

Supporting Information

for

Copper-catalyzed trifluoromethylation of alkenes with an electrophilic trifluoromethylating reagent

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Full experimental details, analytical data and spectra of the target compounds

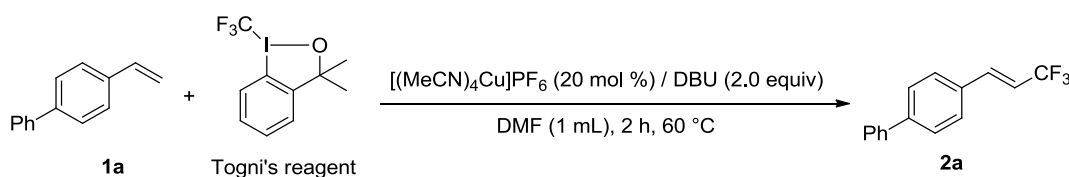
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1. General information

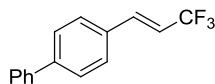
^1H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, with TMS as the internal standard. ^{19}F NMR spectra were recorded at 376 MHz with CFCl_3 (positive for downfield shifts) as the external standard. High resolution mass data were recorded on a Waters Micromass GCT Premier instrument. All reactions were monitored by TLC with Huanghai GF₂₅₄ silica gel coated plates. Flash column chromatography was carried out using 300–400 mesh silica gel.

2. General procedure for the trifluoromethylation of terminal alkenes



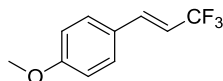
Into a solution of 4-vinylbiphenyl (90 mg, 0.5 mmol) in DMF (1 mL) was added Togni's reagent (415 mg, 1.25 mmol) and DBU (152 mg, 1 mmol), followed by $[(\text{MeCN})_4\text{Cu}]\text{PF}_6$ (37 mg, 0.1 mmol). The reaction mixture was stirred at 60 °C for 2 h. After being cooled to room temperature, the mixture was subjected to column chromatography to afford pure product **2a**.

(E)-4-(3,3,3-Trifluoroprop-1-en-1-yl)-1,1'-biphenyl (**2a**)^[1]



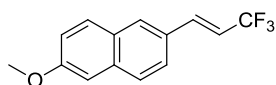
White solid, 90% yield; ^1H NMR (400 MHz, CDCl_3): δ 7.69 – 7.34 (m, 9H), 7.19 (dq, $J = 16.0$ Hz, 2.0 Hz, 1H), 6.25 (dq, $J = 16.0$ Hz, 6.6 Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3): δ -63.24 (dd, $J = 6.6$ Hz, 2.0 Hz, 3F). GC-MS: 248 $[\text{M}]^+$.

(E)-1-Methoxy-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (**2b**)^[1]



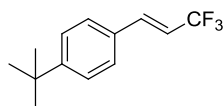
Colorless oil, 91% yield; ^1H NMR (400 MHz, CDCl_3): δ 7.40 (d, $J = 8.8$ Hz, 2H), 7.09 (dq, $J = 16.0$ Hz, 2.0 Hz, 1H), 6.91 (d, $J = 8.8$ Hz, 2H), 6.06 (dq, $J = 16.0$ Hz, 6.6 Hz, 1H) 3.84 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3): δ -62.89 (dd, $J = 6.6$ Hz, 2.0 Hz, 3F). GC-MS: 202 $[\text{M}]^+$.

(E)-2-Methoxy-6-(3,3,3-trifluoroprop-1-en-1-yl)naphthalene (**2c**)^[1]



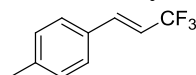
White solid, 88% yield; ^1H NMR (400 MHz, CDCl_3): δ 7.79 (s, 1H), 7.77 – 7.69 (m, 2H), 7.60 – 7.52 (m, 1H), 7.27 (dq, $J = 16.0$ Hz, 2.0 Hz, 1H), 7.21 – 7.10 (m, 2H), 6.26 (dq, $J = 16.0$ Hz, 6.5 Hz, 1H), 3.94 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3): δ –63.00 (dd, $J = 6.5$ Hz, 2.0 Hz, 3F). GC-MS: 252 $[\text{M}]^+$.

(*E*)-1-(*tert*-Butyl)-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (**2d**)^[1]



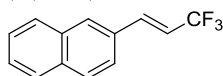
Colorless oil, 88% yield; ^1H NMR (400 MHz, CDCl_3): δ 7.49 – 7.31 (m, 4H), 7.13 (dq, $J = 16.1$ Hz, 2.1 Hz, 1H), 6.16 (dq, $J = 16.1$ Hz, 6.6 Hz, 1H), 1.33 (s, 9H). ^{19}F NMR (376 MHz, CDCl_3): δ –63.17 (dd, $J = 6.6$ Hz, 2.1 Hz, 3F). GC-MS: 228 $[\text{M}]^+$.

