

Supporting Information

N-Heterocyclic Carbene Adsorption States on Pt(111) and Ru(0001)

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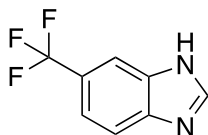
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General

Reactions were performed in flame-dried flasks with reagent grade solvents, with exception of CH₂Cl₂ and pentanes, they were distilled from calcium hydride prior to use. Work-up purifications were performed using commercial reagent-grade solvents. 2-nitro-4-(trifluoromethyl) aniline was purchased from Alfa Aesar; trifluoromethanesulfonyl anhydride, chloroform-*d*, methanol-*d*₄, and 2-bromopropane-1,1,1,2,3,3,3-*d*₇ were purchased from Sigma-Aldrich. 1,3-diisopropyl-1*H*-benzo[*d*]imidazol-3-ium hydrogen carbonate was synthesized following reported procedure from 1,3-diisopropyl-1*H*-benzo[*d*]imidazol-3-ium trifluoromethanesulfonate.¹

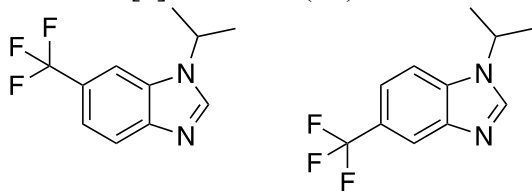
High-resolution mass spectrometric (HRMS) data were obtained from a Thermo Fisher Scientific Exactive (ESI) or an Applied Biosystems/MDS Sciex QStar XL QqTOF instrument (EI). ¹H, ¹³C, and ¹⁹F NMR spectra were recorded on Bruker Instruments (Neo-500 and Neo-700) operating at denoted spectrometer frequency given in megahertz (MHz) at 25 °C. ¹H chemical shifts are referenced to the residual protons of the deuterated solvents CDCl₃ (at δ = 7.26 ppm) and CD₃OD (at δ = 3.31 ppm); ¹³C chemical shifts are referenced to the CDCl₃ and CD₃OD signals at δ = 77.16 and 49.00 ppm, respectively. ¹⁹F NMR spectra were calibrated using CFCl₃ (δ = 0.0 ppm) as an external reference. The following abbreviations are used to describe NMR signals: s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, and m = multiplet. Coupling constants obtained from ¹H NMR spectra are associated with an error and reported to the first decimal point (the digital resolution in ¹H NMR spectra and ¹³C NMR is 0.11 Hz and 0.64 Hz respectively). Assignments for newly synthesized compounds were supported by additional NMR experiments (COSY, HSQC, and HMBC). All data were processed using MestReNova 11.0 software.

6-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (1)



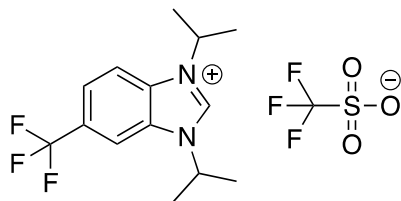
Modified from a previously reported procedure.² Formic acid (90 mL, 1.92 mol, 88% wt/vol in H₂O) was added to a solution of 2-nitro-4-(trifluoromethyl)aniline (2.648g, 12.8 mmol), iron powder (7.18 g, 128.6 mmol), and ammonium chloride (6.87g, 128.6 mmol) in 2-propanol (150 mL). This resulting mixture was refluxed for 6 h followed by cooling to r.t. and filtered through a fritted funnel to remove unreacted iron powder. The dark grey solid was then washed with more 2-propanol (3 × 20 mL). Volatiles from the filtrate were evaporated under reduced pressure, and any remaining acid was neutralized by careful addition of saturated NaHCO₃ (aq.) until a pH 6 was achieved. This suspension was extracted using CH₂Cl₂ (4 × 50 mL) and combined organic layers were dried over anhydrous sodium sulfate and concentrated to give **1** as a white crystalline solid (2.21 g, 84%). ¹H NMR (700 MHz, Chloroform-*d*) δ 8.26 (s, 1H, N=CH-NH), 7.99 (s, 1H, C-CH=C(-CH)-CF₃), 7.74 (d, *J* = 8.5 Hz, 1H, -CH=CH-C-CF₃), 7.57 (d, *J* = 8.4 Hz, 1H, -CH=CH-C-CF₃). ¹³C NMR (176 MHz, Chloroform-*d*) δ 142.74 (s, N=C-N), 139.35 (s, N-C), 137.82 (s, C-N), 124.91 (q, F₃C-C, ²*J*(¹⁹F, ¹³C) = 31.8 Hz), 124.80 (q, F₃C-C, ¹*J*(¹⁹F, ¹³C) = 272.14 Hz), 120.24 (q, F₃C-C-C(H), ³*J*(¹⁹F, ¹³C) = 3.82 Hz), 115.68 (s, F₃C-C=C(H)-C(H)), 113.92 (s, F₃C-C=CH-CH). ¹⁹F NMR (471 MHz, Chloroform-*d*) δ -61.25 (s, CF₃). HRMS (ESI): *m/z* [M+H]⁺ calcd for C₈H₅F₃N₂, 187.04776, found 187.04773.

