**Supplementary Material**

**Fast and efficient direct conversion of 2-aminopyridine into 2,3-disubstituted imidazo[1,2-a]pyridines**

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1. **Description of 2D NMR spectra**

The NMR spectra of imidazo[1,2-a]pyridines 3 show a doublet for a methyl group, CH neighbour to CH₃, and a quaternary carbon at 123-125 ppm. The vinylated products 4 show characteristic signals for a terminal C=CH₂, close to o-protons of Ar-3 (NOESY), C₉-1 of Ar-3 (HMBC), and C₉-3 (HMBC). The spectra of compound 5e show an additional singlet for aromatic CH, which is close to CH-5 (NOESY), o-protons of 4-MeOPh-2 (NOESY), and C₉-2 (HMBC); no CH-CH₃ and only one 4-methoxyphenyl group. The spectra of pyrido[1,2-a]pyrimidine 6f show a singlet for a methyl group, an additional singlet for aromatic CH and a quaternary carbon at 65 ppm.

**2-Phenyl-3-(1-phenylethyl)imidazo[1,2-a]pyridine (3a).** COSY cross peaks 1.841/5.048, 6.592/7.140, 6.592/7.627, 7.140/7.679, 7.269/7.339, 7.403/7.483, 7.483/7.778; NOESY cross peaks 1.841/5.048, 1.841/7.627, 5.048/7.778, 6.592/7.140, 6.592/7.627, 7.140/7.679, 7.269/7.339, 7.269/7.627 (weak), 7.403/7.483, 7.483/7.778; HSQC cross peaks 1.841/16.70, 5.048/33.78, 6.592/111.56, 7.140/123.74, 7.269/126.61, 7.269/126.80, 7.339/128.81, 7.403/127.68, 7.483/128.42, 7.627/124.53, 7.679/117.78, 7.778/128.92; HMBC cross peaks 1.841/33.78, 1.841/122.96, 1.841/141.11, 5.048/16.70, 5.048/122.96, 5.048/126.80, 5.048/141.11, 5.048/143.76 (weak), 6.592/117.78, 6.592/124.53, 7.140/124.53, 7.140/144.86,
2-(4-Methylphenyl)-3-(1-(4-methylphenyl)ethyl)imidazo[1,2-a]pyridine (3b). COSY cross peaks 1.691/4.889, 6.463/7.025, 6.463/7.515, 7.025/7.555, 7.174/7.555; NOESY cross peaks 1.691/4.889, 1.691/7.025, 1.691/7.515, 2.230/7.025, 2.315/7.174, 4.889/7.025, 4.889/7.515, 6.463/7.025, 6.463/7.515, 7.025/7.555, 7.174/7.555; HSQC cross peaks 1.691/16.75, 2.230/20.95, 2.315/21.29, 4.889/33.49, 6.463/111.45 (td, 1H, J 1.12, 6.8, CH-6), 7.025/123.61, 7.025/126.74, 7.025/129.52, 7.174/129.18, 7.174/129.52, 7.577/111.71, 7.555/128.82; HMBC cross peaks 1.691/33.49, 1.691/122.96, 1.691/138.12, 2.230/129.52, 2.230/136.16, 2.315/129.18, 2.315/137.43, 4.889/16.75, 4.889/129.96, 4.889/126.74 (weak), 4.889/138.12, 6.463/117.71, 6.463/124.64, 7.025/20.95, 7.025/33.49, 7.025/124.64, 7.025/126.74, 7.025/129.52, 7.025/136.16, 7.025/138.18, 7.025/144.83, 7.174/21.29, 7.174/129.18, 7.174/132.18, 7.515/123.61, 7.515/144.83, 7.555/111.45, 7.555/128.82, 7.555/137.43, 7.555/143.74.

