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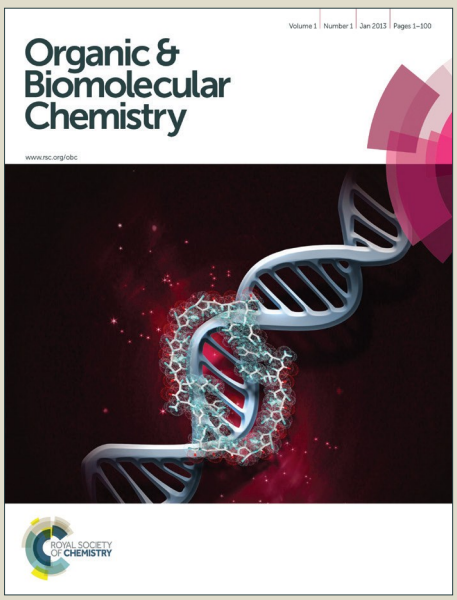

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Facile synthesis of 4- and 7-azaindoles from corresponding imines by palladium-catalyzed cascade C-C and C-N coupling

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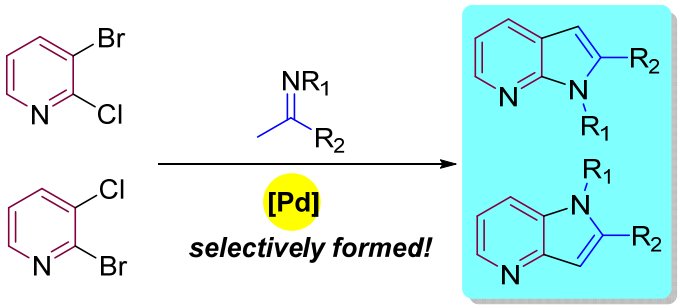


Abstract: The cyclization of 2,3-dihalopyridines with readily available imines provides a convenient and regioselective approach to 4- and 7-azaindoles. The regioselectivity can be controlled by the choice of the halogen atoms at the pyridine ring (chlorine versus bromine).

Introduction

Azaindoles are considered as biologically important core structures, as these function as bioisosteres of the prevalent subunit indole in biological systems (Figure 1).[1] A great number of heterocycles derived from the azaindole moiety exhibit interesting biological properties for medicinal applications. For example, 7-azatryptophan (**Aza1**, Figure 2) has been used as fluorescent marker for characterizing protein interactions.[2] Derivative **Aza2** has been used as HIV-attachment inhibitor[3] and **Aza3** as anti-tubercular[4] agent. The binding selectivity and bioavailability of azaindoles can be well controlled by varying their substituents.[5] Therefore, there has been an increasing number of azaindole-derived drug candidates recently developed and released in the pharmaceutical industry.

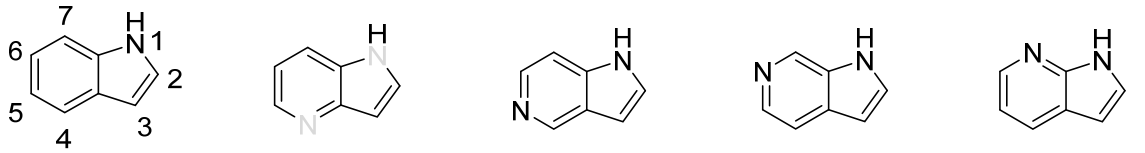


Figure 1: Indole and azaindoles

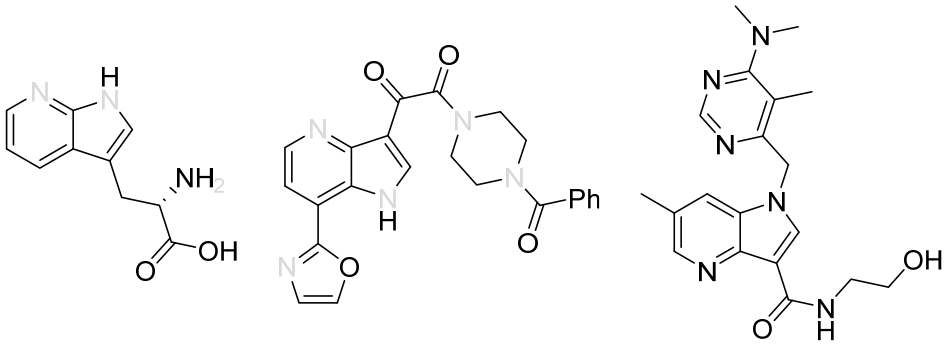


Figure 2: Biologically relevant azaindole-derived compounds

Many syntheses of azaindoles start from the pyridine ring, followed by a ring closure to form the pyrrole ring. In classic chemistry, the cyclization was accomplished through different ways, including reactions developed by Fischer,[6] Madelung,[7] Reissert,[8] Bartoli[9] and

Chichibabin.[10] These classical strategies, however, are limited by their harsh conditions, low yields, and low functional group compatibility. These shortcomings have been gradually solved in modern chemistry by the use of palladium with its greater C-C and C-N formation potential together with its higher functional group tolerance. A number of new syntheses for azaindole have been developed, as shown in Figure 3, including the (a, b) C-N/Heck reaction,[11, 12] (c) Suzuki/C-N reaction,[13] (d) C-N/C-N-cross coupling reactions,[14] as well as (e) alkynyl amine cyclizations[15] and the (f) Larock synthesis.[16]

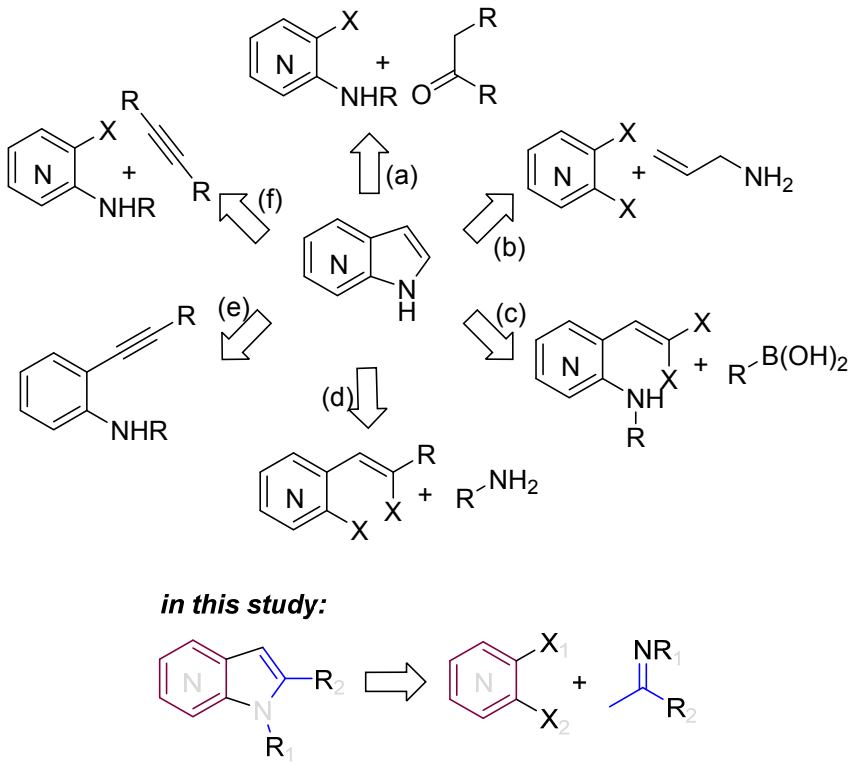


Figure 3: Palladium catalyzed azaindole syntheses

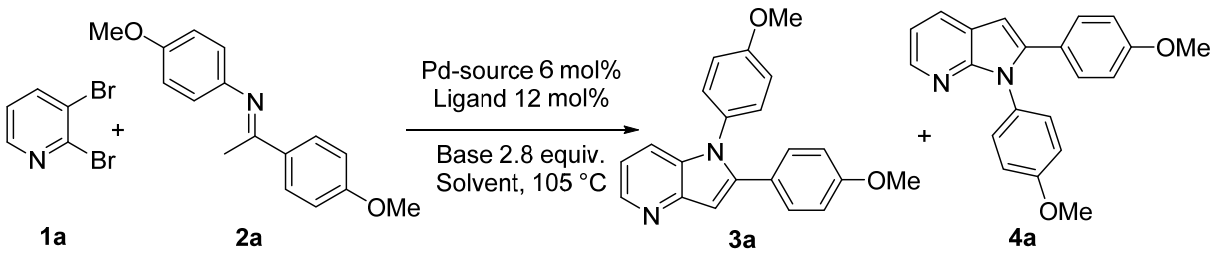
Our goal was to develop a strategy which allows for the preparation of azaindoles from simple starting materials in a facile manner. Herein, we describe a convenient synthesis of both 4- and 7-azaindoles which has, to the best of our knowledge, not been previously reported. The protocol is operationally simple using commercially available or easily available starting materials.

Results and discussion

The reaction of dihalopyridine **1a** with imine **2a** was chosen for the optimization process (Table 1). At the beginning we applied the conditions used by Barluenga *et al*[17] for the

synthesis of indoles by an analogous reaction of 1,2-dibromobenzene. However, these conditions only produced a regioisomeric mixture of azaindoles **3a** and **4a** which were each isolated only in 6% yield (entry 1, Table 1). Subsequently, we tested bidentate ligands, namely S-Phos, BINAP, XantPhos and DavePhos, but these conditions failed completely to deliver the expected results. Therefore, we turned our attention to monodentate ligands (entries 2–7, Table 1). Remarkably higher yields were obtained with the ligands PPh_3, CataCXium A and PCy_3 (entries 4, 6 and 7). Next, we checked the robustness of this system by varying the palladium sources, bases, solvents and temperatures. We found a catalyst system which allowed a regioselective formation of 7-azaindole (entry 9), however, the conversion was only moderate. In contrast, a high conversion was obtained in case of the catalyst system $Pd(OAc)_2/PCy_3$ with the base NaO*t*Bu in dioxane at 105 °C. However, the regioselectivity was low and a 2:3 mixture of regioisomers **3a** and **4a** was obtained in 91% yield (entry 8). Notably, these conditions are identical to those of Ackermann's carbazole synthesis by reaction of anilines with *ortho*-dihalobenzenes.[18] To improve the regioselectivity, we decided to employ 2-bromo-3-chloropyridine (**1b**) in the reaction with imine **2a** (Scheme 1, Figure 4). Palladium catalyzed cross-coupling reactions of heterocyclic dihalides usually proceed by initial attack at the more electron deficient position of the heterocycle. Position 2 of the pyridine is more electron deficient than position 3. Obviously, this difference in reactivity was not sufficient in case of 2,3-dibromopyridine in order to achieve a good regioselectivity. In case of **1b** two different leaving groups are present. The better leaving group bromine is located at position 2. Therefore, two effects operate in the same direction and the selectivity is higher. In order to obtain a high yield we employed the conditions of entry 8 of Table 1. Much to our satisfaction, under these conditions, the reaction afforded 4-azaindole **3a** in very good yield (80%) and with excellent regioselectivity.

