Supporting Information

Hydride transfer initiated ring expansion of pyrrolidines toward highly functionalized tetrahydro-1-benzoazepines

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1. General Information

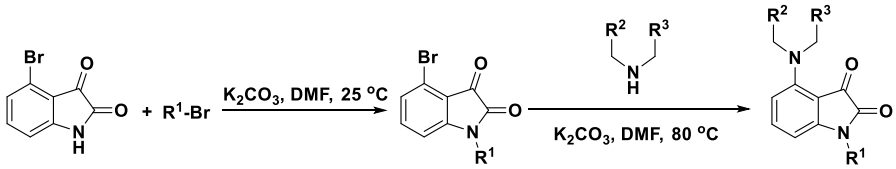
All commercially available reagents, unless otherwise indicated, were used without further purification. All the solvents used in the reaction were distilled prior to use. Thin layer chromatography (TLC) was used to monitor the reaction on Merck 60 F254 precoated silica gel plate (0.2 mm thickness). TLC spots were visualized by UV-light irradiation on Spectroline Model ENF-24061/F 254 nm. The products were isolated and purified by flash column chromatography (200-300 mesh silica gel) eluted with the gradient of petroleum ether and ethyl acetate. Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on a Bruker 500 MHz NMR spectrometer ($CDCl_3$ or DMSO-d_6 solvent).

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

2. Experimental Procedures

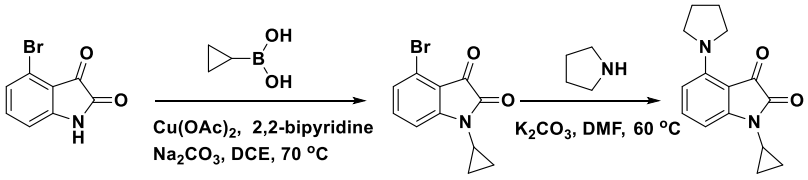
2.1 General Procedure for the Synthesis of 1

a. **General Procedure for the Synthesis of 1a-1e, 1g, 1h, 1o**



A round-bottomed flask was charged with 4-bromoindoline-2,3-dione (5 mmol), K_2CO_3 (10 mmol) and DMF (50.0 mL). Alkyl bromide (7.5 mmol) was added dropwise at room temperature. The mixture was stirred at room temperature under an air atmosphere. Upon completion of the reaction as indicated by TLC analysis, pyrrolidine (7.5 mmol) was added dropwise at room temperature, the mixture was stirred at 60 °C. Upon completion of the reaction as indicated by TLC analysis, the mixture was diluted with water (100 mL), and extracted with EtOAc (3 x 100 mL). The combined extracts were washed with brine (3 x 50 mL), dried, filtered, and concentrated in vacuum and the residue was directly purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether) to afford the desired products.

b. **General Procedure for the Synthesis of 1f**

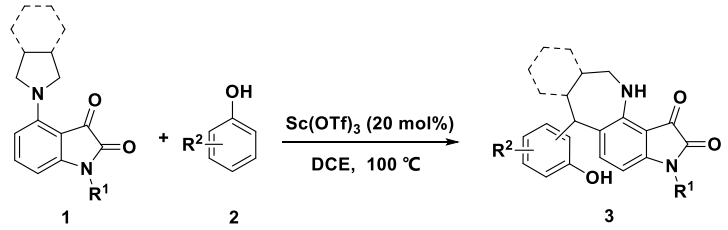


A round-bottomed flask was charged with 4-bromoindoline-2,3-dione (5 mmol), cyclopropylboronic acid (10 mmol), Na_2CO_3 (10 mmol) and dichloroethane (30.0 mL). A suspension of $Cu(OAc)_2$ (5 mmol) and 2, 2-bipyridine (5 mmol) in 20 ml hot dichloroethane was added at room temperature. The mixture

was warmed to 70 ℃ and stirred for 2-4 h. The resulting mixture was cooled to room temperature and an aqueous HCl solution was added (1N, 50 mL). The organic layer was separated and the aqueous layer was extracted 3 times with CH_2Cl_2. The combined organic layers were washed with brine, dried over sodium sulfate and concentrated under reduced pressure to afford the crude product 4-bromo-1-cyclopropylindoline-2, 3-dione.

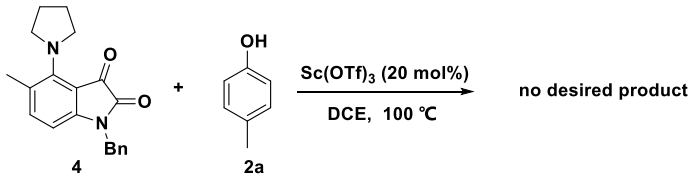
To the solution of 4-bromo-1-cyclopropylindoline-2, 3-dione (5 mmol) in 50 mL DMF, pyrrolidine (7.5 mmol) was added dropwise at room temperature, the mixture was stirred at 60 °C. Upon completion of the reaction as indicated by TLC analysis, the mixture was diluted with water (100 mL), and extracted with EtOAc (3 x 100 mL). The combined extracts were washed with brine (3 x 50 mL), dried, filtered, and concentrated in vacuum and the residue was directly purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether) to afford the desired product 1.1 g.

2.2 General Procedure for the Synthesis of 3

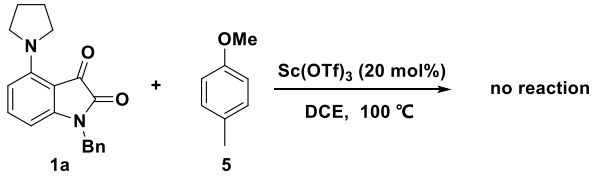


A sealed tube was charged with substituted isatin **1** (0.1 mmol), $Sc(OTf)_3$ (0.02 mmol) and distilled dichloroethane (2.0 mL). Substituted phenol **2** (0.3 mmol) was added dropwise at room temperature. The mixture was then stirred at 100 °C under air atmosphere. Upon completion of the reaction as indicated by TLC analysis, the mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether) to afford the desired products **3**.

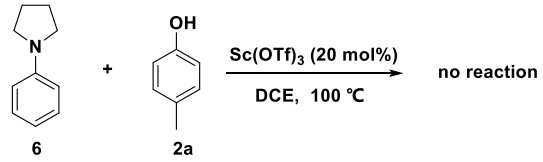
2.3 Control Experiments



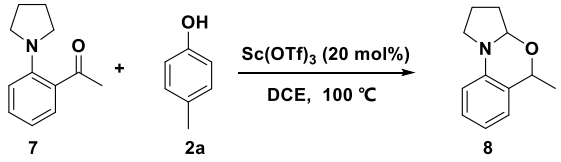
A sealed tube was charged with substituted isatin **4** (0.1 mmol), $Sc(OTf)_3$ (0.02 mmol) and distilled dichloroethane (2.0 mL). Substituted phenol **2a** (0.3 mmol) was added dropwise at room temperature. The mixture was then stirred at 100 °C under air atmosphere. No desired product was obtained.



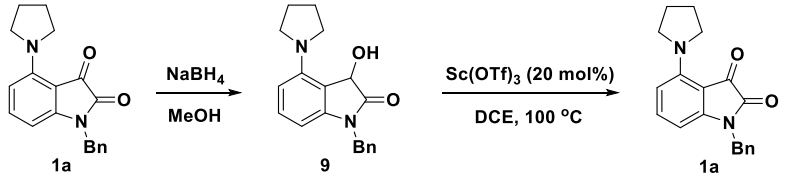
A sealed tube was charged with substituted isatin **1a** (0.1 mmol), $Sc(OTf)_3$ (0.02 mmol) and distilled dichloroethane (2.0 mL), 1-methoxy-4-methylbenzene **5** (0.3 mmol) was added dropwise at room temperature. The mixture was then stirred at 100 °C under air atmosphere. No reaction proceeded.



A sealed tube was charged with 1-phenylpyrrolidine **6** (0.1 mmol), $Sc(OTf)_3$ (0.02 mmol) and distilled dichloroethane (2.0 mL). Substituted phenol **2a** (0.3 mmol) was added dropwise at room temperature. The mixture was then stirred at 100 °C under air atmosphere. No reaction proceeded.



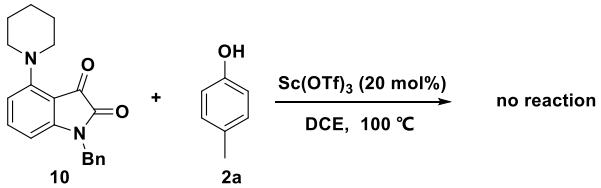
A sealed tube was charged with 1-(2-(pyrrolidin-1-yl)phenyl)ethan-1-one **7** (0.1 mmol), $Sc(OTf)_3$ (0.02 mmol) and distilled dichloroethane (2.0 mL). Substituted phenol **2a** (0.3 mmol) was added dropwise at room temperature. The mixture was then stirred at 100 °C under air atmosphere. Upon completion of the reaction as indicated by TLC analysis, the mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether) to afford product **8** in 38% yield.



A round-bottomed flask was charged with 1-benzyl-4-(pyrrolidin-1-yl)indoline-2,3-dione **1a** (1 mmol) and methanol (10.0 mL). The solution was then cooled down to 0 °C and $NaBH_4$ (1.2 mmol) was added in portions. The mixture was then allowed to stir at room temperature. Upon completion of the reaction as indicated by TLC analysis, the mixture was quench with ice water and extracted 3 times with ethyl acetate. The combined organic layers were washed with brine, dried over sodium sulfate and concentrated under reduced pressure to afford product **9**.[1]

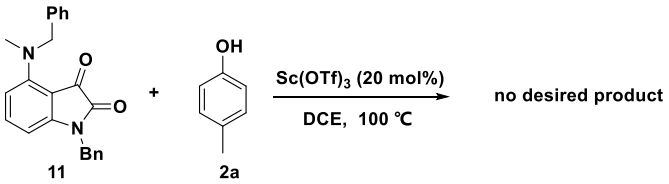
A sealed tube was charged with 1-benzyl-3-hydroxy-4-(pyrrolidin-1-yl)indolin-2-one **9** (0.1 mmol), $Sc(OTf)_3$ (0.02 mmol) and distilled dichloroethane (2.0 mL). The mixture was then stirred at 100 °C under air atmosphere. After 10 min. **9** was converted to **1a**.

2.4 Inert Substrates

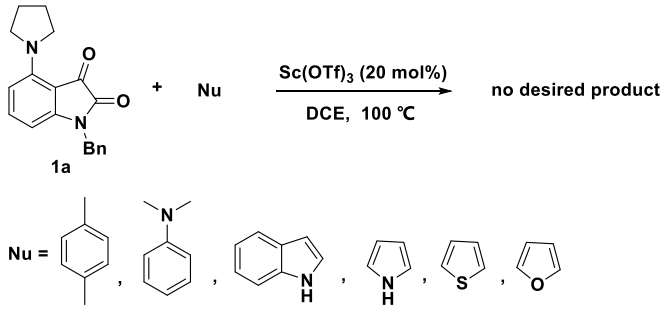


A sealed tube was charged with substituted isatin **10** (0.1 mmol), $Sc(OTf)_3$ (0.02 mmol) and distilled dichloroethane (2.0 mL). Substituted phenol **2a** (0.3 mmol) was added dropwise at room temperature. The mixture was then stirred at 100 °C under air atmosphere. No reaction proceeded.

[1] M. Silvi, I. Chatterjee, Y. Liu and P Melchiorreet, *Angew. Chem., Int. Ed.*, 2014, **52**, 10780-10783.



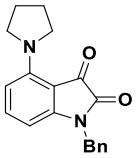
A sealed tube was charged with substituted isatin **11** (0.1 mmol), $Sc(OTf)_3$ (0.02 mmol) and distilled dichloroethane (2.0 mL). Substituted phenol **2a** (0.3 mmol) was added dropwise at room temperature. The mixture was then stirred at 100 °C under air atmosphere. No desired product was obtained.



A sealed tube was charged with substituted isatin **1a** (0.1 mmol), $Sc(OTf)_3$ (0.02 mmol) and distilled dichloroethane (2.0 mL), nucleophiles (0.3 mmol) was added at room temperature. The mixture was then stirred at 100 °C under air atmosphere. No desired products were obtained.

3. Characterization Data of Products

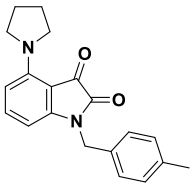
1-benzyl-4-(pyrrolidin-1-yl)indoline-2,3-dione (1a)



Flash column chromatography on silica gel (ethyl acetate: petroleum ether, 1:15) gave the product (1.4 g, 90% yield) as a red solid, mp: 73-75 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 25.2 Hz, 5H), 7.12 (t, *J* = 8.1 Hz, 1H), 6.33 (d, *J* = 8.9 Hz, 1H), 5.97 (d, *J* = 7.3 Hz, 1H), 4.89 (s, 2H), 3.60 (s, 4H), 2.00 (s, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 177.98, 160.16, 150.38, 148.08, 137.34, 135.60, 128.77, 127.69, 127.27, 111.40, 102.65, 97.86, 51.62, 43.74, 25.62. **HRMS (ESI)**: calcd. for $C_{19}H_{19}N_2O_2$ $[M+H]^+$: 307.1441, found: 307.1443.

1-(4-methylbenzyl)-4-(pyrrolidin-1-yl)indoline-2,3-dione (1b)

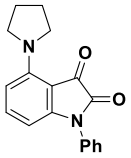


Flash column chromatography on silica gel (ethyl acetate: petroleum ether, 1:15) gave the product (1.5 g, 92% yield) as a red solid, mp: 118-119 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, *J* = 7.6 Hz, 2H), 7.15 – 7.07 (m, 3H), 6.32 (d, *J* = 8.9 Hz, 1H), 5.98 (d, *J* = 7.3 Hz, 1H), 4.85 (s, 2H), 3.59 (s, 4H), 2.31 (s, 3H), 1.99 (s, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 178.07, 160.11, 150.43, 148.05, 137.40, 137.33, 132.57, 129.42, 127.29, 111.32, 102.65,

97.89, 51.59, 43.50, 25.61, 21.06. **HRMS (ESI)**: calcd. for $C_{20}H_{21}N_2O_2$ $[M+H]^+$: 321.1598, found: 321.1597.

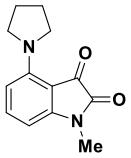
1-phenyl-4-(pyrrolidin-1-yl)indoline-2,3-dione (1c)



Flash column chromatography on silica gel (ethyl acetate: petroleum ether, 1:15) gave the product (1.3 g, 86% yield) as a red solid, mp: 105-107 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 9.1 Hz, 3H), 7.16 (t, *J* = 8.1 Hz, 1H), 6.41 (d, *J* = 8.9 Hz, 1H), 6.00 (d, *J* = 7.3 Hz, 1H), 3.64 (s, 4H), 2.03 (s, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 177.45, 159.30, 151.28, 148.32, 137.33, 133.48, 129.56, 128.29, 126.61, 111.50, 102.82, 98.32, 51.71, 25.65. **HRMS (ESI)**: calcd. for $C_{18}H_{17}N_2O_2$ $[M+H]^+$: 293.1285, found: 293.1287.

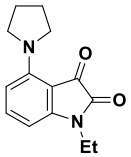
1-methyl-4-(pyrrolidin-1-yl)indoline-2,3-dione (1d)



Flash column chromatography on silica gel (ethyl acetate: petroleum ether, 1:15) gave the product (1.0 g, 90% yield) as a red solid, mp: 103-104 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (t, *J* = 8.0 Hz, 1H), 6.38 (d, *J* = 8.9 Hz, 1H), 6.06 (d, *J* = 7.2 Hz, 1H), 3.60 (s, 4H), 3.20 (s, 3H), 2.00 (s, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 178.27, 160.07, 151.42, 147.91, 137.36, 111.46, 102.38, 96.72, 51.59, 26.12, 25.62. **HRMS (ESI)**: calcd. for $C_{13}H_{15}N_2O_2$ $[M+H]^+$: 231.1128, found: 231.1130.

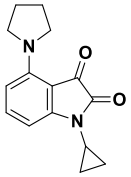
1-ethyl-4-(pyrrolidin-1-yl)indoline-2,3-dione (1e)



Flash column chromatography on silica gel (ethyl acetate: petroleum ether, 1:15) gave the product (1.1 g, 88 % yield) as a red solid, mp: 100-101 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (t, *J* = 8.1 Hz, 1H), 6.37 (d, *J* = 8.9 Hz, 1H), 6.08 (d, *J* = 7.3 Hz, 1H), 3.74 (d, *J* = 7.2 Hz, 2H), 3.59 (s, 3H), 2.00 (s, 4H), 1.28 (t, *J* = 7.2 Hz, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 178.56, 159.71, 150.44, 148.16, 137.37, 111.26, 102.64, 96.88, 51.62, 34.74, 25.68, 13.06. **HRMS (ESI)**: calcd. for $C_{14}H_{17}N_2O_2$ $[M+H]^+$: 245.1285, found: 245.1288.

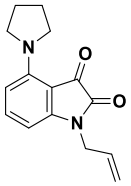
1-cyclopropyl-4-(pyrrolidin-1-yl)indoline-2,3-dione (1f)



Flash column chromatography on silica gel (ethyl acetate: petroleum ether, 1:15) gave the product (1.1 g, 86% yield) as a red solid, mp: 124-125 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.23 (m, 1H), 6.38 (t, *J* = 7.7 Hz, 2H), 3.58 (s, 4H), 2.63 (d, *J* = 3.4 Hz, 1H), 2.00 (s, 4H), 1.05 (q, *J* = 6.1 Hz, 2H), 0.96 (s, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 178.29, 160.42, 151.74, 147.78, 137.43, 110.98, 102.54, 98.07, 51.56, 25.62, 22.04, 6.14. **HRMS (ESI)**: calcd. for $C_{15}H_{17}N_2O_2$ $[M+H]^+$: 257.1285, found: 257.1286.

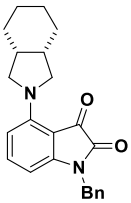
1-allyl-4-(pyrrolidin-1-yl)indoline-2,3-dione (1g)



Flash column chromatography on silica gel (ethyl acetate: petroleum ether, 1:15) gave the product (1.2 g, 93 % yield) as a red solid, mp: 97-99 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (t, *J* = 8.1 Hz, 1H), 6.37 (d, *J* = 8.9 Hz, 1H), 6.07 (d, *J* = 7.3 Hz, 1H), 5.84 (ddt, *J* = 16.0, 10.4, 5.3 Hz, 1H), 5.25 (dd, *J* = 21.6, 13.8 Hz, 2H), 4.33 (d, *J* = 5.1 Hz, 2H), 3.60 (s, 4H), 2.01 (d, *J* = 5.8 Hz, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 178.04, 159.74, 150.49, 148.06, 137.34, 131.32, 117.74, 111.31, 102.59, 97.60, 51.60, 42.28, 25.62. **HRMS (ESI)**: calcd. for $C_{15}H_{17}N_2O_2$ $[M+H]^+$: 257.1285, found: 257.1283.

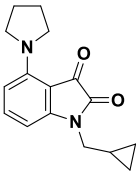
1-benzyl-4-(octahydro-2*H*-isoindol-2-yl)indoline-2,3-dione (1h)



Flash column chromatography on silica gel (ethyl acetate: petroleum ether, 1:15) gave the product (1.5 g, 90% yield) as a red solid, mp: 117-118 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 25.9 Hz, 5H), 7.10 (t, *J* = 8.0 Hz, 1H), 6.31 (d, *J* = 8.9 Hz, 1H), 5.96 (d, *J* = 7.2 Hz, 1H), 4.89 (s, 2H), 3.55 (d, *J* = 58.6 Hz, 4H), 2.33 (s, 2H), 1.62 (dd, *J* = 37.6, 10.0 Hz, 6H), 1.51 – 1.36 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 177.92, 160.20, 150.38, 148.73, 137.24, 135.65, 128.77, 127.68, 127.30, 111.22, 102.53, 97.66, 43.74, 36.97, 25.63, 22.65. **HRMS (ESI)**: calcd. for $C_{22}H_{23}N_2O_2$ $[M+H]^+$:347.1754, found:347.1756.

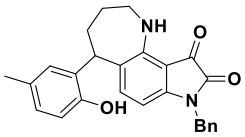
1-(cyclopropylmethyl)-4-(pyrrolidin-1-yl)indoline-2,3-dione (1o)



Flash column chromatography on silica gel (ethyl acetate: petroleum ether, 1:15) gave the product (1.1 g, 85% yield) as a red solid, mp: 81-84 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (t, *J* = 8.1 Hz, 1H), 6.37 (d, *J* = 8.9 Hz, 1H), 6.15 (d, *J* = 7.3 Hz, 1H), 3.60 (s, 4H), 3.57 (d, *J* = 7.0 Hz, 2H), 2.00 (s, 4H), 1.23 – 1.11 (m, 1H), 0.53 (q, *J* = 5.2 Hz, 2H), 0.40 (t, *J* = 5.1 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 178.56, 160.08, 151.08, 148.16, 137.36, 111.20, 102.64, 97.21, 51.64, 44.33, 25.68, 9.87, 3.99. **HRMS (ESI)**: calcd. for $C_{16}H_{19}N_2O_2$ $[M+H]^+$: 271.1441, found: 271.1443.

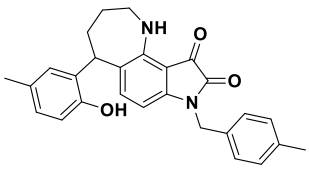
8-benzyl-5-(2-hydroxy-5-methylphenyl)-1,2,3,4,5,8-hexahydroazepino[2,3-*e*]indole-9,10-dion e (3a)



Flash column chromatography on silica gel (ethyl acetate: petroleum ether, 1:8) gave the product (24.3 mg, 59% yield) as a red solid, mp: 105-107 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.40 – 7.16 (m, 5H), 6.97 – 6.85 (m, 2H), 6.72 (d, *J* = 8.0 Hz, 1H), 6.54 (d, *J* = 7.7 Hz, 1H), 5.76 (d, *J* = 7.7 Hz, 1H), 5.28 (s, 1H), 4.77 (q, *J* = 15.6 Hz, 2H), 4.58 (dd, *J* = 10.5, 2.3 Hz, 1H), 3.74 (ddd, *J* = 12.8, 7.8, 3.5 Hz, 1H), 3.46 – 3.31 (m, 1H), 2.45 (ddd, *J* = 16.4, 12.2, 5.9 Hz, 1H), 2.25 (s, 3H), 2.13 – 2.04 (m, 1H), 2.04 – 1.90 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 181.43, 160.84, 152.20, 150.95, 147.20, 139.31, 135.57, 130.15, 130.07, 129.48, 128.80, 128.29, 127.83, 127.53, 127.39, 115.91, 103.65, 98.72, 44.11, 43.88, 40.30, 31.02, 27.17, 20.71. **HRMS (ESI)**: calcd. for $C_{26}H_{25}N_2O_3$ $[M+H]^+$: 413.1860, found: 413.1907.

