Gold Catalysis: Mild Conditions for the Transformation of Alkynyl Epoxides to Furans

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Abstract: Gold(III) chloride catalyzes the isomerization of alkynyl epoxides to furans under mild conditions. Additional functional groups like hydroxy groups or aryl bromides do not need to be protected.

Keywords: alkynes; epoxides; furans; gold; homogeneous catalysis

Introduction

Furans are an important class of heterocyclic compounds which are extensively used as synthetic building blocks[1] and appear as a subunit in many natural products and substances of relevance for industry.[2] Thus the synthesis of furans has always been of importance.[3]

Since alkynyloxiranes are nowadays easily accessible by either a Sonogashira coupling[4] of an alkyne and a vinyl halide and a subsequent epoxidation[5] or nucleophilic ring closure of propargylic alcohols with a leaving group in the homopropargylic position,[6] the isomerization of alkynyloxiranes to furans looks quite attractive, especially for highly substituted furans. Thus several groups have already addressed this rearrangement. In 1975 Queguiner et al.[7] and in 1981 Berbalk et al. described the Hg(II)/acid-catalyzed reaction.[8] Queguiner et al. also reported an isomerization by NaOEt in ethanol.[7b] Ten years later Marshall et al. discovered that this rearrangement can also be induced by stoichiometric amounts of base using either potassium hydride in THF/HMPA at room temperature or KO*t*-Bu/18-crown-6 in *t*-BuOH at 60 °C.[9] This reaction is initiated by an elimination to an cumulenyl alkoxide and thus depended on the propargylic position. Similar results with *in situ* formed alkynyloxiranes were obtained by Katrizky et al.[10] A related class of starting materials, alkynyloxiranes with leaving groups in the propargylic position, furnished furans upon treatment with stoichiometric amounts of SmI_2 and catalytic amounts of Pd(0) or Pd(II) in the case of a sequential procedure developed by Aurrechoechea et al.[11] Finally, in 1994 McDonald et al.[12] reported a molybdenum-catalyzed and last year Liu et al.[13] reported a ruthenium-catalyzed isomerization of alkynyloxiranes with a terminal alkyne to the corresponding furan. Another reaction that converts alkynyl epoxides to furans, not by isomerization but rather by the reaction with an external carbon nucleophile, is palladium-catalyzed and was published by Tsuji et al. in 1987.[14]

These approaches to furan in principle allow a perfect regiocontrol in the synthesis of 2-, 3-, 2,3-, 2,4-, 2,5-, 2,3,5- and even 2,3,4,5-substituted furans. But the reactions mentioned above also have some limitations. The disadvantages of the Hg-catalysis are obvious, the base-catalysis depends on a C–H bond in the propargylic position and therefore allows the synthesis of furans which possess a substituent in the 2-position, the latter is also true for the SmI_2. Furthermore, the catalysis by the strong bases will also be problematic when other eliminations are possible or epimerizations of chiral centers are possible. The molybdenum and ruthenium catalysts are limited to a terminal alkyne in the substrate for the formation of the intermediate vinylidene species. We were looking for a catalyst that had the potential of the Hg catalyst without using this problematic metal, would not need terminal alkynes and would work under less acidic or, respectively, less basic conditions. In the context of the recent investigation of the addition of heteronucleophiles to alkynes,[15] we have now investigated $AuCl_3$ as a catalyst for this transformation.

Results and Discussion

The synthesis of the starting materials followed the sequence mentioned above. Sonogashira coupling of **1** and **2** afforded the 1,3-enynes **3**. Epoxidation of the latter with mCPBA yielded the alkynyloxiranes **4** (Scheme 1).

Compound **4** was then subjected to a catalytic amount of $AuCl_3$ in acetonitrile at room temperature. The conversions of **4a** (entry 1) and **4b** (entry 2) proceeded in high yields, the primary alcohol group did not cause any problems (Table 1).

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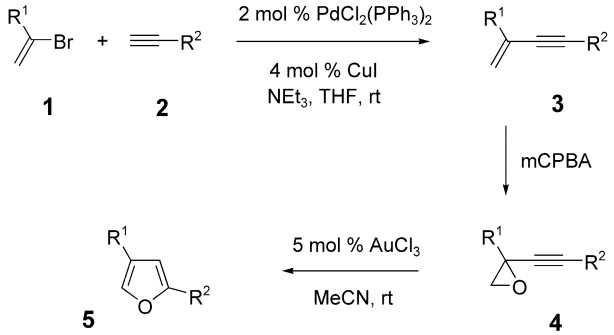
Table 1. Yield of the gold-catalyzed isomerization of **4** to **5**.

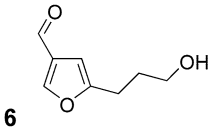
Entry	Starting material	Product (isolated yield)
1	**4a**	**5a** (80%)
2	**4b**	**5b** (84%)
3	**4c**	**5c** (56%)
4	**4d**	**5d** (53%)
5	**4e**	**5e** (25%)
6	**4f**	**5f** (25%)
7	**4g**	**5g** (0%), **6** (69%)



1a R^1 = Me
1b R^1 = $(CH_2)_2OH$
1c R^1 = $CH(OCH_2CH_3)_2$

2a R^2 = $(CH_2)_3OH$
2b R^2 = $(CH_2)_4OH$
2c R^2 = Ph
2d R^2 = 4-Br-Ph
2e R^2 = $(CH_2)_2CO_2$menthyl
2f R^2 = Pr

