

SUPPORTING INFORMATION

Magnetically Recoverable Nickel-Palladium Alloy Nanocatalysts for the C-H Arylation Reactions

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Experimental details

Materials

Oleylamine (OAm) (>70%), 1-octadecene (ODE, 90%), palladium (II) acetylacetonate ($\text{Pd}(\text{acac})_2$, 99%), nickel(II) acetylacetonate ($\text{Ni}(\text{acac})_2$, 97%), Cobalt(II) acetylacetonate ($\text{Co}(\text{acac})_2$, 97%), iron(III) acetylacetonate ($\text{Fe}(\text{acac})_3$, 97%), benzyl ether (BE, 99%), 1,2-tetradecanediol (1,2-TDD, 97%), borane-tert-bütylamine (BTB, 97%), hexanes (99%), ethanol (99%), acetone (97%), Phosphorus pentoxide (P_2O_5 , 95%), Potassium peroxodisulfate ($\text{K}_2\text{S}_2\text{O}_8$, 95%), potassium permanganate (KMnO_4), hydrogen peroxide (H_2O_2 , 30%), sodium nitrate (NaNO_3 , 99%), sulfuric acid (H_2SO_4 , 98%), dimethylformamide (DMF, >99%) and were purchased from Sigma-Aldrich[®] used as received. Natural graphite flakes (average particle size: 325 mesh) were purchased from Alfa-Aesar. All organic compounds received from commercially sources. A deionized water was distilled using a Milli-Q water purification system.

Instrumentation

All low-resolution transmission electron microscope (TEM) images were recorded on a Hitachi HT7700 TEM instrument equipped with the EXALENS HR-TEM lens operated at 120 kV. X-ray diffraction (XRD) patterns were recorded on a Panalytical Empyrean diffractometer with Cu-K α radiation (40 kV, 15 mA, 1.54051 Å) over a 2 θ range from 10°–90° at room temperature. Elemental analysis measurements were carried out on an Agilent Technologies 7700x inductively coupled plasma-mass spectroscopy (ICP-MS) after each sample was completely dissolved in aqua-regia (HCl/HNO₃: 3/1 v/v ratio). X-ray photoelectron spectra (XPS) were recorded on Thermo Scientific K-Alpha spectrometer using an Al K α (h ν : 1486.6 eV) radiation. ¹H NMR and ¹³C NMR experiments were performed on either 400 MHz Varian and 400 MHz Bruker Avance II instruments using CDCl₃, DMSO-*d*₆, MeOD, Acetone-*d*₆ as the solvent with tetramethylenesilane (TMS) as internal standard at room temperature, and the coupling constants *J* are given in hertz. The multiplicity is designated as s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet.

Compound Characterization

3-Phenylimidazo[1,2-*a*]pyridine (3a).^[1] Light yellow crystal, 94 mg from bromobenzene (97% yield, 30:70 EtOAc/hexane) and 93 mg from iodobenzene (96% yield). ¹H NMR (400 MHz, CDCl₃): δ 8.18 (d, *J* = 6.9 Hz, 1H), 7.59 – 7.50 (m, 2H), 7.45 – 7.33 (m, 4H), 7.32 – 7.24 (m, 1H), 7.09 – 6.99 (m, 1H), 6.65 (t, *J* = 6.9 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 146.0, 132.3, 129.2, 129.2, 128.2, 128.0, 125.7, 124.3, 123.3, 118.1, 112.6.

3-(4-Nitrophenyl)imidazo[1,2-*a*]pyridine (3b).^[1] Yellow solid, 116 mg from 1-bromo-4-nitrobenzene (97% yield, 30:70 EtOAc/hexane) and 115 mg from 1-iodo-4-nitrobenzene (96% yield). ¹H NMR (400 MHz, CDCl₃): δ 8.35 (d, *J* = 7.0 Hz, 1H), 8.33 – 8.26 (m, 2H), 7.79 (s, 1H), 7.73 – 7.64 (m, 3H), 7.28 – 7.20

(m, 1H), 6.87 (t, $J = 6.8$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 147.3, 146.8, 135.9, 134.7, 127.5, 125.5, 124.8, 123.7, 123.2, 118.8, 113.6.

