# Supporting Information

# One-pot synthesis of 1,2-disubstituted 4-,5-,6- and 7-azaindoles from amino-*o*-halopyridines *via* N-arylation/Sonogashira/cyclization reaction

Sara I. Purificação,† Marina J. D. Pires,† Rafael Rippel, A. Sofia Santos, and M. Manuel B. Marques[a,*]

[a]LAQV@REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia
Universidade Nova de Lisboa, Campus de Caparica
2829-516 Caparica, Portugal
E-mail: mmbmarques@fct.unl.pt

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## General information

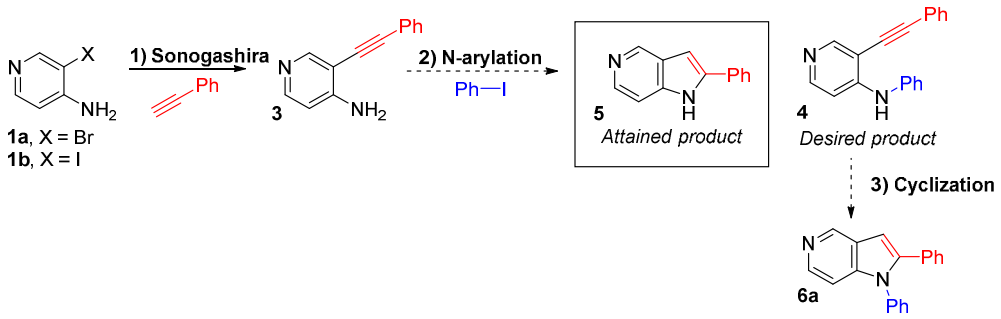
All reagents and solvents were acquired commercially and usually used without further purification. The solvents used during the reactions were dried and distilled using typical methods. Analytical TLC was performed on Merck Kieselgel GF 254, 0.2 mm plates supported on aluminum. Preparative TLC was performed using Merk Kieselgel $60GS_{254}$ silica gel for TLC supported on a glass surface with the described eluent for each case. Column chromatography was performed using Merck Kieselgel 60A silica gel (70-200 mesh) and the described eluent for each case.

Melting points were measured using a Reichert Thermovar melting point apparatus, equipped with a Kofler plate. Measured melting points were not corrected.

NMR spectra were acquired with Bruker ARX 400 or Bruker Avance III 400 spectrometers. $^{1}$H-NMR and $^{13}$C-NMR spectra were measured at 400 and 101 MHz, respectively. The samples were prepared on 5 or 3 mm NMR tubes using $CDCl_3$, $MeOD_4$ or DMSO-$d_6$ as solvents and the corresponding trace of $CHCl_3$, MeOH or DMSO as reference signals. The NMR signals are described with chemical shift (δ, in ppm), source of signal (R-H) and relative intensity of signal multiplicity (nH, with n being the number of protons) of NMR signals are described as singlet (s), broad singlet (br s), doublet of doublets (dd), triplet of doublets (td), doublet (d), triplet (t) and multiplet (m) with coupling constant (J) being given in Hz. IR spectra were acquired using a Perkin Elmer, Spectrum Two FT-IR spectrophotometer. Transmittance of the sample was acquired on between 4000 and 450 $cm^{-1}$ and the samples were supported on NaCl pellets. The IR bands are classified as weak (w), medium (m) or strong (s), and broad (br) when such is the case.

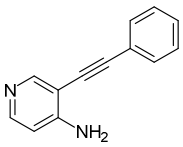
PTLC means preparative thin layer chromatography and ATR means attenuated total reflectance.

## A) Route I – Sonogashira reaction followed by N-arylation




### *1) Sonogashira*

**From 1b:**
**3-(Phenylethynyl)pyridin-4-amine (3)**[1]



DMF was previously degassed 7 times by applying vacuum when the mixture is completely frozen and then flushed with nitrogen. Three solutions were prepared with the degassed DMF and the solids were dried under vacuum before DMF addition:

Solution A – A round-bottom flask was charged with 4-amino-3-iodopyridine (**1b**, 1 equiv, 100 mg, 0.45 mmol), DIPEA (3.2 equiv, 253 µL, 1.45 mmol) and DMF (0.95 mL) and the final solution degassed thrice.

Solution B – A round-bottom flask was charged with CuI (5 mol %, 4.33 mg, 0.023 mmol), $PdCl_2(PPh_3)_2$ (3 mol %, 9.77 mg, 0.014 mmol) and DMF (0.95 mL) and the final solution degassed thrice.

Solution C – A round-bottom flask was charged with phenylacetylene (98%, 2.1 equiv, 107 µL, 0.95 mmol) and DMF (1.9 mL) and the final solution degassed thrice.

To solution B, solution A was added via syringe, then degassed twice; and finally, solution C. The mixture was degassed one more time and then allowed to warm up to rt and stirred for an overnight. After reaction completion (18 h), DCM (3.8 mL) was added to the residue and washed with sat. $NH_4Cl$ (3.8 mL) and water. The combined organic layers were dried over anhydrous sodium sulphate, the desiccant filtered and the product concentrated and vacuum dried.[1]

The product was isolated after purification by column chromatography (silica gel normal, with gradient EtOAc:hexane (1:1) to EtOAc:hexane: EtOH (5:5:1)) with quantitative yield (89 mg, 0.46 mmol) as pale yellow solid.

**IR ($cm^{-1}$) (ATR):** 3450, 2922, 2206, 1736, 1638, 756, 688

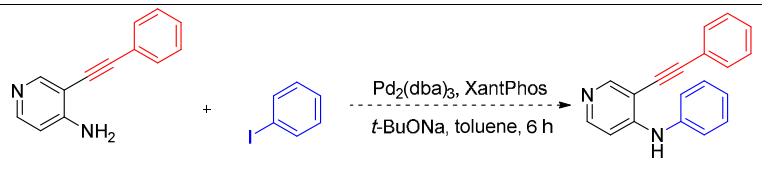
**$^1$H NMR (400 MHz, $CDCl_3$) δ:** 8.40 (s,1H), 8.11 (d, *J* = 5.6 Hz,1H), 7.53 (dd, *J* = 6.5, 3.1 Hz,2H), 7.41 – 7.32 (m, 3H), 6.70 (d, *J* = 5.8 Hz, 1H), 5.25 (br s, 2H)

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ:** 154.1, 150.8, 147.4, 131.7, 129.0, 128.6, 122.4, 108.5, 105.2, 97.8, 81.9

Spectral data were in accordance with literature.[1]

## *2) N-arylation (C-N coupling) attempts of 3*

**General procedure:** A sealed tube equipped with a magnetic stir bar was charged with $Pd_2(dba)_3$ (4 mol %, 3.39 mg, 0.0037 mmol), XantPhos (8 mol %, 4.29 mg, 0.0074 mmol), *t*-BuONa (2 equiv, 17.81 mg, 0.19 mmol) and aminopyridine **3** (1 equiv, 18 mg, 0.093 mmol ) and dry toluene (C = 0.2 M, 0.5 mL), followed by iodobenzene (1.2 equiv, 12.72 µL, 0.11 mmol). The reaction was stirred for 6 hours with temperature. The crude reaction product was filtered through a celite pad. The products were isolated after purification by column chromatography.

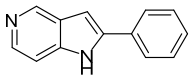



**3** **4**

| entry | 3 (equiv) | phenyl iodide (equiv) | temperature (ºC) | 4 yield (%)[a] |
|---|---|---|---|---|
| **1** | 1 | 1.2 | 110 | - |
| **2** | 1 | 1.2 | 60 | - |

[a] *No desired product **4** was attained, though this reaction resulted in compound **5**:*

**2-Phenyl-*1H*-pyrrolo[3,2-*c*]pyridine (5)**[2]




**Purification:** Silica gel, dichloromethane/methanol with gradient

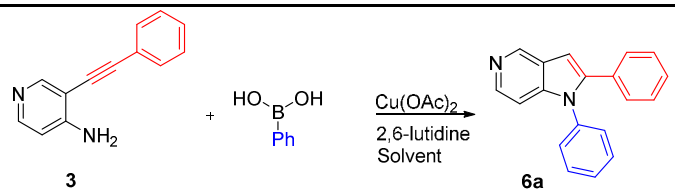
**Appearance:** White solid

**Yield:** Traces

**$^1$H NMR (400 MHz, DMSO-d$_6$) δ:** 11.97 (s, 1H), 8.82 (s, 1H), 8.17 (d, *J* = 4.3 Hz, 1H), 7.90 (d, *J* = 7.3 Hz, 2H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.38 – 7.35 (m, 2H), 7.04 (s, 1H)

Spectral data were in accordance with literature.[2]

**Alternative investigated procedures:**

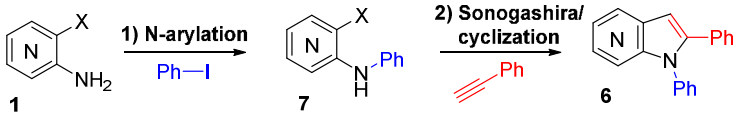



**3** **6a**

| entry | boronic acid (equiv) | $Cu(OAc)_2$ (equiv) | 2,6-lutidine (equiv) | conditions | procedure adapted from literature | yield (%) |
|---|---|---|---|---|---|---|
| **1** [a] | 1.5 | 0.1 | 1.1 | toluene, rt to 120 °C | *J. Org. Chem.*, **2014**, *79* (19), pp 9000–9008[3] | - |
| **2** [b] | 2 | 1.5 | 2 | dichloromethane, rt | *Org. Lett.*, **2012**, *14* (7), pp 1764–1767[4] | - |
| **3** [a] | 1.5 | 1 | 1.1 | toluene, 50 °C | *J. Org. Chem.*, **2014**, *79* (19), pp | 4 |

[a] Dodecanoic acid was used. [b] Atmosphere $O_2$.

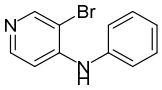
## B) Route II – Stepwise N-arylation followed by Sonogashira/cyclization reaction




### *1) N-arylation*

**General procedure:** A sealed tube equipped with a magnetic stir bar was charged with $Pd_2(dba)_3$ (4 mol %, 21 mg, 0.023 mmol), XantPhos (8 mol %, 26.8 mg, 0.046 mmol), *t*-BuONa (2 equiv, 111 mg, 1.56 mmol) and 4-amino-3-bromopyridine **7a** (1 equiv, 100 mg, 0.578 mmol) and dry toluene (2.9 mL, C = 0.2 M), followed by iodobenzene (1.2 equiv, 77.6 µL, 0.693 mmol). The reaction was stirred for 6 hours at 110°C. The crude reaction product was filtered through a celite pad. The desired products were isolated after purification by column chromatography (silica gel, EtOAc: hexane with gradient).

**3-Bromo-*N*-phenylpyridin-4-amine (7a)**[5]



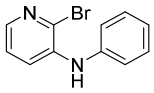

**Appearance:** Beige solid

**Yield:** 87% (124.8 mg , 0.5 mmol of **7a** from 100 mg, 0.578 mmol of starting 4-amino-3-bromopyridine)

**$^1$H NMR (400 MHz, $CDCl_3$) δ:** 8.47 (s, 1H), 8.12 (d, *J* = 5.6 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.34 – 7.13 (m, 3H), 6.90 (d, *J* = 5.7 Hz, 1H), 6.57 (s, 1H)

Spectral data were in accordance with literature.[5]

**2-Bromo-*N*-phenylpyridin-3-amine**[5]



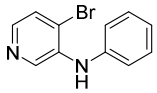

**Appearance:** Yellow solid

**Yield:** 99% (143.4 mg, 0.575 mmol from 100 mg of starting 3-amino-2-bromopyridine)

**$^1$H NMR (400 MHz, $CDCl_3$) δ:** 7.84 (dd, *J* = 4.5, 1.5 Hz, 1H), 7.42 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.35 (t, *J* = 7.9 Hz, 2H), 7.18 – 7.04 (m, 4H), 6.14 (br s, 1H)

Spectral data were in accordance with literature.[5]

**4-Bromo-*N*-phenylpyridin-3-amine**[5]



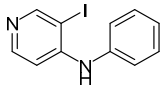
**Appearance:** Beige solid

**Yield:** 79% (113.4 mg, 0.455 mmol from 100 mg of starting 3-amino-4-bromopyridine)

**$^1$H NMR (400 MHz, $CDCl_3$) δ:** 8.50 (s, 1H), 7.92 (d, *J* = 5.1 Hz, 1H), 7.45 (d, *J* = 5.1 Hz, 1H), 7.35 (t, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 7.7 Hz, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 5.96 (s, 1H)

Spectral data were in accordance with literature.[5]

**3-Iodo-*N*-phenylpyridin-4-amine (7b)**



**Appearance:** White solid

**Yield:** 22% (44 mg, 0.15 mmol of **7b** from 150 mg , 0.68 mmol of starting 4-amino-3-iodopyridine)

**M.p.:** 74- 76 ºC

**IR (ATR) $\nu_{max}$ ($cm^{-1}$):** 3370, 2923, 2852, 1735, 1572, 1503, 1405, 1228, 1007, 698

**$^1$H NMR (400 MHz, $CDCl_3$) δ:** 8.66 (s, 1H), 8.12 (br s, 1H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.25 – 7.20 (m, 3H), 6.85 (d, *J* = 4.0 Hz, 1H), 6.43 (br s, 1H)

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ:** 156.8, 150.7, 149.0, 138.6, 129.8, 125.7, 123.6, 107.9, 84.6.

**GS-MS calcd for $C_{11}H_9IN_2$ (M+):** 295.9; **Found:** 295.9

## *2) Sonogashira and cyclization reaction*

**General procedure from 7a, with X=Br:** DMF was previously degassed 7 times by applying vacuum when the mixture is completely frozen and then flushed with nitrogen.

Three solutions were prepared with the degassed DMF and the solids were dried under vacuum before DMF addition:

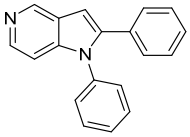
Solution A – A round-bottom flask was charged with **7a, X=Br** (1 equiv, 90 mg, 0.36 mmol), DIPEA (3.2 equiv, 202 µL , 1.15 mmol) and DMF (0.76 mL) and the final solution degassed thrice.

Solution B – A round-bottom flask was charged with CuI (5 mol %, 3.46 mg, 0.018 mmol), $PdCl_2(PPh_3)_2$ (3 mol %,7.82 mg, 0.011 mmol) and DMF (0.76 mL) and the final solution degassed thrice.

Solution C – A round-bottom flask was charged with phenylacetylene (98%, 86 µL, 0.76 mmol, 2.1 equiv) and DMF (1.5 mL) and the final solution degassed thrice.

To solution B, solution A was added via syringe, then degassed twice; and finally, solution C. The mixture was degassed one more time and then allowed to warm up to 110 ºC and stirred for 24 h. After reaction completion, DMF was evaporated; DCM was added to the residue and washed with sat. $NH_4Cl$ and water. The combined organic layers were dried over anhydrous sodium sulphate, the desiccant filtered and the product concentrated and vacuum dried.[1]

**1,2-Diphenyl-5-azaindole (6a)**



**Purification:** Column chromatography (silica gel flash, EtOAc:hexane with gradient to EtOAc:MeOH 10%) and PTLC ($CHCl_3$:MeOH 3%)

**Appearance:** Beige solid

**Yield:** 60% (59 mg, 0.22 mmol of **6a** from 90 mg, 0.36 mmol of starting **7a**)

**M.p.:** 176-178 ºC

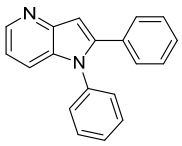
**IR (cm-1) (ATR):** 2924, 1739, 1591, 1461, 1379, 1215, 753, 695

**$^1$H NMR (400 MHz, MeOD-$d_4$) δ:** 8.89 (s, 1H), 8.19 (d, *J* = 4.9 Hz, 1H), 7.53 – 7.42 (m, 3H), 7.33 – 7.23 (m, 8H), 6.98 (s, 1H)

**$^{13}$C NMR (101 MHz, MeOD-$d_4$) δ:** 144.5, 144.2, 143.4, 141.0, 138.5, 132.6, 130.8, 130.2, 129.4, 129.4, 128.9, 126.7, 107.4, 103.5

**HRMS (EI) calcd for $C_{19}H_{14}N_2$ (M+1):** 271.1191; **Found:** 271.1229

**1,2-Diphenyl-4-azaindole (6b)**[6]



**Purification:** PTLC using EtOAc/hexane (1:1) followed by PTLC using EtOAc/hexane (4:1)

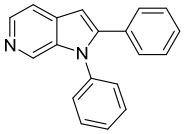
**Appearance:** Yellow solid

**Yield:** 27% (14.4 mg, 0.053 mmol of **6b** from 50 mg , 0.2 mmol of starting 2-bromo-*N*-phenylpyridin-3-amine)

**$^1$H NMR (400 MHz, $CDCl_3$) δ:** 8.51 (d, *J* = 3.8 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.44 – 7.37 (m, 3H), 7.29 – 7.23 (m, 7H), 7.09 (dd, *J* = 8.3, 4.6 Hz, 1H), 7.01 (s, 1H)

Spectral data were in accordance with literature.[6]

**1,2-Diphenyl-6-azaindole (6c)**



**Purification:** PTLC using EtOAc/hexane (1:1) followed by PTLC using EtOAc/hexane/EtOH (5:5:1)

**Appearance:** Yellow solid

**Yield:** 47% (17.4 mg, 0.064 mmol of **6c** from 33.9 mg, 0.14 mmol of starting 4-bromo-*N*-phenylpyridin-3-amine)

**M.p.:** 106-107 °C

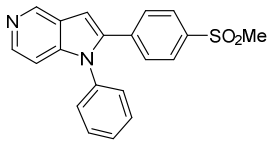
**IR ($cm^{-1}$) (NaCl):** 3044, 2923, 2853, 1596, 1498

**$^1$H NMR (400 MHz, $CDCl_3$) δ:** 8.66 (s, 1H), 8.33 (d, *J* = 5.2 Hz, 1H), 7.56 (d, *J* = 5.3, 1H), 7.46 – 7.39 (m, 3H), 7.28 – 7.26 (m, 7H), 6.78 (s, 1H)

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ:** 144.2, 140.0, 137.5, 135.9, 134.1, 133.1, 131.5, 129.6, 129.3, 128.5, 128.4, 128.0, 127.8, 114.8, 102.8. Note: one carbon is masked.

**HRMS (EI) calcd for $C_{19}H_{14}N_2$ (M+1):** 271.1190; **Found:** 271.1229

**2-(4-(Methylsulphonyl)phenyl)-1-phenyl-5-azaindole (6k)**




**Purification:** Silica gel flash, EtOAc/hexane (1:1)

**Appearance:** Pale yellow solid

**Yield:** 32% (22.4 mg, 0.064 mmol of **6k** from 50 mg, 0.2 mmol of starting **7a**)

**M.p.:** 174-177 ºC

**IR (cm$^{-1}$) (NaCl):** 2929, 1729, 1595, 1501, 1314, 1149, 769

**$^1$H NMR (400 MHz, $CDCl_3$) δ:** 8.97 (s, 1H), 8.28 (d, *J* = 4.2 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.42 – 7.37 (m, 5H), 7.20 – 7.14 (m, 3H), 6.94 (s, 1H), 2.99 (s, 3H)

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ:** 143.2, 141.1, 140.3, 139.8, 136.8, 136.6, 130.2, 129.6, 128.8, 127.7, 127.6, 106.4, 104.8, 44.5. Note: two carbons are masked

**HRMS (EI) calcd for $C_{20}H_{16}N_2O_2S$ (M+1):** 349.0966; **Found:** 349.1005

**General procedure from 7b, with X=I:** DMF was previously degassed 7 times by applying vacuum when the mixture is completely frozen and then flushed with nitrogen.

Three solutions were prepared with the degassed DMF and the solids were dried under vacuum before DMF addition:

Solution A – A round-bottom flask was charged with **7b** (1 equiv, 20 mg, 0.068 mmol), DIPEA (3.2 equiv, 37.7 µL, 0.22 mmol) and DMF (0.14 mL) and the final solution degassed thrice.