3 - 5:
a R^1 = Me, R^2 = $(CH_2)_3OH$
b R^1 = Me, R^2 = $(CH_2)_4OH$
c R^1 = $(CH_2)_2OH$, R^2 = Ph
d R^1 = $(CH_2)_2OH$, R^2 = 4-Br-Ph
e R^1 = $(CH_2)_2OH$, R^2 = $(CH_2)_2CO_2$menthyl
f R^1 = $(CH_2)_2OH$, R^2 = $(CH_2)_2Me$
g R^1 = $CH(OCH_2CH_3)$, R^2 = $(CH_2)_3OH$



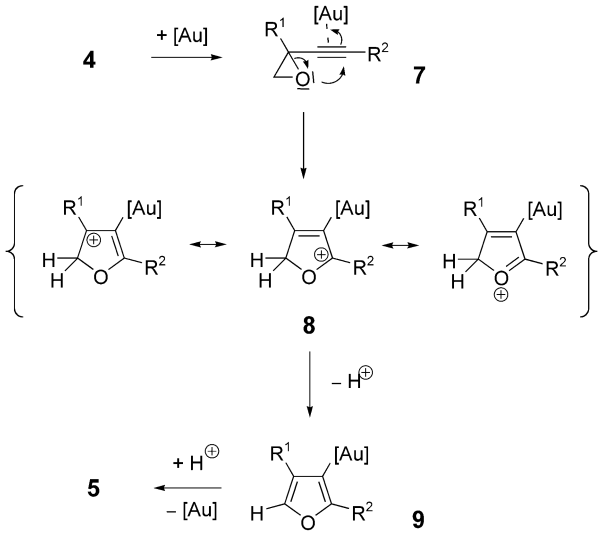
Scheme 1. Sequence to the alkynyl epoxides **4** and their gold-catalyzed isomerization to **5**.

With the aryl substituent in **4c** and **4d**, the yield dropped to 56% (entry 3) and 53% (entry 4). The same is true for **4e** and **4f** (25%, entries 5 and 6), which suggests that the low yield is connected to the $(CH_2)OH$ substituent in all the substrates **4c**–**f** (for example, an elimination followed by a polymerization of the vinylfuran).

Quite nice is the reaction of the diethyl acetal **4g**, where the isomerization to the furan is connected with a deprotection of the furylic acetal to the furylaldehyde **6** in 67% yield over both steps (entry 7). The NMR spectra taken during the reaction provide evidence for the deprotection of the aldehyde taking place in the second phase of the reaction when the furan was already formed and the acetal is activated by the furyl (benzyl-like) position. Usually it is synthetically challenging to position a formyl group in the 4-position of the furan ring.

For the mechanism of the reaction we assume that like in many other cases[16] the gold activates the carbon-carbon triple bond for the addition of a nucleophile by co-ordination as shown in **7**. In this case the epoxide-oxygen would attack at the distal position of the alkyne, the gold will form a σ-bond to the other carbon atom of the alkyne and the resulting species **8** only has to loose a proton to form the aromatic furan **9** and finally the product **5** after proto-demetallation (Scheme 2).

If the mechanism depicted in Scheme 2 is correct, one proton must migrate to the 3- or 4-position of the furan ring during the reaction. Thus the maximum number of substituents on the furan ring tolerated by this reaction would be three. Further studies are needed to clarify this point.



Scheme 2. Mechanistic proposal for the gold-catalyzed isomerization of **4** to **5**.

Conclusion

In conclusion, with gold(III) chloride the isomerization is possible under mild conditions and tolerates a number of functional groups.

Experimental Section

6-Methylhept-6-en-4-yn-1-ol (3a)

To a stirred solution of 2-bromopropene (**1a**; 1.81 g, 15.0 mmol) and triethylamine (1.52 g, 15.0 mmol) in THF (5 mL), CuI (76.1 mg, 400 μmol) and $(PPh_3)_2PdCl_2$ (140 mg, 200 μmol) were added. A solution of 4-pentyn-1-ol (2a; 84.1 mg, 10.0 mmol) in THF (5 mL) was added dropwise at room temperature. The reaction mixture was allowed to stir at room temperature for 17 h. The solvent was evaporated and the column chromatography of the crude product (silica gel, 10% EtOAC-hexane) afforded **3a** as a yellow viscous oil; yield: 1.13 g (91%). IR (film): $\nu = 3350$, 3080, 2930, 2860, 2200, 1610 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): $\delta = 5.19$ (d, $J =$ 1.7 Hz, 1H), 5.14 (d, $J =$ 1.7 Hz, 1H), 3.76 (t, $J =$ 6.1 Hz, 2H), 2.43 (t, $J = 6.1$ Hz, 2H), 1.86 (s, 3H), 1.79 (m, 2H), 1.58 (s, 1H, OH); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 127.39$ (s), 121.02 (d), 88.76 (s), 82.76 (s), 62.14 (t), 31.66 (t), 24.09 (q), 16.18 (t); MS (EI, 70 eV): *m/z* (%): 124 (36)[M^+], 105 (25), 91 (100), 79 (56), 65 (23), 53 (23), 41 (16); anal. calcd. for $C_8H_{12}O$: C 77.38, H 9.74; found: C 77.26, H 9.73.

