Supporting Information for

Catalytic Enantioselective Diels-Alder Reactions of Benzoquinones and Vinylindoles with Chiral Magnesium Phosphate Complexes

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Content

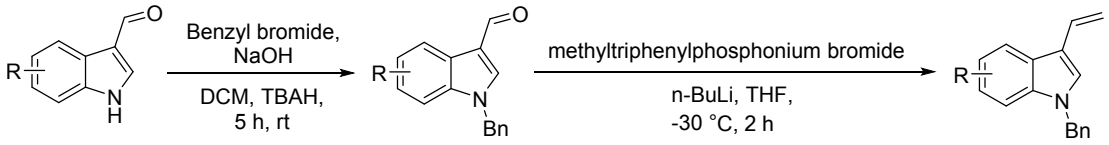
1. General Considerations

General Methods. ^{1}H, ^{13}C NMR spectra were recorded on Bruker AVANCE IIITM HD NanoBAY (400 MHz)and Bruker AVANCE III (600 MHz) instruments with chemical shifts reported relative to tetramethylsilane (TMS). Chemical shifts (δ) are reported in ppm relative to residual solvent signals for ^{1}H and ^{13}C NMR (^{1}H NMR: 7.26 ppm for $CDCl_3$, 7.16 ppm for C_6D_6, 2.50 ppm for DMSO-d_6, 2.05 ppm for acetone-d_6; ^{13}C NMR: 77.0 ppm for $CDCl_3$, 128.0 ppm for C_6D_6, 39.5 ppm for DMSO-d_6, 29.8 ppm for acetone-d_6). The HRMS data were measured on a Thermo Fisher Q Exactive HF LC-MS. Optical rotations were measured on a Rudolph Research Analytical Autopol IV polarimeter (λ 589) using a 700-μL cell with a path length of 1dm. The enantiomeric excess (ee) of the products was determined by chiral stationary phase HPLC (Chiralpak AD-H or Chiralpak OD-H or Chiralpak IA-H columns), using a UV detector operating at 254 nm. Melting points were measured on a Büchi smp-20 apparatus.

Materials. All reactions were carried out in flame-dried or oven-dried screw-cap test tubes and were allowed to proceed under a dry argon atmosphere with magnetic stirring. Analytical grade solvents and commercially available reagents were used as received, unless otherwise stated. Solvents were purified by passing through the column of activated alumina before use. Chromatographic purifications were performed using 200-300 mesh silica. Molecular Sieves (4Å) were flame-dried under high vacuum before use. Catalysts were prepared in some steps from (*R*)-BINOL, respectively, following literature procedures.[1] 3-Vinylindoles **2a-2r** were prepared by a Wittig reaction from the corresponding aldehydes, following a literature procedure as outlined below, and were stored at -20 °C. Racemic samples were prepared using Magnesium TRIP-Phosphoric Acid as a catalyst at room temperature.

2. General procedure for preparation of the 3-vinylindoles substrates

Synthesis of 3-vinylindoles substrates:



A) General procedure for protection of 3-vinylindoles:[2]

To a flame – dried flask equipped with a stir bar was added the corresponding enone (1 equiv) and DCM. Sodium hydroxide (2.5 equiv) and tetrabutylammonium hydrogensulfate (TBAH) (0.2 equiv) were then added as single portions. The reaction mixture was stirred at room temperature under nitrogen atmosphere for 0.5 hour. Benzyl bromide (1.2 equiv) was then added dropwise and the reaction was allowed to stir for 5 hours. After completion, the reaction was quenched with saturated NH_4Cl solution and extracted with DCM. The combined organic layers were washed with brine solution and then dried

over Na_2SO_4. After solvent was removed by rotary evaporation, the crude product was purified via flash column chromatography with a gradient of an appropriate eluent on silica gel (petroleum ether – ethyl acetate, 4:1).

B) The preparation of 3-vinylindoles through a Wittig reaction:[3]

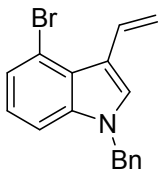
To a solution of methyltriphenylphosphonium bromide (1.5 equiv) in anhydrous THF under argon at -30 °C, n-BuLi (2.5 M in n-hexane; 1.5 equiv) was slowly added. The mixture was stirred at the indicated temperature for 1h. Then the solution of an indole-3-carboxaldehyde (1 equiv) in anhydrous THF was added dropwise to the ylide formed, the reaction was stirred at -30 °C for 1h. The resulting suspension was poured into Ether-H_2O (300:1, 30mL). The precipitate was filtered through a funnel and the filtrate was dried over Na_2SO_4. The solvent was evaporated under vacuum, the crude product was purified by flash chromatography on neutral aluminium oxide (petroleum ether – ethyl acetate, 30:1) and recrystallization give product **2a-2r**.

1-benzyl-3-vinyl-1H-indole (2a)

2a

White solid, 249mg, yield: 85%; M.P.: 76 – 78 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 6.9, 1.2 Hz, 1H), 7.30 – 7.28 (m, 4H), 7.23 – 7.15 (m, 3H), 7.13 (d, *J* = 7.2 Hz, 2H), 6.88 (dd, *J* = 17.8, 11.3 Hz, 1H), 5.69 (dd, *J* = 17.8, 1.3 Hz, 1H), 5.30 (s, 2H), 5.15 (dd, *J* = 11.3, 1.3 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.20, 137.14, 129.34, 128.85, 127.77, 127.64, 126.88, 126.44, 122.32, 120.34, 120.21, 114.84, 110.39, 110.00, 50.06. HRMS (ESI) calcd for $C_{17}H_{15}N$ $[M+H]^+$: 234.1277, found: 234.1279.

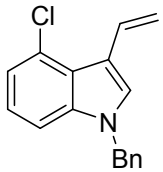
1-benzyl-4-bromo-3-vinyl-1H-indole (2b)



2b

Yellow solid, 339mg, yield: 87%; M.P.: 52 – 54 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 17.5, 10.9 Hz, 1H), 7.27 – 7.15 (m, 5H), 7.09 (d, *J* = 8.2 Hz, 1H), 7.00 (d, *J* = 7.1 Hz, 2H), 6.87 (t, *J* = 7.9 Hz, 1H), 5.36 (dd, *J* = 17.5, 1.7 Hz, 1H), 5.18 (s, 2H), 5.02 (dd, *J* = 10.9, 1.7 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.70, 135.54, 128.42, 127.84, 126.84, 125.68, 125.22, 124.10, 123.42, 121.61, 115.39, 113.56, 109.84, 108.24, 49.26. HRMS (ESI) calcd for $C_{17}H_{14}BrN$ $[M+H]^+$: 312.0382, found: 312.0384.

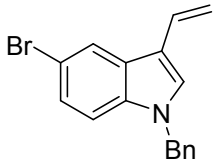
1-benzyl-4-chloro-3-vinyl-1H-indole (2c)



2c

Yellow solid, 265mg, yield: 79%; M.P.: 48 – 50 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 17.5, 10.9 Hz, 1H), 7.34 – 7.23 (m, 4H), 7.12 (d, *J* = 8.2 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 3H), 7.02 (t, *J* = 7.8 Hz, 1H), 5.45 (d, *J* = 17.5 Hz, 1H), 5.26 (s, 2H), 5.08 (d, *J* = 10.9 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.95, 136.66, 129.59, 128.92, 127.92, 126.80, 126.77, 125.86, 122.39, 121.07, 115.94, 110.95, 108.75, 50.33. HRMS (ESI) calcd for $C_{17}H_{14}ClN$ $[M+H]^+$: 268.0888, found: 268.0890.

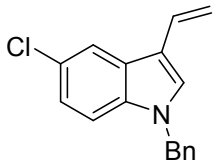
1-benzyl-5-bromo-3-vinyl-1H-indole (2d)



2d

White solid, 328mg, yield: 84%; M.P.: 50 – 52 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 1.7 Hz, 1H), 7.32 – 7.24 (m, 4H), 7.17 (s, 1H), 7.14 – 7.03 (m, 3H), 6.80 (dd, *J* = 17.8, 11.4 Hz, 1H), 5.64 (dd, *J* = 17.8, 1.2 Hz, 1H), 5.24 (s, 2H), 5.17 (dd, *J* = 11.4, 1.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.63, 135.77, 128.93, 128.60, 128.45, 127.95, 126.78, 125.12, 122.89, 114.46, 113.62, 111.45, 111.13, 50.28. HRMS (ESI) calcd for $C_{17}H_{14}BrN$ $[M+H]^+$: 312.0382, found: 312.0386.

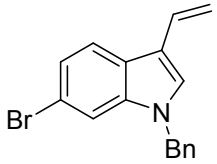
1-benzyl-5-chloro-3-vinyl-1H-indole (2e)



2e

White solid, 278mg, yield: 83%; M.P.: 42 – 44 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.33 – 7.27 (m, 3H), 7.16 (s, 1H), 7.14 – 7.10 (m, 2H), 7.06 (d, *J* = 6.9 Hz, 2H), 6.79 (dd, *J* = 17.8, 11.3 Hz, 1H), 5.63 (d, *J* = 17.8 Hz, 1H), 5.21 (s, 2H), 5.16 (d, *J* = 11.3 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.68, 135.53, 128.94, 128.68, 128.68, 127.95, 127.42, 126.80, 126.04, 122.58, 119.84, 114.53, 111.03, 111.02, 50.30. HRMS (ESI) calcd for $C_{17}H_{14}ClN$ $[M+H]^+$: 268.0888, found: 268.0891.

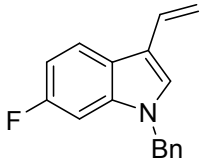
1-benzyl-6-bromo-3-vinyl-1H-indole (2f)



2f

White solid, 328mg, yield: 84%; M.P.: 94 – 95 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.4 Hz, 1H), 7.42 (s, 1H), 7.34 – 7.25 (m, 4H), 7.17 – 7.04 (m, 3H), 6.82 (dd, *J* = 17.8, 11.3 Hz, 1H), 5.65 (d, *J* = 17.8 Hz, 1H), 5.22 (s, 2H), 5.17 (d, *J* = 11.3 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.96, 136.53, 128.97, 128.74, 127.97, 126.80, 125.28, 123.42, 121.51, 115.96, 115.06, 112.91, 111.14, 50.09. HRMS (ESI) calcd for $C_{17}H_{14}BrN$ $[M+H]^+$: 312.1382, found: 312.0390.

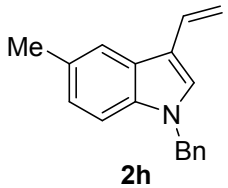
1-benzyl-6-fluoro-3-vinyl-1H-indole (2g)



2g

White solid, 274mg, yield: 87%; M.P.: 93 – 95 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 9.4, 5.3 Hz, 1H), 7.35 – 7.27 (m, 3H), 7.17 (s, 1H), 7.12 (d, *J* = 7.1 Hz, 2H), 6.93 (ddd, *J* = 9.4, 6.2, 2.4 Hz, 2H), 6.83 (dd, *J* = 17.8, 11.3 Hz, 1H), 5.66 (dd, *J* = 17.8, 1.0 Hz, 1H), 5.22 (s, 2H), 5.16 (dd, *J* = 11.3, 1.0Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.76, 159.18, 137.27, 136.60, 128.97, 128.92, 127.98, 127.88, 127.86, 126.83, 122.95, 121.14, 121.07, 115.01, 110.79, 108.88, 108.71, 96.56, 96.39, 50.26. HRMS (ESI) calcd for $C_{17}H_{14}FN$ $[M+H]^+$: 252.1183, found: 252.1184.

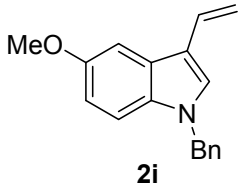
1-benzyl-5-methyl-3-vinyl-1H-indole (2h)



2h

White solid, 270mg, yield: 87%; M.P.: 47 – 49 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.33 – 7.26 (m, 3H), 7.17 (t, *J* = 4.1 Hz, 2H), 7.13 (d, *J* = 7.0 Hz, 2H), 7.05 (dd, *J* = 8.3, 1.1 Hz, 1H), 6.89 (dd, *J* = 17.8, 11.3 Hz, 1H), 5.71 (dd, *J* = 17.8, 1.4 Hz, 1H), 5.27 (s, 2H), 5.17 (dd, *J* = 11.3, 1.4 Hz, 1H), 2.50 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.19, 134.50, 128.41, 128.38, 127.72, 126.69, 126.59, 125.71, 125.56, 122.75, 118.99, 113.22, 108.93, 108.58, 48.99, 20.56, 20.53. HRMS (ESI) calcd for $C_{18}H_{17}N$ $[M+H]^+$: 248.1434, found: 248.1436.

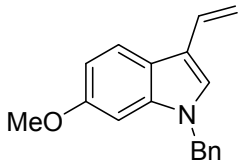
1-benzyl-5-methoxy-3-vinyl-1H-indole (2i)



2i

White solid, 254mg, yield: 77%; M.P.: 57 – 59 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 – 7.25 (m, 4H), 7.20 – 7.04 (m, 4H), 6.91 – 6.81 (m, 2H), 5.62 (dd, *J* = 17.8, 1.1 Hz, 1H), 5.25 (s, 2H), 5.13 (dd, *J* = 11.3, 1.1 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.61, 137.17, 132.42, 129.35, 128.83, 128.11, 127.73, 126.80, 114.34, 112.23, 110.72, 109.80, 102.34, 100.00, 55.94, 50.28. HRMS (ESI) calcd for $C_{18}H_{17}NO$ $[M+H]^+$: 264.1383, found: 264.1386.

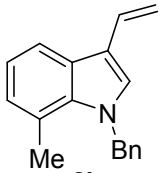
1-benzyl-6-methoxy-3-vinyl-1H-indole (2j)



2j

White solid, 267mg, yield: 81%; M.P.: 59 – 61°C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.7 Hz, 1H), 7.28 – 7.23 (m, 3H), 7.11 (d, *J* = 7.0 Hz, 2H), 7.06 (s, 1H), 6.83 (ddd, *J* = 15.4, 10.2, 8.2 Hz, 2H), 6.71 (d, *J* = 2.2 Hz, 1H), 5.66 (dd, *J* = 17.8, 1.3 Hz, 1H), 5.21 (s, 2H), 5.12 (dd, *J* = 11.3, 1.3 Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.55, 138.11, 137.07, 129.45, 128.85, 127.74, 126.86, 121.03, 120.75, 114.88, 110.15, 109.63, 108.24, 93.75, 55.67, 50.01. HRMS (ESI) calcd for $C_{18}H_{17}NO$ $[M+H]^+$: 264.1383, found: 264.1385.

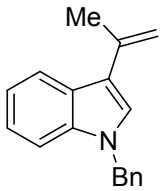
1-benzyl-7-methyl-3-vinyl-1H-indole (2k)



2k

White solid, 267mg, yield: 86%; M.P.: 64 – 66 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 7.6, 4.8 Hz, 1H), 7.30 – 7.19 (m, 3H), 7.11 (s, 1H), 7.05 (td, *J* = 7.6, 4.4 Hz, 1H), 6.87 (ddd, *J* = 15.3, 13.4, 5.7 Hz, 4H), 5.66 (dd, *J* = 17.8, 3.6 Hz, 1H), 5.50 (s, 2H), 5.14 (dd, *J* = 11.3, 3.6 Hz, 1H), 2.49 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.29, 135.85, 129.25, 129.09, 128.92, 127.62, 127.45, 125.51, 125.25, 121.34, 120.44, 118.14, 114.73, 110.46, 52.29, 19.62. HRMS (ESI) calcd for $C_{18}H_{17}N$ $[M+H]^+$: 248.1434, found: 248.1436.

1-benzyl-3-(prop-1-en-2-yl)-1H-indole (2l)[4]

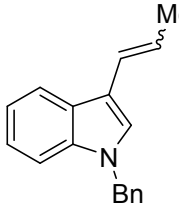


2l

To a flame – dried flask equipped with a stir bar was added the 1-(1H-indol-3-yl)ethan-1-one (1 equiv) and DCM. Sodium hydroxide (2.5 equiv) and tetrabutylammonium hydrogensulfate (TBAH) (0.2 equiv) were then added as single portions. The reaction mixture was stirred at room temperature under nitrogen atmosphere for 0.5 hour. Benzyl bromide (1.2 equiv) was then added dropwise and the reaction was allowed to stir for 5 hours. After completion, the reaction was quenched with saturated NH_4Cl solution and extracted with DCM. The combined organic layers were washed with brine solution and then dried over Na_2SO_4. After solvent was removed by rotary evaporation, the crude product was purified via flash column chromatography with a gradient of an appropriate eluent on silica gel (petroleum ether – ethyl acetate, 4:1).

To a stirred suspension of methyltriphenylphoshonium bromide (1.5 equiv) in THF, cooled to 0 ^oC, n-BuLi (1.5 equiv, 2.5 M in hexanes) was slowly added. The resulting yellow suspension was stirred for 2 h at the same temperature, then 1-(1-benzyl-1H-indol-3-yl) ethan-1-one (1.0 equiv) was added in one portion. The mixture was stirred overnight at room temperature, and then it poured into Ether-H_2O (300:1, 30 mL). The precipitate was filtered through a funnel and the filtrate was dried over Na_2SO_4. The solvent was evaporated under vacuum; the crude product was purified by flash chromatography on neutral aluminium oxide (petroleum ether-ethyl acetate, 30:1) to give the title compound in 67% yield as a white solid. 208mg. M.P.: 88 – 90 ^oC. ^1H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.1 Hz, 1H), 7.40 – 7.26 (m, 7H), 7.21 (d, *J* = 7.4 Hz, 2H), 5.62 (s, 1H), 5.38 (s, 2H), 5.17 (s, 1H), 2.28 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.64, 136.18, 127.71, 127.58, 126.58, 125.76, 125.64, 125.06, 120.99, 120.08, 119.07, 116.45, 108.86, 108.54, 48.91, 22.26. HRMS (ESI) calcd for $C_{18}H_{17}N$ $[M+H]^+$: 248.1434, found: 248.1437.

(E/Z)-1-benzyl-3-(prop-1-en-1-yl)-1H-indole (2m)[5]

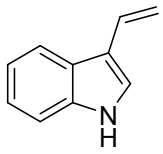


2m

To a suspension of ethyltriphenylphosphonium bromide (1.5 equiv) in THF (20 mL) was added phenyllithium in 2.5 M n-BuLi solution (1.5 equiv) at room temperature and the mixture was stirred for 10 min. The solution was cooled to -78 ^oC and an indole-3-carboxaldehyde (1 equiv) in THF (10 mL) was added dropwise. After stirring for 5 min at -78 ^oC and then the mixture was stirred for overnight at room temperature. After cooling to 0 ^oC, the reaction mixture was quenched by saturated aqueous NH_4Cl solution and extracted with Et_2O (×3). The combined organic layers were washed with brine, dried over Na_2SO_4, and evaporated in vacuo. The residue was purified by flash chromatography on neutral aluminium oxide (elution with hexane) to give **2m** as a 4:1 *E/Z* mixture in 57% yield. 212mg. M.P.: 66 – 68 ^oC. ^1H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.7 Hz, 0.2H), 7.69 (d, *J* = 7.8 Hz, 0.8H), 7.27

(dt, *J* = 18.5, 5.3 Hz, 4H), 7.22 – 7.09 (m, 5H), 6.67 (dd, *J* = 11.3, 0.9 Hz, 0.8H), 6.56 (dd, *J* = 15.9, 1.5 Hz, 0.2H), 6.19 (dq, *J* = 15.9, 6.6 Hz, 0.2H), 5.75 (dq, *J* = 11.3, 7.0 Hz, 0.8H), 5.34 (s, 1.6H), 5.27 (s, 0.4H), 1.91 (dt, *J* = 8.2, 2.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.42, 135.94, 128.80, 128.78, 128.22, 127.64, 126.82, 126.71, 126.02, 123.15, 122.45, 122.17, 122.07, 120.47, 120.17, 119.76, 119.58, 119.22, 113.08, 109.80, 109.61, 50.15, 49.97, 18.99, 15.69. HRMS (ESI) calcd for $C_{18}H_{17}N$ $[M+H]^+$: 248.1434, found: 248.1440.

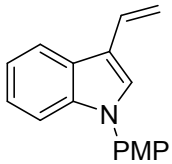
3-vinyl-1H-indole (2n)



2n

White solid, 319mg, yield: 89%; M.P.: 80 – 81 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 – 7.69 (m, 2H), 7.32 (d, *J* = 7.7 Hz, 1H), 7.26 – 7.12 (m, 3H), 6.89 (dd, *J* = 17.8, 11.3 Hz, 1H), 5.70 (d, *J* = 17.8 Hz, 1H), 5.17 (d, *J* = 11.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.78, 129.45, 125.67, 123.47, 122.53, 120.38, 120.13, 115.88, 111.33, 110.79. HRMS (ESI) calcd for $C_{10}H_9N$ $[M+H]^+$: 143.1890, found: 143.1883.

1-(4-methoxyphenyl)-3-vinyl-1H-indole (2o)[3]



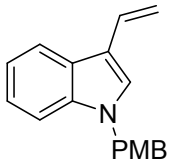
2o

1H-indole-3-carbaldehyde (1.5 equiv), CuOAc (1.1 equiv) and the 4-iodoanisole (1.0 equiv) were placed in a reaction vessel under a stream of argon. The reaction vessel was evacuated and backfilled with argon. Anhydrous DMA (10 mL) was then added by syringe at room temperature under a stream of argon and the mixture was stirred under argon at 160 °C for 48 h. After this period, the reaction was then allowed to cool to room temperature and had been treated with a saturated aqueous NH_4Cl solution and extracted with EtOAc. The organic extract was washed with brine, dried, filtered and concentrated under reduced pressure, and the residue was purified by flash chromatography on silica gel with a mixture of hexane and ethyl acetate (5:1) as eluent to give the product for the next step.

And then to a solution of methyltriphenylphosphonium bromide (1.5 equiv) in anhydrous THF under argon at -30 °C, n-BuLi (2.5 M in n-hexane; 1.5 equiv) was slowly added. The mixture was stirred at the indicated temperature for 1h. Then the solution of the product of the last step (1 equiv) in anhydrous THF was added dropwise to the ylide formed, the reaction was stirred at -30 °C for 1h. The resulting suspension was poured into Ether-H_2O (300:1, 30 mL). The precipitate was filtered through a funnel and the filtrate was dried over Na_2SO_4. The solvent was evaporated under vacuum; the crude product was purified by flash chromatography on neutral aluminium oxide (petroleum ether-ethyl acetate, 30:1) and recrystallization give **2o** as a white solid in 62% yield. 233mg. M.P.: 56 – 58 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 7.2, 1.7 Hz, 1H), 7.37 – 7.33 (m, 1H), 7.32 – 7.26 (m, 3H), 7.15 (dq, *J* = 5.6, 1.9 Hz, 2H), 6.97 – 6.92 (m, 2H), 6.86 (dd, *J* = 17.8, 11.3 Hz, 1H), 5.68 (dd, *J* = 17.8, 1.2 Hz, 1H), 5.14 (dd, *J* = 11.3, 1.2 Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (151 MHz,

$CDCl_3$) δ 158.42, 137.25, 132.32, 129.08, 127.45, 126.68, 126.07, 122.71, 120.68, 120.26, 115.83, 114.78, 111.08, 110.68, 55.63. HRMS (ESI) calcd for $C_{17}H_{15}NO$ $[M+H]^+$: 250.1226, found: 250.1224.

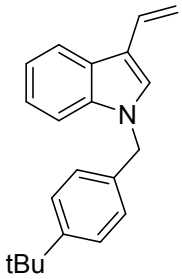
1-(4-methoxybenzyl)-3-vinyl-1H-indole (2p)



2p

Following the general procedure, the title compound was obtained from 1H-indole-3-carbaldehyde and 4-methoxybenzyl bromide as a white solid in 85% yield. 281mg. M.P.: 66 – 68 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.0 Hz, 1H), 7.27 (d, *J* = 7.9 Hz, 1H), 7.21 – 7.12 (m, 3H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.90 – 6.77 (m, 3H), 5.67 (d, *J* = 17.8 Hz, 1H), 5.17 (s, 2H), 5.13 (d, *J* = 11.2 Hz, 1H), 3.74 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.19, 137.15, 129.38, 129.07, 128.36, 127.49, 126.48, 122.23, 120.31, 120.15, 114.70, 114.20, 110.25, 110.01, 109.94, 55.33, 55.31, 49.56. HRMS (ESI) calcd for $C_{18}H_{17}NO$ $[M+H]^+$: 264.1383, found: 264.1385.

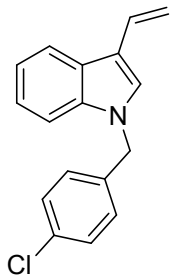
1-(4-(tert-butyl)benzyl)-3-vinyl-1H-indole (2q)



2q

Following the general procedure, the title compound was obtained between 1H-indole-3-carbaldehyde and 4-tert-butylbenzyl bromide as a white solid in 85% yield. 308mg. M.P.: 51 – 53 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 7.1, 1.0 Hz, 1H), 7.32 – 7.27 (m, 3H), 7.21 – 7.14 (m, 3H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.87 (dd, *J* = 17.8, 11.3 Hz, 1H), 5.68 (dd, *J* = 17.8, 1.4 Hz, 1H), 5.22 (s, 2H), 5.13 (dd, *J* = 11.3, 1.4 Hz, 1H), 1.27 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.76, 137.27, 134.14, 129.38, 127.56, 126.68, 126.46 125.74, 122.23, 120.29, 120.13, 114.81, 110.26, 109.99, 49.71, 34.55, 31.35. HRMS (ESI) calcd for $C_{21}H_{23}N$ $[M+H]^+$: 290.1903, found: 290.1904.

1-(4-chlorobenzyl)-3-vinyl-1H-indole (2r)



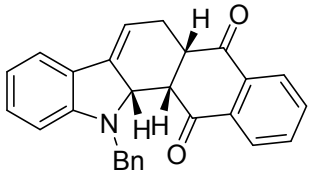
2r

Following the general procedure, the title compound was obtained from 1H-indole-3-carbaldehyde and 4-chlorobenzyl chloride as a white solid in 76% yield. 255mg. M.P.: 59 – 61 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 6.5, 1.7 Hz, 1H), 7.27 (d, *J* = 1.7 Hz, 2H), 7.23 – 7.17 (m, 4H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.88 (dd, *J* = 17.8, 11.3 Hz, 1H), 5.70 (dd, *J* = 17.8, 1.3 Hz, 1H), 5.26 (s, 2H), 5.17 (dd, *J* = 11.3, 1.3 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.03, 135.62, 133.59, 129.12, 129.01, 128.14, 127.30, 126.50, 122.43, 120.39, 120.32, 115.13, 110.66, 109.82, 49.45. HRMS (ESI) calcd for $C_{17}H_{14}ClN$ $[M+H]^+$: 268.0888, found:268.0891.

3. General procedure for the organocatalytic, enantioselective Diels-Alder reaction

4 Å MS (30 mg) were added to a reaction tube and flame dried in situ. Then substrate **1a-1i** (1 equiv, 0.05 mmol), catalyst Mg[**P4**]$_2$ (3.6 mg, 5 mol%) and **2a-2r** (1.5 equiv, 0.075 mmol) were added, and then the tube was removed under argon. The resulting mixture was stirred at -25 ^{o}C for 10 min. Then anhydrous methylcyclohexane (1 mL) was added via a syringe. The mixture was then stirred overnight at the same temperature to give the crude product. The crude product was purified by washing with hexane and MeOH to give the pure D-A corresponding product **3a-3i** and **4b-4r**. Then the product **3a-3i** and **4b-4r** was analyzed by HPLC.

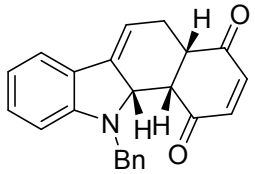
(5a*S*,12a*S*,12b*S*)-12-benzyl-6,12,12a,12b-tetrahydro-5*H*-naphtho[2,3-*a*]carbazole-5,13(5a*H*)-dione (3a)



3a

Yellow solid, 18mg, yield: 91%; M.P.: 141 – 143 ^{o}C. $[\alpha]^{20}_{D}$ = +281.7°(c 0.43, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 8H), 7.13 (t, *J* = 7.4 Hz, 1H), 6.72 (t, *J* = 7.4 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 6.58 – 6.46 (m, 2H), 5.75 (dd, *J* = 8.0, 3.9 Hz, 1H), 4.42 (dd, *J* = 50.2, 15.7 Hz, 2H), 4.12 – 4.06 (m, 1H), 3.34 (t, *J* = 5.2 Hz, 1H), 3.17 (dd, *J* = 13.8, 8.3 Hz, 1H), 2.55 – 2.39 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.25, 196.57, 154.00, 140.59, 138.75, 137.99, 137.65, 129.88, 128.64, 127.73, 127.44, 125.90, 120.50, 118.38, 109.88, 109.07, 64.68, 52.37, 47.51, 46.30, 26.94. HRMS (ESI) calcd for $C_{27}H_{21}NO_2$ $[M+H]^+$: 392.1645, found: 392.1647. The enantiomeric excess was determined to be 96% by HPLC analysis on Chiralpak AD column (20% isopropanol/hexane, 1 mL/min), UV 254 nm, t_1 (minor) = 12.4 min, t_2 (major) = 14.9 min.

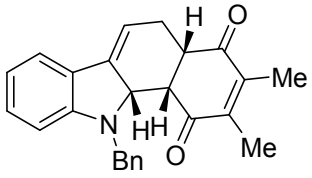
(4a*S*,11a*S*,11b*S*)-11-benzyl-5,11,11a,11b-tetrahydro-1*H*-benzo[*a*]carbazole-1,4(4a*H*)-dione (3b)



3b

Red solid, 17mg, yield: 98%; M.P.: 128-130 ^{o}C. $[\alpha]^{20}_{D}$ = +280°(c 0.25, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 6H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.72 (t, *J* = 7.5 Hz, 1H), 6.63 (d, *J* = 7.9 Hz, 1H), 6.50 (d, *J* = 50.2 Hz, 2H), 5.74 (d, *J* = 2.8 Hz, 1H), 4.42 (dd, *J* = 50.2, 15.7 Hz, 2H), 4.13 – 4.02 (m, 1H), 3.34 (t, *J* = 4.6 Hz, 1H), 3.16 (dd, *J* = 13.3, 7.6 Hz, 1H), 2.55 – 2.40 (m, 2H).^{13}C NMR (151 MHz, $CDCl_3$) δ 200.22, 196.54, 154.01, 140.59, 138.79, 138.00, 137.66, 129.88, 128.64, 127.74, 127.43, 125.90, 120.49, 118.37, 109.86, 109.05, 64.69, 52.36, 47.52, 46.27, 26.95. HRMS (ESI) calcd for $C_{23}H_{19}NO_2$ $[M+H]^+$: 342.1489, found: 342.1496. The enantiomeric excess was determined to be 97% by HPLC analysis on Chiralpak OD column (30% isopropanol/hexane, 1 mL/min), UV 254 nm, t_1 (minor) = 22.1 min, t_2 (major) = 33.3 min.

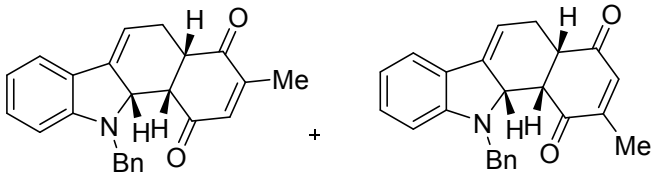
(4a*S*,11a*S*,11b*S*)-11-benzyl-2,3-dimethyl-5,11,11a,11b-tetrahydro-1*H*-benzo[*a*]carbazole-1,4(4a*H*)-dione (3c)



3c

Yellow solid, 18mg, yield: 95%; M.P.: 150 – 152 °C. $[\alpha]^{20}_D$ = +174.3°(c 0.54, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 5H), 7.25 – 7.22 (m, 1H), 7.13 (t, *J* = 7.4 Hz, 1H), 6.69 (dt, *J* = 24.8, 6.1 Hz, 2H), 5.71 (dd, *J* = 7.9, 3.8 Hz, 1H), 4.44 (q, *J* = 15.8 Hz, 2H), 4.10 – 4.03 (m, 1H), 3.32 (t, *J* = 5.2 Hz, 1H), 3.20 – 3.15 (m, 1H), 2.48 (ddt, *J* = 18.5, 7.4, 3.6 Hz, 1H), 2.34 (dtd, *J* = 13.3, 8.7, 4.2 Hz, 1H), 1.87 (d, *J* = 9.0 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.98, 197.18, 153.84, 146.13, 141.89, 138.81, 138.03, 129.80, 128.57, 127.79, 127.38, 125.93, 120.47, 118.17, 109.77, 108.70, 64.50, 51.87, 47.51, 45.73, 27.42, 13.15, 12.61. HRMS (ESI) calcd for $C_{25}H_{23}NO_2$ $[M+H]^+$: 370.1802, found: 370.1810. The enantiomeric excess was determined to be 98% by HPLC analysis on Chiralpak OD column (20% isopropanol/hexane, 1 mL/min), UV 254 nm t_1 (minor) = 11.5 min, t_2 (major) = 13.4 min.

(4a*S*,11a*S*,11b*S*)-11-benzyl-3-methyl-5,11,11a,11b-tetrahydro-1*H*-benzo[*a*]carbazole-1,4(4a*H*)-dione and (4a*S*,11a*S*,11b*S*)-11-benzyl-2-methyl-5,11,11a,11b-tetrahydro-1*H*-benzo[*a*]carbazole-1,4 (4a*H*)-dione (3d and 3d')

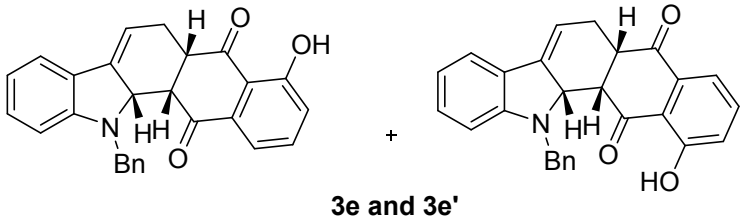


3d and 3d'

Orange solid, 17mg, yield: 93%; M.P.: 174 – 176 °C. $[\alpha]^{20}_D$ = +180.0°(c 0.5, $CHCl_3$,). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 6H), 7.18 – 7.08 (m, 1H), 6.74-6.61 (m, 2H), 6.36 (d, *J* = 39.3 Hz, 1H), 5.77 – 5.68 (m, 1H), 4.53 – 4.34 (m, 2H), 4.11 – 4.04 (m, 1H), 3.32 (dt, *J* = 34.8, 5.2 Hz, 1H), 3.20 – 3.10 (m, 1H), 2.50 (ddd, *J* = 14.8, 7.5, 3.7 Hz, 1H), 2.40 (dtd, *J* = 13.5, 8.9, 4.3 Hz, 1H), 1.89 (t, *J* = 13.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.00, 197.51, 153.85, 151.12, 138.65, 137.98, 137.42, 134.53, 129.81, 128.79, 128.57, 127.87, 127.74, 125.96, 120.49, 118.34, 118.12, 109.91, 108.87, 76.70, 64.57, 52.14, 47.81, 46.34, 27.12, 16.10. HRMS (ESI) calcd for $C_{24}H_{21}NO_2$ $[M+H]^+$: 356.1645, found: 356.1653. The enantiomeric excess was determined to be 82% and 96% by HPLC analysis on Chiralpak IA column (15% isopropanol/hexane, 1 mL/min), UV 254 nm, 3d: t_1 (minor) = 7.8 min, t_2 (major) = 8.5 min; 3d': t_1 (minor) = 9.9 min, t_2 (major) = 10.6 min.

(5a*S*,12a*S*,12b*S*)-12-benzyl-4-hydroxy-6,12,12a,12b-tetrahydro-5*H*-naphth

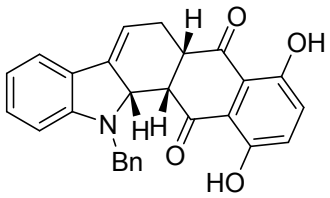
o[2,3-*a*]carbazole-5,13(5a*H*)-dione and (5a*S*,12a*S*,12b*S*)-12-benzyl-1-hydroxy-6,12,12a,12b-tetrahydro-5*H*-naphth o[2,3-*a*]-carbazole-5,13(5a*H*)-dione (3e and 3e')



3e and 3e'

Orange solid, 17mg, yield: 85%; M.P.: 179 – 181 °C. $[\alpha]^{20}_D$ = +172.0°(c 0.42, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 11.89 (s, 0.87H), 11.81 (s, 0.05H), 7.59 (t, *J* = 7.9 Hz, 1H), 7.36 – 7.28 (m, 4H), 7.26 – 7.11 (m, 5H), 6.78 – 6.62 (m, 2H), 5.68 (d, *J* = 3.6 Hz, 1H), 4.53 – 4.37 (m, 2H), 4.24 – 4.22 (m, 0.07H), 4.20 – 4.13 (m, 0.93H), 3.49 (t, *J* = 4.3 Hz, 0.07H), 3.46 (t, *J* = 4.4 Hz, 0.93H), 3.36 – 3.27 (m, 1H), 2.77 – 2.69 (m, 1H), 2.41 – 2.30 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 202.10, 197.71, 160.88, 153.82, 138.96, 137.96, 136.64, 132.58, 130.19, 128.69, 127.66, 127.53, 125.86, 124.50, 120.51, 118.67, 118.30, 109.71, 108.69, 65.29, 52.28, 47.21, 46.37, 26.66. HRMS (ESI) calcd for $C_{27}H_{21}NO_3$ $[M+H]^+$: 408.1594, found: 408.1605. The enantiomeric excess was determined to be 97% and 97% by HPLC analysis on Chiralpak AD column (20% isopropanol/hexane, 1 mL/min), UV 365 nm, 3e: t_1 (minor) = 9.07 min, t_2 (major) = 11.48 min; 3e': t_1 (minor) = 10.13 min, t_2 (major) = 13.23 min.

(5a*S*,12a*S*,12b*S*)-12-benzyl-1,4-dihydroxy-6,12,12a,12b-tetrahydro-5*H*-na phtho[2,3-*a*]carbazole-5,13(5a*H*)-dione (3f)

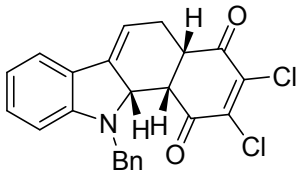


3f

Purple solid, 20mg, yield: 96%; M.P.: 182 – 184 °C. $[\alpha]^{20}_D$ = +251.3°(c 0.19, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 12.39 (s, 1H), 11.60 (s, 1H), 7.34 (d, *J* = 7.0 Hz, 2H), 7.28 (d, *J* = 7.0 Hz, 2H), 7.23 – 7.14 (m, 5H), 6.73 (t, *J* = 7.4 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 5.70 (s, 1H), 4.47 (dd, *J* = 46.4, 15.8 Hz, 2H), 4.26 – 4.17 (m, 1H), 3.44 (t, *J* = 5.2 Hz,1H), 3.28 – 3.19 (m, 1H), 2.77 – 2.68 (m, 1H), 2.42 – 2.35 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 204.01, 200.62, 172.84, 155.90, 154.36, 153.88, 138.83, 137.96, 134.62, 130.17, 128.98, 128.66, 128.01, 127.62, 127.51, 125.81, 120.50, 118.35, 114.09, 111.99, 111.87, 109.54, 108.73, 65.04 , 52.32, 46.44, 45.86, 27.51. HRMS (ESI) calcd for $C_{27}H_{21}NO_4$ $[M+H]^+$: 424.1543, found: 424.1548. The enantiomeric excess was determined to be 85% by HPLC analysis on Chiralpak IA column (15% isopropanol/hexane, 1 mL/min), UV 254 nm, t_1 (minor) = 8.92 min, t_2 (major) = 11.21 min.

(4a*S*,11a*S*,11b*S*)-11-benzyl-2,3-dichloro-5,11,11a,11b-tetrahydro-1*H*-benz

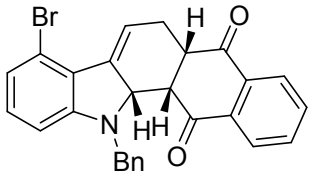
o[*a*]carbazole-1,4(4a*H*)-dione (3h)



3h

Red brown solid, 15mg, yield: 75%; M.P.: 134 – 136 °C. $[\alpha]^{20}_{D}$ = +146.3°(c 0.35, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 6H), 7.16 (t, *J* = 7.4 Hz, 1H), 6.74 (t, *J* = 7.4 Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 5.76 – 5.68 (m, 1H), 4.51 (d, *J* = 15.6 Hz, 1H), 4.34 (d, *J* = 15.6 Hz, 1H), 4.16 – 4.08 (m, 1H), 3.35 (td, *J* = 8.3, 5.4 Hz, 1H), 3.29 (t, *J* = 5.0 Hz, 1H), 2.61 – 2.56 (m, 1H), 2.45 – 2.37 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 189.57, 185.91, 153.88, 144.91, 142.50, 138.97, 137.72, 130.21, 128.73, 127.82, 127.68, 125.58, 120.61, 118.68, 109.32, 109.15, 64.63, 52.52, 47.42, 45.21, 26.92. HRMS (ESI) calcd for $C_{23}H_{17}Cl_2NO_2$ $[M+H]^+$: 410.0709, found: 410.0709. The enantiomeric excess was determined to be 29% by HPLC analysis on Chiralpak IA column (20% isopropanol/hexane, 1 mL/min), UV 254 nm, t_1 (minor) = 7.88 min, t_2 (major) = 8.82 min.

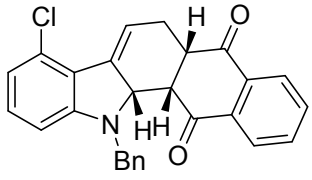
(5a*S*,12a*S*,12b*S*)-12-benzyl-8-bromo-6,12,12a,12b-tetrahydro-5*H*-naphtho [2,3-*a*]carbazole-5,13(5a*H*)-dione (4b)



4b

Yellow solid, 22mg, yield: 92%; M.P.: 152 – 154 °C. $[\alpha]^{20}_{D}$ = +120.4°(c 0.51, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 – 8.01 (m, 1H), 7.91 – 7.85 (m, 1H), 7.72 (dd, *J* = 5.3, 3.4 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 4H), 7.21 (t, *J* = 6.5 Hz, 1H), 6.93 (t, *J* = 8.0 Hz, 1H), 6.83 (d, *J* = 7.9 Hz, 1H), 6.55 (d, *J* = 7.9 Hz, 1H), 6.49 (d, *J* = 3.5 Hz, 1H), 4.51 – 4.40 (m, 2H), 4.31 – 4.27 (m, 1H), 3.59 (t, *J* = 4.2 Hz, 1H), 3.36 (dd, *J* = 15.0, 8.0 Hz, 1H), 2.78 – 2.71 (m, 1H), 2.39 – 2.30 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.05, 194.80, 155.76, 137.44, 137.08, 135.16, 134.63, 134.08, 132.42, 130.25, 128.71, 127.48, 127.25, 126.37, 122.40, 117.97, 114.70, 106.92, 64.78, 51.38, 47.15, 46.86, 27.12. HRMS (ESI) calcd for $C_{27}H_{20}BrNO_2$ $[M+H]^+$: 470.0750, found: 470.0752. The enantiomeric excess was determined to be 91% by HPLC analysis on Chiralpak IA column (15% isopropanol/hexane, 1 mL/min), UV 254 nm, t_1 (minor) = 9.67 min, t_2 (major) = 10.53 min.

(5a*S*,12a*S*,12b*S*)-12-benzyl-8-chloro-6,12,12a,12b-tetrahydro-5*H*-naphtho [2,3-*a*]carbazole-5,13(5a*H*)-dione (4c)

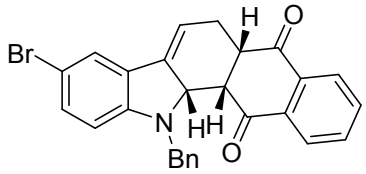


4c

Yellow solid, 20mg, yield: 96%; M.P.: 182 – 184 °C. $[\alpha]^{20}_{D}$ = +208.9°(c 0.37, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 – 7.94 (m, 1H), 7.93 – 7.81 (m, 1H), 7.79 – 7.61 (m, 2H), 7.24 (d, *J* = 33.5 Hz, 5H), 7.01 (t, *J* = 7.2 Hz, 1H), 6.65 (d, *J* = 7.4 Hz, 1H), 6.51 (d, *J* = 7.4 Hz, 1H), 6.34 (d, *J* = 3.7 Hz, 1H), 4.46 (dd, *J* = 42.2, 15.9 Hz, 2H), 4.34 – 4.19 (m, 1H), 3.73 – 3.47 (m, 1H), 3.45 – 3.25 (m, 1H), 2.86 – 2.56 (m, 1H), 2.45 – 2.13 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.13, 194.92, 155.48, 137.47, 136.47, 135.14, 134.68, 134.13, 132.38,

130.08, 129.70, 128.72, 127.50, 127.26, 126.38, 122.87, 119.19, 114.94, 106.43, 64.74, 51.43, 47.16, 46.84, 27.27. HRMS (ESI) calcd for $C_{27}H_{20}ClNO_2$ $[M+H]^+$: 426.1255, found: 426.1256. The enantiomeric excess was determined to be 93% by HPLC analysis on Chiralpak IA column (15% isopropanol/hexane, 1 mL/min), UV 254 nm, t_1 (minor) = 9.23 min, t_2 (major) = 10.00 min.

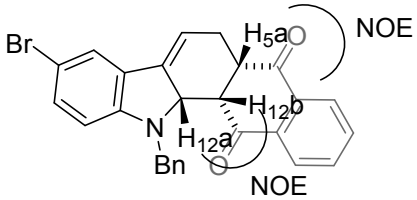
(5a*S*,12a*S*,12b*S*)-12-benzyl-9-bromo-6,12,12a,12b-tetrahydro-5*H*-naphtho [2,3-*a*]carbazole-5,13(5a*H*)-dione (4d)



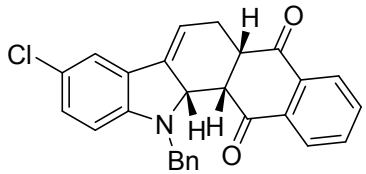
4d

Yellow solid, 23mg, yield: 96%; M.P.: 150 – 152 °C. $[\alpha]^{20}_D$ = +116.7°(c 0.6, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 – 7.99 (m, 1H), 7.89 – 7.83 (m, 1H), 7.74 – 7.68 (m, 2H), 7.34 (d, *J* = 1.7 Hz, 1H), 7.27 (dt, *J* = 15.0, 7.3 Hz, 4H), 7.23 – 7.17 (m, 2H), 6.51 (d, *J* = 8.5 Hz, 1H), 5.68 (q, *J* = 3.7 Hz, 1H), 4.43 (s, 2H), 4.21 (p, *J* = 4.0 Hz, 1H), 3.53 (t, *J* = 4.4 Hz, 1H), 3.35 (ddd, *J* = 10.8, 7.9, 4.7 Hz, 1H), 2.70 – 2.67 (m, 1H), 2.35 – 2.26 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.92, 194.84, 152.76, 137.52, 135.18, 134.65, 134.06, 132.25, 128.69, 128.19, 127.58, 127.52, 127.24, 126.35, 123.38, 111.13, 109.96, 109.93, 65.04, 51.77, 47.41, 47.09, 26.88. HRMS (ESI) calcd for $C_{27}H_{20}BrNO_2$ $[M+H]^+$: 470.0750, found: 470.0753. The enantiomeric excess was determined to be 95% by HPLC analysis on Chiralpak IA column (15% isopropanol/hexane, 1 mL/min), UV 254 nm, t_1 (minor) = 11.01 min, t_2 (major) = 15.31 min.

The relative configuration of the title compound was tentatively assigned by means of NMR NOESY experiments. Irradiation at 3.35 ppm (H_5a) gives a signal at 4.21 ppm (H_{12}b). Irradiation at 4.21 ppm (H_{12}b) gives signals at 3.35 ppm (H_5a) and 3.53 ppm (H_{12}a). Therefore, a 5a,12b-*cis* and 12a,12b-*cis* configuration can be assumed.



(5a*S*,12a*S*,12b*S*)-12-benzyl-9-chloro-6,12,12a,12b-tetrahydro-5*H*-naphtho [2,3-*a*]carbazole-5,13(5a*H*)-dione (4e)

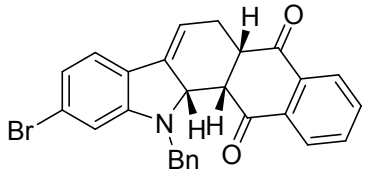


4e

Yellow solid, 21mg, yield: 98%; M.P.: 161 – 163 °C. $[\alpha]^{20}_D$= +140.0°(c 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dt, *J* = 7.4, 3.3 Hz, 1H), 7.92 – 7.81 (m, 1H), 7.77 – 7.66 (m, 2H), 7.33 – 7.18 (m, 6H), 7.07 (dd, *J* = 8.5, 2.1 Hz, 1H), 6.55 (d, *J* = 8.5 Hz, 1H), 5.69 (q, *J* = 3.8 Hz, 1H), 4.44 (s, 2H), 4.22 (p, *J* = 4.1 Hz, 1H), 3.52 (t, *J* = 4.5 Hz, 1H), 3.36 (ddd, *J* = 10.7, 7.8, 4.7 Hz,

1H), 2.67 (ddt, *J* = 19.5, 7.8, 3.8 Hz, 1H), 2.30 (ddt, *J* = 19.5, 10.7, 4.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.88, 193.81, 151.39, 136.64, 136.61, 134.21, 133.61, 133.02, 131.35, 128.41, 127.66, 126.58, 126.48, 126.21, 125.32, 121.98, 119.49, 110.05, 108.41, 64.20, 50.98, 46.41, 46.15, 25.87. HRMS (ESI) calcd for $C_{27}H_{20}ClNO_2$ $[M+H]^+$: 426.1255, found: 426.1259. The enantiomeric excess was determined to be 96% by HPLC analysis on Chiralpak IA column (15% isopropanol/hexane, 1 mL/min), UV 254 nm, t_1 (minor) = 11.61 min, t_2 (major) = 15.70 min.

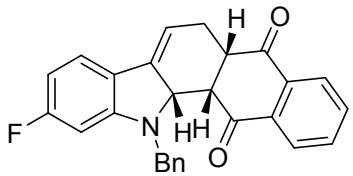
(5a*S*,12a*S*,12b*S*)-12-benzyl-10-bromo-6,12,12a,12b-tetrahydro-5*H*-naphth o[2,3-*a*]carbazole-5,13(5a*H*)-dione (4f)



4f

Yellow solid, 22mg, yield: 95%; M.P.: 152 – 154 °C. $[\alpha]^{20}_D$= +232.2°(c 0.31, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 – 7.99 (m, 1H), 7.89 – 7.83 (m, 1H), 7.74 – 7.68 (m, 2H), 7.29 – 7.27 (m, 4H), 7.21 (t, *J* = 6.5 Hz, 1H), 7.10 (d, *J* = 7.8 Hz, 1H), 6.86 – 6.77 (m, 2H), 5.67 (d, *J* = 3.4 Hz, 1H), 4.44 (s, 2H), 4.27 – 4.19 (m, 1H), 3.51 (t, *J* = 4.2 Hz, 1H), 3.39 – 3.28 (m, 1H), 2.67 – 2.62 (m, 1H), 2.33 – 2.20 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.01, 194.90, 154.82, 137.61, 137.33, 135.15, 134.69, 134.10, 132.34, 128.75, 127.58, 127.26, 126.36, 125.19, 123.73, 121.43, 120.86, 111.43, 110.46, 64.90, 51.44, 47.34, 47.01, 26.87. HRMS (ESI) calcd for $C_{27}H_{20}BrNO_2$ $[M+H]^+$: 470.0750, found: 470.0767. The enantiomeric excess was determined to be 90% by HPLC analysis on Chiralpak OD column (15% isopropanol/hexane, 1 mL/min), UV 254 nm, t_1 (major) = 14.57 min, t_2 (minor) = 21.78 min.

