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Rhodium(III)-catalyzed directed C−H benzylation and allylation of indoles with organosilicon reagents

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Supporting Information

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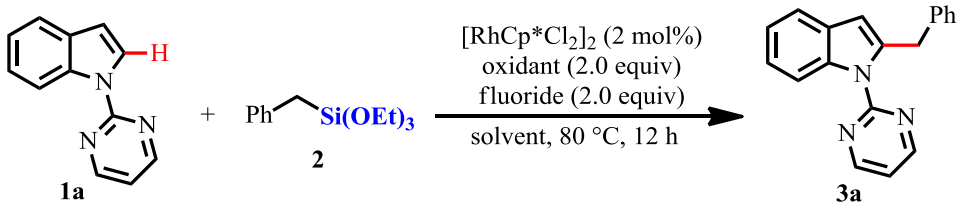
General Information

Unless otherwise noted, all reagents and solvents were purchased from commercial suppliers and used without further purification. ^{1}H-NMR and ^{13}C-NMR spectra were recorded at 25 ℃ on a Bruker Advance 400M NMR spectrometers ($CDCl_3$ as solvent). Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of $SiMe_4$ (δ 0.00 singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); dt (doublet of triplets); m (multiplets) and etc. Coupling constants are reported as a *J* value in Hz. ^{13}C NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ 77.00 triplet). High resolution mass spectral analysis (HRMS) was performed on Water XEVO G2 Q-TOF (Waters Corporation). Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system.

All 2-pyrimidylindoles were prepared readily from the corresponding *N-H* indoles with 2-chloropyrimidine according to the literature.[1] Benzyltriethoxysilane and allyltrimethoxysilane were purchased from commercial sources and used as received. 2-*d* indole were prepared according to the literature[2] and *d*-**1a** was prepared using the same method noted above.[3] Unless otherwise noted, all reactions were carried out under air atmosphere.

Table of Optimization of Reaction Conditions



Entry	Oxidant	Fluoride	Solvent	Yield[a,b] (%)
1	$Cu(OAc)_2$	AgF	DCE	74
2	$Cu(OAc)_2$	AgF	dioxane	89
3	$Cu(OAc)_2$	AgF	toluene	85
4	$Cu(OAc)_2$	AgF	DMF	33
5	$Cu(OAc)_2$	AgF	DMSO	10
6	$Cu(OAc)_2$	AgF	MeCN	18
7	$Cu(OAc)_2$	AgF	DCM	78
8	$Cu(OAc)_2$	AgF	acetone	81
9	$Cu(OAc)_2$	AgF	DME	80
10	$Cu(OAc)_2$	AgF	H_2O	38
11	**$Cu(OAc)_2$**	**AgF**	**THF**	**94**
12	$Cu(OAc)_2$	AgF	*t*-AmylOH	90
13	$Cu(OAc)_2$	KF	THF	trace
14	$Cu(OAc)_2$	CsF	THF	trace
15	$Cu(OAc)_2$	TBAF	THF	trace
16	$Cu(OAc)_2$	—	THF	0
17	—	AgF	THF	84
18[c]	$Cu(OAc)_2$	AgF	THF	53
19[d]	$Cu(OAc)_2$	AgF	THF	0
20[e]	$Cu(OAc)_2$	AgF	THF	67

[a] Unless otherwise noted, all reactions were carried out as follows: **1a** (0.3 mmol), **2** (0.6 mmol, 2.0 equiv), $[RhCp^*Cl_2]_2$ (2 mol%), $Cu(OAc)_2$ (2.0 equiv), fluoride (2.0 equiv), solvent (2 mL), at 80 °C for 12 h. [b] Isolated yields. [c] $[RhCp^*Cl_2]_2$ (1 mol%) was used. [d] No $[RhCp^*Cl_2]_2$. [e] 1.0 equiv of **2** was used.

Experimental section

Typical procedure for rhodium(III)-catalyzed benzylation of 2-pyrimidylindole with benzyltriethoxysilane (3a)

1a (58.5 mg, 0.3 mmol), **2** (152.6 mg, 0.6 mmol), $[RhCp^*Cl_2]_2$ (3.7 mg, 0.006 mmol), AgF (76.0 mg, 0.6 mmol) and $Cu(OAc)_2$ (109.0 mg, 0.6 mmol) were sequentially weighed into an oven-dried sealed tube. THF (2 mL) was added *via* syringe and the reaction mixture was stirred at 80 ℃ for 12 h. After cooling to ambient temperature, the mixture was extracted with EtOAc (3×10 mL). The combined organic layer was dried over anhydrous Na_2SO_4. The solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel using petroleum ether/EtOAc (9:1) to afford the desired product **3a** (80.4 mg, 94%).

Typical procedure for rhodium(III)-catalyzed benzylation of 2-phenylpyridine with benzyltriethoxysilane (5a)

4a (46.6 mg, 0.3 mmol), **2** (114.5 mg, 0.45 mmol), $[RhCp^*Cl_2]_2$ (3.7 mg, 0.006 mmol), AgF (76.0 mg, 0.6 mmol) and $Cu(OAc)_2$ (109.0 mg, 0.6 mmol) were sequentially weighed into an oven-dried sealed tube. THF (2 mL) was added *via* syringe and the reaction mixture was stirred at 80 ℃ for 12 h. After cooling to ambient temperature, the mixture was extracted with EtOAc (3×10 mL). The combined organic layer was dried over anhydrous Na_2SO_4. The solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel using petroleum ether/EtOAc (9:1) to afford the desired product **3a** (50.8 mg, 69%).

Typical procedure for rhodium(III)-catalyzed allylation of 2-pyrimidylindole with allyltrimethoxysilane (7a)

1a (58.5 mg, 0.3 mmol), **6** (97.3 mg, 0.6 mmol), $[RhCp^*Cl_2]_2$ (3.7 mg, 0.006 mmol), AgF (76.0 mg, 0.6 mmol) and $Cu(OAc)_2$ (109.0 mg, 0.6 mmol) were sequentially weighed into an oven-dried sealed tube. THF (2 mL) was added *via* syringe and the reaction mixture was stirred at 80 ℃ for 12 h. After cooling to ambient temperature,

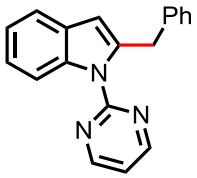
the mixture was extracted with EtOAc (3×10 mL). The combined organic layer was dried over anhydrous Na_2SO_4. The solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel using petroleum ether/EtOAc (15:1) to afford the desired product **7a** (52.9 mg, 75%).

Typical procedure for the synthesis of free (*NH*)-indoles [1]

An oven-dried sealed tube (15 mL) containing **3a** (57.0 mg, 0.2 mmol), EtONa (40.8 mg, 0.6 mmol), was evacuated and purged with nitrogen gas three times. DMSO (3 mL) was added *via* syringe and the reaction mixture was stirred at 100 ^oC for 24 h under N_2. After cooling to room temperature, the resulting mixture was quenched with water (10 mL) and extracted with EtOAc (10 mL×3). The combined organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel using petroleum ether/EtOAc (15:1) to give the desired product **8a** (33.6 mg, 81%).

Experimental Data

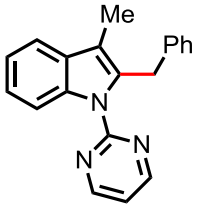
2-benzyl-1-(pyrimidin-2-yl)-1H-indole (3a)



3a

Purified by flash chromatography on silica gel (eluent: PE:EA=9:1) to give the desired product **3a** in 94% yield. Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 4.8 Hz, 2H), 8.26 (dd, *J* = 8.3, 0.6 Hz, 1H), 7.53-7.47 (m, 1H), 7.26 -7.11 (m, 7H), 7.02 (t, *J* = 4.8 Hz, 1H), 6.31 (d, *J* = 0.7 Hz, 1H), 4.56 (s, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 158.09, 157.96, 140.50, 139.33, 137.11, 129.09, 128.96, 128.17, 126.03, 122.74, 121.81, 119.86, 116.93, 113.88, 107.84, 35.94; HRMS m/z $[M+1]^+$ calculated for $C_{19}H_{16}N_3$: 286.1344, found: 286.1344.

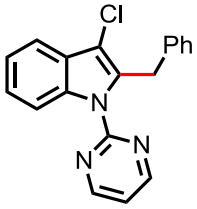
2-benzyl-3-methyl-1-(pyrimidin-2-yl)-1H-indole (3b)



3b

Purified by flash chromatography on silica gel (eluent: PE:EA=9:1) to give the desired product **3b** in 76% yield. Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 4.8 Hz, 2H), 8.24-8.21 (m, 1H), 7.58-7.57 (m, H), 7.26-7.25 (m, 1H), 7.24-7.23 (m, 1H), 7.13-7.07 (m, 2H), 7.05-6.96 (m, 4H), 4.65 (s, 2H), 2.36 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 158.05, 157.88, 140.00, 136.37, 134.66, 130.30, 128.06, 128.04, 125.57, 123.07, 121.48, 118.19, 116.59, 114.55, 113.69, 31.98, 9.06; HRMS m/z $[M+1]^+$ calculated for $C_{20}H_{18}N_3$: 300.1501, found: 300.1499.

2-benzyl-3-chloro-1-(pyrimidin-2-yl)-1H-indole (3c)

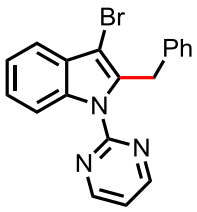


3c

Purified by flash chromatography on silica gel (eluent: PE:EA=9:1) to give the

desired product **3c** in 88% yield. White solid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 4.8 Hz, 2H), 8.30-8.26 (m, 1H), 7.69-7.65 (m, 1H), 7.34-7.28 (m, 2H), 7.14-7.09 (m, 2H), 7.07-7.03 (m, 4H), 4.76 (s, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 158.01, 157.57, 138.82, 135.30, 134.77, 128.16, 128.10, 126.79, 125.86, 124.20, 122.40, 117.91, 114.14, 111.35, 31.87; HRMS m/z $[M+1]^+$ calculated for $C_{19}H_{15}ClN_3$: 320.0955, found: 320.0956.

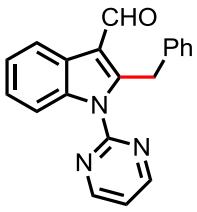
2-benzyl-3-bromo-1-(pyrimidin-2-yl)-1H-indole (3d)



3d

Purified by flash chromatography on silica gel (eluent: PE:EA=9:1) to give the desired product **3d** in 74% yield. White solid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 4.8 Hz, 2H), 8.23-8.21 (m, 1H), 7.63-7.61 (m, 1H), 7.33-7.29 (m, 2H), 7.13-7.08 (m, 2H), 7.07-7.00 (m, 4H), 4.77 (s, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 158.06, 157.52, 138.69, 136.51, 135.93, 128.21, 128.14, 128.10, 125.87, 124.21, 122.48, 119.04, 117.43, 113.98, 99.43, 32.99; HRMS m/z $[M+1]^+$ calculated for $C_{19}H_{15}BrN_3$: 364.0449, found: 364.0444.

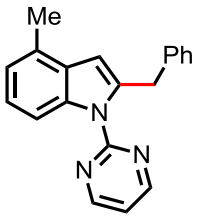
2-benzyl-1-(pyrimidin-2-yl)-1H-indole-3-carbaldehyde (3e)



3e

Purified by flash chromatography on silica gel (eluent: PE:EA=9:1) to give the desired product **3e** in 87% yield.. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.43 (s, 1H), 8.76 (d, *J* = 4.8 Hz, 2H), 8.44-8.41 (m, 1H), 7.92-7.90 (m, 1H), 7.39-7.31 (m, 2H), 7.22 (t, *J* = 4.8 Hz, 1H), 7.13-7.03 (m, 3H), 6.96-6.94 (m, 2H), 4.96 (s, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 185.85, 158.52, 156.94, 149.22, 137.66, 136.57, 128.40, 128.12, 126.40, 125.93, 124.62, 124.03, 121.31, 118.98, 118.00, 112.89, 30.96; HRMS m/z $[M+1]^+$ calculated for $C_{20}H_{16}N_3O$: 314.1293, found: 314.1290.

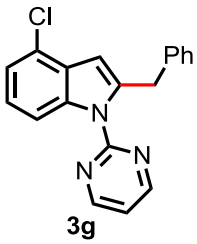
2-benzyl-4-methyl-1-(pyrimidin-2-yl)-1H-indole (3f)



3f

Purified by flash chromatography on silica gel (eluent: PE:EA=9:1) to give the desired product **3f** in 81% yield. Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 4.8 Hz, 2H), 8.19 (d, *J* = 8.5 Hz, 1H), 7.30 (s, 1H), 7.24-7.20 (m, 2H), 7.18-7.13 (m, 3H), 7.07-7.02 (m, 2H), 6.27 (d, *J* = 0.8 Hz, 1H), 4.58 (s, 2H), 2.44 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 158.19, 157.89, 140.51, 139.51, 135.40, 131.16, 129.35, 128.95, 128.14, 125.97, 124.14, 119.73, 116.67, 113.80, 107.76, 36.09, 21.30; HRMS m/z $[M+1]^+$ calculated for $C_{20}H_{18}N_3$: 300.1501, found: 300.1502.

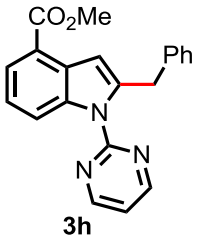
2-benzyl-4-chloro-1-(pyrimidin-2-yl)-1H-indole (3g)



3g

Purified by flash chromatography on silica gel (eluent: PE:EA=9:1) to give the desired product **3g** in 88% yield. White solid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 4.8 Hz, 2H), 8.15-8.11 (m, 1H), 7.25-7.09 (m, 8H), 6.48 (d, *J* = 0.8 Hz, 1H), 4.58 (s, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 158.11, 157.84, 140.30, 138.82, 137.76, 128.92, 128.28, 127.75, 126.19, 125.08, 123.31, 121.55, 117.47, 112.41, 105.75, 35.82; HRMS m/z $[M+1]^+$ calculated for $C_{19}H_{15}ClN_3$: 320.0955, found: 320.0959.

methyl 2-benzyl-1-(pyrimidin-2-yl)-1H-indole-4-carboxylate (3h)

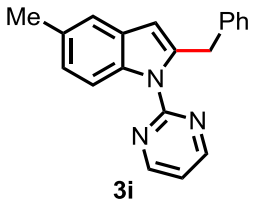


3h

Purified by flash chromatography on silica gel (eluent: PE:EA=4:1) to give the desired product **3h** in 80% yield. White solid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 4.8 Hz, 2H), 8.42 (d, *J* = 8.3 Hz, 1H), 7.95 (dd, *J* = 7.6, 0.5 Hz, 1H), 7.27 (t, *J* = 8.3 Hz, 1H), 7.20 -7.09 (m, 7H), 4.62 (s, 2H), 3.96 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 166.80, 157.11, 156.73, 141.52, 137.90, 136.87, 127.76, 127.20, 125.09,

123.84, 120.99, 119.74, 117.30, 116.49, 107.46, 50.72, 34.64; HRMS m/z $[M+1]^+$ calculated for $C_{21}H_{18}N_3O_2$: 344.1399, found: 344.1395.

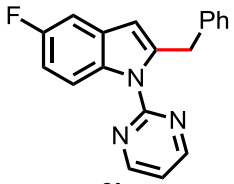
2-benzyl-5-methyl-1-(pyrimidin-2-yl)-1H-indole (3i)



3i

Purified by flash chromatography on silica gel (eluent: PE:EA=9:1) to give the desired product **3i** in 83% yield. Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 4.8 Hz, 2H), 8.08 (dd, *J* = 8.4, 0.5 Hz, 1H), 7.24-7.20 (m, 2H), 7.17-7.12 (m, 4H), 7.06 (t, *J* = 4.8 Hz, 1H), 7.01-6.98 (m, 1H), 6.38 (d, *J* = 0.9 Hz, 1H), 4.59 (s, 2H), 2.51 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 158.16, 157.98, 139.73, 139.46, 136.89, 129.22, 128.92, 128.67, 128.17, 125.99, 122.84, 122.18, 116.95, 111.36, 106.23, 35.89, 18.59; HRMS m/z $[M+1]^+$ calculated for $C_{20}H_{18}N_3$: 300.1501, found: 300.1501.

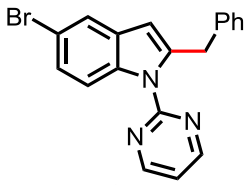
2-benzyl-5-fluoro-1-(pyrimidin-2-yl)-1H-indole (3j)



3j

Purified by flash chromatography on silica gel (eluent: PE:EA=9:1) to give the desired product **3j** in 90% yield. Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 4.8 Hz, 2H), 8.25 (dd, *J* = 9.1, 4.7 Hz, 1H), 7.25-7.21 (m, 2H), 7.20-7.13 (m, 4H), 7.08 (td, *J* = 4.8, 0.9 Hz, 1H), 6.99-6.93 (m, 1H), 6.27 (s, 1H), 4.58 (s, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 158.91 (d, J_{C-F} = 235.6 Hz), 158.00, 142.33, 139.04, 133.49, 129.81 (d, J_{C-F} = 10.1 Hz), 128.98, 128.25, 126.16, 117.08, 115.02 (d, J_{C-F} = 9.0 Hz), 110.51, 110.26, 107.66 (d, J_{C-F} = 4.0 Hz), 105.03 (d, J_{C-F} = 23.4 Hz), 36.15; HRMS m/z $[M+1]^+$ calculated for $C_{19}H_{15}FN_3$: 304.1250, found: 304.1252.

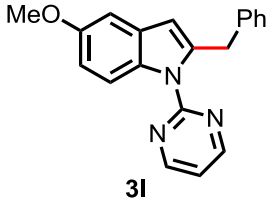
2-benzyl-5-bromo-1-(pyrimidin-2-yl)-1H-indole (3k)



3k

Purified by flash chromatography on silica gel (eluent: PE:EA=9:1) to give the desired product **3k** in 82% yield. White solid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 4.8 Hz, 2H), 8.15-8.11 (m, 1H), 7.24-7.10 (m, 8H), 6.48 (d, *J* = 0.9 Hz, 1H), 4.58 (s, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 158.11, 157.84, 141.30, 138.82, 137.77, 128.92, 128.28, 127.75, 126.19, 125.08, 123.31, 121.55, 117.48, 112.40, 107.75, 35.82; HRMS m/z $[M+1]^+$ calculated for $C_{19}H_{15}BrN_3$: 364.0449, found: 364.0447.

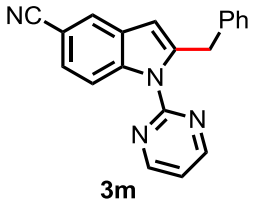
2-benzyl-5-methoxy-1-(pyrimidin-2-yl)-1H-indole (3l)



3l

Purified by flash chromatography on silica gel (eluent: PE:EA=5:1) to give the desired product **3l** in 81% yield. White solid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 4.8 Hz, 2H), 8.24 (dd, *J* = 9.1, 0.6 Hz, 1H), 7.25-7.13 (m, 5H), 7.03 (t, *J* = 4.8 Hz, 1H), 6.98 (d, *J* = 2.5 Hz, 1H), 6.87 (dd, *J* = 9.1, 2.6 Hz, 1H), 6.25 (d, *J* = 0.8 Hz, 1H), 4.58 (s, 2H), 3.85 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 158.13, 157.89, 155.38, 141.26, 139.45, 132.01, 129.87, 128.99, 128.18, 126.02, 116.63, 115.13, 111.68, 107.95, 102.30, 55.69, 36.26; HRMS m/z $[M+1]^+$ calculated for $C_{20}H_{18}N_3O$: 316.1450, found: 316.1448.

2-benzyl-1-(pyrimidin-2-yl)-1H-indole-5-carbonitrile (3m)

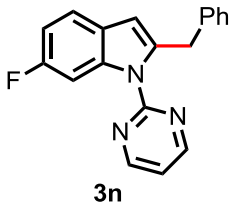


3m

Purified by flash chromatography on silica gel (eluent: PE:EA=3:1) to give the desired product **3m** in 89% yield. White solid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 4.8 Hz, 2H), 8.27 (d, *J* = 8.7 Hz, 1H), 7.82 (d, *J* = 1.5 Hz, 1H), 7.46 (dd, *J* = 8.7, 1.6 Hz, 1H), 7.26-7.21 (m, 2H), 7.20-7.12 (m, 4H), 6.35 (s, 1H), 4.56 (s, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 158.32, 157.51, 143.32, 138.85, 138.38, 128.97, 128.92, 128.41, 126.44, 125.84, 124.85, 120.42, 118.06, 114.65, 107.30, 104.82,

35.81; HRMS m/z $[M+1]^+$ calculated for $C_{20}H_{15}N_4$: 311.1297, found: 311.1295.

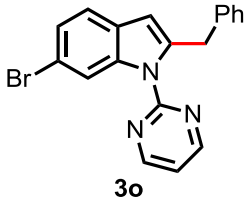
2-benzyl-6-fluoro-1-(pyrimidin-2-yl)-1H-indole (3n)



3n

Purified by flash chromatography on silica gel (eluent: PE:EA=9:1) to give the desired product **3n** in 84% yield. Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 4.8 Hz, 2H), 8.08 (dd, *J* = 11.1, 2.4 Hz, 1H), 7.40 (dd, *J* = 8.5, 5.6 Hz, 1H), 7.26-7.20 (m, 2H), 7.19-7.14 (m, 3H), 7.09 (t, *J* = 4.8 Hz, 1H), 6.97-6.92 (m, 1H), 6.28 (d, *J* = 0.8 Hz, 1H), 4.57 (s, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 160.19 (d, J_{C-F} = 235.6 Hz), 158.01, 141.06 (d, J_{C-F} = 3.9 Hz), 139.22, 137.16 (d, J_{C-F} = 12.7 Hz), 128.96, 128.23, 126.11, 125.41, 120.22 (d, J_{C-F} = 9.9 Hz), 117.12, 110.01 (d, J_{C-F} = 24.1 Hz), 107.62, 101.58, 101.29, 36.13; HRMS m/z $[M+1]^+$ calculated for $C_{19}H_{15}FN_3$: 304.1250, found: 304.1244.

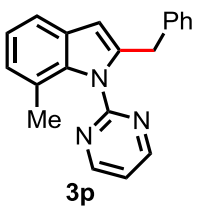
2-benzyl-6-bromo-1-(pyrimidin-2-yl)-1H-indole (3o)



3o

Purified by flash chromatography on silica gel (eluent: PE:EA=9:1) to give the desired product **3o** in 89% yield. White solid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 4.8 Hz, 2H), 8.49-8.47 (m, 1H), 7.37-7.34 (m, 1H), 7.29 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.25-7.20 (m, 2H), 7.19-7.13 (m, 3H), 7.10 (t, *J* = 4.8 Hz, 1H), 6.28 (dd, *J* = 1.8, 1.0 Hz, 1H), 4.55 (s, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 158.09, 157.80, 141.38, 138.97, 137.75, 128.96, 128.26, 127.93, 126.18, 124.98, 120.92, 117.30, 117.08, 116.35, 107.61, 36.00; HRMS m/z $[M+1]^+$ calculated for $C_{19}H_{15}BrN_3$: 364.0449, found: 364.0448.

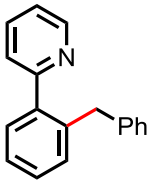
2-benzyl-7-methyl-1-(pyrimidin-2-yl)-1H-indole (3p)



3p

Purified by flash chromatography on silica gel (eluent: PE:EA=9:1) to give the desired product **3p** in 82% yield. Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 4.8 Hz, 2H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.18-7.06 (m, 5H), 7.03-6.99 (m, 2H), 6.96 (d, *J* = 7.2 Hz, 1H), 6.37 (s, 1H), 4.17 (s, 2H), 1.95 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 158.68, 158.09, 140.34, 138.27, 136.64, 129.34, 128.68, 128.09, 126.04, 125.20, 121.70, 121.26 118.83, 118.07, 105.34, 34.02, 19.98; HRMS m/z $[M+1]^+$ calculated for $C_{20}H_{18}N_3$: 300.1501, found: 300.1499.

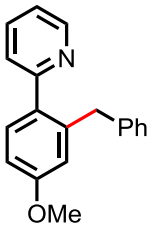
2-(2-benzylphenyl)pyridine (5a)



5a

Purified by flash chromatography on silica gel (eluent: PE:EA=9:1) to give the desired product **5a** in 69% yield. Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.67 (ddd, *J* = 4.9, 1.8, 1.0 Hz, 1H), 7.64 (td, *J* = 7.7, 1.8 Hz, 1H), 7.40-7.36 (m, 1H), 7.34-7.27 (m, 2H), 7.26-7.13 (m, 5H), 7.12-7.07 (m, 1H), 6.98-6.95 (m, 2H), 4.12 (s, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 159.91, 149.05, 141.26, 140.62, 138.78, 136.11, 130.60, 129.83, 128.83, 128.39, 128.14, 126.29, 125.67, 124.17, 121.68, 38.76; HRMS m/z $[M+1]^+$ calculated for $C_{18}H_{16}N$: 246.1283, found: 246.1281.

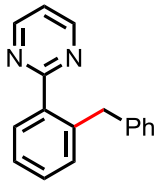
2-(2-benzyl-4-methoxyphenyl)pyridine (5b)



5b

Purified by flash chromatography on silica gel (eluent: PE:EA=5:1) to give the desired product **5b** in 63% yield. Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.66 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 7.62 (td, *J* = 7.7, 1.9 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.26-7.21 (m, 1H), 7.20-7.14 (m, 3H), 7.14-7.08 (m, 1H), 7.01-6.97 (m, 2H), 6.84 (dd, J = 8.4, 2.7 Hz, 1H), 6.76 (d, J = 2.6 Hz, 1H), 4.13 (s, 2H), 3.78 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 159.70, 159.58, 149.04, 141.08, 140.38, 136.07, 133.49, 131.18, 128.83, 128.18, 125.74, 124.20, 121.35, 116.29, 111.48, 55.21, 38.98; HRMS m/z $[M+1]^+$ calculated for $C_{19}H_{18}NO$: 276.1388, found: 276.1386.

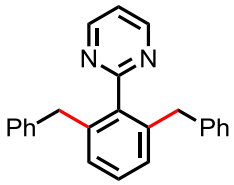
2-(2-benzylphenyl)pyrimidine (5c)



5c

Purified by flash chromatography on silica gel (eluent: PE:EA=9:1) to give the desired product **5c** in 73% yield (mono:di=1:1.5). Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.79 (d, J = 4.9 Hz, 2H), 7.79-7.77 (m, 1H), 7.40-7.33 (m, 2H), 7.26-7.23 (m, 1H), 7.19-7.15 (m, 3H), 7.11-7.07 (m, 1H), 7.04-7.02 (m, 2H), 4.39 (s, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 167.60, 156.83, 141.37, 139.85, 138.29, 131.08, 130.60, 129.53, 128.93, 128.10, 126.44, 125.61, 118.58, 39.01; HRMS m/z $[M+1]^+$ calculated for $C_{17}H_{15}N_2$: 247.1235, found: 247.1237.

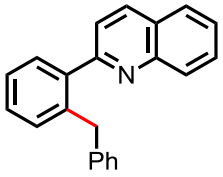
2-(2,6-dibenzylphenyl)pyrimidine (5c´)



5c´

Purified by flash chromatography on silica gel (eluent: PE:EA=9:1) to give the desired product **5c´**. White solid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.70 (d, J = 4.9 Hz, 2H), 7.26 (t, J = 8.4 Hz, 1H), 7.17-7.13 (m, 5H), 7.12-7.07 (m, 4H), 6.95-6.90 (m, 4H), 3.83 (s, 4H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 167.80, 156.70, 140.56, 139.02, 138.90, 128.88, 128.66, 128.20, 128.11, 125.72, 118.74, 39.30; HRMS m/z $[M+1]^+$ calculated for $C_{24}H_{21}N_2$: 337.1705, found: 337.1707.

2-(2-benzylphenyl)quinoline (5d)

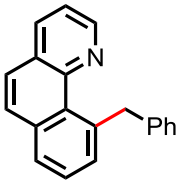


5d

Purified by flash chromatography on silica gel (eluent: PE:EA=9:1) to give the desired product **5d** in 64% yield. White solid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.14 (t, J = 8.0 Hz, 2H), 7.84 (dd, J = 8.2, 1.2 Hz, 1H), 7.77-7.73 (m, 1H), 7.58-7.54 (m, 1H), 7.52-7.48 (m, 1H), 7.40 (d, J = 8.4 Hz, 1H), 7.39-7.34 (m, 2H), 7.31-7.28 (m, 1H),

7.17-7.07 (m, 3H), 7.00-6.96 (m, 2H), 4.20 (s, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 160.10, 147.74, 141.25, 140.87, 139.12, 136.10, 130.80, 129.91, 129.62, 129.57, 128.91, 128.62, 128.13, 127.46, 126.71, 126.44, 126.41, 125.69, 122.40, 38.92; HRMS m/z $[M+1]^+$ calculated for $C_{22}H_{18}N$: 296.1439, found: 276.1437.

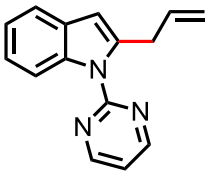
10-benzylbenzo[*h*]quinoline (5e)



5e

Purified by flash chromatography on silica gel (eluent: PE:EA=9:1) to give the desired product **5e** in 86% yield. White solid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.92 (dd, J = 4.3, 1.9 Hz, 1H), 8.11 (dd, J = 8.0, 1.9 Hz, 1H), 7.85 (dd, J = 7.8, 1.4 Hz, 1H), 7.82 (d, J = 8.8 Hz, 1H), 7.63 (dd, J = 15.1, 8.1 Hz, 2H), 7.55 (dd, J = 7.3, 1.4 Hz, 1H), 7.43 (dd, J = 8.0, 4.3 Hz, 1H), 7.30-7.26 (m, 2H), 7.25-7.19 (m, 2H), 7.15-7.10 (m, 1H), 5.40 (s, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 148.14, 147.02, 143.02, 140.51, 135.47, 135.29, 131.81, 129.60, 129.11, 128.82, 127.89, 127.41, 127.38, 127.30, 125.57, 125.18, 120.75, 43.43; HRMS m/z $[M+1]^+$ calculated for $C_{20}H_{16}N$: 270.1283, found: 276.1285.

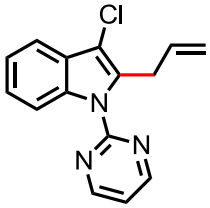
2-allyl-1-(pyrimidin-2-yl)-1H-indole (7a)



7a

Purified by flash chromatography on silica gel (eluent: PE:EA=10:1) to give the desired product **7a** in 75% yield. Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.78 (d, *J* = 4.8 Hz, 2H), 8.27 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.55 (dd, *J* = 6.9, 1.4 Hz, 1H), 7.26-7.17 (m, 2H), 7.13 (t, *J* = 4.8 Hz, 1H), 6.50 (d, *J* = 0.8 Hz, 1H), 6.00 (ddt, *J* = 16.6, 10.1, 6.5 Hz, 1H), 5.10-5.01 (m, 2H), 4.00-3.95 (m, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 158.18, 158.06, 139.73, 137.04, 135.55, 129.21, 122.63, 121.77, 119.80, 117.03, 116.37, 113.75, 106.44, 34.02; HRMS m/z $[M+1]^+$ calculated for $C_{15}H_{14}N_3$: 236.1188, found: 236.1190.