1-isopropyl-6-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (**2a**) and 1-isopropyl-5-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (**2b**)



Synthesized from **1** following a reported procedure³ with slight modifications. 2-bromopropane (3.96 g, 32.23 mmol) was added dropwise over 10 min to a solution of **1** (2.01 g, 10.7 mmol) and potassium hydroxide (1.808 g, 32.23 mmol) in dimethyl sulfoxide (20 mL). The resulting mixture was stirred overnight at rt. Water (20 mL) was added to the mixture and product was extracted with methylene chloride (3 × 50 mL). The combined organic layer was dried over anhydrous sodium sulfate, filtered and evaporated to give a mixture of **2a** and **2b** as a yellow oil (1.472 g, 60%). ¹H NMR (700 MHz, Chloroform-*d*) δ 8.10 (s, 1H), 8.07 (d, *J* = 6.7 Hz, 2H), 7.85 (d, *J* = 8.5 Hz, 1H), 7.69 (d, *J* = 1.8 Hz, 1H), 7.53 – 7.45 (m, 3H), 4.64 (m, 2H, N-CH-(CH₃)₂), 1.60 (m, 12H, N-CH-(CH₃)₂). ¹³C NMR (176 MHz, Chloroform-*d*) δ 146.17, 143.49, 142.59, 142.16, 135.28, 132.76, 124.96 (q, F₃C-C, ²*J*(¹⁹F, ¹³C) = 32.43 Hz), 124.9 (q, F₃C-C, ¹*J*(¹⁹F, ¹³C) = 271.48 Hz), 124.86 (q, F₃C-C, ¹*J*(¹⁹F, ¹³C) = 272.12 Hz), 124.66 (q, F₃C-C, ²*J*(¹⁹F, ¹³C) = 5.16 Hz), 120.84, 119.59 (q, ³*J*(¹⁹F, ¹³C) = 3.82 Hz), 119.09 (q, ³*J*(¹⁹F, ¹³C) = 3.18 Hz), 118.11 (q, ³*J*(¹⁹F, ¹³C) = 4.45 Hz), 110.63, 107.9 (q, ³*J*(¹⁹F, ¹³C) = 4.45 Hz), 48.20 (s, N-CH-(CH₃)₂), 48.15 (s, N-CH-(CH₃)₂), 22.64 (s, N-CH-(CH₃)₂), 22.55 (s, N-CH-(CH₃)₂). ¹⁹F NMR (471 MHz, Chloroform-*d*) δ -61.08 (s, CF₃), -61.14 (s, CF₃); two different signals are presumably from two possible isomers. HRMS (ESI): *m/z* [M+H]⁺ calcd for C₁₁H₁₁F₃N₂, 229.09471, found 229.09410.

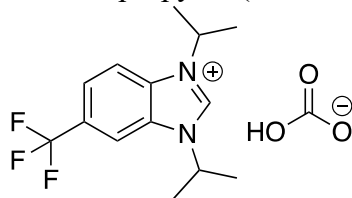
1,3-diisopropyl-6-(trifluoromethyl)-1*H*-benzo[*d*]imidazol-3-ium trifluoromethanesulfonate (**3**):



Preparation of isopropyl triflate: Modified from a previously reported procedure.¹ Dry CH₂Cl₂ (10 mL) was taken in a flame dried round-bottomed flask and cooled to -78 °C followed by consecutive addition of 2-propanol (1.12 mL) and pyridine (1.18 mL). Trifluoromethanesulfonyl anhydride (2.46 mL, 14.70 mmol) was added to the reaction mixture at -78 °C dropwise over 30 min resulting in the gradual formation of a white precipitate. The resulting mixture was then stirred at that temperature for another 30 min and at rt. for additional 30 min. After this time, 10 mL dry pentane was added to the slurry, stirred for ca. 5 min, and let the precipitate settle down.