(*E*)-1-Methyl-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (**2e**)^[1]



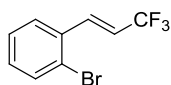
White solid, 92% yield; ^1H NMR (400 MHz, CDCl_3): δ 7.35 (d, $J = 8.0$ Hz, 2H), 7.20 (d, $J = 8.0$ Hz, 2H), 7.12 (dq, $J = 16.1$ Hz, 2.0 Hz, 1H), 6.16 (dq, $J = 16.1$ Hz, 6.6 Hz, 1H), 2.38 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3): δ –63.16 (dd, $J = 6.6$ Hz, 2.0 Hz, 3F). GC-MS: 186 $[\text{M}]^+$.

(*E*)-2-(3,3,3-Trifluoroprop-1-en-1-yl)naphthalene (**2f**)^[1]



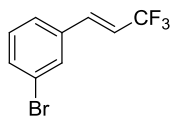
White solid, 92% yield; ^1H NMR (400 MHz, CDCl_3): δ 7.90 – 7.75 (m, 4H), 7.60 (d, $J = 8.8$ Hz, 1H), 7.57 – 7.45 (m, 2H), 7.32 (dd, $J = 16.0$ Hz, 1.5 Hz, 1H), 6.16 (dq, $J = 16.0$ Hz, 6.6 Hz, 1H), 2.38 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3): δ –63.20 (dd, $J = 6.6$ Hz, 1.5 Hz, 3F). GC-MS: 222 $[\text{M}]^+$.

(*E*)-1-Bromo-2-(3,3,3-trifluoroprop-1-en-1-yl)benzene (**2g**)^[2]



Colorless oil, 93% yield; ^1H NMR (400 MHz, CDCl_3): δ 7.66 – 7.47 (m, 3H), 7.39 – 7.29 (m, 1H), 7.25 – 7.20 (m, 1H), 6.16 (dq, $J = 16.0$ Hz, 6.4 Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3): δ –63.67 (dd, $J = 6.4$ Hz, 2.1 Hz, 3F). GC-MS: 250 $[\text{M}]^+$.

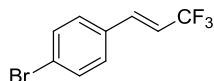
(*E*)-1-Bromo-3-(3,3,3-trifluoroprop-1-en-1-yl)benzene (**2h**)^[3]



Colorless oil, 92% yield; ^1H NMR (400 MHz, CDCl_3): δ 7.61 (t, $J = 1.6$ Hz, 1H), 7.51 (dt, $J = 7.8$ Hz, 1.6 Hz, 1H), 7.38 (dt, $J = 7.8$ Hz, 1.6 Hz, 1H), 7.27 (t, $J = 7.8$ Hz, 1H),

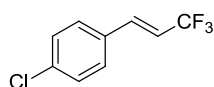
7.08 (dq, $J = 16.1$ Hz, 2.1 Hz, 1H), 6.21 (dq, $J = 16.1$ Hz, 6.4 Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3): $\delta -63.64$ (dd, $J = 6.4$ Hz, 2.1 Hz, 3F). GC-MS: 250 $[\text{M}]^+$.

(*E*)-1-Bromo-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (**2i**)^[4]



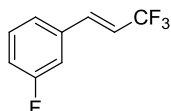
Colorless oil, 93% yield; ^1H NMR (400 MHz, CDCl_3): δ 7.53 (d, $J = 8.4$ Hz, 2H), 7.32 (d, $J = 8.4$ Hz, 2H), 7.09 (dq, $J = 16.1$ Hz, 2.0 Hz, 1H), 6.20 (dq, $J = 16.1$ Hz, 6.5 Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3): $\delta -63.52$ (dd, $J = 6.5$ Hz, 2.1 Hz, 3F). GC-MS: 250 $[\text{M}]^+$.

(*E*)-1-Chloro-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (**2j**)^[4]



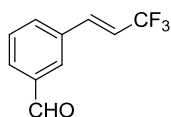
Colorless oil, 86% yield; ^1H NMR (400 MHz, CDCl_3): δ 7.44 – 7.31 (m, 4H), 7.11 (dq, $J = 16.0$ Hz, 2.0 Hz, 1H), 6.18 (dq, $J = 16.0$ Hz, 6.4 Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3): $\delta -63.48$ (dd, $J = 6.4$ Hz, 2.0 Hz, 3F). GC-MS: 206 $[\text{M}]^+$.

(*E*)-1-Fluoro-3-(3,3,3-trifluoroprop-1-en-1-yl)benzene (**2k**)^[5]



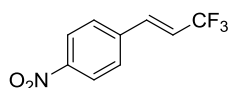
Colorless oil, 63% yield; ^1H NMR (400 MHz, CDCl_3): δ 7.41 – 7.32 (m, 1H), 7.25 – 7.20 (m, 1H), 7.19 – 7.05 (m, 3H), 6.21 (dq, $J = 16.0$ Hz, 6.4 Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3): $\delta -63.63$ (dd, $J = 6.4$ Hz, 2.0 Hz, 3F), -112.41 (td, $J = 9.0$ Hz, 5.9 Hz, 1F). GC-MS: 190 $[\text{M}]^+$.