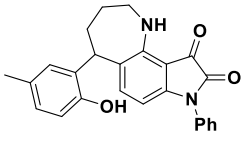
5-(2-hydroxy-5-methylphenyl)-8-(4-methylbenzyl)-1,2,3,4,5,8-hexahydroazepino[2,3-*e*]indole -9,10-dione (3b)



Flash column chromatography on silica gel (ethyl acetate: petroleum ether, 1:8) gave the product (19.2 mg, 45% yield) as a red solid, mp: 177-179 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.15 (d, *J* = 7.5 Hz, 2H), 7.09 (d, *J* = 7.5 Hz, 2H), 6.93 (d, *J* = 7.9 Hz, 1H), 6.89 (s, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.54 (d, *J* = 7.6 Hz, 1H), 5.78 (d, *J* = 7.6 Hz, 1H), 5.05 (s, 1H), 4.81 – 4.66 (m, 2H), 4.57 (d, *J* = 10.2 Hz, 1H), 3.81 – 3.66 (m, 1H), 3.47 – 3.33 (m, 1H), 2.44 (dd, *J* = 19.5, 8.7 Hz, 1H), 2.29 (s, 3H), 2.25 (s, 3H), 2.13 – 2.04 (m, 1H), 1.97 (s, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 181.59, 160.80, 152.16, 150.90, 147.30, 139.30, 137.60, 132.54, 130.19, 130.13, 129.48, 128.30, 127.57, 127.24, 115.86, 103.65, 98.79, 44.12, 43.64, 40.31, 30.98, 27.15, 21.12, 20.74. **HRMS (ESI)**: calcd. for $C_{27}H_{27}N_2O_3$ $[M+H]^+$: 427.2016, found: 427.2017.

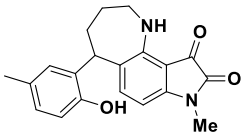
5-(2-hydroxy-5-methylphenyl)-8-phenyl-1,2,3,4,5,8-hexahydroazepino[2,3-*e*]indole-9,10-dion e (3c)



Flash column chromatography on silica gel (ethyl acetate: petroleum ether, 1:8) gave the product (20.7 mg, 52% yield) as a red solid, mp: 136-137 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.36 (d, *J* = 7.6 Hz, 3H), 6.94 (d, *J* = 8.2 Hz, 2H), 6.70 (d, *J* = 7.8 Hz, 1H), 6.63 (d, *J* = 7.7 Hz, 1H), 5.88 (d, *J* = 7.7 Hz, 1H), 4.90 (s, 1H), 4.62 (d, *J* = 10.0 Hz, 1H), 3.84 – 3.69 (m, 1H), 3.46 (dd, *J* = 13.6, 5.0 Hz, 1H), 2.61 – 2.44 (m, 1H), 2.26 (s, 3H), 2.17 – 1.94 (m, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 180.97, 159.92, 152.46, 150.84, 147.96, 139.46, 133.43, 130.24, 129.53, 128.32, 128.17, 127.34, 126.06, 115.78, 103.75, 99.12, 44.21, 40.55, 30.84, 27.07, 20.74. **HRMS (ESI)**: calcd. for $C_{25}H_{23}N_2O_3$ $[M+H]^+$: 399.1703, found: 399.1679.

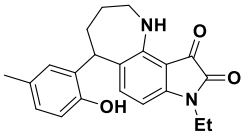
5-(2-hydroxy-5-methylphenyl)-8-methyl-1,2,3,4,5,8-hexahydroazepino[2,3-*e*]indole-9,10-dione (3d)



Flash column chromatography on silica gel (ethyl acetate: petroleum ether, 1:8) gave the product (23.2 mg, 69% yield) as a red solid, mp: 197-200 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (s, 1H), 7.03 – 6.88 (m, 2H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.65 (d, *J* = 7.5 Hz, 1H), 5.84 (d, *J* = 7.5 Hz, 1H), 5.61 (s, 1H), 5.30 (s, 2H), 4.62 (d, *J* = 10.2 Hz, 1H), 3.85 – 3.64 (m, 1H), 3.40 (dd, *J* = 13.3, 4.9 Hz, 1H), 3.09 (s, 3H), 2.58 – 2.41 (m, 1H), 2.27 (s, 3H), 2.17 – 1.90 (m, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 181.83, 160.79, 152.01, 150.84, 148.26, 139.34, 130.26, 130.23, 129.61, 128.32, 127.23, 115.82, 103.41, 97.64, 77.29, 77.03, 76.78, 44.20, 40.65, 30.90, 27.06, 26.04, 20.76. **HRMS (ESI)**: calcd. for $C_{20}H_{21}N_2O_3$ $[M+H]^+$: 337.1547, found: 337.1530.

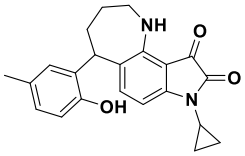
8-ethyl-5-(2-hydroxy-5-methylphenyl)-1,2,3,4,5,8-hexahydroazepino[2,3-*e*]indole-9,10-dione (3e)



Flash column chromatography on silica gel (ethyl acetate: petroleum ether, 1:2) gave the product (19.6 mg, 56% yield) as a red solid, mp: 234-235 °C.

^{1}H NMR (500 MHz, DMSO) δ 9.21 (s, 1H), 7.56 (s, 1H), 6.92 (d, *J* = 9.0 Hz, 2H), 6.78 (d, *J* = 7.9 Hz, 1H), 6.62 (d, *J* = 7.7 Hz, 1H), 6.17 (d, *J* = 7.7 Hz, 1H), 4.64 (d, *J* = 9.2 Hz, 1H), 3.68 (dd, *J* = 9.7, 3.4 Hz, 1H), 3.63 (dd, *J* = 14.4, 7.2 Hz, 2H), 3.51 (dd, *J* = 13.8, 4.1 Hz, 1H), 2.53 – 2.43 (m, 1H), 2.23 (s, 3H), 1.94 (ddd, *J* = 15.0, 8.9, 5.4 Hz, 2H), 1.86 (dd, *J* = 12.7, 8.5 Hz, 1H), 1.17 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (125 MHz, DMSO) δ 181.94, 160.09, 152.73, 152.06, 147.08, 139.51, 130.27, 130.19, 128.17, 127.75, 115.53, 103.14, 98.16, 55.39, 43.85, 34.61, 30.78, 27.09, 20.88, 13.48. **HRMS (ESI)**: calcd. for $C_{21}H_{23}N_2O_3$ $[M+H]^+$: 351.1703, found: 351.1704.

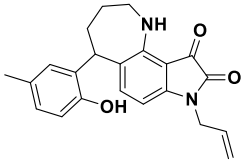
8-cyclopropyl-5-(2-hydroxy-5-methylphenyl)-1,2,3,4,5,8-hexahydroazepino[2,3-*e*]indole-9,10-dione (3f)



Flash column chromatography on silica gel (ethyl acetate: petroleum ether, 1:8) gave the product (17.8 mg, 49% yield) as a red solid, mp: 91-94 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.01 – 6.89 (m, 2H), 6.71 (t, *J* = 8.6 Hz, 2H), 6.16 (d, *J* = 7.7 Hz, 1H), 4.85 (s, 1H), 4.59 (d, *J* = 9.8 Hz, 1H), 3.76 – 3.65 (m, 1H), 3.41 (dd, *J* = 13.6, 5.3 Hz, 1H), 2.58 (s, 1H), 2.49 (dt, *J* = 15.6, 5.9 Hz, 1H), 2.28 (s, 3H), 2.10 (dd, *J* = 13.0, 7.3 Hz, 1H), 1.98 (d, *J* = 5.2 Hz, 2H), 0.98 (d, *J* = 6.0 Hz, 2H), 0.88 (s, 2H), 0.85 (d, *J* = 6.8 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 181.85, 161.23, 151.84, 150.85, 148.62, 139.52, 130.29, 130.22, 129.65, 128.31, 126.78, 115.84, 103.59, 99.04, 44.26, 40.72, 30.97, 29.72, 27.10, 21.93, 20.76, 5.94, 0.02. **HRMS (ESI)**: calcd. for $C_{22}H_{23}N_2O_3$ $[M+H]^+$: 363.1703, found: 363.1706.

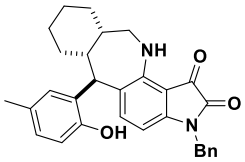
8-allyl-5-(2-hydroxy-5-methylphenyl)-1,2,3,4,5,8-hexahydroazepino[2,3-*e*]indole-9,10-dione (3g)



Flash column chromatography on silica gel (ethyl acetate: petroleum ether, 1:8) gave the product (20.3 mg, 56% yield) as a red solid, mp: 90-93 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.00 – 6.90 (m, 2H), 6.73 (d, *J* = 8.0 Hz, 1H), 6.64 (d, *J* = 7.7 Hz, 1H), 5.88 (d, *J* = 7.7 Hz, 1H), 5.78 (ddd, *J* = 22.5, 10.6, 5.5 Hz, 1H), 5.21 (dd, *J* = 19.3, 13.9 Hz, 2H), 5.08 (s, 1H), 4.60 (dd, *J* = 10.4, 2.5 Hz, 1H), 4.23 (d, *J* = 5.3 Hz, 2H), 3.74 (ddd, *J* = 12.8, 8.0, 3.7 Hz, 1H), 3.42 (ddd, *J* = 13.7, 10.0, 5.8 Hz, 1H), 2.49 (ddd, *J* = 16.3, 12.1, 6.0 Hz, 1H), 2.27 (s, 3H), 2.16 – 2.07 (m, 1H), 2.03 – 1.90 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 181.55, 160.46, 152.19, 150.94, 147.36, 139.38, 131.35, 130.21, 130.12, 129.52, 128.31, 127.22, 118.05, 115.87, 103.59, 98.58, 44.18, 42.41, 40.45, 30.95, 27.11, 20.76. **HRMS (ESI)**: calcd. for $C_{22}H_{23}N_2O_3$ $[M+H]^+$: 363.1703, found: 363.1706.

3-benzyl-6-(2-hydroxy-5-methylphenyl)-3,6,6a,7,8,9,10,10a,11,12-decahydrobenzo[5,6]azepino[2,3-*e*]indole-1,2-dione (3h)

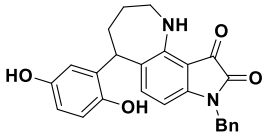


Flash column chromatography on silica gel (ethyl acetate: petroleum ether, 1:4) gave the product (20.3 mg, 63% yield) as a red solid, mp: 83-85 °C with 20:1 dr.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.1 Hz, 1H), 7.31 – 7.22 (m, 6H), 7.03 (s, 1H), 6.94 (d, *J* = 8.1 Hz, 1H), 6.70 (d, *J* = 8.1 Hz, 1H), 6.51 (d, *J* = 7.7 Hz, 1H), 5.72 (d, *J* = 7.7 Hz, 1H), 5.02 (s, 1H), 4.75 (q, *J* = 15.6 Hz, 2H), 4.18 (d, *J* = 10.4 Hz, 1H), 4.04 – 3.94 (m, 1H), 3.13 (dd, *J* = 13.7, 7.9 Hz, 1H), 2.38 (d, *J* = 5.6 Hz, 2H), 2.30 (s, 3H), 1.72 (d, *J* = 12.5 Hz, 1H), 1.58 (d, *J* = 4.2 Hz, 3H), 1.50 (d, *J* = 9.7 Hz, 1H), 1.13 (dd, *J* = 20.0, 12.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 181.39, 160.95,

151.66, 151.41, 147.07, 138.20, 135.62, 130.18, 129.96, 128.79, 128.34, 127.81, 127.54, 126.49, 125.70, 116.32, 103.51, 98.38, 46.45, 43.83, 41.15, 37.05, 32.26, 29.20, 25.53, 22.20, 20.83. **HRMS (ESI)**: calcd. for $C_{30}H_{31}N_2O_3$ $[M+H]^+$: 467.2329, found: 467.2334.

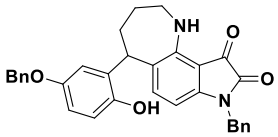
8-benzyl-5-(2,5-dihydroxyphenyl)-1,2,3,4,5,8-hexahydroazepino[2,3-*e*]indole-9,10-dione (3i)



Flash column chromatography on silica gel (ethyl acetate: petroleum ether, 1:2) gave the product (16.6 mg, 40% yield) as a red solid, mp: 133-134 °C.

^{1}H NMR (500 MHz, DMSO) δ 8.68 (s, 1H), 8.58 (s, 1H), 7.54 (s, 1H), 7.32 (d, *J* = 2.9 Hz, 4H), 7.26 (d, *J* = 3.6 Hz, 1H), 6.66 – 6.52 (m, 3H), 6.45 (d, *J* = 8.5 Hz, 1H), 6.41 (s, 1H), 6.03 (d, *J* = 7.6 Hz, 1H), 4.78 (s, 2H), 4.52 (d, *J* = 9.2 Hz, 1H), 3.57 (d, *J* = 8.0 Hz, 1H), 3.54 – 3.42 (m, 3H), 2.37 (d, *J* = 5.0 Hz, 1H), 1.86 (t, *J* = 13.8 Hz, 2H), 1.77 (s, 1H); **^{13}C NMR** (125 MHz, DMSO) δ 181.46, 160.56, 152.16, 150.15, 147.37, 147.22, 139.86, 136.80, 131.13, 129.12, 127.96, 127.93, 127.88, 116.54, 116.22, 114.03, 103.32, 98.82, 44.04, 43.27, 30.57, 26.86. **HRMS (ESI)**: calcd. for $C_{25}H_{23}N_2O_4$ $[M+H]^+$: 415.1652, found: 415.1662.

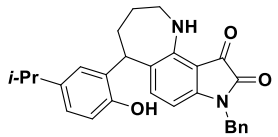
8-benzyl-5-(5-(benzyloxy)-2-hydroxyphenyl)-1,2,3,4,5,8-hexahydroazepino[2,3-*e*]indole-9,10-dione (3j)



Flash column chromatography on silica gel (ethyl acetate: petroleum ether, 1:8) gave the product (21.2 mg, 42% yield) as a red solid, mp: 193-194 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.38 – 7.11 (m, 10H), 6.67 (s, 2H), 6.64 (s, 1H), 6.49 (d, *J* = 7.4 Hz, 1H), 5.70 (d, *J* = 7.3 Hz, 1H), 4.89 (s, 2H), 4.80 (s, 1H), 4.72 (s, 2H), 4.49 (d, *J* = 9.8 Hz, 1H), 3.56 (s, 1H), 3.29 (d, *J* = 9.9 Hz, 1H), 2.34 (s, 1H), 1.98 (d, *J* = 8.6 Hz, 1H), 1.86 (s, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 180.44, 159.75, 151.83, 151.15, 146.33, 146.16, 138.49, 136.07, 134.50, 129.95, 127.81, 127.52, 126.88, 126.84, 126.48, 126.44, 125.91, 115.96, 115.53, 112.59, 102.66, 97.76, 69.66, 43.20, 42.84, 39.67, 29.70, 25.82. **HRMS (ESI)**: calcd. for $C_{32}H_{29}N_2O_4$ $[M+H]^+$: 505.2122, found: 505.2133.

8-benzyl-5-(2-hydroxy-5-isopropylphenyl)-1,2,3,4,5,8-hexahydroazepino[2,3-*e*]indole-9,10-di one (3k)

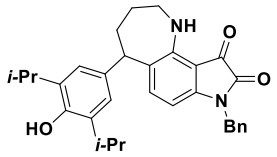


Flash column chromatography on silica gel (ethyl acetate: petroleum ether, 1:8) gave the product (20.3 mg, 46% yield) as a red solid, mp: 100-101 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.34 – 7.20 (m, 5H), 7.00 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.95 (d,

J = 2.1 Hz, 1H), 6.72 (d, *J* = 8.2 Hz, 1H), 6.54 (d, *J* = 7.7 Hz, 1H), 5.78 (d, *J* = 7.7 Hz, 1H), 4.83 (s, 1H), 4.79 (d, *J* = 5.8 Hz, 1H), 4.59 (dd, *J* = 10.6, 2.7 Hz, 1H), 3.77 (ddt, *J* = 12.8, 8.9, 3.6 Hz, 1H), 3.41 (dtd, *J* = 13.9, 5.9, 3.9 Hz, 1H), 2.82 (dt, *J* = 13.8, 6.9 Hz, 1H), 2.52 – 2.39 (m, 1H), 2.10 (dtd, *J* = 10.4, 7.4, 3.0 Hz, 1H), 1.19 (dd, *J* = 6.9, 2.7 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 181.53, 160.79, 152.11, 150.98, 147.28, 141.51, 139.14, 135.57, 129.31, 128.80, 127.82, 127.78, 127.49, 127.19, 125.44, 115.75, 103.66, 98.70, 44.12, 43.86, 40.56, 33.42, 31.02, 27.20, 24.34, 24.20, 1.04. **HRMS (ESI)**: calcd. for $C_{28}H_{29}N_2O_3$ $[M+H]^+$: 441.2173, found: 441.2207.

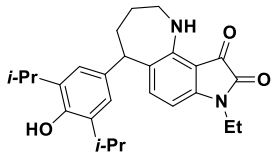
8-benzyl-5-(4-hydroxy-3,5-diisopropylphenyl)-1,2,3,4,5,8-hexahydroazepino[2,3-*e*]indole-9,10-dione (3l)



Flash column chromatography on silica gel (ethyl acetate: petroleum ether, 1:8) gave the product (30.4 mg, 63% yield) as a red solid, mp: 209-210 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.39 – 7.19 (m, 6H), 6.82 (s, 2H), 6.57 (d, *J* = 7.7 Hz, 1H), 5.79 (d, *J* = 7.7 Hz, 1H), 4.88 (d, *J* = 15.8 Hz, 1H), 4.81 – 4.69 (m, 2H), 4.24 (dd, *J* = 9.8, 2.6 Hz, 1H), 3.60 (ddd, *J* = 18.0, 10.1, 5.9 Hz, 1H), 3.35 (dq, *J* = 13.9, 5.4 Hz, 1H), 3.14 (tt, *J* = 13.7, 6.8 Hz, 2H), 2.37 (ddd, *J* = 15.6, 11.6, 5.8 Hz, 1H), 2.16 (dtd, *J* = 10.8, 7.9, 2.9 Hz, 1H), 2.01 – 1.88 (m, 2H), 1.27 – 1.17 (m, 12H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 181.53, 160.86, 152.17, 148.50, 147.19, 140.47, 135.66, 135.59, 133.80, 128.85, 128.79, 128.31, 127.78, 127.45, 127.37, 123.35, 103.52, 98.41, 46.05, 43.88, 43.83, 31.73, 27.35, 26.70, 22.78. **HRMS (ESI)**: calcd. for $C_{31}H_{35}N_2O_3$ $[M+H]^+$: 483.2642, found: 483.2625.

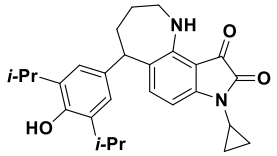
8-ethyl-5-(4-hydroxy-3,5-diisopropylphenyl)-1,2,3,4,5,8-hexahydroazepino[2,3-*e*]indole-9,10-dione (3m)



Flash column chromatography on silica gel (ethyl acetate: petroleum ether, 1:8) gave the product (23.1 mg, 55% yield) as a red solid, mp: 116-118 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (s, 1H), 6.87 (s, 2H), 6.68 (d, *J* = 7.7 Hz, 1H), 5.91 (d, *J* = 7.7 Hz, 1H), 4.76 (s, 1H), 4.28 (dd, *J* = 9.6, 2.5 Hz, 1H), 3.69 (tq, *J* = 14.2, 7.3 Hz, 2H), 3.58 (ddd, *J* = 11.4, 10.1, 5.7 Hz, 1H), 3.35 (dq, *J* = 13.9, 5.5 Hz, 1H), 3.17 (dq, *J* = 13.7, 6.8 Hz, 2H), 2.40 (tt, *J* = 9.9, 5.8 Hz, 1H), 2.19 (dtd, *J* = 10.6, 7.9, 2.9 Hz, 1H), 2.02 – 1.91 (m, 2H), 1.24 (dt, *J* = 8.6, 4.3 Hz, 16H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 182.08, 160.44, 152.22, 148.47, 147.21, 140.49, 135.72, 133.80, 128.10, 123.34, 103.35, 97.46, 46.06, 43.81, 34.77, 31.65, 27.35, 26.67, 22.82, 13.23. **HRMS (ESI)**: calcd. for $C_{26}H_{33}N_2O_3$ $[M+H]^+$: 421.2486, found: 421.2498.

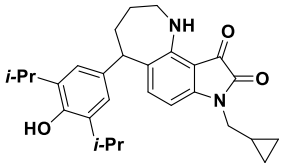
8-cyclopropyl-5-(4-hydroxy-3,5-diisopropylphenyl)-1,2,3,4,5,8-hexahydroazepino[2,3-*e*]indole-9,10-dione (3n)



Flash column chromatography on silica gel (ethyl acetate: petroleum ether, 1:8) gave the product (28.1 mg, 65% yield) as a red solid, mp: 163-164 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (s, 1H), 6.86 (s, 2H), 6.70 (d, *J* = 7.7 Hz, 1H), 6.17 (d, *J* = 7.7 Hz, 1H), 4.76 (s, 1H), 4.28 (dd, *J* = 9.6, 2.5 Hz, 1H), 3.57 (ddd, *J* = 11.6, 10.0, 5.5 Hz, 1H), 3.38 – 3.27 (m, 1H), 3.16 (dt, *J* = 13.7, 6.8 Hz, 2H), 2.66 – 2.55 (m, 1H), 2.40 (tt, *J* = 9.9, 5.8 Hz, 1H), 2.18 (dtd, *J* = 10.6, 7.9, 3.0 Hz, 1H), 2.00 – 1.88 (m, 2H), 1.25 (dd, *J* = 6.8, 4.8 Hz, 13H), 0.98 (t, *J* = 7.4 Hz, 2H), 0.93 – 0.84 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 181.81, 161.32, 151.87, 148.47, 148.42, 140.68, 135.78, 133.79, 127.90, 123.34, 103.35, 98.65, 46.06, 43.83, 31.64, 27.35, 26.68, 22.83, 21.93, 5.95, 5.93. **HRMS (ESI)**: calcd. for $C_{27}H_{33}N_2O_3$ $[M+H]^+$: 433.2486, found: 433.2485.

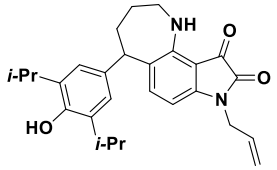
8-(cyclopropylmethyl)-5-(4-hydroxy-3,5-diisopropylphenyl)-1,2,3,4,5,8-hexahydroazepino[2,3-*e*]indole-9,10-dione (3o)



Flash column chromatography on silica gel (ethyl acetate: petroleum ether, 1:8) gave the product (33.0 mg, 74% yield) as a red solid, mp: 64-66 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (s, 1H), 6.87 (s, 2H), 6.68 (d, *J* = 7.6 Hz, 1H), 5.96 (d, *J* = 7.6 Hz, 1H), 4.76 (s, 1H), 4.28 (d, *J* = 8.7 Hz, 1H), 3.59 (dd, *J* = 13.5, 4.8 Hz, 1H), 3.56 – 3.45 (m, 2H), 3.35 (dd, *J* = 13.7, 5.6 Hz, 1H), 3.16 (dt, *J* = 13.4, 6.7 Hz, 2H), 2.40 (dt, *J* = 14.7, 7.3 Hz, 1H), 2.26 – 2.14 (m, 1H), 2.02 – 1.92 (m, 2H), 1.61 (s, 1H), 1.35 – 1.17 (m, 14H), 0.51 (d, *J* = 7.5 Hz, 2H), 0.36 (d, *J* = 4.2 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 182.06, 160.80, 152.20, 148.48, 147.80, 140.48, 135.73, 133.80, 128.06, 123.36, 103.36, 97.79, 46.07, 44.41, 43.83, 31.70, 27.35, 26.69, 22.82, 9.97, 4.02, 3.93. **HRMS (ESI)**: calcd. for $C_{28}H_{35}N_2O_3$ $[M+H]^+$: 447.2642, found: 447.2640.

