Electronic Supplementary Information

Bifunctional Phosphine Ligand-Enabled Gold-Catalyzed

Direct Cycloisomerization of Alkynyl Ketones to 2,5-Disubstituted Furans

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1. General information

All glassware was thoroughly oven-dried. Solvents were dried according to standard methods prior to use. All commercially available reagents were obtained from chemical suppliers and used after proper purification if necessary. Thin-layer chromatography (TLC) plates were visualized by exposure to ultraviolet light. Flash chromatography was carried out using silica gel (100-200 mesh). Melting points are uncorrected. NMR spectra were recorded with tetramethylsilane as the internal standard. ¹H NMR and ¹³C NMR spectra of CDCl₃ solutions were recorded at 500 and 125 MHz (Bruker Avance), respectively and resonances (δ) are given in parts per million relatives to tetramethylsilane. Data for ¹H NMR are reported as follows: chemical shift (δ ppm), mul-tiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet), integration, coupling constant (Hz) and assignment. Data for ¹³C NMR are reported as chemical shift. GC-MS experiments were performed with an Agilent 6890N GC system equipped with a 5973N mass-selective detector with EI source; High resolution mass spectra (HRMS) were obtained on a TOF MS instrument with EI or ESI source.

2. Preparation of bifunctional Ligands L1, L3-L5, and corresponding LAu(I)Cl catalysts

L1,¹ L3-L5² were prepared according to previous reports. The corresponding LAu(I)Cl catalysts were prepared by ligand exchanging of Me₂SAuCl with L1 and L3-L5, respectively.^{1,2}

3. General procedure for the synthesis of substrates 1



General Procedure A:³

$$\begin{array}{c} O \\ R^{1} \\ \hline CI \end{array} + = R^{2} \end{array} \xrightarrow{\begin{array}{c} Pd(PPh_{3})_{2}Cl_{2} \\ Cul, Et_{3}N \\ \hline THF, 1 h, rt \end{array}} P^{1} \\ R^{1} \\ R^{2} \\ R^{2} \end{array}$$

According to a modified literature procedure, using standard Schlenk line, to a flame-dried round bottom flask equipped with stir bar under N₂ atmosphere was added acid chloride (5.0 mmol, 1.0 equiv), PdCl₂(PPh₃)₂ (70.0 mg, 0.10 mmol, 2.0 mol %), CuI (38 mg, 0.20 mmol, 4.0 mol %), Et₃N (0.70 mL, 5.0 mmol, 1.0 equiv), and alkyne (5.0 mmol, 1.0 equiv) in dry THF (15.0 mL) at room temperature. The resulting reaction mixture was stirred at room temperature under N₂ and monitored by TLC until starting materials were completely consumed about 1 h. The reaction was quenched with saturated aqueous ammonium chloride (15.0 mL). The aqueous layer was extracted with EtOAc (3 × 15.0 mL). The combined organic layers were washed with brine (15.0 mL), dried over MgSO₄, filtered, and concentrated in vacuo. The resulting crude product was purified by silica gel flash column chromatography (eluent: petroleum ether/ EtOAc = 40/1).

General Procedure B:4



To a dried schlenk tube under N₂ atmosphere was added alkyne **S1** (5.0 mmol, 1.0 equiv) and anhydrous THF (10 mL), and the solution was cooled to -78 °C. Then the solution of *n*-BuLi in THF (5.5 mmol, 1.1 equiv) was added dropwise into the solution while the temperature was maintained at -78 °C. The mixture was stirred for 0.5 h at -78 °C, aldehyde (5.0 mmol, 1.0 equiv) was added. After that, the resulting mixture was stirred for 12 h at room temperature. Upon reaction completion, the reaction system was quenched with saturated aqueous ammonium chloride (15 mL). The mixture was extracted with EtOAc (3×15 mL). The combined organic layers were washed with brine and dried over anhydrous MgSO₄, filtered, and concentrated in vacuo. The resulting crude product was purified by silica gel flash column chromatography (eluent: petroleum ether/ EtOAc =

20/1) afforded the products S2.

To the solution of alkynol **S2** in anhydrous CH_2Cl_2 (10 mL), Dess-Martin periodinane (1.5 equiv) was added portion-wise at room temperature. After the mixture was stirred for about 2 h, the saturated aqueous solution of $Na_2S_2O_3$ was added excessively. The mixture was extracted with CH_2Cl_2 (3×15 mL). The combined organic layers were washed with brine and dried over anhydrous MgSO₄, filtered, and concentrated in vacuo. The resulting crude product was purified by silica gel flash column chromatography (eluent: petroleum ether/ EtOAc = 40/1) afforded the products **1**.

Substrates 1a³, 1b⁵, 1d, 1e⁵, 1f⁶, 1g⁷, 1i, 1k, 1l, 1n¹⁰, 1p¹¹, 1r, 1s¹², 1t¹³, 1u¹⁴, 1v, 1w, 1za¹⁵, 1zb and 1zc were prepared following the *general procedure A*. 1c⁵, 1h⁸, 1j, 1m, 1o,⁹ 1q, and 1x-1z¹⁶ were prepared following the *general procedure B*. Among them, 1a³, 1b⁵, 1c⁵, 1e⁵, 1f⁶, 1g⁷, 1h⁸, 1n¹⁰, 1p¹¹, 1s¹², 1t¹³, 1u¹⁴, 1za,¹⁵ 1o⁹ and 1x-1z¹⁶ are known compounds and their NMR spectroscopy data were consisted with those known data.

