Supporting Information

Organocatalytic Cascade Aldimine Condensation/[1,6]-Hydride Transfer/Mannich-Type Cyclization : Sustainable Access to Indole-2,3-Fused Diazocanes

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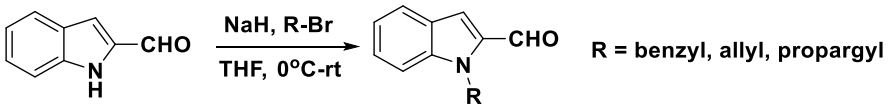
1. General Information

Unless otherwise noted, all reagents and solvents were purchased from the commercial sources 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 isolated and purified by flash column chromatography (200-300 mesh silica gel) eluted with the gradient of petroleum ether and ethyl acetate. Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on a Bruker 500 MHz NMR spectrometer ($CDCl_3$ solvent). The chemical shifts were reported in parts per million (ppm), downfield from $SiMe_4$ (δ 0.0). 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 (ESI-TOF) was performed on Waters Q-TOF-MS.

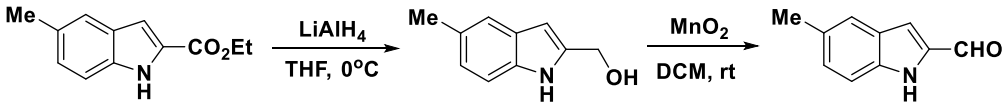
2. General Procedure

2.1 General procedure for the synthesis of 1b, 1c, 1d.[1]



To a stirred solution of 1H-indole-2-carbaldehyde (0.8 g, 5.7 mmol) in anhydrous THF (30 mL) at 0 ℃ was added NaH (60% dispersion in mineral oil, 0.3 g, 14.3 mmol). The mixture was stirred at 0 ℃ for 30 minutes. To the stirred solution was added R-Br (6.8 mmol) in THF (2 mL) dropwise at 0 ℃, then the reaction mixture was allowed to warm to room temperature and stirred until the starting material disappeared (monitored by TLC). The reaction was quenched by the dropwise addition of EtOH at 0 ℃. After evaporation of the solvent, the crude product was directly purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether = 1:200) to afford the desired products **1b-1d** (**1b**, 90% yield; **1c**, 83% yield; **1d**, 75% yield).

2.2 General procedure for the synthesis of 1j.[2]

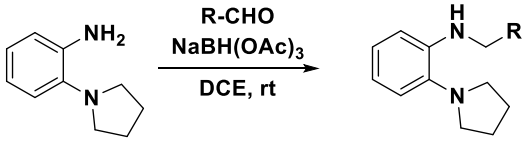


To a stirred solution of ethyl 5-methyl-1H-indole-2-carboxylate (2.2 g, 10.6 mmol) in 30 mL THF at 0 ℃ dropwisely added lithium aluminum hydride solution (2.5M, in THF 5.0 mL, 12.7 mmol) and the reaction mixture was stirred at 0 ℃ until completion of the reaction as indicated by TLC analysis. The reaction was quenched with H_2O, 15% NaOH and H_2O before it was filtered and rinsed with THF. The organic phase was dried (anhydrous Na_2SO_4) and concentrated to give (5-methyl-1H-indol-2-yl)methanol in 71% yield (1.2 g).

To a stirred solution of crude (5-methyl-1H-indol-2-yl)methanol (1.2 g, 7.5 mmol) in anhydrous DCM (20 mL) at 10 ℃ was added MnO_2 (3.3 g, 37.5 mmol). The reaction mixture was stirred at room temperature for 24 hours. Then the mixture was diluted with DCM and filtered through a pad of celite and washed with DCM. After evaporation of the solvent, the crude product was directly purified by flash column

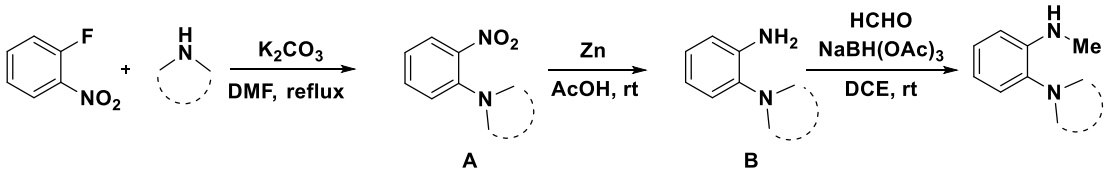
chromatography on silica gel (eluent: ethyl acetate/petroleum ether = 1:100) to afford 5-methyl-1H-indole-2-carbaldehyde in 65% yield (0.78 g).

2.3 General procedure for the synthesis of 2a, 2l, 2m, 2n, 2o, 2p, 2q, 2r, 2s.[3]



To a stirred solution of 2-(pyrrolidin-1-yl)aniline (0.4 g, 2.5 mmol) in DCE (10 mL) was added aldehyde (2.8 mmol) for 30 minutes. $NaHB(OAc)_3$ (1.1 g, 5.0 mmol) was added to the stirred solution, then the mixture was stirred at room temperature until completion of the reaction as indicated by TLC analysis. The solution was basified with sat. $NaHCO_3$ solution, extracted with ethyl acetate (3 x 25 mL) and subsequently dried with Na_2SO_4. After evaporation of the solvent, the crude product was directly purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether = 1:500) to afford the desired products (**2a**, 45% yield; **2l**, 47% yield; **2m**, 45% yield; **2n**, 90% yield; **2o**, 85% yield; **2p**, 75% yield; **2q**, 80% yield; **2r**, 80% yield; **2s**, 65% yield).

2.4 General procedure for the synthesis of 2t, 2u.[3, 4]

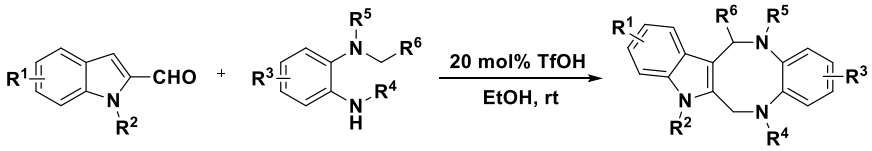


To a stirred solution of 1-fluoro-2-nitrobenzene (0.7 g, 5.0 mmol) and potassium carbonate (1.4 g, 10.0 mmol, 2 equiv.) in DMF (20 mL) was added the amine (6.0 mmol, 1.2 equiv.). The resulting reaction mixture was heated under reflux until completion of the reaction as indicated by TLC analysis. The mixture was subsequently allowed to cool to room temperature, diluted with water (5 mL), and extracted with ethyl acetate (2 x 25 mL). The combined organic layers were washed with a saturated NaCl solution (2 x 25 mL) and subsequently dried with Na_2SO_4. After evaporation of the solvent directly purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether = 1:500) to afford the desired product **A** (**A-2t**, 86% yield; **A-2u**, 90% yield).

To a stirred solution of compound **A** (4.3 mmol) in AcOH (8 mL) was added zinc powder (1.4 g, 21.5 mmol, 5 equiv.) portion wise for 10 minutes. The resulting reaction mixture was stirred at room temperature until completion of the reaction as indicated by TLC analysis. The solution was filtered and evaporated at reduced pressure. The residue was basified with sat. $NaHCO_3$ solution, extracted with ethyl acetate (3 x 25 mL) and subsequently dried with Na_2SO_4. After evaporation of the solvent, the crude product was directly purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether = 1:200) to afford the desired product **B** (**B-2t**, 60% yield; **B-2u**, 70% yield).

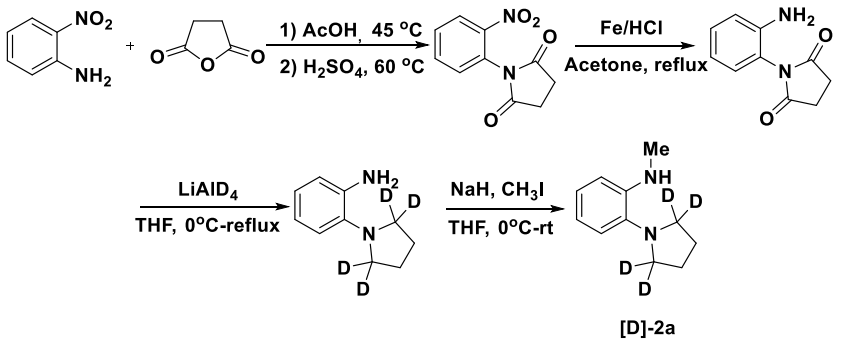
To a stirred solution of compound **B** (2.5 mmol) in DCE (10 mL) was added aldehyde (2.8 mmol) for 30 minutes. $NaHB(OAc)_3$ (1.1 g, 5.0 mmol) was added to the stirred solution, then the resulting mixture was stirred at room temperature until completion of the reaction as indicated by TLC analysis. The solution was basified with sat. $NaHCO_3$ solution, extracted with ethyl acetate (3 x 25 mL) and subsequently dried with Na_2SO_4. After evaporation of the solvent, the crude product was directly purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether = 1:500) to afford the desired product (**2t,** 45% isolated yield; **2u,** 55% isolated yield).

2.5 General procedure for the synthesis of 3.



A sealed tube was charged with **1** (0.1 mmol), **2** (0.2 mmol), TfOH (0.02 mmol, 3.0 mg) and EtOH (1.0 mL). The mixture was stirred at room temperature under an air atmosphere. After 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 = 1:250) to afford the desired product **3**.

2.6 General procedure for the synthesis of [D]-2a.[5, 6]



To a vigorously stirred solution of the 2-nitroaniline (5.5 g, 40.0 mmol) in acetic acid (30 mL), the anhydride (4.4 g, 44.0 mmol) was added in one lot. The reaction mixture was stirred further for 10 minutes at 45 ℃. The clear solution turned into slurry, then the concentrated sulfuric acid (9.2 g, 93.8 mmol) was added in one lot. The temperature of reaction was then maintained at 60 ℃ for 30 – 45 minutes. The cooled mixture was poured onto crushed ice. The solid separated was collected, washed with aqueous sodium bicarbonate and then with water, and recrystallized from aqueous ethanol to afford the desired product 1-(2-nitrophenyl)pyrrolidine-2,5-dione (3.1 g, 35% yield).

To a solution of 1-(2-nitrophenyl)pyrrolidine-2,5-dione (3.1 g, 14.1 mmol) in 20 mL acetone was added glacial acetic acid (11 mL), water (11 mL) and iron powder (9.5 g, 170 mmol). The reaction mixture was heated to reflux. After 8 h, the reaction was cooled and filtered through pad of celite. The filtrate was concentrated under vacuum. From the filtrate the compound was obtained as a yellow solid then the crude product was directly purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether = 1:100) to afford the desired product 1-(2-aminophenyl)pyrrolidine-2,5-dione (1.5 g, 55% yield).

To ethyl 1-(2-aminophenyl)pyrrolidine-2,5-dione (1.5 g, 7.8 mmol) in 10 mL THF at 0 ℃ was added $LiAlD_4$ (1.6 g, 39.0 mmol, 5 equiv.). The resulting reaction mixture was heated under reflux until completion of the reaction as indicated by TLC analysis. The reaction was quenched by the dropwise addition of H_2O. After evaporation of the solvent directly purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether = 1:200) to afford the desired product

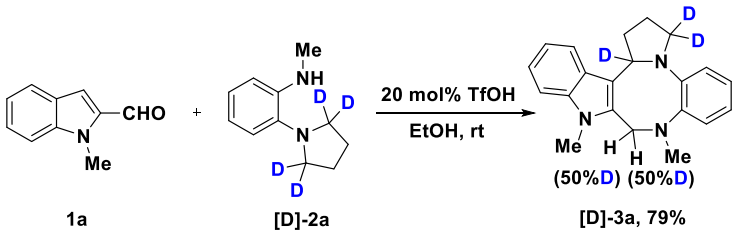
2-(pyrrolidin-1-yl-2,2,5,5-d4)aniline (0.5 g, 40% yield).

To a stirred solution of 2-(pyrrolidin-1-yl-2,2,5,5-d4)aniline (0.5 g, 3.1 mmol) in anhydrous THF (30 mL) at 0 ℃ was added NaH (60%, 0.12 g, 5.0 mmol). The reaction mixture was stirred at 0 ℃ for 30 minutes. To the stirred solution was added CH_3I (0.3 g, 2.4 mmol) in THF (2 mL) dropwise at 0 ℃, then the mixture was allowed to warm to room temperature and stirred until the starting material disappeared (monitored by TLC). The reaction was quenched by the dropwise addition of EtOH at 0 ℃. After evaporation of the solvent directly purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether = 1:500) to afford the desired product **[D]-2a** (0.3 g, 48% yield).

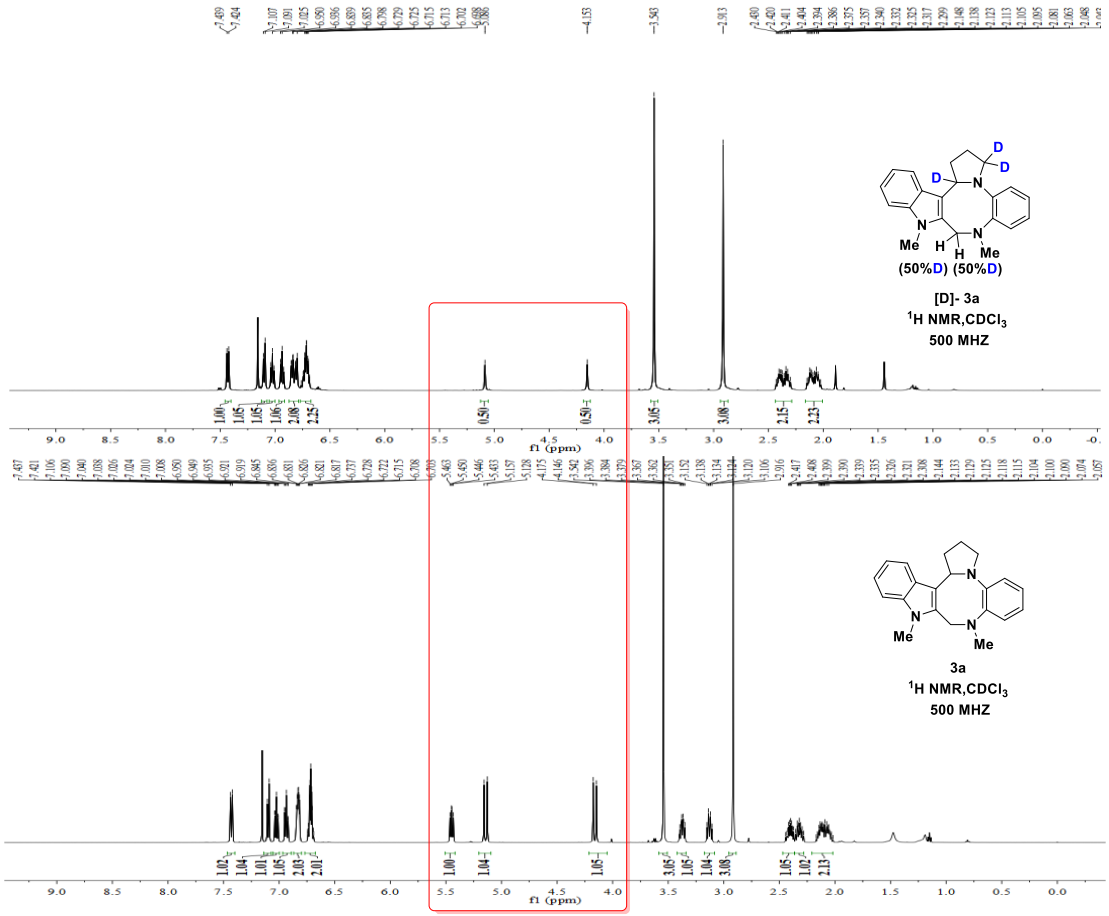
2.7 Reference

1. D. Uredi, D. Motati and E. Watkins, *Org. Lett.*, 2018, **20**, 6336.
2. P. Zheng, S. Wu, C. Mou, W. Xue, Z. Jin and Y. R. Chi, *Org. Lett*., 2019, **21**, 5026.
3. D. M. Wang, M. N. Sun and G. Liu, *J. Comb. Chem*., 2009, **11**, 556.
4. K. Ramakumar , T. Maji , J. J. Partridge and J. A Tunge, *Org. Lett.*, 2017, **19**, 4014.
5. S. V. Patil, K. A. Mahale, K. S. Gosavi, G. B. Deshmukh and N. S. Patil, *Organic Preparations and Procedures International*., 2013, **45**, 314.
6. K. Maji, M. Abbasi, D. Podder, R. Datta and D. Haldar, *ChemistrySelect.*, 2018, **3**, 10220.

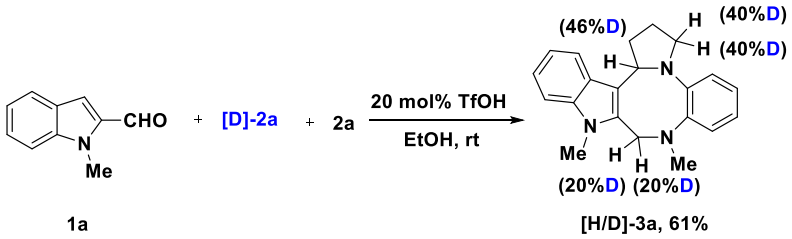
3. Mechanistic Study



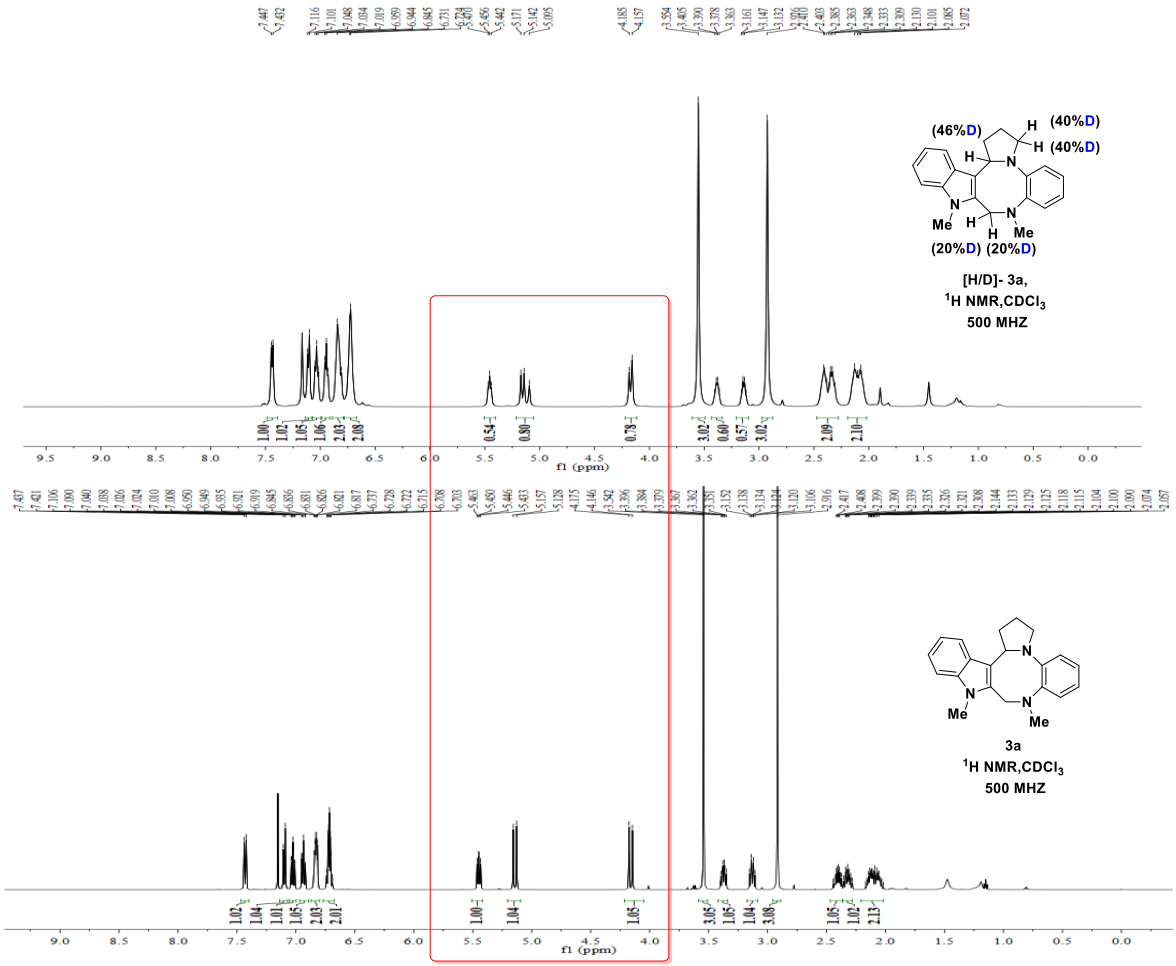
A sealed tube was charged with **1a** (0.1 mmol, 15.9 mg) and deuterated substrate **[D]-2a** (0.2 mmol, 36.1mg), TfOH (0.02 mmol, 3.0 mg) and EtOH (1.0 mL). The mixture was stirred at room temperature under an air atmosphere. After completion of the reaction as indicated by TLC analysis, the mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether = 1:250) to afford the desired product **[D]-3a** as a white solid in 79% yield (25.4 mg).



KIE experiment

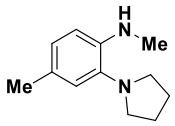


A sealed tube was charged with **1a** (0.1 mmol, 15.9 mg), deuterated substrate **[D]-2a** (0.1 mmol, 18.0 mg), **2a** (0.1 mmol, 17.6 mg) TfOH (0.02 mmol, 3.0 mg) and EtOH (1.0 mL). The mixture was stirred at room temperature under an air atmosphere. The reaction was controlled within 12 h, then the mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether = 1:250) to afford the product **[H/D]-3a** as a yellow solid in 61% yield (19.6 mg).



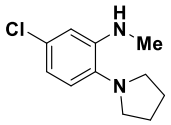
4. Characterization of Products

N,4-dimethyl-2-(pyrrolidin-1-yl)aniline (2l)



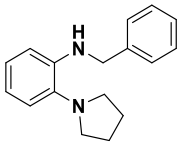
Red oil; 13.3 mg, 35% yield; column chromatography eluent, petroleum ether/EtOAc = 500:1; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 6.76 – 6.71 (m, 2H), 6.45 (d, *J* = 7.7 Hz, 1H), 4.19 (s, 1H), 2.97 – 2.84 (m, 4H), 2.74 (s, 3H), 2.17 (s, 3H), 1.85 – 1.74 (m, 4H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 142.48, 137.29, 125.90, 124.32, 119.15, 109.96, 51.24(2C), 31.36, 24.13(2C), 20.83; HRMS (ESI-TOF) m/z Calcd for $C_{12}H_{19}N_2$ $[M+H]^+$: 191.1543; found: 191.1543.

5-chloro-N-methyl-2-(pyrrolidin-1-yl)aniline (2m)



Red oil; 18.5 mg, 44% yield; column chromatography eluent, petroleum ether/EtOAc = 500:1; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 6.77 (dd, *J* = 8.3, 2.6 Hz, 1H), 6.55 – 6.48 (m, 1H), 6.46 – 6.39 (m, 1H), 4.45 (s, 1H), 2.93 – 2.76 (m, 4H), 2.71 (s, 3H), 1.85 – 1.71 (m, 4H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 145.84, 135.77, 129.63, 119.28, 115.89, 109.50, 51.37(2C), 30.66, 24.08(2C); HRMS (ESI-TOF) m/z Calcd for $C_{11}H_{16}ClN_2$ $[M+H]^+$: 211.0997; found: 211.0997.

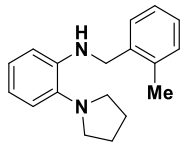
N-benzyl-2-(pyrrolidin-1-yl)aniline (2n)



Yellow oil; 22.0 mg, 87% yield; column chromatography eluent, petroleum ether/EtOAc = 500:1; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.33 – 7.29 (m, 1H), 7.26 (dd, J = 10.3, 4.9 Hz, 1H), 7.18 (t, J = 7.2 Hz, 1H), 6.96 (dd, J = 7.8, 1.4 Hz, 1H), 6.86 (td, J = 7.7, 1.4 Hz, 1H), 6.61 (td, J = 7.6, 1.4 Hz, 1H), 6.51 (dd, J = 7.9, 1.3 Hz, 1H), 4.84 (s, 1H), 4.28 (s, 2H), 3.03 – 2.93 (m, 4H), 1.90 – 1.75 (m, 4H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 142.39, 139.03, 136.24, 127.51(2C), 126.21(2C), 125.91, 123.02, 117.37, 115.87, 109.29, 50.23(2C), 47.31, 23.05(2C); HRMS (ESI-TOF) m/z calcd for

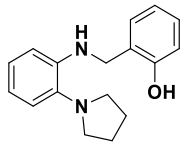
$C_{17}H_{21}N_2$ [M+H]$^+$: 253.1699; found: 253.1701.

N-(2-methylbenzyl)-2-(pyrrolidin-1-yl)aniline (2o)



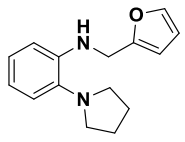
Yellow oil; 17.8 mg, 67% yield; column chromatography eluent, petroleum ether/EtOAc = 500:1; **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.14 – 7.04 (m, 3H), 6.97 – 6.89 (m, 2H), 6.85 – 6.79 (m, 1H), 6.57 (ddd, *J* = 7.5, 2.2, 1.0 Hz, 1H), 6.48 (d, *J* = 7.9 Hz, 1H), 4.76 (s, 1H), 4.18 (s, 2H), 2.99 – 2.88 (m, 4H), 2.22 (s, 3H), 1.88 – 1.71 (m, 4H); **^{13}C NMR (125 MHz, CDCl$_3$)** δ 143.77, 140.25, 138.30, 137.47, 128.67, 128.26, 127.93, 124.53, 124.31, 118.59, 117.11, 110.59, 51.48(2C), 48.63, 24.32(2C), 21.71; HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{23}N_2$ [M+H]$^+$: 267.1856; found: 267.1858.

2-(((2-(pyrrolidin-1-yl)phenyl)amino)methyl)phenol (2p)



Yellow Solid; 16.6 mg, 62% yield; mp 95 – 98 ℃; column chromatography eluent, petroleum ether/EtOAc = 100:1; **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.94 (s, 1H), 7.15 – 7.10 (m, 1H), 7.07 – 7.04 (m, 1H), 7.00 – 6.97 (m, 1H), 6.90 (td, *J* = 7.9, 1.4 Hz, 1H), 6.83 – 6.73 (m, 3H), 4.83 (s, 1H), 4.30 (s, 2H), 2.97 – 2,90(m, 4H), 1.86 – 1.75 (m, 4H); **^{13}C NMR (125 MHz, CDCl$_3$)** δ 157.20, 142.54, 139.68, 129.06, 128.56, 124.07, 123.44, 120.44, 119.98, 118.83, 116.63, 113.83, 51.79(2C), 49.16, 24.43(2C); HRMS (ESI-TOF) m/z Calcd for $C_{17}H_{21}N_2O$ [M+H]$^+$: 269.1648; found: 269.1650.

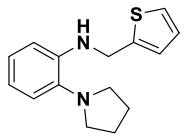
N-(furan-2-ylmethyl)-2-(pyrrolidin-1-yl)aniline (2q)



Yellow oil; 18.9 mg, 78% yield; column chromatography eluent, petroleum ether/EtOAc = 250:1; **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.26 (d, *J* = 0.9 Hz, 1H), 6.94 (dd, *J* = 7.7, 1.1 Hz, 1H), 6.88 (td, *J* = 7.7, 1.3 Hz, 1H), 6.65 – 6.56 (m, 2H), 6.21 (dd, *J* = 3.0, 1.9 Hz, 1H), 6.11 (d, *J* = 2.8 Hz, 1H), 4.78 (s, 1H), 4.23 (s, 2H), 2.99 – 2.85 (m, 4H), 1.87 – 1.73 (m, 4H); **^{13}C NMR (125 MHz, CDCl$_3$)** δ 152.36, 141.97, 140.65, 136.47, 122.99, 117.55, 116.29, 109.46, 109.22, 105.51, 50.28(2C), 40.57, 23.04(2C);

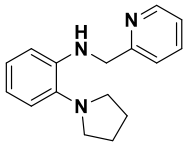
HRMS (ESI-TOF) m/z Calcd for $C_{15}H_{19}N_2O$ $[M+H]^+$: 243.1492; found: 243.1494.