(*E*)-3-(3,3,3-Trifluoroprop-1-en-1-yl)benzaldehyde (**2l**)



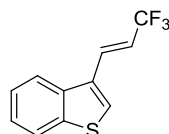
Colorless oil, 84% yield; ^1H NMR (400 MHz, CDCl_3): δ 10.05 (s, 1H), 7.97 (s, 1H), 7.90 (d, $J = 7.6$ Hz, 1H), 7.71 (d, $J = 7.6$ Hz, 1H), 7.59 (t, $J = 7.6$ Hz, 1H), 7.22 (dq, $J = 16.0$ Hz, 2.0 Hz, 1H), 6.32 (dq, $J = 16.0$ Hz, 6.4 Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3): $\delta -63.70$ (dd, $J = 6.4$ Hz, 2.0 Hz, 3F). ^{13}C NMR (100 MHz, CDCl_3): δ 191.52, 136.90, 136.26 (q, $J = 6.8$ Hz), 134.38, 133.08, 131.10, 129.70, 128.13, 123.18 (q, $J = 269.2$ Hz), 117.74 (q, $J = 34.2$ Hz). IR (KBr): 3069, 2928, 2835, 2736, 1702, 1669, 1602, 1310, 1277, 1130, 972, 795, 685, 651, 579 cm^{-1} . GC-MS: 200 $[\text{M}]^+$. HRMS: Calculated for $\text{C}_{10}\text{H}_7\text{OF}_3$: 200.0449; Found: 200.0448.

(*E*)-1-Nitro-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (**2m**)^[6]



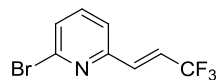
White solid, 76% yield; ¹H NMR (400 MHz, CDCl₃): δ 8.27 (d, *J* = 8.8 Hz, 2H), 7.63 (d, *J* = 8.8 Hz, 2H), 7.22 (dq, *J* = 16.1 Hz, 2.0 Hz, 1H), 6.36 (dq, *J* = 16.1 Hz, 6.4 Hz, 1H). ¹⁹F NMR (376 MHz, CDCl₃): δ -64.02 (dd, *J* = 6.4 Hz, 2.0 Hz, 3F). GC-MS: 217 [M]⁺.

(*E*)-3-(3,3,3-Trifluoroprop-1-en-1-yl)benzo[*b*]thiophene (**2n**)



Colorless oil, 89% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.99 – 7.82 (m, 2H), 7.67 (s, 1H), 7.52 – 7.37 (m, 3H), 6.31 (dq, *J* = 16.0 Hz, 6.4 Hz, 1H). ¹⁹F NMR (376 MHz, CDCl₃): δ -63.42 (dd, *J* = 6.4 Hz, 2.0 Hz, 3F). ¹³C NMR (100 MHz, CDCl₃): δ 140.46, 136.90, 130.25, 129.75 (q, *J* = 7.1 Hz), 126.81 (q, *J* = 1.2 Hz), 125.04, 124.89, 123.50 (q, *J* = 268.9 Hz), 123.06, 121.67, 116.75 (q, *J* = 33.8 Hz). IR (KBr): 3072, 1663, 1511, 1427, 1369, 1298, 1288, 1272, 1128, 964, 891, 757, 730 cm⁻¹. GC-MS: 228 [M]⁺. HRMS: Calculated for C₁₁H₇SF₃: 228.0221; Found: 228.0217.

(*E*)-2-Bromo-6-(3,3,3-trifluoroprop-1-en-1-yl)pyridine (**2o**)



Colorless oil, 70% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.57 (t, *J* = 7.7 Hz, 1H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.28 (d, *J* = 7.7 Hz, 1H), 7.08 (dq, *J* = 15.6 Hz, 2.0 Hz, 1H), 6.86 (dq, *J* = 15.6 Hz, 6.8 Hz, 1H). ¹⁹F NMR (376 MHz, CDCl₃): δ -64.08 (dd, *J* = 6.8 Hz, 2.0 Hz, 3F). ¹³C NMR (100 MHz, CDCl₃): δ 152.79, 142.55, 139.07, 134.90 (q, *J* = 6.7 Hz), 128.70, 123.17 (q, *J* = 269.2 Hz), 122.65, 121.52 (q, *J* = 34.4 Hz). IR (KBr): 3069, 2927, 2854, 1672, 1580, 1557, 1435, 1412, 1331, 1307, 1269, 1163, 1136, 985, 904, 786, 729, 661, 586 cm⁻¹. GC-MS: 251 [M]⁺. HRMS: Calculated for C₈H₅BrNF₃: 250.9557; Found: 250.9559.

References

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