Table 1: Optimization study for the synthesis of 4- and 7-azaindoles **3a** and **4a**



Entry	[Pd]-Source	Ligand	Base	Solvent	Yield (3a:4a)
1	Pd_2dba_3	XPhos	NaO*t*Bu	Dioxane	12%[a] (1:1)[a]
2	Pd_2dba_3	DavePhos	NaO*t*Bu	Dioxane	7%[b] (0:1)[b]
3	Pd_2dba_3	P*t*Bu_3	NaO*t*Bu	Dioxane	-
4	Pd_2dba_3	PPh_3	NaO*t*Bu	Dioxane	39%[b] (1:0)[b]
5	Pd_2dba_3	P(*o*-Tol)$_3$	NaO*t*Bu	Dioxane	-
6	Pd_2dba_3	CataCXium A	NaO*t*Bu	Dioxane	53%[b] (1:2)[b]
7	Pd_2dba_3	PCy_3	NaO*t*Bu	Dioxane	73%[b] (2:1)[b]
8	$Pd(OAc)_2$	PCy_3	NaO*t*Bu	Dioxane	91%[a] (2:3)[a]
9	$Pd(OAc)_2$	PCy_3	K_2CO_3	Dioxane	39%[b] (0:1)[b]

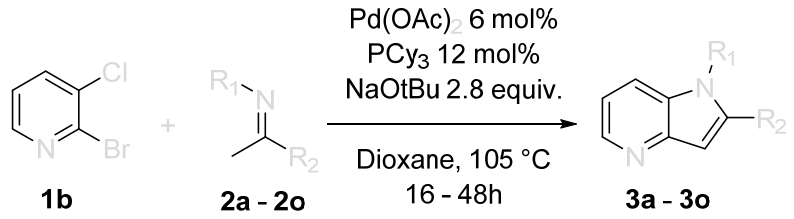
Reaction conditions: 2,3-dibromopyridine (0.1 mmol), imine **3j** (0.11 mmol), [Pd]-source (0.06 mol), ligand (0.012 mmol), NaO*t*Bu (0.28 mmol) 105 °C, 48h.

[a] isolated yield; [b] determined by NMR

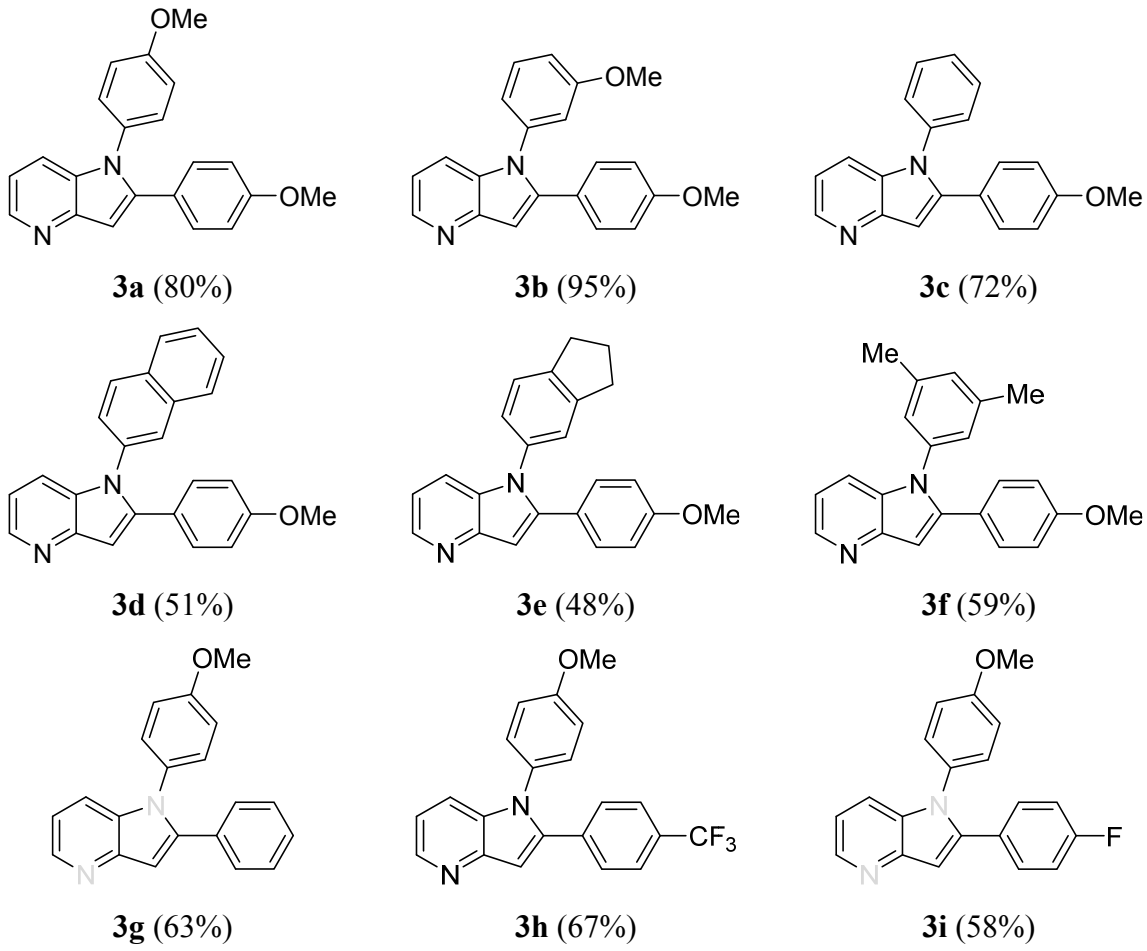
The result of our optimization allowed us to study the preparative scope of the reaction. The reaction of **1b** with imines **2b-o** afforded 4-azaindoles **3b-o** in moderate to high yields. The highest yield was achieved (95%) for the electron rich system **3b**. The yields of electron rich products **3g** and **3h** were also relatively high. In comparison, the lowest was observed for **3e** (48%). However, no clear trend between the chemical structures of the imines and the reaction yields was observed.

The structures of 4-azaindole **3c** was independently confirmed by X-ray crystal structure analysis (Figure 5). The phenyl group located at the 1-position of the azaindole ring is twisted out of the aromatic plane, due to steric effects between the pyridine and the phenyl ring located at the 2-position. Two **3c** molecules orientate in two different directions in order that

the electronic repulsion of the two methoxyl groups and the two phenyl rings located at the 1-position of both molecules **3c** are reduced. A π-π stacking interaction was not clearly observed.



Scheme 1. *Reaction conditions*: **1b** (0.3 mmol), **2** (0.33 mmol), $Pd(OAc)_2$ (0.018 mmol), PCy_3 (0.036 mmol), NaO*t*Bu (0.84 mmol), dioxane (6 ml), 105 °C, 16 – 48h.



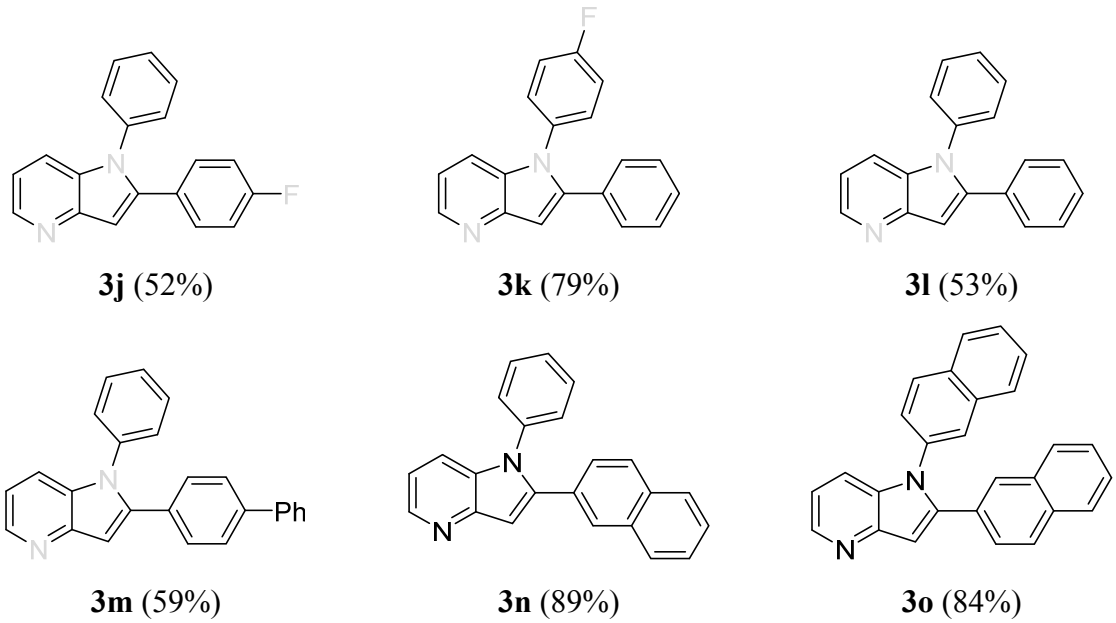


Figure 4: Synthesis of 4-azaindoles

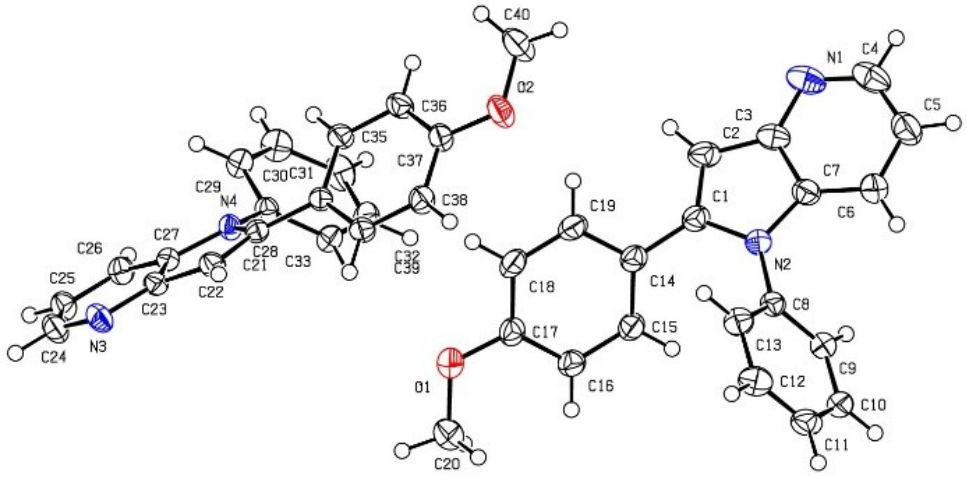
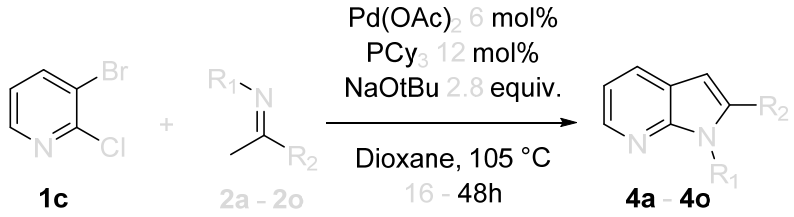


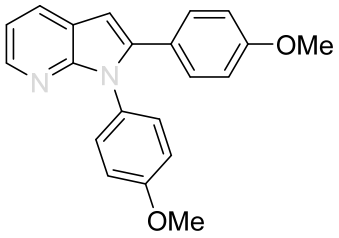
Figure 5: Molecular structure of crystalline azaindole **3c**

The reaction of 3-bromo-2-chloropyridine (**1c**) with imines **2a-o** afforded, under identical conditions, 7-azaindoles **4a-o** with excellent regioselectivity (Scheme 2, Figure 6). The change of the selectivity can be explained by the better leaving group ability of bromine

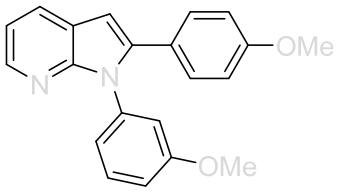
which overrides the higher reactivity usually observed for the more electron deficient and thus more reactive 2-position of the pyridine moiety. No clear trend of the yields was observed depending on the substituents. The highest yield was observed for the large π-system **4o** (86%), while the lowest yield was observed for **4e** and **4f** (both at 47%), presumably due to steric effects.



