Supporting Information

for

Ambient gold-catalyzed O-vinylation of cyclic 1,3-diketone: A vinyl ether synthesis

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General methods, characterization data and NMR spectra of synthesized compounds

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I. General Methods and Materials

All of the reactions dealing with air and/or moisture-sensitive reactions were carried out under an atmosphere of nitrogen using oven/flame-dried glassware. Unless otherwise noted, all commercial reagents and solvents were obtained from the commercial provider and used without further purification. All gold complexes were synthesized from HAuCl₄, which was purchased from Strem. XPhos was purchased from Acros and used as received (stored at 4°C and handled in glovebox). ¹H NMR and ¹³C NMR spectra were recorded on Varian/Agilent 400 MHz spectrometers. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm) or CDCl₃ (δ 7.26 ppm) for ¹H and CDCl₃ (δ 77.0 ppm) for ¹³C. Flash column chromatography was performed on 230-430 mesh silica gel. HRMS were recorded on LTQ-FTUHRA spectrometer.

Representative procedure for Gold-catalyzed O-Vinylation of 1,3-Cyclic Diketone

A 4 mL screw-cap vial was charged with 1,3-cyclohexanedione (46 mg, 0.4 mmol) and alkyne (0.8 mmol, 1.2 equiv.) in dry DCM (0.8 mL), followed by the addition of catalysts XPhosAu(TA)OTf (3.7 mg, 1 mol%) and Cu(OTf)₂ (1.4 mg, 1 mol%). The vial was allowed to stir at rt and monitored by TLC. After the reaction was completed (about 24 h), the reaction mixture was directly purified by flash chromatography on silica gel (ethyl acetate/hexane = 1:3, V/V) to give desired addition product.

Procedure for Synthesis of XPhosAu(TA)OTf

A 20 mL screw-cap vial was charged with XPhosAuCl (355 mg, 0.5 mmol) and 1H-benzotriazole (1.1 equiv.) in dry DCM (5 mL), followed by the addition of AgOTf (1.05 equiv.). The vial was allowed to stir at ambient temperature. After 4h, the reaction mixture was filtered through two celite pads and concentrated in vacuo to give the product as white foam. Pure white powder was obtained via recrystallization through diffusion of hexane into DCM solution of crude product.

For the synthesis of Ph₃PAu(TA)OTf and IPrAu(TA)OTf, see: ref 1-2.
II. Compounds Characterization

1H-NMR (400 MHz, CDCl₃) δ 7.42-7.40 (m, 2H), 7.33-7.30 (m, 2H), 5.43 (d, J = 2.0 Hz, 1H), 5.42 (s, 1H), 4.97 (d, J = 2.4 Hz, 1H), 2.61 (t, J = 6.4 Hz, 2H), 2.31 (t, J = 6.8 Hz, 2H), 2.61 (quint, J = 6.4 Hz, 2H), 2.00 (s, 6H).

13C-NMR (100 MHz, CDCl₃) δ 199.6, 176.5, 154.9, 133.2, 129.3, 128.7, 125.0, 106.5, 101.9, 36.5, 28.2.


1H-NMR (400 MHz, CDCl₃) δ 7.37-7.35 (m, 2H), δ 6.87-6.84 (m, 2H), 5.31 (t, J = 1.6 Hz, 1H), 4.87 (d, J = 1.6 Hz, 1H), 3.80 (s, 3H), 2.63 (t, J = 1.6 Hz, 2H), 2.34 (t, J = 1.6 Hz, 2H), 2.05-2.02 (m, 2H).

13C-NMR (100 MHz, CDCl₃) δ 199.7, 176.7, 160.3, 154.6, 126.4, 125.6, 114.0, 106.3, 99.9, 55.2, 36.4, 28.1, 21.0.

HRMS Calculated for C₁₅H₁₇O₃ [M+H]^+: 245.1172, Found: 245.1172.

1H-NMR (400 MHz, CDCl₃) δ 7.61 (d, J = 8.0 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H), 5.57 (d, J = 2.4 Hz, 1H), 5.39 (s, 1H), 5.13 (d, J = 2.0 Hz, 1H), 2.64 (t, J = 6.2 Hz, 2H), 2.34 (t, J = 6.6 Hz, 2H), 2.06 (quint, J = 6.4 Hz, 2H).

