

Supporting Information
for
Gold(I)-catalyzed formation of furans from
 γ -acyloxyalkynyl ketones

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General procedures, characterization data and NMR spectra
for compounds 1a–l, 2a–l and 3

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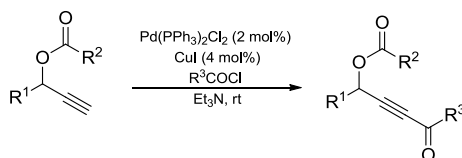
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General Information:

Proton (^1H NMR) and carbon (^{13}C NMR) nuclear magnetic resonance spectra were recorded on 300, 400 or 500 MHz instruments. The chemical shifts are given in part per million (ppm) on the delta scale. The solvent peak was used as reference value. For ^1H NMR: $\text{CDCl}_3 = 7.26$ ppm. For ^{13}C NMR: $\text{CDCl}_3 = 77.16$ ppm. Data are presented as follow: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet), coupling constants (J/Hz) and integration. Assignments were determined either on the basis of unambiguous chemical shifts or coupling patterns, COSY, HMQC, HMBC, NOESY experiments to fully interpreted spectra for related compounds. Infrared spectra were recorded neat with Hewlett-Packard spectrometer. Wavelengths of maximum absorbance (ν_{max}) are quoted in wave numbers (cm^{-1}). High resolution mass spectra (HRMS) data were recorded on a microTOF spectrometer equipped with orthogonal electrospray interface (ESI). The parent ions $[\text{M}]^+$, $[\text{M} + \text{H}]^+$, $[\text{M} + \text{Li}]^+$ or $[\text{M} + \text{Na}]^+$ are quoted. Analytical thin-layer chromatography (TLC) was carried out on silica gel 60 F254 plates or basic alumina (63–200 μm) with visualization by ultraviolet light, cerium ammonium molybdate (CAM) or potassium permanganate dip. Flash-column chromatography was carried out using silica gel 60 (40–63 μm) or basic Al_2O_3 (63–200 μm) and the procedure included the subsequent evaporation of solvents in vacuo. Reagents and solvents were purified using standard means. Dichloroethane ($(\text{CH}_2\text{Cl})_2$), and triethylamine (NEt_3) were distilled from CaH_2 under an argon atmosphere; pyridine was distilled from potassium carbonate; diisopropylamine (DIPA) was distilled from KOH; and tetrahydrofuran (THF) was dried using Glasstechnology GT S100 device. Anhydrous reactions were carried out in flame-dried glassware and under an argon atmosphere.

CuI (98%) and DMA ($\geq 99.5\%$) was purchased from Sigma Aldrich. AgSbF_6 (98%) was purchased from STREM Chemicals. AgNTf_2 was prepared from commercially available HNTf_2 (Aldrich) and Ag_2CO_3 [1]. Triphenylphosphinegold(I) chloride was prepared by reduction of NaAuCl_4 with thioldiethanol and subsequent addition of triphenylphosphine [2]. $\text{PPh}_3\text{AuNTf}_2$ catalyst was prepared from the corresponding triphenylphosphinegold(I) chloride and AgNTf_2 [3]. $\text{Cu}(\text{MeCN})_4\text{NTf}_2$ was prepared from commercially available HNTf_2 (Aldrich) and Cu_2O (Acros) [4]. All other chemicals were used as received. All extractive procedures were performed using non distilled solvents and all aqueous solutions used were saturated unless details are given.

Procedure A: preparation of γ -acyloxyalkynyl ketone by Sonogashira reaction [5]



To an oven-dried flask under argon were successively added copper iodide (4 mol %), dichlorobis(triphenylphosphine)palladium (2 mol %) and NEt_3 [0.4 M]. The acyloxyalkyne (1 equiv) previously dissolved in NEt_3 [0.5 M] was added to the catalyst mixture via cannula

¹ Vij, A.; Zheng, Y. Y.; Kirchmeier, R. L.; Shreeve, J. M. *Inorg. Chem.* **1994**, 33, 3281–3288.

² Al'Sa-Ady, A. K.; McAuliffe, C. A.; Parish, R. V.; Sandeank, J. A. *Inorg. Synth.* **1985**, 191–194.

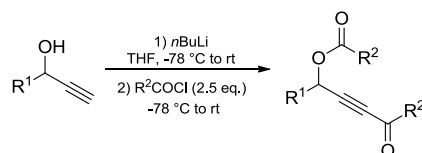
³ Mezailles, N.; Ricard, L.; Gagosz, F. *Org. Lett.* **2005**, 7, 4133–4136.

⁴ Gronnier C.; Kramer S.; Odabachian Y.; Gagosz F. *J. Am. Chem. Soc.* **2012**, 134, 828–831.

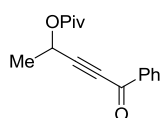
⁵ Schwier, T.; Sromek, A. W.; Yap, D. M. L.; Chernyak, D.; Gevorgyan, V. *J. Am. Chem. Soc.* **2007**, 129, 9868–9878.

and briefly stirred. The acid chloride (1.1 equiv) was then added dropwise. The reaction was stirred at room temperature and monitored by TLC until completion. The mixture was quenched with HCl (1 N) and extracted with Et₂O. The organic layers were washed with HCl (1 N), NaHCO₃ solution and brine, dried over MgSO₄ and concentrated under vacuum. The resulting crude product was purified by flash-column chromatography on silica gel (cyclohexane/EtOAc).