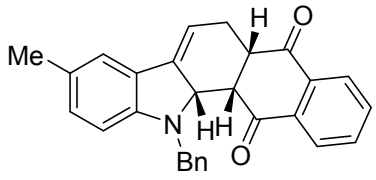
(5a*S*,12a*S*,12b*S*)-12-benzyl-10-fluoro-6,12,12a,12b-tetrahydro-5*H*-naphth o[2,3-*a*]carbazole-5,13(5a*H*)-dione (4g)



4g

Yellow solid, 20mg, yield: 96%; M.P.: 152 – 154 °C. $[\alpha]^{20}_D$= +280.0°(c 0.1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 – 7.99 (m, 1H), 7.90 – 7.85 (m, 1H), 7.74 – 7.70 (m, 2H), 7.29 (dd, *J* = 12.8, 7.2 Hz, 4H), 7.24 – 7.14 (m, 2H), 6.43 – 6.32 (m, 2H), 5.61 (q, *J* = 3.6 Hz, 1H), 4.48 – 4.41 (m, 2H), 4.25 (p, *J* = 3.9 Hz, 1H), 3.54 (t, *J* = 4.7 Hz, 1H), 3.35 (ddd, *J* = 10.8, 8.0, 4.7 Hz, 1H), 2.66 (ddt, *J* = 15.1, 7.5, 3.6 Hz, 1H), 2.33 – 2.24 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.10, 194.95, 137.55, 137.36, 135.17, 134.65, 134.09, 132.39, 128.74, 127.59, 127.57, 127.25, 126.37, 122.11, 121.24, 121.17, 109.02, 104.61, 104.46, 96.30, 96.12, 65.25, 51.49, 47.40, 47.01, 26.82. HRMS (ESI) calcd for $C_{27}H_{20}FNO_2$ $[M+H]^+$: 410.1551, found: 410.1554. The enantiomeric excess was determined to be 85% by HPLC analysis on Chiralpak OD column (20% isopropanol/hexane, 1 mL/min), UV 254 nm, t_1 (major) = 12.74 min, t_2 (minor) = 19.19 min.

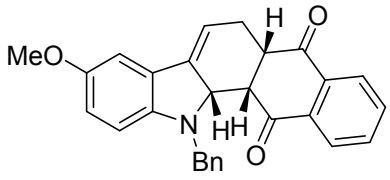
(5a*S*,12a*S*,12b*S*)-12-benzyl-9-methyl-6,12,12a,12b-tetrahydro-5*H*-naphtho[2,3-*a*]carbazole-5,13(5a*H*)-dione (4h)



4h

Orange solid, 19mg, yield: 95%; M.P.: 162 – 164 °C. $[\alpha]^{20}_D$= +181.4°(c 0.47, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 – 8.07 (m, 1H), 8.01 (d, *J* = 4.7 Hz, 1H), 7.86 (d, *J* = 4.7 Hz, 1H), 7.77 (d, *J* = 3.5 Hz, 1H), 7.72 – 7.68 (m, 2H), 7.33 (d, *J* = 7.3 Hz, 1H), 7.24 (d, *J* = 7.3 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 7.00 – 6.94 (m, 2H), 6.60 (d, *J* = 8.0 Hz, 1H), 5.65 (d, *J* = 3.1 Hz, 1H), 4.48 (d, *J* = 15.6 Hz, 1H), 4.37 (d, *J* = 15.5 Hz, 1H), 4.13 (s, 1H), 3.46 (d, *J* = 3.7 Hz, 1H), 3.37 (d, *J* = 11.2 Hz, 1H), 2.65 (d, *J* = 19.0 Hz, 1H), 2.35 – 2.23 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.35, 194.99, 152.04, 138.85, 138.35, 135.42, 134.57, 133.87, 132.37, 130.46, 128.56, 127.76, 127.58, 127.31, 127.15, 126.34, 120.99, 109.16, 108.93, 65.55, 52.95, 47.70, 47.51, 26.92, 20.78. HRMS (ESI) calcd for $C_{28}H_{23}NO_2$ $[M+H]^+$: 406.1802, found: 406.1812. The enantiomeric excess was determined to be 92% by HPLC analysis on Chiralpak IA column (10% isopropanol/hexane, 1 mL/min), UV 254 nm, t_1 (minor) = 10.59 min, t_2 (major) = 15.50 min.

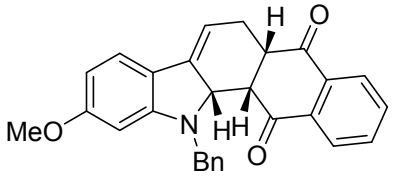
(5a*S*,12a*S*,12b*S*)-12-benzyl-9-methoxy-6,12,12a,12b-tetrahydro-5*H*-naphtho[2,3-*a*]carbazole-5,13(5a*H*)-dione (4i)



4i

Orange solid, 19mg, yield: 92%; M.P.: 144 – 146 °C. $[\alpha]^{20}_D$= +176.7°(c 0.43, $CHCl_3$, 85% ee). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 – 7.95 (m, 1H), 7.91 – 7.81 (m, 1H), 7.75 – 7.63 (m, 2H), 7.34 (d, *J* = 7.4 Hz, 2H), 7.23 (d, *J* = 7.4 Hz, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 6.87 (d, *J* = 1.5 Hz, 1H), 6.79 – 6.73 (m, 1H), 6.61 (d, *J* = 8.6 Hz, 1H), 5.66 (d, *J* = 3.4 Hz, 1H), 4.48 (d, *J* = 15.4 Hz, 1H), 4.29 (d, *J* = 15.4 Hz, 1H), 4.14 – 4.07 (m, 1H), 3.76 (s, 3H), 3.44 – 3.31 (m, 2H), 2.71 – 2.59 (m, 1H), 2.31 (ddd, *J* = 15.0, 9.9, 4.6 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.20, 195.03, 153.27, 148.80, 138.86, 138.44, 135.49, 134.57, 133.85, 132.35, 128.55, 127.84, 127.34, 127.14, 126.32, 116.23, 110.13, 109.69, 106.04, 66.23, 66.18, 56.10, 56.05, 54.00, 47.73, 26.92. HRMS (ESI) calcd for $C_{28}H_{23}NO_3$ $[M+H]^+$: 422.1751, found: 422.1760. The enantiomeric excess was determined to be 85% by HPLC analysis on Chiralpak IA column (15% isopropanol/hexane, 1 mL/min), UV 254 nm, t_1 (minor) = 13.42 min, t_2 (major) = 18.99 min.

(5a*S*,12a*S*,12b*S*)-12-benzyl-10-methoxy-6,12,12a,12b-tetrahydro-5*H*-naphtho[2,3-*a*]carbazole-5,13(5a*H*)-dione (4j)

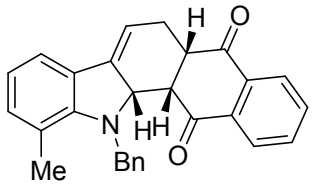


4j

Orange solid, 20mg, yield: 93%; M.P.: 140 – 142 °C. $[\alpha]^{20}_D$= +210.0°(c 0.29, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 – 7.99 (m, 1H), 7.89 – 7.84 (m, 1H), 7.72 – 7.64 (m, 2H), 7.31 (d, *J* = 7.2 Hz,

2H), 7.26 (s, 1H), 7.25 – 7.15 (m, 3H), 6.33 – 6.18 (m, 2H), 5.51 (d, *J* = 2.6 Hz, 1H), 4.51 – 4.40 (m, 2H), 4.25 – 4.13 (m, 1H), 3.76 (s, 3H), 3.55 – 3.44 (m, 1H), 3.33 (dd, *J* = 14.9, 7.8 Hz, 1H), 2.72 – 2.56 (m, 1H), 2.32 – 2.24 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.42, 195.08, 162.04, 155.34, 138.14, 137.91, 135.29, 134.57, 133.96, 132.44, 128.65, 127.67, 127.41, 127.19, 126.36, 121.15, 119.41, 107.08, 103.72, 94.91, 65.37, 55.38, 51.79, 47.56, 47.19, 26.85. HRMS (ESI) calcd for $C_{28}H_{23}NO_3$ $[M+H]^+$: 422.1751, found: 422.1748. The enantiomeric excess was determined to be 96% by HPLC analysis on Chiralpak AD column (15% isopropanol/hexane, 1 mL/min), UV 254 nm, t_1 (major) = 22.08 min, t_2 (minor) = 30.04 min.

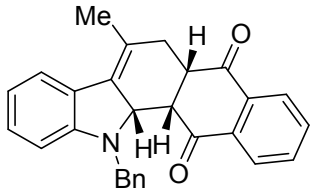
(5a*S*,12a*S*,12b*S*)-12-benzyl-11-methyl-6,12,12a,12b-tetrahydro-5*H*-naphtho[2,3-*a*]carbazole-5,13(5a*H*)-dione (4k)



4k

Yellow solid, 20mg, yield: 98%; M.P.: 163 – 165 °C. $[\alpha]^{20}_D$ = +140.0°(c 0.5, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 – 7.96 (m, 1H), 7.89 – 7.84 (m, 1H), 7.69 (q, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 7.4 Hz, 2H), 7.24 (t, *J* = 7.5 Hz, 2H), 7.17 (t, *J* = 7.5 Hz, 2H), 6.98 (d, *J* = 7.4 Hz, 1H), 6.73 (t, *J* = 7.4 Hz, 1H), 5.62 (d, *J* = 3.5 Hz, 1H), 4.92 (d, *J* = 16.5 Hz, 1H), 4.34 (d, *J* = 16.5 Hz, 1H), 4.11 – 4.04 (m, 1H), 3.34 (dd, *J* = 15.5, 7.2 Hz, 2H), 2.70 – 2.58 (m, 1H), 2.41 (s, 3H), 2.30 – 2.24 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.40, 195.12, 152.66, 139.69, 139.28, 135.39, 134.55, 133.87, 133.23, 132.45, 128.57, 127.26, 126.24, 126.23, 120.97, 119.53, 118.34, 108.78, 67.42, 55.55, 48.14, 47.70, 26.89, 19.51. HRMS (ESI) calcd for $C_{28}H_{23}NO_2$ $[M+H]^+$: 406.1802, found: 406.1804. The enantiomeric excess was determined to be 97% by HPLC analysis on Chiralpak IA column (10% isopropanol/hexane, 1 mL/min), UV 254 nm, t_1 (minor) = 8.73 min, t_2 (major) = 9.45 min.

(5a*S*,12a*S*,12b*S*)-12-benzyl-7-methyl-6,12,12a,12b-tetrahydro-5*H*-naphtho[2,3-*a*]carbazole-5,13(5a*H*)-dione (4l)

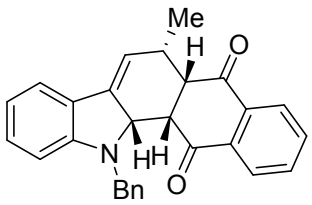


4l

Yellow solid, 19mg, yield: 93%; M.P.: 139 – 141 °C. $[\alpha]^{20}_D$= +157.5°(c 0.57, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 – 7.99 (m, 1H), 7.87 – 7.82 (m, 1H), 7.70 (dd, *J* = 5.4, 3.5 Hz, 2H), 7.39 (d, *J* = 7.4 Hz, 1H), 7.32 (d, *J* = 7.4 Hz, 2H), 7.26 (d, *J* = 14.9 Hz, 3H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.10 (t, *J* = 7.7 Hz, 1H), 6.72 (t, *J* = 7.5 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 4.44 (q, *J* = 16.1 Hz, 2H), 4.26 – 4.14 (m, 1H), 3.55 (t, *J* = 4.4 Hz, 1H), 3.37 – 3.31 (m, 1H), 2.69 – 2.52 (m, 1H), 2.25 – 2.17 (m, 1H), 1.88 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.26, 195.02, 154.33, 138.17, 135.52, 134.58, 133.90, 132.45, 131.07, 128.84, 128.59, 127.58, 127.23, 127.11, 126.98, 126.37, 123.81, 120.69, 117.90, 108.25, 65.88, 52.07, 47.55, 47.02, 33.91, 18.99. HRMS (ESI) calcd for $C_{28}H_{23}NO_2$ $[M+H]^+$: 406.1802, found: 406.1805. The enantiomeric excess

was determined to be >99% by HPLC analysis on Chiralpak IA column (10% isopropanol/hexane, 1 mL/min), UV 254 nm, t_1 (minor) = 10.65 min, t_2 (major) = 16.05 min.

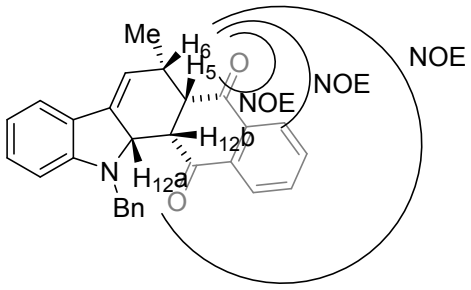
(5a*S*,6*S*,12a*S*,12b*S*)-12-benzyl-6-methyl-6,12,12a,12b-tetrahydro-5*H*-naphtho[2,3-*a*]carbazole-5,13(5a*H*)-dione (4m)



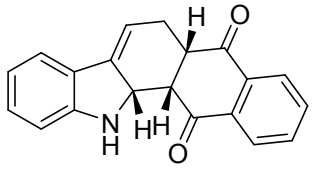
4m

Orange solid, 14mg, yield: 70%; M.P.: 136 – 138 °C. $[\alpha]^{20}_D$= +135.6°(c 0.64, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 5.0, 3.4 Hz, 1H), 7.88 (dd, *J* = 5.0, 3.4 Hz, 1H), 7.70 (dd, *J* = 5.0, 3.4 Hz, 2H), 7.30 (dd, *J* = 23.7, 7.3 Hz, 3H), 7.24 (d, *J* = 7.3 Hz, 2H), 7.20 – 7.13 (m, 2H), 6.74 – 6.66 (m, 2H), 5.61 – 5.55 (m, 1H), 4.45 (d, *J* = 33.3 Hz, 2H), 4.17 (d, *J* = 3.7 Hz, 1H), 3.49 (t, *J* = 3.7 Hz, 1H), 2.93 (dd, *J* = 10.0, 4.2 Hz, 1H), 2.56 – 2.47 (m, 1H), 1.18 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.56, 194.71, 154.05, 138.15, 137.72, 135.38, 134.45, 133.88, 132.89, 129.92, 128.60, 127.71, 127.36, 127.15, 126.32, 126.02, 120.53, 118.22, 115.84, 108.81, 65.05, 56.17, 52.36, 48.80, 32.94, 20.04. HRMS (ESI) calcd for $C_{28}H_{23}NO_2$ $[M+H]^+$: 406.1802, found: 406.1806. The enantiomeric excess was determined to be 83% by HPLC analysis on Chiralpak OD column (20% isopropanol/hexane, 1 mL/min), UV 365 nm, t_1 (minor) = 11.82 min, t_2 (major) = 17.83 min.

The relative configuration of the title compound was tentatively assigned by means of NMR NOESY experiments. Irradiation at 2.5 ppm (H_5a) gives a signal at 2.93 ppm (H_{12}b), 3.49 ppm (H_{12}b) and 4.17 ppm (H_{12}a). Therefore, a 5a,6,12a,12b-*cis* configuration can be assumed.



(5a*S*,12a*S*,12b*S*)-6,12,12a,12b-tetrahydro-5H-naphtho[2,3-*a*]carbazole-5,13(5a*H*)-dione (4n)

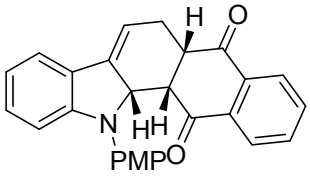


4n

Orange solid, 12mg, yield: 77%; M.P.: 137 – 139 °C. $[\alpha]^{20}_D$= +233.1°(c 0.36, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 – 8.01 (m, 1H), 7.96 – 7.87 (m, 1H), 7.77 – 7.69 (m, 2H), 7.30 (d, *J* = 7.4 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.81 (dd, *J* = 16.8, 7.9 Hz, 2H), 5.80 (d, *J* = 3.2 Hz, 1H), 4.55 (s, 1H), 4.33 (s, 1H), 3.90 (t, *J* = 5.0 Hz, 1H), 3.48 (dd, *J* = 14.3, 7.3 Hz, 1H), 2.66 – 2.59 (m, 1H), 2.52 – 2.46 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.79, 195.21, 133.56, 133.11, 131.96,

128.55, 126.16, 125.52, 119.67, 118.96, 111.14, 109.90, 58.61, 47.93, 46.23, 25.55. HRMS (ESI) calcd for $C_{20}H_{15}NO_2$ $[M+H]^+$: 302.1176, found: 302.1172. The enantiomeric excess was determined to be 48% by HPLC analysis on Chiralpak IA column (20% isopropanol/hexane, 1 mL/min), UV 254 nm, t_1 (minor) = 4.69 min, t_2 (major) = 6.30 min.

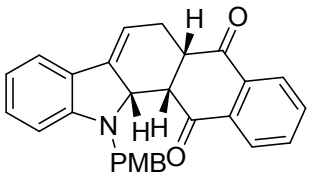
(5a*S*,12a*S*,12b*S*)-12-(4-methoxyphenyl)-6,12,12a,12b-tetrahydro-5*H*-naphtho[2,3-*a*]carbazole-5,13(5a*H*)-dione (4o)



4o

Yellow solid, 18mg, yield: 85%; M.P.: 132 – 134 °C. $[\alpha]^{20}_D$= +221.3°(c 0.47, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 6.2, 2.7 Hz, 1H), 7.91 – 7.87 (m, 1H), 7.75 – 7.69 (m, 2H), 7.32 (d, *J* = 7.3 Hz, 1H), 7.24 (d, *J* = 8.8 Hz, 2H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.81 – 6.66 (m, 2H), 5.72 (d, *J* = 3.6 Hz, 1H), 4.79 – 4.73 (m, 1H), 3.95 – 3.84 (m, 2H), 3.79 (s, 2H), 3.48 (ddd, *J* = 12.2, 7.9, 4.7 Hz, 1H), 2.75 (ddt, *J* = 14.9, 7.3, 3.5 Hz, 1H), 2.43 – 2.33 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.28, 195.04, 151.78, 138.43, 135.46, 134.59, 134.09, 132.44, 129.74, 127.27, 126.53, 125.43, 120.58, 118.33, 114.86, 109.62, 108.52, 65.36, 55.49, 47.50, 46.65, 27.12. HRMS (ESI) calcd for $C_{27}H_{21}NO_3$ $[M+Na]^+$: 430.1414, found: 430.1413. The enantiomeric excess was determined to be 5% by HPLC analysis on Chiralpak IA column (20% isopropanol/hexane, 1 mL/min), UV 254 nm, t_1 (minor) = 12.41 min, t_2 (major) = 13.49 min.

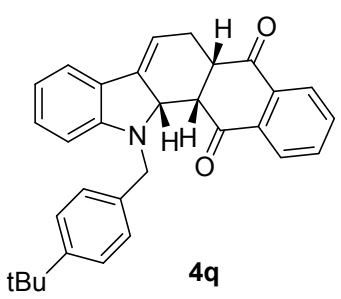
(5a*S*,12a*S*,12b*S*)-12-(4-methoxybenzyl)-6,12,12a,12b-tetrahydro-5*H*-naphtho[2,3-*a*]carbazole-5,13(5a*H*)-dione (4p)



4p

Orange solid, 20mg, yield: 93%; M.P.: 133 – 135 °C. $[\alpha]^{20}_D$= +121.7°(c 0.86, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 5.9, 3.1 Hz, 1H), 7.87 (dd, *J* = 5.9, 3.1 Hz, 1H), 7.70 (dd, *J* = 5.1, 3.8 Hz, 2H), 7.25 (dd, *J* = 21.8, 7.9 Hz, 3H), 7.14 (t, *J* = 7.7 Hz, 1H), 6.78 (d, *J* = 8.5 Hz, 2H), 6.71 (t, *J* = 8.1 Hz, 2H), 5.67 (dd, *J* = 6.9, 3.3 Hz, 1H), 4.40 (dd, *J* = 45.4, 15.5 Hz, 2H), 4.18 – 4.11 (m, 1H), 3.72 (s, 3H), 3.49 (t, *J* = 4.5 Hz, 1H), 3.36 (ddd, *J* = 12.2, 7.8, 4.7 Hz, 1H), 2.68 – 2.63 (m, 1H), 2.34 – 2.26 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.36, 195.07, 158.87, 153.96, 138.73, 135.35, 134.60, 133.94, 132.38, 129.98, 129.83, 128.95, 127.18, 126.35, 126.21, 120.47, 118.18, 113.96, 109.43, 108.94, 64.96, 55.24, 51.72, 47.68, 47.32, 26.92. HRMS (ESI) calcd for $C_{28}H_{23}NO_3$ $[M+H]^+$: 422.1751, found: 422.1752. The enantiomeric excess was determined to be 91% by HPLC analysis on Chiralpak IA column (10% isopropanol/hexane, 1 mL/min), UV 254 nm, t_1 (minor) = 19.13 min, t_2 (major) = 24.57 min.

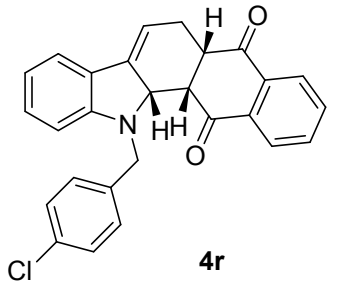
(5a*S*,12a*S*,12b*S*)-12-(4-(tert-butyl)benzyl)-6,12,12a,12b-tetrahydro-5*H*-naphtho[2,3-*a*]carbazole-5,13(5a*H*)-dione (4q)



4q

Yellow solid, 21mg, yield: 94%; M.P.: 146 – 148 °C. $[\alpha]^{20}_{D}$= +160.2°(c 0.62, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 6.4, 2.4 Hz, 1H), 7.88 – 7.86 (m, 1H), 7.72 (ddd, *J* = 6.1, 5.4, 3.6 Hz, 2H), 7.32 – 7.26 (m, 5H), 7.18 (t, *J* = 7.6 Hz, 1H), 6.74 (dd, *J* = 12.3, 4.9 Hz, 2H), 5.69 (dd, *J* = 7.0, 3.4 Hz, 1H), 4.54 (d, *J* = 15.3 Hz, 1H), 4.36 (d, *J* = 15.3 Hz, 1H), 4.18 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.39 – 3.33 (m, 2H), 2.67 (ddd, *J* = 15.6, 7.2, 3.6 Hz, 1H), 2.32 (ddd, *J* = 15.6, 7.2, 3.6 Hz, 1H), 1.21 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.26, 195.01, 153.95, 150.41, 138.66, 135.56, 135.01, 134.51, 133.76, 132.31, 129.81, 127.71, 127.11, 126.26, 126.14, 125.45, 120.46, 118.12, 109.42, 108.77, 65.00, 51.81, 47.67, 47.32, 34.40, 31.21, 26.89, 22.66, 14.12. HRMS (ESI) calcd for $C_{31}H_{29}NO_2$ $[M+H]^+$: 448.2271, found: 448.2276. The enantiomeric excess was determined to be 96% by HPLC analysis on Chiralpak IA column (15% isopropanol/hexane, 1 mL/min), UV 254 nm, t_1 (minor) = 8.06 min, t_2 (major) = 10.37 min.

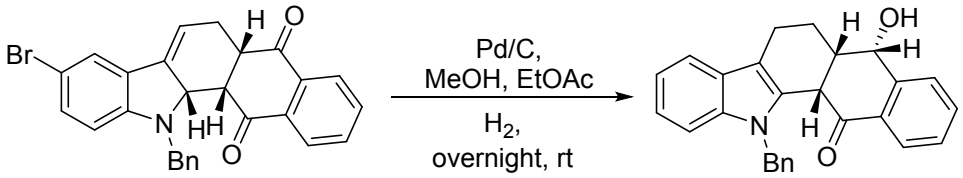
(5a*S*,12a*S*,12b*S*)-12-(4-chlorobenzyl)-6,12,12a,12b-tetrahydro-5*H*-naphtho[2,3-*a*]carbazole-5,13(5a*H*)-dione (4r)



4r

Yellow solid, 19mg, yield: 90%; M.P.: 162 – 164 °C. $[\alpha]^{20}_{D}$= +220.0°(c 0.5, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 – 8.00 (m, 1H), 7.87 (dd, *J* = 5.6, 3.2 Hz, 1H), 7.72 (dd, *J* = 5.6, 3.2 Hz, 2H), 7.29 (d, *J* = 7.3 Hz, 3H), 7.24 (d, *J* = 8.3 Hz, 2H), 7.13 (t, *J* = 7.7 Hz, 1H), 6.73 (t, *J* = 7.4 Hz, 1H), 6.58 (d, *J* = 8.0 Hz, 1H), 5.70 (dd, *J* = 7.0, 3.4 Hz, 1H), 4.41 (q, *J* = 16.2 Hz, 2H), 4.22 – 4.16 (m, 1H), 3.59 (t, *J* = 4.4 Hz, 1H), 3.43 – 3.36 (m, 1H), 2.68 (ddt, *J* = 14.8, 7.4, 3.5 Hz, 1H), 2.37 – 2.29 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.12, 194.91, 153.74, 138.50, 136.87, 135.26, 134.66, 134.06, 133.00, 132.41, 129.87, 128.83, 127.24, 126.36, 126.19, 120.52, 118.48, 109.76, 108.74, 65.49, 51.90, 47.61, 47.27, 26.93. HRMS (ESI) calcd for $C_{27}H_{20}ClNO_2$ $[M+H]^+$: 426.1255, found: 426.1260. The enantiomeric excess was determined to be 79% by HPLC analysis on Chiralpak IA column (10% isopropanol/hexane, 1 mL/min), UV 254 nm, t_1 (minor) = 15.82 min, t_2 (major) = 23.34 min.

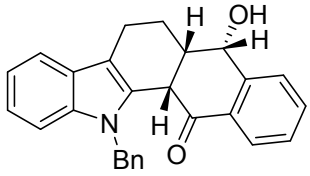
4. General procedure for the reduction reaction of 4d[6]



4d **4d-1**

4d (70mg, 0.15mmol) was completely dissolved in EtOAc, and then 10 mol% Pd/C (70mg, 0.033mol) was added as a single portion. Anhydrous MeOH was then added by syringe at room temperature under a stream of hydrogen and the mixture was stirred overnight under hydrogen gas. The mixture was filtered through Celite, and the solvents were removed via rotary evaporation. The product was purified by flash chromatography (petroleum ether-ethyl acetate, 3:1) to give 50mg (85%) of a yellow solid.

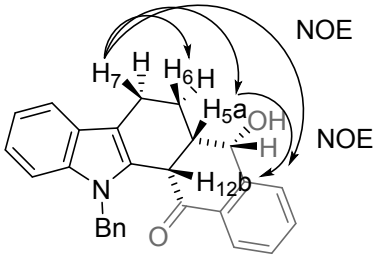
(5*S*,5a*S*,12b*S*)-12-benzyl-5-hydroxy-5,5a,6,7,12,12b-hexahydro-13*H*-naphtho[2,3-*a*]carbazol-13-one (4d-1)



4d-1

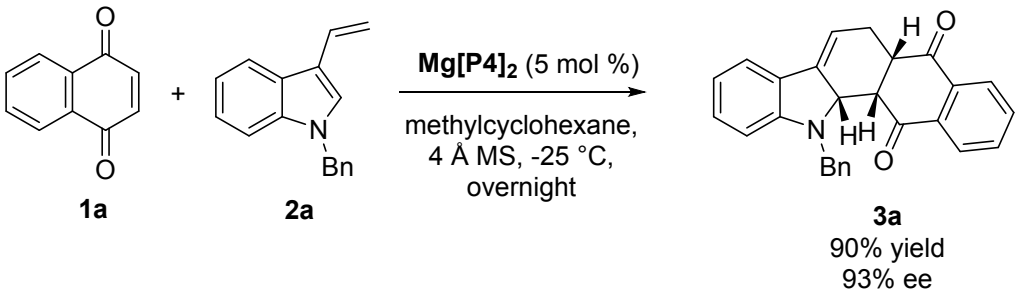
Light yellow solid, 34mg, yield: 85%; M.P.: 190 – 192 °C. $[\alpha]^{20}_{D}$= +193.7°(c 0.32, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.8 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.26 – 7.19 (m, 4H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.96 (d, *J* = 7.4 Hz, 2H), 5.61 (dd, *J* = 44.3, 17.5 Hz, 2H), 5.27 (s, 1H), 3.75 (d, *J* = 3.4 Hz, 1H), 2.92 (dd, *J* = 16.0, 5.8 Hz, 1H), 2.76 (dd, *J* = 16.5, 10.6 Hz, 2H), 2.32 (d, *J* = 5.0 Hz, 1H), 2.14 (dd, *J* = 13.0, 5.3 Hz, 1H), 1.43 (dt, *J* = 12.9, 6.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.28, 143.61, 138.70, 137.39, 134.64, 132.64, 130.11, 128.76, 127.85, 127.45, 127.14, 126.71, 125.96, 125.68, 121.70, 119.08, 118.35, 110.52, 109.69, 69.82, 47.14, 45.99, 43.71, 29.73, 20.46, 18.78. HRMS (ESI) calcd for $C_{27}H_{23}NO_2$ $[M+H]^+$: 394.1802, found: 394.1800. The enantiomeric excess was determined to be 93% by HPLC analysis on Chiralpak IA column (20% isopropanol/hexane, 1 mL/min), UV 254 nm, t_1 (minor) = 11.00 min, t_2 (major) = 13.50 min.

The relative configuration of the title compound was tentatively assigned by means of NMR NOESY experiments. Irradiation at 2.14 ppm (H_7) gives signals at 1.43 ppm (H_6) and 2.76 ppm (H_5a) and at 2.92 ppm (H_{12}b). Irradiation at 2.76 ppm (H_5a) gives signals at 2.92 ppm (H_{12}b). Therefore, a 5a,12b-*cis* configuration can be assumed.



5. A detailed synthetic method example at a minimum 1 mmol scale

A representative example: 4 Å MS (30 mg) was added to a reaction tube and flame dried in situ. The tube was back-filled with argon and substrate 1a (1 equiv, 1 mmol), catalyst $Mg[P4]_2$ (360 mg, 5 mol%) and 2a (1.5 equiv, 1.25 mmol) were added. The resulting mixture was stirred at -25 ^oC for 10 min. Then anhydrous methylcyclohexane (100 mL) was added via a syringe. The mixture was then stirred overnight at the same temperature to give the crude product. The crude product was purified by washing with hexane and MeOH to give the product 3a. Then the product 3a was analyzed by HPLC. Yellow solid, 353mg, yield: 90%, The enantiomeric excess was determined to be 93% by HPLC analysis on Chiralpak AD column (20% isopropanol/hexane, 1 mL/min), UV 254 nm, t_1 (minor) = 12.4 min, t_2 (major) = 14.9 min. The ee value has a slight decrease from 96% to 93%.



1a **2a** **3a**
90% yield
93% ee

(5a*S*,12a*S*,12b*S*)-12-benzyl-6,12,12a,12b-tetrahydro-5*H*-naphtho[2,3-*a*]carbazole-5,13(5a*H*)-dione (3a)

Yellow solid, 353mg, Yield: 90%, The enantiomeric excess was determined to be 93% by HPLC analysis on Chiralpak AD column (20% isopropanol/hexane, 1 mL/min), UV 254 nm, t_1 (minor) = 12.5 min, t_2 (major) = 14.9 min. The ee value has a slight decreased from 96% to 93%.

6. References

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7. Copies of NMR spectra and HPLC Chromatograms

1-benzyl-3-vinyl-1H-indole (2a)

Figure S1. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of 2a

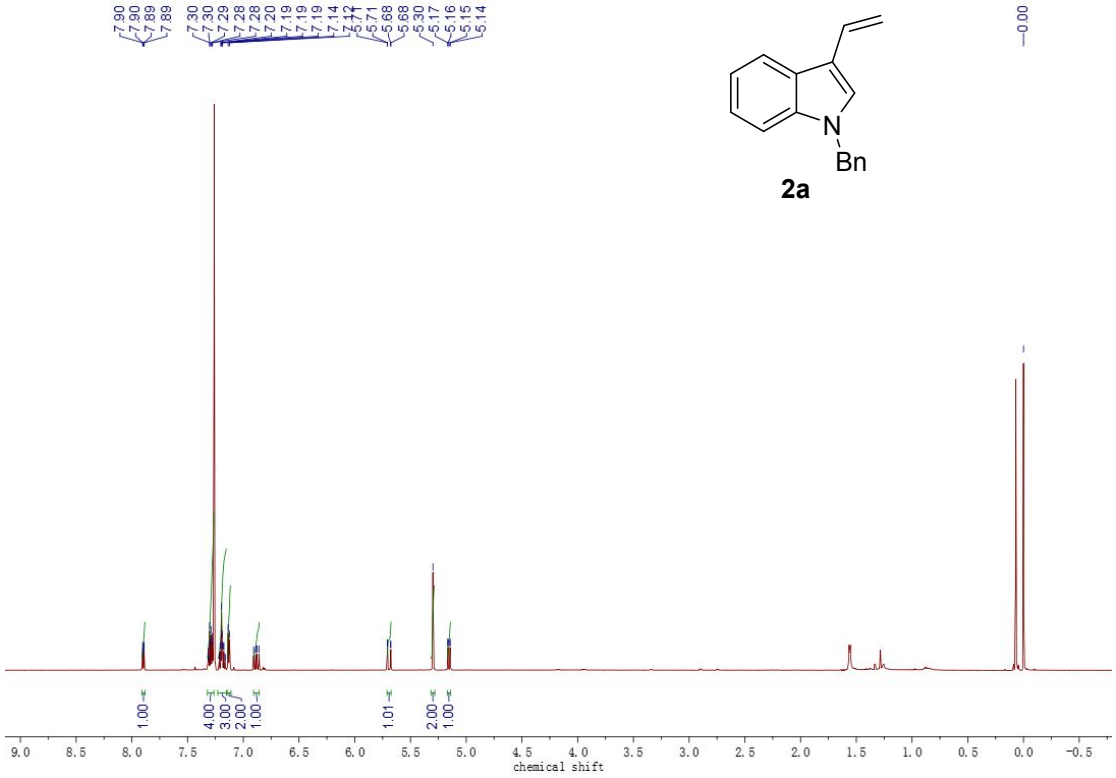
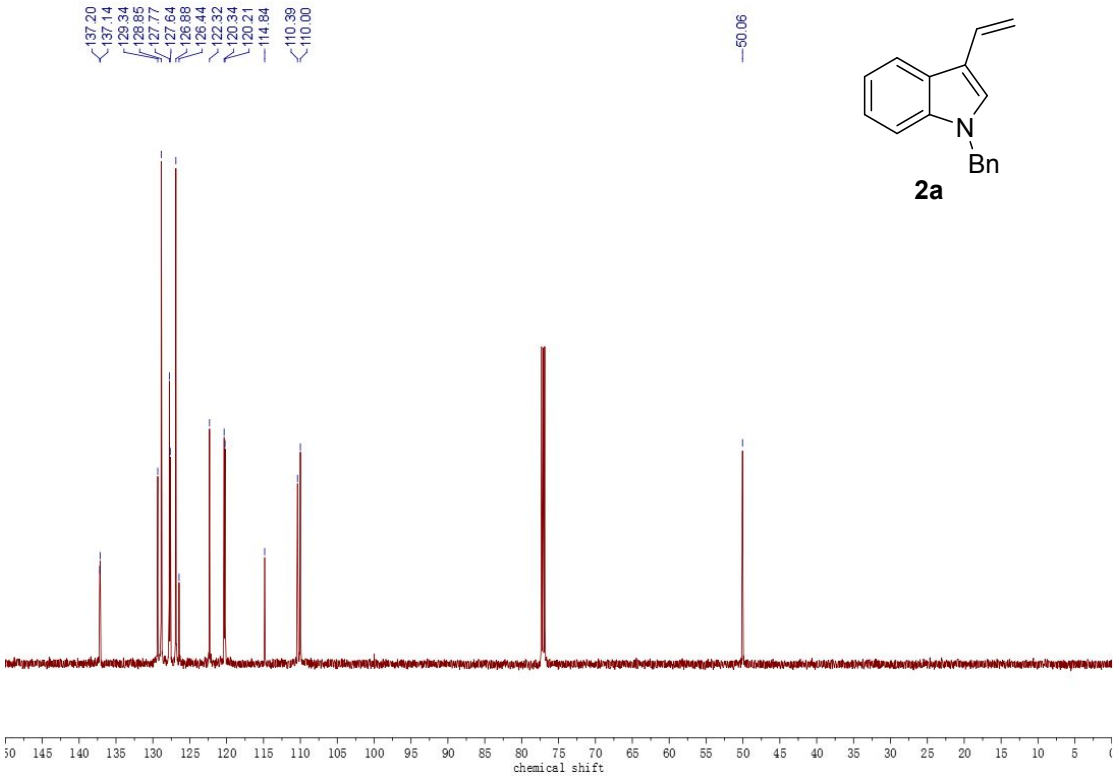


Figure S2. ^{13}C NMR (151MHz, $CDCl_3$) spectrum of 2a



1-benzyl-4-bromo-3-vinyl-1H-indole (2b)

Figure S3. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of 2b

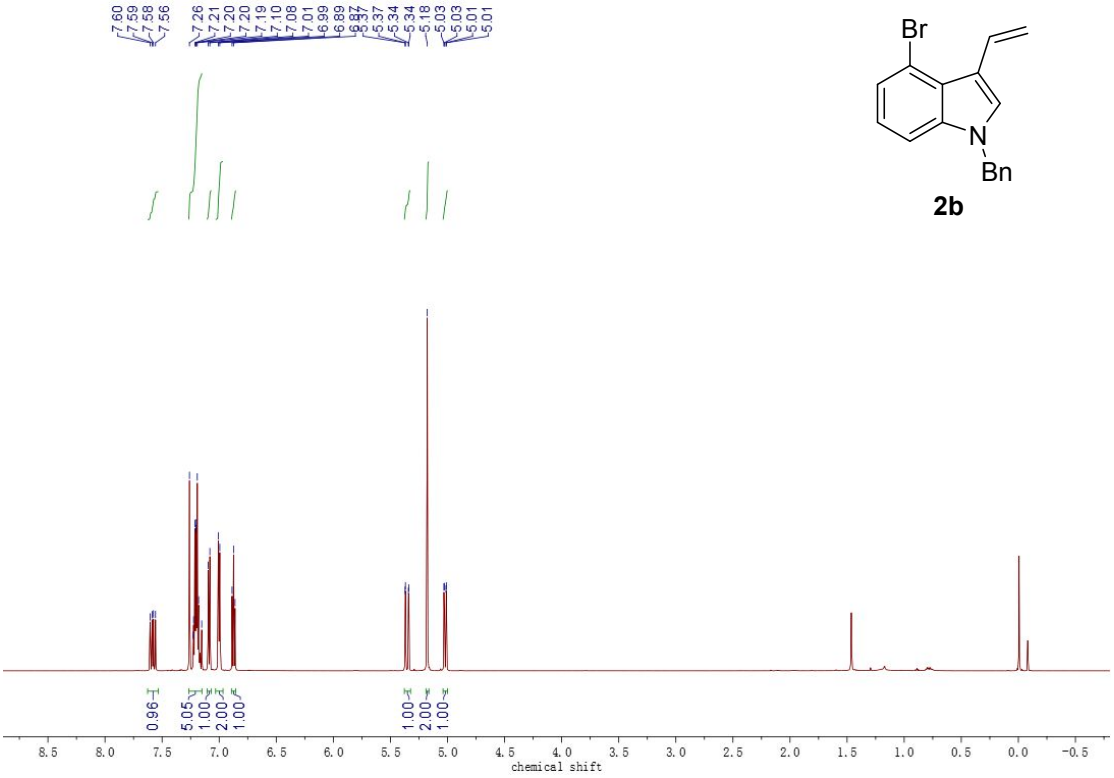
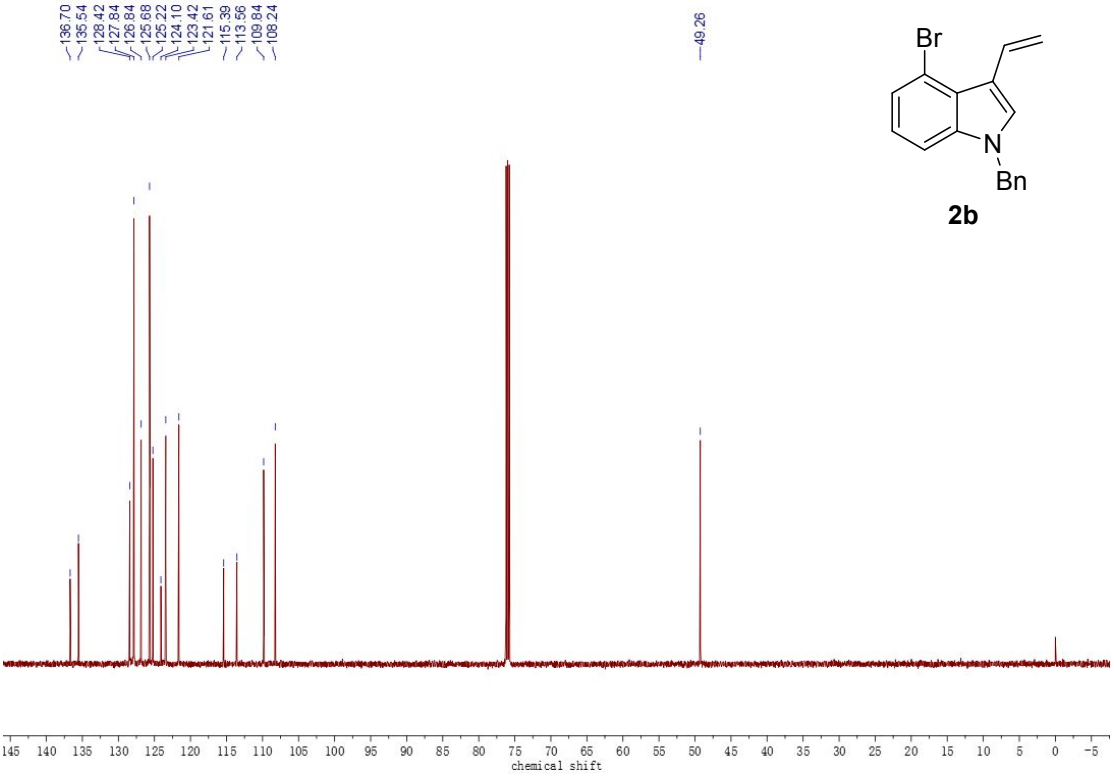
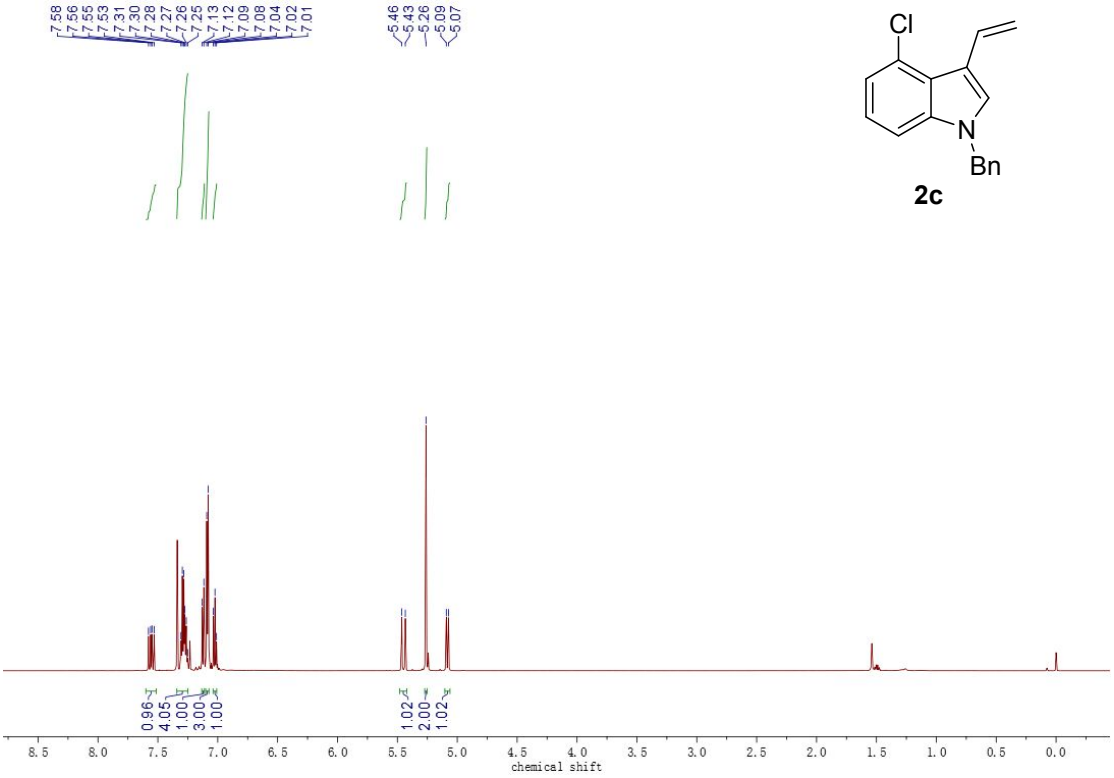


Figure S4. ^{13}C NMR (151MHz, $CDCl_3$) spectrum of 2b



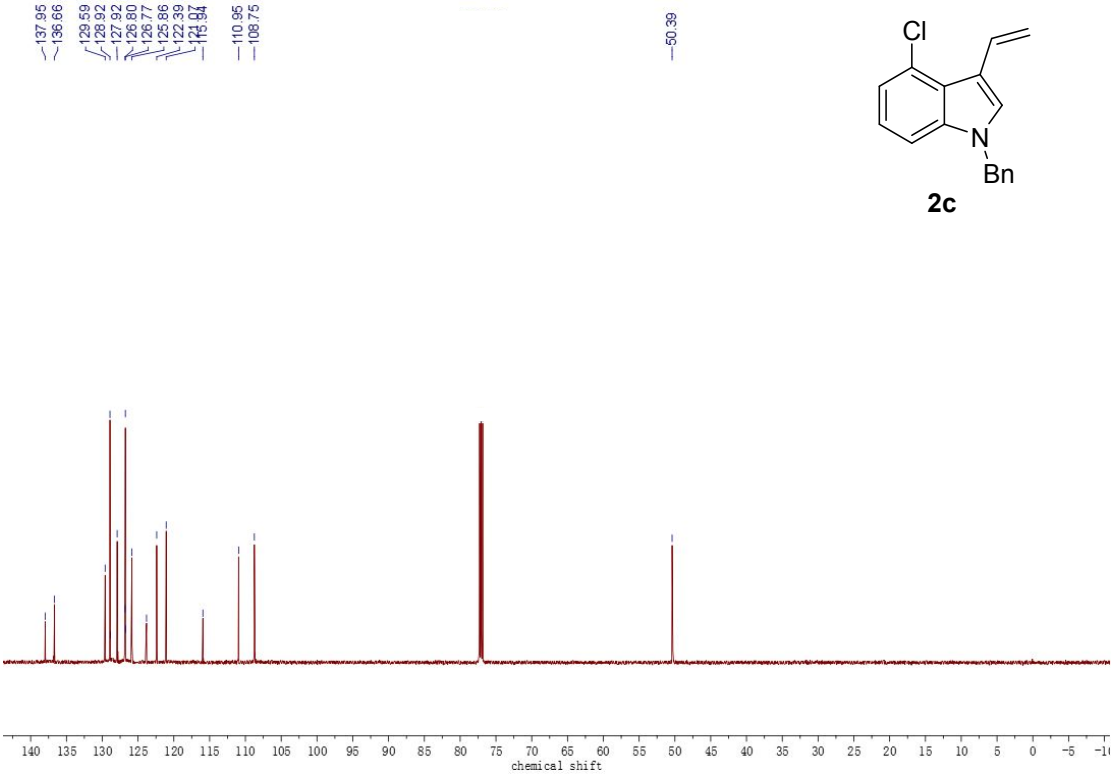
1-benzyl-4-chloro-3-vinyl-1H-indole (2c)

Figure S5. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of 2c



2c

Figure S6. ^{13}C NMR (151MHz, $CDCl_3$) spectrum of 2c



2c

1-benzyl-5-bromo-3-vinyl-1H-indole (2d)