8-allyl-5-(4-hydroxy-3,5-diisopropylphenyl)-1,2,3,4,5,8-hexahydroazepino[2,3-*e*]indole-9,10-dione (3p)

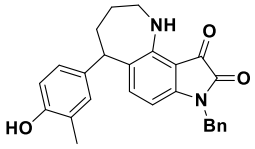


Flash column chromatography on silica gel (ethyl acetate: petroleum ether, 1:8) gave the product (18.6 mg, 43% yield) as a red solid, mp: 63-64 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.53 (s, 1H), 6.86 (s, 2H), 6.86 (s, 2H), 6.65 (d, *J* = 7.7 Hz, 1H), 6.65 (d, *J* = 7.7 Hz, 1H), 5.90 (d, *J* = 7.7 Hz, 1H), 5.90 (d, *J* = 7.7 Hz, 1H), 5.81 (ddd, *J* = 22.5, 10.5, 5.4 Hz, 1H), 5.81 (ddd, *J* = 22.5, 10.5, 5.4 Hz, 1H), 5.22 (dd, *J* = 19.6, 13.8 Hz, 2H), 4.75 (s, 1H), 4.36 – 4.18 (m, 3H), 3.59 (ddd, *J* = 16.4, 10.2, 5.9 Hz, 1H), 3.35 (dq, *J* = 13.9, 5.5 Hz, 1H), 3.21 – 3.08 (m, 2H), 2.40 (tt, *J* = 10.0, 5.8 Hz, 1H), 2.18 (dtd, *J* = 10.7, 7.9, 2.9 Hz, 1H), 1.96 (dq, *J* = 12.2, 6.0 Hz,

2H), 1.24 (dd, *J* = 6.8, 4.1 Hz, 13H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 181.58, 160.50, 152.17, 148.48, 147.28, 140.52, 135.66, 133.79, 131.43, 128.21, 123.34, 117.91, 103.40, 98.21, 46.05, 43.84, 42.37, 31.66, 27.34, 26.67, 22.81. **HRMS (ESI)**: calcd. for $C_{27}H_{33}N_2O_3$ $[M+H]^+$: 433.2486, found: 433.2487.

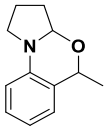
8-benzyl-5-(4-hydroxy-3-methylphenyl)-1,2,3,4,5,8-hexahydroazepino[2,3-*e*]indole-9,10-dion e (3q)



Flash column chromatography on silica gel (ethyl acetate: petroleum ether, 1:8) gave the product (15.8 mg, 38% yield) as a red solid, mp: 95-98 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.35 – 7.26 (m, 5H), 6.90 (s, 1H), 6.89 – 6.82 (m, 1H), 6.74 (d, *J* = 8.2 Hz, 1H), 6.63 (d, *J* = 7.7 Hz, 1H), 5.81 (d, *J* = 7.7 Hz, 1H), 4.82 (dd, *J* = 32.5, 15.7 Hz, 2H), 4.19 (dd, *J* = 9.0, 2.3 Hz, 1H), 3.56 – 3.42 (m, 1H), 3.33 (dd, *J* = 13.3, 6.3 Hz, 1H), 2.42 – 2.29 (m, 1H), 2.22 (s, 3H), 2.14 (ddd, *J* = 14.0, 9.4, 2.7 Hz, 1H), 1.97 – 1.86 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 181.49, 160.84, 152.38, 152.27, 147.31, 140.88, 136.06, 135.63, 130.71, 128.83, 127.84, 127.74, 127.50, 126.73, 123.89, 114.97, 103.54, 98.47, 45.70, 43.86, 43.83, 31.22, 26.33, 15.93. **HRMS (ESI)**: calcd. for $C_{26}H_{25}N_2O_3$ $[M+H]^+$: 413.1860, found: 413.1861.

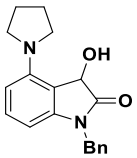
5-methyl-1,2,3,3a-tetrahydro-5*H*-benzo[*d*]pyrrolo[2,1-*b*][1,3]oxazine (8)



Flash column chromatography on silica gel (ethyl acetate: petroleum ether, 1:100) gave the product (7.2 mg, 38% yield) as a colorless oil with 3.3:1 dr.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (t, *J* = 7.7 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.73 (t, *J* = 7.5 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 5.03 (t, *J* = 5.2 Hz, 1H), 4.99 (dd, *J* = 12.8, 6.4 Hz, 1H), 3.59 – 3.54 (m, 1H), 3.25 (dd, *J* = 16.0, 8.3 Hz, 1H), 2.32 – 2.28 (m, 1H), 2.06 (td, *J* = 7.0, 3.7 Hz, 1H), 1.93 – 1.88 (m, 2H), 1.55 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 143.21, 127.80, 126.44, 124.26, 117.75, 114.64, 88.84, 73.12, 49.48, 32.42, 22.38, 20.29. **HRMS (ESI)**: calcd. for $C_{12}H_{16}NO$ $[M+H]^+$: 190.1226, found: 190.1227.

1-benzyl-3-hydroxy-4-(pyrrolidin-1-yl)indolin-2-one (9)

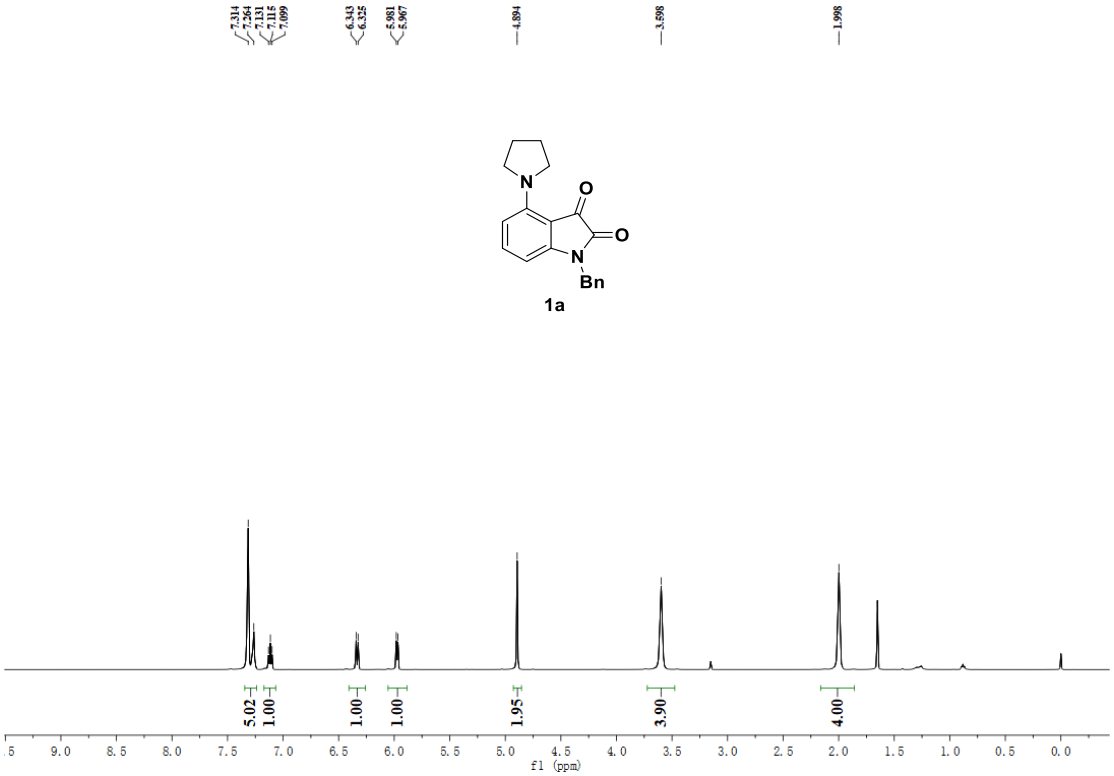


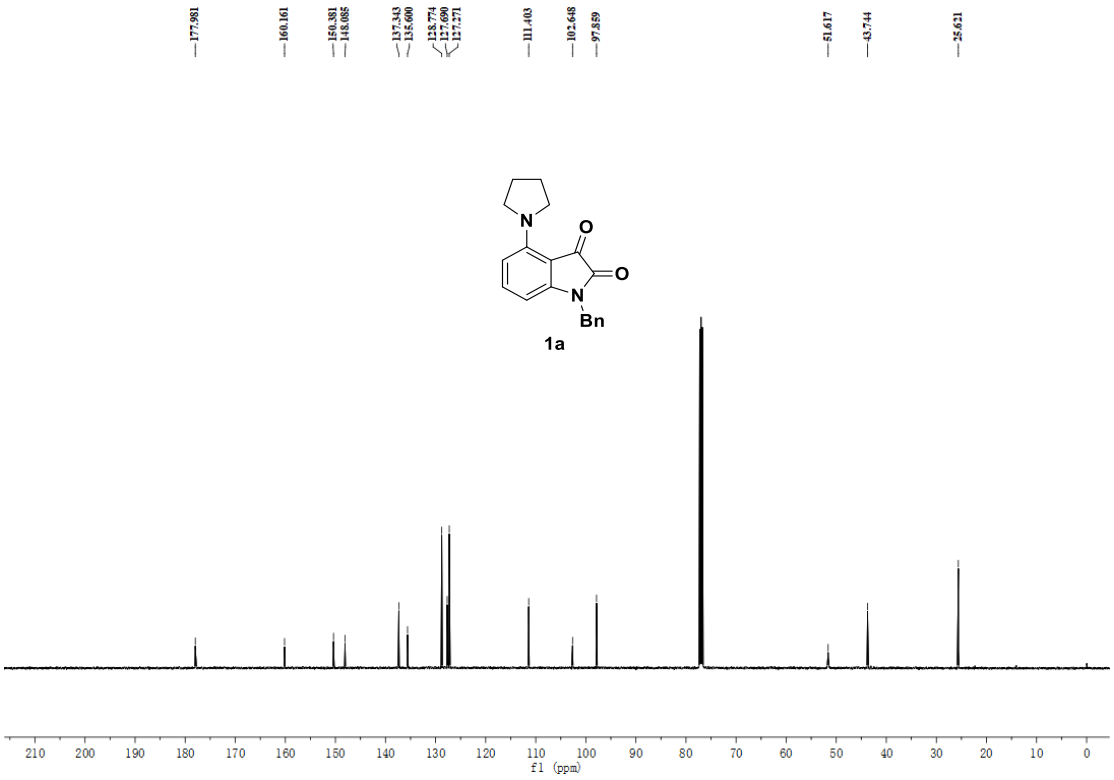
White solid, mp: 132-133 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 5H), 7.04 (t, *J* = 8.1 Hz, 1H), 6.33 (d, *J* = 8.5 Hz, 1H), 6.09 (d, *J* = 7.5 Hz, 1H), 5.23 (s, 1H), 4.85 (dd, *J* = 34.8, 15.7 Hz, 2H), 3.71 (dd, *J* = 14.4, 7.3 Hz, 2H), 3.43 (s, 1H), 3.35 (s, 2H), 2.08 – 1.87 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 176.52, 146.24, 145.40, 135.81, 130.62, 128.74, 127.54, 127.14, 109.95, 107.64, 98.29, 69.93, 48.37, 43.67, 25.41. **HRMS (ESI)**: calcd. for $C_{19}H_{21}N_2O_2$ $[M+H]^+$: 309.1598, found: 309.1597.

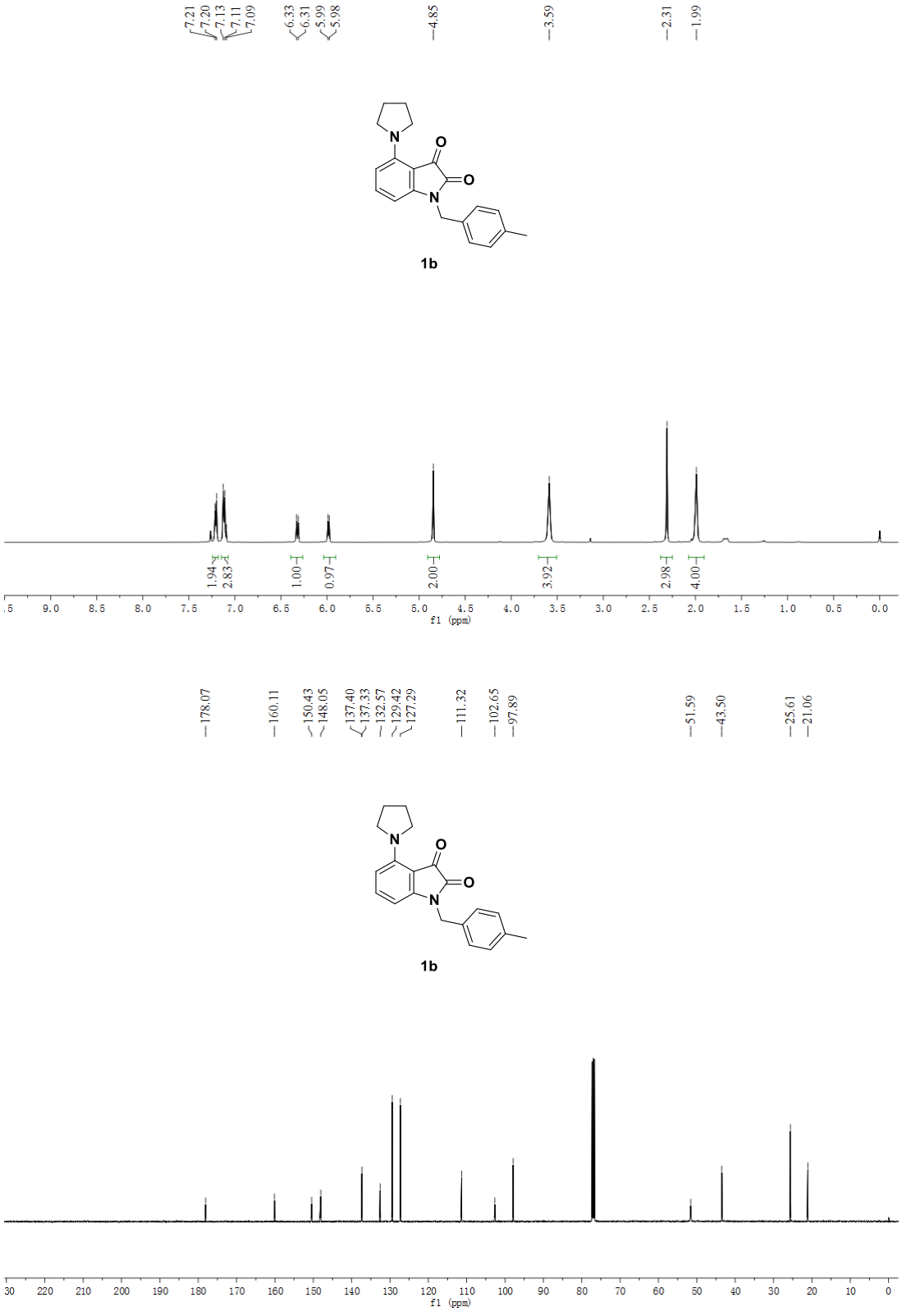
4. ^{1}H and ^{13}C-NMR Spectra

1-benzyl-4-(pyrrolidin-1-yl)indoline-2,3-dione (1a)

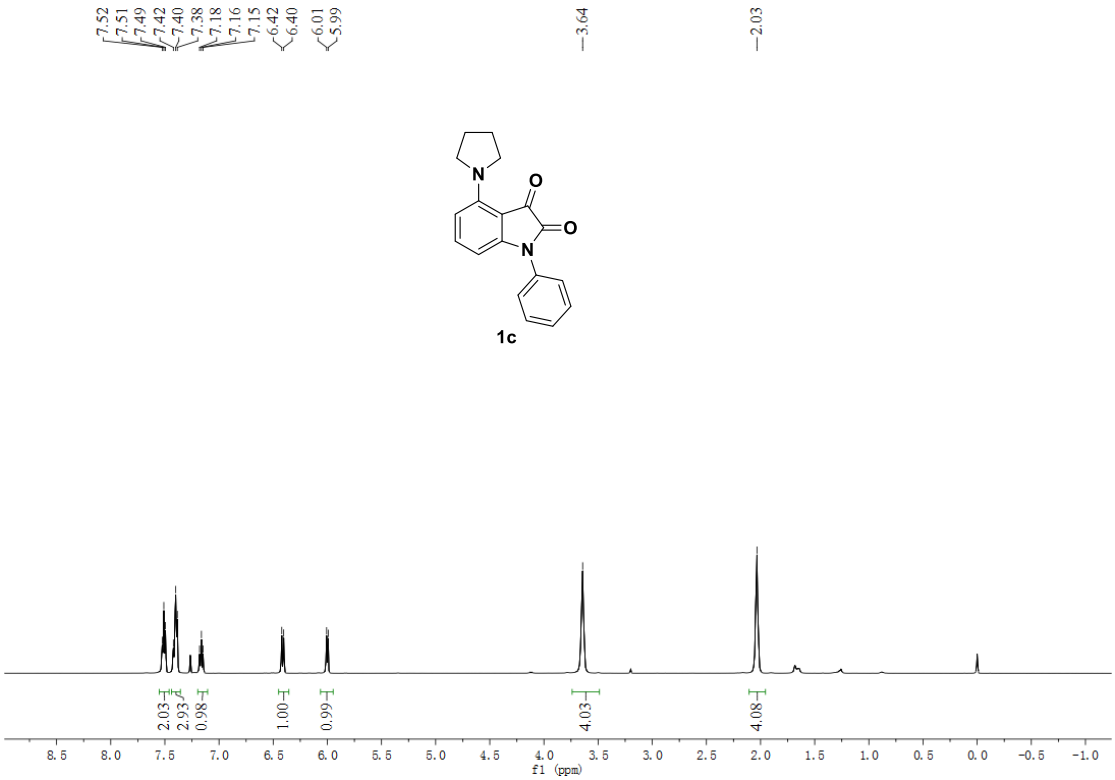


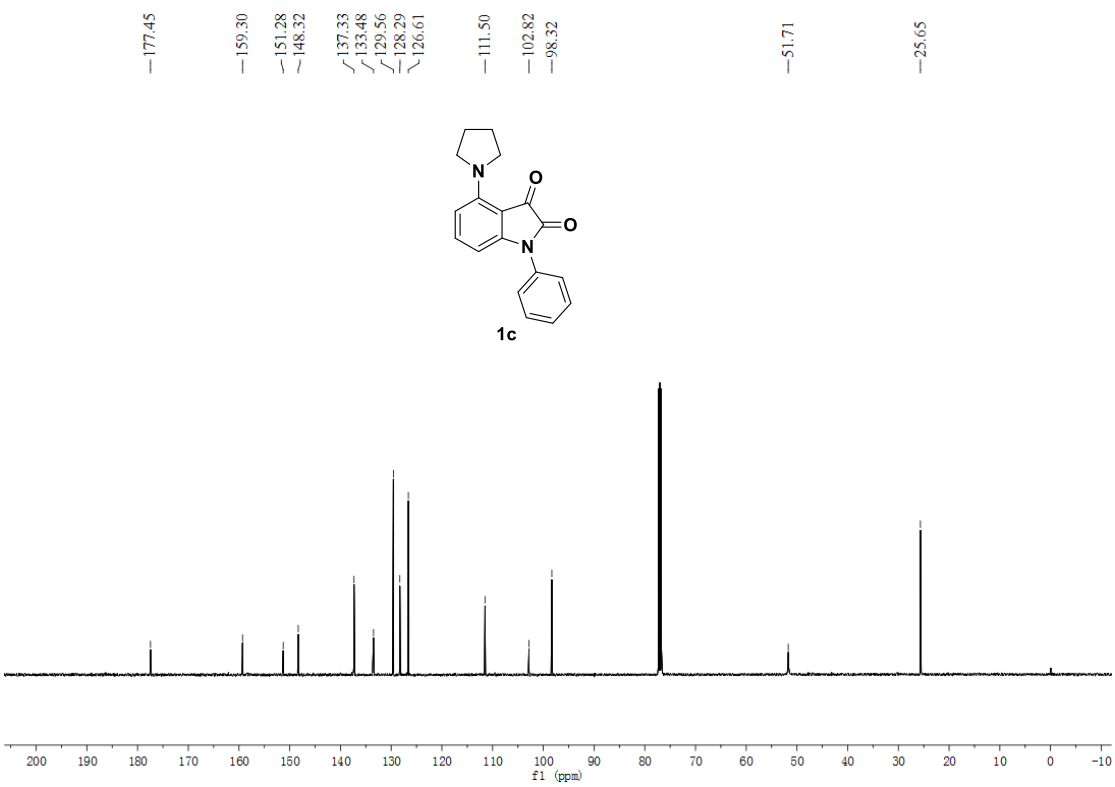


1-(4-methylbenzyl)-4-(pyrrolidin-1-yl)indoline-2,3-dione (1b)