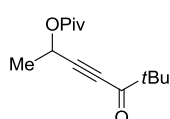
Procedure B: preparation of γ -acyloxyalkynyl ketone by condensation [5]



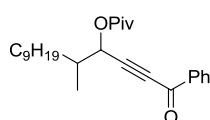
To a stirred solution of propargyl alcohol (1 equiv) in THF [0.5 M] under argon at $-78\text{ }^{\circ}\text{C}$, was dropwise added *n*-BuLi ([1.6 M] in hexanes, 2.2 equiv). The resulting solution was then allowed to warm to room temperature and stirred for 0.5 to 1 hour. A solution of acid chloride (2.5 equiv) in THF [1.8 M] under argon at $-78\text{ }^{\circ}\text{C}$ was added via cannula to the mixture. The reaction was then allowed to warm to room temperature and stirred for 2 to 7 hours (monitored by TLC). The reaction was quenched with NH₃ (aqueous solution) and extracted with Et₂O. The organic layers were washed with HCl (1 N), NaHCO₃ and brine, dried over MgSO₄ and concentrated under vacuum. The resulting crude product was purified by column chromatography on silica gel (cyclohexane/EtOAc).



5-Oxo-5-phenylpent-3-yn-2-yl pivalate (1a) [5]: Prepared following the **Procedure A** in 63% yield (1.06 g, 4.10 mmol) from 1.00 g (6.48 mmol) of but-3-yn-2-yl pivalate. Colorless oil; TLC *R_f* 0.60 (cyclohexane/EtOAc 25%); ¹H NMR (400 MHz, CDCl₃) δ 1.26 (s, 9H), 1.63 (d, *J* = 6.8 Hz, 3H), 5.66 (q, *J* = 6.8 Hz, 1H), 7.48 (dd, *J* = 8.1, 7.5 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 8.10 (d, *J* = 8.1 Hz, 2H); ¹³C NMR (125.8 MHz, CDCl₃) δ 20.5, 27.2, 38.9, 59.8, 82.0, 92.0, 128.7, 129.7, 134.4, 136.6, 177.3, 177.6.

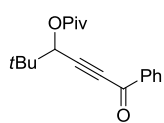


6,6-Dimethyl-5-oxohept-3-yn-2-yl pivalate (1b): Prepared following the **Procedure B** in 38% yield (1.30 g, 5.45 mmol) from 1.00 g (14.30 mmol) of but-3-yn-2-yl pivalate. Colorless oil; TLC *R_f* 0.40 (pentane/Et₂O 5%); IR (neat) ν_{max} 1007, 1035, 1079, 1133, 1274, 1366, 1396, 1460, 1479, 1675, 1736, 2217, 2872, 2936, 2971 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.18 (s, 9H), 1.22 (s, 9H), 1.55 (d, *J* = 6.8 Hz, 3H), 5.55 (q, *J* = 6.8 Hz, 1H); ¹³C NMR (125.8 MHz, CDCl₃) δ 20.4, 26.0, 27.1, 38.9, 45.0, 59.7, 81.3, 91.4, 177.2, 193.7; HRMS 261.148 (C₁₄H₂₁O₃ + Na calcd 261.146).

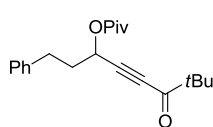


5-Methyl-1-oxo-1-phenyltetradec-2-yn-4-yl pivalate (1c): Prepared following the **Procedure A** in 56% yield (229 mg, 0.57 mmol, mixture 50/50 of 2 diastereoisomers) from 300 mg (1.02 mmol) of 4-methyltridec-1-yn-3-yl pivalate. Colorless oil; TLC *R_f* 0.56 (cyclohexane/EtOAc 10%); IR (neat) ν_{max} 977, 1031, 1133, 1259, 1312, 1365, 1396, 1450, 1582, 1598, 1650, 1736, 2208, 2226, 2854, 2924, 2958, 3067 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 0.83–0.92 (m, 6H), 1.10 (d, *J* = 6.9 Hz, 3H, Diastereoisomer 1), 1.11 (d, *J* = 6.9 Hz, 3H, Diastereoisomer 2), 1.21–1.33 (m, 28H), 1.26–1.27 (m, 18H), 1.35–1.45 (m, 2H), 1.52–1.64 (m, 2H), 1.95–2.05 (m, 2H), 5.50 (d, *J* = 5.0 Hz, 1H, Diastereoisomer 2), 5.52 (d, *J* = 5.4 Hz, 1H, Diastereoisomer 1), 7.50–7.45 (m, 4H), 7.59–7.64 (m, 2H), 8.08–8.12 (m, 4H); ¹³C NMR (125.8 MHz, CDCl₃) δ

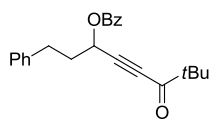
14.27 (x2), 15.3, 15.6, 22.8 (x2), 27.0, 27.1, 27.2 (x2), 29.5 (x2), 29.6 (x2), 29.7 (x2), 29.8, 29.9, 32.0 (x2), 32.4, 32.7, 37.2, 37.5, 39.1, 39.2, 67.4, 67.8, 83.2, 83.5, 90.5, 91.1, 128.7 (x2), 129.7 (x2), 134.4 (x2), 136.7 (x2), 177.3, 177.4, 177.50, 177.53; HRMS 421.270 ($C_{26}H_{38}O_3 + Na$ calcd 421.271).