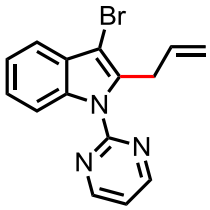
2-allyl-3-chloro-1-(pyrimidin-2-yl)-1H-indole (7b)



7b

Purified by flash chromatography on silica gel (eluent: PE:EA=10:1) to give the desired product **7b** in 47% yield. Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.78 (d, *J* = 4.8 Hz, 2H), 8.29-8.26 (m, 1H), 7.62-7.60 (m, 1H), 7.33-7.26 (m, 2H), 7.17 (t, *J* = 4.8 Hz, 1H), 5.88 (ddt, *J* = 17.1, 10.1, 6.0 Hz, 1H), 4.96-4.87 (m, 2H), 4.09 (dt, *J* = 6.0, 1.6 Hz, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 158.17, 157.76, 135.18, 134.54, 134.04, 126.88, 124.01, 122.33, 117.74, 117.43, 115.91, 114.00, 110.55, 30.23; HRMS m/z $[M+1]^+$ calculated for $C_{15}H_{13}ClN_3$: 270.0798, found: 270.0797.

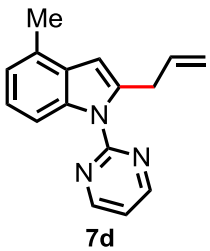
2-allyl-3-bromo-1-(pyrimidin-2-yl)-1H-indole (7c)



7c

Purified by flash chromatography on silica gel (eluent: PE:EA=10:1) to give the desired product **7c** in 43% yield. Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.79 (d, *J* = 4.8 Hz, 2H), 8.24-8.21 (m, 1H), 7.58-7.55 (m, 1H), 7.33-7.27 (m, 2H), 7.18 (t, *J* = 4.8 Hz, 1H), 5.87 (ddt, *J* = 17.1, 10.1, 6.0 Hz, 1H), 4.96-4.87 (m, 2H), 4.10 (dt, *J* = 6.0, 1.6 Hz, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 158.23, 157.73, 135.82, 135.73, 134.48, 128.30, 124.04, 122.44, 118.88, 117.58, 115.98, 113.86, 98.49, 31.37; HRMS m/z $[M+1]^+$ calculated for $C_{15}H_{13}BrN_3$: 314.0293, found: 314.0292.

2-allyl-4-methyl-1-(pyrimidin-2-yl)-1H-indole (7d)

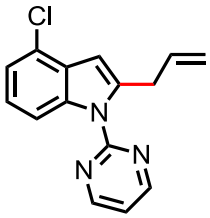


7d

Purified by flash chromatography on silica gel (eluent: PE:EA=10:1) to give the desired product **7d** in 67% yield. Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.78 (d, *J* = 4.8 Hz, 2H), 8.08 (dd, *J* = 8.4, 0.6 Hz, 1H), 7.16-7.12 (m, 2H), 7.01-6.97 (m, 1H),

6.52 (dd, *J* = 1.8, 0.9 Hz, 1H), 6.01 (ddt, *J* = 16.6, 10.1, 6.5 Hz, 1H), 5.05 (tq, *J* = 10.0, 1.5 Hz, 2H), 3.97 (ddd, *J* = 6.5, 2.5, 1.3 Hz, 2H), 2.54 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 158.25, 158.06, 139.06, 136.80, 135.68, 129.12, 128.77, 122.71, 122.13, 117.03, 116.33, 111.27, 104.83, 34.07, 18.58; HRMS m/z $[M+1]^+$ calculated for $C_{16}H_{16}N_3$: 250.1344, found: 250.1343.

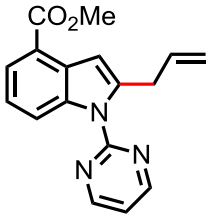
2-allyl-4-chloro-1-(pyrimidin-2-yl)-1H-indole (7e)



7e

Purified by flash chromatography on silica gel (eluent: PE:EA=10:1) to give the desired product **7e** in 46% yield. Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 4.8 Hz, 2H), 8.15-8.11 (m, 1H), 7.20-7.17 (m, 2H), 7.13 (t, *J* = 7.9 Hz, 1H), 6.62 (d, *J* = 0.8 Hz, 1H), 5.99 (ddt, *J* = 16.7, 10.1, 6.5 Hz, 1H), 5.11-5.02 (m, 2H), 3.96 (dq, *J* = 6.5, 1.3 Hz, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 158.19, 157.94, 140.64, 137.68, 135.06, 127.85, 125.01, 123.18, 121.50, 117.54, 116.80, 112.35, 104.45, 33.99; HRMS m/z $[M+1]^+$ calculated for $C_{15}H_{13}ClN_3$: 270.0798, found: 270.0796.

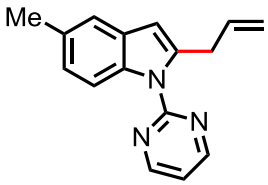
methyl 2-allyl-1-(pyrimidin-2-yl)-1H-indole-4-carboxylate (7f)



7f

Purified by flash chromatography on silica gel (eluent: PE:EA=5:1) to give the desired product **7f** in 49% yield. Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.81 (d, *J* = 4.8 Hz, 2H), 8.42 (dt, *J* = 8.3, 0.8 Hz, 1H), 7.94 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.26 (t, *J* = 8. Hz, H), 7.19 (t, *J* = 4.8 Hz, 2H), 6.00 (ddt, *J* = 16.6, 10.1, 6.5 Hz, 1H), 5.09-5.00 (m, 2H), 4.01-3.97 (m, 5H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 167.86, 158.22, 157.88, 142.08, 137.78, 135.11, 129.17, 124.81, 121.86, 120.66, 118.23, 117.58, 116.70, 107.08, 51.75, 33.93; HRMS m/z $[M+1]^+$ calculated for $C_{17}H_{16}N_3O_2$: 294.1243, found: 294.1240.

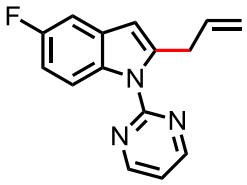
2-allyl-5-methyl-1-(pyrimidin-2-yl)-1H-indole (7g)



7g

Purified by flash chromatography on silica gel (eluent: PE:EA=10:1) to give the desired product **7g** in 64% yield. Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 4.8 Hz, 2H), 8.16 (d, *J* = 8.5 Hz, 1H), 7.32 (s, 1H), 7.11 (td, *J* = 4.8, 0.6 Hz, 1H), 7.04 (d, *J* = 8.5 Hz, 1H), 6.41 (s, 1H), 5.99 (ddt, *J* = 16.6, 10.1, 6.5 Hz, 1H), 5.10-4.99 (m, 2H), 3.96 (d, *J* = 6.4 Hz, 2H), 2.44 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 158.29, 157.99, 139.79, 135.72, 135.34, 131.12, 129.48, 124.02, 119.68, 116.76, 116.25, 113.65, 106.31, 34.19, 21.31; HRMS m/z $[M+1]^+$ calculated for $C_{16}H_{16}N_3$: 250.1344, found: 250.1343.

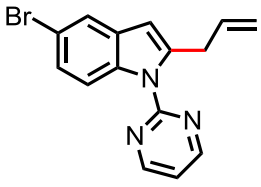
2-allyl-5-fluoro-1-(pyrimidin-2-yl)-1H-indole (7h)



7h

Purified by flash chromatography on silica gel (eluent: PE:EA=10:1) to give the desired product **7h** in 51% yield. Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.78 (d, *J* = 4.8 Hz, 2H), 8.23 (dd, *J* = 9.1, 4.7 Hz, 1H), 7.16 (dt, *J* = 7.0, 3.7 Hz, 2H), 6.94 (td, *J* = 9.2, 2.6 Hz, 1H), 6.45 (d, *J* = 0.8 Hz, 1H), 5.99 (ddt, *J* = 16.7, 10.1, 6.5 Hz, 1H), 5.11-5.02 (m, 2H), 3.96 (dd, *J* = 6.5, 1.2 Hz, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 158.92 (d, J_{C-F} = 235.6 Hz), 158.09, 141.53, 135.29, 133.42, 129.93 (d, J_{C-F} = 10.1 Hz), 117.16, 116.62, 114.88 (d, J_{C-F} = 9.0 Hz), 110.40, 110.16, 106.29 (d, J_{C-F} = 4.0 Hz), 104.98 (d, J_{C-F} = 23.4 Hz), 34.23; HRMS m/z $[M+1]^+$ calculated for $C_{15}H_{13}FN_3$: 254.1094, found: 254.1092.

2-allyl-5-bromo-1-(pyrimidin-2-yl)-1H-indole (7i)

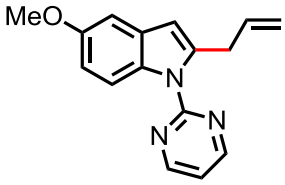


7i

Purified by flash chromatography on silica gel (eluent: PE:EA=9:1) to give the

desired product **7i** in 56% yield. White solid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.78 (d, *J* = 4.8 Hz, 2H), 8.15 (d, *J* = 8.9 Hz, 1H), 7.65 (d, *J* = 1.9 Hz, 1H), 7.30 (dd, *J* = 8.9, 2.0 Hz, 1H), 7.16 (t, *J* = 4.8 Hz, 1H), 6.45-6.40 (m, 1H), 5.97 (ddt, *J* = 16.7, 10.2, 6.5 Hz, 1H), 5.09-5.01 (m, 2H), 3.95 (dd, *J* = 6.5, 1.2 Hz, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 158.14, 157.93, 141.16, 135.73, 135.15, 130.96, 125.31, 122.30, 117.35, 116.72, 115.46, 114.95, 105.69, 34.06; HRMS m/z $[M+1]^+$ calculated for $C_{15}H_{13}BrN_3$: 314.0293, found: 314.0291.

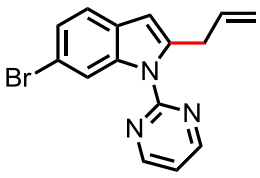
2-allyl-5-methoxy-1-(pyrimidin-2-yl)-1H-indole (7j)



7j

Purified by flash chromatography on silica gel (eluent: PE:EA=9:1) to give the desired product **7j** in 85% yield. Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.75 (d, *J* = 4.8 Hz, 2H), 8.22 (d, *J* = 9.1 Hz, 1H), 7.11 (t, *J* = 4.8 Hz, 1H), 7.01 (d, *J* = 2.6 Hz, 1H), 6.85 (dd, *J* = 9.1, 2.6 Hz, 1H), 6.42 (d, *J* = 0.8 Hz, 1H), 6.06-6.96 (m, 1H), 5.10-5.00 (m, 2H), 3.99-3.92 (m, 2H), 3.86 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 158.23, 158.00, 155.39, 140.52, 135.67, 131.97, 130.01, 116.74, 116.35, 114.99, 111.54, 106.53, 102.31, 55.74, 34.35; HRMS m/z $[M+1]^+$ calculated for $C_{16}H_{16}N_3O$: 266.1293, found: 266.1297.

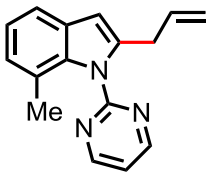
2-allyl-6-bromo-1-(pyrimidin-2-yl)-1H-indole (7k)



7k

Purified by flash chromatography on silica gel (eluent: PE:EA=9:1) to give the desired product **7k** in 41% yield. White solid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.79 (d, *J* = 4.8 Hz, 2H), 7.38 (d, *J* = 8.3 Hz, 1H), 7.29 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.17 (t, *J* = 4.8 Hz, 1H), 6.45 (d, *J* = 0.8 Hz, 1H), 5.97 (ddt, *J* = 16.7, 10.2, 6.5 Hz, 1H), 5.10-5.01 (m, 2H), 3.94 (dd, *J* = 6.5, 1.2 Hz, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 158.18, 157.87, 140.57, 137.68, 135.18, 128.05, 124.95, 120.85, 117.39, 116.97, 116.67, 116.22, 106.24, 34.06; HRMS m/z $[M+1]^+$ calculated for $C_{15}H_{13}BrN_3$: 314.0293, found: 314.0294.

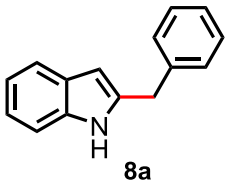
2-allyl-7-methyl-1-(pyrimidin-2-yl)-1H-indole (7l)



7l

Purified by flash chromatography on silica gel (eluent: PE:EA=10:1) to give the desired product **7l** in 50% yield. Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.85 (d, *J* = 4.9 Hz, 2H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.30 (t, *J* = 4.8 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 7.2 Hz, 1H), 6.44 (s, 1H), 5.83 (ddt, *J* = 16.7, 10.2, 6.5 Hz, 1H), 4.93-4.84 (m, 2H), 3.54 (dd, *J* = 6.5, 1.1 Hz, 2H), 1.96 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 158.77, 158.24, 139.67, 136.60, 134.62, 129.48, 125.08, 121.68, 121.22, 119.07, 118.02, 116.34, 104.06, 32.15, 20.02; HRMS m/z $[M+1]^+$ calculated for $C_{16}H_{16}N_3$: 250.1344, found: 250.1344.

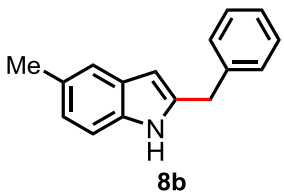
2-benzyl-1H-indole (8a)



8a

Purified by flash chromatography on silica gel (eluent: PE:EA=15:1) to give the desired product **8a** in 81% yield. Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.56 (d, J = 7.6 Hz, 1H), 7.38-7.30 (m, 2H), 7.30-7.20 (m, 4H), 7.14-7.04 (m, 2H), 6.34 (s, 1H), 4.13 (s, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 138.48, 137.75, 136.23, 128.81, 128.70, 128.64, 126.71, 121.28, 119.96, 119.69, 110.44, 101.06, 34.68; HRMS m/z $[M+1]^+$ calculated for $C_{16}H_{16}N_3$: 208.1126, found: 208.1130.

2-benzyl-5-methyl-1H-indole (8b)



8b

Purified by flash chromatography on silica gel (eluent: PE:EA=15:1) to give the desired product **8b** in 84% yield. Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ7.65 (s, 1H), 7.37-7.28 (m, 3H), 7.25 (t, J = 7.6 Hz, 3H), 7.12 (d, J = 8.2 Hz, 1H), 6.94 (d, J = 8.1 Hz, 1H), 6.25 (s, 1H), 4.10 (s, 2H), 2.43 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ

138.60, 137.81, 134.50, 128.88, 128.85, 128.77, 128.65, 126.64, 122.76, 119.68, 110.08, 100.62, 34.69, 21.42; HRMS m/z $[M+1]^+$ calculated for $C_{16}H_{16}N_1$: 222.1283, found: 222.1285.

References

1 Ackermann, L.; Lygin, A. V. *Org. Lett.* **2011**, *13*, 3332.

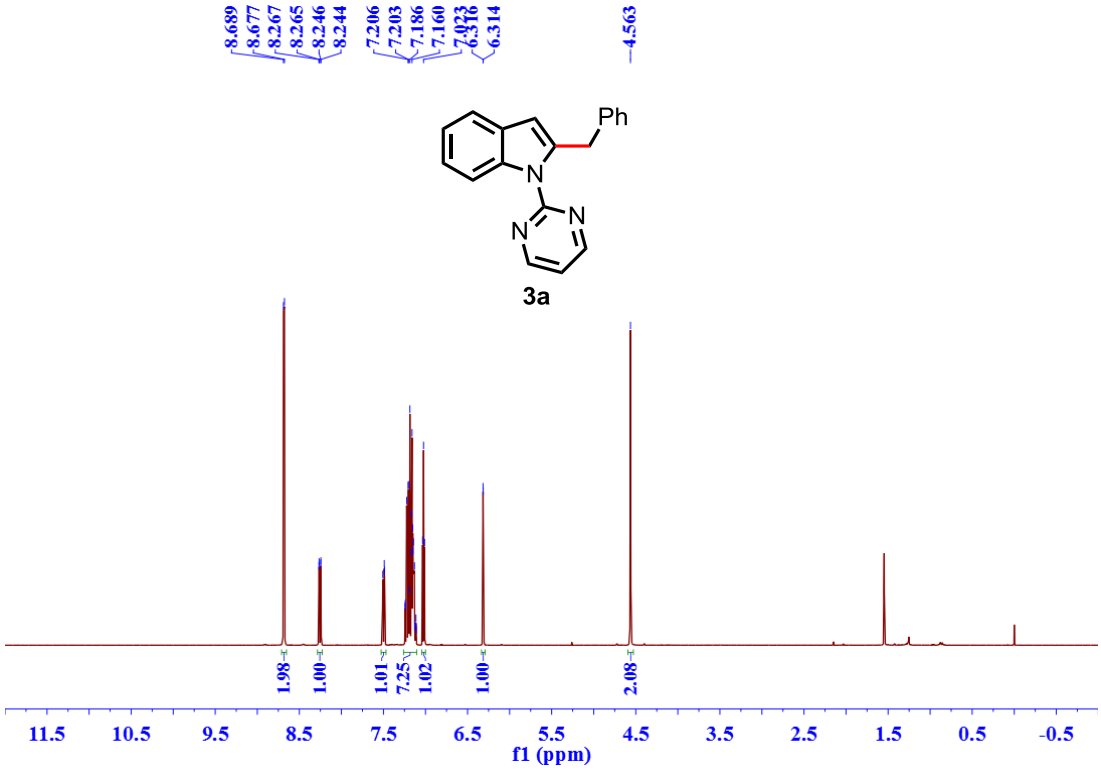
2 Maresh, J. J.; Giddings, L.-A.; Friedrich, A.; Loris, E. Panjikar, A.; S.; Trout, B. L.; Stckigt, J.; Peters, B.; O′Connor, S. E. *J. Am. Chem. Soc.* **2008**, *130*, 710.

3 M.-Z. Lu, P. Lu, Y.-H. Xu, T.-P. Loh, *Org. Lett.*, **2014**, *16*, 2614.

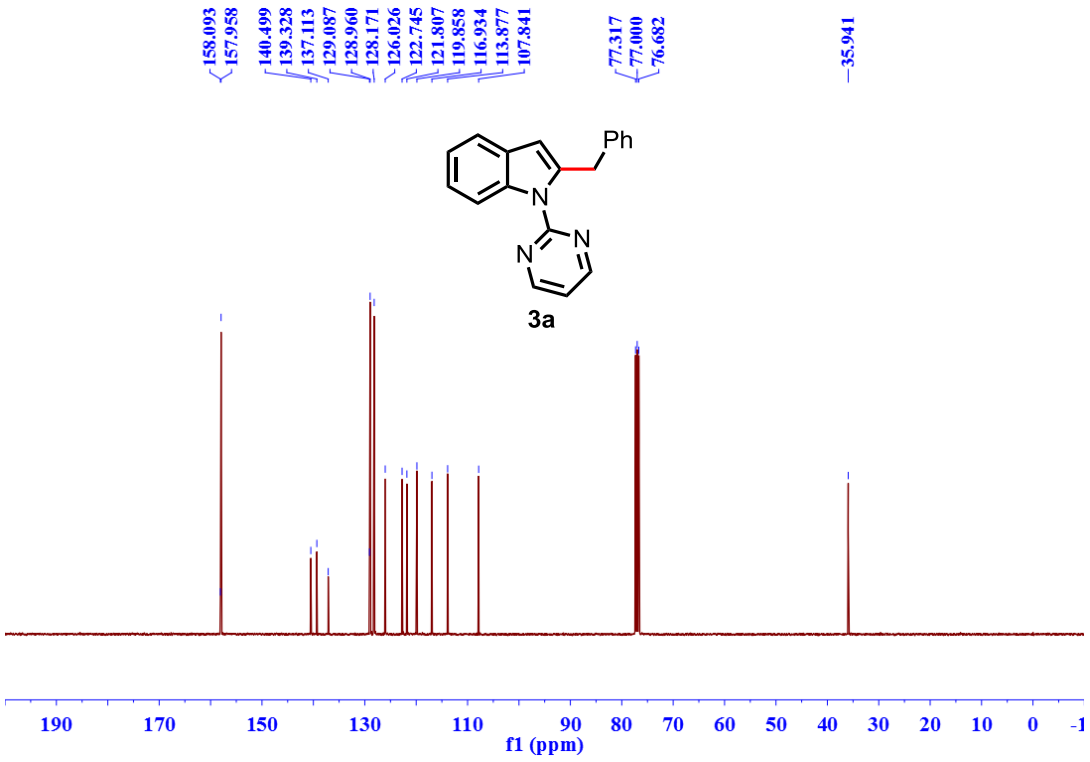
^{1}H and ^{13}C NMR Spectra of Products

2-benzyl-1-(pyrimidin-2-yl)-1H-indole (3a)

^{1}H-NMR (400 MHz, $CDCl_3$)

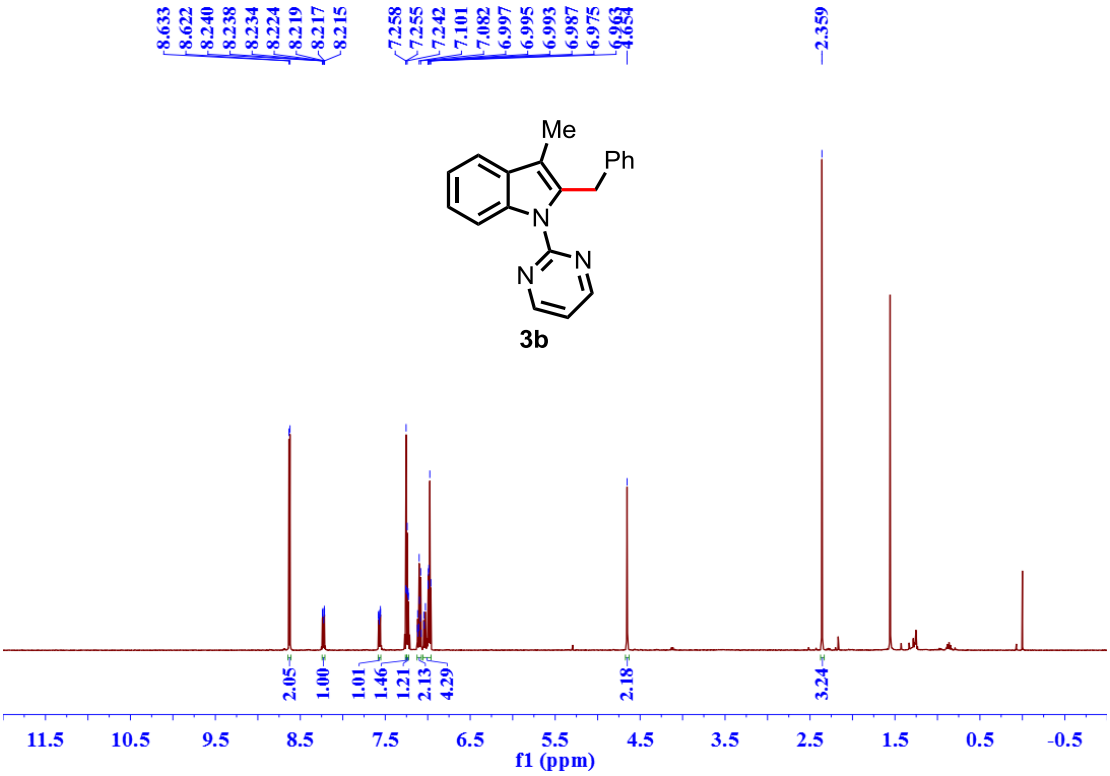


^{13}C-NMR (100 MHz, $CDCl_3$)

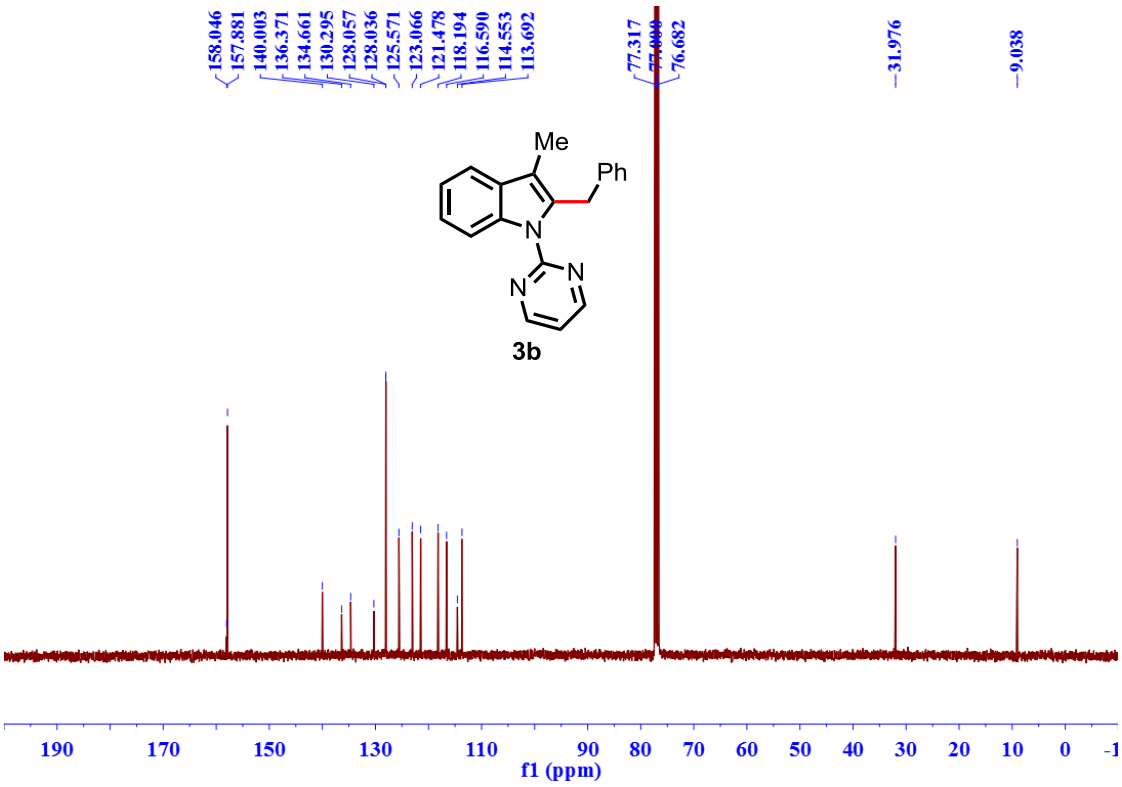


2-benzyl-3-methyl-1-(pyrimidin-2-yl)-1H-indole (3b)

^{1}H-NMR (400 MHz, $CDCl_3$)

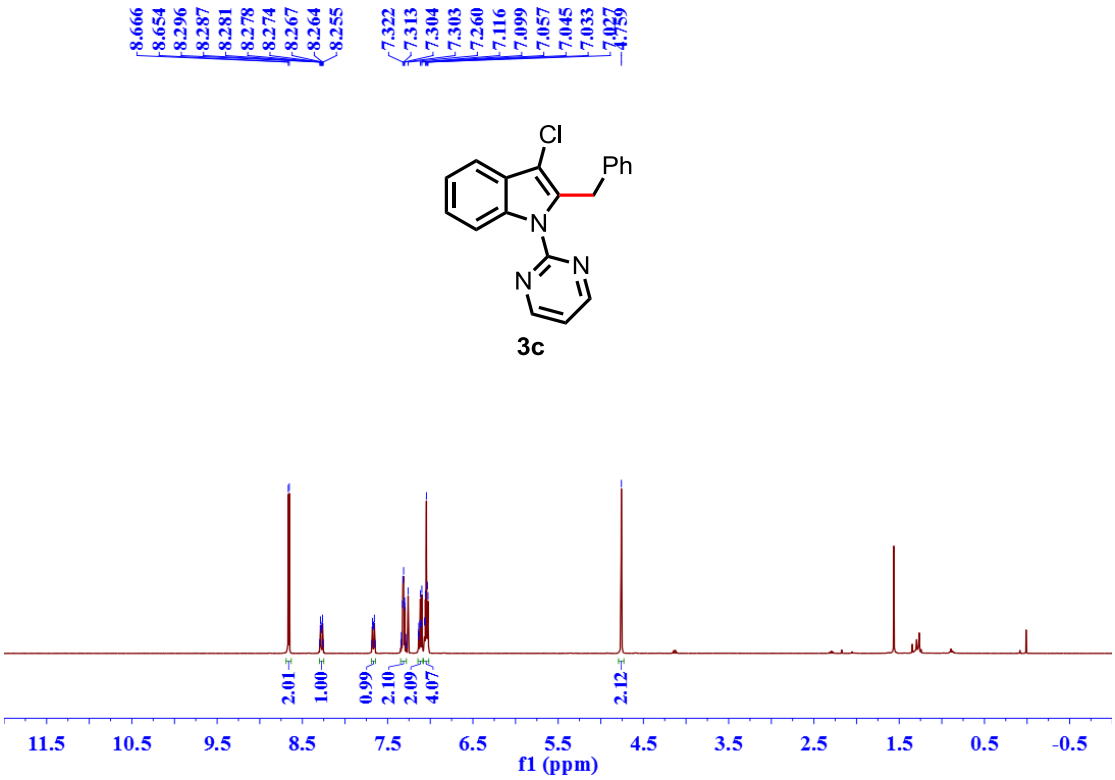


^{13}C-NMR (100 MHz, $CDCl_3$)