2 (1.12 g, 4.90 mmol) was added into a separate round-bottomed flask and dissolved in dry CH₂Cl₂ (5.0 mL). Clear supernatant from aforementioned freshly prepared isopropyl triflate was transferred with a syringe and resulting mixture was stirred at 35 °C for 14 h under argon atmosphere. Reaction mixture was quenched with saturated NaHCO₃ solution (aq.), extracted with CH₂Cl₂ (3 × 50 mL), dried over anhyd. Na₂SO₄, and concentrated resulting a pale yellow solid as crude. The crude product was then purified by washing with diethyl ether (3 × 50 mL), producing compound **3** as a fluffy white solid (1.34 g, 65%). ¹H NMR (700 MHz, Chloroform-*d*) δ 10.04 (s, 1H, N-CH-N), 8.07 (s, 1H, CF₃-C=CH-C), 8.00 (d, *J* = 8.2 Hz, 1H, CF₃-C-CH=CH), 7.91 (d, *J* = 8.6 Hz, 1H, CF₃-C-CH=CH-), 5.15 – 5.05 (m, 2H, N-CH-(CH₃)₂), 1.85 – 1.80 (m, 12H, , N-CH-(CH₃)₂). ¹³C NMR (176 MHz, CDCl₃) δ 141.95 (s, N-CH-N), 133.09 (s, CF₃-C=CH-C), 130.85 (s, CF₃-C-CH=CH-C), 129.84 (q, F₃C-C, ²*J*(¹⁹F, ¹³C) = 34.46 Hz), 129.00, 124.19 (s, CF₃-C-CH=CH), 123.34 (q, F₃C-C, ¹*J*(¹⁹F, ¹³C) = 271.90 Hz), 120.73 (q, F₃C-SO₃, ¹*J*(¹⁹F, ¹³C) = 321.33 Hz), 115.24 (s, CF₃-C-CH=CH), 111.81 (q, ³*J*(¹⁹F, ¹³C) = 4.19 Hz, CF₃-C=CH-C), 53.26 (s, N-CH-(CH₃)₂), 53.18 (s, N-CH-(CH₃)₂), 21.95 (s, N-CH-(CH₃)₂), 21.87 (s, N-CH-(CH₃)₂). ¹⁹F NMR (471 MHz, CDCl₃) δ -62.14 (s, C-CF₃), -78.92 (s, CF₃SO₃⁻). HRMS (ESI): *m/z* [*M*]⁺ calcd for C₁₄H₁₈F₃N₂, 271.14166, found 271.14078; *m/z* [*M*]⁻ calcd for CO₃F₃S, 148.95257, found 148.95367.

1,3-diisopropyl-6-(trifluoromethyl)-1*H*-benzo[*d*]imidazol-3-ium hydrogen carbonate (**4**)



Preparation of bicarbonate resin: The resin was prepared from commercial Amberlyst A26 hydroxide resin modified from a previously reported procedure.¹ 100 g (0.8 meq/mL) of the hydroxide resin was suspended in 100 mL MilliQ water and carbon dioxide was bubbled through the solution for 1 h. The conversion of resin was tested similar to the previously reported procedure.