Figure S7. ^{1}H NMR (400MHz, $CDCl_3$) spectrum of 2d

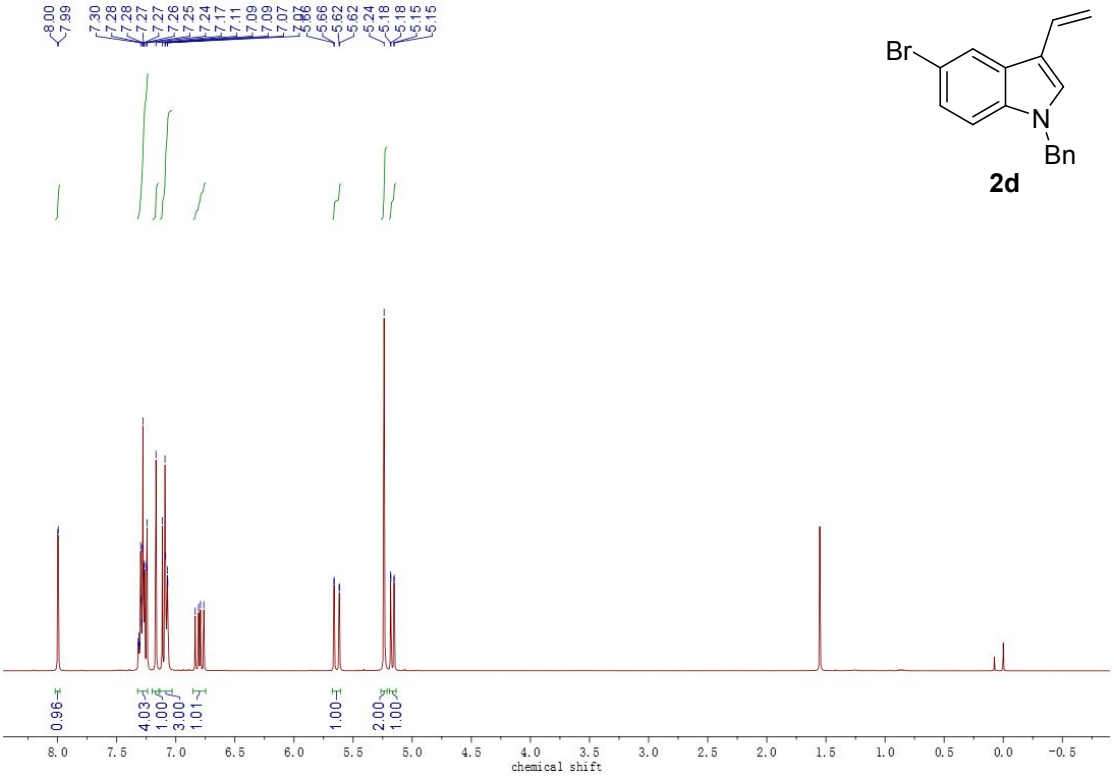
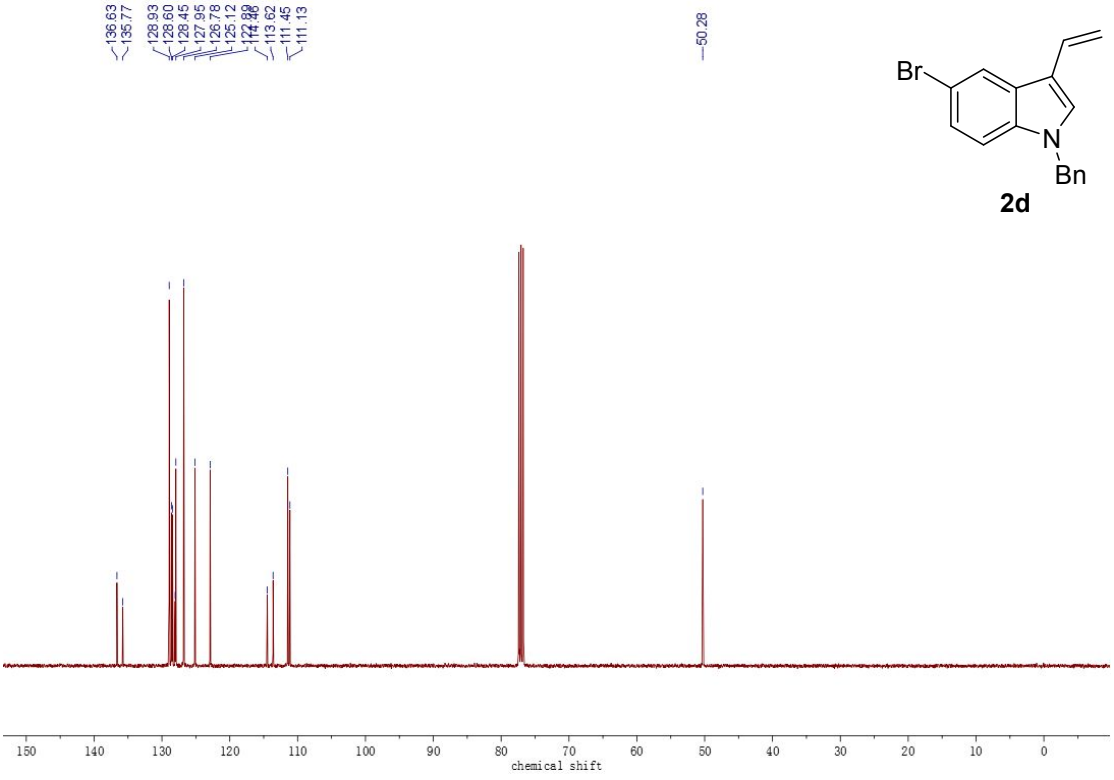
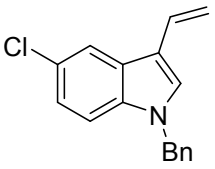


Figure S8. ^{13}C NMR (101MHz, $CDCl_3$) spectrum of 2d



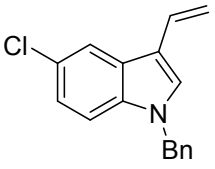
1-benzyl-5-chloro-3-vinyl-1H-indole (2e)

Figure S9. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of 2e



2e

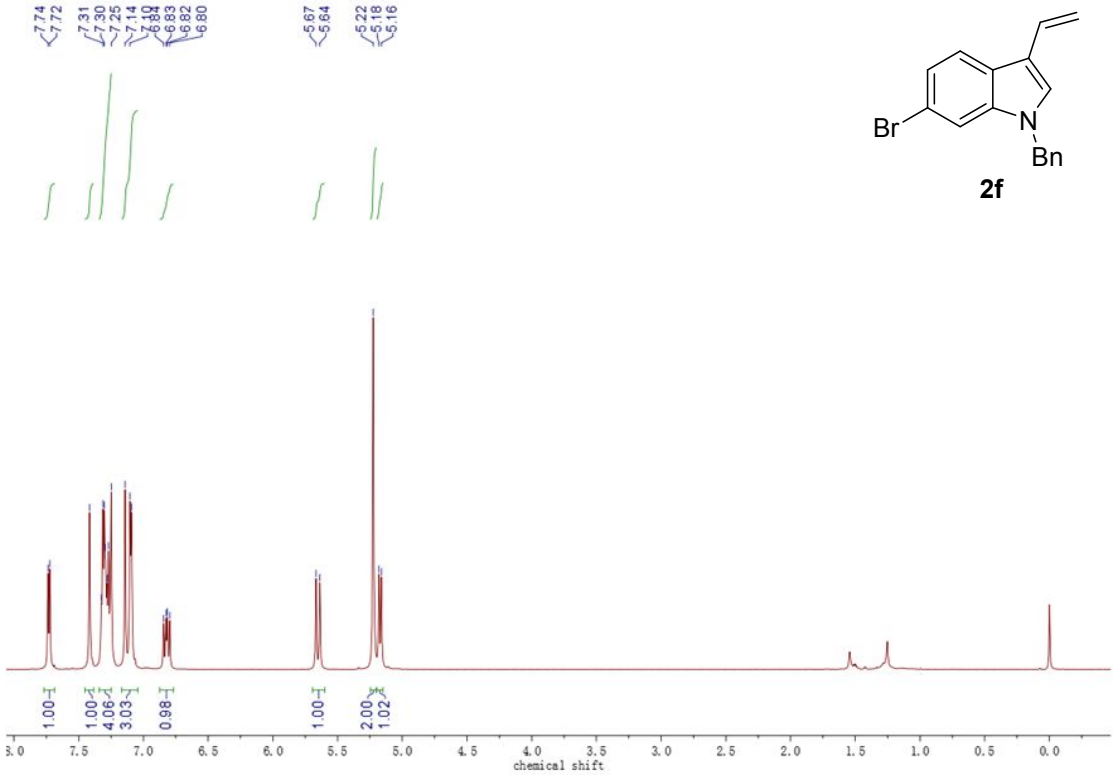
Figure S10. ^{13}C NMR (151MHz, $CDCl_3$) spectrum of 2e



2e

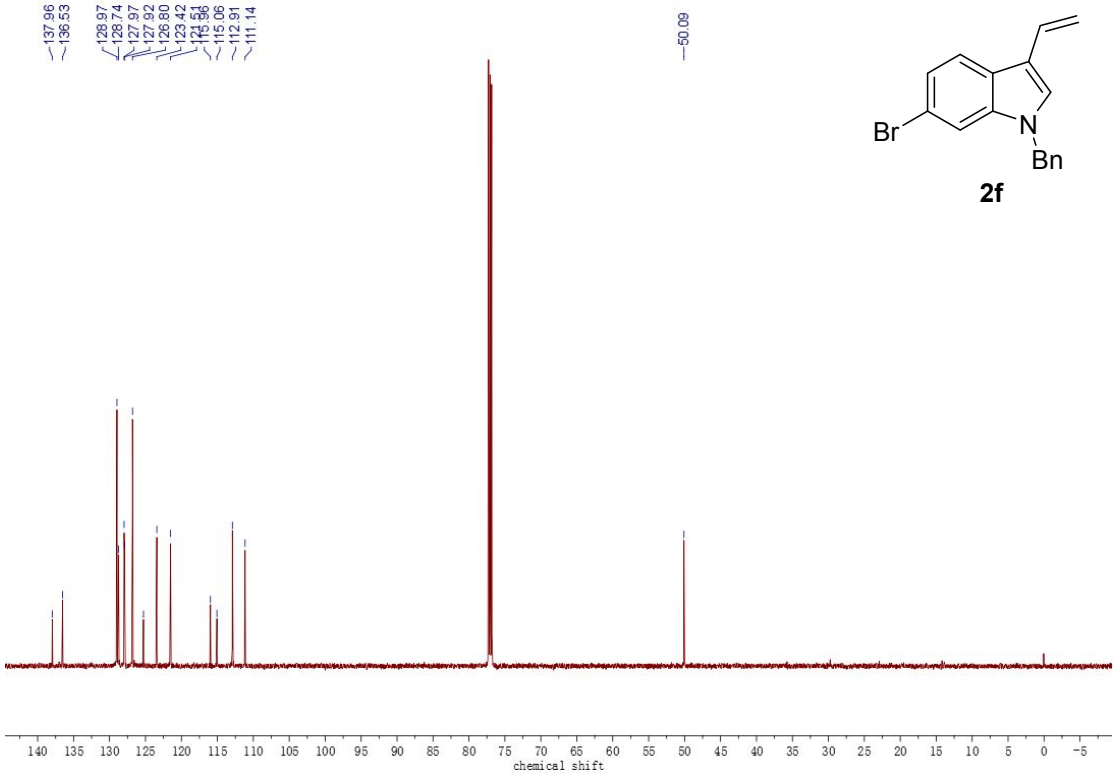
1-benzyl-6-bromo-3-vinyl-1H-indole (2f)

Figure S11. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of 2f



2f

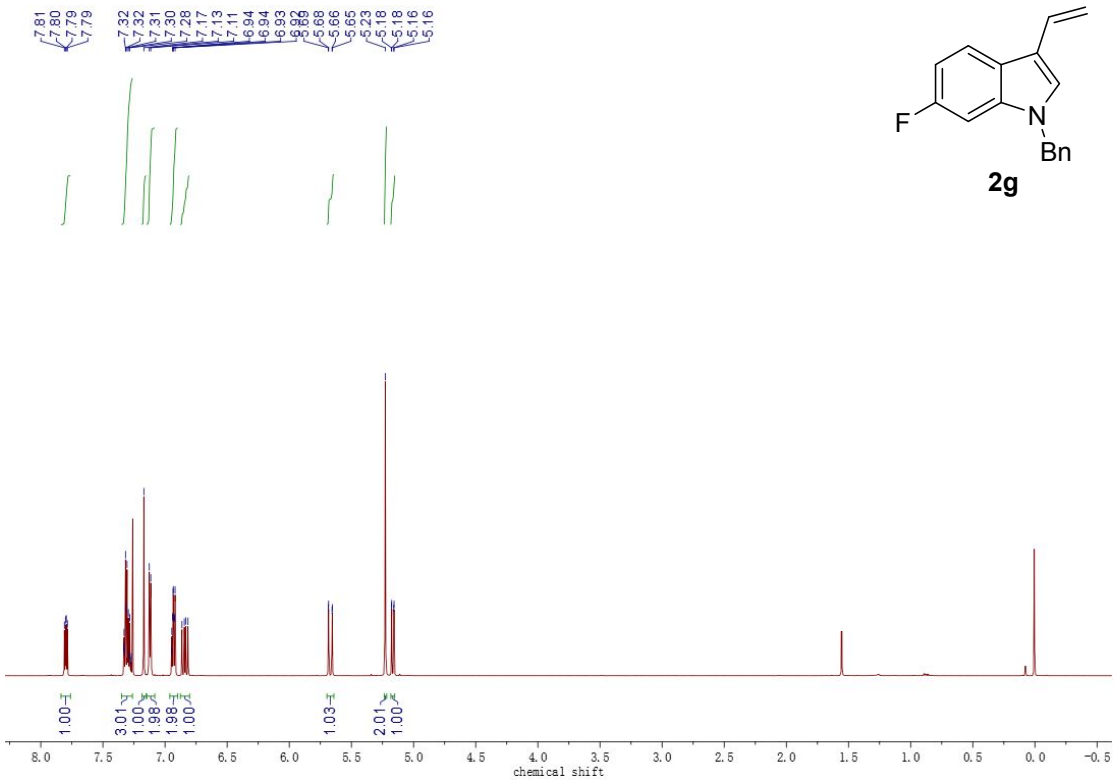
Figure S12. ^{13}C NMR (151MHz, $CDCl_3$) spectrum of 2f



2f

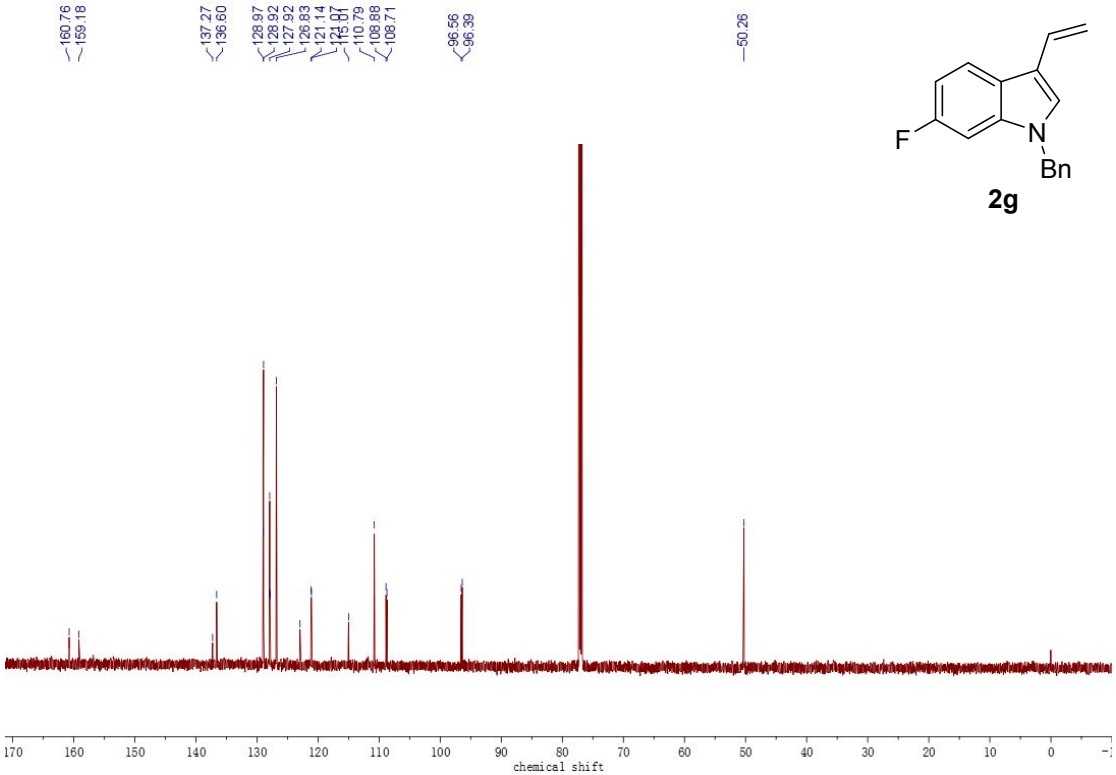
1-benzyl-6-fluoro-3-vinyl-1H-indole (2g)

Figure S13. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of 2g



2g

Figure S14. ^{13}C NMR (151MHz, $CDCl_3$) spectrum of 2g



2g

1-benzyl-5-methyl-3-vinyl-1H-indole (2h)

Figure S15. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of 2h

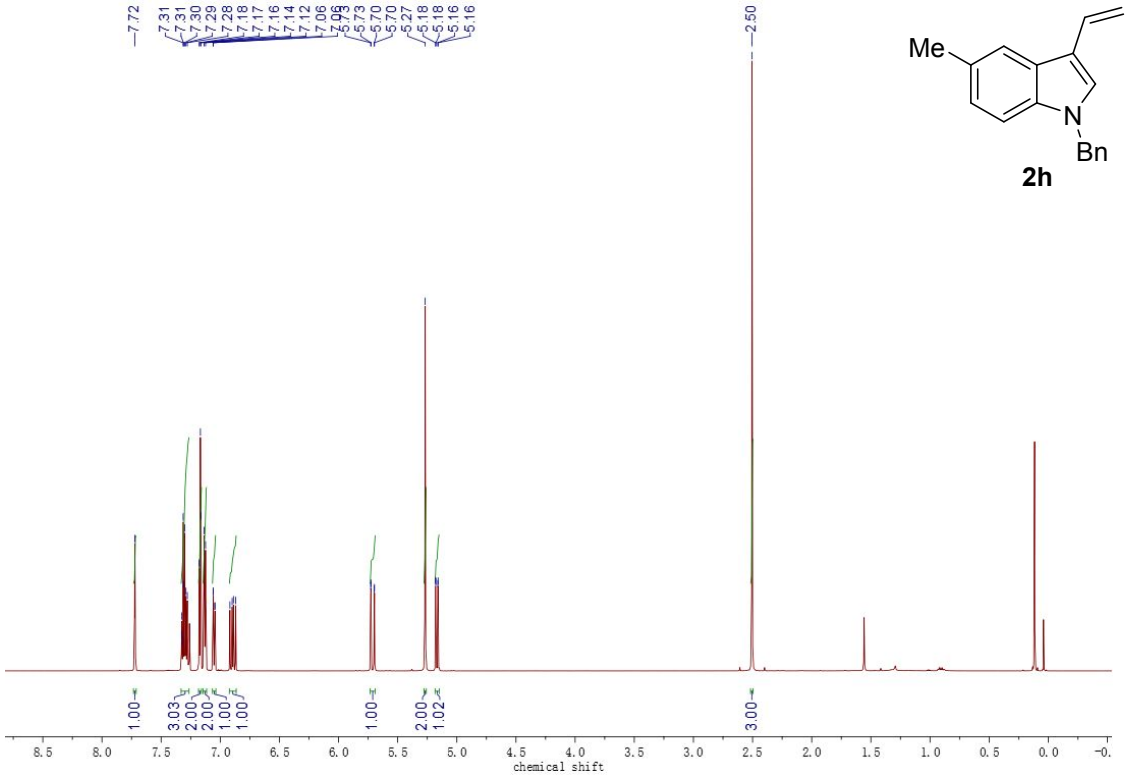
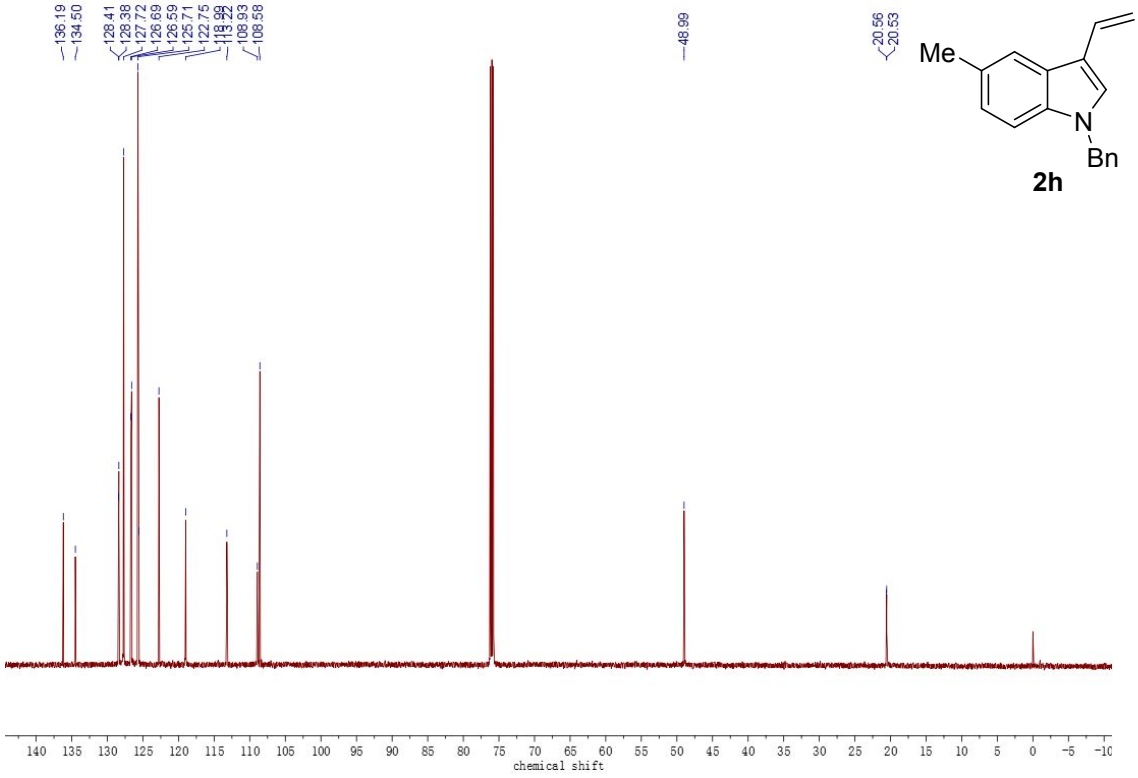


Figure S16. ^{13}C NMR (151MHz, $CDCl_3$) spectrum of 2h



1-benzyl-5-methoxy-3-vinyl-1H-indole (2i)

Figure S17. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of 2i

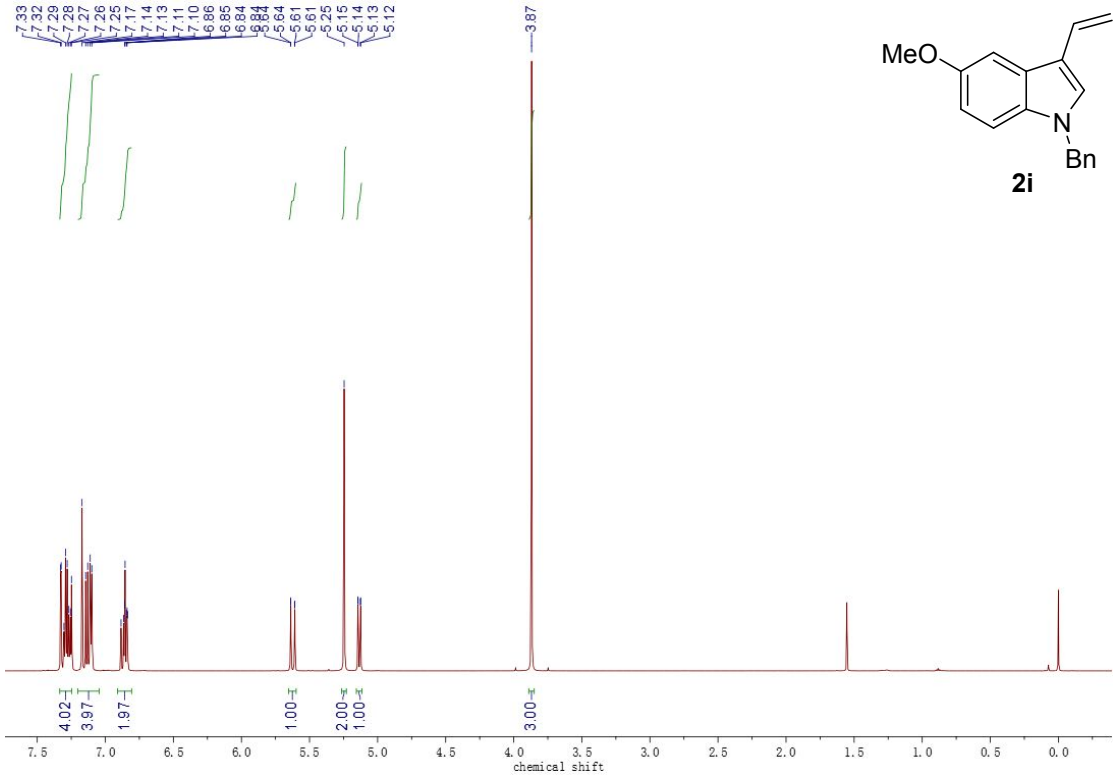
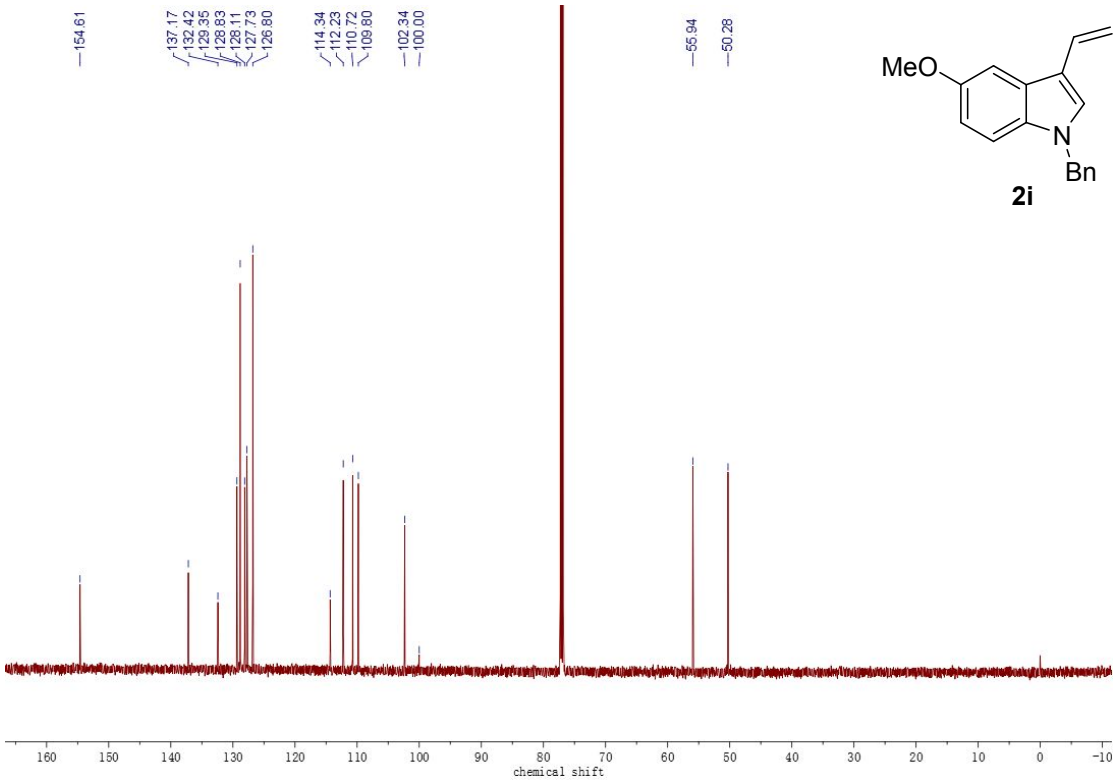
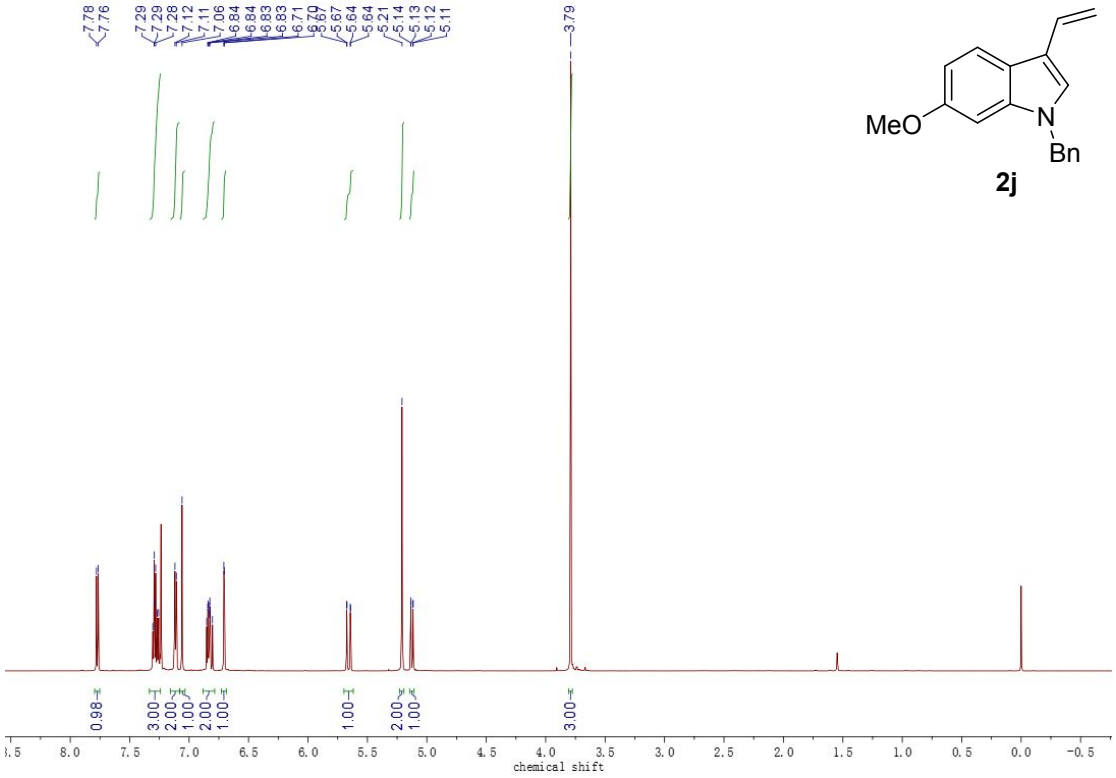


Figure S18. ^{13}C NMR (151MHz, $CDCl_3$) spectrum of 2i



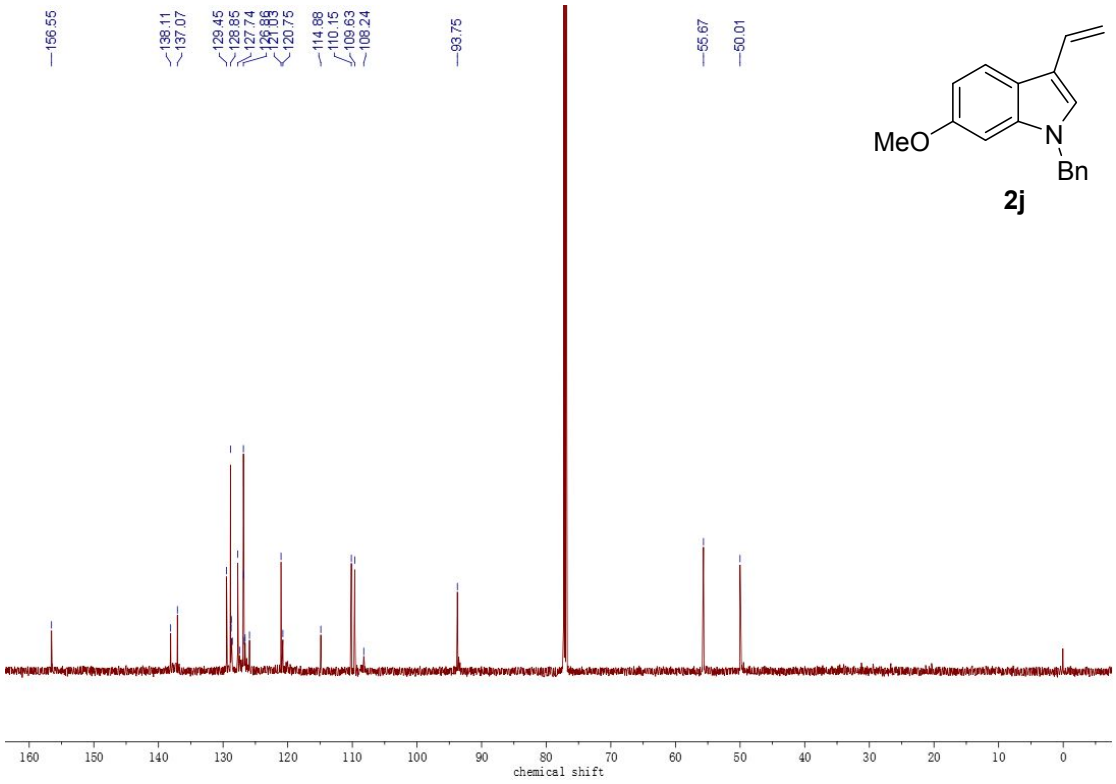
1-benzyl-6-methoxy-3-vinyl-1H-indole (2j)

Figure S19. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of 2j



2j

Figure S20. ^{13}C NMR (151MHz, $CDCl_3$) spectrum of 2j



2j

1-benzyl-7-methyl-3-vinyl-1H-indole (2k)

Figure S21. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of 2k

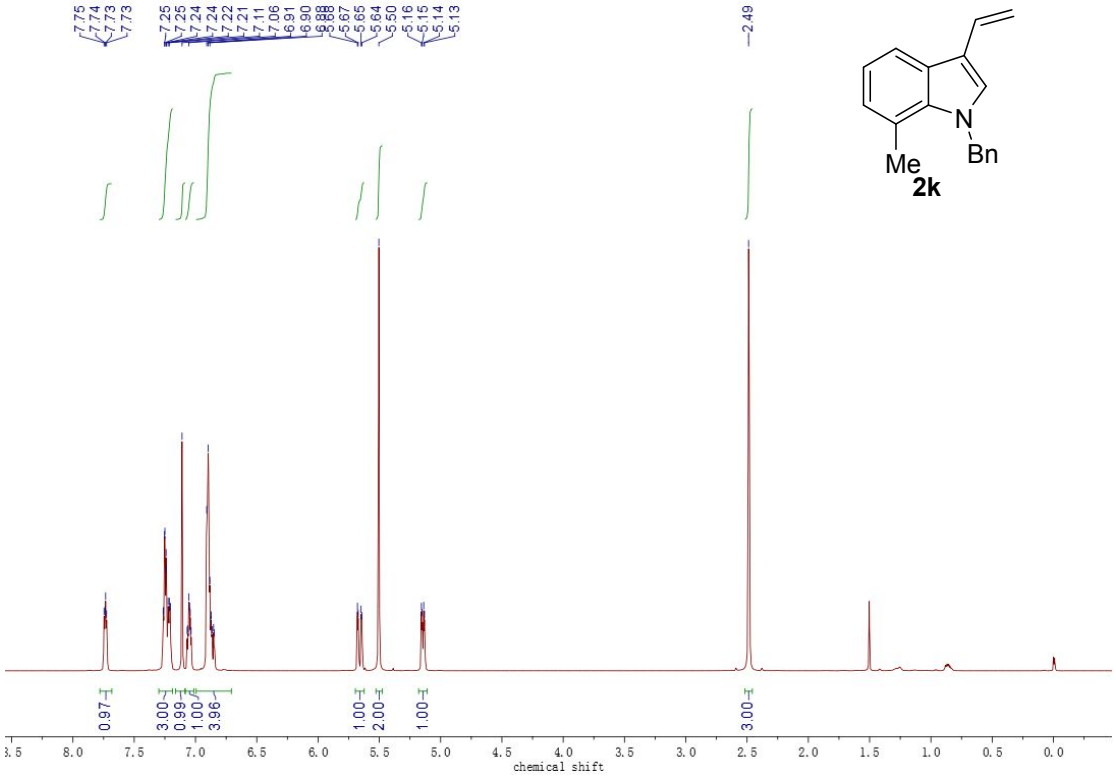
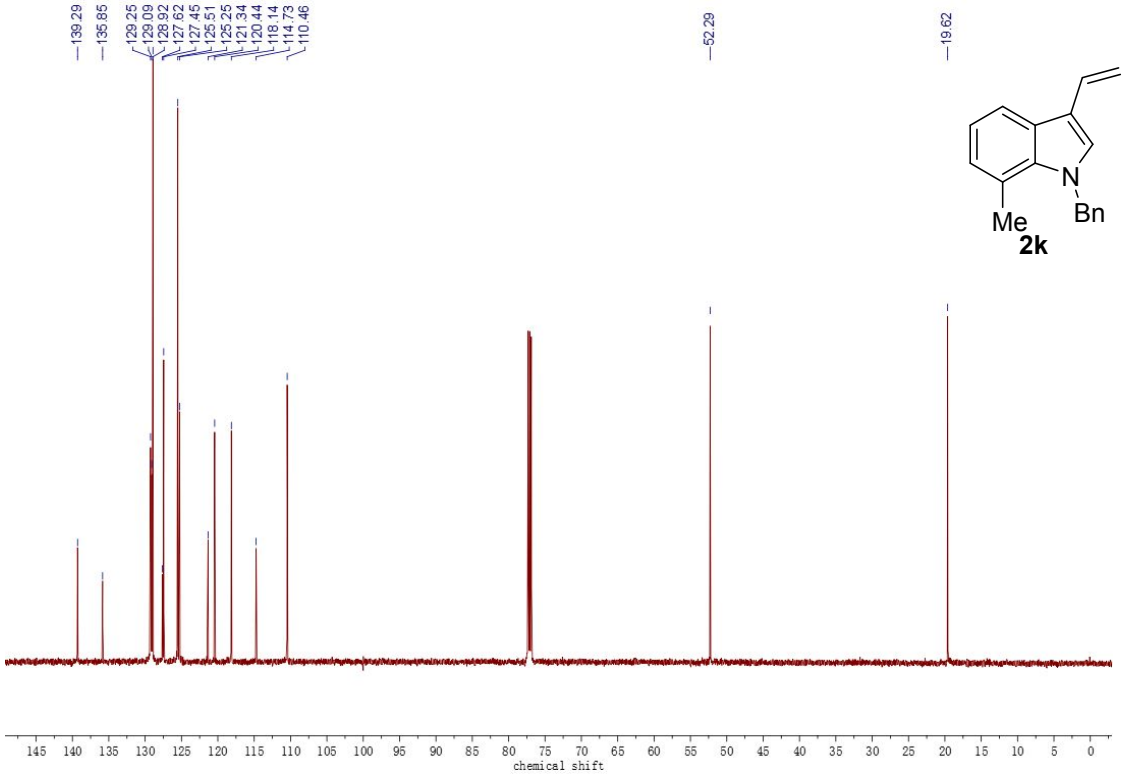


Figure S22. ^{13}C NMR (151MHz, $CDCl_3$) spectrum of 2k



1-benzyl-3-(prop-1-en-2-yl)-1H-indole (2l)

Figure S23. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of 2l

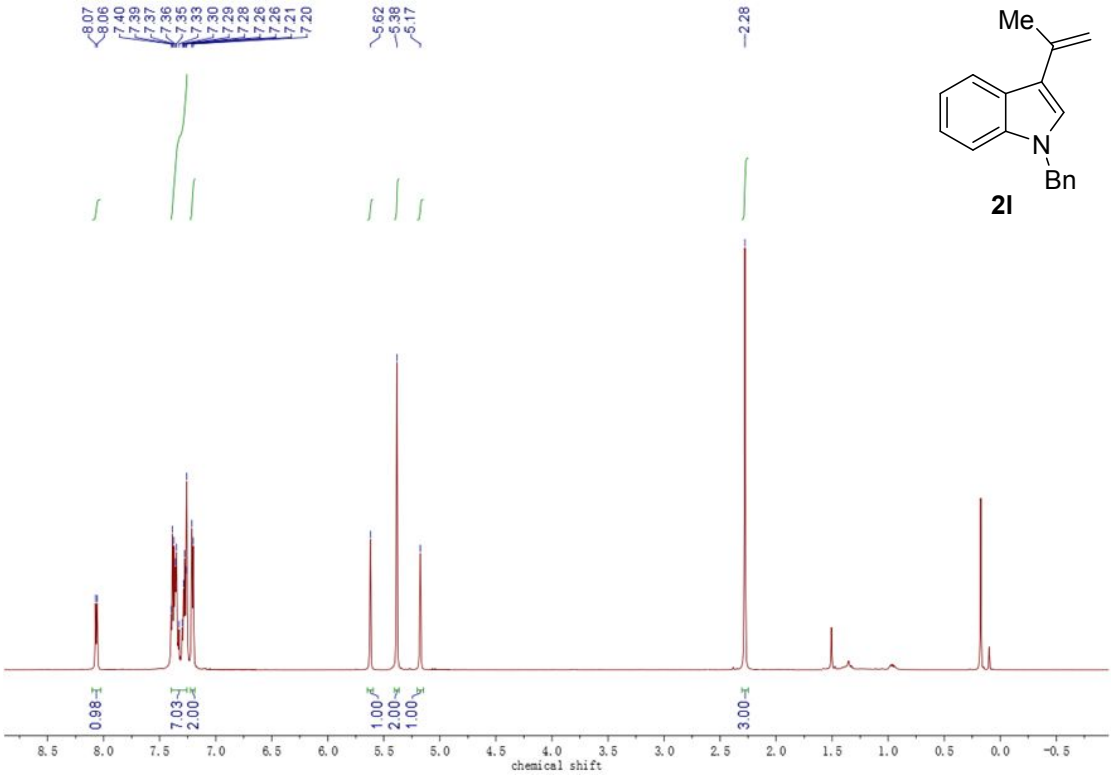
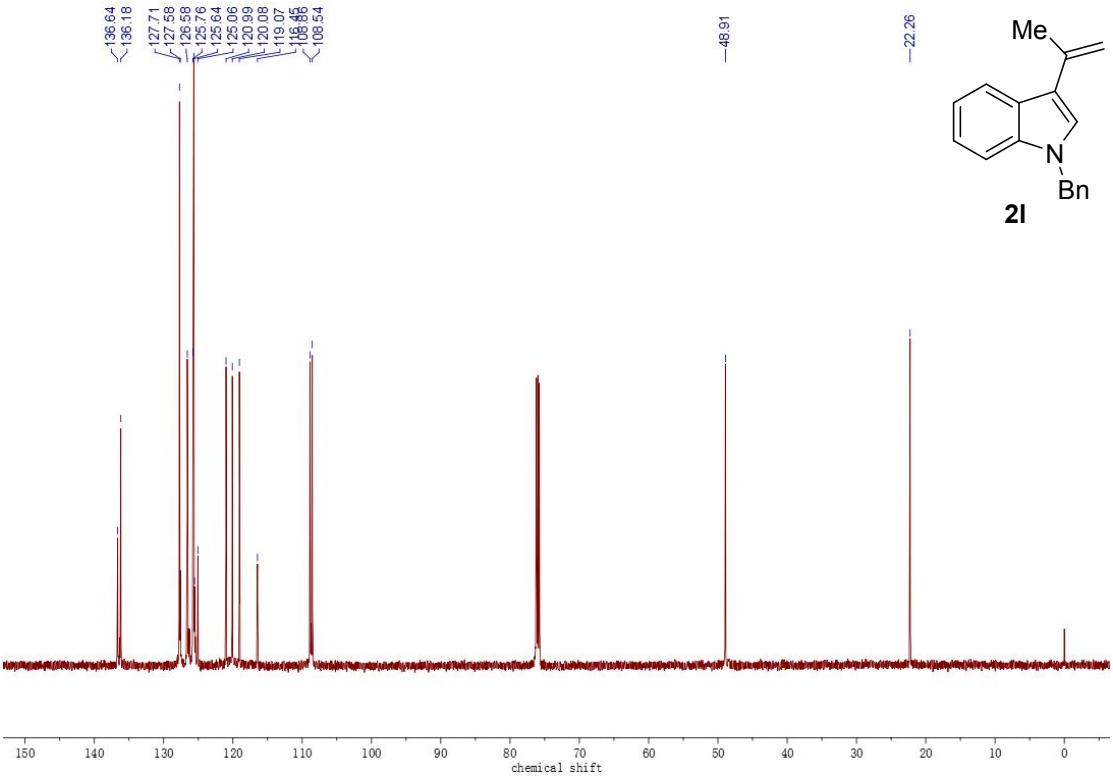


Figure S24. ^{13}C NMR (151MHz, $CDCl_3$) spectrum of 2l



(E/Z)-1-benzyl-3-(prop-1-en-1-yl)-1H-indole (2m)

Figure S25. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of 2m

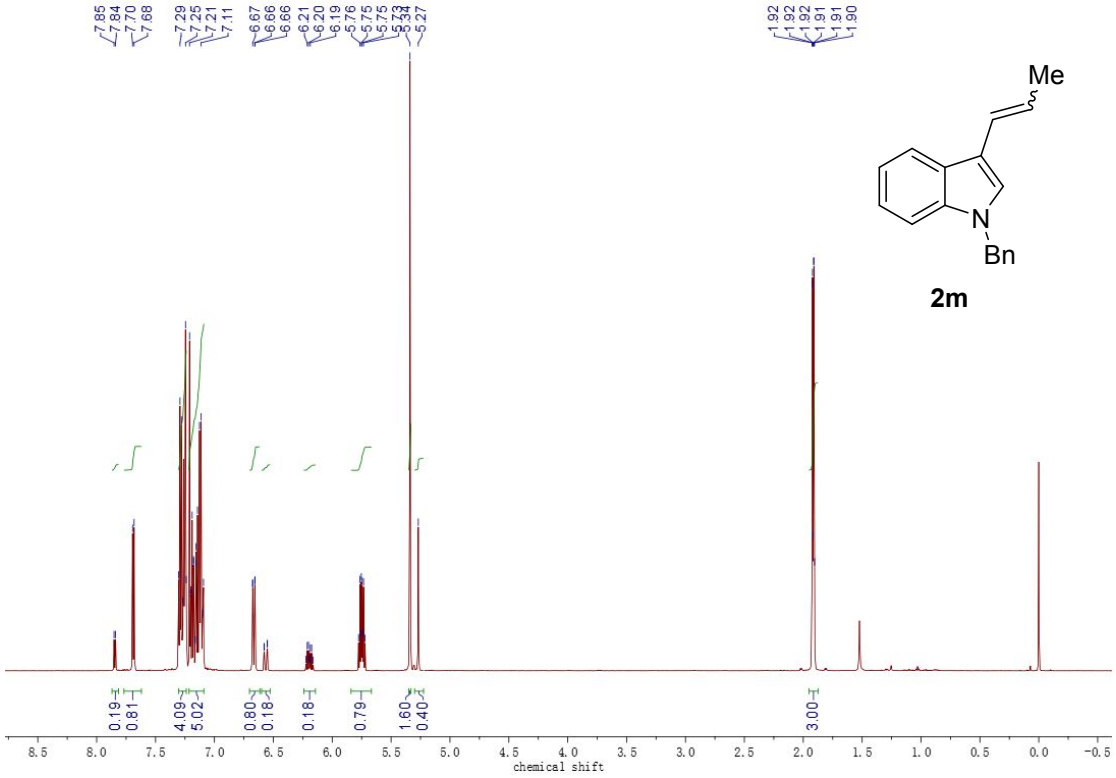
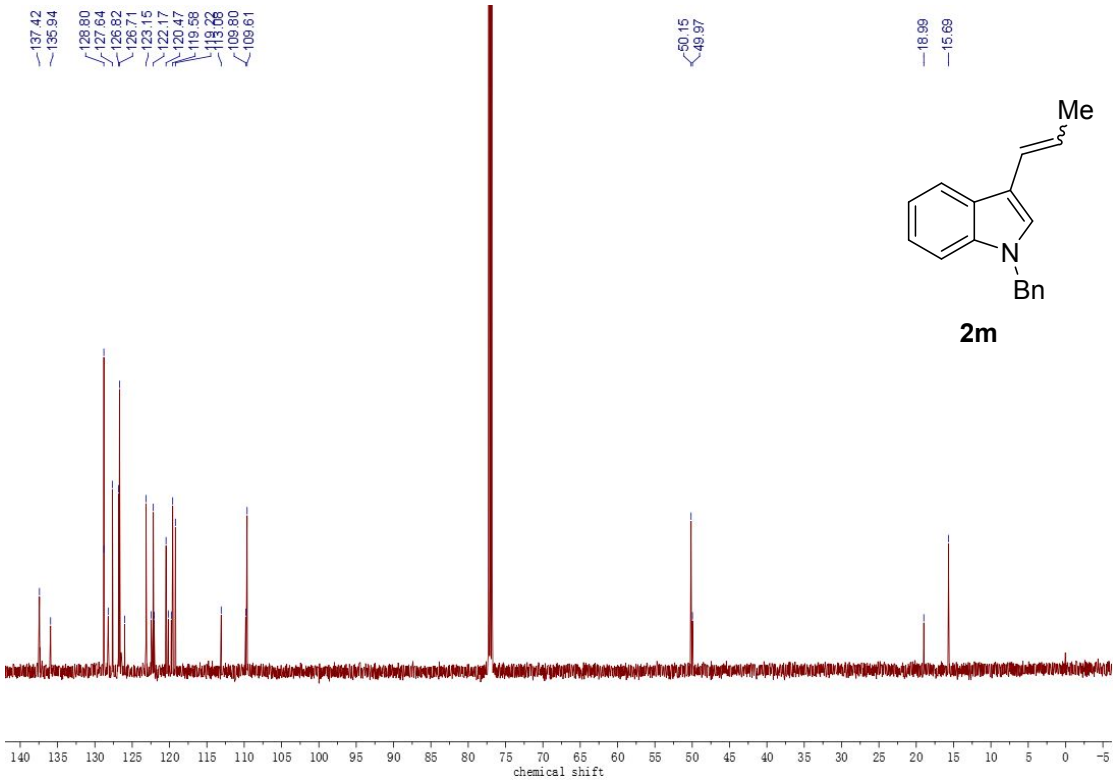
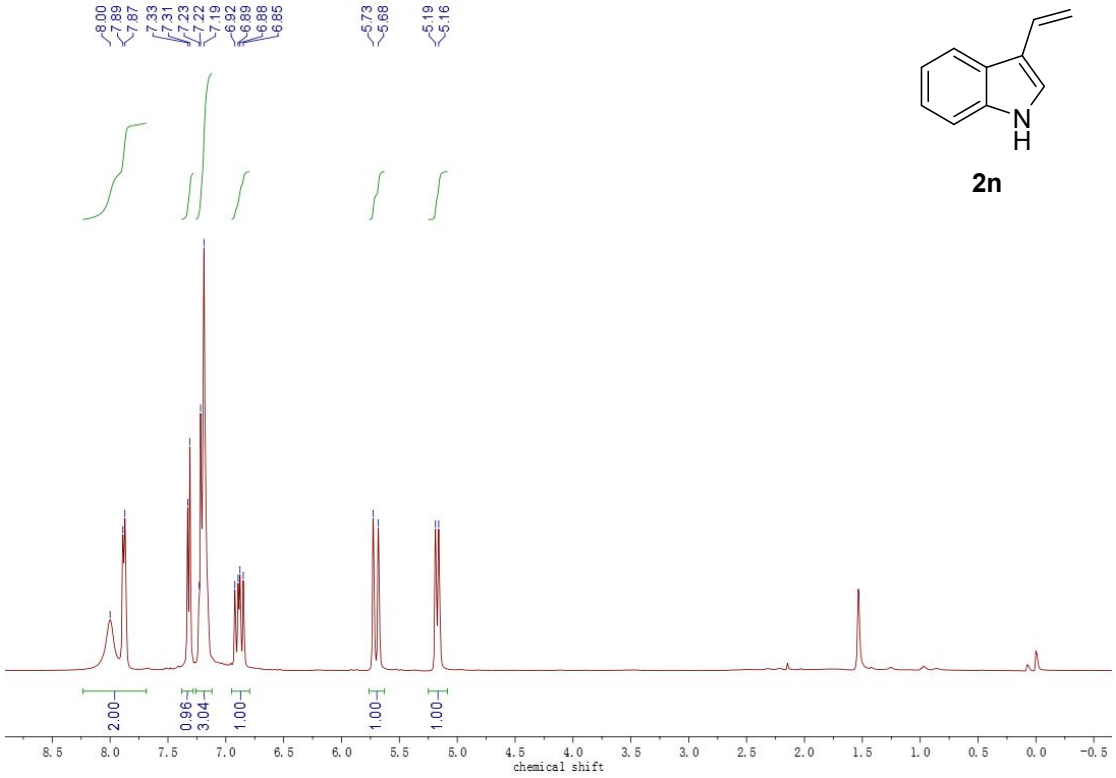