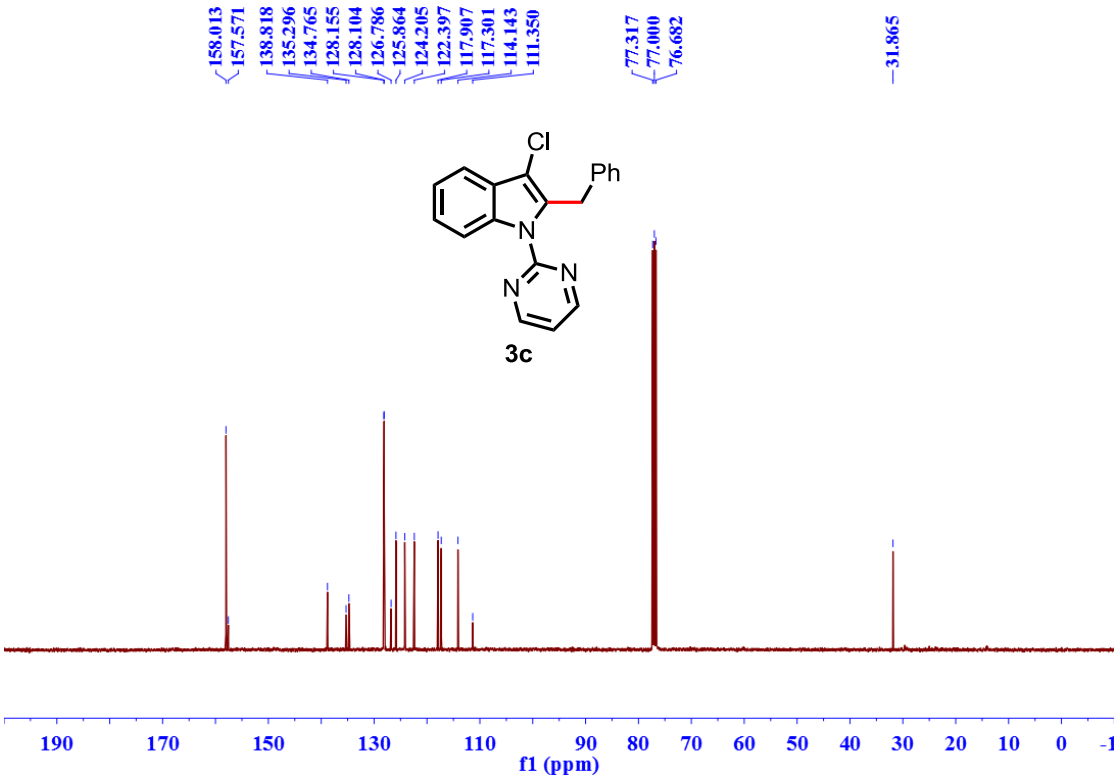


2-benzyl-3-chloro-1-(pyrimidin-2-yl)-1H-indole (3c)

^{1}H-NMR (400 MHz, $CDCl_3$)

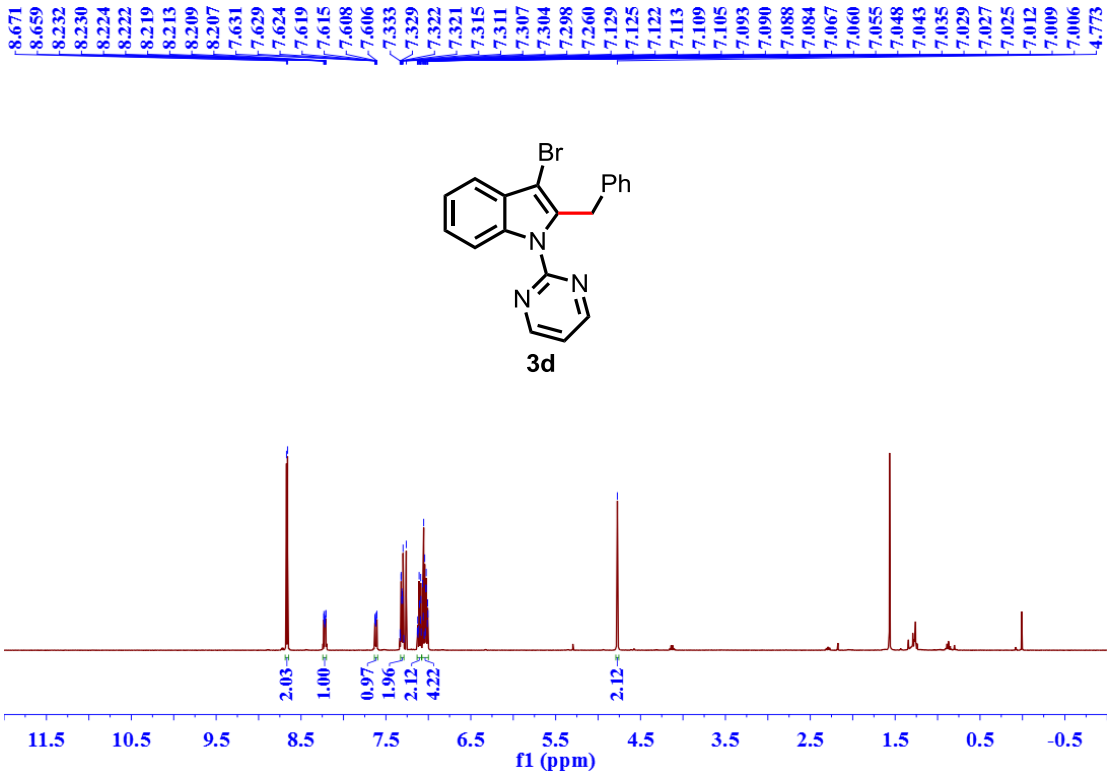


^{13}C-NMR (100 MHz, $CDCl_3$)

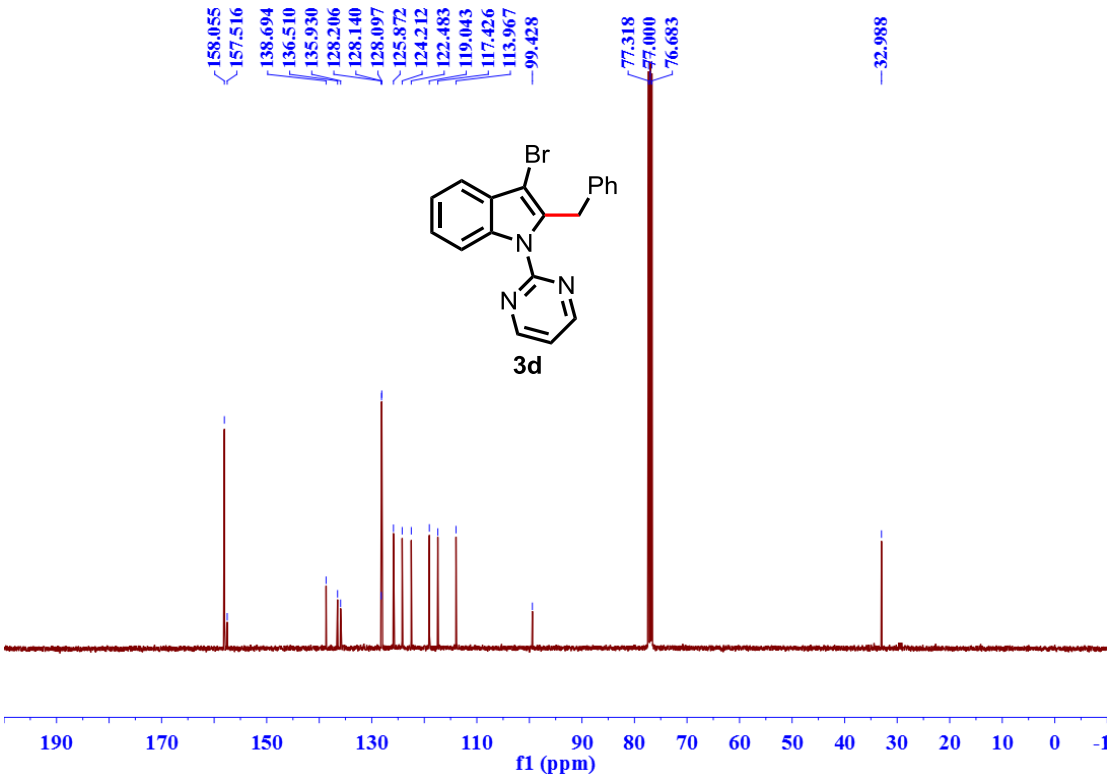


2-benzyl-3-bromo-1-(pyrimidin-2-yl)-1H-indole (3d)

^{1}H-NMR (400 MHz, $CDCl_3$)

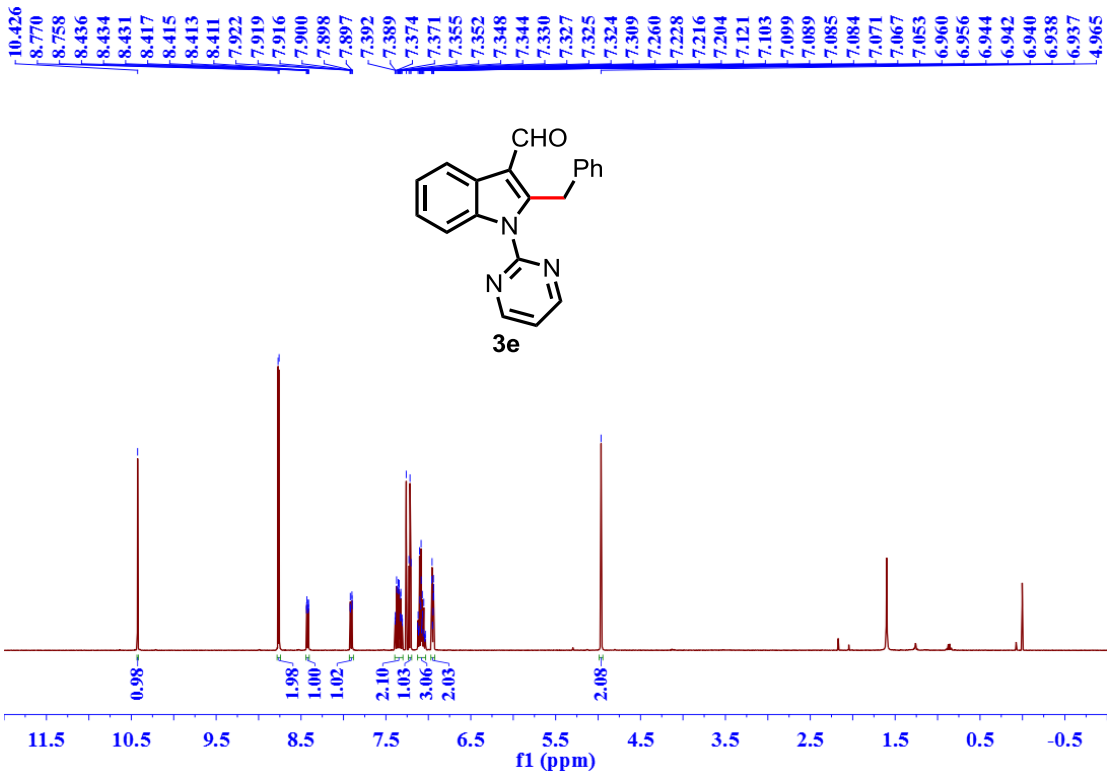


^{13}C-NMR (100 MHz, $CDCl_3$)

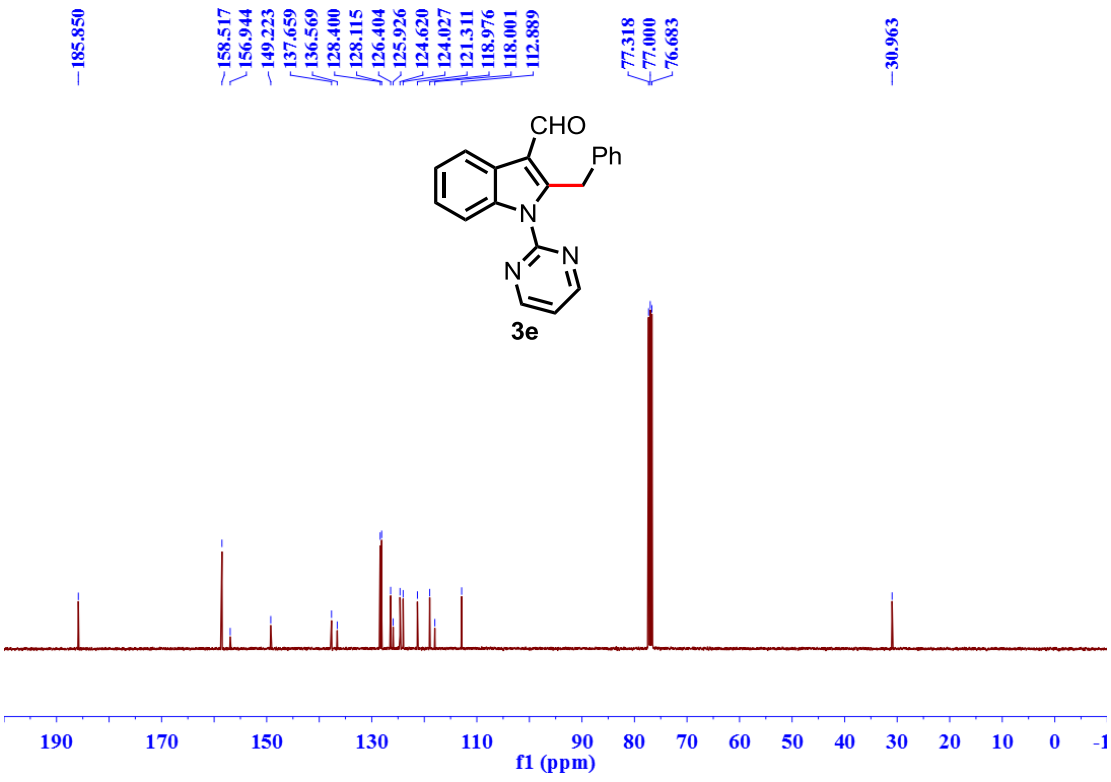


2-benzyl-1-(pyrimidin-2-yl)-1H-indole-3-carbaldehyde (3e)

^{1}H-NMR (400 MHz, $CDCl_3$)

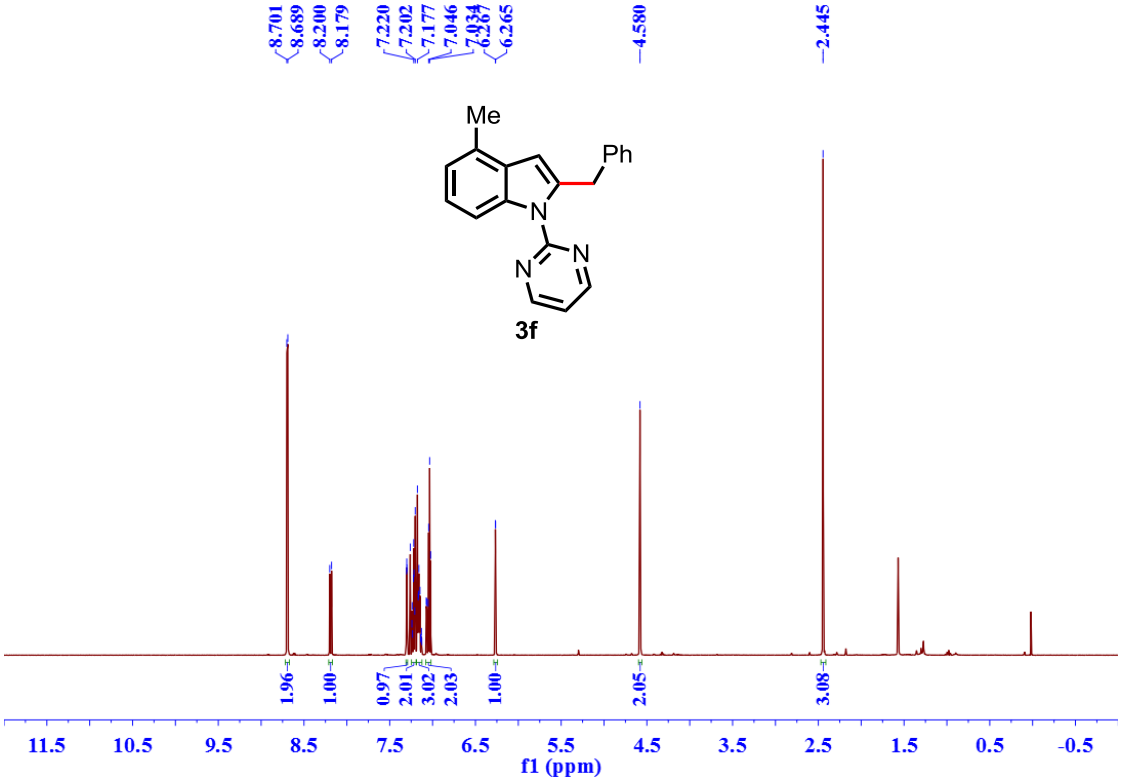


^{13}C-NMR (100 MHz, $CDCl_3$)

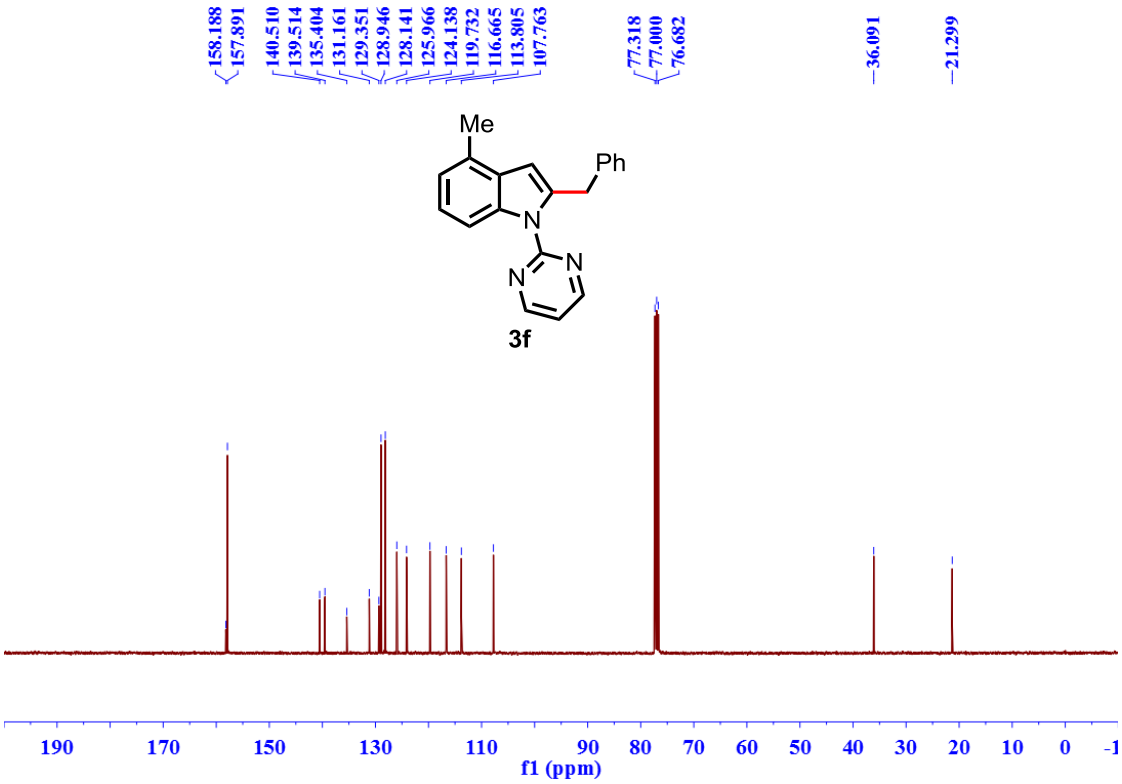


2-benzyl-4-methyl-1-(pyrimidin-2-yl)-1H-indole (3f)

^{1}H-NMR (400 MHz, $CDCl_3$)

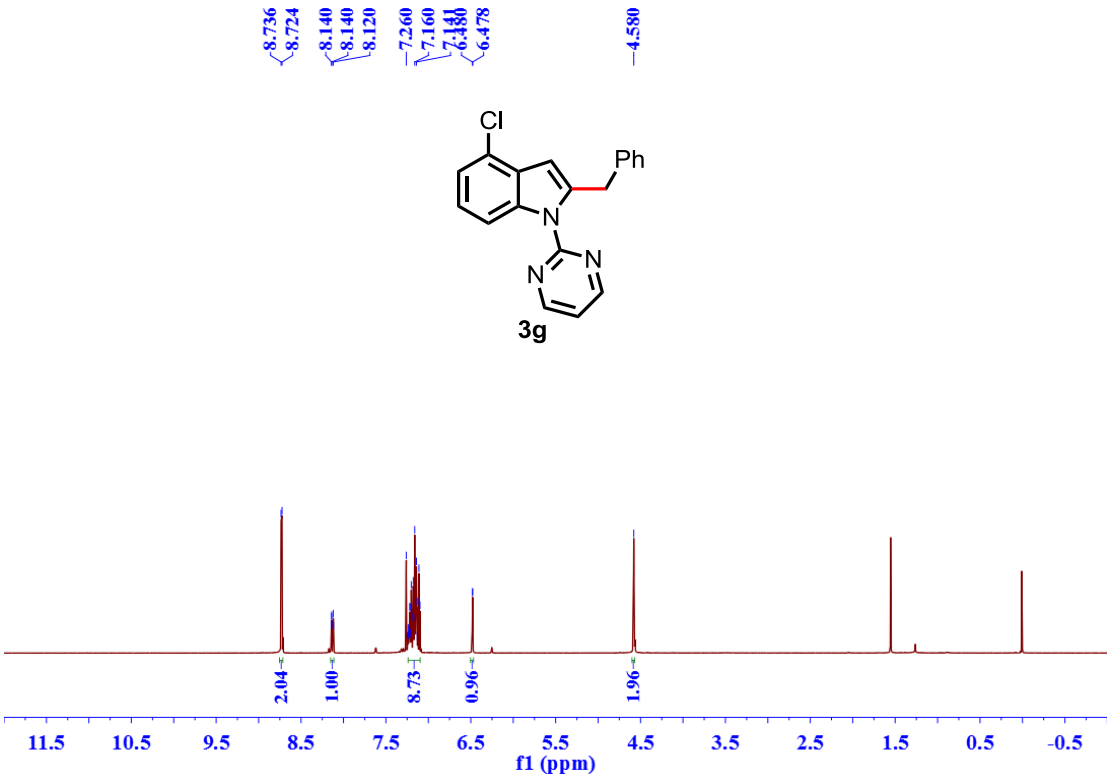


^{13}C-NMR (100 MHz, $CDCl_3$)

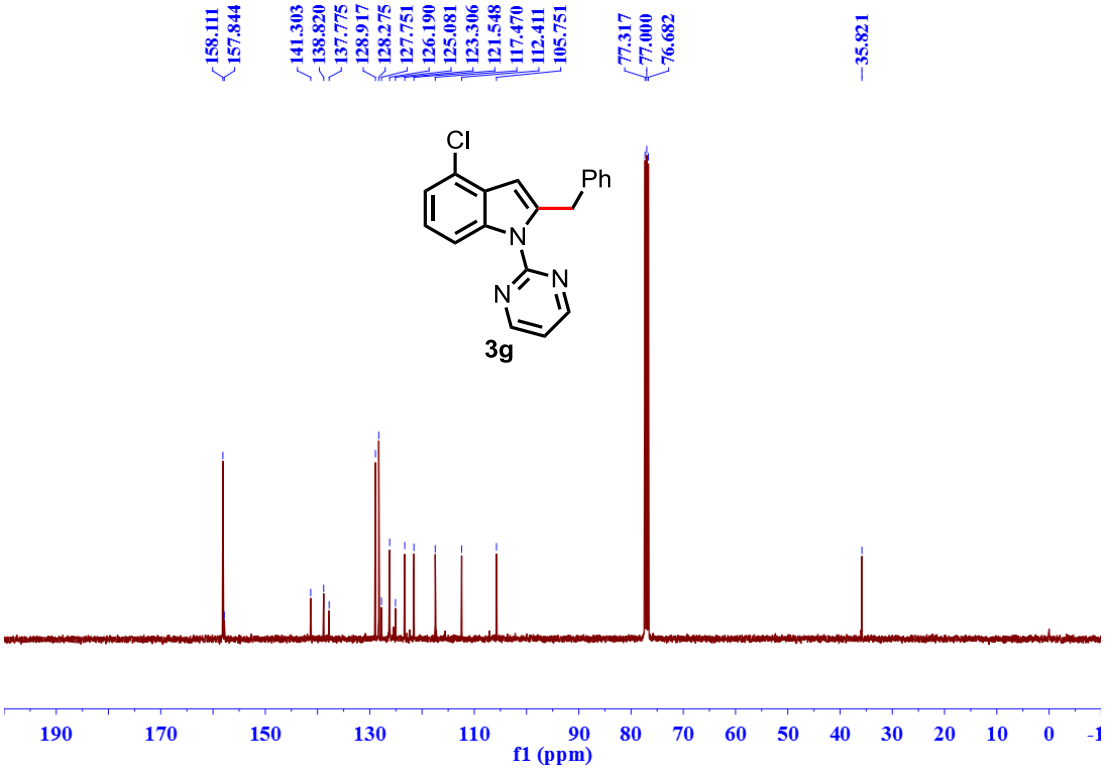


2-benzyl-4-chloro-1-(pyrimidin-2-yl)-1H-indole (3g)

^{1}H-NMR (400 MHz, $CDCl_3$)

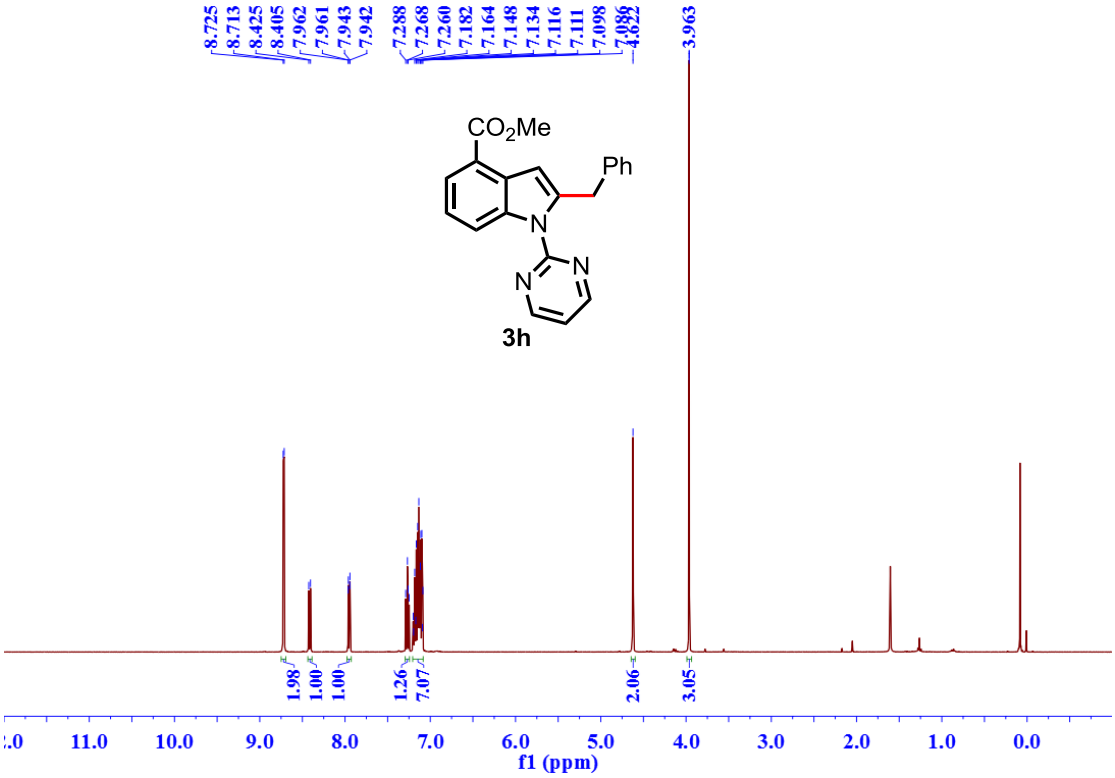


^{13}C-NMR (100 MHz, $CDCl_3$)

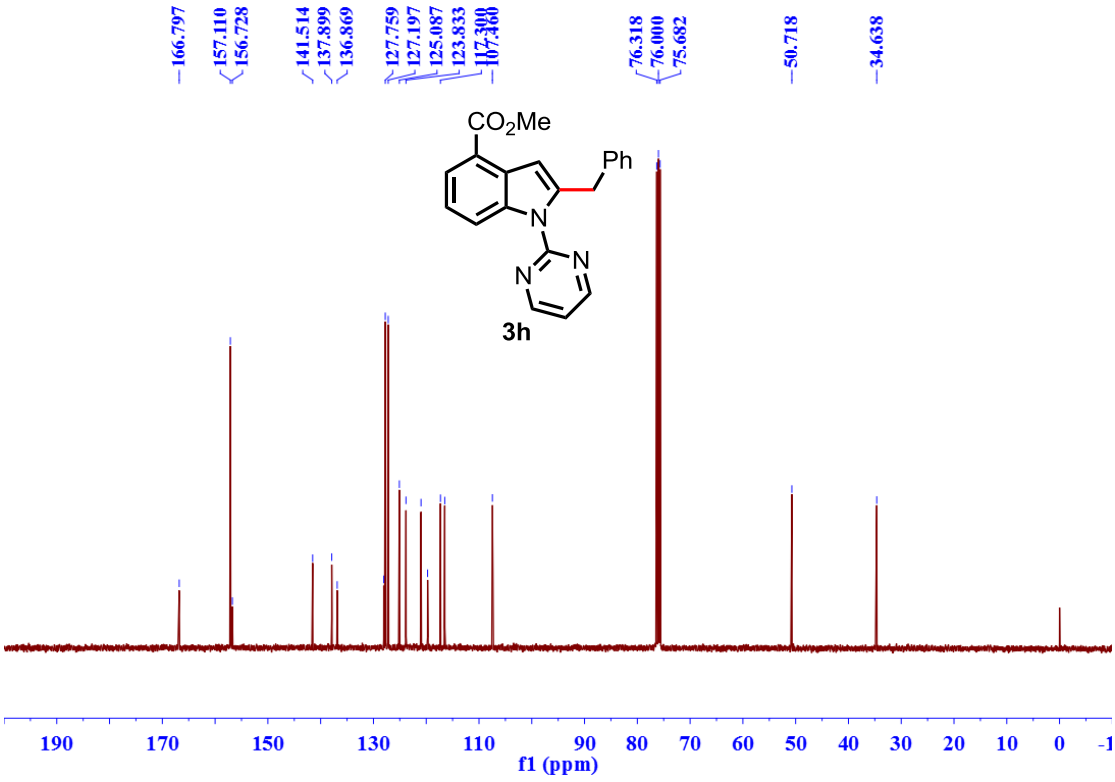


methyl 2-benzyl-1-(pyrimidin-2-yl)-1H-indole-4-carboxylate (3h)

^{1}H-NMR (400 MHz, $CDCl_3$)

