Electronic Supplementary Information (ESI)

Nickel-catalysed chemoselective C-3 alkylation of indoles with alcohols through borrowing hydrogen method

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1. General Information

All the starting compounds employed in this study were procured from commercial suppliers and were used without further purification. Potassium tert-butoxide, potassium hydroxide and indole were purchased from Sigma Aldrich. Glasswares were dried overnight at 160 °C. Toluene was dried by heating over sodium with benzophenone as an indicator. For thin layer chromatography (TLC), Merck pre-coated silica gel 60 F254 aluminium foils with detection under UV lamp at 254 nm were used. Column chromatography was performed using SD Fine silica gel 60-120 mesh using a gradient of ethyl acetate and hexane as mobile phase. High-resolution mass spectra were recorded on a Waters QTOF mass spectrometer. IR spectra were recorded on a Perkin–Elmer FT IR spectrometer as KBr pellet, as indicated, with ν_{max} in inverse centimetres. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz Bruker Biospin Advance III FT-NMR spectrometer. NMR shifts are reported as delta (δ) units in parts per million (ppm) and coupling constants (J) are reported in Hertz (Hz). Chemical shifts (δ) are quoted to the nearest 0.01 ppm relative to tetramethylsilane (δ 0.00 ppm) in $CDCl_3$ (δ 7.26 ppm). Carbon chemical shifts are internally referenced to the deuterated solvent signals in $CDCl_3$ (δ 77.1 ppm).

2. Synthesis of 1[S1]

The azo-phenolate ligand (**L**) was synthesized following our reported procedure.[1] A methanolic solution of **L (**1 mmol) was taken in a 100-mL round-bottom flask and to it KOH (1 mmol) was added and the mixture was stirred at room temperature for 30 min. Then, 0.5 mmol of $Ni(OAc)_2$ was added to the reaction mixture and refluxed for another 30 min. Immediate precipitate was obtained during the reflux. After completion of the reaction, the solution was filtered to obtain dark brown colored product in 82% yield. The desired product was fully characterized by ^{1}H, ^{13}C NMR spectroscopies.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45-8.44 (d, 2H), 7.35-7.25 (m, 5H), 1.29 (s, 9H), 1.01 (s, 9H) ppm.

^{13}C NMR (400 MHz, $CDCl_3$): δ 148.81, 144.38, 139.59, 130.80, 128.64, 125.76, 124.85, 124.80, 122.46, 122.10, 35.70, 34.37, 31.62, 29.56 ppm.

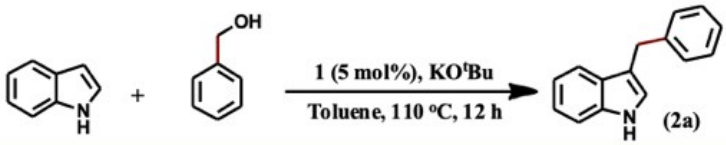
3. General Procedure for C-3 alkylation of indole

Procedure for C-3 alkylation of indole: In a typical reaction, 25 mL Schlenk flask was charged with primary (2 mmol) / secondary alcohols (2.2 mmol), indole (1 mmol), KO^{t}Bu (0.7 mmol), **1** (5 mol%) in 2 mL toluene. The mixture was packed under anaerobic atmosphere. The reaction mixture was stirred at 110 ^{o}C for 12 h. The reaction mixture was cooled to room temperature upon completion and concentrated *in vacuo.* The residue was purified by column chromatography using hexane/ethyl acetate (10:1) as eluent to afford pure products. The desired products were fully characterized by ^{1}H, ^{13}C NMR spectroscopies.

Procedure for C-3 alkylation using 2-(2-aminophenyl) ethanol: In a typical reaction, 25 mL Schlenk flask was charged with primary alcohols (2.2 mmol), 2-(2-aminophenyl) ethanol (1 mmol), KO^{t}Bu (0.7 mmol), **1** (5 mol%) in 2 mL toluene. The mixture was packed under anaerobic atmosphere. The reaction mixture was stirred at 110 ^{o}C for 12 h. The reaction mixture was cooled to room temperature upon completion and concentrated *in vacuo.* The residue was purified by column chromatography using hexane/ethyl acetate (10:1) as eluent to afford pure products. The desired products were fully characterized by ^{1}H, ^{13}C NMR spectroscopies.

4. Optimization Table:

Table S1: Screening reaction condition for C-3 alkylation of indole

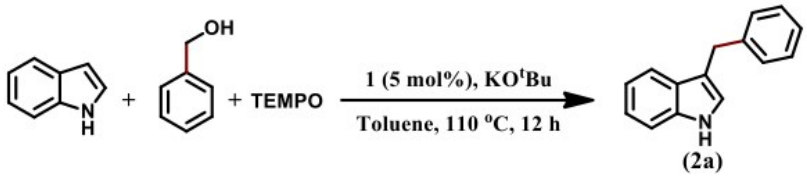


Entry	Catalyst loading	Base	Yield% (2a)
1	**1** (2.5 mol%)	KO^{t}Bu (0.25 eq)	16
2	**1** (5 mol%)	KO^{t}Bu (0.25 eq)	39
3	**1** (5 mol%)	KO^{t}Bu (0.5 eq)	56
4	**1** (5 mol%)	KO^{t}Bu (0.7 eq)	79
5	**1** (2.5 mol%)	KO^{t}Bu (0.7 eq)	61
6	**1** (5 mol%)	KOH (0.7 eq)	23
7	**1** (5 mol%)	NaOH (0.7 eq)	15
8	**1** (5 mol%)	K_2CO_3 (0.7 eq)	n.r
9	**1** (5 mol%)	NaO^{t}Bu (0.7 eq)	67
10	**1** (5 mol%)	-	n.r
11	-	KO^{t}Bu (0.7 eq)	n.r
12	$NiCl_2$	KO^{t}Bu (0.7 eq)	11

Reaction conditions: **1** (5 mol%, with respect to indole), indole (1 mmol), primary alcohol (2 mmol), KO^{t}Bu (0.7 mmol), toluene (2 mL), 110 °C (oil bath), 12 h.

5. Control experiments

5.a) Radical quenching experiment

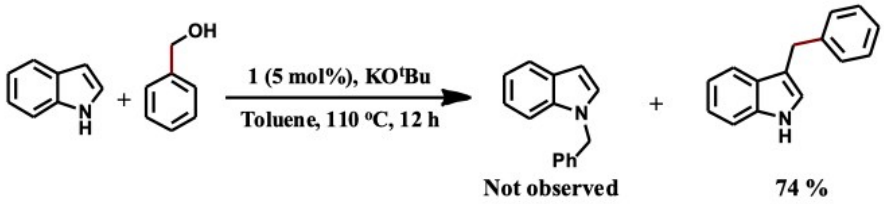


In a typical reaction, 25 mL Schlenk flask was charged with benzyl alcohol (2 mmol), indole (1 mmol), KO^{t}Bu (0.7 mmol), **1** (5 mol%) **1** and varying equivalent of TEMPO, in 2 mL toluene and connected to condenser under nitrogen flow. The reaction mixture was stirred at 110 °C for 12 h. The product yield was quantified by GC-MS.

Table S2: Quantification of product formation by addition of varying equivalence of radical quencher

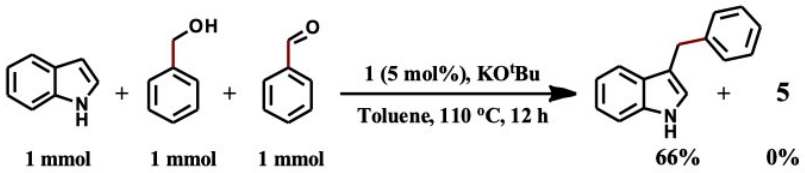
Entry	TEMPO equivalence	(2a) Yield (%)
1.	0.5 eq	21%
2.	1.0 eq	trace

5.b) N-alkylation of indole



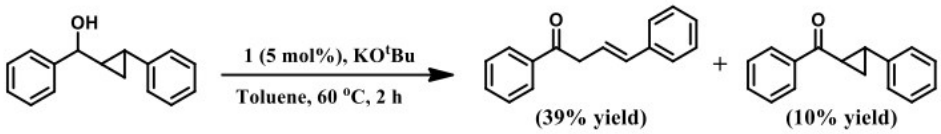
In a typical reaction, 25 mL Schlenk flask was charged with benzyl alcohol (2 mmol), indole (1 mmol), KO^{t}Bu (0.7 mmol), **1** (5 mol%) in 2 mL toluene. The mixture was packed under anaerobic atmosphere. The reaction mixture was stirred at 110 °C for 12 h. 1-(Phenyl methyl)-1*H*-Indole, was not obtained indicating N-alkylation of indole does not occur.

5.c)



In a typical reaction 25 mL schlenk flask was charged with **1** (5 mol%), KO^{t}Bu (0.7 mmol), benzaldehyde (1 mmol), benzyl alcohol (1 mmol), and indole (1 mmol) in 2 mL toluene. The reaction mixture was stirred for 12 h at 110°C. The product yield was quantified by GC-MS. The product **2a** was isolated in 66% yield.

5.d) Ring opening probe reaction:



In a typical reaction 25 mL Schlenk flask was charged with **1** (5 mol%), KO^{t}Bu (25 mol%), phenyl-(2-phenylcyclopropyl) methanol (1 mmol) in 2 mL toluene. The reaction mixture was stirred for 2 h at 60 ^{o}C. The ring opened product was separated by column chromatography in 39% yield. The desired product was characterized by ^{1}H NMR spectroscopy.

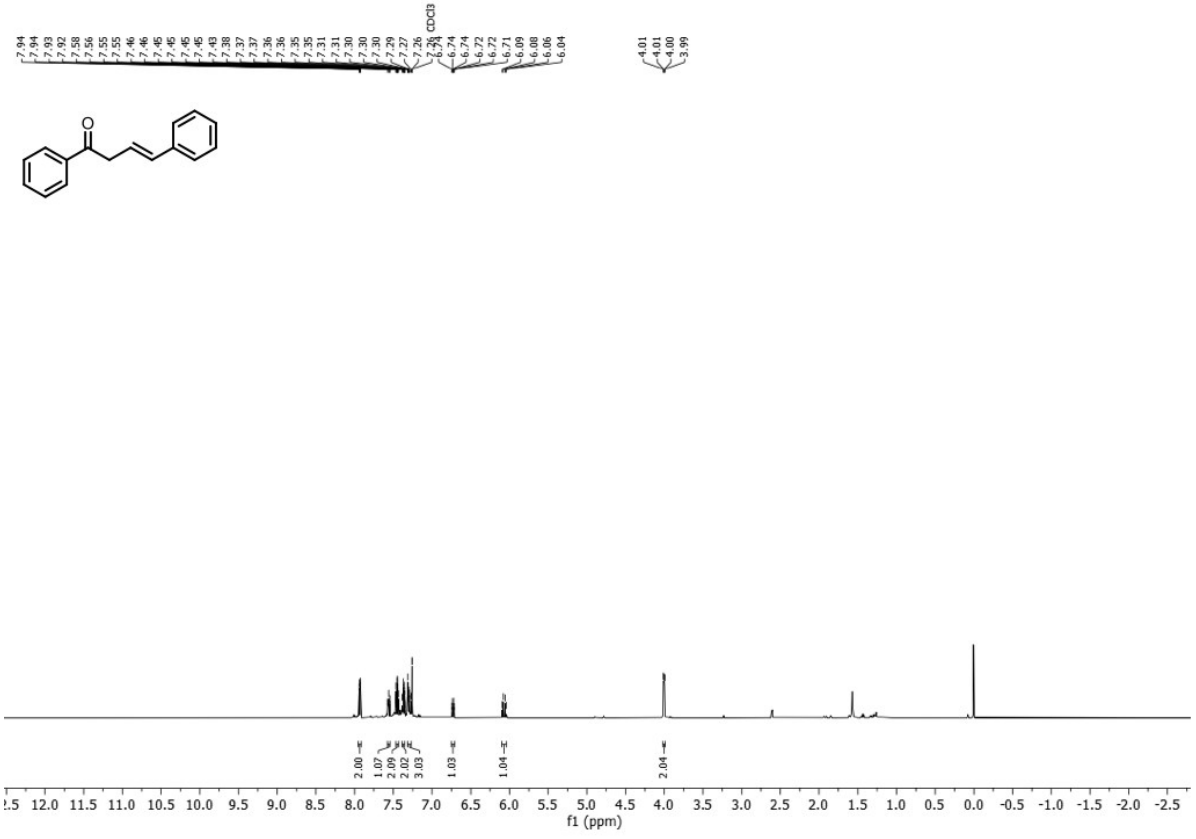


Figure S1. ^{1}H NMR spectrum of ring opened product in $CDCl_3$.

5.e) Procedure for intercepting ketyl radical intermediate

A 25 mL Schlenk flask was charged with **1** (5 mol%), KO^{t}Bu (25 mol%), 4-nitro benzyl alcohol (1 mmol) in 2 mL toluene. The solution was stirred for 5 min. After that, 0.6 equiv of BHT was added and the reaction mixture was stirred for 2 h at 60 ^{o}C. The trapped BHT adduct was detected by mass spectrometry. HRMS (ESI) m/z calcd for $C_{22}H_{28}NO_4Na$ (M+Na = 393.1906 (experimental), 393.1916 (calculated).

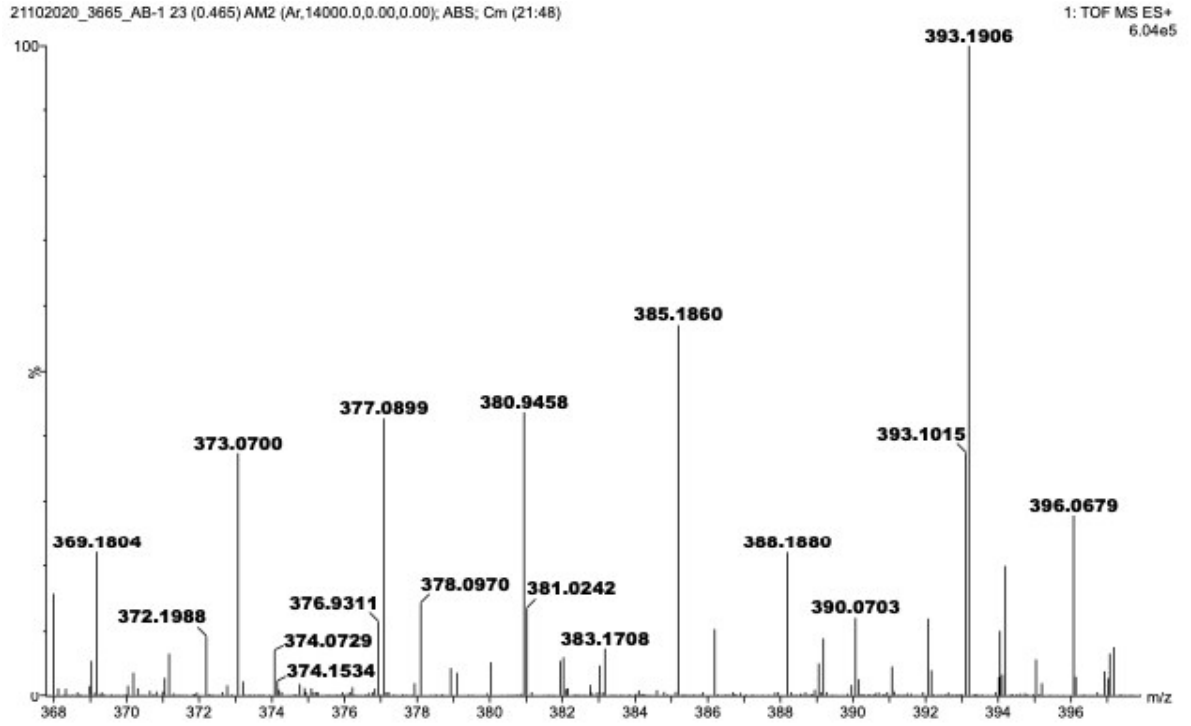


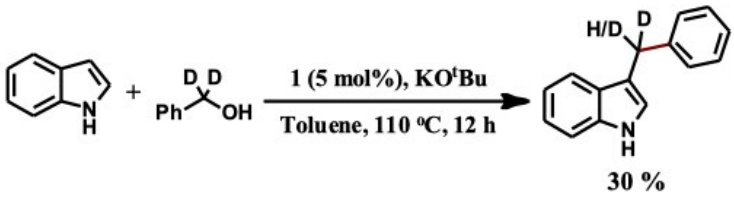
Figure S2. Mass spectrum of ketyl-BHT adduct.

5.f) Synthetic application: Gram scale synthesis

A large-scale reaction was performed in a 50-mL Schlenk flask with **1** (270 mg, 0.4 mmol), KO^{t}Bu (666 mg, 5.9 mmol), indole (1 g, 8.5 mmol), benzyl alcohol (1.8 g, 17.1 mmol) in 30 mL toluene and the mixture was packed under N_2 atmosphere. The reaction mixture was stirred at 110 ^{o}C for 12 h. The reaction mixture was cooled to room temperature upon completion and concentrated *in vacuo.* The residue was purified by column chromatography using ethyl acetate and petroleum ether (10-15%) as eluent to afford pure products. 3-(phenylmethyl)- 1*H*-Indole was obtained as white solid in (1.2 g) 68% yield.

6. Deuterium incorporation studies

Scheme S1:



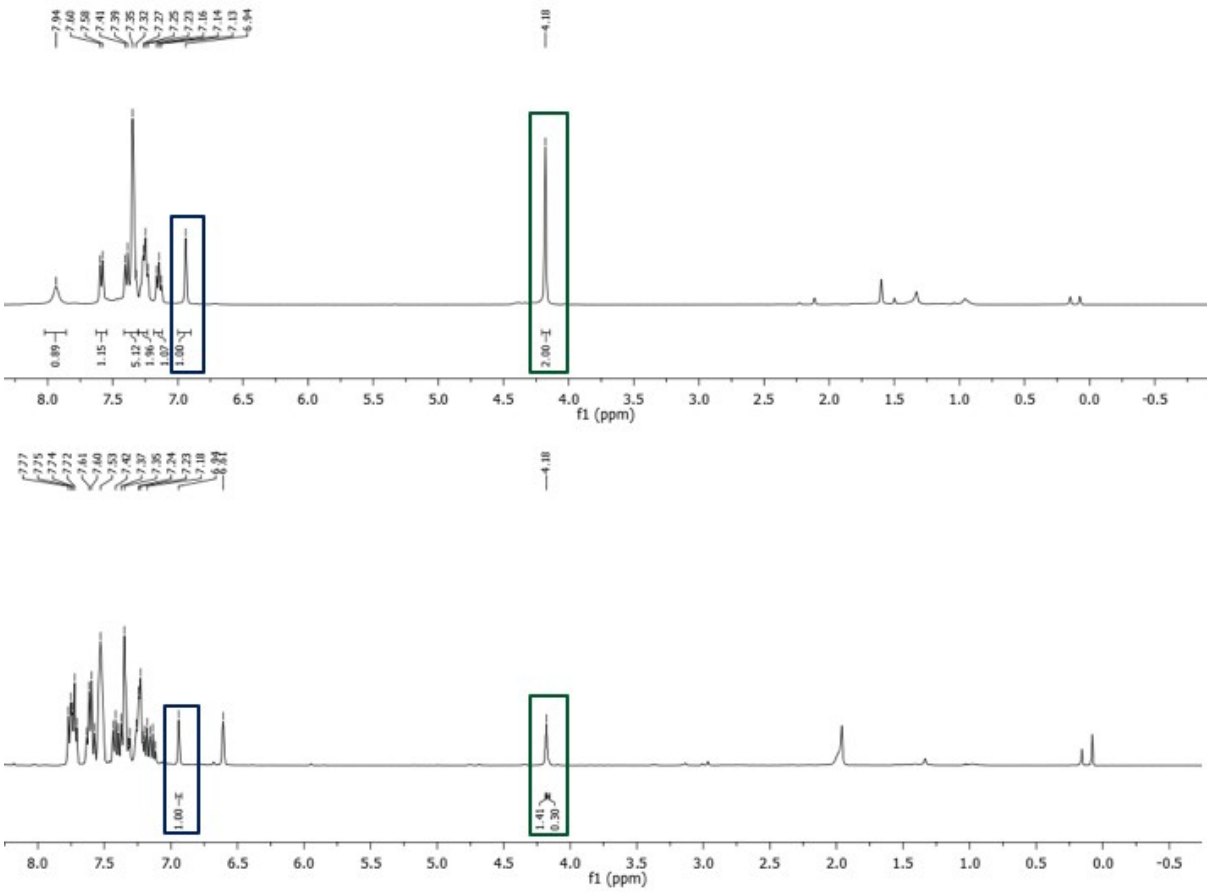


Figure S3. ^{1}H NMR spectrum of **2a (above)** in $CDCl_3$; ^{1}H NMR spectrum of **Scheme S1(below)** in $CDCl_3$.