2-(4-Fluorophenyl)-3-(1-(4-fluorophenyl)ethyl)imidazo[1,2-a]pyridine (3c). COSY cross peaks 1.800/4.900, 6.611/7.145, 6.611/7.577, 6.998/7.180, 7.145/7.673, 7.145/7.642; NOESY cross peaks 1.800/4.900, 1.800/7.180, 1.800/7.577, 4.900/17.04 (weak), 4.900/7.025, 6.611/7.145, 6.611/7.577, 6.998/7.180, 7.145/7.642, 7.145/7.673; HSQC cross peaks 1.800/7.025, 4.900/33.27, 6.611/111.92, 6.998/115.44, 6.998/115.59, 7.145/115.67, 7.145/115.81, 7.145/124.14, 7.180/128.33, 7.180/128.38, 7.577/124.39, 7.642/117.87, 7.673/130.57, 7.673/130.62; HMBC cross peaks 1.800/33.27, 1.800/122.62, 1.800/136.63, 1.800/136.65, 4.900/17.04, 4.900/115.67 (weak), 4.900/115.81 (weak), 4.900/122.62, 4.900/126.33, 4.900/128.38, 4.900/136.63, 4.900/136.65, 4.900/142.86 (weak), 6.611/117.87, 6.611/124.39, 6.998/115.67, 6.998/115.81, 6.998/115.98, 6.998/116.08, 6.998/124.14, 7.145/115.81, 7.145/124.39, 7.145/130.99, 7.145/131.01, 7.145/144.90, 7.145/161.81, 7.145/163.44, 7.180/33.27, 7.180/128.33, 7.180/128.38, 7.180/160.80, 7.180/162.43, 7.577/111.92, 7.577/124.14, 7.577/144.90, 7.642/111.92, 7.642/144.90 (weak), 7.673/130.57, 7.673/130.62, 7.673/142.86, 7.673/161.81, 7.673/163.44.

2-(Naphthalen-1-yl)-3-(1-(naphthalen-1-yl)ethyl)imidazo[1,2-a]pyridine (3d). COSY cross peaks 1.754/4.751, 6.578/7.145, 6.578/7.727, 7.145/7.697; NOESY cross peaks 1.754/4.751, 1.754/7.727, 4.751/7.727, 6.578/7.145, 6.578/7.727, 7.145/7.697; HSQC cross peaks 1.754/17.56, 4.751/34.70, 6.578/111.91, 7.145/123.97, 7.697/117.90, 7.727/124.36; HMBC cross peaks 1.754/34.70, 1.754/124.57, 1.754/139.07, 4.751/17.56, 4.751/139.07, 4.751/143.07, 6.578/117.90, 7.145/124.36, 7.145/144.81, 7.643/143.07, 7.727/123.97, 7.727/144.81.

2-(4-Methoxyphenyl)-3-(1-(4-methoxyphenyl)ethyl)imidazo[1,2-a]pyridine (3e). COSY cross peaks 1.774/4.928, 6.559/7.099, 6.559/7.601, 6.838/7.146, 6.991/7.668, 7.099/7.626; NOESY cross peaks 1.774/4.928, 1.774/7.146, 1.774/7.601, 3.776/6.838, 3.848/6.991, 4.928/7.146 (weak), 4.928/7.601, 6.559/7.099, 6.559/7.601, 6.838/7.146, 6.991/7.668, 7.099/7.626, 7.146/7.668, 7.146/7.601; HSQC cross peaks 1.774/16.88, 3.776/55.27, 3.848/55.33, 4.928/33.08, 6.559/111.50, 6.838/114.17, 6.991/113.95, 7.099/123.68, 7.146/127.87,
7.601/124.60, 7.626/117.58, 7.668/130.10; HMBC cross peaks 1.774/33.08, 1.774/122.73, 1.774/133.10, 3.776/158.22, 3.848/159.32, 4.928/16.88, 4.928/122.73, 4.928/127.52 (weak), 4.928/133.10, 6.559/117.58, 6.559/124.60, 6.838/114.17, 6.838/133.10, 6.838/158.22 (weak), 6.991/119.55, 6.991/127.52, 6.991/159.32 (weak), 7.099/124.60, 7.099/144.77, 7.146/33.08, 7.146/127.87, 7.146/158.22, 7.601/123.68, 7.601/144.77, 7.626/111.50, 7.668/130.10, 7.668/143.38, 7.668/159.32.