Resin-HCO₃⁻ suspended in water was measured out using a graduated cylinder (2 mL) and transferred to a 20 mL vial. The water was carefully removed, and the resin was washed with methanol (3 × 5 mL) and finally, this resin was suspended in methanol (5 mL). **3** (0.14 g, 0.32 mmol) was dissolved in methanol (2 mL) in a separate vial and this solution was added to the vial with resin. This mixture was stirred for 0.5 h. The reaction was stopped by passing this mixture through a cotton plug to remove resin beads and they were washed with additional methanol (3 × 2 mL). Solvent was evaporated and the resulting solid residue was triturated in diethyl ether (3 × 10 mL) to give **4** as an off-white solid (0.074 g, 70%). ¹H NMR (700 MHz, Methanol-*d*₄) δ 8.50 (s, 1H, CF₃-C=CH-C), 8.28 (d, *J* = 8.8 Hz, 1H, CF₃-C-CH=CH-), 8.02 (d, *J* = 8.8, 1H, CF₃-C-CH=CH-), 5.19 (sept, *J* = 6.7 Hz, 1H, N-CH-(CH₃)₂), 5.14 (sept, *J* = 6.7 Hz, 1H, N-CH-(CH₃)₂), 1.76 (m, 12H, N-CH-(CH₃)₂). ¹³C NMR (176 MHz, Methanol-*d*₄) δ 161.43 (s, HCO₃⁻), 141.71 (broad, N-CH-N), 134.68 (s, CH-C-N), 132.55 (s, CH-C-N), 130.28 (q, ²*J*(¹⁹F, ¹³C) = 33.82 Hz, CF₃-C-), 125.18 (q, CF₃-C, ¹*J*(¹⁹F, ¹³C) = 271.15 Hz), 124.84 (q, CF₃-C-CH=CH-, ³*J*(¹⁹F, ¹³C) = 3.31 Hz), 116.37 (s, CF₃-C-CH=CH-C), 113.15 (q, CF₃-C=CH-C, ³*J*(¹⁹F, ¹³C) = 4.26 Hz), 53.48 (s, N-CH-(CH₃)₂), 53.22 (s, N-CH-(CH₃)₂), 22.22 (s, N-CH-(CH₃)₂), 22.07 (s, N-CH-(CH₃)₂). ¹⁹F NMR (471 MHz, CDCl₃) δ -61.22 (s, C-CF₃). HRMS (ESI): *m/z* [M]⁺ calcd for C₁₄H₁₈F₃N₂, 271.14166, found 271.14047.

1. Crudden, C. M.; Horton, J. H.; Narouz, M. R.; Li, Z.; Smith, C. A.; Munro, K.; Baddeley, C. J.; Larrea, C. R.; Drevniok, B.; Thanabalasingam, B.; McLean, A. B.; Zenkina, O. V.; Ebralidze, II; She, Z.; Kraatz, H. B.; Mosey, N. J.; Saunders, L. N.; Yagi, A., Simple direct formation of self-assembled N-heterocyclic carbene monolayers on gold and their application in biosensing. *Nat. Commun.* **2016**, *7*, 12654.
2. Crudden, C. M.; Horton, J. H.; Ebralidze, II; Zenkina, O. V.; McLean, A. B.; Drevniok, B.; She, Z.; Kraatz, H. B.; Mosey, N. J.; Seki, T.; Keske, E. C.; Leake, J. D.; Rousina-Webb, A.; Wu, G., Ultra stable self-assembled monolayers of N-heterocyclic carbenes on gold. *Nat. Chem.* **2014**, *6*, 409-14.
3. Gao, G. L.; Yang, C.; Xia, W., Selective C-H trifluoromethylation of benzimidazoles through photoredox catalysis. *Chem Commun.* **2017**, *53*, 1041-1044.

Table SI 1. Assignment of RAIRS bands observed in the experiments on Ru(0001) in the 300-500 K temperature range.

Band Frequencies (cm⁻¹)	Assignments
3017 (very weak)	$\nu(\text{C-H})$ aromatic ring
2954	$\nu_{\text{asym}}(\text{CH}_3)$
2919	$\nu_{\text{sym}}(\text{CH}_3)$
2848-2860	$\nu(\text{CH})$ isopropyl
1623 (at 300 K)	OCO vibration or $\nu(\text{CC})$
1593 (at 300 K)	OCO vibration or $\nu(\text{CC})$
1466	$\delta_{\text{asym}}(\text{CH}_3)$
1353	$\delta_{\text{sym}}(\text{CH}_3)$
1330	$\nu_{\text{sym}}(\text{C-CF}_3)$
1268	$(\text{CFx})_{\text{adsorbed}}$
1185	$\nu_{\text{asym}}(\text{CF}_3)$ in-plane
1147	$\nu_{\text{asym}}(\text{CF}_3)$ out-of-plane
1065	$\delta(\text{CH})$ in-plane