Supporting Information

Halogen Bond-catalyzed Pictet-Spengler Reaction

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1. General Information

All chemicals were purchased from commercial suppliers and used as received. Unless otherwise noted, all reactions were carried out under air. Reactions with chemicals sensitive to moisture or oxygen were carried out under an argon atmosphere using standard Schlenk techniques. Anhydrous tetrahydrofuran (THF) was obtained from an *Inert* PS-MD-6 solvent purification system. Methanol was dried using a standard method and stored over molecular sieves.[1]

Yields refer to isolated yields of compounds estimated to be >95% pure as determined by ^{1}H-NMR spectroscopy.

Thin layer chromatography was performed on fluorescence indicator marked precoated silica gel 60 plates (*Macherey-Nagel*, POLYGRAM SIL G/UV254) and visualized by UV light (254 nm/366 nm). Flash column chromatography was performed on silica gel (40 – 63 µm) with the solvents given in the procedures.

NMR spectra were recorded on a *Bruker* AVANCE NEO 600 MHz spectrometer with BBO probe head and a *Bruker* AVANCE NEO 600 MHz spectrometer with TXI probe head at 25 °C. Chemical shifts for ^{1}H-NMR spectra are reported as δ (parts per million) relative to the residual proton signal of $CDCl_3$ at 7.26 ppm (s), DMSO-d_6 at 2.50 ppm (quint) or MeOH-d_4 at 3.31 ppm (quint). Chemical shifts for ^{13}C-NMR spectra are reported as δ (parts per million) relative to the signal of $CDCl_3$ at 77.0 ppm (t), DMSO-d_6 at 39.5 ppm (sept) or MeOH-d_4 at 49.0 ppm (sept). Chemical shifts for ^{19}F-NMR spectra are reported as δ (parts per million) relative to the signal of $Si(CH_3)_4$ at 0.0 ppm. The following abbreviations are used to describe splitting patterns: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sept = septet, m = multiplet. Coupling constants *J* are given in Hz.

ESI and APCI mass spectra were recorded on an *Advion* Expression CMS^{L} via ASAP probe or direct inlet. EI mass spectra were recorded on an *Agilent* 5977A Series GC/MSD system. HR-EI mass spectra were recorded on a double-focusing mass spectrometer ThermoQuest MAT 95 XL from *Finnigan MAT*. HR-ESI mass spectra were recorded on a *Bruker* Impact II. All Signals are reported with the quotient from mass to charge *m/z*.

Optical Rotations were measured on an *Anton Paar* MCP 150 polarimeter at 20 °C in an appropriate solvent.

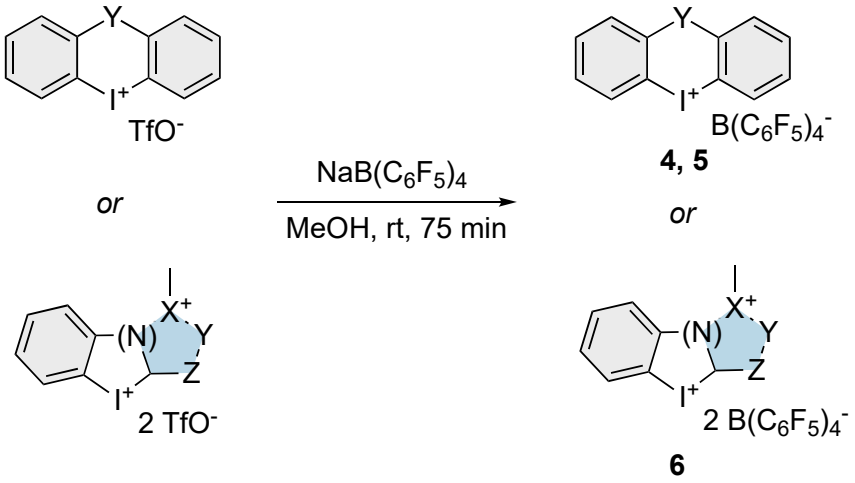
IR spectra were recorded on a *Thermo Scientific* Nicolet iS10 spectrometer with a diamond ATR unit. The absorption bands are reported in cm^{-1}.

Melting points of solids were measured on a *Büchi* M-5600 Melting Point apparatus and are uncorrected. The measurements were performed with a heating rate of 2 °C/min and the melting point temperatures T are reported in °C.

2. Synthesis of Catalysts

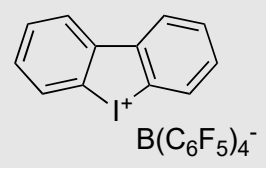
Dibenzoiodonium triflates, *N*-heterocyclic iodazinium bistriflates and sodium tetrakis(pentafluorophenyl)borate were synthesized according to literature procedures.[2,3]

2.1. General Procedure for Anion Exchange of Iodolium Triflates with Sodiumtetrakis(pentafluorophenyl) Borate (GP1)



To a solution of dibenzoiodonium triflates or *N*-heterocyclic iodazinium bistriflates (100 µmol, 1.0 eq.) in dry MeOH (0.05 M) was added sodium tetrakis(pentafluorophenyl)borate (1.0 eq. for each triflate anion) and stirred for 75 min at rt. After removal of the solvent, the residue was treated with H_2O (10 mL) and DCM (10 mL), the phases were separated and the aqueous phase was extracted with DCM (3 x 5 mL). The combined organic phases were dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The residue was dissolved in DCM/Et_2O (1:1, 2 mL) and triturated with *n*-pentane (10 mL). The formed precipitate was further washed with *n*-pentane (2 x 5 mL) to obtain diaryliodonium tetrakis(pentafluorophenyl)borates **4** or **5** or *N*-heterocyclic iodazinium tetrakis(pentafluorophenyl)borates **6**.

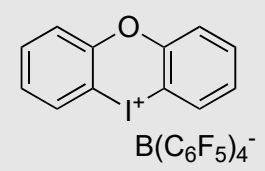
Dibenzo[*b,d*]iodoli-5-ium tetrakis(pentafluorophenyl)borate (4a)



Following GP1, the reaction of dibenzo[*b,d*]iodol-5-ium triflate (42.8 mg) and $NaB(C_6F_5)_4$ (70.2 mg, 100 µmol, 1.00 eq.) gave the product **4a** (87.2 mg, 91.0 µmol, 91%) as an off-white solid.

^{1}H-NMR (600 MHz, DMSO-*d*$_6$) δ = 8.46 (d, *J* = 6.5 Hz, 2H), 8.22 (d, *J* = 8.3 Hz, 2H), 7.84 (t, *J* = 7.2 Hz, 2H), 7.69 (t, *J* = 7.0 Hz, 2H).
^{13}C-NMR (150 MHz, DMSO-*d*$_6$) δ = 148.0 (d, *J* = 239.8 Hz), 142.2, 138.1 (d, *J* = 246.7 Hz), 136.1 (d, *J* = 245.7 Hz), 131.5, 131.1, 131.1, 127.4, 124.4 – 123.1 (m), 122.1.
^{19}F-NMR (565 MHz, DMSO-*d*$_6$) δ = - 132.4 (d, *J* = 13.3 Hz, 8F), -161.5 (t, *J* = 21.5 Hz, 4F), -166.0 (t, *J* = 19.0 Hz, 8F).
HRMS (ESI): *m/z* [M-B(C_6F_5)$_4^-$]$^+$ calcd for $C_{12}H_8I^+$: 278.9665; found 278.9662.
IR (ATR) $\tilde{\nu}$ = 3099, 1645, 1513, 1456, 1270, 1082, 967, 746, 661.
Mp = 252 – 253 °C (decomp.).

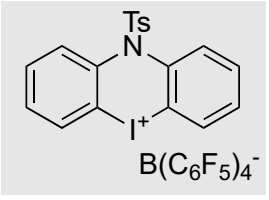
Dibenzo[*b,e*][1,4]iodaoxin-5-ium tetrakis(pentafluorophenyl) borate (5a)



Following GP1, the reaction of dibenzo[*b,e*][1,4]iodaoxin-5-ium triflate (44.4 mg) and NaB(C_6F_5)$_4$ (70.2 mg, 100 µmol, 1.00 eq.) gave the product **5a** (69.8 mg, 71.6 µmol, 72%) as a colorless solid.

^{1}H-NMR (600 MHz, DMSO-*d*$_6$) δ = 8.03 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.73 (dd, *J* = 8.1, 1.6 Hz, 2H), 7.69 (ddd, *J* = 8.3, 7.1, 1.4 Hz, 2H), 7.46 (td, *J* = 7.8, 7.2, 1.6 Hz, 2H).
^{13}C-NMR (150 MHz, DMSO-*d*$_6$) δ =153.4, 147.5 (d, *J* = 241.5 Hz), 137.7 (d, *J* = 242.6 Hz), 135.6 (d, *J* = 247.1 Hz), 133.5, 133.5, 128.2, 123.8 – 122.8 (m), 121.6, 102.3.
^{19}F-NMR (565 MHz, DMSO-*d*$_6$) δ = -132.4 (d, *J* = 13.0 Hz, 8F), -161.3 (t, *J* = 21.5 Hz, 4F), -165.9 (t, *J* = 20.7 Hz, 8F).
HRMS (ESI): *m/z* [M-B(C_6F_5)$_4^-$]$^+$ calcd for $C_{12}H_8IO^+$: 294.9614; found 294.9611.
IR (ATR) $\tilde{\nu}$ = 3605, 2358, 1644, 1513, 1452, 1263, 1085, 974.
Mp = 219 – 221 °C.

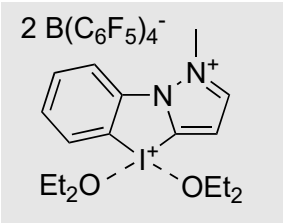
10-Tosyl -10*H*-dibenzo[*b,e*]iodazin-5-ium tetrakis(pentafluoro-phenyl)borate (5b)



Following GP1, the reaction of 10-tosyl-10*H*-dibenzo[*b,e*]iodazin-5-ium triflate (59.7 mg) and NaB(C_6F_5)$_4$ (70.2 mg, 100 µmol, 1.00 eq.) gave the product **5b** (100 mg, 88.7 µmol, 89%) as a colorless solid.

^{1}H-NMR (600 MHz, DMSO-*d*$_6$) δ = 7.98 (dd, *J* = 8.1, 1.5 Hz, 4H), 7.80 – 7.73 (m, 2H), 7.61 – 7.54 (m, 2H), 7.46 – 7.32 (m, 4H), 2.43 (s, 3H).
^{13}C-NMR (150 MHz, DMSO-*d*$_6$) δ = 148.0 (d, *J* = 241.0 Hz), 145.9, 138.1 (d, *J* = 246.5 Hz), 137.4, 136.1 (d, *J* = 245.2 Hz), 135.8, 134.6, 133.0, 132.3, 131.3, 131.1, 127.6, 114.3, 21.7.
^{19}F-NMR (565 MHz, DMSO-*d*$_6$) δ = -132.4 (d, *J* = 13.0 Hz, 8F), -161.3 (t, *J* = 21.5 Hz, 4F), -165.9 (t, *J* = 20.7 Hz, 8F).
HRMS (ESI): *m/z* [M-B(C_6F_5)$_4^-$]$^+$ calcd for $C_{19}H_{15}INO_2S^+$: 447.9863; found 447.9859.
IR (ATR) $\tilde{\nu}$ = 2923, 1645, 1514, 1456, 1348, 1272, 1158, 1083, 973.
Mp = 222 – 224 °C.

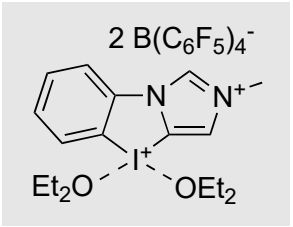
2-Methylbenzo[*d*]imidazo[5,1-*b*][1,3]iodazole-2,4-diium tetrakis(pentafluorophenyl)borate dietherate complex (6a)



Following GP1, the reaction of 2-methylbenzo[*d*]imidazo[5,1-*b*][1,3]iodazole-2,4-diium bistriflate (58.2 mg) and NaB(C_6F_5)$_4$ (140 mg, 200 µmol, 2.00 eq.) gave the product **6a** (161 mg, 98.0 µmol, 98%) as a colorless solid.

^{1}H-NMR (600 MHz, DMSO-*d*$_6$) δ = 8.87 (s, 1H), 8.59 (d, *J* = 8.5 Hz, 1H), 8.37 (d, *J* = 8.3 Hz, 1H), 8.00 (t, *J* = 7.7 Hz, 1H), 7.82 (t, *J* = 7.9 Hz, 1H), 7.43 (s, 1H), 4.78 (s, 3H), 3.38 (q, *J* = 7.0 Hz, 8H), 1.09 (t, *J* = 7.0 Hz, 12H).
^{13}C NMR (150 MHz, DMSO-*d*$_6$) δ = 147.5 (br d, *J* = 241.0 Hz), 143.4, 137.6 (br d, *J* = 245.3 Hz), 135.6 (br d, *J* = 245.5 Hz), 135.0, 132.2, 131.4, 130.6, 125.0 – 121.5 (br s/m), 119.3, 112.7, 112.1, 64.9, 42.4, 15.1.
^{19}F-NMR (565 MHz, DMSO-*d*$_6$) δ = -132.4 (d, *J* = 13.1 Hz, 16F), -161.3 (t, *J* = 21.6 Hz, 8F), -165.9 (t, *J* = 20.6 Hz, 16F).
HRMS (ESI): *m/z* [M+H-2B(C_6F_5)$_4^-$]$^+$ calcd for $C_{10}H_{10}IN_2^+$: 284.9883; found 284.9881.
IR (ATR) $\tilde{\nu}$ = 3144, 2981, 1644, 1513, 1456, 1411, 1274, 1083, 974.
Mp = 115 – 119 °C.
The analytical data is in accordance with the literature data.[3]

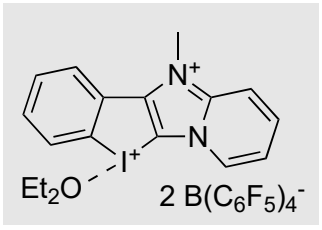
2-Methylbenzo[d]imidazo[5,1-*b*][1,3]iodazole-2,4-diium tetrakis(pentafluorphenyl)borate dietherate complex (6b)



Following GP1, the reaction of 2-methylbenzo[d]imidazo[5,1-*b*][1,3]iodazole-2,4-diium bistriflate (58.2 mg) and $NaB(C_6F_5)_4$ (140 mg, 200 µmol, 2.00 eq.) gave the product **6b** (116 mg, 68.6 µmol, 69%) as a colorless solid.

^{1}H-NMR (600 MHz, DMSO-*d*$_6$) δ = 10.56 (s, 1H), 8.35 (d, *J* = 6.8 Hz, 1H), 8.20 (d, *J* = 8.3 Hz, 1H), 8.14 (s, 1H), 7.99 (t, *J* = 7.2 Hz, 1H), 7.77 (t, *J* = 7.9 Hz, 1H), 4.12 (s, 3H), 3.38 (q, *J* = 7.0 Hz, 4H), 1.09 (t, *J* = 7.0 Hz, 6H).
^{13}C-NMR (150 MHz, DMSO-*d*$_6$) δ = 147.5 (d, *J* = 239.0 Hz), 137.6 (d, *J* = 243.2 Hz), 135.8, 135.6 (d, *J* = 245.0 Hz), 134.3, 132.4, 131.3, 131.1, 126.7, 123.9 – 121.8 (m), 118.7, 113.8, 102.7, 64.9, 37.7, 15.2.
^{19}F-NMR (565 MHz, DMSO-*d*$_6$) δ = -132.4 (d, *J* = 13.0 Hz, 16F), -161.3 (t, *J* = 21.5 Hz, 8F), -165.9 (t, *J* = 20.7 Hz, 16F).
HRMS (ESI): *m/z* $[M+H-2B(C_6F_5)_4^-]^+$ calcd for $C_{19}H_{15}INO_2S^+$: 284.9878; found 284.9882.
IR (ATR) $\tilde{\nu}$ = 3160, 2983, 1645, 1514, 1456, 1374, 1272, 1083, 974.
Mp = 177 – 179 °C
The analytical data is in accordance with the literature data.[3]

11-Methylbenzo[4',5']iodolo[3',2':4,5]imidazo[1,2-*a*]pyridin-5,11-diium tetrakis(pentafluorphenyl)borat etherate complex (6c)

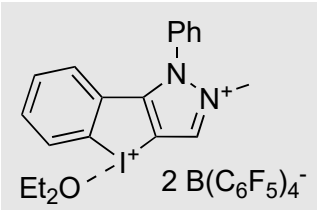


Following GP1, the reaction of 11-methylbenzo[4',5']-iodolo[3',2':4,5]imidazo[1,2-*a*]pyridin-5,11-diium bistriflate (63.2 mg) and $NaB(C_6F_5)_4$ (140 mg, 200 µmol, 2.00 eq.) gave the product **6c** (158 mg, 96.2 µmol, 96%) as a colorless solid.

^{1}H-NMR (600 MHz, DMSO-*d*$_6$) δ = 9.41 (d, *J* = 6.8 Hz, 1H), 8.67 (d, *J* = 6.5 Hz, 1H), 8.59 (s, 1H), 8.52 (d, *J* = 8.5 Hz, 1H), 8.33 – 8.24 (m, 1H), 8.01 (t, *J* = 7.4 Hz, 1H), 7.90 – 7.80 (m, 2H), 4.54 (s, 3H), 3.37 (q, *J* = 7.0 Hz, 4H), 1.08 (t, *J* = 7.0 Hz, 6H).
^{13}C-NMR (150 MHz, DMSO-*d*$_6$) δ = 147.5 (d, *J* = 240.6 Hz), 143.91, 143.4, 137.7 (d, *J* = 245.5 Hz), 135.7, 135.6 (d, *J* = 245.9 Hz), 132.0 (d, *J* = 142.0 Hz), 131.4, 130.2, 128.0, 127.2, 126.8, 123.6 – 122.6 (m), 118.1, 112.0, 64.9, 33.9, 15.2.

^{19}F-NMR (565 MHz, DMSO-*d*$_6$) δ = -132.4 (d, *J* = 13.0 Hz, 16F), -161.3 (t, *J* = 21.5 Hz, 8F), -165.9 (t, *J* = 20.7 Hz, 16F).
HRMS (ESI): *m/z* [M+H-2B(C_6F_5)$_4^-$]$^+$ calcd for $C_{14}H_{12}IN_2^+$: 335.0040; found 335.0035.
IR (ATR) $\tilde{\nu}$ =
Mp = 183 – 185 °C.

2-Methyl-1-phenyl-1*H*-benzo[*4,5*]iodolo[3,2-*c*]pyrazole-2,4-diium tetrakis(pentafluorphenyl)borate etherate complex (6d)



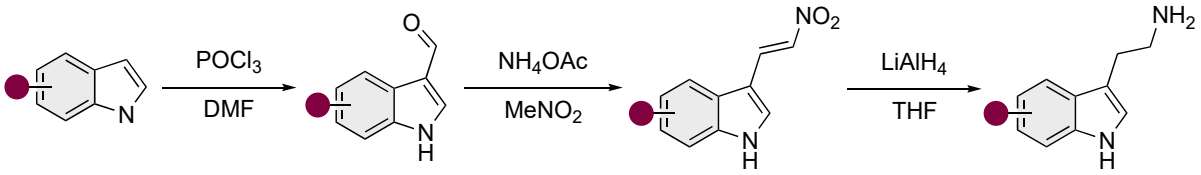
Following GP1, the reaction of 2-methyl-1-phenyl-1*H*-benzo[*4,5*]iodolo[3,2-*c*]pyrazole-2,4-diium bistriflate (65.8 mg) and NaB(C_6F_5)$_4$ (140 mg, 200 µmol, 2.00 eq.) gave the product **6d** (158 mg, 92.0 µmol, 92%) as a colorless solid.

^{1}H-NMR (600 MHz, DMSO-*d*$_6$) δ = 9.17 (s, 1H), 8.44 (d, *J* = 8.4 Hz, 1H), 8.00 – 7.95 (m, 1H), 7.93 – 7.88 (m, 4H), 7.82 (t, *J* = 8.6 Hz, 1H), 7.69 (t, *J* = 7.2 Hz, 1H), 6.78 (d, *J* = 6.5 Hz, 1H), 4.05 (s, 3H), 3.37 (q, *J* = 7.0 Hz, 4H), 1.08 (t, *J* = 7.0 Hz, 6H).
^{13}C-NMR (150 MHz, DMSO-*d*$_6$) δ = 151.6, 147.5 (d, *J* = 240.9 Hz), 138.7, 137.7 (d, *J* = 244.5 Hz), 135.6 (d, *J* = 245.3 Hz), 134.1, 133.9, 131.9, 131.5, 131.2, 130.7, 129.3, 128.8, 126.9, 126.3, 124.4 – 122.4 (m), 95.7, 64.9, 38.4, 15.2.
^{19}F-NMR (565 MHz, DMSO-*d*$_6$) δ = -132.4 (d, *J* = 13.0 Hz, 16F), -161.3 (t, *J* = 21.5 Hz, 8F), -165.9 (t, *J* = 20.7 Hz, 16F).
HRMS (ESI): *m/z* [M+H-2B(C_6F_5)$_4^-$]$^+$ calcd for $C_{16}H_{12}IN_2^+$: 361.0185; found 361.0192.
IR (ATR) $\tilde{\nu}$ = 3101, 1645, 1513, 1456, 1273, 1084, 973.
Mp = 200 – 202 °C.

3. Synthesis of Starting Material

All indoles **S1**, benzaldehydes **2**, tryptamine (**S4a**), tryptophol, and methyl *D*-tryptophanate were purchased commercially.

3.1. General Procedure for Synthesis of Tryptamines (GP2)



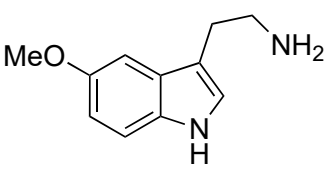
S1 **S2** **S3** **S4**

A modified literature procedure was used.[4] $POCl_3$ (10.0 mmol, 2.0 eq.) was added to DMF (5 mL) at 0 °C and the mixture was stirred for 20 min. At this temperature indole **S1** (5.00 mmol, 1.0 eq.) in DMF (10 mL) was added over 20 min via syringe pump and stirred for an additional 15 min at rt before being heated to 40 °C for 1 h. After cooling to 0 °C ice-water (10 mL) and NaOH (3 M, 15 mL) were added and the resulting mixture was heated to 90 °C for 0.5 h. EtOAc (25 mL) was added at rt and the resulting phases were separated. The aqueous phase was extracted with EtOAc (3 x 20 mL), dried over Na_2SO_4, and the solvent was removed under reduced pressure to obtain the crude **S2**, which was used without further purification in the next step.

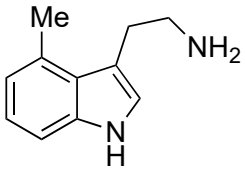
A modified literature procedure was used.[5] To a solution of **S2** (5.00 mmol, 1.00 eq.) in $MeNO_2$ (20 mL) was added NH_4OAc (1.16 g, 15.0 mmol, 3.00 eq.) and the mixture was heated to 90 °C for 2.5 h. After removal of the solvent, EtOAc (30 mL) and H_2O (20 mL) were added, the phases were separated and the aqueous phase was extracted with EtOAc (3 x 20 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure to obtain the crude **S3**, which was used without further purification in the next step.

Under an argon atmosphere, a solution of **S3** (5.00 mmol) in dry THF (25 mL) was added to a suspension of $LiAlH_4$ (1.14 g, 30.0 mmol, 6.0 eq.) in THF (25 mL) at 0 °C. The reaction mixture was warmed to rt and stirred for 36 h before it was quenched by the dropwise addition of water until effervescence ceased. The mixture was diluted with Et_2O (50 mL) before the addition of a sat. aq. solution of Rochelle's salt (50 mL) and the resulting biphasic mixture was stirred for an additional 24 h. The phases were separated and the aqueous phase was extracted with HCl (1 M, 50 mL) and subsequently basified with NaOH (3 M). After the addition of Et_2O (50 mL) the phases were separated, extracted with Et_2O (3 x 40 mL), dried over Na_2SO_4, and the solvent was removed under reduced pressure to obtain **S4**.

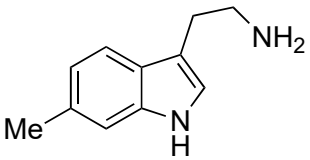
The following substrates were synthesized according to GP2 and their analytical data is in accordance with the literature data:[6]



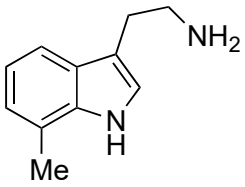
S4c
42% (over 3 steps)



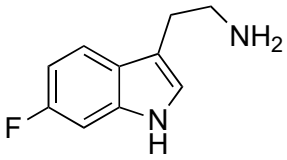
S4b
60% (over 3 steps)



S4d
58% (over 3 steps)



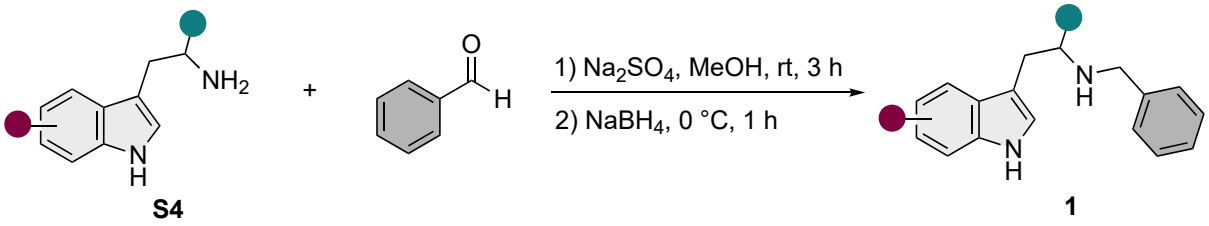
S4e
86% (over 3 steps)



S4f
72% (over 3 steps)

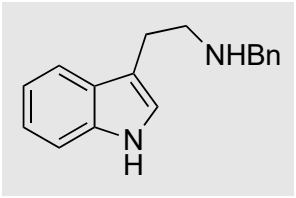
Figure S1. Tryptamines **S4** synthesized according to GP2.

3.2. General Procedure for *N*-Benzylation of Tryptamines (GP3)



To a solution of tryptamine derivate **S4** (1.0 eq.) and benzaldehyde derivate (1.2 eq.) in MeOH (5 mL mmol^{-1}) was added Na_2SO_4 (500 mg mmol^{-1}) and the resulting suspension was stirred for 3 h at rt. Afterward, the mixture was cooled to 0 °C, $NaBH_4$ (1.2 eq.) was added slowly and the mixture was stirred for 1 h at rt. After removal of the solvent, the residue was treated with H_2O (5 mL mmol^{-1}) and extracted with EtOAc (3 x 10 mL mmol^{-1}). The combined phases were washed with brine (5 mL mmol^{-1}), dried over Na_2SO_4, and the solvent was removed under reduced pressure. The crude was purified by column chromatography (DCM/MeOH 25:1 → 10:1) to obtain *N*-benzyl-protected tryptamines **1**.

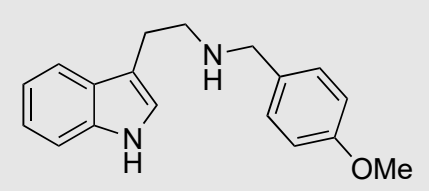
***N*-Benzyl-2-(1*H*-indol-3-yl)ethan-1-amine (1a)**



Following GP3, the reaction of tryptamine (**S4a**, 801 mg, 5.00 mmol) and benzaldehyde (612 µL, 637 mg, 6.00 mmol) gave the product **1a** (1.10 g, 4.39 mmol, 88%) as a brownish oil.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 8.00 (s, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.31 – 7.18 (m, 5H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 7.03 (s, 1H), 4.70 (s, 1H), 3.82 (m, 2H), 3.01 (m, 4H).
^{13}C-NMR (150 MHz, $CDCl_3$) δ = 140.5, 136.5, 128.5, 128.3, 127.6, 127.0, 122.2, 122.0, 119.4, 119.1, 114.2, 111.2, 54.1, 49.5, 25.9.
MS (APCI): *m/z* = 251.0 $[M+H]^+$.
IR (ATR) $\tilde{\nu}$ = 3414, 3298, 3100, 3058, 2918, 1620, 1454, 1224 1029, 1009, 872, 737.
The analytical data is in accordance with the literature data.[7]

2-(1*H*-Indol-3-yl)-*N*-(4-methoxybenzyl)ethan-1-amine (1b)



Following GP3, the reaction of tryptamine (**S4a**, 320 mg, 2.00 mmol) and 4-methoxybenzaldehyde (292 µL, 326 mg, 2.40 mmol) gave the product **1b** (503 mg, 1.79 mmol, 90%) as an off-white solid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.96 (s, 1H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.23 – 7.16 (m, 3H), 7.15 – 7.08 (m, 1H), 7.03 (d, *J* = 2.3 Hz, 1H), 6.87 – 6.80 (m, 2H), 3.79 (s, 3H), 3.76 (s, 2H), 3.04 – 2.93 (m, 4H). *Note: The aliphatic N-H is not observable due to signal broadening.*

^{13}C-NMR (150 MHz, $CDCl_3$) δ = 158.7, 136.5, 132.5, 129.5, 127.6, 122.2, 122.0, 119.4, 119.1, 114.2, 113.9, 111.2, 55.4, 53.4, 49.4, 25.9.

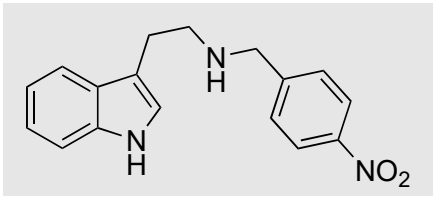
MS (APCI) *m/z* = 280.9 $[M+H]^+$.

IR (ATR) $\tilde{\nu}$ = 3416, 2915, 2838, 1611, 1510, 1450, 1243, 1176, 1031, 816, 738.

Mp = 153 – 155 °C.

The analytical data is in accordance with the literature data.[8]

2-(1*H*-Indol-3-yl)-*N*-(4-nitrobenzyl)ethan-1-amine (1c)



Following GP3, the reaction of tryptamine (**S4a**, 320 mg, 2.00 mmol) and 4-nitrobenzaldehyde (363 mg, 2.40 mmol) gave the product **1c** (580 mg, 1.96 mmol, 98%) as a brown solid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 8.13 (d, *J* = 8.7 Hz, 2H), 7.99 (s, 1H), 7.60 (d, *J* = 8.9 Hz, 1H), 7.44 (d, *J* = 8.9 Hz, 2H), 7.38 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 2.3 Hz, 1H), 3.90 (s, 2H), 3.06 – 2.99 (m, 2H), 3.00 – 2.92 (m, 2H). *Note: The N-H is not observable due to signal broadening.*

^{13}C-NMR (150 MHz, $CDCl_3$) δ = 148.2, 147.1, 136.4, 128.5, 127.3, 123.5, 122.1, 121.9, 119.3, 118.8, 113.7, 111.1, 53.0, 49.3, 25.7.

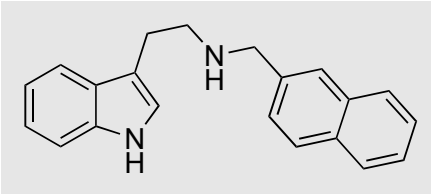
MS (APCI): *m/z* = 295.9 $[M+H]^+$.

IR (ATR) $\tilde{\nu}$ = 3301, 3144, 2921, 2851, 1599, 1477, 1445, 1335, 1150, 1011, 988.

Mp = 60 – 62 °C.

The analytical data is in accordance with the literature data.[7]

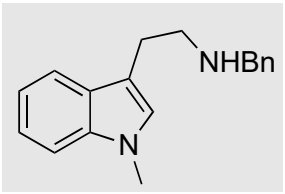
2-(1*H*-Indol-3-yl)-*N*-(naphthalen-2-ylmethyl)ethan-1-amine (1d)



Following GP3, the reaction of tryptamine (**S4a**, 320 mg, 2.00 mmol) and 2-naphthaldehyde (375 mg, 2.40 mmol) gave the product **1d** (413 mg, 1.37 mmol, 69%) as an off-white solid.

^{1}H-NMR (600 MHz, DMSO-d_6) δ = 10.76 (s, 1H), 7.90 – 7.82 (m, 3H), 7.80 (s, 1H), 7.54 – 7.41 (m, 4H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.13 (d, *J* = 2.3 Hz, 1H), 7.05 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1H), 6.94 (t, *J* = 7.6 Hz, 1H), 3.93 (s, 2H), 2.98 – 2.75 (m, 4H). *Note: The aliphatic N-H is not observable due to signal broadening.*
^{13}C-NMR (150 MHz, DMSO-d_6) δ = 138.6, 136.2, 133.0, 132.1, 127.5, 127.5, 127.3, 126.7, 125.9, 125.9, 125.4, 122.5, 120.8, 118.3, 118.1, 112.6, 111.3, 79.2, 64.0, 52.9, 49.5, 25.4.
MS (APCI): *m/z* = 300.9 $[M+H]^+$.
IR (ATR) $\tilde{\nu}$ = 3050, 2900, 2846, 1477, 1380, 1229, 1077, 849.
Mp = 97 – 99 °C.
The analytical data is in accordance with the literature data.[9]

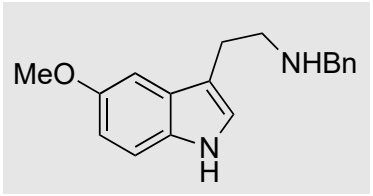
***N*-benzyl-2-(1-methyl-1*H*-indol-3-yl)ethan-1-amine (1e)**



Following GP3, the reaction of 2-(1-methyl-1*H*-indol-3-yl)ethan-1-amine (93.2 mg, 535 µmol) and benzaldehyde (65.5 µl, 642 µmol) gave the product **1e** (127 mg, 480 µmol, 90%) as a brownish oil.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.60 (d, *J* = 7.9 Hz, 1H), 7.31 – 7.20 (m, 7H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.87 (s, 1H), 3.82 (s, 2H), 3.74 (s, 3H), 2.99 (s, 4H). *Note: The aliphatic N-H is not observable due to signal broadening.*
^{13}C-NMR (150 MHz, $CDCl_3$) δ = 140.4, 137.3, 128.5, 128.3, 127.0, 126.9, 123.2, 121.7, 119.2, 118.8, 112.6, 109.3, 54.0, 49.7, 32.7, 25.8.
MS (APCI): *m/z* = 265.1 $[M+H]^+$.
IR (ATR) $\tilde{\nu}$ = 3025, 2912, 1452, 1325, 1289, 1125, 1011, 733.
The analytical data is in accordance with the literature data.[10]

***N*-Benzyl-2-(5-methoxy-1*H*-indol-3-yl)ethan-1-amine (1f)**



Following GP3, the reaction of **S4b** (396 mg, 2.08 mmol) and benzaldehyde (255 µl, 265 mg, 2.50 mmol) gave the product **1f** (570 mg, 2.03 mmol, 98%) as an off-white solid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.97 (s, 1H), 7.30 (d, *J* = 6.5 Hz, 4H), 7.24 (d, *J* = 8.8 Hz, 2H), 7.04 (d, *J* = 2.6 Hz, 1H), 6.99 (d, *J* = 2.5 Hz, 1H), 6.86 (dd, *J* = 8.7, 2.5 Hz, 1H), 3.85 (s, 3H), 3.83 (s, 2H), 3.01 – 2.96 (m, 4H). *Note: The aliphatic N-H is not observable due to signal broadening.*

^{13}C-NMR (150 MHz, $CDCl_3$) δ = 154.0, 140.5, 131.6, 128.5, 128.2, 128.0, 127.0, 122.9, 113.9, 112.4, 112.0, 100.8, 56.1, 54.0, 49.4, 25.9.

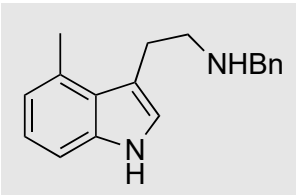
MS (APCI): *m/z* = 281.1 $[M+H]^+$.

IR (ATR) $\tilde{\nu}$ = 3375, 3020, 2882, 2857, 1584, 1450, 1210, 1103, 828, 751.

Mp = 81 – 83 °C.

The analytical data is in accordance with the literature data.[7]

***N*-Benzyl-2-(4-methyl-1*H*-indol-3-yl)ethan-1-amine (1g)**



Following GP3, the reaction of **S4c** (521 mg, 2.99 mmol) and benzaldehyde (336 µL, 349 mg, 3.29 mmol) gave the product **1g** (743 mg, 2.78 mmol, 93%) as an off-white solid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 8.13 (s, 1H), 7.33 (d, *J* = 4.5 Hz, 4H), 7.29 – 7.24 (m, 1H), 7.18 (d, *J* = 8.2 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 2.5 Hz, 1H), 6.86 (dq, *J* = 7.1, 1.0 Hz, 1H), 3.86 (s, 2H), 3.17 (t, *J* = 7.1 Hz, 2H), 3.00 (t, *J* = 7.1 Hz, 2H), 2.71 (s, 3H). *Note: The aliphatic N-H is not observable due to signal broadening.*

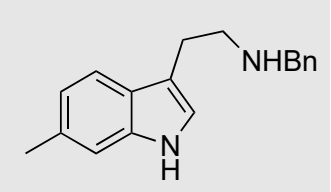
^{13}C-NMR (150 MHz, $CDCl_3$) δ = 140.5, 136.9, 131.0, 128.5, 128.3, 127.0, 126.0, 122.2, 122.1, 121.1, 114.9, 109.2, 54.1, 50.8, 27.7, 20.5.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{18}H_{21}N_2^+$: 265.1699; found 265.1694.

IR (ATR) $\tilde{\nu}$ = 3260, 3175, 2928, 2855, 1438, 1345, 1147, 1066, 895, 754.

Mp = 89 – 91 °C.

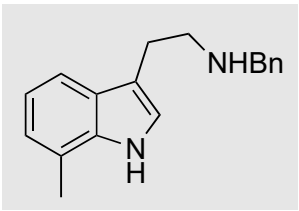
***N*-Benzyl-2-(4-methyl-1*H*-indol-3-yl)ethan-1-amine (1h)**



Following GP3, the reaction of **S4d** (503 mg, 2.89 mmol) and benzaldehyde (354 µL, 378 mg, 3.46 mmol) gave the product **1h** (703 mg, 2.66 mmol, 92%) as an orange semi-solid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.94 (m, 1H), 7.53 – 7.48 (m, 1H), 7.38 (d, *J* = 3.5 Hz, 1H), 7.33 – 7.28 (m, 4H), 7.25 – 7.22 (m, 1H), 7.14 (d, *J* = 2.5 Hz, 1H), 6.99 – 6.91 (m, 2H), 3.82 (s, 1H), 2.99 (s, 4H), 2.47 (s, 3H). *Note: The aliphatic N-H is not observable due to signal broadening.*
^{13}C-NMR (150 MHz, $CDCl_3$) δ = 140.5, 137.0, 131.9, 128.7, 128.5, 128.3, 127.1, 127.0, 125.4, 121.1, 118.7, 111.2, 54.0, 49.5, 25.9, 21.8.
MS (APCI): *m/z* = 265.1 $[M+H]^+$.
IR (ATR) $\tilde{\nu}$ = 3294, 3031, 2908, 2834, 1624, 1453, 1337, 1087, 804, 729.
The analytical data is in accordance with the literature data.[11]

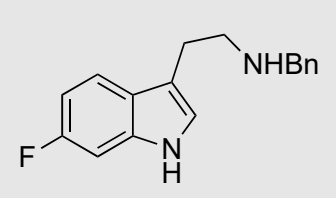
***N*-Benzyl-2-(7-methyl-1*H*-indol-3-yl)ethan-1-amine (1i)**



Following GP3, the reaction of **S4e** (753 mg, 4.32 mmol) and benzaldehyde (485 µL, 504 mg, 3.46 mmol) gave the product **1i** (1.12 g, 4.24 mmol, 98%) as an orange solid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.95 (s, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 6.4 Hz, 4H), 7.27 – 7.22 (m, 1H), 7.06 (t, *J* = 7.4 Hz, 1H), 7.04 – 7.00 (m, 2H), 3.83 (s, 2H), 3.01 (s, 4H), 2.49 (s, 3H). *Note: The aliphatic N-H is not observable due to signal broadening.*
^{13}C-NMR (150 MHz, $CDCl_3$) δ = 140.5, 136.1, 128.5, 128.2, 127.1, 127.0, 122.7, 121.8, 120.4, 119.6, 116.8, 114.7, 54.1, 49.6, 26.0, 16.7.
MS (APCI): *m/z* = 265.2 $[M+H]^+$.
IR (ATR) $\tilde{\nu}$ = 3025, 2853, 1452, 1348, 1114, 1094, 816, 734.
Mp = 69 – 71 °C.
The analytical data is in accordance with the literature data.[12]

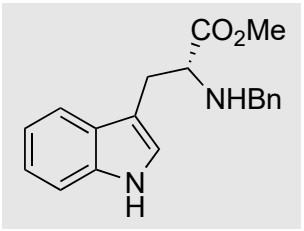
_N_-Benzyl-2-(4-methyl-1_H_-indol-3-yl)ethan-1-amine (1j)



Following GP3, the reaction of **S4f** (634 mg, 3.56 mmol) and benzaldehyde (436 µL, 453 mg, 4.27 mmol) gave the product **1j** (298 mg, 1.11 mmol, 31%) as an orange solid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 8.02 (s, 1H), 7.49 (dd, *J* = 8.7, 5.3 Hz, 1H), 7.32 – 7.26 (m, 4H), 7.25 – 7.22 (m, 1H), 7.02 (dd, *J* = 9.6, 2.5 Hz, 1H), 6.99 (s, 1H), 6.90 – 6.84 (m, 1H), 3.82 (s, 2H), 2.98 (s, 4H). *Note: The aliphatic N-H is not observable due to signal broadening.*
^{13}C NMR (151 MHz, $CDCl_3$) δ = 160.2 (d, *J* = 238.1 Hz), 140.3, 136.4 (d, *J* = 12.5 Hz), 128.5, 128.2, 127.1, 124.2, 122.2 (d, *J* = 3.8 Hz), 119.8 (d, *J* = 9.8 Hz), 114.3, 108.2 (d, *J* = 24.5 Hz), 97.5 (d, *J* = 25.6 Hz), 54.0, 49.3, 25.8.
^{19}F-NMR (565 MHz, $CDCl_3$) δ = -121.3 (td, *J* = 9.5, 5.2 Hz).
HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{17}H_{18}FN_2^+$: 269.1449; found 269.1442.
IR (ATR) $\tilde{\nu}$ = 3334, 3054, 2919, 2853, 1626, 1450, 1344, 1144, 1105, 843, 750.
Mp = 80 – 82 °C.

