

Supporting Information

Sulfonato-imino copper(II) complexes : fast and general Chan-Evans-Lam coupling of amines and anilines

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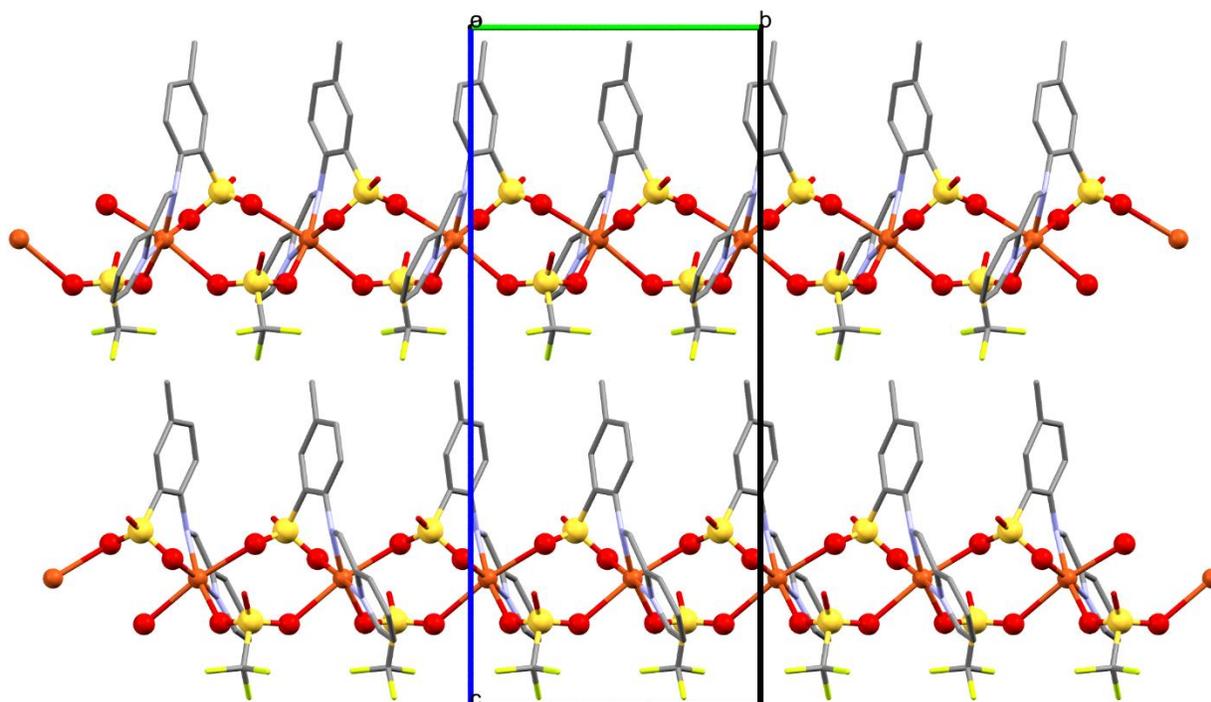


Figure S1. Packing diagram showing the 1D-coordination polymer formed by **2** along the *b*-axis due to bridging coordination of the sulfonate and triflate groups.