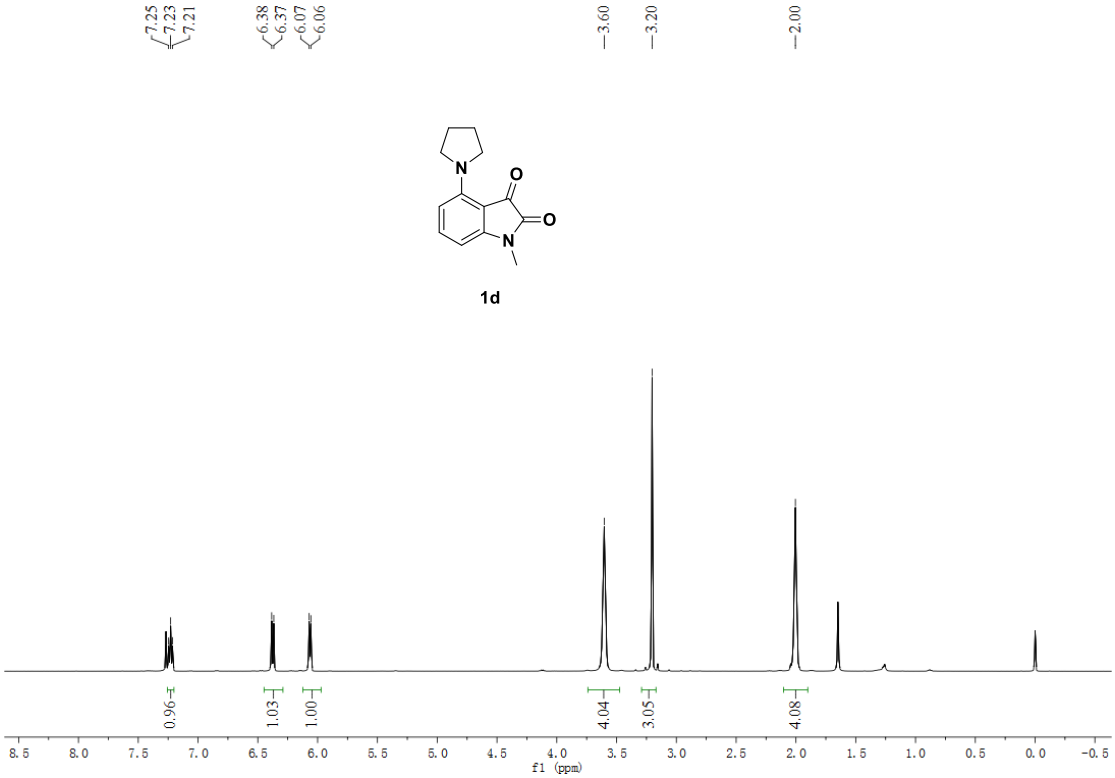


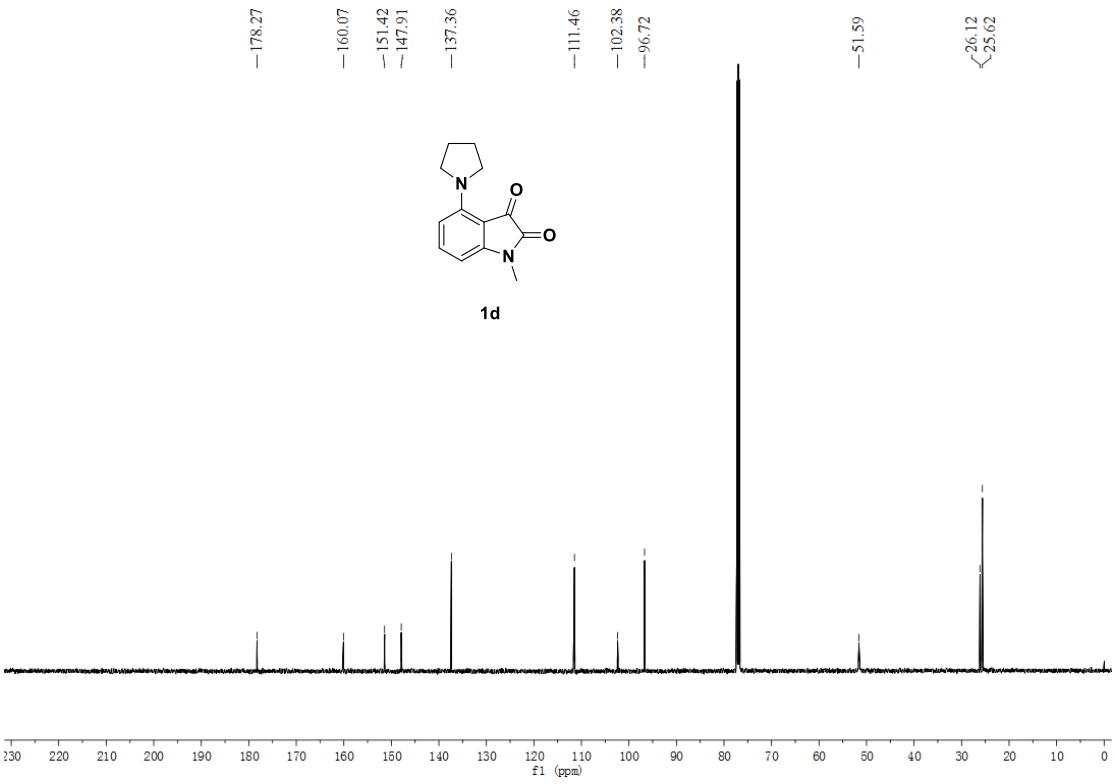
1-phenyl-4-(pyrrolidin-1-yl)indoline-2,3-dione (1c)



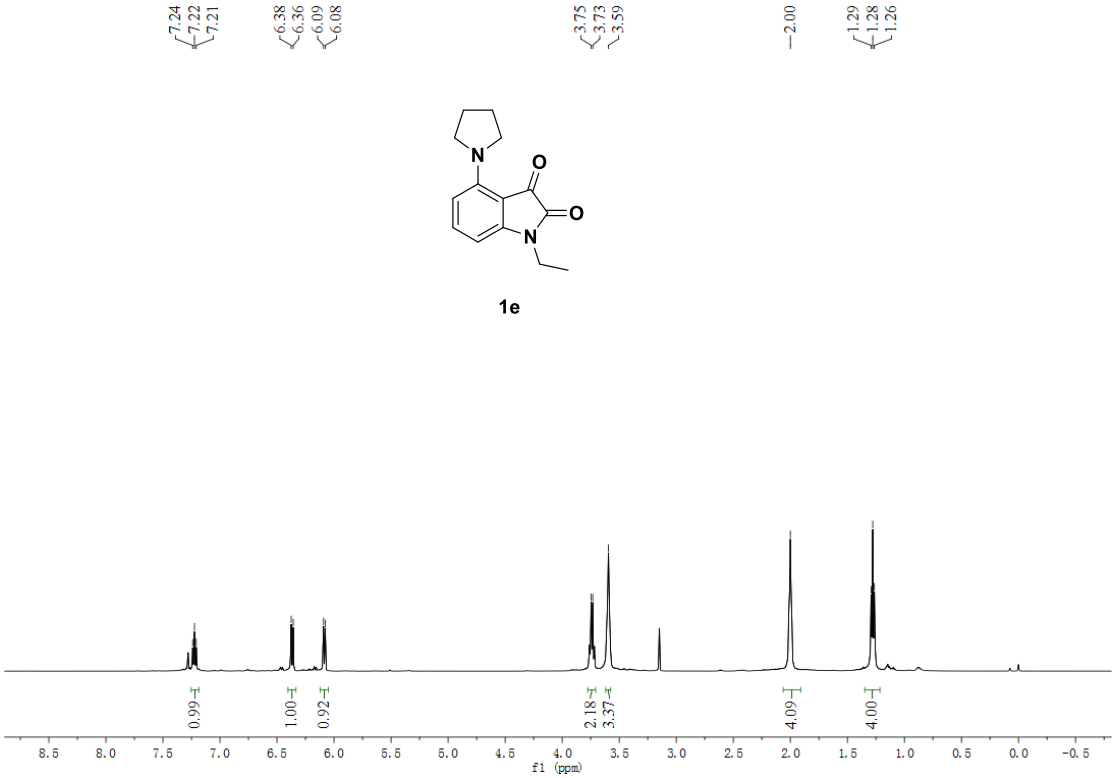


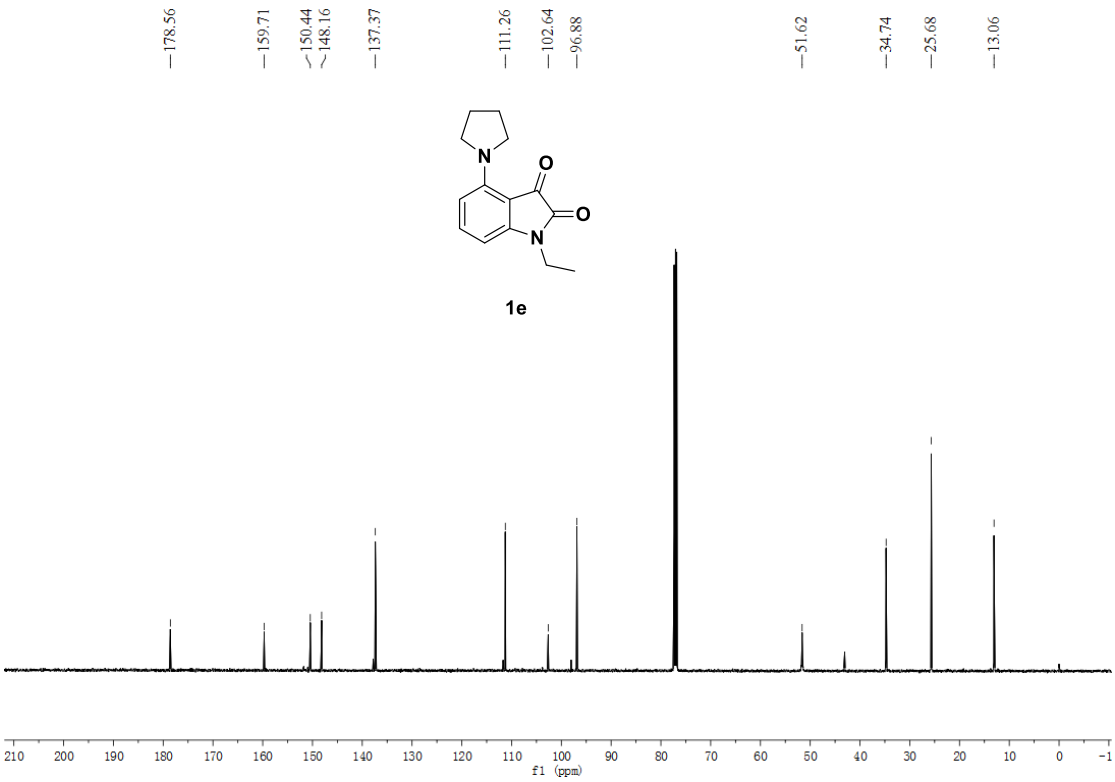
1-methyl-4-(pyrrolidin-1-yl)indoline-2,3-dione (1d)



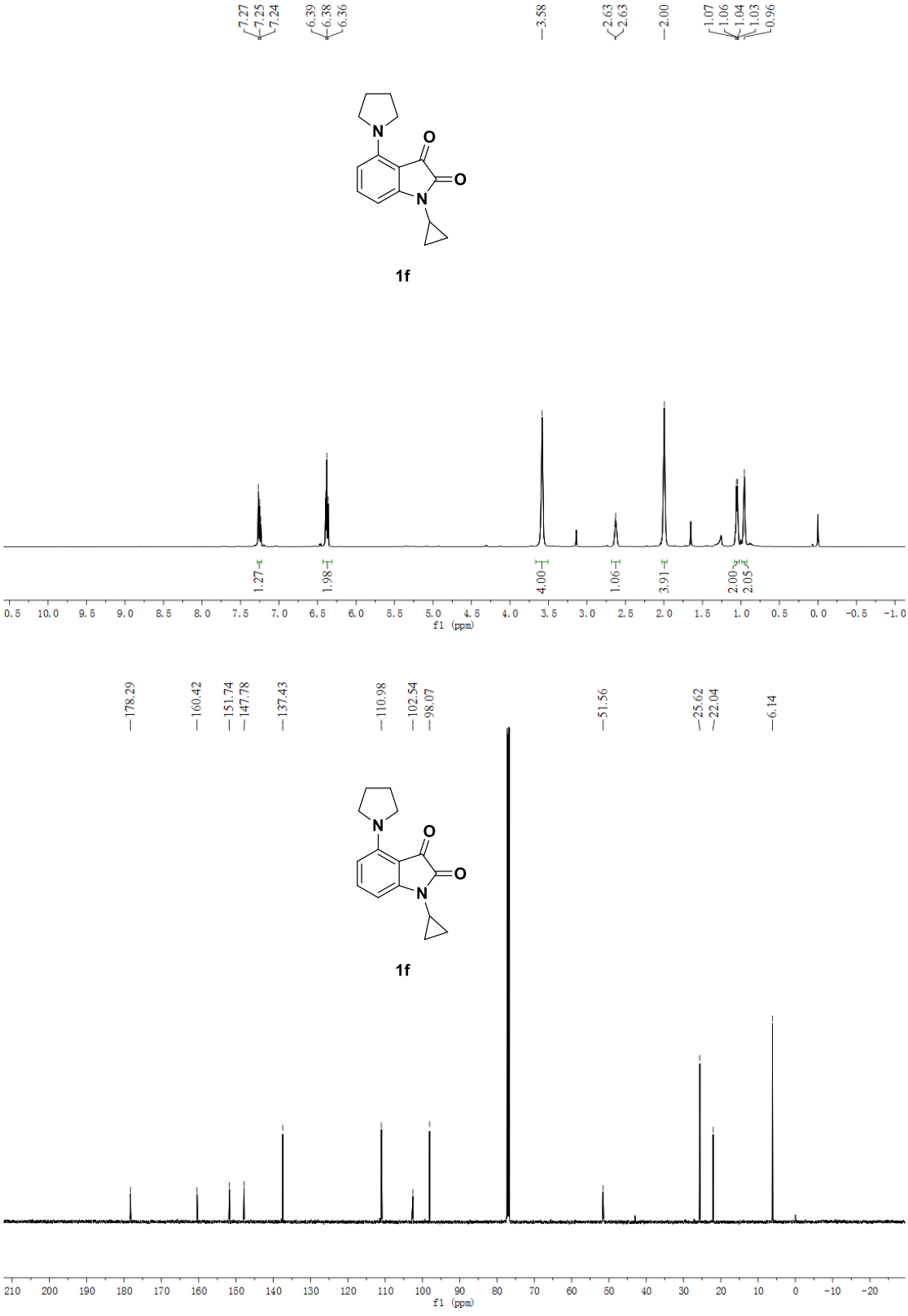


1-ethyl-4-(pyrrolidin-1-yl)indoline-2,3-dione (1e)

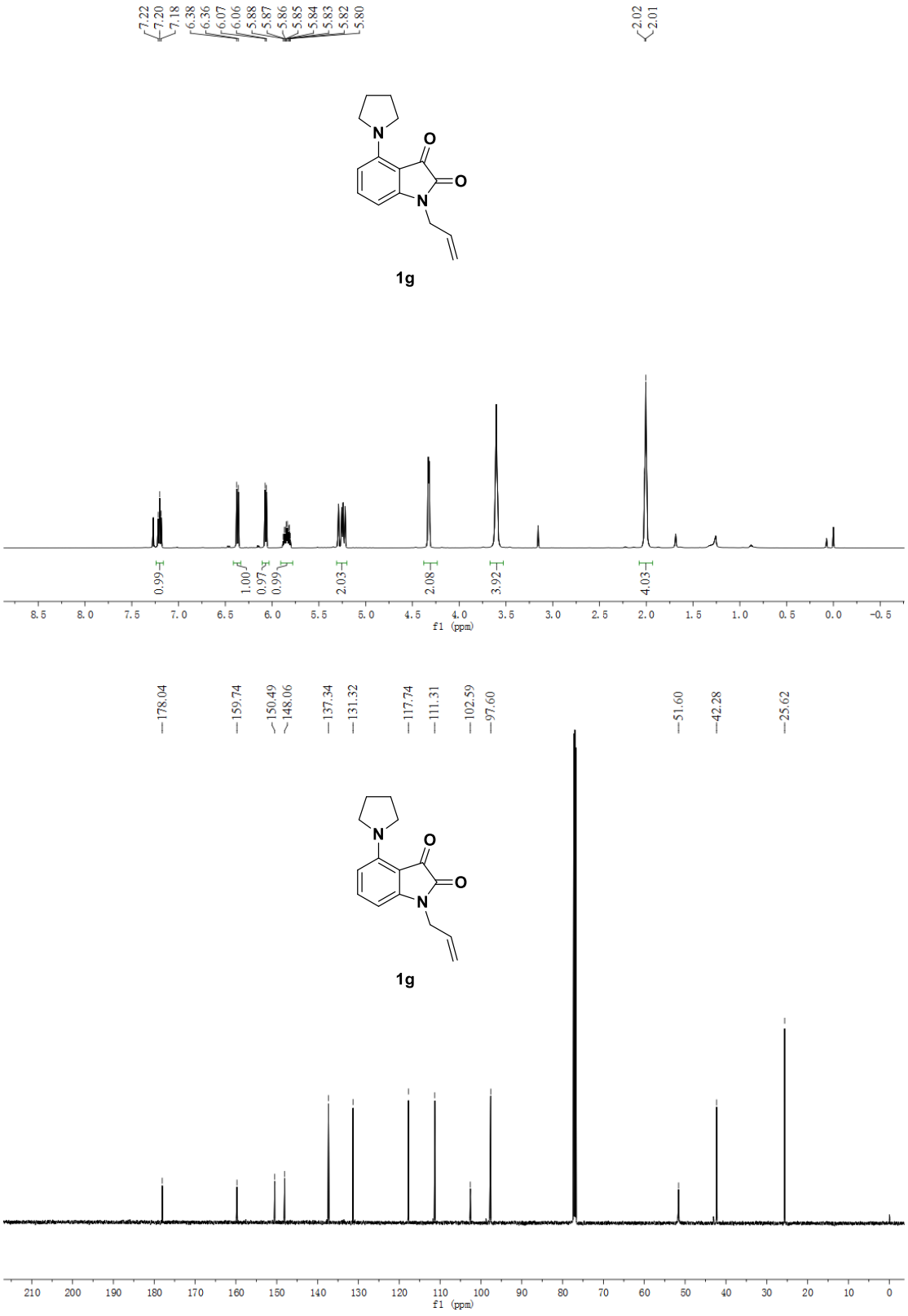




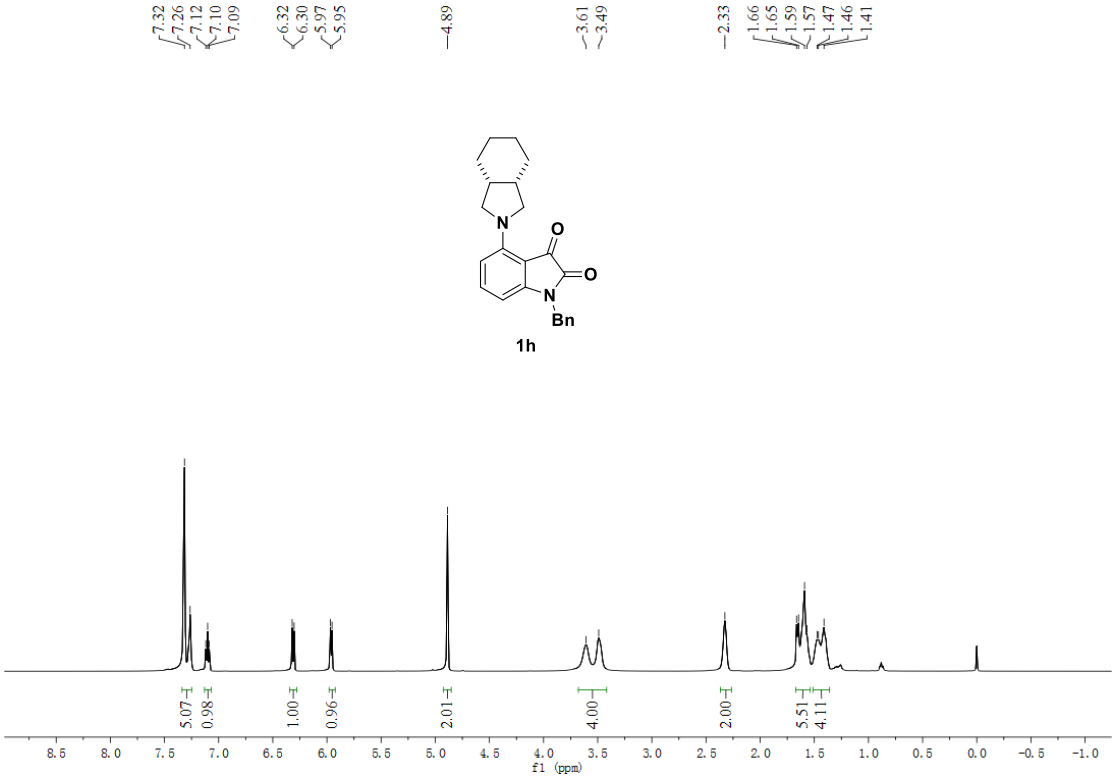
1-cyclopropyl-4-(pyrrolidin-1-yl)indoline-2,3-dione (1f)

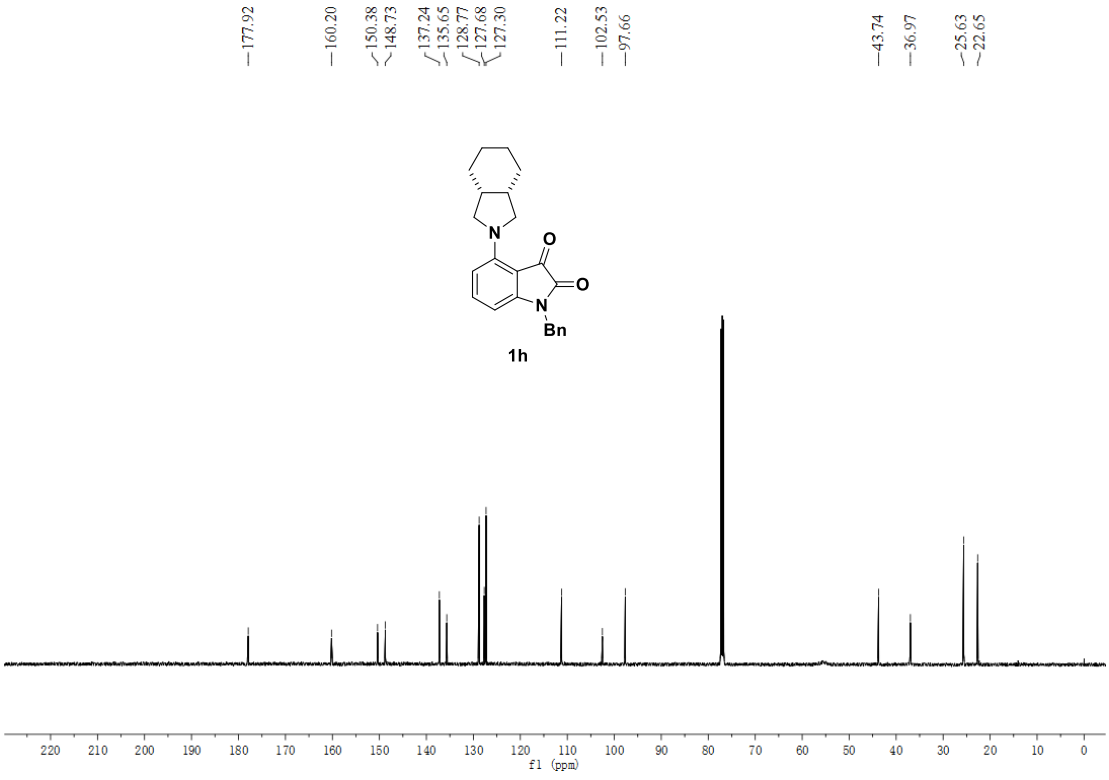


1-cyclopropyl-4-(pyrrolidin-1-yl)indoline-2,3-dione (1g)