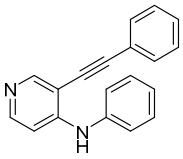
Solution B – A round-bottom flask was charged with CuI (5 mol %, 0.6 mg, 0.034 mmol), $PdCl_2(PPh_3)_2$ (3 mol %, 1.45 mg, 0.02 mmol) and DMF (0.14 mL) and the final solution degassed thrice.

Solution C – A round-bottom flask was charged with phenylacetylene (98%, 2.1 equiv, 15.9 µL, 0.14 mmol) and DMF (0.3 mL) and the final solution degassed thrice.

To solution B, solution A was added via syringe, then degassed twice; and finally, solution C. The mixture was degassed one more time and then allowed to warm up to rt and stirred for an overnight to achieve the Sonogashira product; then the reaction was stirred at 110 ºC for 5 h. After reaction completion, DCM was added to the residue and washed with sat. $NH_4Cl$ and water. The combined organic layers were dried over anhydrous sodium sulphate, the desiccant filtered and the product concentrated and vacuum dried.[1]

The product **6a** was isolated after purification by column chromatography (silica gel flash, EtOAc:hexane (1:1)) with 66% yield as pale beige solid (12 mg, 0.044 mmol of **6a** from 20 mg, 0.068 mmol of starting **7b**). Spectral data were in accordance with the product **6a** isolated from the reaction using "**General procedure from 7a, with X=Br".**

*Sonogashira intermediate* **4** *(N-phenyl-3-(phenylethynyl)pyridin-4-amine) synthesis and isolation:*



**Note:** DMF was previously degassed 7 times by applying vacuum when the mixture is completely frozen and then flushed with nitrogen.

Three solutions were prepared with the degassed DMF and the solids were dried under vacuum before DMF addition:

Solution A – A round-bottom flask was charged with **7b, X=I** (1 equiv, 20 mg, 0.068 mmol), DIPEA (3.2 equiv, 37.7 µL, 0.22 mmol) and DMF (0.14 mL) and the final solution degassed thrice.

Solution B – A round-bottom flask was charged with CuI (5 mol %, 0.6 mg, 0.034 mmol), $PdCl_2(PPh_3)_2$ (3 mol %, 1.45 mg, 0.02 mmol) and DMF (0.14 mL) and the final solution degassed thrice.

Solution C – A round-bottom flask was charged with phenylacetylene (98%, 2.1 equiv, 15.9 µL, 0.14 mmol) and DMF (0.3 mL) and the final solution degassed thrice.

To solution B, solution A was added via syringe, then degassed twice; and finally, solution C. The mixture was degassed one more time and then allowed to warm up to rt and stirred for an overnight. After reaction completion, DCM was added to the residue and washed with sat. $NH_4Cl$ and water. The combined organic layers were dried over anhydrous sodium sulphate, the desiccant filtered and the product concentrated and vacuum dried.[1]

**Purification:** Silica gel flash, EtOAc/hexane (1:1)

**Appearance:** Beige solid

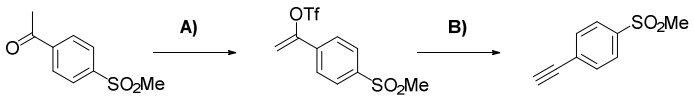
**Yield:** 70% (12.7 mg , 0.047 mmol of **4** from 20 mg, 0.068 mmol of starting **7b**)

**IR ($cm^{-1}$) (ATR):** 2920, 2858, 1583, 1567, 1513, 1496, 752

**$^1$H NMR (400 MHz, $CDCl_3$) δ:** 8.55 (s, 1H), 8.21 (d, *J* = 4.0 Hz, 1H), 7.61 – 7.56 (m, 2H), 7.48 – 7.38 (m, 5H), 7.34 – 7.22 (m, 3H), 6.97 (d, *J* = 5.8 Hz, 1H), 6.92 (br s, 1H)

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ:** 152.0, 151.4, 148.7, 138.6, 131.8, 129.8, 129.2, 128.7, 125.6, 123.4, 122.4, 106.3, 105.9, 98.4, 82.1

*Synthesis of 1-ethynyl-4-(methylsulphonyl)benzene*[7]




**A)** To a solution of 4-(methylsulphonyl)acetophenone (1 equiv, 500 mg, 2.5 mmol) in dry toluene (10 mL), 2,4,6-collidine (2 equiv, 671 µL, 5 mmol) was added at 0 ºC under $N_2$. This mixture was stirred for 5 minutes, then $Tf_2O$ (2 equiv, 847 µL, 5 mmol) was added dropwise and the reaction was stirred for an overnight at rt, then 2 h at 50 ºC. The crude reaction product was filtered through a celite pad and washed with ethyl acetate. The product was isolated after purification by column chromatography (silica gel flash, ethyl acetate: cyclohexane with gradient) with 69% yield as a beige solid (574 mg, 1.74 mmol of the desired product from 500 mg of 4-(methylsulphonyl)acetophenone).

**M.p.:** 48-50 ºC

**IR (KBr) $\nu_{max}$ ($cm^{-1}$):** 1426, 1314, 1226, 1142, 942

**$^1$H NMR (400 MHz, $CDCl_3$) δ:** 8.01 (d, J = 8.0 Hz, 2H), 7.75 (d, J = 8.0 Hz, 2H), 5.80 (d, J = 3.6 Hz, 1H), 5.59 (d, J = 3.7 Hz, 1H), 3.08 (s, 3H)

**B)** To a solution of 1-(4-(methylsulphonyl)phenyl)vinyl trifluoromethanesulphonate (1 equiv, 364 mg, 1.1 mmol) in dry THF (11 mL) freshly prepared, TBAF 1 M in THF (2.5 equiv, 2.76 mL) was added dropwise under $N_2$. After 10 min at rt the reaction was complete. Ethyl acetate (50 mL) was added and extracted thrice with water (10 mL). The combined aqueous layers were then extracted with more ethyl acetate and finally the combined organic layers washed with brine. Combined organic layers were dried over anhydrous sodium sulphate, the desiccant filtered and the product concentrated and vacuum dried.[8] The product was isolated after purification by column chromatography (silica gel flash, ethyl acetate:hexane (1:1)) with 68% yield as a light yellow solid (135 mg, 0.75 mmol of the desired product from 364 mg of 1-(4-(methylsulphonyl)phenyl)vinyl trifluoromethanesulphonate).

**M.p.:** 94-97 ºC (Lit. 100-101 ºC)[7]

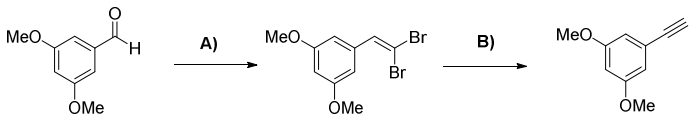
**IR (NaCl) $\nu_{max}$ ($cm^{-1}$):** 3246, 2107, 1301, 1278, 1150

**$^1$H NMR (400 MHz, $CDCl_3$) δ:** 7.91 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 8.5 Hz, 2H), 3.29 (s, 1H), 3.06 (s, 3H)

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ:** 140.5, 133.1, 128.1, 127.5, 81.9, 81.4, 44.6

Spectral data were in accordance with literature.[7]

*Synthesis of 1-ethynyl-3,5-dimethoxybenzene*[9]




**A)** To a solution of 3,5-dimethoxybenzaldehyde (1 equiv, 581 mg, 3.5 mmol) and carbon tetrabromide (2 equiv, 2.317 g, 7 mmol) in dry dichloromethane (10 mL) was added triphenylphosphine (4 equiv, 3.654 g, 14 mmol) in portions over a period of 20 mins at 0 ºC under inert atmosphere. The reaction mixture was stirred at 0 ºC for 2 h. After reaction completion, the mixture was quenched with water (15 mL). Then reaction mixture was extracted with dichloromethane (2 x 20 mL) and combined organic layers were washed with brine (10 mL). The combined organic layers were dried over anhydrous sodium sulphate, the desiccant filtered and the product concentrated and vacuum dried. The product was isolated after purification by column chromatography (silica gel, ethyl acetate:hexane (1:1)) with quantitative yield (1.3 g, 3.98 mmol) as a beige solid.

**$^1$H NMR (400 MHz, $CDCl_3$) δ:** 7.42 (s, 1H), 6.69 (d, *J* = 4 Hz, 2H), 6.45 (s, 1H), 3.80 (s, 6H)

Spectral data were in accordance with literature.[10]

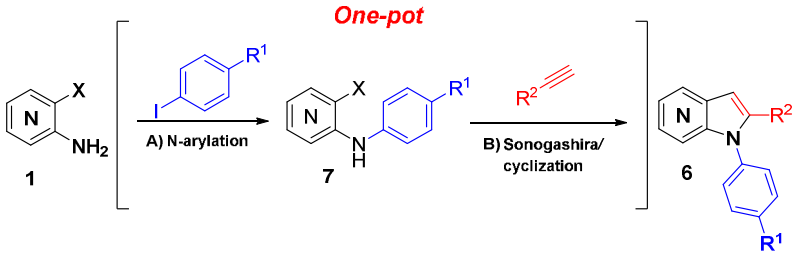
**B)** To a solution of 1-(2,2-dibromovinyl)-3,5-dimethoxybenzene (1 equiv, 1.28 g, 3.98 mmol) in dry $CH_3CN$ (7.96 mL) was added DBU (2.38 mL, 4 equiv, 15.9 mmol) dropwise over a period of 10 mins at room temperature. The reaction mixture was allowed to stir at room temperature for 16 h. After reaction completion, the mixture was cooled at 15 °C and quenched by dropwise addition of 5N aqueous HCl (10 mL) over a period of 15 mins and stirred for 5 mins. The reaction mixture was extracted with EtOAc/hexane (1:1, 2 x 10 mL); organic layers were washed with water (10 mL). The combined organic layers were dried over anhydrous sodium sulphate, the desiccant filtered and the product concentrated and vacuum dried. The product was

isolated after purification by column chromatography (silica gel, ethyl acetate:hexane (2:1)) with 35% yield (217.7 mg, 1.34 mmol) as a beige solid.

**$^1$H NMR (400 MHz, $CDCl_3$) δ:** 6.65 (d, *J* = 2 Hz, 2H), 6.47 (s, 1H), 3.78 (s, 6H), 3.04 (s, 1H)

Spectral data were in accordance with literature.[10]

## General procedure for the one-pot N-arylation/Sonogashira/cyclization reaction with amino-*o*-bromopyridines




**A)** A sealed tube equipped with a magnetic stir bar was charged with $Pd_2(dba)_3$ (4 mol %, 42.34 mg, 0.04 mmol), XantPhos (8 mol %, 53.51 mg, 0.092 mmol), *t*-BuONa (2 equiv, 222.2 mg, 2.31 mmol) and amino-*o*-bromopyridine (**1**) (1 equiv, 200 mg, 1.16 mmol). The tube was sealed with a suba-seal, evacuated and backfilled with $N_2$ thrice, then dry toluene (C = 0.2 M, 5.8 mL) was added, followed by the aryl iodide (1.2 equiv, 158.67 µL, 1.39 mmol), and the tube sealed under $N_2$. The reaction was stirred for 6 hours at 110 ºC. The crude reaction product (**7**) was concentrated and vacuum dried.

**B)** DMF was previously degassed 7 times by applying vacuum when the mixture is completely frozen and then flushed with $N_2$.

Three solutions were prepared with the degassed DMF and the solids were dried under vacuum before DMF addition:

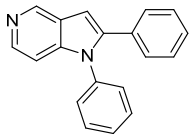
Solution A – A round-bottom flask was charged with the crude product **7** (1 equiv, 287.97 mg, 1.16 mmol), DIPEA (3.2 equiv, 644.35 µL, 3.7 mmol) and DMF (2.4 mL) and the final solution degassed thrice.

Solution B – A round-bottom flask was charged with CuI (5 mol %, 11.01 mg, 0.058 mmol), $PdCl_2(PPh_3)_2$ (3 mol %, 4.87 mg, 0.035 mmol) and DMF (2.4 mL) and the final solution degassed twice.

Solution C – A round-bottom flask was charged with phenylacetylene (2.1 equiv, 266.61 µL, 2.43 mmol) and DMF (4.8 mL) and the final solution degassed thrice.

To solution B, solution A was added via syringe, then degassed twice; and finally, solution C. The mixture was degassed one more time and then allowed to warm up to 110 ºC and stirred for 24 h. Toluene was added to the residue and washed thrice with water, then sat. $NH_4Cl$. The combined aqueous layers were then washed with toluene to take off remain product. Combined organic layers were dried with anhydrous sodium sulphate, filtered and concentrated. The desired product was isolated after purification by chromatography.

**1,2-Diphenyl-5-azaindole (6a)**



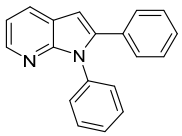
**Purification:** PTLC using EtOAc/hexane (1:1) followed by PTLC using EtOAc/hexane (1:2)

**Appearance:** Beige solid

**Yield:** 49% (22.8 mg, 0.084 mmol of **6a** from 30 mg, 0.17 mmol of starting 4-amino-3-bromopyridine); 84% (263.53 mg, 0.97 mmol of **6a** from 200 mg, 1.16 mmol of starting 4-amino-3-bromopyridine).

Spectral data were in accordance with the product **6a** isolated from the reaction using the previously described approaches.

**1,2-Diphenyl-7-azaindole (6d)**[11]



**Purification:** PTLC using toluene/hexane (2:1) followed by PTLC using toluene/hexane (3:1)

**Appearance:** Beige solid

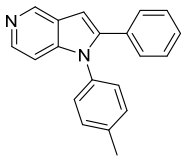
**Yield:** 22% (14.0 mg, 0.052 mmol of **6d** from 40 mg, 0.23 mmol of starting 2-amino-3-bromopyridine)

**IR ($cm^{-1}$) (NaCl):** 3058, 2923, 2853, 1596, 1498.

**$^1$H NMR (400 MHz, $CDCl_3$) δ:** 8.27 (d, *J* = 4.04 Hz, 1H), 7.90 (d, *J* = 7.64, 1H), 7.35 – 7.18 (m, 10H), 7.09 – 7.06 (m, 1H), 6.67 (s, 1H).

Spectral data were in accordance with literature.[11]

**2-Phenyl-1-(*p*-tolyl)-5-azaindole (6e)**



**Purification:** PTLC using EtOAc/hexane (1:1) followed by PTLC using EtOAc/hexane (1:2)

**Appearance:** Brown oil

**Yield:** 62% (40.7 mg, 0.14 mmol of **6e** from 40 mg, 0.23mmol of starting 4-amino-3-bromopyridine)

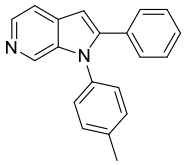
**IR ($cm^{-1}$) (NaCl):** 3037, 2926, 2852, 1597, 1514, 1463

**$^1$H NMR (400 MHz, $CDCl_3$) δ:** 8.96 (s, 1H), 8.28 (d, *J* = 5.8 Hz, 1H), 7.26 – 7.20 (m, 7H), 7.15 (d, *J* = 5.8 Hz, 1H), 7.09 (d, *J* = 8.1 Hz, 2H), 6.83 (s, 1H), 2,40 (s, 3H)

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ:** 143.7, 142.7, 142.0, 141.6, 137.9, 134.8, 130.2, 131.8, 129.1, 128.4, 128.0, 127.5, 125.2, 105.9, 102.4, 21.3

**HRMS (EI) calcd for $C_{20}H_{16}N_2$ (M+1):** 285.1347; **Found:** 285.1386

**2-Phenyl-1-(*p*-tolyl)-6-azaindole (6f)**



**Purification:** PTLC using EtOAc/hexane (1:1) followed by PTLC using EtOAc/hexane (1:4)

**Appearance:** Brown solid

**Yield:** 38% (24.9 mg, 0.088 mmol of **6f** from 40 mg, 0.23 mmol of starting 3-amino-4-bromopyridine)

**M.p.:** 98-100 °C

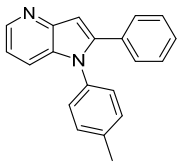
**IR ($cm^{-1}$) (NaCl):** 3035, 2919, 2849, 1596, 1512, 1460

**$^1$H NMR (400 MHz, $CDCl_3$) δ:** 8.55 (s, 1H), 8.23 (d, *J* = 5.3 Hz, 1H), 7.48 (d, *J* = 5 Hz, 1H), 7.21 – 7.15 (m, 7H), 7.07 (d, *J* = 8.2 Hz, 2H), 6,69 (s, 1H), 2.34 (s, 3H)

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ:** 144.3, 139.8, 138.0, 137.5, 134.8, 134.2, 133.0, 131.6, 130.3, 129.4, 128.5, 127.9, 127.6, 114.7, 102.6, 21.3

**HRMS (EI) calcd for $C_{20}H_{16}N_2$ (M+1):** 285.1347; **Found:** 285.1384

**2-Phenyl-1-(*p*-tolyl)-4-azaindole (6g)**



**Purification:** PTLC using EtOAc/hexane (1:1) followed by PTLC using EtOAc/hexane (1:3)

**Appearance:** Yellow oil

**Yield:** 32% (21.0 mg, 0.074 mmol of **6g** from 40 mg, 0.23 mmol of starting 3-amino-2-bromopyridine)

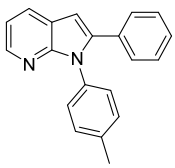
**IR ($cm^{-1}$) (NaCl):** 3040, 2928, 2858, 1596, 1512, 1419

**$^1$H NMR (400 MHz, $CDCl_3$) δ:** 8.42 (d, *J* = 4.4 Hz, 1H), 7.45 (d, *J* = 8.6 Hz, 1H), 7.23 – 7.14 (m, 8H), 7.04-7-02 (m, 2H), 6.91 (s, 1H), 2.33 (s, 3H)

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ:** 144.3, 144.1, 140.7, 137.7, 135.1, 131.9, 130.2, 129.6, 129.2, 128.4, 128.1, 127.6, 117.8, 117.1, 104.3, 21.3

**HRMS (EI) calcd for $C_{20}H_{16}N_2$ (M+1):** 285.1347; **Found:** 285.1386

**2-Phenyl-1-(*p*-tolyl)-7-azaindole (6h)**



**Purification:** PTLC using EtOAc/hexane (1:20) followed by PTLC using toluene/hexane (2:1)

**Appearance:** Orange solid

**Yield:** 35% (23.3 mg, 0.082 mmol of **6h** from 40 mg, 0.23 mmol of starting 2-amino-3-bromopyridine)

**M.p.:** 118-121 °C

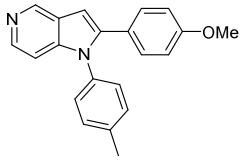
**IR ($cm^{-1}$) (NaCl):** 3040, 2923, 2853, 1596, 1516, 1414

**$^1$H NMR (400 MHz, $CDCl_3$) δ:** 8.24 (d, *J* = 3.8 Hz, 1H), 7.87 (d, *J* = 7.4 Hz, 1H), 7.26 – 7.17 (m, 9H), 7.03 (dd, *J* = 7.8, 4.8 Hz, 1H), 6.64 (s, 1H), 2.30 (s, 3H)

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ:** 150.2, 143.7, 141.2, 137.3, 134.5, 132.3, 129.9, 129.05, 128.5, 128.4, 128.2, 127.9, 120.9, 117.0, 101.2, 21.3

**HRMS (EI) calcd for $C_{20}H_{16}N_2$ (M+1):** 285.1347; **Found:** 285.1386

**2-(4-Methoxyphenyl)-1-(*p*-tolyl)-5-azaindole (6i)**




**Purification:** PTLC using EtOAc/hexane (1:1) followed by PTLC using EtOAc/hexane/EtOH (5:5:0.5)

**Appearance**: Yellow oil

**Yield:** 45% (32.7 mg, 0.1 mmol of **6i** from 40 mg, 0.23 mmol of starting 4-amino-3-bromopyridine)

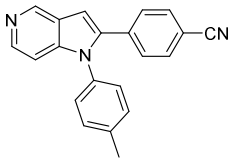
**IR ($cm^{-1}$) (NaCl):** 3041, 2926, 2833, 1607, 1500, 1459, 1255

**$^1$H NMR (400 MHz, $CDCl_3$) δ:** 8.89 (s, 1H), 8.19 (d, *J* = 5.84 Hz, 1H), 7.19 – 7.08 (m, 6H), 7.03 (d, *J* = 8.08 Hz, 1H), 6.74 – 6.71 (m, 3H), 3.72 (s, 3H), 2.34 (s, 3H)

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ:** 159.6, 142.7, 140.8, 140.5, 137.4, 134.7, 130.4, 130.3, 127.8, 127.5, 125.2, 124.0, 113.9, 106.0, 101.5, 55.4, 21.3

**HRMS (EI) calcd for $C_{21}H_{18}N_2O$ (M+1):** 315.1452; **Found:** 315.1492

**4-(2-Benzonitrile)-1-(p-tolyl)-5-azaindole (6j)**




**Purification:** PTLC using EtOAc/hexane (1:1) followed by PTLC using EtOAc/hexane (2:1)

**Appearance:** Pale yellow solid

**Yield:** 23% (12.5 mg, 0.04 mmol of **6j** from 30 mg, 0.17 mmol of starting 4-amino-3-bromopyridine)

**M.p. :** 127-130 °C

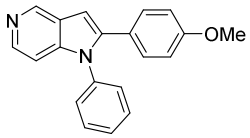
**IR ($cm^{-1}$) (NaCl):** 3042, 2923, 2853, 2225, 1512, 1457.