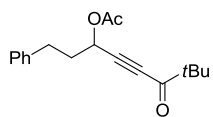
2,2-Dimethyl-6-oxo-6-phenylhex-4-yn-3-yl pivalate (1d): Prepared following the **Procedure A** in 70% yield (1.30 g, 4.33 mmol) from 1.20 g (6.12 mmol) of 4,4-dimethylpent-1-yn-3-yl pivalate. White solid; mp 54 °C; TLC R_f 0.40 (cyclohexane/EtOAc 10%); IR (neat) ν_{max} 1110, 1266, 1313, 1366, 1395, 1448, 1478, 1580, 1596, 1638, 1739, 2238, 2871, 2935, 2972, 3071 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$) δ 1.11 (s, 9H), 1.28 (s, 9H), 5.30 (s, 1H), 7.48 (dd, $J = 7.5, 7.3$ Hz, 2H), 7.61 (t, $J = 7.2$ Hz, 1H), 8.10 (d, $J = 7.5$ Hz, 2H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 25.9, 27.2, 35.9, 39.2, 71.5, 83.3, 90.6, 128.8, 129.7, 134.4, 136.8, 177.3, 177.5; HRMS 323.163 ($C_{19}H_{24}O_3 + Na$ calcd 323.162).



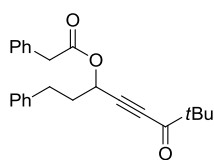
7,7-Dimethyl-6-oxo-1-phenyloct-4-yn-3-yl pivalate (1e): Prepared following the **Procedure A** in 84% yield (553 mg, 1.68 mmol) from 489 mg (2.00 mmol) of 5-phenylpent-1-yn-3-yl pivalate. Colorless oil; TLC R_f 0.50 (cyclohexane/ CH_2Cl_2 50%); IR (neat) ν_{max} 699, 745, 1032, 1130, 1275, 1365, 1478, 1496, 1674, 1736, 2214, 2870, 2933, 2969, 3029 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$) δ 1.19 (s, 9H), 1.24 (s, 9H), 2.11–2.23 (m, 2H), 2.79 (t, $J = 8.0$ Hz, 2H), 5.74 (t, $J = 6.8$ Hz, 1H), 7.18 (d, $J = 7.7$ Hz, 2H), 7.21 (t, $J = 7.2$ Hz, 1H), 7.30 (dd, $J = 7.7, 7.2$ Hz, 2H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 26.0, 27.2, 31.3, 35.7, 39.0, 45.0, 62.8, 82.2, 90.3, 126.5, 128.5, 128.8, 140.3, 177.2, 193.7; HRMS 351.193 ($C_{21}H_{28}O_3 + Na$ calcd 351.194).



7,7-Dimethyl-6-oxo-1-phenyloct-4-yn-3-yl benzoate (1f): Prepared following the **Procedure A** in 70% yield (478 mg, 1.37 mmol) from 518 mg (1.96 mmol) of 5-phenylpent-1-yn-3-yl benzoate. Colorless oil; TLC R_f 0.23 (pentane/ Et_2O 5%); IR (neat) ν_{max} 711, 745, 1025, 1067, 1094, 1141, 1261, 1476, 1672, 1723, 2214, 2868, 2931, 2968, 3028 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) δ 1.21 (s, 9H), 2.23–2.42 (m, 2H), 2.89 (t, $J = 7.9$ Hz, 2H), 5.74 (t, $J = 6.6$ Hz, 1H), 7.18–7.25 (m, 3H), 7.27–7.34 (m, 2H), 7.47 (dd, $J = 8.3, 7.5$ Hz, 2H), 7.60 (t, $J = 7.5$ Hz, 1H), 8.04 (d, $J = 8.3$ Hz, 2H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 26.0, 31.5, 35.9, 45.0, 63.5, 82.6, 90.0, 126.5, 128.5, 128.6, 128.8, 129.4, 129.9, 133.6, 140.2, 165.4, 193.6; HRMS 371.158 ($C_{23}H_{24}O_3 + Na$ calcd 371.163).