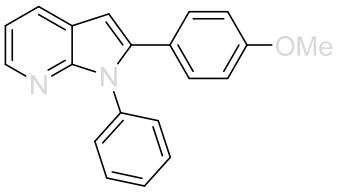
Scheme 2. Reaction conditions: **1c** (0.3 mmol), **2** (0.33 mmol), $Pd(OAc)_2$ (0.018 mmol), PCy_3 (0.036 mmol), NaO*t*Bu (0.84 mmol), Dioxane (6 ml), 105 °C, 16 – 48h.



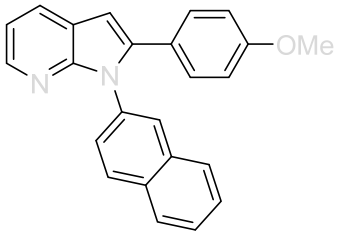
4a (81%)



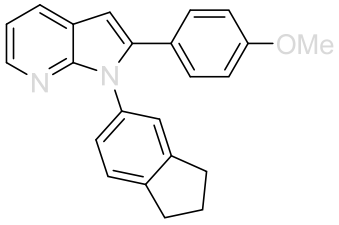
4b (75%)



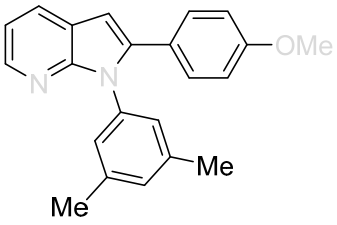
4c (70%)



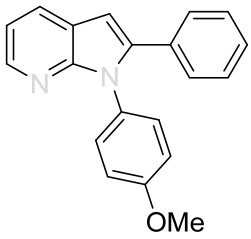
4d (68%)



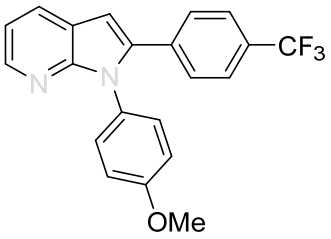
4e (47%)



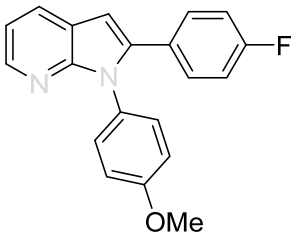
4f (47%)



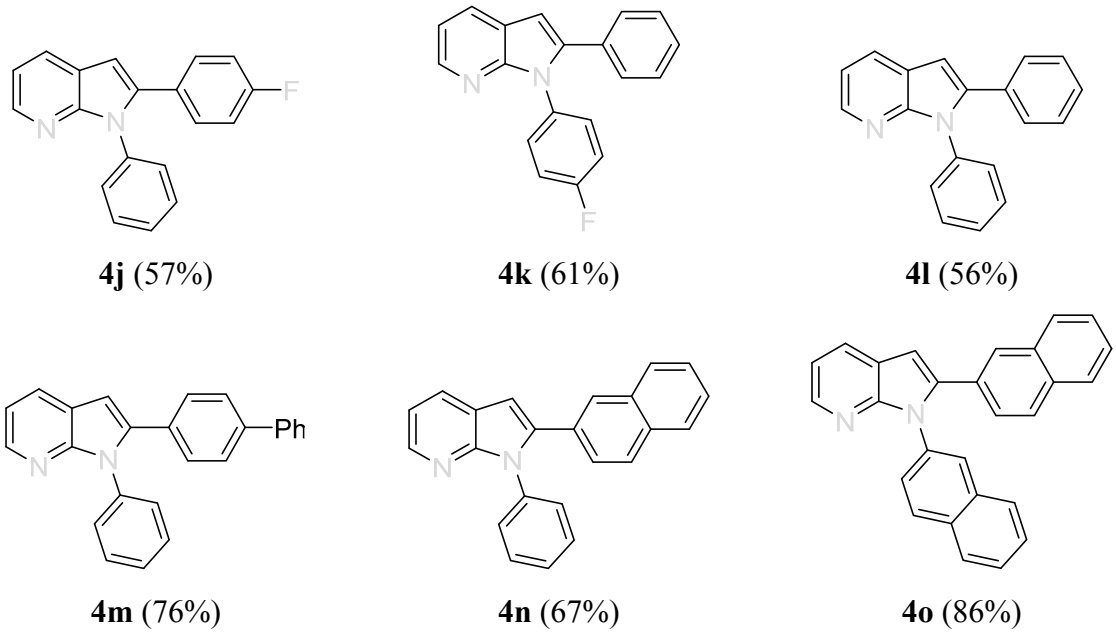
4g (72%)



4h (63%)



4i (59%)



4j (57%) **4k** (61%) **4l** (56%)

4m (76%) **4n** (67%) **4o** (86%)

Figure 6: Synthesis of 7-azaindoles

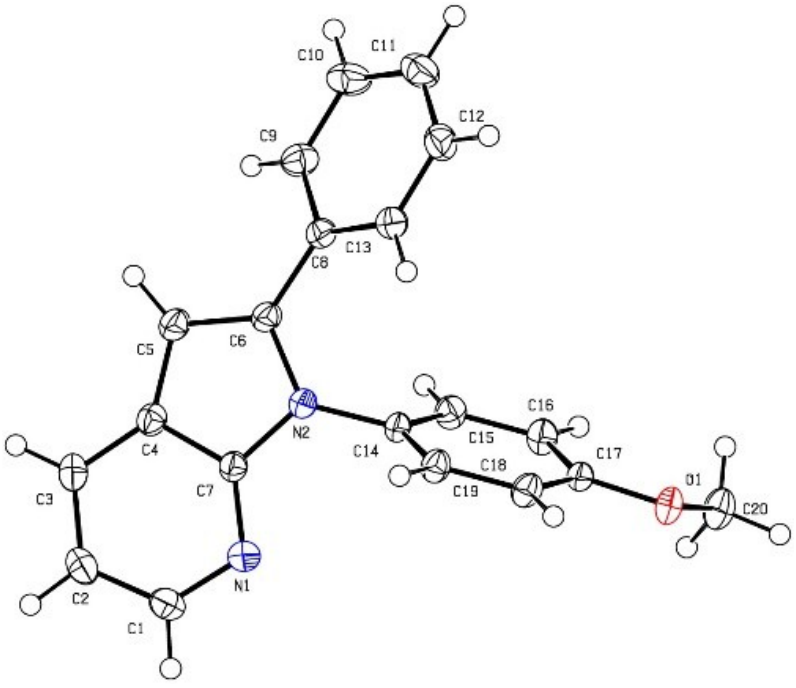


Figure 7: Molecular structure of azaindole **4g**

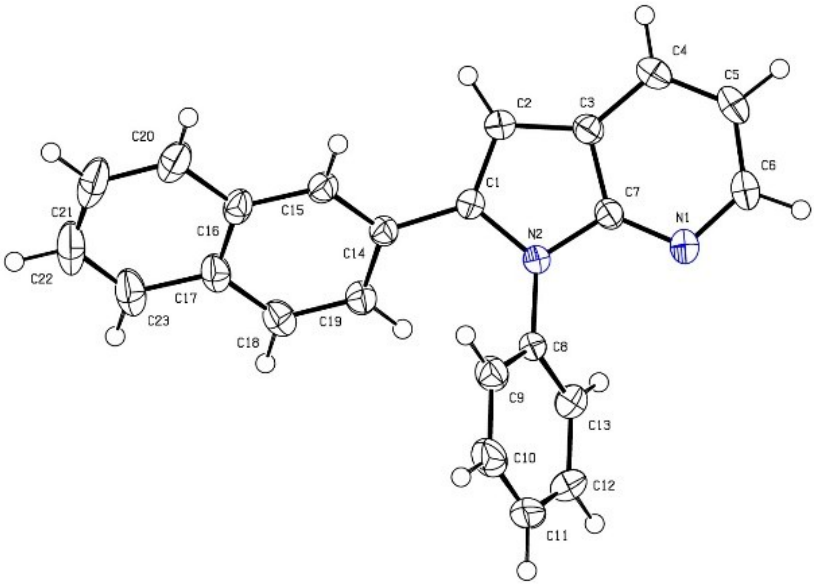


Figure 8: Molecular structure of azaindole **4n**

The structures of 4-azaindoles **4g** and **4n** were independently confirmed by X-ray crystal structure analysis (Figures 7 and 8). The phenyl rings located at the 1-position are twisted out of plane, due to the steric effect. In comparison, the naphthalene and the phenyl ring located at the 2-position are twisted only slightly out of the plane of the azaindole ring.

Conclusion

In conclusion, we have developed a convenient synthesis of 4- and 7-azaindoles. The yields varied from moderate to very good. The regioselectivity can be controlled by the choice of the leaving groups of the pyridine moiety.

Experimental section

General information: Hexane, ethyl acetate and dichloromethane were dried and distilled using standard methods. Molecular sieves were dried in the oven at 300 °C for 12 hours. Other chemicals and solvents, if not otherwise cited, are commercially available and were used without further purification. Column chromatography was performed using normal silica gel with particle size from 0.006 to 0.043 mm. NMR measurements were carried out with Bruker AVANCE 250 II (built 2006), Bruker AVANCE 300 III (built 2007) and Bruker

AVANCE 500 (built 2001) spectrometers. NMR peaks were adjusted according to the standard ^{1}H- and ^{13}C-NMR signals of $CDCl_3$ at 7.260 and 77.160 ppm, respectively. For multiplicity description, abbreviations s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and dd (doublet doublet) were used. IR measurements were recorded on a Nicolet 380 FT-IR spectrometer using ATR sampling technique for both liquids and solids. To report peaks, abbreviations w (weak), m (medium) and s (strong) were used. GC/MS measurements were conducted on a Finnigan MAT 95-XP device with HP-5 capillary column using helium carrier gas and using electron ionization (EI) scan technique. Yield calculation via ^{1}H-NMR technique was carried out using dimethyl sulfone as internal standard.

General procedure for the synthesis of imines: A mixture of ketone (10.0 mmol), amine (10.0 mmol), $NaHCO_3$ (4.20 g) and molecular sieve 4Å (8.00 g) in dried toluene (10.0 ml) in a flask was heated to 80 °C or refluxed for 12 hours overnight. The reaction was controlled on the next day for completion by TLC. After completion, the mixture was taken up in dichloromethane and filtered through zeolite. The solvents were evaporated under reduced pressure. The products were purified by recrystallization in heptane/ethyl acetate mixture or by Kugelrohr distillation under reduced pressure.

