Electronic Supplementary Information

Aromatic Trifluoromethylation Catalytic in Copper

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General. All reactions were carried out under a nitrogen atmosphere in flame-dried glassware. Syringes which were used to transfer anhydrous solvents or reagents were purged with argon prior to use. Starting materials, reagents, and dry solvent were purchased from commercial suppliers and used without further purification. ^{1}H NMR spectra (400 MHz) were recorded using Me_4Si as an internal standard (0 ppm). ^{19}F NMR spectra (376 MHz) were recorded using hexafluorobenzene (C_6F_6) as an internal standard (0 ppm). Splitting patterns were reported as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad.

General procedure of Cu(I)-catalyzed aromatic trifluoromethylation.
To a mixture of CuI (19.1 mg, 0.10 mmol), 1,10-phenanthroline (18.0 mg, 0.10 mmol), KF (116 mg, 2.0 mmol), 4-iodonitrobenzene (249 mg, 1.0 mmol), NMP (1 mL), and DMF (1 mL) was added triethyl(trifluoromethyl)silane (368 mg, 2.0 mmol) at room temperature. The reaction mixture was stirred at 60 °C in an atmosphere of nitrogen for 24 h and quenched with water. The aqueous layer was extracted with ether and the combined organic phase was dried over Na_2SO_4. Purification by column chromatography on silica gel (hexane/ethyl acetate = 98/2) gave 133 mg (70%) of 4–nitro(trifluoromethyl)benzene (**3a**)[1] as a white solid; mp 37 °C; ^{1}H NMR (400 MHz, $CDCl_3$) 7.84 (d, J = 8.8 Hz, 2H), 8.37 (d, J = 8.8 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) 98.6 (s, 3F); EI-MS m/z (%) 191 (M^+, 60), 145 (100).

3-Nitro(trifluoromethyl)benzene (3b) [2]
The title compound was prepared according to the general procedure and purified by column chromatography (hexane:AcOEt=98:2) to give a pale yellow oil (63% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$) 7.74 (t, J = 7.7 Hz, 1H), 7.98 (d, J = 7,7 Hz, 1H), 8.45 (d, J = 7.7 Hz, 1H), 8.52 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) 98.8 (s, 3F); EI-MS m/z (%) 191 (M^+, 61), 145 (100).

4-Trifluoromethylbenzonitrile (3c) [3]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 98.2 (s, 3F); EI-MS *m/z* (%) 171 (M^+, 100), 152 (33), 121 (41).

Ethyl 4-Trifluoromethylbenzoate (3d) [1]
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.42 (t, *J* = 7.2 Hz, 3H), 4.42 (q, *J* = 7.2 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 8.17 (d, *J* = 8.0 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 98.7 (s, 3F); EI-MS *m/z* (%) 218 (M^+, 14), 190 (37), 173 (100), 145 (39).

4-Chloro(trifluoromethyl)benzene (3e) [1]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 8.3 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 99.2 (s, 3F); EI-MS *m/z* (%) 182 ($M+2^+$, 32), 180 (M^+, 100), 161 (36), 145 (35).

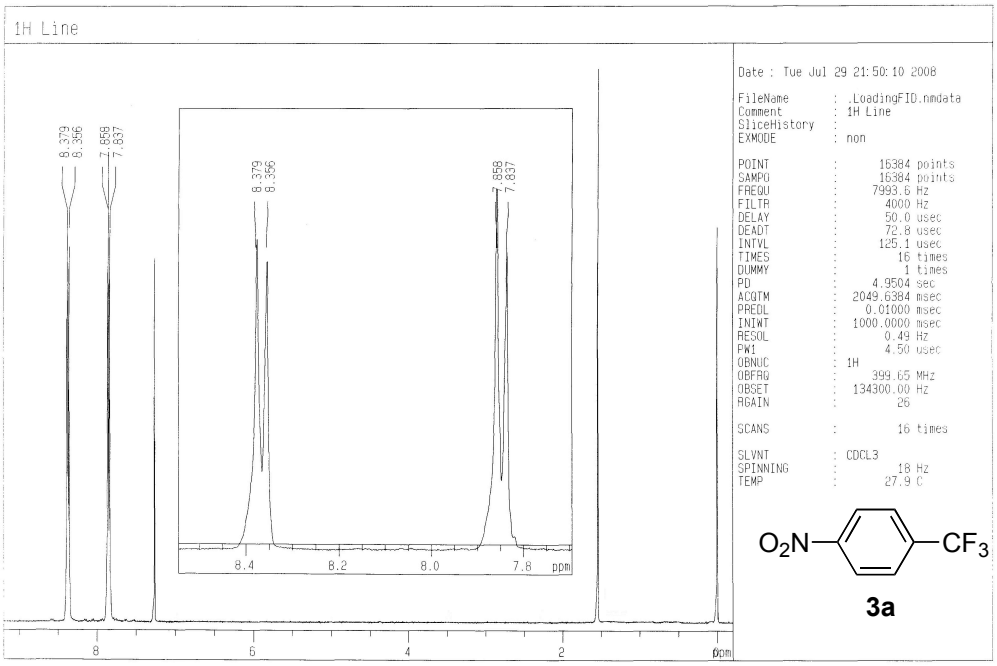
4-Butyl(trifluoromethyl)benzene (3f) [4]
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.53 (t, *J* = 8.0 Hz, 3H), 1.31-1.37 (m, 2H), 1.54-1.61 (m, 2H), 2.66 (t, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 8.6 Hz, 2H), 7.52 (d, *J* = 8.6 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 99.5 (s, 3F); EI-MS *m/z* (%) 202 (M^+, 36), 160 (100).