Characterization of Unknown Starting Materials.



AccordingtoGeneralProcedureA,1-(4-(dimethylamino)phenyl)hept-2-yn-1-one(1d)was obtained asyellow solid (0.80 g, 70% isolated yield, m.p. = 52-53 °C).

¹H NMR (500 MHz, CDCl₃): δ 7.97 (d, J = 8.5 Hz, 2H), 6.58 (d, J = 9.0 Hz, 2H), 3.01 (s, 6H), 2.43 (t, J = 7.0 Hz, 2H), 1.65–1.55 (m, 2H), 1.51–1.40 (m, 2H), 0.92 (t, J = 7.5 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 176.4, 154.0, 131.8, 125.4, 110.5, 94.4, 79.9, 40.0, 30.0, 22.0, 18.8, 13.6.

HRMS (ESI) for C₁₅H₂₀NO [M+H]⁺: calcd: 230.1539, found: 230.1543.



According to *General Procedure A*, **2-(hept-2-ynoyl)phenyl acetate** (1i) was obtained as colorless oil (1.07 g, 88% isolated yield).

¹H NMR (500 MHz, CDCl₃): δ 8.17 (dd, J = 8.0, 1.5 Hz, 1H), 7.54 (td, J = 7.8, 1.5 Hz, 1H), 7.32 (t, J = 7.5 Hz, 1H), 7.06 (d, J = 8.0 Hz, 1H), 2.42 (t, J = 7.3 Hz, 2H), 2.32 (s, 3H), 1.62–1.53 (m, 2H), 1.48–1.38 (m,

2H), 0.91 (t, J = 7.3 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 175.8, 169.2, 149.8, 134.3, 133.2, 129.0, 125.8, 123.7, 96.1, 80.2, 29.5, 21.8, 20.7, 18.6, 13.2.

HRMS (ESI) for C₁₅H₁₇O₃ [M+H]⁺: calcd: 245.1172, found: 245.1175.



According to *General Procedure B*, **1-(3-Methylphenyl)hept-2-yn-1-one** (1j) was obtained as colorless oil (0.77 g, 77% isolated yield). ¹H NMR (500 MHz, CDCl₃): δ 7.95 (d, J = 8.0 Hz, 2H), 7.43–7.31 (m,

¹J 2H), 2.51 (t, *J* = 7.0 Hz, 2H), 2.42 (s, 3H), 1.71–1.62 (m, 2H), 1.56–1.47 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 178.3, 138.2, 136.9, 134.6, 129.7, 128.3, 126.9, 96.5, 79.7, 29.8, 22.0, 21.2, 18.8, 13.4.

HRMS (ESI) for C₁₅H₁₇O₃ [M+H]⁺: calcd: 245.1172, found: 245.1175.



AccordingtoGeneralProcedureA,1-(3-(trifluoromethyl)phenyl)hept-2-yn-1-one(1k)wasobtainedascolorless oil (1.03 g, 81% isolated yield).

¹H NMR (500 MHz, CDCl₃): δ 8.36 (s, 1H), 8.29 (d, J = 7.8 Hz, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.60 (t, J = 7.8 Hz, 1H), 2.51 (t, J = 7.1 Hz, 2H), 1.70-1.60 (m, 2H), 1.56-1.43 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 176.5, 137.3, 132.4, 131.1 (q, *J* = 32.8 Hz), 130.0 (q, *J* = 3.5 Hz), 129.2, 126.2 (q, *J* = 3.8 Hz), 123.6 (q, *J* = 270.9 Hz), 98.3, 79.2, 29.6, 22.0, 18.8, 13.3.

HRMS (ESI) for C₁₄H₁₄F₃O [M+H]⁺: calcd: 255.0991, found: 255.0988.



According to *General Procedure A*, **1-(3-chlorophenyl)hept-2-yn-1-one** (11) was obtained as colorless oil (0.94 g, 85% isolated yield).

¹H NMR (500 MHz, CDCl₃): δ 8.02 (s, 1H), 7.95 (d, J = 7.5 Hz, 1H),

11 7.49 (d, J = 8.0 Hz, 1H), 7.36 (t, J = 7.9 Hz, 1H), 2.46 (t, J = 7.1 Hz, 2H), 1.65–1.57 (m, 2H), 1.50–1.41 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 176.4, 138.2, 134.6, 133.5, 129.7, 129.1, 127.4, 97.5, 79.1, 29.6,

21.9, 18.7, 13.3.

HRMS (ESI) for C₁₃H₁₄ClO [M+H]⁺: calcd: 221.0728, found: 221.0731.

According



1-(2,4,6-Trimethylphenyl)hept-2-yn-1-one (1m) was obtained as colorless oil (0.80 g, 70% isolated yield).

General

Procedure

В,

¹**H** NMR (500 MHz, CDCl₃): δ 6.87 (s, 2H), 2.41 (t, J = 7.3 Hz, 2H),

to

2.36 (s, 6H), 2.30 (s, 3H), 1.63-1.54 (m, 2H), 1.49-1.39 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 184.7, 139.4, 137.8, 134.6, 128.9, 97.4, 82.5, 29.6, 22.0, 21.1, 19.6, 19.0, 13.4.

HRMS (ESI) for C₁₆H₂₁O [M+H]⁺: calcd: 229.1587, found: 229.1586.



