

Supporting Information Suhre, Reif, Kirsch

# Gold(I)-Catalyzed Synthesis of Highly Substituted Furans

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## Supporting Information

Representative experimental procedures, copies of  $^1\text{H}$  NMR spectra of **3a–q**, and copies of  $^{13}\text{C}$  NMR spectra of **3a–q**.

(23 Pages)

**General experimental details:** All reactions were performed under Argon. All propargyl vinyl ethers **1** were synthesized by the reaction of the corresponding propargylic alcohols with 2-propynoic acid derivatives in the presence of trimethylphosphine.<sup>1</sup> 3-Butin-1-ol was purchased from Acros; and ethyl 2-butynoate, methyl 2-octynoate, ethyl propiolate, ethyl phenylpropiolate and 3-pentyn-2-ol were purchased from Aldrich. All commercially available chemicals were used without further purification. All the other propargylic alcohols were prepared from the corresponding alkynes by addition to paraformaldehyde.<sup>2</sup>  $^1\text{H}$  NMR spectra were obtained on Bruker 500 MHz FT-NMR and 360 MHz FT-NMR spectrometers.  $^{13}\text{C}$  NMR spectra were recorded at 90.6 MHz. Chemical shifts are reported in ppm relative to solvent signal. Multiplicity is indicated as follows: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet); dd (doublet of doublets); etc.; br (broad); app (apparent). High resolution mass spectra and EI were determined on a Finnigan MAT 95S and MAT 8200. Flash chromatography was performed with E. Merck silica gel (43–60  $\mu\text{m}$ ). The eluent used is reported in parentheses. Thin-layer chromatography (TLC) was performed on precoated glass-backed plates (Merck Kieselgel 60 F<sub>254</sub>), and components were visualized by observation under UV light or by treating the plates with  $\text{KMnO}_4/\text{H}_2\text{SO}_4$  followed by heating. For the addition of  $(\text{PPh}_3)\text{AuCl}$  to the reaction mixture, a stock solution was used.

<sup>1</sup> Inanaga, J.; Baba, Y.; Hanamoto, T. *Chem. Lett.* **1993**, 241–244.

<sup>2</sup> Hashmi, A. S. K.; Haufe, P.; Nass, A. R. *Adv. Synth. Catal.* **2003**, 345, 1237–1241.

### General Procedure for the Furan Formation Catalyzed by Gold(I).

**Ethyl 2,4,5-trimethylfuran-3-carboxylate (3a).**<sup>3</sup> (PPh<sub>3</sub>)AuCl (2 mol%, 2.2 mg) and AgBF<sub>4</sub> (2 mol%, 0.9 mg) were added subsequently to a solution of **1a** (40.0 mg, 0.22 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.1 mL), and the reaction vial was sealed, protected from light, and stirred at room temperature. The dark reaction mixture was stirred at room temperature for 4 h (until DC analysis indicated complete conversion). The mixture was concentrated under reduced pressure. Purification of the residue by flash chromatography on silica gel (P/EtOAc = 95/5) gave furan **3a** as a colorless oil (38.0 mg, 0.21 mmol, 95%): R<sub>f</sub> 0.71 (20% EtOAc/hexanes). <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>) δ 1.34 (t, *J* = 7.3 Hz, 3 H), 2.05 (s, 3 H), 2.16 (s, 3 H), 2.49 (s, 3 H), 4.26 (q, *J* = 7.3 Hz, 2 H); <sup>13</sup>C NMR (90.6 MHz, CDCl<sub>3</sub>) δ 9.9, 10.9, 14.1, 14.3, 59.6, 113.8, 114.6, 145.7, 157.2, 165.0; LRMS (EI) 182 (60%) [M<sup>+</sup>], 153 (78%) [M<sup>+</sup>–CH<sub>2</sub>CH<sub>3</sub>], 43 (100%); HRMS 182.0945 [182.0943 calcd for C<sub>10</sub>H<sub>14</sub>O<sub>3</sub><sup>+</sup>].