4-(Imidazo[1,2-*a*]pyridin-3-yl)benzotrile (3c).^[1] Light yellow solid, 105 mg from 4-bromobenzotrile (96% yield, 30:70 EtOAc/hexane) and 107 mg from 4-iodobenzotrile (97% yield). ^1H NMR (400 MHz, CDCl_3): δ 8.30 (d, $J = 7.0$ Hz, 1H), 7.74 – 7.68 (m, 3H), 7.66 – 7.58 (m, 3H), 7.24 – 7.15 (m, 1H), 6.83 (t, $J = 7.4$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 147.0, 134.1, 133.9, 133.1, 127.6, 125.3, 124.0, 123.2, 118.6, 118.5, 113.5, 111.2.

4-(Imidazo[1,2-*a*]pyridin-3-yl)benzaldehyde (3d).^[1] Light yellow solid, 106 mg from 4-bromobenzaldehyde (95% yield, 30:70 EtOAc/hexane) and 108 mg from 4-iodobenzaldehyde (97% yield). ^1H NMR (400 MHz, CDCl_3): δ 9.92 (s, 1H), 8.31 (d, $J = 6.8$ Hz, 1H), 7.88 (d, $J = 8.1$ Hz, 2H), 7.70 (s, 1H), 7.63 – 7.57 (m, 3H), 7.19 – 7.08 (m, 1H), 6.78 (t, $J = 6.8$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 191.3, 146.9, 135.3, 135.2, 134.0, 130.6, 127.4, 125.1, 124.5, 123.4, 118.4, 113.3.

1-(4-(Imidazo[1,2-*a*]pyridin-3-yl)phenyl)ethan-1-one (3e).^[1] Light yellow solid, 115 mg from 1-(4-bromophenyl)ethan-1-one (97% yield, 30:70 EtOAc/hexane) and 114 mg from 1-(4-iodophenyl)ethan-1-one (96% yield). ^1H NMR (400 MHz, CDCl_3): δ 8.32 (d, $J = 7.1$ Hz, 1H), 8.01 (d, $J = 8.4$ Hz, 2H), 7.71 (s, 1H), 7.65 – 7.55 (m, 3H), 7.23 – 7.11 (m, 1H), 6.79 (t, $J = 7.1$ Hz, 1H), 2.57 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 197.2, 146.8, 136.2, 134.0, 133.8, 129.3, 127.3, 124.9, 124.7, 123.4, 118.5, 113.1, 26.6.

Methyl 4-(imidazo[1,2-*a*]pyridin-3-yl)benzoate (3f).^[2] White solid, 106 mg from methyl 4-bromobenzoate (84% yield, 30:70 EtOAc/hexane) and 109 mg from methyl 4-iodobenzoate (86% yield). ^1H NMR (400 MHz, CDCl_3): δ 8.33 (d, $J = 6.9$ Hz, 1H), 8.11 (d, $J = 8.3$ Hz, 2H), 7.72 (s, 1H), 7.65 – 7.58 (m, 3H), 7.22 – 7.10 (m, 1H), 6.81 (t, $J = 6.9$ Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 166.6, 146.8, 133.9, 133.6, 130.6, 129.4, 127.2, 124.8, 123.4, 118.5, 115.6, 113.1, 52.3.

3-(4-(Trifluoromethyl)phenyl)imidazo[1,2-*a*]pyridine (3g).^[1] Light yellow solid, 121 mg from 1-iodo-4-(trifluoromethyl)benzene (92% yield, 30:70 EtOAc/hexane). ^1H NMR (400 MHz, CDCl_3): δ 8.27 (d, $J = 7.0$ Hz, 1H), 7.69 (t, $J = 4.1$ Hz, 3H), 7.62 (t, $J = 7.4$ Hz, 3H), 7.23 – 7.10 (m, 1H), 6.79 (t, $J = 7.4$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 146.7, 133.4, 133.0, 130.1, 129.8, 127.8, 126.4-126.2 (m, 1C), 124.9, 124.3, 123.2, 118.5, 113.1.