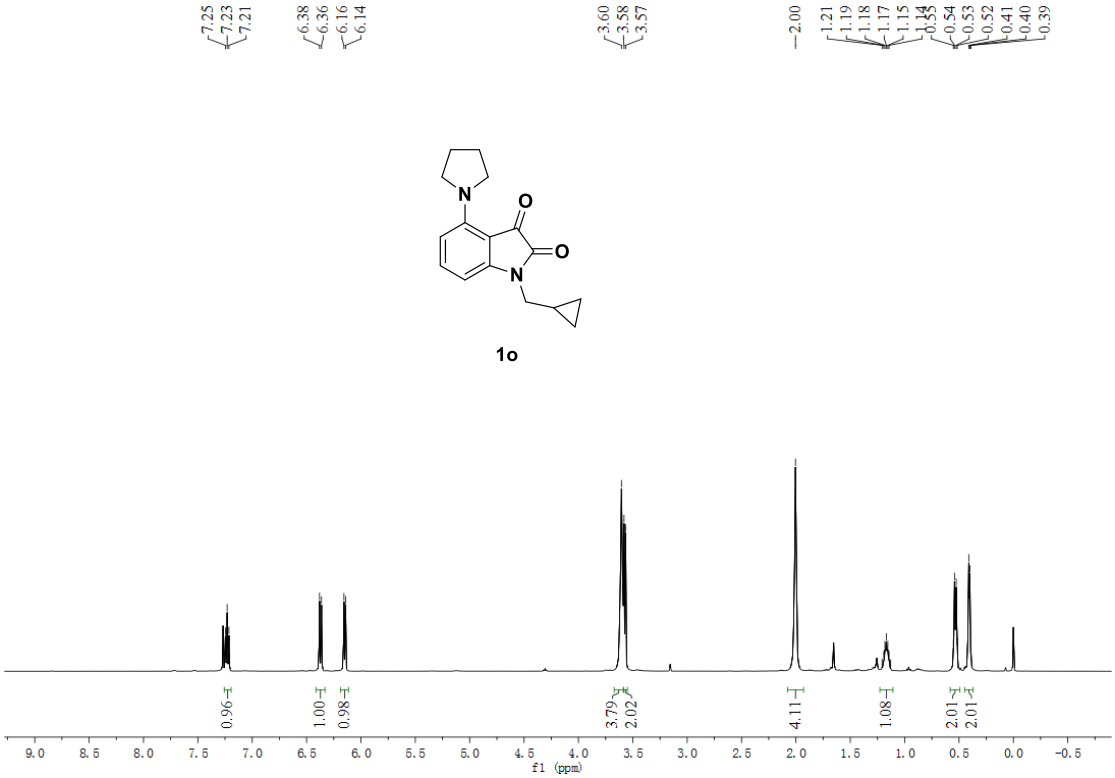


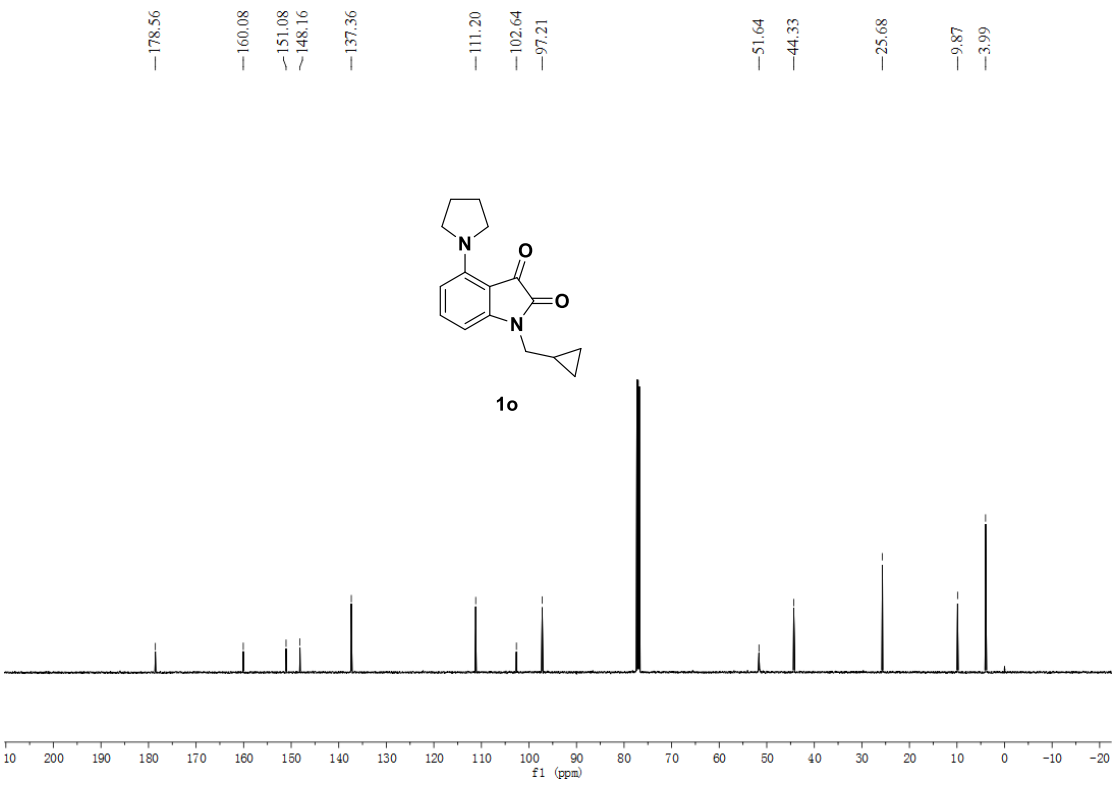
1-benzyl-4-(octahydro-2*H*-isoindol-2-yl)indoline-2,3-dione (1h)



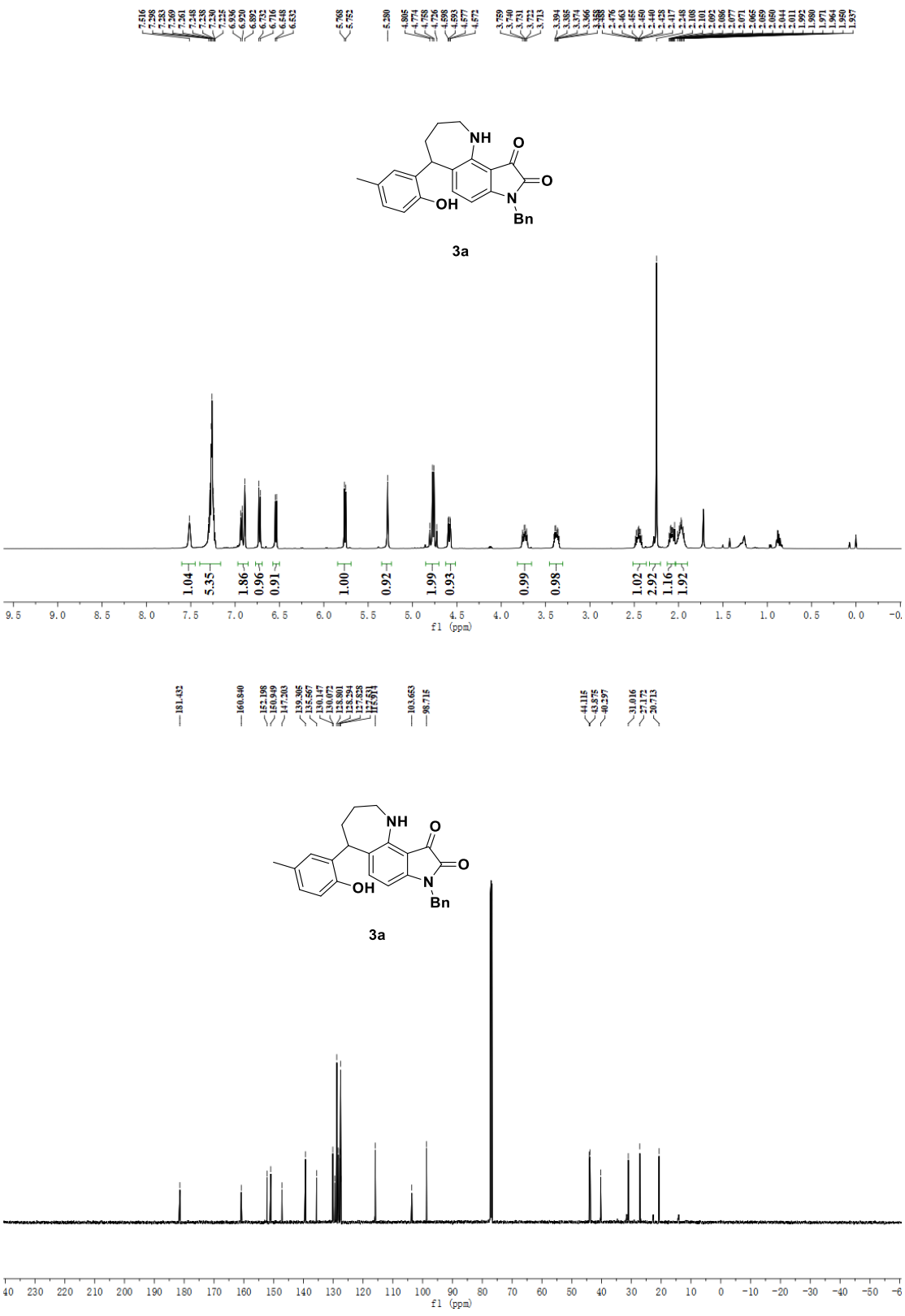


1-(cyclopropylmethyl)-4-(pyrrolidin-1-yl)indoline-2,3-dione (1o)

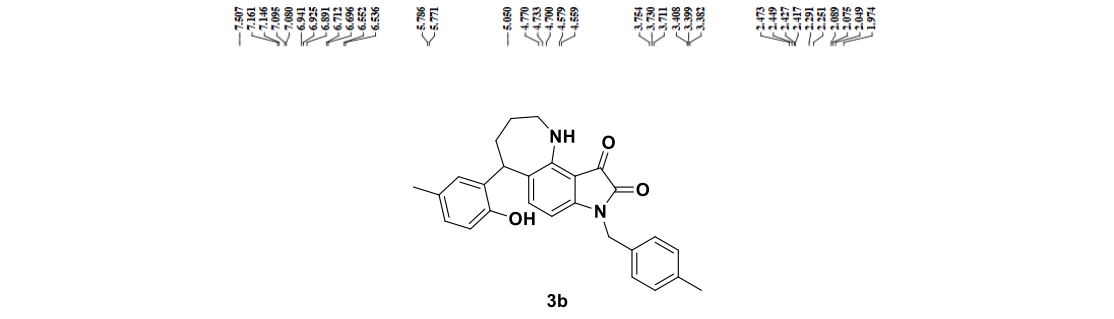


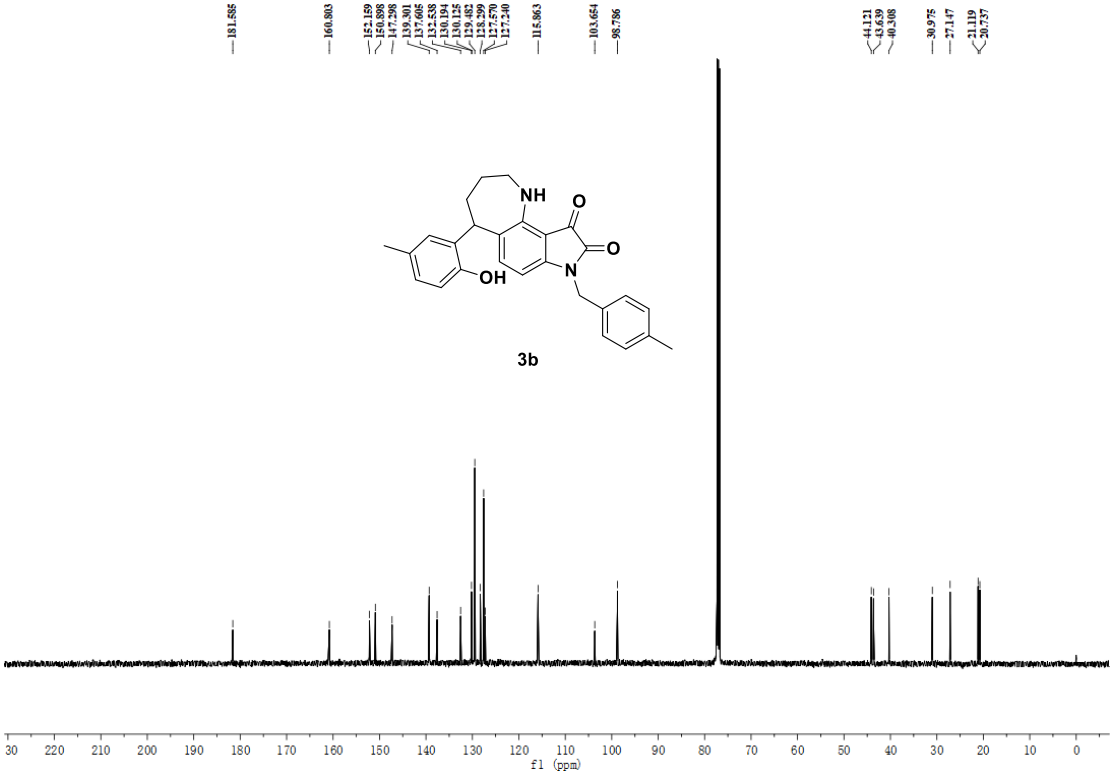


8-benzyl-5-(2-hydroxy-5-methylphenyl)-1,2,3,4,5,8-hexahydroazepino[2,3-*e*]indole-9,10-dion e (3a)

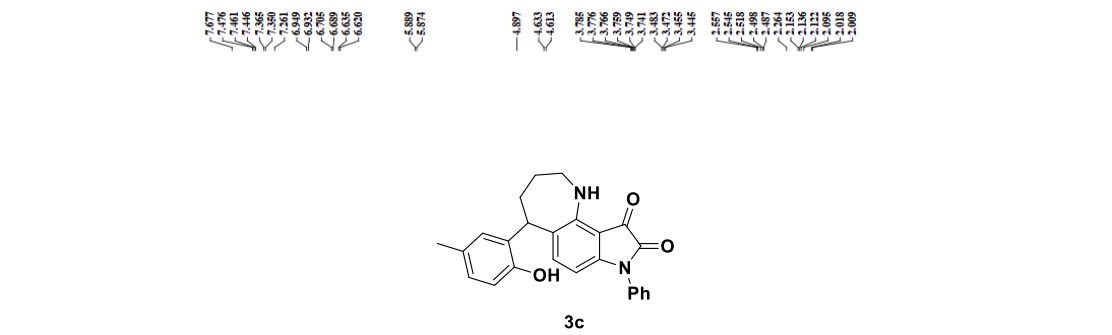


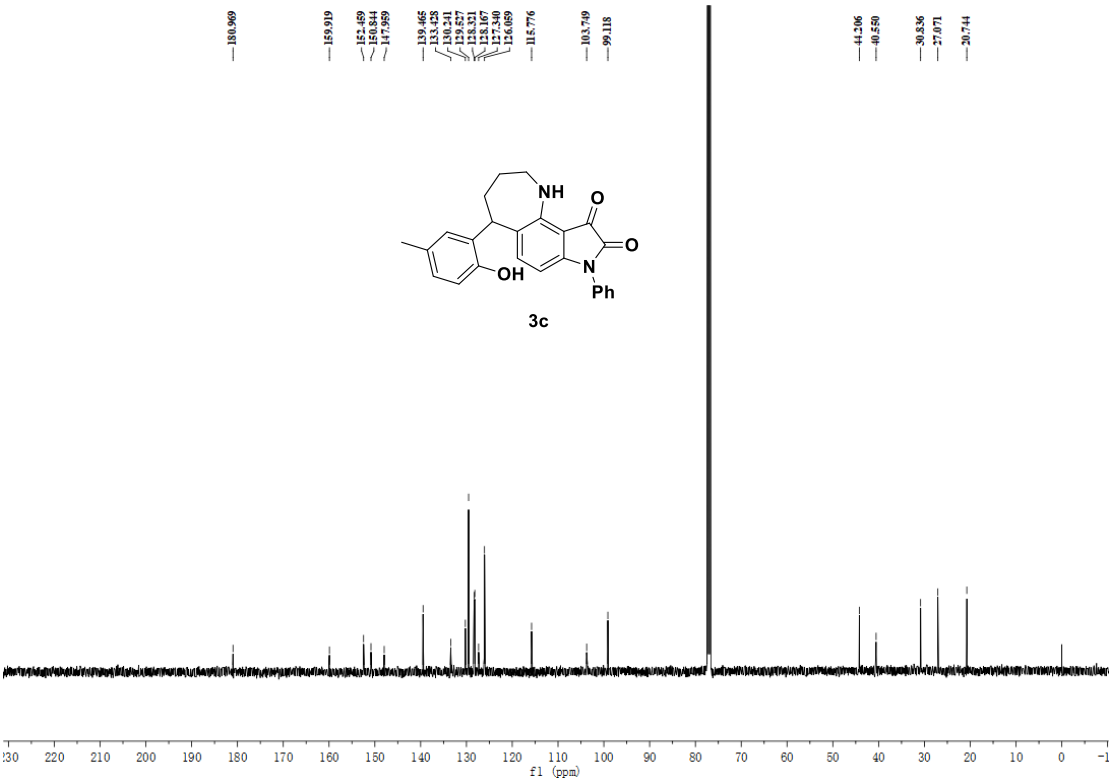
5-(2-hydroxy-5-methylphenyl)-8-(4-methylbenzyl)-1,2,3,4,5,8-hexahydroazepino[2,3-*e*]indole-9,10-dione (3b)



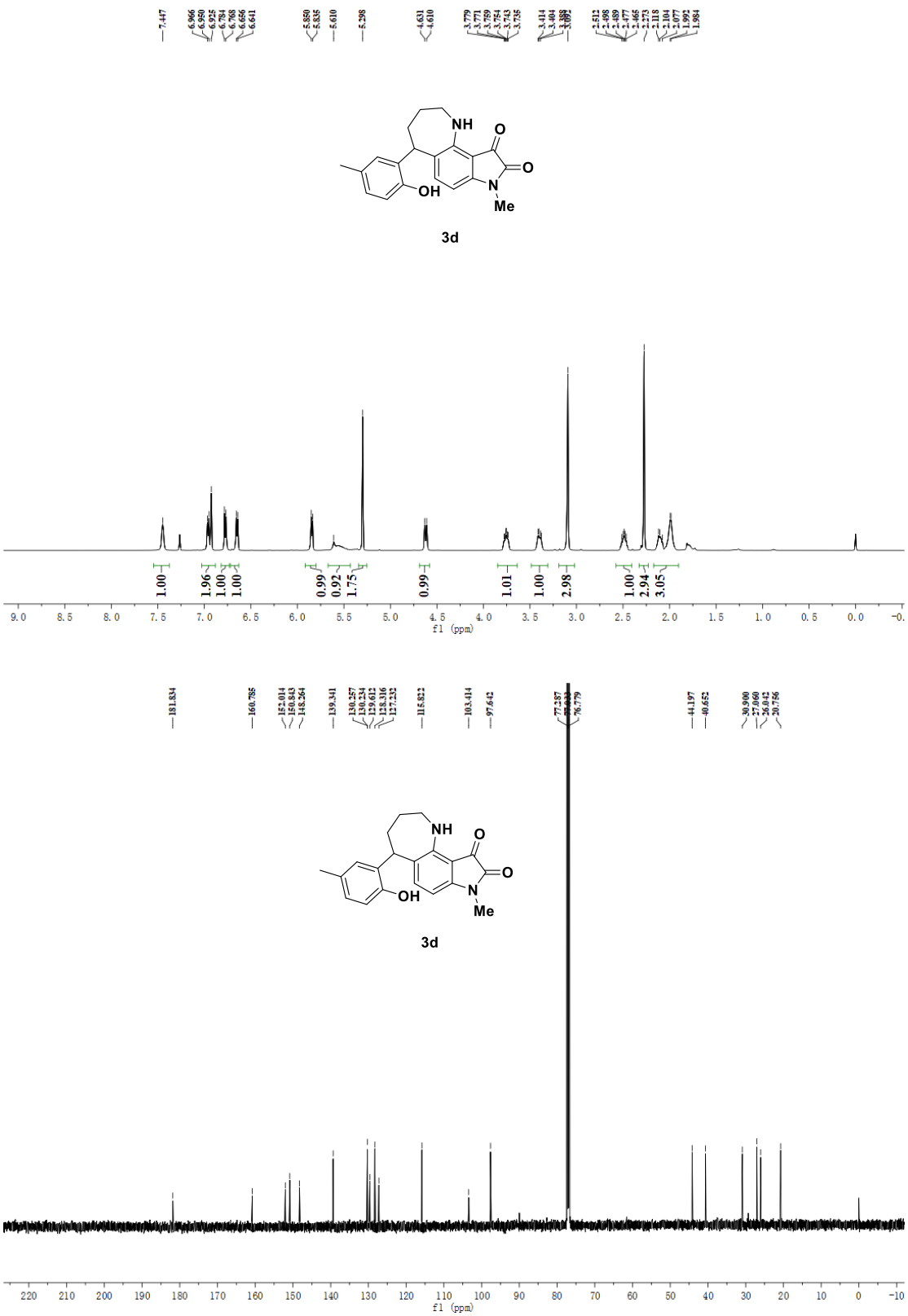


5-(2-hydroxy-5-methylphenyl)-8-phenyl-1,2,3,4,5,8-hexahydroazepino[2,3-*e*]indole-9,10-dion e (3c)