7. $^{1}H,^{13}C$ NMR spectra for synthesized compounds

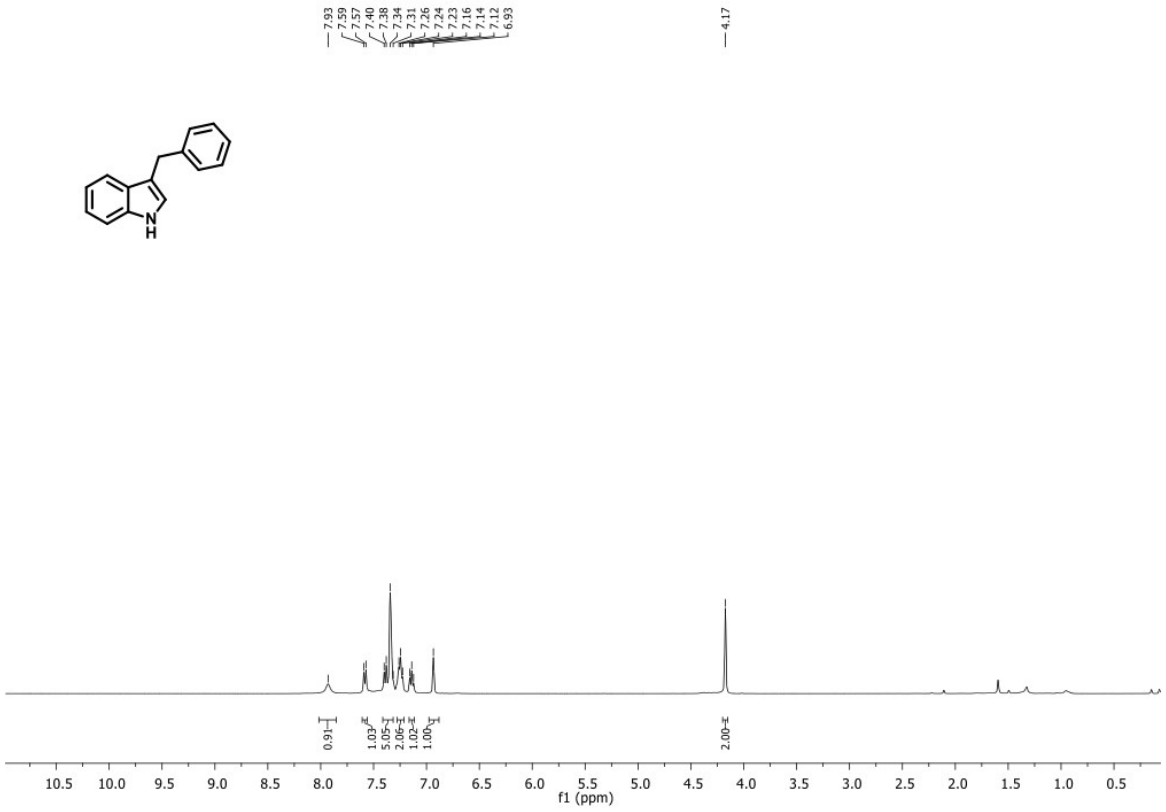


Figure S4. ^{1}H NMR spectrum of **2a** in $CDCl_3$.

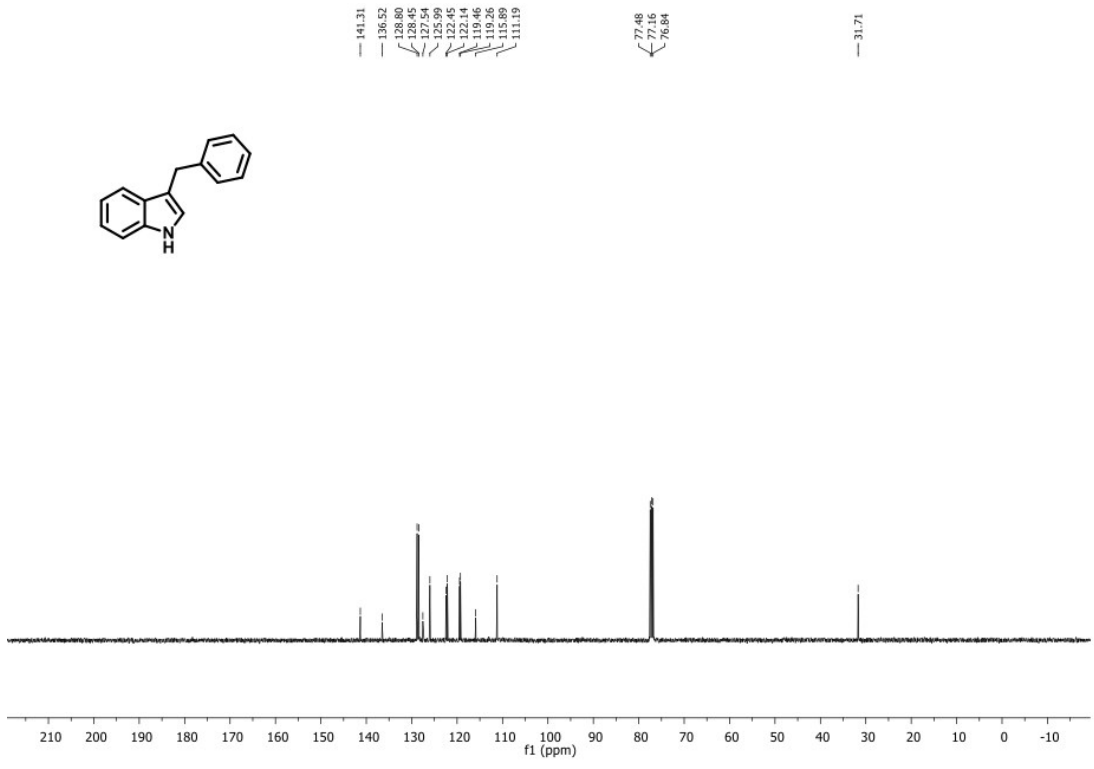


Figure S5. ^{13}C NMR spectrum of **2a** in $CDCl_3$

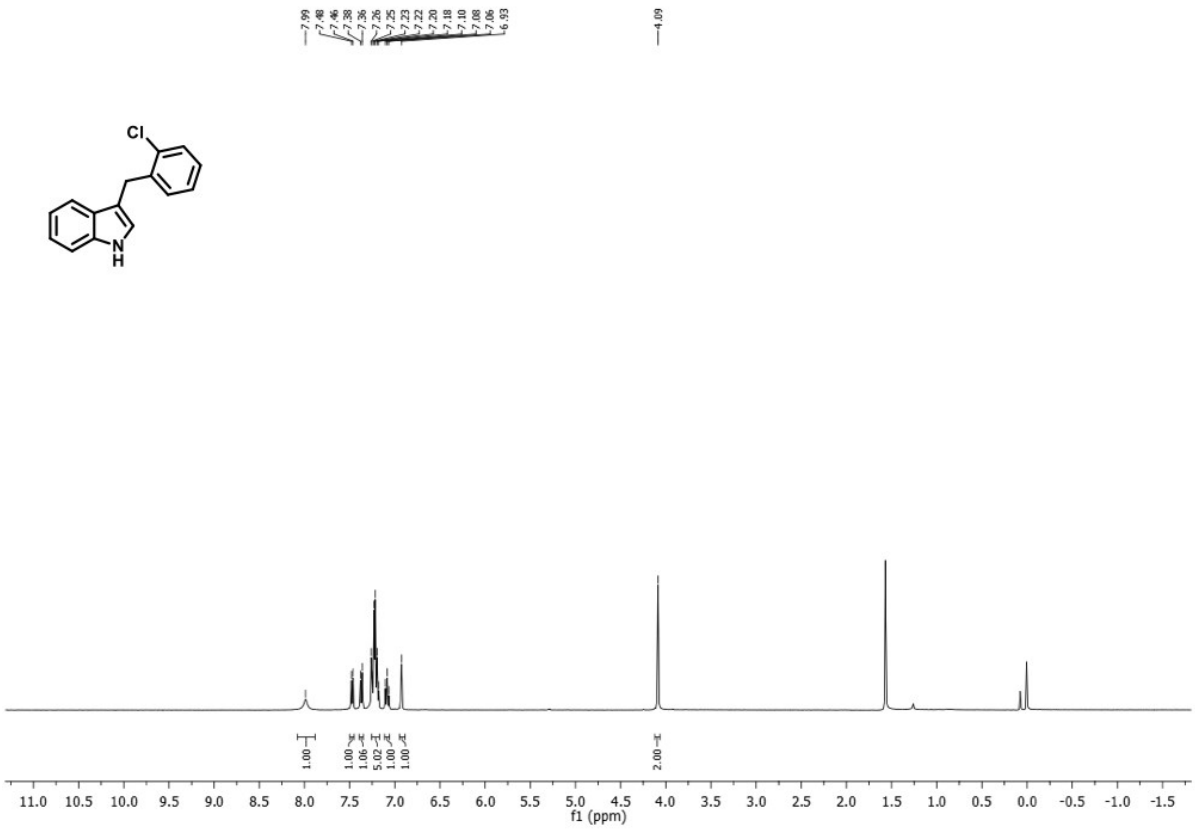


Figure S6. ^{1}H NMR spectrum of **2d** in $CDCl_3$.

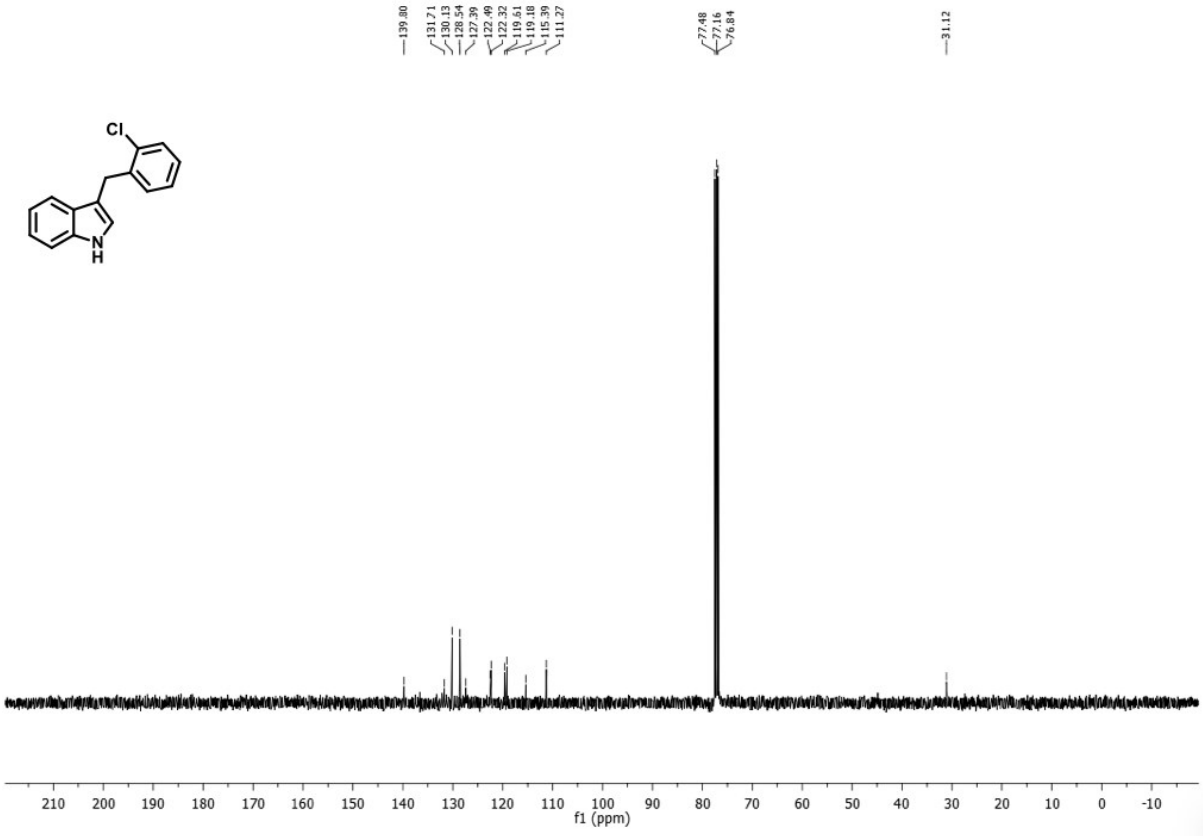


Figure S7. ^{13}C NMR spectrum of **2d** in $CDCl_3$

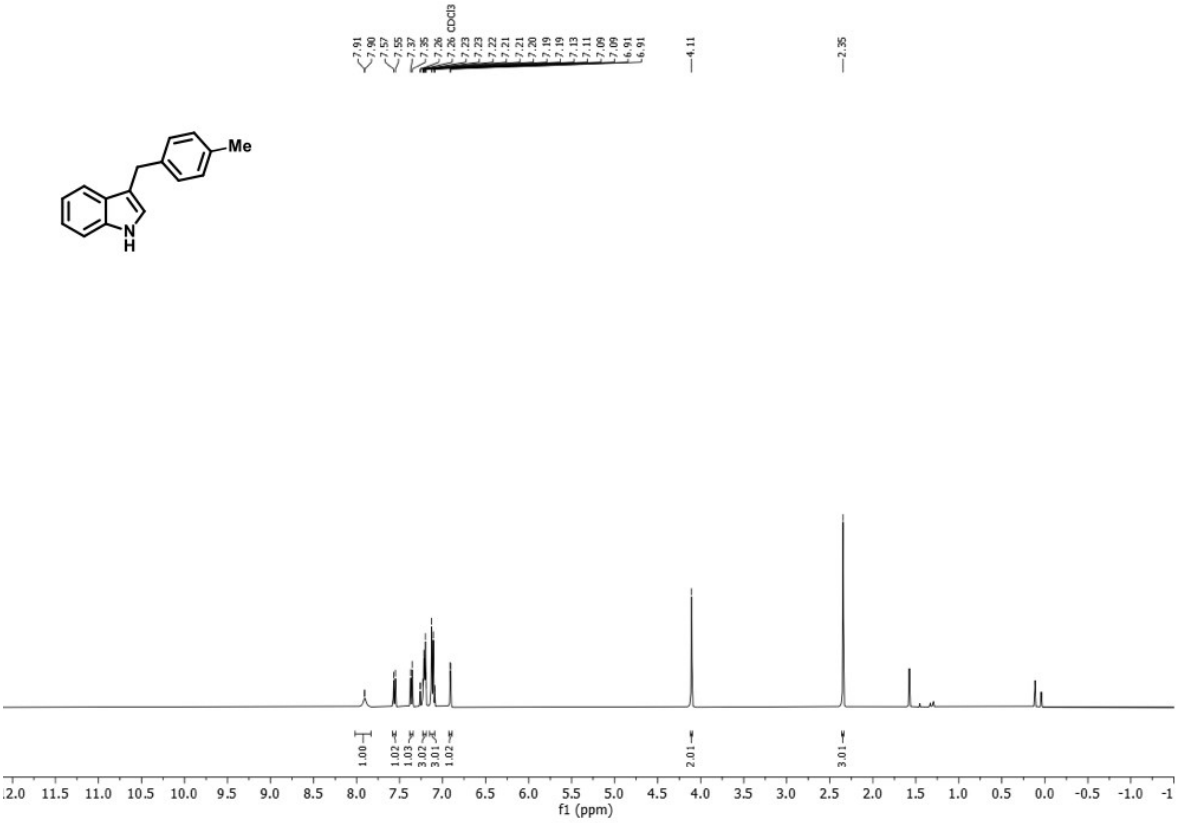


Figure S8. ^{1}H NMR spectrum of **2e** in $CDCl_3$.

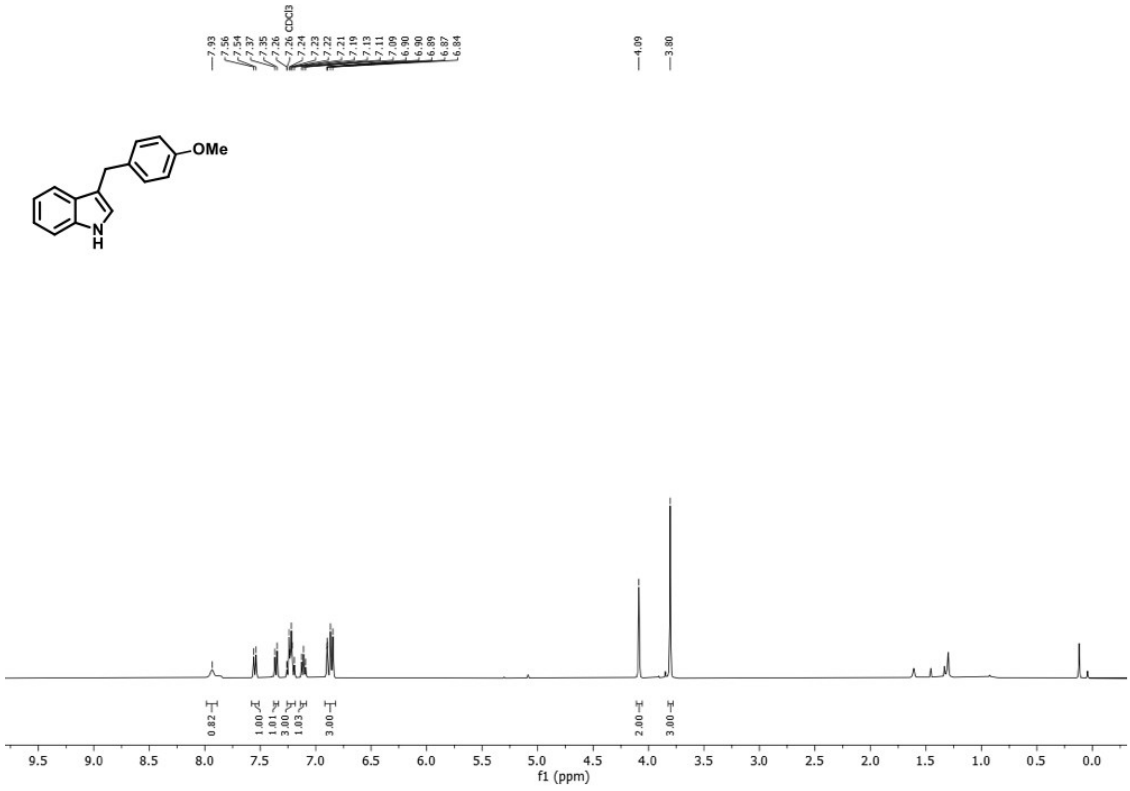


Figure S9. ^{1}H NMR spectrum of **2f** in $CDCl_3$.

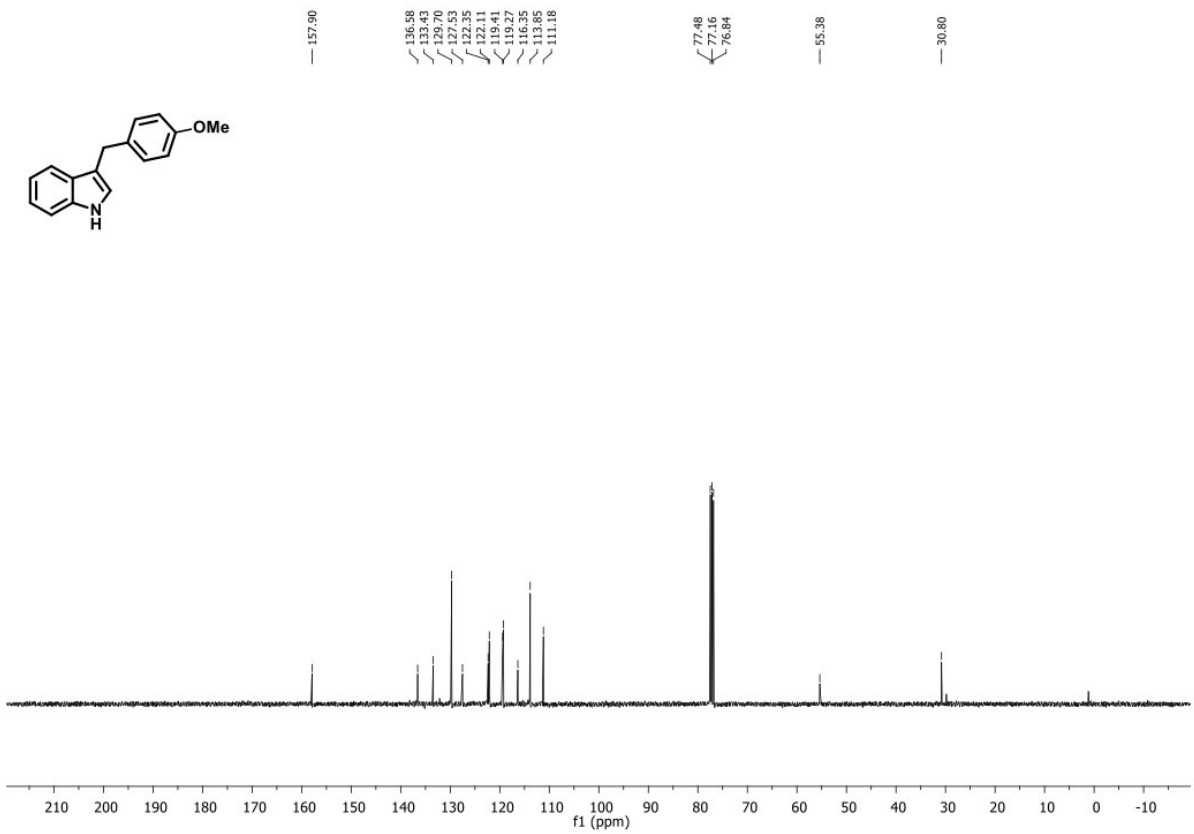


Figure S10. ^{13}C NMR spectrum of **2f** in $CDCl_3$

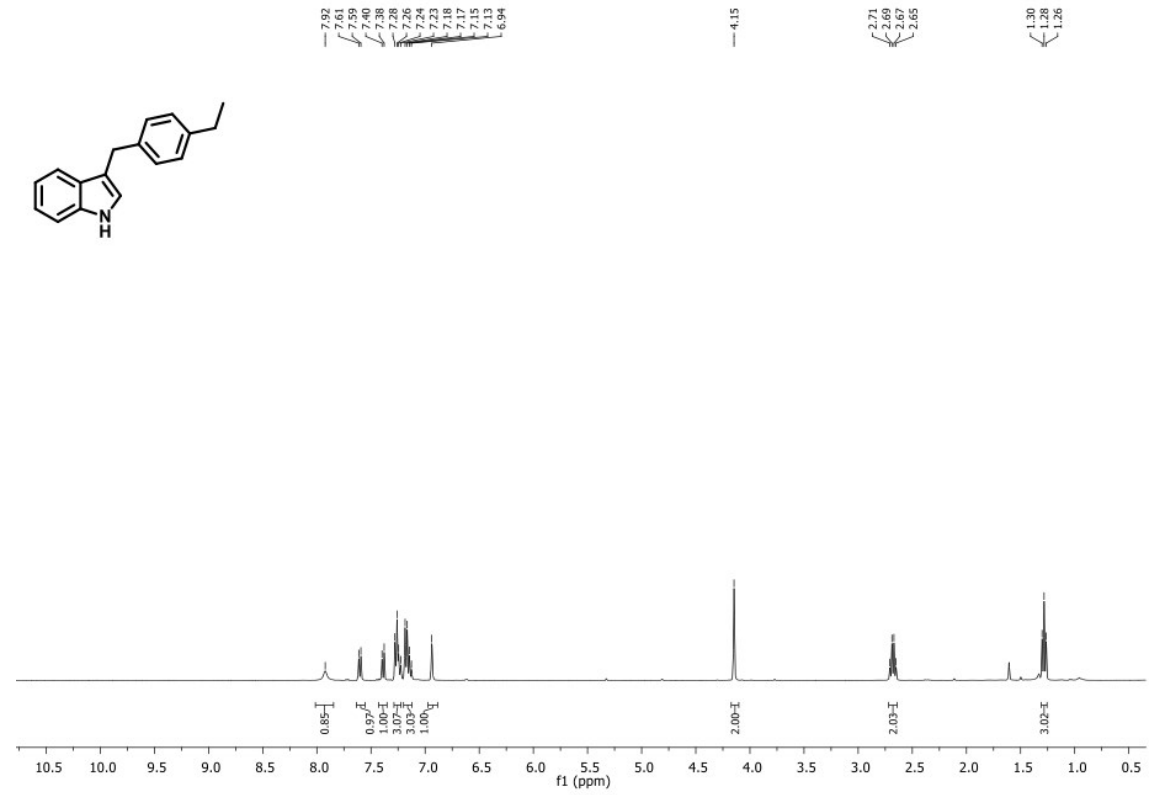


Figure S11. ^{1}H NMR spectrum of **2g** in $CDCl_3$.