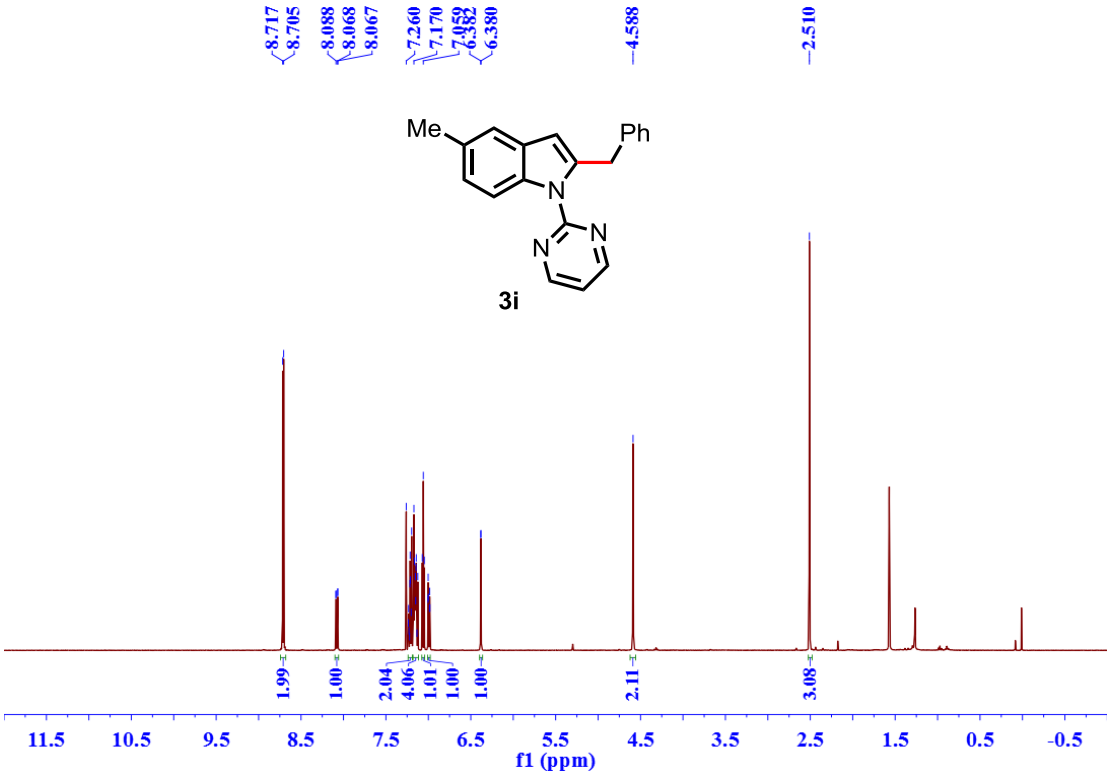


^{13}C-NMR (100 MHz, $CDCl_3$)

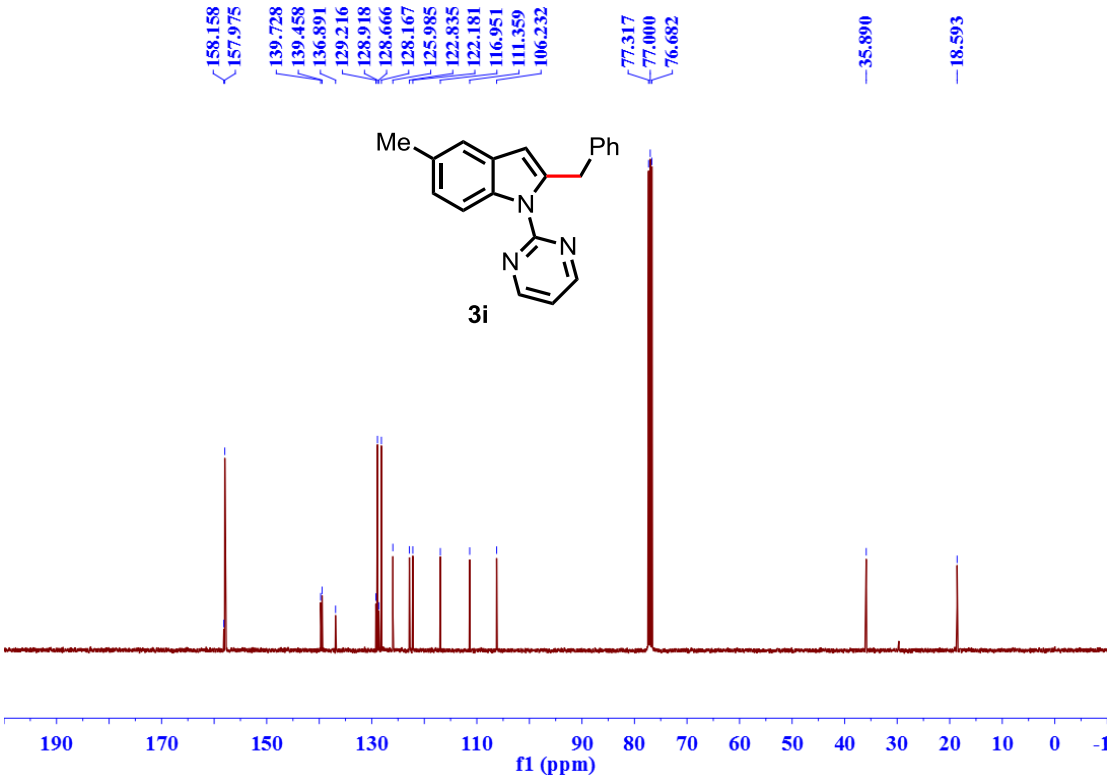


2-benzyl-5-methyl-1-(pyrimidin-2-yl)-1H-indole (3i)

^{1}H-NMR (400 MHz, $CDCl_3$)

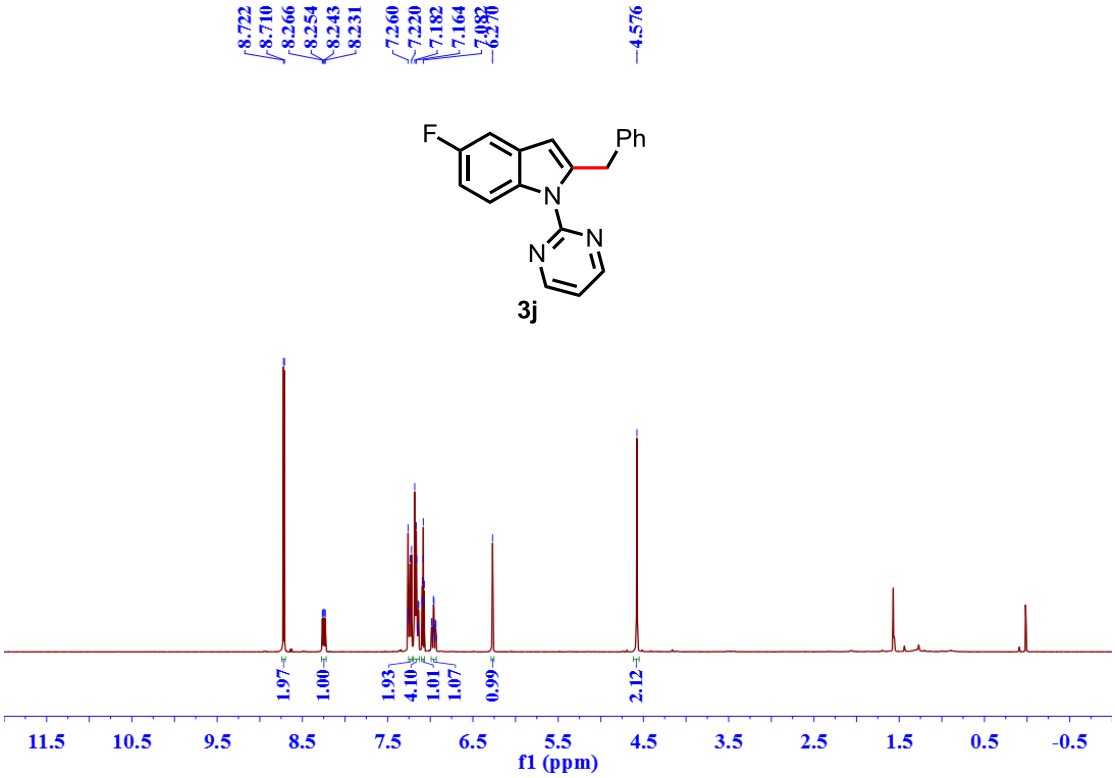


^{13}C-NMR (100 MHz, $CDCl_3$)

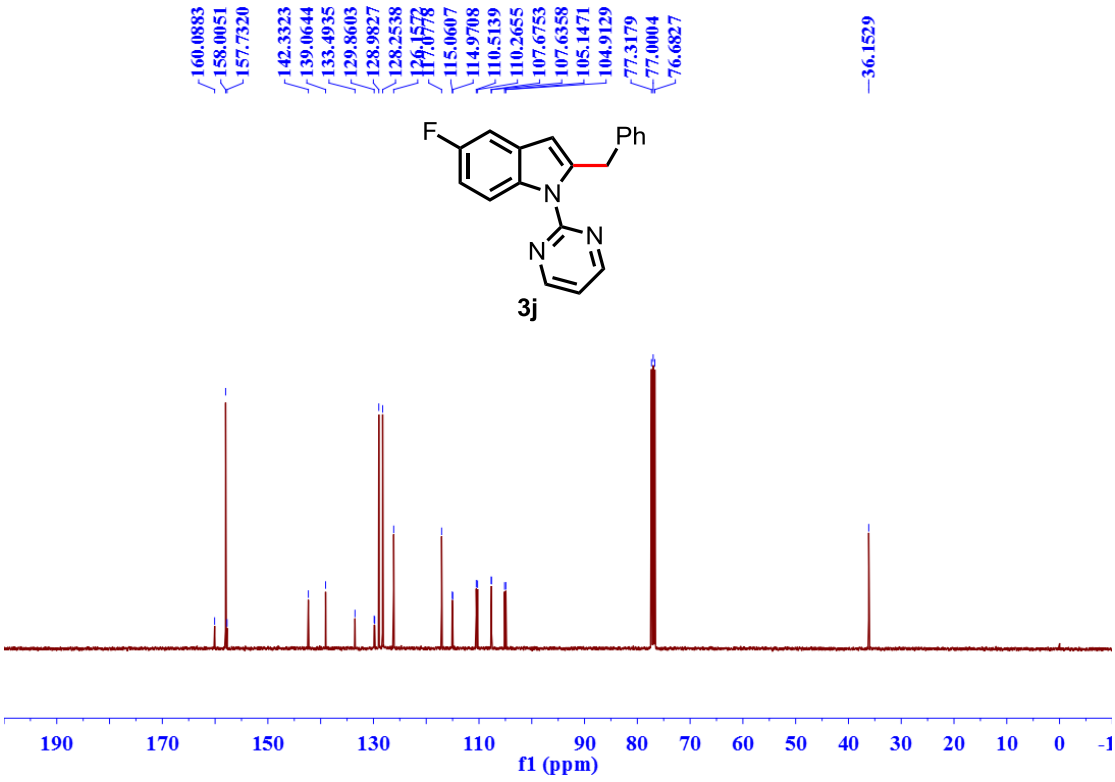


2-benzyl-5-fluoro-1-(pyrimidin-2-yl)-1H-indole (3j)

^{1}H-NMR (400 MHz, $CDCl_3$)

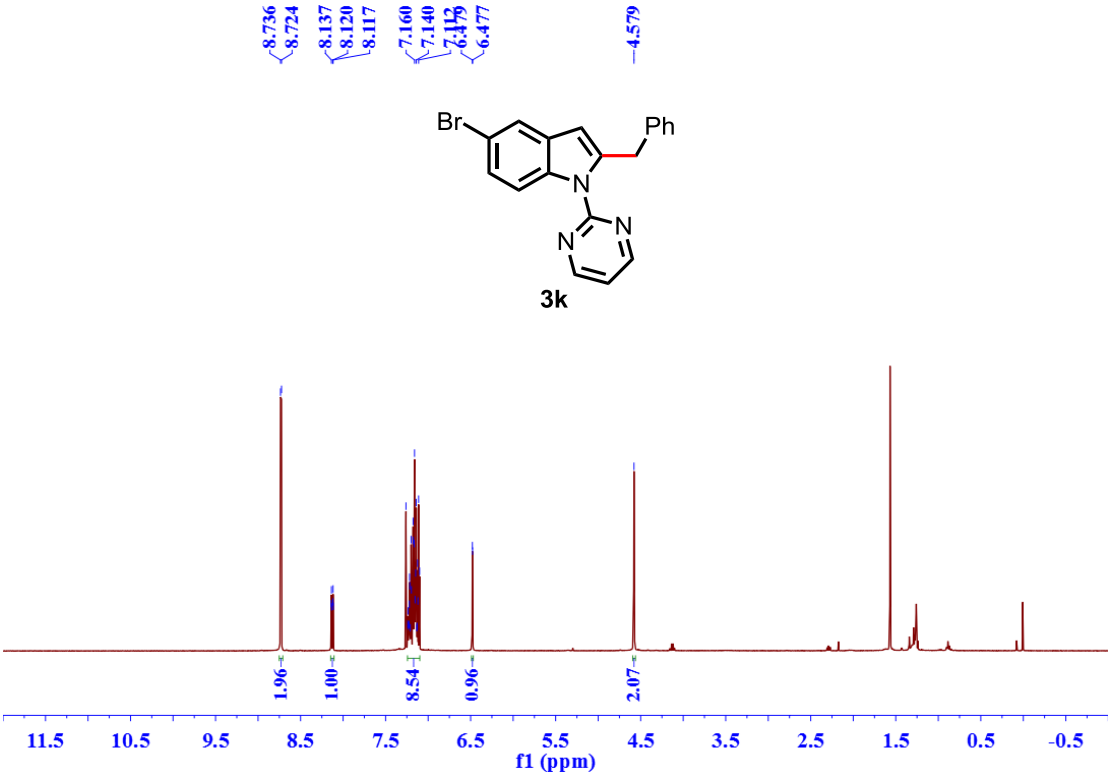


^{13}C-NMR (100 MHz, $CDCl_3$)

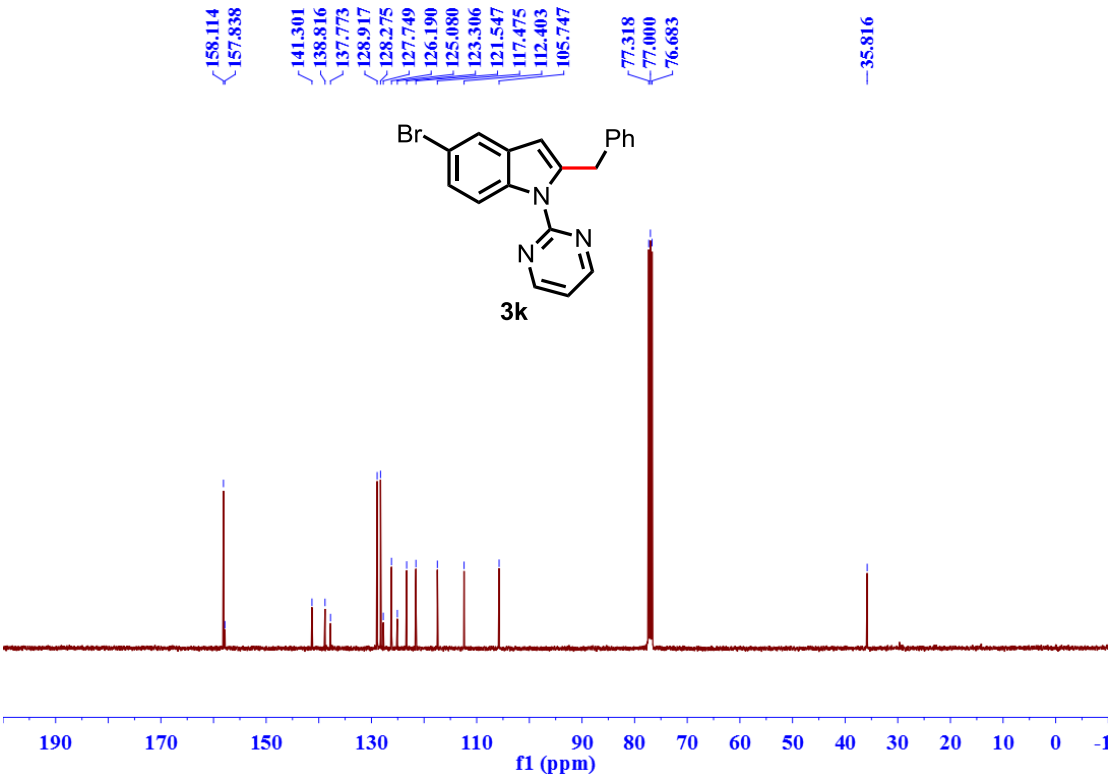


2-benzyl-5-bromo-1-(pyrimidin-2-yl)-1H-indole (3k)

^{1}H-NMR (400 MHz, $CDCl_3$)

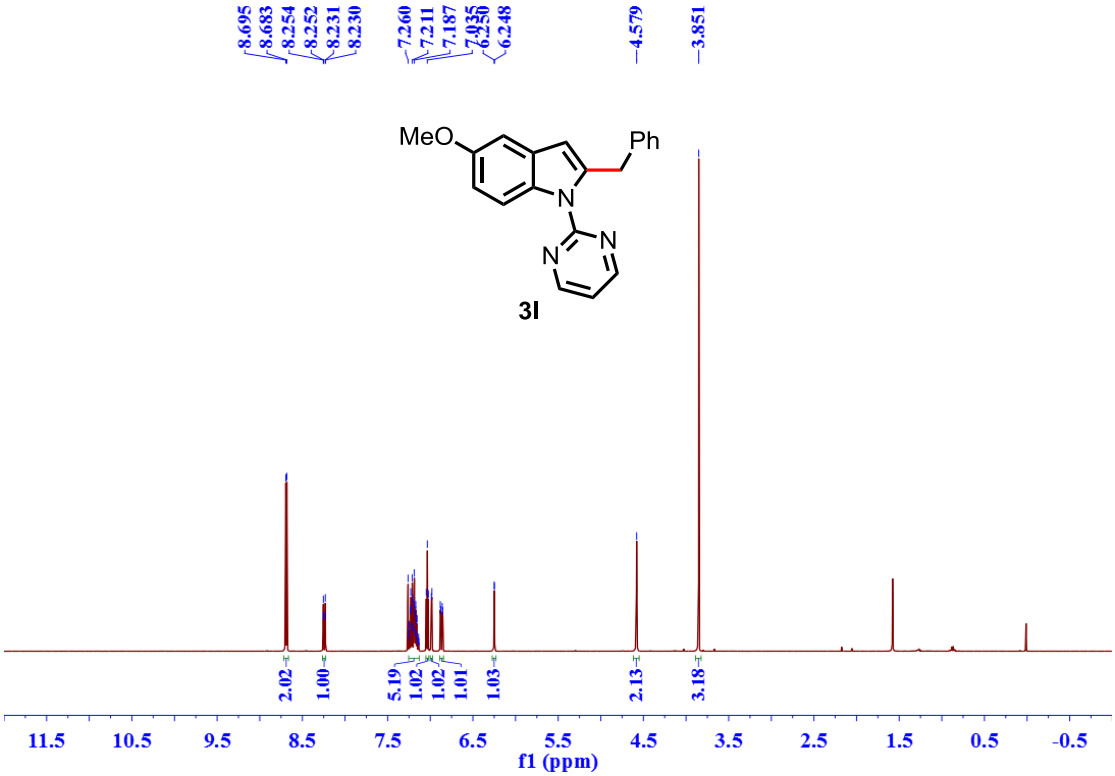


^{13}C-NMR (100 MHz, $CDCl_3$)

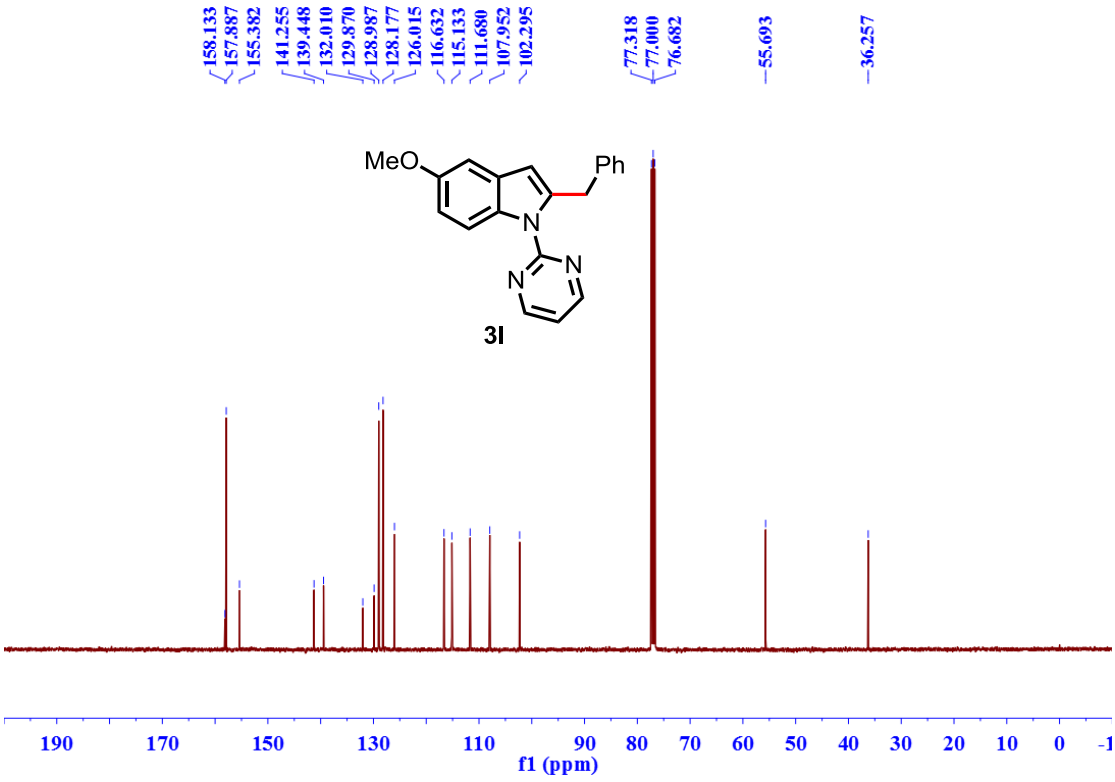


2-benzyl-5-methoxy-1-(pyrimidin-2-yl)-1H-indole (3l)

^{1}H-NMR (400 MHz, $CDCl_3$)

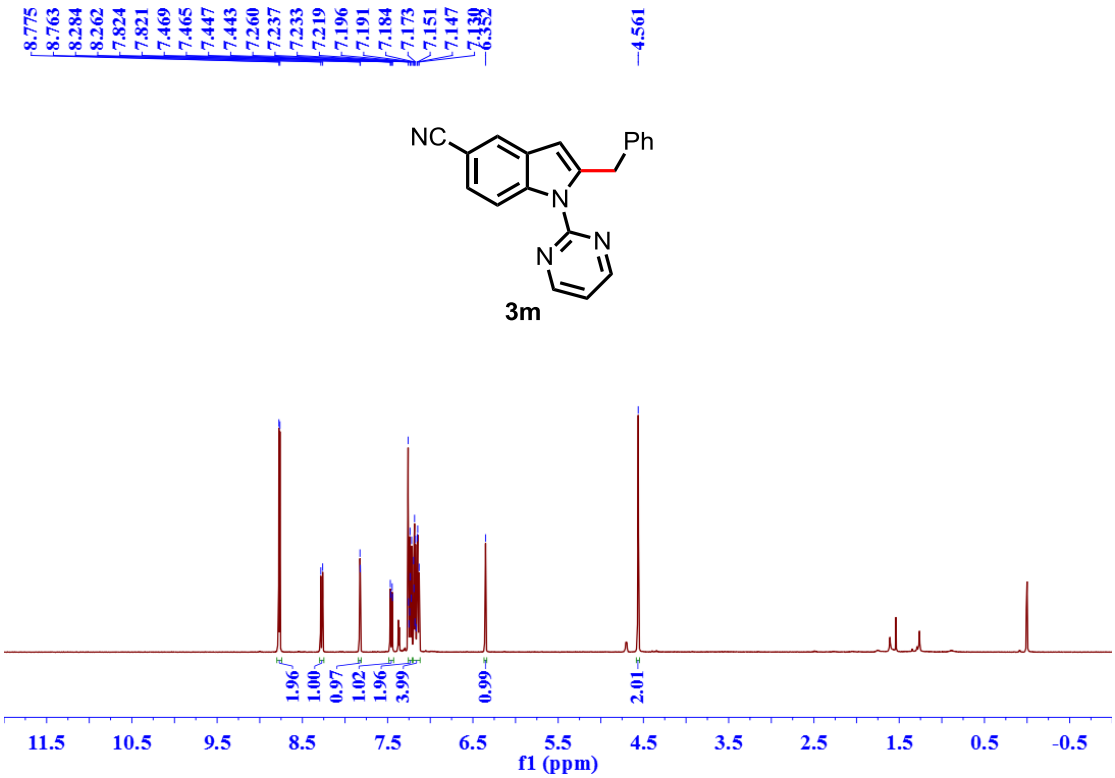


^{13}C-NMR (100 MHz, $CDCl_3$)

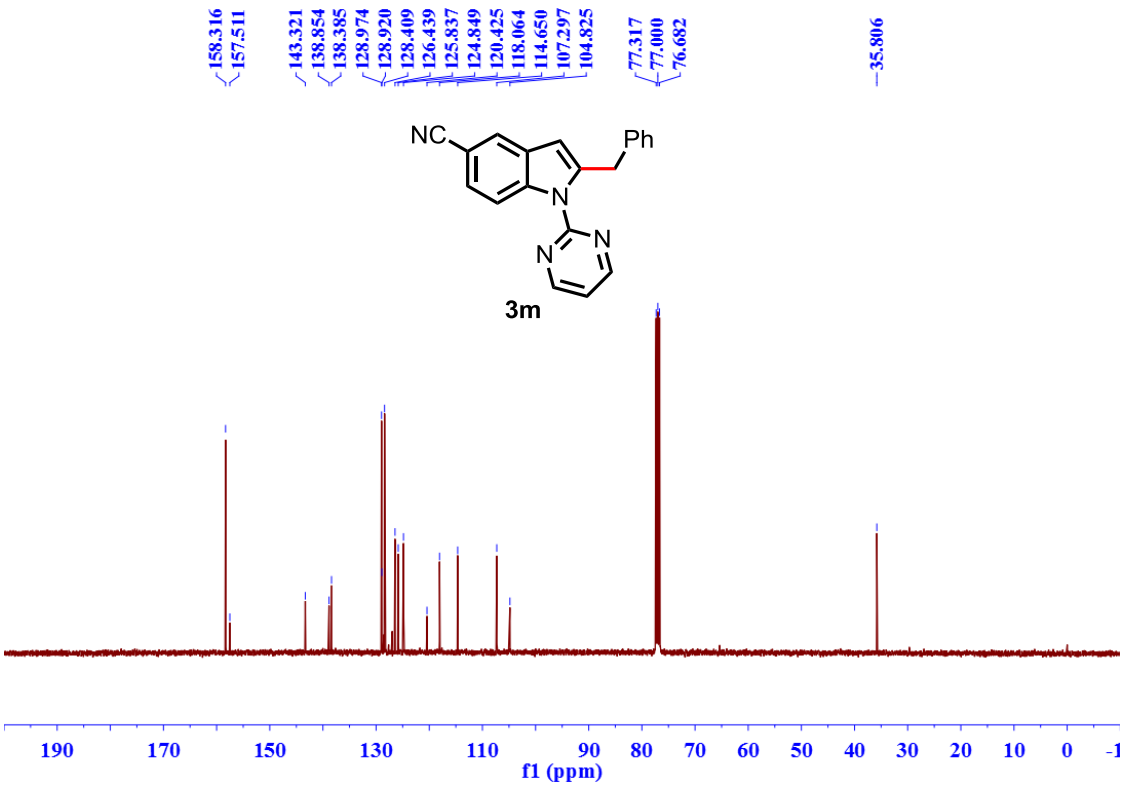


2-benzyl-1-(pyrimidin-2-yl)-1H-indole-5-carbonitrile (3m)

^{1}H-NMR (400 MHz, $CDCl_3$)

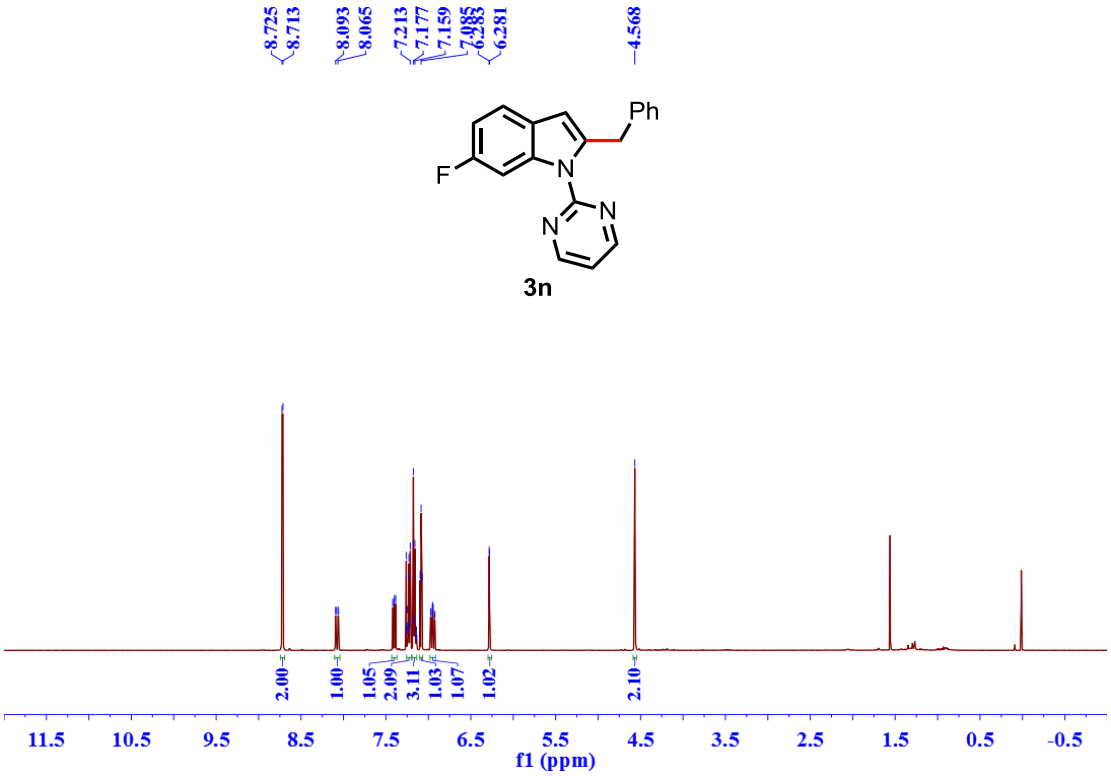


^{13}C-NMR (100 MHz, $CDCl_3$)