2-(pyrrolidin-1-yl)-N-(thiophen-2-ylmethyl)aniline (2r)



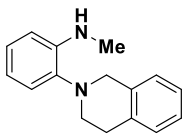
Yellow oil; 17.8 mg, 69% yield; column chromatography eluent, petroleum ether/EtOAc = 250:1; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.00 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.91 – 6.87 (m, 1H), 6.85 – 6.81 (m, 2H), 6.78 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.58 (td, *J* = 7.6, 1.3 Hz, 1H), 6.53 (dd, *J* = 7.9, 1.1 Hz, 1H), 4.78 (s, 1H), 4.34 (s, 2H), 2.96 – 2.84 (m, 4H), 1.82 – 1.67 (m, 4H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 144.25, 143.11, 137.78, 127.03, 124.68, 124.51, 124.26, 118.69, 117.76, 110.81, 51.46(2C), 43.91, 24.38(2C); HRMS (ESI-TOF) m/z Calcd for $C_{15}H_{19}N_2S$ $[M+H]^+$: 259.1263; found: 259.1266.

N-(pyridin-2-ylmethyl)-2-(pyrrolidin-1-yl)aniline (2s)



Yellow oil; 20.5mg, 81% yield; column chromatography eluent, petroleum ether/EtOAc = 250:1; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.49 – 8.42 (m, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.03 – 6.97 (m, 1H), 6.92 (dd, *J* = 7.8, 1.3 Hz, 1H), 6.80 (ddd, *J* = 7.7, 3.1, 1.6 Hz, 1H), 6.57 (ddd, *J* = 7.6, 3.1, 1.6 Hz, 1H), 6.44 – 6.39 (m, 1H), 5.22 (s, 1H), 4.38 (s, 2H), 3.04 – 2.89 (m, 4H), 1.88 – 1.74 (m, 4H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 159.69, 149.25, 143.10, 137.46, 136.70, 124.08, 121.95, 121.28, 118.54, 117.15, 110.51, 51.36(2C), 49.82, 24.20(2C); HRMS (ESI-TOF) m/z Calcd for $C_{16}H_{20}N_3$ $[M+H]^+$: 254.1652; found: 254.1653.

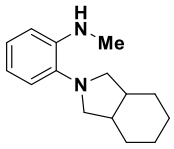
2-(3,4-dihydroisoquinolin-2(1H)-yl)-N-methylaniline (2t)



Yellow oil; 17.6 mg, 37% yield; column chromatography eluent, petroleum ether/EtOAc = 250:1; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.11 – 7.03 (m, 3H), 7.01 – 6.93 (m, 3H), 6.61 (td, J = 7.6, 1.3 Hz, 1H), 6.54 (dd, J = 8.0, 1.1 Hz, 1H), 4.67 (s, 1H), 3.94 (s, 2H), 3.10 (s, 2H), 2.90 (s, 2H), 2.71 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 143.51, 137.78, 134.49, 133.25, 127.86, 125.40, 125.21, 124.61, 124.24, 118.59,

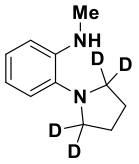
115.50, 108.51, 53.10, 48.48, 29.56, 28.98; HRMS (ESI-TOF) m/z Calcd for $C_{16}H_{19}N_2$ $[M+H]^+$: 239.1543; found: 239.1543.

N-methyl-2-(octahydro-2H-isoindol-2-yl)aniline (2u)



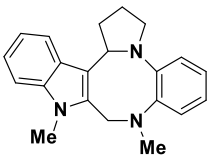
Red oil; 20.7 mg, 45% yield; column chromatography eluent, petroleum ether/EtOAc = 250:1; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 6.98 – 6.82 (m, 2H), 6.66 – 6.46 (m, 2H), 4.12 (s, 1H), 3.16 – 3.03 (m, 2H), 2.96 (dd, J = 8.6, 4.4 Hz, 1H), 2.75 (s, 3H), 2.27 – 2.10 (m, 2H), 1.62 – 1.38 (m, 6H), 1.36 – 1.18 (m, 2H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 143.39, 137.75, 122.07, 116.81, 115.81, 108.89, 54.46(2C), 36.58(2C), 30.08, 25.55(2C), 22.00(2C); HRMS (ESI-TOF) m/z Calcd for $C_{15}H_{23}N_2$ $[M+H]^+$: 231.1856; found: 231.1857.

N-methyl-2-(pyrrolidin-1-yl-2,2,5,5-d4)aniline [D]-2a



Red oil; 13.3 mg, 35% yield; column chromatography eluent, petroleum ether/EtOAc = 500:1; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 6.94 (t, *J* = 7.5 Hz, 2H), 6.61 (t, *J* = 7.5 Hz, 1H), 6.56 (d, *J* = 7.8 Hz, 1H), 4.40 (s, 1H), 2.79 (s, 3H), 1.83 – 1.80 (m, 4H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 144.89, 137.27, 124.31, 118.37, 116.73, 109.77, 51.33(2C), 31.03, 24.19(2C) ; HRMS (ESI-TOF) m/z Calcd for $C_{11}H_{13}D_4N_2$ $[M+H]^+$: 181.1637; found: 181.1638.

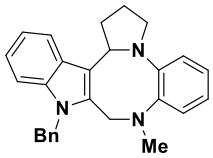
9,11-dimethyl-2,3,9,10,11,15c-hexahydro-1H-benzo[2,3]pyrrolo[1',2':1,8][1,4]diazocino[6,7-b]indole (3a)



White solid; 30.2 mg, 95% yield; mp 192 – 194 ℃; column chromatography eluent, petroleum ether/EtOAc = 250:1; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.43 (d, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 8.2 Hz, 1H), 7.05 – 7.00 (m, 1H), 6.96 – 6.91 (m, 1H), 6.85 – 6.81 (m, 2H), 6.76 – 6.68 (m, 2H), 5.45 (dd, *J* = 8.2, 6.6 Hz, 1H), 5.14 (d, *J* = 14.5 Hz, 1H), 4.16 (d, *J* = 14.5 Hz, 1H), 3.54 (s, 3H), 3.42 – 3.32 (m, 1H), 3.17 – 3.08 (m, 1H),

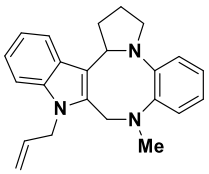
2.92 (s, 3H), 2.46 – 2.36 (m, 1H), 2.36 – 2.28 (m, 1H), 2.20 – 2.01 (m, 2H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 144.00, 143.26, 137.08, 135.03, 126.09, 122.96, 122.14, 120.93, 120.80, 120.65, 118.93 (2C), 114.01, 109.11, 60.88, 52.71, 50.91, 44.20, 31.28, 29.43, 24.02; HRMS (ESI-TOF) m/z Calcd for $C_{21}H_{24}N_3$ $[M+H]^+$: 318.1965; found: 318.1967.

11-benzyl-9-methyl-2,3,9,10,11,15c-hexahydro-1H-benzo[2,3]pyrrolo[1',2':1,8][1,4]diazocino[6,7-b]indole (3b)



Yellow solid; 35.0 mg, 89% yield; mp 90 – 92 ℃; column chromatography eluent, petroleum ether/EtOAc = 200:1; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.51 – 7.45 (m, 1H), 7.12 – 7.05 (m, 3H), 6.99 (dt, J = 6.2, 3.3 Hz, 1H), 6.97 – 6.92 (m, 2H), 6.75 (qd, J = 8.2, 4.2 Hz, 2H), 6.67 (dd, J = 10.0, 4.5 Hz, 2H), 6.63 (dd, J = 7.4, 1.4 Hz, 2H), 5.67 (t, J = 7.5 Hz, 1H), 5.18 (s, 2H), 4.85 (d, J = 14.0 Hz, 1H), 4.12 (d, J = 14.0 Hz, 1H), 3.43 – 3.32 (m, 1H), 3.17 – 3.07 (m, 1H), 2.69 (s, 3H), 2.48 – 2.40 (m, 2H), 2.23 – 2.04 (m, 2H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 143.98, 143.34, 137.75, 136.83, 135.05, 128.80 (2C), 127.17, 126.38, 125.86 (2C), 123.56, 121.86, 121.59, 121.10, 119.96, 119.31, 119.15, 114.37, 109.56, 60.23, 53.25, 50.75, 46.23, 44.04, 30.65, 23.98; HRMS (ESI-TOF) m/z Calcd for $C_{27}H_{28}N_3$ $[M+H]^+$: 394.2278; found: 394.2277.

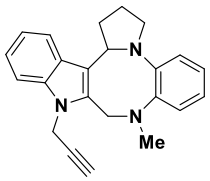
11-allyl-9-methyl-2,3,9,10,11,15c-hexahydro-1H-benzo[2,3]pyrrolo[1',2':1,8][1,4]diazocino[6,7-b]indole (3c)



Colorless oil; 28.7 mg, 83% yield; column chromatography eluent, petroleum ether/EtOAc = 250:1; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.45 (d, *J* = 7.8 Hz, 1H), 7.02 (d, *J* = 7.9 Hz, 1H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.93 (t, *J* = 7.3 Hz, 1H), 6.82 (d, *J* = 7.7 Hz, 1H), 6.78 – 6.70 (m, 2H), 6.68 – 6.61 (m, 1H), 5.80 – 5.69 (m, 1H), 5.65 (t, *J* = 7.5 Hz, 1H), 4.89 (d, *J* = 10.0 Hz, 1H), 4.82 (d, *J* = 14.5 Hz, 1H), 4.53 (s, 2H), 4.38 (d, *J* = 17.5 Hz, 1H), 4.13 (d, *J* = 14.0 Hz, 1H), 3.41 – 3.31 (m, 1H), 3.15 – 3.04 (m,

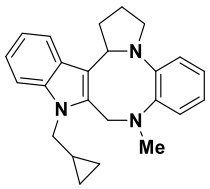
1H), 2.85 (s, 3H), 2.47 – 2,36 (m, 2H), 2.20 – 2.02 (m, 2H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 144.10, 143.37, 136.56, 135.07, 133.08, 126.30, 123.64, 121.80, 121.45, 120.91, 119.84, 119.16, 119.14, 116.35, 114.10, 109.42, 60.16, 53.22, 50.69, 44.97, 44.25, 30.62, 24.02; HRMS (ESI-TOF) m/z Calcd for $C_{23}H_{26}N_3$ $[M+H]^+$: 344.2121; found: 344.2122.

9-methyl-11-(prop-2-yn-1-yl)-2,3,9,10,11,15c-hexahydro-1H-benzo[2,3]pyrrolo[1',2':1,8][1,4]diazocino[6,7-b]indole (3d)



White solid; 23.6 mg, 69% yield; mp 152 – 154 ℃; column chromatography eluent, petroleum ether/EtOAc = 250:1; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.44 (d, *J* = 7.9 Hz, 1H), 7.21 – 7.17 (m, 1H), 7.06 (ddd, *J* = 8.2, 7.1, 1.1 Hz, 1H), 6.97 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 6.87 – 6.80 (m, 2H), 6.76 – 6.68 (m, 2H), 5.43 (dd, *J* = 8.3, 6.6 Hz, 1H), 5.17 (d, *J* = 14.0 Hz, 1H), 4.77 – 4.65 (m, 2H), 4.23 (d, *J* = 14.5 Hz, 1H), 3.42 – 3.34 (m, 1H), 3.17 – 3.09 (m, 1H), 2.94 (s, 3H), 2.46 – 2.29 (m, 2H), 2.16 (t, *J* = 2.5 Hz, 1H), 2.15 – 2.02 (m, 2H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 143.96, 143.26, 136.28, 134.30, 126.55, 123.00, 122.17, 121.30, 121.23, 120.56, 119.53, 119.17, 115.27, 109.15, 78.44, 72.43, 60.84, 52.42, 50.90, 44.17, 32.29, 31.13, 24.01; HRMS (ESI-TOF) m/z Calcd for $C_{23}H_{24}N_3$ $[M+H]^+$: 342.1965; found: 342.1965.

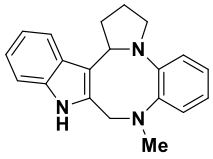
11-(cyclopropylmethyl)-9-methyl-2,3,9,10,11,15c-hexahydro-1H-benzo[2,3]pyrrolo[1',2':1,8][1,4]diazocino[6,7-b]indole (3e)



Pale Yellow oil; 33.2 mg, 93% yield; column chromatography eluent, petroleum ether/EtOAc = 200:1; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.45 (d, *J* = 7.9 Hz, 1H), 7.13 (d, *J* = 8.2 Hz, 1H), 7.03 – 6.98 (m, 1H), 6.96 – 6.86 (m, 2H), 6.77 – 6.72 (m, 2H), 6.69 – 6.64 (m, 1H), 5.69 (dd, *J* = 8.5, 6.3 Hz, 1H), 4.83 (d, *J* = 14.0 Hz, 1H), 4.22 (d, *J* = 14.0 Hz, 1H), 3.87 (qd, *J* = 15.2, 6.3 Hz, 2H), 3.43 – 3.36 (m, 1H), 3.15 – 3.07 (m, 1H), 2.89 (s, 3H), 2.51 – 2.36 (m, 2H), 2.21 – 2.04 (m, 2H), 1.06 – 0.96 (m, 1H), 0.44

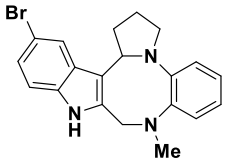
– 0.35 (m, 2H), δ 0.20 (q, J = 5.0 Hz, 2H) ; **^{13}C NMR (125 MHz, $CDCl_3$)** δ 144.55, 143.32, 136.69, 134.87, 126.16, 123.95, 122.25, 121.18, 120.62, 119.58, 119.03, 118.87, 113.75, 109.52, 59.91, 53.54, 50.53, 46.75, 44.42, 30.47, 23.96, 11.72, 4.00, 3.97; HRMS (ESI-TOF) m/z Calcd for $C_{24}H_{28}N_3$ $[M+H]^+$: 358.2278; found: 358.2278.

9-methyl-2,3,9,10,11,15c-hexahydro-1H-benzo[2,3]pyrrolo[1',2':1,8][1,4]diazocino [6,7-b]indole (3f)



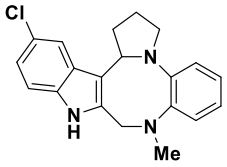
White solid; 23.7 mg, 78% yield; mp 166 – 168 ℃; column chromatography eluent, petroleum ether/EtOAc = 20:1; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.69 (s, 1H), 7.44 (d, *J* = 7.7 Hz, 1H), 7.10 (d, *J* = 7.9 Hz, 1H), 7.00 – 6.92 (m, 2H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.79 – 6.68 (m, 2H), 5.48 (t, *J* = 7.3 Hz, 1H), 4.87 (d, *J* = 14.0 Hz, 1H), 4.13 (d, *J* = 14.0 Hz, 1H), 3.43 – 3.34 (m, 1H), 3.17 – 3.08 (m, 1H), 2.85 (s, 3H), 2.48 – 2.33 (m, 2H), 2.18 – 2.02 (m, 2H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 143.72, 143.64, 135.49, 133.65, 127.05, 123.45, 121.95, 121.70, 121.16, 120.73, 119.35, 119.01, 114.37, 110.81, 60.55, 55.29, 51.00, 44.30, 30.89, 24.22; HRMS (ESI-TOF) m/z Calcd for $C_{20}H_{22}N_3$ $[M+H]^+$: 304.1808; found: 304.1811.

14-bromo-9-methyl-2,3,9,10,11,15c-hexahydro-1H-benzo[2,3]pyrrolo[1',2':1,8][1,4] diazocino[6,7-b]indole (3g)



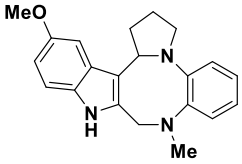
White solid; 32.5 mg, 85% yield; mp 186 – 188 ℃; column chromatography eluent, petroleum ether/EtOAc = 20:1; **^{1}H NMR (500 MHz, DMSO)** δ 11.12 (s, 1H), 7.54 (d, *J* = 1.3 Hz, 1H), 7.18 (d, *J* = 8.5 Hz, 1H), 7.08 (dd, *J* = 8.6, 1.7 Hz, 1H), 6.92 – 6.88 (m, 1H), 6.86 – 6.80 (m, 1H), 6.76 – 6.70 (m, 2H), 5.39 (dd, *J* = 8.2, 6.8 Hz, 1H), 4.96 (d, *J* = 14.0 Hz, 1H), 4.26 (d, *J* = 14.0 Hz, 1H), 3.35 – 3.31 (m, 1H), 3.10 – 3.02 (m, 1H), 2.86 (s, 3H), 2.48 – 2.39 (m, 1H), 2.24 – 2.15 (m, 1H), 2.15 – 2.08 (m, 1H), 2.08 – 1.98 (m, 1H); **^{13}C NMR (125 MHz, DMSO)** δ 144.04, 142.88, 136.60, 134.53, 128.59, 123.21, 122.93, 122.33, 121.08, 120.98, 120.85, 113.50, 112.67, 111.68, 60.55, 54.67, 51.09, 44.14, 31.19, 24.30; HRMS (ESI-TOF) m/z Calcd for $C_{20}H_{21}BrN_3$ $[M+H]^+$: 382.0913; found: 382.0915.

14-chloro-9-methyl-2,3,9,10,11,15c-hexahydro-1H-benzo[2,3]pyrrolo[1',2':1,8][1,4]diazocino[6,7-b]indole (3h)



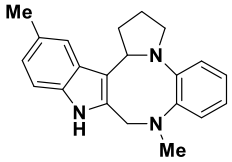
White solid; 27.7mg, 82% yield; mp 200 – 202 ℃; column chromatography eluent, petroleum ether/EtOAc = 20:1; **^{1}H NMR (500 MHz, DMSO)** δ 11.10 (s, 1H), 7.41 (s, 1H), 7.22 (d, *J* = 8.5 Hz, 1H), 6.97 (d, *J* = 8.5 Hz, 1H), 6.94 – 6.88 (m, 1H), 6.86 – 6.80 (m, 1H), 6.77 – 6.70 (m, 2H), 5.42 (t, *J* = 7.4 Hz, 1H), 4.95 (d, *J* = 14.0 Hz, 1H), 4.26 (d, *J* = 14.5 Hz, 1H), 3.36 – 3.30 (m, 1H), 3.11 – 3.01 (m, 1H), 2.86 (s, 3H), 2.48 – 2.38 (m, 1H), 2.27 – 2.20 (m, 1H), 2.17 – 2.08 (m, 1H), 2.08 – 1.97 (m, 1H); **^{13}C NMR (125 MHz, DMSO)** δ 143.98, 142.96, 136.81, 134.32, 127.86, 123.68, 122.99, 122.25, 121.14, 120.89, 120.66, 117.88, 113.00, 112.75, 60.48, 54.75, 51.06, 44.15, 31.11, 24.30; HRMS (ESI-TOF) m/z Calcd for $C_{20}H_{21}ClN_3$ $[M+H]^+$: 338.1419; found: 338.1418.

14-methoxy-9-methyl-2,3,9,10,11,15c-hexahydro-1H-benzo[2,3]pyrrolo[1',2':1,8][1,4]diazocino[6,7-b]indole (3i)



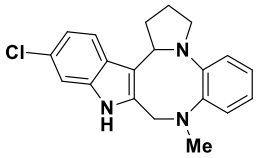
White solid; 22.7mg, 68% yield; mp 80 – 82 ℃; column chromatography eluent, petroleum ether/EtOAc = 20:1; **^{1}H NMR (500 MHz, DMSO)** δ 10.68 (s, 1H), 7.11 (d, *J* = 8.7 Hz, 1H), 6.90 (d, *J* = 2.0 Hz, 1H), 6.88 (t, *J* = 2.4 Hz, 2H), 6.78 – 6.70 (m, 2H), 6.64 (dd, *J* = 8.7, 2.4 Hz, 1H), 5.33 (dd, *J* = 8.3, 6.6 Hz, 1H), 5.05 (d, *J* = 14.0 Hz, 1H), 4.22 (d, *J* = 13.5 Hz, 1H), 3.73 (s, 3H), 3.42 – 3.36 (m, 1H), 3.14 – 3.10 (m, 1H), 2.89 (s, 3H), 2.50 – 2.42 (m, 1H), 2.27 – 2.19 (m, 1H), 2.19 – 2.11 (m, 1H), 2.11 – 2.02 (m, 1H); **^{13}C NMR (125 MHz, DMSO)** δ 153.46, 144.46, 142.81, 135.27, 131.03, 127.14, 122.55, 122.50, 121.37, 120.81, 112.72, 112.04, 110.43, 101.16, 61.22, 55.84, 54.67, 51.28, 44.16, 31.32, 24.23; HRMS (ESI-TOF) m/z Calcd for $C_{21}H_{24}N_3O$ $[M+H]^+$: 334.1914; found: 334.1915.

9,14-dimethyl-2,3,9,10,11,15c-hexahydro-1H-benzo[2,3]pyrrolo[1',2':1,8][1,4]diazocino[6,7-b]indole (3j)



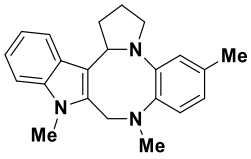
White solid; 26.9 mg, 85% yield; mp 120 – 122 ℃; column chromatography eluent, petroleum ether/EtOAc = 15:1; **^{1}H NMR (500 MHz, DMSO)** δ 10.72 (s, 1H), 7.23 (s, 1H), 7.11 (d, *J* = 8.2 Hz, 1H), 6.95 – 6.90 (m, 1H), 6.88 – 6.80 (m, 2H), 6.78 – 6.72 (m, 2H), 5.45 (dd, *J* = 8.3, 6.9 Hz, 1H), 4.97 (d, *J* = 14.0 Hz, 1H), 4.27 (d, *J* = 14.0 Hz, 1H), 3.38 – 3.35 (m, 1H), 3.14 – 3.05 (m, 1H), 2.89 (s, 3H), 2.49 – 2.40 (m, 1H), 2.35 (s, 3H), 2.34 – 2.27 (m, 1H), 2.23 – 2.13 (m, 1H), 2.12 – 2.01 (m, 1H); **^{13}C NMR (125 MHz, DMSO)** δ 144.16, 143.21, 134.77, 134.26, 127.30, 127.14, 122.87, 122.27, 122.11, 121.11, 120.82, 118.46, 112.25, 111.20, 60.80, 54.97, 51.07, 44.19, 31.17, 24.31, 21.84; HRMS (ESI-TOF) m/z Calcd for $C_{21}H_{24}N_3$ $[M+H]^+$: 318.1965; found: 318.1967.

13-chloro-9-methyl-2,3,9,10,11,15c-hexahydro-1H-benzo[2,3]pyrrolo[1',2':1,8][1,4]diazocino[6,7-b]indole (3k)



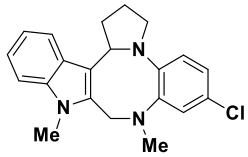
White solid; 25.7 mg, 76% yield; mp 125 – 127 ℃; column chromatography eluent, petroleum ether/EtOAc = 20:1; **^{1}H NMR (500 MHz, DMSO)** δ 11.07 (s, 1H), 7.46 (d, *J* = 8.6 Hz, 1H), 7.28 (d, *J* = 1.9 Hz, 1H), 7.00 – 6.93 (m, 2H), 6.87 – 6.82 (m, 1H), 6.80 – 6.74 (m, 2H), 5.53 (dd, *J* = 8.4, 6.6 Hz, 1H), 4.93 (d, *J* = 14.0 Hz, 1H), 4.32 (d, *J* = 14.0 Hz, 1H), 3.44 – 3.39 (m, 1H), 3.14 –3.05 (m, 1H), 2.90 (s, 3H), 2.52 – 2.43 (m, 1H), 2.36 – 2.26 (m, 1H), 2.23 – 2.13 (m, 1H), 2.13 – 2.02 (m, 1H); **^{13}C NMR (125 MHz, DMSO)** δ 143.84, 143.14, 136.30, 136.05, 125.61, 125.48, 123.14, 122.04, 121.30, 120.67, 120.08, 119.25, 113.07, 111.07, 60.28, 54.87, 50.96, 44.14, 31.01, 24.24; HRMS (ESI-TOF) m/z Calcd for $C_{20}H_{21}ClN_3$ $[M+H]^+$: 338.1419; found: 338.1422.

6,9,11-trimethyl-2,3,9,10,11,15c-hexahydro-1H-benzo[2,3]pyrrolo[1',2':1,8][1,4]diazocino[6,7-b]indole (3l)



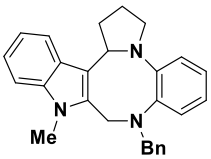
Yellow oil; 19.9 mg, 60% yield; column chromatography eluent, petroleum ether/EtOAc = 200:1; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.45 (d, J = 8.0 Hz, 1H), 7.08 (d, J = 8.2 Hz, 1H), 7.04 – 6.98 (m, 1H), 6.93 (ddd, J = 8.0, 7.0, 1.1 Hz, 1H), 6.80 (d, J = 8.0 Hz, 1H), 6.52 (d, J = 1.5 Hz, 1H), 6.47 (dd, J = 8.0, 1.5 Hz, 1H), 5.74 (dd, J = 8.4, 6.4 Hz, 1H), 4.80 (d, J = 14.0 Hz, 1H), 4.20 (d, J = 14.0 Hz, 1H), 3.51 (s, 3H), 3.42 – 3.34 (m, 1H), 3.15 – 3.06 (m, 1H), 2.86 (s, 3H), 2.50 – 2.34 (m, 2H), 2.26 – 2.07 (m, 2H), 2.06 (s, 3H) ; **^{13}C NMR (125 MHz, $CDCl_3$)** δ 144.05, 140.76, 137.14, 135.44, 133.37, 126.11, 121.92, 121.90, 120.65, 120.31, 119.03, 118.89, 113.63, 109.05, 59.55, 53.80, 50.48, 44.60, 30.48, 29.42, 23.94, 21.00; HRMS (ESI-TOF) m/z Calcd for $C_{22}H_{26}N_3$ $[M+H]^+$: 332.2121; found: 332.2123.

7-chloro-9,11-dimethyl-2,3,9,10,11,15c-hexahydro-1H-benzo[2,3]pyrrolo[1',2':1,8][1,4]diazocino[6,7-b]indole (3m)



White solid; 28.0 mg, 79% yield; mp 60 – 62 ℃; column chromatography eluent, petroleum ether/EtOAc = 200:1; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.40 (d, *J* = 7.9 Hz, 1H), 7.11 (d, *J* = 8.2 Hz, 1H), 7.07 – 7.01 (m, 1H), 6.97 – 6.92 (m, 1H), 6.79 (d, *J* = 8.6 Hz, 1H), 6.69 (d, *J* = 2.4 Hz, 1H), 6.62 (dd, *J* = 8.6, 2.4 Hz, 1H), 5.39 (d, *J* = 14.5 Hz, 1H), 5.17 – 5.11 (m, 1H), 4.09 (d, *J* = 14.5 Hz, 1H), 3.55 (s, 3H), 3.24 – 3.31 (m, , 1H), 3.15 – 3.07 (m, 1H), 2.91 (s, 3H), 2.44 – 2.34 (m, 1H), 2.23 – 2.14 (m, 1H), 2.13 – 1.97 (m, 2H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 145.69, 140.85, 137.10, 134.35, 127.58, 126.02, 122.62, 121.68, 121.16, 119.71, 119.08, 118.83, 114.21, 109.26, 61.99, 51.72, 51.40, 43.82, 31.94, 29.48, 24.03; HRMS (ESI-TOF) m/z Calcd for $C_{21}H_{23}ClN_3$ $[M+H]^+$: 352.1575; found: 352.1577.

