3 General Procedure for Construction of the Lactam Derivatives 3



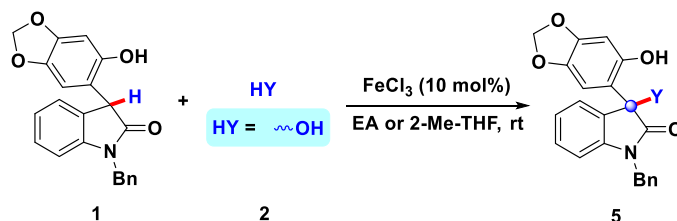
A tube was charged with 3-(2-hydroxyphenyl)indolin-2-one **1** (0.13 mmol), carbon-containing nucleophiles **2** (0.1 mmol), FeCl₃ (10 mol%), and EA (3.0 mL). The mixture was stirred at 40 °C. Upon completion of the reaction as indicated by TLC analysis, the mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate, 8:1) to afford the desired the lactam derivatives **3a-3l**.

2.4 General Procedure for Construction of the Lactam Derivatives 4



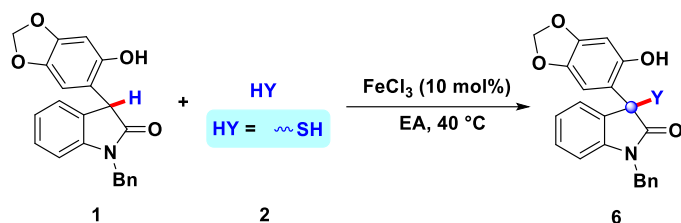
A tube was charged with 3-(2-hydroxyphenyl)indolin-2-one **1** (0.1 mmol), nitrogen-containing nucleophiles **2** (5 equiv., 0.5 mmol), FeCl₃ (10 mol%), and EA (3.0 mL). The mixture was stirred at 40 °C. Upon completion of the reaction as indicated by TLC analysis, the mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate, 20:1) to afford the desired the lactam derivatives **4a-4l**.

2.5 General Procedure for Construction of the Lactam Derivatives 5



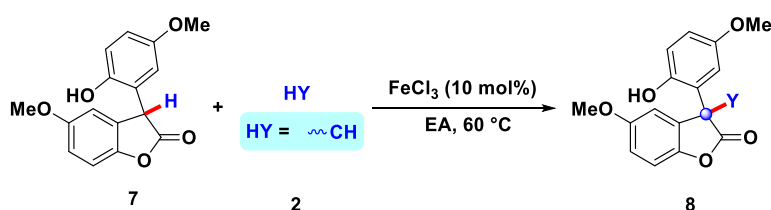
A tube was charged with 3-(2-hydroxyphenyl)indolin-2-one **1** (0.1 mmol), oxygen-containing nucleophiles **2** (0.2 mL), FeCl₃ (10 mol%), and EA (2.8 mL for **5a** and **5b**) or 2-Me-THF (2.8 mL for **5c-5j**). The mixture was stirred at room temperature. Upon completion of the reaction as indicated by TLC analysis, the mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate, 10:1) to afford the desired the lactam derivatives **5a-5j**.

2.6 General Procedure for Construction of the Lactam Derivatives 6



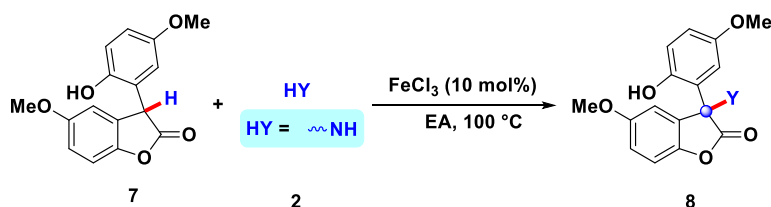
A tube was charged with 3-(2-hydroxyphenyl)indolin-2-one **1** (0.1 mmol), sulfur-containing nucleophiles **2** (2 equiv., 0.2 mmol), FeCl₃ (10 mol%), and EA (3.0 mL). The mixture was stirred at 40 °C. Upon completion of the reaction as indicated by TLC analysis, the mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate, 8:1) to afford the desired the lactam derivatives **6a-6f**.

2.7 General Procedure for Construction of the Lactone Derivatives **8**



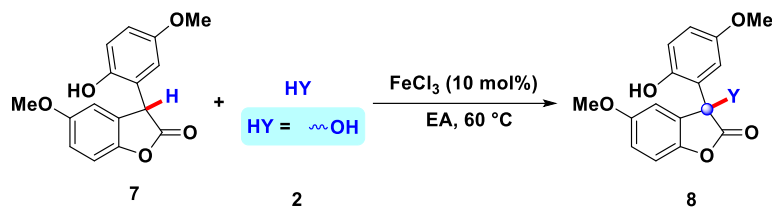
A tube was charged with 3-(2-hydroxyphenyl)benzofuran-2(3H)-one **7** (0.13 mmol), carbon-containing nucleophiles **2** (0.1 mmol), FeCl₃ (10 mol%), and EA (3.0 mL). The mixture was stirred at 60 °C. Upon completion of the reaction as indicated by TLC analysis, the mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate, 8:1) to afford the desired the lactone derivatives **8a-8c**.

2.8 General Procedure for Construction of the Lactone Derivatives **8**



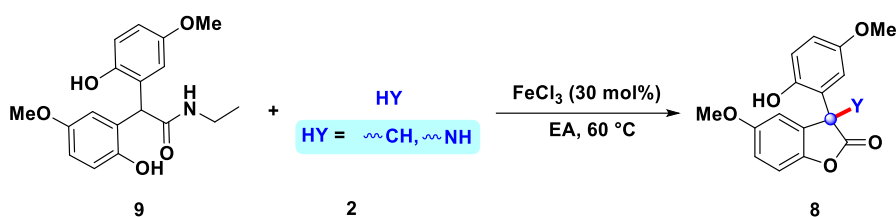
A sealed tube was charged with 3-(2-hydroxyphenyl)benzofuran-2(3H)-one **7** (0.1 mmol), nitrogen-containing nucleophiles **2** (5 equiv., 0.5 mmol), FeCl₃ (10 mol%), and EA (3.0 mL). The mixture was stirred at 100 °C. Upon completion of the reaction as indicated by TLC analysis, the mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate, 15:1) to afford the desired the lactone derivatives **8d-8e**.

2.9 General Procedure for Construction of the Lactone Derivatives **8**



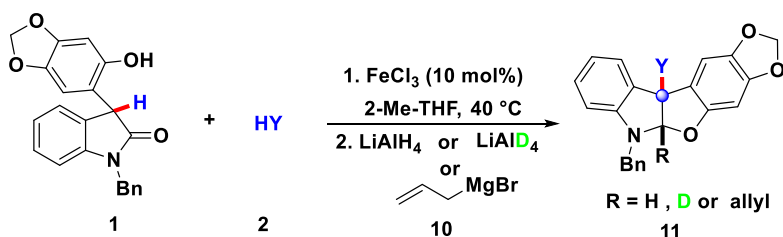
A tube was charged with 3-(2-hydroxyphenyl)benzofuran-2(3*H*)-one **7** (0.1 mmol), oxygen-containing nucleophiles **2** (0.2 mL), FeCl₃ (10 mol%), and EA (3.0 mL). The mixture was stirred at 60 °C. Upon completion of the reaction as indicated by TLC analysis, the mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate, 10:1) to afford the desired the lactone derivative **8f**.

2.10 General Procedure for Construction of the Lactone Derivatives **8**



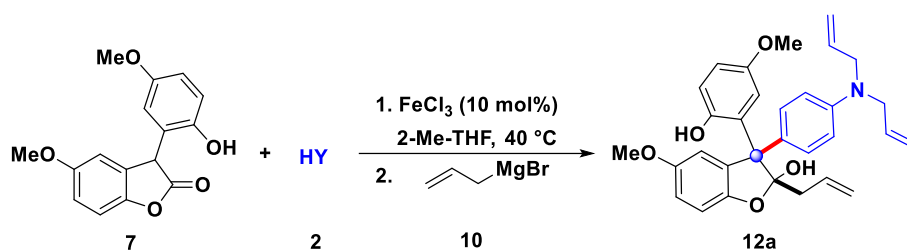
A sealed tube was charged with N-ethyl-2,2-bis(2-hydroxyphenyl)acetamide **9** (0.1 mmol), carbon-containing nucleophiles **2** (1.5 equiv., 0.15 mmol) or nitrogen-containing nucleophiles **2** (5 equiv. 0.5 mmol), FeCl₃ (30 mol%), and EA (3.0 mL). The mixture was stirred at 100 °C. Upon completion of 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 (petroleum ether: ethyl acetate, 10:1) to afford the desired the lactone derivatives **8a-8e**.

2.11 General Procedure for Synthesis of Benzofuroindoline **11**



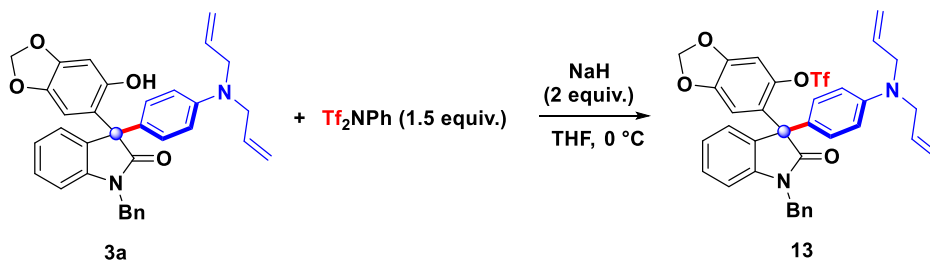
A tube was charged with 3-(2-hydroxyphenyl)indolin-2-one **1** (0.13 mmol), nucleophiles **2** (0.1 mmol), FeCl₃ (10 mol%), and 2-Me-THF (3.0 mL). The mixture was stirred at 40 °C. Upon completion of the reaction as indicated by TLC analysis, H₂O (5 mL) was added dropwise to the system and the resulting solution was extracted with EtOAc (5 mL×3). The combined organic extracts were dried with anhydrous Na₂SO₄ and concentrated in vacuo. The residue could be used in next step without needing to purify. Then LiAlH₄ or LiAlD₄ or allylmagnesium bromide (5 equiv.) was added, and the mixture was stirred in 2-Me-THF (3 mL) at room temperature. 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 (petroleum ether: ethyl acetate, 20:1) to afford the desired the benzofuroindolines **11a-11f**.

2.12 General Procedure for Synthesis of Benzofuran 12



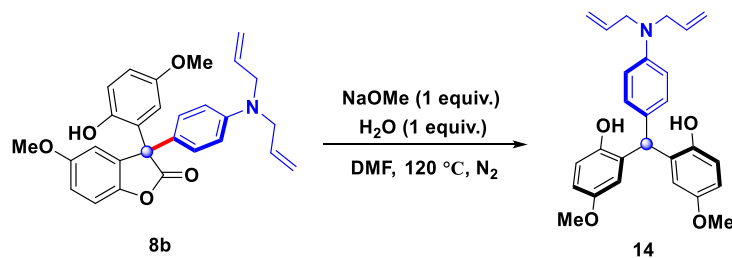
A tube was charged with 3-(2-hydroxyphenyl)benzofuran-2(3*H*)-one **7** (0.13 mmol), nucleophiles **2** (0.1 mmol), FeCl₃ (10 mol%), and 2-Me-THF (3.0 mL). The mixture was stirred at 40 °C. Upon completion of the reaction as indicated by TLC analysis, H₂O (5 mL) was added dropwise to the system and the resulting solution was extracted with EtOAc (5 mL×3). The combined organic extracts were dried with anhydrous Na₂SO₄ and concentrated in vacuo. The residue could be used in next step without needing to purify. Then allylmagnesium bromide (5 equiv.) was added, and the mixture was stirred in 2-Me-THF (3 mL) at room temperature. 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 (petroleum ether: ethyl acetate, 20:1) to afford the desired the benzofuran **12a**.

2.13 General Procedure for Synthesis of the Lactam Derivative 13



To a stirred solution of 3,3-diaryl oxindole **3a** (0.1 mmol) in dry THF (2.0 mL) was added NaH (2 equiv.) at 0 °C, and stirred for 0.5 h. Tf₂NPh (1.5 equiv.) was then added, and the resulting mixture was stirred for 2 h. 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 (petroleum ether: ethyl acetate, 15:1) to give the desired the lactam derivative **13**.

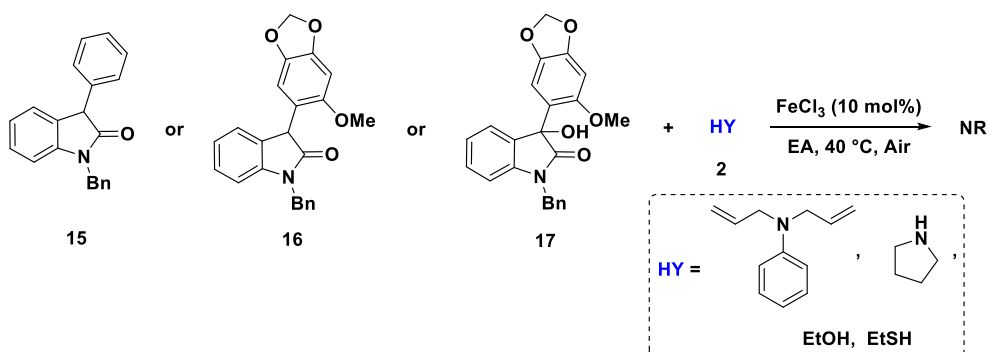
2.14 General Procedure for Synthesis of Triarylmethane 14



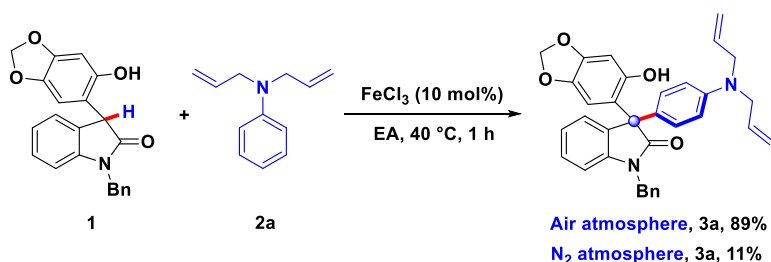
A shrek tube was charged with the lactone derivative **8b** (0.1 mmol), NaOMe (1 equiv.), H₂O (1 equiv.), and DMF (2.0 mL) under N₂ atmosphere. The mixture was stirred at 120 °C. Upon completion of the reaction as indicated by TLC analysis, the mixture was concentrated in vacuum and the residue

was directly purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate, 5:1) to afford the desired triarylmethane **14**.

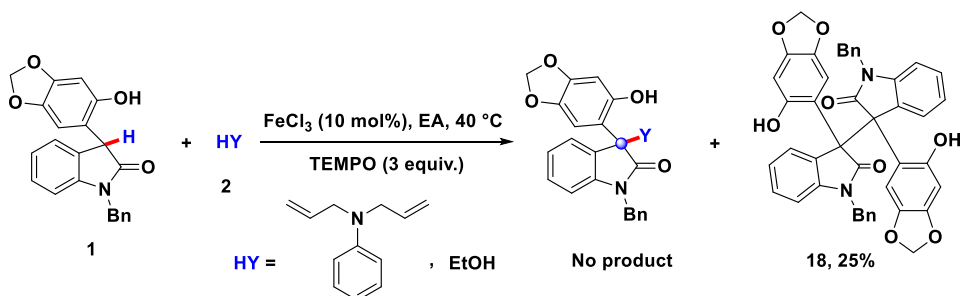
3. Mechanistic Studies



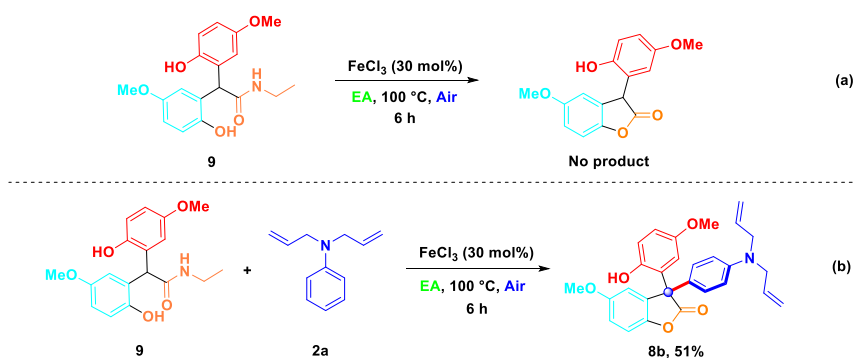
A sealed tube was charged with 3-phenylindolin-2-one **15** or 3-(2-methoxyphenyl)indolin-2-one **16** or 3-hydroxy-3-(2-methoxyphenyl)indolin-2-one **17** (0.1 mmol), nucleophiles **2** (1.5 equiv., 0.15 mmol), FeCl_3 (10 mol%), and EA (3.0 mL). The mixture was stirred at 40 °C. The reaction as indicated by TLC analysis.



A tube was charged with 3-(2-hydroxyphenyl)indolin-2-one **1** (0.13 mmol), nucleophile **2a** (0.1 mmol), FeCl_3 (10 mol%), and EA (3.0 mL) under air or N_2 atmosphere. The mixture was stirred at 40 °C. 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 (petroleum ether: ethyl acetate, 8:1) to afford the desired the lactam derivative **3a** in 89% yield (air) or 11% yield (N_2).

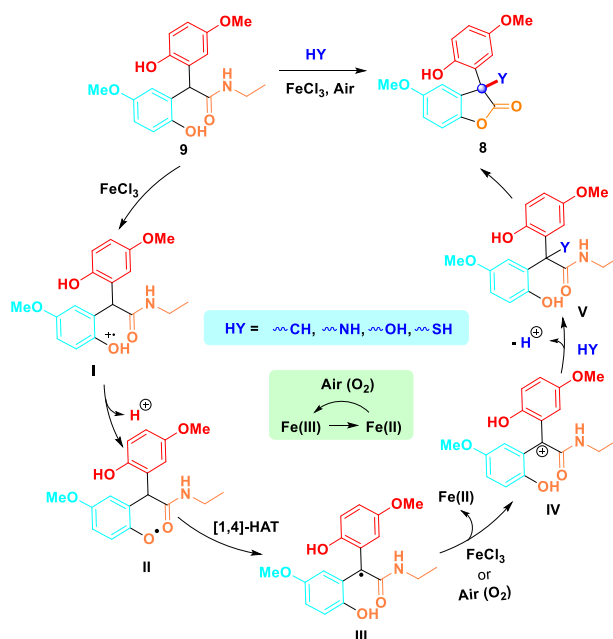


A tube was charged with 3-(2-hydroxyphenyl)indolin-2-one **1** (0.13 mmol), nucleophiles **2** (0.1 mmol), FeCl_3 (10 mol%), TEMPO (3 equiv.), and EA (3.0 mL). The mixture was stirred at 40 °C. The reaction as indicated by TLC analysis, the mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate, 3:1) to afford the desired dimeric product **18**.

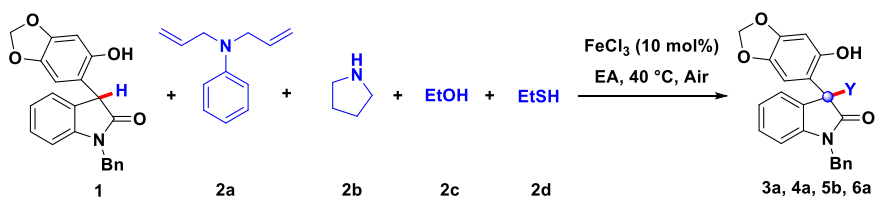


The reaction process of the cyclization for formation of lactones was further investigated. The acyclic substrate **9** bearing *ortho*-hydroxyl benzylic tertiary C(sp³)-H was subjected to the optimal reaction conditions without adding nucleophile. As a result, no cyclic product was observed and substrate **9** was decomposed in 6 h (a). When nucleophile **2a** was added, the cascade CDC/cyclization process took place fluently at the same time (6 h), giving the 3,3-disubstituted lactone **8b** in 51% yield (b). These results indicated that the intramolecular cyclization occurred followed by the CDC process to form the thermodynamically stable lactone (Scheme S1).

Scheme S1. Proposed Mechanism for Formation of Lactone **8** From Acyclic Substrate **9**.



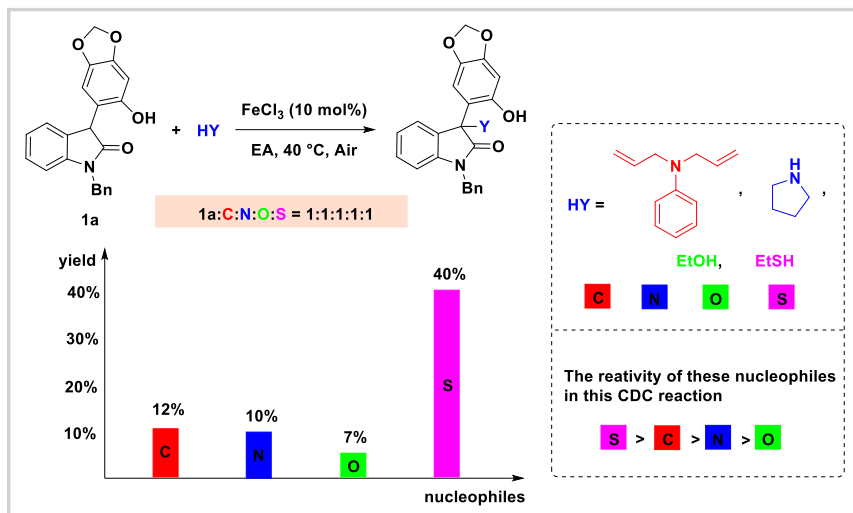
4. Competing Experiments



A tube was charged with 3-(2-hydroxyphenyl)indolin-2-one **1** (0.1 mmol), nucleophile **2a** (0.1 mmol), nucleophile **2b** (0.1 mmol), nucleophile **2c** (0.1 mmol), nucleophile **2d** (0.1 mmol), FeCl₃ (10 mol%), and EA (3.0 mL). The mixture was stirred at 40 °C. The reaction as indicated by TLC analysis,

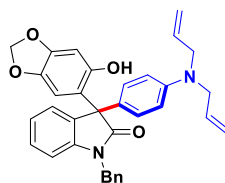
the mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate, 10:1) to afford the desired the lactam derivatives **3a** (12% yield), **4a** (10% yield), **5b** (7% yield), **6a** (40% yield).

Scheme S2. Competing Experiment



5. Characterization of Products

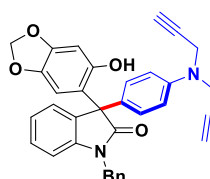
1-benzyl-3-(4-(diallylamino)phenyl)-3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)indolin-2-one (**3a**)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 8:1) afforded the product as a white solid (47.2 mg, 89% yield). M.p. 181 - 183 °C.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.23 (s, 1H), 7.34 – 7.23 (m, 5H), 7.17 – 7.11 (m, 2H), 7.04 (td, $J = 7.5$, 1.1 Hz, 1H), 6.95 – 6.91 (m, 2H), 6.82 – 6.79 (m, 1H), 6.59 – 6.56 (m, 2H), 6.56 (s, 1H), 6.51 (s, 1H), 5.88 (d, $J = 1.4$ Hz, 1H), 5.85 – 5.74 (m, 3H), 5.17 – 5.09 (m, 4H), 5.07 (d, $J = 15.9$ Hz, 1H), 4.90 (d, $J = 15.7$ Hz, 1H), 3.89 – 3.78 (m, 4H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 181.6, 152.7, 148.1, 148.1, 141.2, 140.8, 135.3, 140.0, 133.3, 129.0, 128.2, 127.9, 127.3, 127.3, 126.9, 123.5, 117.3, 116.1, 112.4, 110.2, 108.5, 101.8, 101.25, 61.2, 52.7, 44.4. **HRMS (ESI) m/z**: $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{34}\text{H}_{31}\text{N}_2\text{O}_4^+$ 531.2278; found: 531.2271.

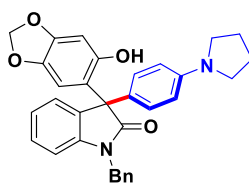
1-benzyl-3-(4-(di(prop-2-yn-1-yl)amino)phenyl)-3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)indolin-2-one (**3b**)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 8:1) afforded the product as a white solid (43.6 mg, 83% yield). M.p. 178 - 180 °C.

¹H NMR (500 MHz, CDCl₃) δ 9.26 (s, 1H), 7.36 – 7.26 (m, 5H), 7.19 (td, *J* = 7.6, 1.5 Hz, 1H), 7.12 – 7.05 (m, 2H), 7.04 – 7.00 (m, 2H), 6.86 – 6.82 (m, 3H), 6.57 (s, 1H), 6.50 (s, 1H), 5.91 (d, *J* = 1.4 Hz, 1H), 5.86 (d, *J* = 1.4 Hz, 1H), 5.08 (d, *J* = 15.7 Hz, 1H), 4.93 (d, *J* = 15.6 Hz, 1H), 4.07 (d, *J* = 2.4 Hz, 4H), 2.22 (t, *J* = 2.4 Hz, 2H). **¹³C NMR** (100 MHz, CDCl₃) δ 181.4, 152.6, 148.3, 147.0, 141.1, 140.9, 135.2, 132.9, 130.84, 129.0, 128.4, 127.9, 127.3, 127.3, 127.0, 123.6, 117.0, 115.4, 110.3, 108.4, 101.9, 101.3, 79.3, 72.7, 61.2, 44.4, 40.2. **HRMS (ESI) m/z:** [M+Na]⁺ calcd for C₃₄H₂₆N₂NaO₄⁺ 549.1784; found: 549.1777.

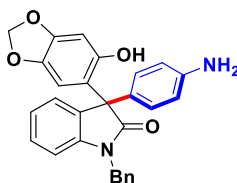
1-benzyl-3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)-3-(4-(pyrrolidin-1-yl)phenyl)indolin-2-one (3c)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 8:1) afforded the product as a white solid (38.3 mg, 76% yield). M.p. 180 - 182 °C.

¹H NMR (500 MHz, CDCl₃) δ 9.22 (s, 1H), 7.33 – 7.22 (m, 5H), 7.16 (td, *J* = 7.6, 1.5 Hz, 1H), 7.09 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.04 (td, *J* = 7.5, 1.0 Hz, 1H), 6.91 – 6.88 (m, 2H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.55 – 6.52 (m, 3H), 6.49 (s, 1H), 5.88 (d, *J* = 1.5 Hz, 1H), 5.82 (d, *J* = 1.5 Hz, 1H), 5.04 (d, *J* = 15.8 Hz, 1H), 4.91 (d, *J* = 15.7 Hz, 1H), 3.43 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 181.7, 152.7, 148.1, 147.1, 141.1, 140.8, 135.3, 133.4, 129.0, 128.1, 127.9, 127.3, 127.3, 126.8, 126.3, 123.6, 117.4, 111.8, 110.2, 108.5, 101.8, 101.2, 61.2, 47.5, 44.3, 25.5. **HRMS (ESI) m/z:** [M+H]⁺ calcd for C₃₂H₂₈N₂O₄⁺ 505.2121; found: 505.2123.

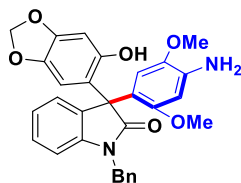
3-(4-aminophenyl)-1-benzyl-3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)indolin-2-one (3d)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 5:1) afforded the product as a white solid (26.5 mg, 59% yield). M.p. 176 - 178 °C.

¹H NMR (500 MHz, CDCl₃) δ 9.22 (s, 1H), 7.33 – 7.22 (m, 5H), 7.16 (td, *J* = 7.6, 1.5 Hz, 1H), 7.09 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.04 (td, *J* = 7.5, 1.0 Hz, 1H), 6.91 – 6.88 (m, 2H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.55 – 6.52 (m, 3H), 6.49 (s, 1H), 5.88 (d, *J* = 1.5 Hz, 1H), 5.82 (d, *J* = 1.5 Hz, 1H), 5.04 (d, *J* = 15.8 Hz, 1H), 4.91 (d, *J* = 15.7 Hz, 1H), 3.43 (s, 2H). **¹³C NMR** (100 MHz, CDCl₃) δ 181.5, 152.5, 148.2, 145.9, 141.2, 140.9, 135.3, 133.1, 129.9, 129.0, 128.3, 127.9, 127.5, 127.3, 126.8, 123.6, 117.4, 115.5, 110.3, 108.6, 101.9, 101.3, 61.2, 44.4. **HRMS (ESI) m/z:** [M+H]⁺ calcd for C₂₈H₂₃N₂O₄⁺ 451.1652; found: 451.1646.

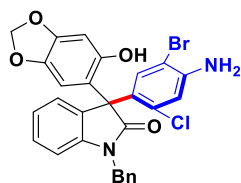
3-(4-amino-2,5-dimethoxyphenyl)-1-benzyl-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)indolin-2-one (3e)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 6:1) afforded the product as a white solid (34.2 mg, 67% yield). M.p. 171 - 173 °C.

¹H NMR (400 MHz, DMSO-*d*₆) δ 9.66 (s, 1H), 7.41 – 7.31 (m, 4H), 7.30 – 7.25 (m, 2H), 7.11 – 7.03 (m, 2H), 6.98 (d, *J* = 7.4 Hz, 1H), 6.56 (s, 1H), 6.33 (s, 1H), 6.29 (s, 1H), 6.20 (s, 1H), 5.96 (s, 1H), 5.92 – 5.89 (m, 1H), 4.97 (s, 2H), 4.84 (s, 2H), 3.50 (s, 3H), 3.12 (s, 3H). **¹³C NMR** (100 MHz, DMSO-*d*₆) δ 182.1, 152.9, 151.9, 148.2, 142.5, 140.7, 140.7, 139.1, 136.6, 132.7, 129.1, 128.5, 128.2, 128.0, 126.2, 123.1, 116.0, 114.0, 112.7, 110.1, 108.6, 101.7, 101.0, 100.2, 59.1, 56.4, 56.3, 43.9. **HRMS (ESI) m/z:** [M+K]⁺ calcd for C₃₀H₂₆KN₂O₆⁺ 549.1422; found: 549.1420.

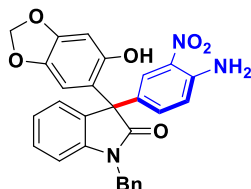
3-(4-amino-5-bromo-2-chlorophenyl)-1-benzyl-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)indolin-2-one (3f)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 5:1) afforded the product as a white solid (26.9 mg, 48% yield). M.p. 184 - 186 °C.

¹H NMR (500 MHz, CDCl₃) δ 9.54 (s, 1H), 7.30 – 7.22 (m, 6H), 7.12 (s, 1H), 7.08 (td, *J* = 7.5, 1.0 Hz, 1H), 6.90 – 6.85 (m, 2H), 6.63 (d, *J* = 3.6 Hz, 2H), 6.21 (s, 1H), 5.93 (d, *J* = 1.5 Hz, 1H), 5.87 (d, *J* = 1.5 Hz, 1H), 5.06 (d, *J* = 15.5 Hz, 1H), 4.78 (d, *J* = 15.5 Hz, 1H), 4.14 (s, 2H). **¹³C NMR** (100 MHz, CDCl₃) δ 180.7, 153.4, 148.8, 144.8, 142.5, 141.4, 134.8, 134.1, 132.9, 130.7, 128.9, 128.8, 127.9, 127.9, 126.4, 126.0, 123.5, 116.9, 115.2, 110.1, 108.3, 107.5, 102.2, 101.5, 61.0, 44.9. **HRMS (ESI) m/z:** [M+H]⁺ calcd for C₂₈H₂₁BrClN₂O₄⁺ 563.0367; found: 563.0370.

3-(4-amino-3-nitrophenyl)-1-benzyl-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)indolin-2-one (3g)

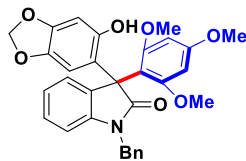


Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 5:1) afforded the product as a white solid (22.7 mg, 46% yield). M.p. 185 - 187 °C.

¹H NMR (400 MHz, DMSO-*d*₆) δ 9.45 (s, 1H), 7.74 (s, 1H), 7.59 (d, *J* = 8.7 Hz, 3H), 7.34 – 7.18 (m, 6H), 7.16 – 7.00 (m, 3H), 6.85 (d, *J* = 7.8 Hz, 1H), 6.37 (s, 1H), 6.29 (s, 1H), 5.91 (s, 2H), 4.90 (q, *J* = 16.0 Hz, 2H). **¹³C NMR** (100 MHz, DMSO-*d*₆) δ 178.0, 150.4, 147.3, 146.3, 143.3, 139.9, 137.0, 131.9,

129.8, 128.9, 128.4, 127.7, 127.6, 126.5, 125.4, 124.8, 122.5, 120.4, 120.1, 109.7, 109.5, 101.4, 98.3, 79.6, 58.2, 43.5. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{28}H_{22}N_3O_6^+$ 496.1503; found: 496.1498.

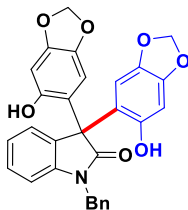
1-benzyl-3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)-3-(2,4,6-trimethoxyphenyl)indolin-2-one (3h)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 9:1) afforded the product as a white solid (44.1 mg, 84% yield). M.p. 187 - 189 °C.

¹H NMR (400 MHz, $CDCl_3$) δ 9.05 (s, 1H), 7.32 – 7.19 (m, 7H), 7.05 (td, $J = 7.5, 1.0$ Hz, 1H), 6.83 (dt, $J = 7.8, 0.8$ Hz, 1H), 6.51 (s, 1H), 6.19 (s, 1H), 6.15 (d, $J = 2.4$ Hz, 1H), 6.06 (d, $J = 2.4$ Hz, 1H), 5.86 (d, $J = 1.4$ Hz, 1H), 5.81 (d, $J = 1.4$ Hz, 1H), 5.00 (d, $J = 15.8$ Hz, 1H), 4.85 (d, $J = 15.8$ Hz, 1H), 3.75 (s, 3H), 3.40 (s, 3H), 3.32 (s, 3H). **¹³C NMR** (100 MHz, $CDCl_3$) δ 182.0, 160.6, 160.4, 158.3, 152.2, 146.8, 142.2, 140.8, 135.9, 131.9, 128.8, 128.3, 127.6, 127.6, 126.4, 123.2, 120.3, 109.5, 108.8, 107.3, 101.0, 100.9, 92.8, 92.6, 57.0, 56.2, 56.1, 55.2, 44.2. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{31}H_{28}NO_7^+$ 526.1860; found: 526.1858.

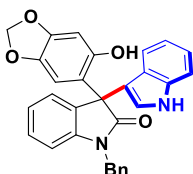
1-benzyl-3,3-bis(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)indolin-2-one (3i)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 5:1) afforded the product as a white solid (43 mg, 87% yield). M.p. 185 - 187 °C.

¹H NMR (400 MHz, $DMSO-d_6$) δ 9.82 (s, 1H), 9.50 (s, 1H), 7.39 – 7.23 (m, 6H), 7.08 (td, $J = 7.5, 1.0$ Hz, 1H), 7.00 (dd, $J = 7.5, 1.3$ Hz, 1H), 6.95 (d, $J = 7.8$ Hz, 1H), 6.58 (s, 1H), 6.36 (s, 1H), 6.31 (s, 1H), 6.18 (s, 1H), 5.97 (s, 1H), 5.92 (d, $J = 3.6$ Hz, 3H), 5.05 (d, $J = 15.9$ Hz, 1H), 4.90 (d, $J = 15.9$ Hz, 1H). **¹³C NMR** (100 MHz, $DMSO-d_6$) δ 181.7, 152.9, 149.8, 148.5, 147.5, 142.6, 141.0, 140.3, 136.4, 131.9, 129.1, 128.7, 127.9, 127.8, 126.2, 123.3, 117.2, 115.9, 110.3, 108.4, 101.8, 101.4, 98.3, 59.3, 44.0. **HRMS (ESI) m/z:** $[M+Na]^+$ calcd for $C_{29}H_{21}NNaO_7^+$ 518.1210; found: 518.1204.

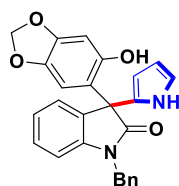
1-benzyl-3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)-3-(1*H*-indol-3-yl)indolin-2-one (3j)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 5:1) afforded the product as a white solid (40.7 mg, 86% yield). M.p. 162 - 164 °C.

¹H NMR (400 MHz, DMSO-*d*₆) δ 11.04 (d, *J* = 2.6 Hz, 1H), 9.38 (s, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.34 – 7.21 (m, 5H), 7.18 (td, *J* = 7.6, 1.6 Hz, 1H), 7.12 – 7.08 (m, 1H), 7.05 – 6.91 (m, 3H), 6.78 (d, *J* = 7.8 Hz, 1H), 6.54 (d, *J* = 2.6 Hz, 1H), 6.41 (s, 2H), 5.88 (dd, *J* = 19.1, 1.1 Hz, 2H), 4.93 (d, *J* = 16.0 Hz, 1H), 4.77 (d, *J* = 16.1 Hz, 1H). **¹³C NMR** (100 MHz, DMSO-*d*₆) δ 177.8, 149.9, 147.0, 143.3, 139.6, 137.9, 137.3, 133.5, 128.9, 127.9, 127.6, 127.5, 126.1, 125.4, 124.3, 123.7, 122.0, 121.8, 119.3, 118.8, 114.0, 112.2, 110.1, 109.0, 101.2, 98.2, 55.5, 43.4. **HRMS (ESI) m/z:** [M+H]⁺ calcd for C₃₀H₂₃N₂O₄⁺ 475.1652; found: 475.1653.

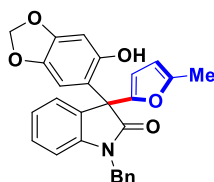
1-benzyl-3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)-3-(1*H*-pyrrol-2-yl)indolin-2-one (3k)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 7:1) afforded the product as a white solid (34.7 mg, 82% yield). M.p. 153 - 155 °C.

¹H NMR (500 MHz, CDCl₃) δ 8.88 (s, 1H), 7.24 – 7.14 (m, 7H), 7.07 – 6.99 (m, 2H), 6.77 (td, *J* = 2.8, 1.4 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 6.33 (d, *J* = 1.1 Hz, 1H), 6.28 (t, *J* = 2.8 Hz, 1H), 6.10 (q, *J* = 2.9 Hz, 1H), 5.90 – 5.89 (m, 1H), 5.81 (d, *J* = 1.6 Hz, 2H), 4.87 (t, *J* = 2.1 Hz, 2H). **¹³C NMR** (100 MHz, CDCl₃) δ 179.1, 149.6, 147.8, 142.1, 141.4, 135.5, 131.7, 128.8, 128.3, 127.6, 127.5, 127.2, 125.2, 123.1, 119.5, 118.7, 109.8, 109.0, 108.9, 108.1, 101.3, 100.0, 55.8, 44.2. **HRMS (ESI) m/z:** [M+H]⁺ calcd for C₂₆H₂₁N₂O₄⁺ 425.1495; found: 425.1497.

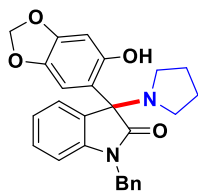
1-benzyl-3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)-3-(5-methylfuran-2-yl)indolin-2-one (3l)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 8:1) afforded the product as a white solid (35.5 mg, 81% yield). M.p. 149 - 151 °C.

¹H NMR (400 MHz, CDCl₃) δ 9.16 (s, 1H), 7.32 – 7.19 (m, 7H), 7.12 (td, *J* = 7.5, 1.1 Hz, 1H), 6.80 – 6.77 (m, 1H), 6.56 (s, 1H), 6.50 (s, 1H), 6.11 (d, *J* = 3.1 Hz, 1H), 5.89 (q, *J* = 1.2 Hz, 2H), 5.84 (d, *J* = 1.5 Hz, 1H), 5.10 (d, *J* = 15.9 Hz, 1H), 4.86 (d, *J* = 15.9 Hz, 1H), 2.20 (d, *J* = 1.1 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 178.8, 152.7, 152.6, 148.8, 148.3, 141.7, 141.0, 134.9, 130.0, 128.9, 128.8, 127.8, 127.0, 126.8, 123.5, 114.4, 110.4, 109.1, 108.1, 106.4, 101.6, 101.3, 57.4, 44.3, 13.7. **HRMS (ESI) m/z:** [M+H]⁺ calcd for C₂₇H₂₂NO₅⁺ 440.1492; found: 440.1491.

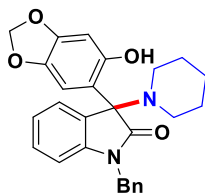
1-benzyl-3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)-3-(pyrrolidin-1-yl)indolin-2-one (4a)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 20:1) afforded the product as a white solid (32.5 mg, 76% yield). M.p. 124 - 126 °C.

¹H NMR (400 MHz, CDCl₃) δ 12.03 (s, 1H), 7.60 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.36 – 7.25 (m, 5H), 7.21 (td, *J* = 7.8, 1.2 Hz, 1H), 7.03 (td, *J* = 7.6, 1.0 Hz, 1H), 6.77 (dd, *J* = 7.9, 1.0 Hz, 1H), 6.50 (s, 1H), 6.15 (s, 1H), 5.80 – 5.78 (m, 2H), 5.00 (d, *J* = 15.5 Hz, 1H), 4.87 (d, *J* = 15.5 Hz, 1H), 2.90 (dt, *J* = 8.2, 5.6 Hz, 2H), 2.73 (s, 2H), 1.79 (q, *J* = 4.7, 2.8 Hz, 4H). **¹³C NMR** (100 MHz, CDCl₃) δ 174.5, 154.7, 148.1, 142.2, 140.1, 135.7, 129.5, 128.9, 128.8, 127.8, 127.4, 125.5, 123.3, 113.9, 109.6, 106.5, 101.0, 99.6, 71.7, 47.0, 43.9, 23.6. **HRMS (ESI) m/z:** [M+H]⁺ calcd for C₂₆H₂₅N₂O₄⁺ 429.1808; found: 429.1806.

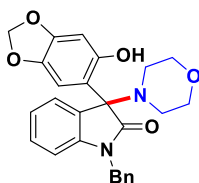
1-benzyl-3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)-3-(piperidin-1-yl)indolin-2-one (4b)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 20:1) afforded the product as a white solid (28.2mg, 64% yield). M.p. 129 - 131 °C.

¹H NMR (400 MHz, CDCl₃) δ 11.85 (s, 1H), 7.56 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.34 – 7.25 (m, 5H), 7.21 (td, *J* = 7.8, 1.3 Hz, 1H), 7.04 (td, *J* = 7.6, 1.1 Hz, 1H), 6.75 (dd, *J* = 7.9, 1.0 Hz, 1H), 6.50 (s, 1H), 6.09 (s, 1H), 5.81 – 5.77 (m, 2H), 4.97 (d, *J* = 15.6 Hz, 1H), 4.88 (d, *J* = 15.6 Hz, 1H), 3.04 (d, *J* = 32.5 Hz, 2H), 2.42 (d, *J* = 67.4 Hz, 2H), 1.65 (s, 6H). **¹³C NMR** (100 MHz, CDCl₃) δ 174.2, 154.6, 148.3, 142.4, 140.1, 135.6, 129.5, 128.9, 128.1, 127.8, 127.4, 125.5, 123.3, 113.1, 109.6, 106.9, 101.0, 99.7, 75.2, 48.1, 43.9, 26.4, 24.2. **HRMS (ESI) m/z:** [M+H]⁺ calcd for C₂₇H₂₇N₂O₄⁺ 443.1965; found: 443.1962.

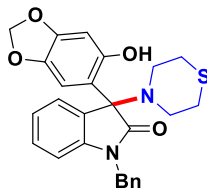
1-benzyl-3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)-3-morpholinoindolin-2-one (4c)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 15:1) afforded the product as a white solid (26.1 mg, 59% yield). M.p. 126 - 128 °C.

¹H NMR (400 MHz, CDCl₃) δ 11.28 (s, 1H), 7.57 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.35 – 7.20 (m, 6H), 7.06 (td, *J* = 7.6, 1.0 Hz, 1H), 6.80 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.49 (s, 1H), 6.13 (s, 1H), 5.81 – 5.78 (m, 2H), 4.99 (d, *J* = 15.5 Hz, 1H), 4.87 (d, *J* = 15.6 Hz, 1H), 3.75 (s, 4H), 2.80 (s, 4H). **¹³C NMR** (100 MHz, CDCl₃) δ 173.8, 154.0, 148.7, 142.5, 140.5, 135.5, 129.8, 129.0, 127.9, 127.4, 127.5, 125.6, 123.5, 112.1, 109.8, 107.1, 101.2, 99.7, 74.7, 67.2, 47.3, 44.0. **HRMS (ESI) m/z:** [M+H]⁺ calcd for C₂₆H₂₅N₂O₅⁺ 445.1758; found: 445.1760.

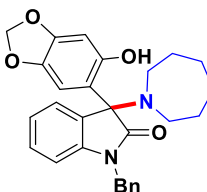
1-benzyl-3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)-3-thiomorpholinoindolin-2-one (4d)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 15:1) afforded the product as a white solid (28.0 mg, 61% yield). M.p. 123 - 125 °C.

¹H NMR (400 MHz, CDCl₃) δ 11.03 (s, 1H), 7.55 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.35 – 7.27 (m, 5H), 7.26 – 7.21 (m, 1H), 7.06 (td, *J* = 7.6, 1.0 Hz, 1H), 6.78 (dd, *J* = 7.9, 1.0 Hz, 1H), 6.50 (s, 1H), 6.08 (s, 1H), 5.83 – 5.80 (m, 2H), 4.97 (d, *J* = 15.6 Hz, 1H), 4.88 (d, *J* = 15.5 Hz, 1H), 3.29 – 2.51 (m, 8H). **¹³C NMR** (100 MHz, CDCl₃) δ 174.0, 154.0, 148.6, 142.4, 140.5, 135.4, 129.8, 128.9, 127.9, 127.4, 125.4, 123.5, 112.4, 109.9, 107.0, 101.1, 99.8, 75.6, 49.7, 44.0, 28.5. **HRMS (ESI) m/z:** [M+H]⁺ calcd for C₂₆H₂₅N₂O₄S⁺ 461.1529; found: 461.1526.

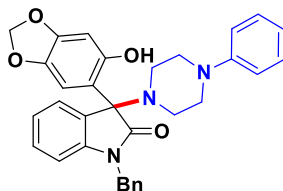
3-(azepan-1-yl)-1-benzyl-3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)indolin-2-one (4e)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 15:1) afforded the product as a white solid (27.8 mg, 61% yield). M.p. 132 - 134 °C.

¹H NMR (400 MHz, CDCl₃) δ 11.70 (s, 1H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.33 – 7.23 (m, 5H), 7.20 (td, *J* = 7.8, 1.2 Hz, 1H), 7.05 – 7.00 (m, 1H), 6.75 (d, *J* = 7.6 Hz, 1H), 6.51 (s, 1H), 6.11 (s, 1H), 5.80 – 5.76 (m, 2H), 4.98 (d, *J* = 15.6 Hz, 1H), 4.85 (d, *J* = 15.6 Hz, 1H), 3.12 (d, *J* = 54.9 Hz, 2H), 2.58 (d, *J* = 41.4 Hz, 2H), 1.75 – 1.47 (m, 8H). **¹³C NMR** (100 MHz, CDCl₃) δ 174.7, 154.2, 148.4, 142.2, 140.1, 135.7, 129.4, 128.9, 127.8, 127.4, 125.0, 123.4, 114.5, 109.6, 106.8, 101.0, 99.8, 75.7, 51.5, 51.1, 43.9, 28.8, 28.5, 26.1. **HRMS (ESI) m/z:** [M+H]⁺ calcd for C₂₈H₂₉N₂O₄⁺ 457.2121; found: 457.2123.

1-benzyl-3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)-3-(4-phenylpiperazin-1-yl)indolin-2-one (4f)

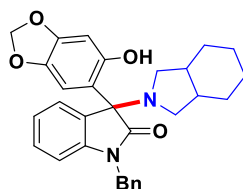


Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 15:1) afforded the product as a white solid (33.2 mg, 64% yield). M.p. 114 - 116 °C.

¹H NMR (400 MHz, CDCl₃) δ 11.31 (s, 1H), 7.59 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.36 – 7.22 (m, 8H), 7.07 (td, *J* = 7.6, 1.0 Hz, 1H), 6.90 – 6.84 (m, 3H), 6.80 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.52 (s, 1H), 6.14 (s, 1H), 5.84 – 5.80 (m, 2H), 5.01 (d, *J* = 15.6 Hz, 1H), 4.88 (d, *J* = 15.6 Hz, 1H), 3.54 (s, 2H), 2.97 (s, 6H). **¹³C NMR**

NMR (100 MHz, CDCl₃) δ 173.9, 154.2, 150.8, 148.6, 142.5, 140.4, 135.5, 129.8, 129.2, 129.0, 127.9, 127.5, 125.7, 123.5, 120.3, 116.4, 112.4, 109.8, 107.1, 101.1, 99.8, 74.6, 49.8, 46.9, 44.0. **HRMS (ESI)** m/z : [M+H]⁺ calcd for C₃₂H₃₀N₃O₄⁺ 520.2230; found: 520.2228.

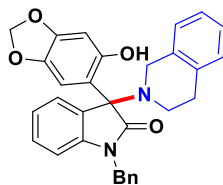
1-benzyl-3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)-3-(octahydro-2*H*-isoindol-2-yl)indolin-2-one (4g)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 20:1) afforded the product as a white solid (31.8 mg, 66% yield). M.p. 117 - 119 °C.

¹H NMR (400 MHz, CDCl₃) δ 12.25 (s, 1H), 7.70 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.40 – 7.24 (m, 5H), 7.19 (td, *J* = 7.7, 1.3 Hz, 1H), 7.02 (td, *J* = 7.6, 1.1 Hz, 1H), 6.78 (dd, *J* = 7.9, 0.9 Hz, 1H), 6.50 (s, 1H), 6.21 (s, 1H), 5.79 (dd, *J* = 8.4, 1.5 Hz, 2H), 5.04 (d, *J* = 15.5 Hz, 1H), 4.87 (d, *J* = 15.5 Hz, 1H), 3.38 – 2.61 (m, 4H), 2.21 – 2.06 (m, 2H), 1.62 – 1.20 (m, 8H). **¹³C NMR** (100 MHz, CDCl₃) δ 175.1, 154.4, 148.3, 141.8, 140.1, 135.8, 130.1, 129.3, 128.9, 127.9, 127.6, 125.1, 123.5, 114.6, 109.5, 106.6, 101.0, 99.5, 71.7, 43.9, 37.3, 37.1, 26.4, 23.1. **HRMS (ESI)** m/z : [M+H]⁺ calcd for C₃₀H₃₁N₂O₄⁺ 483.2278; found: 483.2281.

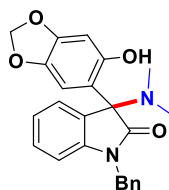
1-benzyl-3-(3,4-dihydroisoquinolin-2(1*H*)-yl)-3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)indolin-2-one (4h)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 20:1) afforded the product as a white solid (29.8 mg, 61% yield). M.p. 121 - 123 °C.

¹H NMR (400 MHz, CDCl₃) δ 11.40 (s, 1H), 7.60 (d, *J* = 67.5 Hz, 1H), 7.39 – 7.24 (m, 6H), 7.17 – 6.97 (m, 4H), 6.83 (dd, *J* = 12.3, 7.6 Hz, 2H), 6.51 (s, 1H), 6.20 (d, *J* = 81.3 Hz, 1H), 5.92 – 5.71 (m, 2H), 5.04 (d, *J* = 15.4 Hz, 1H), 4.90 (s, 1H), 4.12 - 3.62 (m, 2H), 3.57 – 2.58 (m, 4H). **¹³C NMR** (101 MHz, CDCl₃) δ 174.5, 154.9, 148.6, 140.4, 135.7, 133.5, 129.8, 128.9, 128.8, 127.9, 127.6, 126.7, 126.6, 125.9, 123.5, 109.8, 107.0, 101.1, 99.9, 74.6, 49.4, 45.1, 44.0, 29.4. **HRMS (ESI)** m/z : [M+H]⁺ calcd for C₃₁H₂₇N₂O₄⁺ 491.1965; found: 491.1968.