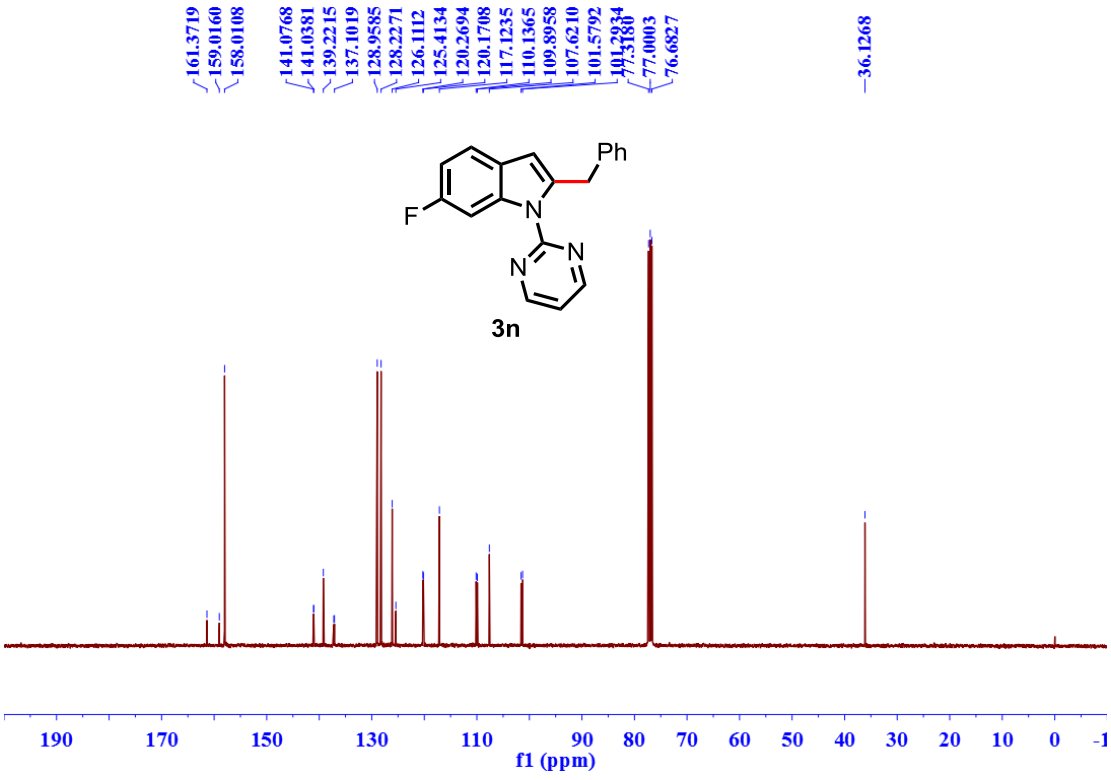


2-benzyl-6-fluoro-1-(pyrimidin-2-yl)-1H-indole (3n)

^{1}H-NMR (400 MHz, $CDCl_3$)

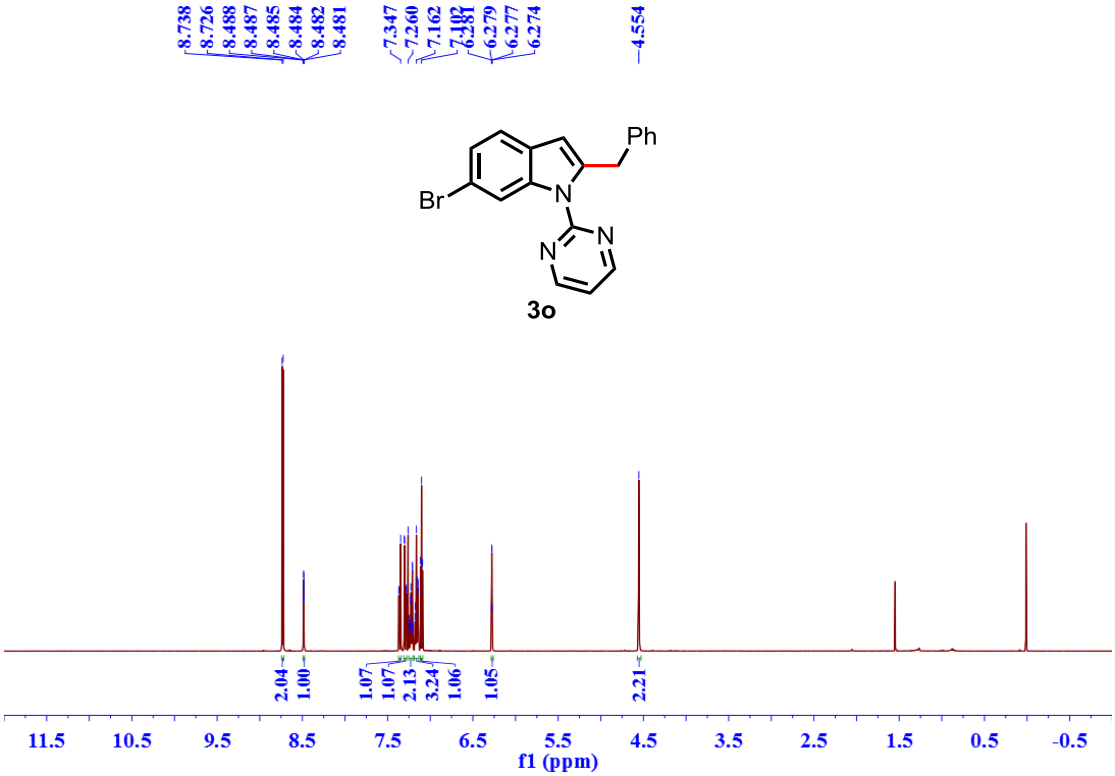


^{13}C-NMR (100 MHz, $CDCl_3$)

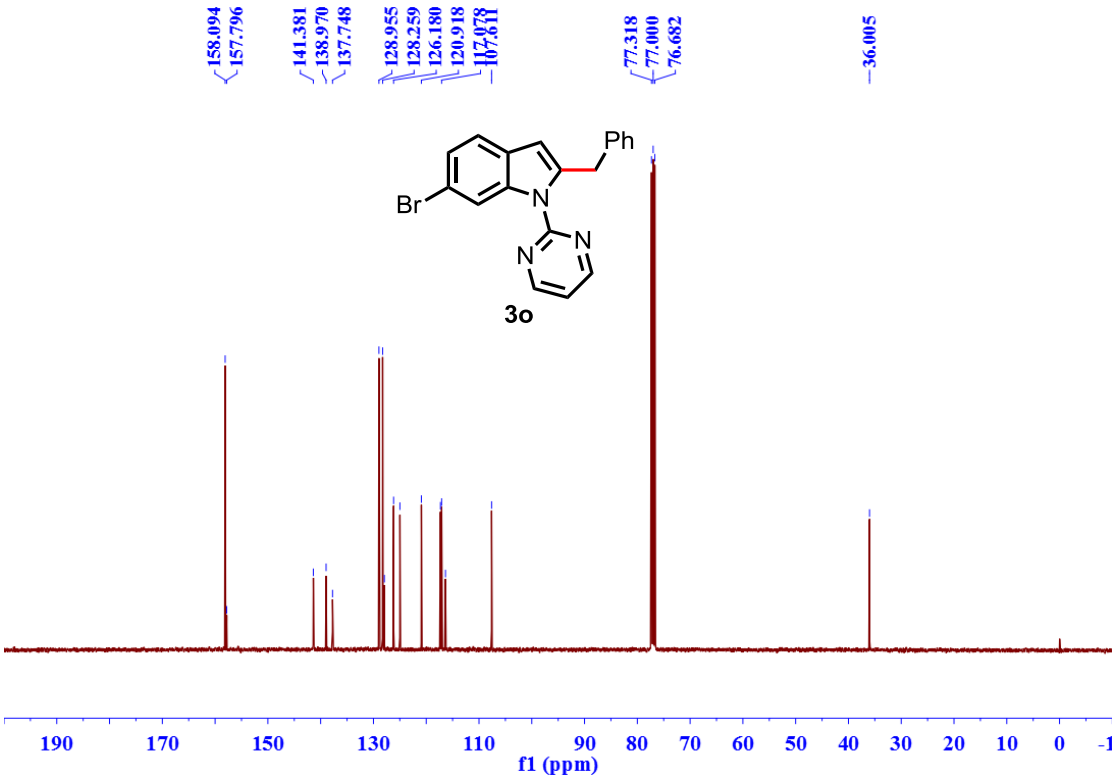


2-benzyl-6-bromo-1-(pyrimidin-2-yl)-1H-indole (3o)

^{1}H-NMR (400 MHz, $CDCl_3$)

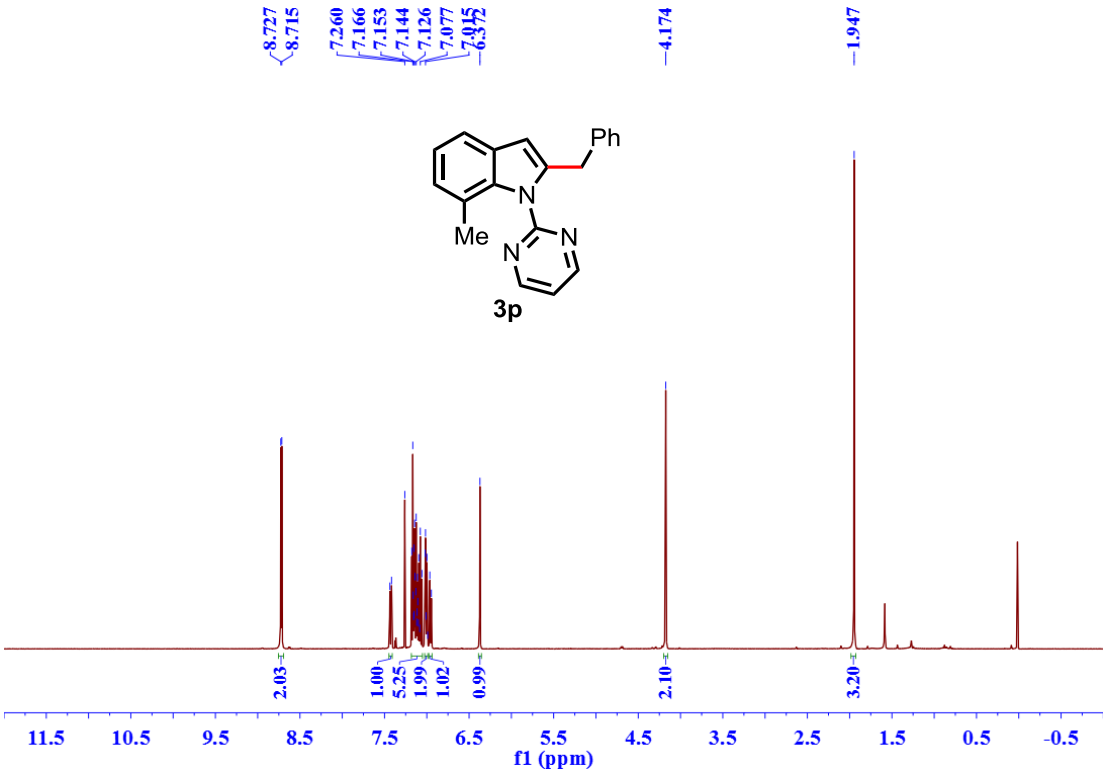


^{13}C-NMR (100 MHz, $CDCl_3$)

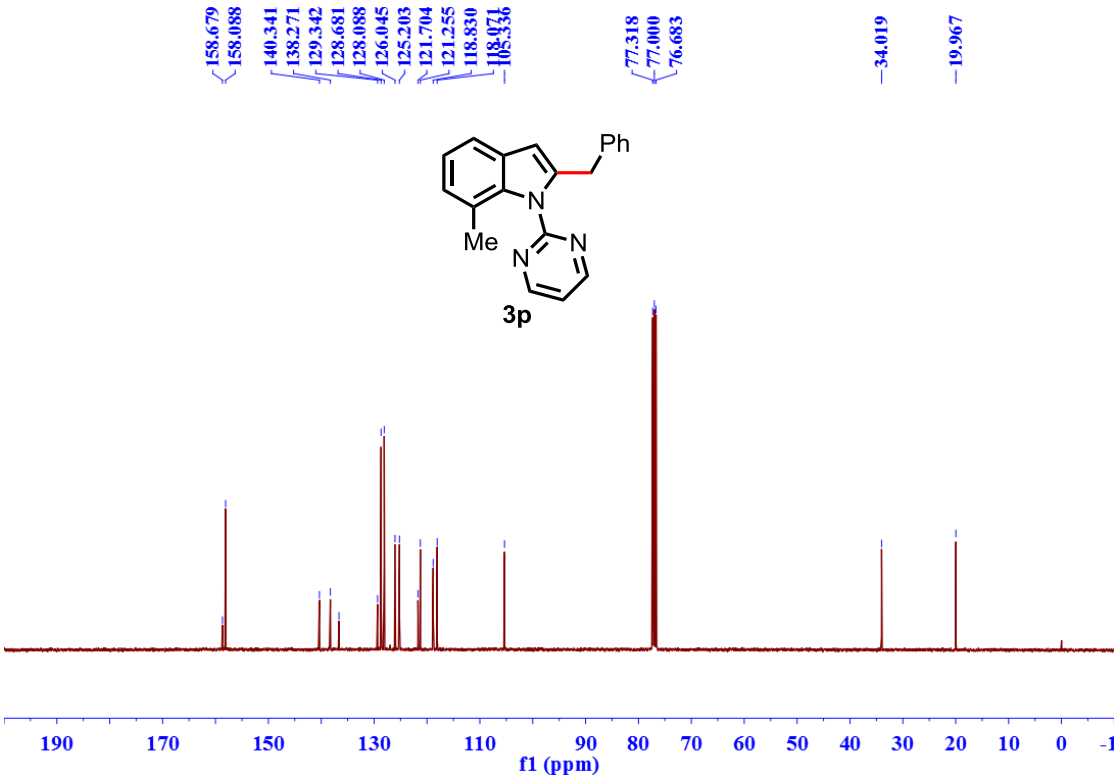


2-benzyl-7-methyl-1-(pyrimidin-2-yl)-1H-indole (3p)

^{1}H-NMR (400 MHz, $CDCl_3$)

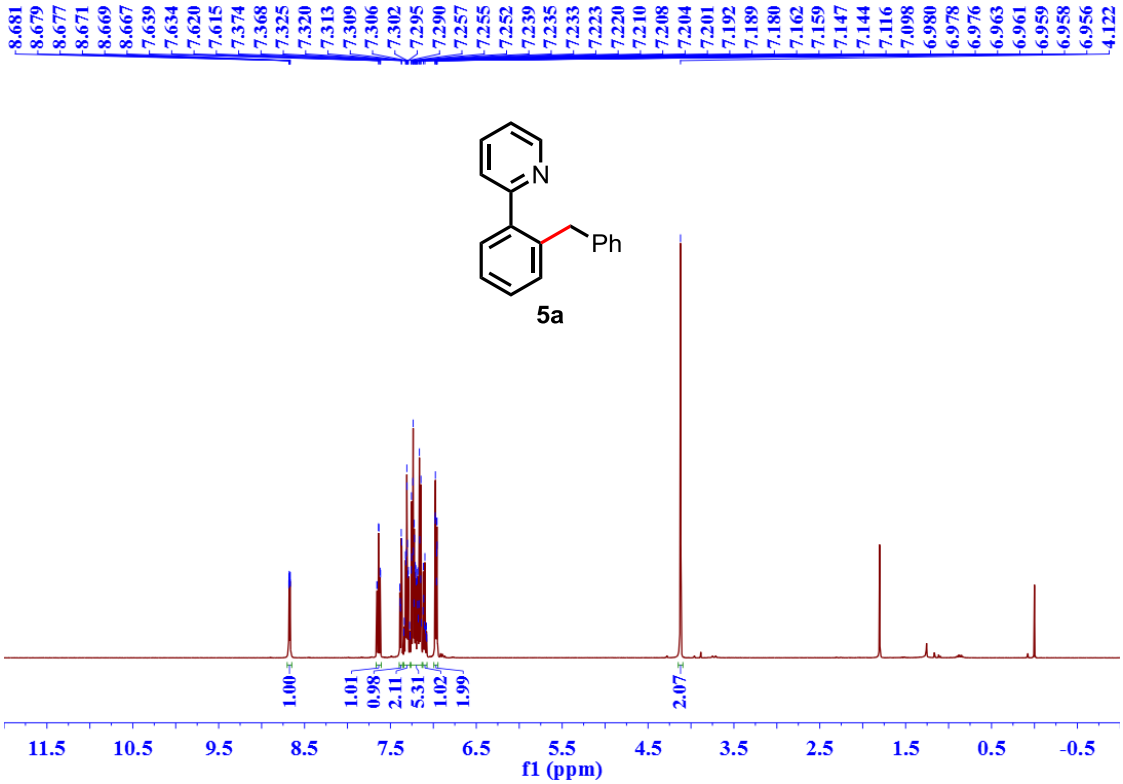


^{13}C-NMR (100 MHz, $CDCl_3$)

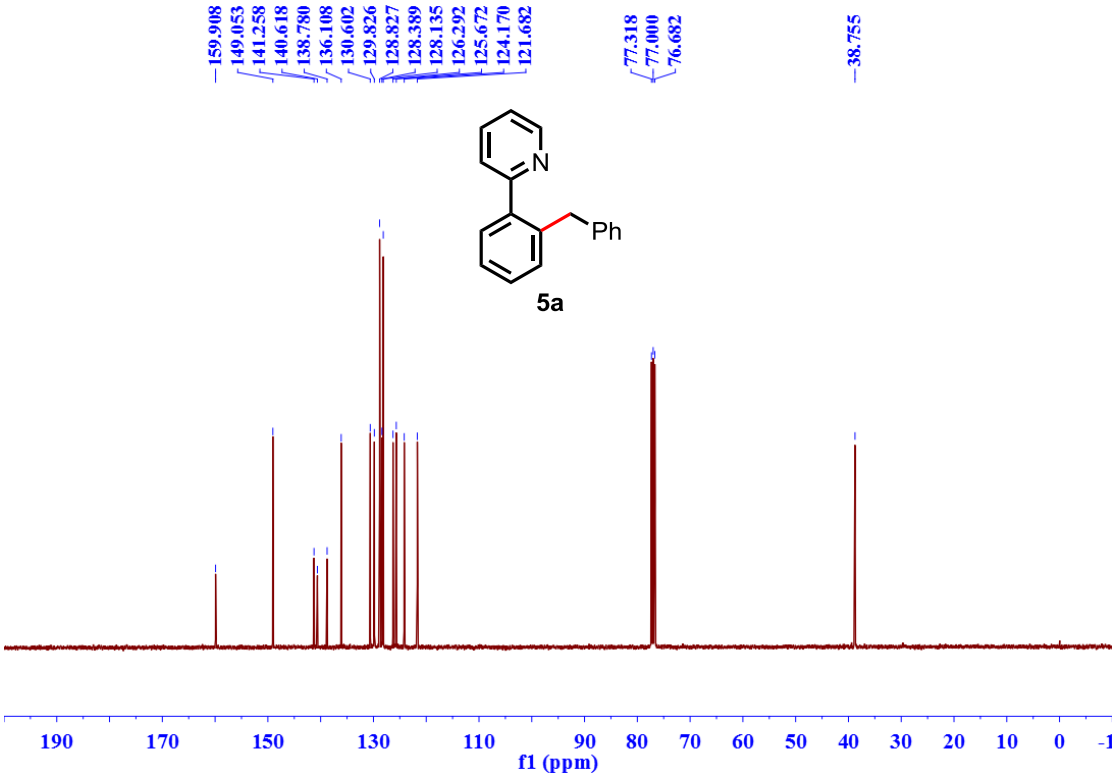


2-(2-benzylphenyl)pyridine (5a)

^{1}H-NMR (400 MHz, $CDCl_3$)

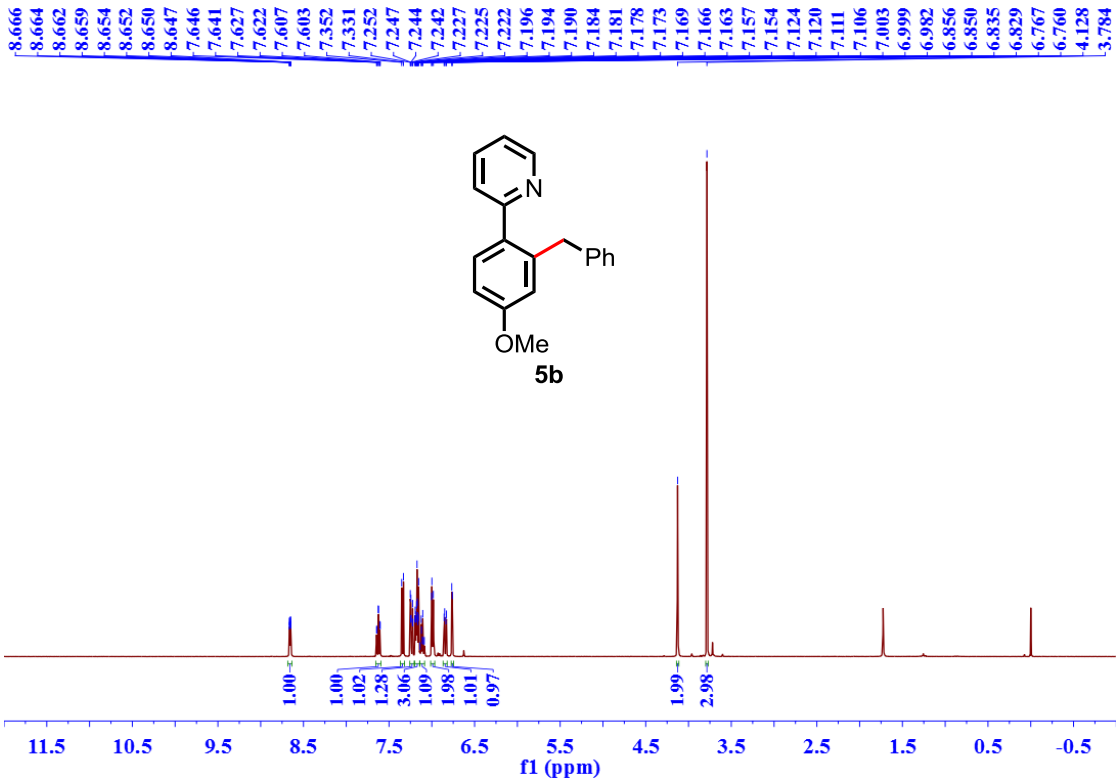


^{13}C-NMR (100 MHz, $CDCl_3$)

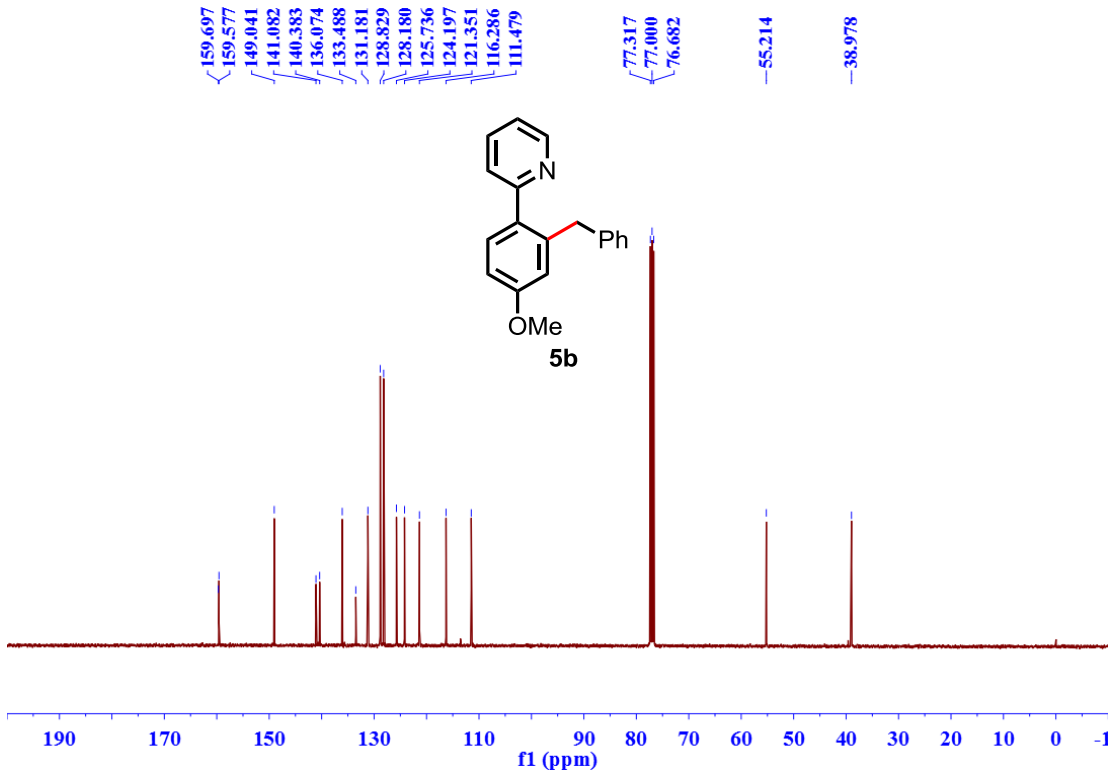


2-(2-benzyl-4-methoxyphenyl)pyridine (5b)

^{1}H-NMR (400 MHz, $CDCl_3$)

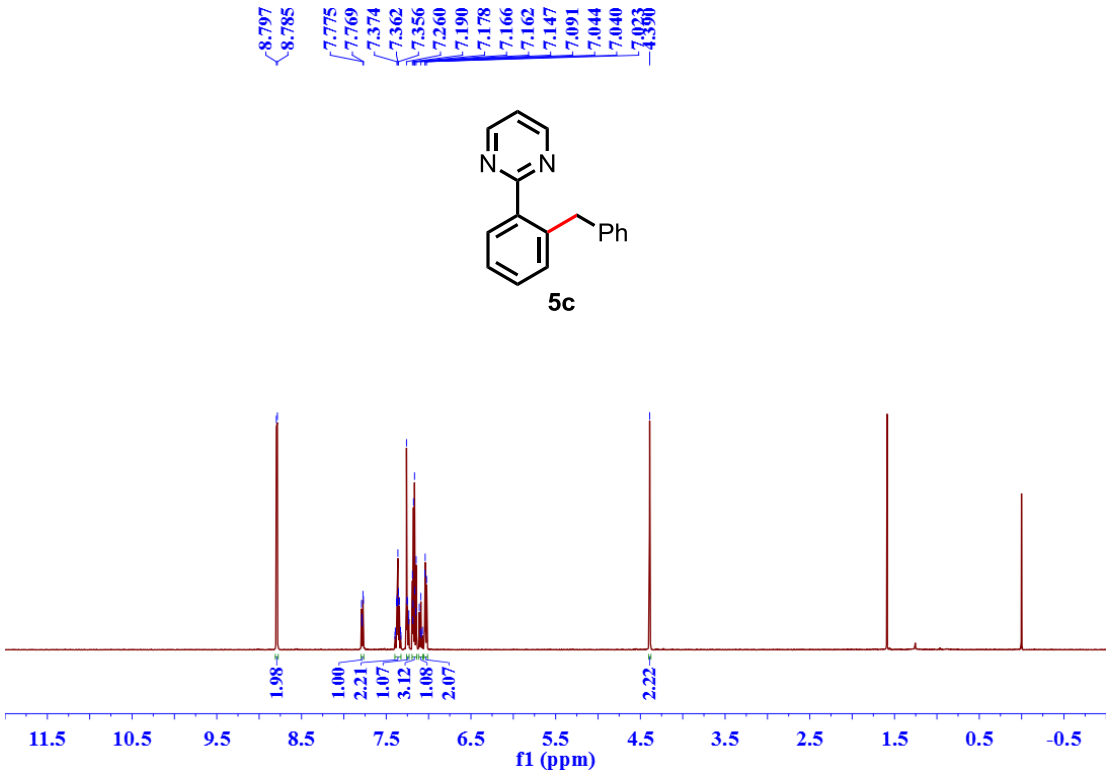


^{13}C-NMR (100 MHz, $CDCl_3$)

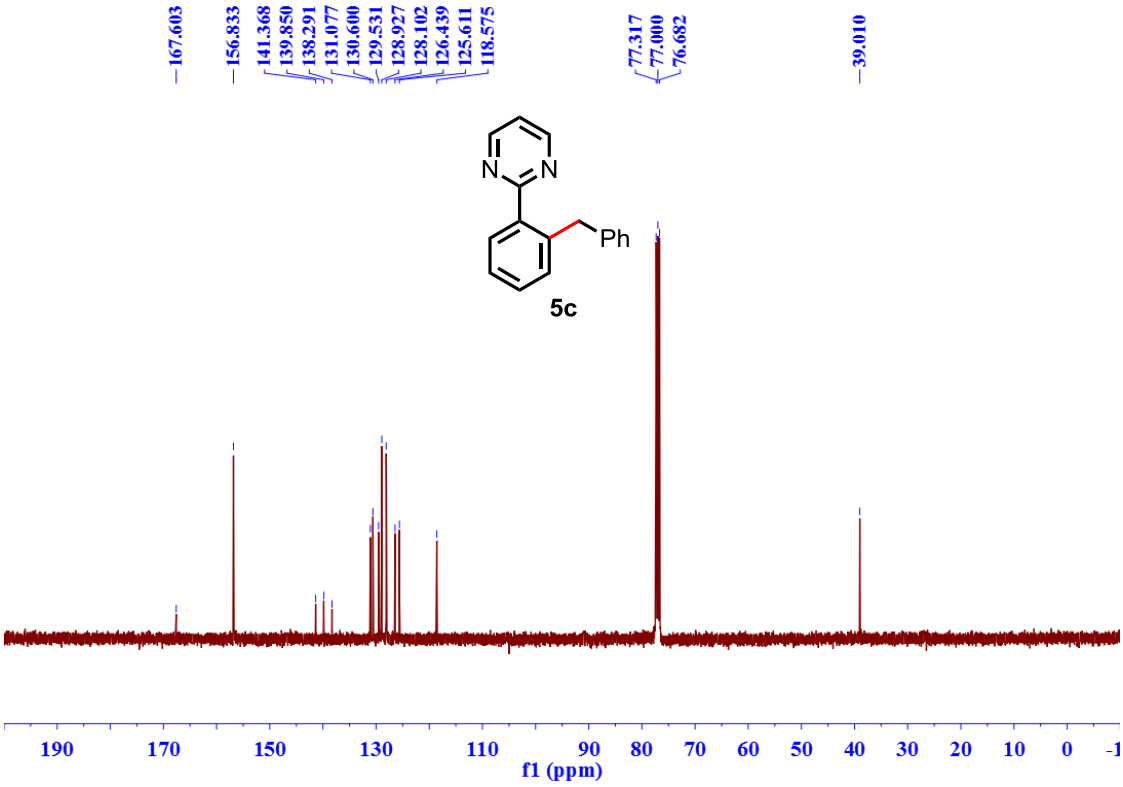


2-(2-benzylphenyl)pyrimidine (5c)

^{1}H-NMR (400 MHz, $CDCl_3$)