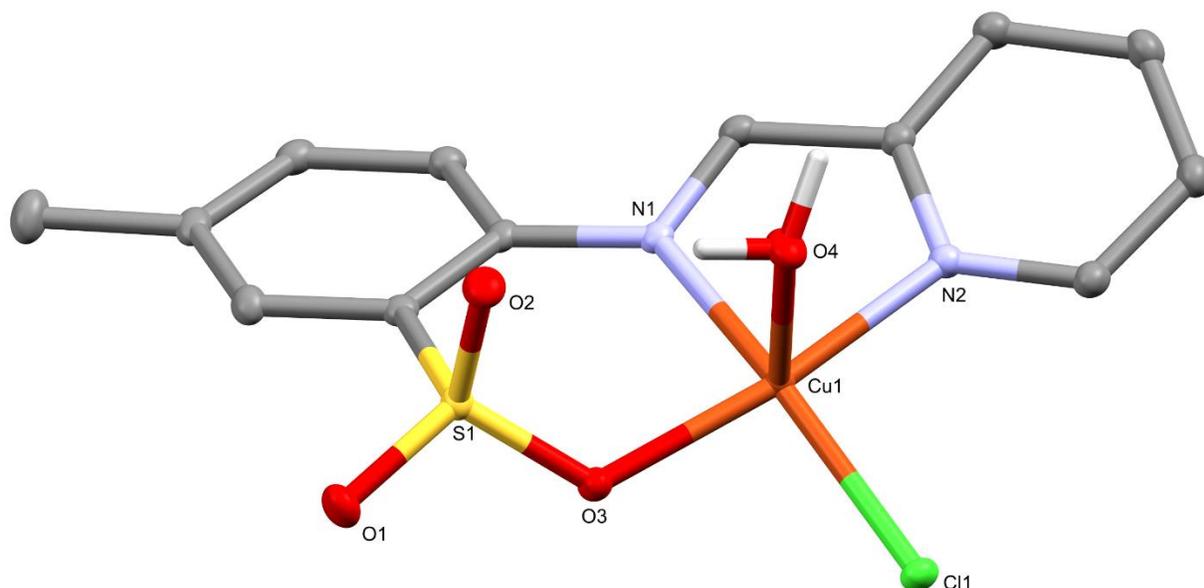


Figure S2. Crystal structure of complex **1**. Hydrogen atoms other than that of water omitted for clarity. Thermal ellipsoids are drawn at 50% probability.

Table S1. Arylation of aniline catalysed by **1**

$\text{PhNH}_2 + \text{PhB(OH)}_2 \xrightarrow{2.5 \text{ mol\% } \mathbf{1}} \text{Ph}_2\text{NH}$				
Entry	Solvent	Additive	Time ^a	Conversion ^b
1	MeCN		320 min	0%
2	MeOH		320 min	86%
3	THF		320 min	67%
4	CH ₂ Cl ₂		320 min	41%
5	toluene		320 min	36%
6	MeOH		320 min	86%
7	MeOH	1 equiv NEt ₃	320 min	0%
8	MeOH	2.5 mol% NEt ₃	320 min	12%
9	MeOH	molecular sieves	320 min	62%
10	MeOH	Using 2 as catalyst	320 min	98%

Conditions: room temperature, air, 1.0 M aniline, 2.5 mol% catalyst, 1.5 equiv. PhB(OH)_2 . ^a Reactions were quenched before full conversion to allow comparisons. ^b Conversion to product, determined by GC-MS and calibrated vs. internal standard.

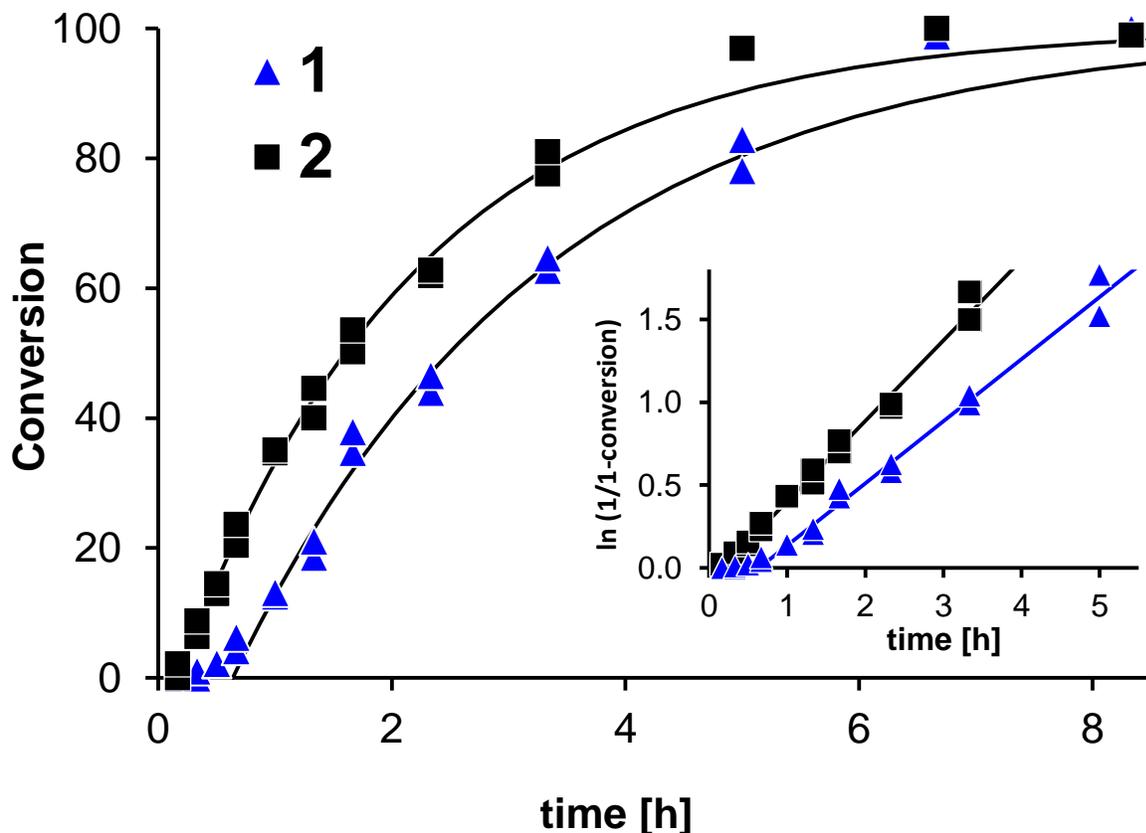
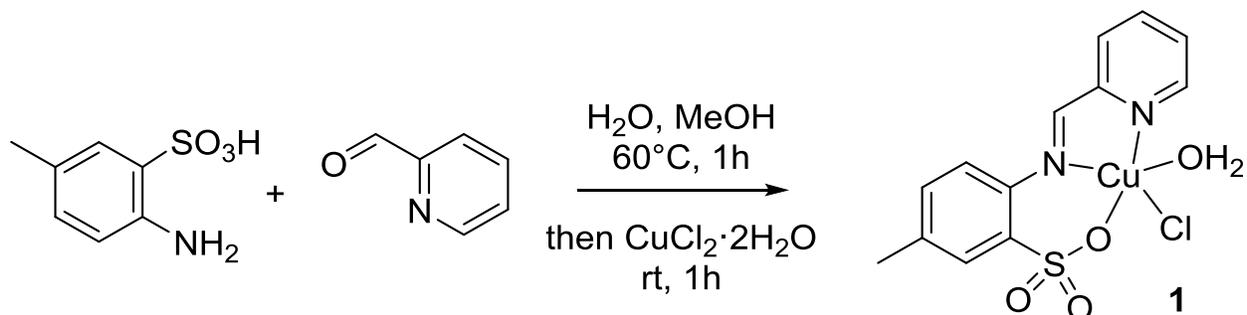