Methyl benzyl-*D*-tryptophanate (1k)

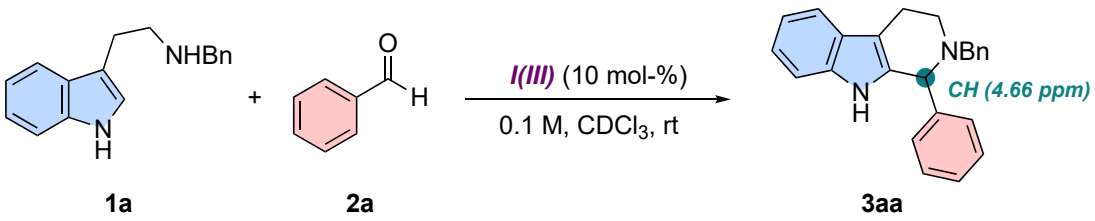


Following GP3, the reaction of methyl *D*-tryptophanate (320 mg, 2.00 mmol) and benzaldehyde (245 µL, 254 mg, 2.40 mmol) gave the product **1k** (571 mg, 1.85 mmol, 93%) as a colorless solid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 8.00 (s, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.41 – 7.33 (m, 1H), 7.25 – 7.15 (m, 6H), 7.10 (t, *J* = 7.0 Hz, 1H), 7.05 (s, 1H), 4.71 (s, 1H), 3.83 (d, *J* = 13.2 Hz, 1H), 3.70 – 3.65 (m, 2H), 3.63 (s, 3H), 3.26 – 3.09 (m, 2H).
^{13}C-NMR (150 MHz, $CDCl_3$) δ = 175.4, 139.8, 136.3, 128.5, 128.3, 127.7, 127.1, 122.9, 122.3, 119.6, 119.0, 111.6, 111.2, 61.4, 52.3, 51.9, 29.4.
MS (APCI): *m/z* = 300.9 $[M+H]^+$.
IR (ATR) $\tilde{\nu}$ = 3287, 3138, 2848, 1739, 1620, 1426, 1207, 1065, 1010, 741.
Mp = 107 – 109 °C.
$[\alpha]_D^{25}$ = +7.9 (c = 1.00, $CHCl_3$).
The analytical data is in accordance with the literature data.[13]

4. Synthesis of Products

4.1. General Procedure for the Time-Dependent ^{1}H-NMR Measurements



1a **2a** **3aa**

To an NMR tube was added the corresponding I(III) catalyst (5.00 µmol, 10 mol-%), a 250 mM stock solution of *N*-benzyltryptamine in $CDCl_3$ (**1a**, 200 µL, 50.0 µmol), a 200 mM stock solution of tetraethylsilane in $CDCl_3$ (TES, 62.5 µL, 12.5 µmol, 0.25 eq.) as the internal standard, followed by $CDCl_3$ (237.5 µL). Additionally, benzaldehyde (**2a**, 6.12 µL, 60.0 µmol, 1.2 eq.) was added, the NMR tube was sealed, shaken, and afterward, time-dependent ^{1}H-NMR measurements were conducted (8 scans, d_1 = 15 s, suitable for integration, an error margin of 5% is assumed). Important measurements were performed at least twice.

The yields were determined as follows: The integral of the ethyl peak of TES (0.51 ppm, q, *J* = 7.9 Hz) was calibrated to 2.00 and/or the integral of the methyl peak of TES (0.93 ppm, t, *J* = 7.9 Hz) was calibrated to 3.00. Afterward, the yields were determined by integrating the CH functionality (4.66 ppm, s, 1H) of the product **3aa**.

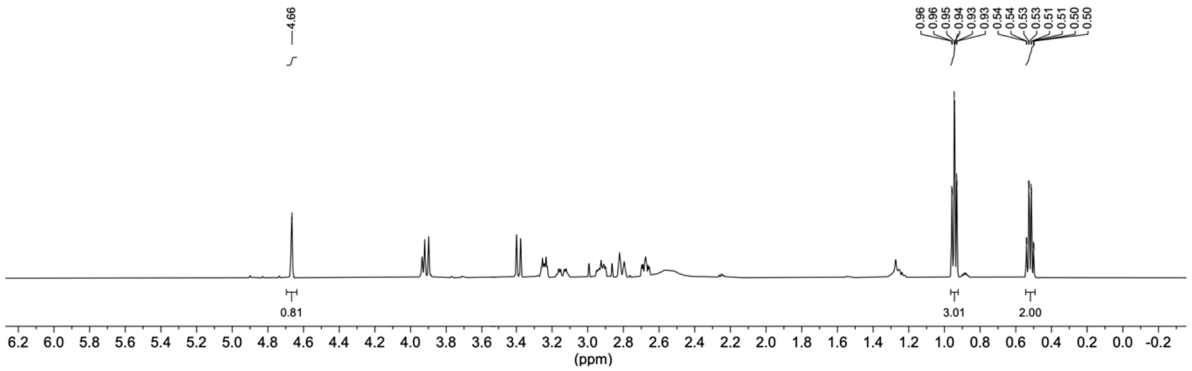


Figure S2. 600 MHz ^{1}H-NMR spectrum for the Pictet Spengler reaction between *N*-benzyltryptamine (**1a**) and benzaldehyde (**2a**) employing iodolium salt **4a** as the XB donor. The spectrum is zoomed in to show the relevant signals for the reaction progress.

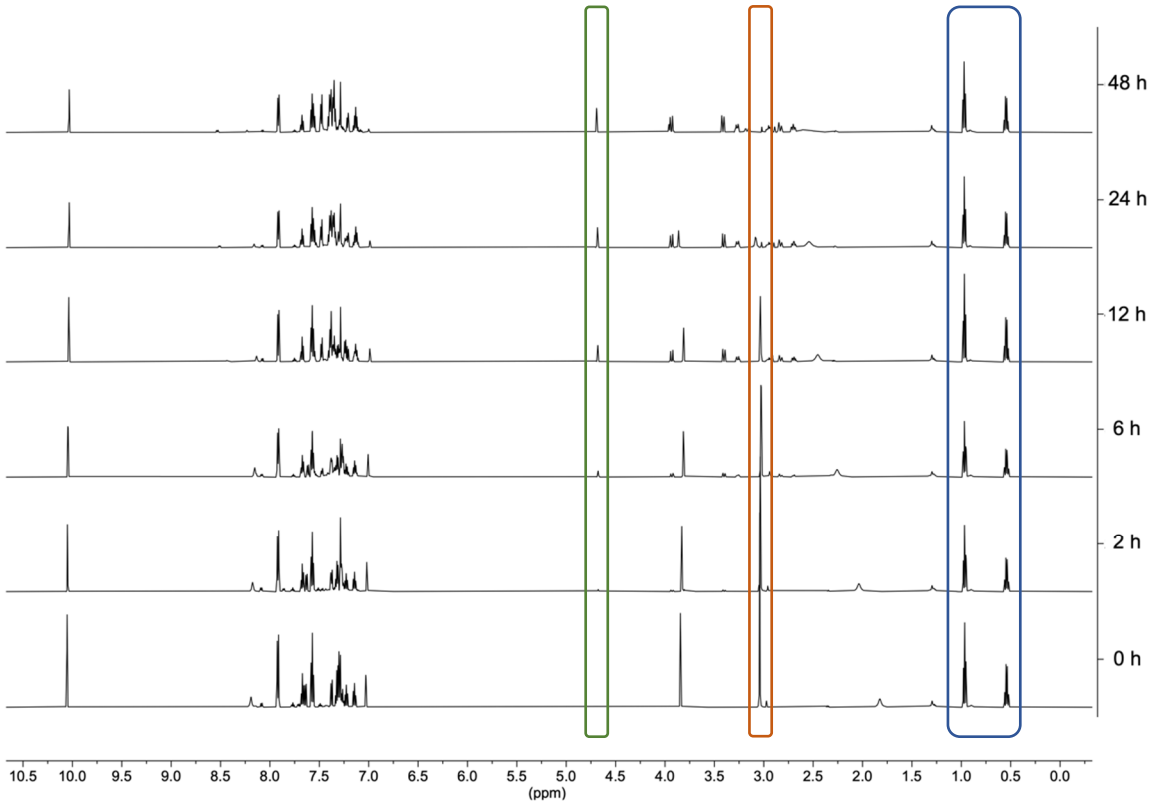


Figure S3. 600 MHz ^{1}H-NMR spectra for the Pictet Spengler reaction between *N*-benzyltryptamine (**1a**) and benzaldehyde (**2a**) employing iodolium salt **4a** (10 mol-%) as the XB donor. Important signals for integration are highlighted as follows: In green: CH signal of the product; in orange: Consumption of the ethylene unit of **1a**; in blue: TES as the internal standard.

4.2. Kinetics of the Time-Dependent ^{1}H-NMR Measurements

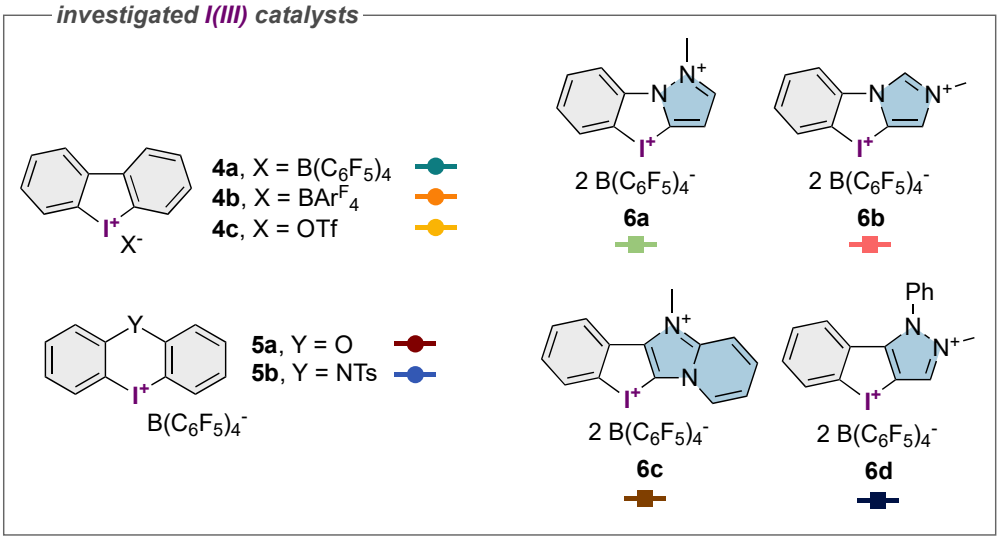


Figure S4. Overview of the investigated I(III) catalysts in this study.

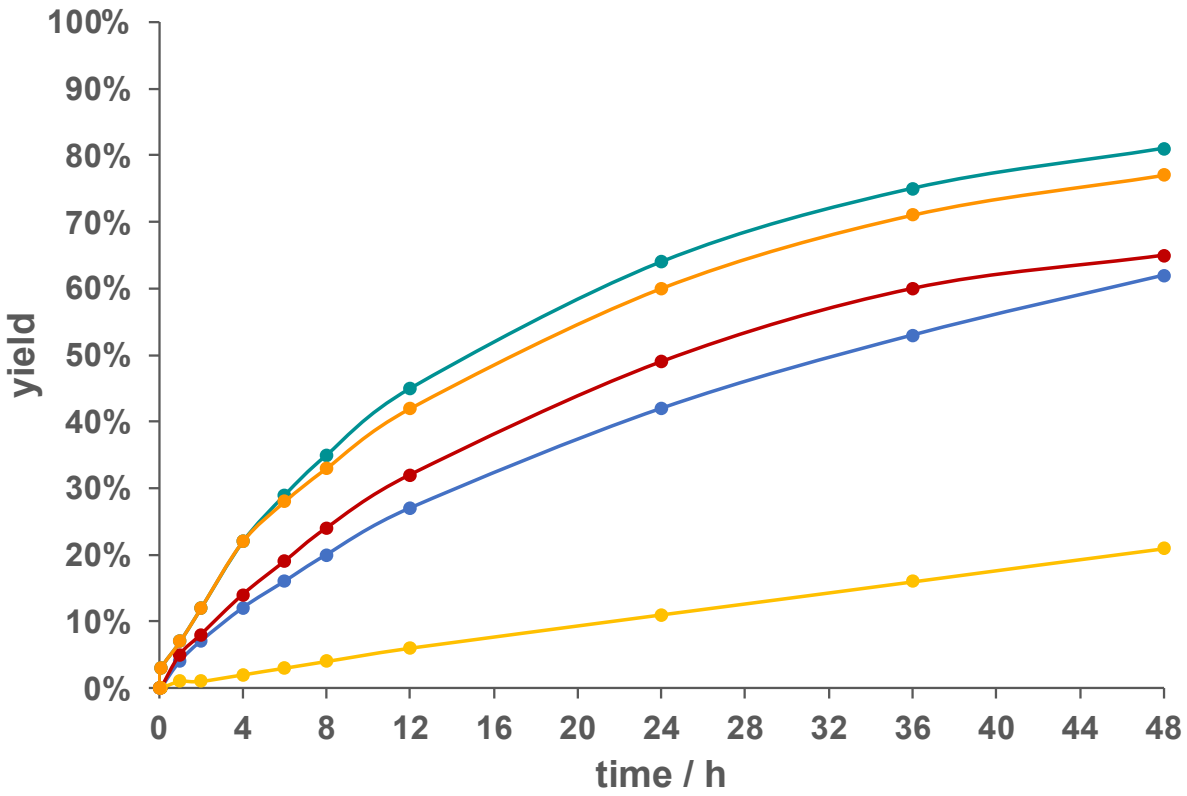


Figure S5. Comparison of monocationic XB catalysts **4** and **5** and various weakly coordinating anions.

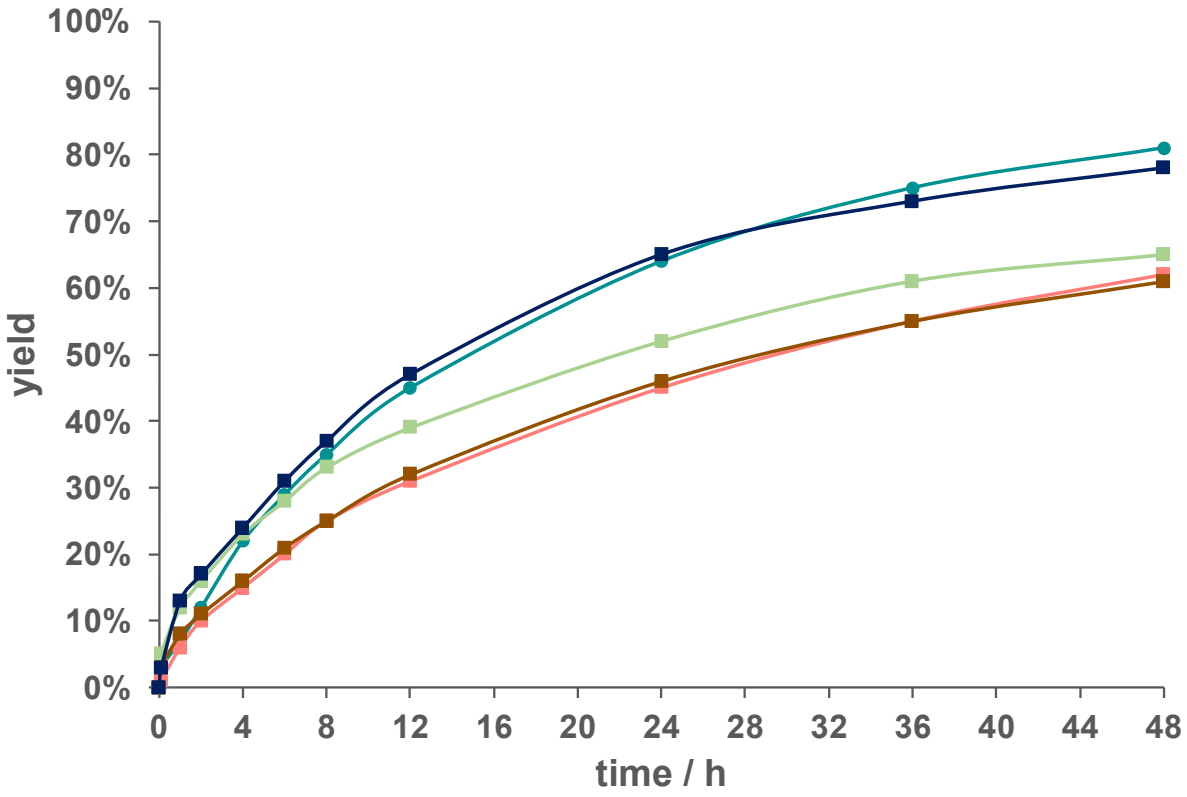


Figure S6. Comparison of **4a** and dicationic *N*-heterocyclic iodazolium salts **6**.

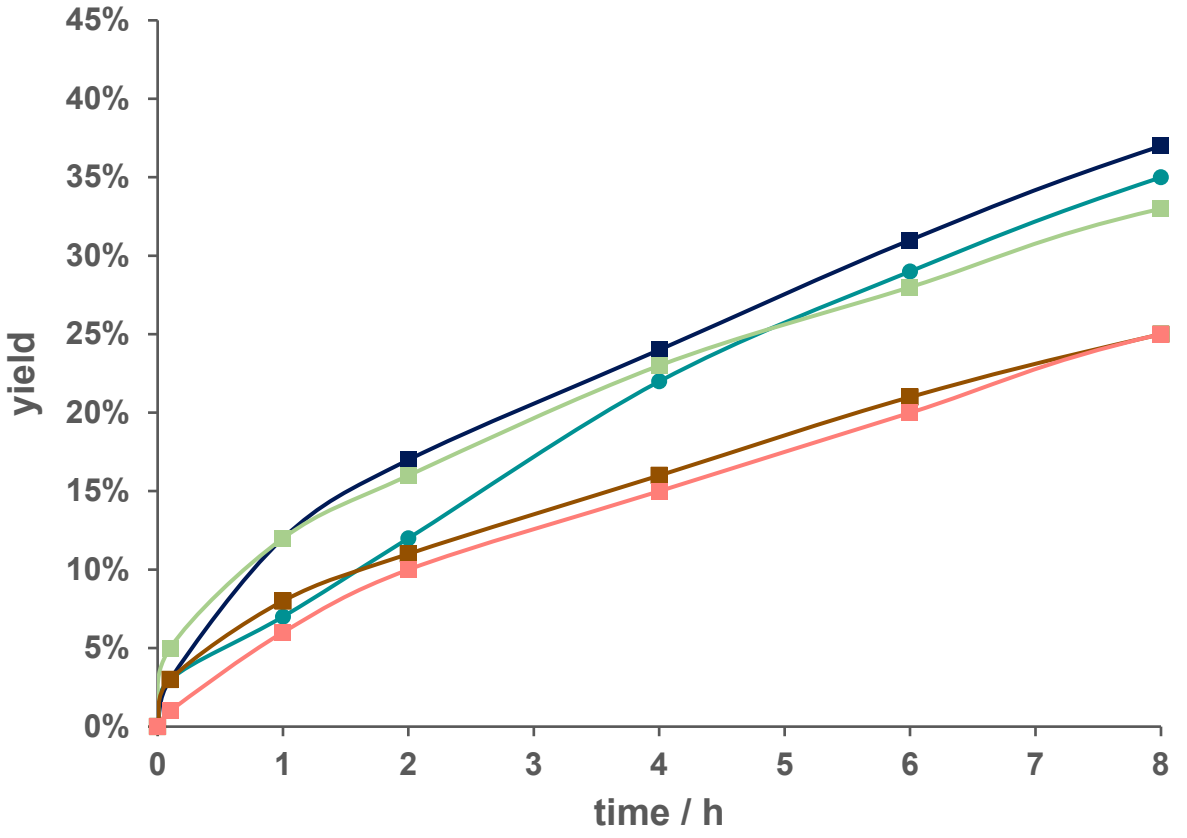


Figure S7. Close-up of the first 8 h for comparing **4a** and dicationic *N*-heterocyclic iodazolium salts **6**.

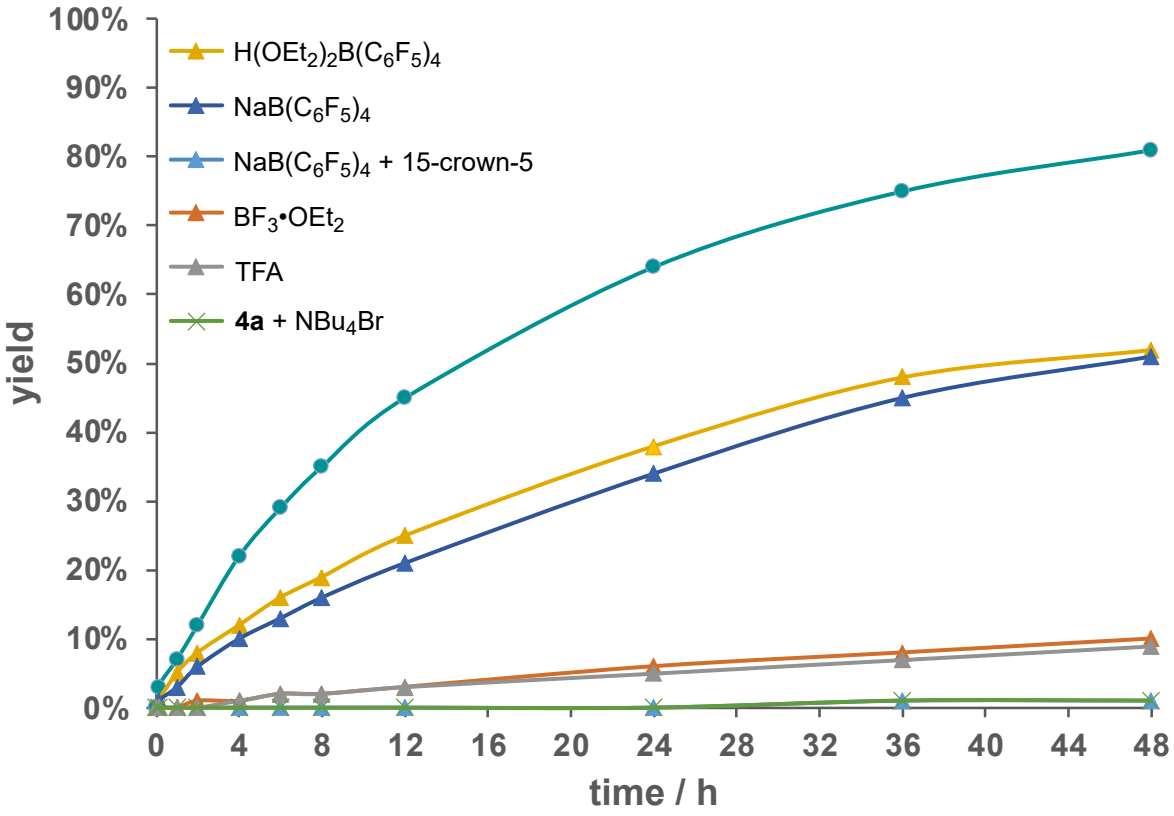
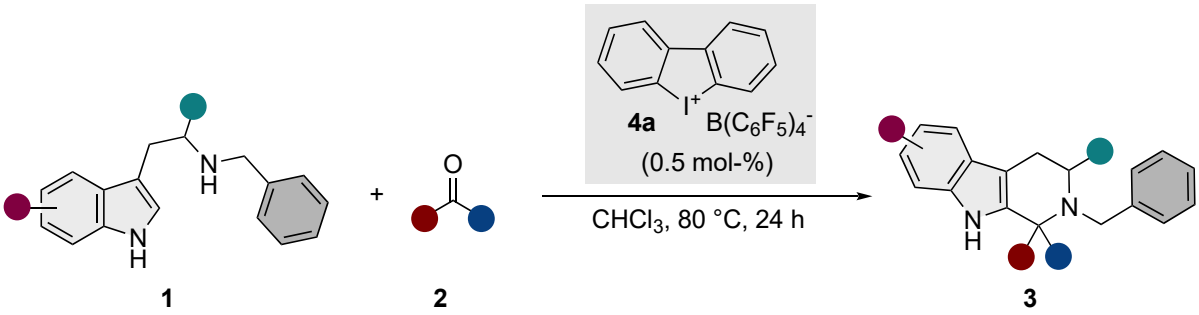


Figure S8. Control experiments.

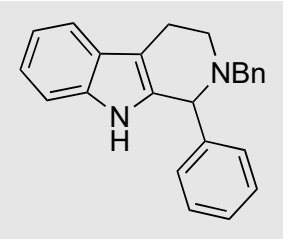
4.3. General Procedure for XB-catalyzed Pictet-Spengler Reaction (GP4)



1 2 3

To a solution of *N*-benzyl-protected tryptamine **1** (100 µmol, 1.0 eq.) and a 10 mM stock solution of the XB catalyst **4a** (50.0 µL, 0.5 mol-%) in $CHCl_3$ (1 mL) was added the carbonyl compound **2** (120 µmol, 1.2 eq.) and the solution was stirred at 80 °C for 24 h. Afterward, MeOH (0.5 mL) and $NaBH_4$ (5.7 mg, 150 µmol, 1.5 eq.) were added successively at 0 °C and the reaction mixture was stirred for 30 min at rt. After filtration through celite and removal of the solvent under reduced pressure, the crude was purified by column chromatography to obtain the cyclized product **3**.

2-Benzyl-1-phenyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole (3aa)



Following GP4, the reaction of **1a** (25.0 mg) and benzaldehyde (12.3 µL, 12.7 mg) gave after column chromatography (cyclohexane/EtOAc 20:1) the product **3aa** (30.1 mg, 88.9 µmol, 89%) as a colorless solid.

Upscaled reaction: To a solution of **1a** (1.25 g, 5.00 mmol, 1.0 eq.) and **4a** (24.0 mg, 25.0 µmol, 0.5 mol-%) in $CHCl_3$ (50 mL) was added benzaldehyde (**2a**, 561µL, 584 mg, 6.00 mmol, 1.2 eq.) and the solution was stirred at 80 °C for 24 h. Afterward, MeOH (25 mL) and $NaBH_4$ (284 mg, 7.50 mmol, 1.5 eq.) were added successively at 0 °C and the reaction mixture was stirred for 30 min at rt. After filtration through celite and removal of the solvent under reduced pressure, the crude was purified by column chromatography (cyclohexane/EtOAc 20:1) to obtain the product **3aa** (1.54 g, 4.55 mmol, 91%) as a colorless solid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.52 (d, *J* = 7.0 Hz, 1H), 7.45 (d, *J* = 6.8 Hz, 2H), 7.39 – 7.29 (m, 7H), 7.25 – 7.23 (m, 2H), 7.19 (d, *J* = 7.3 Hz, 1H), 7.14 – 7.06 (m, 2H), 4.65 (s, 1H), 3.91

(d, *J* = 13.6 Hz, 1H), 3.37 (d, *J* = 13.6 Hz, 1H), 3.27 – 3.19 (m, 1H), 2.97 – 2.87 (m, 1H), 2.86 – 2.76 (m, 1H), 2.72 – 2.61 (m, 1H).

^{13}C-NMR (150 MHz, $CDCl_3$) δ = 141.6, 139.7, 136.4, 135.0, 129.2, 128.9, 128.8, 128.4, 128.2, 127.4, 127.1, 121.6, 119.5, 118.4, 110.9, 109.1, 64.8, 58.5, 48.5, 21.3.

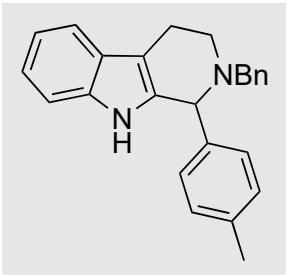
MS (APCI): *m/z* = 339.2 $[M+H]^+$.

IR (ATR) $\tilde{\nu}$ = 3401, 3035, 2907, 2810, 1494, 1452, 1303, 1272, 1123, 744, 696, 672.

Mp = 169 – 170 °C.

The analytical data is in accordance with the literature data.[14]

2-Benzyl-1-(*p*-tolyl)-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole (3ab)



Following GP4, the reaction of **1a** (25.0 mg) and 4-tolualdehyde (14.2 µL, 14.4 mg) gave after column chromatography (cyclohexane/EtOAc 20:1) the product **3ab** (29.9 mg, 84.8 µmol, 85%) as a yellow solid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.53 (d, *J* = 6.9 Hz, 1H), 7.39 – 7.31 (m, 6H), 7.28 – 7.25 (m, 2H), 7.22 – 7.16 (m, 3H), 7.14 – 7.07 (m, 2H), 4.62 (s, 1H), 3.92 (d, *J* = 13.6 Hz, 1H), 3.36 (d, *J* = 13.6 Hz, 1H), 3.27 – 3.21 (m, 1H), 2.97 – 2.90 (m, 1H), 2.84 – 2.77 (m, 1H), 2.70 – 2.62 (m, 1H), 2.37 (s, 3H).

^{13}C-NMR (150 MHz, $CDCl_3$) δ = 139.8, 138.5, 137.9, 136.4, 135.3, 129.6, 129.1, 128.8, 128.3, 127.4, 127.0, 121.5, 119.4, 118.4, 110.9, 109.0, 64.5, 58.4, 48.6, 21.4, 21.3.

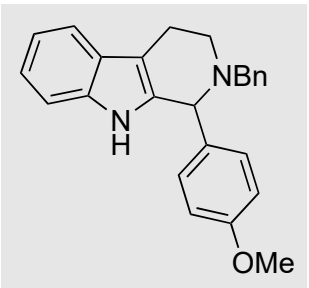
MS (APCI): *m/z* = 353.2 $[M+H]^+$.

IR (ATR) $\tilde{\nu}$ = 3395, 2892, 2839, 1604, 1448, 1363, 1275, 1146, 959, 743.

Mp = 180 – 181 °C.

The analytical data is in accordance with the literature data.[15]

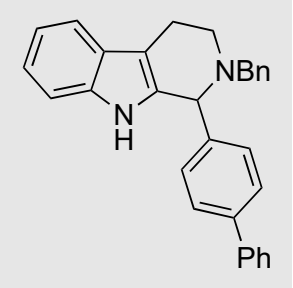
2-Benzyl-1-(4-methoxyphenyl)-2,3,4,9-tetrahydro-1*H*-pyrido-[3,4-*b*]indole (3ac)



Following GP4, the reaction of **1a** (25.0 mg) and 4-methoxybenzaldehyde (16.3 mg) gave after column chromatography (cyclohexane/EtOAc 20:1) the product **3ac** (31.6 mg, 85.8 µmol, 86%) as a yellow solid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.54 (d, *J* = 7.1 Hz, 1H), 7.37 (d, *J* = 8.6 Hz, 4H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.29 – 7.26 (m, 2H), 7.19 (d, *J* = 6.8 Hz, 1H), 7.15 – 7.08 (m, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 4.61 (s, 1H), 3.92 (d, *J* = 13.6 Hz, 1H), 3.82 (s, 3H), 3.36 (d, *J* = 13.6 Hz, 1H), 3.27 – 3.19 (m, 1H), 2.96 – 2.87 (m, 1H), 2.86 – 2.76 (m, 1H), 2.73 – 2.59 (m, 1H).
^{13}C-NMR (150 MHz, $CDCl_3$) δ = 159.3, 139.6, 136.2, 135.1, 133.3, 130.0, 128.6, 128.1, 127.2, 126.8, 121.3, 119.2, 118.2, 114.0, 110.7, 108.8, 63.9, 58.1, 55.2, 48.3, 21.1.
MS (APCI): *m/z* = 369.1 $[M+H]^+$.
IR (ATR) $\tilde{\nu}$ = 3404, 2905, 1722, 1609, 1508, 1462, 1380, 1240, 1155, 1024.
Mp = 194 – 195 °C.
The analytical data is in accordance with the literature data.[16]

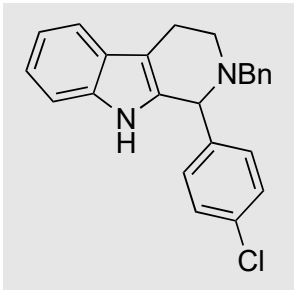
1-([1,1'-Biphenyl]-4-yl)-2-benzyl-2,3,4,9-tetrahydro-1*H*-pyrido-[3,4-*b*]indole (3ad)



Following GP4, the reaction of **1a** (25.0 mg) and 4-phenylbenzaldehyde (21.9 mg) gave after column chromatography (cyclohexane/EtOAc 20:1) the product **3ad** (32.8 mg, 79.1 µmol, 79%) as a colorless solid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.60 (d, *J* = 8.0 Hz, 4H), 7.56 – 7.50 (m, 3H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.41 – 7.31 (m, 6H), 7.29 – 7.24 (m, 1H), 7.21 (d, *J* = 8.7 Hz, 1H), 7.15 – 7.06 (m, 2H), 4.71 (s, 1H), 3.96 (d, *J* = 13.5 Hz, 1H), 3.42 (d, *J* = 13.6 Hz, 1H), 3.27 (ddd, *J* = 11.8, 5.3, 3.7 Hz, 1H), 3.02 – 2.90 (m, 1H), 2.87 – 2.79 (m, 1H), 2.74 – 2.64 (m, 1H).
^{13}C-NMR (150 MHz, $CDCl_3$) δ = 141.1, 140.9, 140.6, 139.7, 136.5, 134.9, 129.6, 128.9, 128.9, 128.4, 127.6, 127.5, 127.4, 127.2, 127.1, 121.7, 119.5, 118.5, 111.0, 109.2, 64.4, 58.5, 48.5, 21.3.
HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{30}H_{27}N_2^+$: 415.2174; found 415.2167.
IR (ATR) $\tilde{\nu}$ = 3406, 2909, 2840, 2754, 1716, 1454, 1365, 1261, 1006, 718, 695.
Mp = 221 – 223 °C.

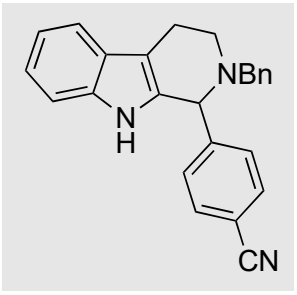
2-Benzyl-1-(4-chlorophenyl)-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole (3ae)



Following GP4, the reaction of **1a** (25.0 mg) and 4-chlorobenzaldehyde (16.9 mg) gave after column chromatography (cyclohexane/EtOAc 20:1) the product **3ae** (35.0 mg, 93.9 µmol, 94%) as a yellow solid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.54 (d, *J* = 7.3 Hz, 1H), 7.40 – 7.38 (m, 2H), 7.37 – 7.31 (m, 6H), 7.30 – 7.27 (m, 1H), 7.25 (s, 1H), 7.23 – 7.19 (m, 1H), 7.17 – 7.08 (m, 2H), 4.64 (s, 1H), 3.88 (d, *J* = 13.5 Hz, 1H), 3.40 (d, *J* = 13.5 Hz, 1H), 3.24 – 3.15 (m, 1H), 2.94 – 2.86 (m, 1H), 2.85 – 2.78 (m, 1H), 2.71 – 2.65 (m, 1H).
^{13}C-NMR (150 MHz, $CDCl_3$) δ = 140.2, 139.4, 136.4, 134.3, 133.9, 130.4, 129.1, 128.8, 128.4, 127.2, 127.2, 121.8, 119.6, 118.5, 111.0, 109.4, 63.8, 58.4, 48.3, 21.1.
MS (APCI): *m/z* = 373.1 $[M+H]^+$.
IR (ATR) $\tilde{\nu}$ = 3398, 3027, 2911, 2826, 1448, 1243, 1013, 1086, 1043, 725, 710.
Mp = 187 – 188 °C.
The analytical data is in accordance with the literature data.[15]

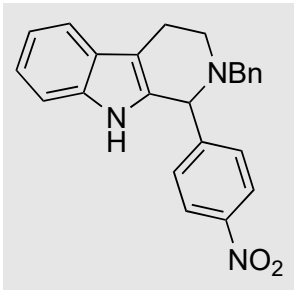
4-(2-Benzyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-1-yl)-benzonitrile (3af)



Following GP4, the reaction of **1a** (25.0 mg) and 4-formylbenzonitrile (15.7 mg) gave after column chromatography (cyclohexane/EtOAc 20:1) the product **3af** (31.5 mg, 86.7 µmol, 87%) as an off-white solid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.64 (d, *J* = 8.3 Hz, 2H), 7.57 – 7.52 (m, 3H), 7.36 – 7.31 (m, 5H), 7.29 (ddd, *J* = 8.6, 5.5, 2.3 Hz, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.19 – 7.10 (m, 2H), 4.74 (s, 1H), 3.82 (d, *J* = 13.5 Hz, 1H), 3.49 (d, *J* = 13.5 Hz, 1H), 3.22 – 3.16 (m, 1H), 2.92 – 2.83 (m, 2H), 2.77 – 2.70 (m, 1H).
^{13}C-NMR (150 MHz, $CDCl_3$) δ = 147.6, 139.0, 136.6, 133.0, 132.6, 129.8, 128.8, 128.5, 127.4, 127.1, 122.2, 119.8, 118.8, 118.6, 112.0, 111.0, 109.8, 63.5, 58.5, 47.8, 20.8.
HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{25}H_{22}N_3^+$: 364.1814; found 364.1805.
IR (ATR) $\tilde{\nu}$ = 3339, 2895, 2811, 2228, 1606, 1451, 1272, 1112, 974, 737.
Mp = 206 – 208 °C.

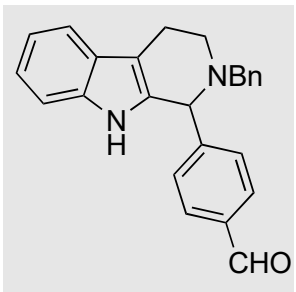
2-Benzyl-1-(4-nitrophenyl)-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole (3ag)



Following GP4, the reaction of **1a** (25.0 mg) and 4-nitrobenzaldehyde (18.1 mg) gave after column chromatography (cyclohexane/EtOAc 20:1) the product **3ag** (35.2 mg, 91.8 µmol, 92%) as a yellow solid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 8.20 (d, *J* = 8.7 Hz, 2H), 7.60 (d, *J* = 8.7 Hz, 2H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.38 – 7.33 (m, 5H), 7.31 – 7.27 (m, 1H), 7.24 (d, *J* = 7.9 Hz, 1H), 7.20 – 7.08 (m, 2H), 4.79 (d, *J* = 1.8 Hz, 1H), 3.83 (d, *J* = 13.5 Hz, 1H), 3.51 (d, *J* = 13.5 Hz, 1H), 3.23 – 3.17 (m, 1H), 2.96 – 2.84 (m, 2H), 2.80 – 2.71 (m, 1H).
^{13}C-NMR (150 MHz, $CDCl_3$) δ = 149.5, 147.7, 138.8, 136.5, 132.7, 129.8, 128.7, 128.5, 127.3, 127.0, 124.0, 122.1, 119.7, 118.6, 111.0, 109.8, 63.1, 58.4, 47.7, 20.6.
MS (APCI): *m/z* = 384.1 $[M+H]^+$.
IR (ATR) $\tilde{\nu}$ = 3392, 2905, 2801, 1606, 1512, 1449, 1273, 1239, 1047, 828, 743.
Mp = 196 – 198 °C.
The analytical data is in accordance with the literature data.[15]

4-(2-Benzyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-1-yl)benzaldehyde (3ah)

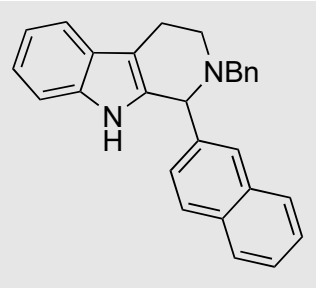


Following GP4, the reaction of **1a** (25.0 mg) and terephtalaldehyde (16.1 mg) gave after column chromatography (cyclohexane/EtOAc 20:1) the product **3ah** (30.0 mg, 81.9 µmol, 82%) as a yellow solid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 9.97 (s, 1H), 7.87 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.57 – 7.52 (m, 1H), 7.40 – 7.31 (m, 5H), 7.29 – 7.27 (m, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.17 – 7.09 (m, 2H), 4.76 (s, 1H), 3.85 (d, *J* = 13.5 Hz, 1H), 3.46 (d, *J* = 13.5 Hz, 1H), 3.23 (dt, *J* = 12.0, 4.8 Hz, 1H), 2.97 – 2.88 (m, 1H), 2.85 (dt, *J* = 15.3, 4.9 Hz, 1H), 2.72 (ddd, *J* = 12.8, 8.9, 4.3 Hz, 1H).
^{13}C-NMR (150 MHz, $CDCl_3$) δ = 192.0, 149.0, 139.2, 136.5, 136.3, 133.5, 130.3, 129.7, 128.8, 128.5, 127.3, 127.1, 122.0, 119.7, 118.6, 111.0, 109.6, 64.1, 58.6, 48.1, 21.0.
HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{25}H_{23}N_2O^+$: 367.1805; found 367.1796.

IR (ATR) $\tilde{\nu}$ = 3377, 3027, 2901, 2800, 1689, 1602, 1575, 1449, 1202, 827, 739.
Mp = 202 – 204 °C.

