Electronic Supplementary Material (ESI) for ChemComm.

Copper-Catalyzed Cross-Coupling of Aryl-, Primary Alkyl-, and Secondary Alkylboranes with Heteroaryl Bromides

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General. Infrared (IR) spectra were recorded on Bruker Tensor II FT-IR Spectrometer, ν_{max} in cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m), and weak (w). ^{1}H NMR spectra were recorded at room temperature on a Varian I400 (400 MHz), Varian VXR400 (400 MHz), Varian I500 (500 MHz), or a Varian I600 (600 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CHCl_3$: δ 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), and integration. ^{13}C NMR spectra were recorded on a Varian I400 (100 MHz) and Varian I500 (125 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 77.16 ppm). High-resolution mass spectrometry (HRMS) was performed on a Thermo Electron Corporation MAT 95XP-Trap (GC/MS). Melting points were obtained on a Thomas Hoover capillary melting point apparatus without correction. Unless otherwise noted, all reactions have been carried out with distilled and degassed solvents under an atmosphere of dry N_2 in oven- (135 °C) and flame-dried glassware with standard vacuum-line techniques. Toluene was purified under a positive pressure of dry argon by passage through columns of activated alumina and Q5 (Grubbs apparatus). All work-up and purification procedures were carried out with reagent grade solvents (purchased from Sigma-Aldrich) in air. Standard column chromatography techniques using ZEOprep 60/40-63 μm silica gel were used for purification.

■ **Reagents and Catalysts:**

4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene (Xantphos) was purchased from Strem and used as received.

Bis(pinacolato)diboron was purchased from Ark Pharm and used as received.

9-Borabicyclo[3.3.1]nonane solution (0.5 M in THF) was purchased from Sigma Aldrich and used as received.

B-Methoxy-9-BBN solution (1.0 M in hexanes) was purchased from Sigma Aldrich and used as received.

Boronic esters were prepared in accordance with literature procedures.[1]

4-Bromobenzotrifluoride was purchased from Sigma-Aldrich and used as received.

1-Bromoisoquinoline was purchased from Sigma-Aldrich and used as received.

3-Bromoisoquinoline was purchased from Ark Pharm and used as received.

2-Bromo-3-methylpyridine was purchased from Matrix Scientific and used as received.

2-Bromo-5-methoxypyridine was purchased from Combi-Blocks and used as received.

(2-Bromophenyl)boronic acid was purchased from Ark Pharm and used as received.

2-Bromopyrazine was purchased from Combi-Blocks and used as received.

2-Bromopyridine was purchased from Sigma-Aldrich and used as received.

2-Bromo-5-(trifluoromethyl)pyridine was purchased from Matrix Scientific and used as received.

4-Chloroiodobenzene was purchased from Combi-Blocks and used as received.

CuBr (99.999%) was purchased from Sigma Aldrich and used as received

CuCl (99.99%) was purchased from Strem and purified by washing with 1M HCl (3 x 3mL), ethanol (3x 3mL), and diethyl ether (3x 3mL) and dried *in vacuo* before use.

CuCl (99.995%) was purchased from Sigma Aldrich and purified by washing with 1M HCl (3 x 3mL), ethanol (3x 3mL), and diethyl ether (3x 3mL) and dried *in vacuo* before use.

CuI (99.999%) was purchased from Sigma Aldrich and used as received.

9-Cyclohexyl-9-borabicyclo[3.3.1]nonane was prepared in accordance with literature procedures.[2]

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[1] Q. Liu, G. Li, J. He, J. Liu, P. Li, A. Lei, *Angew Chem. Int. Ed.* 2010, **49**, 3371.

[2] Y. Yasuda, K. Nagao, Y. Shido, S. Mori, H. Ohmiya, *Chem. Eur. J.* 2015, **21**, 9666.

Cyclohexene was purchased from Sigma Aldrich and used as received.

Cy_3PCuCl was prepared in accordance with literature procedures.[3]

(2,4-Difluoromethyl)phenylboronic acid was purchased from Combi-Blocks and used as received.

2,2-dimethyl-1,3-propanediol was purchased from Alfa Aesar and used as received.

Furan-2-boronic acid was purchased from Combi-Blocks and used as received.

4-Iodoanisole was purchased from Sigma-Aldrich and used as received.

Iodobenzene was purchased from Alfa Aesar and used as received.

2-Iodo-*m*-xylene was purchased from Matrix Scientific and used as received.

4-Iodopyridine was purchased from Combi-Blocks and used as received.

9-Isopropyl-9-borabicyclo[3.3.1]nonane was prepared in accordance with literature procedures.[4]

Isopropylmagnesium chloride solution (2.0 M in THF) was purchased from Sigma Aldrich and used as received.

4-Methylphenylboronic acid was purchased from Combi-Blocks and used as received.

4-Methoxyphenylboronic acid was purchased from Oakwood and used as received.

Naphthalene-1-boronic acid was purchased from Combi-Blocks and used as received.

Pyridine-4-boronic acid pinacol ester was purchased from Combi-Blocks and used as received.

Pinacol was purchased from Combi-Blocks and used as received.

SIMesCuCl was prepared in accordance with literature procedures.[5]

Sodium *tert*-butoxide was purchased from Strem and used as received.

