Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Organic Photoredox Catalyzed C(sp^3)-H Functionalization of Saturated Aza-heterocycles via Cross-Dehydrogenative Coupling Reaction

Yi-Fan Zhang, [a] Han-Nan Chen, [a] Yi Xiao, [a] Zhencun Cui, [b] Wei David Wang*[a] and Guo-Qiang Xu*[a]

[a] State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, MOE Frontiers Science Center for Rare Isotopes, Lanzhou Magnetic Resonance Center, Lanzhou University, Lanzhou 730000 (P.R. China).

[b] Department of Nuclear Medicine, Second Hospital of Lanzhou University, Lanzhou 730030 (P.R. China).

*Corresponding author (s): ww@lzu.edu.cn; gqxu@lzu.edu.cn.

Supporting Information Placeholder

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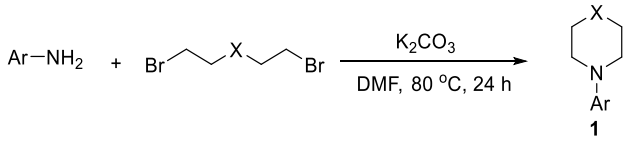
1. General information

All the glassware was thoroughly oven-dried. Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Thin-layer chromatography (TLC) plates were visualized by exposure to ultraviolet light and/or staining with phosphomolybdic acid, followed by heating on a hot plate. Flash chromatography was carried out using silica gel (200-300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-400 (400 MHz) or Agilent Inova 600 MHz. The spectra were recorded in $CDCl_3$ as solvent at room temperature, and ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to the residual solvent peak. The residual solvent signals were used as references, and the chemical shifts were converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.00 ppm). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q=quartet, m = multiplet, dd = doublet), integration, coupling constant (Hz), and assignment. Data for ^{13}C NMR are reported as chemical shifts. HRMS was performed on a Bruker Apex II mass instrument (ESI).

2. Synthesis of substrates

2.1 Synthesis of Cyclic Amines

Cyclic amines were synthesized according to reported procedures with some modifications. [1]



1

General procedure: K_2CO_3 (1.52 g, 11 mmol, 1.1 equiv.) was weighed into an oven-dried 25 mL round-bottom flask with magnetic stirring, and DMF (10 mL, 1.0 M) was added. The appropriate aniline (10 mmol, 1.0 equiv.) was added into the reaction mixture *via* syringes. The reaction system was degassed (10 min) and backfilled with nitrogen. The corresponding dibromide (11 mmol, 1.1 equiv.) was added, and the reaction mixture was heated to 80 ºC for 24 h. After completion, the reaction mixture

was cooled to RT and diluted with EtOAc (20 mL) and H_2O (20 mL). The layers were separated, and the organic layer was extracted with 1 N HCl (3 x 10 mL). The acid layers were combined and adjusted to pH = 8 with 1N NaOH and then extracted with EtOAc (3 x 10 mL). The organic layers were washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered, concentrated, and purified by flash chromatography.

2.2 Synthesis and Characterization of Photocatalyst

Synthesis and Characterization of Photocatalyst according to reported procedures[2].

2.3 Synthesis and Characterization of 2-phenyl-1,2,3,4-tetrahydroisoquinoline

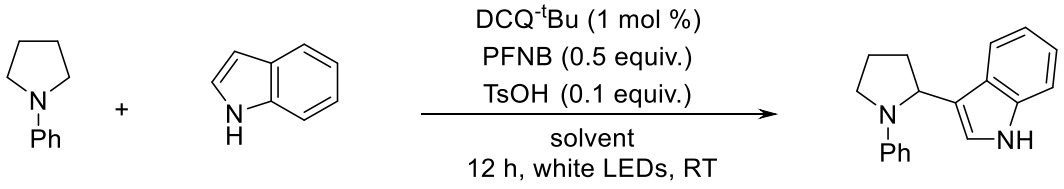
Synthesis and Characterization of 2-phenyl-1,2,3,4-tetrahydroisoquinoline according to reported procedures[3].

2.4 Synthesis and Characterization of (furan-2-yloxy)trimethylsilane

Synthesis and Characterization of (furan-2-yloxy)trimethylsilane according to reported procedures[4].

3. Screening of reaction conditions

Table S1. Optimization of the photocatalyst. [a]



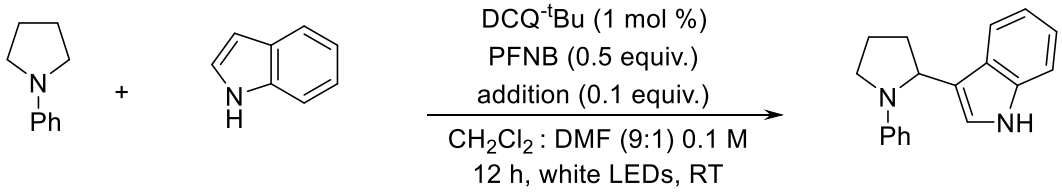
1a **2a** **3a**

Entry	Solvent	Yield (%)[b]
1	DCM	32
2	toluene	NR
3	THF	29
4	CH_3CN	NR
5	DCE	31
6	2-Methyltetrahydrofuran	37
7	hexene	NR
8	EA	28

9	DMF	34
10	H_2O	Trace
11	MeOH	Trace
12	CH_3Cl	39
13	0.2 mL $CHCl_3$ + 0.8 mL DMF	65
14	0.5 mL $CHCl_3$ + 0.5 mL DMF	67
15	0.8 mL $CHCl_3$ + 0.2 mL DMF	78
16	0.2 mL DCM + 0.8 mL DMF	80
17	0.2 mL DCE + 0.8 mL DMFTHF	62
18	0.2 mL THF + 0.8 mL DMF	50
19	0.2 mL 2-Methyltetrahydrofuran + 0.8 mL DMF	68
20	**0.9 mL DCM + 0.1 mL DMF**	**84**
21	0.8 mL DCM + 0.2 mL DMF	80
22	0.7 mL DCM + 0.3 mL DMF	79
23	0.6 mL DCM + 0.4 mL DMF	72

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.13 mmol), PFNB (0.5 equiv.), TsOH (10 mol %) and DCQ (1 mol %) at 25 ºC for 12 h under irradiation with white light. [b] Isolated yield after chromatography. PFNB = pentafluoronitrobenzene.

Table S2. Optimization of the Addition. [a]

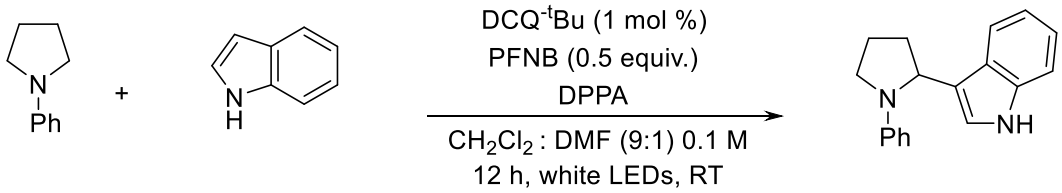


1a **2a** **3a**

Entry	Addition	Yield (%)[b]
1	rac-CPA	85
2	3-Phenylpropionic acid	Trace
3	Propionic acid	Trace
4	Trifluoromethanesulfonic acid	70
5	TsOH	84
6	**DPPA**	**86**

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.13 mmol), PFNB (0.5 equiv.), addition (10 mol %) and DCQ (1 mol %) in CH_2Cl_2 (0.9 mL):DMF (0.1 mLmL) at 25 ºC for 12 h under irradiation with white light. [b] Isolated yield after chromatography. PFNB = pentafluoronitrobenzene. DPPA = Diphenylphosphinic acid.

Table S3. Optimization of the loading of DPPA. [a]

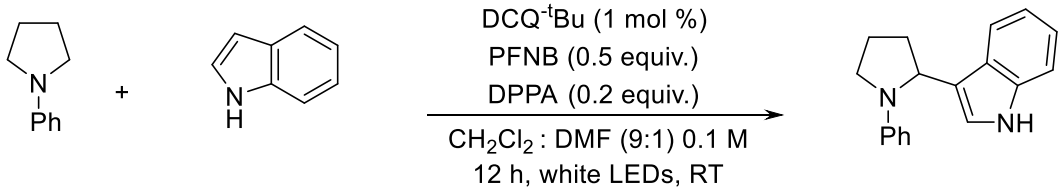


1a **2a** **3a**

Entry	DPPA	Yield (%)[b]
1	0.1 equiv.	86
2	0.3 equiv.	88
3	0.5 equiv.	88
4	1.0 equiv.	88

[a] Reaction conditions: **1** (0.1 mmol), **2a** (0.13 mmol), PFNB (0.5 equiv.), addition (10 mol %) and DCQ (1 mol %) in CH_2Cl_2 (0.9 mL):DMF (0.1 mL) at 25 ºC for 12 h under irradiation with white light. [b] Isolated yield after chromatography. PFNB = pentafluoronitrobenzene. DPPA = Diphenylphosphinic acid.

Table S4. Optimization of the loading of **2a**. [a]

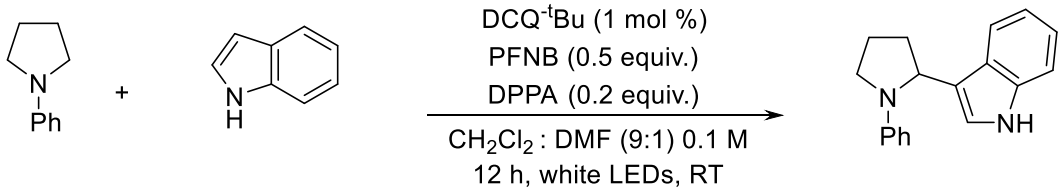


1a **2a** **3a**

Entry	2a	Yield (%)[b]
1	1.0 equiv.	71
2	**1.3 equiv.**	**89**
3	1.5 equiv.	88
4	2.0 equiv.	85

[a] Reaction conditions: **1a** (0.1 mmol), **2a**, PFNB (0.5 equiv.), DPPA (20 mol %) and DCQ-^{t}Bu (1 mol%) in CH_2Cl_2 (0.9 mL): DMF (0.1 mL) at 25 ºC for 12 h under irradiation with white light. [b] Isolated yield after chromatography. PFNB = pentafluoronitrobenzene. DPPA = Diphenylphosphinic acid.

Table S5. Optimization of reaction time. [a]

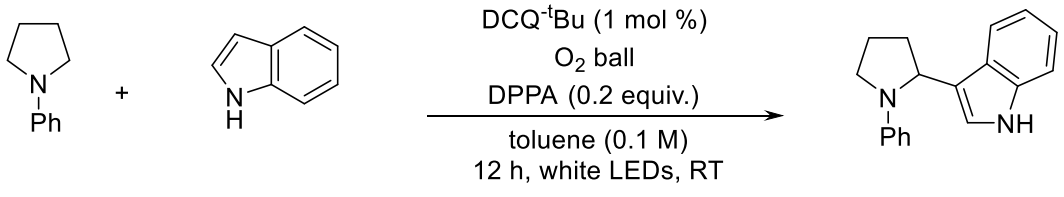


1a **2a** **3a**

Entry	Time	Yield (%)[b]
1	3 h	70
2	6 h	81
3	**12 h**	**89**
4	18 h	89
5	24 h	89
6	30 h	88

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.13 mmol), PFNB (0.5 equiv.), DPPA (20 mol %) and DCQ (1 mol %) in CH_2Cl_2 (0.9 mL): DMF (0.1 mL) at 25 ºC for different time under irradiation with white light. [b] Isolated yield after chromatography. PFNB = pentafluoronitrobenzene. DPPA = Diphenylphosphinic acid.

Table S6. Use O_2 as the oxidant. [a]

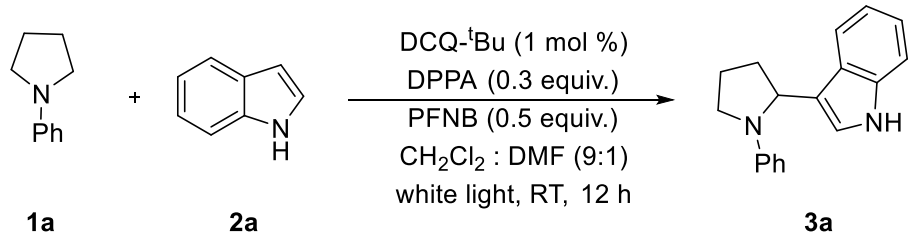


1a **2a** **3a**

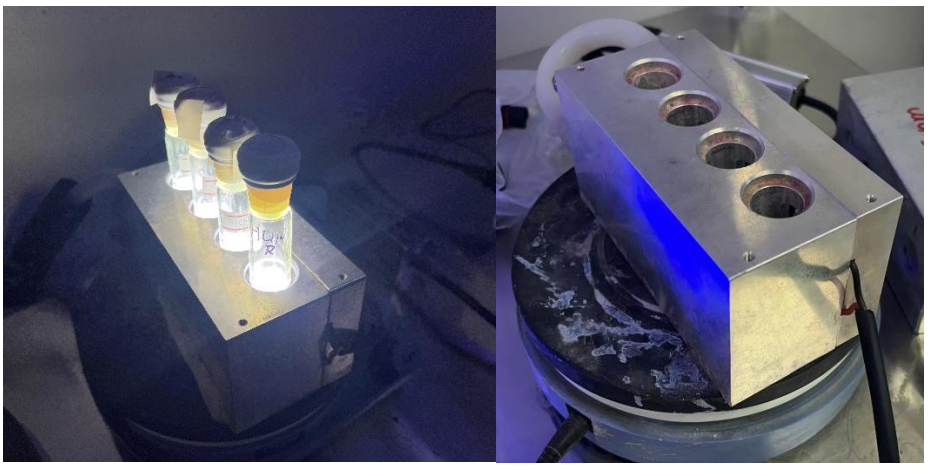
Entry	Time	Yield (%)[b]
1	2 h	25
2	4 h	**53**
3	6 h	52
4	8 h	53

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.13 mmol), O_2 ball, DPPA (20 mol %) and DCQ (1 mol %) in toluene at 25 ºC for different time under irradiation with white light. [b] Isolated yield after chromatography. PFNB = pentafluoronitrobenzene. DPPA = Diphenylphosphinic acid.

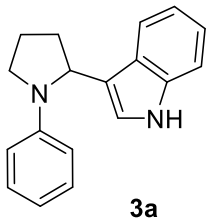
4. General procedure for the synthesis of product 3 and analytical data



General catalysis procedure: A dried 10 mL reaction tube was charged with the photocatalyst (0.001 mol, 0.68 mg), DPPA (0.01 mmol, 6.54 mg), PFNB (0.05 mmol, 6.5 μL), 1-phenylpyrrolidine **1a** (0.13 mmol, 1.3 equiv., 1*H*-indole **2a** (0.1 mmol, 1.0 equiv. and CH_2Cl_2 (0.9 mL) + DMF (0.1 mL). The reaction mixture was degassed by three cycles of freeze-pump-thaw. After the mixture was thoroughly degassed, the vial was placed beside a white LED light. The reaction was stirred at 25 ^oC for 12 h. After completion of the reaction as checked by TLC. The reaction mixture was purified by silica gel flash column chromatography (PE:EA = 10:1) to give the corresponding product. An 18-36W White LED panel was used as light source. Reaction device is shown below.



3-(1-phenylpyrrolidin-2-yl)-1*H*-indole (3a)



3a

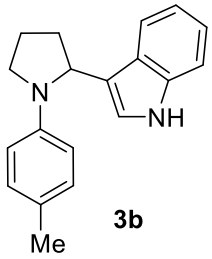
Following the general procedure, compound **3a** was obtained as a gray solid in 89% yield; m.p. = 92-94 °C; R_f = 0.41 (PE:EA = 10:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (s, 1H), 7.58 (d, J = 7.9 Hz, 1H), 7.24 (d, J = 7.2 Hz, 1H), 7.15-7.11 (m, 1H), 7.09-7.03 (m, 3H), 6.71 (d, J = 2.4 Hz, 1H), 6.54 (t, J = 7.2 Hz, 1H), 6.51 (d, J = 8.2 Hz, 2H), 4.98 (d, J = 8.0 Hz, 1H), 3.59-3.53 (m, 1H), 3.26 (td, J = 9.4, 6.6 Hz, 1H), 2.23 (tt, J = 11.7, 7.5 Hz, 1H), 2.08-2.02 (m, 1H), 2.02-1.90 (m, 2H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 147.4, 136.9, 128.9, 125.5, 122.0, 121.9, 119.3, 118.9, 118.6, 115.4, 112.3, 111.3, 56.2, 48.3, 33.6, 23.5;

HRMS (ESI) for $C_{18}H_{18}N_2$ $[M+H]^+$ calcd. 263.1543, found: 263.1542.

3-(1-(p-tolyl)pyrrolidin-2-yl)-1H-indole (3b)



3b

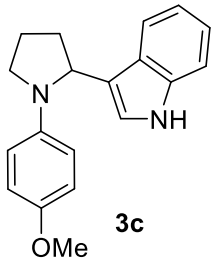
Following the general procedure, compound **3b** was obtained as a gray solid in 76% yield; m.p. = 86-88 °C; R_f = 0.41 (PE:EA = 10:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (s, 1H), 7.65 (dd, J = 7.8, 1.3 Hz, 1H), 7.35-7.30 (m, 1H), 7.24-7.11 (m, 2H), 6.98-6.91 (m, 2H), 6.81 (dd, J = 2.4, 1.1 Hz, 1H), 6.53-6.48 (m, 2H), 5.00 (dt, J = 8.1, 1.5 Hz, 1H), 3.62 (ddd, J = 9.4, 7.4, 2.2 Hz, 1H), 3.30 (td, J = 9.0, 6.7 Hz, 1H), 2.36-2.25 (m, 1H), 2.20 (s, 3H), 2.16-1.94 (m, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 145.5, 136.9, 129.5, 125.7, 124.5, 122.1, 122.0, 119.3, 119.1, 119.0, 112.3, 111.3, 56.4, 48.6, 33.8, 23.7, 20.3;

HRMS (ESI) for $C_{19}H_{20}N_2$ $[M+H]^+$ calcd. 277.1699, found: 277.1701.

3-(1-(4-methoxyphenyl)pyrrolidin-2-yl)-1H-indole (3c)



3c

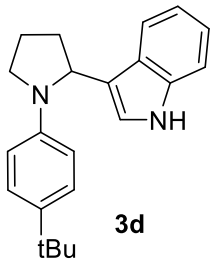
Following the general procedure, compound **3c** was obtained as a brown solid in 82% yield; m.p. = 116-118 ˚C; R_f = 0.40 (PE:EA = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (s, 1H), 7.64 (d, J = 7.8 Hz, 1H), 7.32 (dt, J = 8.2, 1.0 Hz, 1H), 7.23-7.17 (m, 1H), 7.13 (td, J = 7.5, 7.1, 1.2 Hz, 1H), 6.83 (s, 1H), 6.77-6.71 (m, 2H), 6.53 (d, J = 8.5 Hz, 2H), 4.96 (dt, J = 8.2, 1.6 Hz, 1H), 3.69 (s, 3H), 3.62 (t, J = 7.0 Hz, 1H), 3.28 (td, J = 9.0, 6.7 Hz, 1H), 2.39-2.25 (m, 1H), 2.17-1.93 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 150.7, 142.6, 137.0, 125.7, 122.1, 122.0, 119.3, 119.2, 119.0, 114.9, 113.0, 111.3, 56.8, 56.0, 49.1, 33.9, 23.8;

HRMS (ESI) for $C_{19}H_{20}N_2O$ $[M+H]^+$ calcd. 293.1648, found: 293.1649.

3-(1-(4-(tert-butyl)phenyl)pyrrolidin-2-yl)-1H-indole (3d)



3d

Following the general procedure, compound **3af** was obtained as a brown solid in 57% yield; m.p. = 146-148 ˚C; R_f = 0.43 (PE:EA = 10:1);

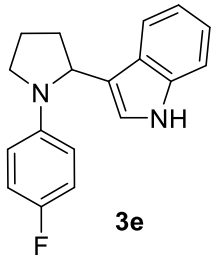
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (s, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.23-7.10 (m, 4H), 6.87 (s, 1H), 6.57-6.52 (m, 2H), 5.01 (d, *J* = 8.6 Hz, 1H), 3.68-3.60 (m, 1H), 3.31 (q, *J* = 8.2, 7.2 Hz, 1H), 2.33-2.21 (m, 1H), 2.14-1.94 (m, 3H), 1.24 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 145.5, 138.1, 137.0, 125.7, 125.7, 122.1, 122.0, 119.3,

119.3, 119.0, 111.9, 111.3, 56.6, 48.6, 33.8, 33.7, 31.6, 23.7;

HRMS (ESI) for $C_{22}H_{26}N_2$ $[M+H]^+$ calcd. 319.2169, found: 319.2173.

3-(1-(4-fluorophenyl)pyrrolidin-2-yl)-1H-indole (3e)



3e

Following the general procedure, compound **3e** was obtained as a gray solid in 73% yield; m.p. = 115-117 ˚C; R_f = 0.30 (PE:EA = 10:1);

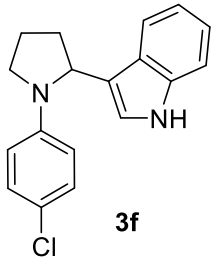
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.88 (s, 1H), 7.64 (d, J = 7.9 Hz, 1H), 7.35 (d, J = 8.1 Hz, 1H), 7.21 (d, J = 7.3 Hz, 1H), 7.15 (t, J = 7.5 Hz, 1H), 6.83 (t, J = 9.9 Hz, 3H), 6.47 (dd, J = 9.2, 4.2 Hz, 2H), 4.99 (d, J = 6.4 Hz, 1H), 3.62 (t, J = 7.0 Hz, 1H), 3.34-3.27 (m, 1H), 2.34 (tt, J = 11.1, 7.7 Hz, 1H), 2.16-1.99 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 155.6, 154.0, 144.2, 137.0, 125.6, 122.1, 121.9, 119.4, 118.9, 118.8, 115.3, 115.2, 112.7, 112.6, 111.3, 56.7, 48.9, 33.9, 23.7;

^{19}F NMR (565 MHz, $CDCl_3$): δ -130.85 ;

HRMS (ESI) for $C_{18}H_{17}FN_2$ $[M+H]^+$ calcd. 281.1449, found: 281.1449.

3-(1-(4-chlorophenyl)pyrrolidin-2-yl)-1H-indole (3f)



3f

Following the general procedure, compound **3ac** was obtained as a brown solid in 66% yield; m.p. = 92-94 ˚C; R_f = 0.42 (PE:EA = 10:1);

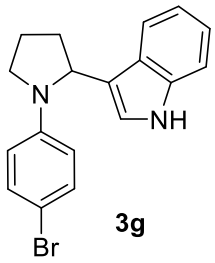
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (s, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 7.09-6.98 (m, 2H), 6.79 (s,

1H), 6.47 (d, *J* = 8.8 Hz, 2H), 5.00 (d, *J* = 7.8 Hz, 1H), 3.66-3.54 (m, 1H), 3.31(q, *J* = 8.8 Hz, 1H), 2.39-2.23 (m, 1H), 2.18 -1.98 (m, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 145.9, 136.9, 128.6, 125.4, 122.1, 121.9, 120.1, 119.4, 118.8, 118.1, 113.3, 111.3, 56.4, 48.5, 33.8, 23.6;

HRMS (ESI) for $C_{17}H_{18}ClN_2$ $[M+H]^+$ calcd. 297.1153, found: 297.1149.

3-(1-(4-bromophenyl)pyrrolidin-2-yl)-1H-indole (3g)



3g

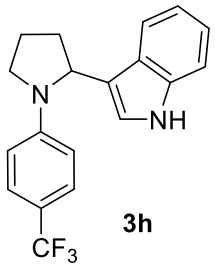
Following the general procedure, compound **3g** was obtained as a brown solid in 59% yield; m.p. = 152-154 °C; R_f = 0.42 (PE:EA = 10:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (s, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.22 (t, *J* = 6.6 Hz, 1H), 7.20-7.12 (m, 3H), 6.78 (s, 1H), 6.42 (d, *J* = 8.9 Hz, 2H), 5.00 (d, *J* = 7.7 Hz, 1H), 3.66-3.52 (m, 1H), 3.31 (q, J = 7.3 Hz, 1H), 2.40-2.24 (m, 1H), 2.17-1.99 (m, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 146.3, 137.0, 131.6, 125.5, 122.2, 122.0, 119.5, 118.9, 118.1, 114.0, 111.4, 107.4, 56.4, 48.5, 33.8, 23.6.

HRMS (ESI) for $C_{18}H_{17}BrN_2$ $[M+H]^+$ calcd. 341.0648, found: 341.0646.

3-(1-(4-(trifluoromethyl)phenyl)pyrrolidin-2-yl)-1H-indole (3h)



3h

Following the general procedure, compound **3h** was obtained as a brown solid in 93% yield; m.p. = 112-114 °C; R_f = 0.28 (PE:EA = 10:1);

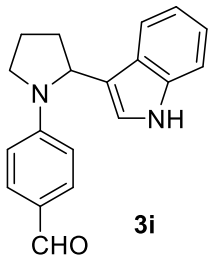
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (s, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.34 (dd, J = 15.3, 8.4 Hz, 3H), 7.25-7.21 (m, 1H), 7.18-7.14 (m, 1H), 6.77 (d, J = 1.4 Hz, 1H), 6.56 (d, J = 8.5 Hz, 2H), 5.11 (d, J = 7.9 Hz, 1H), 3.68-3.63 (m, 1H), 3.39 (td, J = 9.4, 7.0 Hz, 1H), 2.34 (tt, J = 11.7, 7.5 Hz, 1H), 2.20-2.15 (m, 1H), 2.11-2.02 (m, 2H).;

^{13}C NMR (101 MHz, $CDCl_3$): δ 149.4, 137.0, 126.2, 126.2, 125.5, 122.3, 121.9, 121.9, 119.6, 118.9, 117.6, 111.7, 111.4, 56.3, 48.4, 33.7, 23.5;

^{19}F NMR (565 MHz, $CDCl_3$):δ -60.58;

HRMS (ESI) for $C_{19}H_{17}F_3N_2$ $[M+H]^+$ calcd. 331.1417, found: 331.1418.

3-(1-(4-nitrophenyl)pyrrolidin-2-yl)-1H-indole (3i)



3i

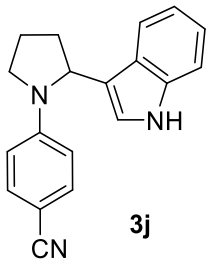
Following the general procedure, compound **3i** was obtained as a white solid in 56% yield; m.p. = 123-125 °C; R_f = 0.31 (PE:EA =1:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.67 (s, 1H), 8.13 (s, 1H), 7.63 (dd, *J* = 7.5 Hz, 2.9 Hz, 3H), 7.38 (d, J = 8.1 Hz, 1H), 7.24 (td, *J* = 7.6 Hz, 0.8 Hz, 1H), 7.18 (td, *J* = 7.6 Hz, 0.8 Hz, 1H), 6.78 (d, *J* = 1.6 Hz, 1H), 6.60 (*d*, J = 8.8 Hz, 2H), 5.23 (d, J = 7.8 Hz, 1H), 3.71 (ddd, J = 8.2 Hz, 7.5 Hz,2.8 Hz, 1H), 3.47 (td, J = 9.5 Hz, 7.5 Hz, 1H), 2.42-2.33 (m, 1H), 2.27-2.19 (m, 1H), 2.16-2.06 (m, 2H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 190.3, 151.7, 136.9, 131.9, 125.3, 125.0, 122.3, 121.8, 119.6, 118.7, 116.8, 112.1, 111.5, 56.4, 48.3, 33.5, 23.3;

HRMS (ESI): for $C_{19}H_{18}N_2O$ $[M+H]^+$ calcd. 291.1492, found: 291.1495.

4-(2-(1H-indol-3-yl)pyrrolidin-1-yl)benzonitrile (3j)



3j

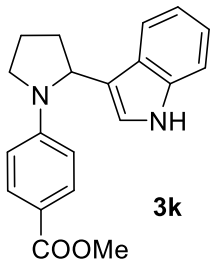
Following the general procedure, compound **3j** was obtained as a white solid in 92% yield; m.p. = 180-182 °C; R_f = 0.2 (PE:EA = 4:1);

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.02 (s, 1H), 7.61 (d, J = 7.9 Hz, 1H), 7.38 (d, J = 8.1 Hz, 1H), 7.34 (d, J = 8.6 Hz, 2H), 7.26-7.21 (m, 1H), 7.16 (t, J = 7.5 Hz, 1H), 6.77 (d, J = 2.4 Hz, 1H), 6.53 (d, J = 8.6 Hz, 2H), 5.14 (d, J = 7.8 Hz, 1H), 3.70-3.64 (m, 1H), 3.46-3.39 (m, 1H), 2.36 (tt, J = 11.5, 7.7 Hz, 1H), 2.24-2.17 (m, 1H), 2.15-2.06 (m, 2H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 149.7, 136.9, 133.2, 125.2, 122.3, 121.7, 120.9, 119.7, 118.7, 116.8, 112.3, 111.4, 96.9, 56.3, 48.2, 33.6, 23.3;

HRMS (ESI) for $C_{19}H_{17}N_3$ $[M+H]^+$ calcd. 288.1595, found: 288.1596.

methyl 4-(2-(1H-indol-3-yl)pyrrolidin-1-yl)benzoate (3k)



3k

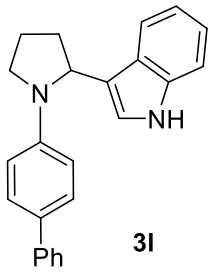
Following the general procedure, compound **3k** was obtained as a brown solid in 84% yield; m.p. = 162-164 °C; R_f = 0.2 (PE:EA = 5:1);

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.01 (s, 1H), 7.72 (d, J = 8.7 Hz, 2H), 7.55 (d, J = 6.8 Hz, 1H), 7.27 (d, J = 8.1 Hz, 1H), 7.14 (t, J = 7.0 Hz, 1H), 7.07 (t, J = 7.5 Hz, 1H), 6.67 (d, J = 1.4 Hz, 1H), 6.45 (d, J = 8.7 Hz, 2H), 5.08 (d, J = 7.8 Hz, 1H), 3.73 (s, 3H), 3.62-3.57 (m, 1H), 3.38-3.31 (m, 1H), 2.26 (tt, J = 11.6, 7.7 Hz, 1H), 2.13-2.08 (m, 1H), 2.02-1.94 (m, 2H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 167.6, 150.4, 136.9, 131.1, 125.3, 122.1, 121.9, 119.4, 118.7, 117.1, 116.4, 111.5, 111.4, 56.23, 51.38, 48.21, 33.52, 23.31;

HRMS (ESI) for $C_{20}H_{20}N_2O_2$ $[M+H]^+$ calcd. 321.1598, found: 321.1597.