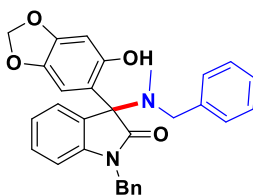
1-benzyl-3-(dimethylamino)-3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)indolin-2-one (4i)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 20:1) afforded the product as a white solid (25.7 mg, 64% yield). M.p. 115 - 117 °C.

¹H NMR (500 MHz, CDCl₃) δ 11.73 (s, 1H), 7.56 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.34 – 7.26 (m, 5H), 7.23 (td, *J* = 7.8, 1.2 Hz, 1H), 7.05 (td, *J* = 7.6, 1.0 Hz, 1H), 6.78 (dd, *J* = 7.9, 1.0 Hz, 1H), 6.51 (s, 1H), 6.10 (s, 1H), 5.82 – 5.79 (m, 2H), 5.01 (d, *J* = 15.5 Hz, 1H), 4.86 (d, *J* = 15.6 Hz, 1H), 2.43 (s, 6H). **¹³C NMR** (100 MHz, CDCl₃) δ 174.0, 154.5, 148.4, 142.4, 140.1, 135.6, 129.6, 128.9, 127.8, 127.4, 125.5, 123.3, 113.4, 109.6, 106.8, 101.0, 99.7, 74.5, 43.9, 39.1. **HRMS (ESI) m/z:** [M+H]⁺ calcd for C₂₄H₂₃N₂O₄⁺ 403.1652; found: 403.1649.

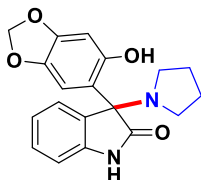
1-benzyl-3-(benzyl(methyl)amino)-3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)indolin-2-one (4j)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 15:1) afforded the product as a white solid (25.8 mg, 54% yield). M.p. 113 - 115 °C.

¹H NMR (400 MHz, CDCl₃) δ 11.55 (s, 1H), 7.72 (s, 1H), 7.37 – 7.22 (m, 11H), 7.08 (td, *J* = 7.6, 1.0 Hz, 1H), 6.80 (dd, *J* = 7.9, 0.9 Hz, 1H), 6.54 (s, 1H), 6.21 (s, 1H), 5.84 – 5.78 (m, 2H), 5.03 (d, *J* = 15.6 Hz, 1H), 4.92 (d, *J* = 15.6 Hz, 1H), 4.22 – 3.10 (m, 2H), 2.32 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 174.2, 154.0, 148.6, 142.3, 140.4, 137.2, 135.6, 129.7, 129.4, 129.0, 128.7, 127.9, 127.7, 127.4, 125.4, 123.5, 113.6, 109.9, 106.9, 101.1, 99.8, 75.0, 55.9, 44.0, 35.3. **HRMS (ESI) m/z:** [M+H]⁺ calcd for C₃₀H₂₇N₂O₄⁺ 479.1965; found: 479.1967.

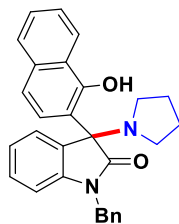
3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)-3-(pyrrolidin-1-yl)indolin-2-one (4k)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 10:1) afforded the product as a white solid (22.6mg, 67% yield). M.p. 130 - 132 °C.

¹H NMR (400 MHz, CDCl₃) δ 12.10 (s, 1H), 9.15 (s, 1H), 7.52 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.29 – 7.24 (m, 1H), 7.06 (td, *J* = 7.6, 1.1 Hz, 1H), 6.95 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.50 (s, 1H), 6.18 (s, 1H), 5.82 – 5.78 (m, 2H), 2.85 (s, 4H), 1.81 (d, *J* = 6.2 Hz, 4H). **¹³C NMR** (100 MHz, CDCl₃) δ 177.1, 154.8, 148.4, 140.5, 140.0, 129.6, 128.6, 125.9, 123.2, 113.3, 110.7, 106.7, 101.0, 99.5, 72.4, 46.9, 23.5. **HRMS (ESI) m/z:** [M+H]⁺ calcd for C₁₉H₁₉N₂O₄⁺ 339.1339; found: 339.1341.

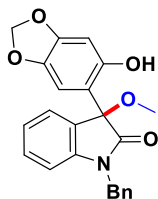
1-benzyl-3-(1-hydroxynaphthalen-2-yl)-3-(pyrrolidin-1-yl)indolin-2-one (4l)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 15:1) afforded the product as a white solid (27.3mg, 63% yield). M.p. 141 - 143 °C.

¹H NMR (400 MHz, CDCl₃) δ 12.83 (s, 1H), 8.41 – 8.38 (m, 1H), 7.69 – 7.65 (m, 1H), 7.60 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.43 (tt, *J* = 6.8, 5.1 Hz, 2H), 7.33 – 7.21 (m, 5H), 7.20 – 7.11 (m, 2H), 7.00 (td, *J* = 7.6, 1.1 Hz, 1H), 6.77 – 6.67 (m, 2H), 4.94 (s, 2H), 3.11 (d, *J* = 43.4 Hz, 2H), 2.49 (d, *J* = 85.2 Hz, 2H), 1.68 – 1.67 (m, 4H). **¹³C NMR** (100 MHz, CDCl₃) δ 174.3, 155.4, 142.6, 135.7, 134.3, 129.5, 128.2, 128.4, 127.8, 127.4, 127.2, 126.7, 125.6, 125.6, 124.9, 124.7, 123.3, 122.9, 118.4, 114.9, 109.7, 75.7, 48.3, 43.9, 26.6, 24.3. **HRMS (ESI) m/z:** [M+H]⁺ calcd for C₂₉H₂₇N₂O₂⁺ 435.2067; found: 435.2064.

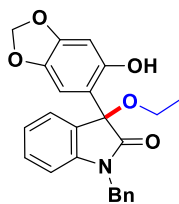
1-benzyl-3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)-3-methoxyindolin-2-one (5a)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 10:1) afforded the product as a white solid (28.0 mg, 72% yield). M.p. 165 - 167 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.94 (s, 1H), 7.42 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.34 – 7.25 (m, 6H), 7.17 (td, *J* = 7.5, 1.0 Hz, 1H), 6.81 (dd, *J* = 7.8, 0.9 Hz, 1H), 6.56 (s, 1H), 6.09 (s, 1H), 5.86 – 5.83 (m, 2H), 4.95 (d, *J* = 15.6 Hz, 1H), 4.86 (d, *J* = 15.6 Hz, 1H), 3.26 (s, 3H). **¹³C NMR** (100 MHz, +9* CDCl₃) δ 176.1, 153.7, 149.1, 143.3, 140.6, 135.1, 130.7, 129.0, 128.0, 127.3, 126.4, 126.0, 123.7, 112.9, 110.3, 107.2, 101.3, 100.6, 86.0, 53.3, 44.1. **HRMS (ESI) m/z:** [M+H]⁺ calcd for C₂₃H₂₀NO₅⁺ 390.1336; found: 390.1337.

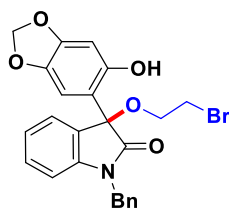
1-benzyl-3-ethoxy-3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)indolin-2-one (5b)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 10:1) afforded the product as a white solid (28.6 mg, 71% yield). M.p. 161 - 163 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.98 (s, 1H), 7.42 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.34 – 7.25 (m, 6H), 7.15 (td, *J* = 7.5, 1.0 Hz, 1H), 6.79 (dt, *J* = 8.0, 0.8 Hz, 1H), 6.55 (s, 1H), 6.04 (s, 1H), 5.83 (q, *J* = 1.4 Hz, 2H), 4.95 – 4.85 (m, 2H), 3.51 – 3.44 (m, 1H), 3.36 – 3.29 (m, 1H), 1.26 (t, *J* = 7.0 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 176.1, 153.7, 149.0, 143.1, 140.5, 135.2, 130.5, 129.0, 127.9, 127.3, 126.8, 126.2, 123.7, 113.1, 110.1, 106.9, 101.2, 100.5, 85.5, 61.6, 44.1, 15.3. **HRMS (ESI) m/z:** [M+H]⁺ calcd for C₂₄H₂₂NO₅⁺ 404.192; found: 404.1495.

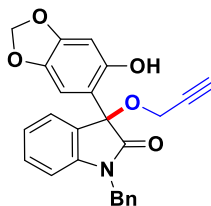
1-benzyl-3-(2-bromoethoxy)-3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)indolin-2-one (5c)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 8:1) afforded the product as a white solid (27.9mg, 58% yield). M.p. 151 - 153 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.82 (s, 1H), 7.47 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.36 – 7.25 (m, 6H), 7.17 (td, *J* = 7.5, 1.0 Hz, 1H), 6.81 (d, *J* = 7.9 Hz, 1H), 6.57 (s, 1H), 6.13 (s, 1H), 5.84 (q, *J* = 1.4 Hz, 2H), 4.96 – 4.85 (m, 2H), 3.73 – 3.66 (m, 1H), 3.59 – 3.53 (m, 1H), 3.48 (t, *J* = 5.7 Hz, 2H). **¹³C NMR** (100 MHz, CDCl₃) δ 175.7, 153.6, 149.2, 143.0, 140.7, 135.0, 130.9, 129.0, 128.0, 127.3, 126.5, 126.0, 123.9, 112.7, 110.4, 107.10 101.4, 100.8, 85.5, 65.6, 44.2, 29.7. **HRMS (ESI) m/z:** [M+H]⁺ calcd for C₂₄H₂₁BrNO₅⁺ 482.0597; found: 482.0596.

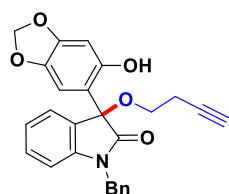
1-benzyl-3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)-3-(prop-2-yn-1-yloxy)indolin-2-one (5d)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 8:1) afforded the product as a white solid (26.4 mg, 64% yield). M.p. 157 - 159 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.85 (s, 1H), 7.47 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.35 – 7.27 (m, 6H), 7.17 (td, *J* = 7.5, 1.0 Hz, 1H), 6.81 (d, *J* = 7.9 Hz, 1H), 6.58 (s, 1H), 6.15 (s, 1H), 5.86 – 5.83 (m, 2H), 4.89 (s, 2H), 4.16 – 4.01 (m, 2H), 2.38 (t, *J* = 2.5 Hz, 1H). **¹³C NMR** (100 MHz, CDCl₃) δ 175.8, 153.8, 149.3, 143.2, 140.7, 134.9, 131.0, 129.0, 128.0, 127.3, 126.8, 125.5, 123.7, 112.4, 110.4, 107.4, 101.4, 100.9, 85.3, 78.5, 75.6, 54.0, 44.2, 29.7. **HRMS (ESI) m/z:** [M+H]⁺ calcd for C₂₅H₂₀NO₅⁺ 414.1336; found: 414.1338.

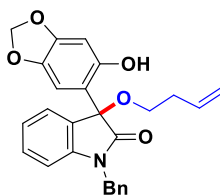
1-benzyl-3-(but-3-yn-1-yloxy)-3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)indolin-2-one (5e)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 8:1) afforded the product as a white solid (26.9 mg, 63% yield). M.p. 149 - 151 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.82 (s, 1H), 7.45 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.34 – 7.24 (m, 6H), 7.15 (td, *J* = 7.6, 1.0 Hz, 1H), 6.80 (d, *J* = 7.9 Hz, 1H), 6.56 (s, 1H), 6.09 (s, 1H), 5.83 (s, 2H), 4.90 (s, 2H), 3.51 (dt, *J* = 8.1, 6.7 Hz, 1H), 3.37 (dt, *J* = 8.2, 6.7 Hz, 1H), 2.52 (td, *J* = 6.7, 2.6 Hz, 2H), 2.05 (t, *J* = 2.7 Hz, 1H). **¹³C NMR** (100 MHz, CDCl₃) δ 175.7, 153.6, 149.1, 143.0, 140.6, 135.1, 130.8, 129.0, 128.7, 128.0, 127.3, 126.3, 123.8, 113.0, 110.2, 106.9, 101.3, 100.7, 85.6, 80.3, 70.3, 63.9, 44.1, 19.9. **HRMS (ESI) m/z:** [M+H]⁺ calcd for C₂₆H₂₁NO₅⁺ 4427.1419; found: 427.1421.

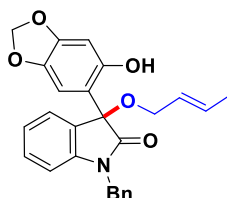
1-benzyl-3-(but-3-en-1-yloxy)-3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)indolin-2-one (5f)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 7:1) afforded the product as a white solid (27.4 mg, 64% yield). M.p. 143 - 145 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.84 (s, 1H), 7.41 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.34 – 7.24 (m, 6H), 7.14 (td, *J* = 7.6, 1.0 Hz, 1H), 6.81 – 6.77 (m, 1H), 6.54 (s, 1H), 6.03 (s, 1H), 5.84 – 5.72 (m, 3H), 5.16 – 5.08 (m, 2H), 4.95 – 4.84 (m, 2H), 3.43 (dt, *J* = 8.3, 6.5 Hz, 1H), 3.31 (dt, *J* = 8.3, 6.3 Hz, 1H), 2.40 – 2.37 (m, 2H). **¹³C NMR** (100 MHz, CDCl₃) δ 175.7, 153.6, 149.0, 143.1, 140.5, 135.2, 134.3, 130.6, 129.0, 127.9, 127.3, 126.7, 126.2, 123.8, 117.6, 113.1, 110.1, 106.8, 101.3, 100.5, 85.6, 65.0, 44.1, 34.0. **HRMS (ESI) m/z:** [M+H]⁺ calcd for C₂₆H₂₄NO₅⁺ 430.1649; found: 430.1646.

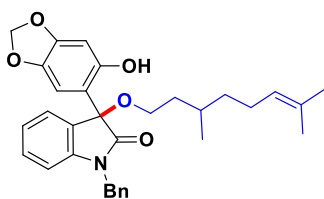
1-benzyl-3-(but-2-en-1-yloxy)-3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)indolin-2-one (5g)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 8:1) afforded the product as a white solid (28.3 mg, 66% yield). M.p. 146 - 148 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.98 (s, 1H), 7.43 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.32 – 7.24 (m, 6H), 7.15 (td, *J* = 7.5, 1.0 Hz, 1H), 6.79 (d, *J* = 7.9 Hz, 1H), 6.55 (s, 1H), 6.06 (s, 1H), 5.82 (q, *J* = 1.4 Hz, 2H), 5.73 – 5.53 (m, 2H), 4.89 (s, 2H), 3.89 – 3.84 (m, 1H), 3.77 – 3.73 (m, 1H), 1.66 (dt, *J* = 6.4, 1.2 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 176.1, 153.7, 149.0, 143.1, 140.5, 135.2, 131.3, 130.6, 129.0, 127.9, 127.3, 126.6, 126.3, 126.0, 123.7, 113.1, 110.2, 107.0, 101.3, 100.6, 85.3, 66.8, 44.1, 17.9. **HRMS (ESI) m/z:** [M+H]⁺ calcd for C₂₆H₂₄NO₅⁺ 430.1649; found: 430.1646.

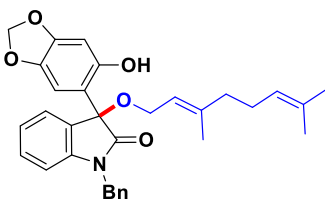
1-benzyl-3-((3,7-dimethyloct-6-en-1-yl)oxy)-3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)indolin-2-one (5h)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 15:1) afforded the product as a white solid (26.6 mg, 52% yield, *dr* = 1:1). M.p. 137 - 139 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.96 (d, *J* = 2.1 Hz, 1H), 7.40 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.32 – 7.22 (m, 6H), 7.14 (td, *J* = 7.5, 1.0 Hz, 1H), 6.80 (d, *J* = 7.9 Hz, 1H), 6.54 (s, 1H), 6.04 (d, *J* = 2.5 Hz, 1H), 5.80 (q, *J* = 1.5 Hz, 2H), 5.08 – 5.03 (m, 1H), 4.95 (dd, *J* = 15.7, 4.4 Hz, 1H), 4.83 (dd, *J* = 15.6, 4.3 Hz, 1H), 3.46 – 3.38 (m, 1H), 3.29 – 3.21 (m, 1H), 2.00 – 1.87 (m, 2H), 1.76 – 1.64 (m, 4H), 1.57 (t, *J* = 1.6 Hz, 4H), 1.50 – 1.37 (m, 1H), 1.31 – 1.21 (m, 1H), 1.15 – 1.04 (m, 1H), 0.82 (dd, *J* = 20.3, 6.6 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 176.0, 176.0, 153.7, 153.7, 148.9, 143.2, 143.1, 140.5, 135.3, 135.3, 131.3, 131.3, 130.6, 129.0, 127.9, 127.4, 127.3, 126.8, 126.7, 126.2, 126.2, 124.7, 124.7, 123.7, 113.3, 113.3, 110.1, 106.9, 101.3, 100.5, 85.5, 64.3, 64.1, 44.1, 37.0, 36.7, 36.6, 29.3, 29.3, 25.8, 25.4, 25.4, 19.4, 19.3, 17.7. **HRMS (ESI) m/z:** [M+H]⁺ calcd for C₃₂H₃₆NO₅⁺ 514.2588; found: 514.2586.

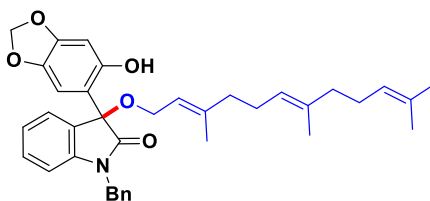
1-benzyl-3-((3,7-dimethylocta-2,6-dien-1-yl)oxy)-3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)indolin-2-one (5i)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 15:1) afforded the product as a white solid (25.0 mg, 49% yield). M.p. 126 - 128 °C.

¹H NMR (500 MHz, CDCl₃) δ 9.00 (s, 1H), 7.44 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.32 – 7.24 (m, 6H), 7.14 (td, *J* = 7.5, 1.0 Hz, 1H), 6.80 (d, *J* = 7.9 Hz, 1H), 6.54 (s, 1H), 6.04 (s, 1H), 5.81 (q, *J* = 1.5 Hz, 2H), 5.38 (tq, *J* = 7.0, 1.3 Hz, 1H), 5.07 – 5.04 (m, 1H), 4.90 (s, 2H), 3.95 (dd, *J* = 10.2, 7.1 Hz, 1H), 3.79 (dd, *J* = 10.2, 6.9 Hz, 1H), 2.06 (dd, *J* = 10.5, 4.9 Hz, 2H), 2.00 (dd, *J* = 9.4, 6.0 Hz, 2H), 1.67 (d, *J* = 1.4 Hz, 3H), 1.56 (dd, *J* = 18.5, 1.4 Hz, 6H). **¹³C NMR** (100 MHz, CDCl₃) δ 176.0, 153.7, 148.9, 143.1, 142.8, 140.5, 135.3, 131.8, 130.6, 129.0, 127.9, 127.4, 126.8, 126.2, 123.8, 123.7, 119.0, 113.2, 110.1, 106.9, 101.2, 100.5, 85.3, 62.6, 44.1, 39.5, 26.3, 25.7, 17.8, 16.5. **HRMS (ESI) m/z:** [M+H]⁺ calcd for C₃₂H₃₄NO₅⁺ 512.2431; found: 512.2433.

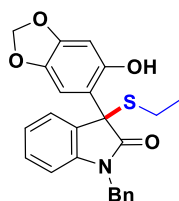
1-benzyl-3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)-3-(((2E,6E)-3,7,11-trimethyldodeca-2,6,10-trien-1-yl)oxy)indolin-2-one (5j)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 15:1) afforded the product as a white solid (24.8mg, 43% yield, *dr* = 1.5:1). M.p. 113 - 115 °C.

¹H NMR (400 MHz, CDCl₃) δ 9.00 (d, *J* = 2.0 Hz, 1H), 7.44 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.33 – 7.26 (m, 6H), 7.15 (td, *J* = 7.6, 1.0 Hz, 1H), 6.82 – 6.77 (m, 1H), 6.54 (s, 1H), 6.03 (s, 1H), 5.81 (d, *J* = 1.8 Hz, 2H), 5.40 – 5.36 (m, 1H), 5.13 – 5.04 (m, 2H), 4.90 (s, 2H), 3.95 (dd, *J* = 10.1, 7.1 Hz, 1H), 3.78 (dd, *J* = 10.1, 7.0 Hz, 1H), 2.11 – 1.93 (m, 8H), 1.69 – 1.66 (m, 5H), 1.61 – 1.57 (m, 5H), 1.55 (d, *J* = 1.4 Hz, 2H). **¹³C NMR** (100 MHz, CDCl₃) δ 175.9, 153.7, 148.9, 143.1, 142.9, 142.8, 140.5, 135.6, 135.5, 135.3, 131.6, 131.3, 130.6, 129.0, 127.9, 127.3, 126.8, 126.3, 124.5, 124.4, 124.3, 123.7, 123.7, 118.9, 118.9, 113.2, 110.1, 106.9, 101.2, 100.5, 85.3, 62.5, 44.1, 39.8, 39.7, 39.5, 32.0, 26.7, 26.6, 26.2, 26.1, 25.8, 25.7, 23.4, 17.7, 17.9, 16.5, 16.5, 16.1. **HRMS (ESI) m/z:** [M+H]⁺ calcd for C₃₇H₄₁NO₅⁺ 579.2984; found: 579.2985.

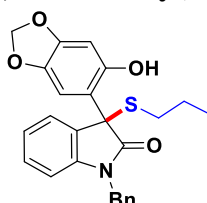
1-benzyl-3-(ethylthio)-3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)indolin-2-one (6a)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 8:1) afforded the product as a white solid (33.1 mg, 79% yield). M.p. 154 - 156 °C.

¹H NMR (400 MHz, CDCl₃) δ 9.08 (s, 1H), 7.44 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.34 – 7.25 (m, 5H), 7.22 (td, *J* = 7.7, 1.3 Hz, 1H), 7.13 (td, *J* = 7.6, 1.1 Hz, 1H), 6.78 (d, *J* = 5.9 Hz, 2H), 6.49 (s, 1H), 5.86 (dd, *J* = 7.9, 1.5 Hz, 2H), 4.98 (d, *J* = 15.7 Hz, 1H), 4.89 (d, *J* = 15.7 Hz, 1H), 2.46 – 2.32 (m, 2H), 1.08 (t, *J* = 7.5 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 178.1, 152.3, 148.6, 141.5, 141.1, 135.2, 129.5, 129.2, 128.9, 127.9, 127.3, 126.3, 123.5, 112.2, 109.9, 108.1, 101.3, 101.0, 58.5, 44.3, 24.1, 13.3. **HRMS (ESI) m/z:** [M+Na]⁺ calcd for C₂₄H₂₁NNaO₄S⁺ 442.1083; found: 442.1077.

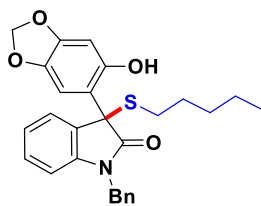
1-benzyl-3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)-3-(propylthio)indolin-2-one (6b)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 8:1) afforded the product as a white solid (32.4 mg, 75% yield). M.p. 147 - 149 °C.

¹H NMR (400 MHz, CDCl₃) δ 9.17 (s, 1H), 7.48 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.32 – 7.26 (m, 5H), 7.23 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.14 (td, *J* = 7.6, 1.1 Hz, 1H), 6.80 (dd, *J* = 7.9, 1.2 Hz, 1H), 6.72 (s, 1H), 6.52 (s, 1H), 5.89 – 5.85 (m, 2H), 5.01 (d, *J* = 15.6 Hz, 1H), 4.87 (d, *J* = 15.7 Hz, 1H), 2.39 – 2.24 (m, 2H), 1.50 – 1.36 (m, 2H), 0.84 (t, *J* = 7.4 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 178.0, 152.5, 148.7, 141.5, 141.1, 135.2, 129.5, 129.2, 128.9, 127.9, 127.4, 126.4, 123.6, 112.0, 109.9, 108.1, 101.3, 101.1, 58.5, 44.3, 32.0, 21.8, 13.6. **HRMS (ESI) m/z:** [M+H]⁺ calcd for C₂₅H₂₄NO₄S⁺ 434.1420; found: 434.1422.

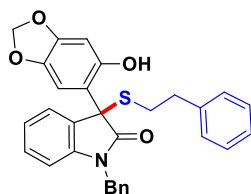
1-benzyl-3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)-3-(pentylthio)indolin-2-one (6c)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 8:1) afforded the product as a white solid (34.1 mg, 74% yield). M.p. 134 - 136 °C.

¹H NMR (400 MHz, CDCl₃) δ 9.04 (s, 1H), 7.41 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.34 – 7.25 (m, 5H), 7.21 (td, *J* = 7.7, 1.4 Hz, 1H), 7.11 (td, *J* = 7.6, 1.1 Hz, 1H), 6.81 (s, 1H), 6.77 (dd, *J* = 7.9, 1.1 Hz, 1H), 6.47 (s, 1H), 5.86 (dd, *J* = 8.9, 1.4 Hz, 2H), 5.00 (d, *J* = 15.7 Hz, 1H), 4.84 (d, *J* = 15.7 Hz, 1H), 2.43 – 2.33 (m, 2H), 1.48 – 1.36 (m, 2H), 1.28 – 1.12 (m, 4H), 0.81 (t, *J* = 7.0 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 178.2, 152.2, 148.5, 141.5, 141.1, 135.3, 129.6, 129.1, 128.9, 127.8, 127.4, 126.1, 123.5, 112.2, 109.9, 108.1, 101.3, 100.9, 58.3, 44.3, 31.0, 29.8, 28.0, 22.2, 13.9. **HRMS (ESI) m/z:** [M+H]⁺ calcd for C₂₇H₂₇NO₄S⁺ 462.1733; found: 462.1732.

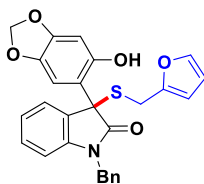
1-benzyl-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)-3-(phenethylthio)indolin-2-one (6d)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 7:1) afforded the product as a white solid (36.1 mg, 73% yield). M.p. 151 - 153 °C.

¹H NMR (400 MHz, CDCl₃) δ 9.01 (s, 1H), 7.40 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.30 – 7.15 (m, 9H), 7.11 (td, *J* = 7.6, 1.1 Hz, 1H), 7.03 – 6.97 (m, 2H), 6.79 – 6.75 (m, 2H), 6.48 (s, 1H), 5.86 (dd, *J* = 7.6, 1.4 Hz, 2H), 5.00 (d, *J* = 15.7 Hz, 1H), 4.84 (d, *J* = 15.7 Hz, 1H), 2.79 – 2.55 (m, 4H). **¹³C NMR** (100 MHz, CDCl₃) δ 178.1, 152.2, 148.7, 141.5, 141.1, 139.8, 135.2, 129.4, 129.3, 128.9, 128.5, 128.4, 127.9, 127.3, 126.4, 126., 123.6, 112.1, 109.9, 108.2, 101.4, 101.0, 58.5, 44.4, 34.9, 31.3. **HRMS (ESI) m/z:** [M+H]⁺ calcd for C₃₀H₂₆NO₄S⁺ 496.1577; found: 496.1578.

1-benzyl-3-((furan-2-ylmethyl)thio)-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)indolin-2-one (6e)

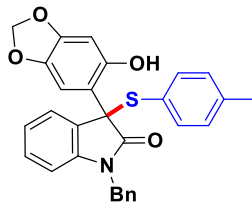


Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 7:1) afforded the product as a white solid (33.4mg, 71% yield). M.p. 145 - 147 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.81 (s, 1H), 7.36 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.31 – 7.25 (m, 6H), 7.21 (td, *J* = 7.7, 1.2 Hz, 1H), 7.10 (td, *J* = 7.6, 1.1 Hz, 1H), 6.88 (s, 1H), 6.75 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.47 (s, 1H), 6.20 (dd, *J* = 3.2, 1.9 Hz, 1H), 5.95 (dd, *J* = 3.3, 0.8 Hz, 1H), 5.88 (dd, *J* = 7.4, 1.5 Hz, 2H), 4.92 (d, *J* = 15.8 Hz, 1H), 4.85 (d, *J* = 15.7 Hz, 1H), 3.71 (q, *J* = 14.0 Hz, 2H). **¹³C NMR** (100 MHz,

CDCl₃) δ 177.7, 152.0, 149.6, 148.7, 142.3, 141.6, 141.3, 135.2, 129.3, 128.9, 128.6, 127.8, 127.3, 126.1, 123.6, 112.1, 110.5, 109.9, 108.2, 108.2, 101.4, 100.9, 58.5, 44.3, 27.1. **HRMS (ESI) m/z:** [M+H]⁺ calcd for C₂₇H₂₂NO₅S⁺ 472.1213; found: 472.1215.

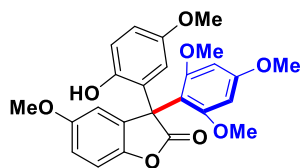
1-benzyl-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)-3-(p-tolylthio)indolin-2-one (6f)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 7:1) afforded the product as a light yellow solid (34.1 mg, 71% yield). M.p. 201 - 203 °C.

¹H NMR (400 MHz, CDCl₃) δ 10.48 (s, 1H), 7.61 (dd, J = 7.4, 1.4 Hz, 1H), 7.24 – 7.11 (m, 5H), 7.06 – 7.02 (m, 2H), 6.88 – 6.84 (m, 2H), 6.83 – 6.79 (m, 2H), 6.68 (s, 1H), 6.64 (s, 1H), 6.49 – 6.46 (m, 1H), 5.86 (dd, J = 17.9, 1.4 Hz, 2H), 4.63 (d, J = 15.8 Hz, 1H), 4.56 (d, J = 15.9 Hz, 1H), 2.27 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 178.0, 153.7, 149.2, 141.7, 141.0, 140.0, 136.9, 134.4, 129.4, 129.2, 129.1, 128.7, 128.0, 127.6, 127.0, 126.2, 123.3, 110.6, 110.1, 108.3, 101.7, 101.4, 63.9, 44.4, 21.4. **HRMS (ESI) m/z:** [M+H]⁺ calcd for C₂₉H₂₄NO₄S⁺ 482.1420; found: 482.1421.

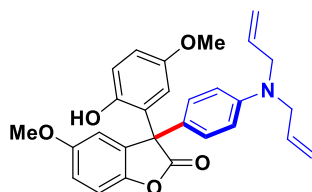
3-(2-hydroxy-5-methoxyphenyl)-5-methoxy-3-(2,4,6-trimethoxyphenyl)benzofuran-2(3H)-one (8a)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 8:1) afforded the product as a white solid (28.9 mg, 64% yield). M.p. 86 - 88 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.17 (s, 1H), 7.08 (d, J = 8.8 Hz, 1H), 6.90 – 6.83 (m, 2H), 6.80 (d, J = 2.7 Hz, 1H), 6.71 (dd, J = 8.7, 3.0 Hz, 1H), 6.36 (d, J = 3.0 Hz, 1H), 6.13 – 6.10 (m, 2H), 3.75 (d, J = 4.3 Hz, 6H), 3.67 (s, 3H), 3.64 (s, 3H), 3.34 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 181.5, 161.1, 160.2, 157.6, 156.9, 153.4, 149.7, 146.9, 131.0, 127.8, 119.1, 115.0, 114.0, 112.6, 112.4, 111.2, 107.7, 92.8, 92.3, 56.2, 56.1, 55.9, 55.8, 55.7, 55.3. **HRMS (ESI) m/z:** [M+H]⁺ calcd for C₂₅H₂₅O₈⁺ 453.1543; found: 453.0546.

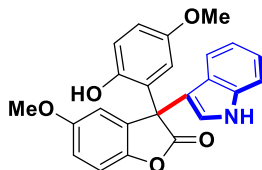
3-(4-(diallylamino)phenyl)-3-(2-hydroxy-5-methoxyphenyl)-5-methoxybenzofuran-2(3H)-one (8b)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 8:1) afforded the product as a white solid (32.4 mg, 71% yield). M.p. 81 - 83 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.12 – 7.05 (m, 3H), 6.83 (dd, *J* = 8.8, 2.7 Hz, 1H), 6.77 – 6.71 (m, 2H), 6.69 (d, *J* = 2.8 Hz, 1H), 6.64 – 6.59 (m, 3H), 5.98 (s, 1H), 5.87 – 5.76 (m, 2H), 5.18 – 5.14 (m, 2H), 5.12 (t, *J* = 1.7 Hz, 2H), 3.89 (dd, *J* = 4.2, 2.5 Hz, 4H), 3.74 (s, 3H), 3.67 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 179.7, 156.6, 153.4, 148.5, 148.1, 146.9, 133.6, 131.8, 128.8, 128.2, 124.1, 118.4, 116.3, 116.2, 113.8, 113.6, 112.3, 112.2, 111.3, 59.3, 55.9, 55.7, 52.7. **HRMS (ESI) m/z:** [M+H]⁺ calcd for C₂₈H₂₈NO₅⁺ 458.1962; found: 458.1960.

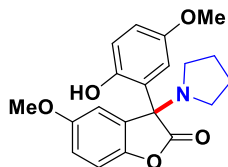
3-(2-hydroxy-5-methoxyphenyl)-3-(1*H*-indol-3-yl)-5-methoxybenzofuran-2(3*H*)-one (8c)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 5:1) afforded the product as a white solid (30.4 mg, 76% yield). M.p. 92 - 94 °C.

¹H NMR (400 MHz, DMSO-*d*₆) δ 11.24 (d, *J* = 2.7 Hz, 1H), 9.52 (s, 1H), 7.49 – 7.43 (m, 2H), 7.19 (d, *J* = 8.7 Hz, 1H), 7.16 – 7.10 (m, 1H), 6.99 – 6.91 (m, 2H), 6.80 – 6.70 (m, 3H), 6.63 (d, *J* = 2.7 Hz, 1H), 6.50 (d, *J* = 3.0 Hz, 1H), 3.70 (s, 3H), 3.45 (s, 3H). **¹³C NMR** (100 MHz, DMSO-*d*₆) δ 176.5, 156.4, 152.2, 148.4, 147.4, 138.0, 132.7, 127.2, 126.7, 125.4, 123.0, 122.1, 119.2, 116.7, 116.1, 113.9, 113.4, 112.4, 111.6, 111.0, 56.1, 55.5, 55.3, 54.3. **HRMS (ESI) m/z:** [M+H]⁺ calcd for C₂₄H₂₀NO₅⁺ 402.1336; found: 402.1337.

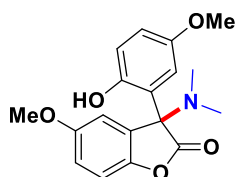
3-(2-hydroxy-5-methoxyphenyl)-5-methoxy-3-(pyrrolidin-1-yl)benzofuran-2(3*H*)-one (8d)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 15:1) afforded the product as a light yellow solid (20.5 mg, 58% yield). M.p. 83 - 85 °C.

¹H NMR (400 MHz, CDCl₃) δ 11.05 (s, 1H), 7.24 (d, *J* = 2.7 Hz, 1H), 7.05 (d, *J* = 8.8 Hz, 1H), 6.89 – 6.85 (m, 2H), 6.77 (dd, *J* = 8.9, 2.9 Hz, 1H), 6.36 (d, *J* = 2.9 Hz, 1H), 3.77 (s, 3H), 3.66 (s, 3H), 3.10 – 2.49 (m, 4H), 1.90 – 1.80 (m, 4H). **¹³C NMR** (100 MHz, CDCl₃) δ 173.5, 157.1, 152.4, 151.3, 146.2, 129.0, 122.5, 118.1, 115.7, 115.1, 112.8, 111.9, 110.6, 72.2, 55.9, 55.7, 23.7. **HRMS (ESI) m/z:** [M+H]⁺ calcd for C₂₀H₂₂NO₅⁺ 356.1492; found: 356.1496.

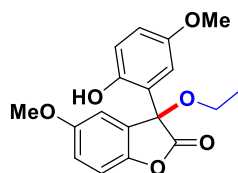
3-(dimethylamino)-3-(2-hydroxy-5-methoxyphenyl)-5-methoxybenzofuran-2(3*H*)-one (8e)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 15:1) afforded the product as a light yellow solid (17.1 mg, 52% yield). M.p. 79 - 81 °C.

¹H NMR (400 MHz, CDCl₃) δ 10.80 (s, 1H), 7.19 (d, *J* = 2.7 Hz, 1H), 7.07 (d, *J* = 8.8 Hz, 1H), 6.89 (dd, *J* = 8.8, 2.8 Hz, 2H), 6.78 (dd, *J* = 8.9, 3.0 Hz, 1H), 6.33 (d, *J* = 3.0 Hz, 1H), 3.77 (s, 3H), 3.66 (s, 3H), 2.44 (d, *J* = 65.6 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 172.7, 157.1, 152.5, 151.1, 146.5, 127.9, 122.1, 118.3, 115.9, 115.1, 113.3, 111.9, 110.6, 74.9, 55.9, 55.7, 39.3. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₁₈H₂₀NO₅⁺ 330.1336; found: 330.1337.

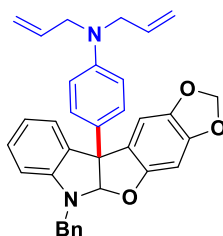
3-ethoxy-3-(2-hydroxy-5-methoxyphenyl)-5-methoxybenzofuran-2(3*H*)-one (8f)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 10:1) afforded the product as a white solid (17.8 mg, 54% yield). M.p. 74 - 76 °C.

¹H NMR (400 MHz, DMSO-*d*₆) δ 9.42 (s, 1H), 7.31 (d, *J* = 3.1 Hz, 1H), 7.21 (d, *J* = 8.8 Hz, 1H), 6.97 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.79 (dd, *J* = 8.7, 3.1 Hz, 1H), 6.65 – 6.59 (m, 2H), 3.75 (s, 3H), 3.67 (s, 3H), 3.30 – 3.20 (m, 2H), 1.18 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 175.1, 156.8, 152.6, 148.3, 147.1, 127.8, 126.6, 116.4, 116.2, 114.6, 112.5, 111.7, 110.5, 79.9, 60.5, 56.1, 55.9, 15.5. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₁₈H₁₉O₆⁺ 331.1176; found: 331.1174.

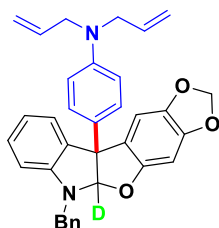
N,N-diallyl-4-(6-benzyl-5a,6-dihydro-10*bH*-[1,3]dioxolo[4',5':5,6]benzofuro[2,3-*b*]indol-10*b*-yl)aniline (11a)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 20:1) afforded the product as a white solid (29.7 mg, 58% yield, *dr* > 20:1). M.p. 112 - 114 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.23 (m, 5H), 7.13 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.03 (td, *J* = 7.7, 1.3 Hz, 1H), 6.96 – 6.91 (m, 2H), 6.77 – 6.70 (m, 2H), 6.63 – 6.57 (m, 2H), 6.45 – 6.38 (m, 2H), 5.95 (s, 1H), 5.90 (d, *J* = 1.4 Hz, 1H), 5.89 – 5.75 (m, 3H), 5.22 – 5.10 (m, 4H), 4.67 – 4.54 (m, 2H), 3.88 (dt, *J* = 4.9, 1.8 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 154.4, 149.3, 147.8, 147.5, 142.1, 137.8, 134.0, 133.2, 130.3, 128.7, 128.6, 128.1, 127.3, 127.1, 124.3, 123.5, 118.7, 116.2, 112.1, 110.8, 106.7, 104.9, 101.2, 93.3, 63.4, 52.8, 49.4. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₃₄H₃₁N₂O₃⁺ 515.2329; found: 515.2326.

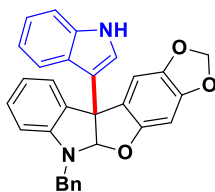
N,N-diallyl-4-((10*bR*)-6-benzyl-5a,6-dihydro-10*bH*-[1,3]dioxolo[4',5':5,6]benzofuro[2,3-*b*]indol-10*b*-yl-5a-*d*)aniline (11b)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 20:1) afforded the product as a white solid (28.3 mg, 55% yield, *dr* > 20:1). M.p. 115 - 117 °C.

¹H NMR (500 MHz, CDCl₃) δ 7.33 – 7.24 (m, 4H), 7.21 (dt, *J* = 7.3, 3.4 Hz, 1H), 7.12 (dd, *J* = 7.2, 2.4 Hz, 1H), 7.02 (td, *J* = 7.7, 2.2 Hz, 1H), 6.93 (dd, *J* = 8.9, 3.0 Hz, 2H), 6.74 – 6.69 (m, 2H), 6.62 – 6.57 (m, 2H), 6.43 (d, *J* = 2.6 Hz, 1H), 6.39 (dd, *J* = 8.0, 2.2 Hz, 1H), 5.88 (s, 1H), 5.87 – 5.76 (m, 3H), 5.19 – 5.10 (m, 4H), 4.66 – 4.53 (m, 2H), 3.87 (dd, *J* = 5.2, 2.4 Hz, 4H). **¹³C NMR** (100 MHz, CDCl₃) δ 154.4, 149.3, 147.8, 147.5, 142.1, 137.8, 134.0, 133.2, 130.3, 128.7, 128.6, 128.1, 127.3, 127.1, 124.3, 123.5, 118.7, 116.2, 112.1, 110.8, 106.7, 104.9, 101.2, 93.3, 63.4, 52.8, 49.4. **HRMS (ESI) m/z:** [M+H]⁺ calcd for C₃₄H₃₀DN₂O₃⁺ 516.2392; found: 516.2390.

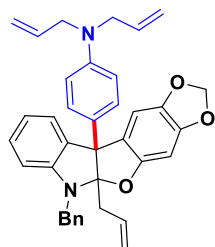
6-benzyl-10b-(1H-indol-3-yl)-5a,10b-dihydro-6H-[1,3]dioxolo[4',5':5,6]benzofuro[2,3-b]indole (11c)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 15:1) afforded the product as a white solid (24.2 mg, 53% yield, *dr* > 20:1). M.p. 124 - 126 °C.

¹H NMR (500 MHz, CDCl₃) δ 7.97 (s, 1H), 7.35 – 7.28 (m, 3H), 7.27 – 7.18 (m, 4H), 7.16 – 7.11 (m, 1H), 7.10 – 7.03 (m, 1H), 6.89 (dd, *J* = 16.2, 3.3 Hz, 3H), 6.76 – 6.68 (m, 2H), 6.49 (s, 1H), 6.46 (d, *J* = 7.9 Hz, 1H), 6.25 (s, 1H), 5.88 (d, *J* = 1.4 Hz, 1H), 5.81 (d, *J* = 1.4 Hz, 1H), 4.70 – 4.58 (m, 2H). **¹³C NMR** (100 MHz, CDCl₃) δ 153.8, 148.8, 147.7, 142.1, 137.8, 137.3, 132.3, 128.6, 128.4, 127.4, 127.3, 125.7, 123.9, 123.7, 123.1, 122.3, 120.1, 119.8, 118.7, 117.7, 111.4, 109.1, 106.8, 104.6, 101.3, 93.5, 58.7, 49.5. **HRMS (ESI) m/z:** [M+H]⁺ calcd for C₃₀H₂₃N₂O₃⁺ 459.1703; found: 459.1705.

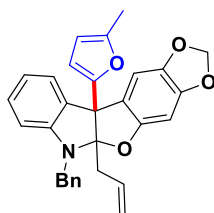
N,N-diallyl-4-(5a-allyl-6-benzyl-5a,6-dihydro-10bH-[1,3]dioxolo[4',5':5,6]benzofuro[2,3-b]indol-10b-yl)aniline (11d)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 20:1) afforded the product as a white solid (34.2 mg, 62% yield, *dr* = 13:1). M.p. 109 - 111 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.27 (d, *J* = 3.5 Hz, 4H), 7.23 – 7.18 (m, 1H), 7.08 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.00 – 6.93 (m, 3H), 6.71 – 6.66 (m, 2H), 6.64 – 6.58 (m, 2H), 6.38 (s, 1H), 6.20 (dd, *J* = 7.9, 0.9 Hz, 1H), 5.91 – 5.79 (m, 4H), 5.43 – 5.32 (m, 1H), 5.19 – 5.15 (m, 2H), 5.15 – 5.13 (m, 2H), 4.74 – 4.51 (m, 4H), 3.90 (dt, *J* = 5.1, 1.7 Hz, 4H), 2.62 – 2.41 (m, 2H). **¹³C NMR** (100 MHz, CDCl₃) δ 153.7, 149.7, 148.0, 147.4, 142.0, 138.8, 134.0, 133.2, 131.8, 130.7, 128.5, 127.9, 127.0, 126.8, 126.6, 124.6, 124.0, 118.6, 117.8, 116.2, 114.5, 111.7, 106.9, 105.1, 101.2, 93.0, 66.5, 52.8, 47.6, 39.6. **HRMS (ESI)** *m/z*: [M+H]⁺ calcd for C₃₇H₃₅N₂O₃⁺ 555.2642; found: 555.2643.

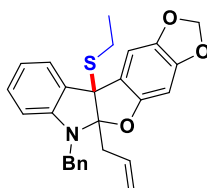
5a-allyl-6-benzyl-10b-(5-methylfuran-2-yl)-5a,10b-dihydro-6H-[1,3]dioxolo[4',5':5,6]benzofuro[2,3-*b*]indole (11e)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 20:1) afforded the product as a white solid (28.2 mg, 61% yield, *dr* = 6:1). M.p. 104 - 106 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.33 – 7.21 (m, 5H), 7.14 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.00 – 6.94 (m, 1H), 6.72 (s, 1H), 6.71 – 6.66 (m, 1H), 6.38 (s, 1H), 6.22 – 6.18 (m, 1H), 6.03 (d, *J* = 3.1 Hz, 1H), 5.91 (dd, *J* = 3.1, 1.1 Hz, 1H), 5.90 (d, *J* = 1.4 Hz, 1H), 5.83 (d, *J* = 1.5 Hz, 1H), 5.49 – 5.39 (m, 1H), 4.82 – 4.72 (m, 2H), 4.62 (q, *J* = 17.0 Hz, 2H), 2.83 – 2.69 (m, 2H), 2.24 (d, *J* = 1.1 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 153.2, 152.7, 150.9, 149.1, 147.9, 142.0, 138.5, 131.3, 130.3, 128.6, 128.5, 126.8, 126.7, 123.6, 122.3, 118.5, 117.4, 114.3, 112.0, 106.9, 106.4, 104.7, 101.3, 93.2, 62.5, 47.2, 38.9, 13.9. **HRMS (ESI)** *m/z*: [M+H]⁺ calcd for C₃₀H₂₆NO₄⁺ 464.1856; found: 464.1854.

5a-allyl-6-benzyl-10b-(ethylthio)-5a,10b-dihydro-6H-[1,3]dioxolo[4',5':5,6]benzofuro[2,3-*b*]indole (11f)

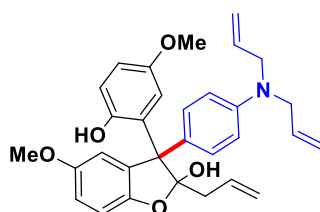


Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 20:1) afforded the product as a white solid (26.0 mg, 59% yield, *dr* = 8:1). M.p. 101 - 103 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.34 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.29 – 7.24 (m, 2H), 7.23 – 7.18 (m, 3H), 6.94 (td, *J* = 7.7, 1.3 Hz, 1H), 6.87 (s, 1H), 6.73 – 6.69 (m, 1H), 6.31 (s, 1H), 6.13 (d, *J* = 7.8 Hz, 1H), 5.91 – 5.83 (m, 3H), 5.20 – 5.13 (m, 1H), 5.04 – 5.00 (m, 1H), 4.66 – 4.54 (m, 2H), 3.14 – 2.99 (m, 2H), 2.29 – 2.17 (m, 2H), 1.14 (t, *J* = 7.5 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 152.5, 148.7, 148.3, 142.3, 138.6, 132.1, 129.2, 129.0, 128.6, 126.9, 126.6, 123.4, 121.6, 118.9, 118.7, 114.2, 106.7, 104.2, 101.4, 93.1, 67.6, 47.9, 40.1, 24.5, 14.1. **HRMS (ESI)** *m/z*: [M+H]⁺ calcd for C₂₇H₂₆NO₃S⁺ 444.1627; found: 444.1624.

2-allyl-3-(4-(diallylamino)phenyl)-3-(2-hydroxy-5-methoxyphenyl)-5-methoxy-2,3

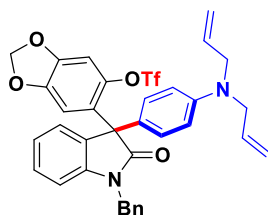
-dihydrobenzofuran-2-ol (12a)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 10:1) afforded the product as a white solid (26.1 mg, 55% yield, *dr* > 20:1). M.p. 93 - 95 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.28 (d, *J* = 2.9 Hz, 1H), 7.12 (d, *J* = 8.5 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 1H), 6.87 (dd, *J* = 8.8, 2.9 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 6.72 – 6.66 (m, 2H), 6.53 – 6.49 (m, 2H), 6.13 (s, 1H), 6.05 – 5.95 (m, 1H), 5.86 – 5.71 (m, 2H), 5.23 (dd, *J* = 10.2, 2.0 Hz, 1H), 5.15 – 5.05 (m, 5H), 4.36 (s, 1H), 3.89 – 3.81 (m, 4H), 3.76 (s, 3H), 3.69 (s, 3H), 2.46 (dd, *J* = 14.1, 5.6 Hz, 1H), 1.92 (dd, *J* = 14.1, 8.6 Hz, 1H). **¹³C NMR** (100 MHz, CDCl₃) δ 154.3, 153.1, 149.9, 149.8, 147.9, 135.1, 133.9, 132.1, 128.2, 127.2, 125.1, 121.3, 118.3, 116.2, 115.9, 113.8, 113.5, 113.4, 112.1, 111.9, 110.9, 64.7, 55.9, 55.7, 52.5, 42.7. **HRMS (ESI) m/z:** [M+H]⁺ calcd for C₃₁H₃₄NO₅⁺ 500.2431; found: 500.2433.

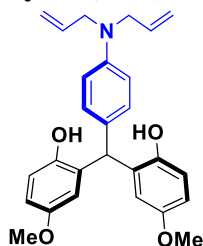
6-(1-benzyl-3-(4-(diallylamino)phenyl)-2-oxoindolin-3-yl)benzo[d][1,3]dioxol-5-yl trifluoromethanesulfonate (13)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 15:1) afforded the product as a white solid (48.3 mg, 73% yield). M.p. 186 - 188 °C.

¹H NMR (500 MHz, CDCl₃) δ 7.27 – 7.17 (m, 5H), 7.07 (t, *J* = 4.2 Hz, 5H), 6.82 (s, 1H), 6.76 (d, *J* = 7.8 Hz, 1H), 6.70 (d, *J* = 11.2 Hz, 3H), 6.04 (q, *J* = 1.5 Hz, 2H), 5.93 – 5.85 (m, 2H), 5.47 (d, *J* = 16.1 Hz, 1H), 5.23 – 5.17 (m, 4H), 4.49 (d, *J* = 16.1 Hz, 1H), 3.96 (dd, *J* = 4.9, 2.5 Hz, 4H). **¹³C NMR** (125 MHz, CDCl₃) δ 177.6, 148.3, 147.6, 146.4, 142.9, 142.5, 136.2, 133.7, 131.2, 129.9, 128.6, 128.5, 128.5, 127.2, 126.8, 125.4, 118.3(q, *J* = 318.8), 116.2, 112.2, 111.4, 110.0, 102.5, 102.1, 102.1, 58.7, 52.8, 43.7. **HRMS (ESI) m/z:** [M+H]⁺ calcd for C₃₅H₃₀F₃N₂O₆S⁺ 663.1771; found: 663.1773.

