Supporting Information

Diversity-Oriented Synthesis of Indole-Fused Scaffolds and Bis(indolyl)methane from *Tosyl*-Protected Tryptamine

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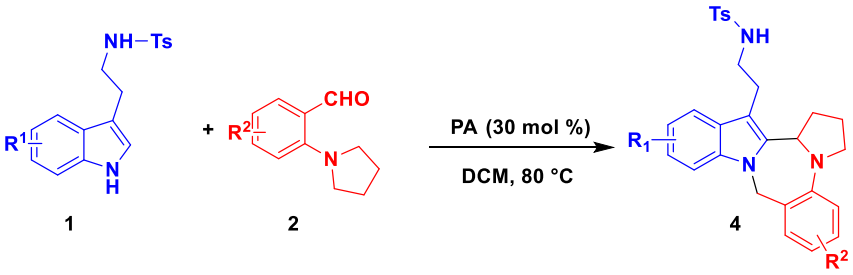
1. General Information

Unless otherwise noted, all reagents and solvents were purchased from the commercial sources (from Adamas-beta) and used as received. Thin layer chromatography (TLC) was used to monitor the reaction on Merck 60 F254 precoated silica gel plate (0.2 mm thickness). TLC spots were visualized by UV-light irradiation on Spectroline Model ENF-24061/F 254 nm. The products were purified by flash column chromatography (200-300 mesh silica gel) eluted with the gradient of petroleum ether and ethyl acetate. Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on a Bruker 500 MHz or 400 MHz NMR spectrometer ($CDCl_3$, DMSO-d_6 or Methanol-d_4 solvent). The chemical shifts were reported in parts per million (ppm), downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ 7.26, singlet), dimethyl sulfoxide-d_6 (δ 2.54, singlet) or methanol-d_4 (δ 4.87, singlet). Multiplicities were afforded as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublets of doublet) or m (multiplets). The number of protons for a given resonance is indicated by nH. Coupling constants were reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) was referenced to the appropriate residual solvent peak. High resolution mass spectral analysis (HRMS) was performed on Waters XEVO G2 Q-TOF. The *ortho*-substituted benzaldehydes were prepared according to the literature.[1]

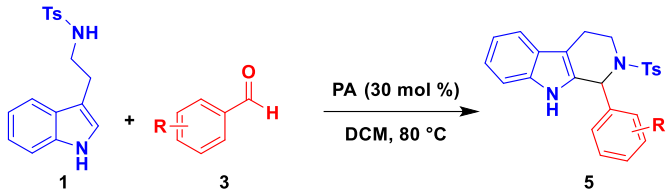
2. General Procedure

2.1 General Procedure for Construction of Indole-1,2-fused 1,4-benzodiazepines 4



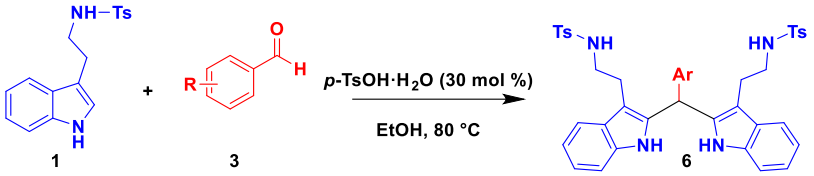
A sealed tube was charged with *tosyl*-protected tryptamine **1** (0.12 mmol, 1.2 equiv.), *N*-alkyl *o*-aminobenzaldehydes **2** (0.1 mmol, 1.0 equiv.), PA (30 mol%, 0.3 equiv.), and DCM (1.0 mL). The mixture was stirred at 80 °C in oil bath. Upon completion of the reaction as indicated by TLC analysis, the mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether, 1:6) to afford the desired indole-1,2-fused 1,4-benzodiazepines **4a**–**4h**.

2.2 General Procedure for Construction of Tetrahydro-*β*-carbolines 5



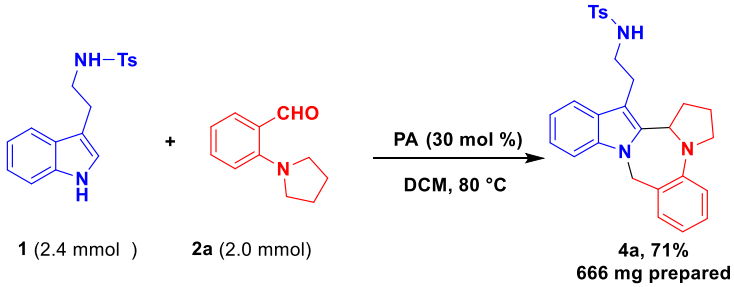
A sealed tube was charged with *tosyl*-protected tryptamine **1** (0.12 mmol, 1.2 equiv.), benzaldehydes **3** (0.1 mmol, 1.0 equiv.), PA (30 mol%, 0.3 equiv.), and DCM (1.0 mL). The mixture was stirred at 80 ℃ in oil bath. Upon completion of the reaction as indicated by TLC analysis, the mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether, 1:30) to afford the desired tetrahydro-*β*-carbolines **5a**–**5m**.

2.3 General Procedure for Construction of 2,2'-Bis(indolyl)methanes 6



A sealed tube was charged with *tosyl*-protected tryptamine **1** (0.22 mmol, 2.2 equiv.), benzaldehydes **3** (0.1 mmol, 1.0 equiv.), *p*-TsOH·H_2O (30 mol%, 0.3 equiv.), and EtOH (1.0 mL). The mixture was stirred at 80 ℃ in oil bath. Upon completion of the reaction as indicated by TLC analysis, the mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether, 1:12) to afford the desired 2,2'-bis(indolyl)methanes **6a**–**6f**.

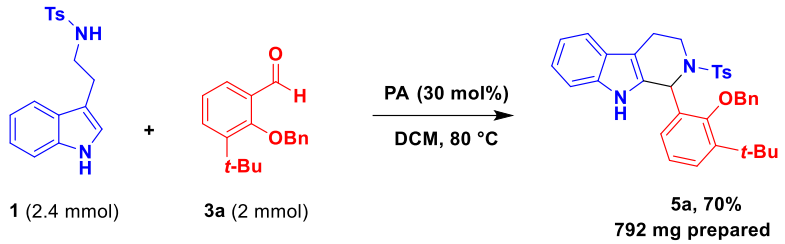
2.4 Large-scale Synthesis of Product 4a



A round-bottom flask was charged with *tosyl*-protected tryptamine **1** (2.4 mmol, 1.2 equiv.), *N*-alkyl *o*-aminobenzaldehyde **2a** (2.0 mmol, 1.0 equiv.), and PA (30 mol%, 0.3 equiv.) in 20.0 mL of DCM. The mixture was stirred at 80 ℃ in oil bath. Upon completion of the reaction as indicated by TLC analysis, the mixture was concentrated in vacuum and the residue was directly purified by flash

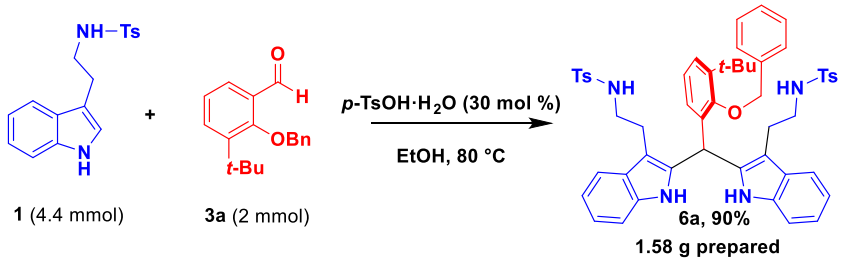
column chromatography on silica gel (ethyl acetate: petroleum ether, 1:6) to give the desired product **4a** in 71% yield.

2.5 Large-scale Synthesis of Product 5a



A round-bottom flask was charged with *tosyl*-protected tryptamine **1** (2.4 mmol, 1.2 equiv.), benzaldehydes **3a** (2.0 mmol, 1.0 equiv.), and PA (30 mol%, 0.3 equiv.) in 20.0 mL of DCM. The mixture was stirred at 80 ℃ in oil bath. Upon completion of the reaction as indicated by TLC analysis, the mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether, 1:30) to give the desired product **5a** in 70% yield.

2.6 Large-scale Synthesis of Product 6a

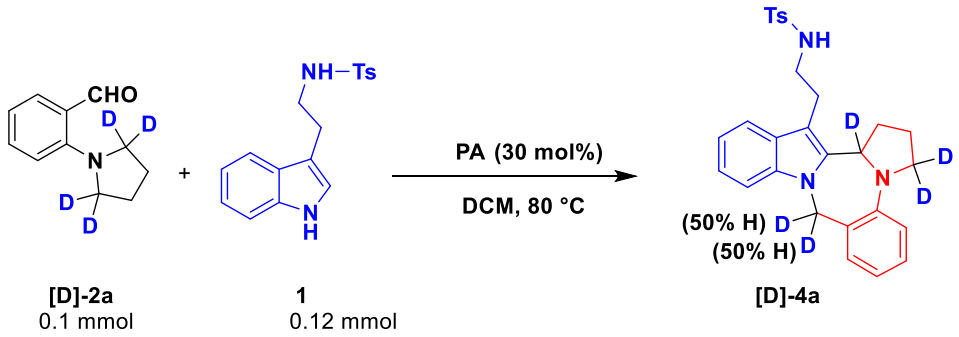


A round-bottom flask was charged with *tosyl*-protected tryptamine **1** (4.4 mmol, 2.2 equiv.), benzaldehydes **3a** (2.0 mmol, 1.0 equiv.), and *p*-TsOH·H_2O (30 mol%, 0.3 equiv.) in 20.0 mL of EtOH. The mixture was stirred at 80 ℃ in oil bath. Upon completion of the reaction as indicated by TLC analysis, the mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether, 1:12) to give the desired product **6a** in 90% yield.

2.7 Deuterium labeling experiments

A sealed tube was charged with *tosyl*-protected tryptamine **1** (0.12 mmol, 1.2 equiv.), *N*-alkyl o-aminobenzaldehyde **[D]-2a** (0.1 mmol, 1.0 equiv.), PA (30 mol%, 0.3 equiv.), and DCM (1.0 mL). The mixture was stirred at 80 °C in oil bath. Upon completion of the reaction as indicated by TLC analysis, the mixture was concentrated in vacuum and the residue was directly purified by flash column

chromatography on silica gel (eluent: ethyl acetate/petroleum ether, 1:6) to afford the desired indole-1,2-fused 1,4-benzodiazepine **[D]-4a** in 68% yield. The deuterated ratio was measured by ^{1}H NMR.

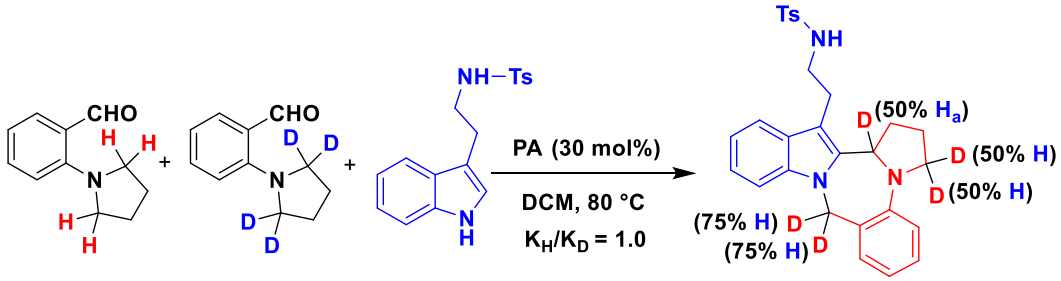


[D]-2a
0.1 mmol

1
0.12 mmol

[D]-4a

A sealed tube was charged with *tosyl*-protected tryptamine **1** (0.1 mmol, 1.2 equiv.), *N*-alkyl o-aminobenzaldehyde **2a** (0.1 mmol, 1.0 equiv.), *N*-alkyl o-aminobenzaldehyde **[D]-2a** (0.1 mmol, 1.0 equiv.), PA (30 mol%, 0.3 equiv.), and DCM (1.0 mL). The mixture was stirred at 80 °C in oil bath. Upon completion of the reaction as indicated by TLC analysis, the mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether, 1:6) to afford the desired indole-1,2-fused 1,4-benzodiazepines **4a** and **[D]-4a** in 64% yield. The ratio of **4a** and **[D]-4a** was measured by ^{1}H NMR.

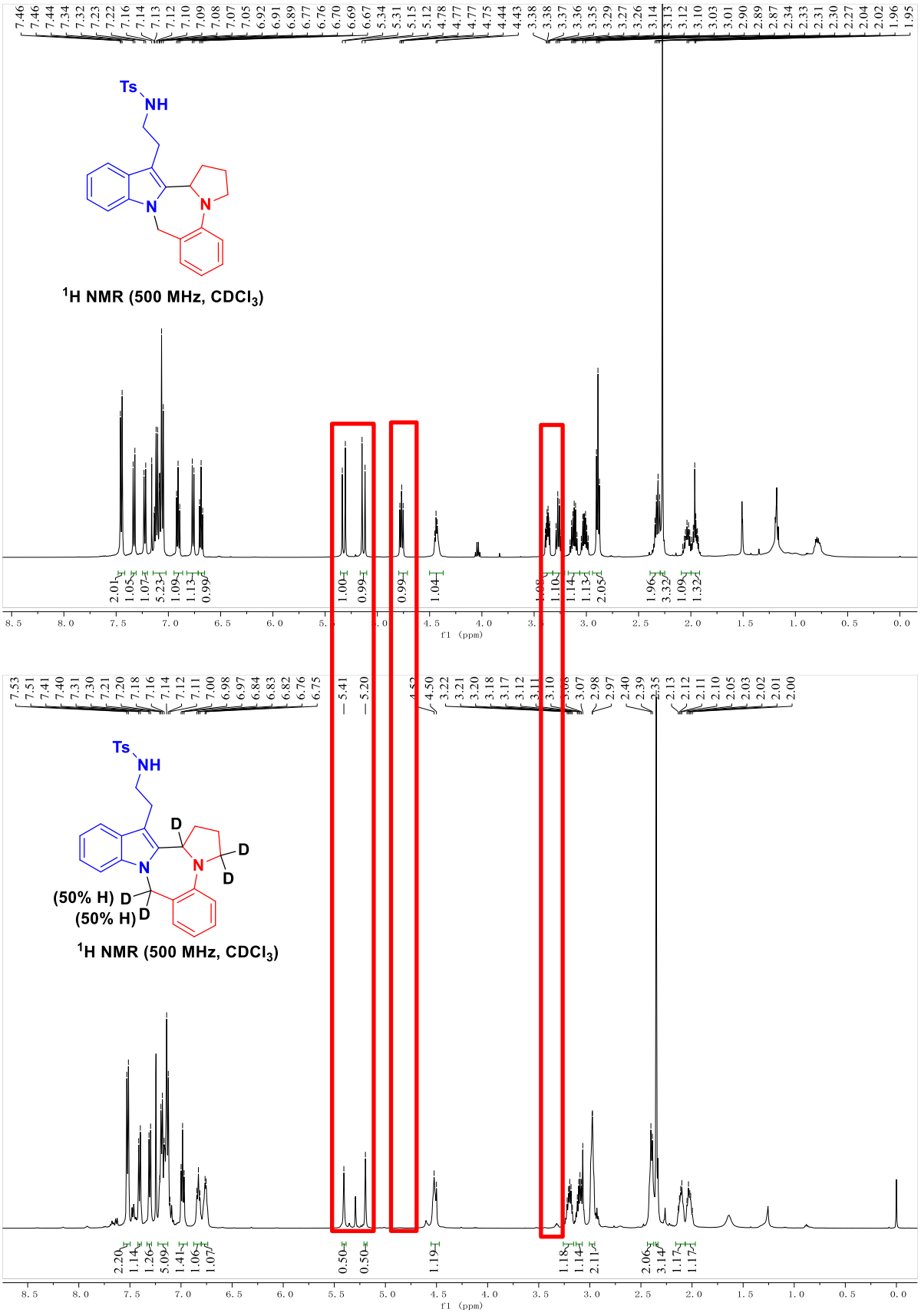


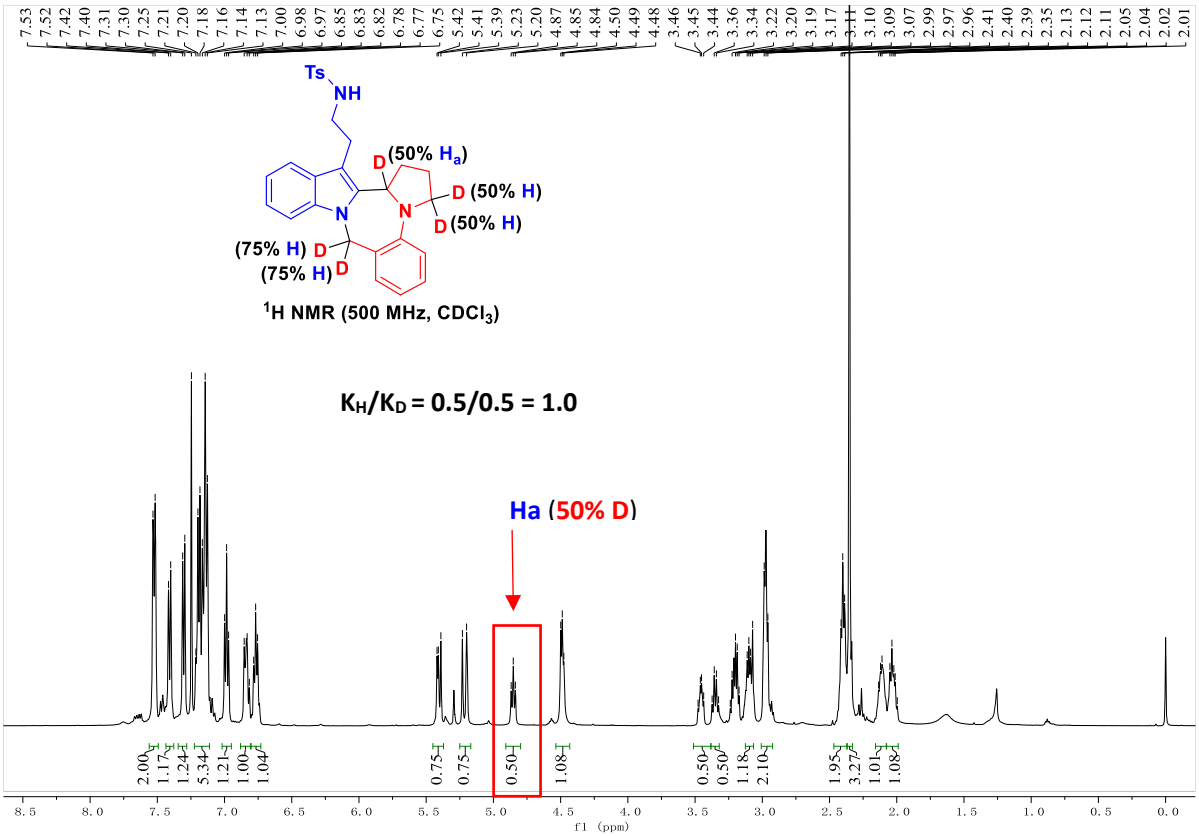
2a
0.1 mmol

[D]-2a
0.1 mmol

1
0.1 mmol

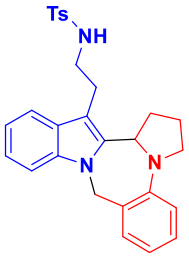
[H/D]-4a


Ts
NH
N
N
^{1}H NMR (500 MHz, CDCl$_3$)
Ts
NH
D
D
D
N
N
(50% H) D
(50% H) D
^{1}H NMR (500 MHz, CDCl$_3$)
f1 (ppm)



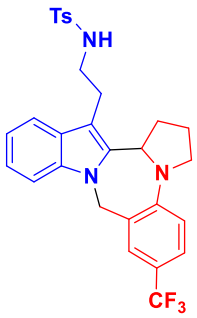
3. Characterization of Products

4-methyl-N-(2-(1,2,3,15b-tetrahydro-9H-benzo[5,6]pyrrolo[2',1':3,4][1,4]diazepino[1,2-a]indol-15-yl)ethyl)benzenesulfonamide (4a).



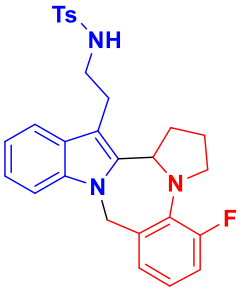
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 6:1) afforded the product as a yellow solid (40.0 mg, 85% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.61 – 7.50 (m, 2H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.35 – 7.30 (m, 1H), 7.25 – 7.12 (m, 5H), 7.01 (s, 1H), 6.86 (dd, *J* = 8.1, 1.1 Hz, 1H), 6.79 (td, *J* = 7.4, 1.1 Hz, 1H), 5.42 (d, *J* = 14.6 Hz, 1H), 5.23 (d, *J* = 14.5 Hz, 1H), 4.87 (dd, *J* = 8.8, 7.0 Hz, 1H), 4.53 (d, *J* = 5.8 Hz, 1H), 3.50 – 3.44 (m, 1H), 3.37 (d, *J* = 8.0 Hz, 1H), 3.22 (dt, *J* = 13.5, 6.8 Hz, 1H), 3.15 – 3.07 (m, 1H), 2.99 (t, *J* = 7.1 Hz, 2H), 2.58 – 2.39 (m, 2H), 2.37 (s, 3H), 2.20 – 2.10 (m, 1H), 2.07 – 1.99 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.2, 143.2, 136.7, 135.6, 135.5, 129.6, 129.3, 128.7, 127.3, 127.0, 127.0, 121.5, 119.7, 119.2, 118.1, 116.6, 108.8, 106.7, 59.9, 49.8, 47.0, 43.5, 31.8, 25.0, 23.0, 21.5. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{28}H_{30}N_3O_2S^+$ 472.2053; found: 472.2050.

4-methyl-N-(2-(7-(trifluoromethyl)-1,2,3,15b-tetrahydro-9H-benzo[5,6]pyrrolo[2',1':3,4][1,4]diazepi no[1,2-a]indol-15-yl)ethyl)benzenesulfonamide (4b).



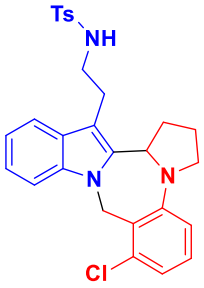
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 6:1) afforded the product as a yellow solid (43.6 mg, 81% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 2H), 7.40 (d, *J* = 8.3 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 2.2 Hz, 1H), 7.25 – 7.20 (m, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.63 (d, *J* = 8.6 Hz, 1H), 5.68 (d, *J* = 15.5 Hz, 1H), 5.48 (dd, *J* = 8.3, 6.5 Hz, 1H), 5.08 (d, *J* = 15.6 Hz, 1H), 4.55 – 4.44 (m, 1H), 3.58 (dt, *J* = 9.2, 7.0 Hz, 1H), 3.40 (td, *J* = 8.4, 5.0 Hz, 1H), 3.24 (dt, *J* = 10.6, 5.7 Hz, 1H), 3.15 – 3.06 (m, 3H), 2.81 – 2.71 (m, 1H), 2.42 (dt, *J* = 12.2, 6.1 Hz, 1H), 2.36 (s, 3H), 2.27 – 2.21 (m, 1H), 2.15 – 2.07 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.3, 143.3, 136.6, 135.5, 134.7, 129.6, 127.3, 126.9, 126.5 (d, *J* = 7.3, 3.5 Hz), 126.1 (d, *J* = 7.2, 3.6 Hz), 126.0, 122.3, 122.0, 119.5, 118.5, 118.5 (d, *J* = 65.0, 32.3 Hz), 114.6, 108.7, 106.7, 58.0, 50.1, 47.0, 43.6, 30.2, 25.0, 24.1, 21.5. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{29}H_{29}F_3N_3O_2S^+$ 540.1927; found: 540.1923.

N-(2-(5-fluoro-1,2,3,15b-tetrahydro-9H-benzo[5,6]pyrrolo[2',1':3,4][1,4]diazepino[1,2-a]indol-15-yl) ethyl)-4-methylbenzenesulfonamide (4c).



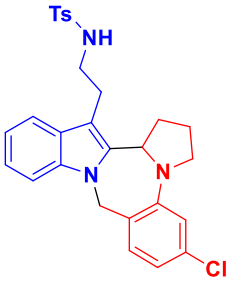
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 6:1) afforded the product as a yellow solid (42.8 mg, 83% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.68 – 7.56 (m, 2H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.24 – 7.14 (m, 3H), 7.05 – 6.95 (m, 3H), 6.86 (td, *J* = 7.9, 4.8 Hz, 1H), 5.33 (d, *J* = 13.8 Hz, 1H), 5.18 – 5.04 (m, 1H), 4.69 (dd, *J* = 9.1, 6.5 Hz, 1H), 4.51 (t, *J* = 6.3 Hz, 1H), 3.81 – 3.73 (m, 1H), 3.58 – 3.42 (m, 1H), 3.28 – 3.12 (m, 2H), 2.88 (t, *J* = 7.2 Hz, 2H), 2.40 (s, 3H), 2.32 (q, *J* = 6.7, 5.8 Hz, 1H), 2.08 – 1.96 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.2 (d, *J* = 247.2 Hz), 143.3, 136.9, 136.2 (d, *J* = 4.3 Hz), 136.0, 135.1, 134.1 (d, *J* = 10.1 Hz), 129.7, 127.4, 127.0, 123.7 (d, *J* = 3.0 Hz), 123.4 (d, *J* = 8.1 Hz), 121.5, 119.4, 118.1, 116.9 (d, *J* = 22.0 Hz), 108.7, 108.3, 59., 50.7, 50.6, 46.4, 46.4, 43.3, 33.7, 24.9, 23.5, 21.5. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{28}H_{29}FN_3O_2S^+$ 490.1959; found: 490.1957.

N-(2-(7-chloro-1,2,3,3a,8,14b-hexahydrobenzo[5,6]cyclopenta[3,4]azepino[1,2-a]indol-14-yl)ethyl)-4 -methylbenzenesulfonamide (4d).



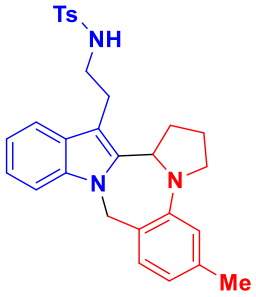
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 6:1) afforded the product as a yellow solid (40.2 mg, 80% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.64 – 7.51 (m, 3H), 7.29 (d, *J* = 7.9 Hz, 1H), 7.25 – 7.15 (m, 3H), 7.11 (t, *J* = 8.1 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 8.1 Hz, 1H), 5.70 (d, *J* = 14.5 Hz, 1H), 5.52 (d, *J* = 14.5 Hz, 1H), 4.71 (dd, *J* = 9.6, 6.6 Hz, 1H), 4.45 (q, *J* = 5.5, 4.7 Hz, 1H), 3.42 (td, *J* = 8.3, 4.1 Hz, 1H), 3.34 (q, *J* = 8.1 Hz, 1H), 3.26 – 3.05 (m, 2H), 2.95 (t, *J* = 7.1 Hz, 2H), 2.50 – 2.41 (m, 1H), 2.37 (s, 3H), 2.32 – 2.24 (m, 1H), 2.17 – 1.99 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.0, 143.3, 136.7, 135.8, 134.7, 132.9, 129.6, 129.3, 127.1, 127.0, 126.8, 121.7, 121.5, 119.3, 117.9, 115.8, 109.4, 107.2, 60.8, 50.1, 43.3, 42.0, 32.4, 25.0, 22.6, 21.5. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{28}H_{29}ClN_3O_2S^+$ 506.1664; found: 506.1663.

