Supporting Information

Ruthenium-Catalyzed Direct C−H Bond Arylations of Heteroarenes

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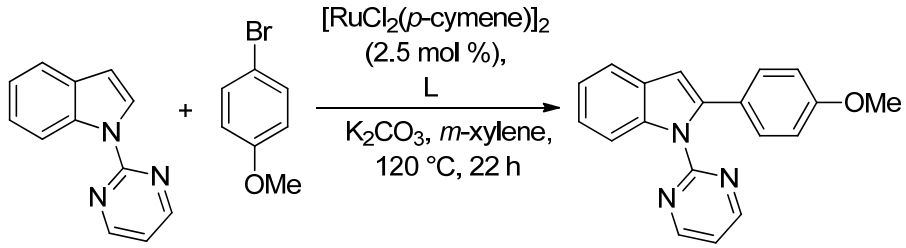
General Remarks

Catalytic reactions were carried out under a N_2 atmosphere using pre-dried glassware. *m*-Xylene was distilled over sodium/benzophenone. The following starting materials were synthesized according to previously described methods: 2-(1*H*-pyrrol-1-yl)pyridine (**8a**),[1] *tert*-butyl 1-(methoxycarbonyl)-2-(1*H*-indol-3-yl)ethylcarbamate,[2] 2-(thiophen-3-yl)pyridine (**10**),[3] 2-(1*H*-pyrrol-3-yl)pyridine (**8c**).[4] Other chemicals were obtained from commercial sources, and were used without further purification. Yields refer to isolated compounds, estimated to be >95 % pure as determined by ^{1}H-NMR and GC. TLC: Macherey-Nagel, TLC plates Alugram® Sil G/UV254. Detection under UV light at 254 nm. Chromatography: Separations were carried out on Merck Silica 60 (0.063–0.200 mm, 70–230 mesh ASTM). IR: measured as KBr pellets or as films between KBr plates. MS: EI-MS: Finnigan MAT 95, 70 eV, DCI-MS: Finnigan MAT 95, 200 eV, reactant gas NH_3; ESI-MS: Finnigan LCQ. High resolution mass spectrometry (HRMS): APEX IV 7T FTICR, Bruker Daltonic. M. p.: Büchi 540 capillary melting point apparatus, values are uncorrected. NMR (^{1}H, ^{13}C, ^{19}F) spectra were recorded at 300 (^{1}H), 75.5 (^{13}C, APT (Attached Proton Test)) and 283 MHz (^{19}F), respectively, on Varian Unity-300 and AMX 300 instruments for $CDCl_3$ solutions if not otherwise specified, chemical shifts (δ) are given in ppm.

Table S-1. Optimization studies for the direct arylation of indole 1a with aryl bromide 2a.[a]

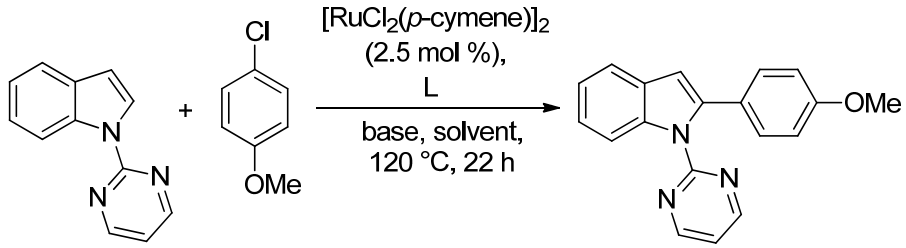


1a **2a** **3a**

Entry	L (mol %)	Yield
1	---	---
2	(1-Ad)CO_2H (10)	71%
3	(1-Ad)CO_2H (30)	84%
4	(1-Ad)CO_2H (30)	---[b]
5	$(1\text{-Ad})_2P(O)H$ (10)	72%
6	PPh_3 (10)	61%
7	*t*-BuCO_2H (30)	68%
8	MesCO_2H (30)	61%
9	PhCO_2H (30)	28%
10	HIMesCl (10)	82%
11	KOAc (30)	57%
12	$[Ru(O_2CMes)_2(p\text{-cymene})]$[c] (**6**)	78%

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), $[RuCl_2(p\text{-cymene})]_2$ (2.5 mol %), L, K_2CO_3 (1.5 mmol), *m*-xylene (2.0 mL), 120 °C, 22 h, yields of isolated products. [b] In NMP (2.0 mL). [c] Instead of $[RuCl_2(p\text{-cymene})]_2$. HIMes = *N*,*N*'-bis-(2,4,6-trimethylphenyl)-imidazol(in)ium.

Table S-2. Optimization studies for the direct arylation of indole 1a with aryl chloride 7a.[a]



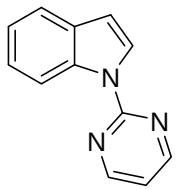
1a **7a** **3a**

Entry	Base	L (mol %)	Solvent	Yield[b]
1	K_2CO_3	---	NMP	---
2	KOAc	---	NMP	14%
3	K_2CO_3	PPh_3 (10)	NMP	---
4	K_2CO_3	$(1\text{-Ad})_2P(O)H$ (10)	NMP	---
5	K_2CO_3	$(1\text{-Ad})CO_2H$ (30)	NMP	---
6	K_2CO_3	---	*m*-xylene	1%
7	K_2CO_3	KOAc (30)	*m*-xylene	17%
8	K_2CO_3	HIMesCl (10)	*m*-xylene	32%
9	K_2CO_3	PPh_3 (10)	*m*-xylene	43%
10	K_2CO_3	PCy_3 (10)	*m*-xylene	68%(60%)
11	K_2CO_3	$t\text{BuCO}_2H$ (30)	*m*-xylene	27%
12	K_2CO_3	$PhCO_2H$ (30)	*m*-xylene	35%
13	K_2CO_3	$(1\text{-Ad})CO_2H$ (30)	*m*-xylene	29%
14	K_2CO_3	$MesCO_2H$ (30)	*m*-xylene	26%
15	K_2CO_3	$(2,4,6\text{-Me}_3C_6H_3)_2P(O)H$ (10)	*m*-xylene	47%
16	K_2CO_3	$(1\text{-Ad})_2P(O)H$ (10)	*m*-xylene	67%(63%)

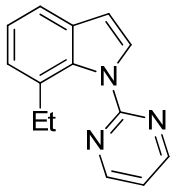
[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), $[RuCl_2(p\text{-cymene})]_2$ (2.5 mol%), L, base (1.5 mmol), solvent (2.0 mL), 120 °C, 22 h. [b] GC-Conversion. In parentheses: isolated yield. HIMes = *N*,*N*'-bis-(2,4,6-trimethylphenyl)imidazol(in)ium.

Representative Procedure A: Synthesis of 1-(pyrimidin-2-yl)-1*H*-indoles (1) and 1-(pyrimidin-2-yl)-1*H*-pyrrole (8b)

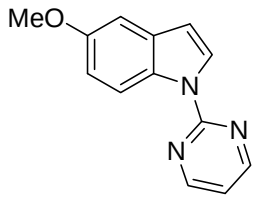
NaH (60% dispersion in mineral oil, 440 mg, 11.0 mmol) was added in portions at 0 °C to a stirred solution of indole (1.17 g, 10.0 mmol) in DMF (25 mL). After stirring for 30 min at 0 °C, 2-chloropyrimidine (1.37 g, 12.0 mmol) was added and the mixture was stirred at 130 °C for 24 h. Then, the reaction mixture was cooled to ambient temperature, poured into H_2O (300 mL) and extracted with EtOAc (4×75 mL). The combined organic phase was dried over Na_2SO_4. After filtration and evaporation of the solvents under reduced pressure, the crude product was purified by column chromatography on silica gel (*n*-hexane/EtOAc: 4/1) to yield **1a** (1.80 g, 92%) as a colorless solid.



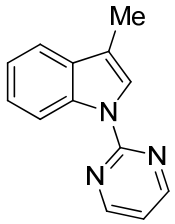
1-(Pyrimidin-2-yl)-1*H*-indole (1a): M. p. = 85−86 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.83 (d, J = 8.4 Hz, 1H), 8.69 (d, J = 4.8 Hz, 2H), 8.29 (d, J = 3.7 Hz, 1H), 7.65 (d, J = 7.7 Hz, 1H), 7.37 (t, J = 7.7 Hz, 1H), 7.26 (t, J = 7.5 Hz, 1H), 7.03 (t, J = 4.8 Hz, 1H), 6.73 (d, J = 3.6 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 158.0 (CH), 157.7 (C_q), 135.3 (C_q), 131.3 (C_q), 125.7 (CH), 123.6 (CH), 122.1 (CH), 120.8 (CH), 116.2 (CH), 116.1 (CH), 106.9 (CH). IR (KBr): 1575, 1525, 1456, 1309, 1204, 1080, 970, 776, 750, 731 cm^{-1}. MS (EI) *m/z* (relative intensity) 195 (100) [M^+], 168 (3), 142 (12), 97 (6). HR-MS (ESI) *m/z* calcd for $C_{12}H_9N_3Na$ [M+Na^+] 218.0689, found 218.0696. The spectral data were in accordance with those reported in the literature.[5]



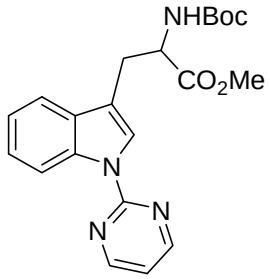
7-Ethyl-1-(pyrimidin-2-yl)-1*H*-indole (1b): The representative procedure A was followed using 7-ethylindole (1.45 g, 10.0 mmol) and 2-chloropyrimidine (1.37 g, 12.0 mmol). After 24 h at 130 °C, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 5/1) yielded **1b** (1.70 g, 76%) as a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz): $\delta = 8.72$ (d, $J = 4.8$ Hz, 2H), 7.85 (d, $J = 3.5$ Hz, 1H), 7.60−7.54 (m, 1H), 7.30−7.24 (m, 2H), 7.06 (t, $J = 4.9$ Hz, 1H), 6.77 (d, $J = 3.5$ Hz, 1H), 2.96 (q, $J = 7.5$ Hz, 2H), 1.11 (t, $J = 7.5$ Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): $\delta = 158.2$ (C_q), 158.0 (CH), 133.7 (C_q), 131.9 (C_q), 130.3 (C_q), 129.9 (CH), 124.5 (CH), 122.2 (CH), 118.7 (CH), 117.3 (CH), 106.8 (CH), 27.6 (CH_2), 13.8 (CH_3). IR (KBr): 1570, 1537, 1481, 1420, 1350, 1271, 1167, 1143, 841, 727 cm^{-1}. MS (EI) *m/z* (relative intensity) 223 (80) [M^+], 208 (100), 130 (20). HR-MS (ESI) *m/z* calcd for $C_{14}H_{14}N_3$ [$M+H^+$] 224.1182, found 224.1188.



5-Methoxy-1-(pyrimidin-2-yl)-1*H*-indole (1c): The representative procedure A was followed using 5-methoxyindole (1.48 g, 10.0 mmol) and 2-chloropyrimidine (1.37 g, 12.0 mmol). After 24 h at 130 °C, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 3/1) yielded **1c** (2.07 g, 91%) as a colorless solid. M. p. = 109−110 °C. ^{1}H-NMR ($CDCl_3$, 300 MHz): $\delta = 8.70$ (d, $J = 9.1$ Hz, 1H), 8.66 (d, $J = 4.8$ Hz, 2H), 8.24 (d, $J = 3.7$ Hz, 1H), 7.09 (d, $J = 2.6$ Hz, 1H), 7.02−6.95 (m, 2H), 6.63 (d, $J = 3.6$ Hz, 1H), 3.89 (s, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): $\delta = 158.0$ (CH), 157.6 (C_q), 155.5 (C_q), 132.1 (C_q), 130.3 (C_q), 126.3 (CH), 117.0 (CH), 115.9 (CH), 112.5 (CH), 106.7 (CH), 103.1 (CH), 55.7 (CH_3). IR (KBr): 1611, 1577, 1436, 1298, 1222, 1158, 848, 767, 727 cm^{-1}. MS (EI) *m/z* (relative intensity) 225 (90) [M^+], 210 (75), 182 (100). HR-MS (ESI) *m/z* calcd for $C_{13}H_{12}N_3O$ [$M+H^+$] 226.0975, found 226.0983.

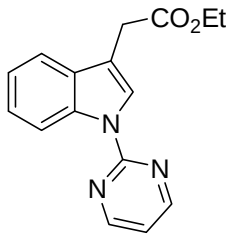


3-Methyl-1-(pyrimidin-2-yl)-1*H*-indole (1d): The representative procedure A was followed using 3-methylindole (1.31 g, 10.0 mmol) and 2-chloropyrimidine (1.37 g, 12.0 mmol). After 24 h at 130 °C, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 5/1) yielded **1d** (1.93 g, 92%) as a colorless solid. M. p. = 76−77 °C. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 8.79 (d, J = 8.2 Hz, 1H), 8.66 (d, J = 4.8 Hz, 2H), 8.05 (s, 1H), 7.57 (d, J = 8.2 Hz, 1H), 7.37 (t, J = 7.7 Hz, 1H), 7.27 (t, J = 7.5 Hz, 1H), 6.98 (t, J = 4.8 Hz, 1H), 2.37 (s, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 158.0 (CH), 157.7 (C_q), 135.6 (C_q), 132.0 (C_q), 123.6 (CH), 122.9 (CH), 121.7 (CH), 118.7 (CH), 116.2 (CH), 116.1 (C_q), 115.5 (CH), 9.8 (CH_3). IR (KBr): 1560, 1457, 1434, 1348, 1250, 1162, 1121, 1017, 802 cm^{-1}. MS (EI) *m/z* (relative intensity) 209 (100) [M$^+$], 130 (55), 77 (14). HR-MS (ESI) *m/z* calcd for $C_{13}H_{12}N_3$ [M+H$^+$] 210.1026, found 210.1028.

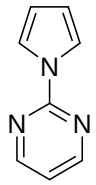


***tert*-Butyl 1-(methoxycarbonyl)-2-{1-(pyrimidin-2-yl)-1*H*-indol-3-yl}ethylcarbamate (1e):** The representative procedure A was followed using Boc-Trp-OMe (1.59 g, 5.0 mmol) and 2-chloropyrimidine (1.37 g, 12.0 mmol). After 24 h at 20 °C, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 2/1) yielded **1e** (1.50 g, 76%) as a colorless solid. M. p. = 175−176 °C. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 8.78 (d, J = 8.3 Hz, 1H), 8.68 (d, J = 4.8 Hz, 2H), 8.09 (s, 1H), 7.55 (d, J = 7.7 Hz, 1H), 7.37−7.09 (m, 2H), 7.03 (t, J = 4.8 Hz, 1H), 5.12 (m, 1H), 4.70 (m, 1H), 3.70 (s, 3H), 3.30 (m, 2H), 1.43 (s, 9H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 172.5 (C_q), 158.1 (CH), 157.5 (C_q), 155.2 (C_q), 135.6 (C_q), 131.2 (C_q), 124.2 (CH), 123.9 (CH), 122.0 (CH), 118.8 (CH), 116.3 (CH), 116.0 (CH), 114.5 (C_q), 79.9 (C_q),

53.9 (CH), 52.3 (CH_3), 28.3 (CH_3), 28.0 (CH_2). IR (KBr): 1735, 1700, 1564, 1521, 1462, 1313, 1223, 1136, 1057, 741 cm^{-1}. MS (ESI) *m/z* (relative intensity) 815 (100) [2M+Na^+], 419 (43) [M+Na^+]. HR-MS (ESI) *m/z* calcd for $C_{21}H_{24}N_4O_4Na$ [M+Na^+] 419.1690, found 419.1687.

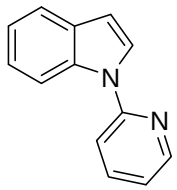


Ethyl 2-{1-(pyrimidin-2-yl)-1*H*-indol-3-yl}acetate (1f): The representative procedure A was followed using ethyl indol-3-yl acetate (1.89 g, 9.30 mmol) and 2-chloropyrimidine (1.37 g, 12.0 mmol). After 24 h at 20 °C, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 3/1) yielded **1f** (2.04 g, 78%) as a yellow solid. M. p. = 109−110 °C. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 8.79 (d, J = 8.4 Hz, 1H), 8.67 (d, J = 4.8 Hz, 2H), 8.26 (s, 1H), 7.61 (d, J = 7.7 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 7.27 (t, J = 7.5 Hz, 1H), 7.01 (t, J = 4.8 Hz, 1H), 4.19 (q, J = 7.2 Hz, 2H), 3.80 (s, 2H), 1.27 (t, J = 7.2 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 171.3 (C_q), 158.0 (CH), 157.6 (C_q), 135.6 (C_q), 130.8 (C_q), 124.5 (CH), 123.9 (CH), 122.0 (CH), 118.9 (CH), 116.3 (CH), 115.9 (CH), 112.9 (C_q), 60.9 (CH_2), 31.5 (CH_2), 14.2 (CH_3). IR (KBr): 2983, 1733, 1559, 1457, 1435, 1310, 1131, 805, 737 cm^{-1}. MS (EI) *m/z* (relative intensity) 281 (27) [M^+], 208 (100). HR-MS (ESI) *m/z* calcd for $C_{16}H_{16}N_3O_2$ [M+H^+] 282.1237, found 282.1235.

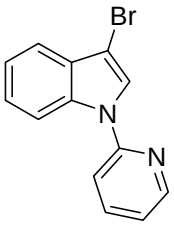


2-(1*H*-Pyrrol-1-yl)pyrimidine (8b): The representative procedure A was followed using pyrrole (1.34 g, 20.0 mmol) and 2-chloropyrimidine (2.75 g, 24.0 mmol). After 24 h at 20 °C, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 3/1) yielded **8b** (1.85 g, 64%) as a colorless solid. M. p. = 89−90 °C. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 8.61

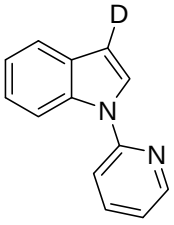
(d, J = 4.8 Hz, 2H), 7.79 (dd, J = 2.4, 2.4 Hz, 2H), 7.04 (t, J = 4.8 Hz, 1H), 6.35 (dd, J = 2.4, 2.4 Hz, 2H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 158.3 (CH), 156.2 (C_q), 119.0 (CH), 117.1 (CH), 111.9 (CH). IR (KBr): 1572, 1478, 1437, 1075, 1057, 1020, 927, 852, 804, 737 cm^{-1}. MS (EI) *m/z* (relative intensity) 145 (42) [M^+], 69 (50), 55 (52), 43 (100). HR-MS (ESI) *m/z* calcd for $C_8H_7N_3Na$ [M+Na^+] 168.0532, found 168.0536. The spectral data were in accordance with those reported in the literature.[6]



1-(Pyridin-2-yl)-1*H*-indole (1g): A mixture of indole (2.93 g, 25.0 mmol), 2-bromopyridine (4.74 g, 30.0 mmol), CuI (478 mg, 2.50 mmol, 10.0 mol %), *N*,*N*'-dimethyl-ethylenediamine (528 mg, 6.00 mmol, 20.0 mol %), K_3PO_4 (14.0 g, 66.0 mmol) in toluene (30 mL) was vigorously stirred at 110 °C under nitrogen atmosphere for 24 h. After cooling the mixture to ambient temperature, the reaction mixture was diluted with EtOAc (200 mL) and washed with H_2O (2×50 mL). The aqueous phase was extracted with EtOAc (2×50 mL), and the combined organic phase was dried over Na_2SO_4. After filtration and evaporation of the solvents *in vacuo*, the crude product was purified by column chromatography on silica gel to give **1g** (4.15 g, 86%) as a yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.58 (d, J = 4.8 Hz, 1H), 8.22 (d, J = 8.3 Hz, 1H), 7.82 (dd, J = 7.7, 7.7 Hz, 1H), 7.74 (d, J = 3.5 Hz, 1H), 7.69 (d, J = 7.7 Hz, 1H), 7.50 (d, J = 8.2 Hz, 1H), 7.32 (t, J = 7.7 Hz, 1H), 6.26−7.15 (m, 2H) 6.73 (d, J = 3.6 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 152.5 (C_q), 149.0 (CH), 138.3 (CH), 135.0 (C_q), 130.4 (C_q), 125.9 (CH), 123.1 (CH), 121.2 (CH), 121.0 (CH), 120.0 (CH), 114.5 (CH), 112.9 (CH), 105.5 (CH). IR (KBr): 1696, 1591, 1523, 1472, 1317, 1277, 1240, 1211, 1016, 741 cm^{-1}. MS (EI) *m/z* (relative intensity) 194 (100) [M^+], 167 (12), 139 (4), 97 (10), 78 (12). HR-MS (ESI) *m/z* calcd for $C_{13}H_{10}N_2Na$ [M+Na^+] 217.0736, found 217.0743. The spectral data were in accordance with those reported in the literature.[7]



3-Bromo-1-(pyridin-2-yl)-1*H*-indole (1h): *N*-Bromosuccinimide (356 mg, 2.00 mmol) was added in portions at 0 °C to a stirred solution of *N*-(2-pyidyl)indole (**1g**) (388 mg, 2.00 mmol) in THF (20 mL). After stirring for 15 min at 0 °C, the reaction mixture was diluted with MTBE (100 mL) and washed with saturated aqueous $Na_2S_2O_3$ (20 mL), brine (50 mL) and dried over Na_2SO_4. After filtration and evaporation of the solvents *in vacuo*, the crude product was purified by column chromatography on silica gel (*n*-hexane/EtOAc: 6/1) to yield **1h** (478 mg, 88%) as a colorless oil. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 8.56 (m, 1H), 8.20 (d, J = 8.3 Hz, 1H), 7.83 (dd, J = 7.9, 1.9 Hz, 1H), 7.79 (s, 1H), 7.63 (d, J = 7.8 Hz, 1H), 7.46 (d, J = 8.3Hz, 1H), 7.39−7.27 (m, 2H), 7.19 (ddd, J = 7.4, 4.9, 0.8 Hz, 1H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 151.7 (C_q), 149.0 (CH), 138.5 (CH), 134.5 (C_q), 129.1 (C_q), 125.0 (CH), 124.2 (CH), 121.9 (CH), 120.5 (CH), 119.6 (CH), 114.4 (CH), 113.1 (CH), 95.4 (C_q). IR (KBr): 1589, 1470, 1449, 1343, 1277, 1211, 1015, 779, 742 cm^{-1}. MS (EI) *m/z* (relative intensity) 274 (100) [M^+], 192 (66), 166 (29), 96 (32), 78 (50). HR-MS (ESI) *m/z* calcd for $C_{13}H_{10}N_2Br$ [$M+H^+$] 273.0022, found 273.0023.

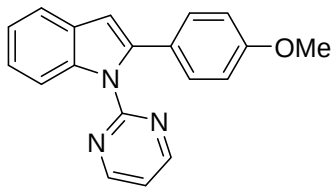


3-Deuterio-1-(pyridin-2-yl)-1*H*-indole ([D_1]-1g): Solution of *t*-BuLi in pentane (2.2 mL, 1.5 M, 3.33 mmol) was added dropwise at −78 °C for 10 min to a stirred solution of **1h** (413 mg, 1.51 mmol) in THF (15 mL). After stirring for 10 min at −78 °C, the reaction mixture was treated with D_2O (1.0 mL), diluted with MTBE (75 mL), washed with H_2O (50 mL), brine (50 mL) and dried over Na_2SO_4. After filtration and evaporation of the solvents *in vacuo*, the crude product was purified by column chromatography on silica gel (*n*-hexane/EtOAc: 6/1) to yield [D_1]-**1g** (265 mg, 90%) as a colorless oil. ^{1}H-NMR ($CDCl_3$,

300 MHz): δ = 8.58 (m, 1H), 8.23 (d, J = 7.7 Hz, 1H), 7.82 (td, J = 8.1, 2.5 Hz, 1H), 7.74 (s, 1H), 7.69 (d, J = 7.7 Hz, 1H), 7.50 (d, J = 8.7 Hz, 1H), 7.32 (t, J = 7.7 Hz, 1H), 7.24 (d, J = 7.6 Hz, 1H), 7.20−7.15 (m, 1H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 152.5 (C_q), 149.0 (CH), 138.3 (CH), 135.0 (C_q), 130.3 (C_q), 125.8 (CH), 123.1 (CH), 121.2 (CH), 121.0 (CH), 120.0 (CH), 114.5 (CH), 112.9 (CH), 105.3 (C_q, J_{C-D} = 24 Hz). IR (KBr): 1695, 1590, 1530, 1510, 1471, 1343, 1276, 1200, 1092, 779, 745 cm^{-1}. MS (EI) *m/z* (relative intensity) 195 (100) [M^+], 168 (10), 97 (12), 78 (15). HR-MS (ESI) *m/z* calcd for $C_{13}H_{10}N_2D^+$ [M+H^+] 196.0980, found 196.0984.

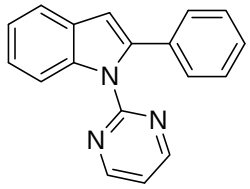
Representative Procedure B: Ruthenium-Catalyzed C−H Bond Arylation of Heteroarenes

A mixture of 1-(pyrimidin-2-yl)-1*H*-indole (**1a**) (97.5 mg, 0.50 mmol), 4-bromoanisole (**2a**) (112 mg, 0.60 mmol), [$RuCl_2$(*p*-cymene)]$_2$ (7.7 mg, 2.5 mol %), **5c** (27.0 mg, 0.15 mmol, 30.0 mol %), K_2CO_3 (207 mg, 1.50 mmol) in *m*-xylene (2.0 mL) was stirred at 120 °C under nitrogen atmosphere for 22 h. After cooling the reaction mixture to ambient temperature, it was diluted with EtOAc (75 mL) and washed with sat. aqueous K_2CO_3 (2×30 mL). The aqueous phase was extracted with EtOAc (2×30 mL), and the combined organic phase was dried over Na_2SO_4. After filtration and evaporation of the solvents *in vacuo*, the crude product was purified by column chromatography on silica gel (*n*-hexane/EtOAc: 4/1) to yield **3a** (125 mg, 84%) as a colorless solid.



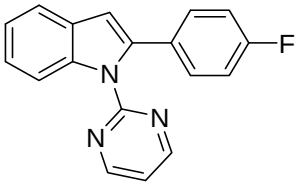
2-(4-Methoxyphenyl)-1-(pyrimidin-2-yl)-1*H*-indole (3a): The representative procedure B was followed using 1-(pyrimidin-2-yl)-1*H*-indole (**1a**) (97.5 mg, 0.50 mmol), 4-chloroanisole (112 mg, 0.60 mmol) and **4** (15.9 mg, 10.0 mol %). After 22 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 5/1) yielded **3a** (92 mg, 61%) as a colorless solid. M. p. = 139−140 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.69 (d, J = 4.8 Hz, 2H), 8.12 (d,

J = 7.5 Hz, 1H), 7.66 (d, J = 7.5 Hz, 1H), 7.32−7.22 (m, 4H), 7.10 (t, J = 4.8 Hz 1H), 6.86 (d, J = 8.9 Hz, 2H), 6.77 (s, 1H), 3.82 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 158.8 (C_q), 158.1 (CH), 158.1 (C_q), 140.2 (C_q), 137.9 (C_q), 129.3 (C_q), 129.3 (CH), 126.4 (C_q), 123.1 (CH), 122.0 (CH), 120.4 (CH), 117.5 (CH), 113.6 (CH), 112.6 (CH), 107.1 (CH), 55.2 (CH_3). IR (KBr): 1608, 1562, 1502, 1422, 1346, 1242, 1178, 1026, 805, 741 cm^{-1}. MS (EI) *m/z* (relative intensity) 301 (100) [M^+], 286 (15), 258 (23), 150 (14), 128 (16). HR-MS (ESI) *m/z* calcd for $C_{19}H_{16}N_3O$ [M+H^+] 302.1288, found 302.1292.

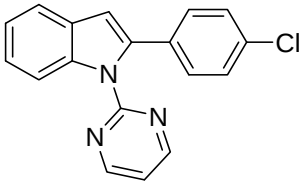


2-Phenyl-1-(pyrimidin-2-yl)-1*H*-indole (3b): The representative procedure B was followed using 1-(pyrimidin-2-yl)-1*H*-indole (**1a**) (97.5 mg, 0.50 mmol) and bromobenzene (94.2 mg, 0.60 mmol). After 22 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 5/1) yielded **3b** (114 mg, 84%) as a colorless solid.

The representative procedure B was followed using 1-(pyrimidin-2-yl)-1*H*-indole (**1a**) (98 mg, 0.50 mmol) and iodobenzene (122 mg, 0.60 mmol). After 22 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 5/1) yielded **3b** (85 mg, 63%) as a colorless solid. M. p. = 126−127 °C. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 8.67 (d, J = 8.4 Hz, 2H), 8.17 (d, J = 8.7 Hz, 1H), 7.68 (d, J = 6.8 Hz, 1H), 7.34−7.24 (m, 7 H), 7.10 (t, J = 4.8 Hz, 1H), 6.83 (s, 1H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 158.1 (CH), 158.1 (C_q), 140.4 (C_q), 138.1 (C_q), 133.9 (C_q), 129.3 (C_q), 128.1 (CH), 128.1 (CH), 127.1 (CH), 123.5 (CH), 122.1 (CH), 120.6 (CH), 117.6 (CH), 112.8 (CH), 108.2 (CH). IR (KBr): 1560, 1424, 1345, 838, 812, 761, 742, 697 cm^{-1}. MS (EI) *m/z* (relative intensity) 271 (100) [M^+], 243 (8), 190 (12), 165 (10), 135 (13). HR-MS (ESI) *m/z* calcd for $C_{18}H_{14}N_3$ [M+H^+] 272.1182, found 272.1184.

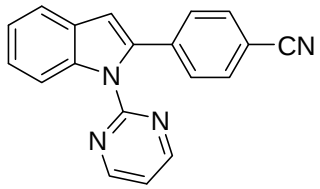


2-(4-Fluorophenyl)-1-(pyrimidin-2-yl)-1*H*-indole (3c): The representative procedure B was followed using 1-(pyrimidin-2-yl)-1*H*-indole (**1a**) (97.5 mg, 0.50 mmol) and 4-fluorobromobenzene (105 mg, 0.60 mmol). After 22 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 5/1) yielded **3c** (124 mg, 86%) as a colorless solid. M. p. = 150−151 °C. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 8.67 (d, J = 4.8 Hz, 2H), 8.16 (d, J = 8.3 Hz, 1H), 7.66 (d, J = 7.2 Hz, 1H), 7.33−7.22 (m, 4H), 7.12 (t, J = 4.9 Hz, 1H), 7.01 (t, J = 8.8 Hz, 2H), 6.78 (s, 1H). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ = 161.9 (C_q, J_{C-F} = 246 Hz), 158.1 (CH), 157.9 (C_q), 139.3 (C_q), 137.9 (C_q), 130.1 (C_q, J_{C-F} = 3 Hz), 129.8 (CH, J_{C-F} = 8 Hz), 129.1 (C_q), 123.6 (CH), 122.2 (CH), 120.6 (CH), 117.5 (CH), 115.0 (CH, J_{C-F} = 22 Hz), 112.8 (CH), 108.1 (CH). ^{19}F-NMR (283 MHz, $CDCl_3$): δ = -106.1 – -106.2 (m). IR (KBr): 1558, 1499, 1420, 1261, 1156, 1015, 839, 798, 750, 674 cm^{-1}. MS (EI) *m/z* (relative intensity) 289 (100) [M^+], 261 (8), 208 (7), 183 (7), 144 (11). HR-MS (EI) *m/z* calcd for $C_{18}H_{12}N_3F$ [M^+] 289.1015, found 289.1014.



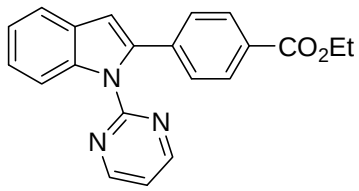
2-(4-Chlorophenyl)-1-(pyrimidin-2-yl)-1*H*-indole (3d): The representative procedure B was followed using 1-(pyrimidin-2-yl)-1*H*-indole (**1a**) (97.5 mg, 0.50 mmol) and 4-chlorobromobenzene (115 mg, 0.60 mmol). After 22 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 5/1) yielded **3d** (128 mg, 84%) as a colorless solid. M. p. = 104−105 °C. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 8.67 (d, J = 4.7 Hz, 2H), 8.18 (d, J = 8.2 Hz, 1H), 7.67 (d, J = 7.7 Hz, 1H), 7.35−7.21 (m, 6H), 7.11 (t, J = 4.8 Hz, 1H), 6.81 (s, 1H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 158.2 (CH), 157.9 (C_q), 139.2 (C_q), 138.1 (C_q), 133.0 (C_q), 132.5 (C_q), 129.3 (CH), 129.2 (C_q), 128.3 (CH), 123.8 (CH), 122.3 (CH), 120.7 (CH), 117.6 (CH), 113.0 (CH), 108.6 (CH). IR (KBr): 1563, 1424, 1346, 1089, 1011, 836, 803, 745,

667 cm^{-1}. MS (EI) *m/z* (relative intensity) 307 (31) [M^+], 305 (100) [M^+], 269 (7), 242 (6), 190 (11), 135 (20). HR-MS (EI) *m/z* calcd for $C_{18}H_{12}N_3Cl$ [M^+] 305.0720, found 305.0721.



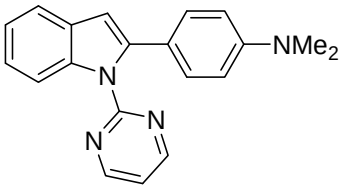
2-(4-Cyanophenyl)-1-(pyrimidin-2-yl)-1*H*-indole (3e): The representative procedure B was followed using 1-(pyrimidin-2-yl)-1*H*-indole (97.5 mg, 0.50 mmol) and 4-bromobenzonitrile (109 mg, 0.60 mmol). After 22 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 3/1) yielded **3e** (108 mg, 73%) as a colorless solid.

The representative procedure B was followed using 1-(pyrimidin-2-yl)-1*H*-indole (97.5 mg, 0.50 mmol), 4-chlorobenzonitrile (82.2 mg, 0.60 mmol) and **4** (15.9 mg, 10 mol %). After 22 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 3/1) yielded **3e** (93 mg, 63%) as a colorless solid. M. p. = 159−160 °C. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 8.67 (d, J = 4.8 Hz, 2H), 8.25 (d, J = 8.4 Hz, 1H), 7.68 (d, J = 7.6 Hz, 1H), 7.59 (d, J = 8.2 Hz, 2H), 7.39−7.25 (m, 4H), 7.15 (t, J = 4.8 Hz, 1H), 6.89 (s, 1H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 158.3 (CH), 157.7 (C_q), 138.8 (C_q), 138.8 (C_q), 138.5 (C_q), 138.3 (C_q), 131.8 (CH), 129.0 (C_q), 128.5 (CH), 124.6 (CH), 122.6 (CH), 121.1 (CH), 118.9 (C_q), 117.7 (CH), 113.3 (CH), 110.3 (CH). IR (KBr): 2224, 1603, 1564, 1449, 1421, 1345, 842, 813, 744 cm^{-1}. MS (EI) *m/z* (relative intensity) 296 (100) [M^+], 268 (10), 215 (8), 190 (8). HR-MS (ESI) *m/z* calcd for $C_{19}H_{13}N_4$ [M+H^+] 297.1135, found 297.1139.