Figure S3. Time-Conversion plots for the arylation of aniline with catalyst 1 (triangles) or 2 (squares). Conditions: 1 M aniline, 1.5 PhB(OH)_2 , 25 mM catalyst, ambient temperature, methanol. Conversion determined from GC-MS by comparison to (calibrated) standard either from disappearance of monomer or appearance of product (both data shown). The inset shows the linearized rate plot.

Experimental Data

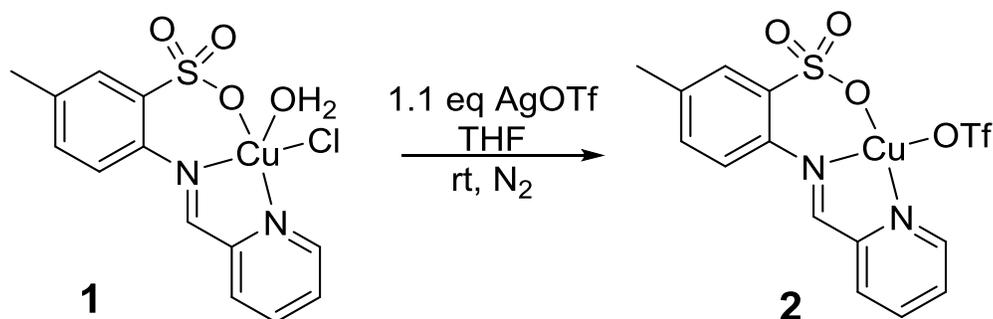
General. Phenyl boronic acid was purified by washing with dichloromethane until the filtrate stayed colorless. All other chemicals were purchased from common commercial suppliers and used without further purification. Elemental analyses were performed by the Laboratoire d'analyse élémentaire (Université de Montreal). UV/vis

spectra were recorded on a Cary Series UV-Vis-NIR spectrophotometer from Agilent Technologie. GC-MS spectra were recorded on a Agilent Technologie GC/MS.



LCuCl(H₂O), 1. To a hot solution (60 °C) of 4-aminotoluene-3-sulfonic acid (184 mg, 1.0 mmol) in water (5 mL) and methanol (10 mL) was added 2-pyridinecarboxaldehyde (95 μL , 1.0 mmol). The mixture was stirred one hour, then copper chloride hydrate (205 mg, 1.1 mmol) was added, resulting in a green solution. Heating was stopped and the solution was stirred another hour. Slow evaporation of solvent afforded green crystals of **1** (321 mg, 82%).

Anal. Calcd. for $\text{C}_{13}\text{H}_{13}\text{ClCuN}_2\text{O}_4\text{S}$: C, 39.80; H, 3.34; N, 7.14; S, 8.17. Found: C, 40.09; H, 3.37; N, 3.37; S, 8.47. UV-vis (DMSO, $1 \cdot 10^{-2}$ M or $1.49 \cdot 10^{-4}$ M) [λ_{max} , nm (ϵ , $\text{M}^{-1} \cdot \text{cm}^{-1}$)] : 338 (97 100), 800 (500).