5-(2-Methyloxiranyl)pent-4-yn-1-ol (4a)

To a stirred solution of **3a** (124 mg, 1.00 mmol) and Na_2HPO_4 (350 mg, 2.47 mmol) in DCM (5 mL) was added mCPBA (362 mg, 2.10 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 3 h and then allowed to warm to room temperature, whereupon it was diluted with ether and quenched with aqueous saturated $NaHCO_3$ solution. The organic layer was washed with 10% NaOH, brine and finally dried over anhydrous $MgSO_4$. The solvent was evaporated and column chromatography (silica gel, 15% EtOAC-hexane) afforded **4a** as a colorless viscous oil; yield: 82.0 mg (59%). IR (film): $\nu =$ 3360, 3040, 2920, 2860, 2220, 1260 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): $\delta = 3.66$ (t, $J = 6.2$ Hz, 2H), 2.92 (d, $J = 5.6$ Hz, 1H), 2.69 (d, $J = 5.6$ Hz, 1H), 2.27 (t, $J = 7.1$ Hz, 2H), 2.21 (br s, 1H, OH), 1.69 (m, 2H), 1.48 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 82.59$ (s), 80.15 (s), 61.56 (t), 55.82 (t), 47.83 (s), 31.29 (t), 23.51 (q), 15.38 (t); MS (EI, 70 eV): *m/z* (%) = 140 (3)[M^+], 125 (3), 109 (27), 95 (11), 82 (100), 70 (3); anal. calcd. for $C_8H_{12}O_2$: C 68.55, H 8.63; found: C 68.72, H 8.57.

3-(4-Methylfuran-2-yl)propan-1-ol (5a)

A solution of $AuCl_3$ in MeCN (66.1 mg; 5% w/w; 3.30 mg, 10.8 μmol $AuCl_3$) was added to a solution of **4a** (30.0 mg, 214 μmol) in MeCN (0.5 mL) at 25 °C. After 17 h (the reaction was monitored by thin layer chromatography) the solvent was evaporated and the residue was purified by column chromatography (silica gel, 12% EtOAC-hexane). The pure compound **5a** was obtained as a yellow viscous liquid; yield: 24.1 mg (80%). IR (film): $\nu = 3375$, 2946, 2887, 2363, 1141, 1072, 1037 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): $\delta = 7.06$ (s, 1H), 5.88 (s, 1H), 3.68 (t, $J = 7.45$ Hz, 2H), 2.68 (m, 2H), 1.98 (s, 3H), 1.88 (m, 2H), 1.48 (br s, 1H, OH); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta =$ 155.89 (s), 137.85 (d), 120.84 (s), 108.26 (d), 62.46 (t), 31.33 (t), 24.73 (t), 10.12 (q); MS (EI, 70 eV): *m/z* (%) = 140 (62) [M^+], 122 (37), 109 (12), 95 (100); HRMS (70 eV): calcd. for $C_8H_{12}O_2$ (M^+): 140.0837; found: 140.0841; anal. calcd. for $C_8H_{12}O_2$: C 68.55, H 8.63; found: C 67.54, H 8.62.

7-Methyloct-7-en-5-yn-1-ol (3b)

The compound **3b** was obtained from 5-hexyn-1-ol (**2b**; 393 mg, 4.00 mmol) and triethylamine (911 mg, 9.00 mmol) in THF (4 mL), CuI (45.7 mg, 240 μmol), $(PPh_3)_2PdCl_2$ (84.2 mg, 120 μmol) and 1a (1.45 g, 12.0 mmol) in THF (4 mL) as described for **3a**. Column chromatography (silica gel, 10% EtOAC-hexane) afforded **3b** as a yellow viscous liquid; yield: 459 mg (83%). IR (film): $\nu = 3320$, 3070, 2920, 2840, 2190, 1610 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): $\delta = 5.19$ (d, $J =$ 1.65 Hz, 1H), 5.13 (d, $J = 1.65$ Hz, 1H), 3.68 (t, $J = 6.2$ Hz, 2H), 2.34 (t, $J = 6.8$ Hz, 2H), 1.86 (s, 3H), 1.69 (m, 2H), 1.63 (m, 2H), 1.48 (s, 1H, OH); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 127.53$ (s), 120.83 (d), 89.23 (s), 82.54 (s), 62.78 (t), 32.19 (t), 25.31 (t), 24.15 (q), 19.36 (t); MS (EI, 70 eV): *m/z* (%) = 138 (26) [M^+], 123 (19), 109 (29), 91 (57), 79 (100); anal. calcd. for $C_9H_{14}O$: C 78.21, H 10.21; found: C 78.61, H 10.11.

6-(2-Methyloxiranyl)hex-5-yn-1-ol (4b)

The compound **4b** was obtained using **3b** (276 mg, 2.00 mmol) and Na_2HPO_4 (710 mg, 5.00 mmol) in DCM (8 mL) and mCPBA (725 mg, 4.20 mmol) as described for **4a**. Column chromatography (silica gel, 15% EtOAC-hexane) furnished pure compound **4b** as a colorless viscous liquid; yield: 212 mg (69%). IR (film): $\nu = 3360$, 3040, 2920, 2850, 2210, 1260 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): $\delta = 3.63$ (t, $J = 6.1$ Hz, 2H), 2.93 (d, $J = 5.6$ Hz, 1H), 2.71 (d, $J = 5.6$ Hz, 1H), 2.21 (t, $J = 6.9$ Hz, 2H), 1.71 (br s, 1H, OH), 1.63 (m, 2H), 1.56 (m, 2H), 1.50 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 82.99$ (s), 80.11 (s), 61.56 (t), 55.88 (t), 47.85 (s), 32.03 (t), 24.96 (t), 23.60 (q), 16.70 (t); MS (EI, 70 eV): *m/z* (%) = 154 (21) [M^+], 123 (55), 109 (25), 95 (92), 91 (100), 81 (26), 67 (53), 57 (9); anal. calcd. for $C_9H_{14}O_2$: C 70.10, H 9.15; found: C 69.74, H 9.07.