N,1-bis(4-methoxyphenyl)ethan-1-imine (2a): ^{1}H NMR (250 MHz, CDCl3) δ 8.03 – 7.85 (m, 2H), 7.00 – 6.84 (m, 4H), 6.80 – 6.71 (m, 2H), 3.87 (s, 3H), 3.82 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 165.1, 161.7, 156.1, 145.5, 132.7, 129.0 (2C), 121.2 (2C), 114.4 (2C), 113.8 (2C), 55.6, 55.5, 17.3. ^{1}H- and ^{13}C-NMR spectral data are in accordance with the literature.[19a]

N-(3-methoxyphenyl)-1-(4-methoxyphenyl)ethan-1-imine (2b): ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.04 – 7.85 (m, 2H), 7.34 – 7.17 (m, 1H), 7.00 – 6.89 (m, 2H), 6.69 – 6.58 (m, 1H), 6.48 – 6.33 (m, 2H), 3.87 (s, 3H), 3.80 (d, J = 3.6 Hz, 3H), 2.22 (s, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 165.1, 161.8, 160.4, 153.1, 130.7, 129.9, 129.1 (2C), 113.8 (2C), 112.2, 109.0, 105.5, 55.6, 55.4, 17.4. ^{1}H-NMR spectral data is in accordance with the literature.[19b]

1-(4-methoxyphenyl)-N-phenylethan-1-imine (2c): ^{1}H NMR (250 MHz, CDCl3) δ 7.95 (d, J = 9.0 Hz, 2H), 7.42 – 7.29 (m, 2H), 7.12 – 7.02 (m, 1H), 7.01 – 6.90 (m, 2H), 6.80 (dd, J = 8.4, 1.2 Hz, 2H), 3.87 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 164.7, 161.7, 152.0, 132.3, 129.0 (2C), 129.0 (2C), 123.2, 119.7 (2C), 113.7 (2C), 55.5, 17.3. ^{1}H- and ^{13}C-NMR spectral data are in accordance with the literature.[19c]

1-(4-methoxyphenyl)-N-(naphthalen-2-yl)ethan-1-imine (2d): Pale yellow crystal, mp. 107 – 108 °C, purified by recrystallization, 61% yield. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.14 – 8.05 (m, 2H), 7.89 – 7.75 (m, 2H), 7.60 (d, J = 8.2 Hz, 1H), 7.53 – 7.35 (m, 3H), 7.06 – 6.97 (m, 2H), 6.79 (dt, J = 4.0, 2.0 Hz, 1H), 3.90 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 166.0, 162.1, 148.3, 134.5, 132.2, 129.4 (2C), 128.3, 126.5, 126.4, 126.2, 125.7, 124.0, 123.4, 114.1, 114.0 (2C), 55.8, 17.8. IR (ATR, cm^{-1}) 3060 (w), 3012 (w), 2975 (w), 2954 (w), 2840 (w), 2050 (w=, 1962 (w), 1913 (w), 1849 (w), 1821 (w), 1788 (w), 1632 (m), 1596 (m), 1504 (m), 1437 (m), 1360 (m), 1307 (m), 1251 (s), 1173 (m), 1024 (m), 960 (m), 838 (s), 777 (s), 572 (m). MS (EI, 70 eV): m/z (%) = 275 (80), $[M]^+$ 276 (16), 261 (20), 260 (100), 217 (20), 127 (64). HRMS (EI): Calculated for $C_{19}H_{17}NO$ $[M]^+$ 275.13047, found 275.13030.

N-(2,3-dihydro-1H-inden-5-yl)-1-(4-methoxyphenyl)ethan-1-imine (2e): Yellow solid, mp. 61 – 62°C, purified by Kugelrohr distillation, 54% yield. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.04 – 7.86 (m, 2H), 7.17 (d, J = 7.9 Hz, 1H), 7.01 – 6.86 (m, 2H), 6.67 (d, J = 1.2 Hz, 1H), 6.61 – 6.48 (m, 1H), 3.87 (s, 3H), 2.90 (t, J = 7.4 Hz, 4H), 2.22 (s, 3H), 2.17 – 2.02 (m, 2H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 161.6, 145.2, 138.9, 132.5, 130.7, 129.0 (2C), 124.6 (2C), 117.7, 115.9, 113.7 (2C), 55.5, 33.2, 32.5, 25.77, 17.3. IR (ATR, cm^{-1}) 3093 (w), 3015 (w), 2967 (w), 2931 (m), 2841 (m), 2062 (w), 2051 (w), 1983 (w), 1923 (w), 1671 (w), 1628 (m), 1598 (s), 1507 (m), 1483 (m), 1444 (m), 1364 (m), 1304 (m), 1255 (s), 1234 (m), 1173 (s), 1118 (m), 1027 (s), 839 (s), 832 (s), 573 (s). MS (EI, 70 eV): m/z (%) = 265 (47), $[M]^+$ 266 (9), 250 (100), 115 (30), 91 (13). HRMS (EI): Calculated for $C_{18}H_{19}ON$ $[M]^+$ 265.14612, found 265.14612.

N-(3,5-dimethylphenyl)-1-(4-methoxyphenyl)ethan-1-imine (2f): Yellow solid, mp. 74 – 75 °C, purified by Kugelrohr distillation, 54% yield. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.08 – 7.85 (m, 2H), 7.04 – 6.88 (m, 2H), 6.72 (s, 1H), 6.42 (s, 2H), 3.87 (s, 3H), 2.31 (s, 6H), 2.26 – 2.17 (m, 3H). 13C NMR (63 MHz, CDCl3) δ 164.4, 161.6 (2C), 151.9, 138.6, 132.4, 130.7, 128.9 (2C), 124.8, 117.4 (2C), 113.7 (2C), 55.5, 21.5, 17.31. IR (ATR, cm^{-1}) 3005 (w), 2959 (w), 2913 (m), 2838 (w), 2732 (w), 2052 (w), 1910 (w), 1626 (m), 1590 (s), 1509 (m), 1454 (m), 1366 (m), 1308 (m), 1251 (s), 1171 (m), 1028 (s), 829 (s), 689 (m), 571 (s). MS (EI, 70 eV): m/z (%) = 253 (51), $[M]^+$ 254 (10), 239 (21), 238 (100), 105 (13), 77 (17). HRMS (EI): Calculated for $C_{17}H_{19}ON$ $[M]^+$ 253.14612, found 253.14642.

N-(4-methoxyphenyl)-1-phenylethan-1-imine (2g): ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.02 – 7.91 (m, 2H), 7.49 – 7.37 (m, 3H), 6.97 – 6.85 (m, 2H), 6.81 – 6.71 (m, 2H), 3.82 (s, 3H), 2.26 (s, 3H). 13C NMR (63 MHz, $CDCl_3$) δ 166.0, 156.1, 144.9, 139.9, 130.5, 128.5 (2C),

127.3 (2C), 120.9 (2C), 114.4 (2C), 55.9, 17.5. ^{1}H- and ^{13}C-NMR spectral data are in accordance with the literature.[17]

N-(4-methoxyphenyl)-1-(4-(trifluoromethyl)phenyl)ethan-1-imine (2h): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, J = 8.1 Hz, 2H), 7.69 (d, J = 8.2 Hz, 2H), 6.93 (dd, J = 9.3, 2.7 Hz, 2H), 6.83 – 6.66 (m, 2H), 3.83 (s, 3H), 2.28 (s, 3H). 19F NMR (282 MHz, $CDCl_3$) δ -62.7. 13C NMR (63 MHz, CDCl3): δ 164.4, 156.3, 144.1, 142.9, 131.9 (q, J = 32.4 Hz), 127.5 (2C), 125.4 (q, J = 3.8 Hz) (2C), 124.1 (q, J = 269.9 Hz), 120.7 (2C), 114.3 (2C), 55.5, 17.4. ^{1}H- and ^{13}C-NMR spectral data are in accordance with the literature.[19d]

1-(4-fluorophenyl)-N-(4-methoxyphenyl)ethan-1-imine (2i): Orange solid, mp. 66 – 67 °C, purified by Kugelrohr distillation, 51% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 – 7.92 (m, 2H), 7.17 – 7.05 (m, 2H), 6.96 – 6.86 (m, 2H), 6.79 – 6.69 (m, 2H), 3.82 (s, 3H), 2.24 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -110.7. 13C NMR (126 MHz, $CDCl_3$) δ 164.5, 164.4 (d, J = 250.4 Hz), 156.2, 144.8, 136.1 (d, J = 3.1 Hz), 129.3 (d, J = 8.6 Hz) (2C), 120.9 (2C), 115.4 (d, J = 21.6 Hz) (2C), 114.4 (2C), 55.7, 17.4. ^{1}H- and ^{19}F-NMR spectral data are in accordance with the literature.[19e]

1-(4-fluorophenyl)-N-phenylethan-1-imine (2j): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 – 7.94 (m, 2H), 7.35 (t, J = 7.8 Hz, 2H), 7.21 – 7.05 (m, 3H), 6.84 – 6.76 (m, 2H), 2.22 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -105.34. 13C NMR (75 MHz, $CDCl_3$) δ 164.6 (d, J = 252 Hz), 164.5, 152.8, 136.1, 130.2 (d, J = 8.6 Hz), 130.2, 124.6, 120.2, 116.7 (d, J = 21.5 Hz), 17.5. ^{1}H- and ^{13}C-NMR spectral data are in accordance with the literature.[19f]

N-(4-fluorophenyl)-1-phenylethan-1-imine (2k): ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.24 (s, 3H), 6.74-6.78 (m, 2H), 7.04-7.08 (m, 2H), 7.43-7.49 (m, 3H), 7.96-7.99 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5, 159.5 (d, J = 241 Hz), 147.8 (d, J = 2.4 Hz), 139.5, 130.7, 128.4 (2C), 127.3 (2C), 120.8 (d, J = 8.2 Hz) (2C), 115.7 (d, J = 22 Hz) (2C), 17.4. ^{1}H- and ^{13}C-NMR spectral data are in accordance with the literature.[19c]

N,1-diphenylethan-1-imine (2l): Yellow solid, mp. 40 – 41 °C, purified by Kugelrohr distillation, 51% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 – 7.94 (m, 2H), 7.50 – 7.42 (m, 3H), 7.39 – 7.31 (m, 2H), 7.12 – 7.05 (m, 1H), 6.83 – 6.77 (m, 2H), 2.24 (s, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 165.5, 152.9, 140.3, 131.2, 129.7, 129.0, 128.0, 123.8, 120.0, 17.2. ^{1}H- and ^{13}C-NMR spectral data are in accordance with the literature.[17]

1-([1,1'-biphenyl]-4-yl)-N-phenylethan-1-imine (2m): Yellow solid, mp. 136 – 137 °C, purified by recrystallization, 71% yield. ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ 8.05 (d, J = 8.4

Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 8.0 Hz, 2H), 7.51-7.42 (m, 2H), 7.40-7.33 (m, 3H), 7.09 (t, J = 7.2 Hz, 1H), 6.81 (d, J = 7.6 Hz, 2H), 2.26 (s, 3H). 13C NMR (63 MHz, $CDCl_3$) δ 165.2, 151.9, 143.3, 140.6, 138.5, 129.1 (2C), 129.0 (2C), 127.9, 127.8 (2C), 127.3 (2C), 127.2 (2C), 123.4, 119.6 (2C), 17.5. ^{1}H- and ^{13}C-NMR spectral data are in accordance with the literature.[19g]

1-(naphthalen-2-yl)-N-phenylethan-1-imine (2n): ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 8.35 (s, 1H), 8.23 (d, J = 8.8 Hz, 2H), 7.96-7.85 (m, 3H), 7.59-7.48 (m, 2H), 7.38 (dd, J = 7.6 Hz, 7.6 Hz, 2H), 7.12 (t, J = 7.6 Hz, 1H), 6.84 (d, J = 7.6 Hz, 2H), 2.36 (s, 3H). 13C NMR (63 MHz, $CDCl_3$) δ 165.5, 151.8, 137.0, 134.6, 133.1, 129.1 (2C), 129.1, 128.2, 127.8 (2C), 127.3, 126.5, 124.4, 123.5, 119.6 (2C), 17.5. ^{1}H- and ^{13}C-NMR spectral data are in accordance with the literature.[19f]

N,1-di(naphthalen-2-yl)ethan-1-imine (2o): Brown crystal, mp. 136 – 137 °C, purified by recrystallization, yield 47%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.41 (dd, J = 8.7, 1.8 Hz, 1H), 8.02 – 7.80 (m, 5H), 7.63 (m, 1H), 7.60 – 7.54 (m, 2H), 7.52 – 7.39 (m, 3H), 6.86 (d, J = 7.2 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.7, 134.8, 134.4, 133.1, 129.7, 129.2, 128.6, 128.3, 128.2, 128.1, 127.9, 127.5, 126.6, 126.3, 126.2, 126.1, 125.6, 124.5, 123.8, 123.6, 113.8, 17.9. IR (ATR, cm^{-1}) 3468 (w), 3397 (w), 3239 (w), 3084 (w), 3050 (m), 3006 (w), 2963 (w), 2852 (w), 2704 (w), 2561 (w), 1938 (w), 1915 (w), 1848 (w), 1690 (w), 1625 (s), 1570 (m), 1504 (m), 1433 (w), 1387 (m), 1366 (m), 1292 (m), 1293 (m), 1223 (m), 1129 (m), 1080 (m), 1014 (m), 858 (m), 802 (m), 777 (s), 747 (m), 868 (m). MS (EI, 70 eV): m/z (%) = 295 (74), $[M]^+$ 296 (17), 281 (23), 280 (100), 153 (15), 127 (67), 126 (29). HRMS (EI): Calculated for $C_{22}H_{17}N$ $[M]^+$ 295.13555, found 295.13563.