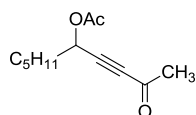


7,7-Dimethyl-6-oxo-1-phenyloct-4-yn-3-yl acetate (1g): Prepared following the **Procedure A** in 57% yield (331 mg, 1.16 mmol) from 410 mg (2.03 mmol) of 5-phenylpent-1-yn-3-yl acetate. Colorless oil; TLC R_f 0.28 (pentane/ Et_2O 10%); IR (neat) ν_{max} 699, 745, 1023, 1222, 1369, 1476, 1673, 1745, 2213, 2869, 2933, 2969, 3028 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$) δ 1.20 (s, 9H), 2.10 (s, 3H), 2.11–2.23 (m, 2H), 2.79 (t, $J = 7.9$ Hz, 2H), 5.47 (t, $J = 6.7$ Hz, 1H), 7.18 (d, $J = 7.8$ Hz, 2H), 7.21 (t, $J = 7.5$ Hz, 1H), 7.30 (dd, $J = 7.8, 7.5$ Hz, 2H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 21.0, 26.0, 31.4, 35.7, 45.0, 63.0, 82.4, 89.9, 126.5, 128.5, 128.8, 140.23, 169.8, 193.6; HRMS 309.149 ($C_{18}H_{22}O_3 + Na$ calcd 309.147).



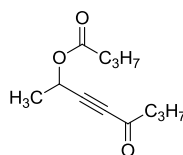
7,7-Dimethyl-6-oxo-1-phenyloct-4-yn-3-yl 2-phenylacetate (1h):

Prepared following the **Procedure A** in 66% yield (204 mg, 0.56 mmol) from 489 mg (0.86 mmol) of 5-phenylpent-1-yn-3-yl 2-phenylacetate. Colorless oil; TLC R_f 0.27 (pentane/Et₂O 15%); IR (neat) $\nu_{\max}$ 1131, 1240, 1455, 1476, 1496, 1672, 2213, 2868, 2931, 2968, 3029, 3063, 3087 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.54 (s, 9H), 2.06–2.24 (m, 2H), 2.71 (t, J = 7.8 Hz, 2H), 3.65 (s, 2H), 5.47 (t, J = 6.6 Hz, 1H), 7.10 (d, J = 7.6 Hz, 2H), 7.20 (t, J = 7.3 Hz, 1H), 7.25–7.37 (m, 7H); ¹³C NMR (125.8 MHz, CDCl₃) δ 26.0, 31.2, 35.7, 41.3, 45.0, 63.3, 82.5, 89.7, 126.5, 127.5, 128.5, 128.7, 128.8, 129.4, 133.5, 140.2, 170.3, 193.6; HRMS 385.176 (C₂₄H₂₆O₃ + Na calcd 385.177).



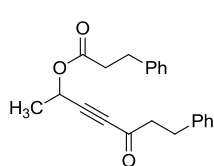
2-Oxodec-3-yn-5-yl acetate (1i) [6]: Prepared following the **Procedure B**

in 52% yield (2.11 g 10.03 mmol) from 2.8 mL (19.68 mmol) of oct-1-yn-3-ol. Colorless oil; TLC R_f 0.50 (cyclohexane/EtOAc 20%); ¹H NMR (300 MHz, CDCl₃) δ 0.90 (t, J = 6.9 Hz, 3H), 1.27–1.37 (m, 4H), 1.38–1.50 (m, 2H), 1.76–1.86 (m, 2H), 2.10 (s, 3H), 2.35 (s, 3H), 5.46 (t, J = 6.7 Hz, 1H); ¹³C NMR (75.5 MHz, CDCl₃) δ 14.1, 21.0, 22.6, 24.7, 31.3, 32.7, 34.1, 63.4, 84.3, 88.5, 169.9, 184.



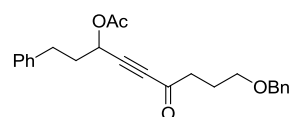
5-Oxo-oct-3-yn-2-yl butyrate (1j): Prepared following the **Procedure B** in

58% yield (876 mg, 4.17 mmol) from 0.5 mL (7.13 mmol) of but-3-yn-2-ol. Colorless oil; TLC R_f 0.38 (pentane/Et₂O 20%); IR (neat) $\nu_{\max}$ 1023, 1078, 1159, 1245, 1350, 1456, 1678, 1742, 2216, 2876, 2937, 2965 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 0.93 (t, J = 7.4 Hz, 3H), 0.96 (t, J = 7.4 Hz, 3H), 1.53 (d, J = 6.8 Hz, 3H), 1.67 (qt, J = 7.4, 7.4 Hz, 2H), 1.68 (qt, J = 7.4, 7.4 Hz, 2H), 2.32 (t, J = 7.4 Hz, 2H), 2.53 (t, J = 7.4 Hz, 2H), 5.56 (q, J = 6.8 Hz, 1H); ¹³C NMR (125.8 MHz, CDCl₃) δ 13.6, 13.7, 17.5, 18.5, 20.6, 36.1, 47.3, 59.4, 83.1, 89.3, 172.4, 187.6; HRMS 233.116 (C₁₂H₁₈O₃ + Na calcd 233.115).



5-Oxo-7-phenylhept-3-yn-2-yl 3-phenylpropanoate (1k): Prepared

following the **Procedure B** in 45% yield (1.89 g, 5.69 mmol) from 1 mL (12.76 mmol) of but-3-yn-2-ol. Yellowish oil; TLC R_f 0.31 (pentane/Et₂O 20%); IR (neat) $\nu_{\max}$ 698, 748, 1030, 1076, 1087, 1138, 1229, 1453, 1496, 1678, 1740, 2220, 2934, 3028 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.50 (d, J = 6.9 Hz, 3H), 2.67 (t, J = 7.6 Hz, 2H), 2.89 (t, J = 7.6 Hz, 2H), 2.97 (m, 4H), 5.54 (q, J = 6.9 Hz, 1H), 7.16–7.23 (m, 6H), 7.26–7.32 (m, 4H); ¹³C NMR (125.8 MHz, CDCl₃) δ 20.5, 29.7, 30.9, 35.8, 47.0, 59.7, 83.1, 89.6, 126.5, 126.5, 128.4, 128.5, 128.7, 128.7, 140.1, 140.2, 171.6, 186.3; HRMS 357.144 (C₂₂H₂₂O₃ + Na calcd 357.146).