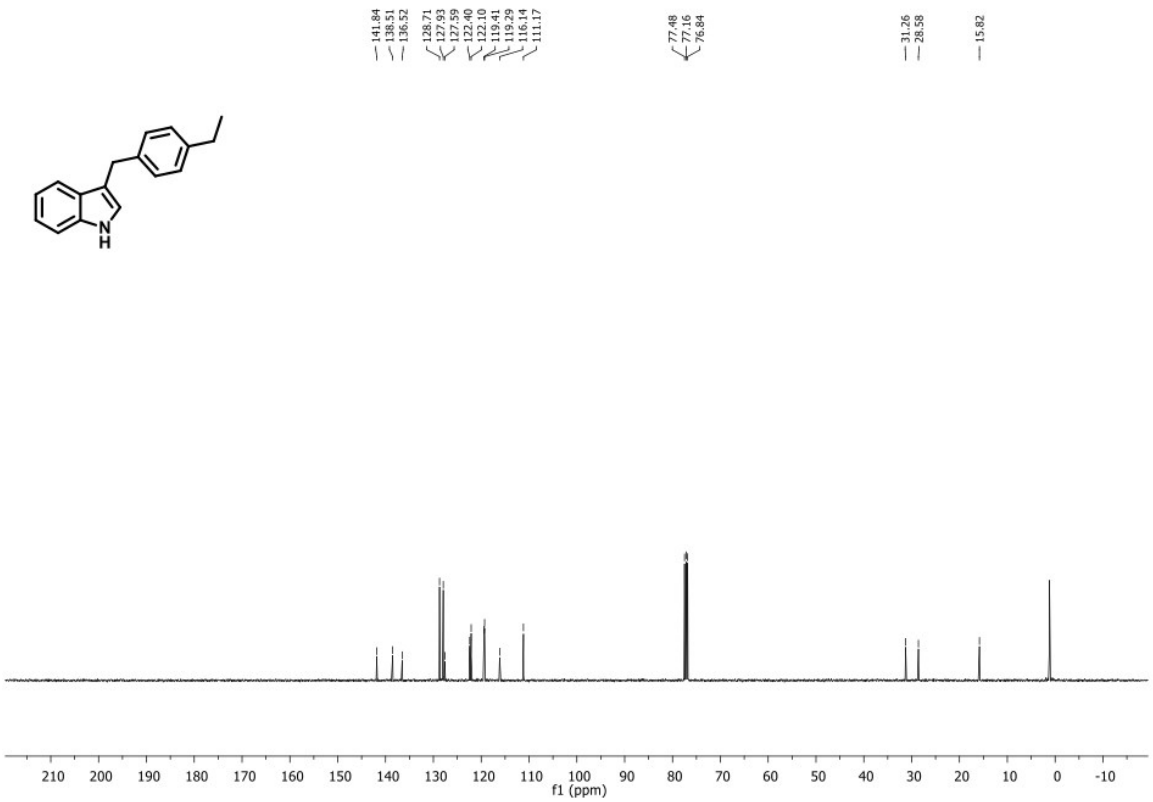


Figure S12. ^{13}C NMR spectrum of **2g** in $CDCl_3$

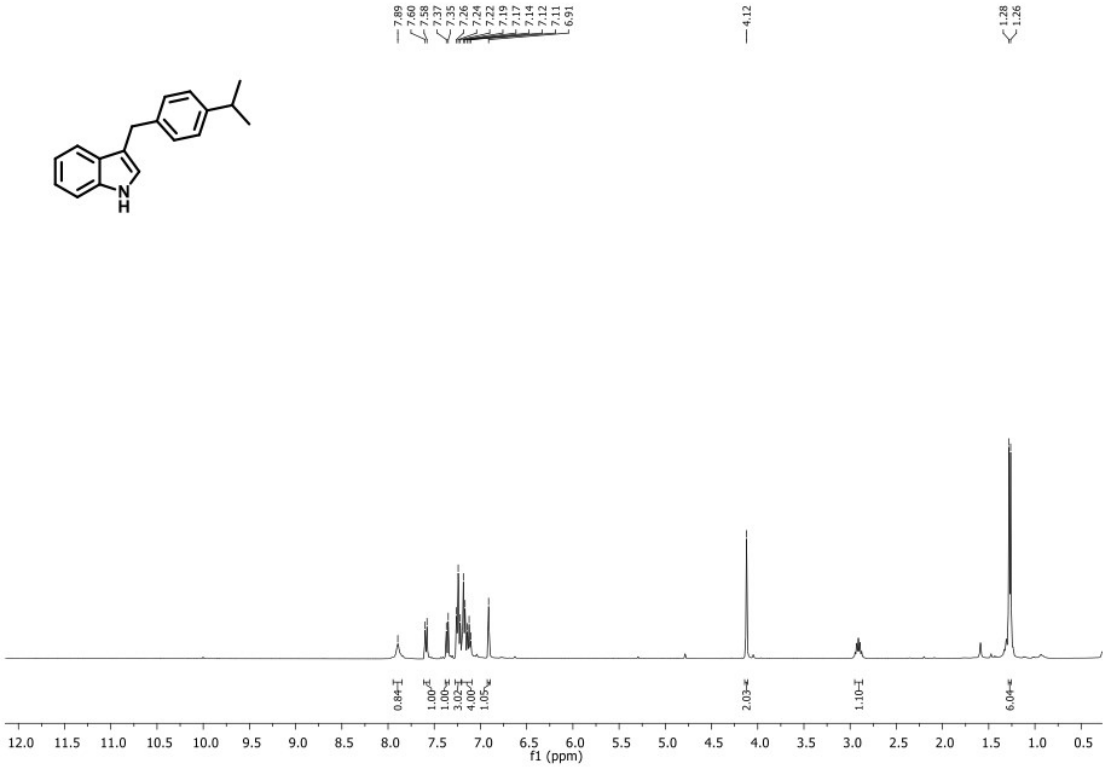


Figure S13. ^{1}H NMR spectrum of **2h** in $CDCl_3$.

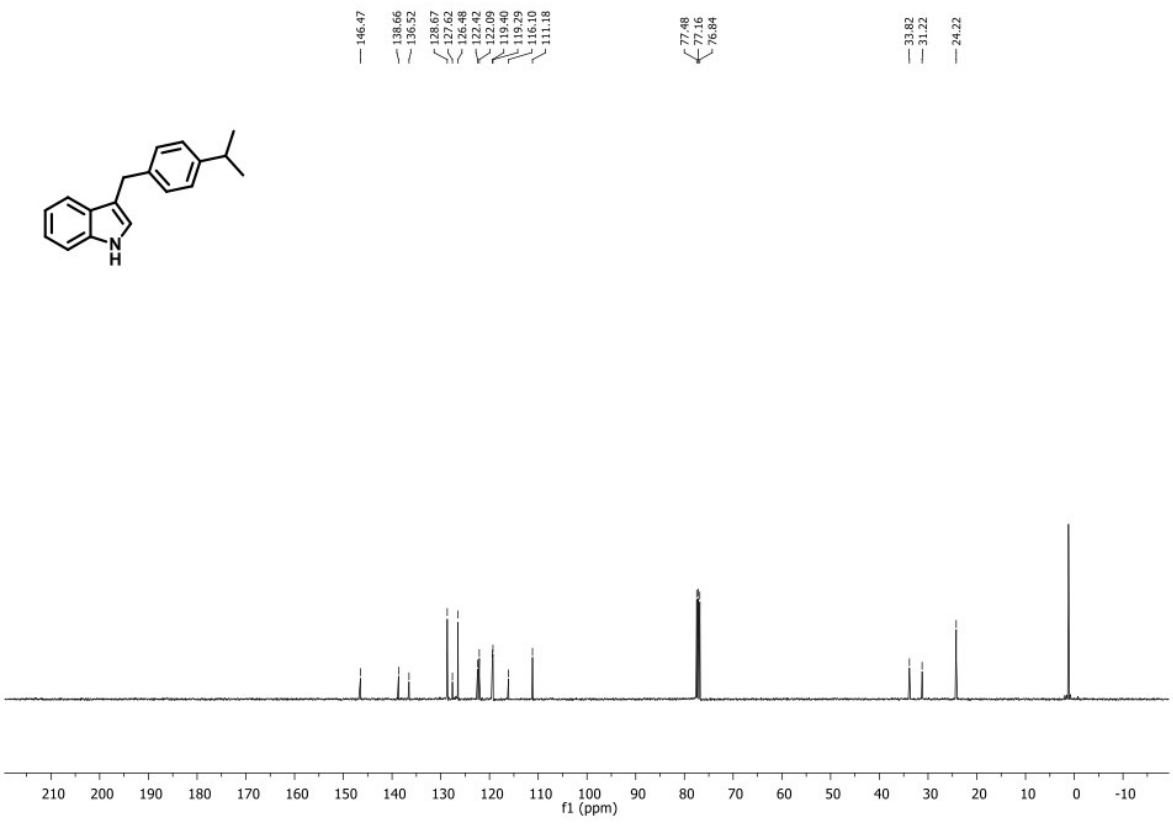


Figure S14. ^{13}C NMR spectrum of **2h** in $CDCl_3$

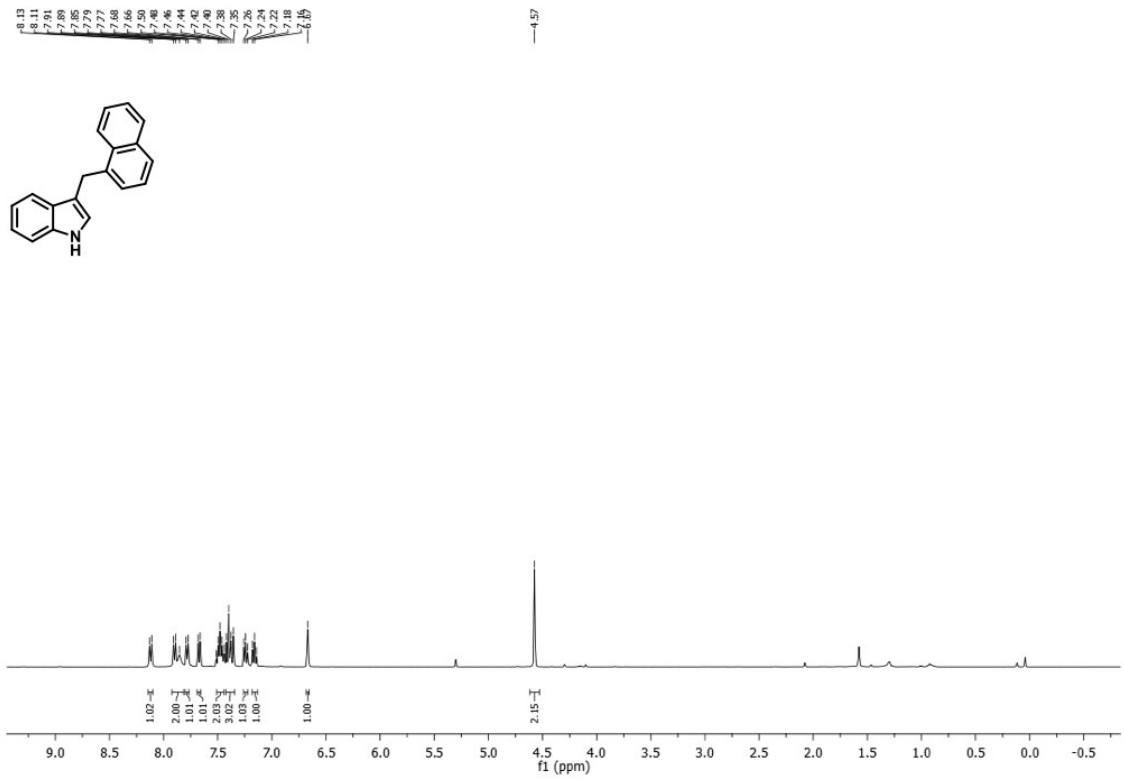


Figure S15. ^{1}H NMR spectrum of **2i** in $CDCl_3$.

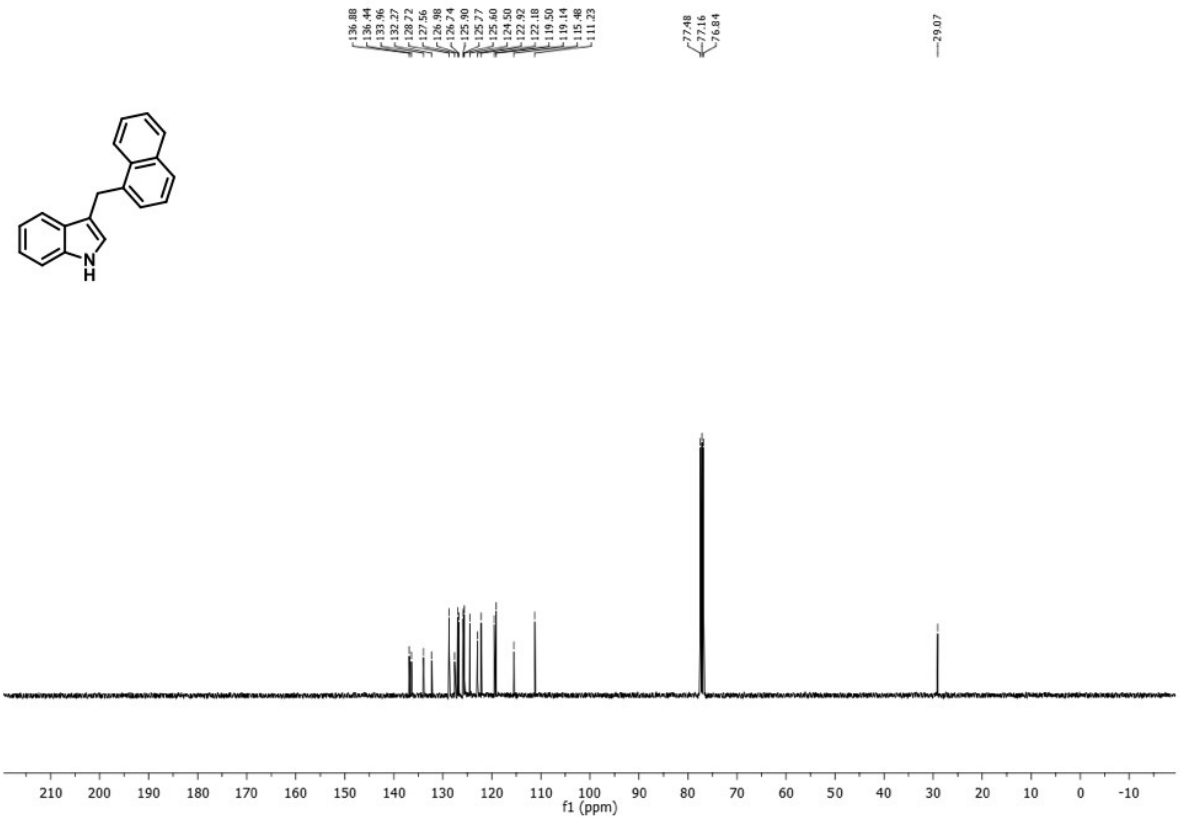


Figure S16. ^{13}C NMR spectrum of **2i** in $CDCl_3$

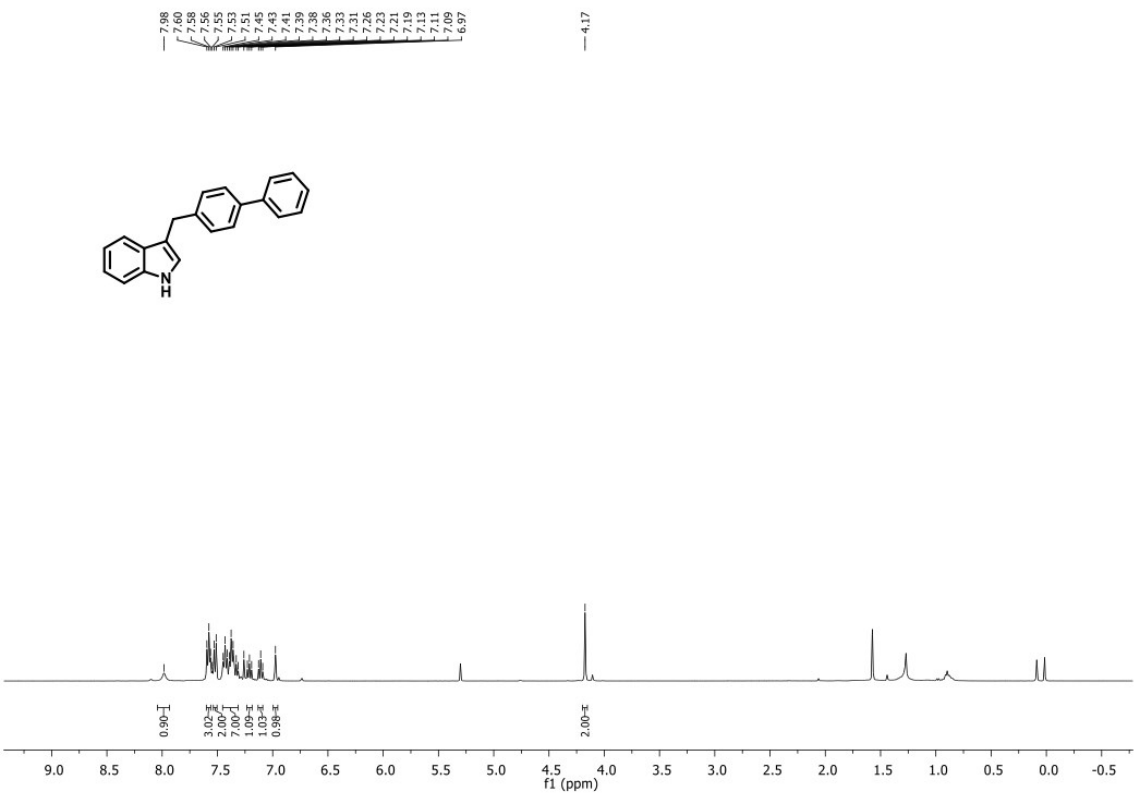


Figure S17. ^{1}H NMR spectrum of **2j** in $CDCl_3$.