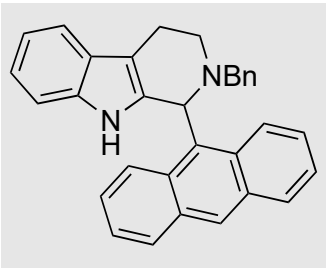
2-Benzyl-1-(naphthalen-2-yl)-2,3,4,9-tetrahydro-1*H*-pyrido-[3,4-*b*]indole (3ai)



Following GP4, the reaction of **1a** (25.0 mg) and 2-naphthaldehyde (18.7 mg) gave after column chromatography (cyclohexane/EtOAc 20:1) the product **3ai** (36.2 mg, 93.2 µmol, 93%) as a colorless solid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.92 – 7.82 (m, 4H), 7.63 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.58 – 7.49 (m, 3H), 7.37 (d, *J* = 7.0 Hz, 2H), 7.35 – 7.30 (m, 2H), 7.28 – 7.26 (m, 2H), 7.17 – 7.08 (m, 3H), 4.82 (s, 1H), 3.98 (d, *J* = 13.5 Hz, 1H), 3.41 (d, *J* = 13.6 Hz, 1H), 3.34 – 3.27 (m, 1H), 3.04 – 2.96 (m, 1H), 2.88 – 2.82 (m, 1H), 2.76 – 2.69 (m, 1H).
^{13}C-NMR (150 MHz, $CDCl_3$) δ = 139.5, 139.1, 136.4, 134.8, 133.4, 133.2, 128.9, 128.8, 128.3, 128.0, 127.9, 127.8, 127.3, 127.0, 126.6, 126.3, 126.2, 121.6, 119.4, 118.4, 110.9, 109.2, 65.0, 58.5, 48.5, 21.4.
HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{28}H_{25}N_2^+$: 389.2018; found 389.2012.
IR (ATR) $\tilde{\nu}$ = 3409, 2891, 2805, 1466, 1363, 1244, 1128, 987, 905, 736.
Mp = 213 – 215 °C.

1-(Anthracen-9-yl)-2-benzyl-2,3,4,9-tetrahydro-1*H*-pyrido-[3,4-*b*]indole (3aj)

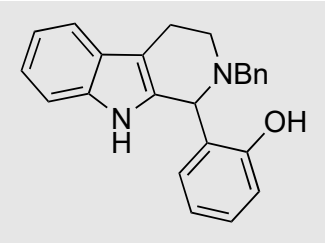


Following GP4, the reaction of **1a** (25.0 mg) and anthracene-9-carbaldehyde (24.8 mg) gave after column chromatography (cyclohexane/EtOAc 20:1) the product **3aj** (16.8 mg, 38.3 µmol, 38%) as a yellow solid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 9.13 (dt, *J* = 9.2, 1.0 Hz, 1H), 8.66 (dt, *J* = 9.1, 1.0 Hz, 1H), 8.52 (s, 1H), 8.12 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.99 – 7.93 (m, 1H), 7.62 (ddd, *J* = 9.0, 6.5, 1.5 Hz, 1H), 7.58 – 7.53 (m, 2H), 7.42 – 7.38 (m, 1H), 7.29 (ddd, *J* = 9.2, 6.5, 1.4 Hz, 1H), 7.18 – 7.11 (m, 3H), 7.10 – 7.06 (m, 3H), 7.02 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 2H), 6.96 (dt, *J* = 8.1, 1.0 Hz, 1H),

6.24 (s, 1H), 3.69 (d, *J* = 13.4 Hz, 1H), 3.47 (ddd, *J* = 11.4, 5.5, 1.6 Hz, 1H), 3.29 – 3.18 (m, 2H), 2.97 (ddt, *J* = 15.3, 3.5, 1.6 Hz, 1H), 2.79 (td, *J* = 11.5, 3.9 Hz, 1H).
^{13}C-NMR (150 MHz, $CDCl_3$) δ = 139.8, 136.2, 136.2, 132.3, 132.2, 131.4, 131.0, 130.1, 130.0, 129.2, 128.9, 128.5, 128.1, 127.8, 127.3, 126.9, 126.8, 125.6, 125.3, 124.9, 122.9, 121.3, 119.4, 118.2, 111.0, 108.4, 60.3, 59.1, 51.3, 22.2.
HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{32}H_{27}N_2^+$: 439.2169; found 439.2162.
IR (ATR) $\tilde{\nu}$ = 3413, 3050, 2919, 2790, 1445, 1293, 1016, 887, 730.
Mp = 142 – 144 °C.

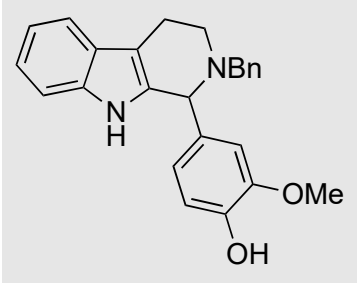
2-(2-Benzyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-1-yl)-phenol (3ak)



Following GP4, the reaction of **1a** (25.0 mg) and salicylaldehyde (12.5 µL, 14.7 mg) gave after column chromatography (cyclohexane/EtOAc 20:1) the product **3ak** (24.2 mg, 68.3 µmol, 68%) as a yellow solid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 10.94 (s, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.37 (qd, *J* = 8.4, 7.8, 1.6 Hz, 4H), 7.34 – 7.27 (m, 4H), 7.20 (d, *J* = 8.1 Hz, 1H), 7.14 – 7.05 (m, 2H), 6.96 (t, *J* = 8.0 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 4.80 (t, *J* = 2.1 Hz, 1H), 4.18 (d, *J* = 13.1 Hz, 1H), 3.43 (d, *J* = 13.1 Hz, 1H), 3.38 (s, 1H), 2.96 – 2.87 (m, 1H), 2.86 – 2.79 (m, 1H), 2.67 – 2.56 (m, 1H).
^{13}C-NMR (150 MHz, $CDCl_3$) δ = 157.2, 136.8, 136.5, 131.8, 130.0, 129.8, 128.9, 128.8, 127.8, 127.1, 123.6, 122.1, 119.7, 119.7, 118.5, 117.6, 111.1, 108.9, 65.2, 59.2, 48.6, 21.2.
HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{24}H_{23}N_2O^+$: 355.1810; found 355.1803.
IR (ATR) $\tilde{\nu}$ = 3435, 3322, 2920, 1593, 1479, 1260, 1073, 749.
Mp = 183 – 185 °C.

4-(2-Benzyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-1-yl)-2-methoxyphenol (3al)

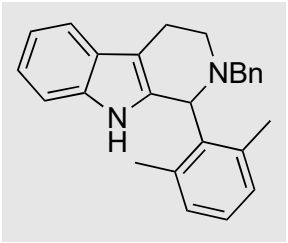


Following GP4, the reaction of **1a** (25.0 mg) and 4-hydroxy-3-methoxybenzaldehyde (18.3 mg) gave after column

chromatography (cyclohexane/EtOAc 4:1) the product **3al** (27.4 mg, 71.3 µmol, 71%) as an orange solid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.52 (dd, *J* = 7.3, 1.5 Hz, 1H), 7.38 – 7.29 (m, 5H), 7.27 (d, *J* = 7.7 Hz, 1H), 7.21 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.15 – 7.08 (m, 2H), 7.01 (s, 1H), 6.97 – 6.90 (m, 2H), 5.65 (s, 1H), 4.57 (s, 1H), 3.95 (d, *J* = 13.7 Hz, 1H), 3.83 (s, 3H), 3.33 (d, *J* = 13.7 Hz, 1H), 3.26 (ddd, *J* = 11.8, 5.4, 3.0 Hz, 1H), 2.94 (dddd, *J* = 15.0, 9.7, 5.1, 1.9 Hz, 1H), 2.82 – 2.75 (m, 1H), 2.65 (td, *J* = 10.9, 4.1 Hz, 1H).
^{13}C-NMR (150 MHz, $CDCl_3$) δ = 147.3, 145.7, 139.8, 136.4, 135.4, 133.3, 128.7, 128.3, 127.4, 127.0, 122.1, 121.6, 119.4, 118.4, 114.0, 110.9, 110.6, 108.8, 64.9, 58.4, 56.1, 49.0, 21.5.
HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{25}H_{25}N_3O_2^+$: 385.1911; found 385.1903.
IR (ATR) $\tilde{\nu}$ = 3466, 3372, 2929, 2839, 1603, 1507, 1452, 1227, 1033, 819, 741.
Mp = 196 – 198 °C.

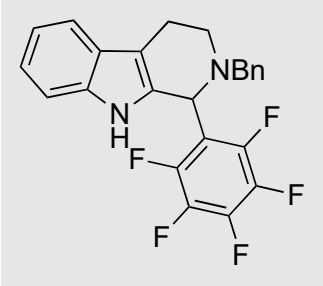
2-Benzyl-1-(2,6-dimethylphenyl)-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole (3am)



Following GP4, the reaction of **1a** (25.0 mg) and 2,6-dimethylbenzaldehyde (16.1 mg) gave after column chromatography (cyclohexane/EtOAc 20:1) the product **3am** (9.2 mg, 25.1 µmol, 25%) as an off-white solid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.50 – 7.47 (m, 1H), 7.31 – 7.27 (m, 4H), 7.24 – 7.18 (m, 3H), 7.15 – 7.11 (m, 1H), 7.11 – 7.07 (m, 3H), 7.00 (d, *J* = 7.5 Hz, 1H), 5.16 (s, 1H), 3.89 (d, *J* = 13.1 Hz, 1H), 3.29 (dd, *J* = 11.7, 5.6 Hz, 1H), 3.20 (d, *J* = 13.3 Hz, 1H), 2.90 (q, *J* = 8.7 Hz, 1H), 2.76 (d, *J* = 15.1 Hz, 1H), 2.57 (s, 3H), 2.52 (td, *J* = 11.6, 3.9 Hz, 1H), 2.20 (s, 3H).
^{13}C-NMR (150 MHz, $CDCl_3$) δ = 140.3, 140.2, 138.2, 136.0, 135.9, 134.8, 130.9, 128.8, 128.3, 128.3, 128.0, 127.2, 126.8, 121.3, 119.5, 118.2, 110.9, 109.3, 61.0, 58.7, 50.6, 21.9, 21.8, 20.0.
HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{26}H_{27}N_2^+$: 367.2169; found 367.2167.
IR (ATR) $\tilde{\nu}$ = 3390, 2921, 2851, 1467, 1453, 1260, 1094, 1027, 800, 750.
Mp = 157 – 159 °C.

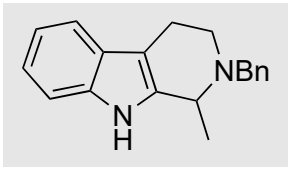
2-Benzyl-1-(perfluorophenyl)-2,3,4,9-tetrahydro-1*H*-pyrido-[3,4-*b*]indole (3an)



Following GP4, the reaction of **1a** (25.0 mg) and pentafluorobenzaldehyde (14.4 µL, 23.5 mg) gave after column chromatography (cyclohexane/EtOAc 10:1) the product **3an** (38.9 mg, 90.8 µmol, 91%) as a yellow solid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.56 (d, *J* = 7.7 Hz, 1H), 7.41 (s, 1H), 7.36 – 7.30 (m, 4H), 7.28 – 7.25 (m, 2H), 7.16 (dtd, *J* = 22.0, 7.1, 1.2 Hz, 2H), 5.27 (s, 1H), 3.85 (d, *J* = 13.6 Hz, 1H), 3.61 (d, *J* = 13.6 Hz, 1H), 3.25 (dt, *J* = 11.7, 4.3 Hz, 1H), 2.95 (dddd, *J* = 14.8, 9.6, 5.1, 2.1 Hz, 1H), 2.87 – 2.79 (m, 1H), 2.71 (ddd, *J* = 12.8, 9.9, 4.0 Hz, 1H).
^{13}C-NMR (150 MHz, $CDCl_3$) δ = 146.0 (br d, *J* = 250.7 Hz), 141.1 (br d, *J* = 256.5 Hz), 138.9, 137.7 (br d, *J* = 251.2 Hz), 136.4, 130.9, 128.5, 127.3, 127.0, 122.2, 119.9, 118.7, 115.1 (br s/m), 111.0, 110.8, 59.5, 54.8, 49.3, 21.2. *Note: One carbon signal is missing due to overlap.*
^{19}F-NMR (565 MHz, $CDCl_3$) δ = -140.6 (d, *J* = 21.6 Hz), -153.9 (t, *J* = 20.8 Hz), -161.5 (td, *J* = 21.7, 8.4 Hz).
HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{24}H_{18}F_5N_2^+$: 429.1385; found 429.1378.
IR (ATR) $\tilde{\nu}$ = 3453, 2842, 1521, 1499, 1451, 1302, 1114, 989, 828, 738.
Mp = 128 – 130 °C.

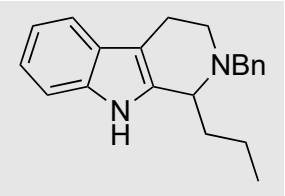
2-Benzyl-1-methyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole (3ao)



Following GP4, the reaction of **1a** (25.0 mg) and acetaldehyde (27.9 µL, 22.1 mg, 500 µmol, 5.0 eq.) gave after column chromatography (cyclohexane/EtOAc 20:1 to 4:1) the product **3ao** (24.1 mg, 87.2 µmol, 87%) as an orange oil.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.64 (s, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.41 (d, *J* = 7.2 Hz, 2H), 7.36 – 7.29 (m, 3H), 7.27 (d, *J* = 7.4 Hz, 1H), 7.15 (t, *J* = 6.9 Hz, 1H), 7.10 (t, *J* = 6.9 Hz, 1H), 3.92 (d, *J* = 13.7 Hz, 1H), 3.85 (t, *J* = 6.7 Hz, 1H), 3.71 (d, *J* = 13.6 Hz, 1H), 3.25 – 3.17 (m, 1H), 2.90 – 2.80 (m, 2H), 2.69 – 2.63 (m, 1H), 1.47 (d, *J* = 6.7 Hz, 3H).
^{13}C-NMR (150 MHz, $CDCl_3$) δ = 139.7, 136.5, 136.0, 128.9, 128.4, 127.5, 127.1, 122.1, 121.6, 119.5, 118.3, 110.8, 108.0, 57.6, 52.3, 45.9, 19.6.
HRMS (EI, 70 eV): *m/z* = $[M]^+$ calcd for $C_{19}H_{20}N_2^+$: 276.1621; found 276.1617.
IR (ATR) $\tilde{\nu}$ = 3401, 2910, 1485, 1302, 1155, 1085, 1028, 826, 737, 695.

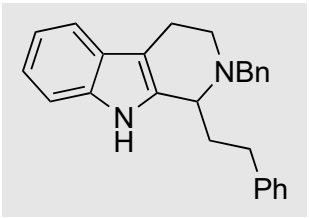
2-Benzyl-1-propyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole (3ap)



Following GP4, the reaction of **1a** (25.0 mg) and butyraldehyde (10.8 µL, 8.7 mg) gave after column chromatography (cyclohexane/EtOAc 10:1) the product **3ap** (27.2 mg, 89.4 µmol, 89%) as a yellow oil.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.62 (s, 1H), 7.53 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.42 – 7.38 (m, 2H), 7.37 – 7.31 (m, 3H), 7.30 – 7.27 (m, 1H), 7.17 (ddd, *J* = 8.0, 7.1, 1.3 Hz, 1H), 7.13 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 3.83 – 3.73 (m, 2H), 3.65 (dd, *J* = 8.1, 5.1 Hz, 1H), 3.27 (ddd, *J* = 12.5, 9.3, 5.0 Hz, 1H), 3.01 – 2.88 (m, 2H), 2.60 (ddd, *J* = 15.6, 5.0, 2.8 Hz, 1H), 1.80 (dtt, *J* = 10.1, 8.0, 5.0 Hz, 1H), 1.76 – 1.68 (m, 1H), 1.57 – 1.40 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H).
^{13}C-NMR (150 MHz, $CDCl_3$) δ = 140.0, 135.9, 135.8, 129.1, 128.3, 127.5, 127.0, 121.5, 119.4, 118.2, 110.8, 107.9, 57.4, 56.5, 44.8, 37.1, 19.6, 18.0, 14.3.
MS (APCI): *m/z* = 305.2 $[M+H]^+$.
IR (ATR) $\tilde{\nu}$ = 3408, 3027, 2928, 2869, 1452, 1299, 1154, 1009, 737.
The analytical data is in accordance with the literature data.[12]

2-Benzyl-1-phenethyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole (3aq)

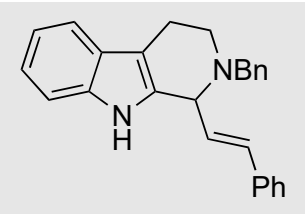


Following GP4, the reaction of **1a** (25.0 mg) and 3-phenylpropanal (15.9 µL, 16.1 mg) gave after column chromatography (cyclohexane/EtOAc 10:1) the product **3aq** (30.5 mg, 83.2 µmol, 83%) as a yellow oil.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.55 – 7.52 (m, 1H), 7.48 – 7.43 (m, 3H), 7.41 – 7.37 (m, 2H), 7.35 – 7.31 (m, 1H), 7.31 – 7.26 (m, 3H), 7.22 – 7.15 (m, 2H), 7.15 – 7.09 (m, 3H), 3.87 – 3.75 (m, 2H), 3.72 – 3.67 (m, 1H), 3.30 (ddd, *J* = 13.4, 9.7, 4.9 Hz, 1H), 3.01 (ddd, *J* = 13.4, 5.3, 3.1 Hz, 1H), 2.93 (dddd, *J* = 15.1, 9.6, 5.2, 1.4 Hz, 1H), 2.84 (ddd, *J* = 14.2, 9.3, 5.1 Hz, 1H), 2.74 (ddd, *J* = 13.8, 9.3, 7.1 Hz, 1H), 2.62 (ddd, *J* = 15.6, 5.0, 3.1 Hz, 1H), 2.20 – 2.11 (m, 1H), 2.04 (dddd, *J* = 14.1, 9.3, 7.3, 4.4 Hz, 1H).
^{13}C-NMR (150 MHz, $CDCl_3$) δ = 142.6, 140.0, 135.9, 135.2, 129.2, 128.6, 128.5, 128.4, 127.4, 127.2, 125.9, 121.5, 119.5, 118.2, 110.8, 108.2, 57.5, 56.1, 44.7, 36.6, 32.5, 17.9.
MS (APCI): *m/z* = 367.2 $[M+H]^+$.

IR (ATR) $\tilde{\nu}$ = 3409, 3025, 2929, 2842, 1494, 1452, 1299, 1106, 1010, 732.
The analytical data is in accordance with the literature data.[17]

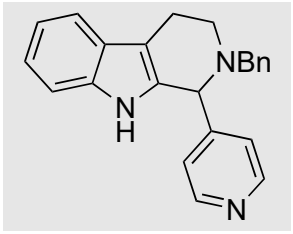
(*E*)-2-Benzyl-1-styryl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]-indole (3ar)



Following GP4, the reaction of **1a** (25.0 mg) and cinnamaldehyde (15.1 µL, 15.8 mg) gave after column chromatography (cyclohexane/EtOAc 20:1 to 10:1) the product **3ar** (15.6 mg, 42.8 µmol, 43%) as an orange oil.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.70 (s, 1H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.43 (dd, *J* = 17.0, 7.5 Hz, 4H), 7.35 (q, *J* = 6.9 Hz, 4H), 7.30 – 7.26 (m, 3H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.38 (dd, *J* = 15.9, 8.5 Hz, 1H), 4.33 (d, *J* = 8.6 Hz, 1H), 4.17 (d, *J* = 13.6 Hz, 1H), 3.54 (d, *J* = 13.6 Hz, 1H), 3.23 (dt, *J* = 10.4, 4.9 Hz, 1H), 2.79 (tt, *J* = 15.4, 6.5 Hz, 2H), 2.66 (td, *J* = 10.8, 4.6 Hz, 1H).
^{13}C-NMR (150 MHz, $CDCl_3$) δ = 139.4, 136.4, 136.3, 133.9, 133.3, 130.1, 129.0, 128.9, 128.4, 128.2, 127.7, 127.1, 126.7, 121.8, 119.5, 118.5, 111.0, 109.1, 62.8, 58.8, 48.2, 21.4.
HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{26}H_{25}N_2^+$: 365.2012; found 365.2004.
IR (ATR) $\tilde{\nu}$ = 3397, 3025, 2920, 2850, 2324, 1450, 1301, 1266, 967, 732.

2-Benzyl-1-(pyridin-4-yl)-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]-indole (3as)

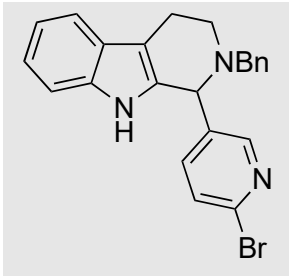


Following GP4, the reaction of **1a** (25.0 mg) and isonicotinaldehyde (11.3 µL, 12.9 mg) gave after column chromatography (cyclohexane/EtOAc 1:1) the product **3as** (31.4 mg, 92.5 µmol, 93%) as a yellow solid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 8.57 (d, *J* = 6.0 Hz, 2H), 7.56 – 7.50 (m, 2H), 7.37 – 7.32 (m, 6H), 7.29 – 7.22 (m, 2H), 7.18 – 7.09 (m, 2H), 4.67 (s, 1H), 3.83 (d, *J* = 13.4 Hz, 1H), 3.49 (d, *J* = 13.5 Hz, 1H), 3.19 (dt, *J* = 12.2, 4.9 Hz, 1H), 2.93 – 2.81 (m, 2H), 2.73 (ddd, *J* = 12.5, 8.1, 4.7 Hz, 1H).
^{13}C-NMR (150 MHz, $CDCl_3$) δ = 150.9, 150.4, 139.0, 136.6, 132.7, 128.8, 128.5, 127.4, 127.1, 124.0, 122.1, 119.8, 118.6, 111.1, 109.8, 63.1, 58.6, 47.8, 20.8.
MS (APCI): *m/z* = 340.2 $[M+H]^+$.

IR (ATR) $\tilde{\nu}$ = 3252, 3028, 2842, 1601, 1449, 1414, 1293, 1155, 822, 749.
Mp = 204 – 206 °C.
The analytical data is in accordance with the literature data.[18]

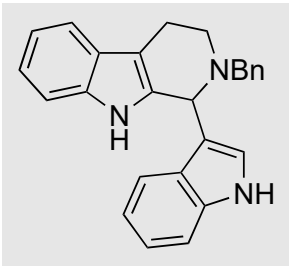
2-Benzyl-1-(6-bromopyridin-3-yl)-2,3,4,9-tetrahydro-1*H*-pyrido-[3,4-*b*]indole (3at)



Following GP4, the reaction of **1a** (25.0 mg) and 6-bromonicotinaldehyde (22.3 mg) gave after column chromatography (cyclohexane/EtOAc 10:1) the product **3at** (36.8 mg, 88.0 µmol, 88%) as a colorless solid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 8.37 (d, *J* = 2.6 Hz, 1H), 7.57 (dd, *J* = 8.3, 2.6 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.50 (s, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.35 – 7.29 (m, 4H), 7.29 – 7.23 (m, 2H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 4.70 (s, 1H), 3.83 (d, *J* = 13.5 Hz, 1H), 3.48 (d, *J* = 13.5 Hz, 1H), 3.19 (dt, *J* = 12.1, 4.9 Hz, 1H), 2.91 – 2.82 (m, 2H), 2.74 (ddd, *J* = 12.6, 8.2, 4.7 Hz, 1H).
^{13}C-NMR (150 MHz, $CDCl_3$) δ = 150.5, 142.0, 139.4, 138.9, 137.1, 136.6, 132.7, 128.7, 128.7, 128.6, 127.4, 127.0, 122.2, 119.8, 118.6, 111.1, 110.1, 60.6, 58.3, 47.9, 20.8.
HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{23}H_{21}BrN_3^+$: 418.0913; found 418.0905.
IR (ATR) $\tilde{\nu}$ = 3166, 3100, 2921, 2842, 1585, 1560, 1450, 1280, 1092, 750.
Mp = 222 – 224 °C.

2-Benzyl-1-(1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole (3au)

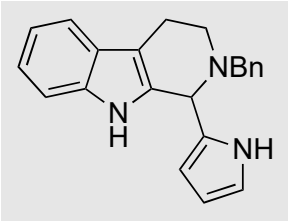


Following GP4, the reaction of **1a** (25.0 mg) and 1*H*-indole-3-carbaldehyde (17.4 mg) gave after column chromatography (cyclohexane/EtOAc 10:1 to 2:1) the product **3au** (27.8 mg, 73.6 µmol, 74%) as a yellow solid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 8.09 (s, 1H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.57 – 7.51 (m, 1H), 7.42 (s, 1H), 7.36 (d, *J* = 8.2 Hz, 1H), 7.32 (d, *J* = 7.4 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.21 – 7.17 (m, 2H), 7.15 – 7.12 (m, 1H), 7.11 – 7.08 (m, 2H), 7.05 (t, *J* = 7.5 Hz,

1H), 5.02 (s, 1H), 4.04 (d, *J* = 13.4 Hz, 1H), 3.40 (d, *J* = 13.4 Hz, 1H), 3.30 (dt, *J* = 12.0, 4.7 Hz, 1H), 3.00 – 2.91 (m, 1H), 2.85 (dt, *J* = 15.3, 4.5 Hz, 1H), 2.69 (ddd, *J* = 13.1, 9.1, 4.3 Hz, 1H).
^{13}C-NMR (151 MHz, $CDCl_3$) δ = 140.1, 136.8, 136.1, 135.4, 129.0, 128.3, 127.5, 126.9, 126.8, 124.3, 122.5, 121.3, 120.5, 120.0, 119.3, 118.3, 115.8, 111.2, 111.0, 108.6, 58.4, 57.1, 48.7, 21.3.
HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{26}H_{24}N_3^+$: 378.1965; found 378.1961.
IR (ATR) $\tilde{\nu}$ = 3402, 2926, 1552, 1452, 1301, 1092, 1009, 818, 738.
Mp = 163 – 165 °C.

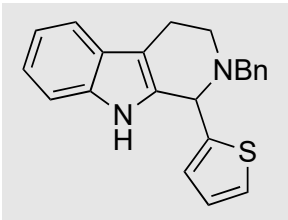
2-Benzyl-1-(1*H*-pyrrol-2-yl)-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole (3av)



Following GP4, the reaction of **1a** (25.0 mg) and 1*H*-pyrrole-2-carbaldehyde (11.4 mg) gave after column chromatography (cyclohexane/EtOAc 10:1 to 4:1) the product **3av** (14.6 mg, 44.6 µmol, 45%) as an orange solid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 8.36 (s, 1H), 7.52 – 7.49 (m, 1H), 7.47 – 7.43 (m, 1H), 7.34 (d, *J* = 4.5 Hz, 4H), 7.29 – 7.25 (m, 1H), 7.20 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.13 (td, *J* = 7.5, 1.4 Hz, 1H), 7.10 (ddd, *J* = 8.3, 7.1, 1.2 Hz, 1H), 6.74 (td, *J* = 2.6, 1.6 Hz, 1H), 6.32 (ddd, *J* = 3.9, 2.5, 1.5 Hz, 1H), 6.19 (q, *J* = 2.7 Hz, 1H), 4.78 (s, 1H), 3.97 (d, *J* = 13.7 Hz, 1H), 3.41 (d, *J* = 13.7 Hz, 1H), 3.24 (ddd, *J* = 11.8, 5.3, 3.5 Hz, 1H), 2.87 (dddd, *J* = 15.1, 9.6, 5.3, 2.1 Hz, 1H), 2.78 (dtd, *J* = 15.3, 4.3, 1.7 Hz, 1H), 2.66 (ddd, *J* = 11.8, 9.6, 4.4 Hz, 1H).
^{13}C-NMR (150 MHz, $CDCl_3$) δ = 139.2, 136.2, 133.8, 130.4, 128.9, 128.4, 127.3, 127.1, 121.8, 119.5, 118.6, 118.4, 111.0, 108.8, 108.6, 108.0, 58.4, 57.8, 48.8, 21.3.
HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{22}H_{22}N_3^+$: 328.1808; found 328.1805.
IR (ATR) $\tilde{\nu}$ = 3414, 3343, 2903, 2811, 1450, 1300, 1115, 1025, 803, 726.
Mp = 148 – 150 °C.

2-Benzyl-1-(thiophen-2-yl)-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]-indole (3aw)

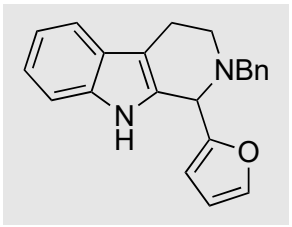


Following GP4, the reaction of **1a** (25.0 mg) and thiophene-2-carbaldehyde (11.1 µL, 13.5 mg) gave after column

chromatography (cyclohexane/EtOAc 10:1) the product **3aw** (33.6 mg, 97.5 µmol, 98%) as a yellow solid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.54 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.47 – 7.44 (m, 3H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.33 – 7.27 (m, 2H), 7.24 (dt, *J* = 8.0, 0.9 Hz, 1H), 7.16 (ddd, *J* = 8.1, 7.0, 1.4 Hz, 1H), 7.14 – 7.10 (m, 2H), 7.01 (dd, *J* = 5.1, 3.5 Hz, 1H), 5.04 (s, 1H), 4.02 (d, *J* = 13.6 Hz, 1H), 3.50 (d, *J* = 13.5 Hz, 1H), 3.27 (dt, *J* = 12.1, 5.0 Hz, 1H), 2.91 – 2.79 (m, 2H), 2.73 (ddd, *J* = 12.7, 8.3, 4.6 Hz, 1H).
^{13}C-NMR (150 MHz, $CDCl_3$) δ = 146.1, 139.4, 136.3, 134.1, 128.8, 128.4, 127.3, 127.2, 126.4, 126.3, 121.8, 119.5, 118.6, 111.0, 108.7, 59.3, 58.3, 48.0, 20.9. *Note: One signal is missing due to overlap.*
MS (APCI): *m/z* = 344.2 $[M+H]^+$.
IR (ATR) $\tilde{\nu}$ = 3393, 2914, 2822, 2753, 1451, 1364, 1286, 1114, 955, 742.
Mp = 172 – 174 °C.
The analytical data is in accordance with the literature data.[15]

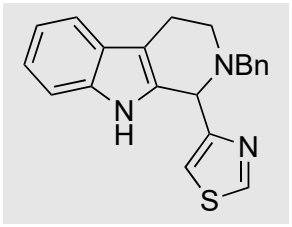
2-Benzyl-1-(furan-2-yl)-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]-indole (3ax)



Following GP4, the reaction of **1a** (25.0 mg) and furan-2-carbaldehyde (9.94 µL, 11.5 mg) gave (cyclohexane/EtOAc 10:1) the product **3ax** (29.6 mg, 90.1 µmol, 90%) as an orange oil.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.63 (s, 1H), 7.54 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.46 – 7.41 (m, 3H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.25 (m, 2H), 7.16 (ddd, *J* = 8.1, 7.1, 1.3 Hz, 1H), 7.12 (ddd, *J* = 8.0, 7.1, 1.1 Hz, 1H), 6.37 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.25 (d, *J* = 3.2 Hz, 1H), 4.96 (s, 1H), 3.86 (d, *J* = 13.7 Hz, 1H), 3.71 (d, *J* = 13.7 Hz, 1H), 3.28 – 3.20 (m, 1H), 2.93 – 2.78 (m, 3H).
^{13}C-NMR (150 MHz, $CDCl_3$) δ = 153.9, 142.7, 139.1, 136.2, 131.8, 129.0, 128.4, 127.2, 127.2, 121.9, 119.5, 118.5, 111.0, 110.4, 109.5, 109.2, 58.2, 56.2, 46.9, 20.4.
MS (APCI): *m/z* = 329.2 $[M+H]^+$.
IR (ATR) $\tilde{\nu}$ = 3404, 2842, 1521, 1495, 1451, 1301, 1114, 1009, 736.
The analytical data is in accordance with the literature data.[19]

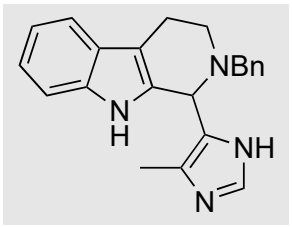
4-(2-Benzyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-1-yl)thiazole (3ay)



Following GP4, the reaction of **1a** (25.0 mg) and thiazole-4-carbaldehyde (13.6 mg) gave (cyclohexane/EtOAc 4:1) the product **3ay** (29.6 mg, 85.7 µmol, 86%) as a yellow solid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ 8.84 (d, *J* = 2.3 Hz, 1H), 8.31 (s, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 2H), 7.44 (s, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.29 (m, 2H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 5.18 (s, 1H), 4.06 (d, *J* = 14.0 Hz, 1H), 3.72 (d, *J* = 14.0 Hz, 1H), 3.35 – 3.26 (m, 1H), 2.94 – 2.78 (m, 3H).
^{13}C-NMR (150 MHz, $CDCl_3$) δ = 158.2, 153.4, 139.4, 136.3, 133.2, 128.5, 128.5, 127.2, 127.0, 121.7, 119.4, 118.4, 115.0, 111.1, 108.4, 59.6, 58.7, 47.9, 20.3.
MS (APCI): *m/z* = 346.2 $[M+H]^+$.
IR (ATR) $\tilde{\nu}$ = 3395, 2913, 2820, 2752, 1451, 1250, 1114, 815, 758.
Mp = 153 – 155 °C.
The analytical data is in accordance with the literature data.[18]

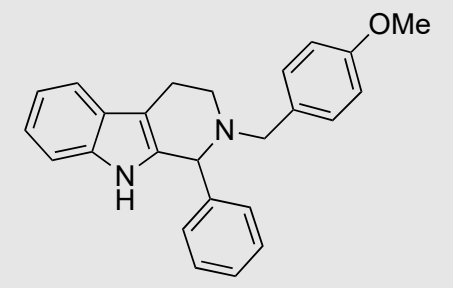
2-Benzyl-1-(4-methyl-1*H*-imidazol-5-yl)-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole (3az)



Following GP4, the reaction of **1a** (25.0 mg) and 4-methyl-1*H*-imidazole-5-carbaldehyde (13.2 mg) gave after column chromatography (DCM/MeOH 20:1 to 10:1) the product **3az** (26.5 mg, 77.3 µmol, 77%) as a yellow solid.

^{1}H-NMR (600 MHz, MeOD-d_4) δ = 7.51 (s, 1H), 7.41 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.32 – 7.26 (m, 4H), 7.22 (dt, *J* = 8.1, 1.0 Hz, 2H), 7.01 (ddd, *J* = 8.2, 7.0, 1.3 Hz, 1H), 6.96 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 4.87 (t, *J* = 1.7 Hz, 1H), 3.79 (d, *J* = 13.3 Hz, 1H), 3.43 (d, *J* = 13.3 Hz, 1H), 3.19 (dt, *J* = 11.8, 4.9 Hz, 1H), 2.85 – 2.74 (m, 2H), 2.65 (ddd, *J* = 11.7, 8.4, 4.5 Hz, 1H), 2.07 (s, 3H). *Note: The N-H signals are not observable due to exchange.*
^{13}C-NMR (150 MHz, MeOD-d_4) δ = 140.6, 138.2, 134.9, 134.6, 130.1, 129.2, 128.2, 128.0, 121.9, 119.6, 118.7, 111.9, 109.2, 59.3, 57.4, 49.3, 22.0, 10.8. *Note: Two signals are missing due to overlap.*
HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{22}H_{23}N_4^+$: 343.1917; found 343.1909.
IR (ATR) $\tilde{\nu}$ = 3414, 3341, 3058, 2902, 2811, 1450, 1300, 1268, 1115, 788.
Mp = 211 – 213 °C.

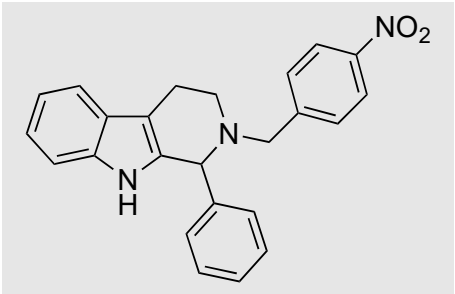
2-(4-Methoxybenzyl)-1-phenyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole (3ba)



Following GP4, the reaction of **1b** (28.0 mg) and benzaldehyde (12.3 µL, 12.7 mg) gave after column chromatography (cyclohexane/EtOAc 20:1) the product **3ba** (35.3 mg, 95.8 µmol, 96%) as a colorless solid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.54 (d, *J* = 7.9 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.36 – 7.31 (m, 1H), 7.29 – 7.26 (m, 3H), 7.21 – 7.17 (m, 1H), 7.15 – 7.08 (m, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 4.65 (d, *J* = 1.9 Hz, 1H), 3.85 (d, *J* = 13.3 Hz, 1H), 3.82 (s, 3H), 3.34 (d, *J* = 13.3 Hz, 1H), 3.28 – 3.21 (m, 1H), 2.95 – 2.87 (m, 1H), 2.85 – 2.78 (m, 1H), 2.70 – 2.62 (m, 1H).
^{13}C-NMR (150 MHz, $CDCl_3$) δ = 158.8, 141.7, 136.4, 135.0, 131.6, 130.0, 129.1, 128.9, 128.2, 127.3, 121.6, 119.4, 118.4, 113.7, 110.9, 109.1, 64.5, 57.8, 55.4, 48.2, 21.2.
MS (APCI): *m/z* = 369.2 $[M+H]^+$.
IR (ATR) $\tilde{\nu}$ = 3405, 2901, 1607, 1511, 1451, 1364, 1266, 1235, 1036.
Mp = 138 – 139 °C.
The analytical data is in accordance with the literature data.[20]

2-(4-Nitrobenzyl)-1-phenyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole (3ca)

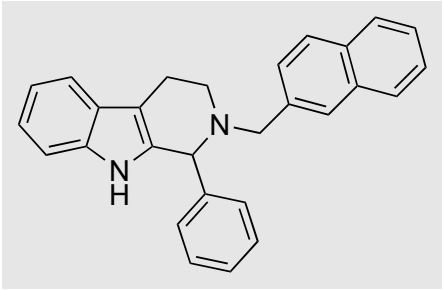


Following GP4, the reaction of **1c** (29.5 mg) and benzaldehyde (12.3 µL, 12.7 mg) gave after column chromatography (cyclohexane/EtOAc 20:1) the product **3ca** (35.7 mg, 93.1 µmol, 93%) as a yellow solid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 8.20 – 8.15 (m, 2H), 7.54 (dd, *J* = 7.9, 5.4 Hz, 3H), 7.48 – 7.43 (m, 2H), 7.42 – 7.37 (m, 2H), 7.37 – 7.33 (m, 1H), 7.28 (s, 1H), 7.21 – 7.17 (m, 1H), 7.16 – 7.08 (m, 2H), 4.68 (s, 1H), 3.96 (d, *J* = 14.5 Hz, 1H), 3.50 (d, *J* = 14.5 Hz, 1H), 3.19 – 3.10 (m, 1H), 3.01 – 2.92 (m, 1H), 2.87 – 2.79 (m, 1H), 2.75 – 2.67 (m, 1H).
^{13}C-NMR (150 MHz, $CDCl_3$) δ = 147.9, 147.2, 141.0, 136.4, 134.6, 129.2, 129.1, 129.1, 128.5, 127.2, 123.6, 121.8, 119.6, 118.4, 111.0, 108.9, 65.1, 57.9, 49.0, 21.5.

MS (APCI): *m/z* = 384.1 $[M+H]^+$.
IR (ATR) $\tilde{\nu}$ = 3408, 2905, 2836, 1600, 1511, 1318, 1093, 864, 735.
Mp = 190 – 192 °C.
The analytical data is in accordance with the literature data.[21]

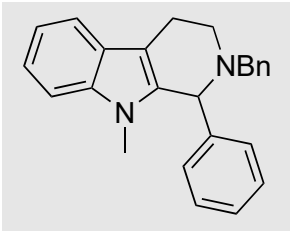
2-(Naphthalen-2-ylmethyl)-1-phenyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole (3da)



Following GP4, the reaction of **1d** (30.0 mg) and benzaldehyde (12.3 µL, 12.7 mg) gave after column chromatography (cyclohexane/EtOAc 20:1) the product **3da** (35.3 mg, 90.9 µmol, 91%) as a yellow solid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.87 – 7.81 (m, 3H), 7.79 (s, 1H), 7.54 (t, *J* = 9.0 Hz, 2H), 7.51 – 7.45 (m, 4H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.28 (bs, 1H), 7.21 (d, *J* = 8.4 Hz, 1H), 7.18 – 7.09 (m, 2H), 4.72 (s, 1H), 4.07 (d, *J* = 13.5 Hz, 1H), 3.56 (d, *J* = 13.5 Hz, 1H), 3.32 – 3.23 (m, 1H), 2.97 – 2.89 (m, 1H), 2.86 – 2.79 (m, 1H), 2.76 – 2.69 (m, 1H).
^{13}C-NMR (150 MHz, $CDCl_3$) δ = 141.6, 137.3, 136.4, 134.9, 133.5, 132.9, 129.2, 128.9, 128.2, 128.0, 127.8, 127.4, 127.3, 127.2, 126.1, 125.6, 121.7, 119.5, 118.4, 110.9, 109.1, 64.7, 58.6, 48.4, 21.2. *Note: One carbon signal is missing due to overlap.*
MS (APCI): *m/z* = 389.2 $[M+H]^+$.
IR (ATR) $\tilde{\nu}$ = 3401, 2946, 2916, 2815, 1598, 1454, 1303, 1157, 1119, 1011.
Mp = 212 – 213 °C.
The analytical data is in accordance with the literature data.[15]

2-Benzyl-9-methyl-1-phenyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole (3ea)



Following GP4, the reaction of **1e** (26.4 mg) and benzaldehyde (12.3 µL, 12.7 mg) gave after column chromatography (cyclohexane/EtOAc 20:1) the product **3ea** (32.1 mg, 91.1 µmol, 91%) as a colorless solid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.62 (d, *J* = 7.9 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.33 – 7.21 (m, 6H), 7.16 (t, *J* = 7.2 Hz, 1H), 7.12 (d, *J* = 7.3 Hz, 2H), 4.87 (s, 1H),

3.85 – 3.76 (m, 2H), 3.27 (d, *J* = 1.9 Hz, 3H), 3.12 – 2.98 (m, 2H), 2.92 – 2.86 (m, 1H), 2.81 – 2.73 (m, 1H).

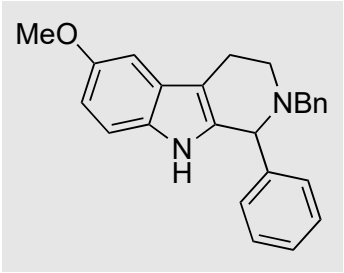
^{13}C-NMR (150 MHz, $CDCl_3$) δ = 140.9, 139.9, 137.3, 134.5, 129.4, 129.2, 128.5, 128.3, 127.6, 127.2, 126.9, 121.3, 119.0, 118.4, 108.9, 108.7, 59.8, 57.6, 44.4, 29.7, 19.1.

