Palladium-Catalyzed Amination of *N*-free-2-chloro-7-azaindole

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Supporting Information

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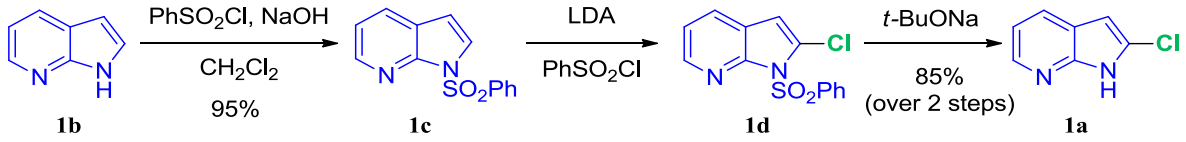
Complementary data

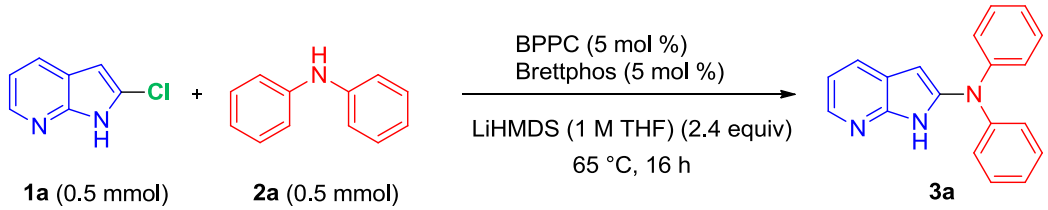
2-chloro-7-azaindole **1a** was prepared in three steps from the commercially available 7-azaindole **1b**, with an overall yield of 80% (Scheme S1). The first step was the sulfonylation at position 1[1] in order to direct the introduction of chlorine at position 2 of 7-azaindole in the second step. Then, deprotection of the sulfonyl group under basic conditions[2] offered the desired compound **1a**.

Scheme S1: Synthesis of 2-chloro-7-azaindole **1a**



We perform a kinetic study for C-2 amination of *N*-free-2-chloro-7-azaindole **1a** with diphenylamine **2a** (Table S1). We observed that an optimal yield was obtained for a reaction time of 16 h. This could be explained by the steric hindrance of the amine, which is then hindered to bind to the species obtained after the oxidative addition in the catalytic cycle.

Table S1: Kinetic study of C-2 amination of 2-chloro-7-azaindole **1a** with diphenylamine **2a**[a]



entry	time (h)	yield (%)
1	1	traces
2	4	15
3	8	35
4	16	70
5	24	60
6	48	60

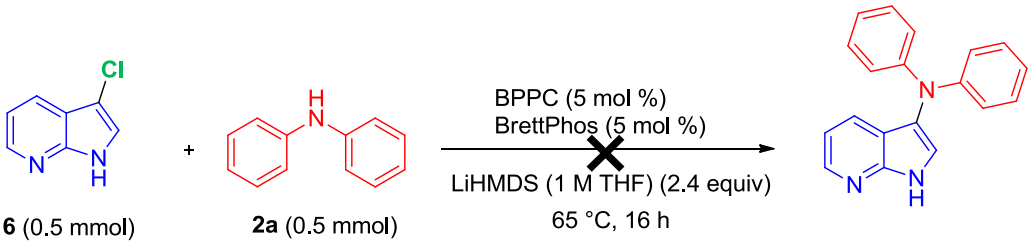
[a] Reaction conditions: 2-chloro-7-azaindole (0.5 mmol), amine (0.5 mmol), BrettPhos (5 mol %), BrettPhos precatalyst (5 mol %), LiHMDS (1.2 mmol, 1 M in THF), 65 °C, 16 h.

[1] Sandham, D.A.; Adcock, C.; Bala, K.; Brown, Z.; Dubois, G.; Wilson, C. *Bioorg. Med. Chem.*, **2009**, *19*, 4794-4798.

[2] Chaulet, C.; Croix, C.; Basset, J.; Pujol, M.-D.; Viaud-Massuard, M.C. *Synlett*, **2010**, *10*, 1481-1484.

We wanted to extend our methodology to amination on position 3 of 7-azaindole. 3-chloro-7-azaindole **6** was synthesized according to known procedure.[3] Then, **6** was engaged in the same conditions to perform amination as described for **1a**, however no reaction occurred (Scheme S2).

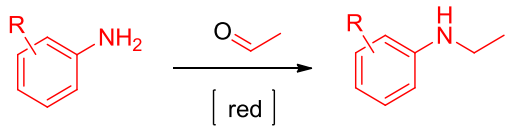
Scheme S2: Failed attempt of C-3 amination on 3-chloro-7-azaindole **6** with **2a**[a]



[a] Reaction conditions: 3-chloro-7-azaindole (0.5 mmol), diphenylamine (0.5 mmol), BrettPhos (5 mol %), BrettPhos precatalyst (5 mol %), LiHMDS (1.2 mmol, 1 M in THF), 65 °C, 16 h.

To explore the robustness of our methodology, we decided to synthesize various N-ethylanilines and use them as amine partner in Buchwald amination. Therefore, we performed reductive amination on acetaldehyde using various anilines in presence of a reducer (Scheme S3, see experimental sections for further information).

Scheme S3: Reductive aminations of acetaldehyde with various anilines.

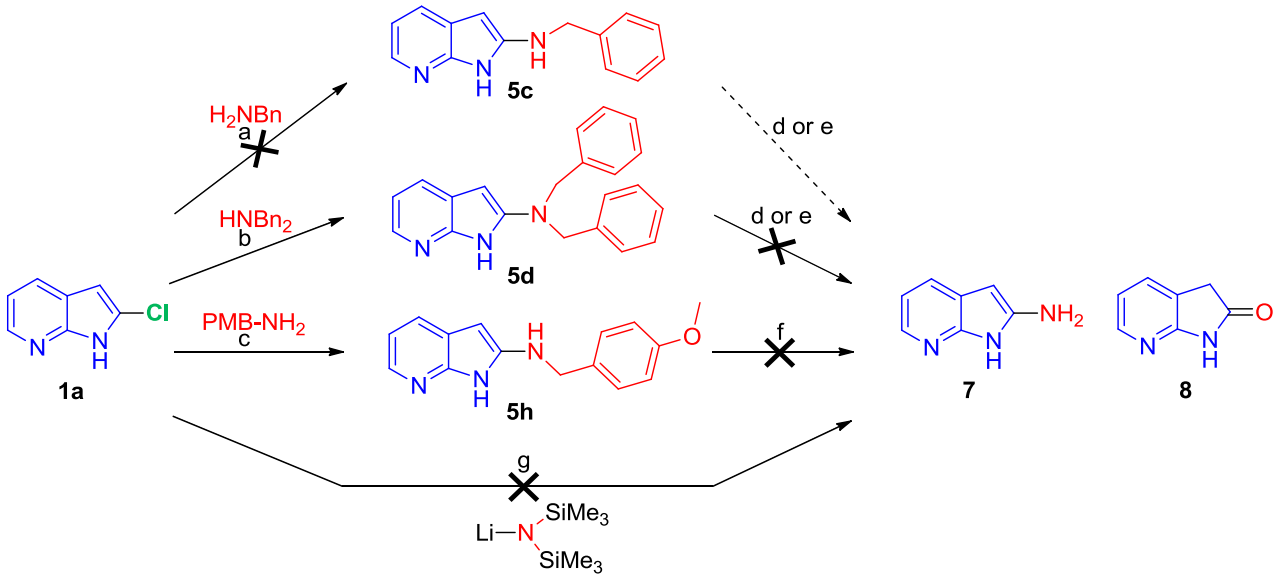


Finally, we attempted to access 2-amino-7-azaindole **7** from **1a** through three different pathways. First, we wanted to use benzylamine or dibenzylamine in presence of **1a** under our optimized Buchwald-Hartwig coupling conditions to obtain **5c** or **5d** respectively. Though we failed to obtain **5c**, we obtained **5d**, which we engaged in a deprotection of the benzyl moiety to obtain **7** according to two procedures: potassium tert-butoxide in dmso or palladium on carbone with dihydrogen in acetic acid. Unfortunately, degradation led to an unidentified mixture within no desired product **7** could be found. Then, coupling of paramethoxybenzylamine with **1a** followed by deprotection using cerium ammonium nitrate in a mixture of acetonitrile and water did not give compound **7**. Finally, coupling in presence

[3] Minakata, S.; Hamada, T.; Komatsu, M.; Tsuboi, H.; Kikuta, H.; Ohshiro, Y. *J. Agric. Food Chem.*, **1997**, 45, 2345–2348.

of LiHMDS as an ammoniac surrogate did not give **7**. In all final reactions, no trace of compound **8**[4] could have been observed (either by TLC monitoring or NMR and MS analysis).

Scheme S4: Failed attempts to access 2-amino-7-azaindole **7**[a]



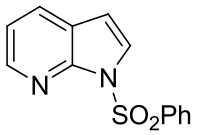
[a] Reaction conditions: a) **1a** (0.5 mmol), benzylamine (0.5 mmol), BrettPhos (5 mol %), BrettPhos precatalyst (5 mol %), LiHMDS (1.2 mmol, 1 M in THF), 65 °C, 16 h. b) **1a** (0.5 mmol), dibenzylamine (0.5 mmol), BrettPhos (20 mol %), BrettPhos precatalyst (20 mol %), LiHMDS (1.2 mmol, 1 M in THF), 65 °C, 16 h, 42%. c) **1a** (0.5 mmol), paramethoxybenzylamine (0.5 mmol), BrettPhos (5 mol %), BrettPhos precatalyst (5 mol %), LiHMDS (1.2 mmol, 1 M in THF), 65 °C, 16 h, 11%. d) **5d** (0.2 mmol), $Pd(OH)_2$/C (10 mol %), Pd/C (10 mol %), H_2, AcOH, rt. e) **5d** (0.2 mmol), *t*-BuOK (1.4 mmol), DMSO, THF, rt. f) **5h** (0.1 mmol), CAN (0.25 mmol), ACN/H_2O : 2/1, rt. g) **1a** (0.5 mmol), BrettPhos (5 mol %), BrettPhos precatalyst (5 mol %), LiHMDS (1.7 mmol, 1 M in THF), 65 °C, 16 h.

[4] Popowycz, F.; Routier, S.; Joseph, B.; Mérour, J.-Y. *Tetrahedron* **2007**, *63*, 1031-1064.

General Reagent Information: All chemicals were used as received from the commercial sources. 7-azaindole was purchased from Alfa Aesar Chemicals. The benzene sulfonyl chloride was purchased from Aldrich Chemical Co. The LDA solution and LiHMDS solution in THF were purchased from Aldrich Chemical Co. in Sure-Seal bottles and used as received. *tert*-butanol, toluene, dichloromethane, and dimethoxy-ethane were purchased from Aldrich Chemical Co. in Sure-Seal bottles and used as received. Anhydrous cesium carbonate, potassium carbonate and tribasic potassium phosphate were purchased from Aldrich Chemical Co. Ligands (triphenylphosphine, Xantphos, bdCyp, Ruphos, Binap and Josiphos CyPF-*t*Bu), $Pd(OAc)_2$ and Pd_2dba_3 were purchased from Aldrich Chemical Co. BrettPhos and BrettPhos precatalyst were purchased from Strem Chemicals Inc. All reactions were carried out under a nitrogen atmosphere. Aminations were carried out in screw-cap test-tubes with Teflon seals under an atmosphere of nitrogen. Flash chromatography was performed on silica gel Merck Kieselgel 60 (0.073-0.230 nm). When necessary, neutralization of silica was performed using 0.3% Et_3N in eluent, while conditioning the column and during elution for the purifications of sensitive products.

General Analytical Information: Yields reported for the preparation of starting materials refer to a single experiment whereas those reported for the C,N-cross coupling products products are an average of at least two independent runs. NMR spectra were acquired as solutions in the indicated solvents on a Bruker Advance DRX 300 spectrometer at 300 and 75 MHz field strengths for 1 H and 13 C nuclei, respectively. Chemical shifts are reported in parts per million (ppm, δ), downfield from tetramethylsilane (TMS, δ = 0.00 ppm), and are referenced to the residual solvent. Coupling constants are reported in Hertz (Hz). The following abbreviations are used singularly or in combination to indicate the multiplicity of signals: s singlet, d doublet, t triplet, q quartet, m multiplet and br broad. NMR spectra were acquired at 300 K unless otherwise indicated. Melting points were determined Buchi Melting point B-540. High resolution mass spectra were obtained using electrospray ionization from " Département d'Analyse Chimique Biologique et Médicale, de l'Université François Rabelais de Tours."

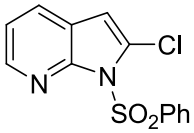
1-(Phenylsulfonyl)-1*H*-pyrrolo[2,3-*b*]pyridine 1c



To a solution of 7-azaindole **1b** (5.00 g, 42.3 mmol, 1 equiv) in CH_2Cl_2 (100 mL) were added NaOH (5.08 g, 127 mmol, 3 equiv) and benzyltriethylammonium chloride (410 mg, 1.27 mmol, 0.03 equiv). Phenylsulfonyl chloride (5.43 mL, 42.3 mmol, 1 equiv) was dropped into the reaction mixture under ice bath. The reaction mixture was stirred for 2 h at room temperature, and then 30 mL of water were added. The crude was washed with brine (1*50 mL). The organic extracts were dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification of the residue by silica gel column chromatography (Cy/EtOAc: 7/3) and precipitation from MeOH gave **1c** (10.2 g, 95%) as a white solid.

Mp = 129.0-129.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.43 (dd, *J* = 4.8, 1.5 Hz, 1H), 8.20 (m, 2H), 7.84 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.73 (d, *J* = 4.0 Hz, 1H), 7.61 – 7.52 (m, 1H), 7.52 – 7.43 (m, 2H), 7.18 (dd, *J* = 7.9, 4.8 Hz, 1H), 6.60 (d, *J* = 4.0 Hz, 1H). ^{13}C NMR (75 MHz, DMSO) δ 146.7, 144.7, 137.6, 134.7, 130.2, 129.6, 127.5, 126.8, 122.5, 119.4, 106.1. HRMS (ESI): m/z calcd for $C_{13}H_{11}N_2O_2S$ $(M+H)^+$: 259.0496; found 259.0532.

2-Chloro-1-(phenylsulfonyl)-1*H*-pyrrolo[2,3-*b*]pyridine 1d

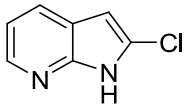


To a cold solution (-35 °C) of 1-(phenylsulfonyl)-1*H*-pyrrolo[2,3-*b*]pyridine **1c** (1.50 g, 5.81 mmol, 1.0 equiv) in dry THF (30 mL) was added slowly under argon, lithium diisopropylamide solution 2 M in THF (7.0 mL, 13.9 mmol, 2.4 equiv). The resultant brown precipitate was stirred for 30 min at -35 °C before the addition of benzene sulfonyl chloride (1.5 mL, 11.6 mmol, 2.0 equiv). The resulting solution was stirred for 2 h at -35 °C. Then, 10 mL of distilled water and 20 mL of ethyl acetate were added. The mixture was washed with a saturated solution of NaCl (20 mL). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated *in vacuo*. Flash chromatography on silica gel (Cy/EtOAc: 8/2) gave the desired compound **1d** (1.50 g, 90%) as a pale yellow solid.

Mp = 138.7-141.1 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.47 (dd, *J* = 4.9, 1.6 Hz, 1H), 8.20 (ddd, *J* = 7.1, 3.1, 1.8 Hz, 2H), 7.74 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.63 – 7.55 (m, 1H), 7.54 – 7.45 (m, 2H), 7.19 (dt, *J* = 7.8, 4.9 Hz, 1H), 6.54 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.4,

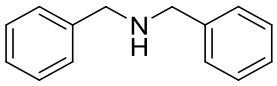
144.9, 138.9, 134.4, 129.3, 128.3, 128.0, 126.4, 121.2, 119.9, 106.8. HRMS (ESI): m/z calcd for $C_{13}H_{10}ClN_2O_2S$ $(M+H)^+$: 294.0044; found 293.0143.

2-Chloro-1*H*-pyrrolo[2,3-*b*]pyridine 1a



Under argon atmosphere, to a solution of 2-chloro-1-(phenylsulfonyl)-1H-pyrrolo[2,3-b]pyridine **1d** (3.36 g, 11.5 mmol, 1.0 equiv) in dioxane (40 mL) was added sodium *tert*-butoxyde (2.21 g, 22.9 mmol, 2.0 equiv). The resulting mixture was stirred at 80 °C for 2 h. Then, 60 mL of EtOAc were added, and the residue was washed with brine (30 mL). The organic extracts were dried over $MgSO_4$, filtered and concentrated *in vacuo*. Flash chromatography on silica gel (Cy/EtOAc: 7/3) gave **1a** as a pale yellow solid (1.70 g, 95%).
Mp = 157.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.24 (s, 1H), 8.33 (dd, *J* = 5.0, 1.5 Hz, 1H), 7.91 (dt, *J* = 4.4, 1.5 Hz, 1H), 7.15 (dd, *J* = 5.0, 4.4 Hz, 1H), 6.41 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.2, 141.0, 128.8, 126.2, 122.0, 116.6, 98.7. HRMS (ESI): m/z calcd for $C_7H_6ClN_2$ $(M+H)^+$: 154.0112; found 153.0214.

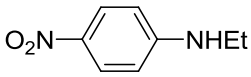
Dibenzylamine 2a



To a solution of benzylamine (1.3 mL, 12 mmol, 1.2 equiv) in methanol (20 mL) was added slowly benzaldehyde (1.0 mL, 10 mmol, 1.0 equiv). The reaction mixture was left stirring for 30 min, and then $NaBH_4$ (190 mg, 5 mmol, 2 equiv) was added slowly. The reaction was left running for another 16 h, and then concentrated *in vacuo*. The product was dissolved into dichloromethane (40 mL) and water (40 mL). The aqueous phase was extracted with dichloromethane (3*20 mL). Combined organic extracts were dried over $MgSO_4$, filtered and evaporated *in vacuo*. Flash chromatography on silica gel (Cy/EtOAc, 9/1) gave the desired product as a colorless oil (1.2 g, 62%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 – 7.23 (m, 10H), 3.84 (s, 4H), 2.27 (s, 1H). This experimental data is in agreement with those described in the literature.[5]

***N*-Ethyl-4-nitroaniline 2p**



To a solution of 4-nitroaniline (1.00 g, 7.24 mmol, 1.0 equiv) in dichloroethane (20 mL) was added acetaldehyde at -20 °C (1.2 mL, 21.4 mmol, 3.0 equiv). Sodium triacetoxyborohydride (1.84 g, 8.69 mmol, 1.2 equiv) and acetic acid (0.8 mL, 14.5 mmol, 2 equiv) were added and the reaction mixture was left stirring for 30 h at room temperature. The crude mixture was dissolved with 40 mL of ethyl acetate, and washed with a solution of NaOH 1 N (10 mL). The aqueous phase was extracted with ethyl acetate (3*20 mL). Combined organic extracts were dried over $MgSO_4$, filtered and evaporated *in vacuo*. Flash chromatography on silica gel (Cy/EtOAc: 9/1) gave the desired product as an orange solid (960 mg, 80%).

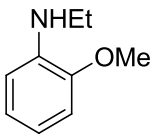
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (m, 2H), 6.54 (m, 2H), 4.49 (s, 1H), 3.28 (q, J = 7.2 Hz, 2H), 1.33 (t, J = 7.2 Hz, 3H). This experimental data is in agreement with those described in the literature.[6]

[5] Miriyala, B.; Bhattacharyya, S.; Williamson, J.S. *Tetrahedron*, **2004**, *60*, 1463-1471
[6] Katritzky, A.R.; Laurenzo, K.S. *J. Org. Chem*., **1988**, *53*, 3978-3982

General procedure A for the preparation of *N*-Ethyl-X-methoxyaniline

Methoxy-aniline (5 mmol, 1 equiv) was dissolved in acetonitrile (25 mL) and stirred at room temperature. 5% Pd/C (2 mol %) and ammonium formate (60 mmol, 12 equiv) dissolved in H_2O (6 mL) was then added to the reaction mixture while stirring. The reaction was monitored by TLC for the disappearance of the spot (lowest R_f) corresponding to the primary amine intermediate. The reaction mixture was then filtered, washed with methanol and the filtrate evaporated *in vacuo*. The residue was dissolved in CH_2Cl_2 and the organic layer was washed with a saturated solution of NaCl (20 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated *in vacuo*. Flash chromatography on silica gel gave the desired product.

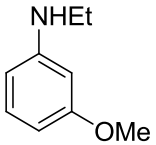
_N_-Ethyl-2-methoxyaniline 2m



Following the general procedure A. The crude was purified by flash chromatography on silica gel (Cy/EtOAc: 1/0 to 98/2) to provide the desired compound **2m**(470 mg, 60%) as an orange oil.

^{1}H NMR (300 MHz, CDCl3) δ 6.90 (dd, *J* = 7.6, 1.5 Hz, 1H), 6.79 (dd, *J* = 7.9, 1.4 Hz, 1H), 6.70 (dd, *J* = 7.6, 1.4 Hz, 1H), 6.65 (m, 1H), 4.11 (s, 1H), 3.87 (s, 3H), 3.19 (q, *J* = 7.1 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H). This experimental data is in agreement with those described in the literature[7].

_N_-Ethyl-3-methoxyaniline 2n



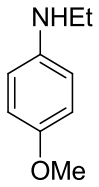
Following the general procedure A. The crude was purified by flash chromatography on silica gel (Cy/EtOAc: 1/0 to 95/5) to provide the desired compound **2n** (602 mg, 80%) as a yellow oil .

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 (t, *J* = 8.1 Hz ,1H), 6.29 (ddd, *J* = 8.1, 2.3, 0.8 Hz, 1H), 6.26 (ddd, *J* = 8.1, 2.3, 0.8 Hz, 1H), 6.21 (t, *J* = 2.3 Hz, 1H), 3.81 (s, 3H), 3.51 (s, 1H), 3.18

[7] Nacario, R.; Kotakonda, S.; Fouchard, D.M.; Tillekeratne, L.V.; Hudson, R.A. *Org. Lett*., **2005**, *7*, 471-474

(q, *J* = 7.2 Hz, 2H), 1.28 (t, *J* = 7.2 Hz, 3H). This experimental data is in agreement with those described in the literature[7].

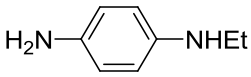
N-Ethyl-4-methoxyaniline 2o



Following the general procedure A. The crude was purified by flash chromatography on silica gel (Cy/EtOAc: 98/2 to 95/5) to provide the desired compound **2o** (530 mg, 70%) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.82 (m, 2H), 6.62(m, 2H), 3.78 (s, 3H), 3.14 (q, *J* = 7.1 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H). This experimental data is in agreement with those described in the literature.[7]

N^1-Ethylbenzene-1,4-diamine 2k



To a solution of *N*-ethyl-4-nitroaniline **2k** (550 mg, 3.31 mmol, 1 equiv) in ethyl acetate (15 mL) was added palladium on charcoal (55 mg, 0.1% mass). The mixture was stirred for 4 h at room temperature, then filtered on Celite® and washed with ethyl acetate (30 mL). The filtrate was evaporated *in vacuo*. Flash chromatography on silica gel (Cy/EtOAc: 6/4) gave the desired product (380 mg, 85%) as a dark purple oil.

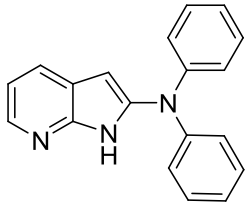
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.64 (d, *J* = 8.4 Hz, 2H), 6.55 (d, *J* = 8.4 Hz, 2H), 3.10 (q, *J* = 7.1 Hz, 2H), 2.63 (s, 1H), 1.25 (t, *J* = 7.1 Hz, 3H). This experimental data is in agreement with those described in the literature.[8]

[8] Rodriguez, F.; Rozas, I.; Ortega, J.E.; Erdozain, A.M.; Meana, J.J.; Callado, L.F. *J. Med. Chem*., **2009**, *52*, 601-609

General procedure B for Buchwald-Hartwig reaction

A screw-cap test-tube, equipped with a magnetic stir bar, was charged with 2-chloro-1*H*-pyrrolo[2,3-*b*]pyridine **3** (76 mg, 0.5 mmol, 1 equiv), BrettPhos (13.5 mg, 0.025 mmol, 0.05 equiv) and BrettPhos precatalyst (20.0 mg, 0.025 mmol, 0.05 equiv). The vial was evacuated and backfilled with argon. LiHMDS solution 1 M in THF (1.2 mL, 1.20 mmol, 2.4 equiv) was added *via* syringe, followed by the amine (0.5 mmol, 1.0 equiv) (amines that were solids at room temperature were added with the catalyst). The vial was sealed with a teflon screw-cap and the reaction mixture was heated at 65 °C until completion. The solution was allowed to cool to room temperature, quenched by the addition of 1 M HCl (1 mL), diluted with EtOAc and washed with a saturated aqueous solution of $NaHCO_3$. After extracting with 3 portions of EtOAc, the combined organic layers were washed with brine, dried over $MgSO_4$, and then concentrated *in vacuo*. Flash chromatography on silica gel gave the desired product.

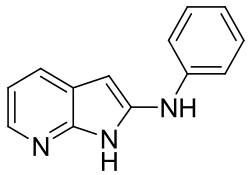
***N*,*N*-Diphenyl-1*H*-pyrrolo[2,3-*b*]pyridin-2-amine 3a**



Following the general procedure B. The crude was purified by flash chromatography on silica gel (Cy/EtOAc: 1/0 to 95/5) to provide the desired compound **3a** (100 mg, 70%) as a white solid.

Mp = 170-172 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.40 (dd, *J* = 5.0, 1.5 Hz, 1H), 7.35 – 7.27 (m, 4H), 7.27 – 7.20 (m, 4H), 7.15 – 7.07 (m, 2H), 6.85 (dd, *J* = 7.7, 5.0 Hz, 1H), 5.79 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.0, 143.7, 139.5, 129.6, 129.5, 129.5, 126.4, 124.3, 124.2, 121.1, 117.9, 89.0. HRMS (ESI): m/z calcd for $C_{19}H_{16}N_3$ $(M+H)^+$: 286.1299; found: 286.1335.

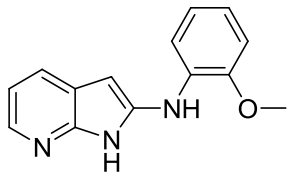
***N*-Phenyl-1*H*-pyrrolo[2,3-*b*]pyridin-2-amine 3b**



Following the general procedure B. The crude was purified by flash chromatography on silica gel (Cy/EtOAc: 1/1) to provide the desired compound **3b** (61 mg, 60%) as a red solid.