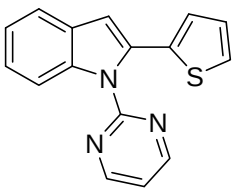


Ethyl 4-{1-(pyrimidin-2-yl)-1*H*-indol-2-yl}benzoate (3f): The representative procedure B was followed using 1-(pyrimidin-2-yl)-1*H*-indole (**1a**) (97.5 mg, 0.50 mmol) and ethyl 4-bromobenzoate (137.4 mg, 0.60 mmol). After 22 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 4/1) yielded **3f** (144 mg, 84%) as a colorless oil. ^{1}H-NMR

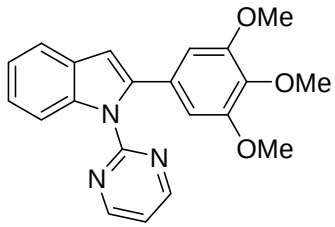
($CDCl_3$, 300 MHz): δ = 8.64 (d, J = 4.8 Hz, 2H), 8.21 (d, J = 8.1 Hz, 1H), 7.99 (d, J = 8.2 Hz, 2H), 7.67 (d, J = 7.2 Hz, 1H), 7.37−7.23 (m, 4H), 7.09 (t, J = 4.8 Hz, 1H), 6.90 (s, 1H), 4.39 (q, J = 7.0 Hz, 2H), 1.40 (q, J = 7.0 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 166.3 (C_q), 158.1 (CH), 157.9 (C_q), 139.3 (C_q), 138.4 (C_q), 138.4 (C_q), 129.3 (CH), 129.1 (C_q), 128.8 (C_q), 127.8 (CH), 124.1 (CH), 122.3 (CH), 120.9 (CH), 117.6 (CH), 113.0 (CH), 109.5 (CH), 60.9 (CH_2), 14.3 (CH_3). IR (KBr): 1728, 1615, 1562, 1510, 1425, 1346, 1247, 1031, 911, 835 cm^{-1}. MS (EI) *m/z* (relative intensity) 343 (100) [M^+], 314 (62), 270 (18), 190 (10), 134 (20). HR-MS (EI) *m/z* calcd for $C_{21}H_{17}N_3O_2$ [M^+] 343.1321, found 343.1322.



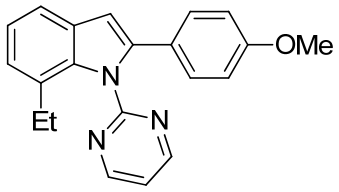
2-{4-(*N*,*N*-dimethylamino)phenyl}-1-(pyrimidin-2-yl)-1*H*-indole (3g): The representative procedure B was followed using 1-(pyrimidin-2-yl)-1*H*-indole (**1a**) (97.5 mg, 0.50 mmol) and 4-dimethylamino bromobenzene (120.0 mg, 0.60 mmol). After 22 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 4/3) yielded **3g** (131 mg, 83%) as a colorless solid. M. p. = 171−172 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.71 (d, J = 4.9 Hz, 2H), 8.05 (m, 1H), 7.62 (m, 1H), 7.26−7.11 (m, 5H), 6.71 (s, 1H), 6.66 (d, J = 8.8 Hz, 2H), 2.96 (s, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 158.4 (C_q), 158.2 (CH), 149.5 (C_q), 141.1 (C_q), 137.9 (C_q), 129.6 (CH), 129.0 (CH), 122.7 (CH), 121.8 (CH), 120.2 (CH), 117.5 (CH), 112.3 (CH), 112.1 (C_q), 112.1 (C_q), 106.2 (CH), 40.5 (CH_3). IR (KBr): 2893, 1609, 1561, 1508, 1421, 1347, 1260, 1200, 794, 743 cm^{-1}. MS (EI) *m/z* (relative intensity) 314 (100) [M^+], 297 (14), 270 (7), 157 (6). HR-MS (EI) *m/z* calcd for $C_{20}H_{18}N_4$ [M^+] 314.1531, found 314.1528.



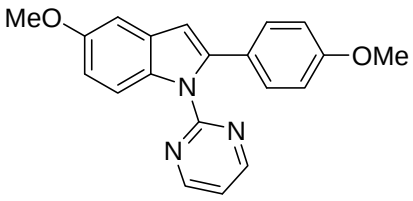
1-(Pyrimidin-2-yl)-2-(thiophen-2-yl)-1*H*-indole (3h): The representative procedure B was followed using 1-(pyrimidin-2-yl)-1*H*-indole (**1a**) (97.5 mg, 0.50 mmol) and 2-bromothiophene (97.8 mg, 0.60 mmol). After 22 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 4/1) yielded **3h** (58 mg, 42%) as a colorless solid. M. p. = 98−99 °C. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 8.75 (d, J = 4.8 Hz, 2H), 8.02 (d, J = 8.3 Hz, 1H), 7.64 (d, J = 6.4 Hz, 1H), 7.33−7.15 (m, 3H), 7.17 (t, J = 4.9 Hz, 1H), 6.99 (m, 1H), 6.94 (dd, J = 3.6, 1.2 Hz, 1H), 6.88 (s, 1H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 158.3 (CH), 157.7 (C_q), 138.0 (C_q), 135.3 (C_q), 133.4 (C_q), 128.9 (C_q), 126.9 (CH), 126.4 (CH), 125.6 (CH), 123.7 (CH), 122.1 (CH), 120.6 (CH), 118.0 (CH), 112.5 (CH), 108.6 (CH). IR (KBr): 1560, 1452, 1423, 1341, 1257, 1216, 851, 823, 784, 744 cm^{-1}. MS (EI) *m/z* (relative intensity) 277 (100) [M$^+$], 244 (17), 138 (8). HR-MS (ESI) *m/z* calcd for $C_{16}H_{12}N_3S$ [M+H$^+$] 278.0746, found 278.0746.



2-(3,4,5-Trimethoxyphenyl)-1-(pyrimidin-2-yl)-1*H*-indole (3i): The representative procedure B was followed using 1-(pyrimidin-2-yl)-1*H*-indole (**1a**) (97.5 mg, 0.50 mmol) and 3,4,5-trimethoxy bromobenzene (148 mg, 0.60 mmol). After 22 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 1/1) yielded **3i** (156 mg, 86%) as a colorless solid. M. p. = 92−93 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.71 (d, J = 4.9 Hz, 2H), 8.05 (d, J = 7.9 Hz, 1H), 7.65 (d, J = 6.9 Hz, 1H), 7.26 (m, 2H), 7.13 (t, J = 4.8 Hz, 1H), 6.82 (s, 1H), 6.50 (s, 2H), 3.86 (s, 3H), 3.71 (s, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 158.2 (CH), 158.1 (C_q), 152.8 (C_q), 140.2 (C_q), 138.0 (C_q), 137.3 (C_q), 129.2 (C_q), 129.1 (C_q), 123.5 (CH), 122.1 (CH), 120.6 (CH), 117.7 (CH), 112.4 (CH), 107.6 (CH), 105.4 (CH), 60.4 (CH_3), 56.0 (CH_3). IR (KBr): 1568, 1501, 1417, 1351, 1237, 1128, 998, 814, 743 cm^{-1}. MS (EI) *m/z* (relative intensity) 361 (100) [M$^+$], 346 (50), 260 (27). HR-MS (ESI) *m/z* calcd for $C_{21}H_{20}N_3O_3$ [M+H$^+$] 362.1499, found 362.1498.

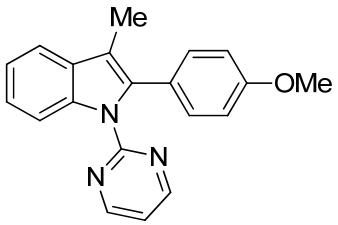


7-Ethyl-2-(4-methoxyphenyl)-1-(pyrimidin-2-yl)-1*H*-indole (3j): The representative procedure B was followed using 7-ethyl-1-(pyrimidin-2-yl)-1*H*-indole (**1b**) (112 mg, 0.50 mmol) and 4-bromoanisole (**2a**) (112 mg, 0.60 mmol). After 22 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 4/1) yielded **3j** (150 mg, 91%) as a colorless solid. M. p. = 148−149 °C. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 8.74 (d, J = 4.9 Hz, 2H), 7.56 (d, J = 7.7 Hz, 1H), 7.27 (d, J = 8.8 Hz, 2H), 7.22 (t, J = 4.9 Hz, 1H), 7.18 (dd, J = 7.6, 7.6 Hz, 1H), 7.06 (d, J = 6.8 Hz, 1H), 6.79 (d, J = 8.8 Hz, 2H), 6.73 (s, 1H), 3.78 (s, 3H), 2.34 (q, J = 7.5 Hz, 2H), 0.97 (t, J = 7.5 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 160.3 (C_q), 158.9 (C_q), 158.1 (CH), 142.0 (C_q), 136.9 (C_q), 130.1 (CH), 129.6 (C_q), 128.0 (C_q), 125.3 (C_q), 123.2 (CH), 121.3 (CH), 119.7 (CH), 118.5 (CH), 113.5 (CH), 104.8 (CH), 55.1 (CH_2), 25.2 (CH_3), 14.3 (CH_3). IR (KBr): 1563, 1502, 1418, 1243, 1176, 1035, 826, 803, 743 cm^{-1}. MS (EI) *m/z* (relative intensity) 329 (100) [M^+], 314 (43), 270 (14), 164 (12), 135 (14). HR-MS (ESI) *m/z* calcd for $C_{21}H_{20}N_3O$ [M+H^+] 330.1601, found 330.1598.

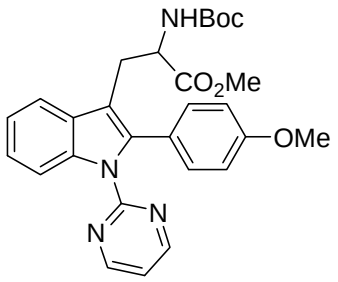


5-Methoxy-2-(4-methoxyphenyl)-1-(pyrimidin-2-yl)-1*H*-indole (3k): The representative procedure B was followed using 5-methoxy-1-(pyrimidin-2-yl)-1*H*-indole (**1c**) (113 mg, 0.50 mmol) and 4-bromoanisole (**2a**) (112 mg, 0.60 mmol). After 22 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 2/1) yielded **3k** (125 mg, 76%) as a colorless solid. M. p. = 111−112 °C. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 8.64 (d, J = 4.9 Hz, 2H), 8.05 (d, J = 9.0 Hz, 1H), 7.22 (d, J = 8.8 Hz, 2H), 7.10 (d, J = 2.5 Hz, 1H), 7.06 (t, J = 4.8 Hz, 1H), 6.91 (dd, J = 9.0, 2.6 Hz, 1H), 6.85 (d, J = 8.8 Hz, 2H), 6.68 (s, 1H), 3.88 (s, 3H), 3.81 (s, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 158.8 (C_q), 158.1 (CH), 155.5 (C_q), 155.5 (C_q), 140.8 (C_q), 132.9 (C_q), 130.0 (C_q), 129.3 (CH), 126.5 (C_q), 117.3 (CH), 113.7 (CH),

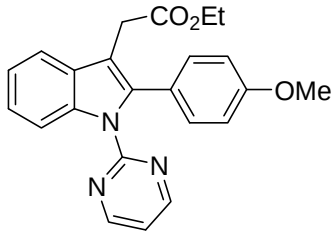
113.5 (CH), 112.4 (CH), 107.2 (CH), 102.5 (CH), 55.7 (CH_3), 55.2 (CH_3). IR (KBr): 1612, 1563, 1425, 1338, 1297, 1217, 1149, 909, 807, 732 cm^{-1}. MS (EI) *m/z* (relative intensity) 331 (100) [M^+], 316 (10), 288 (28), 244 (12). HR-MS (ESI) *m/z* calcd for $C_{20}H_{18}N_3O_2$ [$M+H^+$] 332.1394, found 332.1389.



2-(4-Methoxyphenyl)-3-methyl-1-(pyrimidin-2-yl)-1*H*-indole (3l): The representative procedure B was followed using 3-methyl-1-(pyrimidin-2-yl)-1*H*-indole (**1d**) (105 mg, 0.50 mmol) and 4-bromoanisole (**2a**) (112 mg, 0.60 mmol). After 22 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 5/1) yielded **3l** (129 mg, 82%) as a colorless solid. M. p. = 120−121 °C. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 8.60 (d, J = 4.8 Hz, 2H), 8.18 (d, J = 8.8 Hz, 1H), 7.64 (d, J = 7.1 Hz, 1H), 7.35−7.26 (m, 2H), 7.22 (d, J = 8.6 Hz, 2H), 7.00 (t, J = 4.8 Hz, 1H), 6.90 (d, J = 8.7 Hz, 2H), 3.84 (s, 3H), 2.38 (s, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 158.4 (C_q), 158.1 (C_q), 157.9 (CH), 136.7 (C_q), 135.7 (C_q), 130.7 (CH), 130.5 (C_q), 126.0 (C_q), 123.4 (CH), 121.6 (CH), 118.7 (CH), 116.8 (CH), 114.2 (C_q), 113.3 (CH), 112.7 (CH), 55.1 (CH_3), 9.4 (CH_3). IR (KBr): 1560, 1508, 1420, 1344, 1292, 1173, 1035, 806, 705 cm^{-1}. MS (EI) *m/z* (relative intensity) 315 (100) [M^+], 300 (10), 272 (12), 236 (15). HR-MS (ESI) *m/z* calcd for $C_{20}H_{18}N_3O$ [$M+H^+$] 316.1444, found 316.1438.

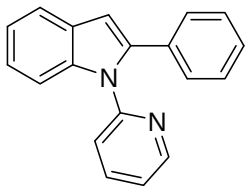


***tert*-Butyl 1-(methoxycarbonyl)-2-{2-(4-methoxyphenyl)-1-(pyrimidin-2-yl)-1*H*-indol-3-yl}ethylcarbamate (3m):** The representative procedure B was followed using *tert*-butyl 1-(methoxycarbonyl)-2-(1-(pyrimidin-2-yl)-1*H*-indol-3-yl)ethylcarbamate (**1e**) (198 mg, 0.50 mmol), 4-bromoanisole (**2a**) (112 mg, 0.60 mmol) **5c** (54.0 mg, 0.30 mmol, 60.0 mol %) and $[RuCl_2(p\text{-cymene})]_2$ (15.3 mg, 5.0 mol %). After 22 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 2/1) yielded **3m** (103 mg, 41%) as a colorless solid. M. p. = 84−85 °C. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 8.58 (d, J = 4.8 Hz, 2H), 8.08 (d, J = 8.1 Hz, 1H), 7.66 (d, J = 7.0 Hz, 1H), 7.32−7.23 (m, 2H), 7.03 (d, J = 8.7 Hz, 2H), 7.03 (t, J = 4.8 Hz, 1H), 6.87 (d, J = 8.6 Hz, 2H), 4.78 (d, J = 7.9 Hz, 1H), 4.51 (m, 1H), 3.83 (s, 3H), 3.63(I)/3.49(II) (s, 3H), 3.29 (m, 2H), 1.34(I)/1.16(II) (s, 9H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 172.7 (C_q), 158.9 (C_q), 157.9 (CH), 157.7 (C_q), 155.0 (C_q), 137.8 (C_q), 136.5 (C_q) 131.2 (CH), 129.3 (C_q), 125.2 (C_q), 123.7 (CH), 121.9 (CH), 119.0 (CH), 117.2 (CH), 113.7 (CH), 112.8 (CH), 112.7 (C_q), 79.5 (C_q), 55.2 (CH_3), 53.7 (CH), 52.1 (CH_3), 28.2 (CH_3), 27.3 (CH_2). IR (KBr): 3431, 1700, 1615, 1560, 1507, 1456, 1366, 1246, 911, 734 cm^{-1}. MS (ESI) *m/z* (relative intensity) 1027 (100) [2M+Na$^+$], 525 (86) [M+Na$^+$]. HR-MS (ESI) *m/z* calcd for $C_{28}H_{30}N_4O_5Na$ [M+Na$^+$] 525.2108, found 525.2105.

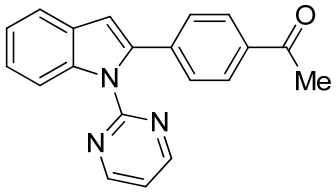


Ethyl 2-{2-(4-methoxyphenyl)-1-(pyrimidin-2-yl)-1*H*-indol-3-yl}acetate (3n): The representative procedure B was followed using 2-{1-(pyrimidin-2-yl)-1*H*-indol-3-yl}acetate (**1f**) (141 mg, 0.50 mmol) and 4-bromoanisole (**2a**) (112 mg, 0.60 mmol). After 22 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 2/1) yielded **3n** (159 mg, 82%) as a colorless solid. M. p. = 91−92 °C. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 8.59 (d, J = 4.8 Hz, 2H), 8.14 (d, J = 8.6 Hz, 1H), 7.70 (d, J = 8.6 Hz, 1H), 7.34−7.24 (m, 4H), 7.03 (t, J = 4.8 Hz, 1H), 6.88 (d, J = 8.8 Hz, 2H), 4.18 (q, J = 7.2 Hz, 2H), 3.83 (s, 3H), 3.73 (s, 2H), 1.26 (t, J = 7.1 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 171.7 (C_q), 158.9 (C_q), 157.9 (CH), 137.8 (C_q), 136.6 (C_q), 131.0 (CH), 129.3 (C_q), 129.3 (C_q), 125.0 (C_q), 123.6 (CH), 121.9 (CH), 119.1 (CH), 117.2 (CH), 113.4 (CH), 112.8 (CH), 111.3 (C_q), 60.8 (CH_2),

55.1 (CH_3), 31.2 (CH_2), 14.2 (CH_3). IR (KBr): 1732, 1615, 1562, 1509, 1368, 1247, 1031, 835, 733 cm^{-1}. MS (EI) *m/z* (relative intensity) 387 (42) [M^+], 314 (100), 270 (14), 234 (8). HR-MS (ESI) *m/z* calcd for $C_{23}H_{20}N_3O_3$ [$M-H^+$] 386.1510, found 386.1509.

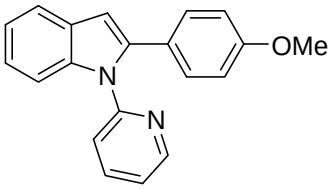


2-Phenyl-1-(pyridin-2-yl)-1*H*-indole (3o): The representative procedure B was followed using 1-(pyridin-2-yl)-1*H*-indole (**1g**) (97.0 mg, 0.50 mmol) and bromobenzene (94.2 mg, 0.60 mmol). After 22 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 5/1) yielded **3o** (123 mg, 91%) as a colorless solid. M. p. = 126−127 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.65 (m, 1H), 8.71−7.60 (m, 3H), 8.30−7.18 (m, 8H), 6.90 (d, *J* = 8.1 Hz, 1H), 6.82 (s, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 152.1 (C_q), 149.2 (CH), 140.0 (C_q), 138.5 (C_q), 137.7 (CH), 132.7 (C_q), 128.7 (CH), 128.7 (C_q), 128.3 (CH), 127.4 (CH), 123.0 (CH), 122.0 (CH), 121.6 (CH), 121.3 (CH), 120.6 (CH), 111.5 (CH), 105.6 (CH). IR (KBr): 1581, 1475, 1375, 1290, 1213, 1151, 1097, 1072, 1046, 740 cm^{-1}. MS (EI) *m/z* (relative intensity) 270 (76) [M^+], 169 (100), 134 (25). HR-MS (ESI) *m/z* calcd for $C_{19}H_{15}N_2$ [$M+H^+$] 271.1230, found 271.1233. The spectral data were in accordance with those reported in the literature.[8]

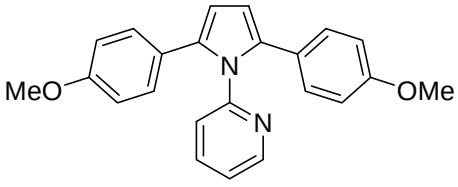


2-(4-Acetylphenyl)-1-(pyrimidin-2-yl)-1*H*-indole (3p): The representative procedure B was followed using 1-(pyrimidin-2-yl)-1*H*-indole (**1a**) (97.5 mg, 0.50 mmol), 4-chloroacetophenone (92.8 mg, 0.60 mmol) and **4** (15.9 mg, 10 mol %). After 22 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 2/1) yielded **3p**

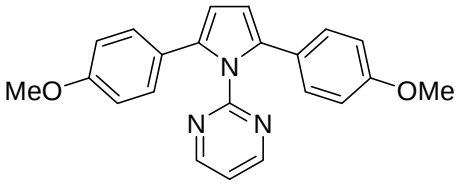
(99 mg, 63%) as a colorless solid. M. p. = 147−148 °C. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 8.67 (d, J = 4.8 Hz, 2H), 8.20 (d, J = 7.8 Hz, 1H), 7.90 (d, J = 8.6 Hz, 2H), 7.67 (d, J = 7.7 Hz, 1H), 7.38 (d, J = 8.1 Hz, 2H), 7.35−7.23 (m, 2H), 7.13 (t, J = 4.8 Hz, 1H), 6.90 (s, 1H), 2.61 (s, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 197.6 (C_q), 158.2 (CH), 157.9 (C_q), 139.2 (C_q), 138.7 (C_q), 138.5 (C_q), 135.4 (C_q), 129.1 (C_q), 128.2 (CH), 128.0 (CH), 124.2 (CH), 122.4 (CH), 121.0 (CH), 117.7 (CH), 113.1 (CH), 109.7 (CH), 26.6 (CH_3). IR (KBr): 1679, 1603, 1561, 1421, 1345, 1182, 956, 811, 742 cm^{-1}. MS (EI) *m/z* (relative intensity) 313 (100) [M^+], 298 (14), 270 (32). HR-MS (ESI) *m/z* calcd for $C_{20}H_{16}N_3O$ [M+H^+] 314.1288, found 314.1290.



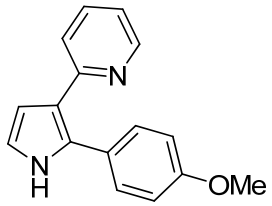
2-(4-Methoxyphenyl)-1-(pyridin-2-yl)-1*H*-indole (3q): The representative procedure B was followed using 1-(pyridin-2-yl)-1*H*-indole (**1g**) (97.0 mg, 0.50 mmol), 1-chloro-4-methoxybenzene (85.5 mg, 0.60 mmol) and **5c** (27.0 mg, 0.15 mmol, 30 mol %). After 22 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 6/1) yielded **3q** (113 mg, 75%) as a colorless solid. M. p. = 124−125 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.66 (m, 1H), 8.70−7.60 (m, 3H), 8.26−7.17 (m, 5H), 6.89 (d, J = 8.1 Hz, 1H), 6.83 (d, J = 8.9 Hz, 2H), 6.75 (d, J = 0.6 Hz, 1H), 3.80 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 159.0 (C_q), 152.1 (C_q), 149.0 (CH), 139.8 (C_q), 138.3 (C_q), 137.8 (CH), 130.0 (CH), 128.8 (C_q), 125.1 (C_q), 122.7 (CH), 122.1 (CH), 121.5 (CH), 121.3 (CH), 120.3 (CH), 113.8 (CH), 111.4 (CH), 104.7 (CH), 55.2 (CH_3). IR (KBr): 1568, 1450, 1371, 1244, 1173, 1111, 1075, 843, 790, 742 cm^{-1}. MS (EI) *m/z* (relative intensity) 300 (100) [M^+], 285 (10), 256 (18), 207 (16), 150 (11), 128 (13). HR-MS (ESI) *m/z* calcd for $C_{20}H_{17}N_2O$ [M+H^+] 301.1335, found 301.1332.



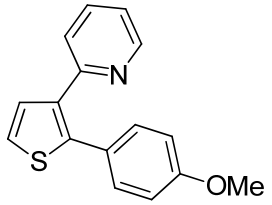
2-{2,5-bis(4-Methoxyphenyl)-1*H*-pyrrol-1-yl}pyridine (9a): The representative procedure B was followed using 2-(1*H*-pyrrol-1-yl)pyridine (**8a**) (72.0 mg, 0.50 mmol), 4-bromoanisole (**2a**) (224 mg, 1.20 mmol) **5c** (54.0 mg, 0.30 mmol, 60.0 mol %) and $[RuCl_2(p\text{-cymene})]_2$ (15.3 mg, 5.0 mol %). After 22 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 1/1) yielded **9a** (120 mg, 67%) as a colorless solid. M. p. = 130−131 °C. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 8.46 (ddd, J = 4.8, 1.8, 0.6 Hz, 1H), 7.56 (td, J = 7.7, 1.9 Hz, 1H), 7.18 (ddd, J = 7.4, 4.8, 1.0 Hz, 1H), 7.04 (d, J = 8.8 Hz, 4 H), 6.96 (d, J = 7.8 Hz, 1H), 6.74 (d, J = 8.8 Hz, 4 H), 6.40 (s, 2H), 3.76 (s, 6 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 158.1 (CH), 152.4 (C_q), 148.8 (CH), 137.5 (C_q), 135.4 (C_q), 129.6 (CH), 125.9 (C_q), 123.8 (CH), 122.4 (CH), 113.4 (CH), 109.4 (CH), 55.1 (CH_3). IR (KBr): 1612, 1500, 1471, 1436, 1379, 1332, 1291, 1177, 830, 779 cm^{-1}. MS (EI) *m/z* (relative intensity) 356 (100) [M^+], 341 (29). HR-MS (ESI) *m/z* calcd for $C_{23}H_{20}N_2O_2Na$ [M+Na^+] 379.1417, found 379.1413.



2-{2,5-bis(4-Methoxyphenyl)-1*H*-pyrrol-1-yl}pyrimidine (9b): The representative procedure B was followed using 2-(1*H*-pyrrol-1-yl)pyrimidine (**8b**) (72.5 mg, 0.50 mmol), 4-bromoanisole (**2a**) (224 mg, 1.20 mmol) **5c** (54.0 mg, 0.30 mmol, 60.0 mol %) and $[RuCl_2(p\text{-cymene})]_2$ (15.3 mg, 5.0 mol %). After 22 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 1/1) yielded **9b** (128 mg, 72%) as a colorless solid. M. p. = 188−189 °C. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 8.61 (d, J = 4.8 Hz, 2H), 7.15 (t, J = 4.8 Hz, 1H), 7.04 (d, J = 8.8 Hz, 4H), 6.75 (d, J = 8.8 Hz, 4H), 6.38 (s, 2H), 3.76 (s, 6H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 158.8 (C_q), 158.3 (CH), 135.8 (C_q), 129.4 (CH), 126.1 (C_q), 119.3 (C_q), 119.2 (CH), 113.5 (CH), 110.1 (CH), 55.1 (CH_3). IR (KBr): 1610, 1566, 1501, 1430, 1250, 1028, 843, 794, 776, 742 cm^{-1}. MS (EI) *m/z* (relative intensity) 357 (100) [M^+], 342 (45), 299 (5), 270 (5). HR-MS (ESI) *m/z* calcd for $C_{22}H_{19}N_3O_2Na$ [M+Na^+] 380.1369, found 380.1368.



2-{2-(4-Methoxyphenyl)-1*H*-pyrrol-3-yl}pyridine (9c): The representative procedure B was followed using 2-(1*H*-pyrrol-3-yl)pyridine (**8c**) (86.4 mg, 0.60 mmol) and 4-bromoanisole (**2a**) (93.5 mg, 0.50 mmol). After 22 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 1/1) yielded **9c** (89 mg, 71%) as a colorless solid. M. p. = 196−197 °C. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 8.54 (d, J = 4.8 Hz, 1H), 8.28 (br s, 1H), 7.42 (td, J = 7.5, 1.8 Hz, 1H), 7.31 (d, J = 8.5 Hz, 2H), 7.17 (d, J = 8.0 Hz, 1H), 7.00 (m, 1H), 6.87 (d, J = 8.5 Hz, 2H), 6.83 (t, J = 2.5 Hz, 1H), 6.72 (t, J = 2.7 Hz, 1H), 3.81 (s, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 159.0 (C_q), 155.4 (C_q), 149.3 (CH), 135.6 (CH), 130.3 (C_q), 129.5 (CH), 125.9 (C_q), 122.2 (CH), 121.1 (C_q), 120.2 (CH), 117.9 (CH), 114.1 (CH), 110.6 (CH), 55.3 (CH_3). IR (KBr): 3002, 1594, 1559, 1493, 1290, 1250, 1153, 1027, 834, 747 cm^{-1}. MS (EI) *m/z* (relative intensity) 250 (75) [M^+], 249 (100), 234 (18), 206 (37), 57 (55). HR-MS (EI) *m/z* calcd for $C_{16}H_{14}N_2O$ [M^+] 250.1106, found 250.1100.

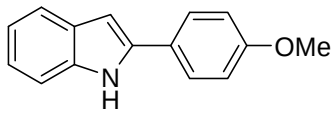


2-{2-(4-Methoxyphenyl)thiophen-3-yl}pyridine (11): The representative procedure B was followed using 2-(thiophen-3-yl)pyridine (**10**) (96.6 mg, 0.60 mmol) and 4-bromoanisole (**2a**) (93.5 mg, 0.50 mmol). After 22 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc: 3/1) yielded **11** (110 mg, 82%) as a colorless oil. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 8.61 (m, 1H), 7.47−7.42 (m, 2H), 7.27 (d, J = 5.3 Hz, 1H), 7.24 (d, J = 8.8 Hz, 2H), 7.12−7.06 (m, 2H), 6.82 (d, J = 8.8 Hz, 2H), 3.79 (s, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 159.3 (C_q), 154.9 (C_q), 149.5 (CH), 141.0 (C_q), 137.2 (C_q), 135.7 (CH), 130.7 (CH), 130.1

(CH), 126.5 (C_q), 123.8 (CH), 123.8 (CH), 121.4 (CH), 114.0 (CH), 55.2 (CH_3). IR (KBr): 1608, 1586, 1541, 1465, 1291, 1177, 1102, 991, 886, 746 cm^{-1}. MS (EI) *m/z* (relative intensity) 267 (83) [M^+], 266 (100), 251 (20), 223 (50), 112 (13). HR-MS (EI) *m/z* calcd for $C_{16}H_{13}NOS$ [M^+] 267.0718, found 267.0711.

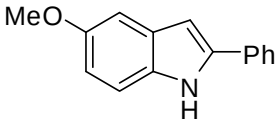
Representative Procedure C: Ruthenium-Catalyzed Direct Arylation of 1-(Pyrimidin-2-yl)-1*H*-indoles and Cleavage of the Pyrimidyl Group

A mixture of 1-(pyrimidin-2-yl)-1*H*-indole (**1a**) (97.5 mg, 0.50 mmol), 4-bromoanisole (**2a**) (112 mg, 0.60 mmol), $[RuCl_2(p\text{-cymene})]_2$ (7.7 mg, 2.5 mol %), **5c** (27.0 mg, 0.15 mmol, 30.0 mol %), K_2CO_3 (207 mg, 1.50 mmol) in *m*-xylene (2.0 mL) was stirred at 120 °C under nitrogen atmosphere for 22 h. After cooling the mixture to ambient temperature, DMSO (4.0 mL) and sodium ethoxide (102 mg, 1.50 mmol) were added, and the reaction mixture was stirred at 100 °C under nitrogen atmosphere for 24 h. After cooling to ambient temperature, the reaction mixture was diluted with EtOAc (75 mL) and washed with H_2O (2×30 mL). The aqueous phase was extracted with EtOAc (2×30 mL), and the combined organic phase was dried over Na_2SO_4. After filtration and evaporation of the solvents *in vacuo*, the crude product was purified by column chromatography on silica gel (*n*-hexane/EtOAc: 4/1) to yield **12a** (86 mg, 77%) as a colorless solid.