**$^1$H NMR (400 MHz, $CDCl_3$) δ:** 8.96 (s, 1H), 8.26 (d, *J* = 5.1 Hz, 1H), 7.49 (d, *J* = 8.04 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 7.13 (d, *J* = 5.8 Hz, 1H), 7.03 (d, *J* = 7.9 Hz, 2H), 6.92 (s, 1H), 2.37 (s, 3H)

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ:** 143.5, 143.3, 141.4, 138.9, 135.9, 134.2, 132.3, 130.7, 129.3, 128.7, 127.3, 124.8, 118.6, 111.7, 106.4, 104.4, 21.3

**HRMS (EI) calcd for $C_{21}H_{15}N_3$ (M+1):** 310.1230; **Found:** 310.1337

**2-(4-Methoxyphenyl)-1-phenyl-5-azaindole (6l)**




**Purification:** PTLC using EtOAc/hexane (1:1) followed by PTLC using EtOAc/hexane (2:1)

**Appearance:** Yellow solid

**Yield:** 44% (22.7 mg, 0.076 mmol of **6l** from 30 mg, 0.17 mmol of starting 4-amino-3-bromopyridine)

**M.p.:** 123-125 °C

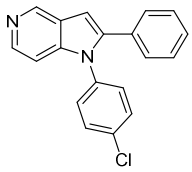
**IR ($cm^{-1}$) (NaCl):** 3040, 2933, 2839, 1610, 1498, 1460, 1251

**$^1$H NMR (400 MHz, $CDCl_3$) δ:** 8.88 (s, 1H), 8.20 (d, *J* = 5.6 Hz, 1H), 7.37 – 7.31 (m, 3H), 7.16 – 7.09 (m, 5H), 6.72 (d, *J* = 7. 9 Hz, 3H), 3.70 (s, 3H)

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ:** 159.6, 143.2, 142.5, 142.1, 141.1, 137.5, 130.4, 129.6, 127.9, 127.8, 125.3, 124.0, 113.9, 105.9, 101.7, 55.4

**HRMS (EI) calcd for $C_{20}H_{16}N_2O$ (M+1):** 301.1296; **Found:** 301.1336

**1-(4-Chlorophenyl)-2-phenyl-5-azaindole (6m)**




**Purification:** PTLC using EtOAc/hexane (1:1) followed by PTLC using EtOAc/hexane (2:1)

**Appearance:** Yellow oil

**Yield:** 52% (36.4 mg, 0.12 mmol of **6m** from 40 mg, 0.23 mmol of starting 4-amino-3-bromopyridine)

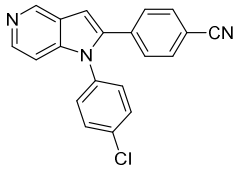
**IR (cm-1) (NaCl):** 3042, 2923, 2848, 1497, 1462, 744.

**$^1$H NMR (400 MHz, $CDCl_3$) δ:** 8.89 (s, 1H), 8.23 (d, *J* = 5.0 Hz, 1H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.21 – 7.16 (m, 5H), 7.07 (d, *J* = 8.5 Hz, 3H), 6.76 (s, 1H)

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ:** 143.8, 142.4, 141.8, 135.9, 133.8, 131.3, 129.8, 129.1, 128.9, 128.6, 128.3, 127.7, 125.2, 105.7, 102.9

**HRMS (EI) calcd for $C_{19}H_{15}ClN_2$ (M+1):** 305.0845; **Found:** 305.0840

**1-(4-Chlorophenyl)-2-(4-benzonitrile)-5-azaindole (6n)**




**Purification:** PTLC using EtOAc/hexane (1:1) followed by PTLC using EtOAc/hexane (1:2)

**Appearance:** Yellow solid

**Yield:** 39% (29.8 mg, 0.09 mmol of **6n** from 40 mg, 0.23 mmol of starting 4-amino-3-bromopyridine)

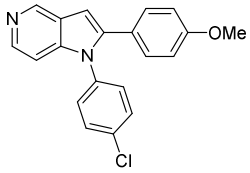
**IR ($cm^{-1}$) (NaCl):** 3054, 2919, 2844, 2229, 1605, 1493

**$^1$H NMR (400 MHz, $CDCl_3$) δ:** 9.01 (s, 1H), 8.35 (d, *J* = 5.4 Hz, 1H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 3H), 6.97 (s, 1H)

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ:** 144.5, 142.7, 139.4, 135.8, 135.4, 134.4, 132.3, 130.3, 129.9.129.3, 128.8, 124.9, 118.5, 111.7, 105.8, 104.9

**HRMS (EI) calcd for $C_{20}H_{12}ClN_3$ (M+1):** 330.0753; **Found:** 330.0791

**1-(4-Chlorophenyl)-2-(4-methoxyphenyl)-5-azaindole (6o)**




**Purification:** PTLC using EtOAc/hexane (1:1) followed by PTLC using EtOAc/hexane (1:2)

**Appearance:** Brown oil

**Yield:** 68% (52.3 mg, 0.16 mmol of **6o** from 40 mg, 0.23 mmol of starting 4-amino-3-bromopyridine)

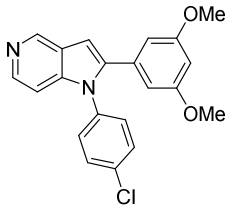
**IR (cm$^{-1}$) (NaCl):** 3040, 2961, 2839, 1614, 1502, 1405, 1256

**$^1$H NMR (400 MHz, $CDCl_3$) δ:** 8.88 (s, 1H), 8.23 (d, *J* = 4.8 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.10 – 7.05 (m, 5H), 6.75 (d, *J* = 8.5 Hz, 2H), 6.70 (s, 1H), 3.73 (s, 3H)

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ:** 159.7, 143.6, 142.3, 141.8, 141.7, 133.7, 130.4, 136.1, 129.9, 128.9, 125.4, 123.7, 114.1, 105.6, 102.1, 55.4

**HRMS (EI) calcd for $C_{20}H_{15}ClN_2O$ (M+1):** 335.0907; **Found:** 335.0945.

**1-(4-Chlorophenyl)-2-(3,5-dimethoxyphenyl)-5-azaindole (6p)**




**Purification:** PTLC using EtOAc/hexane (1:1)

**Appearance:** Yellow oil

**Yield:** 60% (50.3 mg, 0.14 mmol of **6p** from 40 mg, 0.23 mmol of starting 4-amino-3-bromopyridine)

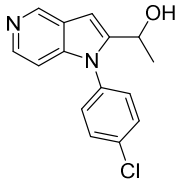
**IR (cm$^{-1}$) (NaCl):** 3042, 2958, 2838, 1597, 1492, 1203, 759

**$^1$H NMR (400 MHz, $CDCl_3$) δ:** 8.89 (s, 1H), 8.24 (d, *J* = 5.3 Hz, 1H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.12 (d, *J* = 8.5 Hz, 2H), 7.07 (d, *J* = 5.7 Hz, 1H), 6.78 (s, 1H), 6.31 – 6.30 (m, 3H), 3.58 (s, 6H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ:** 160.1, 143.9, 142.3, 141.9, 141.7, 133.8, 132.9, 129.8, 128.8, 128.6, 128.5, 125.1, 107.3, 105.6, 103.0, 100.5, 55.3.

**HRMS (EI) calcd for $C_{21}H_{17}ClN_2O_2$ (M+1):** 365.1012; **Found:** 365.1052.

**1-(4-Chlorophenyl)-2-(ethyl-1-ol)-5-azaindole (6q)**




**Purification:** PTLC using EtOAc/hexane (1:1) followed by PTLC using $CHCl_3$/MeOH (5%)

**Appearance:** Yellow solid

**Yield:** 54% (34.1 mg, 0.13 mmol of **6q** from 40 mg, 0.23 mmol of starting 4-amino-3-bromopyridine)

**M.p.:** 155-158 °C

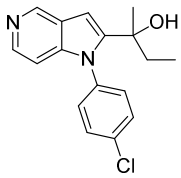
**IR ($cm^{-1}$) (NaCl):** 3341, 3047, 2973, 2853, 1492, 1467, 814.

**$^1$H NMR (400 MHz, $CDCl_3$) δ:** 8.82 (s, 1H), 8.17 (s, 1H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.21 (s, 1H), 6.90 (d, *J* = 4.4 Hz, 1H), 6.68 (s, 1H), 4.79 (q, *J* = 6 Hz, 1H), 1.97 (s, OH) 1.53 (d, *J* = 6.5 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$) δ:** 145.6, 143.8, 142.3, 141.6, 135.2, 134.9, 130.1, 129.5, 125.5, 105.6, 99.4, 62.2, 22.9.

**HRMS (EI) calcd for $C_{15}H_{13}ClN_2O$ (M+1):** 273.0750; **Found:** 273.0791.

**1-(4-Chlorophenyl)-2-(2-butyl-2-ol)-5-azaindole (6r)**




**Purification:** PTLC using EtOAc/hexane (1:1) followed by PTLC using $CHCl_3$/MeOH (10%)

**Appearance:** Brown oil

**Yield:** 45% (32.7 mg, 0.11 mmol of **6f** from 40 mg, 0.23 mmol of starting 4-amino-3-bromopyridine)

**IR ($cm^{-1}$) (NaCl):** 3341, 2973, 2878, 1492, 809.

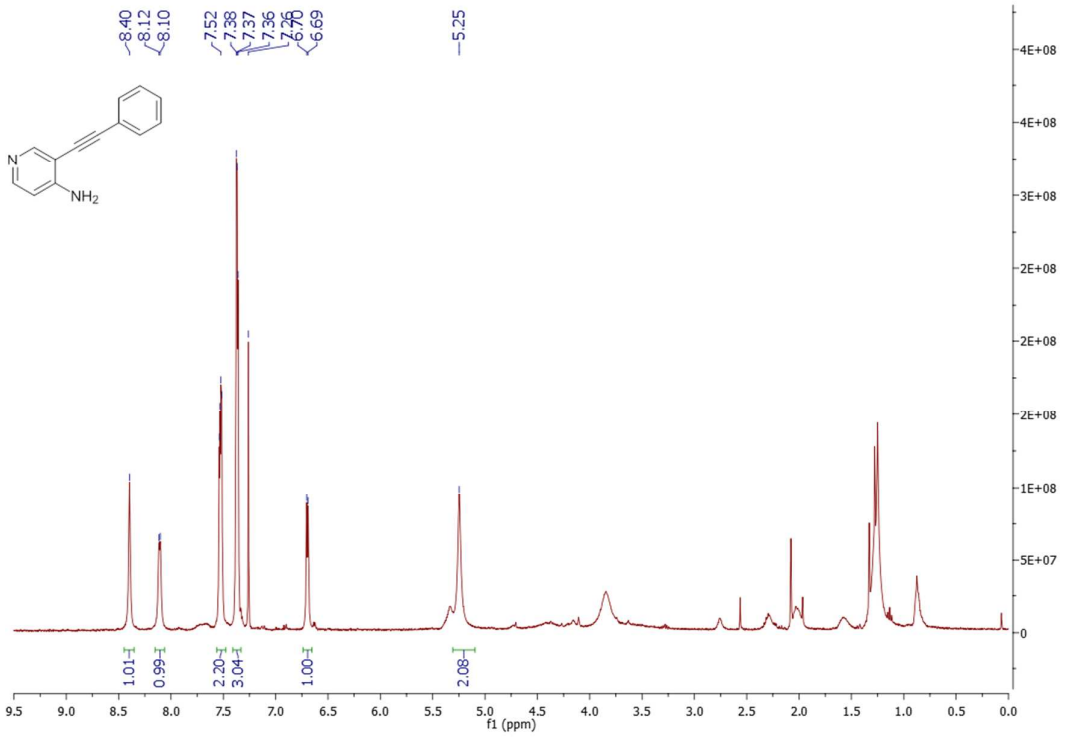
**$^1$H NMR (400 MHz, $CDCl_3$) δ:** 8.73 (s, 1H), 8.07 (d, *J* = 5.3 Hz, 1H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 6.62 (d, *J* = 5.5 Hz, 1H), 6.57 (s, 1H), 2.42 (s, OH), 1.62 (q, *J* = 7.2 Hz, 2H), 1.49 (s, 3H), 0.71 (t, *J* = 7.4 Hz, 3H).

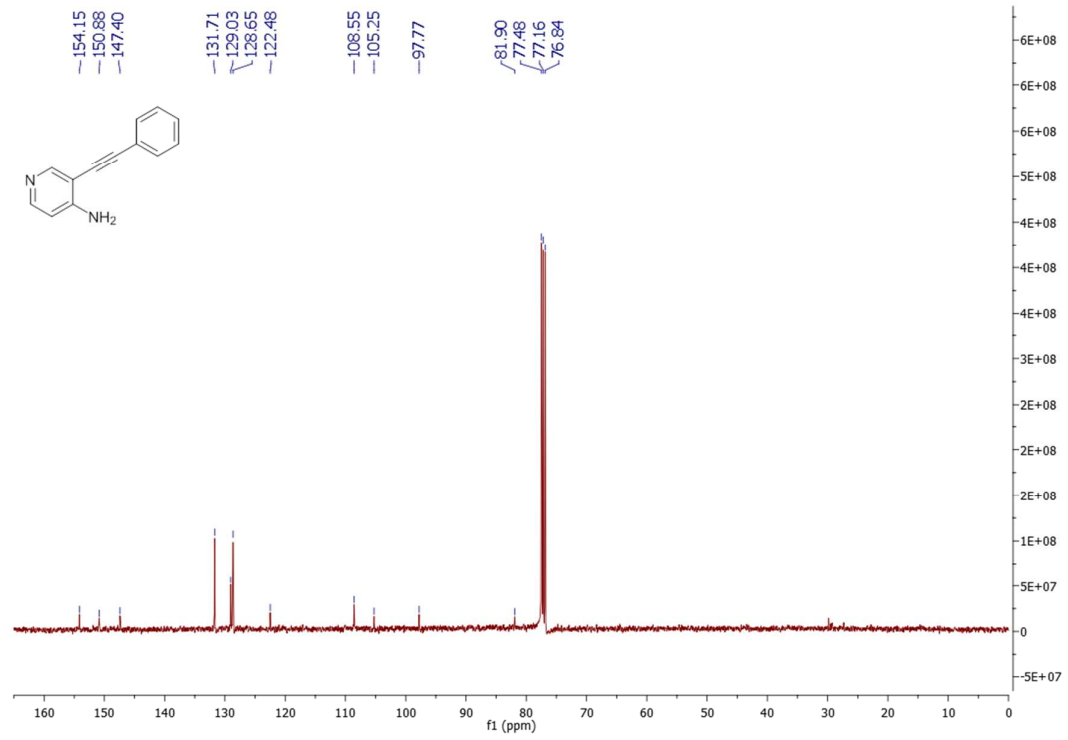
**$^{13}$C NMR (101 MHz, $CDCl_3$) δ:** 147.3, 144.0, 143.2, 141.2, 137.0, 135.0, 131.4, 130.6, 129.6, 123.8, 105.6, 100.9, 72.9, 34.6, 28.4, 8.8.