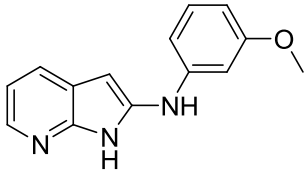
Mp = 165 °C; ^{1}H NMR (300 MHz, DMSO) δ 11.08 (s, 1H), 8.53 (s, 1H), 7.93 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.61 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.30 – 7.22 (m, 2H), 7.18 – 7.12 (m, 2H), 6.92 (dd, *J* = 7.7, 4.8 Hz, 1H), 6.84 (ddd, *J* = 8.4, 2.3, 1.1 Hz, 1H), 5.90 (s, 1H). ^{13}C NMR (75 MHz, DMSO) δ 146.3, 142.9, 140.6, 138.9, 129.2, 124.2, 121.8, 119.8, 115.8, 115.6, 82.1. HRMS (ESI): m/z calcd for $C_{13}H_{12}N_3$ $(M+H)^+$: 210.0986; found: 210.1022.

_N_-(2-Methoxyphenyl)-1_H_-pyrrolo[2,3-_b_]pyridin-2-amine 3c



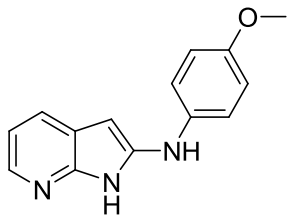
Following the general procedure A. The crude was purified by flash chromatography on silica gel (Cy/EtOAc: 1/1) to provide the desired compound **3c** (86 mg, 72%) as a red solid.
Mp = 155.6 °C; ^{1}H NMR (300 MHz, DMSO) δ 10.81 (s, 1H), 7.91 (dd, J = 4.8, 1.5 Hz, 1H), 7.85 (s, 1H), 7.61 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.41 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.04 (dd, *J* = 7.7, 1.6 Hz, 1H), 6.98 – 6.84 (m, 3H), 5.97 (s, 1H), 3.90 (s, 3H). ^{13}C NMR (75 MHz, DMSO) δ 147.5, 145.6, 140.3, 138.8, 131.0, 124.2, 122.0, 121.0, 120.2, 115.6, 114.1, 110.9, 80.4, 55.8. HRMS (ESI): m/z calcd for $C_{14}H_{14}N_3O$ $(M+H)^+$: 240.1092; found: 240.1127.

_N_-(3-Methoxyphenyl)-1_H_-pyrrolo[2,3-_b_]pyridin-2-amine 3d



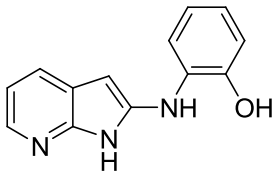
Following the general procedure B. The crude was purified by flash chromatography on silica gel (Cy/EtOAc: 4/6 to 2/8) to provide the desired compound **3d** (68 mg, 60%) as a red solid.
Mp = 151 °C; ^{1}H NMR (300 MHz, DMSO) δ 11.11 (s, 1H), 8.55 (s, 1H), 7.94 (dd, J = 4.8, 1.5 Hz, 1H), 7.62 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.16 (t, *J* = 8.0 Hz, 2H), 6.93 (dd, *J* = 7.7, 4.8 Hz, 2H), 6.75-6.71 (m, 2H), 6.43 (dd, *J* = 7.9, 2.1 Hz, 1H), 5.91 (s, 1H), 3.72 (s, 3H). ^{13}C NMR (75 MHz, DMSO) δ 160.2, 146.3, 144.2, 140.3, 139.1, 130.0, 124.4, 121.7, 115.6, 108.4, 105.3, 101.4, 82.5, 54.9. HRMS (ESI): m/z calcd for $C_{14}H_{14}N_3O$ $(M+H)^+$: 240,1092; found: 240.1128.

_N_-(4-Methoxyphenyl)-1_H_-pyrrolo[2,3-_b_]pyridin-2-amine 3e



Following the general procedure B. The crude was purified by flash chromatography on silica gel (Cy/EtOAc: 3/7 to 1/9) to provide the desired compound **3e** (28 mg, 25%) as a red solid. Mp = 162 °C; ^{1}H NMR (300 MHz, DMSO) δ 10.93 (s, 1H), 8.24 (s, 1H), 7.87 (dd, *J* = 4.9, 1.5 Hz, 1H), 7.53 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.13 (m, 2H), 6.91 – 6.84 (m, 3H), 5.71 (s, 1H), 3.71 (s, 3H). ^{13}C NMR (75 MHz, DMSO) δ 153.6, 146.4, 142.4, 138.2, 135.9, 123.5, 122.2, 118.4, 115.5, 114.6, 79.6, 55.3. HRMS (ESI): m/z calcd for $C_{14}H_{14}N_3O$ $(M+H)^+$: 240.1092; found: 240.1128.

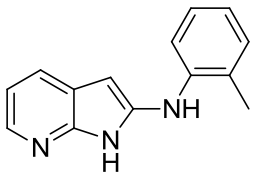
2-(1_H_-Pyrrolo[2,3-_b_]pyridin-2-ylamino)phenol 3f



Following the general procedure B. The crude was purified by flash chromatography on silica gel (Cy/EtOAc: 3/7 to EtOAc/MeOH 9/1) to provide the desired compound **3f** (54 mg, 50%) as a green solid.

Mp = 132.4 °C; ^{1}H NMR (300 MHz, DMSO) δ 10.77 (s, 1H), 9.94 (s, 1H), 7.88 (dd, *J* = 4.9, 1.5 Hz, 1H), 7.74 (s, 1H), 7.58 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.36 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.90 (dd, *J* = 7.6, 4.9 Hz, 1H), 6.87 (dd, *J* = 7.6, 1.8 Hz, 1H), 6.81 (td, *J* = 7.6, 1.8 Hz, 1H), 6.74 (td, *J* = 7.5, 1.7 Hz, 1H), 5.92 (s, 1H). ^{13}C NMR (75 MHz, DMSO) δ 145.6, 145.4, 140.8, 138.5, 130.0, 123.8, 122.2, 120.2, 119.6, 115.5, 114.5, 114.5, 79.4. HRMS (ESI): m/z calcd for $C_{13}H_{12}N_3O$ $(M+H)^+$: 226.0935; found: 226.0972.

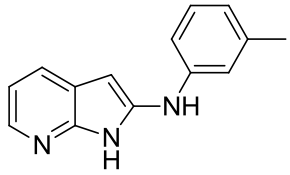
_N_-(2-Tolyl)-1_H_-pyrrolo[2,3-_b_]pyridin-2-amine 3g



Following the general procedure B. The crude was purified by flash chromatography on silica gel (Cy/EtOAc: 1/0 to 6/4) to provide the desired compound **3f** (54 mg, 50%) as a dark red solid.

^{1}H NMR (300 MHz, DMSO) δ 10.74 (s, 1H), 8.40 (dd, *J* = 5.1, 1.5 Hz, 1H), 7.97 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.30-6.70 (m, 6H), 2.12 (s, 3H). ^{13}C NMR (75 MHz, DMSO) δ 165.4, 156.2, 146.4, 145.3, 133.1, 130.3, 128.8, 126.5, 124.3, 119.7, 117.7, 113.0, 17.7. HRMS (ESI): m/z calcd for $C_{14}H_{14}N_3$ $(M+H)^+$: 224.1109; found: 224.1141.

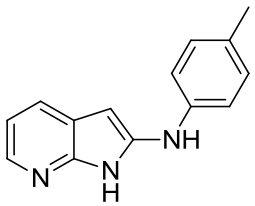
N-(3-Tolyl)-1*H*-pyrrolo[2,3-*b*]pyridin-2-amine 3h



Following the general procedure B. The crude was purified by flash chromatography on silica gel (Cy/EtOAc: 9/1 to 6/4) to provide the desired compound **3h** (18 mg, 16%) as a dark red solid.

^{1}H NMR (300 MHz, DMSO) δ 10.43 (s, 1H), 8.38 (dd, 5.0, 1.6 Hz, 1H), 8.05 – 7.74 (m, 2H), 7.28 (dd, *J* = 7.7, 5.0 Hz, 1H), 7.09 – 6.80 (m, 3H), 2.33 (s, 3H). ^{13}C NMR (75 MHz, DMSO) δ 156.1, 155.3, 147.1, 145.1, 138.4, 133.1, 128.9, 125.5, 122.1, 121.4, 119.0, 117.7, 112.8, 21.1. HRMS (ESI): m/z calcd for $C_{14}H_{14}N_3$ $(M+H)^+$: 224.1109; found: 224.1152.

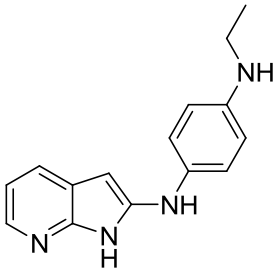
N-(4-Tolyl)-1*H*-pyrrolo[2,3-*b*]pyridin-2-amine 3i



Following the general procedure B. The crude was purified by flash chromatography on silica gel (Cy/EtOAc: 9/1 to 6/4) to provide the desired compound **3f** (13 mg, 11%) as a dark red solid.

^{1}H NMR (300 MHz, DMSO) δ 10.48 (s, 1H), 8.38 (dd, *J* = 5.1, 1.7 Hz, 1H), 8.20-7.70 (m, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 7.12 – 6.91 (m, 2H), 2.31 (d, *J* = 5.9 Hz, 3H). ^{13}C NMR (75 MHz, DMSO) δ 156.1, 155.4, 144.5, 134.0, 133.7, 133.1, 132.7, 129.7, 129.4, 122.0, 121.0, 118.6, 117.7, 114.8, 20.6. HRMS (ESI): m/z calcd for $C_{14}H_{14}N_3$ $(M+H)^+$: 224.1109; found: 224.1172.

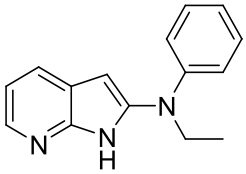
N^1-Ethyl-N^4-(1*H*-pyrrolo[2,3-*b*]pyridin-2-yl)benzene-1,4-diamine 3k



Following the general procedure A. The crude was purified by flash chromatography on silica gel (Cy/EtOAc: 3/7 to EtOAc/MeOH 95/5) to provide the desired compound **3k** (32 mg, 25%) as a dark solid.

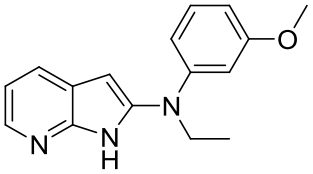
Mp = 111.0 °C; ^{1}H NMR (300 MHz, DMSO) δ 10.71 (s, 1H), 7.87 (s, 1H), 7.80 (dd, *J* = 4.9, 1.5 Hz, 1H), 7.45 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.03 – 6.96 (m, 2H), 6.83 (dd, *J* = 7.6, 4.9 Hz, 1H), 6.55 (m, 2H), 5.53 (s, 1H), 2.98 (m, 3H), 1.15 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, DMSO) δ 146.5, 144.2, 144.0, 137.5, 131.4, 122.8, 122.5, 119.8, 115.4, 112.8, 77.8, 37.9, 14.5. HRMS (ESI): m/z calcd for $C_{15}H_{17}N_4$ $(M+H)^+$: 253.1408; found: 253.2789.

***N*-Ethyl-N-phenyl-1*H*-pyrrolo[2,3-*b*]pyridin-2-amine 3l**



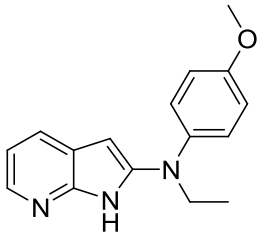
Following the general procedure B. The crude was purified by flash chromatography on silica gel (Cy/EtOAc: 7/3 to 1/1) to provide the desired compound **3l** (86 mg, 72%) as a red solid. Mp = 108.0-111.0 °C; ^{1}H NMR (300 MHz, DMSO) δ 11.43 (s, 1H), 7.96 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.62 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.29 (m, 2H), 7.12 – 7.07 (m, 2H), 6.97 (m, 1H), 6.92 (dd, *J* = 7.7, 4.8 Hz, 1H), 5.76 (s, 1H), 3.82 (q, *J* = 7.0 Hz, 2H), 1.16 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, DMSO) δ 146.8, 146.1, 144.1, 139.5, 129.2, 124.7, 121.6, 121.3, 119.9, 115.6, 85.9, 46.1, 12.8. HRMS (ESI): m/z calcd for $C_{15}H_{16}N_3$ $(M+H)^+$: 238.1299; found: 238.1335.

***N*-Ethyl-*N*-(3-methoxyphenyl)-1*H*-pyrrolo[2,3-*b*]pyridin-2-amine 3n**



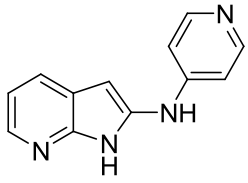
Following the general procedure B. The crude was purified by flash chromatography on silica gel (Cy/EtOAc: 6/4 to 1/1) to provide the desired compound **3n** (80 mg, 60%) as a brown solid. Mp = 103.4-104.4 °C; ^{1}H NMR (300 MHz, DMSO) δ 11.43 (s, 1H), 7.98 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.64 (dt, *J* = 7.7, 1.6 Hz, 1H), 7.19 (t, *J* = 8.1 Hz, 1H), 6.95 (dd, *J* = 7.7, 4.8 Hz, 1H), 6.64 (m, 1H), 6.61 – 6.51 (m, 2H), 5.81 (s, 1H), 3.79 (q, *J* = 7.2 Hz, 2H), 3.71 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, DMSO) δ 160.2, 147.4, 146.7, 143.6, 139.8, 129.9, 124.9, 121.2, 115.6, 111.9, 106.6, 105.4, 86.7, 55.0, 46.1, 12.8. HRMS (ESI): m/z calcd for $C_{16}H_{18}N_3O$ $(M+H)^+$: 268.1405; found: 268.1439.

_N_-Ethyl-N-(4-methoxyphenyl)-1_H_-pyrrolo[2,3-_b_]pyridin-2-amine 3o



Following the general procedure B. The crude was purified by flash chromatography on silica gel (Cy/EtOAc: 4/6 to 3/7) to provide the desired compound **3o** (88 mg, 67%) as a red solid. Mp = 125.6-126.9 °C; ^{1}H NMR (300 MHz, DMSO) δ 11.12 (s, 1H), 7.83 (dd, *J* = 4.9, 1.6 Hz, 1H), 7.45 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.17 (m, 2H), 6.95 (m, 2H), 6.85 (dd, *J* = 7.7, 4.9 Hz, 1H), 5.30 (s, 1H), 3.76 (s, 3H), 3.72 (q, *J* = 7.0 Hz, 2H), 1.12 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, DMSO) δ 156.2, 147.0, 146.8, 138.3, 137.8, 125.8, 123.0, 122.1, 115.5, 114.7, 80.6, 55.3, 46.5, 12.8. HRMS (ESI): m/z calcd for $C_{16}H_{18}N_3O$ $(M+H)^+$: 268.1405; found: 268.1441.

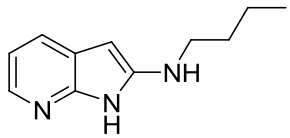
_N_-(Pyridin-4-yl)-1_H_-pyrrolo[2,3-_b_]pyridin-2-amine 5a



Following the general procedure B. The crude was purified by flash chromatography on silica gel (EtOAc/MeOH: 1/0 to 9/1) to provide the desired compound **5a** (64 mg, 62%) as a yellow solid.

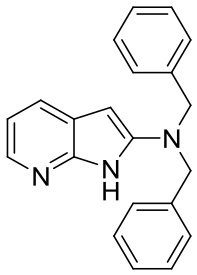
Mp = 212.6-215.1 °C; ^{1}H NMR (300 MHz, DMSO) δ 11.46 (s, 1H), 9.16 (s, 1H), 8.24 (dd, *J* = 4.8, 1.5 Hz, 2H), 8.05 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.74 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.02 – 6.97 (m, 3H), 6.11 (s, 1H).^{13}C NMR (75 MHz, DMSO) δ 150.1, 149.7, 146.3, 140.5, 137.2, 125.7, 121.0, 115.8, 109.5, 86.7. HRMS (ESI): m/z calcd for $C_{12}H_{11}N_4$ $(M+H)^+$: 211.0939; found: 211.0977.

_N_-Butyl-1_H_-pyrrolo[2,3-_b_]pyridin-2-amine 5b



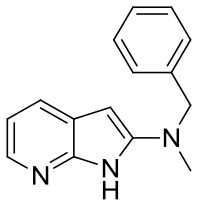
Following the general procedure B. The crude was purified by flash chromatography on silica gel (Cy/EtOAc: 6/4 to 1/1) to provide the desired compound **5b** (60 mg, 65%) as a grey solid. Mp = 96.6-98.1 °C; ^{1}H NMR (300 MHz, DMSO) δ 11.93 (s, 1H), 8.22 (dd, *J* = 4.6, 1.3 Hz, 1H), 7.91 (dd, *J* =7.8, 1.3 Hz, 1H), 7.08 (dd, *J* = 7.8, 4.6 Hz, 1H), 6.36 (s, 1H), 3.65 (t, *J* = 7.3 Hz, 2H), 1.88 (s, 1H), 1.50 – 1.33 (m, 2H), 1.31 – 1.18 (m, 2H), 0.83 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, DMSO) δ 146.5, 143.0, 137.3, 128.2, 119.5, 116.2, 96.4, 47.2, 29.7, 19.3, 13.7. HRMS (ESI): m/z calcd for $C_{11}H_{16}N_3$ $(M+H)^+$: 190.1299; found: 190.1338.

_N_,_N_-Dibenzyl-1_H_-pyrrolo[2,3-_b_]pyridin-2-amine 5d



Following the general procedure B. The crude was purified by flash chromatography on silica gel (Cy/EtOAc: 8/2 to 6/4) to provide the desired compound **5d** (50 mg, 30%) as a red solid. Mp = 159.5 °C; ^{1}H NMR (300 MHz, DMSO) δ 11.40 (s, 1H), 7.79 (dd, *J* = 4.9, 1.5 Hz, 1H), 7.38 (dd, *J* = 7.7, 1.5 Hz, 1H),7.44 – 7.17 (m, 10H), 6.82 (dd, *J* = 7.7, 4.9 Hz, 1H), 5.26 (s, 1H), 4.55 (s, 4H). ^{13}C NMR (75 MHz, DMSO) δ 148.3, 147.3, 138.1, 137.0, 128.4, 127.4, 126.9, 122.8, 122.3, 115.5, 77.8, 53.1. HRMS (ESI): m/z calcd for $C_{21}H_{20}N_3$ $(M+H)^+$: 314.1612; found: 314.1647.

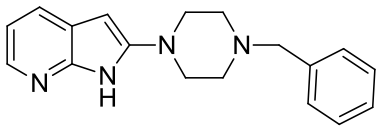
_N_-Benzyl-_N_-methyl-1_H_-pyrrolo[2,3-_b_]pyridin-2-amine 5e



Following the general procedure B. The crude was purified by flash chromatography on silica gel (Cy/EtOAc: 9/1 to 4/6) to provide the desired compound **5e** (51 mg, 43%) as a dark red solid.

^{1}H NMR (300 MHz, DMSO) δ 7.80 (dd, *J* = 4.9, 1.5 Hz, 1H), 7.43 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.38 (d, *J* = 7.4 Hz, 1H), 7.35-7.20 (m, 5H), 6.84 (dd, *J* = 7.4, 4.9 Hz, 1H), 4.54 (s, 2H), 2.86 (s, 3H). ^{13}C NMR (75 MHz, DMSO) δ 149.25, 147.44, 137.83, 136.94, 128.71, 128.58, 128.40 (2 C), 127.60 (2 C), 127.06, 122.87, 122.26, 115.42, 76.96, 55.10, 37.21. HRMS (ESI): m/z calcd for $C_{15}H_{16}N_3$ $(M+H)^+$: 238.1266; found: 238.1278.

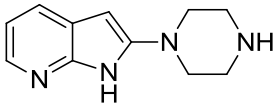
2-(4-Benzylpiperazin-1-yl)-1*H*-pyrrolo[2,3-*b*]pyridine 5f



Following the general procedure B. The crude was purified by flash chromatography on silica gel (Cy/EtOAc: 1/9 to EtOAc/MeOH 9/1) to provide the desired compound **5f** (69 mg, 50%) as a yellow solid.

Mp = 199.5-203.6 °C; ^{1}H NMR (300 MHz, DMSO) δ 11.23 (s, 1H), 7.85 (dd, *J* = 4.9, 1.5 Hz, 1H), 7.51 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.37 – 7.21 (m, 5H), 6.86 (dd, *J* = 7.6, 4.9 Hz, 1H), 5.41 (s, 1H), 3.53 (s, 2H), 3.34 (m, 4H), 3.22 (m, 4H). ^{13}C NMR (75 MHz, DMSO) δ 149.5, 147.3, 138.0, 137.9, 128.9, 128.2, 127.0, 123.4, 122.0, 115.4, 78.6, 62.0, 51.8, 47.9. HRMS (ESI): m/z calcd for $C_{18}H_{21}N_4$ $(M+H)^+$: 293.1721; found: 293.1758.

2-(Piperazin-1-yl)-1*H*-pyrrolo[2,3-*b*]pyridine 5g

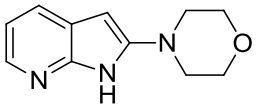


Following the general procedure B. The crude was purified by flash chromatography on silica gel (EtOAc/MeOH: 10:0 to 8:2) to provide the desired compound **5g** (8 mg, 8%) as a brown solid.

1H NMR (300 MHz, DMSO) δ 11.37 (s, 1H), 7.89 (d, J = 4.9 Hz, 1H), 7.56 (d, J = 7.7 Hz, 1H), 6.90 (dd, J = 7.6, 4.9 Hz, 1H), 5.54 (s, 1H), 3.38 (s, 4H), 3.11 – 3.07 (m, 1H), 1.17 (t, J =

7.3 Hz, 4H). 13C NMR (75 MHz, DMSO) δ 149.2, 147.2, 138.3, 123.7, 121.9, 115.5, 79.2, 47.3 (x2), 39.7 (x2). HRMS (ESI): m/z calcd for C11H14N4 $(M^+H)^+$: 203.1252; found: 203.1284.

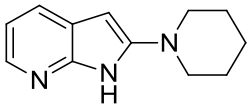
4-(1*H*- Pyrrolo[2,3-*b*]pyridin-2-yl)morpholine 5h



Following the general procedure B. The crude was purified by flash chromatography on silica gel (Cy/EtOAc: 1/9 to 0/10) to provide the desired compound **5g** (31 mg, 30%) as a brown solid.

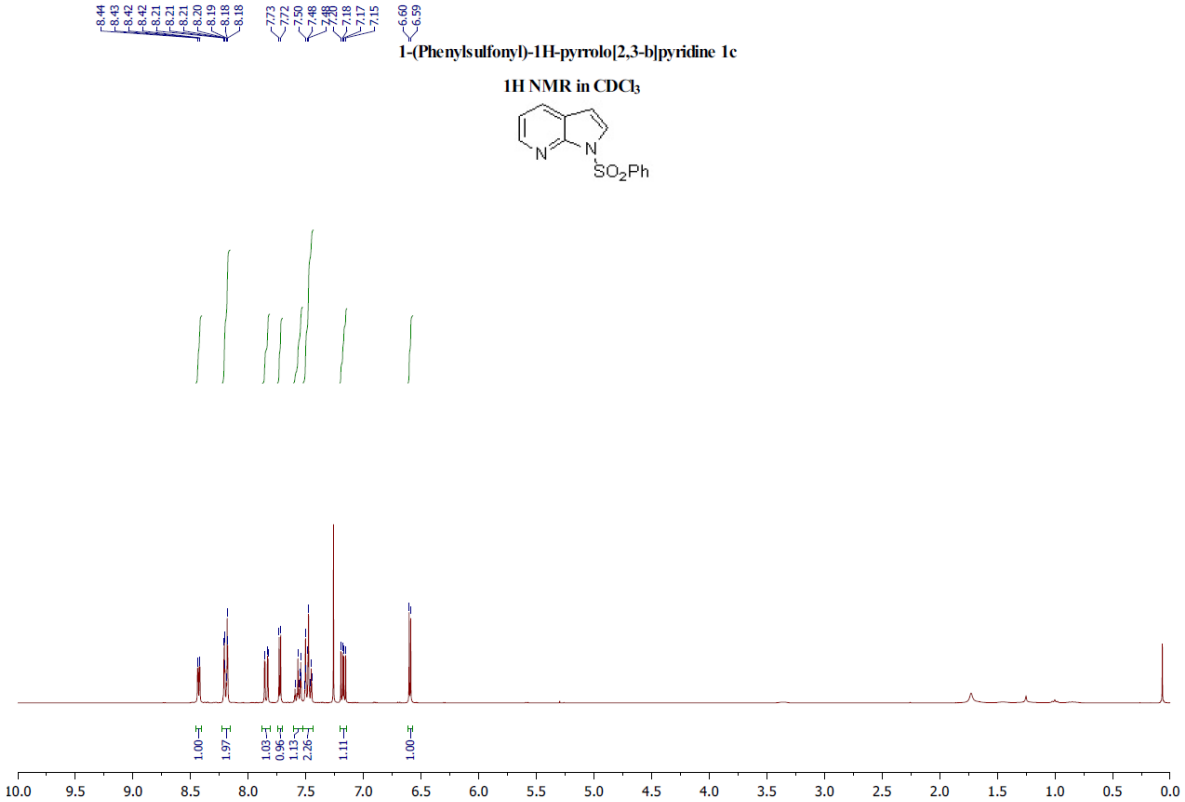
^{1}H NMR (300 MHz, DMSO) δ 11.33 (s, 1H), 7.88 (dd, *J* = 4.8, 1.5 Hz, 1H), 7.55 (dd, *J* = 7.6, 1.5 Hz, 1H), 6.89 (dd, *J* = 7.6, 4.9 Hz, 1H), 5.46 (s, 1H), 3.85 – 3.66 (m, 4H), 3.25 – 3.08 (m, 4H). ^{13}C NMR (75 MHz, DMSO) δ 150.0, 147.7, 138.7, 124.1, 122.2, 115.9, 79.1, 66.0 (x2), 48.6 (x2). HRMS (ESI): m/z calcd for $C_{11}H_{13}N_3O$ $(M^+H)^+$: 204.1092; found: 204.1130.