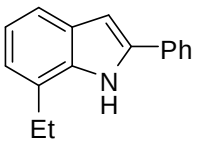


2-(4-Methoxyphenyl)-1*H*-indole (12a): M. p. = 226−227 °C. ^{1}H-NMR ($CDCl_3$/DMSO-[d_6], 300 MHz): δ = 10.13 (br s, 1H), 7.27 (d, J = 8.7 Hz, 2H), 7.09 (d, J = 7.7 Hz, 1H), 6.96 (d, J = 7.9 Hz, 1H), 6.64 (dd, J = 7.5, 7.5 Hz, 1H), 6.57 (dd, J = 7.5, 7.5 Hz, 1H), 6.51 (d, J = 8.7 Hz, 2H), 6.22 (d, J = 2.1 Hz, 1H), 3.40 (s, 3H). ^{13}C-NMR ($CDCl_3$/DMSO-[d_6], 75 MHz): δ = 158.5 (C_q), 137.6 (C_q), 136.6 (C_q), 128.6 (C_q), 126.0 (CH), 124.9 (C_q), 120.7 (CH), 119.3 (CH), 118.9 (CH), 113.6 (CH), 110.6 (CH), 97.1 (CH), 54.7 (CH_3). IR (KBr): 3411, 1550, 1502, 1456, 1246, 1179, 1031 cm^{-1}. MS (EI) *m/z* (relative intensity) 223 (100)

[M^+], 208 (70), 180 (25). HR-MS (ESI) *m/z* calcd for $C_{15}H_{13}NO$ [M^+] 223.0997, found 223.0999. The spectral data were in accordance with those reported in the literature.[9]

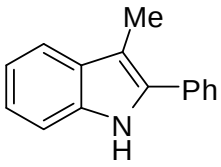


5-Methoxy-2-phenyl-1*H*-indole (12b): The representative procedure C was followed using 5-methoxy-1-(pyrimidin-2-yl)-1*H*-indole (**1c**) (338 mg, 1.50 mmol) and bromobenzene (283 mg, 1.80 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 1/1) yielded **12b** (240 mg, 72%) as a colorless solid. M. p. = 164−165 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.23 (br s, 1H), 7.66−7.63 (m, 2H), 7.44 (dd, J = 7.6, 7.6 Hz, 2H), 7.34−7.28 (m, 2H), 7.09 (d, J = 2.4 Hz, 1H), 6.86 (dd, J = 8.8, 2.5 Hz, 1H), 6.77 (dd, J = 2.2, 0.8 Hz, 1H), 3.87 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 154.5 (C_q), 138.6 (C_q), 132.4 (C_q), 132.0 (C_q), 129.7 (C_q), 129.0 (CH), 127.6 (CH), 125.0 (CH), 112.6 (CH), 111.6 (CH), 102.3 (CH), 99.8 (CH), 55.8 (CH_3). IR (KBr): 3420, 1618, 1586, 1475, 1446, 1214, 1149, 843, 802, 735 cm^{-1}. MS (EI) *m/z* (relative intensity) 223 (100) [M^+], 208 (62), 180 (85), 152 (23). HR-MS (EI) *m/z* calcd for $C_{15}H_{13}NO$ [M^+] 223.0997, found 223.0994. The spectral data were in accordance with those reported in the literature.[10]



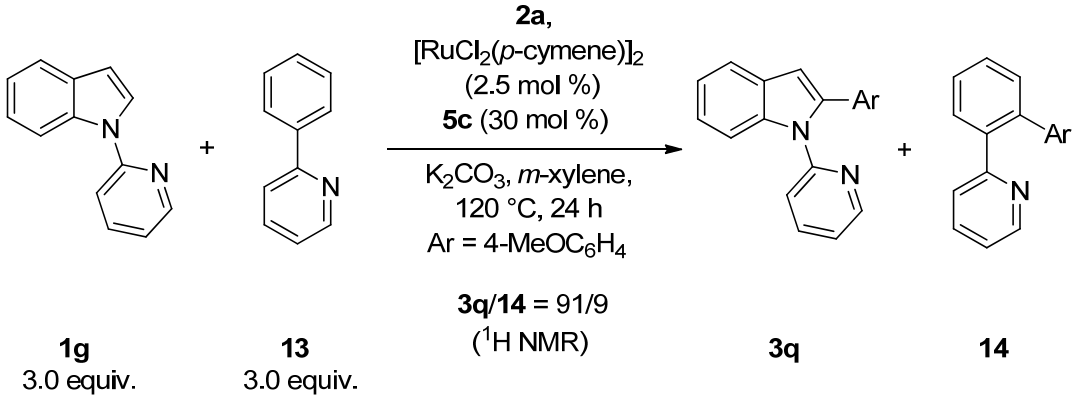
7-Ethyl-2-phenyl-1*H*-indole (12c): The representative procedure C was followed using 7-ethyl-1-(pyrimidin-2-yl)-1*H*-indole (**1b**) (335 mg, 1.50 mmol) and bromobenzene (283 mg, 1.80 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 2/1) yielded **12c** (225 mg, 68%) as a colorless solid. M. p. = 53−54 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.21 (br s, 1H), 7.70−7.67 (m, 2H), 7.51−7.42 (m, 3H), 7.35−7.30 (m, 1H), 7.12−7.03 (m, 2H), 6.84 (d, J = 2.1 Hz, 1H), 2.92 (q, J = 7.6 Hz, 2H), 1.42 (t, J = 7.6 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 137.5 (C_q), 135.6 (C_q), 132.6 (C_q), 129.0 (CH), 127.6 (CH), 126.2 (C_q), 126.2 (C_q), 125.2 (CH), 120.9 (CH), 120.5 (CH), 118.4 (CH), 100.6 (CH), 24.0 (CH_2), 13.8 (CH_3). IR (KBr): 3440, 2959, 1601, 1482, 1451, 1430, 1356, 1255, 1065, 743

cm^{-1}. MS (EI) *m/z* (relative intensity) 221 (95) [M^+], 206 (100), 178 (18), 103 (31). HR-MS (EI) *m/z* calcd for $C_{16}H_{15}N$ [M^+] 221.1204, found 221.1209. The spectral data were in accordance with those reported in the literature.[11]



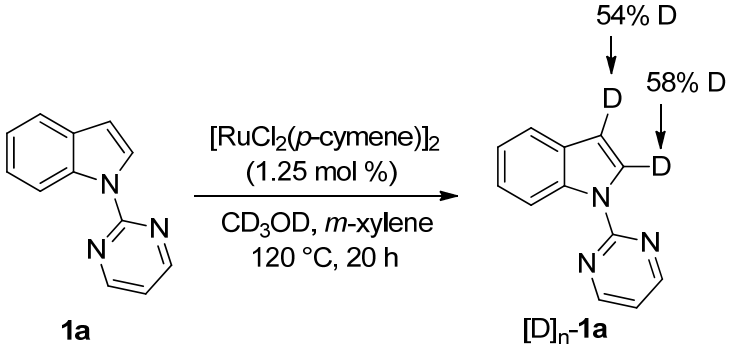
3-Methyl-2-phenyl-1*H*-indole (12d): The representative procedure C was followed using 3-methyl-1-(pyrimidin-2-yl)-1*H*-indole (**1d**) (314 mg, 1.50 mmol) and bromobenzene (283 mg, 1.80 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 2/1) yielded **12d** (228 mg, 73%) as a colorless solid. M. p. = 94−95 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.98 (br s, 1H), 7.65−7.56 (m, 3H), 7.48 (t, J = 7.7 Hz, 2H), 7.38−7.33 (m, 2H), 7.22−7.13 (m, 2H), 2.47 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 135.8 (C_q), 134.0 (C_q), 133.3 (C_q), 130.0 (C_q), 128.8 (CH), 127.7 (CH), 127.3 (CH), 122.3 (CH), 119.5 (CH), 118.9 (CH), 110.6 (CH), 108.7 (C_q), 9.6 (CH_3). IR (KBr): 3417, 1601, 1441, 1330, 1235, 1119, 1032, 917, 738 cm^{-1}. MS (EI) *m/z* (relative intensity) 207 (100) [M^+], 206 (91), 178 (10), 130 (24), 102 (11), 77 (18). HR-MS (EI) *m/z* calcd for $C_{15}H_{13}N$ [M^+] 207.1048, found 207.1053. The spectral data were in accordance with those reported in the literature.[12]

Scheme S-1. Intermolecular Competition Experiments with 2-Phenylpyridine and 1-(Pyridin-2-yl)-1*H*-indole (1g)



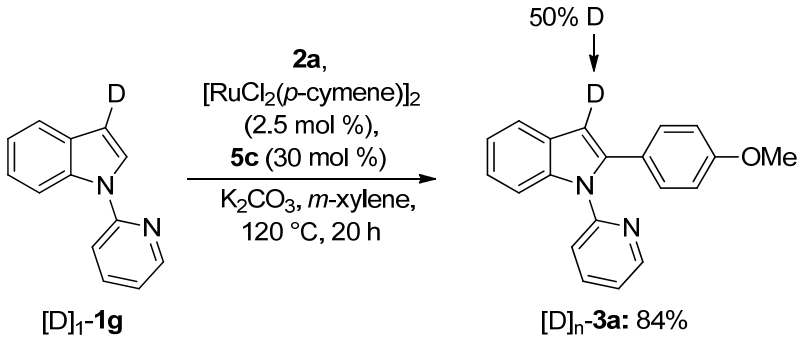
A mixture of 2-phenylpyridine (**13**) (233 mg, 1.50 mmol), 1-(pyridin-2-yl)-1*H*-indole (**1g**) (291 mg, 1.50 mmol) 4-bromoanisole (**2a**) (93.5 mg, 0.50 mmol), $[RuCl_2(p\text{-cymene})]_2$ (7.7 mg, 2.5 mol %), **5c** (27.0 mg, 0.15 mmol, 30 mol %), K_2CO_3 (207 mg, 1.50 mmol) in *m*-xylene (2.0 mL) was stirred at 120 °C under nitrogen atmosphere for 22 h. At ambient temperature, the reaction mixture was diluted with EtOAc (75 mL) and washed with saturated aqueous K_2CO_3 (2×30 mL). The aqueous phase was extracted with EtOAc (30 mL), and the combined organic phase was dried over Na_2SO_4. After filtration and evaporation of the solvents *in vacuo*, the mixture was analyzed by GC-MS to show complete conversion of 4-bromoanisole (**2a**). The ratio of **3q**/**14** in the crude mixture of products was determined to be 91/9 by ^{1}H-NMR.

Scheme S-2a. Experiments with Isotopically-Labeled Compounds



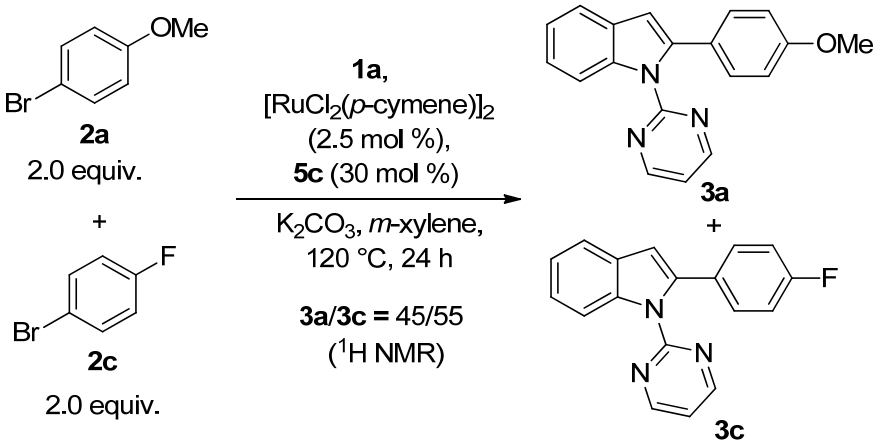
A mixture of 1-(pyrimidin-2-yl)-1*H*-indole (**1a**) (195 mg, 1.00 mmol), $[RuCl_2(p\text{-cymene})]_2$ (7.7 mg, 2.5 mol %), CD_3OD (0.5 mL) and *m*-xylene (1.5 mL) was stirred at 120 °C under nitrogen atmosphere for 22 h. At ambient temperature, the reaction mixture was diluted with EtOAc (75 mL) and washed with saturated aqueous K_2CO_3 (2×30 mL). The aqueous phase was extracted with EtOAc (30 mL), and the combined organic phase was dried over Na_2SO_4. After filtration and evaporation of the solvents *in vacuo*, the crude products were purified by column chromatography on silica gel (*n*-hexane/EtOAc: 4/1) to yield $[D_n]$-**1a** (190 mg, 97%) as a colorless solid. The deuterium incorporation was determined to be 58% at the position C-2 and 54% at the position C-3 of the indole **1a** by ^1H NMR.

Scheme S-2b. Experiments with Isotopically-Labeled Compounds



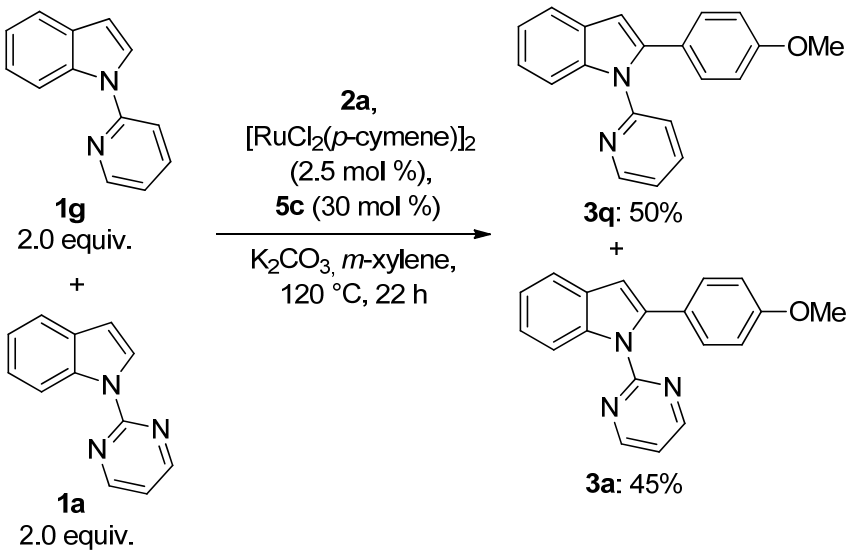
A mixture of 3-deuterio-1-(pyridin-2-yl)-1*H*-indole ([D_1]-**1g**) (97.5 mg, 0.50 mmol), 4-bromoanisole (**2a**) (112 mg, 0.60 mmol), [$RuCl_2$(*p*-cymene)]$_2$ (7.7 mg, 2.5 mol %), **5c** (27.0 mg, 0.15 mmol, 30 mol %) and K_2CO_3 (207 mg, 1.50 mmol) in *m*-xylene (2.0 mL) was stirred at 120 °C under nitrogen atmosphere for 22 h. At ambient temperature, the reaction mixture was diluted with EtOAc (75 mL) and washed with saturated aqueous K_2CO_3 (2×30 mL). The aqueous phase was extracted with EtOAc (30 mL), and the combined organic phase was dried over Na_2SO_4. After filtration and evaporation of the solvents *in vacuo*, the crude product was purified by column chromatography on silica gel (*n*-hexane/EtOAc: 6/1) to yield **3a**/[D_1]-**3a** (126 mg, 84%) as a colorless solid. The ratio of indoles **3a**/[D_1]-**3a** in the mixture of products was determined to be 50/50 by ^{1}H NMR.

Scheme S-3. Intermolecular Competition Experiments with 4-Bromoanisole (2a) and 4-Bromofluorobenzene (2c)



A mixture of 1-(pyrimidin-2-yl)-1*H*-indole (**1a**) (97.5 mg, 0.50 mmol), 4-bromoanisole (**2a**) (187 mg, 1.00 mmol), 4-bromofluorobenzene (**2c**) (175 mg, 1.00 mmol), $[RuCl_2(p\text{-cymene})]_2$ (7.7 mg, 2.5 mol %), **5c** (27.0 mg, 0.15 mmol, 30 mol %) and K_2CO_3 (207 mg, 1.5 mmol) in *m*-xylene (2.0 mL) was stirred at 120 °C under nitrogen atmosphere for 22 h. At ambient temperature, the reaction mixture was diluted with EtOAc (75 mL) and washed with saturated aueous K_2CO_3 (2×30 mL). The aqueous phase was extracted with EtOAc (30 mL), and the combined organic phase was dried over Na_2SO_4. After filtration and evaporation of the solvents *in vacuo*, the mixture was analyzed by GC-MS to show complete conversion of the indole **1a**. The ratio of **3a**/**3c** in the crude mixture of products was determined to be 45/55 by ^{1}H-NMR.

Scheme S-4. Intermolecular Competition Experiments with 1-(Pyridin-2-yl)-1*H*-indole (1g) and 1-(Pyrimidin-2-yl)-1*H*-indole (1a)



A mixture of 1-(pyridin-2-yl)-1*H*-indole (**1g**) (194 mg, 1.00 mmol), 1-(pyrimidin-2-yl)-1*H*-indole (**1a**) (195 mg, 1.00 mmol), 4-bromoanisole (**2a**) (93.5 mg, 0.50 mmol), $[RuCl_2(p\text{-cymene})]_2$ (7.7 mg, 2.5 mol %), **5c** (27.0 mg, 0.15 mmol, 30 mol %) and K_2CO_3 (207 mg, 1.50 mmol) in *m*-xylene (2.0 mL) was stirred at 120 °C under nitrogen atmosphere for 22 h. At ambient temperature, the reaction mixture was diluted with EtOAc (75 mL) and washed with saturated aqueous K_2CO_3 (2×30 mL). The aqueous phase was extracted with EtOAc (30 mL), and the combined organic phase was dried over Na_2SO_4. After filtration and evaporation of the solvents *in vacuo*, the crude products were purified by column chromatography on silica gel (*n*-hexane/EtOAc: 5/1) to give indoles **3q** (75 mg, 50%) and **3a** (68 mg, 45%).

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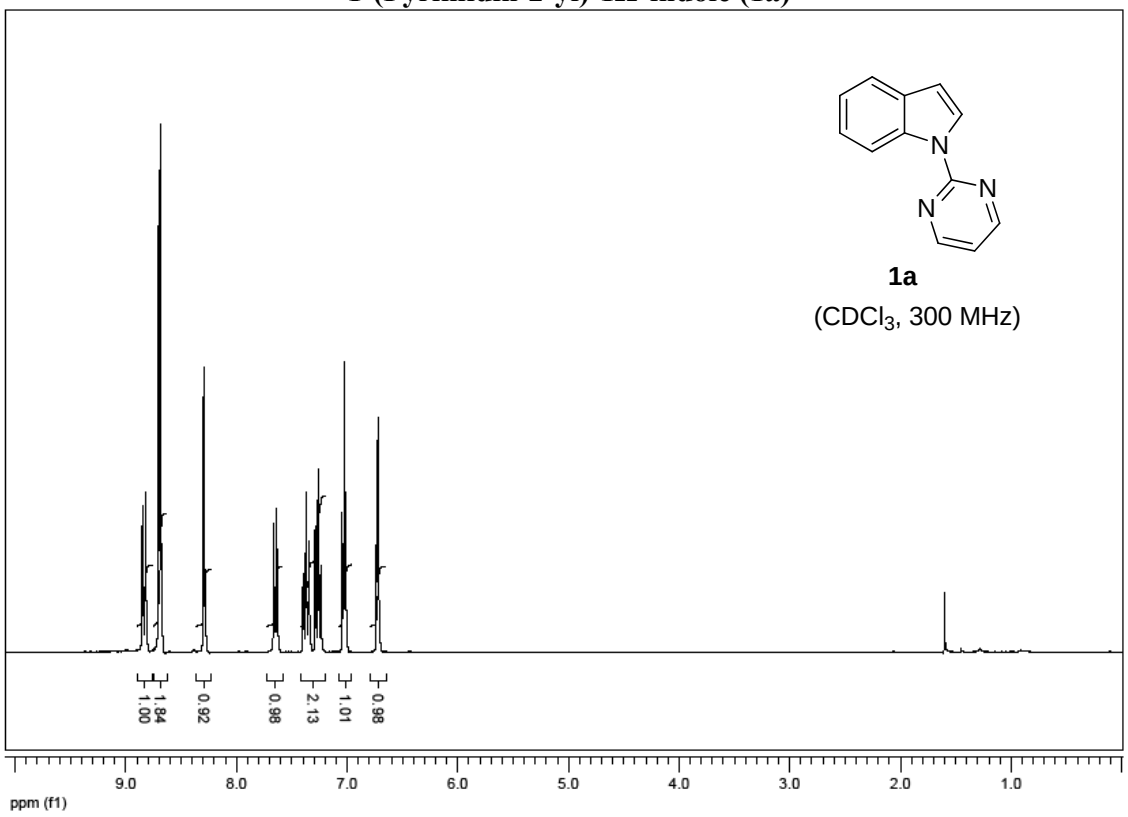
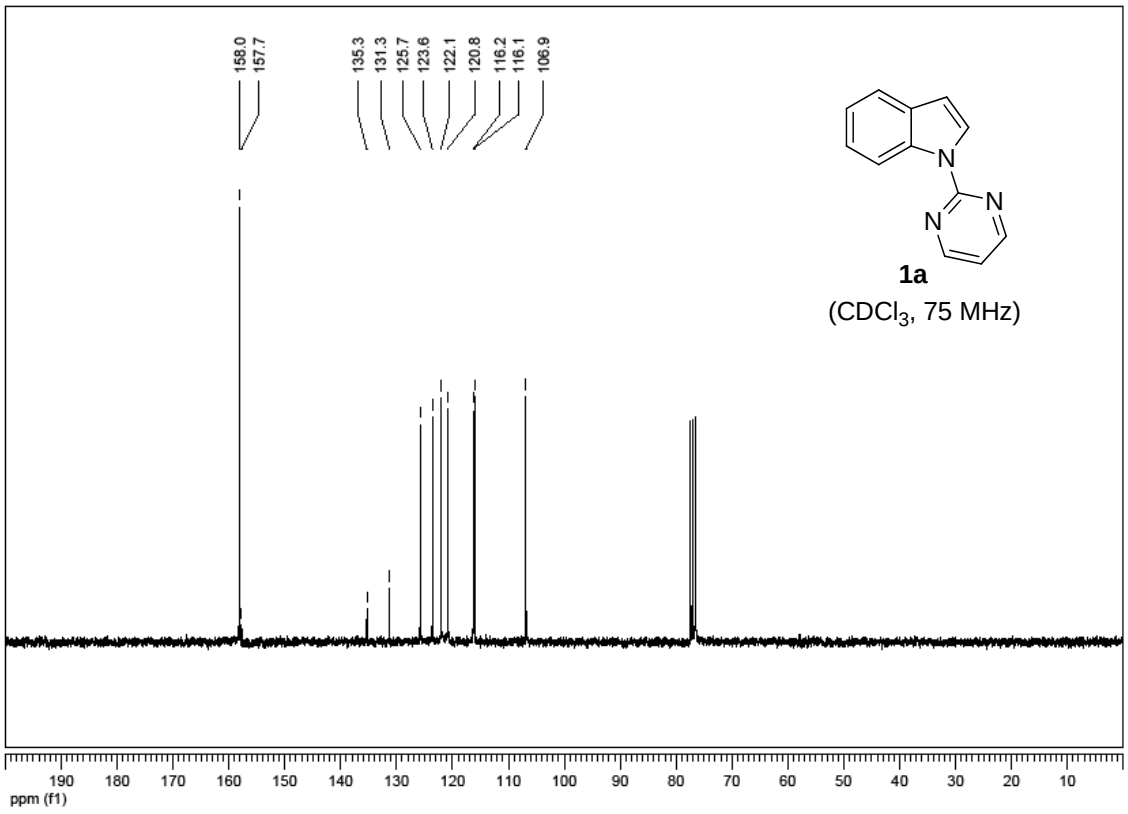
1-(Pyrimidin-2-yl)-1*H*-indole (1a)



1a

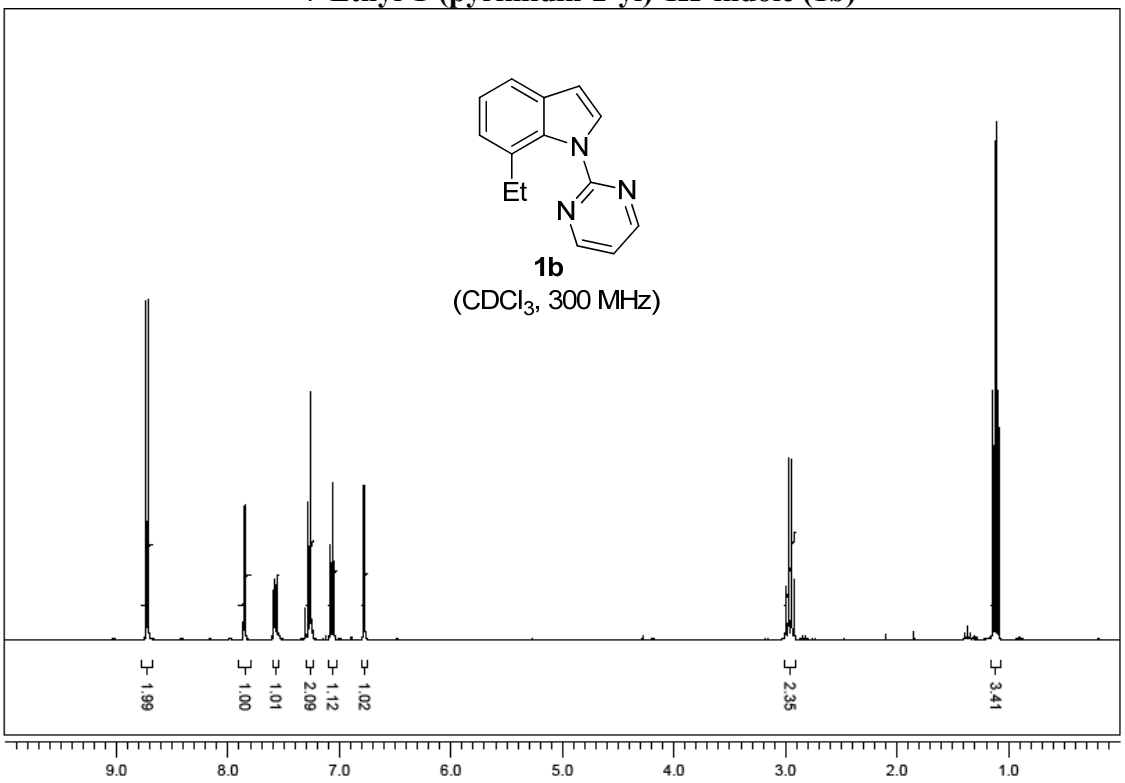
($CDCl_3$, 300 MHz)

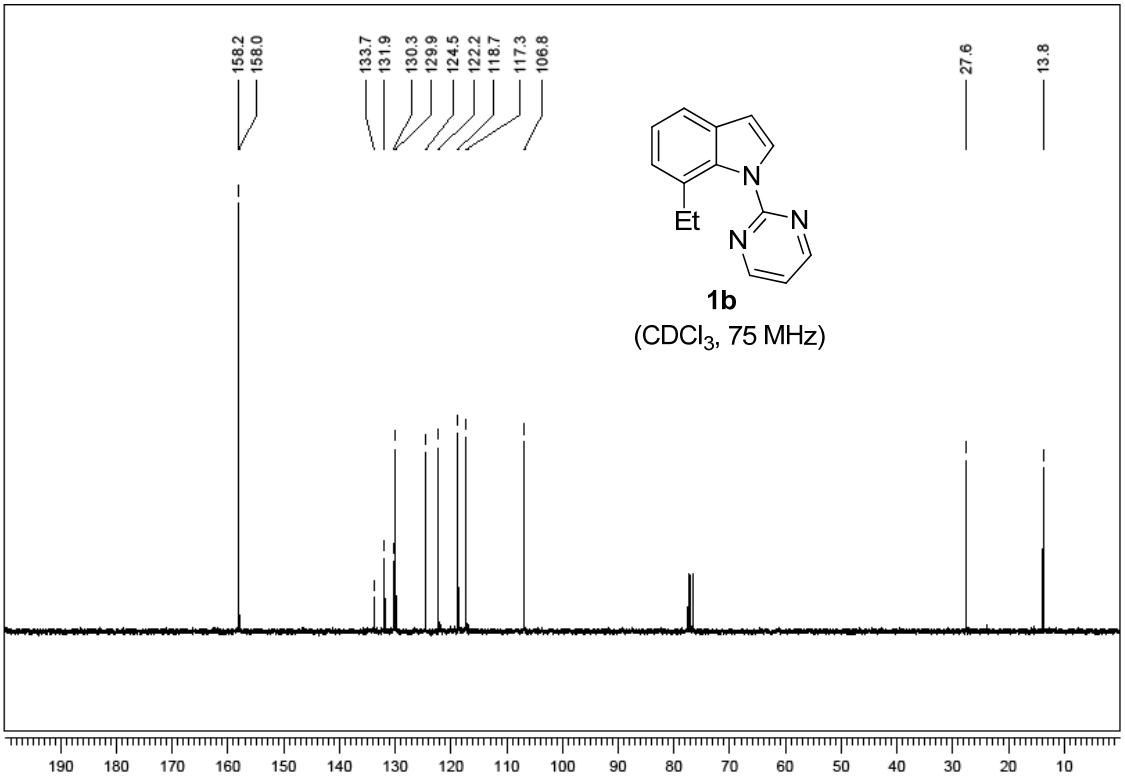


1a

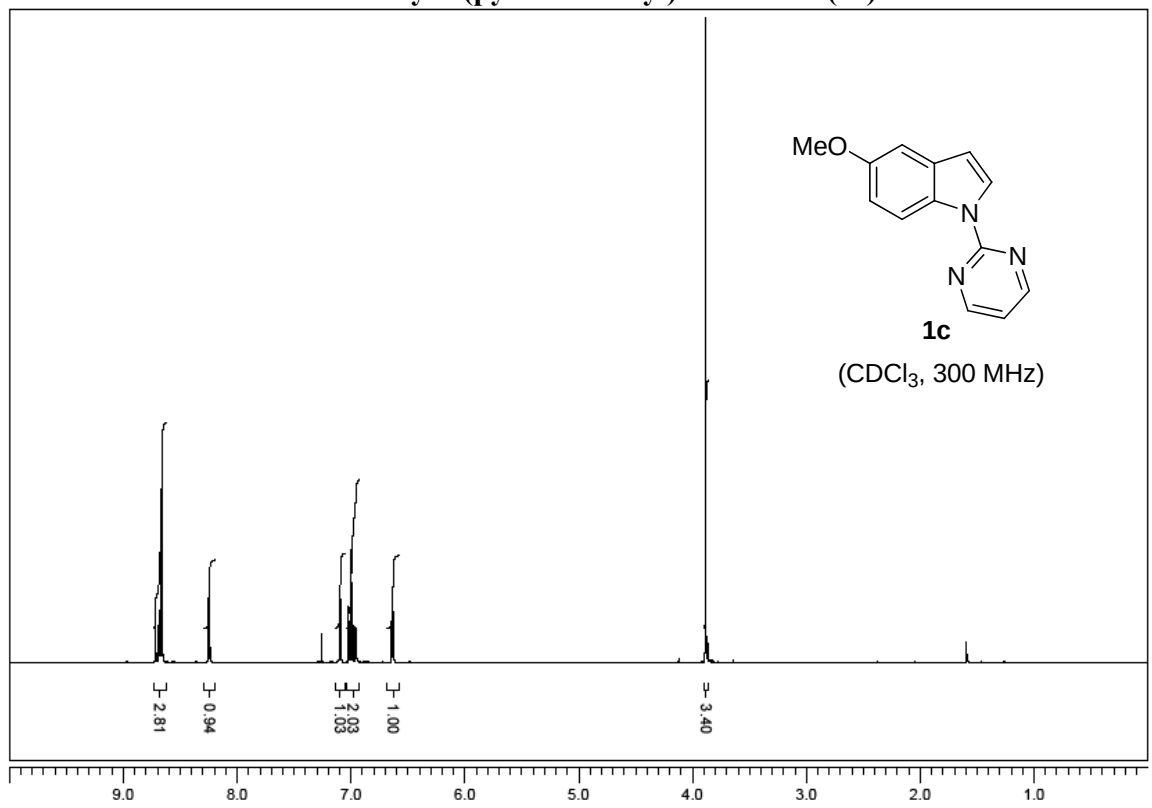
($CDCl_3$, 75 MHz)

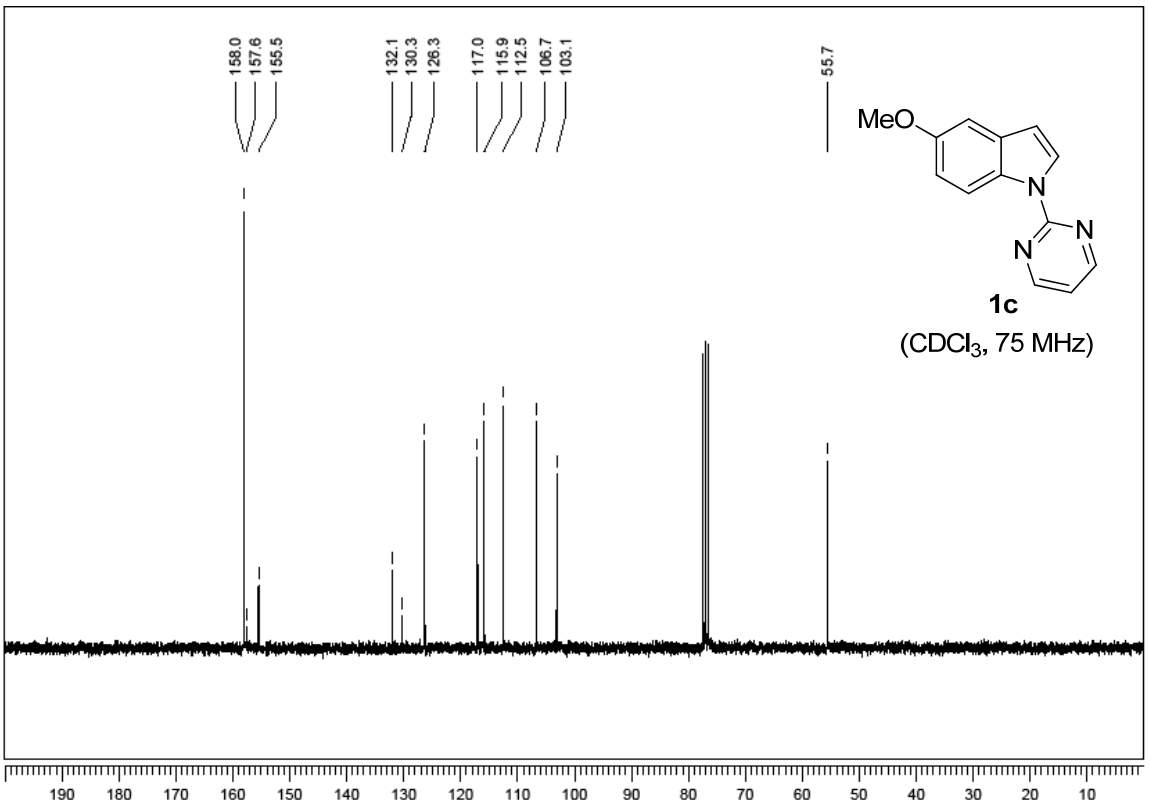
7-Ethyl-1-(pyrimidin-2-yl)-1*H*-indole (1b)



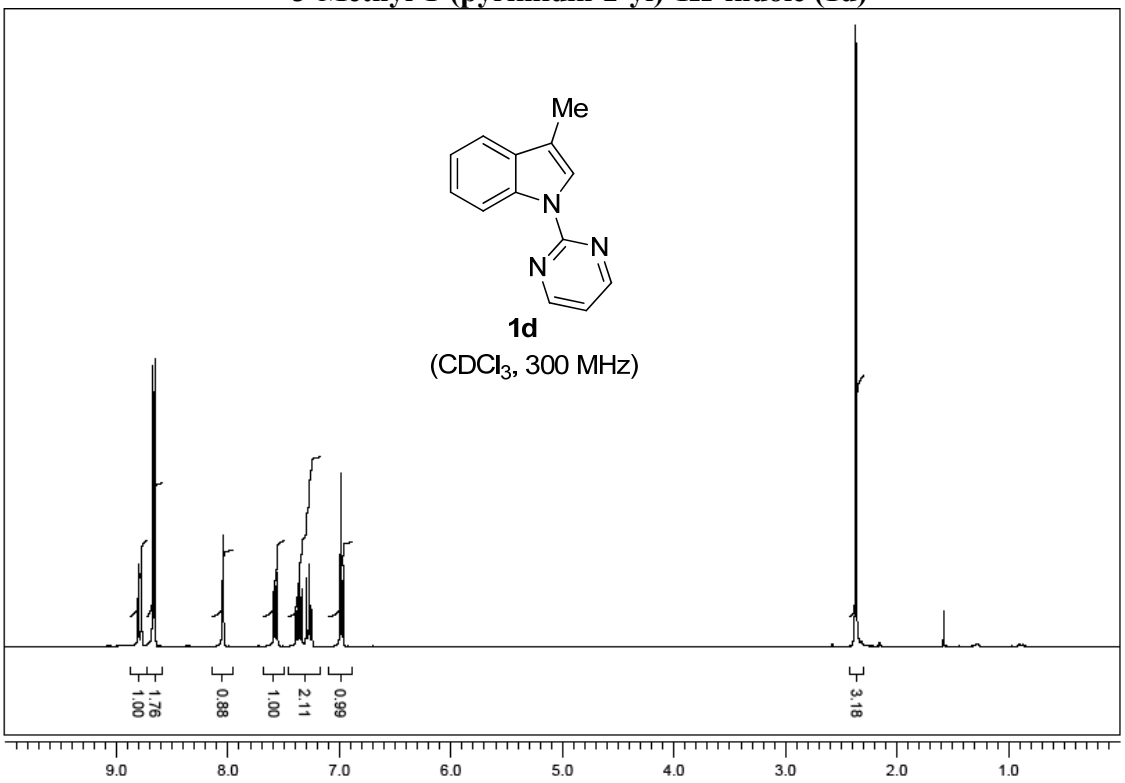


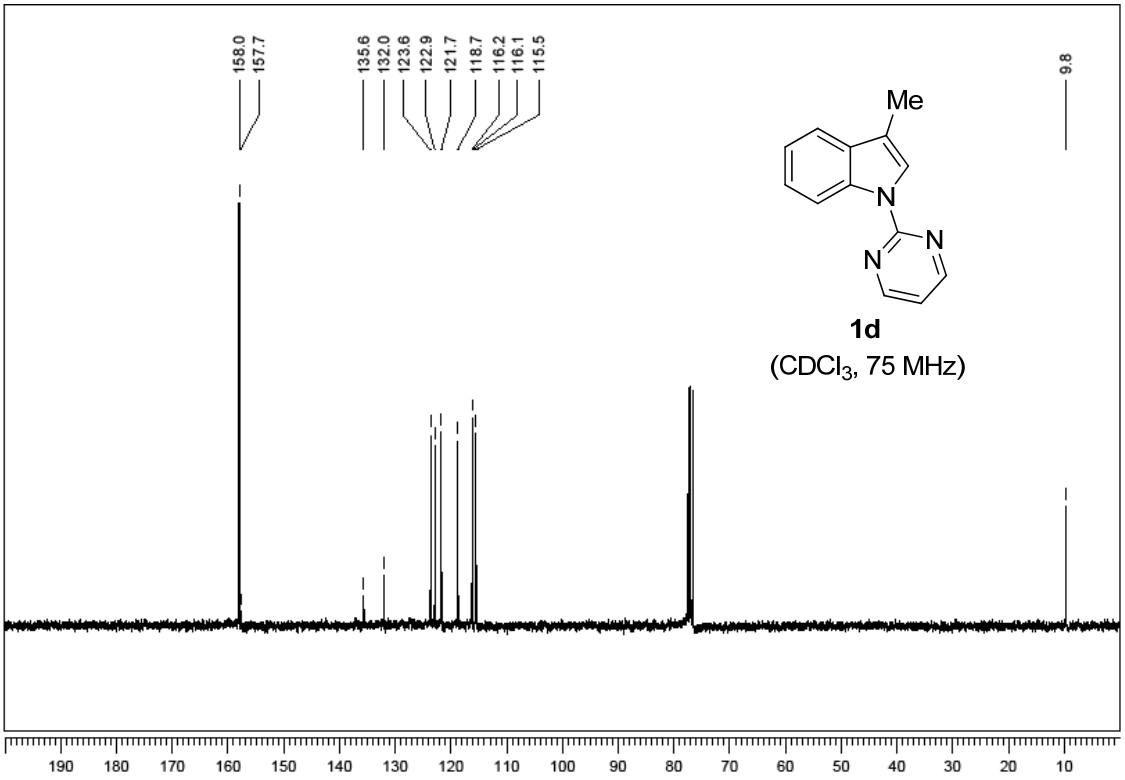
5-Methoxy-1-(pyrimidin-2-yl)-1*H*-indole (1c)