**HRMS (EI) calcd for $C_{17}H_{17}ClN_2O$ (M+1):** 301.1063; **Found:** 301.1101.

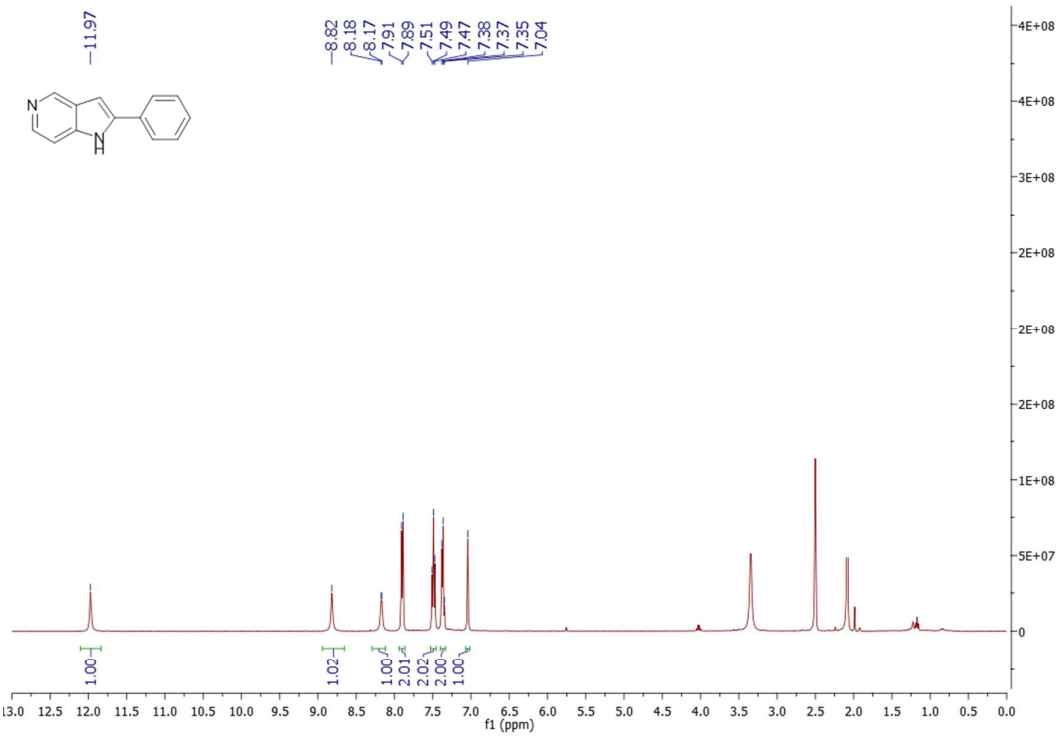
# NMR spectra of intermediates

**3-(Phenylethynyl)pyridin-4-amine (3)**

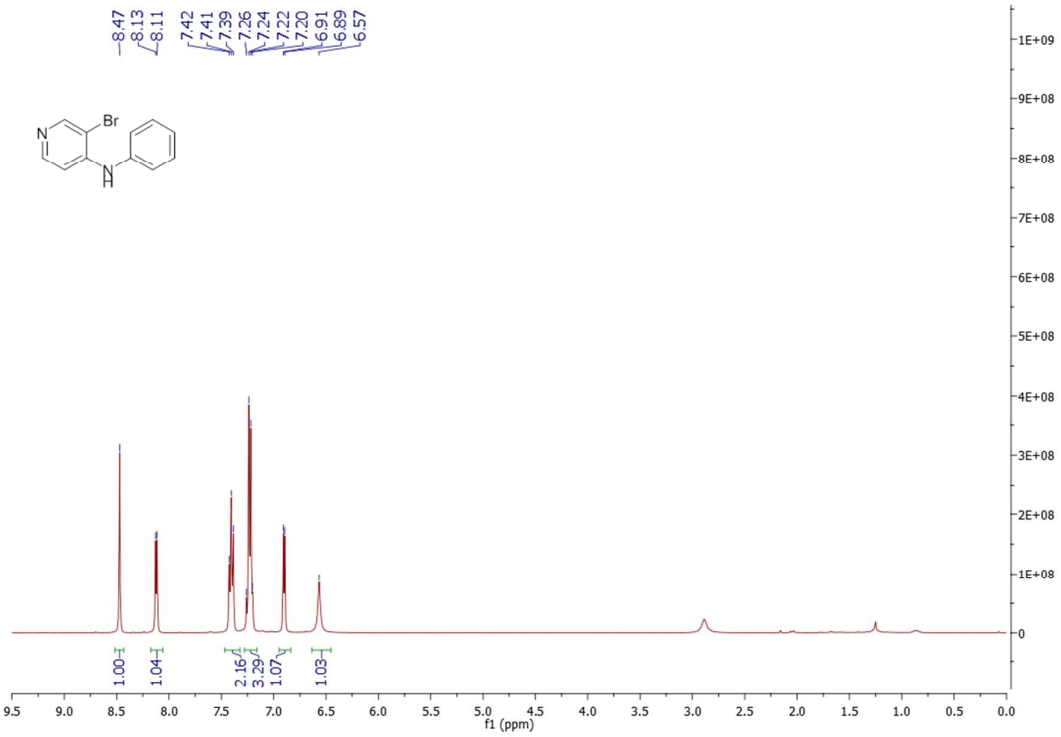


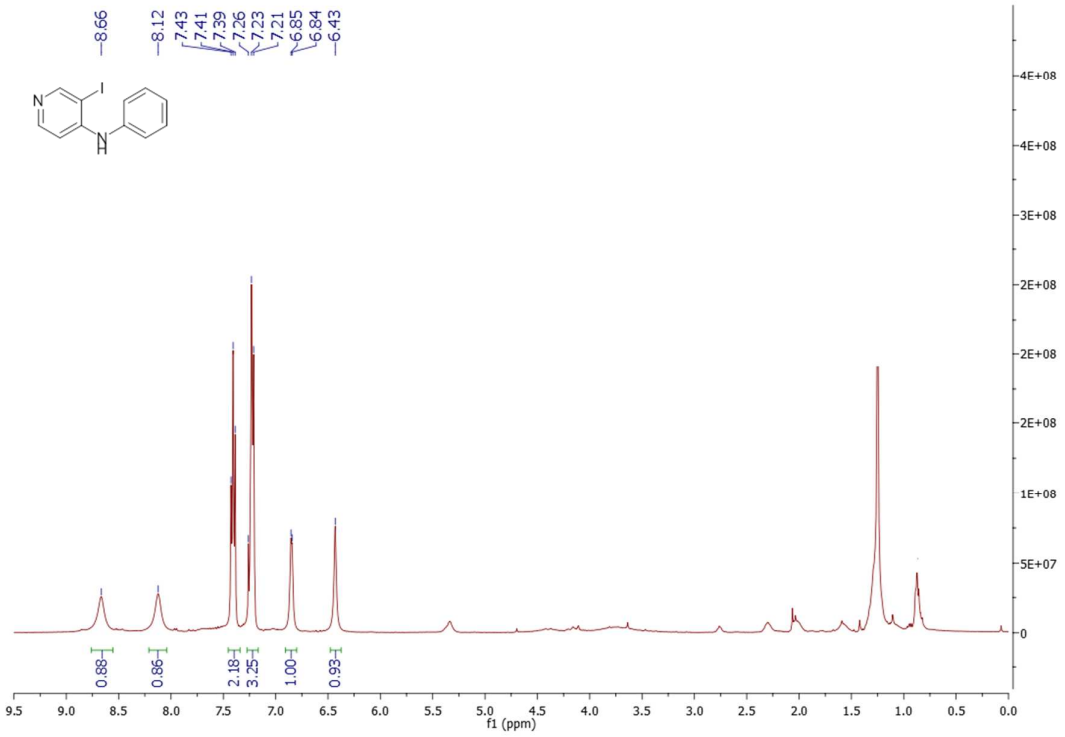
**2-Phenyl-1*H*-pyrrolo[3,2-*c*]pyridine (5)**

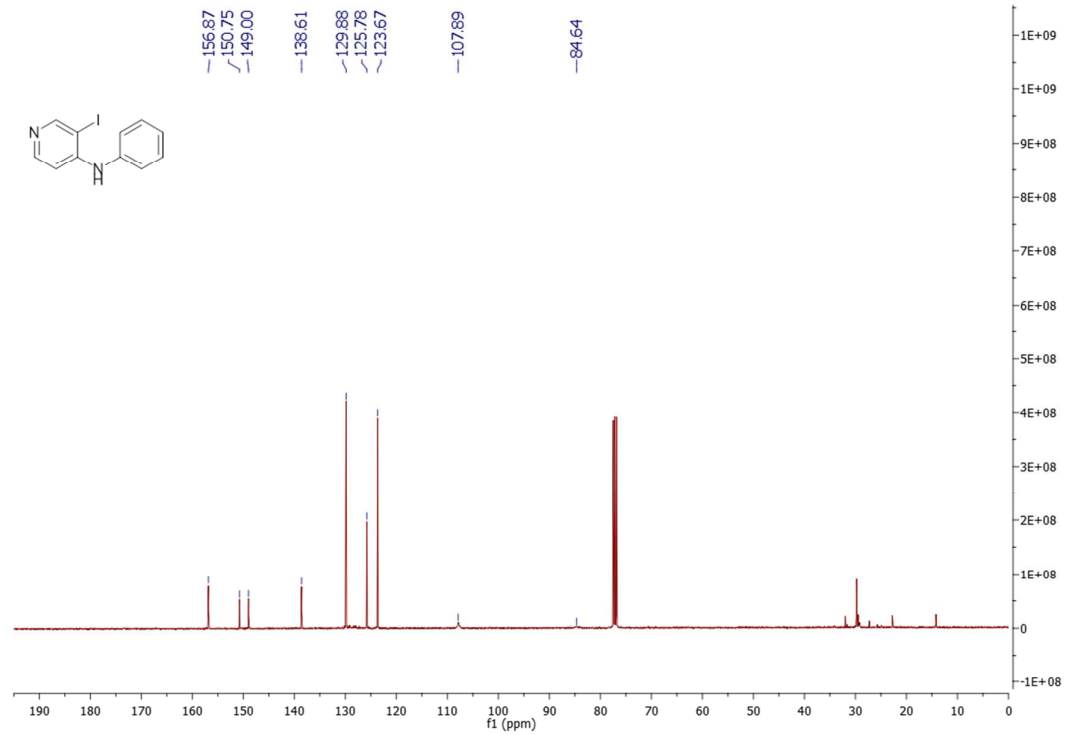



**3-Bromo-*N*-phenylpyridin-4-amine (7a)**

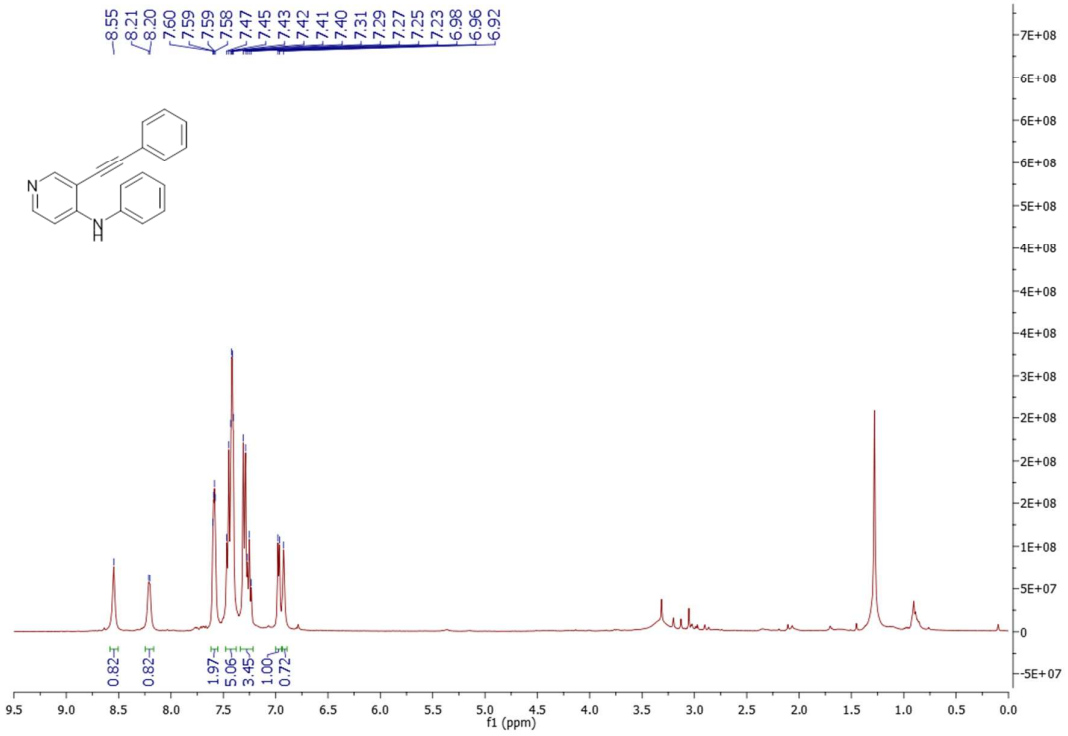


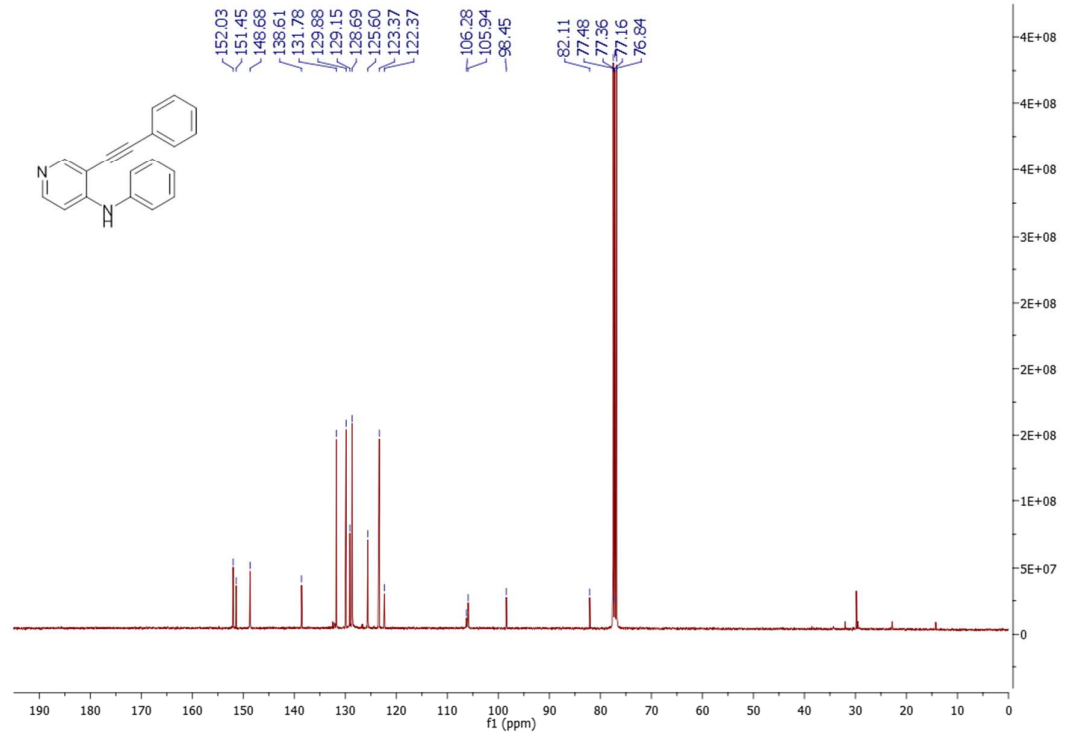
**3-Iodo-*N*-phenylpyridin-4-amine (7b)**



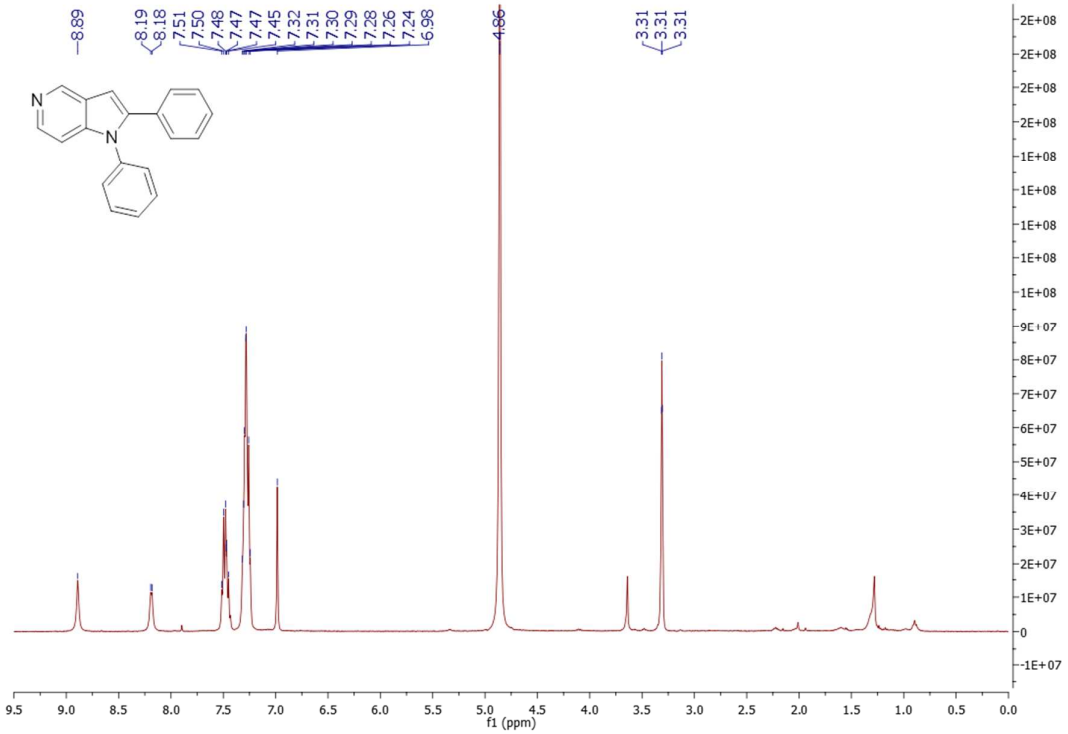
***N*-Phenyl-3-(phenylethynyl)pyridin-4-amine (4)**

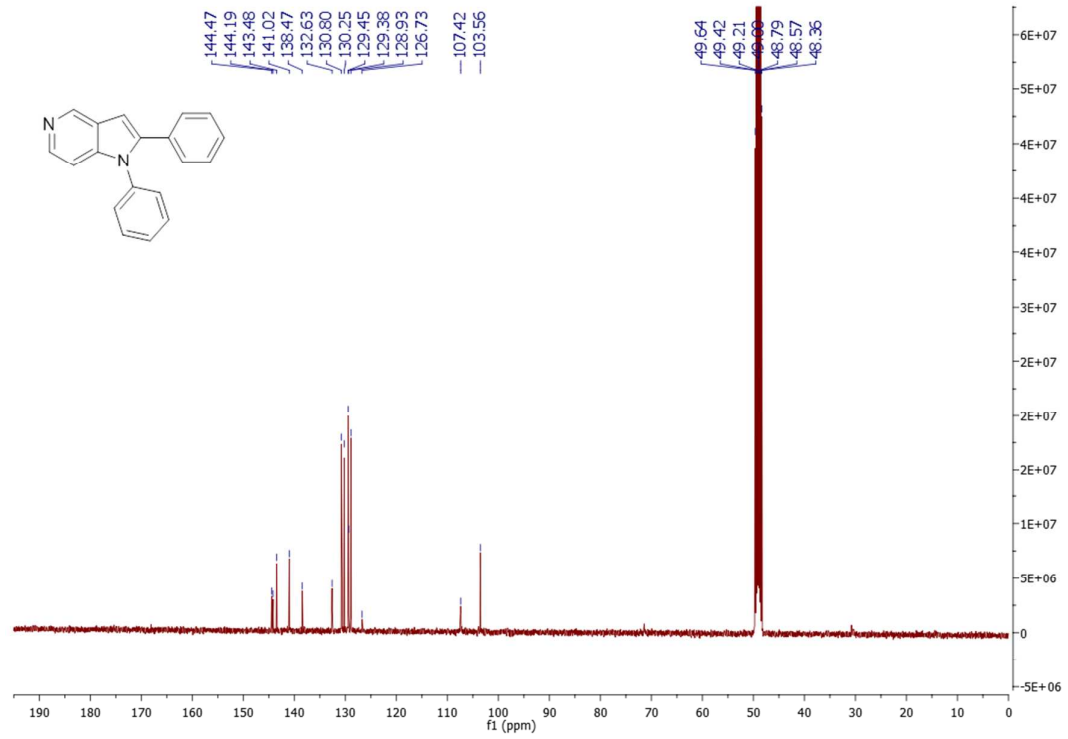


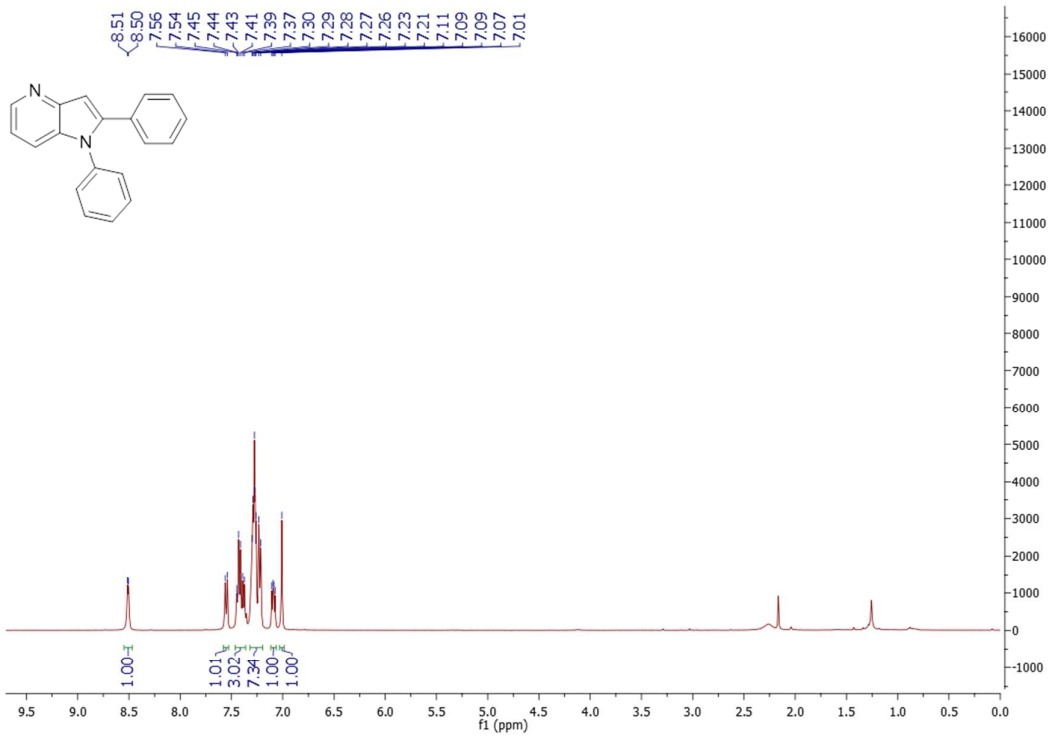
# NMR spectra of 1,2-disubstituted azaindoles