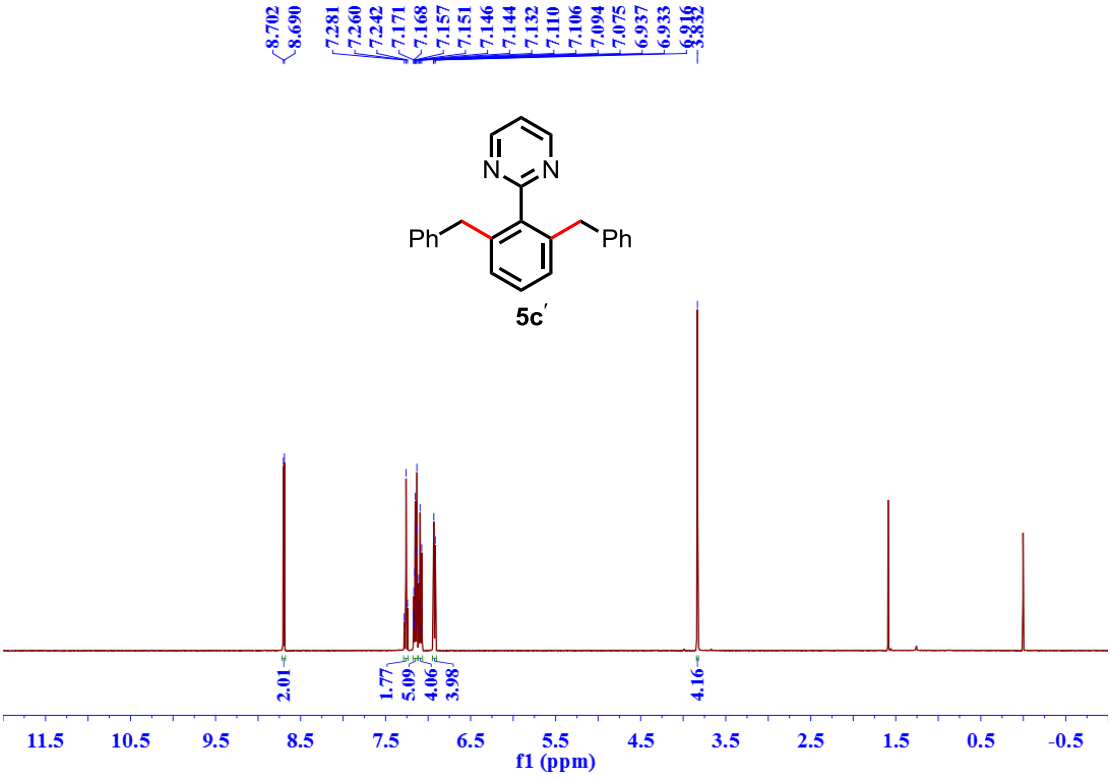


^{13}C-NMR (100 MHz, $CDCl_3$)

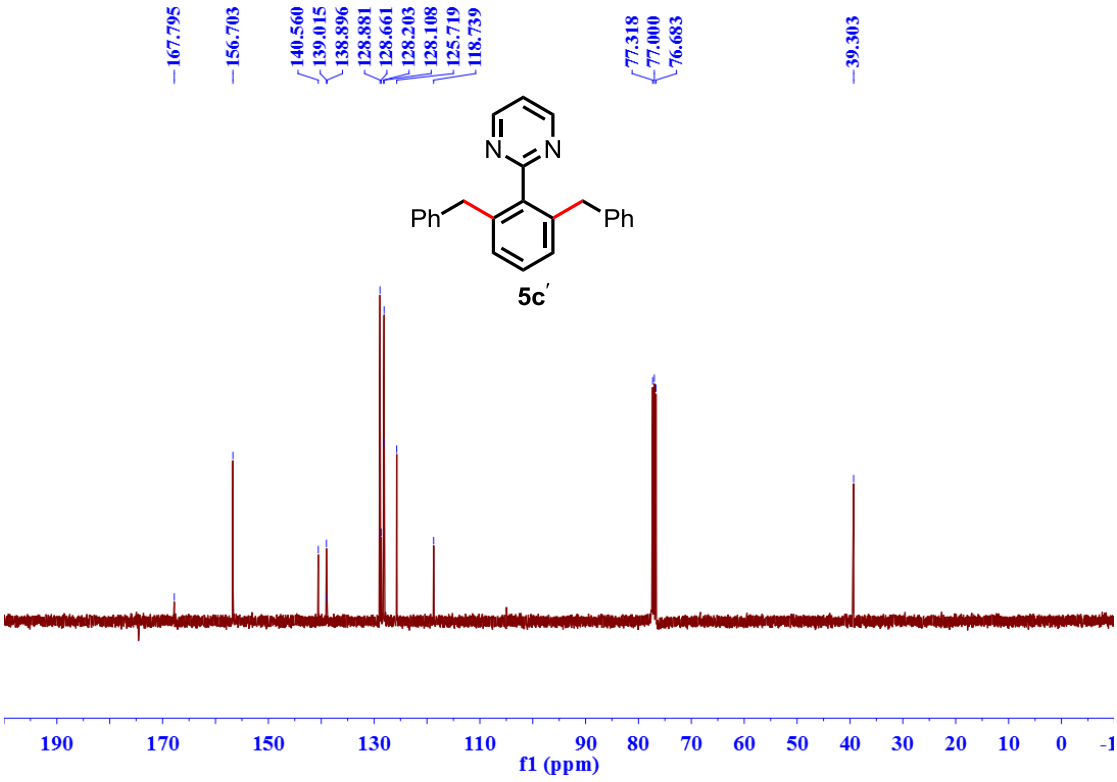


2-(2,6-dibenzylphenyl)pyrimidine (5c´)

^{1}H-NMR (400 MHz, $CDCl_3$)

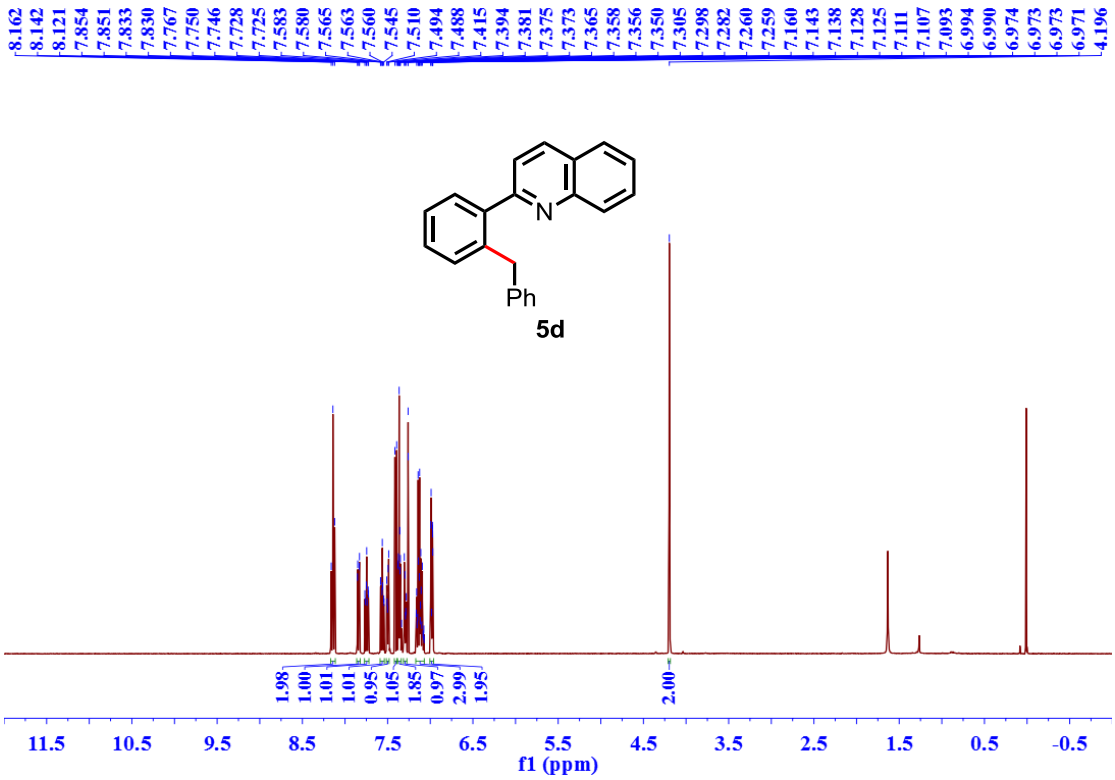


^{13}C-NMR (100 MHz, $CDCl_3$)

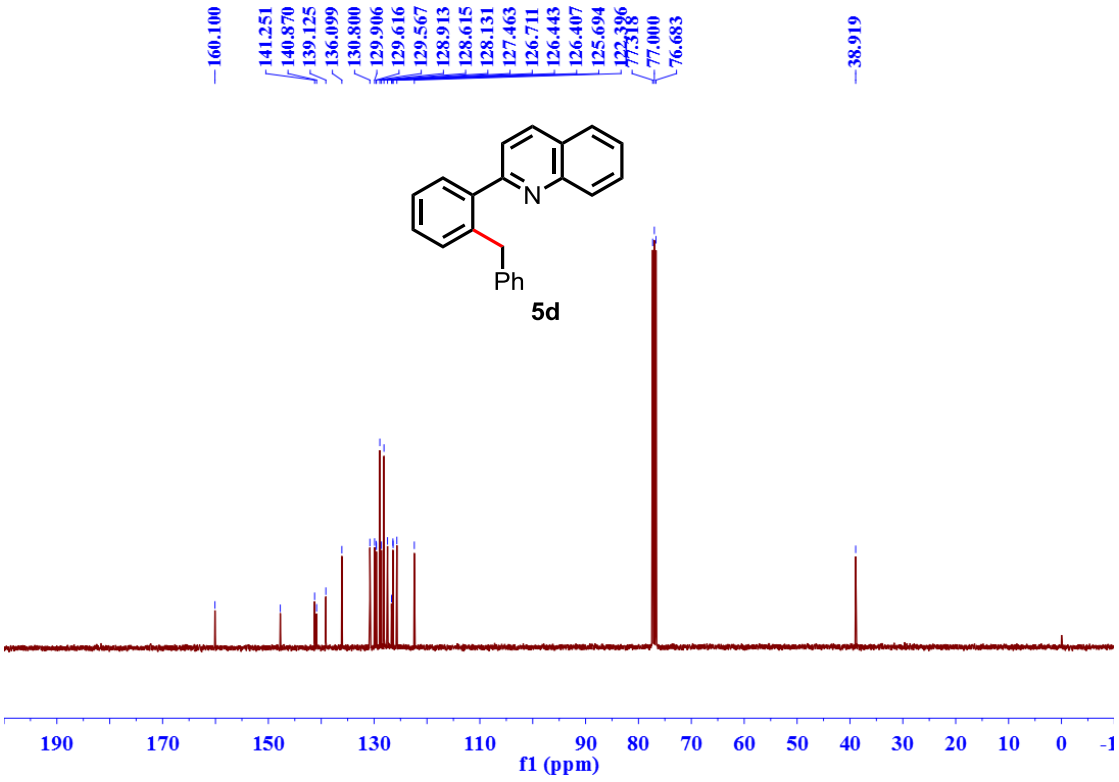


2-(2-benzylphenyl)quinoline (5d)

^{1}H-NMR (400 MHz, $CDCl_3$)

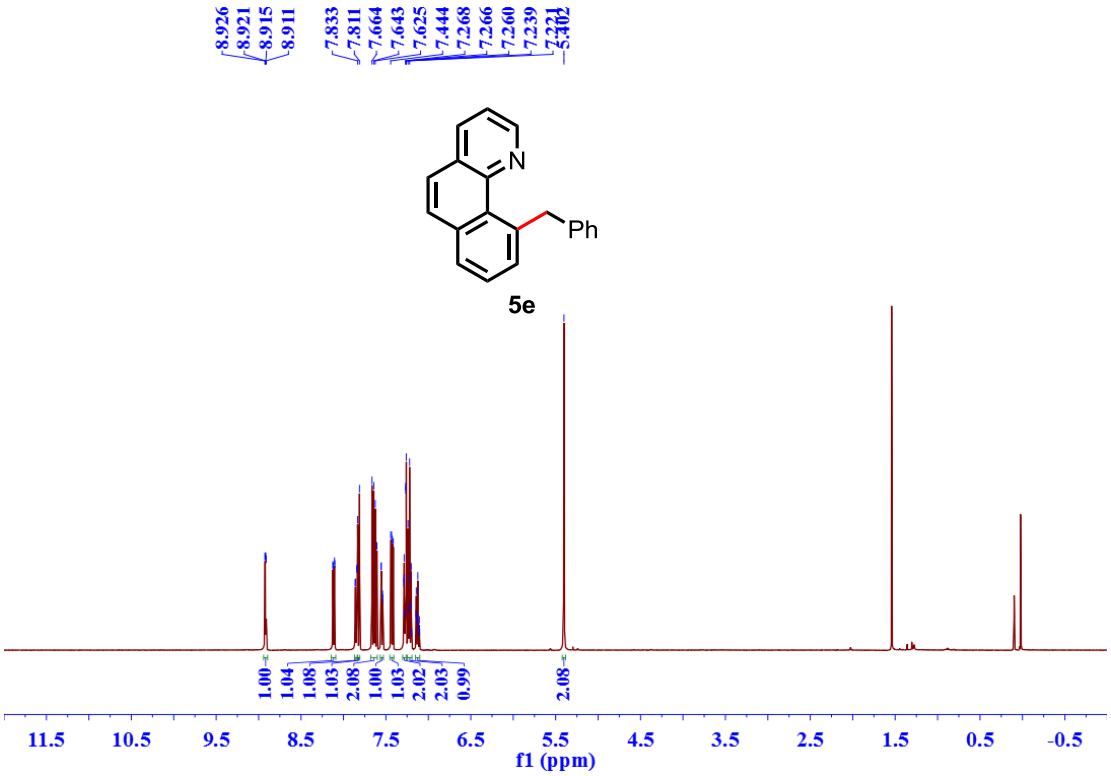


^{13}C-NMR (100 MHz, $CDCl_3$)

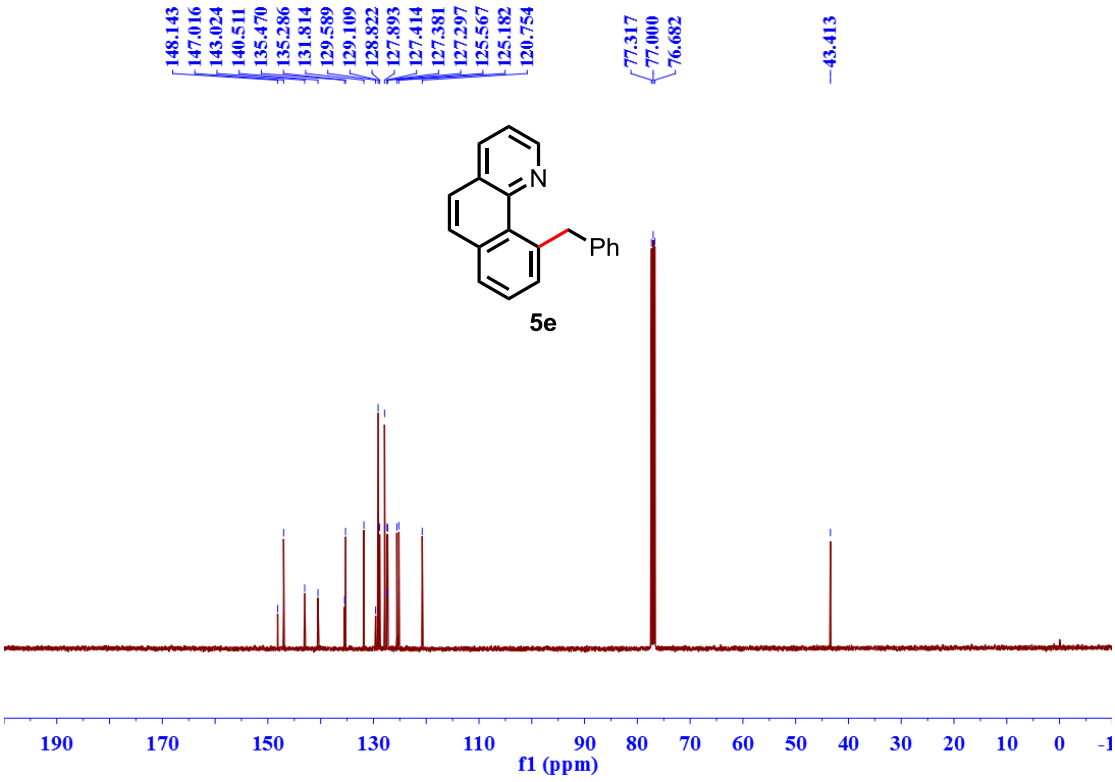


10-benzylbenzo[*h*]quinoline (5e)

^{1}H-NMR (400 MHz, $CDCl_3$)

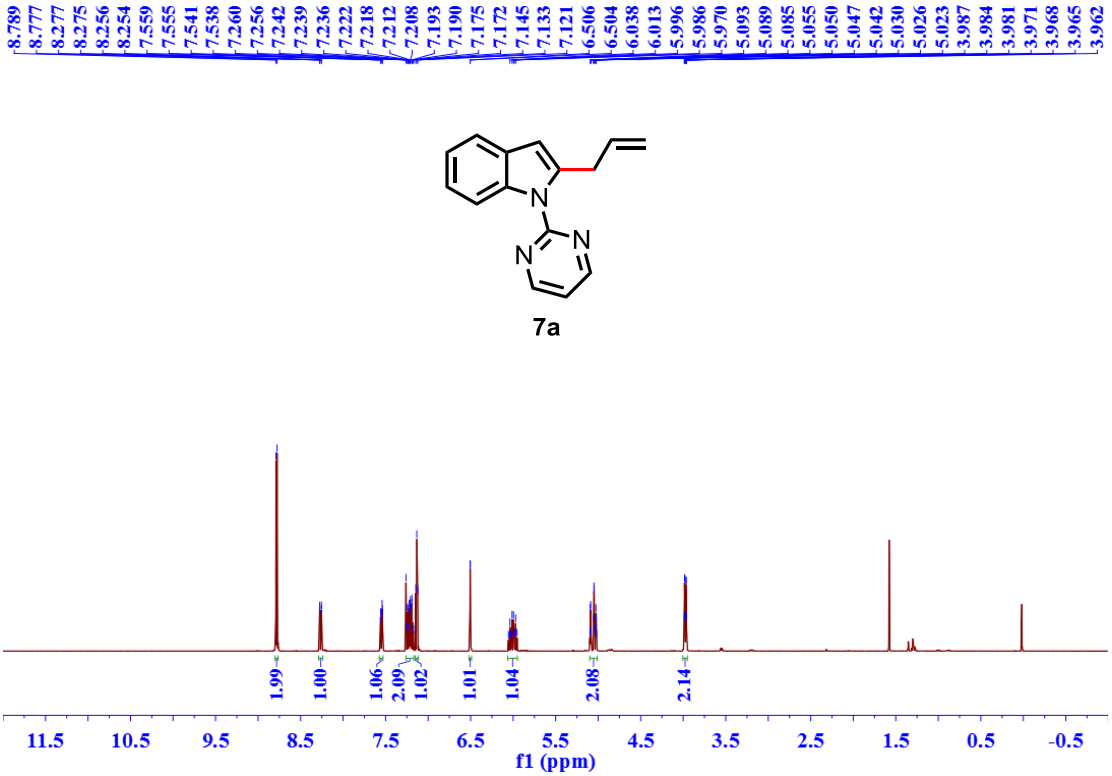


^{13}C-NMR (100 MHz, $CDCl_3$)

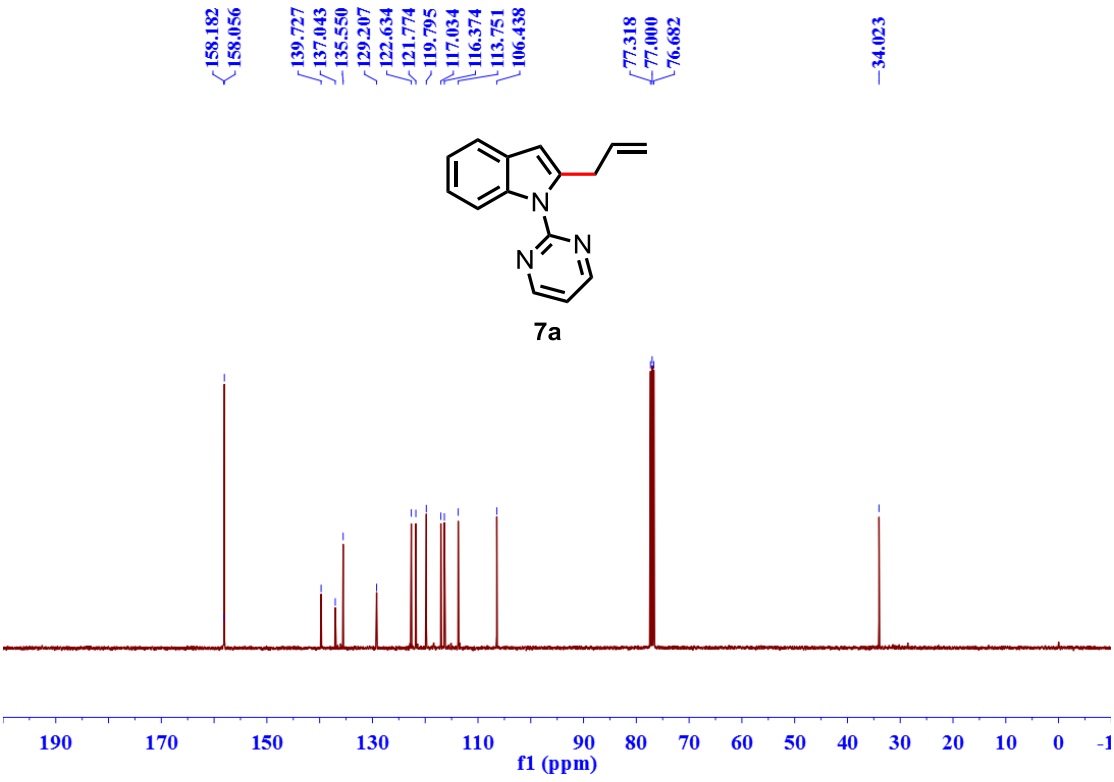


2-allyl-1-(pyrimidin-2-yl)-1H-indole (7a)

^{1}H-NMR (400 MHz, $CDCl_3$)

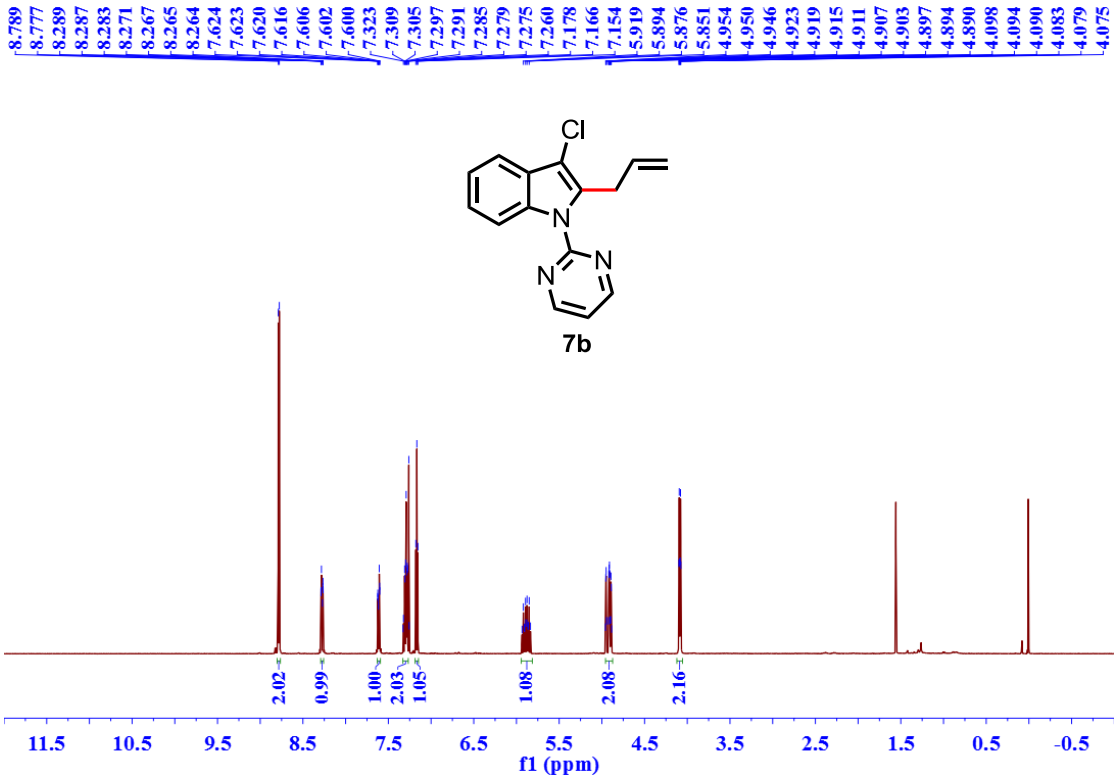


^{13}C-NMR (100 MHz, $CDCl_3$)

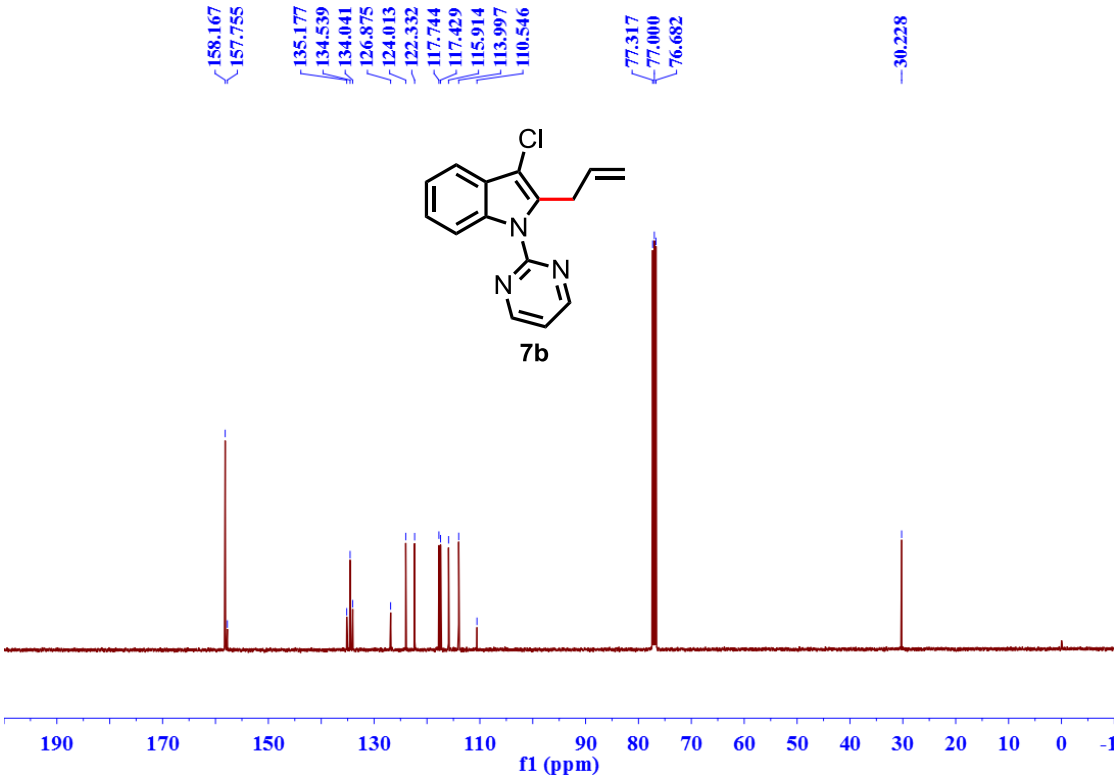


2-allyl-3-chloro-1-(pyrimidin-2-yl)-1H-indole (7b)

^{1}H-NMR (400 MHz, $CDCl_3$)

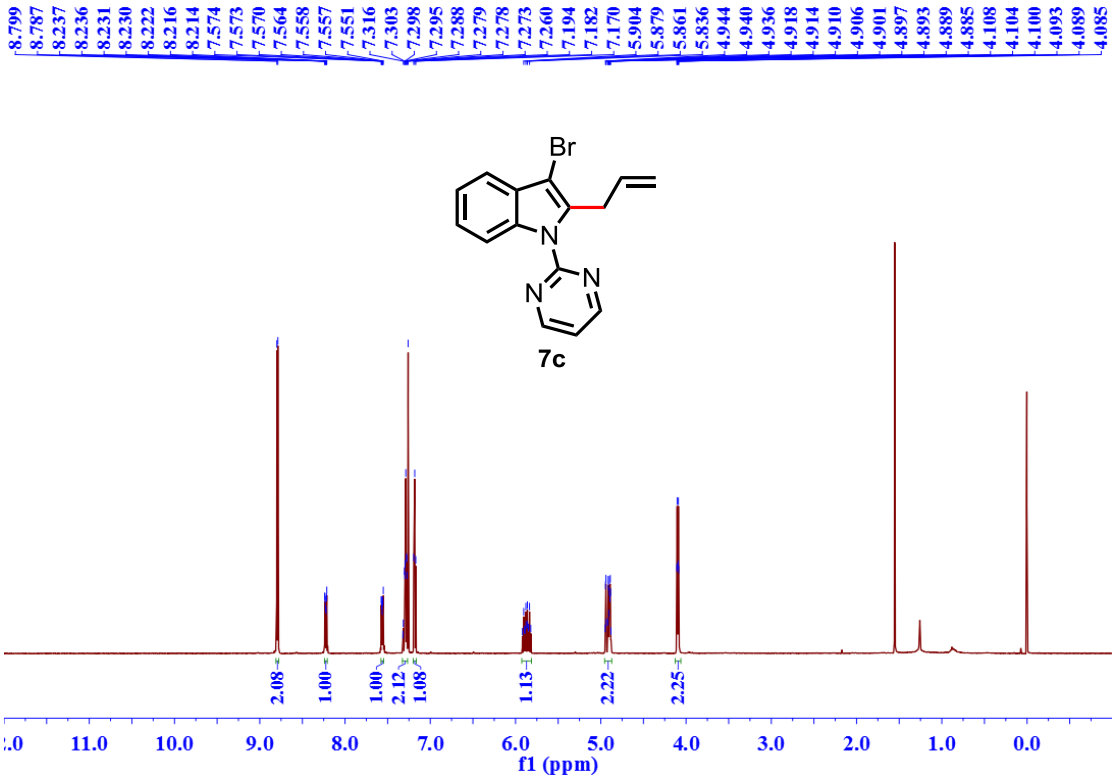


^{13}C-NMR (100 MHz, $CDCl_3$)