2,2'-((4-(diallylamino)phenyl)methylene)bis(4-methoxyphenol) (14)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 5:1) afforded the product as a white solid (26.2 mg, 61% yield). M.p. 106 - 108 °C.

¹H NMR (500 MHz, CDCl₃) δ 6.93 – 6.88 (m, 2H), 6.68 (d, *J* = 8.7 Hz, 2H), 6.63 – 6.53 (m, 4H), 6.41 (d, *J* = 3.0 Hz, 2H), 5.81 – 5.72 (m, 2H), 5.60 (s, 1H), 5.12 – 5.03 (m, 4H), 4.80 (s, 2H), 3.86 – 3.77 (m, 4H), 3.59 (s, 6H). **¹³C NMR** (100 MHz, CDCl₃) δ 153.81, 147.89, 147.54, 133.96, 130.56, 129.90, 127.10, 117.02, 116.21, 116.13, 112.67, 112.27, 55.59, 52.76, 44.41. **HRMS (ESI) m/z:** [M+H]⁺ calcd for C₂₇H₃₀NO₄⁺ 432.2169; found: 432.2167.

Reference

1. Shi, H.; Wang, L.; Li, S.-S.; Liu, Y.; Xu, L. *Org. Chem. Front.* **2020**, *7*, 747-755.

6. Crystal Structures and Data

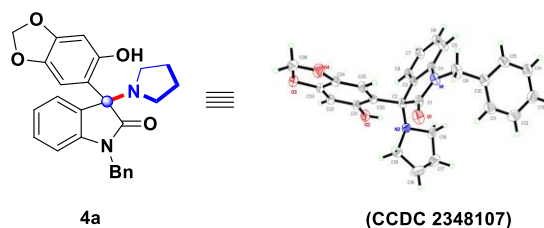


Table S2. Crystal data and structure refinement for **4a**.

Identification code	4a
Empirical formula	C ₂₆ H ₂₃ N ₂ O ₄
Formula weight	427.46
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 10.8116(11) Å alpha = 90 deg. b = 14.9897(14) Å beta = 94.585(3) deg. c = 13.0257(12) Å gamma = 90 deg.
Volume	2104.2(3) Å ³
Z, Calculated density	4, 1.349 Mg/m ³
Absorption coefficient	0.092 mm ⁻¹
F(000)	900
Crystal size	0.410 x 0.370 x 0.350 mm
Theta range for data collection	2.075 to 25.007 deg.
Limiting indices	-12 ≤ h ≤ 12, -17 ≤ k ≤ 13, -15 ≤ l ≤ 15
Reflections collected / unique	9970 / 3690 [R(int) = 0.0448]
Completeness to theta = 25.007	99.4 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3690 / 36 / 290
Goodness-of-fit on F ²	1.029
Final R indices [I > 2σ(I)]	R1 = 0.0551, wR2 = 0.1398
R indices (all data)	R1 = 0.0903, wR2 = 0.1568
Extinction coefficient	0.0187(18)
Largest diff. peak and hole	0.434 and -0.288 e.Å ⁻³

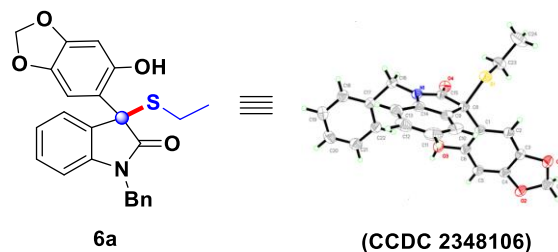
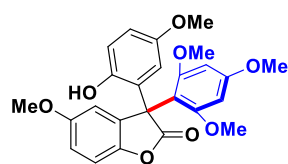
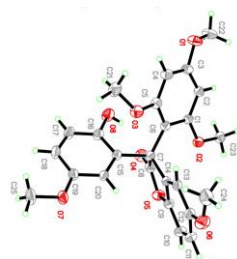


Table S3. Crystal data and structure refinement for **6a**.

Identification code	6a
Empirical formula	C ₂₅ H ₂₅ NO ₅ S
Formula weight	451.52
Temperature	293(2) K
Wavelength	1.54184 Å
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 12.9521(5) Å alpha = 90 deg. b = 19.0400(8) Å beta = 96.104(4) deg. c = 9.3837(5) Å gamma = 90 deg.
Volume	2300.97(18) Å ³
Z, Calculated density	4, 1.303 Mg/m ³
Absorption coefficient	1.552 mm ⁻¹
F(000)	952
Crystal size	0.120 x 0.120 x 0.110 mm
Theta range for data collection	3.432 to 67.244 deg.
Limiting indices	-14 ≤ h ≤ 15, -22 ≤ k ≤ 19, -8 ≤ l ≤ 11
Reflections collected / unique	8265 / 4108 [R(int) = 0.0219]
Completeness to theta = 67.244	99.8 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4108 / 0 / 293
Goodness-of-fit on F ²	1.034
Final R indices [I > 2σ(I)]	R1 = 0.0419, wR2 = 0.1046
R indices (all data)	R1 = 0.0548, wR2 = 0.1134
Extinction coefficient	n/a
Largest diff. peak and hole	0.161 and -0.172 e.Å ⁻³



8a



(CCDC 2348105)

Table S4. Crystal data and structure refinement for **8a**.

Identification code	8a
Empirical formula	C ₃₃ H ₂₈ N ₂ O ₅
Formula weight	532.57
Temperature	139(2) K
Wavelength	1.54184 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 9.8268(5) Å alpha = 79.621(4) deg. b = 12.1370(6) Å beta = 68.485(5) deg. c = 12.7460(6) Å gamma = 66.793(5) deg.
Volume	1298.70(13) Å ³
Z, Calculated density	2, 1.362 Mg/m ³
Absorption coefficient	0.747 mm ⁻¹
F(000)	560
Crystal size	0.220 x 0.210 x 0.210 mm
Theta range for data collection	3.731 to 67.244 deg.
Limiting indices	-7 ≤ h ≤ 11, -11 ≤ k ≤ 14, -14 ≤ l ≤ 15
Reflections collected / unique	8360 / 4655 [R(int) = 0.0177]
Completeness to theta = 67.244	99.7 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4655 / 362 / 426
Goodness-of-fit on F ²	1.030
Final R indices [I > 2σ(I)]	R1 = 0.0722, wR2 = 0.1891
R indices (all data)	R1 = 0.0817, wR2 = 0.1993
Extinction coefficient	n/a
Largest diff. peak and hole	0.413 and -0.388 e.Å ⁻³

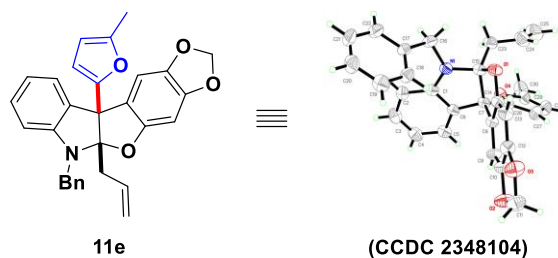
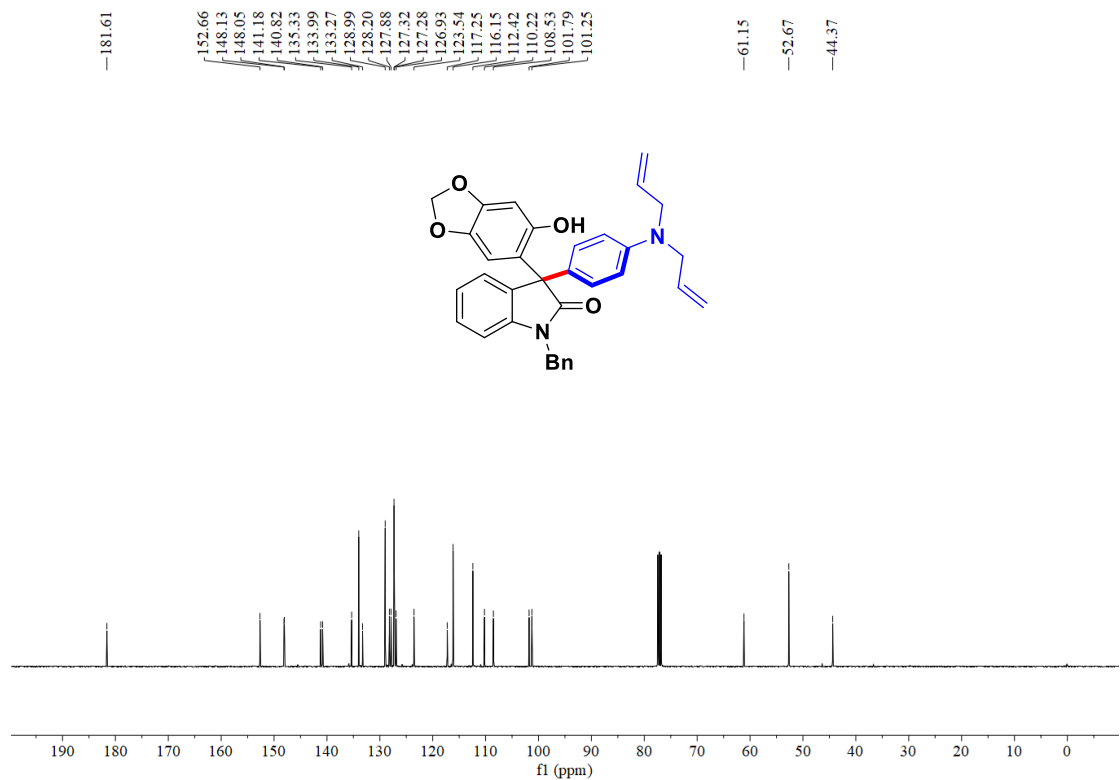
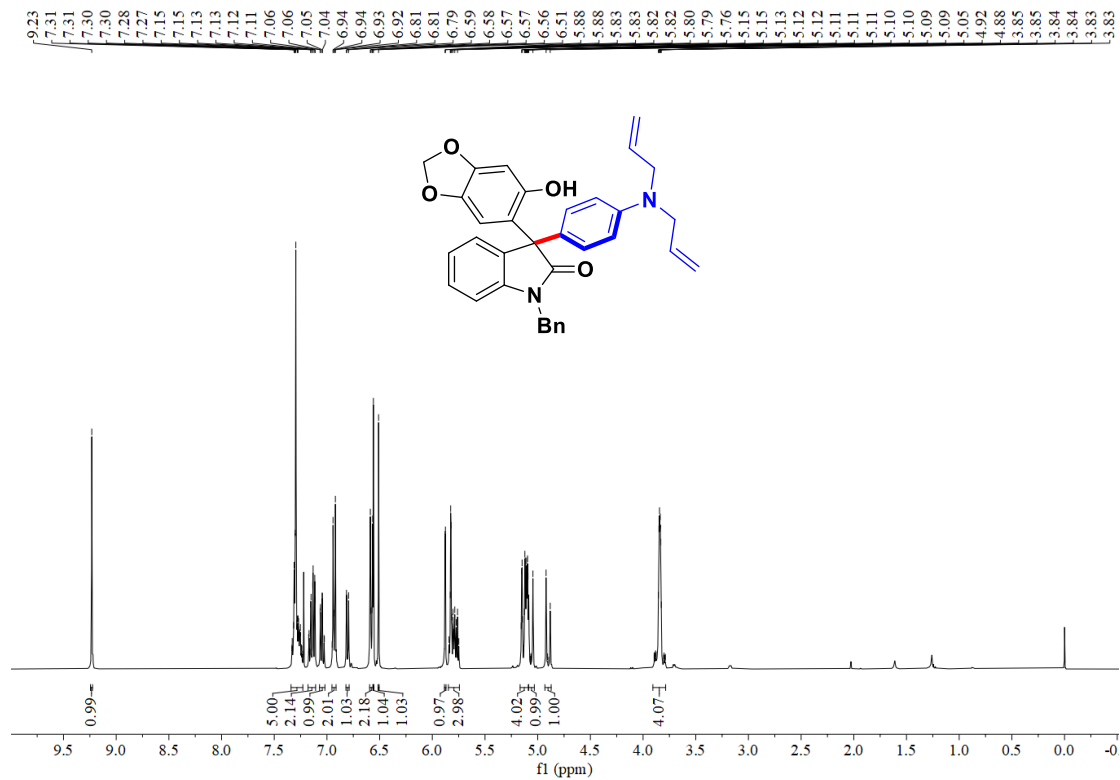


Table S5. Crystal data and structure refinement for **11e**.

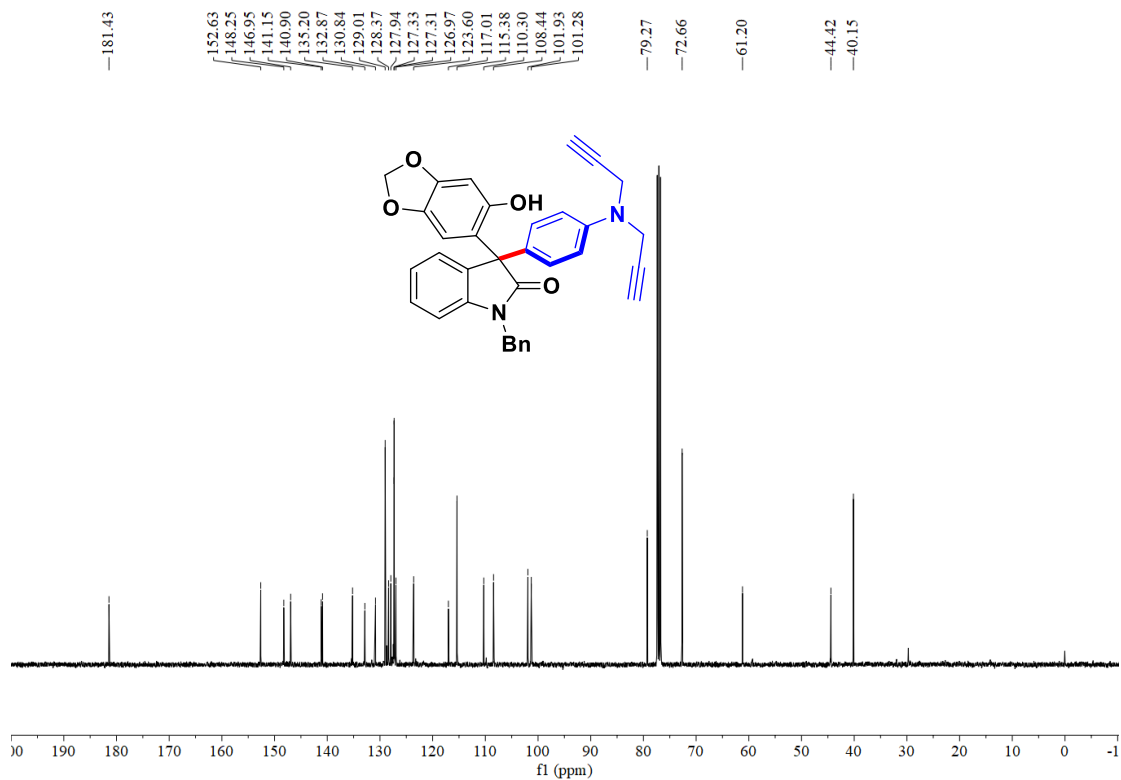
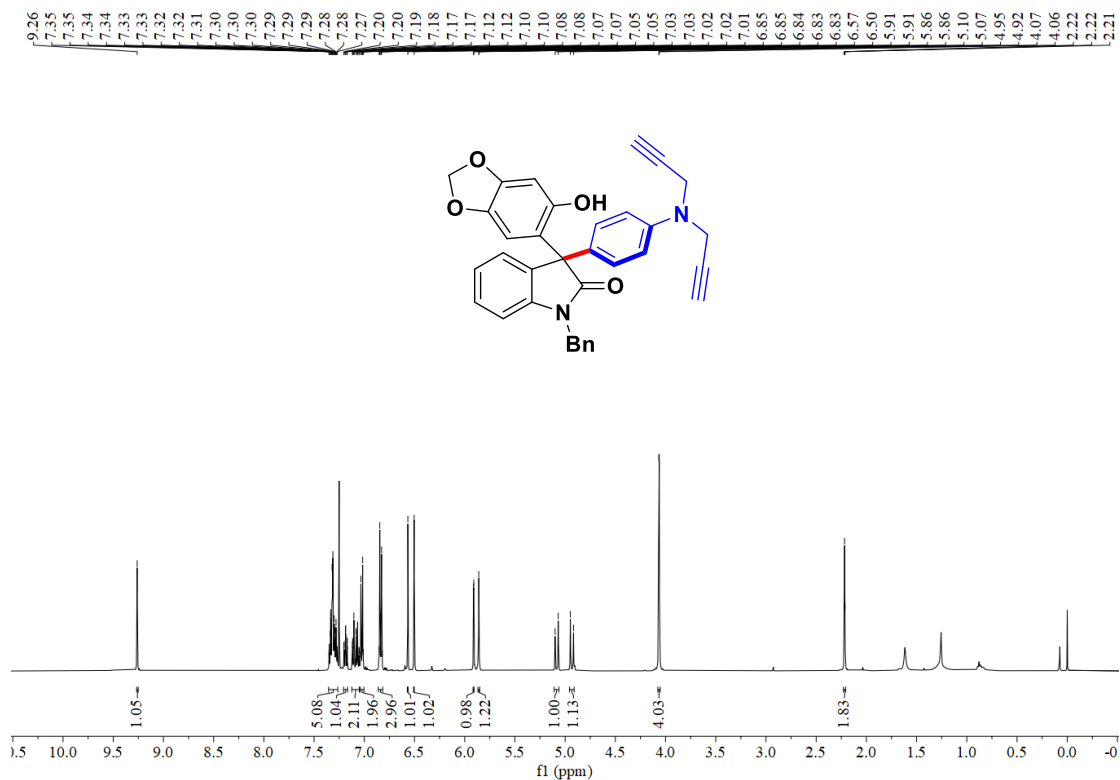
Identification code	11e
Empirical formula	C ₃₀ H ₂₅ NO ₄
Formula weight	463.51
Temperature	273(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 8.7819(5) Å alpha = 97.784(2) deg. b = 10.3472(6) Å beta = 97.527(2) deg. c = 13.4614(8) Å gamma = 91.588(2) deg.
Volume	1200.21(12) Å ³
Z, Calculated density	2, 1.283 Mg/m ³
Absorption coefficient	0.085 mm ⁻¹
F(000)	488
Crystal size	0.230 x 0.210 x 0.200 mm
Theta range for data collection	2.342 to 25.016 deg.
Limiting indices	-10 ≤ h ≤ 10, -12 ≤ k ≤ 12, -16 ≤ l ≤ 16
Reflections collected / unique	17738 / 4221 [R(int) = 0.0473]
Completeness to theta = 25.016	99.6 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4221 / 0 / 317
Goodness-of-fit on F ²	1.151
Final R indices [I > 2σ(I)]	R1 = 0.0792, wR2 = 0.1382
R indices (all data)	R1 = 0.1261, wR2 = 0.1627
Extinction coefficient	n/a
Largest diff. peak and hole	0.300 and -0.209 e.Å ⁻³

7. ¹H and ¹³C NMR Spectra

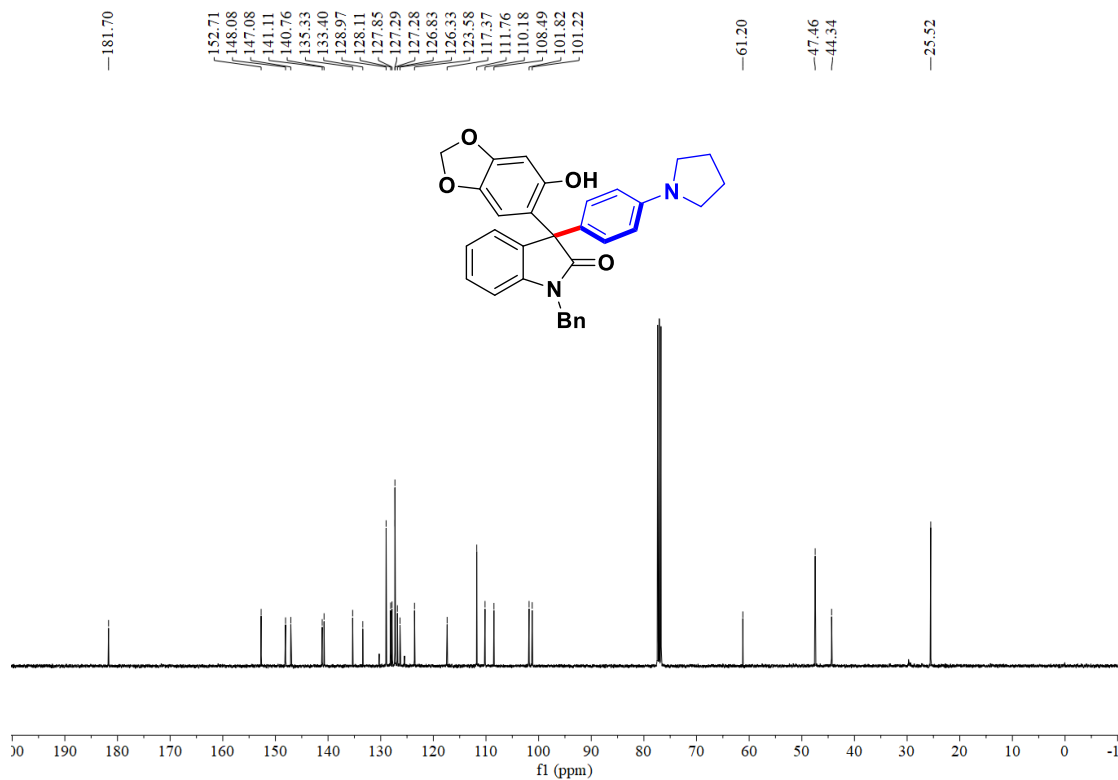
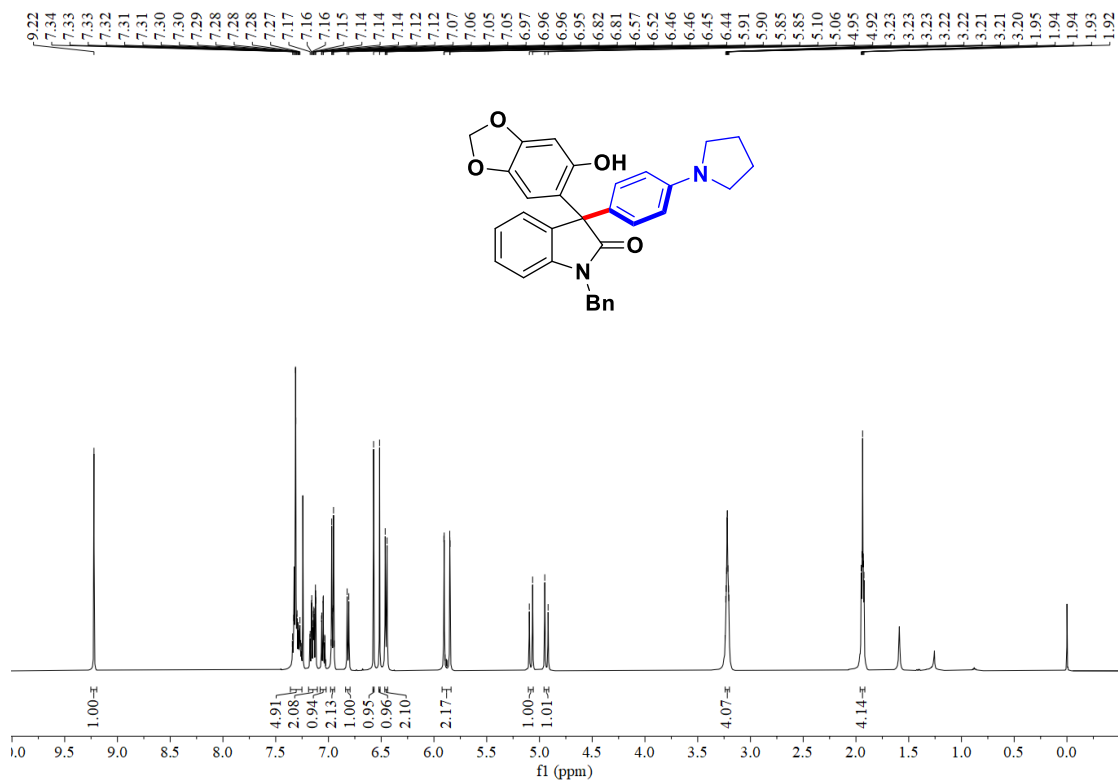
1-benzyl-3-(4-(diallylamino)phenyl)-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)indolin-2-one (3a)



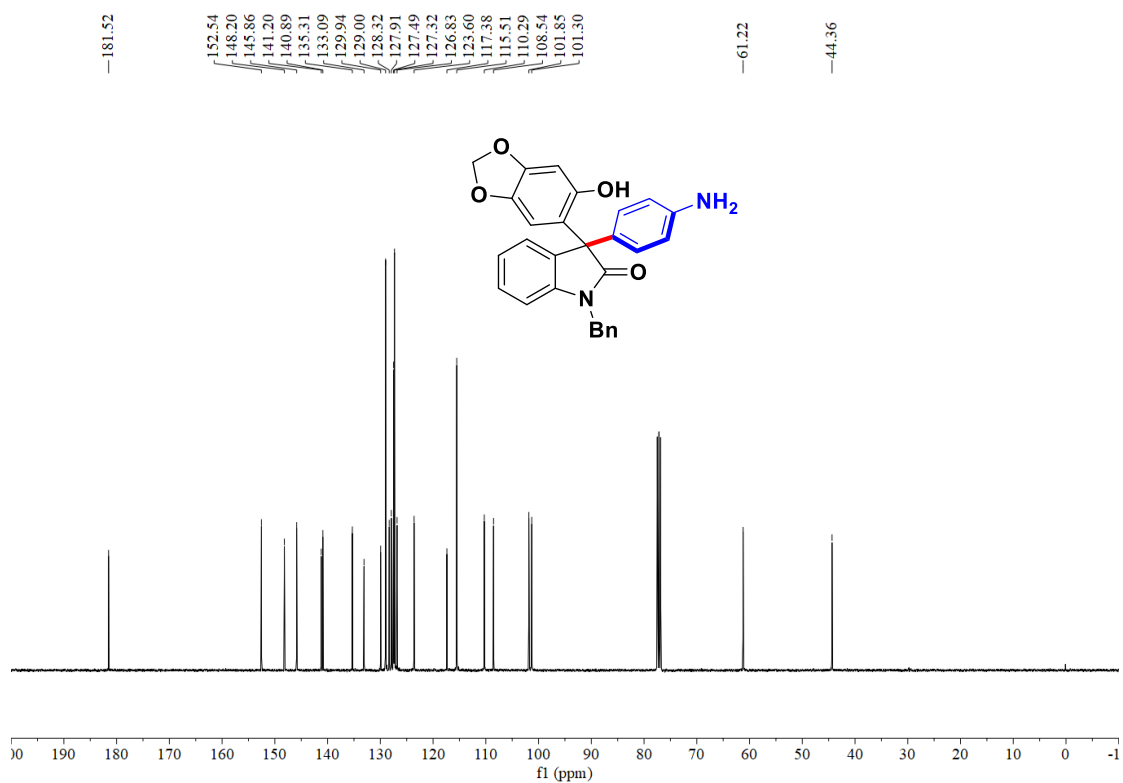
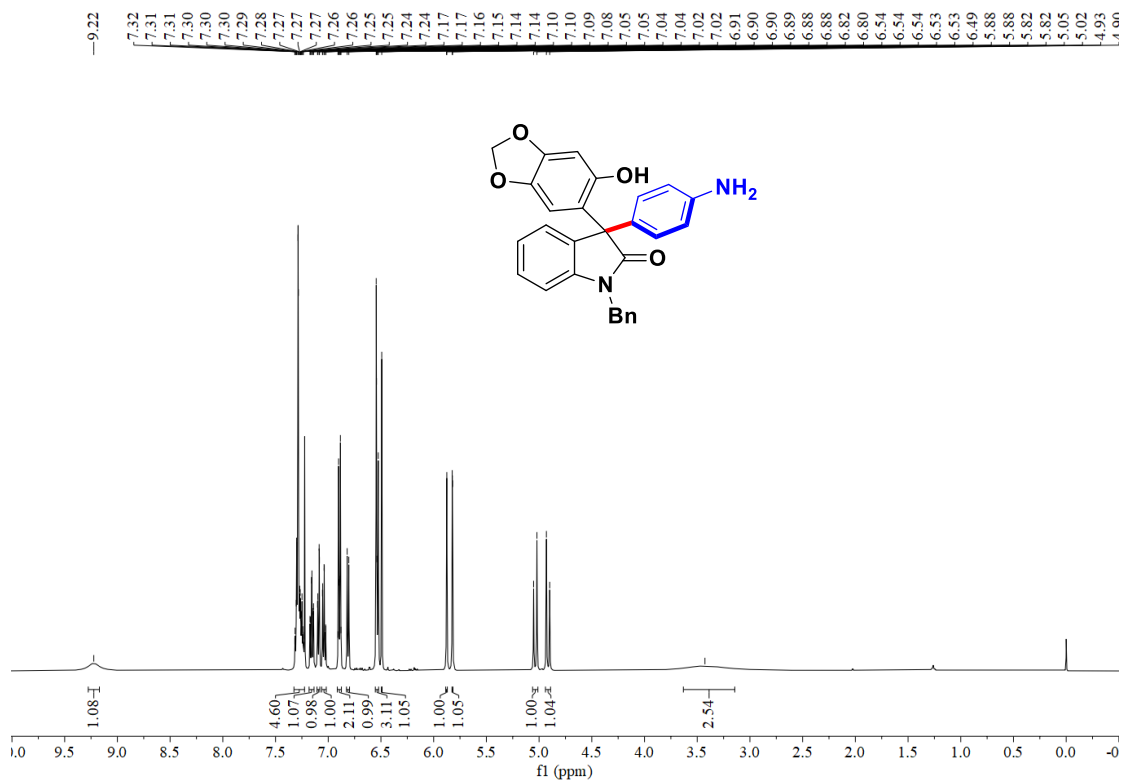
1-benzyl-3-(4-(di(prop-2-yn-1-yl)amino)phenyl)-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)indolin-2-one (3b)



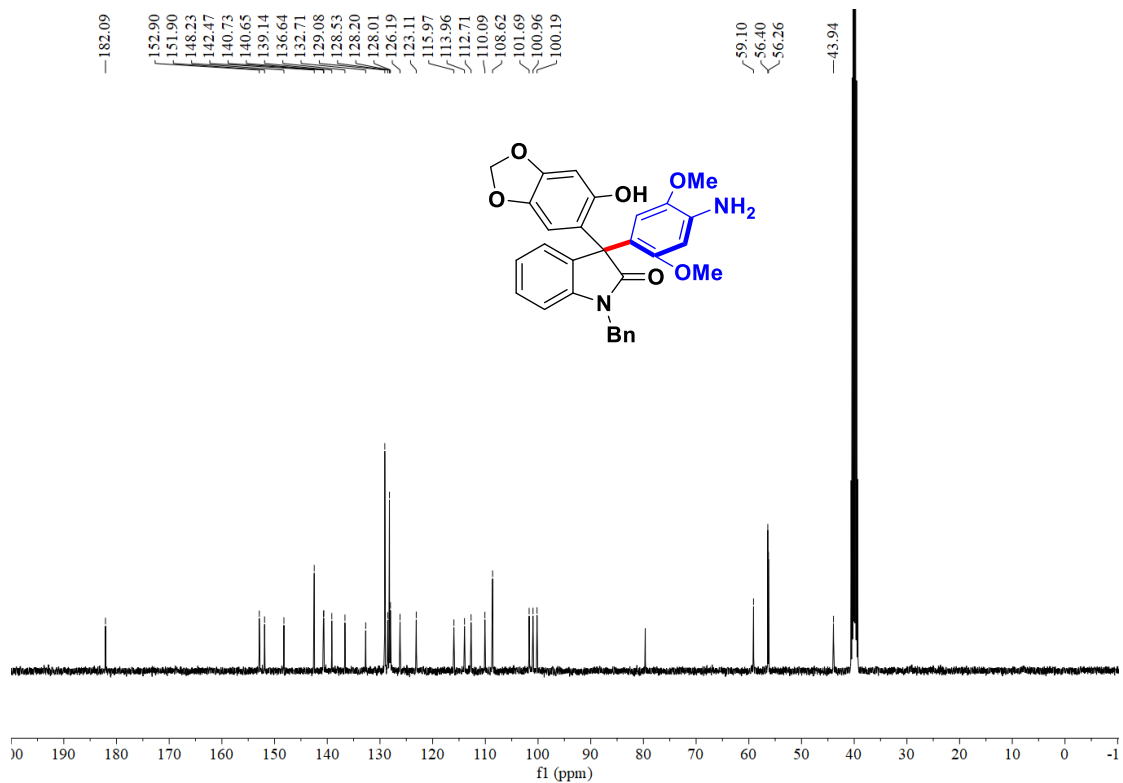
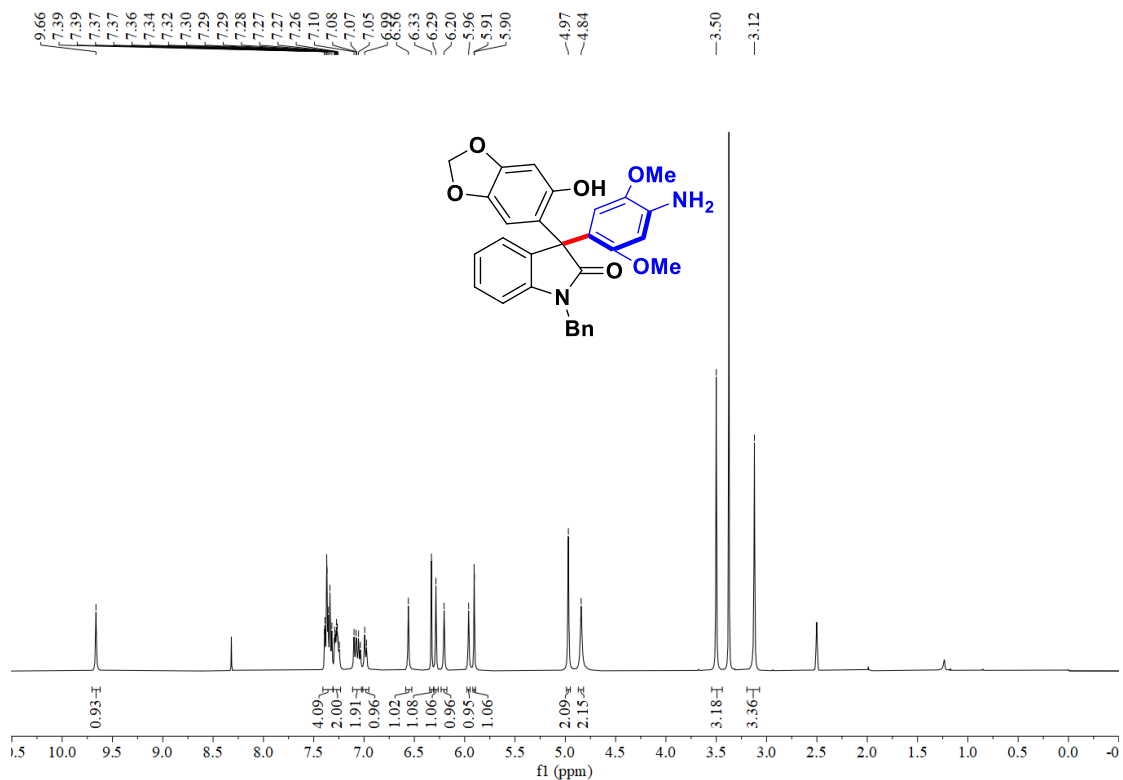
1-benzyl-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)-3-(4-(pyrrolidin-1-yl)phenyl)indolin-2-one (3c)



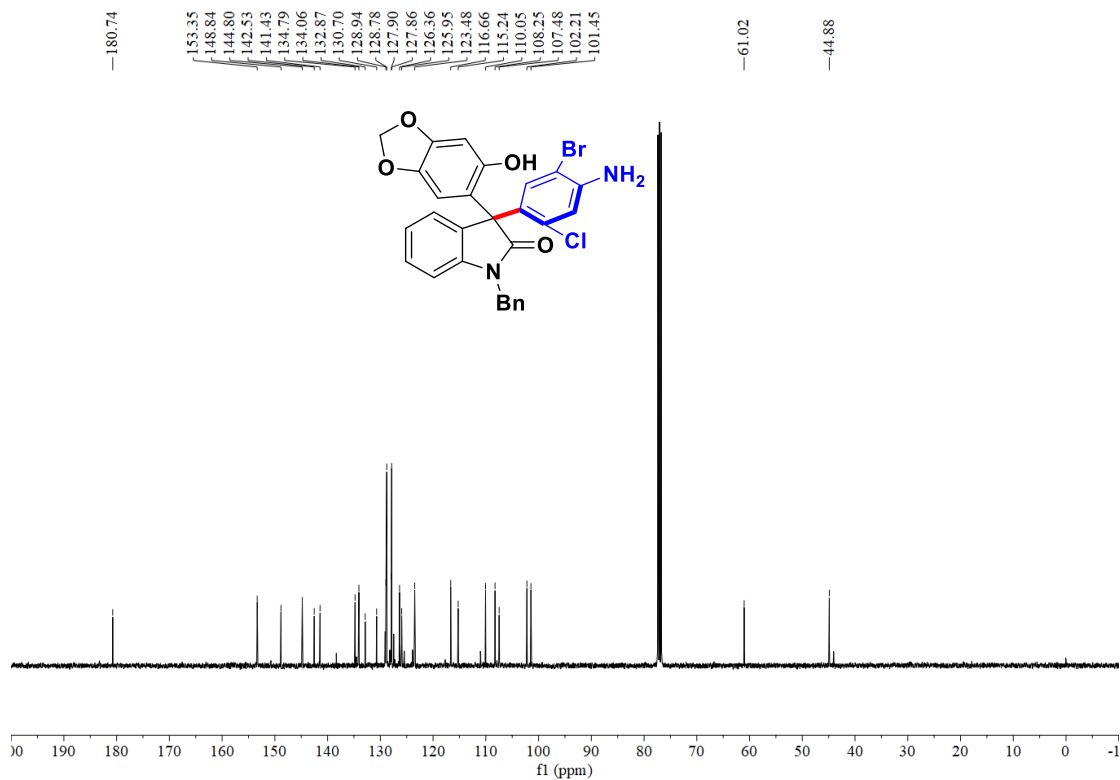
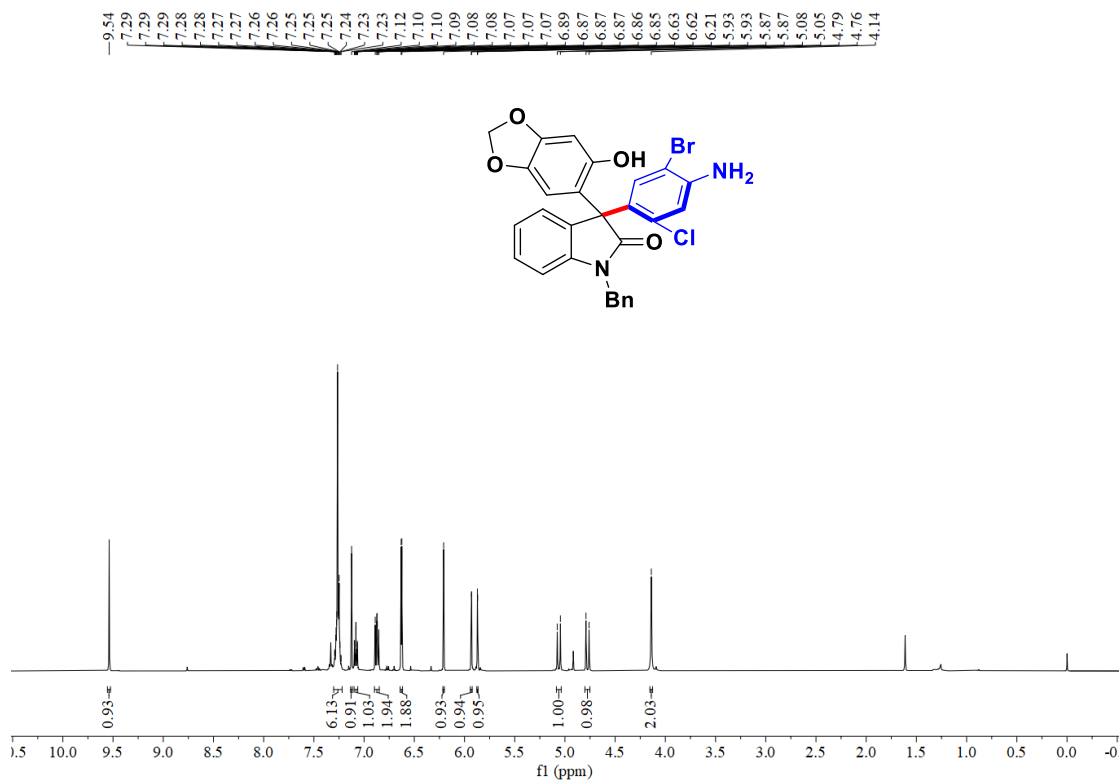
**3-(4-aminophenyl)-1-benzyl-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)indolin-2-one
(3d)**



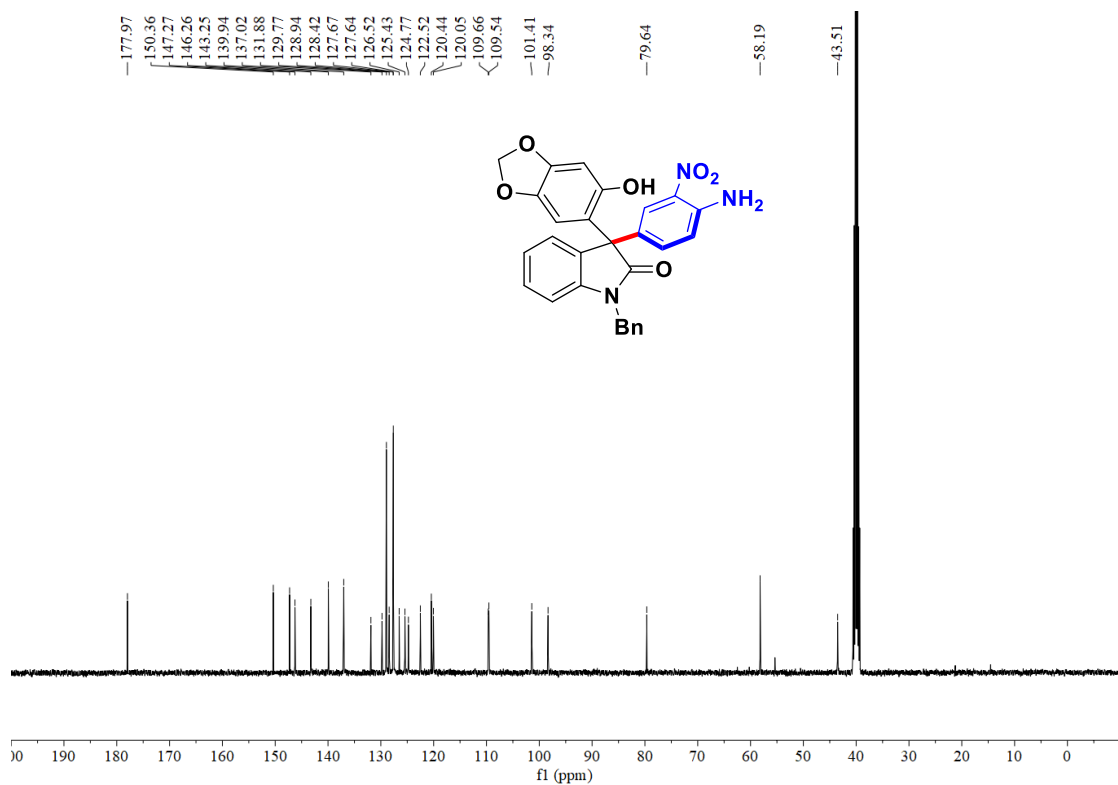
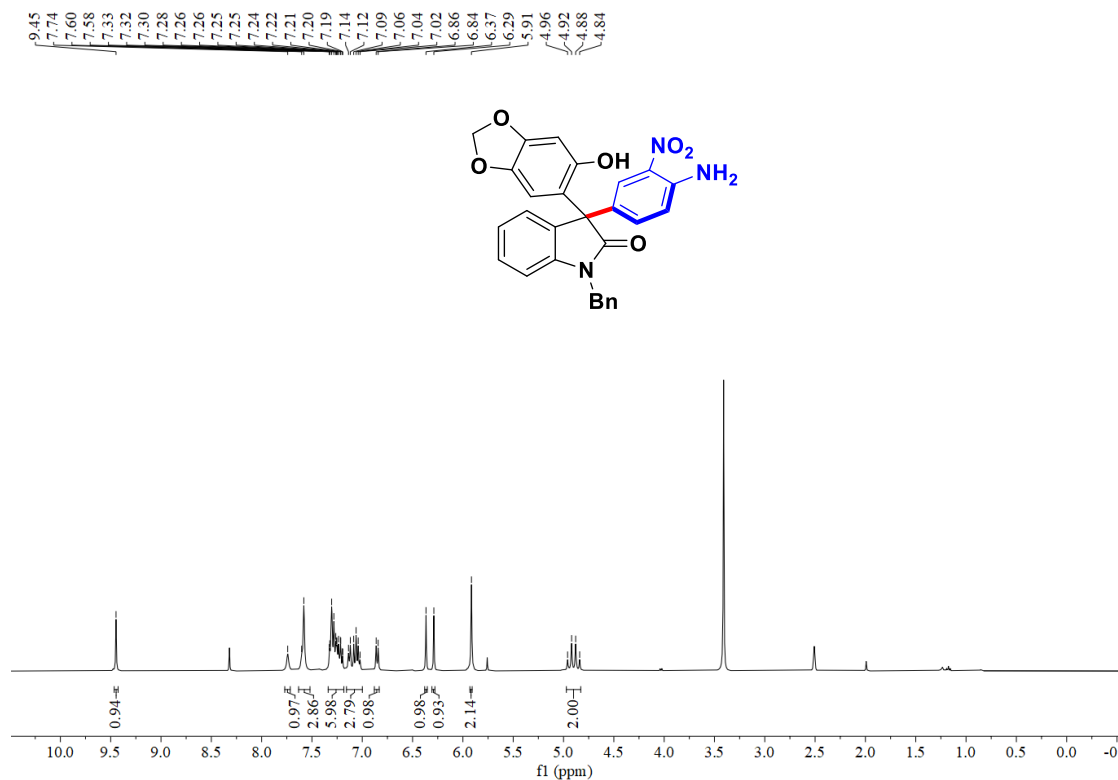
3-(4-amino-2,5-dimethoxyphenyl)-1-benzyl-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)indolin-2-one (3e)



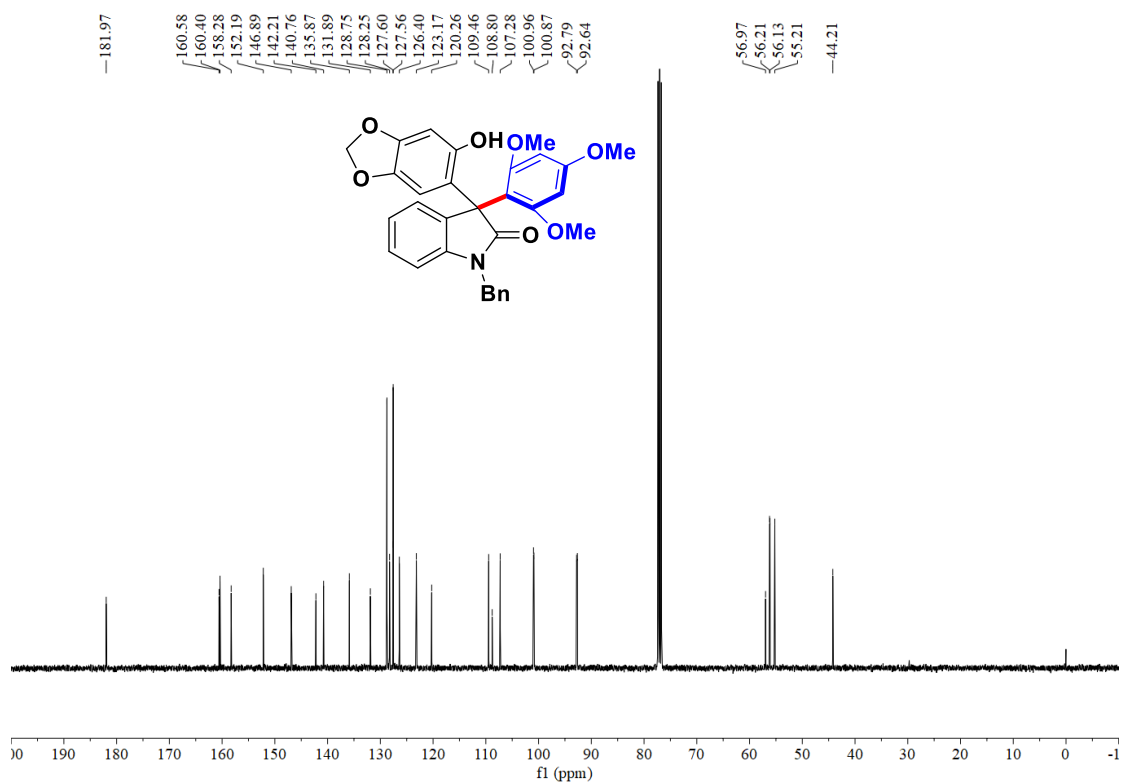
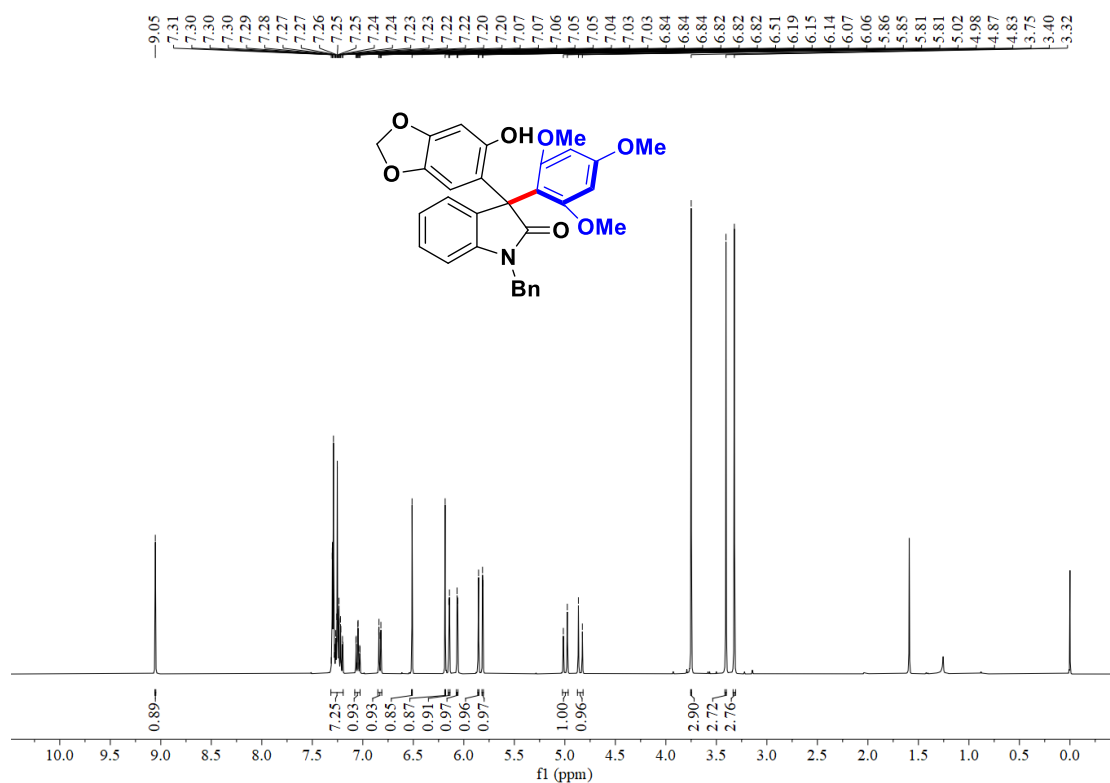
3-(4-amino-5-bromo-2-chlorophenyl)-1-benzyl-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)indolin-2-one (3f)