13C-NMR (100 MHz, CDCl₃) δ 199.3, 176.0, 153.5, 136.6, 126.0, 125.7 (q, J = 3.8 Hz), 125.3, 104.6, 104.1, 36.4, 28.1, 21.0.

HRMS Calculated for C_{14}H_{14}FO_{2} [M+H]^+: 233.0972, Found: 233.0971.

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\text{HRMS Calculated for C}_{14}\text{H}_{14}\text{ClO}_{2} [M+H]^+: 249.0677, \text{Found: 249.0678.}
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\text{HRMS Calculated for C}_{15}\text{H}_{17}O_{2} [M+H]^+: 229.1223, \text{Found: 229.1224.}
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\text{HRMS Calculated for C}_{12}\text{H}_{13}O_{2}S [M+H]^+: 221.0631, \text{Found: 221.0631.}
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\text{HRMS Calculated for C}_{18}\text{H}_{19}FeO_{2} [M+H]^+: 323.0734, \text{Found: 321.0729.}
\]
$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 5.41 (s, 1H), 4.64 (m, 1H), 4.51 (m, 1H), 2.41 (t, $J = 6.3$ Hz, 2H), 2.26 (t, $J = 6.8$ Hz, 2H), 1.98-1.90 (m, 3H), 1.79-1.57 (m, 4H), 1.17-1.04 (m, 6H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 199.6, 176.7, 162.2, 105.2, 99.2, 40.7, 36.4, 30.5, 28.3, 25.8, 25.7, 21.0.

HRMS Calculated for C$_{14}$H$_{21}$O$_2$ [M+H]$^+$: 221.1536, Found: 221.1535.

Obtained as inseparable mixtures (6b:6b$'$=1:0.4).

Major isomer (6b):
$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 7.37-7.35 (m, 2H), $\delta$ 5.56 (s, 1H), 4.80 (dd, $J = 1.6$, 1.0 Hz, 1H), 4.60 (d, $J = 1.6$ Hz, 1H), 2.59 (quint, $J = 8.0$ Hz, 1H), 2.50 (t, $J = 6.4$ Hz, 2H), 2.36 (t, $J = 6.4$ Hz, 2H), 1.84-1.80 (m, 2H), 1.71-1.47 (m, 6H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 199.8, 176.8, 161.0, 105.4, 99.5, 42.9, 36.6, 30.6, 28.4, 24.8, 21.1.

HRMS Calculated for C$_{13}$H$_{19}$O$_2$ [M+H]$^+$: 207.1380, Found: 207.1378.

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 5.60 (s, 1H), 4.75 (d, $J = 2.0$ Hz, 1H), 4.57 (d, $J = 1.6$ Hz, 1H), 4.48 (t, $J = 6.8$ Hz, 2H), 2.35 (t, $J = 6.8$ Hz, 2H), 2.02 (quint, $J = 6.4$ Hz, 2H), 1.49 (tt, $J = 8.4$, 5.2 Hz, 1H), 0.75-0.70 (m, 2H), 0.61-0.57 (m, 2H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 199.7, 176.7, 158.3, 105.6, 98.9, 36.5, 28.2, 21.1, 13.0, 6.0.

HRMS Calculated for C$_{11}$H$_{15}$O$_2$ [M+H]$^+$: 179.1067, Found: 179.1066.

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 5.91 (t, $J = 5.4$ Hz, 1H), 5.42 (s, 1H), 4.94 (d, $J = 1.2$ Hz, 1H), 4.69 (d, $J = 0.8$ Hz, 1H), 2.56 (t, $J = 6.2$ Hz, 2H), 2.35 (t, $J = 6.4$ Hz, 2H), 2.15-2.10 (m, 4H), 2.03 (quint, $J = 6.6$ Hz, 2H), 1.71-1.66 (m, 2H), 1.60-1.55 (m, 2H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 199.9, 177.5, 155.8, 129.0, 126.7, 105.2, 99.9, 36.5, 28.1, 25.5, 24.6, 22.1, 21.6, 21.1.

