Supplementary Material (ESI) for Green Chemistry

Supplementary Information

Towards Sustainable Homogeneous Gold Catalysis: Cycloisomerization of Functionalized Allenes in Water

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General remarks

All reactions were carried out in demineralized water. The reactions were monitored by Thin Layer Chromatography (on Silica Gel 60 F_{254} from Merck) and the TLC's were stained with potassium permanganate solution or anisaldehyde solution. Flash chromatography was performed on silica gel from Macherey-Nagel (Kieselgel 60M, 0.04-0.063 mm) with a mixture of cyclohexane and ethyl acetate as eluent. The NMR spectra were recorded with a Bruker DRX 400 spektrometer and the deuterated solvent $CDCl_3$ ($\delta = 7.26$ (^1H) and $\delta = 77.2$ (^{13}C)) was used as internal standard. The signals of the major component of a diastereomeric mixture or a mixture of rotamers are marked with an asterisk (*). HR mass spectra were recorded using either EI ionization on a Finnigan MAT 830 or FAB ionization on a JEOL SX102A spectrometer.

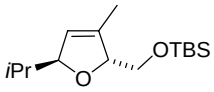
Starting materials

Chloroauric acid hydrate and lithium chloride (99%) were purchased from Aldrich and sodium tetrachloroaurate dihydrate from Alfa Aesar. The reagents were used without further purification. Due to the hygroscopic nature of these reagents, stock solutions in water were prepared directly after opening the package.
Used stock solutions in water: $HAuCl_4$ (10.3 mM), $NaAuCl_4$ (5.03 mM), LiCl (0.2 M).

General procedure for the gold-catalyzed cycloisomerization

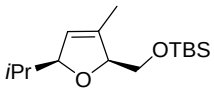
To a mixture of the allene **1** (50 mg) and 9 mL of demineralized water is added LiCl (1 equiv.; 0.2 M stock solution in water) and $HAuCl_4$ (5 mol%; 10.3 mM stock solution in H_2O). The yellow solution is stirred at room temperature until TLC control indicates full conversion. The aqueous solution is extracted three times with diethylether and the organic solvent is removed by evaporation. Purification of the crude product by flash chromatography (silica gel, cyclohexane / ethyl acetate) affords the 2,5-dihydrofurans **2**.

Analytical data for compounds 2a-e, 2g, 2h, 4a, 4b, 6a, 6b, 8



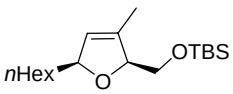
2-(*tert*-Butyldimethylsilyloxymethyl)-3-methyl-5-isopropyl-2,5-dihydrofuran (**2a**)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.46-5.40 (m, 1H, 4-H), 4.56-4.53 (m, 2H, 2-H + 5-H), 3.67-3.62 (m, 2H, 2-CH_2), 1.75 (s, 3H, 3-CH_3) 1.75-1.60 (m, 1H, 5-CH), 0.91-0.83 (m, 15H, SiC(CH_3)$_3$ + CH(CH_3)$_2$), 0.05 (s, 6H, Si(CH_3)$_2$).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.8 (x, C-3), 123.4 (+, C-4), 90.8 (+, C-2), 88.4 (+, C-5), 65.4 (–, 2-CH_2), 33.8 (+, 5-CH), 26.0 (+, SiC(CH_3)$_3$), 18.4 (x, SiC(CH_3)$_3$), 18.2/18.0 (2+, CH(CH_3)$_2$), 13.1 (+, 3-CH_3), -5.2/-5.3 (2+, Si(CH_3)$_2$).