Sodium *tert*-butoxide (99.9%) was purchased from Sigma Aldrich and used as received.**4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane** was prepared in accordance with literature procedures.[6]

***Tert*-butyl 2-bromobenzoate** was purchased from Combi-Blocks and used a received.

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[3] G. A. Bowmaker, S. E. Boyd, J. V. Hanna, R. D. Hart, P. C. Healy, B. W. Skelton, A. H. White, *J. Chem. Soc., Dalton Trans* 2002, 2722.

[4] G. Y. Fang, O.A. Wallner, N. Di Blasio, X. Ginesta, J. N. Harvey, V. K. Aggarwal, *J. Amer. Chem. Soc.* 2007, **129**, 14632.

[5] S. Diez-Gonzalez, E. C. Escudero-Adan, J. Benet-Buchholz, E. D. Stevens, A. M. Z. Slawinc, S. P. Nolan, *Dalton Trans.* 2010, **39**, 7595.

[6] Y. Lee, A. Hoveyda, *J. Am. Chem. Soc*. 2009, **131**, 3160.

Thiophene-2-boronic acid was purchased from Combi-Blocks and used as received.

2-tolylboronic acid was purchased from Matrix Scientific and used as received.

Tricyclohexylphosphine (PCy_3) was purchased from Sigma-Aldrich and used as received.

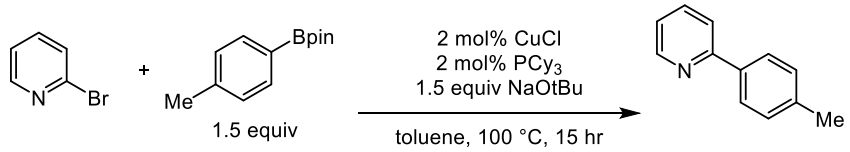
2-(Trifluoromethyl)phenylboronic acid was purchased from Matrix Scientific and used as received.

XantphosCuCl was prepared in accordance with literature procedures.[7]

■ Control Reactions

To verify that the reaction is catalyzed by Cu, several control reactions were performed, as shown in Table 1. Note that the Cu(I) sources and PCy_3 were used individually in these reactions, instead of using pre-ligated Cu complexes, as this does not have a significant effect on yield (Table 1, entries 1-2). No product was observed in the absence of CuCl, though moderate yield of product was obtained in the absence of PCy_3 (Table 1, entries 3-5). To investigate whether the reaction is catalyzed by other metal contaminates, various sources of Cu(I) in high purity were attempted, including CuCl from different suppliers (Table 1, entry 6) as well as CuBr and CuI (Table 1, entry 7 and 8, respectively). Additionally, high purity NaO*t*-Bu was used in a control reaction (Table 1, entry 9). All of these reactions provided the desired product in excellent yield.

Table 1: Control Reactions



entry	change	yield (%)[a]
1	none	81
2	Cy_3PCuCl instead of CuCl and PCy_3	94
3	no CuCl	<2
4	no PCy_3	46
5	no CuCl, no PCy_3	<2
6	CuCl (Aldrich, 99.995%) instead of CuCl (Strem, 99.99%)	92
7	CuI (Aldrich, 99.999%) instead of CuCl	89
8	CuBr (Aldrich, 99.999%) instead of CuCl	76
9	NaOtBu (Aldrich, 99.9%) instead of NaOtBu (Strem, 98%)	88

[a] Yield determined by analysis of the crude ^1H NMR with an internal standard.

[7] K. Semba, T. Fujihara, T. Xu, J. Terao, Y. Tsuji, *Adv. Synth. Catal.* 2012, **354**, 1542.

■ General Procedure A: Coupling of aryl bromides and aryl boronic esters

In an N_2 filled glovebox, to a 13 x 100 mm screw-capped vial was added PCy_3-CuCl (3.80 mg, 10.0 μmol, 2.00 mol%), boronic ester (0.750 mmol, 1.50 equiv), NaO*t*-Bu (72.1 mg, 0.750 mmol, 1.50 equiv). The vial was sealed with a rubber septum and then removed from the glovebox. Aryl bromide (0.50 mmol, 1.5 equiv) was added via microsyringe and was immediately followed by addition of 0.50 mL (1.00 M) of toluene via syringe. Note: If the aryl bromide is a solid, it was added in the glovebox. The septum was quickly replaced with a Teflon-lined screw cap and then placed in a preheated 100 ºC aluminum heating block and allowed to stir for 15 hours. The reaction was then quenched upon addition of H_2O (1.0 mL) and the mixture was extracted with EtOAc (3 x 1.0 mL). The combined organic layers were concentrated via rotovap. The residue was purified by silica gel column chromatography to obtain the desired product.