Figure S26. ^{13}C NMR (151MHz, $CDCl_3$) spectrum of 2m



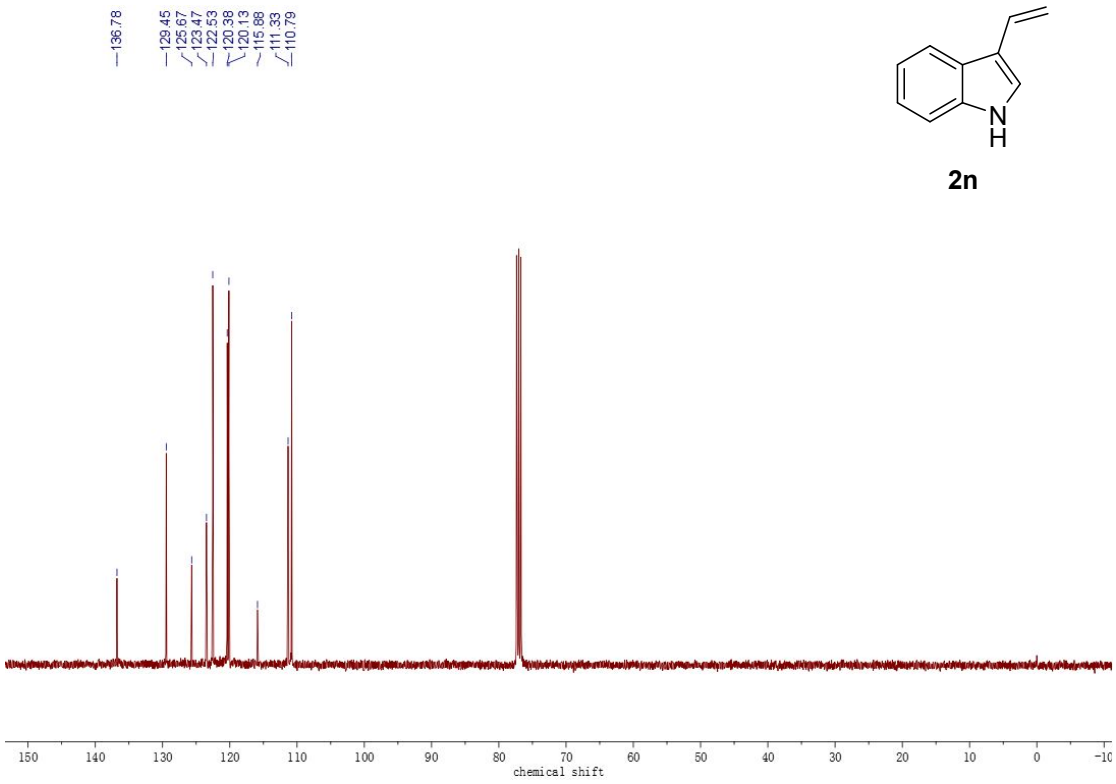
3-vinyl-1H-indole (2n)

Figure S27. ^{1}H NMR (400MHz, $CDCl_3$) spectrum of 2n



2n

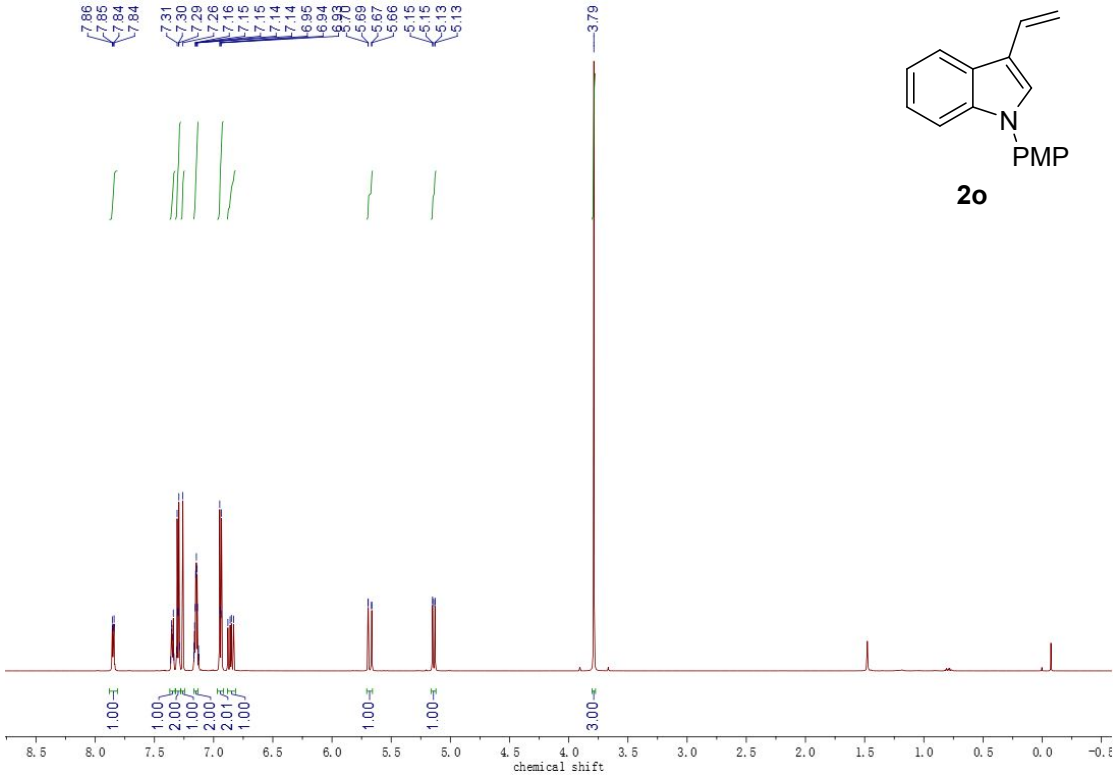
Figure S28. ^{13}C NMR (101MHz, $CDCl_3$) spectrum of 2n



2n

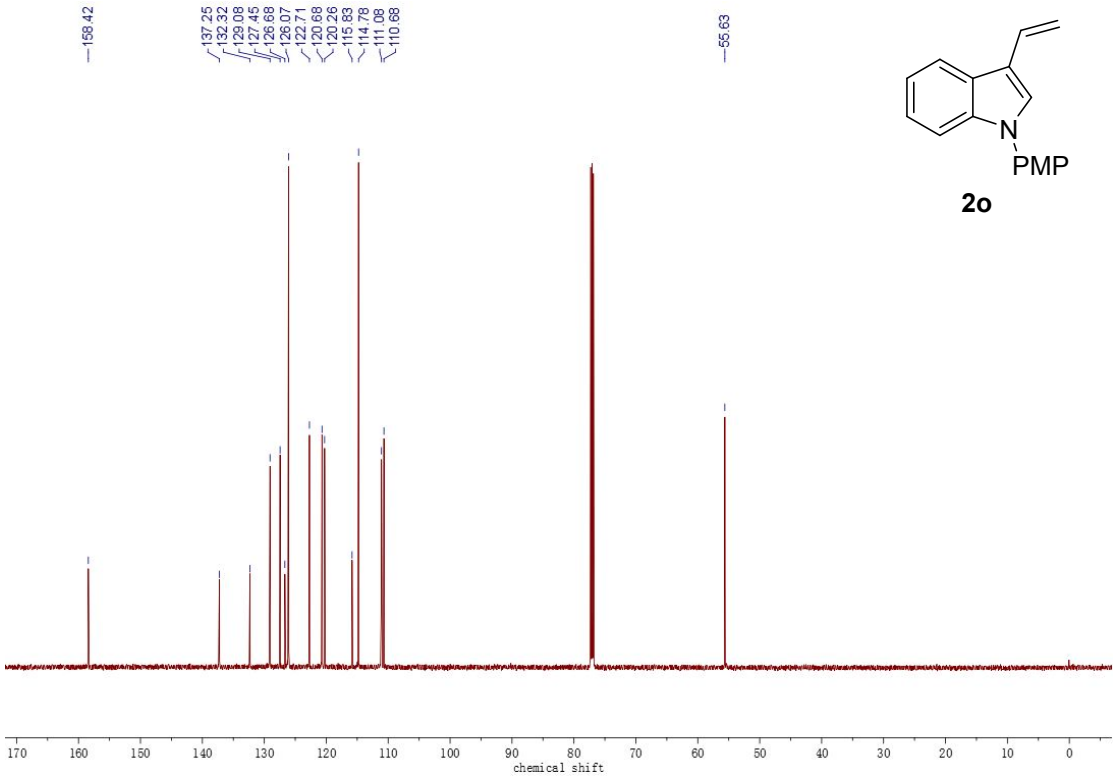
1-(4-methoxyphenyl)-3-vinyl-1H-indole (2o)

Figure S29. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of 2o



2o

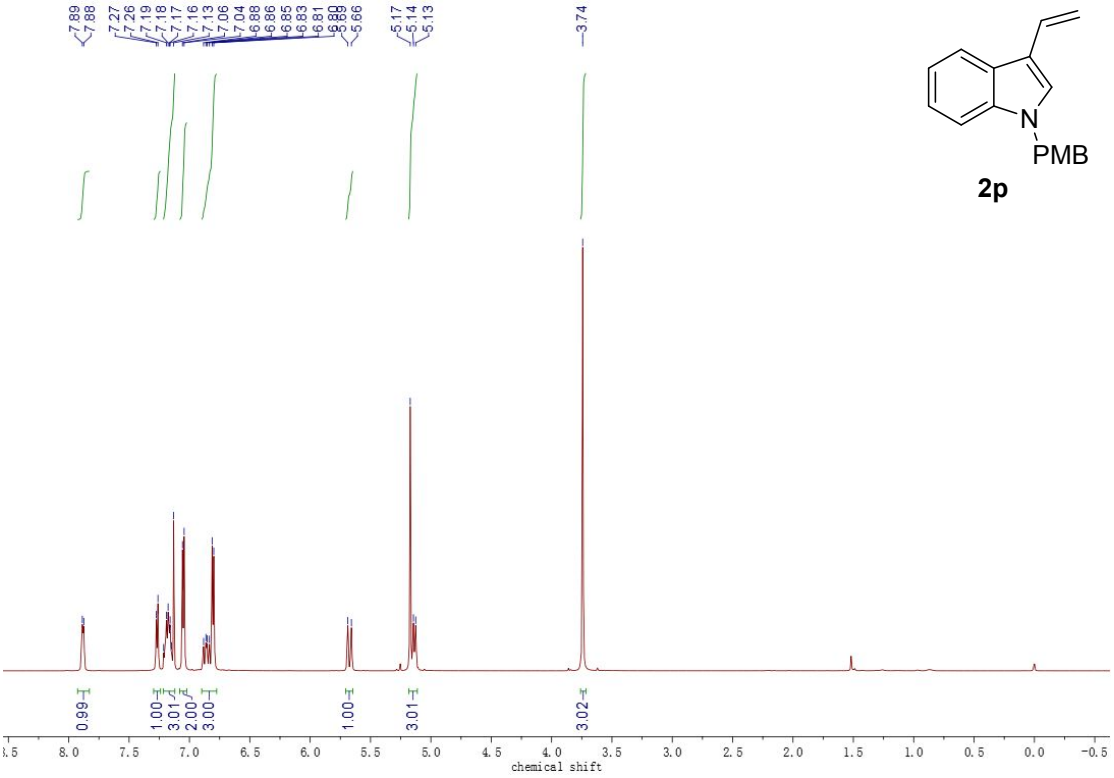
Figure S30. ^{13}C NMR (151MHz, $CDCl_3$) spectrum of 2o



2o

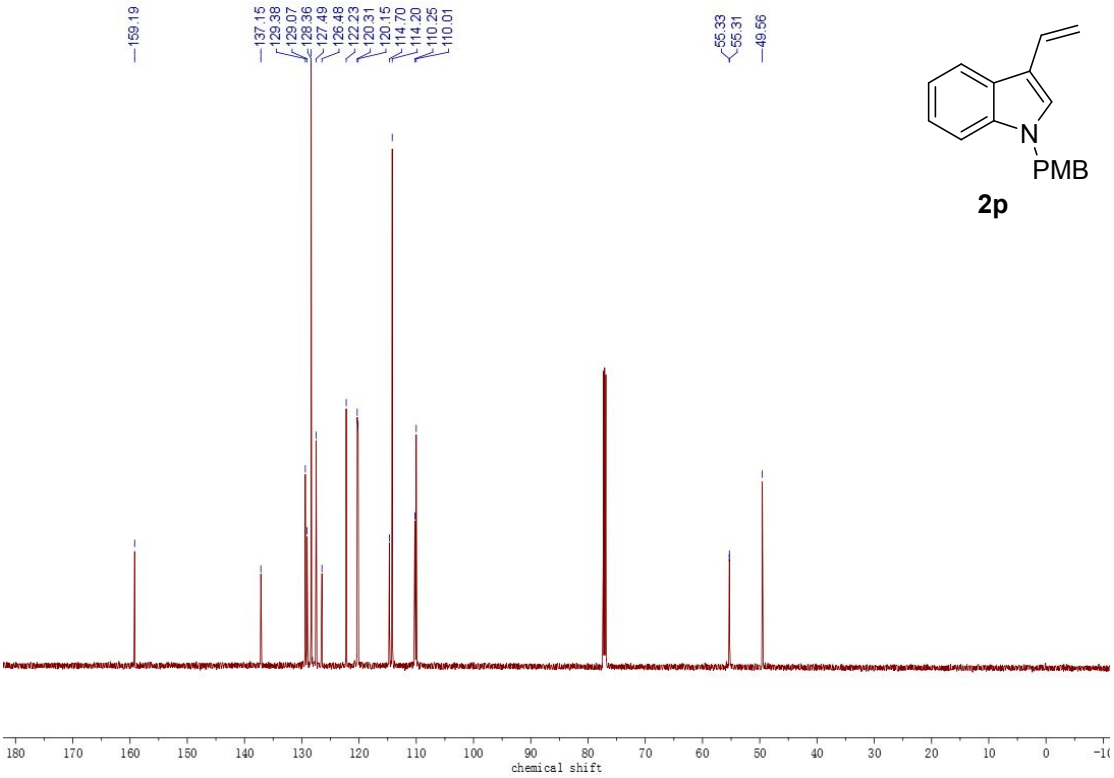
1-(4-methoxybenzyl)-3-vinyl-1H-indole (2p)

Figure S31. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of 2p



2p

Figure S32. ^{13}C NMR (151MHz, $CDCl_3$) spectrum of 2p



2p

1-(4-(tert-butyl)benzyl)-3-vinyl-1H-indole (2q)

Figure S33. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of 2q

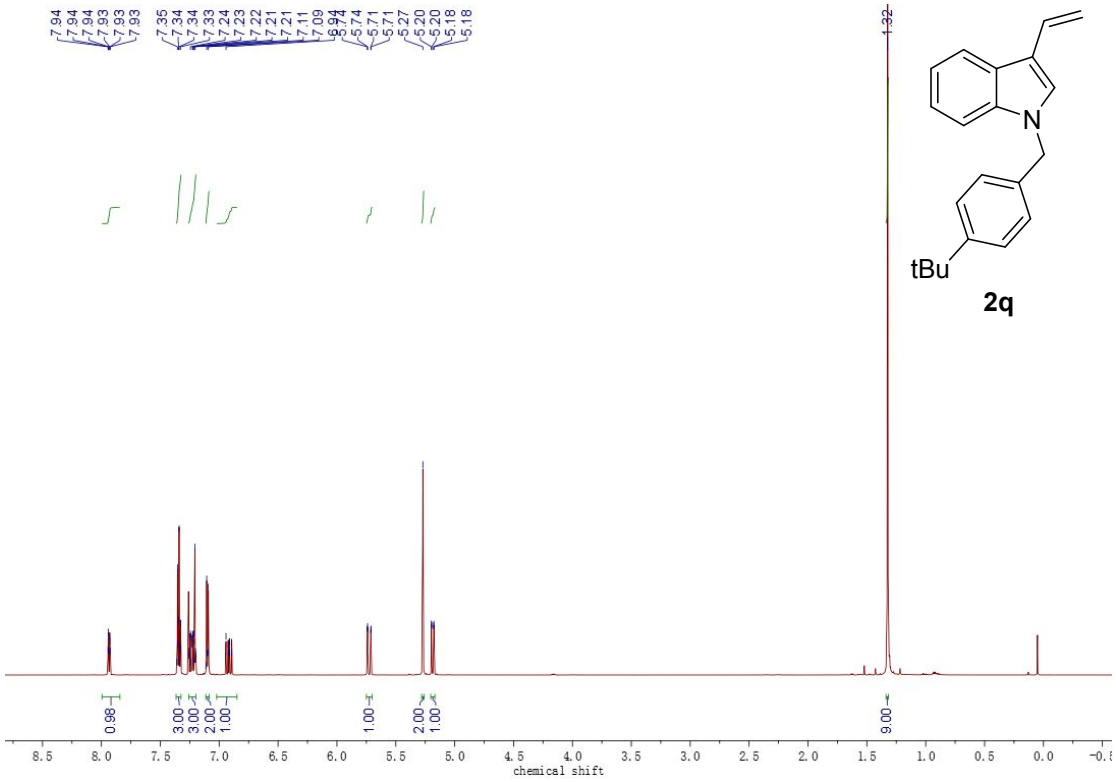
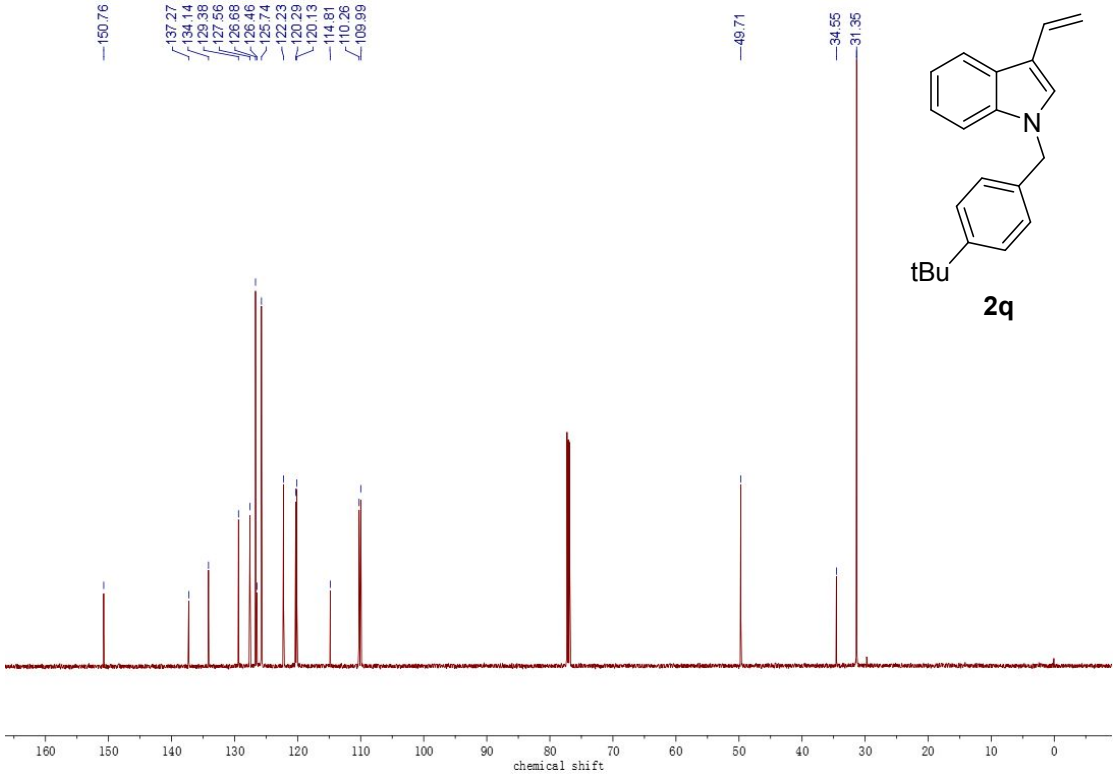


Figure S34. ^{13}C NMR (151MHz, $CDCl_3$) spectrum of 2q



1-(4-chlorobenzyl)-3-vinyl-1H-indole (2r)

Figure S35. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of 2r

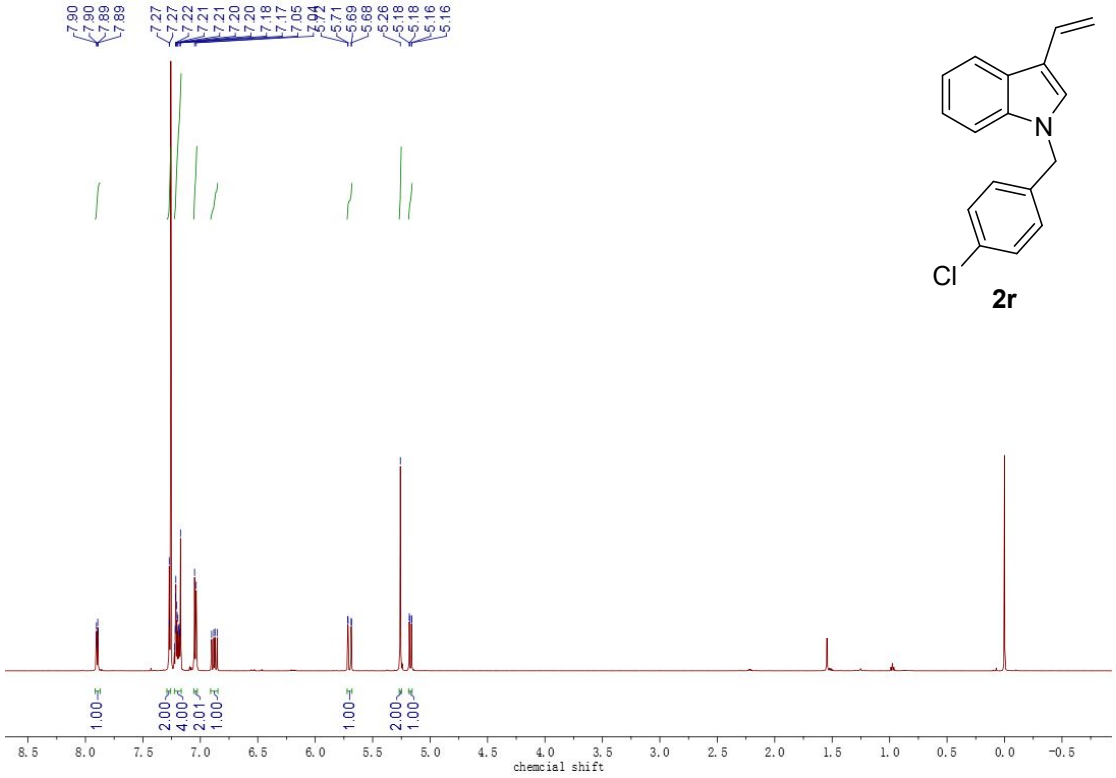
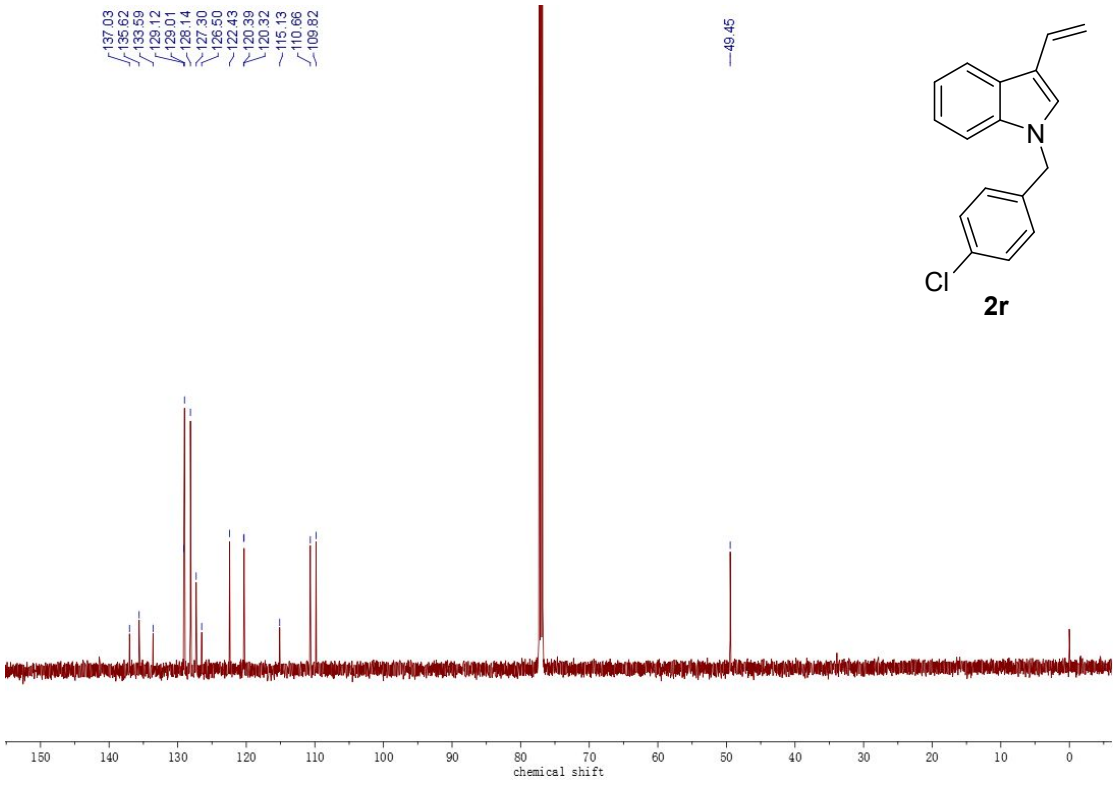
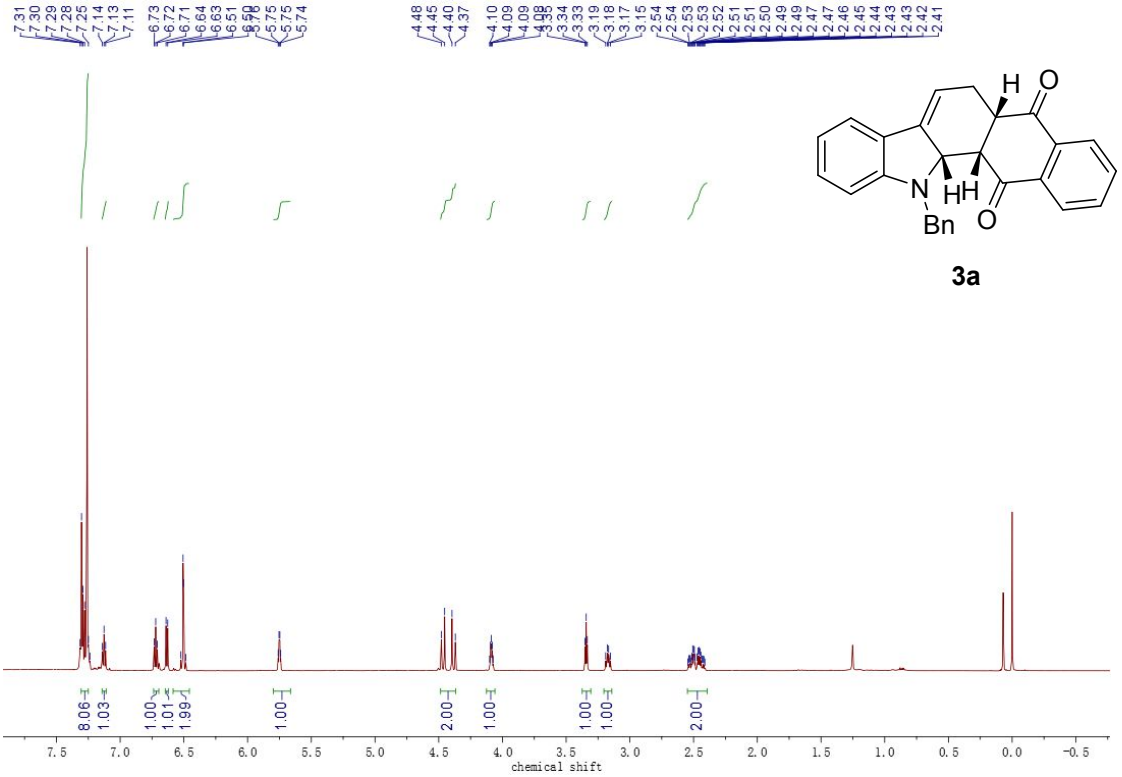


Figure S36. ^{13}C NMR (151MHz, $CDCl_3$) spectrum of 2r



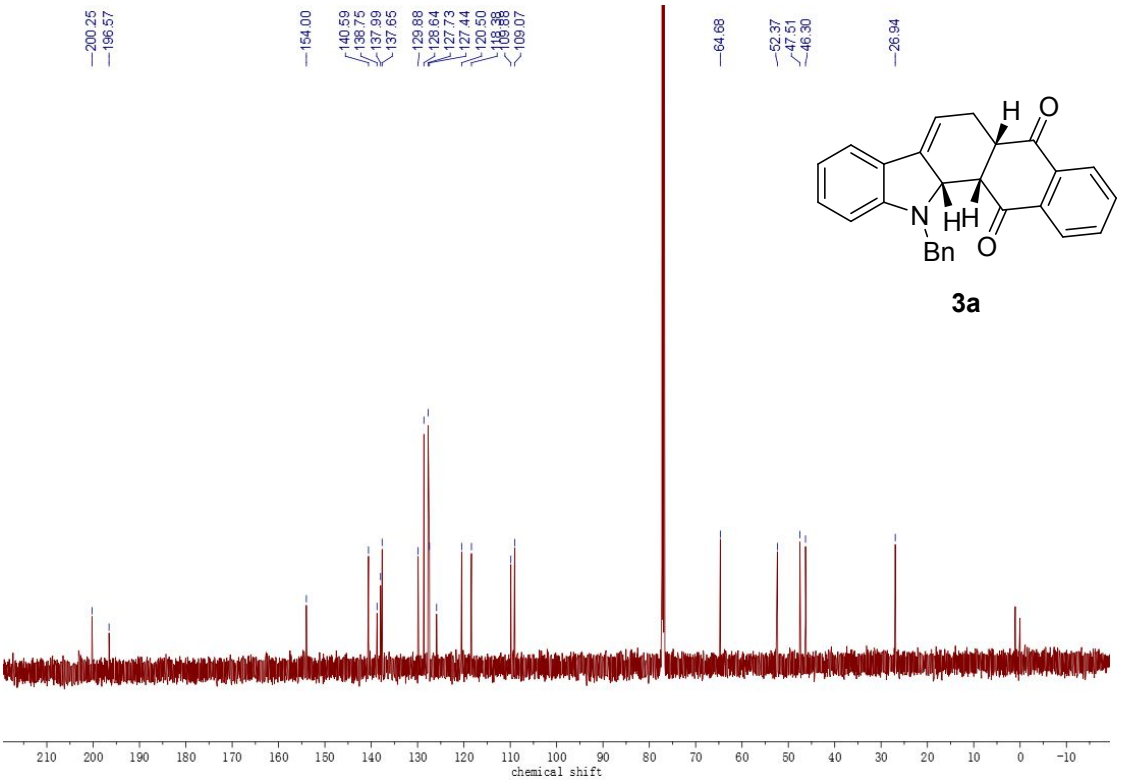
(5a*S*,12a*S*,12b*S*)-12-benzyl-6,12,12a,12b-tetrahydro-5*H*-naphtho[2,3-*a*]carbazole-5,13(5a*H*)-dione (3a)

Figure S37. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of 3a



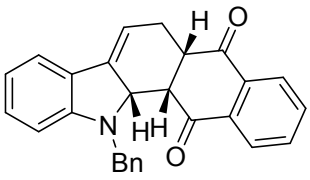
3a

Figure S38.^{13}C NMR (151MHz, $CDCl_3$) spectrum of 3a

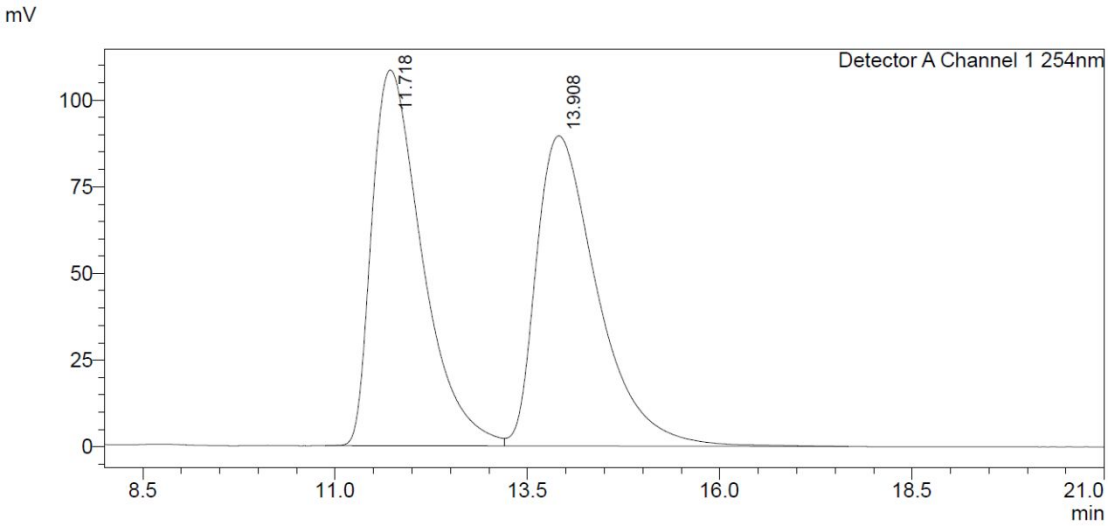


3a

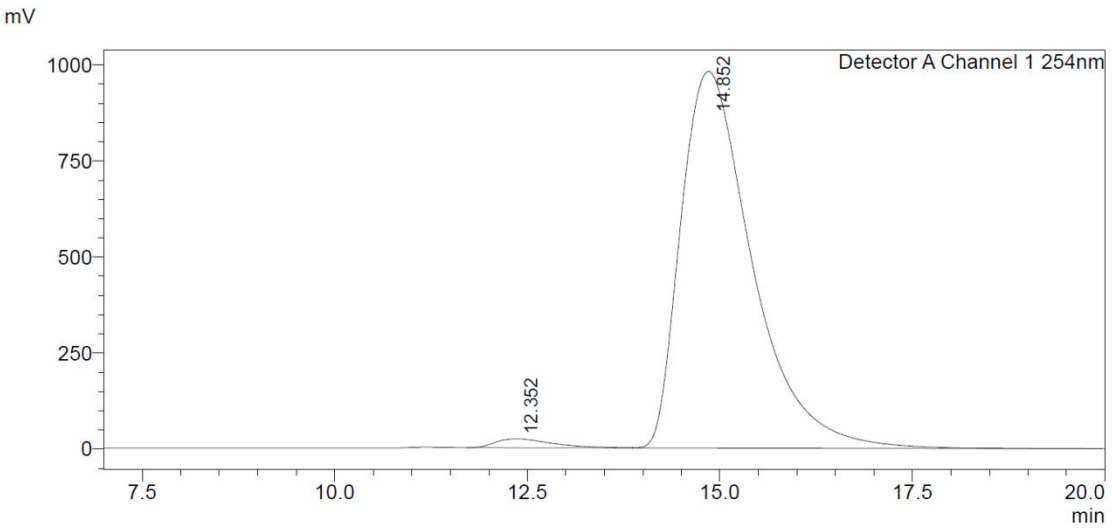
Figure S39. HPLC spectrum of 3a



3a (The top one is racemic, and the bottom one is chiral)



Peak#	Ret. Time	Area	Height	Conc.	Area%
1	11.718	4924652	108350	49.796	49.796
2	13.908	4965098	89467	50.204	50.204
Total		9889750	197817		100.000



Peak#	Ret. Time	Area	Height	Conc.	Area%
1	12.352	1171623	22960	1.818	1.818
2	14.852	63284870	980067	98.182	98.182
Total		64456493	1003026		100.000

(4a*S*,11a*S*,11b*S*)-11-benzyl-5,11,11a,11b-tetrahydro-1*H*-benzo[*a*]carbazole-1,4(4a*H*)-dione (3b)

Figure S40. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of 3b

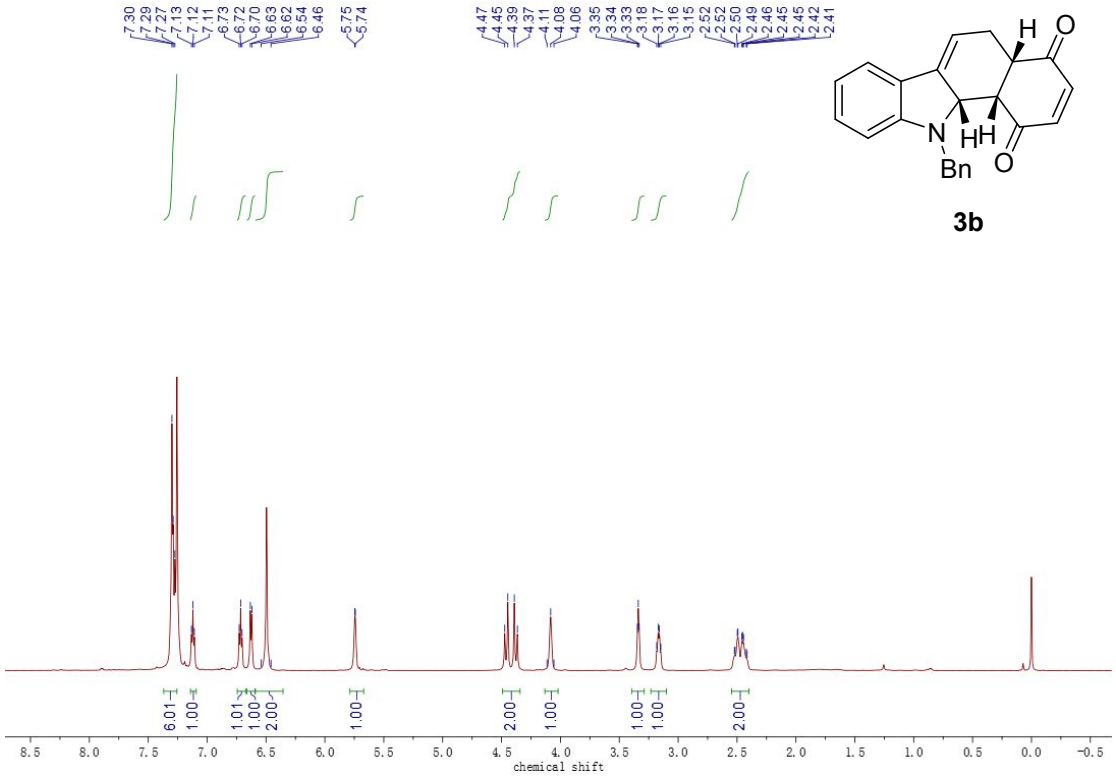


Figure S41. ^{13}C NMR (151MHz, $CDCl_3$) spectrum of 3b

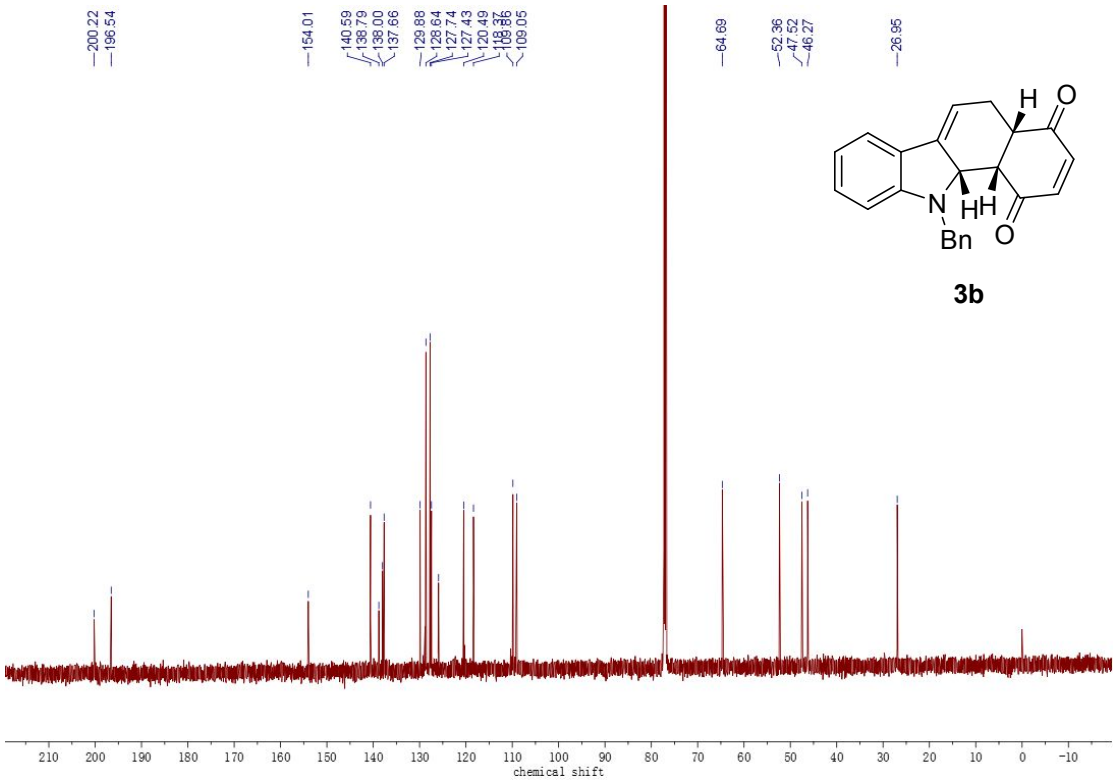
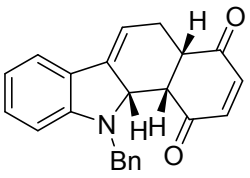
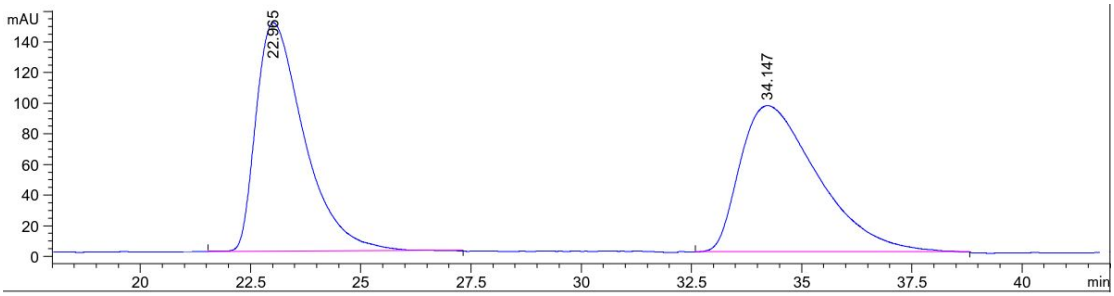


Figure S42. HPLC spectrum of 3b

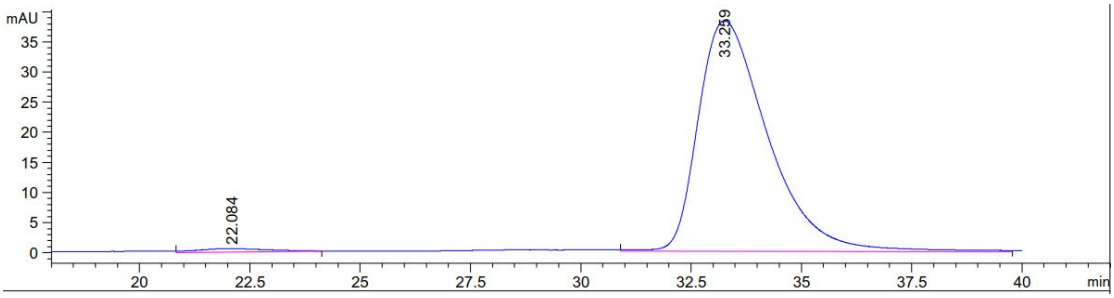


3b (The top one is racemic, and the bottom one is chiral)



Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.965	MM	1.2827	1.15252e4	149.75708	49.3014
2	34.147	MM	2.0614	1.18518e4	95.82256	50.6986
Totals :				2.33770e4	245.57964	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.084	MM	1.9017	63.66054	5.57939e-1	1.4867
2	33.259	MM	1.8366	4218.44775	38.28151	98.5133
Totals :				4282.10829	38.83945	

(4a*S*,11a*S*,11b*S*)-11-benzyl-2,3-dimethyl-5,11,11a,11b-tetrahydro-1*H*-benzo[*a*]carbazole-1,4(4a*H*)-dione (3c)

Figure S43. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of 3c

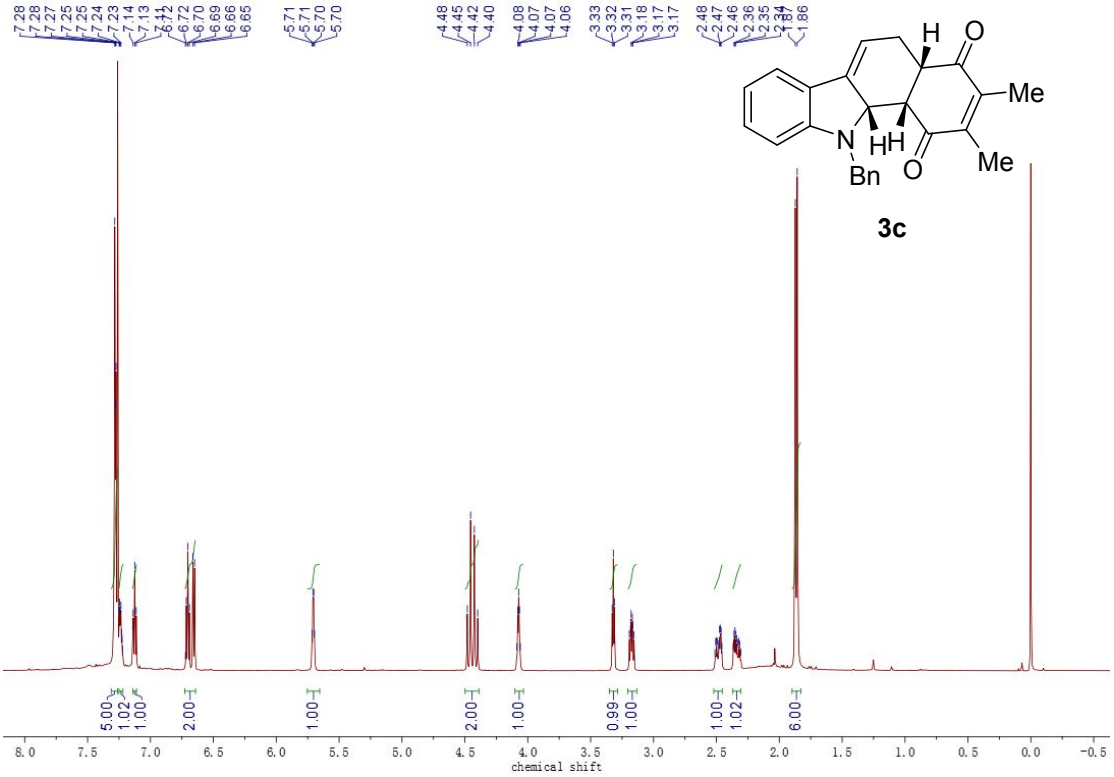


Figure S44. ^{13}C NMR (151MHz, $CDCl_3$) spectrum of 3c

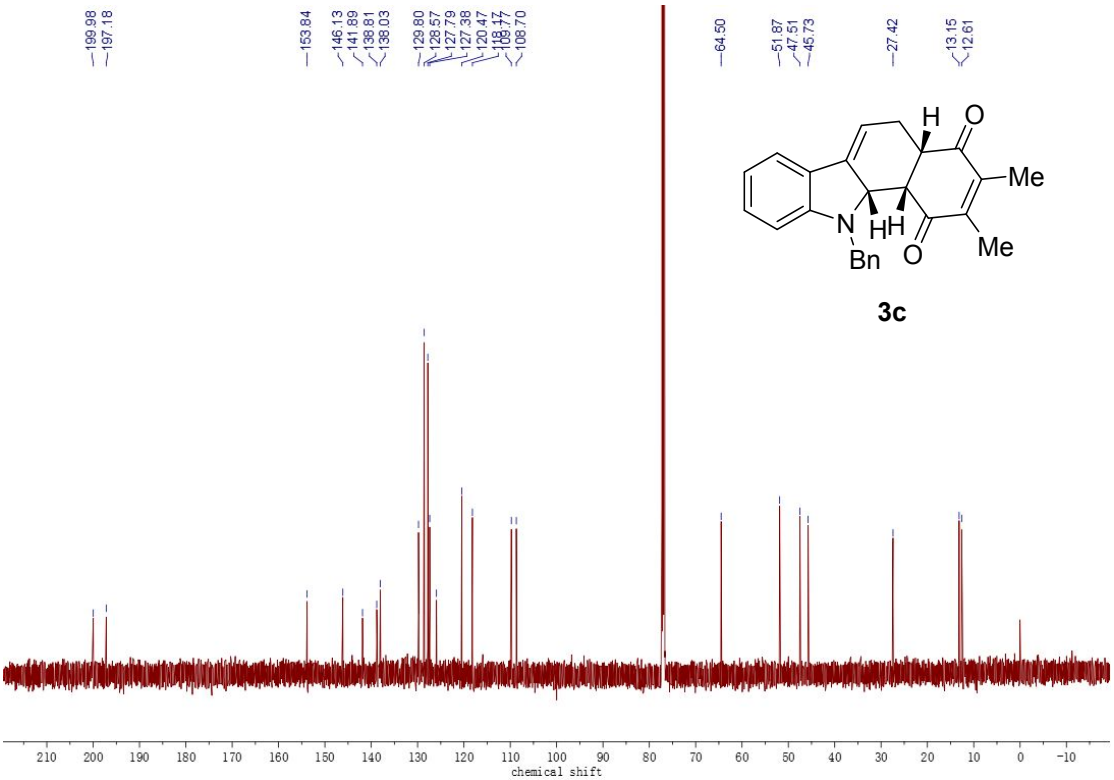
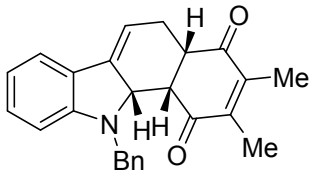
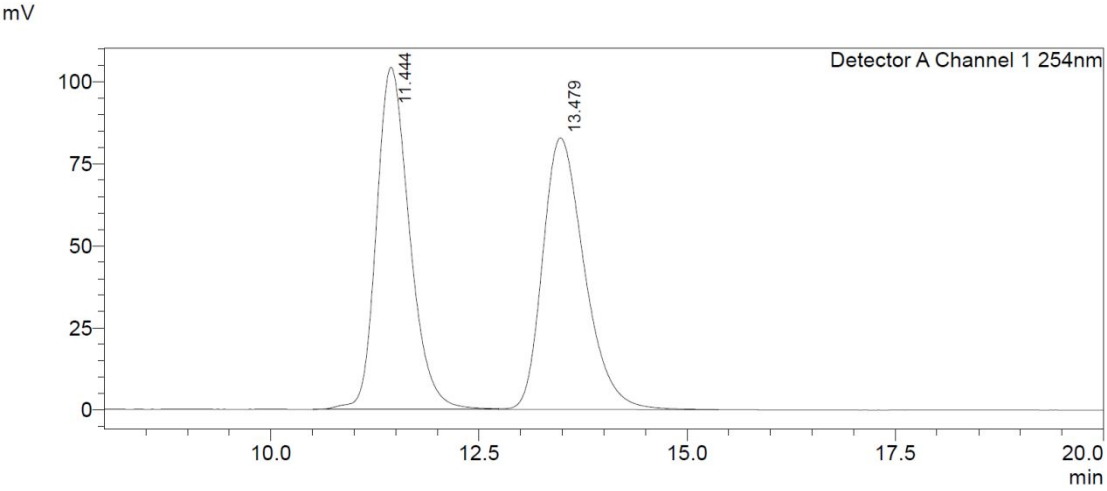