2-(*tert*-Butyldimethylsilyloxymethyl)-3-methyl-5-isopropyl-2,5-dihydrofuran (**2b**)

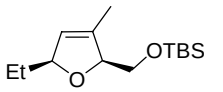
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.46-5.44 (m, 1H, 4-H), 4.58-4.52 (m, 1H, 5-H), 4.44-4.37 (m, 1H, 2-H), 3.67 (d, ^3J(H,H) = 4.8 Hz, 2H, 2-CH_2), 1.73 (s, 3H, 3-CH_3) 1.69-1.62 (m, 1H, 5-CH), 0.92 (d, ^3J(H,H) = 6.8 Hz, 3H, CH(CH_3)$_2$), 0.88 (s, 9H, SiC(CH_3)$_3$), 0.85 (d, ^3J(H,H) = 6.8 Hz, 3H, CH(CH_3)$_2$), 0.06/0.05 (s, 6H, Si(CH_3)$_2$).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.8 (x, C-3), 123.8 (+, C-4), 90.8 (+, C-2), 88.1 (+, C-5), 66.0 (–, 2-CH_2), 34.0 (+, 5-CH), 26.1 (+, SiC(CH_3)$_3$), 18.9/18.3 (2+, CH(CH_3)$_2$), 18.5 (x, SiC(CH_3)$_3$), 13.1 (+, 3-CH_3), -5.2/-5.3 (2+, Si(CH_3)$_2$).
IR (KBr): ν (cm^{-1}) = 3069 (w, C-H), 2957 (s, C-H), 2929 (s, C-H), 2896 (s, C-H), 2858 (s, C-H), 1666 (m, C=C).
HRMS (FAB) calcd for $[M-H]^+$ $C_{15}H_{29}O_2Si^+$ 269.1937, obsd 269.1964.



2-(*tert*-Butyldimethylsilyloxymethyl)-5-hexyl-3-methyl-2,5-dihydrofuran (**2c**)

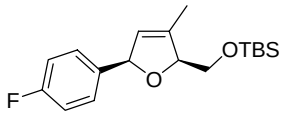
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.43 (s, 1H, 4-H), 4.70-4.62 (m, 1H, 5-H), 4.57-4.52 (m, 1H, 2-H), 3.66 (d, ^3J(H,H) = 4.3 Hz, 2H, 2-CH_2), 1.72 (s, 3H, 3-CH_3) 1.58-1.23 (m, 10H, Hex-CH_2), 0.91-0.84 (m, 12H, Hex-CH_3 + SiC(CH_3)$_3$), 0.06/0.05 (s, 6H, Si(CH_3)$_2$).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.7 (x, C-3), 125.6 (+, C-4), 88.2 (+, C-2), 85.6 (+, C-5), 65.8 (–, 2-CH_2), 37.3 (–, 5-CH_2), 32.0 (–, CH_2), 29.6 (–, CH_2), 26.1 (+, SiC(CH_3)$_3$), 25.7

(–, CH_2), 22.8 (–, CH_2), 18.5 (x, Si*C*$(CH_3)_3$), 14.2 (+, CH_3), 13.0 (+, 3-CH_3), -5.2/-5.3 (2+, Si$(CH_3)_2$).



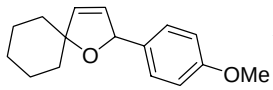
2-(*tert*-Butyldimethylsilyloxymethyl)-5-ethyl-3-methyl-2,5-dihydrofuran (**2d**)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.43-5.40 (m, 1H, 4-H), 4.63-4.57 (m, 1H, 5-H), 4.56-4.50 (m, 1H, 2-H), 3.64 (d, ^3J(H,H) = 4.5 Hz, 2H, 2-CH_2), 1.70 (s, 3H, 3-CH_3) 1.57-1.43 (m, 2H, 5-CH_2), 0.90-0.84 (m, 12H, 5-CH_3 + SiC(C*H*$_3)_3$), 0.04/0.03 (s, 6H, Si(C*H*$_3)_2$).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.1 (x, C-3), 125.2 (+, C-4), 88.2 (+, C-2), 86.7 (+, C-5), 65.9 (–, 2-CH_2), 29.9 (–, 5-CH_2), 26.1 (+, SiC(*C*$H_3)_3$), 18.5 (x, Si*C*$(CH_3)_3$), 13.0 (+, 3-CH_3), 9.8 (+, 5-CH_2*C*H_3), -5.2/-5.3 (2+, Si$(CH_3)_2$).