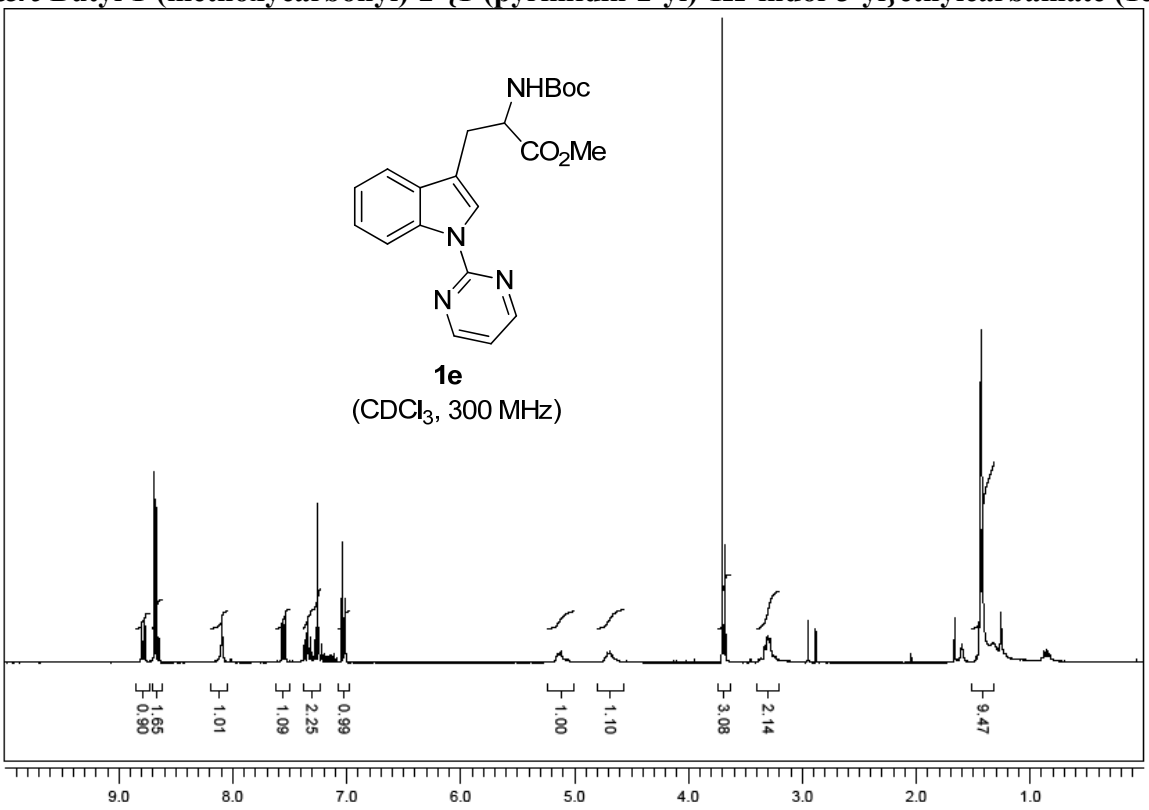


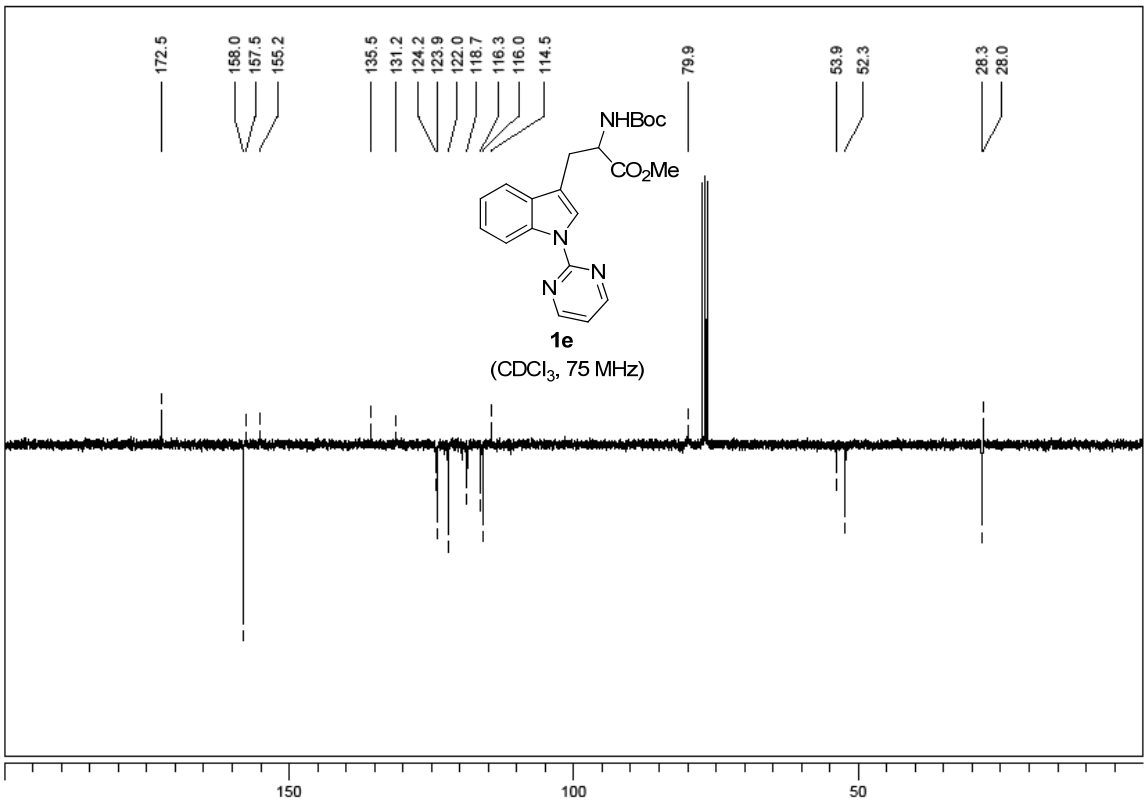
3-Methyl-1-(pyrimidin-2-yl)-1*H*-indole (1d)



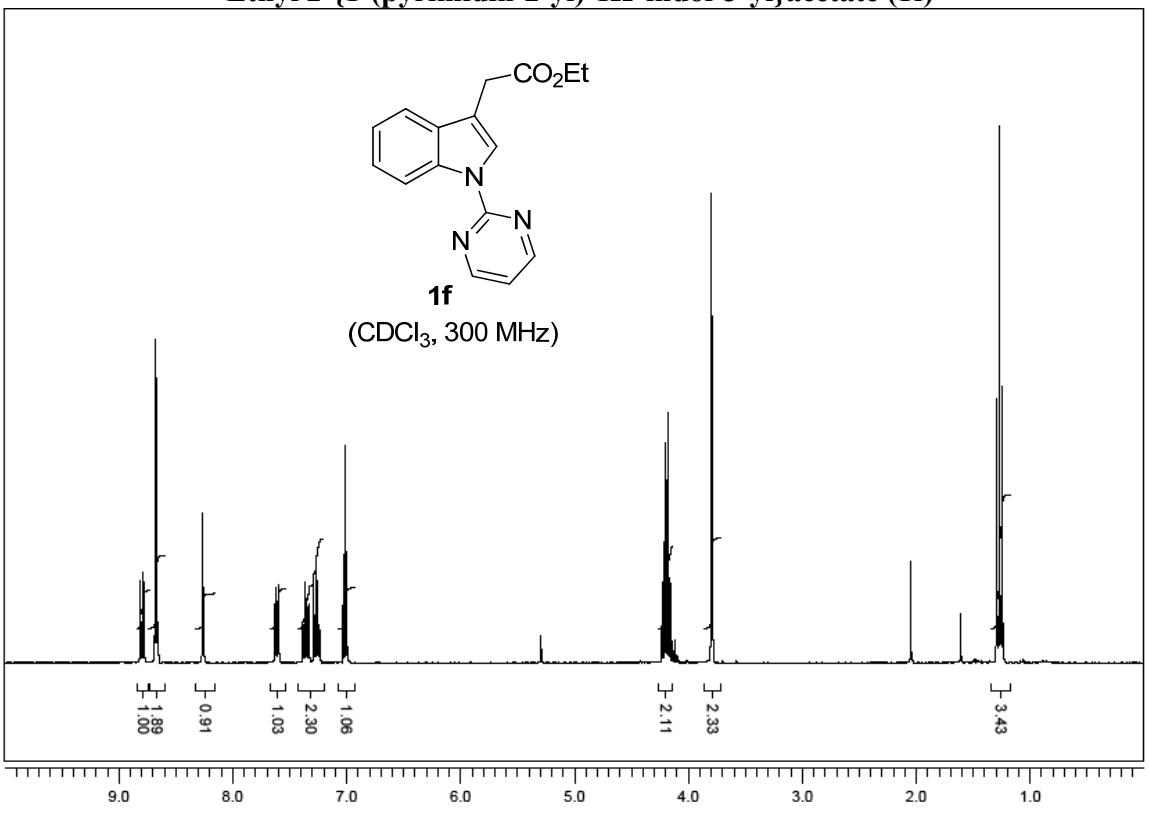


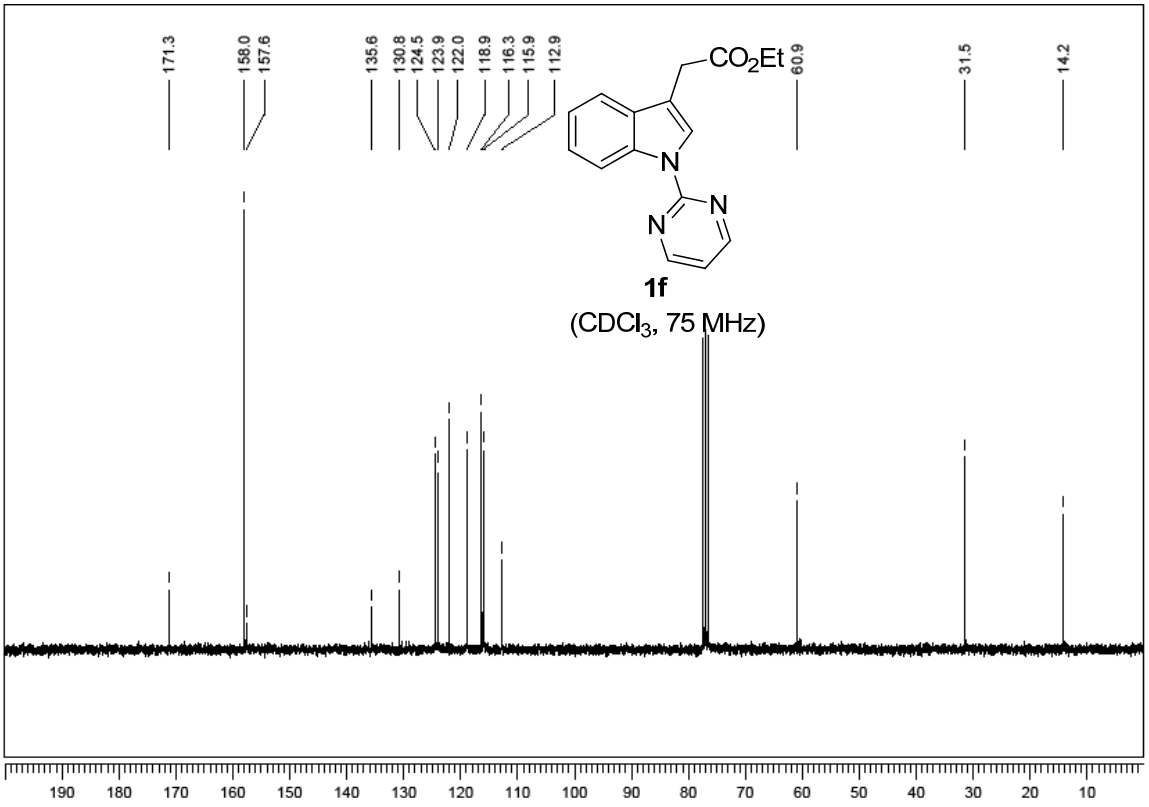
tert-Butyl 1-(methoxycarbonyl)-2-{1-(pyrimidin-2-yl)-1*H*-indol-3-yl}ethylcarbamate (1e)



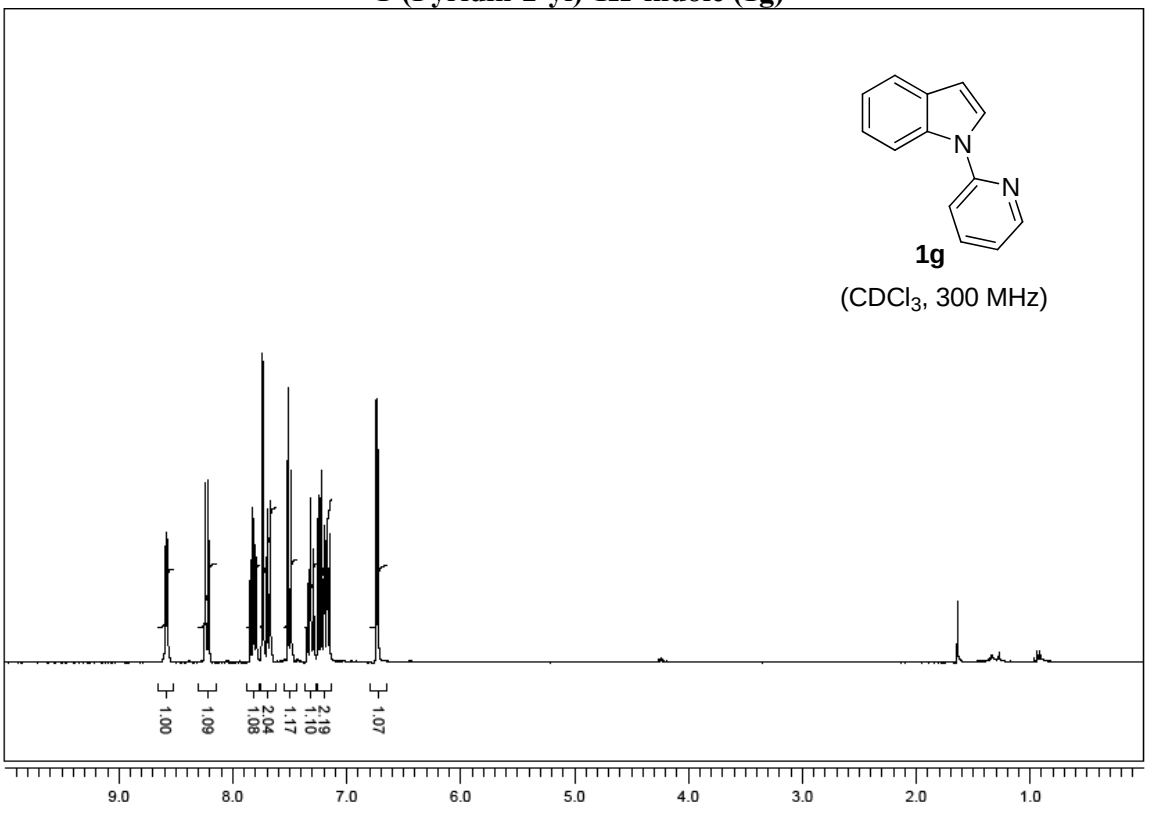


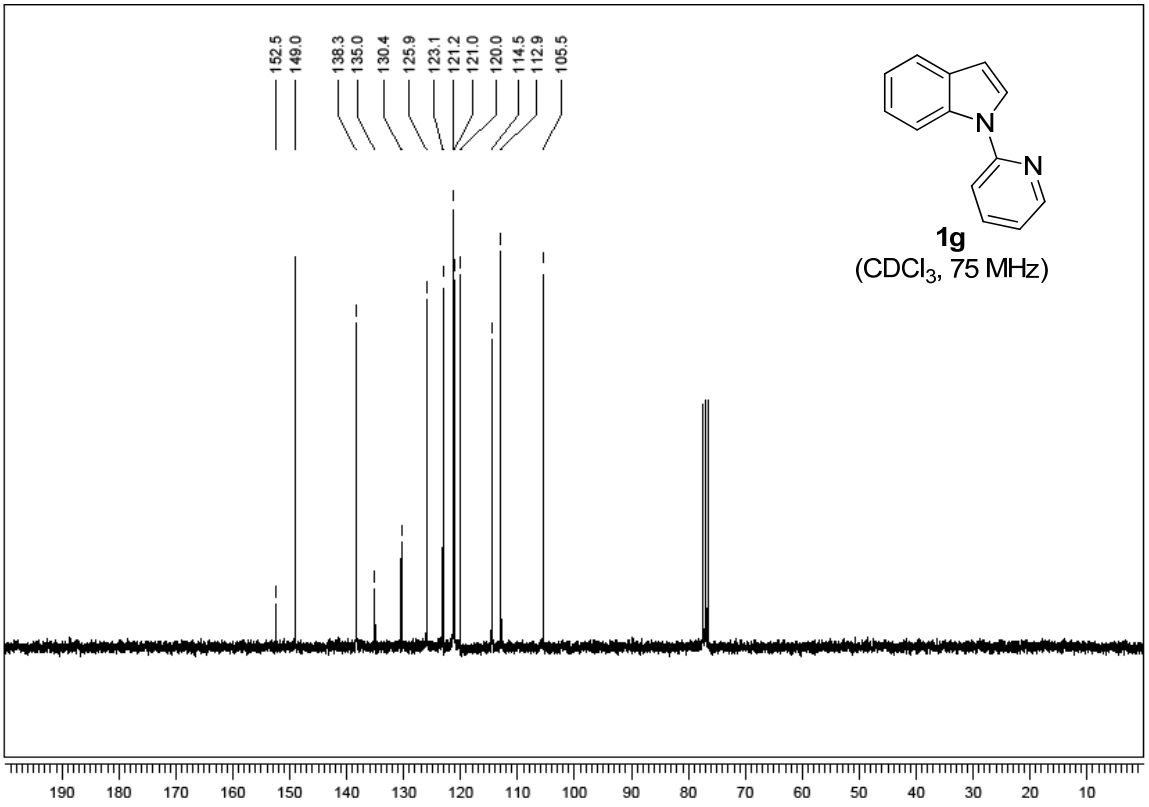
Ethyl 2-{1-(pyrimidin-2-yl)-1*H*-indol-3-yl}acetate (1f)



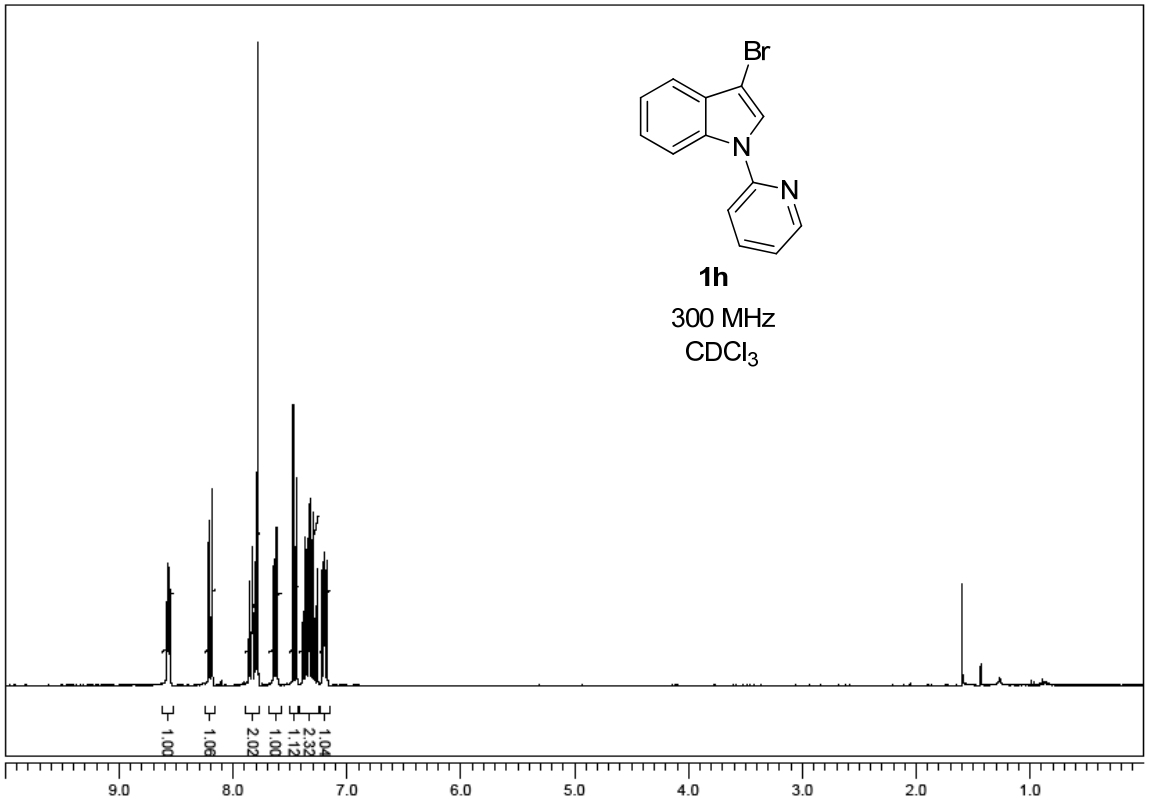


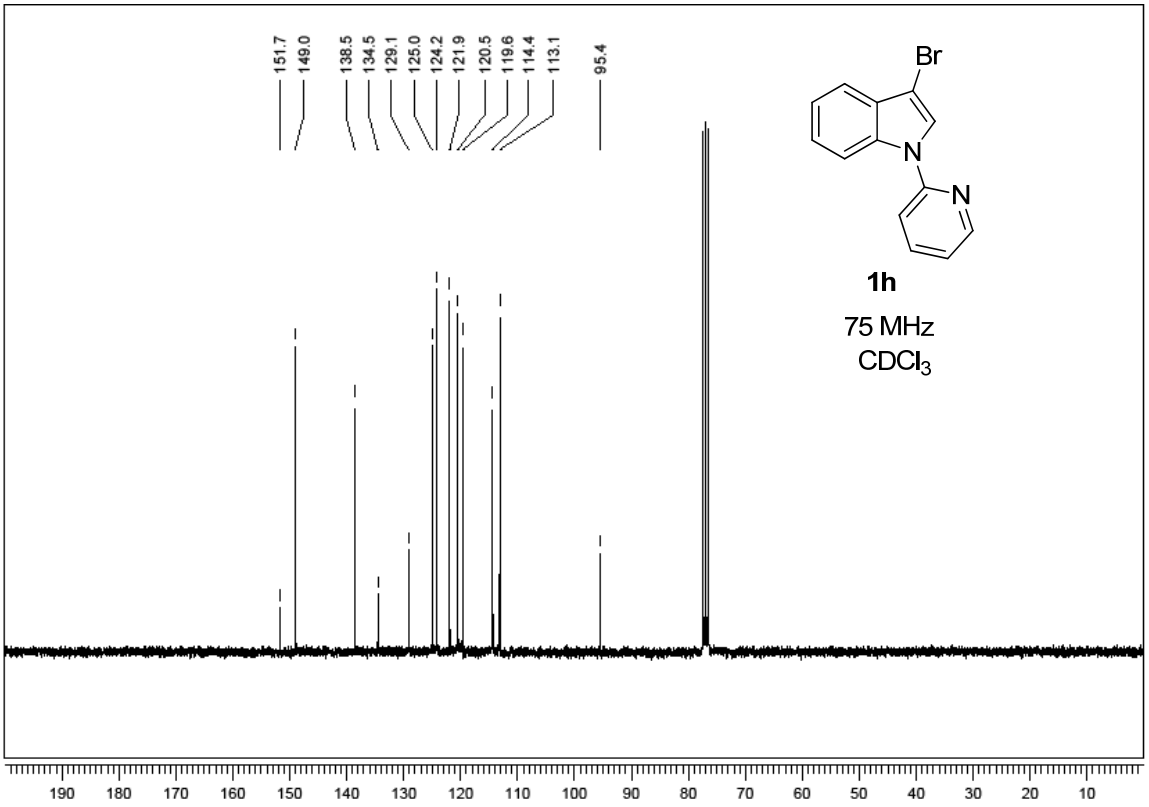
1-(Pyridin-2-yl)-1*H*-indole (1g)



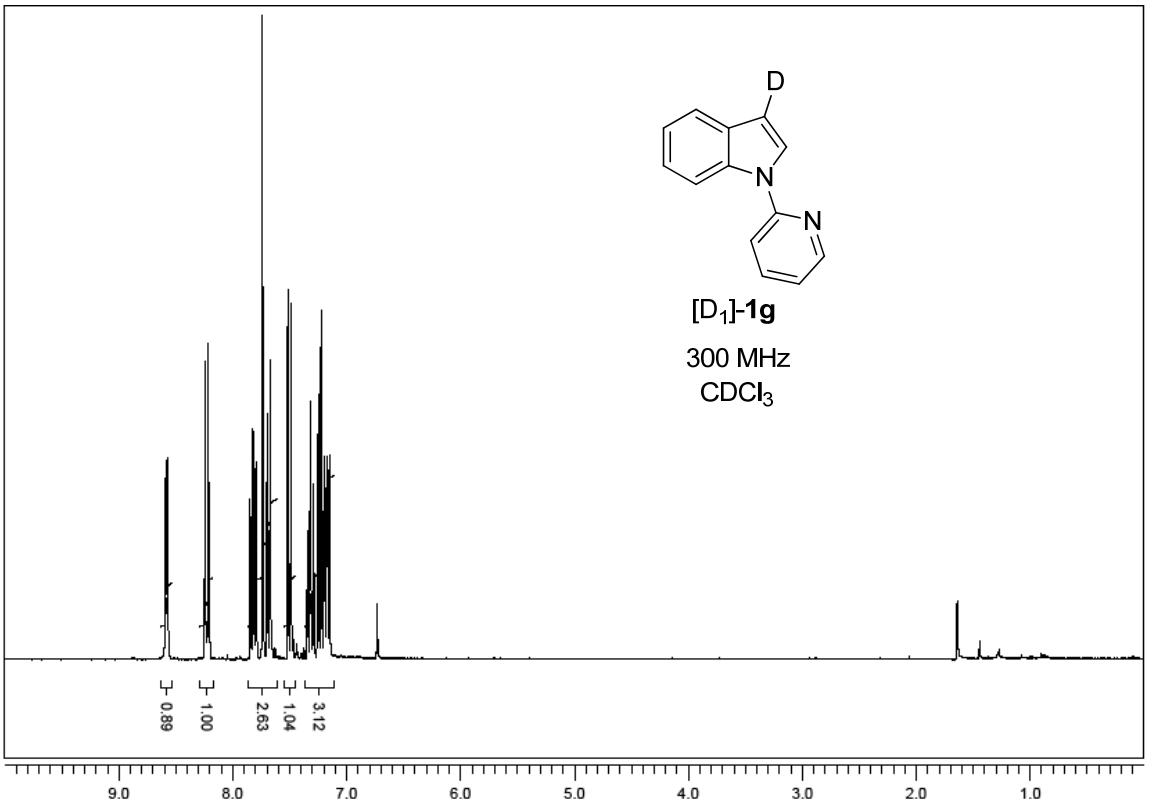


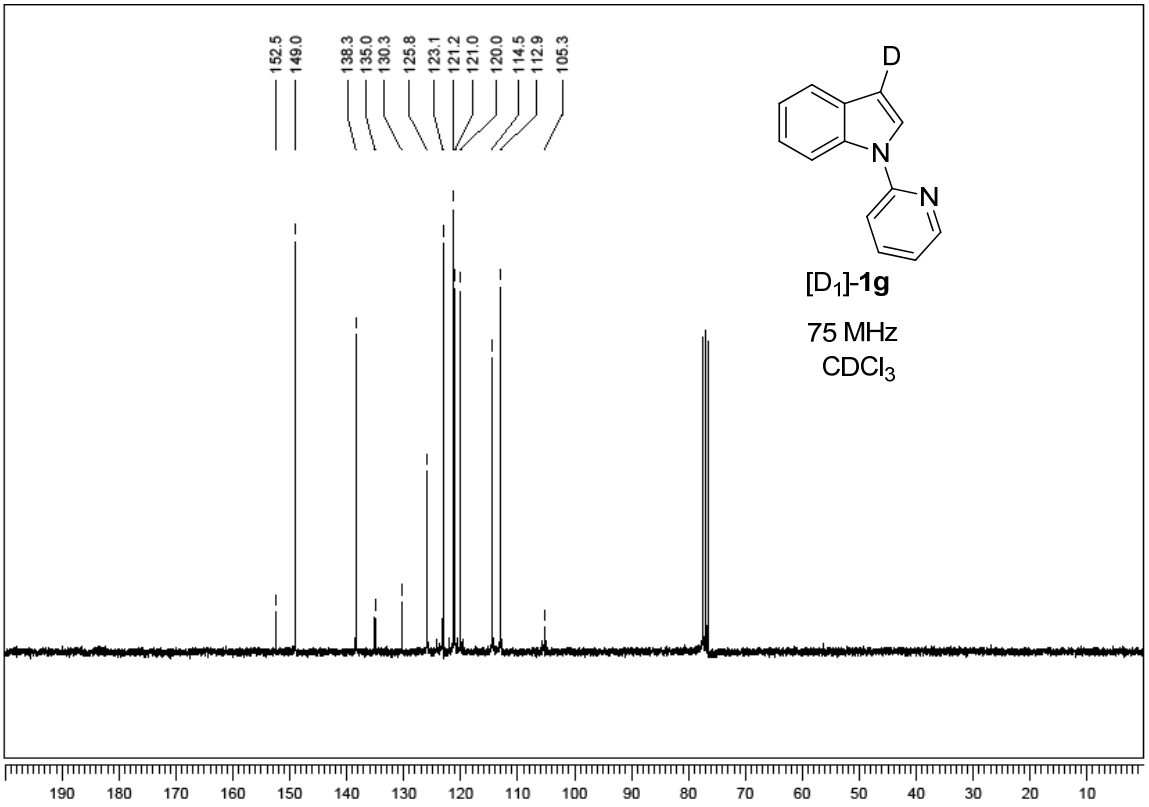
3-Bromo-1-(pyridin-2-yl)-1*H*-indole (1h)



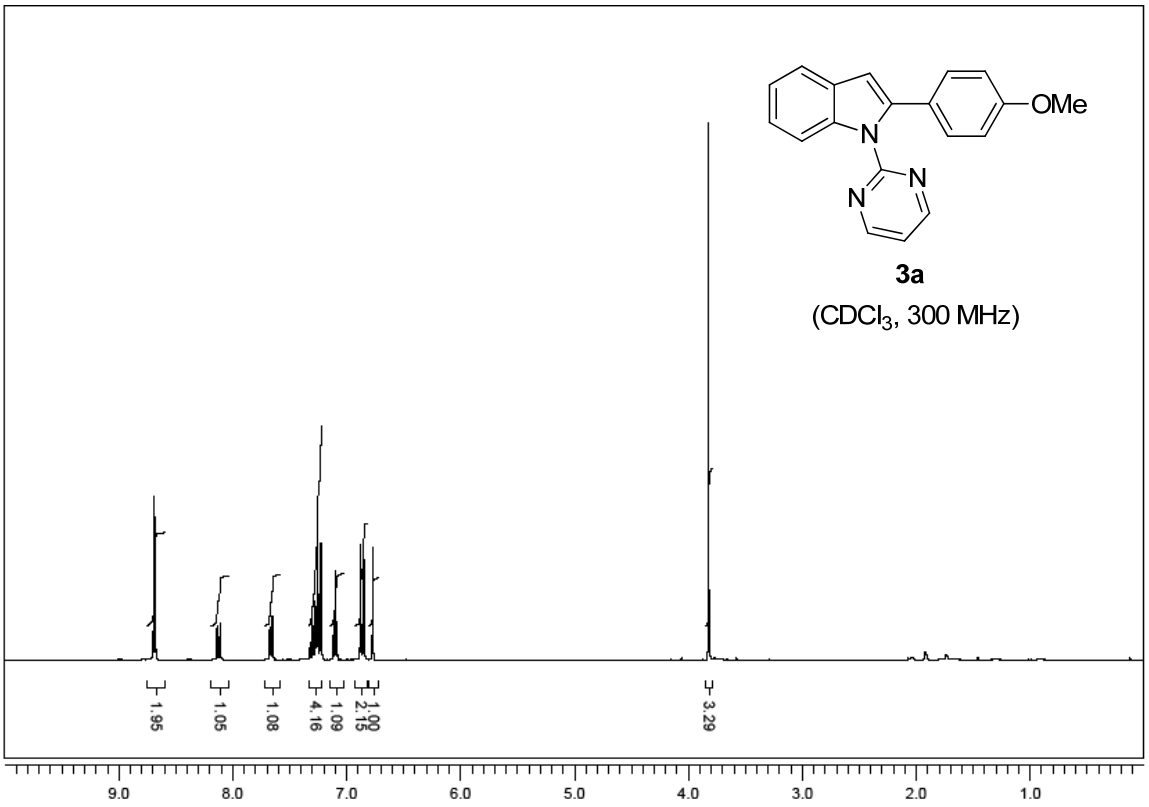


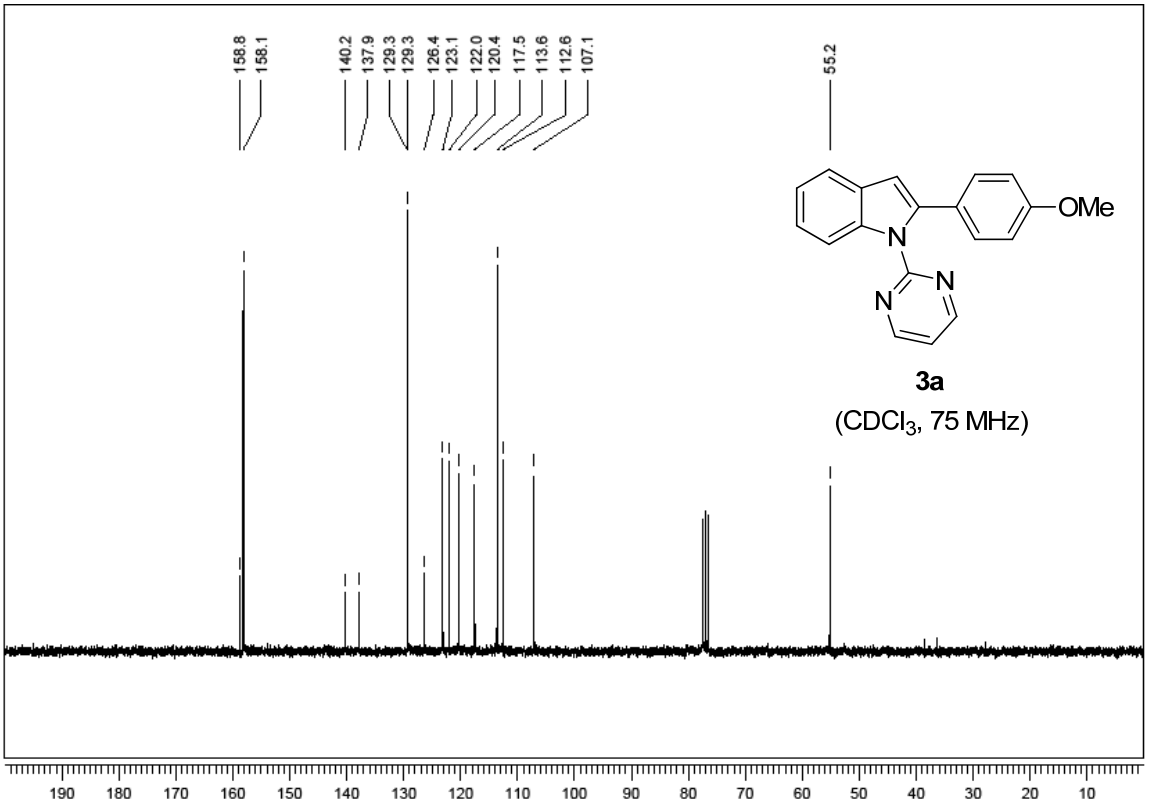
3-Deuterio-1-(pyridin-2-yl)-1*H*-indole ([D$_1$]-1g)