4-(4-Methylfuran-2-yl)butan-1-ol (5b)

A solution of $AuCl_3$ in MeCN (255 mg; 5% w/w, 12.8 mg, 42.0 μmol $AuCl_3$) was added to a solution of **4b** (130 mg, 843 μmol) in MeCN (1 mL) at 25 °C. After 17 h (the reaction was monitored by thin layer chromatography) the solvent was evaporated and residue was purified by column chromatography (silica gel, 10% EtOAC-hexane). The pure compound **5b** was obtained in as a colorless viscous liquid; yield: 109 mg (84%). IR (film): $\nu = 3320$, 2920, 2850, 1610, 1100, 1040 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): $\delta = 7.05$ (s, 1H), 5.86 (s, 1H), 3.66 (t, $J = 6.4$ Hz, 2H), 2.60 (m, $J = 7.3$ Hz, 2H), 1.97 (s, 3H), 1.69 (m, 2H), 1.61 (m, 2H), 1.36 (br s, 1H, OH); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 156.35$ (s), 137.69 (d), 120.78 (s), 108.09 (d),

63.02 (t), 32.51 (t), 28.09 (t), 24.59 (t), 10.14 (q); MS (EI, 70 eV): *m/z* (%) = 154 (54) [M$^+$], 108 (49), 95 (100), 84 (15), 67 (15), 41 (13); anal. calcd. for $C_9H_{14}O_2$: C 70.10, H 9.15; found: C 69.57, H 9.18.

3-Methylene-5-phenylpent-4-yn-1-ol (3c)

The compound **3c** was obtained from 3-bromo-3-buten-1-ol (**1b**; 604 mg, 4.00 mmol) and triethylamine (607 mg, 6.00 mmol) in THF (3 mL), CuI (30.5 mg, 160 μmol), $(PPh_3)_2PdCl_2$ (56.2 mg, 80.0 μmol) and phenylacetylene (**2c**; 540 mg, 6.00 mmol) in THF (3 mL) in analogy to **3a**. Column chromatography (silica gel, 10% EtOAC-hexane) furnished pure compound **3c** as a yellow viscous liquid; yield: 490 mg (71%). IR (film): ν = 3070, 3040, 2860, 2220, 1650, 1600 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.43 (m, 2H), 7.32 (m, 3H), 5.55 (d, *J* = 1.1 Hz, 1H), 5.41 (d, *J* = 1.1 Hz, 1H), 3.88 (t, *J* = 6.0 Hz, 2H), 2.52 (t, *J* = 6.1 Hz, 2H), 1.62 (br s, 1H, OH); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 131.94 (d, 2C), 128.74 (d), 128.67 (d, 2C), 128.34 (s), 124.15 (t), 123.22 (s), 90.27 (s), 89.16 (s), 61.23 (t), 40.88 (t); MS (EI, 70 eV): *m/z* (%) = 172 (100) [M$^+$], 141 (70), 115 (46), 102 (17), 77 (17); anal. calcd. for $C_{12}H_{12}O$: C 83.69, H 7.02; found: C 83.28, H 7.08.

2-(2-Phenylethynyloxiranyl)ethanol (4c)

The compound **4c** was obtained using **3c** (172 mg, 1.00 mmol) and Na_2HPO_4 (350 mg, 2.46 mmol) in DCM (5 mL) and mCPBA (362 mg, 2.10 mmol) as described for **4a**. Column chromatography (silica gel, 15% EtOAC-hexane) furnished **4c** as a colorless viscous liquid; yield: 58.4 mg (31%). IR (film): ν = 3620 (OH), 3040, 2940, 2860, 2220, 1650, 1590 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.39 (m, 2H), 7.28 (m, 3H), 3.92 (m, 2H), 3.10 (d, *J* = 5.4 Hz, 1H), 2.93 (d, *J* = 5.4 Hz, 1H), 2.15 (br s, 1H, OH), 2.11 (m, 1H), 2.01 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 132.18 (d), 129.14 (d, 2C), 128.69 (d, 2C), 122.05 (s), 87.17 (s), 83.96 (s), 59.79 (t), 54.81 (t), 49.99 (s), 39.05 (t); MS (EI, 70 eV): *m/z* (%) = 188 (21) [M$^+$], 172 (5), 145 (3), 127 (100), 102 (20), 77 (20); anal. calcd. for $C_{12}H_{12}O_2$: C 76.57, H 6.43; found: C 76.02, H 6.32.