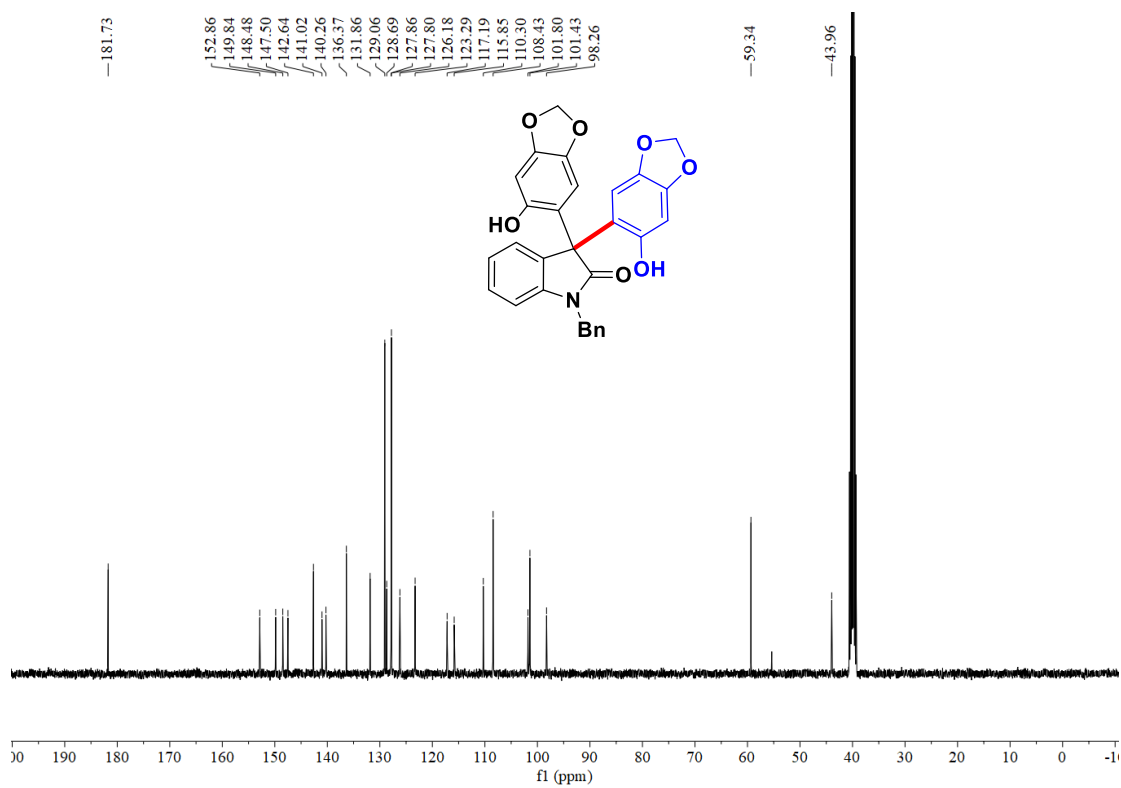
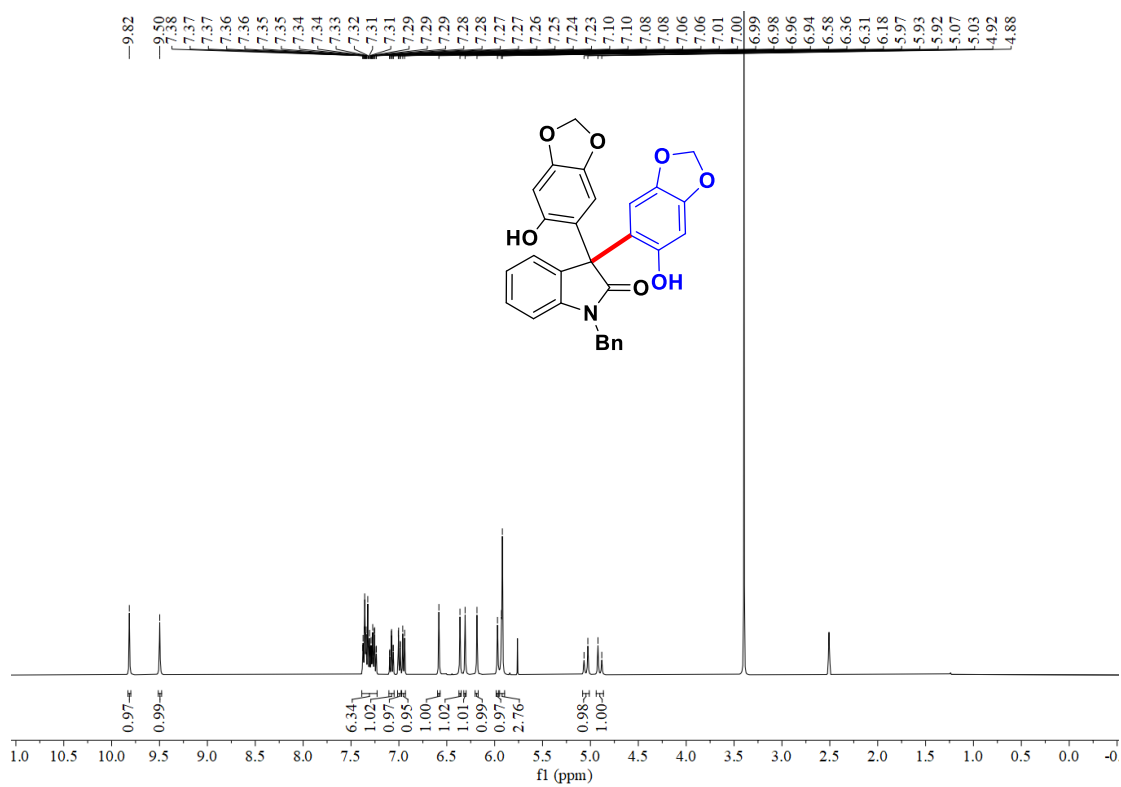
3-(4-amino-3-nitrophenyl)-1-benzyl-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)indolin-2-one (3g)



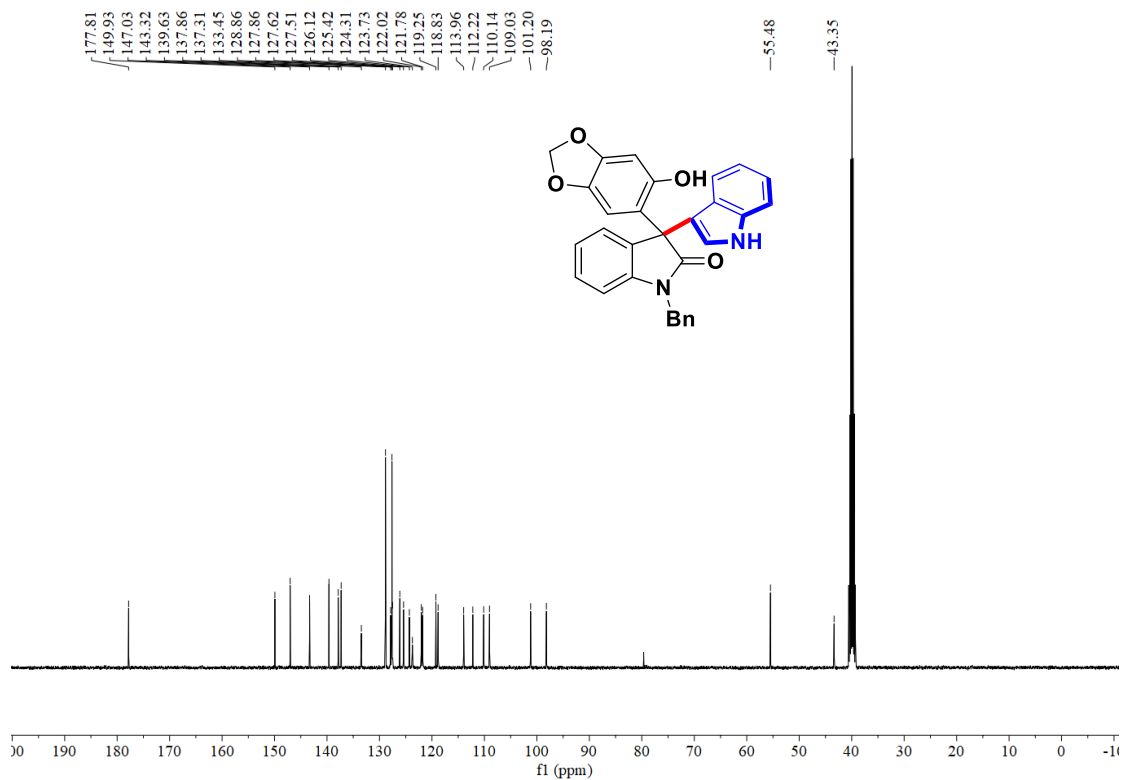
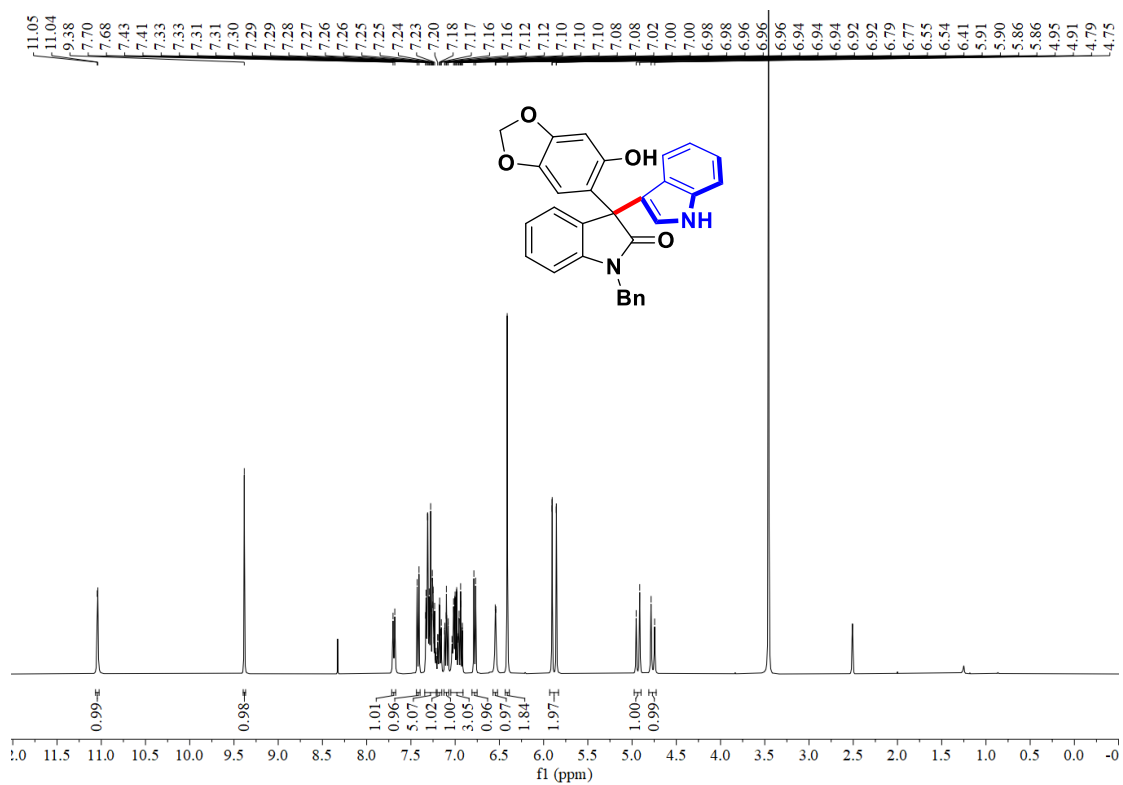
1-benzyl-3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)-3-(2,4,6-trimethoxyphenyl)indolin-2-one (3h)



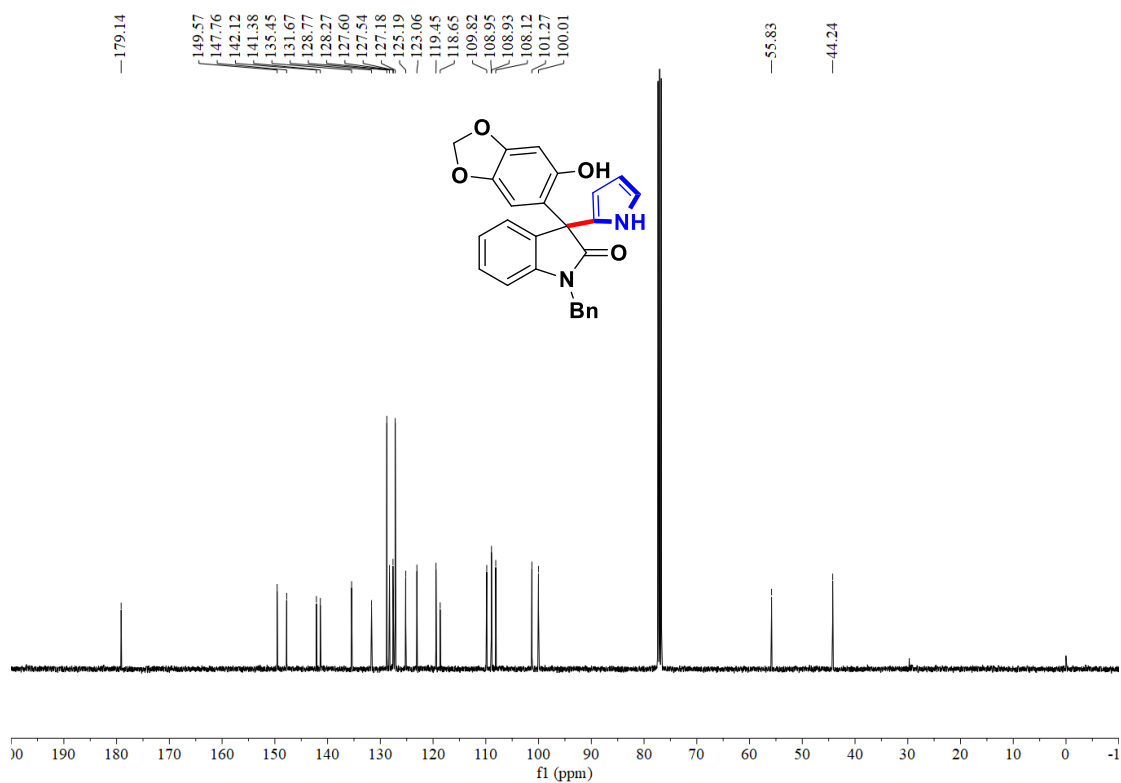
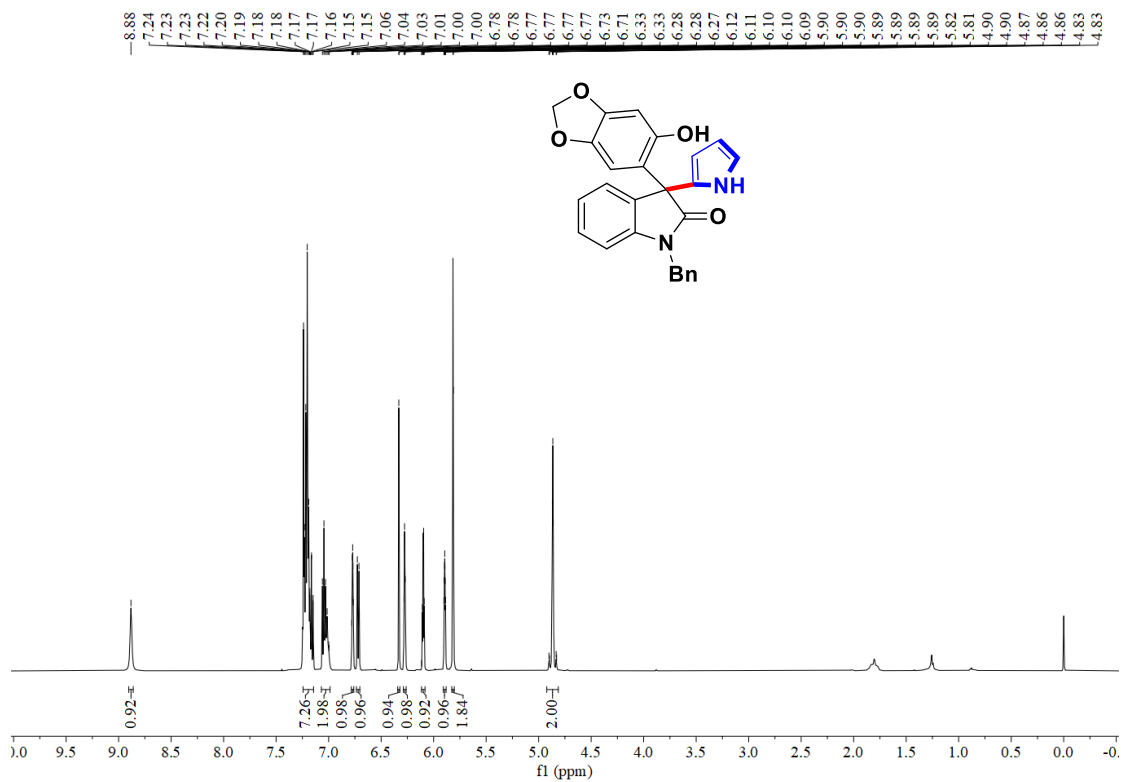
1-benzyl-3,3-bis(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)indolin-2-one (3i)



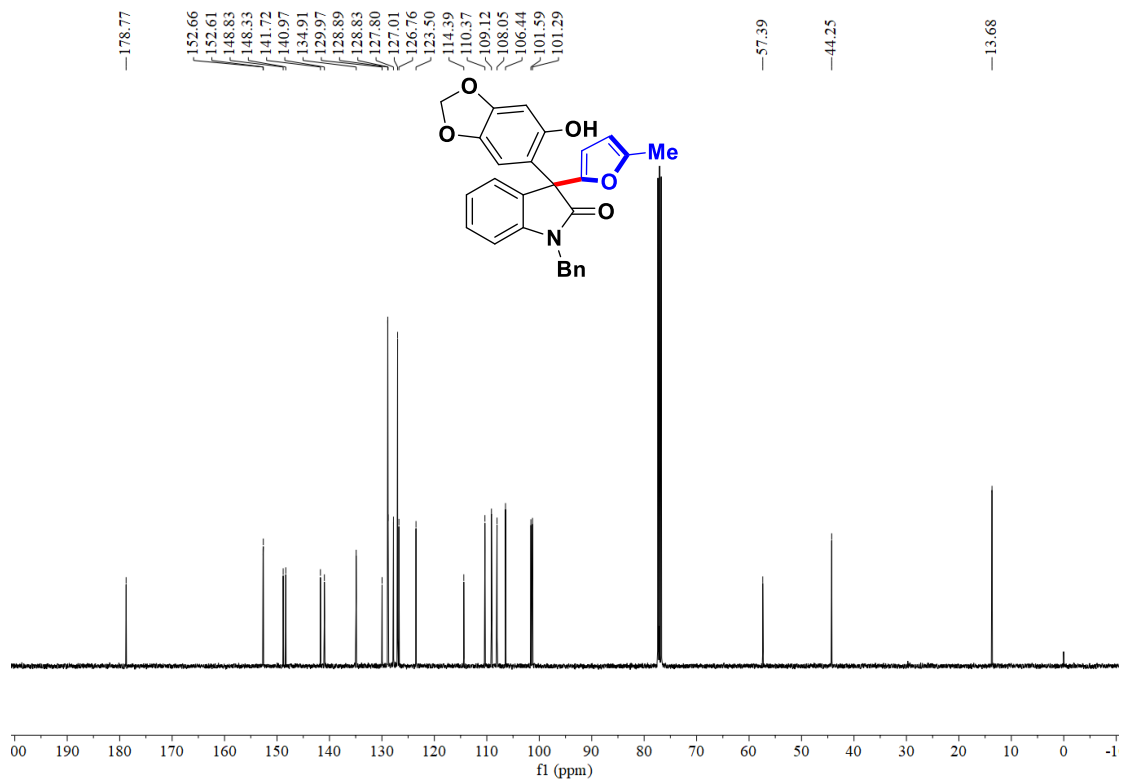
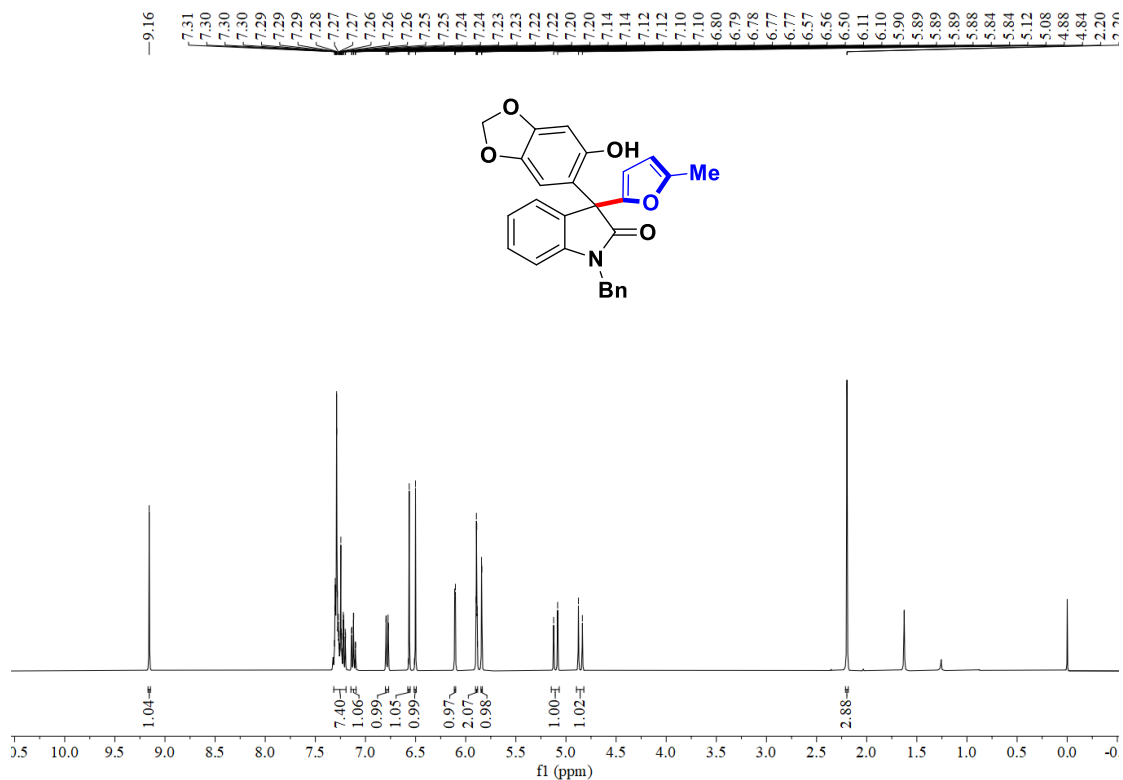
1-benzyl-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)-3-(1*H*-indol-3-yl)indolin-2-one
(3j)



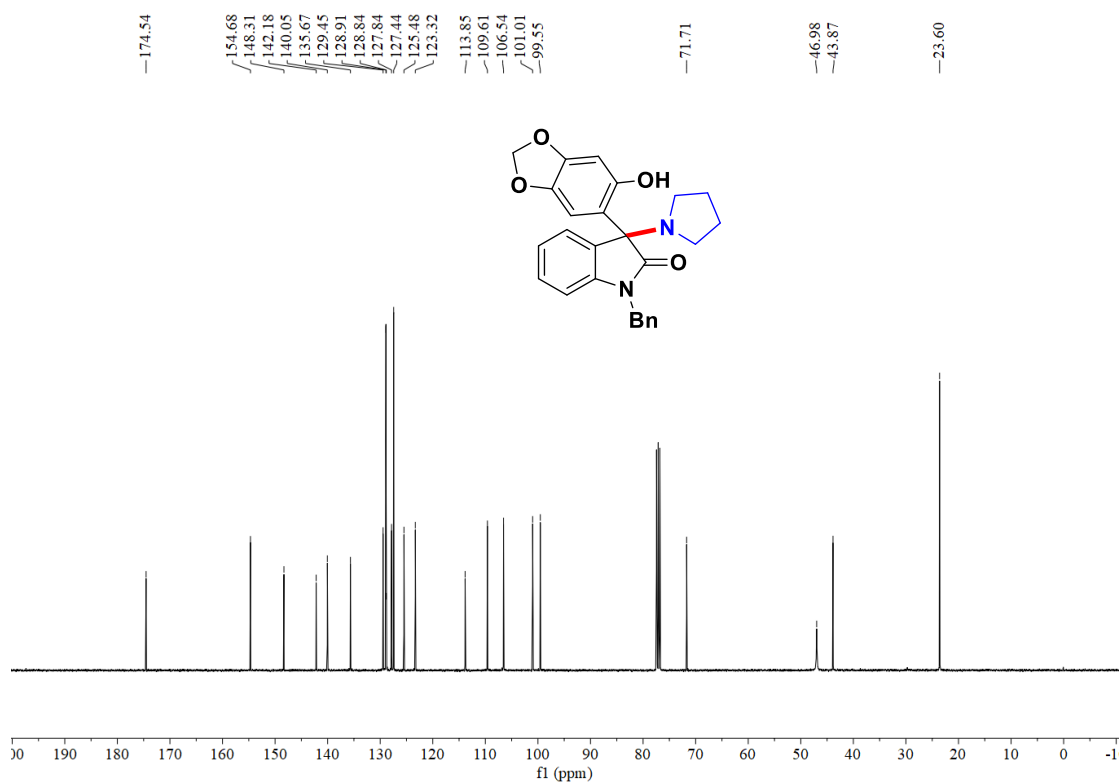
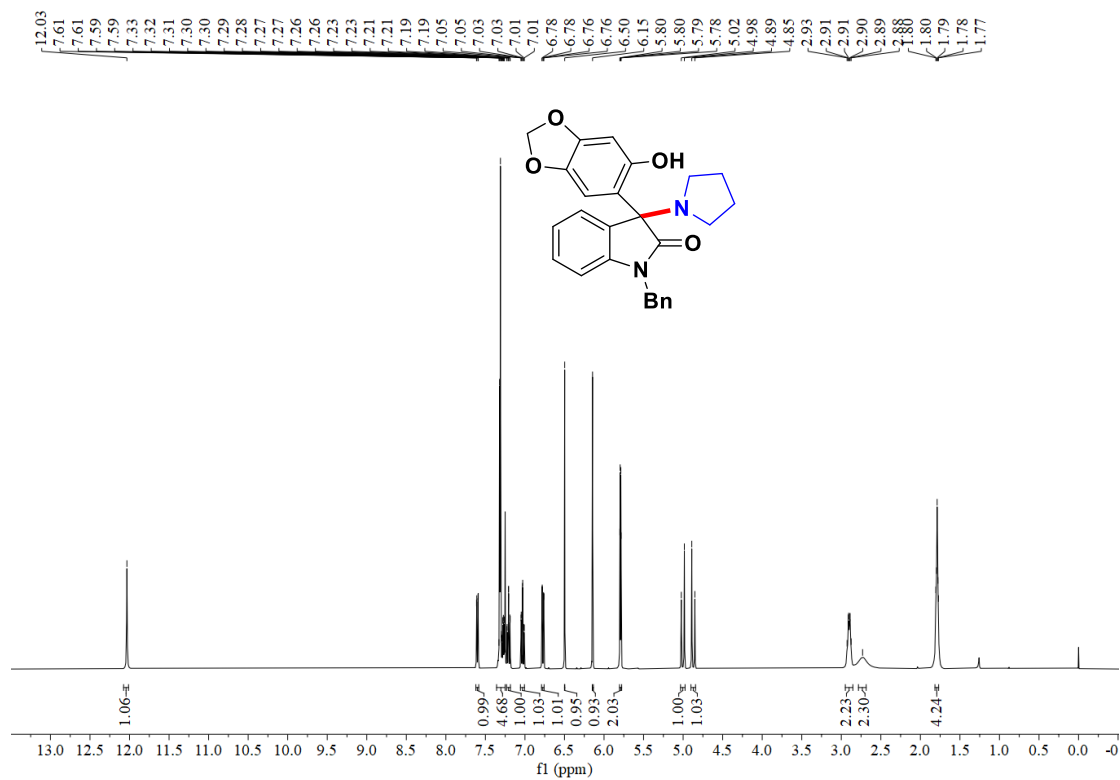
**1-benzyl-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)-3-(1*H*-pyrrol-2-yl)indolin-2-one
(3k)**



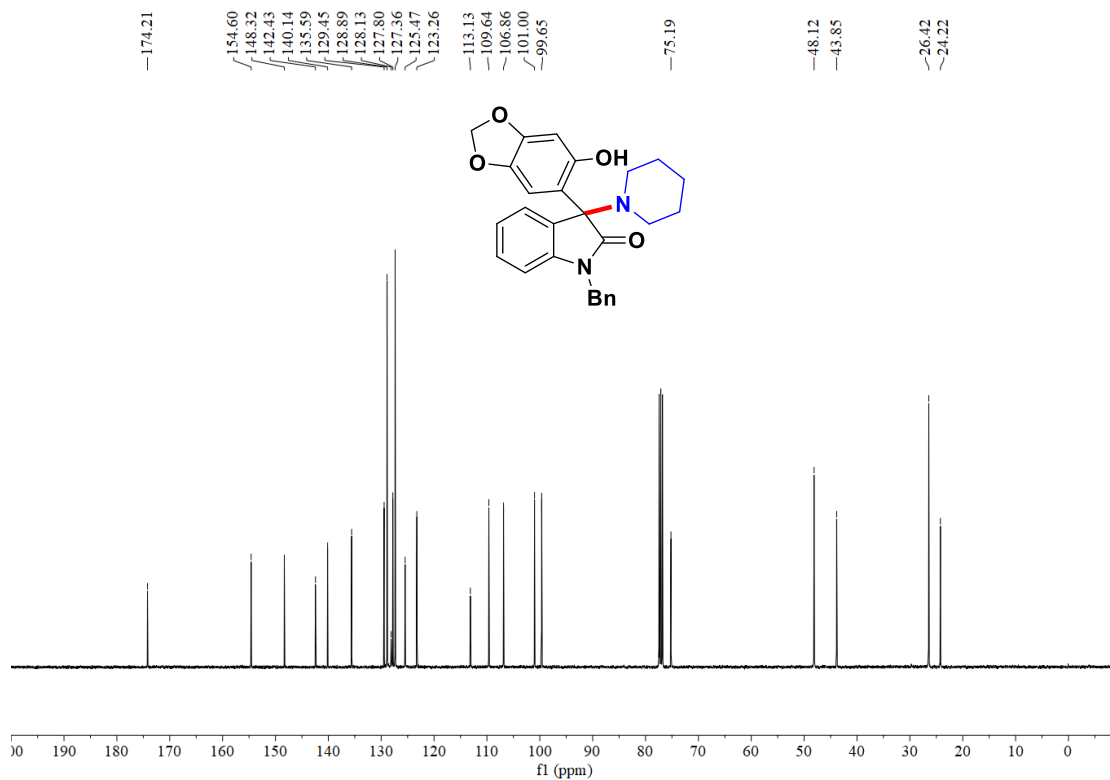
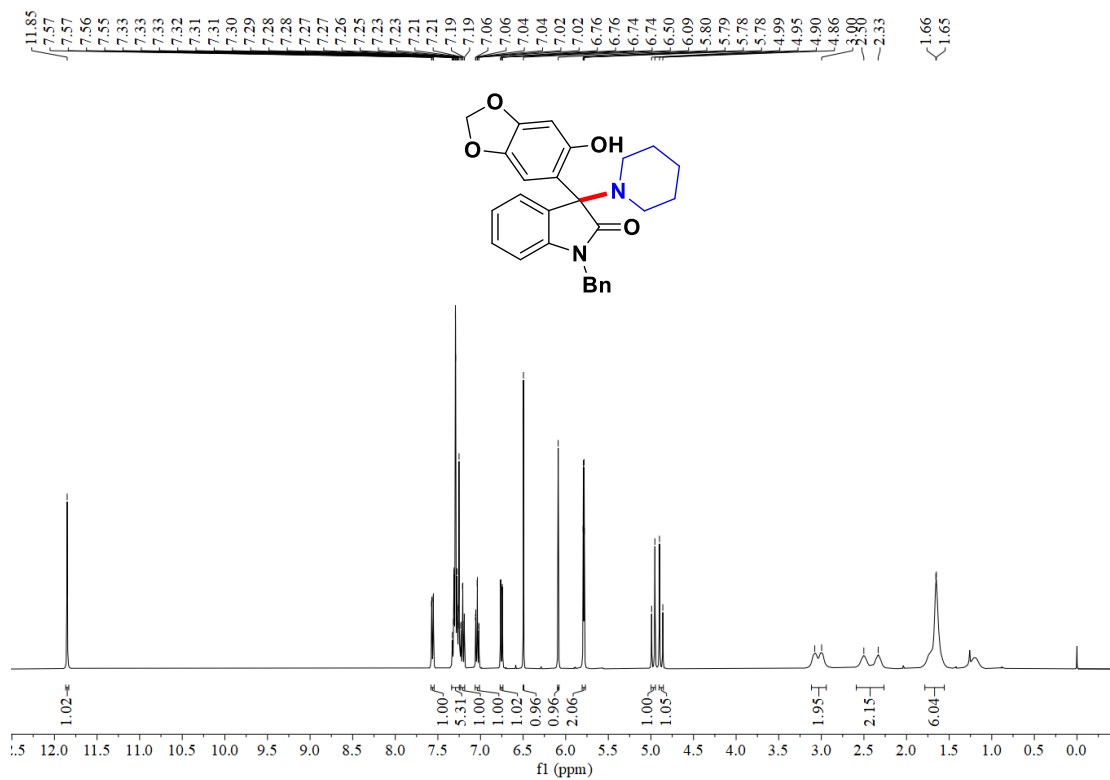
1-benzyl-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)-3-(5-methylfuran-2-yl)indolin-2-one (3l)



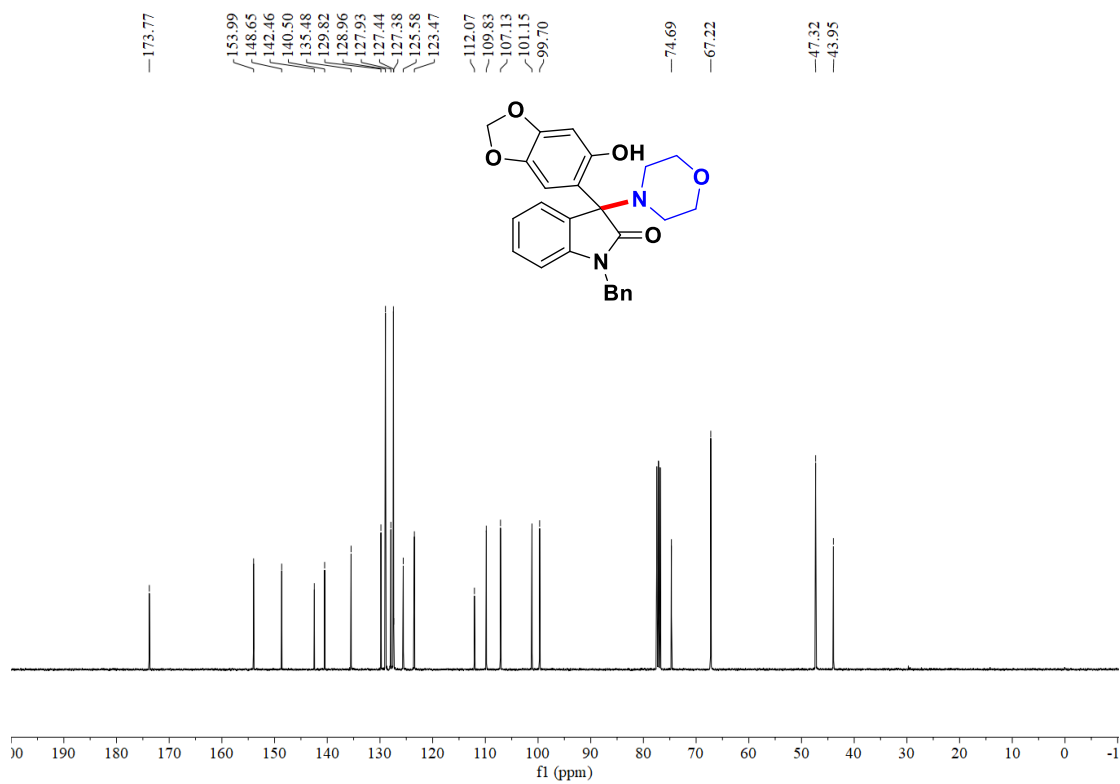
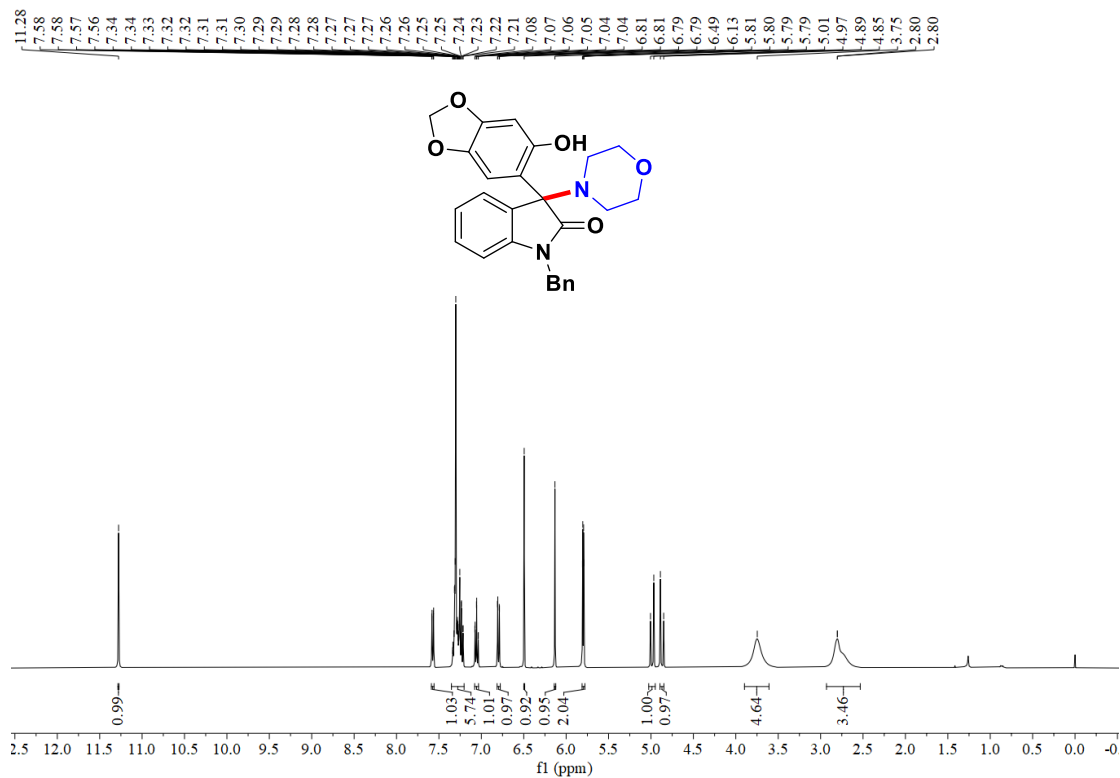
**1-benzyl-3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)-3-(pyrrolidin-1-yl)indolin-2-one
(4a)**



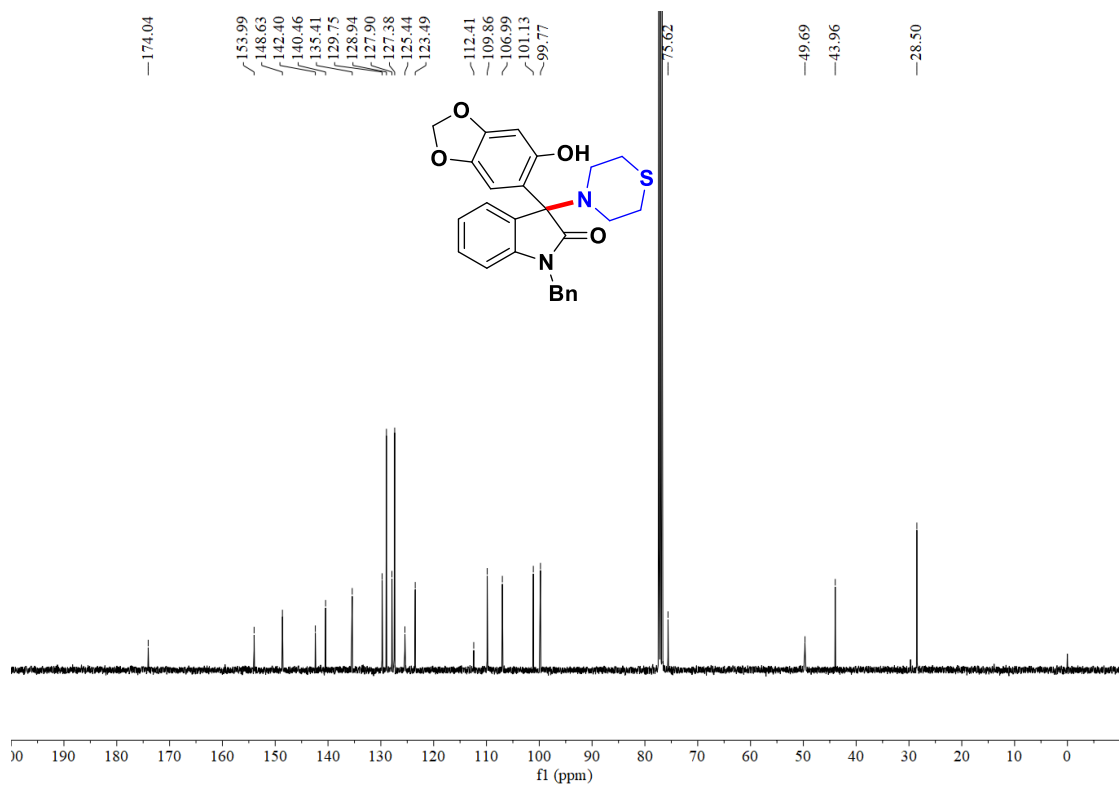
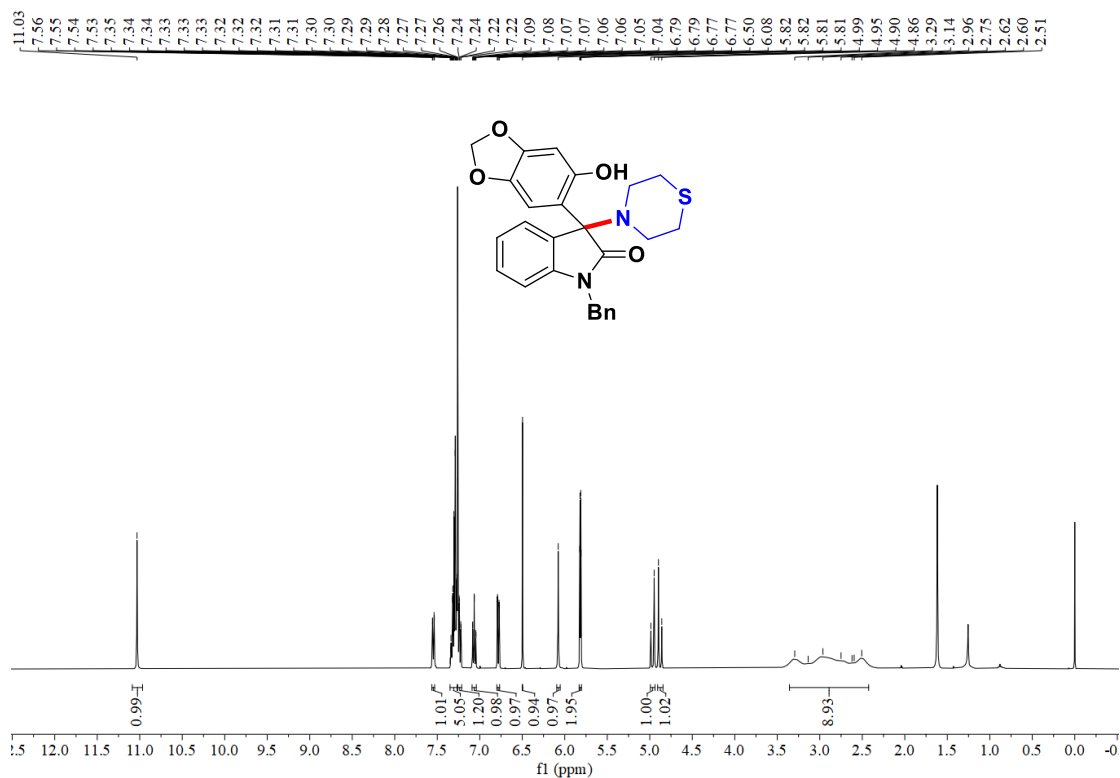
**1-benzyl-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)-3-(piperidin-1-yl)indolin-2-one
(4b)**



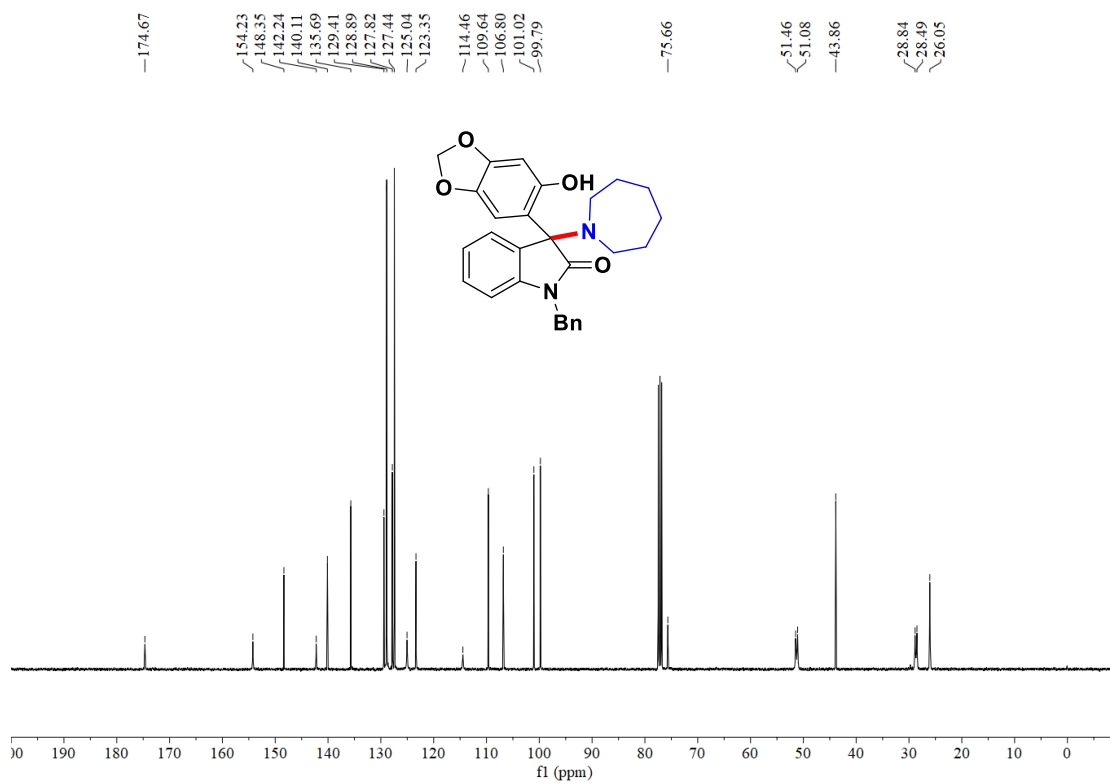
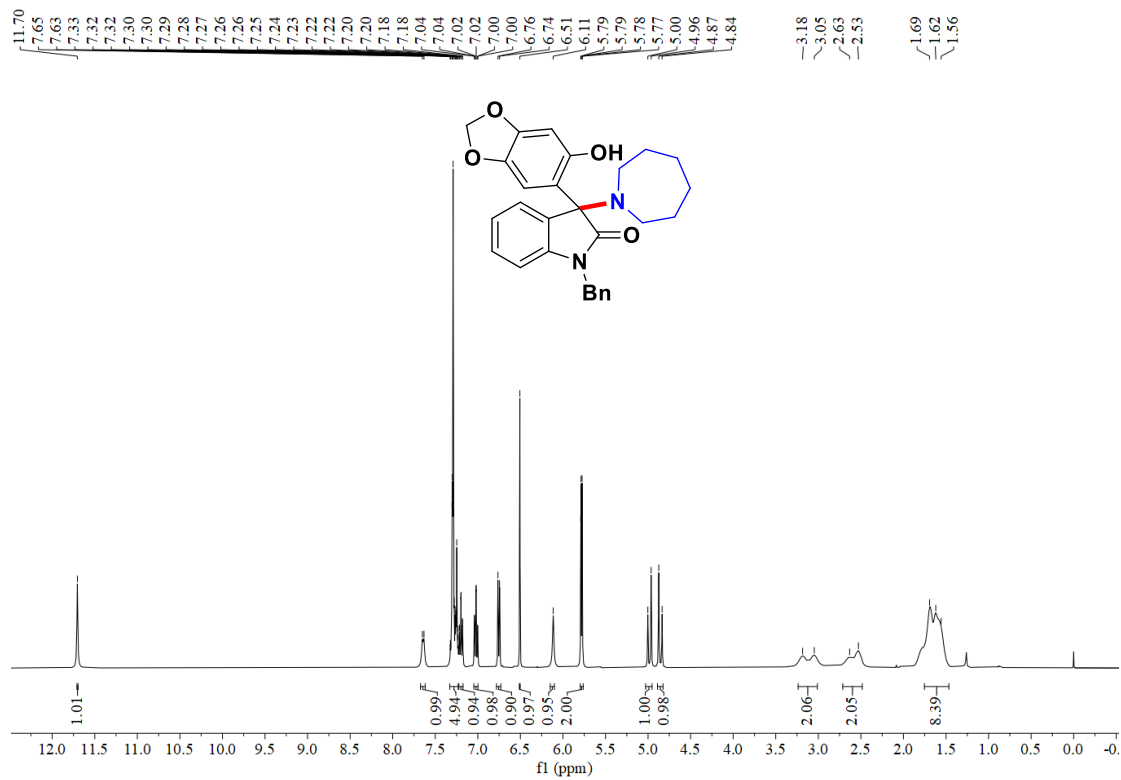
1-benzyl-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)-3-morpholinoindolin-2-one (4c)