9-(Benzyloxy)-6-oxo-1-phenylnon-4-yn-3-yl acetate (1l): To a

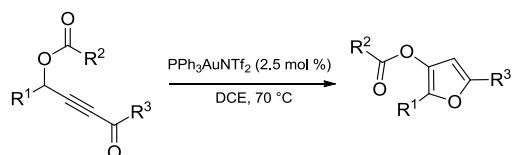
stirred solution of 1-(benzyloxy)-7-hydroxy-9-phenylnon-5-yn-4-one [7] (500 mg, 1.31 mmol) in dichloromethane was added at once a mixture of pyridinium chlorochromate (430 mg, 2 mmol) and SiO₂ (430 mg). After 5 h of stirring at room temperature, the reaction mixture was filtered through a pad of Celite® (CH₂Cl₂) and the filtrate was concentrated in vacuo. The crude product was purified by flash chromatography (cyclohexane/EtOAc 10-20%) to afford **1l** as a pale yellow oil (460 mg, 1.22 mmol, 93%). TLC R_f 0.45 (cyclohexane/EtOAc 25%); IR (neat) $\nu_{\max}$ 698, 737, 1025, 1101, 1155, 1220, 1369, 1454, 1496, 1677, 1743, 2217, 2859, 2931, 3028 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.97 (tt, J = 6.0, 7.3 Hz, 2H), 2.09 (s, 3H), 2.10–2.19 (m, 2H),

⁶ Sromek, A. W.; Kel'in, A. V.; Gevorgyan, V. *Angew. Chem., Int. Ed.* **2004**, 43, 2280–2282.

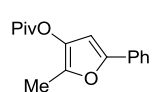
⁷ This compound was synthesized according to the sequence described by Singh, M.; Argade, N. P. *J. Org. Chem.* **2010**, 75, 3121–3124.

2.71 (t, $J = 7.3$ Hz, 2H), 2.78 (t, $J = 7.9$ Hz, 2H), 3.50 (t, $J = 6.1$ Hz, 2H), 4.49 (s, 2H), 5.45 (t, $J = 6.67$ Hz, 1H), 7.16–7.34 (m, 10H); ^{13}C NMR (125.8 MHz, CDCl_3) δ 20.9, 24.0, 31.3, 35.6, 42.4, 62.9, 69.0, 73.0, 84.1, 88.2, 126.5, 127.7, 128.5, 128.5, 128.7, 138.4, 140.2, 169.8, 186.9; HRMS 401.174 ($\text{C}_{24}\text{H}_{26}\text{O}_4 + \text{Na}$ calcd 401.172).

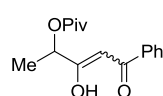
Procedure C: gold(I)-catalyzed formation of furans from γ -acyloxyalkynyl ketones



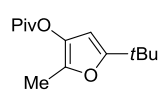
In an oven-dried flask, γ -acyloxyalkynyl ketone (0.4 mmol) was dissolved in dichloroethane [0.1 M] and heated to 70 °C under an argon atmosphere. $\text{Ph}_3\text{PAuNTf}_2$ (2.5 mol %) was then added to the stirred solution at 70 °C. The reaction was monitored by thin-layer chromatography until completion. The solvent was then removed in vacuo and the crude residue was purified by flash chromatography on silica gel (pentane/ Et_2O).



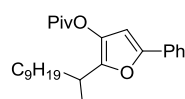
2-Methyl-5-phenylfuran-3-yl pivalate (2a) [5]: Prepared following the **Procedure C** in 95% yield (99 mg, 0.38 mmol) from 102 mg (0.40 mmol) of **1a**. White solid; mp 57 °C; TLC R_f 0.60 (Pentane/ Et_2O 5%); ^1H NMR (400 MHz, CDCl_3) δ 1.35 (s, 9H), 2.26 (s, 3H), 6.64 (s, 1H), 7.23 (t, $J = 7.3$ Hz, 1H), 7.36 (dd, $J = 7.9$, 7.3 Hz, 2H), 7.59 (d, $J = 7.8$ Hz, 2H); ^{13}C NMR (125.8 MHz, CDCl_3) δ 10.8, 27.3, 39.2, 102.1, 123.4, 127.3, 128.7, 131.0, 135.9, 139.8, 150.1, 176.2.