2-(5-Phenylfuran-3-yl)ethanol (5c)

A solution of $AuCl_3$ in MeCN (96.0 mg; 5% w/w, 4.80 mg, 15.8 μmol $AuCl_3$) was added to a solution of **4c** (39.9 mg, 212 μmol) in MeCN (0.5 mL) at 25 °C. After 27 h (the reaction was monitored by thin layer chromatography) the solvent was evaporated and residue was purified by column chromatography (silica gel, 8% EtOAC-hexane). Compound **5c** was obtained as a yellow viscous liquid; yield: 22.4 mg (56%). IR (film): ν = 3383, 2925, 2885, 1617, 1580, 1123 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.52 (m, 2H), 7.26 (s, 1H), 7.24 (m, 2H), 7.14 (m, 1H), 6.48 (s, 1H), 3.72 (t, *J* = 6.3 Hz, 2H), 2.61 (t, *J* = 6.3 Hz, 1H), 1.57 (br s, 1H, OH); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 154.76 (s), 139.76 (d), 131.14 (s), 129.01 (d, 2C), 127.74 (d), 124.07 (d, 2C), 123.73 (s), 106.73 (d), 62.85 (t), 28.83 (t); MS (EI, 70 eV): *m/z* (%) = 187 (49) [M$^+$], 159 (9), 105 (100), 91 (5), 77 (32); anal. calcd. for $C_{12}H_{12}O_2$: C 76.57, H 6.43; found: C 76.72, H 6.07.

5-(4-Bromophenyl)-3-methylenepent-4-yn-1-ol (3d)

The compound **3d** was obtained using **1b** (680 mg, 4.50 mmol) and triethylamine (683 mg, 6.75 mmol) in THF (3 mL), CuI (34.3 mg, 180 μmol), $(PPh_3)_2PdCl_2$ (63.2 mg, 90.0 μmol) and 1-bromo-4-ethynylbenzene (**2d**; 905 mg, 5.00 mmol) in THF (3 mL) as described for **3a**. Column chromatography (silica gel, 10% EtOAC-hexane) afforded **3d** as a yellow solid; yield: 418 mg (37%). IR (film): ν = 3360, 2840, 1600, 800, 580 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.39 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 5.51 (d, *J* = 1.2 Hz, 1H), 5.39 (d, *J* = 1.2 Hz, 1H), 3.82 (t, *J* = 6.2 Hz, 2H), 2.46 (t, *J* = 6.2 Hz, 2H), 1.74 (br s, 1H, OH); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 133.32 (d, 2C), 131.92 (d, 2C), 128.09 (s), 124.56 (t), 122.94 (s), 122.16 (s), 90.29 (s), 89.07 (s), 61.12 (t), 40.69 (t); MS (EI, 70 eV): *m/z* (%) = 252 (98)/250 (100) [M$^+$], 206 (8), 171 (15), 153 (19), 128 (89), 95 (14), 77 (3); anal. calcd. for $C_{12}H_{11}BrO$: C 57.39, H 4.42, Br 31.82; found: C 58.07, H 4.17, Br 30.23.

2-[2-(4-Bromophenylethynyl)oxiranyl]ethanol (4d)

The compound **4d** was obtained using **3d** (309 mg, 1.23 mmol) and Na_2HPO_4 (436 mg, 3.07 mmol) in DCM (6 mL) and mCPBA (425 mg, 2.46 mmol)as described for **4a**. Column chromatography (silica gel, 15% EtOAC-hexane) afforded **4d** as a yellow solid; yield: 53.6 mg (16%). IR (film): ν = 3370, 3060, 2912, 2852, 2190, 820 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.39 (d, *J* = 8.4 Hz, 2H), 7.26 (m, *J* = 8.4 Hz, 2H), 3.91 (m, 2H), 3.09 (d, *J* = 5.4 Hz, 1H), 2.94 (d, *J* = 5.4 Hz, 1H), 2.08 (m, 1H), 2.02 (m, 1H), 1.22 (br s, 1H, OH); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 133.62 (d, 2C), 131.95 (d, 2C), 123.53 (s), 121.09 (s), 88.48 (s), 82.85 (s), 59.75 (t), 54.75 (t), 49.90 (s), 38.96 (t); MS (EI, 70 eV): *m/z* (%) = 268 (28)/266 (29) [M$^+$], 238 (76), 236 (77), 207 (80), 205 (66), 182 (15), 157 (6), 129 (54), 126 (85), 73 (100); HRMS (70 eV): calcd. for $C_{12}H_{11}{}^{79}BrO_2$ (M$^+$): 265.9942; found: 265.9928/calcd. for $C_{12}H_{11}{}^{81}BrO_2$ (M$^+$): 267.9922; found: 267.9908.

2-[5-(4-Bromophenyl)-furan-3-yl]ethanol (5d)

A solution of $AuCl_3$ in MeCN (54.1 mg; 5% w/w, 2.71 mg, 8.92 μmol $AuCl_3$) was added to a solution of **4d** (32.1 mg, 120 μmol) in MeCN (0.5 mL) at 25 °C. After 27 h (the reaction was monitored by thin layer chromatography) the solvent was evaporated and residue was purified by column chromatography (silica gel, 10% EtOAC-hexane). The pure compound **5d** was obtained as yellow solid; yield: 17.1 mg (53%). IR (film): ν = 3411, 3061, 2924, 2854, 1584, 1265, 1067, 822 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.49 (m, 4H), 7.34 (s, 1H), 6.59 (s, 1H), 3.83 (t, *J* = 6.3 Hz, 2H), 2.72 (t, *J* = 6.3 Hz, 2H), 1.56 (brs, 1H, OH); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 153.66 (s), 140.08 (d), 132.15 (d, 2C), 130.06 (s), 125.57 (d, 2C), 123.99 (s), 121.48 (s), 107.36 (d), 62.82 (t), 28.76 (t); MS (EI, 70 eV): *m/z* (%) = 268 (99)/266 (28) [M$^+$], 237 (24), 235 (24), 200 (13), 183 (33), 128 (83); HRMS (70 eV): calcd. for $C_{12}H_{11}{}^{79}BrO_2$ (M$^+$): 265.9942; found: 265.9943/calcd. for $C_{12}H_{11}{}^{81}BrO_2$ (M$^+$): 267.9922; found: 267.9922.