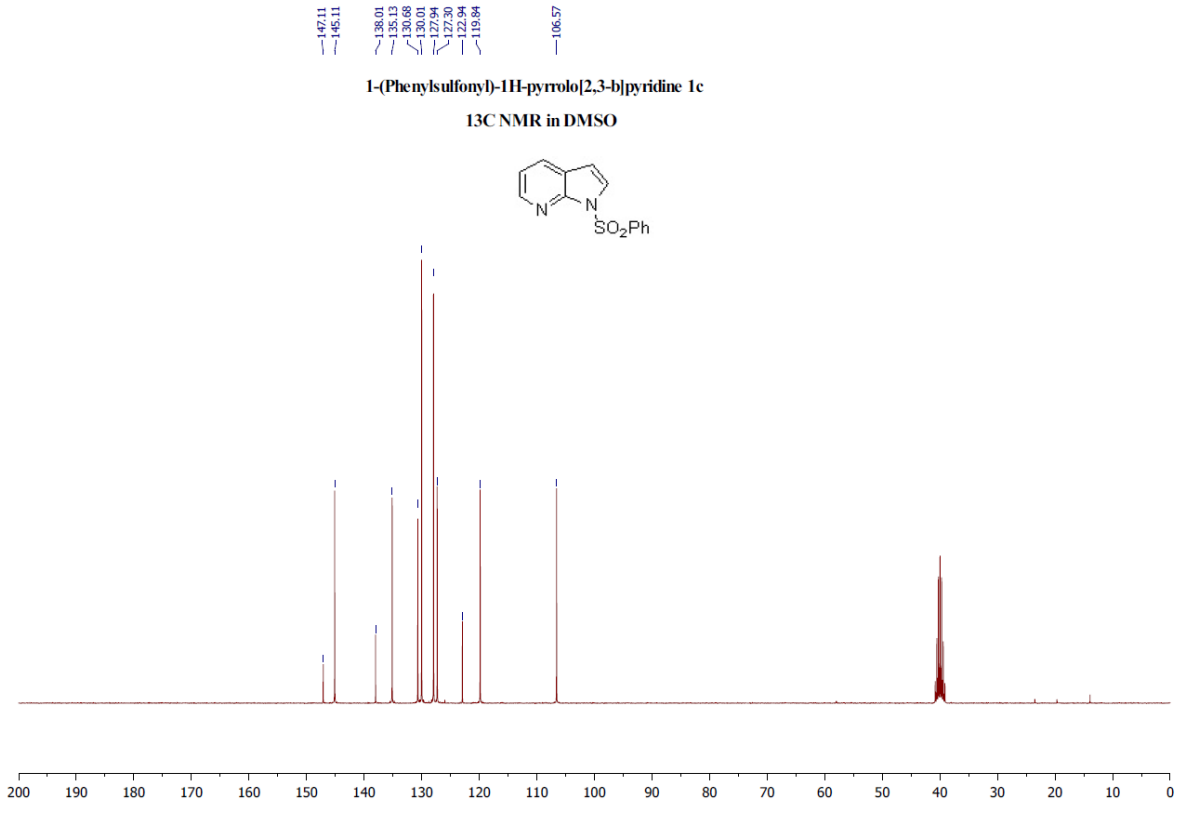
2-(Piperidin-1-yl)-1*H*-pyrrolo[2,3-*b*]pyridine 5i

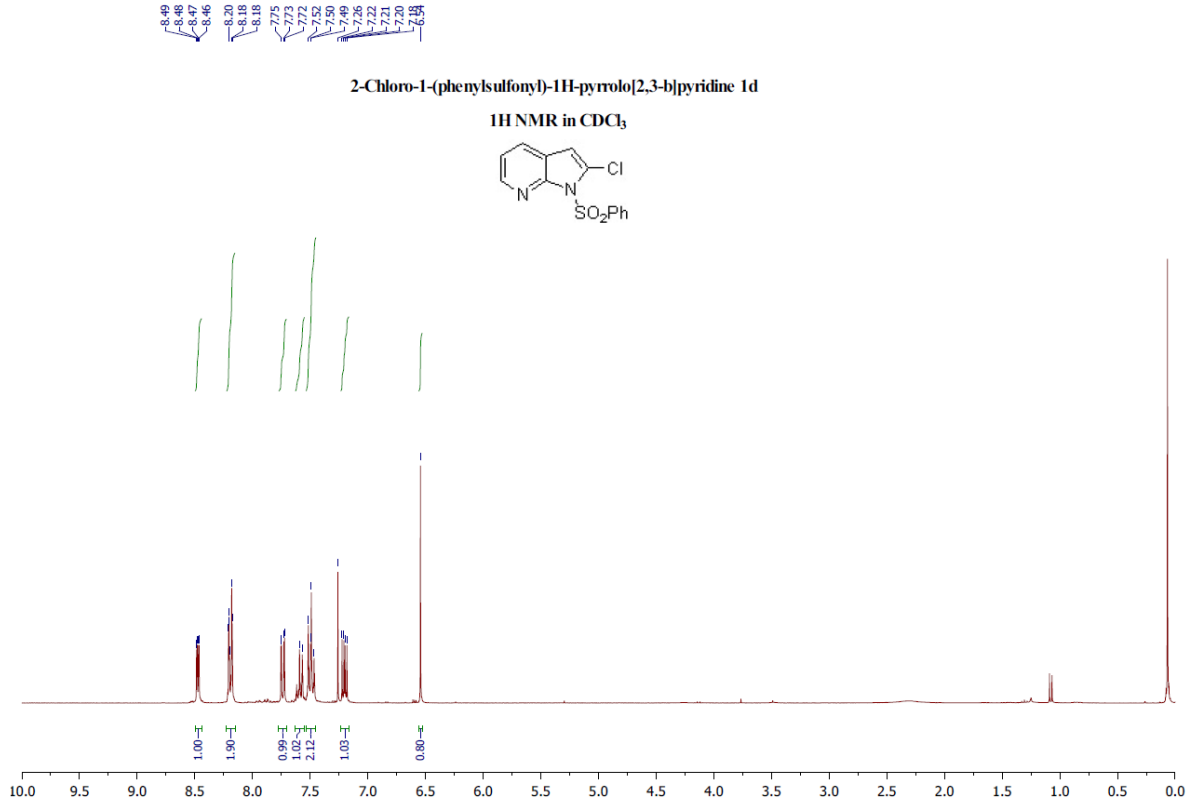


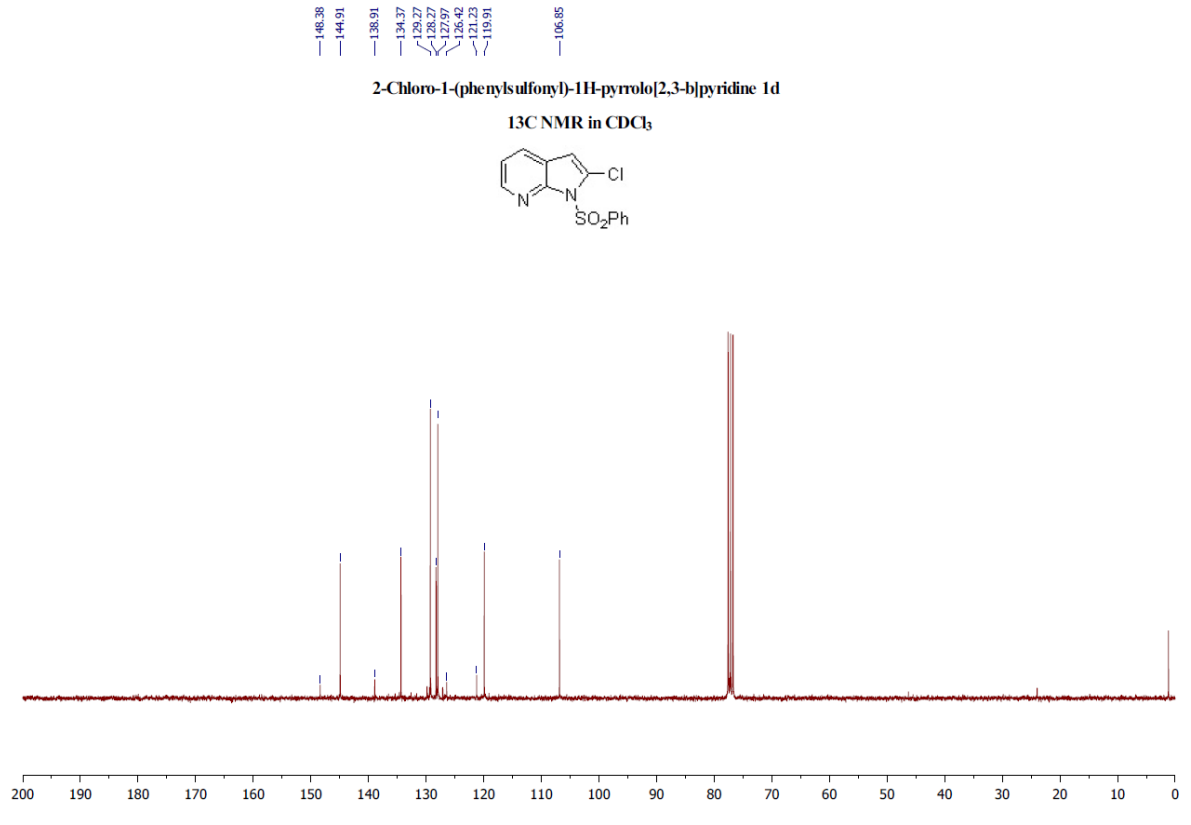
Following the general procedure B. The crude was purified by flash chromatography on silica gel (Cy/EtOAc: 3/7) to provide the desired compound **5i** (18 mg, 18%) as a dark brown solid.

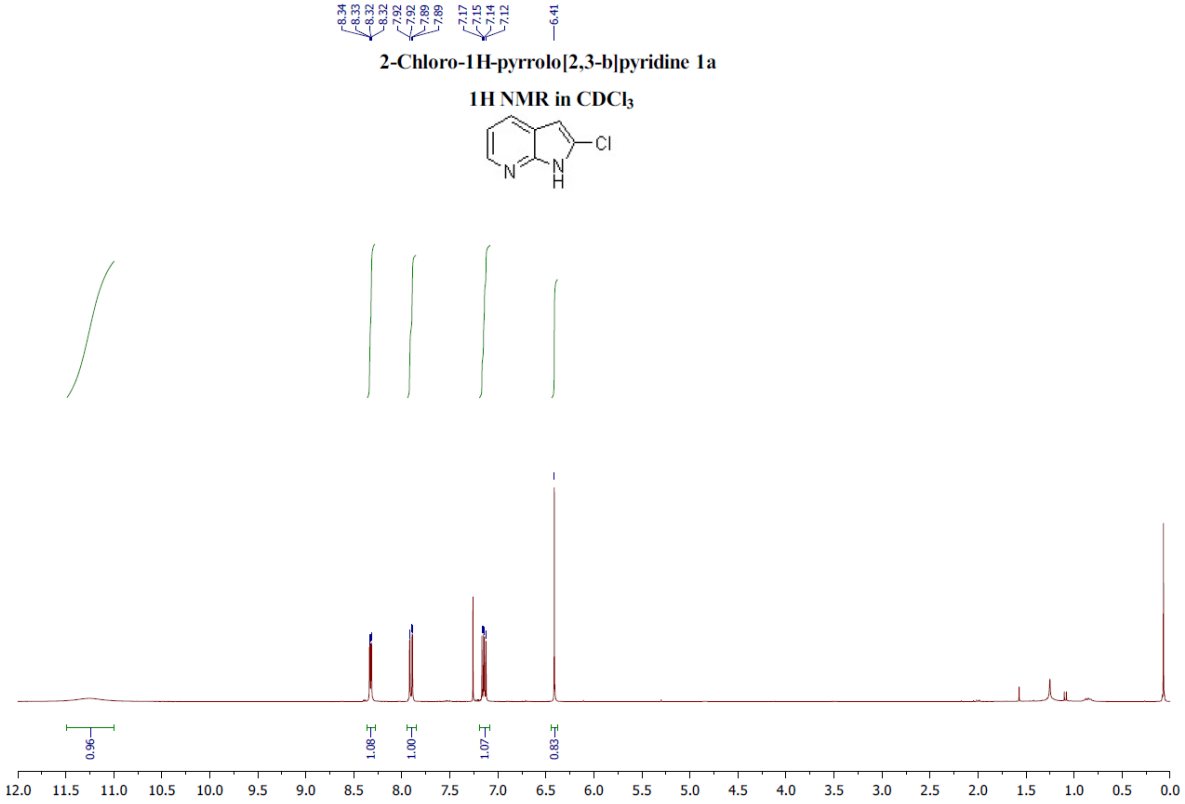
^{1}H NMR (300 MHz, DMSO) δ 11.16 (s, 1H), 7.82 (dd, *J* = 4.9, 1.5 Hz, 1H), 7.47 (dd, *J* = 7.6, 1.5 Hz, 1H), 6.84 (dd, *J* = 7.6, 4.9 Hz, 1H), 5.38 (d, *J* = 1.8 Hz, 1H), 3.24 – 3.09 (m, 3H), 1.71 – 1.47 (m, 6H). ^{13}C NMR (75 MHz, DMSO) δ 150.0, 147.2, 137.6, 123.0, 122.2, 115.3, 78.2, 48.8, 24.7, 23.8. HRMS (ESI): m/z calcd for $C_{12}H_{15}N_3$ $(M^+H)^+$: 202.1300; found: 202.1328.

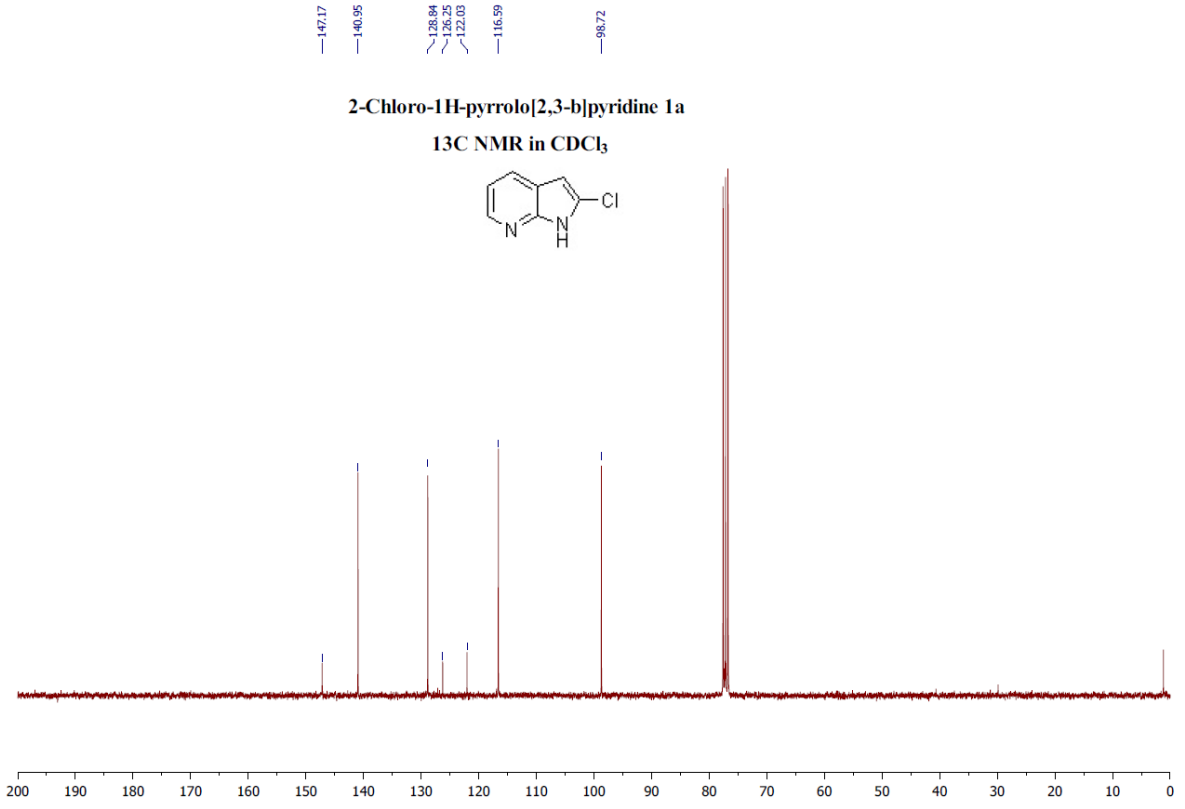

8.44
8.43
8.42
8.42
8.42
8.21
8.21
8.21
8.20
8.19
8.18
8.18
7.73
7.72
7.50
7.48
7.48
7.20
7.18
7.17
7.15
6.60
6.59
1-(Phenylsulfonyl)-1H-pyrrolo[2,3-b]pyridine 1c
1H NMR in CDCl3
N
N
SO2Ph
1.00
1.97
1.03
0.96
1.13
2.26
1.11
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

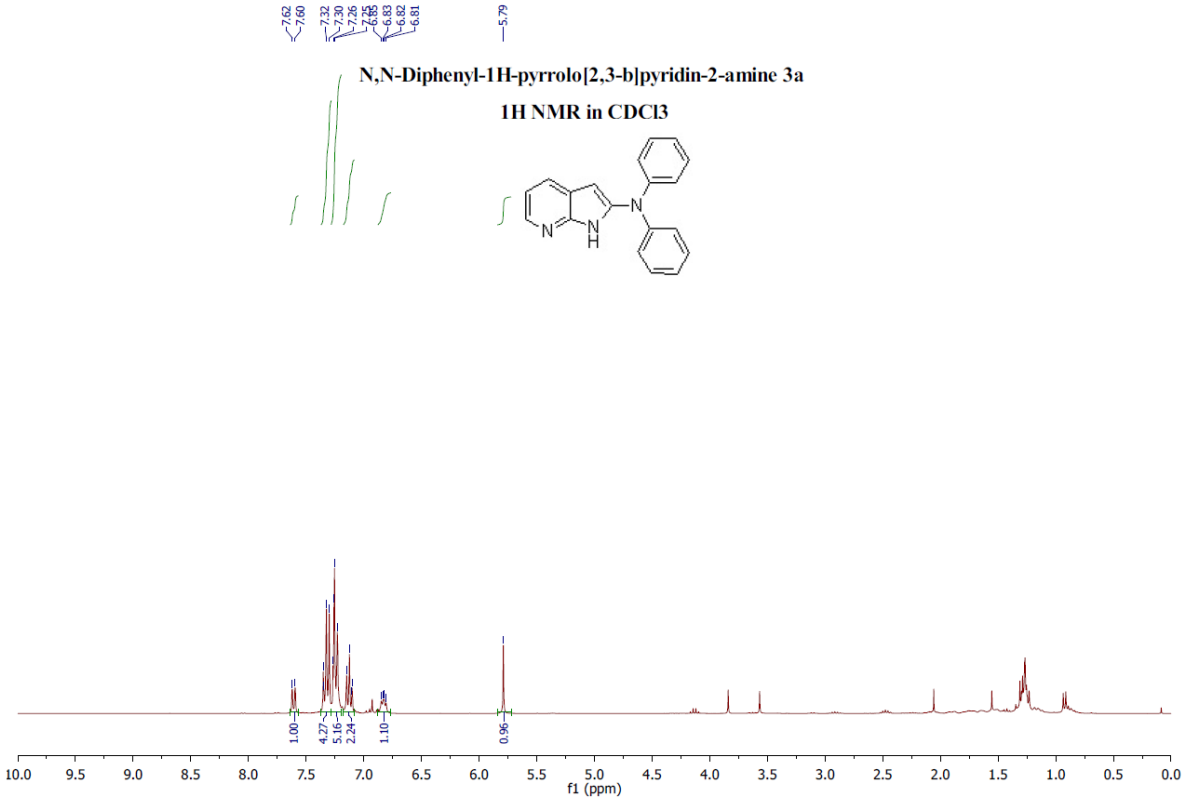

147.11
145.11
138.01
135.13
130.68
130.01
127.94
127.30
122.94
119.84
106.57
1-(Phenylsulfonyl)-1H-pyrrolo[2,3-b]pyridine 1c
13C NMR in DMSO
N
N
SO2Ph
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

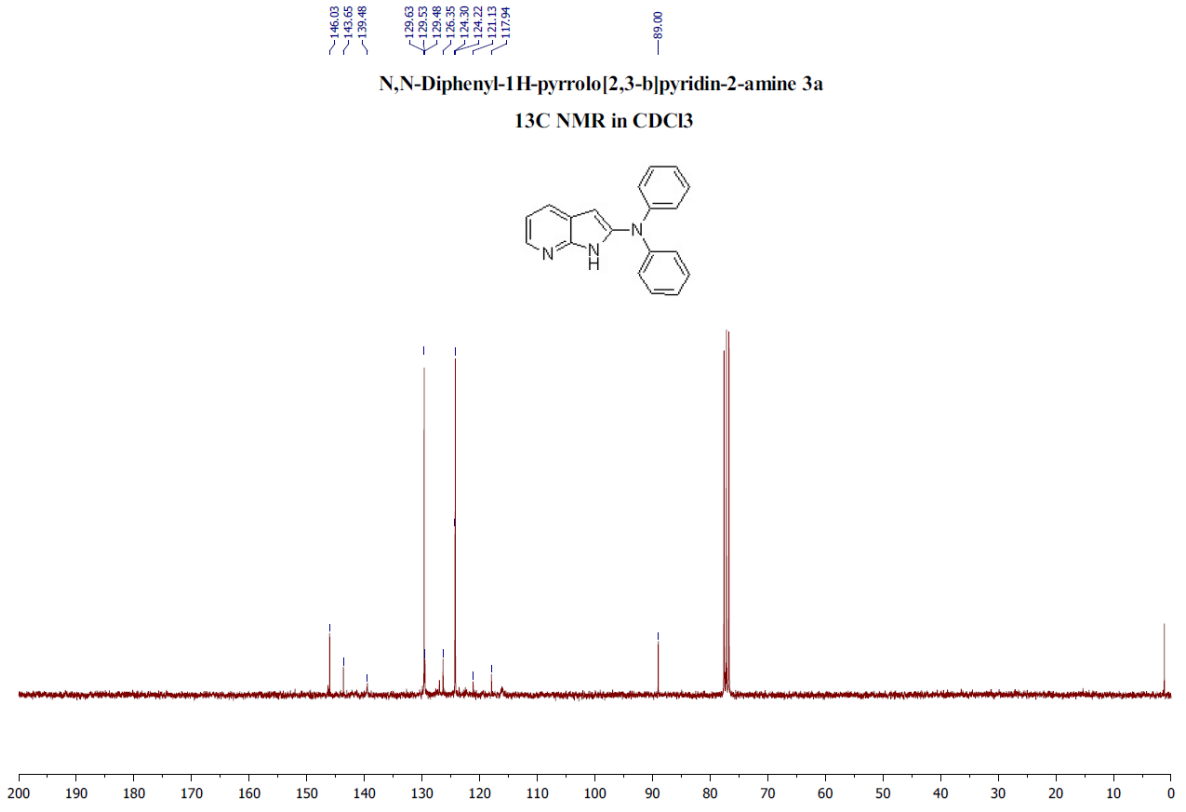

8.49
8.48
8.47
8.46
8.20
8.18
8.18
7.75
7.73
7.72
7.72
7.52
7.50
7.49
7.26
7.22
7.21
7.20
7.18
6.54
2-Chloro-1-(phenylsulfonyl)-1H-pyrrolo[2,3-b]pyridine 1d
1H NMR in CDCl3
Cl
N
N
SO2Ph
1.00
1.90
0.99
1.02
2.12
1.03
0.80
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

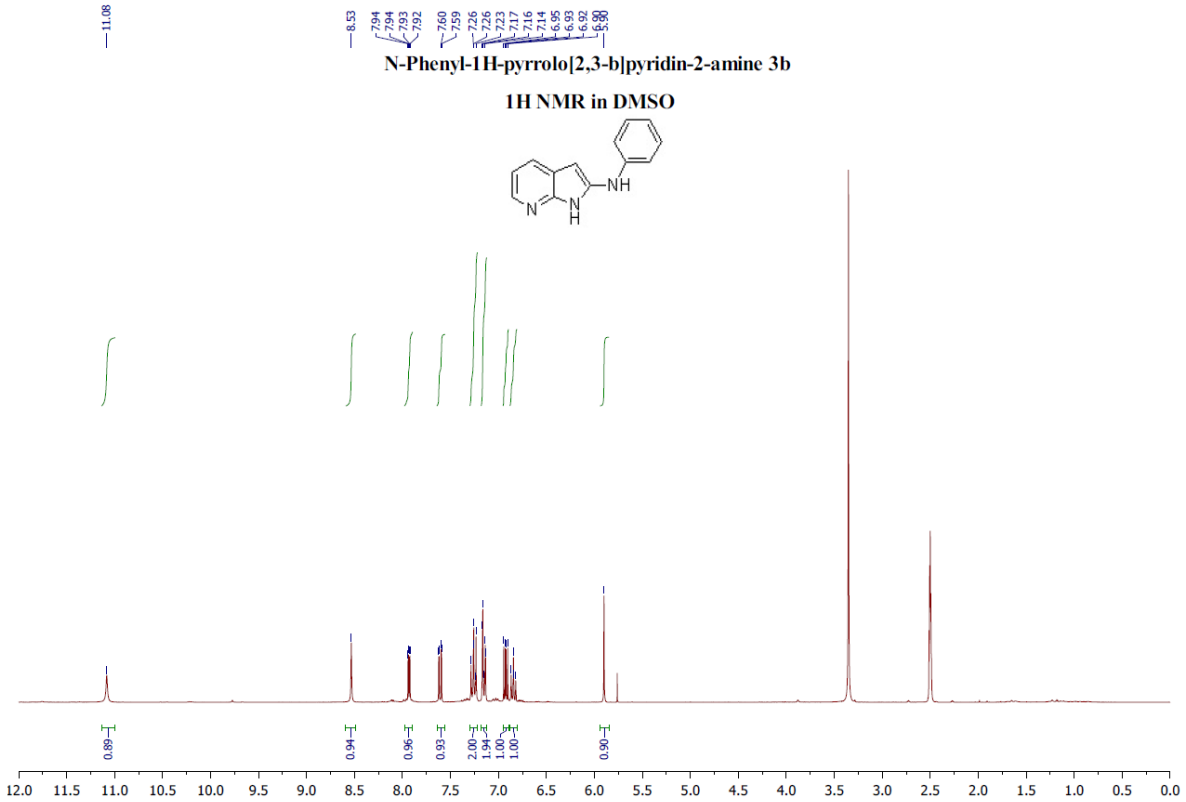

148.38
144.91
138.91
134.37
129.27
128.27
127.97
126.42
121.23
119.91
106.85
2-Chloro-1-(phenylsulfonyl)-1H-pyrrolo[2,3-b]pyridine 1d
13C NMR in CDCl3
Cl
N
N
SO2Ph
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