N-(2-(6-chloro-1,2,3,15b-tetrahydro-9H-benzo[5,6]pyrrolo[2',1':3,4][1,4]diazepino[1,2-a]indol-15-yl) ethyl)-4-methylbenzenesulfonamide (4e).



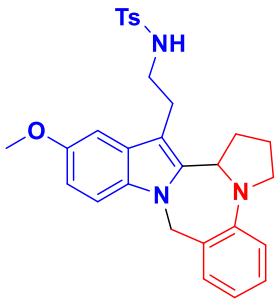
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 6:1) afforded the product as a yellow solid (41.0 mg, 82% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.65 – 7.57 (m, 2H), 7.41 (d, *J* = 8.3 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.20 (t, *J* = 7.7 Hz, 3H), 7.14 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.01 (d, *J* = 7.9 Hz, 1H), 6.89 (s, 1H), 5.23 (d, *J* = 13.9 Hz, 1H), 5.01 (d, *J* = 14.0 Hz, 1H), 4.92 (dd, *J* = 9.1, 6.1 Hz, 1H), 4.36 (t, *J* = 6.1 Hz, 1H), 3.95 (td, *J* = 8.7, 8.3, 3.4 Hz, 1H), 3.25 – 3.18 (m, 1H), 3.13 (d, *J* = 6.7 Hz, 2H), 2.85 (t, *J* = 7.1 Hz, 2H), 2.39 (s, 3H), 2.33 – 2.26 (m, 1H), 2.15 – 2.00 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.3, 138.6, 136.8, 136.4, 135.4, 133.8, 130.5, 129.7, 127.6, 127.1, 126.8, 125.1, 121.6, 119.4, 118.2, 109.3, 108.6, 58.2, 51.2, 46.5, 43.4, 35.5, 24.9, 24.7, 21.5. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{28}H_{29}ClN_3O_2S^+$ 506.1664; found: 506.1666.

4-methyl-N-(2-(6-methyl-1,2,3,15b-tetrahydro-9H-benzo[5,6]pyrrolo[2',1':3,4][1,4]diazepino[1,2-a]i ndol-15-yl)ethyl)benzenesulfonamide (4f).



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 6:1) afforded the product as a yellow solid (40.2. mg, 83% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.32 (d, *J* = 7.9 Hz, 1H), 7.24 – 7.10 (m, 3H), 7.06 (d, *J* = 7.5 Hz, 1H), 7.00 (t, *J* = 7.4 Hz, 1H), 6.69 (d, *J* = 1.6 Hz, 1H), 6.60 (dd, *J* = 7.6, 1.6 Hz, 1H), 5.38 (d, *J* = 14.5 Hz, 1H), 5.20 (d, *J* = 14.5 Hz, 1H), 4.84 (dd, *J* = 8.8, 6.9 Hz, 1H), 4.66 – 4.42 (m, 1H), 3.53 – 3.42 (m, 1H), 3.36 (q, *J* = 8.1 Hz, 1H), 3.22 (dt, *J* = 13.4, 6.7 Hz, 1H), 3.11 (dd, *J* = 12.8, 6.4 Hz, 1H), 2.98 (t, *J* = 7.1 Hz, 2H), 2.52 – 2.31 (m, 5H), 2.30 (s, 3H), 2.18 – 2.09 (m, 1H), 2.05 (td, *J* = 7.8, 4.1 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.1, 143.2, 139.1, 136.7, 135.6, 135.6, 129.6, 128.6, 127.3, 127.0, 124.2, 121.4, 120.4, 119.1, 118.0, 117.4, 108.8, 106.6, 59.9, 49.8, 46.7, 43.5, 31.8, 25.0, 23.0, 21.5. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{29}H_{32}N_3O_2S^+$ 486.2210; found: 486.2213.

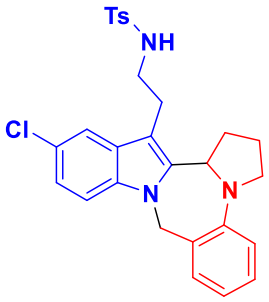
4-methyl-N-(2-(13-methoxy-1,2,3,15b-tetrahydro-9H-benzo[5,6]pyrrolo[2',1':3,4][1,4]diazepino[1,2-a]indol-15-yl)ethyl)-benzenesulfonamide (4g).



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 6:1) afforded the product **4g** as a yellow solid (36.3 mg, 71% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.46 (m, 2H), 7.30 (dd, *J* = 8.9, 1.4 Hz, 1H), 7.20 (t, *J* = 7.7 Hz, 1H), 7.13 (dd, *J* = 11.4, 7.7 Hz, 3H), 6.88 – 6.82 (m, 2H), 6.80 – 6.74 (m, 2H), 5.34 (d, *J* = 14.4 Hz, 1H), 5.18 (d, *J* = 14.5 Hz, 1H), 4.79 (dd, *J* = 9.0, 6.8 Hz, 1H), 4.49 (t, *J* = 6.2 Hz, 1H), 3.77 (d, *J* = 1.4 Hz, 3H), 3.44 (td, *J* = 8.5, 4.4 Hz, 1H), 3.34 (q, *J* = 8.1 Hz, 1H), 3.18 (dt, *J* = 13.1, 6.6 Hz, 1H), 3.11 – 3.03 (m, 1H), 2.94 (t, *J* = 7.0 Hz, 2H), 2.35 (s, 5H), 2.16 – 2.07 (m, 1H), 2.06 – 1.98 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 153.9, 147.3, 143.2, 136.6, 136.1, 131.0, 129.5, 129.2, 128.6, 127.6, 127.3, 127.0, 119.9, 116.8, 111.5, 109.6, 106.3, 100.1, 60.0, 56.0, 49.8, 47.2, 43.3, 31.9, 25.0, 22.9, 21.5. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{29}H_{32}N_3O_3S^+$ 502.2158; found: 502.2156.

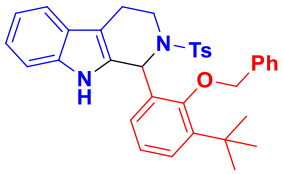
4-methyl-N-(2-(13-chloro-1,2,3,15b-tetrahydro-9H-benzo[5,6]pyrrolo[2',1':3,4][1,4]diazepino[1,2-a]indol-15-yl)ethyl)-benzenesulfonamide (4h).



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 6:1) afforded the product **4h** as a yellow solid (37.5 mg, 74% yield).

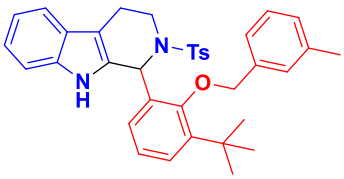
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.46 (m, 2H), 7.30 (d, *J* = 8.7 Hz, 1H), 7.25 – 7.13 (m, 5H), 7.11 (dt, *J* = 8.7, 1.8 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.79 (t, *J* = 7.4 Hz, 1H), 5.35 (d, *J* = 14.5 Hz, 1H), 5.19 (d, *J* = 14.5 Hz, 1H), 4.81 (t, *J* = 7.9 Hz, 1H), 4.45 (t, *J* = 6.2 Hz, 1H), 3.46 (td, *J* = 8.4, 4.3 Hz, 1H), 3.35 (q, *J* = 8.1 Hz, 1H), 3.23 – 3.11 (m, 1H), 3.09 – 3.01 (m, 1H), 2.90 (t, *J* = 7.2 Hz, 2H), 2.48 – 2.39 (m, 1H), 2.37 (s, 4H), 2.16 – 1.98 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 147.2, 143.4, 137.1, 136.4, 134.0, 129.7, 129.5, 128.7, 128.3, 127.0, 126.9, 124.8, 121.7, 120.1, 117.5, 116.9, 109.8, 106.4, 59.9, 49.8, 47.2, 43.1, 31.9, 24.8, 22.9, 21.5. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{28}H_{29}ClN_3O_2S^+$ 506.1664; found: 506.1667.

1-(2-(benzyloxy)-3-(tert-butyl)phenyl)-2-tosyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (5a).



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 30:1) afforded the product as a white solid (40.3 mg, 73% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.00 (s, 1H), 7.64 – 7.57 (m, 4H), 7.44 – 7.36 (m, 4H), 7.35 – 7.30 (m, 2H), 7.20 – 7.16 (m, 1H), 7.14 – 7.06 (m, 4H), 7.04 – 6.96 (m, 1H), 6.66 (d, *J* = 1.6 Hz, 1H), 5.36 (d, *J* = 12.1 Hz, 1H), 5.28 (d, *J* = 12.1 Hz, 1H), 4.46 – 4.36 (m,1H), 3.69 (d, *J* = 1.5 Hz, 1H), 2.66 – 2.59 (m, 1H), 2.50 – 2.42 (m, 1H), 2.35 (s, 3H), 1.55 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.9, 143.9, 143.4, 137.9, 136.8, 135.8, 135.6, 132.3, 129.8, 128.9,128.3, 127.6, 127.3, 126.7, 126.0, 126.0, 125.1, 125.0, 121.9, 119.2, 118.0, 111.0, 107.4, 52.1, 52.1, 42.7, 35.5, 31.7, 21.5, 20.1. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{35}H_{37}N_2O_3S^+$ 565.2519; found: 565.2517.

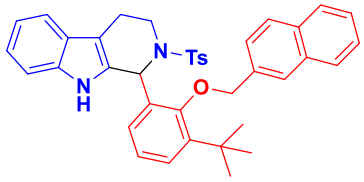
1-(3-(tert-butyl)-2-((3-methylbenzyl)oxy)phenyl)-2-tosyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (5b).



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 30:1) afforded the product as a white solid (39.8 mg, 70% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.96 (s, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.33 (q, *J* = 7.7 Hz, 3H), 7.25 – 7.17 (m, 3H), 7.10 (d, *J* = 8.1 Hz, 2H), 7.06 – 6.98 (m, 4H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.59 (s, 1H), 5.28 – 5.13 (m, 2H), 4.33 (dd, *J* = 14.2, 5.3 Hz, 1H), 3.66 – 3.55 (m,

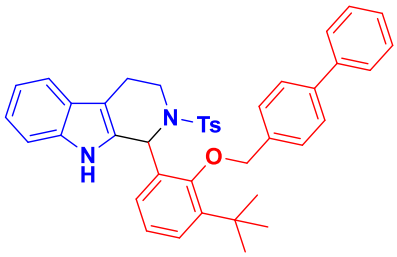
1H), 2.53 (dd, *J* = 15.5, 3.7 Hz, 1H), 2.39 – 2.32 (m, 1H), 2.29 (s, 3H), 2.27 (s, 3H), 1.47 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.0., 143.9, 143.4, 138.6, 138.1, 136.9, 135.9, 135.7, 132.5, 129.8, 129.1, 128.8, 128.1, 127.6, 126.8, 126.0, 125.1, 125.0, 124.4, 121.9, 119.2, 118.0, 110.9, 107.2, 52.2, 42.6, 35.5, 31.8, 21.6, 21.5, 20.1. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{36}H_{39}N_2O_3S^+$ 579.2676; found: 579.2672.

1-(3-(tert-butyl)-2-(naphthalen-2-ylmethoxy)phenyl)-2-tosyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (5c).



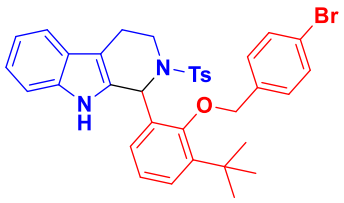
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 30:1) afforded the product as a white solid (42.0 mg, 68% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.06 (s, 1H), 7.94 – 7.84 (m, 2H), 7.79 (dd, *J* = 7.3, 2.0 Hz, 1H), 7.72 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.54 – 7.46 (m, 2H), 7.41 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.36 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.16 (d, *J* = 8.1 Hz, 1H), 7.09 (dt, *J* = 17.4, 8.0 Hz, 2H), 6.98 (dd, *J* = 13.4, 7.8 Hz, 3H), 6.73 (s, 1H), 5.55 – 5.41 (m, 2H), 4.46 – 4.35 (m, 1H), 3.76 – 3.62 (m, 1H), 2.65 – 2.57 (m, 1H), 2.45 – 2.35 (m, 1H), 2.28 (s, 3H), 1.59 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.1, 144.0, 143.3, 138.0, 136.0, 135.7, 134.4, 133.3, 133.2, 132.3, 129.8, 128.9, 128.2, 127.8, 127.7, 126.7, 126.5, 126.4, 126.4, 126.1, 125.2, 125.1, 125.0, 121.9, 119.2, 118.0, 111.0, 107.4, 52.3, 42.6, 35.6, 31.8, 21.5, 20.1. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{39}H_{39}N_2O_3S^+$ 615.2676; found: 615.2673.

(2-([1,1'-biphenyl]-4-ylmethoxy)-3-(tert-butyl)phenyl)-2-tosyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (5d).



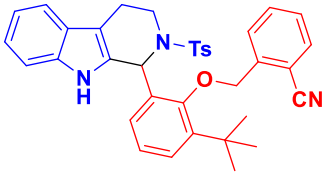
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 30:1) afforded the product as a white solid (46.0 mg, 72% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.00 (s, 1H), 7.67 – 7.60 (m, 8H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.40 – 7.33 (m, 4H), 7.20 (d, *J* = 8.1 Hz, 1H), 7.09 (t, *J* = 7.7 Hz, 4H), 7.01 (td, *J* = 7.5, 7.0, 1.0 Hz, 1H), 6.68 (d, *J* = 1.6 Hz, 1H), 5.42 (d, *J* = 12.2 Hz, 1H), 5.32 (d, *J* = 12.2 Hz, 1H), 4.47 – 4.37 (m, 1H), 3.74 – 3.62 (m, 1H), 2.67 – 2.59 (m, 1H), 2.51 – 2.42 (m, 1H), 2.31 (s, 3H), 1.57 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.9, 143.9, 143.4, 141.2, 140.6, 138.0, 135.9, 135.8, 135.7, 132.4, 129.8, 128.9, 127.8, 127.7, 127.6, 127.5, 127.2, 126.8, 126.1, 125.2, 125.1, 121.9, 119.3, 118.1, 111.1, 107.5, 52.1, 42.7, 35.5, 31.8, 21.5, 20.2. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{41}H_{41}N_2O_3S^+$ 641.2832; found: 641.2833.

1-(2-((4-bromobenzyl)oxy)-3-(tert-butyl)phenyl)-2-tosyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (5e).



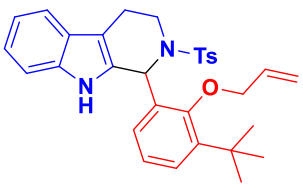
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 30:1) afforded the product as a white solid (45.2 mg, 70% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.81 (s, 1H), 7.59 – 7.51 (m, 4H), 7.48 – 7.44 (m, 2H), 7.36 – 7.31 (m, 3H), 7.19 (s, 1H), 7.15 – 7.06 (m, 4H), 7.05 – 6.99 (m, 1H), 6.59 (d, *J* = 1.7 Hz, 1H), 5.29 (s, 1H), 5.23 (d, *J* = 12.3 Hz, 1H), 4.42 – 4.32 (m, 1H), 3.72 – 3.61 (m, 1H), 2.67 – 2.60 (m, 1H), 2.51 – 2.43 (m, 1H), 2.36 (s, 3H), 1.53 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.8, 143.9, 143.5, 137.9, 135.9, 135.8, 135.7, 132.1, 132.1, 129.8, 129.0, 127.7, 126.7, 126.1, 125.3, 125.2, 122.3, 122.1, 119.4, 118.1, 111.0, 107.6, 76.5, 52.0, 42.6, 35.5, 31.7, 21.5, 20.2. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{35}H_{36}BrN_2O_3S^+$ 643.1625; found: 643.1628.

2-((2-(tert-butyl)-6-(2-tosyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indol-1-yl)phenoxy)methyl)benzonitrile (5f).



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 30:1) afforded the product as a white solid (40.5 mg, 69% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.73 (s, 1H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.73 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.62 (td, *J* = 7.8, 1.4 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.45 (td, *J* = 7.6, 1.2 Hz, 1H), 7.36 (dt, *J* = 7.9, 1.5 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.22 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.16 – 7.10 (m, 1H), 7.11 – 7.00 (m, 4H), 6.64 (d, *J* = 1.6 Hz, 1H), 5.57 – 5.43 (m, 2H), 4.30 – 4.14 (m, 1H), 3.70 – 3.48 (m, 1H), 2.70 – 2.60 (m, 1H), 2.59 – 2.49 (m, 1H), 2.33 (s, 3H), 1.51 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.4, 144.1, 143.3, 140.6, 138.0, 136.0, 135.1, 133.4, 133.3, 131.7, 129.6, 128.5, 128.4, 128.1, 126.9, 126.3, 126.1, 125.3, 122.2, 119.5, 118.1, 117.7, 111.3, 110.6, 108.3, 75.2, 51.7, 41.8, 35.5, 31.7, 21.5, 20.3. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{36}H_{36}N_3O_3S^+$ 590.2472; found: 590.2476.

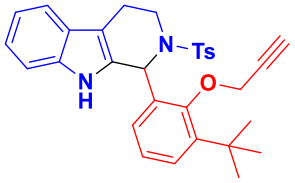
1-(2-(allyloxy)-3-(tert-butyl)phenyl)-2-tosyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (5g).



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 30:1) afforded the product as a white solid (34.5 mg, 68% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.09 (s, 1H), 7.76 – 7.68 (m, 2H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.30 (td, *J* = 7.7, 1.6 Hz, 2H), 7.25 (s, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.14 – 7.08 (m, 1H), 7.03 (t, *J* = 7.8 Hz, 2H), 6.58 (d, *J* = 1.6 Hz, 1H), 6.32 – 6.17 (m, 1H), 5.60 (dt, *J* = 17.2,

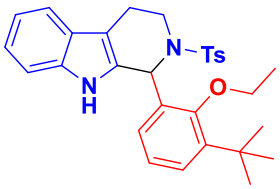
1.6 Hz, 1H), 5.37 (dd, *J* = 10.6, 1.5 Hz, 1H), 4.90 – 4.81 (m, 1H), 4.75 – 4.66 (m, 1H), 4.41 – 4.30 (m, 1H), 3.70 – 3.59 (m, 1H), 2.69 – 2.59 (m, 1H), 2.57 – 2.47 (m, 1H), 2.37 (s, 3H), 1.49 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.9, 143.9, 143.4, 138.0, 135.6, 135.6, 133.4, 132.5, 129.7, 127.5, 126.9, 126.1, 125.0, 124.9, 121.9, 119.2, 118.1, 118.0, 111.0, 107.5, 75.9, 52.1, 42.5, 35.4, 31.5, 21.5, 20.3. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{31}H_{35}N_2O_3S^+$ 515.2363; found: 515.2365.

1-(3-(tert-butyl)-2-(prop-2-yn-1-yloxy)phenyl)-2-tosyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (5h).



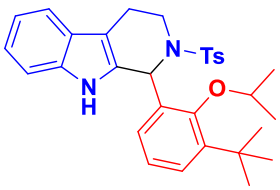
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 30:1) afforded the product as a white solid (32.5 mg, 63% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.97 (s, 1H), 7.77 (d, *J* = 7.9 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 7.26 – 7.21 (m, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 7.09 (t, *J* = 7.6 Hz, 1H), 7.02 (dt, *J* = 14.9, 7.6 Hz, 2H), 6.64 (s, 1H), 4.98 – 4.82 (m, 2H), 4.34 (dd, *J* = 14.2, 5.3 Hz, 1H), 3.72 – 3.62 (m, 1H), 2.69 – 2.57 (m, 2H), 2.53 – 2.43 (m, 1H), 2.34 (s, 3H), 1. 47 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.7, 144.0, 143.4, 137.9, 135.9, 135.8, 132.2, 129.7, 127.4, 126.9, 126.1, 125.5, 125.3, 122.0, 119.2, 118.0, 111.1, 107.5, 78.9, 76.4, 62.8, 52.0, 42.5, 35.3, 31.5, 21.5, 20.2. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{31}H_{33}N_2O_3S^+$ 513.2206; found: 513.2207.

1-(3-(tert-butyl)-2-ethoxyphenyl)-2-tosyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (5i).



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 30:1) afforded the product as a white solid (33.2 mg, 66% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.19 (s, 1H), 7.79 – 7.70 (m, 2H), 7.38 (d, *J* = 7.9 Hz, 1H), 7.30 – 7.26 (m, 3H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.15 – 7.09 (m, 1H), 7.07 – 6.97 (m, 2H), 6.57 (s, 1H), 4.47 – 4.33 (m, 2H), 4.27 – 4.16 (m, 1H), 3.69 – 3.57 (m, 1H), 2.71 – 2.57 (m, 2H), 2.38 (s, 3H), 1.61 (t, *J* = 7.0 Hz, 3H), 1.49 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.1, 143.8, 143.4, 138.0, 135.7, 135.5, 132.6, 129.7, 127.6, 126.9, 126.2, 125.0, 124.7, 122.0, 119.3, 118.1, 111.0, 107.6, 70.9, 51.9, 42.4, 35.3, 31.5, 21.5, 20.4, 15.7. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{30}H_{35}N_2O_3S^+$ 503.2363; found: 503.2361.

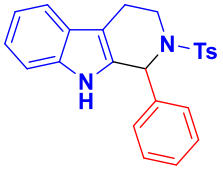
1-(3-(tert-butyl)-2-isopropoxyphenyl)-2-tosyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (5j).



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 30:1) afforded the product

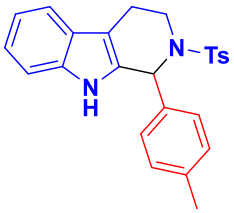
as a white solid (28.0 mg, 54% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.55 (s, 1H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 1H), 7.29 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.24 (s, 1H), 7.23 – 7.18 (m, 3H), 7.13 – 7.07 (m, 1H), 7.04 – 6.94 (m, 2H), 6.69 (s, 1H), 4.88 – 4.74 (m, 1H), 4.41 – 4.30 (m, 1H), 3.58 – 3.44 (m, 1H), 2.64 – 2.54 (m, 2H), 2.36 (s, 3H), 1.51 (d, *J* = 6.2 Hz, 3H), 1.46 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.2, 144.2, 143.3, 138.3, 135.8, 135.5, 132.9, 129.7, 128.3, 127.0, 126.1, 124.1, 124.0, 121.89, 119.2, 118.0, 111.0, 107.7, 76.2, 53.2, 42.3, 35.5, 31.9, 22.7, 21.7, 21.5, 20.5. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{31}H_{37}N_2O_3S^+$ 517.2519; found: 517.2516.

1-phenyl-2-tosyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (5k).



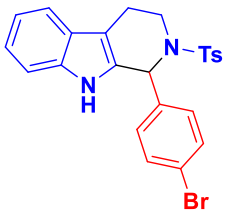
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 30:1) afforded the product as a white solid (32.1 mg, 80% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.62 – 7.53 (m, 2H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.37 – 7.26 (m, 6H), 7.18 (s, 1H), 7.13 – 7.02 (m, 3H), 6.34 (s, 1H), 4.00 (dd, *J* = 14.5, 5.5 Hz, 1H), 3.38 – 3.22 (m, 1H), 2.69 – 2.53 (m, 2H), 2.29 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.2, 139.3, 137.9, 136.1, 130.4, 129.5, 128.7, 128.6, 128.4, 126.8, 126.6, 122.3, 119.6, 118.3, 111.0, 109.9, 55.0, 39.5, 21.4, 20.1. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{24}H_{23}N_2O_2S^+$ 403.1475; found: 403.1472.

1-(p-tolyl)-2-tosyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (5l).



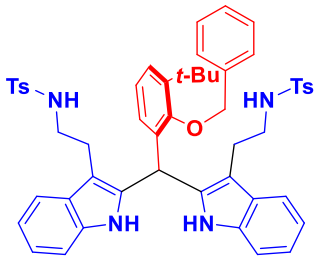
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 30:1) afforded the product as a white solid (32.4 mg, 78% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.62 – 7.57 (m, 2H), 7.44 – 7.40 (m, 1H), 7.28 (d, *J* = 1.3 Hz, 1H), 7.20 – 7.16 (m, 3H), 7.14 – 7.06 (m, 5H), 6.31 (s, 1H), 4.05 – 3.96 (m, 1H), 3.37 – 3.26 (m, 1H), 2.67 – 2.54 (m, 2H), 2.35 (s, 3H), 2.29 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.2, 138.3, 138.0, 136.3, 136.1, 130.6, 129.4, 129.3, 128.6, 126.9, 126.6, 122.3, 119.6, 118.3, 111.0, 109.8, 55.6, 39.4, 21.4, 21.2, 20.2. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{25}H_{25}N_2O_2S^+$ 417.1631; found: 417.1633.

1-(4-bromophenyl)-2-tosyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (5m).



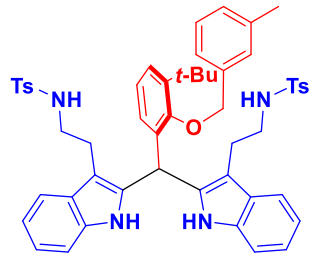
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 30:1) afforded the product as a white solid (39.4 mg, 82% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.57 – 7.51 (m, 2H), 7.41 – 7.34 (m, 3H), 7.24 (s, 1H), 7.18 – 7.12 (m, 3H), 7.10 – 7.03 (m, 3H), 6.25 (s, 1H), 3.97 (dd, *J* = 14.5, 5.6 Hz, 1H), 3.29 – 3.14 (m, 1H), 2.63 – 2.57 (m, 1H), 2.52 (s, 1H), 2.27 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.5, 138.4, 137.7, 136.2, 131.7, 130.3, 129.7, 129.5, 126.8, 126.5, 122.6, 122.5, 119.7, 118.4, 111.1, 110.1, 55.3, 39.5, 21.4, 20.1. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{24}H_{22}BrN_2O_2S^+$ 481.0580; found: 481.0581.

N,N'-((((2-(benzyloxy)-3-(tert-butyl)phenyl)methylene)bis(1H-indole-2,3-diyl))bis(ethane-2,1-diyl))bis(4-methylbenzenesulfonamide) (6a).