2-Chloro-5-(trifluoromethyl)pyridine (3g) [5]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.5 Hz, 1H), 7.89 (d, *J* = 8,5 Hz, 1H), 8.69 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 99.4 (s, 3F); EI-MS *m/z* (%) 183 ($M+2^+$, 33), 181 (M^+, 100), 162 (12), 146 (80), 126 (27).

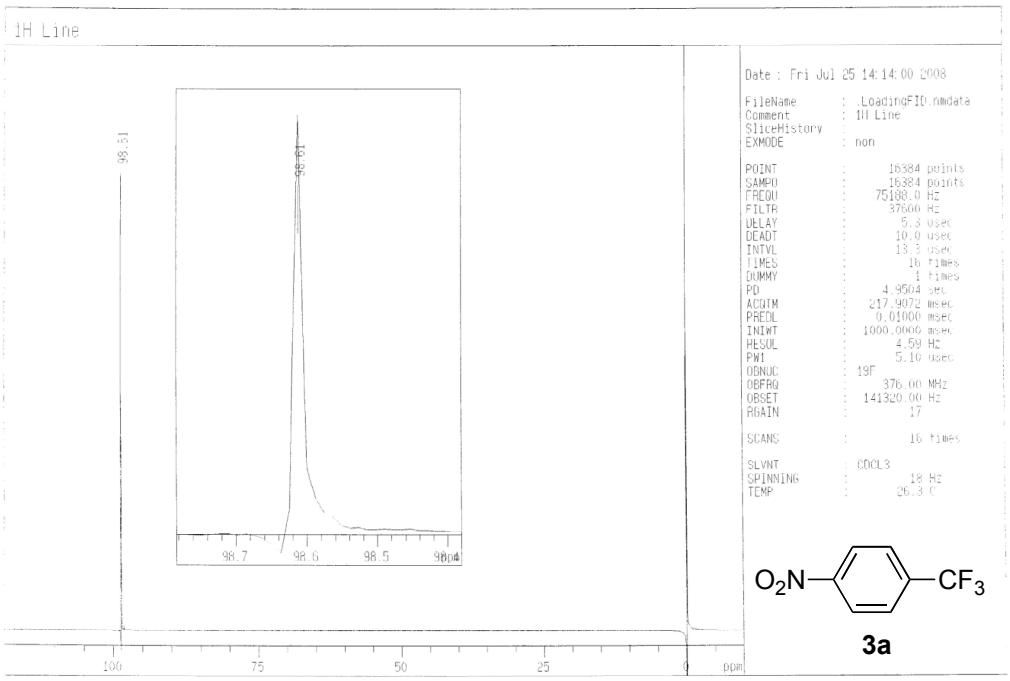
2-Trifluoromethylquinoline (3h) [6]
The title compound was prepared according to the general procedure and purified by column chromatography (hexane:AcOEt=98:2) to give a white solid (95% isolated yield); mp 57 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (t, *J* = 7.6 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.84 (t, *J* = 7.6 Hz, 1H), 7.92 (d, *J* = 8.8 Hz, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), δ 8.36 (d, *J* = 8.8 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 94.2 (s, 3F); EI-MS *m/z* (%) 197 (M^+, 100), 178 (3), 128 (63).

5-Methyl-2-trifluoromethylthiophene (3i) [7]
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 3H), 6.63-6.67 (m, 1H), 7.15 (d, *J* = 4.0 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 106.7 (s, 3F); EI-MS *m/z* (%) 166 (M^+, 100), 147 (13), 97 (56).