3-(3-Nitrophenyl)imidazo[1,2-*a*]pyridine (3h).^[3] Brownish solid, 113 mg from 1-bromo-3-nitrobenzene (94% yield, 30:70 EtOAc/hexane) and 111 mg from 1-iodo-3-nitrobenzene (93% yield). ^1H NMR (400 MHz, CDCl_3): δ 8.37 (m, 1H), 8.30 – 8.25 (m, 1H), 8.19 – 8.17 (m, 1H), 7.87 – 7.80 (m, 1H), 7.74 (m, 1H), 7.66 – 7.62 (m, 2H), 7.25 – 7.17 (m, 1H), 6.84 (t, $J = 6.8$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 148.9, 146.8, 133.9, 133.5, 131.2, 130.4, 125.1, 123.3, 122.9, 122.7, 122.1, 118.7, 113.4.

3-(Imidazo[1,2-*a*]pyridin-3-yl)benzotrile (3i).^[2] Light brownish solid, 108 mg from 3-bromobenzotrile (98% yield, 30:70 EtOAc/hexane) and 106 mg from 3-iodobenzotrile (97% yield). ¹H NMR (400 MHz, CDCl₃): δ 8.22 (d, *J* = 7.0 Hz, 1H), 7.76 (s, 1H), 7.73 – 7.70 (m, 1H), 7.65 (s, 1H), 7.62 – 7.52 (m, 3H), 7.19 – 7.12 (m, 1H), 6.80 (t, *J* = 7.3 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 146.7, 133.6, 131.9, 131.3, 130.9, 130.8, 130.3, 125.0, 123.4, 122.9, 118.5, 118.3, 113.6, 113.3.

3-(Imidazo[1,2-*a*]pyridin-3-yl)benzaldehyde (3j).^[2] Light yellow solid, 106 mg from 3-bromobenzaldehyde (95% yield, 30:70 EtOAc/hexane) and 102 mg from 3-iodobenzaldehyde (92% yield). ¹H NMR (400 MHz, CDCl₃): δ 10.07 (s, 1H), 8.33 (d, *J* = 7.0 Hz, 1H), 8.06 (s, 1H), 7.93 – 7.86 (m, 1H), 7.84 – 7.78 (m, 1H), 7.75 (s, 1H), 7.72 – 7.63 (m, 2H), 7.27 – 7.17 (m, 1H), 6.85 (t, *J* = 7.3 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 191.8, 146.5, 137.2, 133.6, 133.2, 130.4, 130.1, 129.5, 128.2, 124.8, 124.3, 123.1, 118.4, 113.1.

2-(Imidazo[1,2-*a*]pyridin-3-yl)benzaldehyde (3k).^[2] Brownish oil, 102 mg from 2-bromobenzaldehyde (92% yield, 30:70 EtOAc/hexane) and 105 mg from 2-iodobenzaldehyde (94% yield). ¹H NMR (400 MHz, CDCl₃): δ 9.80 (s, 1H), 8.02 (d, *J* = 7.8 Hz, 1H), 7.87 (d, *J* = 6.9 Hz, 1H), 7.71 – 7.62 (m, 2H), 7.62 (s, 1H), 7.58 – 7.44 (m, 2H), 7.25 – 7.13 (m, 1H), 6.77 (t, *J* = 6.9 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 191.1, 146.2, 134.8, 134.7, 134.5, 131.3, 131.1, 129.5, 129.4, 125.5, 123.4, 120.9, 118.1, 113.4.