3-(1-([1,1'-biphenyl]-4-yl)pyrrolidin-2-yl)-1H-indole (3l)



3l

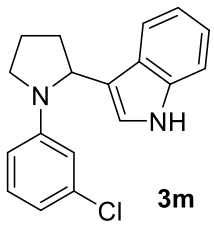
Following the general procedure, compound **3l** was obtained as a gray solid in 72% yield; m.p. = 153-155 °C; R_f = 0.43 (PE:EA = 10:1);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.87 (s, 1H), 7.67 (d, J = 7.8 Hz, 1H), 7.49 (d, J = 6.8 Hz, 2H), 7.40 (d, J = 8.7 Hz, 2H), 7.38-7.32 (m, 3H), 7.23-7.19 (m, 2H), 7.16 (t, J = 7.5 Hz, 1H), 6.87 (s, 1H), 6.65 (d, J = 8.4 Hz, 2H), 5.11 (d, J = 7.9 Hz, 1H), 3.73-3.66 (m, 1H), 3.43-3.36 (m, 1H), 2.34 (tt, J = 11.7, 7.5 Hz, 1H), 2.19-2.13 (m, 1H), 2.13-2.00 (m, 2H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 146.8, 141.3, 136.9, 128.5, 128.2, 127.5, 126.1, 125.7, 125.5, 122.0, 122.0, 119.4, 118.9, 118.5, 112.6, 111.3, 56.3, 48.4, 33.6, 23.5;

HRMS (ESI) for $C_{24}H_{22}N_2$ $[M+H]^+$ calcd. 339.1856, found: 339.1859.

3-(1-(3-chlorophenyl)pyrrolidin-2-yl)-1H-indole (3m)



3m

Following the general procedure, compound **3m** was obtained as a white solid in 82% yield; m.p. = 135-137 °C; R_f = 0.27 (PE:EA = 4:1);

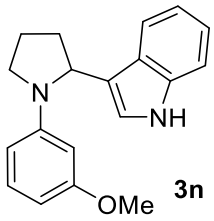
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.79 (s, 1H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.23-7.18 (m, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 6.98 (t, *J* = 8.0 Hz, 1H), 6.75 (d,

J = 2.3 Hz, 1H), 6.57 (d, *J* = 7.6 Hz, 2H), 6.41 (d, *J* = 8.4 Hz, 1H), 5.03 (d, *J* = 7.9 Hz, 1H), 3.62-3.55 (m, 1H), 3.35-3.28 (m, 1H), 2.30 (tt, *J* = 11.7, 7.6 Hz, 1H), 2.17-2.10 (m, 1H), 2.08-1.96 (m, 2H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 148.4, 136.9, 134.7, 129.7, 125.4, 122.0, 121.9, 119.4, 118.8, 117.9, 115.3, 111.9, 111.3, 110.7, 56.3, 48.4, 33.6, 23.4;

HRMS (ESI) for $C_{18}H_{17}ClN_2$ $[M+H]^+$ calcd. 297.1153, found: 297.1156.

3-(1-(3-methoxyphenyl)pyrrolidin-2-yl)-1H-indole (3n)



3n

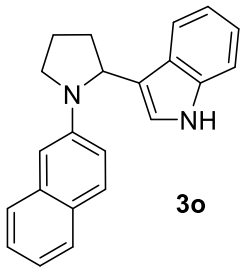
Following the general procedure, compound **3n** was obtained as a white solid in 76% yield; m.p. = 110-112 °C; R_f = 0.4 (PE:EA = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (s, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.05 (t, *J* = 8.1 Hz, 1H), 6.84 (s, 1H), 6.23 (ddd, *J* = 7.8, 5.0, 2.3 Hz, 2H), 6.19 (s, 1H), 5.08 (d, *J* = 7.9 Hz, 1H), 3.72 (s, 3H), 3.67-3.62 (t, *J* = 9.0 Hz, 1H), 3.37 (td, *J* = 9.4, 6.7 Hz, 1H), 2.33 (tt, *J* = 11.7, 7.4 Hz, 1H), 2.15 (dd, *J* = 11.9, 6.0 Hz, 1H), 2.11-2.00 (m, 2H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 160.5, 148.8, 136.9, 129.5, 125.5, 122.0, 121.9, 119.2, 118.8, 118.5, 111.2, 105.7, 100.3, 98.6, 56.3, 55.0, 48.4, 33.7, 23.5;

HRMS (ESI) for $C_{19}H_{20}N_2O[M+H]^+$ calcd. 293.1648, found: 293.1649.

3-(1-(naphthalen-2-yl)pyrrolidin-2-yl)-1H-indole (3o)



3o

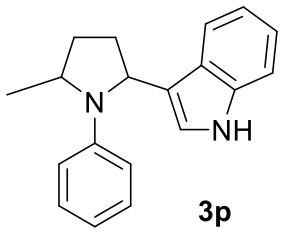
Following the general procedure, compound **3o** was obtained as white solid in 63% yield; m.p. =112-114 °C; R_f = 0.39 (PE:EA = 10:1);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.86 (s, 1H), 7.71 (d, J = 7.8 Hz, 1H), 7.63 (d, J = 8.1 Hz, 1H), 7.60-7.55 (m, 2H), 7.37 (d, J = 8.1 Hz, 1H), 7.31 (ddd, J = 8.2, 6.7, 1.3 Hz, 1H), 7.25 (td, J = 8.1, 7.6, 1.3 Hz, 1H), 7.22-7.17 (m, 1H), 7.16-7.10 (m, 1H), 6.98 (dd, J = 9.0, 2.5 Hz, 1H), 6.85-6.80 (m, 2H), 5.24 (d, J = 7.9 Hz, 1H), 3.81-3.72 (m, 1H), 3.54-3.45 (m, 1H), 2.39 (tt, J = 11.3, 7.9 Hz, 1H), 2.22 (ddt, J = 11.2, 4.4, 1.9 Hz, 1H), 2.18-2.07 (m, 2H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 145.3, 136.9, 135.1, 128.5, 127.5, 126.2, 126.0, 125.8, 125.6, 122.2, 122.0, 121.2, 119.4, 119.0, 118.6, 116.4, 111.3, 105.1, 56.3, 48.5, 33.7, 23.6;

HRMS (ESI) for $C_{22}H_{20}N_2$ $[M+H]^+$ calcd. 313.1699, found: 313.1701.

3-(5-methyl-1-phenylpyrrolidin-2-yl)-1H-indole (3p)



3p

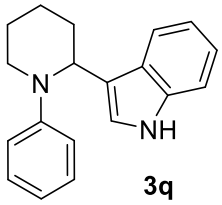
Following the general procedure, compound **3p** was obtained as white solid in 84% yield; m.p. =102-104 °C; R_f = 0.73 (PE:EA = 2:1);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.72 (s, 1H), 7.59 (d, J = 6.8 Hz, 1H), 7.26 (d, J = 8.1 Hz, 1H), 7.15-7.12 (m, 1H), 7.09-7.06 (m, 2H), 7.03-6.99 (m, 1H), 6.87 (d, J = 1.3 Hz, 1H), 6.59-6.54 (m, 3H), 4.91 (dd, J = 7.3, 4.5 Hz, 1H), 3.85 (h, J = 6.2 Hz, 1H), 2.32-2.23 (m, 1H), 2.09-1.98 (m, 2H), 1.66 (ddt, J = 10.9, 7.3, 5.8 Hz, 1H), 1.35 (d, J = 6.0 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 147.8, 137.0, 128.8, 125.5, 122.1, 121.9, 119.3, 119.0, 115.9, 113.5, 112.9, 111.3, 59.7, 55.2, 32.8, 32.7, 21.1;

HRMS (ESI) for $C_{19}H_{20}N_2$ $[M+H]^+$ calcd. 277.1699, found: 277.1698.

3-(1-phenylpiperidin-2-yl)-1H-indole (3q)



3q

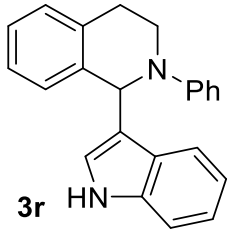
Following the general procedure, compound **3q** was obtained as a white oil in 48% yield; R_f = 0.31 (PE:EA = 10:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (s, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.32 (d, J = 8.1 Hz, 1H), 7.19-7.12 (m, 3H), 7.10 (d, J = 7.1 Hz, 1H), 6.96 (d, J = 7.7 Hz, 2H), 6.91 (d, J = 3.2 Hz, 1H), 6.72 (t, J = 7.3 Hz, 1H), 5.08 (t, J = 4.9 Hz, 1H), 3.45 (dt, J = 12.8, 4.8 Hz, 1H), 3.38 (dt, J = 12.7, 6.4 Hz, 1H), 2.17 (dh, J = 15.1, 3.8 Hz, 1H), 2.10 (ddt, J = 13.6, 8.8, 4.4 Hz, 1H), 1.82-1.70 (m, 3H), 1.58-1.64 (m, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 151.29, 136.28, 128.83, 126.51, 122.52, 121.83, 119.66, 119.22, 118.58, 117.20, 117.07, 111.01, 53.77, 48.08, 31.23, 25.47, 21.26;

HRMS (ESI) for $C_{19}H_{20}N_2$ $[M+H]^+$ calcd. 177.1699, found: 177.1700.

1-(1H-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3r)



3r

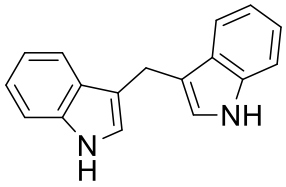
Following the general procedure, compound **3r** was obtained as white solid in 89% yield; m.p. = 146-148 °C; R_f = 0.6 (PE:EA = 2:1);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.88 (s, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.33-7.26 (m, 2H), 7.26-7.20 (m, 3H), 7.20-7.11 (m, 4H), 7.06-6.99 (m, 3H), 6.81-6.74 (m, 1H), 6.64-6.56 (m, 1H), 6.17 (s, 1H), 3.62 (dd, J = 7.7, 4.5 Hz, 2H), 3.06 (dt, J = 15.7, 7.7 Hz, 1H), 2.80 (dt, J = 16.3, 4.5 Hz, 1H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 149.8, 137.4, 136.6, 135.6, 129.2, 128.9, 128.1, 126.7, 126.5, 125.7, 124.2, 122.1, 120.1, 119.7, 119.3, 118.1, 115.9, 111.1, 56.7, 42.3, 26.7;

HRMS (ESI) for $C_{23}H_{20}N_2$ $[M+H]^+$ calcd. 325.1699, found: 325.1703.

di(1*H*-indol-3-yl)methane (4a)



4a

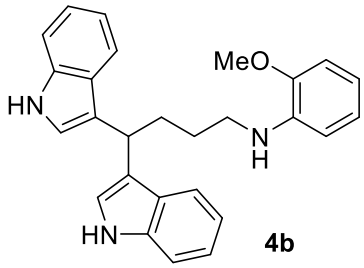
Following the general procedure, compound **4a** was obtained as a white solid in 45% yield; m.p. = 126-128 ˚C; R_f = 0.48 (PE:EA = 2:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (s, 2H), 7.62 (d, J = 7.9 Hz, 2H), 7.35 (d, J = 8.2 Hz, 2H), 7.22-7.15 (m, 2H), 7.12 -7.05 (m, 2H), 6.95-6.88 (m, 2H), 4.24 (s, 2H);

^{13}C NMR (101 MHz, CDCl3): δ 136.5, 127.6, 122.2, 121.9, 119.3, 119.2, 115.7, 111.1, 21.2;

HRMS (ESI) for $C_{16}H_{16}N_2$ $[M+H]^+$ calcd. 247.1300, found: 247.1299.

N-(4,4-di(1*H*-indol-3-yl)butyl)-2-methoxyaniline (4b)



4b

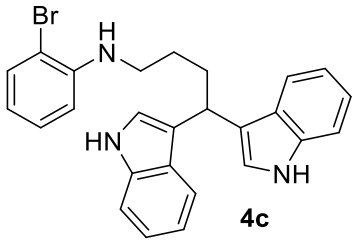
Following the general procedure, compound **4b** was obtained as a white solid in 40% yield; m.p. = 76-78 ˚C; R_f = 0.38 (PE:EA = 5:1);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.88 (s, 2H), 7.61 (dd, J = 7.9, 1.1 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 7.16 (ddd, J = 8.2, 7.0, 1.2 Hz, 2H), 7.05 (ddd, J = 8.0, 7.0, 1.0 Hz, 2H), 6.98 (d, J = 2.3 Hz, 2H), 6.86 (td, J = 7.6, 1.4 Hz, 1H), 6.76 (dd, J = 7.9, 1.4 Hz, 1H), 6.66 (td, J = 7.6, 1.5 Hz, 1H), 6.57 (dd, J = 7.8, 1.6 Hz, 1H), 4.53 (t, J = 7.5 Hz, 1H), 4.18 (s, 1H), 3.81 (s, 3H), 3.17 (t, J = 7.1 Hz, 2H), 2.40-2.31 (m, 2H), 1.79 (p, J = 7.2 Hz, 2H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 146.7, 138.4, 136.6, 127.0, 121.8, 121.5, 121.3, 120.0, 119.6, 119.0, 116.1, 111.1, 109.8, 109.3, 55.3, 43.8, 33.8, 33.2, 28.1;

HRMS (ESI) for $C_{27}H_{27}N_3O$ $[M+H]^+$ calcd. 410.2227, found:410.2228.

3-(1-(2-bromophenyl)pyrrolidin-2-yl)-1H-indole (4c)



4c

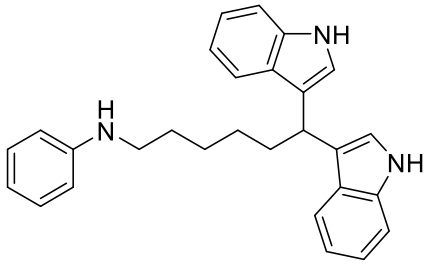
Following the general procedure, compound **4c** was obtained as a white solid in 43% yield; m.p. = 45-47 °C; R_f = 0.4 (PE:EA = 5:1);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.85 (s, 2H), 7.60 (d, J = 7.9 Hz, 2H), 7.39 (d, J = 6.3 Hz, 1H), 7.31 (d, J = 8.1 Hz, 2H), 7.15 (t, J = 7.9 Hz, 2H), 7.11 (t, J = 7.7 Hz, 1H), 7.04 (t, J = 7.5 Hz, 2H), 6.97 (d, J = 2.3 Hz, 2H), 6.57-6.50 (m, 2H), 4.52 (t, J = 7.5 Hz, 1H), 4.23 (s, 1H), 3.17 (q, J = 6.9 Hz, 2H), 2.35 (q, J = 7.6 Hz, 2H), 1.78 (p, J = 7.2 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 145.1, 136.6, 132.3, 128.4, 127.0, 121.9, 121.5, 119.9, 119.6, 119.1, 117.4, 111.2, 111.1, 109.6, 43.8, 33.9, 33.0, 27.9;

HRMS (ESI) for $C_{26}H_{24}BrN_3$ $[M+H]^+$ calcd. 458.1226, found: 458.1229.

N-(6,6-di(1*H*-indol-3-yl)hexyl)aniline (4d)



4d

Following the general procedure, compound **4d** was obtained as brown solid in 42% yield; m.p. = 60-62 °C; R_f = 0.50 (PE:EA = 2:1);

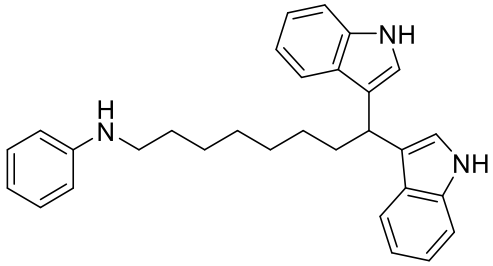
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.85 (s, 2H), 7.59 (d, J = 7.9 Hz, 2H), 7.31 (d, J = 8.5 Hz, 2H), 7.15 (td, J = 7.1, 4.2 Hz, 4H), 7.07-7.00 (m, 2H), 6.96 (d, J = 2.3 Hz, 2H), 6.68

(t, J = 7.3 Hz, 1H), 6.57 (d, J = 7.6 Hz, 2H), 4.47 (t, J = 7.4 Hz, 1H), 3.03 (t, J = 7.0 Hz, 2H), 2.23 (d, J = 7.3 Hz, 2H), 1.56 (t, J = 6.7 Hz, 2H), 1.45 (p, J = 3.4 Hz, 4H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 148.3, 136.6, 129.2, 127.1, 121.7, 121.4, 120.3, 119.6, 119.0, 117.2, 112.8, 111.1, 44.0, 35.7, 34.0, 29.4, 28.0, 27.2;

HRMS (ESI) for $C_{28}H_{29}N_3$ $[M+H]^+$ calcd. 408.2434, found:408.2436.

N-(8,8-di(1H-indol-3-yl)octyl)aniline (4e)



4e

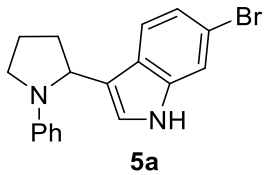
Following the general procedure, compound **4e** was obtained as brown oil in 40% yield; R_f = 0.51 (PE:EA = 2:1);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.88 (s, 2H), 7.59 (d, J = 7.9 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 7.20-7.11 (m, 4H), 7.03 (ddd, J = 8.0, 7.0, 1.0 Hz, 2H), 6.99 (d, J = 2.3 Hz, 2H), 6.68 (t, J = 7.3 Hz, 1H), 6.58 (dd, J = 8.7, 1.1 Hz, 2H), 4.47 (t, J = 7.4 Hz, 1H), 3.05 (t, J = 7.1 Hz, 2H), 2.21 (q, J = 7.4 Hz, 2H), 1.60-1.29 (m, 10H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 148.5, 136.6, 129.2, 127.1, 121.7, 121.4, 120.5, 119.7, 119.0, 117.0, 112.7, 111.0, 43.9, 35.8, 34.0, 29.6, 29.5, 29.3, 28.2, 27.1;

HRMS (ESI) for $C_{30}H_{33}N_3$ $[M+H]^+$ calcd. 436.2747, found:436.2751.

6-bromo-3-(1-phenylpyrrolidin-2-yl)-1H-indole (5a)



5a

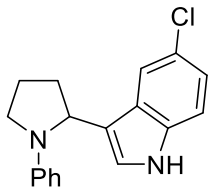
Following the general procedure, compound **5a** was obtained as a brown solid in 82% yield; m.p. = 152-154 °C; R_f = 0.26 (PE:EA = 10:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (s, 1H), 7.77 (d, J = 1.8 Hz, 1H), 7.28 (dd, J = 8.6, 1.9 Hz, 1H), 7.19 (d, J = 8.6 Hz, 1H), 7.15 (dd, J = 8.7, 7.2 Hz, 2H), 6.81 (d, J = 1.4 Hz, 1H), 6.63 (t, J = 7.3 Hz, 1H), 6.56 (d, J = 7.6 Hz, 2H), 4.97 (d, J = 8.1 Hz, 1H), 3.67-3.60 (m, 1H), 3.33 (q, J = 8.4 Hz, 1H), 2.37-2.24 (m, 1H), 2.12-1.98 (m, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 147.4, 135.6, 129.0, 127.3, 124.9, 123.3, 121.5, 118.6, 115.7, 112.8, 112.7, 112.3, 56.0, 48.4, 33.8, 23.6;

HRMS (ESI) for $C_{18}H_{17}BrN_2$ $[M+H]^+$ calcd. 341.0648, found: 341.0649.

5-chloro-3-(1-phenylpyrrolidin-2-yl)-1H-indole (5b)



5b

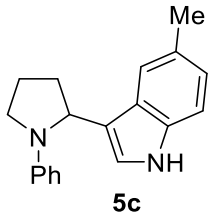
Following the general procedure, compound **5b** was obtained as a brown solid in 85% yield; m.p. = 142-144 $^{\circ}$C ; R_f = 0.31 (PE:EA = 10:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (s, 1H), 7.54 (d, J = 8.4 Hz, 1H), 7.32 (d, J = 1.8 Hz, 1H), 7.19-7.08 (m, 3H), 6.82 (d, J = 1.4 Hz, 1H), 6.63 (t, J = 7.3 Hz, 1H), 6.56 (d, J = 7.6 Hz, 2H), 5.00 (d, J = 8.1 Hz, 1H), 3.64 (ddd, J = 9.6, 6.2, 3.0 Hz, 1H), 3.39-3.29 (m, 1H), 2.36-2.24 (m,1H), 2.12-1.97 (m, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 147.3, 137.2, 129.0, 128.0, 124.1, 122.6, 120.1, 119.7, 119.0, 115.6, 112.2, 111.2, 56.1, 48.4, 33.8, 23.6;

HRMS (ESI) for $C_{18}H_{17}ClN_2$ $[M+H]^+$ calcd. 297.1153, found: 297.1153.

5-methyl-3-(1-phenylpyrrolidin-2-yl)-1H-indole (5c)



5c

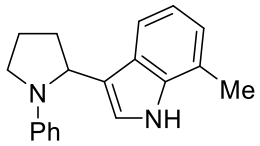
Following the general procedure, compound **5c** was obtained as a brown solid in 72% yield; m.p. = 94-96 °C; R_f = 0.35 (PE:EA = 10:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (s, 1H), 7.43 (s, 1H), 7.21 (d, J = 7.1 Hz, 1H), 7.17-7.10 (m, 2H), 7.03 (d, J = 10.0 Hz, 1H), 6.75 (d, J = 1.9 Hz, 1H), 6.60 (d, J = 8.1 Hz, 1H), 6.57 (d, J = 7.9 Hz, 2H), 5.02 (d, J = 7.9 Hz, 1H), 3.62 (t, J = 6.9 Hz, 1H), 3.38-3.28 (m, 1H), 2.49 (s, 3H), 2.35-2.23 (m, 1H), 2.16-1.95 (m, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 147.5, 135.2, 128.9, 128.6, 125.8, 123.5, 122.2, 118.5, 118.1, 115.4, 112.3, 111.0, 56.2, 48.3, 33.6, 23.5, 21.62;

HRMS (ESI) for $C_{19}H_{20}N_2$ $[M+H]^+$ calcd. 277.1699, found: 277.1700.

7-methyl-3-(1-phenylpyrrolidin-2-yl)-1H-indole (5d)



5d

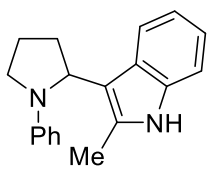
Following the general procedure, compound **5d** was obtained as a brown solid in 84% yield; m.p. = 102-104 °C; R_f = 0.4 (PE:EA = 10:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (s, 1H), 7.50 (d, J = 6.8 Hz, 1H), 7.12 (dd, J = 8.7, 7.2 Hz, 2H), 7.07 (t, J = 7.5 Hz, 1H), 7.00 (d, J = 7.1 Hz, 1H), 6.76 (d, J = 1.4 Hz, 1H), 6.61 (t, J = 7.3 Hz, 1H), 6.59-6.54 (m, 2H), 5.04 (d, J = 7.9 Hz, 1H), 3.66-3.59 (m, 1H), 3.33 (td, J = 9.1, 6.7 Hz, 1H), 2.43 (s, 3H), 2.35-2.24 (m, 1H), 2.15-1.95 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 147.5, 136.5, 128.9, 125.1, 122.6, 121.8, 120.6, 119.6, 119.2, 116.6, 115.5, 112.3, 56.4, 48.4, 33.7, 23.6, 16.6;

HRMS (ESI) for $C_{19}H_{20}N_2$ $[M+H]^+$ calcd. 279.1699, found: 277.1701.

2-methyl-3-(1-phenylpyrrolidin-2-yl)-1H-indole (5e)



5e

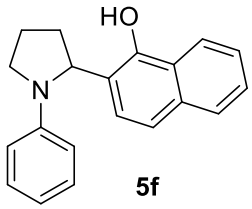
Following the general procedure, compound **5e** was obtained as a brown solid in 54% yield; m.p. =118-120 °C; R_f = 0.35 (PE:EA = 10:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (s, 1H), 7.50 (d, J = 8.5 Hz, 1H), 7.23 (d, J = 6.5 Hz, 1H), 7.14-7.01 (m, 4H), 6.63-6.50 (m, 3H), 5.02 (dd, J = 7.8, 2.8 Hz, 1H), 3.65 (ddd, J = 9.5, 6.5, 3.4 Hz, 1H), 3.45-3.35 (m, 1H), 2.41-2.29 (m, 1H), 2.22 (s, 3H), 2.13-1.97 (m, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 147.4, 135.1, 130.4, 128.9 ,127.4, 120.9, 119.2, 118.2 115.3, 113.2, 111.9, 110.1, 56.2, 48.9, 35.1, 24.5, 12.0;

HRMS (ESI) for $C_{19}H_{20}N_2$ $[M+H]^+$ calcd. 277.1699, found: 277.1699.

2-(1-phenylpyrrolidin-2-yl)naphthalen-1-ol (5f)



5f

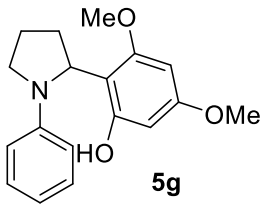
Following the general procedure, compound **5f** was obtained as a brown oil in 72% yield; R_f = 0.52 (PE:EA = 10:1);

^{1}H NMR (600 MHz, $CDCl_3$): δ 10.09 (s, 1H), 8.06 (d, J = 7.5 Hz, 1H), 7.70-7.64 (m, 1H), 7.38-7.28 (m, 3H), 7.15 (d, J = 8.4 Hz, 1H), 7.13-7.07 (m, 2H), 6.79 (dd, J = 16.8, 8.1 Hz, 3H), 4.60 (dd, J = 8.3, 5.8 Hz, 1H), 3.90-3.84 (m, 1H), 3.28-3.21 (m, 1H), 2.43-2.34 (m, 1H), 2.18-2.05 (m, 2H), 2.01-1.93 (m, 1H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 151.5, 148.6, 133.4, 129.0, 127.2, 126.0, 125.5, 125.3, 125.0, 121.9, 120.4, 119.3, 116.1, 77.2, 77.0, 76.7, 66.6, 52.3, 35.6, 24.3;

HRMS (ESI) for $C_{20}H_{19}NO$ $[M+H]^+$ calcd. 290.1539, found: 290.1540.

3,5-dimethoxy-2-(1-phenylpyrrolidin-2-yl)phenol (5g)



5g

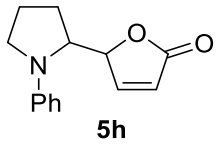
Following the general procedure, compound **5g** was obtained as a white solid in 78% yield; m.p. = 94-96 °C; R_f = 0.42 (PE:EA = 10:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.32 (s, 1H), 7.20 (t, J = 7.1 Hz, 2H), 6.92 – 6.82 (m, 3H), 6.06 (d, J = 2.4 Hz, 1H), 5.96 (d, J = 2.3 Hz, 1H), 4.91 (dd, J = 8.2, 5.5 Hz, 1H), 3.87-3.78 (m, 4H), 3.73 (s, 3H), 3.19 (dd, J = 16.3, 8.0 Hz, 1H), 2.43-2.31 (m, 1H), 2.18-2.06 (m, 1H), 2.04-1.92 (m, 2H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 160.1, 158.4, 157.5, 149.0, 129.0, 120.5, 116.2, 107.0, 93.9, 90.6, 60.0, 55.6, 55.2, 52.2, 34.2, 24.4;

HRMS (ESI) for $C_{18}H_{21}NO_3$ $[M+H]^+$ calcd. 300.1594, found:300.1594.

5-(1-phenylpyrrolidin-2-yl)furan-2(5H)-one (5h)



5h

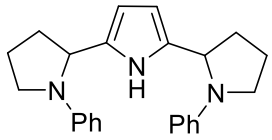
Following the general procedure, compound **5h** was obtained as a colorless liquid in 76% yield; R_f = 0.35 (PE:EA = 4:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (dd, J = 8.7, 7.3 Hz, 2H), 7.05 (q, J = 1.7 Hz, 1H), 6.71 (t, J = 7.3 Hz, 1H), 6.50 (d, J = 7.7 Hz, 2H), 4.83-4.71 (m, 2H), 4.53 (dt, J = 8.8, 2.0 Hz, 1H), 3.63-3.55 (m, 1H), 3.34-3.25 (m, 1H), 2.31-2.19 (m, 1H), 2.11-1.88 (m, 4H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 173.0, 146.4, 146.2, 135.4, 129.2, 116.5, 112.2, 70.3, 55.5, 48.4, 31.2, 23.2;

HRMS (ESI) for $C_{14}H_{16}N_2$ $[M+H]^+$ calcd. 230.1176, found: 230.1178.