**1,2-Diphenyl-5-azaindole (6a)**

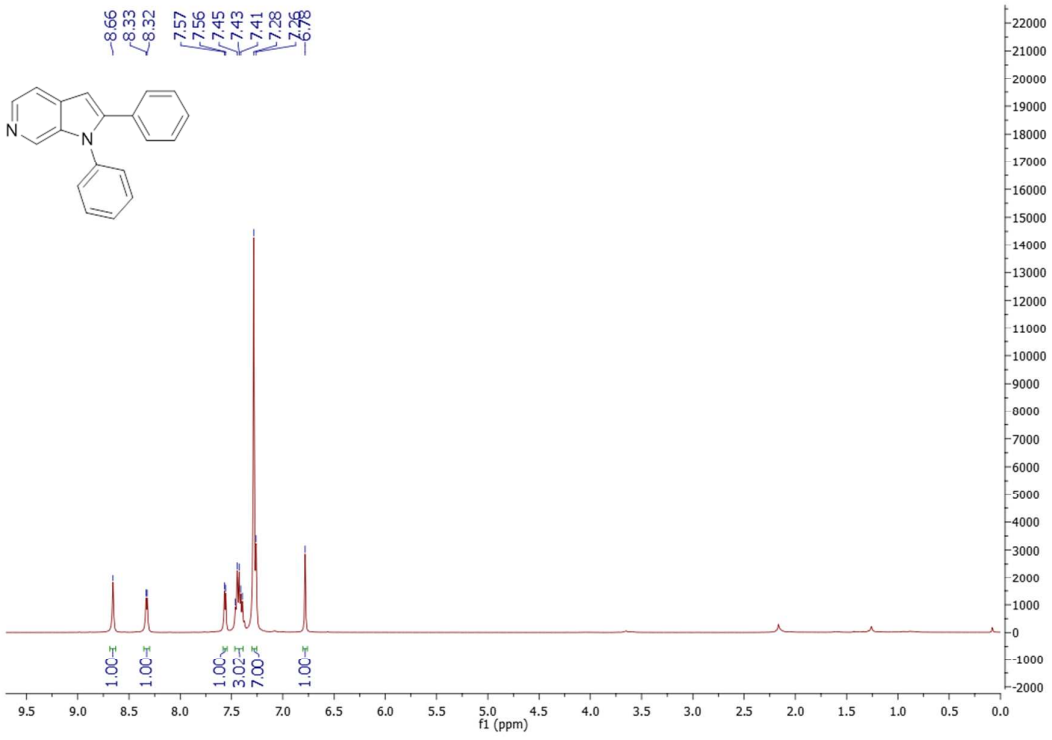


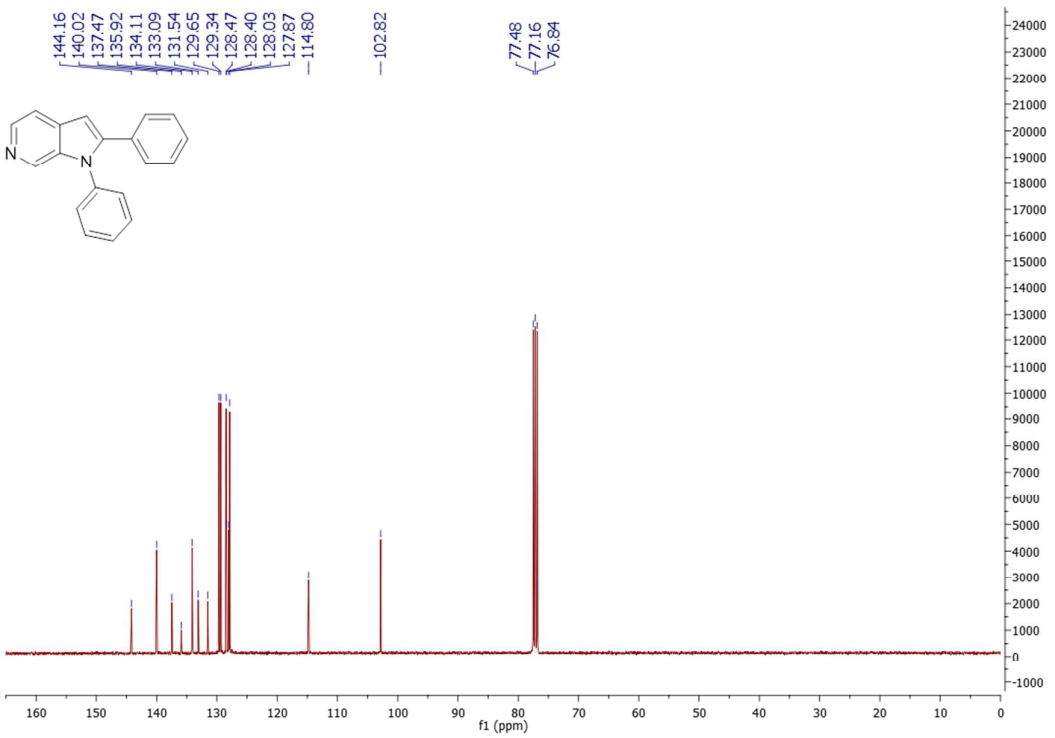



**1,2-Diphenyl-4-azaindole (6b)**

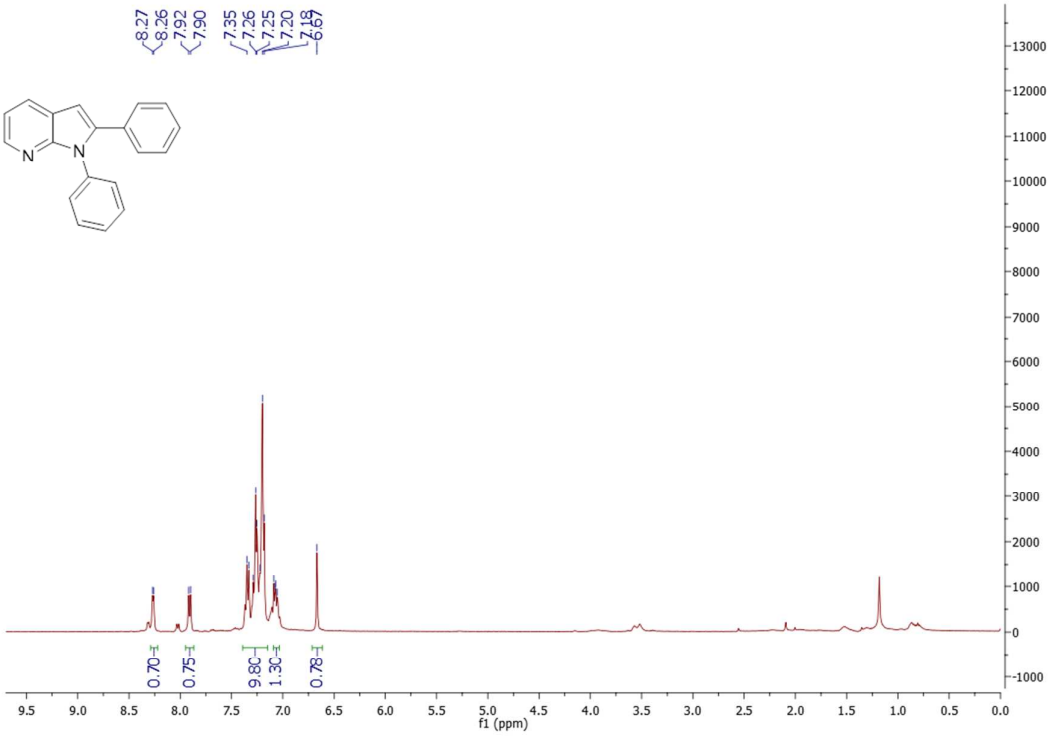



**1,2-Diphenyl-6-azaindole (6c)**

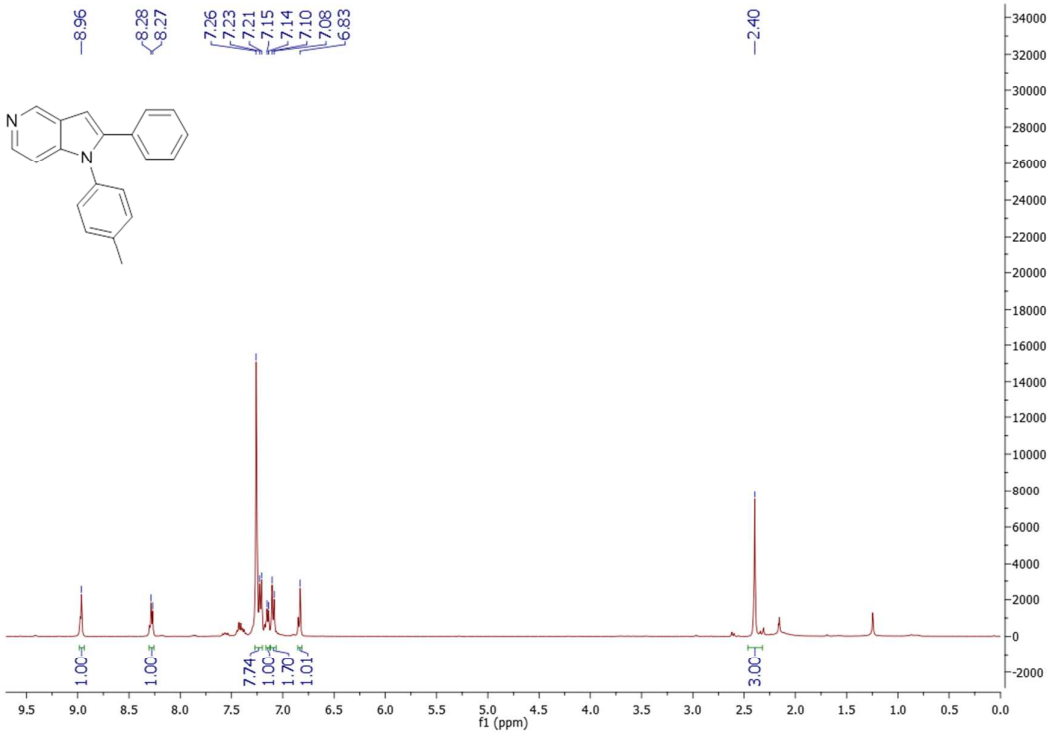


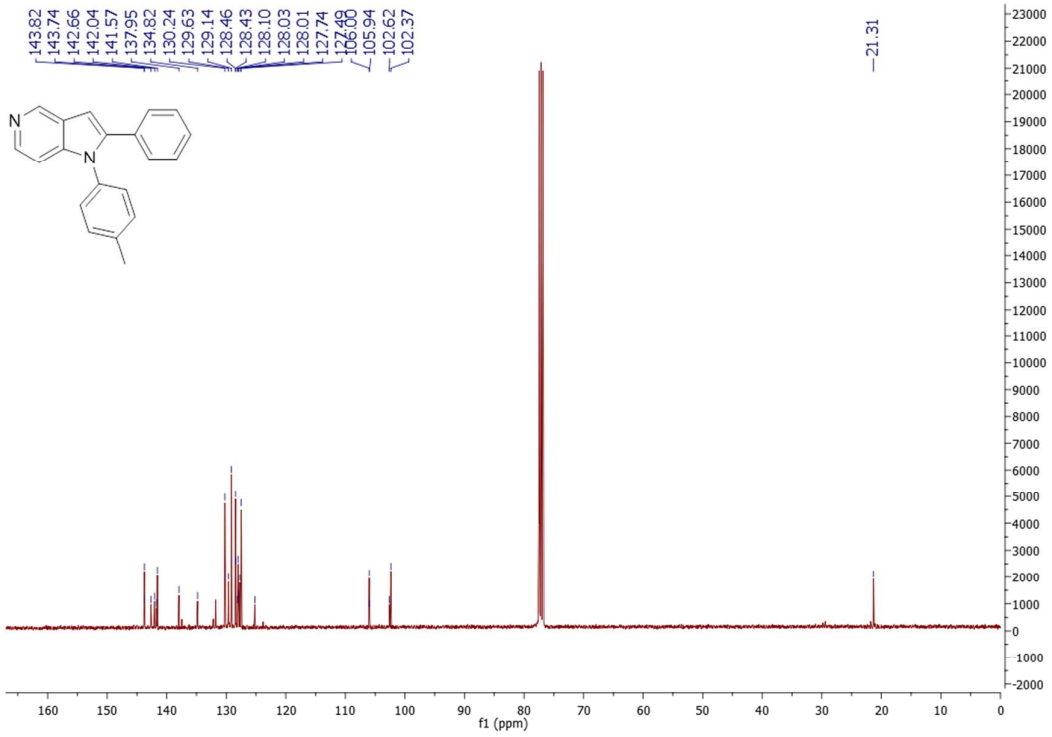



**1,2-Diphenyl-7-azaindole (6d)**

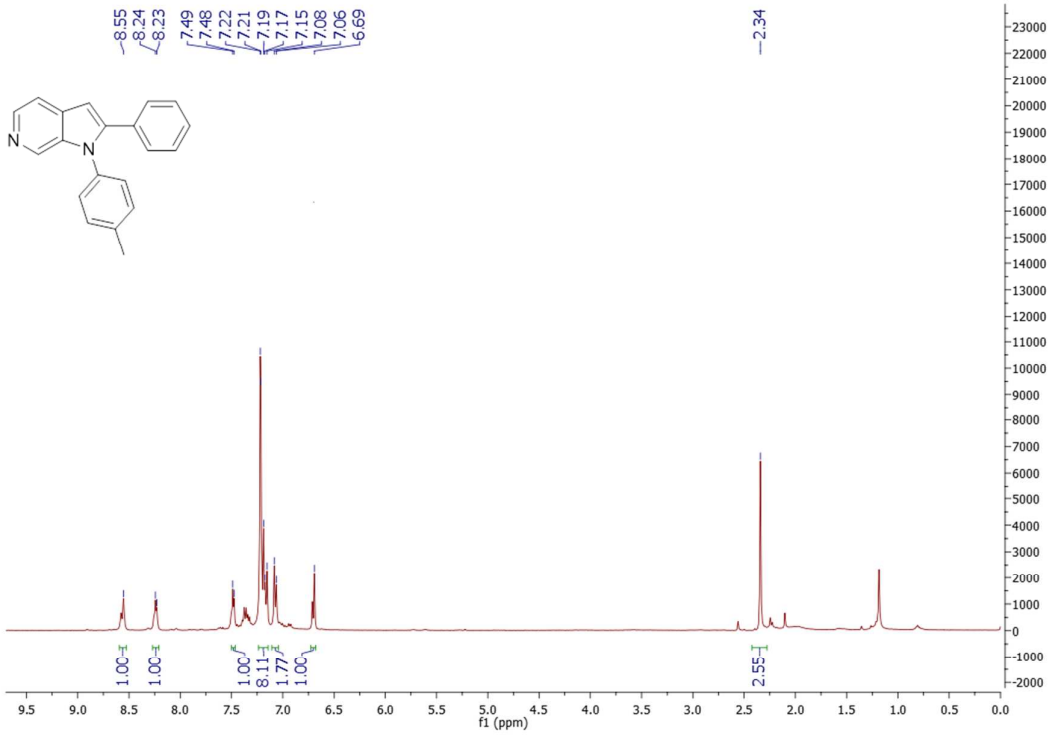


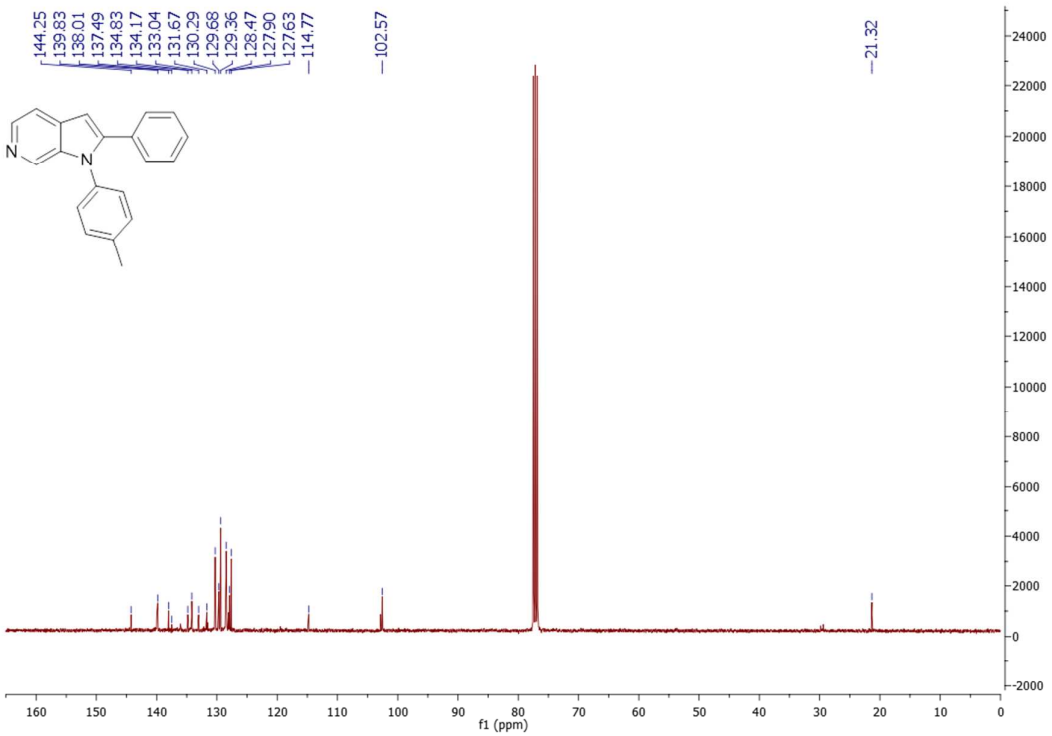
**2-Phenyl-1-(*p*-tolyl)-5-azaindole (6e)**



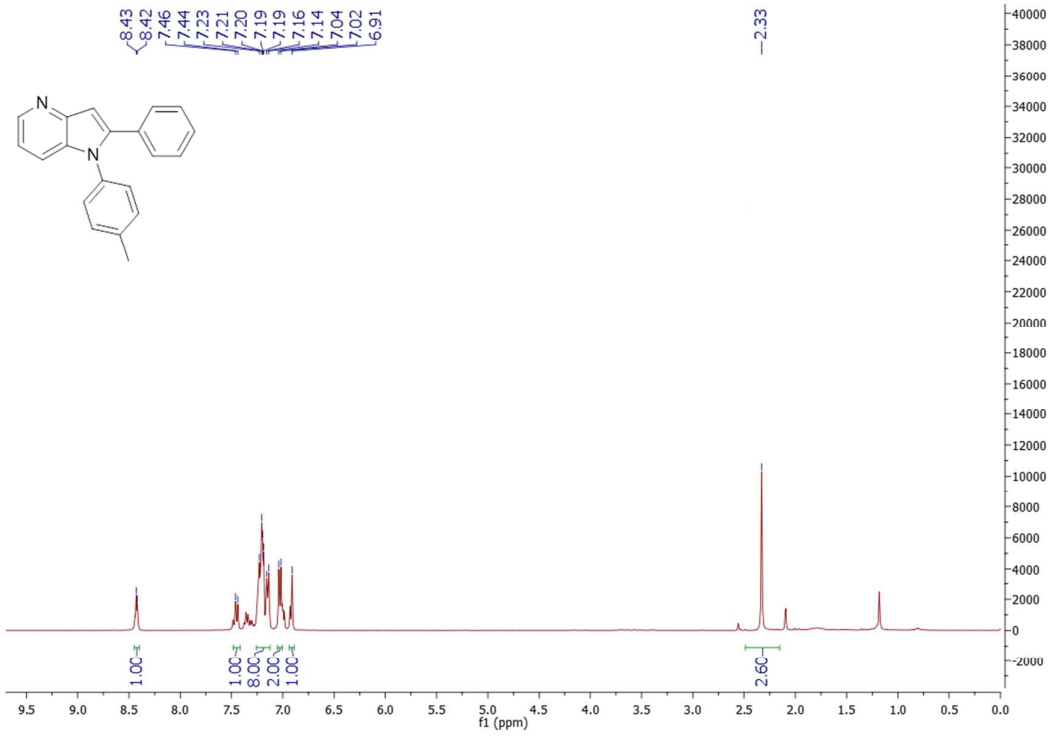



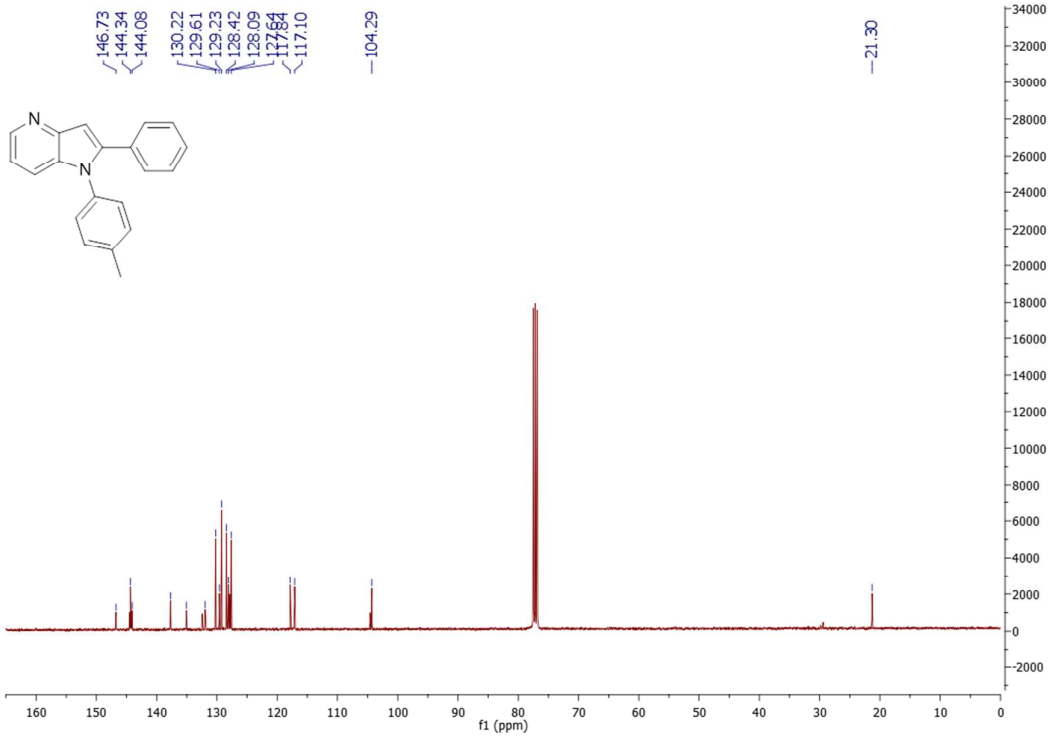
**2-Phenyl-1-(*p*-tolyl)-6-azaindole (6f)**