**Methyl 4,5-dimethyl-2-pentylfuran-3-carboxylate (3b).** Following the general procedure, **3b** (58.2 mg, 0.26 mmol, 97%) was obtained as a pale yellow oil from **1b** (60.0 mg, 0.27 mmol). The reaction was conducted in CH<sub>2</sub>Cl<sub>2</sub> (1.35 mL) in the presence of (PPh<sub>3</sub>)AuCl (2 mol%, 2.7 mg) and AgBF<sub>4</sub> (2 mol%, 1.1 mg) at 23 °C for 15 h. The residue was purified by flash chromatography on silica (3% EtOAc/pentane): R<sub>f</sub> 0.73 (20% EtOAc/hexanes). <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>) δ 0.89 (t, *J* = 6.8 Hz, 3 H), 1.25–1.34 (m, 4 H), 1.55–1.62 (m, 2 H), 2.05 (s, 3 H), 2.16 (s, 3 H), 2.88 (t, *J* = 7.7 Hz, 2 H), 3.79 (s, 3 H); <sup>13</sup>C NMR (90.6 MHz, CDCl<sub>3</sub>) δ 9.9, 11.0, 13.9, 22.4, 27.9, 28.0, 31.4, 50.8, 113.1, 114.4, 145.8, 161.5, 165.4; LRMS (EI) 224 (30%) [M<sup>+</sup>], 167 (100%), 43 (28%); HRMS 224.1413 [224.1412 calcd for C<sub>13</sub>H<sub>20</sub>O<sub>3</sub><sup>+</sup>].

**Ethyl 4,5-dimethyl-2-phenylfuran-3-carboxylate (3c).** Following the general procedure, **3c** (45.1 mg, 0.18 mmol, 90%) was obtained as a colorless oil from **1c** (50.0 mg, 0.20 mmol). The reaction was conducted in CH<sub>2</sub>Cl<sub>2</sub> (1.00 mL) in the presence of (PPh<sub>3</sub>)AuCl (2 mol%, 2.0 mg) and AgBF<sub>4</sub> (2 mol%, 0.8 mg) at 23 °C for 2 h. The residue was purified by flash chromatography on silica (2% EtOAc/pentane): R<sub>f</sub> 0.63 (20% EtOAc/hexanes). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.29 (t, *J* = 7.1 Hz, 3 H), 2.12 (s, 3 H), 2.28 (s, 3 H), 4.27 (q, *J* = 7.1 Hz, 2 H), 7.30–7.41 (m, 3

<sup>3</sup> Minami, I.; Yuhara, M.; Watanabe, H.; Tsuji, J. *J. Organomet. Chem.* **1987**, *334*, 225–242.

H), 7.72–7.79 (m, 2 H);  $^{13}\text{C}$  NMR (90.6 MHz,  $\text{CDCl}_3$ )  $\delta$  9.9, 11.3, 14.1, 60.2, 114.7, 116.3, 127.9, 128.2, 128.6, 130.6, 147.6, 155.1, 164.8; LRMS (EI) 244 (100%) [ $\text{M}^+$ ], 216 (30%) [ $\text{M}^+ - \text{C}_2\text{H}_4$ ], 199 (42%); HRMS 244.1098 [244.1099 calcd for  $\text{C}_{15}\text{H}_{16}\text{O}_3^+$ ].