Figure S45. HPLC spectrum of 3c

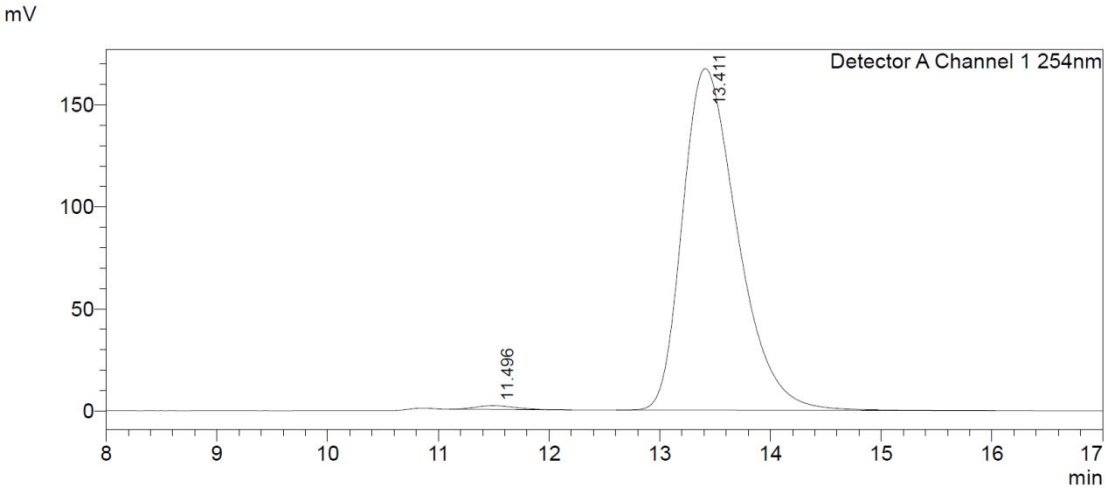


3c (The top one is racemic, and the bottom one is chiral)



Detector A Channel 1 254nm

Peak	Ret. Time	Area	Height	Area%	Conc.
1	11.444	2887145	104188	49.983	49.983
2	13.479	2889104	82711	50.017	50.017
Total		5776249	186898	100.000	



Detector A Channel 1 254nm

Peak	Ret. Time	Area	Height	Area%	Conc.
1	11.496	47770	1870	0.819	0.819
2	13.411	5782979	167468	99.181	99.181
Total		5830749	169338	100.000	

(4a*S*,11a*S*,11b*S*)-11-benzyl-3-methyl-5,11,11a,11b-tetrahydro-1*H*-benzo[*a*]carbazole-1,4(4a*H*)-dione and (4a*S*,11a*S*,11b*S*)-11-benzyl-2-methyl-5,11,11a,11b-tetrahydro-1*H*-benzo[*a*]carba-zole-1,4(4a*H*)-dione (3d and 3d')

Figure S46. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of 3d and 3d'

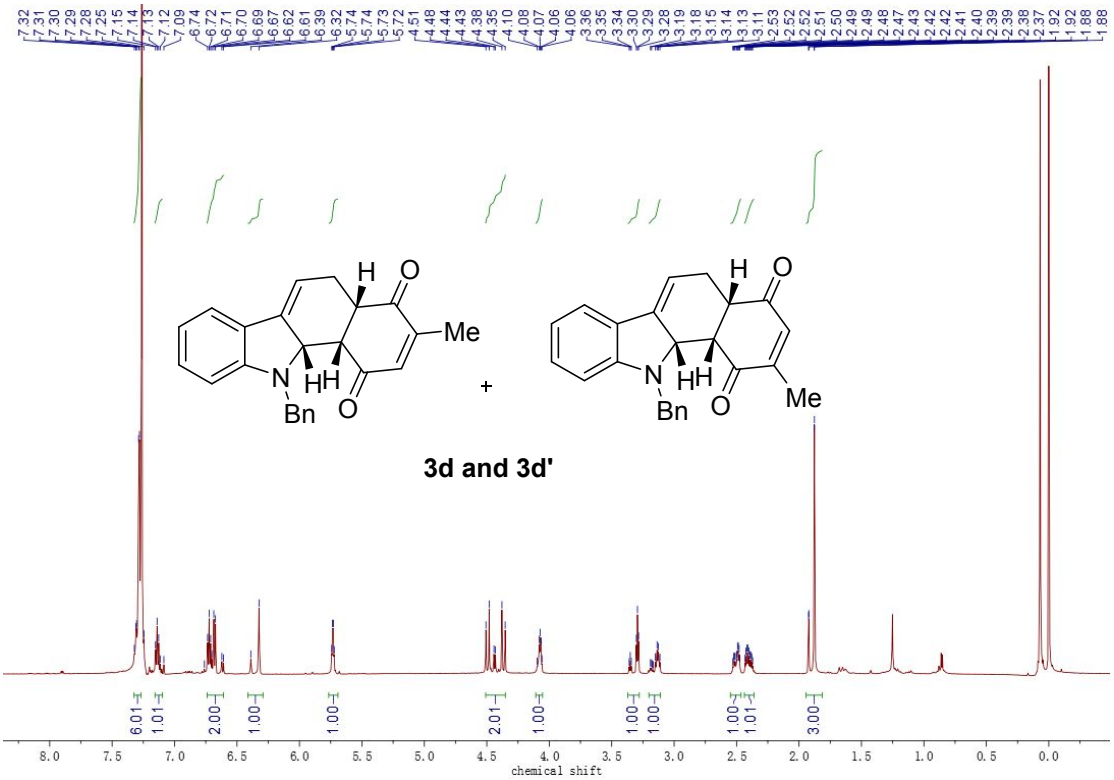


Figure S47. ^{13}C NMR (151MHz, $CDCl_3$) spectrum of 3d and 3d'

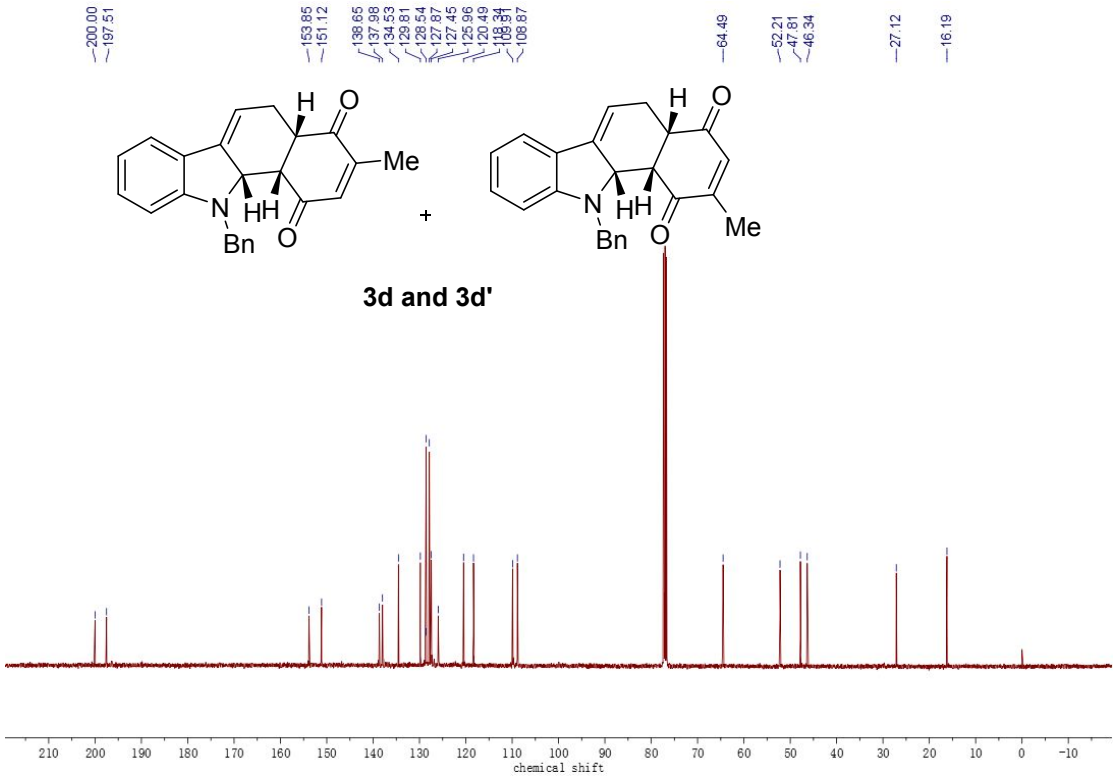
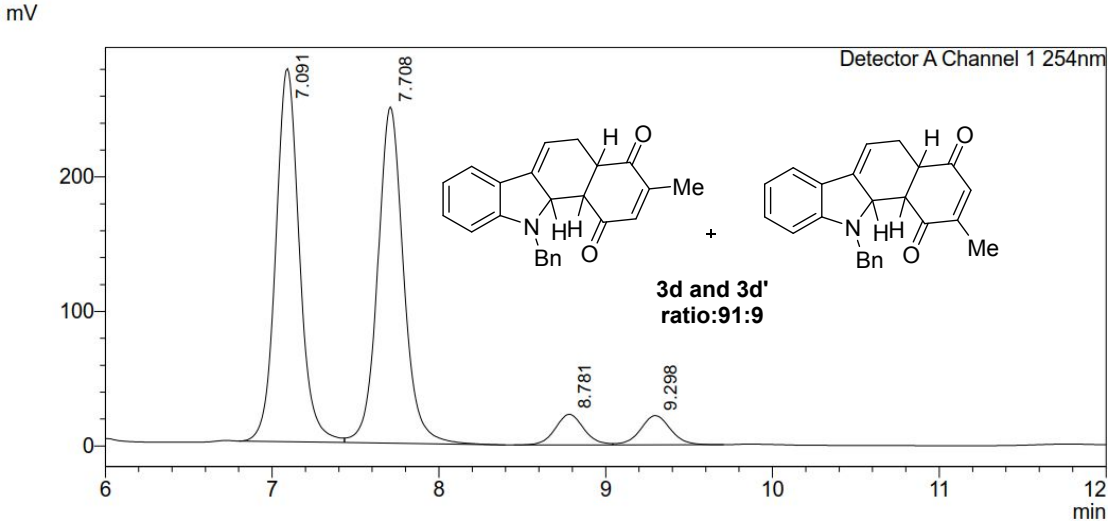


Figure S48. HPLC spectrum of 3d and 3d'

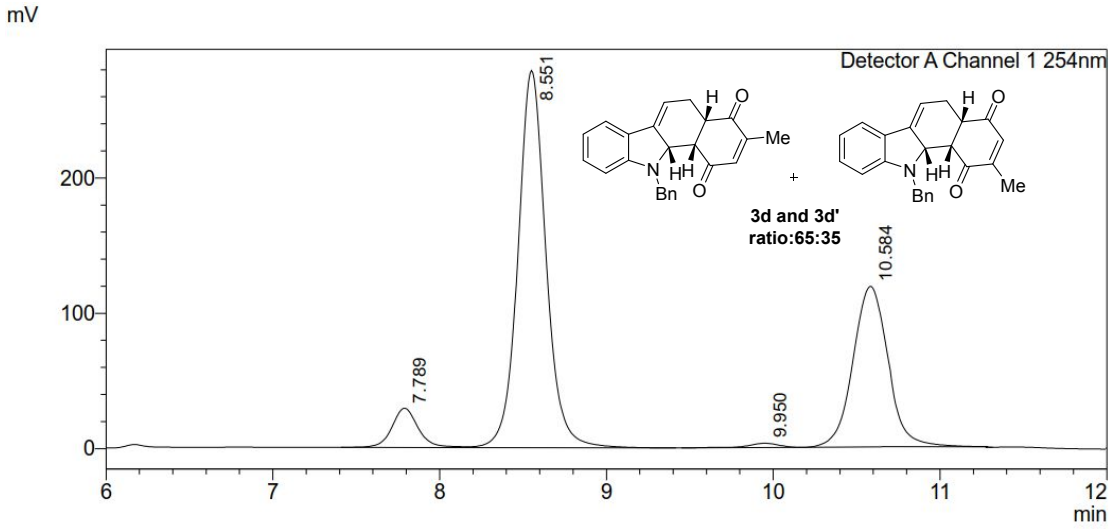
3d and 3d' (The top one is racemic, and the bottom one is chiral)



Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	7.091	2717134	277432	45.524	45.524

Peak#	Ret. Time	Area	Height	Conc.	Area%
2	7.708	2707090	250094	45.356	45.356
3	8.781	271620	22759	4.551	4.551
4	9.298	272688	21752	4.569	4.569
Total		5968532	572036		100.000



Peak#	Ret. Time	Area	Height	Conc.	Area%
1	7.789	317341	28955	5.740	5.740
2	8.551	3265517	278780	59.066	59.066
3	9.950	42335	3202	0.766	0.766
4	10.584	1903352	118724	34.428	34.428
Total		5528545	429661		100.000

(5a*S*,12a*S*,12b*S*)-12-benzyl-4-hydroxy-6,12,12a,12b-tetrahydro-5*H*-naphtho[2,3-*a*]carbazole-5,13(5a*H*)-dione and (5a*S*,12a*S*,12b*S*)-12-benzyl-1-hydroxy-6,12,12a,12b-tetrahydro-5*H*-naphtho[2,3-*a*]carbazole-5,13(5a*H*)-dione (3e and 3e')

Figure S49. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of 3e and 3e'

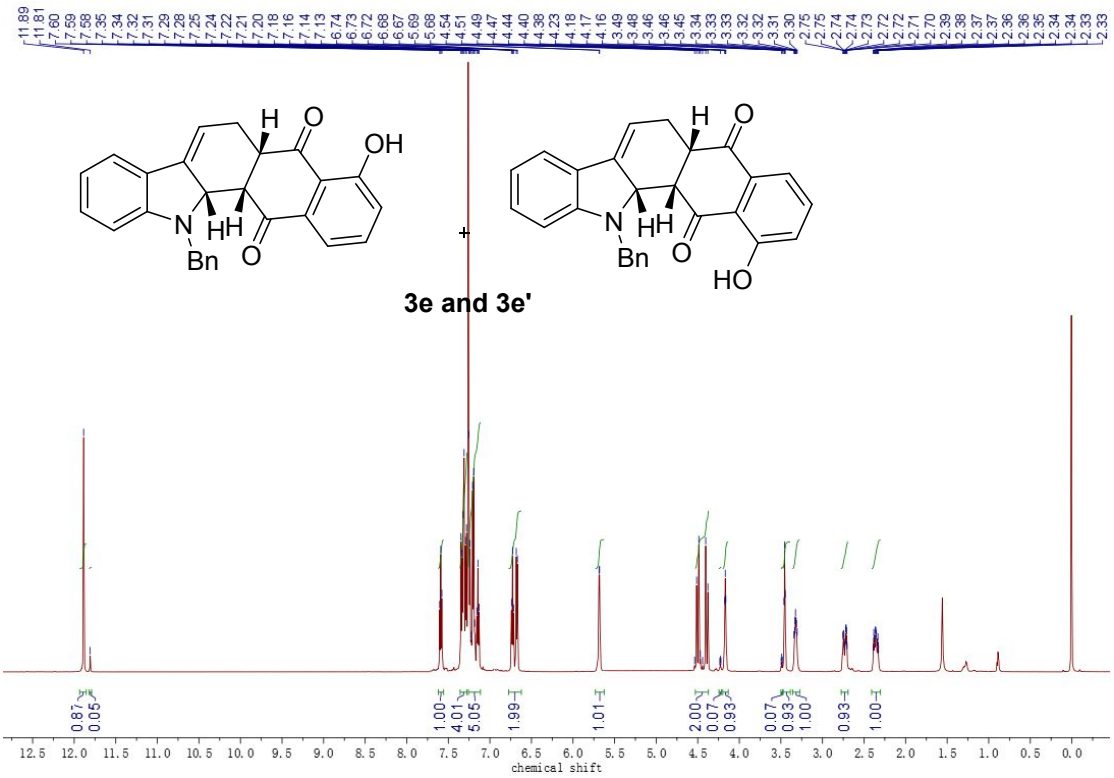


Figure S50. ^{13}C NMR (151MHz, $CDCl_3$) spectrum of 3e and 3e'

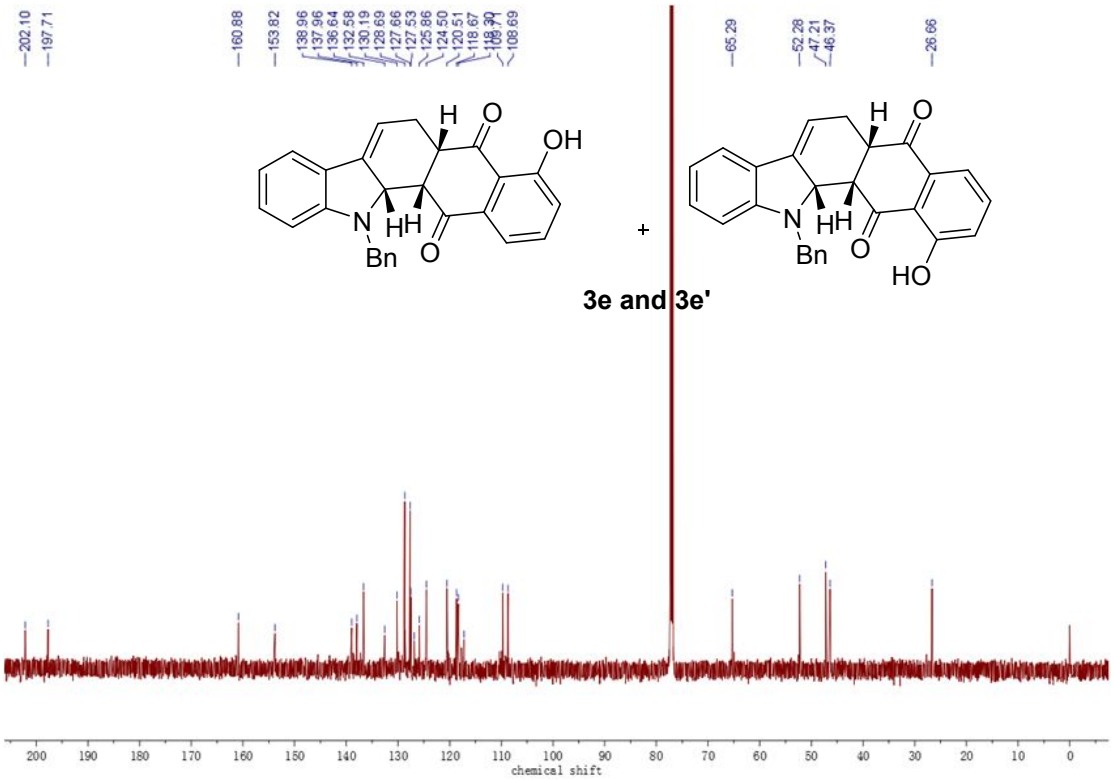
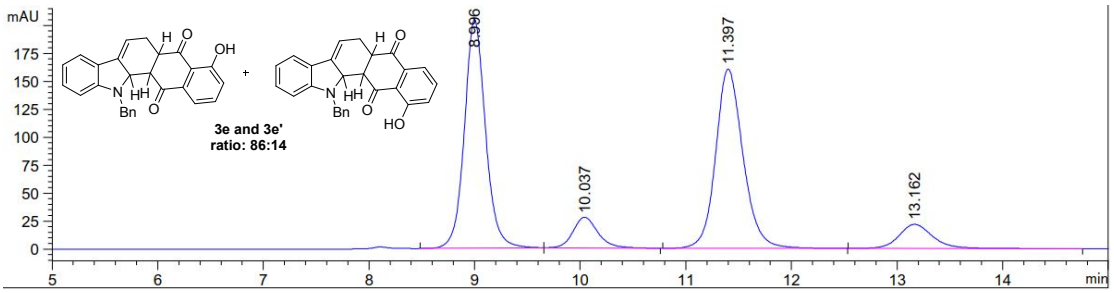


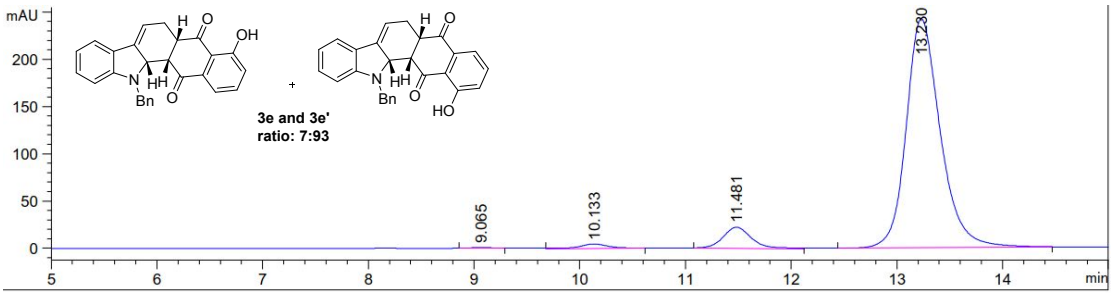
Figure S51. HPLC spectrum of 3e and 3e'

3e and 3e' (The top one is racemic, and the bottom one is chiral)



Signal 2: DAD1 B, Sig=365,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.996	BB	0.2121	2841.61572	204.51073	42.6091
2	10.037	BB	0.2481	446.62421	27.40537	6.6970
3	11.397	BB	0.2749	2897.87451	160.30252	43.4527
4	13.162	BB	0.3389	482.91556	21.59663	7.2412
Totals :				6669.03000	413.81525	



Signal 2: DAD1 B, Sig=365,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.065	MM	0.2078	10.39936	8.34021e-1	0.1736
2	10.133	MM	0.3292	94.03818	4.76059	1.5697
3	11.481	MM	0.3166	426.49530	22.44905	7.1192
4	13.230	MM	0.3748	5459.86328	242.75932	91.1375
Totals :				5990.79612	270.80299	

(5a*S*,12a*S*,12b*S*)-12-benzyl-1,4-dihydroxy-6,12,12a,12b-tetrahydro-5*H*-naphtho[2,3-*a*]carbazole-5,13(5a*H*)-dione (3f)

Figure S52. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of 3f

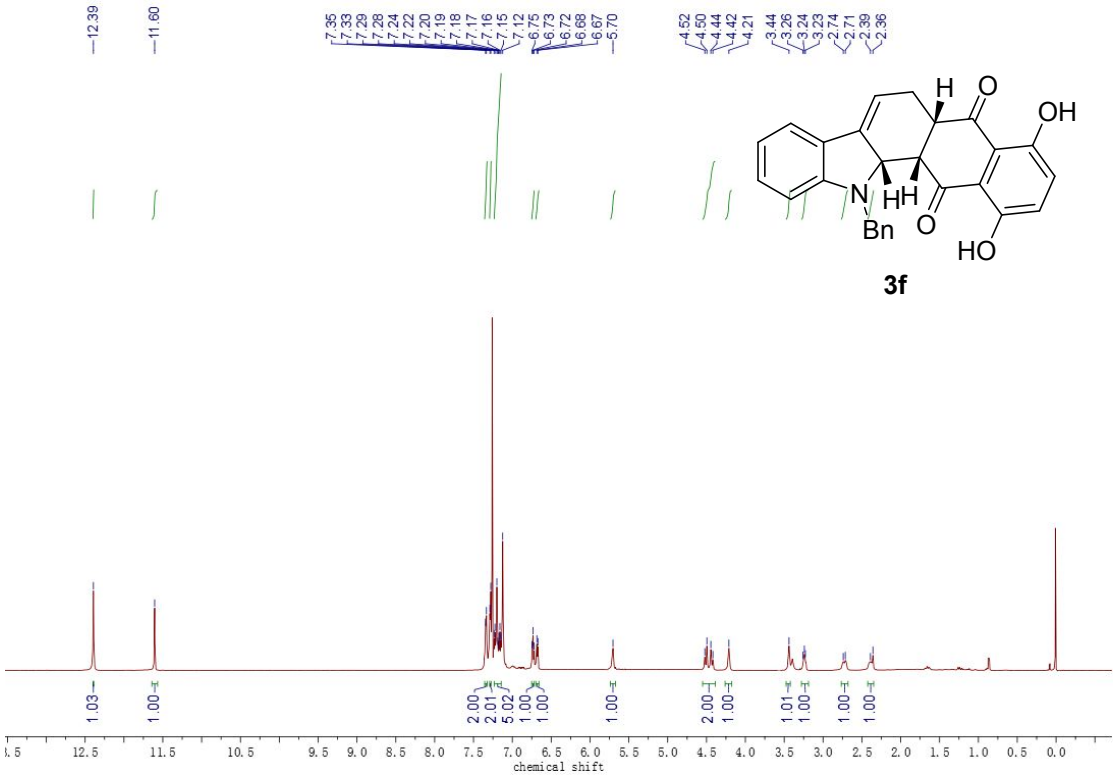


Figure S53. ^{13}C NMR (151MHz, $CDCl_3$) spectrum of 3f

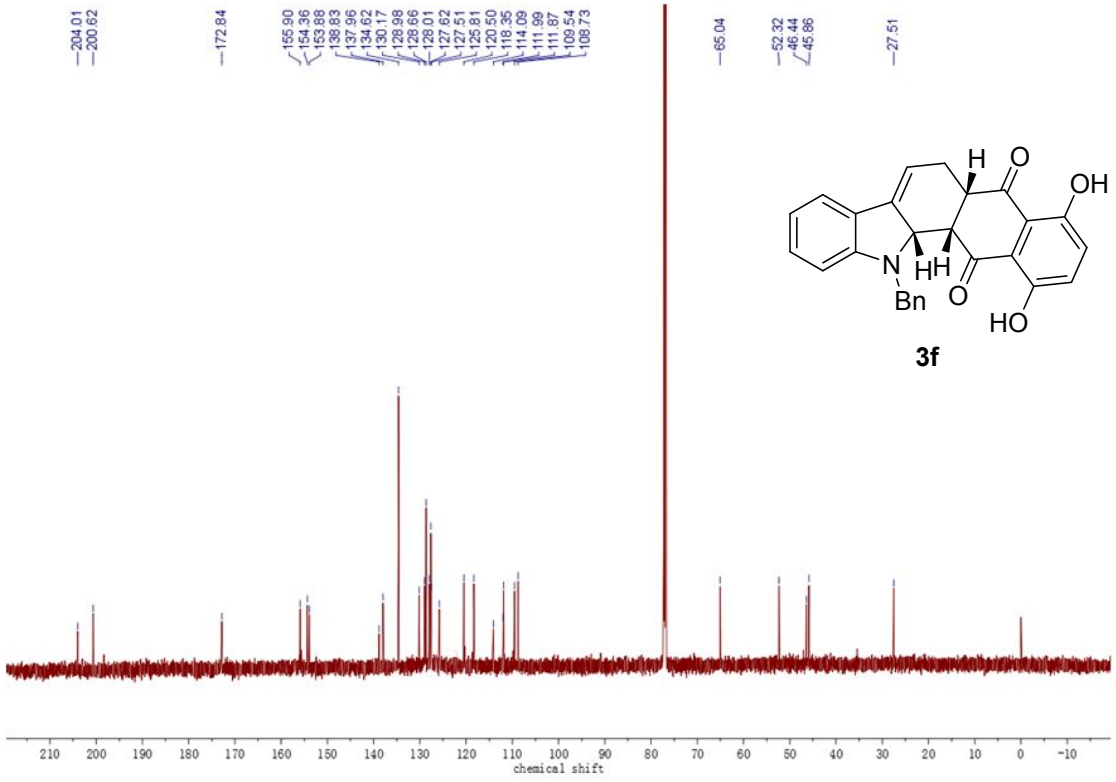
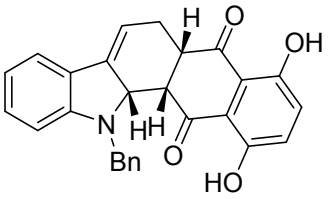
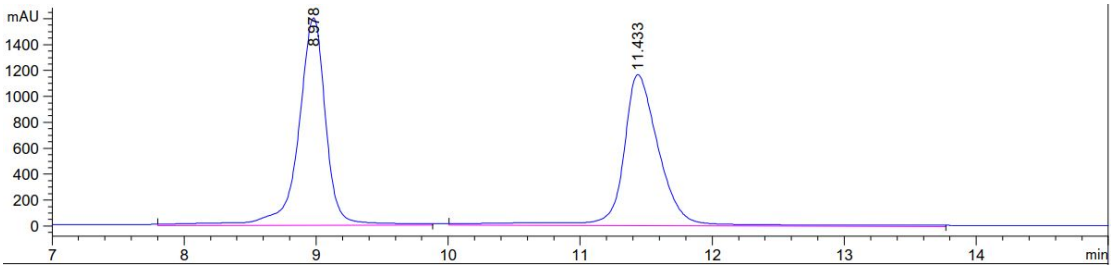


Figure S54. HPLC spectrum of 3f

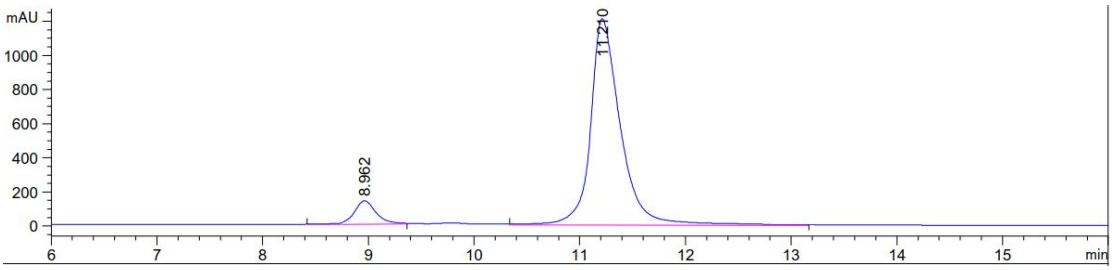


3f (The top one is racemic, and the bottom one is chiral)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.978	MM	0.2428	2.33431e4	1602.43994	50.5501
2	11.433	MM	0.3260	2.28351e4	1167.54492	49.4499
Totals :				4.61782e4	2769.98486	



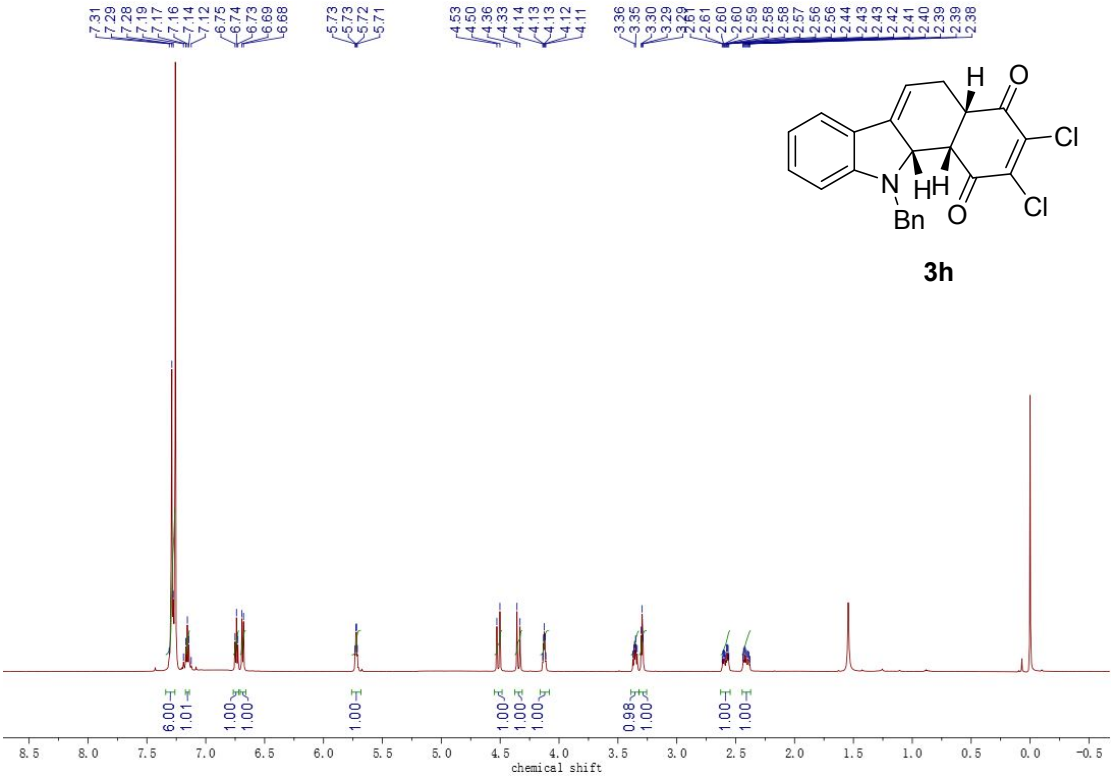
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.962	MM	0.2403	1989.16333	137.96635	7.6068
2	11.210	MM	0.3329	2.41606e4	1209.45483	92.3932
Totals :				2.61498e4	1347.42119	

(4a*S*,11a*S*,11b*S*)-11-benzyl-2,3-dichloro-5,11,11a,11b-tetrahydro-1*H*-benz

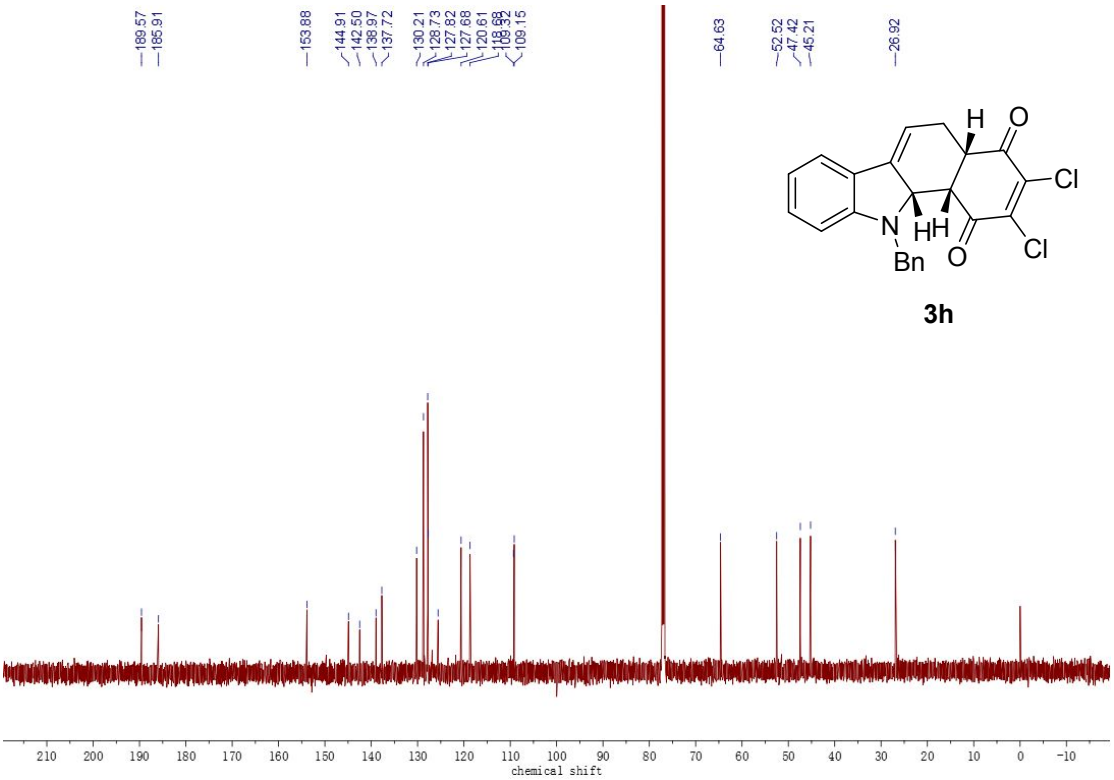
o[*a*]carbazole-1,4(4a*H*)-dione (3h)

Figure S55. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of 3h



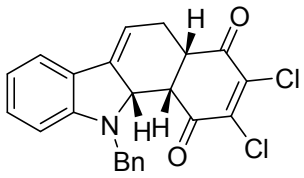
3h

Figure S56. ^{13}C NMR (151MHz, $CDCl_3$) spectrum of 3h

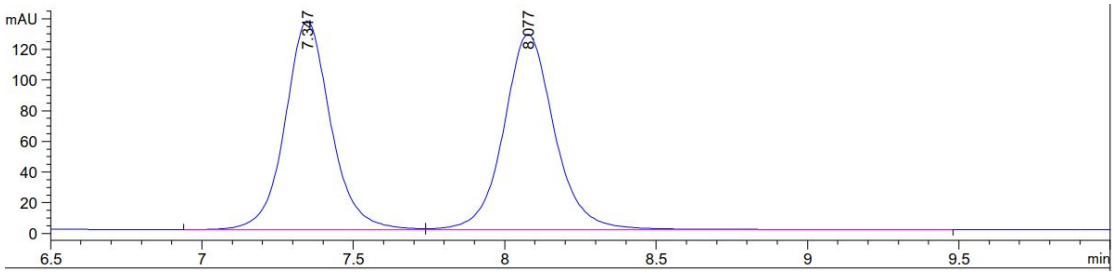


3h

Figure S57. HPLC spectrum of 3h

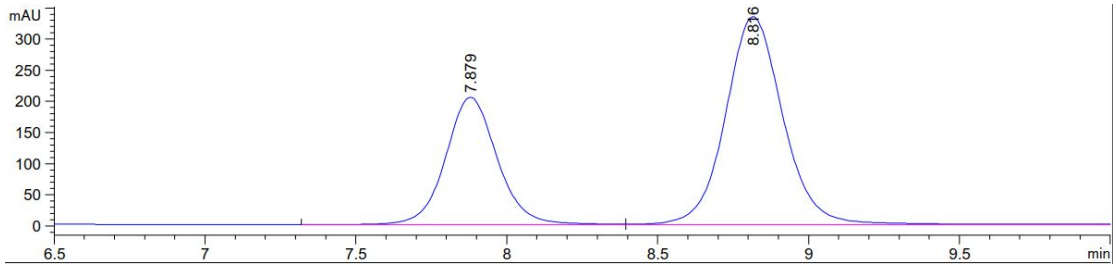


3h (The top one is racemic, and the bottom one is chiral)



Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.347	BV	0.1603	1428.26379	136.19902	49.0044
2	8.077	VB	0.1760	1486.30042	127.52252	50.9956
Totals :				2914.56421	263.72154	



Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.879	BV	0.1811	2436.79175	204.38507	35.5032
2	8.816	VB	0.2029	4426.79883	333.43723	64.4968
Totals :				6863.59058	537.82230	

(5a*S*,12a*S*,12b*S*)-12-benzyl-8-bromo-6,12,12a,12b-tetrahydro-5*H*-naphtho

[2,3-*a*]carbazole-5,13(5a*H*)-dione (4b)

Figure S58. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of 4b

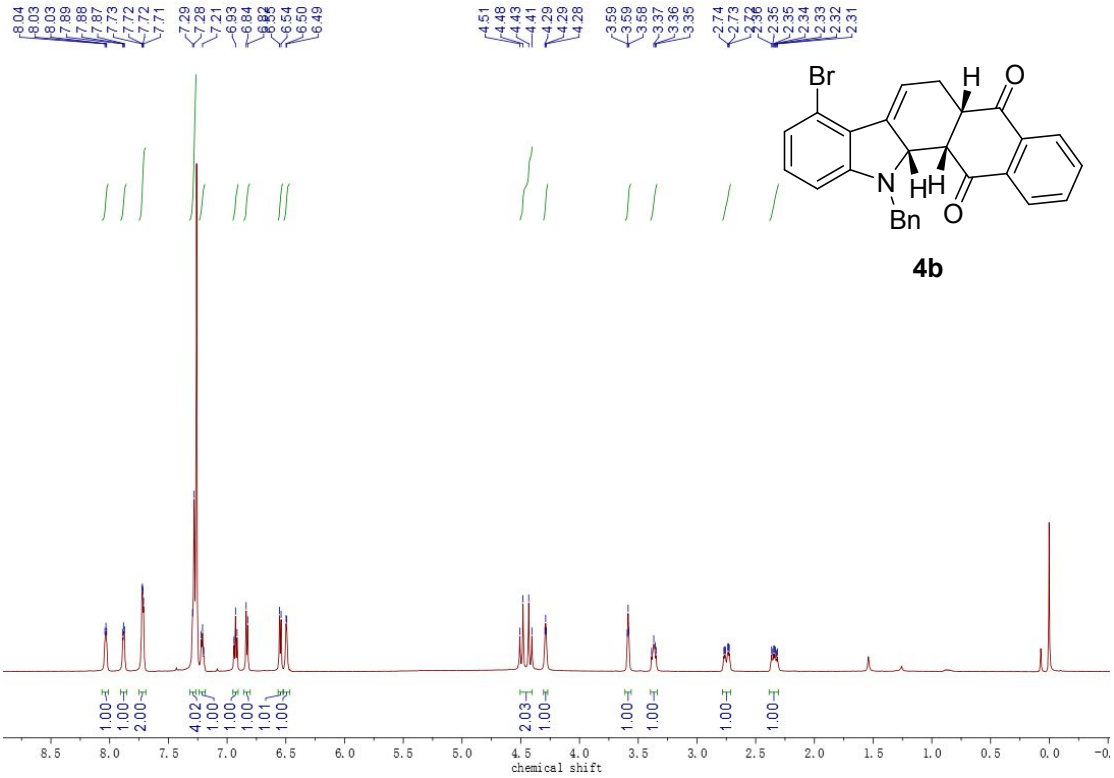


Figure S59. ^{13}C NMR (151MHz, $CDCl_3$) spectrum of 4b

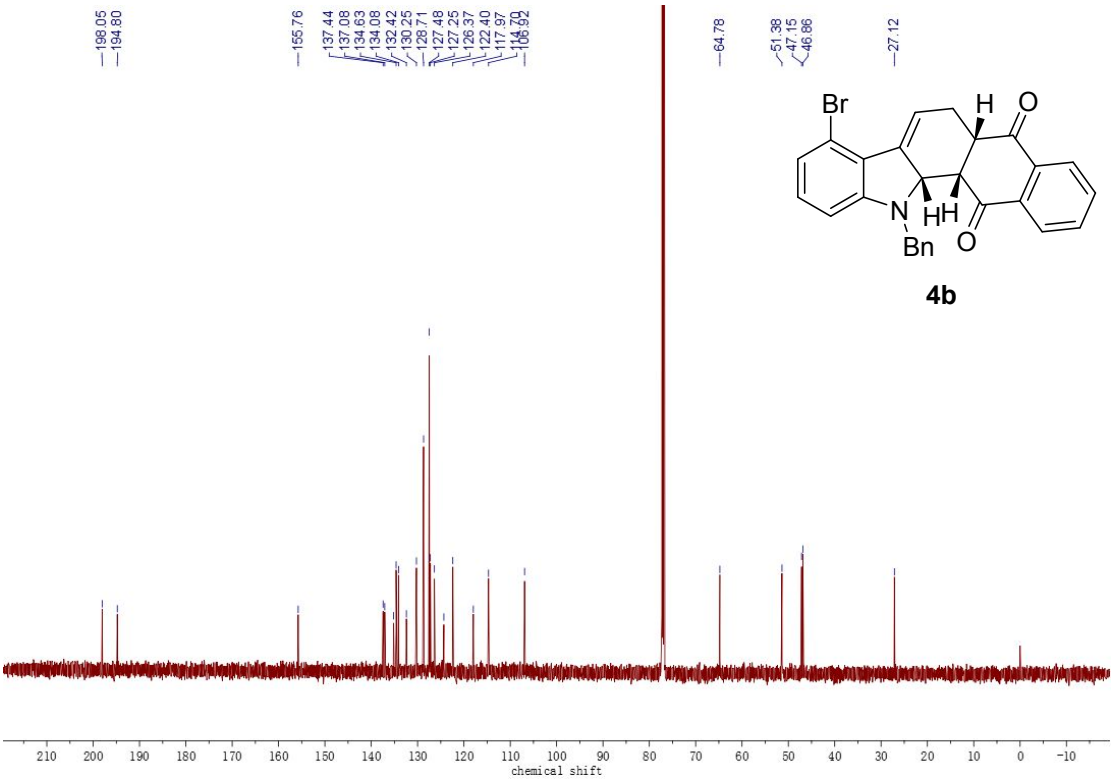
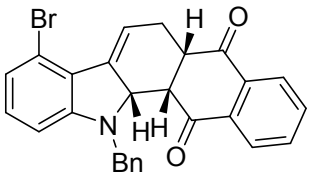
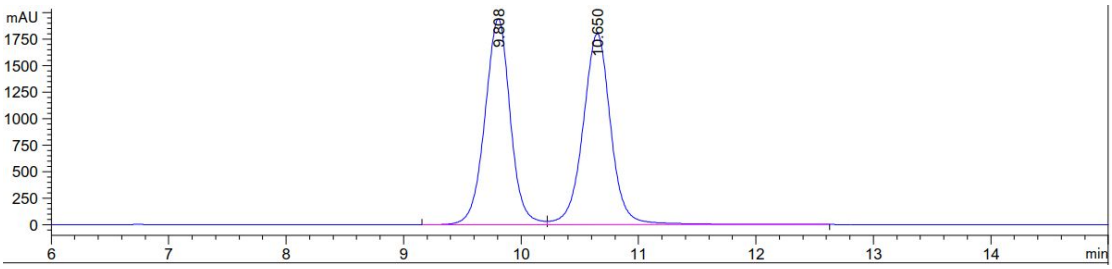


Figure S60. HPLC spectrum of 4b

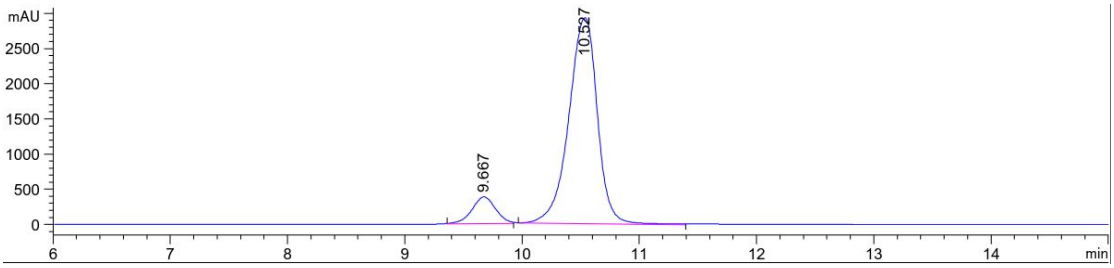


4b (The top one is racemic, and the bottom one is chiral)



Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.808	BV	0.2290	2.90761e4	1938.37561	49.5564
2	10.650	VBA	0.2501	2.95966e4	1797.44495	50.4436
Totals :				5.86726e4	3735.82056	



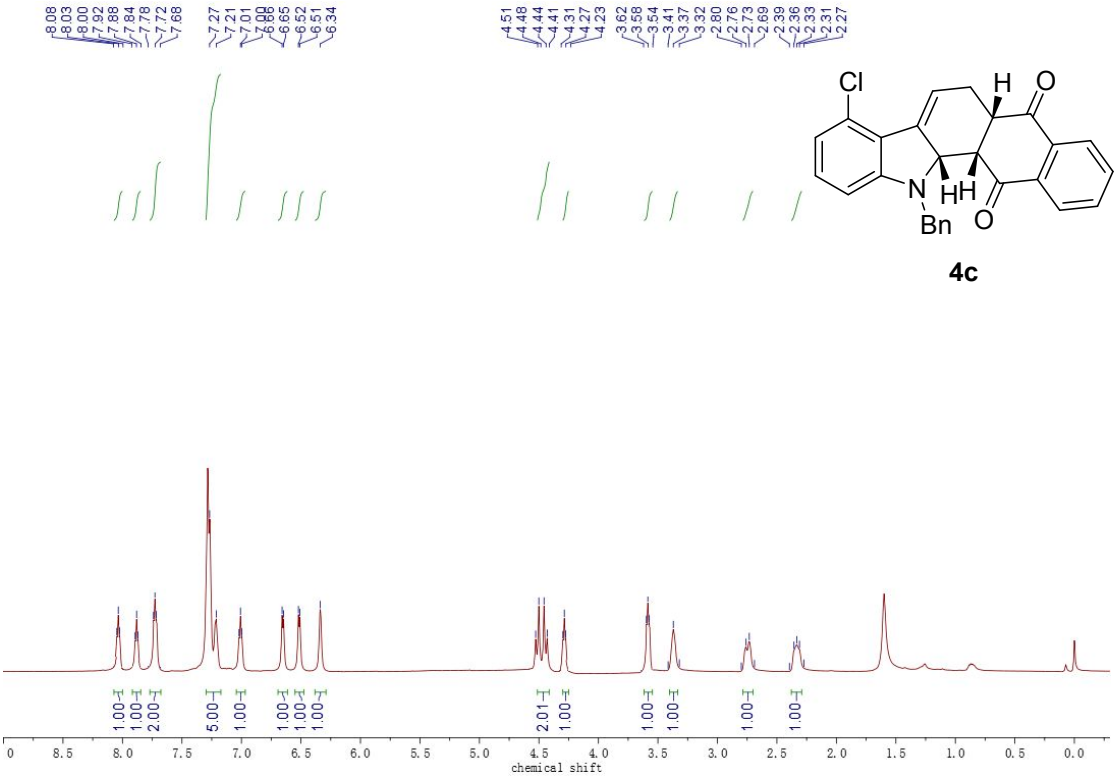
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.667	MM	0.2334	2424.0472	238.15424	4.6713
2	10.527	MM	0.2818	4.94683e4	2925.92139	95.3287
Totals :				5.18923e4	3164.07562	