■ General Procedure B: Coupling of aryl bromides and alkyl boronic esters

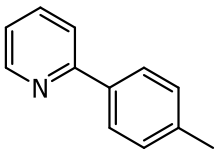
In an N_2 filled glovebox, to a 13 x 100 mm screw-capped vial was added SIMes-CuCl (10.1 mg, 25.0 μmol, 5.00 mol%), alkyl boronic ester (0.750 mmol, 1.50 equiv), NaO*t*-Bu (72.1 mg, 0.750 mmol, 1.50 equiv). The vial was sealed with a rubber septum and then removed from the glovebox. Aryl bromide (0.500 mmol, 1.5 equiv) was added via microsyringe and was immediately followed by addition of 0.50 mL (1.00 M) of toluene via syringe. Note: If the aryl bromide is a solid, it was added in the glovebox. The septum was quickly replaced with a Teflon-lined screw cap and then placed in a preheated 140 ºC aluminum heating block and allowed to stir for 15 hours. The reaction was then quenched upon addition of H_2O (1.0 mL) and the mixture was extracted with EtOAc (3 x 1.0 mL). The combined organic layers were concentrated via rotovap. The residue was purified by silica gel column chromatography to obtain the desired product.

■ General Procedure C: Coupling of aryl bromides and alkyl-9-BBN reagents

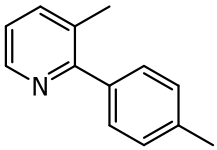
In an N_2 filled glovebox, to a 13 x 100 mm screw-capped vial was added SIMes-CuCl (10.1 mg, 25.0 μmol, 5.00 mol%) and NaO*t*-Bu (72.1 mg, 0.750 mmol, 1.50 equiv). The vial was sealed with a rubber septum and then removed from the glovebox. Aryl bromide (0.500 mmol, 1.5 equiv) was added via microsyringe and was immediately followed by

addition of a solution of alkyl-9-BBN (0.750 mmol, 1.50 equiv) in 0.50 mL of toluene via syringe. The septum was quickly replaced with a Teflon-lined screw cap and then placed in a preheated 140 ºC aluminum heating block and allowed to stir for 15 hours. The reaction was then quenched upon addition of H_2O (1.0 mL) and the mixture was extracted with EtOAc (3 x 1.0 mL). The combined organic layers were concentrated via rotovap. The residue was purified by silica gel column chromatography to obtain the desired product.

■ **Characterization Data:**



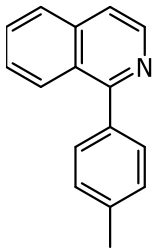
2-(p-tolyl)pyridine (8): The title compound was prepared according to general procedure A. Purification by column chromatography (30:1 hexanes/ethyl acetate) yields **8** as a colorless oil (92% avg. yield of two runs). All characterization data are in agreement with previous literature.[8] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.68 (dt, J = 4.9, 1.6 Hz, 1H), 7.93 – 7.85 (m, 2H), 7.77 – 7.66 (m, 2H), 7.28 (m, 2H), 7.20 (m, 1H), 2.41 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$):** 157.5, 149.6, 138.9, 136.7, 136.6, 129.5, 126.8, 121.8, 120.2, 21.3.



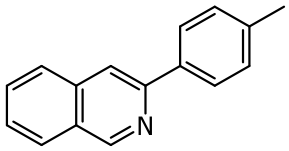
3-methyl-2-(p-tolyl)pyridine (16): The title compound was prepared according to general procedure A. Purification by column chromatography (30:1 hexanes/ethyl acetate) yields **16** as a colorless oil (97% avg. yield of two runs). All characterization data are in agreement with previous literature.[9] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.51 (dd, J = 4.8, 1.7 Hz, 1H), 7.58 – 7.50 (m, 1H), 7.43 (d, J = 6.3 Hz, 2H), 7.25 (d, J = 7.7 Hz, 2H),

[8] L. Ackermann, A. R. Kapdi, S. Fenner, C. Kornhaaß, C. Schulzke, *Chem. Eur. J.* 2011, **17**, 2965.
[9] K. Joydev, K. P. J. Laha, P. Sagarkumar, *Org. Lett.* 2015, **17**, 5890.

7.14 (dd, J = 7.6, 4.8 Hz, 1H), 2.40 (s, 3H), 2.35 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 158.7, 147.0, 138.4, 137.8, 137.6, 130.7, 128.9, 128.8, 121.8, 21.3, 20.2.



1-(p-tolyl)isoquinoline (17): The title compound was prepared according to general procedure A. Purification by column chromatography (30:1 hexanes/ethyl acetate) yields **17** as a colorless oil (94% avg. yield of two runs). All characterization data are in agreement with previous literature.[10] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.60 (d, J = 5.7, 1H), 8.13 (d, J = 8.5 Hz, 1H), 7.87 (d, J = 8.2 Hz, 1H), 7.68 (tt, J = 8.8, 1.8 Hz, 1H), 7.65 – 7.57 (m, 3H), 7.53 (ddd, J = 10.0, 5.1, 3.2 Hz, 1H), 7.34 (d, J = 7.7 Hz, 2H), 2.46 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 160.8, 142.3, 138.4, 136.9, 136.8, 129.9, 129.9, 129.1, 127.7, 127.1, 127.0, 126.8, 119.7, 21.4.



3-(p-tolyl)isoquinoline (18): The title compound was prepared according to general procedure A. Purification by column chromatography (1:1 hexanes/dichloromethane) yields **18** as a white solid (39% avg. yield of two runs). All characterization data are in agreement with previous literature.[11] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 9.30 (s, 1 H), 8.03-8.00 (m, 3 H), 7.94 – 7.92 (d, J = 8.4 Hz, 1 H), 7.82 – 7.79 (d, J = 8.4 Hz, 1 H), 7.65 – 7.61 (t, J = 7.6 Hz, 1 H), 7.54 – 7.50 (t, J = 7.6 Hz, 1 H), 7.30 – 7.28 (d, J = 8.0 Hz, 2 H), 2.40 (s, 3 H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 152.2, 151.1, 138.3, 136.7, 136.6, 130.3, 129.4, 127.5, 127.4, 126.8, 126.7, 126.7, 115.8, 21.2.