2-(4-Phenyl)-3-(1-(4-phenyl)vinyl)imidazo[1,2-a]pyridine (4a). COSY cross peaks 5.580/6.170, 6.653/7.177, 6.653/7.634, 7.177/7.685, 7.264/7.333, 7.333/7.387, 7.333/7.934; NOESY cross peaks 5.580/6.170, 6.170/7.387, 6.653/7.177, 6.653/7.634, 7.177/7.685, 7.264/7.333, 7.333/7.387, 7.333/7.934; HSQC cross peaks 5.580/121.42, 6.170/121.42, 6.653/112.24, 7.177/124.71, 7.264/127.63, 7.333/128.32, 7.333/128.78, 7.333/129.06, 7.387/126.17, 7.634/124.28, 7.685/117.35, 7.934/127.88; HMBC cross peaks 5.580/120.12, 5.580/137.58, 6.170/120.12, 6.170/137.58, 6.653/117.35, 6.653/124.28, 7.177/124.28, 7.177/144.81, 7.264/127.88, 7.333/128.32, 7.333/128.78, 7.333/129.06, 7.333/133.93, 7.333/137.58, 7.387/126.17, 7.387/128.78, 7.387/137.58, 7.634/112.24, 7.634/124.71, 7.634/144.81, 7.685/112.24, 7.685/144.81 (weak), 7.934/127.88, 7.934/143.37.

2-(4-Methoxyphenyl)-3-(1-(4-methoxyphenyl)vinyl)imidazo[1,2-a]pyridine (4e). COSY cross peaks 5.485/6.087, 6.660/7.174, 6.660/7.668, 6.863/7.330, 6.898/7.903, 7.174/7.668; NOESY cross peaks 3.809/6.863, 3.824/6.898, 5.485/6.087, 6.087/7.330, 6.660/7.174, 6.660/7.668, 6.863/7.330, 6.898/7.903, 7.174/7.668; HSQC cross peaks 5.485/119.10, 6.087/119.10, 6.660/111.99, 6.863/114.37, 6.898/113.76, 7.174/124.41, 7.330/127.48, 7.668/124.23, 7.668/117.12, 7.934/129.06; HMBC cross peaks 5.485/119.54, 5.485/130.11, 5.485/137.17 (weak), 6.087/119.54, 6.087/130.11, 6.087/137.17 (weak), 6.660/117.12, 6.660/124.23, 6.863/114.37, 6.863/130.11, 6.863/160.08 (weak), 6.898/113.76, 6.898/126.75, 6.898/159.20 (weak), 7.174/124.23, 7.174/144.80, 7.330/127.48, 7.330/137.17, 7.330/160.08, 7.668/111.99, 7.668/124.41, 7.668/144.80, 7.903/129.06, 7.903/143.12, 7.903/159.20.

2-(4-Nitrophenyl)-3-(1-(4-nitrophenyl)vinyl)imidazo[1,2-a]pyridine (4f). COSY cross peaks 6.821/7.316, 6.821/7.738, 7.316/7.728, 7.528/8.193, 8.039/8.176; NOESY cross peaks 5.889/6.473, 5.889/7.738, 5.889/8.039 (weak), 6.473/7.528, 6.473/8.039 (weak), 6.821/7.316, 6.821/7.738, 7.316/7.728, 7.528/8.193, 8.039/8.176; HSQC cross peaks 5.889/125.69, 6.473/125.69, 6.821/113.56, 7.316/126.23, 7.528/126.96, 7.728/117.95, 7.738/123.90, 8.039/128.22, 8.176/123.83, 8.193/124.54; HMBC cross peaks 5.889/120.34, 5.889/135.76 (weak), 5.889/143.35, 6.473/120.34, 6.473/135.76 (weak), 6.473/143.35, 6.821/117.95, 6.821/123.90, 7.316/123.90, 7.316/145.45, 7.528/126.96, 7.728/135.76, 7.528/148.08, 7.728/113.56, 7.728/145.45 (weak), 7.738/126.23, 7.738/145.45 (weak), 8.039/123.83 (weak), 8.039/128.22, 8.039/141.17, 8.039/147.10, 8.176/123.83, 8.176/128.22 (weak), 8.176/139.99, 8.176/147.10, 8.193/124.54, 8.193/143.35, 8.193/148.08.

2-(4-Methoxyphenyl)imidazo[1,2-a]pyridine (5e). COSY cross peaks 6.748/7.152, 6.748/8.081, 6.988/7.901, 7.152/7.620; NOESY cross peaks 3.862/6.988, 6.748/7.152,
6.748/8.081, 6.988/7.901, 7.152/7.620, 7.764/7.901, 7.764/8.081; HSQC cross peaks 3.862/55.33, 6.748/112.25, 6.988/114.15, 7.152/124.47, 7.620/117.28, 7.764/107.26, 7.901/127.30, 8.081/125.49; HMBC cross peaks 3.862/159.58, 6.748/117.28, 6.748/125.49, 6.988/114.15, 6.988/127.30, 7.152/145.63, 7.620/107.26 (weak), 7.620/112.25, 7.620/145.63, 7.764/145.72, 7.901/107.26 (weak), 7.901/112.25, 7.901/126.50 (weak), 7.901/127.30, 7.901/145.72, 7.901/159.58, 8.081/112.25, 8.081/124.47, 8.081/145.63.