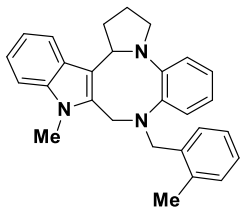
9-enzyl-11-methyl-2,3,9,10,11,15c-hexahydro-1H-benzo[2,3]pyrrolo[1',2':1,8][1,4]diazocino[6,7-b]indole (3n)



White solid; 32.4 mg, 82% yield; mp 80 – 82 ℃; column chromatography eluent, petroleum ether/EtOAc = 100:1; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.43 (d, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 7.4 Hz, 2H), 7.26 (t, *J* = 7.5 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.05

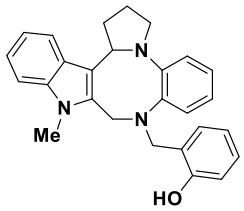
(d, *J* = 8.1 Hz, 1H), 7.02 – 6.96 (m, 2H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.85 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.78 – 6.73 (m, 1H), 6.73 – 6.68 (m, 1H), 5.47 (dd, *J* = 7.9, 6.9 Hz, 1H)，4.94 (d, *J* = 14.0 Hz, 1H), 4.36 – 4.24 (m, 2H), 4.09 (d, *J* = 13.5 Hz, 1H), 3.43 – 3.34 (m, 1H), 3.32 (s, 3H), 3.15 – 3.06 (m, 1H), 2.47 – 2.35 (m, 1H), 2.34 – 2.24 (m, 1H), 2.15 – 2.00 (m, 2H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 144.32, 144.22, 139.53, 137.06, 135.00, 128.47 (2C), 128.45 (2C), 127.16, 126.10, 123.70, 123.47, 122.27, 120.85, 120.73, 118.91, 118.87, 113.90, 109.08, 61.74, 60.85, 51.05, 49.07, 31.57, 29.22, 24.18; HRMS (ESI-TOF) m/z Calcd for $C_{27}H_{30}N_3$ $[M+H]^+$: 394.2278; found: 394.2279.

11-methyl-9-(2-methylbenzyl)-2,3,9,10,11,15c-hexahydro-1H-benzo[2,3]pyrrolo[1',2':1,8][1,4]diazocino[6,7-b]indole (3o)



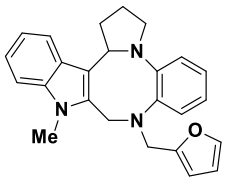
White solid; 35.0 mg, 86% yield; mp 96 – 98 ℃; column chromatography eluent, petroleum ether/EtOAc = 250:1; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.42 (d, *J* = 7.9 Hz, 1H), 7.16 (s, 1H), 7.13 (d, *J* = 4.7 Hz, 2H), 7.05 – 6.95 (m, 4H), 6.93 – 6.89 (m, 1H), 6.85 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.74 (td, *J* = 7.7, 1.5 Hz, 1H), 6.70 (td, *J* = 7.7, 1.4 Hz, 1H), 5.48 (dd, *J* = 8.0, 6.8 Hz, 1H), 4.92 (d, *J* = 14.0 Hz, 1H), 4.29 (d, *J* = 14.5 Hz, 1H), 4.24 (d, *J* = 13.5 Hz, 1H), 4.07 (d, *J* = 14.0 Hz, 1H), 3.45 – 3.34 (m, 1H), 3.30 (s, 3H), 3.16 – 3.05 (m, 1H), 2.45 – 2.35 (m, 1H), 2.34 – 2.26 (m, 1H), 2.24 (s, 3H), 2.15 – 1.99 (m, 2H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 144.45, 144.16, 139.54, 138.06, 137.09, 135.15, 129.20, 128.38, 127.90, 126.13, 125.48, 123.63, 123.37, 122.28, 120.81, 120.75, 118.93, 118.90, 113.93, 109.11, 61.67, 60.87, 51.08, 49.05, 31.61, 29.22, 24.26, 21.57; HRMS (ESI-TOF) m/z Calcd for $C_{28}H_{30}N_3$ $[M+H]^+$: 408.2434; found: 408.2433.

2-((11-methyl-1,2,3,10,11,15c-hexahydro-9H-benzo[2,3]pyrrolo[1',2':1,8][1,4]diazocino[6,7-b]indol-9-yl)methyl)phenol (3p)



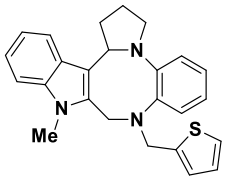
White solid; 22.1 mg, 54% yield; mp 86 – 88 ℃; column chromatography eluent, petroleum ether/EtOAc = 100:1; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.93 (s, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.19 – 7.13 (m, 1H), 7.07 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.05 (dd, *J* = 7.1, 4.5 Hz, 2H), 7.02 – 6.98 (m, 1H), 6.97 (dd, *J* = 8.1, 1.3 Hz, 1H), 6.92 – 6.86 (m, 3H), 6.78 (tdd, *J* = 7.8, 3.3, 1.3 Hz, 2H), 4.82 (dd, *J* = 8.8, 7.7 Hz, 1H), 4.67 (d, *J* = 13.0 Hz, 1H), 4.38 (d, *J* = 14.0 Hz, 1H), 4.20 (d, *J* = 13.0 Hz, 1H), 4.13 (d, *J* = 14.0 Hz, 1H), 3.46 (s, 3H), 3.36 – 3.30 (m, 1H), 3.30 – 3.24 (m, 1H), 2.42 – 2.33 (m, 1H), 2.31 – 2.19 (m, 1H), 2.18 – 2.03 (m, 2H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 157.56, 146.56, 144.30, 137.11, 133.53, 129.29, 129.07, 126.68, 126.21, 125.33, 123.75, 122.72, 121.19, 121.16, 119.72, 119.03, 118.90, 116.61, 113.05, 109.26, 62.69, 62.33, 51.05, 49.58, 31.76, 29.28, 24.15; HRMS (ESI-TOF) m/z Calcd for $C_{27}H_{28}N_3O$ $[M+H]^+$: 410.2227; found: 410.2227.

9-(furan-2-ylmethyl)-11-methyl-2,3,9,10,11,15c-hexahydro-1H-benzo[2,3]pyrrolo[1',2':1,8][1,4]diazocino[6,7-b]indole (3q)



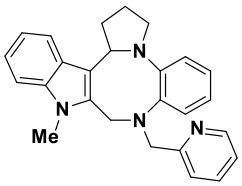
White solid; 32.6 mg, 85% yield; mp 126 – 128 ℃; column chromatography eluent, petroleum ether/EtOAc = 250:1; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.42 (d, *J* = 7.9 Hz, 1H), 7.31 (d, *J* = 0.9 Hz, 1H), 7.05 (d, *J* = 8.1 Hz, 1H), 7.02 – 6.97 (m, 2H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.81 (dd, *J* = 8.0, 1.4 Hz, 1H), 6.79 – 6.74 (m, 1H), 6.72 – 6.67 (m, 1H), 6.25 (dd, *J* = 2.9, 1.9 Hz, 1H), 6.18 (d, *J* = 3.1 Hz, 1H), 5.48 (dd, *J* = 8.1, 6.6 Hz, 1H), 4.92 (d, *J* = 13.5 Hz, 1H), 4.32 – 4.17 (m, 3H), 3.37 (s, 3H), 3.36 – 3.30 (m, 1H), 3.09 – 3.02 (m, 1H), 2.44 – 2.26 (m, 2H), 2.15 – 1.99 (m, 2H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 153.42, 144.70, 143.33, 142.00, 137.08, 134.86, 126.12, 124.28, 124.27, 122.00, 120.74, 120.55, 118.91, 118.90, 113.84, 110.38, 109.07, 108.03, 60.36, 53.96, 50.81, 49.31, 31.35, 29.13, 24.00; HRMS (ESI-TOF) m/z Calcd for $C_{25}H_{26}N_3O$ $[M+H]^+$: 384.2070; found: 384.2073.

11-methyl-9-(thiophen-2-ylmethyl)-2,3,9,10,11,15c-hexahydro-1H-benzo[2,3]pyrrolo[1',2':1,8][1,4]diazocino[6,7-b]indole (3r)



Pale Yellow oil; 31.9 mg, 80% yield; column chromatography eluent, petroleum ether/EtOAc = 200:1; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.44 (d, *J* = 8.0 Hz, 1H), 7.16 (dd, *J* = 5.0, 0.8 Hz, 1H), 7.05 – 7.01 (m, 2H), 7.01 – 6.97 (m, 1H), 6.93 – 6.90 (m, 2H), 6.87 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.82 – 6.78 (m, 1H), 6.75 (dd, *J* = 8.1, 1.4 Hz, 1H), 6.70 – 6.66 (m, 1H), 5.79 (t, *J* = 7.4 Hz, 1H), 4.68 (d, *J* = 13.5 Hz, 1H), 4.48 (d, *J* = 14.5 Hz, 1H), 4.35 (d, *J* = 14.5 Hz, 1H), 4.27 (d, *J* = 13.5 Hz, 1H), 3.42 – 3.39 (m, 1H), 3.36 (s, 3H), 3.13 – 3.01 (m, 1H), 2.47 – 2.36 (m, 2H), 2.20 – 2.01 (m, 2H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 145.25, 143.60, 142.82, 137.12, 134.96, 126.55, 126.09, 125.77, 125.16, 125.05, 124.50, 121.31, 120.69, 119.92, 119.01, 118.92, 113.44, 109.04, 59.56, 56.68, 50.57, 50.21, 30.85, 29.27, 24.05; HRMS (ESI-TOF) m/z Calcd for $C_{25}H_{26}N_3S$ $[M+H]^+$: 400.1842; found: 400.1842.

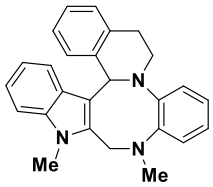
11-methyl-9-(pyridin-2-ylmethyl)-2,3,9,10,11,15c-hexahydro-1H-benzo[2,3]pyrrolo[1',2':1,8][1,4]diazocino[6,7-b]indole (3s)



White solid; 21.3 mg, 54% yield; mp 68 – 70 ℃; column chromatography eluent, petroleum ether/EtOAc = 250:1; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.47 (d, *J* = 4.4 Hz, 1H), 7.51 (td, *J* = 7.7, 1.7 Hz, 1H), 7.42 (dd, *J* = 11.1, 8.0 Hz, 2H), 7.05 (dd, *J* = 7.0, 3.9 Hz, 2H), 7.02 – 6.98 (m, 1H), 6.96– 6.90 (m, 2H), 6.83 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.76 – 6.71 (m, 1H), 6.70 – 6.65 (m, 1H), 5.56 (dd, *J* = 8.2, 6.6 Hz, 1H), 5.09 (d, *J* = 14.0 Hz, 1H), 4.49 (q, *J* = 15.4 Hz, 2H), 4.18 (d, *J* = 14.0 Hz, 1H), 3.41-3.37 (m, 1H), 3.37 (s, 3H), 3.16 – 3.07 (m, 1H), 2.47 – 2.28 (m, 2H), 2.15 – 1.98 (m, 2H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 159.68, 149.09, 143.99, 143.35, 137.10, 136.64, 134.87, 126.04, 123.79, 122.78, 122.65, 122.22, 122.09, 120.84, 120.77, 118.96(2C), 113.85, 109.14, 63.32, 60.66, 51.05, 50.38, 31.42, 29.35, 24.22; HRMS (ESI-TOF) m/z Calcd for

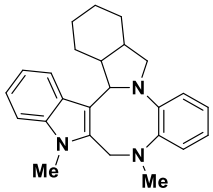
$C_{26}H_{27}N_4$ $[M+H]^+$: 395,2230; found: 395.2231.

12,14-dimethyl-5,6,12,13,14,18c-hexahydrobenzo[2,3]indolo[2',3':6,7][1,4]diazocino[8,1-a]isoquinoline (3t)



Pale Yellow solid; 23.9 mg, 63% yield; mp 180 – 182 ℃; column chromatography eluent, petroleum ether/EtOAc = 200:1; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.50 (d, *J* = 7.8 Hz, 1H), 7.15 – 7.11 (m, 2H), 7.10 – 6.98 (m, 5H), 6.89 (t, *J* = 7.6 Hz, 1H), 6.84 – 6.79 (m, 1H), 6.66 (td, *J* = 7.7, 1.3 Hz, 1H), 6.55 (dd, *J* = 8.1, 1.2 Hz, 1H), 5.74 (d, *J* = 13.5 Hz, 1H), 5.47 (s, 1H), 3.91 (d, *J* = 14.0 Hz, 1H), 3.57 (s, 3H), 3.51 – 3.44 (m, 1H), 3.39 – 3.30 (m, 1H), 3.26 (ddd, *J* = 11.1, 5.6, 1.5 Hz, 1H), 3.01 (s, 3H), 2.85 – 2.78 (m, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 146.89, 144.93, 140.57, 136.90, 134.19, 133.24, 128.57, 127.81, 127.27, 126.19, 125.90, 125.77, 124.15, 121.13, 121.05, 119.29, 119.16, 118.68, 116.54, 109.27, 62.71, 52.18, 50.13, 43.87, 30.81, 29.42; HRMS (ESI-TOF) m/z Calcd for $C_{26}H_{26}N_3$ $[M+H]^+$: 380.2121; found: 380.2121.

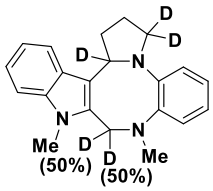
11,13-dimethyl-1,3,4,4a,5,11,12,13,17c,17d-decahydro-2H-benzo[2,3]isoindolo[2',1':1,8][1,4]diazocino[6,7-b]indole (3u)



White solid; 26.4 mg, 71% yield; mp 122 – 124 ℃; column chromatography eluent, petroleum ether/EtOAc = 150:1; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.64 (d, *J* = 8.0 Hz, 1H), 7.33 – 7.29 (m, 1H), 7.23 – 7.18 (m, 1H), 7.14 – 7.07 (m, 2H), 6.96 – 6.86 (m, 3H), 5.46 (d, *J* = 15.0 Hz, 1H), 5.28 (d, *J* = 6.5 Hz, 1H), 4.23 (d, *J* = 14.5 Hz, 1H), 3.74 (s, 3H), 3.56 (dd, *J* = 8.8, 6.5 Hz, 1H), 3.36 (dd, *J* = 8.8, 5.0 Hz, 1H), 3.06 (s, 3H), 2.93 – 2.79 (m, 1H), 2.60 – 2.48 (m, 1H), 1.90 – 1.76 (m, 6H), 1.71 – 1.55 (m, 2H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 145.04, 142.17, 137.12, 135.87, 126.33, 122.83, 122.43, 121.90, 120.76, 119.93, 119.30, 118.96, 114.16, 109.20, 64.76, 55.89, 50.97, 44.67, 43.68, 37.21, 29.42, 27.54, 26.39, 24.07, 23.23; HRMS (ESI-TOF) m/z Calcd

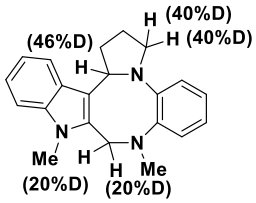
for $C_{25}H_{30}N_3$ $[M+H]^+$: 372.2434; found: 372.2437.

[D]-3a



White soild; 26.3 mg, 83% yield; column chromatography eluent, petroleum ether/EtOAc =250:1; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.43 (d, *J* = 7.9 Hz, 1H), 7.10 (d, *J* = 8.2 Hz, 1H), 7.02 (t, *J* = 7.3 Hz, 1H), 6.94 (t, *J* = 7.3 Hz, 1H), 6.88 – 6.79 (m, 2H), 6.77 – 6.67 (m, 2H), 5.09 (s, 0.5H), 4.15 (s, 0.5H), 3.54 (s, 3H), 2.91 (s, 3H), 2.47 – 2.27 (m, 2H), 2.18 – 2.00 (m, 2H); HRMS (ESI-TOF) m/z Calcd for $C_{21}H_{20}D_4N_3$ $[M+H]^+$: 322.2216; found: 322.2220.

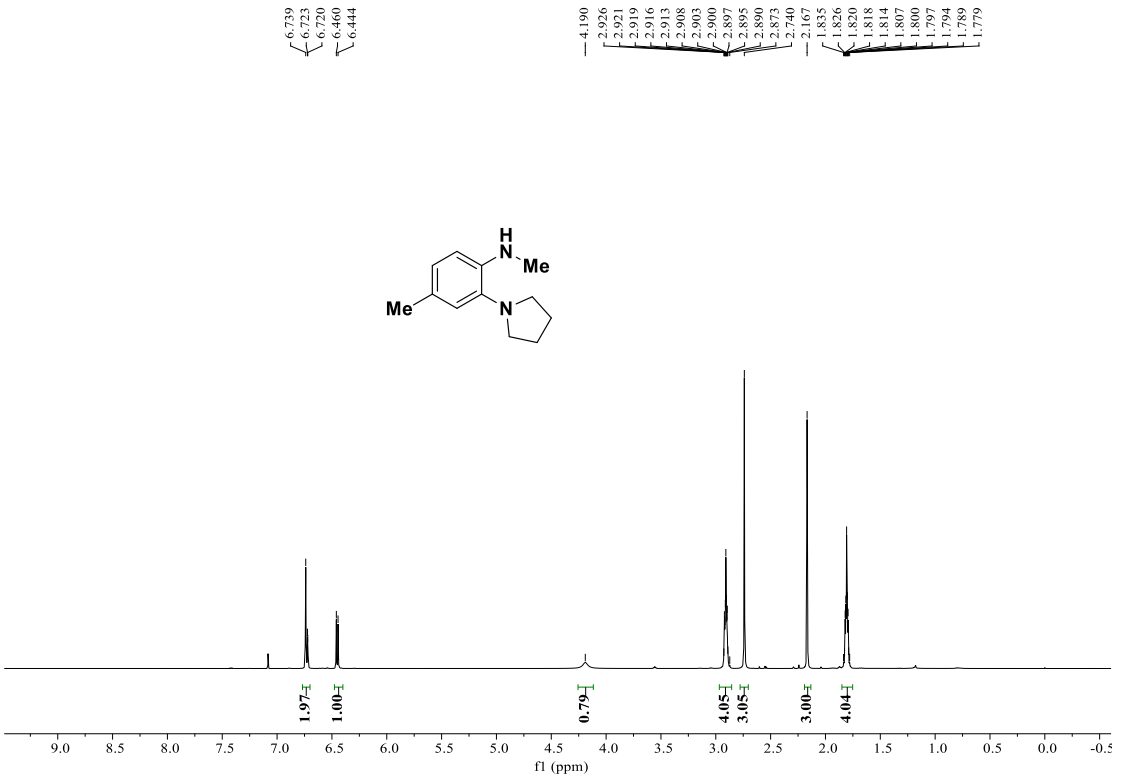
[H/D]-3a

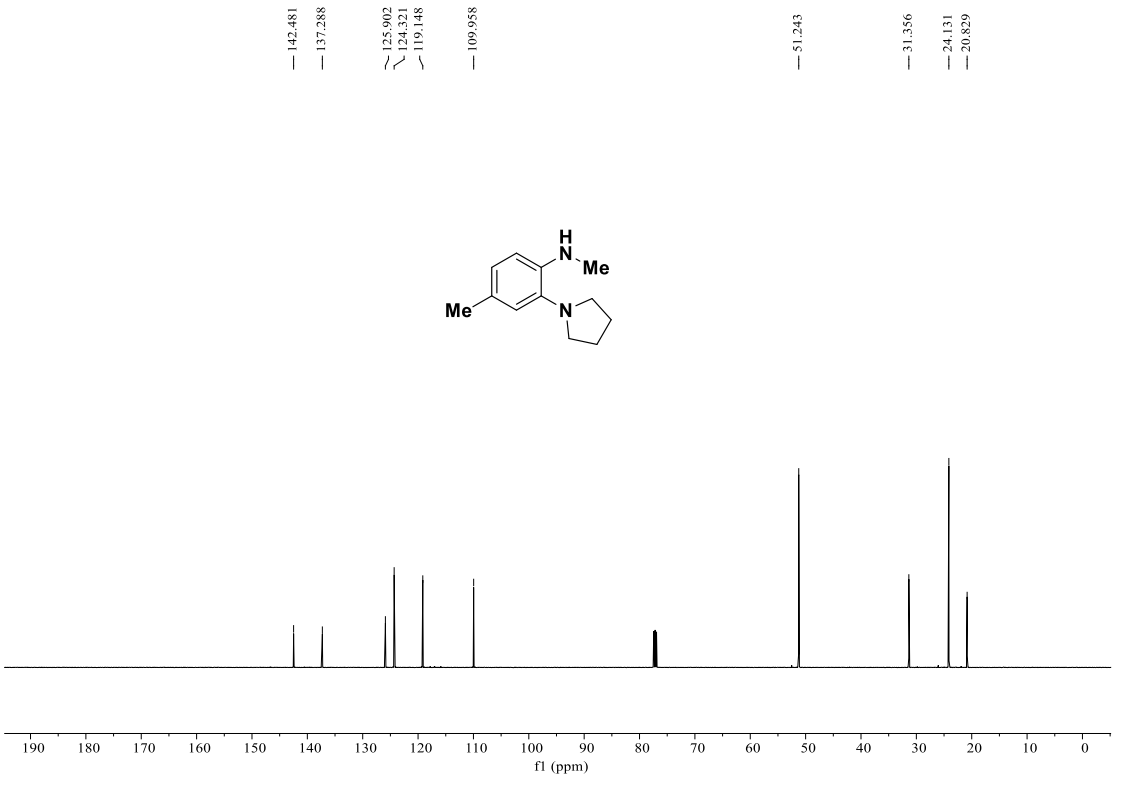


White solid; 19.3 mg, 61% yield; column chromatography eluent, petroleum ether/EtOAc = 250:1; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.44 (d, J = 7.7 Hz, 1H), 7.11 (d, J = 7.9 Hz, 1H), 7.03 (t, J = 7.2 Hz, 1H), 6.94 (t, J = 7.1 Hz, 1H), 6.87 – 6.78 (m, 2H), 6.77 – 6.66 (m, 2H), 5.46 (t, J = 7.1 Hz, 1H), 5.23 – 5.05 (m, 1H), 4.17 (d, J = 13.7 Hz, 1H), 3.55 (s, 3H), 3.38 (dd, J = 13.4, 7.6 Hz, 1H), 3.14 (dd, J = 14.5, 7.0 Hz, 1H), 2.93 (s, 3H), 2.48 – 2.26 (m, 2H), 2.20 – 2.00 (m, 2H).

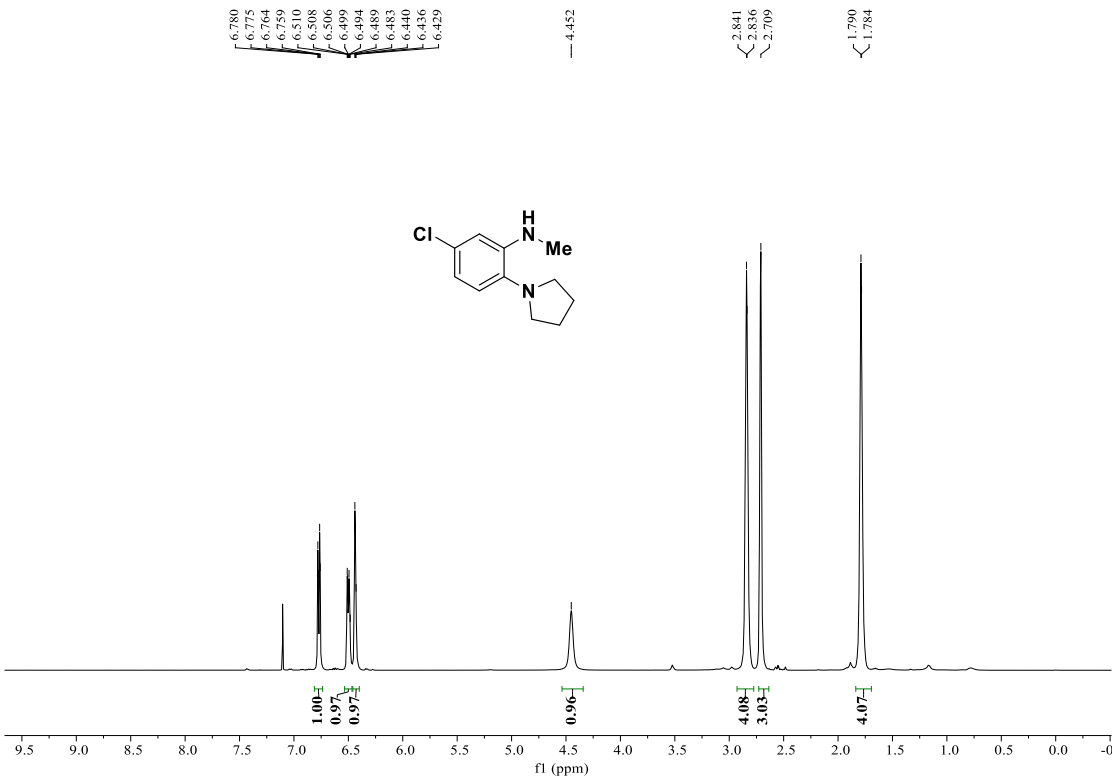
5. ^{1}H and ^{13}C NMR Spectra

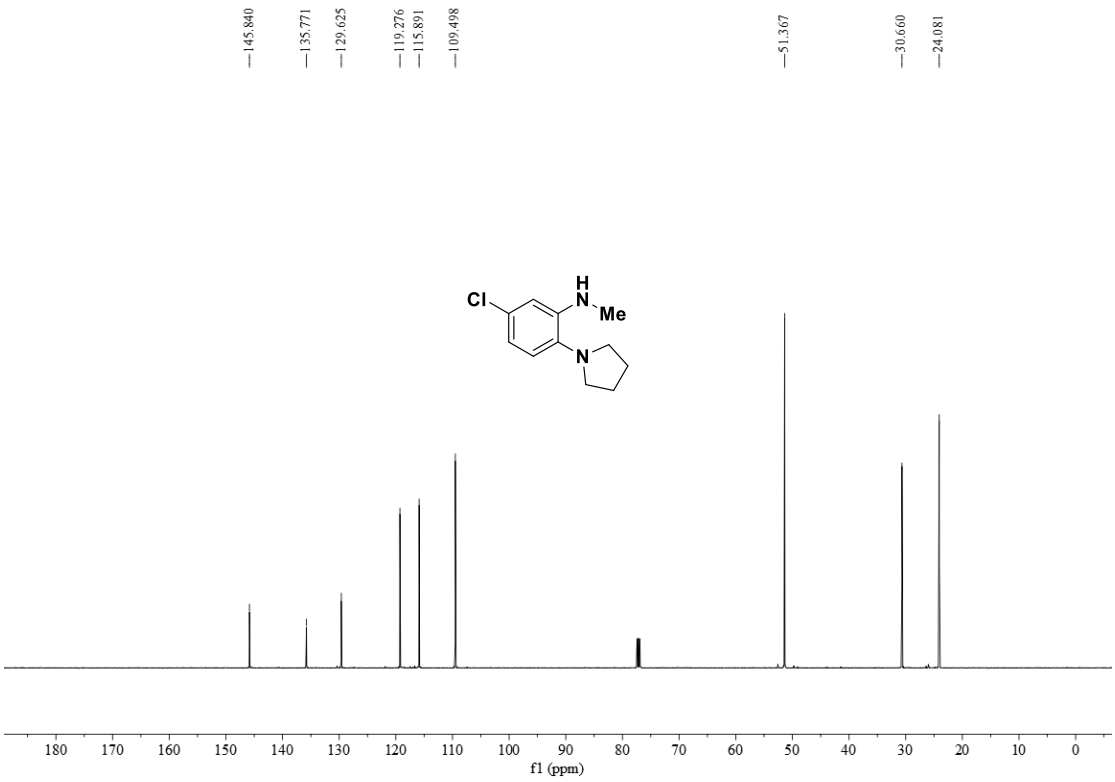
N,4-dimethyl-2-(pyrrolidin-1-yl)aniline (2l)