According to *General Procedure B*, **1-phenyloct-3-yn-2-one (1q)** was obtained as colorless oil (0.78 g, 78% isolated yield).

¹H NMR (500 MHz, CDCl₃): δ 7.38–7.33 (m, 2H), 7.32–7.23 (m, 3H),

3.82 (s, 2H), 2.33 (t, *J* = 7.0 Hz, 2H), 1.55–1.44 (m, 2H), 1.40–1.31 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 185.4, 133.3, 129.8, 128.6, 127.2, 96.5, 80.7, 52.2, 29.6, 21.8, 18.6, 13.4.

HRMS (ESI) for C₁₄H₁₇O [M+H]⁺: calcd: 201.1274, found: 201.1278.



According to *General Procedure A*, **1-phenylnon-1-en-4-yn-3-one** (**1r**) was obtained as colorless oil (0.94 g, 89% isolated yield). ¹H NMR (500 MHz, CDCl₃): δ 7.77 (dd, J = 16.1, 1.5 Hz, 1H), 7.51

(dd, J = 6.3, 3.1 Hz, 2H), 7.37 (dd, J = 4.8, 2.0 Hz, 3H), 6.72 (dd, J =

16.1, 2.0 Hz, 1H), 2.42 (t, *J* = 7.1 Hz, 2H), 1.65–1.54 (m, 2H), 1.52–1.41 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 178.2, 147.8, 133.8, 130.7, 128.8, 128.3, 128.3, 94.8, 79.1, 29.6, 21.8, 18.5, 13.3.

HRMS (ESI) for C₁₅H₁₇O [M+H]⁺: calcd: 213.1274, found: 213.1277.



AccordingtoGeneralProcedureA,1-phenyl-5-((tetrahydro-2H-pyran-2-yl)oxy)pent-2-yn-1-one(1v)was obtained as colorless oil (1.02 g, 79% isolated yield).

¹**H NMR (500 MHz, CDCl₃):** δ 8.12 (d, J = 8.5 Hz, 2H), 7.57–7.51 (m, 1H), 7.42 (t, J = 7.8 Hz, 2H), 4.66 (t, J = 3.3 Hz, 1H), 3.93 (dt, J = 9.7, 6.7 Hz, 1H), 3.89–3.82 (m, 1H), 3.65 (dt, J = 9.7, 6.7 Hz, 1H), 3.52–3.45 (m, 1H), 2.76 (t, J = 6.8 Hz, 2H), 1.87–1.75 (m, 1H), 1.74–1.65 (m, 1H), 1.63–1.45 (m, 4H).

¹³C NMR (125 MHz, CDCl₃): δ 177.8, 136.6, 133.8, 129.4, 128.3, 98.6, 93.4, 79.9, 64.4, 62.0, 30.3, 25.2, 20.6, 19.1.

HRMS (ESI) for C₁₆H₁₉O₃ [M+H]⁺: calcd: 259.1329, found: 259.1334.



¹³C NMR (125 MHz, CDCl₃): δ 178.0, 136.7, 133.9, 129.6, 128.4, 93.5, 80.3, 60.1, 23.4, -0.6.

HRMS (ESI) for C₁₄H₁₉O₂Si [M+H]⁺: calcd: 247.1149, found: 247.1145.



¹H NMR (500 MHz, CDCl₃): δ 7.82 (d, J = 7.5 Hz, 2H), 7.72 (d, J = 8.0 Hz, 2H), 7.63 – 7.56 (m, 1H), 7.41 (t, J = 7.8 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 4.33 (s, 2H), 2.93 (s, 3H), 2.20 (s, 3H).
¹³C NMR (125 MHz, CDCl₃): δ 176.7, 144.2, 135.8, 134.3, 133.6, 129.7, 129.3, 128.5, 127.7, 86.4, 83.5, 40.0, 34.8, 21.3.

HRMS (ESI) for C₁₈H₁₈NO₃S [M+H]⁺: calcd: 328.1002, found: 328.1004.



According to *General Procedure A*, 4-chloro-1-phenylbut-2-yn-1-one (1zc) was obtained as yellow solid (0.62g, 70% isolated yield, m.p. = 33-35 °C). ¹H NMR (500 MHz, CDCl₃): δ 8.13 (dd, J = 8.5, 1.0 Hz, 2H), 7.67–7.61 (m, 1H), 7.51 (t, J = 7.8 Hz, 2H), 4.39 (s, 2H). ¹³C NMR (125 MHz, CDCl₃): δ 177.0, 136.0, 134.5, 129.6, 128.7, 87.6, 83.1, 29.4.

HRMS (ESI) for C₁₀H₈ClO [M+H]⁺: calcd: 179.0258, found: 179.0254.

4. General procedure for the synthesis of products 2



A mixture of catalyst L3AuCl (3.0 mg, 0.004 mmol, 2 mol %), NaBARF (17.7 mg, 0.02 mmol, 10 mol %), alkynyl ketone 1 (0.20 mmol, 1.0 equiv) and anhydrous DCE (2.0 mL) were added to a reaction tube equipped with a stir bar. The resulting mixture was stirred at 60-80 °C under N₂ condition for the time indicated in Table 2. Upon completion (monitored by TLC), the reaction solution was concentrated in vacuo. The crude product was purified by column chromatography on silica gel to afford pure products 2.

Characterization of products.