2-(1-phenylpyrrolidin-2-yl)-1H-pyrrole (5i)



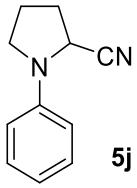
Following the general procedure, compound **5i** was obtained as a colorless liquid in 47% yield, 1.3:1 d.r.; R_f = 0.62 (PE:EA = 10:1);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.95 (s, 1H), 7.16 (t, *J* = 7.6 Hz, 4H), 6.68 (t, *J* = 7.2 Hz, 2H), 6.56 (d, J = 8.4 Hz, 4H), 5.91 (d, *J* = 2.4 Hz, 2H), 4.69-4.66 (m, 2H), 3.56-3.49 (m, 2H), 3.24-3.20 (m, 2H), 2.22-2.18 (m, 2H), 2.03-1.98 (m, 4H); 1.94-1.91 (m, 2H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 147.9, 147.8, 133.2, 133.1, 128.9(7), 128.9(6), 116.4, 116.3, 112.6, 112.4, 104.2, 104.1(9), 57.6, 57.5, 48.7, 48.6(8), 35.2, 34.7, 23.8, 23.7;

HRMS (ESI) for $C_{24}H_{27}N_3$ $[M+H]^+$ calcd. 358.2278, found: 358.2278.

1-phenylpyrrolidine-2-carbonitrile (5j)



5j

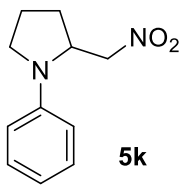
Following the general procedure, compound **5j** was obtained as a brown oil in 80% yield; R_f =0.34 (PE:EA = 10:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (dd, J = 8.7, 7.2 Hz, 2H), 6.84 (t, J = 7.4 Hz, 1H), 6.70 (d, J = 7.7 Hz, 2H), 4.44 (d, J = 7.4 Hz, 1H), 3.47 (td, J = 8.2, 7.6, 2.9 Hz, 1H), 3.42-3.33 (m, 1H), 2.47-2.37 (m, 1H), 2.35-2.15 (m, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 145.2, 129.5, 119.3, 118.2, 112.7, 49.1, 47.4, 31.5, 23.9;

HRMS (ESI) for $C_{11}H_{12}N_2$ $[M+H]^+$ calcd.173.1073, found: 173.1074.

2-(nitromethyl)-1-phenylpyrrolidine (5k)



5k

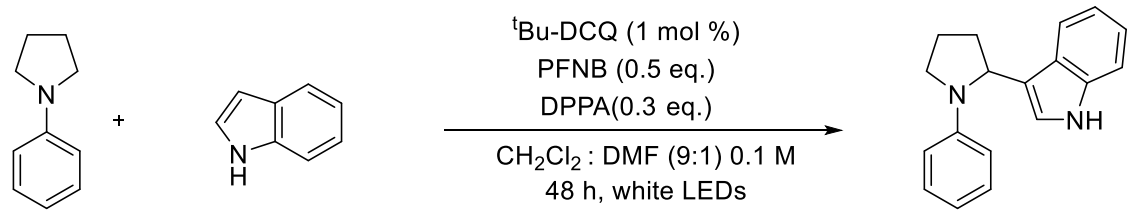
Following the general procedure, compound **5k** was obtained as a yellow oil in 84% yield; R_f = 0.54 (PE:EA = 10:1);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.31-7.27 (m, 2H), 6.78 (t, *J* = 7.3 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 2H), 4.63 (dd, *J* = 11.6, 3.1 Hz, 1H), 4.47-4.38 (m, 1H), 4.19 (ddd, *J* = 11.2, 9.8, 1.2 Hz, 1H), 3.49 (t, *J* = 8.1 Hz, 1H), 3.21 (td, *J* = 9.1, 6.6 Hz, 1H), 2.19-2.03 (m, 4H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 145.7, 129.6, 117.3, 112.0, 75.8, 55.7, 47.3, 29.2, 22.7;

HRMS (ESI) for $C_{11}H_{14}N_2O_2$ $[M+H]^+$ calcd. 207.1128, found: 207.1129.

5. Gram-scale reaction



General procedure： A dried 10 mL reaction tube was charged with the photocatalyst (34.2 mg, 0.05 mmol, 1 mol %), Diphenylphosphinic acid (0.3 mmol, 650 mg), PFNB (2.5 mmol, 0.33 mL), 1-phenylpyrrolidine **1a** (6.5 mmol, 1.3 equiv., 0.95 mL), 1H-indole **2a** (5.0 mmol, 1.0 equiv., 585.9 mg) and 45 mL CH_2Cl_2 + 5 mL DMF. The reaction mixture was degassed by three cycles of freeze-pump-thaw. After the mixture was thoroughly degassed, the reaction was under the irradiation of the white LEDs for 48 h. After completion of the reaction as checked by TLC. The reaction mixture was purified by silica gel flash column chromatography (petroleum PE/EA=10:1) to give the product **3a** (943.0 mg, 72% yield).

6. Mechanistic investigations

6.1 Luminescence quenching experiments

Stern-Volmer experiments were conducted on an Agilent Technologies Cary Eclipse Fluorescence Spectrophotometer using the Cary Eclipse Scan Application. Rigorously purged (with nitrogen) solutions of each component were prepared prior to each set of experiments. Luminescence quenching experiments were run with toluene as the solvent. The solutions were irradiated at 410 nm and the luminescence was measured from 440 nm to 700 nm (emission maximum is at 530 nm). The concentration of DCQ-^{t}Bu stock solution was 0.15 mM in toluene, the concentration of N-Ph-pyrrolidine stock solution was 3.00 mM in toluene, the concentration of 1*H*-Indole stock solution was 3.00 mM in toluene and the concentration of PFNB stock solution was 3 mM in toluene. All of the gradient concentration of mixed solutions was used at once for experiments after prepared by methods as follows: 2 mL of stock solution was added 8 mL toluene in 10 mL volumetric flask to form 0.6 mM solution. 1.2 mM (4 mL + 6mL), 1.8 mM (6 mL + 4 mL) and 2.4 mM (8 mL + 2 mL) was prepared by the same operation, finally each of the solution was diluted to 2/3 of original concentration when used for experiments. After being stirred with a thin glass rod, the emission spectrum was collected. Linear regression of I0/I against concentration is done in Origin.

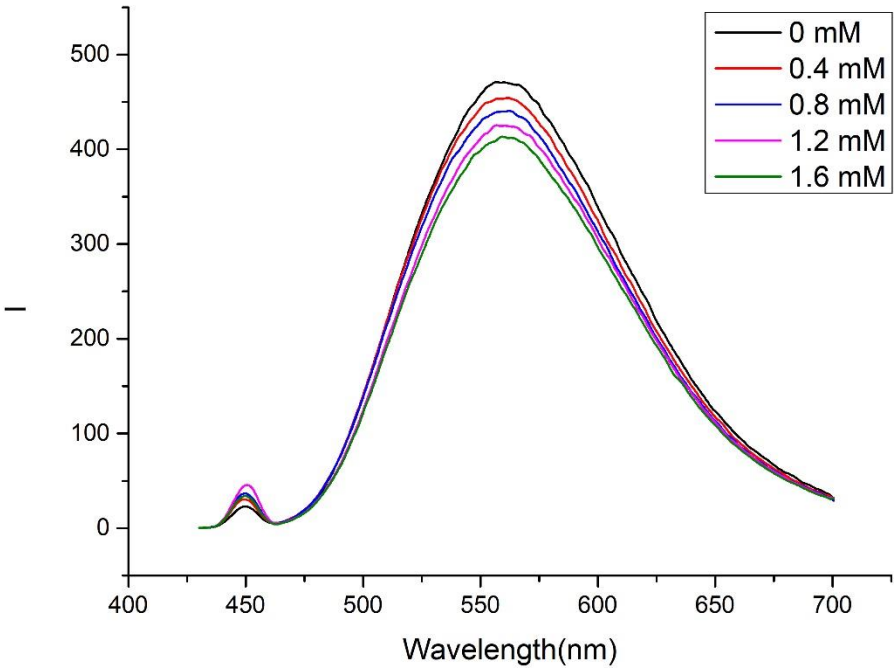


Figure S1. Fluorescence quenching data with DCQ-^{t}Bu and variable N-Ph pyrrolidine.

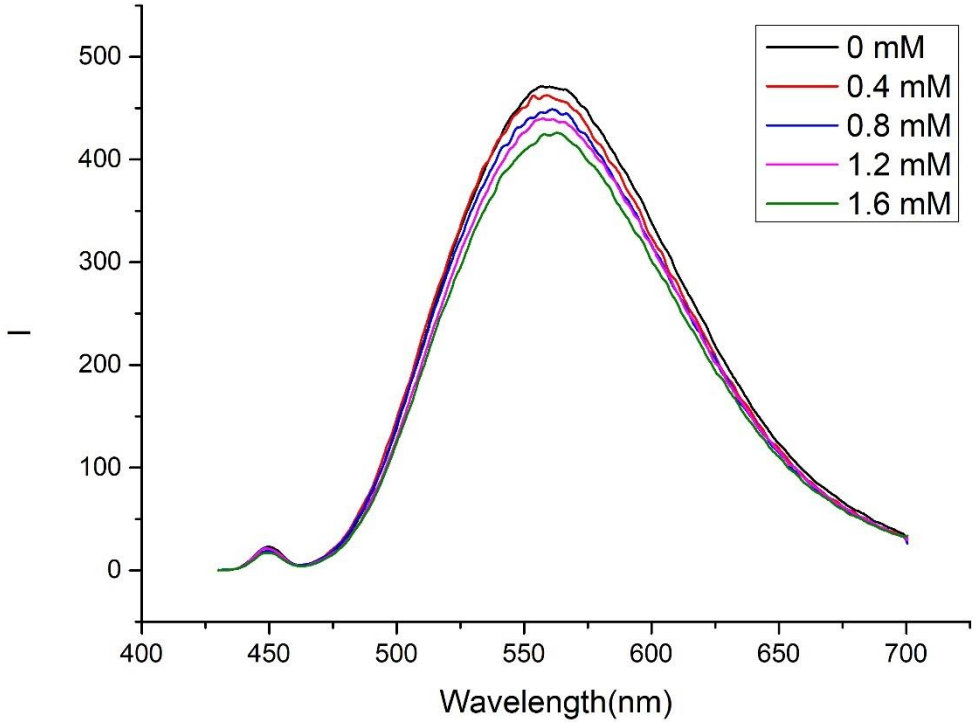


Figure S2. Fluorescence quenching data with DCQ-tBu and variable PFNB.

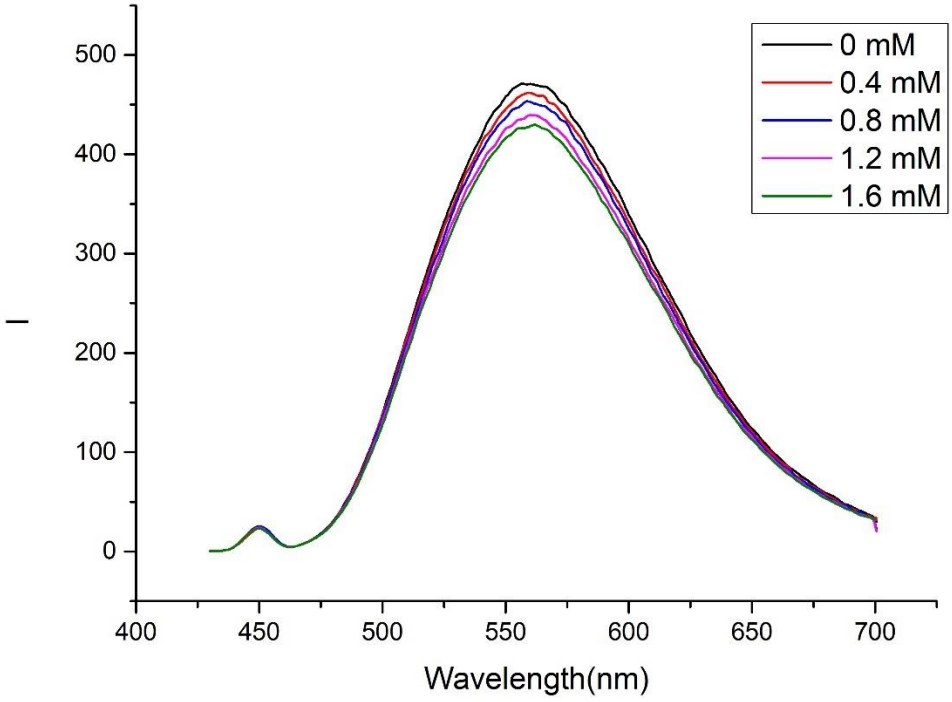


Figure S3. Fluorescence quenching data with DCQ-^{t}Bu and variable 1*H*-Indole

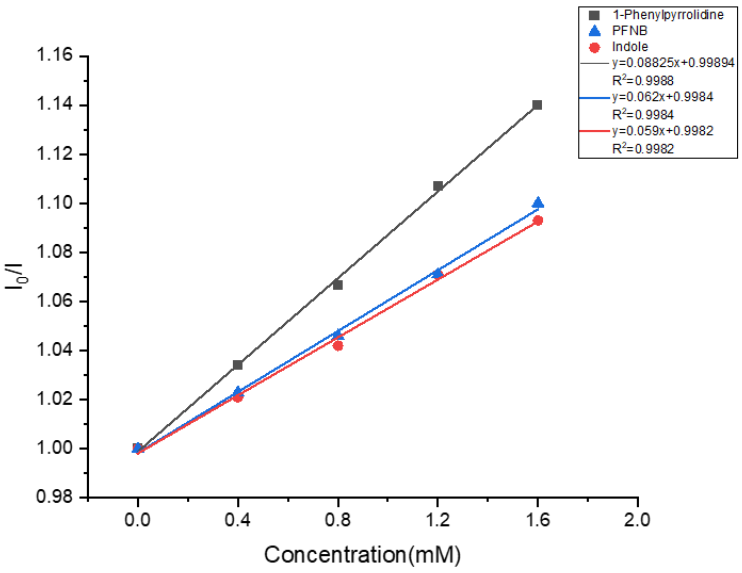
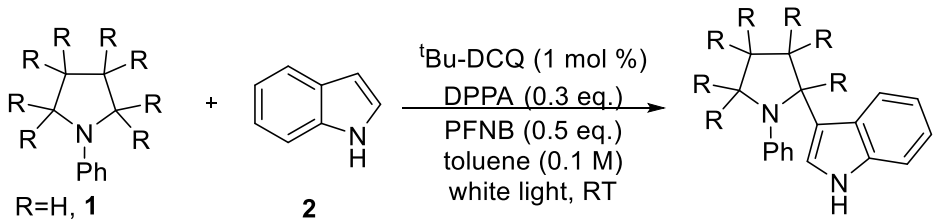


Figure S4. Stern-Volmer plot of DCQ with **1a**, **2a**, and PFNB.

6.2 Kinetic isotope effect



10 min: 18% conversion, k_H:k_D = 2.20 : 1
20 min: 29% conversion, k_H:k_D = 1.85 : 1

A dried 10 mL reaction tube was charged with the photocatalyst (0.001 mol, 0.68 mg), DPPA (0.03 mmol, 6.4 mg), PFNB (0.05 mmol, 6.5 μL), tertiary arylamine **1** (0.065 mmol, 0.65 equiv.) and **1**-d_8 (0.065 mmol, 0.65 equiv.), *1H*-indole **2a** (0.1 mmol, 1.0 equiv.) and 1.0 mL toluene. The reaction mixture was degassed by three cycles of freeze-pump-thaw. After the mixture was thoroughly degassed, the vial was placed

beside a white LED light. The reaction was stirred at 25 ºC for 10min and 20 min. The yields and k_H/k_D ratios were determined by the ^{1}H NMR spectrum.

Figure S5. ^{1}H NMR of the reaction mixture after reacting 10 min.

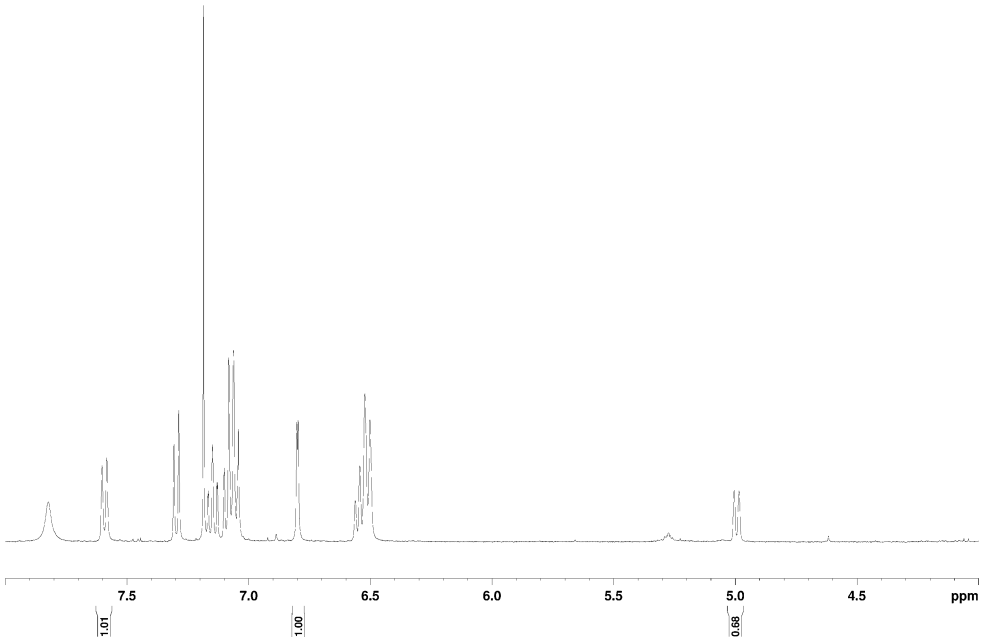
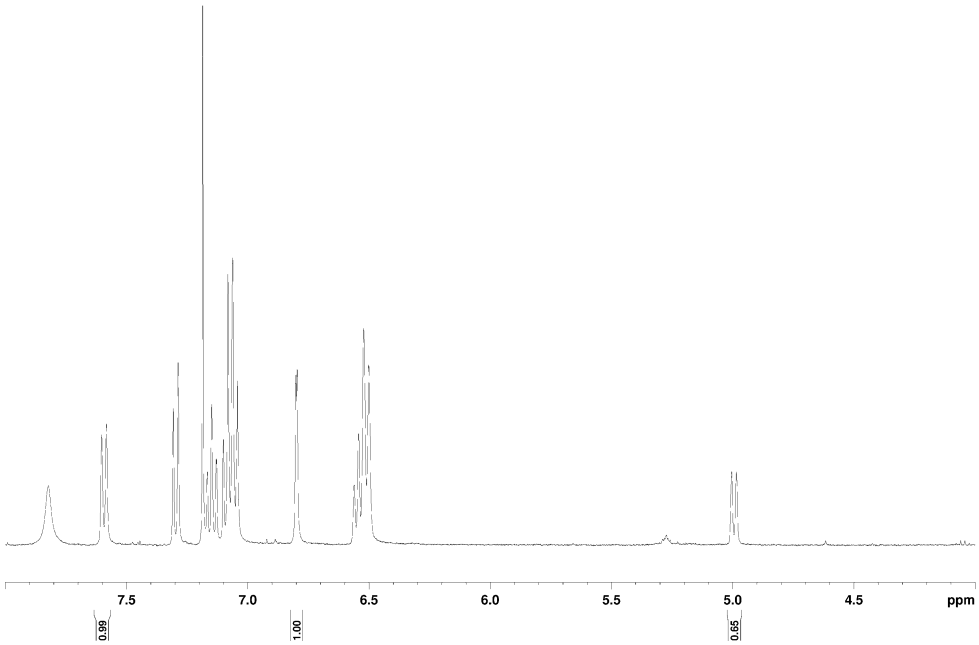
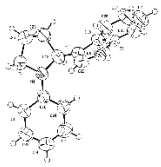


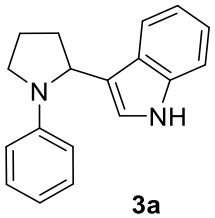
Figure S6. ^{1}H NMR of the reaction mixture after reacting 20 min.


7.5
7.0
6.5
6.0
5.5
5.0
4.5
ppm
0.99
1.00
0.65

7. X-Ray crystallographic data of product 3a

The crystal structure **3a** has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: CCDC 2270021.



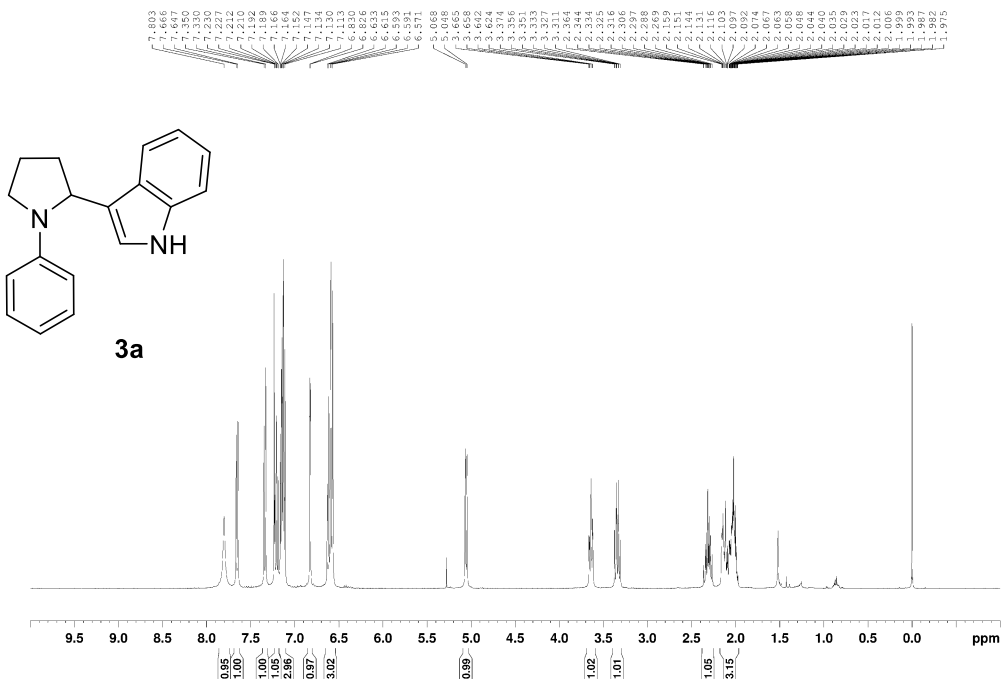


3a

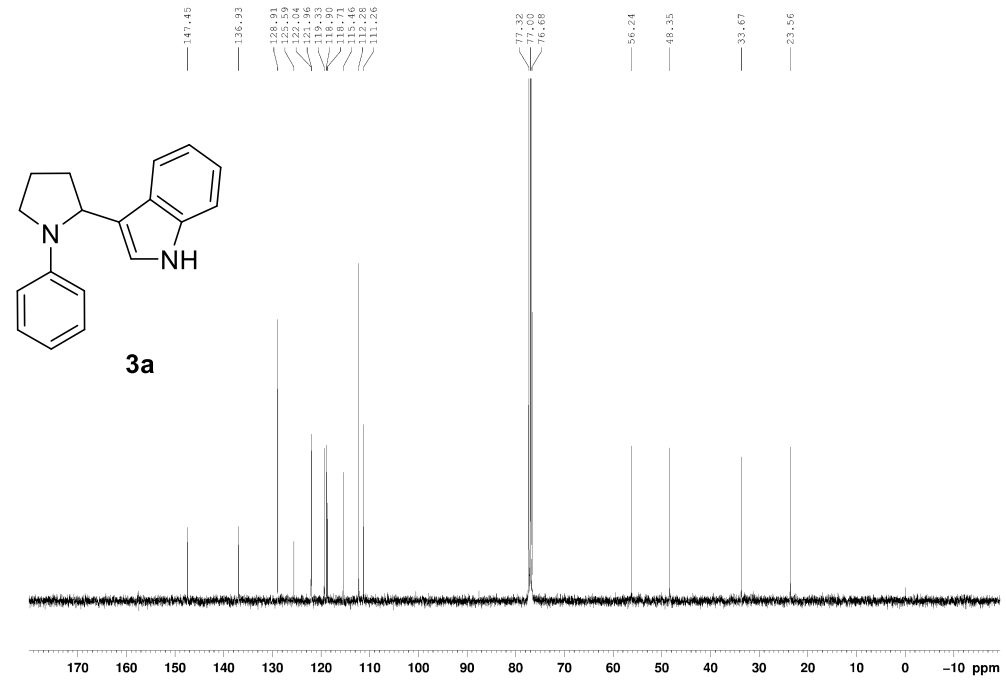
Bond precision:	C-C = 0.0024 A	Wavelength=1.54184	
Cell:	a=13.9327(3)	b=11.0108(3)	c=19.2787(4)
	alpha=90	beta=103. 663(2)	gamma=90
Temperature:	301 K		
	Calculated	Reported	
Volume	2873.86(12)	2873.84(11)	
Space group	P 21/n	P 1 21/n 1	
Hall group	-P 2yn	-P 2yn	
Moiety formula	C18 H18 N2	2(C18 H18 N2)	
Sum formula	C18 H18 N2	C36 H36 N4	
Mr	262.34	524.69	
Dx,g cm-3	1.213	1.213	
Z	8	4	
Mu (mm-1)	0.550	0.550	
F000	1120.0	1120.0	
F000’	1122.90		
h,k,lmax	17,13,24	17,13,24	
Nref	6027	5716	
Tmin,Tmax	0.906,0.936	0.609,1.000	
Tmin’	0.906		
Correction method= # Reported T Limits: Tmin=0.609 Tmax=1.000			
AbsCorr = MULTI-SCAN			
Data completeness= 0.948		Theta(max)= 76.374	
R(reflections)= 0.0406(4190)		wR2(reflections)= 0.1229(5716)	
S = 1.055		Npar= 370	

8. NMR spectra of compounds

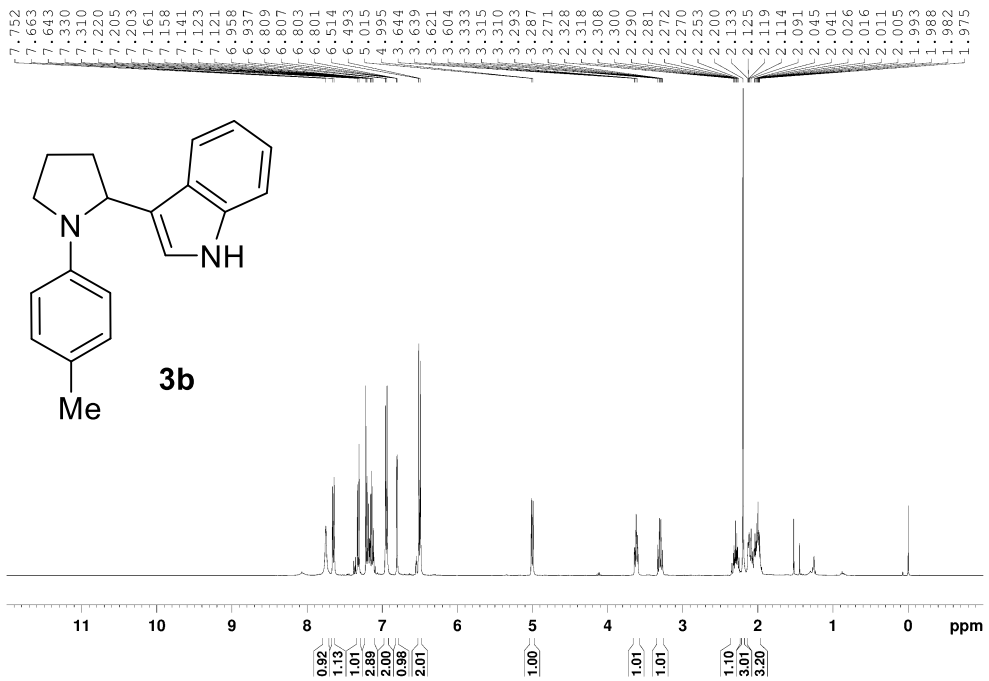
^{1}H NMR of **3a** ($CDCl_3$, 400 MHz)



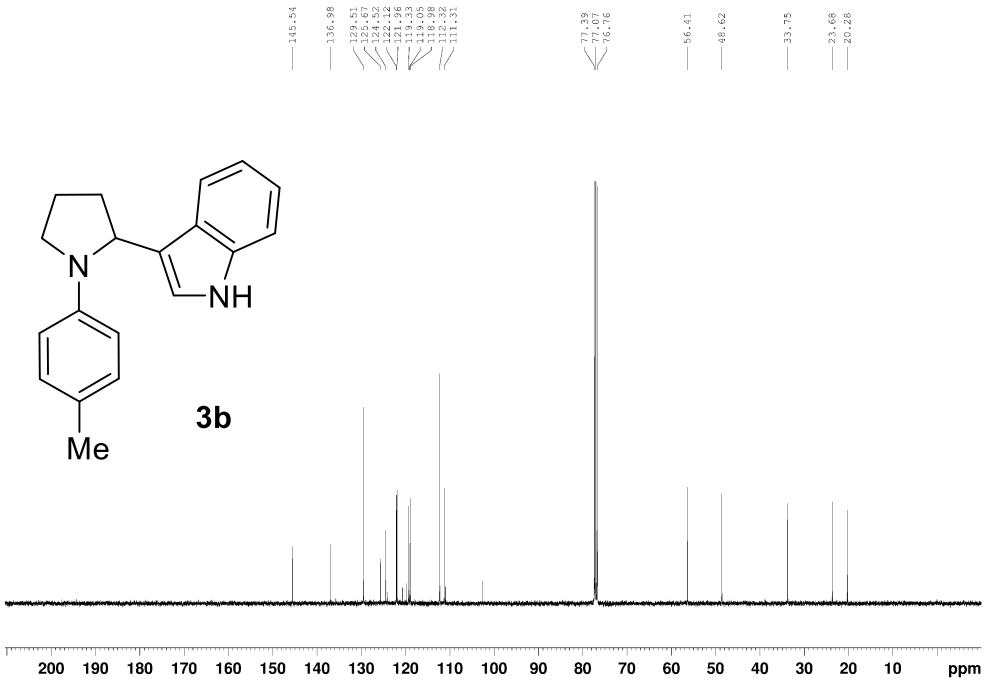
^{13}C NMR of **3a** ($CDCl_3$, 101 MHz)