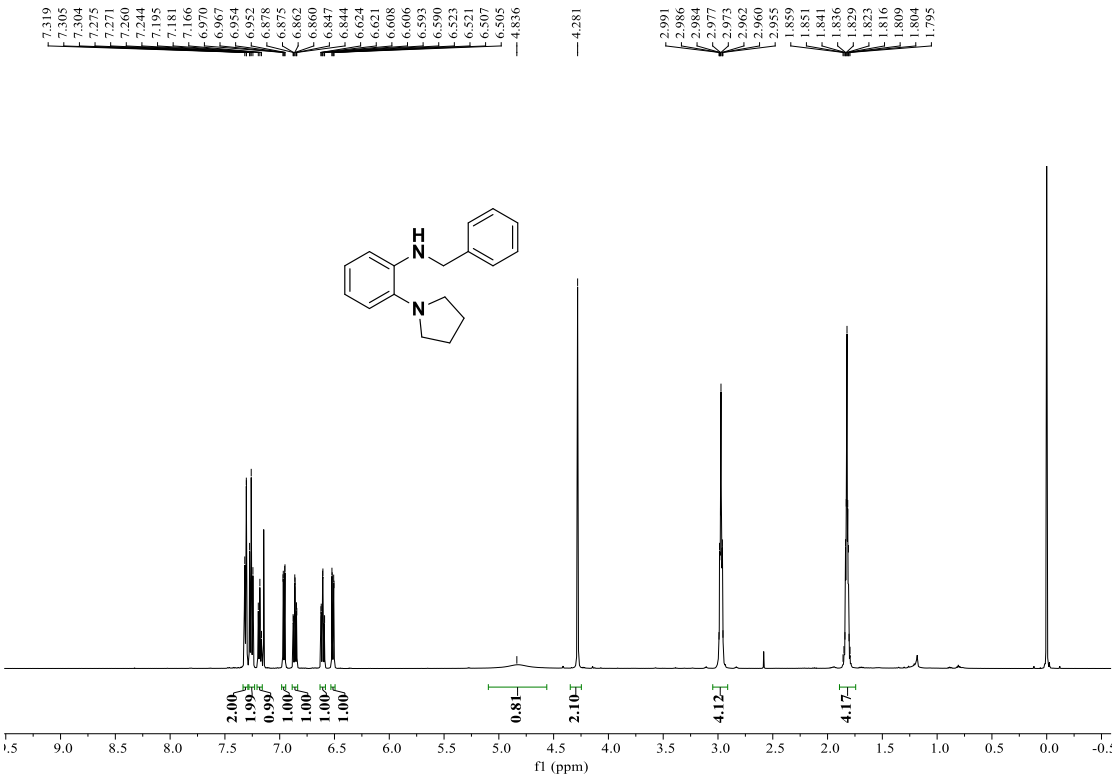


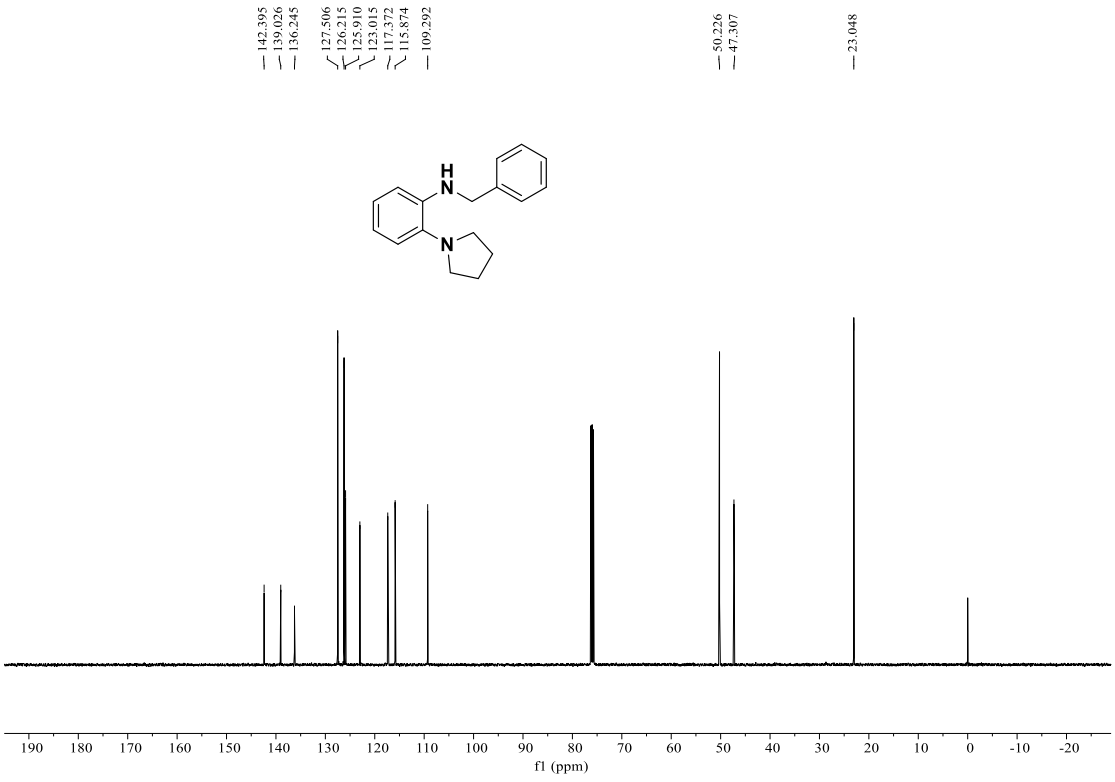
5-chloro-N-methyl-2-(pyrrolidin-1-yl)aniline (2m)



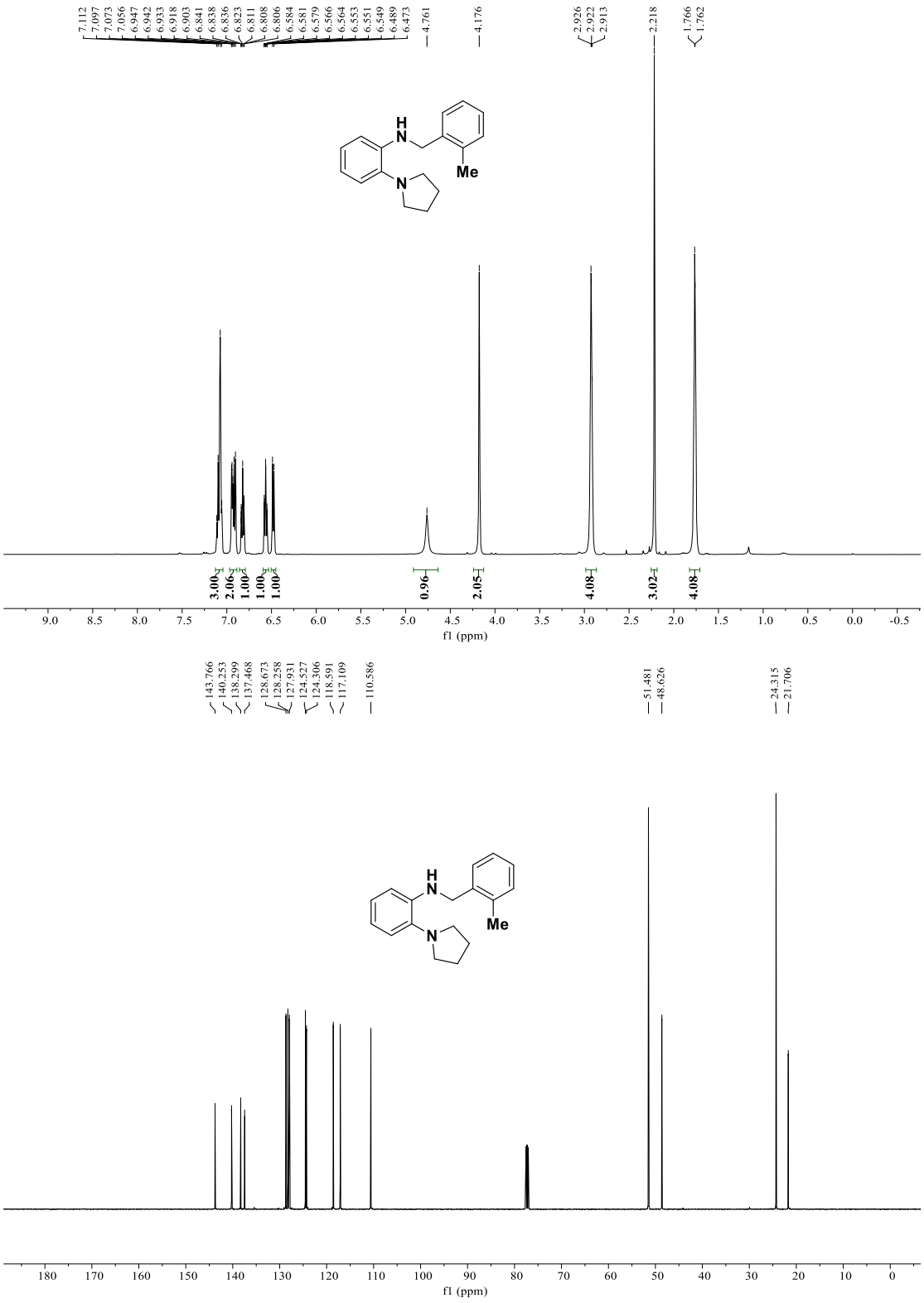


N-benzyl-2-(pyrrolidin-1-yl)aniline (2n)

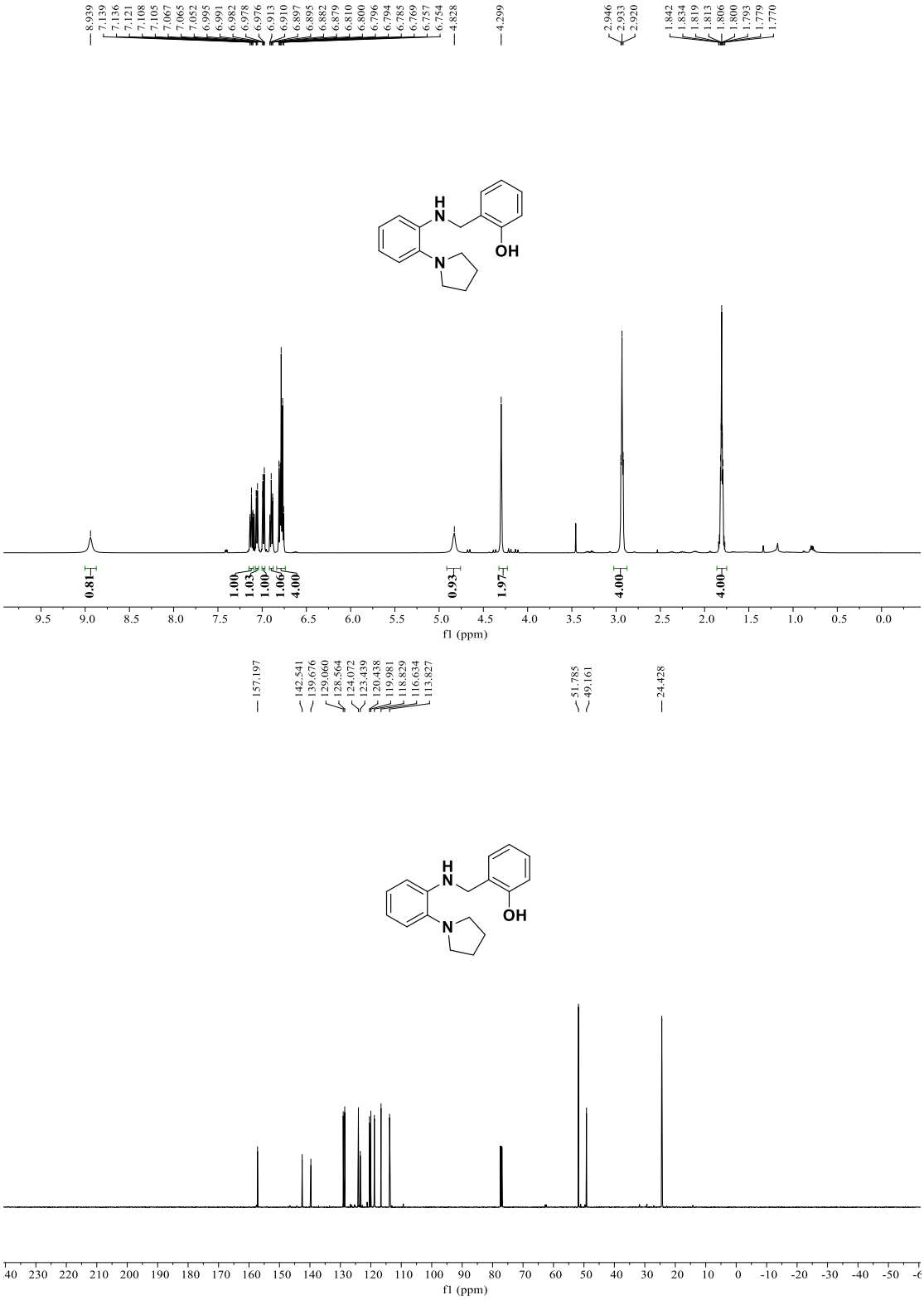




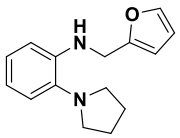
N-(2-methylbenzyl)-2-(pyrrolidin-1-yl)aniline (2o)

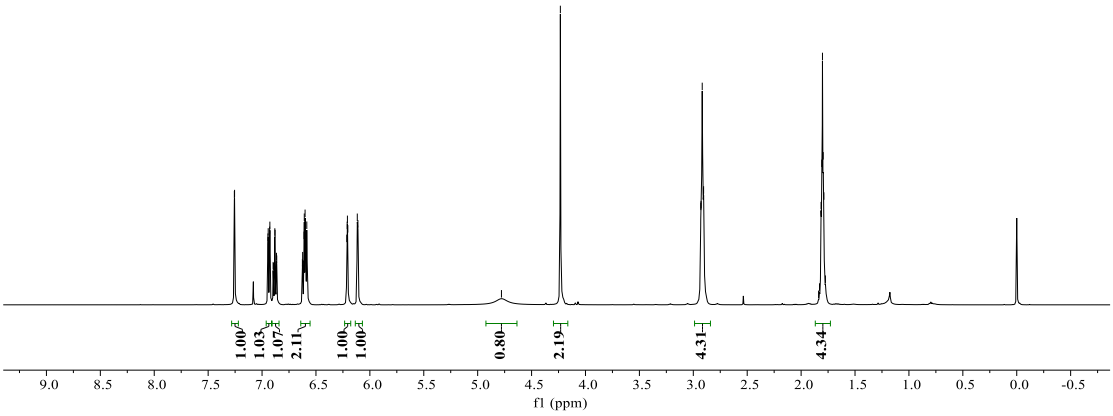


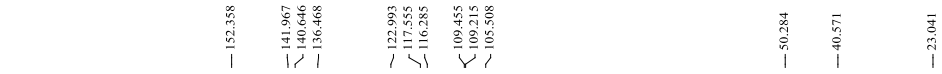
2-(((2-(pyrrolidin-1-yl)phenyl)amino)methyl)phenol (2p)

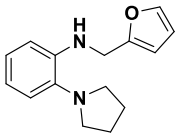


N-(furan-2-ylmethyl)-2-(pyrrolidin-1-yl)aniline (2q)

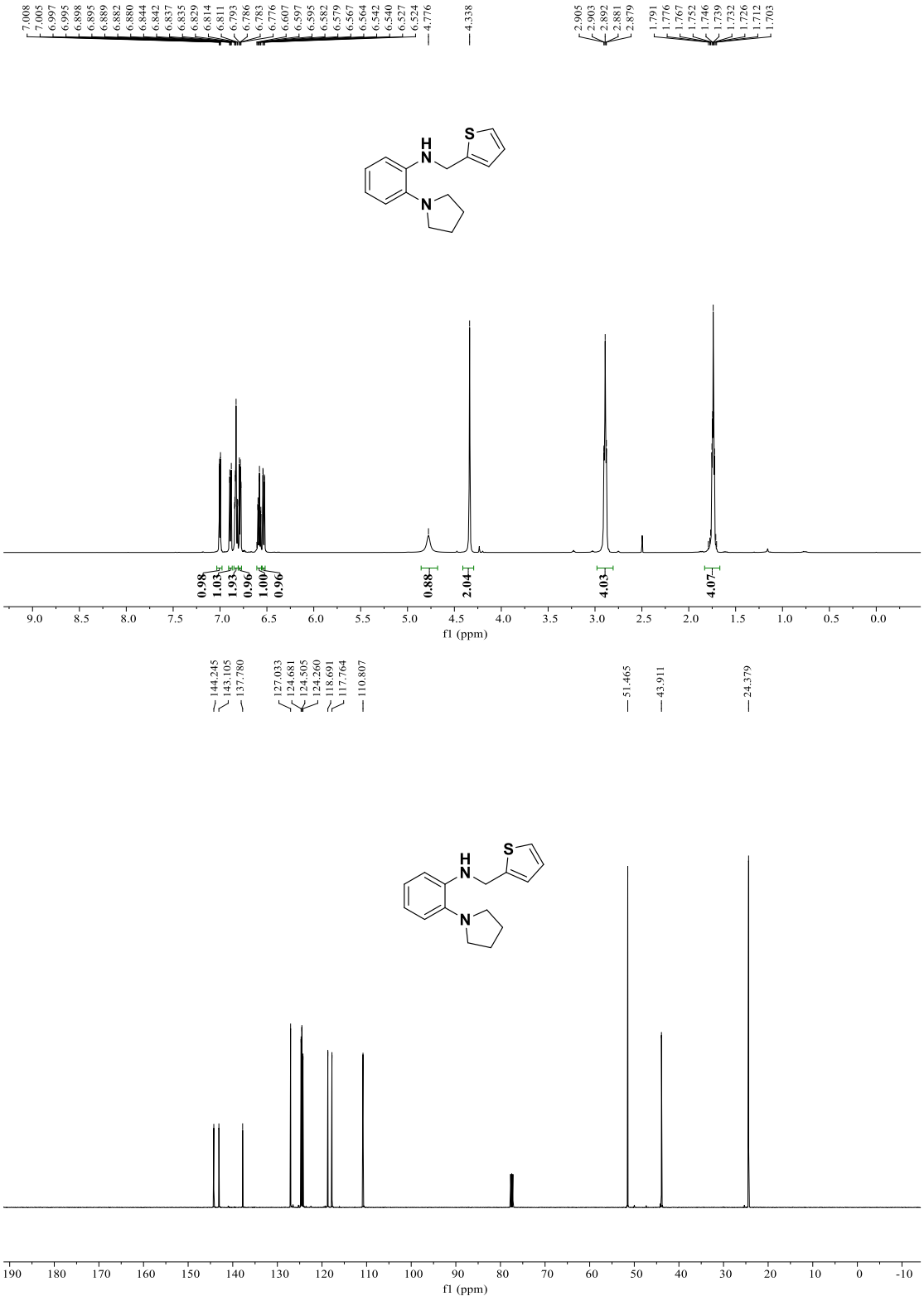




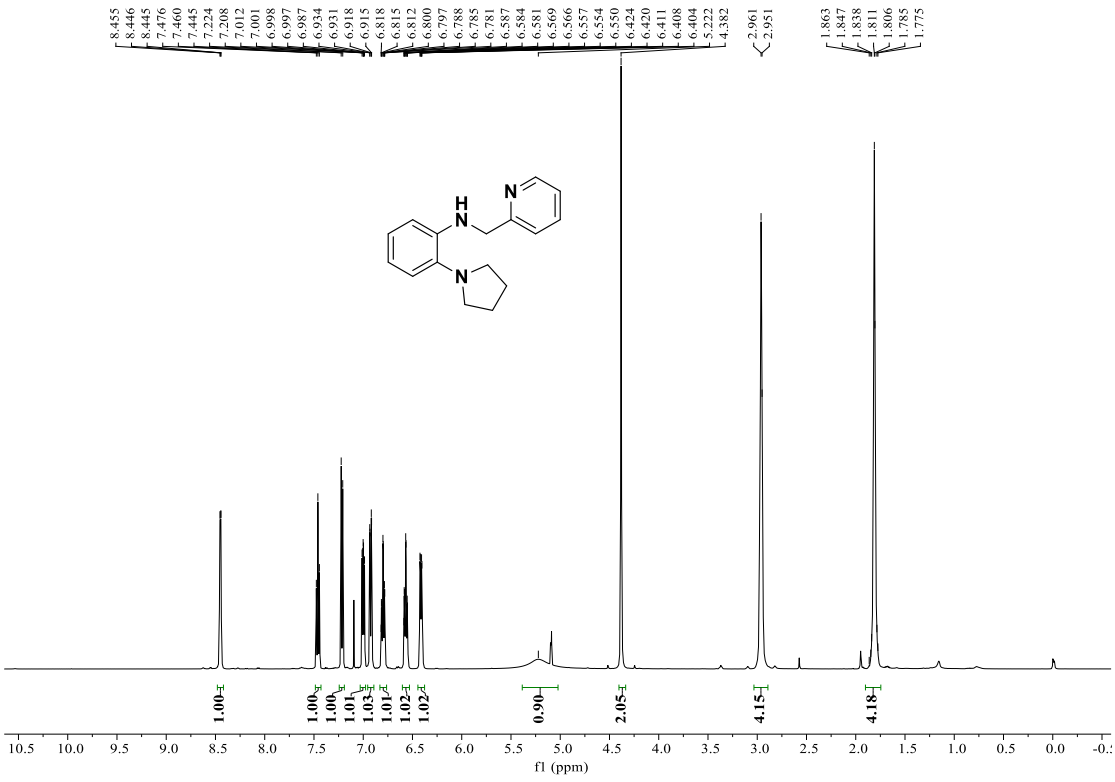


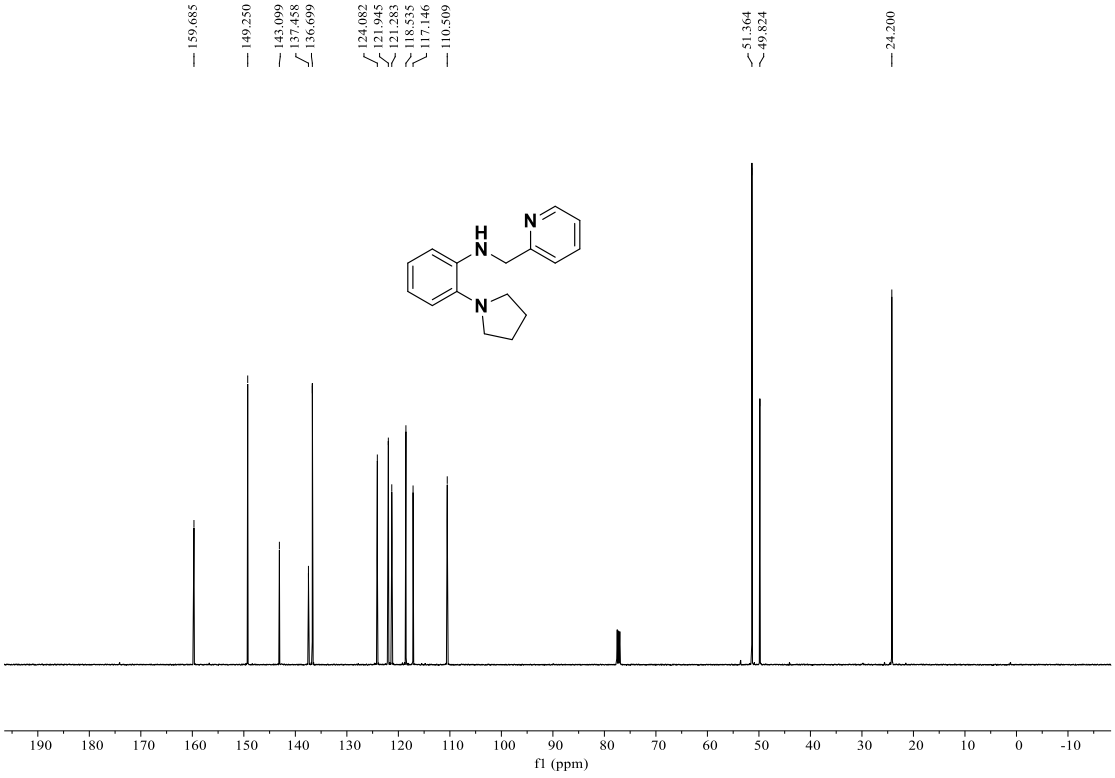


2-(pyrrolidin-1-yl)-N-(thiophen-2-ylmethyl)aniline (2r)

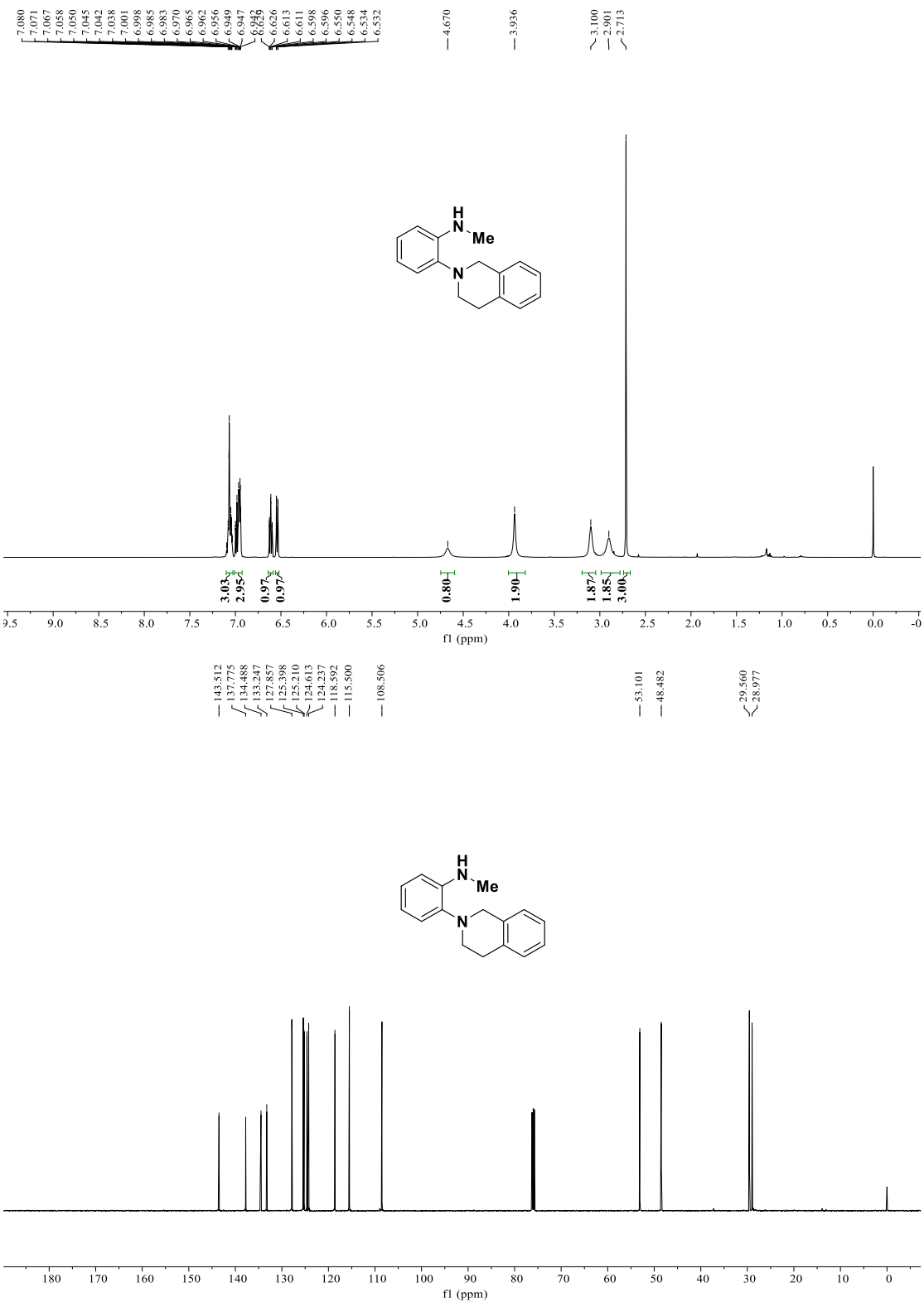


N-(pyridin-2-ylmethyl)-2-(pyrrolidin-1-yl)aniline (2s)