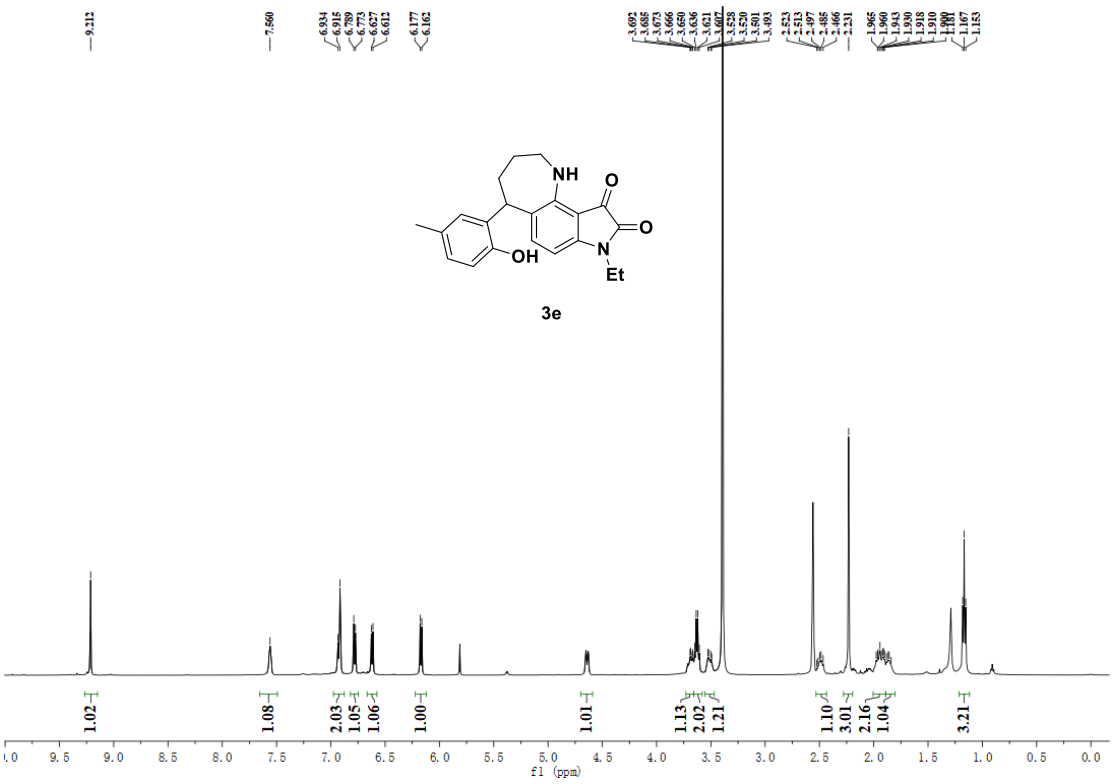


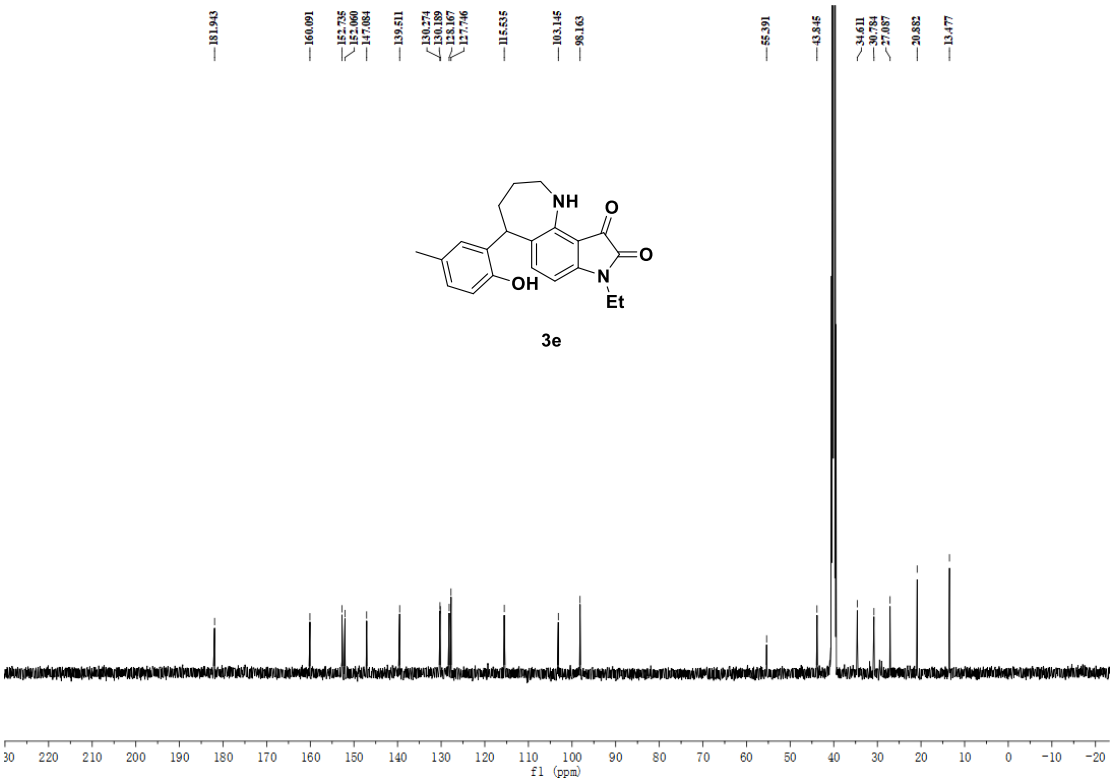


5-(2-hydroxy-5-methylphenyl)-8-methyl-1,2,3,4,5,8-hexahydroazepino[2,3-*e*]indole-9,10-dion e (3d)

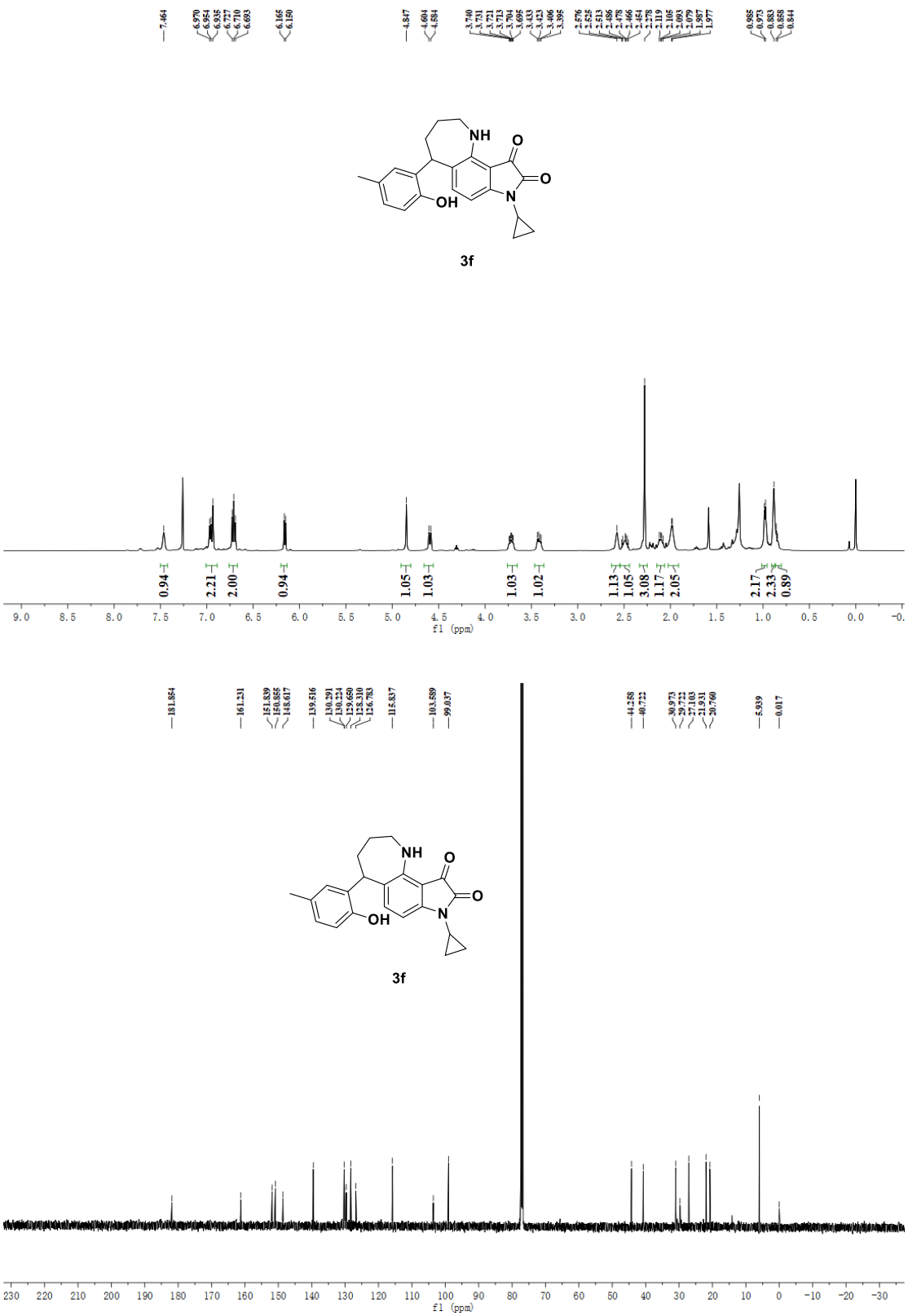


8-ethyl-5-(2-hydroxy-5-methylphenyl)-1,2,3,4,5,8-hexahydroazepino[2,3-*e*]indole-9,10-dione (3e)

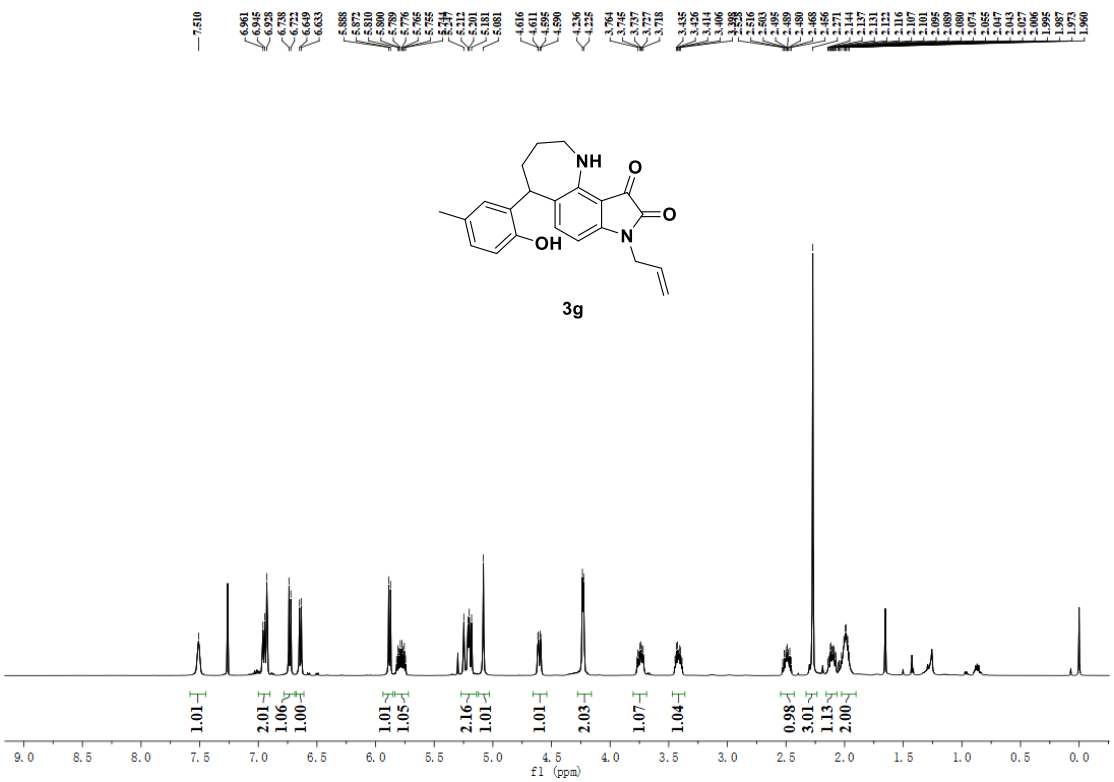


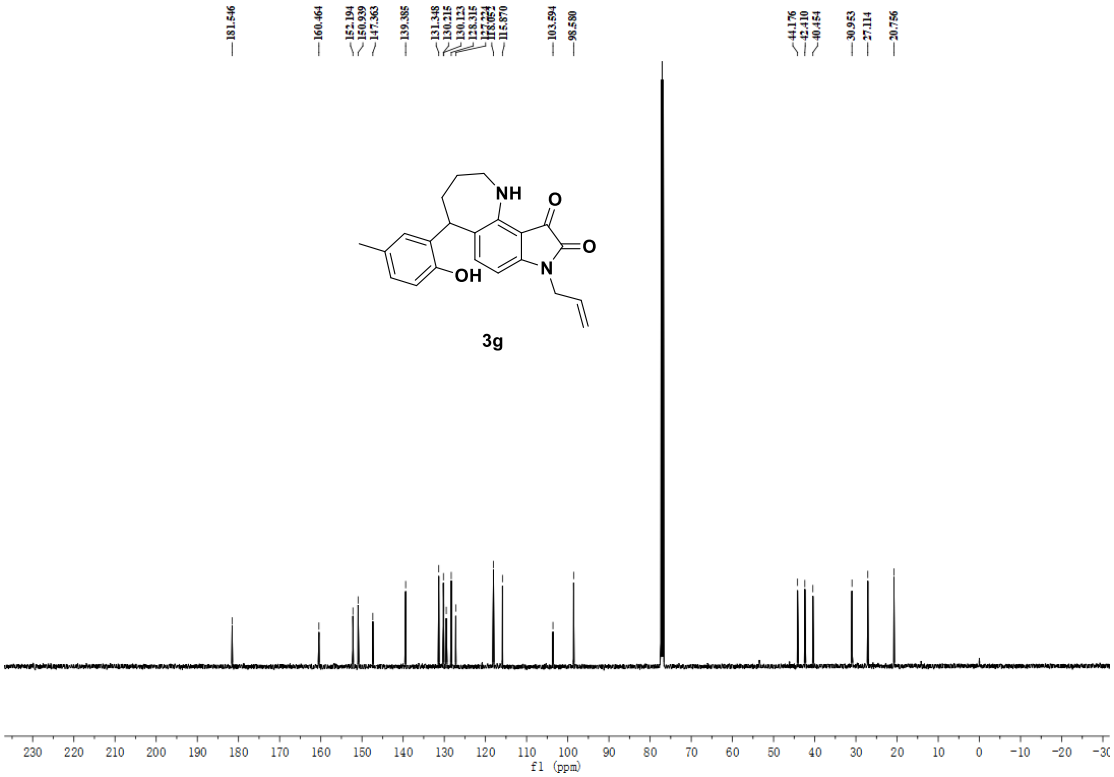


8-cyclopropyl-5-(2-hydroxy-5-methylphenyl)-1,2,3,4,5,8-hexahydroazepino[2,3-*e*]indole-9,10-dione (3f)

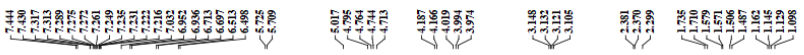


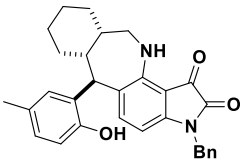
8-allyl-5-(2-hydroxy-5-methylphenyl)-1,2,3,4,5,8-hexahydroazepino[2,3-*e*]indole-9,10-dione (3g)



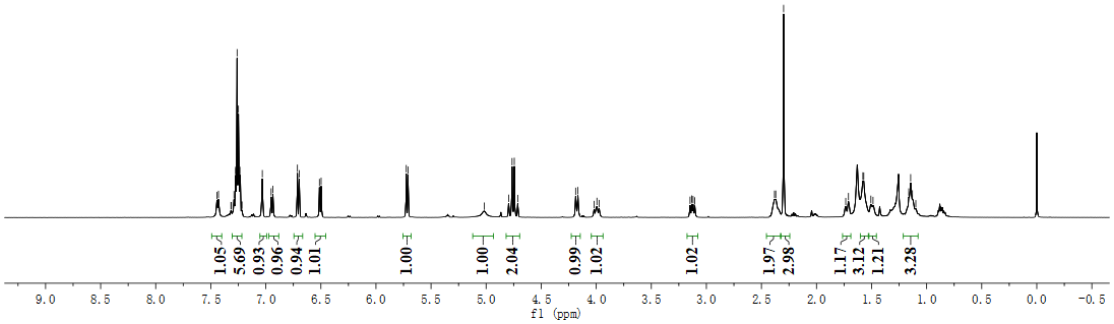


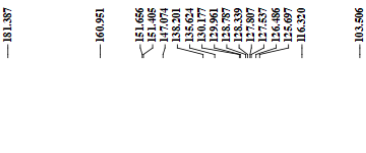
3-benzyl-6-(2-hydroxy-5-methylphenyl)-3,6,6a,7,8,9,10,10a,11,12-decahydrobenzo[5,6]azepino[2,3-*e*]indole-1,2-dione (3h)





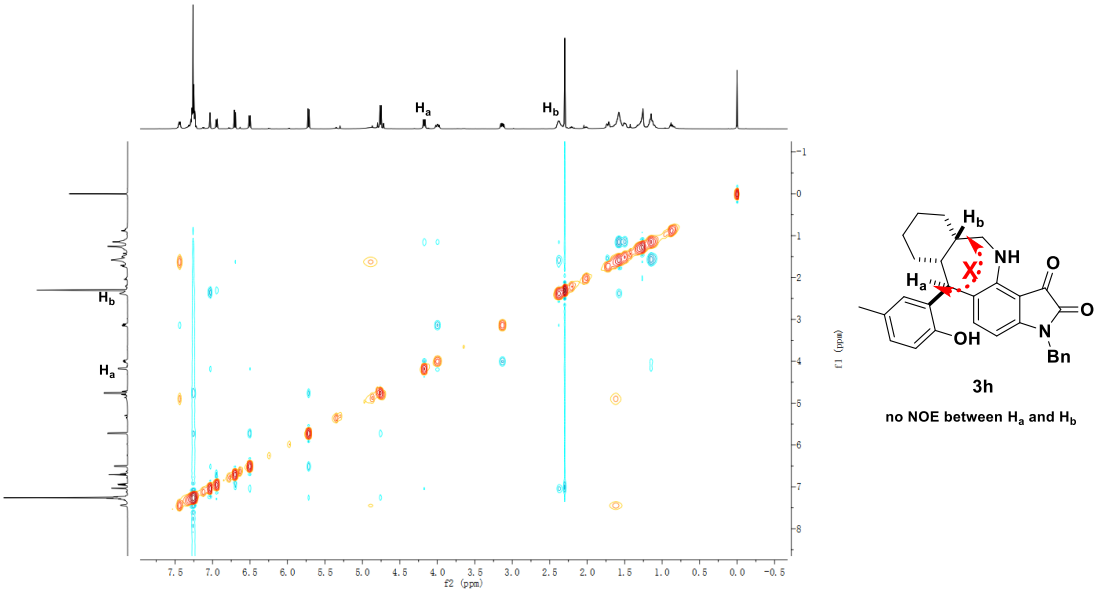
3h



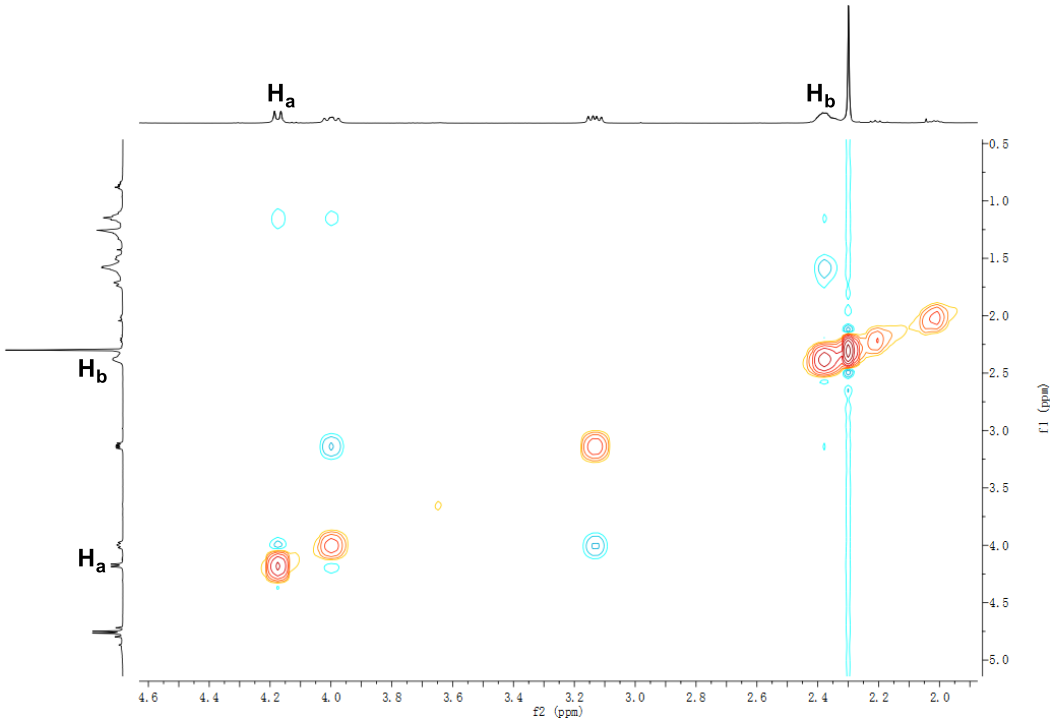


3h

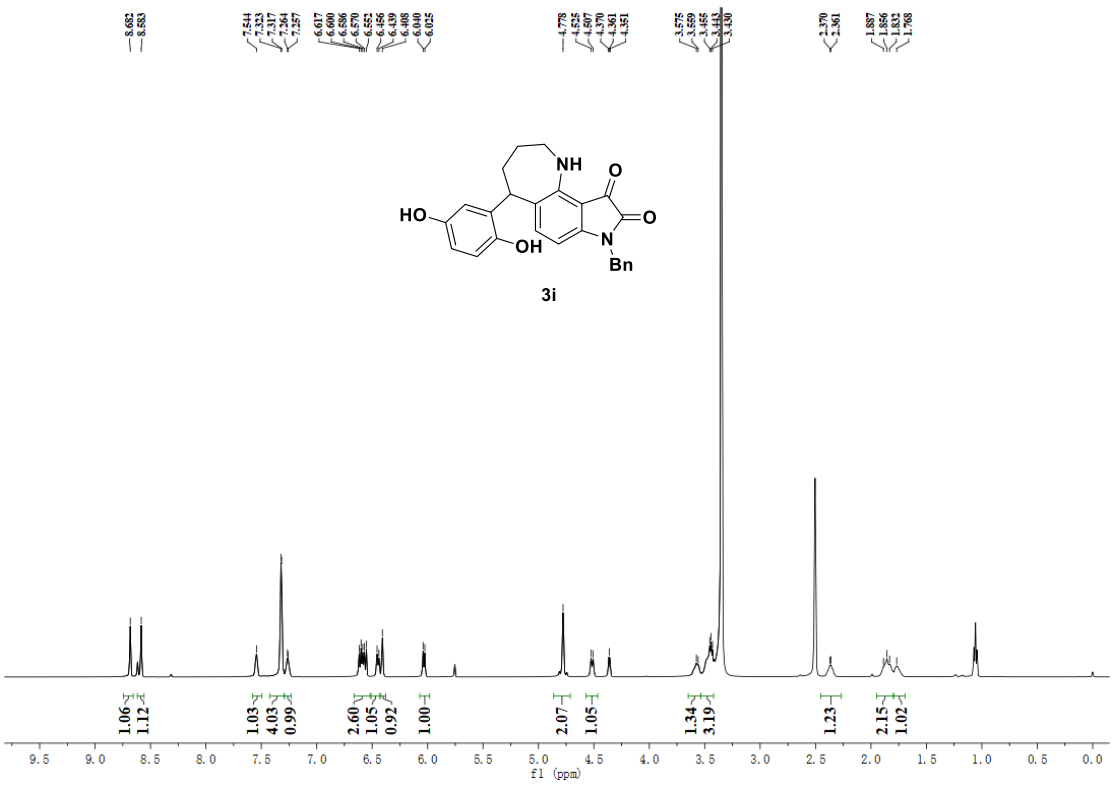
NOE spectra of 3-benzyl-6-(2-hydroxy-5-methylphenyl)-3,6,6a,7,8,9,10,10a,11,12-decahydro benzo[5,6]azepino[2,3-*e*]indole-1,2-dione (3h)

