-Supporting Information-

A novel catalytic process for trifluoromethylation of bromoaromatic compounds

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Materials. 1-Bromo-naphthalene, *para*-bromo-phenol, *ortho*-bromo-phenol, *ortho*-bromo-aniline, *para*-bromoaniline, 1-bromo-3-methyl-4-nitrobenzene, 9-bromo-anthracene, $(CH_3)_3SiCF_3$ and CsF were purchased from Aldrich Co. 4-Bromo-2-phenyl-aniline was obtained from Interchim Co. Anhydrous toluene (with molecular sieves and septum), Sodium dodecyl sulphate (SDS) (electrophoretic grade) and cetyltrimethylammonium bromide (CTAB) (electrophoretic grade) were obtained from Sigma-Aldrich Co. The purity of these surfactants was ascertained tensiometrically. [CinnamylPdCl]₂ was prepared as described previously,^{S1} and stored at -20 °C. Cyclohexyl BrettPhos was prepared according to literature procedure.^{S2} All other reagents from commercial sources were used as received. All reactions were performed under an atmosphere of argon. Flash chromatography was performed with Merck silica gel 60 (230-400 mesh ASTM).

General procedure for trifluoromethylation. 1-Bromonaphthalene (207 mg, 1.00 mmol, 1 eq), cyclohexyl BrettPhos (6.40 mg, 0.012 mmol, 10 mol%), (cinnamylPdCl)₂ (10.4 mg, 0.02 mmol, 2 mol%), (CH₃)₃SiCF₃ (0.228 mL, 2.00 mmol, 2 eq) and CsF (304 mg, 2.00 mmol, 2 eq) were added to a SDS (60 mmol) toluene (10 mL) solution the mixture was agitated for 6 hr under an argon atmosphere in a 50 cm³ baffled glass reactor equipped with a six-blade turbine agitator of 0.3 cm diameter. The speed of agitation was maintained at 1.67 Hz. Isothermal conditions were maintained at 110 °C. After cooling to room temperature, a solution of CTAB (60 mM) in toluene (5 mL) solution was added to the reaction mixture which was agitated for an additional 10 min. The mixture was filtered through a plug of Celite, the fiiltrate concentrated under reduced pressure, and then purified by flash chromatography on silica gel using hexane to give the 1-(trifluoromethyl)naphthalene as a colorless oil; yield: 173 mg (88% yield). The experiments were performed in replicates of three. The variation in the results from the reported average values was within \pm 0.75 %.

General analytical information. All the products formed were identified using ¹H NMR (300 MHz), ¹³C NMR (75.46 MHz), ¹⁹F NMR (282 MHz). Peak positions are given in parts per million (δ) from tetramethylsilane (¹H and ¹³C) and FCCl₃ (¹⁹F) as internal standards; coupling constant values (*J*) are given in Hertz. The yields are determined by comparing the integration of the ¹⁹F NMR resonance in the products to that of of 4-fluorotoluene (-118.0 ppm. Percent conversion was determined using a gas chromatograph (Chemito 8610) with a flame ionization detector. A 4 m. long and 0.37 cm internal diameter S.S. column packed with 10% SE-30 on chromosorb WHP was employed for the analysis. Nitrogen at the flow rate of 0.5 x 10⁻⁷ m³ sec⁻¹ was used as carrier gas.

Analytical data for trifluoromethyl aromatic compounds.

1-(Trifluoromethyl)naphthalene.



Colorless liquid, boiling point: 187 °C. (Found: C, 67.80; H, 3.50. $C_{10}H_7F$ requires C, 67.35; H, 3.60%); $\delta_H(300 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$: 7.70 (1 H, d, *J* 3 Hz, C3), 7.75 (1 H, t, *J* 6 Hz, C6), 7.82 (1 H, t, *J* 6, C7), 7.88 (1 H, d, *J* 6 Hz, C2), 8.20 (1 H, d, *J* 3 Hz, C4), 8.23 (1 H, d, *J* 6 Hz, C5), 8.52 (1 H, d, *J* 3 Hz, C8). $\delta_C(75.46 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$: 123.5 (d, C3), 123.7 (d, C2), 124.2 (s, C*F₃), 125.4 (d, C1), 126.02 (d, C8), 126.8 (d, C6), 128.1 (d, C7), 129.4 (C4a), 131.9 (C8a), 133.8 (d, C4). $\delta_F(282 \text{ MHz}; \text{CDCl}_3; \text{FCCl}_3)$: -60.3.^{S3}

2-Methyl-1-nitro-4-(trifluoromethyl)benzene.