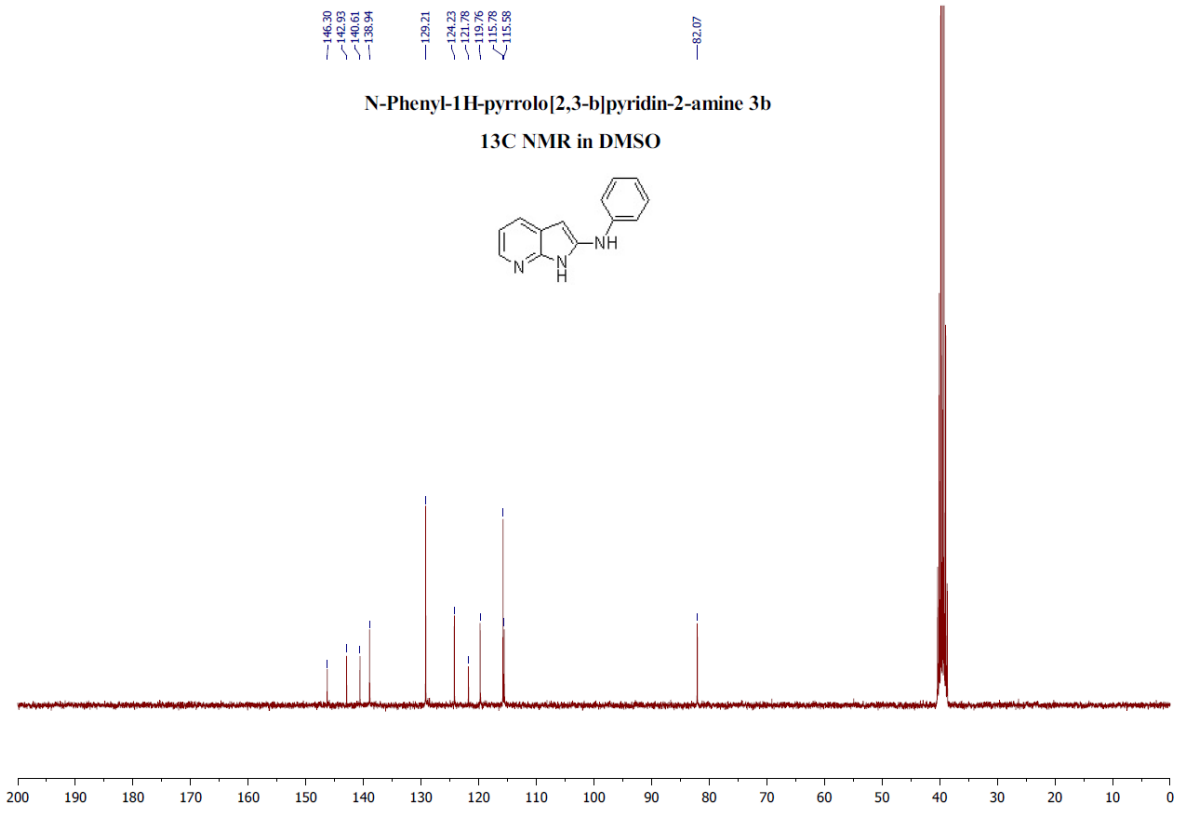

8.34
8.33
8.32
8.32
7.92
7.92
7.89
7.89
7.17
7.15
7.14
7.12
6.41
2-Chloro-1H-pyrrolo[2,3-b]pyridine 1a
1H NMR in CDCl3
Cl
N
H
0.96
1.08
1.00
1.07
0.83
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

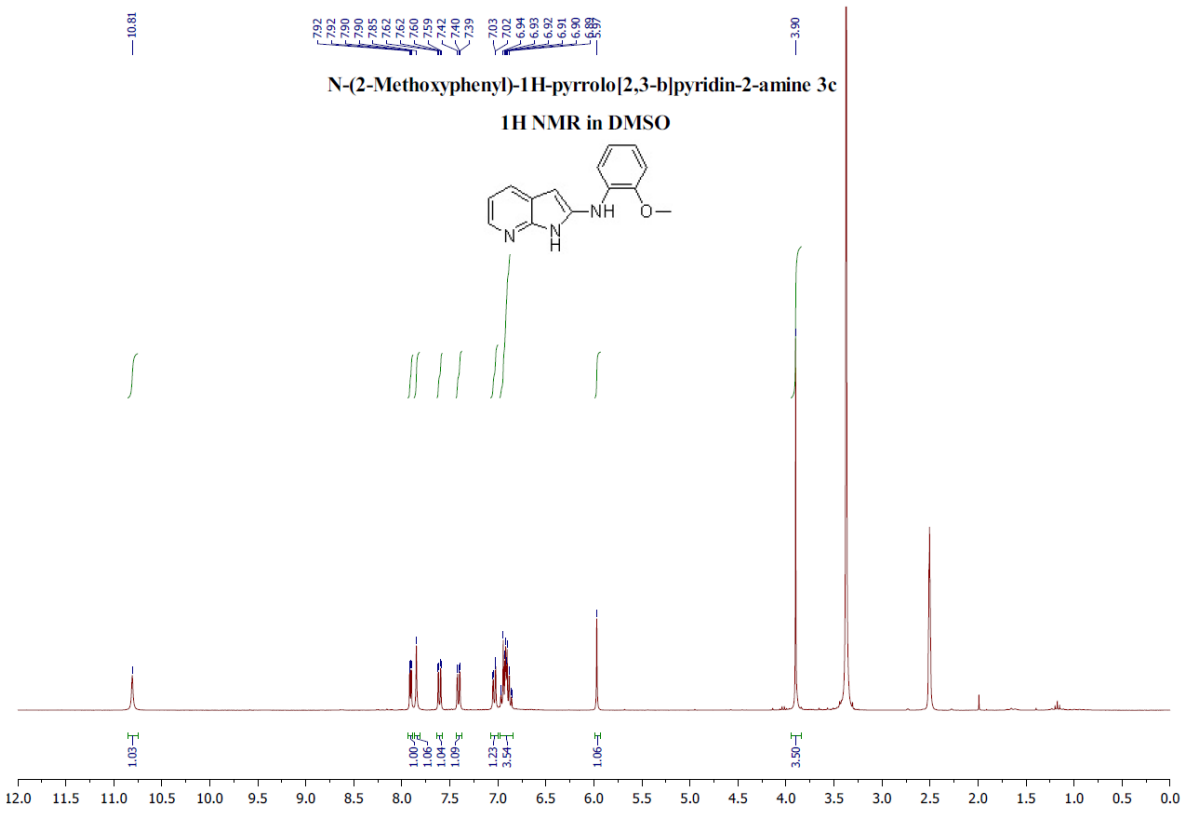

147.17
140.95
128.84
126.25
122.03
116.59
98.72
2-Chloro-1H-pyrrolo[2,3-b]pyridine 1a
13C NMR in CDCl3
Cl
N
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

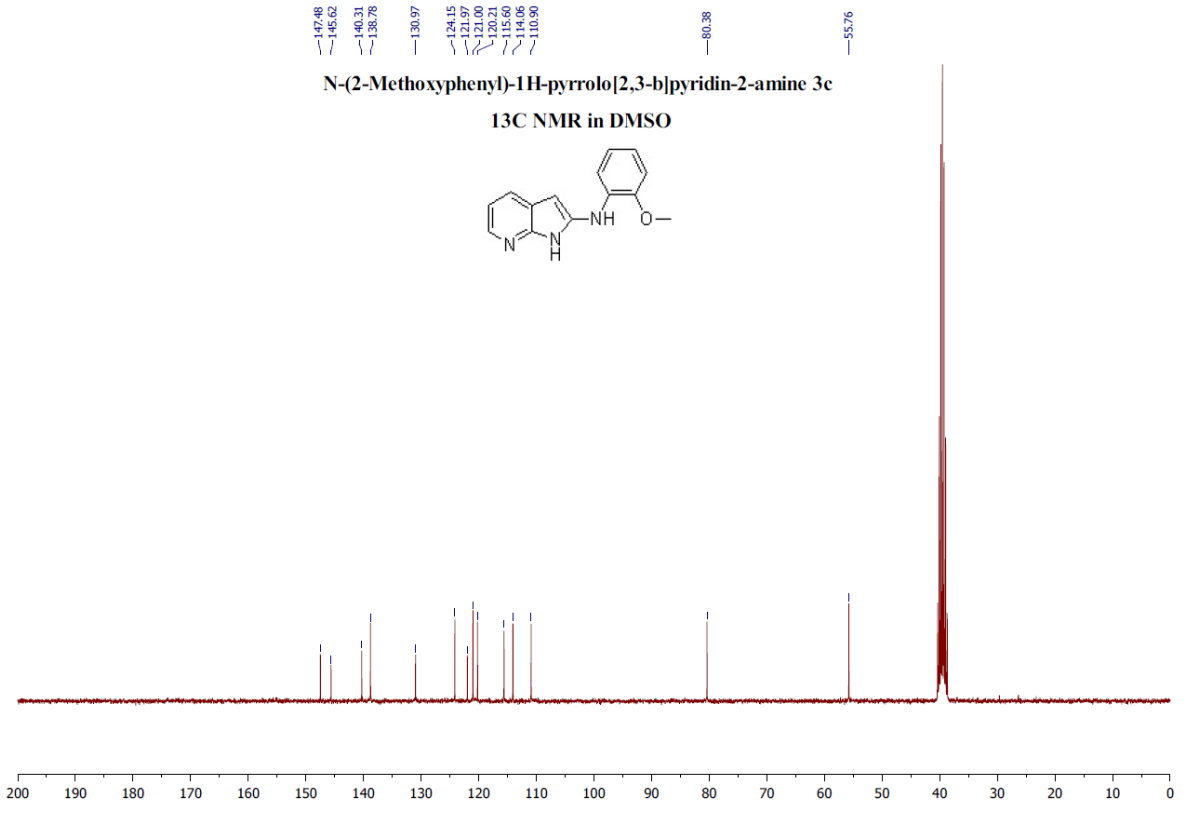

7.62
7.60
7.32
7.30
7.26
6.83
6.82
6.81
5.79
N,N-Diphenyl-1H-pyrrolo[2,3-b]pyridin-2-amine 3a
1H NMR in CDCl3
1.00
4.27
5.16
2.24
1.10
0.96
f1 (ppm)

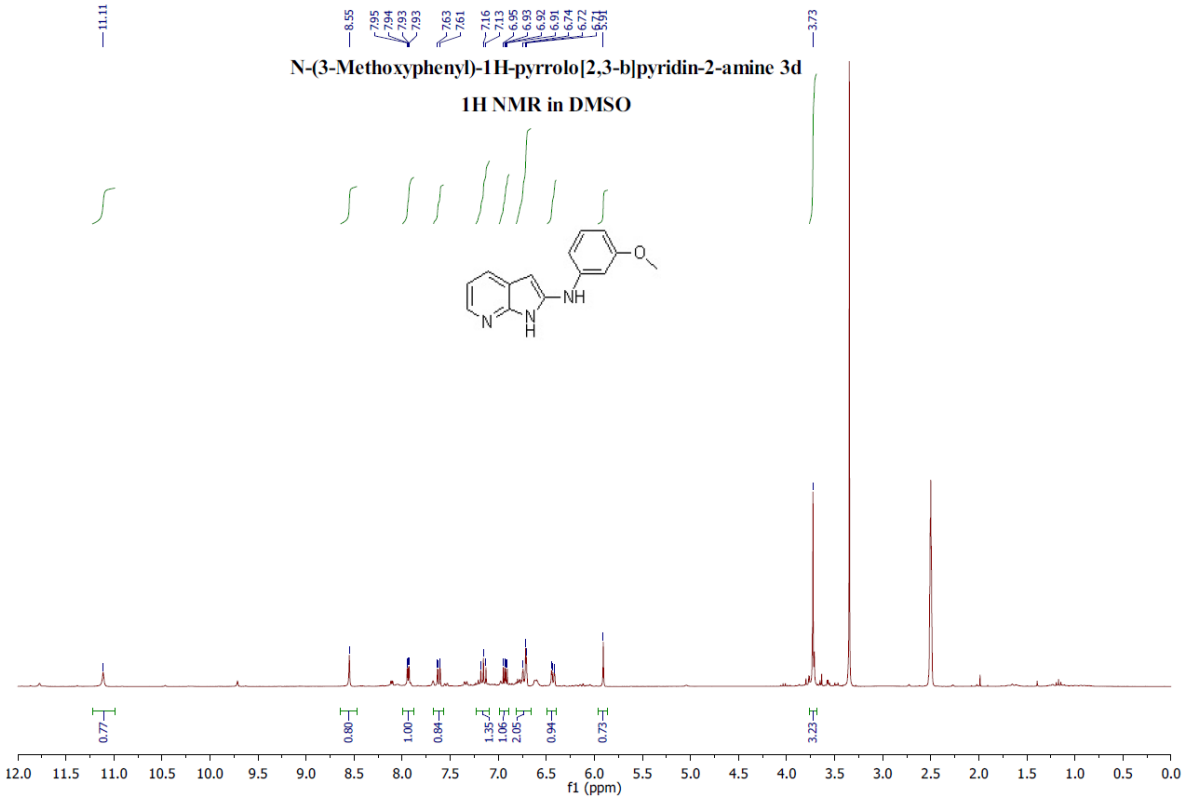

146.03
143.65
139.48
129.63
129.53
129.48
126.35
124.30
124.22
121.13
117.94
89.00
N,N-Diphenyl-1H-pyrrolo[2,3-b]pyridin-2-amine 3a
13C NMR in CDCl3

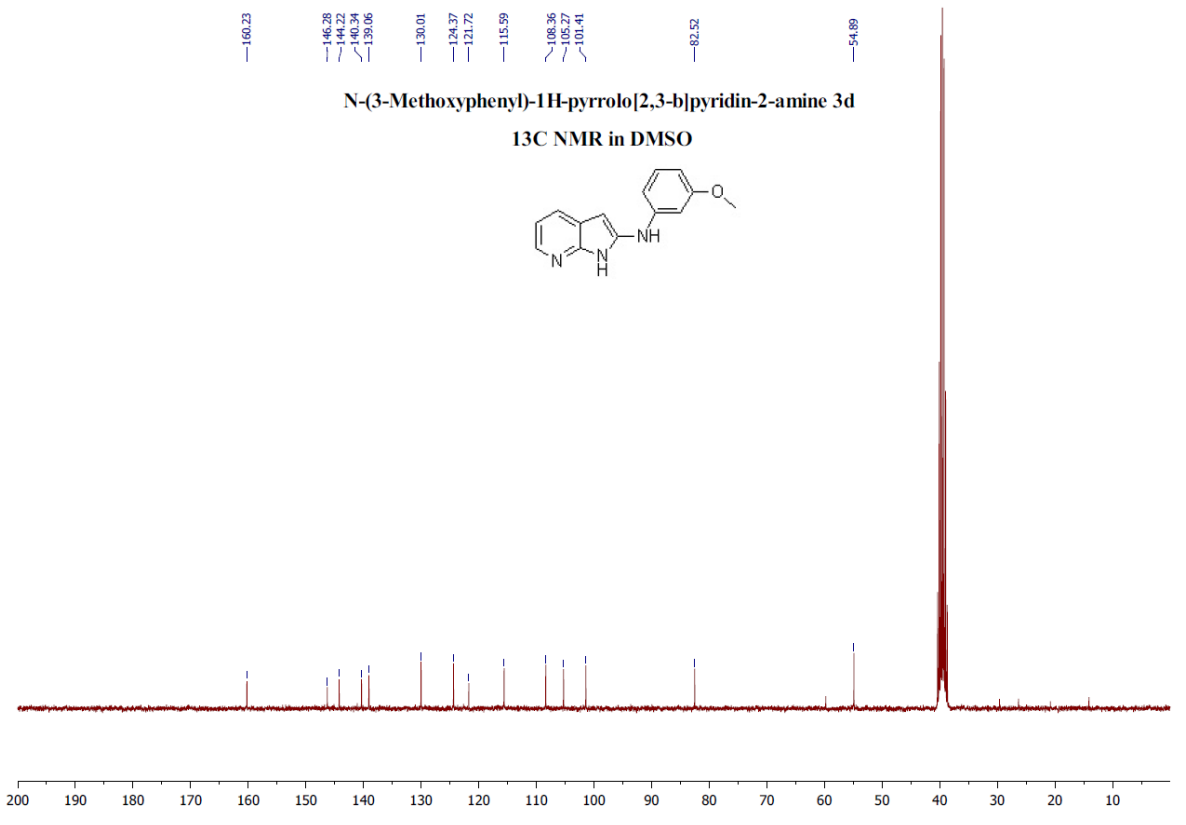

11.08
8.53
7.94
7.94
7.93
7.92
7.60
7.59
7.26
7.26
7.23
7.17
7.16
7.14
6.95
6.93
6.92
5.90
5.88
N-Phenyl-1H-pyrrolo[2,3-b]pyridin-2-amine 3b
1H NMR in DMSO
NH
N
H
0.89
0.94
0.96
0.93
2.00
1.94
1.00
1.00
0.90
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

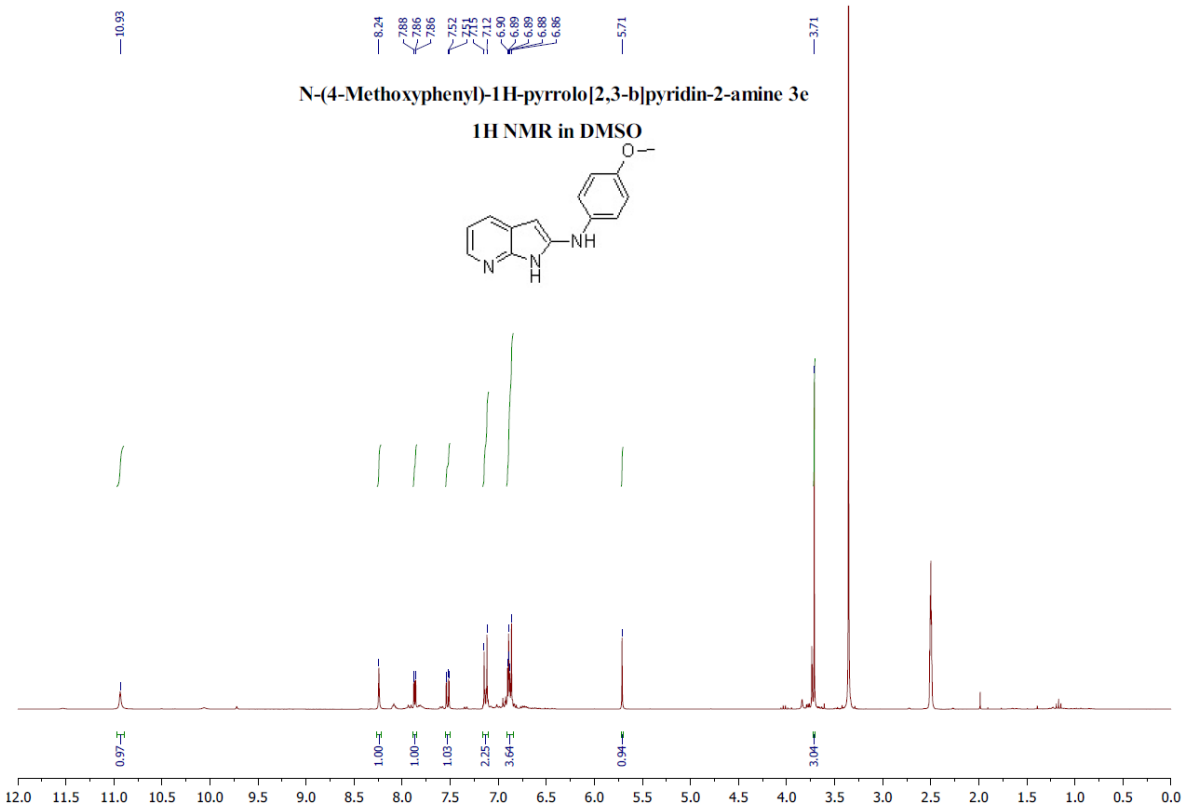

146.30
142.93
140.61
138.94
129.21
124.23
121.78
119.76
115.78
115.58
82.07
N-Phenyl-1H-pyrrolo[2,3-b]pyridin-2-amine 3b
13C NMR in DMSO
NH
N
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

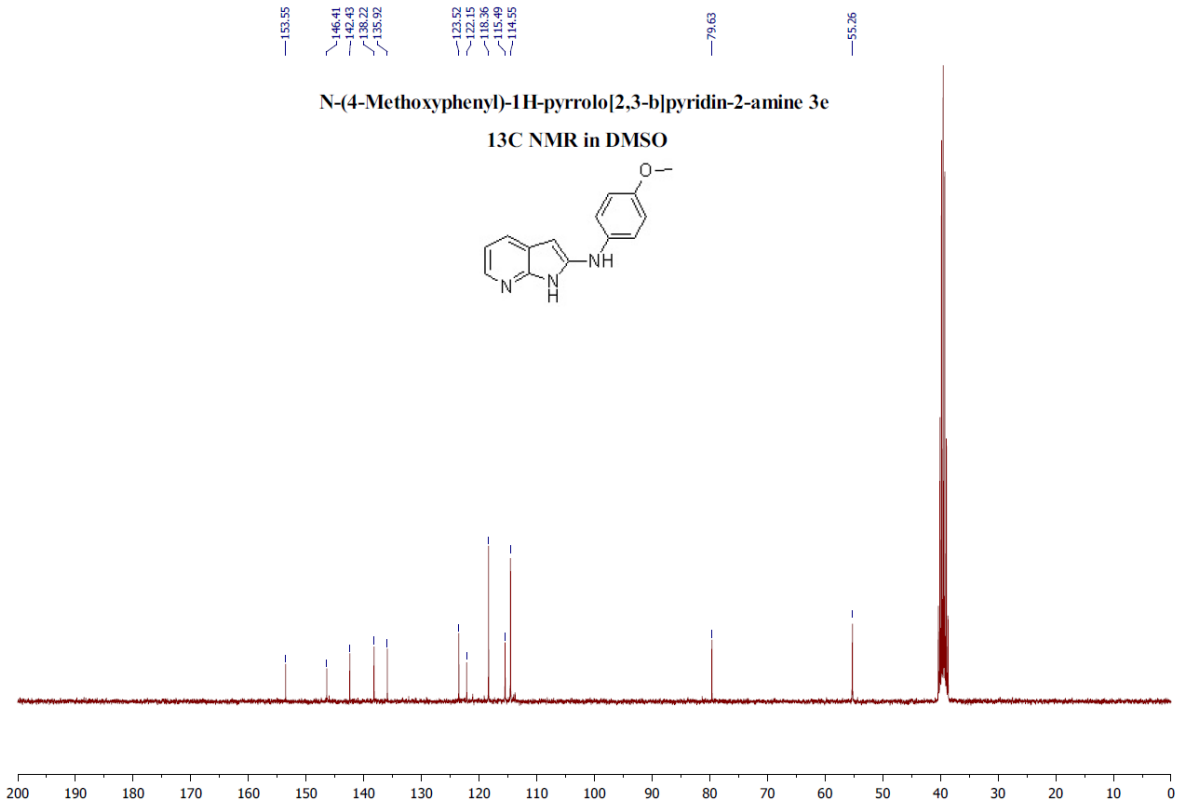

10.81
7.92
7.92
7.90
7.90
7.85
7.62
7.62
7.60
7.59
7.42
7.40
7.39
7.03
7.02
6.94
6.93
6.92
6.91
6.90
6.89
5.97
3.90
N-(2-Methoxyphenyl)-1H-pyrrolo[2,3-b]pyridin-2-amine 3c
1H NMR in DMSO
NH
O
N
H
1.03
1.00
1.06
1.04
1.09
1.23
3.54
1.06
3.50
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

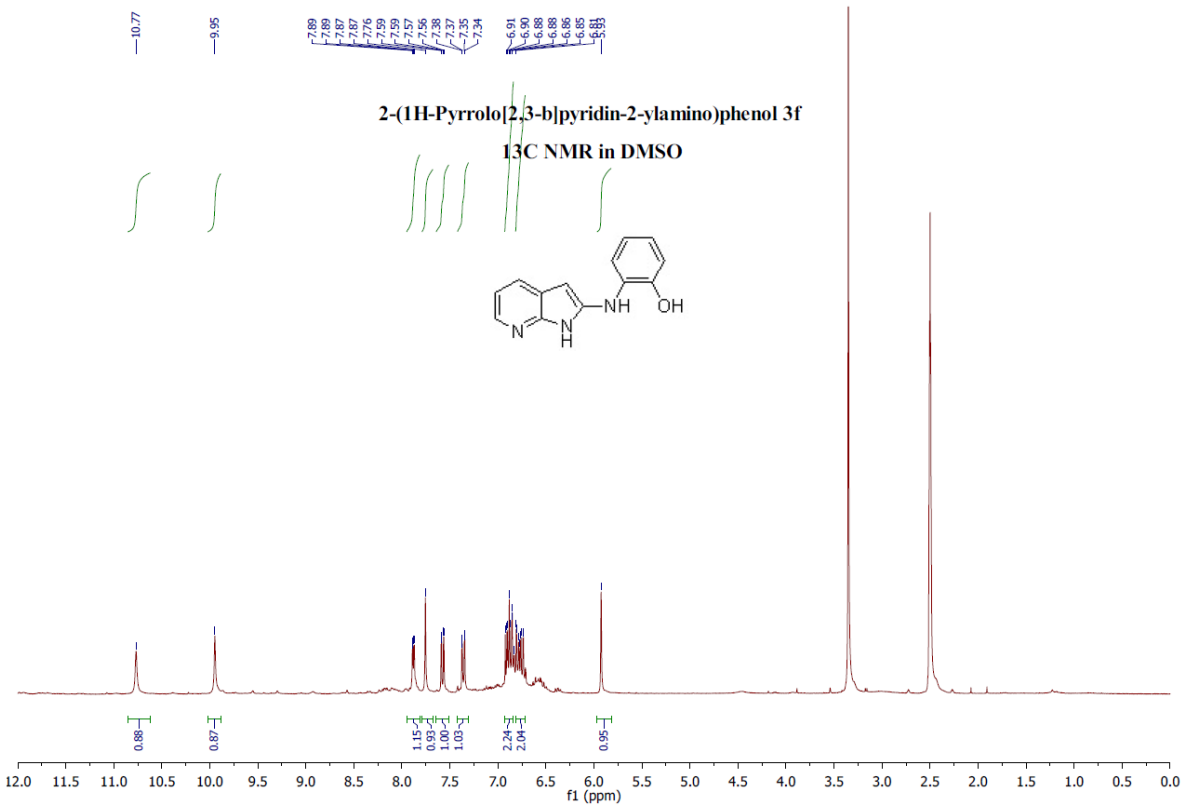

147.48
145.62
140.31
138.78
130.97
124.15
121.97
121.00
120.21
115.60
114.06
110.90
80.38
55.76
N-(2-Methoxyphenyl)-1H-pyrrolo[2,3-b]pyridin-2-amine 3c
13C NMR in DMSO
NH
O
N
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