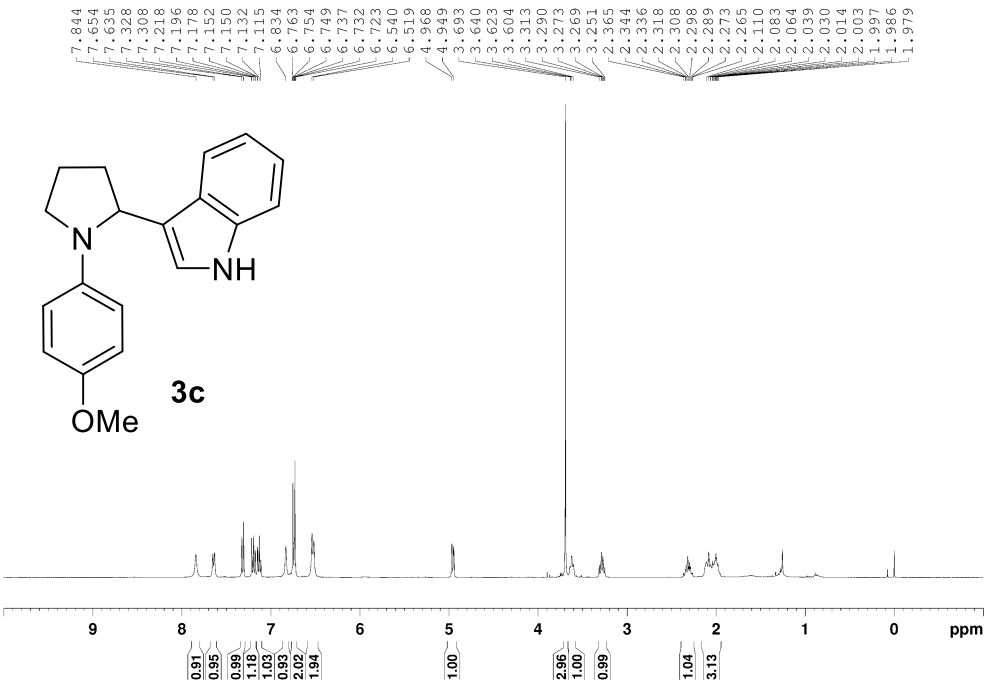
^{1}H NMR of **3b** ($CDCl_3$, 400 MHz)



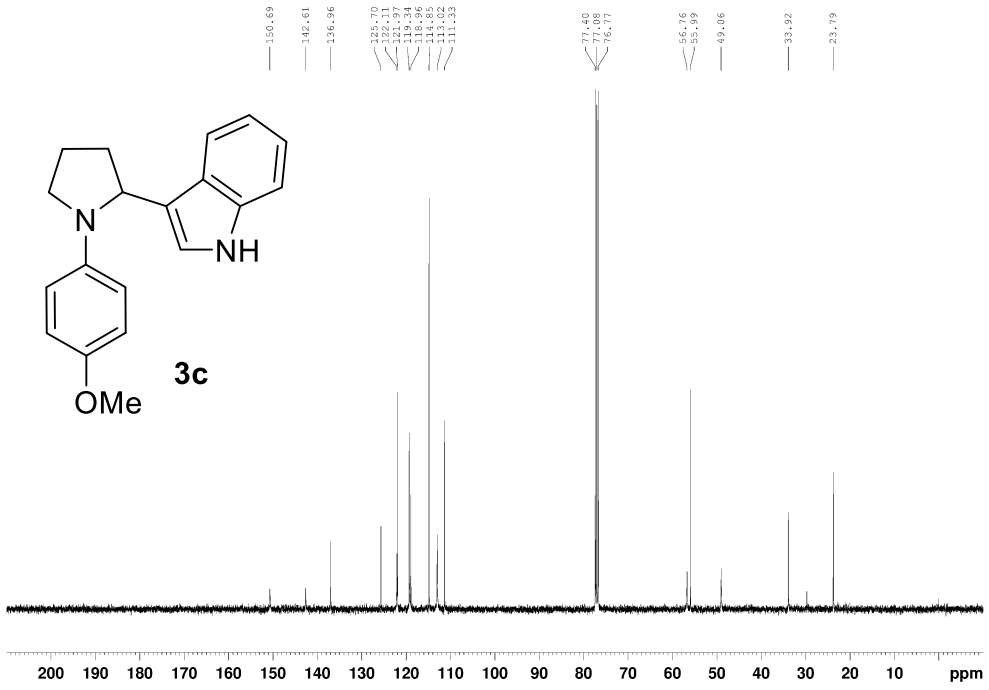
^{13}C NMR of **3b** ($CDCl_3$, 101 MHz)



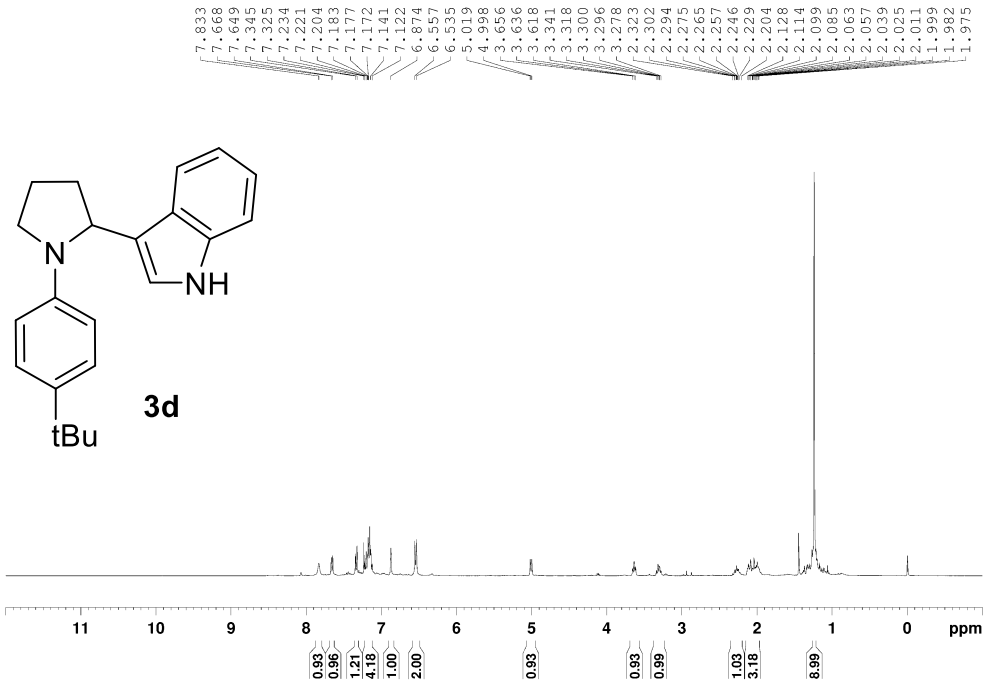
^{1}H NMR of **3c** ($CDCl_3$, 400 MHz)



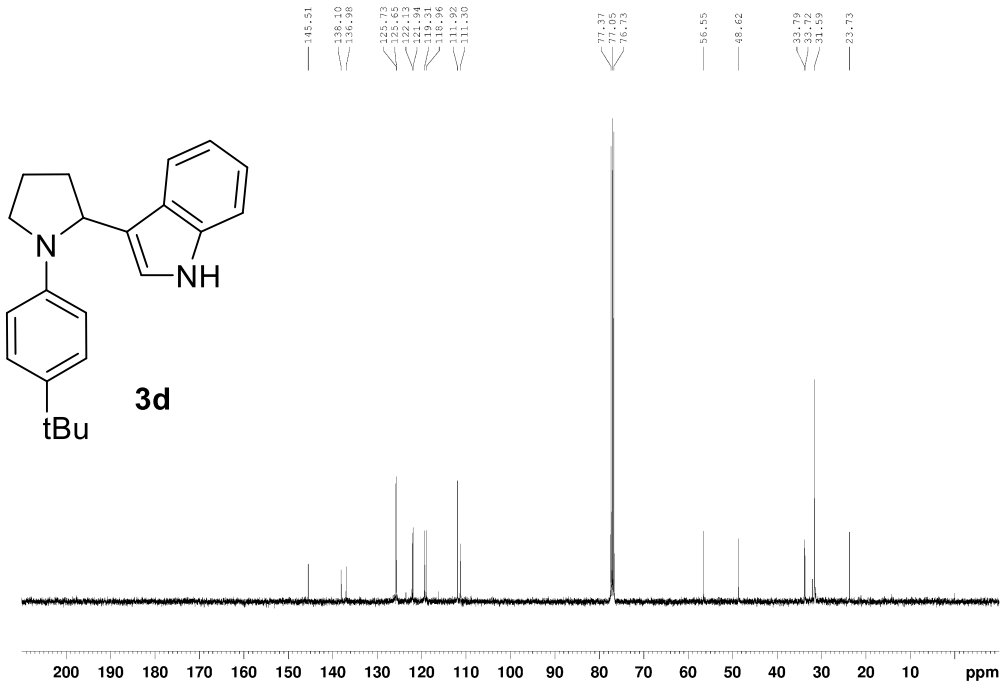
^{13}C NMR of **3c** ($CDCl_3$, 101 MHz)



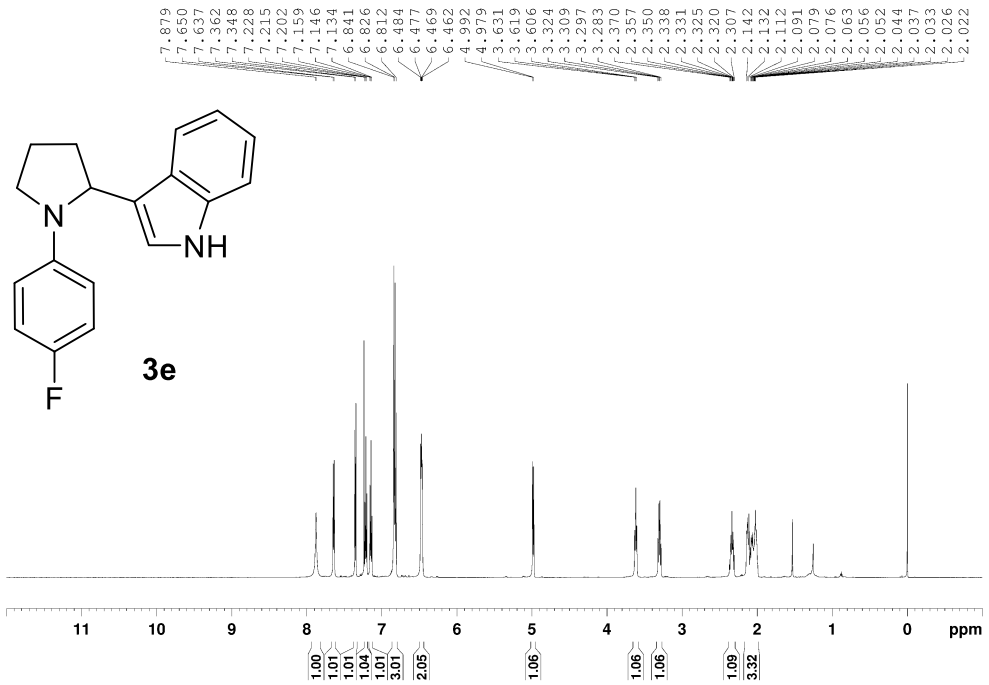
^{1}H NMR of **3d** ($CDCl_3$, 400 MHz)



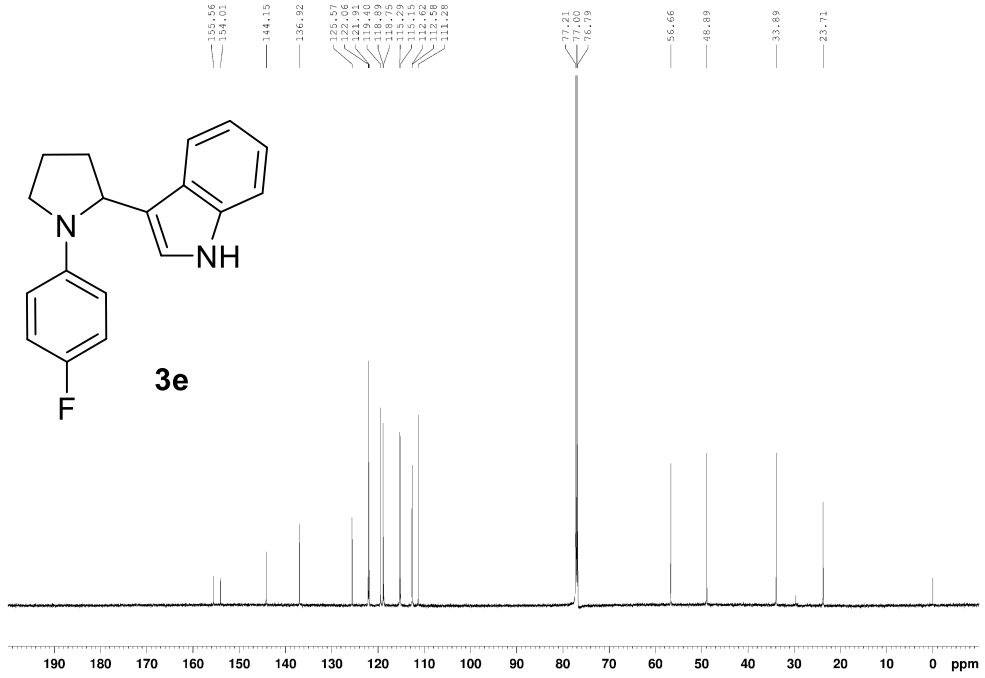
^{13}C NMR of **3d** ($CDCl_3$, 101 MHz)



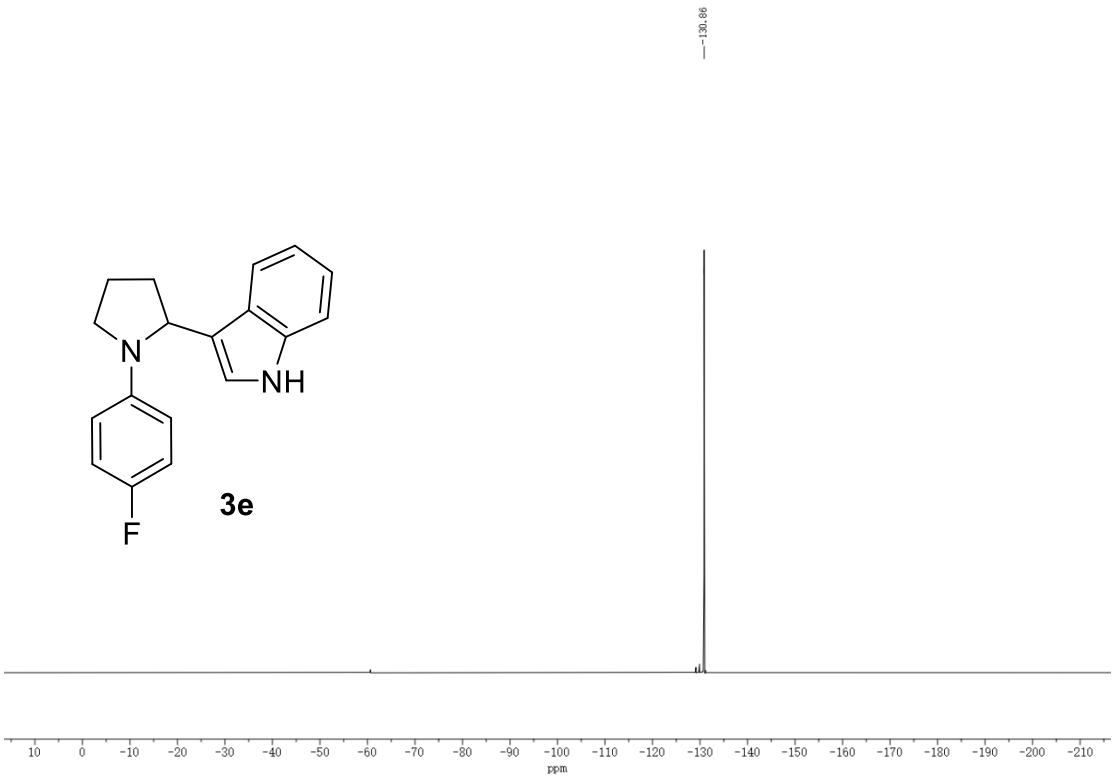
^{1}H NMR of **3e** ($CDCl_3$, 400 MHz)



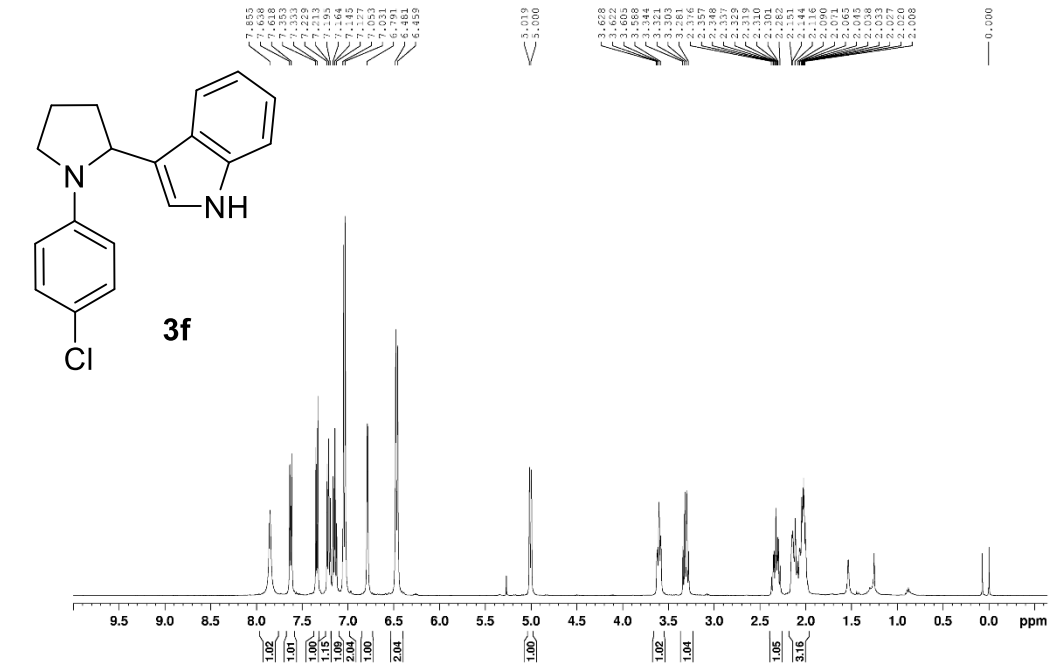
^{13}C NMR of **3e** ($CDCl_3$, 101 MHz)



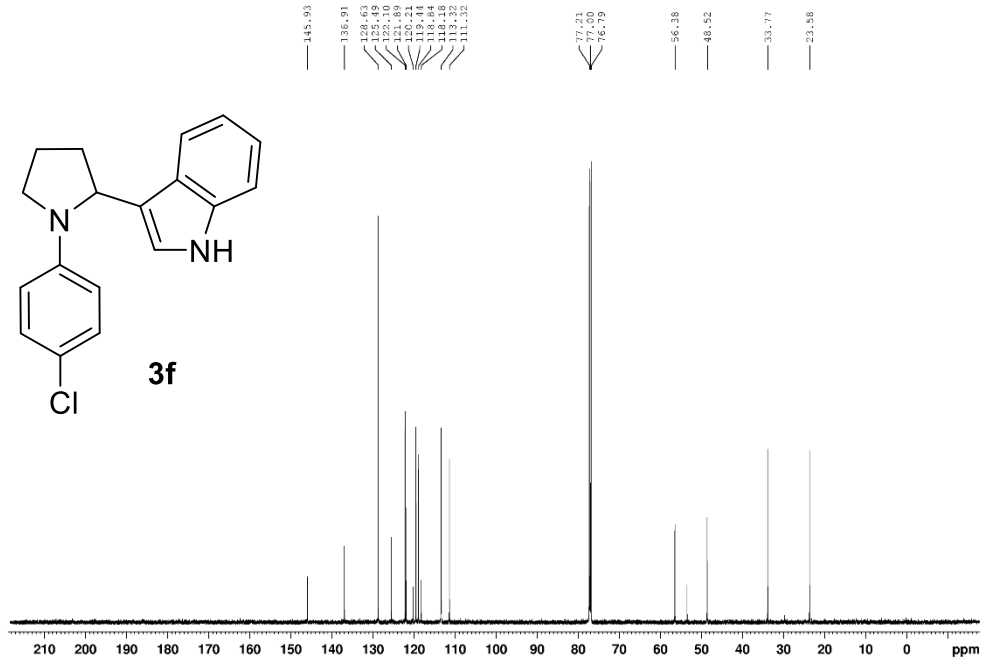
F^{19} NMR of **3e** ($CDCl_3$, 565 MHz)



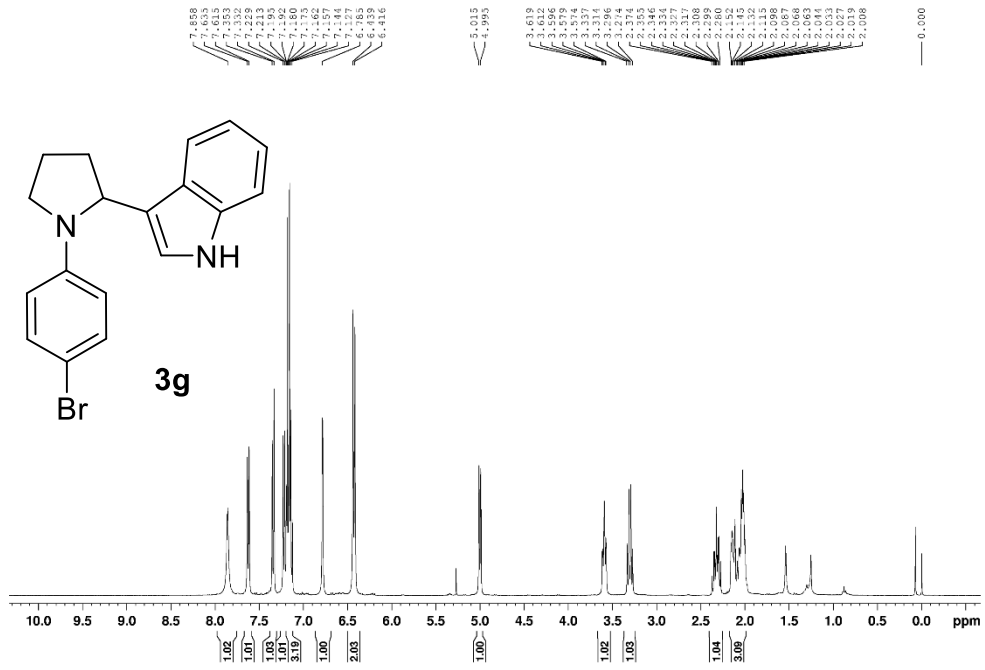
^1H NMR of **3f** ($CDCl_3$, 600 MHz)



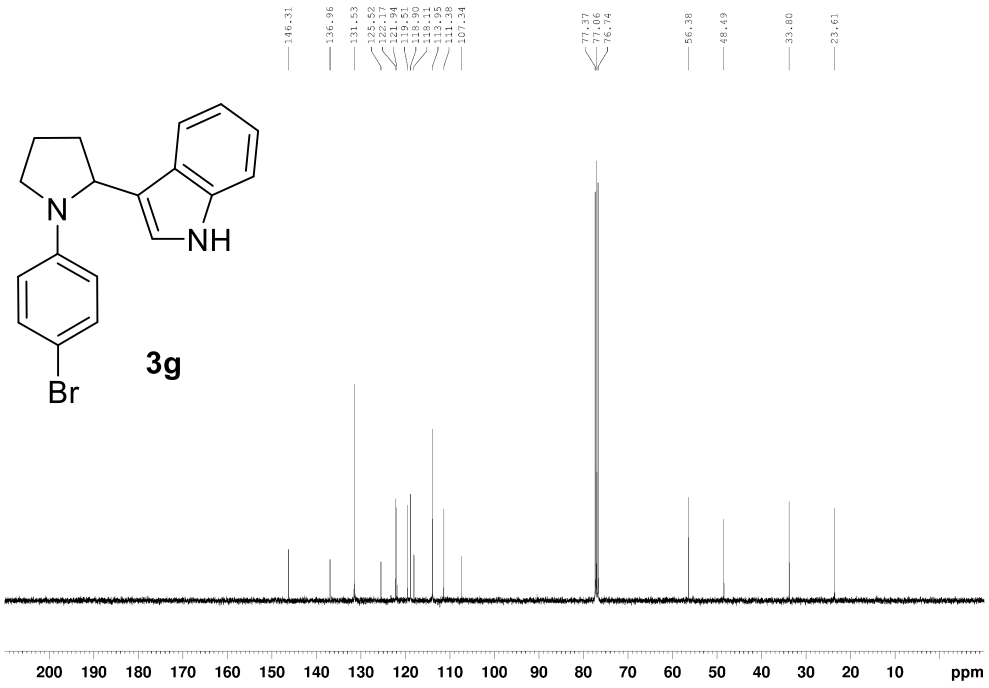
^{13}C NMR of **3f** ($CDCl_3$, 151 MHz)



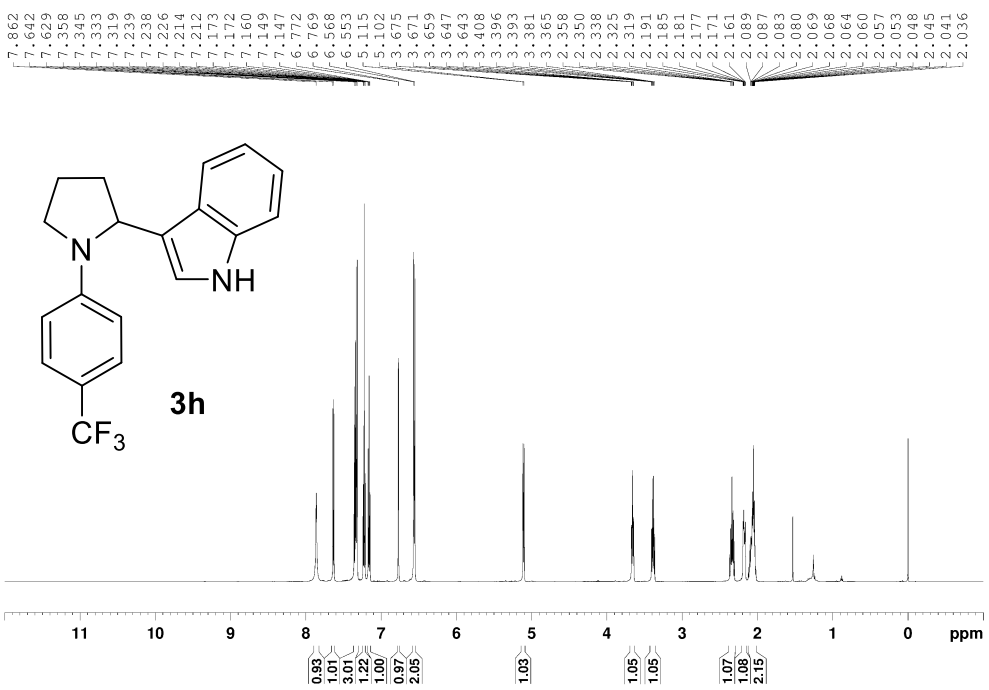
^{1}H NMR of **3g** ($CDCl_3$, 400 MHz)



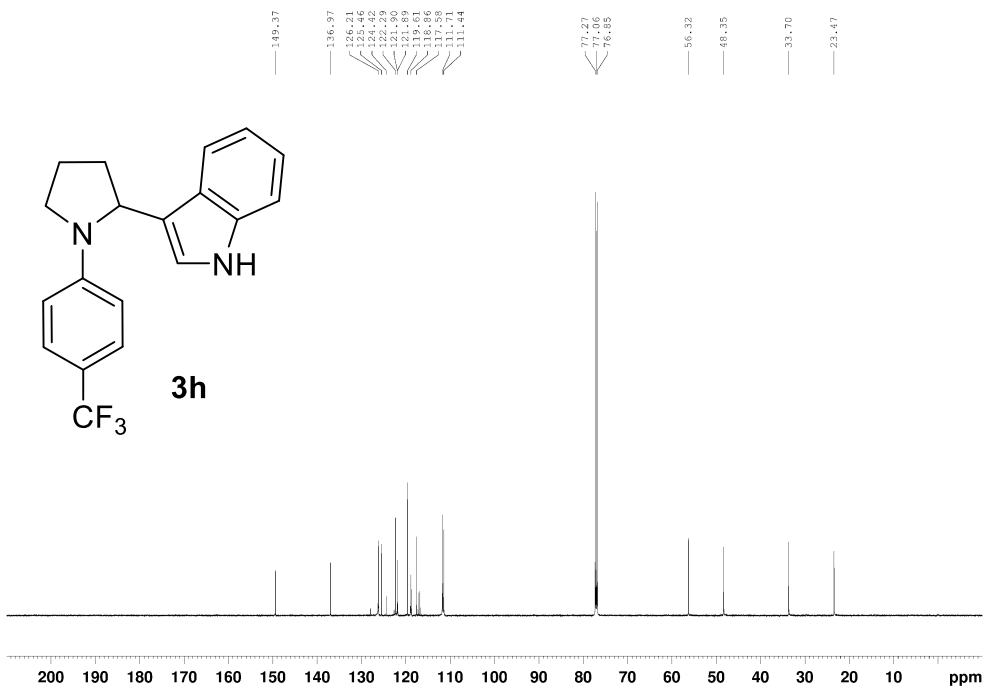
^{13}C NMR of **3g** ($CDCl_3$, 101 MHz)