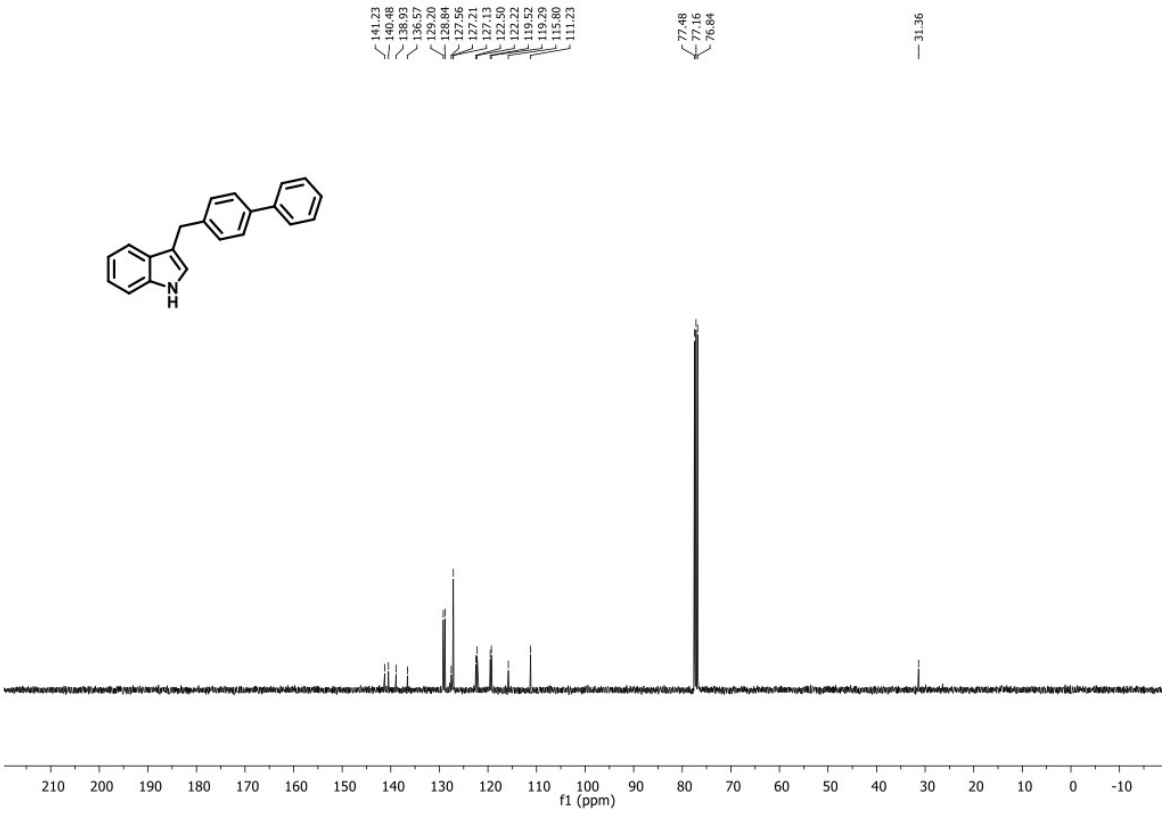


Figure S18. ^{13}C NMR spectrum of **2j** in $CDCl_3$

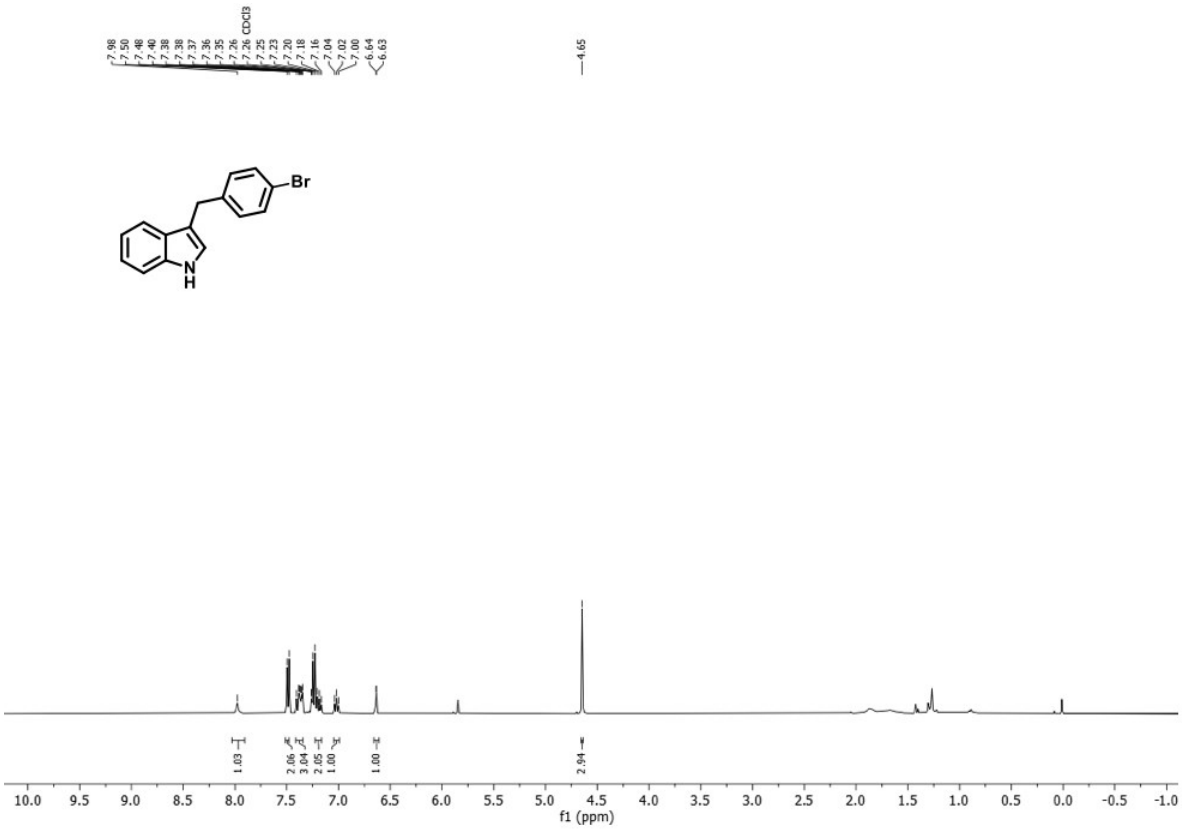


Figure S19. ^{1}H NMR spectrum of **2m** in $CDCl_3$.

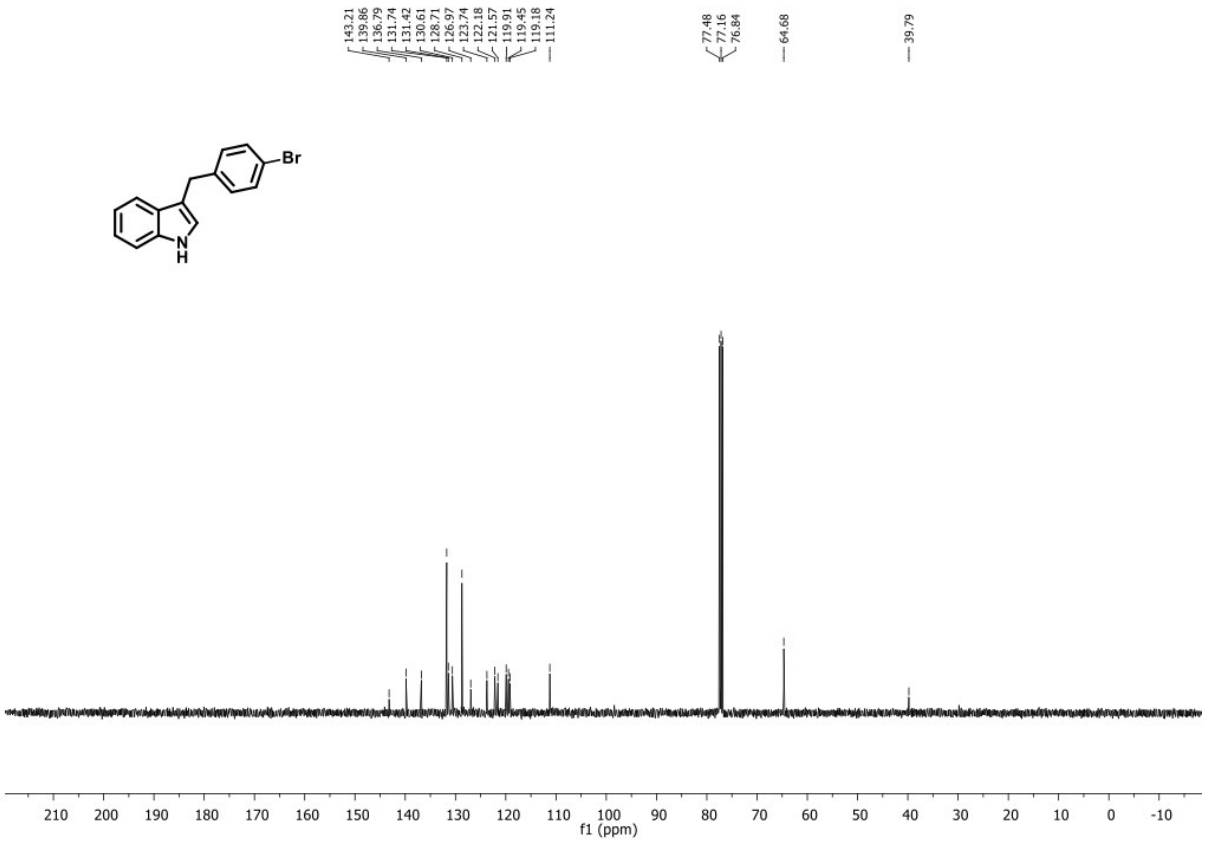


Figure S20. ^{13}C NMR spectrum of **2m** in $CDCl_3$

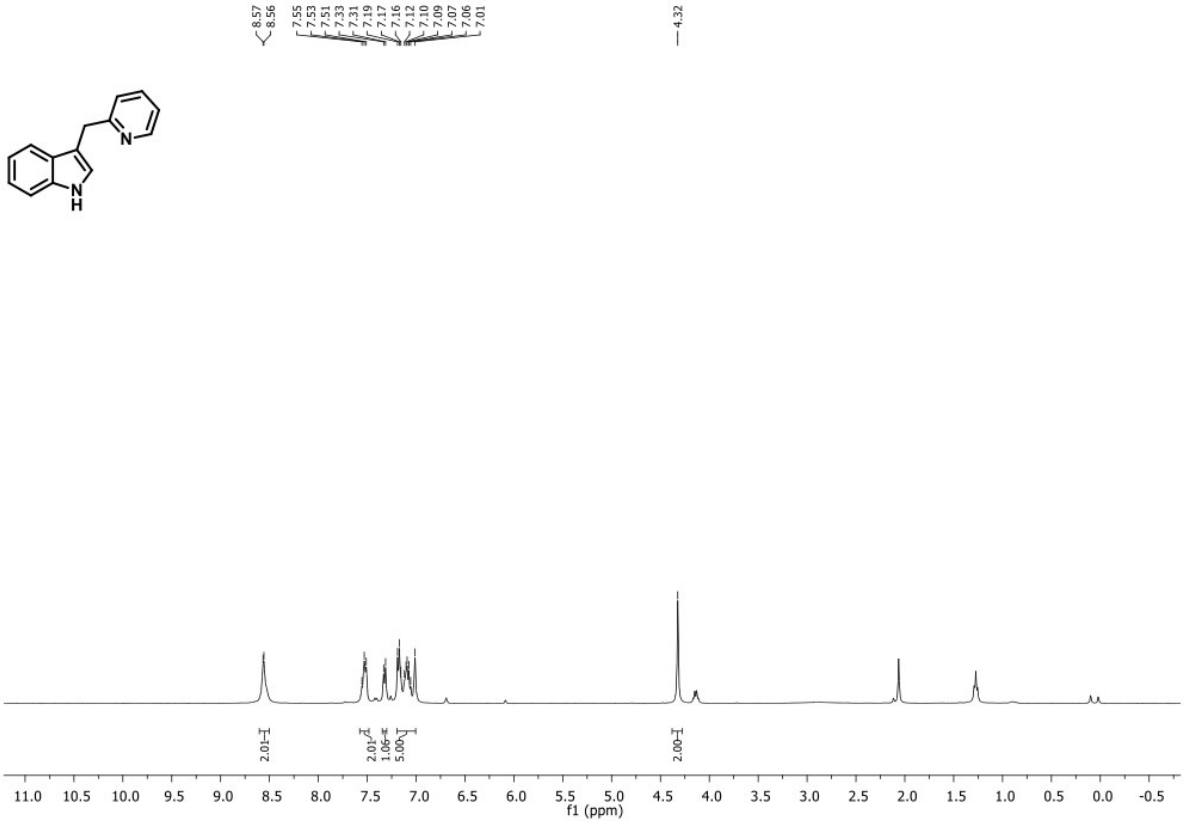


Figure S21. ^{1}H NMR spectrum of **2n** in $CDCl_3$.

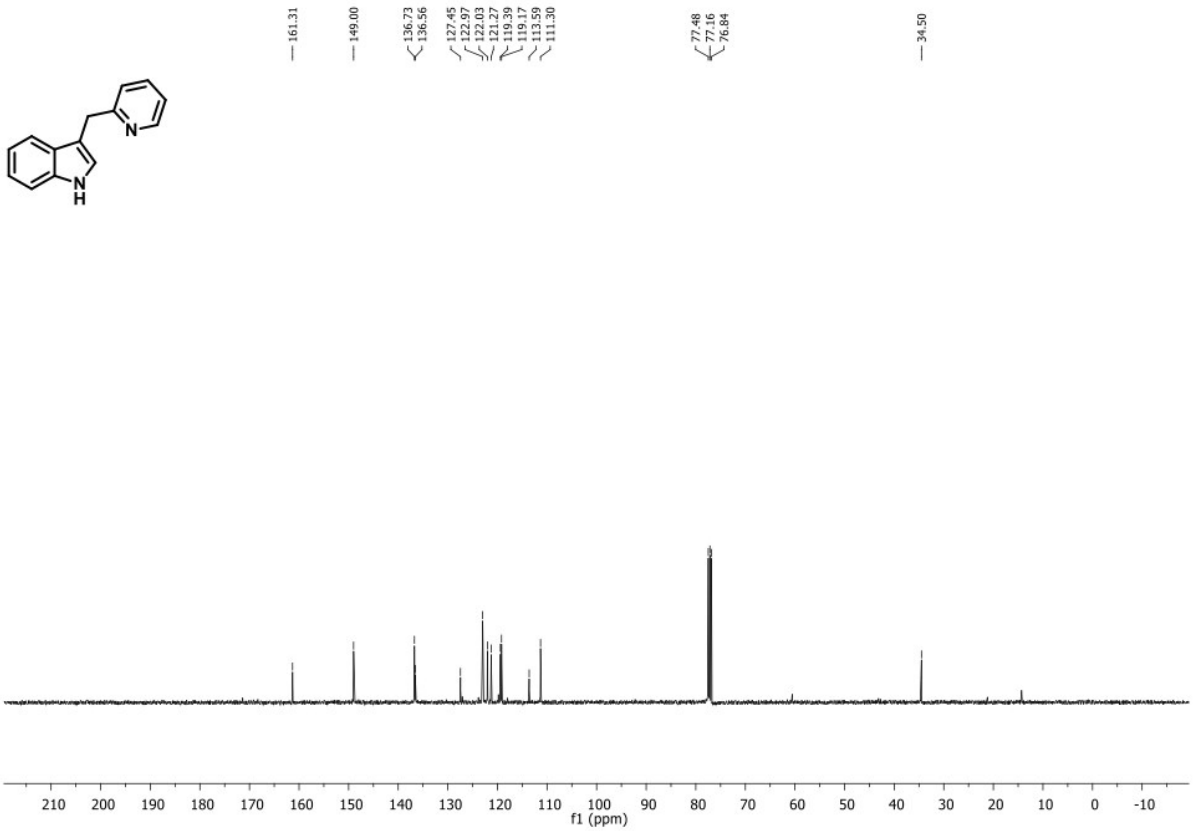


Figure S22. ^{13}C NMR spectrum of **2n** in $CDCl_3$

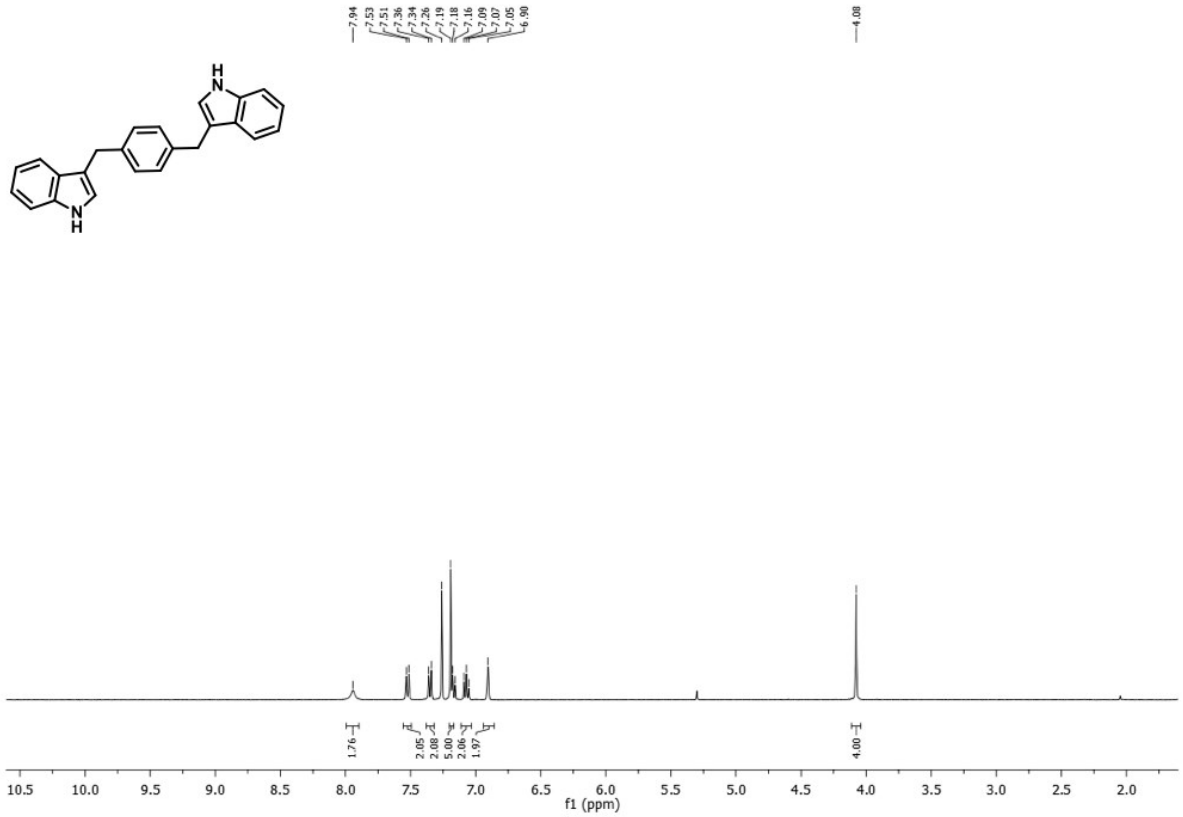


Figure S23. ^{1}H NMR spectrum of **2p** in $CDCl_3$.