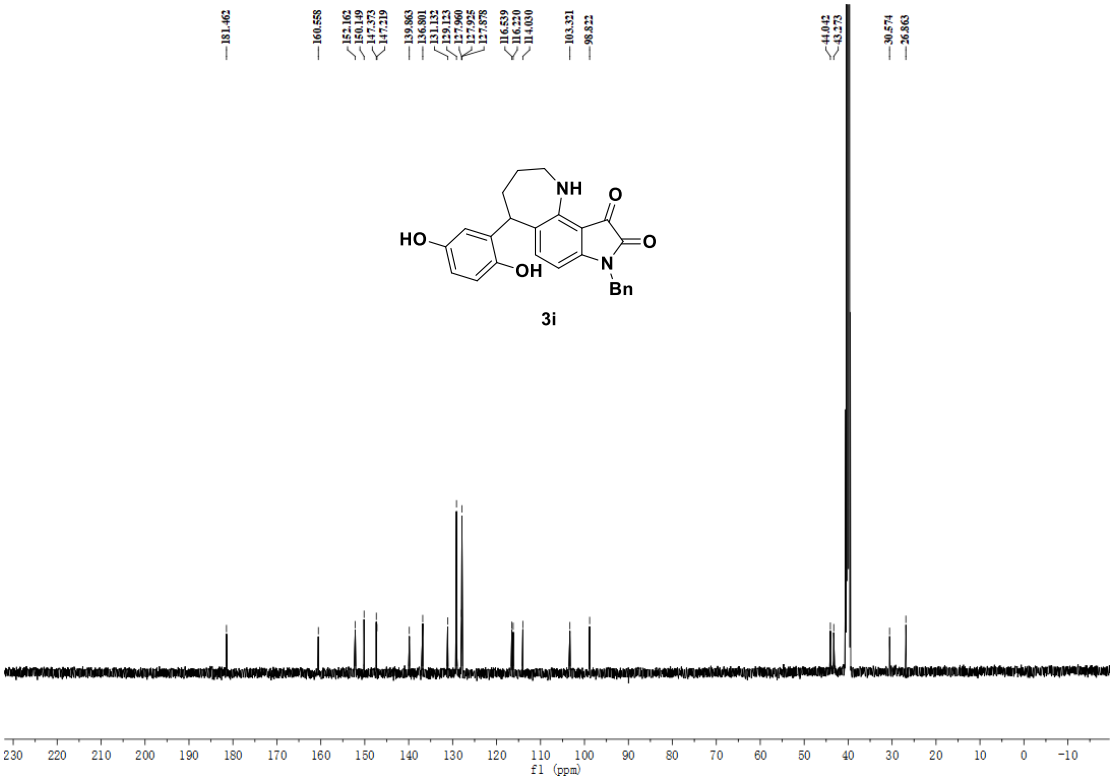


Amplification of NOE spectra

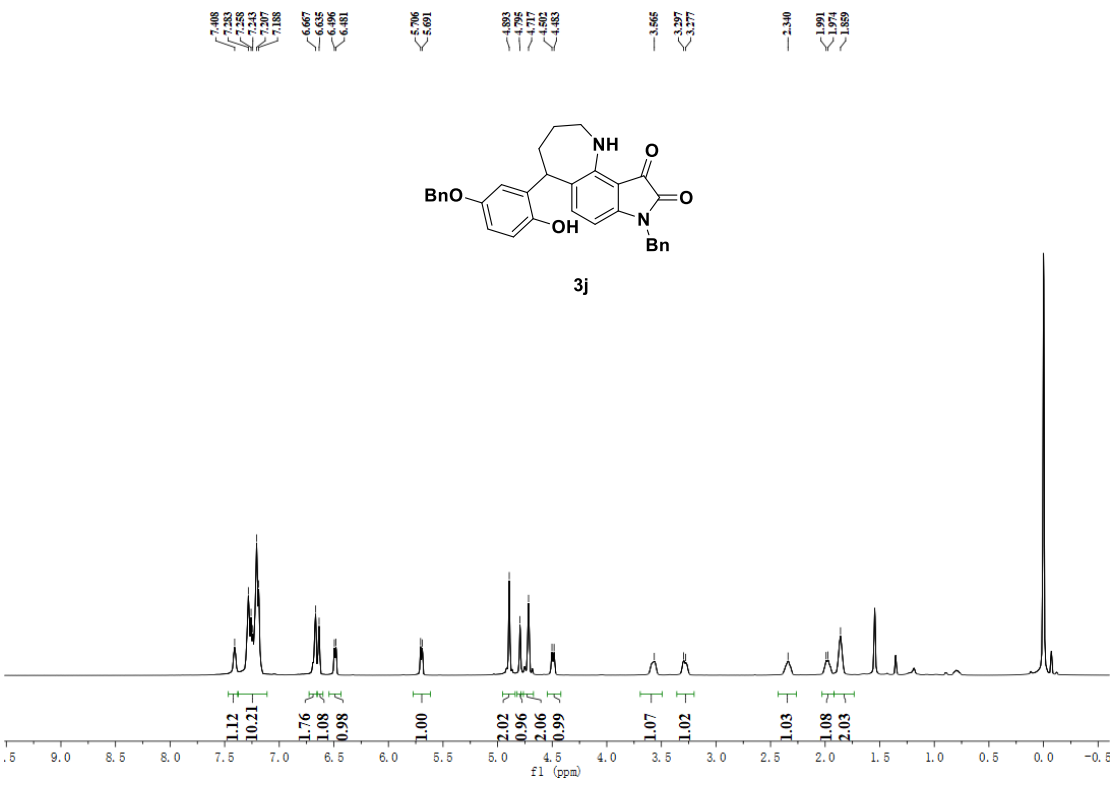


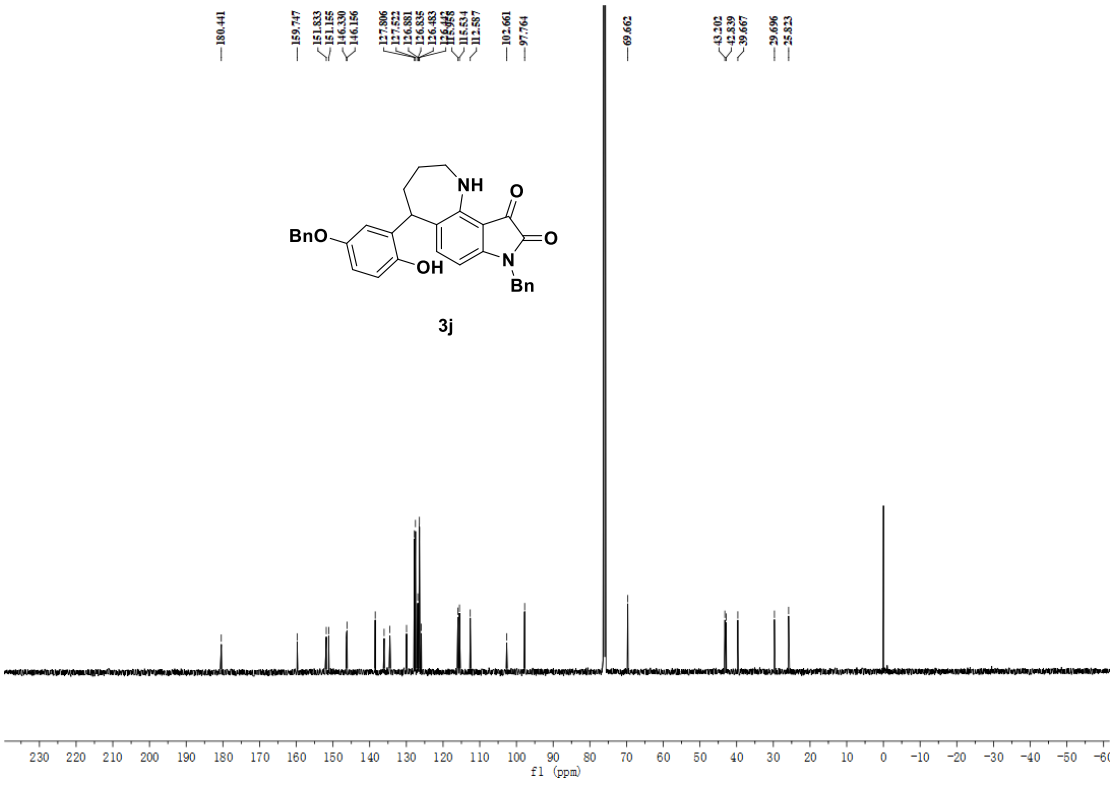
8-benzyl-5-(2,5-dihydroxyphenyl)-1,2,3,4,5,8-hexahydroazepino[2,3-*e*]indole-9,10-dione (3i)



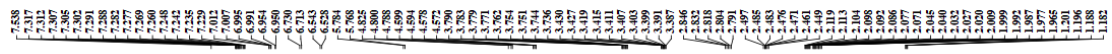


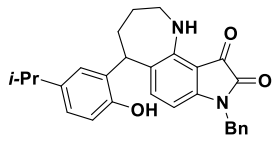
8-benzyl-5-(5-(benzyloxy)-2-hydroxyphenyl)-1,2,3,4,5,8-hexahydroazepino[2,3-*e*]indole-9,10-dione (3j)



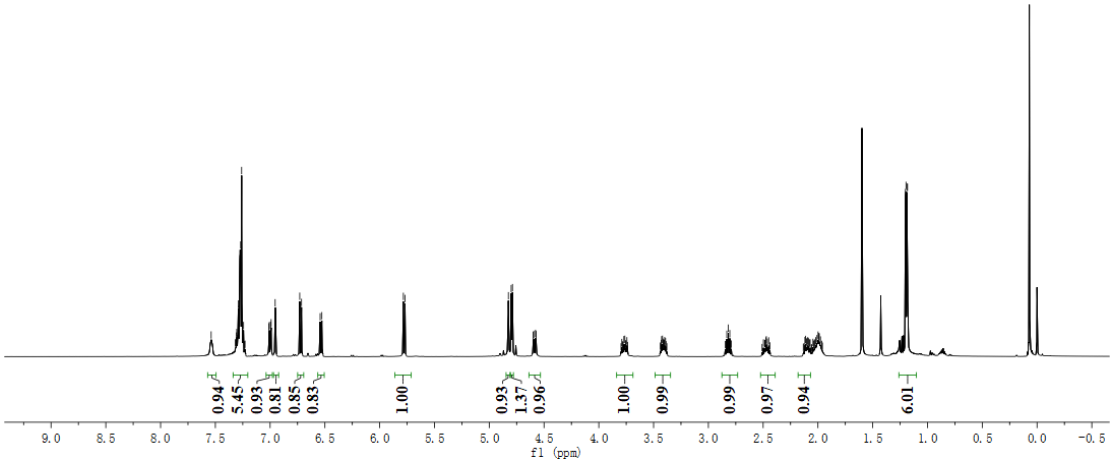


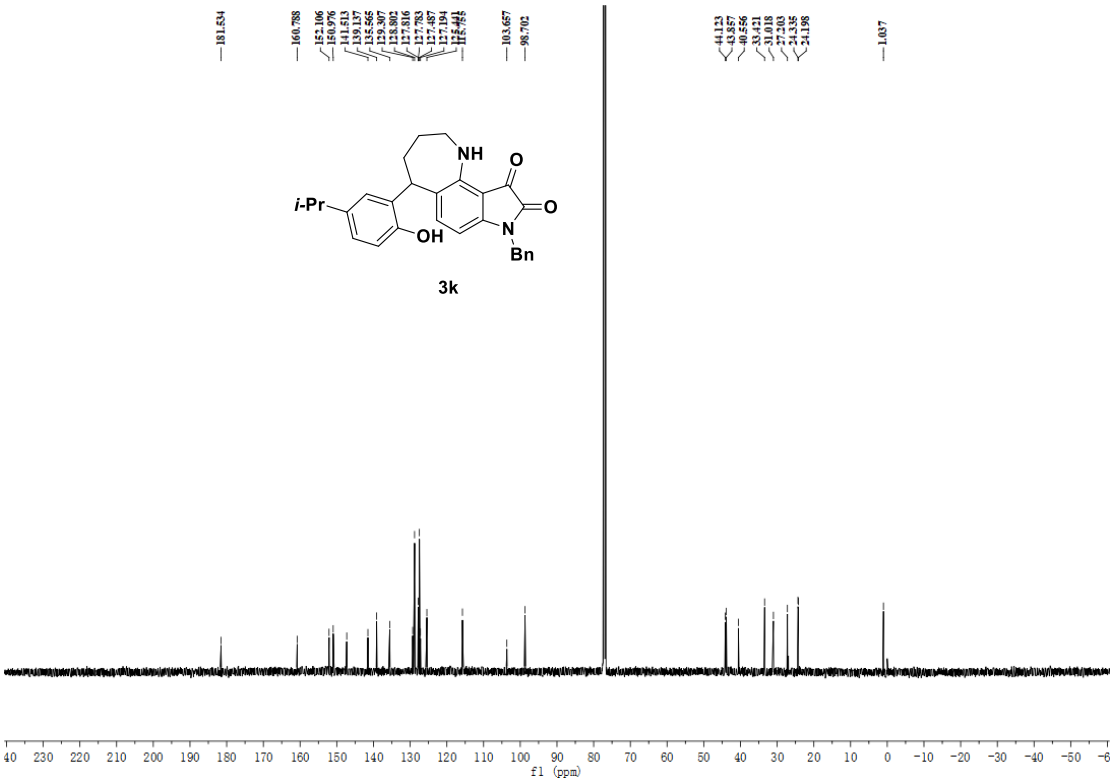
8-benzyl-5-(2-hydroxy-5-isopropylphenyl)-1,2,3,4,5,8-hexahydroazepino[2,3-*e*]indole-9,10-dione (3k)





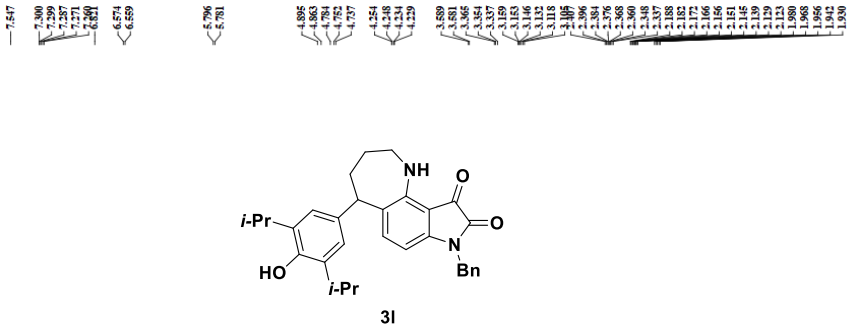
3k



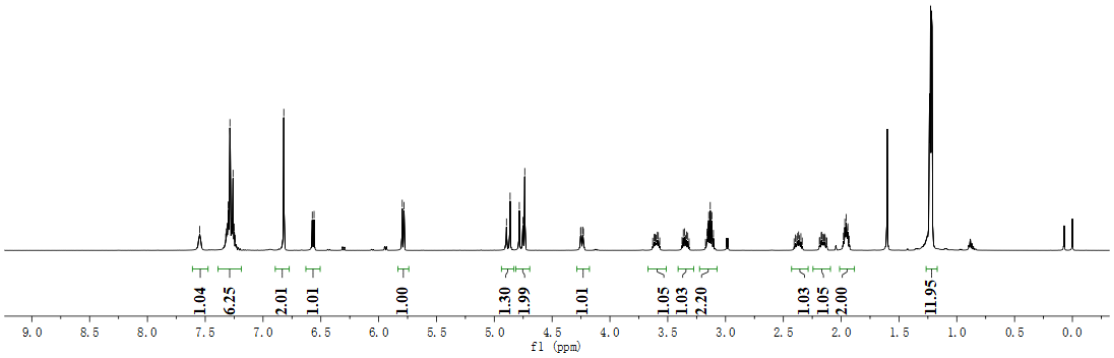


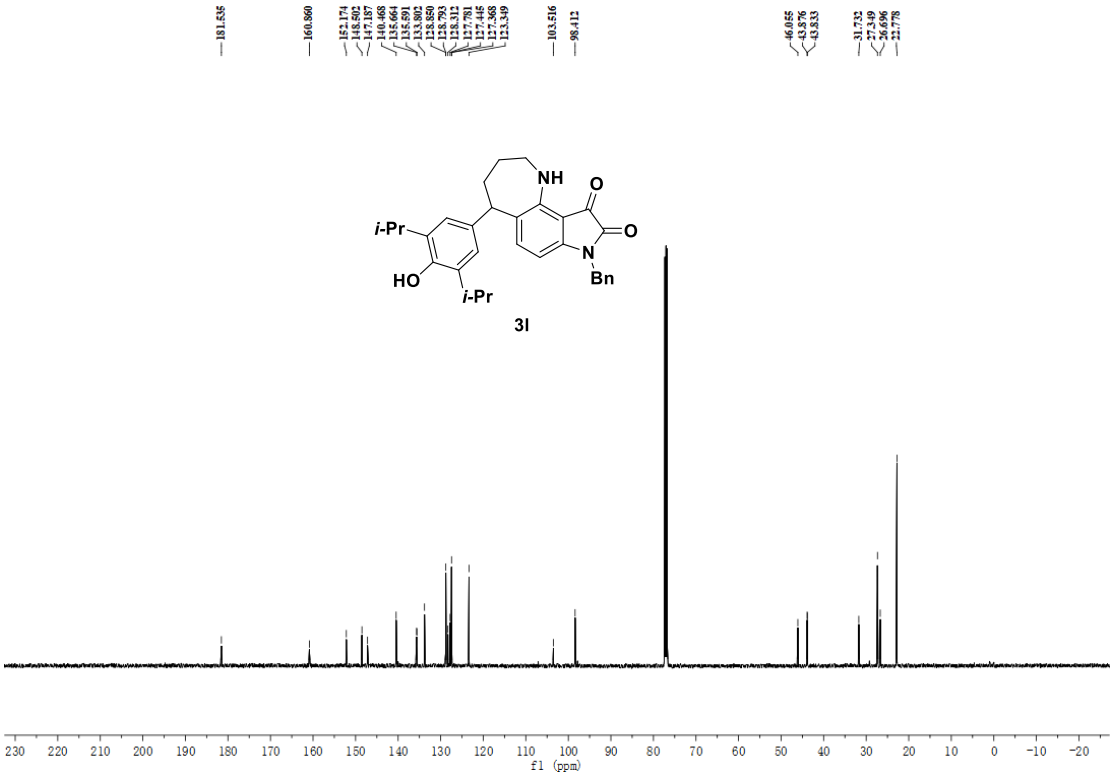
3k

8-benzyl-5-(4-hydroxy-3,5-diisopropylphenyl)-1,2,3,4,5,8-hexahydroazepino[2,3-*e*]indole-9,10-dione (3l)