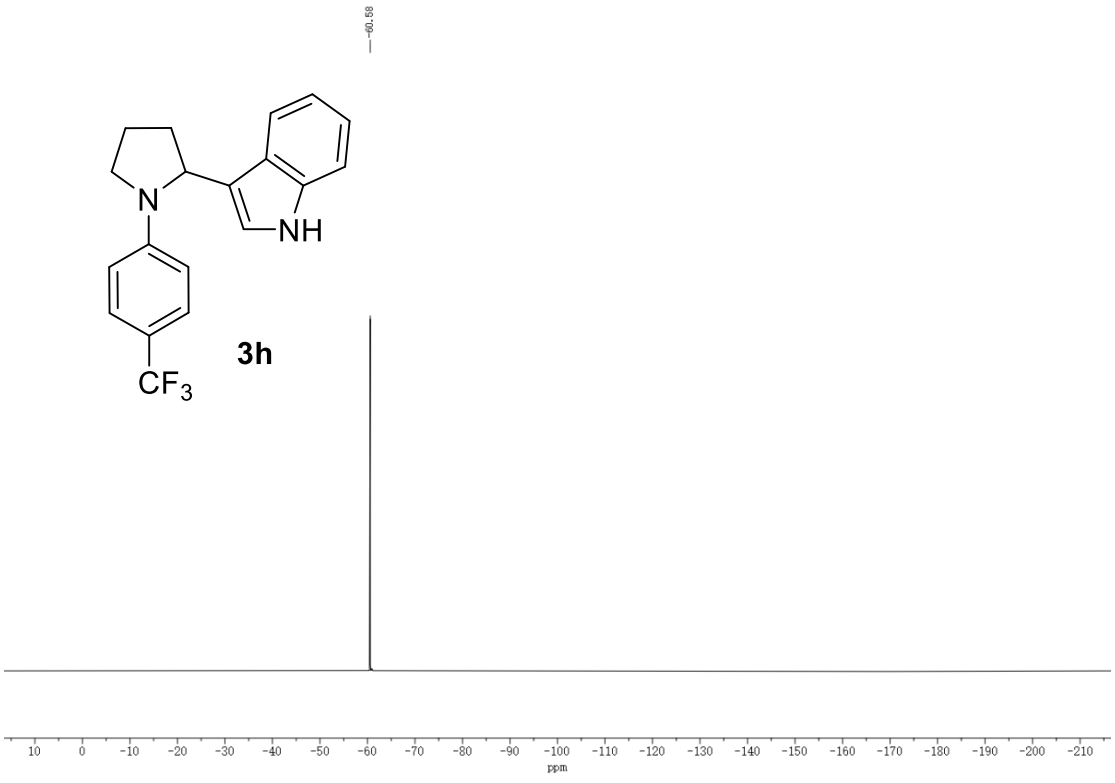
^{1}H NMR of **3h** ($CDCl_3$, 600 MHz)



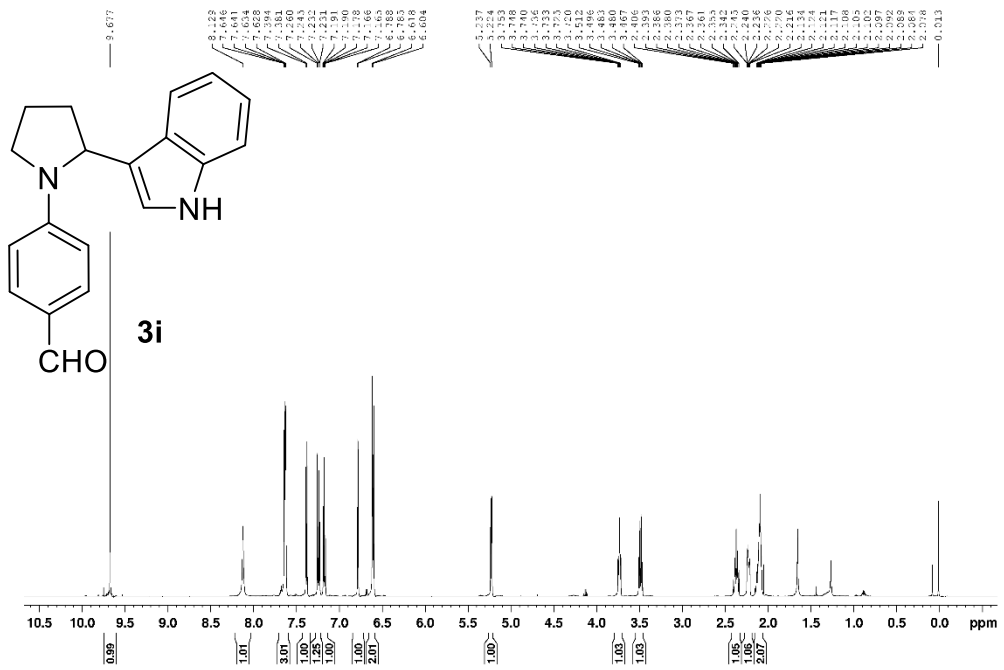
^{13}C NMR of **3h** ($CDCl_3$, 151 MHz)



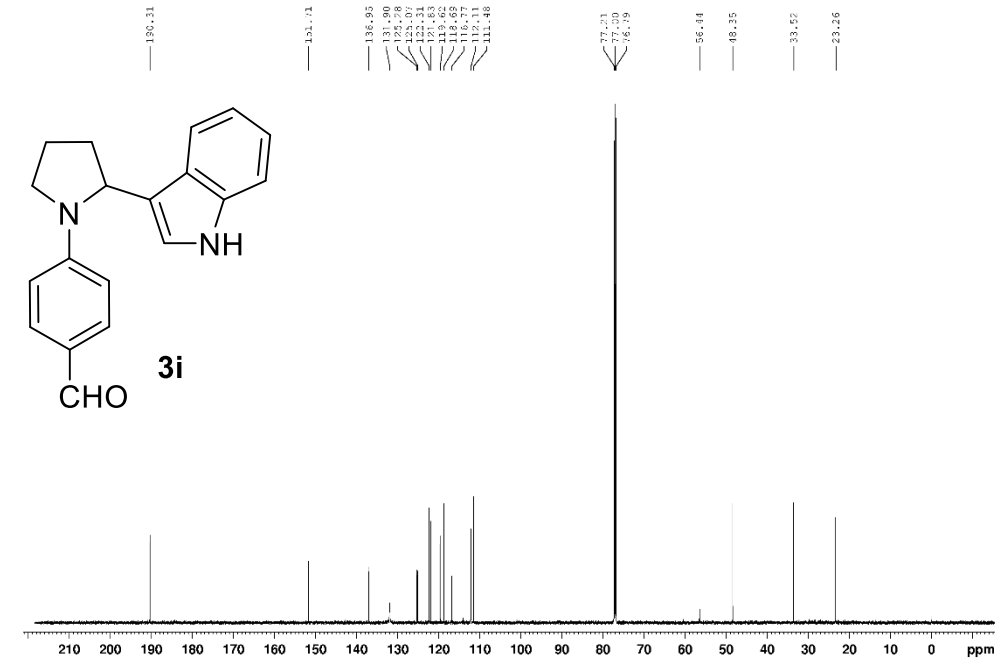
^{19}F NMR of **3h** ($CDCl_3$, 565 MHz)



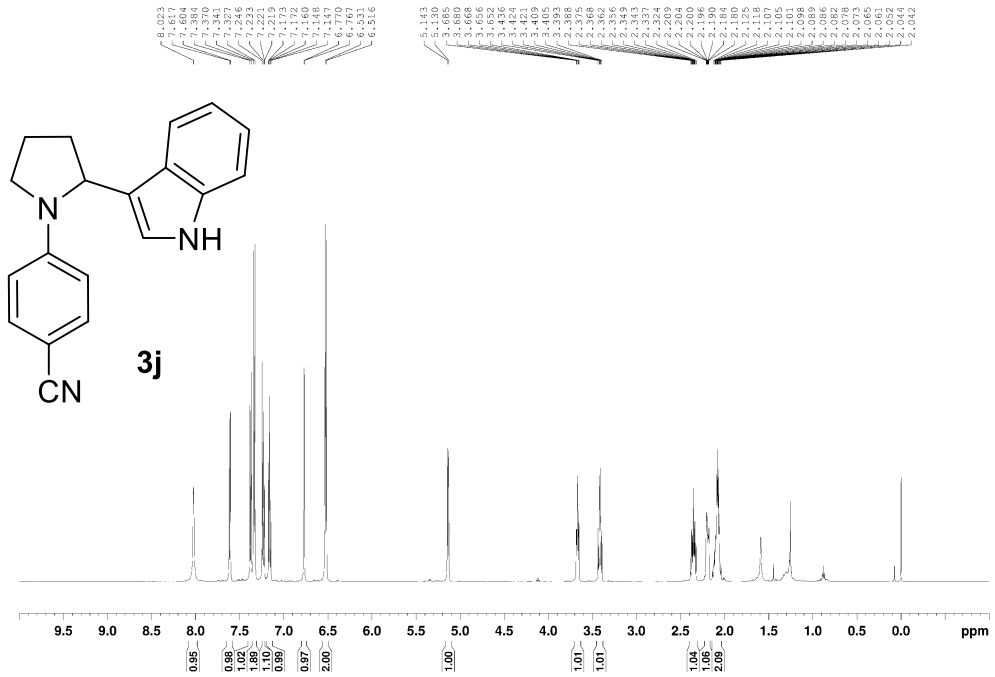
^{1}H NMR of **3i** ($CDCl_3$, 400 MHz)



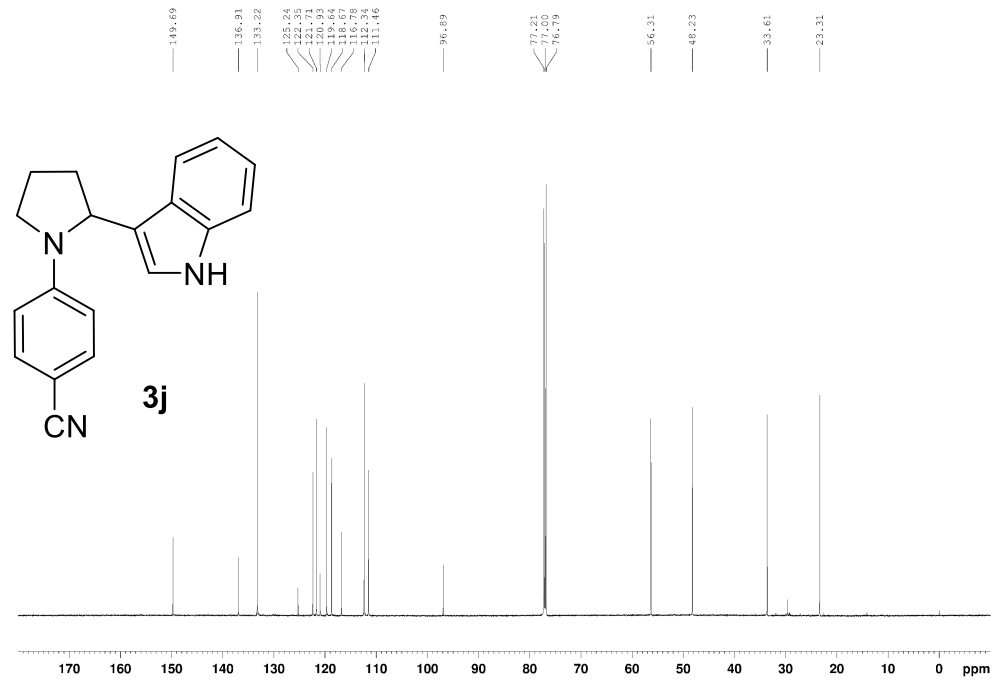
^{13}C NMR of **3i** ($CDCl_3$, 101 MHz)



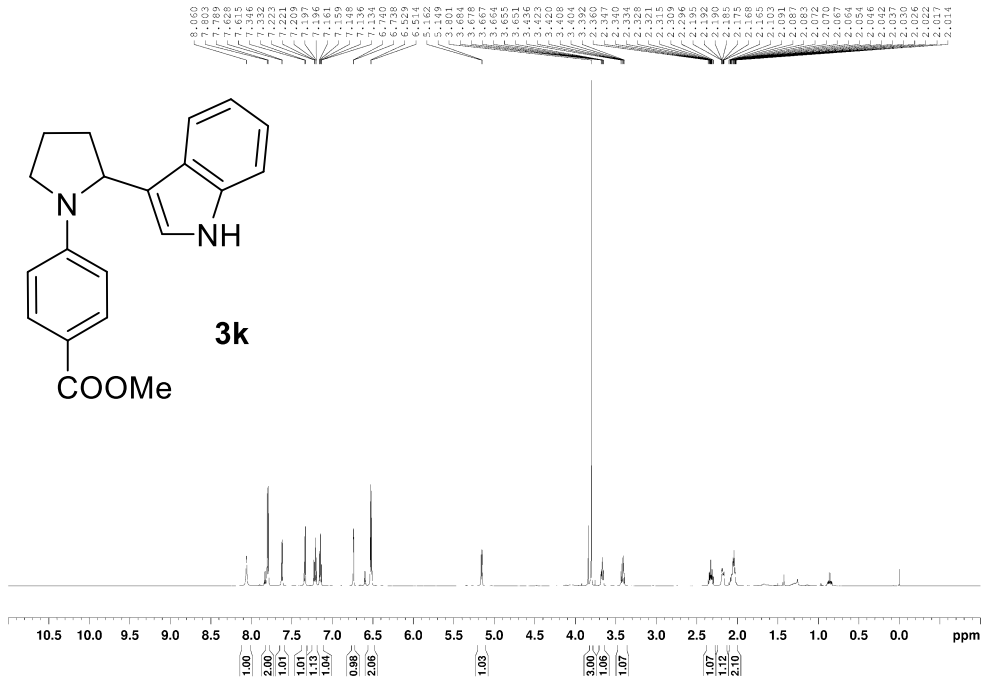
^{1}H NMR of **3j** ($CDCl_3$, 400 MHz)



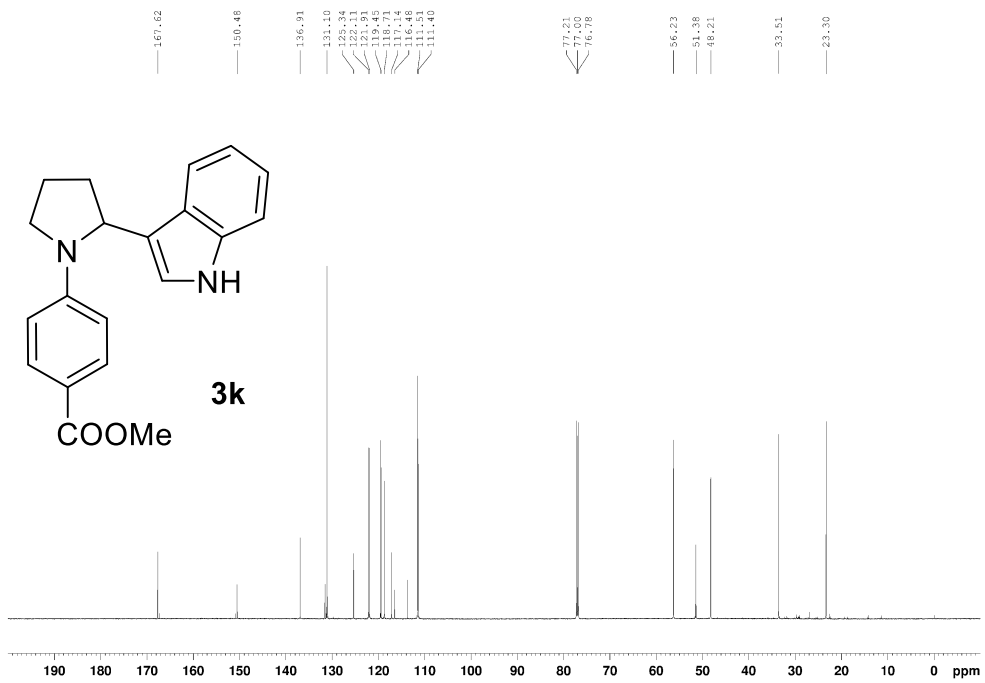
^{13}C NMR of **3j** ($CDCl_3$, 101 MHz)



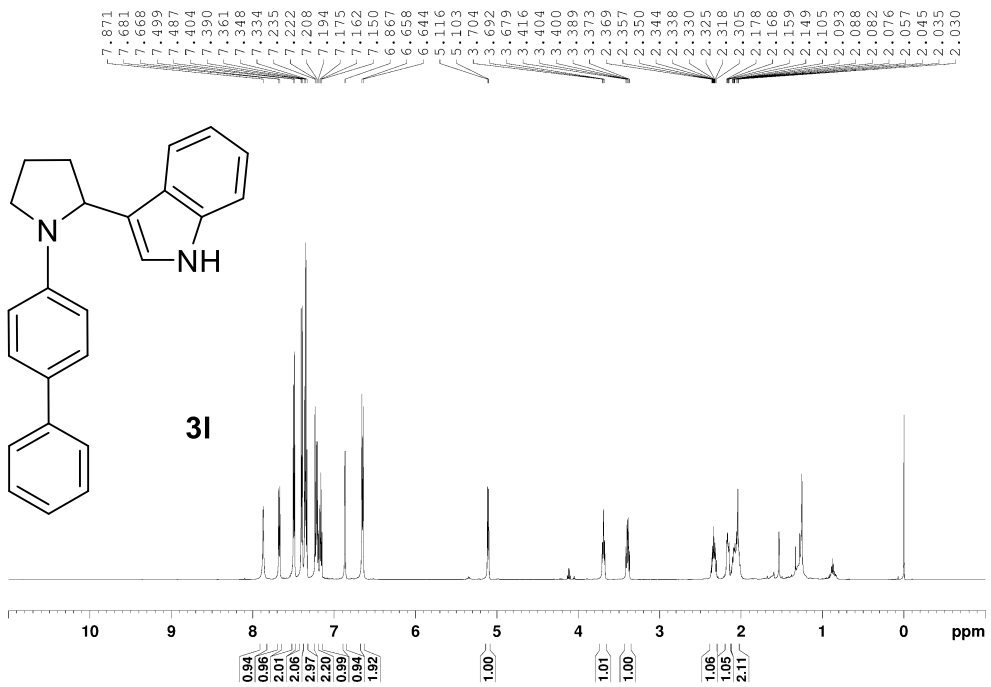
^{1}H NMR of **3k** ($CDCl_3$, 400 MHz)



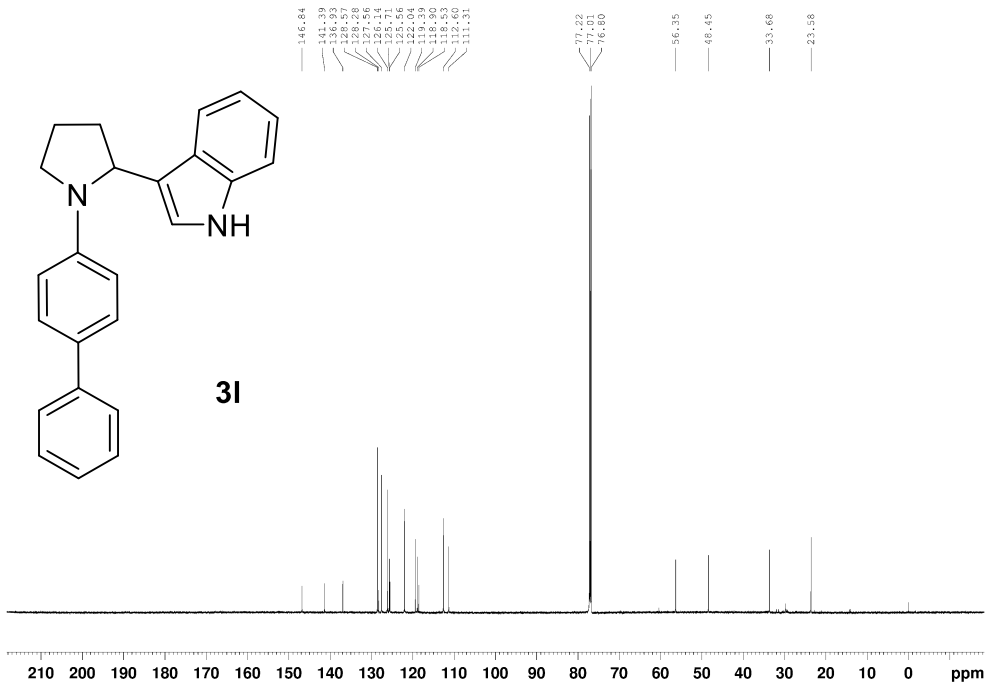
^{13}C NMR of **3k** ($CDCl_3$, 101 MHz)



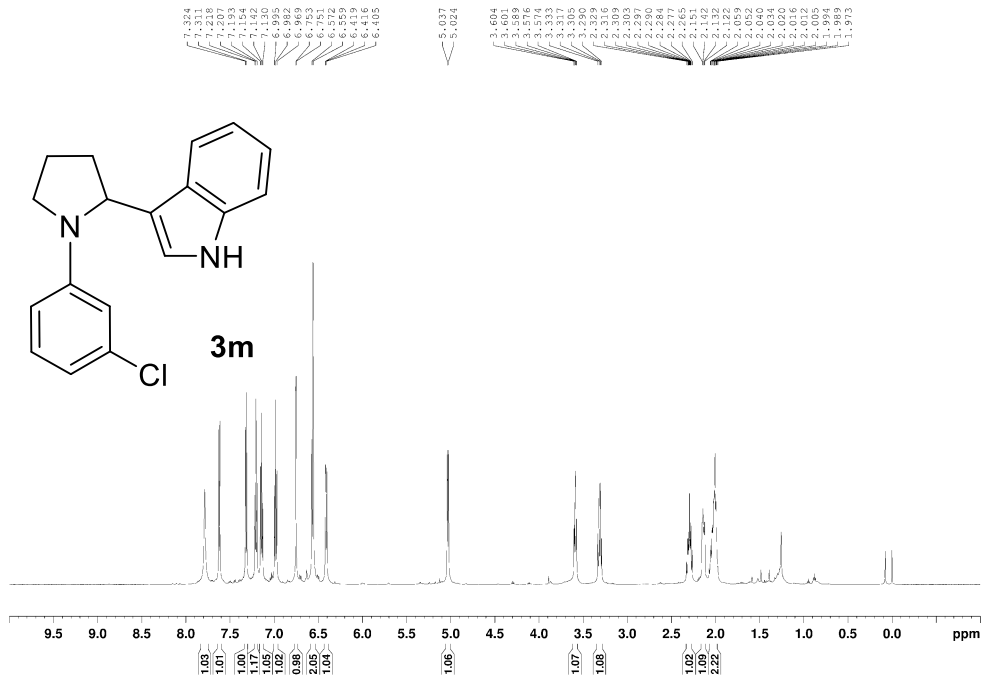
^{1}H NMR of **3l** ($CDCl_3$, 400 MHz)



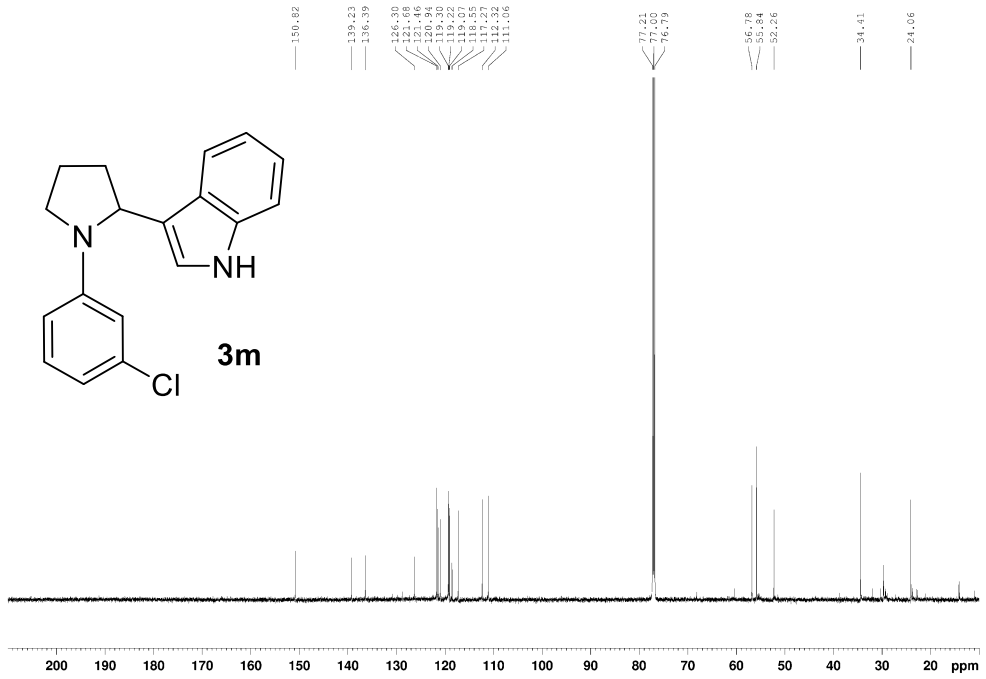
^{13}C NMR of **3l** ($CDCl_3$, 101 MHz)



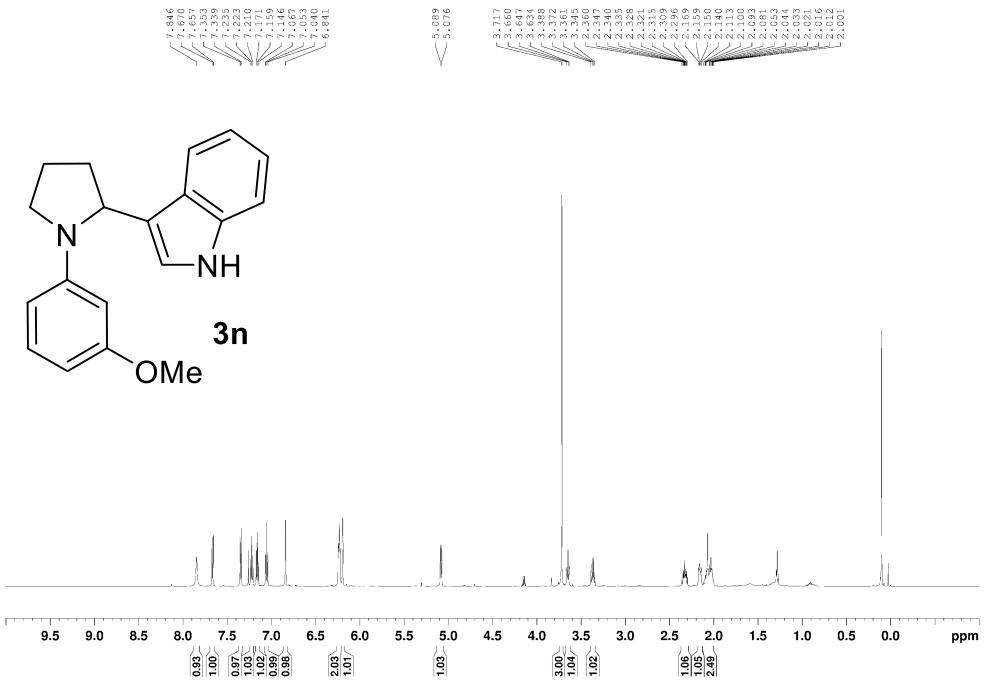
^{1}H NMR of **3m** ($CDCl_3$, 400 MHz)



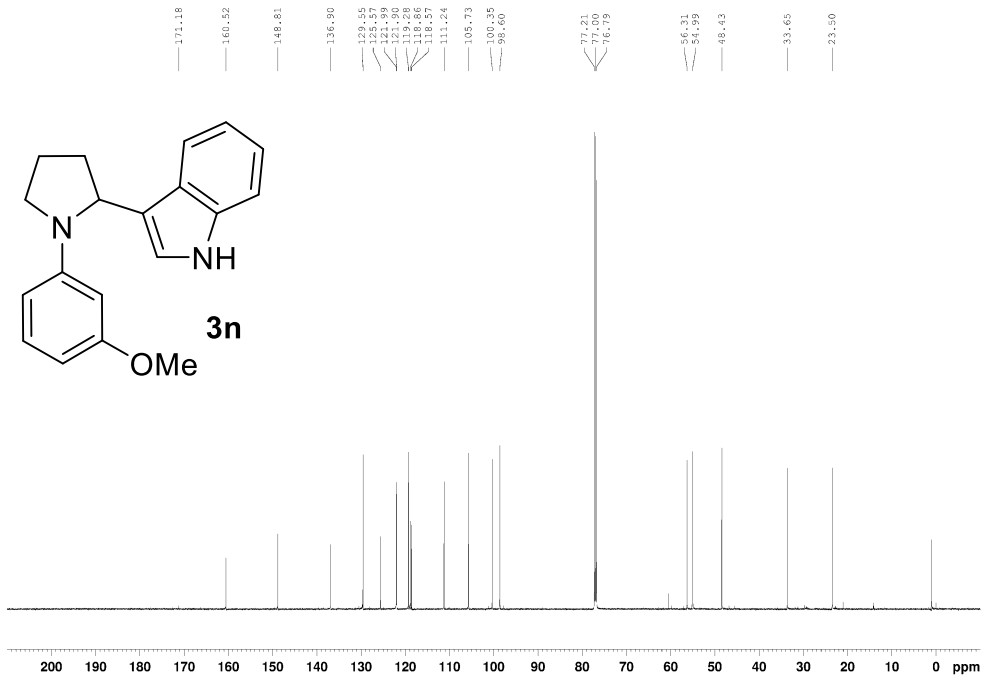
^{13}C NMR of **3m** ($CDCl_3$, 101 MHz)