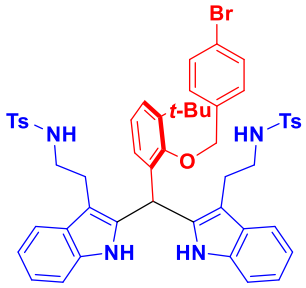
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 12:1) afforded the product as a white solid (81.5. mg, 93% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 5.1 Hz, 2H), 7.39 (dd, *J* = 8.0, 4.4 Hz, 6H), 7.34 – 7.26 (m, 4H), 7.21 (d, *J* = 8.9 Hz, 4H), 7.14 – 7.02 (m, 8H), 6.98 (d, *J* = 6.5 Hz, 2H), 6.38 (s, 1H), 4.72 (s, 2H), 4.52 (t, *J* = 6.4 Hz, 2H), 2.88 – 2.73 (m, 4H), 2.73 – 2.58 (m, 4H), 2.34 (s, 6H), 1.38 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.8, 144.5, 143.0, 137.0, 136.8, 135.1, 135.1, 134.3, 129.6, 128.7, 128.5, 128.1, 127.6, 127.5, 127.0, 126.1, 124.8, 122.0, 120.1, 118.6, 111.3, 109.2, 75.7, 42.8, 35.6, 35.3, 31.2, 25.1, 21.5. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{52}H_{55}N_4O_5S_2^+$ 879.3608; found: 879.3607.

N,N'-((((3-(tert-butyl)-2-((3-methylbenzyl)oxy)phenyl)methylene)bis(1H-indole-2,3-diyl))bis(ethane-2,1-diyl))bis(4-methylbenzenesulfonamide) (6b).



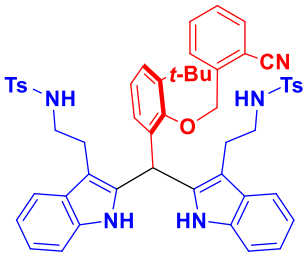
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 12:1) afforded the product as a white solid (72.8. mg, 82% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92 (s, 2H), 7.43 (dd, *J* = 8.4, 1.9 Hz, 6H), 7.34 (dd, *J* = 7.3, 2.3 Hz, 1H), 7.26 – 7.07 (m, 13H), 7.06 – 6.98 (m, 3H), 6.39 (s, 1H), 4.71 (s, 2H), 4.51 (t, *J* = 6.4 Hz, 2H), 2.93 – 2.85 (m, 2H), 2.83 – 2.77 (m, 2H), 2.77 – 2.71 (m, 2H), 2.69 – 2.62 (m, 2H), 2.37 (s, 6H), 2.27 (s, 3H), 1.42 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.9, 144.5, 143.0, 138.1, 137.0, 136.8, 135.1, 135.1, 134.3, 129.5, 128.7, 128.7, 128.5, 128.4, 128.2, 127.5, 126.9, 126.8, 124.7, 124.7, 123.2, 122.0, 120.0, 111.3, 109.2, 75.8, 42.8, 35.6, 35.4, 31.3, 25.1, 21.5, 21.5. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{53}H_{57}N_4O_5S_2^+$ 893.3765; found: 893.3768.

N,N'-((((2-((4-bromobenzyl)oxy)-3-(tert-butyl)phenyl)methylene)bis(1H-indole-2,3-diyl))bis(ethane-2,1-diyl))bis(4-methylbenzenesulfonamide) (6c).



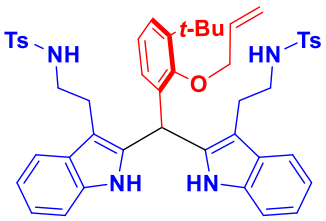
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 12:1) afforded the product as a white solid (81.1. mg, 85% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (s, 2H), 7.43 (td, *J* = 6.2, 3.0 Hz, 8H), 7.34 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.25 (d, *J* = 4.6 Hz, 2H), 7.19 – 7.07 (m, 10H), 7.02 (t, *J* = 7.8 Hz, 1H), 6.96 (dd, *J* = 7.6, 1.8 Hz, 1H), 6.47 (s, 1H), 4.72 (d, *J* = 6.6 Hz, 4H), 3.00 – 2.90 (m, 2H), 2.87 – 2.75 (m, 4H), 2.72 – 2.64 (m, 2H), 2.37 (s, 6H), 1.38 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.6, 144.4, 143.1, 136.7, 136.1, 135.2, 135.1, 134.3, 131.6, 129.6, 128.6, 128.1, 128.0, 127.5, 127.0, 124.9, 122.0, 121.4, 120.1, 118.5, 111.3, 109.2, 74.8, 42.8, 35.5, 35.4, 31.2, 25.2, 21.5. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{52}H_{54}BrN_4O_5S_2^+$ 957.2714; found: 957.2711.

N,N'-((((3-(tert-butyl)-2-((2-cyanobenzyl)oxy)phenyl)methylene)bis(1H-indole-2,3-diyl))bis(ethane-2,1-diyl))bis(4-methylbenzenesulfonamide) (6d).



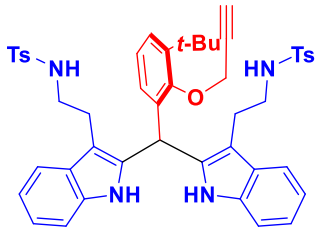
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 12:1) afforded the product as a white solid (80.6. mg, 90% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 (s, 2H), 7.76 (d, *J* = 7.9 Hz, 1H), 7.64 (t, *J* = 7.7 Hz, 1H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.47 (d, *J* = 7.9 Hz, 4H), 7.41 (d, *J* = 7.9 Hz, 2H), 7.38 – 7.32 (m, 2H), 7.25 (s, 2H), 7.17 (t, *J* = 7.6 Hz, 2H), 7.14 – 7.07 (m, 6H), 7.04 (t, *J* = 7.8 Hz, 1H), 6.95 (d, *J* = 7.8 Hz, 1H), 6.53 (s, 1H), 4.89 (d, *J* = 5.5 Hz, 4H), 3.02 – 2.92 (m, 2H), 2.83 (dd, *J* = 13.0, 6.7 Hz, 2H), 2.76 (dt, *J* = 15.4, 7.8 Hz, 2H), 2.69 – 2.61 (m, 2H), 2.37 (s, 6H), 1.38 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.4, 144.2, 143.1, 140.7, 136.7, 135.2, 135.1, 134.3, 133.6, 132.5, 129.6, 128.6, 128.3, 127.9, 127.6, 127.5, 127.0, 125.2, 122.1, 120.1, 118.5, 116.9, 111.3, 109.4, 109.1, 73.6, 42.7, 35.5, 35.3, 31.3, 25.0, 21.5. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{53}H_{54}N_5O_5S_2^+$ 904.3561; found: 904.3565.

N,N'-((((2-(allyloxy)-3-(tert-butyl)phenyl)methylene)bis(1H-indole-2,3-diyl))bis(ethane-2,1-diyl))bis(4-methylbenzenesulfonamide) (6e).



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 12:1) afforded the product as a white solid (70.3. mg, 88% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 (s, 2H), 7.50 (d, *J* = 8.0 Hz, 4H), 7.45 (d, *J* = 7.9 Hz, 2H), 7.30 (dd, *J* = 7.7, 2.0 Hz, 1H), 7.25 (d, *J* = 3.5 Hz, 2H), 7.15 (dd, *J* = 11.7, 7.7 Hz, 6H), 7.09 (t, *J* = 7.5 Hz, 2H), 7.01 – 6.94 (m, 2H), 6.40 (s, 1H), 5.94 – 5.85 (m, 1H), 5.38 (dd, *J* = 17.4, 2.0 Hz, 1H), 5.14 (dd, *J* = 10.7, 2.0 Hz, 1H), 4.78 (t, *J* = 6.2 Hz, 2H), 4.23 – 4.12 (m, 2H), 3.08 – 2.98 (m, 2H), 2.95 – 2.84 (m, 4H), 2.83 – 2.75 (m, 2H), 2.37 (s, 6H), 1.38 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.8, 144.4, 143.1, 136.8, 135.3, 135.0, 134.3, 133.0, 129.6, 128.7, 128.0, 127.3, 127.0, 124.7, 122.0, 120.0, 118.5, 116.5, 111.3, 109.0, 74.8, 42.9, 35.5, 35.1, 31.1, 25.2, 21.5. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{48}H_{53}N_4O_5S_2^+$ 829.3452; found: 829.3453

N,N'-((((3-(tert-butyl)-2-(prop-2-yn-1-yloxy)phenyl)methylene)bis(1H-indole-2,3-diyl))bis(ethane-2,1-diyl))bis(4-methylbenzenesulfonamide) (6f).



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 12:1) afforded the product as a white solid (69.0. mg, 84% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93 (s, 2H), 7.51 (d, *J* = 8.0 Hz, 4H), 7.45 (d, *J* = 7.9 Hz, 2H), 7.29 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.25 (d, *J* = 3.1 Hz, 2H), 7.15 (dd, *J* = 12.3, 7.6 Hz, 6H), 7.08 (t, *J* = 7.4 Hz, 2H), 7.02 – 6.94 (m, 2H), 6.46 (s, 1H), 4.76 (t, *J* = 6.5 Hz, 2H), 4.29 (d, *J* = 2.6 Hz, 2H), 3.10 – 3.01 (m, 2H), 3.01 – 2.80 (m, 6H), 2.41 (d, *J* = 2.5 Hz, 1H), 2.36 (s, 6H), 1.40 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.1, 144.6, 143.1, 136.8, 135.1, 134.9, 134.4, 129.6, 128.7, 128.1, 127.5, 127.1, 125.3, 122.1, 120.1, 118.6, 111.3, 109.2, 78.5, 76.4, 62.3, 42.9, 35.5, 35.4, 31.2, 25.1, 21.5. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{48}H_{51}N_4O_5S_2^+$ 827.3295; found: 827.3294.

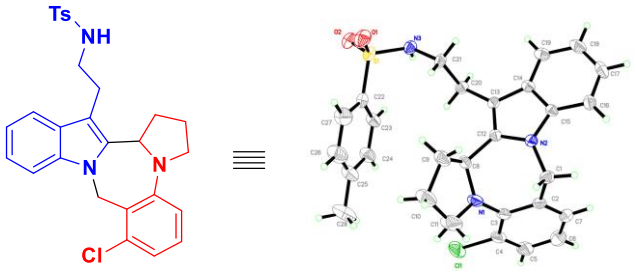
Reference:

1. (a) I. D. Jurberg, B. Peng, E. Wçstefeld, M. Wasserloos, N. Maulide, *Angew. Chem. Int. Ed.*, 2012, **51**, 1950; (b) L. Cao, F. Hu, H. Sun, X. Zhang and S.-S. Li, *Org. Chem. Front.*, 2022, **9**, 1668–1674.

4. Crystal Structures and Data

4.1 Crystal sample preparation and crystal structure determination of 4d

To a 10 mL vial, the corresponding samples (15.0 mg) were dissolved in 2 mL ethyl acetate, then 4.0 mL petroleum ether was slowly dropwise into the above solution. The vial, which was not screwed down, was carefully setting in a clean place at room temperature, and wait for the crystals to precipitate. The crystal was confirmed by X-ray crystallographic. The type of the device that used for the crystal measurement was “Xcalibur, Eos, Gemini”.



ORTEP diagram of compound **4d**, thermal ellipsoids are drawn on 30% probability level

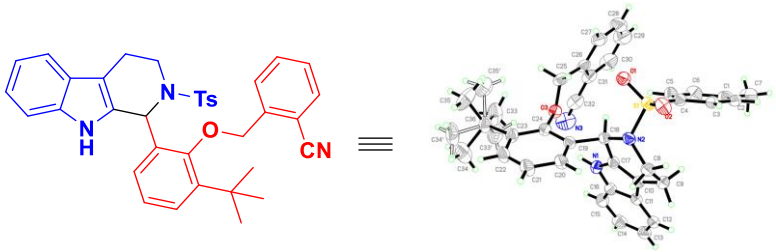
Crystal data and structure refinement for **4d**

Identification code	**4d**
Empirical formula	$C_{28}H_{28}ClN_3O_2S$
Formula weight	506.04
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 9.7670(9) A alpha = 73.207(2) deg.
	b = 12.1981(12) A beta = 83.479(4) deg.
	c = 12.7598(12) A gamma = 79.591(3) deg.
Volume	1428.4(2) A^3
Z, Calculated density	2, 1.177 Mg/m^3
Absorption coefficient	0.234 mm^-1
F(000)	532
Crystal size	0.45 x 0.30 x 0.16 mm
Theta range for data collection	2.12 to 25.02 deg.
Limiting indices	-11<=h<=11, -14<=k<=14, -8<=l<=15

Reflections collected / unique	6918 / 4940 [R(int) = 0.0382]
Completeness to theta = 25.02	97.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9635 and 0.9019
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4940 / 0 / 317
Goodness-of-fit on F^2	1.019
Final R indices [I>2sigma(I)]	R1 = 0.0661, wR2 = 0.1639
R indices (all data)	R1 = 0.0967, wR2 = 0.1779
Largest diff. peak and hole	0.262 and -0.345 e.A^-3

4.2 Crystal sample preparation and crystal structure determination of 5f

To a 10 mL vial, the corresponding samples (20.0 mg) were dissolved in 1 mL ethyl acetate, then 4.0 mL petroleum ether was slowly dropwise into the above solution. The vial, which was not screwed down, was carefully setting in a clean place at room temperature, and wait for the crystals to precipitate. The crystal was confirmed by X-ray crystallographic. The type of the device that used for the crystal measurement was "Xcalibur, Eos, Gemini".



5f **CCDC 2320457**

ORTEP diagram of compound **5f**, thermal ellipsoids are drawn on 30% probability level

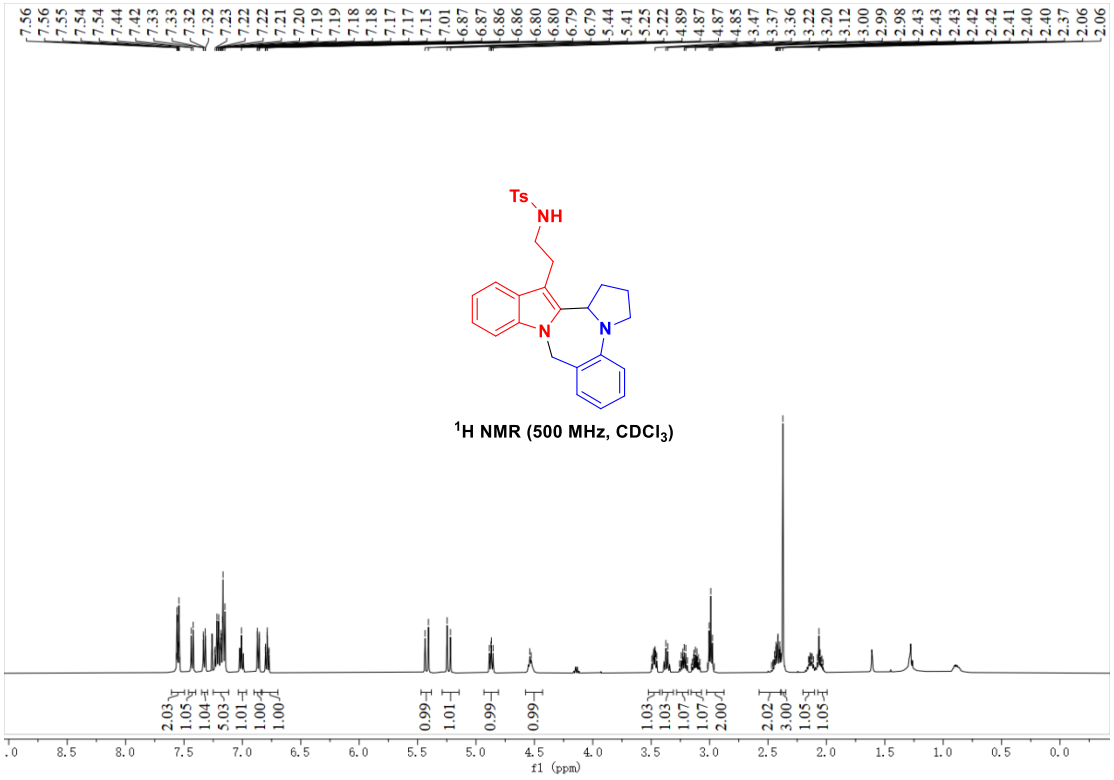
Crystal data and structure refinement for **5f**.

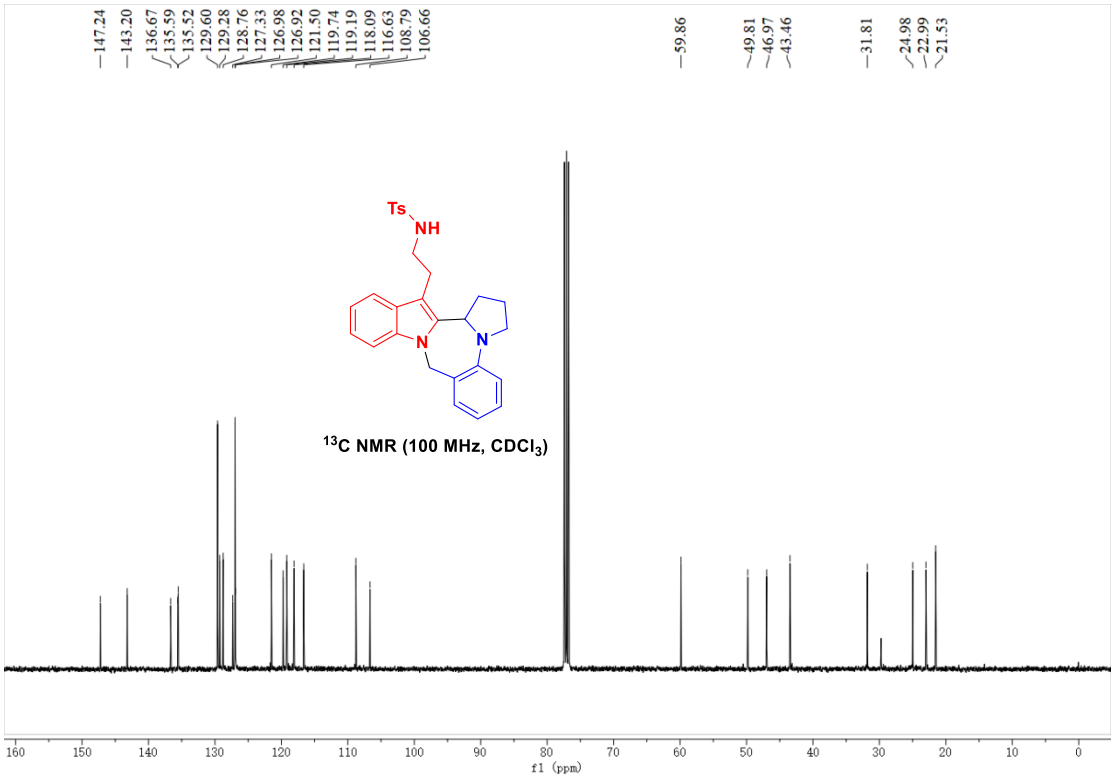
Identification code	**5f**
Empirical formula	$C_{36}H_{35}N_3O_3S$
Formula weight	1179.46
Temperature	293(2) K
Wavelength	1.54184 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 17.2157(4) A alpha = 90 deg.
	b = 9.9039(2) A beta = 99.352(2) deg.
	c = 18.6383(4) A gamma = 90 deg.
Volume	3135.64(12) A^3
Z, Calculated density	2, 1.249 Mg/m^3
Absorption coefficient	1.232 mm^-1
F(000)	1248
Crystal size	0.130 x 0.120 x 0.120 mm
Theta range for data collection	2.601 to 67.234 deg.
Limiting indices	-20<=h<=20, -11<=k<=11, -17<=l<=22
Reflections collected / unique	20552 / 5615 [R(int) = 0.0305]
Completeness to theta = 67.234	100.0 %

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5615 / 126 / 423
Goodness-of-fit on F^2	1.028
Final R indices [I>2sigma(I)]	R1 = 0.0455, wR2 = 0.1226
R indices (all data)	R1 = 0.0548, wR2 = 0.1307
Extinction coefficient	n/a
Largest diff. peak and hole	0.290 and -0.336 e.A^-3

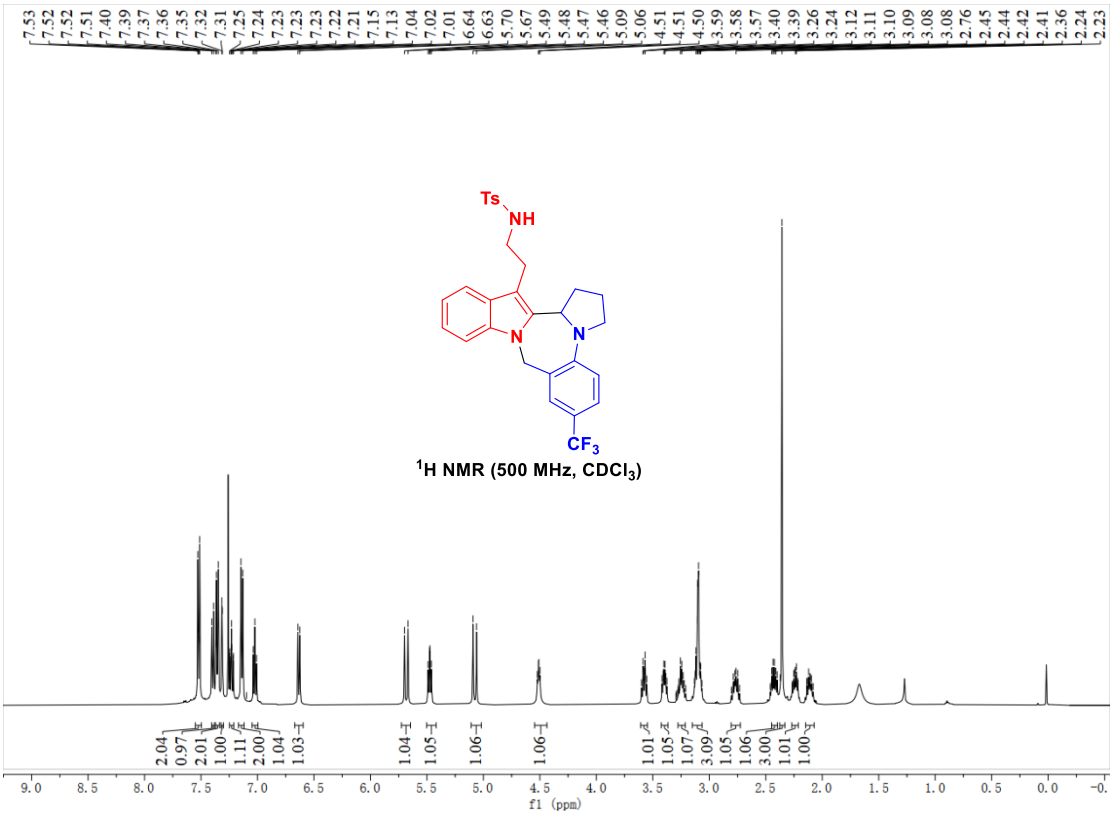
5. ^{1}H and ^{13}C NMR Spectra

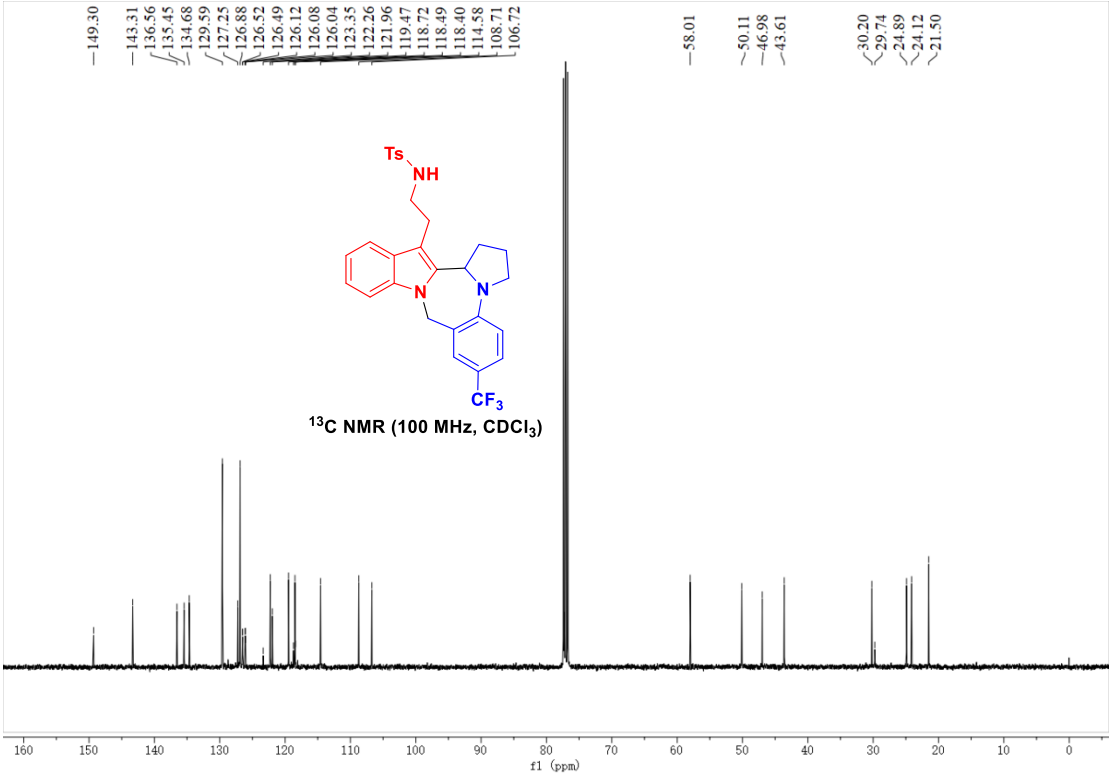
4-methyl-*N*-(2-(1,2,3,15b-tetrahydro-9*H*-benzo[5,6]pyrrolo[2',1':3,4][1,4]diazepino[1,2-*a*]indol-15-yl)ethyl)benzenesulfonamide (4a)