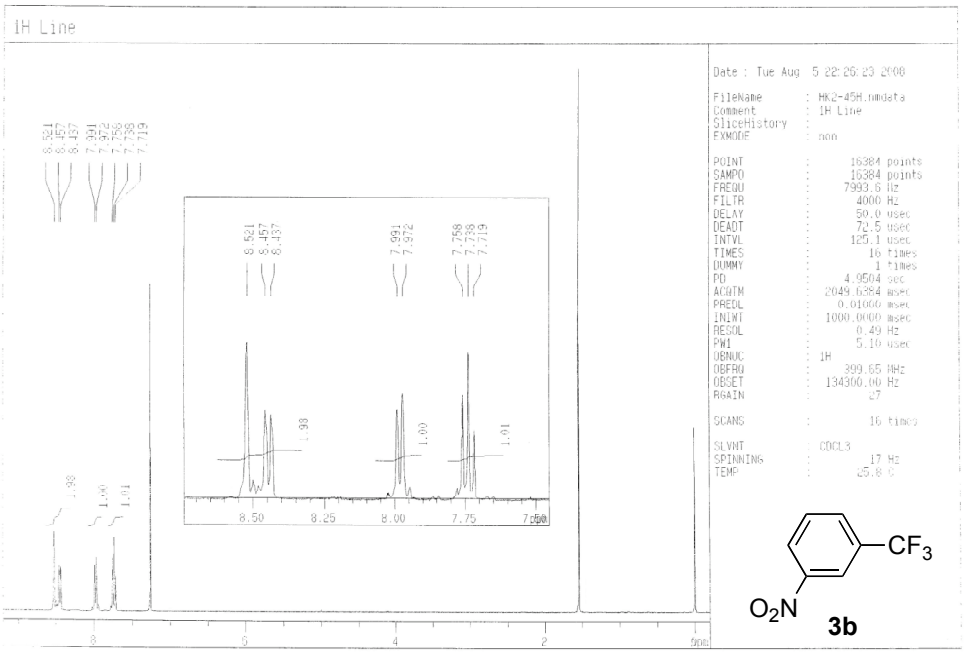
^{1}H NMR Spectrum of Compound **3a**



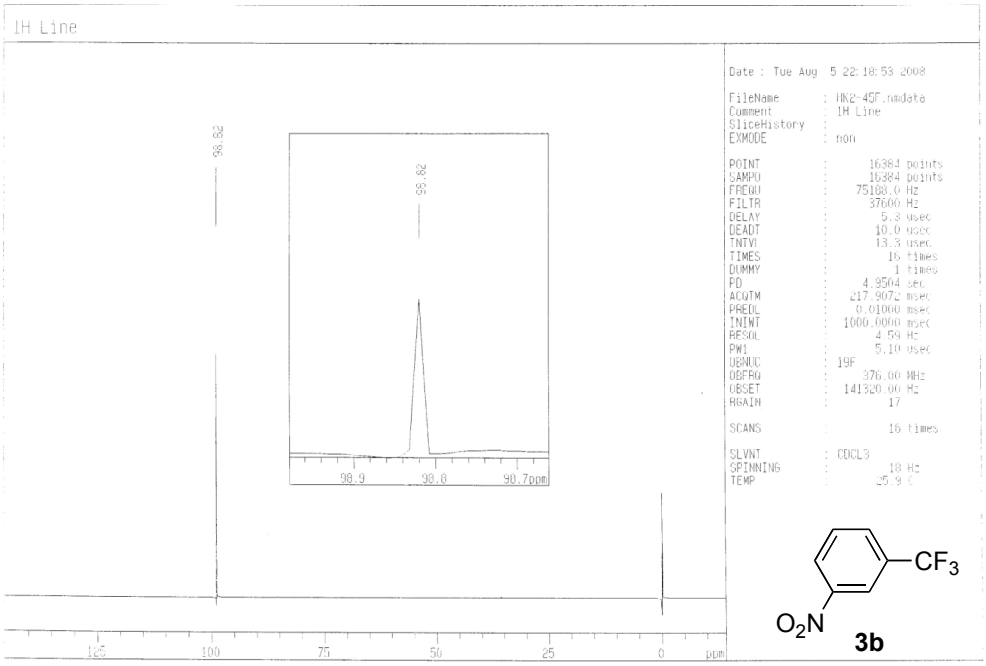
^{19}F NMR Spectrum of Compound **3a**



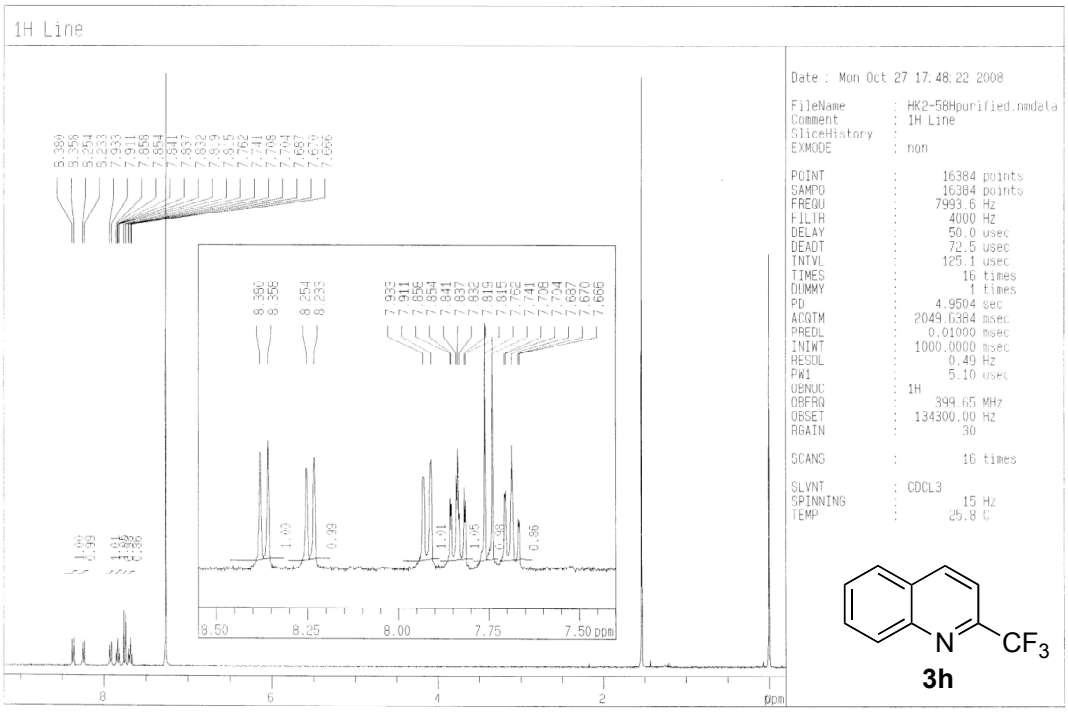
^{1}H NMR Spectrum of Compound **3b**