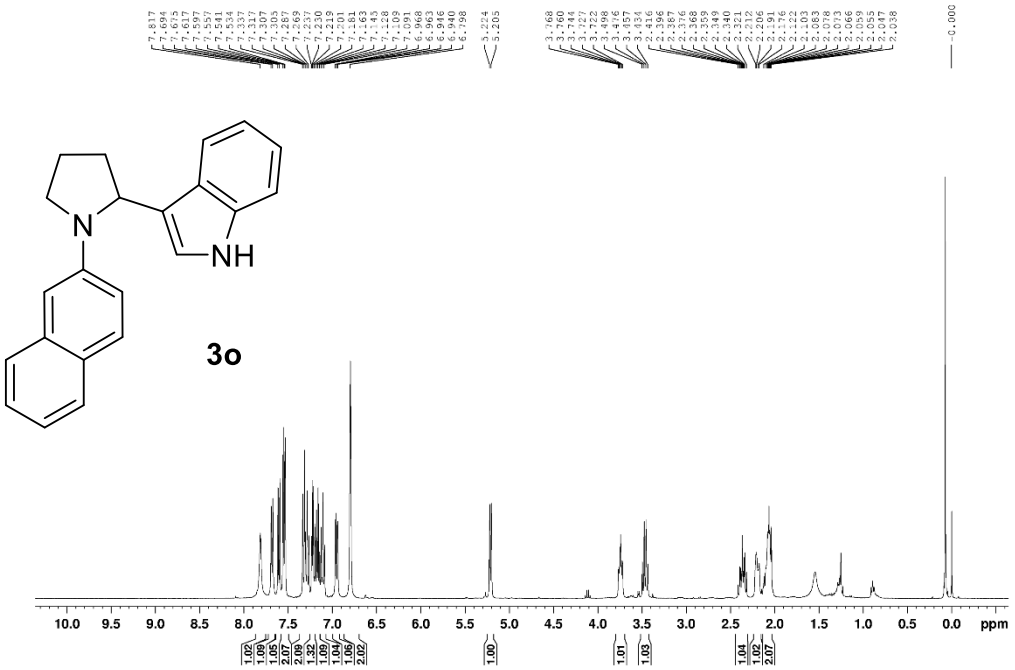
^{1}H NMR of **3n** ($CDCl_3$, 600 MHz)



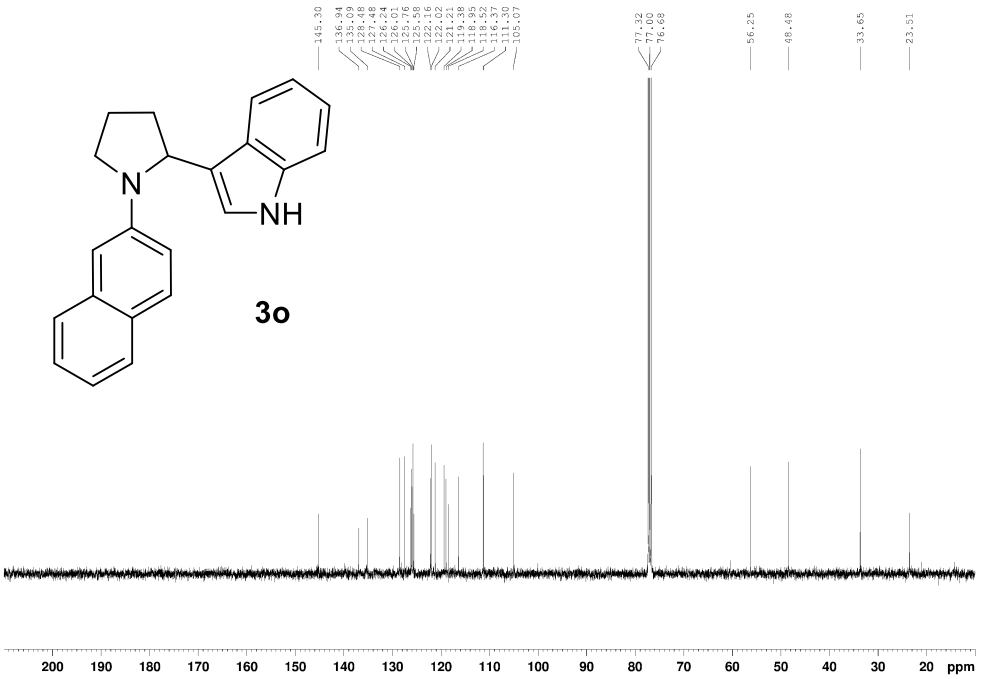
^{13}C NMR of **3n** ($CDCl_3$, 600 MHz)



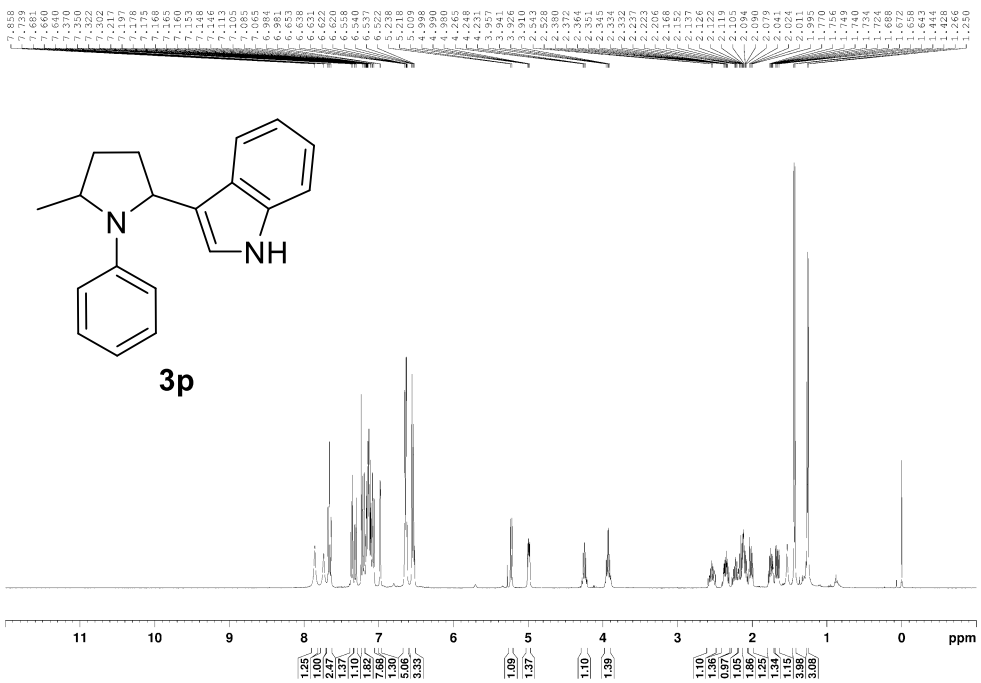
^{1}H NMR of **3o** ($CDCl_3$, 400 MHz)



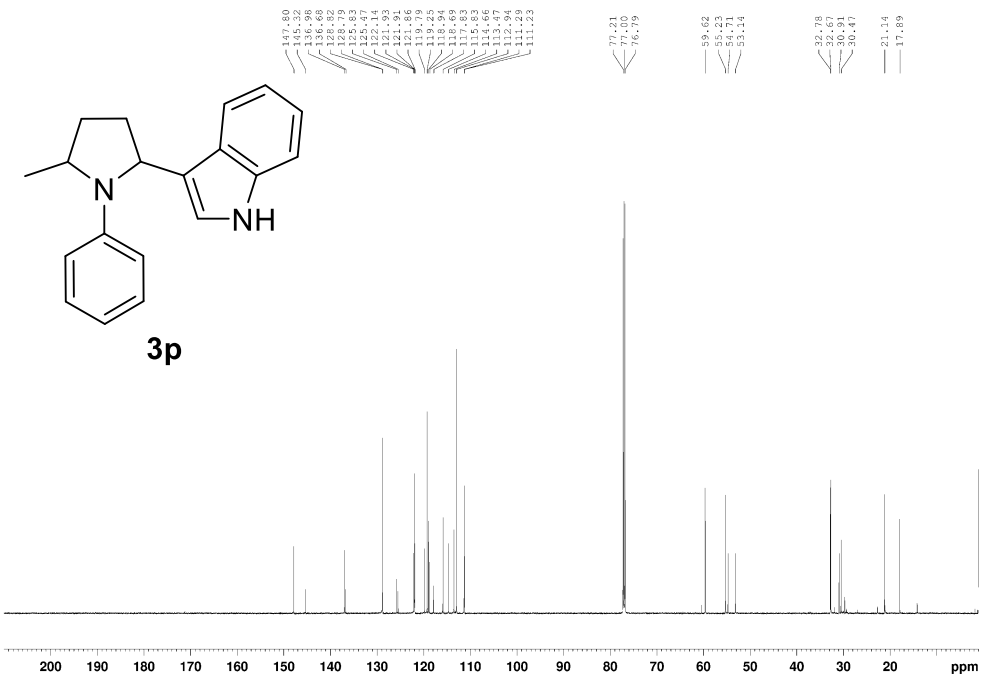
^{13}C NMR of **3o** ($CDCl_3$, 101 MHz)



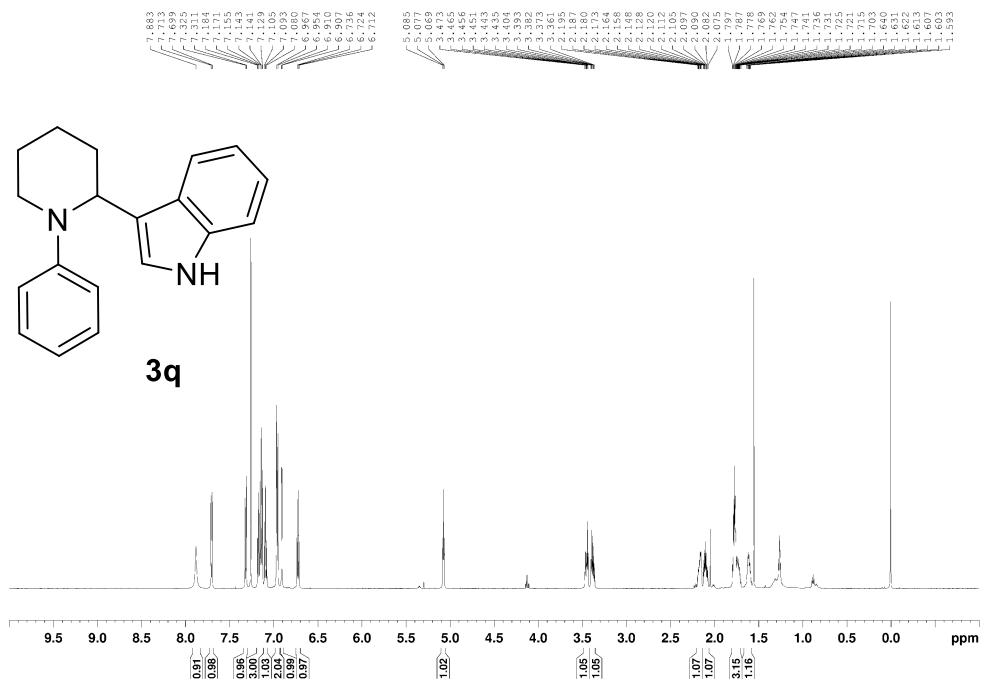
^{1}H NMR of **3p** ($CDCl_3$, 400 MHz)



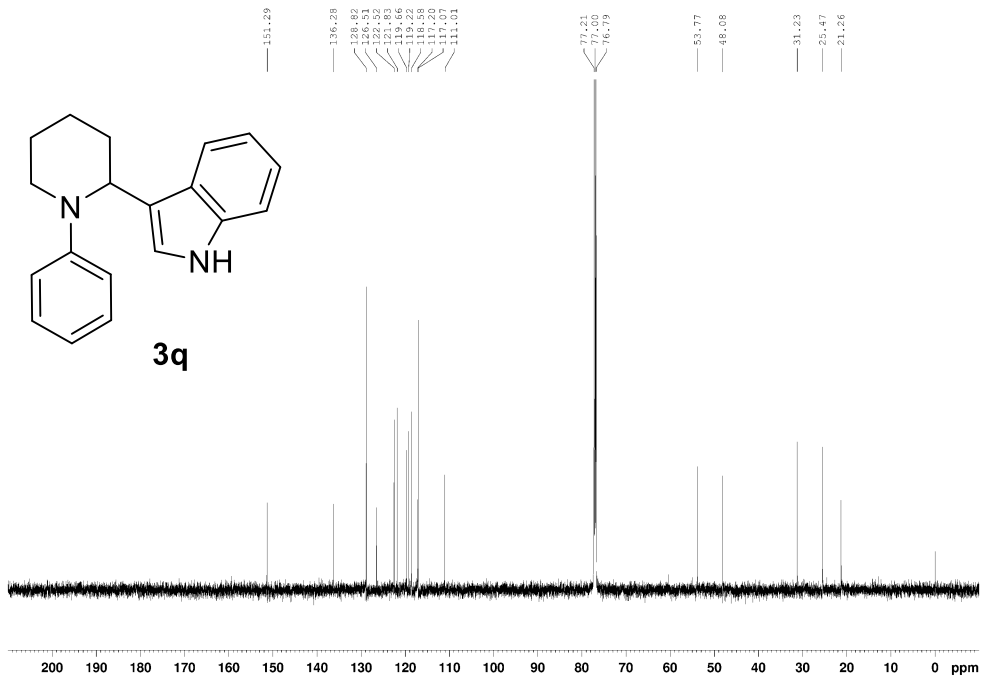
^{13}C NMR of **3p** ($CDCl_3$, 101 MHz)



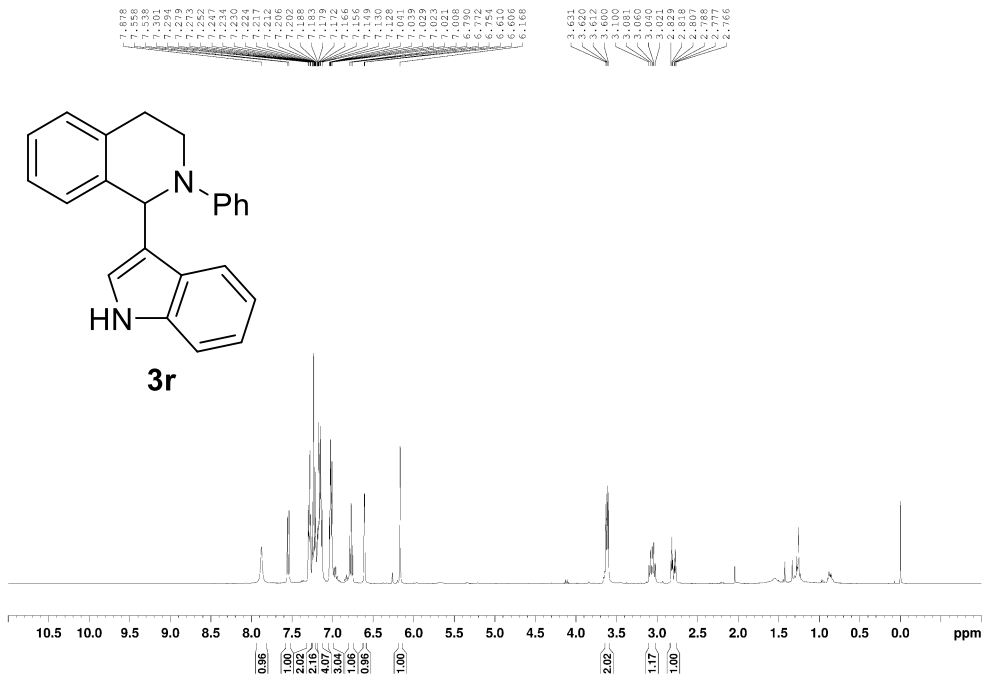
^{1}H NMR of **3q** ($CDCl_3$, 400 MHz)



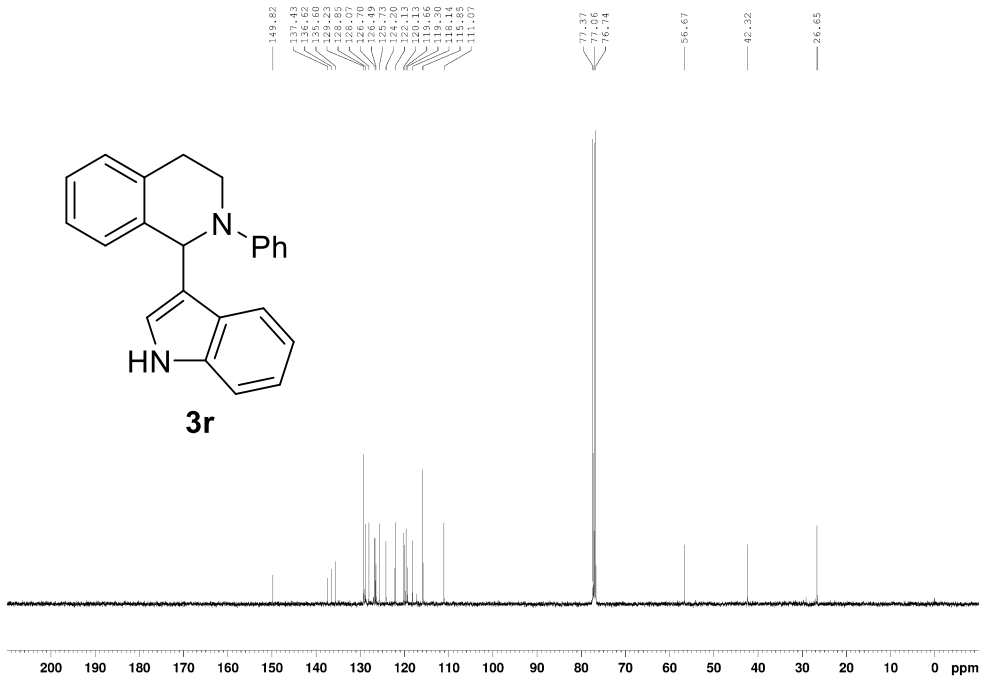
^{13}C NMR of **3q** ($CDCl_3$, 101 MHz)



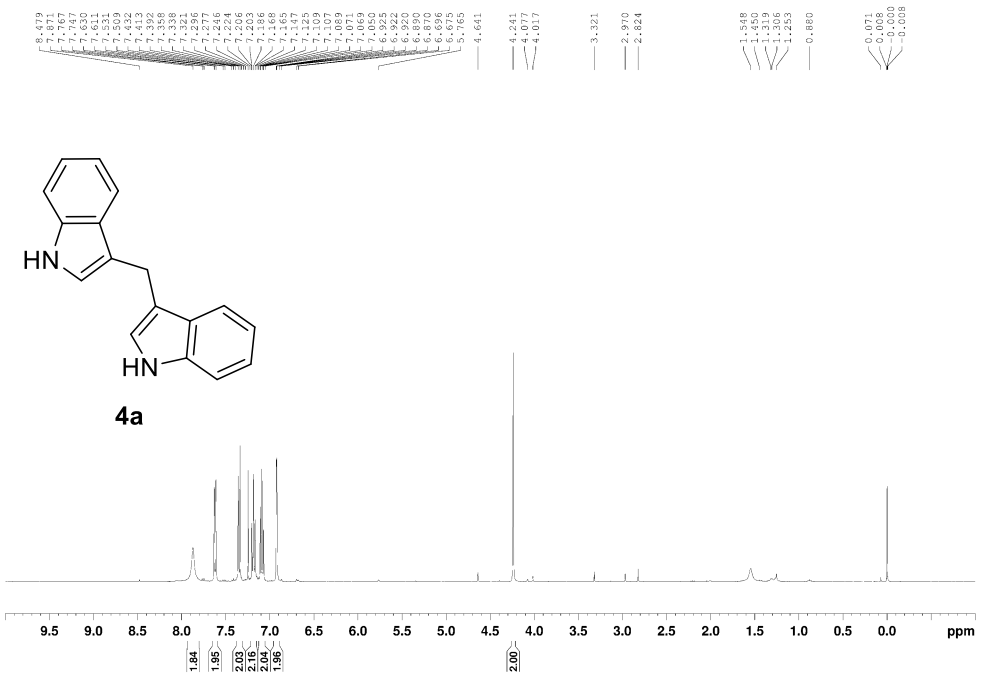
^{1}H NMR of **3r** ($CDCl_3$, 400 MHz)



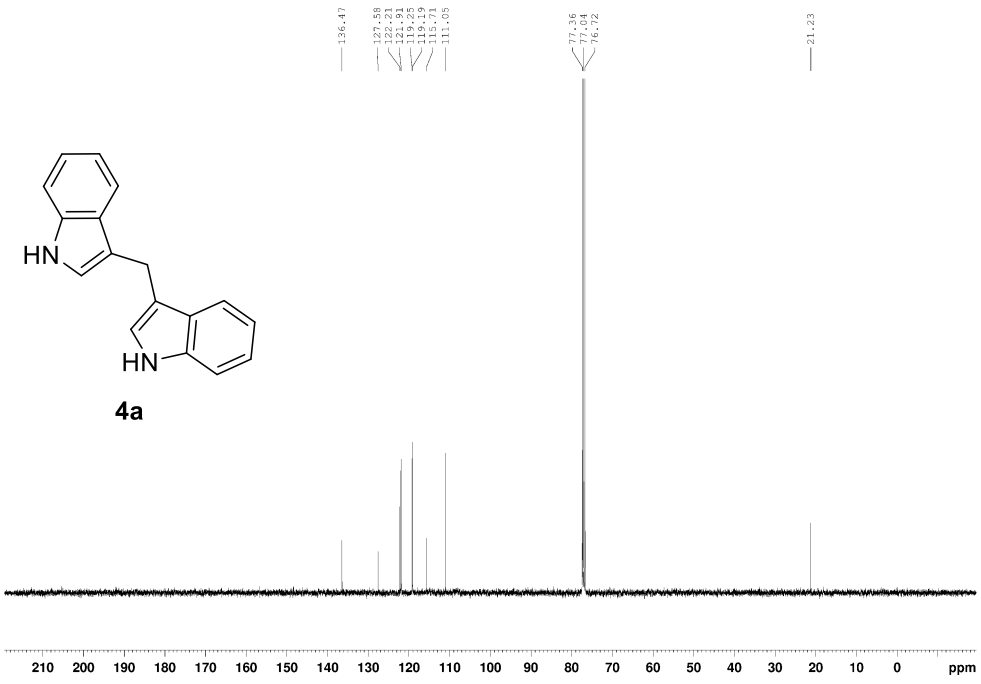
^{13}C NMR of **3r** ($CDCl_3$, 101 MHz)



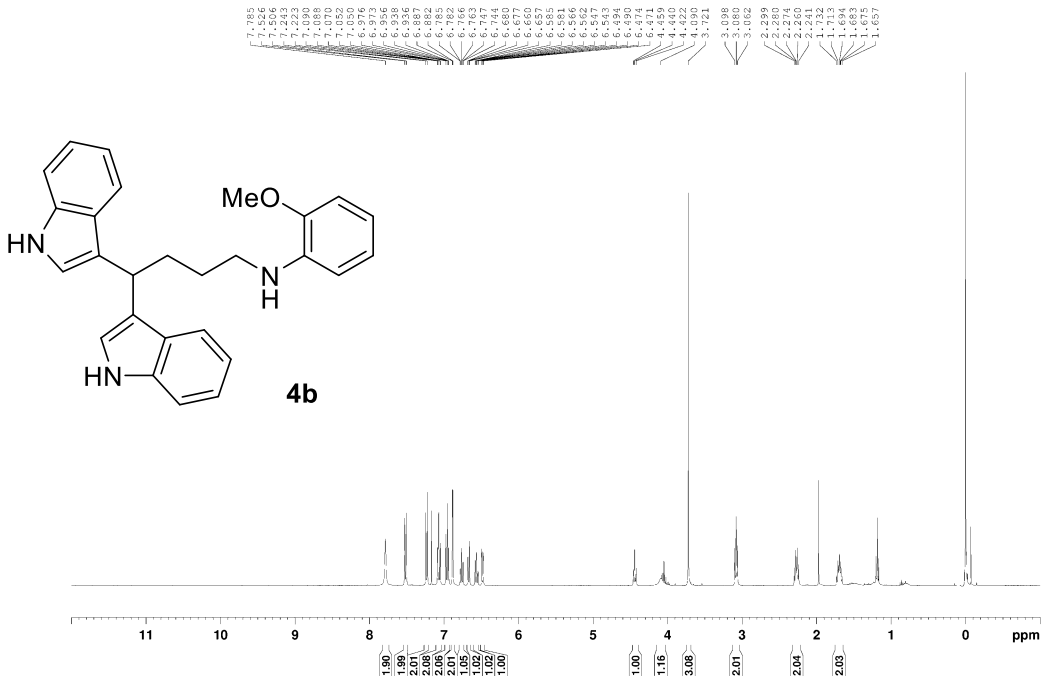
^{1}H NMR of **4a** ($CDCl_3$, 400 MHz)



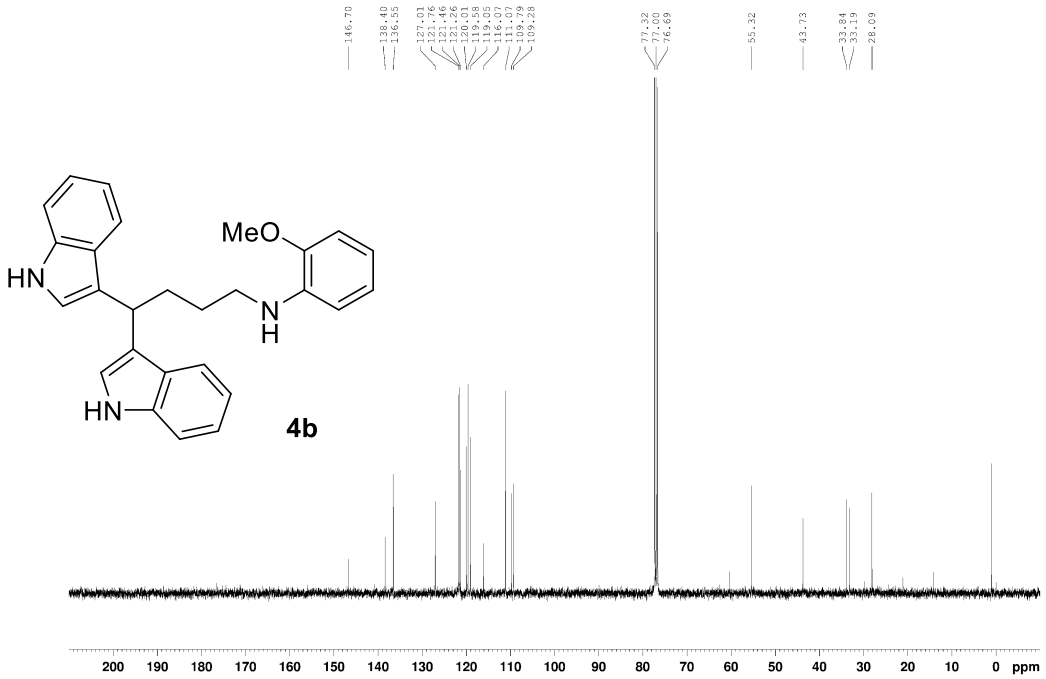
^{13}C NMR of **4a** ($CDCl_3$, 101 MHz)



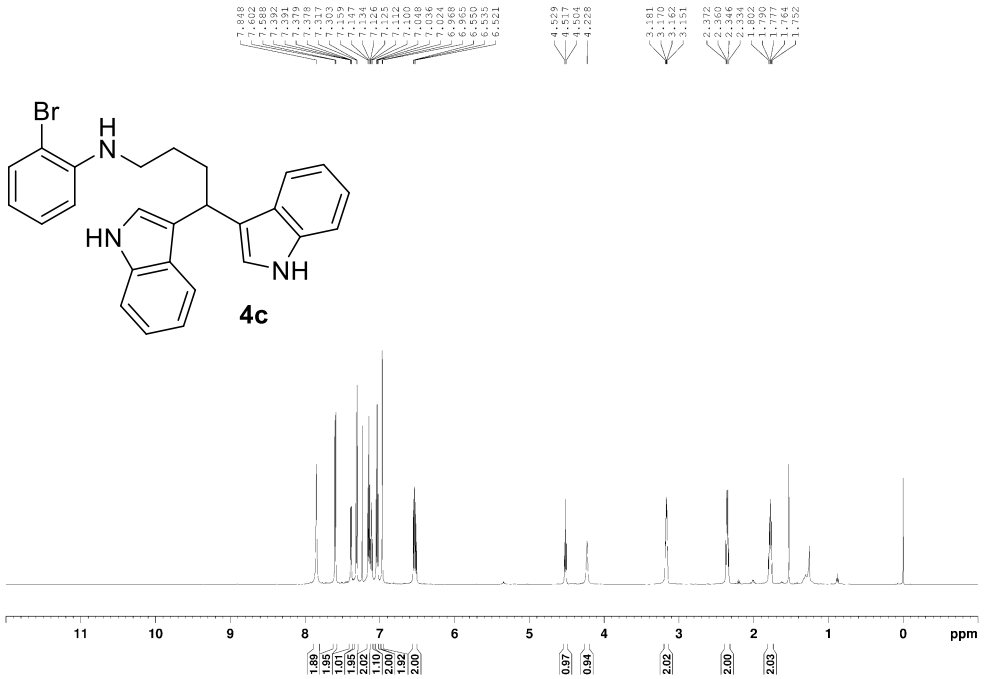
^{1}H NMR of **4b** ($CDCl_3$, 600 MHz)