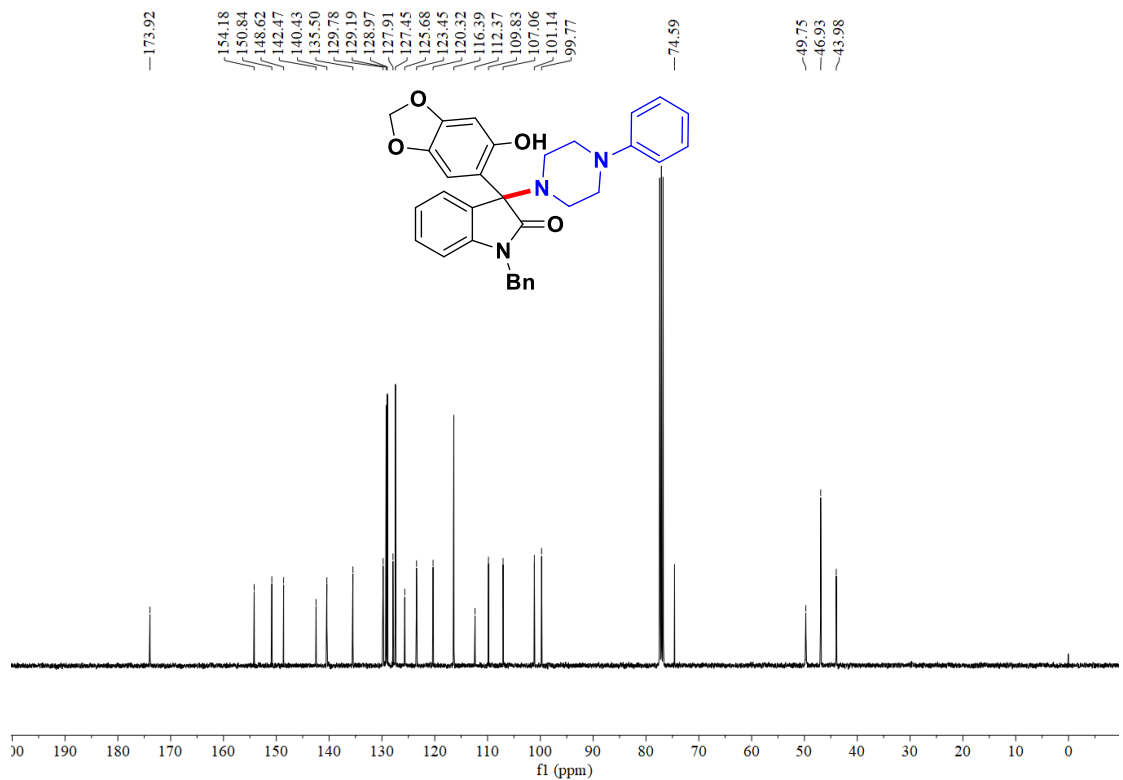
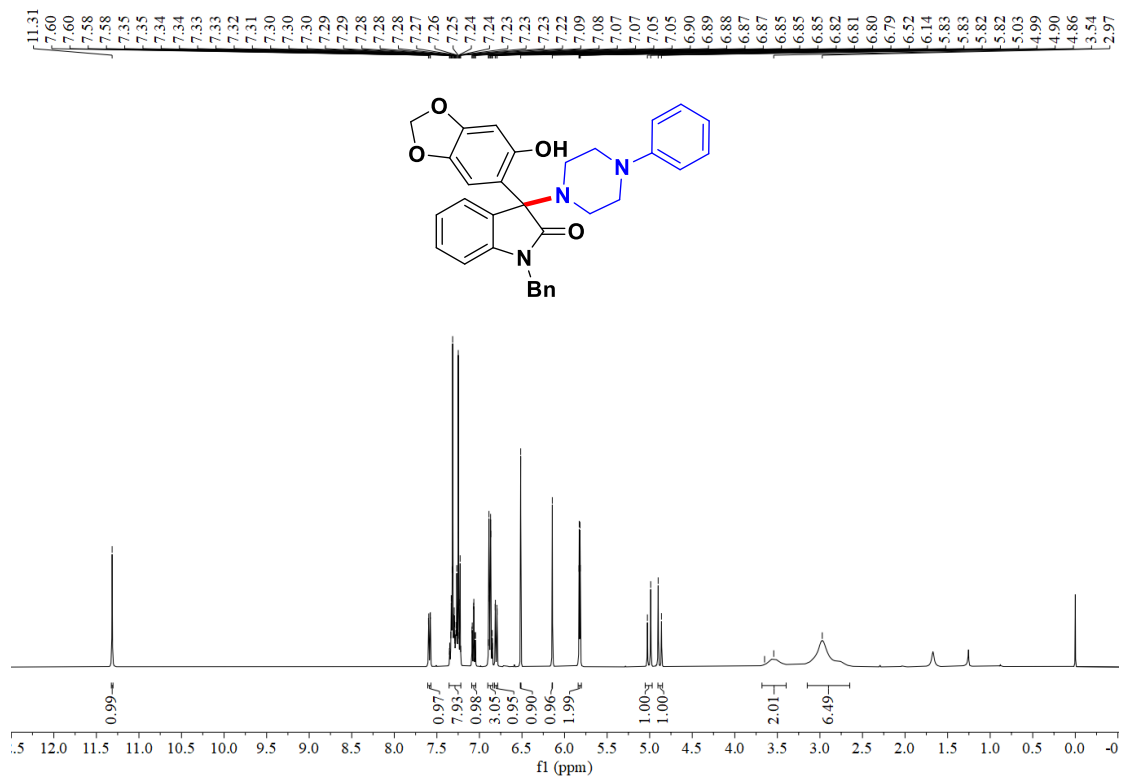
**1-benzyl-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)-3-thiomorpholinoindolin-2-one
(4d)**



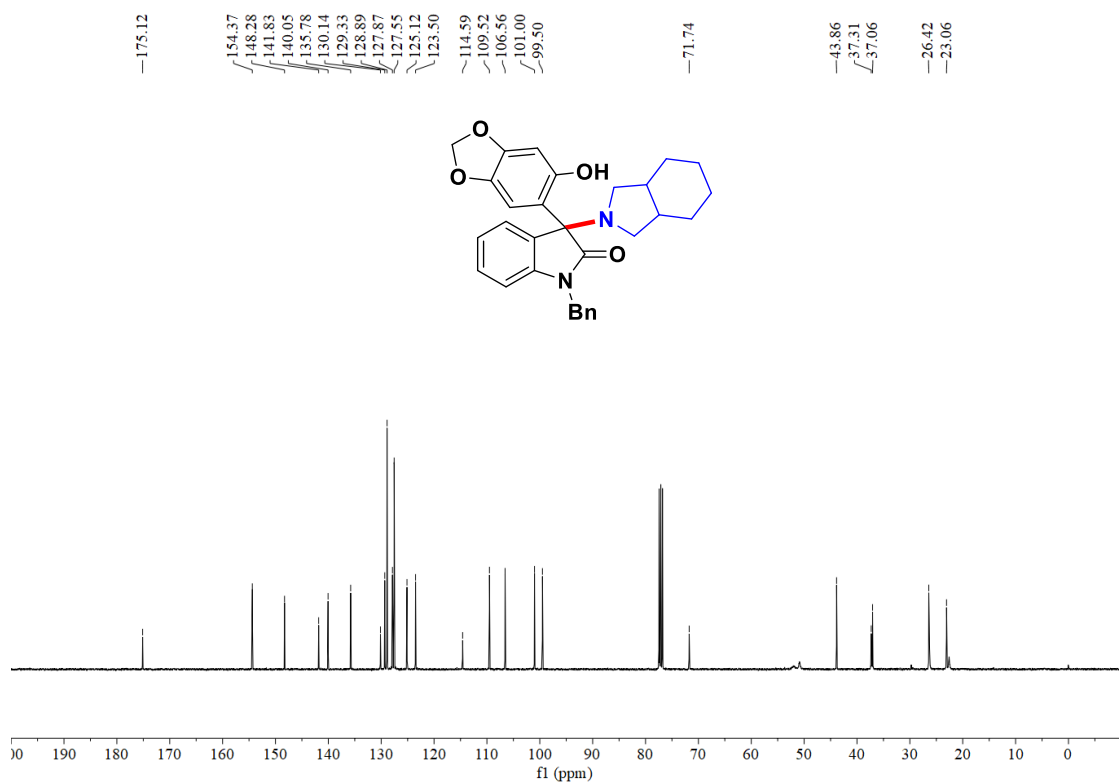
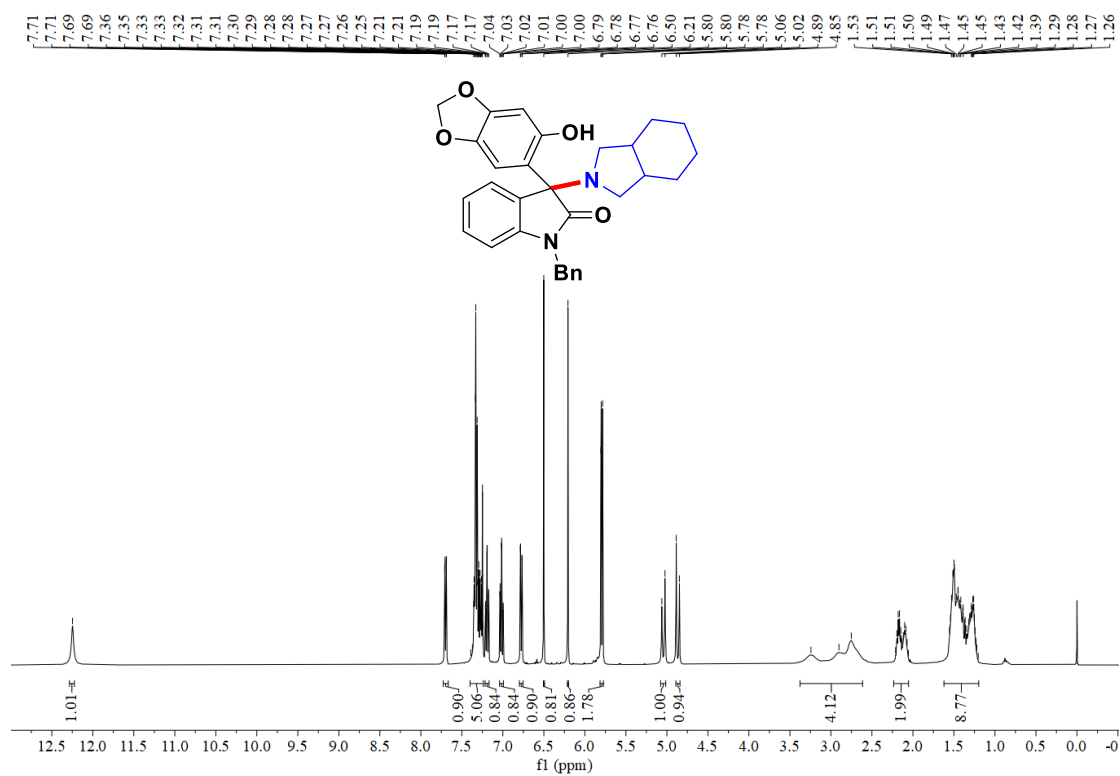
3-(azepan-1-yl)-1-benzyl-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)indolin-2-one (4e)



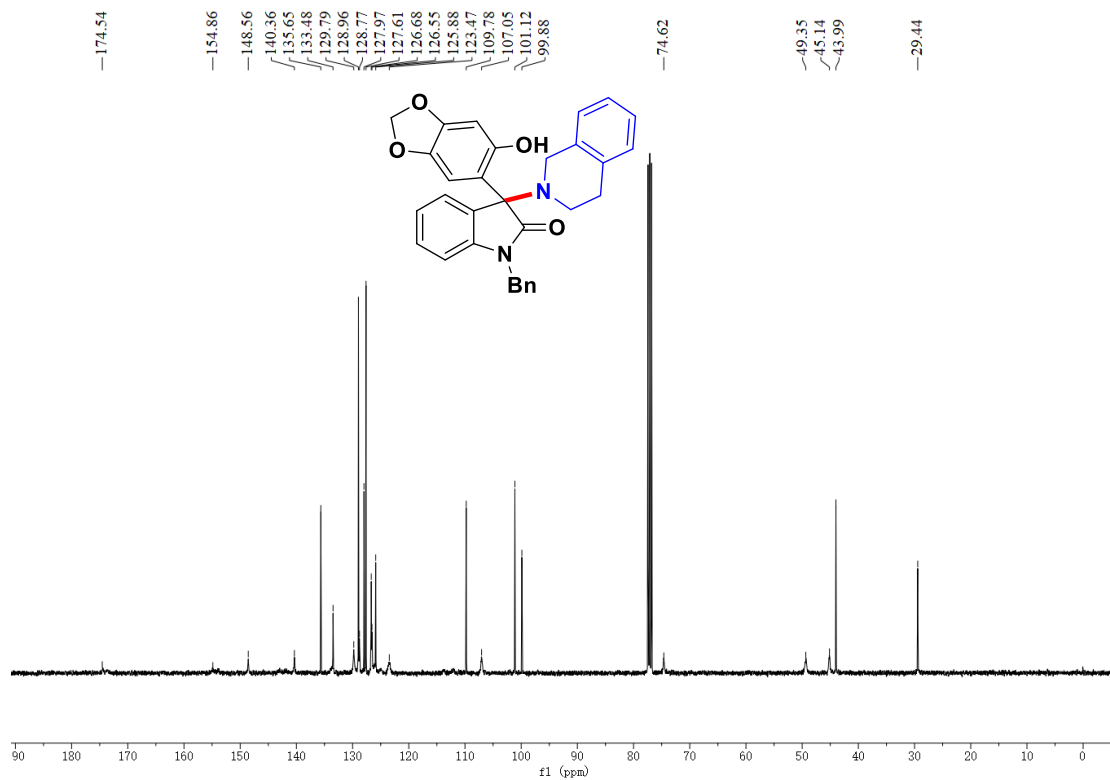
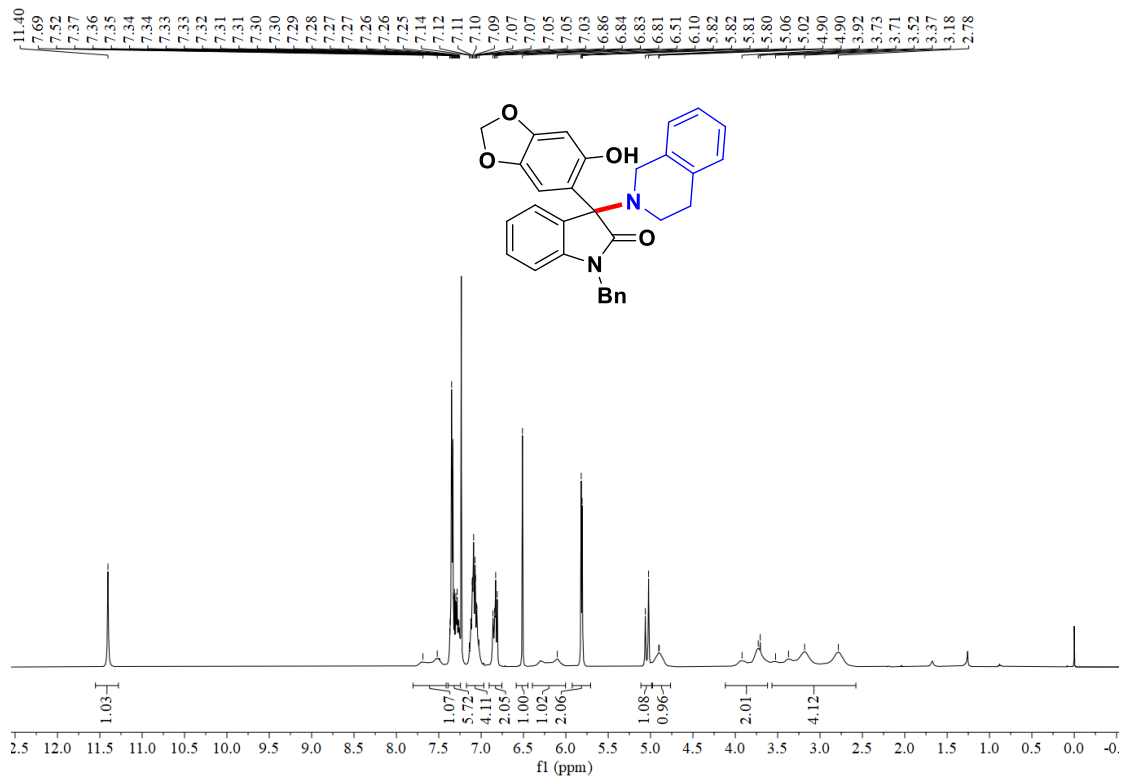
1-benzyl-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)-3-(4-phenylpiperazin-1-yl)indolin-2-one (4f)



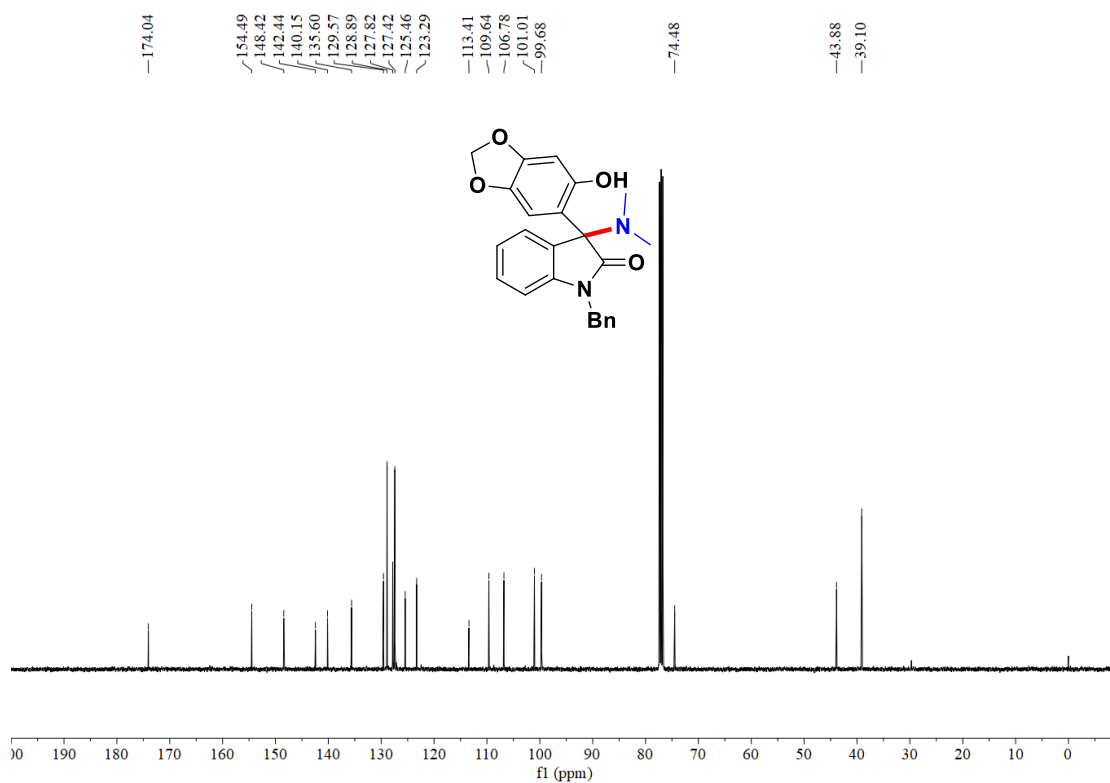
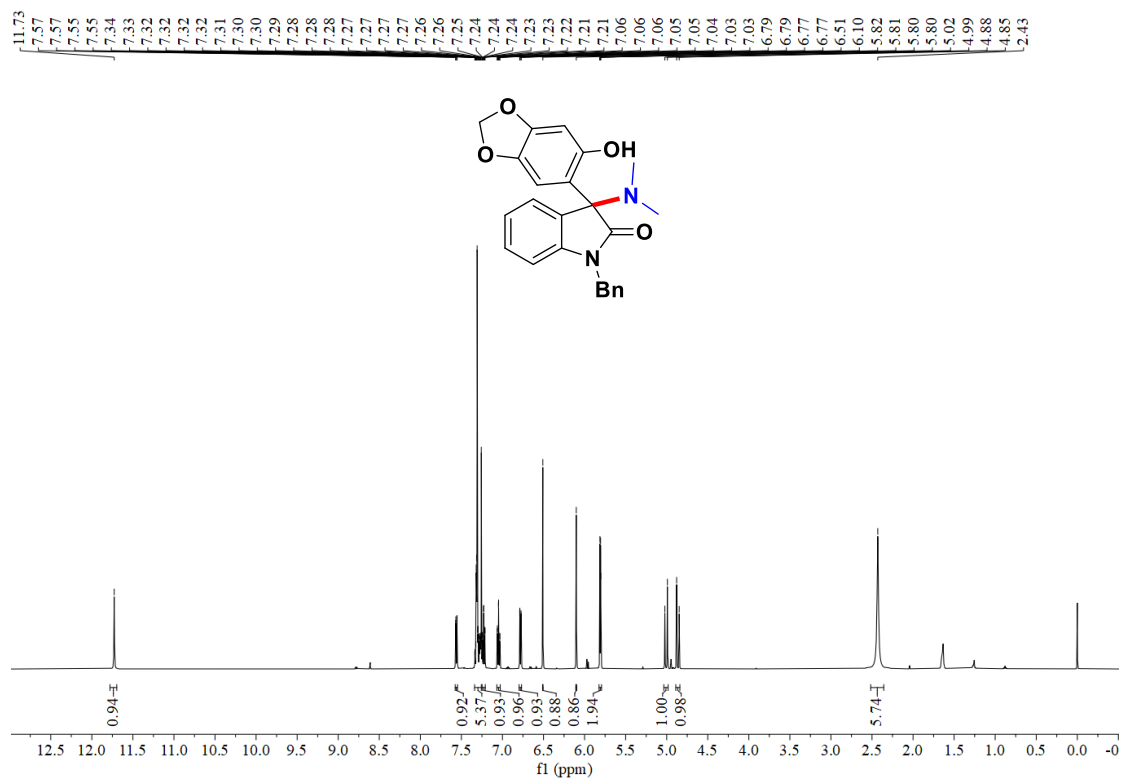
1-benzyl-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)-3-(octahydro-2H-isoindol-2-yl)indolin-2-one (4g)



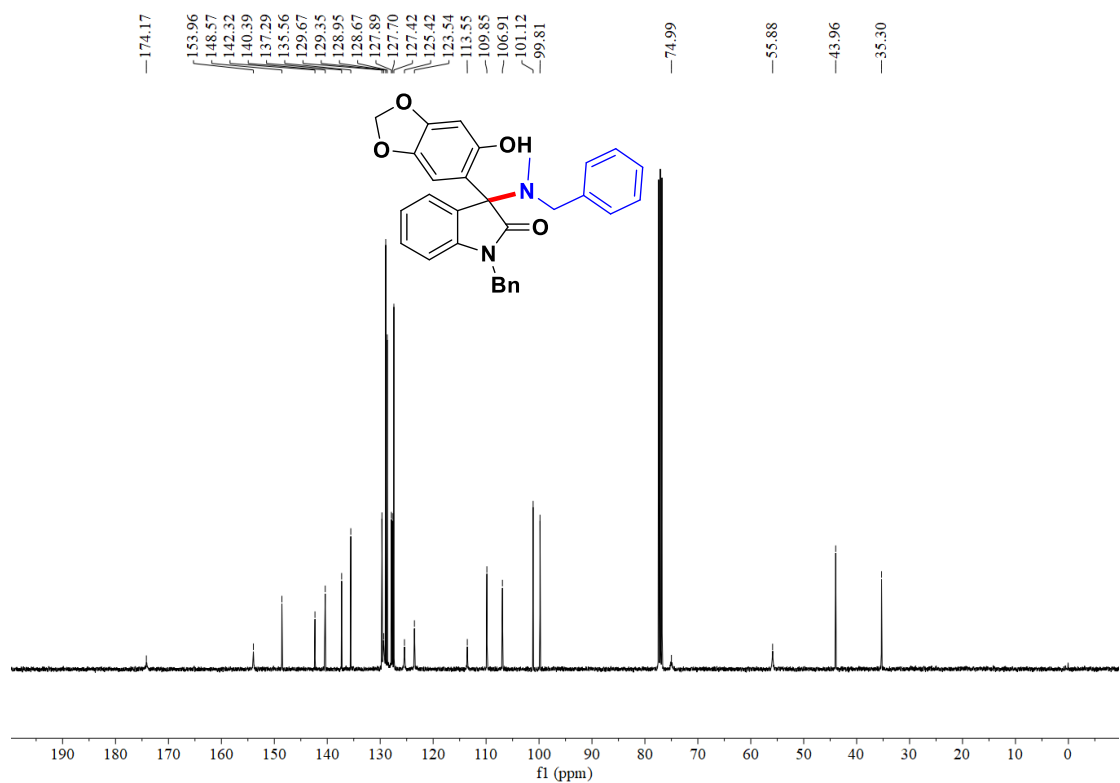
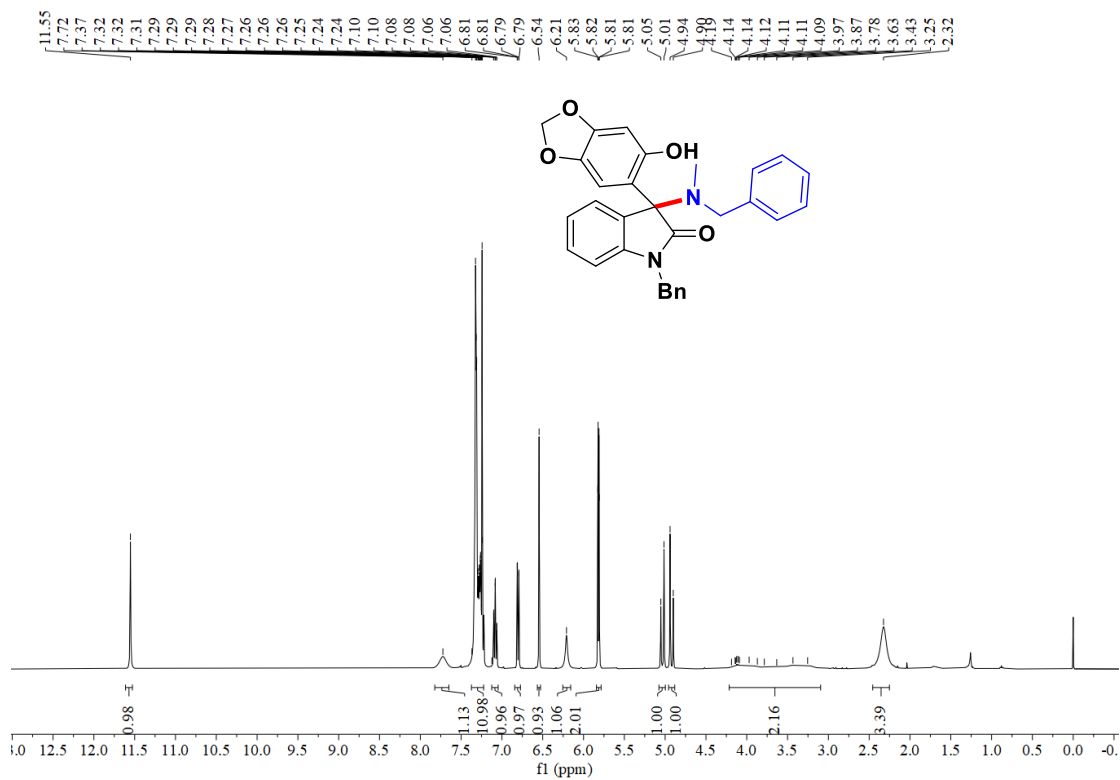
1-benzyl-3-(3,4-dihydroisoquinolin-2(1*H*)-yl)-3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)indolin-2-one (4h)



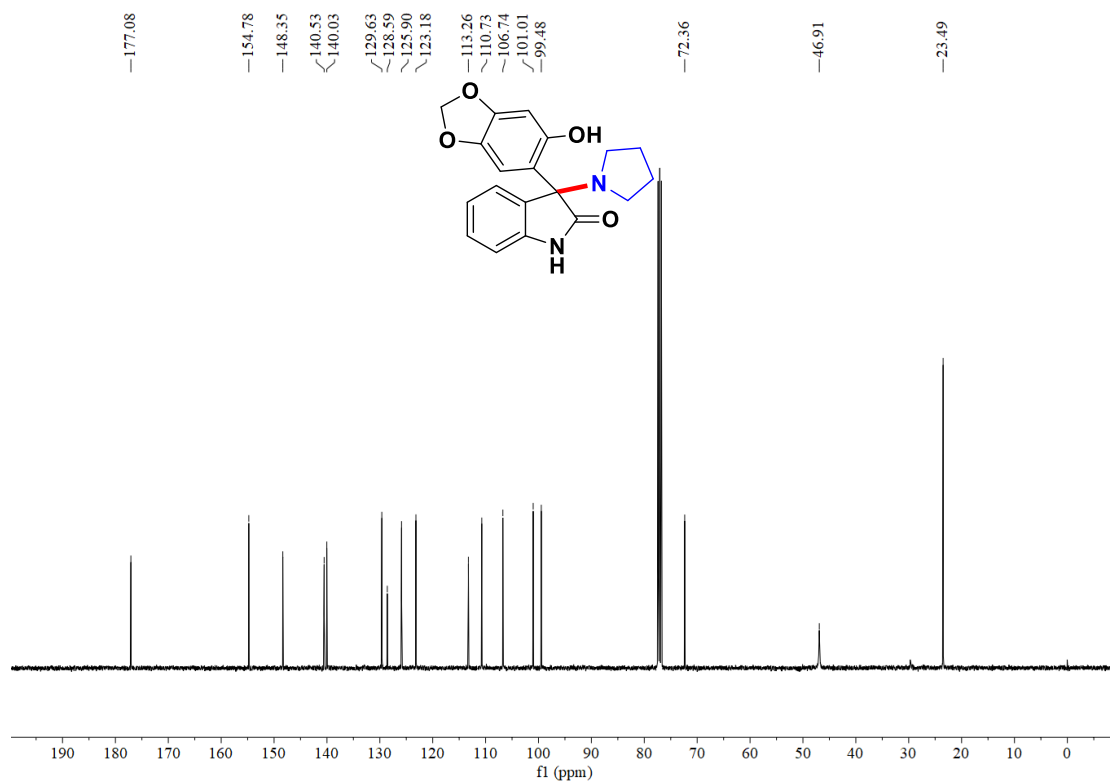
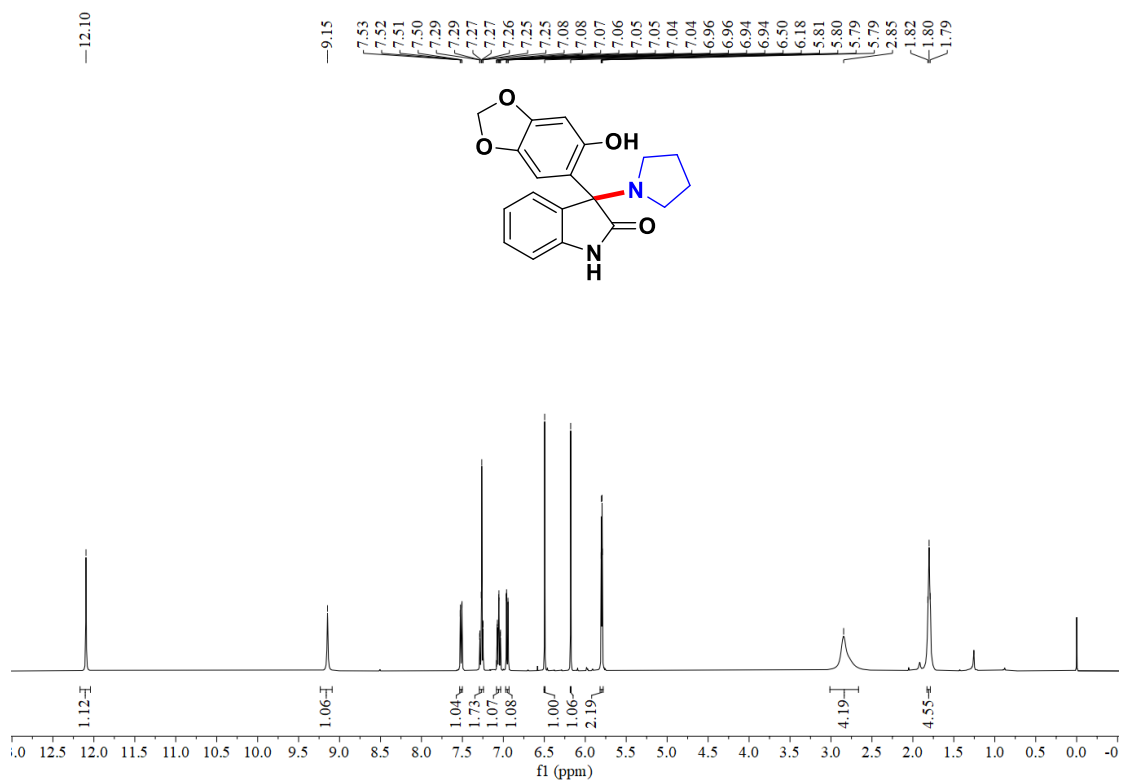
1-benzyl-3-(dimethylamino)-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)indolin-2-one
(4i)



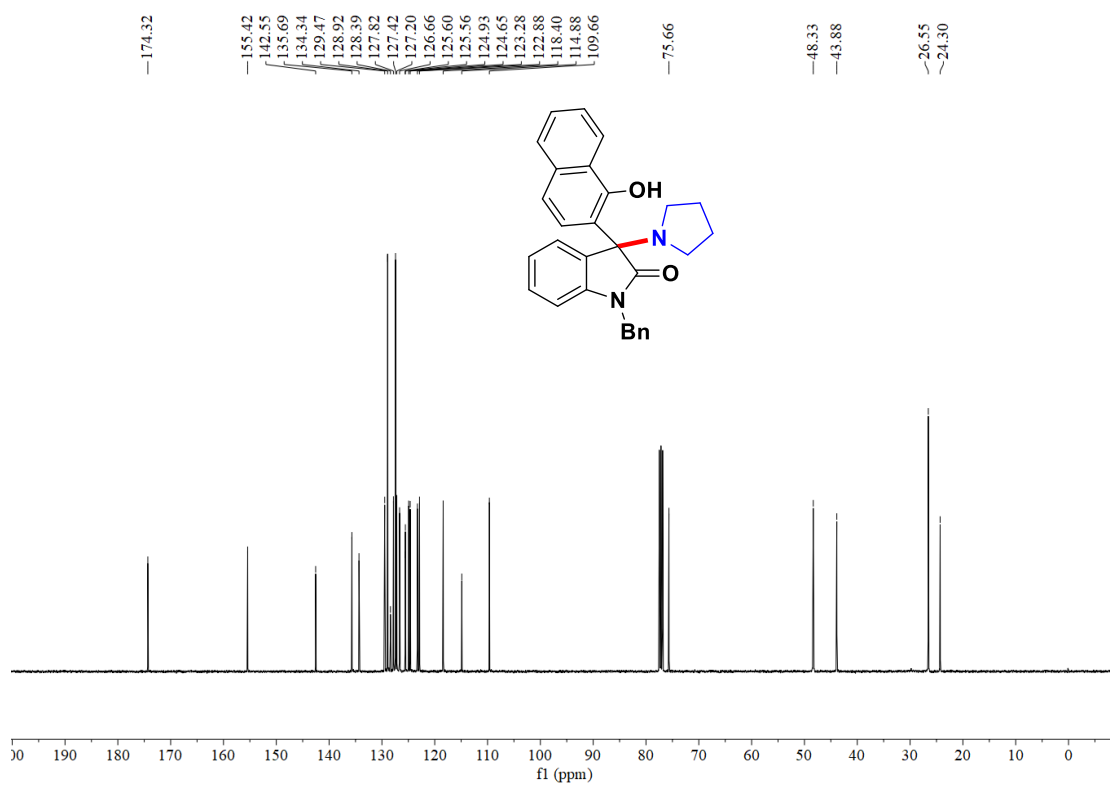
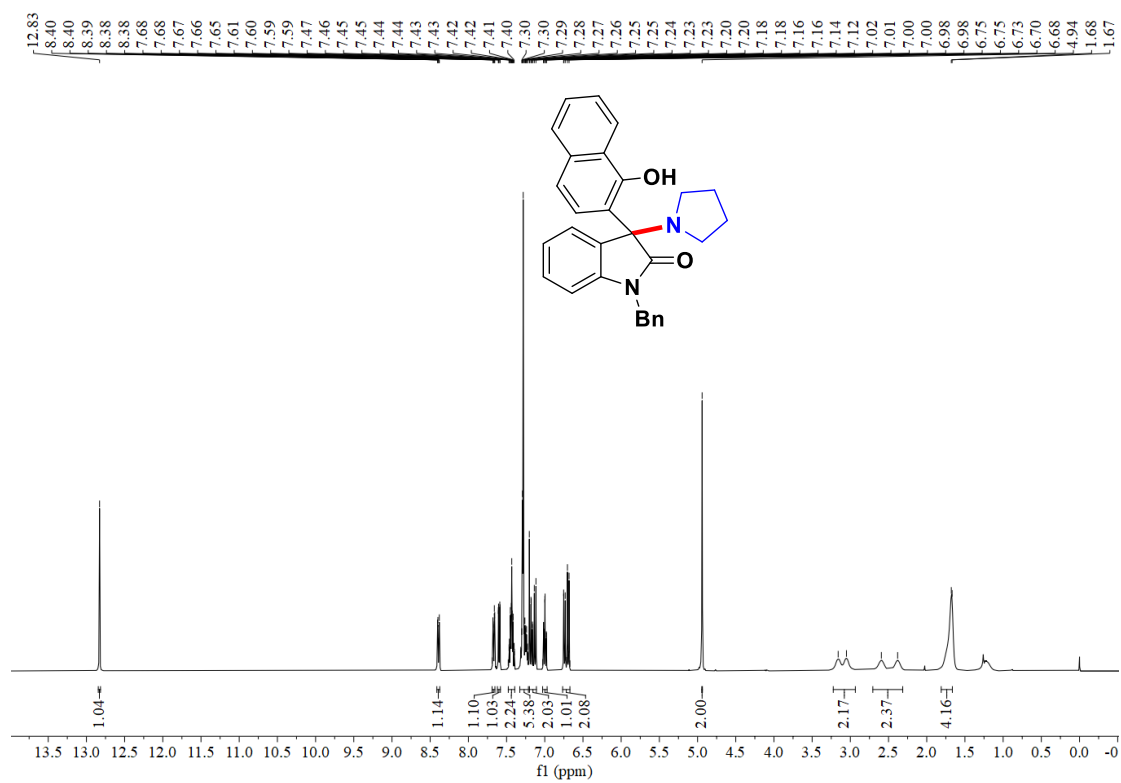
1-benzyl-3-(benzyl(methyl)amino)-3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)indolin-2-one (4j)



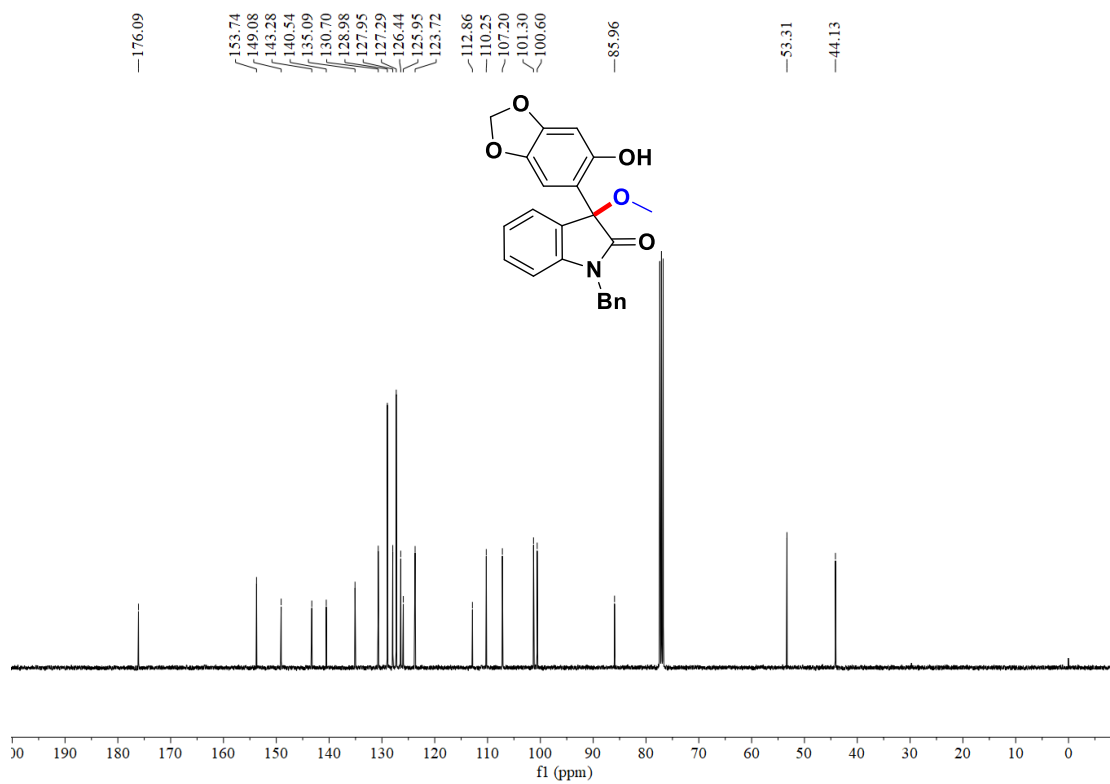
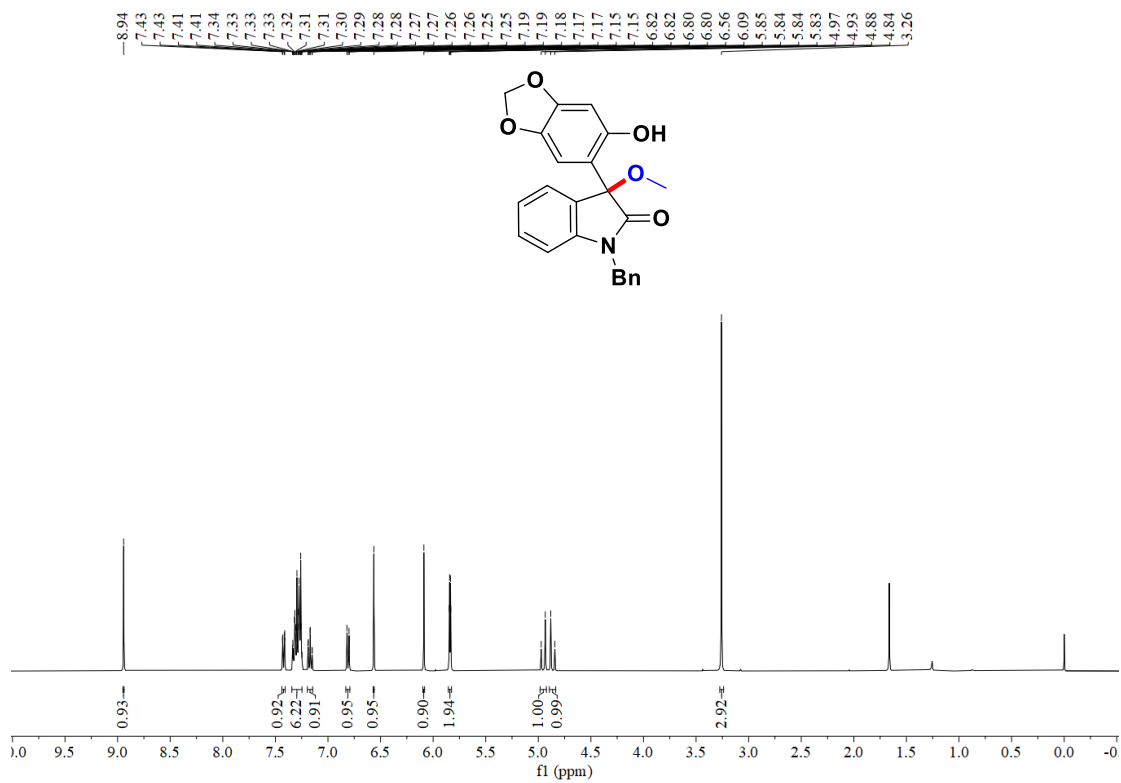
3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)-3-(pyrrolidin-1-yl)indolin-2-one (4k)



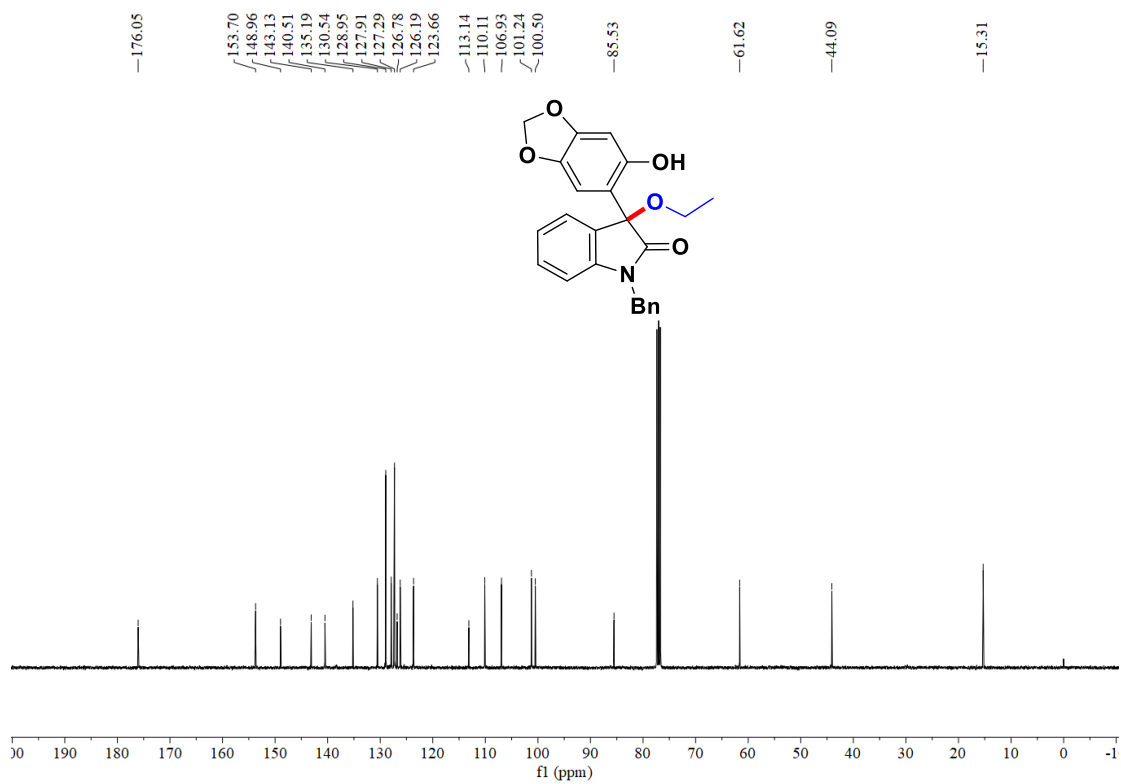
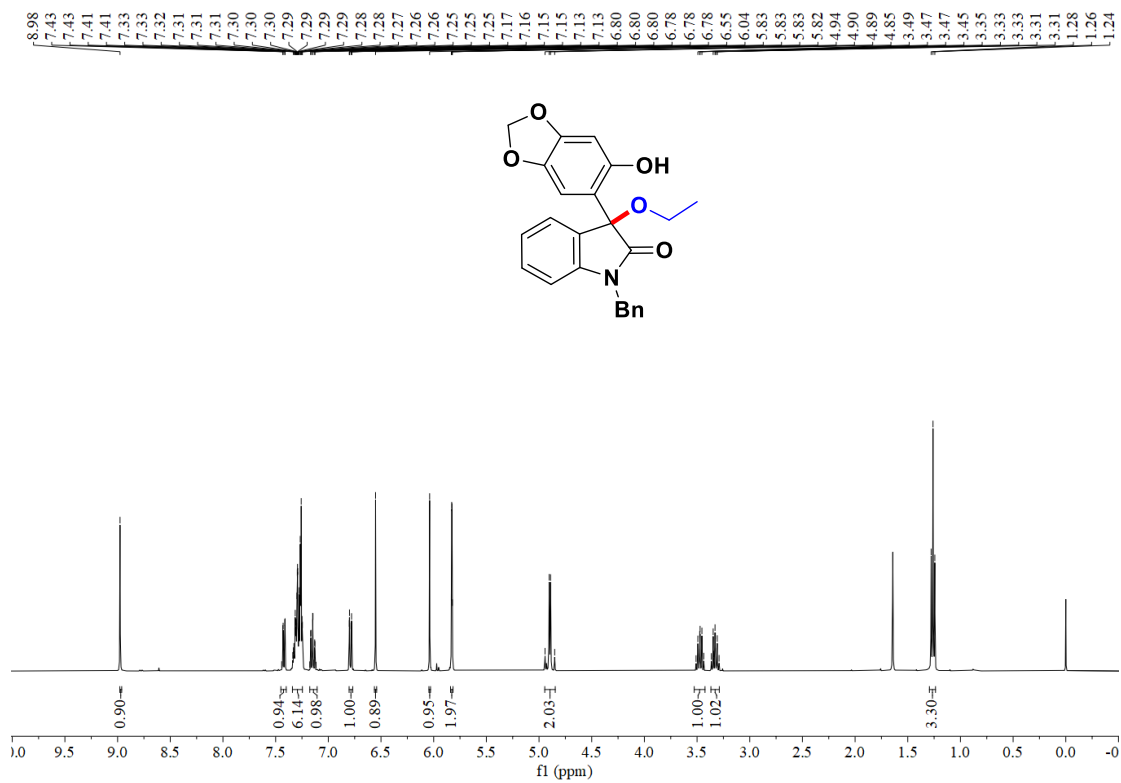
1-benzyl-3-(1-hydroxynaphthalen-2-yl)-3-(pyrrolidin-1-yl)indolin-2-one (4l)



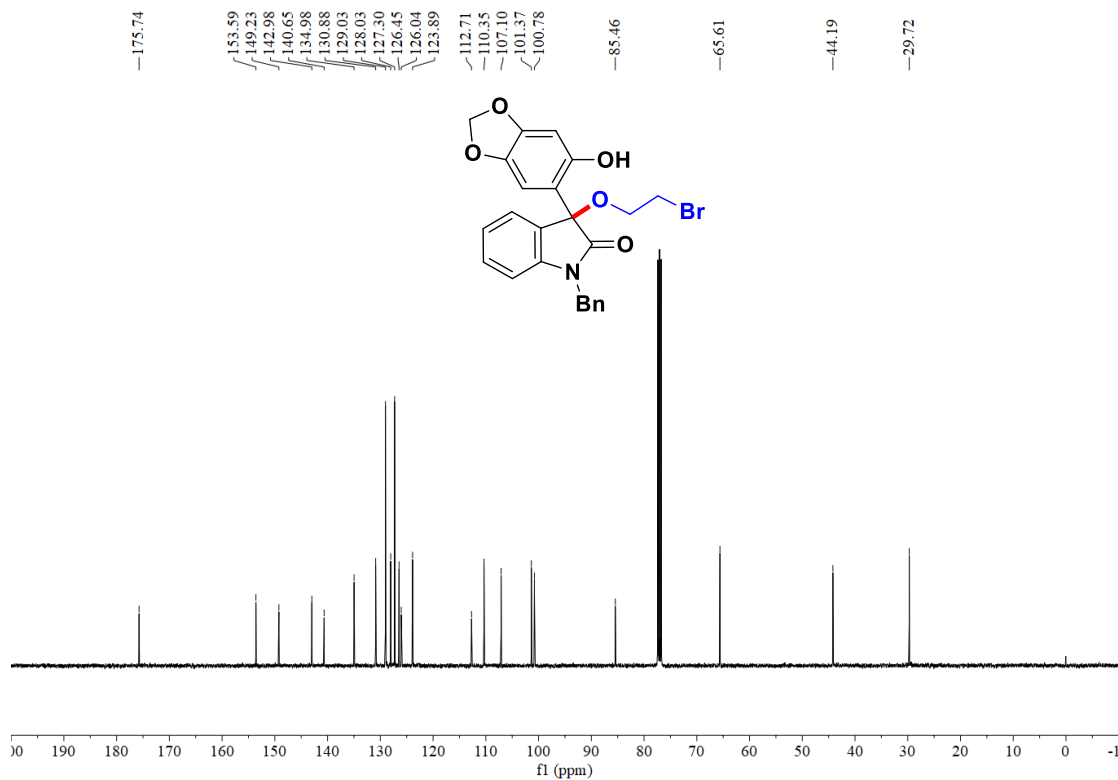
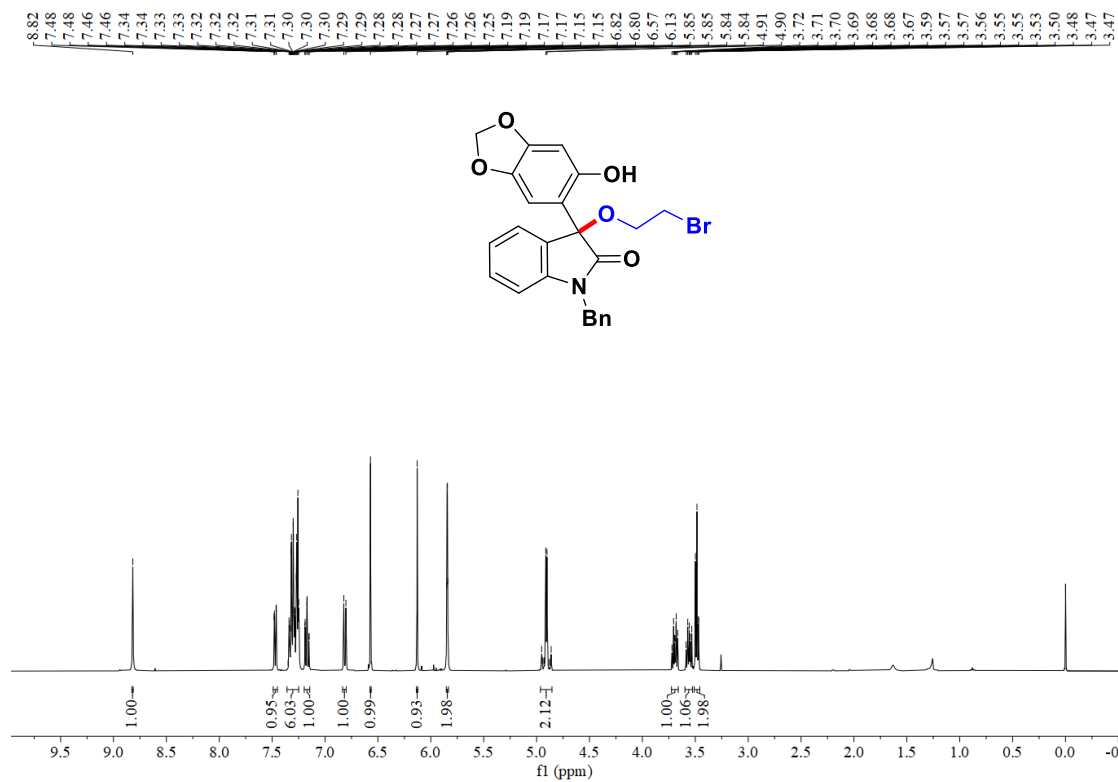
1-benzyl-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)-3-methoxyindolin-2-one (5a)