(m, 2H), 7.32–7.15 (m, 1H), 6.60 (d, J = 3.5 Hz, 1H), 6.11 (d, J = 3.5 Hz, 1H), 2.71 (t, J = 7.5 Hz, 2H), 1.92–1.66 (m, 2H), 1.05 (t, *J* = 7.5 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 156.3, 152.2, 131.3, 128.6, 126.7, 123.4, 107.0, 105.6, 30.2, 21.5, 13.8.





yield).

¹**H NMR (500 MHz, CDCl₃):** δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 7.5 Hz, 2H), 6.51 (d, *J* = 3.5 Hz, 1H), 6.07 (d, *J* = 3.5 Hz, 1H), 2.68 (t, *J* = 7.5 Hz, 2H), 2.37 (s, 3H), 1.81–1.69 (m, 2H), 1.03 (t, *J* = 7.5 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 155.9, 152.4, 136.5, 129.3, 128.7, 123.4, 106.8, 104.9, 30.2, 21.5, 21.2, 13.8.

HRMS (ESI) for C₁₄H₁₇O [M+H]⁺: calcd: 201.1274, found: 201.1278.



2-(4-methoxyphenyl)-5-propylfuran (2c) was obtained as colorless oil at 60 °C after 2 h (eluent: PE to PE/EA = 50:1, 41.9 mg, 97% isolated yield).

¹**H NMR (500 MHz, CDCl₃):** δ 7.62–7.58 (m, 2H), 6.96–6.91 (m, 2H), 6.44 (d, *J* = 3.2 Hz, 1H), 6.07 (d, *J* = 3.2 Hz, 1H), 3.85 (s, 3H), 2.69 (t, *J* = 7.5 Hz, 2H), 1.79–1.71 (m, 2H), 1.04 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 158.6, 155.5, 152.1, 124.7, 124.5, 114.0, 106.8, 104.0, 55.3, 30.2, 21.5, 13.8.

HRMS (ESI) for C₁₄H₁₇O₂ [M+H]⁺: calcd: 217.1223, found: 217.1228.



2-(4-(dimethylamino)phenyl)-5-propylfuran (2d) was obtained as colorless oil at 60 °C after 2 h (eluent: PE/EA = 40:1, 45.8 mg, 91% isolated yield).

¹**H NMR (500 MHz, CDCl₃):** δ 7.58–7.52 (m, 2H), 6.79–6.74 (m, 2H), 6.37 (d, *J* = 3.0 Hz, 1H), 6.05 (d, *J* = 3.0 Hz, 1H), 3.00 (s, 6H), 2.68 (t, *J* = 7.3 Hz, 2H), 1.80–1.70 (m, 2H), 1.04 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 154.8, 153.0, 149.6, 124.6, 120.5, 112.6, 106.6, 102.6, 40.6, 30.2, 21.5, 13.8.

HRMS (ESI) for C₁₅H₂₀NO [M+H]⁺: calcd: 230.1539, found: 230.1534.



2-(4-fluorophenyl)-5-propylfuran (2e) was obtained as colorless oil at 60 °C after 2 h (eluent: PE to PE/EA = 100:1, 37.5 mg, 92% isolated

yield).

¹**H** NMR (500 MHz, CDCl₃): δ 7.65–7.59 (m, 2H), 7.11–7.05 (m, 2H), 6.50 (d, J = 3.2 Hz, 1H), 6.08 (d, J = 3.2 Hz, 1H), 2.68 (t, J = 7.5 Hz, 2H), 1.80–1.71 (m, 2H), 1.04 (t, J = 7.5 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 161.8 (d, J = 244.5 Hz), 156.3, 151.4, 127.7, 125.0 (d, J = 7.9 Hz), 115.6 (d, J = 21.8 Hz), 107.0, 105.3 (d, J = 1.1 Hz), 30.1, 21.5, 13.8.

HRMS (ESI) for C₁₃H₁₄FO [M+H]⁺: calcd: 205.1023, found: 205.1028.



2-(4-nitrophenyl)-5-propylfuran (2f) was obtained as yellow oil at 60 °C after 2 h (eluent: PE to PE/EA = 20:1, 43.9 mg, 95% isolated yield).

¹H NMR (500 MHz, CDCl₃): δ 8.24–8.19 (m, 2H), 7.74–7.70 (m, 2H), 6.79 (d, J = 3.0 Hz, 1H), 6.17 (d, J = 3.0 Hz, 1H), 2.70 (t, J = 7.5 Hz, 2H), 1.82–1.69 (m, 2H), 1.03 (t, J = 7.5 Hz, 3H).
¹³C NMR (125 MHz, CDCl₃): δ 158.9, 150.0, 145.9, 136.8, 124.3, 123.3, 110.1, 108.1, 30.2, 21.3, 13.7.

HRMS (ESI) for C₁₃H₁₄NO₃ [M+H]⁺: calcd: 232.0968, found: 232.0971.



2-(4-Cyanophenyl)-5-propylfuran (2g) was obtained as colorless oil at 60 °C after 2 h (eluent: PE to PE/EA = 50:1, 40.1 mg, 95% isolated yield).

¹H NMR (500 MHz, CDCl₃): δ 7.72–7.66 (m, 2H), 7.66–7.59 (m, 2H), 6.72 (d, J = 3.3 Hz, 1H), 6.14 (d, J = 3.3 Hz, 1H), 2.69 (t, J = 7.5 Hz, 2H), 1.81–1.68 (m, 2H), 1.02 (t, J = 7.4 Hz, 3H).
¹³C NMR (125 MHz, CDCl₃): δ 158.3, 150.2, 135.0, 132.5, 123.4, 119.1, 109.5, 109.1, 107.8, 30.2, 21.3, 13.7.