White powder, melting point: 40 °C. (Found C, 46.89; H, 3.10; N, 6.91; O, 15.52. C_8H_9FO requires C, 46.84; H, 2.95; N, 6.83; O, 15.60%); $\delta_H(300 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$: 2.35 (3 H, s, C2-*CH**₃), 7.71 (1 H, d, *J* 6, C5), 7.8 (1 H, s, C3) and 8.15 (1 H, d, *J* 6, C6). $\delta_C(75.46 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$: 18.5 (d, CH₃),123.1 (d, C5), 124.2 (C*F₃), 124.8 (d, C6), 128.01 (d, C3), 132.8 (s, C2), 137.5 (C4) and 151.8 (d, C1). $\delta_F(282 \text{ MHz}; \text{CDCl}_3; \text{FCCl}_3)$: -63.3.^{S3}

4-(Trifluoromethyl)phenol.



Off-white crystals, melting point: 47 °C. (Found: C, 51.75; H, 3.23; O, 9.90. $C_7H_3F_3O$ requires C, 51.86; H, 3.11; O, 9.87%);^{S4} $\delta_H(300 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$: 5.96 (1 H, br s, Ar-OH*), 6.82 (2 H, dd, *J* 8.2, C2,C6) and 7.64 (2 H, dd, C3,C5). $\delta_C(75.46 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$: 118.1 (q, C2,C6), 122.8 (C4), 124.4 (C*F_3), 129.1 (q, C3,C5), and 157.8 (C1). $\delta_F(282 \text{ MHz}; \text{CDCl}_3; \text{FCCl}_3)$: -61.5.^{S5}

2-(Trifluoromethyl)phenol.



Light yellow solid, melting point: 44 °C. (Found: C, 52.2; H, 3.20; O, 9.70. C_7H_7FO requires C, 51.86; H, 3.11; O, 9.87%);^{S4} $\delta_H(300 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$: 5.05 (1 H, br s, Ar-O*H**), 6.90 (1 H, d, *J* 8 C6), 7.02 (1 H, s, C4), 7.40 (1 H, t, *J* 8.2, C5) and 7.60 (1 H, d, *J* 7.8, C3); $\delta_C(75.46 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$: 118.4 (d, C6), 120.4 (C2), 121.8 (d, C4), 124.4 (C*F₃), 126.8 (d, C3), 134.1 (C5), 156.8 (C1); $\delta_F(282 \text{ MHz}; \text{CDCl}_3; \text{FCCl}_3)$: -60.4.^{S5}

2- Hydroxy-5-(trifluoromethyl)benzaldehyde.



White solid, melting point: 61 °C. (Found: C, 50.50; H, 2.70; O, 16.78. $C_8H_5F_3O_2$ requires C, 50.54; H, 2.65; O, 16.83%); $\delta_{H}(300 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$: 7.20 (1 H, d, *J* 9.6, C6), 7.80 (1 H, d, *J* 9.6, C5), 8.05 (1 H, s, C3) and 10.50 (1 H, s, CH*O); $\delta_C(75.46 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$: 118.9 (d, C6), 123.6 (C4), 124.4 (C*F_3), 128.0 (d, C3), 135.4 (d, C5), 137.6 (C2), 167.1 (C1) and 200.2 (HC*O). $\delta_F(282 \text{ MHz}; \text{CDCl}_3; \text{FCCl}_3)$: -62.2.⁸⁶

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2-(Trifluoromethyl)-aniline.



White powder, melting point: 35 °C. (Found: C, 52.30; H, 3.80; N, 8.90. $C_7H_6F_3N$ requires C, 52.18; H, 3.75; N, 8.69%);^{S7} $\delta_H(300 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$: 4.05 (1 H, br s, Ar-N H_2 *), 6.78 (1 H, d, *J* 9.6, C6), 6.95 (1 H, t, *J* 6, C4), 7.15 (1 H, t, *J* 6, C5) and 7.41 (1 H, d, *J* 7.8, C3); $\delta_C(75.46 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$: 110.9 (C2), 118.7 (d, C6), 120.01 (d, C4), 124.5 (C*F_3), 127.4 (d, C3), 133.6 (d, C5), 145.5 (C1); $\delta_F(282 \text{ MHz}; \text{CDCl}_3; \text{FCCl}_3)$: -59.5.⁸⁸

4-(Trifluoromethyl)-aniline.