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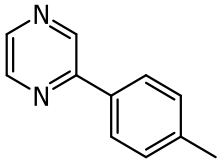
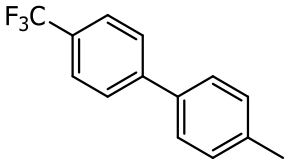
[10] S. Thapa. A. Kafle, S. K. Gurung, A. Montoya, P. Riedel, R. Giri, *Angew. Chem. Int. Ed.* 2015, **54**, 8236.

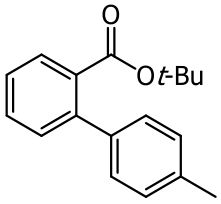
[11] Y.-N. Niu, Z.-Y. Yan, G.-L. Gao, H.-L.Wang, X.-Z. Shu, K.-G. Ji, Y.-M. Liang *J. Org. Chem.* 2009, **74**, 2893.



2-(p-tolyl)pyrazine (19): The title compound was prepared according to general procedure A. Purification by column chromatography (20:1 hexanes/ethyl acetate) yields **19** as a white solid (54% avg. yield of two runs). All characterization data are in agreement with previous literature.[12] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 9.00 (s, 1H), 8.59 – 8.61 (m, 1H), 8.45 (d, J = 2.4 Hz, 1H), 7.91 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 7.8 Hz, 2H), 2.42 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 152.9, 144.2, 142.7, 142.1, 140.2, 133.7, 129.9, 126.9, 21.5.



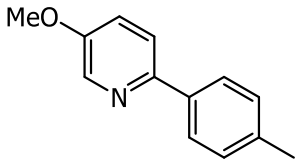
4-methyl-4'-(trifluoromethyl)-1,1'-biphenyl (22): The title compound was prepared according to general procedure A. Purification by column chromatography (hexanes) yields **22** as a white solid (37% avg. yield of two runs). All characterization data are in agreement with previous literature. [13] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.68 (s, 4H), 7.49 (d, J = 7.8 Hz, 2H), 7.27 (d, J = 7.9 Hz, 2H), 2.41 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 144.8, 138.3, 137.0, 129.8, 129.2 (q, J = 32.5 Hz), 127.3, 127.3, 125.8 (q, J = 3.8 Hz), 124.5 (q, J = 270.0 Hz), 21.3.



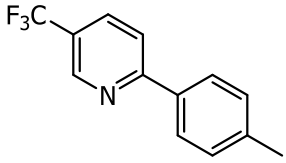
tert-butyl 4'-methyl-[1,1'-biphenyl]-2-carboxylate (9): The title compound was prepared according to general procedure A. Purification by column chromatography (30:1 hexanes/ethyl acetate) yields **9** as a colorless oil (52% avg. yield of two runs). All

[12] S. Thapa. A. Kafle, S. K. Gurung, A. Montoya, P. Riedel, R. Giri, *Angew. Chem. Int. Ed.* 2015, **54**, 8236.
[13] S. Shi, G. Meng, M. Szoztak, *Angew. Chem. Int. Ed.* 2016, **55**, 6959.

characterization data are in agreement with previous literature.[14] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.69 (d, J = 7.6 Hz, 1H), 7.52 (t, J = 7.4 Hz, 1H), 7.41 (t, J = 7.4 Hz, 1H), 7.33 (d, J = 7.6 Hz, 1H), 7.23 (d, J = 8.0 Hz, 1H), 7.18 (d, J = 8.0 Hz, 1H), 2.41 (s, 3H), 1.29 (s, 9H) ppm; **^{13}C NMR (100 MHz, $CDCl_3$)**: d 167.8, 140.6, 137.6, 135.5, 135.5, 131.8, 129.7, 129.5, 129.1, 129.0, 128.9, 127.8, 125.4, 80.1, 28.2, 17.2.



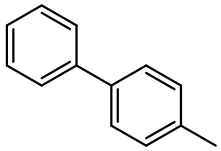
5-methoxy-2-(p-tolyl)pyridine (20): The title compound was prepared according to general procedure A. Purification by column chromatography (20:1 hexanes/ethyl acetate) yields **20** as a white solid (62% avg. yield of two runs). **m.p:** 70-72 ºC **IR (neat)**: 3009 (w), 2933 (w), 1577 (m), 1566 (m), 1278 (s). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.38 (s, 1H), 7.83 (d, J = 8.3 Hz, 2H), 7.64 (d, J = 8.7 Hz, 1H), 7.25 (d, J = 8.3 Hz, 4H), 3.90 (s, 3H), 2.40 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 154.6, 150.2, 138.0, 137.0 136.4, 129.4, 126.2, 121.3, 120.5, 55.7, 21.2. **HRMS (EI):** Calculated for $C_{13}H_{13}NO$ [M^+]: 199.0992, Found: 199.0986.