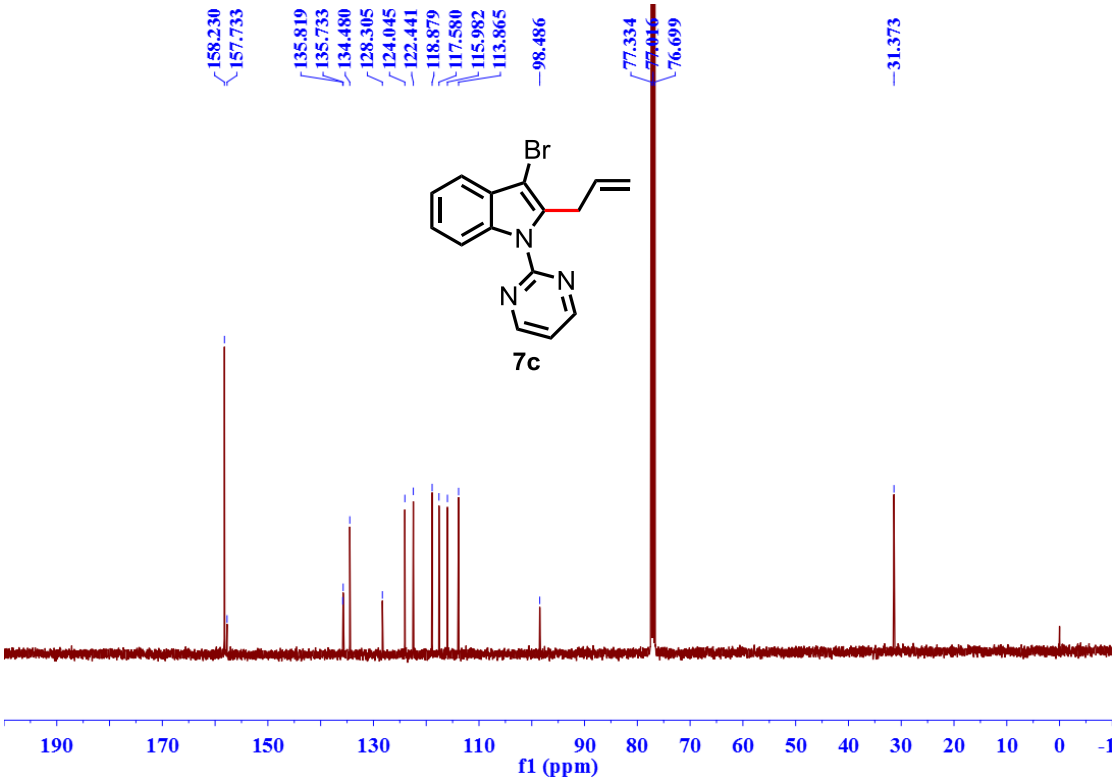


2-allyl-3-bromo-1-(pyrimidin-2-yl)-1H-indole (7c)

^{1}H-NMR (400 MHz, $CDCl_3$)

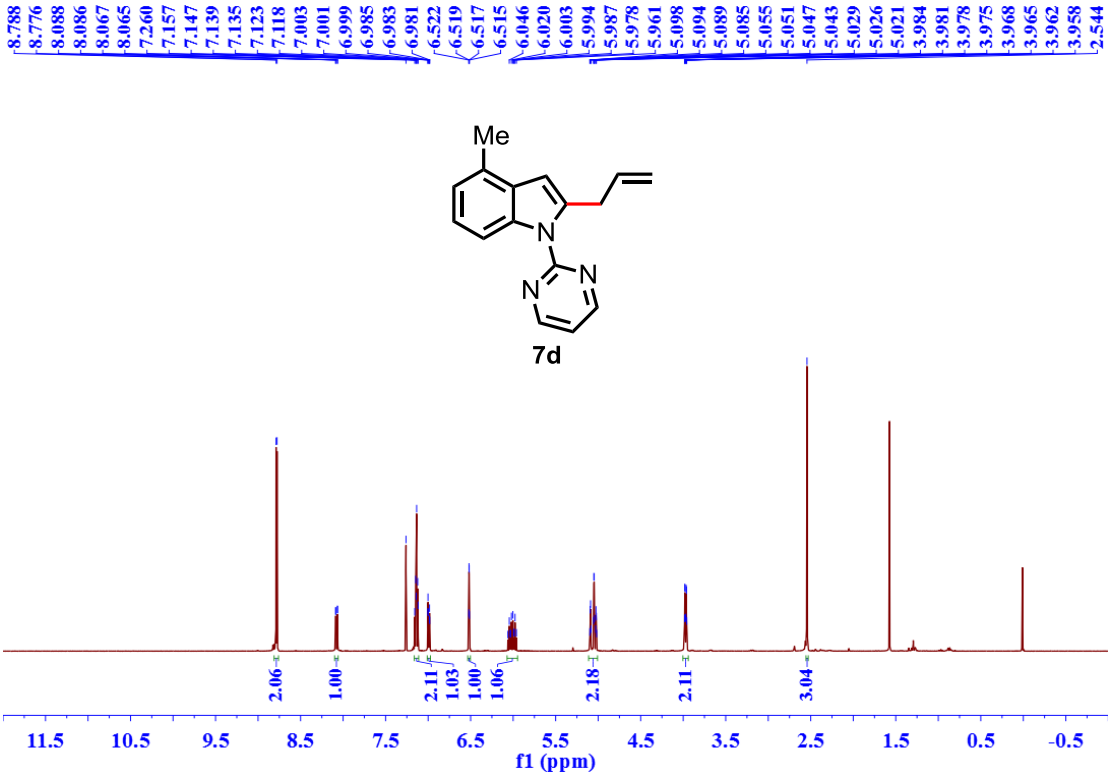


^{13}C-NMR (100 MHz, $CDCl_3$)

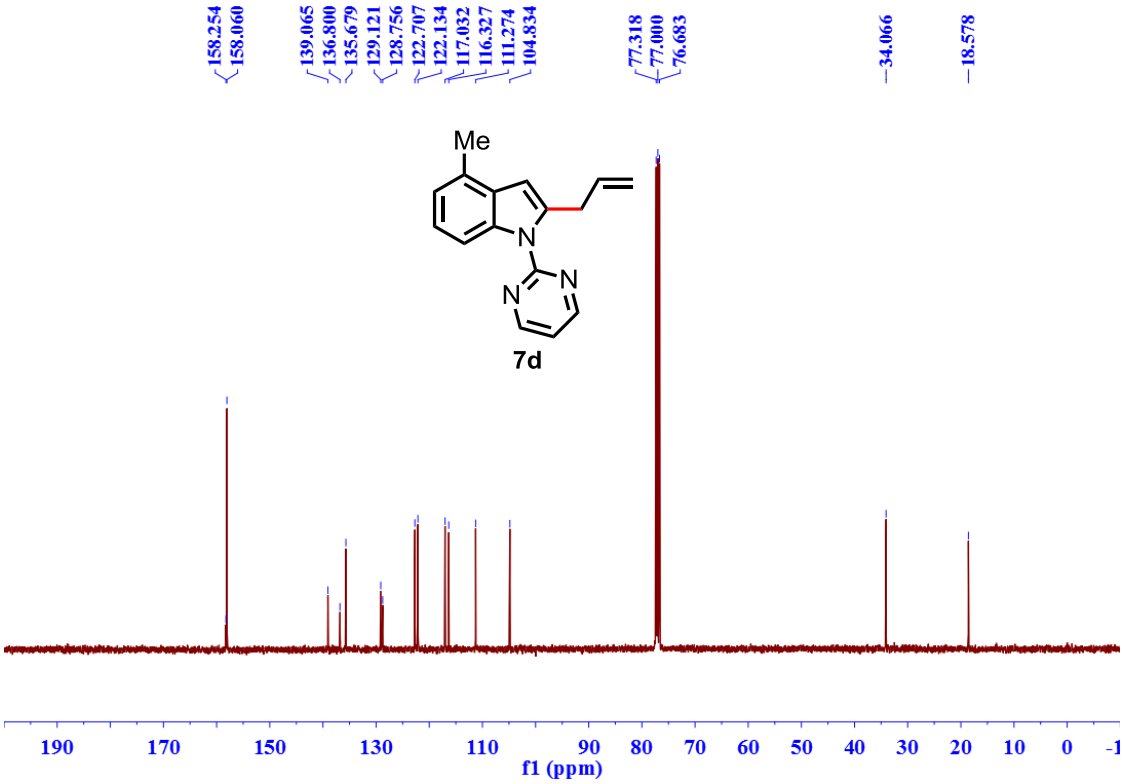


2-allyl-4-methyl-1-(pyrimidin-2-yl)-1H-indole (7d)

^{1}H-NMR (400 MHz, $CDCl_3$)

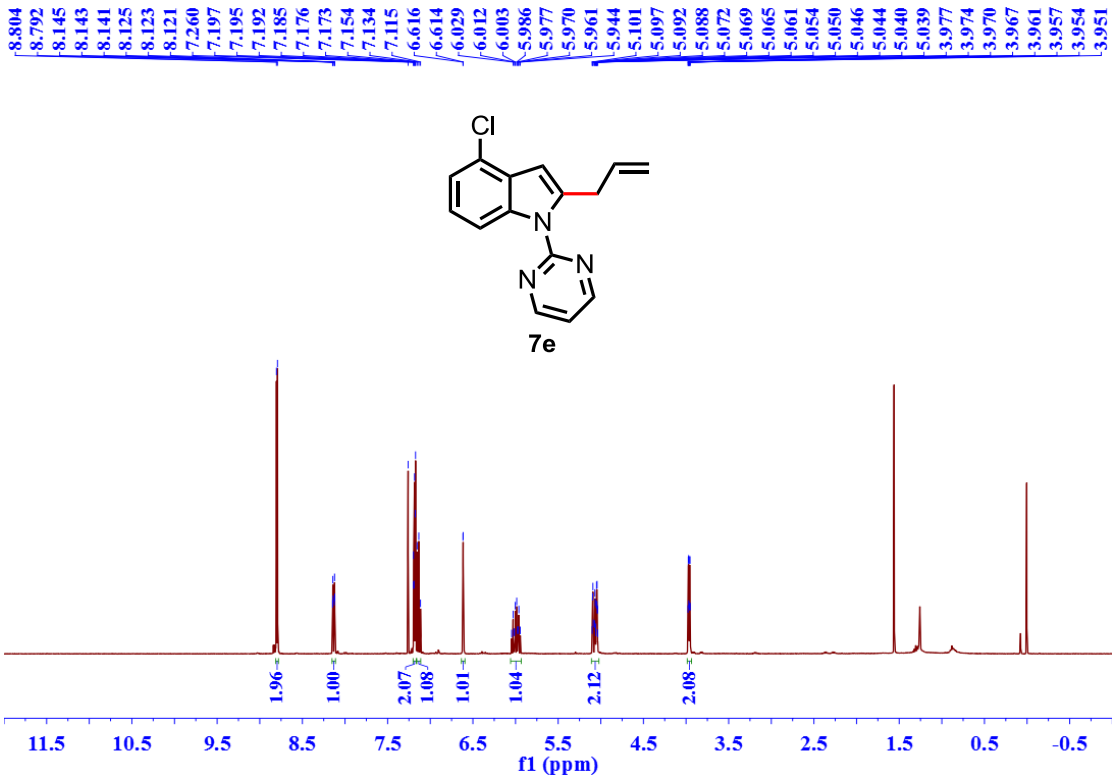


^{13}C-NMR (100 MHz, $CDCl_3$)

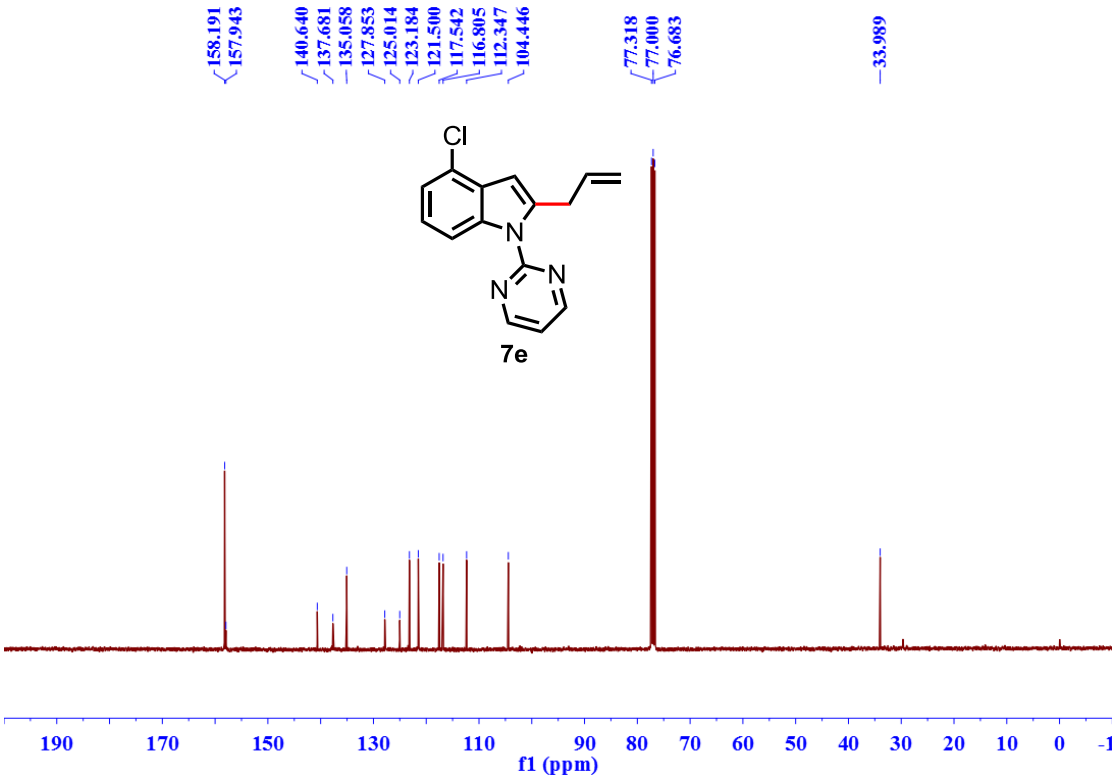


2-allyl-4-chloro-1-(pyrimidin-2-yl)-1H-indole (7e)

^{1}H-NMR (400 MHz, $CDCl_3$)

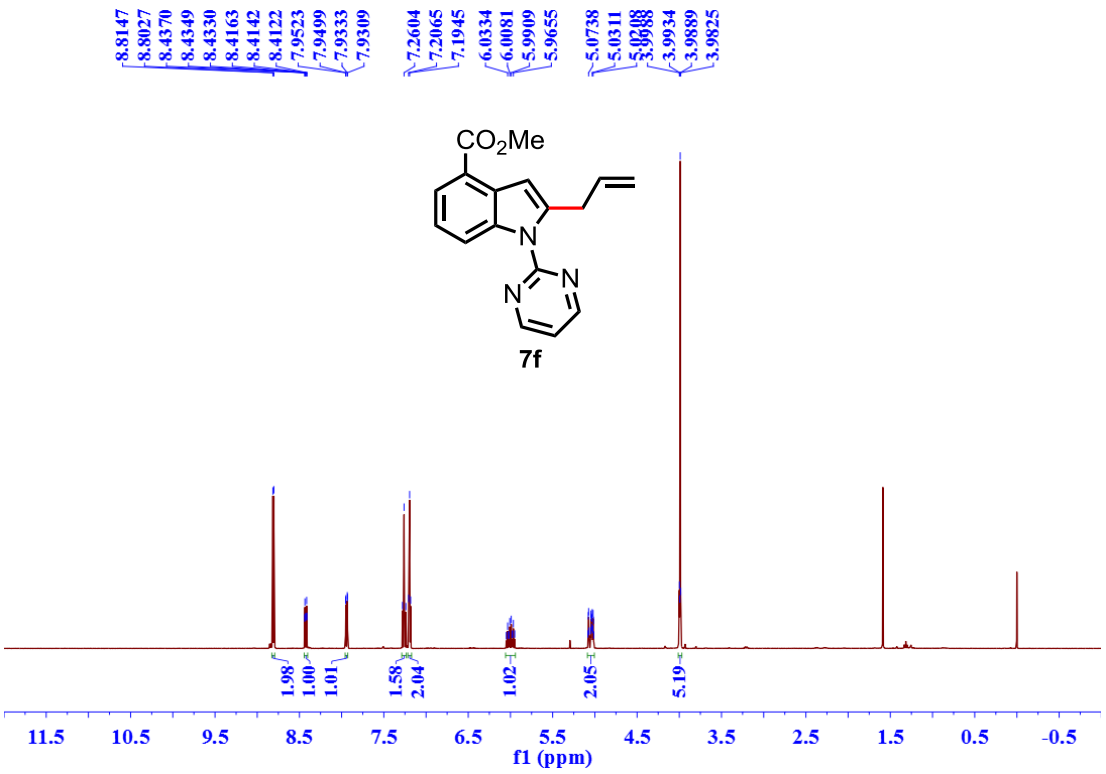


^{13}C-NMR (100 MHz, $CDCl_3$)

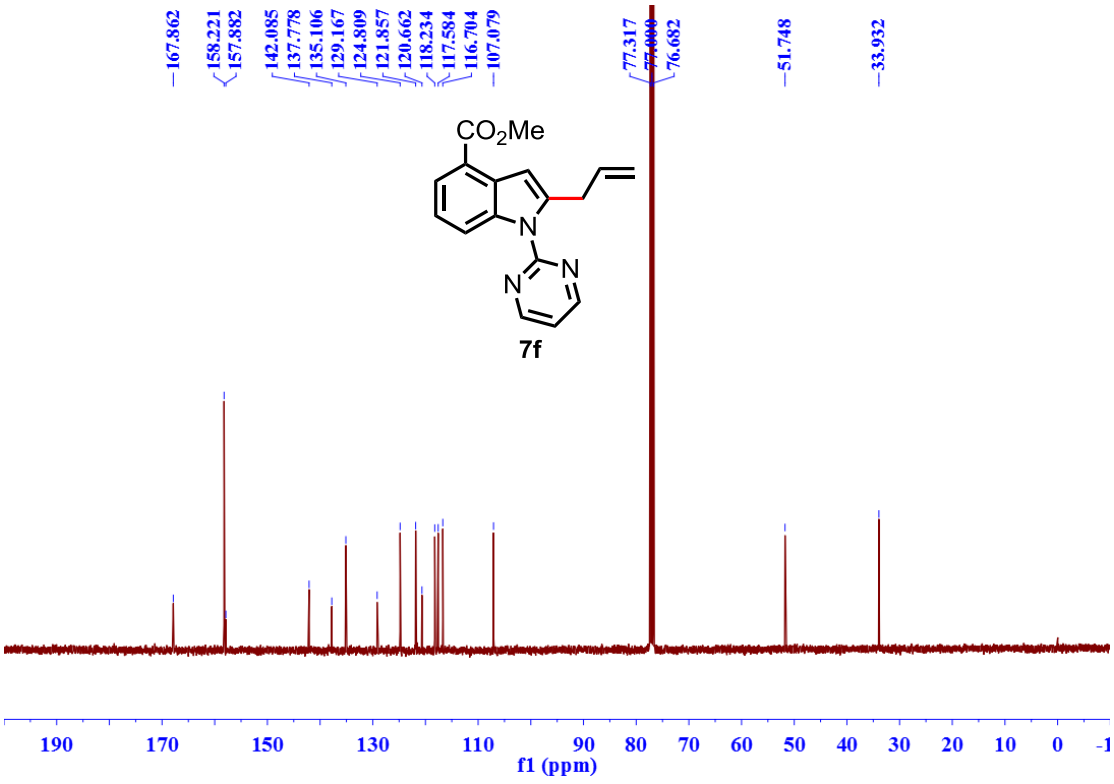


methyl 2-allyl-1-(pyrimidin-2-yl)-1H-indole-4-carboxylate (7f)

^{1}H-NMR (400 MHz, $CDCl_3$)

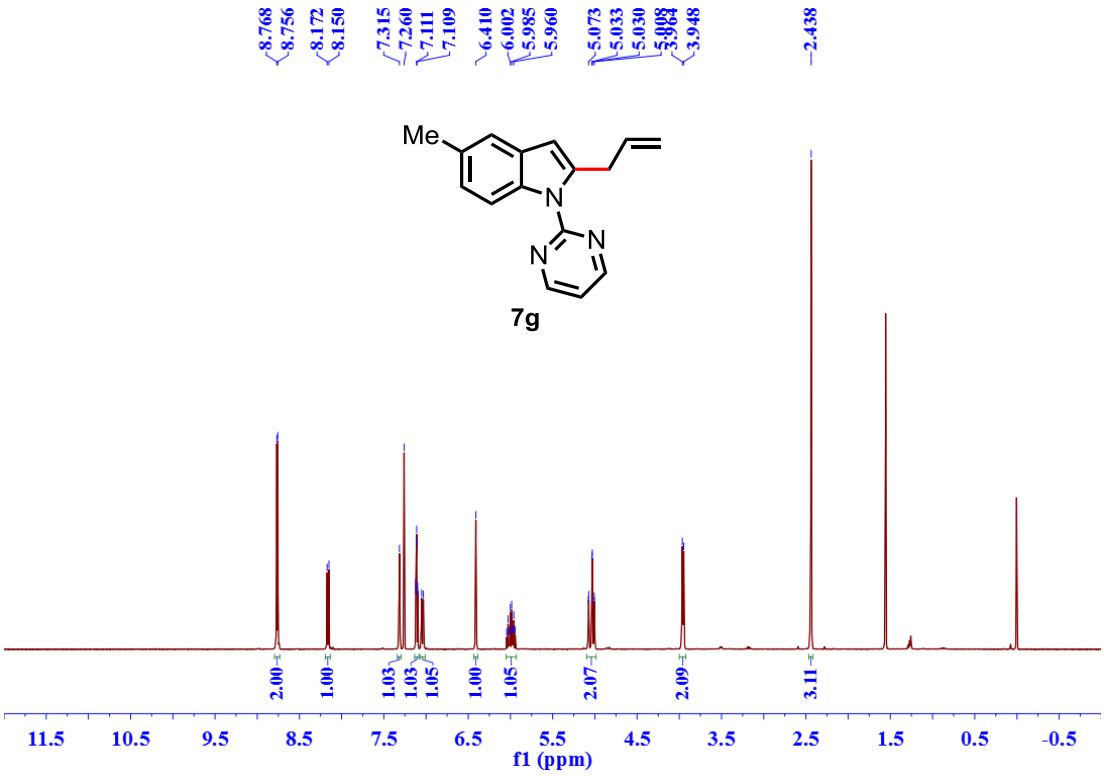


^{13}C-NMR (100 MHz, $CDCl_3$)

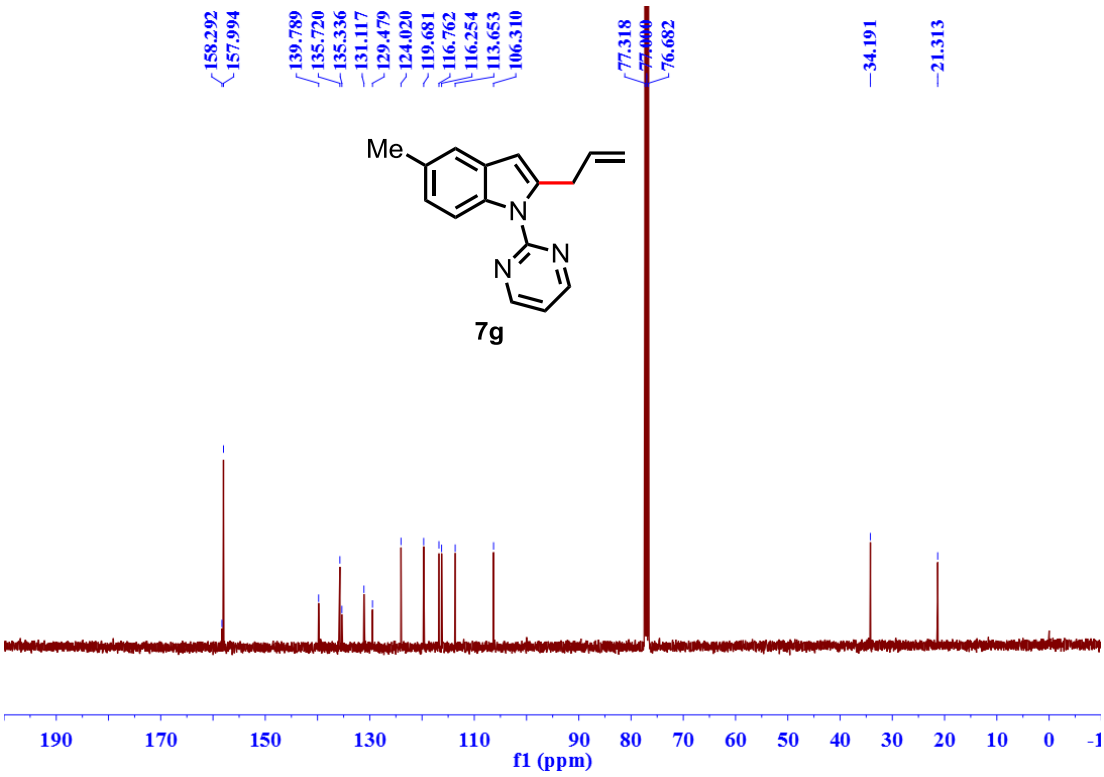


2-allyl-5-methyl-1-(pyrimidin-2-yl)-1H-indole (7g)

^{1}H-NMR (400 MHz, $CDCl_3$)

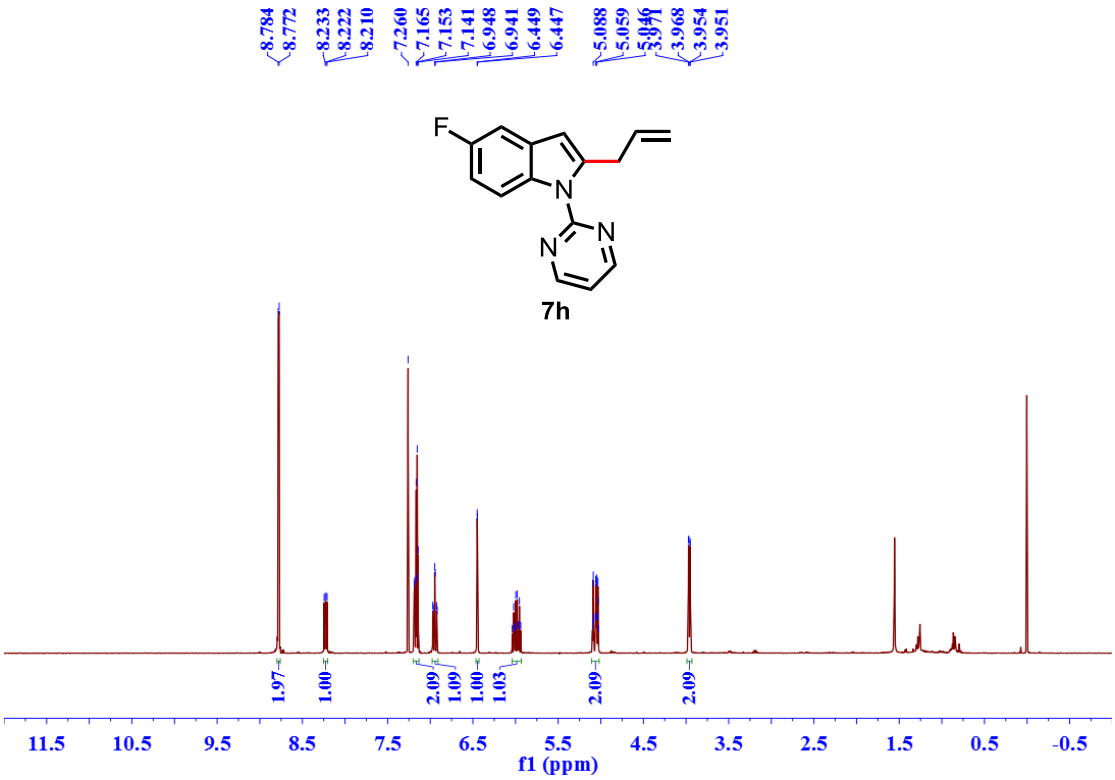


^{13}C-NMR (100 MHz, $CDCl_3$)

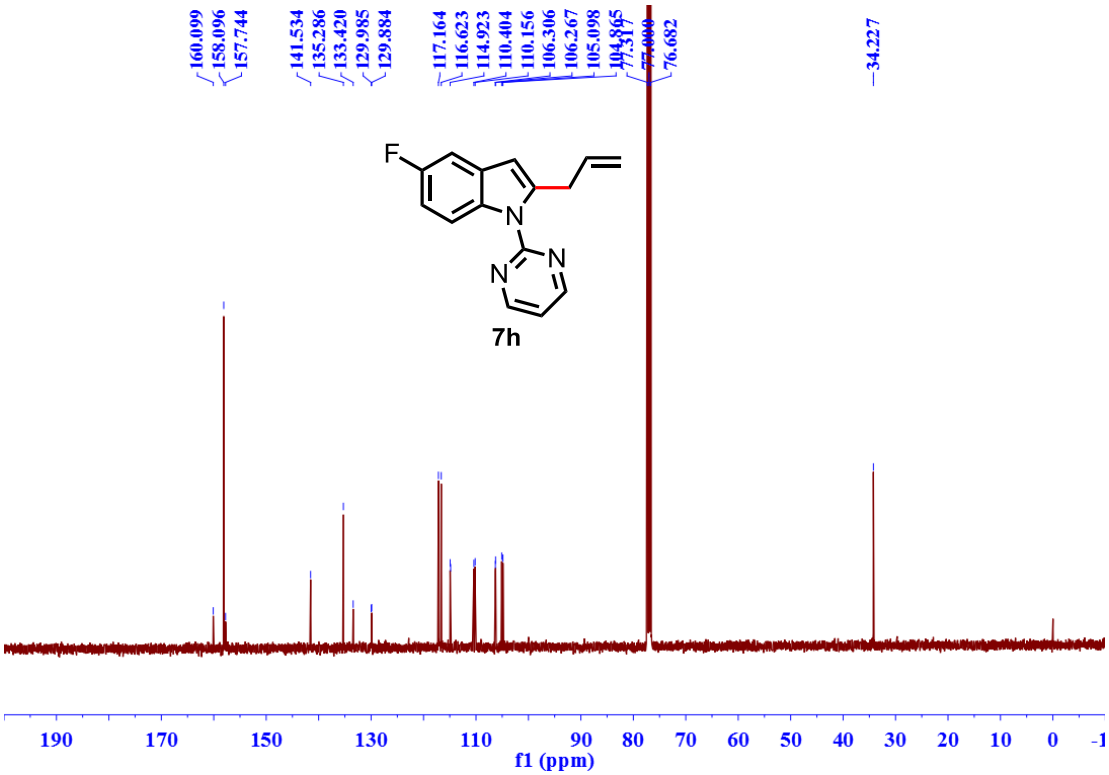


2-allyl-5-fluoro-1-(pyrimidin-2-yl)-1H-indole (7h)

^{1}H-NMR (400 MHz, $CDCl_3$)