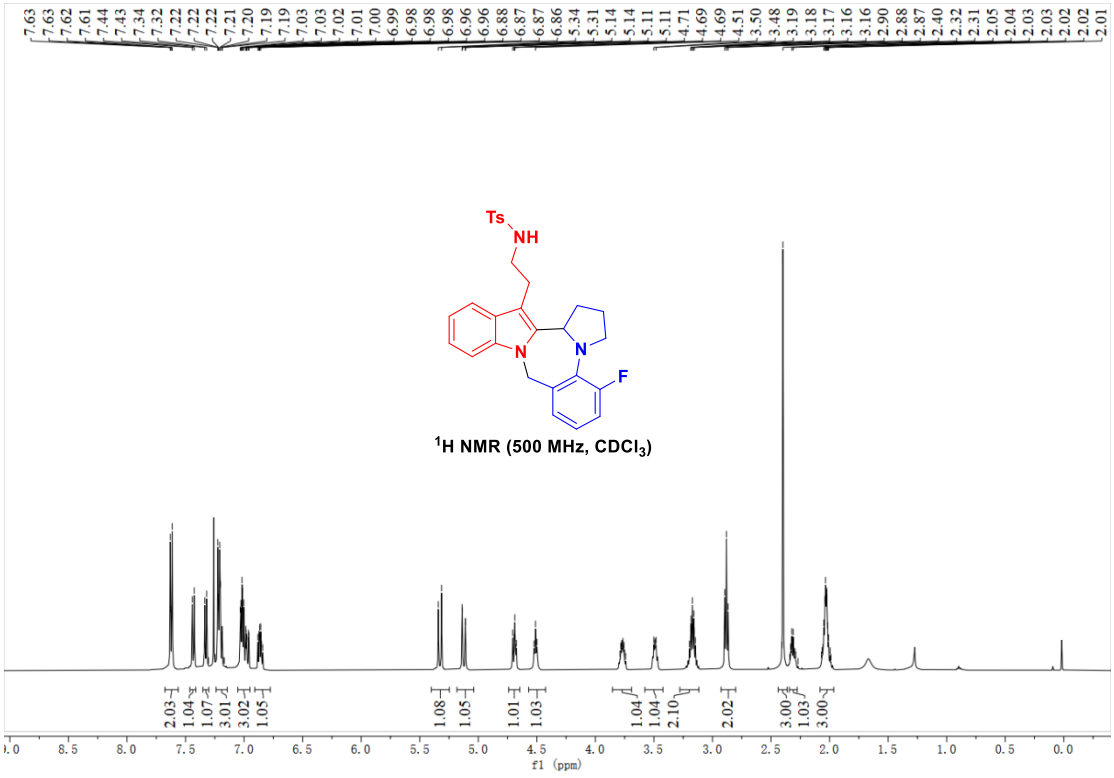


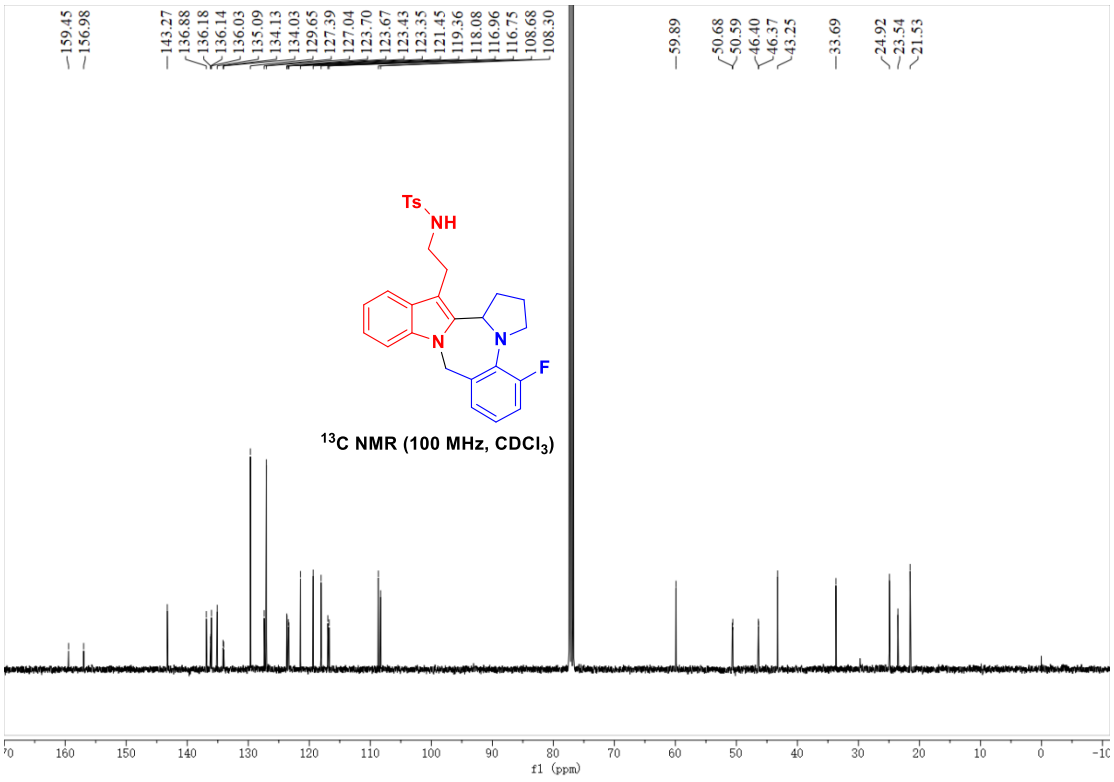
4-methyl-*N*-(2-(7-(trifluoromethyl)-1,2,3,15b-tetrahydro-9*H*-benzo[5,6]pyrrolo[2',1':3,4][1,4]diazepino[1,2-*a*]indol-15-yl)ethyl)benzenesulfonamide (4b)



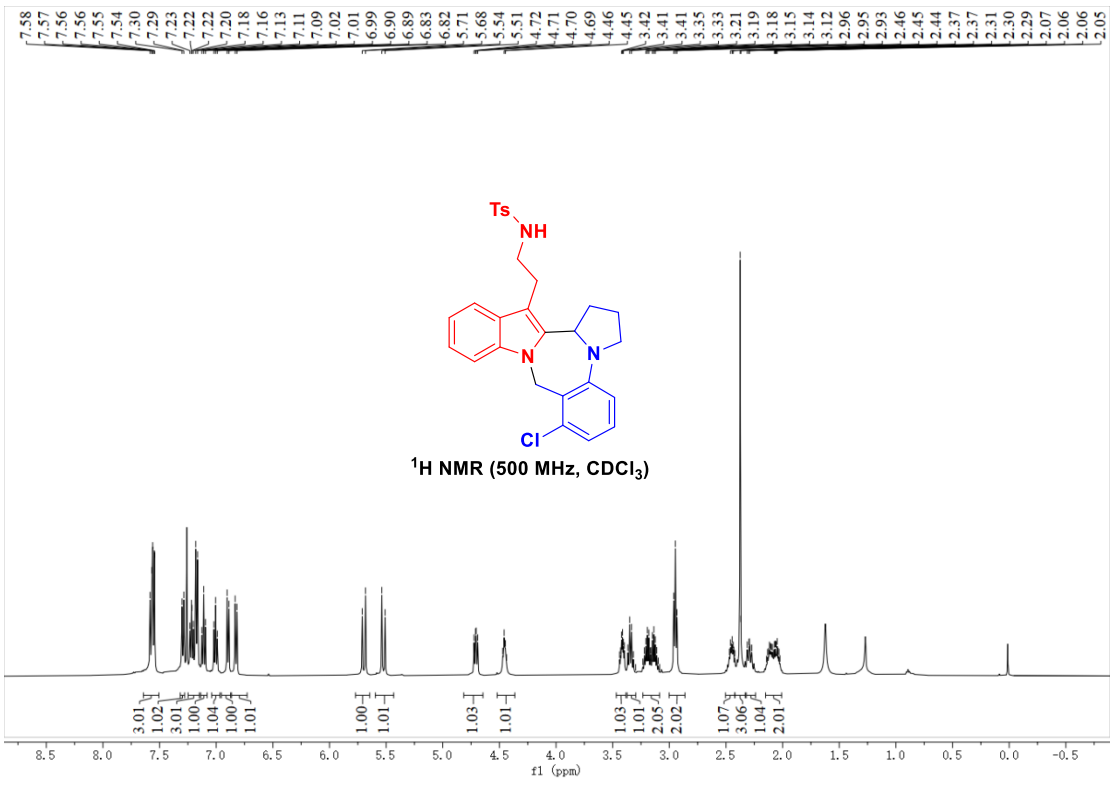


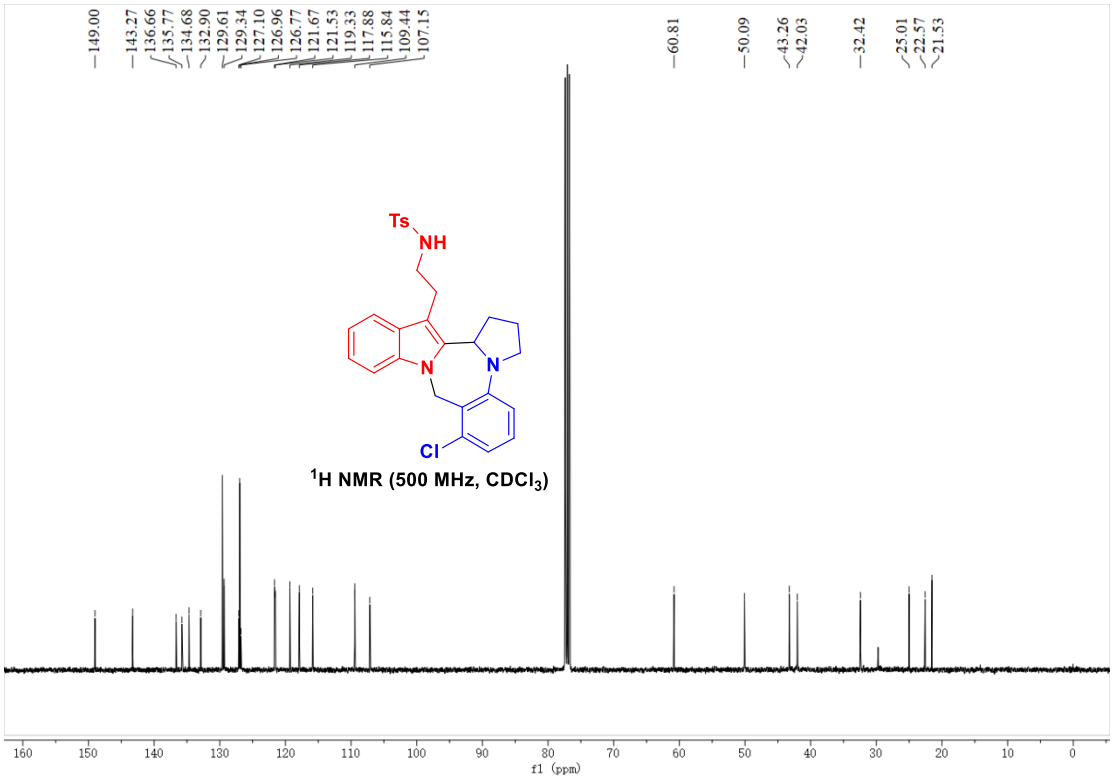
_N_-(2-(5-fluoro-1,2,3,15b-tetrahydro-9_H_-benzo[5,6]pyrrolo[2',1':3,4][1,4]diazepino[1,2-_a_]indol-15-yl)ethyl)-4-methylbenzenesulfonamide (4c)



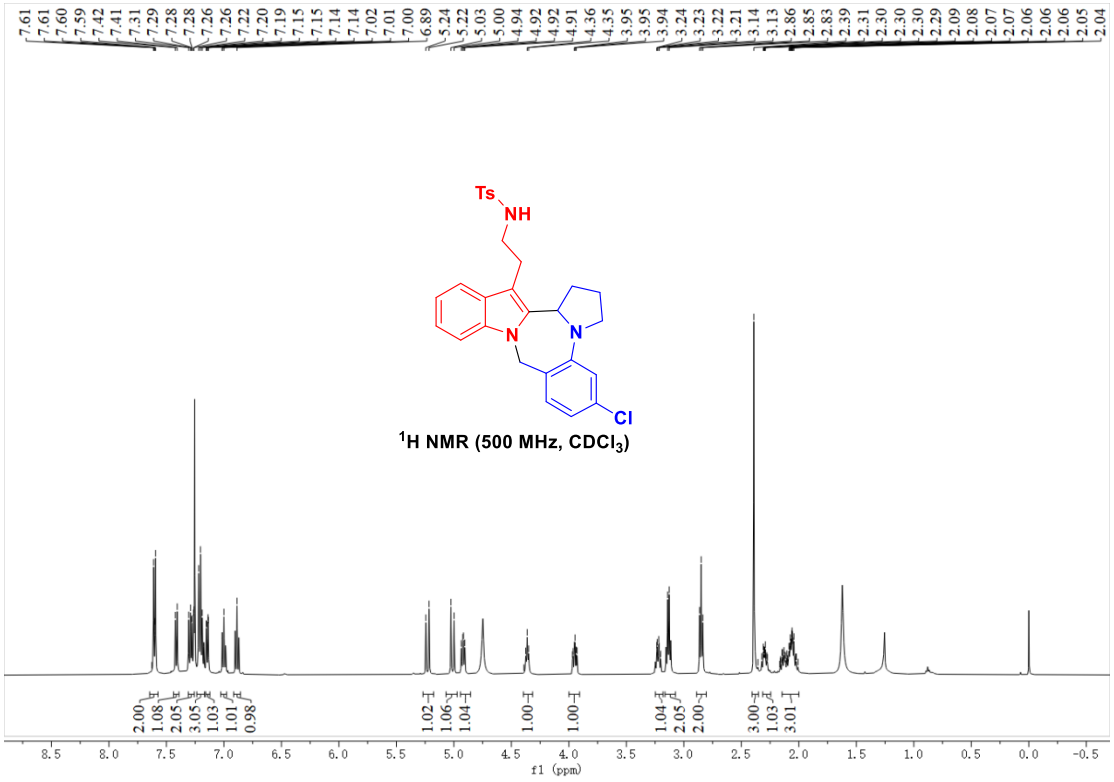


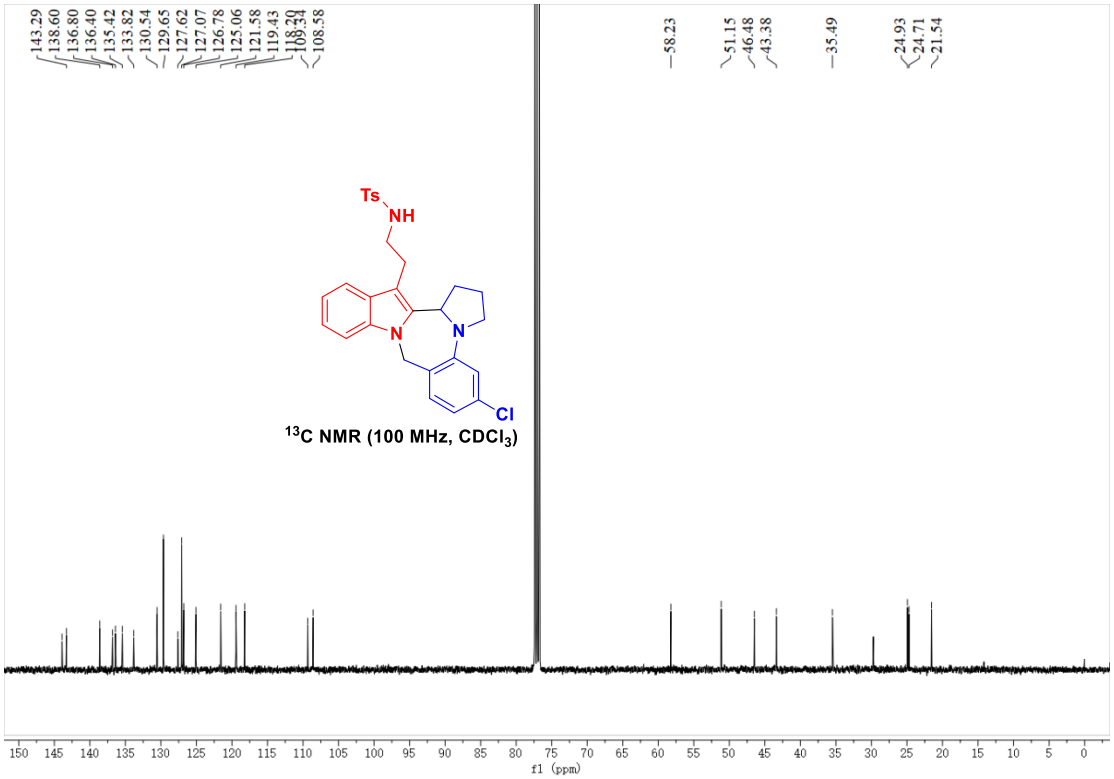
_N_-(2-(7-chloro-1,2,3,3a,8,14b-hexahydrobenzo[5,6]cyclopenta[3,4]azepino[1,2-_a_]indol-14-yl)ethyl)-4-methylbenzenesulfonamide (4d)



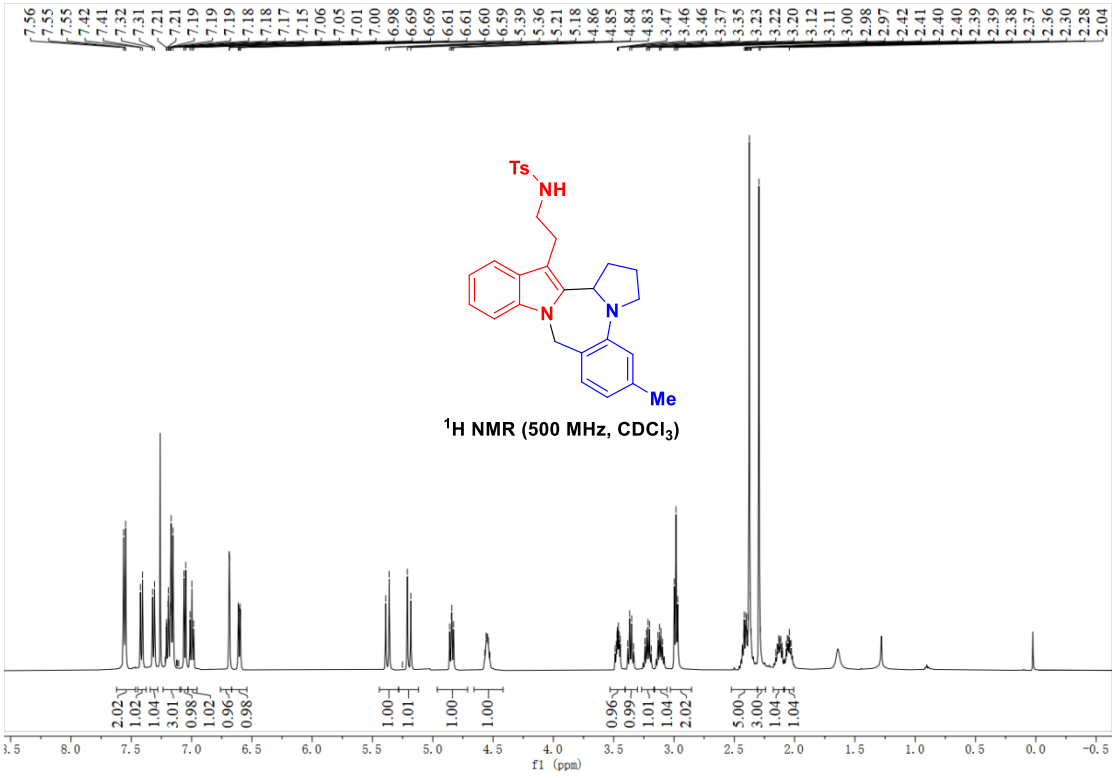


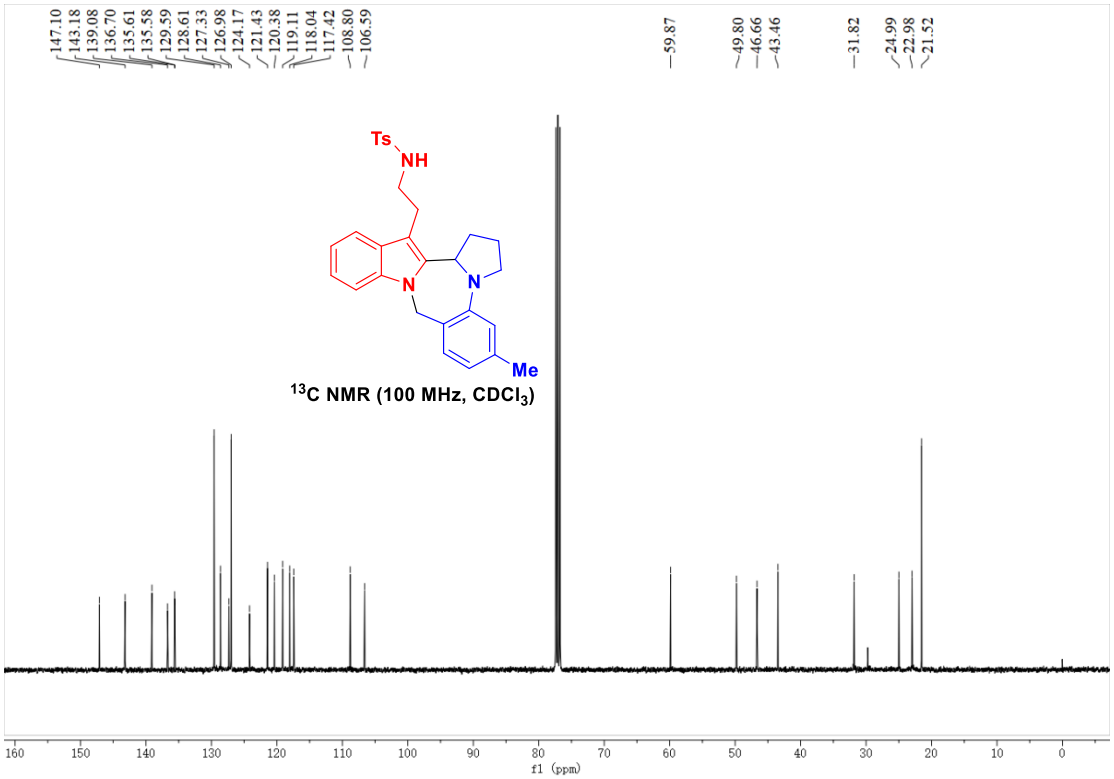
_N_-(2-(6-chloro-1,2,3,15b-tetrahydro-9_H_-benzo[5,6]pyrrolo[2',1':3,4][1,4]diazepino[1,2-_a_]indol-15-yl)ethyl)-4-methylbenzenesulfonamide (4e)



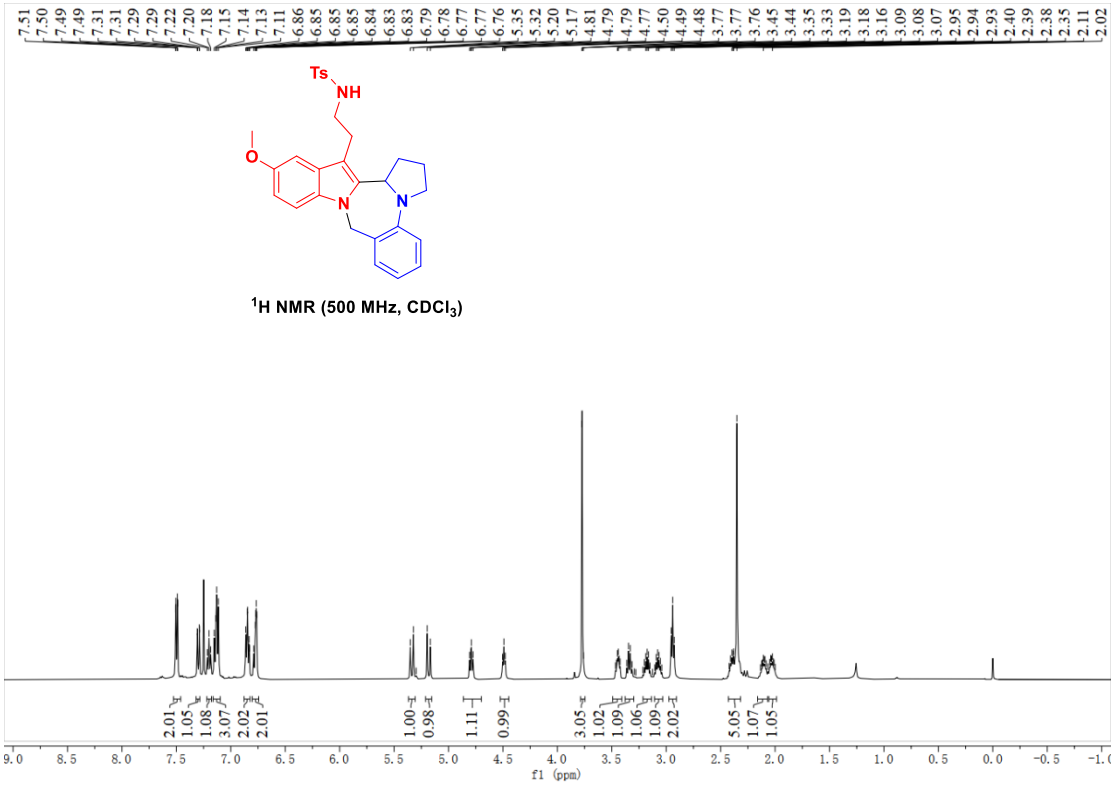


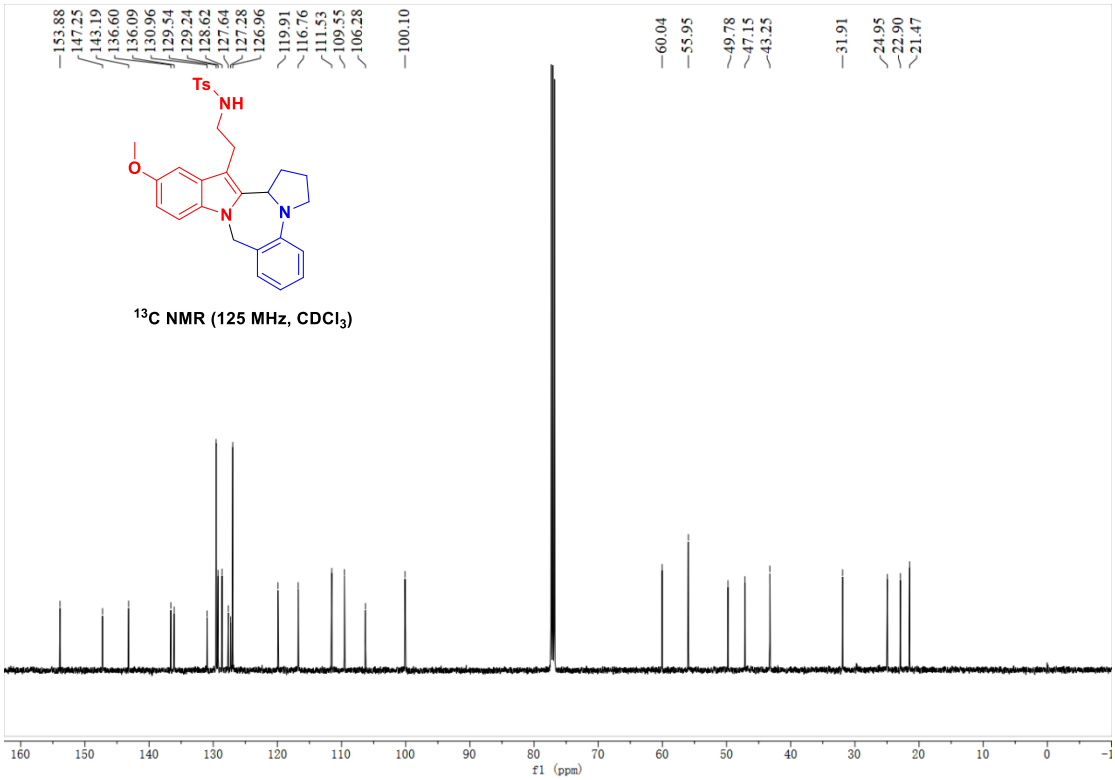
4-methyl-*N*-(2-(6-methyl-1,2,3,15b-tetrahydro-9*H*-benzo[5,6]pyrrolo[2',1':3,4][1,4]diazepino[1,2-*a*]indol-15-yl)ethyl)benzenesulfonamide (4f)