LCuOTf, 2. Complex **1** (391, 1.0 mmol) was dissolved in dry THF (5 mL) under nitrogen atmosphere to give a green solution. Silver triflate (28 mg, 1.1 mmol) was added. After one hour of reaction at ambient temperature, a precipitate appeared and the colour of the solution intensified. Slow evaporation of the green solution (under N_2), afforded green crystals of **2** (263 mg, 54%).

Anal. Calcd. for $C_{14}H_{11}CuF_3N_2O_6S_2$: C, 34.46; H, 2.27; N, 5.74; S, 13.14. Found: C, 34.10; H, 2.59; N, 5.26; S, 12.61. UV-vis (DMSO, $1.2 \cdot 10^{-2}$ M or $3.35 \cdot 10^{-4}$ M) [λ_{\max} , nm (ϵ , $M^{-1} \cdot cm^{-1}$)] : 338 (62 100), 730 (470).

General procedure for Chan-Evans-Lam couplings. To a solution of amine or aniline (1 mmol) and phenylboronic acid (1.5 mmol) in methanol (1 mL) was added catalyst **1** or **2** (0.025 mmol). Trimethoxybenzene was added as internal standard. The reaction was stirred open to air at ambient temperature or at 50 °C under O_2 atmosphere. After the desired time, the reaction was quenched with a saturated aqueous solution of ammonium chloride. For analysis of conversion, the organic layer was extracted three times with ethyl acetate and filtered through a short silica plug to remove copper complex. Conversion was determined by comparison to trimethoxybenzene. Calibration factors between products and trimethoxybenzene were determined from simultaneous NMR and GC-MS analysis or by analysis of stock solutions prepared from isolated or commercially available products. 1H NMR data of all products agreed with literature data and the only observed species in the reaction mixtures were starting material (if conversion was less than 100%), product and biphenyl side-product from homocoupling reactions.

Isolation of coupling products. To a solution of amine (5 mmol) and phenylboronic acid (7.5 mmol) in methanol (5 mL) was added **2** (0.125 mmol). The reaction mixture was stirred for 12 h open to air at ambient temperature. The mixture was diluted with dichloromethane (20 mL) and washed once with a saturated solution of ammonium chloride and twice with water. Then combined aqueous phases were re-extracted two times with dichloromethane. The combined organic phases were dried, evaporated and purified by column chromatography with hexane/ethyl acetate.

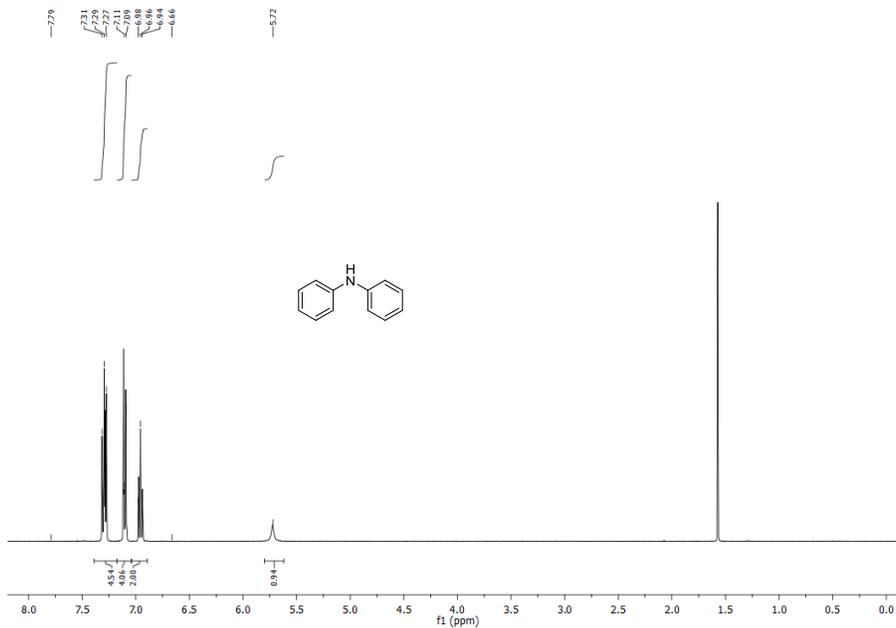


Figure S4. Diphenylamine. White powder, 761 mg, 90%

^1H NMR (400 MHz, CDCl_3): 7.25 (t, $J = 7$ Hz, 2H), 7.05 (d, $J = 7$ Hz, 2H), 6.90 (t, $J = 6$ Hz, 1H), 5.61 (s, 1H); ^{13}C NMR (400 MHz, CDCl_3): 142.8, 129.1, 121.1, 117.8