**Ethyl 4,5-dimethylfuran-3-carboxylate (3d).** Following the general procedure, **3d** (47.9 mg, 0.28 mmol, 75%) was obtained as a yellow oil from **1d** (63.9 mg, 0.38 mmol) which was contaminated with an unknown side product (~3%). The reaction was conducted in benzene (1.90 mL) in the presence of  $(\text{PPh}_3)\text{AuCl}$  (2 mol%, 3.8 mg) and  $\text{AgBF}_4$  (2 mol%, 1.5 mg) at 23 °C for 4 h. The residue was purified by flash chromatography on silica (10%  $\text{Et}_2\text{O}$ /pentane):  $R_f$  0.71 (20%  $\text{EtOAc}$ /hexanes).  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  1.33 (t,  $J = 7.0$  Hz, 3 H), 2.10 (s, 3 H), 2.21 (s, 3 H), 4.27 (q,  $J = 7.0$  Hz, 2 H), 7.82 (s, 1 H);  $^{13}\text{C}$  NMR (90.6 MHz,  $\text{CDCl}_3$ )  $\delta$  9.0, 11.2, 14.3, 59.9, 114.3, 119.3, 146.0, 149.4, 164.1; LRMS (EI) 168 (55%) [ $\text{M}^+$ ], 139 (100%) [ $\text{M}^+ - \text{CH}_2\text{CH}_3$ ], 123 (60%), 43 (62%); HRMS 168.0788 [168.0786 calcd for  $\text{C}_9\text{H}_{12}\text{O}_3^+$ ].

**(4,5-dimethyl-2-phenylfuran-3-yl)(phenyl)methanone (3e).** Following the general procedure, **3e** (35.8 mg, 0.13 mmol, 72%) was obtained as a colorless oil from **1e** (50.0 mg, 0.18 mmol). The reaction was conducted in  $\text{CH}_2\text{Cl}_2$  (0.9 mL) in the presence of  $(\text{PPh}_3)\text{AuCl}$  (2 mol%, 1.8 mg) and  $\text{AgBF}_4$  (2 mol%, 0.7 mg) at 23 °C for 8 h. The residue was purified by flash chromatography on silica (2%  $\text{EtOAc}$ /pentane):  $R_f$  0.59 (20%  $\text{EtOAc}$ /hexanes).  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  1.91 (s, 3 H), 2.33 (s, 3 H), 7.05–7.22 (m, 3 H), 7.28–7.40 (m, 2 H), 7.42–7.51 (m, 3 H), 7.81–7.84 (m, 2 H);  $^{13}\text{C}$  NMR (90.6 MHz,  $\text{CDCl}_3$ )  $\delta$  8.9, 11.4, 116.4, 122.3, 126.6, 127.9, 128.2, 128.3, 129.8, 130.1, 133.0, 137.9, 147.8, 151.5, 193.9; LRMS (EI) 276 (100%) [ $\text{M}^+$ ], 199 (30%) [ $\text{M}^+ - \text{C}_6\text{H}_5$ ], 105 (82%), 77 (91%) [ $\text{C}_6\text{H}_5^+$ ]; HRMS 276.1148 [276.1150 calcd for  $\text{C}_{19}\text{H}_{16}\text{O}_2^+$ ].

**Ethyl 2,5-dimethylfuran-3-carboxylate (3f).**<sup>4</sup> Following the general procedure, **3f** (41.1 mg, 0.24 mmol, 82%) was obtained as a pale yellow oil from **1f** (50.0 mg, 0.29 mmol). The reaction was conducted in  $\text{CH}_2\text{Cl}_2$  (1.45 mL) in the presence of  $(\text{PPh}_3)\text{AuCl}$  (2 mol%, 2.9 mg) and  $\text{AgBF}_4$  (2 mol%, 1.1 mg) at 23 °C for 12 h. The residue was purified by flash chromatography on silica (5%  $\text{EtOAc}$ /pentane):  $R_f$  0.66 (20%  $\text{EtOAc}$ /hexanes).  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  1.32 (t,  $J = 7.1$  Hz, 3 H), 2.23 (s, 3 H), 2.51 (s, 3 H), 4.25 (q,  $J = 7.1$  Hz, 2 H), 6.20 (app. s, 1 H);  $^{13}\text{C}$  NMR

<sup>4</sup> Trahanovsky, W. S.; Chou, C.-H.; Cassady, T. J. *J. Org. Chem.* **1994**, 59, 2613–2615.