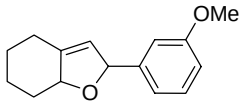
2-(*tert*-Butyldimethylsilyloxymethyl)-5-(4-fluorophenyl)-3-methyl-2,5-dihydrofuran (**2e**)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41-7.36 (m, 1H, Ar-H), 7.29-7.24 (m, 1H, Ar-H), 7.04-6.96 (m, 2H, Ar-H), 5.72-5.68 (m, 1H, 4-H), 5.66-5.62* (m, 1H, 4-H), 5.54-5.51 (m, 1H, 5-H), 5.50-5.48* (m, 1H, 5-H), 4.84-4.79 (m, 1H, 2-H), 4.72-4.67* (m, 1H, 2-H), 3.86-3.74 (m, 2H, 2-CH_2), 1.82 (s, 3H, 3-CH_3), 0.91 (s, 9H, SiC(C*H*$_3)_3$), 0.09/0.08 (s, 6H, Si(C*H*$_3)_2$), 0.07/0.06* (s, 6H, Si(C*H*$_3)_2$).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.7*/161.3 (x, C-4'), 138.5*/138.4 (x, C-1'), 137.7*/137.6 (x, C-3), 128.9/128.8/128.3/128.2/125.5/125.5 (6+, C-2' + C-3' + C-5' + C-6') 115.3/115.0* (+, C-4), 88.9/88.7* (+, C-2), 86.9/86.3* (+, C-5), 65.1*/64.8 (–, 2-CH_2), 26.1*/26.0 (+, SiC(*C*$H_3)_3$), 18.5*/18.4 (x, Si*C*$(CH_3)_3$), 12.8/12.7* (+, 3-CH_3), -5.4/-5.5/-5.6/-5.7 (4+, Si$(CH_3)_2$).
IR (KBr): ν (cm^{-1}) = 2955 (s, C-H), 2929 (s, C-H), 2885 (s, C-H), 2857 (s, C-H), 1727 (m, C=C).
HRMS (EI) calcd for $[M]^+$ $C_{18}H_{27}FO_2Si^+$ 322.1764, obsd 322.1759.



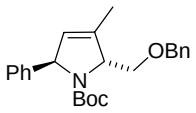
1-Oxa-2-(4-methoxyphenyl)spiro[5.4]-dec-3-ene (**2g**)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23 (d, ^3J(H,H) = 8.7 Hz, 2H, Ar-H), 6.85 (d, ^3J(H,H) = 8.7 Hz, 2H, Ar-H), 6.02-5.97 (m, 1H, 2-H), 5.75-5.70 (m, 2H, 3-H + 4-H), 3.77 (s, 3H, OCH_3), 1.79-1.38 (m, 10H, Cy-CH_2).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.3 (x, C-4'), 134.7 (+, C-3), 134.1 (+, C-4), 129.2, 128.1 (2+, C-2'), 127.8 (x, C-1'), 113.9, 113.6 (2+, C-3'), 90.1 (x, C-5), 86.1 (+, C-2), 55.4 (+, OCH_3), 38.6, 37.6, 22.6, 23.8, 23.5 (5–, Cy-CH_2).
IR (KBr): ν (cm^{-1}) = 3000 (m, C-H), 2933 (s, C-H), 2857 (s, C-H), 1678 (m), 1609 (s), 1512 (s), 1247 (s).
HRMS (EI) calcd for $[M]^+$ $C_{16}H_{20}O_2^+$ 244.1463, obsd 244.1458.