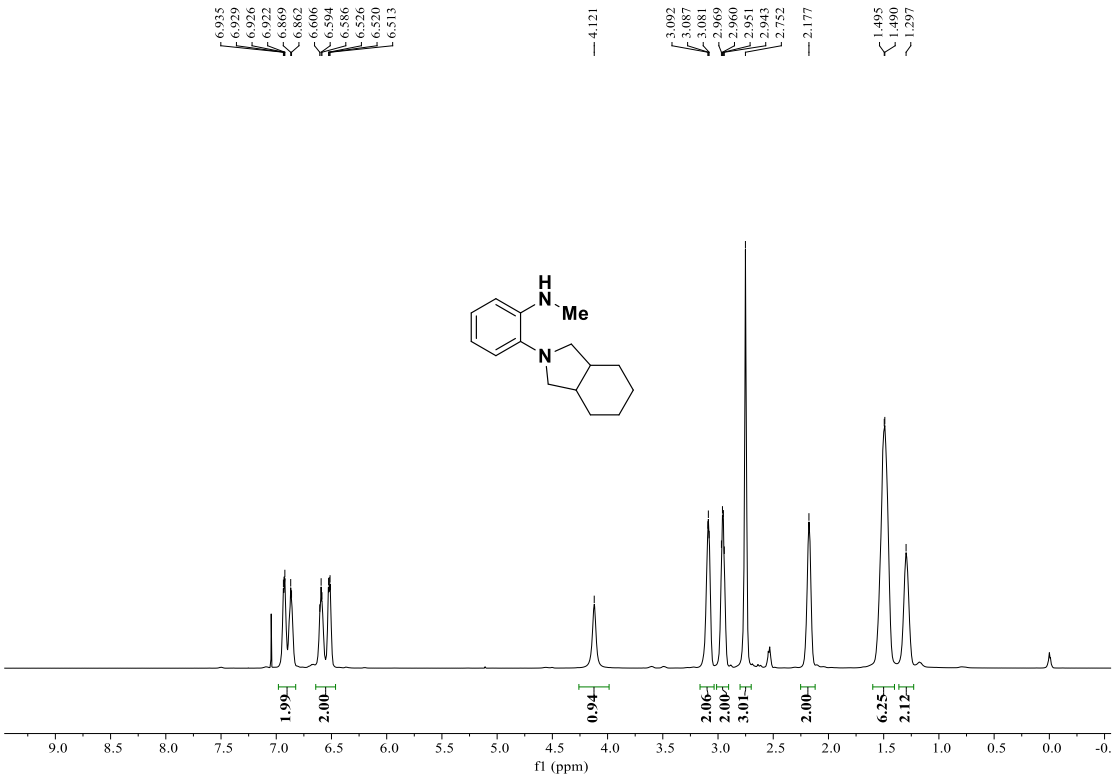


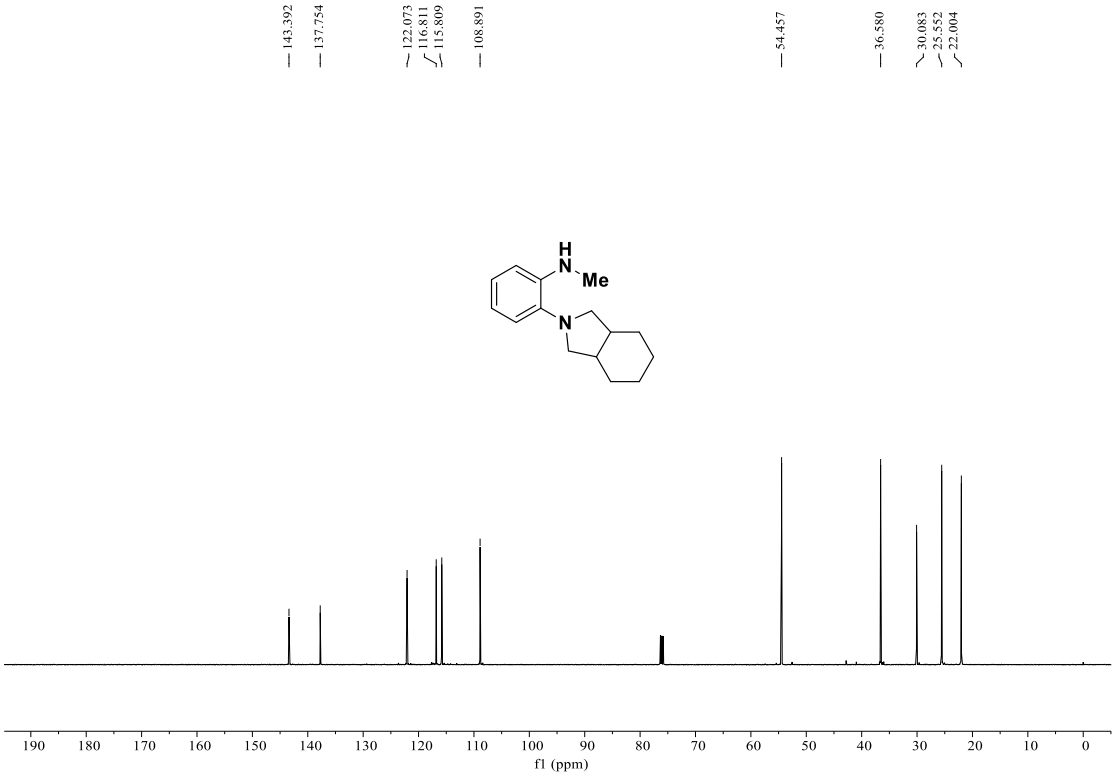


2-(3,4-dihydroisoquinolin-2(1H)-yl)-N-methylaniline (2t)

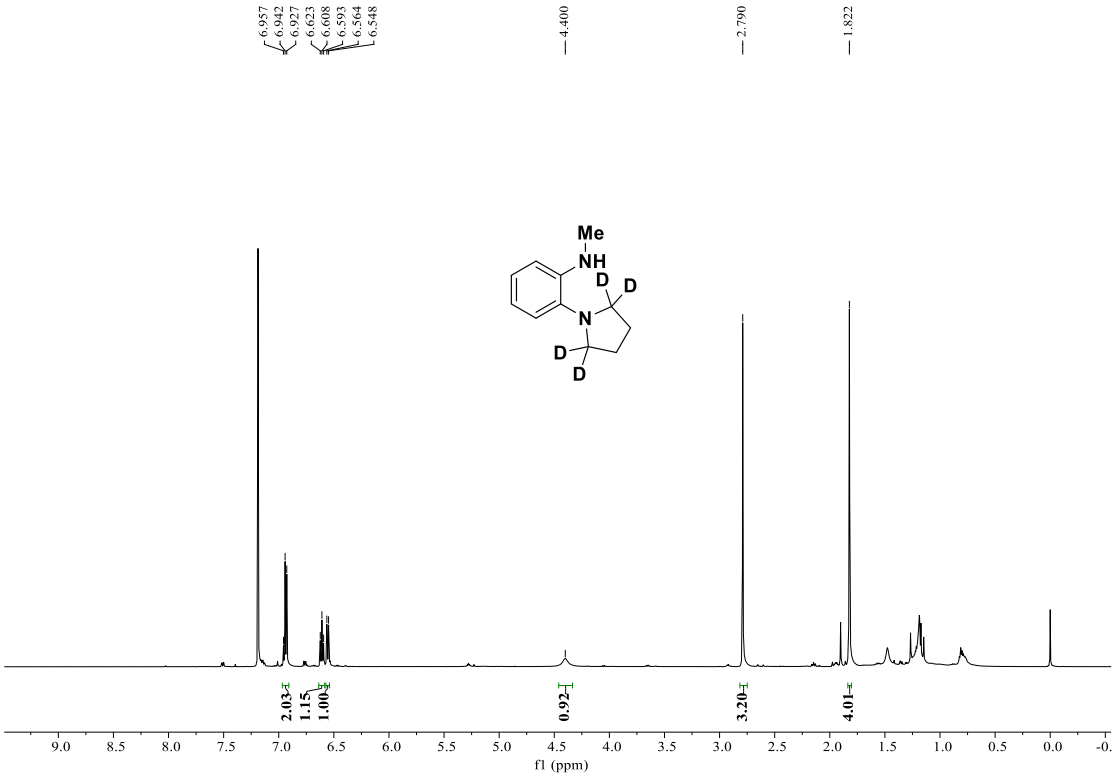


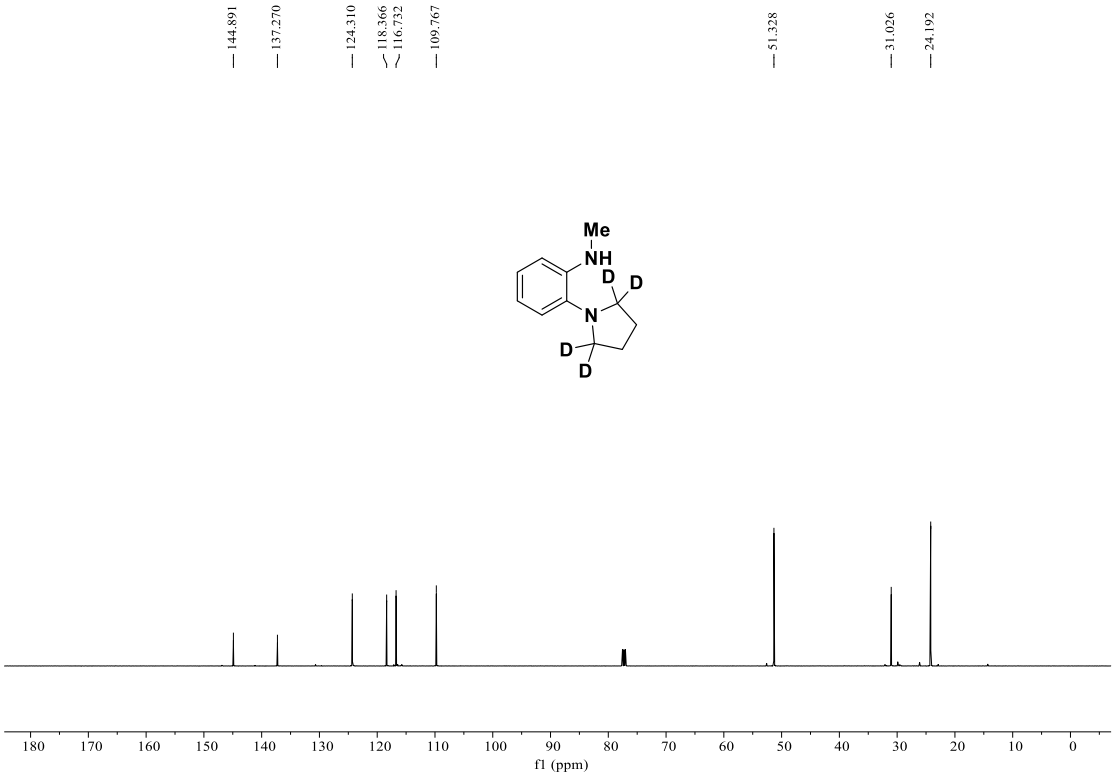
N-methyl-2-(octahydro-2H-isoindol-2-yl)aniline (2u)



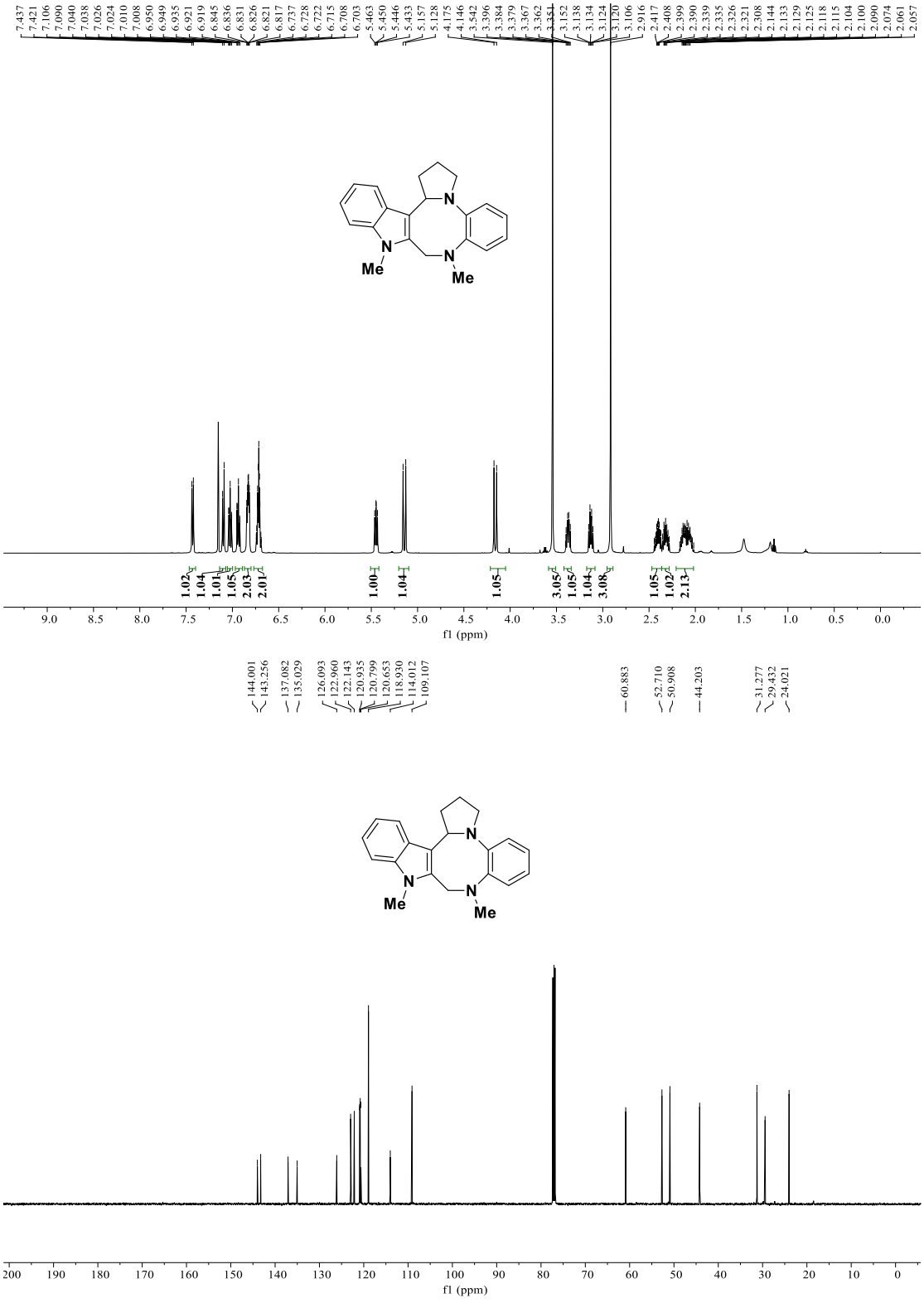


N-methyl-2-(pyrrolidin-1-yl-2,2,5,5-d4)aniline (D-2a)

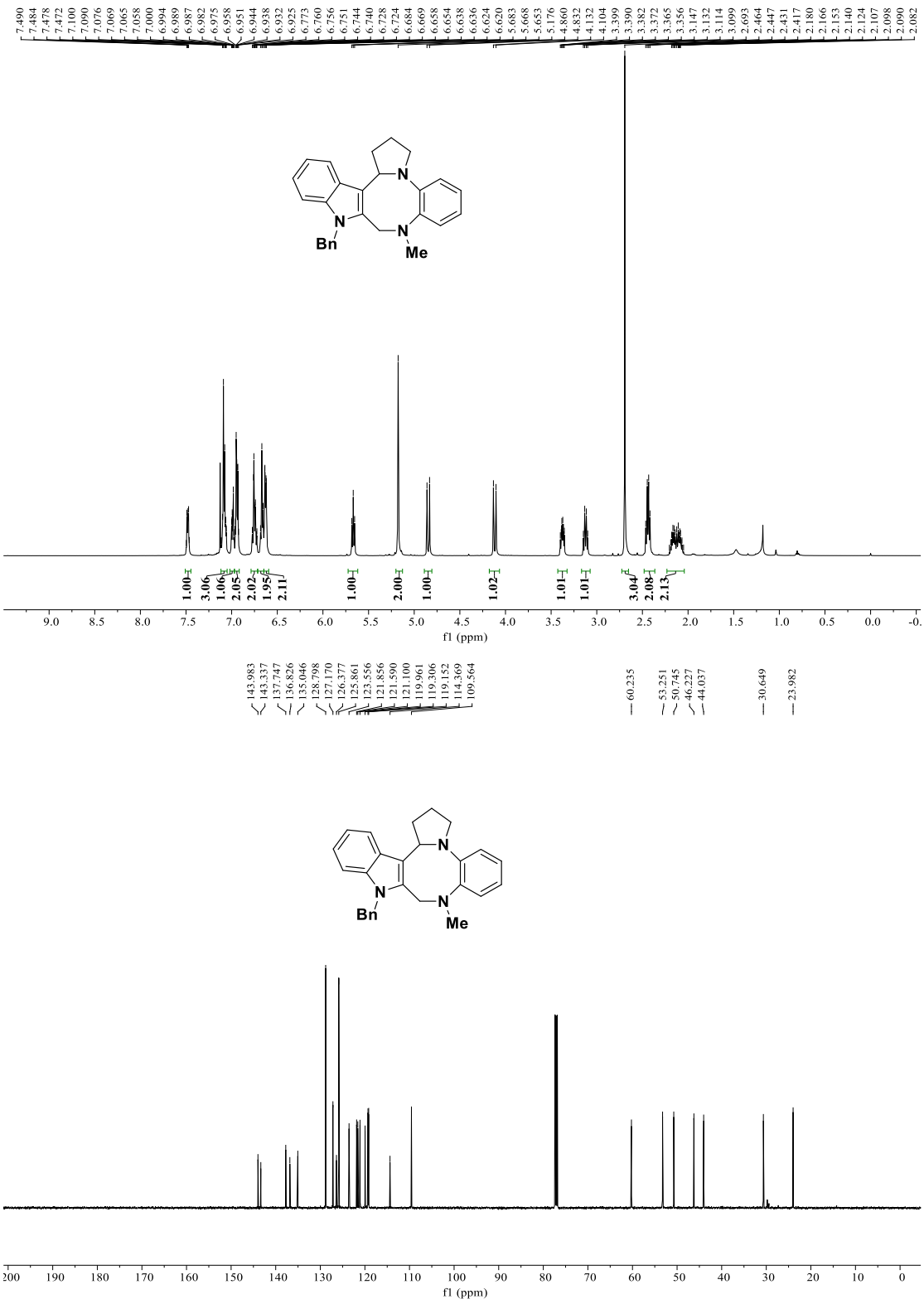




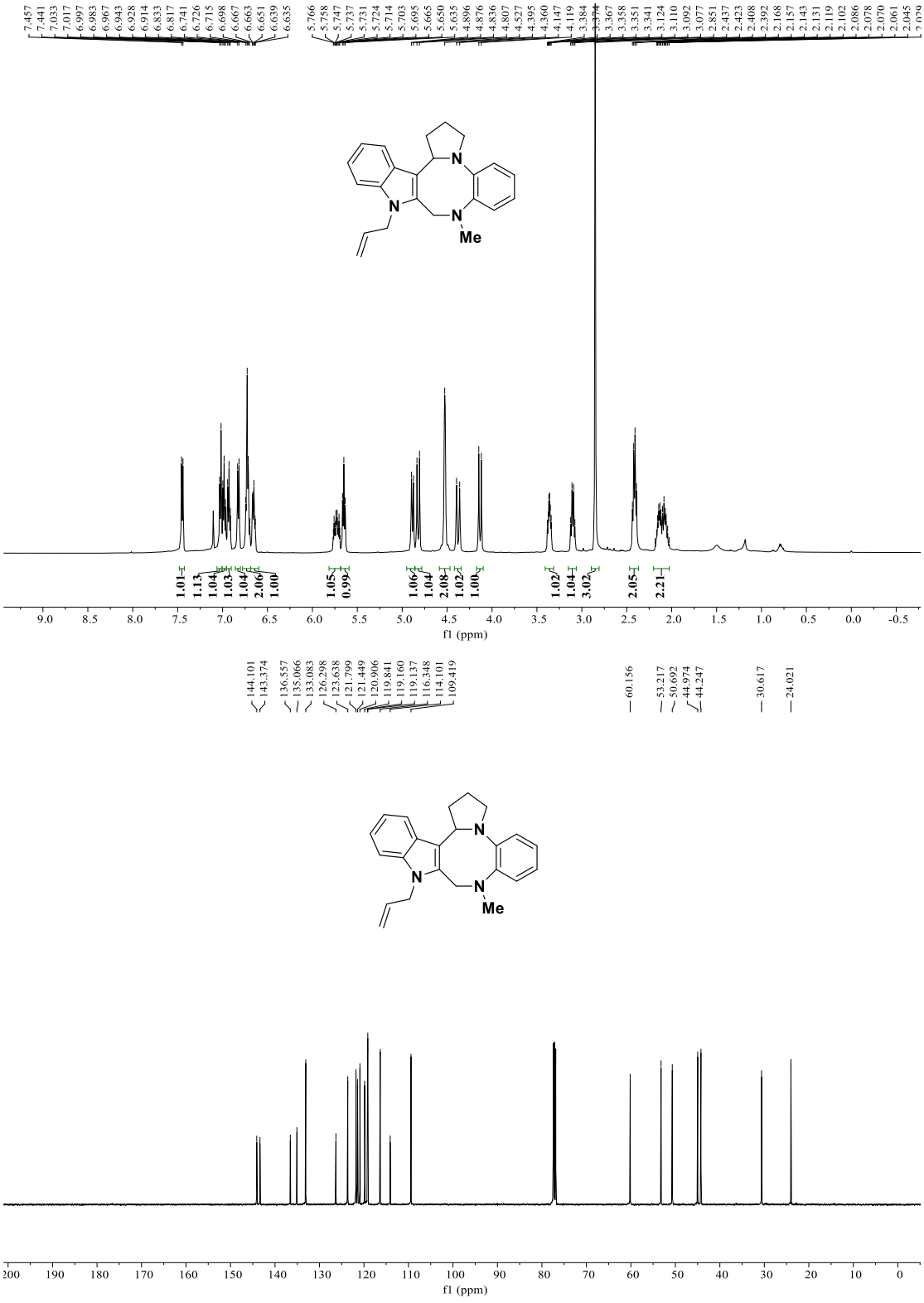
9,11-dimethyl-2,3,9,10,11,15c-hexahydro-1H-benzo[2,3]pyrrolo[1',2':1,8][1,4]diazocino[6,7-b]indole (3a)



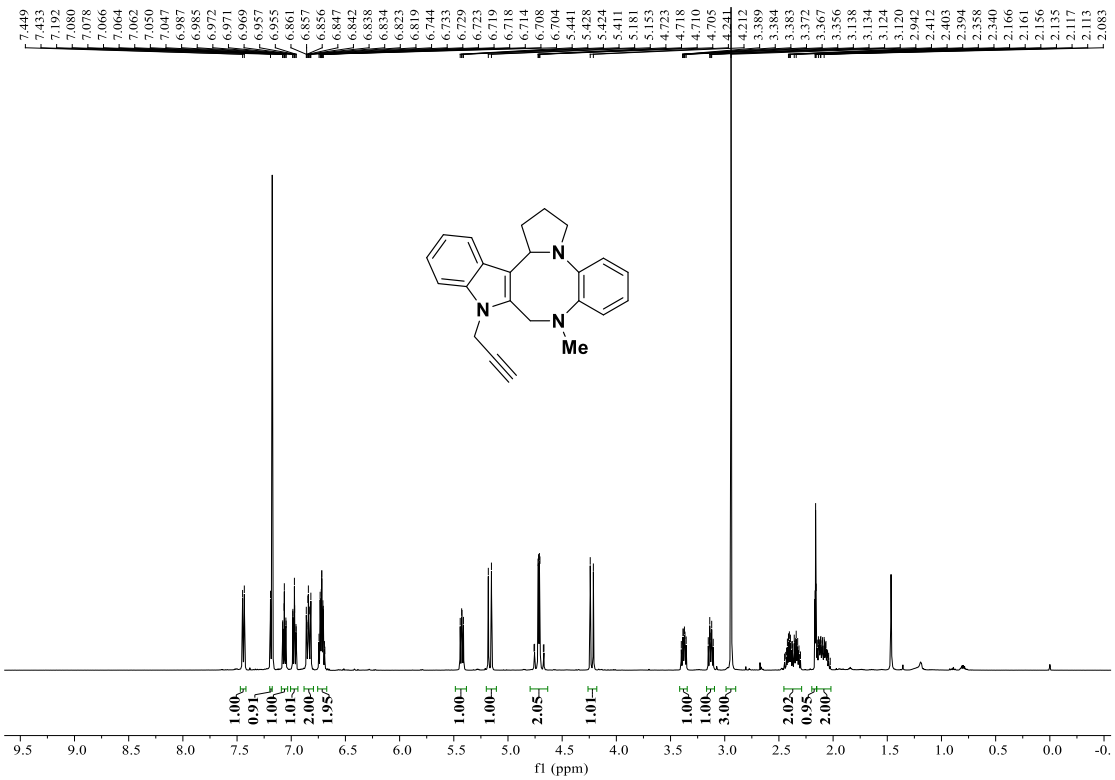
11-benzyl-9-methyl-2,3,9,10,11,15c-hexahydro-1H-benzo[2,3]pyrrolo[1',2':1,8][1,4] diazocino[6,7-b]indole (3b)

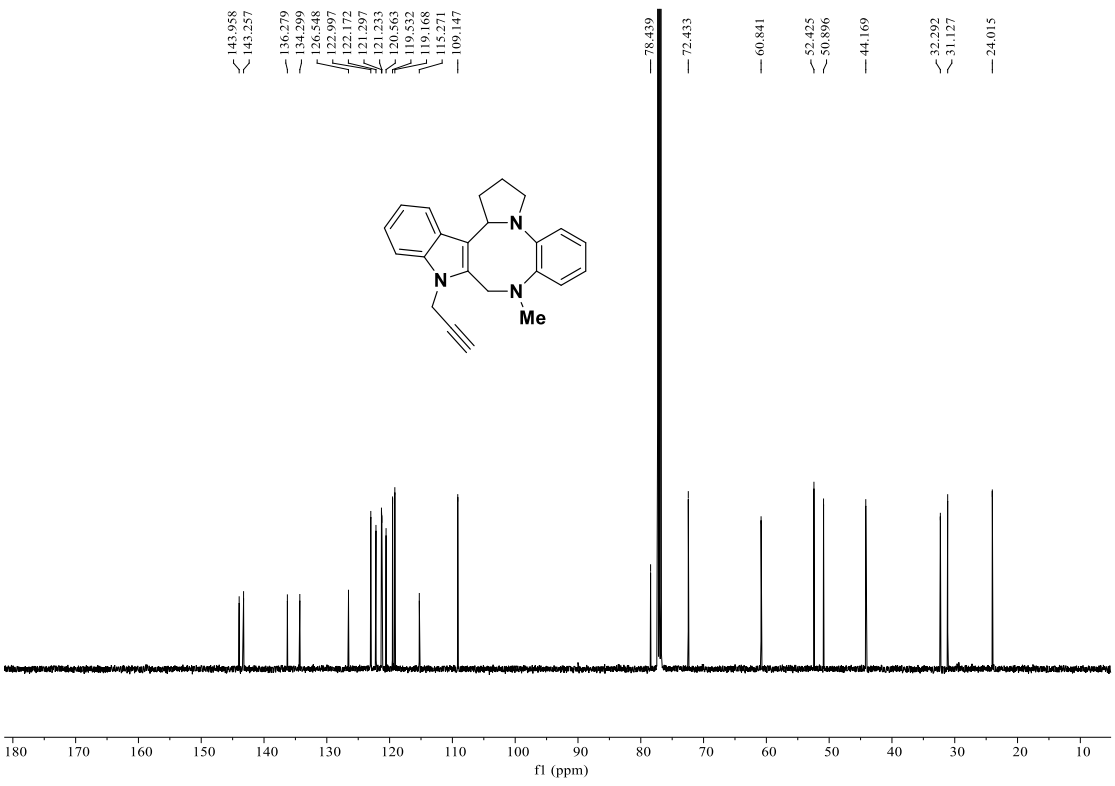


11-allyl-9-methyl-2,3,9,10,11,15c-hexahydro-1H-benzo[2,3]pyrrolo[1',2':1,8][1,4]diazocino[6,7-b]indole (3c)