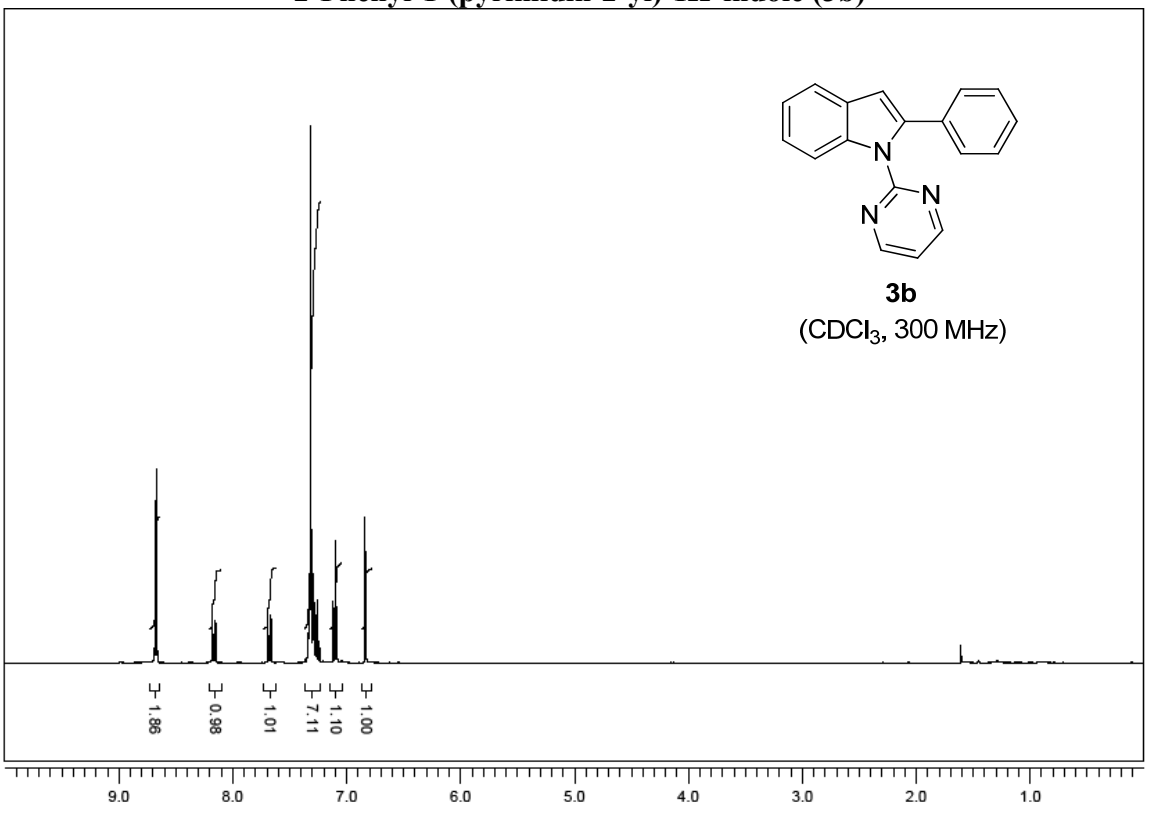


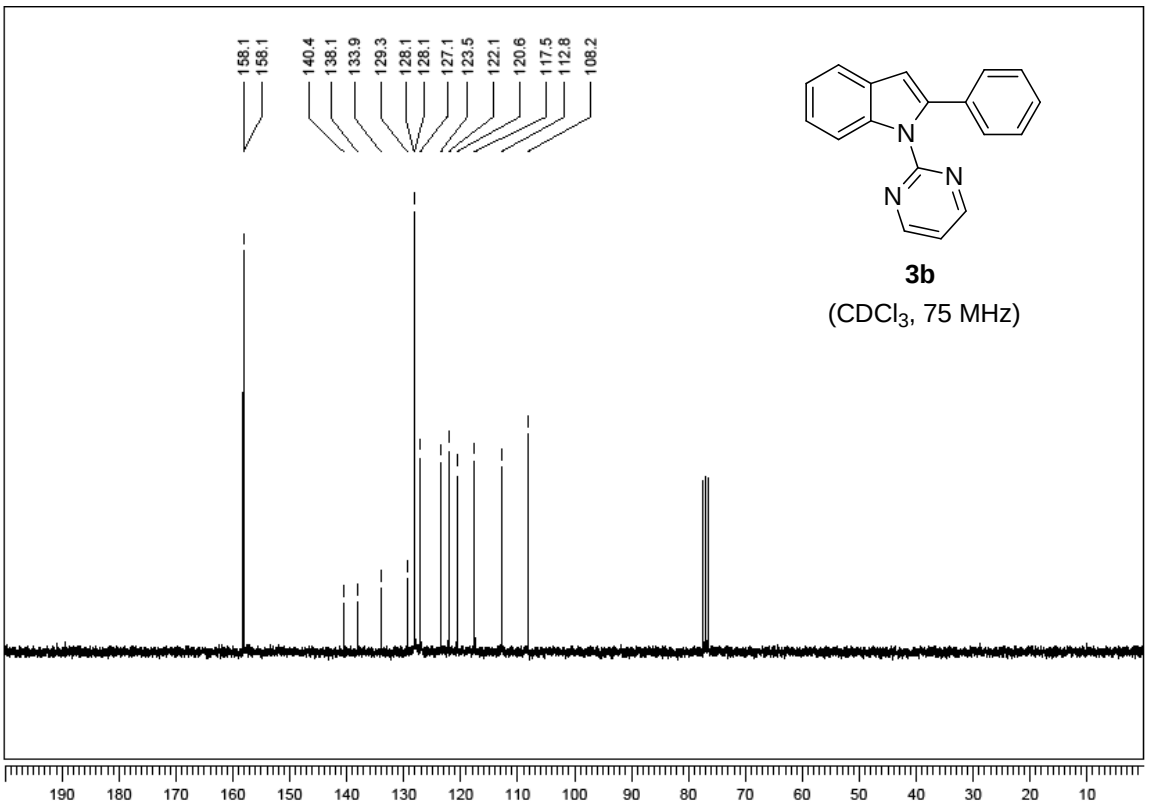
2-(4-Methoxyphenyl)-1-(pyrimidin-2-yl)-1*H*-indole (3a)



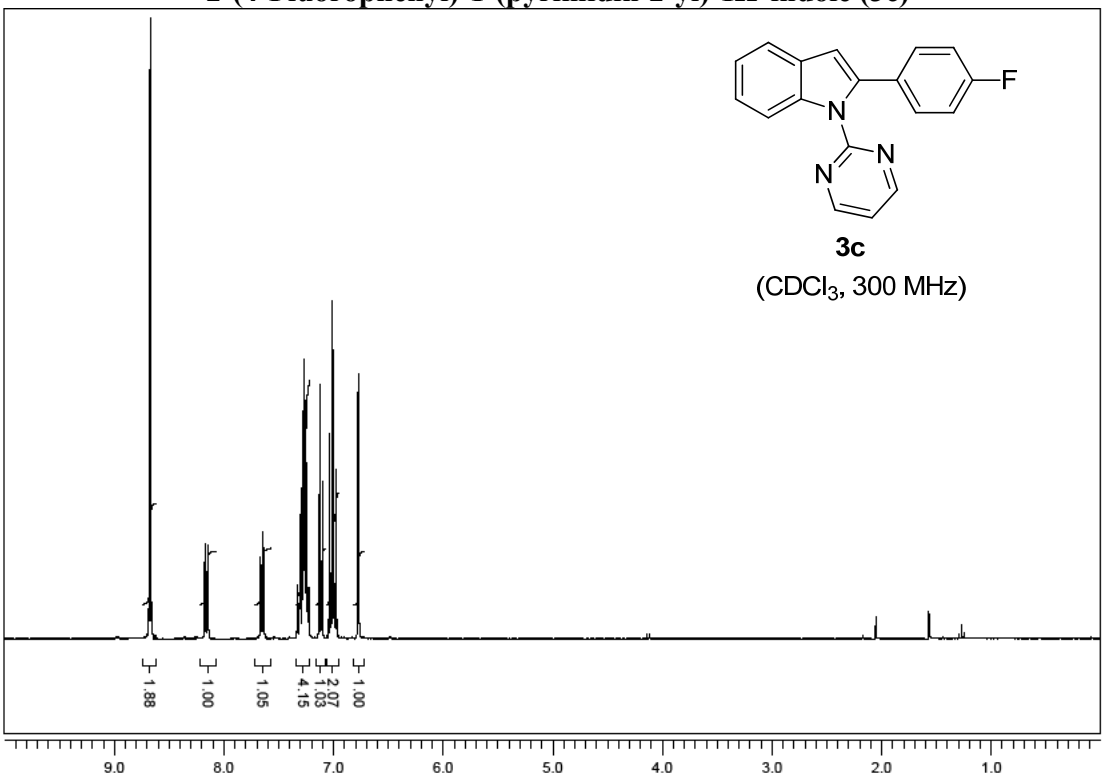


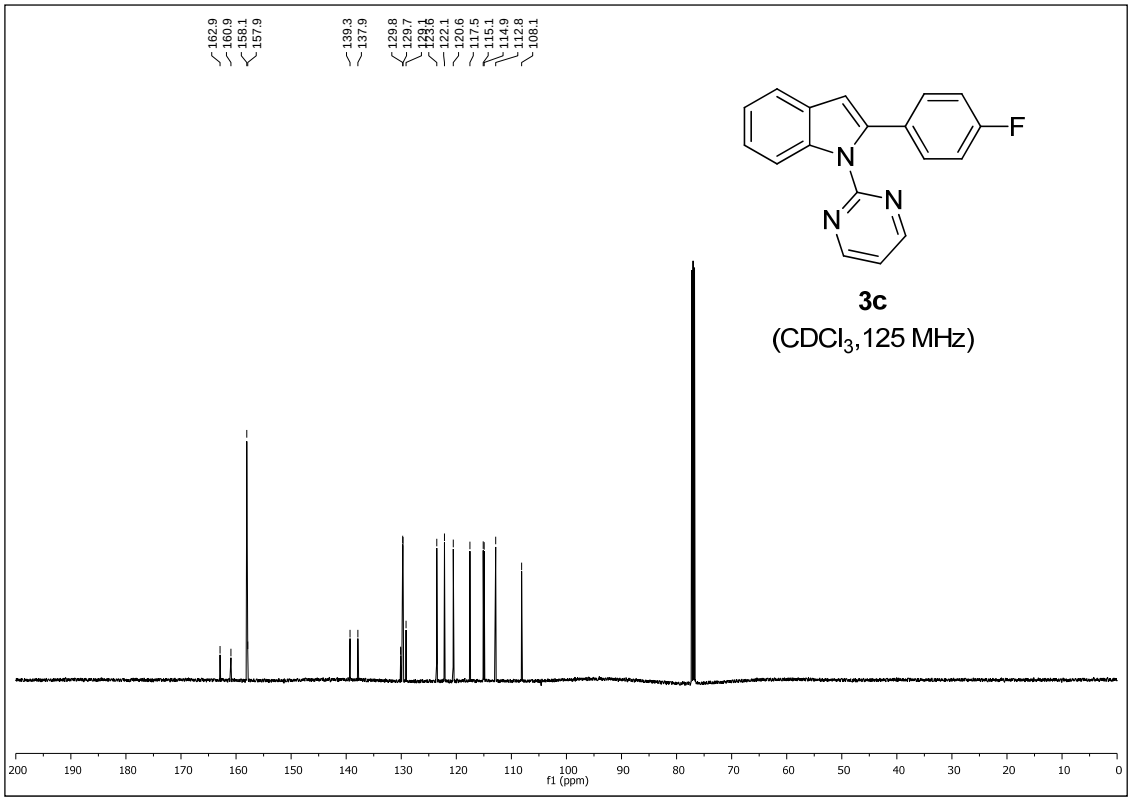
2-Phenyl-1-(pyrimidin-2-yl)-1*H*-indole (3b)



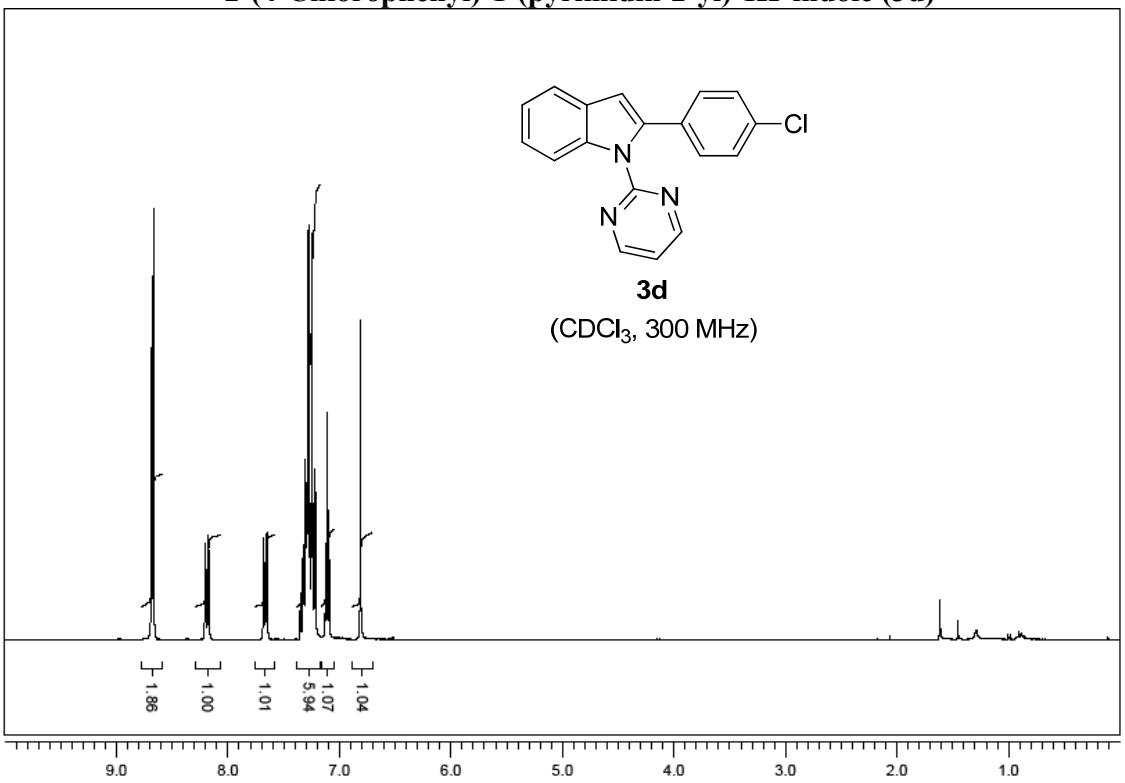


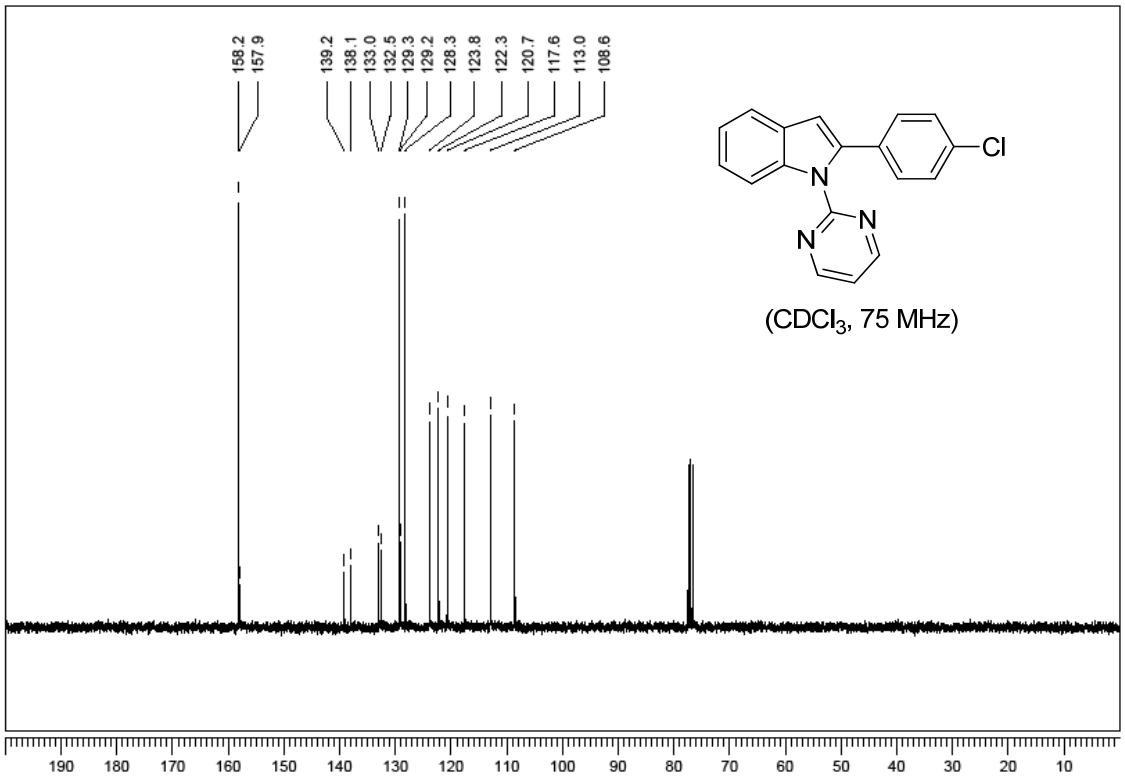
2-(4-Fluorophenyl)-1-(pyrimidin-2-yl)-1*H*-indole (3c)



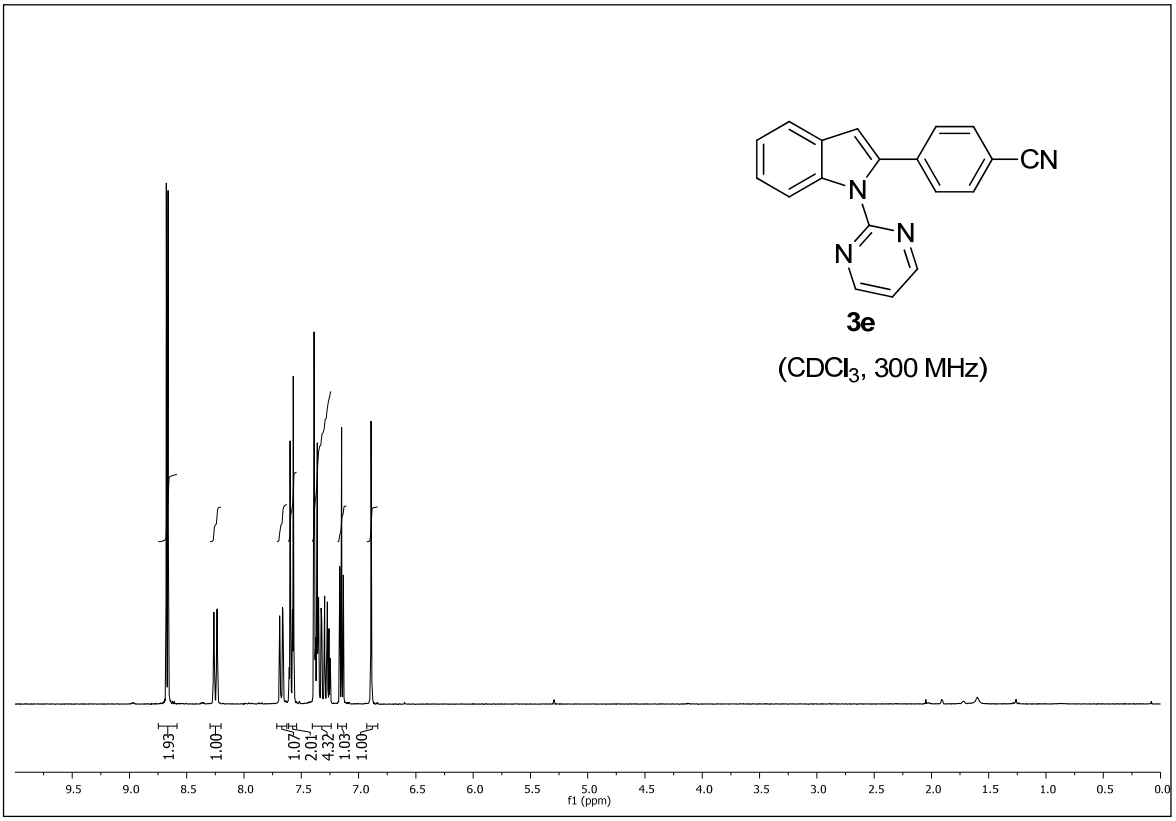


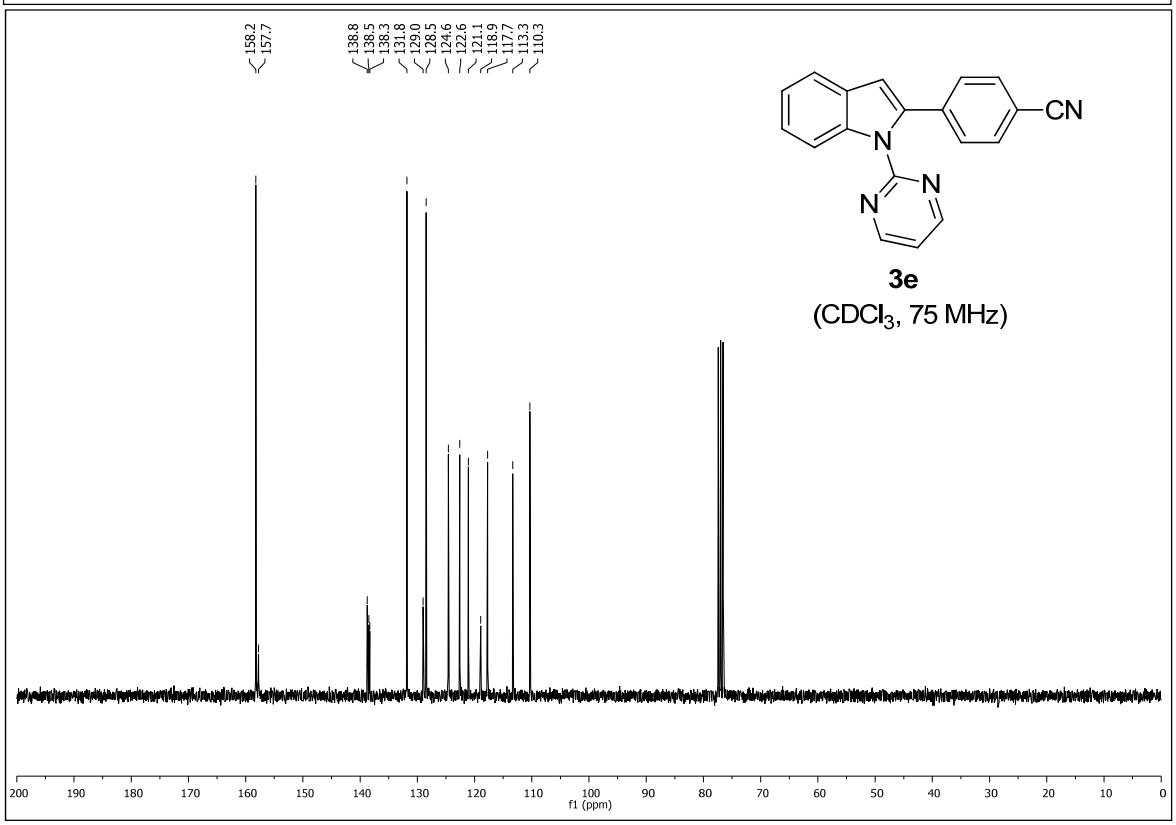
2-(4-Chlorophenyl)-1-(pyrimidin-2-yl)-1*H*-indole (3d)



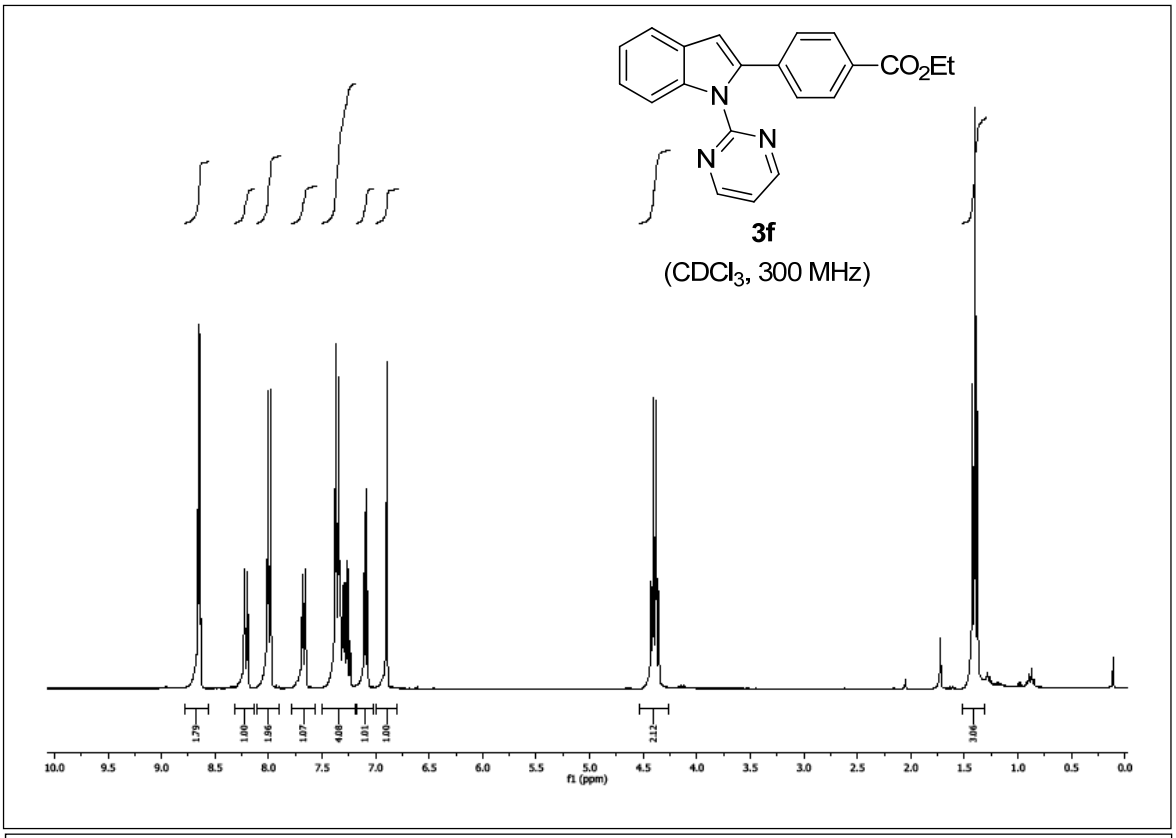


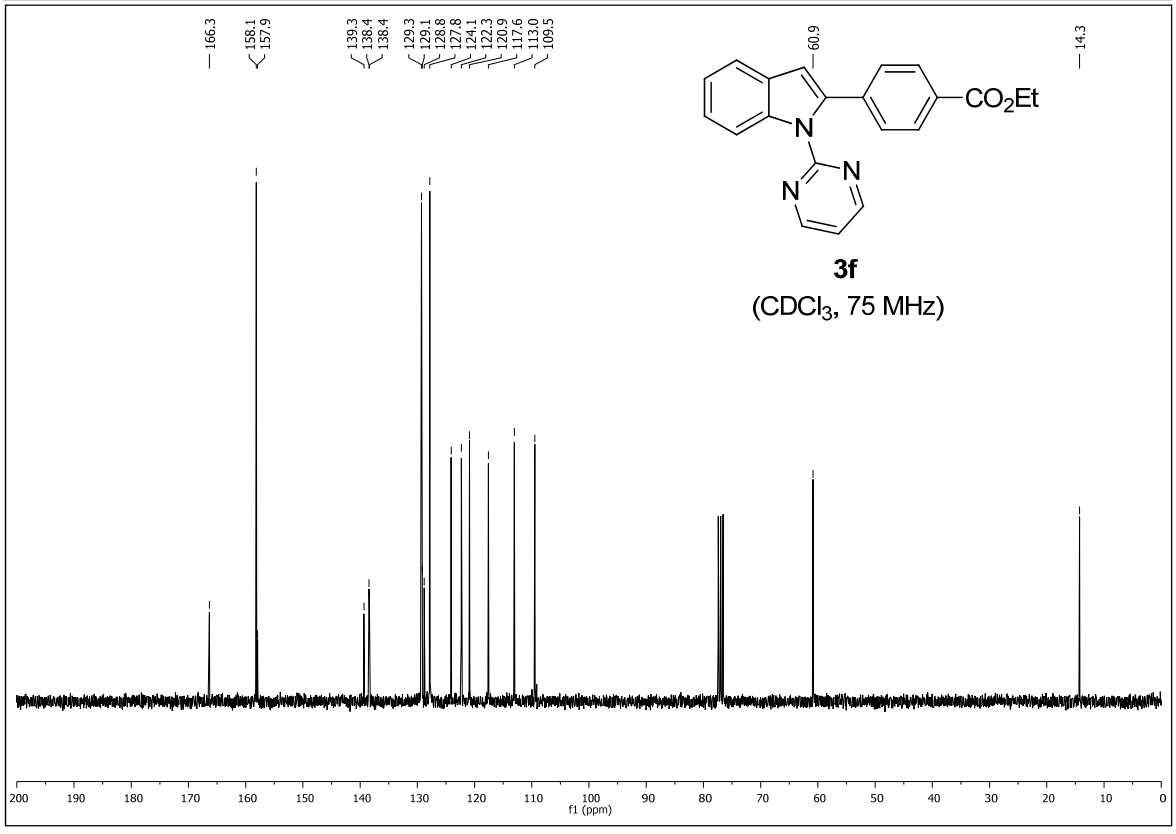
2-(4-Cyanophenyl)-1-(pyrimidin-2-yl)-1*H*-indole (3e)



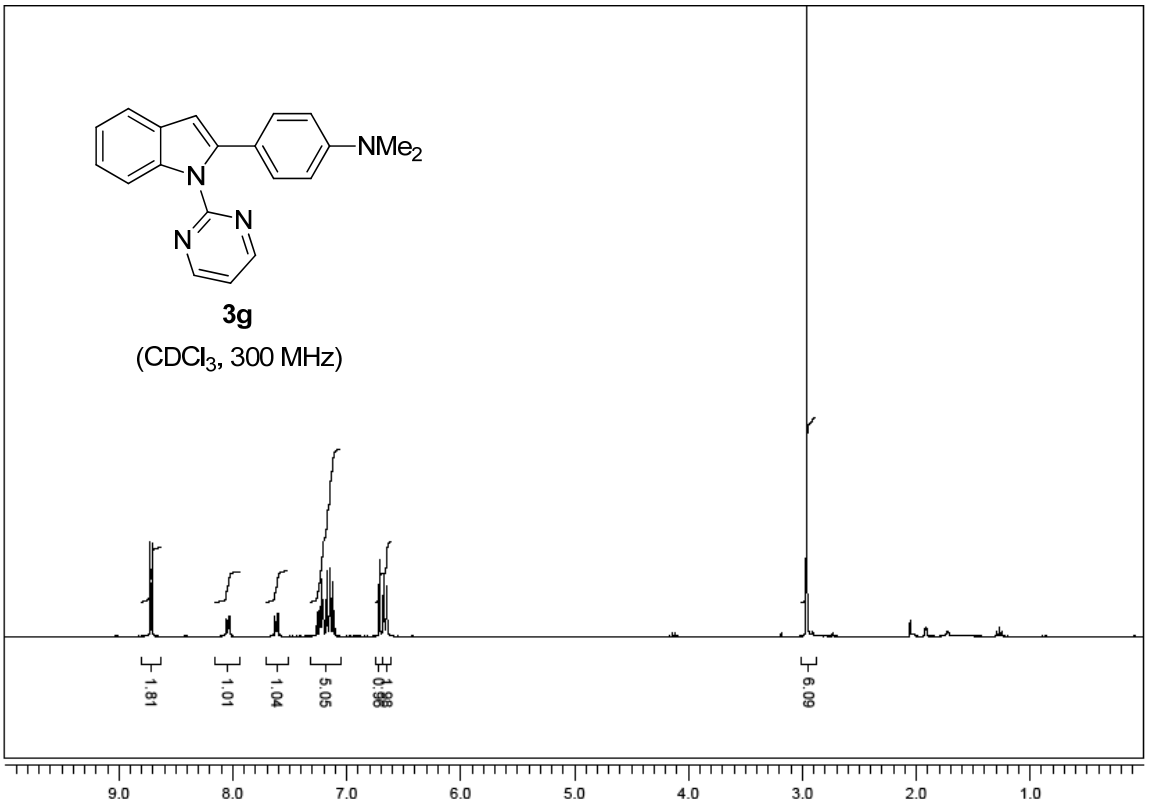


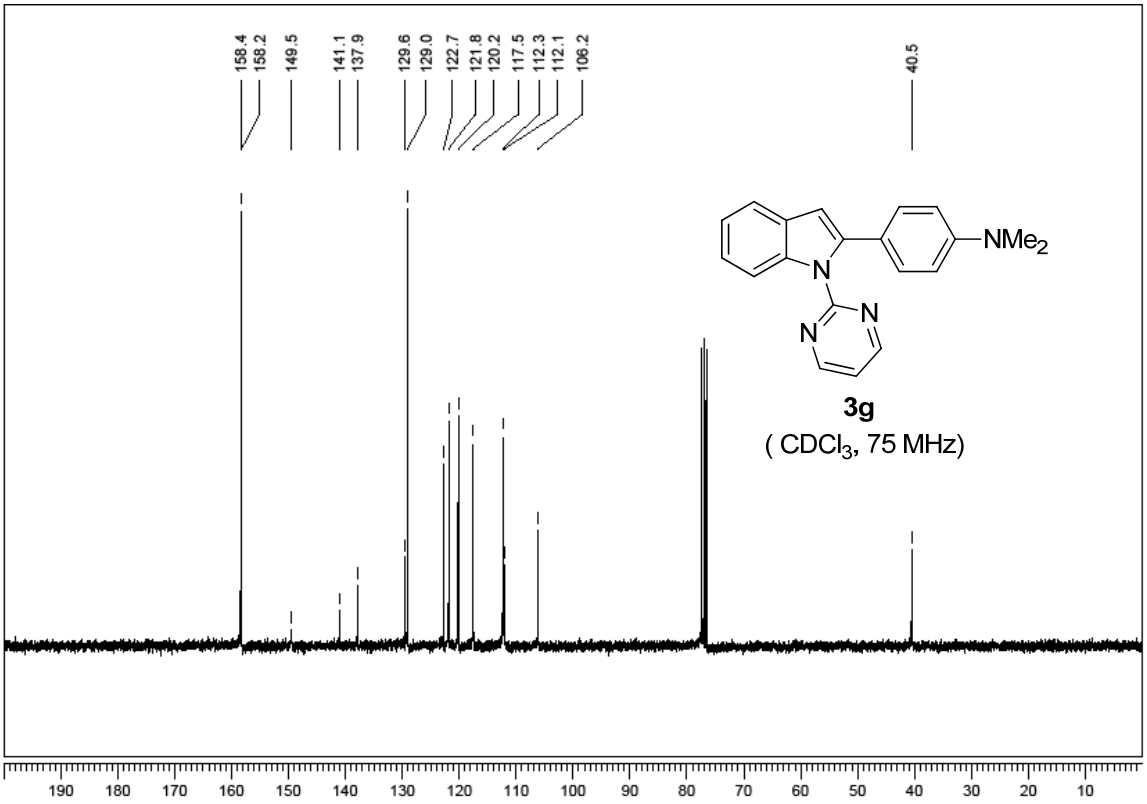
Ethyl 4-{1-(pyrimidin-2-yl)-1*H*-indol-2-yl}benzoate (3f)