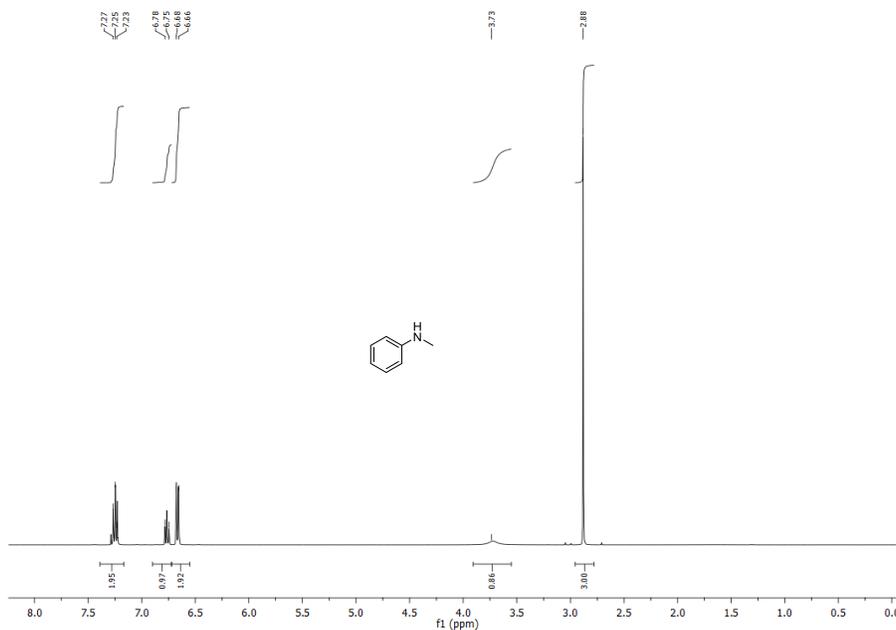


Figure S5. N-Methylaniline. Oil, 471 mg, 88%

^1H NMR (400 MHz, CDCl_3): 7.28 (t, $J = 7$ Hz, 2H), 6.7 (d, $J = 8$ Hz, 2H), 6.55 (t, $J = 8$ Hz, 1H), 3.69 (s, 1H), 2.75 (s, 3H); ^{13}C NMR (400 MHz, CDCl_3): 149.9, 129.5, 117.2, 112.0, 30.6

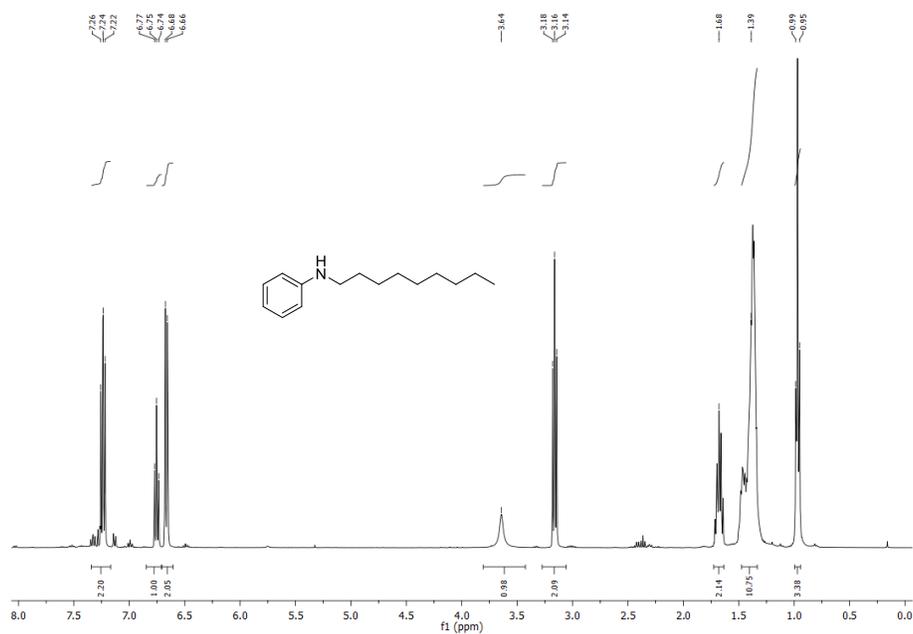


Figure S6. *N*-Octylaniline. Oil, 871 mg , 85%

^1H NMR (400 MHz, CDCl_3): 7.17 (t, $J = 9$ Hz, 2H), 6.70 (t, $J = 9$ Hz, 1H), 6.61 (d, $J = 8$ Hz, 1H), 3.4 (s, 1H), 3.12 (t, $J = 7$ Hz, 2H), 1.60 (m, 2H), 1.28-1.25 (m, 10H), 0.895 (t, $J = 7$ Hz, 3H); ^{13}C NMR (400 MHz, CDCl_3): 148.4, 129.1, 117.0, 112.6, 44.0, 31.8, 30.9, 29.5, 29.2, 27.1, 22.6, 14.0