3-(*p*-Tolyl)imidazo[1,2-*a*]pyridine (3l).^[1] Brownish solid, 76 mg from 1-bromo-4-methylbenzene (73% yield, 30:70 EtOAc/hexane) and 78 mg from 1-iodo-4-methylbenzene (75% yield). ¹H NMR (400 MHz, CDCl₃): δ 8.16 (d, *J* = 6.9 Hz, 1H), 7.54 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.06 – 7.00 (m, 1H), 6.64 (t, *J* = 6.9 Hz, 1H), 2.30 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 145.9, 138.1, 132.2, 129.9, 128.0, 126.3, 125.7, 124.0, 123.4, 118.1, 112.4, 21.3.

3-(4-Methoxyphenyl)imidazo[1,2-*a*]pyridine (3m).^[1] Light yellow solid, 89 mg from 1-bromo-4-methoxybenzene (79% yield, 30:70 EtOAc/hexane) and 90 mg from 1-iodo-4-methoxybenzene (80% yield). ¹H NMR (400 MHz, CDCl₃): δ 8.16 (d, *J* = 7.0 Hz, 1H), 7.58 – 7.55 (m, 2H), 7.44 – 7.31 (m, 2H), 7.13 – 7.05 (m, 1H), 7.01 – 6.90 (m, 2H), 6.69 (t, *J* = 6.8 Hz, 1H), 3.79 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 159.6, 145.8, 132.0, 129.6, 125.5, 123.9, 123.3, 121.6, 118.2, 114.7, 112.3, 55.4.

3-(*m*-Tolyl)imidazo[1,2-*a*]pyridine (3n).^[4] Light yellow oil, 75 mg from 1-bromo-3-methylbenzene (72% yield, 30:70 EtOAc/hexane) and 83 mg from 1-iodo-3-methylbenzene (80% yield). ¹H NMR (400 MHz, CDCl₃): δ 8.31 (d, *J* = 7.0 Hz, 1H), 7.66 (s, 1H), 7.64 (d, *J* = 9.1 Hz, 1H), 7.45 – 7.30 (m, 3H), 7.23 – 7.13 (m, 2H), 6.77 (t, *J* = 7.4 Hz, 1H), 2.41 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 146.1, 139.0, 132.5, 129.2, 129.1, 129.0, 128.7, 125.9, 125.0, 124.1, 123.4, 118.2, 112.4, 21.5.

3-(3-Methoxyphenyl)imidazo[1,2-*a*]pyridine (3o).^[5] Light yellow solid, 80 mg from 1-bromo-3-methoxybenzene (71% yield, 30:70 EtOAc/hexane) and 83 mg from 1-iodo-3-methoxybenzene (74% yield). ¹H NMR (400 MHz, CDCl₃): δ 8.30 (d, *J* = 6.9 Hz, 1H), 7.65 (s, 1H), 7.62 (d, *J* = 9.1 Hz, 1H), 7.36 (t, *J* = 7.9 Hz, 1H), 7.17 – 7.00 (m, 3H), 6.89 (dd, *J* = 8.3, 2.5 Hz, 1H), 6.74 (t, *J* = 6.8 Hz, 1H), 3.80 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 160.4, 146.2, 132.5, 130.6, 130.5, 125.8, 124.6, 123.7, 120.4, 118.3, 113.9, 113.7, 112.9, 55.6.

3-(*o*-Tolyl)imidazo[1,2-*a*]pyridine (3p).^[6] Light yellow oil, 70 mg from 1-bromo-2-methylbenzene (67% yield, 30:70 EtOAc/hexane) and 82 mg from 1-iodo-2-methylbenzene (79% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.66 (d, *J* = 6.8 Hz, 1H), 7.60 (d, *J* = 9.2 Hz, 1H), 7.53 (s, 1H), 7.32 – 7.18 (m, 4H), 7.12 – 7.08 (m, 1H), 6.67 (t, *J* = 6.4 Hz, 1H), 2.07 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 145.5, 138.3, 132.8, 131.1, 130.7, 129.2, 128.2, 126.2, 124.6, 124.0, 123.6, 118.0, 112.2, 19.7.