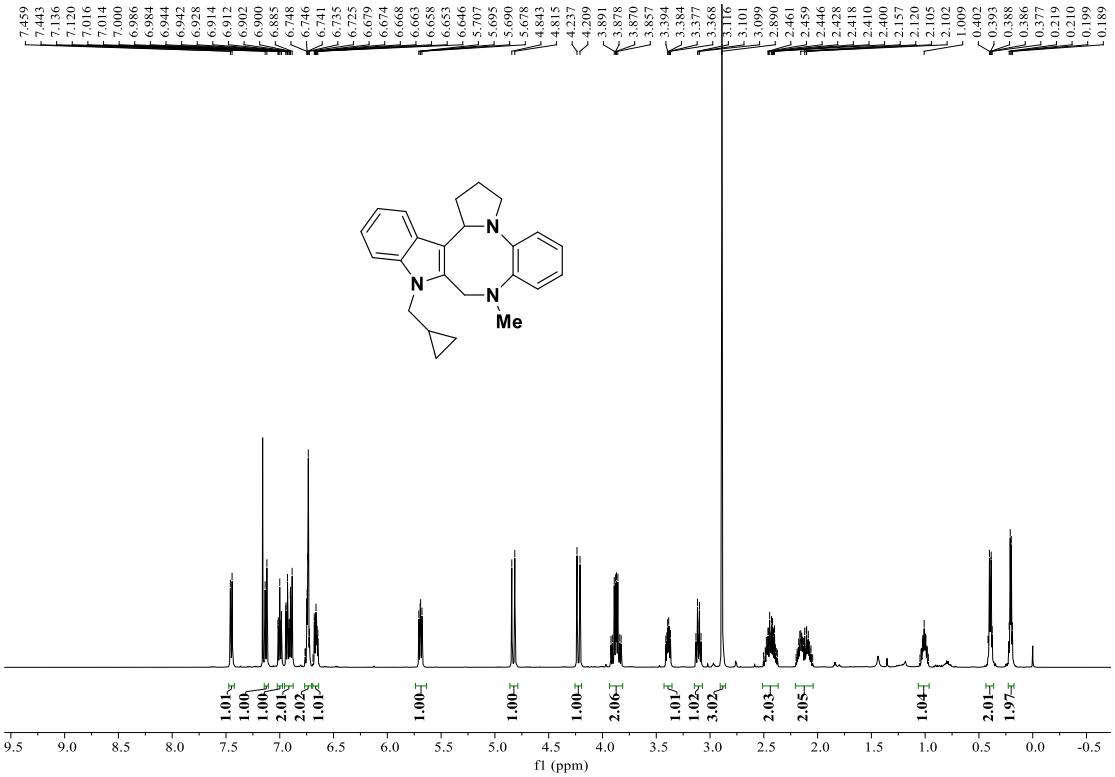


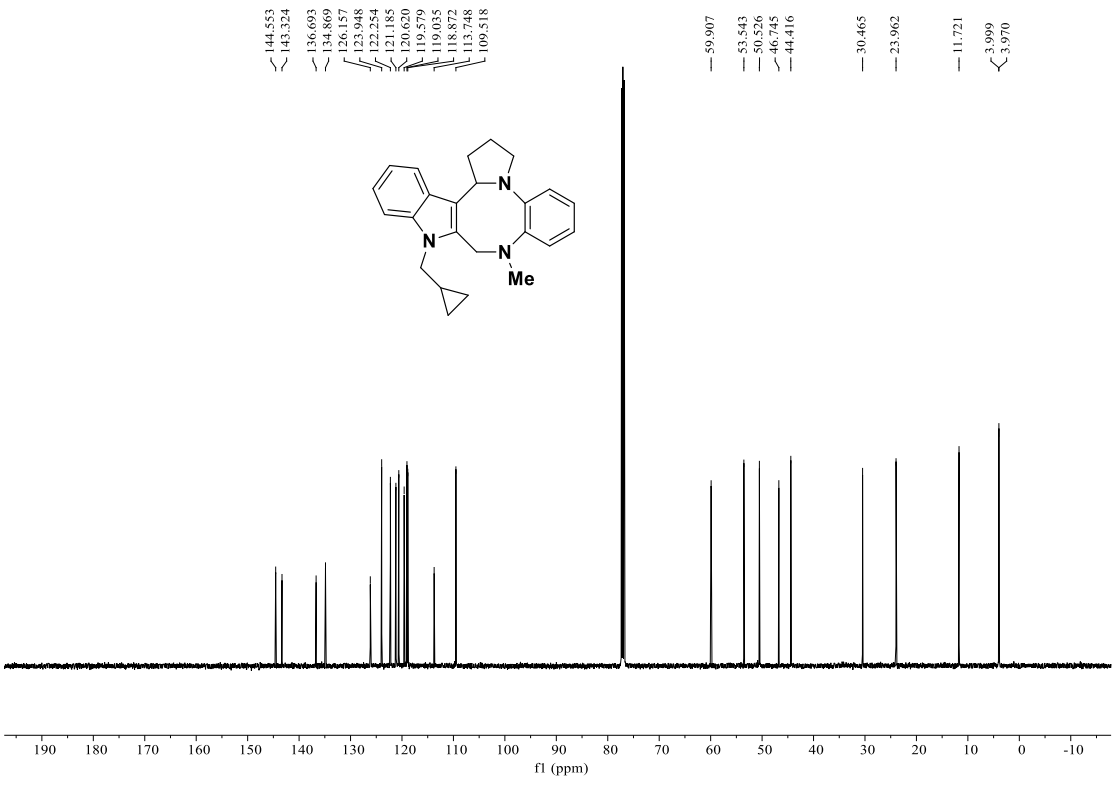
9-methyl-11-(prop-2-yn-1-yl)-2,3,9,10,11,15c-hexahydro-1H-benzo[2,3]pyrrolo[1',2':1,8][1,4]diazocino[6,7-b]indole (3d)



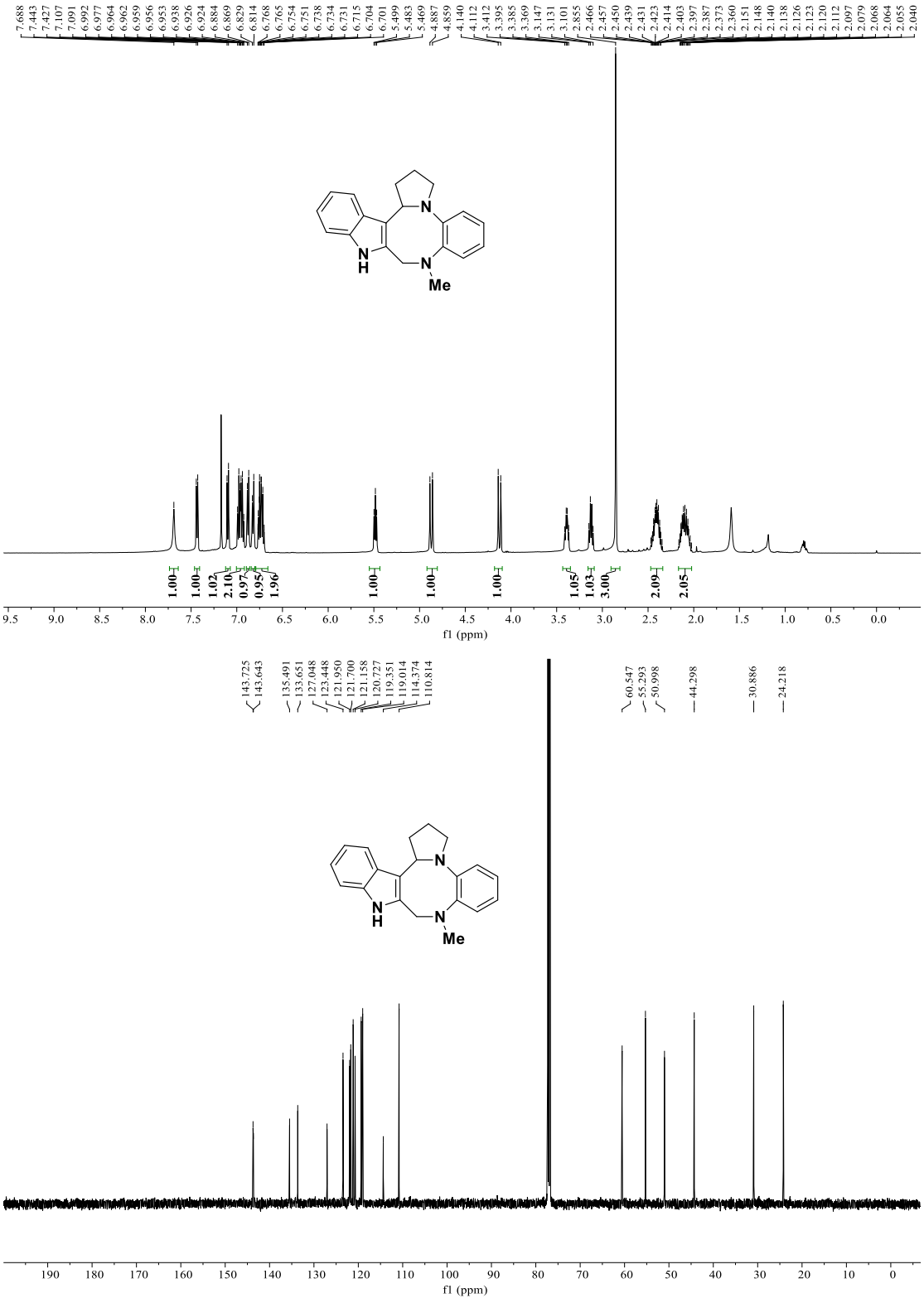


11-(cyclopropylmethyl)-9-methyl-2,3,9,10,11,15c-hexahydro-1H-benzo[2,3]pyrrolo [1',2':1,8][1,4]diazocino[6,7-b]indole (3e)

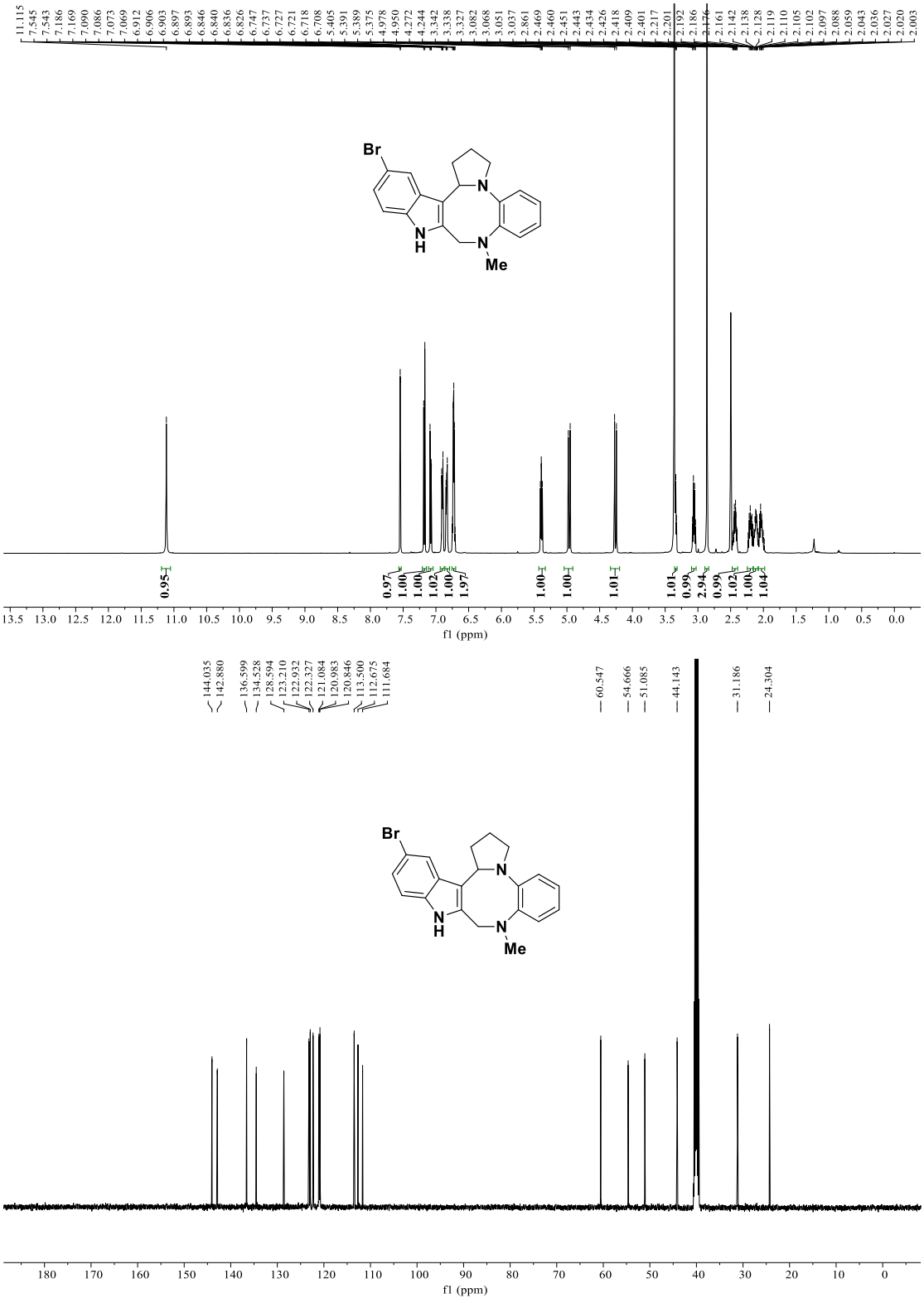




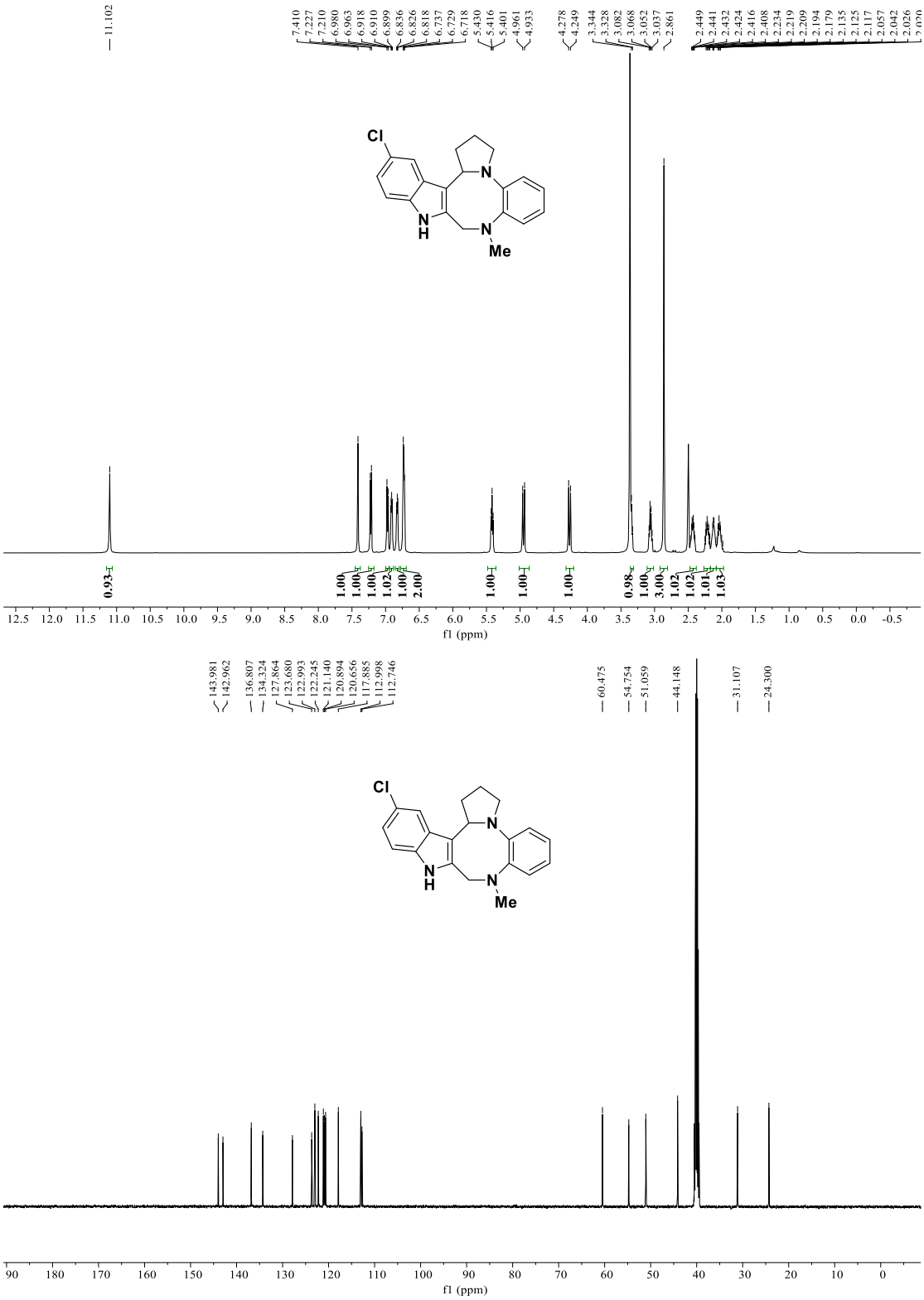
9-methyl-2,3,9,10,11,15c-hexahydro-1H-benzo[2,3]pyrrolo[1',2':1,8][1,4]diazocino [6,7-b]indole (3f)



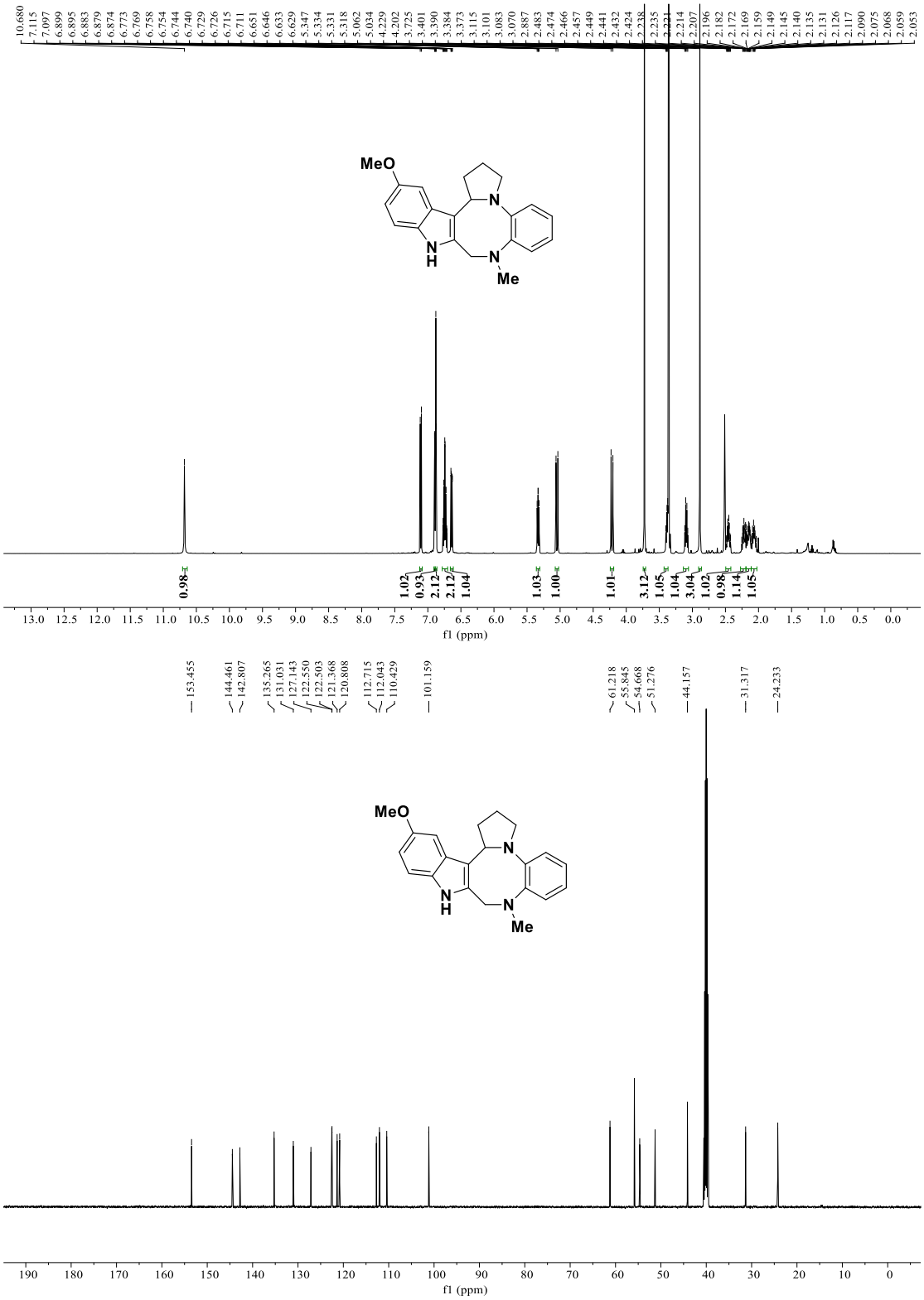
14-bromo-9-methyl-2,3,9,10,11,15c-hexahydro-1H-benzo[2,3]pyrrolo[1',2':1,8][1,4] diazocino[6,7-b]indole (3g)



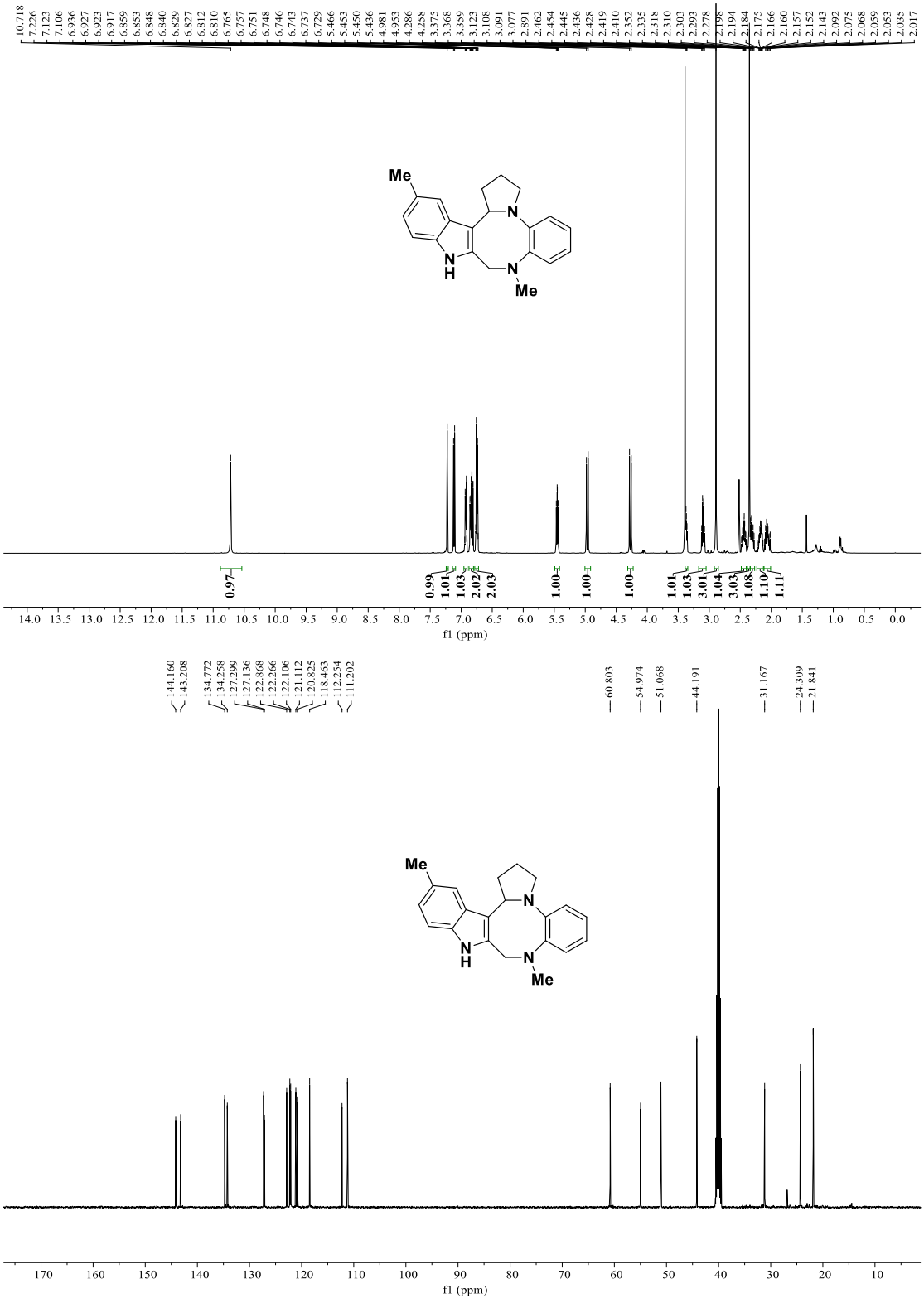
14-chloro-9-methyl-2,3,9,10,11,15c-hexahydro-1H-benzo[2,3]pyrrolo[1',2':1,8][1,4] diazocino[6,7-b]indole (3h)



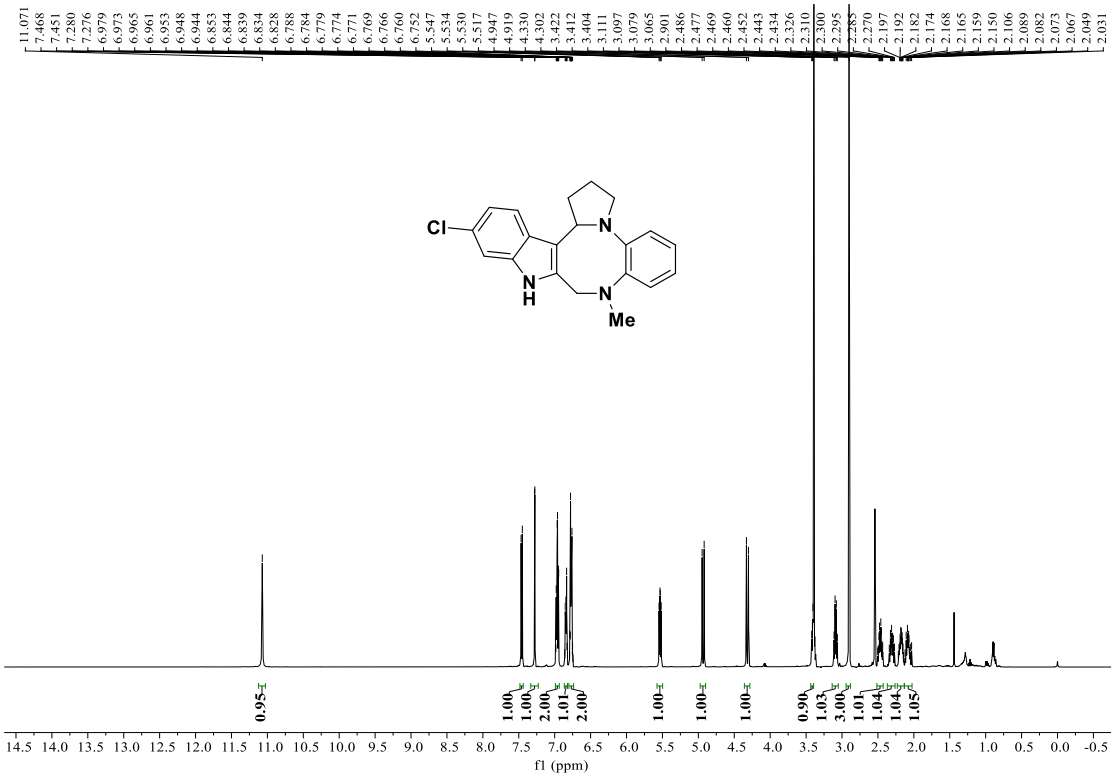
14-methoxy-9-methyl-2,3,9,10,11,15c-hexahydro-1H-benzo[2,3]pyrrolo[1',2':1,8][1,4]diazocino[6,7-b]indole (3i)