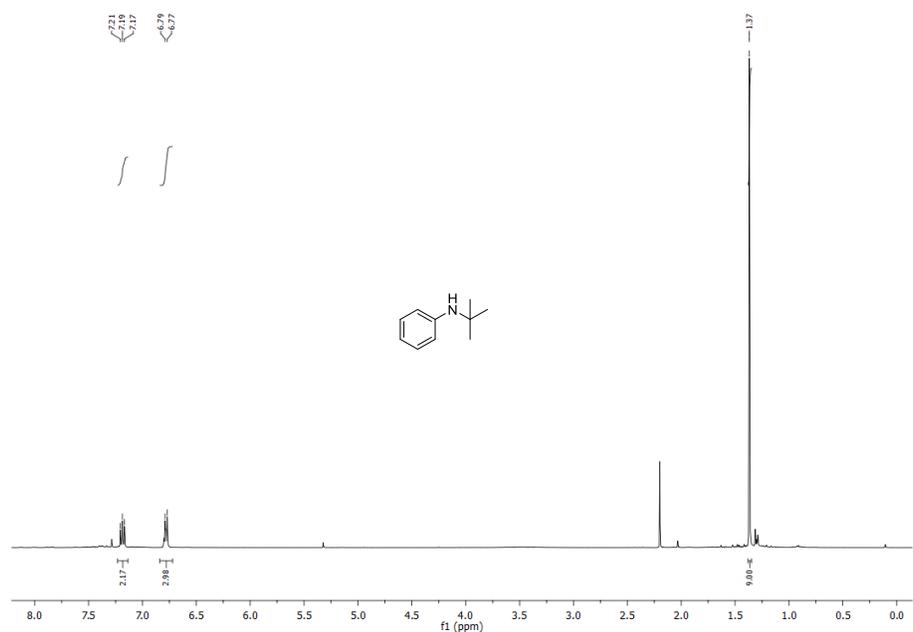


Figure S7. *N-tert*-butylaniline. Oil, 976 mg, 86%

^1H NMR (400 MHz, CDCl_3): 7.27 (t, $J = 8$ Hz, 2H), 6.76 (m, 3H), 1.37 (s, 9H); ^{13}C NMR (400 MHz, CDCl_3): 146.7, 128.8, 118.3, 117.5, 51.5, 30.7

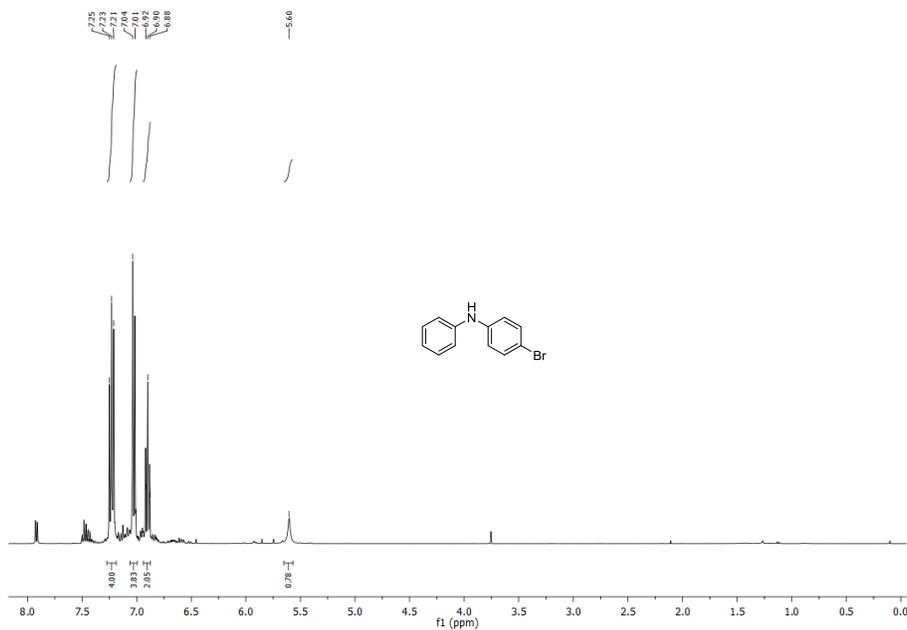


Figure S8. *N*-phenyl-(4-bromo)aniline. White powder, 1.099 mg, 89%

^1H NMR (400 MHz, CDCl_3): 7.34 (d, $J = 9$ Hz, 2H), 7.28 (d, $J = 8$ Hz, 2H), 7.05 (d, $J = 8$ Hz, 2H), 6.86 (m, 3H), 5.66 (s, 1H); ^{13}C NMR (400 MHz, CDCl_3): 142.5, 142.4, 132.2, 129.5, 121.7, 119.0, 118.3, 112.6