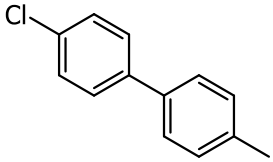
2-(p-tolyl)-5-(trifluoromethyl)pyridine (21): The title compound was prepared according to general procedure A. Purification by column chromatography (5:1 hexanes/ethyl acetate) yields **21** as a light yellow solid (71% avg. yield of two runs). All characterization data are in agreement with previous literature.[15] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.92 (s, 1H), 7.95 (t, J = 8.1 Hz, 3H), 7.82 (d, J = 8.4 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H), 2.43 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 160.66, 146.53 (q, J = 4.0 Hz),

[14] G. Anglis, A. Resani, S. Durdagi, K. Spyridaki, T. Tumova, J. Slaninova, P. Giannopoulos, D. Vlahakos, G. Liapakis, T. Mavromoustakos, J. Matsoukas, *Eur. J. Med. Chem.* 2012, **55**, 358.
[15] S. Chen, G. Tan, W.-Y. Wong, H.-S. Kwok, *Adv. Funct. Mater*. 2011, **21**, 3785.

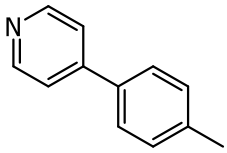
140.34, 135.17, 133.84 (q, J = 3.4 Hz), 129.72, 127.16, 124.49 (q, J = 33.0 Hz), 123.84 (q, J = 272.0 Hz), 119.60, 21.35.



4-methyl-1,1'-biphenyl (33): The title compound was prepared according to general procedure A. Purification by column chromatography (hexanes) yields **33** as a white solid (73% avg. yield of two runs). All characterization data are in agreement with previous literature.[16] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.64 – 7.55 (m, 2H), 7.55 – 7.46 (m, 2H), 7.43 (dd, J = 8.4, 6.9 Hz, 2H), 7.37 – 7.29 (m, 1H), 7.29 – 7.22 (m, 2H), 2.40 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 141.2, 138.4, 137.1, 129.5, 129.5, 128.8, 127.1, 127.0, 126.9, 21.2.



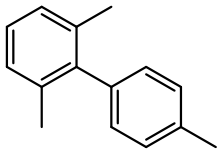
4-chloro-4'-methyl-1,1'-biphenyl (34): The title compound was prepared according to general procedure A. Purification by column chromatography (hexanes) yields **34** as a white solid (83% avg. yield of two runs). All characterization data are in agreement with previous literature.[17] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.53 – 7.48 (m, 2H), 7.45 (d, J = 8.3 Hz, 2H), 7.42 – 7.35 (m, 2H), 7.25 (d, J = 7.9 Hz, 2H), 2.40 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 139.6, 137.5, 137.1, 133.1, 129.6, 128.9, 128.2, 126.8, 21.1.



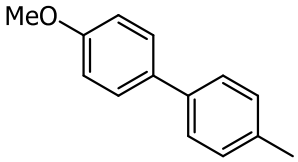
4-(p-tolyl)pyridine (32): The title compound was prepared according to general procedure A. Purification by column chromatography (5:1 hexanes/ethyl acetate) yields

[16] T. Mino, Y. Shirae, M. Sakamoto, T. Fujita, *J. Org. Chem*. 2005, **70**, 2191.
[17] Z. Xiong, N. Wang, M. Dai, A. Li, J. Chen, *Org. Lett.* 2004, **6**, 3337.

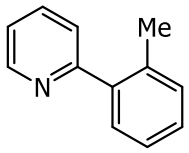
32 as a white solid (85% avg. yield of two runs). All characterization data are in agreement with previous literature.[18] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.62 (d, J = 4.9 2H), 7.65 – 7.36 (m, 3H), 7.37 – 7.10 (m, 3H), 2.40 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 150.2, 148.2, 139.2, 135.1, 129.8, 126.8, 121.3, 21.2.



2,4',6-trimethyl-1,1'-biphenyl (36): The title compound was prepared according to the general procedure A. Purification by column chromatography (pentane) yields **36** as a colorless oil (49% avg. yield of two runs). All characterization data are in agreement with previous literature.[19] **^{1}H NMR (600 MHz, $CDCl_3$)**: δ 7.25 – 7.21 (m, 2H), 7.16 (dd, J = 8.5, 6.5 Hz, 1H), 7.11 (d, J = 7.5 Hz, 2H), 7.05 – 7.02 (m, 2H), 2.42 (s, 3H), 2.05 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 141.8, 138.0, 136.2, 136.0, 129.1, 128.8, 127.2, 126.8, 21.2, 20.9.

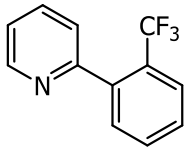


4-methoxy-4'-methyl-1,1'-biphenyl (35): The title compound was prepared according to general procedure A. Purification by column chromatography (pentane) yields **35** as a colorless oil (55% avg. yield of two runs). All characterization data are in agreement with previous literature.[17] **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.51 (d, J = 6.2 Hz, 2H), 7.45 (dd, J = 8.1, 2.2 Hz, 3H), 7.22 (d, J = 7.7 Hz, 2H), 6.96 (d, J = 9.1 Hz, 2H), 3.85 (s, 3H), 2.39 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 159.1, 138.1, 136.5, 133.9, 129.6, 128.1, 126.7, 114.3, 55.5, 21.2.