3-(Pyridin-2-yl)imidazo[1,2-*a*]pyridine (3q).^[2] Light Brownish solid, 56 mg from 2-bromopyridine (57% yield, 30:70 EtOAc/ hexane) and 50 mg from 2-iodopyridine (51% yield). ¹H NMR (400 MHz, CDCl₃): δ 9.94 (d, *J* = 7.1 Hz, 1H), 8.65 (d, *J* = 4.9 Hz, 1H), 8.14 (s, 1H), 7.77 – 7.63 (m, 3H), 7.41 – 7.20 (m, 1H), 7.22 – 7.09 (m, 1H), 6.93 (t, *J* = 6.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 150.7, 148.7, 147.6, 136.5, 134.7, 128.1, 125.5, 123.7, 120.9, 120.4, 117.6, 112.9.

3-(Pyridin-3-yl)imidazo[1,2-*a*]pyridine (3r).^[1] Light yellow solid, 84 mg from 3-bromopyridine (86% yield, 30:70 EtOAc/ hexane) and 87 mg from 3-iodopyridine (89% yield). ¹H NMR (400 MHz, CDCl₃): δ 8.75 (d, *J* = 4.3 Hz, 1H), 8.56 – 8.55 (m, 1H), 8.19 (d, *J* = 7.0 Hz, 1H), 7.82 – 7.73 (m, 1H), 7.66 (s, 1H), 7.60 (d, *J* = 9.1 Hz, 1H), 7.38 – 7.34 (m, 1H), 7.17 – 7.12 (m, 1H), 6.79 – 6.75 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 149.2, 148.8, 146.6, 135.1, 133.3, 125.6, 124.8, 123.9, 123.0, 122.3, 118.4, 113.1.

3-(Naphthalen-1-yl)imidazo[1,2-*a*]pyridine (3s).^[1] Light yellow oil, 93 mg from 1-iodonaphthalene (76% yield, 30:70 EtOAc/hexane). ¹H NMR (400 MHz, CDCl₃): δ 7.89 – 7.84 (m, 2H), 7.73 (s, 1H), 7.69 (d, *J* = 9.1 Hz, 1H), 7.59 (d, *J* = 6.8 Hz, 1H), 7.49 (d, *J* = 4.9 Hz, 2H), 7.47 – 7.40 (m, 2H), 7.33 – 7.28 (m, 1H), 7.16 – 7.08 (m, 1H), 6.57 (t, *J* = 6.7 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 146.0, 134.1, 133.9, 132.2, 129.8, 129.3, 128.9, 127.2, 126.6, 126.4, 125.8, 125.3, 124.6, 124.3, 123.9, 118.1, 112.5.

1,2-Dimethyl-5-phenyl-1H-imidazole (4a).^[7] Light yellow solid, 78 mg from bromobenzene (91% yield, 60:40 EtOAc/hexane) and 74 mg from iodobenzene (86% yield). ¹H-NMR (400 MHz, CDCl₃): δ 7.31 – 7.26 (m, 2H), 7.25 – 7.20 (m, 3H), 6.83 (s, 1H), 3.38 (s, 3H), 2.31 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃): δ 145.9, 133.5, 130.5, 128.6, 128.5, 127.6, 125.7, 31.3, 13.6.

1,2-Dimethyl-5-(4-nitrophenyl)-1H-imidazole (4b).^[7] Yellow solid, 100 mg from 1-bromo-4-nitrobenzene (92% yield, 60:40 EtOAc/hexane) and 92 mg from 1-iodo-4-nitrobenzene (85% yield). ¹H-

NMR (400 MHz, CDCl₃): δ 8.24 – 8.20 (m, 2H), 7.48 – 7.45 (m, 2H), 7.06 (s, 1H), 3.55 (s, 3H), 2.42 (s, 3H). **¹³C-NMR (100 MHz, CDCl₃):** δ 153.7, 148.0, 146.7, 136.9, 131.4, 128.2, 124.2, 31.8, 13.8.