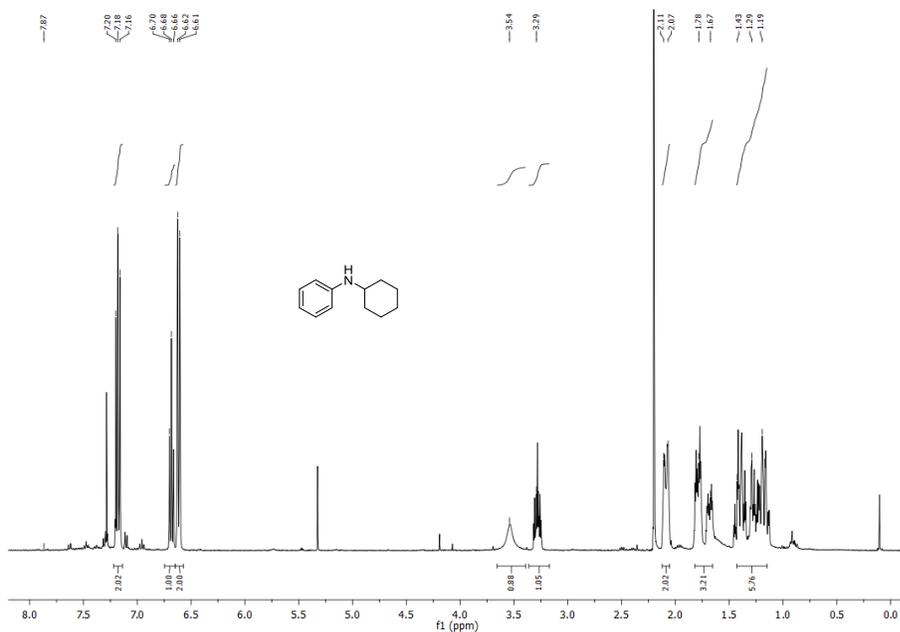


Figure S9. *N*-Cyclohexylaniline. White powder, 787 mg, 90%

^1H NMR (400 MHz, CDCl_3): 7.17 (t, $J = 7$ Hz, 2H), 6.69 (t, $J = 7$ Hz, 1H), 6.62 (d, $J = 7$ Hz, 2H), 3.39 (s, 1H), 3.25 (m, 1H), 2.07 (m, 2H), 1.78 (m, 3H), 1.43 (m, 5H); ^{13}C NMR (400 MHz, CDCl_3): 147.3, 129.1, 116.8, 113.1, 51.6, 33.4, 25.8, 24.9