HRMS (EI, 70 eV): *m/z* = $[M]^+$ calcd for $C_{25}H_{24}N_2^+$: 352.1934; found 352.1934.

IR (ATR) $\tilde{\nu}$ = 3025, 2921, 2839, 1468, 1364, 1178, 1027, 891, 731, 697.

Mp = 76 – 78 °C.

2-Benzyl-6-methoxy-1-phenyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole (3fa)



Following GP4, the reaction of **1f** (28.0 mg) and benzaldehyde (12.3 µL, 12.7 mg) gave after column chromatography (cyclohexane/EtOAc 20:1) the product **3fa** (35.5 mg, 96.3 µmol, 96%) as an off-white solid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.49 – 7.45 (m, 2H), 7.41 – 7.31 (m, 7H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.15 (s, 1H), 7.08 (d, *J* = 8.7 Hz, 1H), 7.00 (d, *J* = 2.5 Hz, 1H), 6.79 (dd, *J* = 8.7, 2.5 Hz, 1H), 4.64 (s, 1H), 3.92 (d, *J* = 13.5 Hz, 1H), 3.87 (s, 3H), 3.38 (d, *J* = 13.6 Hz, 1H), 3.30 – 3.21 (m, 1H), 2.94 – 2.86 (m, 1H), 2.82 – 2.75 (m, 1H), 2.72 – 2.63 (m, 1H).

^{13}C-NMR (150 MHz, $CDCl_3$) δ = 154.1, 141.6, 139.7, 135.9, 131.5, 129.1, 128.9, 128.8, 128.4, 128.2, 127.7, 127.0, 111.6, 111.4, 108.9, 100.7, 64.8, 58.4, 56.1, 48.5, 21.3.

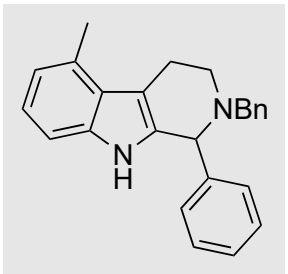
MS (APCI): *m/z* = 369.2 $[M+H]^+$.

IR (ATR) $\tilde{\nu}$ = 3405, 2919, 2840, 1598, 1451, 1296, 1141, 1027, 841, 745.

Mp = 160 – 162 °C.

The analytical data is in accordance with the literature data.[15]

2-Benzyl-5-methyl-1-phenyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole (3ga)



Following GP4, the reaction of **1g** (26.4 mg) and benzaldehyde (12.3 µL, 12.7 mg) gave after column chromatography (cyclohexane/EtOAc 20:1) the product **3ga** (33.5 mg, 95.0 µmol, 95%) as an off-white solid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.50 – 7.46 (m, 2H), 7.42 – 7.36 (m, 4H), 7.36 – 7.32 (m, 3H), 7.28 (m, 1H), 7.22 (s, 1H), 7.03 (d, *J* = 7.7 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 6.9 Hz,

1H), 4.66 (d, *J* = 1.9 Hz, 1H), 3.92 (d, *J* = 13.5 Hz, 1H), 3.36 (d, *J* = 13.5 Hz, 1H), 3.27 – 3.15 (m, 2H), 3.10 (dtd, *J* = 13.6, 3.5, 1.7 Hz, 1H), 2.69 – 2.63 (m, 4H).

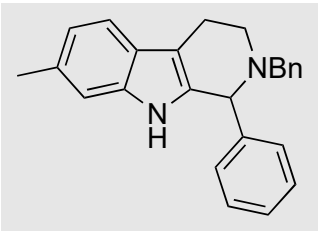
^{13}C-NMR (150 MHz, $CDCl_3$) δ = 141.6, 139.7, 136.4, 134.5, 130.7, 129.2, 128.9, 128.8, 128.3, 128.2, 127.0, 126.3, 121.7, 120.6, 109.4, 108.7, 65.0, 58.5, 48.8, 23.9, 19.7.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{25}H_{25}N_2^+$: 353.2012; found 353.2008.

IR (ATR) $\tilde{\nu}$ = 3385, 2934, 2795, 1492, 1451, 1362, 1274, 959, 746.

Mp = 192 – 194 °C.

2-Benzyl-7-methyl-1-phenyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole (3ha)



Following GP4, the reaction of **1h** (26.4 mg) and benzaldehyde (12.3 µL, 12.7 mg) gave after column chromatography (cyclohexane/EtOAc 20:1) the product **3ha** (31.4 mg, 89.1 µmol, 89%) as an off-white solid.

^{1}H-NMR (600 MHz, $CDCl_3$) ^{1}H NMR (601 MHz, $CDCl_3$) δ 7.45 – 7.41 (m, 2H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.37 – 7.33 (m, 4H), 7.33 – 7.28 (m, 3H), 7.24 (t, *J* = 7.2 Hz, 1H), 7.12 (s, 1H), 6.98 (s, 1H), 6.92 (d, *J* = 8.1 Hz, 1H), 4.63 (s, 1H), 3.89 (d, *J* = 13.5 Hz, 1H), 3.37 (d, *J* = 13.6 Hz, 1H), 3.21 (ddd, *J* = 11.7, 5.2, 3.8 Hz, 1H), 2.91 – 2.84 (m, 1H), 2.77 (dt, *J* = 16.8, 4.8 Hz, 1H), 2.65 (ddd, *J* = 11.8, 9.3, 4.3 Hz, 1H), 2.41 (s, 3H).

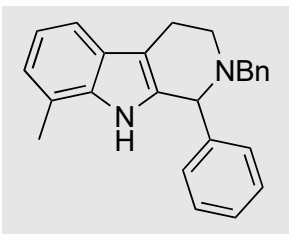
^{13}C-NMR (150 MHz, $CDCl_3$) δ = 141.7, 139.8, 136.9, 134.3, 131.4, 129.1, 128.9, 128.8, 128.3, 128.1, 127.0, 125.2, 121.1, 118.1, 111.0, 108.9, 64.7, 58.5, 48.4, 21.9, 21.3.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{25}H_{25}N_2^+$: 353.2012; found 353.2007.

IR (ATR) $\tilde{\nu}$ = 3444, 3027, 2929, 2825, 1493, 1450, 1316, 1277, 1157, 746.

Mp = 155 – 157 °C.

2-Benzyl-8-methyl-1-phenyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole (3ia)



Following GP4, the reaction of **1i** (26.4 mg) and benzaldehyde (12.3 µL, 12.7 mg) gave after column chromatography (cyclohexane/EtOAc 20:1) the product **3ia** (32.5 mg, 92.2 µmol, 92%) as an off-white solid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.44 – 7.41 (m, 2H), 7.40 – 7.34 (m, 5H), 7.34 – 7.30 (m, 3H), 7.26 – 7.24 (m, 1H), 7.14 (s, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 7.2 Hz, 1H), 4.68 (s, 1H), 3.89 (d, *J* = 13.5 Hz, 1H), 3.41 (d, *J* = 13.5 Hz, 1H), 3.22 (dt, *J* = 12.0, 4.8 Hz, 1H), 2.89

(dddd, *J* = 14.0, 8.6, 5.2, 1.9 Hz, 1H), 2.85 – 2.77 (m, 1H), 2.68 (ddd, *J* = 13.0, 8.7, 4.4 Hz, 1H), 2.34 (s, 3H).

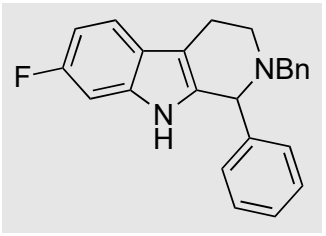
^{13}C-NMR (150 MHz, $CDCl_3$) δ = 141.6, 139.8, 135.9, 134.4, 129.2, 128.9, 128.8, 128.4, 128.2, 127.1, 126.9, 122.4, 120.1, 119.7, 116.2, 109.8, 64.3, 58.4, 48.1, 21.2, 16.8.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{25}H_{25}N_2^+$: 353.2012; found 353.2007.

IR (ATR) $\tilde{\nu}$ = 3451, 2894, 2841, 1493, 1450, 1302, 1120, 1027, 820, 741.

Mp = 173 – 175 °C.

2-Benzyl-7-fluoro-1-phenyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole (3ja)



Following GP4, the reaction of **1j** (26.8 mg) and benzaldehyde (12.3 µL, 12.7 mg) gave after column chromatography (cyclohexane/EtOAc 20:1) the product **3ja** (31.4 mg, 88.1 µmol, 88%) as an off-white solid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.50 – 7.46 (m, 2H), 7.44 – 7.38 (m, 3H), 7.38 – 7.32 (m, 5H), 7.27 (m, 2H), 6.88 (ddd, *J* = 18.1, 9.2, 2.4 Hz, 2H), 4.64 (s, 1H), 3.92 (d, *J* = 13.5 Hz, 1H), 3.38 (d, *J* = 13.5 Hz, 1H), 3.25 (ddd, *J* = 11.8, 5.4, 3.5 Hz, 1H), 2.91 (dddd, *J* = 15.1, 9.8, 5.4, 2.4 Hz, 1H), 2.78 (dt, *J* = 16.8, 4.7 Hz, 1H), 2.67 (m, 1H).

^{13}C-NMR (150 MHz, $CDCl_3$) δ = 159.8 (d, *J* = 237.1 Hz), 141.4, 139.6, 136.3 (d, *J* = 12.5 Hz), 135.3 (d, *J* = 3.8 Hz), 129.1, 129.0, 128.8, 128.4, 128.3, 127.1, 123.9, 119.0 (d, *J* = 10.4 Hz), 109.0, 107.9 (d, *J* = 24.0 Hz), 97.5 (d, *J* = 26.2 Hz), 64.8, 58.4, 48.5, 21.3.

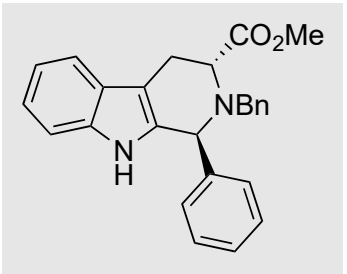
^{19}F-NMR (565 MHz, $CDCl_3$) δ = -121.7 (td, *J* = 9.5, 5.2 Hz).

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{24}H_{22}FN_2^+$: 357.1762; found 357.1752.

IR (ATR) $\tilde{\nu}$ = 3470, 3029, 2941, 2806, 1627, 1489, 1450, 1270, 1131, 830, 733.

Mp = 168 – 170 °C.

Methyl (1*S*,3*R*)-2-benzyl-1-phenyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole-3-carboxylate (3ka)



Following GP4, the reaction of **1k** (30.1 mg) and benzaldehyde (12.3 µL, 12.7 mg) gave after column chromatography (cyclohexane/EtOAc 20:1) the product **3ka** (34.9 mg, 88.0 µmol, 88%) as a colorless solid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.52 (d, *J* = 7.0 Hz, 1H), 7.48 (d, *J* = 6.9 Hz, 2H), 7.38 (s, 1H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.32 – 7.28 (m, 5H), 7.27 – 7.24 (m, 1H), 7.19 (d, *J* = 6.8 Hz, 1H), 7.15

– 7.06 (m, 2H), 5.48 (d, *J* = 1.8 Hz, 1H), 3.96 (t, *J* = 4.6 Hz, 1H), 3.94 – 3.84 (m, 2H), 3.64 (s, 3H), 3.25 – 3.18 (m, 2H).

^{13}C-NMR (150 MHz, $CDCl_3$) δ = 173.7, 142.3, 139.6, 136.6, 135.1, 129.1, 128.9, 128.7, 128.5, 128.2, 127.2, 127.2, 121.7, 119.4, 118.4, 111.0, 106.5, 61.0, 56.2, 54.5, 51.5, 24.6.

MS (APCI) *m/z* = 397.2 $[M+H]^+$.

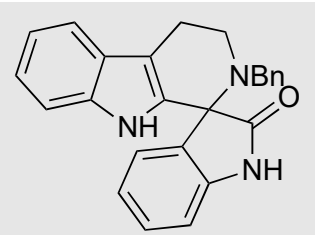
IR (ATR) $\tilde{\nu}$ = 3440, 3330, 2920, 1725, 1465, 1130, 745, 700.

Mp = 221 – 223 °C.

$[\alpha]_D^{25}$ = +77.0 (c = 1.0, MeOH).

The analytical data is in accordance with the literature data.[22]

2'-Benzyl-2',3',4',9'-tetrahydrospiro[indoline-3,1'-pyrido[3,4-*b*]indol]-2-one (7e)



Following GP4, the reaction of **1a** (25.0 mg) and isatin (17.7 mg) gave after column chromatography (cyclohexane/EtOAc 20:1 to 10:1) the product **7e** (33.8 mg, 89.0 µmol, 89%) as a violet solid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 8.46 (s, 1H), 7.54 (d, *J* = 8.3 Hz, 1H), 7.35 – 7.31 (m, 4H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.27 – 7.22 (m, 2H), 7.16 (d, *J* = 7.1 Hz, 1H), 7.14 – 7.04 (m, 3H), 6.92 (d, *J* = 7.8 Hz, 1H), 3.80 – 3.71 (m, 1H), 3.59 – 3.49 (m, 2H), 3.08 – 3.02 (m, 1H), 2.98 – 2.90 (m, 1H), 2.89 – 2.81 (m, 1H).

^{13}C-NMR (150 MHz, $CDCl_3$) δ = 178.7, 141.5, 139.5, 136.7, 130.8, 130.6, 130.0, 128.4, 128.4, 127.2, 127.2, 125.9, 123.9, 122.4, 119.7, 118.8, 112.1, 111.1, 110.4, 67.3, 54.6, 43.6, 21.5.

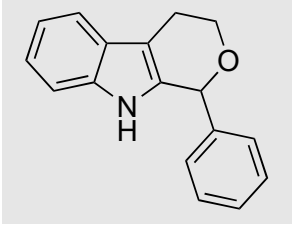
MS (APCI): *m/z* = 380.2 $[M+H]^+$.

IR (ATR) $\tilde{\nu}$ = 3026, 2922, 2840, 1469, 1179, 1011, 891, 731, 697.

Mp = 147 – 149 °C (decomp.).

The analytical data is in accordance with the literature data.[15]

1-Phenyl-1,3,4,9-tetrahydropyrano[3,4-*b*]indole (8)



Following GP4, the reaction of tryptophol (16.1 mg) and benzaldehyde (12.3 µL, 12.7 mg) gave after column chromatography (cyclohexane/EtOAc 20:1 to 10:1) the product **8** (16.8 mg, 67.4 µmol, 67%) as a yellow solid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.56 (d, *J* = 8.4 Hz, 1H), 7.45 (s, 1H), 7.38 (s, 5H), 7.24 (d, *J* = 7.1 Hz, 1H), 7.18 – 7.10 (m, 2H), 5.81 (s, 1H), 4.34 (m, 1H), 4.05 – 3.97 (m, 1H), 3.16 – 3.07 (m, 1H), 2.87 – 2.79 (m, 1H).

^{13}C-NMR (150 MHz, $CDCl_3$) δ = 139.6, 136.2, 133.8, 129.1, 129.0, 128.6, 127.2, 122.1, 119.8, 118.5, 111.1, 108.9, 76.3, 65.1, 22.4.

MS (APCI): *m/z* = 252.2 $[M+H]^+$.

IR (ATR) $\tilde{\nu}$ = 3025, 2922, 2840, 1469, 1365, 1179, 1011, 891, 732, 696.

Mp = 153 – 154 °C.

The analytical data is in accordance with the literature data.[23]

5. NMR Spectra

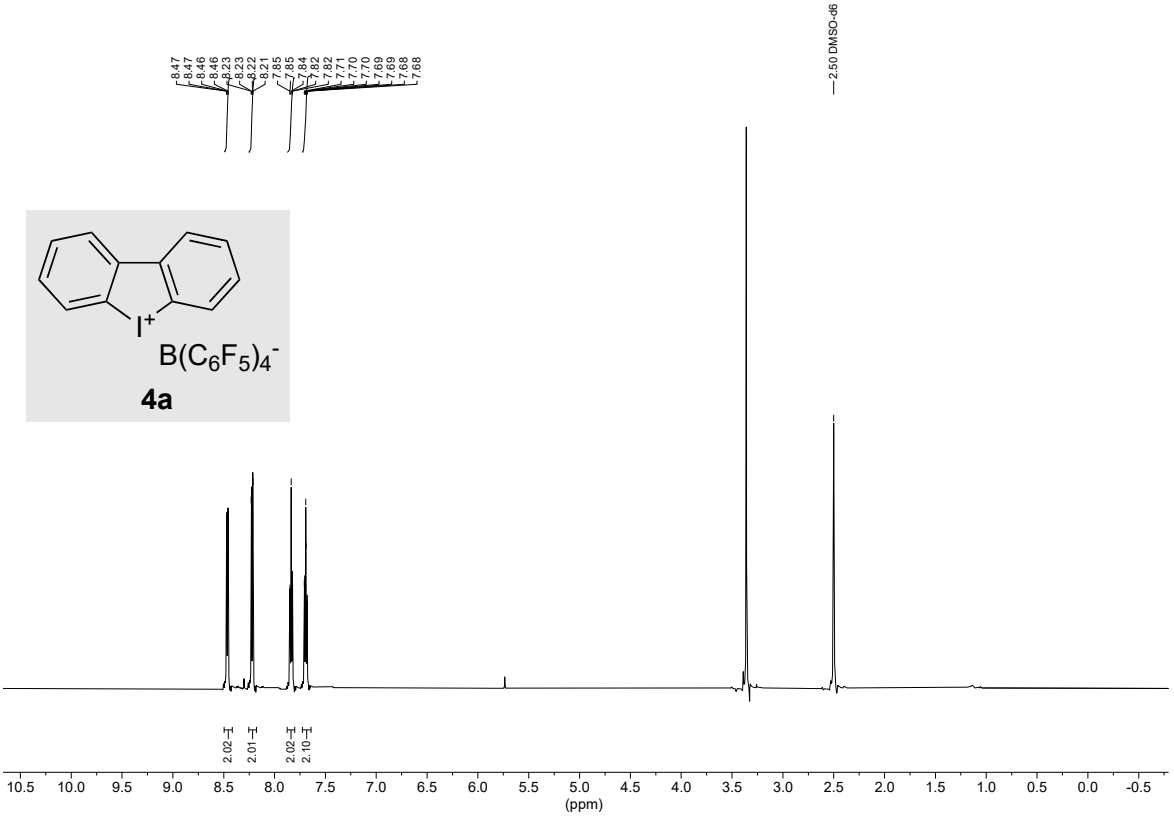


Figure S9. 600 MHz ^{1}H-NMR spectrum of compound **4a** in DMSO-d_6.

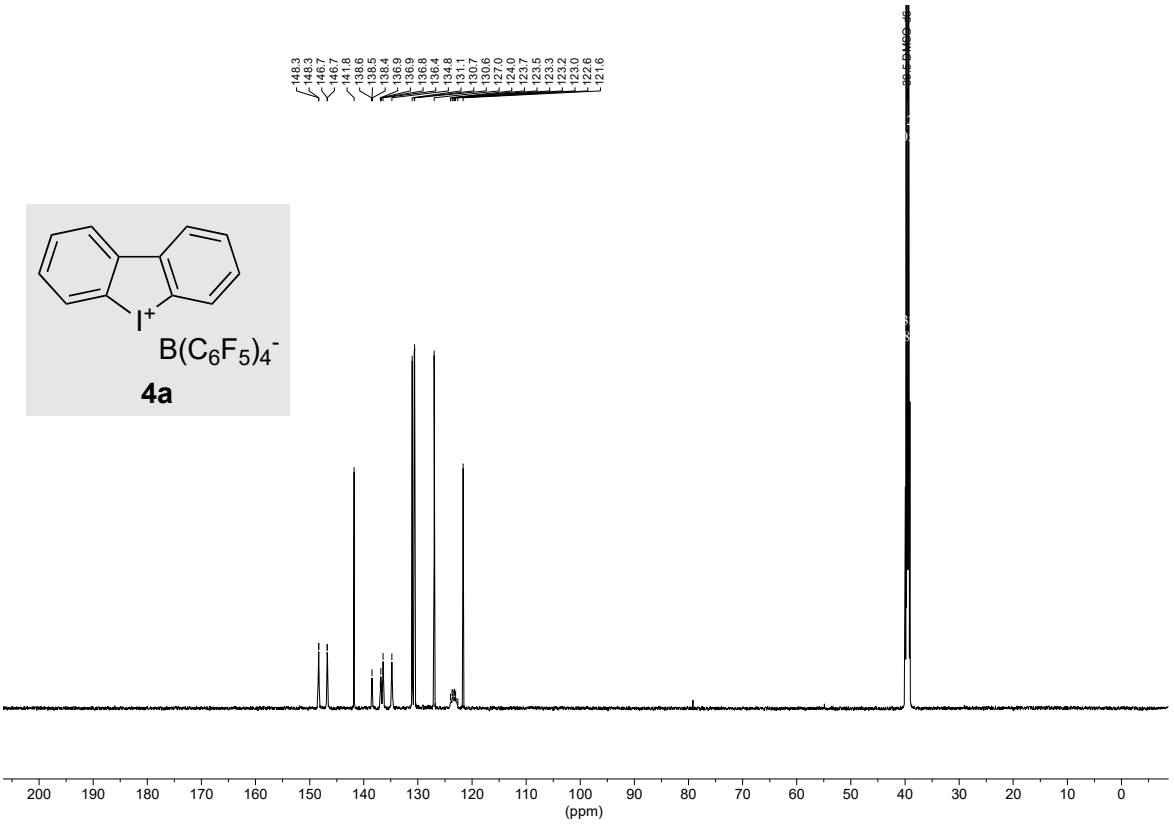


Figure S10. 150 MHz ^{13}C-NMR spectrum of compound **4a** in DMSO-d_6.

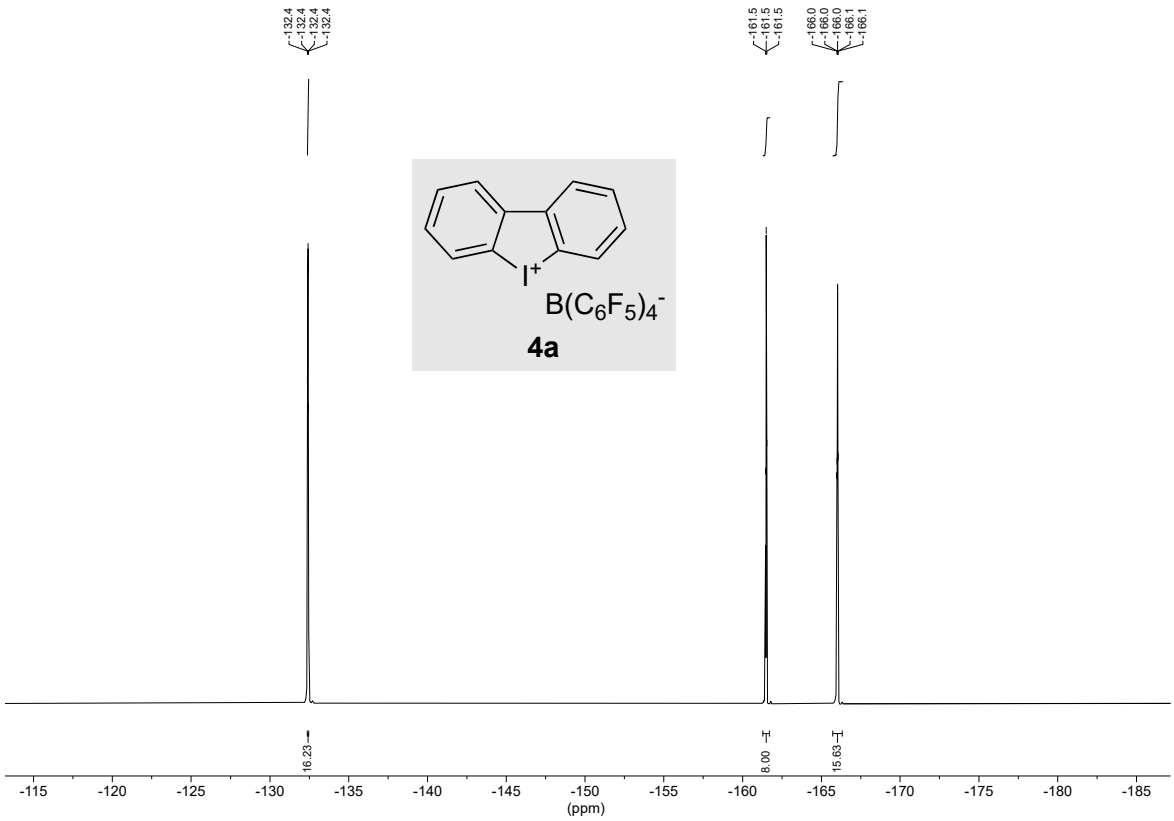


Figure S11. 565 MHz ^{19}F-NMR spectrum of compound **4a** in DMSO-d_6.

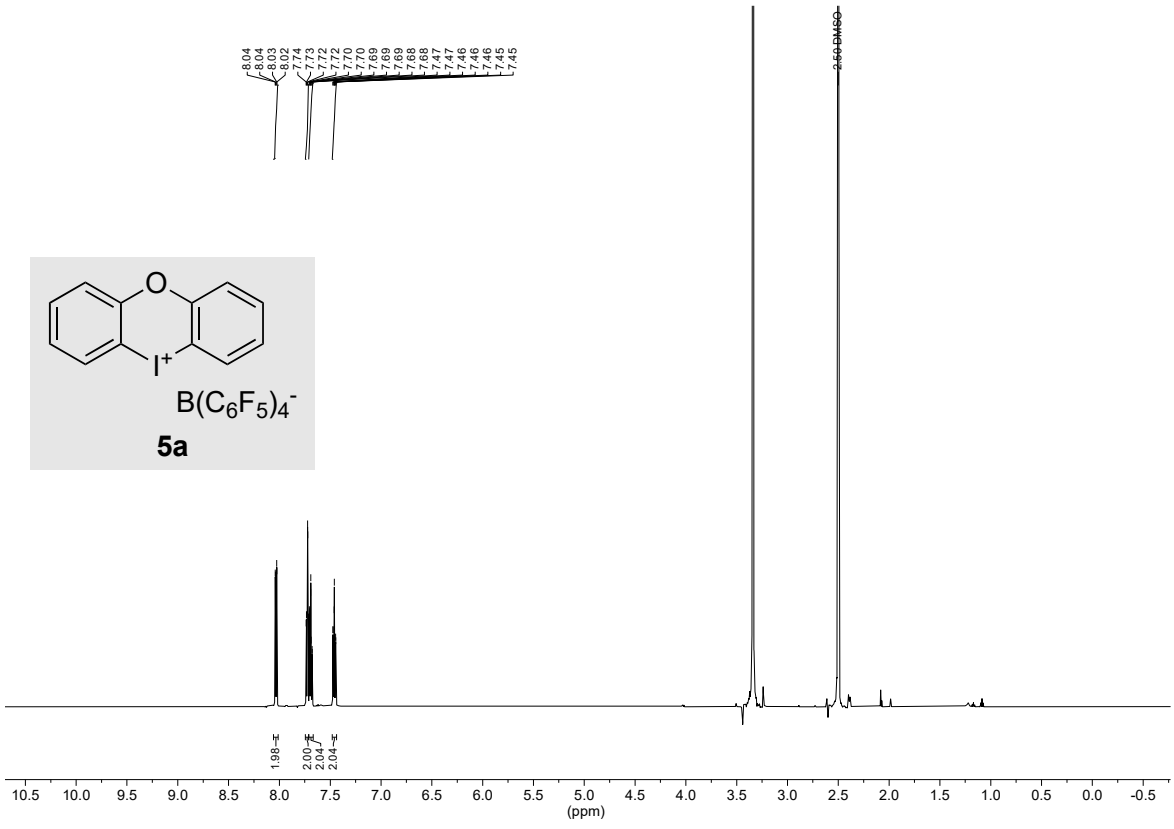


Figure S12. 600 MHz ^{1}H-NMR spectrum of compound **5a** in DMSO-d_6.

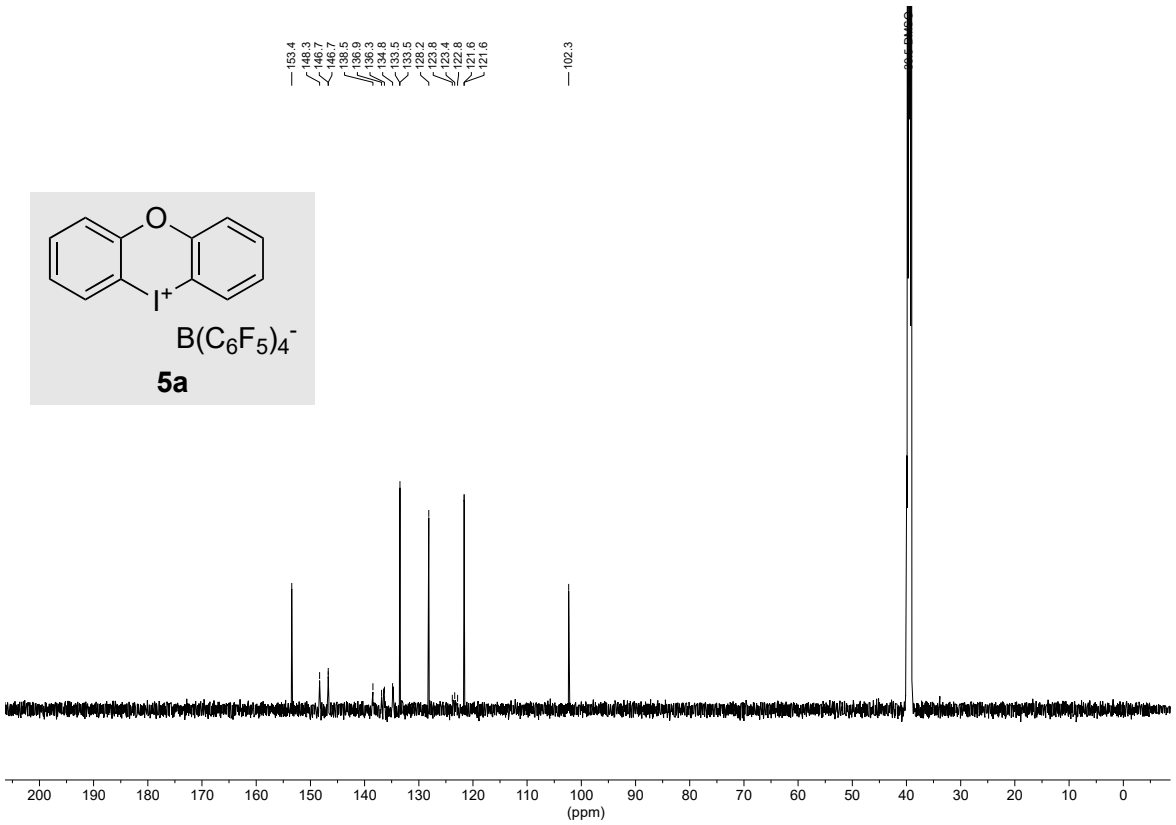


Figure S13. 150 MHz ^{13}C-NMR spectrum of compound **5a** in DMSO-d_6.

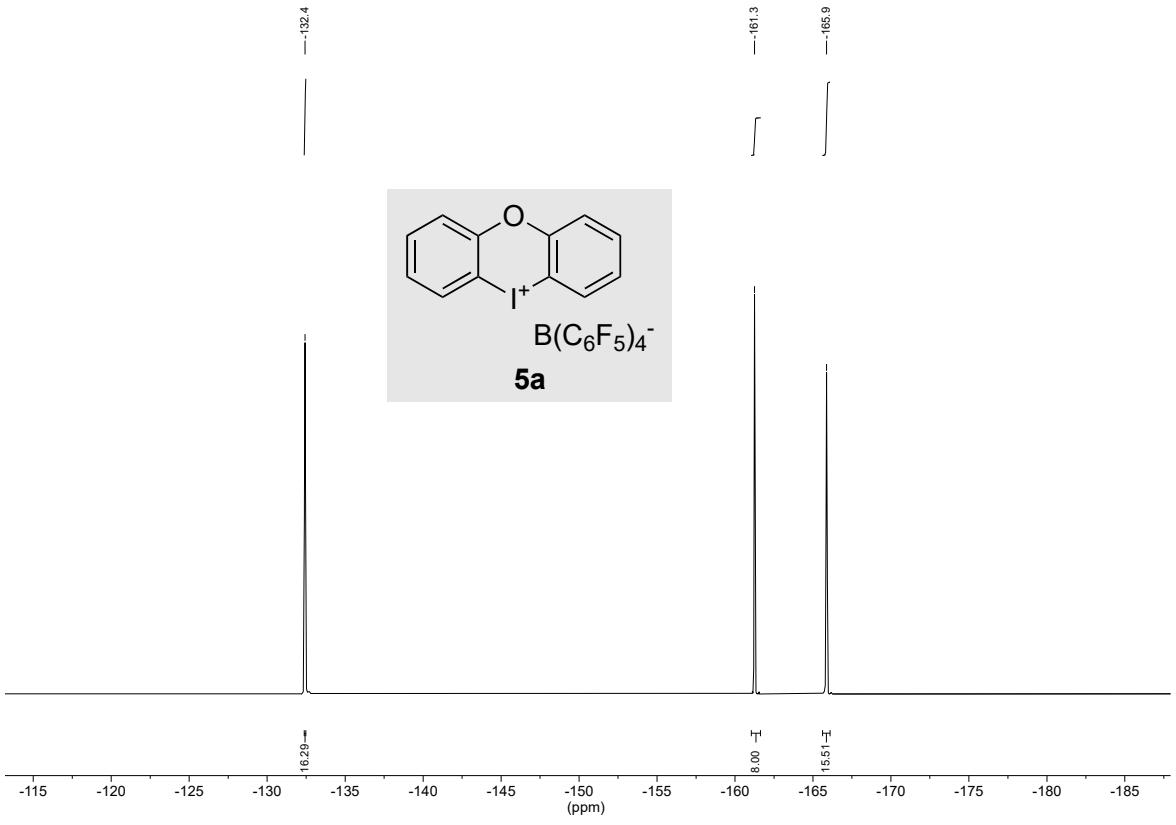


Figure S14. 565 MHz ^{19}F-NMR spectrum of compound **5a** in DMSO-d_6.

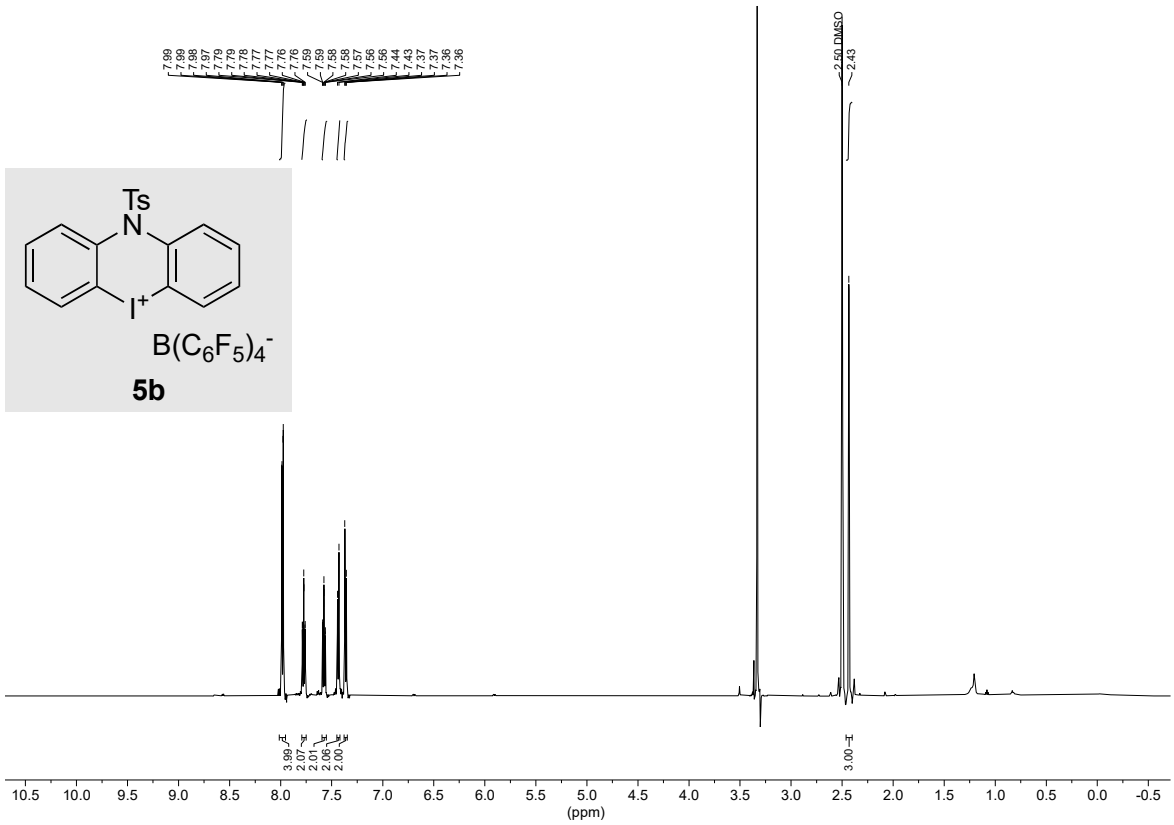


Figure S15. 600 MHz ^{1}H-NMR spectrum of compound **5b** in DMSO-d_6.

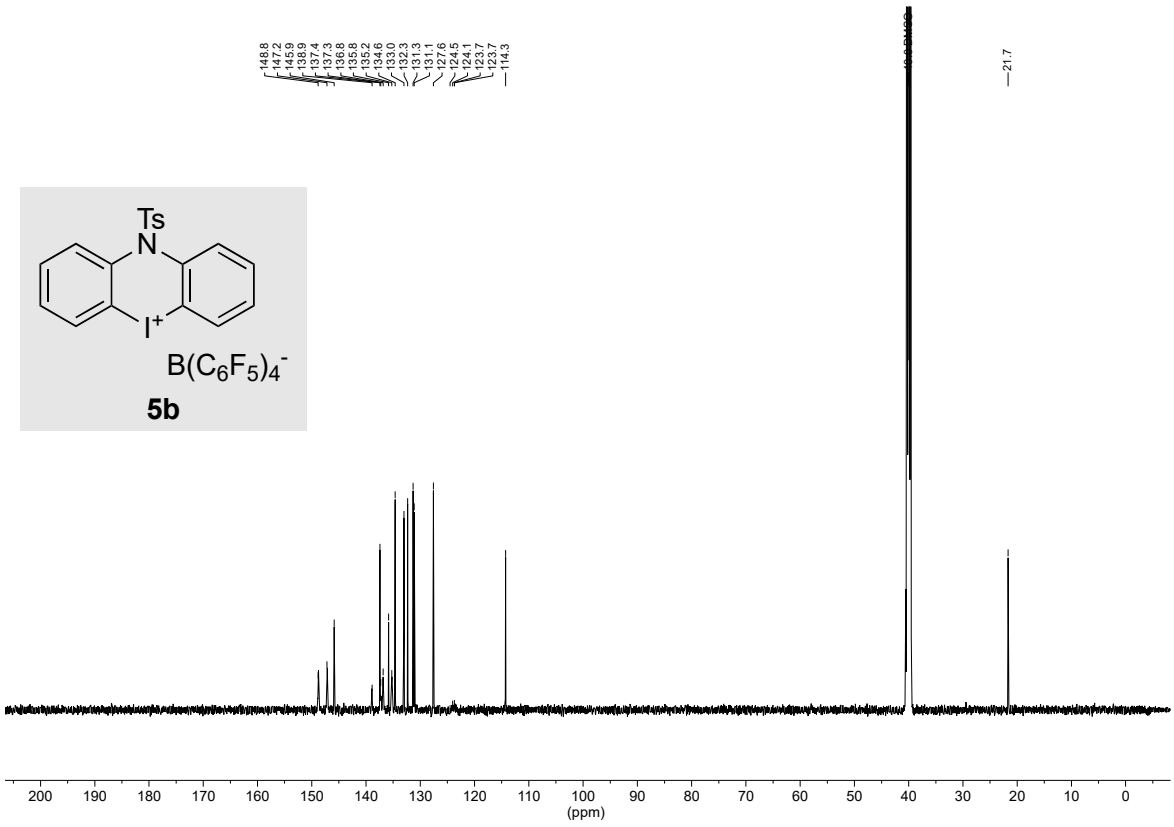


Figure S16. 150 MHz ^{13}C-NMR spectrum of compound **5b** in DMSO-d_6.