3-Hydroxy-5-oxo-5-phenylpent-3-en-2-yl pivalate (3): By-product obtained following the **Procedure C** (at room temperature instead of 70 °C) in 22% yield (22 mg, 0.09 mmol) from 101 mg (0.39 mmol) of **1a**. Yellowish oil; TLC R_f 0.31 (pentane/ Et_2O 5%); IR (neat) ν_{max} 521, 633, 685, 761, 879, 1036, 1060, 1116, 1150, 1278, 1477, 1569, 1598, 1731, 2903, 2958 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.30 (s, 9H), 1.50 (d, $J = 7.0$ Hz, 3H), 5.28 (q, $J = 7.0$ Hz, 1H), 6.30 (s, 1H), 7.46 (dd, $J = 7.5$, 7.1 Hz, 2H), 7.54 (t, $J = 7.1$ Hz, 1H), 7.86 (d, $J = 7.5$ Hz, 2H), 15.79 (s, 1H); ^{13}C NMR (125.8 MHz, CDCl_3) δ 17.9, 27.3, 38.9, 71.9, 92.4, 127.1, 128.9, 132.7, 134.4, 177.6, 182.6, 196.1. HRMS 276.137 ($\text{C}_{16}\text{H}_{20}\text{O}_4 + \text{Na}$ calcd 276.136).

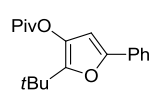


5-(tert-Butyl)-2-methylfuran-3-yl pivalate (2b): Prepared following the **Procedure C** in 93% yield (101 mg, 0.42 mmol) from 108 mg (0.45 mmol) of **1b**. Colorless oil; TLC R_f 0.77 (pentane/ Et_2O 5%); IR (neat) ν_{max} 939, 1028, 1117, 1190, 1241, 1277, 1363, 1395, 1460, 1479, 1652, 1735, 2871, 2914, 2967 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.23 (s, 9H), 1.31 (s, 9H), 2.14 (s, 3H), 5.95 (s, 1H); ^{13}C NMR (125.8 MHz, CDCl_3) δ 10.7, 27.3, 29.0, 32.8, 39.1, 99.3, 134.2, 137.6, 160.5, 176.5; HRMS 261.146 ($\text{C}_{14}\text{H}_{22}\text{O}_3 + \text{Na}$ calcd 261.146).



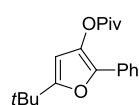
5-Phenyl-2-(undecan-2-yl)furan-3-yl pivalate (2c): Prepared following the **Procedure C** in 90% yield (45 mg, 0.11 mmol) from 49 mg (0.12 mmol) of **1c**. Colorless oil; TLC R_f 0.38 (pentane/ Et_2O 5%); IR (neat) ν_{max} 1113, 1175, 1275, 1397, 1456, 1604, 1754, 2838, 2924, 2971 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.86 (t, $J = 7.0$ Hz, 3H), 1.20–1.27 (m, 14H), 1.29 (d, $J = 7.2$ Hz, 3H), 1.34 (s, 9H), 1.51–1.59 (m, 1H), 1.65–1.74 (m, 1H), 2.83 (dq, $J = 8.4$, 7.2, 5.8 Hz, 1H), 6.65 (s, 1H), 7.22 (t, $J = 7.4$ Hz, 1H), 7.35 (dd, $J = 8.4$, 7.4 Hz, 2H), 7.59 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (125.8 MHz, CDCl_3) δ

14.3, 19.0, 22.8, 27.3, 27.6, 29.5, 29.6, 29.7, 29.7, 31.3, 32.0, 35.6, 39.2, 102.1, 123.4, 127.2, 128.7, 131.1, 135.0, 146.9, 149.6, 176.3; HRMS 421.272 (C₂₆H₃₈O₃ + Na calcd 421.271).

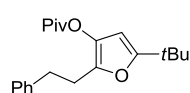


2-(tert-Butyl)-5-phenylfuran-3-yl pivalate (2d): Prepared following the **Procedure C** in 61% yield (63 mg, 0.21 mmol) from 104 mg (0.35 mmol) of **1d**.

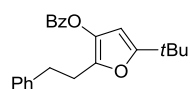
Colorless oil; TLC *R_f* 0.64 (pentane/Et₂O 10%); IR (neat) ν_{max} 1079, 1117, 1156, 1175, 1275, 1460, 1477, 1601, 1745, 2873, 2905, 2963, 2991, 3058 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 1.35 (s, 9H), 1.37 (s, 9H), 6.59 (s, 1H), 7.23 (t, *J* = 7.3 Hz, 1H), 7.35 (dd, *J* = 8.0, 7.3 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 2H); ¹³C NMR (125.8 MHz, CDCl₃) δ 27.3, 29.0, 33.2, 39.1, 102.7, 123.4, 127.3, 128.7, 131.0, 134.0, 148.9, 149.1, 176.4; HRMS 323.161 (C₁₉H₂₄O₃ + Na calcd 323.162).



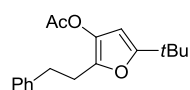
5-(tert-Butyl)-2-phenylfuran-3-yl pivalate (2d'): isolated as a mixture of **2d/2d'** using **Procedure C** from 104 mg (0.35 mmol) of **1d**. TLC *R_f* 0.71 (pentane/Et₂O 10%); ¹H NMR (400 MHz, CDCl₃) δ 1.32 (s, 9H), 1.39 (s, 9H), 6.24 (s, 1H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.38 (dd, *J* = 8.0, 7.3 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 2H); ¹³C NMR (125.8 MHz, CDCl₃) δ 27.4, 29.0, 33.1, 39.3, 101.2, 123.9, 126.7, 128.6, 130.3, 135.7, 138.4, 161.6, 176.0.