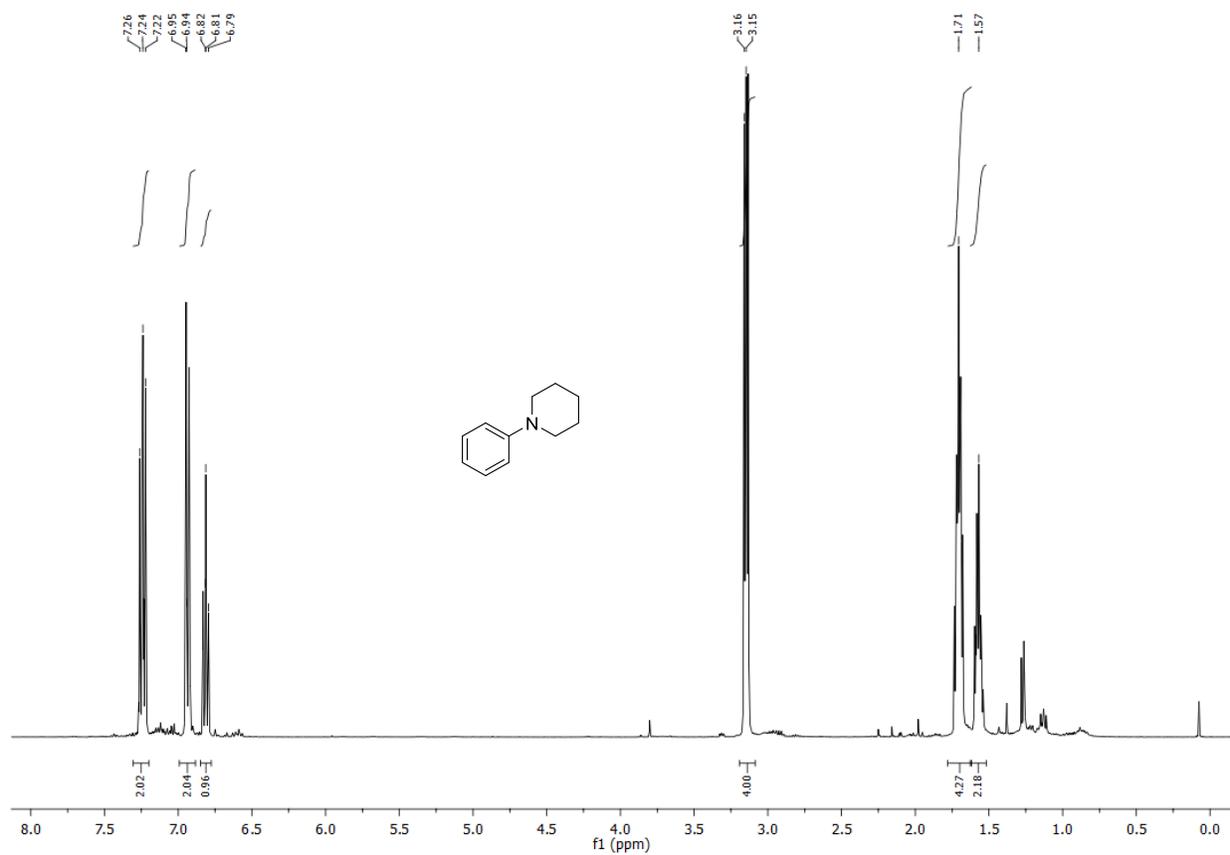


Figure S10. 1-Phenylpiperidine. White powder, 741 mg, 90%

^1H NMR (400 MHz, CDCl_3): 7.29 (t, $J = 7$ Hz, 2H), 6.98 (d, $J = 8$ Hz, 2H), 6.86 (t, $J = 8$ Hz, 1H), 3.19 (m, 4H), 1.76 (m, 4H), 1.61 (m, 2H); ^{13}C NMR (400 MHz, CDCl_3): 152.2, 128.9, 119.1, 116.5, 50.6, 25.8, 24.3

X-ray diffraction studies. Single crystals were obtained directly from isolation of the products as described above. Diffraction data were collected on a Bruker Venture METALJET diffractometer (Ga K α radiation) or a Bruker APEXII with a Cu microsource/Quazar MX using the APEX2 software package.¹ Data reduction was performed with SAINT,² absorption corrections with SADABS.³ Structures were solved by dual-space refinement (SHELXT).⁴ All non-hydrogen atoms were refined anisotropic using full-matrix least-squares on F^2 and hydrogen atoms refined with fixed isotropic U using a riding model (SHELXL97).⁵ Further experimental details can be found in Table S2 and in the supporting information (CIF).

Table S2. Details of X-ray Diffraction Studies

	1	2
Formula	C ₁₃ H ₁₃ ClCuN ₂ O ₄ S	C ₁₄ H ₁₁ CuN ₂ F ₃ O ₆ S ₂
M_w (g/mol); F(000)	392.30; 796	487.91; 1960
T (K); wavelength	100; 1.34190	100; 1.34190
Crystal System	Monoclinic	Orthorombic
Space Group	$P2_1/c$	$Pbca$
Unit Cell: a (Å)	7.9081(2)	14.6171(2)
b (Å)	13.4568(4)	10.0602(2)
c (Å)	14.0019(4)	23.5560(4)
β (°)	104.2800(10)	
V (Å ³)	1444.01(7)	3463.93(10)
Z ; $d_{\text{calcd.}}$ (g/cm ³)	4; 1.805	8; 1.871
μ (mm ⁻¹); Abs. Corr.	10.277; multi-scan	4.698; multi-scan
θ range (°); completeness	4.0-60.7; 0.999	4.8-72.1; 1.000
Collected reflections; R_σ	25548; 0.0274	66922; 0.0089
Unique reflections; R_{int}	3292; 0.0472	3413; 0.0238
Observed Reflections; $R1(F)$	3254; 0.0257	3332; 0.0233
$wR(F^2)$ (all data); GoF(F^2)	0.0735; 1.058	0.0679; 1.055
Residual electron density	0.423	0.416

- (1) *APEX2*, Release 2.1-0; Bruker AXS Inc.: Madison, USA, 2006.
- (2) *SAINT*, Release 7.34A; Bruker AXS Inc.: Madison, USA, 2006.
- (3) Sheldrick, G. M. *SADABS*, Bruker AXS Inc.: Madison, USA, 1996 & 2004.
- (4) Sheldrick, G. *Acta Crystallographica Section A* **2015**, *71*, 3.
- (5) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112.