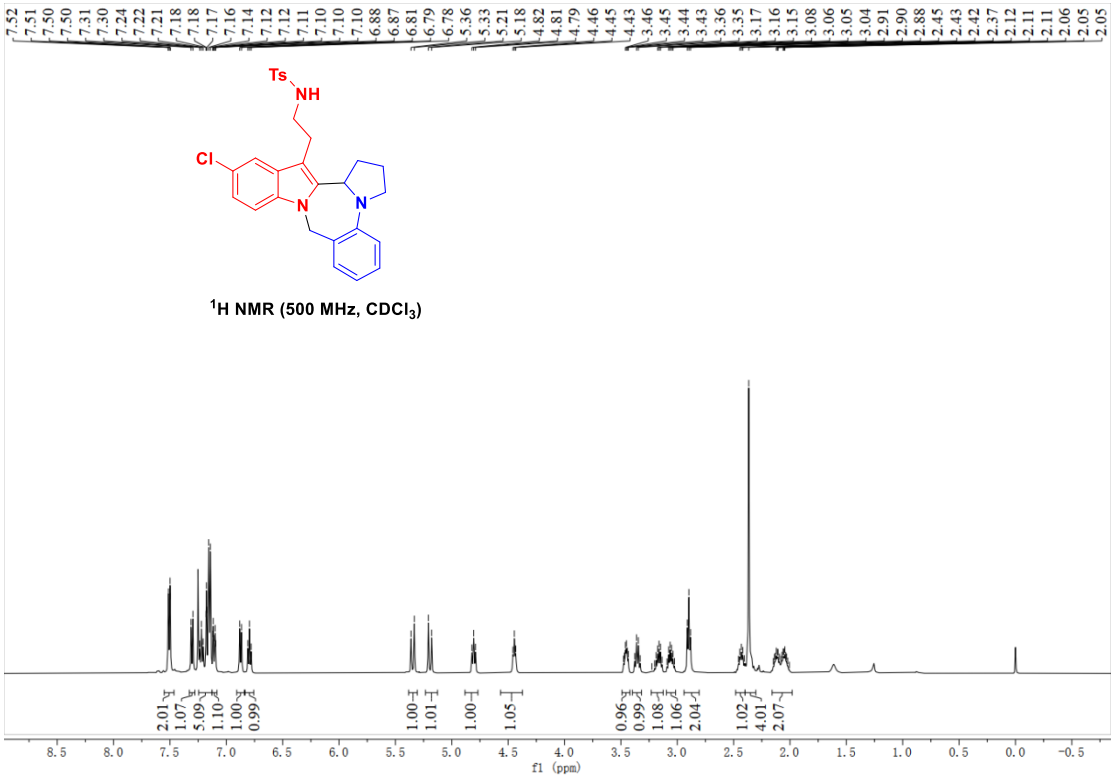


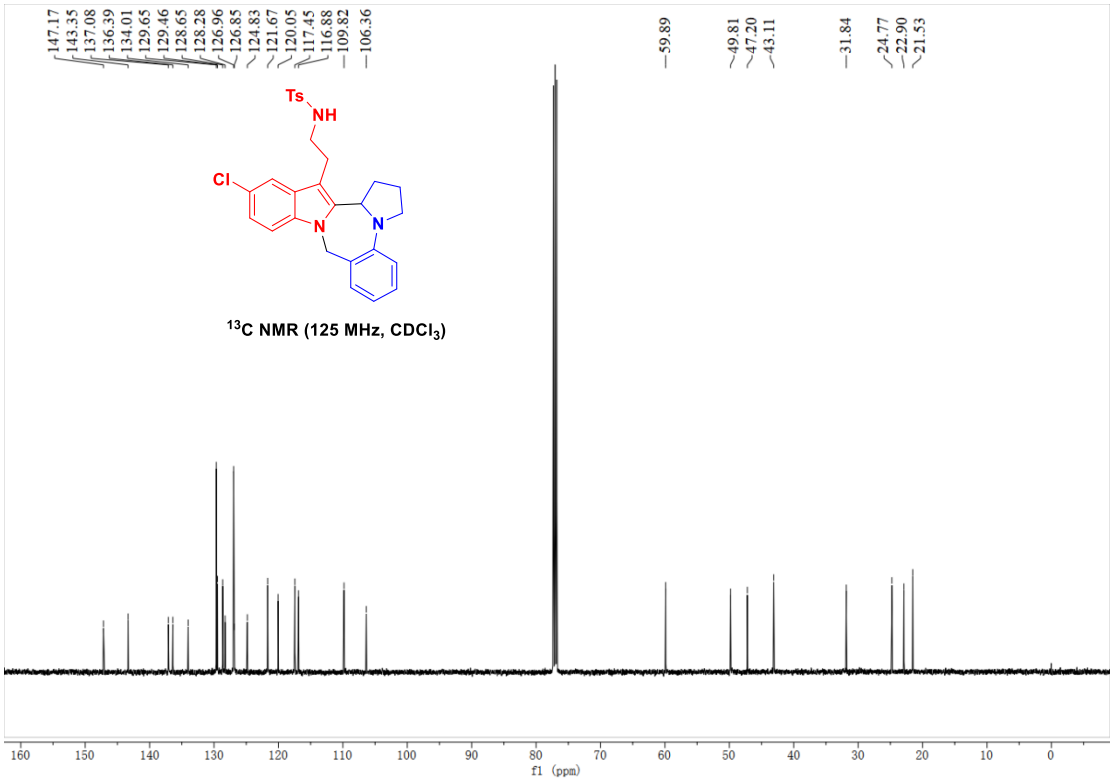
4-methyl-N-(2-(13-methoxy-1,2,3,15b-tetrahydro-9H-benzo[5,6]pyrrolo[2',1':3,4][1,4]diazepino[1,2-a]indol-15-yl)ethyl)-benzenesulfonamide (4g)



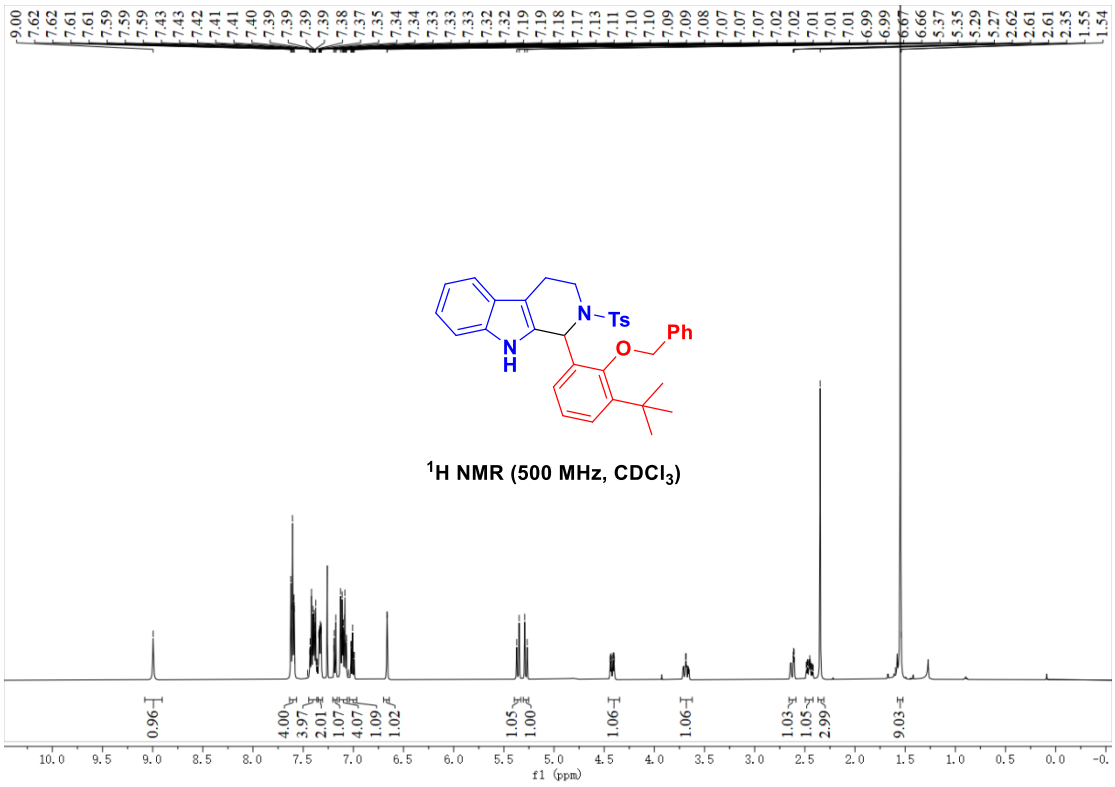


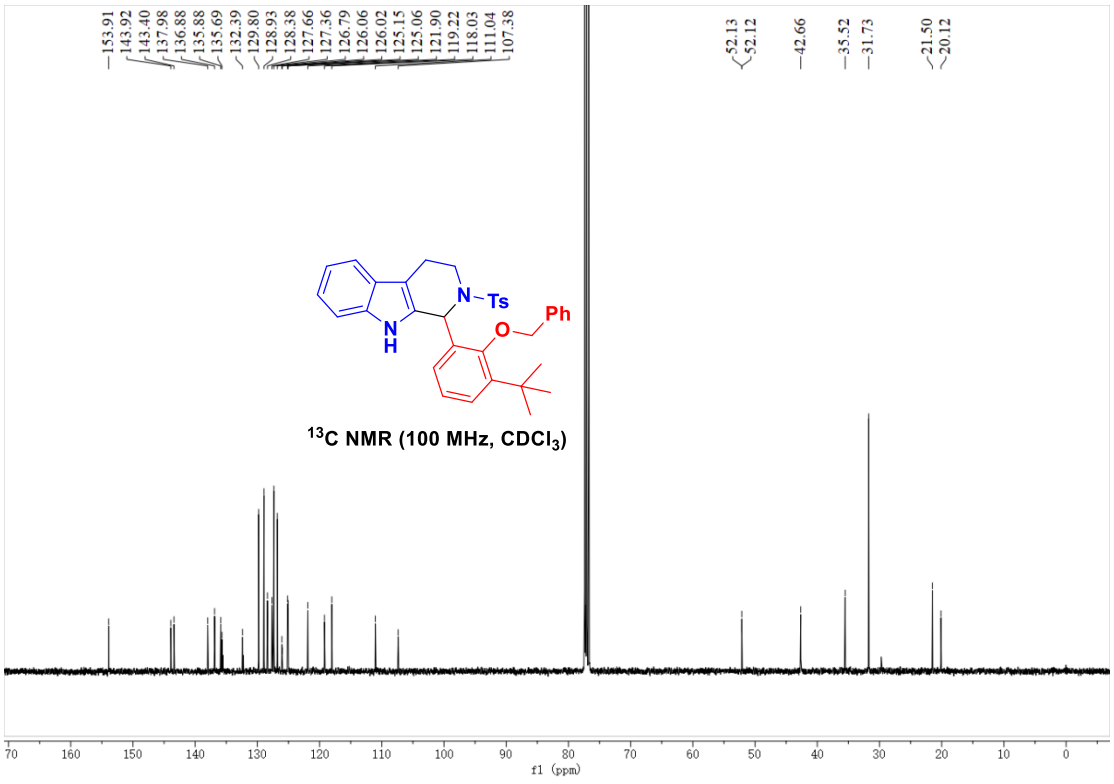
4-methyl-N-(2-(13-chloro-1,2,3,15b-tetrahydro-9H-benzo[5,6]pyrrolo[2',1':3,4][1,4] diazepino[1,2-a]indol-15-yl)ethyl)-benzenesulfonamide (4h)



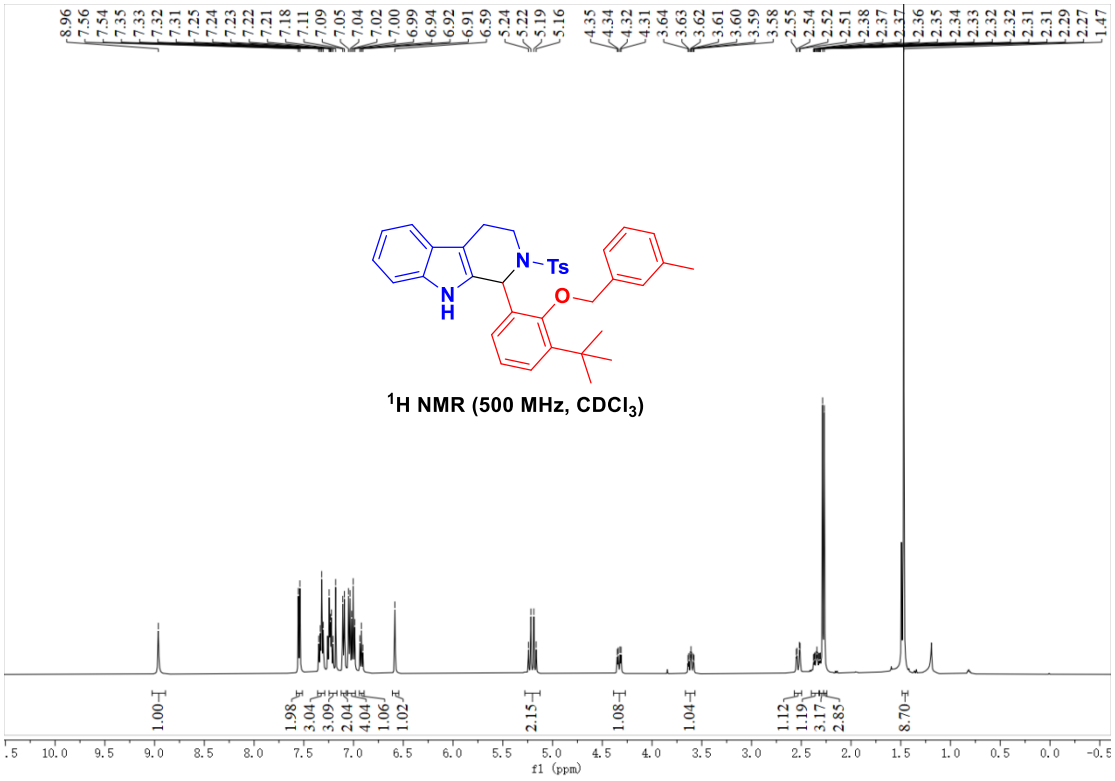


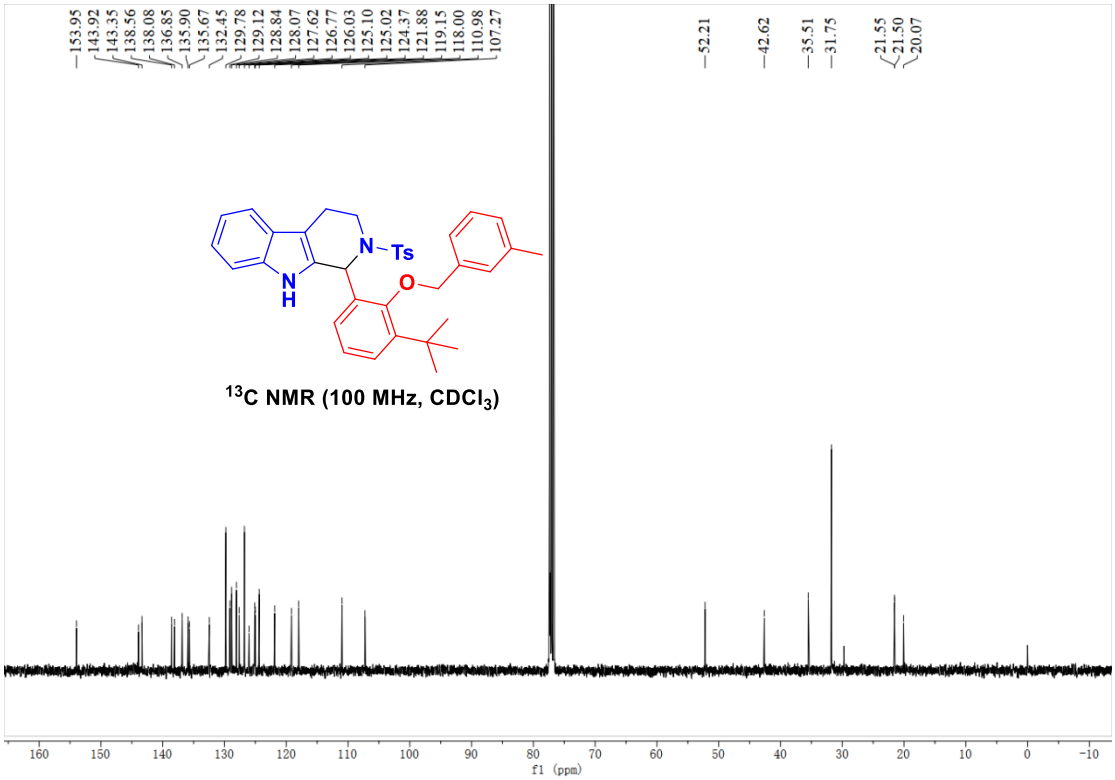
1-(2-(benzyloxy)-3-(*tert*-butyl)phenyl)-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole (5a)



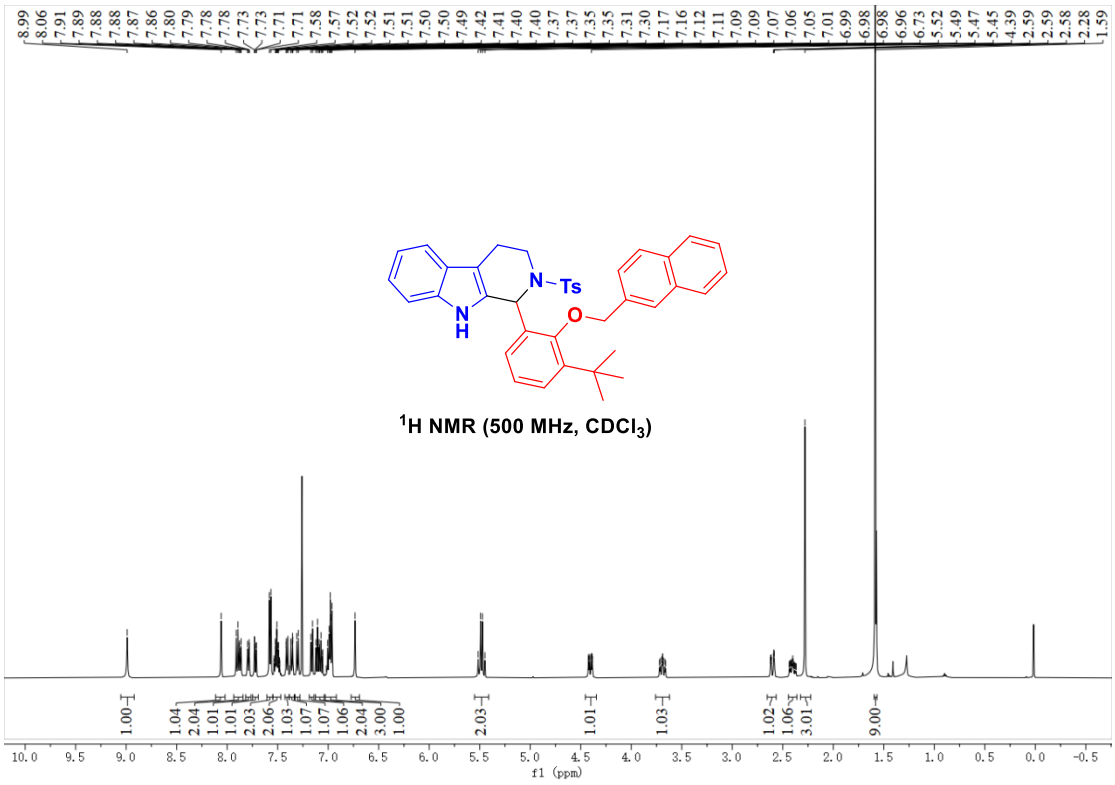


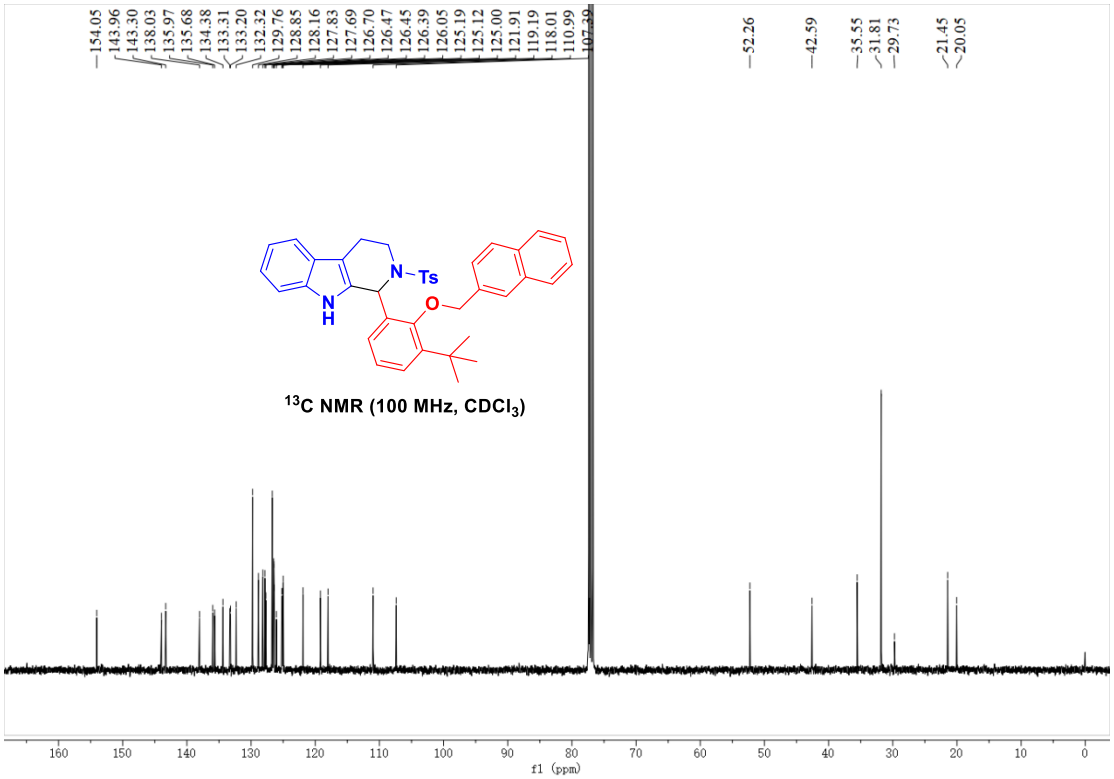
1-(3-(*tert*-butyl)-2-((3-methylbenzyl)oxy)phenyl)-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole (5b)



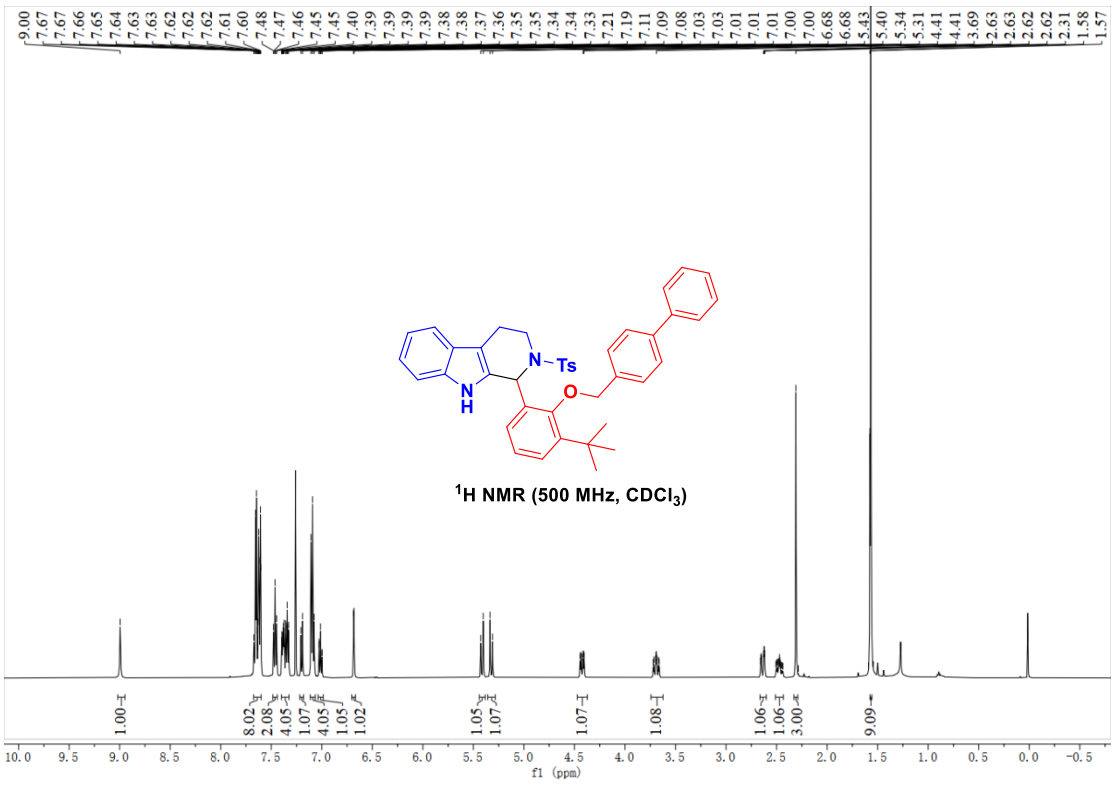


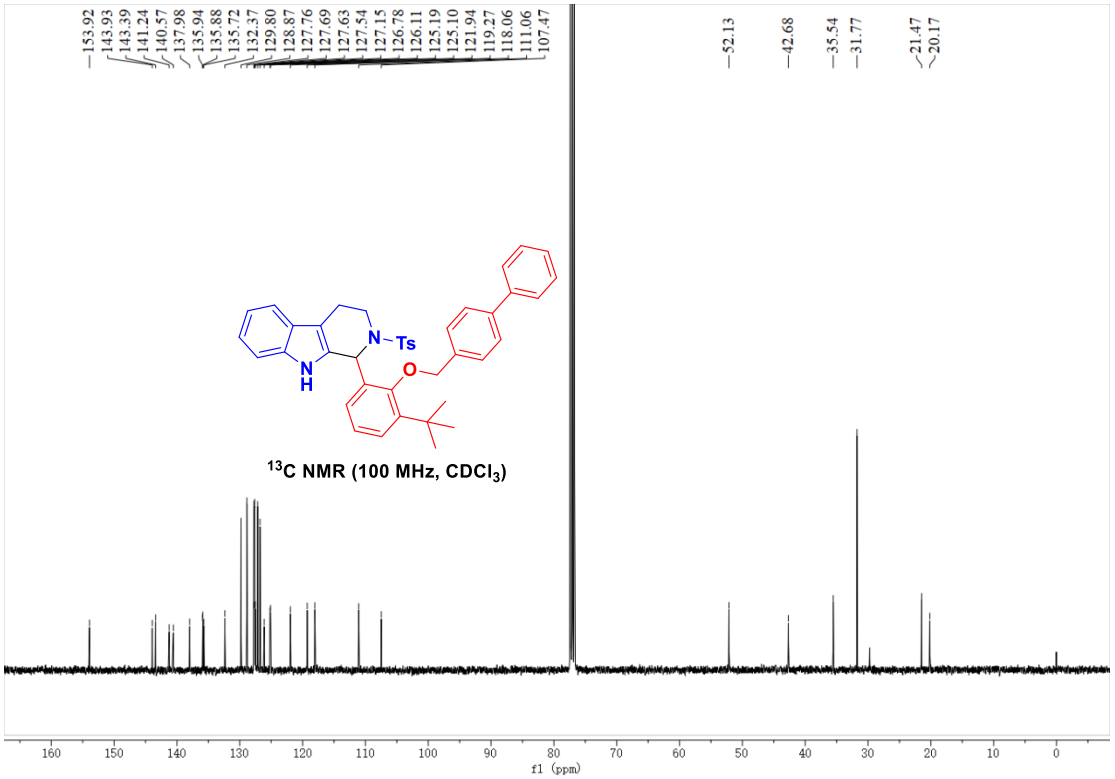
1-(3-(tert-butyl)-2-(naphthalen-2-ylmethoxy)phenyl)-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-b]indole (5c)