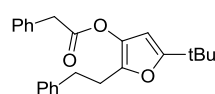
5-(tert-Butyl)-2-phenethylfuran-3-yl pivalate (2e): Prepared following the **Procedure C** in 78% yield (71 mg, 0.22 mmol) from 91 mg (0.28 mmol) of **1e**. Colorless oil; TLC *R_f* 0.52 (pentane/Et₂O 5%); IR (neat) ν_{max} 942, 1029, 1117, 1189, 1273, 1397, 1454, 1748, 2871, 2934, 2966, 3030, 3066, 3088 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 1.25 (s, 9H), 1.28 (s, 9H), 2.82 (t, *J* = 7.6 Hz, 2H), 2.92 (t, *J* = 7.6 Hz, 2H), 5.98 (s, 1H), 7.15 (d, *J* = 7.7 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.28 (dd, *J* = 7.7, 7.4 Hz, 2H); ¹³C NMR (125.8 MHz, CDCl₃) δ 27.3, 27.5, 28.9, 32.9, 34.2, 39.1, 99.3, 126.1, 128.4, 128.5, 134.3, 140.3, 141.4, 160.6, 176.3; HRMS 351.191 (C₂₁H₂₈O₃ + Na calcd 351.193).



5-(tert-Butyl)-2-phenethylfuran-3-yl benzoate (2f): Prepared following the **Procedure C** in 81% yield (75 mg, 0.21 mmol) from 100 mg (0.29 mmol) of **1f**. Colorless oil; TLC *R_f* 0.45 (pentane/Et₂O 10%); IR (neat) ν_{max} 698, 1024, 1057, 1096, 1192, 1260, 1396, 1452, 1741, 2867, 2904, 2930, 2965, 3027 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 1.27 (s, 9H), 2.90 (t, *J* = 7.5 Hz, 2H), 2.96 (t, *J* = 7.5 Hz, 2H), 6.08 (s, 1H), 7.14–7.19 (m, 3H), 7.23–7.27 (m, 2H), 7.48 (dd, *J* = 8.3, 7.5 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 8.07 (d, *J* = 8.3 Hz, 2H); ¹³C NMR (125.8 MHz, CDCl₃) δ 27.6, 29.0, 33.0, 34.1, 99.3, 126.1, 128.4, 128.6, 128.6, 129.4, 130.2, 133.6, 134.3, 140.8, 141.4, 160.8, 164.4; HRMS 371.165 (C₂₃H₂₄O₃ + Na calcd 371.163).

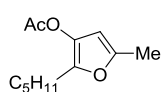


5-(tert-Butyl)-2-phenethylfuran-3-yl acetate (2g): Prepared following the **Procedure C** in 70% yield (71 mg, 0.48 mmol) from 101 mg (0.35 mmol) of **1g**. Colorless oil; TLC *R_f* 0.56 (pentane/Et₂O 10%); IR (neat) ν_{max} 1030, 1094, 1206, 1289, 1366, 1455, 1645, 1759, 2868, 2930, 2964, 3027, 3063, 3073 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 1.23 (s, 9H), 2.16 (s, 3H), 2.82 (t, *J* = 7.8 Hz, 2H), 2.91 (t, *J* = 7.8 Hz, 2H), 5.93 (s, 1H), 7.16 (d, *J* = 7.0 Hz, 2H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.27 (dd, *J* = 7.5, 7.0 Hz, 2H); ¹³C NMR (125.8 MHz, CDCl₃) δ 20.9, 27.4, 28.9, 32.9, 34.1, 99.2, 126.1, 128.4, 128.5, 134.1, 140.6, 141.4, 160.6, 168.8; HRMS 309.145 (C₁₈H₂₂O₃ + Na calcd 309.146).

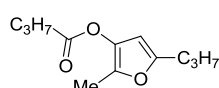


5-(tert-Butyl)-2-phenethylfuran-3-yl 2-phenyl acetate (2h): Prepared following the **Procedure C** in 75% yield (64 mg, 0.18 mmol) from 85 mg (0.23 mmol) of **1h**. Colorless oil; TLC *R_f* 0.42 (pentane/Et₂O 10%); IR (neat) ν_{max} 946, 1121, 1234, 1289, 1397, 1496, 1645, 1757, 2868, 2930, 2965, 3028, 3063, 3086 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 1.21 (s, 9H), 2.72 (t, *J* = 7.7 Hz, 2H), 2.82 (t, *J* =

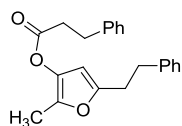
7.7 Hz, 2H), 3.72 (s, 2H), 5.94 (s, 1H), 7.07 (d, $J = 7.6$ Hz, 2H), 7.18 (t, $J = 7.3$ Hz, 1H), 7.25 (t, $J = 7.3$ Hz, 2H), 7.28–7.36 (m, 5H); ^{13}C NMR (125.8 MHz, CDCl_3) δ 27.4, 28.9, 32.9, 34.1, 41.3, 99.1, 126.1, 127.5, 128.4, 128.5, 128.8, 129.4, 133.6, 134.2, 140.6, 141.4, 160.6, 169.3; HRMS 385.176 ($\text{C}_{24}\text{H}_{26}\text{O}_3 + \text{Na}$ calcd 385.177).