(90.6 MHz,  $\text{CDCl}_3$ )  $\delta$  13.1, 13.6, 14.4, 59.9, 106.2, 114.0, 149.8, 157.5, 164.3; LRMS (EI) 168 (52%)  $[\text{M}^+]$ , 139 (100%)  $[\text{M}^+ - \text{CH}_2\text{CH}_3]$ , 123 (74%); HRMS 168.0779 [168.0786 calcd for  $\text{C}_9\text{H}_{12}\text{O}_3^+$ ].

**Methyl 5-methyl-2-pentylfuran-3-carboxylate (3g).** Following the general procedure, **3g** (54.0 mg, 0.25 mmol, 77%) was obtained as a pale yellow oil from **1g** (70.0 mg, 0.33 mmol). The reaction was conducted in  $\text{CH}_2\text{Cl}_2$  (1.45 mL) in the presence of  $(\text{PPh}_3)\text{AuCl}$  (2 mol%, 2.9 mg) and  $\text{AgBF}_4$  (2 mol%, 1.2 mg) at 23 °C for 12 h. The residue was purified by flash chromatography on silica (2% EtOAc/pentane):  $R_f$  0.70 (20% EtOAc/hexanes).  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  0.89 (t,  $J$  = 6.8 Hz, 3 H), 1.31–1.34 (m, 4 H), 1.62–1.66 (m, 2 H), 2.24 (s, 3 H), 2.91 (t,  $J$  = 7.7 Hz, 2 H), 3.79 (s, 3 H), 6.19 (s, 1 H);  $^{13}\text{C}$  NMR (90.6 MHz,  $\text{CDCl}_3$ )  $\delta$  13.2, 13.9, 22.3, 27.5, 27.8, 31.4, 51.1, 106.1, 113.2, 149.9, 161.9, 164.7; LRMS (EI) 210 (25%)  $[\text{M}^+]$ , 153 (100%); HRMS 210.1262 [210.1256 calcd for  $\text{C}_{12}\text{H}_{18}\text{O}_3^+$ ].

**Ethyl 2,5-dimethyl-4-phenylfuran-3-carboxylate (3h).** Following the general procedure, **3h** (52.3 mg, 0.22 mmol, 87%) was obtained as a colorless oil from **1h** (60.0 mg, 0.25 mmol). The reaction was conducted in  $\text{CH}_2\text{Cl}_2$  (1.25 mL) in the presence of  $(\text{PPh}_3)\text{AuCl}$  (2 mol%, 2.5 mg) and  $\text{AgBF}_4$  (2 mol%, 0.9 mg) at 23 °C for 2 h. The residue was purified by flash chromatography on silica (2% EtOAc/pentane):  $R_f$  0.59 (20% EtOAc/hexanes).  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  1.10 (t,  $J$  = 7.2 Hz, 3 H), 2.21 (s, 3 H), 2.59 (s, 3 H), 4.13 (q,  $J$  = 7.2 Hz, 2 H), 7.25–7.38 (m, 5 H);  $^{13}\text{C}$  NMR (90.6 MHz,  $\text{CDCl}_3$ )  $\delta$  11.7, 13.9, 14.0, 59.7, 113.6, 121.4, 126.7, 127.6, 130.0, 133.3, 147.1, 157.4, 164.3; LRMS (EI) 244 (100%)  $[\text{M}^+]$ , 215 (90%)  $[\text{M}^+ - \text{CH}_2\text{CH}_3]$ , 198 (32%); HRMS 244.1095 [244.1099 calcd for  $\text{C}_{15}\text{H}_{16}\text{O}_3^+$ ].