HRMS (ESI) for C₁₄H₁₄NO [M+H]⁺: calcd: 212.1070, found: 212.1073.



2-(2-bromophenyl)-5-propylfuran (2h) was obtained as colorless oil at 60 °C after 2 h (eluent: PE to PE/EA = 100:1, 50.2 mg, 95% isolated yield). ¹H NMR (500 MHz, CDCl₃): δ 7.82 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.65 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.39–7.32 (m, 1H), 7.13 (d, *J* = 3.3 Hz, 1H), 7.12–7.07 (m,

1H), 6.16 (d, *J* = 3.3 Hz, 1H), 2.70 (t, *J* = 7.5 Hz, 2H), 1.84–1.70 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 156.5, 149.5, 134.1, 131.6, 128.3, 127.7, 127.3, 119.2, 111.5, 106.9, 30.2, 21.4, 13.8.

HRMS (ESI) for C₁₃H₁₃BrNaO [M+Na]⁺: calcd: 287.0042, found: 287.0038.



2-(5-propylfuran-2-yl)phenyl acetate (2i) was obtained as colorless oil at 60 °C after 2 h (eluent: PE to PE/EA = 50:1, 46.8 mg, 96% isolated yield). ¹H NMR (500 MHz, CDCl₃): δ 7.82 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.34–7.22 (m, 2H), 7.13 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.61 (d, *J* = 3.2 Hz, 1H), 6.11 (d, *J* = 3.2 Hz, 1H), 2.68 (t, *J* = 7.5 Hz, 2H), 2.39 (s, 3H), 1.80–1.68 (m, 2H), 1.03

(t, J = 7.4 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 169.1, 156.4, 147.9, 145.9, 127.4, 126.5, 126.2, 124.0, 123.3, 109.7, 107.1, 30.1, 21.4, 21.3, 13.7.

HRMS (ESI) for C₁₅**H**₁₇**O**₃ **[M+H]**⁺: calcd: 245.1172, found: 245.1170.

2-(3-methylphenyl)-5-propylfuran (2j) was obtained as colorless oil at 60 °C after 2 h (eluent: PE to PE/EA = 100:1, 32.0 mg, 80% isolated yield). **1H NMR (500 MHz, CDCl₃):** δ 7.53–7.45 (m, 2H), 7.28 (dd, *J* = 9.4, 5.9 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 6.57 (d, *J* = 3.2 Hz, 1H), 6.10 (d, *J* = 3.2 Hz, 1H), 2.70 (t, *J* = 7.5 Hz, 2H), 2.42 (s, 3H), 1.82–1.71 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 156.1, 152.3, 138.2, 131.3, 128.5, 127.6, 124.0, 120.6, 106.9, 105.5, 30.2, 21.5 (2C), 13.8.

HRMS (ESI) for C₁₄H₁₇O [M+H]⁺: calcd: 201.1274, found: 201.1275.



2-(3-(trifluoromethyl)phenyl)-5-propylfuran (2k) was obtained as colorless oil at 60 °C after 2 h (eluent: PE to PE/EA = 100:1, 43.2 mg, 85% isolated yield).

¹H NMR (500 MHz, CDCl₃): δ 7.88 (s, 1H), 7.82–7.76 (m, 1H), 7.51–7.44 (m, 2H), 6.65 (d, J = 3.3 Hz, 1H), 6.12 (d, J = 3.3 Hz, 1H), 2.70 (t, J = 7.5 Hz, 2H), 1.82–1.70 (m, 2H), 1.03 (t, J = 7.4 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 157.3, 150.7, 132.0, 131.2 (q, J = 32.0 Hz), 129.1, 126.3, 124.2 (q,

J = 270.6 Hz), 123.1 (q, J = 3.8 Hz), 120.0 (q, J = 3.9 Hz), 107.3, 107.1, 30.2, 21.4, 13.7. HRMS (ESI) for C₁₄H₁₄F₃O [M+H]⁺: calcd: 255.0991, found: 255.0993.



2-(3-chlorophenyl)-5-propylfuran (2l) was obtained as colorless oil at 60 °C after 2 h (eluent: PE to PE/EA = 100:1, 39.6 mg, 90% isolated yield). **¹H NMR (500 MHz, CDCl₃):** δ 7.64 (t, *J* = 1.5 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.29 (t, *J* = 8.0 Hz, 1H), 7.22–7.18 (m, 1H), 6.60 (d, *J* = 3.2 Hz,

1H), 6.10 (d, J = 3.2 Hz, 1H), 2.69 (t, J = 7.5 Hz, 2H), 1.81–1.70 (m, 2H), 1.03 (t, J = 7.4 Hz, 3H).
¹³C NMR (125 MHz, CDCl₃): δ 157.0, 150.7, 134.7, 133.0, 129.8, 126.6, 123.3, 121.4, 107.2, 106.8, 30.2, 21.4, 13.7.

HRMS (ESI) for C₁₃H₁₃ClNaO [M+Na]⁺: calcd: 243.0547, found: 243.0552.



2-(2,4,6-Trimethylphenyl)-5-propylfuran (2m) was obtained as colorless oil at 60 °C after 2 h (eluent: PE to PE/EA = 100:1, 32.0 mg, 79% isolated yield).