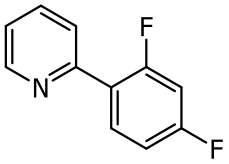


[18] C. A. Fleckenstein, H. Plenio, *Chem. Eur. J*. 2008, **14**, 4267.
[19] L. Bruce, P. Tue, A. Alexander, *Org. Lett*. 2008, **10**, 1333.

2-(o-tolyl)pyridine (23): The title compound was prepared according to general procedure A. Purification by column chromatography (30:1 hexanes/ethyl acetate) yields **23** as a colorless oil (87% avg. yield of two runs). All characterization data are in agreement with previous literature.[20] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.67 (d, J = 4.9 Hz, 1H), 7.72 (d, J = 7.7 Hz, 1H), 7.37 (d, J = 7.9 Hz, 2H), 7.31 – 7.15 (m, 4H), 2.34 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 160.1, 149.2, 140.5, 136.1, 135.7, 130.7, 129.6, 128.3, 125.9, 124.1, 121.6, 20.3.



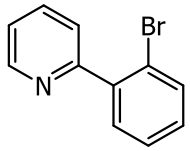
2-(2-(trifluoromethyl)phenyl)pyridine (24): The title compound was prepared according to general procedure A. Purification by column chromatography (30:1 hexanes/ethyl acetate) yields **24** as a colorless oil (55% avg. yield of two runs). All characterization data are in agreement with previous literature.[20] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.69 (d, J = 5.0 Hz, 1H), 7.81 – 7.71 (m, 2H), 7.62 (t, J = 7.6 Hz, 1H), 7.57 – 7.46 (m, 2H), 7.43 (d, J = 7.9 Hz, 1H), 7.31 (ddd, J = 7.6, 4.9, 1.2 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 157.8, 149.1, 140.0 (q, J = 1.7 Hz), 135.9, 131.5, 131.4, 128.3, 128.2 (q, J = 30.4 Hz), 126.3 (q, J = 5.2 Hz), 124.1 (q, J = 272.4 Hz), 123.9 (q, J = 2.0 Hz).



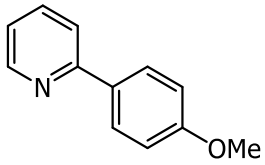
2-(2,4-difluorophenyl)pyridine (27): The title compound was prepared according to general procedure A. Purification by column chromatography (30:1 hexanes/ethyl acetate) yields **27** as a colorless oil (86% avg. yield of two runs). All characterization data are in agreement with previous literature.[21] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.69 (d, J = 4.9 Hz, 1H), 7.98 (td, J = 8.9, 6.7 Hz, 1H), 7.85 – 7.62 (m, 2H), 7.24 (q, J = 4.5 Hz, 1H),

[20] C. Gosmini, C. Bassene-Ernst, M. Durandetti, *Tetrahedron* 2009, **65**, 6141.
[21] A. F. Henwood, A. K. Bansal, D. B. Cordes, A. M. Z. Slawin, D. W. Samuel, E. Zysman-Colman, *J. Mater. Chem. C* 2016, **4**, 3726.

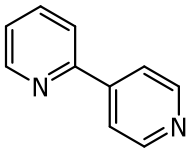
6.99 (t, J = 7.7 Hz, 1H), 6.89 (ddd, J = 11.3, 8.8, 2.5 Hz, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 164.6, 162.1, 159.5, 152.7, 149.9, 136.6, 132.3, 124.4, 122.6, 112.1, 104.5.



2-(2-bromophenyl)pyridine (25): The title compound was prepared according to general procedure A. Purification by column chromatography (20:1 hexanes/ethyl acetate) yields **25** as a clear oil (62% avg. yield of two runs). All characterization data are in agreement with previous literature.[22] **^{1}H NMR (400 MHz, $CDCl_3$):** 7.68 (d, J = 7.6 Hz, 1H), 7.40 - 7.31 (m, 4H), 7.27 (d, J = 8.2 Hz, 2H), 7.20 (ddd, J = 7.8 Hz, J = 6.2 Hz, J = 2.9 Hz, 1H), 2.44 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 142.6, 138.2, 137.3, 133.1, 131.3, 129.2, 128.7, 128.5, 127.3, 122.7, 21.2.



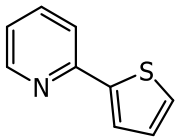
2-(4-methoxyphenyl)pyridine (28): The title compound was prepared according to general procedure A. Purification by column chromatography (10:1 hexanes/ethyl acetate) yields **28** as a white solid (69% avg. yield of two runs). All characterization data are in agreement with previous literature.[20] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.65 (d, J = 4.9 Hz, 1H), 7.95 (d, J = 8.6 Hz, 2H), 7.79 – 7.61 (m, 2H), 7.17 (ddd, J = 7.3, 4.8, 1.4 Hz, 1H), 7.00 (d, J = 9.0 Hz, 2H), 3.87 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 160.5, 157.1, 149.5, 136.6, 132.0, 128.2, 121.4, 119.8, 114.1, 55.3.