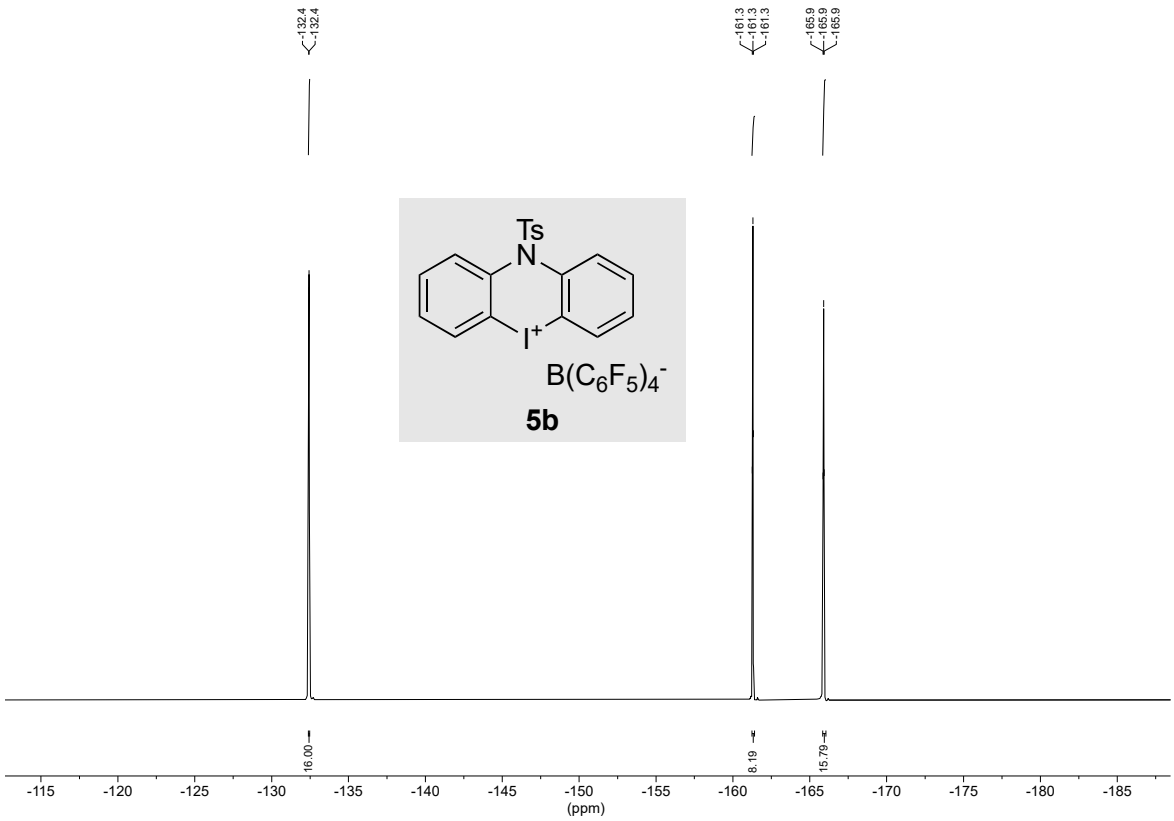


Figure S17. 565 MHz ^{19}F-NMR spectrum of compound **5b** in DMSO-d_6.

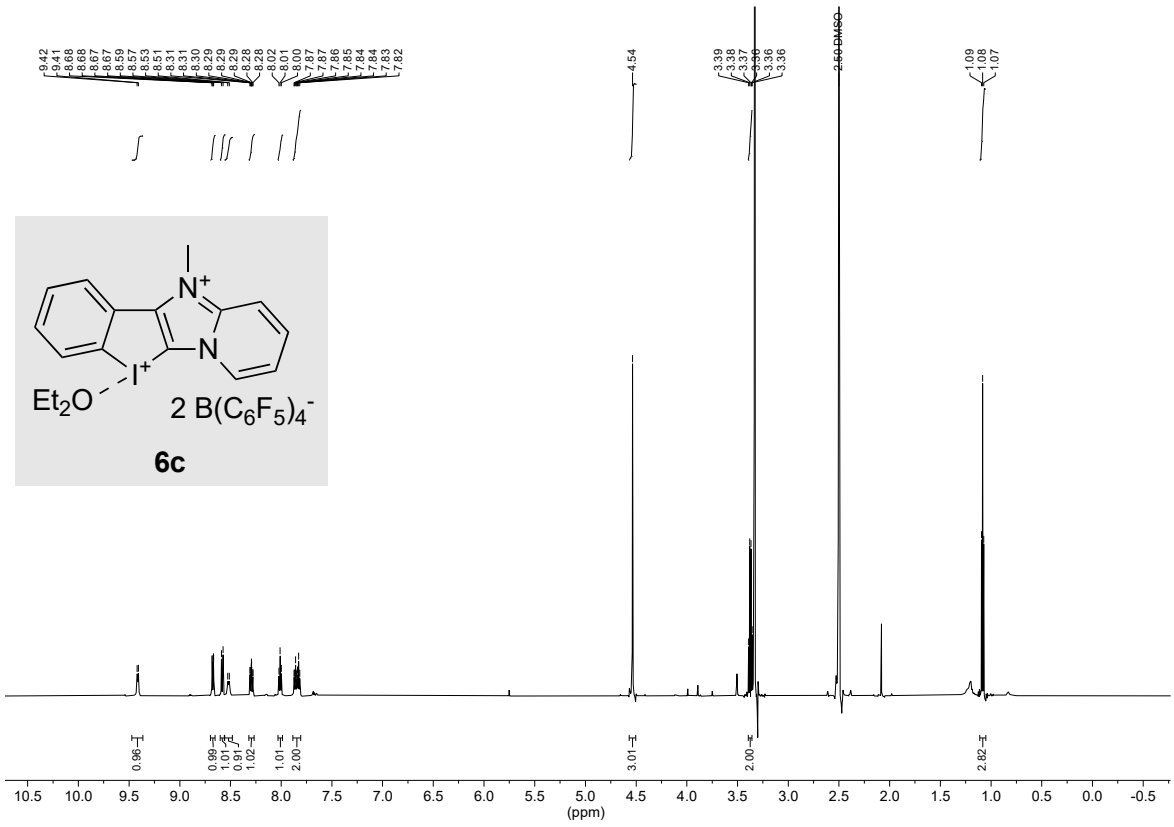


Figure S18. 600 MHz ^{1}H-NMR spectrum of compound **6c** in DMSO-d_6.

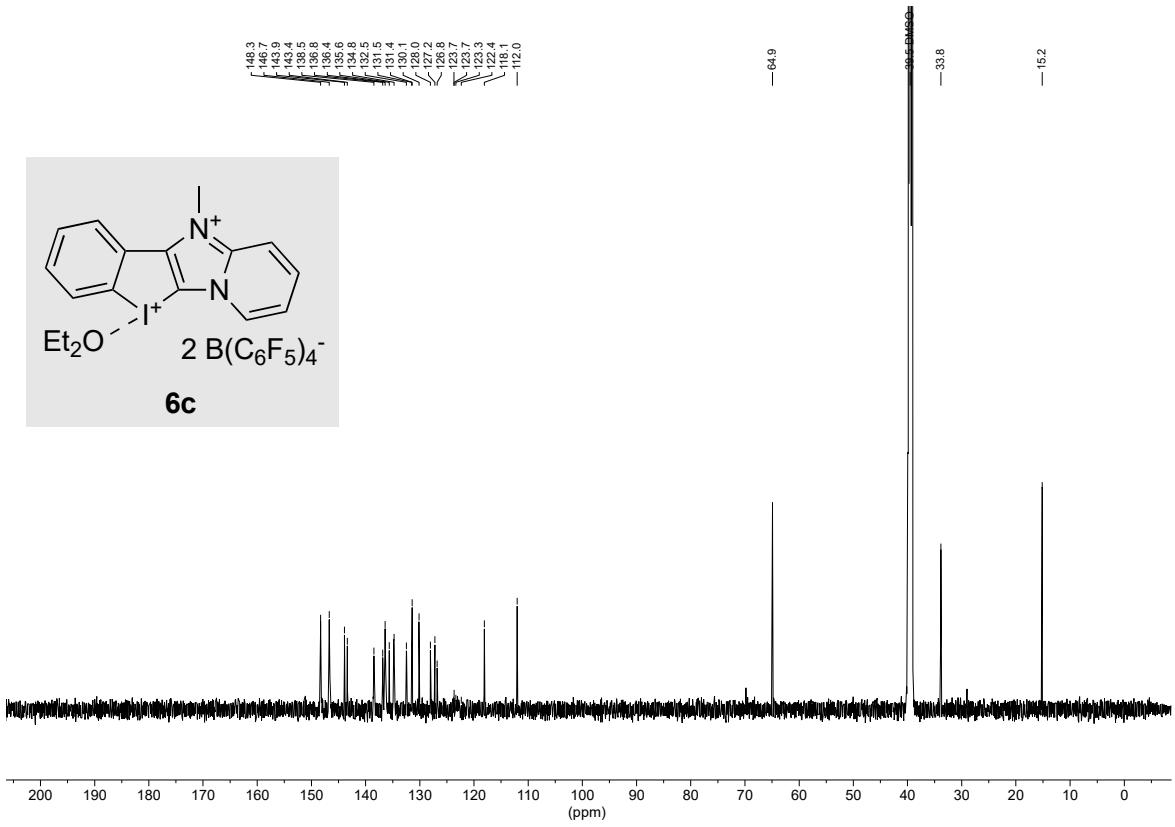


Figure S19. 150 MHz ^{13}C-NMR spectrum of compound **6c** in DMSO-d_6.

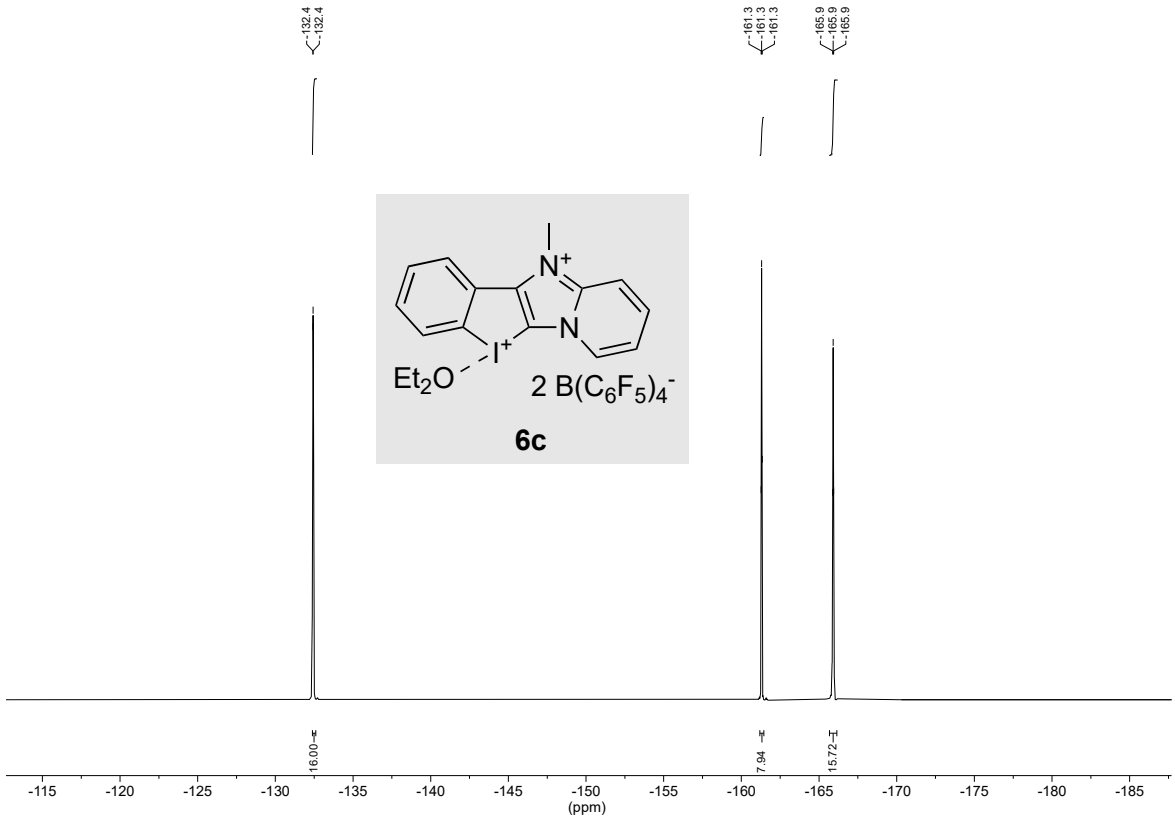


Figure S20. 565 MHz ^{19}F-NMR spectrum of compound **6c** in DMSO-d_6.

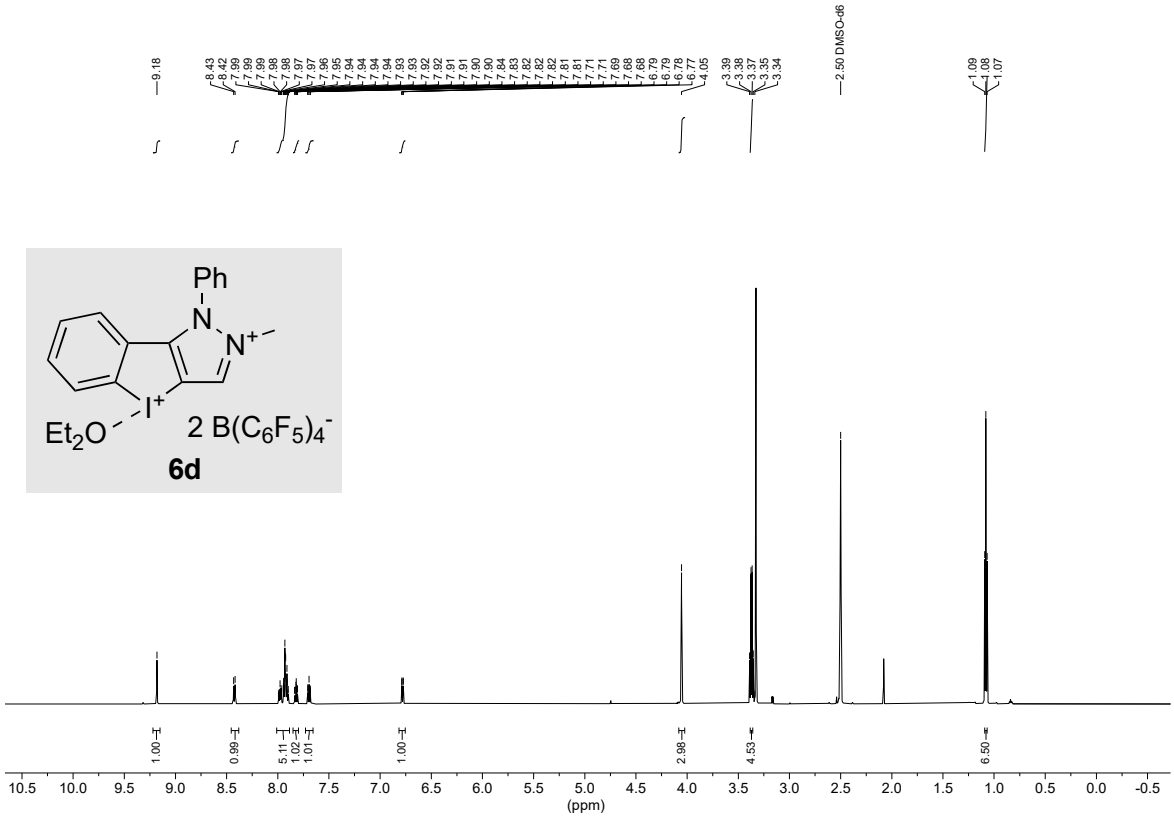


Figure S21. 600 MHz ^{1}H-NMR spectrum of compound **6d** in DMSO-d_6.

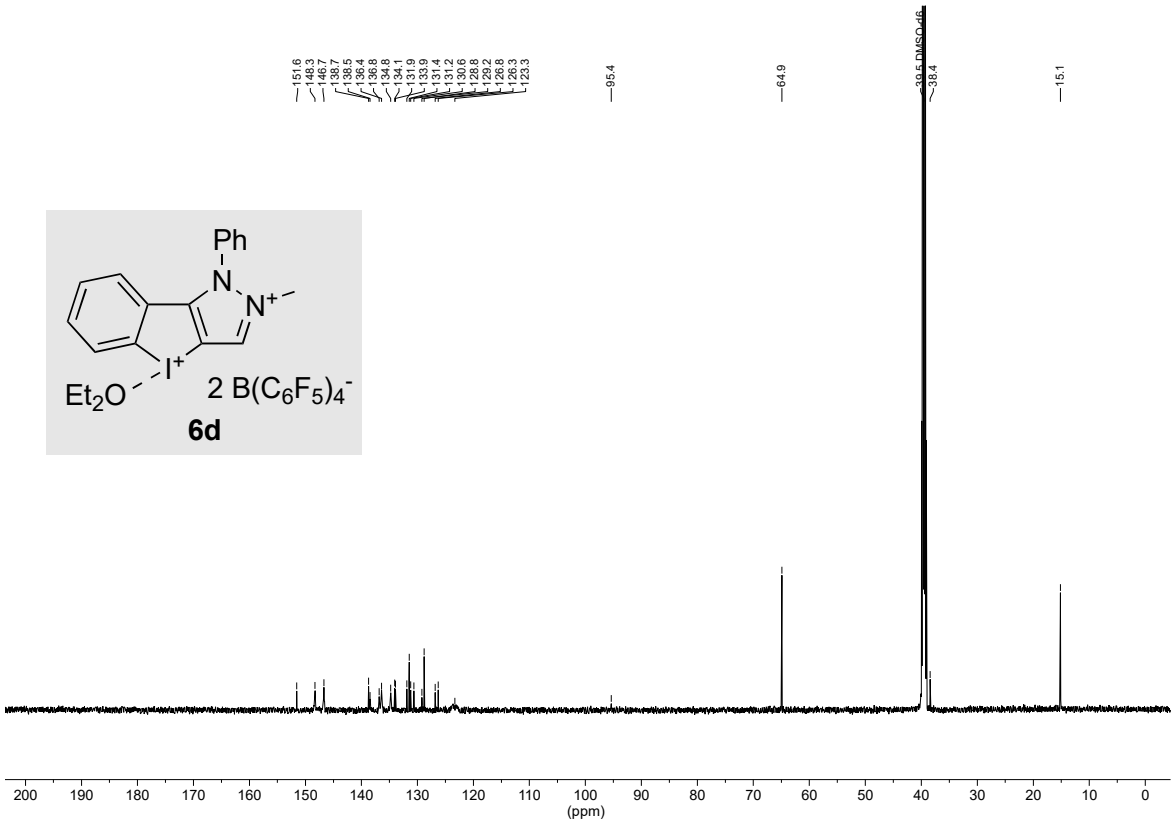


Figure S22. 150 MHz ^{13}C-NMR spectrum of compound **6d** in DMSO-d_6.

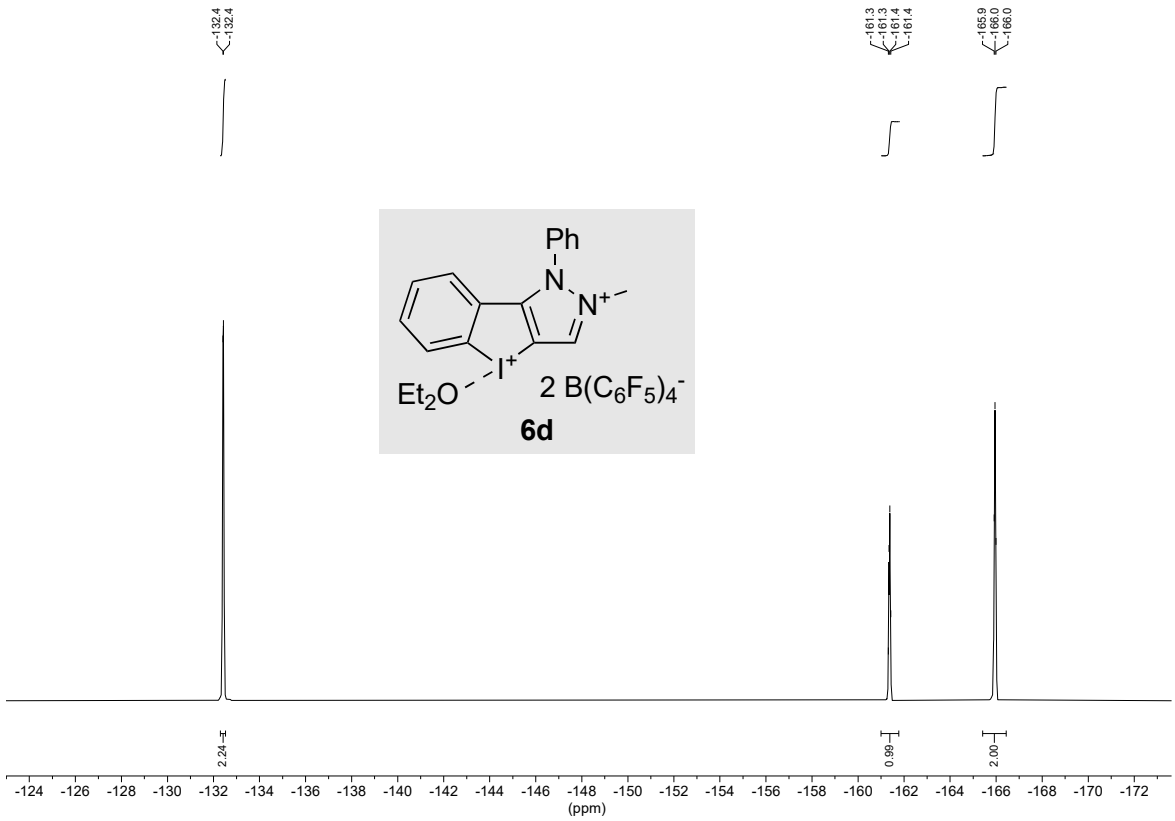


Figure S23. 565 MHz ^{19}F-NMR spectrum of compound **6d** in DMSO-d_6.

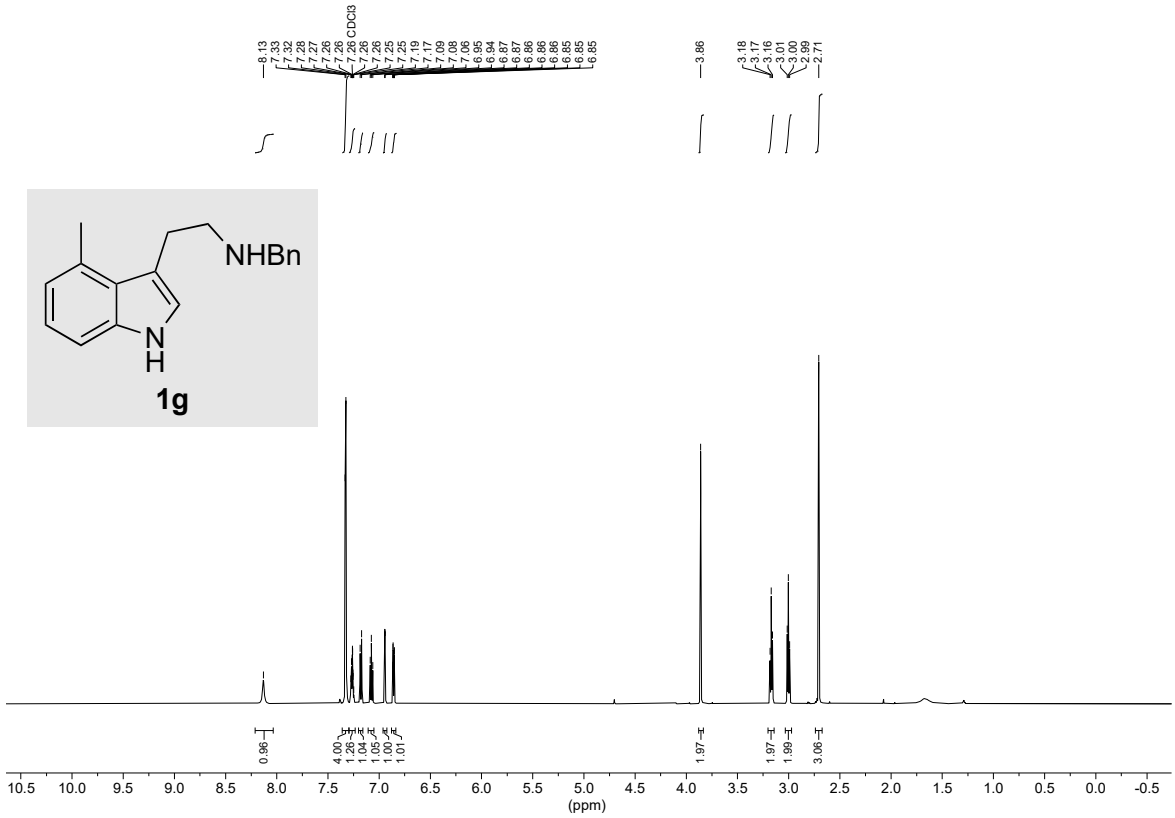


Figure S24. 600 MHz ^{1}H-NMR spectrum of compound **1g** in $CDCl_3$.

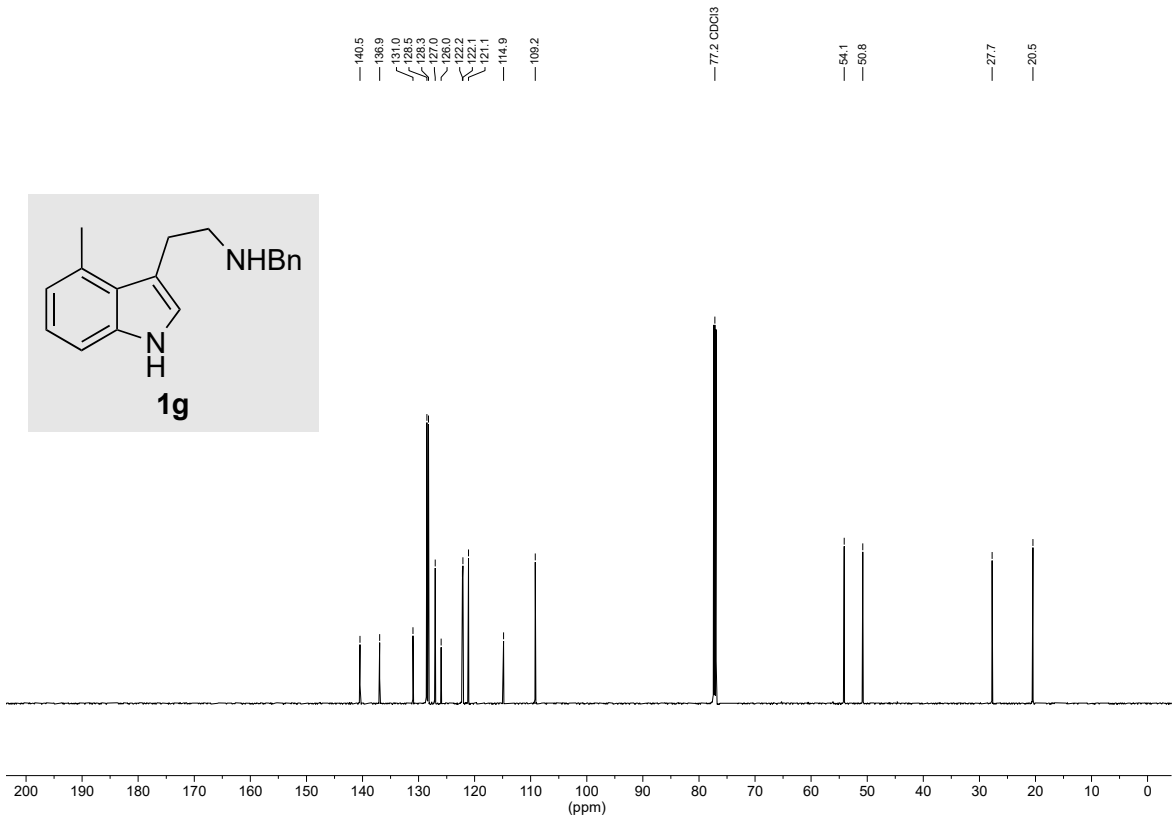


Figure S25. 150 MHz ^{13}C-NMR spectrum of compound **1g** in $CDCl_3$.

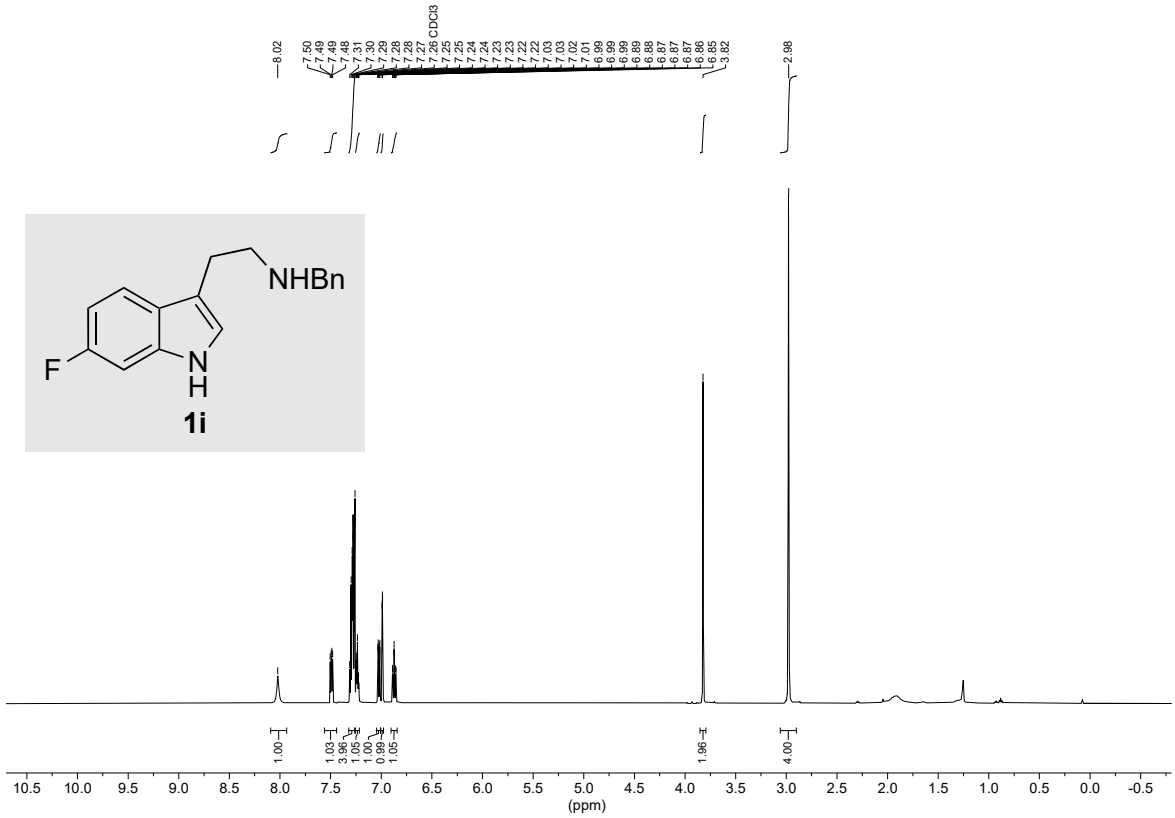


Figure S26. 600 MHz ^{1}H-NMR spectrum of compound **1i** in $CDCl_3$.

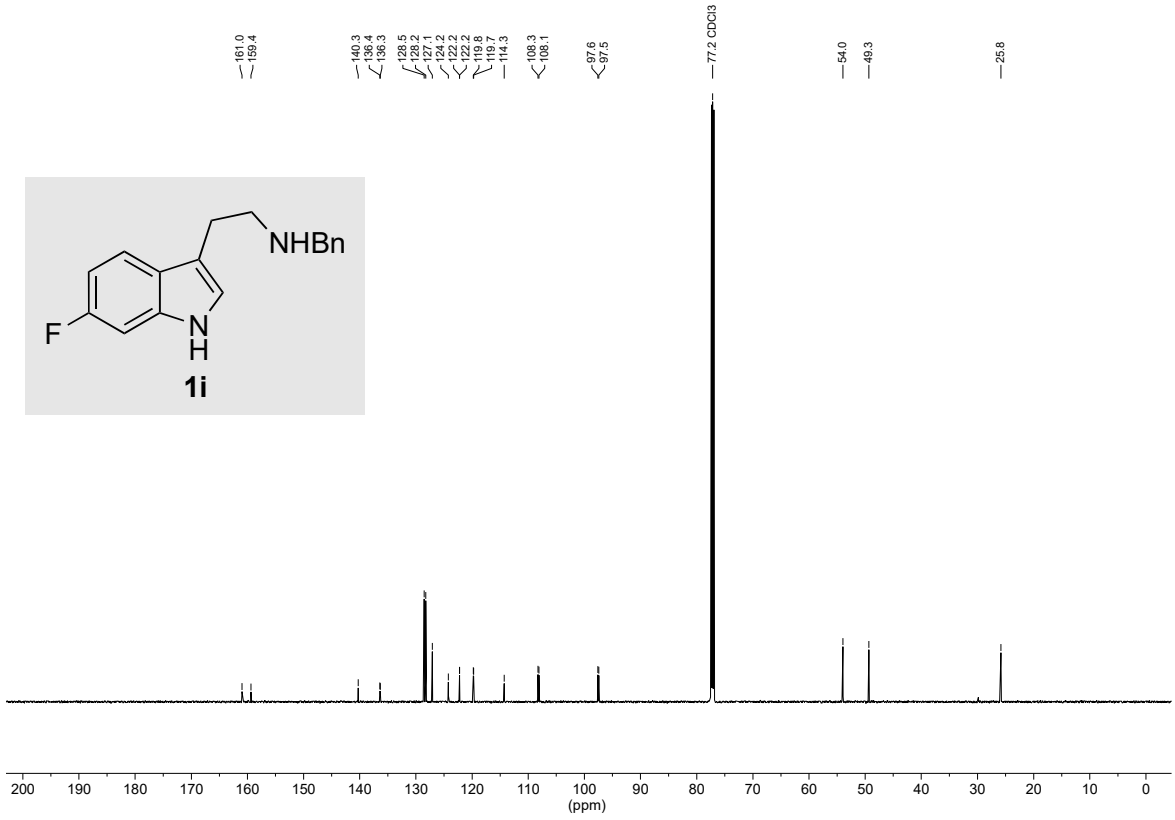


Figure S27. 150 MHz ^{13}C-NMR spectrum of compound **1i** in $CDCl_3$.

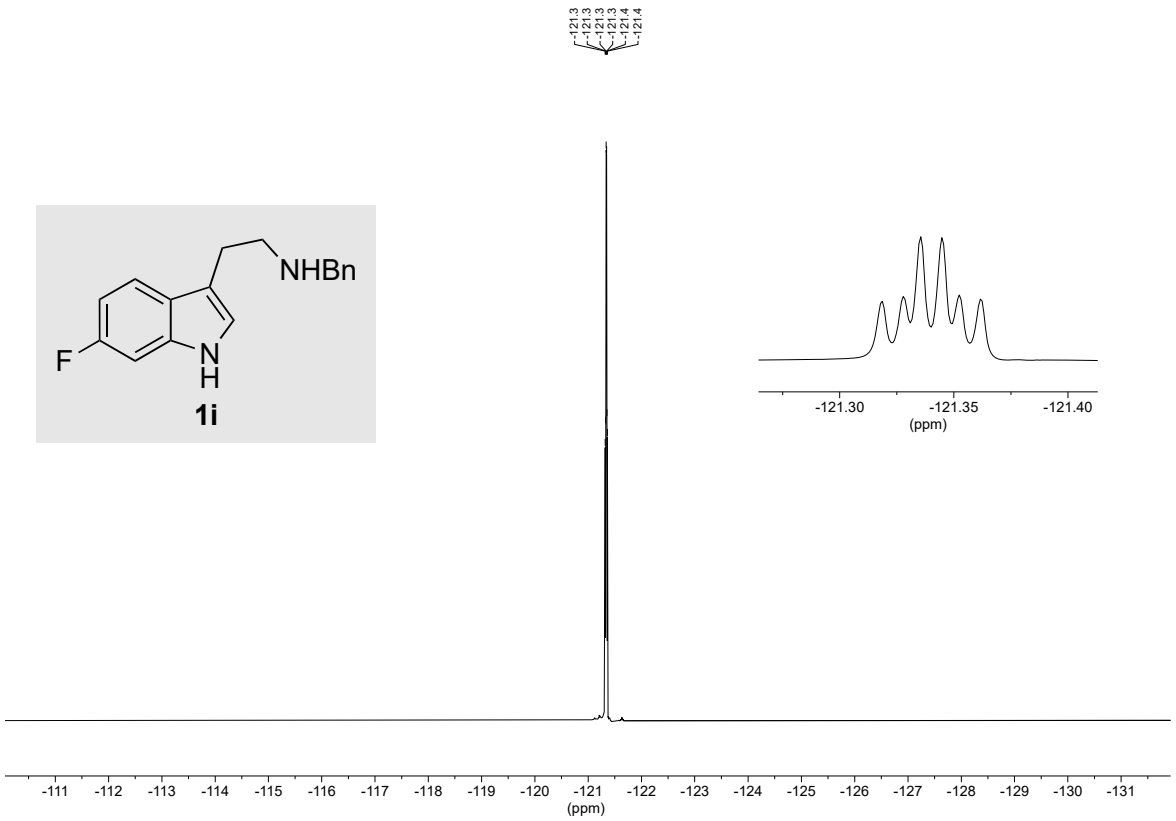


Figure S28. 565 MHz ^{19}F-NMR spectrum of compound **1i** in $CDCl_3$.

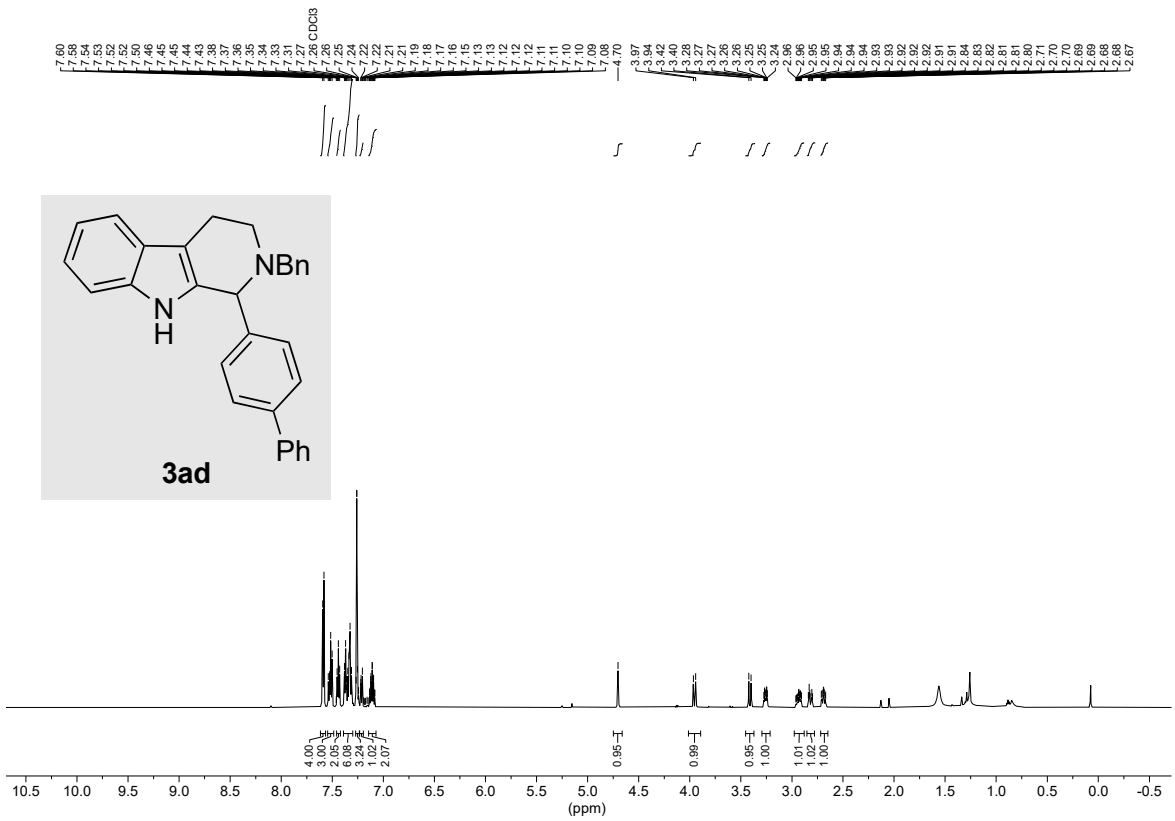


Figure S29. 600 MHz ^{1}H-NMR spectrum of compound **3ad** in $CDCl_3$.

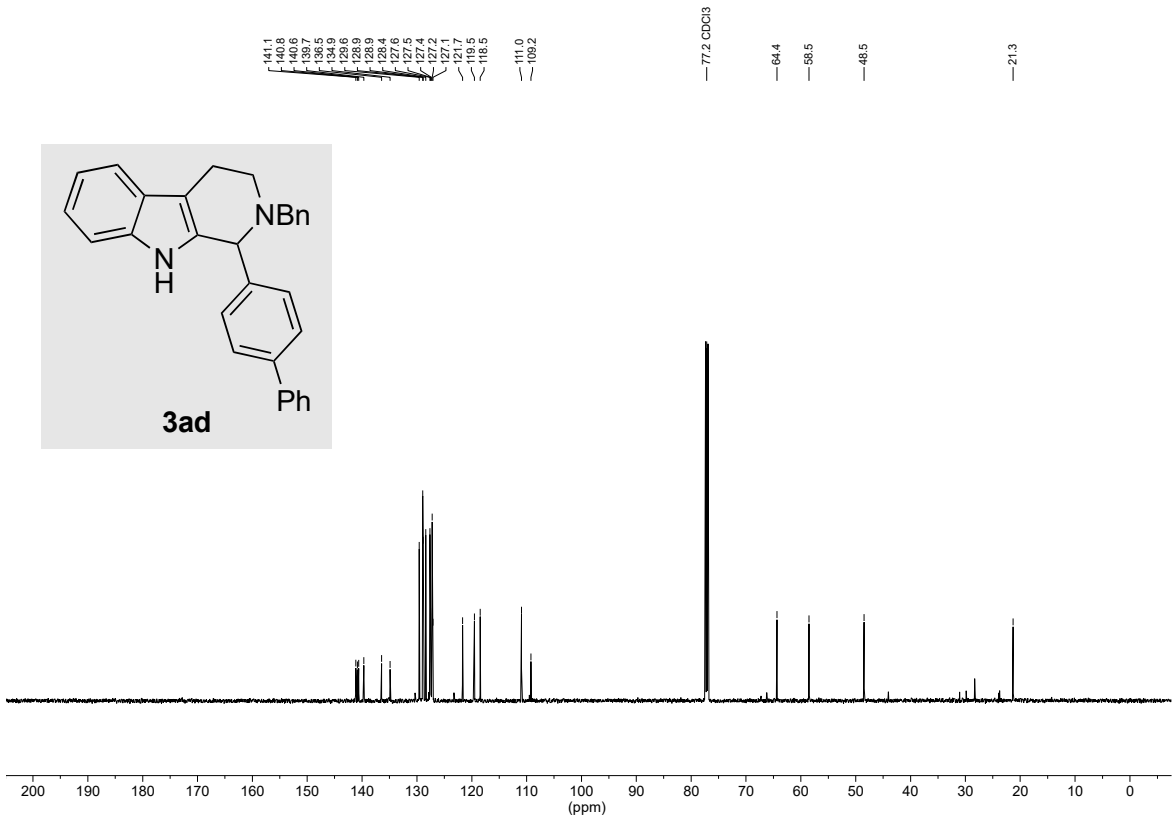


Figure S30. 150 MHz ^{13}C-NMR spectrum of compound **3ad** in $CDCl_3$.