2m ¹H NMR (500 MHz, CDCl₃): δ 6.97 (s, 2H), 6.19 (d, *J* = 3.0 Hz, 1H), 6.12 (d, *J* = 3.0 Hz, 1H), 2.69 (t, *J* = 7.5 Hz, 2H), 2.36 (s, 3H), 2.25 (s, 6H), 1.79–1.71 (m, 2H), 1.03 (t, *J* = 7.5 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 155.3, 150.3, 138.2, 138.0, 128.7, 128.3, 109.6, 105.6, 30.1, 21.7, 21.1, 20.6, 13.7.

HRMS (ESI) for C₁₆H₂₁O [M+H]⁺: calcd: 229.1587, found: 229.1584.



2-(naphthalen-2-yl)-5-propylfuran (2n) was obtained as colorless oil at 60 °C after 2 h (eluent: PE to PE/EA = 100:1, 46.2 mg, 98% isolated yield).

¹H NMR (500 MHz, CDCl₃): δ 8.15 (s, 1H), 7.90 (d, J = 8.0 Hz, 1H),

7.85 (t, *J* = 9.0 Hz, 2H), 7.79 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.54–7.49 (m, 1H), 7.49–7.45 (m, 1H), 6.72 (d, *J* = 3.2 Hz, 1H), 6.17 (d, *J* = 3.2 Hz, 1H), 2.77 (t, *J* = 7.5 Hz, 2H), 1.91–1.73 (m, 2H), 1.09 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 156.7, 152.3, 133.7, 132.5, 128.6, 128.3, 128.1, 127.7, 126.4,

125.6, 122.2, 121.3, 107.2, 106.4, 30.3, 21.5, 13.8.

HRMS (ESI) for C₁₇H₁₇O [M+H]⁺: calcd: 237.1274, found: 237.1271.

2-(thiophen-2-yl)-5-propylfuran (20) was obtained as colorless oil at 60 °C after 2 h (eluent: PE to PE/EA = 100:1, 35.7 mg, 93% isolated yield).

20 ¹H NMR (500 MHz, CDCl₃): δ 7.21 (dd, J = 3.5, 1.0 Hz, 1H), 7.19 (dd, J = 5.0, 1.0 Hz, 1H), 7.03 (dd, J = 5.0, 3.8 Hz, 1H), 6.42 (d, J = 3.5 Hz, 1H), 6.05 (d, J = 3.5 Hz, 1H), 2.66 (t, J = 7.5 Hz, 2H), 1.78–1.68 (m, 2H), 1.02 (t, J = 7.3 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 156.0, 147.7, 134.4, 127.5, 123.3, 121.7, 106.9, 105.8, 30.1, 21.4, 13.7.

HRMS (ESI) for C₁₁H₁₃OS [M+H]⁺: calcd: 193.0682, found: 193.0683.

2-(furan-2-yl)-5-propylfuran (2p) was obtained as colorless oil at 60 °C after 2 h (eluent: PE to PE/EA = 100:1, 33.1 mg, 94% isolated yield).

2p ¹H NMR (500 MHz, CDCl₃): δ 7.42 (d, *J* = 1.0 Hz, 1H), 6.52 (d, *J* = 3.0 Hz, 1H), 6.49 (d, *J* = 3.2 Hz, 1H), 6.47 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.08 (d, *J* = 3.2 Hz, 1H), 2.68 (t, *J* = 7.5 Hz, 2H), 1.80–1.70 (m, 2H), 1.02 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 156.0, 147.0, 144.9, 141.3, 111.2, 106.6, 105.8, 104.1, 30.0, 21.4, 13.7.

HRMS (ESI) for C₁₁H₁₃O₂ [M+H]⁺: calcd: 177.0910, found: 177.0908.

2-benzyl-5-propylfuran $(2q)^{18}$ was obtained as colorless oil at 60 °C after 2 h (eluent: PE to PE/EA = 100:1, 37.6 mg, 94% isolated yield).

2q ¹H NMR (500 MHz, CDCl₃): δ 7.37–7.30 (m, 2H), 7.30–7.23 (m, 3H), 5.91 (dd, *J* = 6.6, 3.0 Hz, 2H), 3.97 (s, 2H), 2.59 (t, *J* = 7.5 Hz, 2H), 1.73–1.61 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 155.4, 152.6, 138.6, 128.7, 128.4, 126.3, 106.7, 105.3, 34.6, 30.1, 21.4, 13.8.



2-propyl-5-styrylfuran (2r) was obtained as colorless oil at 60 °C after 2 h (eluent: PE to PE/EA = 100:1, 41.1 mg, 97% isolated yield).

¹**H NMR (500 MHz, CDCl₃):** δ 7.50 (d, J = 7.0 Hz, 2H), 7.38 (t, J = 7.5 Hz, 2H), 7.30–7.24 (m, 1H), 7.02 (d, J = 16.5 Hz, 1H), 6.90 (d, J =

16.5 Hz, 1H), 6.30 (d, *J* = 3.0 Hz, 1H), 6.08 (d, *J* = 3.0 Hz, 1H), 2.70 (t, *J* = 7.5 Hz, 2H), 1.83–1.72 (m, 2H), 1.06 (t, *J* = 7.5 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 156.6, 151.6, 137.4, 128.6, 127.2, 126.1, 125.5, 116.8, 109.7, 107.1, 30.3, 21.4, 13.8.