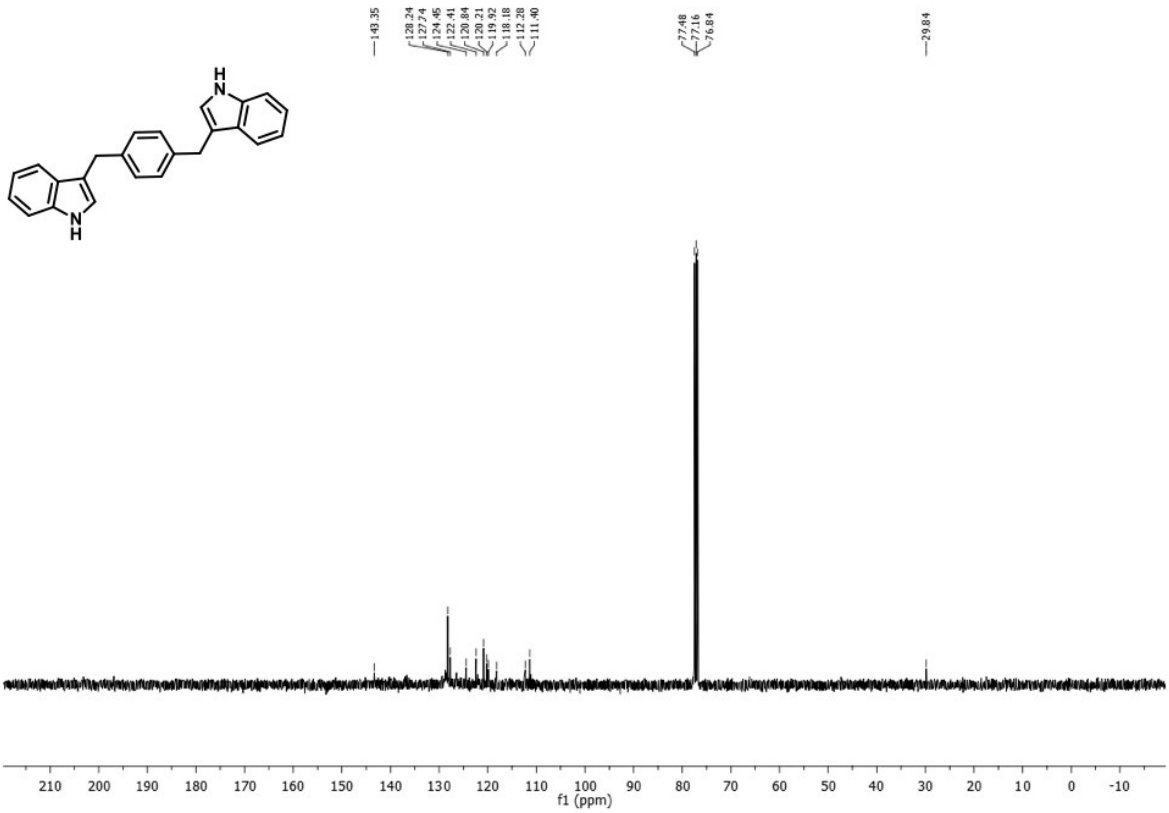


Figure S24. ^{13}C NMR spectrum of **2p** in $CDCl_3$

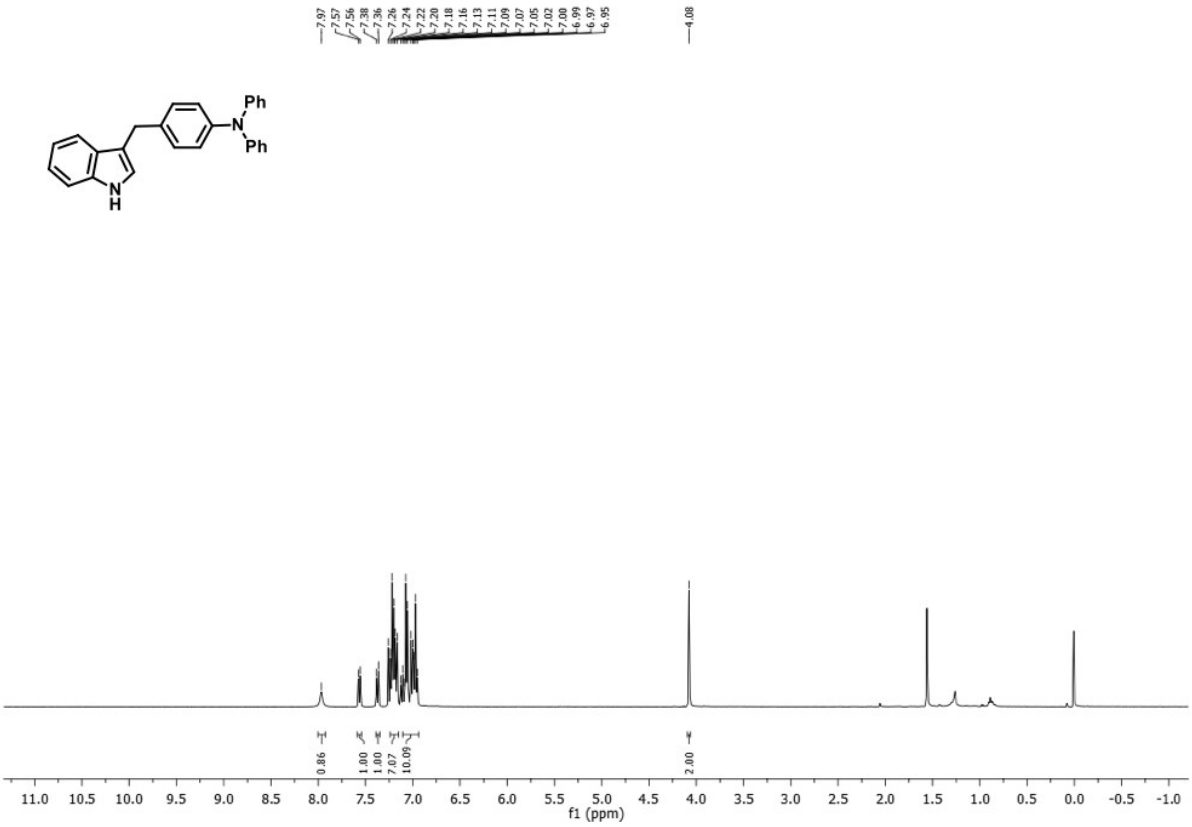


Figure S25. ^{1}H NMR spectrum of **2q** in $CDCl_3$.

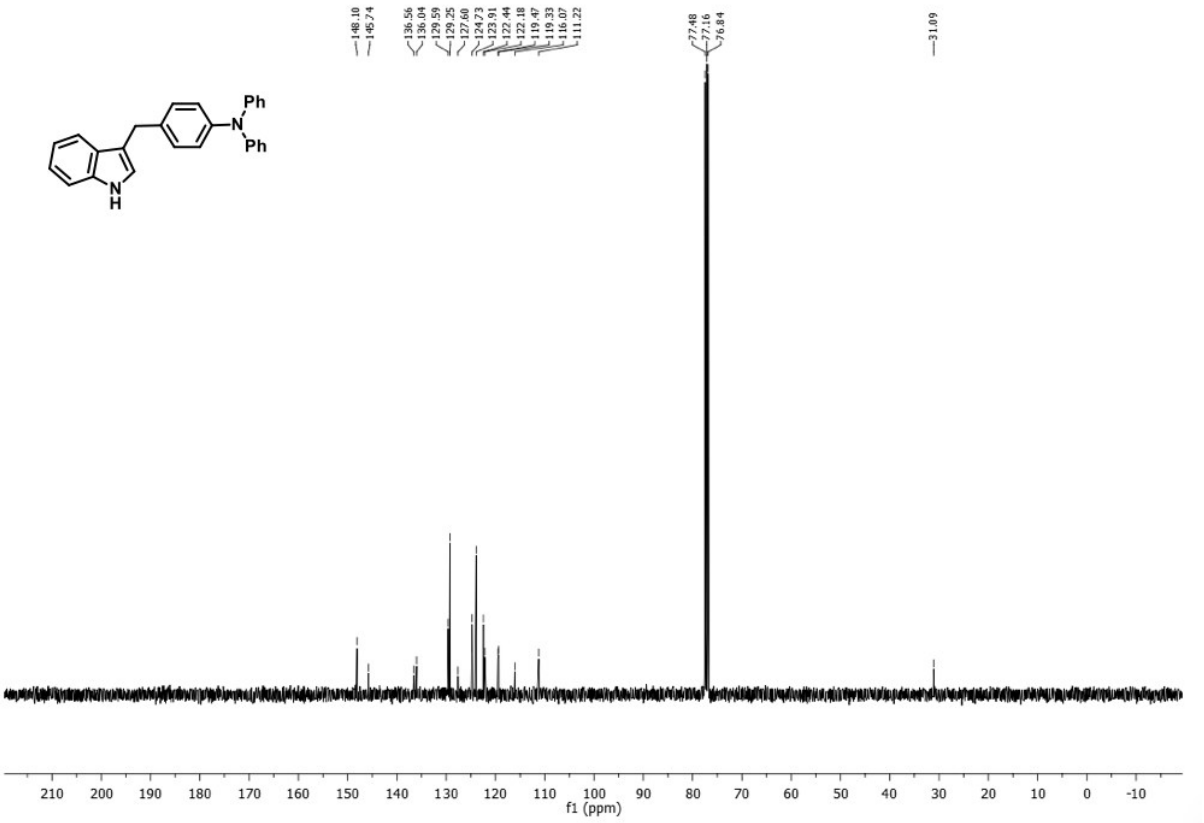


Figure S26. ^{13}C NMR spectrum of **2q** in $CDCl_3$

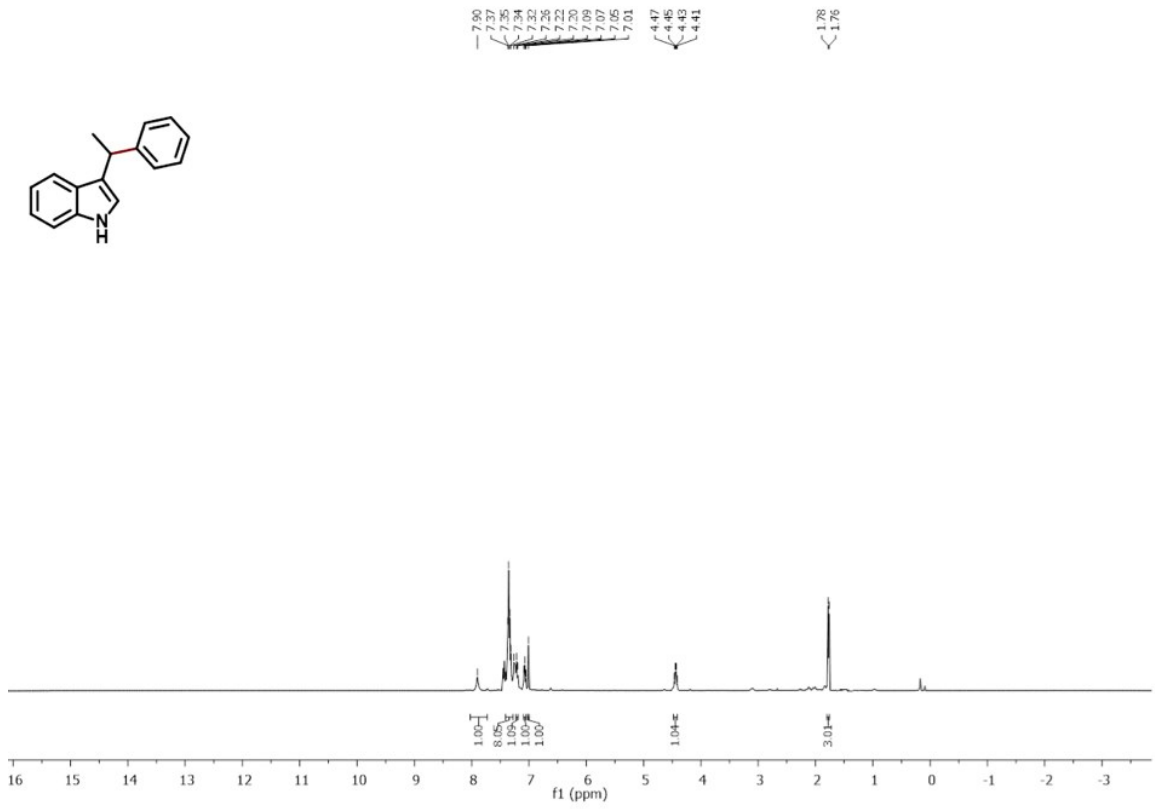


Figure S27. ^{1}H NMR spectrum of **3a** in $CDCl_3$.

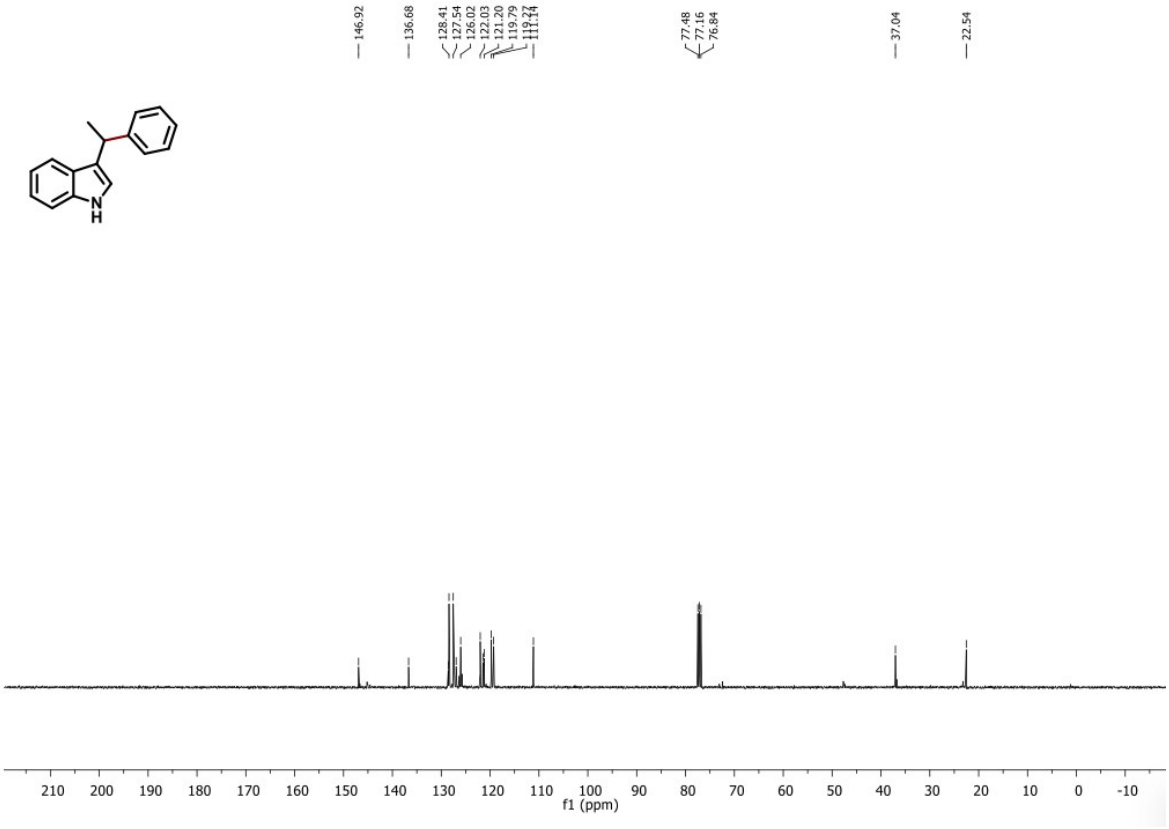


Figure S28. ^{13}C NMR spectrum of **3a** in $CDCl_3$

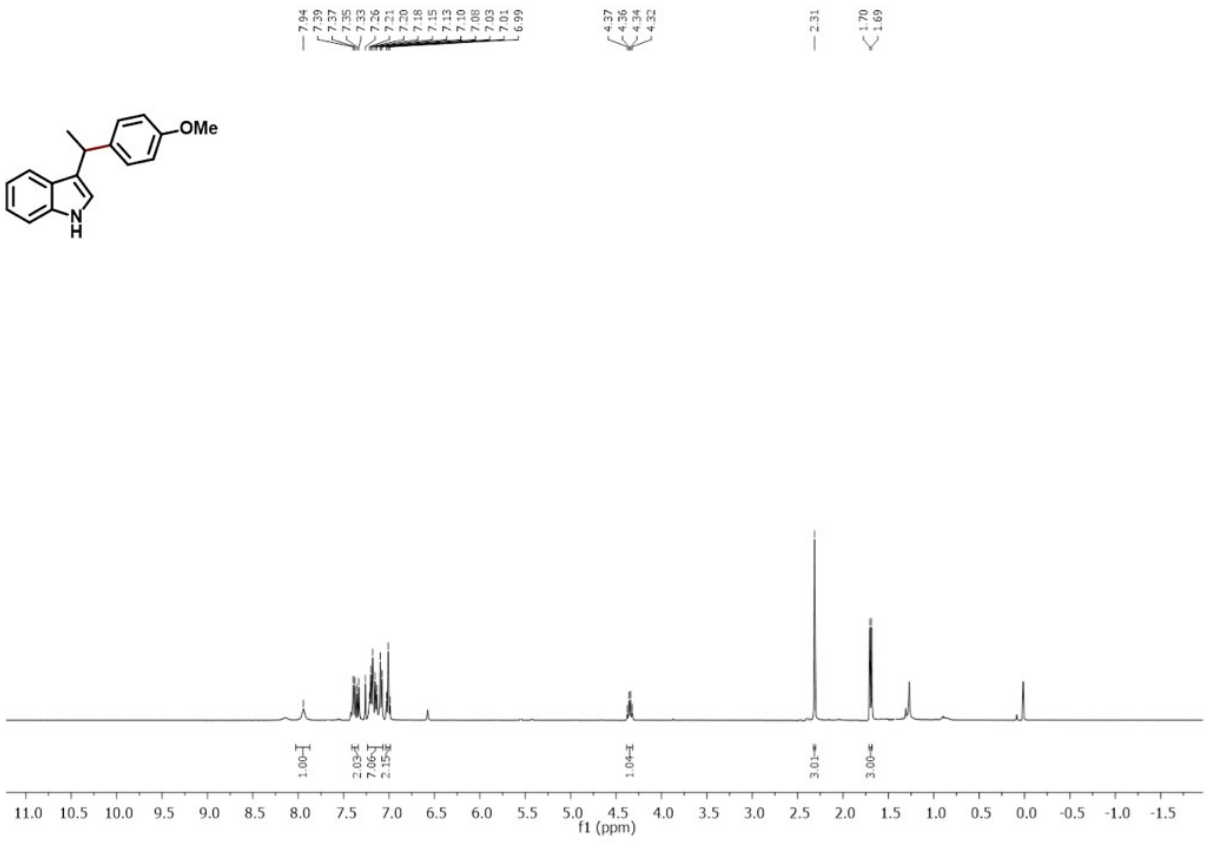


Figure S29. ^{1}H NMR spectrum of **3c** in $CDCl_3$.

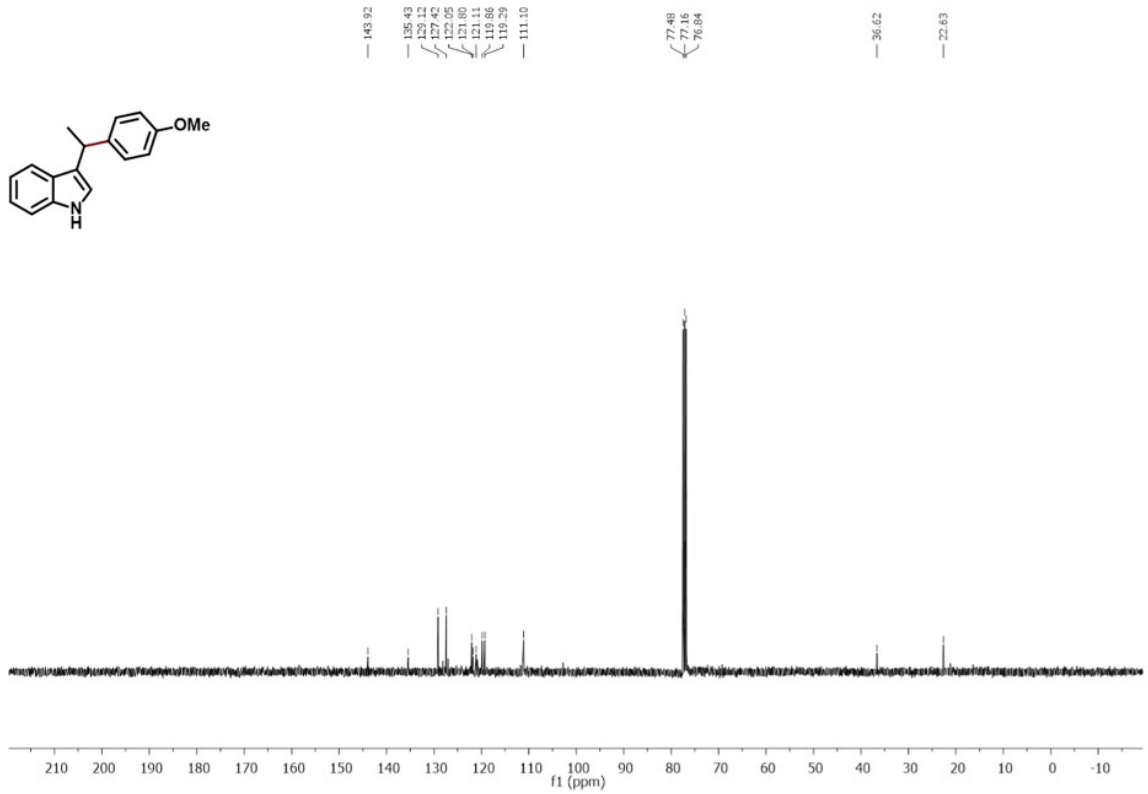


Figure S30. ^{13}C NMR spectrum of **3c** in $CDCl_3$

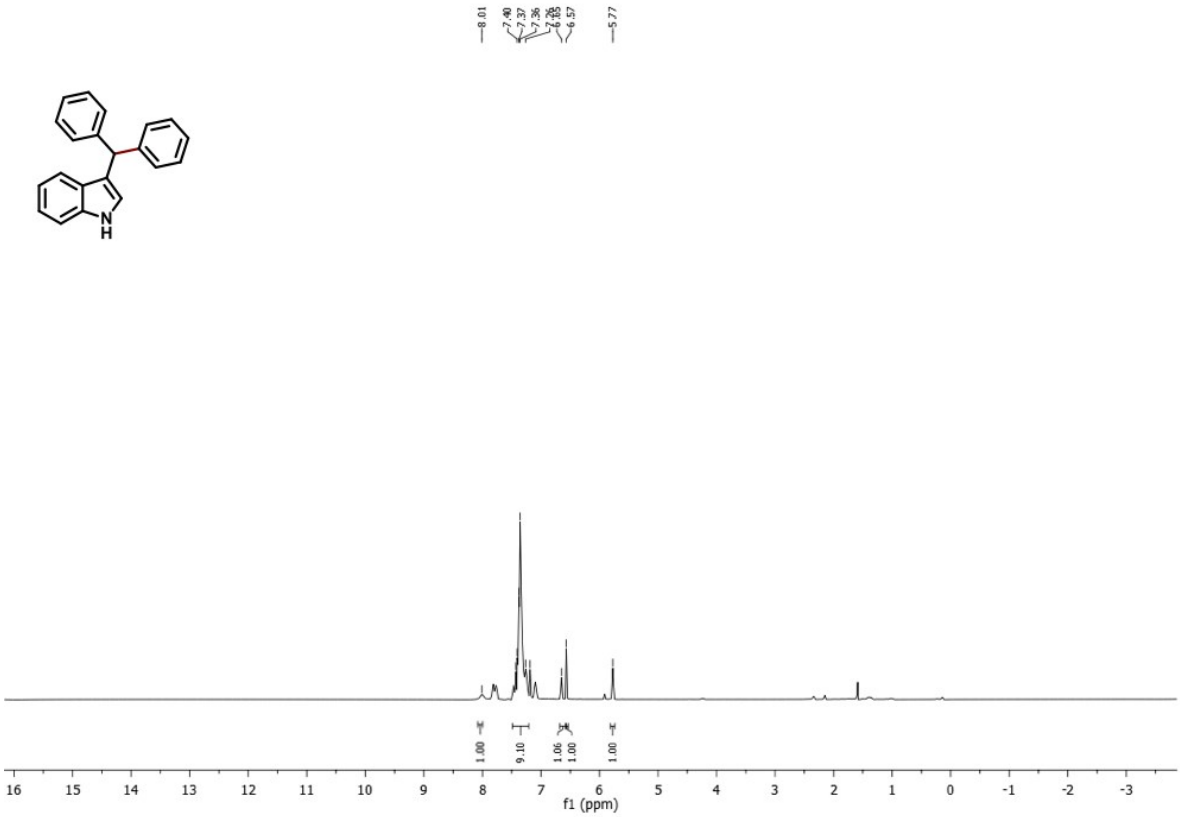


Figure S31. ^{1}H NMR spectrum of **3d** in $CDCl_3$.