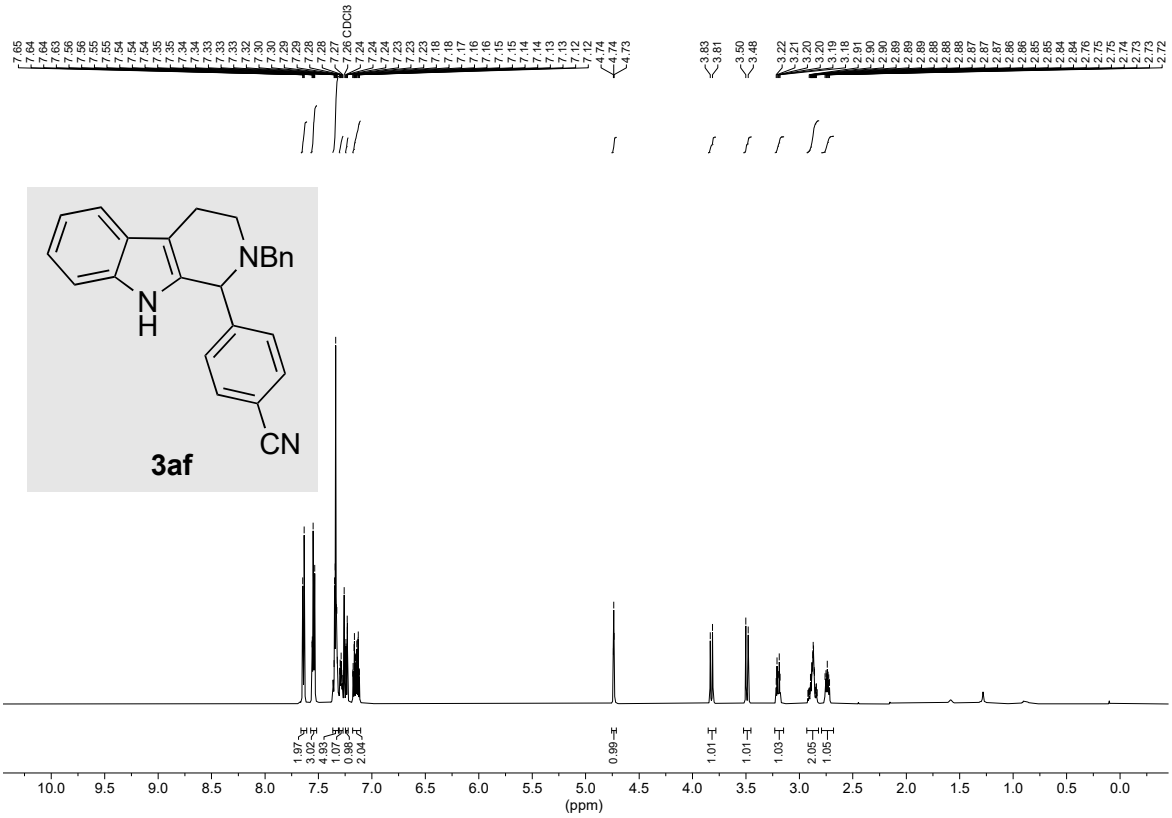


Figure S31. 600 MHz ^{1}H-NMR spectrum of compound **3af** in $CDCl_3$.

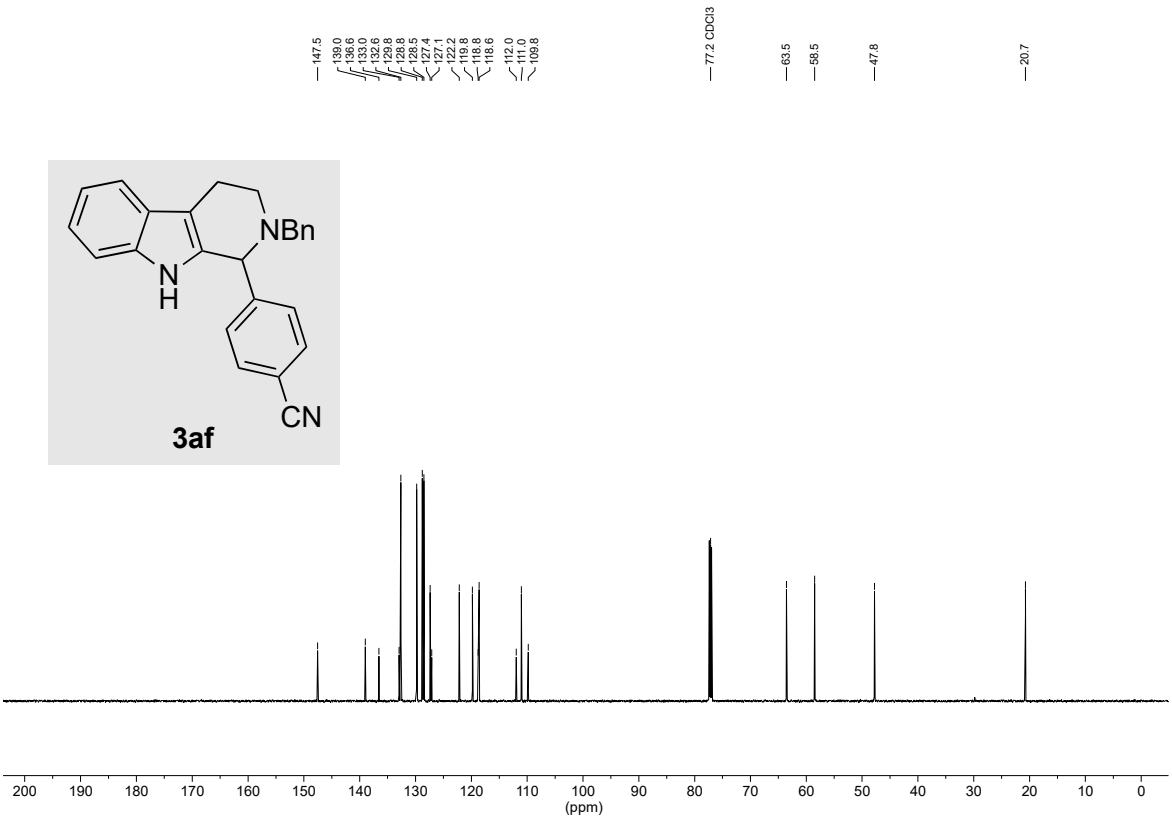


Figure S32. 150 MHz ^{13}C-NMR spectrum of compound **3af** in $CDCl_3$.

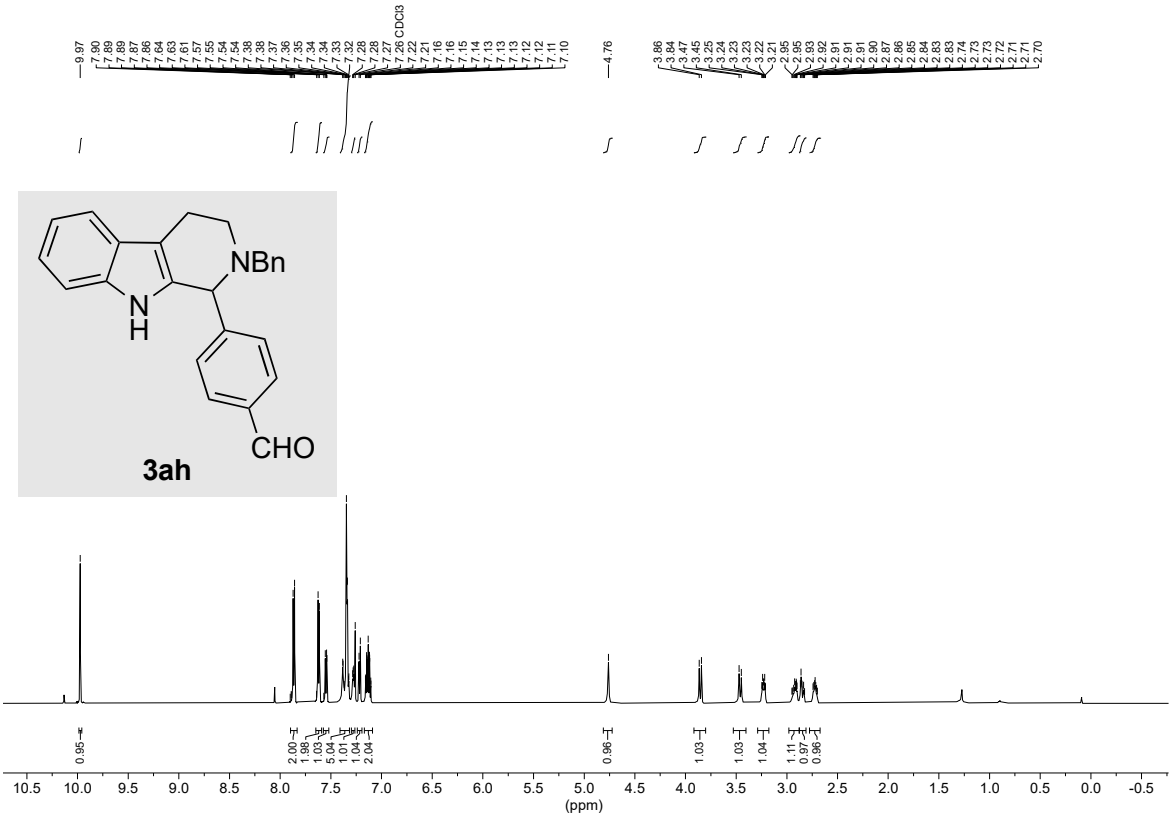


Figure S33. 600 MHz ^{1}H-NMR spectrum of compound **3ah** in $CDCl_3$.

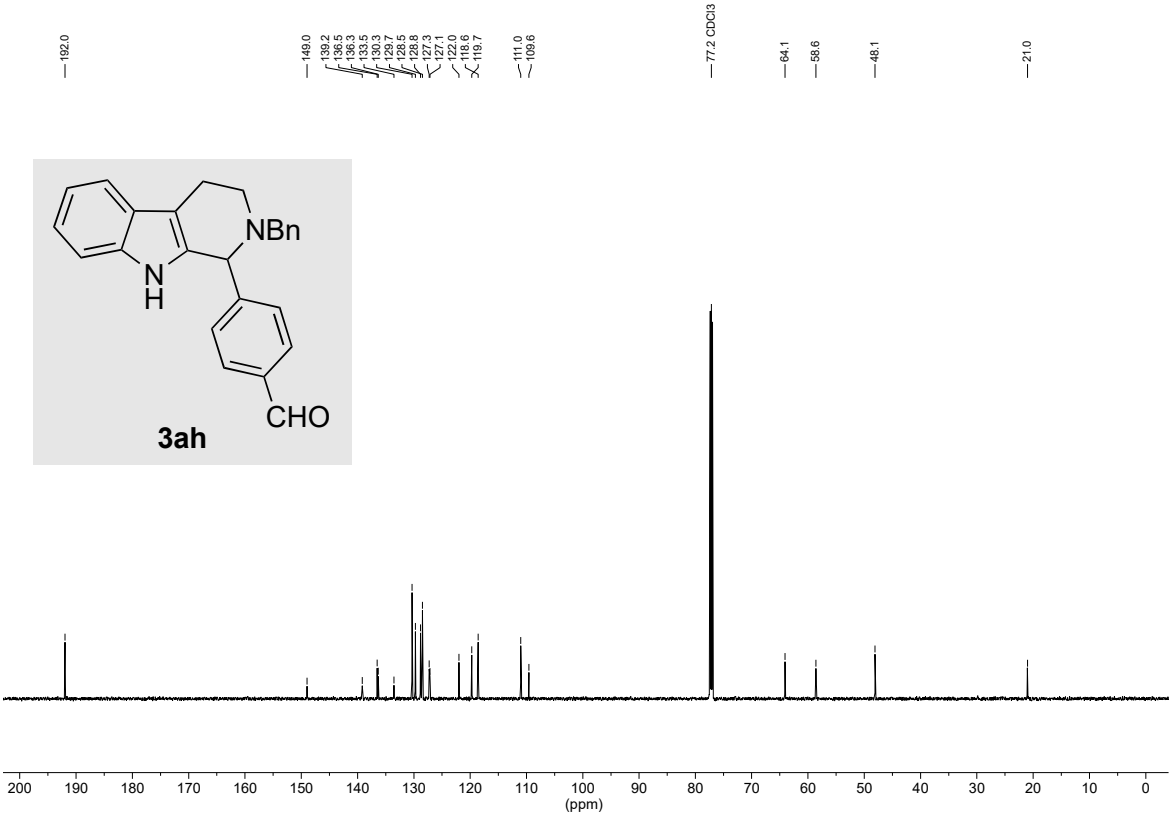


Figure S34. 150 MHz ^{13}C-NMR spectrum of compound **3ah** in $CDCl_3$.

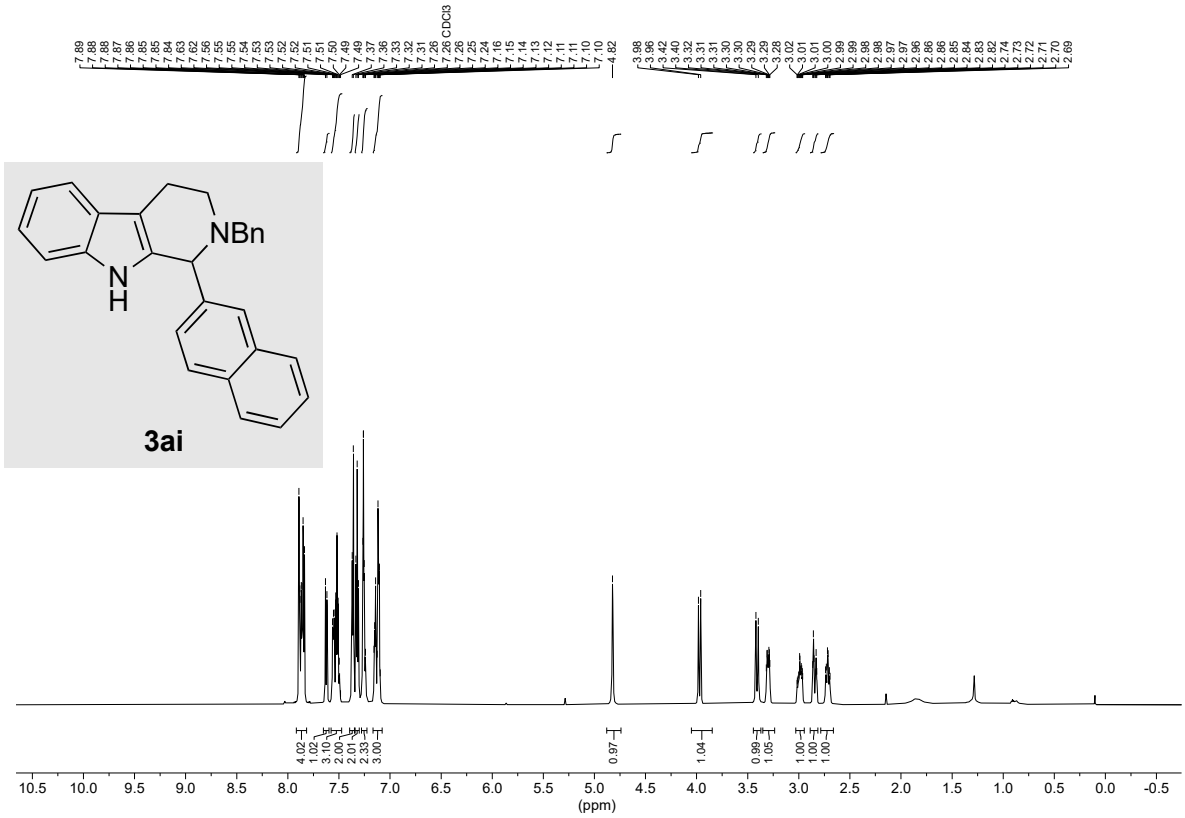


Figure S35. 600 MHz ^{1}H-NMR spectrum of compound **3ai** in $CDCl_3$.

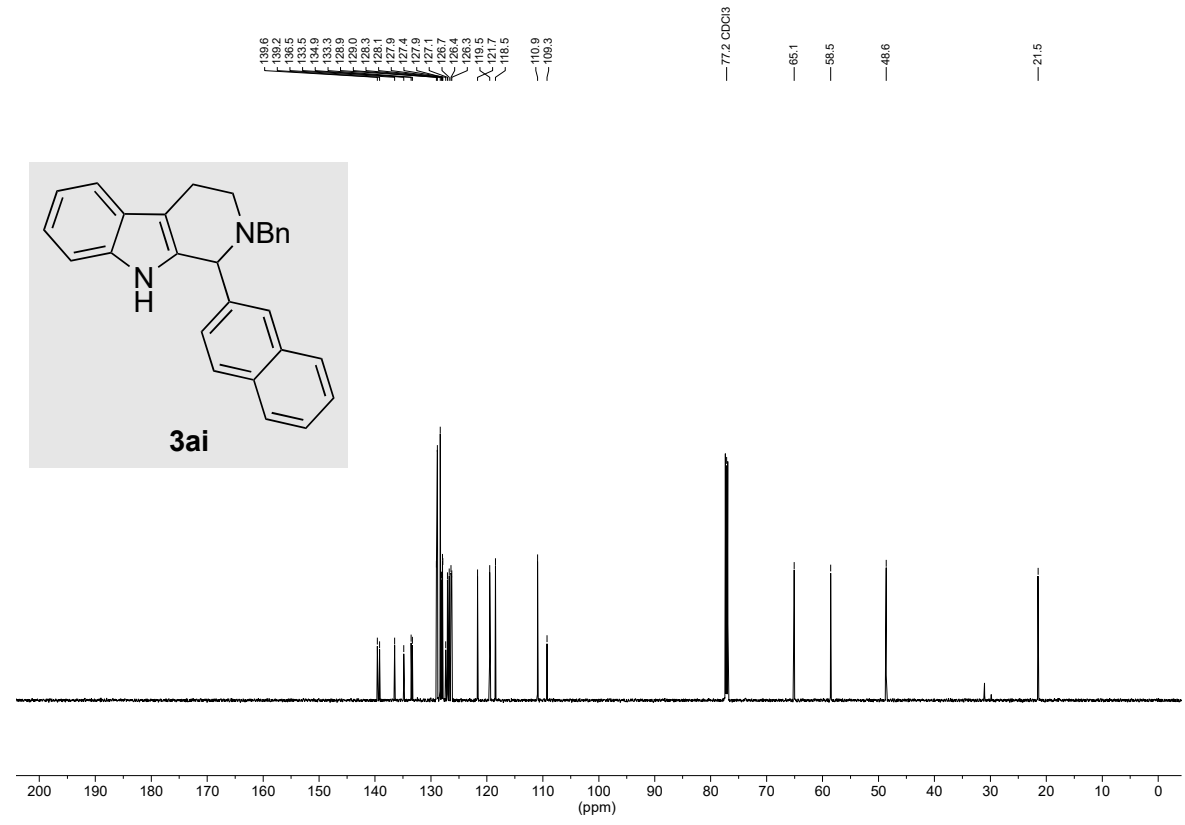


Figure S36. 150 MHz ^{13}C-NMR spectrum of compound **3ai** in $CDCl_3$.

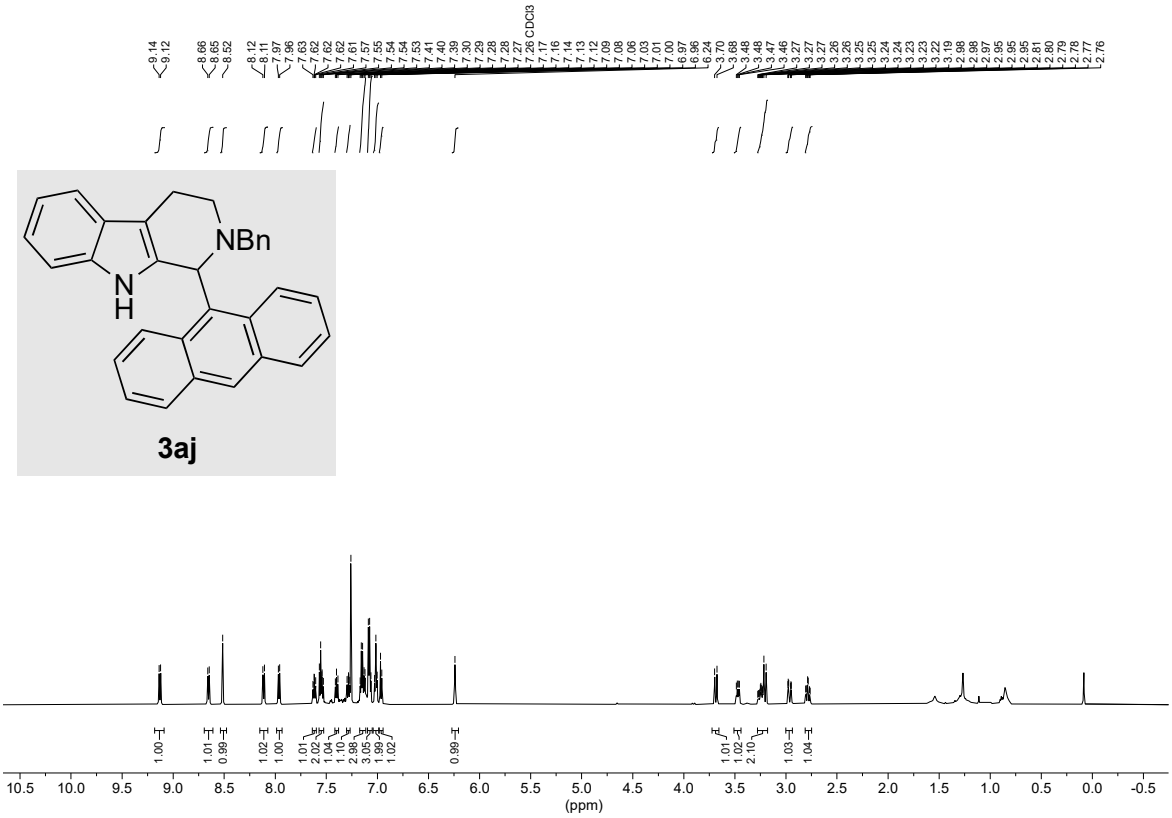


Figure S37. 600 MHz ^{1}H-NMR spectrum of compound **3aj** in $CDCl_3$.

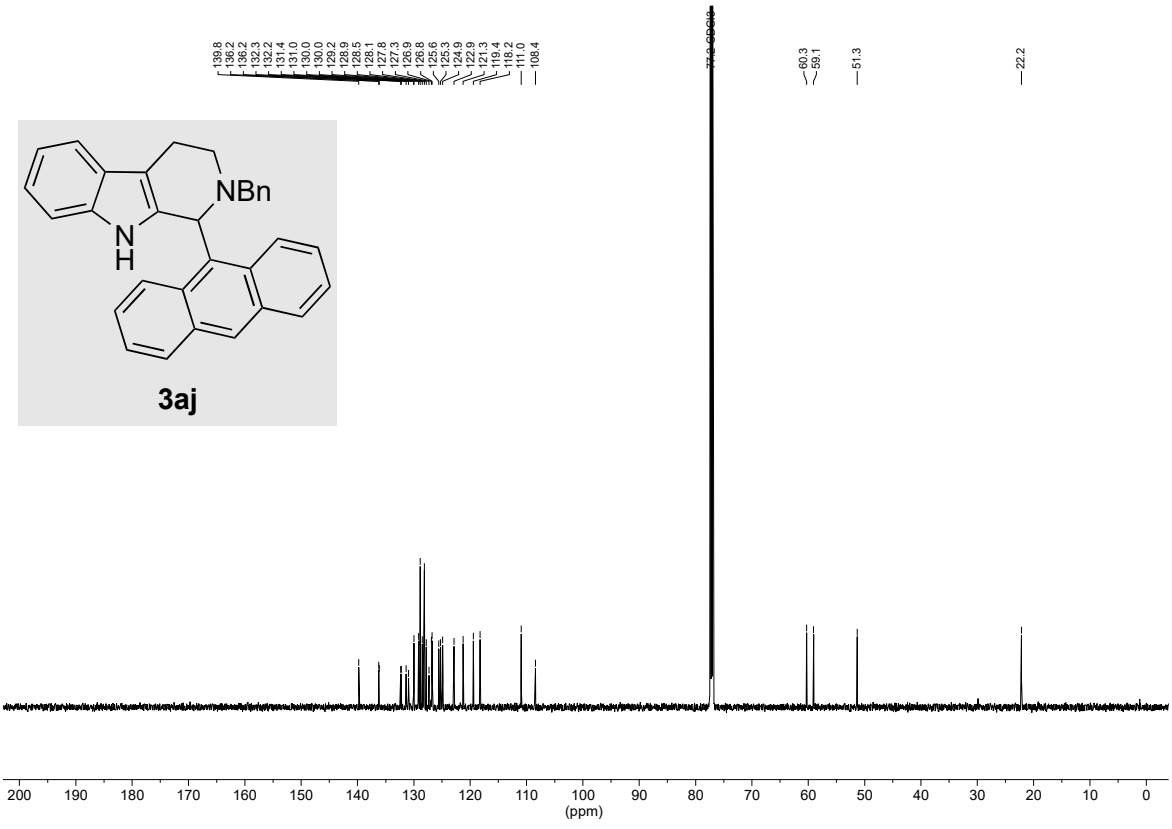


Figure S38. 150 MHz ^{13}C-NMR spectrum of compound **3aj** in $CDCl_3$.

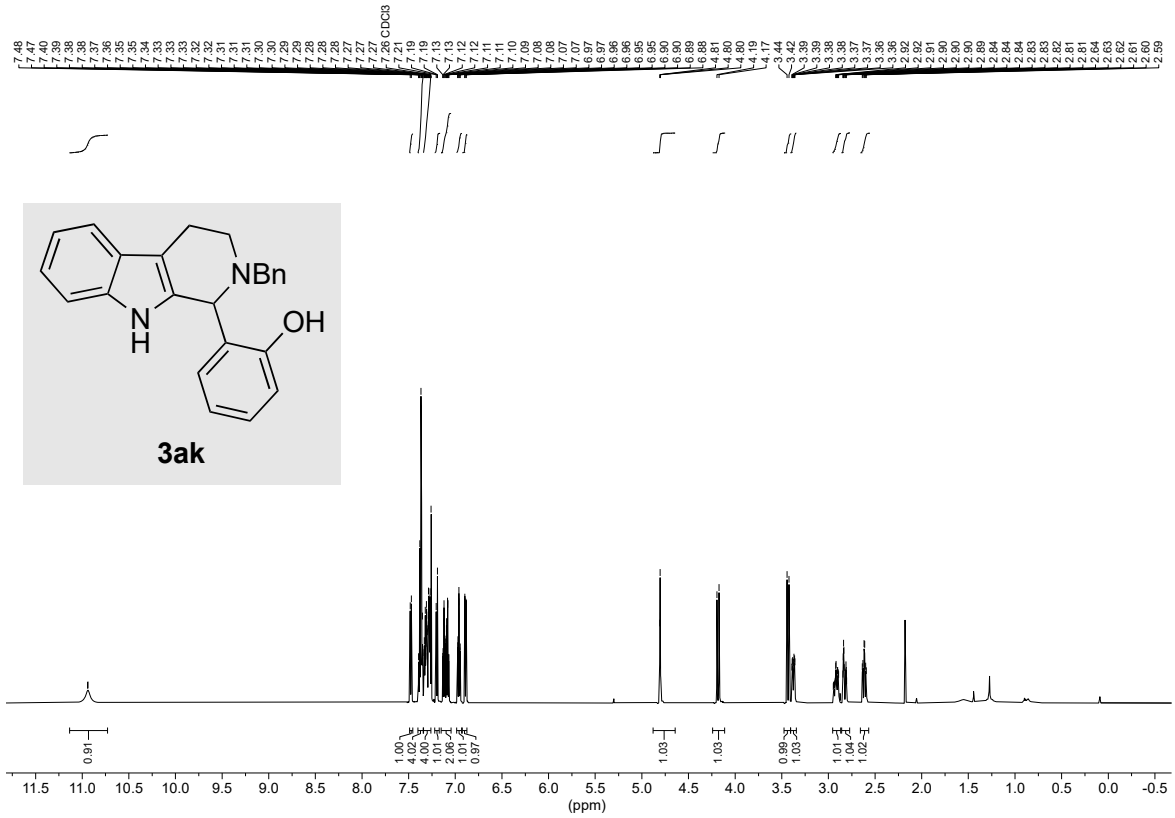


Figure S39. 600 MHz ^{1}H-NMR spectrum of compound **3ak** in $CDCl_3$.

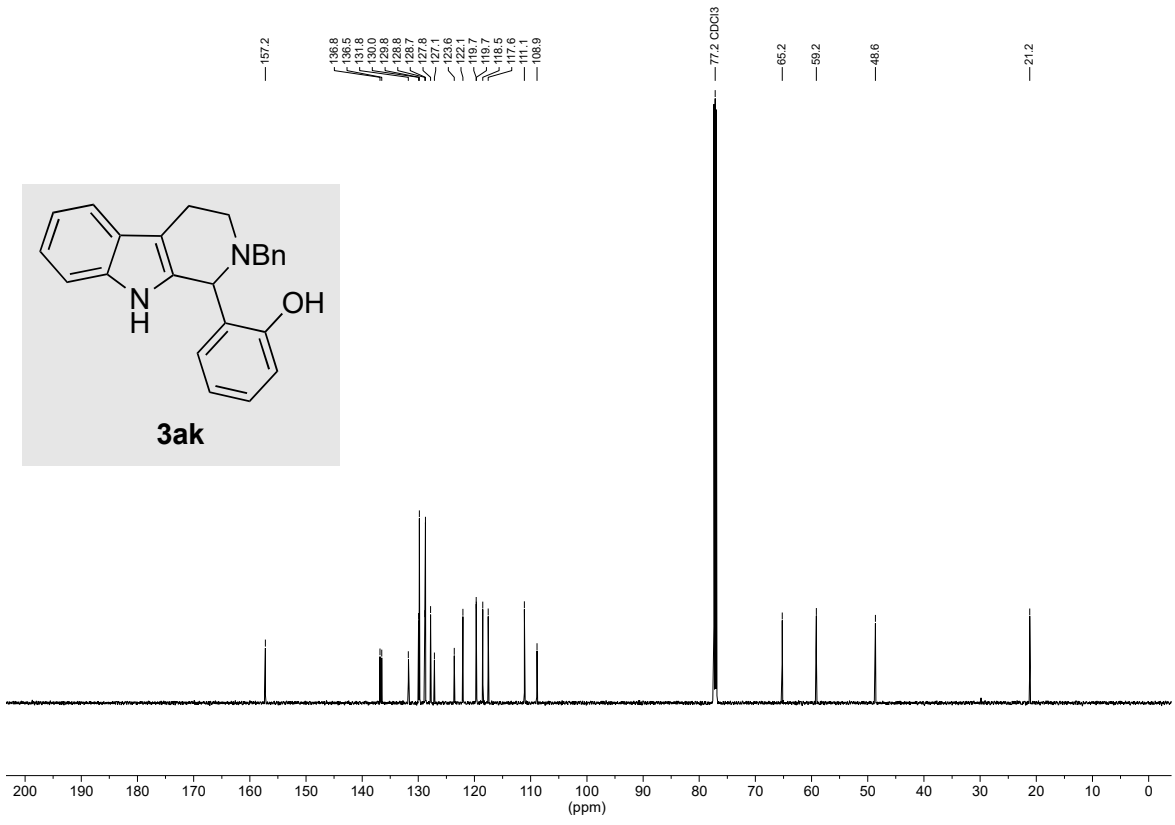


Figure S40. 150 MHz ^{13}C-NMR spectrum of compound **3ak** in $CDCl_3$.

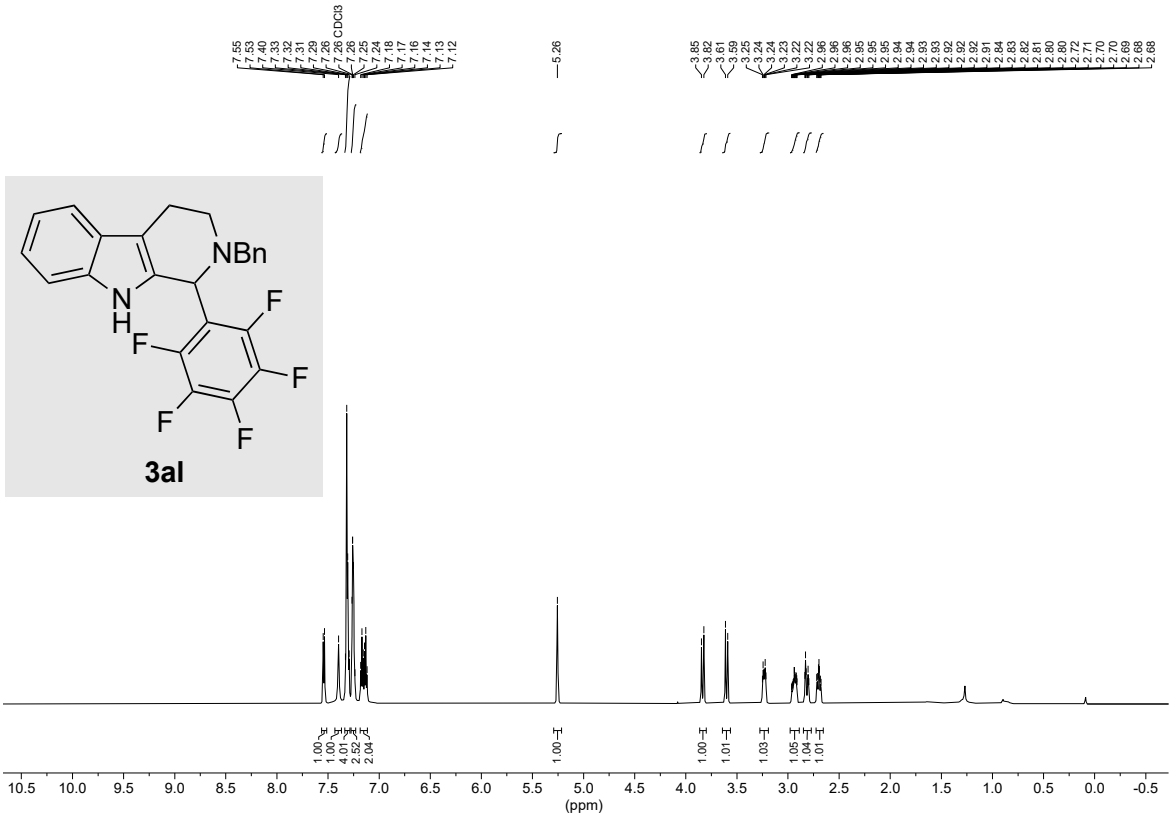


Figure S41. 600 MHz ^{1}H-NMR spectrum of compound **3aI** in $CDCl_3$.

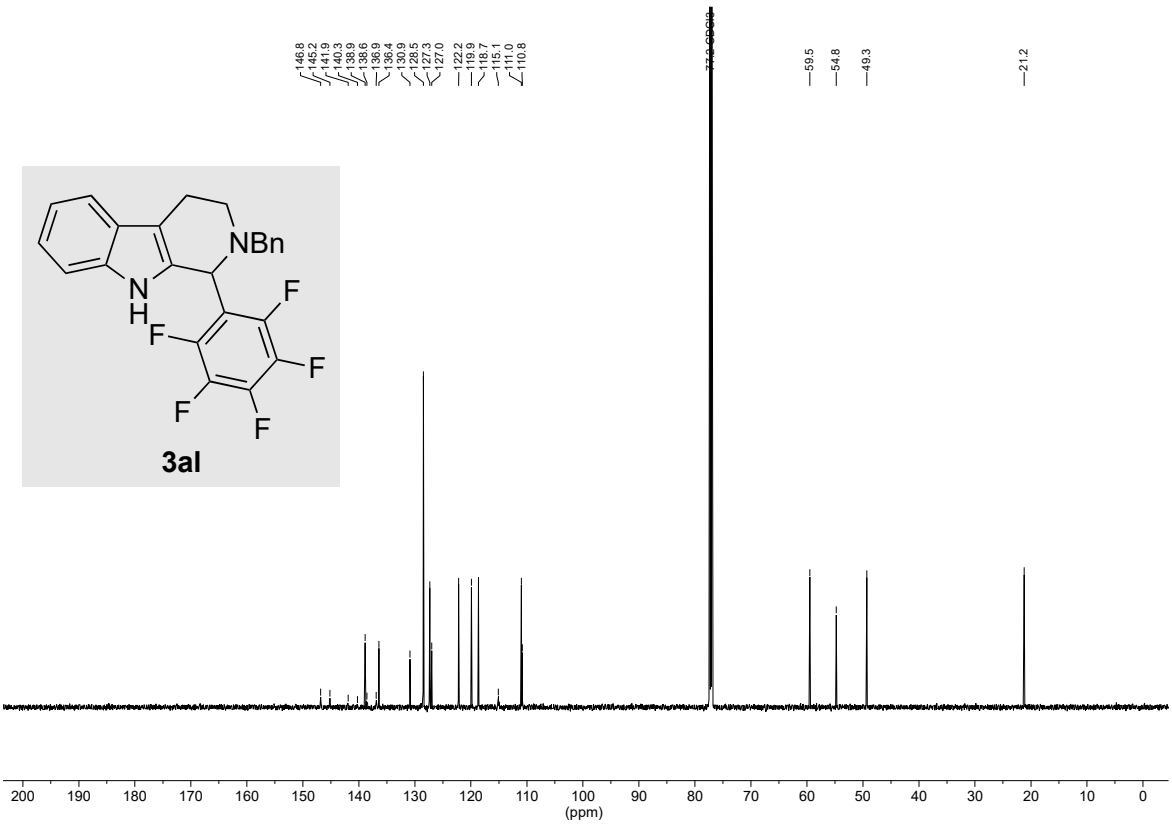


Figure S42. 150 MHz ^{13}C-NMR spectrum of compound **3aI** in $CDCl_3$.

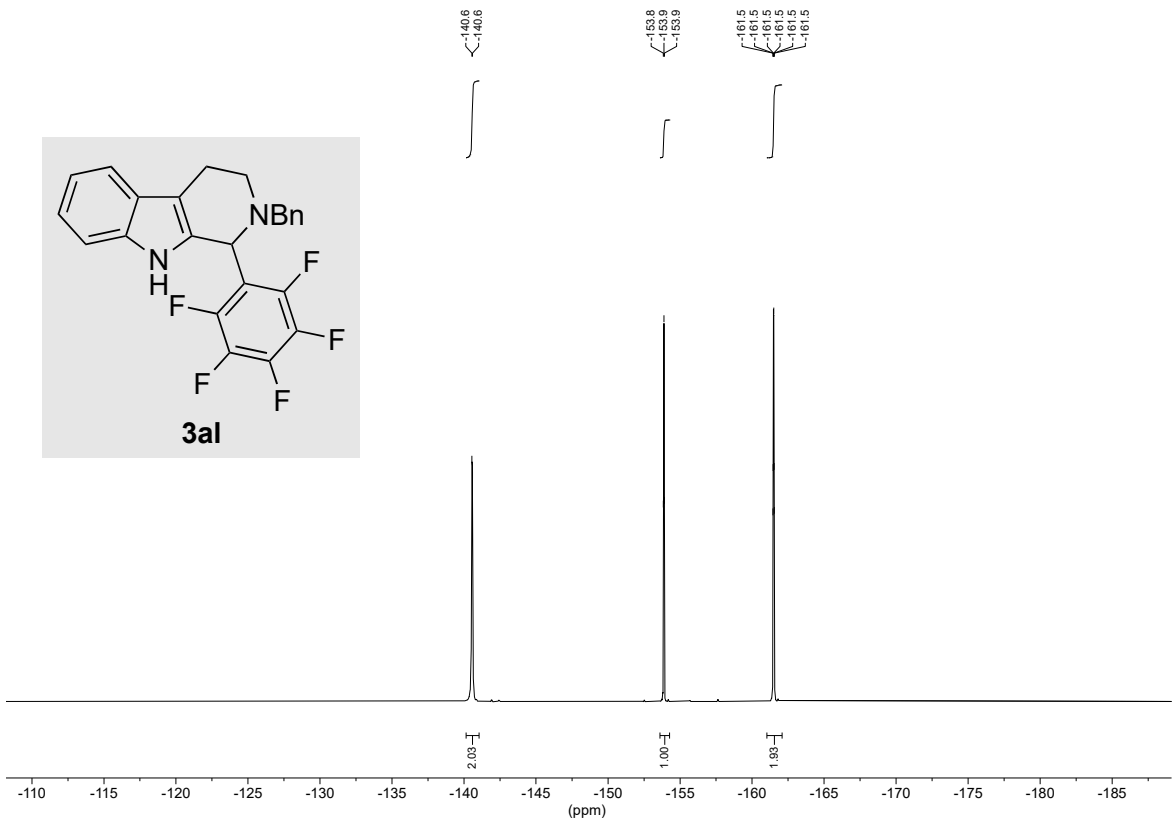


Figure S43. 565 MHz ^{1}H-NMR spectrum of compound **3al** in $CDCl_3$.