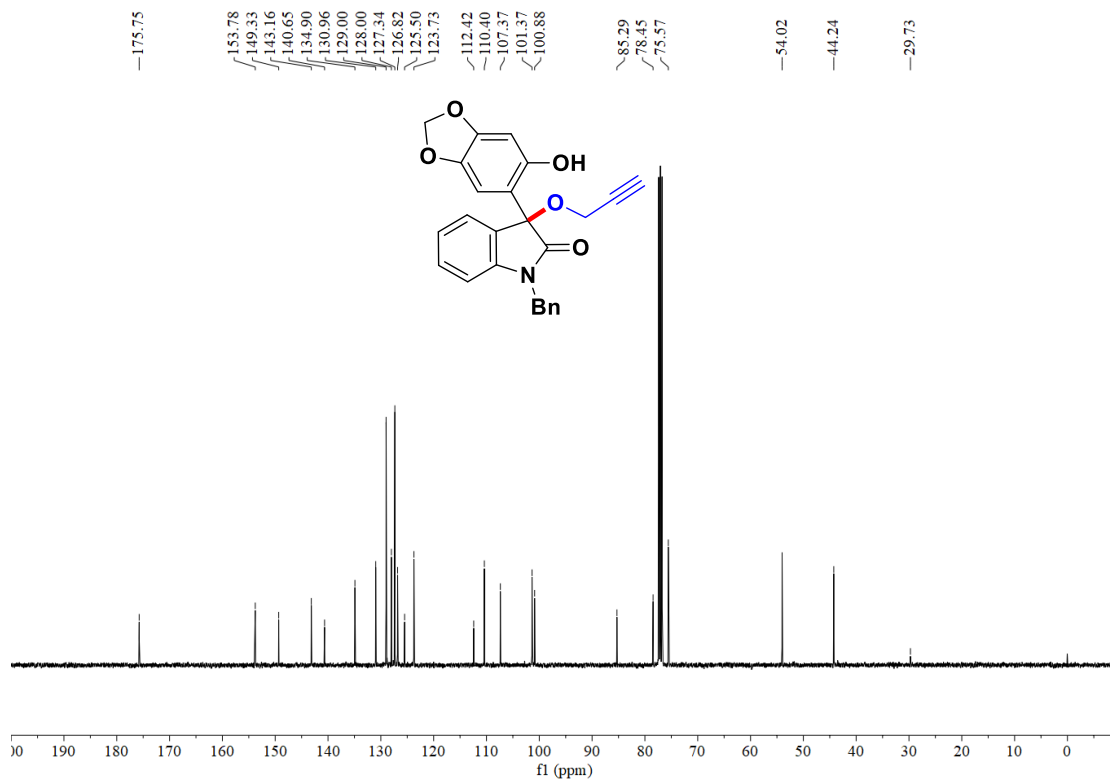
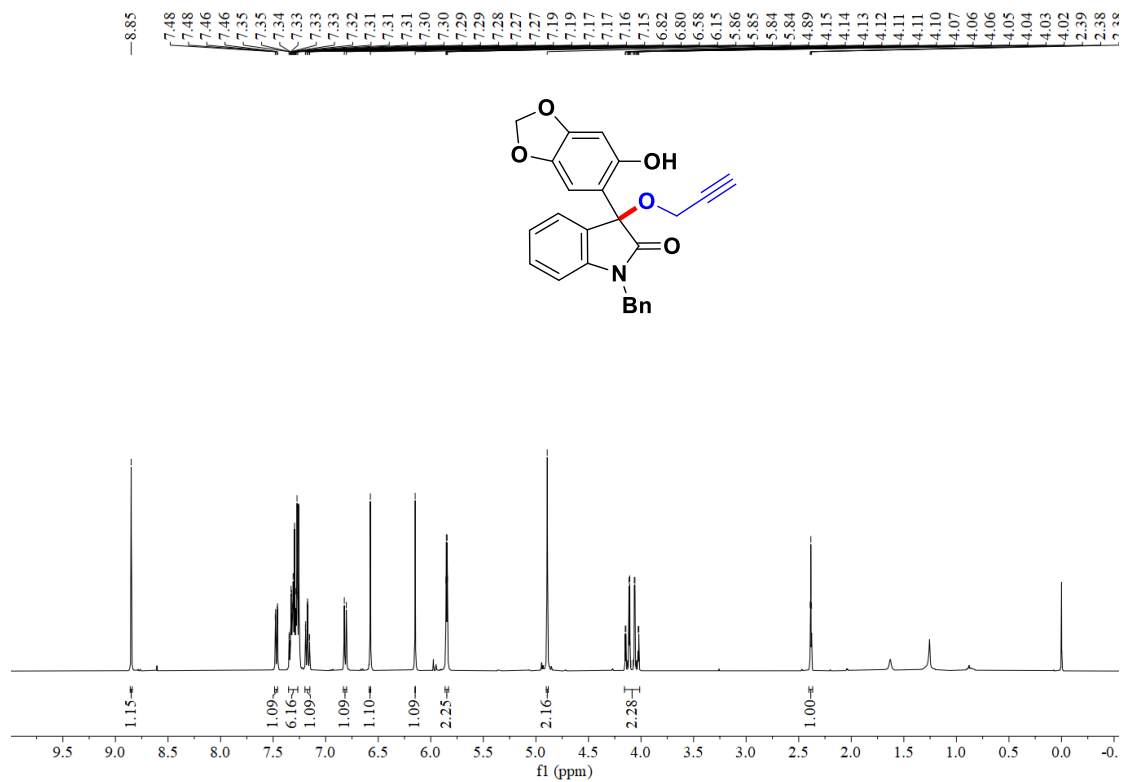
1-benzyl-3-ethoxy-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)indolin-2-one (5b)



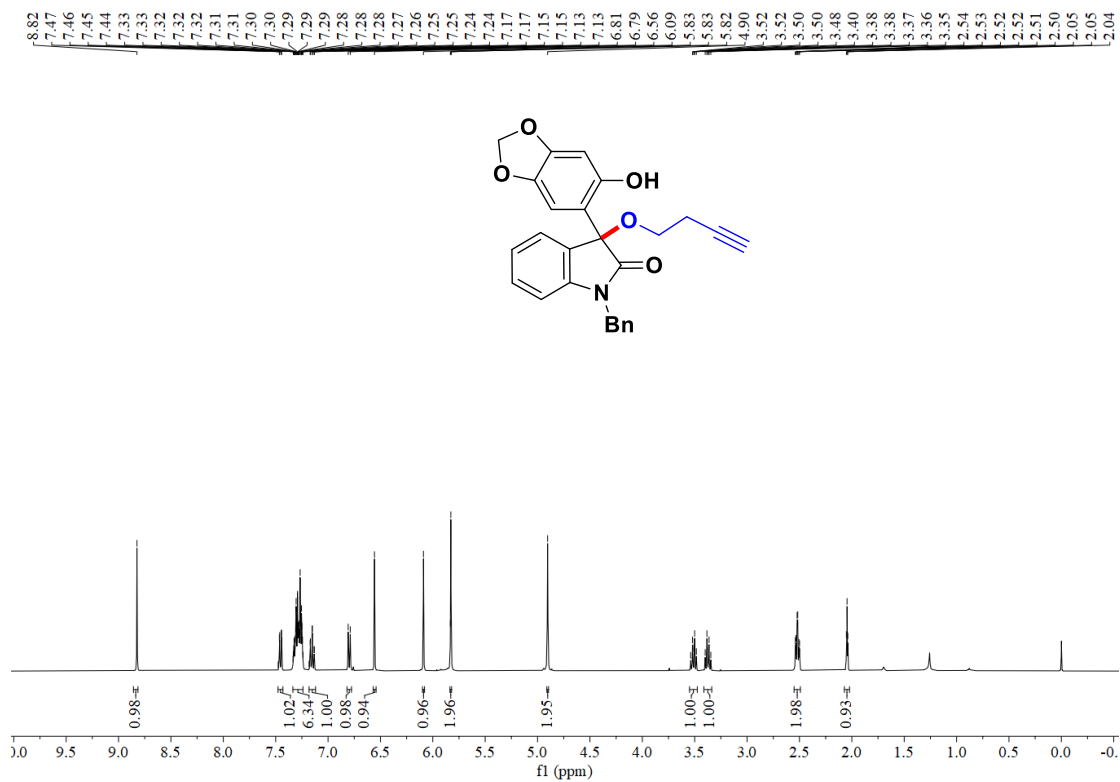
**1-benzyl-3-(2-bromoethoxy)-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)indolin-2-one
(5c)**



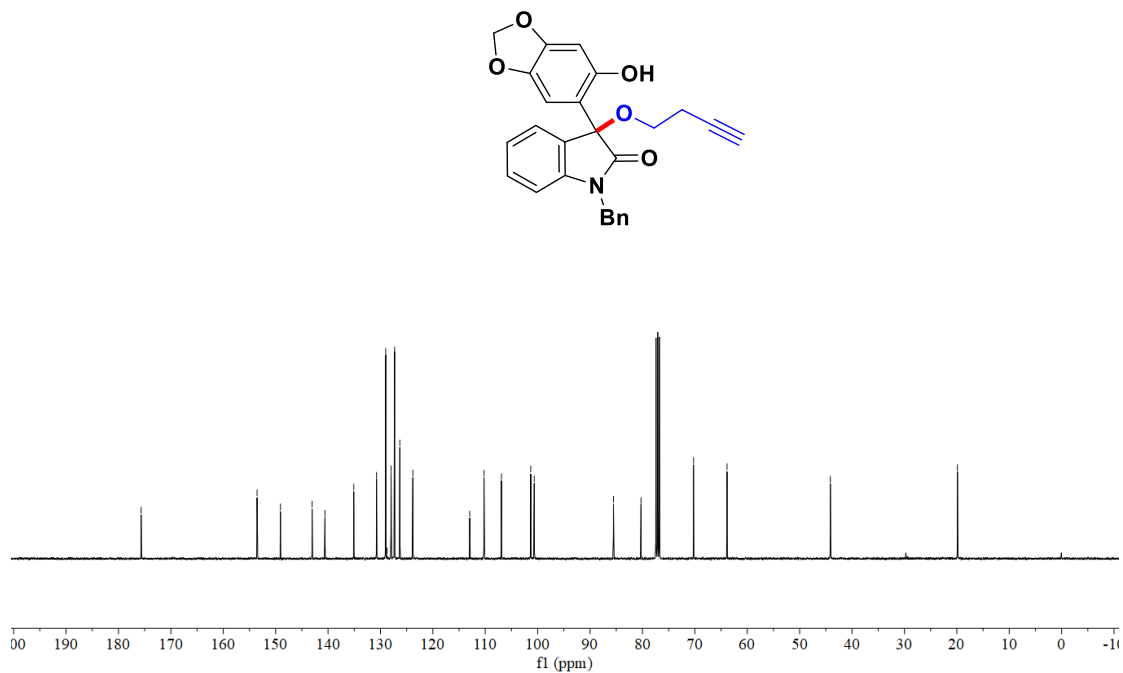
1-benzyl-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)-3-(prop-2-yn-1-yloxy)indolin-2-one (5d)



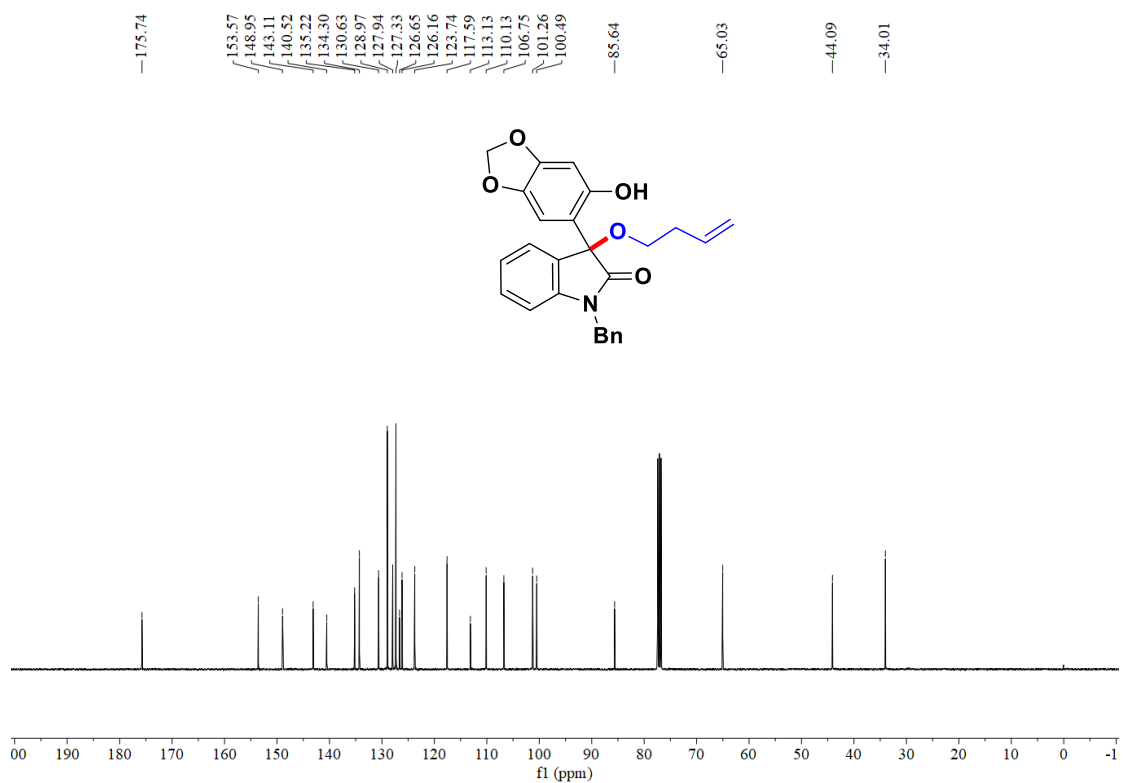
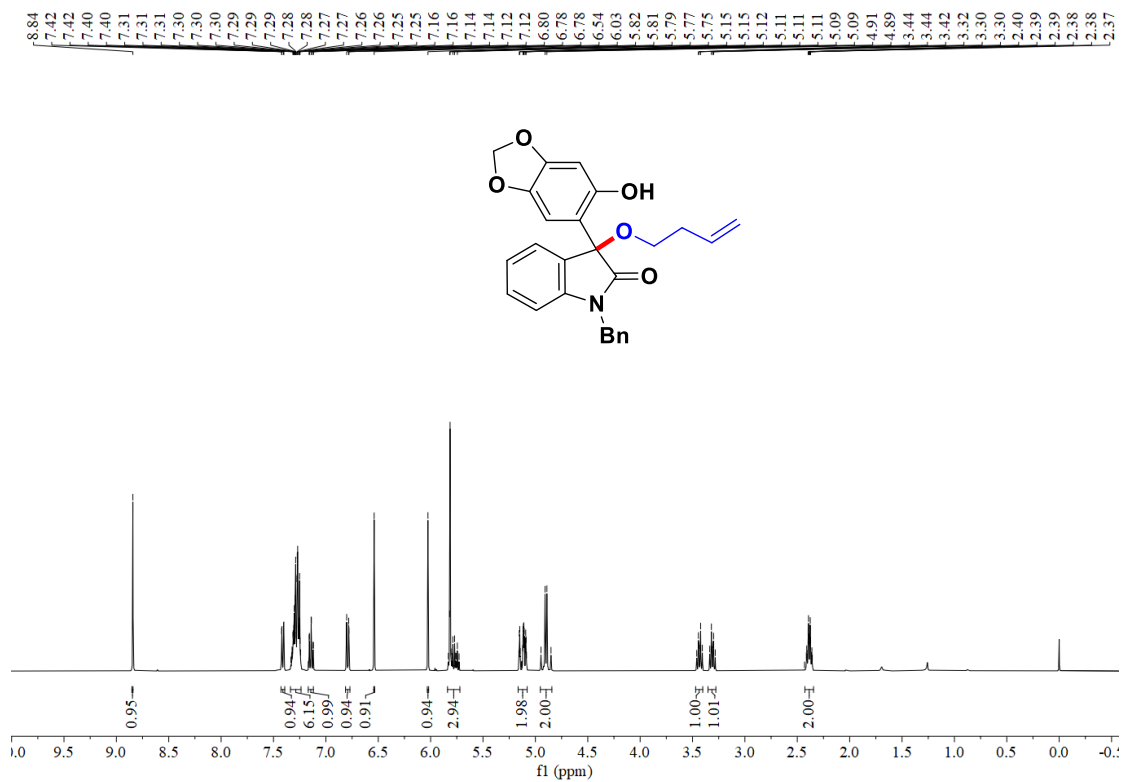
**1-benzyl-3-(but-3-yn-1-yloxy)-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)indolin-2-one
(5e)**



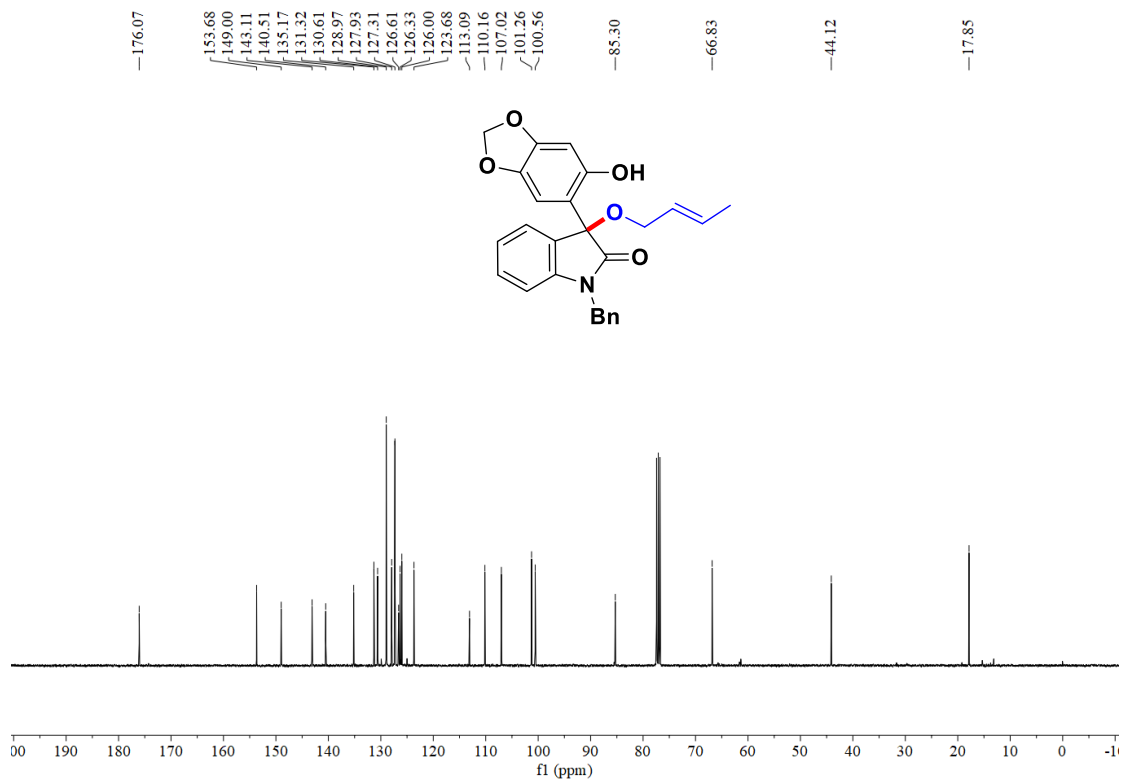
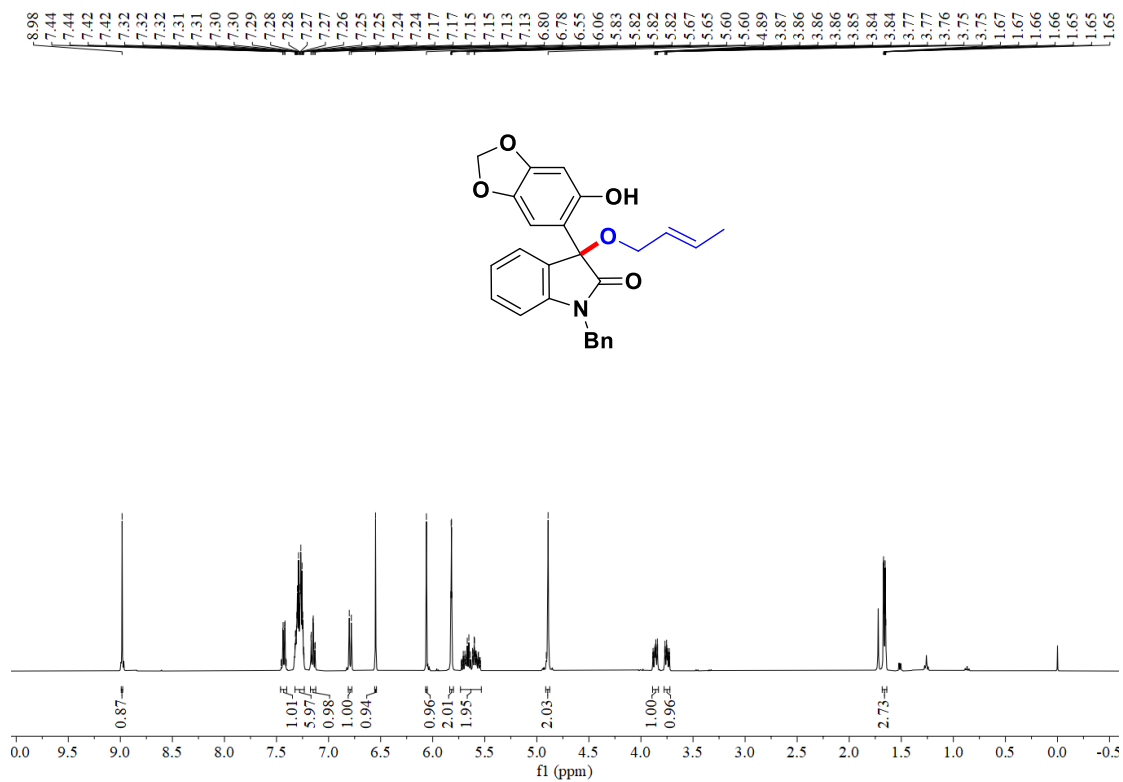
Chemical shifts (ppm): -175.67, 153.55, 149.09, 143.04, 140.59, 135.09, 130.75, 129.00, 128.73, 127.98, 127.30, 126.30, 123.82, 112.96, 110.24, 106.92, 101.32, 100.65, 85.54, 80.27, 70.26, 63.85, 44.14, 19.88.



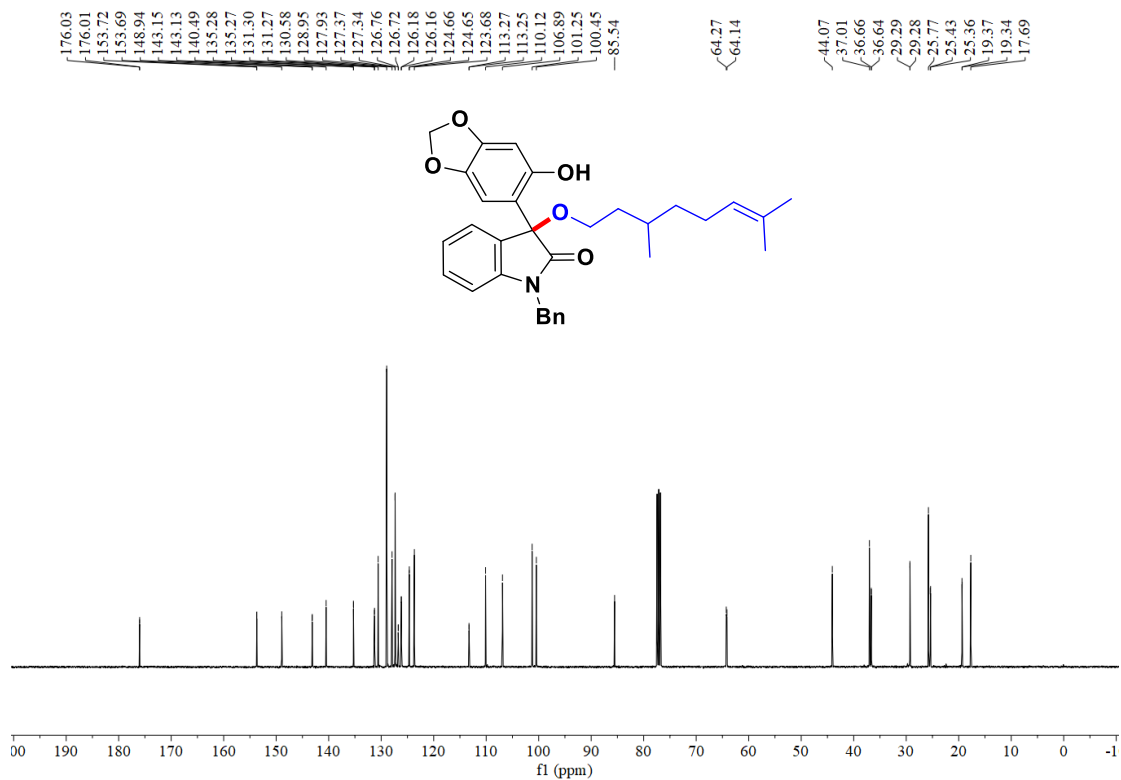
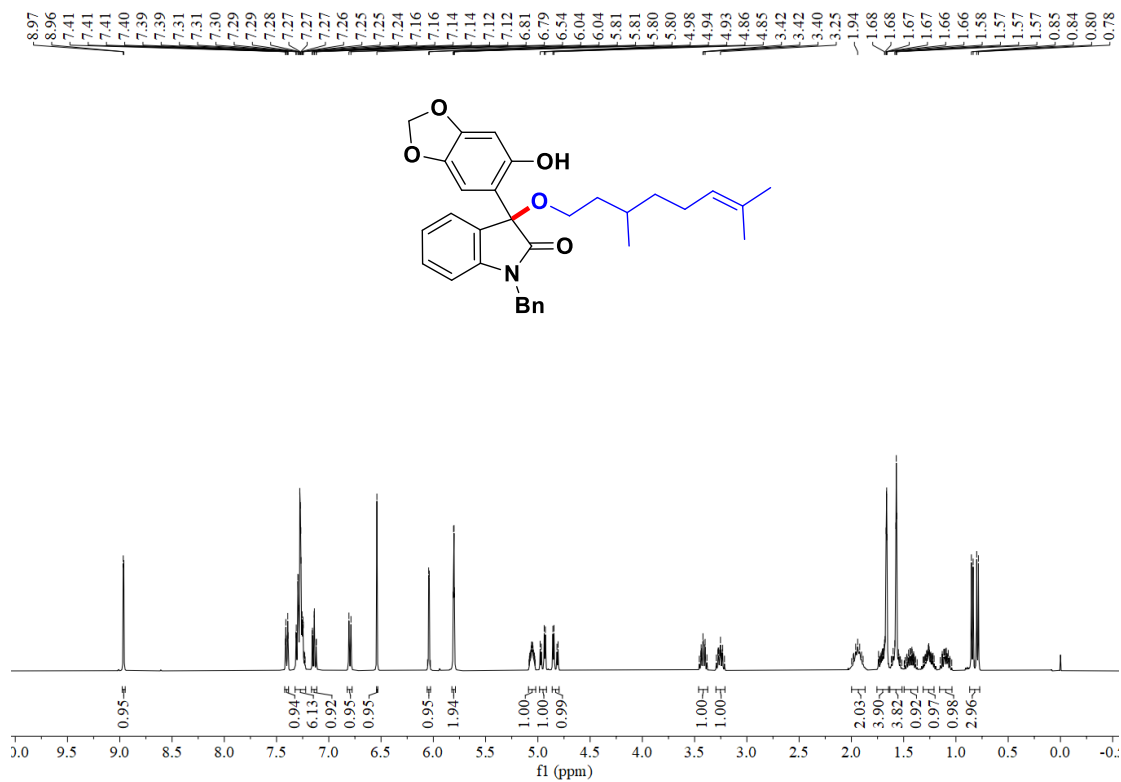
1-benzyl-3-(but-3-en-1-yloxy)-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)indolin-2-one (5f)



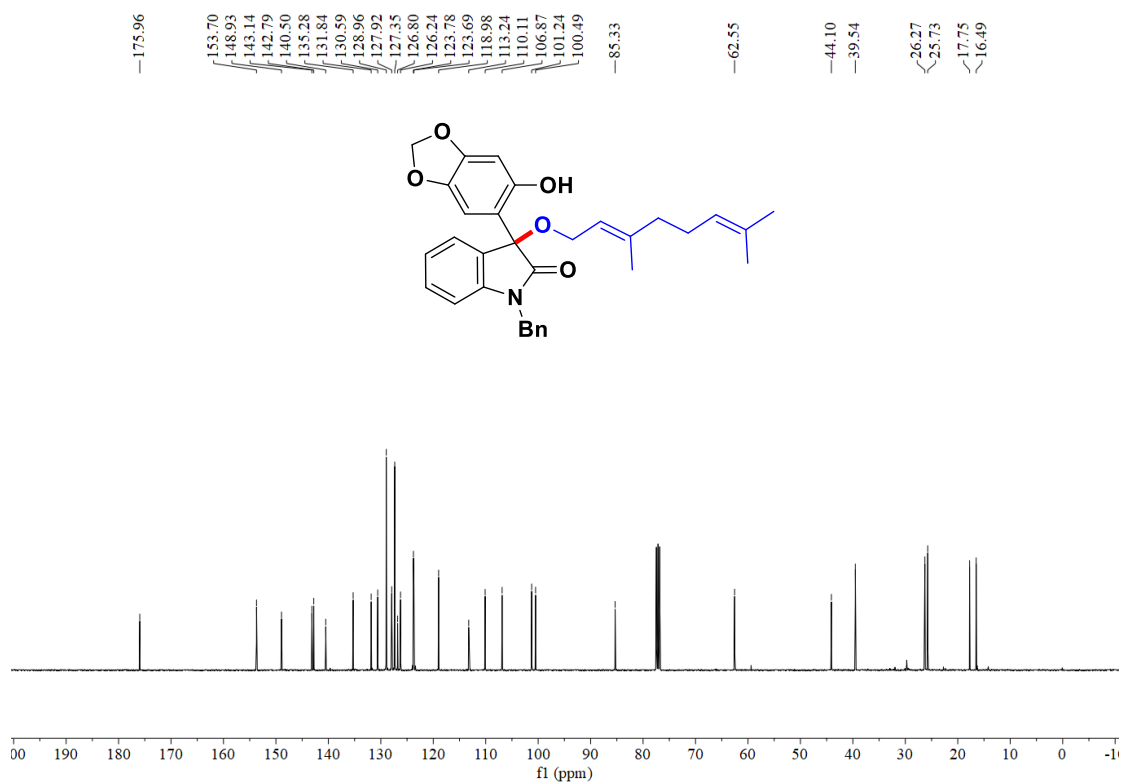
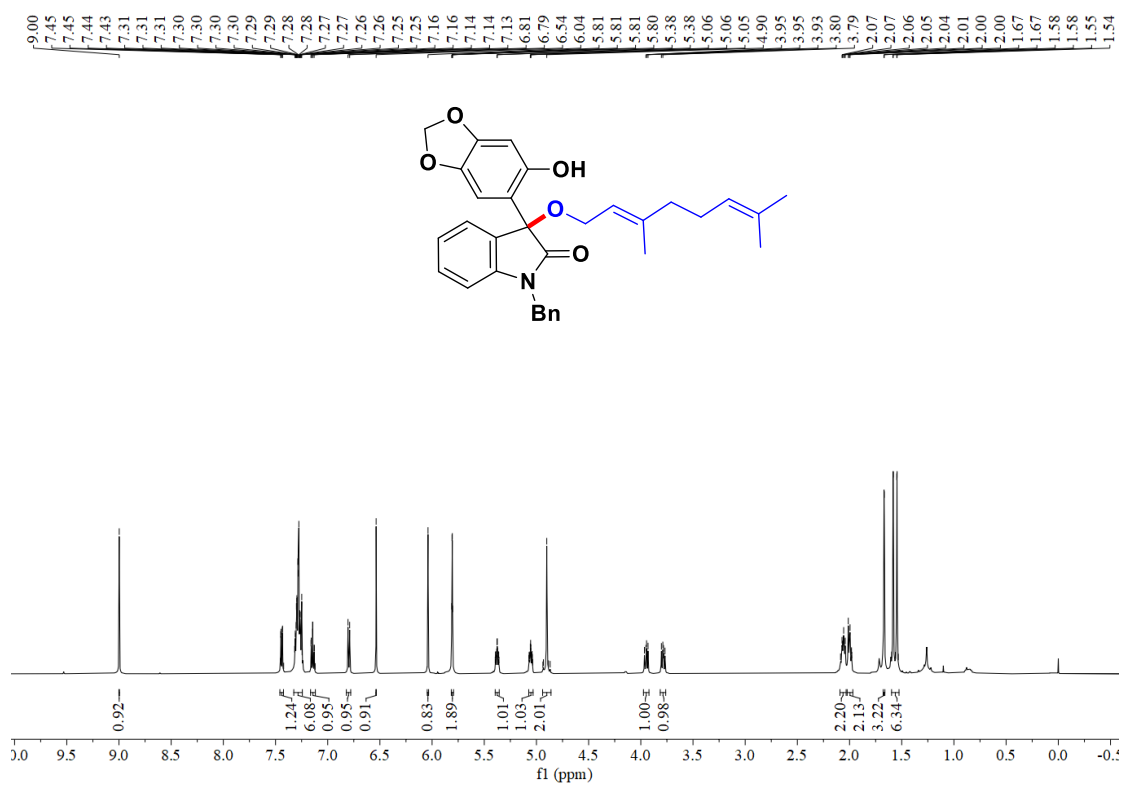
1-benzyl-3-(but-2-en-1-yloxy)-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)indolin-2-one (5g)



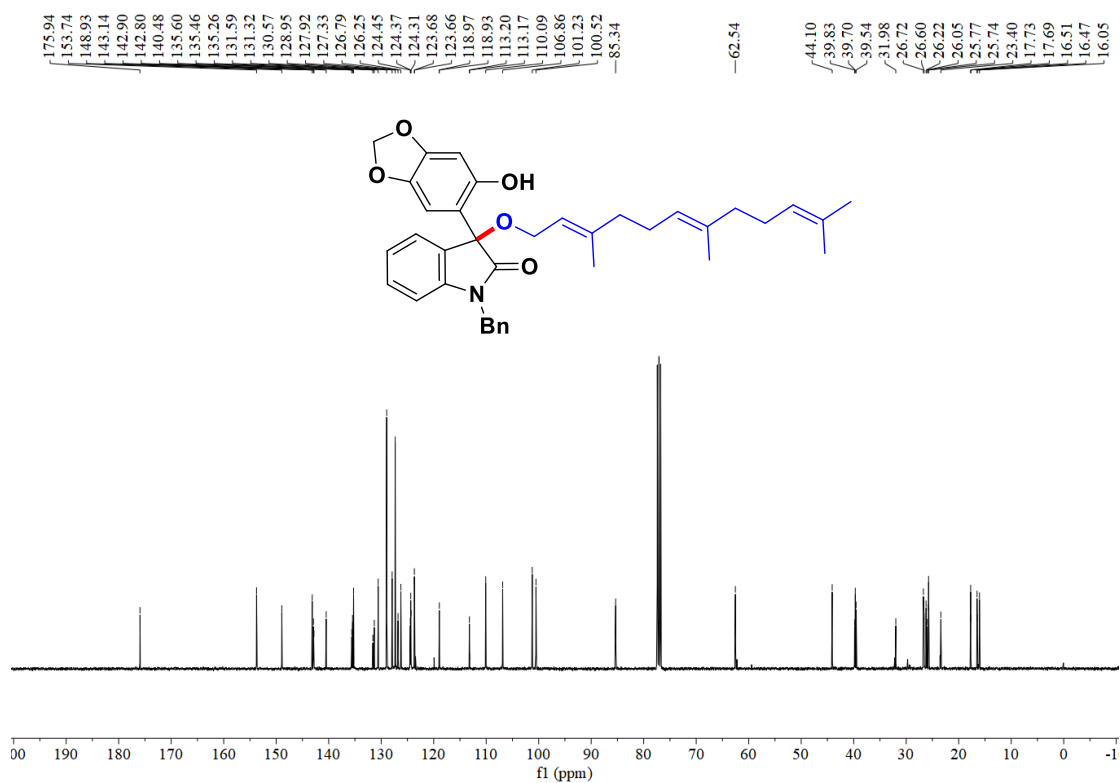
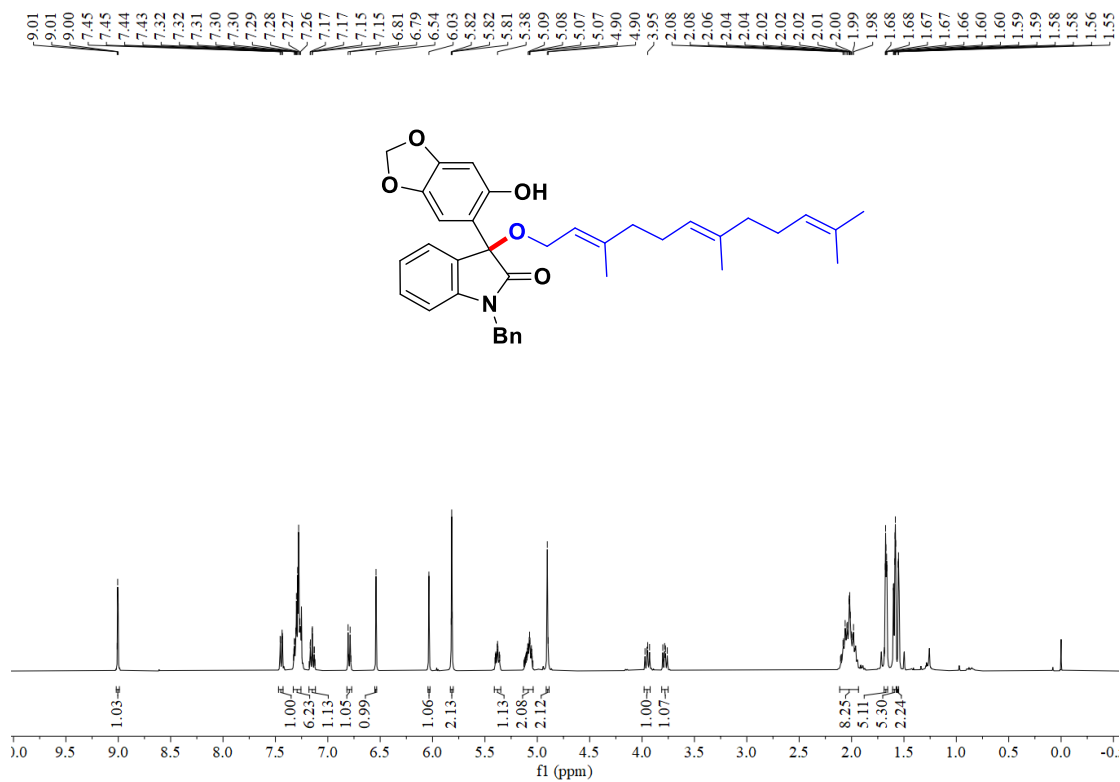
1-benzyl-3-((3,7-dimethyloct-6-en-1-yl)oxy)-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)indolin-2-one (5h)



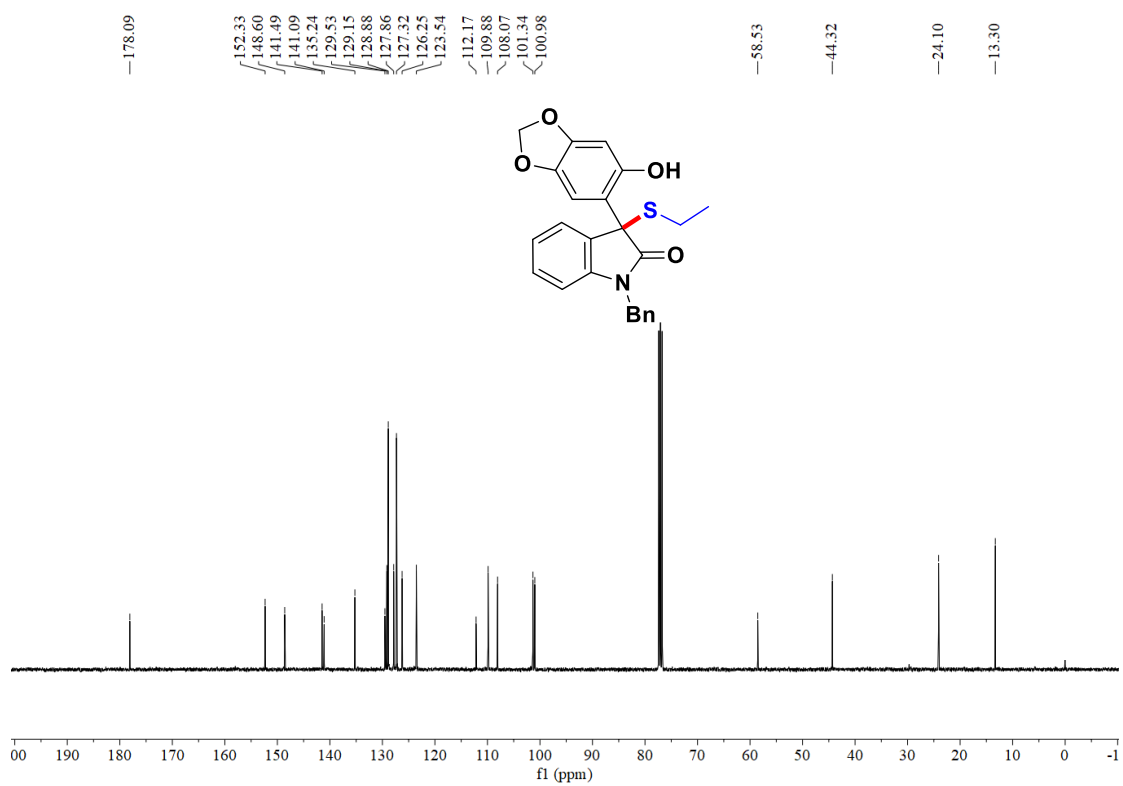
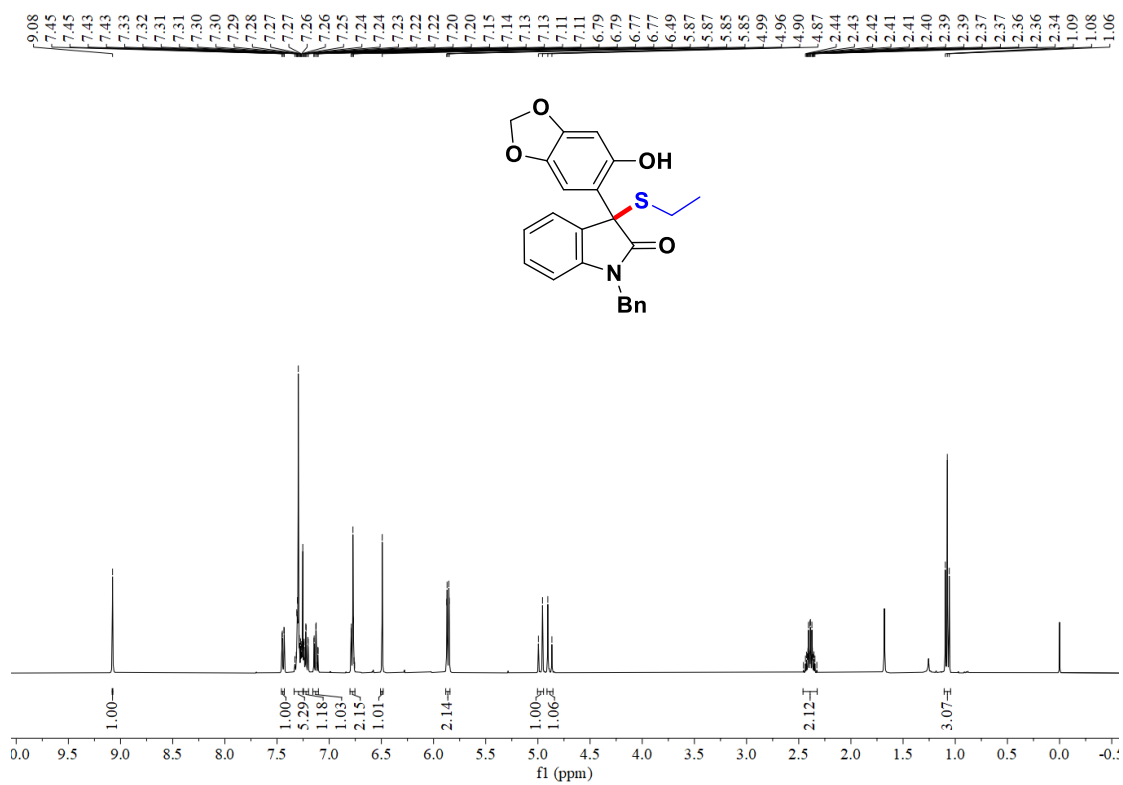
1-benzyl-3-((3,7-dimethylocta-2,6-dien-1-yl)oxy)-3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)indolin-2-one (5i)



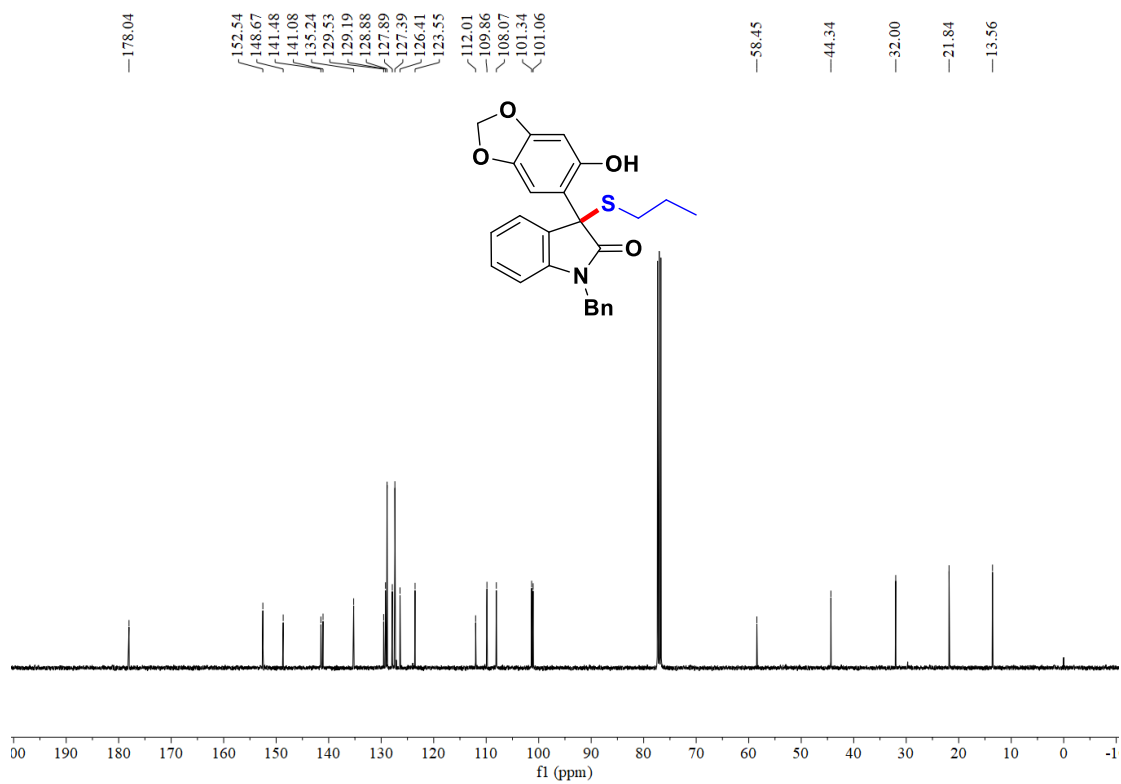
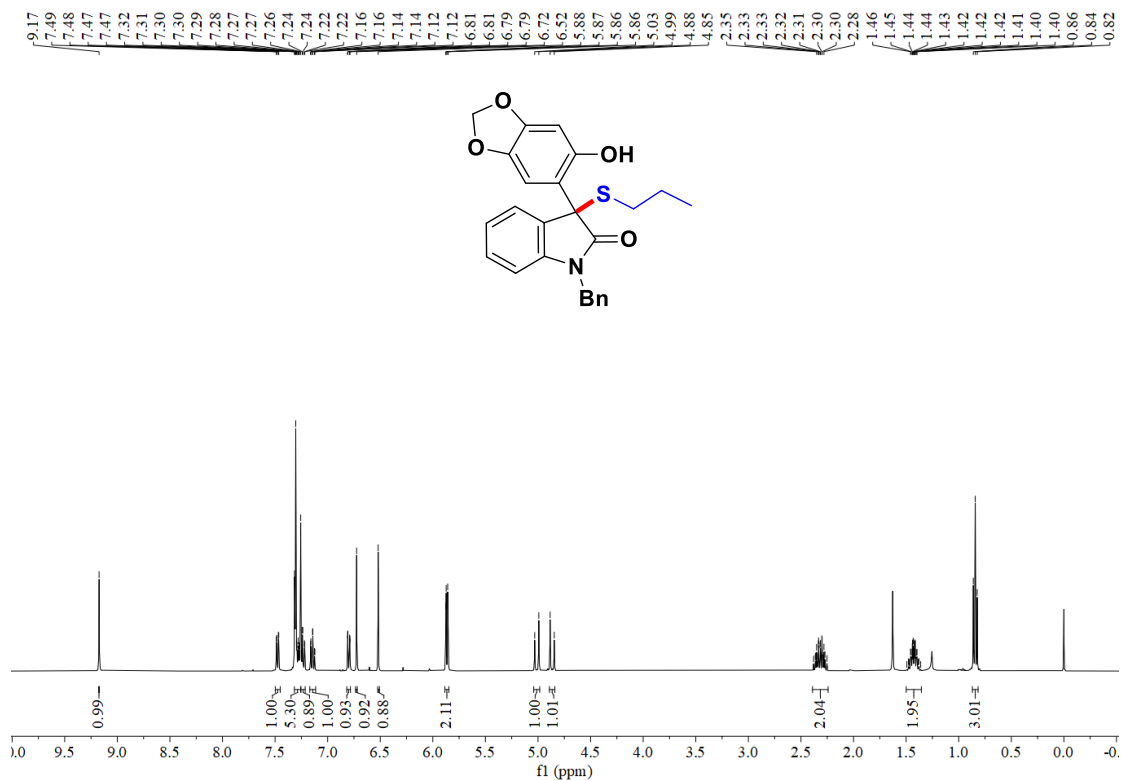
1-benzyl-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)-3-(((2E,6E)-3,7,11-trimethyldodeca-2,6,10-trien-1-yl)oxy)indolin-2-one (5j)