**Ethyl 5-methyl-2,4-diphenylfuran-3-carboxylate (3i).**<sup>5</sup> Following the general procedure, **3i** (63.1 mg, 0.21 mmol, 90%) was obtained as a colorless oil from **1i** (70.1 mg, 0.23 mmol). The reaction was conducted in  $\text{CH}_2\text{Cl}_2$  (1.15 mL) in the presence of  $(\text{PPh}_3)\text{AuCl}$  (2 mol%, 2.3 mg) and  $\text{AgBF}_4$  (2 mol%, 0.9 mg) at 23 °C for 4 h. The residue was purified by flash chromatography on silica (10% EtOAc/pentane):  $R_f$  0.57 (20% EtOAc/hexanes).  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  0.98 (t,  $J$  = 7.0 Hz, 3 H), 2.33 (s, 3 H), 4.09 (q,  $J$  = 7.0 Hz, 2 H), 7.31–7.42 (m, 8 H), 7.82–7.83

<sup>5</sup> Ficini, J.; Claeys, M.; Depezay, J. C. *Tetrahedron Lett.* **1973**, *14*, 3357–3359.

(m, 2 H) ;  $^{13}\text{C}$  NMR (90.6 MHz,  $\text{CDCl}_3$ )  $\delta$  12.0, 13.6, 60.5, 114.9, 122.9, 126.9, 127.6, 127.9, 128.2, 128.7, 129.6, 130.1, 133.0, 148.4, 153.9, 164.6; LRMS (EI) 306 (100%) [ $\text{M}^+$ ], 261 (28%), 105(42%); HRMS 306.1253 [306.1256 calcd for  $\text{C}_{20}\text{H}_{18}\text{O}_3^+$ ].

**Ethyl 5-methyl-4-phenylfuran-3-carboxylate (3j).** Following the general procedure, **3j** (58.8 mg, 0.25 mmol, 84%) was obtained as a colorless oil from **1j** (70.0 mg, 0.30 mmol). The reaction was conducted in benzene (1.50 mL) in the presence of  $(\text{PPh}_3)\text{AuCl}$  (2 mol%, 3.0 mg) and  $\text{AgBF}_4$  (2 mol%, 1.2 mg) at 23 °C for 4 h. The residue was purified by flash chromatography on silica (5% EtOAc/pentane):  $R_f$  0.62 (20% EtOAc/hexanes).  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  0.98 (t,  $J = 7.0$  Hz, 3 H), 2.33 (s, 3 H), 4.09 (q,  $J = 7.0$  Hz, 2 H), 7.31–7.42 (m, 8 H), 7.82–7.83 (m, 2 H) ;  $^{13}\text{C}$  NMR (90.6 MHz,  $\text{CDCl}_3$ )  $\delta$  12.0, 13.6, 60.5, 114.9, 122.9, 126.9, 127.6, 127.9, 128.2, 128.7, 129.6, 130.1, 133.0, 148.4, 153.9, 164.6; LRMS (EI) 230 (100%) [ $\text{M}^+$ ], 185 (67%), 105 (45%), 84 (56%); HRMS 230.0939 [230.0943 calcd for  $\text{C}_{14}\text{H}_{14}\text{O}_3^+$ ].

**Ethyl 4-(2-methoxyphenyl)-5-methyl-2-phenylfuran-3-carboxylate (3k).** Following the general procedure, **3k** (69.1 mg, 0.25 mmol, 99%) was obtained as a colorless oil from **1k** (70.0 mg, 0.26 mmol). The reaction was conducted in  $\text{CH}_2\text{Cl}_2$  (1.30 mL) in the presence of  $(\text{PPh}_3)\text{AuCl}$  (2 mol%, 2.3 mg) and  $\text{AgBF}_4$  (2 mol%, 1.0 mg) at 23 °C for 3 h. The residue was purified by flash chromatography on silica (5% EtOAc/pentane):  $R_f$  0.39 (20% EtOAc/hexanes).  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.03 (t,  $J = 7.2$  Hz, 3 H), 2.17 (s, 3 H), 2.55 (s, 3 H), 3.77 (s, 3 H), 4.06 (q,  $J = 7.2$  Hz, 2 H), 6.89 (d,  $J = 8.2, 0.8$  Hz, 1 H), 6.96 (dt,  $J = 0.8, 7.5$  Hz, 1 H), 7.13 (dd,  $J = 7.5, 1.8$  Hz, 1 H), 7.28 (dt,  $J = 8.2, 1.8$  Hz, 1 H);  $^{13}\text{C}$  NMR (90.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  11.8, 13.8, 13.9, 55.3, 59.5, 110.3, 114.5, 117.3, 120.1, 122.5, 128.5, 131.1, 147.1, 156.6, 157.4, 164.5; LRMS (EI) 274 (100%) [ $\text{M}^+$ ], 213 (92%), 43 (68%); HRMS 274.1206 [274.1205 calcd for  $\text{C}_{16}\text{H}_{18}\text{O}_4^+$ ].