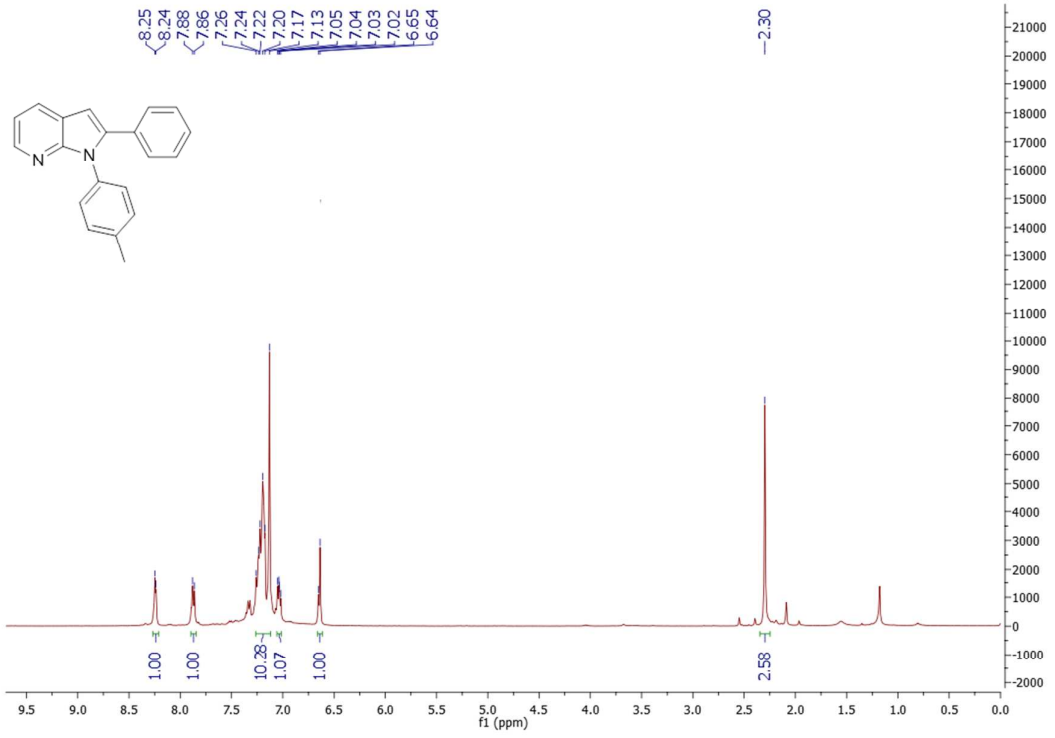



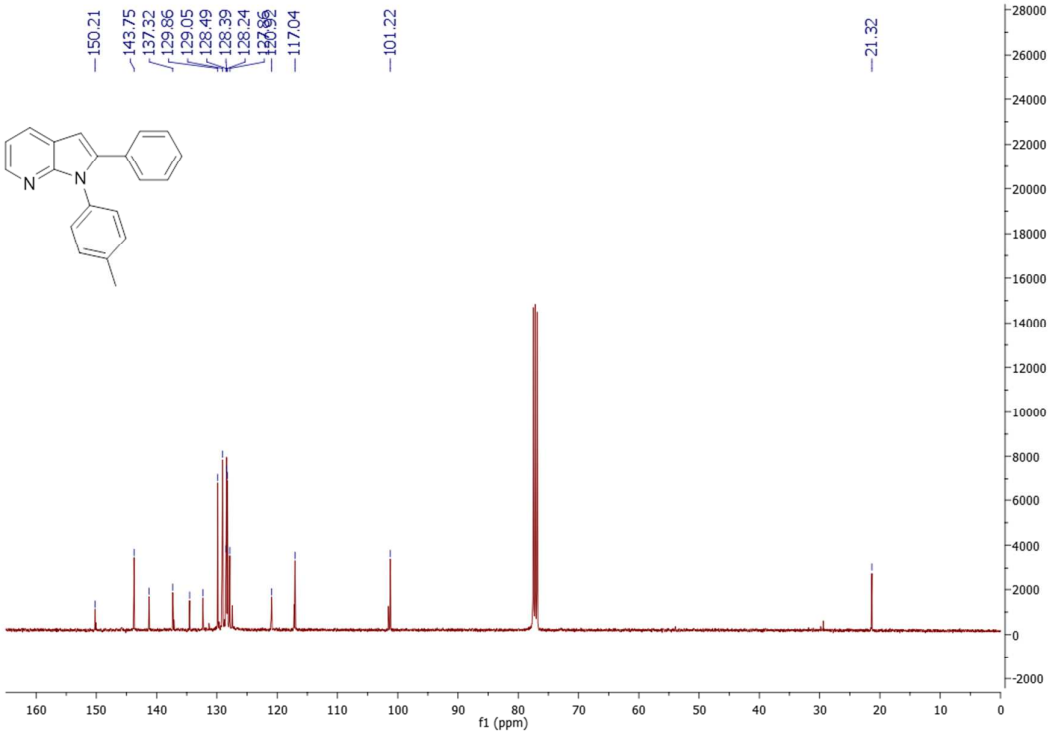
**2-Phenyl-1-(*p*-tolyl)-4-azaindole (6g)**



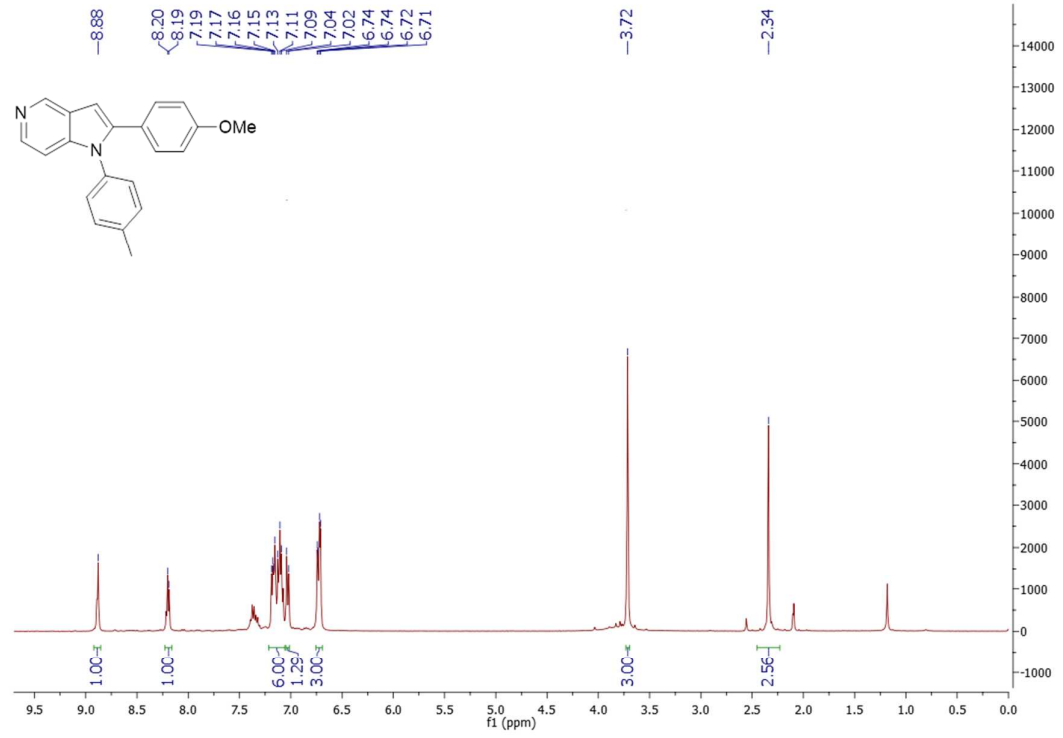



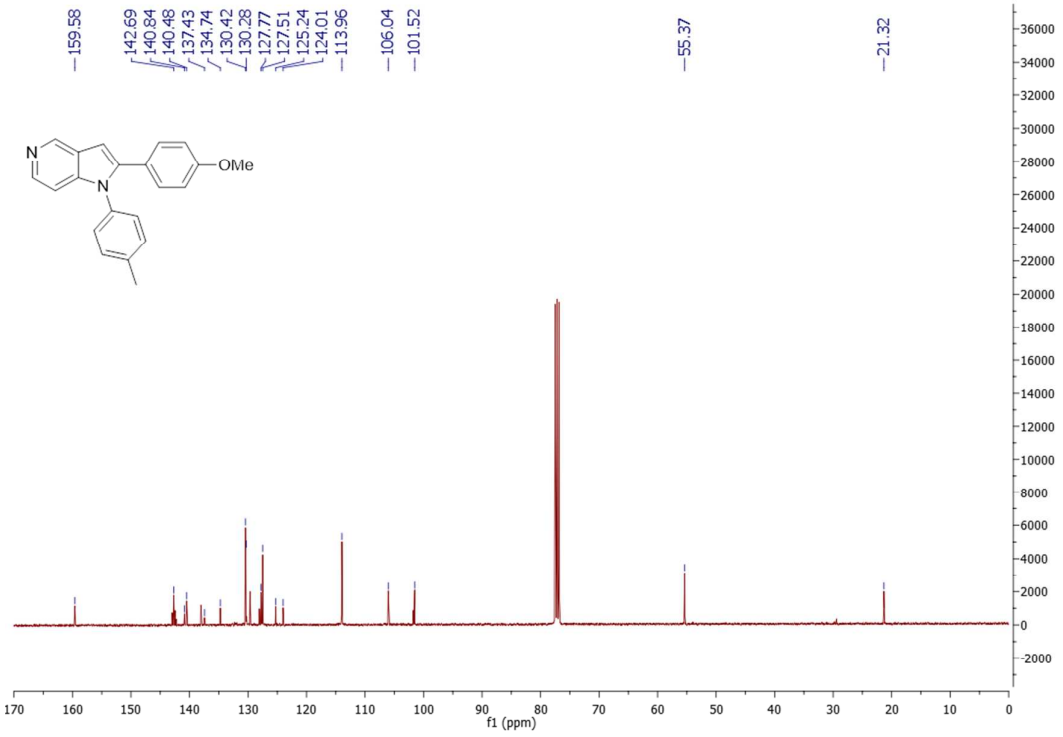
**2-Phenyl-1-(*p*-tolyl)-7-azaindole (6h)**



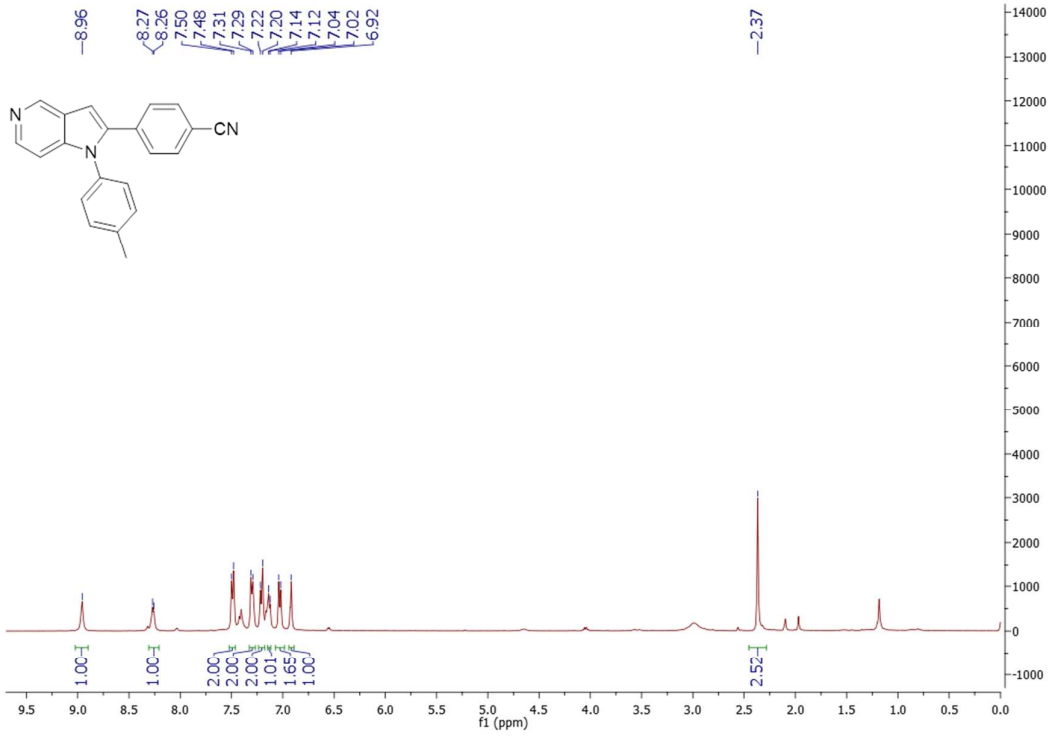



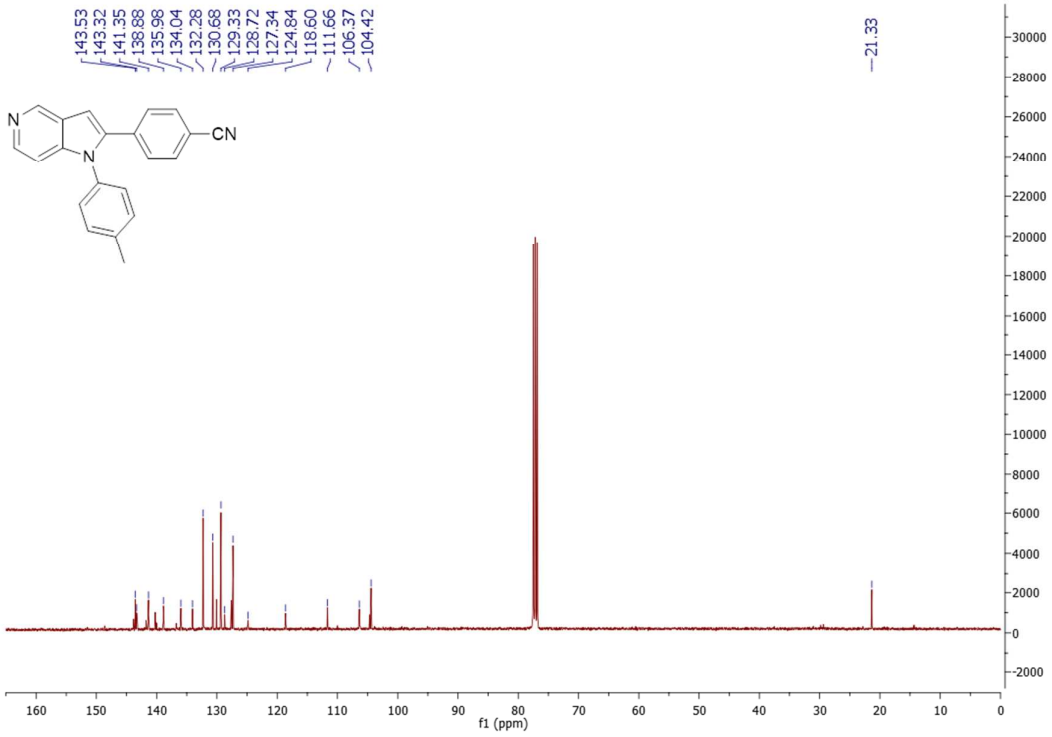
**2-(4-Methoxyphenyl)-1-(*p*-tolyl)-5-azaindole (6i)**



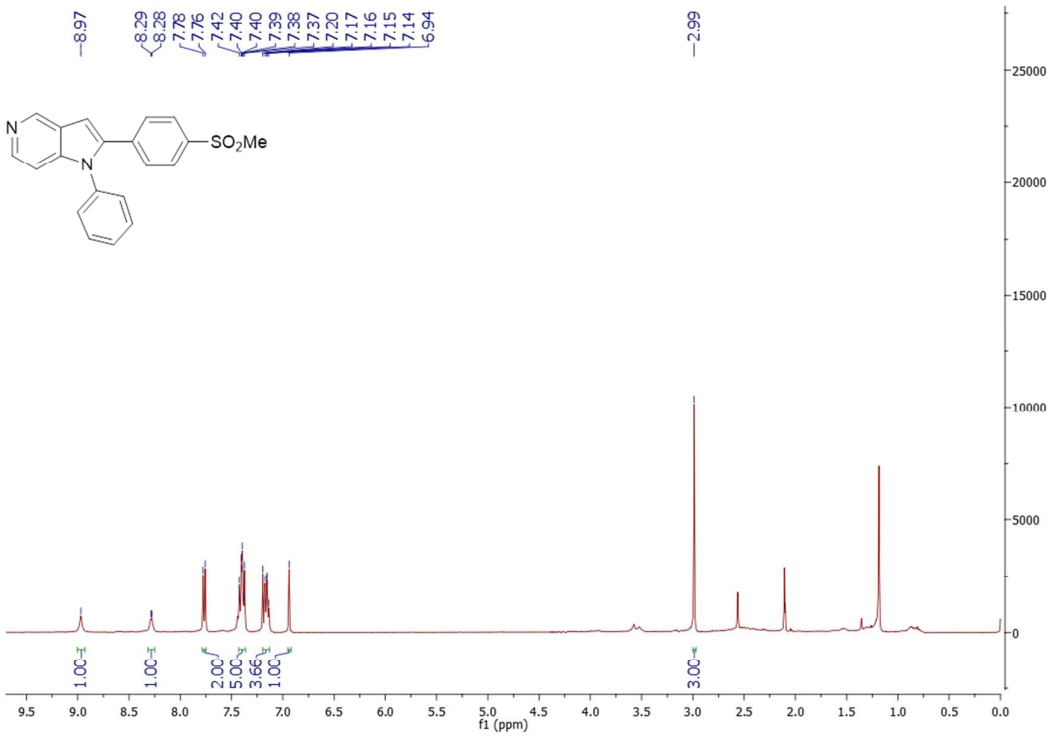



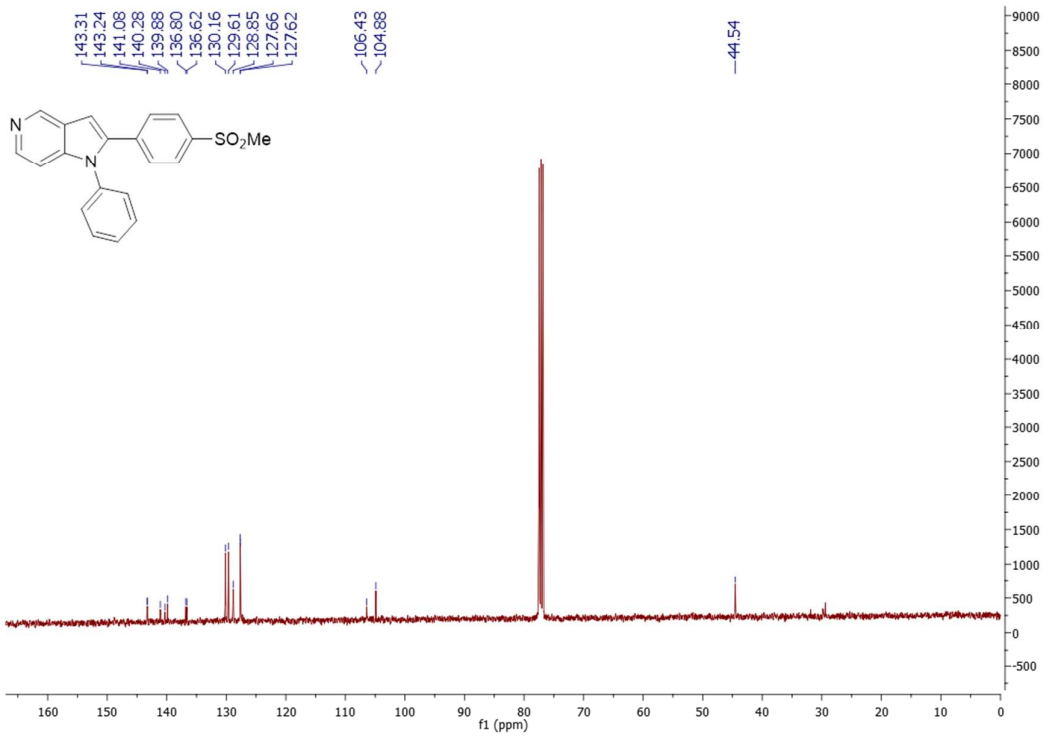
**2-(4-Benzonitrile)-1-(*p*-tolyl)-5-azaindole (6j)**