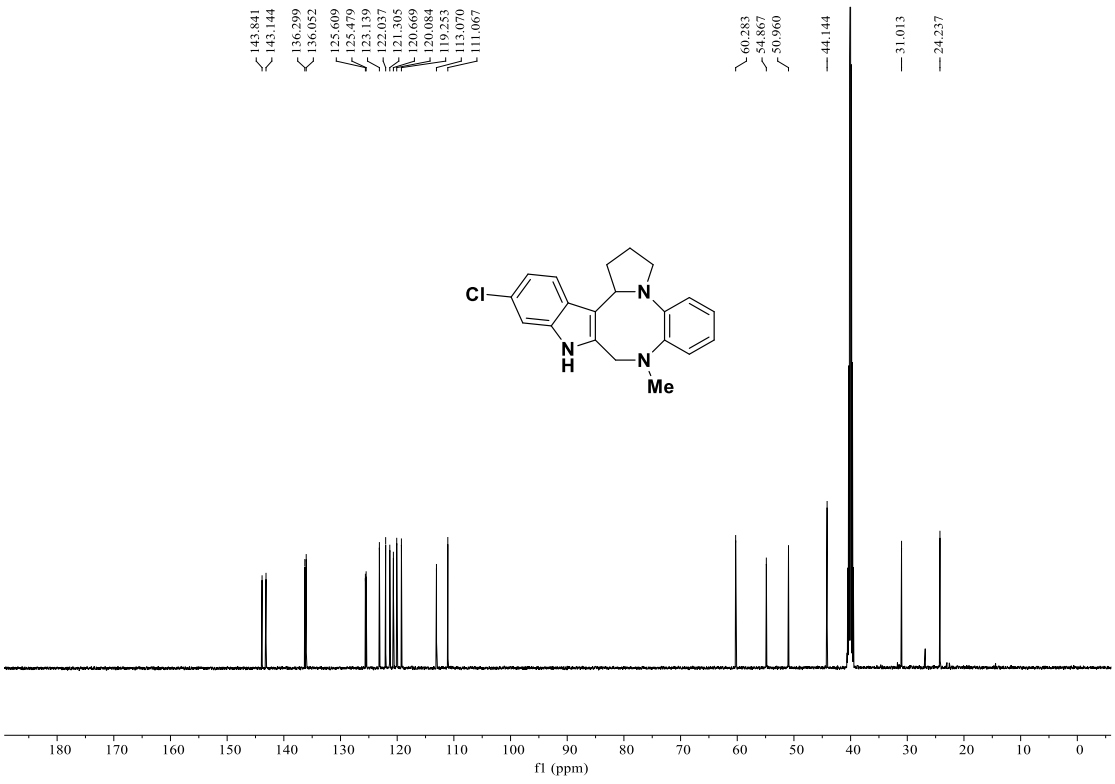


9,14-dimethyl-2,3,9,10,11,15c-hexahydro-1H-benzo[2,3]pyrrolo[1',2':1,8][1,4]diazocino[6,7-b]indole (3j)

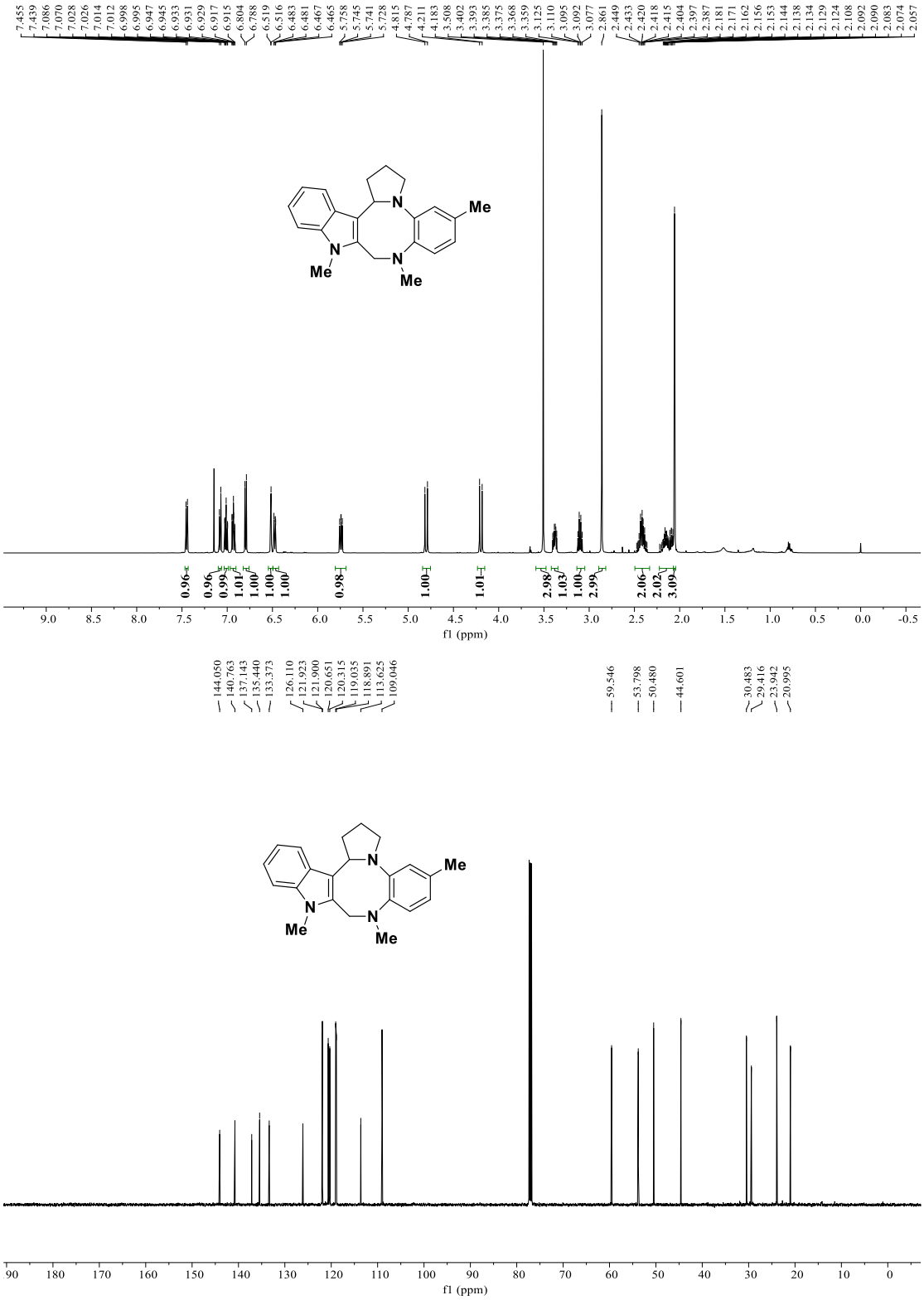


13-chloro-9-methyl-2,3,9,10,11,15c-hexahydro-1H-benzo[2,3]pyrrolo[1',2':1,8][1,4] diazocino[6,7-b]indole (3k)

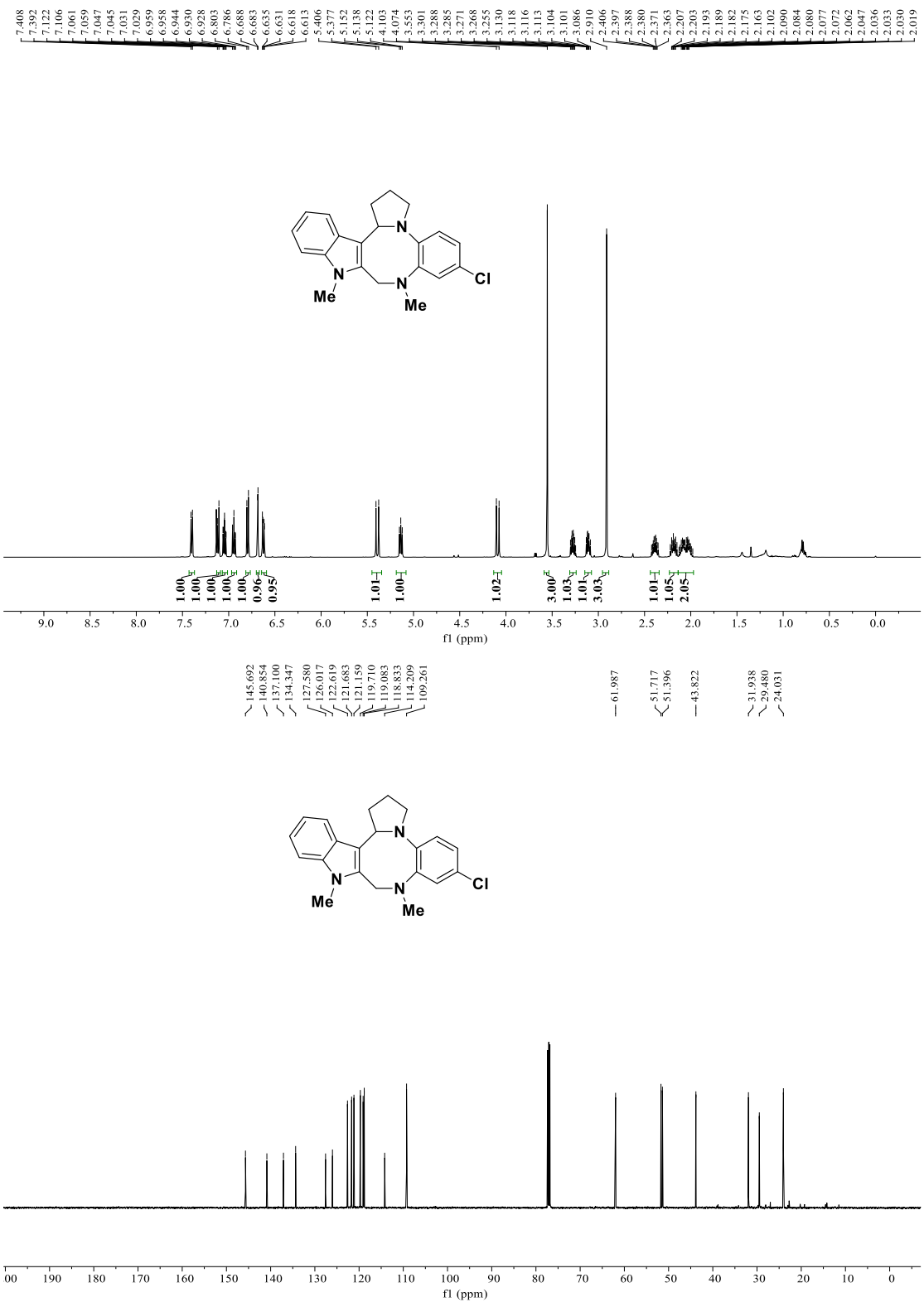




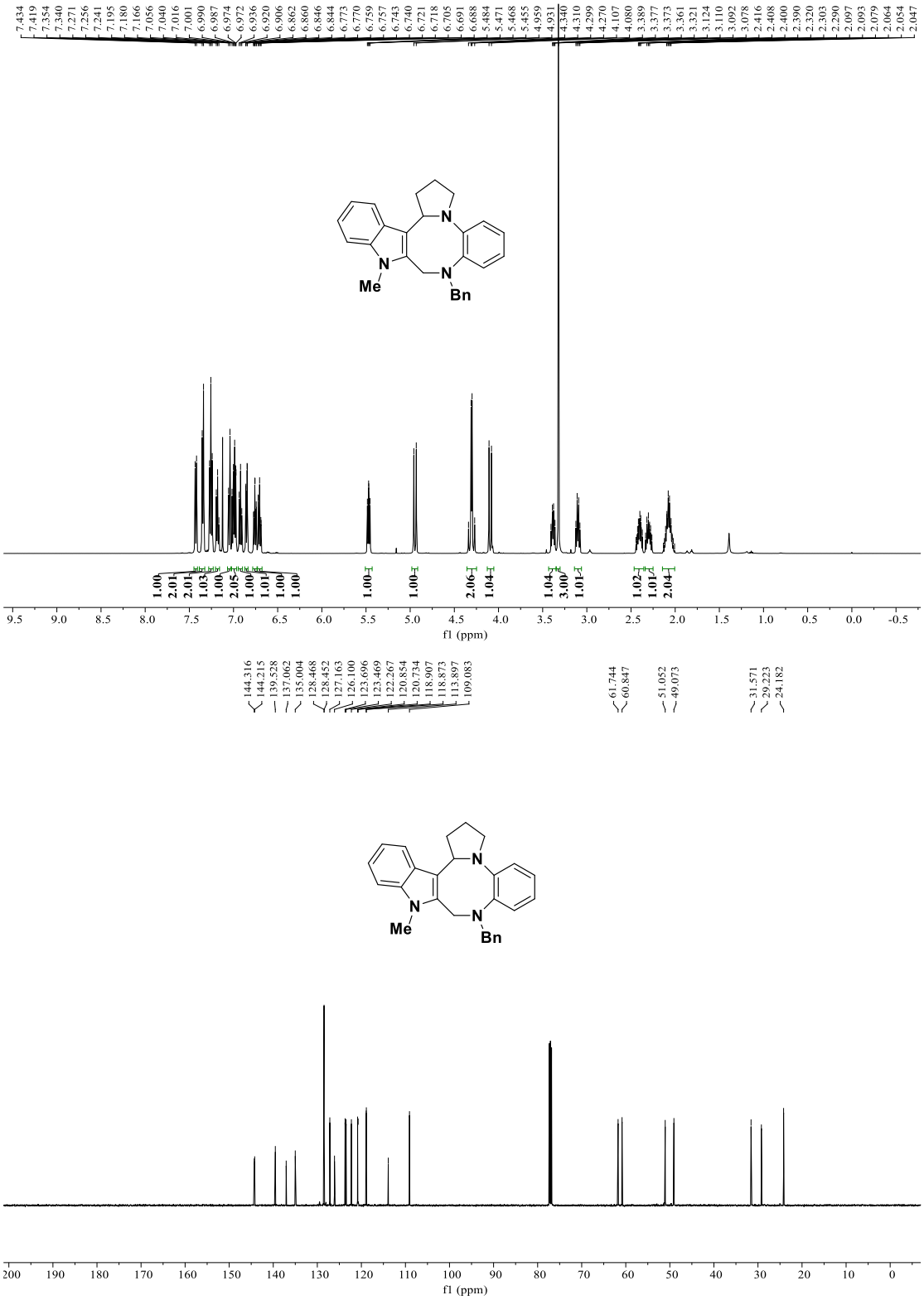
6,9,11-trimethyl-2,3,9,10,11,15c-hexahydro-1H-benzo[2,3]pyrrolo[1',2':1,8][1,4]diazocino[6,7-b]indole (3l)



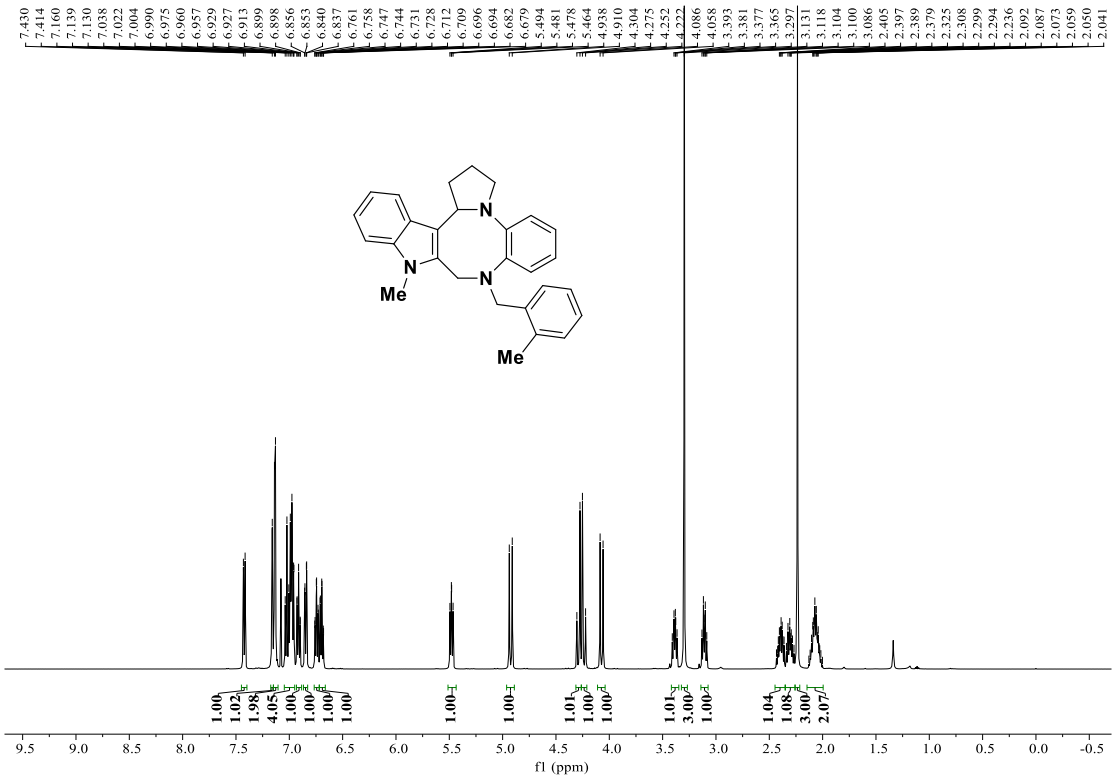
7-chloro-9,11-dimethyl-2,3,9,10,11,15c-hexahydro-1H-benzo[2,3]pyrrolo[1',2':1,8][1,4]diazocino[6,7-b]indole (3m)

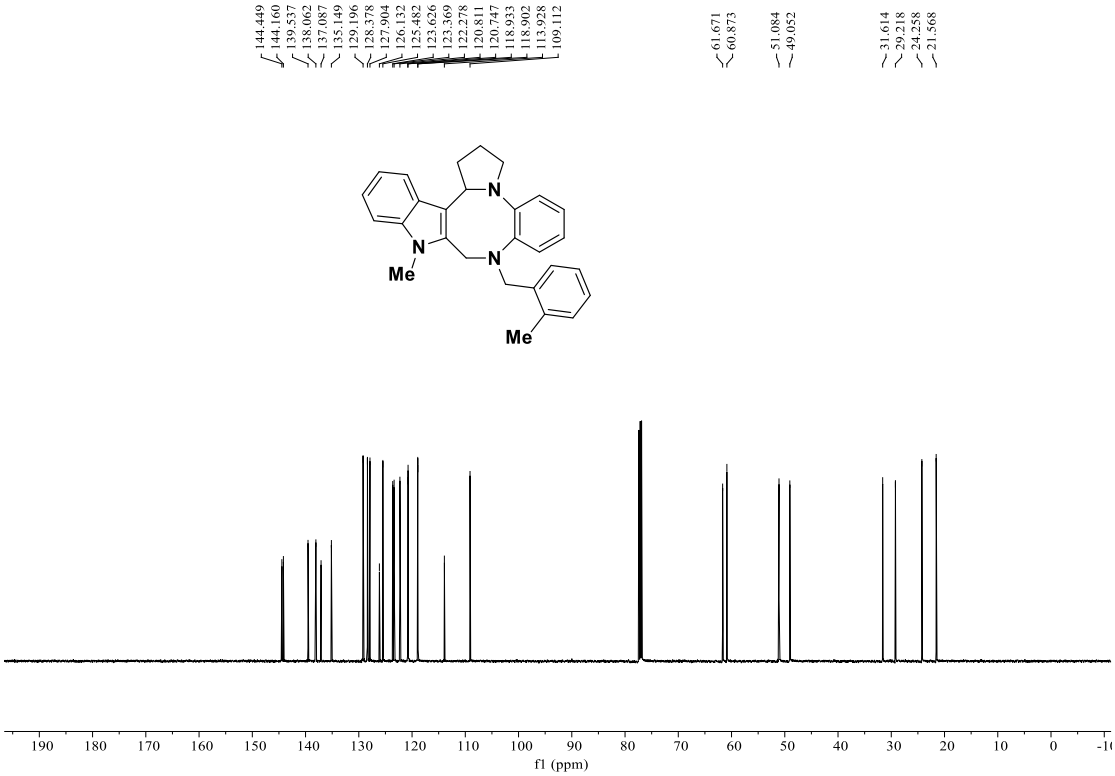


9-enzyl-11-methyl-2,3,9,10,11,15c-hexahydro-1H-benzo[2,3]pyrrolo[1',2':1,8][1,4]diazocino[6,7-b]indole (3n)

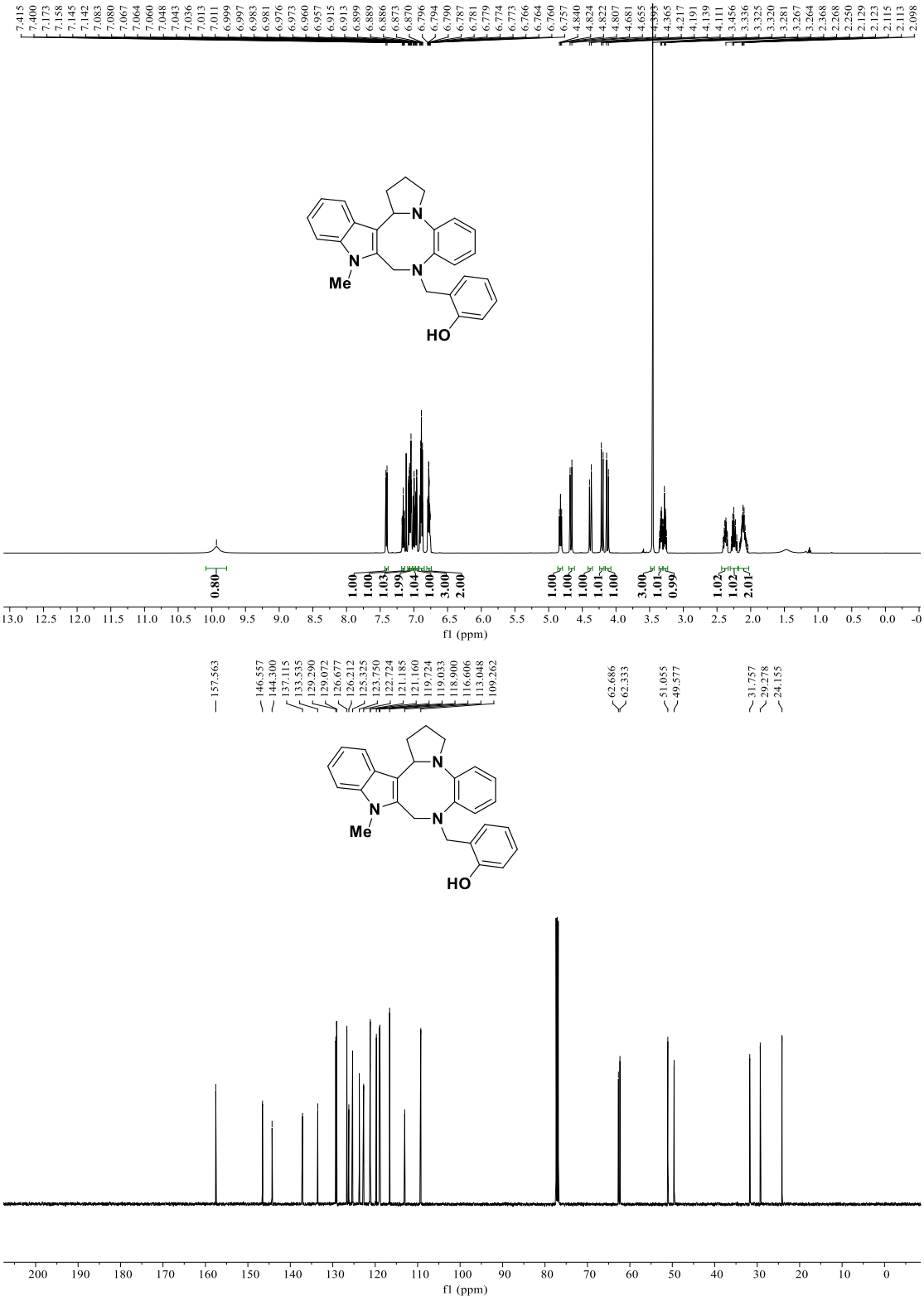


11-methyl-9-(2-methylbenzyl)-2,3,9,10,11,15c-hexahydro-1H-benzo[2,3]pyrrolo[1',2':1,8][1,4]diazocino[6,7-b]indole (3o)

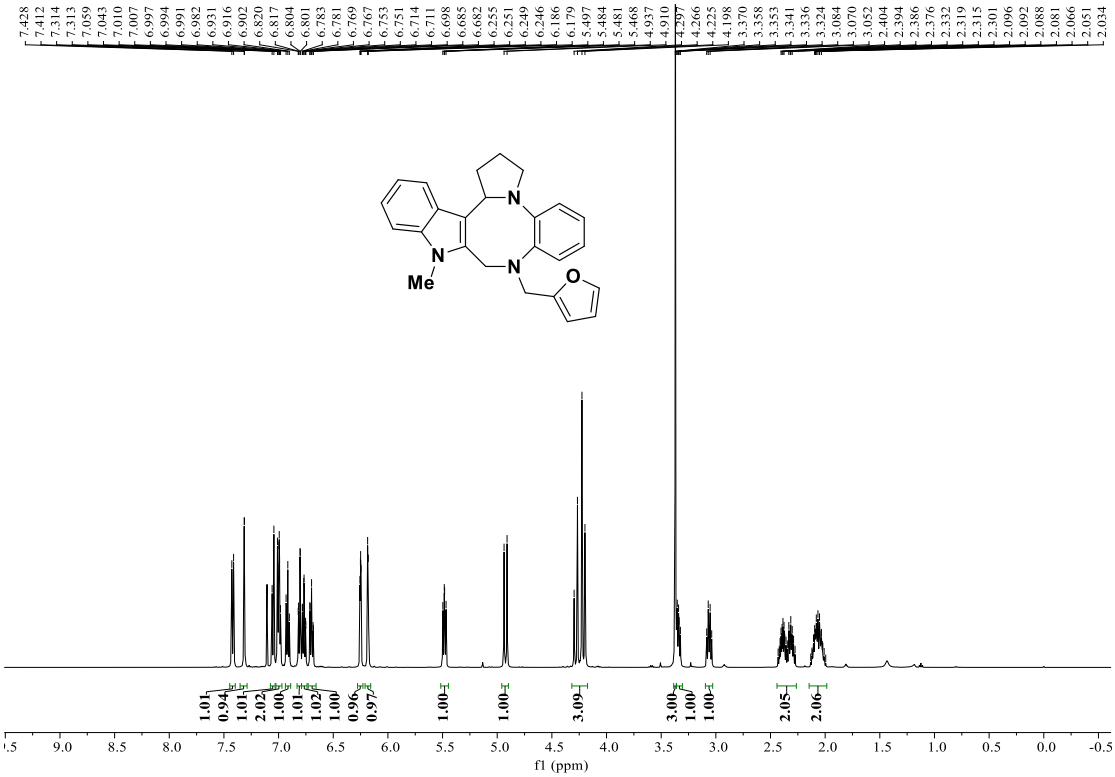


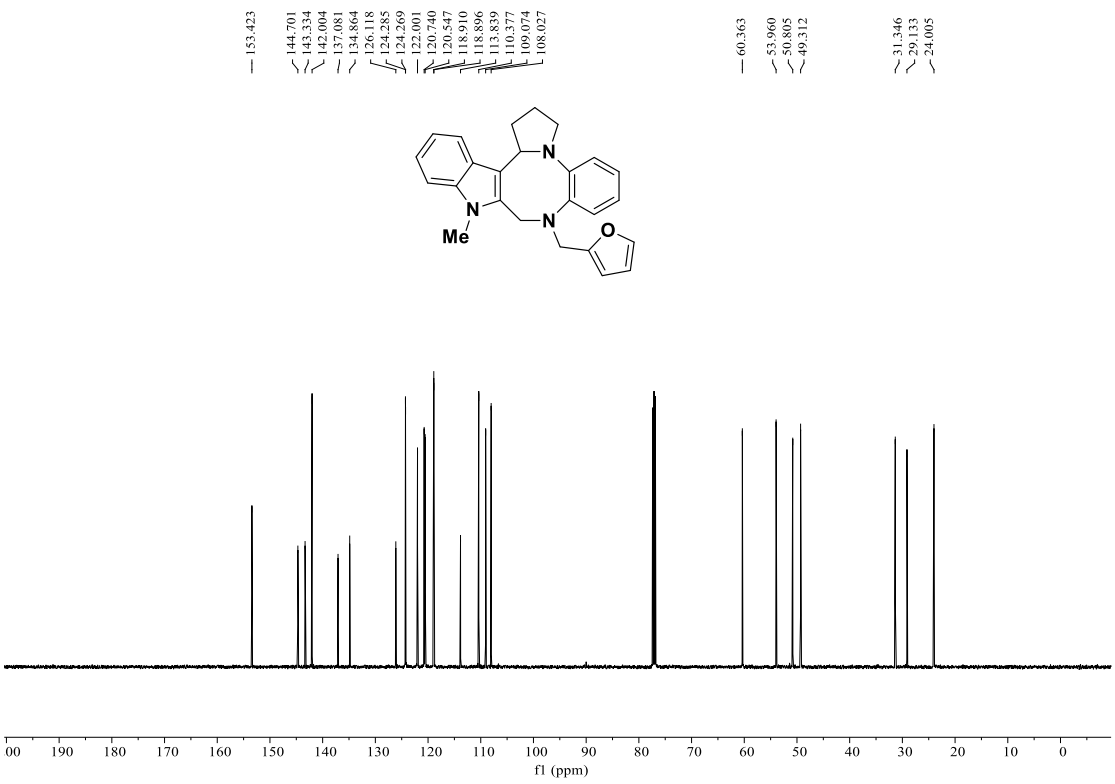


2-((11-methyl-1,2,3,10,11,15c-hexahydro-9H-benzo[2,3]pyrrolo[1',2':1,8][1,4]diazocino[6,7-b]indol-9-yl)methyl)phenol (3p)