4-(1,2-Dimethyl-1H-imidazol-5-yl)benzotrile (4c).^[7] White solid, 86 mg from 4-bromobenzotrile (87% yield, 60:40 EtOAc/hexane) and 82 mg from 4-iodobenzotrile (83% yield). **¹H-NMR (400 MHz, CDCl₃):** δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.00 (s, 1H), 3.51 (s, 3H), 2.40 (s, 3H). **¹³C-NMR (100 MHz, CDCl₃):** δ 147.7, 135.1, 132.6, 131.9, 128.3, 127.9, 118.7, 110.8, 31.5, 13.9.

5-(4-methoxyphenyl)-1,2-dimethyl-1H-imidazole (4d).^[7] White solid, 55 mg from 1-bromo-4-methoxybenzene (54% yield, 60:40 EtOAc/hexane) and 63 mg from 1-iodo-4-methoxybenzene (62% yield). **¹H-NMR (400 MHz, CDCl₃):** δ 7.18 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.80 (s, 1H), 3.75 (s, 3H), 3.39 (s, 3H), 2.35 (s, 3H). **¹³C-NMR (100 MHz, CDCl₃):** δ 159.3, 145.4, 133.3, 130.1, 125.1, 122.9, 114.1, 55.3, 31.2, 13.7.

2,3-Diphenylindolizine (4e).^[8] Brown oil, 118 mg from bromobenzene (85% yield, 5:95 EtOAc/hexane) and 126 mg from iodobenzene (90% yield). **¹H NMR (400 MHz, CDCl₃):** δ 7.86 (d, *J* = 7.4 Hz, 1H), 7.40 – 7.27 (m, 6H), 7.26 – 7.21 (m, 2H), 7.19 – 7.06 (m, 3H), 6.64 – 6.56 (m, 2H), 6.38 – 6.28 (m, 1H). **¹³C NMR (100 MHz, CDCl₃):** δ 136.1, 132.7, 131.9, 131.0, 129.1, 128.9, 128.2, 127.9, 127.8, 126.1, 122.3, 121.5, 119.1, 117.5, 110.5, 99.4.

3-(4-Nitrophenyl)-2-phenylindolizine (4f).^[9] Orange solid, 153 mg from 1-bromo-4-nitrobenzene (94% yield, 6:94 EtOAc/hexane) and 156 mg from 1-iodo-4-nitrobenzene (96% yield). **¹H NMR (400 MHz, CDCl₃):** δ 8.17 (d, *J* = 9.1 Hz, 2H), 8.05 – 8.01 (m, 1H), 7.47 (d, *J* = 9.1 Hz, 2H), 7.38 (d, *J* = 9.0 Hz, 1H), 7.24 – 7.13 (m, 5H), 6.77 – 6.65 (m, 1H), 6.62 (s, 1H), 6.52 – 6.43 (m, 1H). **¹³C NMR (100 MHz, CDCl₃):** δ 146.4, 138.5, 135.4, 134.1, 130.8, 130.1, 129.2, 128.5, 126.8, 124.3, 121.8, 119.5, 119.2, 118.9, 111.6, 101.3.

4-(2-Phenylindolizin-3-yl)benzotrile (4g). Light brown solid, 122 mg from 4-bromobenzotrile (80% yield, mp 126.0–127.0 °C, 5:95 EtOAc/hexane) and 142 mg from 4-iodobenzotrile (93% yield). **¹H NMR (400 MHz, CDCl₃):** δ 8.07 (d, *J* = 7.0 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 9.0 Hz, 1H), 7.35 – 7.24 (m, 5H), 6.83 – 6.73 (m, 1H), 6.72 (s, 1H), 6.58 – 6.50 (m, 1H). **¹³C NMR (100 MHz, CDCl₃):** δ 136.5, 135.4 (2C), 133.8, 132.7, 131.0, 129.6, 129.2, 128.5, 126.7, 121.8, 119.4, 118.9, 118.6, 111.4, 110.7, 100.9. **HRMS (ESI-TOF) m/z:** [M + H]⁺ calcd for C₂₁H₁₅N₂, 295.1230; found 295.1225.