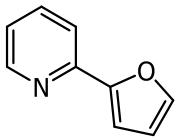
2,4'-bipyridine (29): The title compound was prepared according to general procedure A. Purification by column chromatography (5:1 hexanes/ethyl acetate) yields **29** as a

[22] T. Nguyen, W. Chiu, X. Wang, M. Sattler, J. Love, *Org. Lett.*, 2016, **18**, 5492.

white solid (85% avg. yield of two runs).[23] All characterization data are in agreement with previous literature. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.88 – 8.64 (m, 3H), 7.97 – 7.85 (m, 2H), 7.85 – 7.76 (m, 2H), 7.35 (ddd, J = 6.1, 4.8, 2.5 Hz, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 154.6, 150.4, 150.1, 146.3, 137.0, 123.8, 121.0, 120.8.



2-(thiophen-2-yl)pyridine (30): The title compound was prepared according to general procedure A. Purification by column chromatography (30:1 hexanes/ethyl acetate) yields **30** as a white solid (49% avg. yield of two runs). All characterization data are in agreement with previous literature.[24] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.55 (d, J = 5.0 Hz, 1H), 7.74 – 7.61 (m, 2H), 7.57 (d, J = 3.7 Hz, 1H), 7.38 (d, J = 5.1 Hz, 1H), 7.18 – 7.01 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 152.6, 149.5, 144.8, 136.6, 128.0, 127.5, 124.5, 121.9, 118.7.



2-(furan-2-yl)pyridine (31): The title compound was prepared according to general procedure A. Purification by column chromatography (30:1 hexanes/ethyl acetate) yields **31** as a white solid (34% avg. yield of two runs). All characterization data are in agreement with previous literature.[25] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.59 (d, J = 4.8 Hz, 1H), 7.80 – 7.61 (m, 2H), 7.53 (s, 1H), 7.15 (t, J = 5.9 Hz, 1H), 7.05 (d, J = 3.4 Hz, 1H), 6.54 (s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 153.5, 149.5, 149.3, 143.3, 136.6, 121.9, 118.5, 112.0, 108.5.

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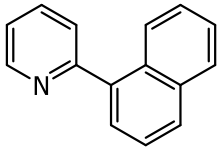
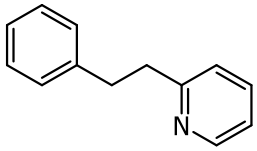
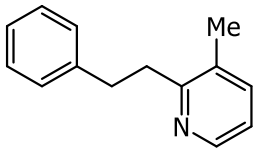
[23] E. Zhang, J. Tang, S. Li, P. Wu, J. Moses, K. B. Sharpless, *Chem.Eur.J.* 2016, **22**, 5692.
[24] M. Tingoli, M. Tiecco, L. Testaferri, R. Andrenacci, R. Balducci, *J. Org. Chem*. 1993, **58**, 6097.
[25] L. Wang, Z.-X. Wang *Org. Lett*. 2007, **9**, 4335.



2-(naphthalen-1-yl)pyridine (26): The title compound was prepared according to general procedure A. Purification by column chromatography (30:1 hexanes/ethyl acetate) yields **26** as a colorless oil (93% avg. yield of two runs). All characterization data are in agreement with previous literature.[23] **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.85 – 8.74 (m, 1H), 8.14 – 8.04 (m, 1H), 7.97 – 7.88 (m, 2H), 7.83 (td, J = 7.7, 1.8 Hz, 1H), 7.65 – 7.53 (m, 3H), 7.53 – 7.43 (m, 2H), 7.34 (ddd, J = 7.5, 4.9, 1.1 Hz, 1H).; **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 159.3, 149.6, 138.5, 136.4, 134.0, 131.2, 128.9, 128.4, 127.5, 126.5, 125.9, 125.6, 125.3, 125.1, 122.1.



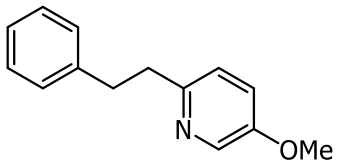
2-phenethylpyridine (39): The title compound was prepared according to general procedure B. Purification by column chromatography (5:1 hexanes/ethyl acetate) yields **39** as a colorless oil (64% avg. yield of two runs). All characterization data are in agreement with previous literature.[26] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.55 (d, J = 4.8 Hz, 1H), 7.54 (td, J = 7.7, 1.9 Hz, 1H), 7.25 (d, J = 6.7 Hz, 3H), 7.22 – 7.14 (m, 4H), 7.14 – 7.03 (m, 2H), 3.06 (m, 4H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 161.5, 149.6, 141.8, 136.6, 128.8, 128.6, 126.2, 123.3, 121.4, 40.5, 36.3.



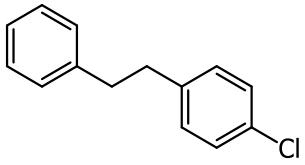
3-methyl-2-phenethylpyridine (40): The title compound was prepared according to general procedure B. Purification by column chromatography (5:1 hexanes/ethyl acetate) yields **40** as a colorless oil (68% avg. yield of two runs). All characterization data are in

[26] M. Lautens, A. Roy, K. Fukuoka, K. Fagnou, B. Martı´n-Matute, *J. Am. Chem. Soc*. 2001, **123**, 5358.

agreement with previous literature.[27] **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.41 (dd, J = 4.9, 1.6 Hz, 1H), 7.38 (dd, J = 7.5, 1.6 Hz, 1H), 7.31 – 7.24 (m, 2H), 7.23 – 7.15 (m, 3H), 7.03 (dd, J = 7.6, 4.8 Hz, 1H), 3.16 – 2.92 (m, 4H), 2.22 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 159.5, 146.7, 142.0, 137.5, 131.1, 128.4, 128.4, 125.9, 121.3, 37.4, 35.0, 18.7.