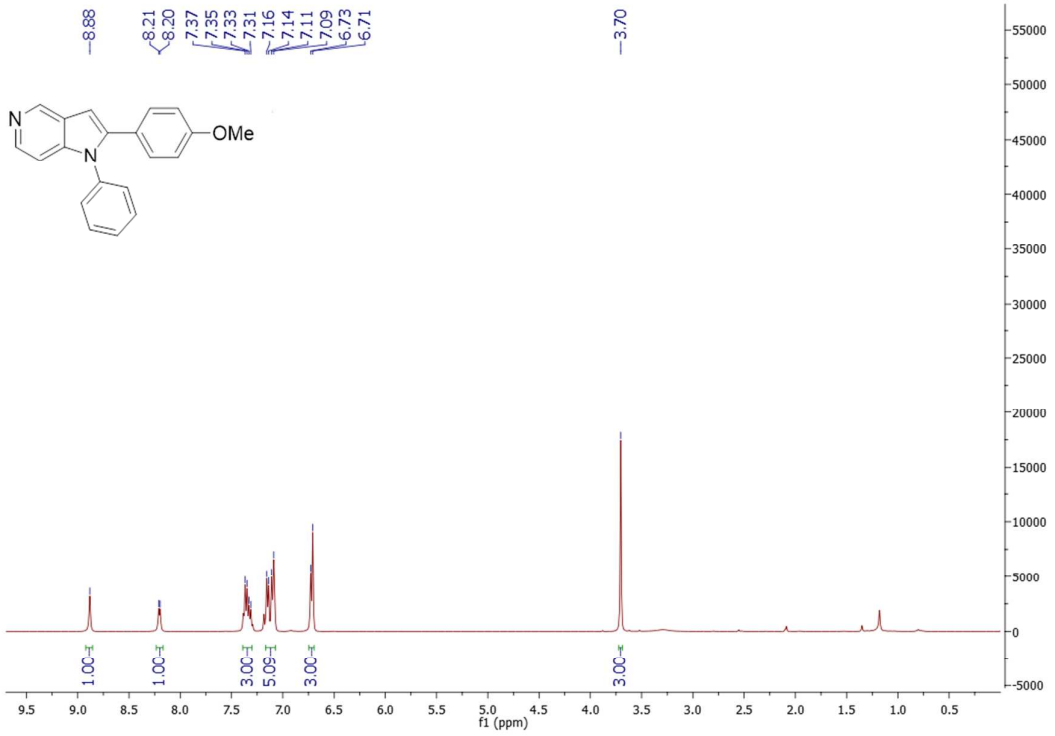



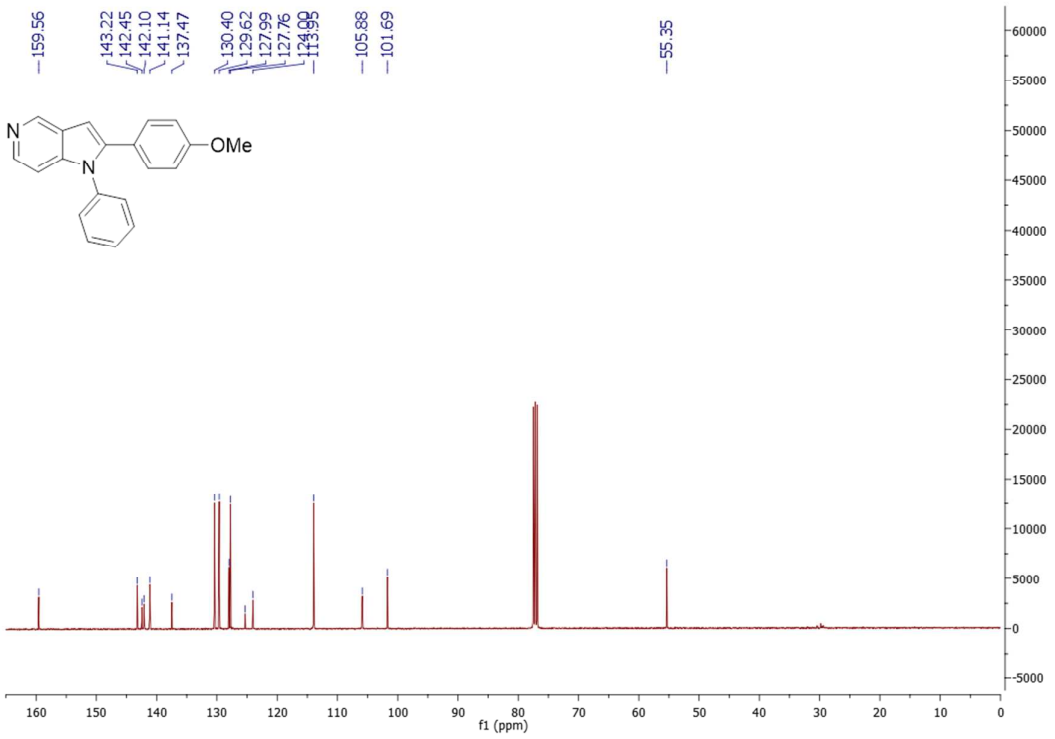
**2-(4-(Methylsulphonyl)phenyl)-1-phenyl-5-azaindole (6k)**



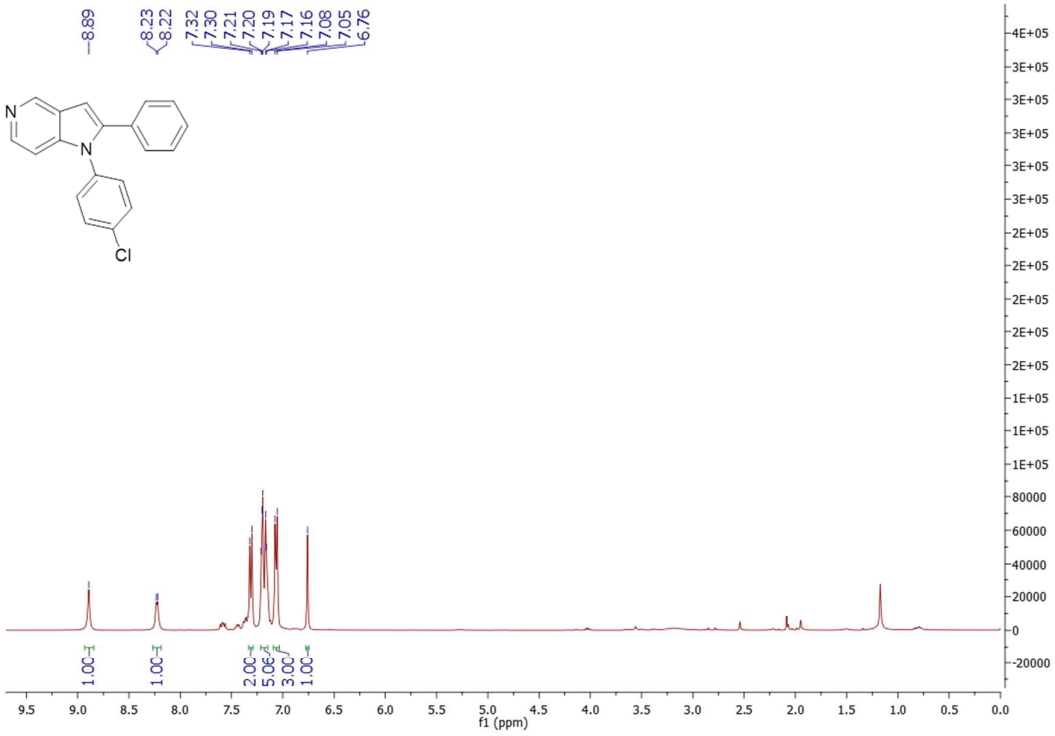



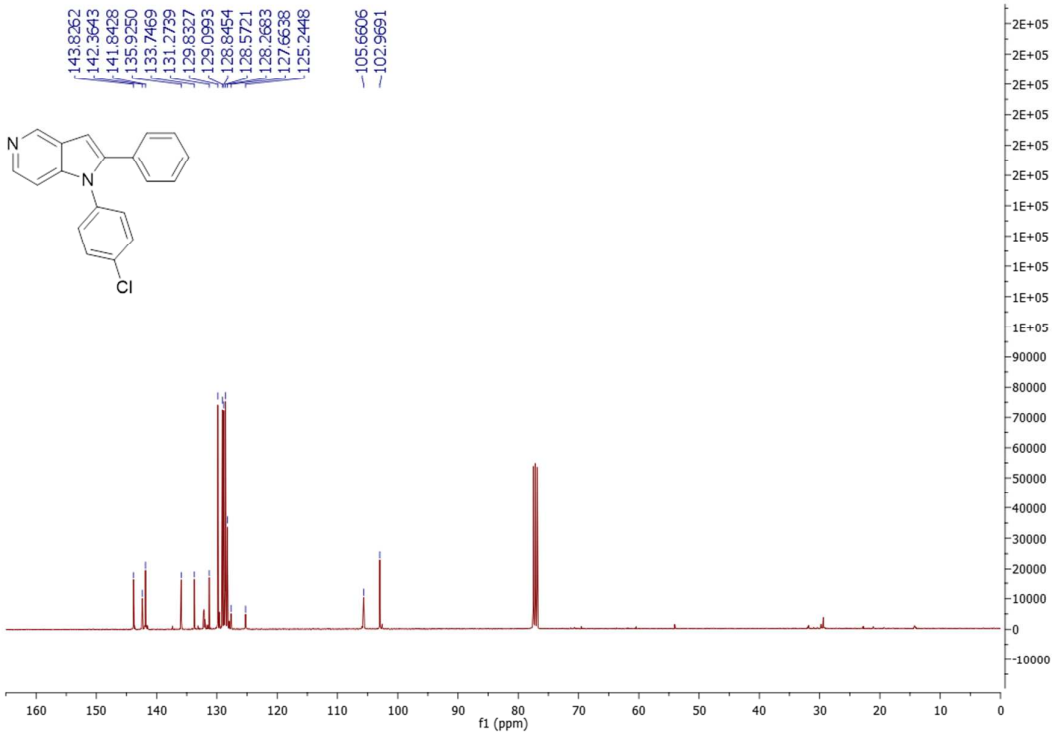
**2-(4-Methoxyphenyl)-1-phenyl-5-azaindole (6l)**



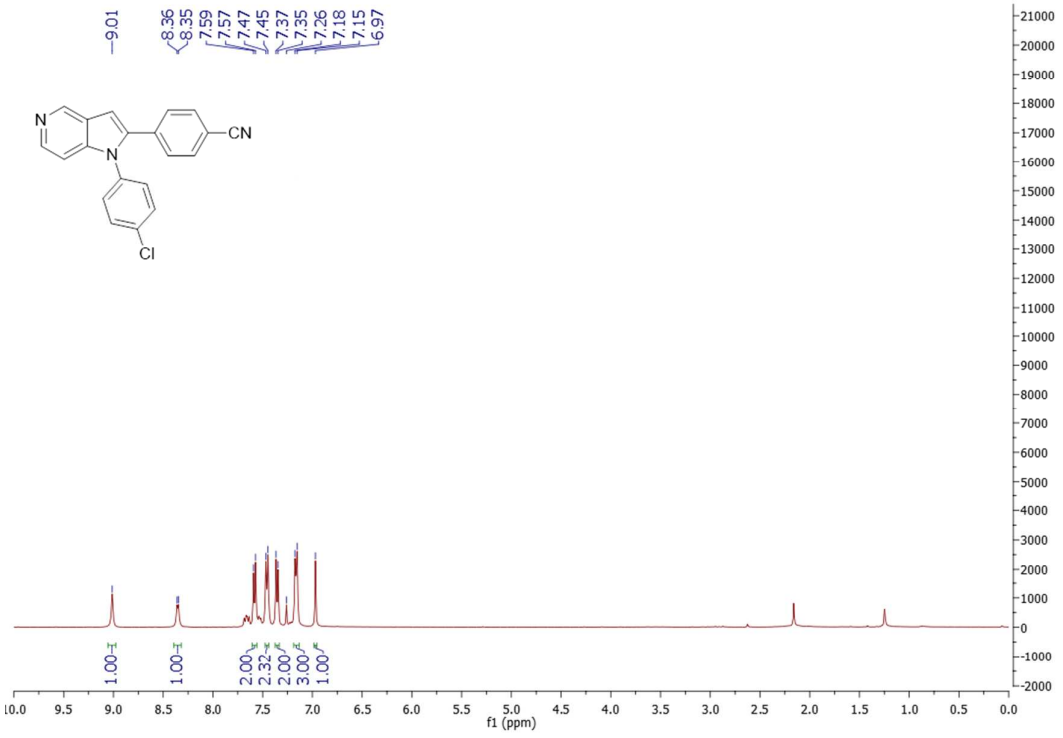



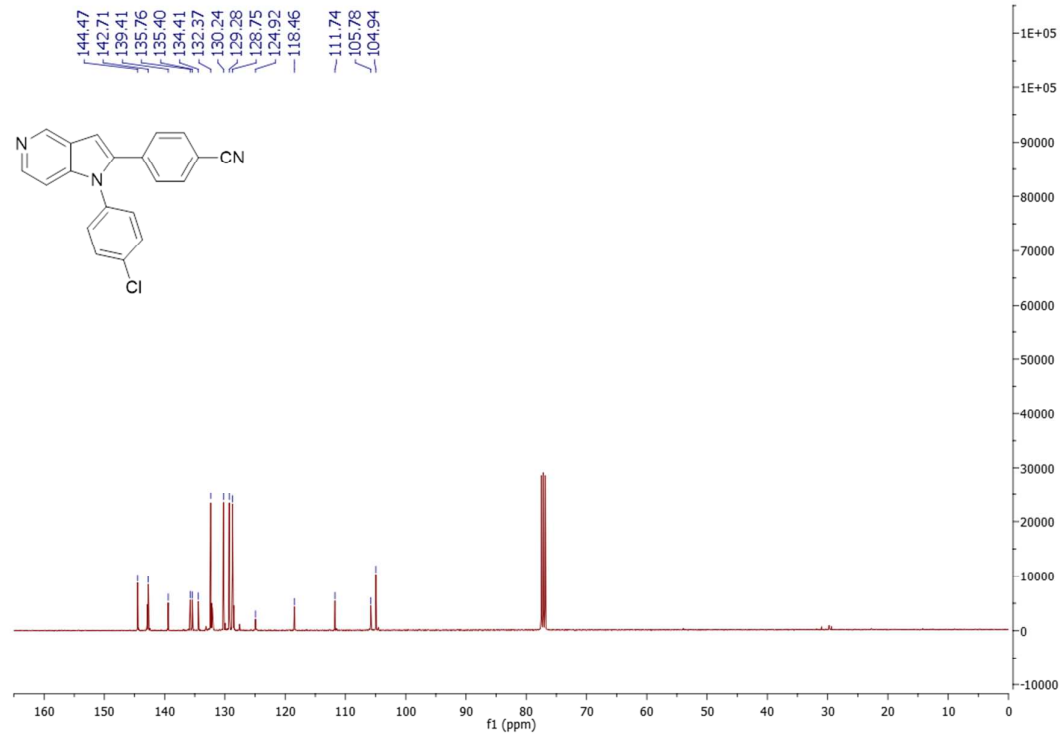
**1-(4-Chlorophenyl)-2-phenyl-5-azaindole (6m)**