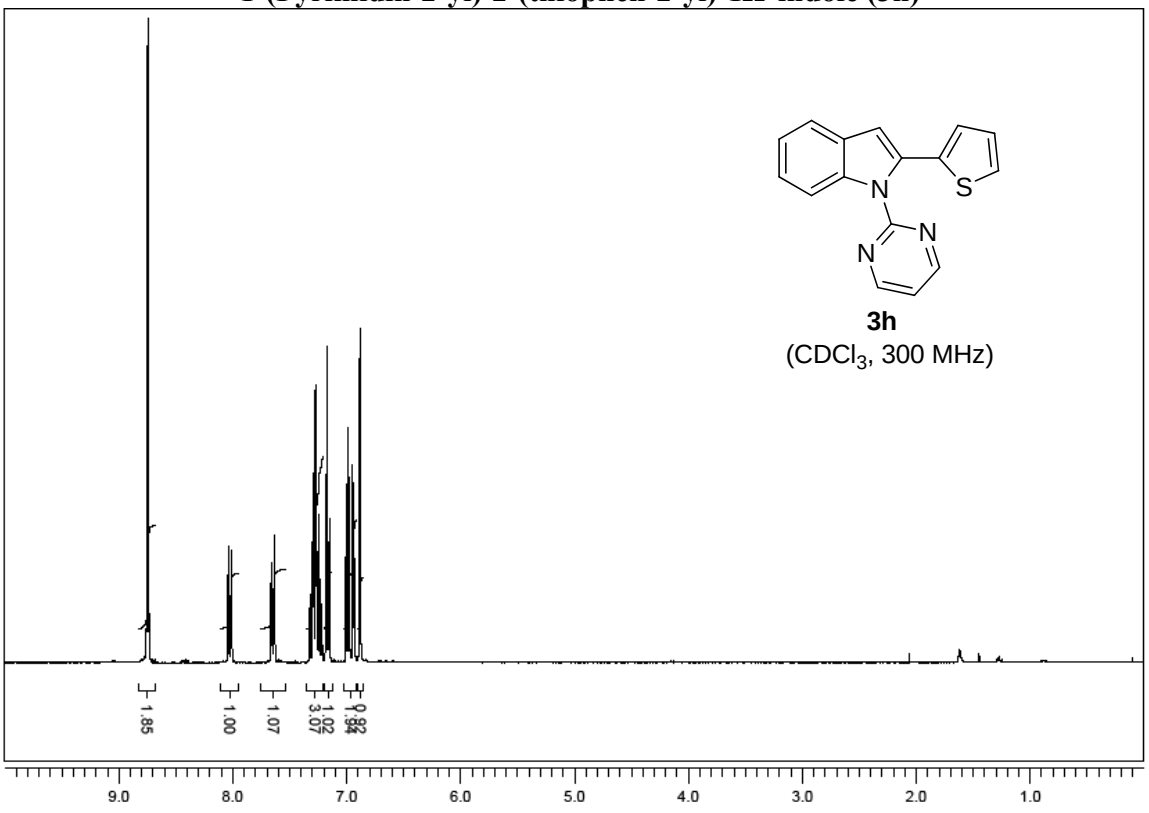


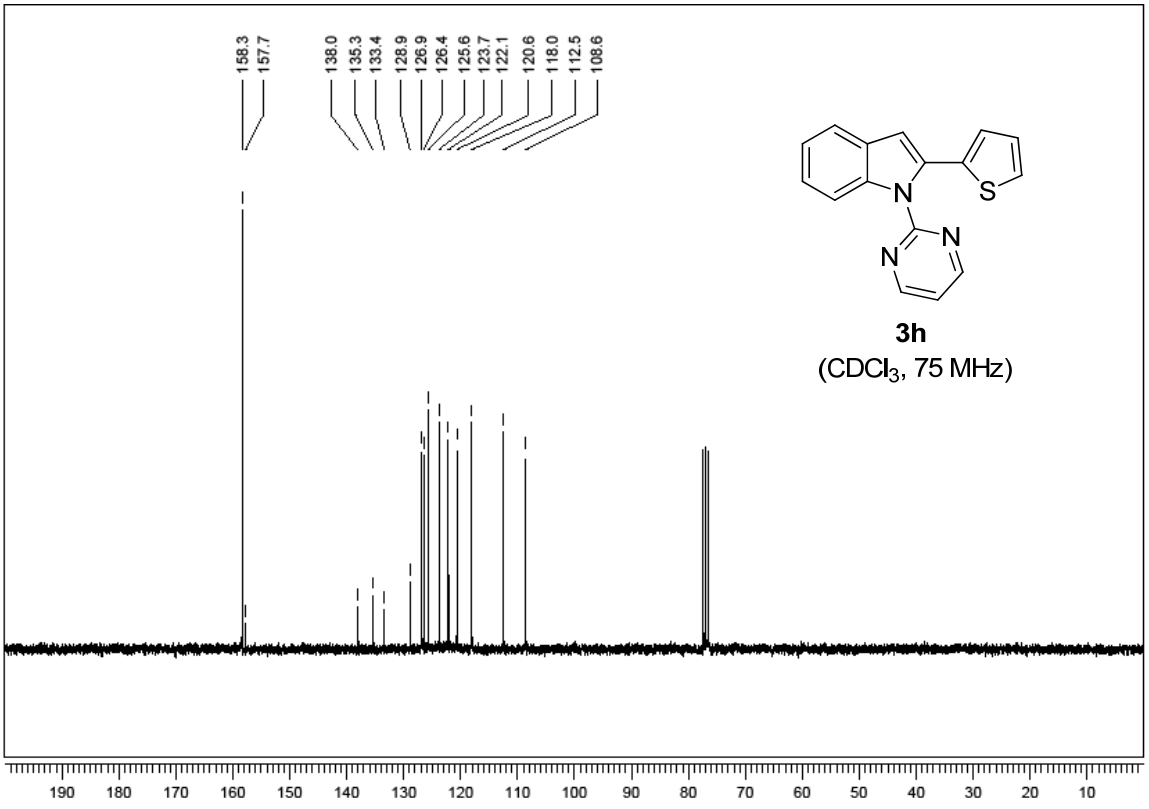
2-{4-(*N*,*N*-Dimethylamino)phenyl}-1-(pyrimidin-2-yl)-1*H*-indole (3g)



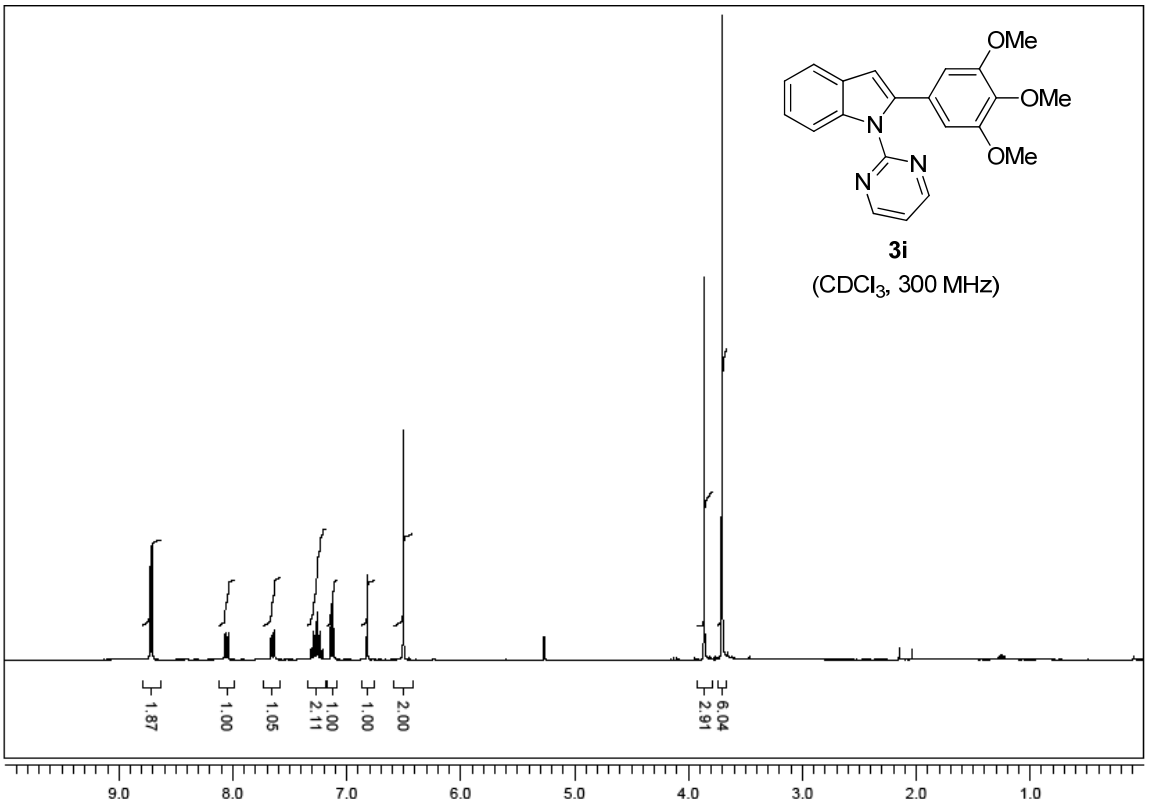


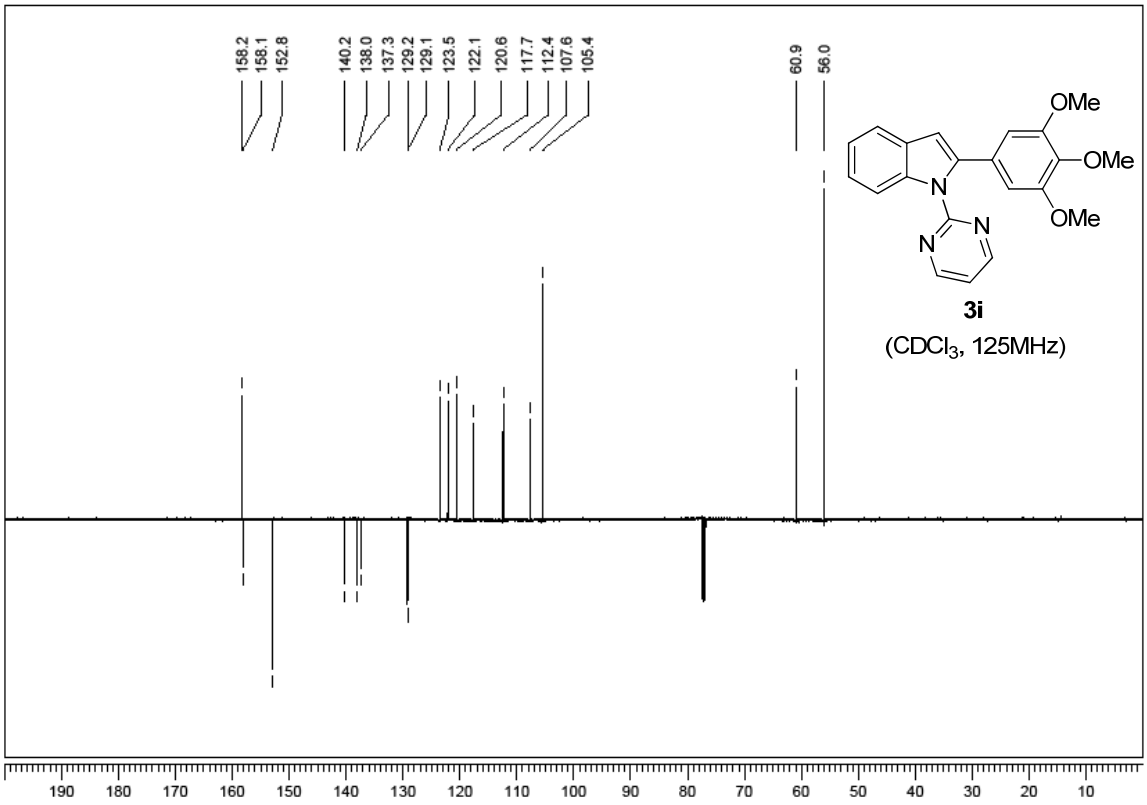
1-(Pyrimidin-2-yl)-2-(thiophen-2-yl)-1*H*-indole (3h)



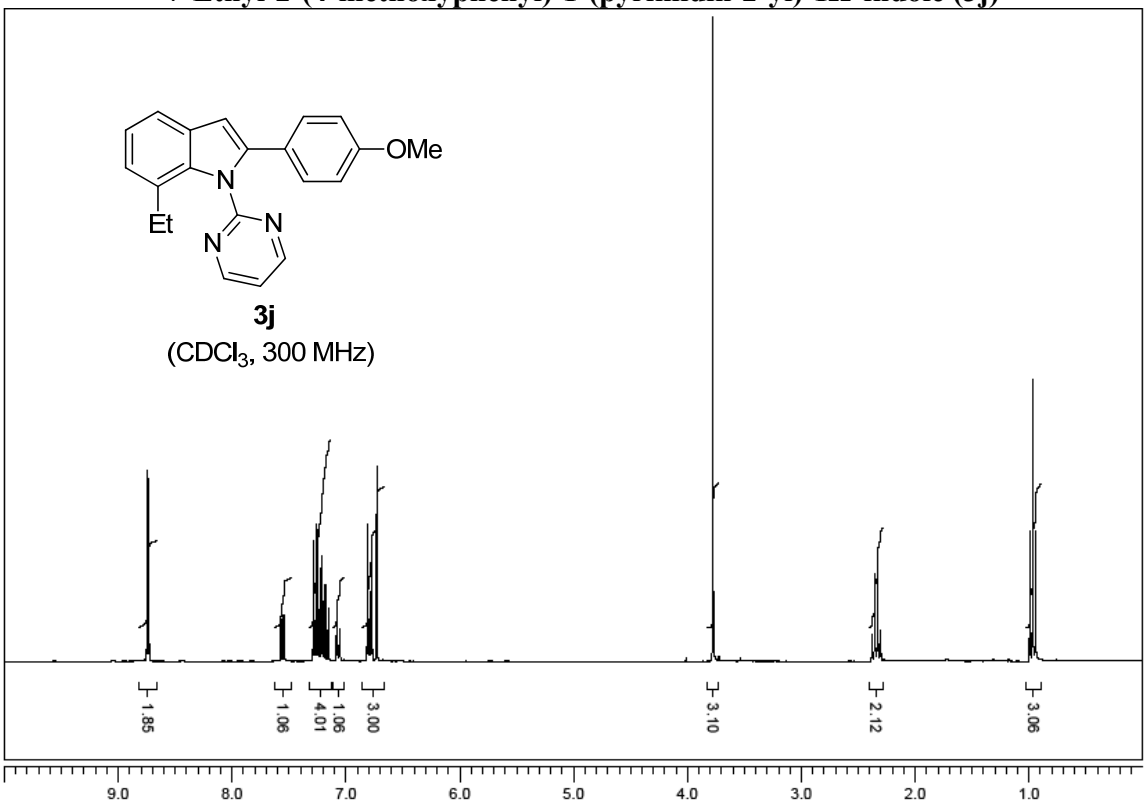


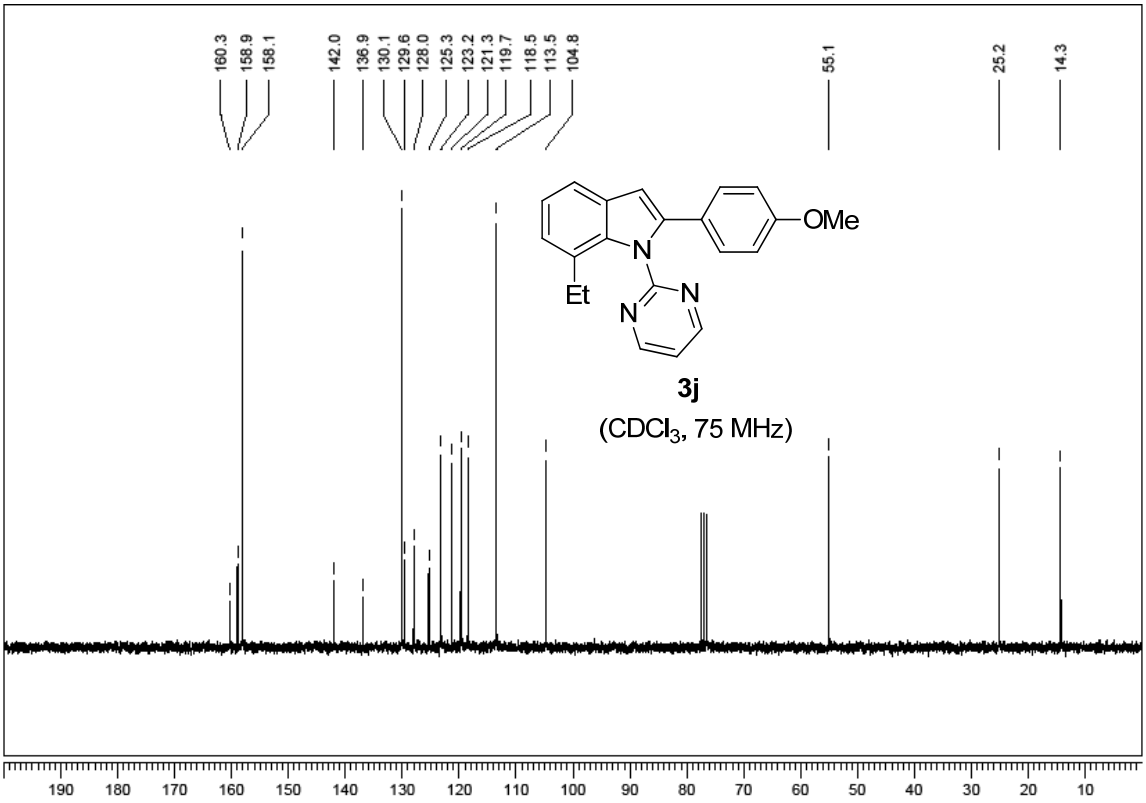
2-(3,4,5-Trimethoxyphenyl)-1-(pyrimidin-2-yl)-1*H*-indole (3i)



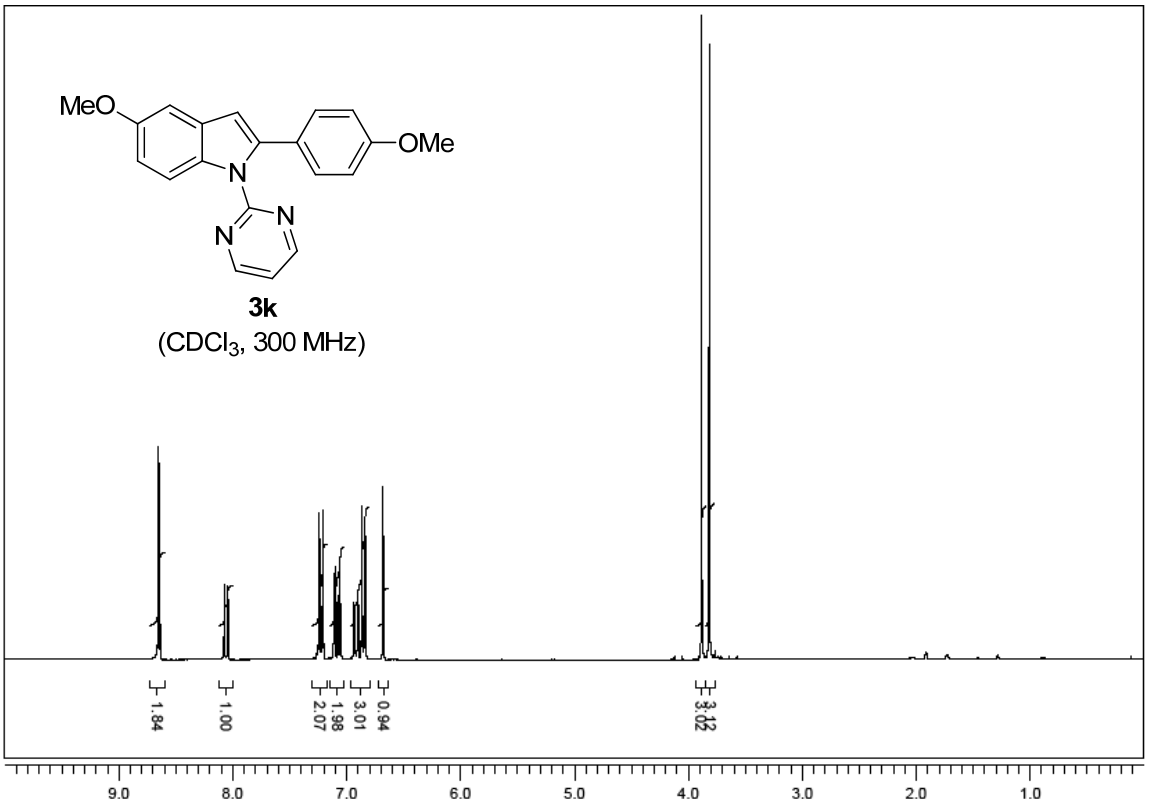


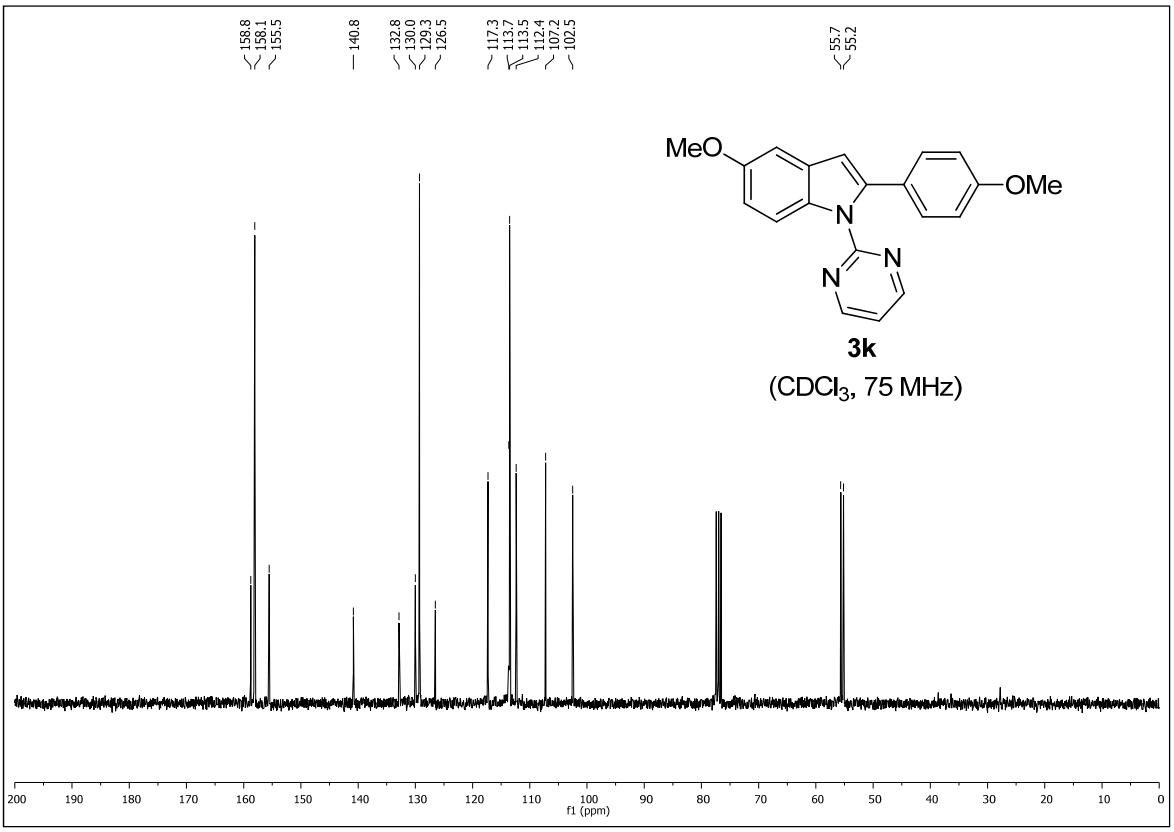
7-Ethyl-2-(4-methoxyphenyl)-1-(pyrimidin-2-yl)-1*H*-indole (3j)



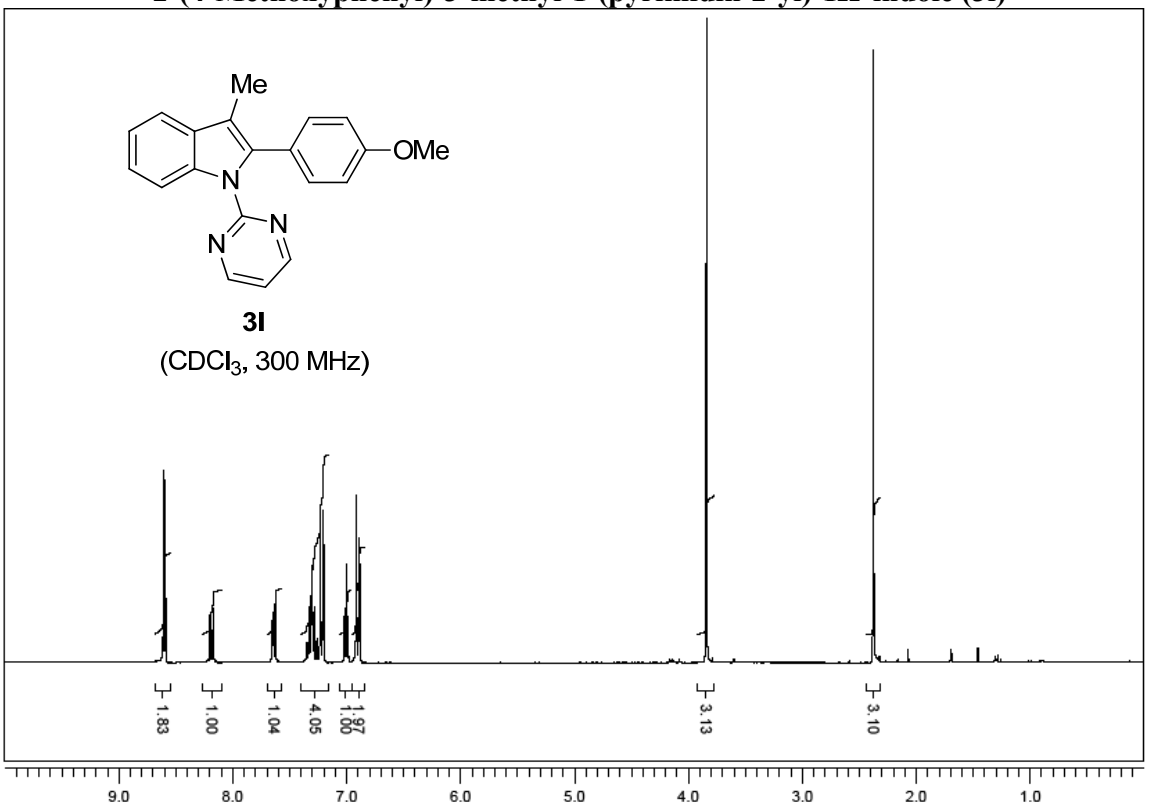


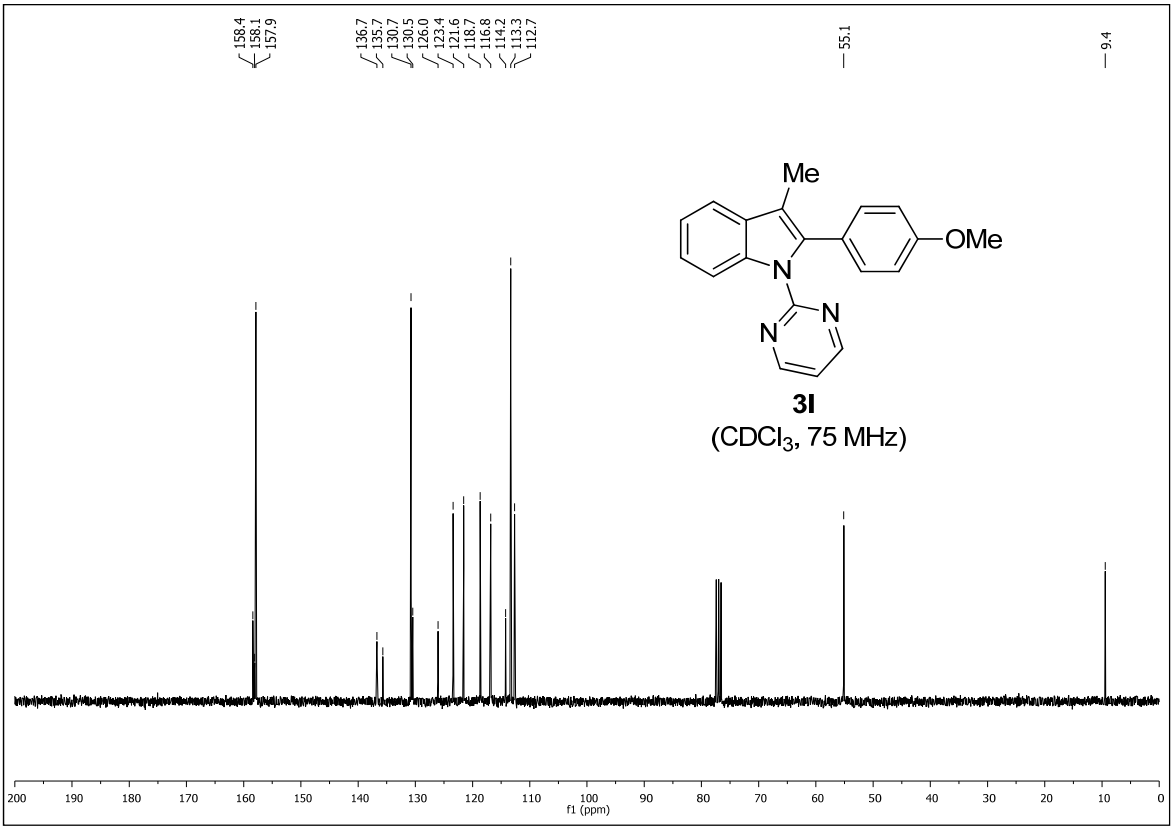
5-Methoxy-2-(4-methoxyphenyl)-1-(pyrimidin-2-yl)-1*H*-indole (3k)



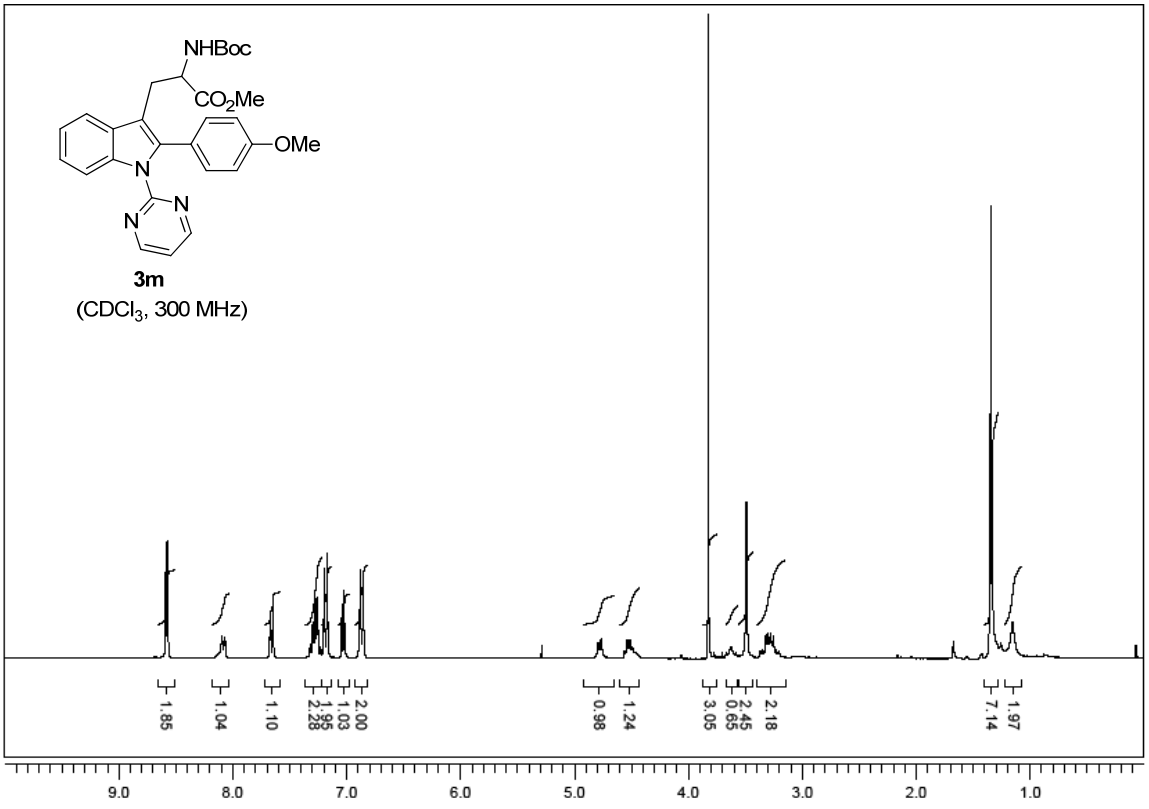


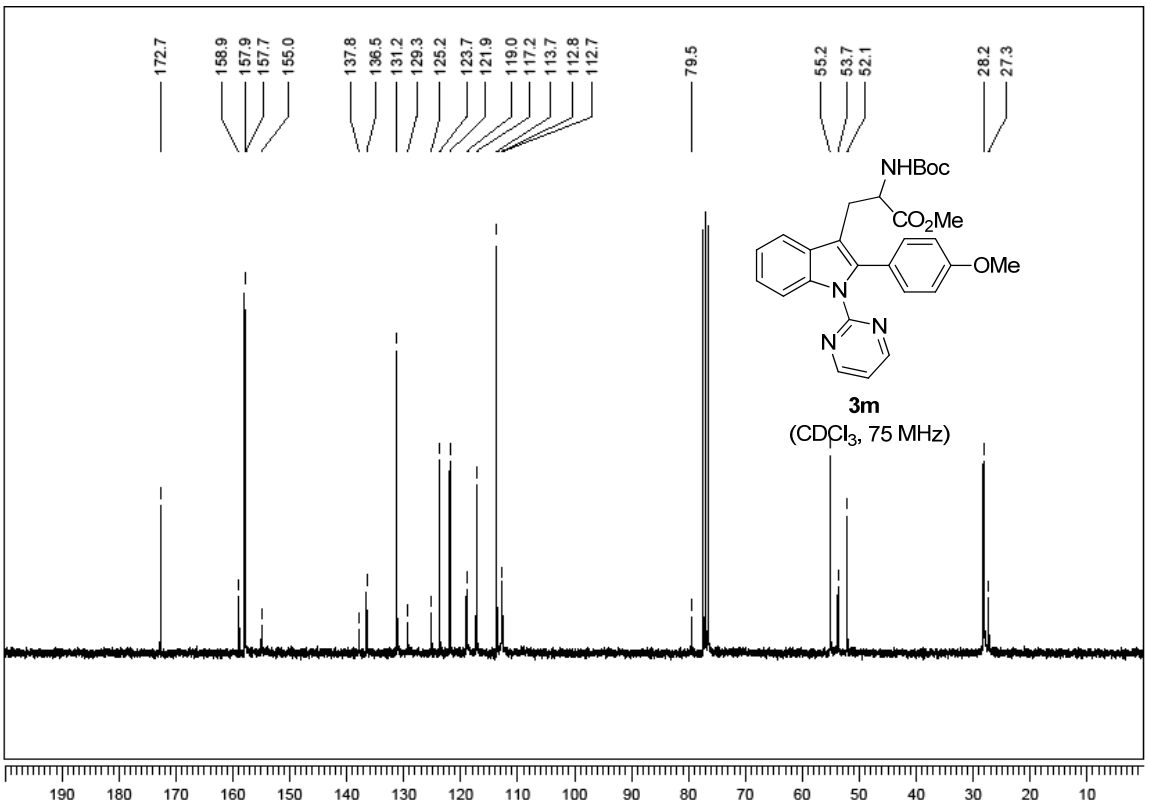
2-(4-Methoxyphenyl)-3-methyl-1-(pyrimidin-2-yl)-1*H*-indole (3l)