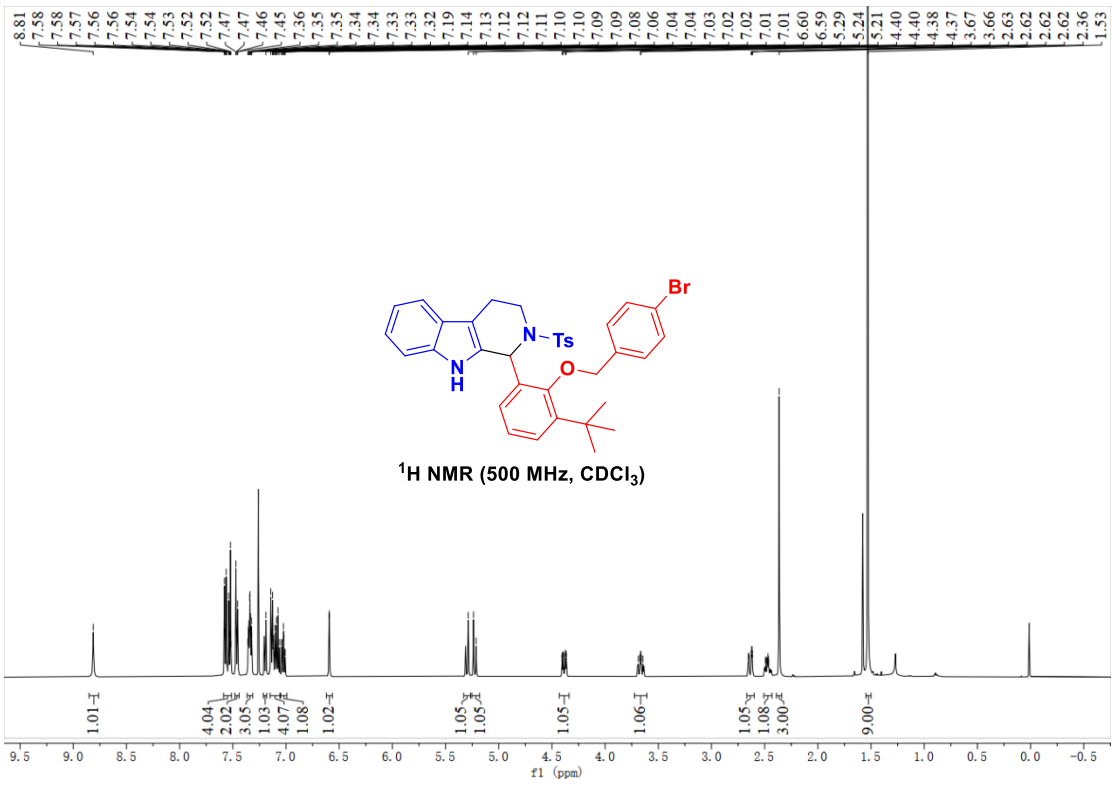


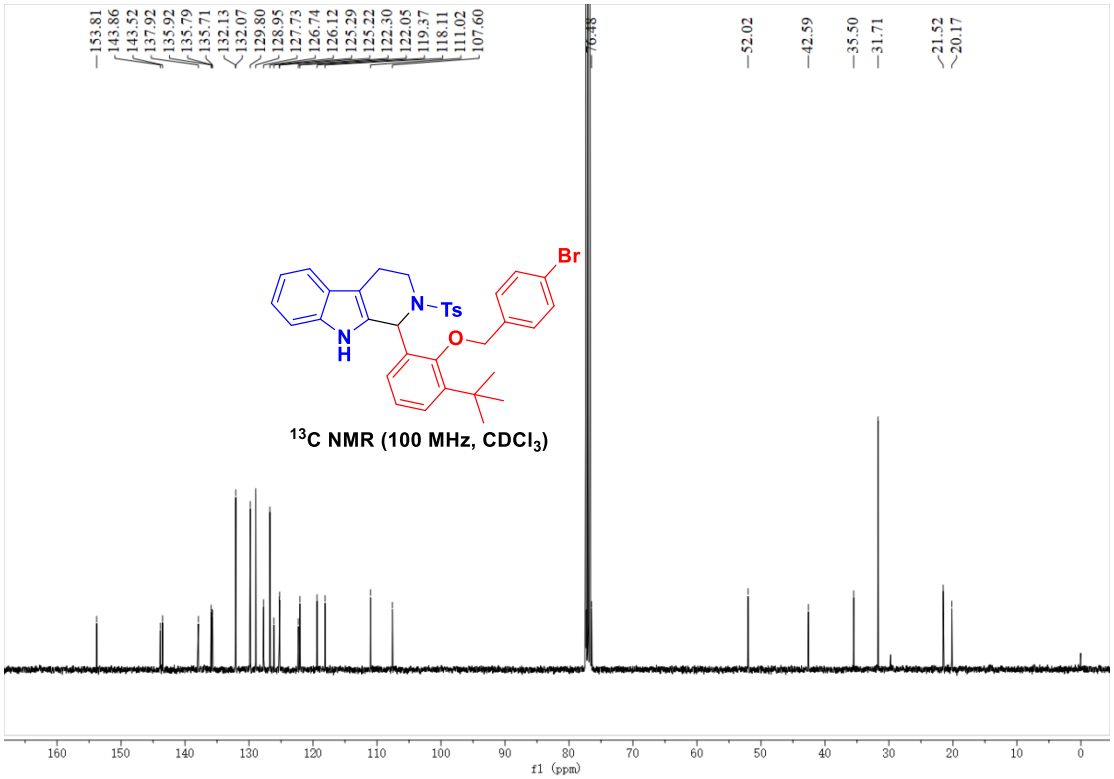
1-(2-([1,1'-biphenyl]-4-ylmethoxy)-3-(*tert*-butyl)phenyl)-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole (5d)



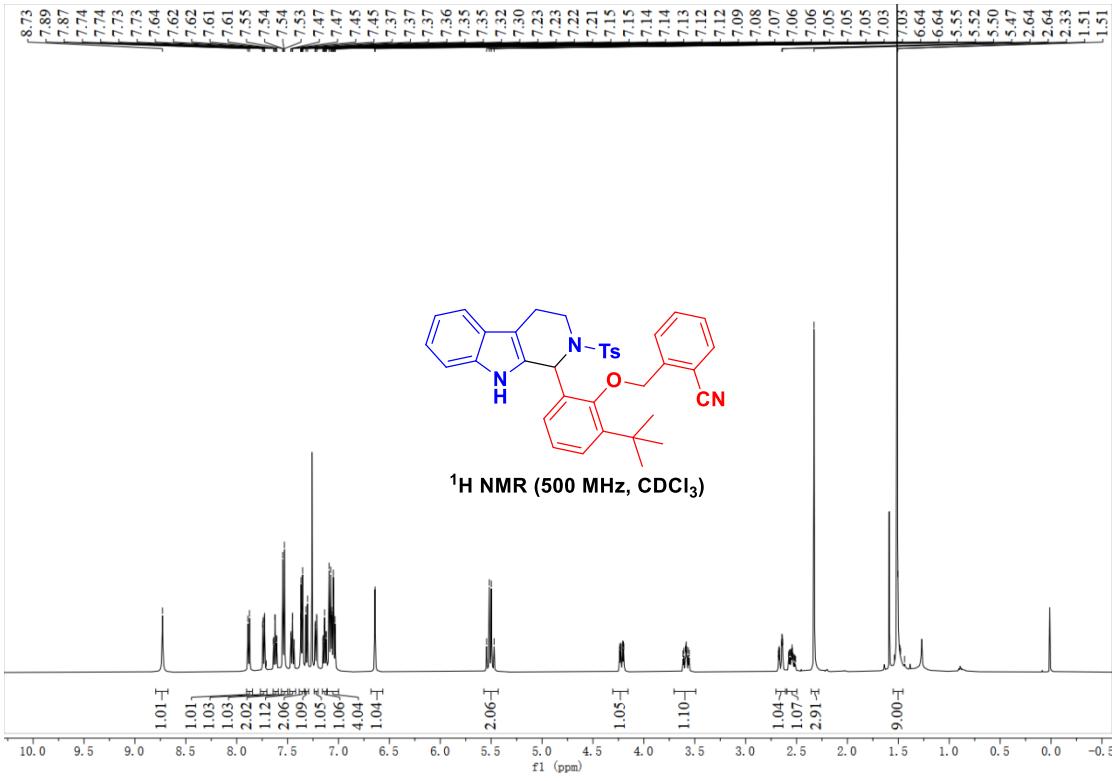


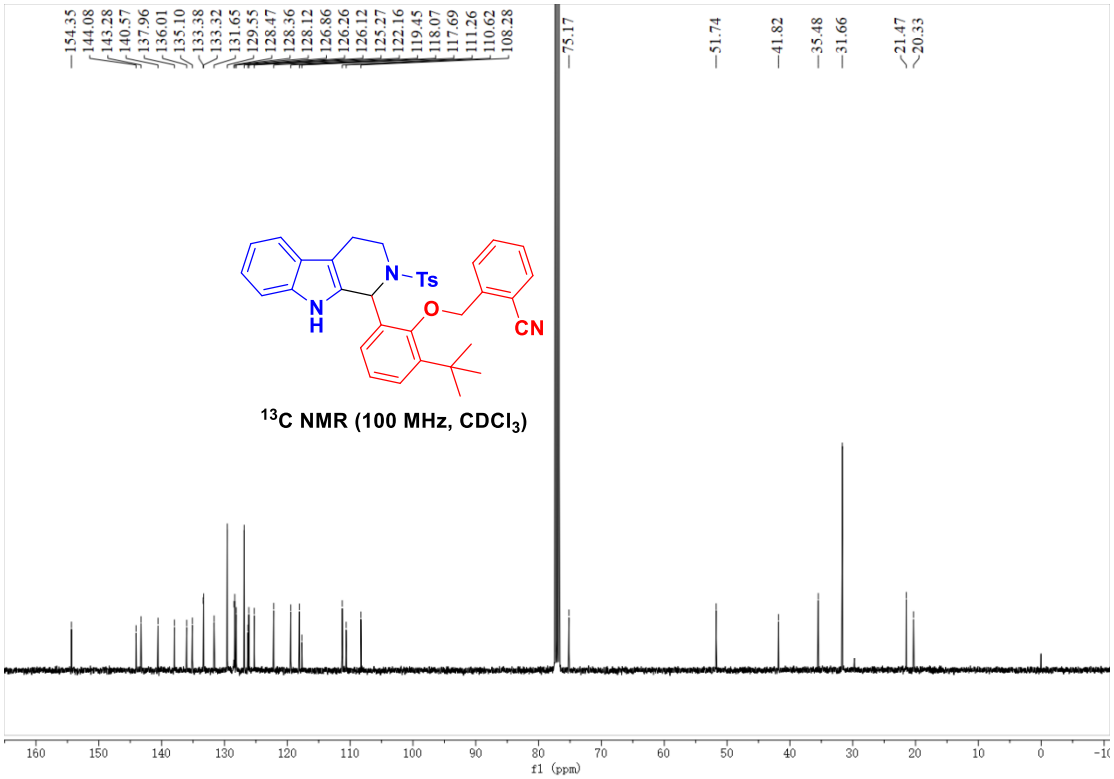
1-(2-((4-bromobenzyl)oxy)-3-(*tert*-butyl)phenyl)-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole (5e)



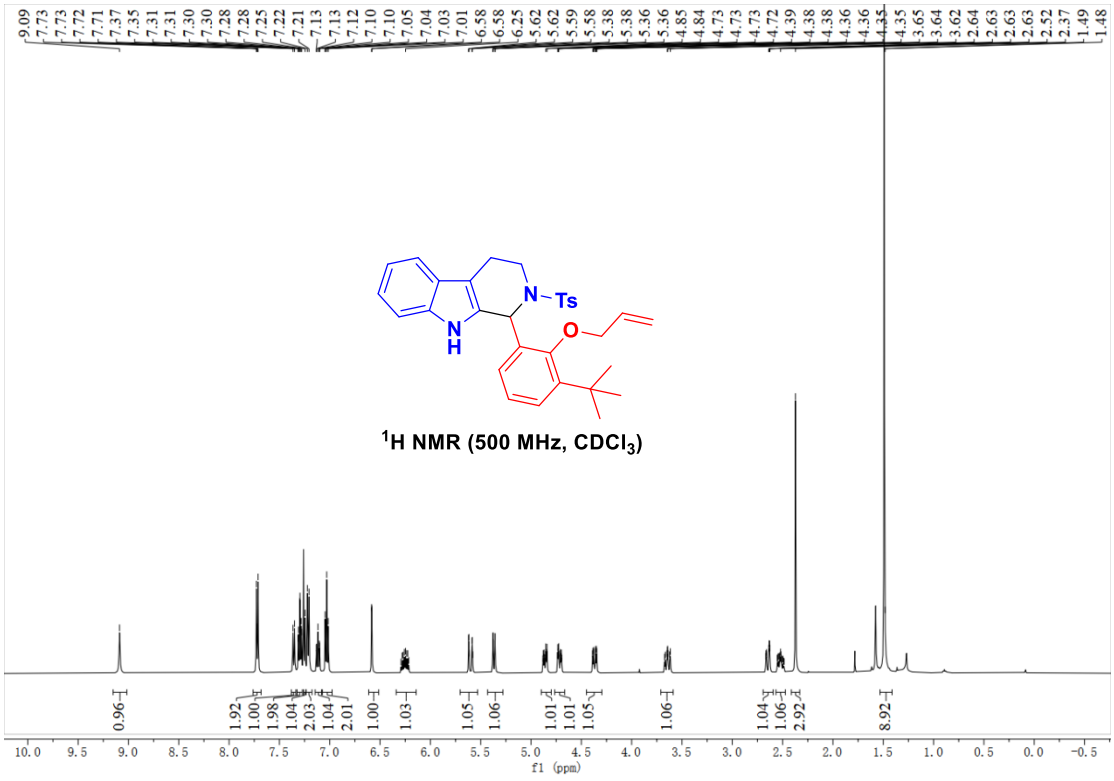


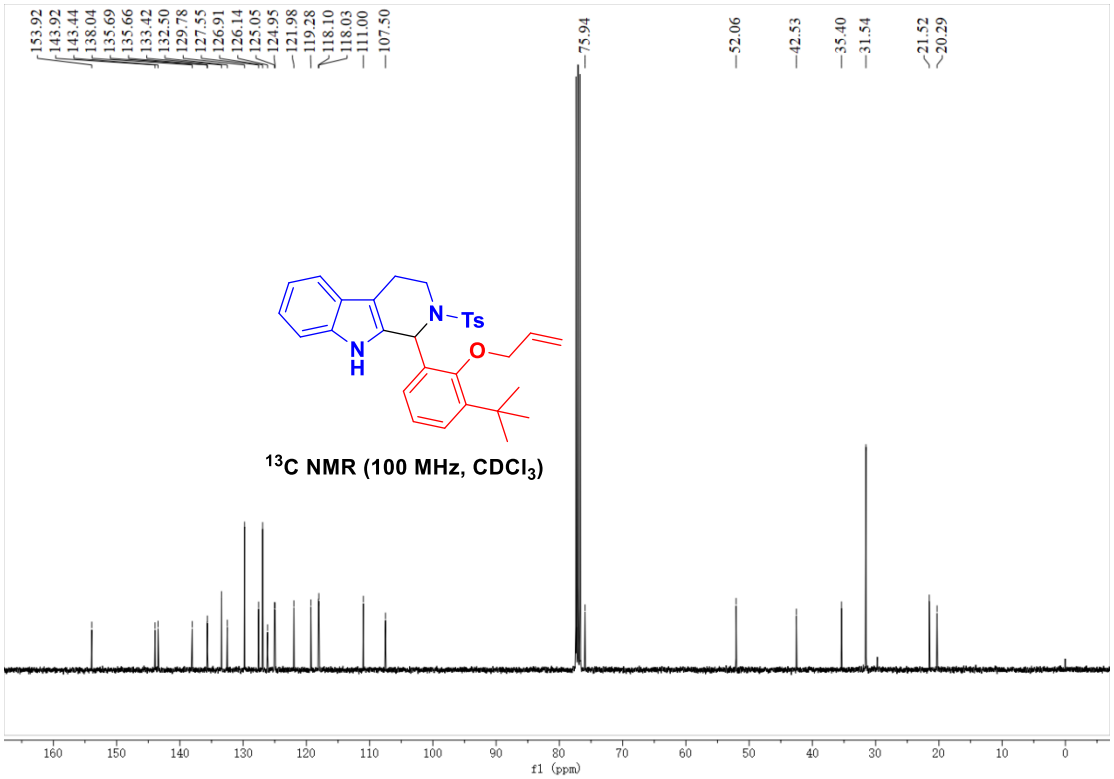
2-((2-(*tert*-butyl)-6-(2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-1-yl)phenoxy)methyl)benzonitrile (5f)



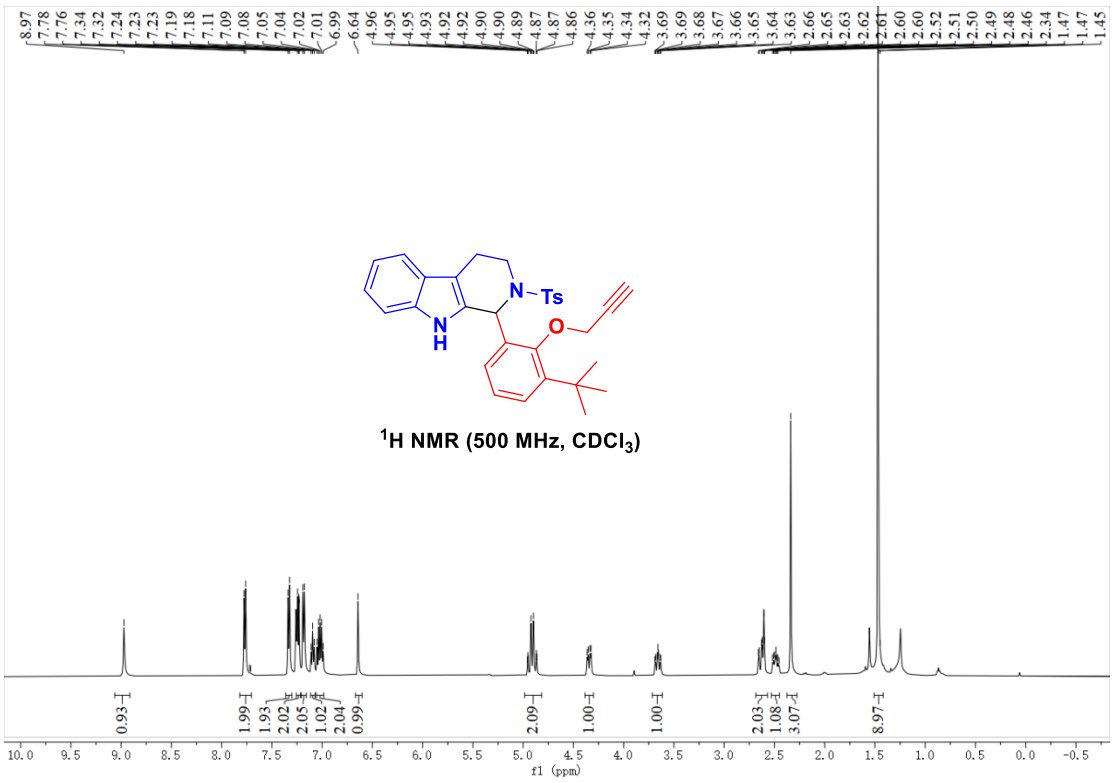


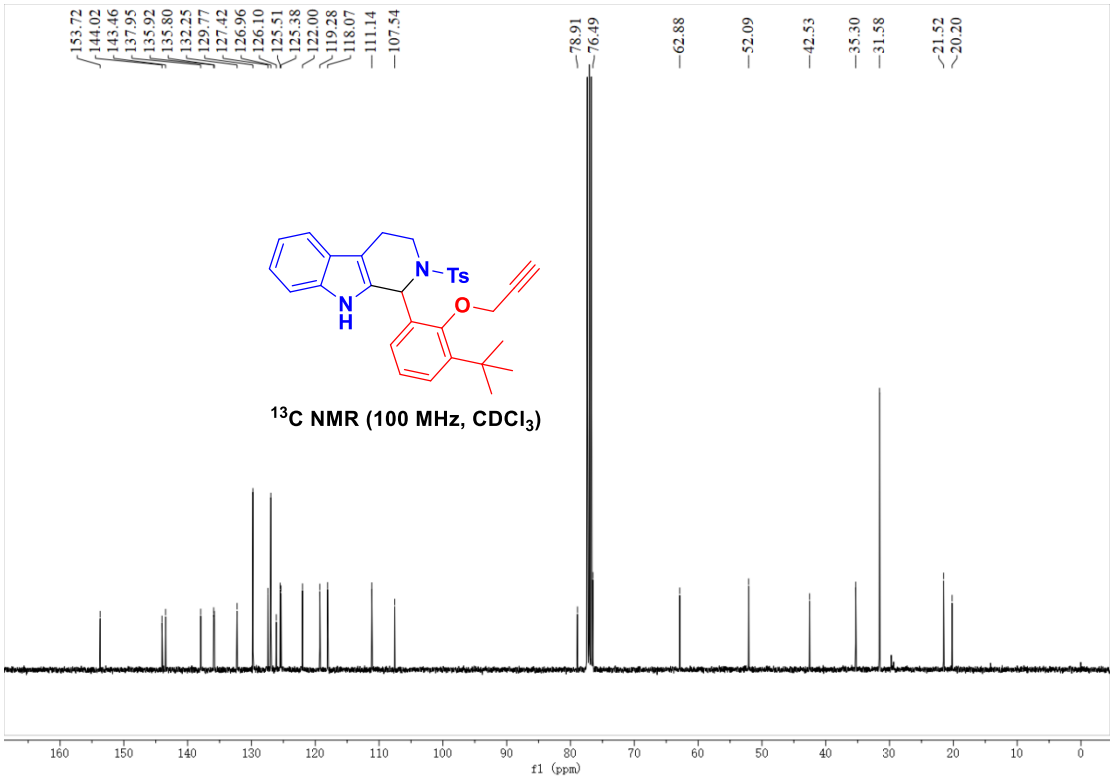
1-(2-(allyloxy)-3-(*tert*-butyl)phenyl)-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole (5g)