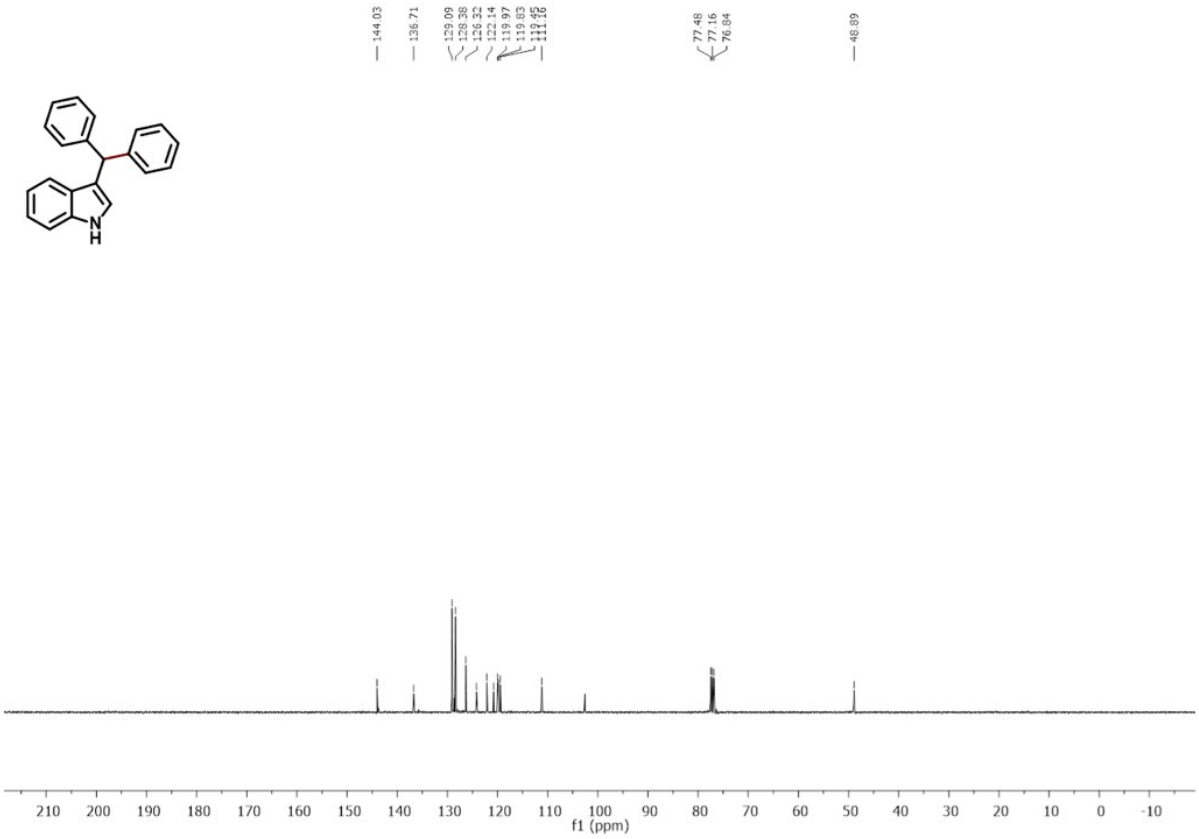


Figure S32. ^{13}C NMR spectrum of **3d** in $CDCl_3$

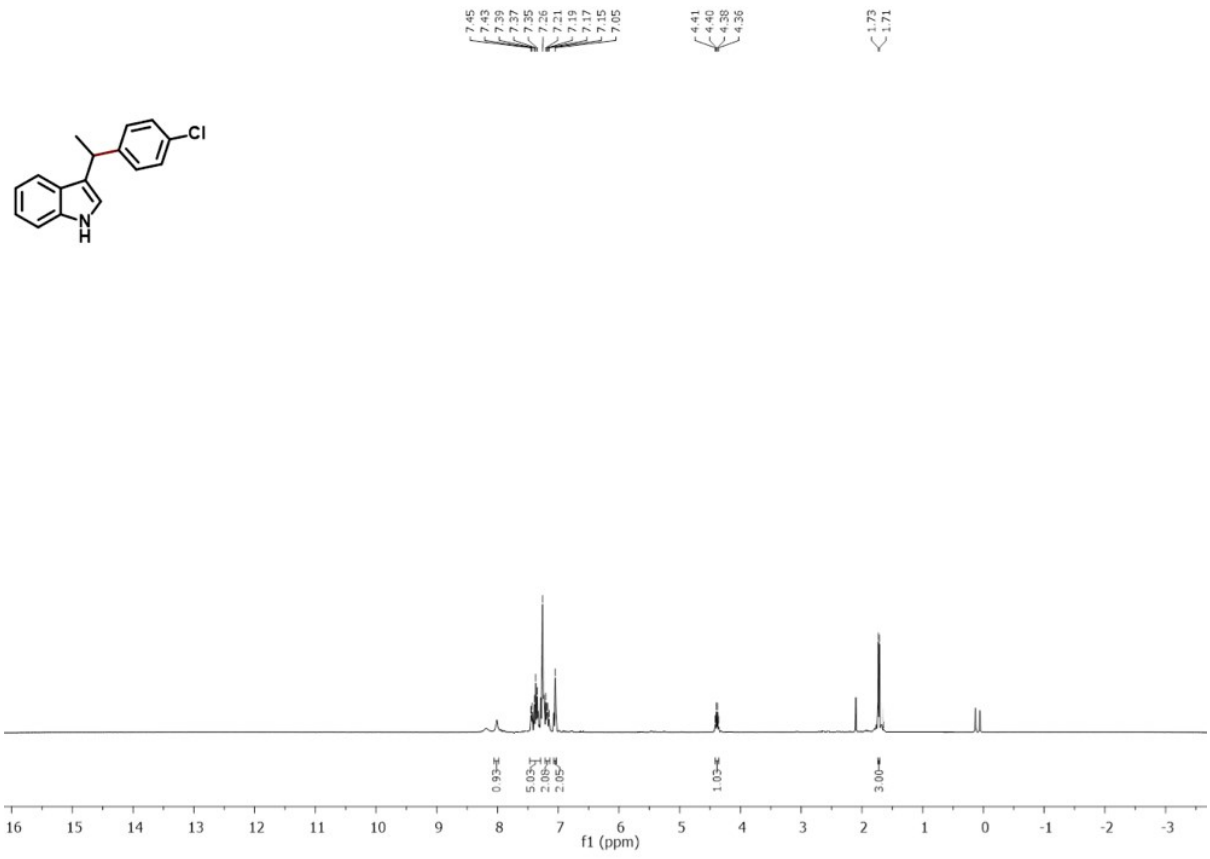


Figure S33. ^{1}H NMR spectrum of **3e** in $CDCl_3$

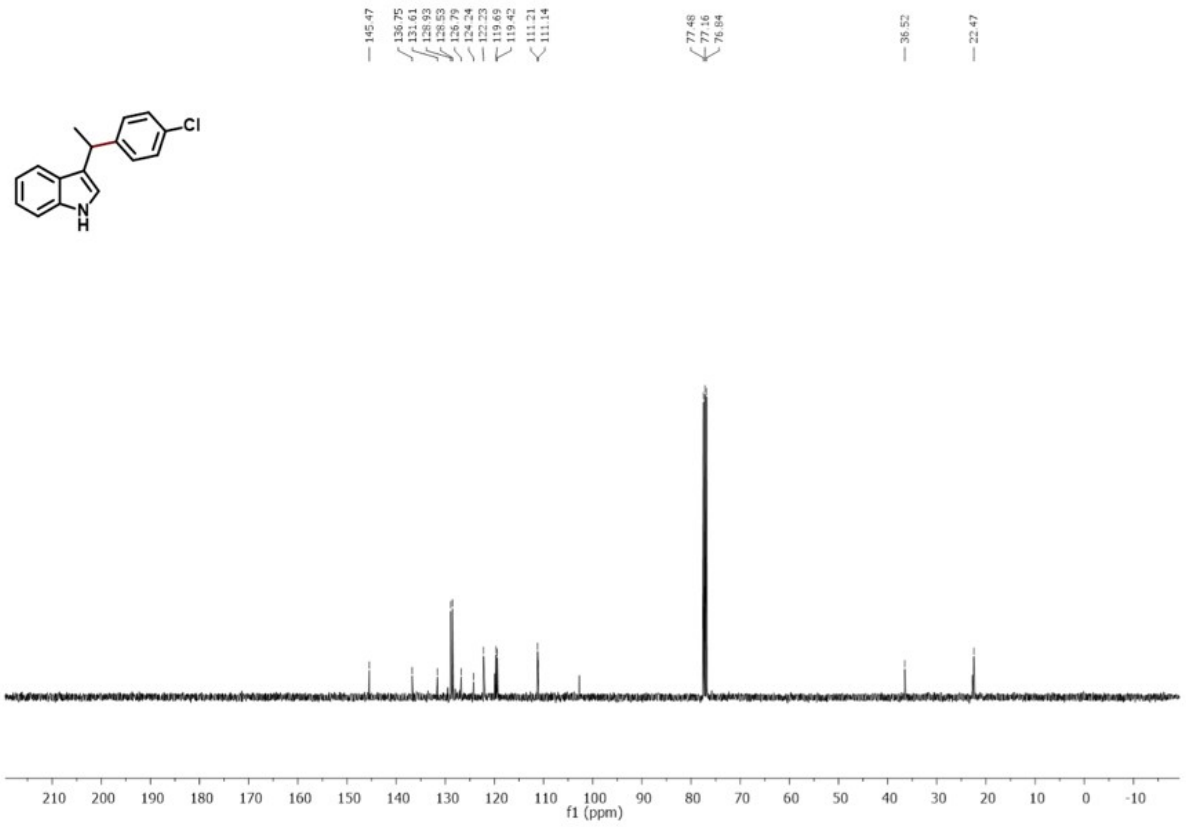


Figure S34. ^{13}C NMR spectrum of **3e** in $CDCl_3$

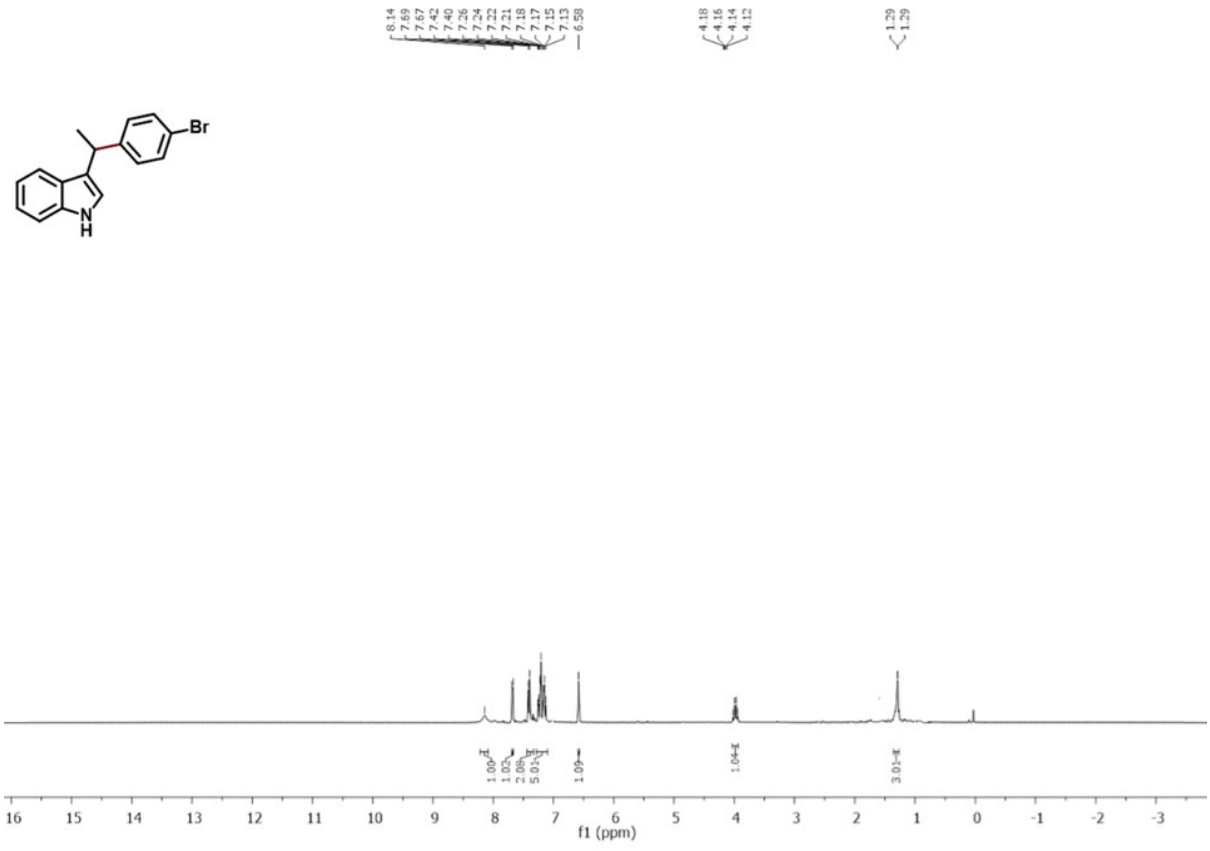


Figure S35. ^{1}H NMR spectrum of **3f** in $CDCl_3$.

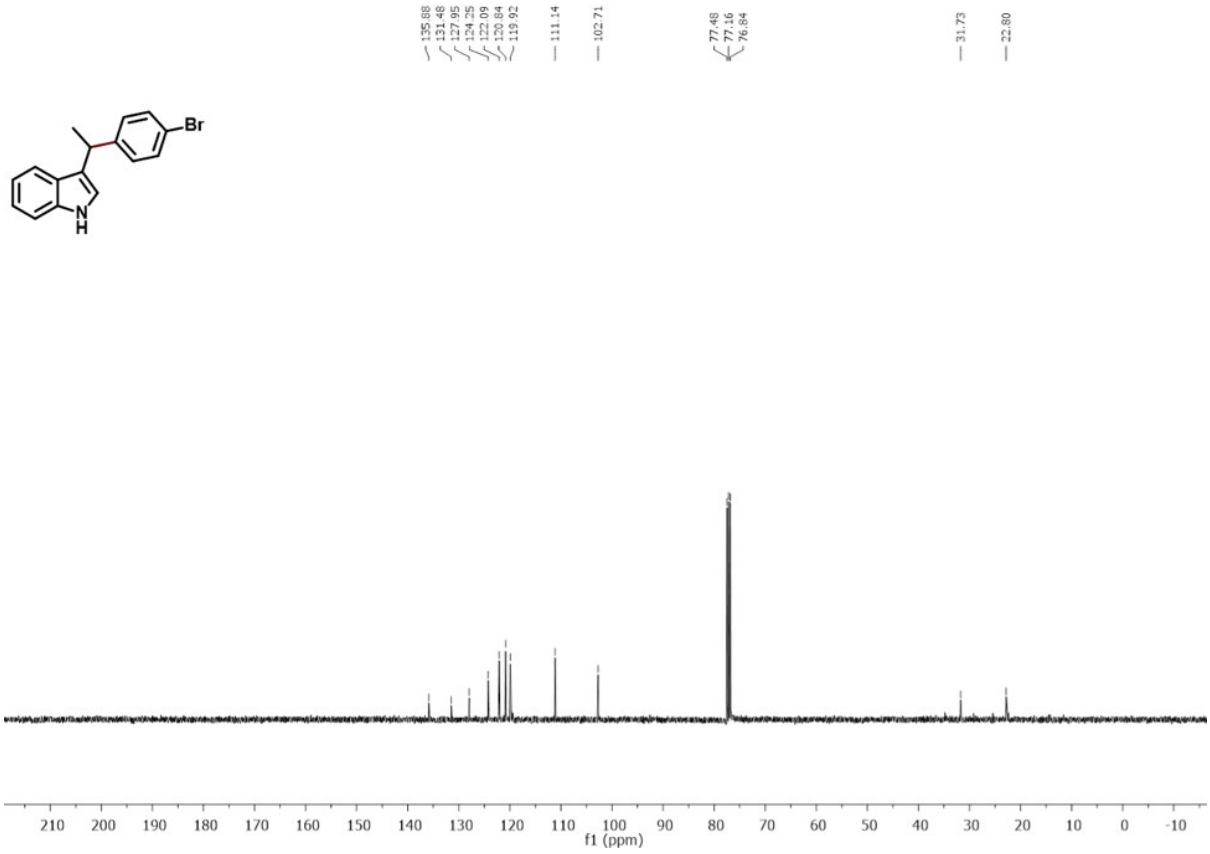


Figure S36. ^{13}C NMR spectrum of **3f** in $CDCl_3$

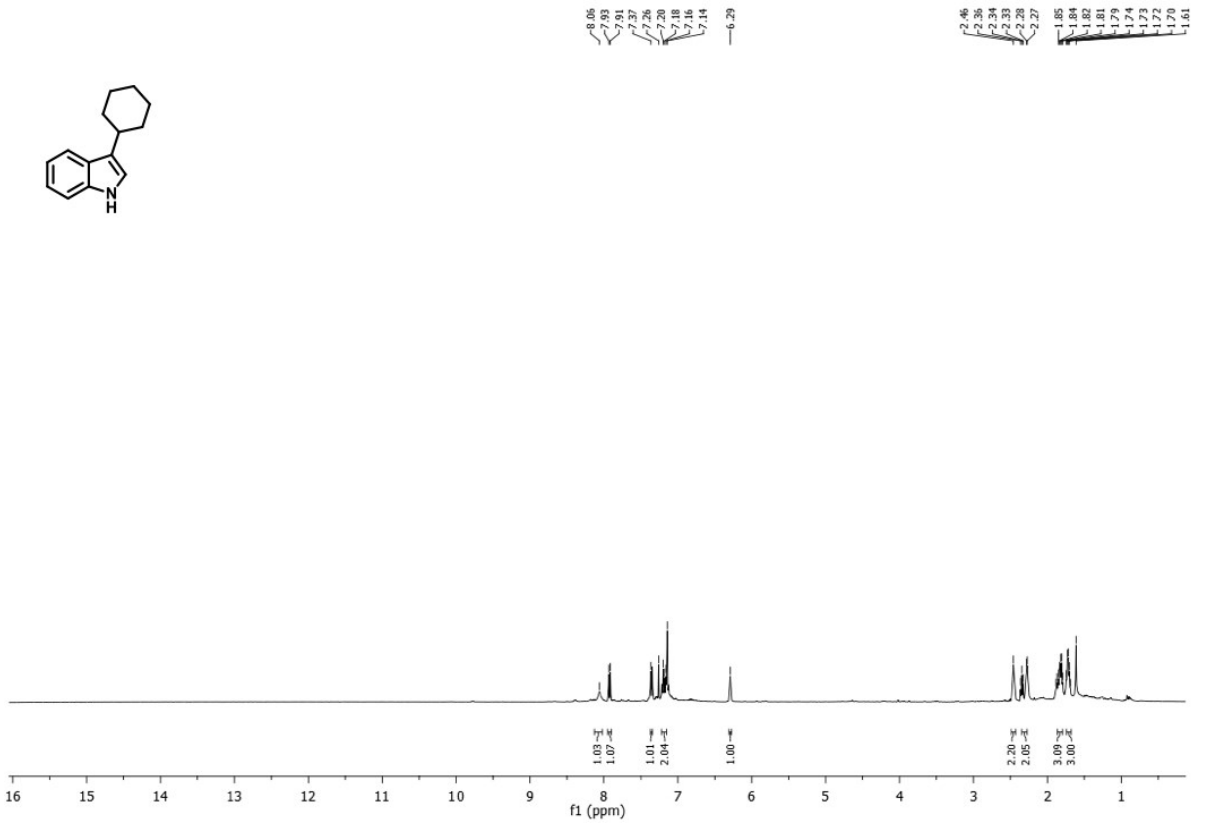


Figure S37. ^{1}H NMR spectrum of **3g** in $CDCl_3$.