HRMS Calculated for C$_{14}$H$_{19}$O$_2$ [M+H]$^+$: 219.1380, Found: 219.1380.
1H-NMR (400 MHz, CDCl₃) δ 5.45 (s, 1H), 4.78 (m, 1H), 4.68 (d, J = 1.6 Hz, 1H), 3.53 (t, J = 6.4 Hz, 2H), 2.44 (t, J = 6.0 Hz, 2H), 2.33-2.29 (m, 4H), 1.98 (quint, J = 6.4 Hz, 2H), 1.94-1.87 (m, 2H).

13C-NMR (100 MHz, CDCl₃) δ 199.5, 175.8, 156.1, 105.5, 102.4, 43.7, 36.5, 29.4, 29.3, 28.3, 21.0.


1H-NMR (400 MHz, CDCl₃) δ 7.43-7.41 (m, 2H), 7.35-7.32 (m, 3H), 5.44 (t, J = 2.4 Hz, 1H), 5.42 (s, 1H), 4.98 (d, J = 2.0 Hz, 1H), 2.49 (s, 2H), 2.19 (s, 2H), 1.10 (s, 2H).

13C-NMR (100 MHz, CDCl₃) δ 199.4, 175.0, 155.0, 133.2, 129.3, 128.7, 125.0, 105.4, 101.9, 50.6, 42.1, 32.7, 28.2.


1H-NMR (400 MHz, CDCl₃) δ 7.44-7.41 (m, 2H), 7.34-7.31 (m, 3H), 5.42 (d, J = 2.8 Hz, 1H), 5.26 (t, J = 1.2 Hz, 1H), 5.04 (d, J = 2.4 Hz, 1H), 2.77-2.74 (m, 2H), 2.47-2.44 (m, 2H).

13C-NMR (100 MHz, CDCl₃) δ 205.5, 188.7, 156.8, 132.6, 129.4, 128.7, 125.0, 108.4, 101.1, 34.3, 28.0.


1H-NMR (400 MHz, CDCl₃) δ 7.33-7.31 (m, 2H), 7.17 (d, J = 5.4, 2.4 Hz, 1H), 5.37 (t, J = 0.9 Hz, 1H), 5.33 (d, J = 2.4 Hz, 1H), 5.00 (d, J = 2.4 Hz, 1H), 2.81-2.78 (m, 2H), 2.53-2.50 (m, 2H).

13C-NMR (100 MHz, CDCl₃) δ 205.5, 188.7, 153.1, 134.8, 126.9, 124.7, 122.7, 108.1, 100.2, 34.4, 28.0.

HRMS Calculated for C₁₁H₁₁O₂ [M+H]+: 207.0474, Found: 207.0473.

Obtained as inseparable mixtures (10d:10d’=1:2.6).

III. ORTEP Drawing of the Crystal Structure

Figure S1. Perspective view of the molecular structure of the \((\text{C}_6\text{H}_5\text{N}_3)\text{Au}[\text{P(}\text{C}_6\text{H}_{11})_2]_2(\text{C}_6\text{H}_5\text{H}_2(\text{i-C}_3\text{H}_7)_3))^+\) cation with the atom labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability.

IV. Reference

V. NMR Spectra of New Compounds

3a $\left(\text{H} \; 400 \text{ MHz}\right)$

3a $\left(\text{C} \; 100 \text{ MHz}\right)$
$3e \ ({}^{1}H \ 400 \ MHz)$

$3e \ ({}^{13}C \ 100 \ MHz)$
3f (1H 400 MHz)

3f (13C 100 MHz)
$3g$ ($^{1}H$ 400 MHz)

$3g$ ($^{13}C$ 100 MHz)
3h (\textsuperscript{1}H 400 MHz)

3h (\textsuperscript{13}C 100 MHz)
$6e$ ($^1H$ 400 MHz)

$6e$ ($^{13}C$ 100 MHz)
10a (\textsuperscript{1}H 400 MHz)

10a (\textsuperscript{13}C 100 MHz)
10b \( (^1\text{H} \ 400 \text{ MHz}) \)

10b \( (^{13}\text{C} \ 100 \text{ MHz}) \)
10d

(1H 400 MHz)

10d'