(5a*S*,12a*S*,12b*S*)-12-benzyl-8-chloro-6,12,12a,12b-tetrahydro-5*H*-naphtho

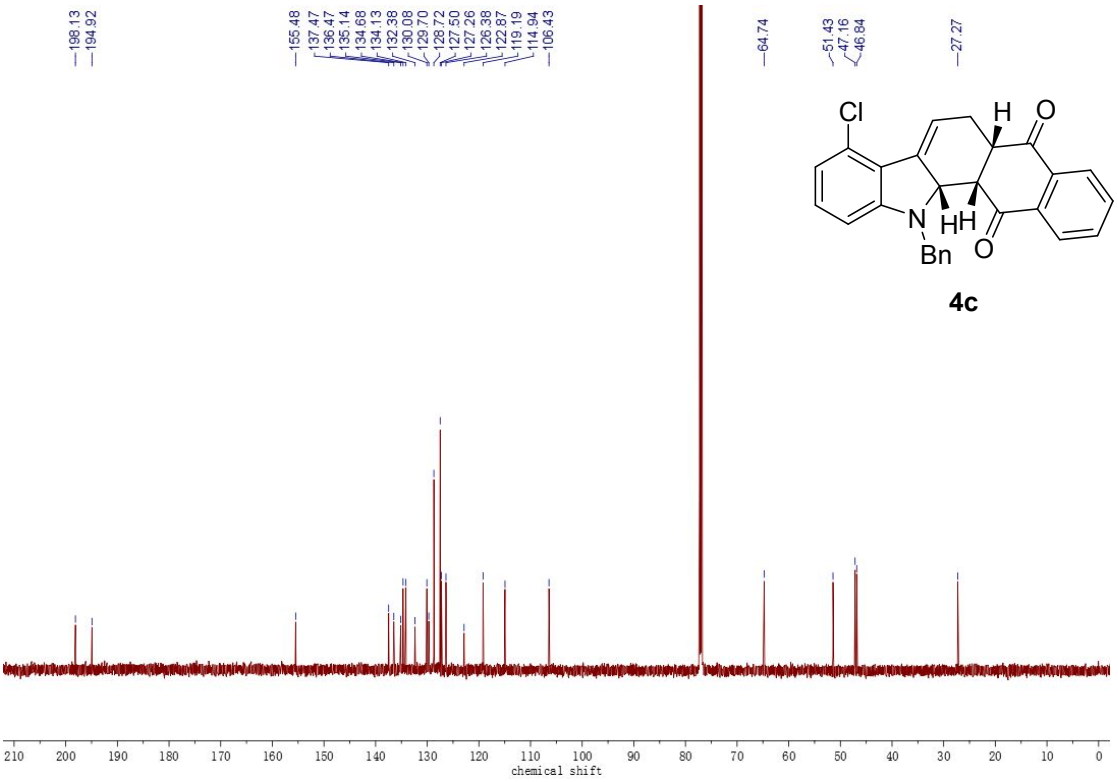
[2,3-*a*]carbazole-5,13(5a*H*)-dione (4c)

Figure S61. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of 4c



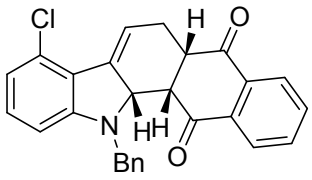
4c

Figure S62. ^{13}C NMR (151MHz, $CDCl_3$) spectrum of 4c

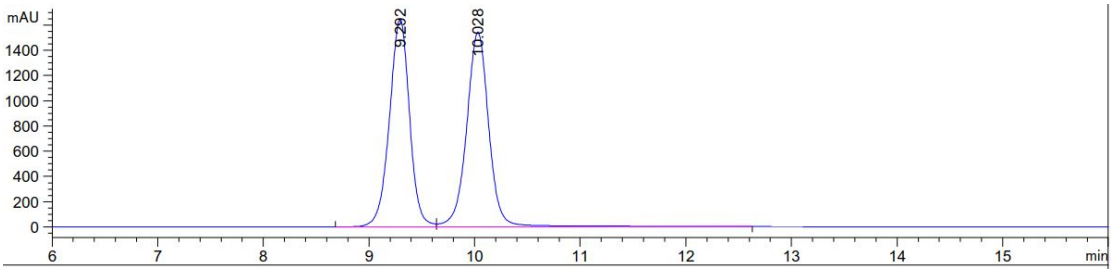


4c

Figure S63. HPLC spectrum of 4c

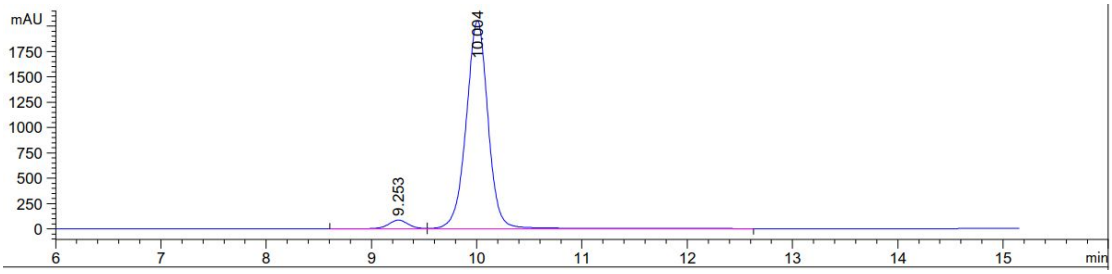


4c (The top one is racemic, and the bottom one is chiral)



Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.292	BV	0.2021	2.17722e4	1648.36963	48.9440
2	10.028	VBA	0.2237	2.27117e4	1543.62305	51.0560
Totals :				4.44839e4	3191.99268	



Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.253	BV	0.1997	1111.04224	85.43491	3.6090
2	10.004	VBA	0.2208	2.96744e4	2051.11548	96.3910
Totals :				3.07854e4	2136.55039	

(5a*S*,12a*S*,12b*S*)-12-benzyl-9-bromo-6,12,12a,12b-tetrahydro-5*H*-naphtho

[2,3-*a*]carbazole-5,13(5a*H*)-dione (4d)

Figure S64. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of 4d

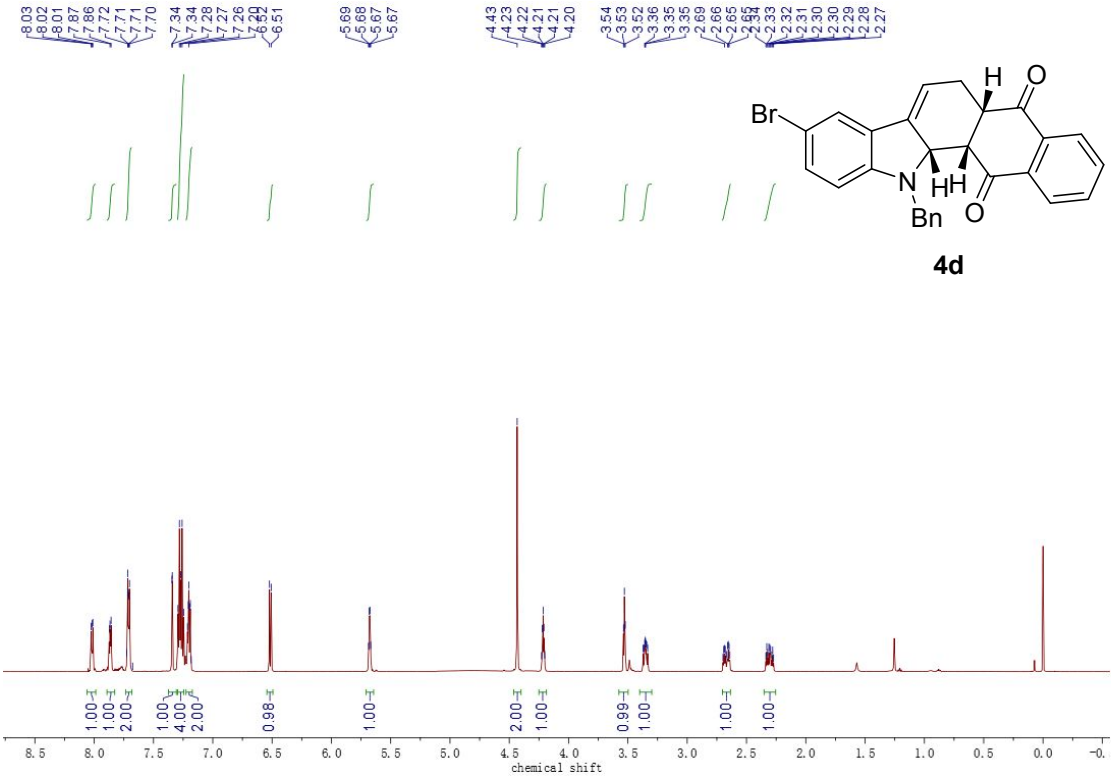


Figure S65. ^{13}C NMR (151MHz, $CDCl_3$) spectrum of 4d

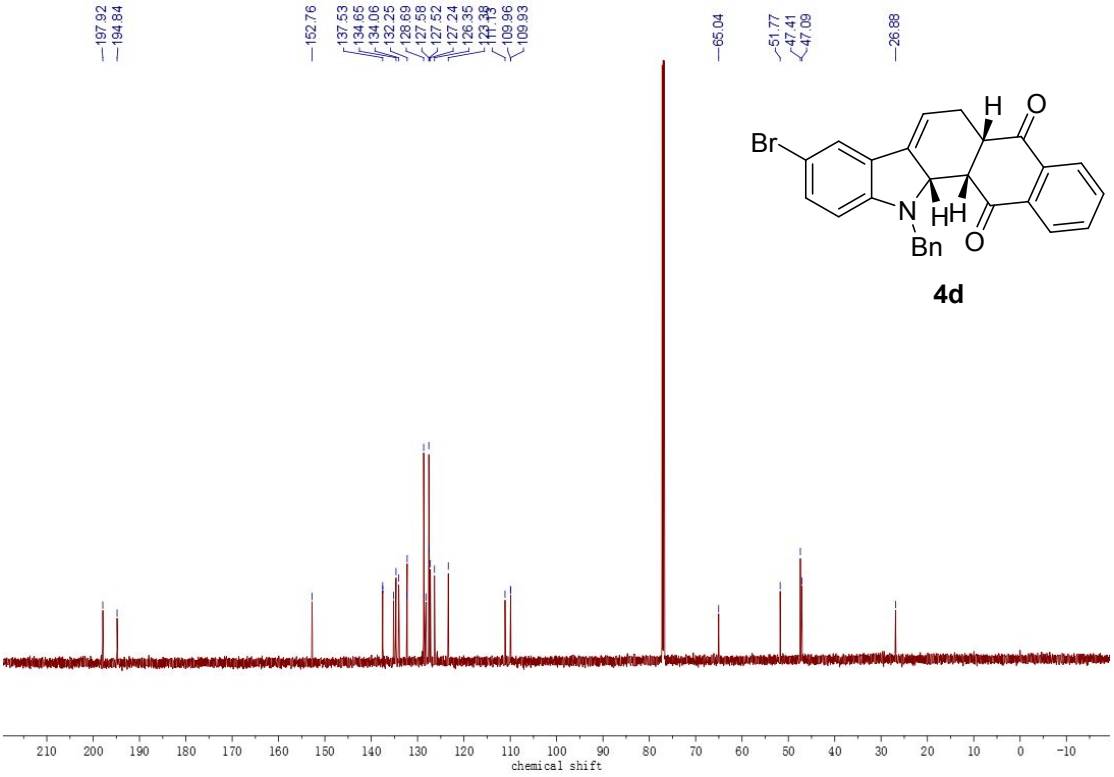
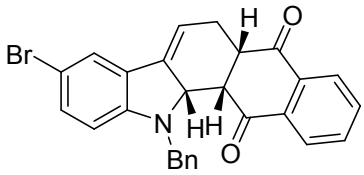
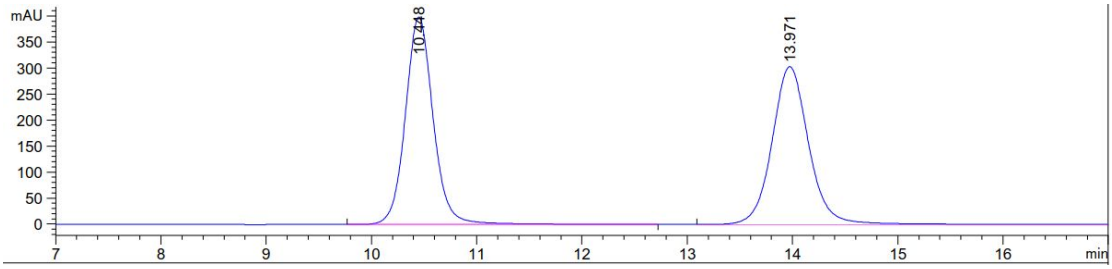


Figure S66. HPLC spectrum of 4d

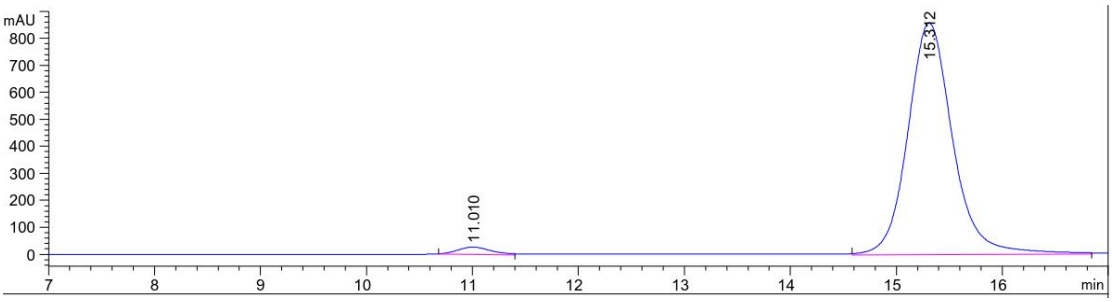


4d (The top one is racemic, and the bottom one is chiral)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

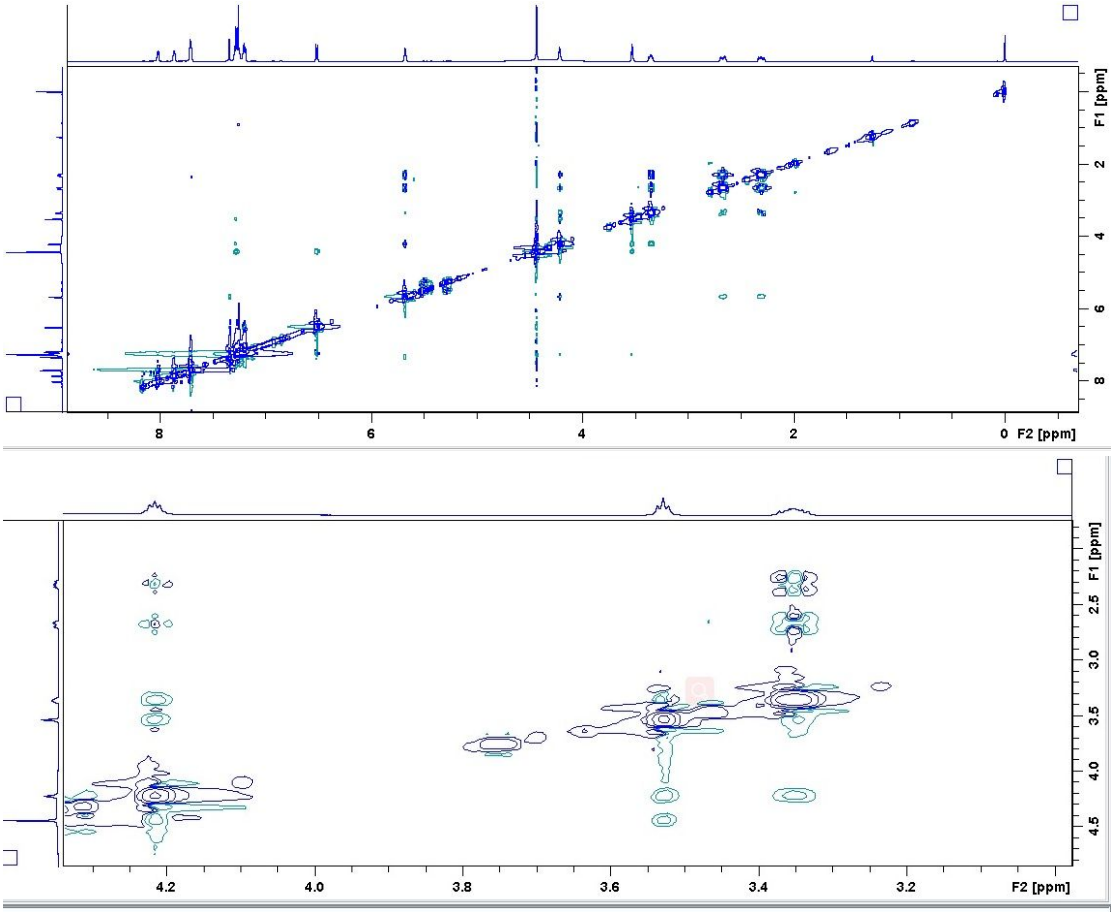
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.448	BB	0.2833	7363.11133	398.92404	49.8553
2	13.971	BB	0.3705	7405.85742	303.64636	50.1447
Totals :				1.47690e4	702.57040	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.010	MM	0.3688	602.62848	27.23625	2.3272
2	15.312	MM	0.4909	2.52922e4	858.64404	97.6728
Totals :				2.58948e4	885.88029	

Figure S67. NOESY NMR (600MHz, $CDCl_3$) spectrum of 4d



(5a*S*,12a*S*,12b*S*)-12-benzyl-9-chloro-6,12,12a,12b-tetrahydro-5*H*-naphtho

[2,3-*a*]carbazole-5,13(5a*H*)-dione (4e)

Figure S68. ^{1}H NMR (400MHz, $CDCl_3$) spectrum of 4e

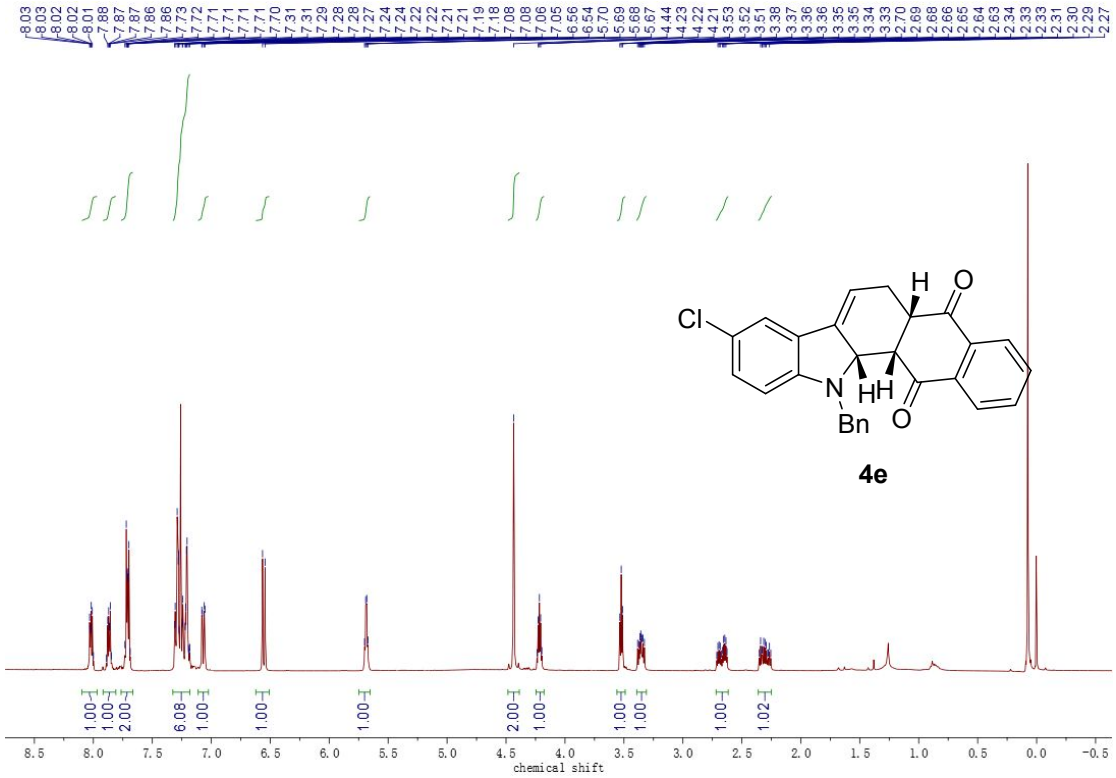


Figure S69. ^{13}C NMR (101MHz, $CDCl_3$) spectrum of 4e

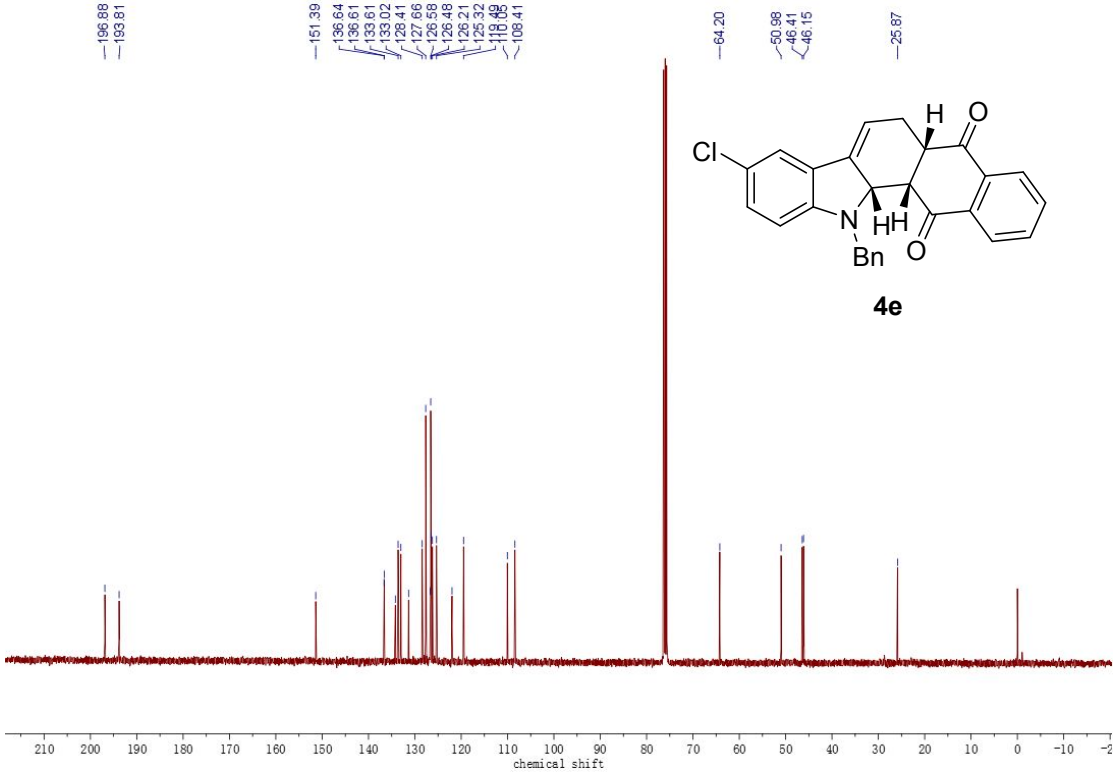
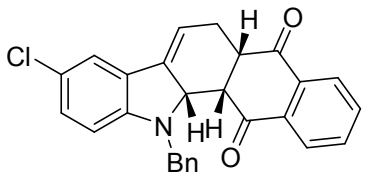
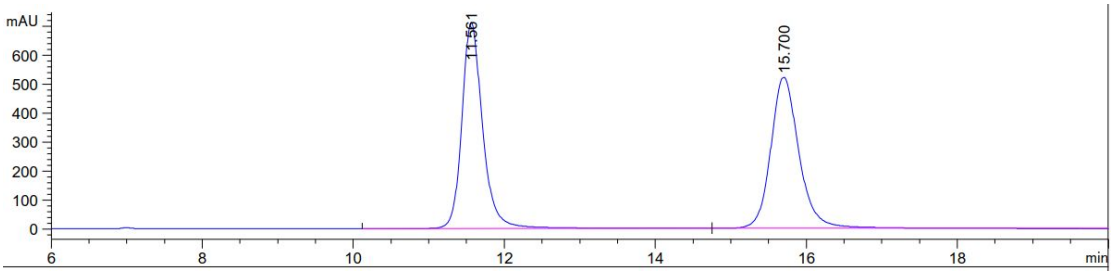


Figure S70. HPLC spectrum of 4e

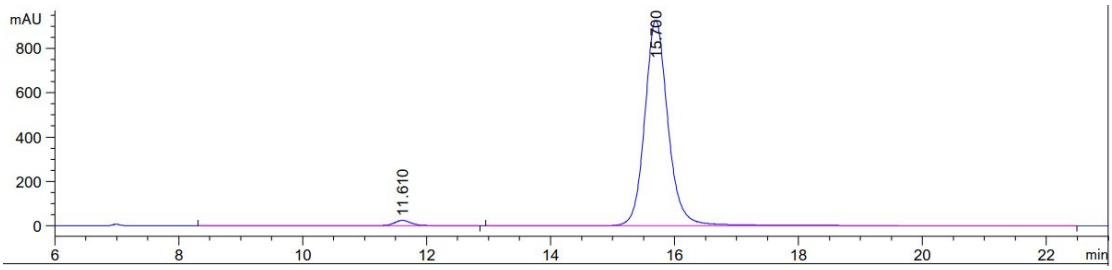


4e (The top one is racemic, and the bottom one is chiral)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.561	VB R	0.2896	1.36232e4	710.90973	49.9336
2	15.700	BB	0.3979	1.36595e4	521.02631	50.0664
Totals :				2.72827e4	1231.93604	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.610	VB R	0.2971	541.36572	24.35772	2.1802
2	15.700	BB	0.3982	2.42892e4	925.33527	97.8198
Totals :				2.48306e4	949.69299	

(5a*S*,12a*S*,12b*S*)-12-benzyl-10-bromo-6,12,12a,12b-tetrahydro-5*H*-naphth

o[2,3-*a*]carbazole-5,13(5a*H*)-dione (4f)

Figure S71. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of 4f

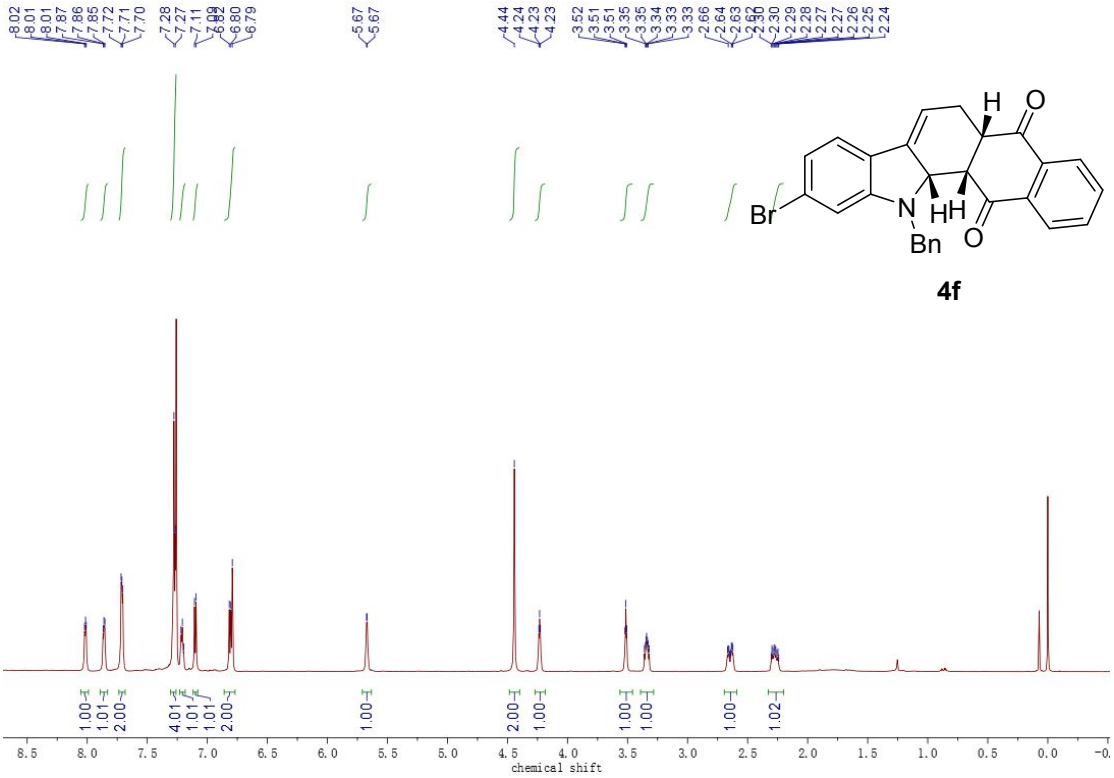


Figure S72. ^{13}C NMR (151MHz, $CDCl_3$) spectrum of 4f

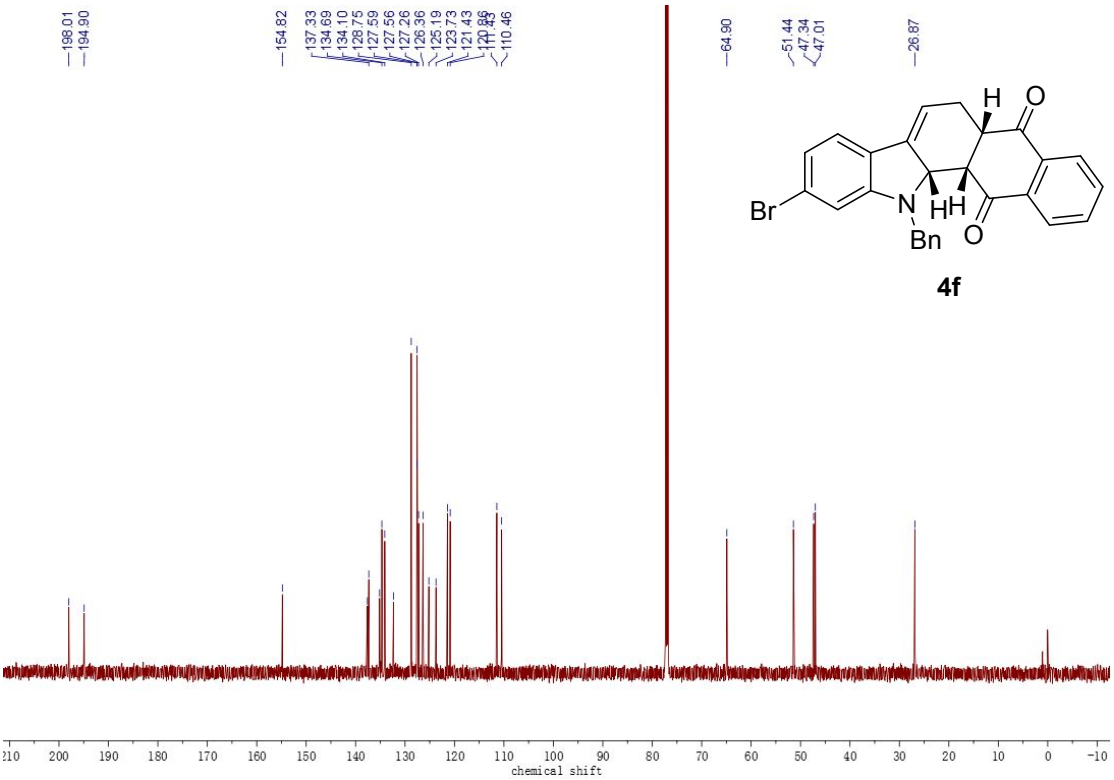
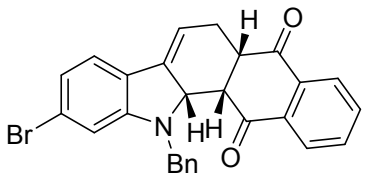
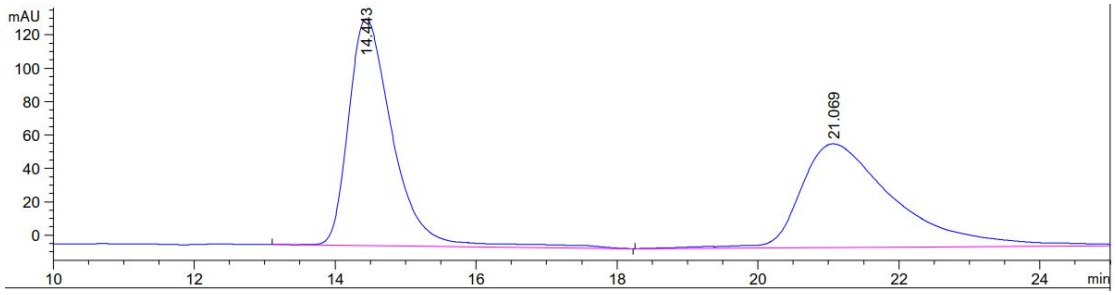


Figure S73. HPLC spectrum of 4f

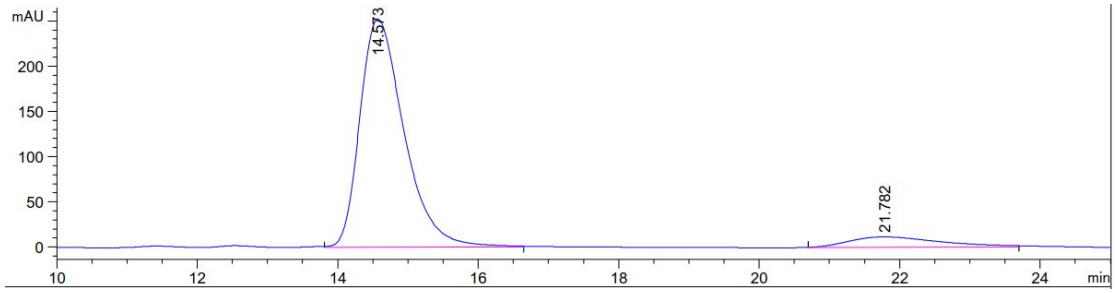


4f (The top one is racemic, and the bottom one is chiral)



Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.443	VV R	0.6657	5958.07080	135.87486	50.4273
2	21.069	BB	1.3909	5857.10205	62.18026	49.5727
Totals :				1.18152e4	198.05512	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.573	MM	0.7275	1.10375e4	252.85777	94.9152
2	21.782	MM	1.0906	591.29822	9.03622	5.0848
Totals :				1.16288e4	261.89399	

(5a*S*,12a*S*,12b*S*)-12-benzyl-10-fluoro-6,12,12a,12b-tetrahydro-5*H*-naphth

o[2,3-*a*]carbazole-5,13(5a*H*)-dione (4g)

Figure S74. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of 4g

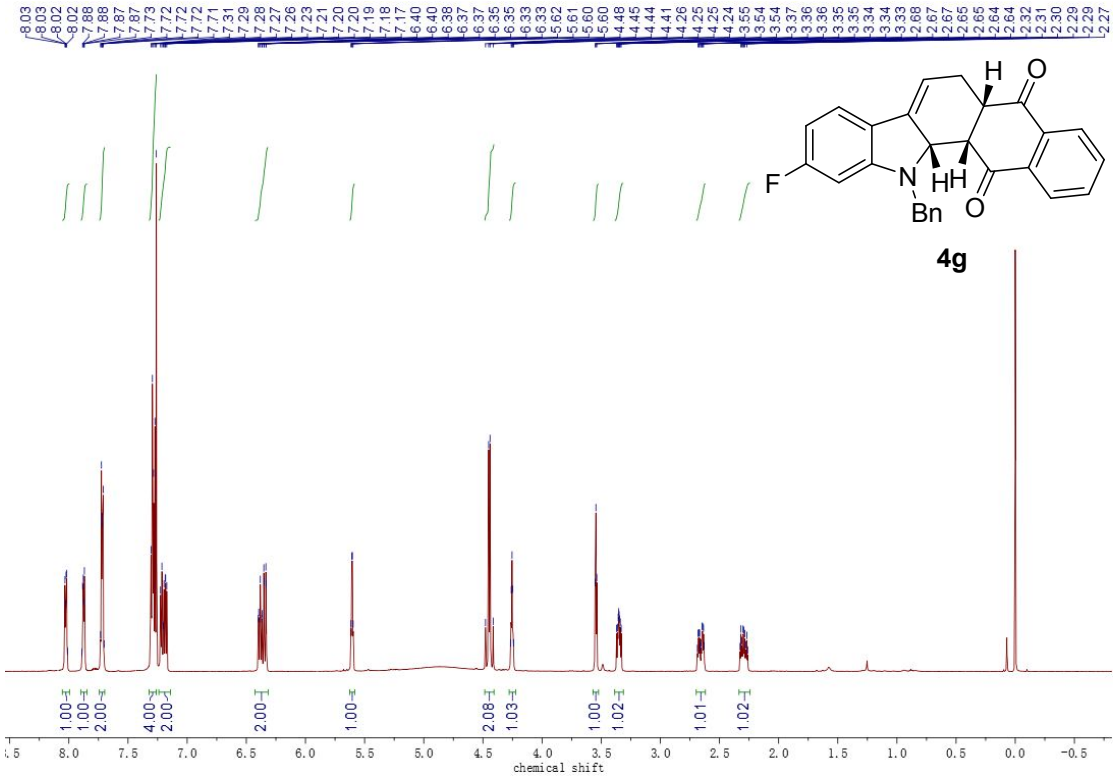


Figure S75.^{13}C NMR (151MHz, $CDCl_3$) spectrum of 4g

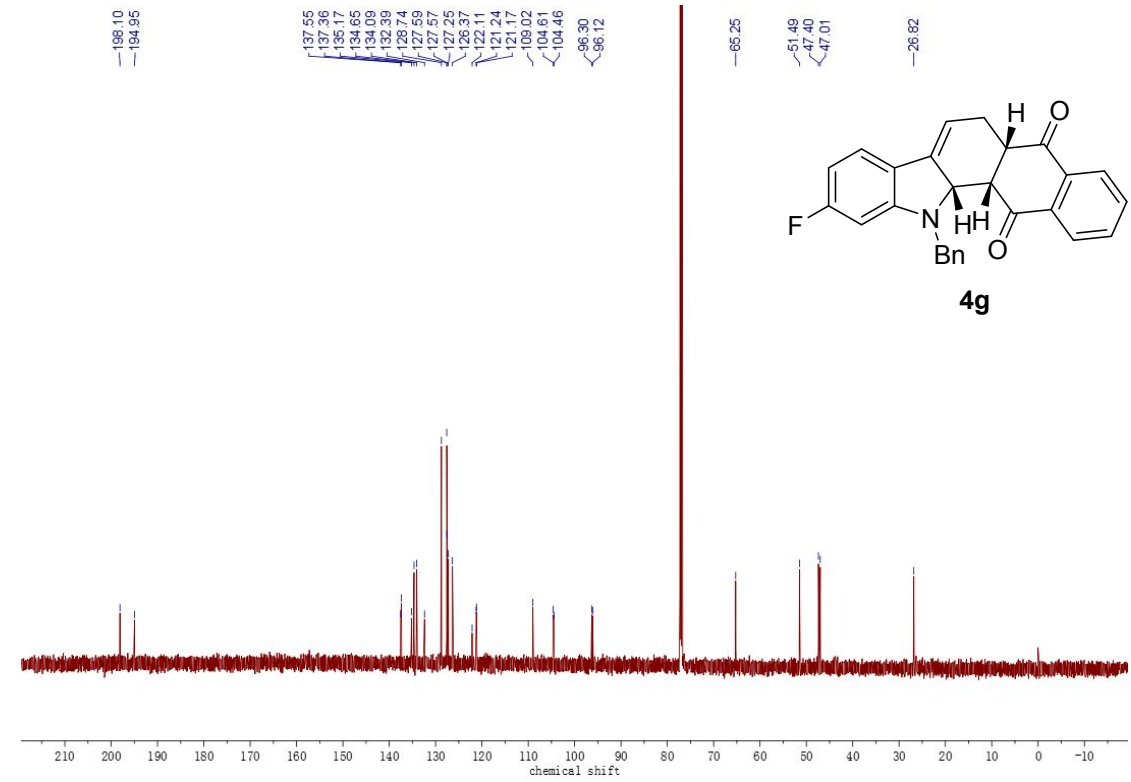
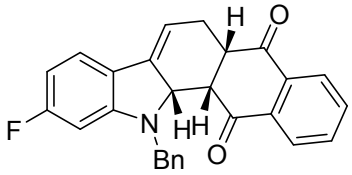
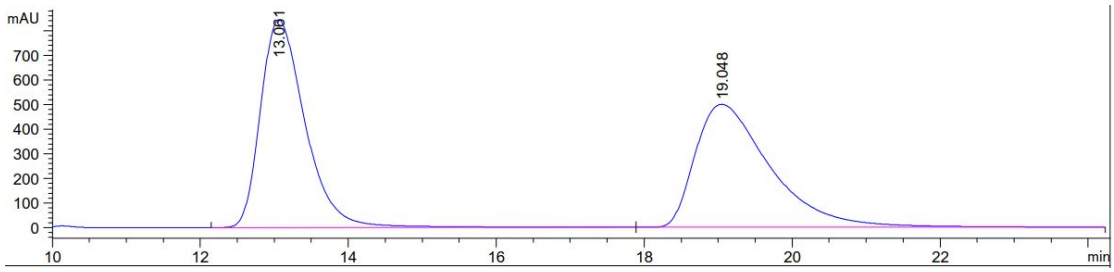


Figure S76. HPLC spectrum of 4g

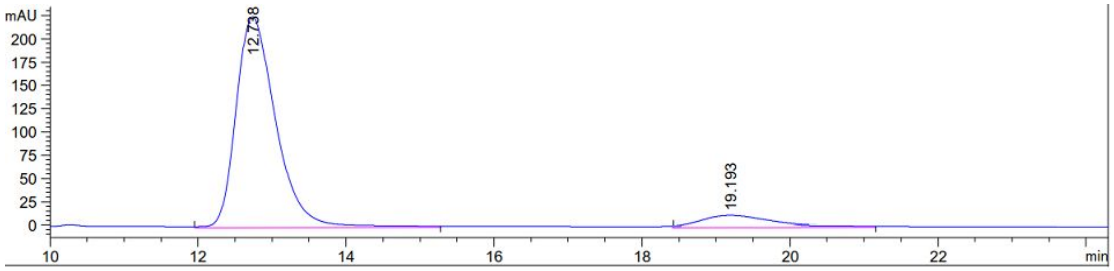


4g (The top one is racemic, and the bottom one is chiral)



Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.061	BB	0.6443	3.53337e4	844.13593	50.0221
2	19.048	BBA	1.0727	3.53025e4	499.41620	49.9779
Totals :				7.06363e4	1343.55212	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.738	MM	0.6232	8451.62891	226.03871	92.6269
2	19.193	MM	0.9740	672.75415	11.51143	7.3731
Totals :				9124.38306	237.55014	

(5a*S*,12a*S*,12b*S*)-12-benzyl-9-methyl-6,12,12a,12b-tetrahydro-5*H*-naphtho

[2,3-*a*]carbazole-5,13(5a*H*)-dione (4h)

Figure S77. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of 4h

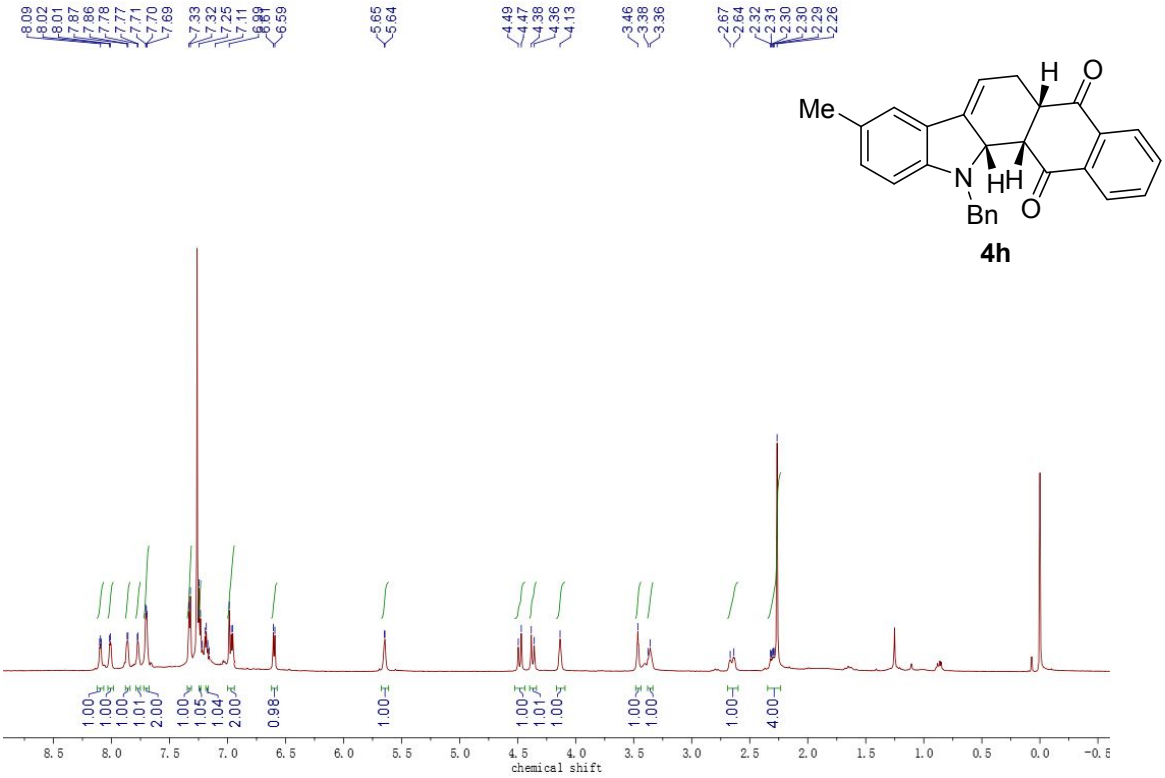


Figure S78. ^{13}C NMR (151MHz, $CDCl_3$) spectrum of 4h

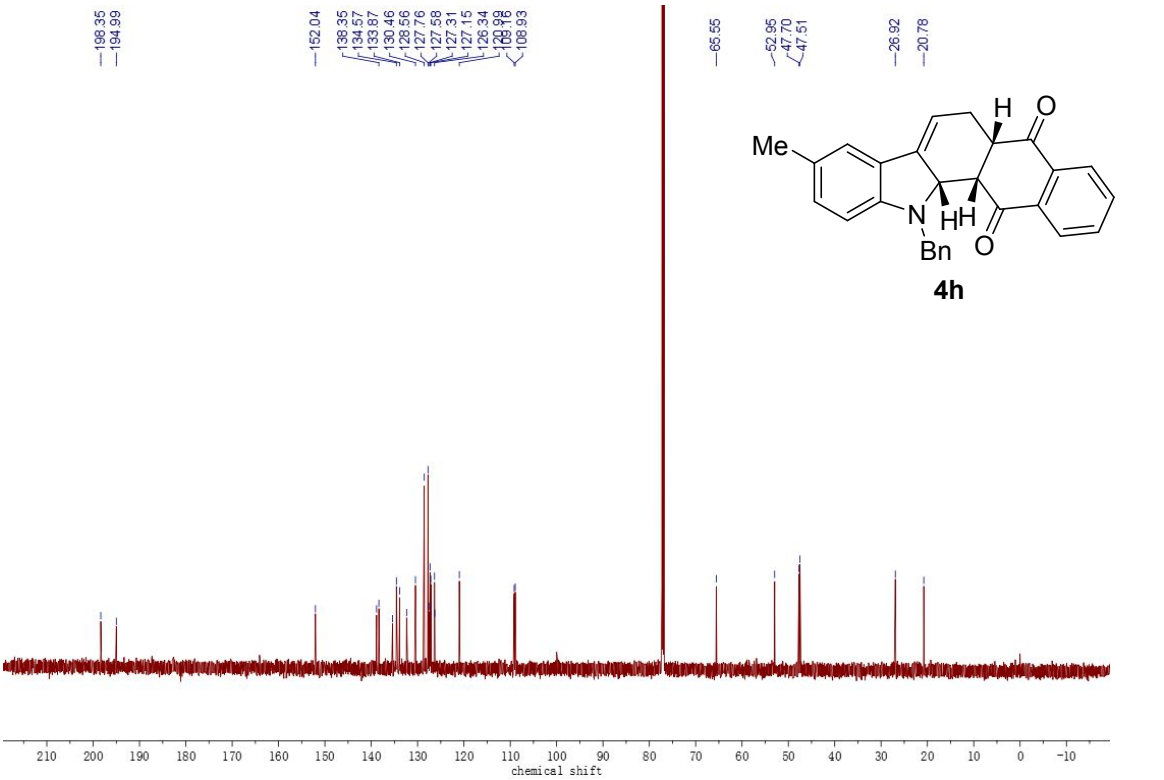
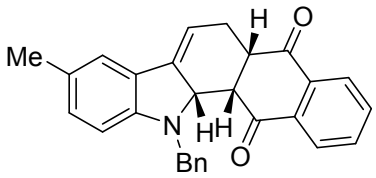
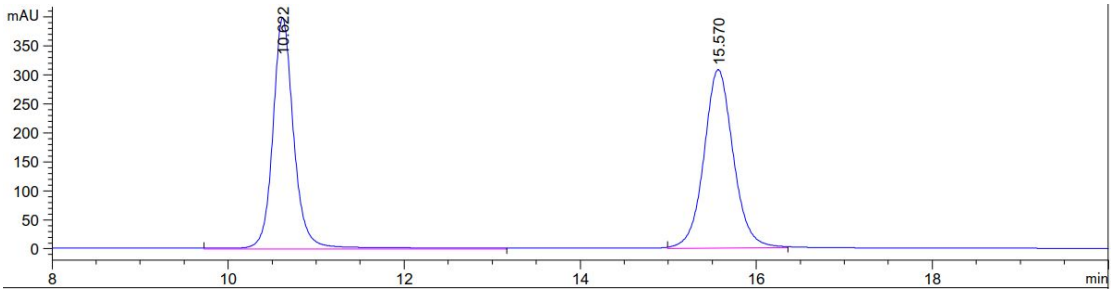


Figure S79. HPLC spectrum of 4h

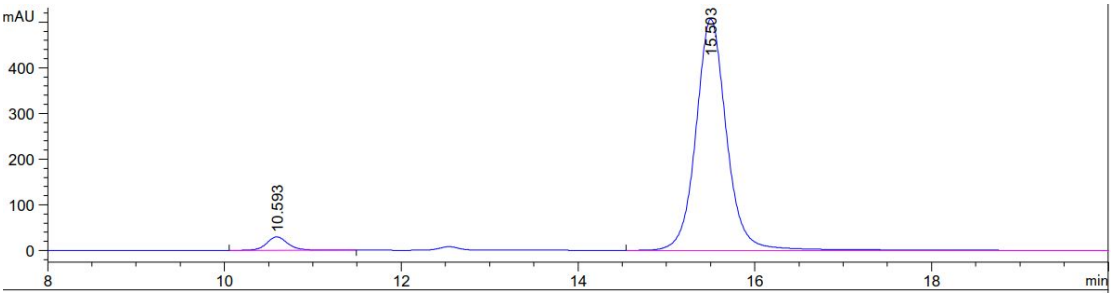


4h (The top one is racemic, and the bottom one is chiral)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.622	MM	0.2845	6812.86133	399.06091	48.8400
2	15.570	MM	0.3860	7136.49805	308.16812	51.1600
Totals :				1.39494e4	707.22903	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.593	BB	0.2563	493.92798	29.36253	3.8812
2	15.503	VBA	0.3658	1.22321e4	506.34439	96.1188
Totals :				1.27261e4	535.70692	

(5a*S*,12a*S*,12b*S*)-12-benzyl-9-methoxy-6,12,12a,12b-tetrahydro-5*H*-napht

ho[2,3-*a*]carbazole-5,13(5a*H*)-dione (4i)