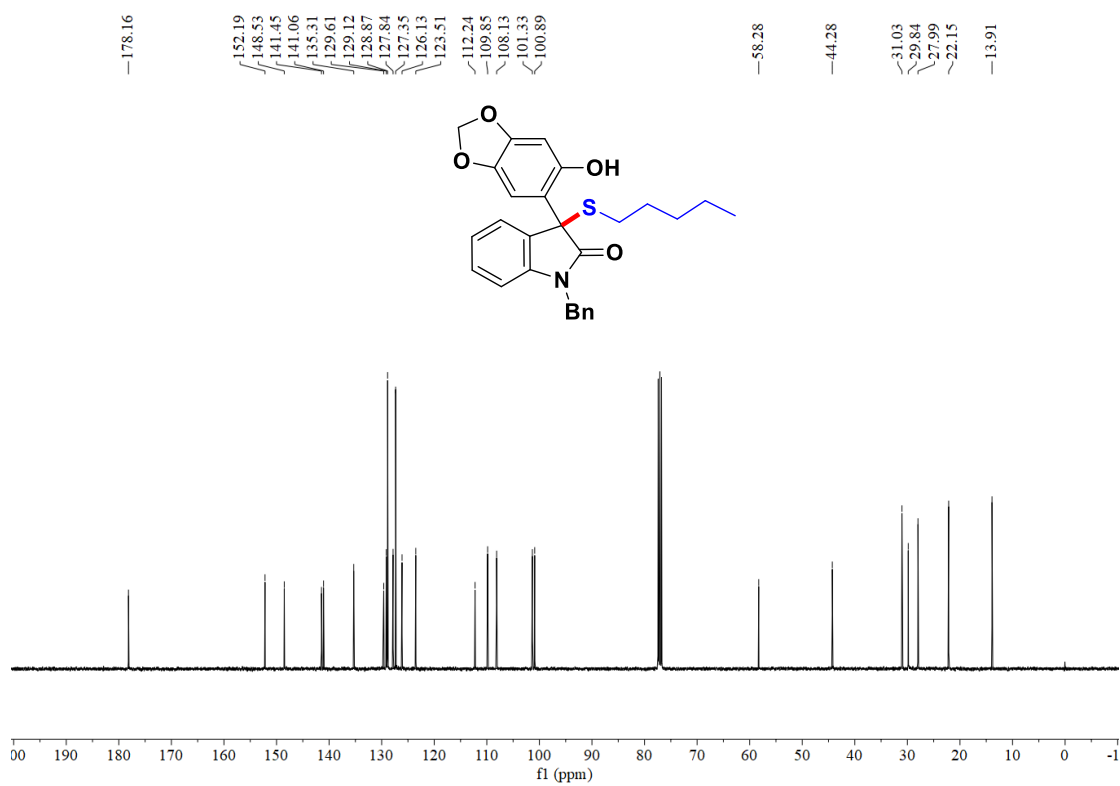
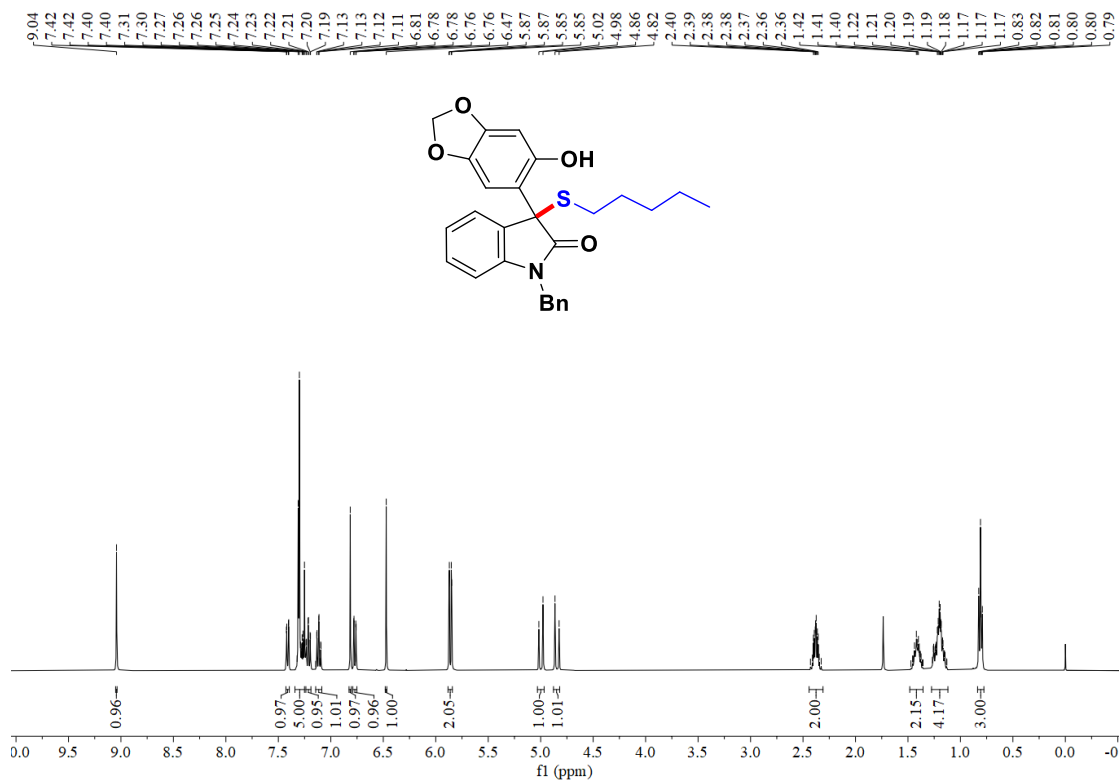
1-benzyl-3-(ethylthio)-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)indolin-2-one (6a)



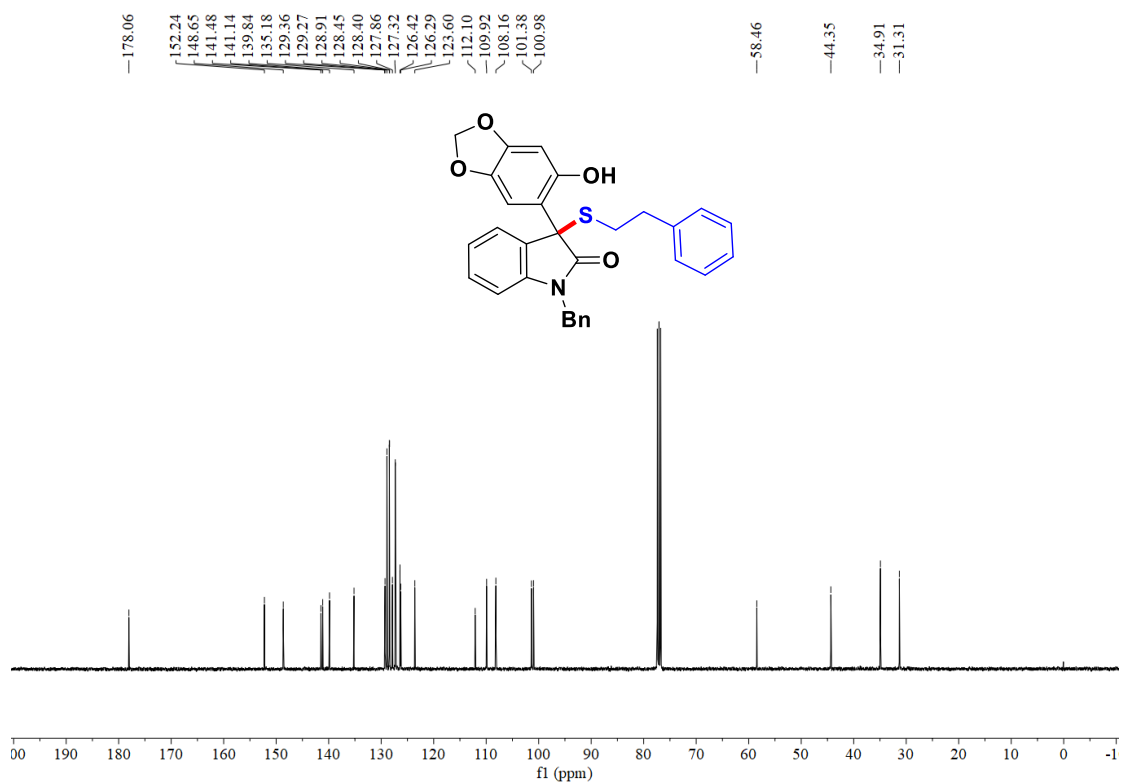
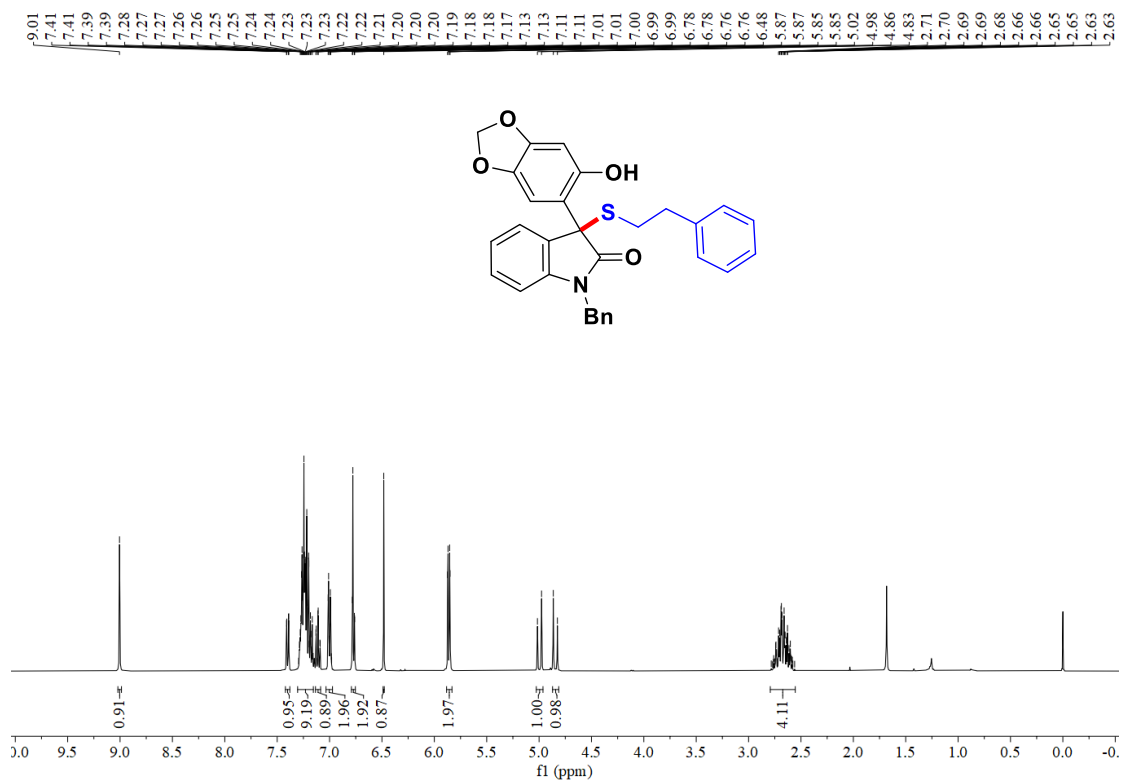
1-benzyl-3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)-3-(propylthio)indolin-2-one (6b)



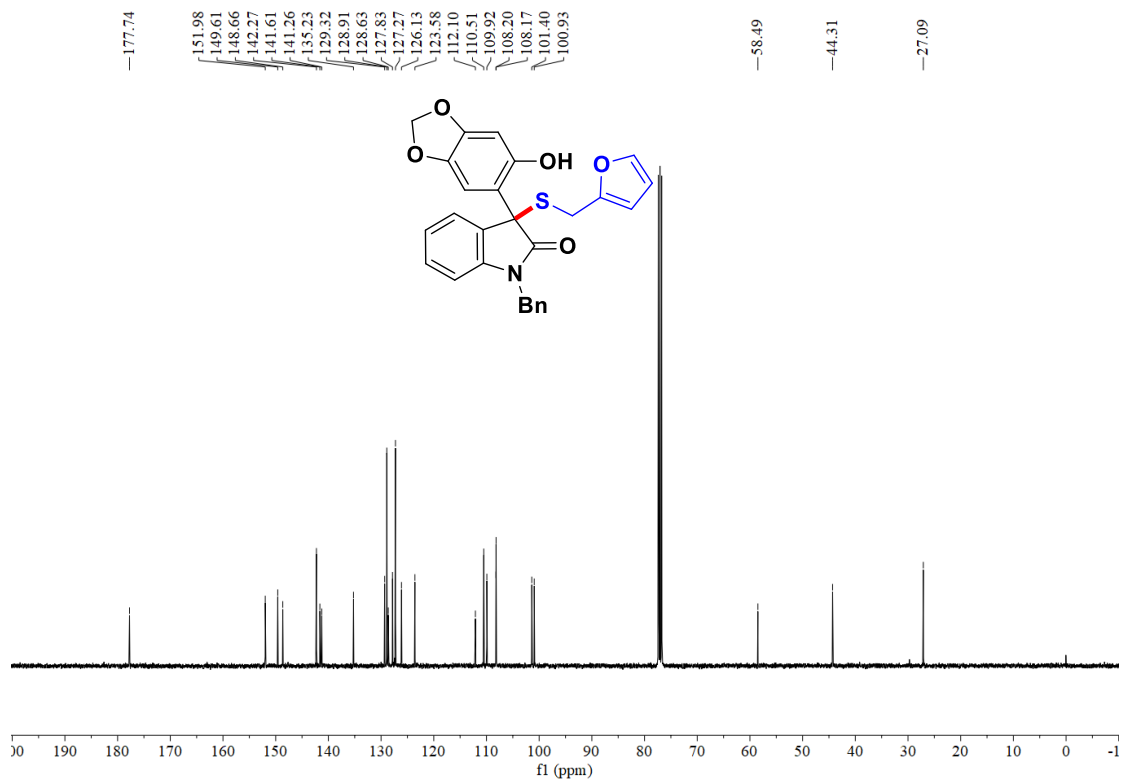
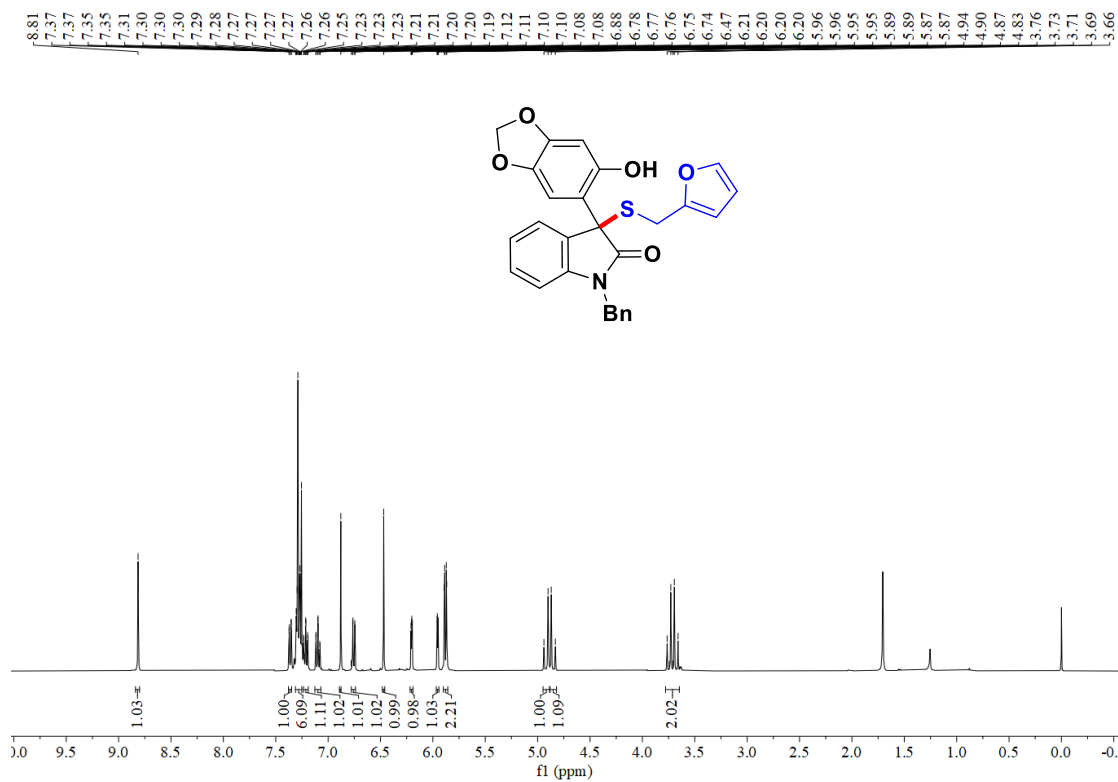
1-benzyl-3-(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)-3-(pentylthio)indolin-2-one (5c)



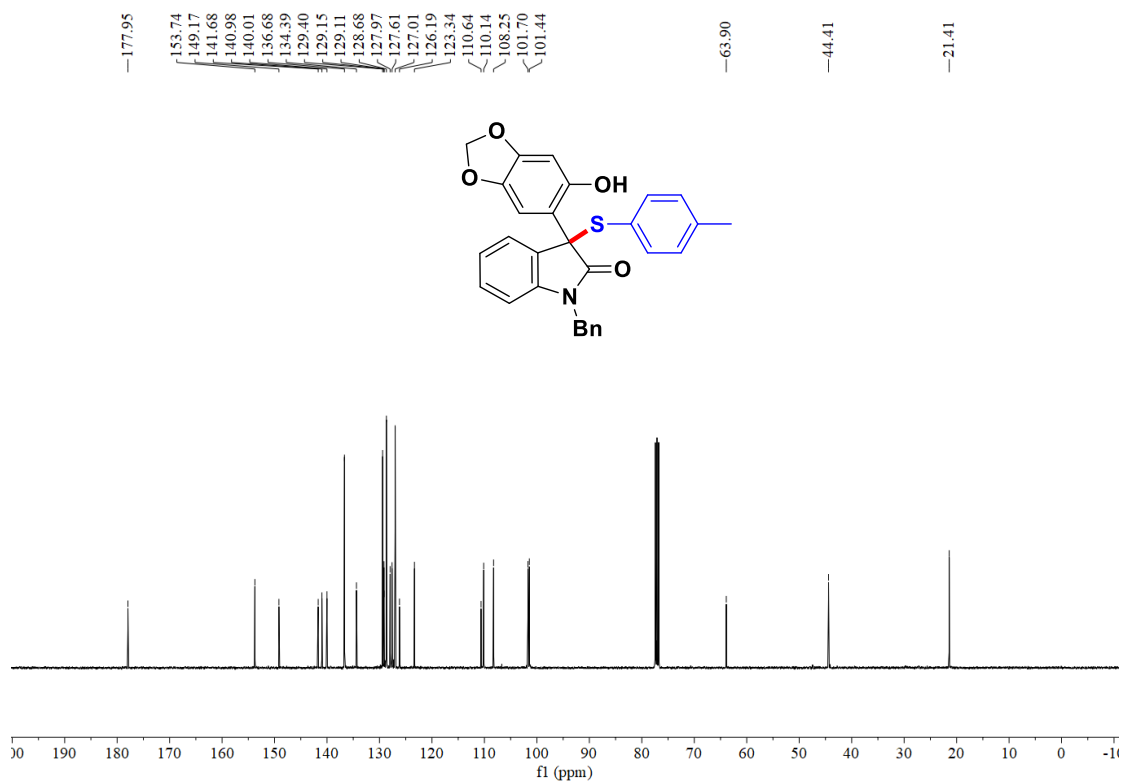
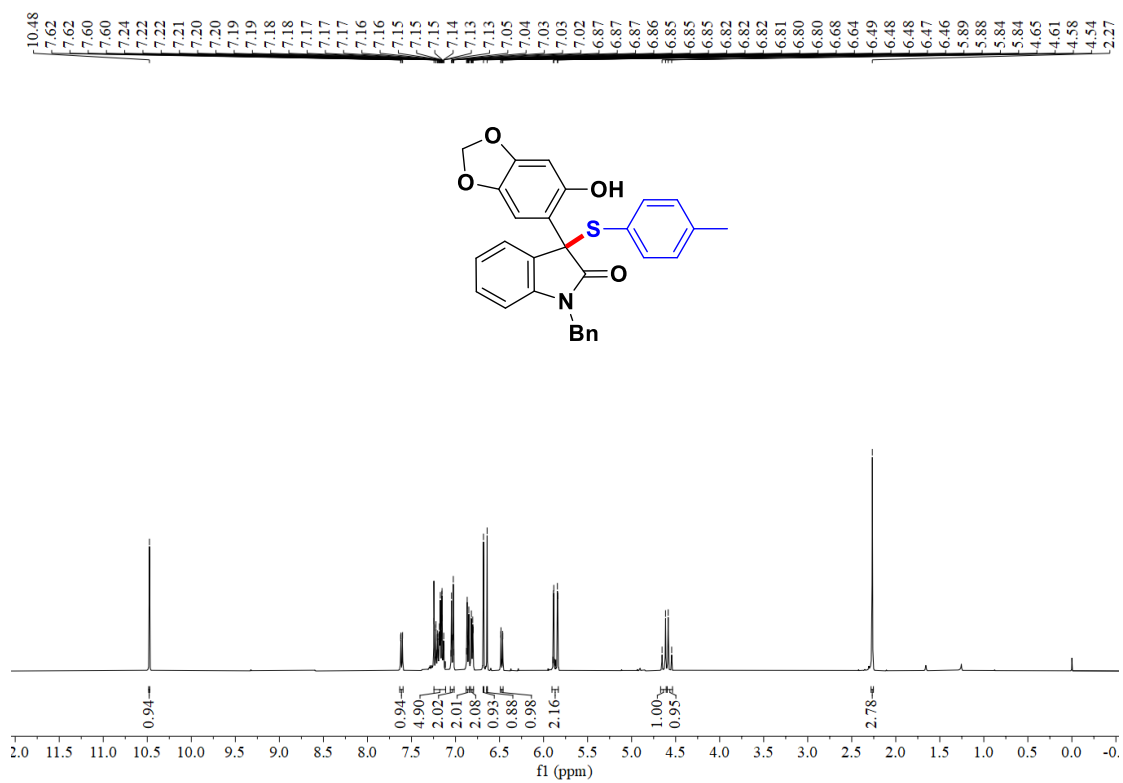
**1-benzyl-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)-3-(phenethylthio)indolin-2-one
(6d)**



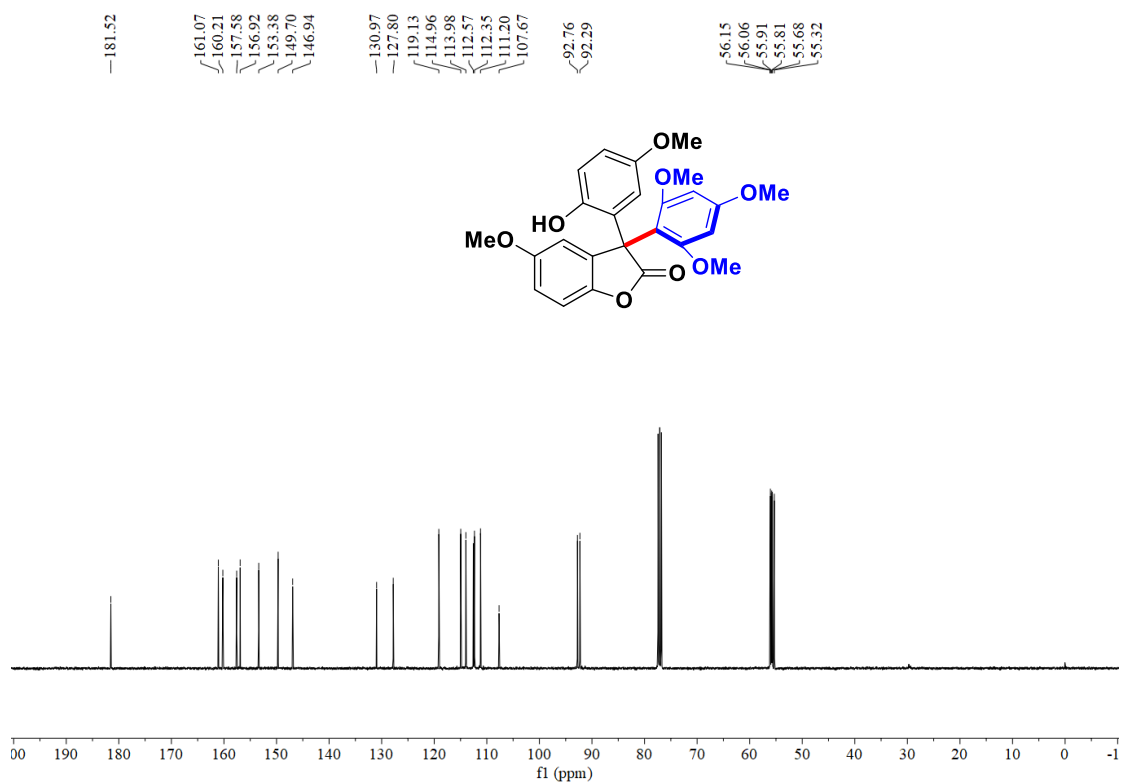
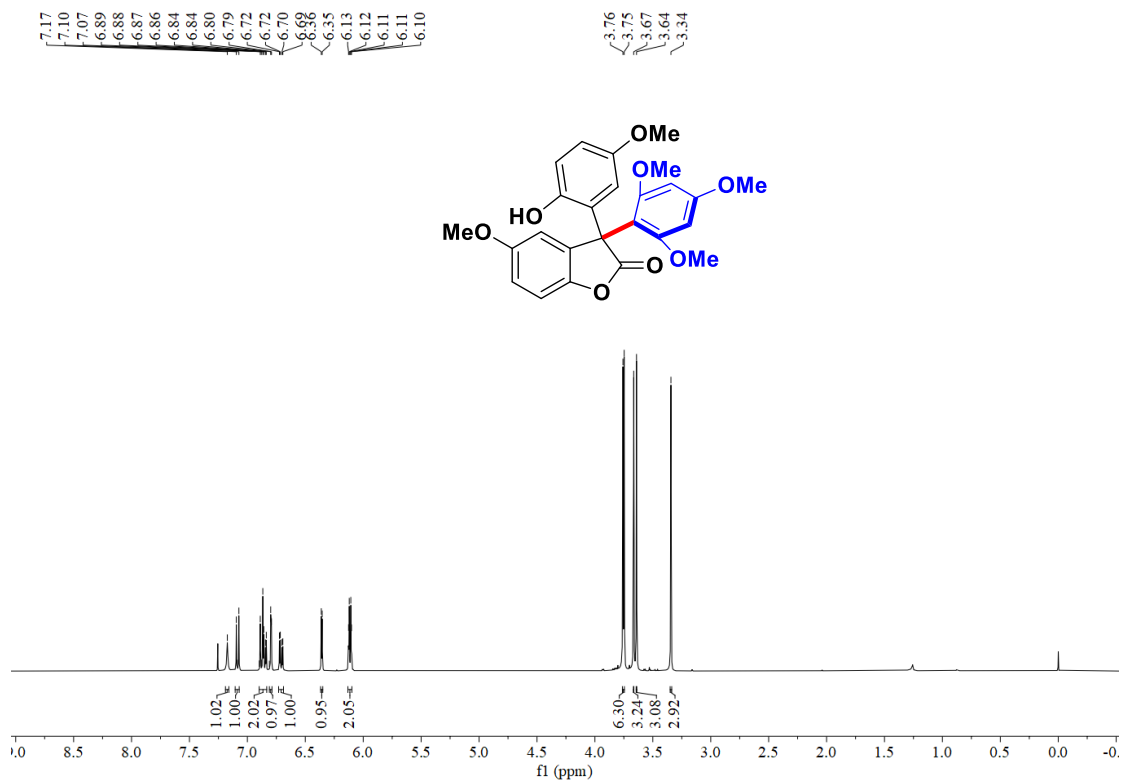
1-benzyl-3-((furan-2-ylmethyl)thio)-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)indolin-2-one (6e)



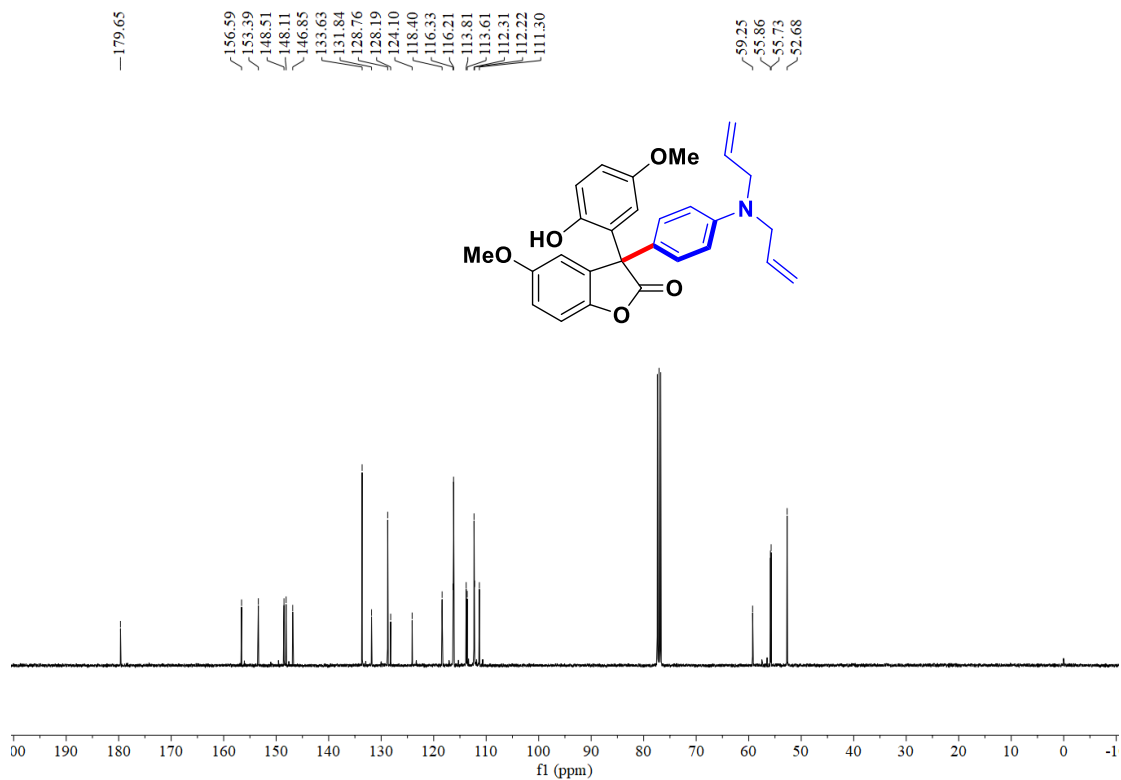
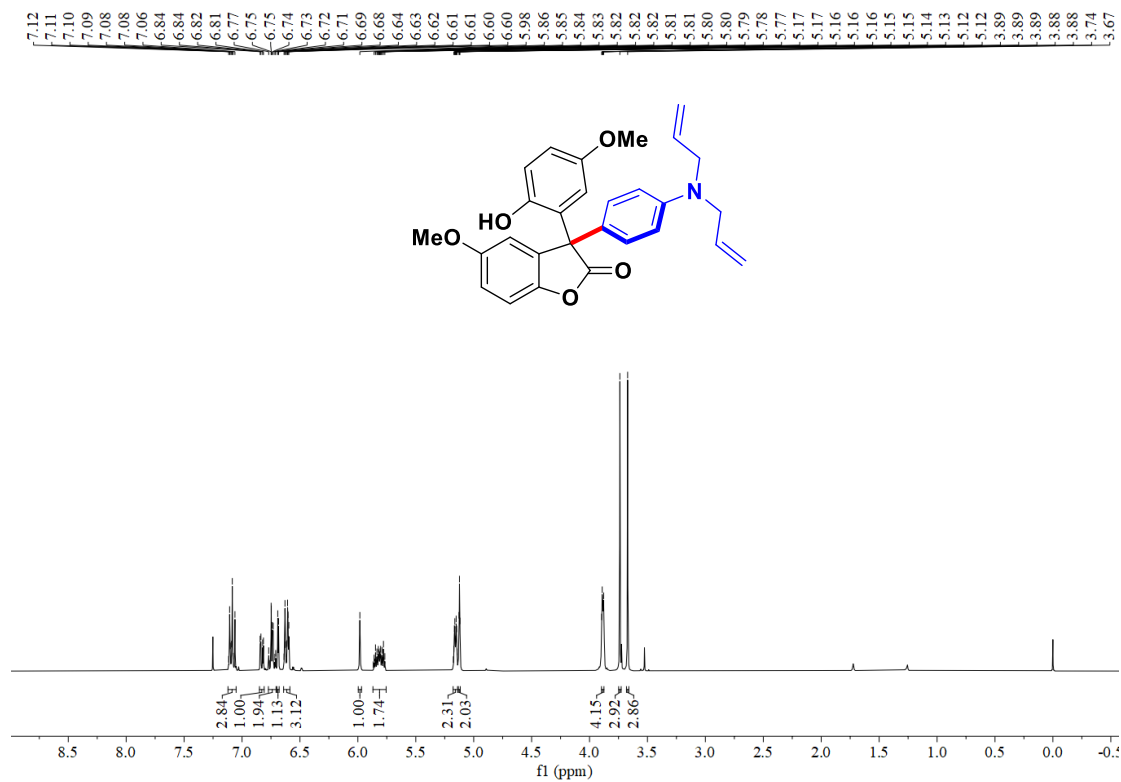
1-benzyl-3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)-3-(p-tolylthio)indolin-2-one (6f)



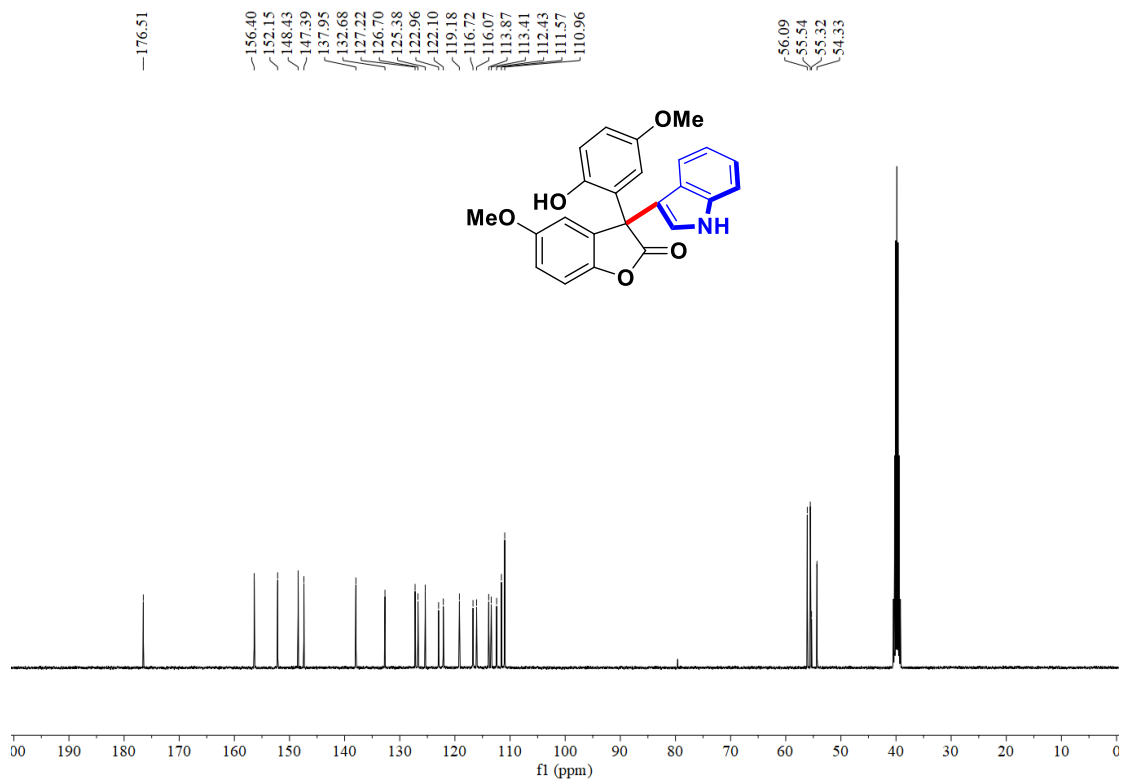
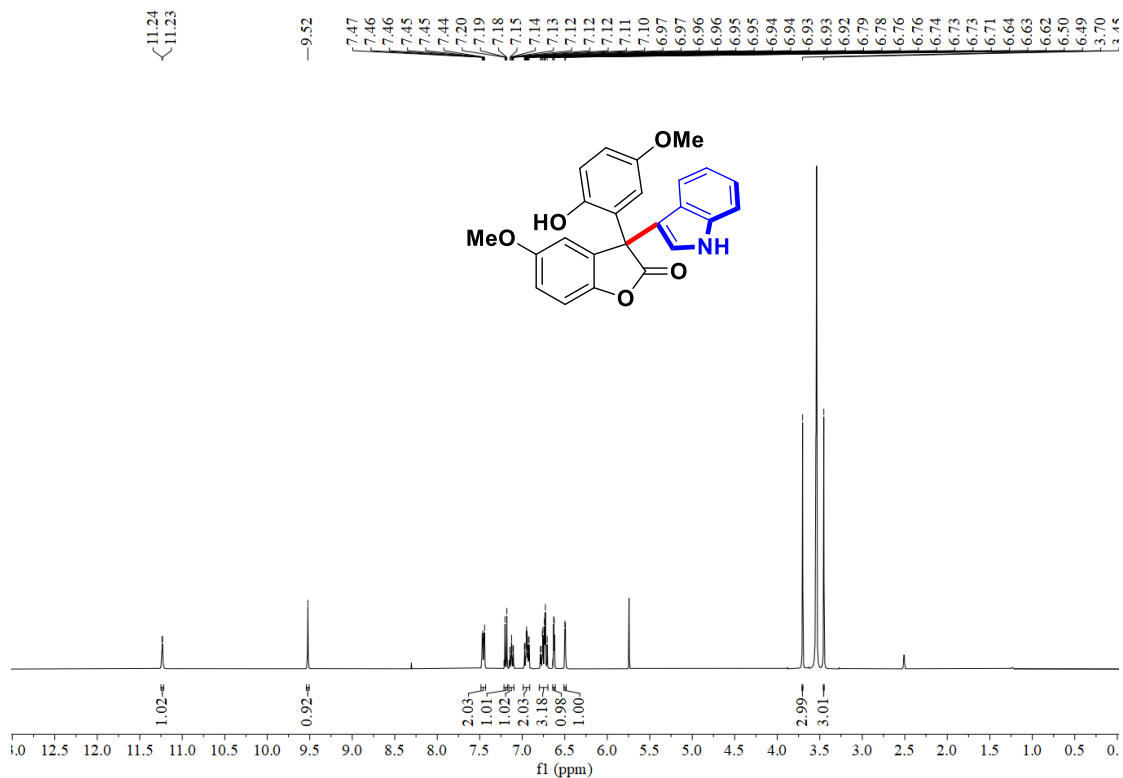
3-(2-hydroxy-5-methoxyphenyl)-5-methoxy-3-(2,4,6-trimethoxyphenyl)benzofuran-2(3H)-one (8a)



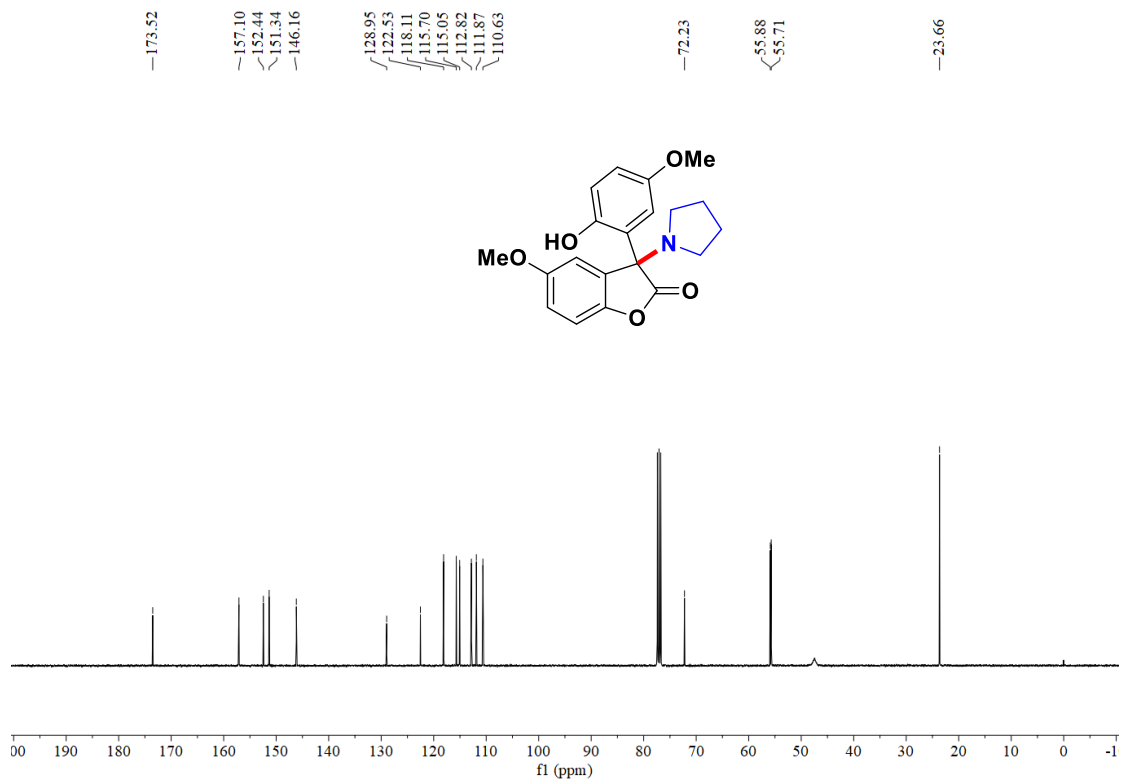
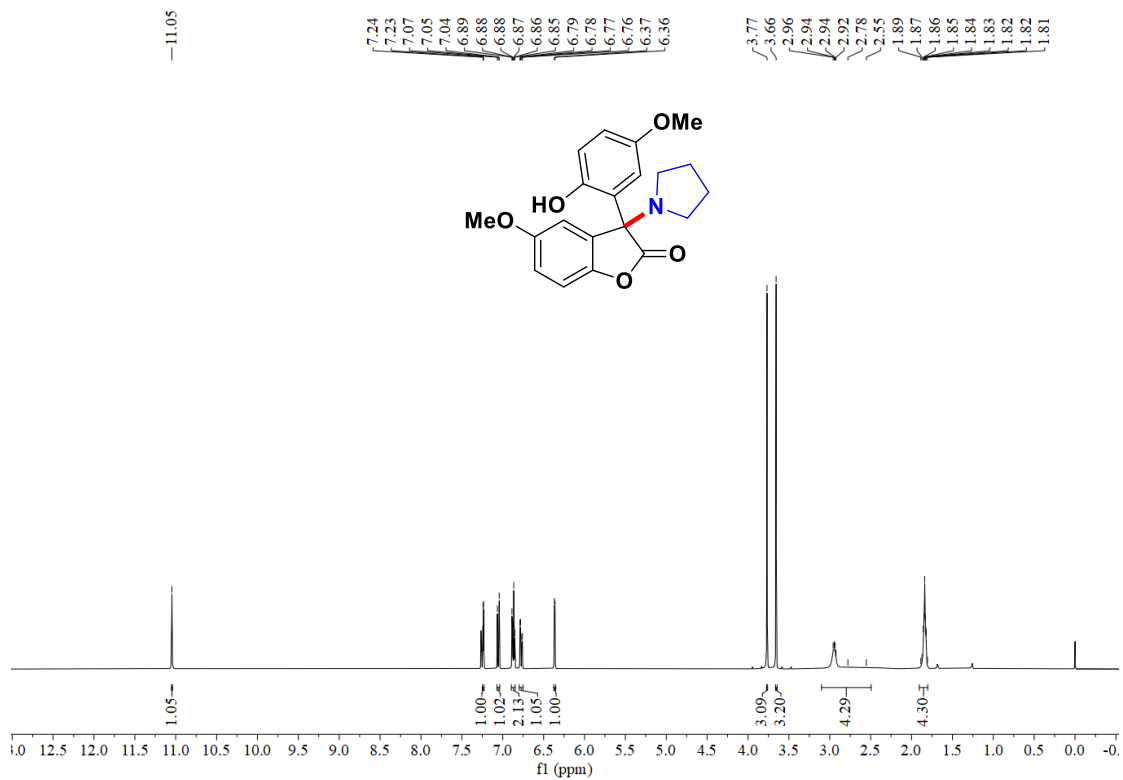
3-(4-(diallylamino)phenyl)-3-(2-hydroxy-5-methoxyphenyl)-5-methoxybenzofuran-2(3H)-one (8b)



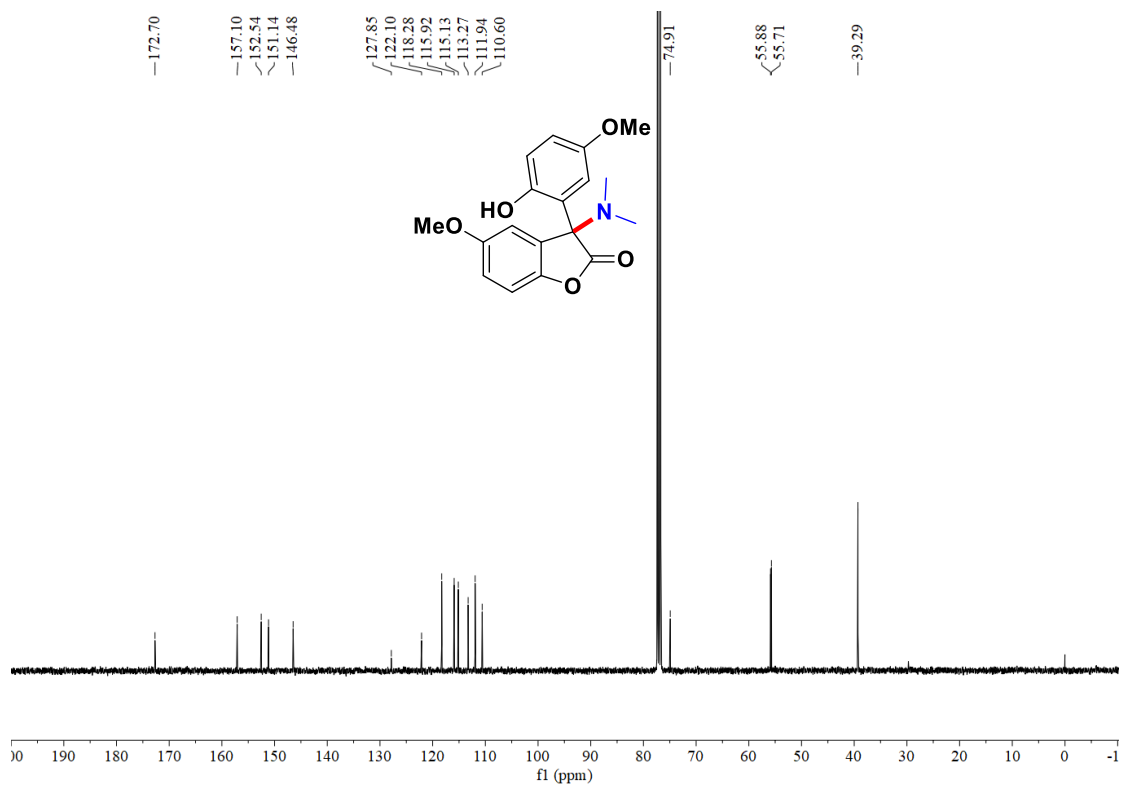
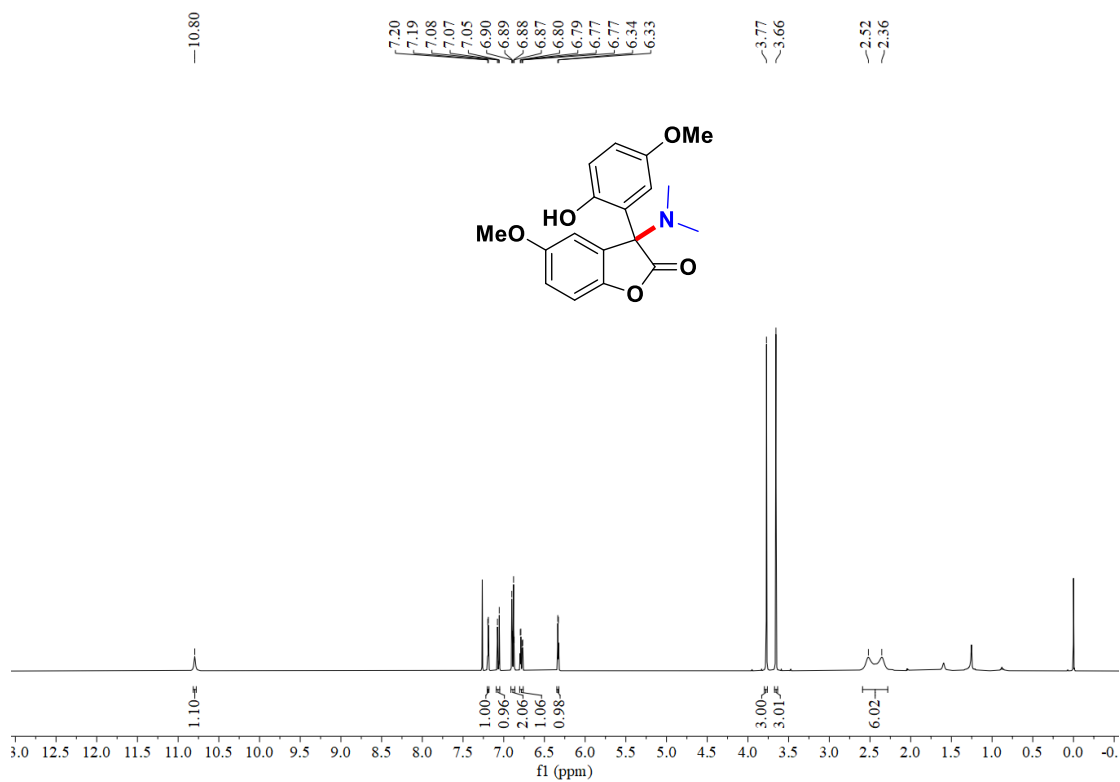
3-(2-hydroxy-5-methoxyphenyl)-3-(1*H*-indol-3-yl)-5-methoxybenzofuran-2(3*H*)-one (8c)