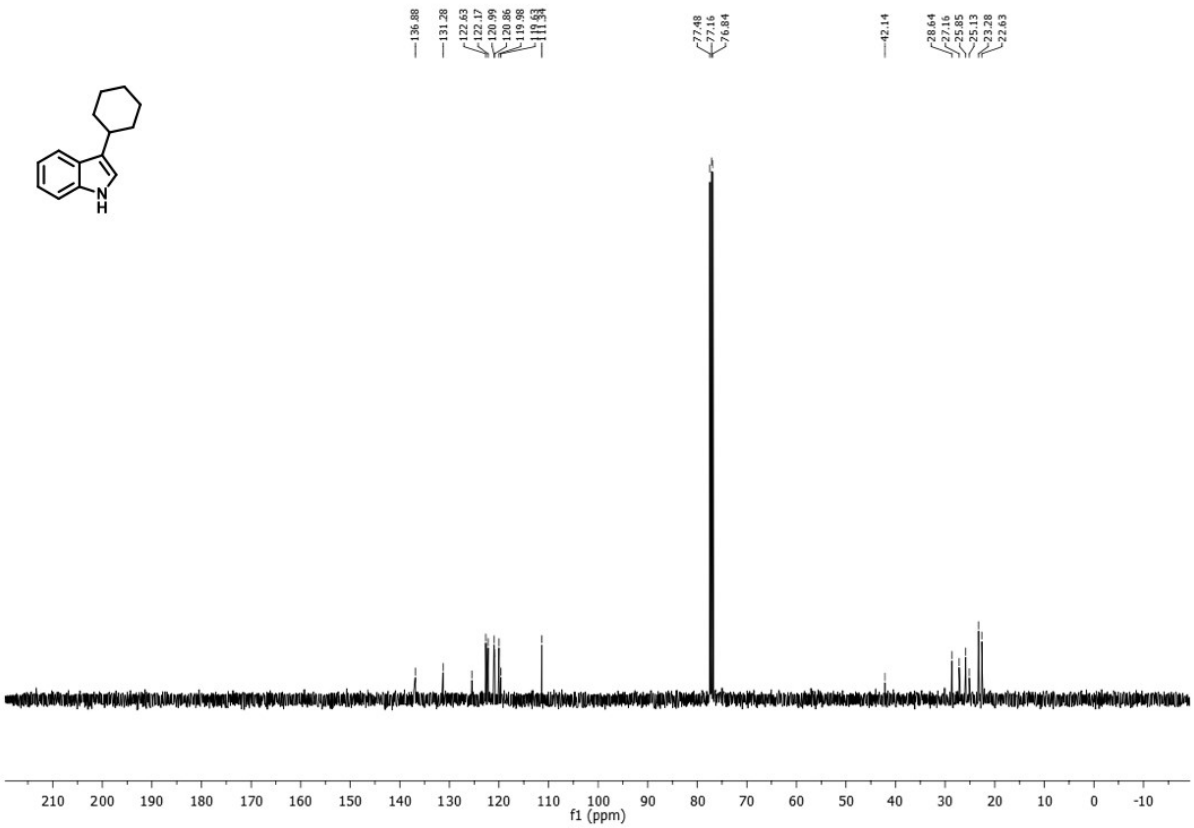


Figure S38. ^{13}C NMR spectrum of **3g** in $CDCl_3$

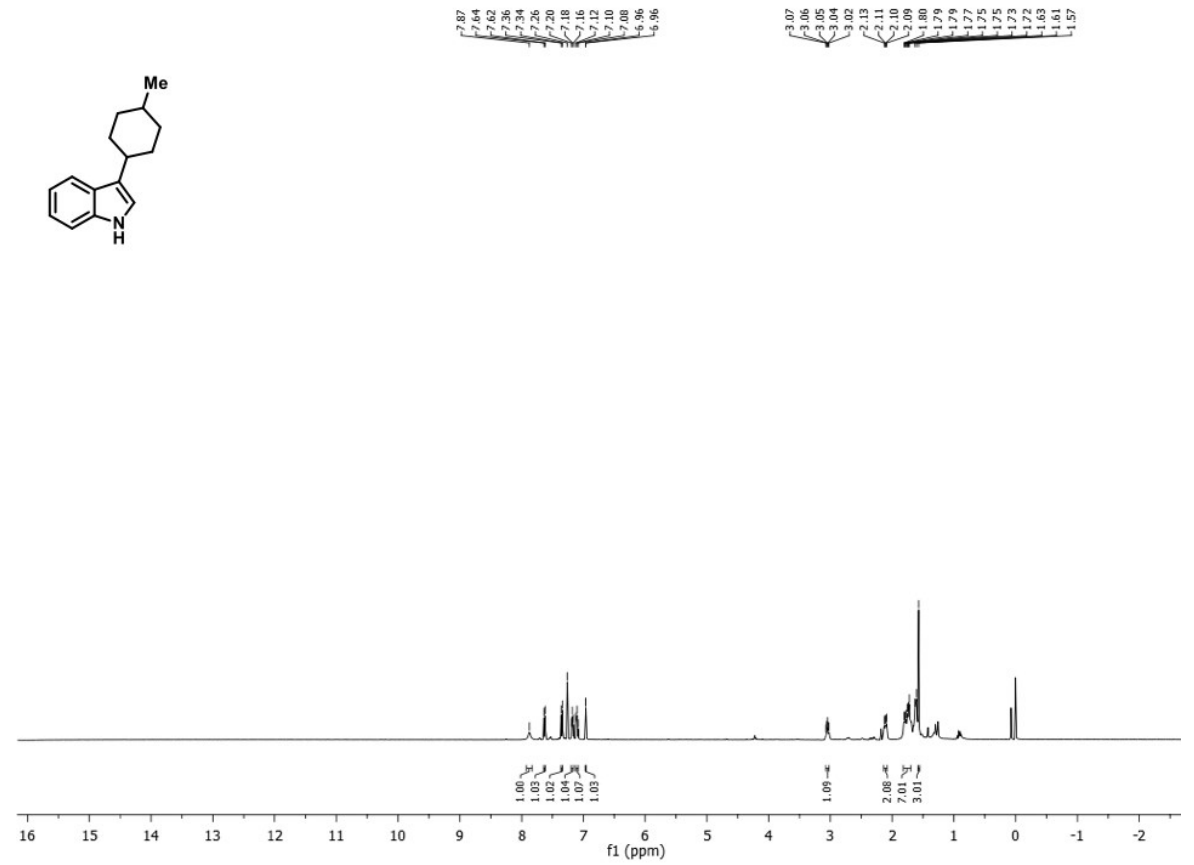


Figure S39. ^{1}H NMR spectrum of **3h** in $CDCl_3$.

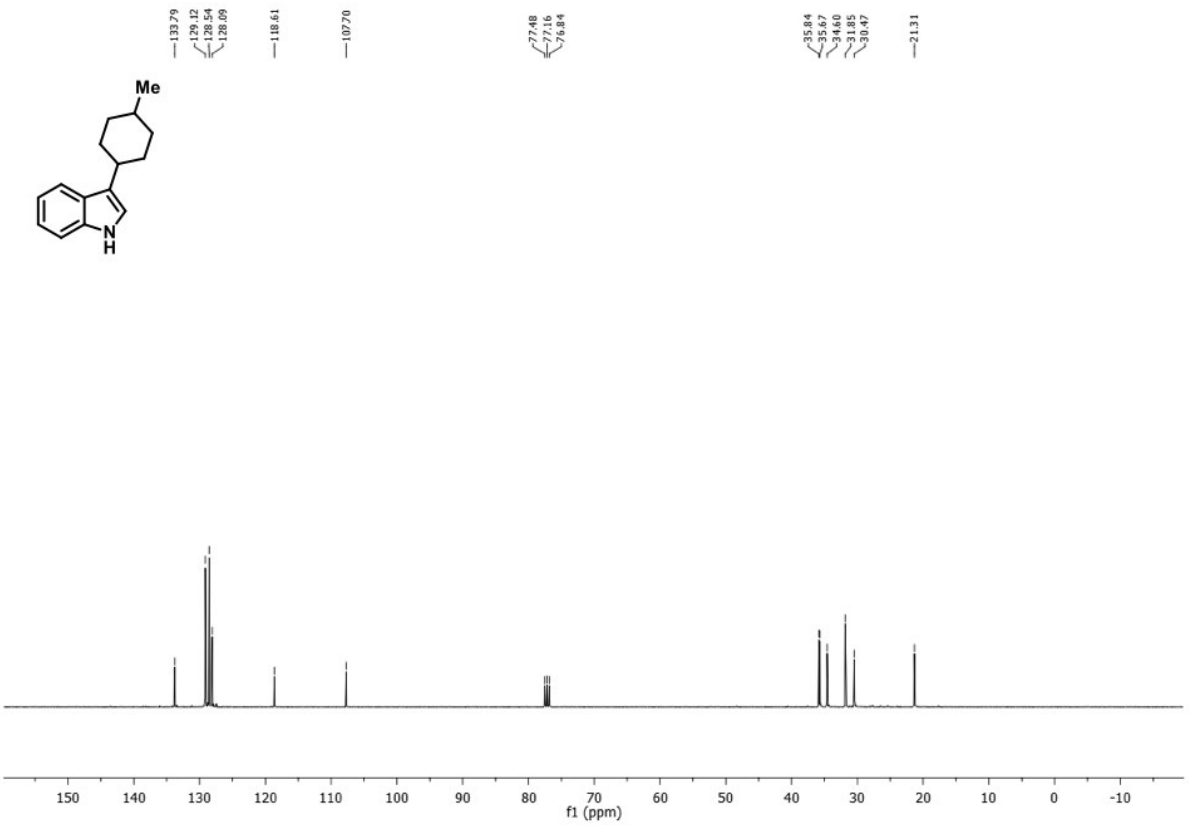


Figure S40. ^{13}C NMR spectrum of **3h** in $CDCl_3$

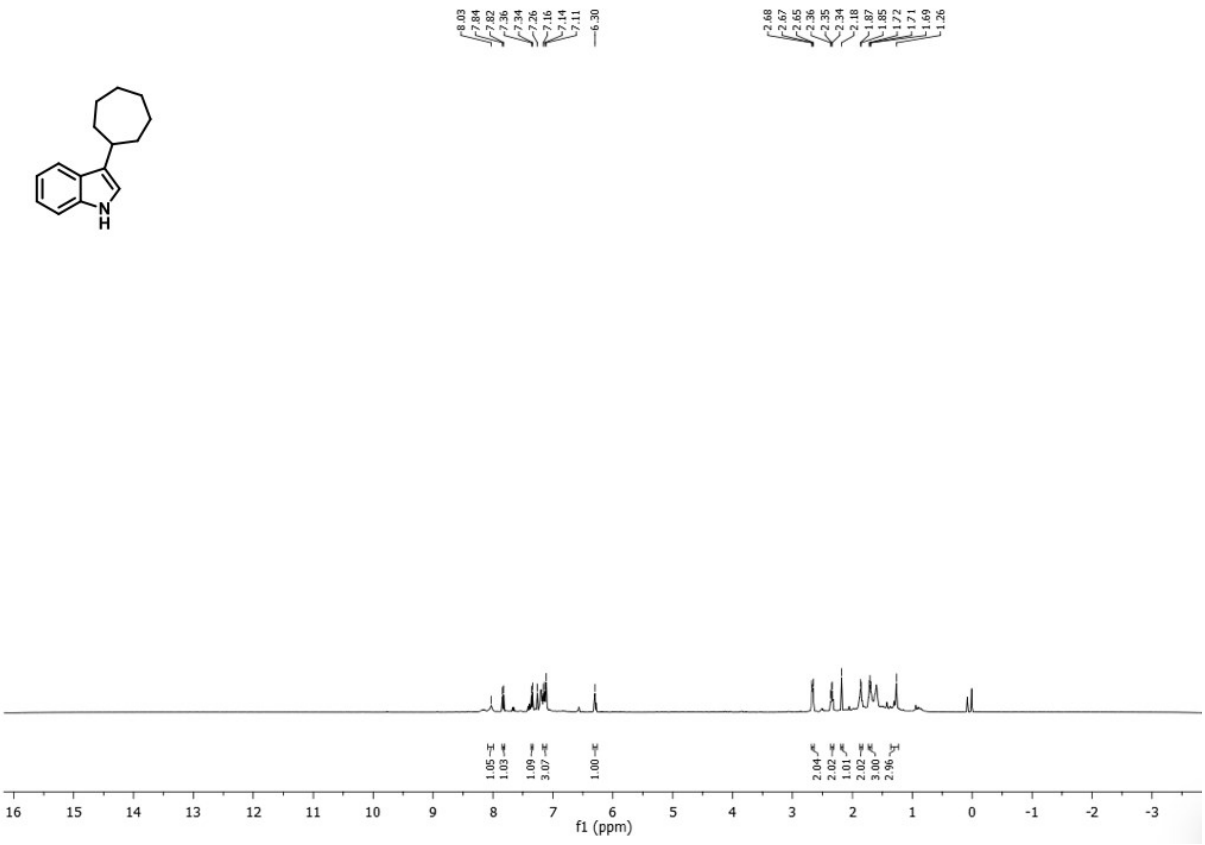


Figure S41. ^{1}H NMR spectrum of **3i** in $CDCl_3$.

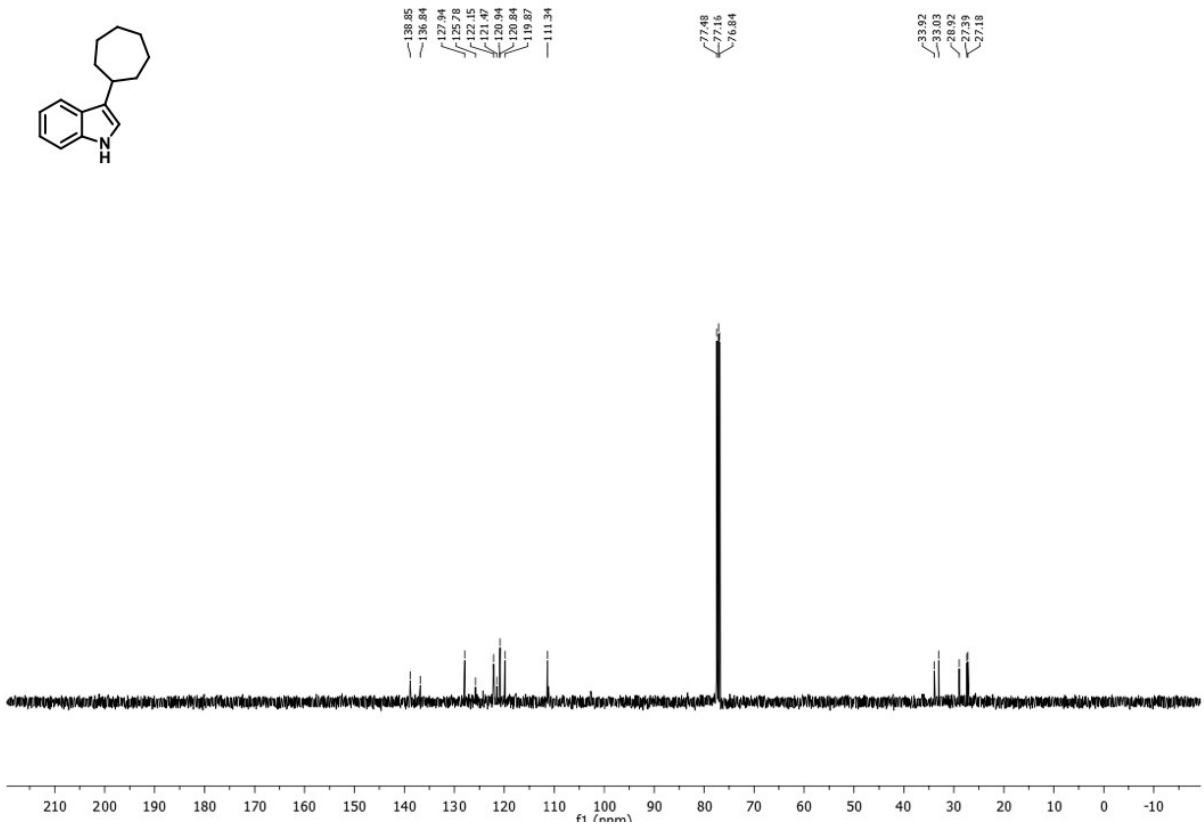


Figure S42. ^{13}C NMR spectrum of **3i** in $CDCl_3$

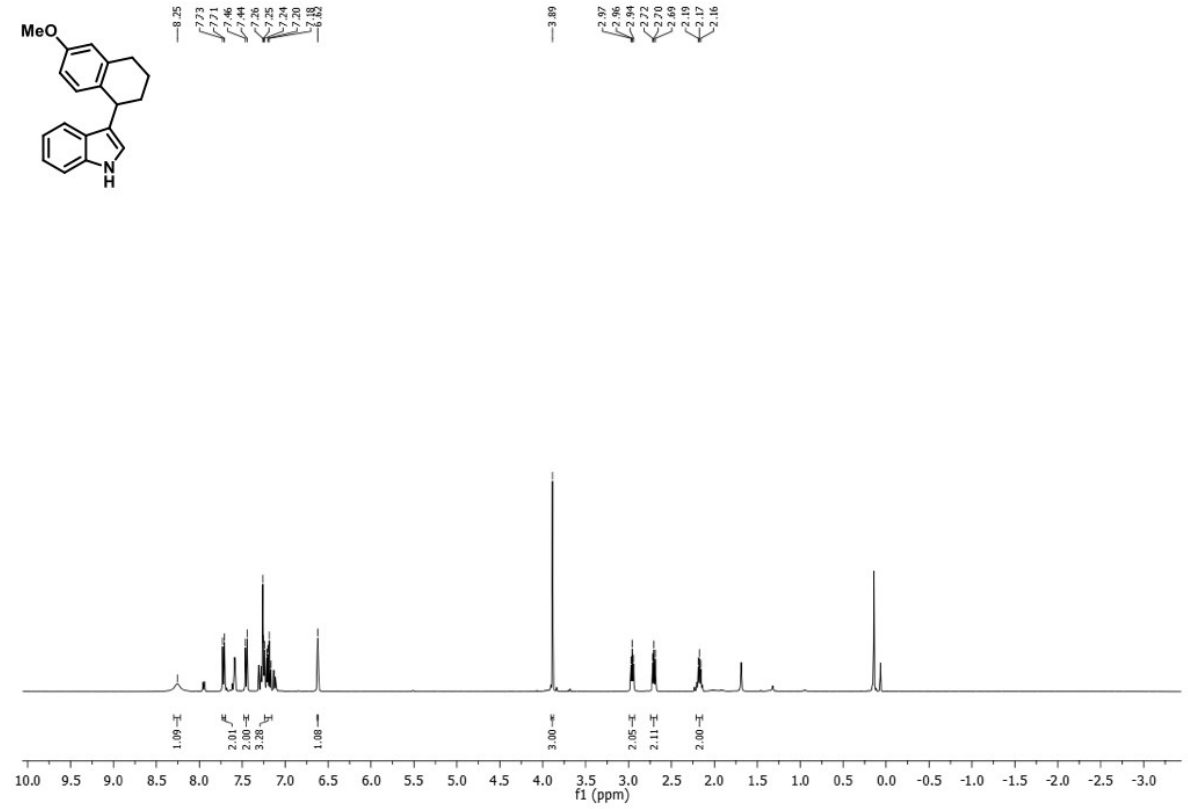


Figure S43. ^{1}H NMR spectrum of **3j** in $CDCl_3$.