HRMS (ESI) for C₁₅H₁₇O [M+H]⁺: calcd: 213.1274, found: 213.1270.



2-pentyl-5-phenylfuran (2s) was obtained as colorless oil at 60 °C after 2 h (eluent: PE to PE/EA = 100:1, 41.5 mg, 97% isolated yield).

¹H NMR (500 MHz, CDCl₃): δ 7.68 (dd, J = 8.3, 1.0 Hz, 2H), 7.40 (t,

J =7.8 Hz, 2H), 7.29–7.21 (m, 1H), 6.59 (d, *J* = 3.0 Hz, 1H), 6.10 (d, *J* = 3.0 Hz, 1H), 2.73 (t, *J* = 7.5 Hz, 2H), 1.80–1.68 (m, 2H), 1.47–1.37 (m, 4H), 0.97 (t, *J* = 7.0 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 156.5, 152.1, 131.3, 128.6, 126.7, 123.3, 106.8, 105.7, 31.4, 28.2, 27.8, 22.5, 14.0.

HRMS (ESI) for C₁₅H₁₉O [M+H]⁺: calcd: 215.1430, found: 215.1433.



2-benzyl-5-phenylfuran $(2t)^{18}$ was obtained as colorless oil at 60 °C after 2 h (eluent: PE to PE/EA = 100:1, 44.4 mg, 95% isolated yield).

¹H NMR (500 MHz, CDCl₃): δ 7.74–7.68 (m, 2H), 7.46–7.34 (m, 6H),

7.34–7.26 (m, 2H), 6.63 (d, J = 3.5 Hz, 1H), 6.14 (d, J = 3.5 Hz, 1H),

4.11 (s, 2H).

¹³C NMR (125 MHz, CDCl₃): δ 154.4, 152.9, 138.1, 131.1, 128.8, 128.6, 128.5, 126.9, 126.5, 123.5, 108.5, 105.8, 34.7.



2-(2-chloroethyl)-5-phenylfuran (2u) was obtained as colorless oil at 60 °C after 2 h (eluent: PE to PE/EA = 100:1, 39.1 mg, 95% isolated yield). ¹H NMR (500 MHz, CDCl₃): δ 7.67 (dd, J = 8.5, 1.0 Hz, 2H), 7.45–7.37

(m, 2H), 7.31–7.23 (m, 1H), 6.61 (d, *J* = 3.3 Hz, 1H), 6.25 (d, *J* = 3.3 Hz, 1H), 3.82 (t, *J* = 7.3 Hz, 2H), 3.20 (t, *J* = 7.3 Hz, 2H).

¹³C NMR (125 MHz, CDCl₃): δ 153.2, 151.5, 130.9, 128.7, 127.2, 123.6, 109.1, 105.7, 42.1, 31.9. HRMS (ESI) for C₁₂H₁₂ClO [M+H]⁺: calcd: 207.0571, found: 207.0575.



2-((5-phenylfuran-2-yl)methoxy)tetrahydro-2H-pyran (2v) was obtained as colorless oil at 60 °C after 2 h (eluent: PE to PE/EA = 40:1, 49.5 mg, 96% isolated yield).

2v ¹**H NMR (500 MHz, CDCl₃):** δ 7.75–7.65 (m, 2H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.27 (t, *J* = 7.5 Hz, 1H), 6.63 (d, *J* = 3.3 Hz, 1H), 6.44 (d, *J* = 3.3 Hz, 1H), 4.80 (t, *J* = 3.5 Hz, 1H), 4.74 (d, *J* = 13.0 Hz, 1H), 4.59 (d, *J* = 13.0 Hz, 1H), 4.03–3.90 (m, 1H), 3.65–3.55 (m, 1H), 1.94–1.82 (m, 1H), 1.81–1.73 (m, 1H), 1.71–1.61 (m, 2H), 1.60–1.51 (m, 2H).

¹³C NMR (126 MHz, CDCl₃): δ 154.1, 151.4, 130.8, 128.6, 127.3, 123.8, 111.5, 105.6, 97.2, 62.0, 60.7, 30.4, 25.4, 19.2.

HRMS (ESI) for C₁₆H₁₉O₃ [M+H]⁺: calcd: 259.1329, found: 259.1326.



trimethyl((5-phenylfuran-2-yl)methoxy)silane (2w) was obtained as colorless oil at 80 °C after 4 h (eluent: PE to PE/EA = 40:1, 41.8 mg, 85% isolated yield).

¹H NMR (500 MHz, CDCl₃): δ 7.70 (dd, J = 8.3, 1.1 Hz, 2H), 7.40 (t, J = 7.8 Hz, 2H), 7.30–7.23 (m, 1H), 6.61 (d, J = 3.5 Hz, 1H), 6.36 (d, J = 3.5 Hz, 1H), 4.69 (s, 2H), 0.19 (s, 9H).

¹³C NMR (125 MHz, CDCl₃): δ 153.7, 153.5, 130.9, 128.6, 127.3, 123.7, 110.0, 105.7, 57.6, -0.3. HRMS (ESI) for C₁₄H₁₉O₂Si [M+H]⁺: calcd: 247.1149, found: 247.1154.