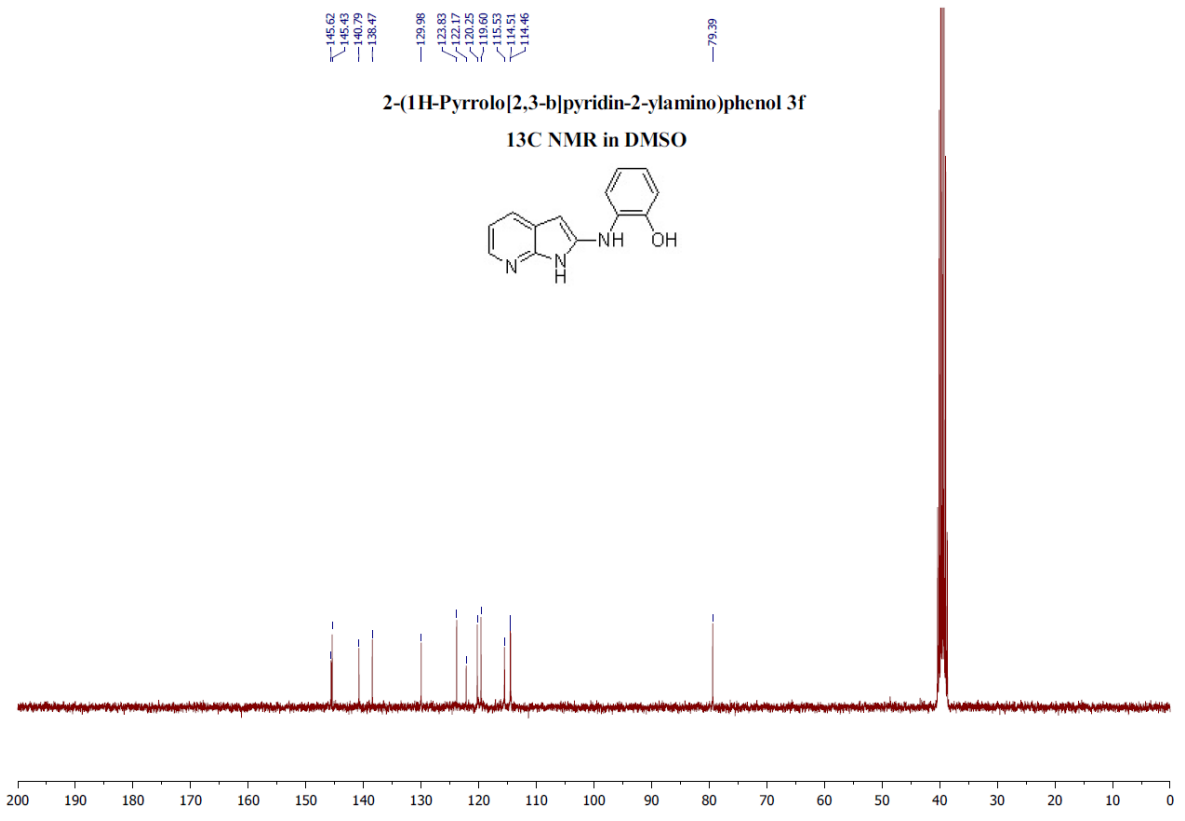

11.11
8.55
7.95
7.94
7.93
7.93
7.63
7.61
7.16
7.13
6.95
6.93
6.92
6.91
6.74
6.72
6.71
5.91
3.73
N-(3-Methoxyphenyl)-1H-pyrrolo[2,3-b]pyridin-2-amine 3d
1H NMR in DMSO
NH
N
H
O
0.77
0.80
1.00
0.84
1.35
1.06
2.05
0.94
0.73
3.23
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

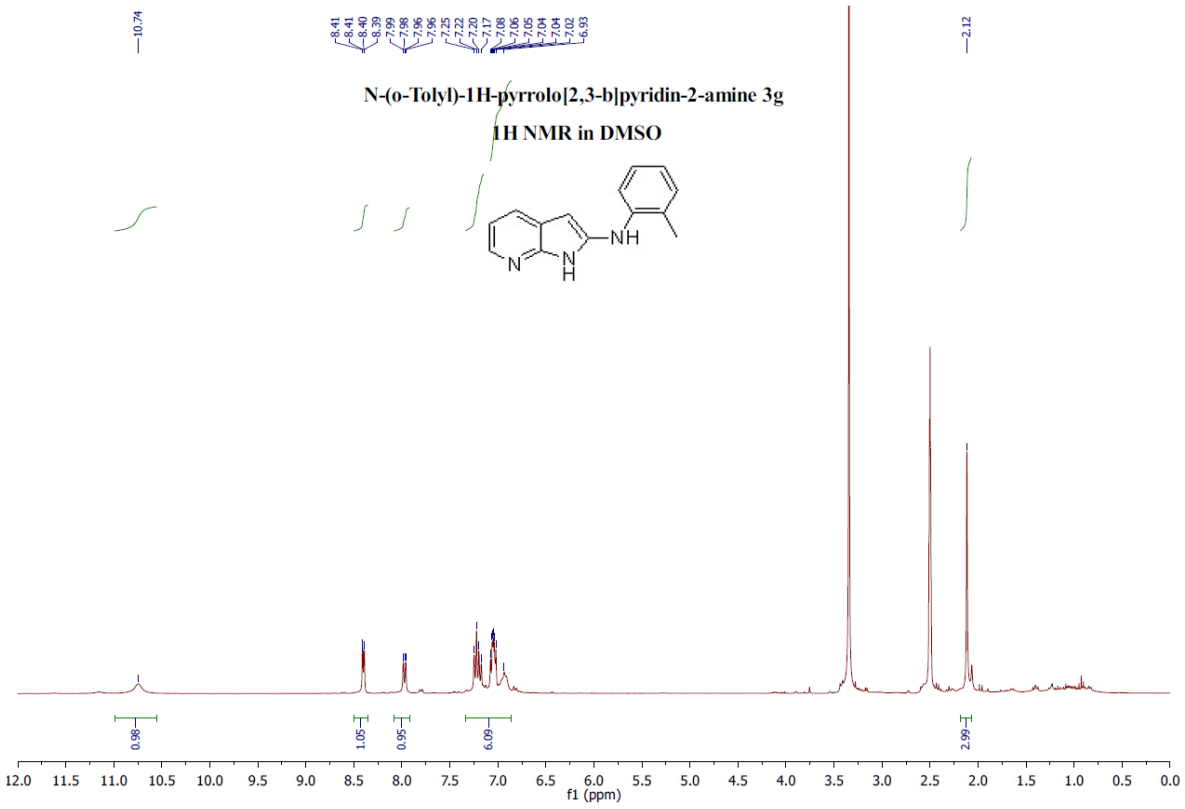

160.23
146.28
144.22
140.34
139.06
130.01
124.37
121.72
115.59
108.36
105.27
101.41
82.52
54.89
N-(3-Methoxyphenyl)-1H-pyrrolo[2,3-b]pyridin-2-amine 3d
13C NMR in DMSO
NH
N
H
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

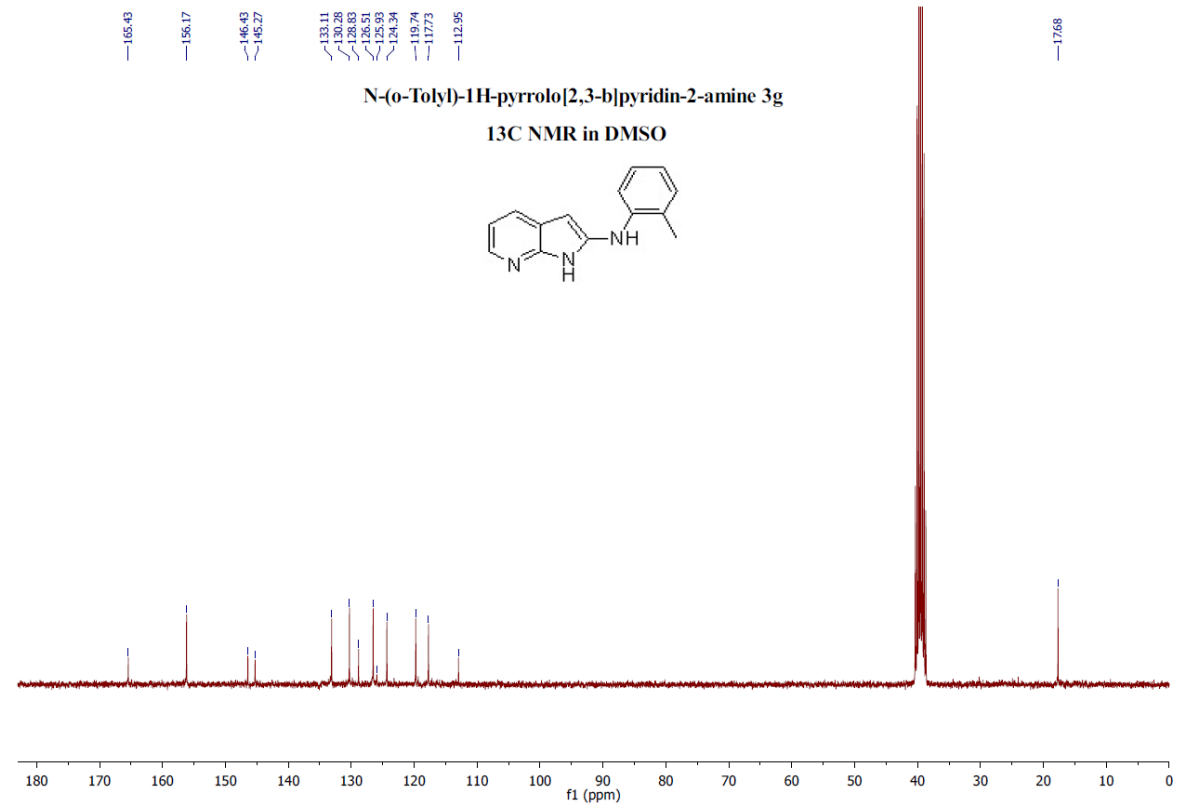

10.93
8.24
7.88
7.86
7.86
7.52
7.51
7.15
7.12
6.90
6.89
6.89
6.88
6.86
5.71
3.71
N-(4-Methoxyphenyl)-1H-pyrrolo[2,3-b]pyridin-2-amine 3e
1H NMR in DMSO
O
NH
N
H
0.97
1.00
1.00
1.03
2.25
3.64
0.94
3.04
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

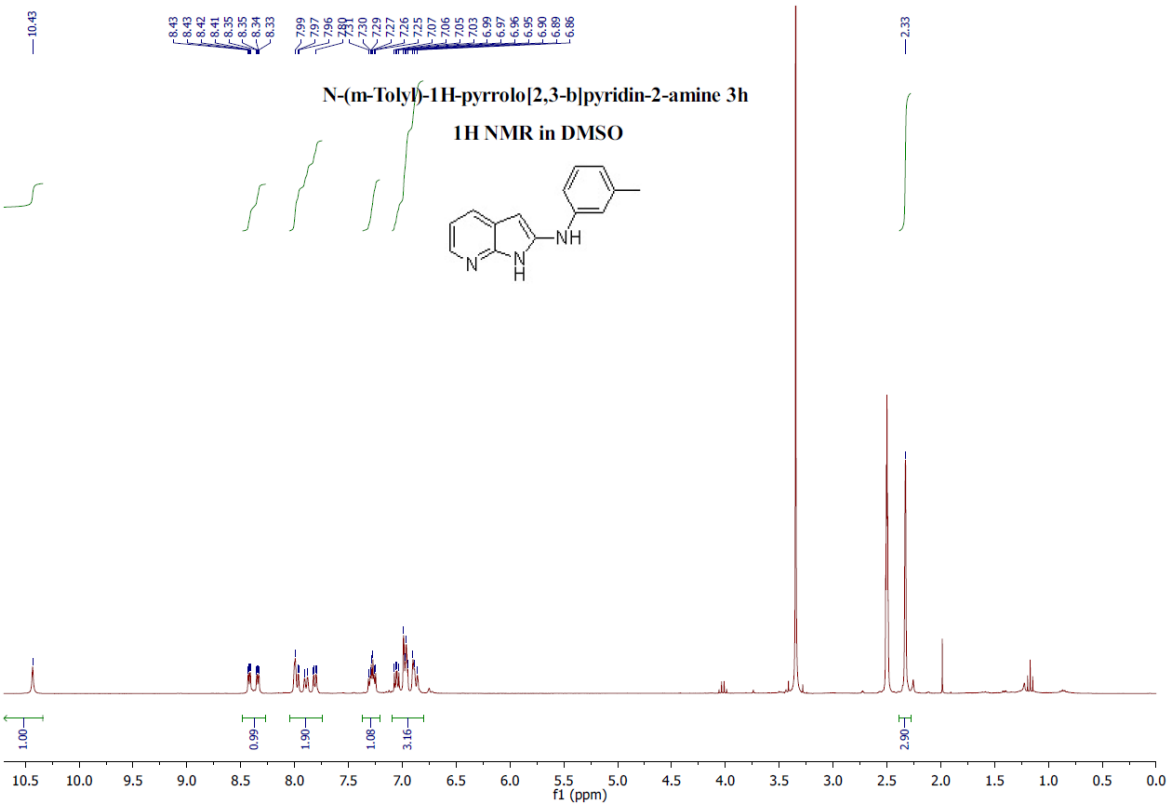

153.55
146.41
142.43
138.22
135.92
123.52
122.15
118.36
115.49
114.55
79.63
55.26
N-(4-Methoxyphenyl)-1H-pyrrolo[2,3-b]pyridin-2-amine 3e
13C NMR in DMSO
O
NH
N
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

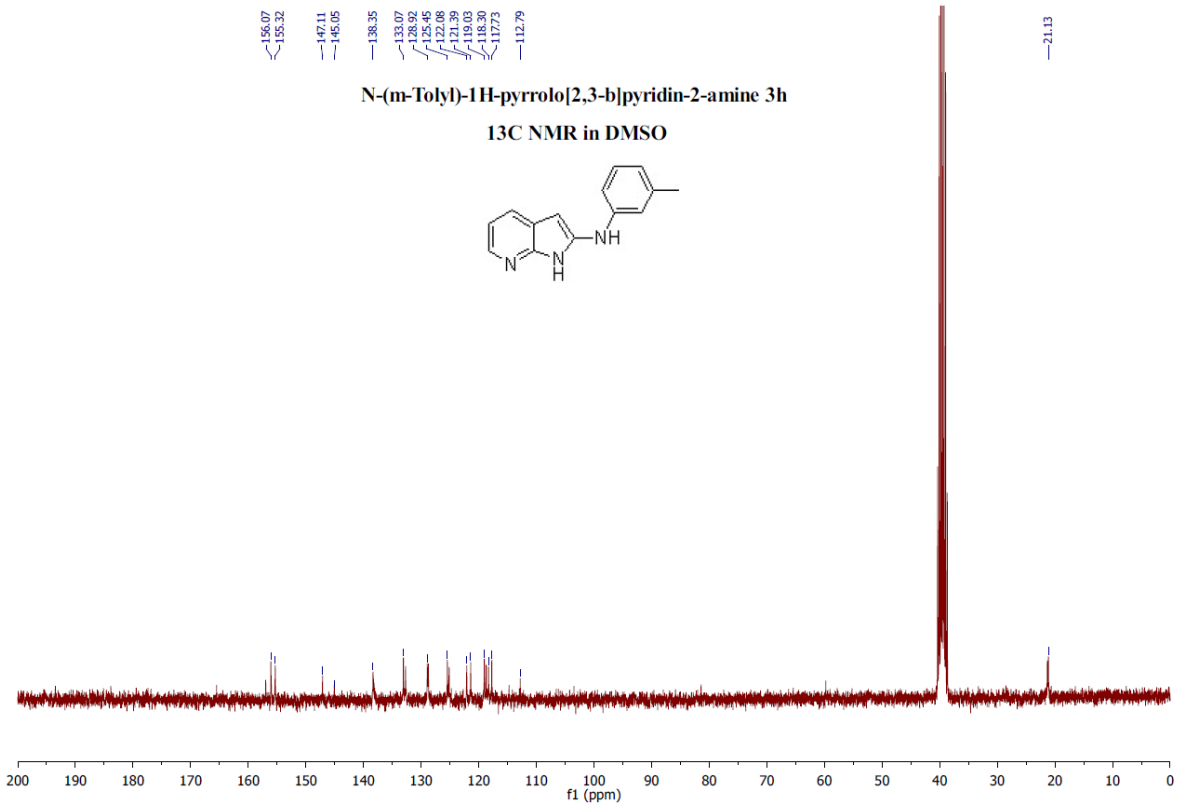

10.77
9.95
7.89
7.89
7.87
7.87
7.76
7.59
7.59
7.57
7.56
7.38
7.37
7.35
7.34
6.91
6.90
6.88
6.88
6.86
6.85
6.81
5.93
2-(1H-Pyrrolo[2,3-b]pyridin-2-ylamino)phenol 3f
13C NMR in DMSO
NH
OH
N
H
0.88
0.87
1.15
0.93
1.00
1.03
2.24
2.04
0.95
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

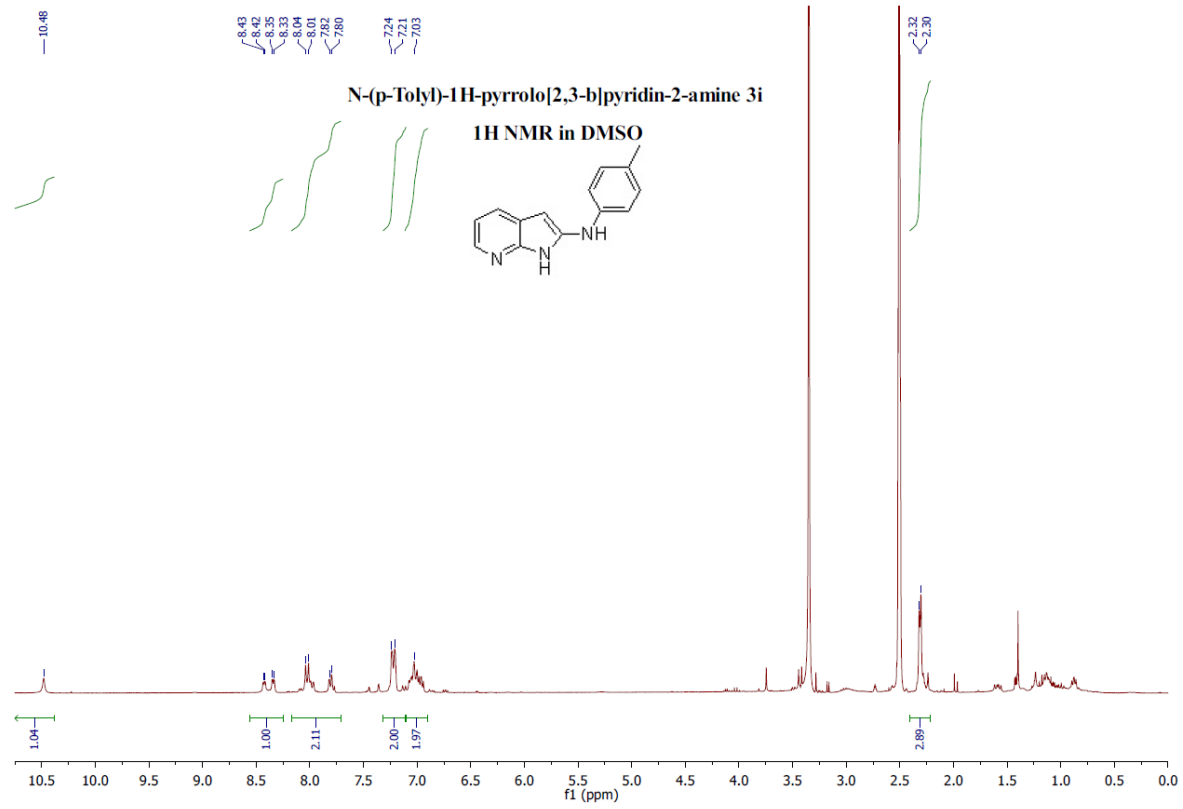

145.62
145.43
140.79
138.47
129.98
123.83
122.17
120.25
119.60
115.53
114.51
114.46
79.39
2-(1H-Pyrrolo[2,3-b]pyridin-2-ylamino)phenol 3f
13C NMR in DMSO
NH
OH
N
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

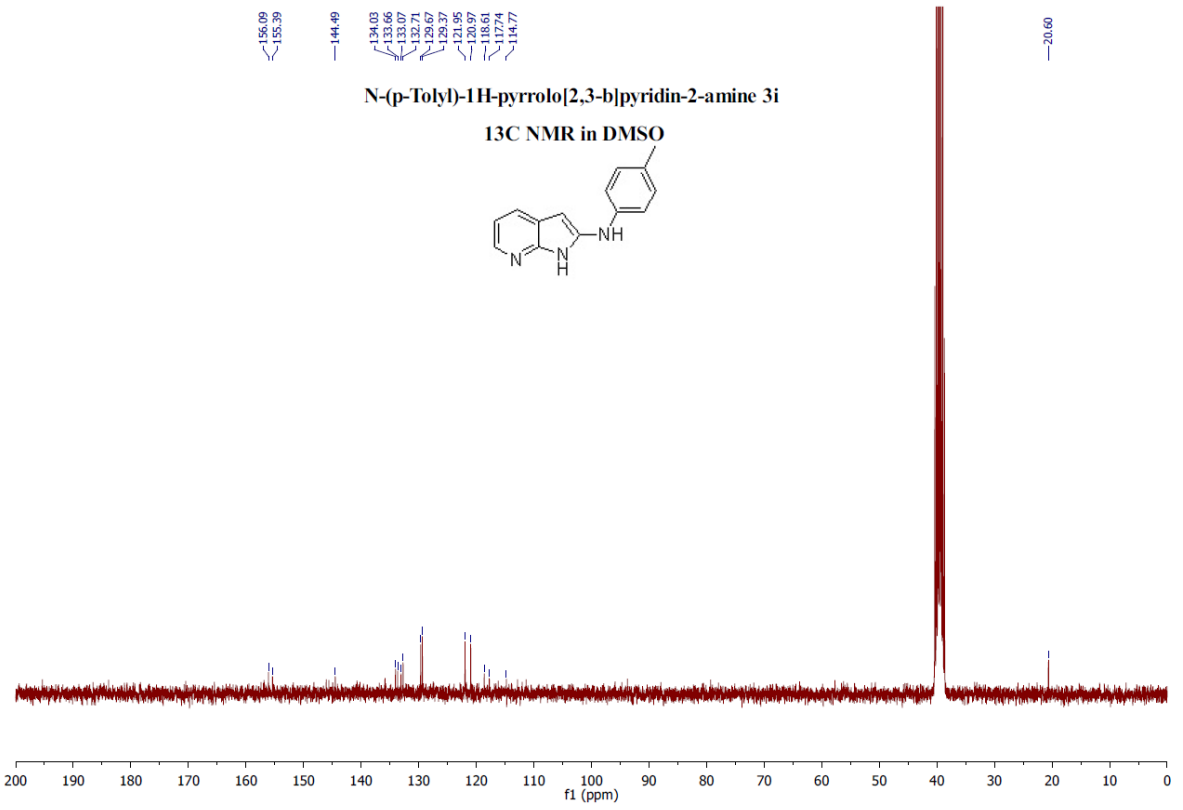

10.74
8.41
8.41
8.40
8.39
7.99
7.98
7.96
7.96
7.25
7.22
7.20
7.17
7.08
7.06
7.05
7.04
7.04
7.02
6.93
2.12
N-(o-Tolyl)-1H-pyrrolo[2,3-b]pyridin-2-amine 3g
1H NMR in DMSO
NH
N
H
0.98
1.05
0.95
6.09
2.99
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

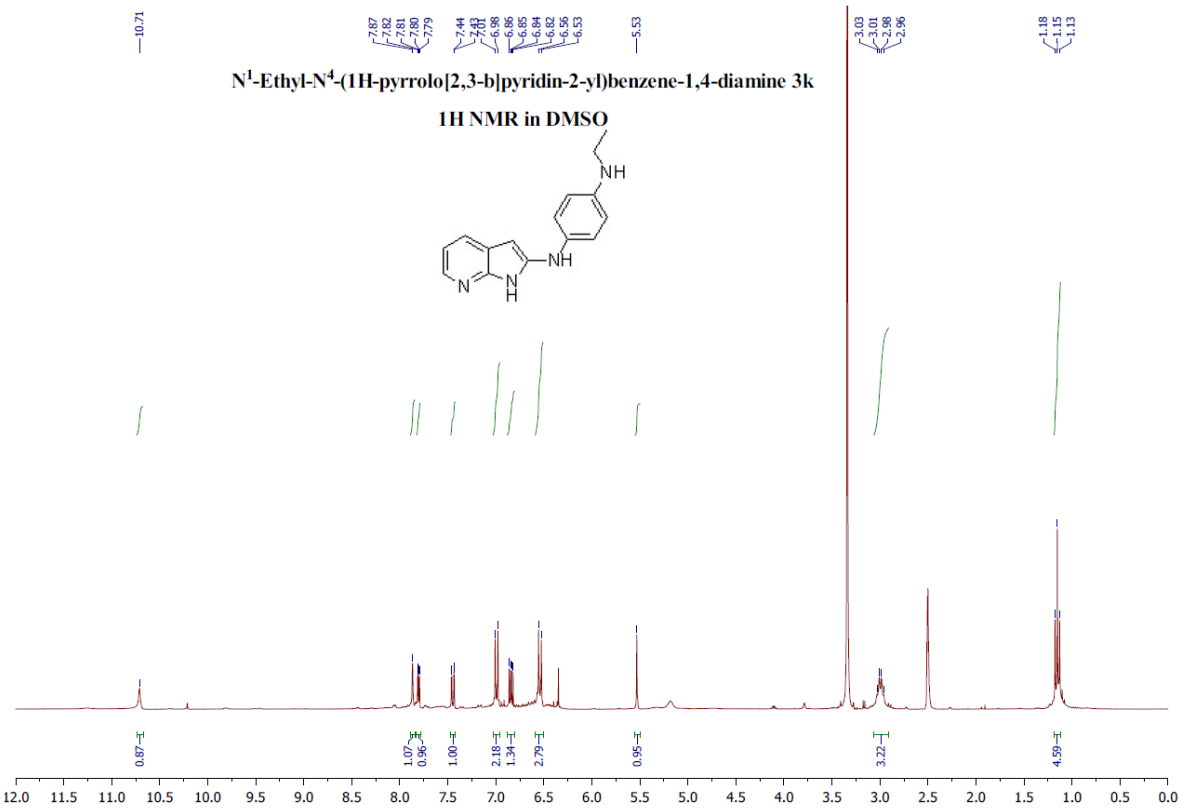

165.43
156.17
146.43
145.27
133.11
130.28
128.83
126.51
125.93
124.34
119.74
117.73
112.95
17.68
N-(o-Tolyl)-1H-pyrrolo[2,3-b]pyridin-2-amine 3g
13C NMR in DMSO
NH
N
H
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