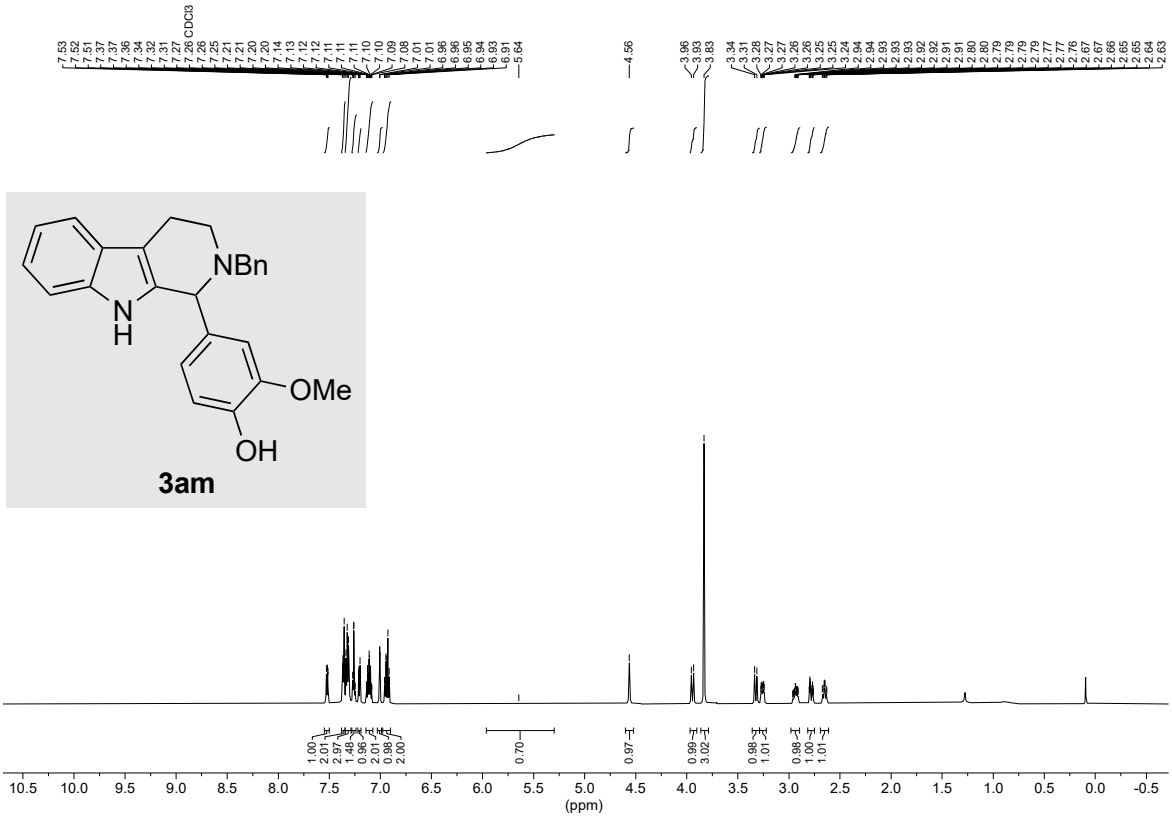


Figure S44. 600 MHz ^{1}H-NMR spectrum of compound **3am** in $CDCl_3$.

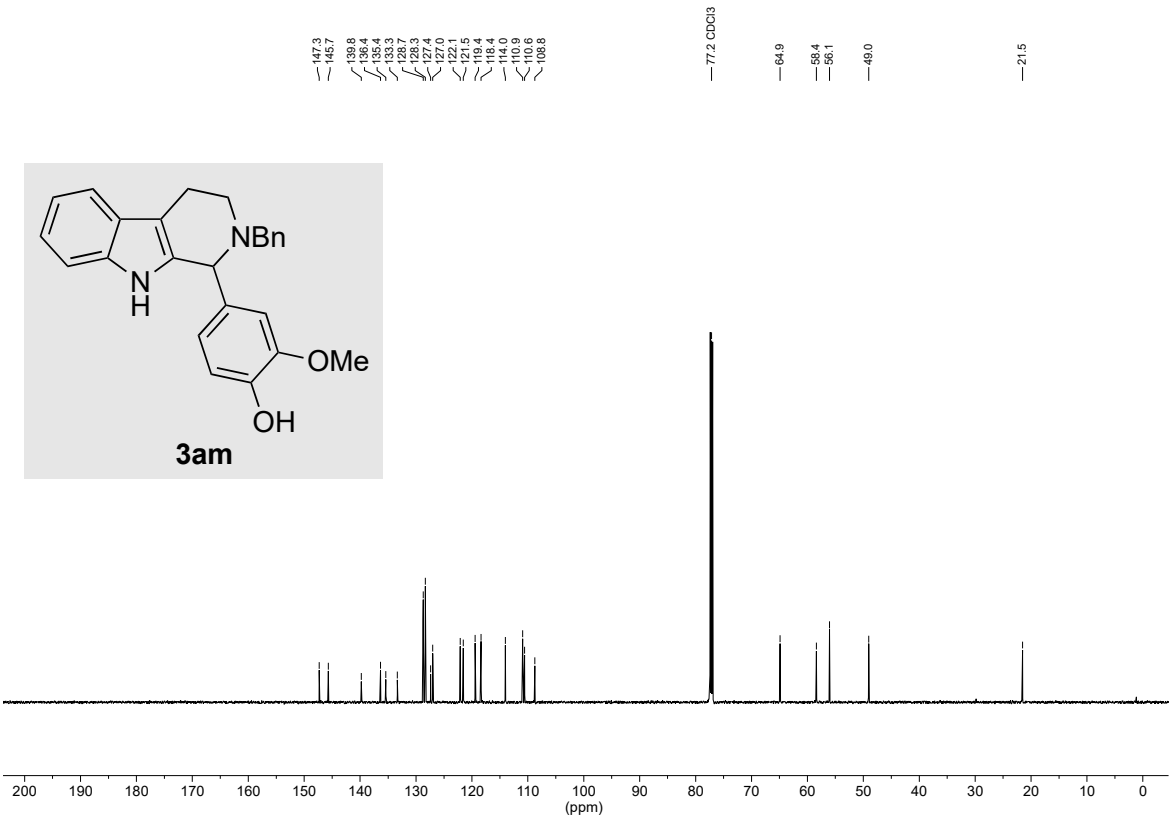


Figure S45. 150 MHz ^{13}C-NMR spectrum of compound **3am** in $CDCl_3$.

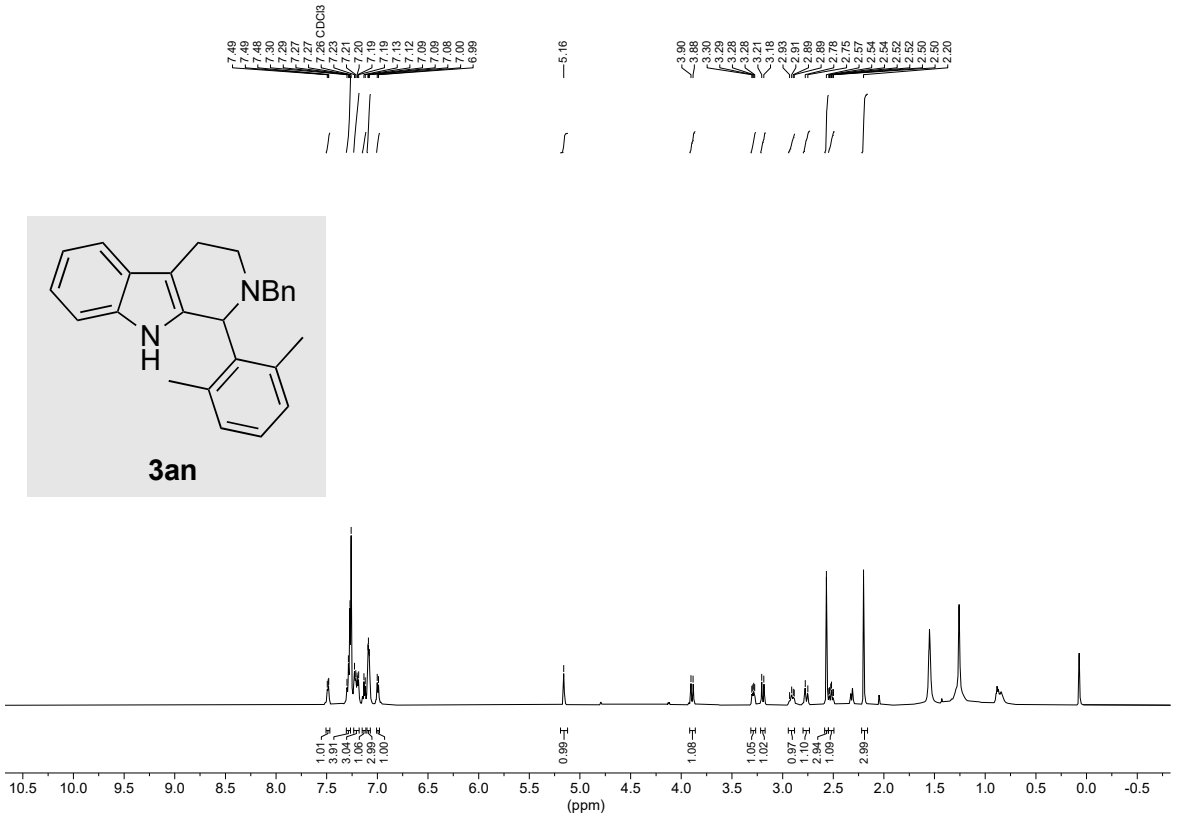


Figure S46. 600 MHz ^{1}H-NMR spectrum of compound **3an** in $CDCl_3$.

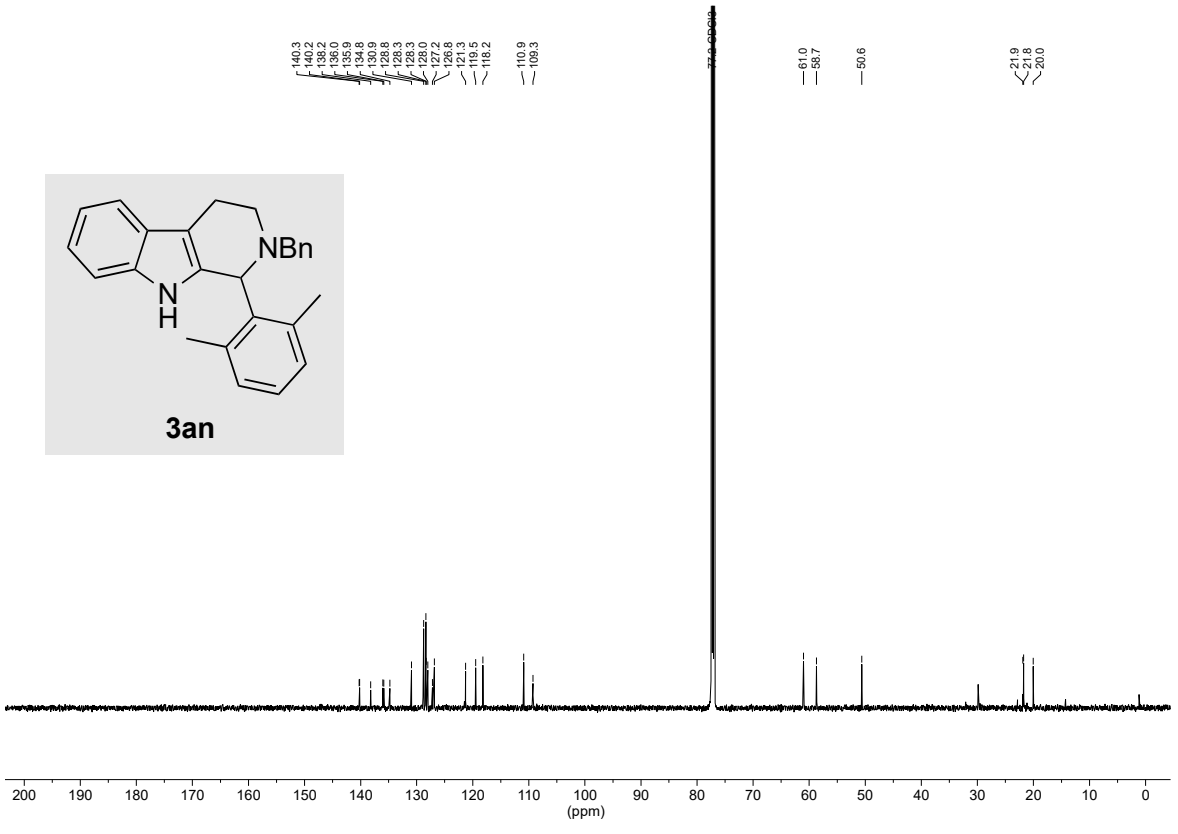


Figure S47. 150 MHz ^{13}C-NMR spectrum of compound **3an** in $CDCl_3$.

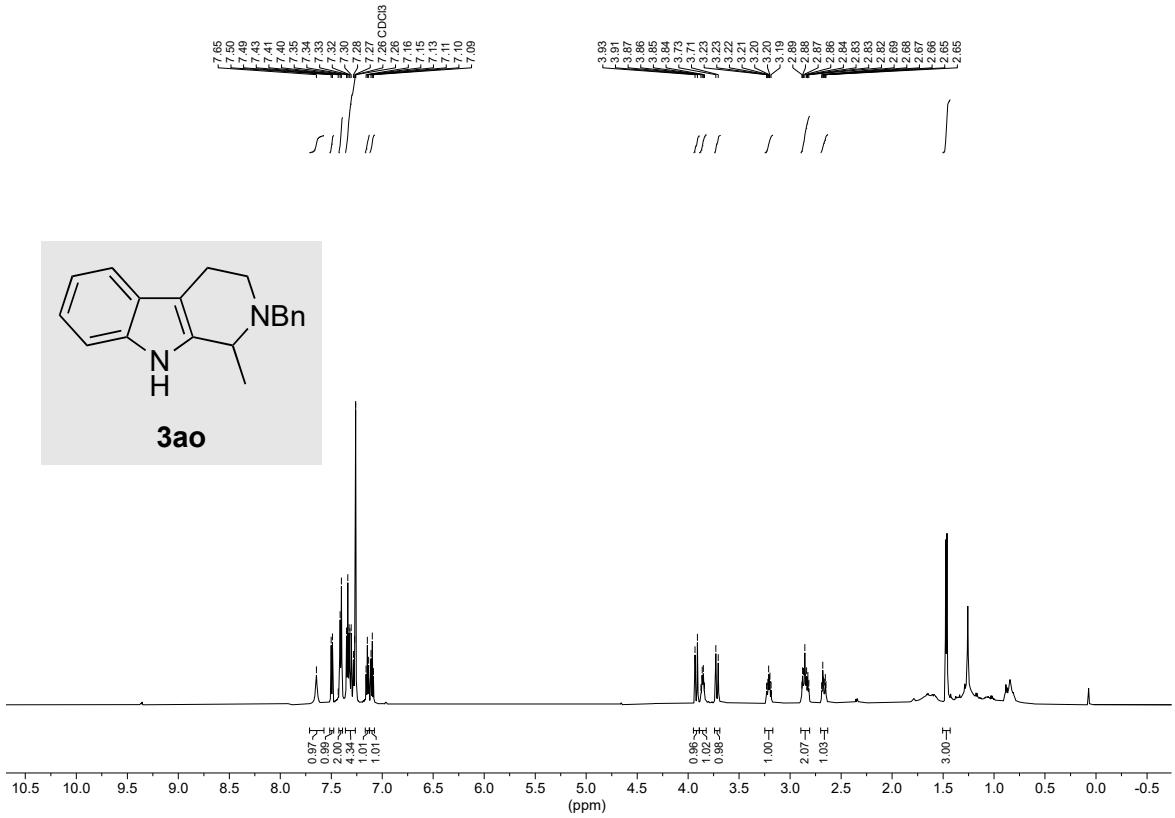


Figure S48. 600 MHz ^{1}H-NMR spectrum of compound **3ao** in $CDCl_3$.

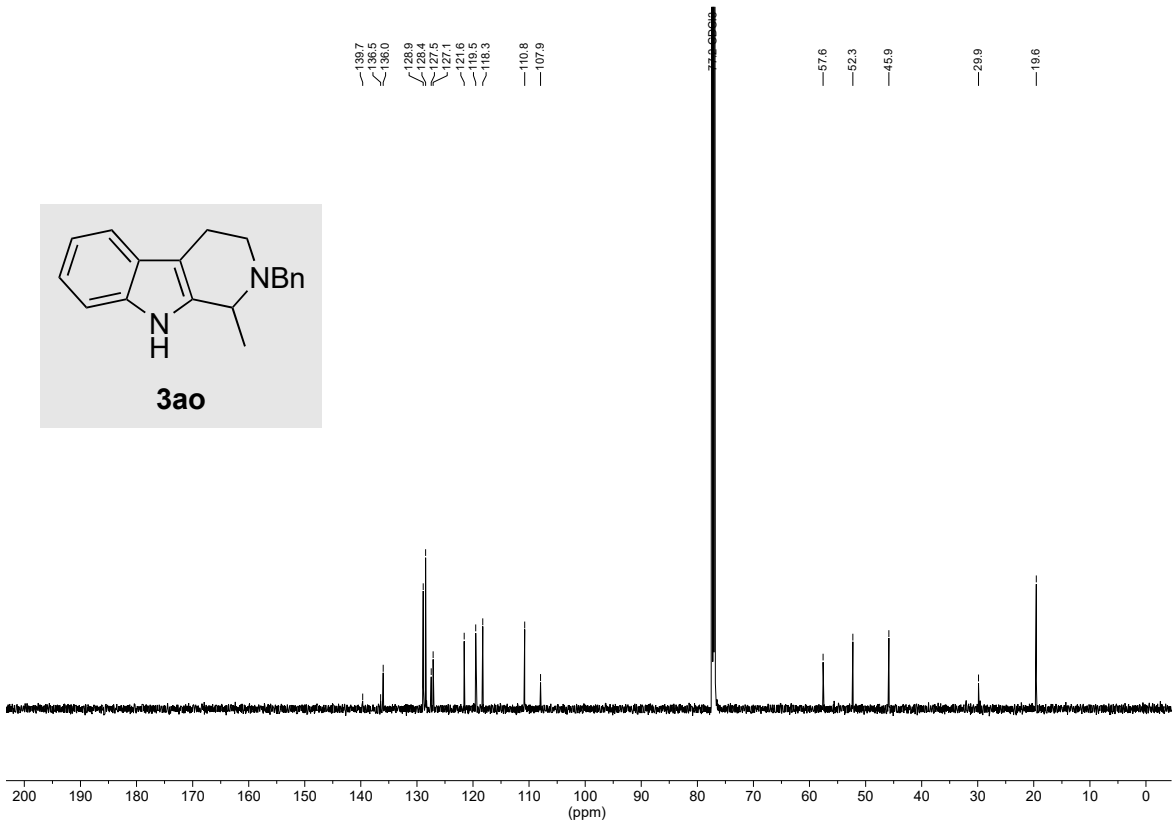


Figure S49. 150 MHz ^{13}C-NMR spectrum of compound **3ao** in $CDCl_3$.

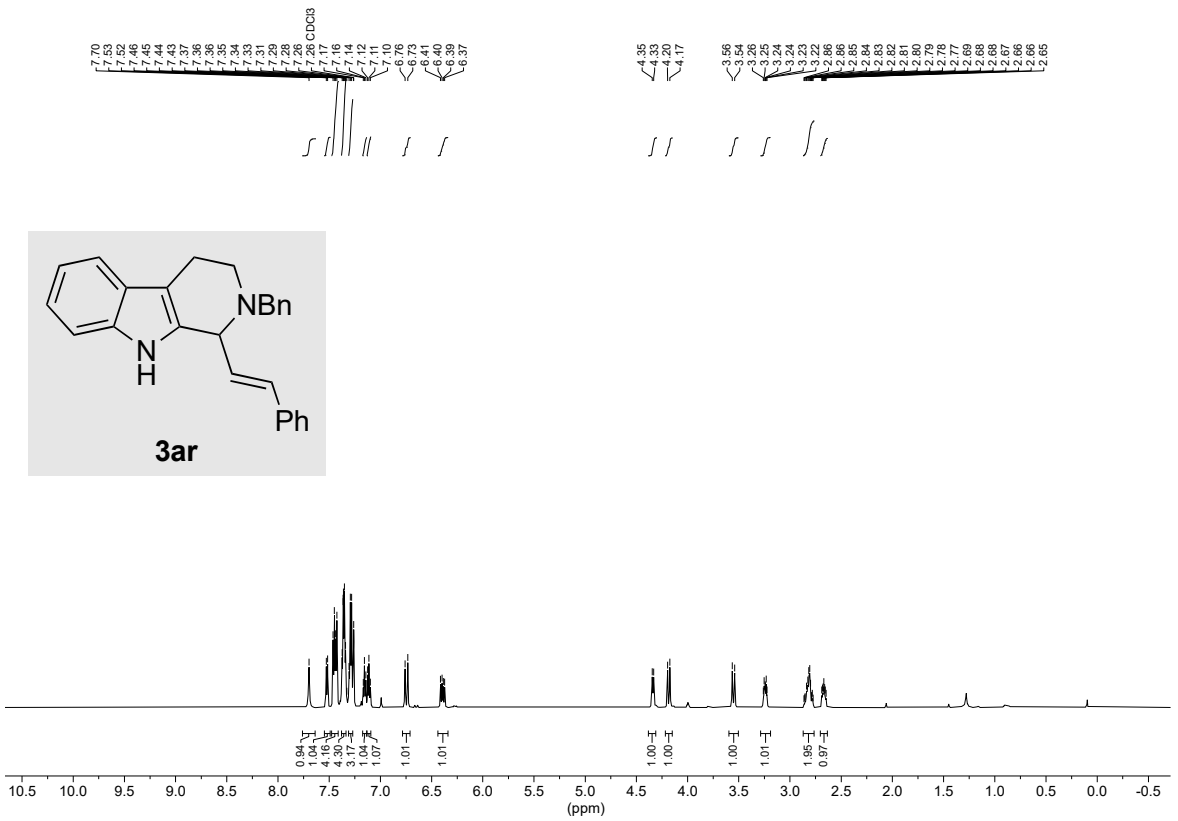


Figure S50. 600 MHz ^{1}H-NMR spectrum of compound **3ar** in $CDCl_3$.

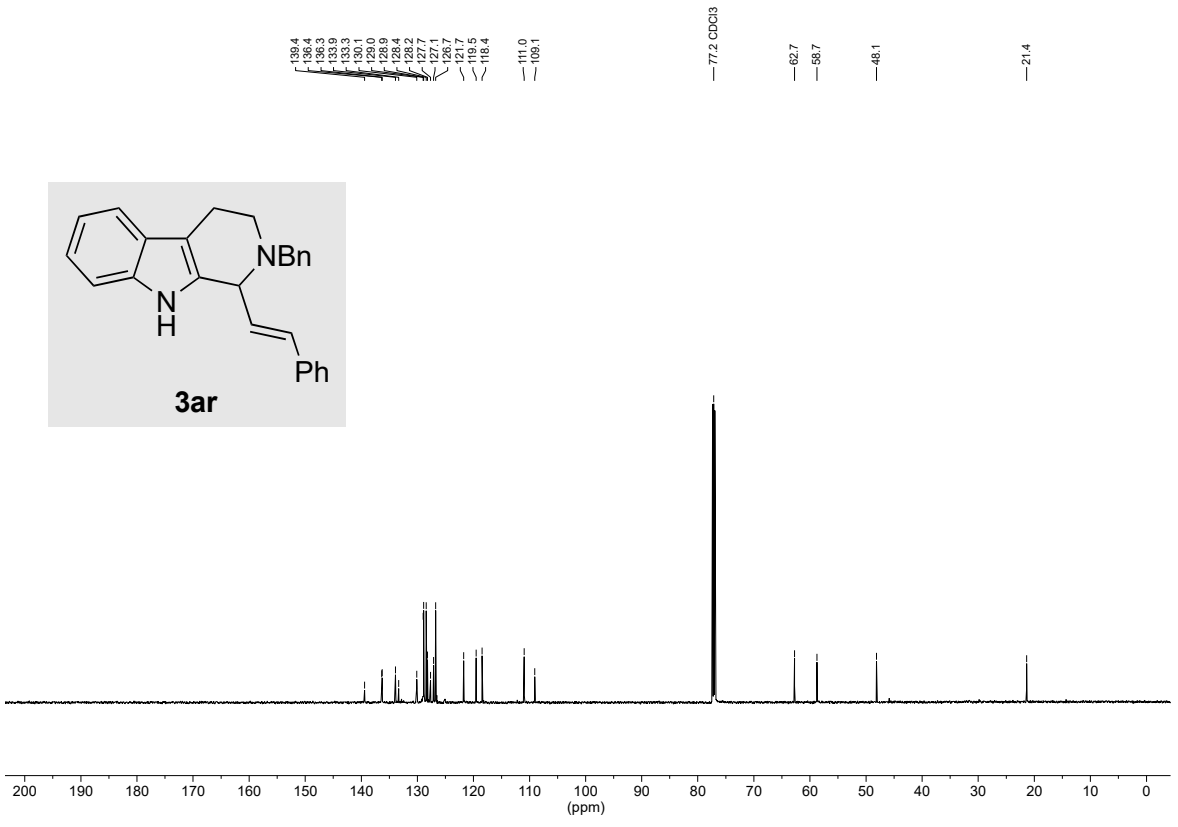


Figure S51. 150 MHz ^{13}C-NMR spectrum of compound **3ar** in $CDCl_3$.

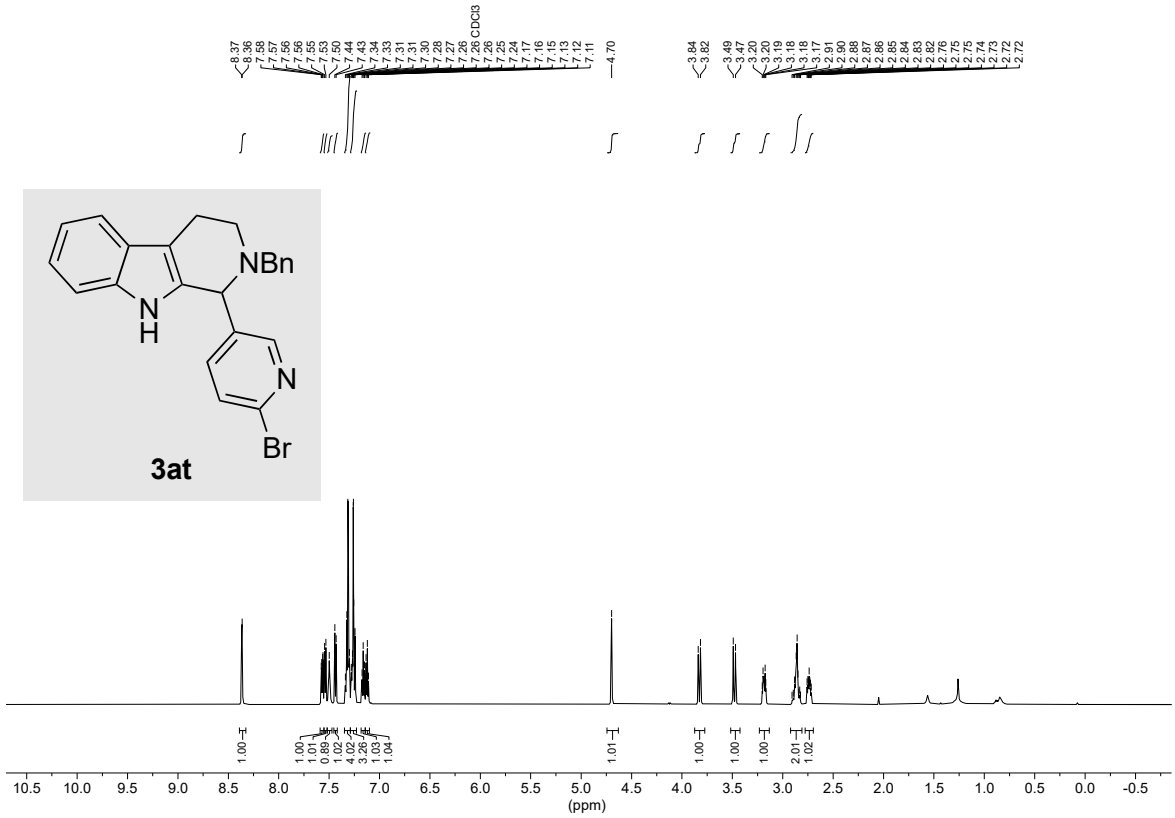


Figure S52. 600 MHz ^{1}H-NMR spectrum of compound **3at** in $CDCl_3$.

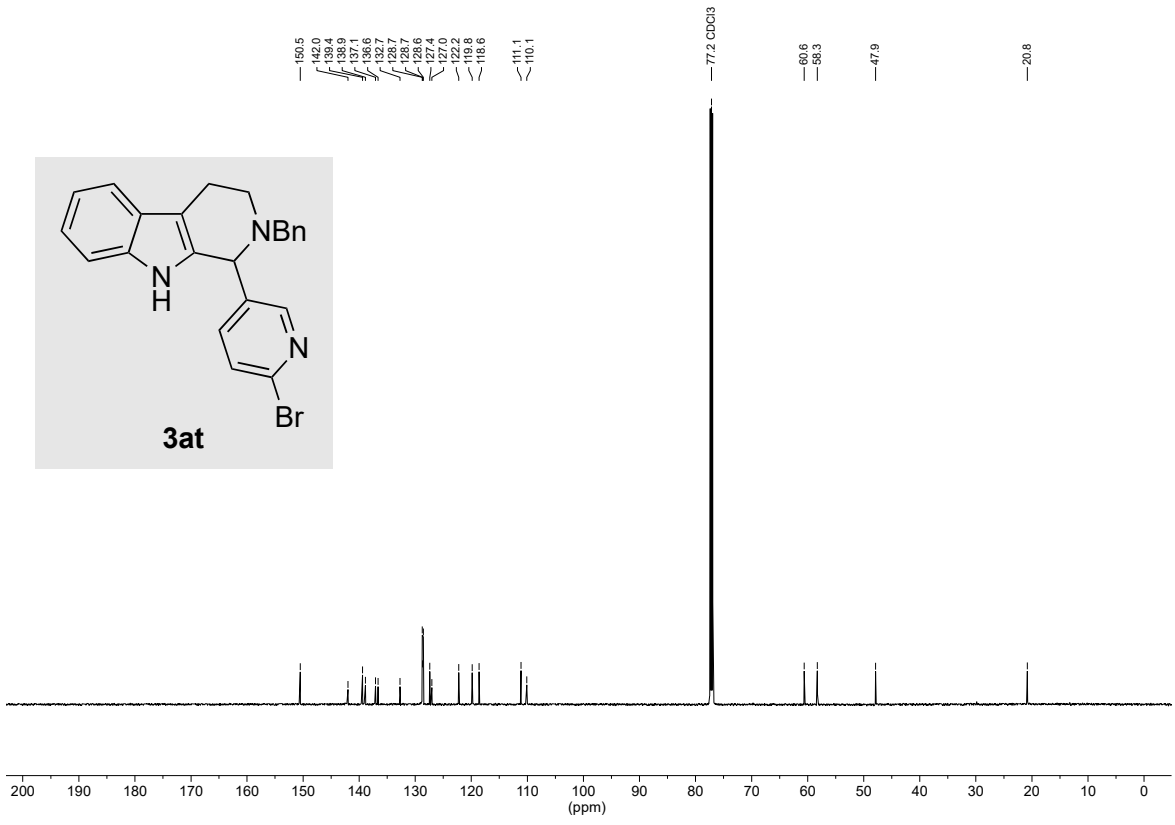


Figure S53. 150 MHz ^{13}C-NMR spectrum of compound **3at** in $CDCl_3$.

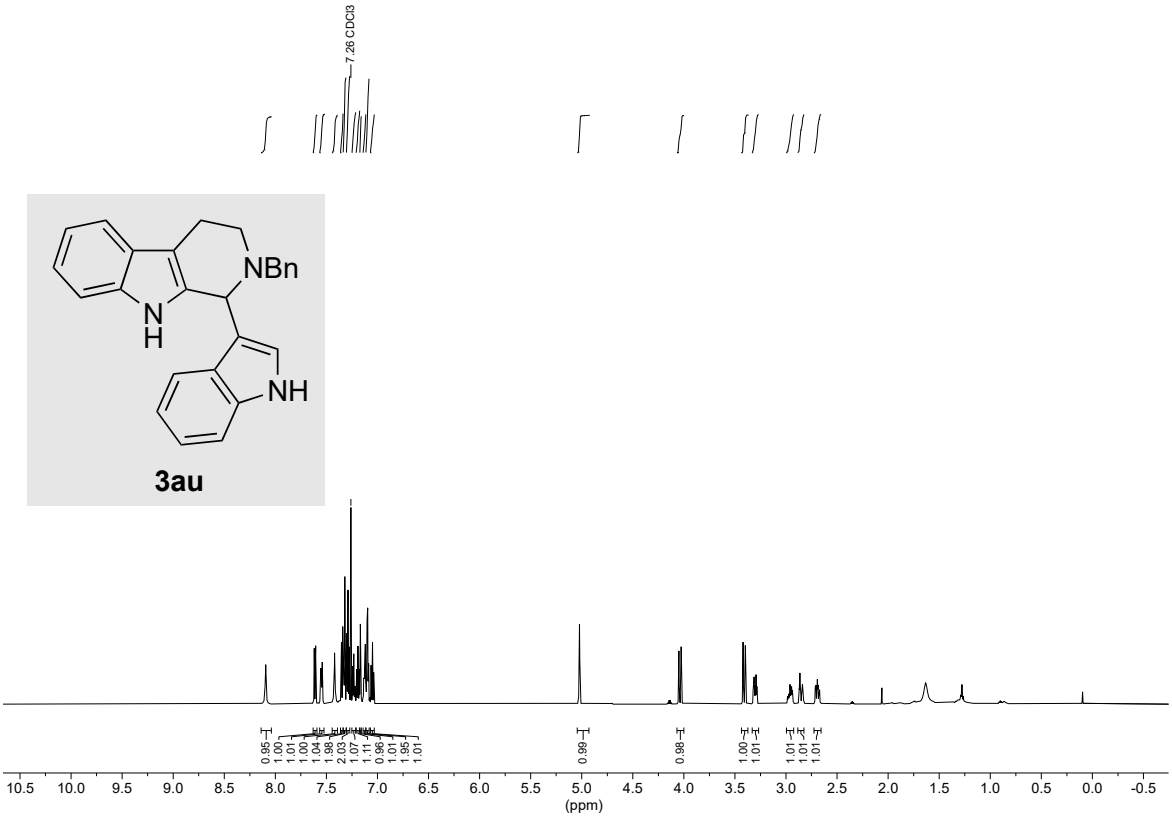


Figure S54. 600 MHz ^{1}H-NMR spectrum of compound **3au** in $CDCl_3$.

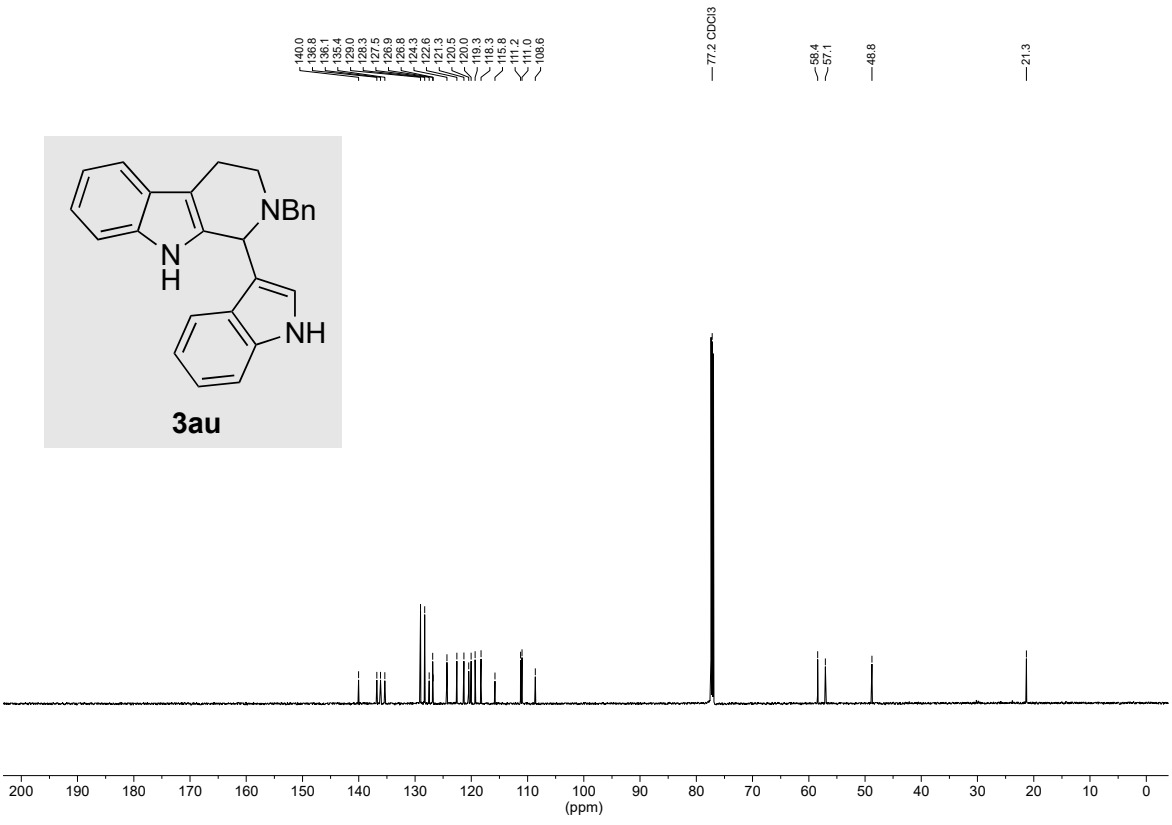


Figure S55. 150 MHz ^{13}C-NMR spectrum of compound **3au** in $CDCl_3$.

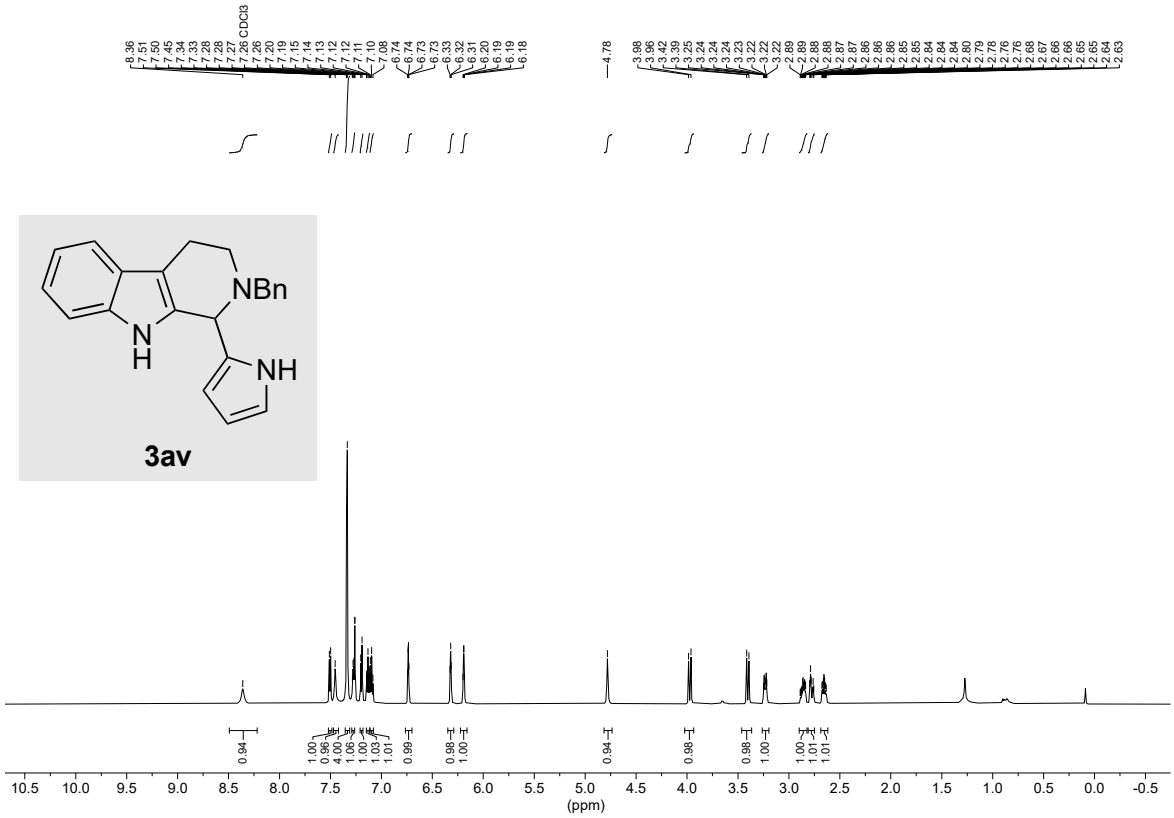


Figure S56. 600 MHz ^{1}H-NMR spectrum of compound **3av** in $CDCl_3$.

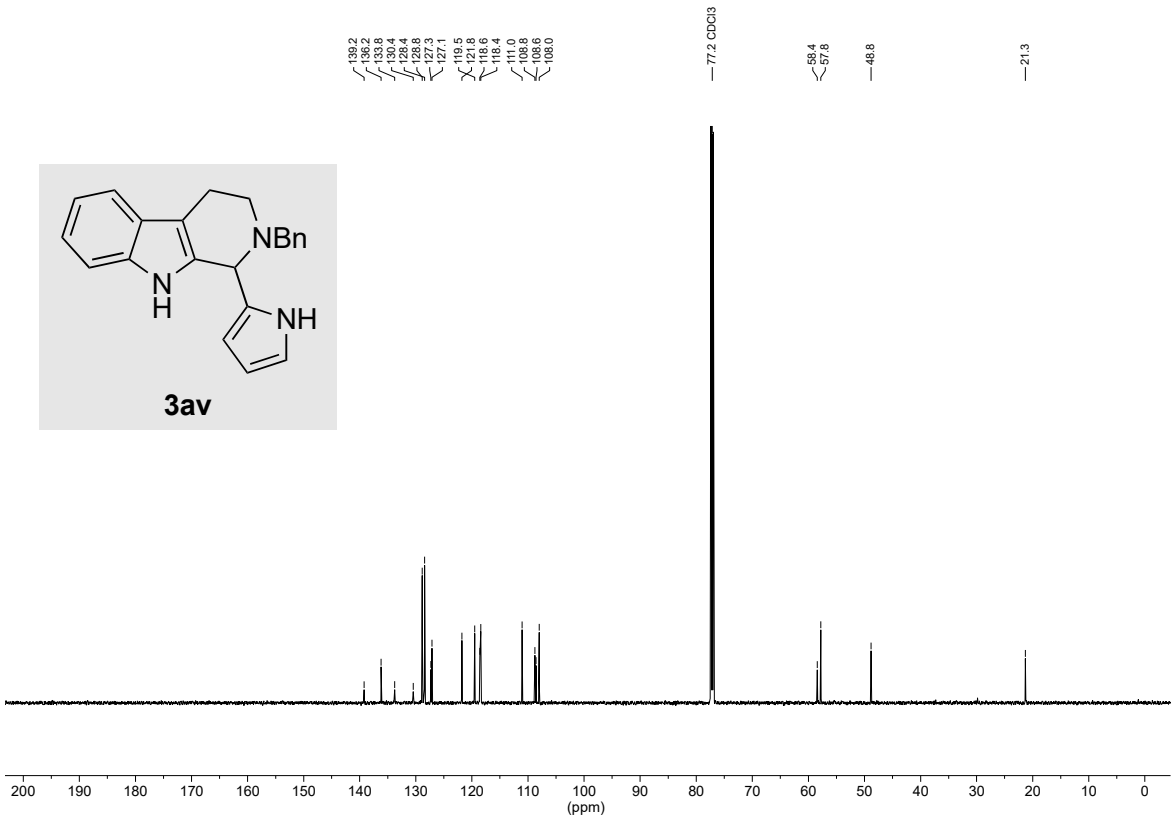


Figure S57. 150 MHz ^{13}C-NMR spectrum of compound **3av** in $CDCl_3$.