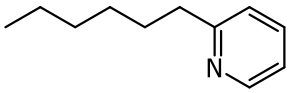


5-methoxy-2-phenethylpyridine (41): The title compound was prepared according to general procedure B. Purification by column chromatography (5:1 hexanes/ethyl acetate) yields **41** as a colorless oil (39% avg. yield of two runs). **IR (neat)**: 3025 (w), 2936 (m), 1572 (m), 1493 (s), 1264 (s). **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.25 (d, J = 3.0 Hz, 1H), 7.30 – 7.21 (m, 2H), 7.20 – 7.14 (m, 3H), 7.08 (dd, J = 8.5, 3.0 Hz, 1H), 6.97 (d, J = 8.5 Hz, 1H), 3.83 (s, 3H), 3.03 (m, 4H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 154.0, 153.3, 141.7, 136.6, 128.5, 128.3, 125.9, 123.0, 121.1, 55.6, 39.2, 36.3. **HRMS (EI):** Calculated for $C_{14}H_{15}NO$ [M^+]: 213.1148, Found: 213.1142.

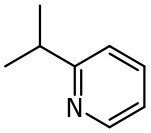


1-chloro-4-phenethylbenzene (42): The title compound was prepared according to general procedure B. Purification by column chromatography (pentane) yields **42** as a colorless oil (60% avg. yield of two runs). All characterization data are in agreement with previous literature.[28] **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.31 – 7.25 (m, 3H), 7.24 (d, J = 8.3 Hz, 2H), 7.22 – 7.18 (m, 1H), 7.17 – 7.13 (m, 2H), 7.09 (dd, J = 8.6, 2.5 Hz, 2H), 2.90 (s, 4H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 141.3, 140.1, 131.6, 129.8, 128.5, 128.4, 128.4, 126.0, 37.8, 37.2.

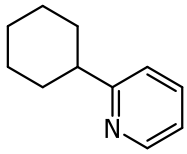
[27] Y. Ogiwara; T. Kochi, F. Kaki *Org. Lett*. 2011, **13**, 3254.
[28] L. Jin, Y. Zhao, L. Zhu, H. Zhang, A. Lei, *Adv. Synth. Catal.* 2009, **351**, 630.



2-hexylpyridine (38): The title compound was prepared according to general procedure B. Purification by column chromatography (10:1 hexane/Et_2O) yields **38** as a colorless oil (61% yield). All characterization data are in agreement with previous literature.[29] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.50 (d, J = 4.7 Hz, 1H), 7.56 (td, J = 7.7, 1.9 Hz, 1H), 7.12 (d, J = 7.7 Hz, 1H), 7.07 (ddd, J = 7.5, 4.9, 1.1 Hz, 1H), 2.79 – 2.73 (m, 2H), 1.73 – 1.68 (m, 2H), 1.30 (m, 6H), 0.96 – 0.73 (m, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 162.5, 149.1, 136.2, 122.7, 120.8, 38.4, 31.7, 29.9, 29.1, 22.6, 14.0.



2-isopropylpyridine (43): The title compound was prepared according to general procedure C. Purification by column chromatography (20:1 hexane/Et_2O) yields **43** as a colorless oil (64% avg. yield of two runs). All characterization data are in agreement with previous literature.[30] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.53 (d, J = 4.6 Hz, 1H), 7.61 (t, J = 7.6, 1H), 7.17 (d, J = 7.7 Hz, 1H), 7.10 (dd, J = 6.8, 5.4 Hz, 1H), 3.07 (m, 1H), 1.30 (d, J = 6.9 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 167.4, 149.1, 136.8, 121.3, 120.9, 36.5, 22.8.



2-cyclohexylpyridine (44): The title compound was prepared according to general procedure C. Purification by column chromatography (20:1 hexane/Et_2O) yields **44** as a colorless oil (67% avg. yield of two runs). All characterization data are in agreement with

[29] J.-F. Soule, H. Miyamura, S. Kobayashi, *J. Am. Chem. Soc.*, 2013, **135**, 10602.
[30] P. C. Too, G. H. Chan, T. L. Tnay, H. Hirao, S. Chiba, *Angew. Chem. Int. Ed.* 2016, **55**, 3719.

previous literature.[31] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.53 (d, J = 4.8 Hz, 1H), 7.59 (dd, J = 8.0, 1.6, 1H), 7.14 (d, J = 8.0, 1H), 7.08 (dd, J = 7.6, 0.8, 1H), 2.69 (t, J = 12.0 Hz, 1H), 1.53 (dt, J = 12.4, 3.2, 2H), 1.42 (td, J = 12.4, 3.2, 2H), 1.28 (td, J = 12.4, 3.2, 1 H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 166.5, 149.0, 136.3, 120.9, 45.6, 32.9, 26.6, 26.1.

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