General procedure for the synthesis of 4-azaindoles: 2-Bromo-3-chloropyridine **1b** (0.3 mmol), imine **2a** – **2o** (0.33 mmol), $Pd(OAc)_2$ (0.018 mmol), PCy_3 (0.036 mmol) and NaO*t*Bu (0.84 mmol) were put into a dried pressure tube. The tube was then evacuated and backfilled three times with argon. Dioxane (6 ml) was added to the tube, evacuated and backfilled three times again. The reaction mixture was sealed and stirred in 10 minutes under room temperature and was subsequently heated at 105 °C for 16 – 48 hours. The reaction was controlled by TLC for completion. After that, it was cooled down to room temperature, taken up in dichloromethane and filtered through zeolite. The solvent was removed by evaporation *in vacuo*. The residue was put into column chromatography using the elute mixture heptane/ethyl acetate.

1,2-bis(4-methoxyphenyl)-1H-pyrrolo[3,2-b]pyridine (3a): Yellow solid, mp. 188 – 189 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.50 – 7.29 (m, 1H), 7.16 (dt, J = 5.0, 2.8 Hz, 2H), 7.12 – 7.00 (m, 2H), 6.96 (dt, J = 13.7, 6.9 Hz, 1H), 6.87 (dt, J = 5.3, 3.2 Hz, 3H), 6.78 – 6.63 (m, 2H), 3.75 (d, J = 9.0 Hz, 3H), 3.71 (s, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 159.4, 158.8, 146.5 (2C), 144.2, 143.8, 132.4, 130.3 (2C), 128.9 (2C), 124.2, 117.5, 116.6, 114.6 (2C), 113.8 (2C), 102.9, 55.5, 55.2. IR (ATR, cm^{-1}) 3122 (w), 3076 (w), 2918 (m), 2848 (w), 2045 (w), 1923 (w), 1716 (w), 1608 (m), 1510 (s), 1498 (s), 1458 (m), 1414 (s), 1247 (s), 1186 (m), 1104 (m), 1025 (s), 923 (m), 834 (s), 800 (s), 789 (s), 729 (m), 644 (w), 580 (s). MS (EI, 70 eV): m/z (%) = 330 (100), $[M]^+$ 331 (24), 315 (28), 243 (17). HRMS (EI): Calculated for $C_{21}H_{18}N_2O_2$ $[M+H]^+$ 331.14410, found 331.14419.

1-(3-methoxyphenyl)-2-(4-methoxyphenyl)-1H-pyrrolo[3,2-b]pyridine (3b): Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.39 (dd, J = 4.7, 1.3 Hz, 1H), 7.46 (d, J = 8.2 Hz, 1H), 7.23 (t, J = 8.1 Hz, 1H), 7.19 – 7.13 (m, 2H), 6.97 (dd, J = 8.3, 4.7 Hz, 1H), 6.86 – 6.80 (m, 2H), 6.76 – 6.69 (m, 3H), 6.67 (t, J = 2.2 Hz, 1H), 3.69 (s, 3H), 3.64 (s, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 160.4, 159.6, 146.9, 144.3, 144.0, 138.8, 132.1, 130.4 (2C), 130.2, 124.3, 120.1, 117.6, 116.9, 113.9 (2C), 113.6, 113.4, 103.7, 55.5, 55.3. IR (ATR, cm^{-1}) 3036 (w), 2002 (w), 2933 (w), 2834 (w), 2926 (w), 2034 (w), 1891 (w), 1676 (w), 1588 (s), 1491 (s), 1454 (m), 1411 (s), 1281 (m), 1246 (s), 1172 (s), 1027 (s), 833 (m), 778 (s), 725 (m), 694 (m), 552 (m). MS (EI, 70 eV): m/z (%) = 330 (100), $[M]^+$ 331 (25), 315 (24), 243 (17). HRMS (EI): Calculated for $C_{21}H_{18}O_2N_2$ $[M]^+$ 330.13628, found 330.13602.

2-(4-methoxyphenyl)-1-phenyl-1H-pyrrolo[3,2-b]pyridine (3c): Yellow solid, mp. 137 – 138 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.43 (d, J = 8.1 Hz, 1H), 7.38 – 7.26 (m, 3H), 7.17 – 7.09 (m, 4H), 6.99 (d, J = 4.6 Hz, 1H), 6.85 (s, 1H), 6.76 – 6.67 (m, 2H), 3.69 (s, 3H). ^{13}C NMR (63 MHz, CDCl3) δ 159.6, 146.8, 144.1, 137.8, 132.2, 130.5 (2C), 129.6 (2C), 127.9 (2C), 127.7, 124.2, 117.6, 116.9, 113.9, 103.6, 55.3. IR (ATR, cm^{-1}) 3117 (w), 3060 (w), 2960 (w), 2834 (w), 1595 (m), 1500 (s), 1414 (s), 1242 (m), 1179 (m), 1023 (m), 834 (m), 782 (s), 700 (s), 598 (m). MS (EI, 70 eV): m/z (%) = 300 (100), $[M]^+$, 301 (23), 285 (39), 255 (27), 128 (10), 77 (10), 51(8). HRMS (EI): Calculated for $C_{20}H_{16}ON_2$ $[M]^+$ 300.12571, found 300.12513

2-(4-methoxyphenyl)-1-(naphthalen-2-yl)-1H-pyrrolo[3,2-b]pyridine (3d): Yellow solid, mp. 140 – 141 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.50 (d, J = 3.5 Hz, 1H), 7.94 (d, J = 8.2 Hz, 2H), 7.56 – 7.44 (m, 2H), 7.44 – 7.29 (m, 3H), 7.22 – 7.13 (m, 2H), 7.07 (d, J = 7.2 Hz, 2H), 6.97 (dd, J = 8.3, 4.6 Hz, 1H), 6.66 (d, J = 8.9 Hz, 2H), 3.69 (s, 3H). ^{13}C NMR (63 MHz,

$CDCl_3$) δ 159.6, 146.8, 145.5, 144.1, 134.5, 134.5, 133.4, 131.2, 129.8 (2C), 129.1, 128.6, 127.5, 127.3, 126.88, 125.7, 124.3, 123.2, 118.2, 116.9, 113.9 (2C), 103.1, 55.3. IR (ATR, cm^{-1}) 3048 (w), 2921 (w), 2850 (w), 1607 (m), 1496 (m), 1417 (m), 1251 (s), 1178 (m), 1024 (m), 842 (m), 806 (s), 797 (s), 773 (s), 590 (m), 539 (m). MS (EI, 70 eV): m/z (%) = 350 (100) $[M]^+$ 351 (22), 335 (17), 305 (20), 153 (11). HRMS (EI): Calculated for $C_{24}H_{18}N_2O$ $[M+H]^+$ 351.14919, found 351.14934

1-(2,3-dihydro-1H-inden-5-yl)-2-(4-methoxyphenyl)-1H-pyrrolo[3,2-b]pyridine (3e): Yellow solid, mp. 51 – 52 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 10.95 – 8.44 (m, 1H), 7.55 – 7.48 (m, 1H), 7.29 (d, J = 1.7 Hz, 1H), 7.28 – 7.23 (m, 2H), 7.10 (s, 1H), 7.06 (dd, J = 8.3, 4.7 Hz, 1H), 6.96 (dd, J = 7.9, 2.0 Hz, 1H), 6.93 (d, J = 0.7 Hz, 1H), 6.86 – 6.80 (m, 2H), 3.81 (s, 3H), 3.05 – 2.86 (m, 4H), 2.20 – 2.08 (m, 2H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 159.5, 146.8, 145.8, 144.2, 144.1, 144.0, 135.8, 132.5, 130.4 (2C), 125.9, 125.1, 124.5, 123.8, 117.7, 116.7, 113.9 (2C), 103.2, 55.4, 33.0, 32.7, 25.7. IR (ATR, cm^{-1}) 3038 (w), 3005 (w), 2924 (m), 2844 (m), 2197 (w), 2058 (w), 2035 (w), 1889 (w), 1722 (w), 1674 (w), 1068 (m), 1596 (w), 1496 (s), 1412 (s), 1281 (m), 1246 (s), 1174 (s), 1028 (m), 832 (m), 780 (s), 726 (m). MS (EI, 70 eV): m/z (%) = 340 (100), $[M]^+$ 341 (25), 325 (18), 156 (12), 115 (6). HRMS (EI): Calculated for $C_{23}H_{20}ON_2$ $[M]^+$ 340.15701, found 340.15685.

1-(3,5-dimethylphenyl)-2-(4-methoxyphenyl)-1H-pyrrolo[3,2-b]pyridine (3f): Yellow solid, mp. 143 – 144 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 8.38 (dd, J = 4.7, 1.4 Hz, 1H), 7.41 (dd, J = 8.2, 2.1 Hz, 1H), 7.19 – 7.13 (m, 2H), 6.96 (dd, J = 8.3, 4.7 Hz, 1H), 6.92 (s, 1H), 6.82 (d, J = 0.7 Hz, 1H), 6.76 – 6.72 (m, 3H), 6.72 – 6.69 (m, 1H), 3.70 (s, 3H), 2.22 (s, 6H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 159.5, 146.9, 144.1, 144.0, 139.3, 137.62, 132.3, 130.4 (2C), 129.5, 125.6 (2C), 124.5, 117.7, 116.7, 113.9 (2C), 103.3, 55.4, 21.4 (2C). IR (ATR, cm^{-1}) 3038 (w), 3008 (w), 2920 (w), 2837 (w), 1610 (m), 1594 (m), 1497 (s), 1413 (s), 1377 (m), 1250 (s), 1177 (m), 1037 (m), 837 (m), 783 (m). MS (EI, 70 eV): m/z (%) = 328 (100), $[M]^+$ 329 (25), 313 (21), 269 (13), 157 (12). HRMS (EI): Calculated for $C_{22}H_{20}ON_2$ $[M]^+$ 328.15701, found 328.15685.

1-(4-methoxyphenyl)-2-phenyl-1H-pyrrolo[3,2-b]pyridine (3g): Yellow solid, mp. 146 – 147 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 8.50 (d, J = 4.1 Hz, 1H), 7.50 (d, J = 8.2 Hz, 1H), 7.35 – 7.25 (m, 5H), 7.17 – 7.11 (m, 2H), 7.08 (dd, J = 8.3, 4.6 Hz, 1H), 6.99 (s, 1H), 6.94 (d, J = 8.9 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 158.9, 146.3, 144.2, 143.9, 132.6, 131.7, 130.2, 129.1 (2C), 128.9 (2C), 128.3 (2C), 127.9, 117.8, 116.9, 114.7 (2C), 103.8, 55.5. IR (ATR, cm^{-1}) 3128 (w), 3012 (w), 2921 (w), 2850 (w), 2044 (w), 1891 (w), 1852 (w),

1597 (m), 1510 (s), 1414 (s), 1245 (s), 1176 (m), 1022 (m), 843 (m), 769 (s), 696 (s), 583 (m). MS (EI, 70 eV): m/z (%) = 300 (100), $[M]^+$ 301 (22), 209 (19), 285 (18), 255 (22), 128 (11). HRMS (EI): Calculated for $C_{20}H_{16}ON_2$ $[M]^+$ 300.12571, found 300.12562.