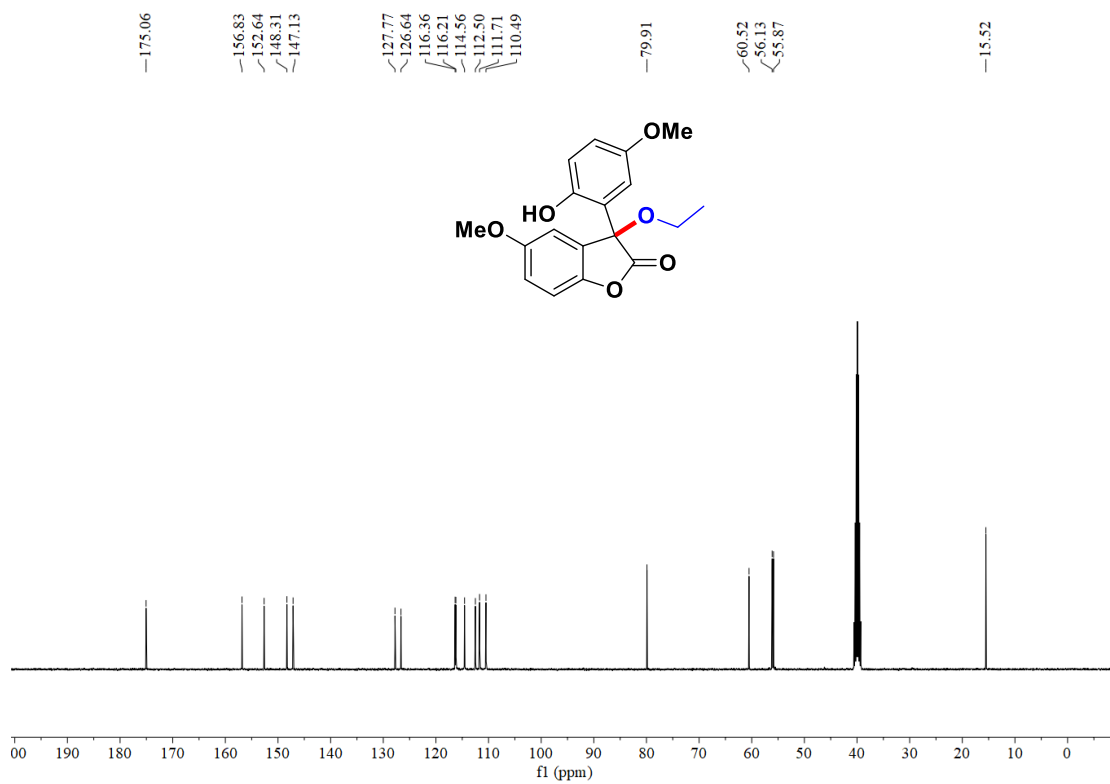
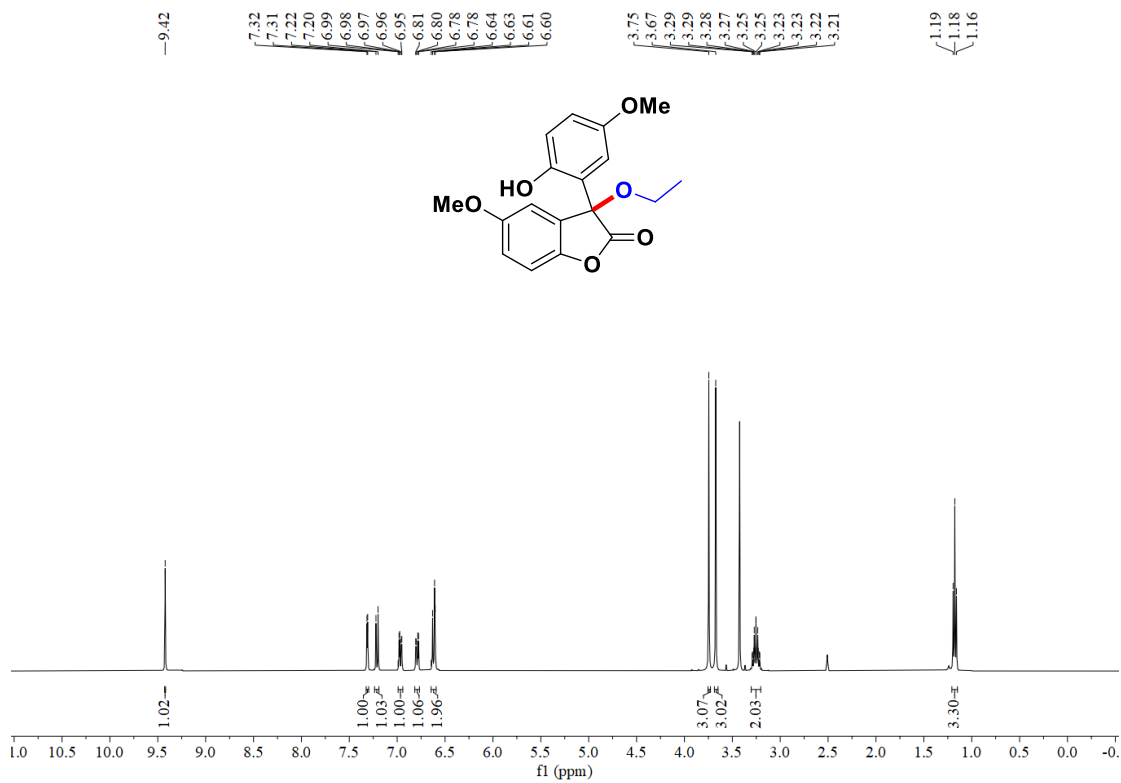
3-(2-hydroxy-5-methoxyphenyl)-5-methoxy-3-(pyrrolidin-1-yl)benzofuran-2(3H)-one (8d)



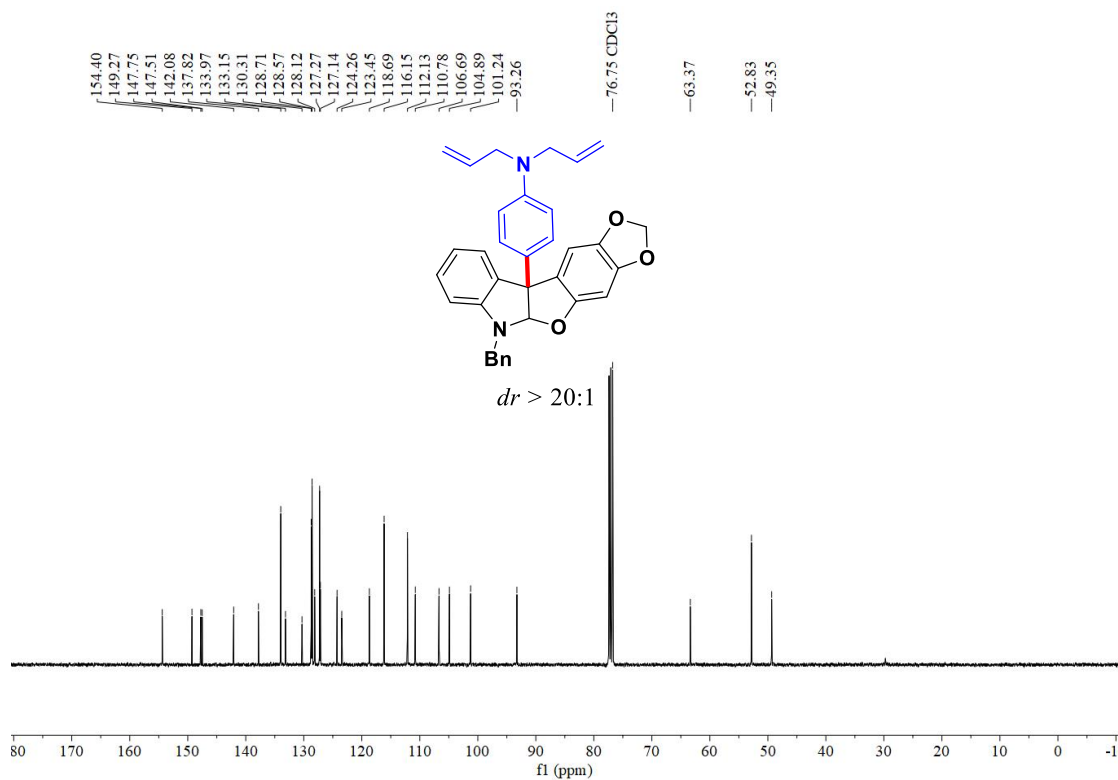
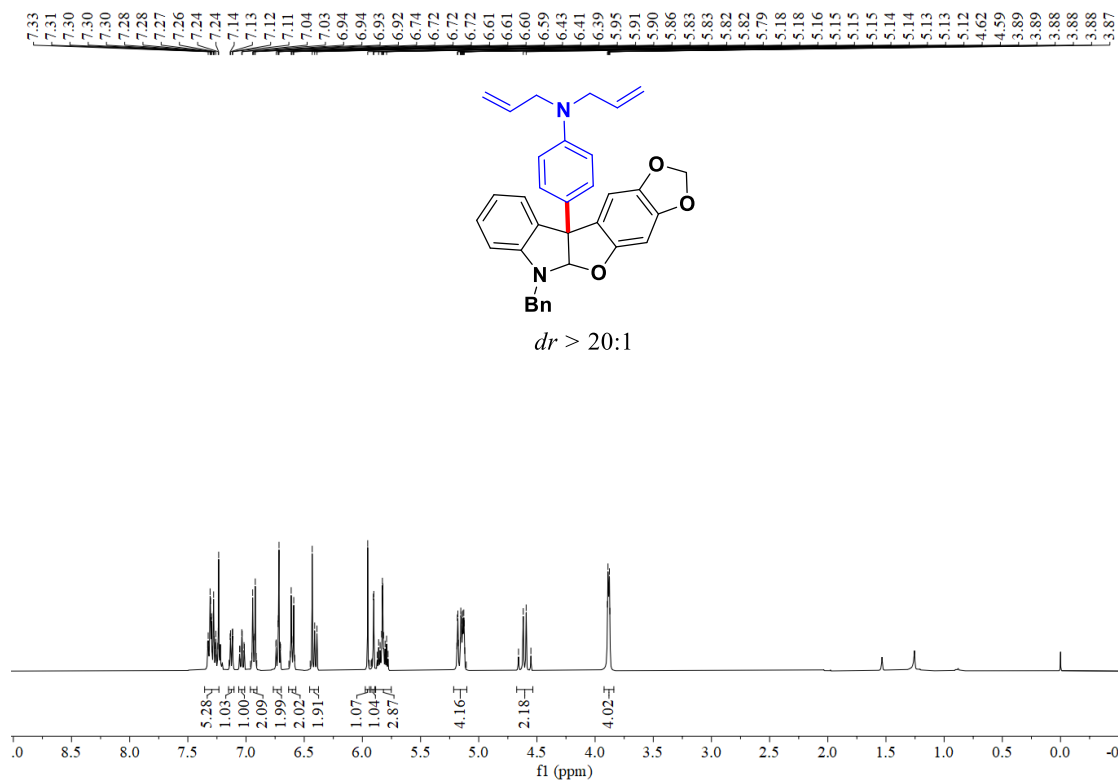
3-(dimethylamino)-3-(2-hydroxy-5-methoxyphenyl)-5-methoxybenzofuran-2(3H)-one (8e)



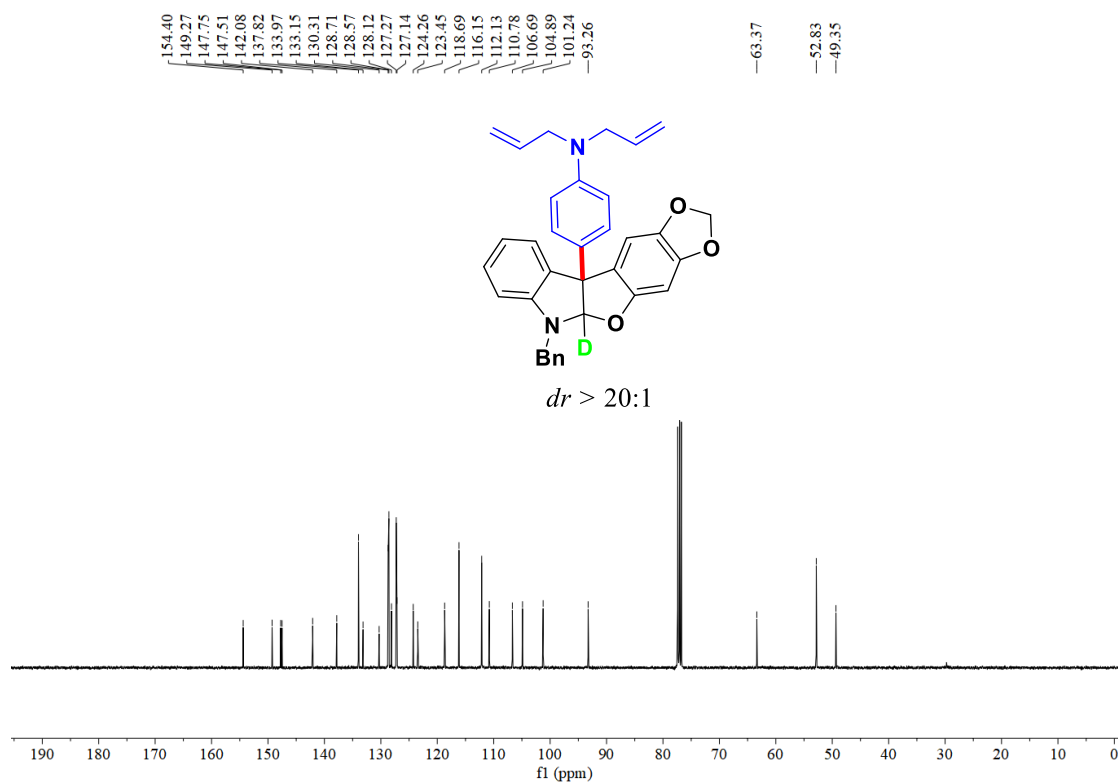
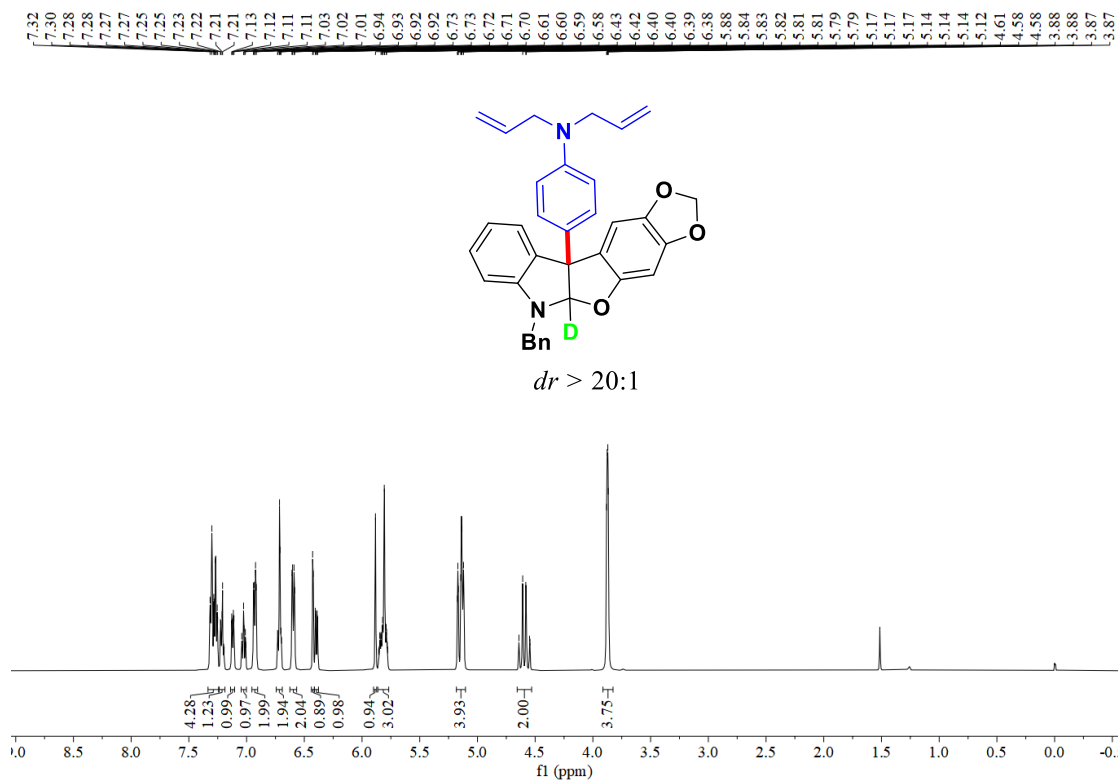
3-ethoxy-3-(2-hydroxy-5-methoxyphenyl)-5-methoxybenzofuran-2(3H)-one (8f)



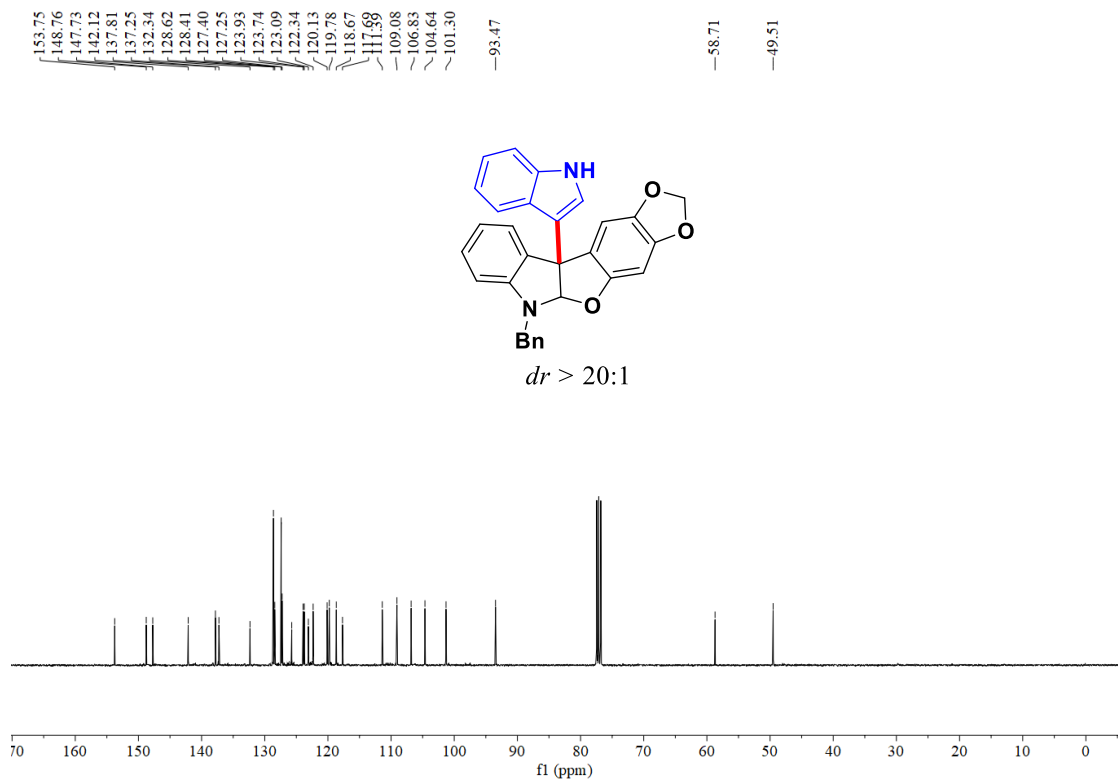
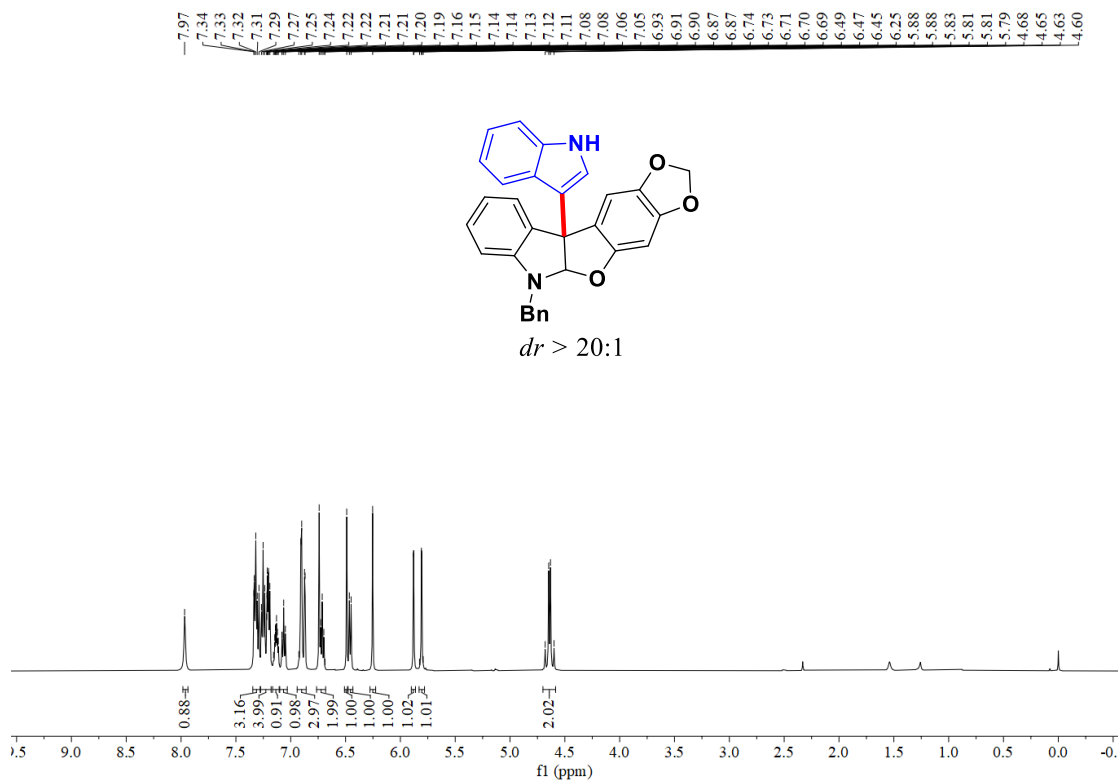
N,N-diallyl-4-(6-benzyl-5a,6-dihydro-10bH-[1,3]dioxolo[4',5':5,6]benzofuro[2,3-b]indol-10b-yl)aniline (11a)



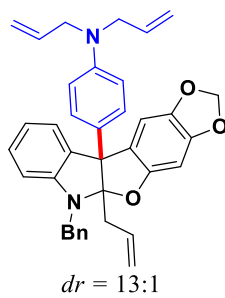
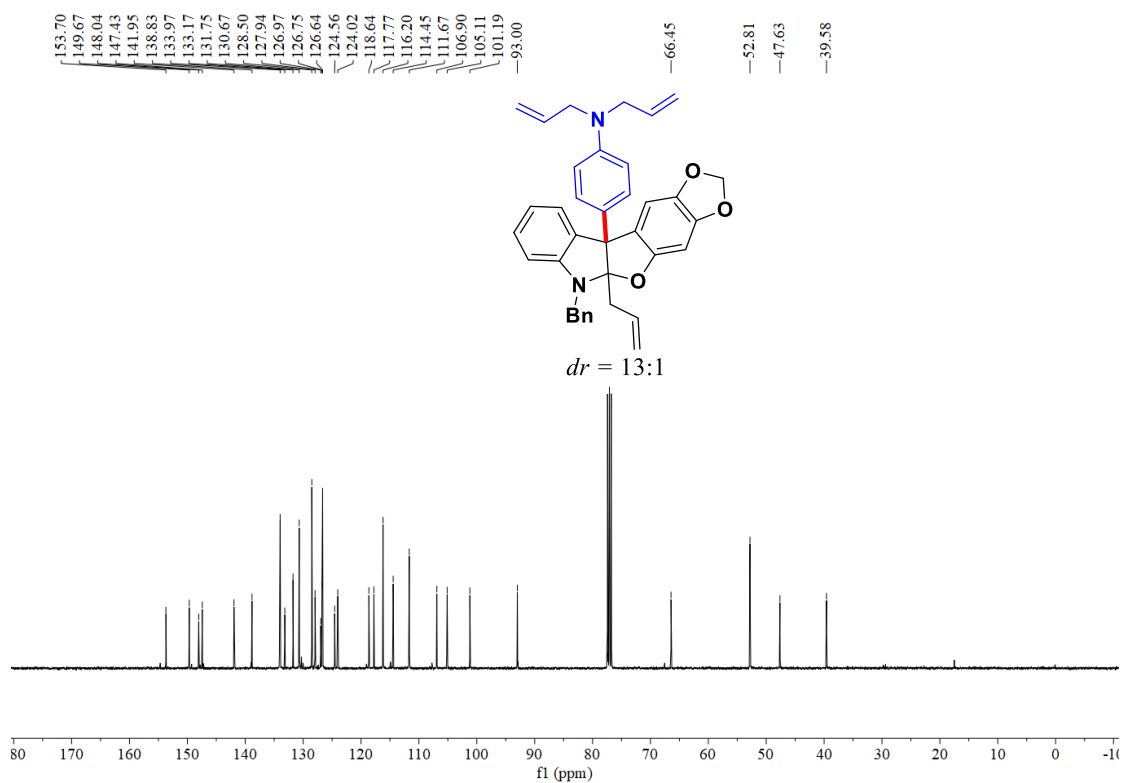
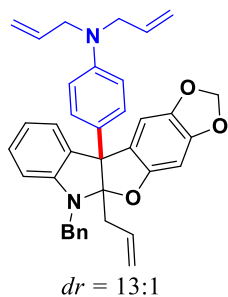
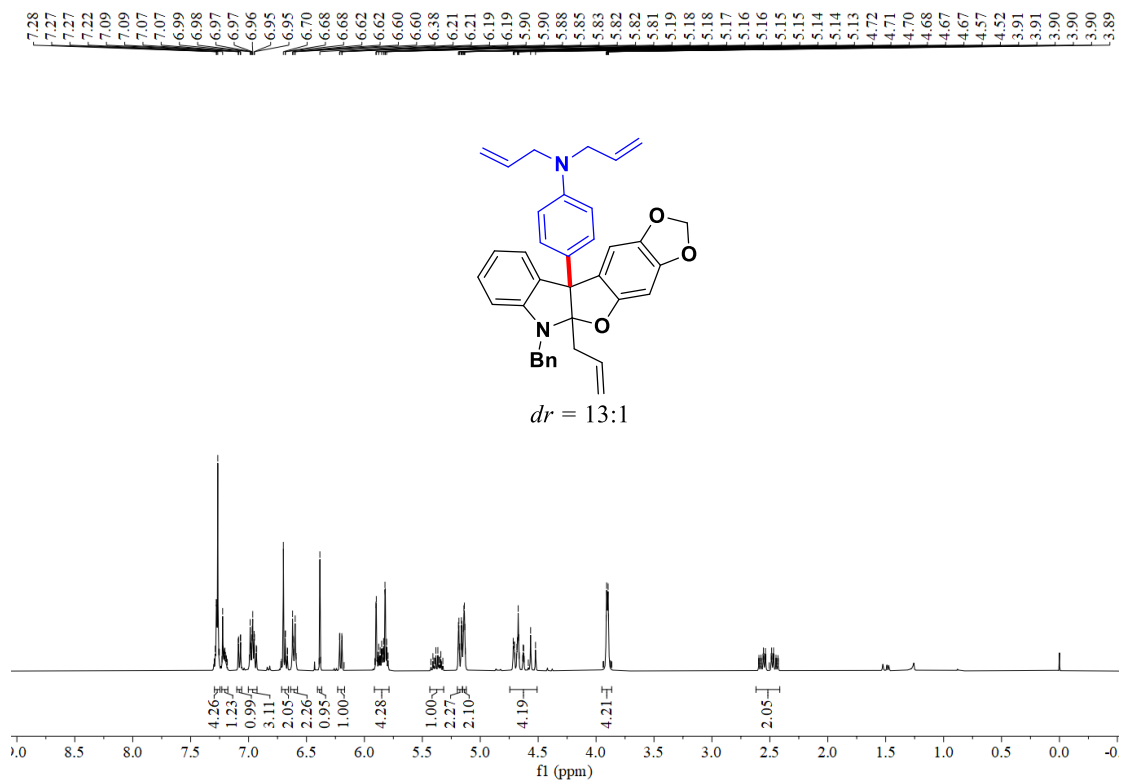
N,N-diallyl-4-((10bR)-6-benzyl-5a,6-dihydro-10bH-[1,3]dioxolo[4',5':5,6]benzofuro[2,3-b]indol-10b-yl-5a-d)aniline (11b)



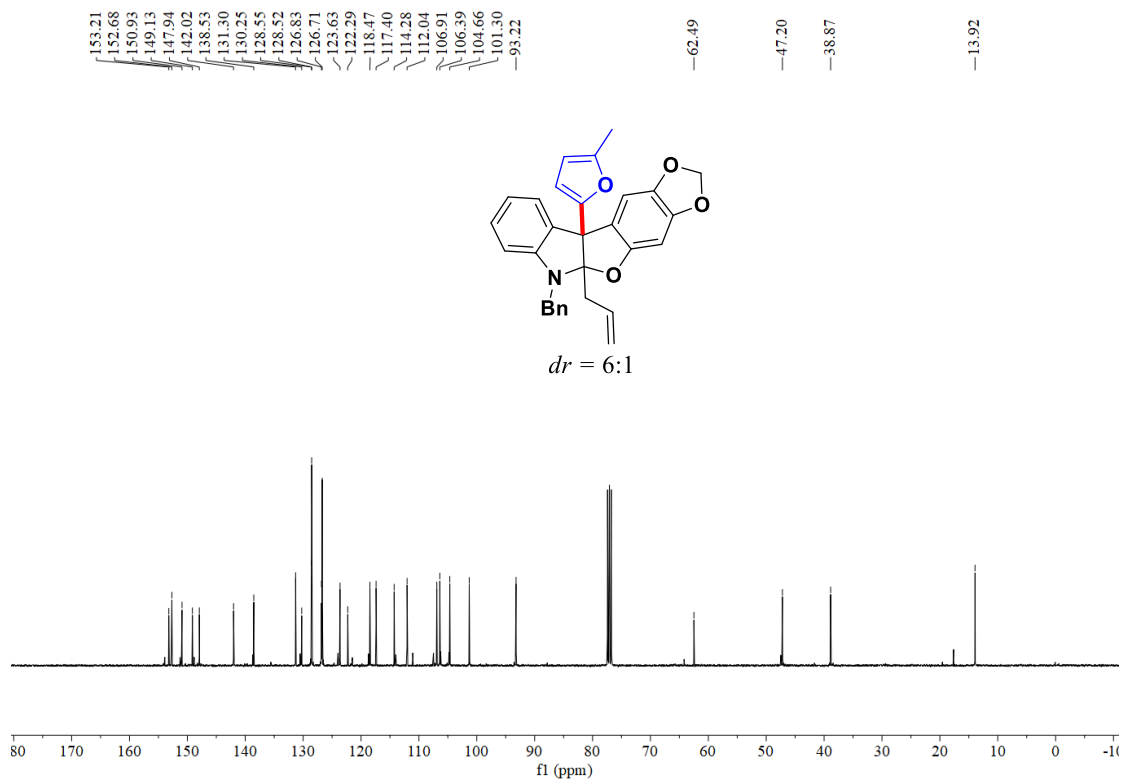
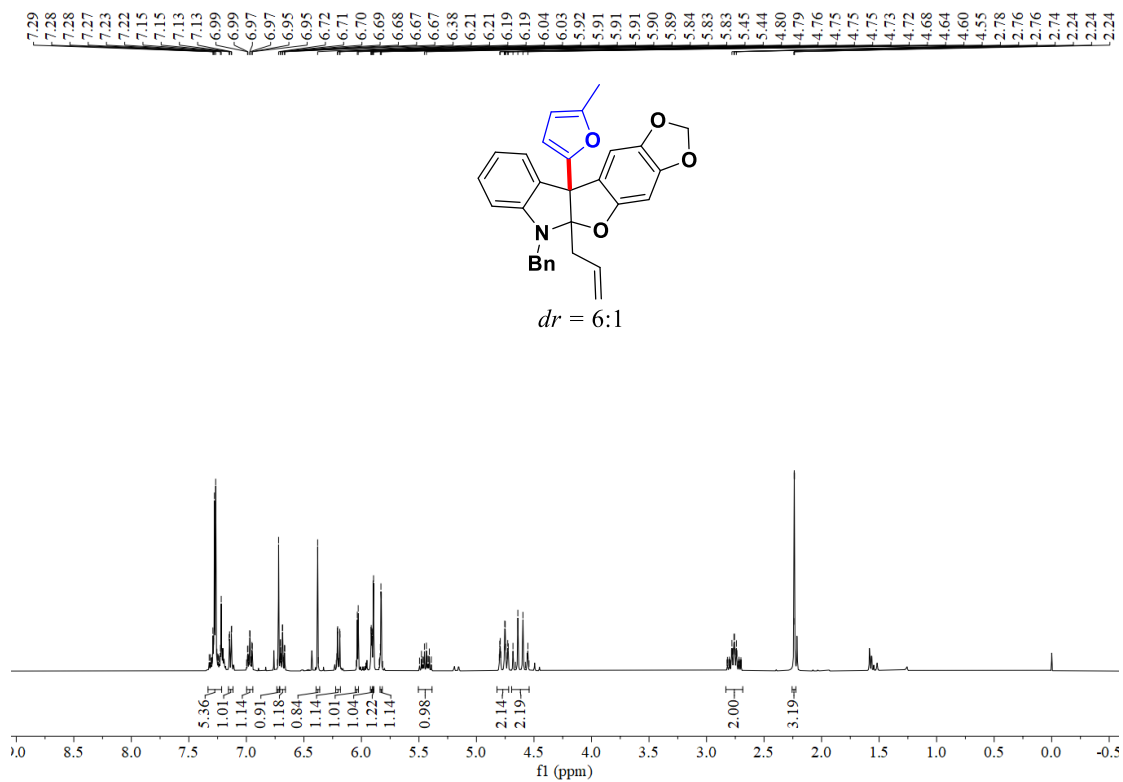
6-benzyl-10b-(1H-indol-3-yl)-5a,10b-dihydro-6H-[1,3]dioxolo[4',5':5,6]benzofuro[2,3-b]indole (11c)



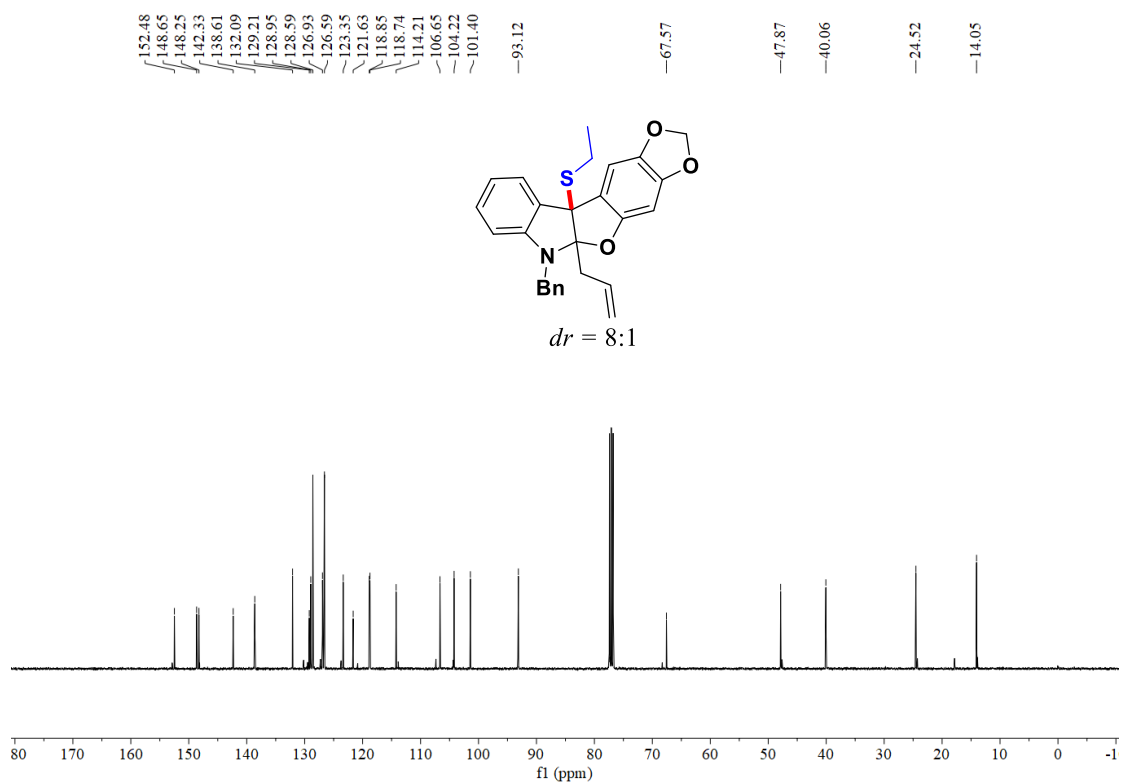
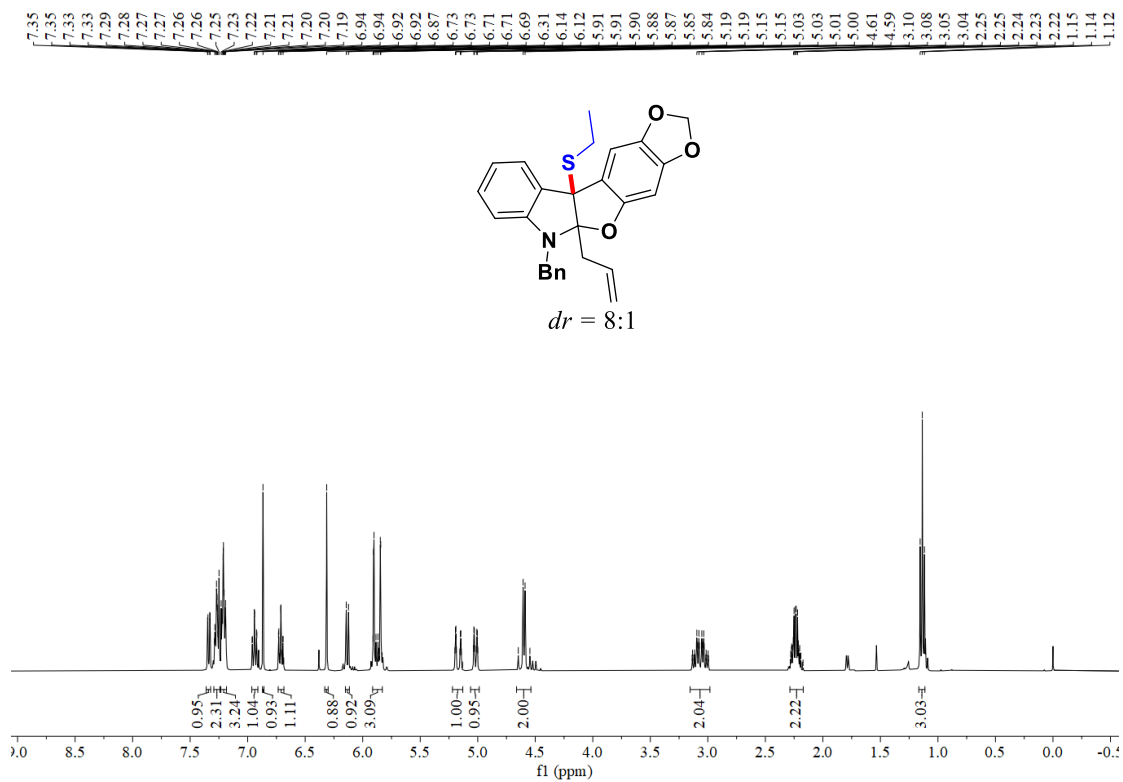
N,N-diallyl-4-(5a-allyl-6-benzyl-5a,6-dihydro-10bH-[1,3]dioxolo[4',5':5,6]benzofuro[2,3-b]indol-10b-yl)aniline (11d)



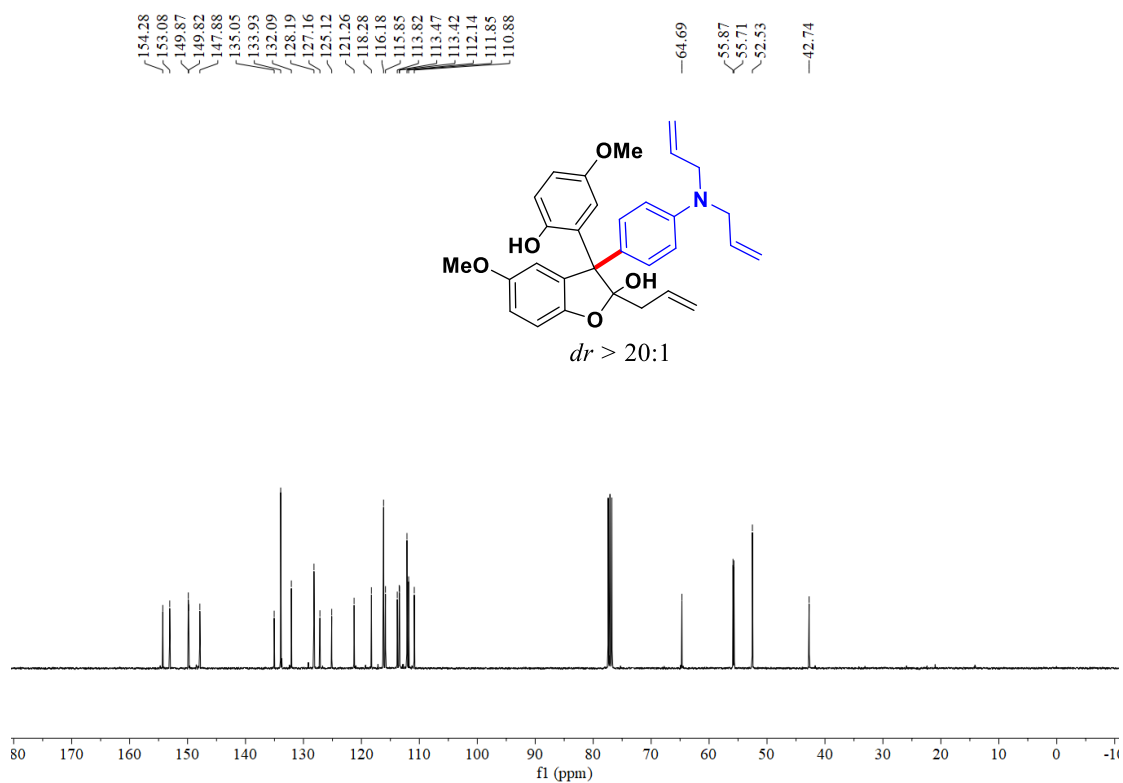
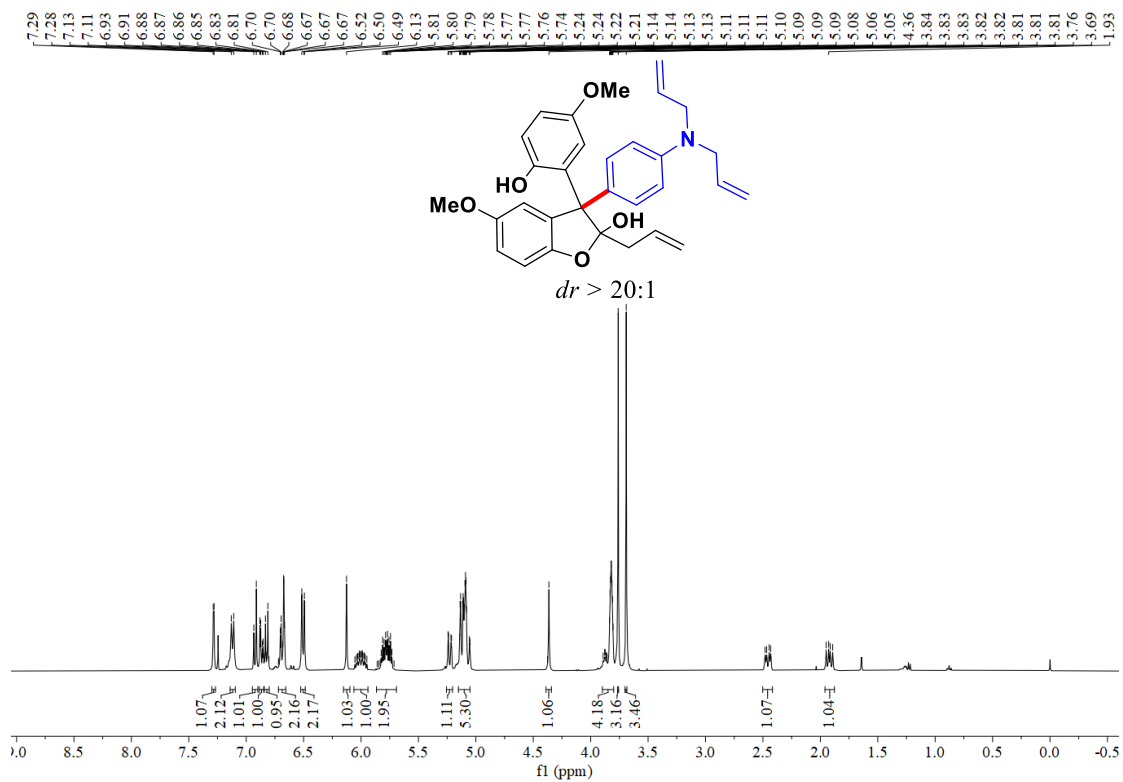
5a-allyl-6-benzyl-10b-(5-methylfuran-2-yl)-5a,10b-dihydro-6H-[1,3]dioxolo[4',5':5,6]benzofuro[2,3-b]indole (11e)



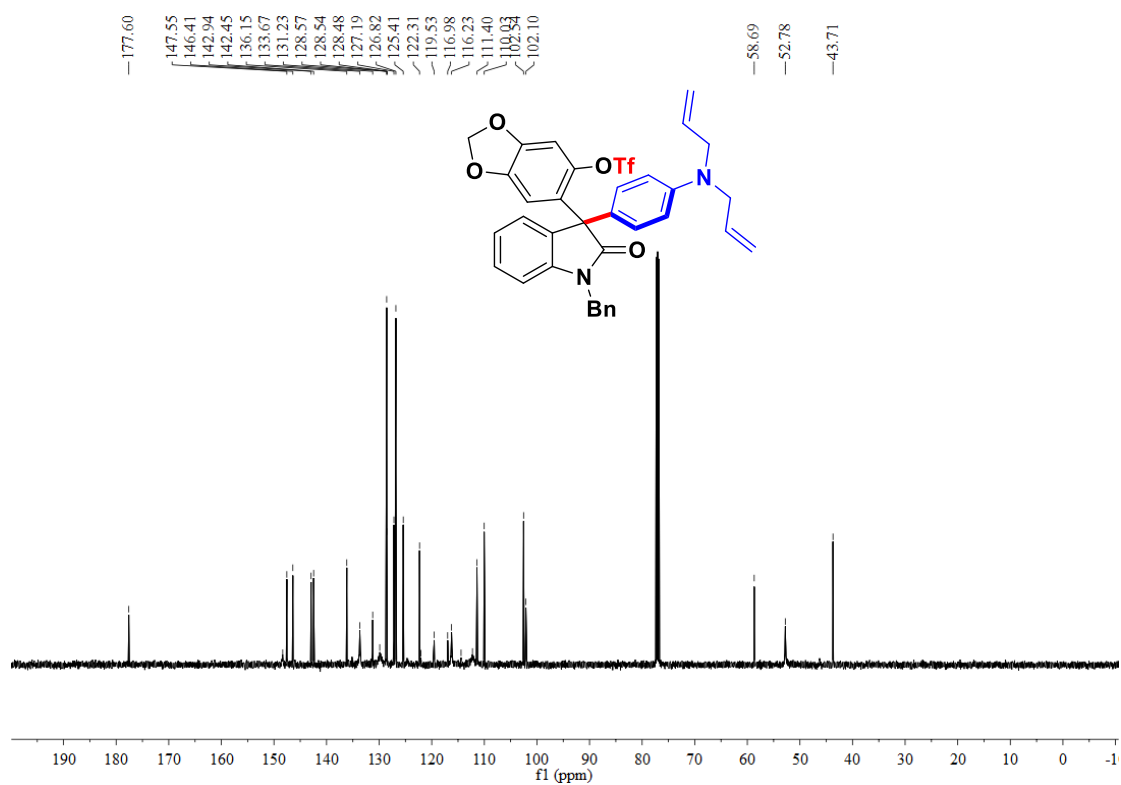
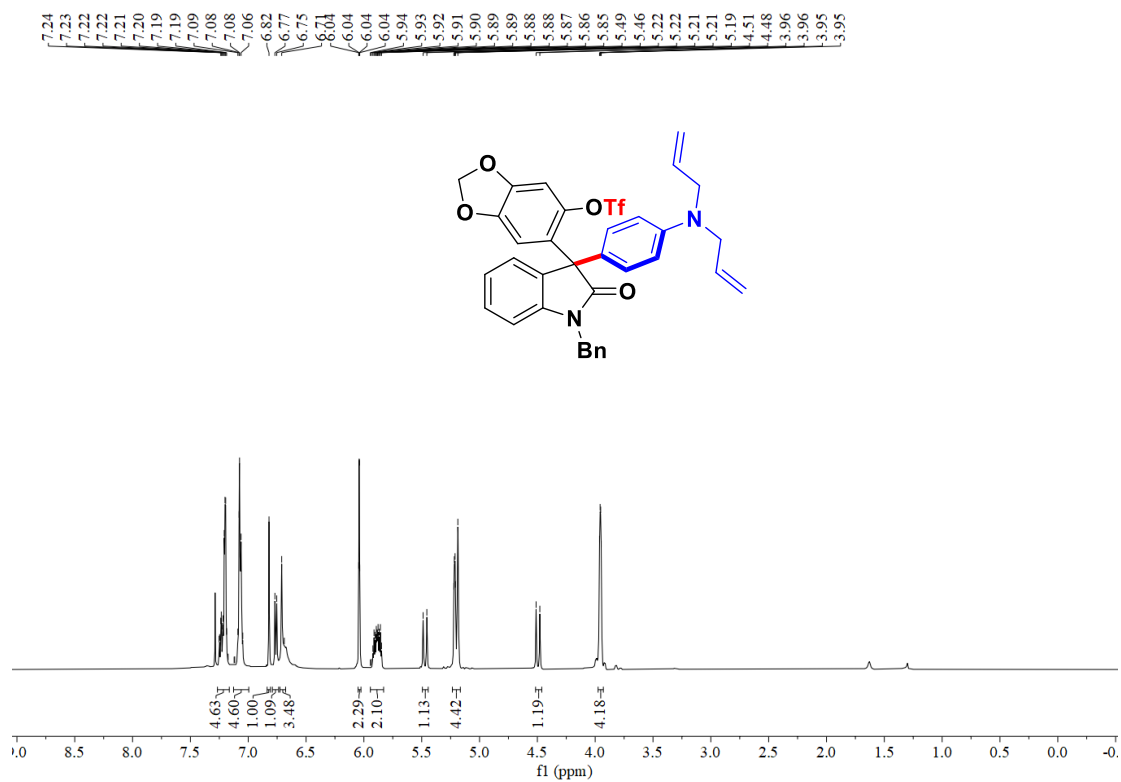
5a-allyl-6-benzyl-10b-(ethylthio)-5a,10b-dihydro-6H-[1,3]dioxolo[4',5':5,6]benzofuro[2,3-b]indole (11f)



2-allyl-3-(4-(diallylamino)phenyl)-3-(2-hydroxy-5-methoxyphenyl)-5-methoxy-2,3-dihydrobenzofuran-2-ol (12a)



6-(1-benzyl-3-(4-(diallylamino)phenyl)-2-oxoindolin-3-yl)benzo[d][1,3]dioxol-5-yl trifluoromethanesulfonate (13)



2,2'-((4-(diallylamino)phenyl)methylene)bis(4-methoxyphenol) (14)