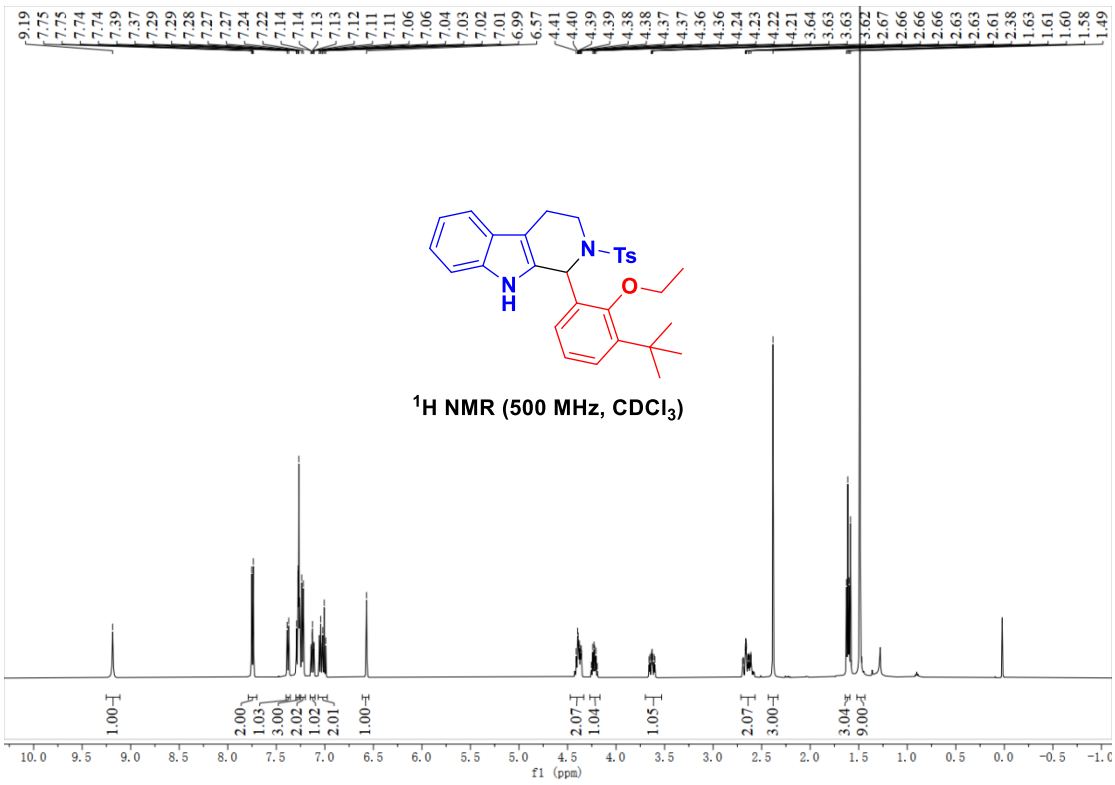


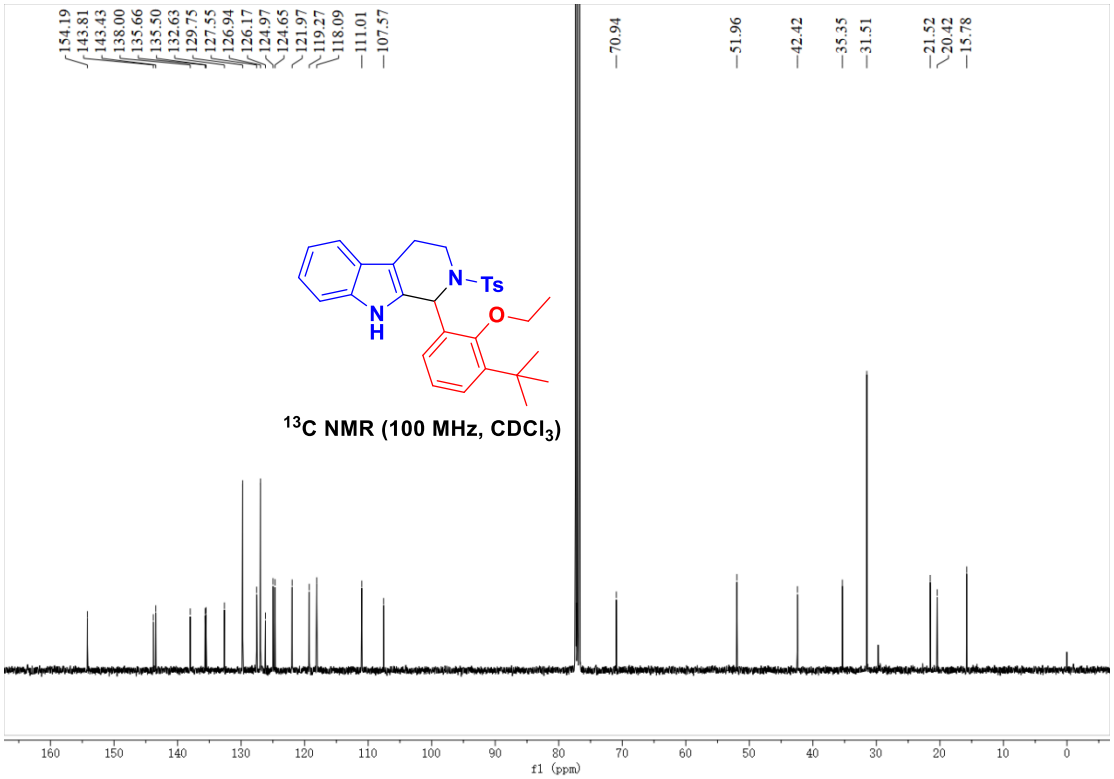
1-(3-(*tert*-butyl)-2-(prop-2-yn-1-yloxy)phenyl)-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole (5h)



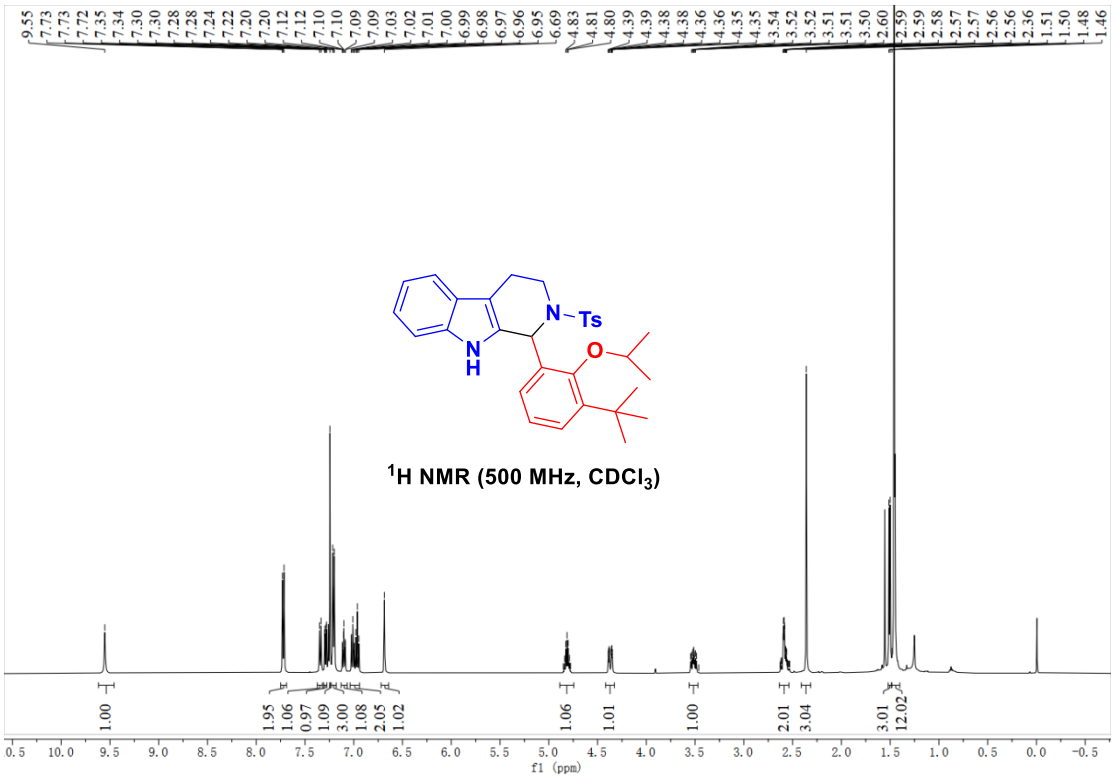


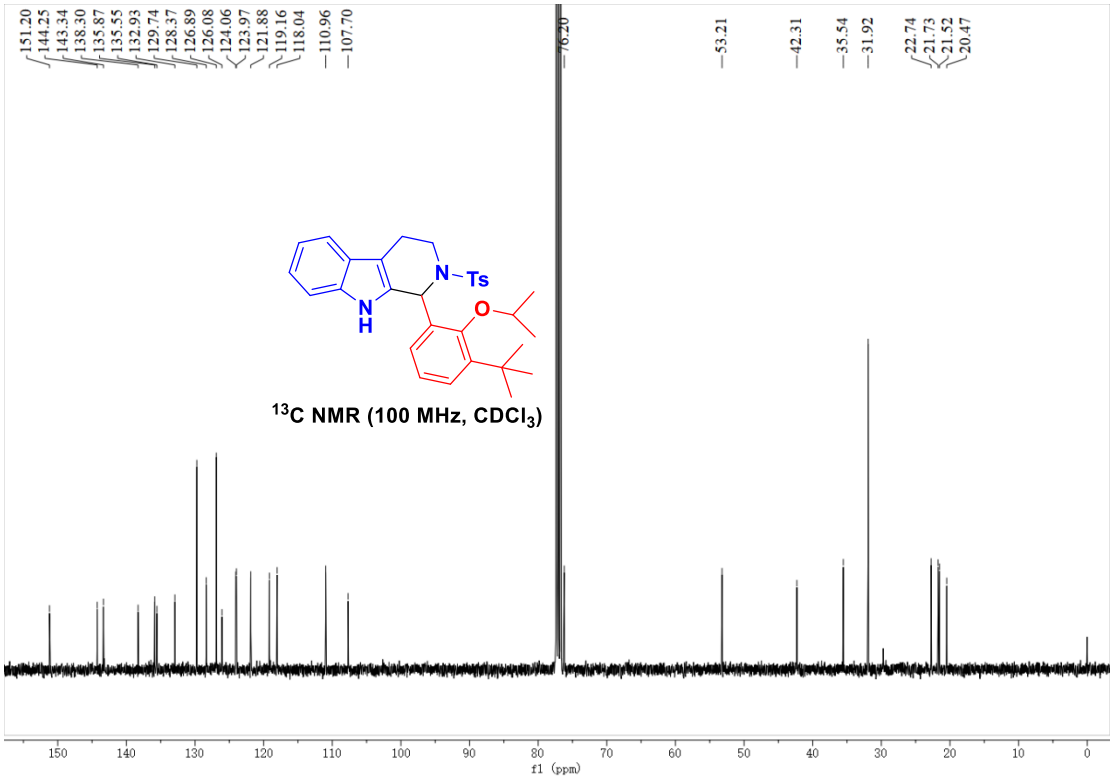
1-(3-(*tert*-butyl)-2-ethoxyphenyl)-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole (5i)



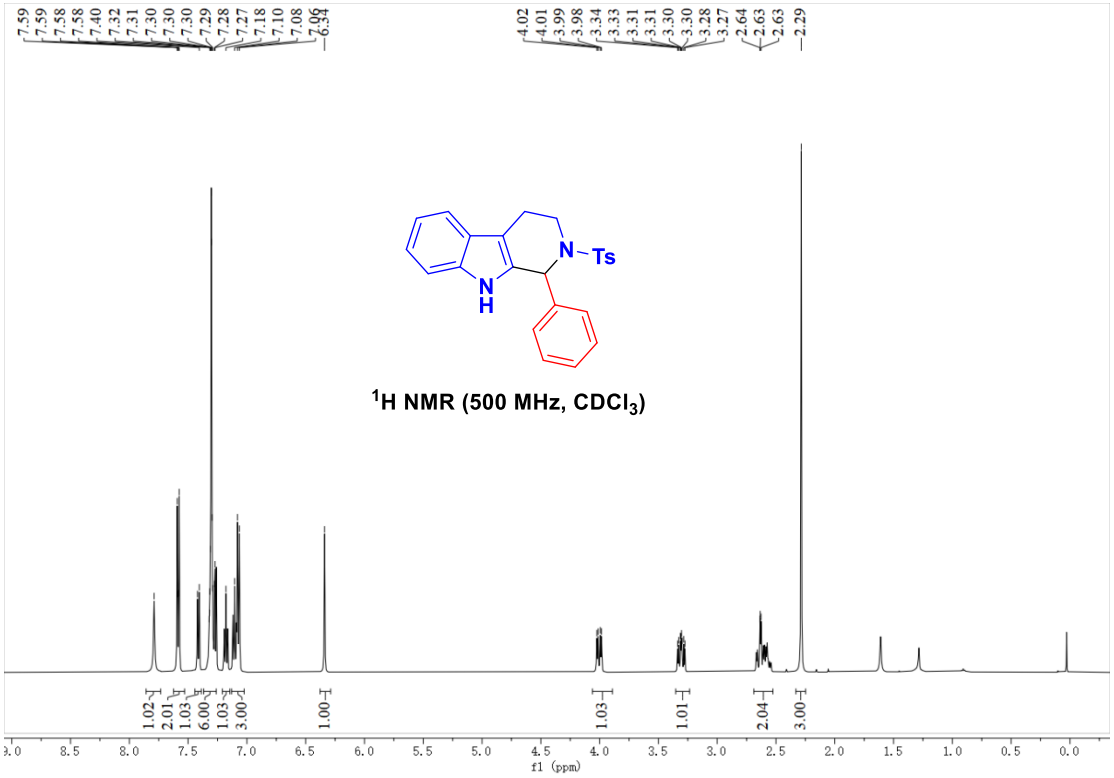


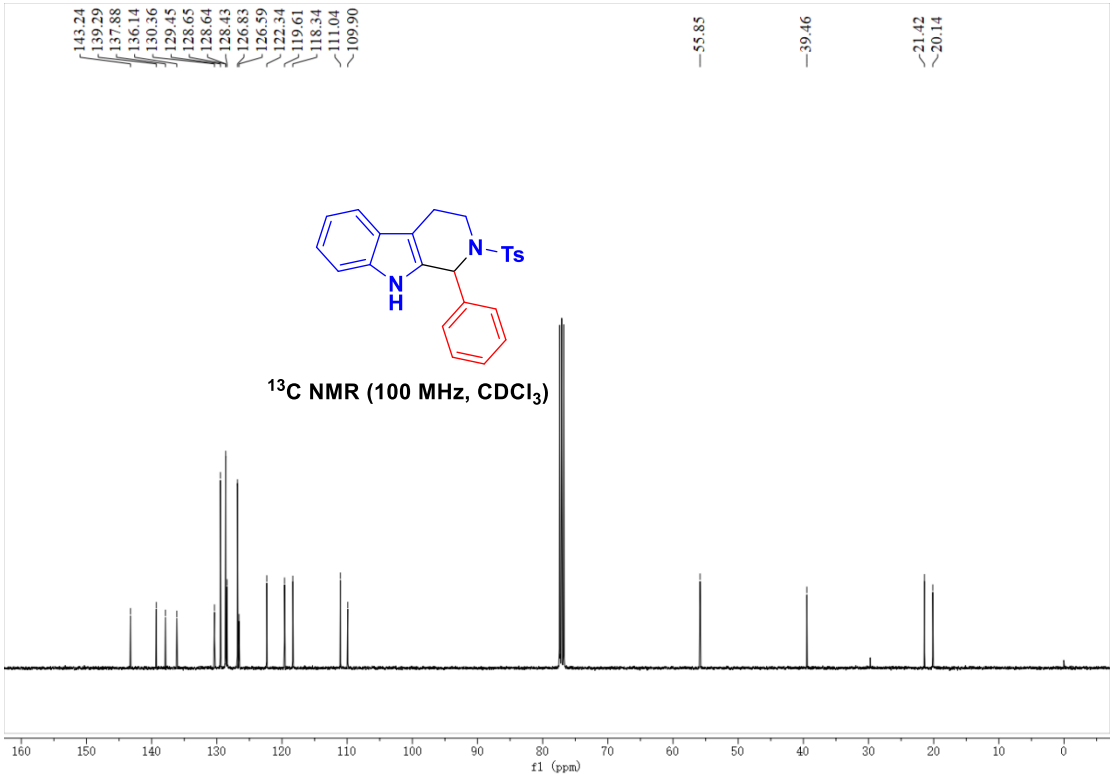
1-(3-(*tert*-butyl)-2-isopropoxyphenyl)-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*] indole (5j)



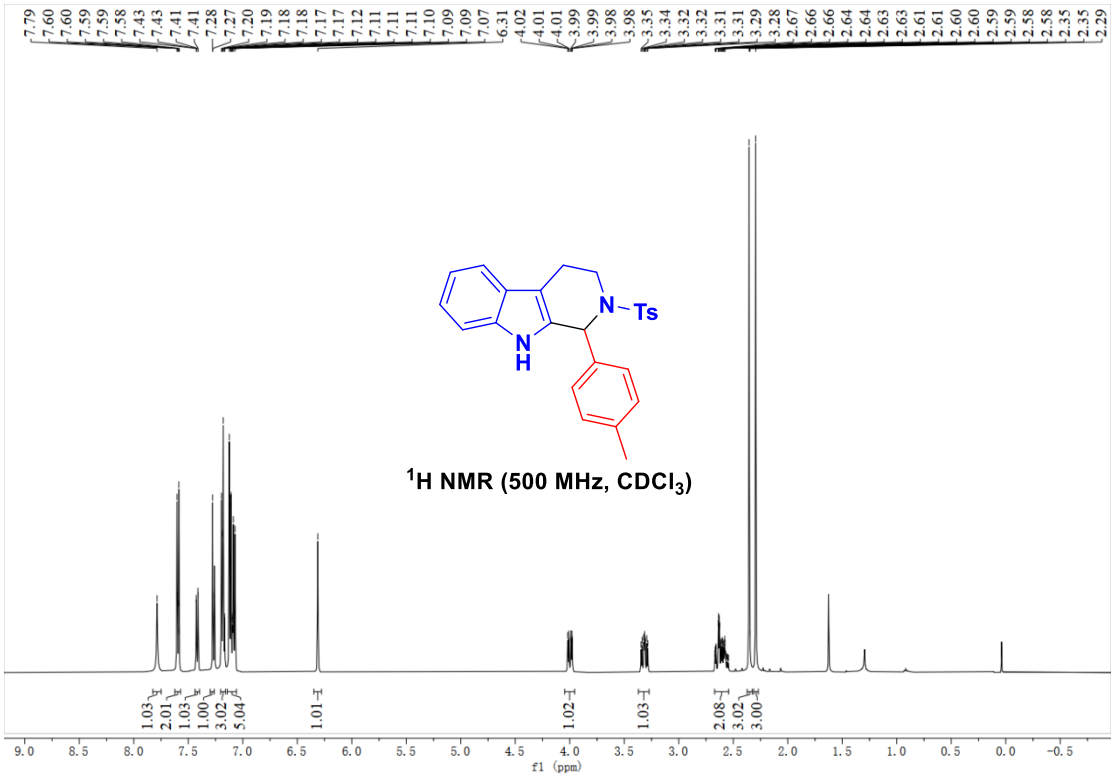


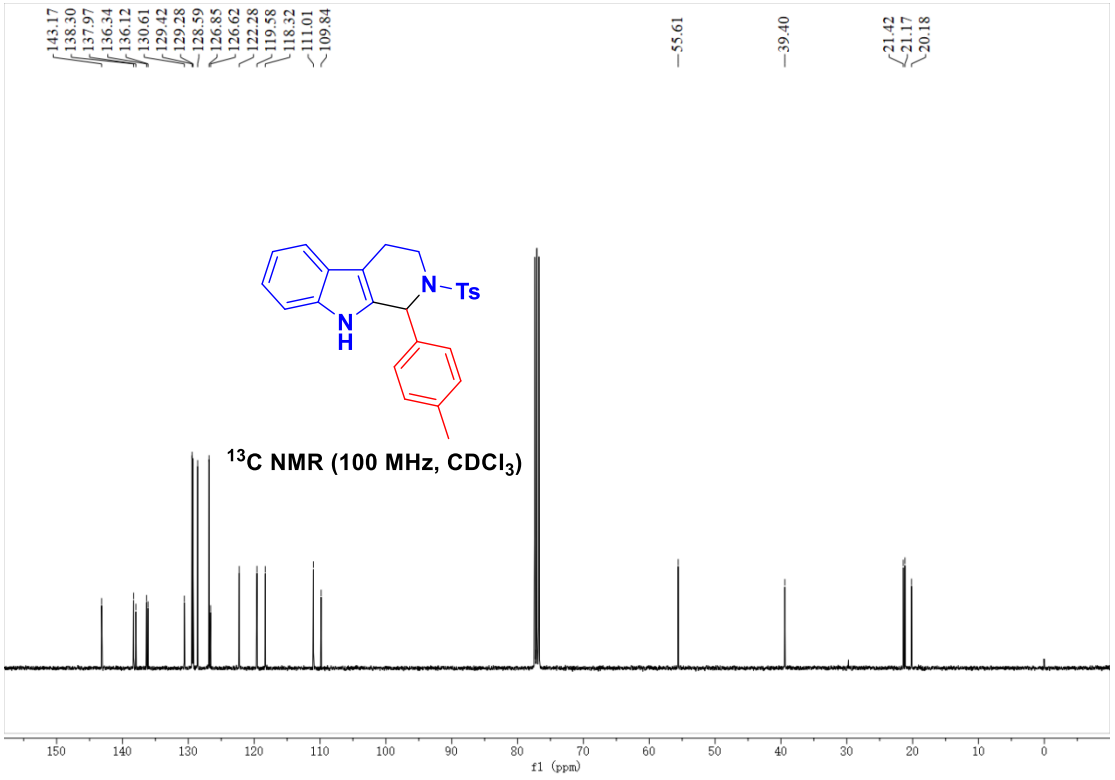
1-phenyl-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole (5k)



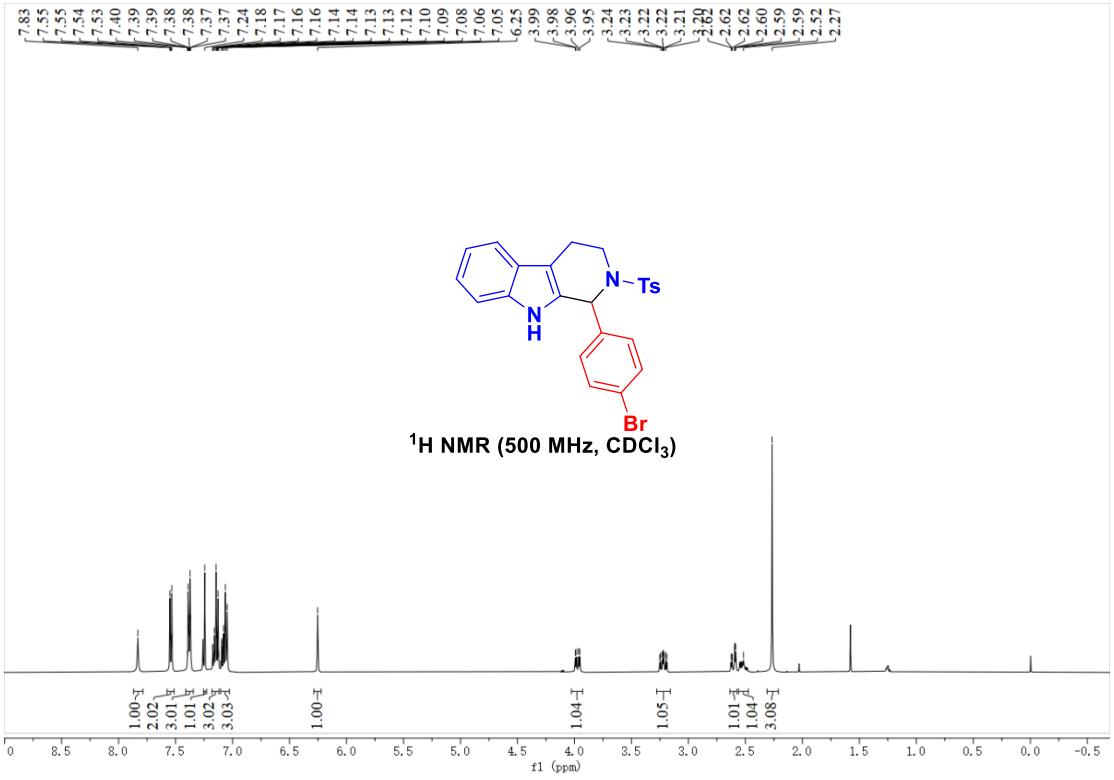


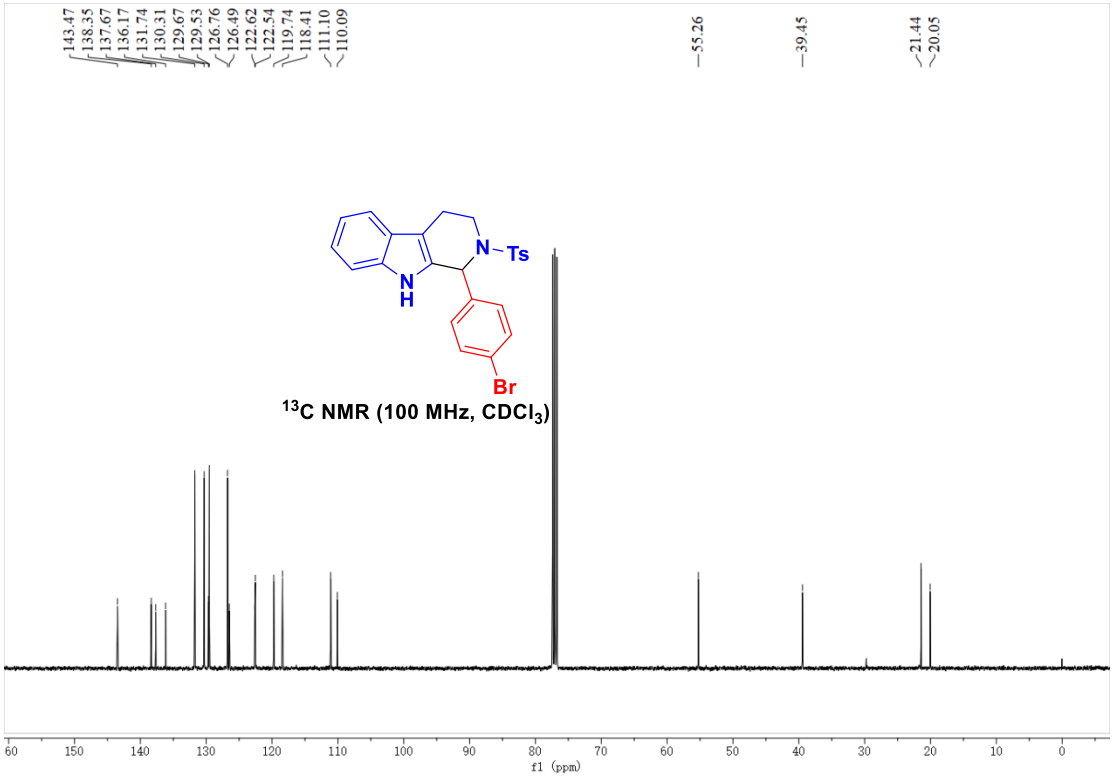
1-(*p*-tolyl)-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole (5l)