Figure S80. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of 4i

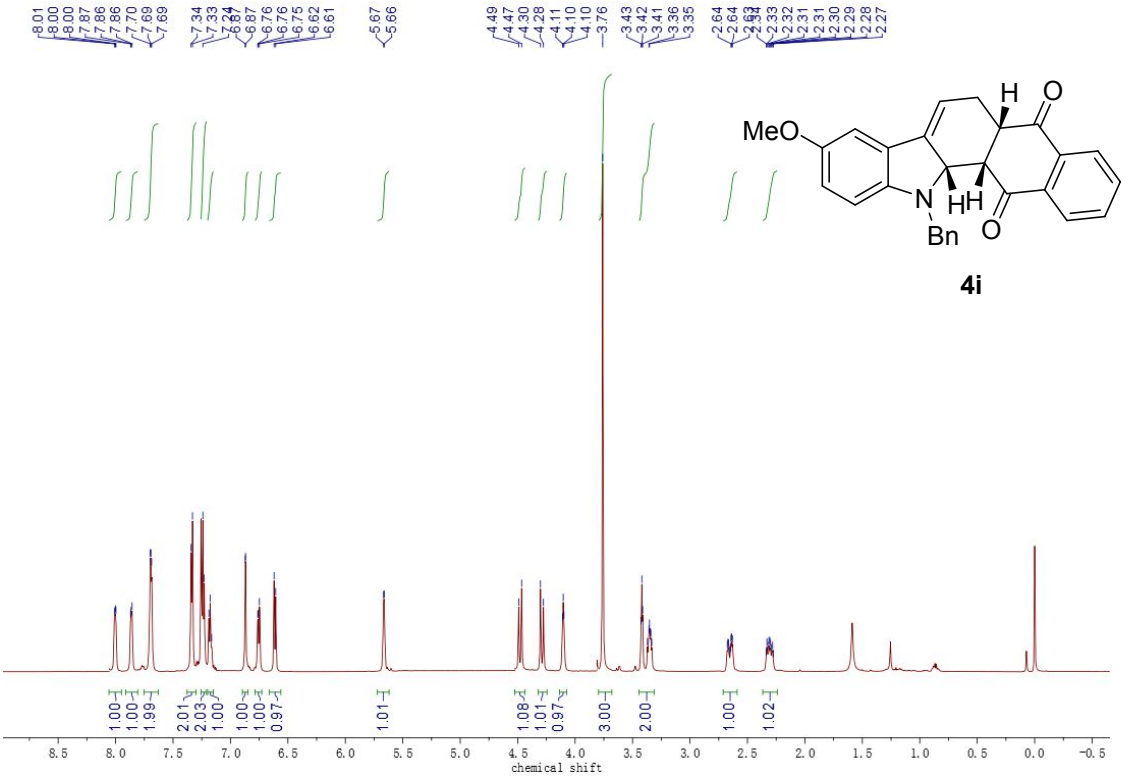


Figure S81. ^{13}C NMR (151MHz, $CDCl_3$) spectrum of 4i

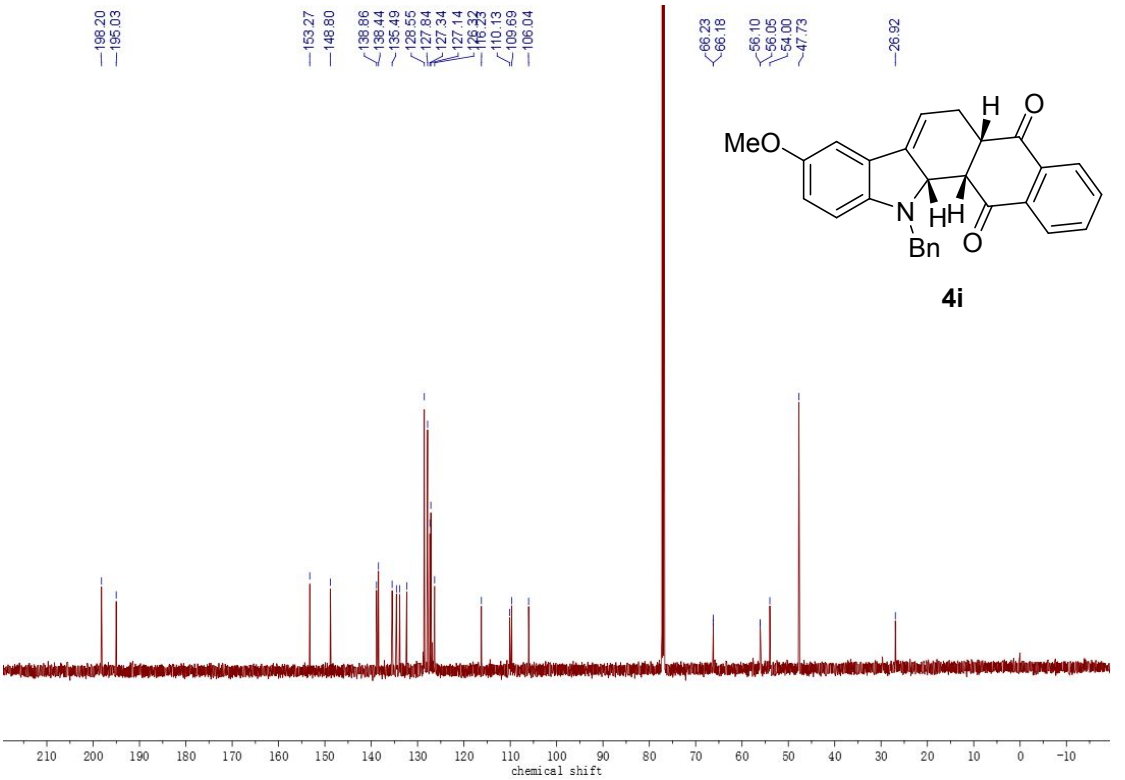
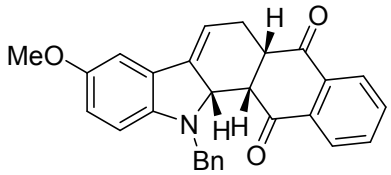
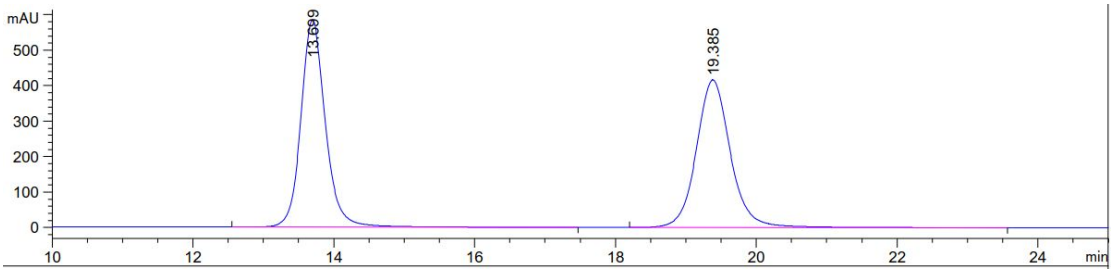


Figure S82. HPLC spectrum of 4i

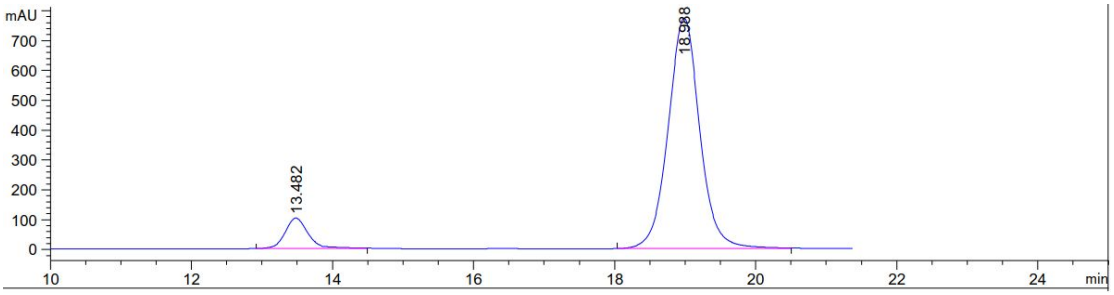


4i (The top one is racemic, and the bottom one is chiral)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.699	BB	0.3661	1.41247e4	584.19623	50.1368
2	19.385	BB	0.5138	1.40476e4	416.22028	49.8632
Totals :				2.81722e4	1000.41650	



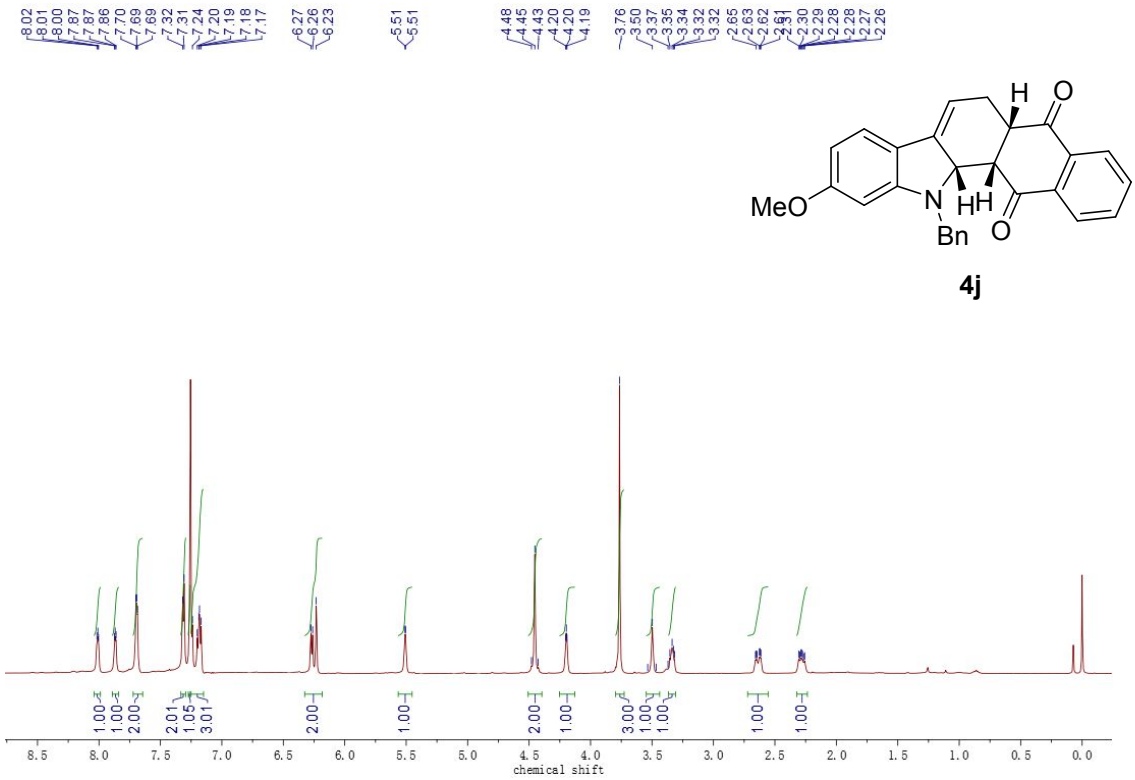
Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.482	MM	0.3396	2000.60400	98.17230	7.6662
2	18.988	MM	0.5202	2.40957e4	772.01215	92.3338
Totals :				2.60963e4	870.18445	

(5a*S*,12a*S*,12b*S*)-12-benzyl-10-methoxy-6,12,12a,12b-tetrahydro-5*H*-naph

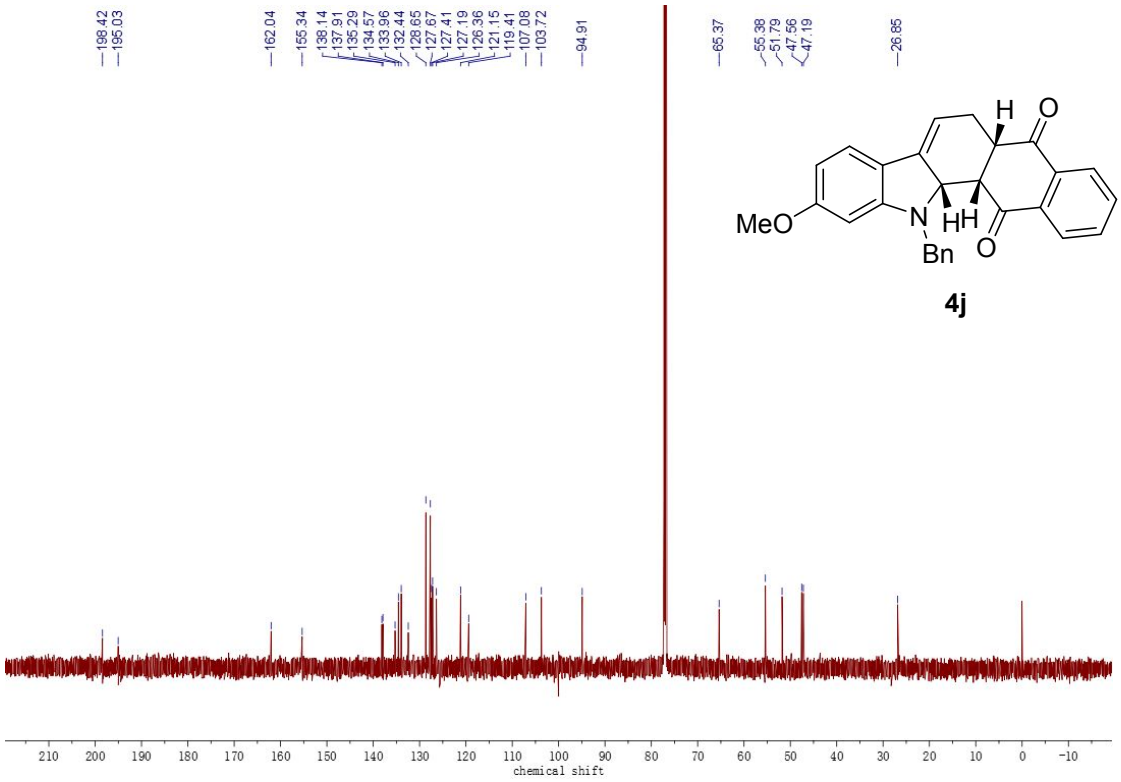
tho[2,3-*a*]carbazole-5,13(5a*H*)-dione (4j)

Figure S83. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of 4j



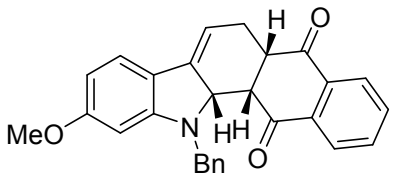
4j

Figure S84. ^{13}C NMR (151MHz, $CDCl_3$) spectrum of 4j

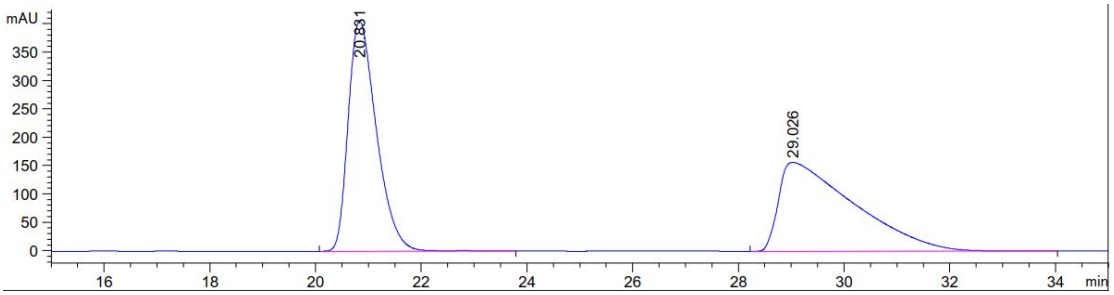


4j

Figure S85. HPLC spectrum of 4j

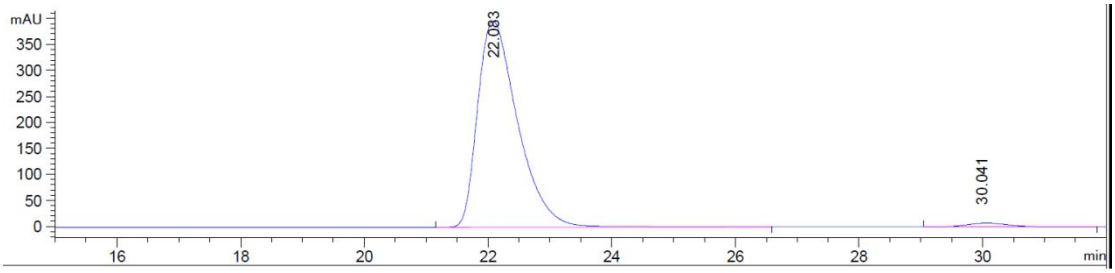


4j (The top one is racemic, and the bottom one is chiral)



Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.831	BV R	0.5674	1.50683e4	406.31296	49.2364
2	29.026	BB	1.4313	1.55356e4	156.88506	50.7636
Totals :				3.06039e4	563.19801	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.083	BB	0.6882	1.78336e4	396.94116	97.9382
2	30.041	BB	0.7717	375.43158	7.50355	2.0618
Totals :				1.82091e4	404.44471	

(5a*S*,12a*S*,12b*S*)-12-benzyl-11-methyl-6,12,12a,12b-tetrahydro-5*H*-naphth

o[2,3-*a*]carbazole-5,13(5a*H*)-dione (4k)

Figure S86. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of 4k

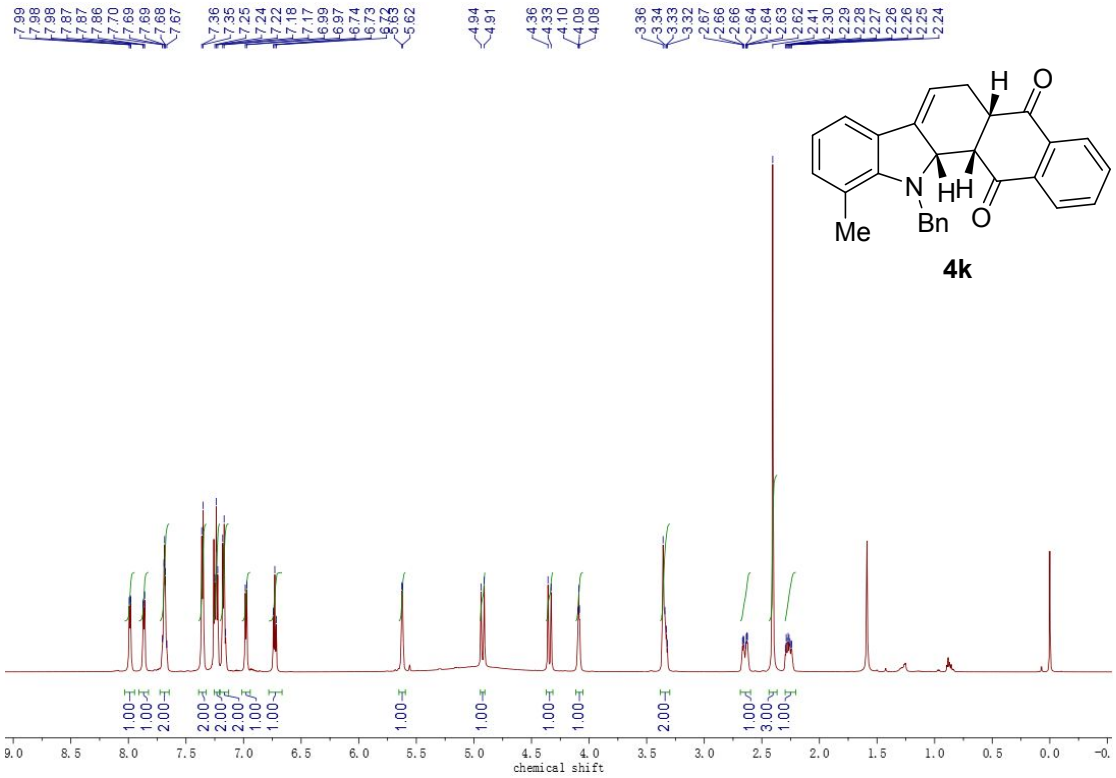


Figure S87. ^{13}C NMR (151MHz, $CDCl_3$) spectrum of 4k

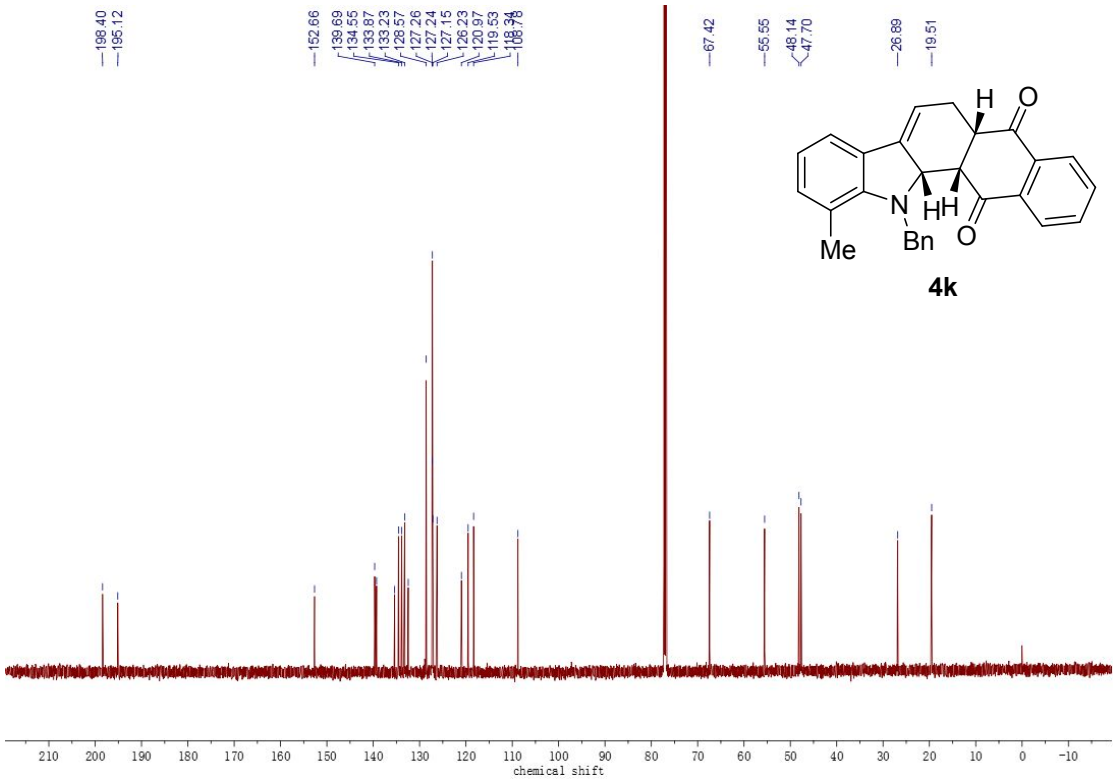
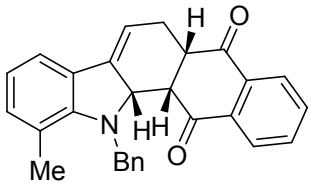
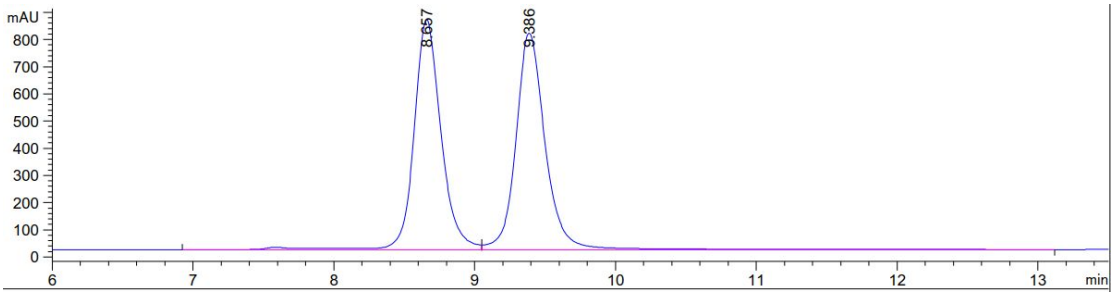


Figure S88. HPLC spectrum of 4k

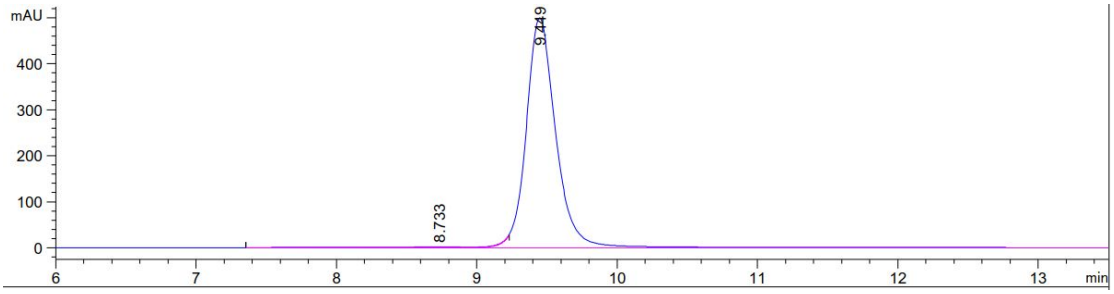


4k (The top one is racemic, and the bottom one is chiral)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.657	VV R	0.1997	1.13524e4	845.34369	49.5303
2	9.386	VB	0.2194	1.15677e4	796.47290	50.4697
Totals :				2.29201e4	1641.81659	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.733	BV E	0.7853	112.09278	1.77371	1.5031
2	9.449	VB R	0.2217	7345.20850	499.02661	98.4969
Totals :				7457.30128	500.80032	

(5a*S*,12a*S*,12b*S*)-12-benzyl-7-methyl-6,12,12a,12b-tetrahydro-5*H*-naphtho

[2,3-*a*]carbazole-5,13(5a*H*)-dione (4l)

Figure S89. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of 4l

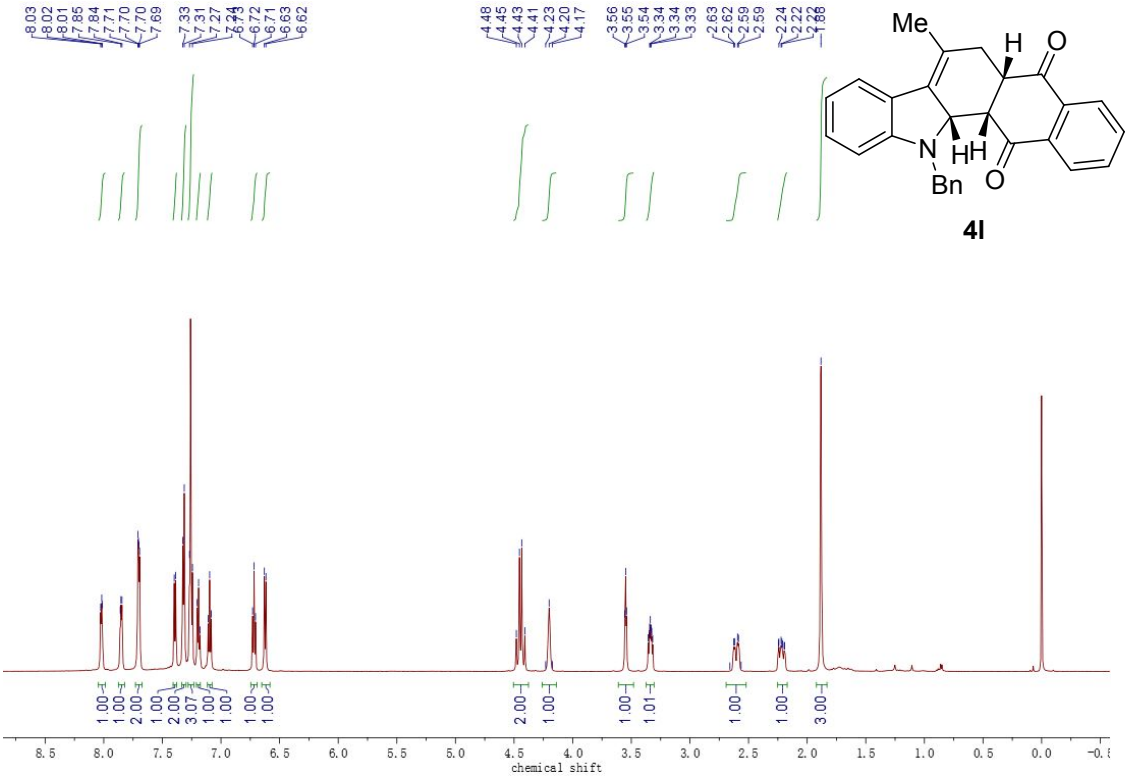


Figure S90. ^{13}C NMR (151MHz, $CDCl_3$) spectrum of 4l

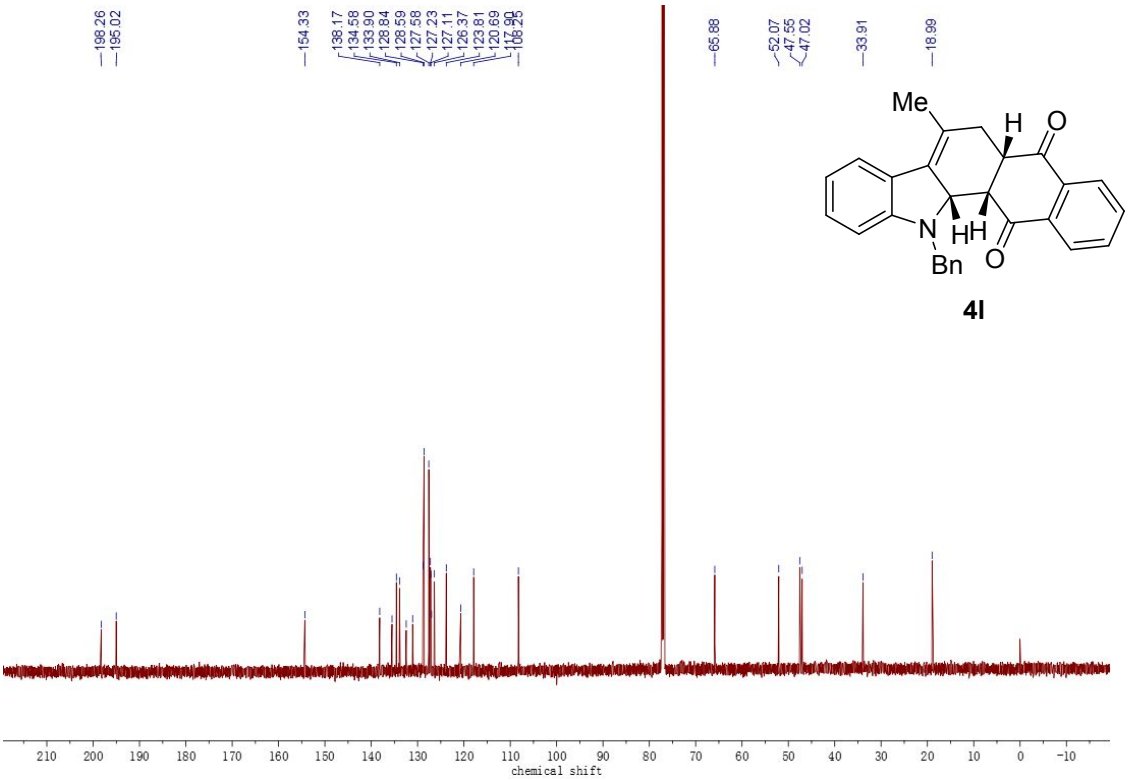
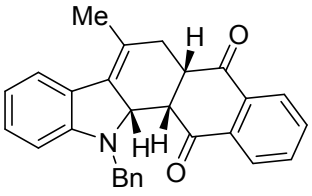
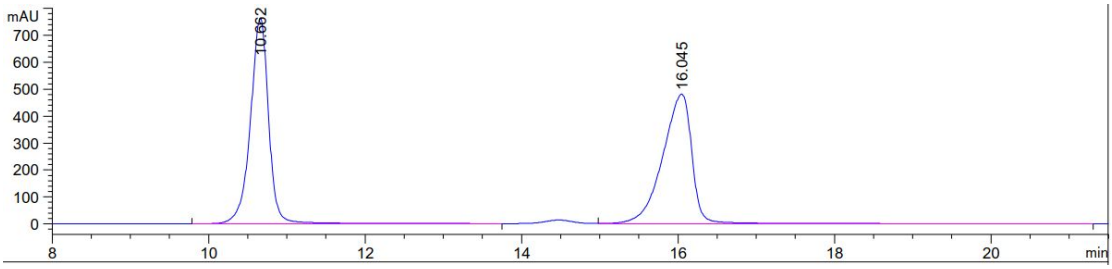


Figure S91. HPLC spectrum of 4l

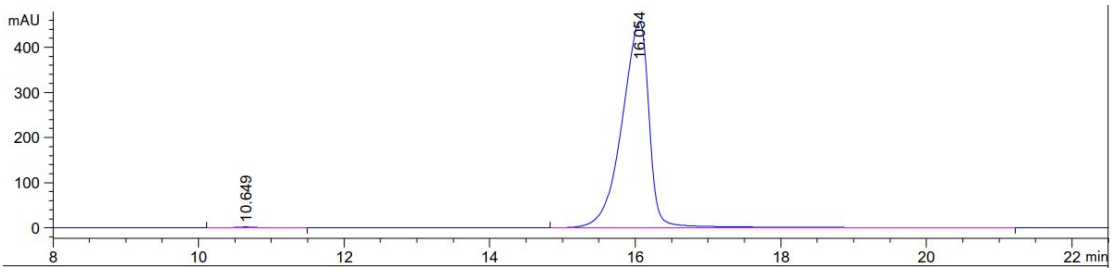


4l (The top one is racemic, and the bottom one is chiral)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.662	BV R	0.2457	1.24332e4	764.22131	49.6393
2	16.045	VV R	0.4014	1.26139e4	481.14987	50.3607
Totals :				2.50471e4	1245.37119	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.649	BB	0.2534	28.65150	1.71062	0.2381
2	16.054	BV R	0.4026	1.20055e4	456.49075	99.7619
Totals :				1.20342e4	458.20138	

(5a*S*,12a*S*,12b*S*)-12-benzyl-6-methyl-6,12,12a,12b-tetrahydro-5*H*-naphtho

[2,3-*a*]carbazole-5,13(5a*H*)-dione (3am)

Figure S92. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of 3am

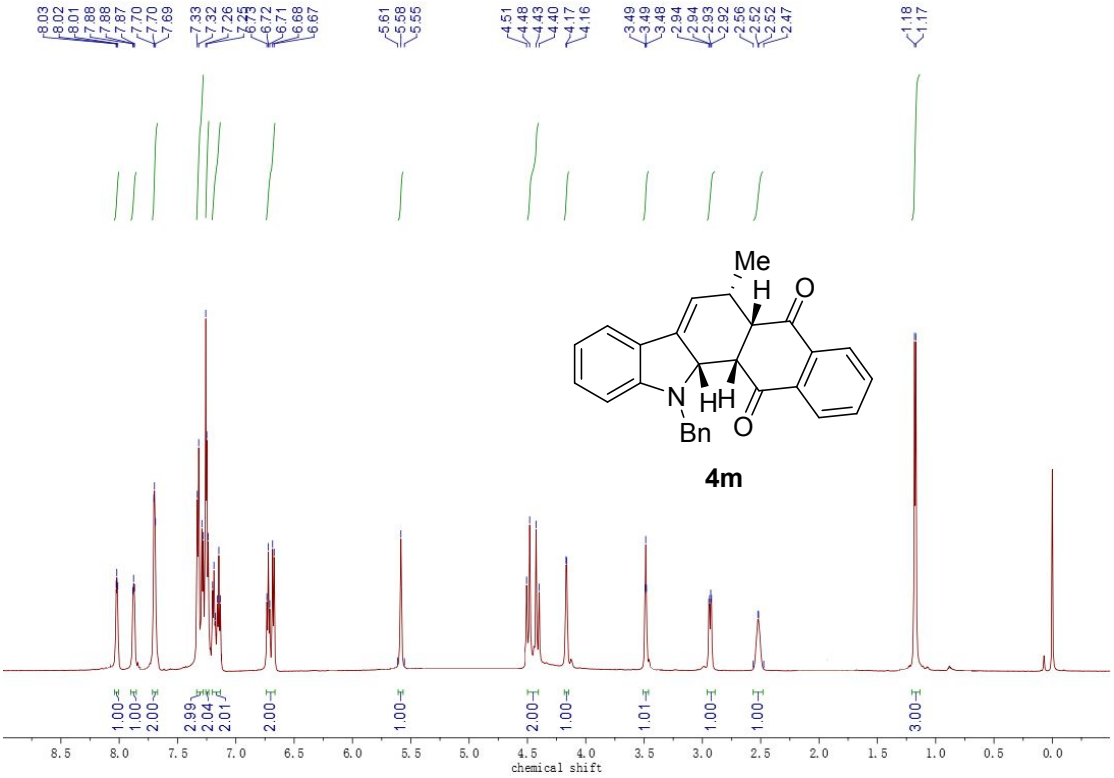


Figure S93. ^{13}C NMR (151MHz, $CDCl_3$) spectrum of 4m

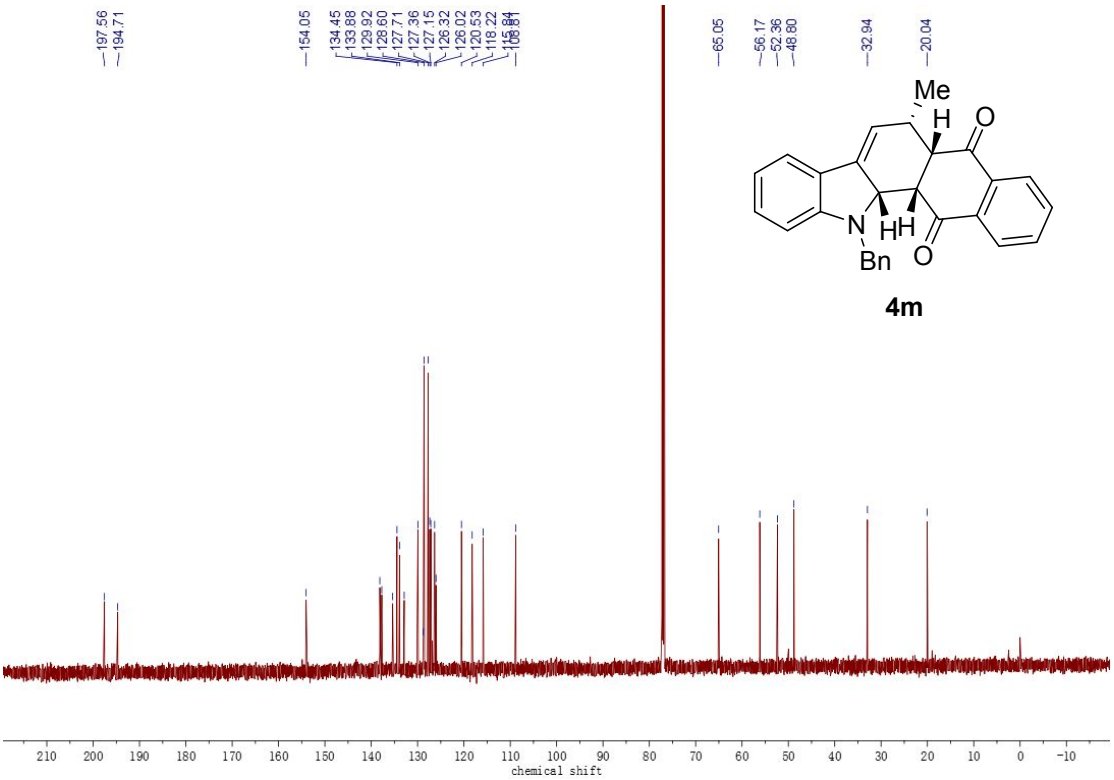
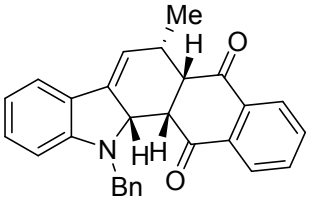
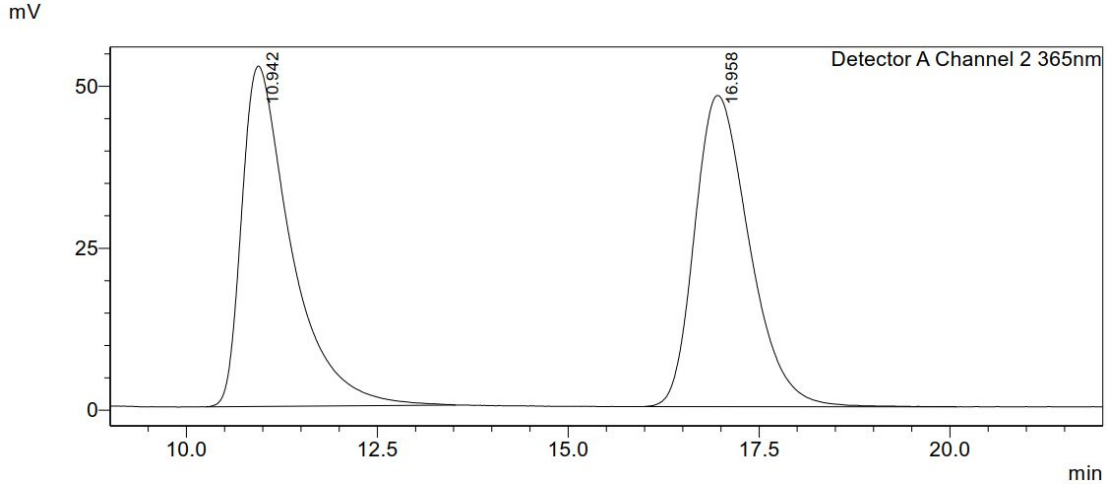


Figure S94. HPLC spectrum of 4m

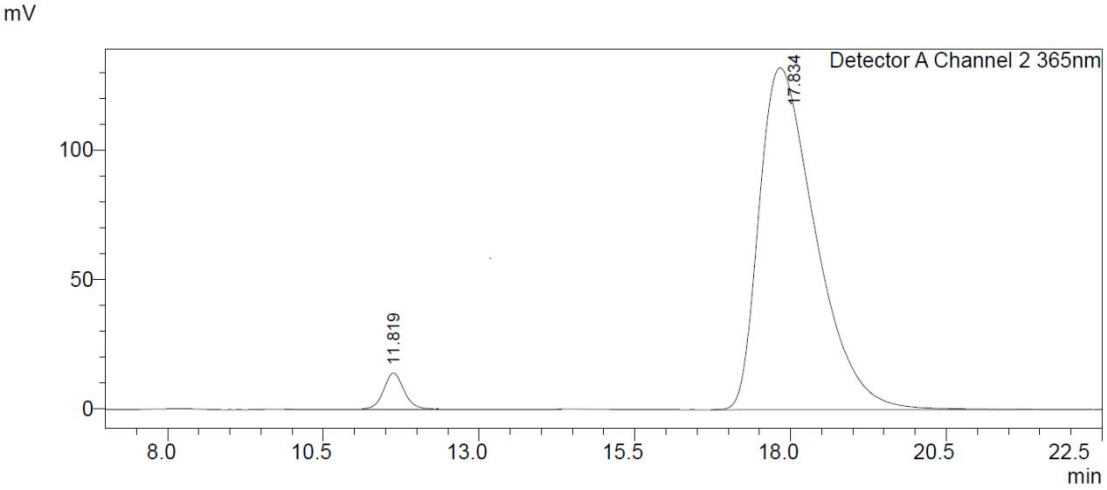


4m (The top one is racemic, and the bottom one is chiral)



Detector A Channel 2 365nm

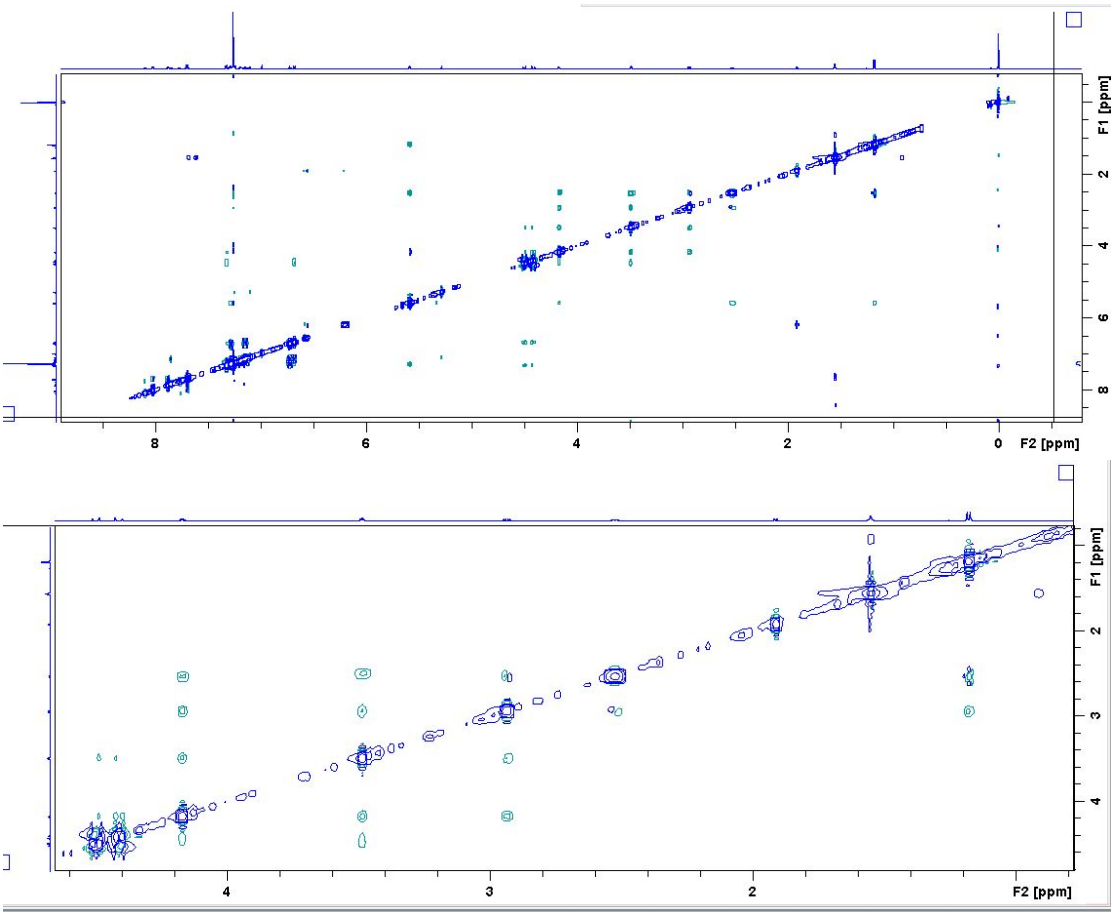
Peak	Ret. Time	Area	Height	Area%	Conc.
1	10.942	2364876	52549	49.655	49.655
2	16.958	2397699	48054	50.345	50.345
Total		4762576	100604	100.000	



Detector A Channel 2 365nm

Peak	Ret. Time	Area	Height	Area%	Conc.
1	11.816	741878	26012	8.186	8.186
2	17.834	8320937	131985	91.814	91.814
Total		9062815	157997	100.000	

Figure S95. NOESY NMR (600MHz, $CDCl_3$) spectrum of 4m



(5a*S*,12a*S*,12b*S*)-6,12,12a,12b-tetrahydro-5*H*-naphtho[2,3-*a*]carbazole-5,1

3(5a*H*)-dione (4n)

Figure S96. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of 4n

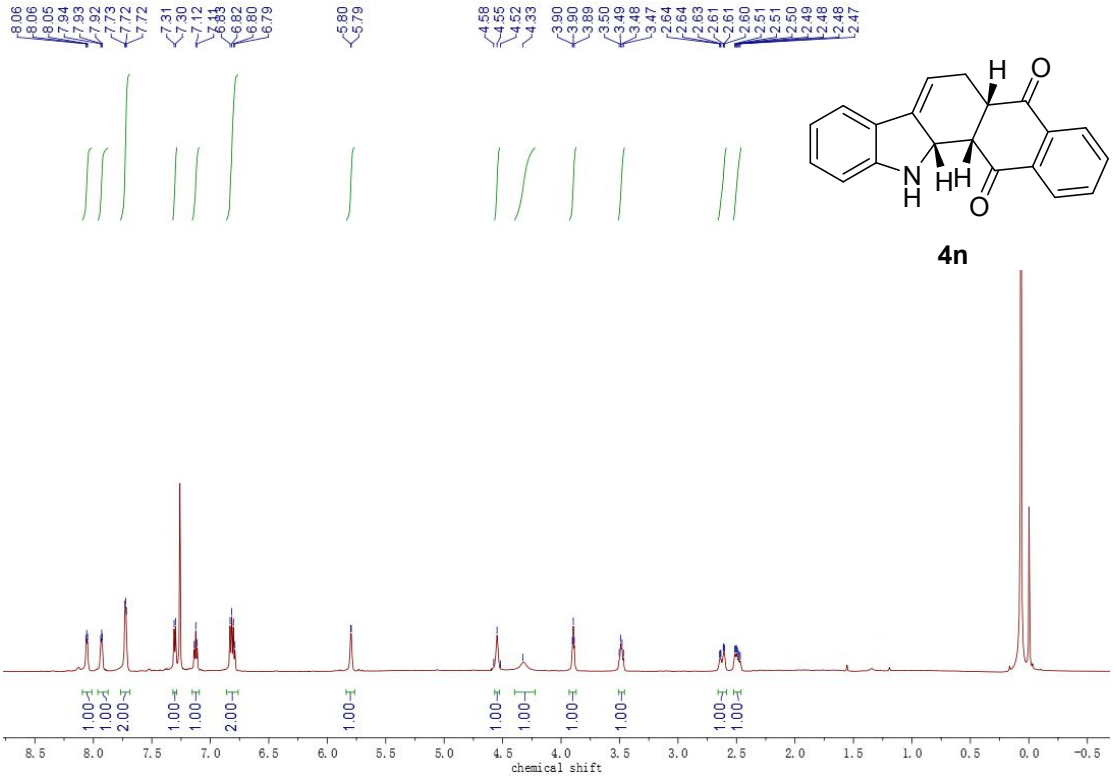


Figure S97. ^{13}C NMR (151MHz, $CDCl_3$) spectrum of 4n

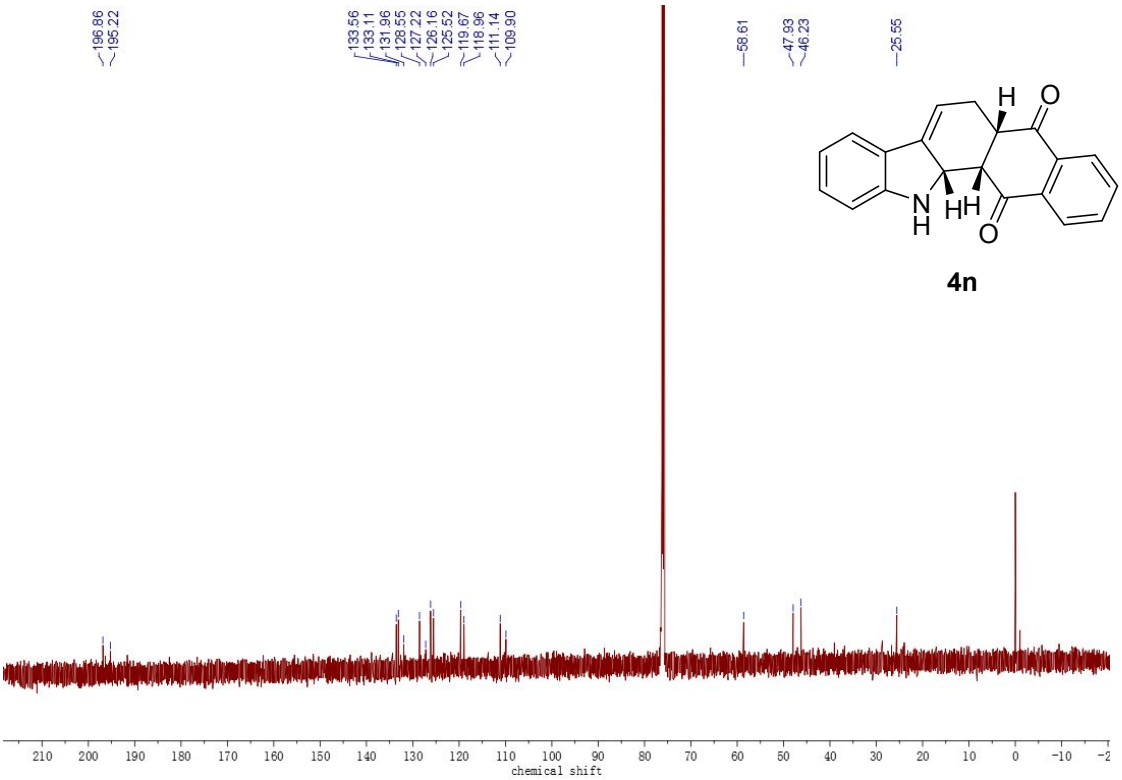
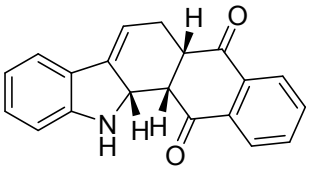
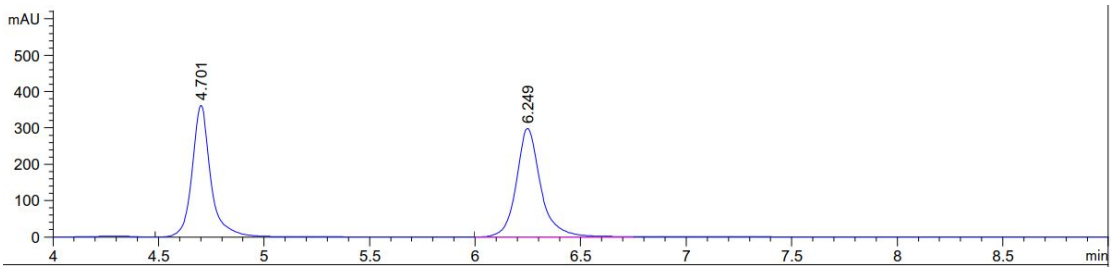