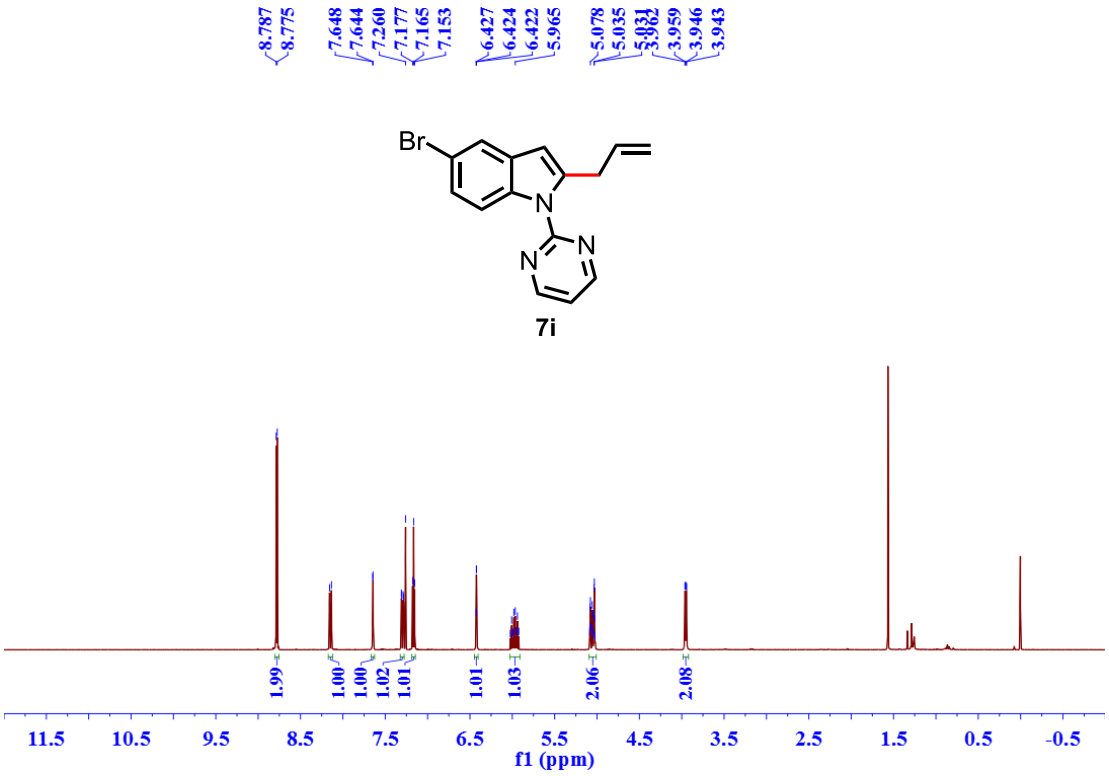


^{13}C-NMR (100 MHz, $CDCl_3$)

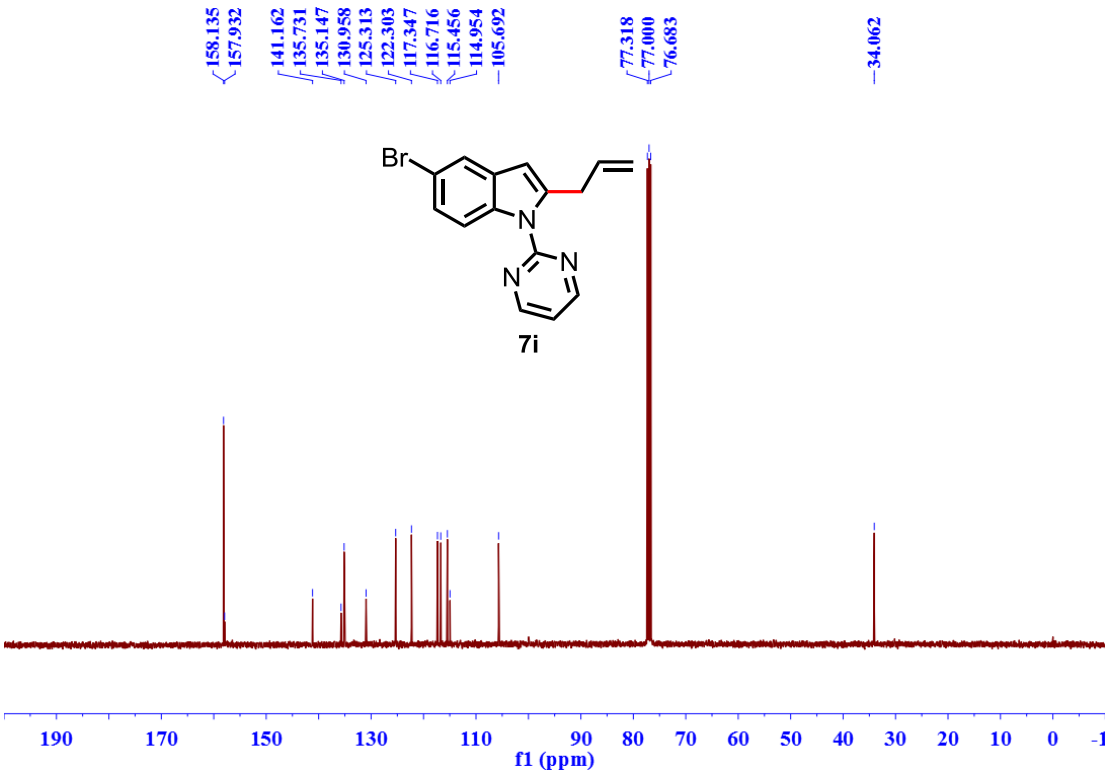


2-allyl-5-bromo-1-(pyrimidin-2-yl)-1H-indole (7i)

^{1}H-NMR (400 MHz, $CDCl_3$)

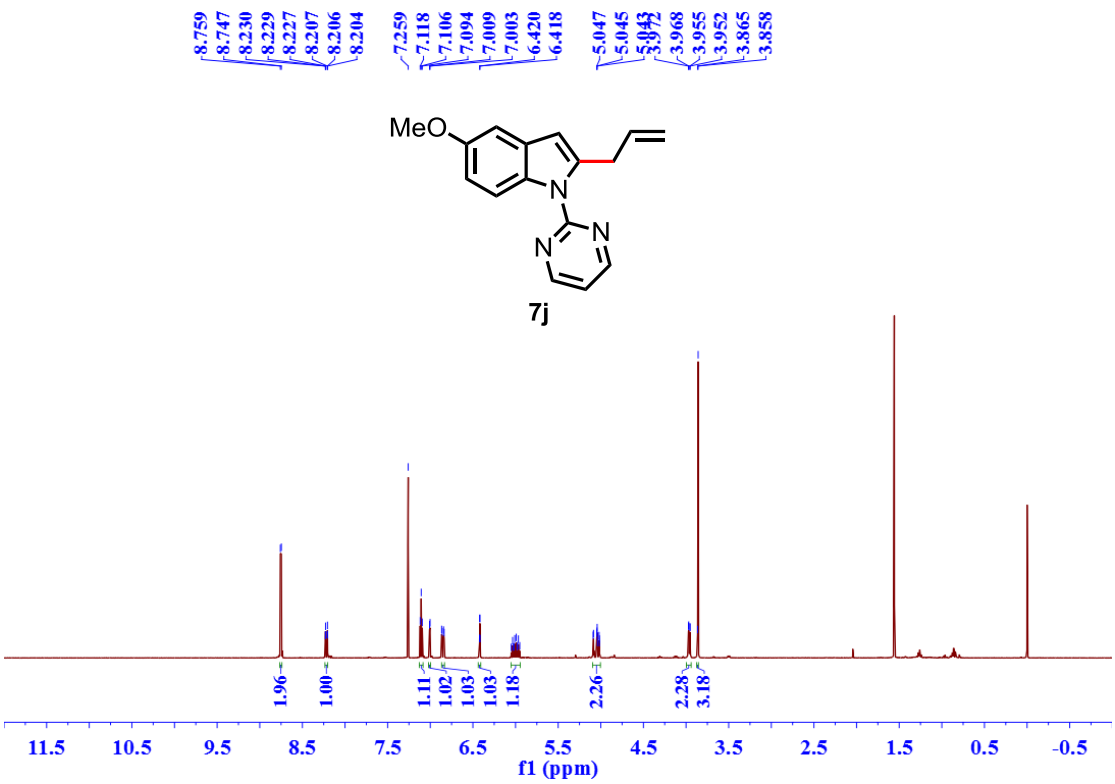


^{13}C-NMR (100 MHz, $CDCl_3$)

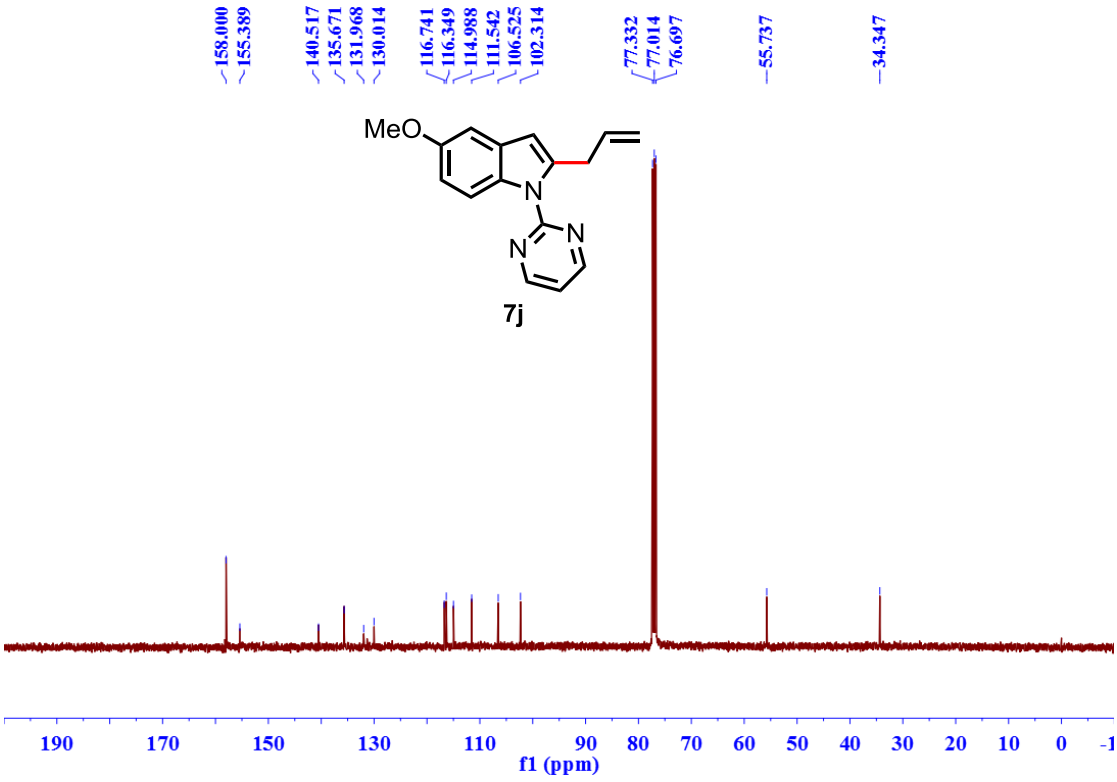


2-allyl-5-methoxy-1-(pyrimidin-2-yl)-1H-indole (7j)

^{1}H-NMR (400 MHz, $CDCl_3$)

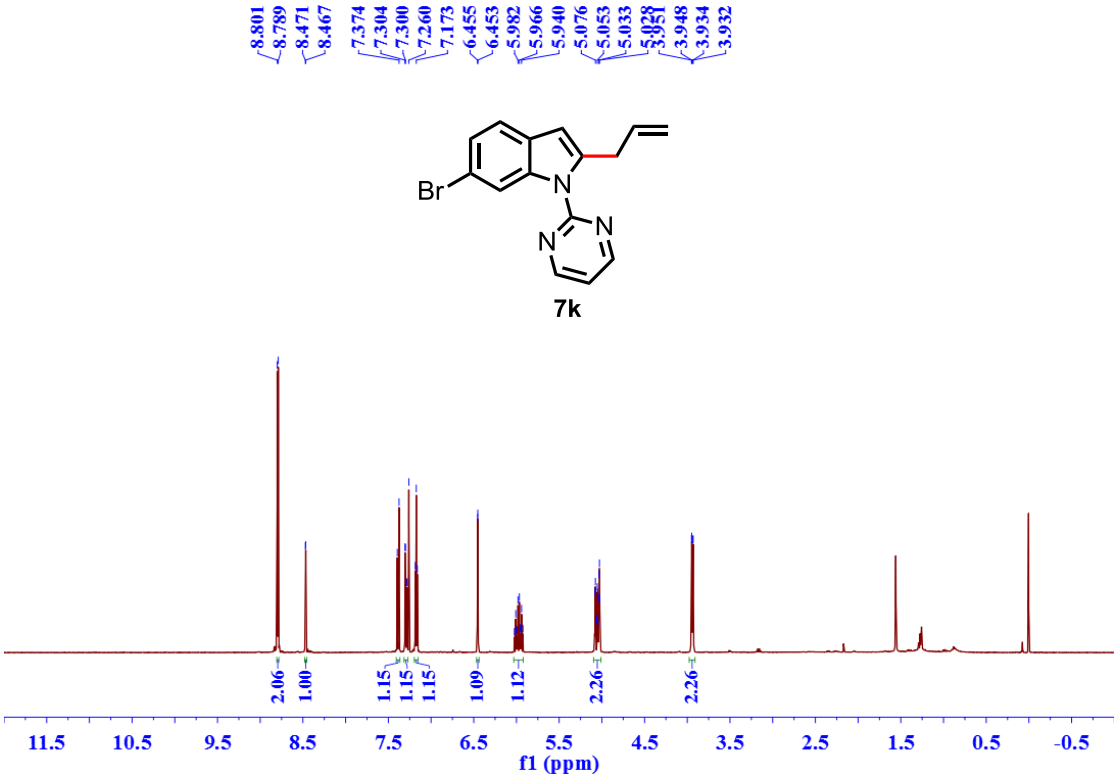


^{13}C-NMR (100 MHz, $CDCl_3$)

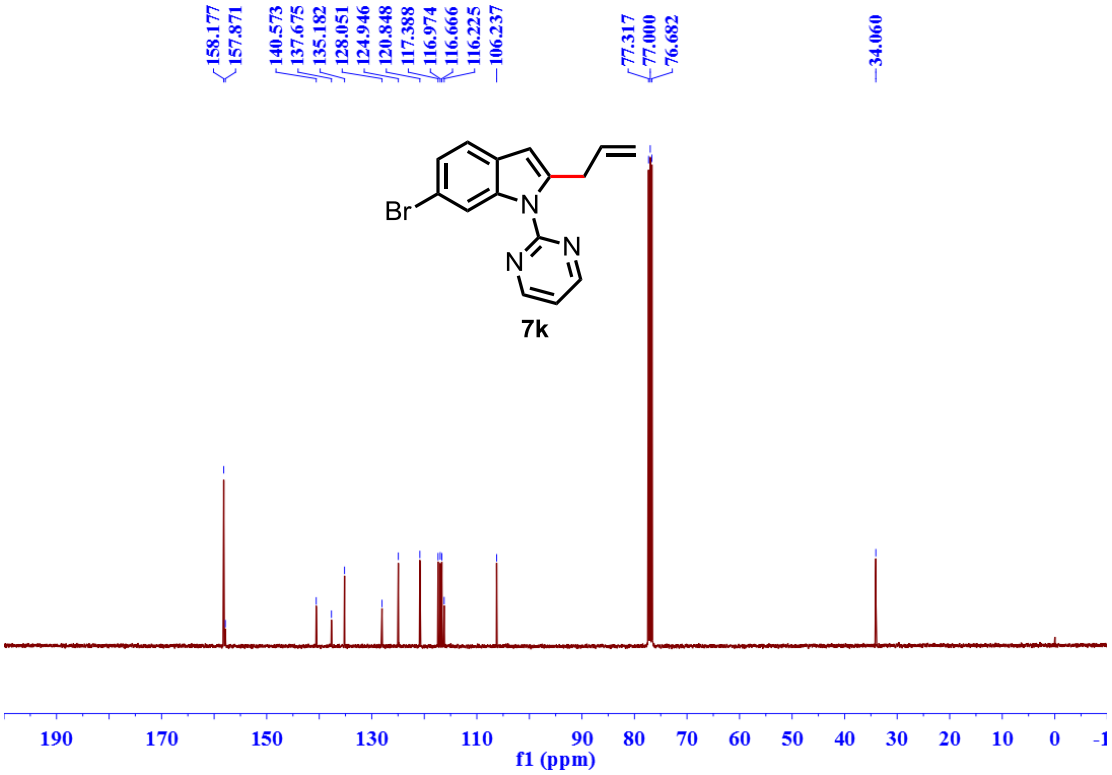


2-allyl-6-bromo-1-(pyrimidin-2-yl)-1H-indole (7k)

^{1}H-NMR (400 MHz, $CDCl_3$)

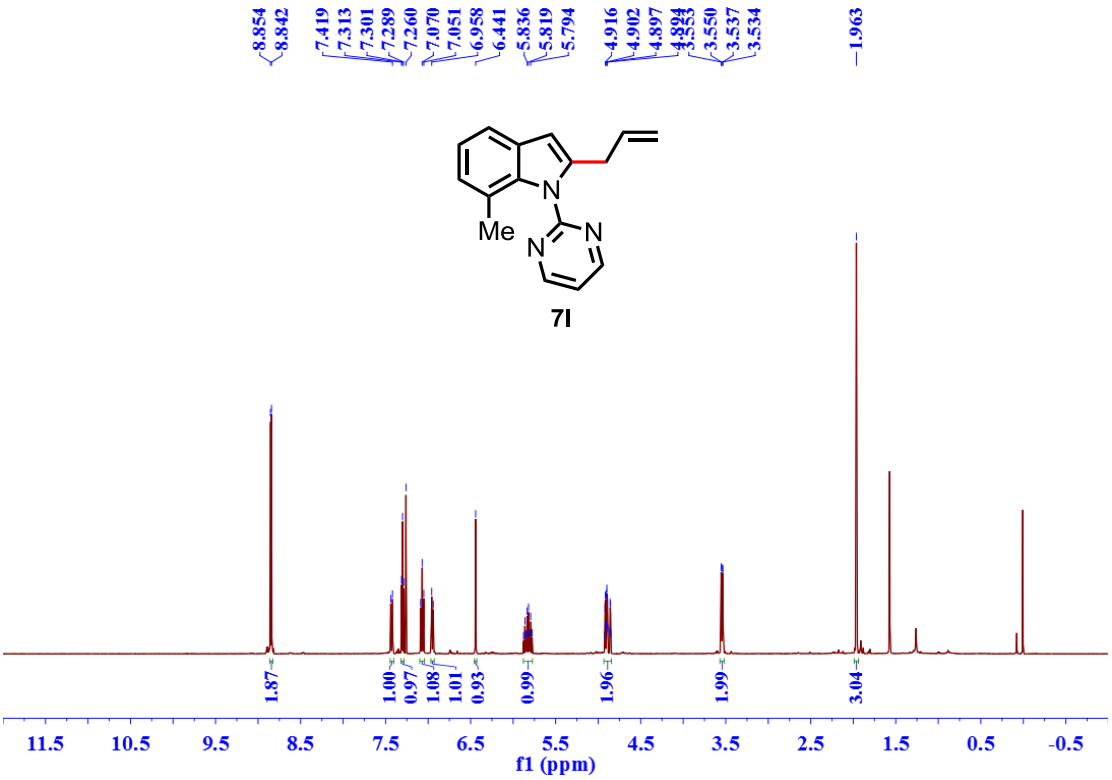


^{13}C-NMR (100 MHz, $CDCl_3$)

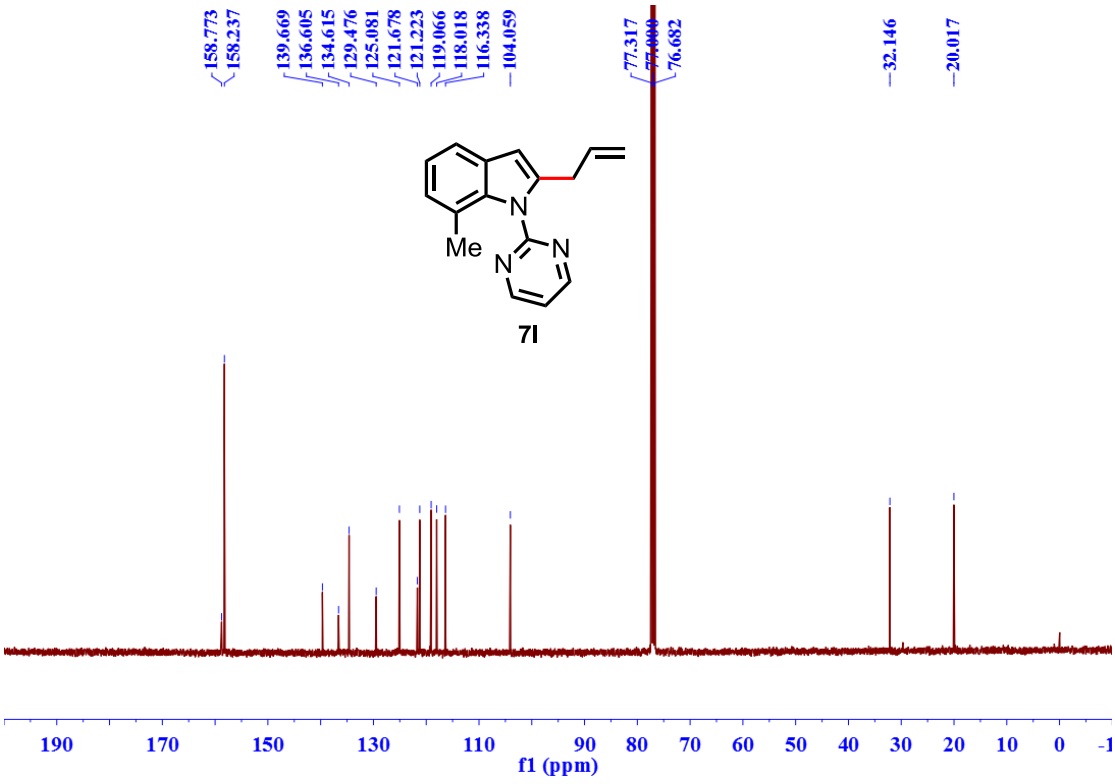


2-allyl-7-methyl-1-(pyrimidin-2-yl)-1H-indole (7l)

^{1}H-NMR (400 MHz, $CDCl_3$)

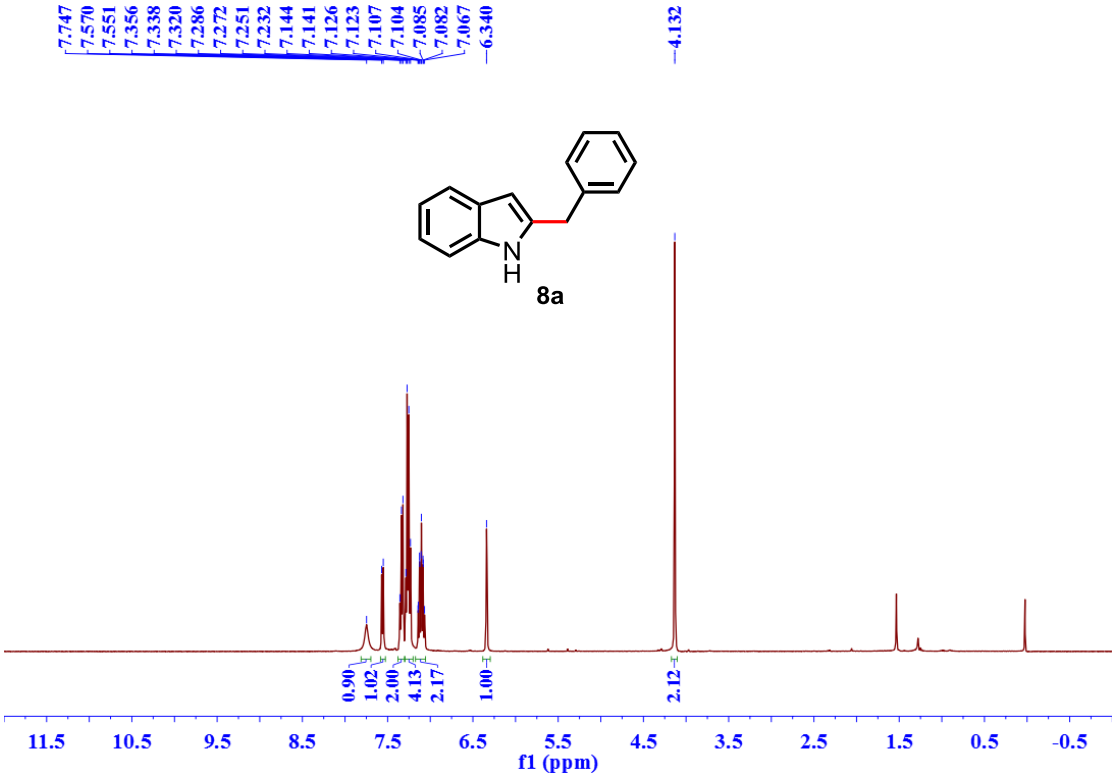


^{13}C-NMR (100 MHz, $CDCl_3$)

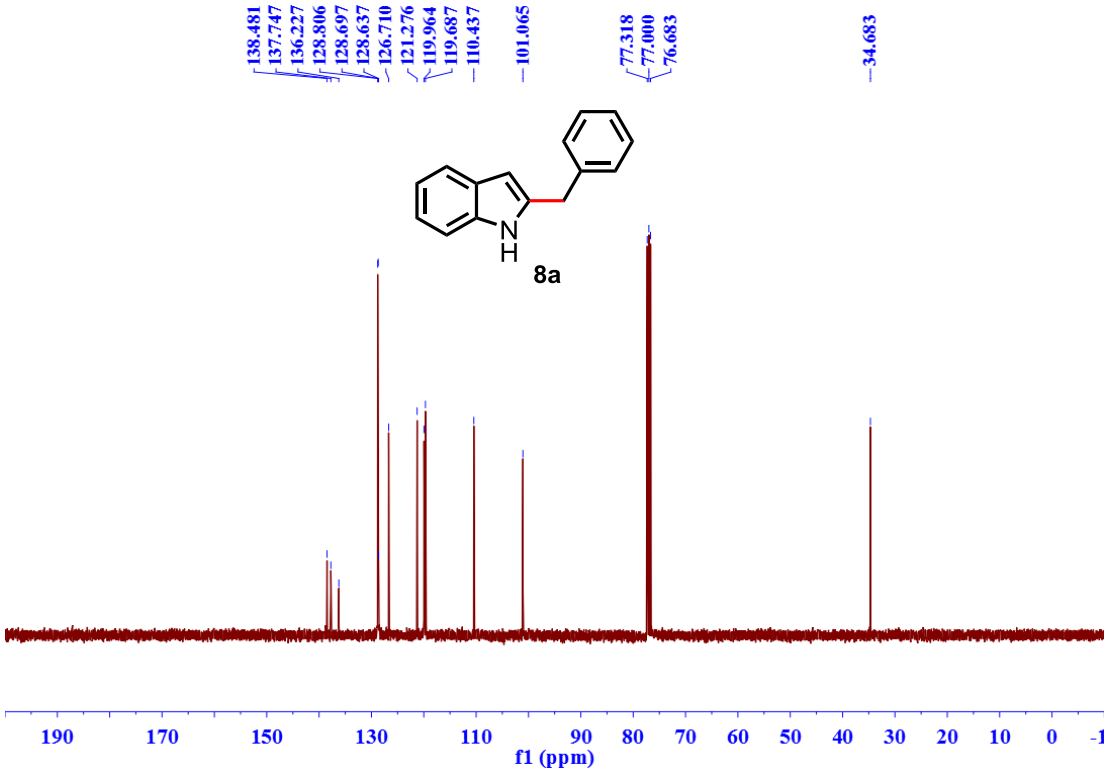


2-benzyl-1H-indole (8a)

^{1}H-NMR (400 MHz, $CDCl_3$)

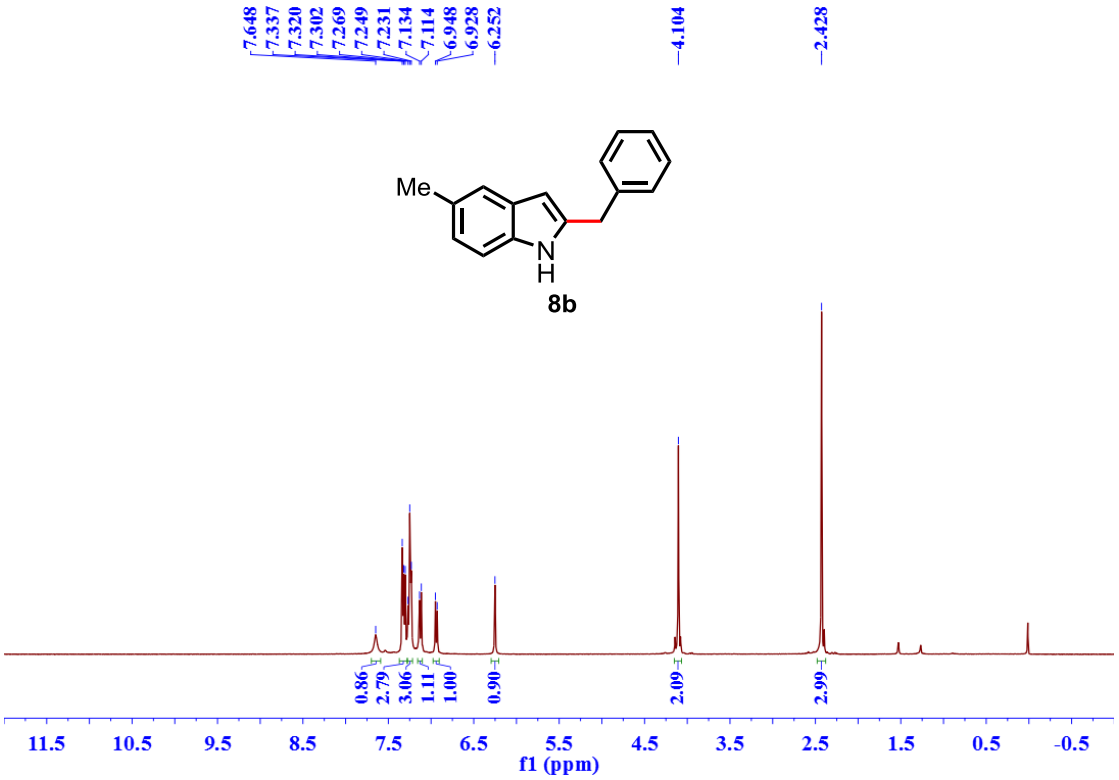


^{13}C-NMR (100 MHz, $CDCl_3$)



2-benzyl-5-methyl-1H-indole (8b)

^{1}H-NMR (400 MHz, $CDCl_3$)



^{13}C-NMR (100 MHz, $CDCl_3$)