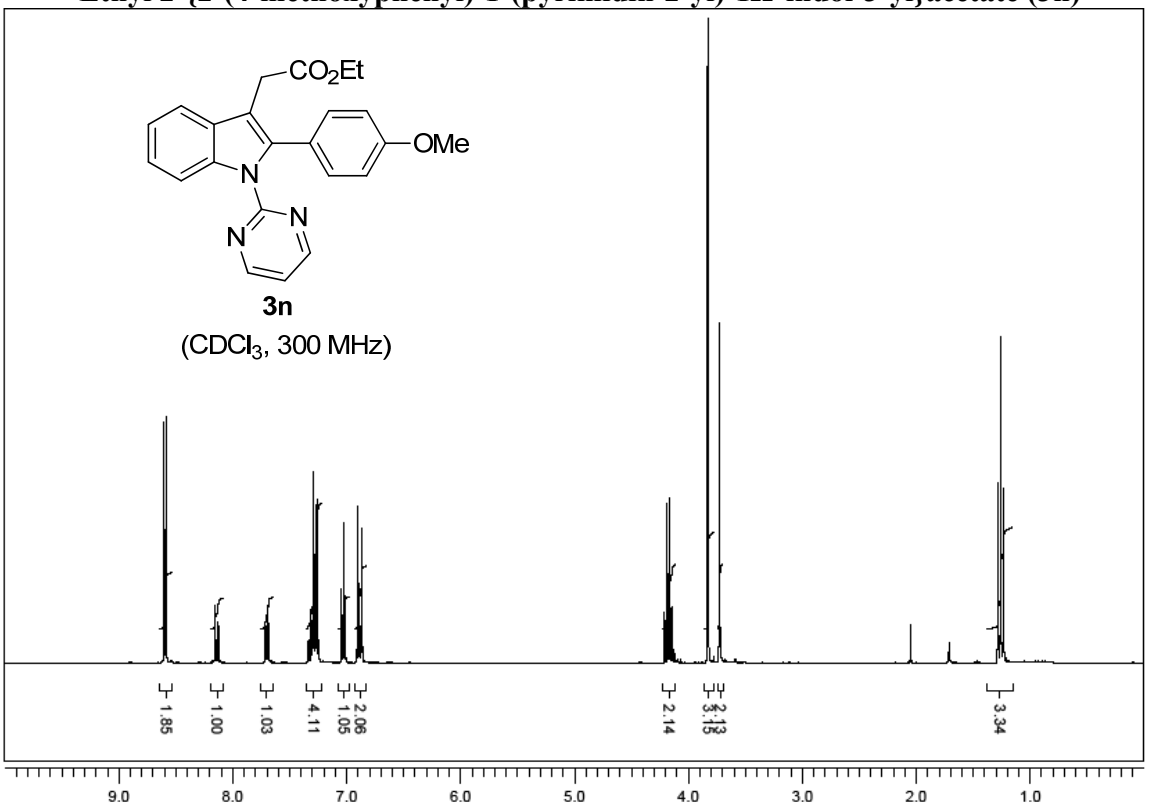


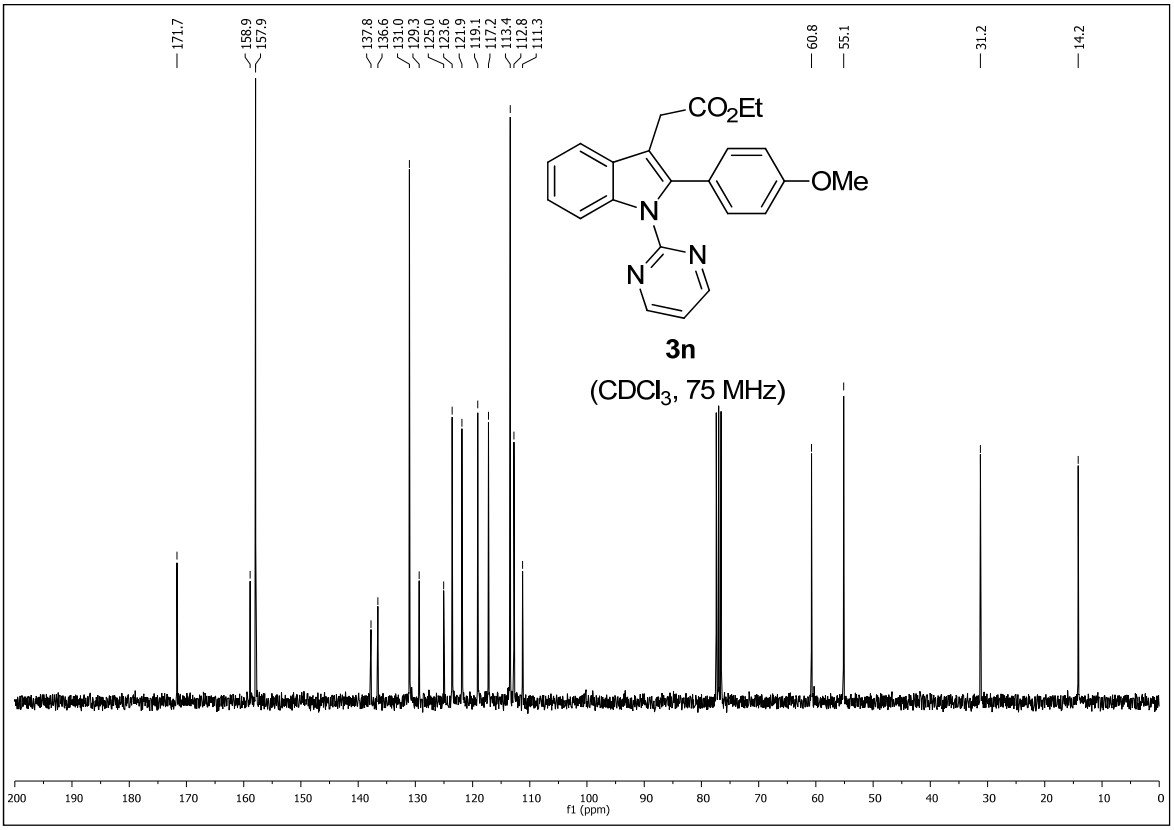
***tert*-Butyl 1-(methoxycarbonyl)-2-{2-(4-methoxyphenyl)-1-(pyrimidin-2-yl)-1*H*-indol-3-yl}ethylcarbamate (3m)**



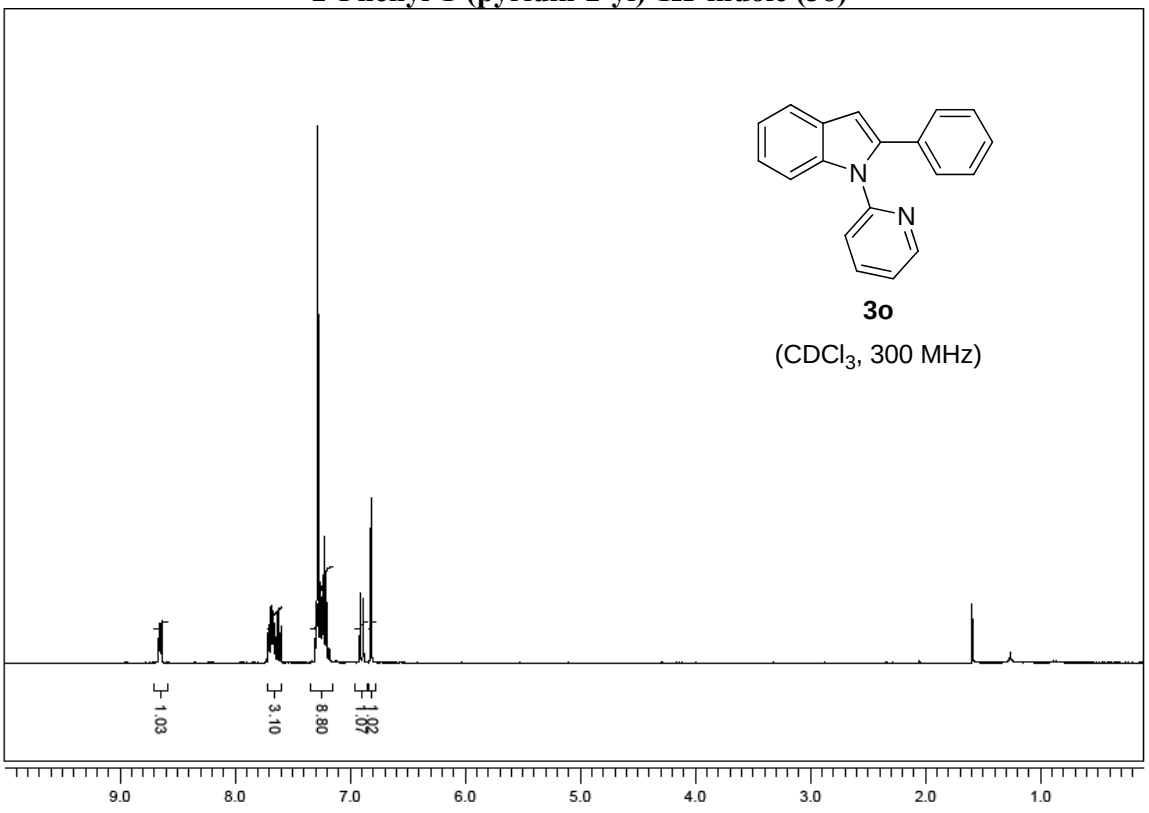


Ethyl 2-{2-(4-methoxyphenyl)-1-(pyrimidin-2-yl)-1*H*-indol-3-yl}acetate (3n)



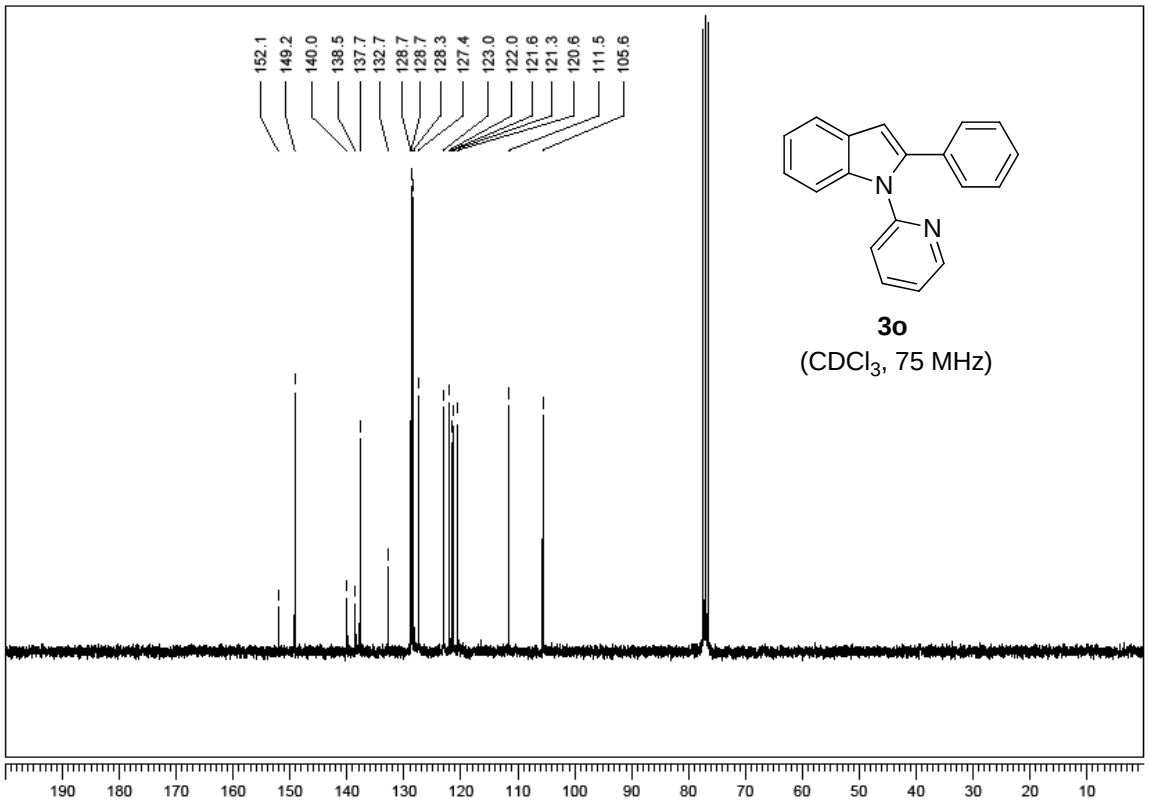


2-Phenyl-1-(pyridin-2-yl)-1*H*-indole (3o)



3o

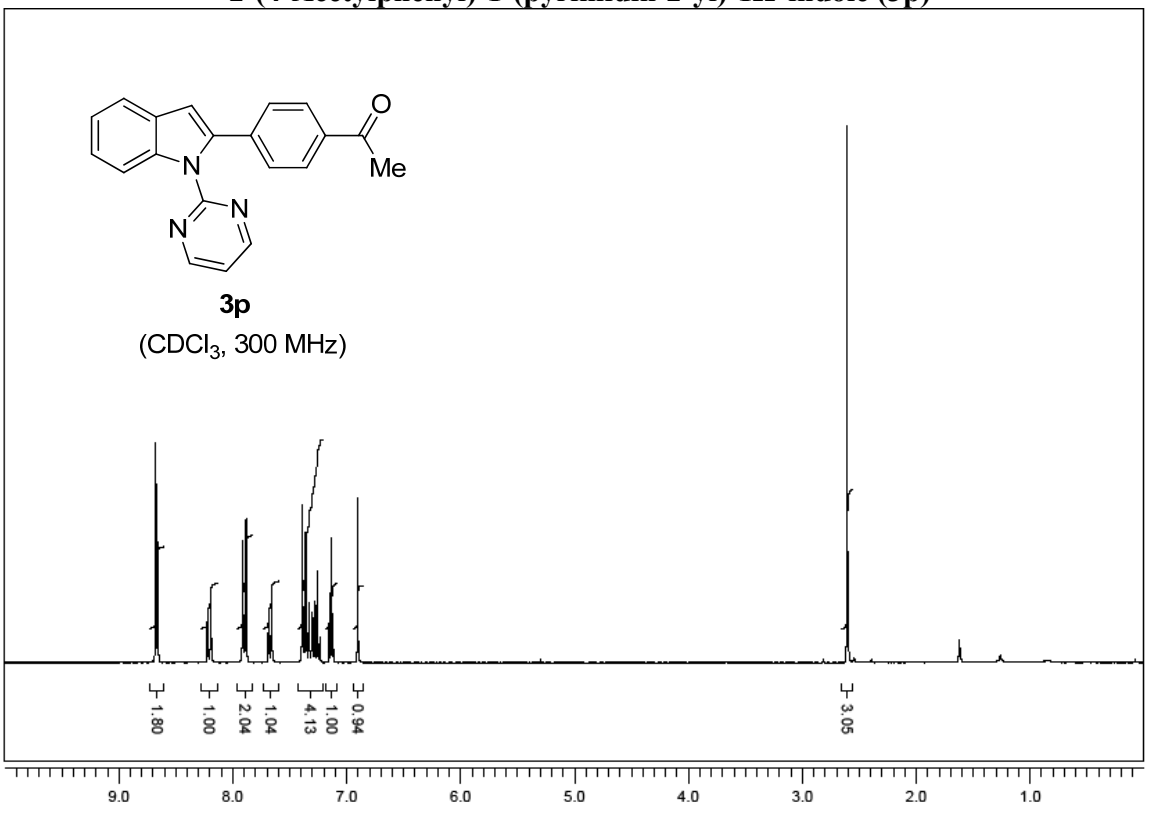
($CDCl_3$, 300 MHz)

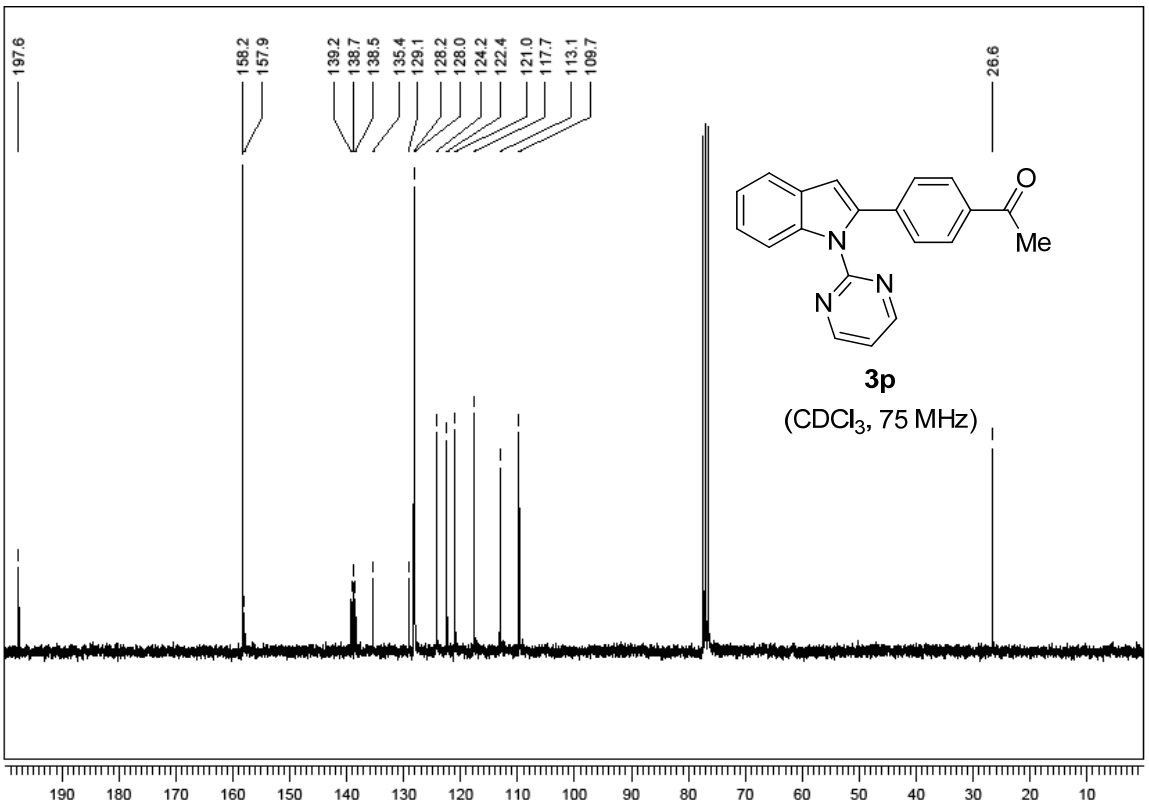


3o

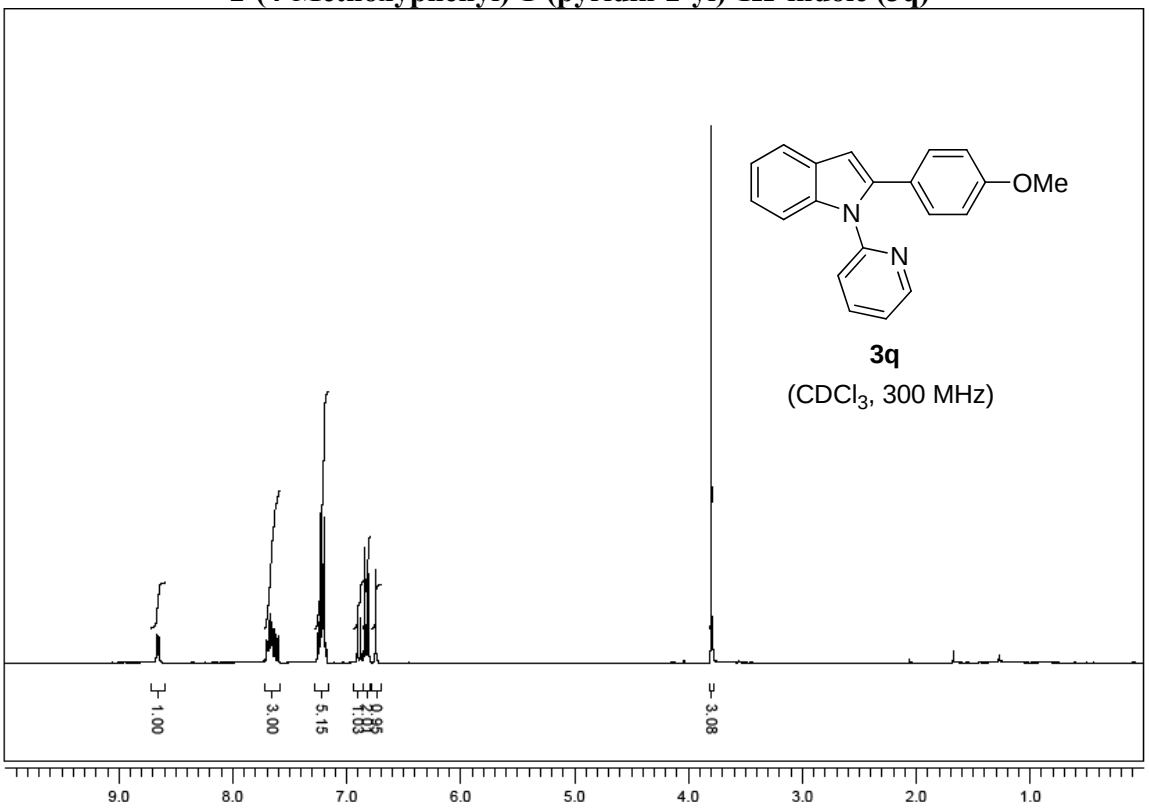
($CDCl_3$, 75 MHz)

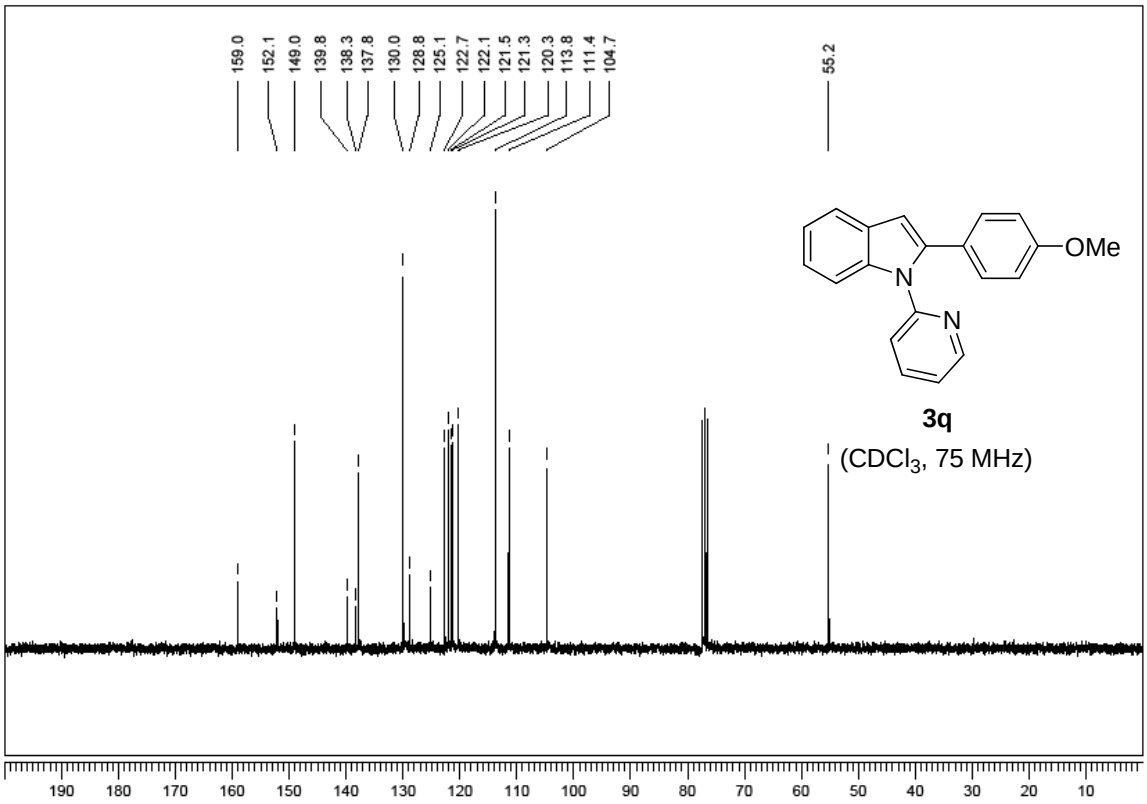
2-(4-Acetylphenyl)-1-(pyrimidin-2-yl)-1*H*-indole (3p)



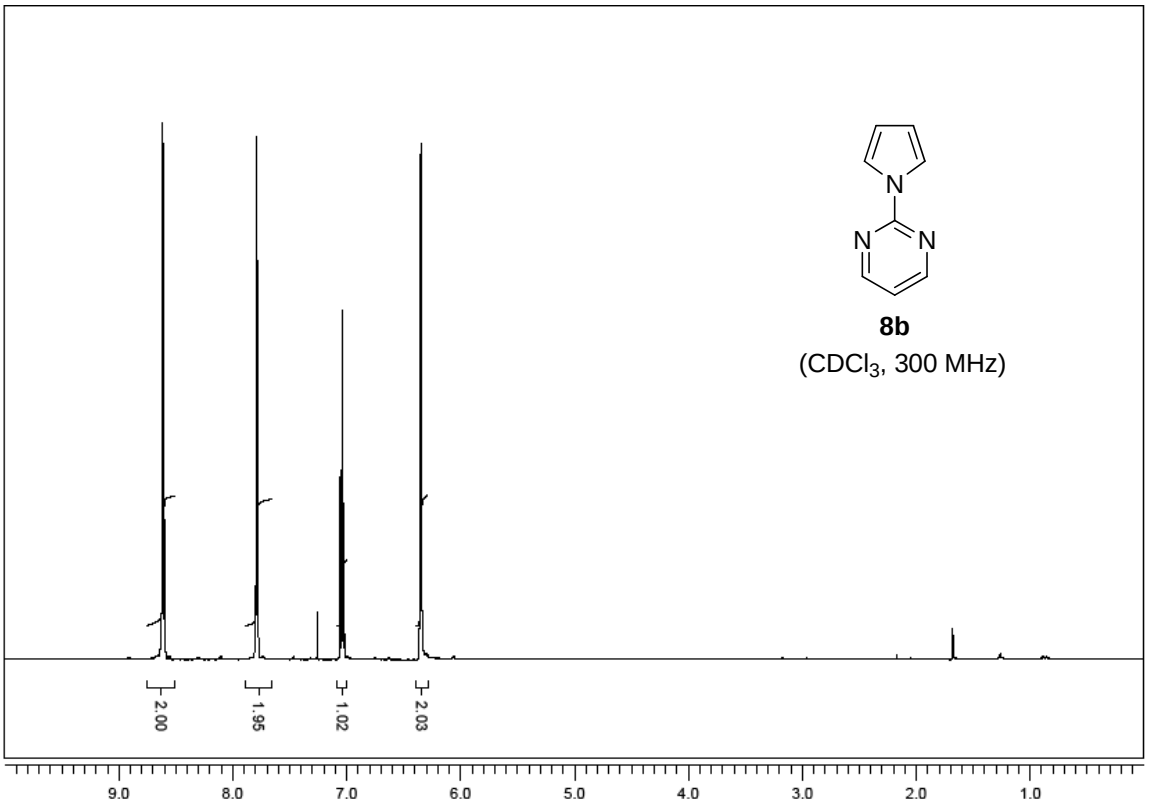


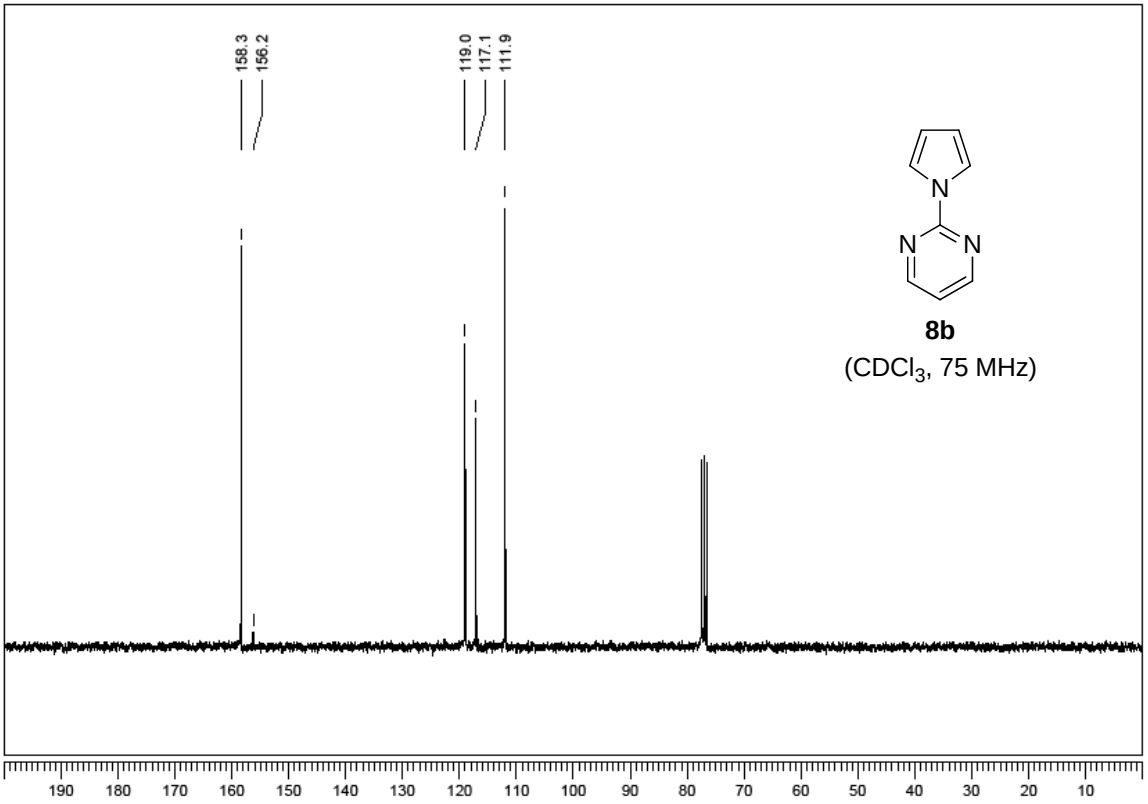
2-(4-Methoxyphenyl)-1-(pyridin-2-yl)-1*H*-indole (3q)



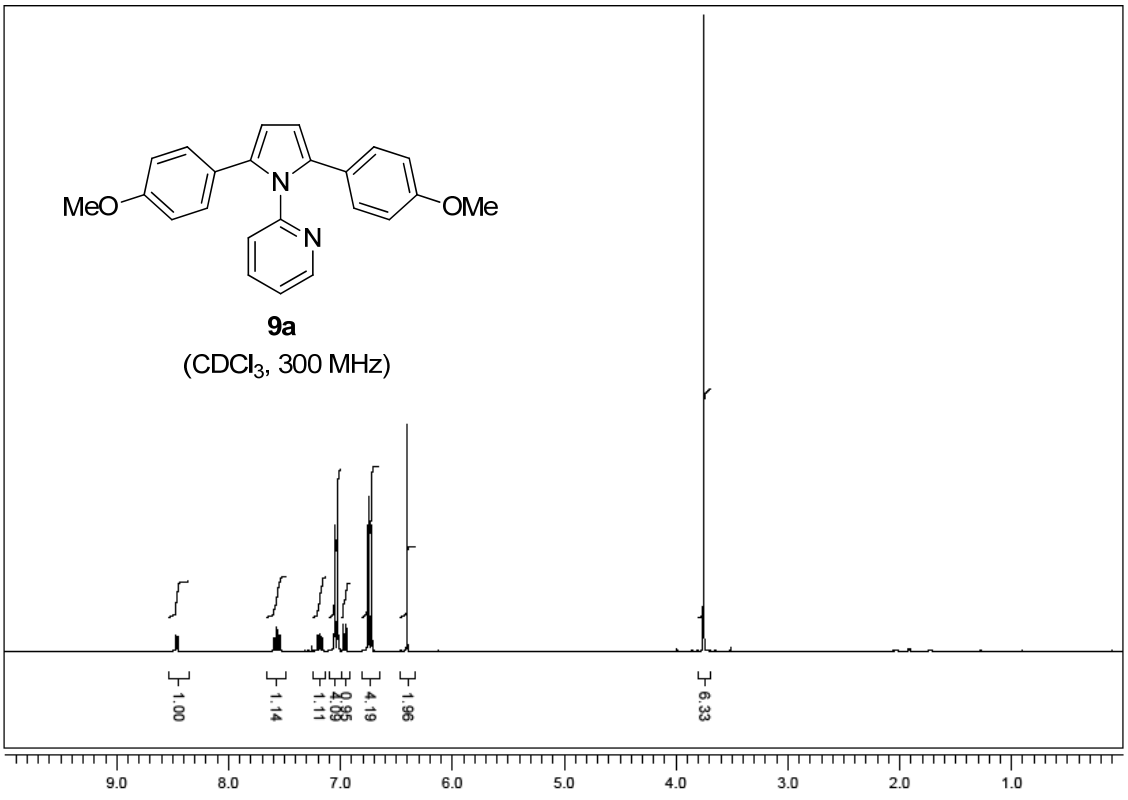


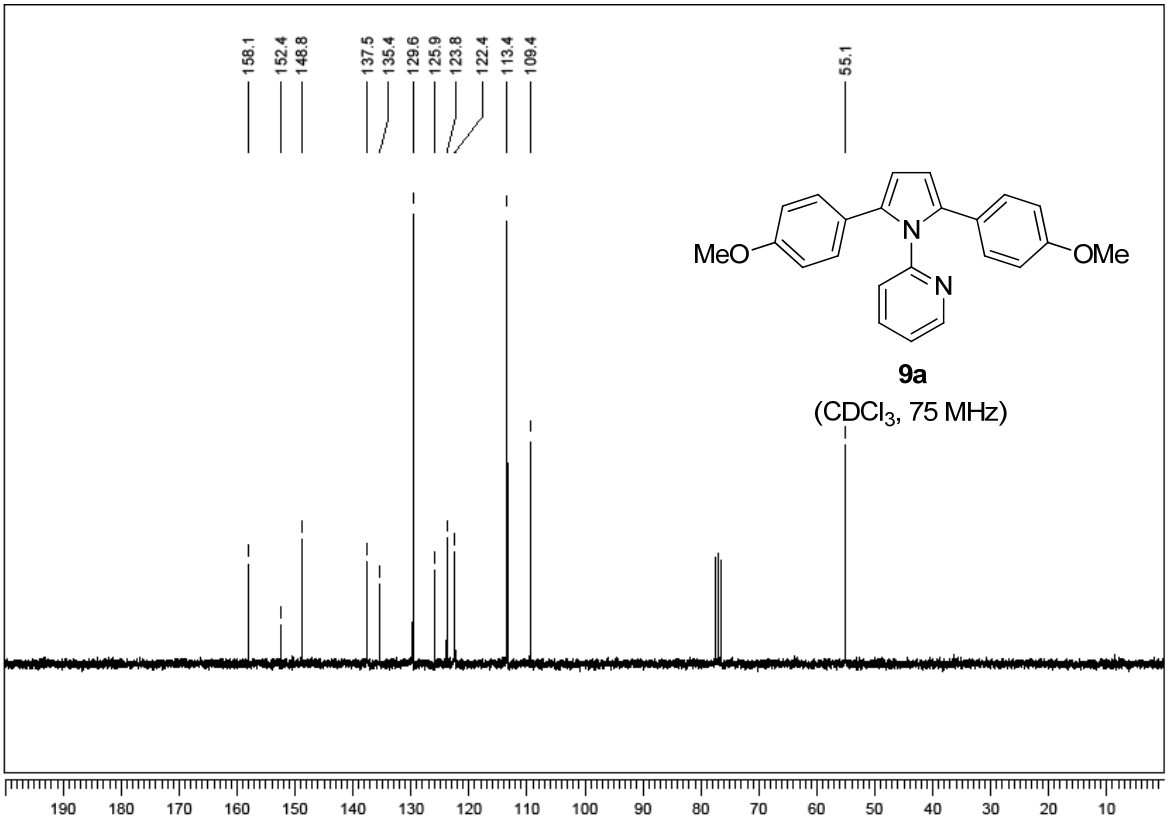
2-(1*H*-Pyrrol-1-yl)pyrimidine (8b)