Pent-4-ynoic Acid 2-Isopropyl-5-methylcyclohexyl Ester (2e)

To a solution of 4-pentynoic acid (491 mg, 5.00 mmol) in CCl_4 (15 mL), L-menthol (859 mg, 5.50 mmol) and 4-toluenesulfonic acid monohydrate (24.7 mg, 130 μmol) were added. The reaction mixture was refluxed for 20 h. The reaction mixture was cooled to room temperature and then diluted with ether. The organic layer was washed with saturated $NaHCO_3$, brine and finally dried over anhydrous $MgSO_4$. The solvent was evaporated and column chromatography (silica gel, 1% EtOAC-hexane) furnished **2e** as a colorless viscous liquid; yield: 1.01 g (85%). IR (film): ν = 3300, 2940, 2850, 2080, 1750, 1360 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ = 4.70 (m, 1H), 2.52 (m, 4H), 1.99 (s, 1H), 1.96 (m, 1H), 1.87 (m, 1H), 1.69 (m, 2H), 1.58 (m, 1H), 1.49 (m, 1H), 1.47 (m, 1H), 0.98 (m, 2H), 0.89 (m, 6H), 0.76 (m, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 171.68 (s), 82.90 (s), 74.97 (d), 69.29 (d), 47.36 (d), 41.23 (t), 34.57 (t), 34.08 (t), 31.72 (d), 26.57 (d), 23.75 (t), 22.36 (q), 21.09 (q), 16.66 (q), 14.87 (t); MS (CI): *m/z* (%) = 237 (100) [M^+], 221 (6), 138 (59), 95 (22), 81 (15); anal. calcd. for $C_{15}H_{24}O_2$: C 76.23, H 10.24; found: C 76.15, H 10.11.

6-(2-Hydroxyethyl)hept-6-en-4-ynoic Acid 2-Isopropyl-5-methylcyclohexyl Ester (3e)

The compound **3e** was obtained using **1b** (755 mg, 5.00 mmol) and triethylamine (607 mg, 6.00 mmol) in THF (3 mL), CuI (30.5 mg, 160 μmol), $(PPh_3)_2PdCl_2$ (56.2 mg, 80.0 μmol) and **2e** (945 mg, 4.00 mmol) in THF (3 mL) as described for 3a. Column chromatography (silica gel, 5% EtOAC-hexane) furnished **3e** as a colorless viscous liquid; yield: 1.32 mg (86%). IR (film): ν = 3440, 3080, 2940, 2850, 2190, 1730 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ = 5.35 (d, 1H), 5.26 (d, 1H), 4.70 (m, 1H), 3.77 (t, *J* = 5.9 Hz, 2H), 2.62 (m, 2H), 2.53 (m, 2H), 2.37 (m, 2H), 1.97 (m, 1H), 1.86 (m, 1H), 1.66 (m, 2H), 1.62 (m, 2H), 1.48 (m, 1H), 1.37 (m, 1H), 1.04 (m, 2H), 0.89 (m, 6H), 0.76 (m, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 171.78 (s), 128.49 (s), 123.17 (t), 89.19 (d), 81.15 (s), 74.92 (d), 61.15 (t), 47.30 (d), 41.25 (t), 40.94 (t), 34.55 (t), 34.29 (t), 31.70 (d), 26.63 (d), 23.75 (t), 22.35 (q), 21.11 (q), 16.66 (q), 15.73 (t); MS (EI, 70 eV): *m/z* (%) = 306 (2) [M^+], 265 (28), 168 (41), 138 (100), 83 (82); anal. calcd. for $C_{19}H_{30}O_3$: C 74.47, H 9.87; found: C 74.33, H 9.77.

5-[2-(2-Hydroxyethyl)oxiranyl]-pent-4-ynoic Acid 2-Isopropyl-5-methylcyclohexyl Ester (4e)

The compound **4e** was obtained using **3e** (306 mg, 1.00 mmol) and Na_2HPO_4 (355 mg, 2.50 mmol) in DCM (5 mL) and mCPBA (362 mg, 2.10 mmol) as described for **4a**. Column chromatography (silica gel, 12% EtOAC-hexane) furnished **4c** as a colorless viscous liquid; yield: 230 mg (71%). IR (film): ν = 3440, 3040, 2940, 2860, 2210, 1730, 1250 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ = 4.62 (m, 1H), 3.76 (m, 2H), 2.89 (d, *J* = 5.5 Hz, 1H), 2.76 (d, *J* = 5.5 Hz, 1H), 2.51 (m, 1H, OH), 2.44 (m, 4H), 1.88 (m, 3H), 1.77 (m, 1H), 1.62 (m, 2H), 1.41 (m, 1H), 1.30 (m, 1H), 1.35 (m, 1H), 0.97 (m, 2H), 0.83 (m, 6H), 0.68 (m, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 171.39 (s), 82.79 (s), 79.04 (s), 74.82 (d), 59.45 (t), 54.39 (t), 49.47 (s), 47.09 (d), 41.04 (t), 39.09 (t), 34.35 (t), 33.73 (t), 31.52 (d), 26.47 (d), 23.58 (t), 22.17 (q), 20.89 (q), 16.49 (q), 14.89 (t); MS (EI, 70 eV): *m/z* (%) = 322 (3) [M^+], 184 (4), 138 (5), 95 (5); anal. calcd. for $C_{19}H_{30}O_4$: C 70.77, H 9.38; found C 70.12, H 9.38.