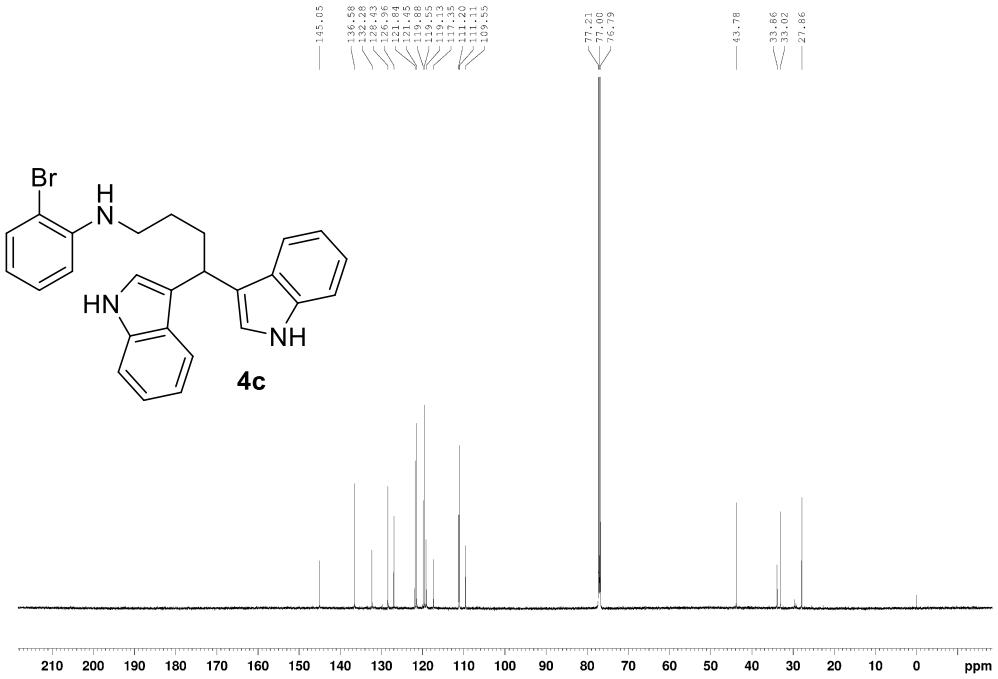
^{13}C NMR of **4b** ($CDCl_3$, 101 MHz)



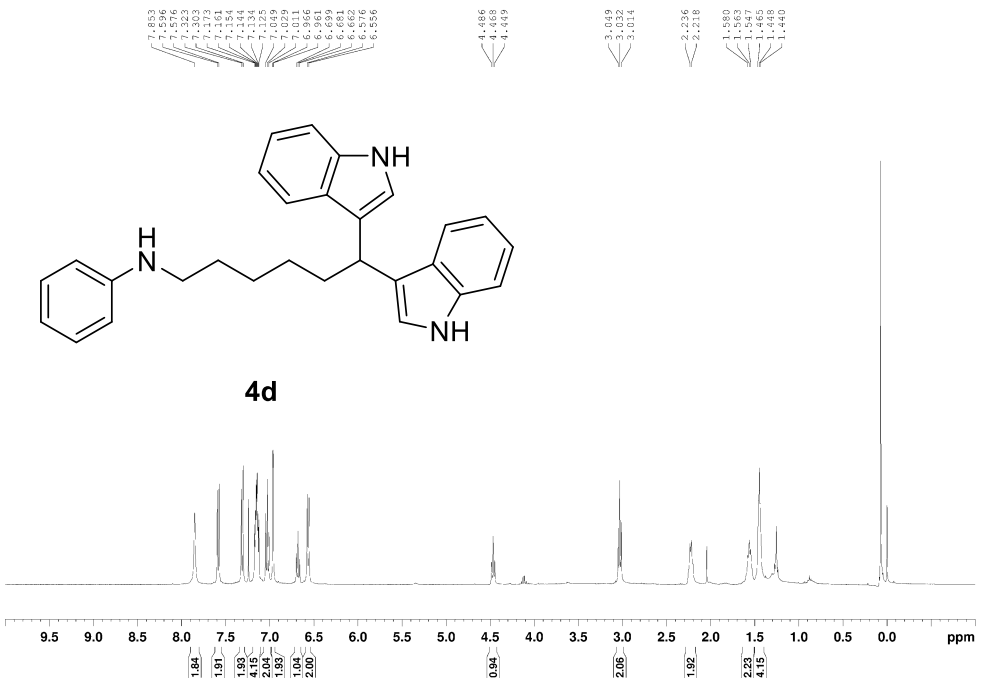
^{1}H NMR of **4c** ($CDCl_3$, 400 MHz)



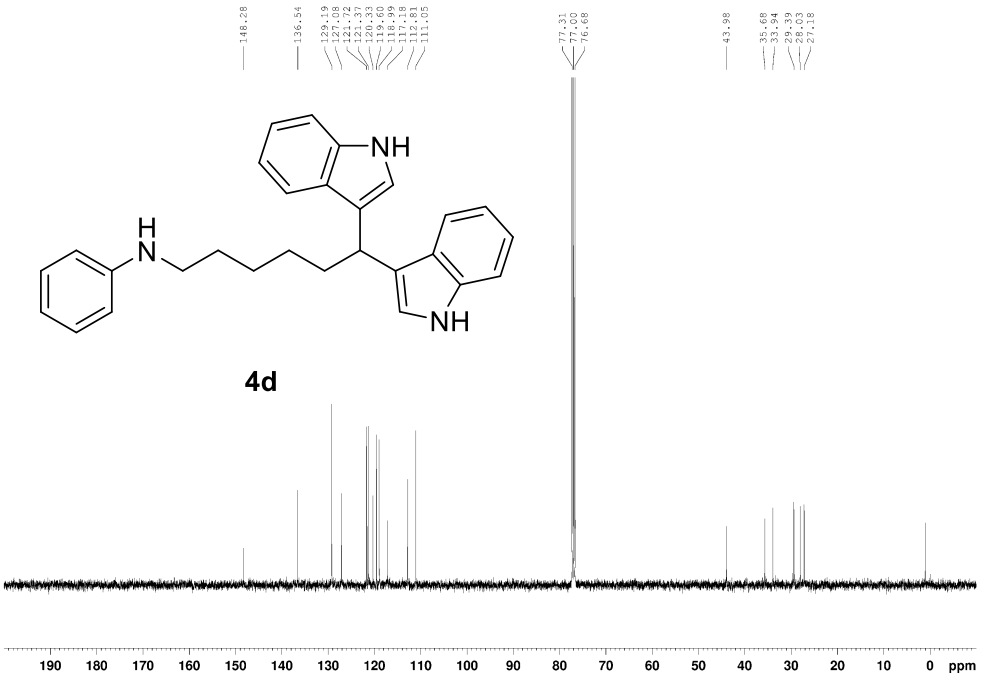
^{13}C NMR of **4c** ($CDCl_3$, 101 MHz)



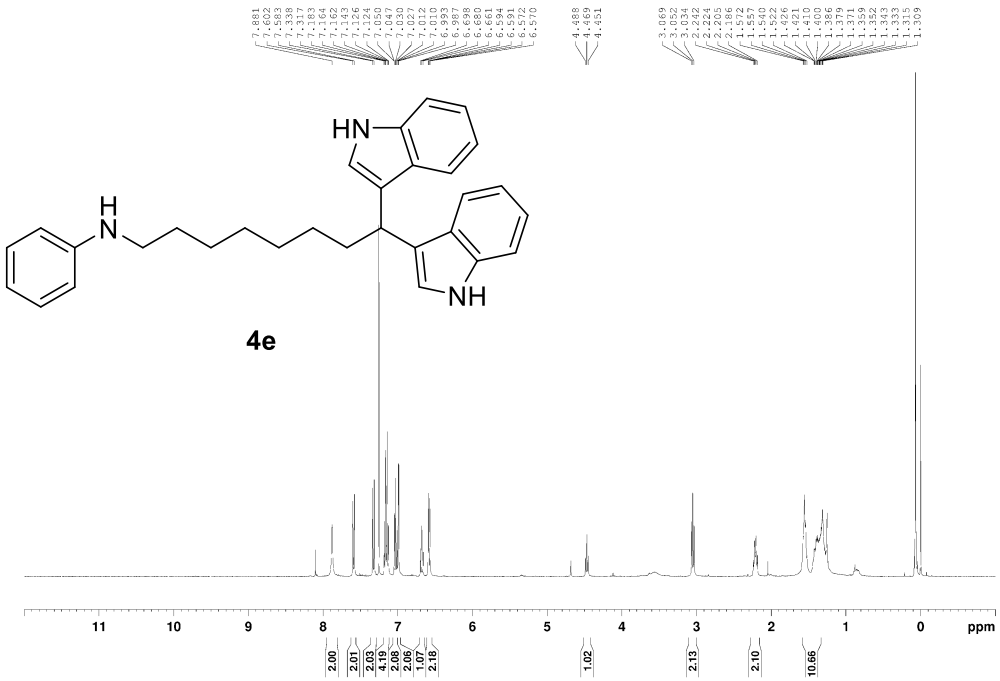
^{1}H NMR of **4d** ($CDCl_3$, 400 MHz)



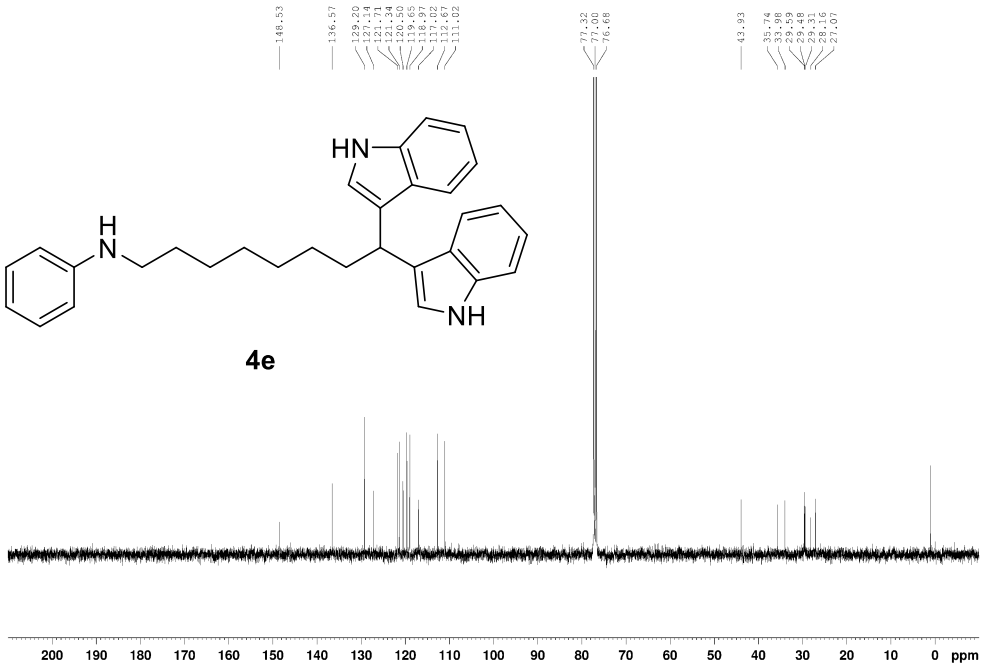
^{13}C NMR of **4d** ($CDCl_3$, 101 MHz)



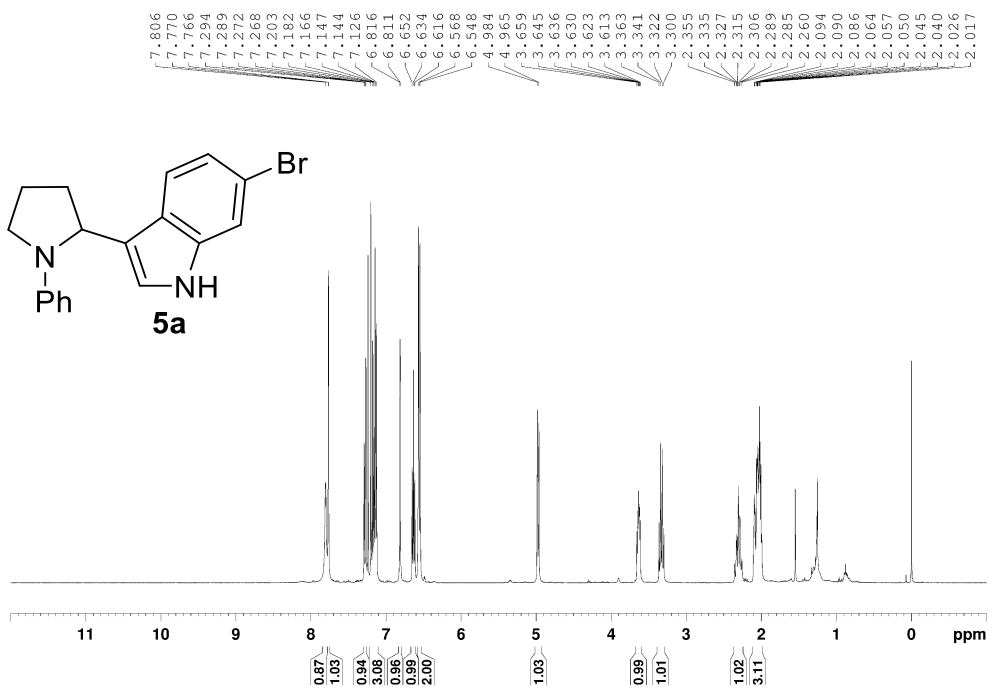
^{1}H NMR of **4e** ($CDCl_3$, 400 MHz)



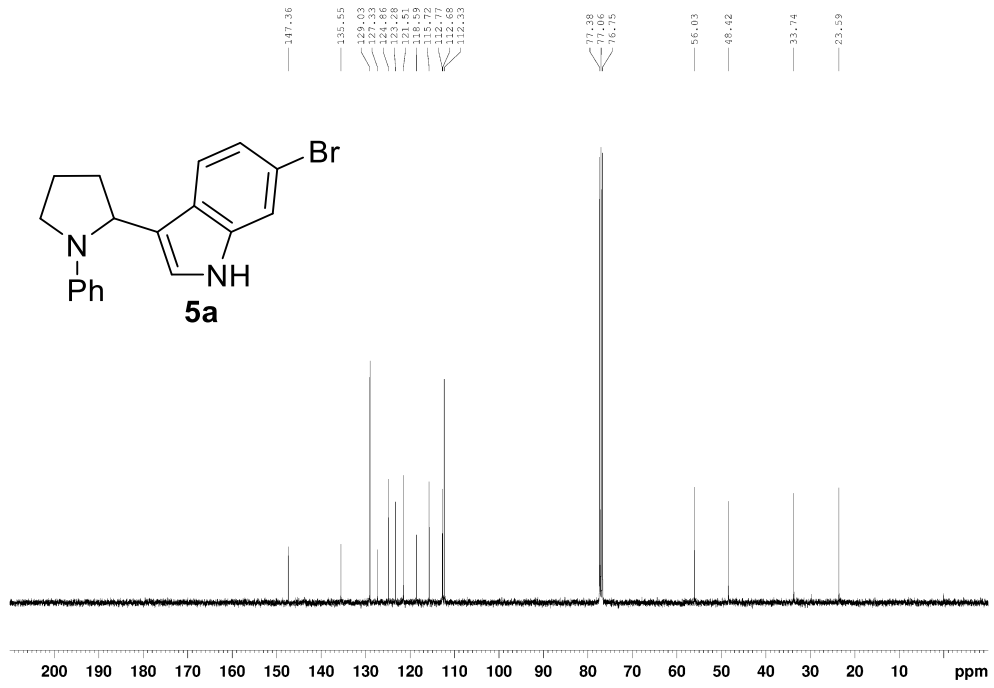
^{13}C NMR of **4e** ($CDCl_3$, 101 MHz)



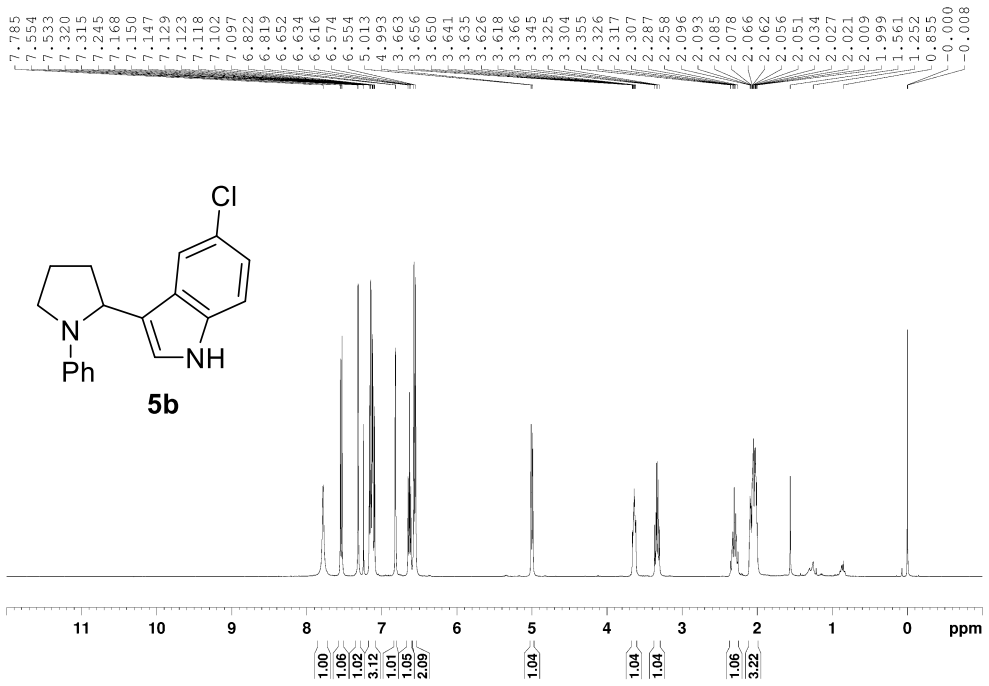
^{1}H NMR of **5a** ($CDCl_3$, 400 MHz)



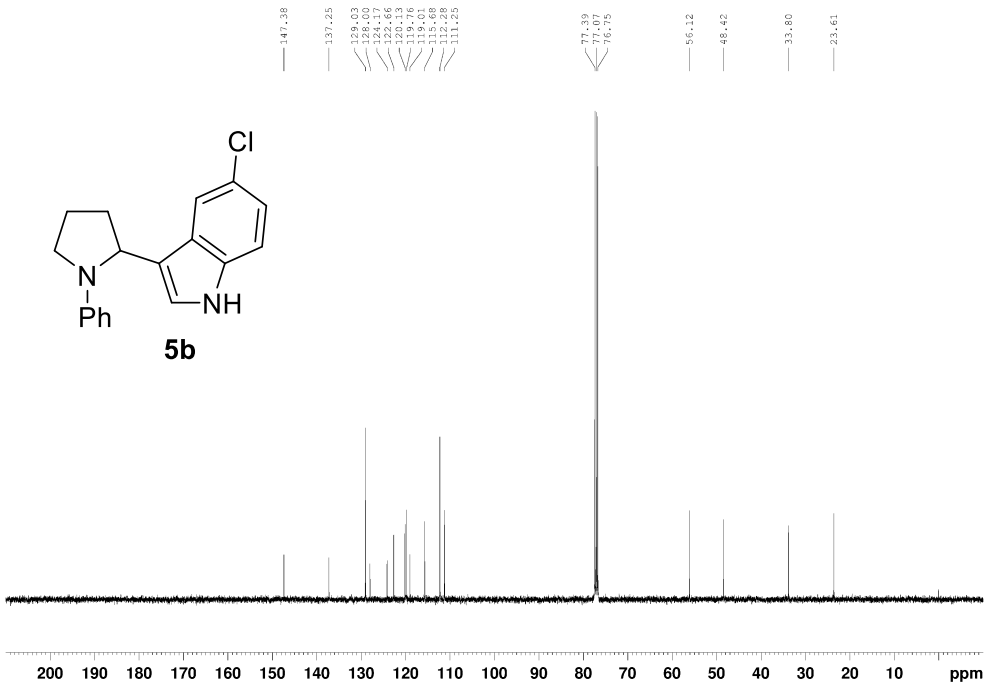
^{13}C NMR of **5a** ($CDCl_3$, 101 MHz)



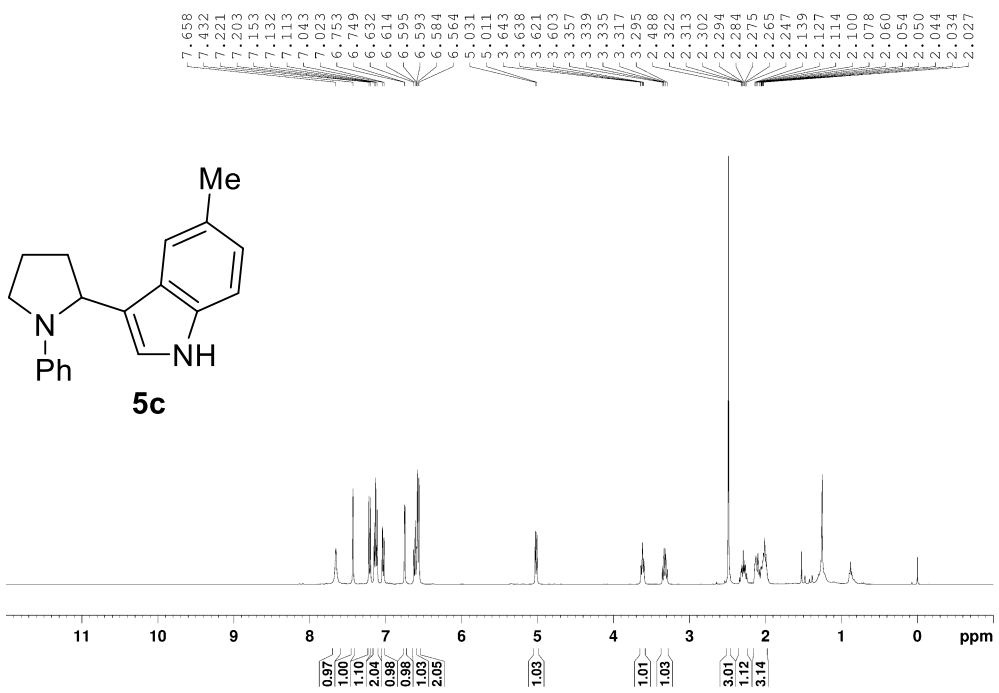
^{1}H NMR of **5b** ($CDCl_3$, 400 MHz)



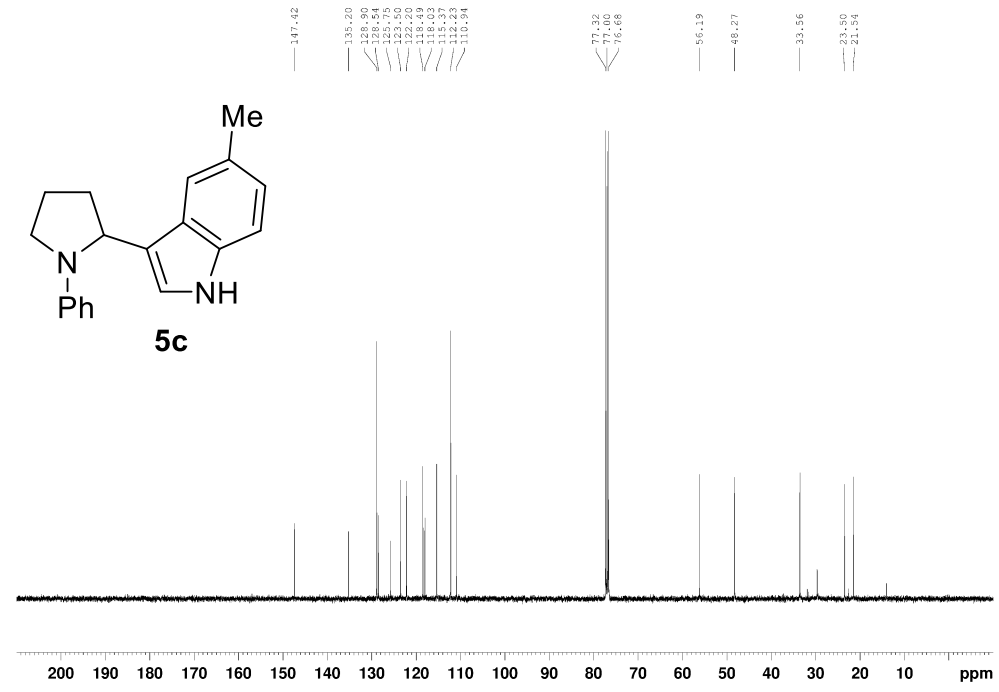
^{13}C NMR of **5b** ($CDCl_3$, 101 MHz)



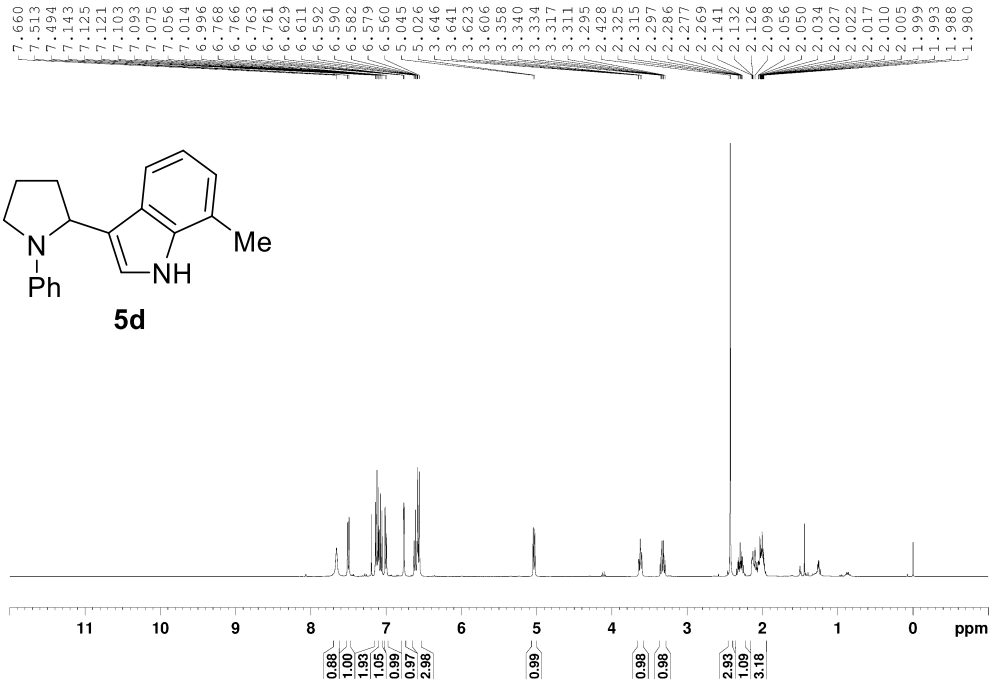
^{1}H NMR of **5c** ($CDCl_3$, 400 MHz)



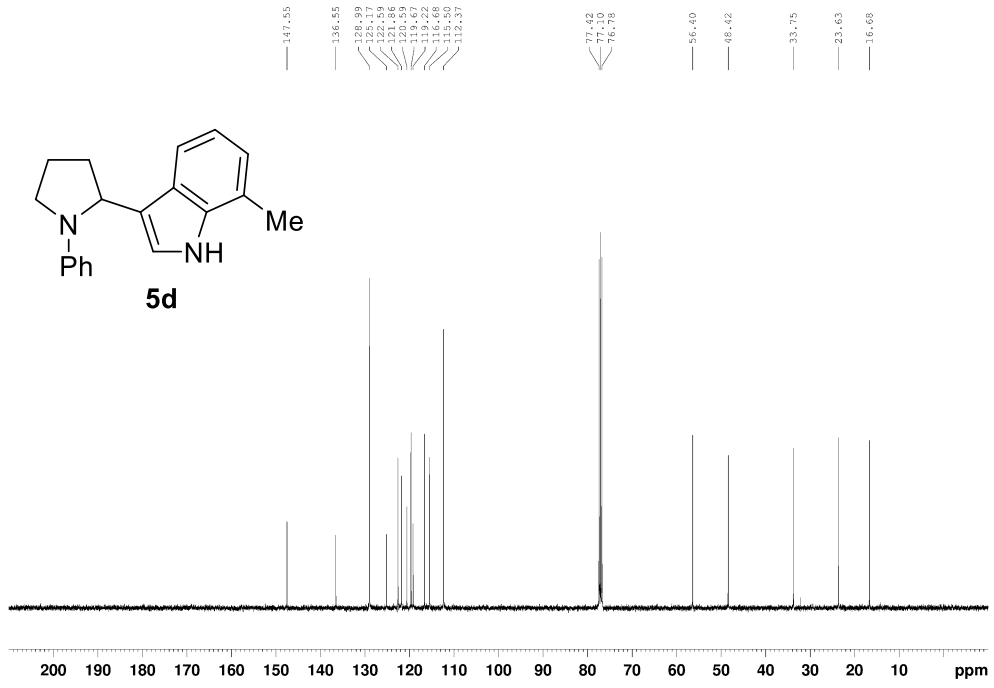
^{13}C NMR of **5c** ($CDCl_3$, 101 MHz)



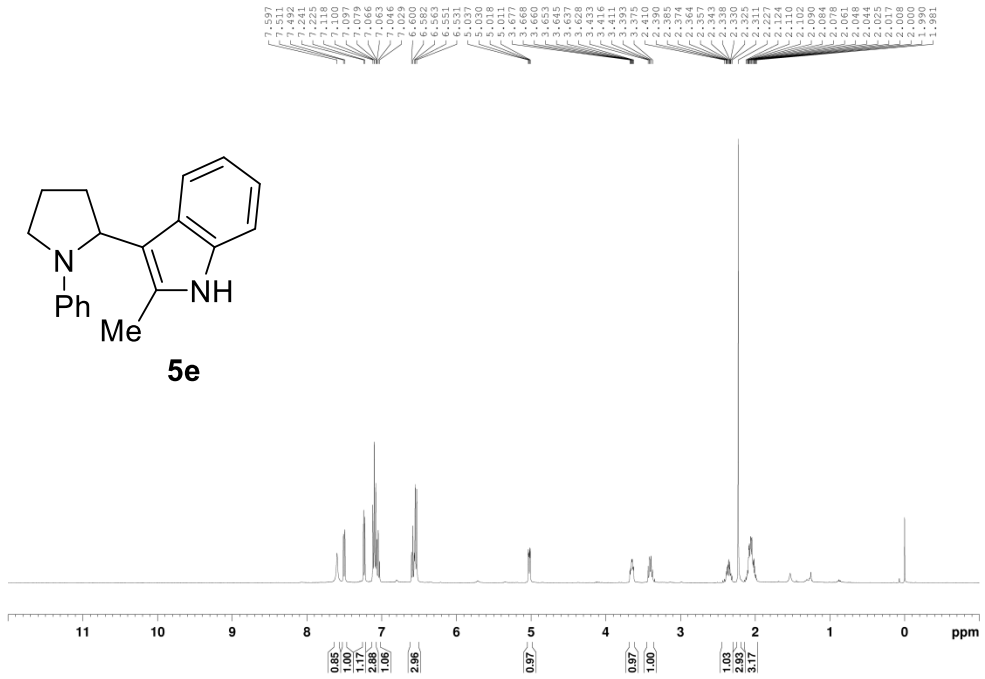
^{1}H NMR of **5d** ($CDCl_3$, 400 MHz)