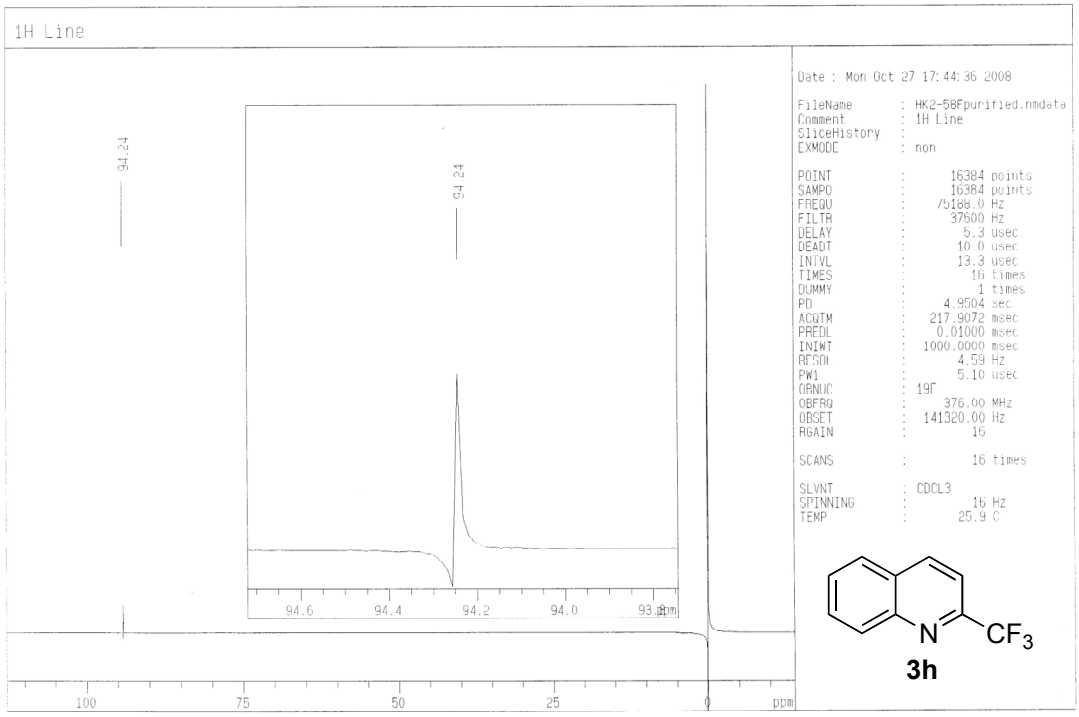
^{19}F NMR Spectrum of Compound **3b**



^{1}H NMR Spectrum of Compound **3h**



^{19}F NMR Spectrum of Compound **3h**



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