1-(4-methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)-1H-pyrrolo[3,2-b]pyridine (3h): Yellow solid, mp. 143 – 144 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.52 (dd, J = 4.6, 1.4 Hz, 1H), 7.56 – 7.47 (m, 3H), 7.41 (d, J = 8.1 Hz, 2H), 7.16 – 7.06 (m, 3H), 7.04 (d, J = 0.7 Hz, 1H), 6.99 – 6.92 (m, 2H), 3.85 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.7. ^{13}C NMR (63 MHz, $CDCl_3$) δ 159.3, 146.4, 144.7, 142.2, 135.4, 133.0, 130.0, 129.8 (q, J = 32.6 Hz), 129.2 (2C), 129.0 (2C), 125.4 (q, J = 3.7 Hz) (2C), 124.1 (q, J = 272.1 Hz), 118.0, 117.7, 115.0 (2C), 105.2, 55.6. IR (ATR, cm^{-1}) 3044 (w), 3014 (w), 2959 (w), 2932 (w), 2840 (w), 1726 (w), 1616 (w), 1514 (s), 1416 (m), 1322 (s), 1317 (s), 1245 (m), 1167 (s), 1109 (s), 1061 (m), 856 (m), 804 (s), 758 (m), 623 (m). MS (EI, 70 eV): m/z (%) = 368 (100), $[M]^+$ 369 (23), 367 (19), 255 (11), 182 (11), 128 (11). HRMS (EI): Calculated for $C_{21}H_{15}ON_2F_3$ $[M]^+$ 368.11310, found 368.11256.

2-(4-fluorophenyl)-1-(4-methoxyphenyl)-1H-pyrrolo[3,2-b]pyridine (3i): Yellow solid, mp. 143 – 144 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.41 (d, J = 4.0 Hz, 1H), 7.39 (d, J = 8.2 Hz, 1H), 7.23 – 7.15 (m, 2H), 7.07 – 7.02 (m, 2H), 6.99 (dd, J = 8.3, 4.6 Hz, 1H), 6.92 (m, 1H), 6.90 – 6.83 (m, 4H), 3.76 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -113.25. ^{13}C NMR (63 MHz, $CDCl_3$) δ 162.6 (d, J = 248.6 Hz), 159.1, 146.5, 144.4, 143.1, 132.6, 131.0 (d, J = 8.2 Hz) (2C), 130.1, 129.0 (2C), 128.1 (d, J = 3.4 Hz), 117.8, 117.2, 115.6 (d, J = 21.7 Hz) (2C), 114.8 (2C), 103.9, 55.6. IR (ATR, cm^{-1}) 3117 (w), 3050 (w=, 3014 (w), 2916 (w), 2835 (w), 1600 (m), 1558 (w), 1515 (s), 1496 (s), 1419 (m), 1359 (m), 1248 (s), 1221 (m), 1158 (m), 1108 (m), 1024 (s), 840 (s), 681 (s), 577 (s). MS (EI, 70 eV): m/z (%) = 318 (100), $[M]^+$ 319 (23), 317 (17), 275 (18), 137 (9). HRMS (EI): Calculated for $C_{20}H_{15}ON_2F$ $[M]^+$ 318.11629, found 318.11615.

2-(4-fluorophenyl)-1-phenyl-1H-pyrrolo[3,2-b]pyridine (3j): Yellow solid, mp. 128 – 129 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.48 (d, J = 8.2 Hz, 1H), 7.42 – 7.28 (m, 3H), 7.26 – 7.08 (m, 4H), 7.08 – 6.97 (m, 1H), 6.95 – 6.82 (m, 3H). 19F NMR (282 MHz, $CDCl_3$) δ -112.85. ^{13}C NMR (63 MHz, $CDCl_3$) δ 162.7 (d, J = 249.0 Hz), 146.1, 143.8, 143.4, 137.3, 131.0 (d, J = 8.2 Hz) (2C), 129.8 (2C), 128.1, 127.9 (2C), 127.8 (d, J = 3.4 Hz), 118.3, 117.3, 115.6 (d, J = 21.7 Hz) (2C), 104.1. IR (ATR, cm^{-1}) 3046 (w), 2920 (w), 2851 (w), 1893 (w), 1596 (m), 1495 (s), 1412 (s), 1359 (m), 1219 (m), 1156 (m), 1013 (m), 835 (s), 798 (s), 782 (s), 696 (s), 594 (s). MS (EI, 70 eV): m/z (%) = 288 (100), $[M]^+$ 289 (20), 287 (47), 286 (15),

120 (7), 77 (12), 51 (12). HRMS (EI): Calculated for $C_{19}H_{13}FN_2$ $[M]^+$ 288.10573, found 288.10600.

1-(4-fluorophenyl)-2-phenyl-1H-pyrrolo[3,2-b]pyridine (3k): Yellow solid, mp. 120 – 121 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (dd, J = 4.6, 1.2 Hz, 1H), 7.49 (d, J = 8.2 Hz, 1H), 7.28 (s, 5H), 7.22 – 7.17 (m, 2H), 7.15 – 7.07 (m, 3H), 6.99 (s, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -113.2. ^{13}C NMR (63 MHz, $CDCl_3$) δ 161.8 (d, J = 248.2 Hz), 146.8, 144.6, 144.1, 133.7 (d, J = 3.0 Hz), 131.6, 129.5 (d, J = 8.5 Hz) (2C), 129.2 (2C), 128.5 (2C), 128.3, 117.6, 117.3, 116.6 (d, J = 22.8 Hz) (2C), 104.7. IR (ATR, cm^{-1}) 3054 (w), 2924 (w), 2853 (w), 1888 (w), 1599 (w), 1560 (w), 1507 (s), 1415 (s), 1221 (s), 1153 (m), 965 (m), 850 (m), 763 (s), 693 (s), 581 (s). MS (EI, 70 eV): m/z (%) = 288 (100), $[M]^+$ 289 (21), 287 (45), 286 (14), 143 (8), 75 (7). HRMS (EI): Calculated for $C_{19}H_{13}NF$ $[M]^+$ 288.10573, found 288.10531.

1,2-diphenyl-1H-pyrrolo[3,2-b]pyridine (3l): Yellow solid, mp. 117 – 118 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.49 (d, J = 4.3 Hz, 1H), 7.54 (d, J = 8.2 Hz, 1H), 7.46 – 7.34 (m, 3H), 7.28 – 7.25 (m, 4H), 7.24 – 7.20 (m, 2H), 7.20 – 7.17 (m, 1H), 7.07 (dd, J = 8.3, 4.6 Hz, 1H), 6.99 (d, J = 0.5 Hz, 1H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 146.7, 144.3, 144.1, 137.8, 132.4, 131.8, 129.6 (2C), 129.2 (2C), 128.4 (2C), 128.2, 127.9 (2C), 127.8, 117.9, 117.2, 104.5. IR (ATR, cm^{-1}) 3046 (w), 2920 (w), 2850 (w), 1595 (m), 1558 (w), 1598 (m), 1454 (w), 1412 (s), 1382 (m), 1327 (m), 1290 (m), 1178 (m), 1113 (m), 963 (m), 769 (s), 690 (s), 604 (s). MS (EI, 70 eV): m/z (%) = 270 (100), $[M]^+$ 271 (21), 269 (52), 268 (18), 77 (12), 51 (14). HRMS (EI): Calculated for $C_{19}H_{14}N_2$ $[M+H]^+$ 271.12297, found 271.12302. ^{1}H- and ^{13}C-NMR spectral data are in accordance with the literature.[19h]

2-([1,1'-biphenyl]-4-yl)-1-phenyl-1H-pyrrolo[3,2-b]pyridine (3m): Yellow solid, mp. 169 – 170 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.45 (d, J = 4.5 Hz, 1H), 7.55 – 7.25 (m, 13H), 7.24 – 7.15 (m, 2H), 7.07 – 6.97 (m, 2H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 146.7, 144.4, 143.7, 140.8, 140.3, 137.7, 132.5, 130.7, 129.7 (2C), 129.5 (2C), 128.9 (2C), 127.92 (2C), 127.9, 127.7, 127.1 (4C), 117.8, 117.2, 104.6. IR (ATR, cm^{-1}) 3113 (w), 3061 (w), 2921 (w), 2851 (w), 1920 (w), 1681 (w), 1596 (m), 1494 (m), 1411 (s), 1353 (m), 844 (m), 805 (m), 785 (m), 769 (s), 698 (s), 605 (m). MS (EI, 70 eV): m/z (%) = 346 (100), $[M]^+$ 347 (27), 345 (32), 269 (8), 77 (11), 51 (7). HRMS (EI): Calculated for $C_{25}H_{18}N_2$ $[M]^+$ 346.14645, found 346.14578.

2-(naphthalen-2-yl)-1-phenyl-1H-pyrrolo[3,2-b]pyridine (3n): Brownish solid, mp. 130 – 131 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.80 – 7.57 (m, 4H), 7.51 (d, J = 8.2 Hz, 1H), 7.44 – 7.13 (m, 8H), 7.11 – 6.97 (m, 2H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 146.6, 144.2,

137.7, 133.2, 132.8, 129.7 (2C), 129.2, 128.6, 128.4, 128.0, 127.9 (2C), 127.8, 126.7, 126.60, 126.6, 118.0, 117.3, 104.8. IR (ATR, cm^{-1}) 3053 (w), 2923 (w), 2851 (w), 1592 (m), 1497 (s), 1414 (s), 1288 (m), 865 (m), 827 (m), 781 (s), 759 (m), 693 (s). MS (EI, 70 eV): m/z (%) = 320 (100), $[M]^+$ 321 (26), 319 (49), 318 (16), 159 (7). HRMS (EI): Calculated for $C_{23}H_{16}N_2$ $[M+H]^+$ 320.13080, found 320.13045.

1,2-di(naphthalen-2-yl)-1H-pyrrolo[3,2-b]pyridine (3o): yellow solid, mp. 157 – 158 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 8.46 (dd, J = 4.6, 1.4 Hz, 1H), 7.85 (dd, J = 8.2, 3.4 Hz, 2H), 7.69 (d, J = 1.3 Hz, 1H), 7.63 – 7.54 (m, 1H), 7.52 – 7.44 (m, 2H), 7.43 – 7.38 (m, 1H), 7.38 – 7.33 (m, 2H), 7.32 – 7.25 (m, 4H), 7.23 (dd, J = 8.6, 1.8 Hz, 1H), 7.19 – 7.15 (m, 1H), 7.04 (ddd, J = 8.2, 1.4, 0.9 Hz, 1H), 6.92 (dd, J = 8.3, 4.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.7, 145.3, 144.4, 134.4, 134.3, 133.6, 133.0, 132.7, 131.1, 129.2, 129.1, 128.5, 128.2, 127.9, 127.8, 127.5, 127.5, 127.2, 126.8, 126.4, 126.3, 125.9, 125.5, 123.1, 118.2, 117.2, 104.4. IR (ATR, cm^{-1}) 3050 (w), 2923 (w), 2850 (w), 1595 (m), 1505 (m), 1465 (m), 1415 (m), 1399 (m), 1284 (m), 1016 (m), 863 (m), 798 (m), 770 (s), 755 (m), 663 (m), 589 (m). MS (EI, 70 eV): m/z (%) = 370 (100), $[M]^+$, 371 (31), 369 (36), 368 (13), 367 (15), 184 (13). HRMS (EI): Calculated for $C_{27}H_{18}N_2$ $[M]^+$ 370.14645, found 370.14572.