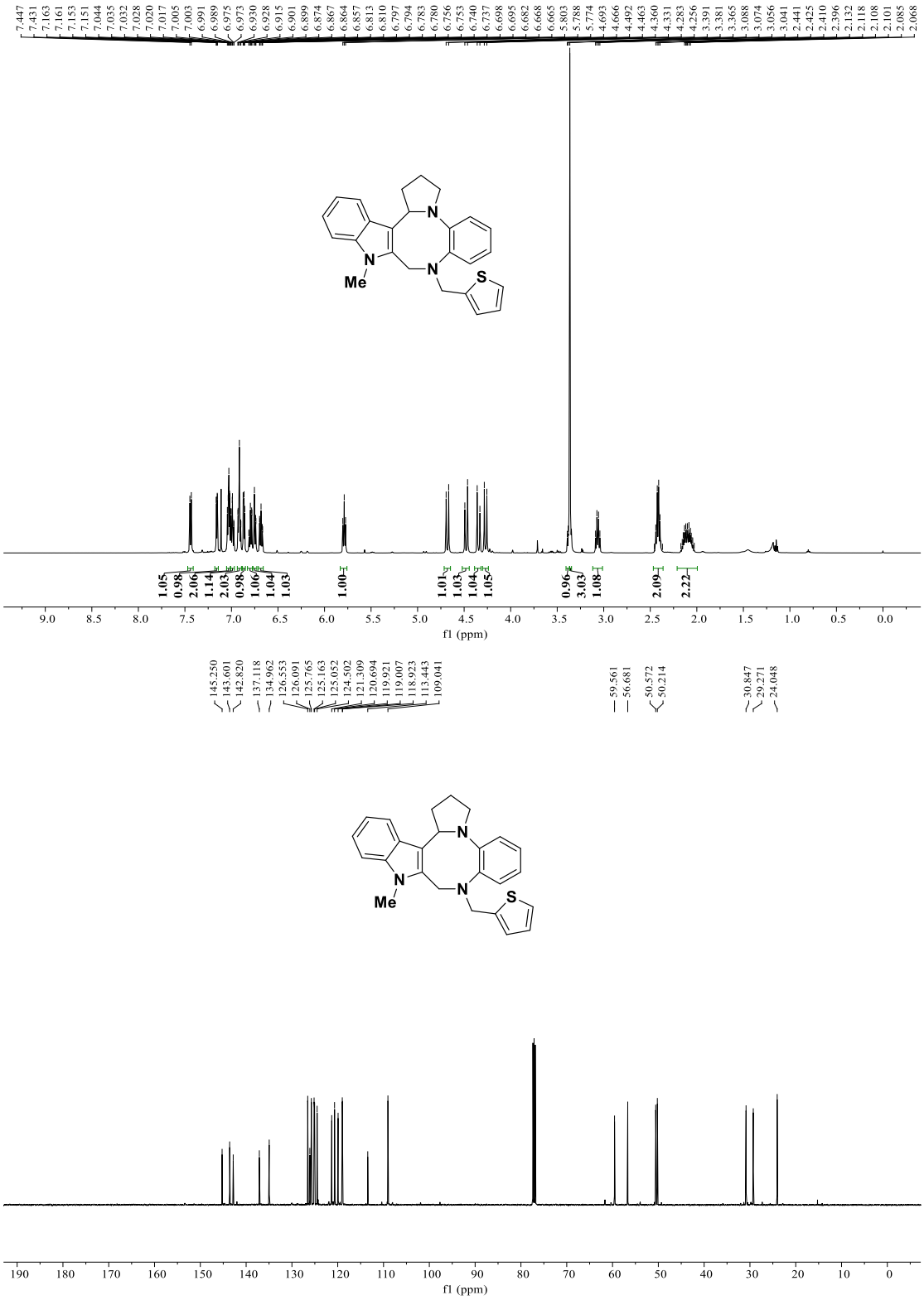


9-(furan-2-ylmethyl)-11-methyl-2,3,9,10,11,15c-hexahydro-1H-benzo[2,3]pyrrolo[1',2':1,8][1,4]diazocino[6,7-b]indole (3q)

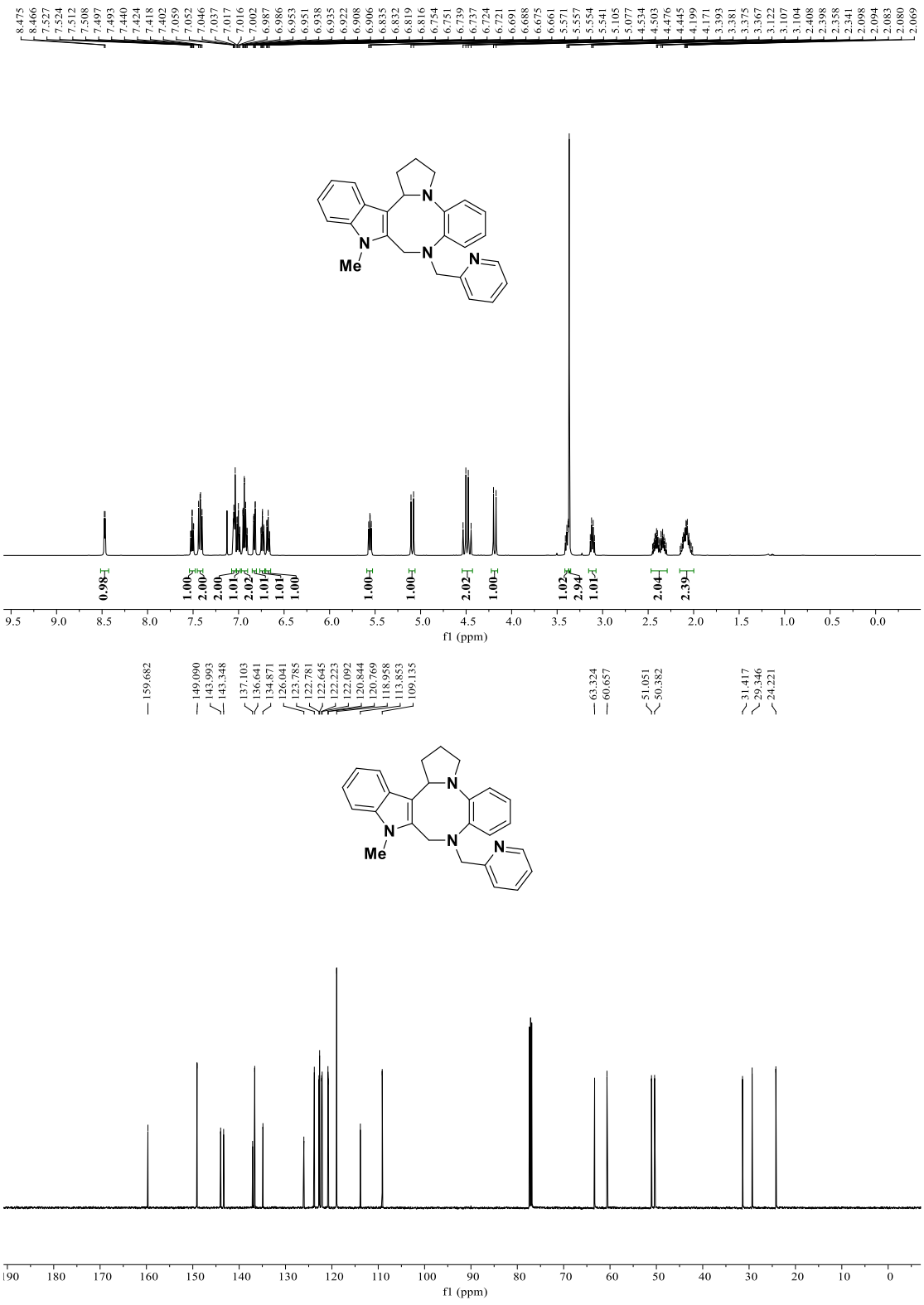




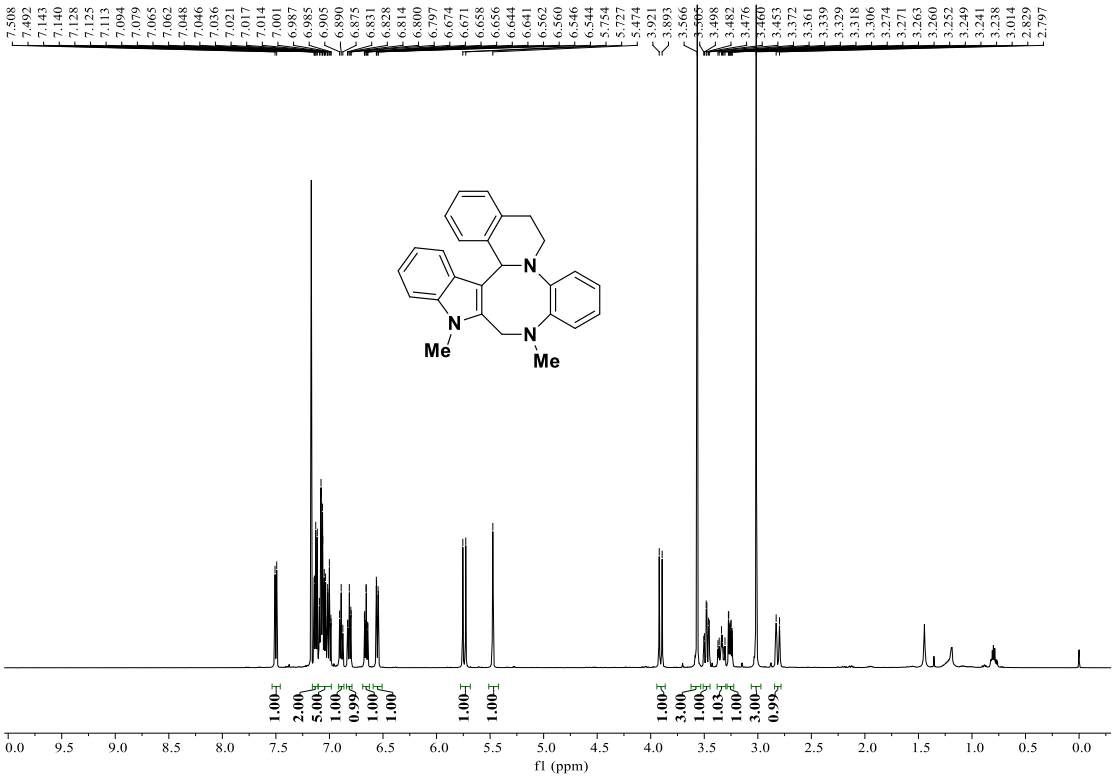
11-methyl-9-(thiophen-2-ylmethyl)-2,3,9,10,11,15c-hexahydro-1H-benzo[2,3]pyrrolo[1',2':1,8][1,4]diazocino[6,7-b]indole (3r)

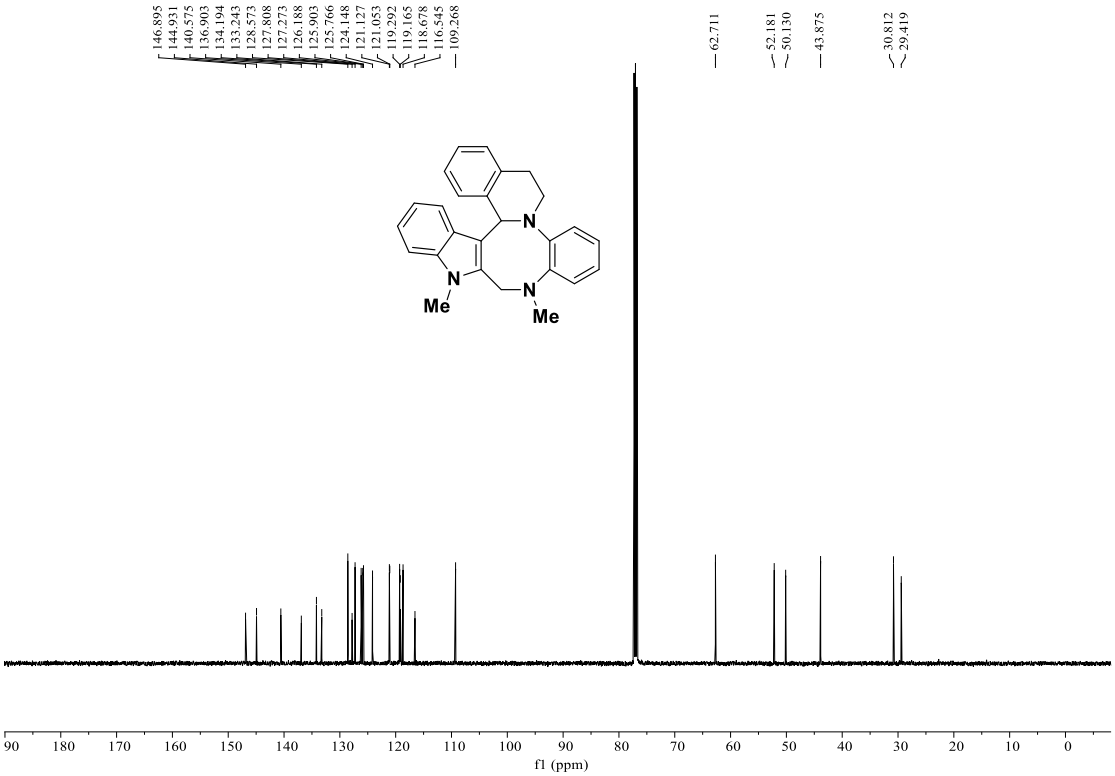


11-methyl-9-(pyridin-2-ylmethyl)-2,3,9,10,11,15c-hexahydro-1H-benzo[2,3]pyrrolo [1',2':1,8][1,4]diazocino[6,7-b]indole (3s)

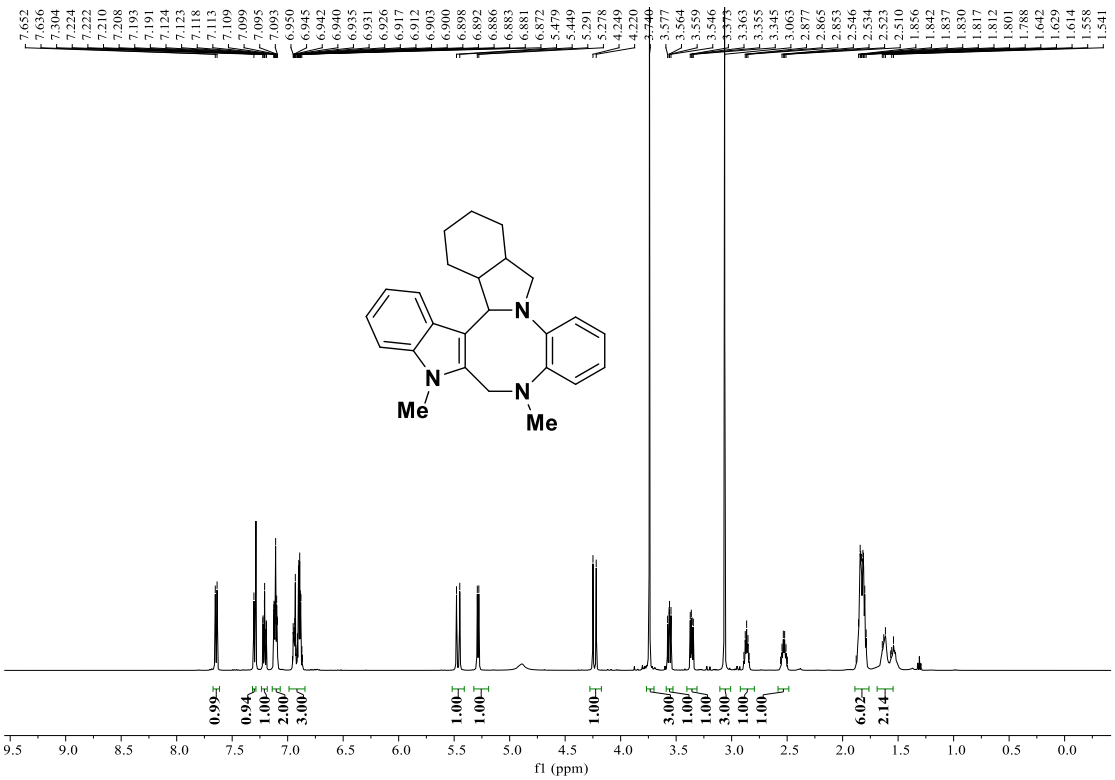


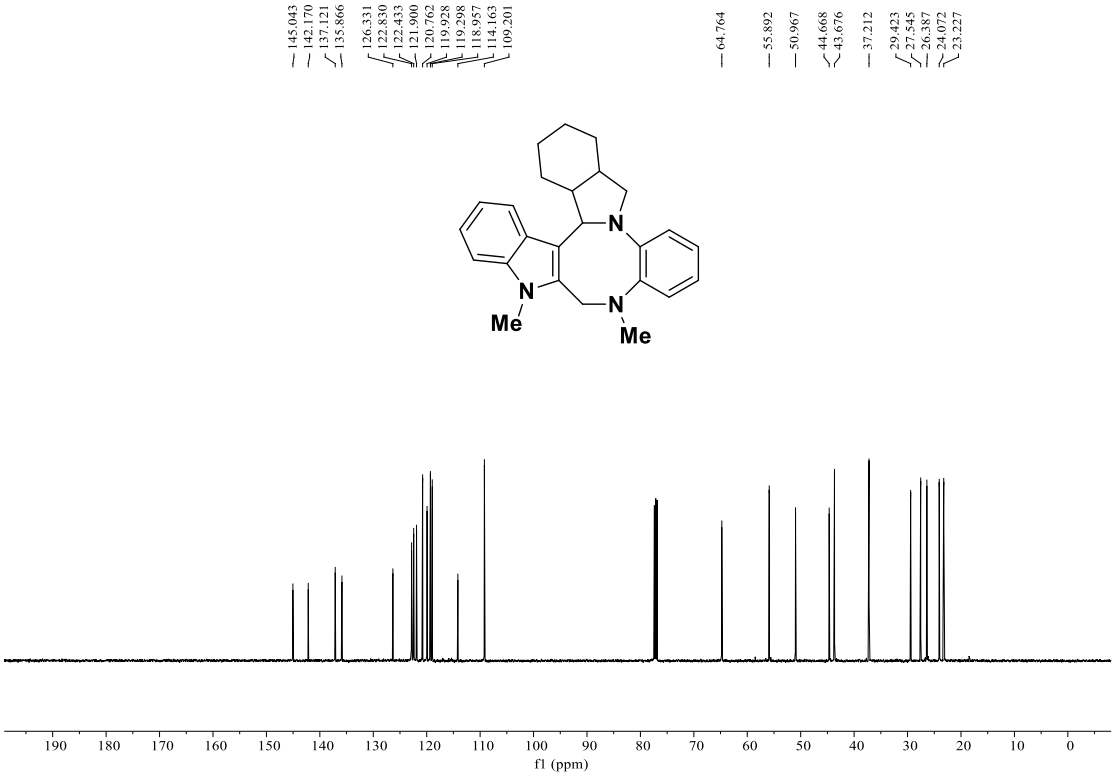
12,14-dimethyl-5,6,12,13,14,18c-hexahydrobenzo[2,3]indolo[2',3':6,7][1,4]diazocino[8,1-a]isoquinoline (3t)



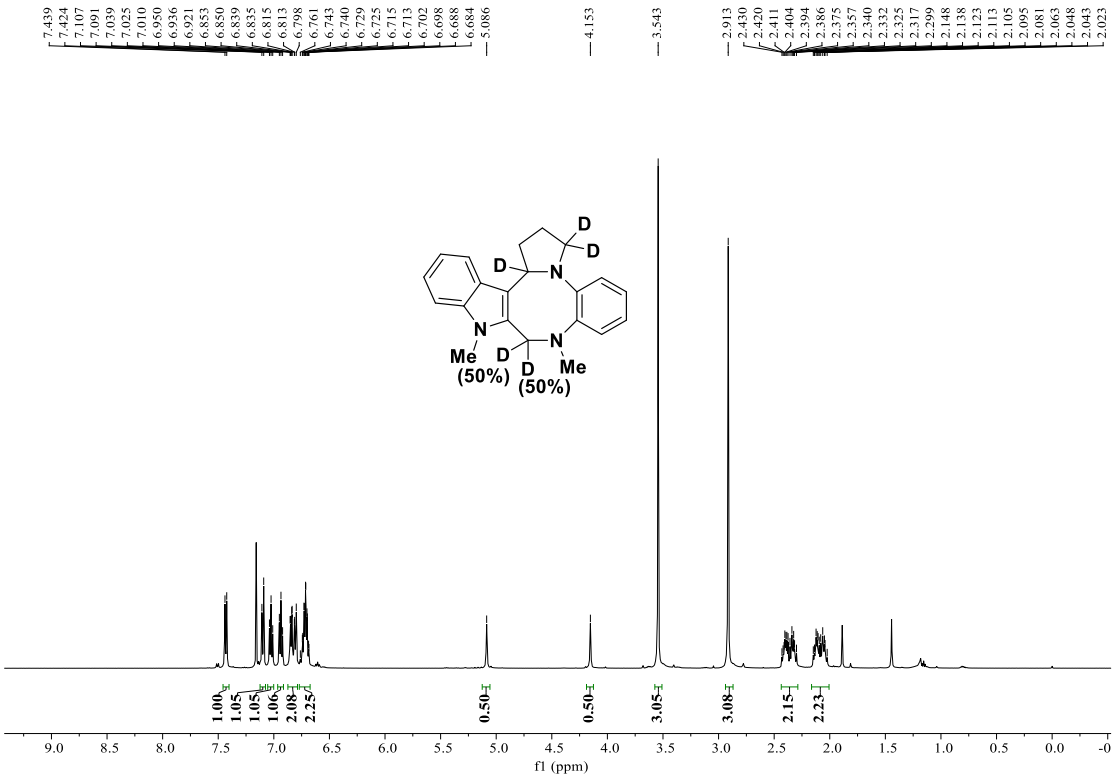


11,13-dimethyl-1,3,4,4a,5,11,12,13,17c,17d-decahydro-2H-benzo[2,3]isoindolo[2',1':1,8][1,4]diazocino[6,7-b]indole (3u)

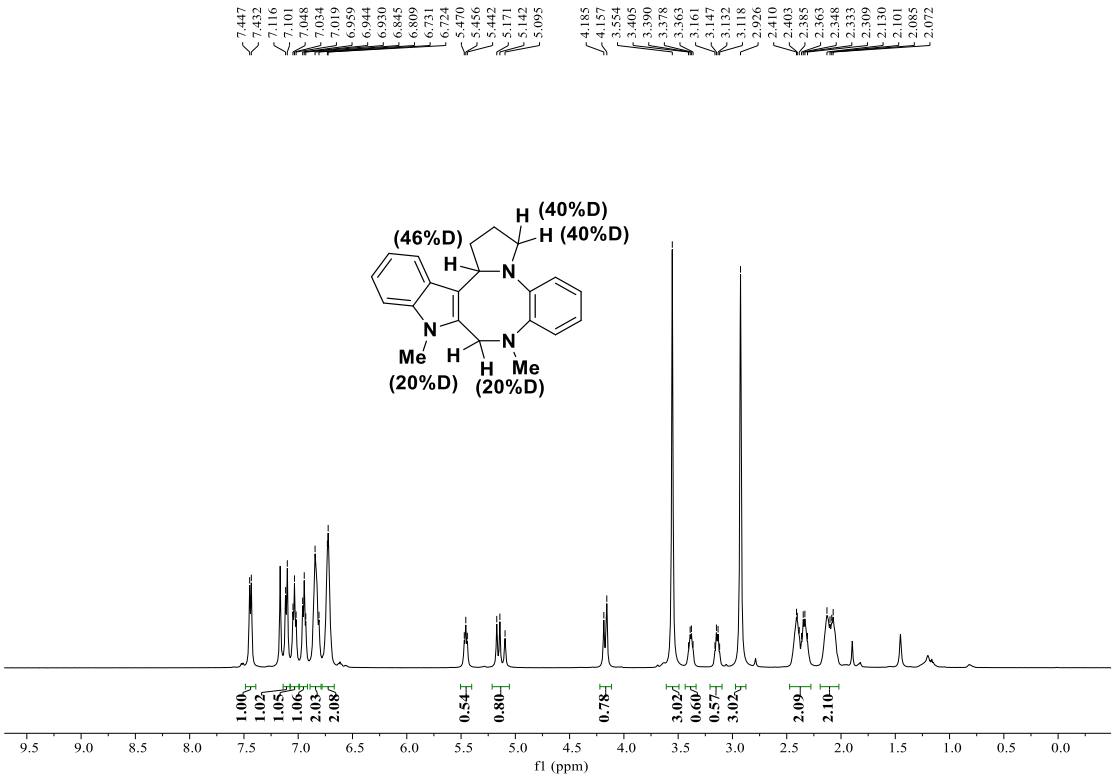




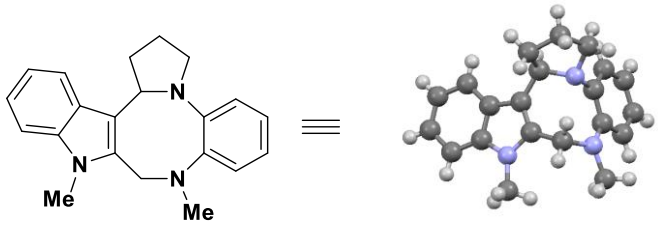
[D]-3a


7.439
7.424
7.107
7.091
7.039
7.025
7.010
6.950
6.936
6.921
6.853
6.850
6.839
6.835
6.815
6.813
6.798
6.761
6.743
6.740
6.729
6.725
6.715
6.713
6.702
6.698
6.688
6.684
5.086
4.153
3.543
2.913
2.430
2.420
2.411
2.404
2.394
2.386
2.375
2.357
2.340
2.332
2.325
2.317
2.299
2.148
2.138
2.123
2.113
2.105
2.095
2.081
2.063
2.048
2.043
2.023
D
D
D
N
N
Me
(50%)
D
D
(50%)
N
Me
1.00
1.05
1.05
1.06
2.08
2.25
0.50
0.50
3.05
3.08
2.15
2.23
f1 (ppm)

[H/D]-3a


7.447
7.432
7.116
7.101
7.048
7.034
7.019
6.959
6.944
6.930
6.845
6.809
6.731
6.724
5.470
5.456
5.442
5.171
5.142
5.095
4.185
4.157
3.554
3.405
3.390
3.378
3.363
3.161
3.147
3.132
3.118
2.926
2.410
2.403
2.385
2.363
2.348
2.333
2.309
2.130
2.101
2.085
2.072
H (40%D)
H (40%D)
(46%D)
H
N
N
Me
(20%D)
H
N
H
H
Me
(20%D)
1.00
1.02
1.05
1.06
2.03
2.08
0.54
0.80
0.78
3.02
0.60
0.57
3.02
2.09
2.10
f1 (ppm)

6. X-ray Crystallography for 3a



CCDC:2077987

Identification code	exp_11691
Empirical formula	C21 H23 N3
Formula weight	317.42
Temperature	293(2) K
Wavelength	1.54184 A
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 15.4459(6) A alpha = 90 deg.
	b = 7.45856(17) A beta = 118.081(5) deg.
	c = 16.2431(6) A gamma = 90 deg.
Volume	1650.99(12) A^3
Z, Calculated density	4, 1.277 Mg/m^3
Absorption coefficient	0.587 mm^-1
F(000)	680
Crystal size	0.120 x 0.110 x 0.110 mm
Theta range for data collection	3.258 to 67.215 deg.
Limiting indices	-13<=h<=18, -4<=k<=8, -19<=l<=17
Reflections collected / unique	5325 / 2962 [R(int) = 0.0166]
Completeness to theta = 67.215	99.8 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2962 / 0 / 220
Goodness-of-fit on F^2	1.060
Final R indices [I>2sigma(I)]	R1 = 0.0450, wR2 = 0.1197
R indices (all data)	R1 = 0.0518, wR2 = 0.1254
Extinction coefficient	0.0038(5)
Largest diff. peak and hole	0.228 and -0.179 e.A^-3