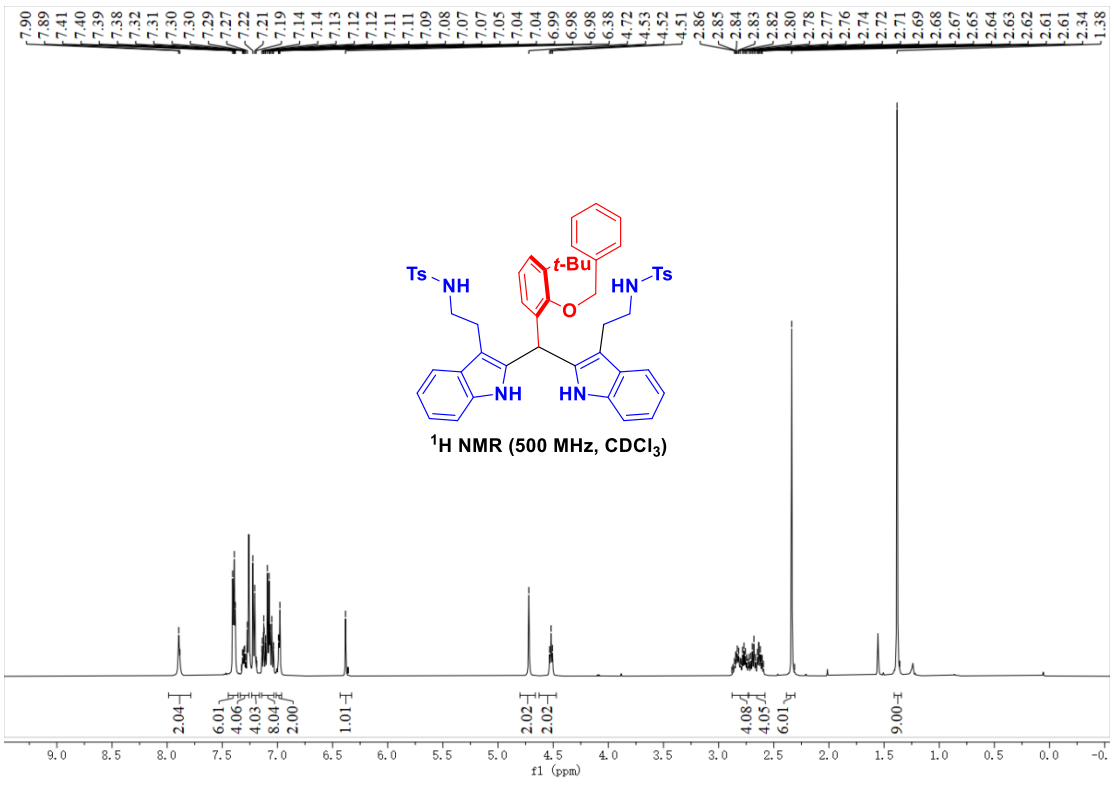


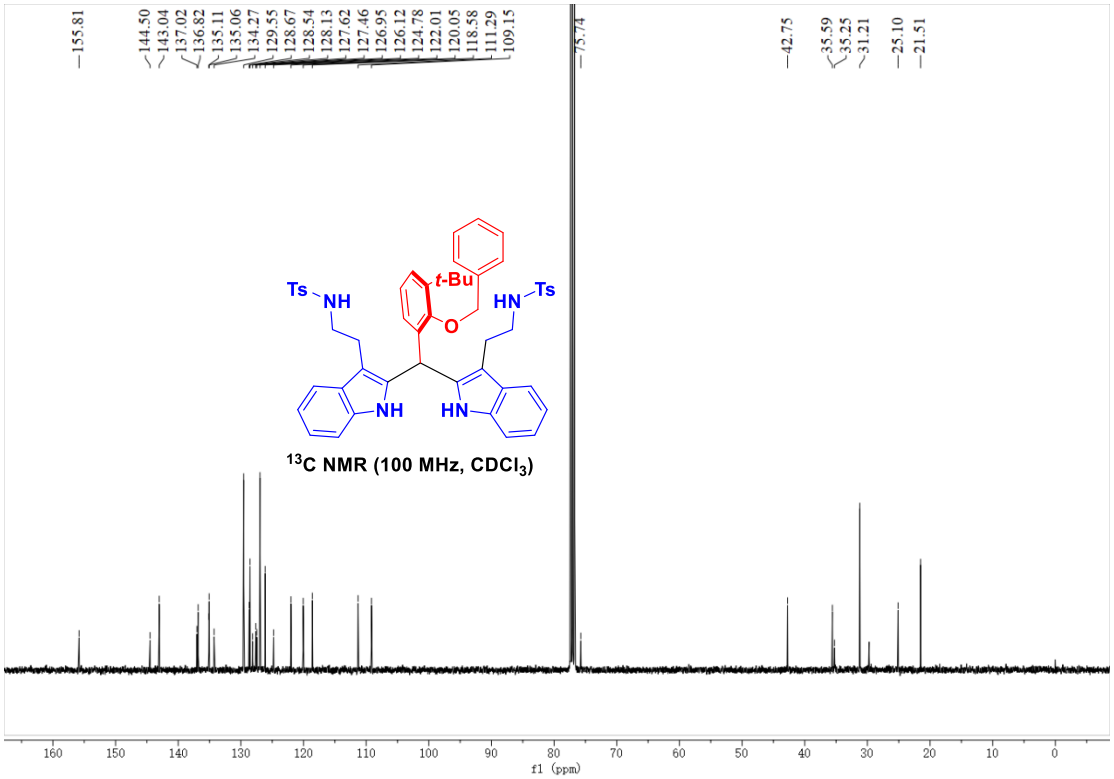
1-(4-bromophenyl)-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole (5m)



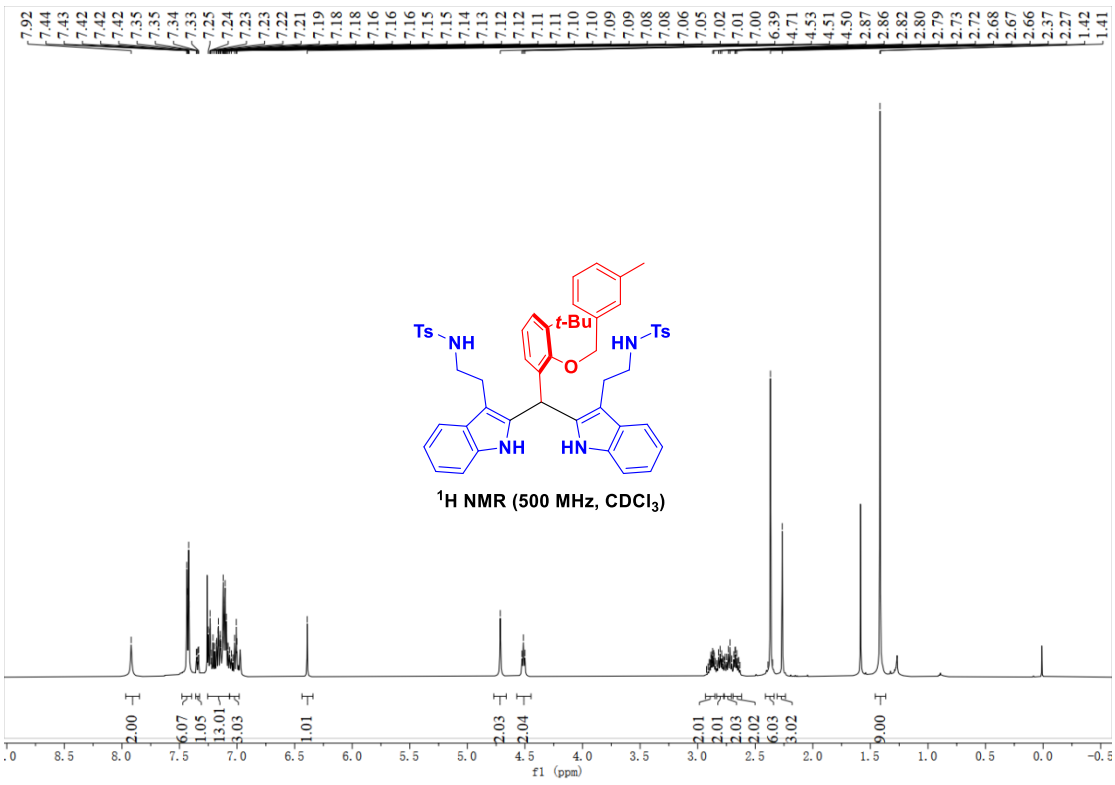


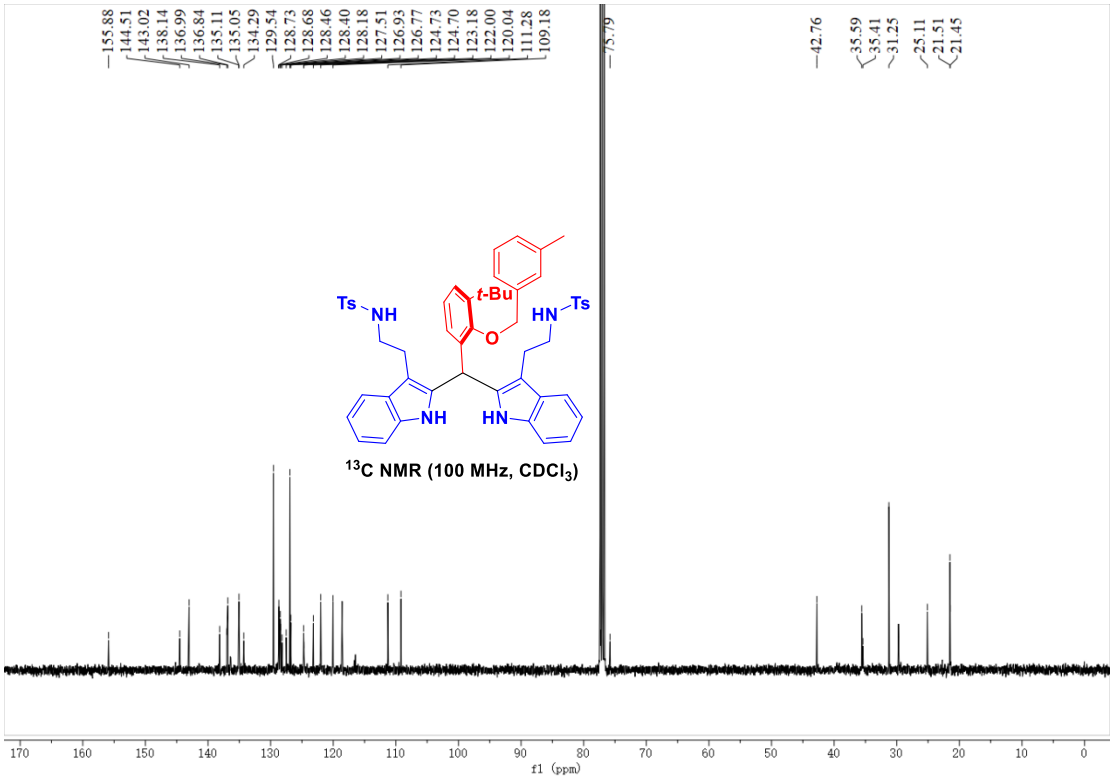
***N*,*N*'-((((2-(benzyloxy)-3-(*tert*-butyl)phenyl)methylene)bis(1*H*-indole-2,3-diyl))bis (ethane-2,1-diyl))bis(4-methylbenzenesulfonamide) (6a)**



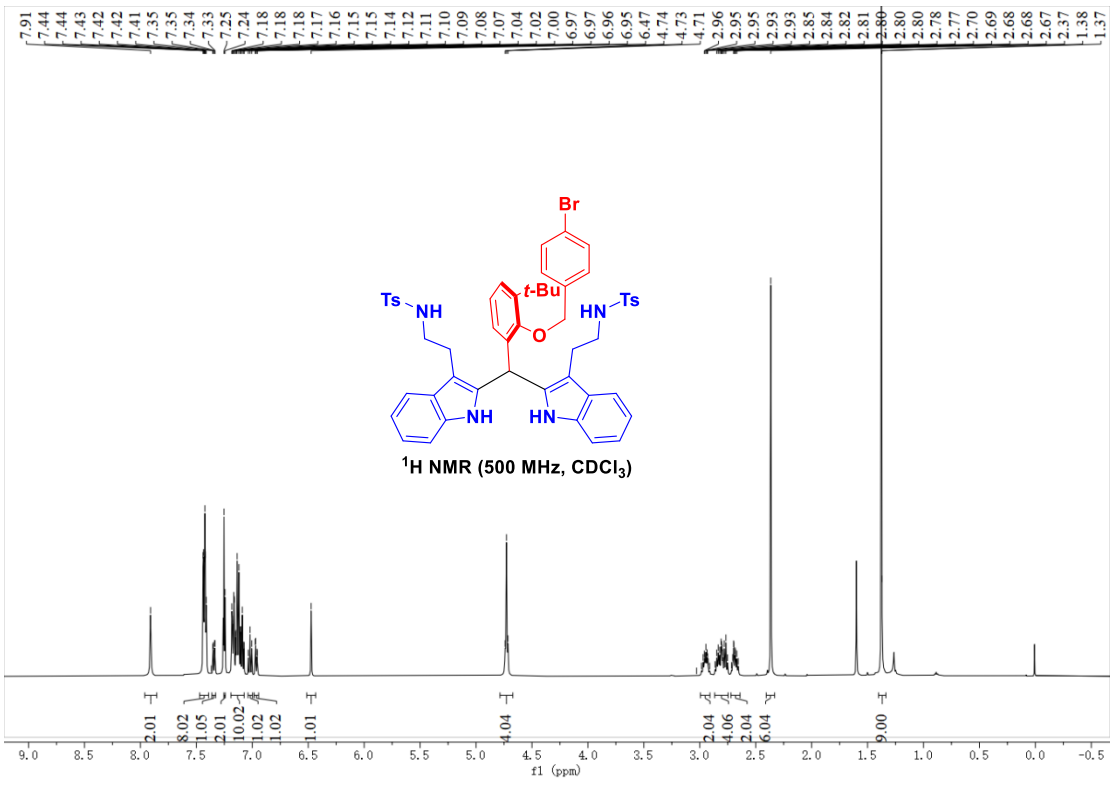


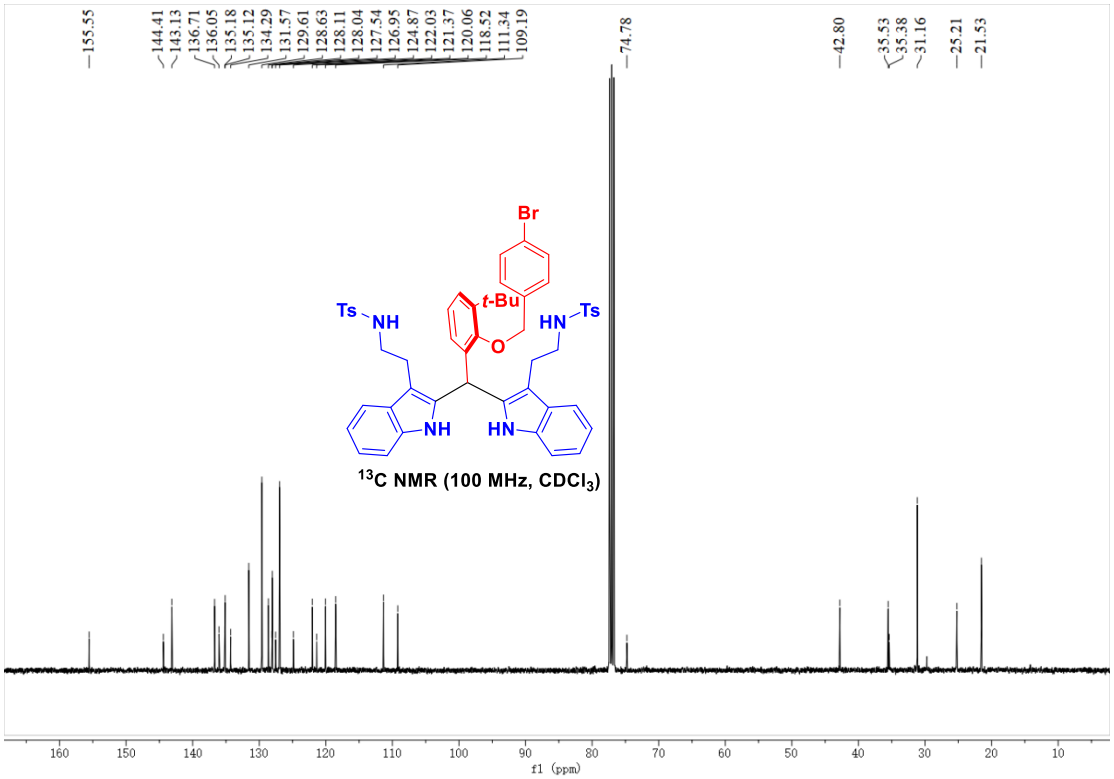
***N*,*N'*-((((3-(*tert*-butyl)-2-((3-methylbenzyl)oxy)phenyl)methylene)bis(1*H*-indole-2,3-diyl))bis(ethane-2,1-diyl))bis(4-methylbenzenesulfonamide) (6b)**



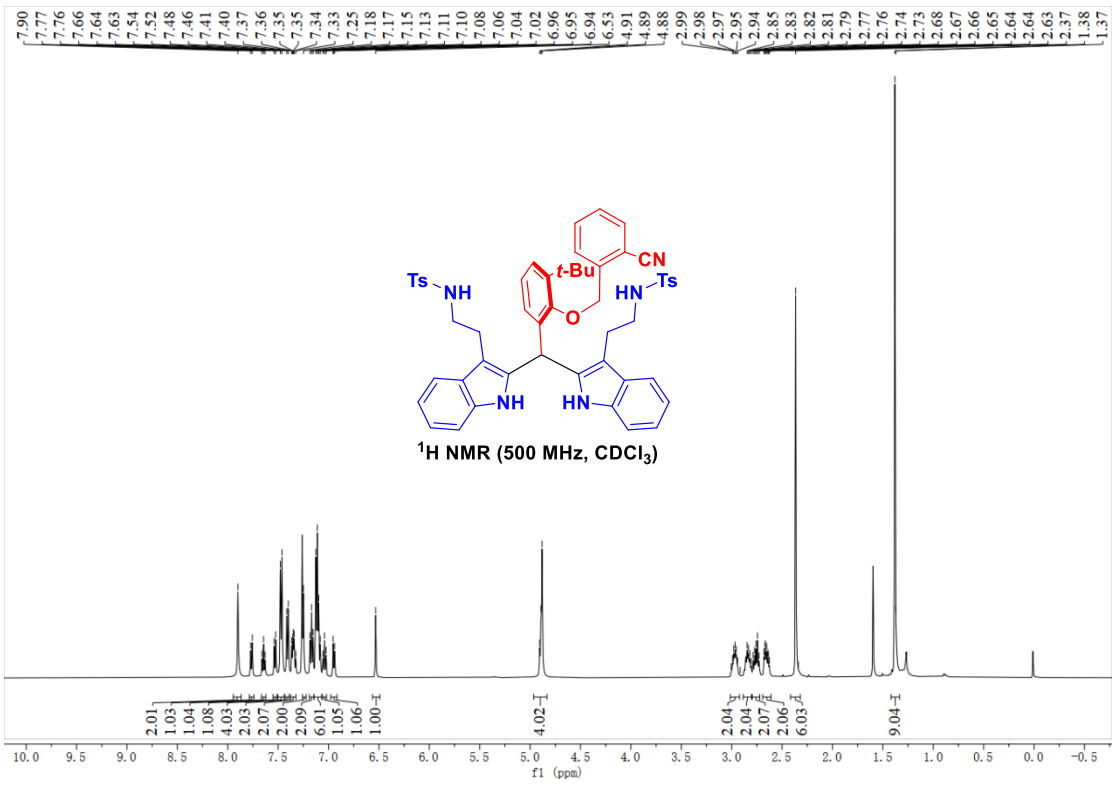


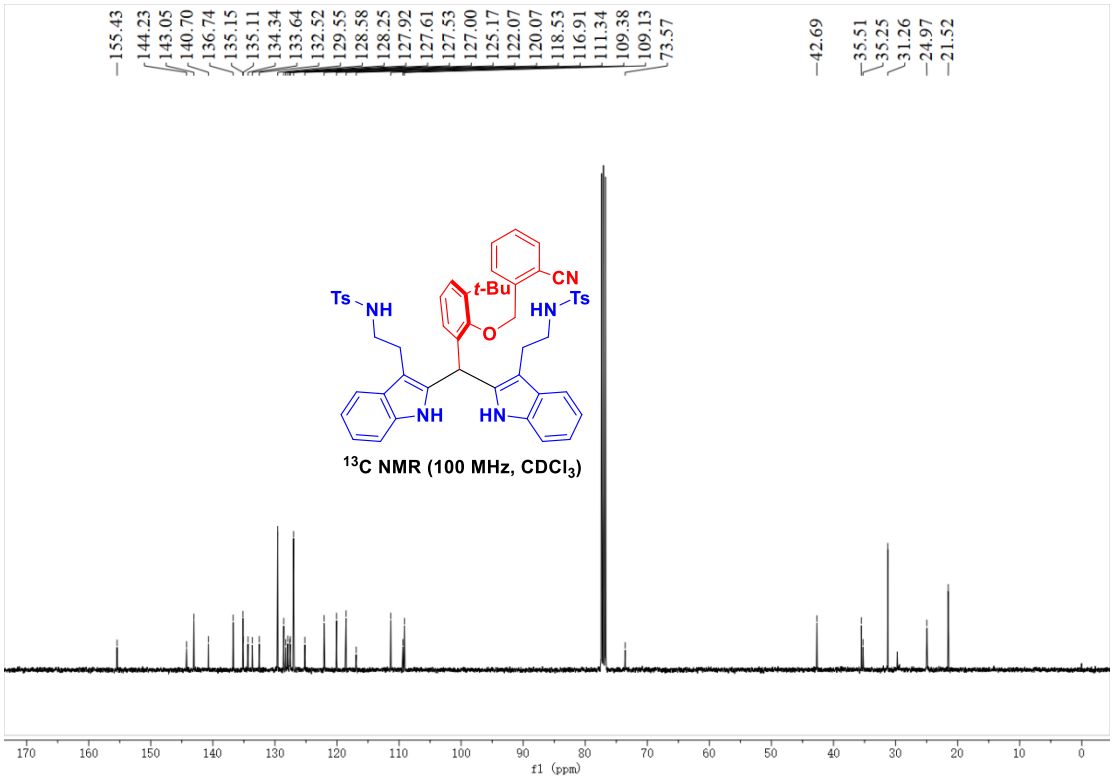
***N*,*N*'-((((2-((4-bromobenzyl)oxy)-3-(*tert*-butyl)phenyl)methylene)bis(1*H*-indole-2,3-diyl))bis(ethane-2,1-diyl))bis(4-methylbenzenesulfonamide) (6c)**



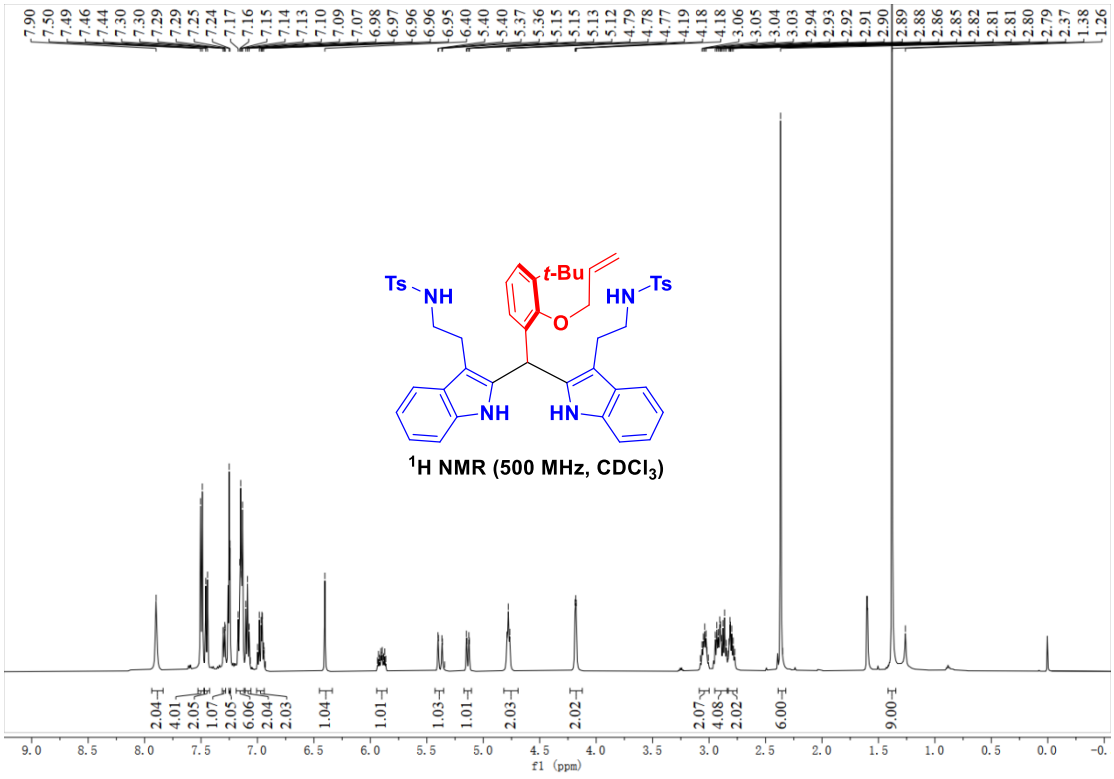


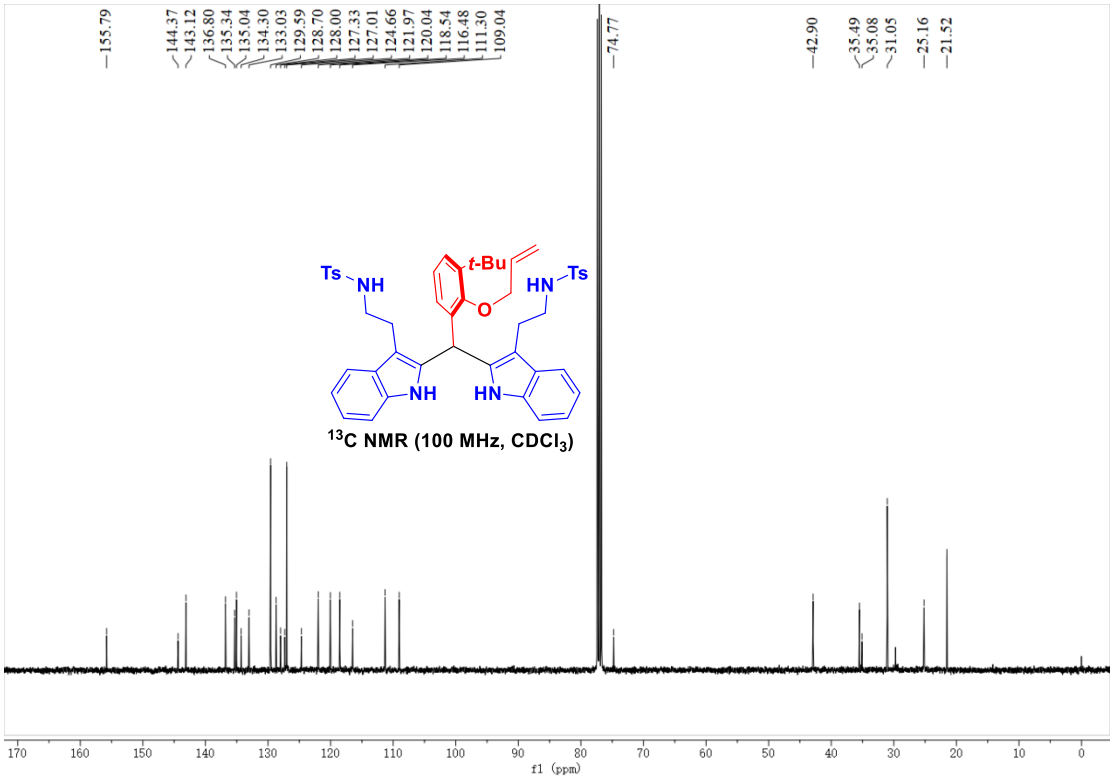
***N*,*N*'-((((3-(*tert*-butyl)-2-((2-cyanobenzyl)oxy)phenyl)methylene)bis(1*H*-indole-2,3-diyl))bis(ethane-2,1-diyl))bis(4-methylbenzenesulfonamide) (6d)**





***N*,*N*'-((((2-(allyloxy)-3-(*tert*-butyl)phenyl)methylene)bis(1*H*-indole-2,3-diyl))bis(ethane-2,1-diyl))bis(4-methylbenzenesulfonamide) (6e)**





***N*,*N*'-((((3-(*tert*-butyl)-2-(prop-2-yn-1-yloxy)phenyl)methylene)bis(1*H*-indole-2,3-diyl))bis(ethane-2,1-diyl))bis(4-methylbenzenesulfonamide) (6f)**