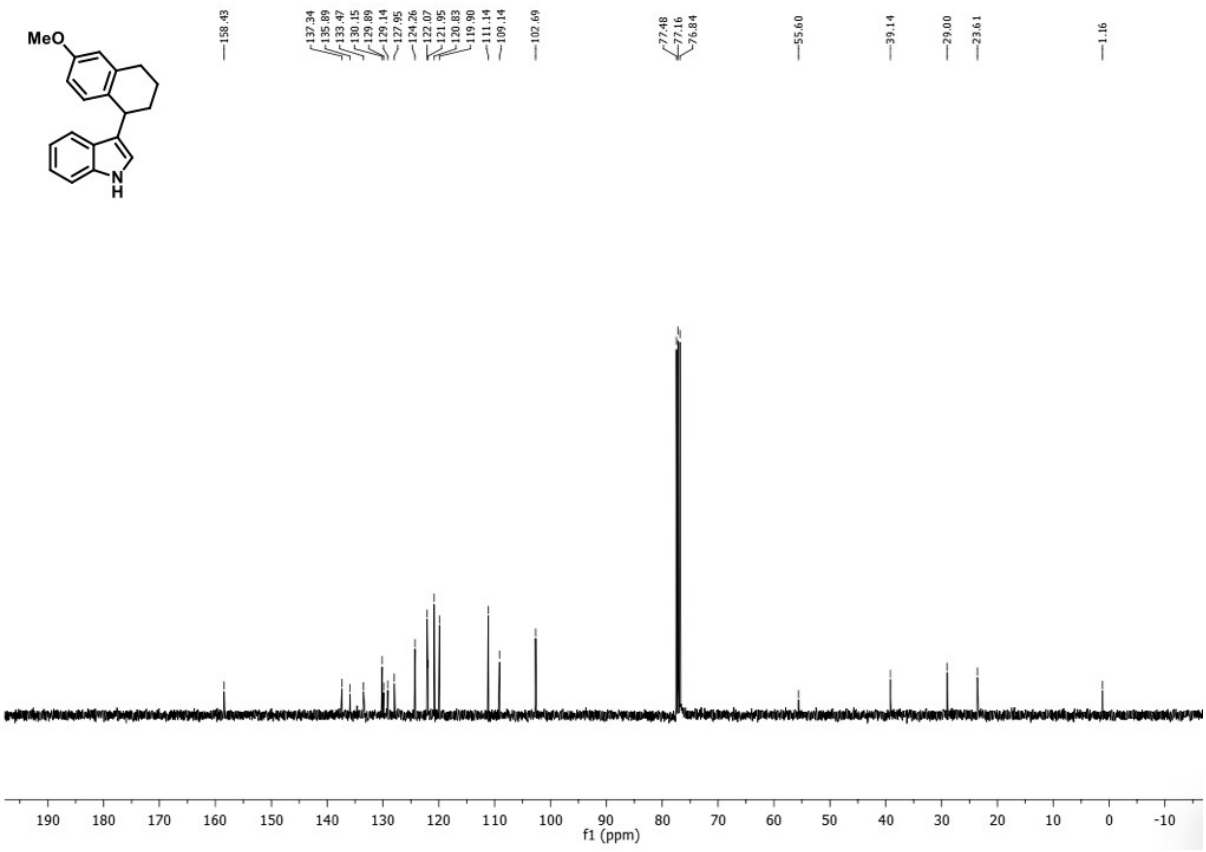


Figure S44. ^{13}C NMR spectrum of **3j** in $CDCl_3$

8. Analytical data for synthesized products

3-(Phenylmethyl)-1*H*-indole (2a): Pink solid (163 mg, 79%), eluent combination: hexane/ethyl acetate (10:1). Spectroscopic data matched those reported in the literature[S4]. ^1H NMR ($CDCl_3$, 400 MHz): δ7.93 (s,1H), 7.59-7.57 (d, 1H), 7.40-7.34 (m, 5H),7.31-7.23 (m, 2H), 7.16-7.12 (t, 1H), 6.93 (s, 1H), 4.17 (s, 2H) ppm.; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 141.31, 136.52, 128.80, 128.45, 127.54, 125.99, 122.45, 122.14, 119.46, 119.26, 115.89, 111.19, 31.71 ppm.

3-(2-Methylbenzyl)-1*H*-indole (2b): Brown solid (160 mg, 74%), eluent combination: hexane/ethyl acetate (10:1). Spectroscopic data matched those reported in the literature[S2]. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.76 (s, 1H), 7.70 (d, 1H), 7.40 (d, 1H), 7.33 (t, 2H), 7.27−7.23 (m, 3H), 7.17 (d, 1H), 6.92 (s, 1H), 4.22 (s, 2H), 2.46 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 139.05, 136.42, 130.09, 129.37, 127.53, 126.14, 125.91, 122.35, 122.02, 119.30, 115.18, 111.04, 29.23, 19.47.ppm

3-(2-Methoxybenzyl)-1*H*-indole (2c): Brown solid (190 mg, 81%), eluent combination: hexane/ethyl acetate (10:1). Spectroscopic data matched those reported in the literature [S2]. ^1H NMR ($CDCl_3$, 400 MHz): 7.93 (s, 1H), 7.56-7.54 (d, 1H), 7.37-7.35 (d, 1H), 7.26-7.19 (m, 3H), 7.11 (t, 1H), 6.90 (s, 1H), 6.84 (d, 2H), 4.09 (s, 2H), 3.80 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 157.90, 136.58, 133.43, 129.70, 127.53, 122.35, 122.11, 119.41, 199.27, 116.35, 113.85, 55.38, 30.80 ppm.

3-(2-Chlorobenzyl)-1*H*-indole (2d): Pink solid (174 mg, 73%), eluent combination: hexane/ethyl acetate (10:1). Spectroscopic data matched those reported in the literature [S2]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.99 (s, 1H), 7.48-7.46 (d,1H), 7.38-7.36 (m, 1H), 7.25-7.18 (m, 5H), 7.10-7.06 (m, 1H) 6.93 (s, 1H), 4.09 (s, 2H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 139.80, 131.71, 130.13, 128.54, 127.39, 122.49, 122.32, 119.61, 119.18, 115.39, 111.27, 31.12 ppm.

3-(4-Methylbenzyl)-1*H*-indole (2e): Pinkish solid (161 mg, 73%), eluent combination: hexane/ethyl acetate (10:1). Spectroscopic data matched those reported in the literature [S2]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.91 (s, 1H), 7.57-7.55 (d, 1H), 7.37-7.35 (d, 1H), 7.26−7.19 (m, 3H), 7.13−7.09 (m, 3H), 6.91 (s, 1H), 4.11 (s, 2H), 2.35 (s, 3H) ppm.

3-(4-Methoxybenzyl)-1*H*-indole (2f): Brown solid (142 mg, 76%), eluent combination: hexane/ethyl acetate (10:1). Spectroscopic data matched those reported in the literature [S2]. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.93 (s, 1H), 7.56-7.54 (d, 1H), 7.37-7.35 (d, 1H), 7.26-7.19 (m, 3H), 7.13-7.11 (t, 1H), 6.90-6.84 (m, 3H), 4.09 (s, 2H), 3.80 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 157.90, 136.58, 133.43, 129.70, 127.53, 122.35, 122.11, 119.41, 119.27, 116.35, 113.85, 111.18, 55.38, 30.80 ppm.

3-(4-Ethylbenzyl)-1*H*-indole (2g): Pink solid (162 mg, 69%), eluent combination: hexane/ethyl acetate (10:1). Spectroscopic data matched those reported in the literature [S3]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.92 (s, 1H), 7.61-7.59 (d, 1H), 7.40-7.38 (d, 1H), 7.28-7.23 (m, 3H), 7.18-7.13 (m, 3H), 6.94 (s, 1H), 4.15 (s, 2H), 2.71-2.65 (m, 2H), 1.30-1.26 (t, 3H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 141.81, 138.51, 136.52, 128.71, 127.93, 127.59, 122.40, 122.10, 119.41, 119.29, 116.14, 111.17, 31.26, 28.58, 15.82 ppm.

3-(4-Isopropylbenzyl)-1*H*-indole (2h): Pink solid (161 mg, 65%) eluent combination: hexane/ethyl acetate (10:1).^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.89 (s, 1H), 7.60-7.58 (d, 1H), 7.37-7.35 (d, 1H), 7.26-7.22 (m, 3H), 7.19-7.11 (m, 4H), 6.91 (s, 1H), 4.12 (s, 2H), 2.9-2.7 (m, 1H), 1.28-1.26 (d, 6H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 146.47, 138.66, 136.52, 128.67, 127.62, 126.48, 122.42, 122.09, 119.40, 119.29, 116.10, 111.18, 33.82, 31.22, 24.22 ppm. IR (KBr pellet): 3412, 2962, 2362, 1262, 1092, 800, 752, 496, 410 cm^{-1}; HRMS (ESI) m/z calcd for $C_{18}H_{18}N$ $(M-H)^+$: 248.1439, found 248.1414.

3-(Naphthalen-2-ylmethyl)-1*H*-indole (2i): Pink solid (191 mg, 75%), eluent combination: hexane/ethyl acetate (10:1). Spectroscopic data matched those reported in the literature. [S2] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.13 (s, 1H), 7.91-7.85 (m, 4H), 7.68-7.66 (d, 1H), 7.46−7.40 (m, 3H), 7.38-7.35 (m, 1H), 7.24-7.22 (m, 1H), 7.18-716 (m, 1H), 6.69 (m, 1H), 4.57 (s, 2H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 136.88, 136.44, 133.96, 132.27, 128.72, 127.56, 126.98, 126.74, 125.90, 125.77, 125.60, 124.50, 122.92, 122.18, 119.50, 119.14, 115.48, 111.23, 29.07 ppm.

3-(Biphenyl-3-ylmethyl)-1*H*-indole (2j): Orange solid (210 mg, 76%), eluent combination: hexane/ethyl acetate (10:1). Spectroscopic data matched those reported in the literature. [S2] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.98 (s, 1H), 7.60-7.56 (m, 3H), 7.55-7.51 (d, 2H), 7.45-7.31 (m, 2H), 7.23-7.19 (t, 1H), 7.13-7.09 (t, 1H), 6.97 (s, 1H), 4.17 (s, 2H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 141.23, 140.48, 138.93, 136.57, 129.20, 128.84, 127.56, 127.21, 127.13, 122.50, 122.22, 119.52, 119.29, 115.80, 111.23, 31.36 ppm.

3-(4-Fluorobenzyl)-1*H*-indole (2k): Pink solid (140 mg, 64%), eluent combination: hexane/ethyl acetate (10:1). Spectroscopic data matched those reported in the literature. [S2] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.99 (br s, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.23−7.14 (m, 3H), 7.13− 6.99 (m, 4H), 4.15 (s, 2H) ppm.

3-(4-Chlorobenzyl)-1*H*-indole (2l): Pink solid (190 mg, 79%), eluent combination: hexane/ethyl acetate (10:1). Spectroscopic data matched those reported in the literature [S2]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.94 (s, 1H), 7.50-7.48 (d, 1H), 7.37-7.35 (d, 1H), 7.26-7.12 (m, 5H), 7.10-7.08 (t, 1H), 6.90 (s, 1H), 4.09 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 139.78, 136.56, 131.69, 130.11, 128.52, 127.35, 122.48, 122.29, 119.58, 119.16, 115.33, 111.27, 31.74 ppm.

3-(4-Bromobenzyl)-1*H*-indole (2m): Brown solid (200 mg, 71%), eluent combination: hexane/ethyl acetate (10:1). Spectroscopic data matched those reported in the literature [S2\4]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.98 (s, 1H), 7.50-7.48 (d, 2H), 7.40-7.35 (m, 3H), 7.25-7.16 (m, 2H), 7.04 -7.0 (t, 1H), 6.64-6.63 (s, 1H), 4.65 (s, 2H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 143.21, 139.86, 136.79, 131.74, 131.42, 130.61, 128.71, 126.97, 123.74, 122.18, 121.57, 119.91,119.45, 119.18, 111.24, 64.68, 39.79 ppm.

3-(Pyridin-2-ylmethyl)-1*H*-indole (2n): Brown solid (160 mg, 77%), eluent combination: hexane/ethyl acetate (10:1). Spectroscopic data matched those reported in the literature [S5]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.57-8.56 (d, 2H), 7.55-7.51 (m, 2H), ppm, 7.33-7.31 (d, 1H), 7.19-7.01 (m, 5H), 4.32 (s, 2H), $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 161.31, 149.00, 136.73, 126.36, 127.45, 122.97, 122.03, 121.27, 119.39, 119.17, 113.59, 111.30, 34.5 ppm.

3-(Furan-2-ylmethyl)-1*H*-indole (2o): Brown solid (150 mg, 76%), eluent combination: hexane/ethyl acetate (10:1). Spectroscopic data matched those reported in the literature [S2]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80 (br s, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.45 (s, 1H), 7.34 (dt, J = 8.0, 7.6 Hz, 2H), 7.27−7.21 (m, 1H), 7.02 (s, 1H), 6.41 (dd, J = 3.0, 2.0 Hz, 1H), 6.16 (d, J = 3.0 Hz, 1H), 4.24 (s, 2H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): ppm.

1,4-Bis((1*H*-indol-3-yl)methyl)benzene (2p): White solid (221 mg, 66%), eluent combination: hexane/ethyl acetate (10:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.94 (s,2H), 7.53-7.51 (d, 2H), 7.36-7.34 (d, 2H),7.19-7.16 (m, 5H), 7.09-7.05 (t, 2H), 6.90 (s,1H), 4.08 (s, 4H) ppm.; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 143.3, 128.2, 127.7, 124.4, 122.4, 120.8, 120.2, 119.9, 118.1, 112.2, 111.4, 29.8 ppm. IR (KBr pellet): 3422, 2916, 2364, 1634, 1456, 1404, 804, 704, 600 cm^{-1}; HRMS (ESI) m/z calcd for $C_{24}H_{19}N_2$ $(M-H)^+$: 335.1548, found: 335.1568.

4-((1*H*-Indol-3-yl)methyl)-N,N-diphenylaniline (2q): Yellow liquid (268 mg, 72%), eluent combination: hexane/ethyl acetate (10:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.97 (s,1H), 7.57-7.56 (d, 1H), 7.38-7.36 (d, 1H),7.24-7.16 (m, 7H), 7.13-6.95 (m, 10H), 4.08 (s, 2H) ppm.; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 148.1, 145.7, 136.5, 136.0, 129.5, 129.2, 127.6, 124.7, 123.9, 122.4, 122.1, 119.4, 119.3, 116.0, 111.2, 31.09 ppm. IR (KBr pellet): 3444, 2922, 2354, 1644, 1260, 1098, 804, 766, 668 cm^{-1}; HRMS (ESI) m/z calcd for $C_{27}H_{23}N_2$ $(M+H)^+$: 375.1861, found: 375.1776.

3-(1-Phenylethyl)-1*H*-indole (3a): Colorless liquid (160 mg, 73%), eluent combination: hexane/ethyl acetate (10:1). Spectroscopic data matched those reported in the literature [S2].

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.90 (s, 1H), 7.37-7.20 (m, 8H), 7.09-7.05 (m, 1H), 7.01 (s, 1H), 4.47-4.41 (q, 1H), 1.78-1.76 (d, 3H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 146.92, 136.68, 128.41, 127.54, 126.02, 122.03, 121.20, 119.79, 119.27, 111.14, 37.04, 22.54 ppm.

3-[1-(p-Tolyl) ethyl]-1*H*-indole (3b): Colorless liquid (162 mg, 69% yield), eluent combination: hexane/ethyl acetate (9:1). Spectroscopic data matched those reported in the literature [S6]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.88 (s, 1H), 7.37 (d, 1H), 7.31 (d, 1H), 7.18−7.15 (m, 2H), 7.12 (d, 1H), 7.07 (d, 2H), 6.99 (t, 2H), 4.33 (q, 1H), 2.29 (s, 3H), 1.68 (d, J =7.3 Hz, 3H) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 143.81, 136.62, 135.33, 129.40, 127.23, 126.29, 121.94, 121.75, 121.06, 119.72, 119.12, 111.03, 36.55, 22.52, 21.05 ppm.

3-[1-(4-Methoxyphenyl) ethyl]-1*H*-indole (3c): Colorless liquid (178 mg, 71% yield), eluent combination: hexane/ethyl acetate (10:1). Spectroscopic data matched those reported in the literature [S7]. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.96 (s, 1H), 7.39-7.33 (m, 2H), 7.21-7.08 (m, 7H), 7.03-6.99 (t, 2H), 4.37-4.32 (q, 1H), 2.31 (s, 3H), 1.70-1.69 (d, 3H), ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): 143.92, 135.43, 129.12, 127.42, 122.05, 121.80, 121.11, 119.86, 119.29, 111.10, 36.62, 22.63 ppm.

3-(Diphenyl methyl)-1*H*-indole (3d): Colorless liquid (180 mg, 64% yield), eluent combination: hexane/ethyl acetate (10:1). Spectroscopic data matched those reported in the literature [S2]. ^{1}H NMR ($CDCl_3$, 400 MHz): 8.01 (s, 1H), 7.40-7.26 (m, 9H), 6.65 (s, 1H), 6.57 (s, 1H), 5.77 (s, 1H), ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): 144.03, 136.71, 129.09, 128.38, 126.32, 122.14, 119.97, 119.83, 119.45, 111.16, 48.89 ppm.

3-[1-(4-Chlorophenyl) ethyl]-1*H*-indole (3e): Colorless liquid (155 mg, 61% yield), eluent combination: hexane/ethyl acetate (8:2). Spectroscopic data matched those reported in the literature [S8]. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.98 (s, 1H), 7.45-7.35 (m, 5H), 7.21-7.15 (m, 2H), 7.05 (t, 2H), 4.41-4.36 (q, 1H), 1.73-1.71 (d, 3H), ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): 145.47, 136.75, 131.61, 128.93, 128.53, 126.79, 124.24, 122.23, 119.69, 119.42, 111.21, 36.52, 22.47 ppm.

3-[1-(4-Bromophenyl) ethyl]-1*H*-indole (3f): Colorless liquid (210 mg, 70% yield), eluent combination: hexane/ethyl acetate (8:2). Spectroscopic data matched those reported in the literature [S9]. ^{1}H NMR ($CDCl_3$, 400 MHz): 8.14 (s, 1H), 7.69-7.67(d, 1H), 7.42-7.40 (d, 2H), 7.24-7.13 (m, 5H), 6.58 (s, 1H), 4.18-4.12 (m, 1H), 1.29 (s, 3H) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): 135.88, 131.48, 127.95, 124.25, 122.09, 120.84, 119.92, 111.14, 102.71, 31.73, 22.80 ppm.

3-Cyclohexyl-1*H*-indole (3g): Colorless liquid (121 mg, 61%), eluent combination: hexane/ethyl acetate (10:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.06 (s,1H), 7.93-7.91 (d, 1H), 7.37 (s, 1H),7.20-7.14 (m, 2H), 6.29 (s,1H), 2.46 (m, 2H), 2.36-2.27 (m, 2H), 1.87-1.79 (m, 3H), 1.74-1.61 (m, 3H) ppm.; ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 136.8, 131.2, 122.6, 122.1, 120.9, 120.8, 119.9, 111.3, 42.1, 28.6, 27.1, 25.8, 25.1, 23.2, 22.6 ppm. IR (KBr pellet): 3420, 2922, 2366, 1634, 1100, 802, 738 cm^{-1}; HRMS (ESI) m/z calcd for $C_{14}H_{16}N$ $(M-H)^+$: 198.1282, found: 198.1259.

3-(4-Methylcyclohexyl)-1*H*-indole (3h): Colorless liquid (138 mg, 65%), eluent combination: hexane/ethyl acetate (10:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.87 (s,1H),

7.64-7.62 (d, 1H), 7.36-7.34 (d, 1H),7.20-7.16 (t, 1H), 7.12-7.08 (t, 1H), 6.96 (s,1H), 3.07-3.02 (m, 1H), 2.13-2.09 (m, 2H), 1.80-1.72 (m, 7H), 1.57 (s, 3H) ppm.; $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ 133.7, 129.1, 128.5, 128.9, 118.6, 107.7, 35.8, 35.6, 34.6, 31.8, 30.4, 21.3 ppm. IR (KBr pellet): 3418, 2920, 1362, 1624, 1260, 1100, 1024, 802, 740, 524, 424 cm^{-1}; HRMS (ESI) m/z calcd for $C_{15}H_{18}N$ $(M-H)^+$: 212.1439, found: 212.1425.

3-Cycloheptyl-1*H*-indole (3i): Colorless liquid (107 mg, 51%), eluent combination: hexane/ethyl acetate (10:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.03 (s,1H), 7.84-7.82 (d, 1H), 7.36-7.34 (d, 1H),7.16-7.11 (m, 3H), 6.30 (t,1H), 2.68-2.65 (m, 2H), 2.36-2.34 (m, 2H), 2.81 (s, 1H), 1.87-1.85 (m, 2H), 1.72-1.69 (m, 3H), 1.26 (s, 1H) ppm.; $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ 138.8, 136.8, 127.9, 125.7, 122.1, 121.4, 120.9, 120.8, 119.8, 111.3, 33.9, 33.0, 28.9, 27.3, 27.1 ppm. IR (KBr pellet): 3404, 2960, 2352, 1456, 1262, 1090, 812, 740 cm^{-1}; HRMS (ESI) m/z calcd for $C_{15}H_{18}N$ $(M-H)^+$: 212.1438, found: 212.1438.

3-(6-Methoxy-1,2,3,4-tetrahydronaphthalen-1-yl)-1*H*-indole (3j): Colorless liquid (163 mg, 59%), eluent combination: hexane/ethyl acetate (10:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.25 (s,1H), 7.73-7.71 (d, 2H), 7.46-7.44 (d, 2H),7.25-7.17 (m, 3H), 6.62 (s,1H), 3.89 (s, 3H), 2.97-2.94 (t, 2H), 2.72-2.69 (t, 2H), 2.19-2.16 (m, 2H) ppm.; $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ 158.4, 137.3, 135.8, 133.4, 130.1, 129.8, 129.1, 127.9, 124.2, 122.0, 121.9, 120.8, 119.9, 111.1, 109.1, 102.6, 55.6, 39.1, 29.0, 23.6 ppm. IR (KBr pellet): 3420, 2934, 2362, 1636, 1492, 1244, 746, 580 cm^{-1}; HRMS (ESI) m/z calcd for $C_{19}H_{18}NO$ $(M-H)^+$: 276.1388, found 276.1409.

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