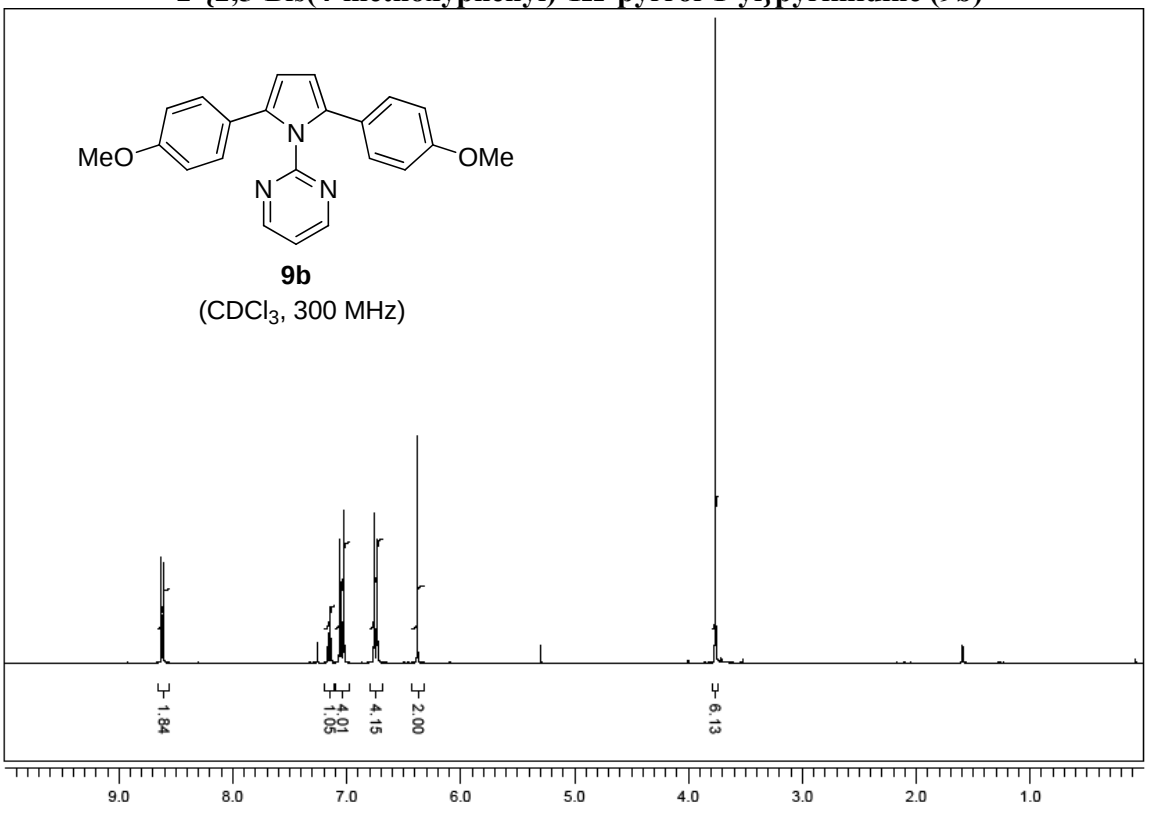


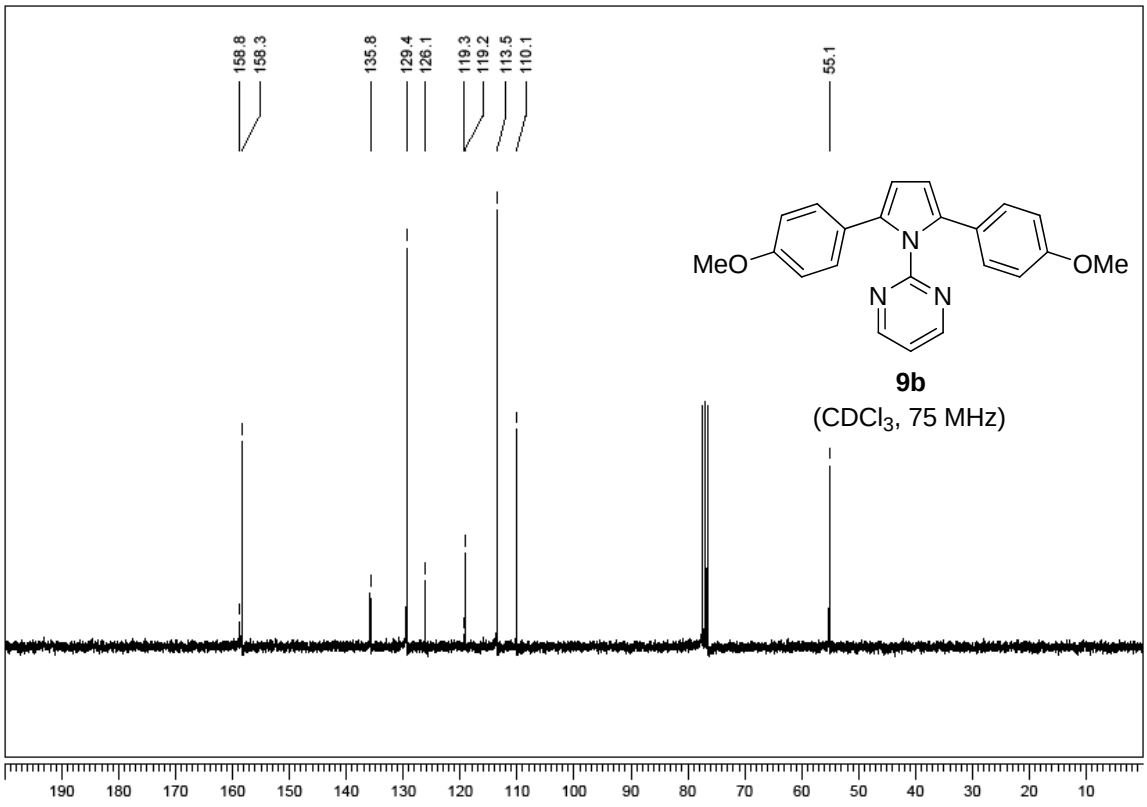
2-{2,5-Bis(4-methoxyphenyl)-1*H*-pyrrol-1-yl}pyridine (9a)



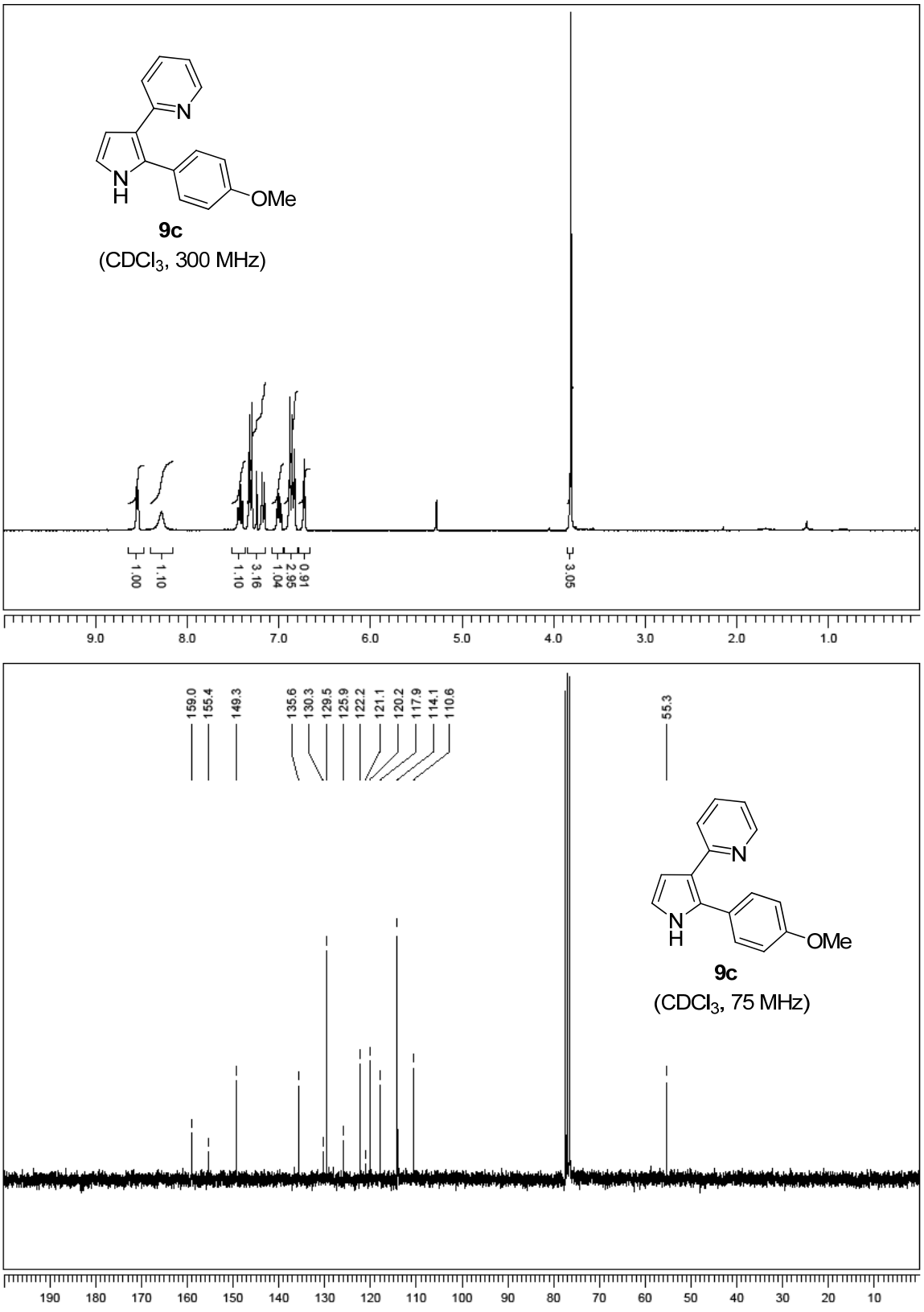


2-{2,5-Bis(4-methoxyphenyl)-1*H*-pyrrol-1-yl}pyrimidine (9b)

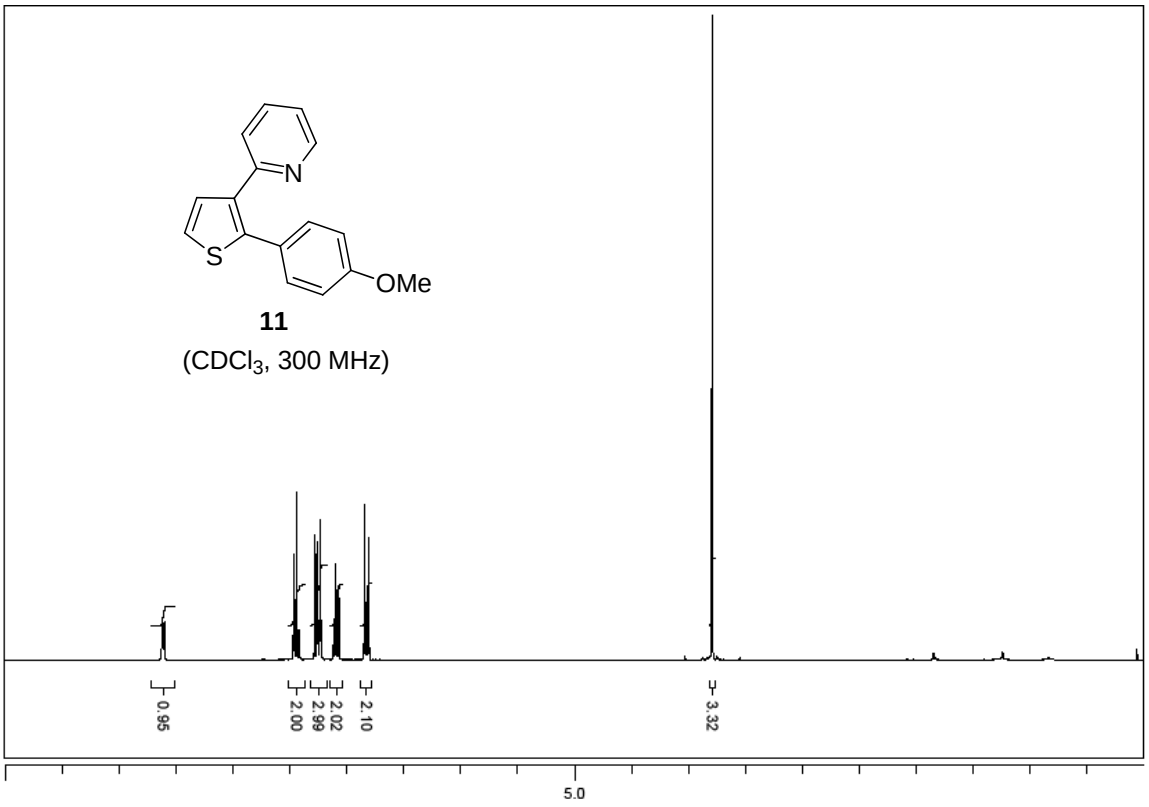


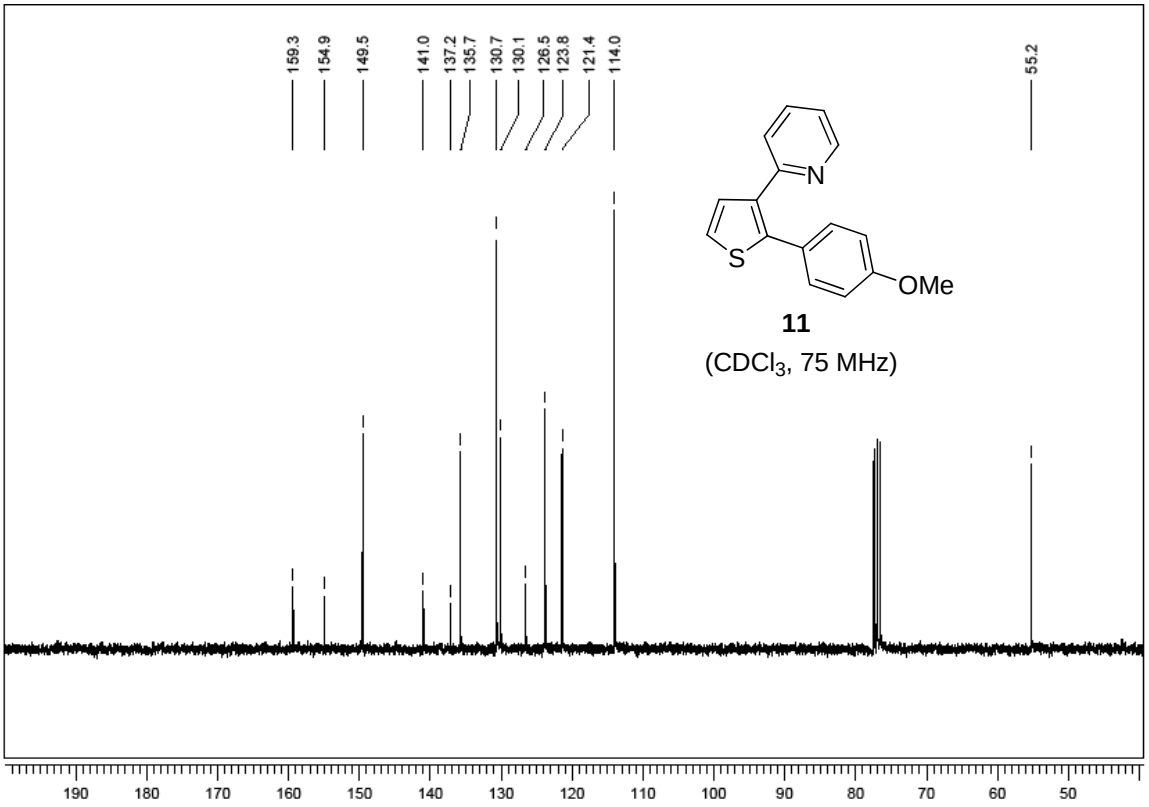


2-{2-(4-Methoxyphenyl)-1*H*-pyrrol-3-yl}pyridine (9c)

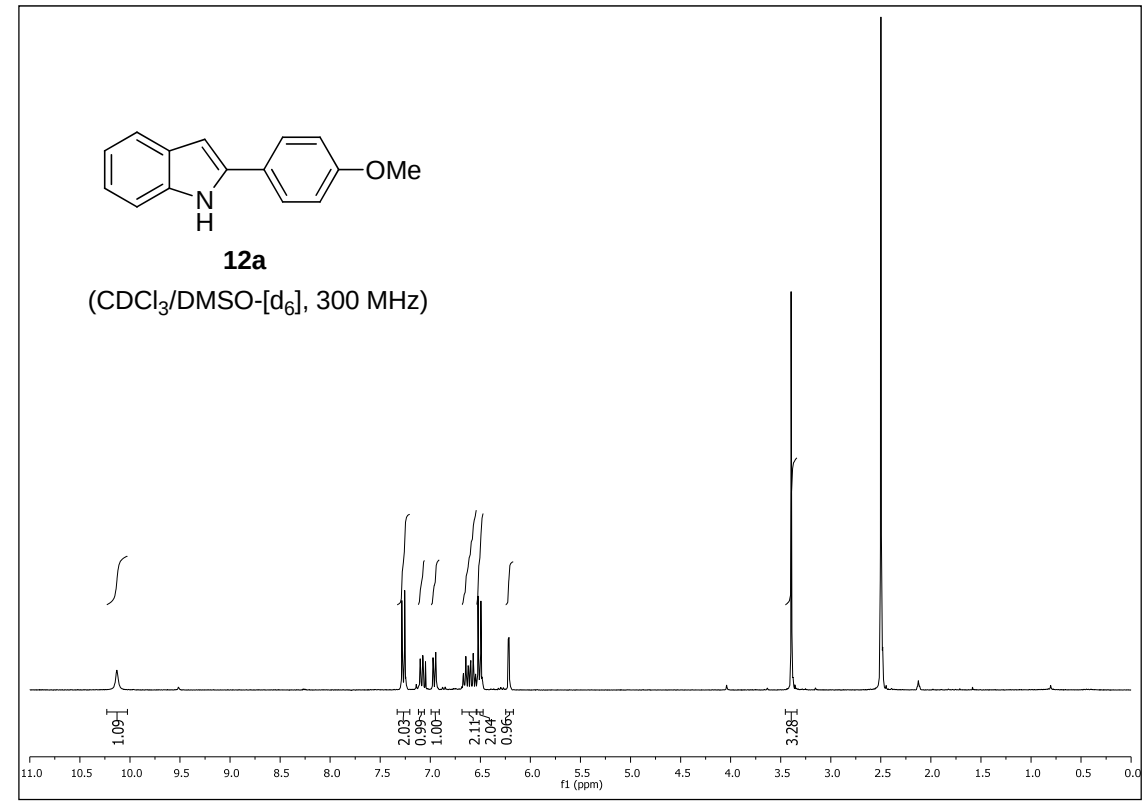


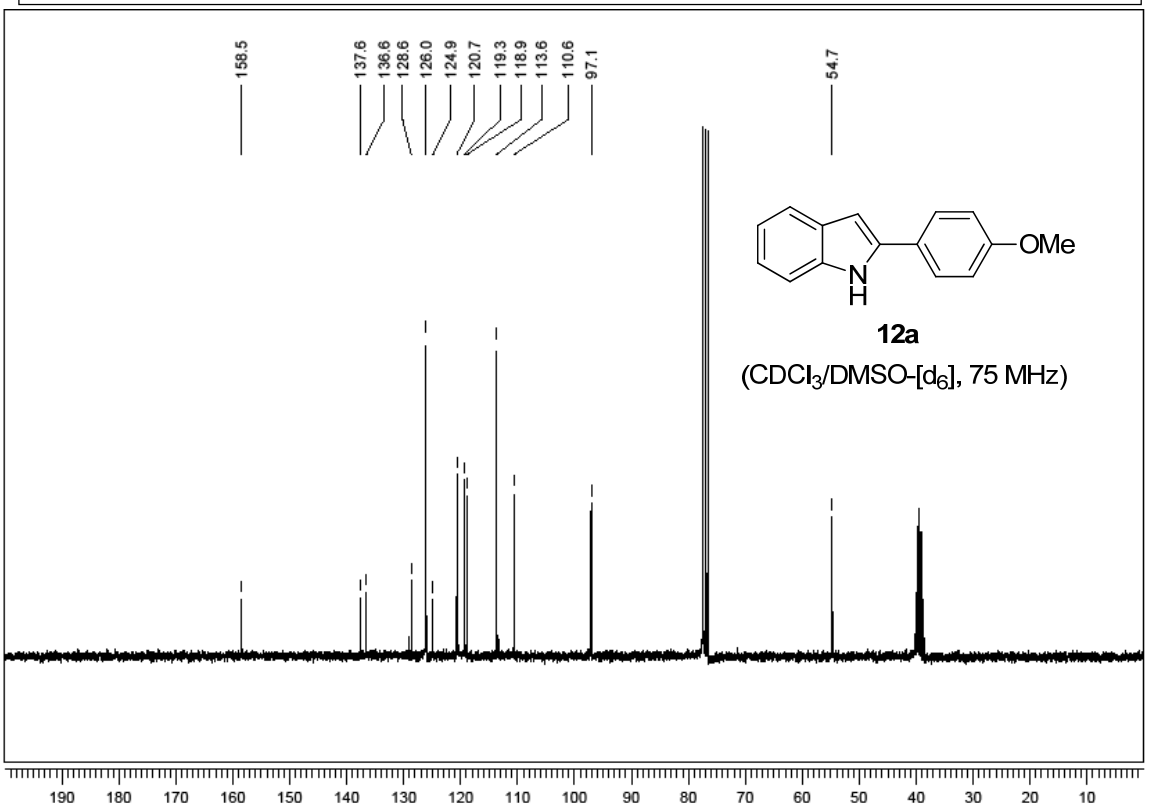
2-{2-(4-Methoxyphenyl)thiophen-3-yl}pyridine (11)



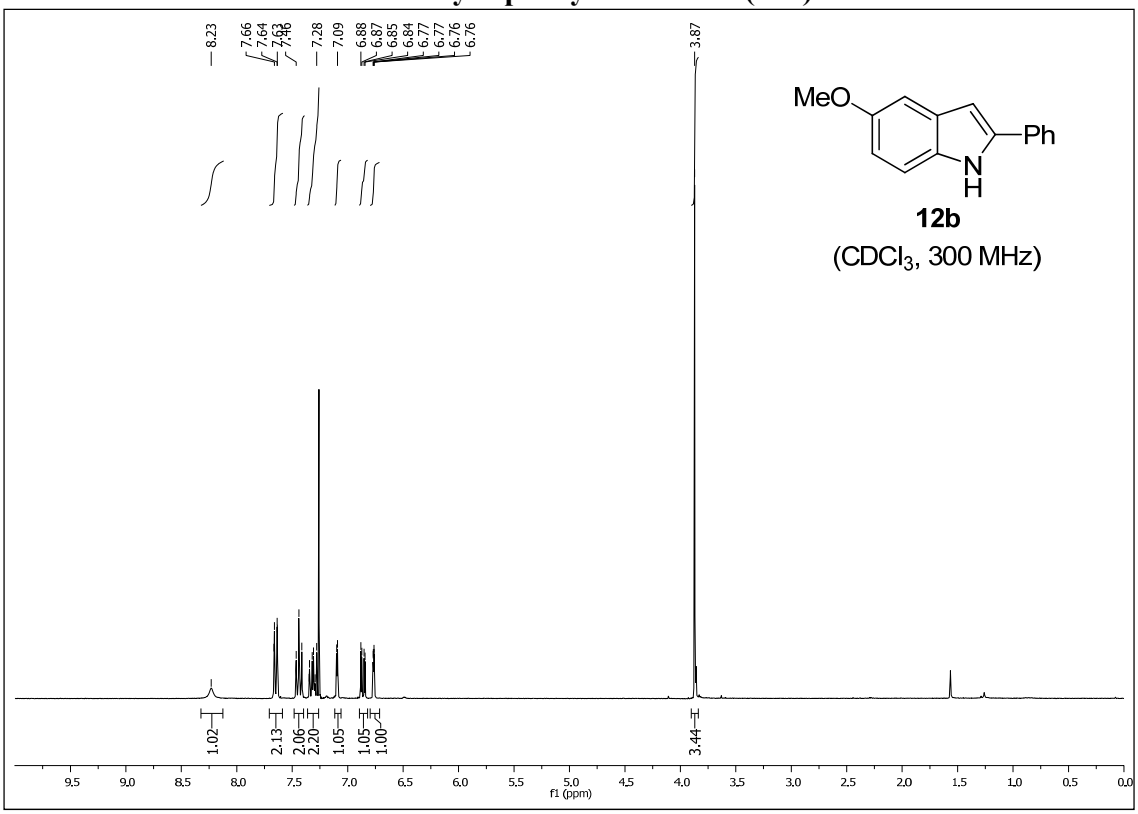


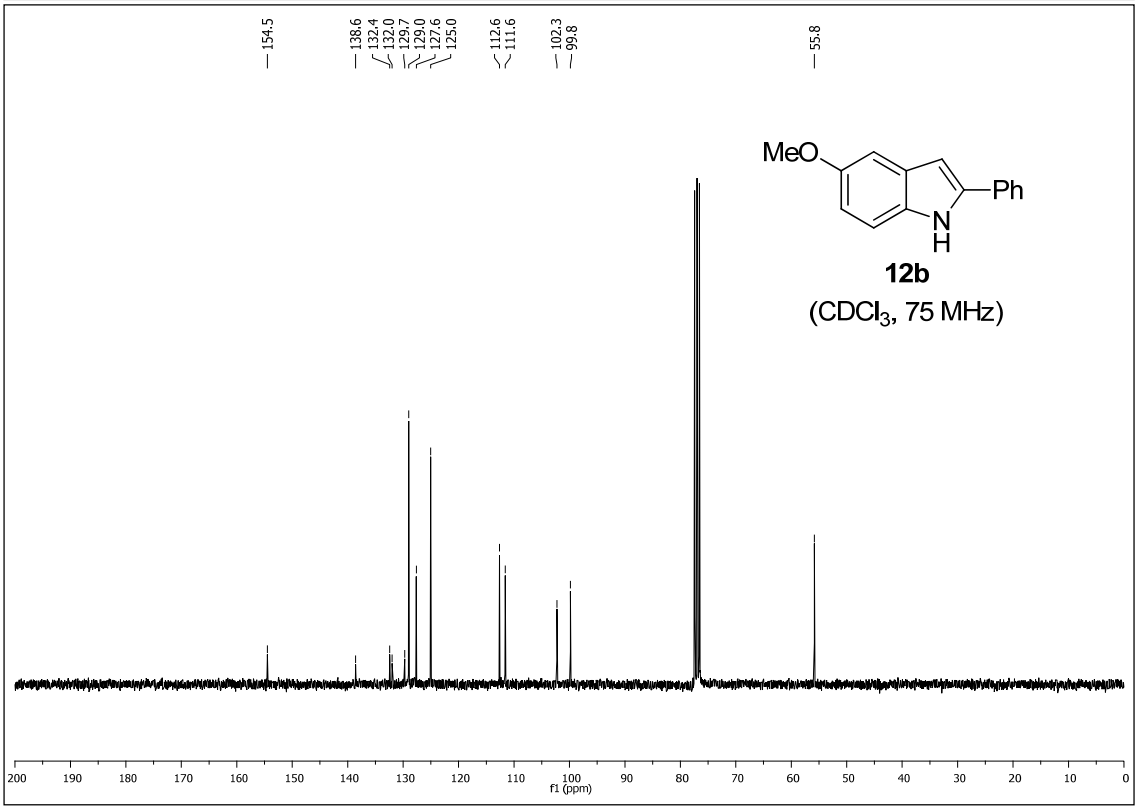
2-(4-Methoxyphenyl)-1*H*-indole (12a)



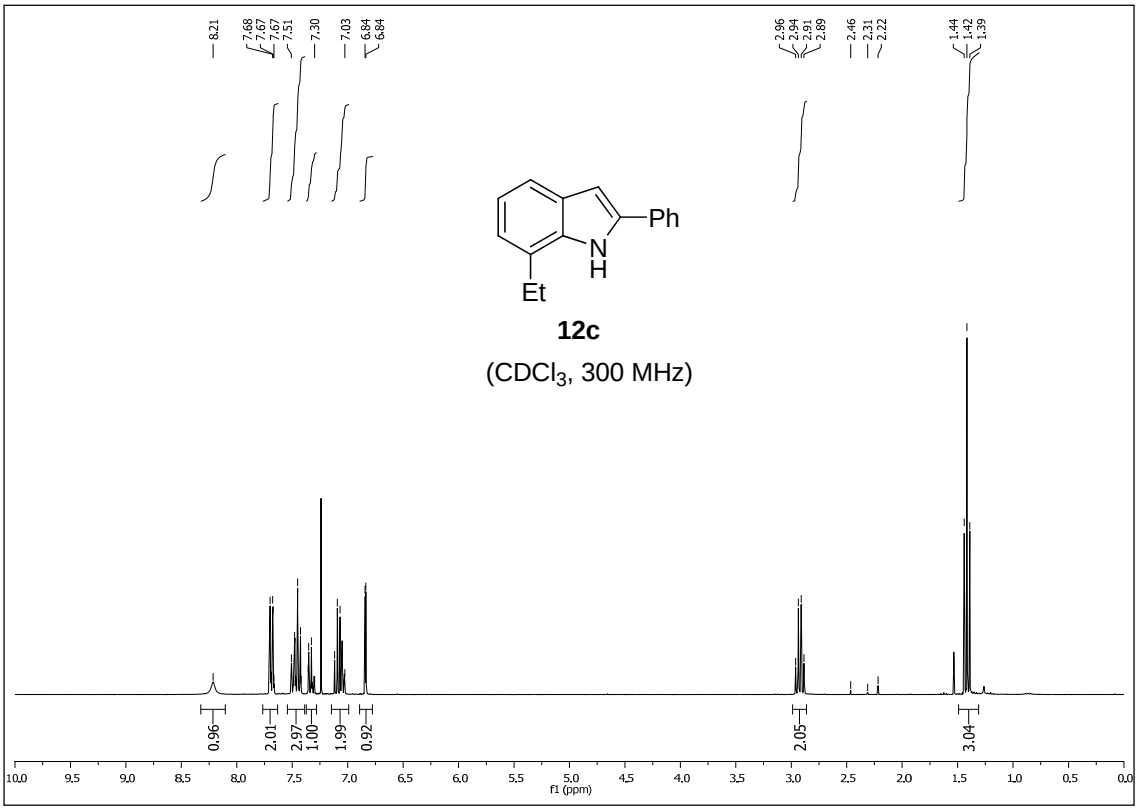


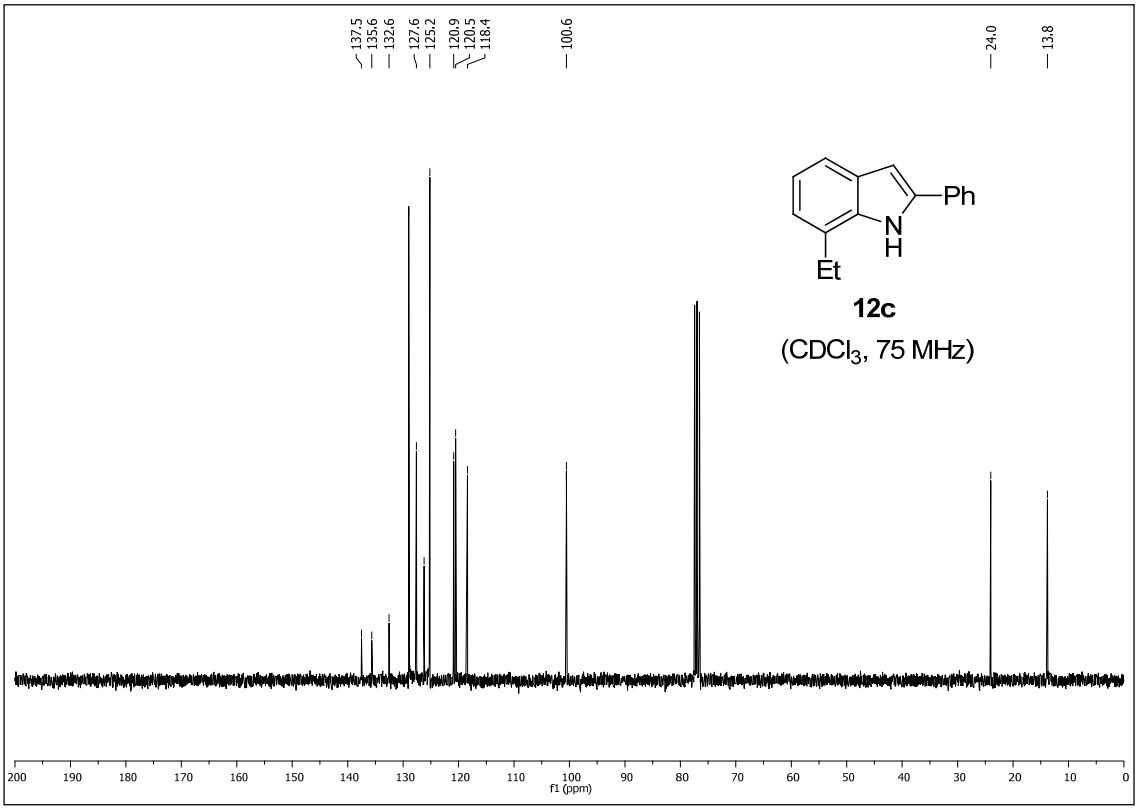
5-Methoxy-2-phenyl-1*H*-indole (12b)





7-Ethyl-2-phenyl-1*H*-indole (12c)





3-Methyl-2-phenyl-1*H*-indole (12d)