**Ethyl 5-methyl-2-phenyl-4-(thiophen-2-yl)furan-3-carboxylate (3l).** Following the general procedure, **3l** (53.2 mg, 0.17 mmol, 89%) was obtained as a colorless oil from **1l** (60.0 mg, 0.19 mmol). The reaction was conducted in  $\text{CH}_2\text{Cl}_2$  (0.95 mL) in the presence of  $(\text{PPh}_3)\text{AuCl}$  (2 mol%, 2.0 mg) and  $\text{AgBF}_4$  (2 mol%, 1.0 mg) at 23 °C for 4 h. The residue was purified by flash chromatography on silica (10% EtOAc/pentane):  $R_f$  0.58 (20% EtOAc/hexanes).  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.08 (t,  $J = 7.3$  Hz, 3 H), 2.36 (s, 3 H), 4.15 (q,  $J = 7.3$  Hz, 2 H), 7.11 (dd,  $J = 5.0$  Hz,  $J = 1.2$  Hz, 1 H), 7.21–7.24 (m, 1 H), 7.33–7.42 (m, 4 H), 7.78–7.81 (m, 2 H);  $^{13}\text{C}$  NMR

(90.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  12.2, 13.7, 60.6, 114.8, 117.9, 123.1, 124.6, 127.6, 128.1, 128.7, 129.2, 130.1, 132.6, 148.8, 153.9, 164.6; LRMS (EI) 312 (100%) [ $\text{M}^+$ ], 284 (12%) [ $\text{M}^+ - \text{C}_2\text{H}_4$ ], 267 (20%); HRMS 312.0826 [312.0820 calcd for  $\text{C}_{18}\text{H}_{16}\text{O}_3\text{S}^+$ ].

**Ethyl 5-methyl-2-phenyl-4-(pyridin-2-yl)furan-3-carboxylate (3m).** Following the general procedure, **3m** (49.0 mg, 0.16 mmol, 82%) was obtained as a pale yellow oil from **1m** (60.0 mg, 0.19 mmol). The reaction was conducted in benzene (2.0 mL) in the presence of  $(\text{PPh}_3)\text{AuCl}$  (2 mol%, 2.0 mg) and  $\text{AgBF}_4$  (2 mol%, 0.9 mg) at 23 °C for 48 h. The residue was purified by flash chromatography on silica (20% EtOAc/pentane):  $R_f$  0.15 (20% EtOAc/hexanes).  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.02 (t,  $J = 7.3$  Hz, 3 H), 2.44 (s, 3 H), 4.12 (q,  $J = 7.3$  Hz, 2 H), 7.21 (ddd,  $J = 7.5$  Hz,  $J = 5.0$  Hz,  $J = 1.1$  Hz, 1 H), 7.34–7.46 (m, 4 H), 7.71 (dt,  $J = 1.8$  Hz,  $J = 7.7$  Hz, 1 H), 7.83–7.87 (m, 2 H), 8.63–8.67 (m, 1 H);  $^{13}\text{C}$  NMR (90.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  12.4, 13.7, 60.5, 114.6, 121.6, 122.8, 124.1, 127.6, 128.2, 128.8, 129.9, 135.8, 149.3, 150.1, 152.6, 153.9, 164.5; LRMS (EI) 307 (25%) [ $\text{M}^+$ ], 234 (44%), 105 (100%); HRMS 307.1211 [307.1208 calcd for  $\text{C}_{19}\text{H}_{17}\text{NO}_3^+$ ].