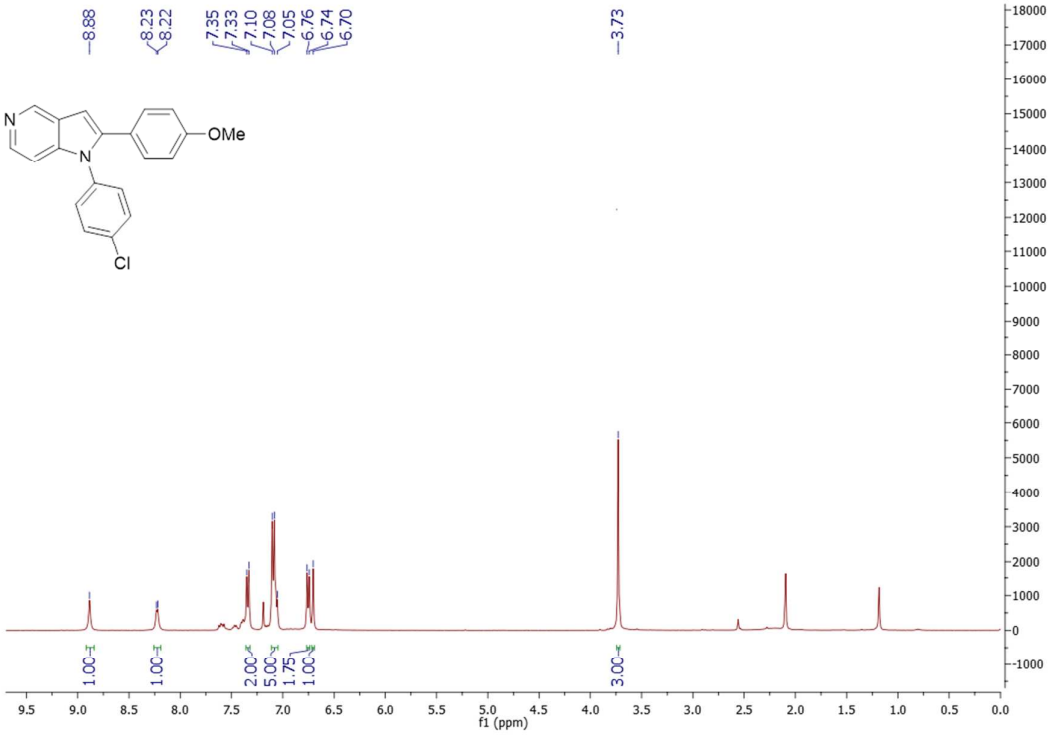



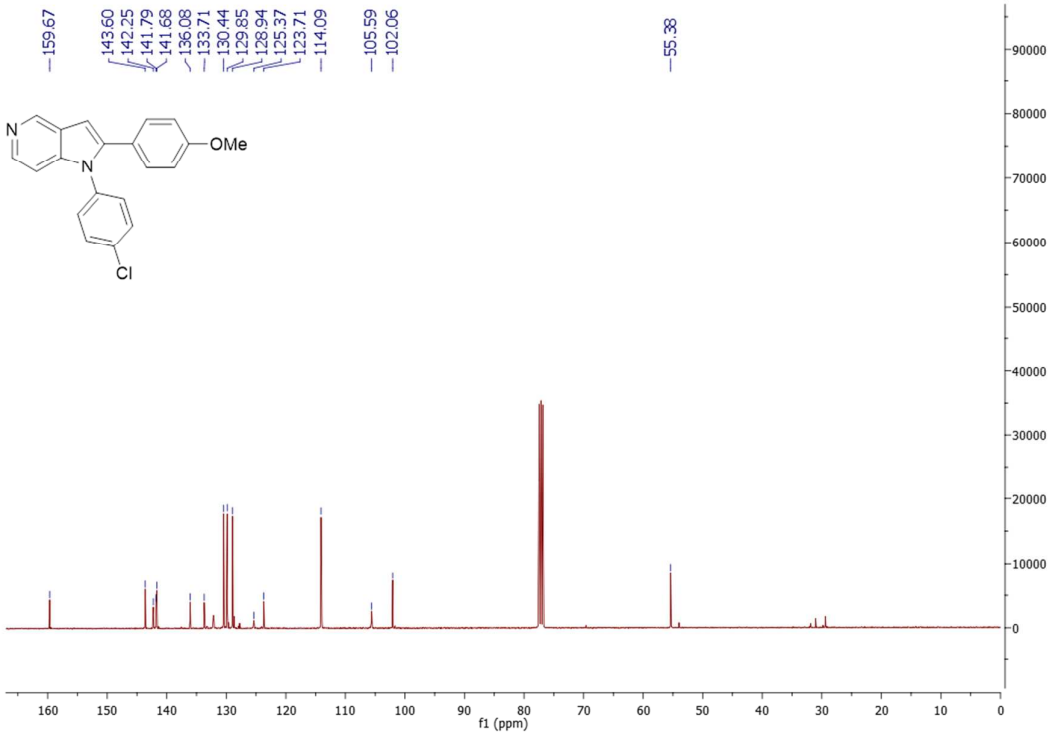
**1-(4-Chlorophenyl)-2-(4-benzonitrile)-5-azaindole (6n)**



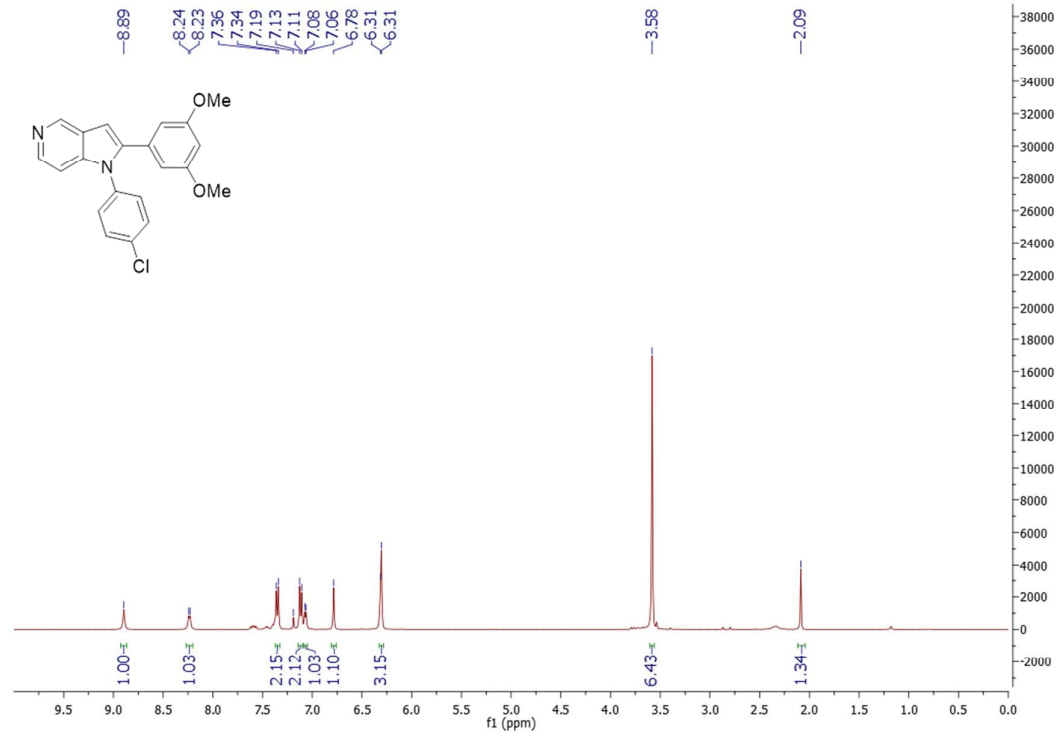



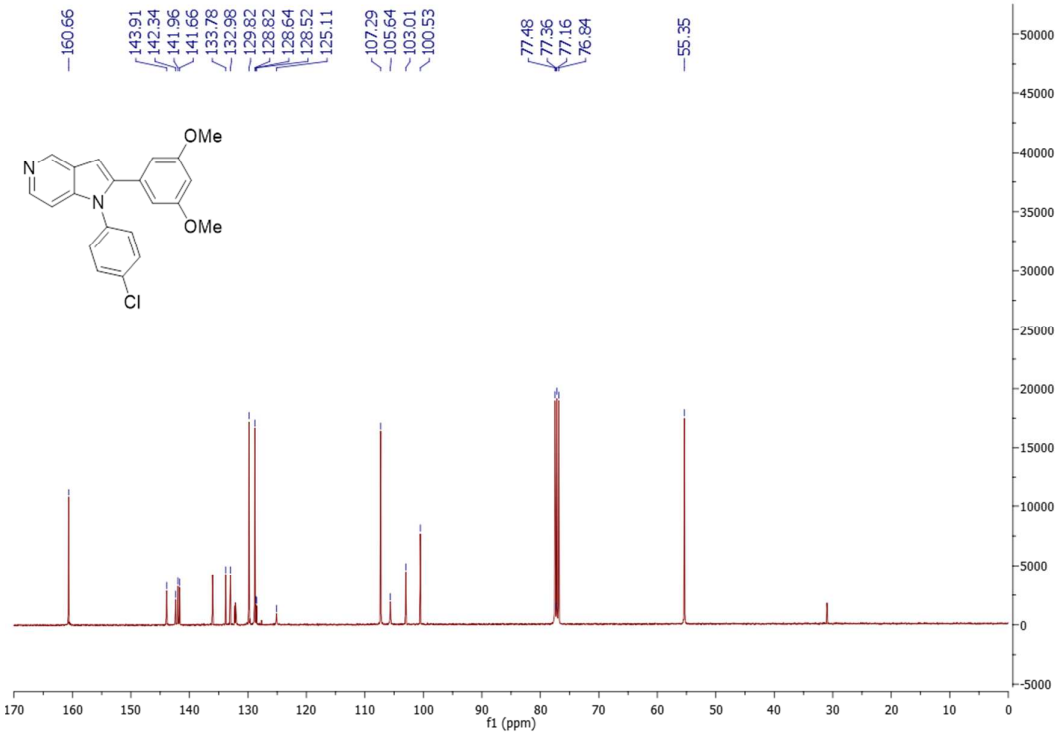
**1-(4-Chlorophenyl)-2-(4-methoxyphenyl)-5-azaindole (6o)**



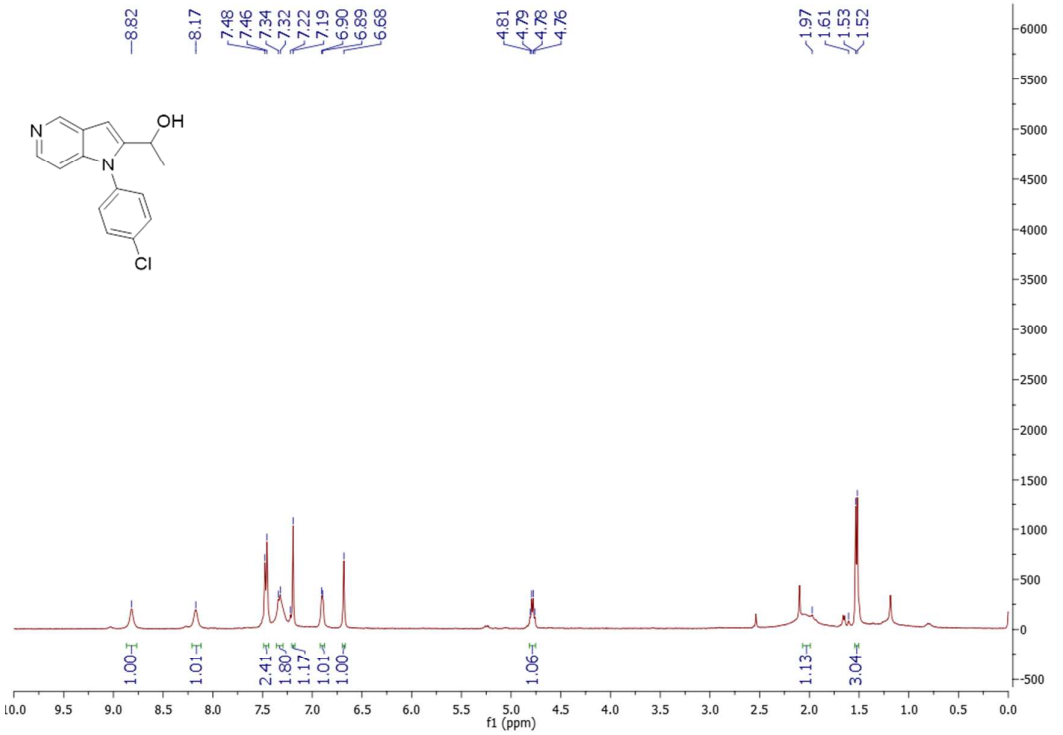



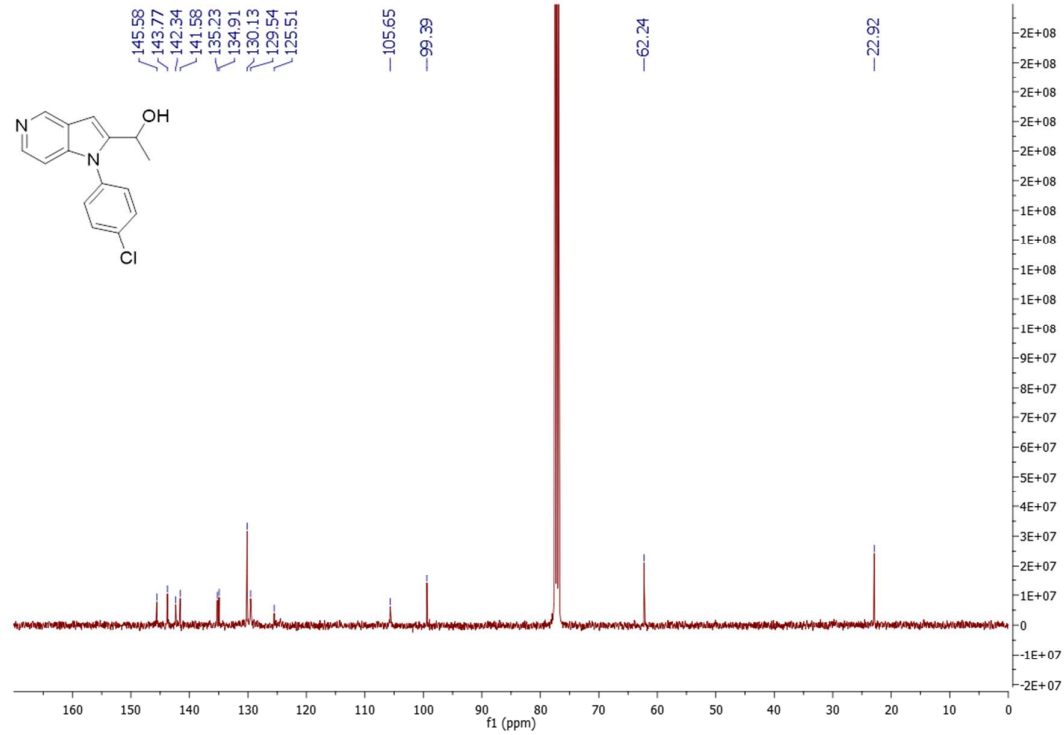
**1-(4-Chlorophenyl)-2-(3,5-dimethoxyphenyl)-5-azaindole (6p)**



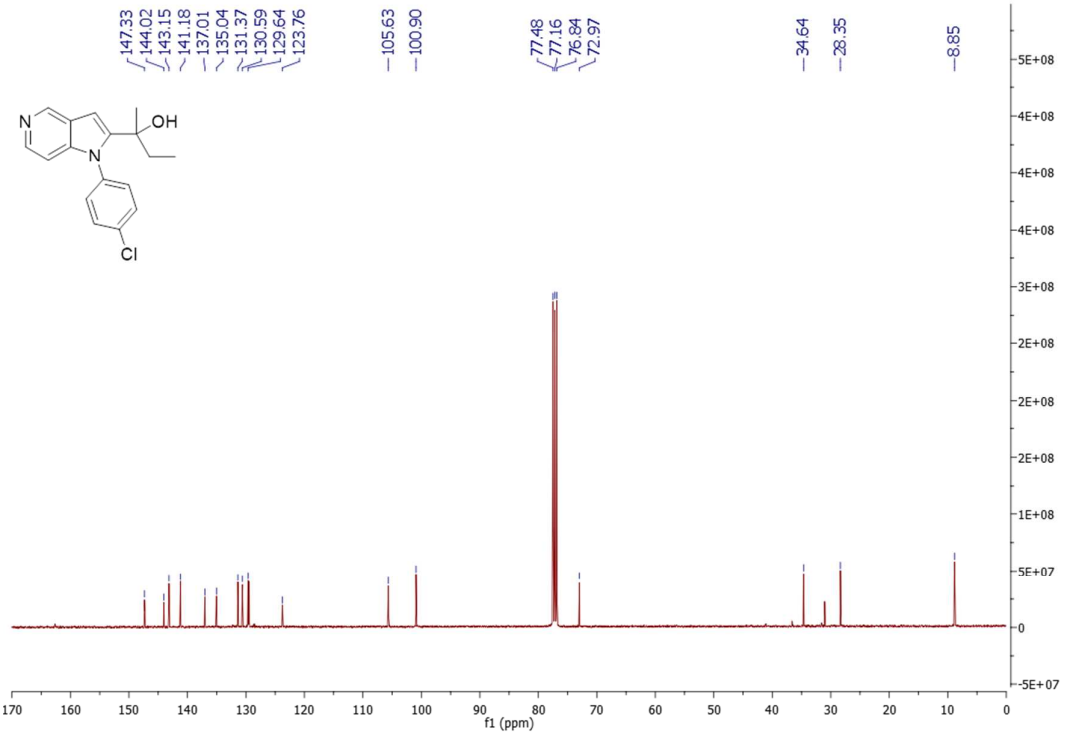



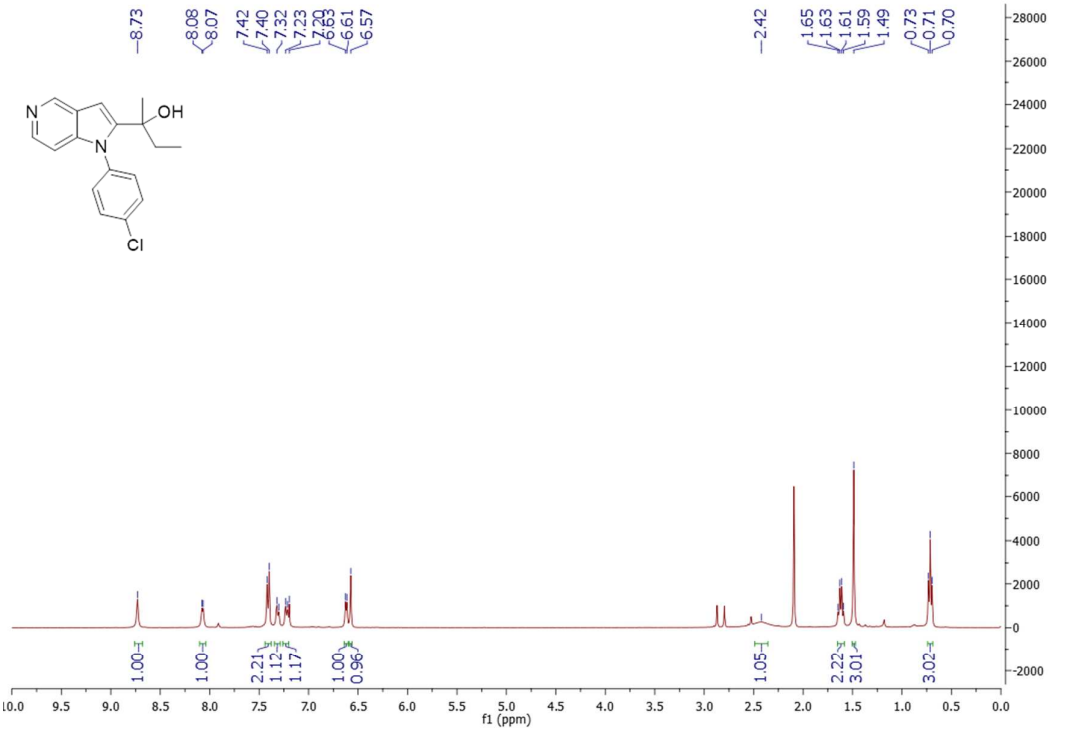
**1-(4-Chlorophenyl)-2-(ethyl-1-ol)-5-azaindole (6q)**



**1-(4-Chlorophenyl)-2-(2-butyl-2-ol)-5-azaindole (6r)**




## References


(1) Lu, X.; Petersen, J. L. and Wang, K. K. *J. Org. Chem.*, **2002**, *67*, 5412-5415.
(2) Spergel, S. H.; Okoro, D. R. and Pitts, W. *J. Org. Chem.*, **2010**, *75*, 5316-5319.
(3) Gao, J.; Shao, Y.; Zhu, J.; Zhu, J.; Mao, H.; Wang, X. and Lv, X. *J. Org. Chem.*, **2014**, *79*, 9000-9008.
(4) Rosenberg, A. J.; Zhao, J. and Clark, D. A. *Org. Lett.*, **2012**, *14*, 1764-1767.

(5) Iwaki, T.; Yasuhara, A. and Sakamoto, T. *J. Chem. Soc., Perkin Trans. 1*, **1999**, 1505-1510.
(6) Crawford, S. M.; Lavery, C. B. and Stradiotto, M. *Chem. Eur. J.*, **2013**, *19*, 16760-16771.
(7) Dell'Acqua, M.; Ronda, L.; Piano, R.; Pellegrino, S.; Clerici, F.; Rossi, E.; Mozzarelli, A.; Gelmi, M. L. and Abbiati, G. *J. Org. Chem.*, **2015**, *80*, 10939-10954.
(8) Moritz, B. J.; Mack, D. J.; Tong, L. and Thomson, R. J. *Angew. Chem., Int. Ed.*, **2014**, *53*, 2988-2991.
(9) Morri, A. K.; Thummala, Y. and Doddi, V. R. *Org. Lett.*, **2015**, *17*, 4640-4643.
(10) Burroughs, L.; Ritchie, J.; Ngwenya, M.; Khan, D.; Lewis, W. and Woodward, S. *Beilstein Journal of Organic Chemistry*, **2015**, *11*, 273-279.
(11) Pham, N. N.; Dang, T. T.; Ngo, N. T.; Villinger, A.; Ehlers, P. and Langer, P. *Org. Biomol. Chem.*, **2015**, *13*, 6047-6058.