2,5-diphenylfuran (2x)¹⁶ was obtained as white solid (m.p. 86-87 °C) at 60 °C after 2 h (eluent: PE to PE/EA = 100:1, 41.9 mg, 95% isolated yield).
¹H NMR (500 MHz, CDCl₃): δ 7.82 (d, J = 7.5 Hz, 4H), 7.47 (t, J = 7.8 Hz, 4H),

4H), 7.34 (t, *J* = 7.4 Hz, 2H), 6.79 (s, 2H).

¹³C NMR (125 MHz, CDCl₃): δ 153.4, 130.8, 128.7, 127.3, 123.7, 107.2.



2-([1,1'-biphenyl]-4-yl)-5-phenylfuran $(2y)^{19}$ was obtained as white solid (m.p. 159-160 °C) at 60 °C after 2 h (eluent: PE to PE/EA = 100:1, 55.1 mg, 93% isolated yield).

¹H NMR (500 MHz, CDCl₃): δ 7.88–7.84 (m, 2H), 7.81 (dd, J = 8.3, 1.1 Hz, 2H), 7.72–7.65 (m, 4H), 7.52–7.44 (m, 4H), 7.42–7.38 (m, 1H), 7.35–7.30 (m, 1H), 6.81 (d, J = 3.5 Hz, 1H), 6.80 (d, J = 3.5 Hz, 1H).

¹³C NMR (125 MHz, CDCl₃): δ 153.5, 153.2, 140.6, 134.0, 130.8, 129.8, 128.8, 128.7, 127.4, 126.9, 124.1, 123.8, 107.5, 107.4.



2-(naphthalen-2-yl)-5-phenylfuran (2z)¹⁹ was obtained as white solid (m.p. 132-134 °C) at 60 °C after 2 h (eluent: PE to PE/EA = 100:1, 50.2 mg, 93% isolated yield).

¹H NMR (500 MHz, CDCl₃): δ 8.27 (s, 1H), 7.95 (d, J = 8.0 Hz, 1H),

7.92–7.84 (m, 5H), 7.58–7.46 (m, 4H), 7.38–7.33 (m, 1H), 6.89 (d, *J* = 3.5 Hz, 1H), 6.82 (d, *J* = 3.5 Hz, 1H).

¹³C NMR (125 MHz, CDCl₃): δ 153.7, 153.4, 133.6, 132.7, 130.8, 128.7, 128.4, 128.2, 128.1, 127.8, 127.4, 126.5, 125.9, 123.8, 122.3, 122.0, 107.9, 107.4.



2-phenoxy-5-phenylfuran $(2za)^{20}$ was obtained as colorless oil at 80 °C after 4 h (eluent: PE to PE/EA = 100:1, 41.5 mg, 88% isolated yield).

¹**H NMR (500 MHz, CDCl₃):** δ 7.64 (dd, J = 8.3, 1.0 Hz, 2H), 7.44–7.35

(m, 4H), 7.30–7.24 (m, 1H), 7.21–7.14 (m, 3H), 6.65 (d, J = 3.5 Hz, 1H),

5.71 (d, *J* = 3.5 Hz, 1H).

¹³C NMR (125 MHz, CDCl₃): δ 156.9, 156.2, 146.4, 130.6, 129.7, 128.7, 126.9, 124.0, 123.0, 117.0, 106.1, 91.3.



N,4-dimethyl-N-(5-phenylfuran-2-yl)benzenesulfonamide (2zb) was obtained as colorless oil at 80 °C after 12 h (eluent: PE/EA = 20:1, 45.1 mg, 69% isolated yield).

2zb

¹**H NMR (500 MHz, CDCl₃):** δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.51–7.46 (m, 2H), 7.38–7.33 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.28–7.24 (m, 1H), 6.61 (d, *J* = 3.3 Hz, 1H), 6.27 (d, *J* = 3.3 Hz, 1H), 3.23 (s, 3H), 2.45 (s, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 150.9, 146.5, 144.1, 134.4, 130.2, 129.6, 128.6, 127.9, 127.6, 123.5, 106.6, 106.1, 37.3, 21.6.

HRMS (ESI) for C₁₈H₁₈NO₃S [M+H]⁺: calcd: 328.1002, found: 328.1006.

Cl 2-chloro-5-phenylfuran (2zc)²¹ was obtained as colorless oil at 60 °C after 2 h (eluent: PE to PE/EA = 100:1, 33.1 mg, 93% isolated yield).

2zc ¹H NMR (500 MHz, CDCl₃): δ 7.64 (d, J = 7.5 Hz, 2H), 7.40 (t, J = 7.8 Hz, 2H), 7.26 (t, J = 7.8 Hz, 1H), 6.64 (d, J = 3.5 Hz, 1H), 6.26 (d, J = 3.5 Hz, 1H).

¹³C NMR (125 MHz, CDCl₃): δ 153.5, 136.0, 130.0, 128.7, 127.7, 123.4, 108.3, 106.9.

5.Scale-up experiment



A mixture of catalyst L3AuCl (30.2 mg, 0.04 mmol, 2 mol %), NaBARF (177.7 mg, 0.2 mmol, 10 mol %), alkynyl ketone **1a** (0.37 g, 2.0 mmol, 1.0 equiv) and anhydrous DCE (20.0 mL) were added to a reaction tube equipped with a stir bar. The resulting mixture was stirred at 60 °C under N₂ condition for 6 h. The reaction solution was concentrated in vacuo. The crude product was purified by column chromatography on silica gel to afford pure products **2a** (0.33 g, 88% yield).

6.References

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7.NMR spectra of products



















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