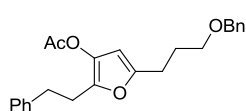
5-Methyl-2-pentylfuran-3-yl acetate (2i) [6]: Prepared following the **Procedure C** in 77% yield (77 mg, 0.37 mmol) from 100 mg (0.48 mmol) of **1i**. Colorless oil; TLC R_f 0.35 (pentane/ Et_2O 5%); ^1H NMR (300 MHz, CDCl_3) δ 0.89 (t, $J = 7.0$ Hz, 3H), 1.25–1.36 (m, 4H), 1.54–1.62 (m, 2H), 2.22 (d, $J = 1.0$ Hz, 3H), 2.23 (s, 3H), 2.48 (t, $J = 7.7$ Hz, 2H), 5.94 (q, $J = 0.9$ Hz, 1H); ^{13}C NMR (125.8 MHz, CDCl_3) δ 14.1, 20.9, 22.5, 25.2, 27.6, 31.4, 102.7, 133.9, 142.3, 148.6, 169.1.



2-Methyl-5-propylfuran-3-yl butyrate (2j): Prepared following the **Procedure C** in 68% yield (71 mg, 0.33 mmol) from 104 mg (0.49 mmol) of **1j**. Colorless oil; TLC R_f 0.58 (pentane/ Et_2O 10%); IR (neat) ν_{max} 943, 1149, 1240, 1372, 1456, 1652, 1761, 2874, 2933, 2962 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.95 (t, $J = 7.5$ Hz, 3H), 1.01 (t, $J = 7.5$ Hz, 3H), 1.62 (qt, $J = 7.5$, 7.5 Hz, 2H), 1.75 (qt, $J = 7.5$, 7.5 Hz, 2H), 2.14 (s, 3H), 2.47 (t, $J = 7.5$ Hz, 2H), 2.49 (t, $J = 7.5$ Hz, 2H), 5.96 (s, 1H); ^{13}C NMR (125.8 MHz, CDCl_3) δ 10.7, 13.8, 13.9, 18.6, 21.3, 30.6, 36.0, 102.1, 134.1, 137.9, 152.8, 171.6; HRMS 233.115 ($\text{C}_{12}\text{H}_{18}\text{O}_3 + \text{Na}$ calcd 233.115).



2-Methyl-5-phenethylfuran-3-yl 3-phenylpropanoate (2k): Prepared following the **Procedure C** in 74% yield (76 mg, 0.23 mmol) from 103 mg (0.31 mmol) of **1k**. Colorless oil; TLC R_f 0.51 (pentane/ Et_2O 20%); IR (neat) ν_{max} 697, 747, 789, 933, 1075, 1135, 1235, 1371, 1453, 1495, 1651, 1758, 2860, 2921, 3027 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 2.09 (s, 3H), 2.83 (t, $J = 7.8$ Hz, 4H), 2.92 (t, $J = 7.8$ Hz, 2H), 3.04 (t, $J = 7.8$ Hz, 2H), 5.93 (s, 1H); 7.18–7.26 (m, 6H), 7.27–7.34 (m, 4H); ^{13}C NMR (125.8 MHz, CDCl_3) δ 10.7, 30.5, 31.1, 34.2, 35.7, 102.5, 126.2, 126.6, 128.5, 128.5, 128.5, 128.7, 134.0, 138.7, 140.2, 141.2, 151.8, 170.9; HRMS 357.145 ($\text{C}_{22}\text{H}_{22}\text{O}_3 + \text{Na}$ calcd 357.146).



5-(3-(Benzyloxy)propyl)-2-phenethylfuran-3-yl acetate (2l): Prepared following the **Procedure C** in 65% yield (68 mg, 0.18 mmol) from 105 mg (0.28 mmol) of **1l**. Colorless oil; TLC R_f 0.43 (cyclohexane/ EtOAc 20%); IR (neat) ν_{max} 578, 697, 734, 1071, 1099, 1206, 1367, 1453, 1495, 1759, 2856, 2925, 3027 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.84 (tt, $J = 7.5$, 6.3 Hz, 2H), 2.08 (s, 3H), 2.58 (t, $J = 7.5$ Hz, 2H), 2.72 (t, $J = 7.7$ Hz, 2H), 2.81 (t, $J = 7.7$ Hz, 2H), 3.43 (t, $J = 6.3$ Hz, 2H), 4.23 (s, 2H), 5.89 (s, 1H), 7.06–7.30 (m, 10H); ^{13}C NMR (125.8 MHz, CDCl_3) δ 20.8, 25.3, 27.4, 28.1, 34.1, 69.4, 73.1, 102.4, 126.2, 127.7, 127.8, 128.5, 128.5, 134.2, 138.7, 141.1, 141.4, 152.4, 168.7; HRMS 402.175 ($\text{C}_{24}\text{H}_{26}\text{O}_4 + \text{Na}$ calcd 402.176).