5-[2-(2-Hydroxyethyl)furan-2-yl]propionic Acid 2-Isopropyl-5-methylcyclohexyl Ester (5e)

A solution of $AuCl_3$ in MeCN (258 mg; 5% w/w, 12.9 mg, 42.5 μmol $AuCl_3$) was added to a solution of **4e** (183 mg, 567 μmol) in MeCN (1 mL) at 25 °C. After 28 h (the reaction was monitored by thin layer chromatography) the solvent was evaporated and residue was purified by column chromatography (silica gel, 18% EtOAC-hexane). Product **5e** was obtained as a yellow viscous liquid; yield: 46.3 mg (25%). IR (film): ν = 3420, 2940, 2850, 1750, 1160, 1030 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.15 (s, 1H), 5.94 (s, 1H), 4.68 (m, 1H), 3.75 (t, *J* = 6.35 Hz, 2H), 2.92 (t, *J* = 7.6 Hz, 2H), 2.61 (m, 4H), 1.96 (m, 1H), 1.79 (m, 1H), 1.66 (m, 3H), 1.53 (br s, 1H), 1.46 (m, 1H), 1.35 (m, 1H), 1.24 (m, 1H), 1.03 (m, 1H), 0.87 (m, 6H), 0.73 (m, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 172.42 (s), 155.22 (s), 138.71 (d), 122.18 (s), 107.12 (d), 74.71 (d), 62.75 (t), 47.31 (d), 41.21 (t), 34.56 (t), 33.25 (t), 31.69 (d), 28.80 (t), 26.55 (d), 24.02 (t), 23.74 (t), 22.35 (q), 21.09 (q), 16.62 (q); MS (EI, 70 eV): *m/z* (%) = 322 (13) [M^+], 184 (95), 138 (100), 95 (94); anal calcd. for $C_{19}H_{30}O_4$: C 70.77, H 9.38; found: C 70.77, H 9.40.

3-Methylenoct-4-yn-1-ol (3f)

The compound **3f** was obtained using 1b (604 mg, 4.00 mmol) and triethylamine (607 mg, 6.00 mmol) in THF (3 mL), CuI (30.5 mg, 160 μmol), $(PPh_3)_2PdCl_2$ (56.2 mg, 80.0 μmol) and 1-pentyne (**2f**; 489 mg, 8.00 mmol) in THF (3 mL) as described for **3a**. Column chromatography (silica gel, 2% EtOAC-hexane) afforded **3f** as a yellow viscous liquid; yield: 226 mg (41%). IR (film): ν = 3330, 3080, 2940, 2850, 2190, 1600 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ = 5.34 (d, *J* = 1.2 Hz, 1H), 5.24 (d, *J* = 0.8 Hz, 1H), 3.79 (m, 2H), 2.39 (t, *J* = 6.0 Hz, 2H), 2.28 (t, *J* = 7.05 Hz, 2H), 1.66 (br s, 1H, OH), 1.54 (m, 2H), 0.99 (t, *J* = 7.45 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 128.79 (s), 122.58 (t), 91.38 (s), 80.64 (s), 62.25 (t), 41.13 (t), 22.45 (t), 21.56 (t), 13.83 (q); MS (EI, 70 eV): *m/z* (%) = 138 (100) [M^+], 109 (38), 95 (75), 81 (22); anal. calcd. for $C_9H_{14}O$: C 78.21, H 10.21; found: C 77.85, H 10.43.

2-(2-Pent-1-ynyloxiranyl)ethanol (4f)

The compound **4f** was obtained using **3f** (258 mg, 1.87 mmol) and Na_2HPO_4 (664 mg, 4.68 mmol) in DCM (8 mL) and mCPBA (678 mg, 3.93 mmol) as described for **4a**. Column chromatography (silica gel, 12% EtOAC-hexane) afforded **4f** as a yellow oil; yield: 170 mg (59%). IR (film): ν = 3400, 3040, 2940, 2860, 2205, 1250 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ = 3.78 (m, 2H), 2.68 (d, *J* = 5.4 Hz, 1H), 2.76 (d, *J* = 5.4 Hz, 1H), 2.67 (br s, 1H, OH), 2.09 (t, *J* = 7.05 Hz, 2H), 1.88 (m, 2H), 1.44 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 84.79 (s), 78.29 (s), 59.49 (t), 54.51 (t), 49.62 (s), 39.22 (t), 21.94 (t), 20.69 (t), 13.54 (q); MS (EI, 70 eV): *m/z* (%) = 154 (2) [M^+], 139 (4), 111 (14), 95 (65), 79 (199), 67 (36); anal. calcd. for $C_9H_{14}O_2$: C 70.10, H 9.15; found: C 70.40, H 9.05.