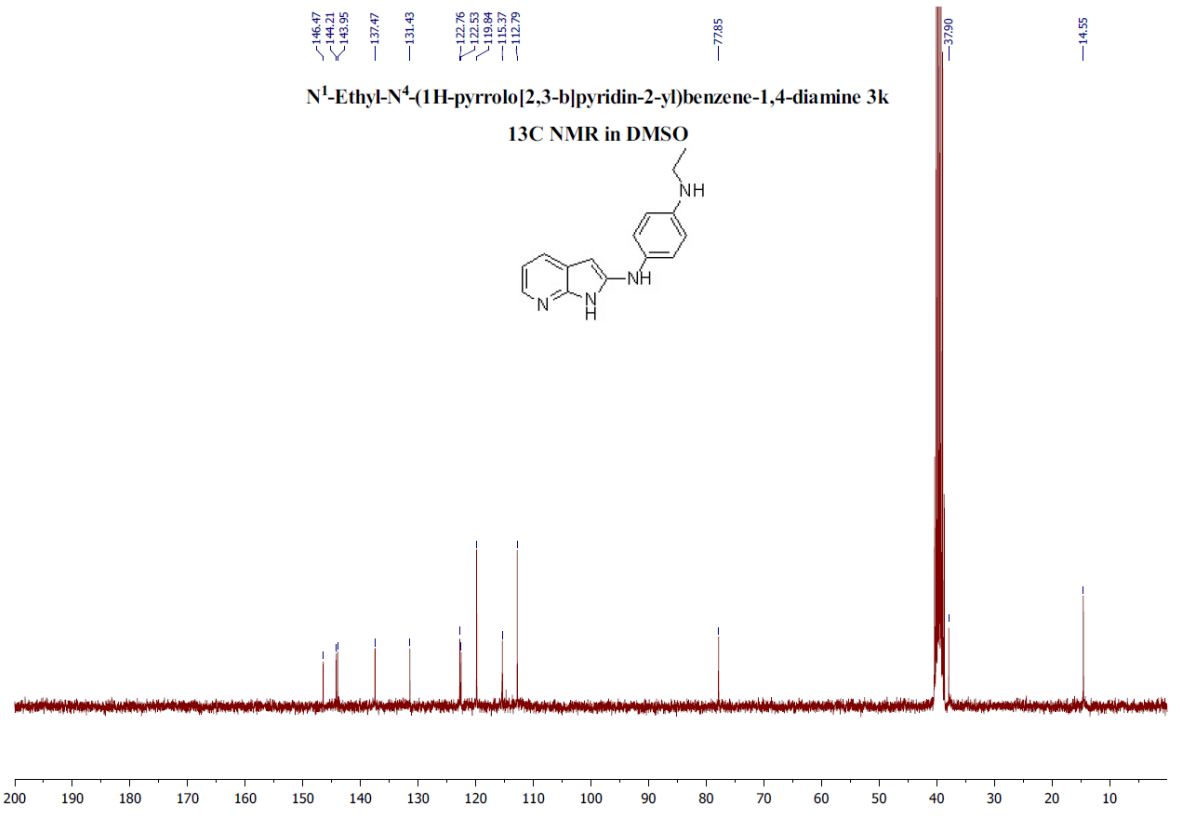

N-(m-Tolyl)-1H-pyrrolo[2,3-b]pyridin-2-amine 3h
1H NMR in DMSO
NH
N
H
f1 (ppm)

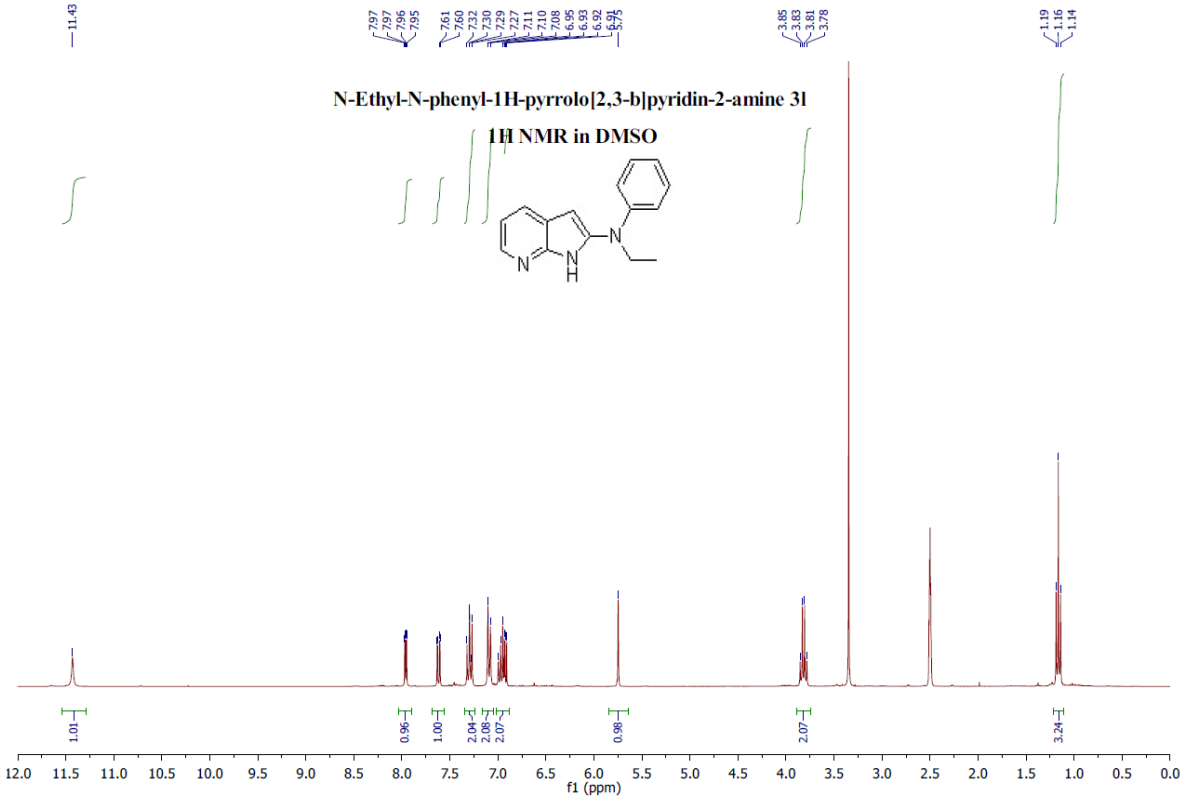

N-(m-Tolyl)-1H-pyrrolo[2,3-b]pyridin-2-amine 3h
13C NMR in DMSO
NH
N
H
f1 (ppm)

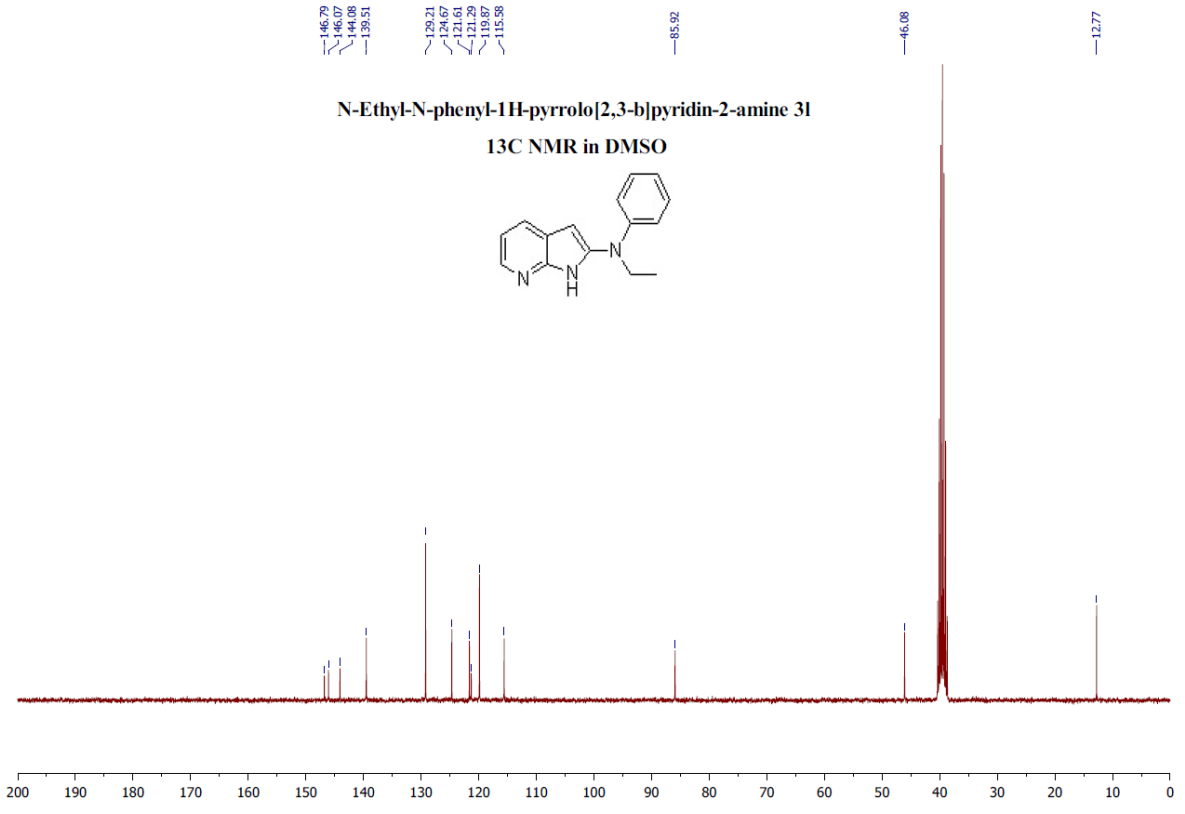

N-(p-Tolyl)-1H-pyrrolo[2,3-b]pyridin-2-amine 3i
1H NMR in DMSO
NH
N
H
f1 (ppm)

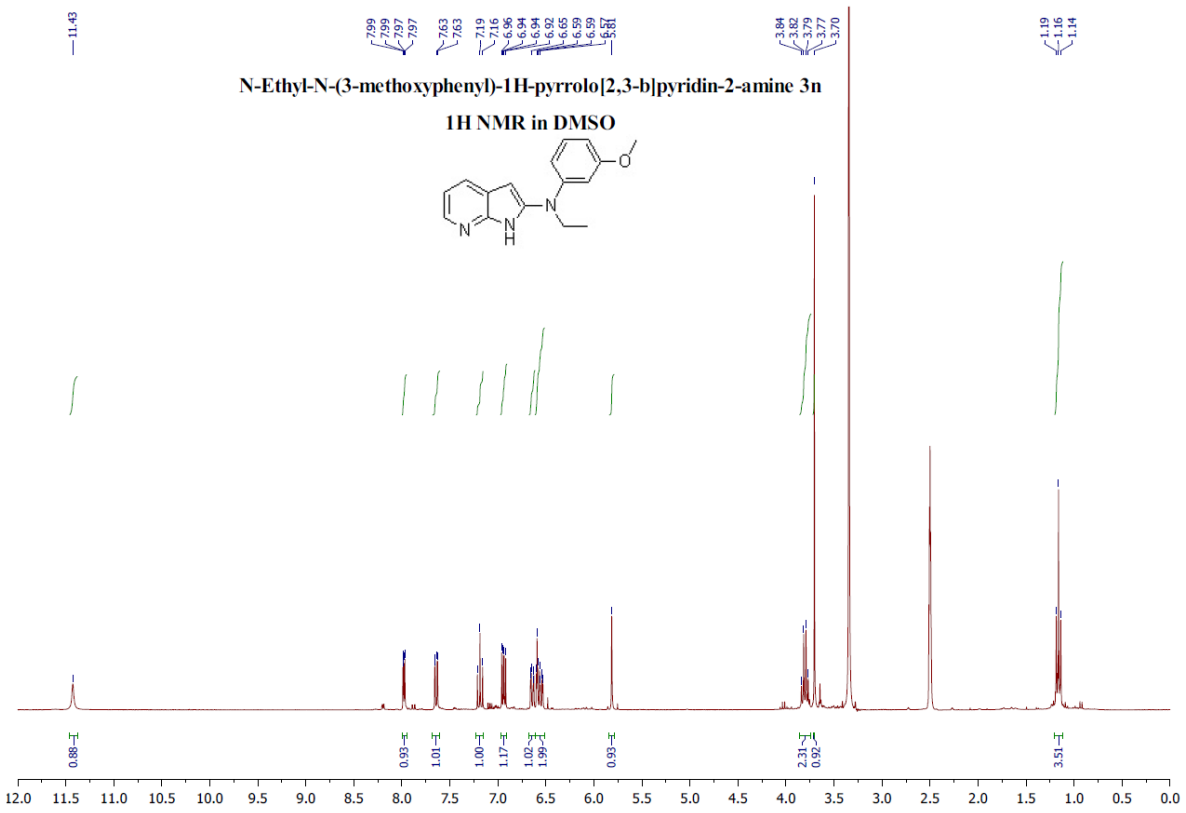

N-(p-Tolyl)-1H-pyrrolo[2,3-b]pyridin-2-amine 3i
13C NMR in DMSO
NH
N
H
f1 (ppm)

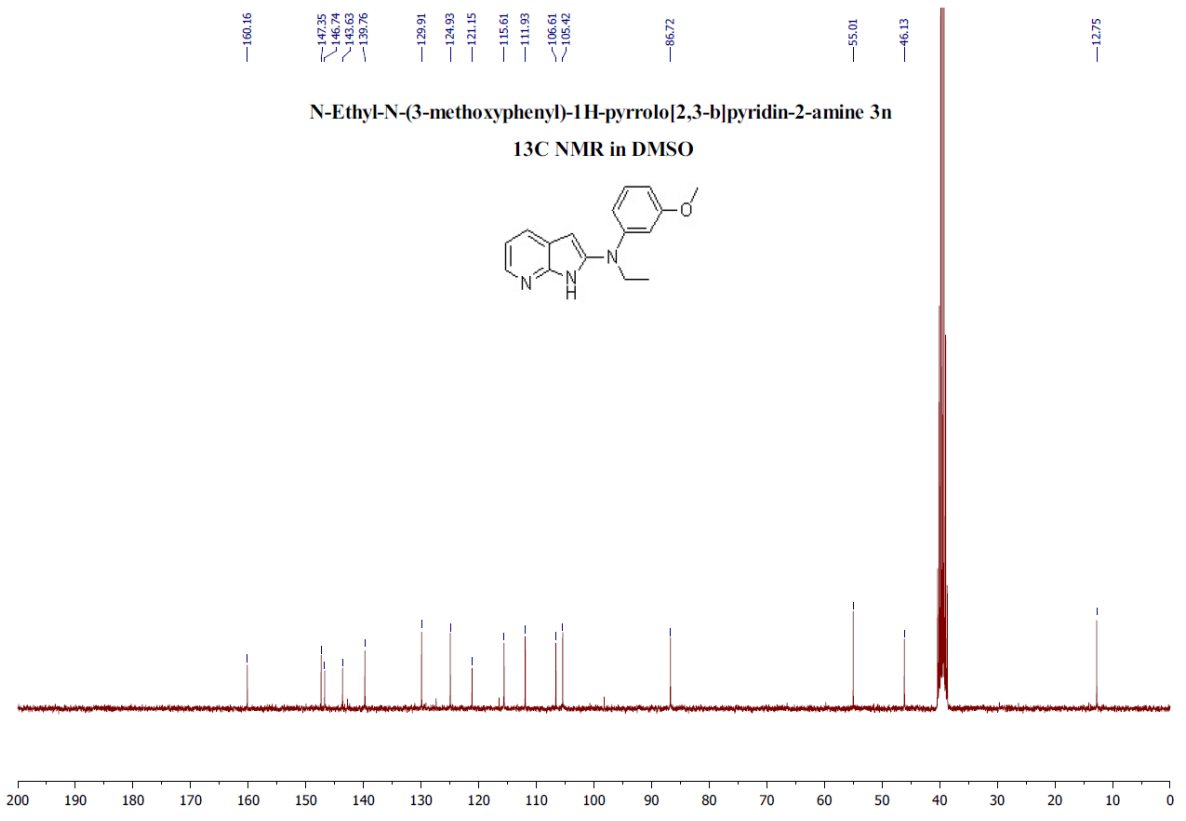

10.71
7.87
7.82
7.81
7.80
7.79
7.44
7.43
7.41
6.98
6.86
6.85
6.84
6.62
6.56
6.53
5.53
3.03
3.01
2.98
2.96
1.18
1.15
1.13
N1-Ethyl-N4-(1H-pyrrolo[2,3-b]pyridin-2-yl)benzene-1,4-diamine 3k
1H NMR in DMSO
NH
NH
N
N
H
0.87
1.07
0.96
1.00
2.18
1.34
2.79
0.95
3.22
4.59
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

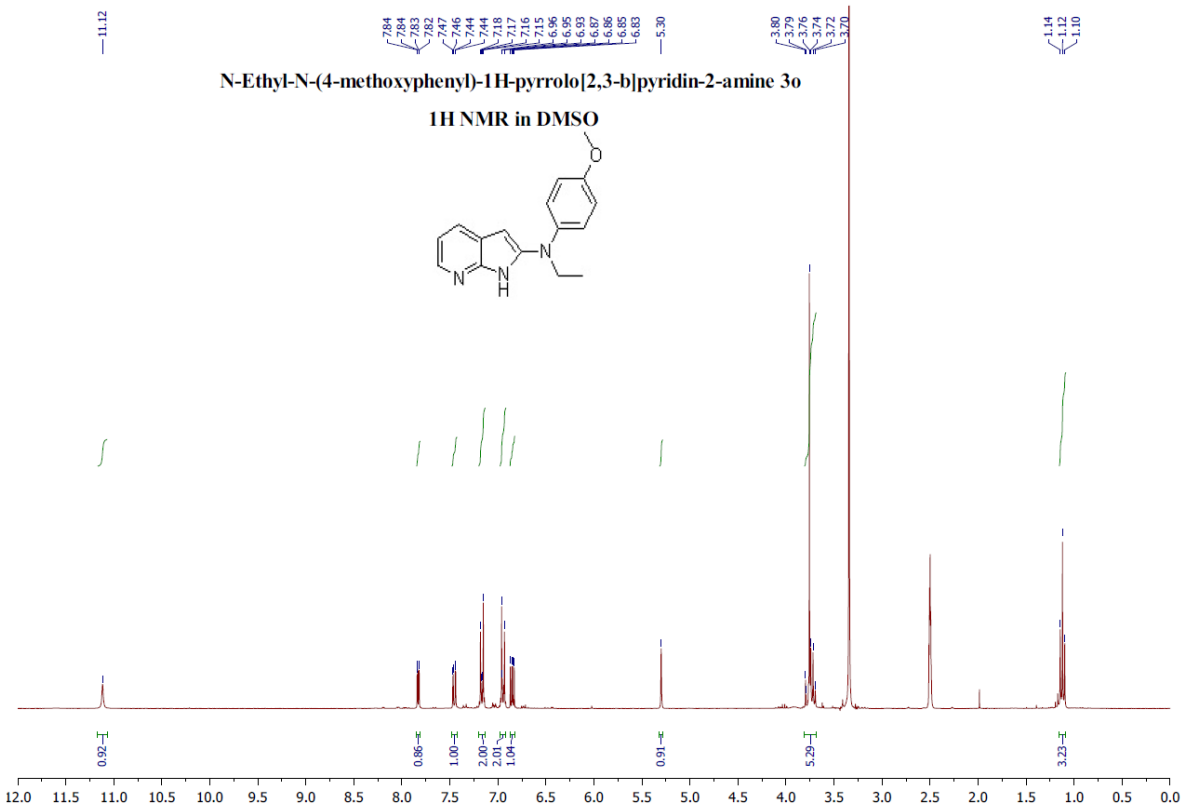

146.47
144.21
143.95
137.47
131.43
122.76
122.53
119.84
115.37
112.79
77.85
37.90
14.55
N1-Ethyl-N4-(1H-pyrrolo[2,3-b]pyridin-2-yl)benzene-1,4-diamine 3k
13C NMR in DMSO
NH
NH
N
N
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

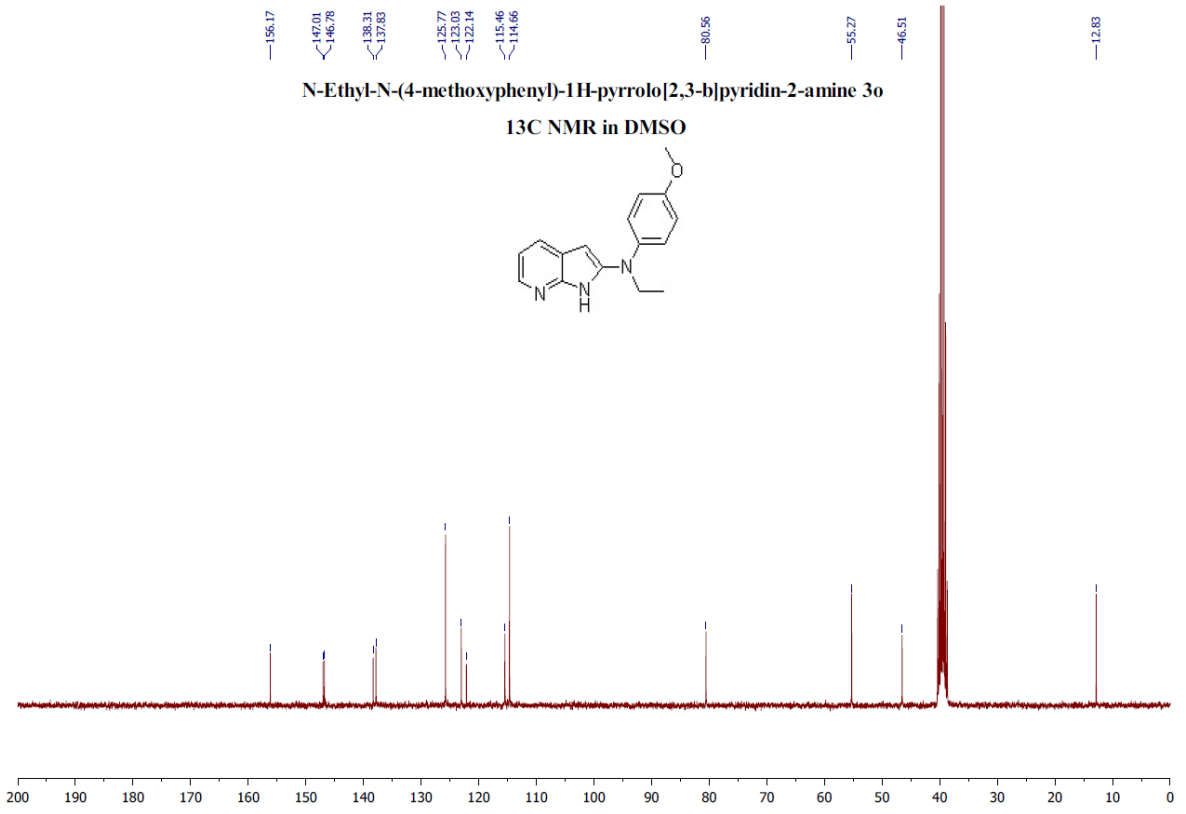

11.43
7.97
7.97
7.96
7.95
7.61
7.60
7.32
7.30
7.29
7.27
7.11
7.10
7.08
6.95
6.93
6.92
6.91
5.75
3.85
3.83
3.81
3.78
1.19
1.16
1.14
N-Ethyl-N-phenyl-1H-pyrrolo[2,3-b]pyridin-2-amine 3l
1H NMR in DMSO
1.01
0.96
1.00
2.04
2.08
2.07
0.98
2.07
3.24
f1 (ppm)

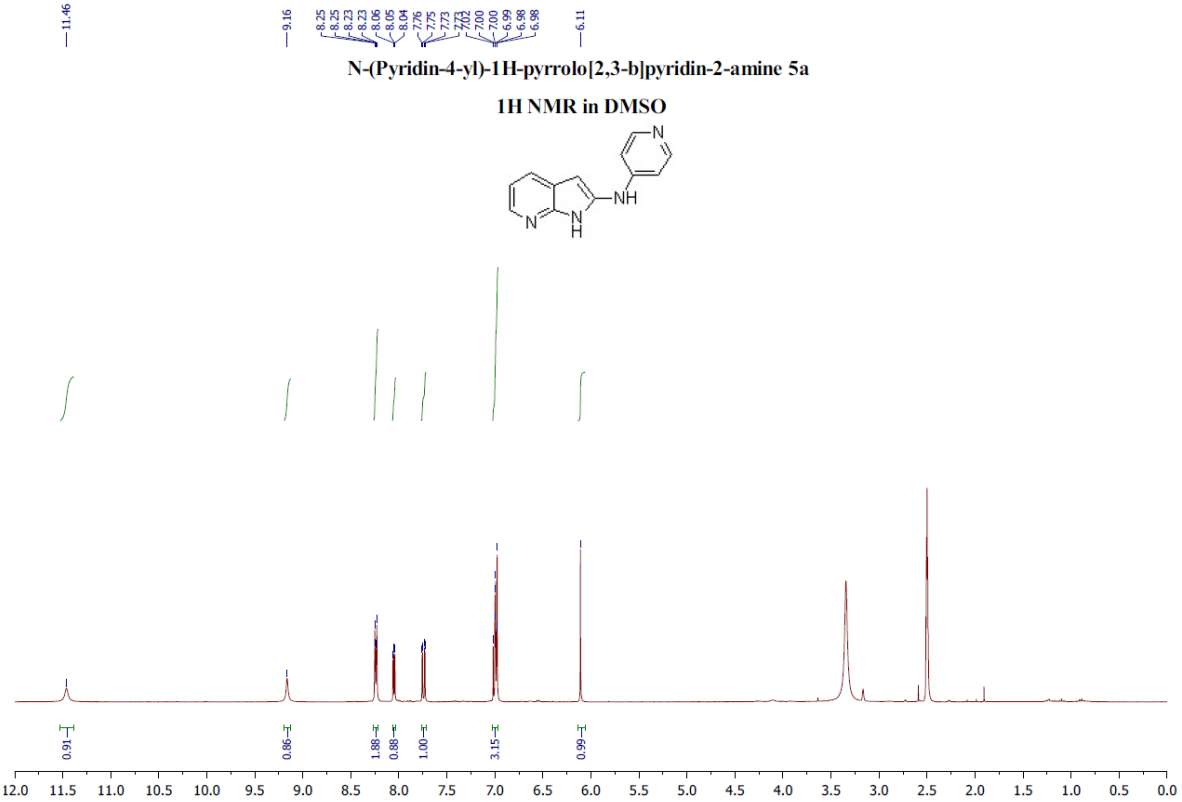

146.79
146.07
144.08
139.51
129.21
124.67
121.61
121.29
119.87
115.58
85.92
46.08
12.77
N-Ethyl-N-phenyl-1H-pyrrolo[2,3-b]pyridin-2-amine 3l
13C NMR in DMSO