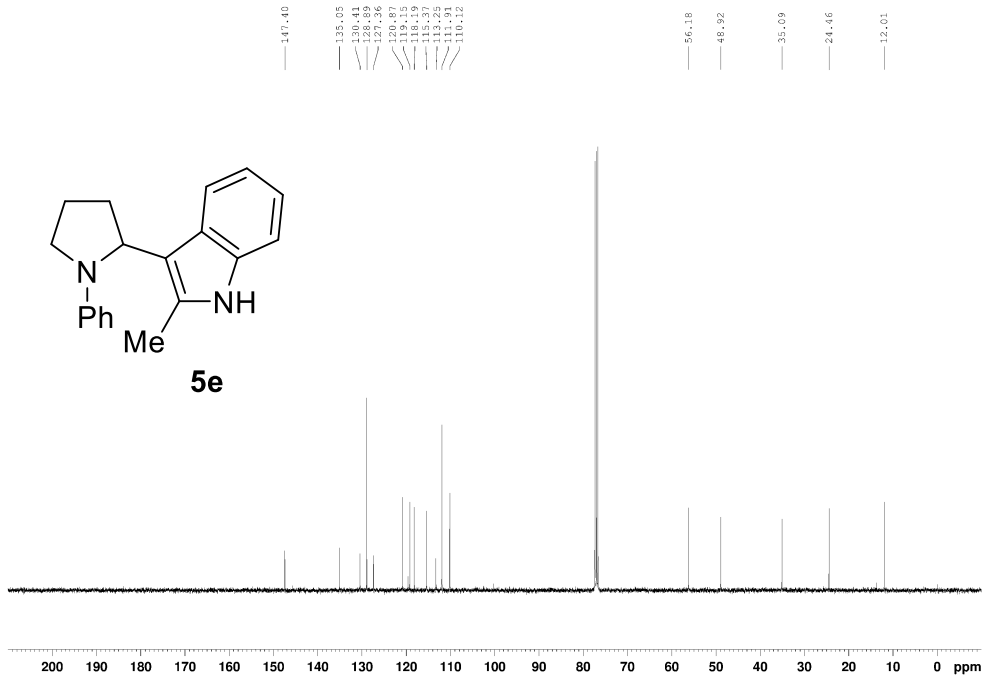
^{13}C NMR of **5d** ($CDCl_3$, 101 MHz)



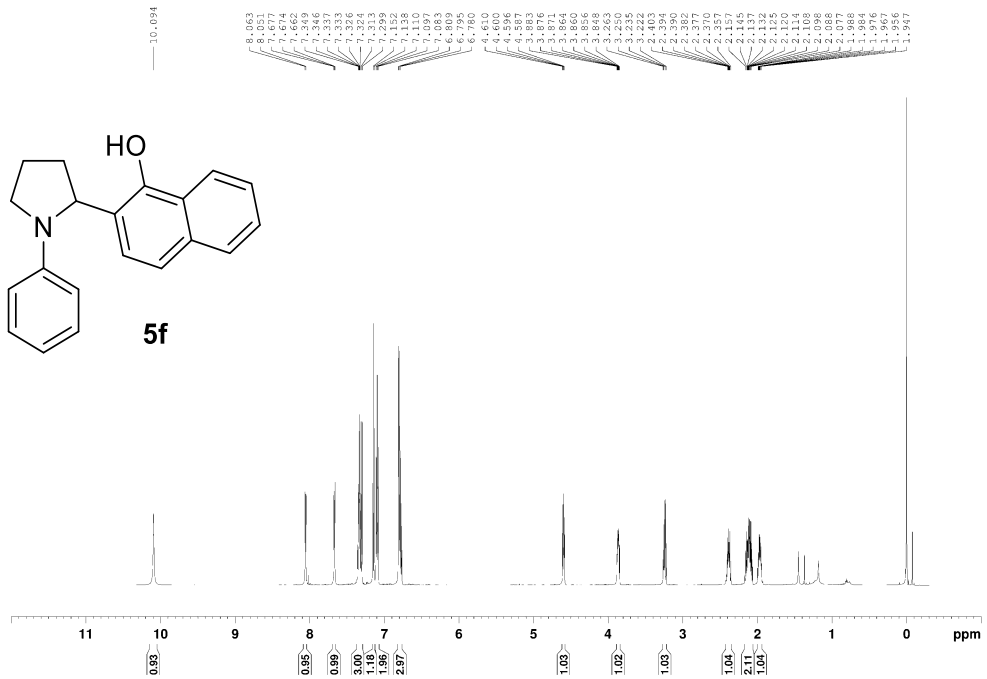
^{1}H NMR of **5e** ($CDCl_3$, 400 MHz)



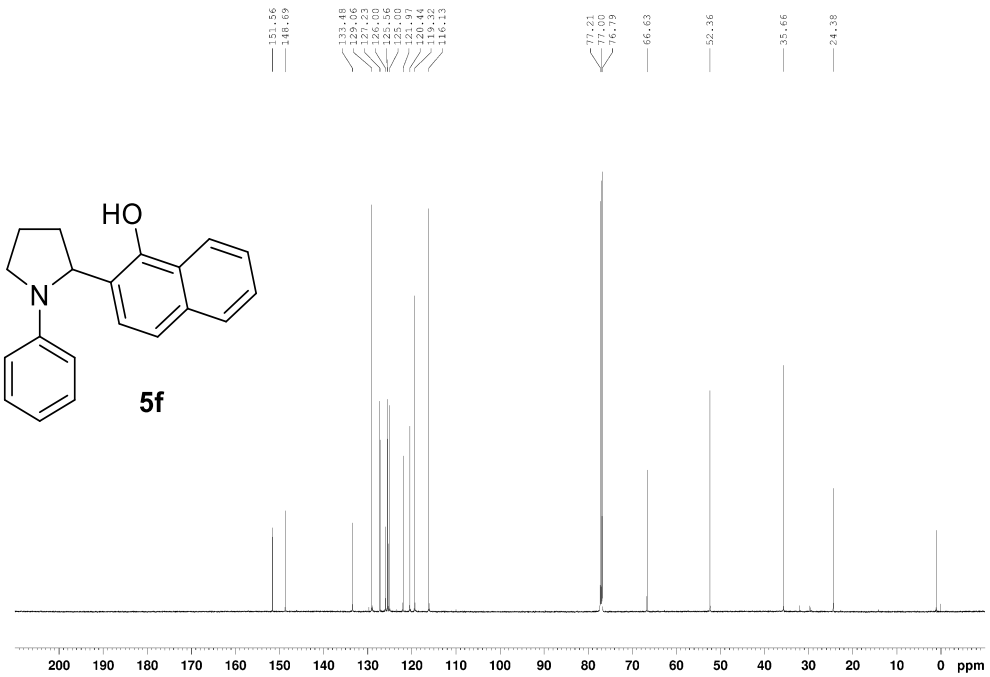
^{13}C NMR of **5e** ($CDCl_3$, 400 MHz)



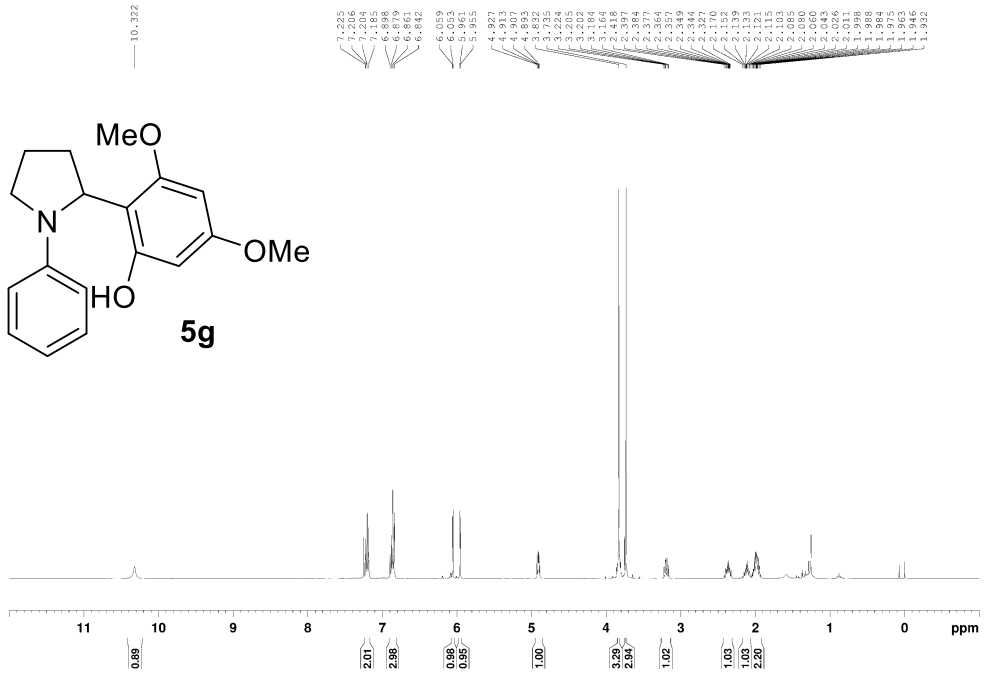
^{1}H NMR of **5f** ($CDCl_3$, 600 MHz)



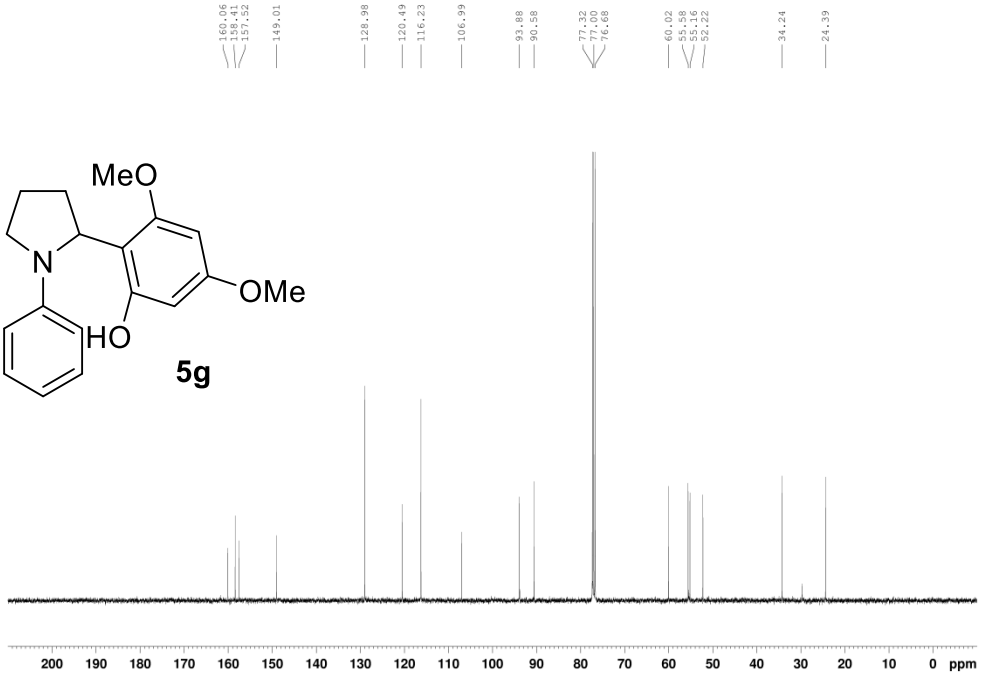
^{13}C NMR of **5f** ($CDCl_3$, 151 MHz)



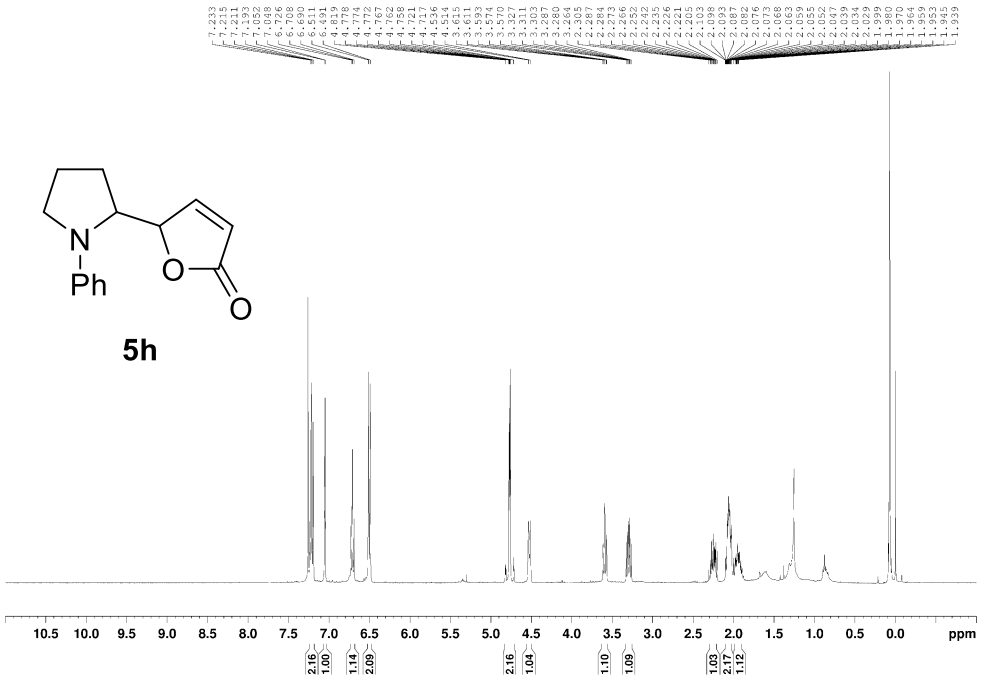
^{1}H NMR of **5g** ($CDCl_3$, 400 MHz)



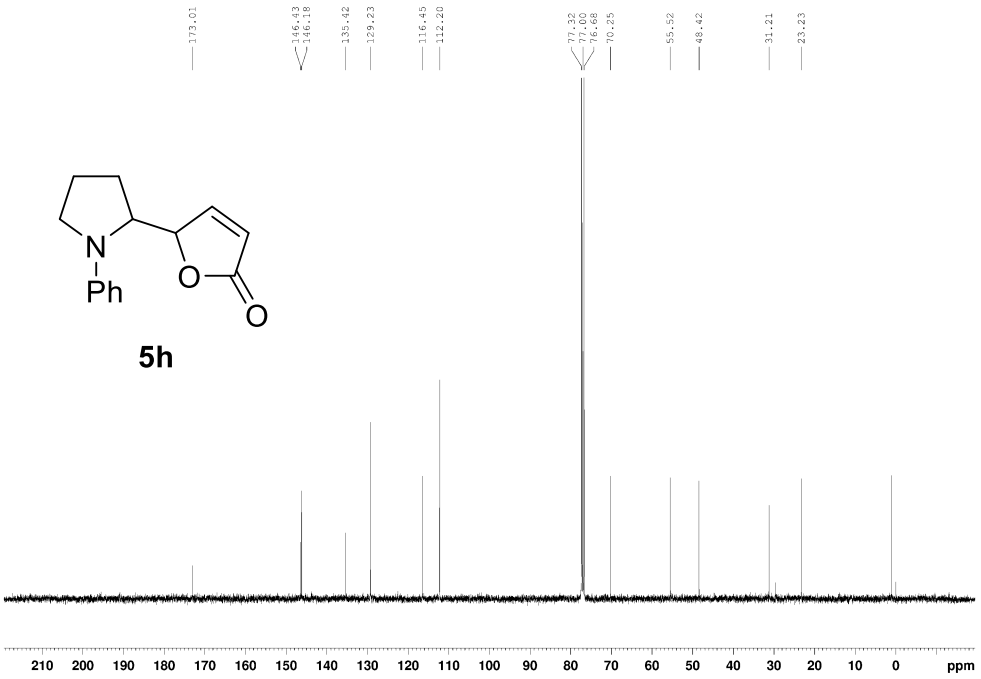
^{13}C NMR of **5g** ($CDCl_3$, 101 MHz)



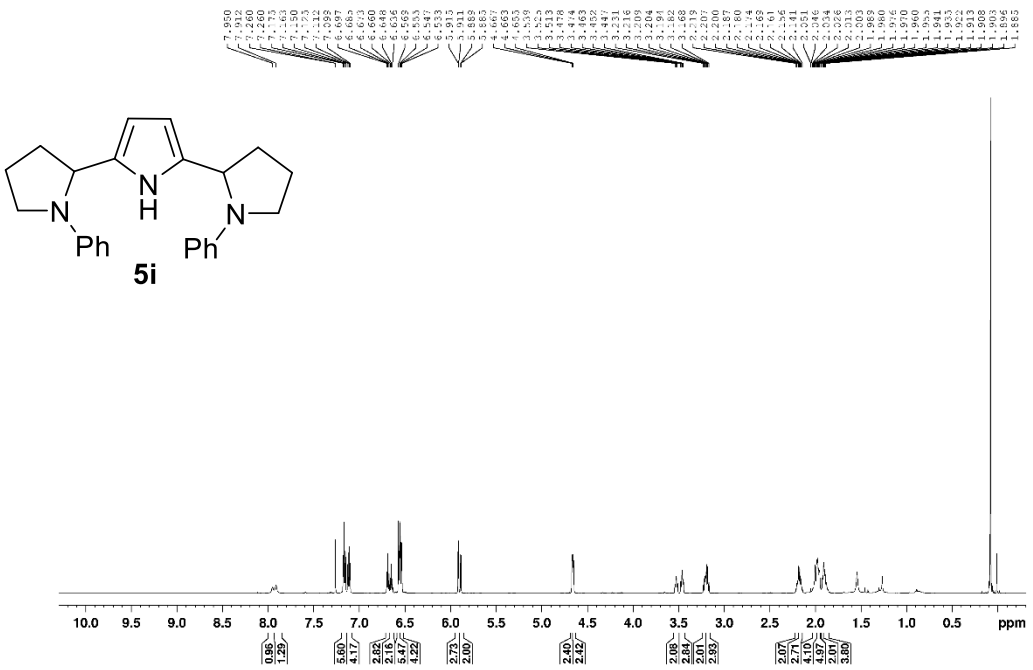
^{1}H NMR of **5h** ($CDCl_3$, 400 MHz)



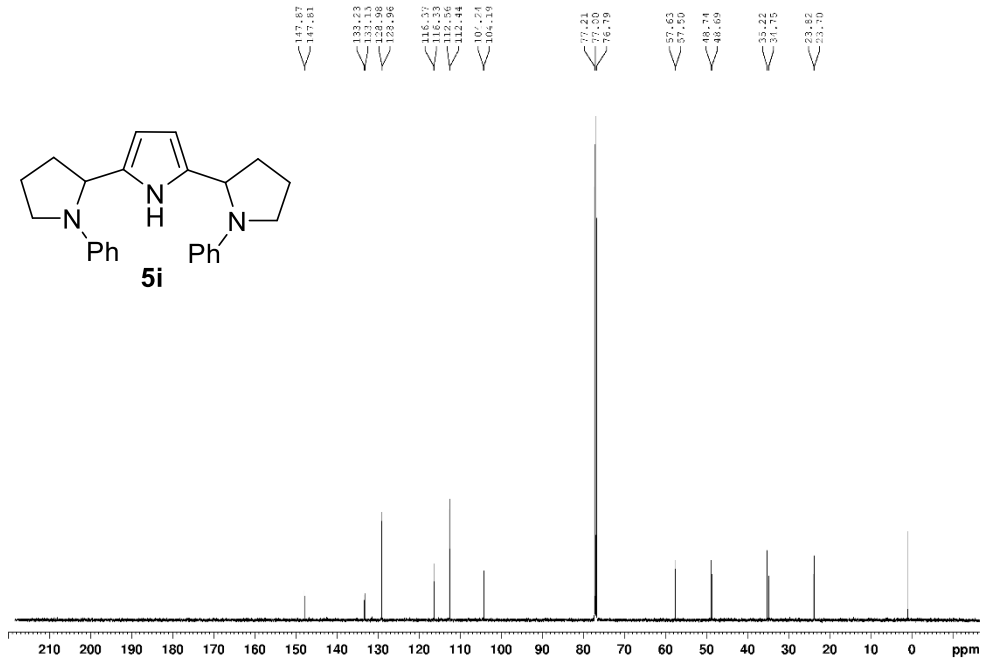
^{13}C NMR of **5h** ($CDCl_3$, 101 MHz)



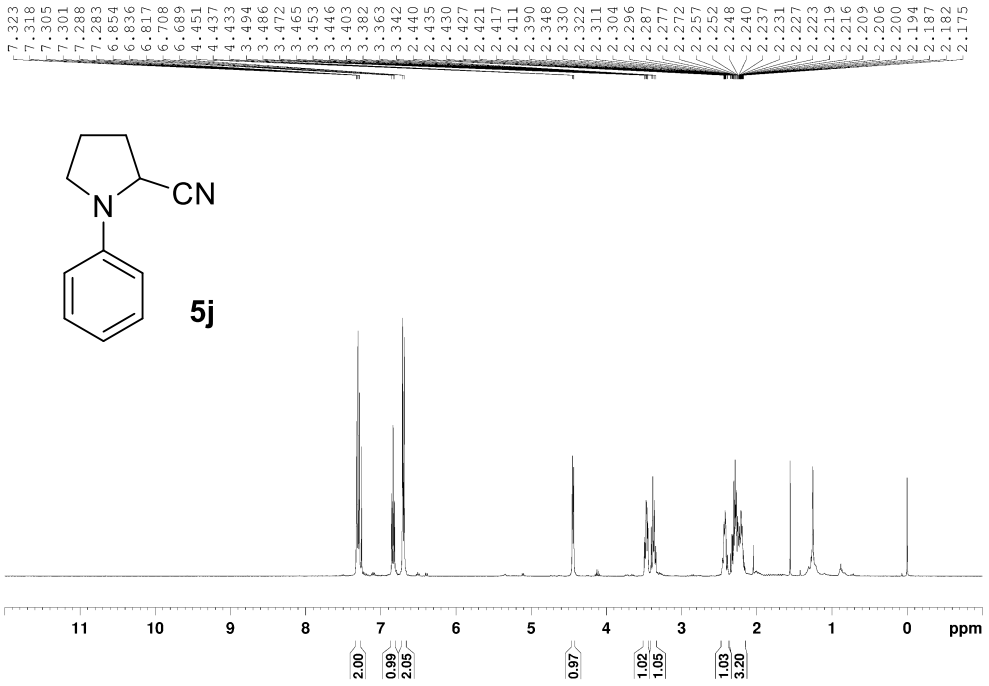
^{1}H NMR of **5i** ($CDCl_3$, 400 MHz)



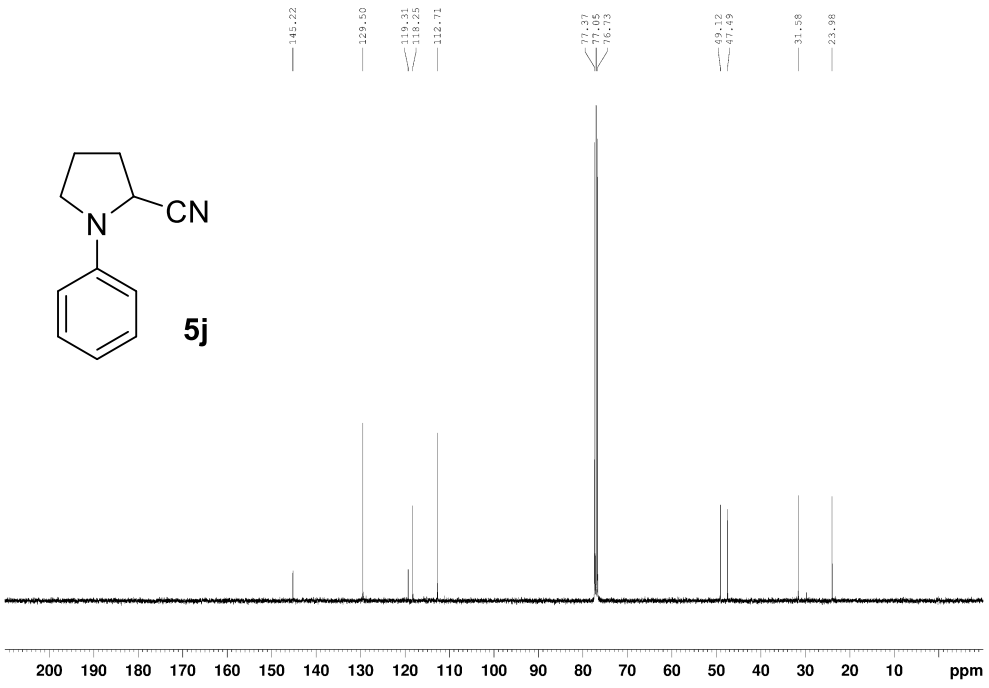
^{13}C NMR of **5i** ($CDCl_3$, 101 MHz)



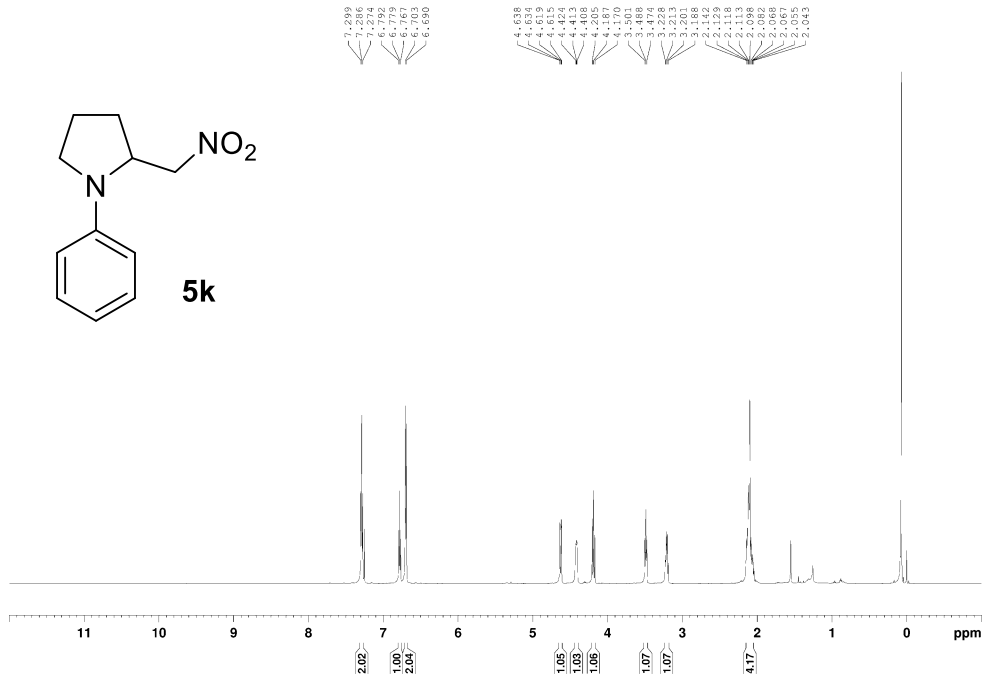
^{1}H NMR of **5j** ($CDCl_3$, 400 MHz)



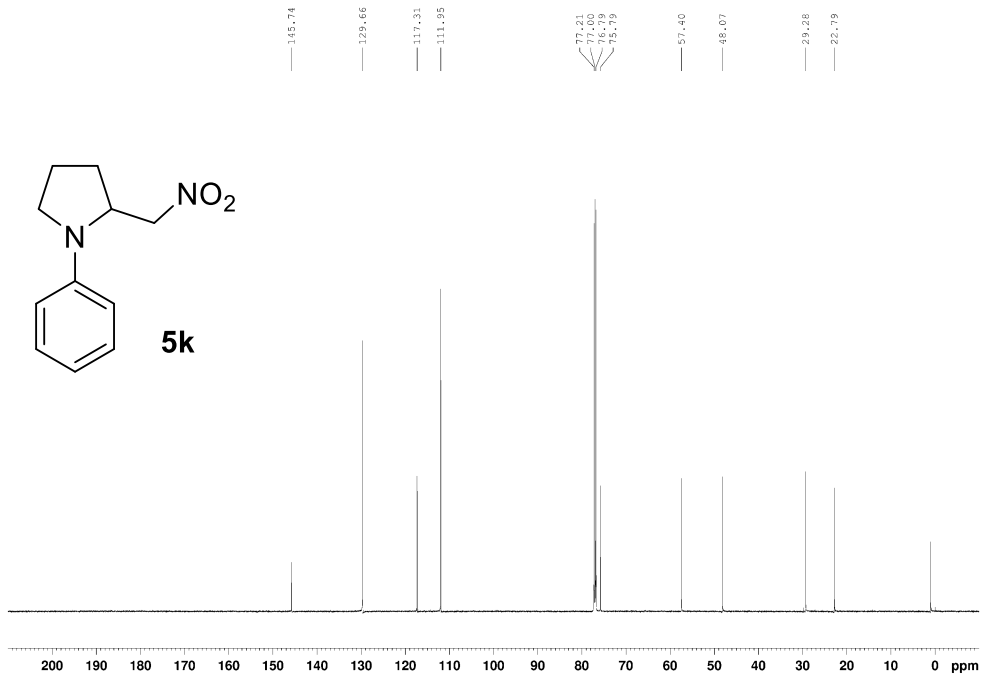
^{13}C NMR of **5j** ($CDCl_3$, 101 MHz)



^{1}H NMR of **5k** ($CDCl_3$, 600 MHz)



^{13}C NMR of **5k** ($CDCl_3$, 151 MHz)



9. References

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