White powder, melting point: 37 °C. (Found: C, 52.32; H, 3.80; N, 8.72. $C_7H_6F_3N$ requires C, 52.18; H, 3.75; N, 8.69%) [S7];^{S7} δ_H (300 MHz; CDCl₃; Me₄Si): 4.10 (1 H, br s, Ar-NH₂*), 6.80 (2 H, dd, *J* 9.6, C2,C6) and 7.48 (2 H, dd, *J* 9.6, C3,C5); δ_C (75.46 MHz; CDCl₃; Me₄Si): 117.5 (q, C2,C6), 124.4 (C*F₃), 126.6 (q, C3,C5), 127.4 (C4), and 152.2 (C1); δ_F (282 MHz; CDCl₃; FCCl₃): -61.3.^{S8}

2-Phenyl-4-(trifluoromethyl)-aniline.



White powder, melting point: 68 °C. (Found: C, 65.60; H, 4.33; N, 5.86. $C_{13}H_{10}F_{3}N$ requires C, 65.82; H, 4.25; N, 5.90%);^{S9} $\delta_{H}(300 \text{ MHz}; \text{CDCl}_{3}; \text{Me}_{4}\text{Si})$: 4.09 (1 H, br s, Ar-NH₂*), 6.70 (1 H, d, J 9.6, C6), 7.20 (1 H, m, J 6, C'2,C'6), 7.37-7.41 (2 H, m, J 7.8, C5,C'4), 7.78 (2 H, m, J 6, C'3,C'5), 8.03 (1 H, s, C3) and 8.79 (1 H, s, C2); $\delta_{C}(75.46 \text{ MHz}; \text{CDCl}_{3}; \text{Me}_{4}\text{Si})$: 117.4 (d, C6), 120.4 (C2), 122.6 (C4), 124.5 (C*F₃), 125.28 (d, C5), 127 (d, C'4), 127.90 (d, C3), 128.1 (q, C'2,C'6), 129.67 (q, C'3,C'5), 140 (C'1), 149.6 (C1); $\delta_{F}(282 \text{ MHz}; \text{CDCl}_{3}; \text{FCCl}_{3})$: -61.4.^{S10}

9-(Trifluoromethyl)anthracene.



Yellow powder, melting point: 50 °C. (Found: C, 72.20; H, 3.72. $C_{10}H_7F$ requires C, 73.17; H, 3.68%); $\delta_{H}(300 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$: 7.62 (2 H, t, *J* 3 Hz, C2,C7), 7.78 (2 H, t, *J* 6 Hz, C3,C6), 8.03 (1 H, s, C4,C5), 8.23 (2 H, d, *J* 8 Hz, C1,C8) and 8.69 (1 H, s, C10); $\delta_C(75.46 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$: 120.9 (C*F₃), 126.02 (d, C3,C6), 126.3 (C9), 126.8 (d, C1,C8), 127.2 (d, C2,C7), 128.2 (d, C4,C5), 128.8 (C10a,C4a), 130.86 (C8a,C9a), and 132.02 (d, C10); $\delta_F(282 \text{ MHz}; \text{CDCl}_3; \text{FCCl}_3)$: -49.5.⁸³



Fig. S1. The ¹H NMR spectra of Naphthalene-BrettPhos-Pd-Br complex in toluene-d₈ and toluene-d₈ + SDS (60 mM).



Fig. S2. The ¹H NMR spectra of Naphthalene-BrettPhos-Pd-CF₃ complex in toluene-d₈ and toluene-d₈ + SDS (60 mM).



← **Fig. S3.** The effect of surfactant concentration (◆ SDS, ■ LABS, ▲ CTAB) on trimethylfluorination of bromonaphthalene in the presence of 10 mol% (cinnamylPdCl)₂, 10 mol % cyclohexyl BrettPhos, 2 eq (CH₃)₃SiCF₃ and 10 mL toluene at 110 °C for 12 h. Each experiment was done three times independently. The variation in the results from the reported average values was within ± 0.75%.



















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