General procedure for the synthesis of 7-azaindoles: 2-Bromo-3-chloropyridine **1c** (0.3 mmol), imine **2a** – **2o** (0.33 mmol), $Pd(OAc)_2$ (0.018 mmol), PCy_3 (0.036 mmol) and NaO*t*Bu (0.84 mmol) were put into a dried pressure tube. The tube was then evacuated and backfilled with argon. Dioxane (6 ml) was added to the tube, evacuated and backfilled again. The reaction mixture was sealed and stirred in 10 minutes under room temperature and subsequently 16 – 48 hours at 105 °C. The reaction was controlled by TLC for completion. After that, it was cooled down to room temperature, taken up in dichloromethane and filtered through zeolite. The solvent was removed by evaporation *in vacuo*. The residue was put into column chromatography using the elute mixture heptane/ethyl acetate.

1,2-bis(4-methoxyphenyl)-1H-pyrrolo[2,3-b]pyridine (4a): White solid, mp. 145 – 146 °C. ^1H NMR (250 MHz, $CDCl_3$) δ 8.22 (dd, J = 4.7, 1.5 Hz, 1H), 7.85 (dd, J = 7.8, 1.5 Hz, 1H), 7.22 – 7.09 (m, 4H), 7.02 (dd, J = 7.8, 4.8 Hz, 1H), 6.92 – 6.82 (m, 2H), 6.78 – 6.69 (m, 2H), 6.56 (s, 1H), 3.75 (s, 3H), 3.71 (s, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 159.3, 158.6, 150.0, 143.2, 141.2, 130.2, 129.9, 129.5, 128.0, 124.6, 120.9, 116.8, 114.4, 113.8, 99.9, 77.5, 77.2, 77.0, 76.5, 55.4, 55.2. IR (ATR, cm^{-1}) 3114 (w), 3049 (w), 3018 (w), 2929 (w), 2835 (w), 2037 (w), 1905 (w), 1833 (w), 1610 (m), 1567 (w), 1515 (s), 1500 (s), 1454 (m), 1371 (m), 1301 (m), 1242 (s), 1184 (m), 1024 (m), 833 (s), 798 (s), 766 (s), 584 (m). MS (EI, 70 eV):

m/z (%) = 330 (83), $[M]^+$ 331 (18), 329 (100), 286 (11), 243 (17), 121 (7). HRMS (EI): Calculated for $C_{21}H_{18}N_2O_2$ $[M+H]^+$ 331.14410, found 331.14454.

1-(3-methoxyphenyl)-2-(4-methoxyphenyl)-1H-pyrrolo[2,3-b]pyridine (4b): Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.30 – 8.04 (m, 1H), 7.83 (t, J = 8.0 Hz, 1H), 7.32 – 7.06 (m, 3H), 7.06 – 6.93 (m, 1H), 6.92 – 6.62 (m, 5H), 6.55 (d, J = 9.6 Hz, 1H), 3.69 (d, J = 9.7 Hz, 3H), 3.63 (d, J = 9.7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.1, 159.5, 150.0, 143.4, 141.2, 138.3, 130.2 (2C), 129.8, 128.1, 124.8, 121.1, 121.0, 117.07, 114.3, 113.9 (2C), 113.5, 100.6, 55.5, 55.4. IR (ATR, cm^{-1}) 3041 (w), 3001 (w), 2933 (w), 2834 (w), 2222 8w), 2032 (w), 1920 (w), 1731 (w), 1604 (m), 1588 (m), 1498 (s), 1455 (m), 1406 (s), 1368 (m), 1283 (m), 1247 (s), 1173 (m), 1028 (m), 833 (m), 802 (m), 767 (m), 692 (m), 612 (m). MS (EI, 70 eV): m/z (%) = 330 (98), $[M]^+$ 331 (20), 329 (100), 243 (16), 121 (13). HRMS (EI): Calculated for $C_{21}H_{18}O_2N_2$ $[M]^+$ 330.13628, found 330.13539.

2-(4-methoxyphenyl)-1-phenyl-1H-pyrrolo[2,3-b]pyridine (4c): Yellow solid, mp. 138 – 139 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 (dd, J = 4.8, 1.6 Hz, 1H), 7.90 – 7.75 (m, 1H), 7.37 – 7.28 (m, 2H), 7.28 – 7.19 (m, 3H), 7.14 – 7.07 (m, 2H), 7.02 (dd, J = 7.8, 4.8 Hz, 1H), 6.75 – 6.63 (m, 2H), 6.56 (s, 1H), 3.68 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.8, 163.5, 159.3, 149.9, 143.3, 141.1, 137.2, 130.6, 130.2, 129.1, 128.5, 128.1, 127.3, 124.6, 121.0, 117.0, 113.8, 113.7, 100.5, 55.2. IR (ATR, cm^{-1}) 3044 (w), 3008 (w), 2953 (m), 2833 (m), 1674 (w), 1608 (m), 1500 (s), 1408 (s), 1368 (m), 1242 (s), 1182 (m), 1024 (s), 836 (m), 799 (s), 766 (s), 696 (s), 597 (s). MS (EI, 70 eV): m/z (%) = 300 (91), $[M]^+$, 301 (18), 299 (100), 285 (8), 255 (31), 128 (18), 51 (9). HRMS (EI): Calculated for $C_{20}H_{16}ON_2$ $[M]^+$ 300.12571, found 300.12482.

2-(4-methoxyphenyl)-1-(naphthalen-2-yl)-1H-pyrrolo[2,3-b]pyridine (4d): Yellow solid, mp. 123 – 124 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.13 (dd, J = 4.8, 1.6 Hz, 1H), 7.91 (dd, J = 7.8, 1.6 Hz, 1H), 7.87 – 7.77 (m, 2H), 7.48 – 7.30 (m, 3H), 7.29 – 7.18 (m, 2H), 7.10 – 6.97 (m, 3H), 6.69 (s, 1H), 6.62 – 6.47 (m, 2H), 3.58 (s, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 159.3, 150.9, 143.4, 142.5, 134.4, 134.2, 131.7, 129.5 (2C), 129.0, 128.5, 128.3, 128.1, 127.6, 127.0, 126.4, 125.5, 124.6, 123.5, 120.9, 116.9, 113.7 (2C), 100.0. IR (ATR, cm^{-1}) 3604 (w), 3388 (w), 3044 (w), 2961 (w), 2835 (w), 1609 (m), 1497 (s), 1469 (m), 1425 (m), 1298 (m), 1245 (s), 1176 (m), 1024 (m), 833 (m), 798 (s), 761 (s). MS (EI, 70 eV): m/z (%) = 350 (100) $[M]^+$, 351 (23), 349 (87), 305 (29), 243 (25), 153 (13). HRMS (EI): Calculated for $C_{24}H_{18}N_2O$ $[M+H]^+$ 351.14919, found 351.14934.

1-(2,3-dihydro-1H-inden-5-yl)-2-(4-methoxyphenyl)-1H-pyrrolo[2,3-b]pyridine (4e): Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 (dd, J = 4.7, 1.6 Hz, 1H), 7.83 (dd, J = 7.7, 1.7 Hz, 1H), 7.19 – 7.12 (m, 3H), 7.11 (s, 1H), 7.00 (dd, J = 7.8, 4.8 Hz, 1H), 6.94 (d, J = 7.8 Hz, 1H), 6.76 – 6.68 (m, 2H), 6.55 (s, 1H), 3.70 (s, 1H), 2.84 (t, J = 7.0 Hz, 4H), 2.09 – 1.93 (m, 2H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 159.3, 150.3, 145.3, 143.8, 143.3, 141.4, 135.3, 130.3 (2C), 128.0, 126.5, 125.0, 124.8, 124.6, 121.0, 116.8, 113.9 (2C), 100.0, 55.4, 33.1, 32.8, 25.7. IR (ATR, cm^{-1}) 3042 (w), 2944 (m), 2839 (w), 1675 (w), 1609 (m), 1499 (s), 1407 (m), 1248 (s), 1176 (m), 1030 (m), 834 (m), 803 (m), 769 (m). MS (EI, 70 eV): m/z (%) = 340 (79), $[M]^+$ 341 (17), 339 (100), 296 (10), 115 (12). HRMS (EI): Calculated for $C_{23}H_{19}ON_2$ $[M]^+$ 339.14919, found 339.14923.

1-(3,5-dimethylphenyl)-2-(4-methoxyphenyl)-1H-pyrrolo[2,3-b]pyridine (4f): Yellow solid, mp. 95 – 96 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.29 – 8.14 (m, 1H), 7.86 – 7.80 (m, 1H), 7.17 (d, J = 3.6 Hz, 1H), 7.13 (s, 1H), 7.01 (dd, J = 7.8, 4.8 Hz, 1H), 6.90 (s, 1H), 6.85 (s, 2H), 6.72 (d, J = 8.8 Hz, 2H), 6.55 (s, 1H), 3.71 (s, 3H), 2.22 (s, 6H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 159.3, 150.2, 143.3, 141.3, 138.7, 137.1, 130.7, 130.2 (2C), 129.6, 128.0, 126.5 (2C), 124.9, 121.0, 116.8, 113.8 (2C), 113.2, 100.1, 55.3, 21.5. IR (ATR, cm^{-1}) 3040 (w), 3006 (w), 2917 (w), 2836 (w), 1609 (m), 1546 (w), 1498 (s), 1473 (m), 1405 (s), 1369 (m), 1247 (s), 1175 (m), 1026 (m), 836 (m), 801 (m), 767 (m), 696 (m). MS (EI, 70 eV): m/z (%) = 328 (99), $[M]^+$ 329 (21), 327 (100), 313 (12), 312 (14), 269 (17), 157 (12), 135 (10). HRMS (EI): Calculated for $C_{22}H_{19}ON_2$ $[M-H]^+$ 327.14919, found 327.14906.

1-(4-methoxyphenyl)-2-phenyl-1H-pyrrolo[2,3-b]pyridine (4g): Yellow solid, mp. 188 – 189 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.24 (dd, J = 4.7, 1.6 Hz, 1H), 7.87 (dd, J = 7.8, 1.6 Hz, 1H), 7.28 – 7.11 (m, 7H), 7.03 (dd, J = 7.8, 4.7 Hz, 1H), 6.90 – 6.82 (m, 1H), 6.63 (s, 1H), 3.74 (s, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 158.7, 150.1, 143.5, 141.2, 132.2, 129.8, 129.4 (2C), 128.9 (2C), 128.3, 128.3 (2C), 127.7, 120.8, 116.9, 114.4 (2C), 100.9, 55.4. IR (ATR, cm^{-1}) 3067 (w), 3043 (w), 3010 (w), 2840 (w), 1901 (w), 1856 (w), 1604 (w), 1510 (m), 1419 (m), 1236 (s), 1025 (s), 842 (m), 806 (m), 752 (s), 693 (s), 556 (s). MS (EI, 70 eV): m/z (%) = 300 (68), $[M]^+$ 301 (13), 299 (100), 256 (27), 128 (9). HRMS (EI): Calculated for $C_{20}H_{15}ON_2$ $[M]^+$ 299.11789, found 299.11775.