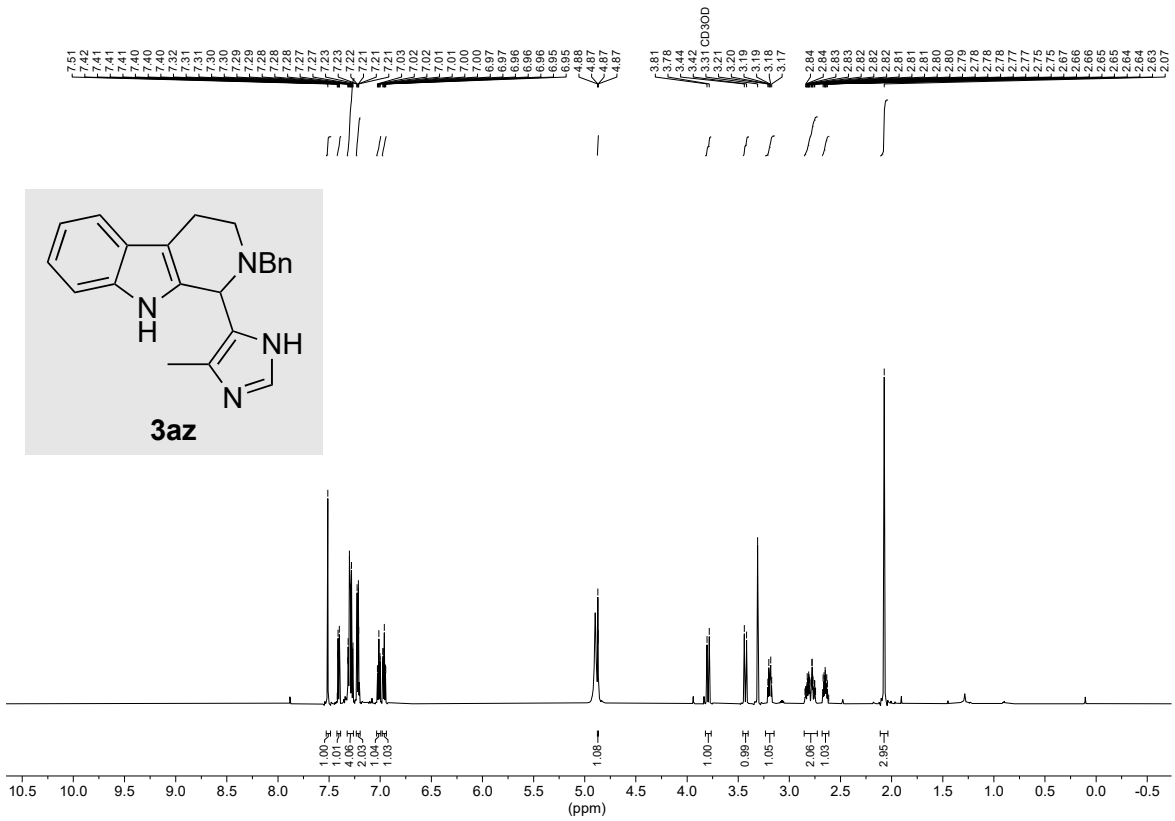


Figure S58. 600 MHz ^{1}H-NMR spectrum of compound **3az** in MeOD-d_4.

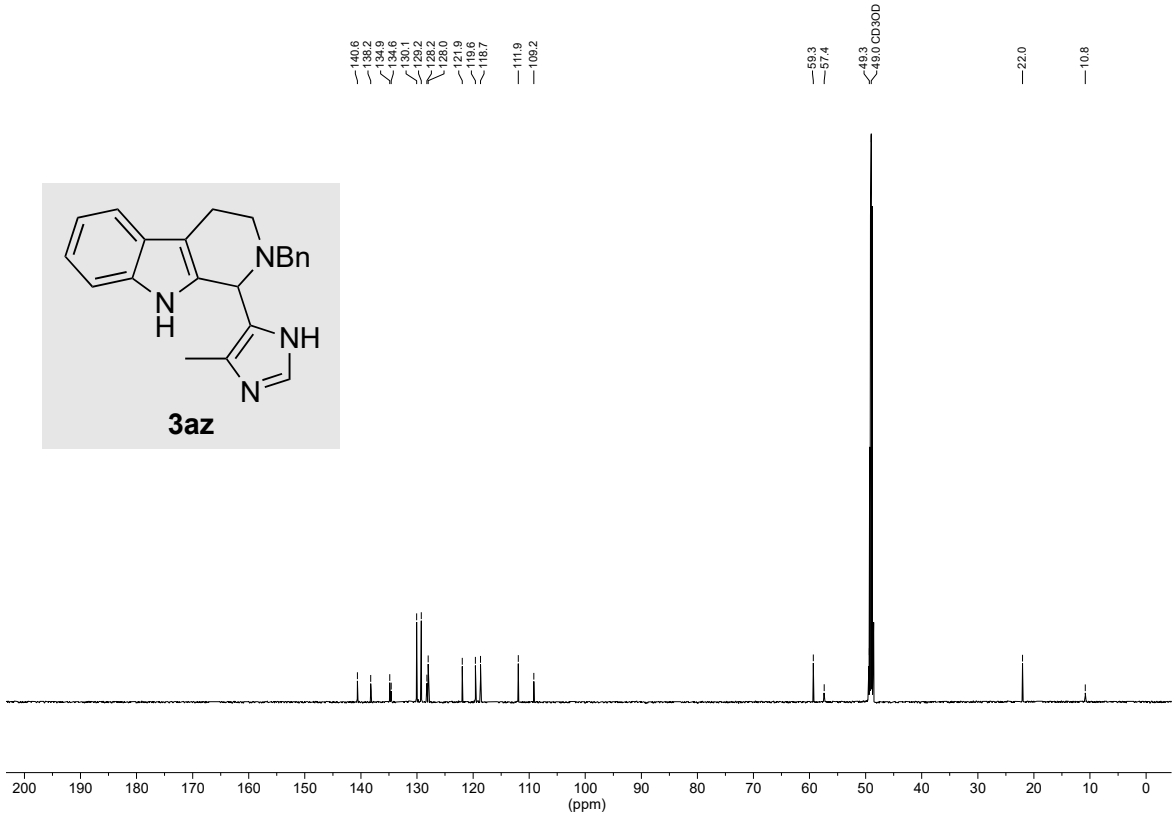


Figure S59. 150 MHz ^{13}C-NMR spectrum of compound **3az** in MeOD-d_4.

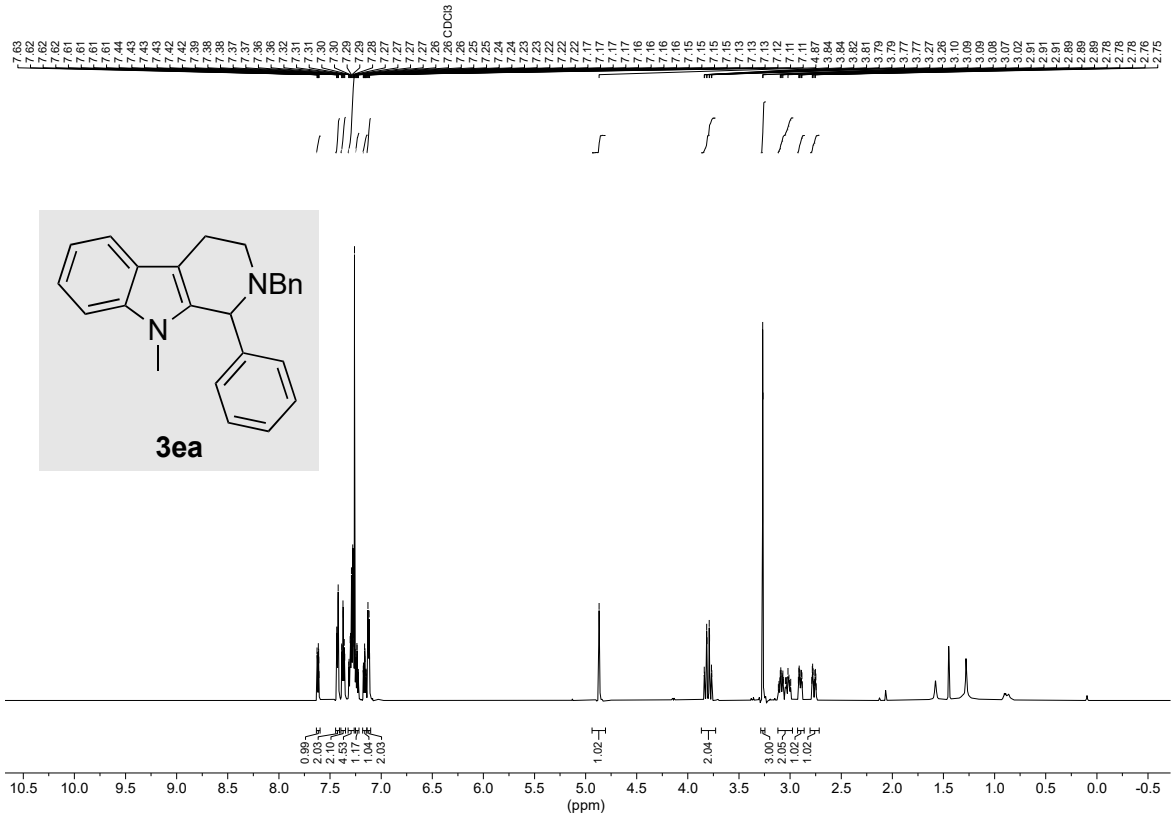


Figure S60. 600 MHz ^{1}H-NMR spectrum of compound **3ea** in $CDCl_3$.

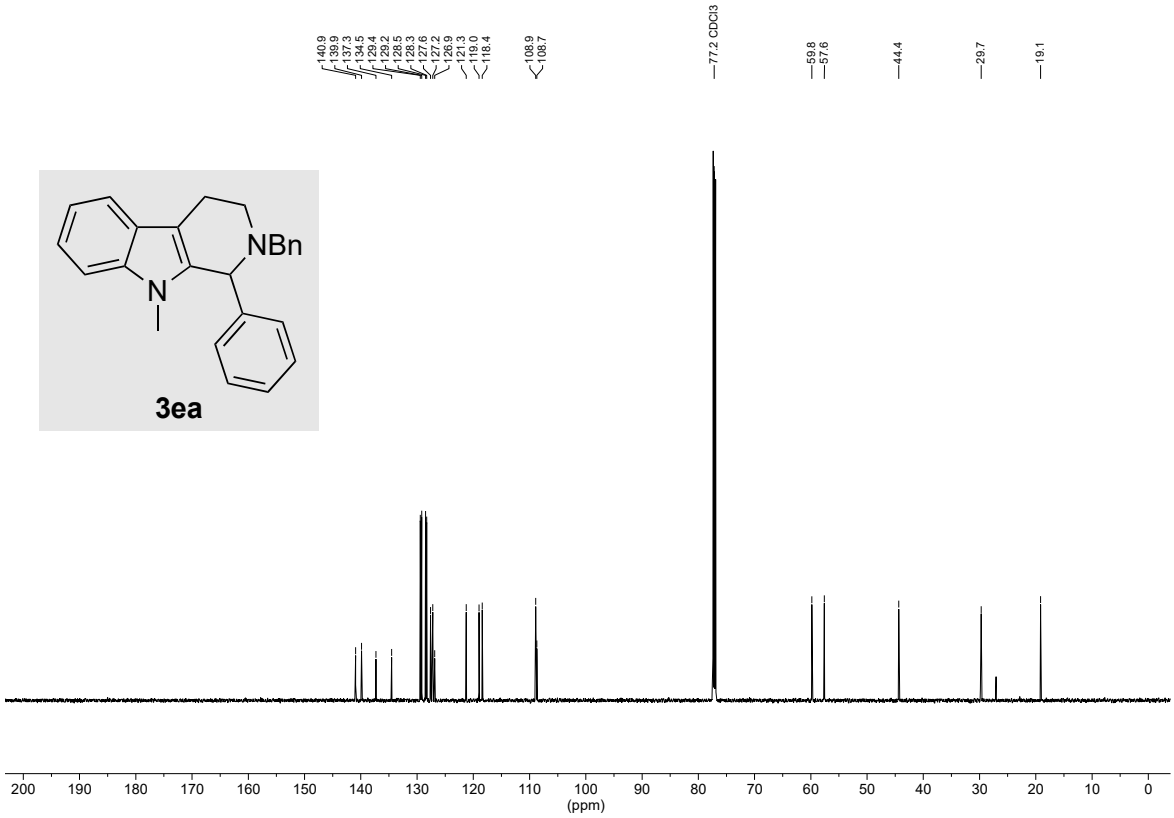


Figure S61. 150 MHz ^{13}C-NMR spectrum of compound **3ea** in $CDCl_3$.

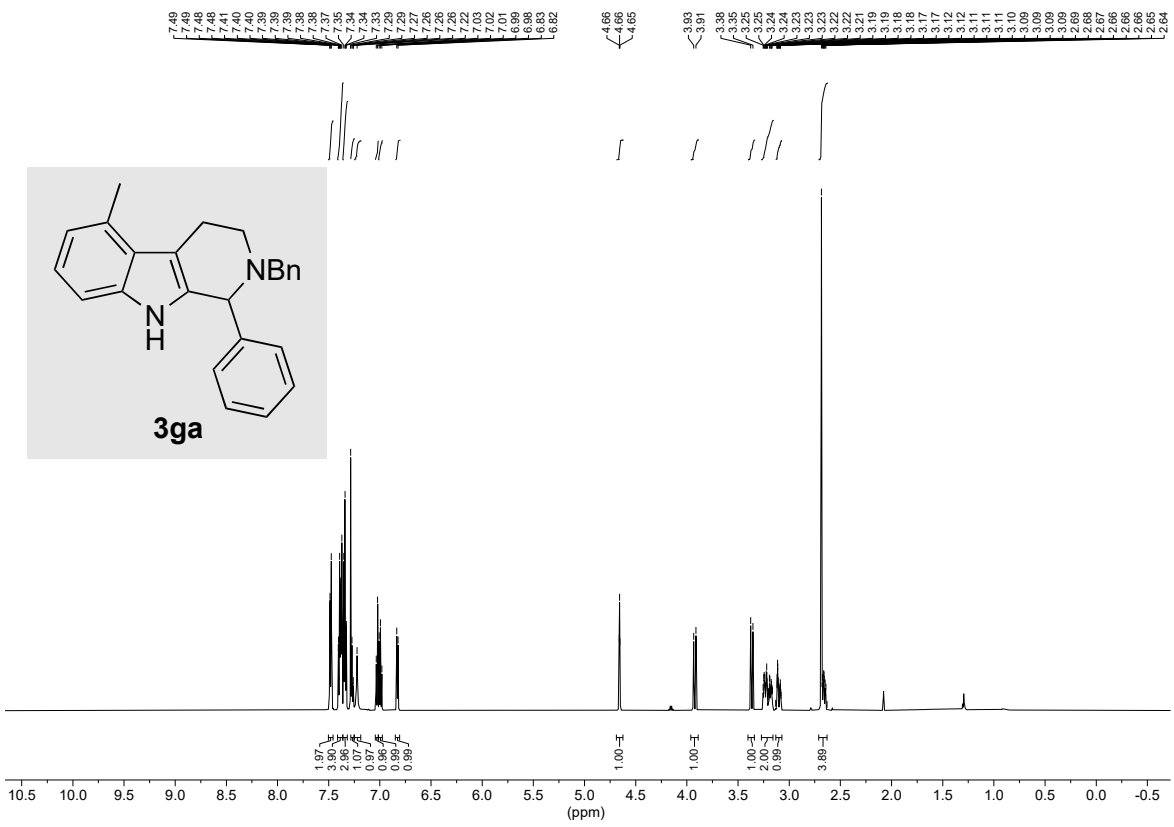


Figure S62. 600 MHz ^{1}H-NMR spectrum of compound **3ga** in $CDCl_3$.

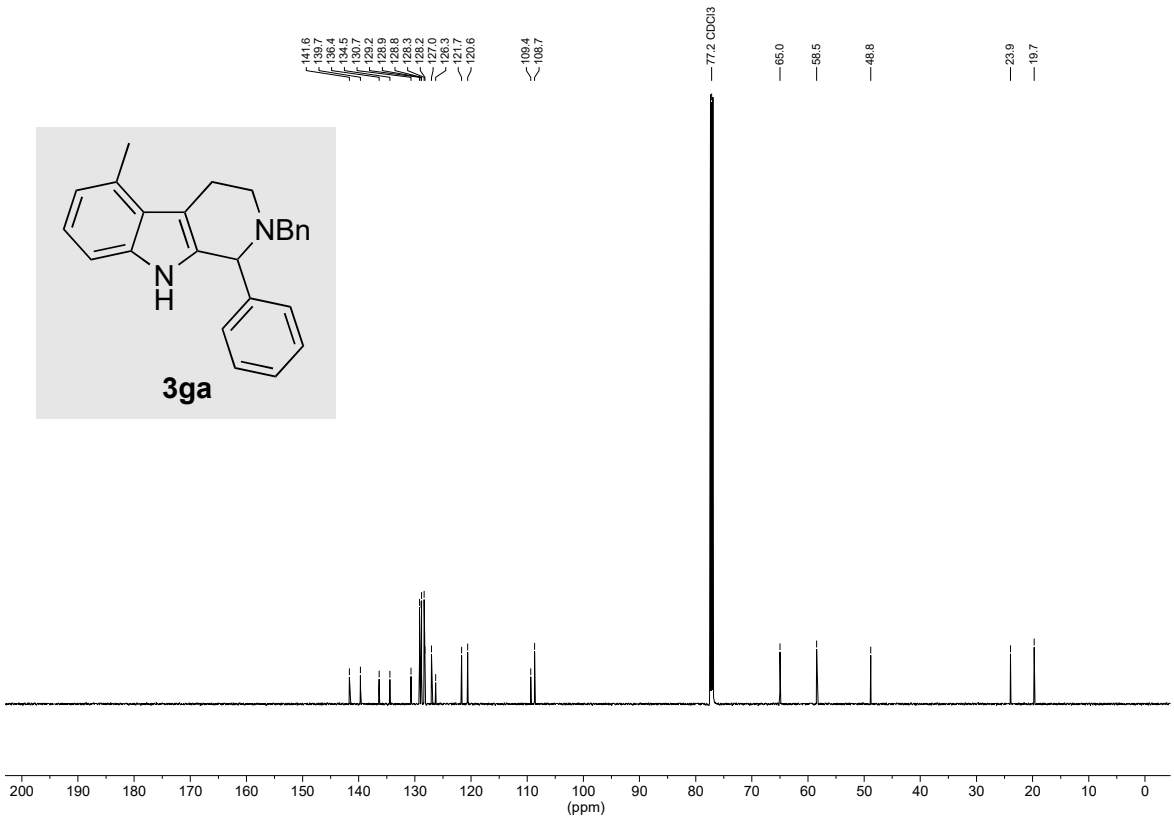


Figure S63. 150 MHz ^{13}C-NMR spectrum of compound **3ga** in $CDCl_3$.

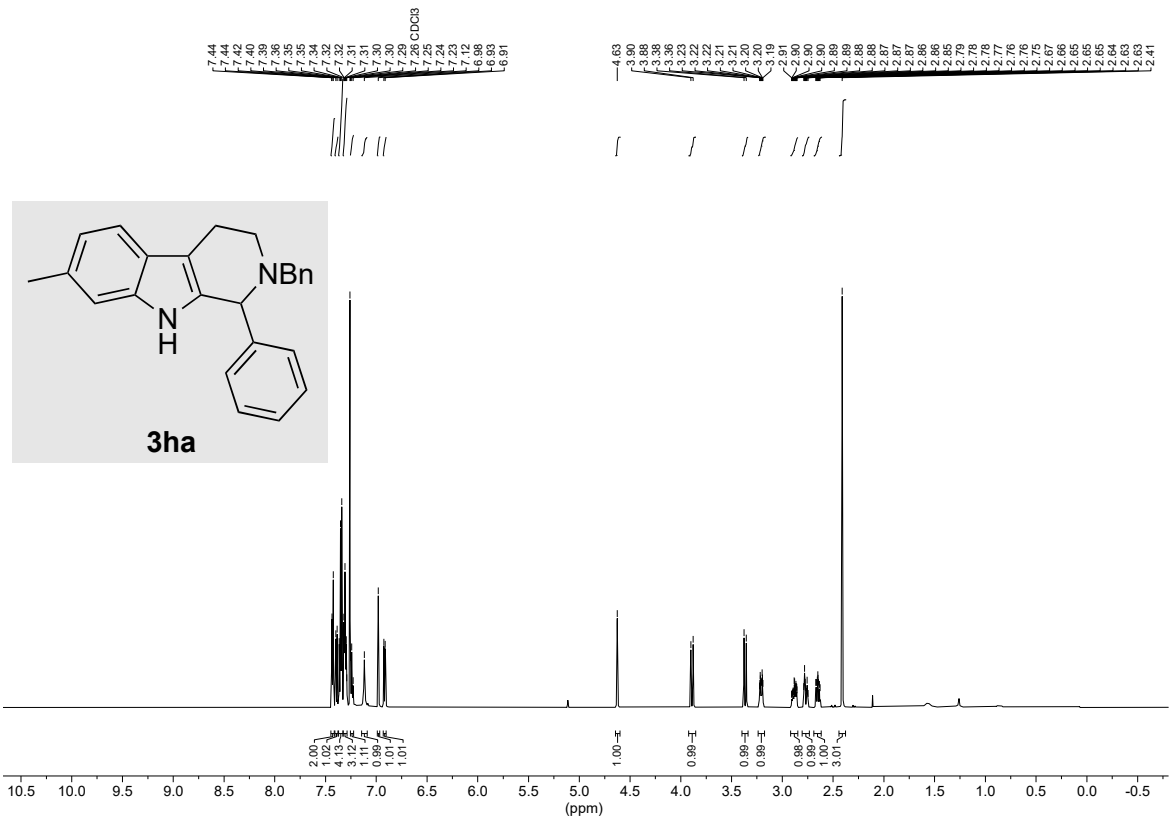


Figure S64. 600 MHz ^{1}H-NMR spectrum of compound **3ha** in $CDCl_3$.

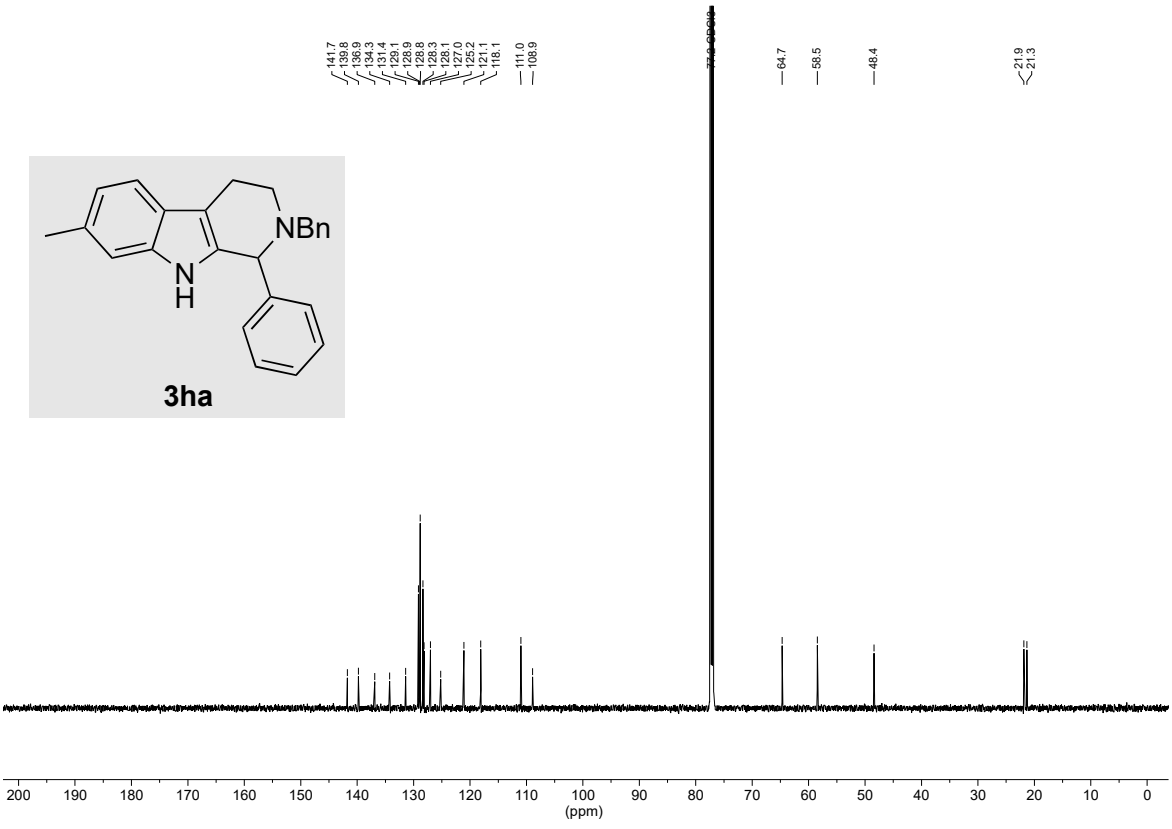


Figure S65. 150 MHz ^{13}C-NMR spectrum of compound **3ha** in $CDCl_3$.

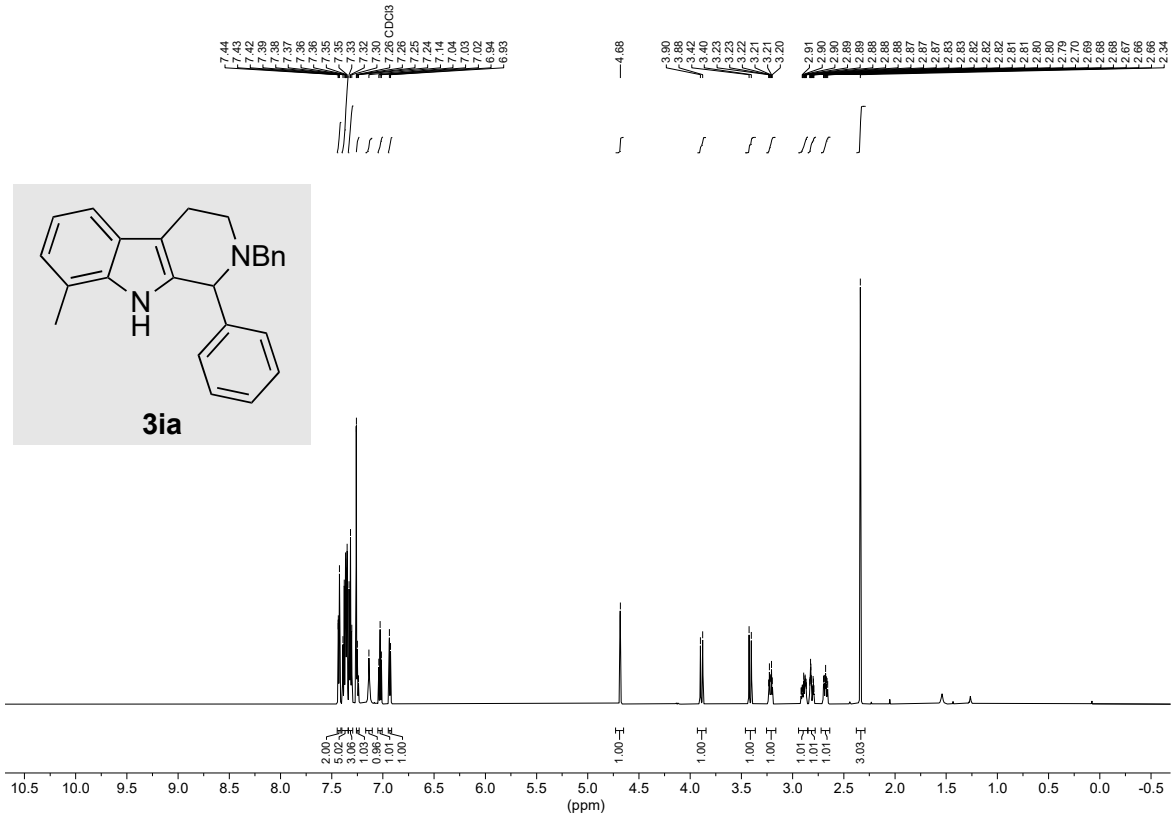


Figure S66. 600 MHz ^{1}H-NMR spectrum of compound **3ia** in $CDCl_3$.

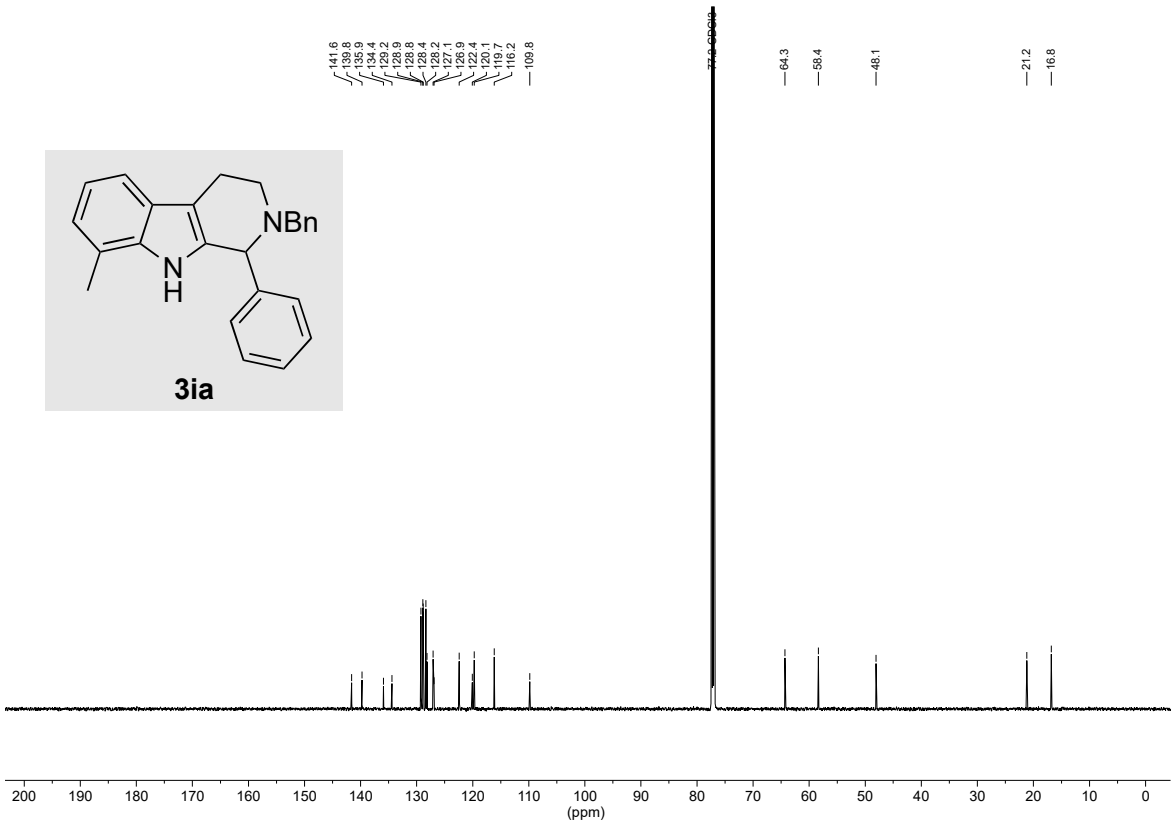


Figure S67. 150 MHz ^{13}C-NMR spectrum of compound **3ia** in $CDCl_3$.

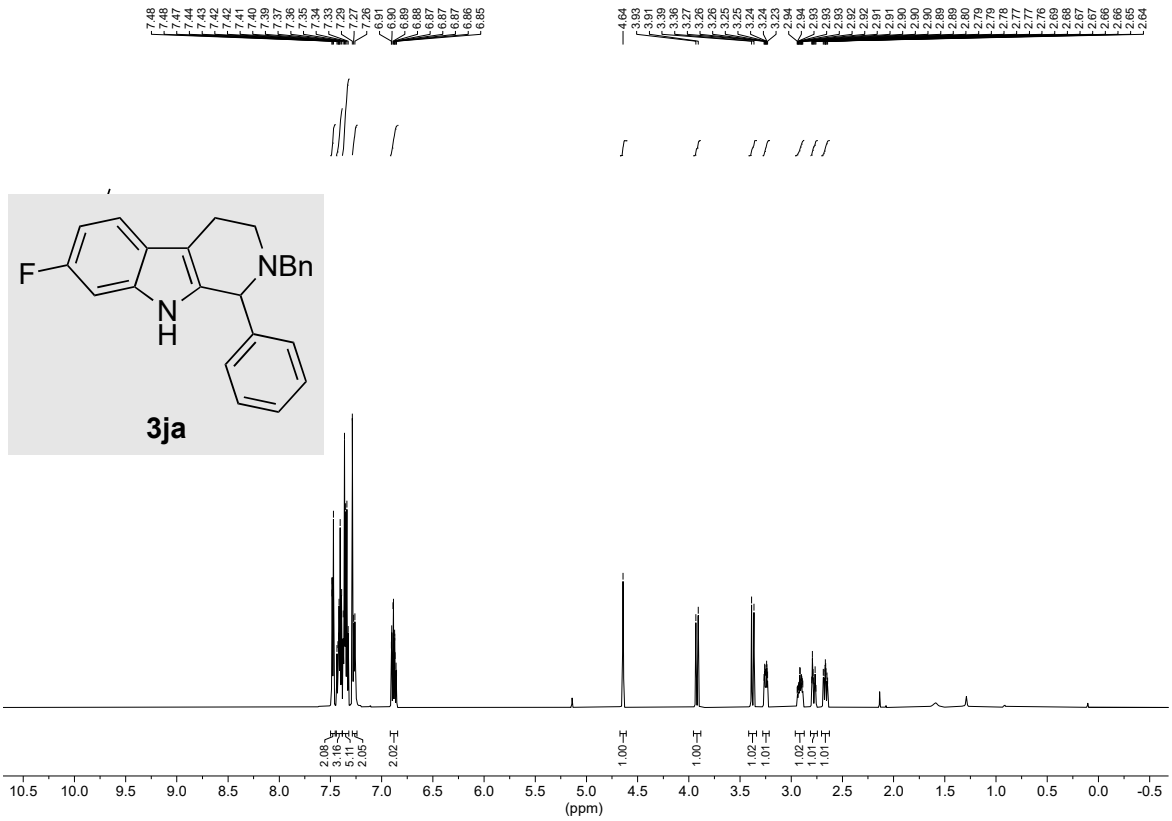


Figure S68. 600 MHz ^{1}H-NMR spectrum of compound **3ja** in $CDCl_3$.

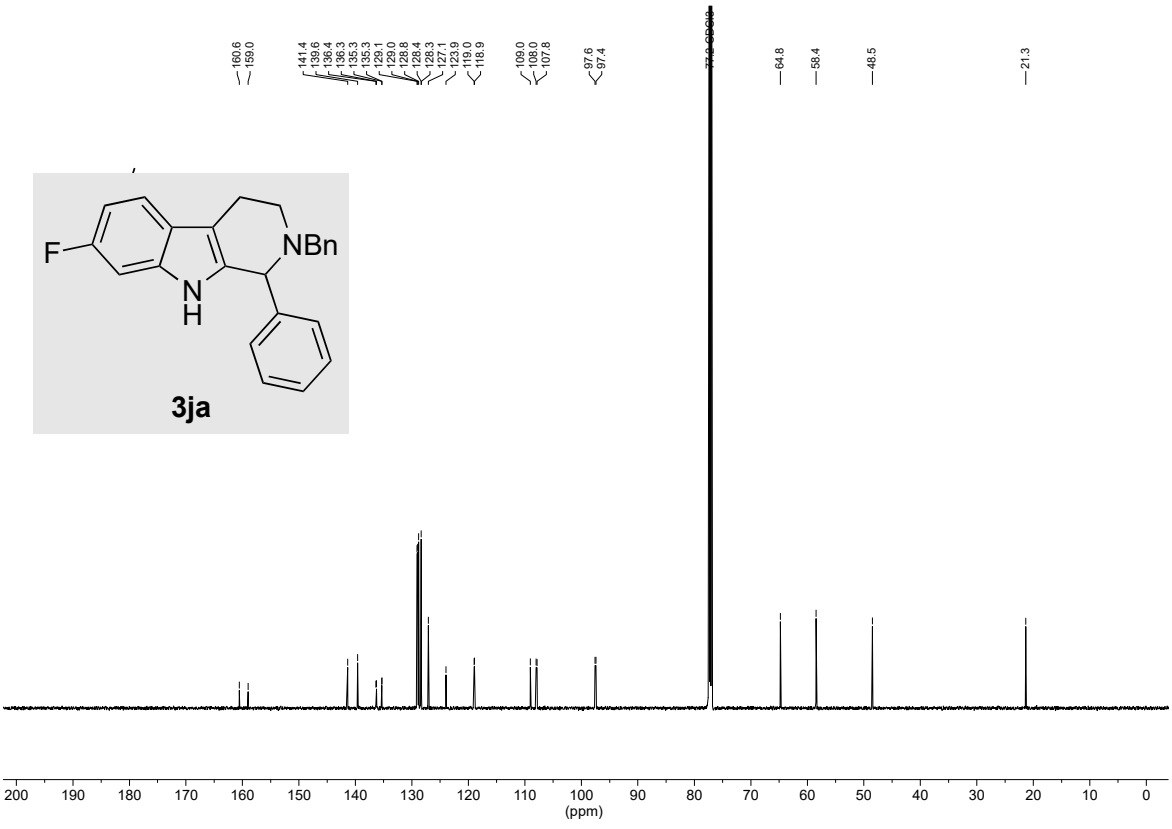


Figure S69. 150 MHz ^{13}C-NMR spectrum of compound **3ja** in $CDCl_3$.

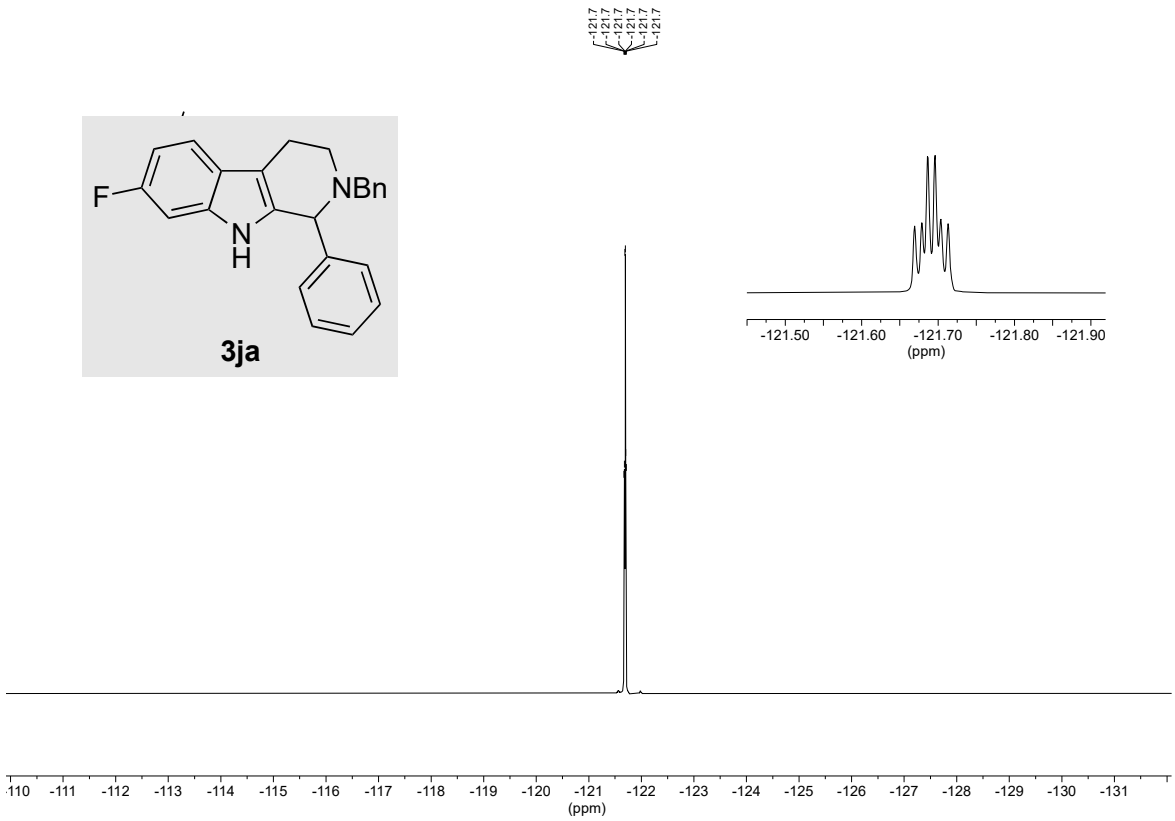


Figure S70. 565 MHz ^{19}F-NMR spectrum of compound **3ja** in $CDCl_3$.

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