2-Phenyl-3-(*p*-tolyl)indolizine (4h).^[8] Brown oil, 110 mg from 1-bromo-4-methylbenzene (75% yield, 4:96 EtOAc/hexane) and 136 mg from 1-iodo-4-methylbenzene (93% yield). **¹H NMR (400 MHz, CDCl₃):**

δ 7.86 – 7.78 (m, 1H), 7.31 (d, J = 9.0 Hz, 1H), 7.27 – 7.22 (m, 2H), 7.22 – 7.11 (m, 6H), 7.11 – 7.04 (m, 1H), 6.64 – 6.53 (m, 2H), 6.37 – 6.25 (m, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 137.6, 136.2, 132.6, 130.9, 129.9, 128.9, 128.2 (2C), 127.7, 126.1, 122.4, 121.6, 119.1, 117.3, 110.4, 99.3, 21.4.

5-Phenylfuran-2-carbonitrile (4i).^[10] White solid, 64 mg from bromobenzene (70% yield, 2:98 EtOAc/hexane) and 69 mg from iodobenzene (75% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.77 – 7.71 (m, 2H), 7.51 – 7.37 (m, 3H), 7.19 (d, J = 3.7 Hz, 1H), 6.75 (d, J = 3.7 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 158.7, 129.5, 129.0, 128.7, 125.1, 124.9, 124.0, 111.9, 106.0.

5-(4-Acetylphenyl)furan-2-carbonitrile (4j).^[11] White solid, 103 mg from 4'-bromoacetophenone (91% yield, 7:93 EtOAc/hexane) and 93 mg from 4'-iodoacetophenone (82% yield). ^1H NMR (400 MHz, CDCl_3): δ 8.05 (d, J = 8.5 Hz, 2H), 7.83 (d, J = 8.5 Hz, 2H), 7.22 (d, J = 3.7 Hz, 1H), 6.89 (d, J = 3.7 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 197.1, 157.3, 137.3, 132.5, 129.1, 126.1, 124.9, 123.9, 111.5, 108.0, 26.7.

5-(4-Cyanophenyl)furan-2-carbonitrile (4k).^[12] White solid, 91 mg from 4-bromobenzonitrile (87% yield, 3:97 EtOAc/hexane) and 96 mg from 4-iodobenzonitrile (92% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.75 (d, J = 8.5 Hz, 2H), 7.66 (d, J = 8.5 Hz, 2H), 7.14 (d, J = 3.7 Hz, 1H), 6.83 (d, J = 3.7 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 156.2, 132.9, 132.3, 126.6, 125.2, 123.9, 118.2, 112.8, 111.3, 108.7.

5-(*p*-Tolyl)furan-2-carbonitrile (4l).^[13] White-off solid, 45 mg from 1-bromo-4-methylbenzene (45% yield, 2:98 EtOAc/hexane) and 62 mg from 1-iodo-4-methylbenzene (63% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.63 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.2 Hz, 2H), 7.17 (d, J = 3.7 Hz, 1H), 6.69 (d, J = 3.7 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 159.0, 139.8, 129.7, 126.1, 124.8, 124.8, 124.0, 112.1, 105.3, 21.4.

2-(4-(Methylsulfonyl)phenyl)-3-phenylimidazo[1,2-*a*]pyridine (6a).^[14] Light Brown solid, from bromobenzene (trace) and 168 mg from iodobenzene (96% yield, 10:90 EtOAc/hexane). ^1H NMR (400 MHz, CDCl_3): δ 7.84 (d, J = 6.9 Hz, 1H), 7.78 (d, J = 8.5 Hz, 2H), 7.73 (d, J = 8.5 Hz, 2H), 7.59 (d, J = 9.1 Hz, 1H), 7.52 – 7.41 (m, 3H), 7.37 – 7.32 (m, 2H), 7.19 – 7.11 (m, 1H), 6.69 (t, J = 6.8 Hz, 1H), 2.95 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 145.0, 140.1, 139.9, 138.8, 130.6, 129.9, 129.5, 129.1, 128.5, 127.3, 125.5, 123.6, 122.7, 117.7, 112.9, 44.5.