4-Methyl-2,4-bis(4-nitrophenyl)-4H-pyrido[1,2-a]pyrimidine (6f). COSY cross peaks 6.039/6.743, 6.039/6.962, 6.723/6.962, 7.636/8.173, 7.834/8.093; NOESY cross peaks 2.111/5.106, 2.111/6.743, 2.111/7.636, 5.106/7.636 (weak), 5.106/7.834, 6.039/6.743, 6.039/6.962, 6.723/6.962, 7.636/8.173, 7.834/8.093; HSQC cross peaks 2.111/29.32, 5.106/110.05, 6.723/124.83, 6.743/133.47, 6.962/134.71, 7.636/127.35, 7.834/126.39, 8.093/123.44, 8.173/124.16; HMBC cross peaks 2.111/64.90, 2.111/105.05, 2.111/152.87, 5.106/29.32, 5.106/64.90, 5.106/144.89, 5.106/152.87 (weak), 6.039/124.83, 6.039/133.47, 6.723/110.05, 6.743/134.71, 6.743/151.48, 6.962/133.47, 6.962/151.48, 7.636/127.35, 7.636/147.33, 7.834/126.39, 7.834/140.11, 7.834/147.41, 8.093/123.44, 8.093/144.89, 8.093/147.41 (weak), 8.173/124.16, 8.173/147.33 (weak), 8.173/152.87.

2. Crystallography
2-Phenyl-3-(1-phenylethyl)imidazo[1,2-a]pyridine (3a). Crystals of 3a were obtained from a CH2Cl2/heptane solution. An ORTEP view of the molecule is reported on Figure 2 together with the atomic labeling scheme. Selected bond lengths [Å]: C11–N12 1.312(6), C21–N22 1.330(6), N12–C13 1.346(6), N22–C23 1.382(6), C13–C14 1.358(7), C23–C24 1.397(6), C116–C117 1.544(6), C216–C217 1.551(6), C14–C116 1.516(6), C24–C216 1.502(6). Compound 3a crystallizes in the monoclinic centrosymmetric P 21/c space group, with two independent molecules in the asymmetric unit (Table S1). Both R and S enantiomers are present in the crystals as seen on Figure S1. The majority of bond lengths and angles are comparable in the two independent molecules. The ring systems are nearly planar with respective rmsd of (0.0122, 0.0114), (0.0095, 0.0041) and (0.0051, 0.0049) for the imidazo[1,2-a]pyridine, 2-phenyl and the 3-phenyl substituents in the two molecules. The angles between the mean planes of the imidazole/2-phenyl and imidazole/3-phenyl rings are also similar in the two molecules: 39.1(2)o, 42.8(2)o and 79.9(2)o, 86.2(2)o, respectively. The crystal packing does not show hydrogen bonding or weak interactions. The lack of such interaction, usually associated with the stabilization of the crystal structure, is probably responsible for the difficulties in the obtainment of single crystals. The main structural dissimilarity between the two molecules in the ASU relates to the positioning of the phenyl from the substituent at the 3 position, which is clearly demonstrated by the overlay of the two molecules shown on Figure 3a. Thus, the angle between the mean planes of the imidazole and 3-phenyl moiety in the two molecules is 79.9(2)o and 86.2(2)o, respectively. Even slighter differences are observed for the 2-phenyl moiety in the two molecules; the angle between the imidazo[1,2-a]pyridine and 2-phenyl mean planes is 39.1(2)o and 42.8(2)o.
2-(4-Phenyl)-3-(1-(4-phenyl)vinyl)imidazo[1,2-a]pyridine (4a). Compound 4a crystallizes from heptane in the monoclinic centrosymmetric $P 2_1/c$ space group, with two independent molecules in the asymmetric unit (Table S1). An ORTEP view of the molecule is reported on Figure 4 together with the atomic labeling scheme. Selected bond lengths [Å]: C11–N12 1.333(3), N12–C13 1.375(3), C13–C14 1.376(3), C13–C110 1.474(3), C21–N22 1.327(3), N22–C23 1.379(3), C23–C24 1.369(3), C23–C210 1.477(3). The majority of bond lengths and angles are comparable in the two independent molecules. The ring systems are nearly planar with respective rmsd of (0.0106, 0.0125), (0.0012, 0.0012) and (0.0054, 0.0067) for the imidazo[1,2-a]pyridine, 2-phenyl and the 3-phenyl substituents in the two molecules. The angles between the mean planes of the imidazole/3-phenyl rings are also similar in the two molecules: 84.2(2)$^\circ$ and 77.9(2)$^\circ$, respectively. On the other hand the angle between the mean planes of the imidazole/2-phenyl rings is quite different 16.2(2)$^\circ$, 46.6(2)$^\circ$. Similarly to 3a the crystal packing (Figure 3b) does not show hydrogen bonding or weak interactions. As in 3a, the dissimilarity between the two molecules in the ASU of 4a is associated to the rotation of the phenyl along C13-C110/C23-C210 (Figure 3b). The rotation of the phenyl ring C-C bond is 63.31$^\circ$ and thus “obliges” the existence of two molecules per ASU (Figure S2).