**Ethyl 4-(cyclohexylmethyl)-5-methyl-2-phenylfuran-3-carboxylate (3n).** Following the general procedure, **3n** (51.0 mg, 0.15 mmol, 73%) was obtained as a colorless oil from **1n** (70.0 mg, 0.21 mmol). The reaction was conducted in  $\text{CH}_2\text{Cl}_2$  (1.0 mL) in the presence of  $(\text{PPh}_3)\text{AuCl}$  (2 mol%, 1.9 mg) and  $\text{AgBF}_4$  (2 mol%, 1.0 mg) at 23 °C for 5 h. The residue was purified by flash chromatography on silica (2% EtOAc/pentane):  $R_f$  0.69 (20% EtOAc/hexanes).  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.72–1.02 (m, 2 H), 1.06–1.19 (m, 3 H), 1.28 (t,  $J = 7.0$  Hz, 3 H), 1.42–1.50 (m, 1 H), 1.61–1.72 (m, 5 H), 2.27 (s, 3 H), 2.42 (d,  $J = 7.0$  Hz, 2 H), 4.27 (q,  $J = 7.0$  Hz, 2 H), 7.36–7.38 (m, 3 H), 7.73 (d,  $J = 6.8$  Hz, 2 H);  $^{13}\text{C}$  NMR (90.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  11.7, 14.0, 26.4, 26.6, 32.0, 33.3, 39.0, 60.2, 114.4, 119.6, 127.9, 128.1, 128.5, 130.7, 148.4, 154.9, 164.9; LRMS (EI) 326 (75%) [ $\text{M}^+$ ], 244 (100%), 43 (92%); HRMS 326.1878 [326.1882 calcd for  $\text{C}_{21}\text{H}_{26}\text{O}_3^+$ ].

**Ethyl 4-(2-tert-butyltrimethylsilyloxyethyl)-5-methyl-2-phenylfuran-3-carboxylate (3o).** Following the general procedure, **3o** (43.2 mg, 0.11 mmol, 72%) was obtained as a colorless oil from **1o** (60.0 mg, 0.15 mmol). The reaction was conducted in  $\text{CH}_2\text{Cl}_2$  (0.75 mL) in the presence of  $(\text{PPh}_3)\text{AuCl}$  (2 mol%, 1.7 mg) and  $\text{AgBF}_4$  (2 mol%, 0.9 mg) at 23 °C for 3 h. The residue was

purified by flash chromatography on silica (5% Et<sub>2</sub>O/pentane): R<sub>f</sub> 0.71 (20% EtOAc/hexanes). <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>): δ 0.00 (s, 6 H), 0.87 (s, 9 H), 1.26 (t, *J* = 7.0 Hz, 3 H), 2.30 (s, 3 H), 2.80 (t, *J* = 6.7 Hz, 2 H), 3.76 (t, *J* = 6.7 Hz, 2 H), 4.26 (q, *J* = 7.0 Hz, 2 H), 7.36–7.39 (m, 3 H), 7.70–7.73 (m, 2 H); <sup>13</sup>C NMR (90.6 MHz, CDCl<sub>3</sub>): δ –5.4, 11.6, 14.0, 18.4, 25.9, 28.1, 60.2, 63.3, 114.2, 117.6, 127.9, 128.3, 128.6, 130.7, 149.4, 155.2, 164.5; LRMS (EI) 388 (1%) [M<sup>+</sup>], 331 (7%) [M<sup>+</sup>–C<sub>4</sub>H<sub>9</sub>], 219 (24%), 147 (41%), 84 (100%); HRMS 331.1363 [331.1365 calcd for fragment C<sub>18</sub>H<sub>23</sub>O<sub>4</sub>Si<sup>+</sup>]; HRMS 388.2077 [388.2070 calcd for C<sub>22</sub>H<sub>32</sub>O<sub>4</sub>Si<sup>+</sup>].