2-(4-(Methylsulfonyl)phenyl)-3-(4-nitrophenyl)imidazo[1,2-*a*]pyridine (6b). Yellow solid, 173 mg from 1-bromo-4-nitrobenzene (88% yield, mp 123.0-124.0 °C, 10:90 EtOAc/hexane) and 182 mg from 1-iodo-4-nitrobenzene (93% yield). ^1H NMR (400 MHz, CDCl_3): δ 8.33 (d, J = 8.7 Hz, 2H), 7.97 (d, J = 7.0 Hz, 1H), 7.80 (d, J = 8.5 Hz, 2H), 7.72 (d, J = 8.5 Hz, 2H), 7.65 (d, J = 9.1 Hz, 1H), 7.59 (d, J = 8.7 Hz, 2H), 7.32 – 7.22 (m, 1H), 6.86 – 6.77 (m, 1H), 2.99 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 147.9, 145.8, 141.9,

139.7, 139.2, 135.9, 131.3, 129.0, 127.6, 126.4, 125.0, 123.1, 120.1, 118.2, 113.8, 44.5. **HRMS (ESI-TOF) m/z:** [M + H]⁺ calcd for C₂₀H₁₆N₃O₄S, 394.0856; found 394.0857.

4-(2-(4-(Methylsulfonyl)phenyl)imidazo[1,2-*a*]pyridin-3-yl)benzotrile (6c). White-off solid, 150 mg from 4-bromobenzotrile (80% yield, mp 242.0-243.0 °C, 10:90 EtOAc/hexane) and 155 mg from 4-iodobenzotrile (83% yield). **¹H NMR (400 MHz, CDCl₃):** δ 7.93 (d, *J* = 6.9 Hz, 1H), 7.83 – 7.86 (m, 4H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.66 (d, *J* = 9.1 Hz, 1H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.29 – 7.22 (m, 1H), 6.80 (t, *J* = 6.7 Hz, 1H), 2.99 (s, 3H). **¹³C NMR (100 MHz, CDCl₃):** δ 145.7, 141.6, 139.6, 139.2, 134.0, 133.5, 131.1, 128.9, 127.6, 126.2, 123.0, 120.4, 118.2, 118.1, 113.6, 113.1, 44.5. **HRMS (ESI-TOF) m/z:** [M + H]⁺ calcd for C₂₁H₁₆N₃O₂S, 374.0958; found 374.0954.

2-(4-(Methylsulfonyl)phenyl)-3-(*p*-tolyl)imidazo[1,2-*a*]pyridine (6d). yellow solid, from 1-bromo-4-methylbenzene (trace) and 149 mg from 1-iodo-4-methylbenzene (82% yield, mp 178.9-179.9 °C, 8:92 EtOAc/hexane). **¹H NMR (400 MHz, CDCl₃):** δ 7.83 (d, *J* = 7.0 Hz, 1H), 7.80 (d, *J* = 8.6 Hz, 2H), 7.74 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 9.1 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.17 – 7.12 (m, 1H), 6.70 – 6.65 (m, 1H), 2.95 (s, 3H), 2.39 (s, 3H). **¹³C NMR (100 MHz, CDCl₃):** δ 144.9, 140.0, 139.96, 139.6, 138.7, 130.6, 130.5, 128.4, 127.3, 126.0, 125.4, 123.6, 122.8, 117.7, 112.7, 44.5, 21.5. **HRMS (ESI-TOF) m/z:** [M + H]⁺ calcd for C₂₁H₁₈N₂O₂S, 363.1162; found 363.1158.

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NMR Spectra





































