2-(4-Methoxyphenyl)imidazo[1,2-a]pyridine (5e). Crystals of 5e, suitable for single crystal X-ray analysis (Table S1), were obtained by slow evaporation from CHCl$_3$/ethyl acetate solution. An ORTEP view of the molecule is reported on Figure 5 together with the atomic labeling scheme. Selected bond lengths [Å]: C1–N2 1.329(3), N2–C3 1.374(3), C3–C4 1.377(3), C3–C10 1.468(3). Compound 5e crystallizes in the orthorhombic noncentrosymmetric $Pna2_1$ space group, with one independent molecule in the asymmetric unit. The noncentrosymmetry is due to the packing of the molecules as no chiral centers are present. The majority of bond lengths and angles are comparable with those of compound 3a. The ring systems are nearly planar with respective rmsd of 0.0102 and 0.0084 Å for imidazo[1,2-a]pyridine and 2-phenyl. The angle between the mean planes of the imidazole/2-phenyl ring is 12.5(4)$^\circ$ while in 3a the values ranged between 39$^\circ$ and 43$^\circ$. The crystal packing of the molecules of 5e does not show typical hydrogen bonds however, weak C-H⋯π interactions can be detected. The main structural dissimilarity between compounds 3a and 5e relates to the positioning of the 2-phenyl with respect to the imidazo[1,2-a]pyridine one (Figure 3a).
### Table S1. Crystal data for 3a, 4a and 5e

| Compound |     |     |     |
|----------|-----|-----|-----|
|          | 3a  | 4a  | 5e  |
| **Formula** | C₂₁H₁₈N₂ | C₂₁H₁₆N₂ | C₁₄H₁₂N₂O₁ |
| **MW**   | 298.37 | 296.365 | 224.26 |
| Crystal system | Monoclinic | Monoclinic | Orthorhombic |
| **Space group** | P2₁/c | P2₁/c | Pna2₁ |
| **a [Å]** | 25.370(4) | 9.6379(6) | 6.3186(4) |
| **b [Å]** | 6.0454(11) | 8.3186(7) | 7.1021(5) |
| **c [Å]** | 21.181(2) | 40.816(2) | 24.4768(14) |
| **α, β, γ [°]** | 90/87.341(11)/90 | 90/103.038(6)/90 | 90/90/90 |
| **V [Å³]** | 3245.1(8) | 3188.1(4) | 1098.4(2) |
| **Z**    | 4 | 4 | 4 |
| **F₀₀₀** | 1264 | 1248 | 472 |
| **D_{calculated} [Mg m⁻³]** | 1.221 | 1.235 | 1.356 |
| **Crystal size, [mm]** | 0.15x0.14x0.12 | 0.24x0.22x0.24 | 0.35x0.25x0.25 |
| **Reflections collected/unique** | 11281/5731 | 14219/6442 | 3617/1837 |
| **Reflections observed [I > 2σ(I)]** | 2182 | 3445 | 1661 |
| **Parameters** | 419 | 415 | 155 |
| **R indices [F² > 2σ(F²)], R₁/ wR** | 0.044/0.056 | 0.062/0.12 | 0.040/0.103 |
| **R indices [F², all data], R/ wR₁** | 0.030/0.082 | 0.13/0.15 | 0.047/0.096 |
Figure S1. Crystal packing of 3a. The R and S stereo centers are shown along with the symmetry operations for generating the molecules.

Figure S2. Crystal packing of 4a.