1-(4-methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)-1H-pyrrolo[2,3-b]pyridine (4h): Yellow solid, mp. 158 – 159 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 (dd, J = 4.7, 1.6 Hz, 1H), 7.89 (dd, J = 7.8, 1.6 Hz, 1H), 7.45 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 7.23 – 7.11 (m, 2H), 7.05 (dd, J = 7.8, 4.7 Hz, 1H), 6.94 – 6.83 (m, 2H), 6.70 (s, 1H), 3.75 (s, 3H). ^{13}C

NMR (63 MHz, $CDCl_3$) δ 159.0, 150.5, 144.5, 139.5, 135.8, 129.7 (q, J = 32.6 Hz), 129.6, 129.5 (2C), 129.0 (2C), 128.9, 125.4 (q, J = 3.8 Hz) (2C), 124.2 (q, J = 272.1 Hz), 120.6, 117.3, 114.7 (2C), 102.3, 55.6. IR (ATR, cm^{-1}) 3020 (w), 2971 (w), 2843 (w), 2549 (w), 2315 (w), 2051 (w), 1934 (w), 1869 (w), 1613 (m), 1567 (w), 1515 (s), 1468 (m), 1442 (m), 1323 (s), 1300 (m), 1250 (s), 1162 (s), 1115 (s), 1028 (m), 918 (m), 844 (s), 800 (s), 764 (s), 591 (m), 561 (m). MS (EI, 70 eV): m/z (%) = 368 (69), $[M]^+$ 369 (13), 367 (100), 324 (22), 323 (10), 255 (7). HRMS (EI): Calculated for $C_{21}H_{14}ON_2F_3$ $[M]^+$ 367.10527, found 367.10514.

2-(4-fluorophenyl)-1-(4-methoxyphenyl)-1H-pyrrolo[2,3-b]pyridine (4i): Yellow solid, mp. 173 – 174 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 8.24 (dd, J = 4.7, 1.6 Hz, 1H), 7.86 (dd, J = 7.8, 1.6 Hz, 1H), 7.23 – 7.10 (m, 4H), 7.04 (dd, J = 7.8, 4.7 Hz, 1H), 6.94 – 6.83 (m, 4H), 6.59 (s, 1H), 3.75 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -113.6. ^{13}C NMR (63 MHz, $CDCl_3$) δ 162.5 (d, J = 248.2 Hz), 158.9, 150.2, 143.9, 140.3, 130.8 (d, J = 8.1 Hz) (2C), 129.8, 129.6 (2C), 128.5, 128.4, 120.8, 117.1, 115.5 (d, J = 21.7 Hz) (2C), 114.6 (2C), 100.9, 55.6. IR (ATR, cm^{-1}) 3103 (w), 3014 (w), 2969 (w), 2841 (w), 2050 (w), 1893 (w), 1602 (w), 1511 (s), 1496 (s), 1297 (m), 1245 (s), 1152 (m), 1106 (m), 1029 (m), 834 (s), 813 (s), 773 (s), 581 (s). MS (EI, 70 eV): m/z (%) = 318 (67), $[M]^+$ 319 (12), 317 (100), 274 (29), 273 (21), 137 (7), 63 (8). HRMS (EI): Calculated for $C_{20}H_{14}ON_2F$ $[M-H]^+$ 317.10847, found 317.10836.

2-(4-fluorophenyl)-1-phenyl-1H-pyrrolo[2,3-b]pyridine (4j): White solid, mp. 141 – 142 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 8.34 (d, J = 3.7 Hz, 1H), 8.03 – 7.91 (m, 1H), 7.48 – 7.23 (m, 7H), 7.15 (dd, J = 7.8, 4.7 Hz, 1H), 7.02 – 6.90 (m, 2H), 6.70 (s, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -113.4. ^{13}C NMR (63 MHz, $CDCl_3$) δ 162.6 (d, J = 248.4 Hz), 149.8, 143.8, 140.3, 136.9, 130.8 (d, J = 8.2 Hz) (2C), 129.3 (2C), 128.6, 128.5 (2C), 128.4 (d, J = 3.4 Hz), 127.7, 121.0, 117.3, 115.5 (d, J = 21.7 Hz) (2C), 101.5. IR (ATR, cm^{-1}) 3064 (w), 3043 (w), 2921 (w), 1589 (m), 1543 (m), 1496 (s), 1424 (m), 1402 (m), 1220 (s), 1157 (m), 840 (s), 802 (s), 768 (s), 691 (s), 592 (s), 539 (m). MS (EI, 70 eV): m/z (%) = 288 (62), $[M]^+$ 289 (10), 287 (100), 286 (21), 143 (6), 51 (7). HRMS (EI): Calculated for $C_{19}H_{13}FN_2$ $[M+H]^+$ 289.11355, found 289.11359.

1-(4-fluorophenyl)-2-phenyl-1H-pyrrolo[2,3-b]pyridine (4k): Yellow solid, mp. 164 – 165 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 8.31 (dd, J = 4.7, 1.6 Hz, 1H), 7.95 (dd, J = 7.8, 1.6 Hz, 1H), 7.35 – 7.20 (m, 7H), 7.16 – 7.04 (m, 3H), 6.71 (d, J = 3.6 Hz, 1H). ^{19}F NMR (282 MHz, CDCl3) δ -114.4. ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.7 (d, J = 247.1 Hz), 150.1, 143.8, 141.2, 133.1 (d, J = 3.2 Hz), 132.0, 130.1 (d, J = 8.6 Hz) (2C), 129.1 (2C), 128.6, 128.5 (2C), 128.1, 121.0, 117.3, 116.1 (d, J = 22.8 Hz) (2C), 101.6. IR (ATR, cm^{-1}) 3110 (w), 3059 (w), 3008

(w), 2924 (w), 1907 (w), 1858 (w), 1675 (w), 1568 (w), 1508 (m), 1420 (m), 1208 (m), 1096 (w), 852 (m), 804 (s), 747 (s). 698 (s), 552 (m). MS (EI, 70 eV): m/z (%) = 288 (60), $[M]^+$ 289 (10), 287 (100), 286 (21), 75 (11). HRMS (EI): Calculated for $C_{19}H_{12}FN_2$ $[M-H]^+$ 287.09790, found 287.09747.

1,2-diphenyl-1H-pyrrolo[2,3-b]pyridine (4l): White solid, mp. 130 – 132 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.33 (dd, J = 4.7, 1.6 Hz, 1H), 7.97 (dd, J = 7.8, 1.6 Hz, 1H), 7.48 – 7.26 (m, 10H), 7.14 (dd, J = 7.8, 4.7 Hz, 1H), 6.74 (s, 1H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 150.1, 143.8, 141.3, 137.2, 132.3, 129.2 (2C), 129.1 (2C), 128.5 (3C), 128.4 (2C), 127.9, 127.5, 121.0, 117.2, 101.6. IR (ATR, cm^{-1}) 3116 (w), 3064 (w), 2925 (w), 1852 (w), 1594 (m), 1540 (m), 1496 (s), 1474 (m), 1425 (m), 1401 (m), 1370 (m), 1224 (s), 1158 (m), 841 (m), 799 (s), 767 (s), 692 (s), 593 (s). MS (EI, 70 eV): m/z (%) = 270 (59), $[M]^+$ 271 (11), 269 (100), 268 (21), 135 (8). HRMS (EI): Calculated for $C_{19}H_{14}N_2$ $[M+H]^+$ 271.12297, found 271.12322. ^{1}H- and ^{13}C-NMR spectral data are in accordance with the literature.[19i]

2-([1,1'-biphenyl]-4-yl)-1-phenyl-1H-pyrrolo[2,3-b]pyridine (4m): White solid, mp. 182 – 183 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.36 (dd, J = 4.7, 1.5 Hz, 1H), 7.99 (dd, J = 7.8, 1.5 Hz, 1H), 7.63 – 7.33 (m, 14H), 7.15 (dd, J = 7.8, 4.7 Hz, 1H), 6.80 (s, 1H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 150.2, 143.8, 140.9, 140.5, 140.4, 137.2, 131.1, 129.3 (2C), 129.3 (2C), 128.9 (2C), 128.6 (2C), 128.5, 127.6, 127.5 (2C), 127.1 (2C), 127.0, 121.0, 117.2, 101.6. IR (ATR, cm^{-1}) 3110 (w), 3050 (w), 3034 (w), 3001 (w), 1591 (w), 1500 (m), 1421 (m), 1293 (w), 1247 (w), 997 (w), 842 (m), 807 (m), 760 (s), 694 (s), 610 (w). MS (EI, 70 eV): m/z (%) = 345 (100), $[M]^+$, 347 (19), 346 (84), 268 (8), 173 (6), 77 (9). HRMS (EI): Calculated for $C_{25}H_{18}N_2$ $[M+H]^+$ 347.15419, found 347.15428.

2-(naphthalen-2-yl)-1-phenyl-1H-pyrrolo[2,3-b]pyridine (4n): Yellow solid, mp. 180 – 181 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.37 (dd, J = 4.7, 1.5 Hz, 1H), 8.01 (dd, J = 7.8, 1.5 Hz, 1H), 7.90 – 7.65 (m, 4H), 7.54 – 7.43 (m, 2H), 7.43 – 7.30 (m, 6H), 7.17 (dd, J = 7.8, 4.7 Hz, 1H), 6.87 (s, 1H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 150.1, 143.8, 141.2, 137.2, 133.3, 132.8, 129.7, 129.3 (2C), 128.6, 128.5 (2C), 128.3, 128.3, 127.9, 127.8, 127.5, 126.6, 126.6, 126.5, 121.1, 117.3, 102.0. IR (ATR, cm^{-1}) 3053 (w), 2923 (w), 2851 (w), 1957 (w), 1930 (w), 1879 (w), 1865 (w), 1674 (w), 1592 (m), 1499 (m), 1416 (s), 1293 (m), 827 (m), 802 (s), 772 (s), 755 (s), 596 (s), 578 (m). MS (EI, 70 eV): m/z (%) = 320 (68), $[M]^+$ 321 (15), 319 (100), 318 (22), 317 (10), 159 (13). HRMS (EI): Calculated for $C_{23}H_{16}N_2$ $[M+H]^+$ 321.13862, found 321.13885.

1,2-di(naphthalen-2-yl)-1H-pyrrolo[2,3-b]pyridine (4o): Yellow solid, mp. 168 – 169 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.29 (dd, J = 4.7, 1.6 Hz, 1H), 8.07 (dd, J = 7.8, 1.6 Hz, 1H), 7.96 – 7.87 (m, 2H), 7.75 (d, J = 1.3 Hz, 1H), 7.71 – 7.64 (m, 1H), 7.60 – 7.51 (m, 2H), 7.51 – 7.45 (m, 2H), 7.45 – 7.42 (m, 1H), 7.42 – 7.34 (m, 4H), 7.31 (dd, J = 8.6, 1.8 Hz, 1H), 7.17 (dd, J = 7.8, 4.7 Hz, 1H), 7.00 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.2, 144.0, 142.5, 134.4, 134.2, 133.0, 132.6, 131.7, 129.5, 129.1, 128.5, 128.4, 128.2, 127.7, 127.7, 127.5 (2C), 127.1, 126.5, 126.3, 126.2, 125.8, 125.5, 123.4, 120.8, 117.1, 101.4. IR (ATR, cm^{-1}) 3052 (w), 2922 (w), 2851 (w), 1929 (w), 1595 (m), 1415 (m), 1297 (m), 958 (w), 786 (m), 768 (s), 758 (s). MS (EI, 70 eV): m/z (%) = 370 (99), $[M]^+$ 371 (28), 369 (100), 367 (16), 243 (25), 184 (10), 127 (11), 77 (6). HRMS (EI): Calculated for $C_{27}H_{18}N_2$ $[M]^+$ 370.14645, found 370.14531.

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