2-(5-Propylfuran-3-yl)ethanol (5f)

A solution of $AuCl_3$ in MeCN (472 mg; 5% w/w, 23.6 mg, 77.8 μmol $AuCl_3$) was added to a solution of **4f** (160 mg, 1.04 mmol) in MeCN (1 mL) at 25 °C. After 9 h (the reaction was monitored by thin layer chromatography) the solvent was evaporated and residue was purified by column chromatography (silica gel, 8% EtOAC-hexane). The pure compound **5f** was obtained as a yellow viscous liquid; yield: 40.3 mg (25%). IR (film): ν = 3411, 2964, 2871, 1613, 1256, 1053 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.15 (s, 1H), 5.91 (s, 1H), 3.76 (t, *J* = 6.35 Hz, 2H), 2.63 (t, *J* = 6.4 Hz, 2H), 2.55 (t, *J* = 7.6 Hz, 2H), 1.64 (m, 2H), 1.62 (br s, 1H, OH), 0.95 (t, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 154.44 (s), 138.25 (d), 122.01 (s), 106.54 (d), 62.78 (t), 30.44 (t), 28.84 (t), 21.61 (t), 14.09 (q); MS (EI, 70 eV): *m/z* (%) = 154 (56) [M^+], 136 (2), 125 (100), 111 (5), 95 (9), 67 (12).

6-Diethoxymethylhept-6-en-4-yn-1-ol (3g)

The compound **3g** was obtained using 2-bromo-3,3-diethoxypropene (**1c**; 2.09 g, 10.0 mmol) and triethylamine (911 mg, 9.00 mmol) in THF (4 mL), CuI (45.7 mg, 240 μmol), $(PPh_3)_2PdCl_2$ (84.2 mg, 120 μmol) and **2a** (505 mg, 6.00 mmol) in THF (4 mL) as described for 3a. Column chromatography (silica gel, 10% EtOAC-hexane) furnished **3g** as a yellow viscous liquid; yield: 695 mg (55%). IR (film): ν = 3400, 3090, 2960, 2860, 2250, 1610, 1110 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ = 5.79 (s, 1H), 5.71 (s, 1H), 5.02 (s, 1H), 3.96 (t, *J* = 5.8 Hz, 2H), 3.84 (m, 2H), 3.71 (m, 2H), 2.65 (t, *J* = 6.9 Hz, 2H), 2.15 (br s, 1H, OH), 1.99 (m, 2H), 1.42 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 130.12 (s), 122.79 (t), 101.53 (d), 91.24 (s), 78.99 (s), 62.14 (t), 61.89 (t, 2C), 31.44 (t), 16.54 (t), 15.43 (q, 2C); MS (EI, 70 eV): *m/z* (%) = 212 (2) [M^+], 167 (8), 103 (100), 75 (60), 47 (57); anal. calcd. for $C_{12}H_{20}O_3$: C 67.89, H 9.50; found: C 67.15, H 9.64.

5-[(2-Diethoxymethyloxiranyl)]pent-4-yn-1-ol (4g)

The compound **4g** was obtained using 3 g (425 mg, 2.00 mmol) and Na_2HPO_4 (710 mg, 5.00 mmol) in DCM (8 mL) and mCPBA (725 mg, 4.20 mmol) as described for **4a**. Column chromatography (silica gel, 18% EtOAC-hexane) furnished **4g** as a yellow oil; yield: 139 mg (30%). IR (film): ν = 3420, 3050, 2960, 2860, 2220, 1100, 900 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ = 4.36 (s, 1H), 3.68 (m, 4H), 3.55 (m, 2H), 2.96 (d, *J* = 5.8 Hz, 1H), 2.89 (d, *J* =5.8 Hz, 1H), 2.31 (t, *J* = 6.9 Hz, 2H), 2.29 (br s, 1H, OH), 1.71 (m, 2H), 1.17 (m, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 101.69 (d), 85.04 (s), 76.57 (s,), 63.79 (t), 63.60 (t), 61.57 (t), 51.62 (s), 51.18 (t), 31.11 (t), 15.73 (t), 15.37 (q), 15.34 (q); MS (EI, 70 eV): *m/z* (%) = 228 (3) [M^+], 183 (12), 125 (6), 103 (100), 75 (27), 47 (26); anal. calcd. for $C_{12}H_{20}O_4$: C 63.14, H 8.83; found: C 63.11, H 8.65.

5-(3-Hydroxypropyl)furan-2-carbaldehyde (6)

A solution of $AuCl_3$ in MeCN (88.3 mg; 5% w/w, 4.41 mg, 14.5 μmol $AuCl_3$) was added to a solution of **4g** (66.2 mg, 290 μmol) in MeCN (0.5 mL) at 25 °C. After 1 h (the reaction was monitored by thin layer chromatography) the solvent was evaporated and residue was purified by column chromatography (silica gel, 30% EtOAC-hexane). Compound **6** was obtained as a yellow viscous liquid; yield: 30.7 mg (69%). IR (film): ν = 3400, 2920, 2860, 2710, 2240, 1680, 1120, 1040 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ = 9.85 (s, 1H), 7.95 (s, 1H), 6.41 (s, 1H), 3.69 (t, *J* = 6.3 Hz, 2H), 2.76 (t, *J* = 7.6 Hz, 2H), 1.90 (m, 2H), 1.88 (br s, 1H, OH); ^{13}C NMR ($CDCl_3$, 500 MHz): δ = 184.99 (d), 159.09 (s), 150.91 (d), 129.81 (s), 102.48 (d), 61.93 (t), 30.73 (t), 24.48 (t); MS (EI, 70 eV): *m/z* (%) = 154 (49) [M^+], 136 (100), 109 (60), 79 (22); HRMS (70 eV): calcd. for $C_8H_{10}O_3$ (M^+): 154.0630; found: 154.0630.

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