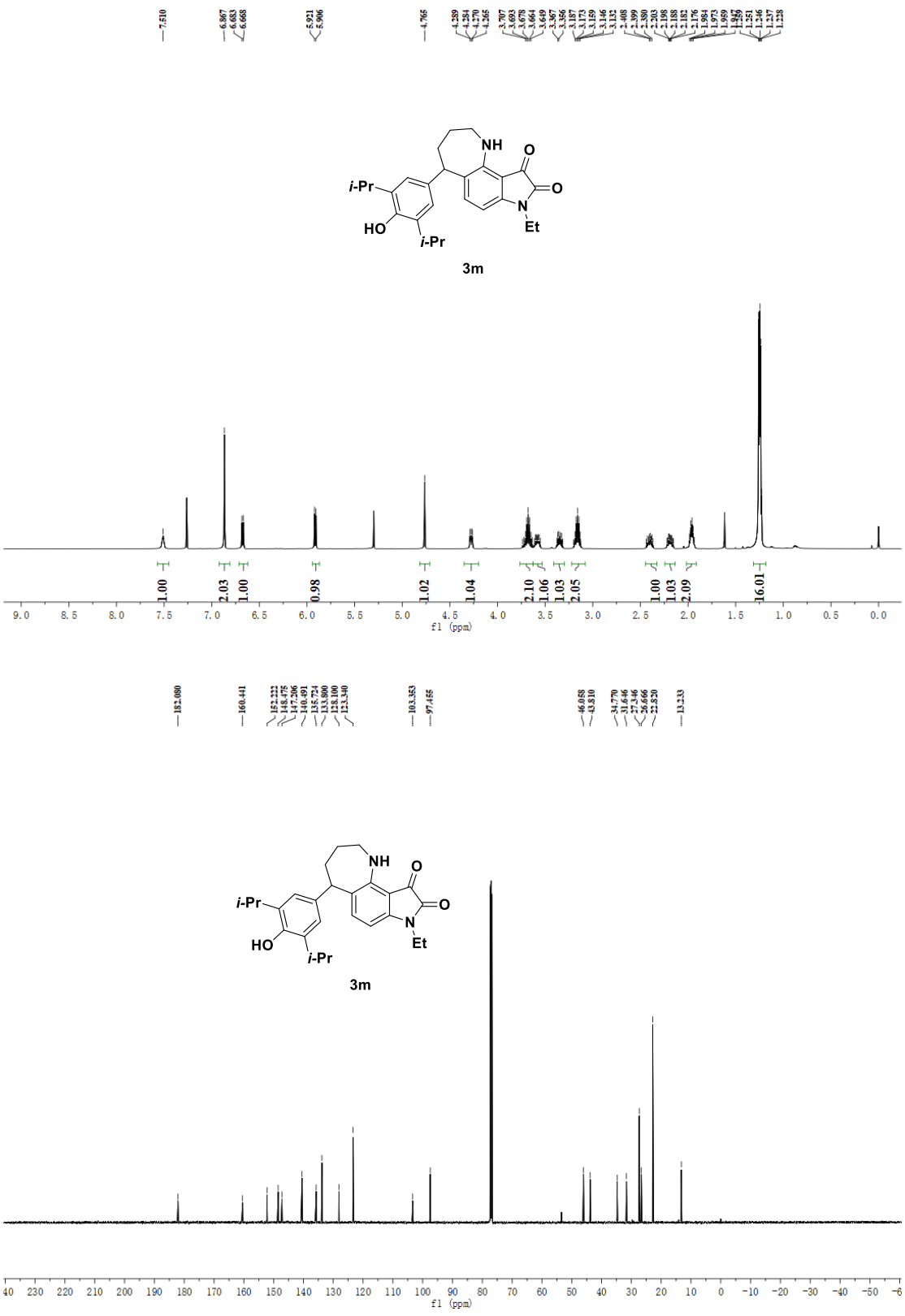
3l



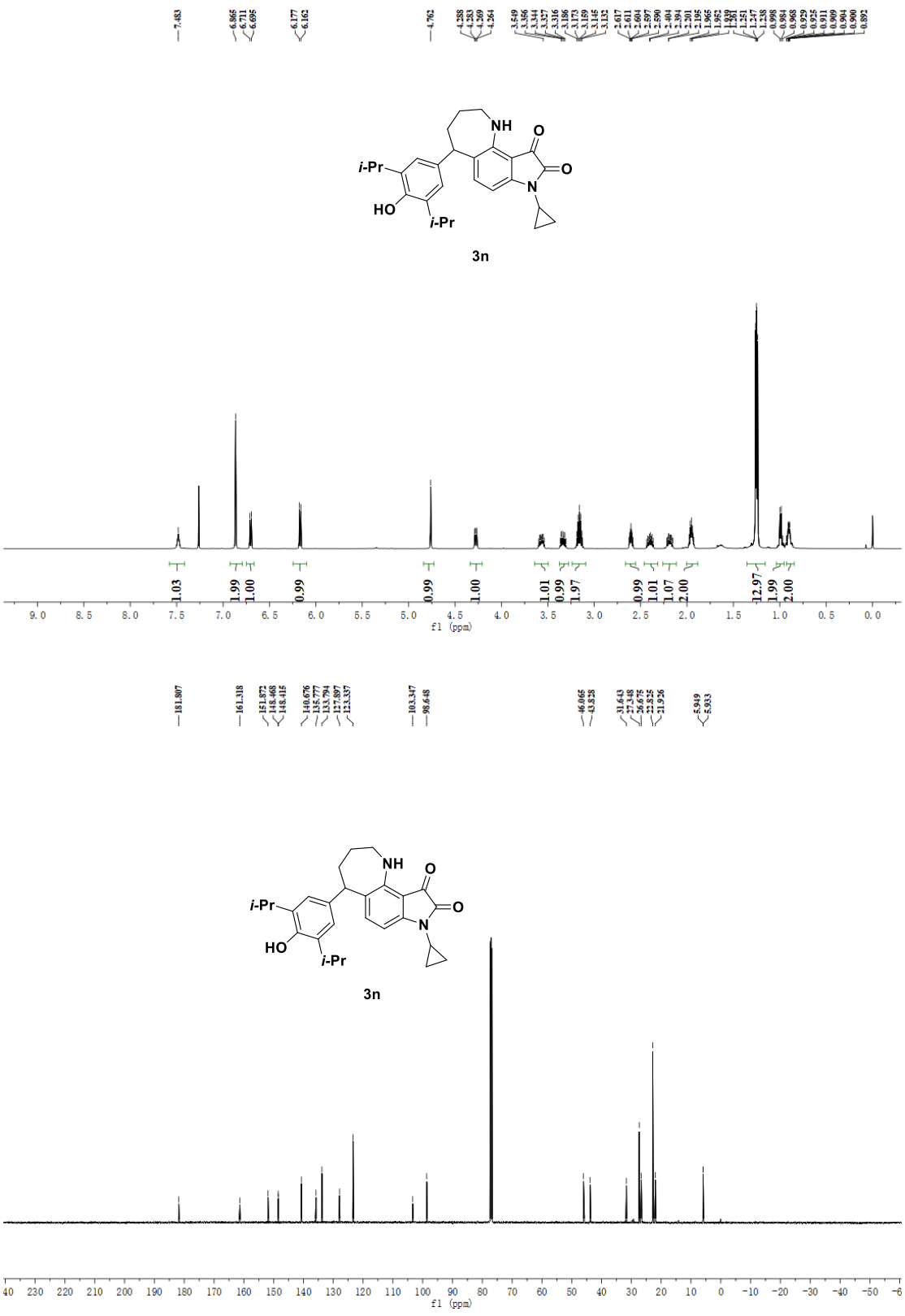


3l

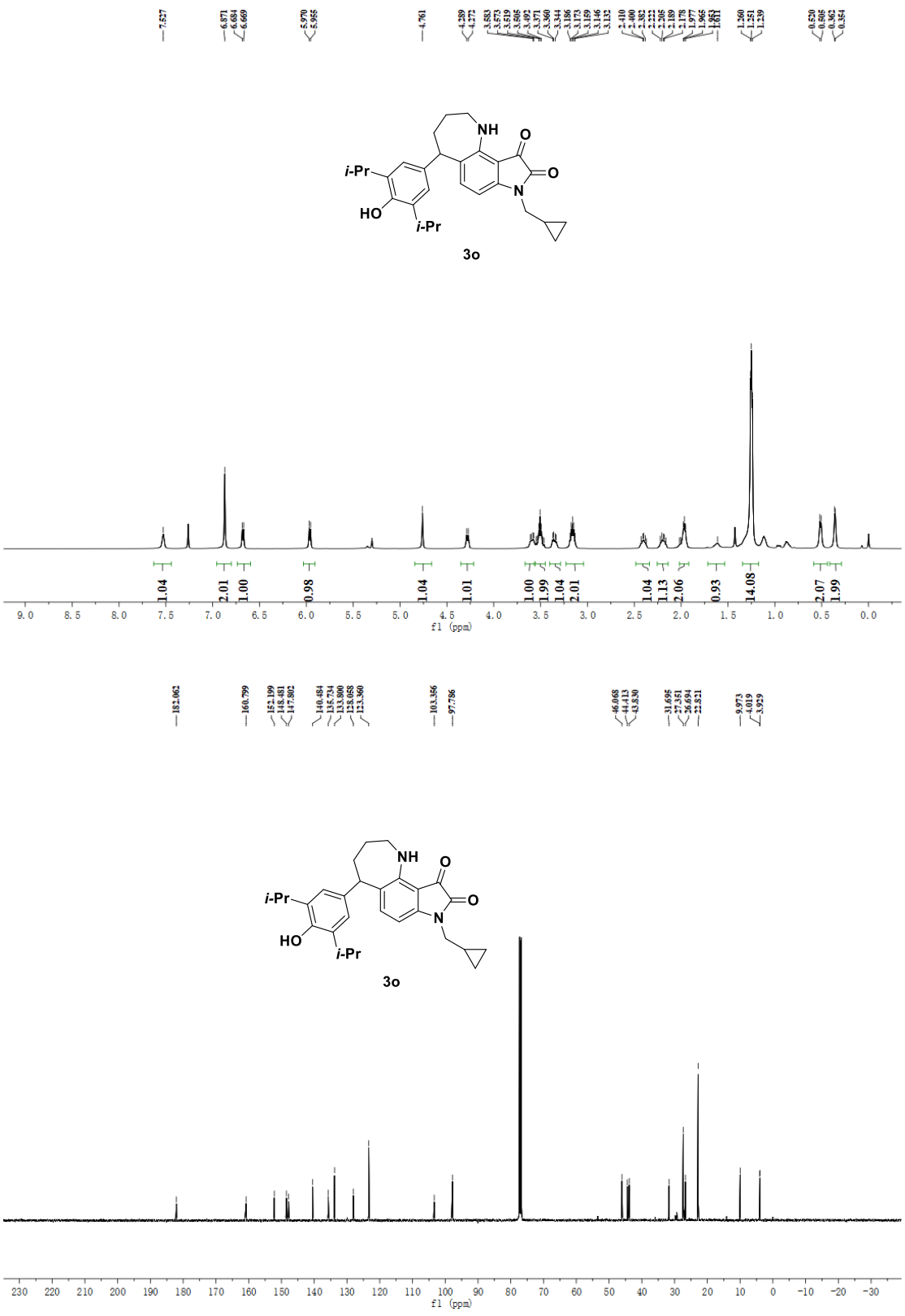
8-ethyl-5-(4-hydroxy-3,5-diisopropylphenyl)-1,2,3,4,5,8-hexahydroazepino[2,3-*e*]indole-9,10-dione (3m)



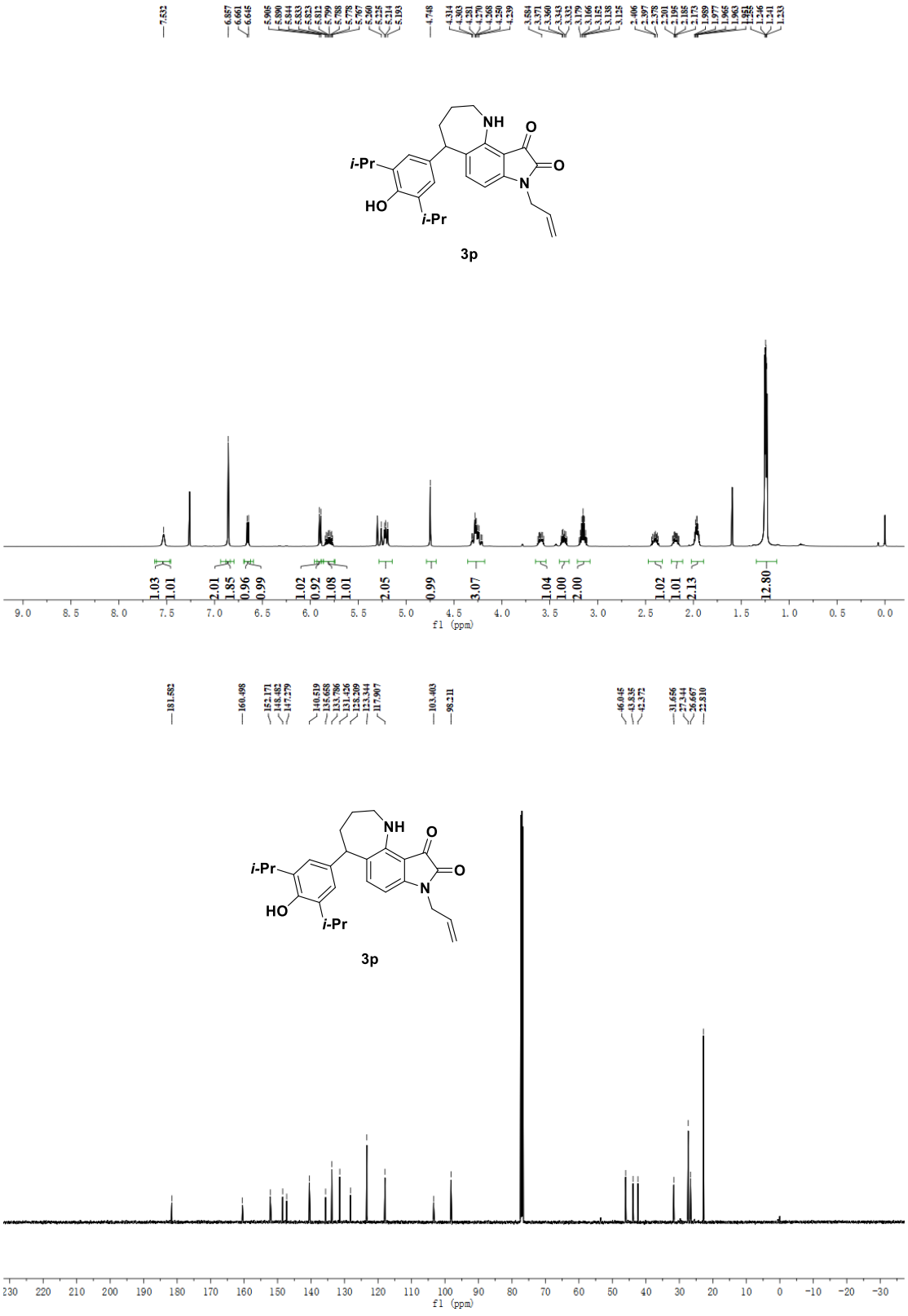
8-cyclopropyl-5-(4-hydroxy-3,5-diisopropylphenyl)-1,2,3,4,5,8-hexahydroazepino[2,3-*e*]indole-9,10-dione (3n)



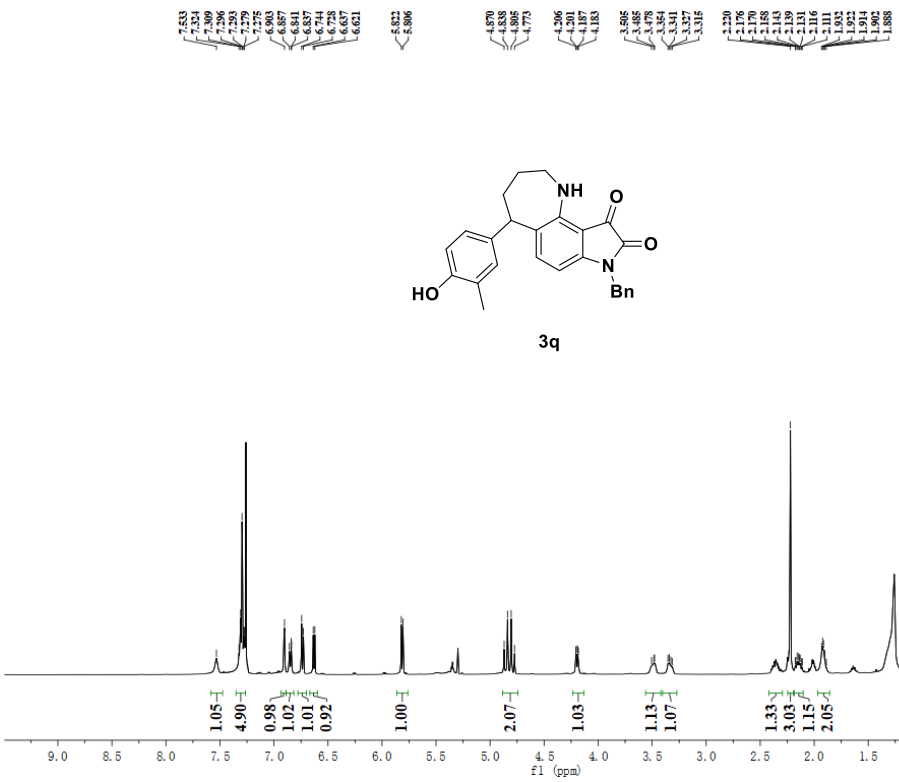
8-(cyclopropylmethyl)-5-(4-hydroxy-3,5-diisopropylphenyl)-1,2,3,4,5,8-hexahydroazepino[2, 3-*e*]indole-9,10-dione (3o)



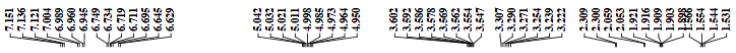
8-allyl-5-(4-hydroxy-3,5-diisopropylphenyl)-1,2,3,4,5,8-hexahydroazepino[2,3-*e*]indole-9,10-dione (3p)

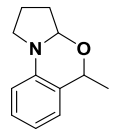


8-benzyl-5-(4-hydroxy-3-methylphenyl)-1,2,3,4,5,8-hexahydroazepino[2,3-*e*]indole-9,10-dion e (3q)



5-methyl-1,2,3,3a-tetrahydro-5*H*-benzo[*d*]pyrrolo[2,1-*b*][1,3]oxazine (8)





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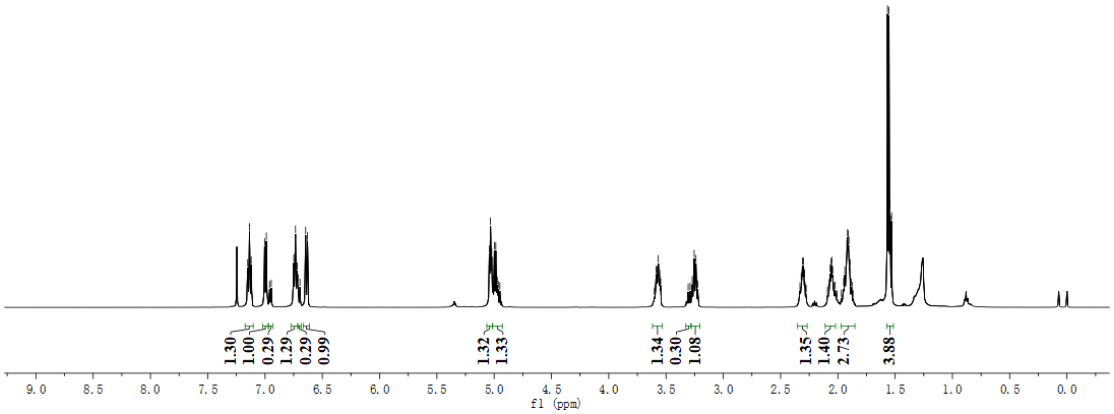

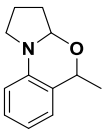

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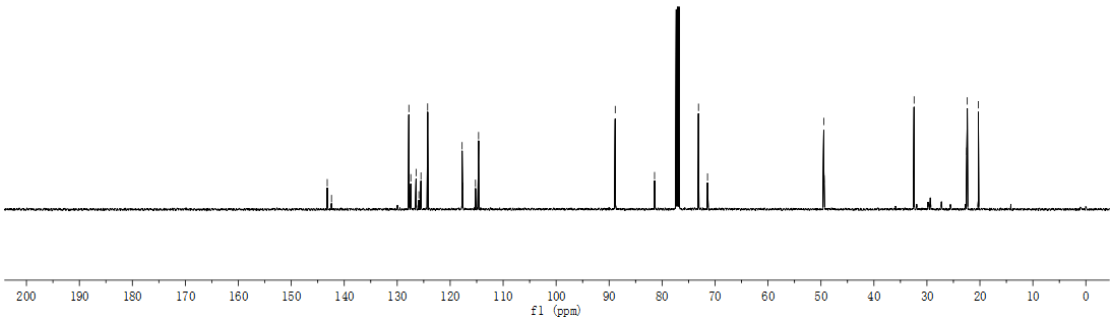
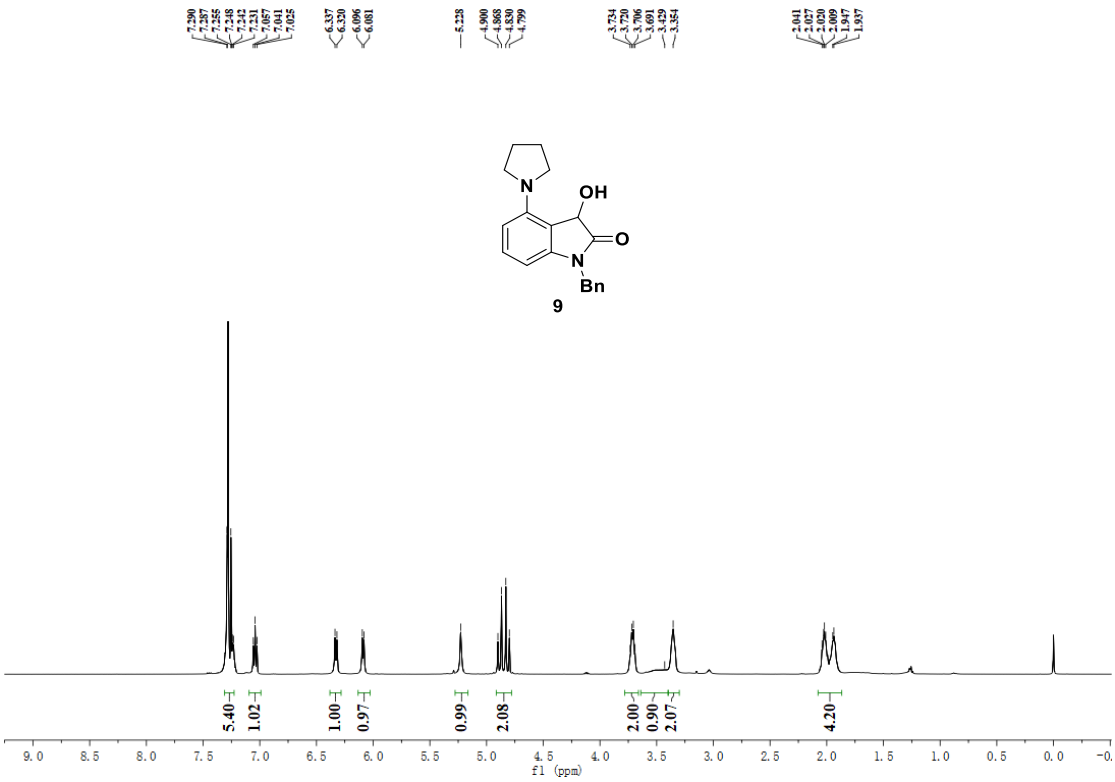
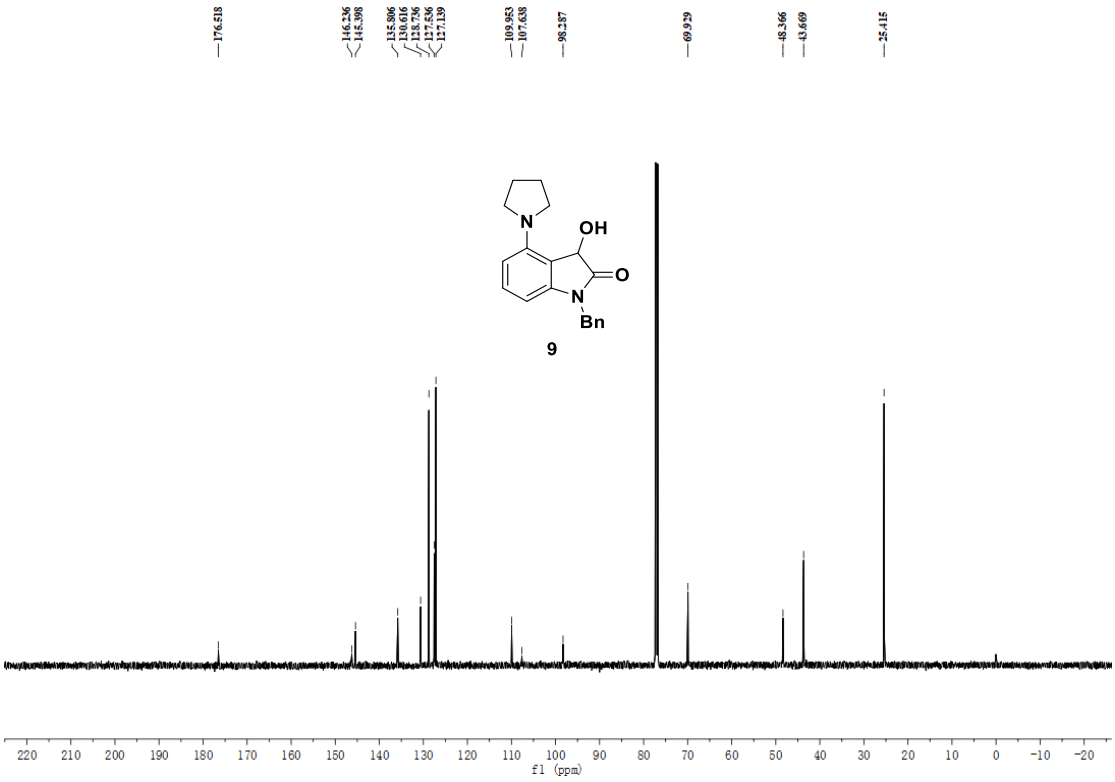
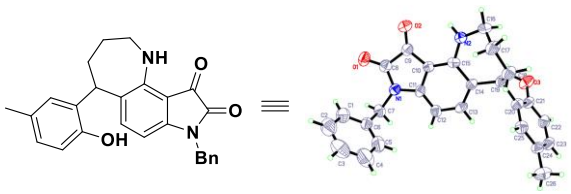


1-benzyl-3-hydroxy-4-(pyrrolidin-1-yl)indolin-2-one (9)





5. X-ray Crystallography of 3a



3a (CCDC 1829218)

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

Identification code	**3a**
Empirical formula	$C_{26}H_{24}N_2O_3$
Formula weight	412.47
Temperature	293(2) K
Wavelength	1.54184 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 7.4591(17) A alpha = 102.784(17) deg.
	b = 12.033(3) A beta = 94.976(16) deg.
	c = 12.1333(18) A gamma = 99.04(2) deg.
Volume	1040.5(4) A^3
Z, Calculated density	2, 1.317 Mg/m^3
Absorption coefficient	0.694 mm^-1
F(000)	436
Crystal size	0.08 x 0.07 x 0.07 mm
Theta range for data collection	3.77 to 67.24 deg.
Limiting indices	-8<=h<=8, -14<=k<=14, -14<=l<=9
Reflections collected / unique	6312 / 3691 [R(int) = 0.0865]
Completeness to theta = 67.24	99.0 %
Max. and min. transmission	0.9530 and 0.9466
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3691 / 0 / 283
Goodness-of-fit on F^2	0.917
Final R indices [I>2sigma(I)]	R1 = 0.0775, wR2 = 0.1627
R indices (all data)	R1 = 0.2325, wR2 = 0.2573
Extinction coefficient	0.0020(6)
Largest diff. peak and hole	0.194 and -0.236 e.A^-3