Figure S98. HPLC spectrum of 4n

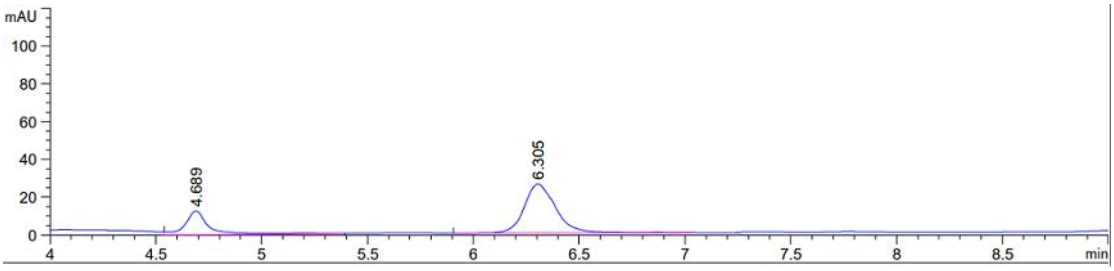


4n (The top one is racemic, and the bottom one is chiral)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.701	MM	0.1032	2256.42188	364.25891	48.5430
2	6.249	MM	0.1332	2391.87671	299.35306	51.4570
Totals :				4648.29858	663.61197	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.689	VV R	0.1100	104.23135	12.66841	26.0547
2	6.305	BV	0.1630	295.81680	25.95681	73.9453
Totals :				400.04816	38.62521	

(5a*S*,12a*S*,12b*S*)-12-(4-methoxyphenyl)-6,12,12a,12b-tetrahydro-5*H*-napht

ho[2,3-*a*]carbazole-5,13(5a*H*)-dione (4o)

Figure S99. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of 4o

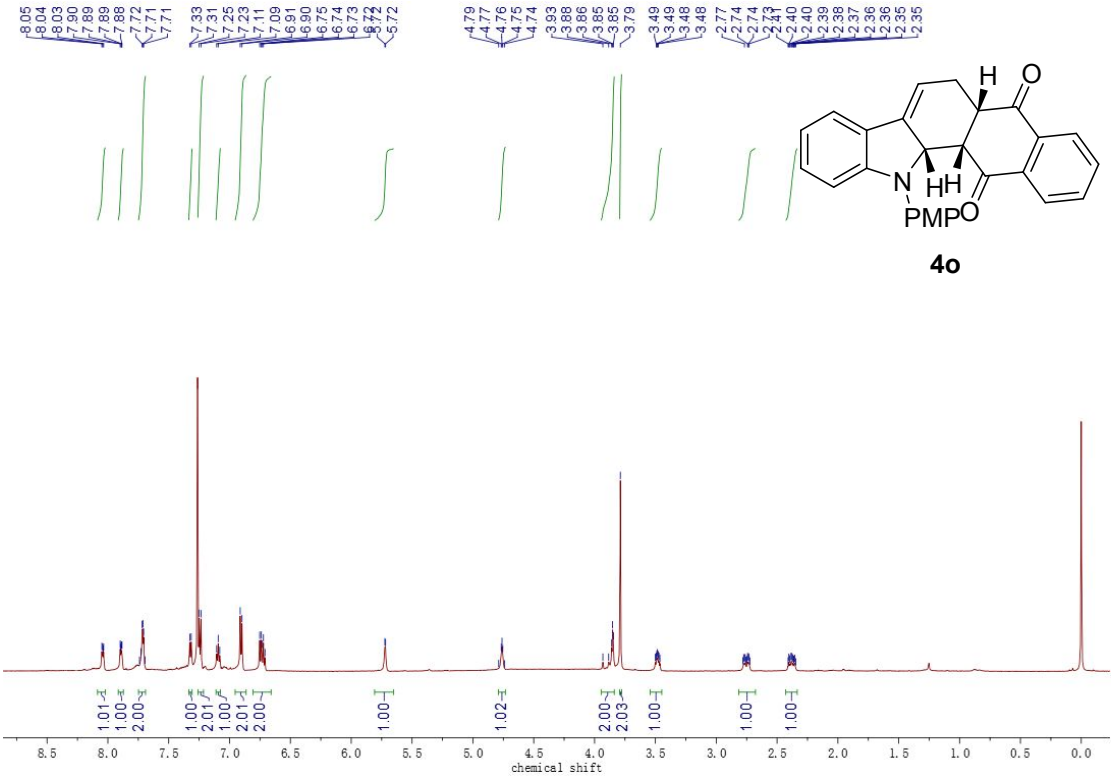


Figure S100. ^{13}C NMR (151MHz, $CDCl_3$) spectrum of 4o

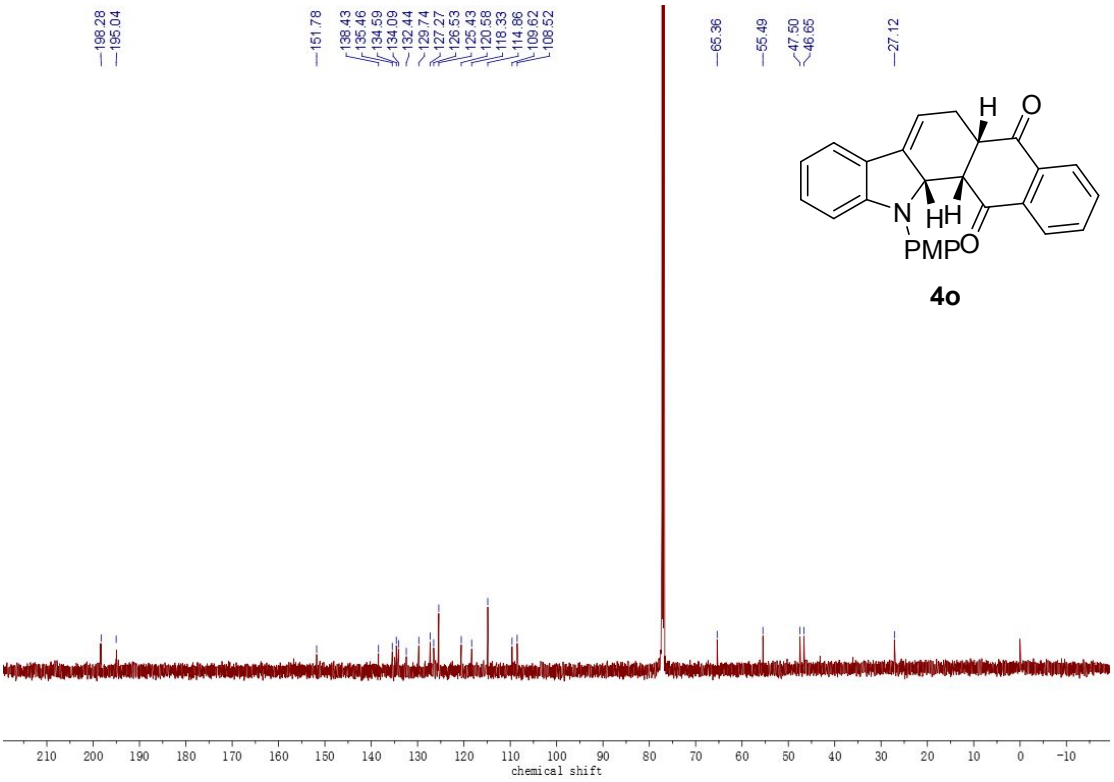
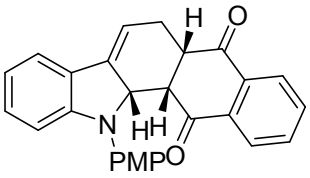
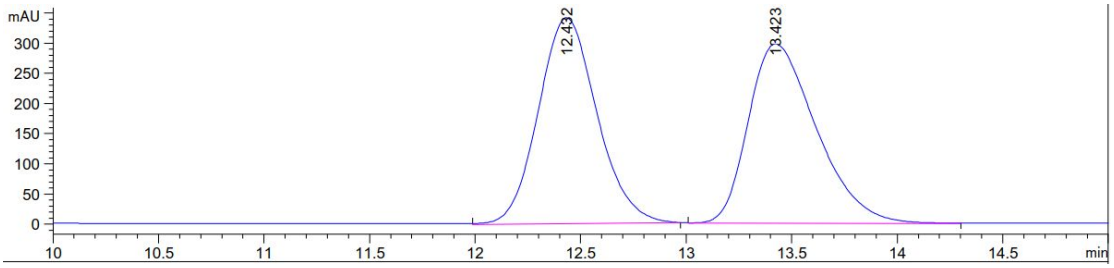


Figure S101. HPLC spectrum of 4o

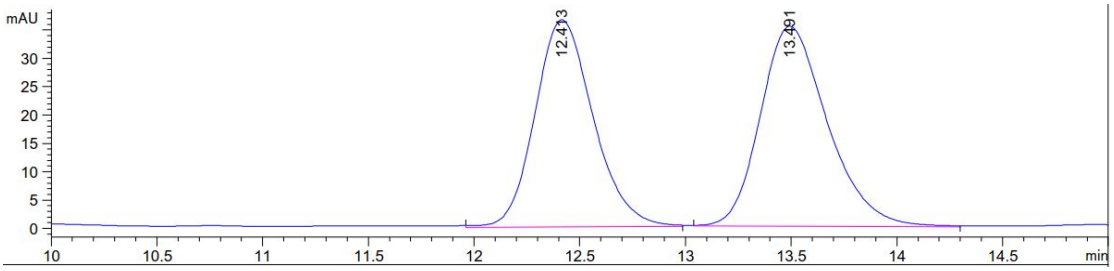


4o (The top one is racemic, and the bottom one is chiral)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.432	MM	0.3221	6603.14502	341.71100	49.6960
2	13.423	MM	0.3743	6683.92480	297.60675	50.3040
Totals :				1.32871e4	639.31775	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.413	MM	0.3190	700.04437	36.57253	47.3318
2	13.491	MM	0.3679	778.97064	35.28646	52.6682
Totals :				1479.01501	71.85899	

(5a*S*,12a*S*,12b*S*)-12-(4-methoxybenzyl)-6,12,12a,12b-tetrahydro-5*H*-napht

ho[2,3-*a*]carbazole-5,13(5a*H*)-dione (4p)

Figure S102. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of 4p

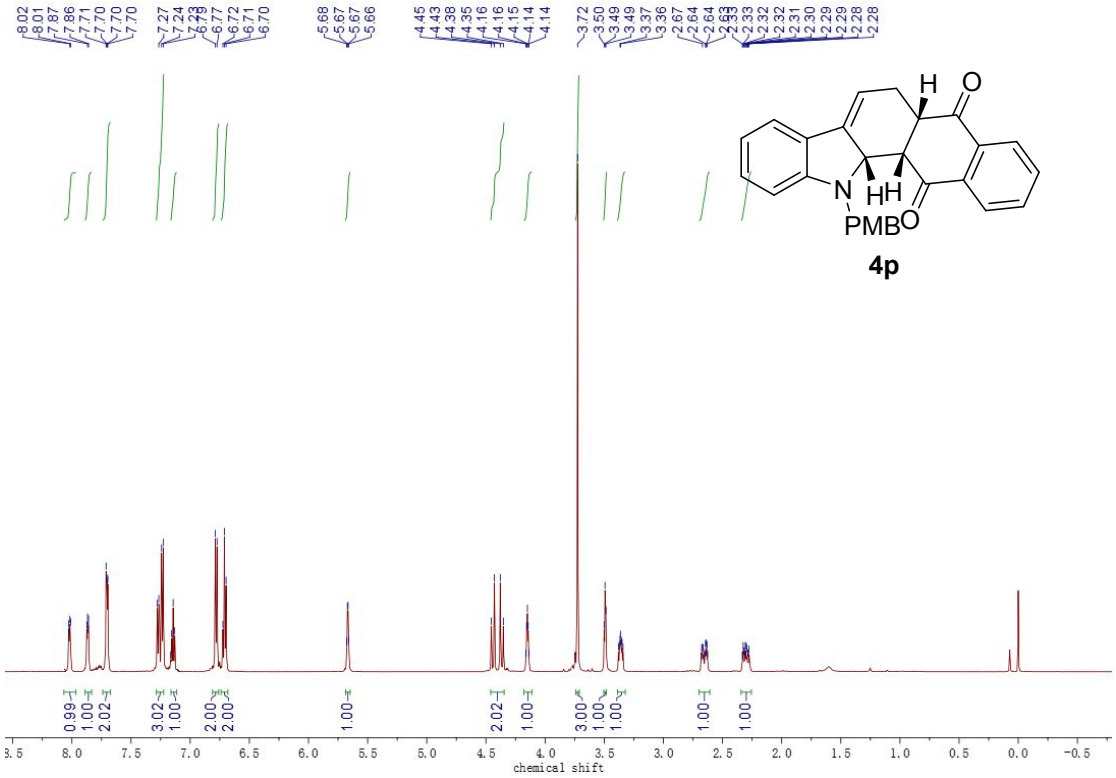


Figure S103. ^{13}C NMR (151MHz, $CDCl_3$) spectrum of 4p

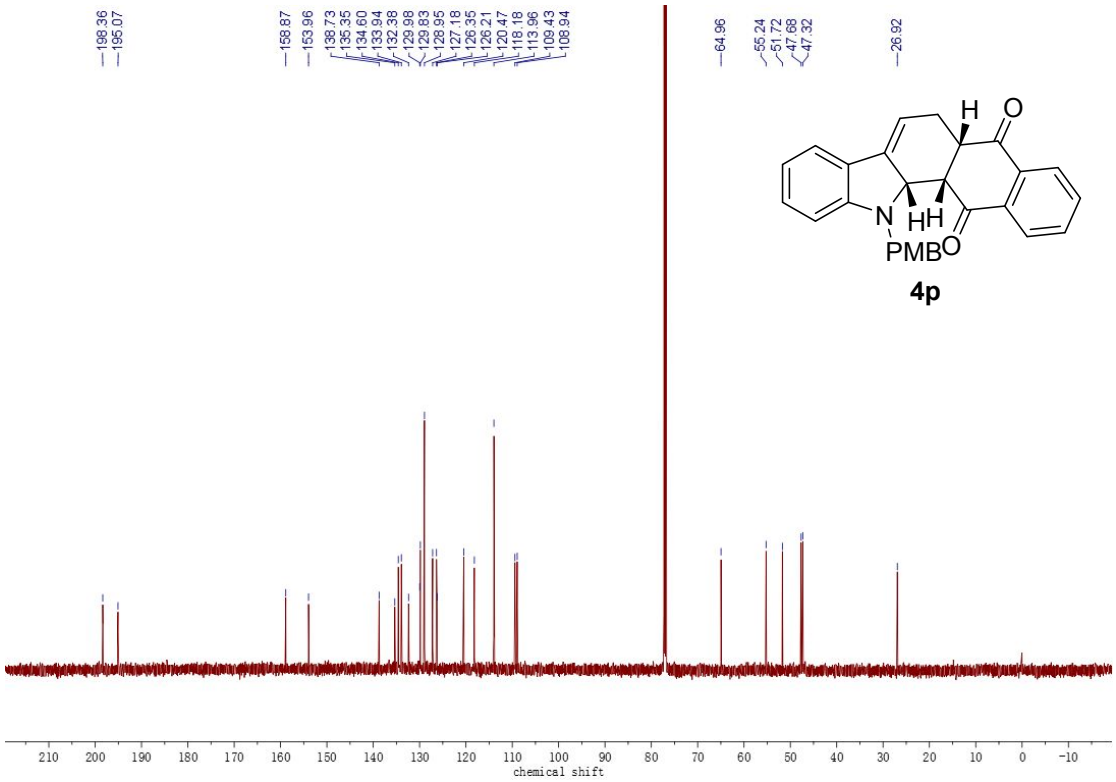
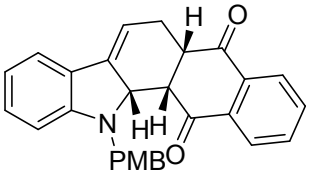
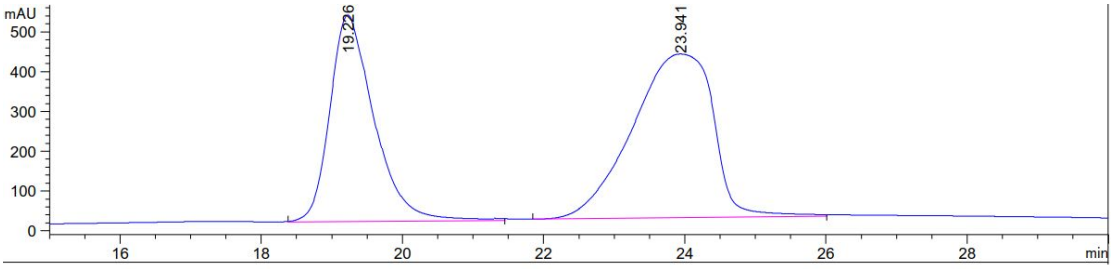


Figure S104. HPLC spectrum of 4p

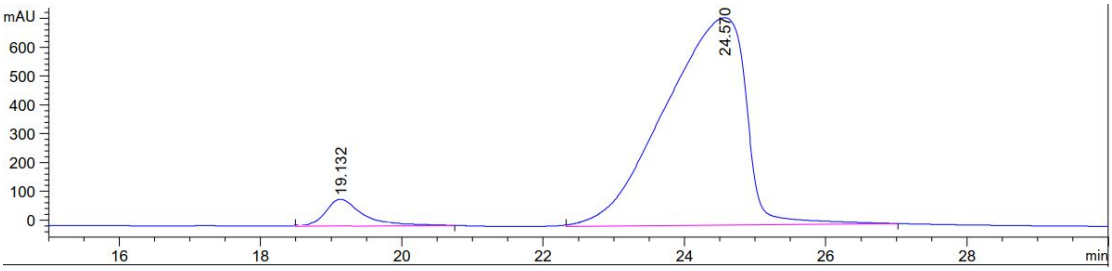


4p (The top one is racemic, and the bottom one is chiral)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.226	MM	1.0601	3.29921e4	518.70599	50.1117
2	23.941	MM	1.3308	3.28451e4	411.34277	49.8883
Totals :				6.58373e4	930.04877	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.132	MM	0.5128	2668.26953	86.72807	4.4186
2	24.570	MM	1.3377	5.77183e4	719.12042	95.5814
Totals :				6.03865e4	805.84850	

(5a*S*,12a*S*,12b*S*)-12-(4-(tert-butyl)benzyl)-6,12,12a,12b-tetrahydro-5*H*-nap

htho[2,3-*a*]carbazole-5,13(5a*H*)-dione (4q)

Figure S105. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of 4q

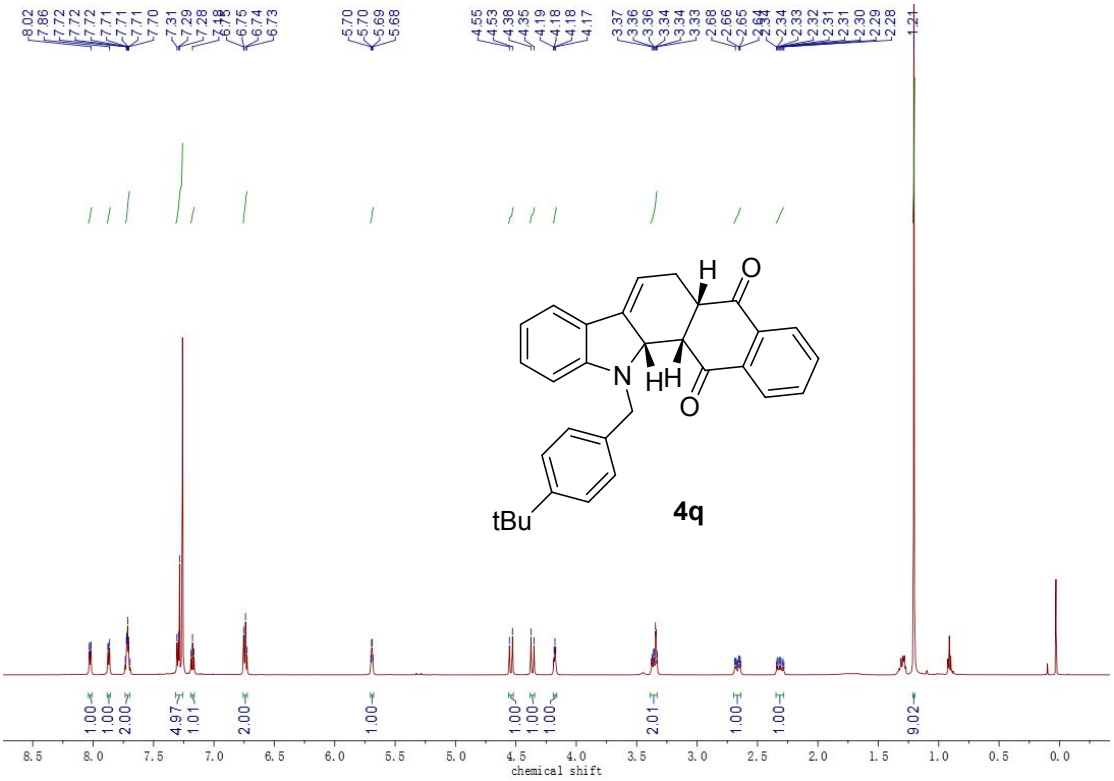


Figure S106. ^{13}C NMR (151MHz, $CDCl_3$) spectrum of 4q

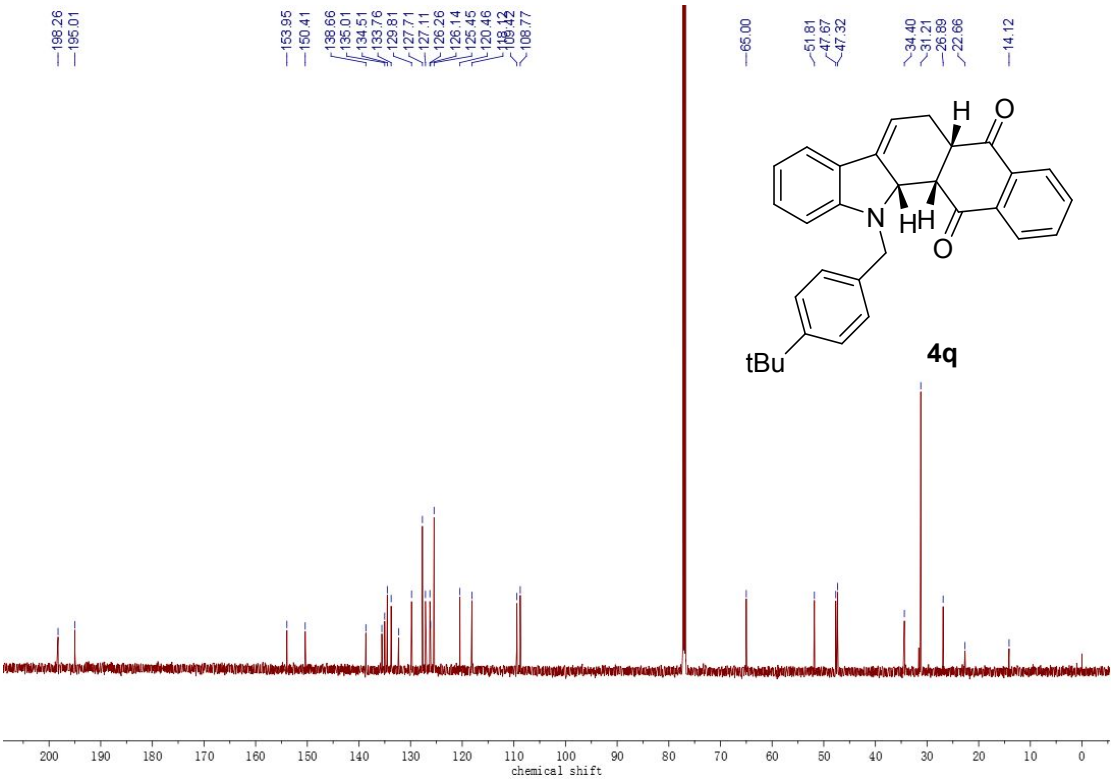
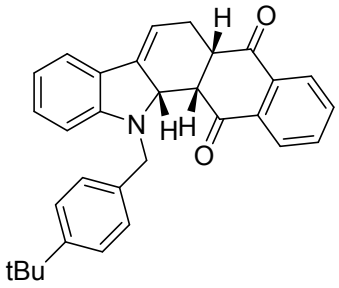
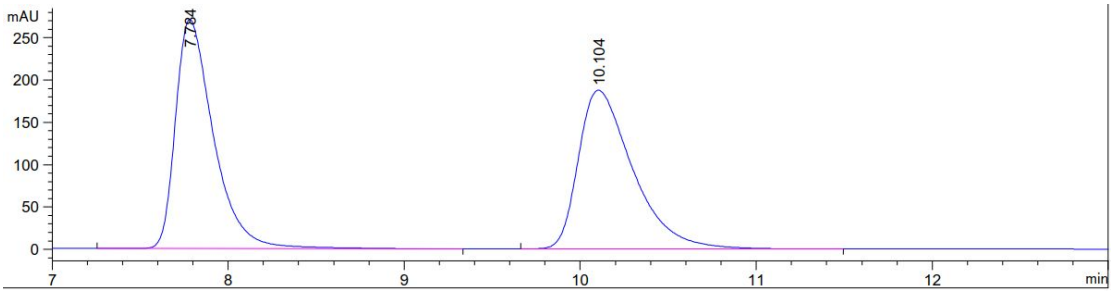


Figure S107. HPLC spectrum of 4q

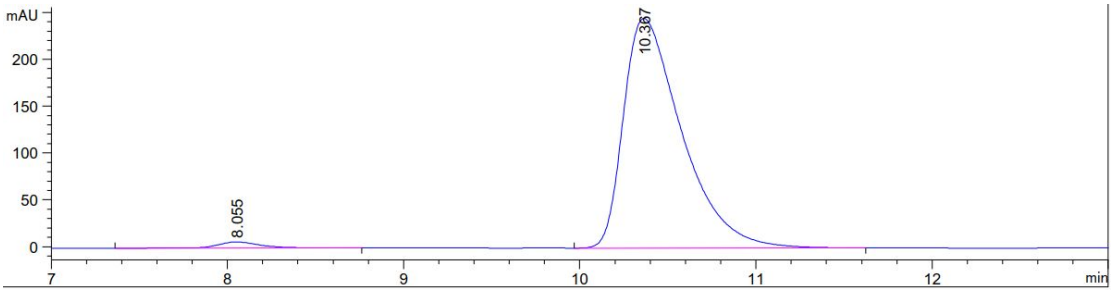


4q (The top one is racemic, and the bottom one is chiral)



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.784	BB	0.2275	4074.92578	270.83435	50.2940
2	10.104	BB	0.3269	4027.28174	187.29085	49.7060
Totals :				8102.20752	458.12520	



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.055	BB	0.2533	110.80417	6.55222	1.9271
2	10.367	BB	0.3464	5639.04834	245.14120	98.0729
Totals :				5749.85251	251.69343	

(5a*S*,12a*S*,12b*S*)-12-(4-chlorobenzyl)-6,12,12a,12b-tetrahydro-5*H*-naphth o[2,3-*a*]carbazole-5,13(5a*H*)-dione (4r)

Figure S108. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of 4r

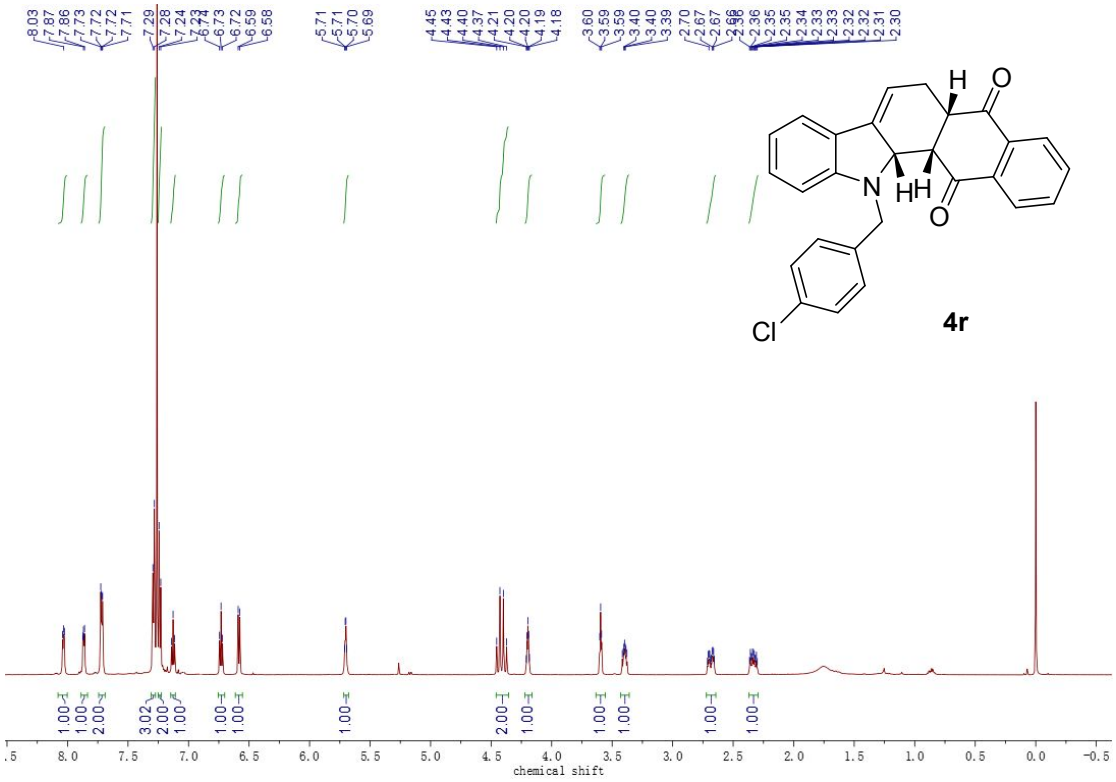


Figure S109. ^{13}C NMR (151MHz, $CDCl_3$) spectrum of 4r

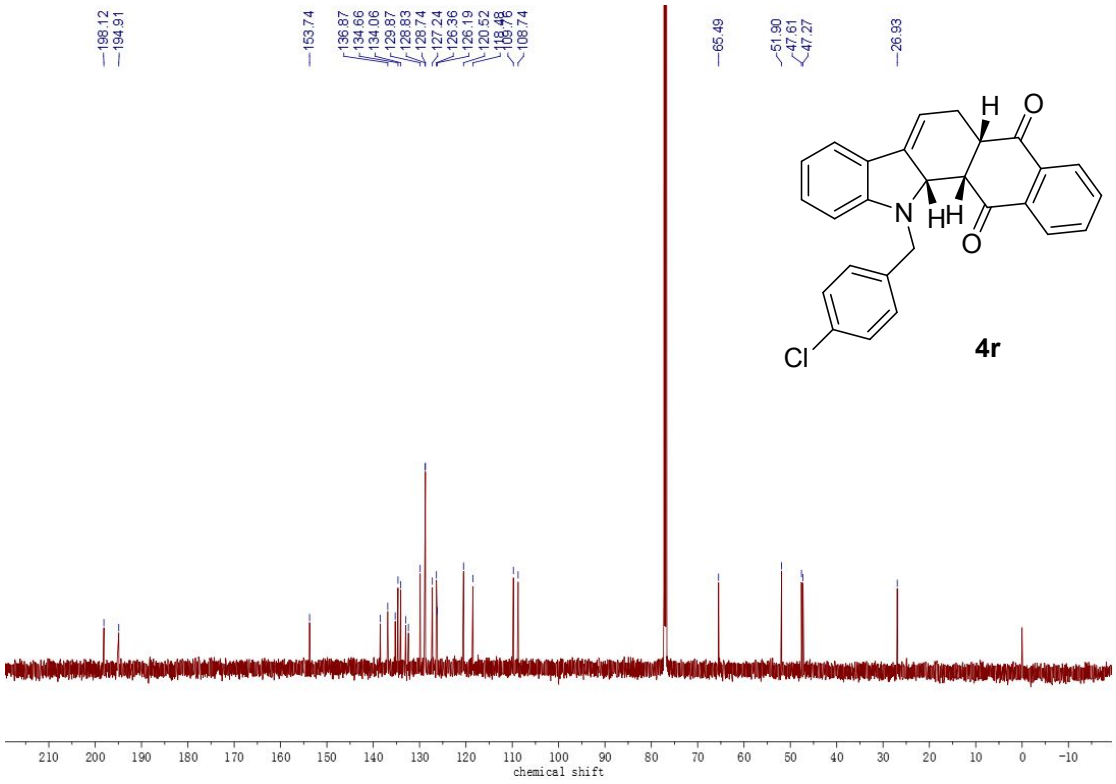
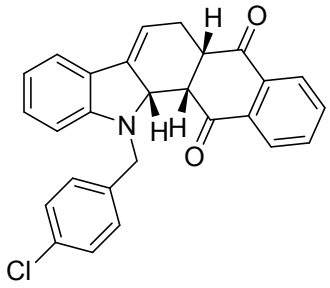
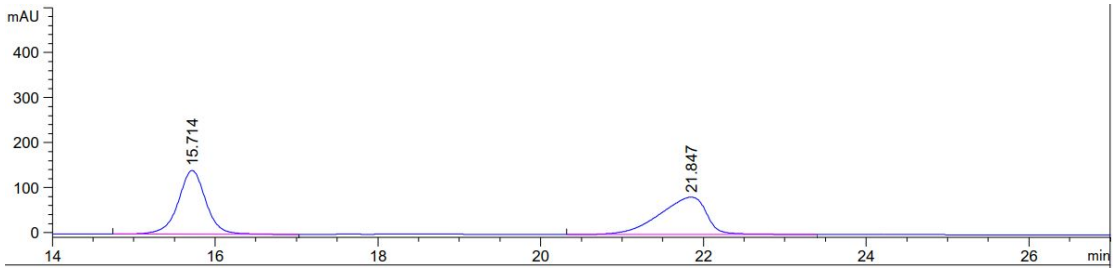


Figure S110. HPLC spectrum of 4r

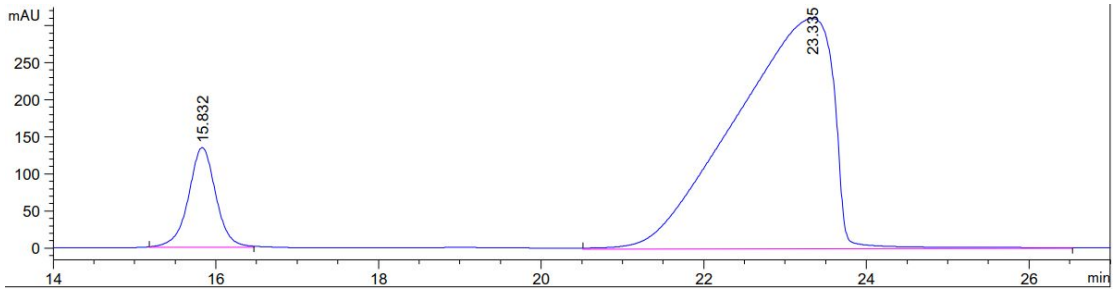


4r (The top one is racemic, and the bottom one is chiral)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.714	BB	0.3589	3362.33350	141.67412	49.9900
2	21.847	BB	0.6386	3363.67432	83.02781	50.0100
Totals :				6726.00781	224.70193	



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.832	MM	0.3890	3133.49341	134.24651	10.6499
2	23.335	MM	1.4104	2.62892e4	310.66104	89.3501
Totals :				2.94227e4	444.90755	

(5*S*,5a*S*,12b*S*)-12-benzyl-5-hydroxy-5,5a,6,7,12,12b-hexahydro-13*H*-naphtho[2,3-*a*]carbazol-13-one (4d-1)

Figure S111. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of 4d-1

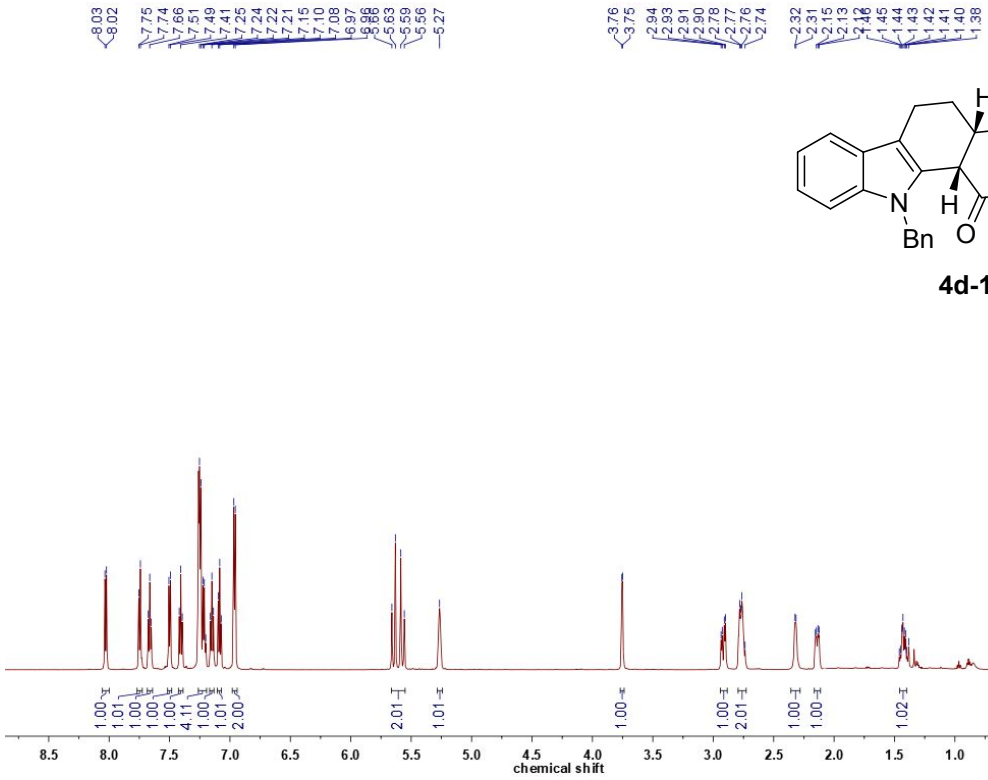


Figure S112. ^{13}C NMR (151MHz, $CDCl_3$) spectrum of 4d-1

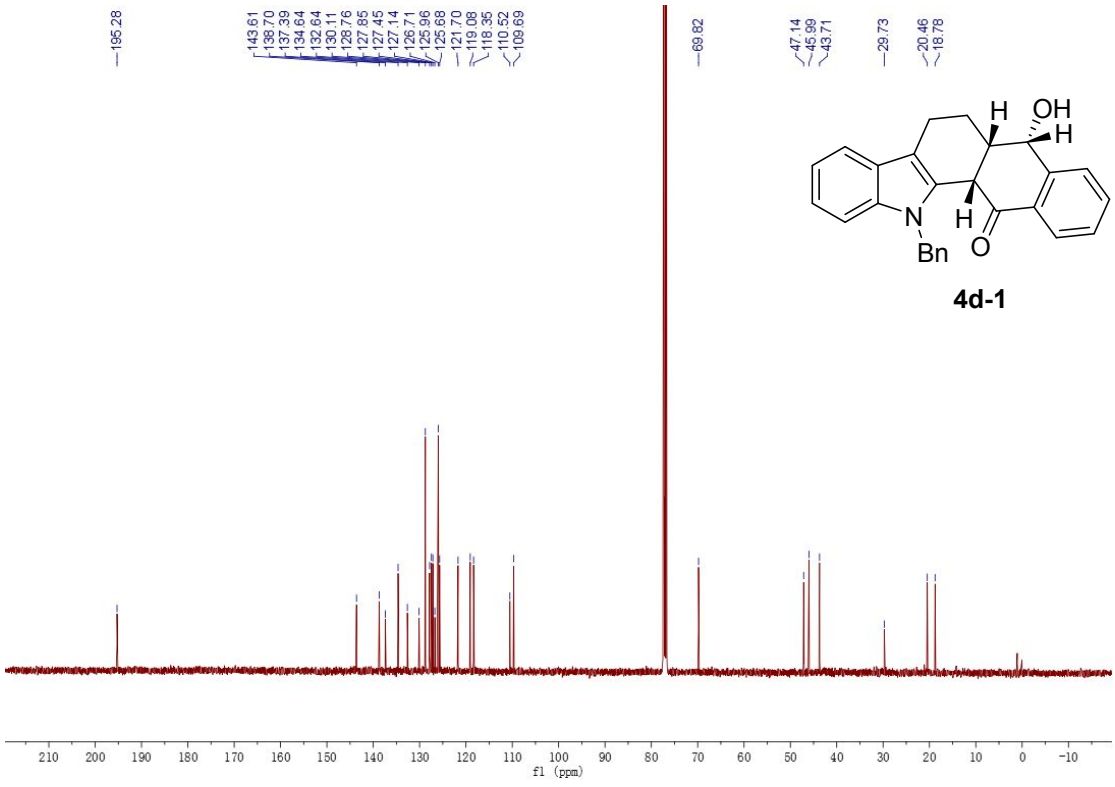
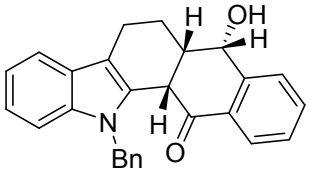
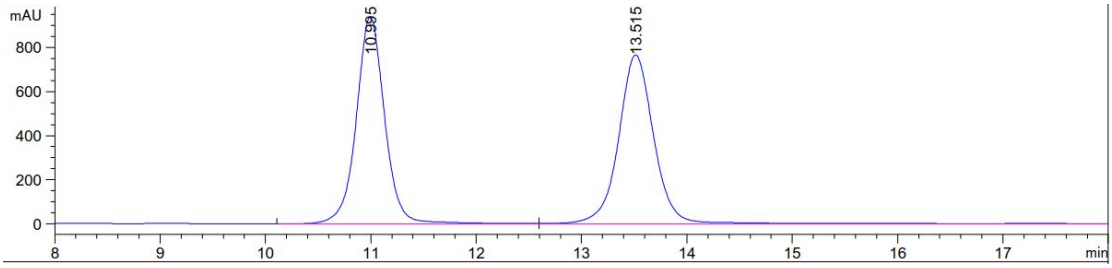


Figure S113. HPLC spectrum of 4d-1

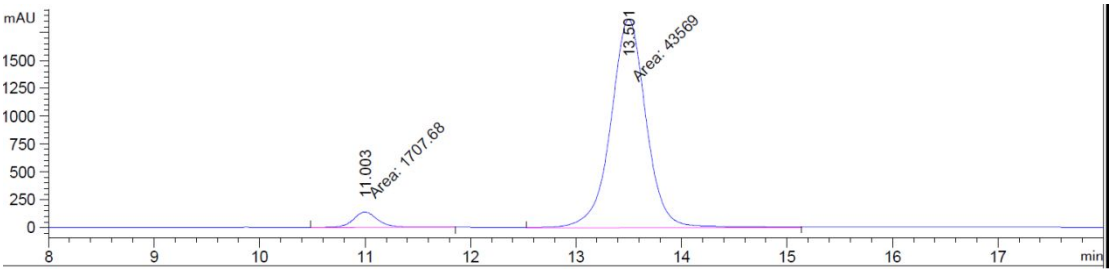


4d-1 (The top one is racemic, and the bottom one is chiral)



Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.995	BV	0.2874	1.76746e4	939.91205	49.4886
2	13.515	VV R	0.3543	1.80398e4	766.24023	50.5114
Totals :				3.57144e4	1706.15228	



Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.003	MM	0.1947	1707.68250	146.18575	3.7717
2	13.501	MM	0.3888	4.35690e4	1867.72107	96.2283
Totals :				4.52767e4	2013.90681	

Figure S114. NOESY NMR (600MHz, $CDCl_3$) spectrum of 4d-1

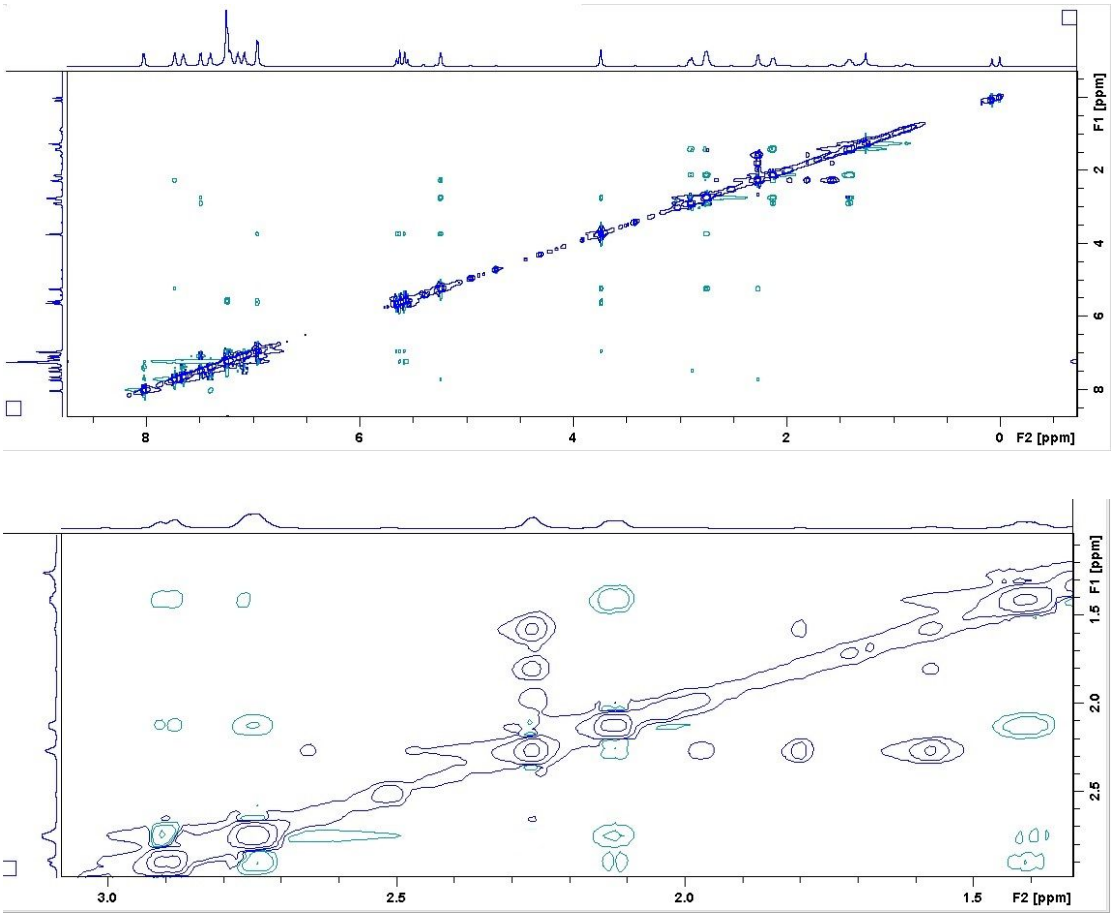
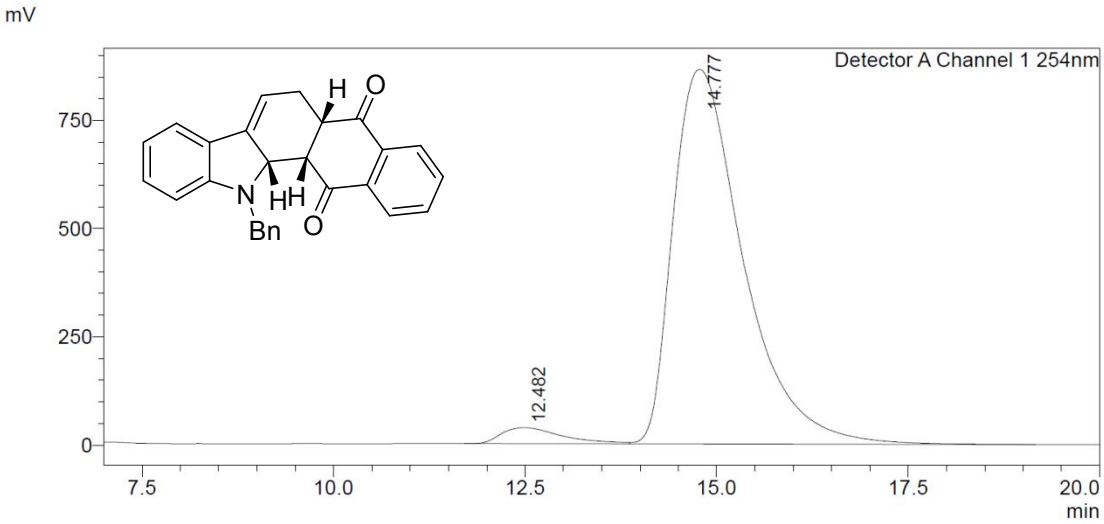


Figure S115. HPLC spectrum of 3a at a minimum 1 mmol scale



Peak#	Ret. Time	Area	Height	Conc.	Area%
1	12.482	2040286	37118	3.567	3.567
2	14.777	55155904	864956	96.433	96.433
Total		57196190	902073		100.000