**Ethyl 4-(*tert*-butyldimethylsilyl)-2,5-dimethylfuran-3-carboxylate (3p).** Following the general procedure, **3p** (57.8 mg, 0.20 mmol, 83%) was obtained as a colorless oil from **1p** (70.0 mg, 0.25 mmol). The reaction was conducted in CH<sub>2</sub>Cl<sub>2</sub> (1.25 mL) in the presence of (PPh<sub>3</sub>)AuCl (2 mol%, 2.5 mg) and AgBF<sub>4</sub> (2 mol%, 1.0 mg) at 23 °C for 4 h. The residue was purified by flash chromatography on silica (2% EtOAc/pentane): R<sub>f</sub> 0.80 (20% EtOAc/hexanes). <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>): δ 0.26 (s, 6 H), 0.91 (s, 9 H), 1.33 (t, *J* = 7.3 Hz, 3 H), 2.29 (s, 3 H), 2.46 (s, 3 H), 4.25 (q, *J* = 7.3 Hz, 2 H); <sup>13</sup>C NMR (90.6 MHz, CDCl<sub>3</sub>): δ –2.6, 13.9, 14.4, 15.2, 18.5, 27.1, 59.9, 110.1, 118.7, 156.6, 156.7, 165.3; LRMS (EI) 282 (4%) [M<sup>+</sup>], 225 (100%) [M<sup>+</sup>–C<sub>4</sub>H<sub>9</sub>], 197 (95%), 75 (68%); HRMS 282.1653 [282.1651 calcd for C<sub>15</sub>H<sub>26</sub>O<sub>3</sub>Si<sup>+</sup>].

**Ethyl 5-ethyl-4-methyl-2-phenylfuran-3-carboxylate (3q).**<sup>6</sup> Following the general procedure, **3q** (27.3 mg, 0.10 mmol, 45%) was obtained as a pale yellow oil from **1q** (60.0 mg, 0.23 mmol). The reaction was conducted in CH<sub>2</sub>Cl<sub>2</sub> (1.20 mL) in the presence of (PPh<sub>3</sub>)AuCl (2 mol%, 2.4 mg) and AgBF<sub>4</sub> (2 mol%, 1.0 mg) at 38 °C for 24 h. The residue was purified by flash chromatography on silica (2% EtOAc/pentane): R<sub>f</sub> 0.67 (20% EtOAc/hexanes). <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>): δ 1.24 (t, *J* = 7.7 Hz, 3 H), 1.29 (t, *J* = 7.0 Hz, 3 H), 2.13 (s, 3 H), 2.26 (q, *J* = 7.7 Hz, 2 H), 4.27 (q, *J* = 7.0 Hz, 2 H), 7.38–7.39 (m, 3 H), 7.74–7.77 (m, 2 H); <sup>13</sup>C NMR (90.6 MHz, CDCl<sub>3</sub>): δ 9.8, 12.8, 14.1, 19.2, 60.2, 114.7, 115.4, 127.9, 128.2, 128.6, 130.7, 152.7, 154.9, 164.8; LRMS (EI) 258 (5%) [M<sup>+</sup>], 220 (12%), 185 (25%), 147 (28%), 105 (100%); HRMS 258.1249 [258.1256 calcd for C<sub>16</sub>H<sub>18</sub>O<sub>3</sub><sup>+</sup>].

<sup>6</sup> Antonioletti, R.; Cecchini, C.; Ciani, B.; Magnanti, S. *Tetrahedron Lett.* **1995**, *36*, 9019–9022.



