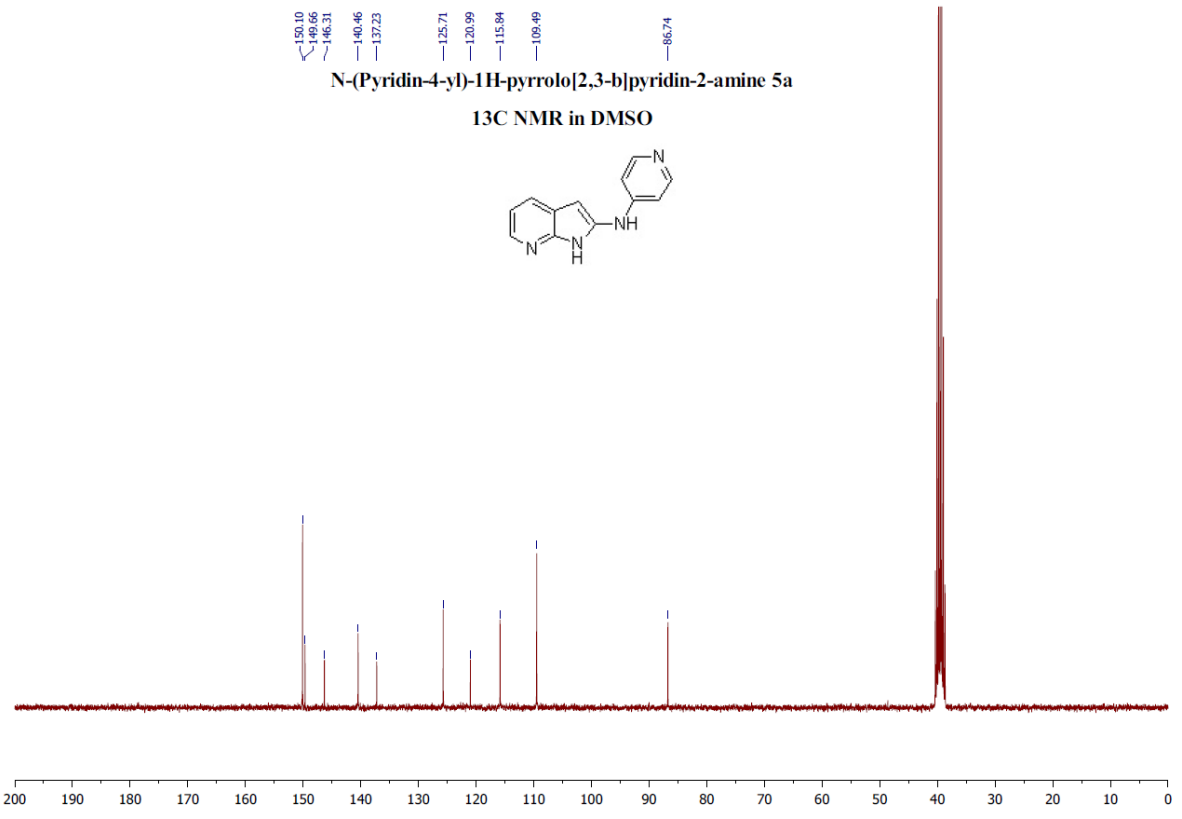

11.43
7.99
7.99
7.97
7.97
7.63
7.63
7.19
7.16
6.96
6.94
6.94
6.92
6.65
6.59
6.59
6.57
5.81
3.84
3.82
3.79
3.77
3.70
1.19
1.16
1.14
N-Ethyl-N-(3-methoxyphenyl)-1H-pyrrolo[2,3-b]pyridin-2-amine 3n
1H NMR in DMSO
0.88
0.93
1.01
1.00
1.17
1.02
1.99
0.93
2.31
0.92
3.51
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

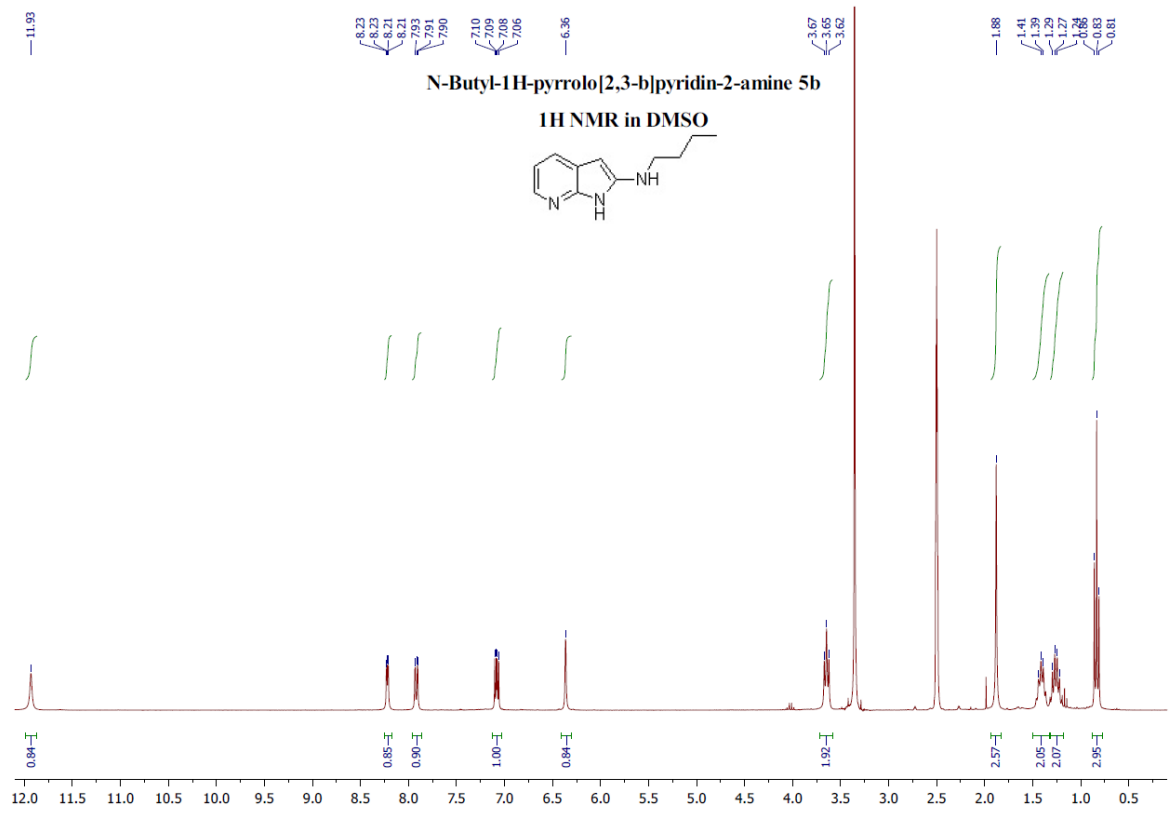

160.16
147.35
146.74
143.63
139.76
129.91
124.93
121.15
115.61
111.93
106.61
105.42
86.72
55.01
46.13
12.75
N-Ethyl-N-(3-methoxyphenyl)-1H-pyrrolo[2,3-b]pyridin-2-amine 3n
13C NMR in DMSO
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

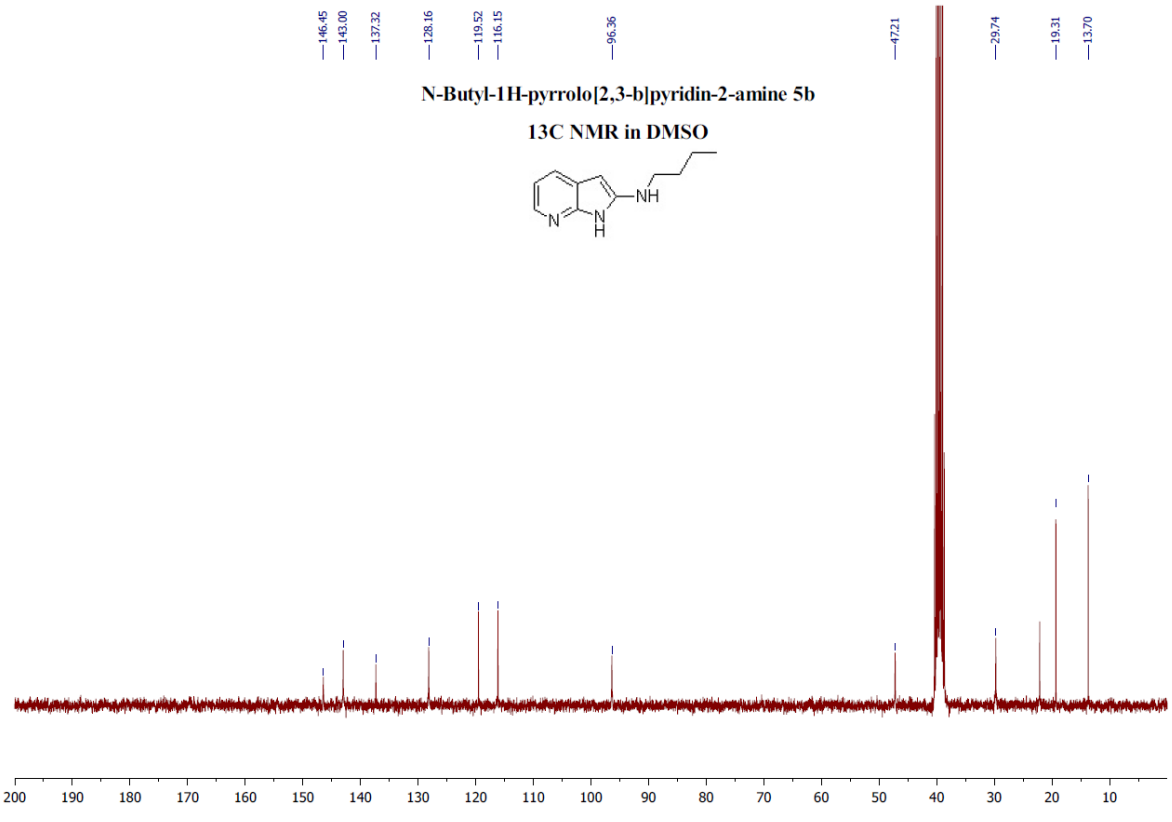

11.12
7.84
7.84
7.83
7.82
7.47
7.46
7.44
7.44
7.18
7.17
7.16
7.15
6.96
6.95
6.93
6.87
6.86
6.85
6.83
5.30
3.80
3.79
3.76
3.74
3.72
3.70
1.14
1.12
1.10
N-Ethyl-N-(4-methoxyphenyl)-1H-pyrrolo[2,3-b]pyridin-2-amine 3o
1H NMR in DMSO
O
N
N
H
0.92
0.86
1.00
2.00
2.01
1.04
0.91
5.29
3.23
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

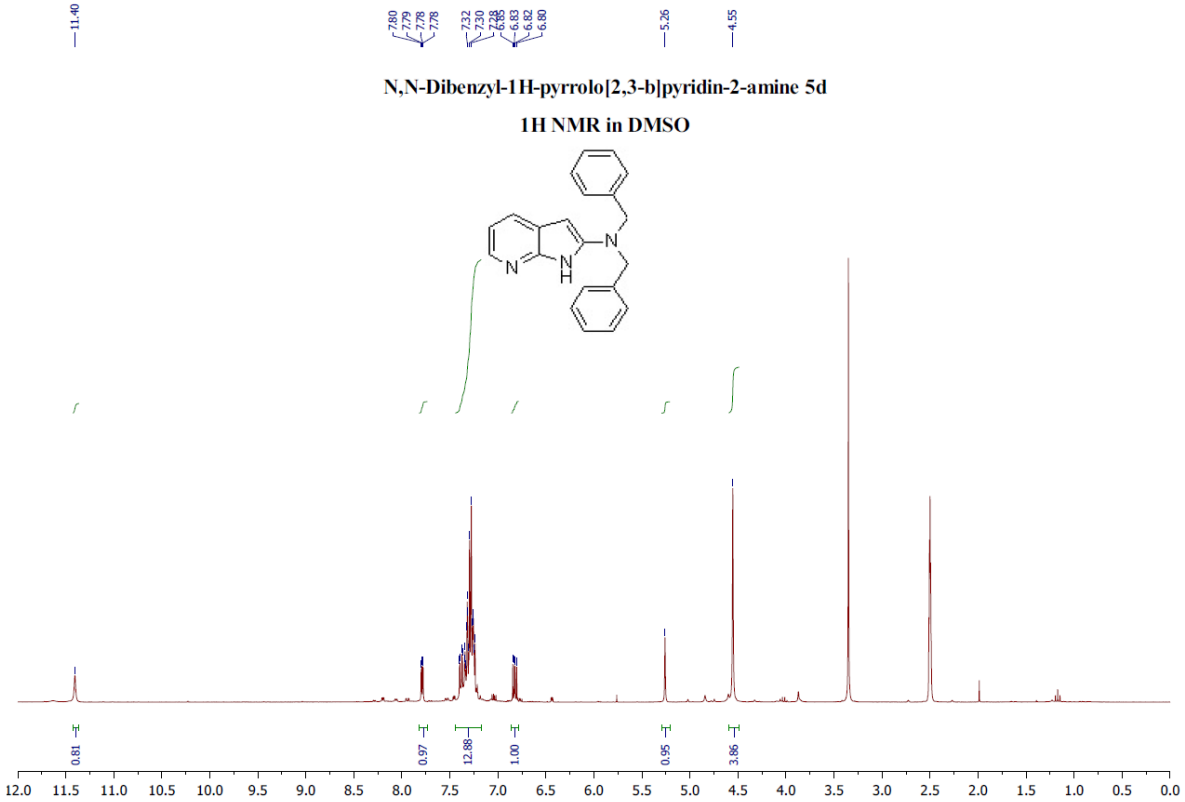

156.17
147.01
146.78
138.31
137.83
125.77
123.03
122.14
115.46
114.66
80.56
55.27
46.51
12.83
N-Ethyl-N-(4-methoxyphenyl)-1H-pyrrolo[2,3-b]pyridin-2-amine 3o
13C NMR in DMSO
O
N
N
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


11.46
9.16
8.25
8.25
8.23
8.23
8.06
8.05
8.04
7.76
7.75
7.73
7.72
7.00
7.00
6.99
6.98
6.98
6.11
N-(Pyridin-4-yl)-1H-pyrrolo[2,3-b]pyridin-2-amine 5a
1H NMR in DMSO
N
NH
N
H
0.91
0.86
1.88
0.88
1.00
3.15
0.99
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


150.10
149.66
146.31
140.46
137.23
125.71
120.99
115.84
109.49
86.74
N-(Pyridin-4-yl)-1H-pyrrolo[2,3-b]pyridin-2-amine 5a
13C NMR in DMSO
N
NH
N
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

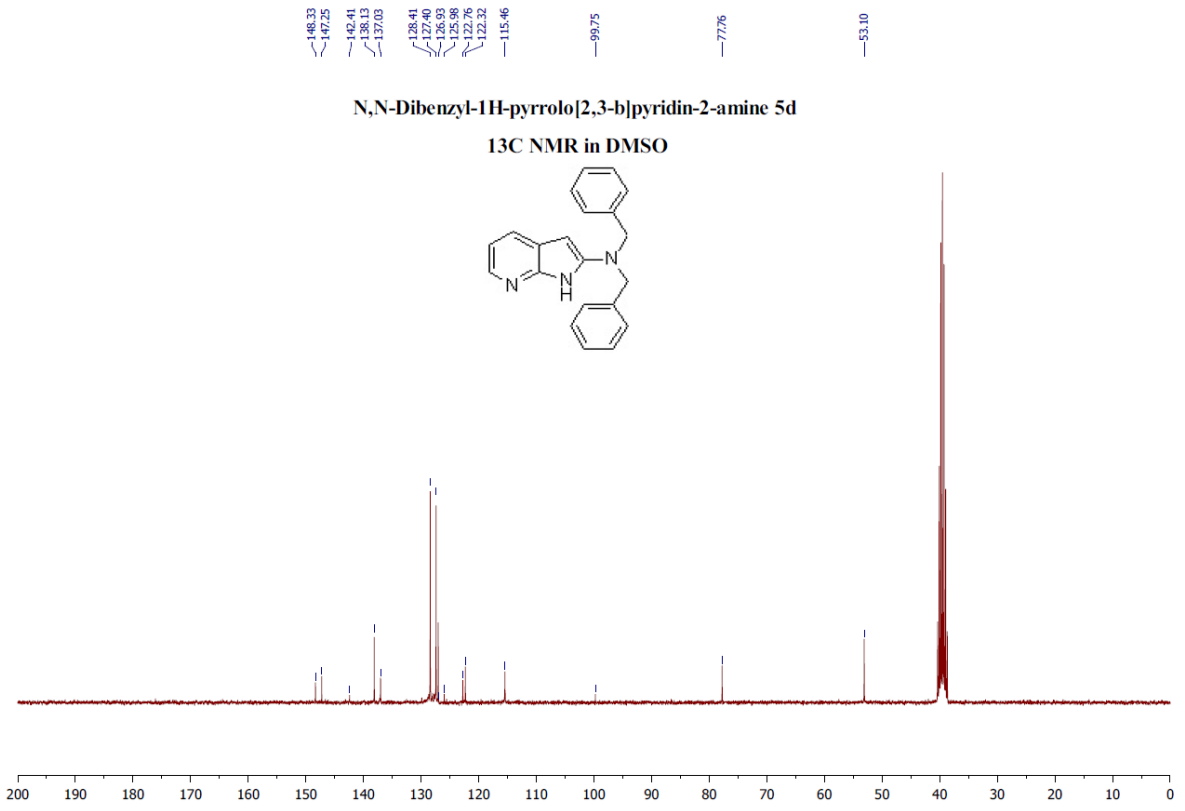

11.93
8.23
8.23
8.21
8.21
7.93
7.91
7.90
7.10
7.09
7.08
7.06
6.36
3.67
3.65
3.62
1.88
1.41
1.39
1.29
1.27
1.24
0.86
0.83
0.81
N-Butyl-1H-pyrrolo[2,3-b]pyridin-2-amine 5b
1H NMR in DMSO
NH
N
H
0.84
0.85
0.90
1.00
0.84
1.92
2.57
2.05
2.07
2.95
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5


146.45
143.00
137.32
128.16
119.52
116.15
96.36
47.21
29.74
19.31
13.70
N-Butyl-1H-pyrrolo[2,3-b]pyridin-2-amine 5b
13C NMR in DMSO
NH
N
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10



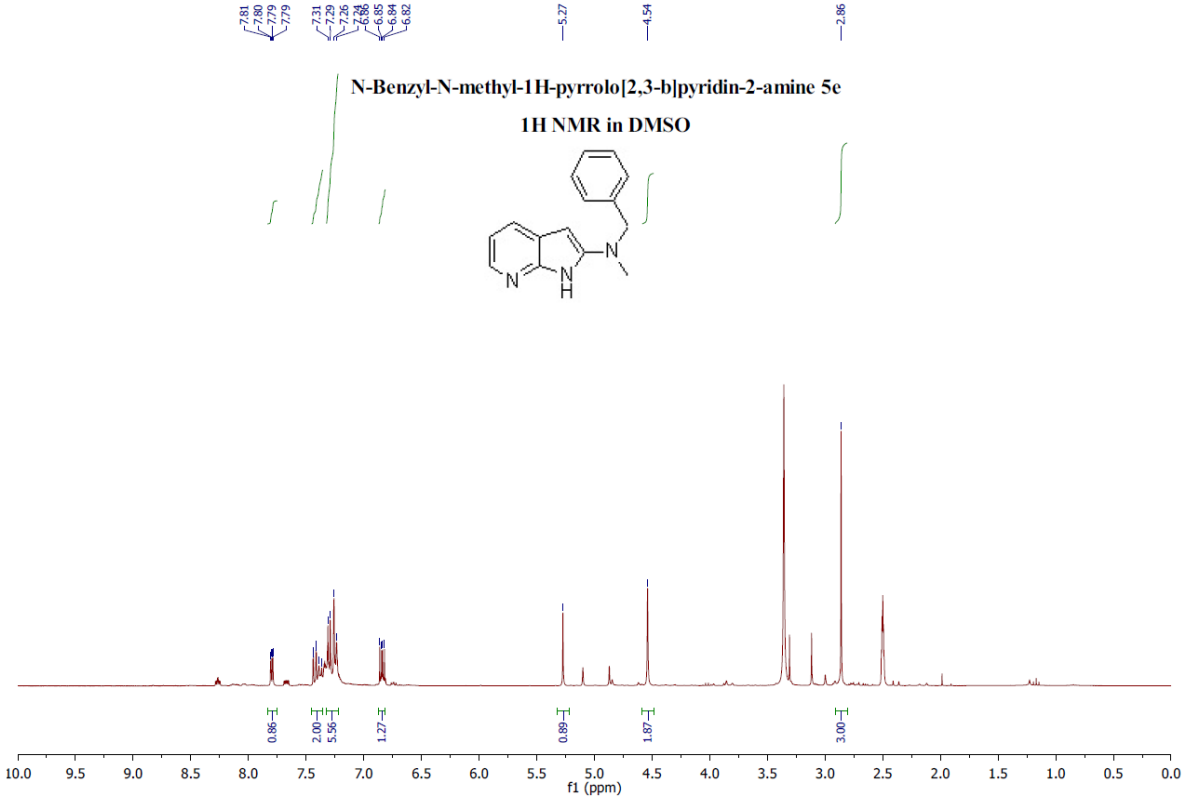
N,N-Dibenzyl-1H-pyrrolo[2,3-b]pyridin-2-amine 5d

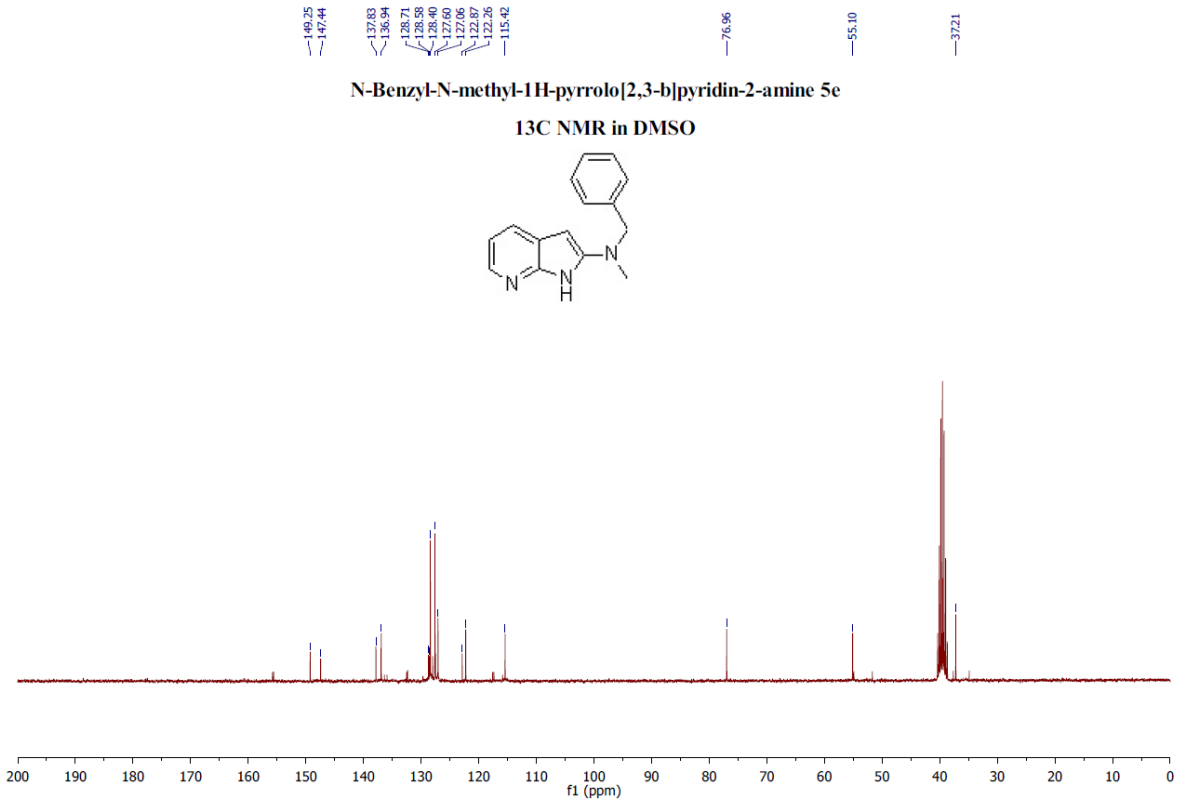
1H NMR in DMSO

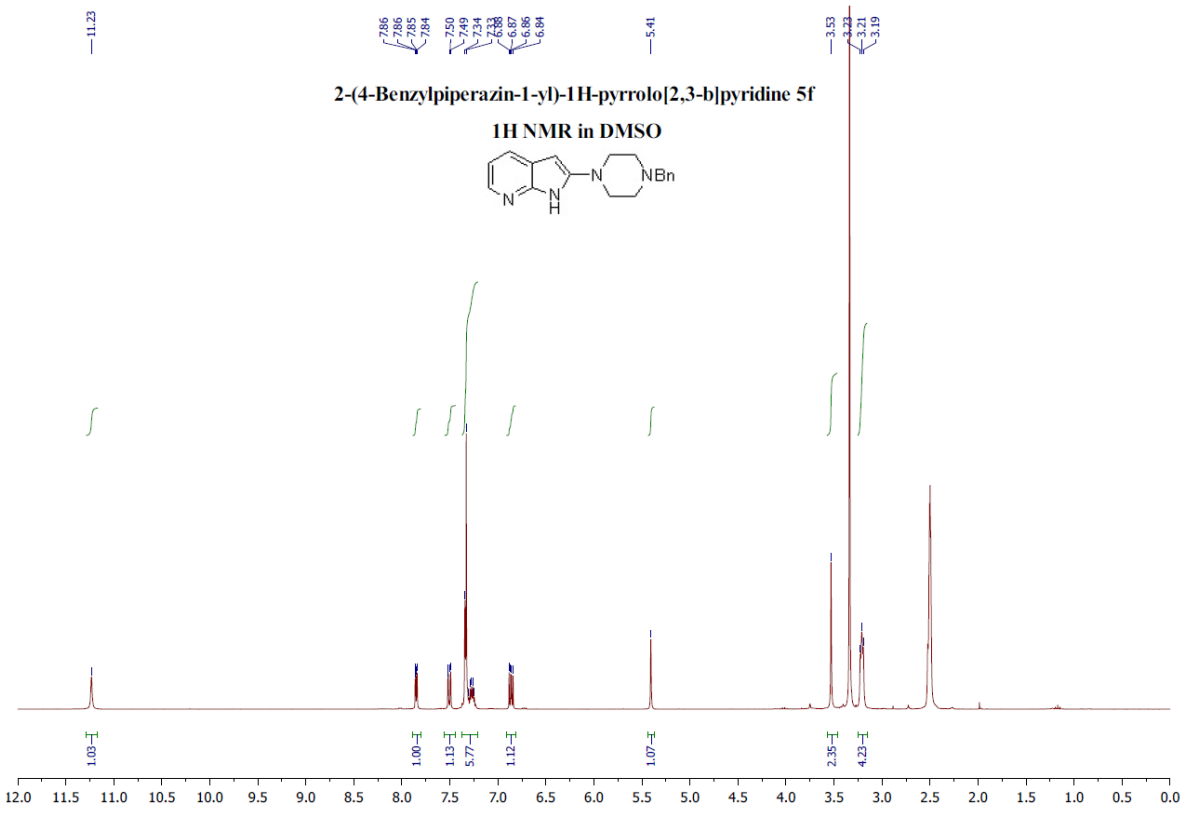


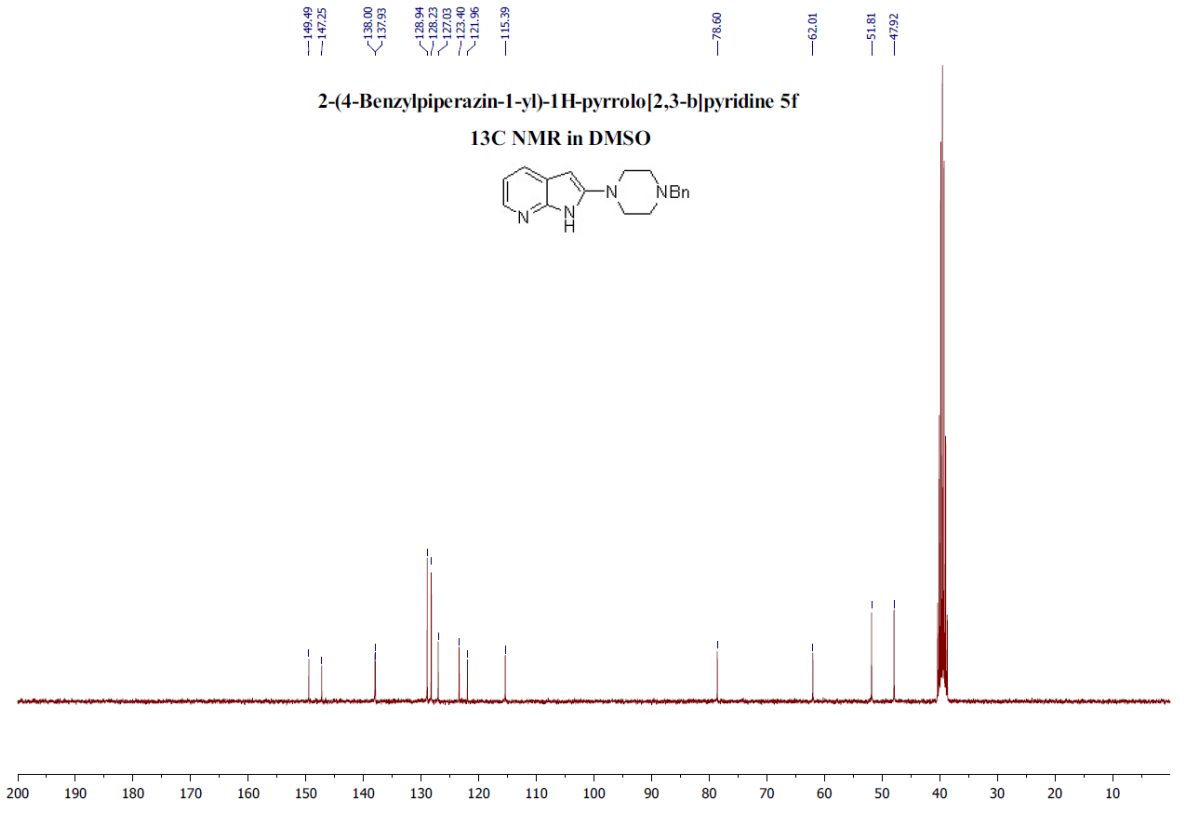
N,N-Dibenzyl-1H-pyrrolo[2,3-b]pyridin-2-amine 5d

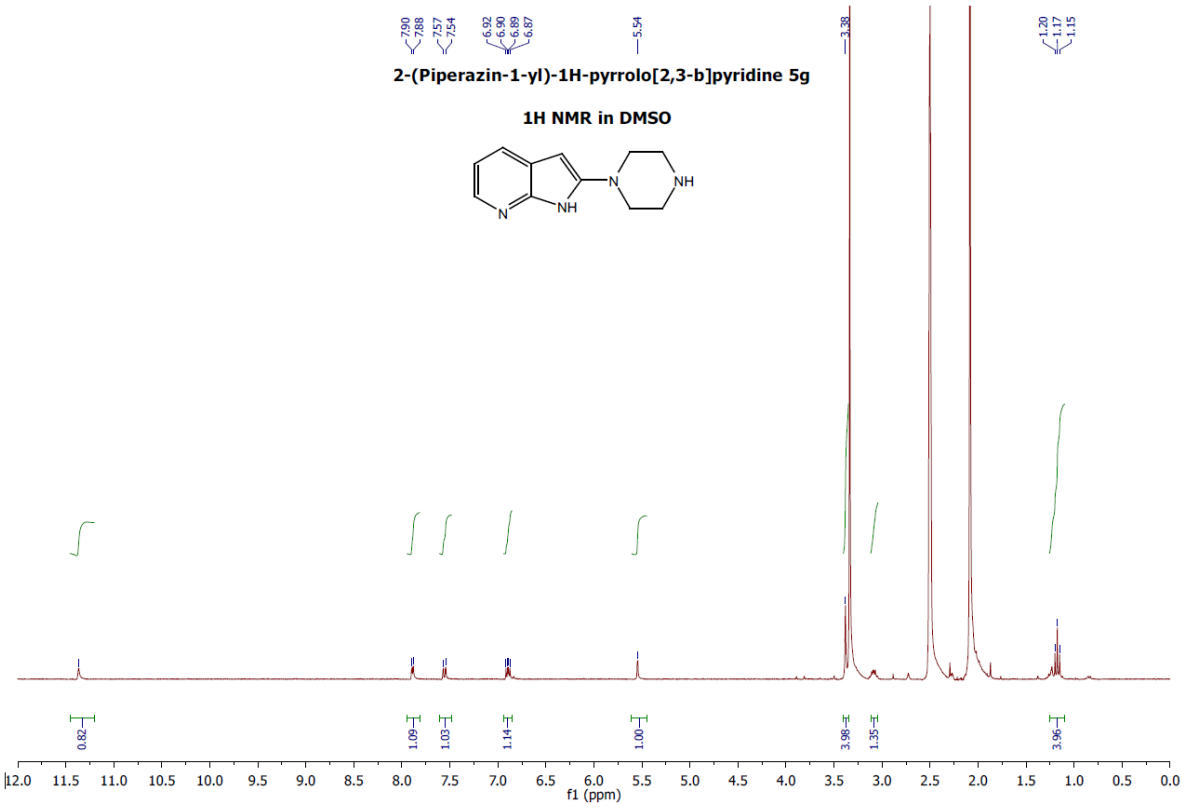
13C NMR in DMSO

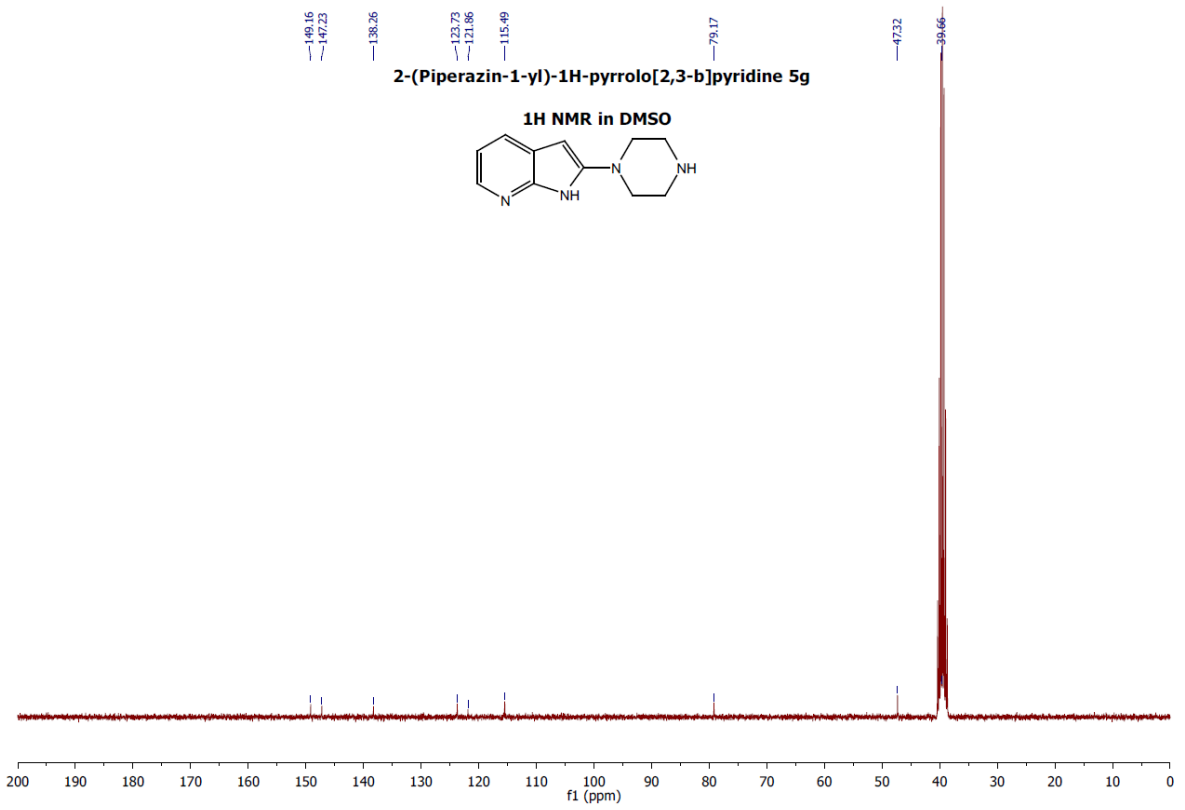

7.81
7.80
7.79
7.79
7.31
7.29
7.26
7.24
6.86
6.85
6.84
6.82
5.27
4.54
2.86
N-Benzyl-N-methyl-1H-pyrrolo[2,3-b]pyridin-2-amine 5e
1H NMR in DMSO
N
N
H
0.86
2.00
5.56
1.27
0.89
1.87
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

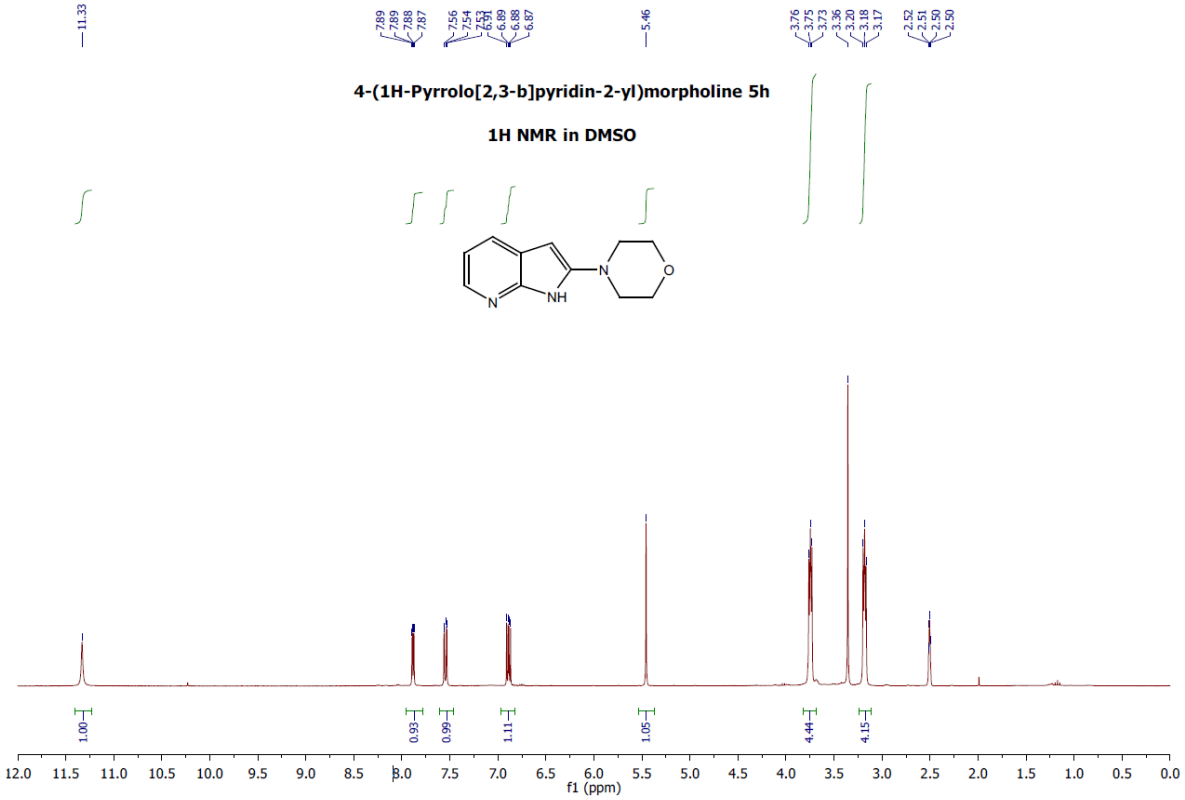

149.25
147.44
137.83
136.94
128.71
128.58
128.40
127.60
127.06
122.87
122.26
115.42
76.96
55.10
37.21
N-Benzyl-N-methyl-1H-pyrrolo[2,3-b]pyridin-2-amine 5e
13C NMR in DMSO
N
N
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

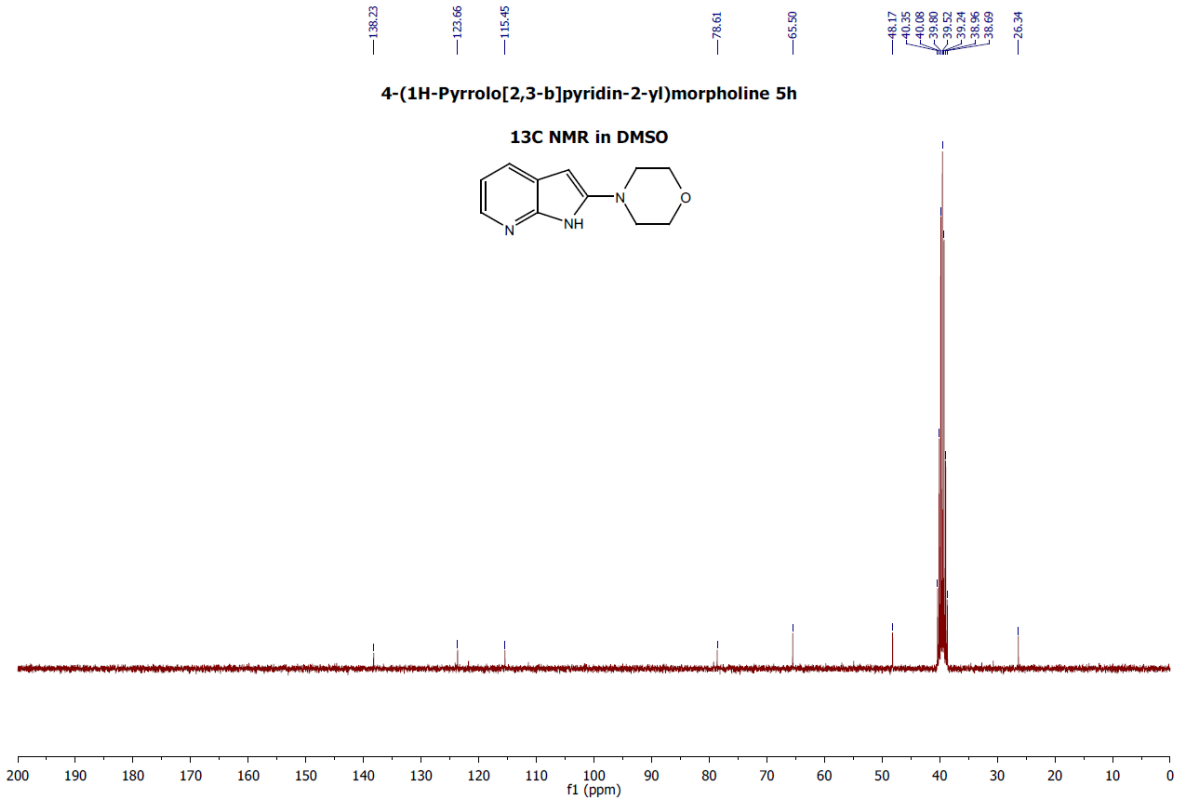

11.23
7.86
7.86
7.85
7.84
7.50
7.49
7.34
7.33
6.87
6.86
6.84
5.41
3.53
3.33
3.21
3.19
2-(4-Benzylpiperazin-1-yl)-1H-pyrrolo[2,3-b]pyridine 5f
1H NMR in DMSO
N
N
H
N
NBn
1.03
1.00
1.13
5.77
1.12
1.07
2.35
4.23
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

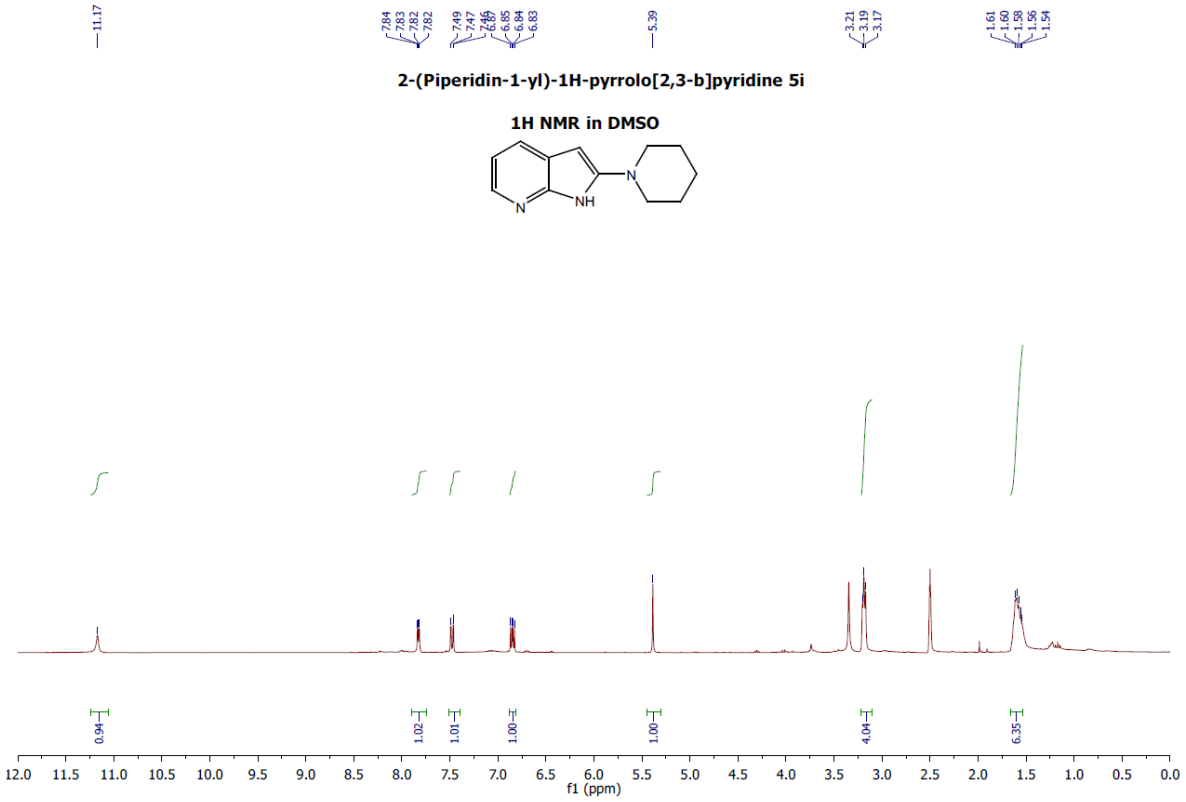

149.49
147.25
138.00
137.93
128.94
128.23
127.03
123.40
121.96
115.39
78.60
62.01
51.81
47.92
2-(4-Benzylpiperazin-1-yl)-1H-pyrrolo[2,3-b]pyridine 5f
13C NMR in DMSO
N
N
H
N
NBn
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

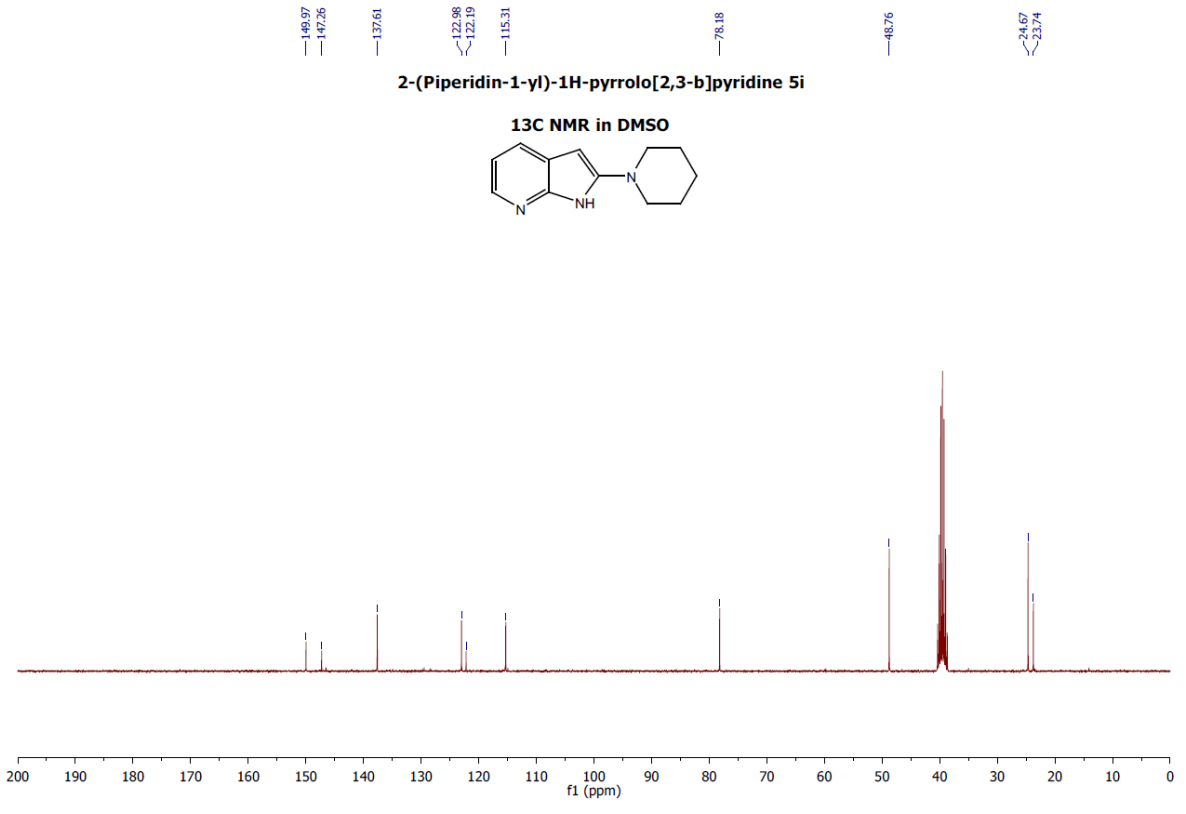

7.90
7.88
7.57
7.54
6.92
6.90
6.89
6.87
5.54
3.38
1.20
1.17
1.15
2-(Piperazin-1-yl)-1H-pyrrolo[2,3-b]pyridine 5g
1H NMR in DMSO
NH
N
NH
0.82
1.09
1.03
1.14
1.00
3.98
1.35
3.96
f1 (ppm)


149.16
147.23
138.26
123.73
121.86
115.49
79.17
47.32
39.66
2-(Piperazin-1-yl)-1H-pyrrolo[2,3-b]pyridine 5g
1H NMR in DMSO
NH
N
NH
f1 (ppm)


11.33
7.89
7.89
7.88
7.87
7.56
7.54
7.53
6.91
6.89
6.88
6.87
5.46
3.76
3.75
3.73
3.36
3.20
3.18
3.17
2.52
2.51
2.50
2.50
4-(1H-Pyrrolo[2,3-b]pyridin-2-yl)morpholine 5h
1H NMR in DMSO
N
NH
O
1.00
0.93
0.99
1.11
1.05
4.44
4.15
f1 (ppm)


138.23
123.66
115.45
78.61
65.50
48.17
40.35
40.08
39.80
39.52
39.24
38.96
38.69
26.34
4-(1H-Pyrrolo[2,3-b]pyridin-2-yl)morpholine 5h
13C NMR in DMSO
N
NH
O
f1 (ppm)


11.17
7.84
7.83
7.82
7.82
7.49
7.47
7.46
6.85
6.84
6.83
5.39
3.21
3.19
3.17
1.61
1.60
1.58
1.56
1.54
2-(Piperidin-1-yl)-1H-pyrrolo[2,3-b]pyridine 5i
1H NMR in DMSO
N
NH
N
0.94
1.02
1.01
1.00
1.00
4.04
6.35
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


149.97
147.26
137.61
122.98
122.19
115.31
78.18
48.76
24.67
23.74
2-(Piperidin-1-yl)-1H-pyrrolo[2,3-b]pyridine 5i
13C NMR in DMSO
N
NH
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)