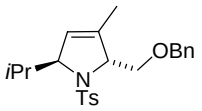
2-(3-Methoxyphenyl)-2,4,5,6,7,7a-hexahydrobenzofuran (**2h**)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29-7.22 (m, 1H, 5'-H), 6.95-6.85 (m, 2H, 4'-H + 6-H'), 6.83-6.78 (m, 1H, 2'-H), 5.73 (d, ^3J(H,H) = 5.0 Hz, 1H, 2-H), 5.45-5.43*/5.37-5.34 (m, 1H, 3-H), 4.74-4.67*/4.64-4.57 (m, 1H, 5-H), 3.80 (s, 3H, OCH_3), 2.63-2.54 (m, 1H, 4-H/5-H/6-H/7-H), 2.33-2.23 (m, 1H, 4-H/5-H/6-H/7-H), 2.11-2.00 (m, 1H, 4-H/5-H/6-H/7-H), 1.88-1.79 (m, 2H, 4-H/5-H/6-H/7-H), 1.43-1.17 (m, 3H, 4-H/5-H/6-H/7-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9*/159.8 (x, C-3'), 144.8*/144.6 (x, C-3a), 142.8*/142.7 (x, C-1'), 129.6*/129.5 (+, C-5'), 120.0/119.3* (+, C-3/C-6'), 119.1/118.7* (+, C-3/C-6'), 113.1/113.0* (+, C-2'/C-4'), 112.4/111.8* (+, C-2'/C-4'), 87.3/87.2* (+, C-2), 85.3/85.1* (+, C-7a), 55.4*/55.3 (+, OCH_3), 36.5/35.7*, 27.4*/27.2, 26.9*/26.8, 23.5/23.4 (4+, C-4 + C-5 + C-6 + C-7).
IR (KBr): ν (cm^{-1}) = 2998 (m, C-H), 2935 (s, C-H), 2856 (s, C-H), 1670 (m), 1601 (s), 1487 (s), 1436 (s), 1264 (s).
HRMS (EI) calcd for $[M]^+$ $C_{15}H_{18}O_2^+$ 230.1307, obsd 230.1301.



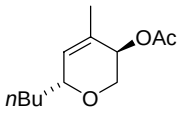
tert-Butyl 2-(benzyloxymethyl)-3-methyl-5-phenyl-2,5-dihydro-2*H*-pyrrole-1-carboxylate (**4a**)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37-7.15 (m, 10H, Ar-H), 5.45-5.40 (m, 1H, 4-H), 5.36-5.30 (m, 1H, 5-H), 4.72-4.68 (m, 1H, 2-H), 4.63 (d, ^2J(H,H) = 12.4 Hz, 1H, CH_2Ph), 4.56 (d, ^2J(H,H) = 12.4 Hz, 1H, CH_2Ph), 4.13 (dd, ^2J(H,H) = 10.3 Hz, ^3J(H,H) = 3.8 Hz, 1H, 2-CH_2), 3.72 (dd, ^2J(H,H) = 10.3 Hz, ^3J(H,H) = 2.0 Hz, 1H, 2-CH_2), 1.80 (s, 3H, 3-CH_3), 1.35/1.09* (s, 9H, $OC(CH_3)_3$).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.7*/152.9 (x, OCON), 143.8*/142.6, 138.8*/138.4 (2x, Ar-C), 135.3 (x, C-3), 128.5/128.4*, 128.4/128.2*, 127.7/127.6*, 127.6/127.5*, 127.1*/127.0, 126.7*/126.6, 126,4*/126.2 (7+, Ar-C + C-4), 79.7/79.5* (x, O*C*$(CH_3)_3$), 73.5/73.4* (–, *C*H_2Ph), 68.8/67.1* (–, 2-CH_2), 68.8*/68.5, 67.5*/67.4 (2+, C-2 + C-5), 28.5*/28.1 (+, $OC(CH_3)_3$), 14.1/13.9* (+, 3-CH_3).



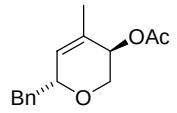
2-(Benzyloxymethyl)-5-isopropyl-3-methyl-1-tosyl-2,5-dihydro-2*H*-pyrrole (**4b**)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, ^3J(H,H) = 8.1 Hz, 2H, Ar-H), 7.31-7.25 (m, 3H, Ar-H), 7.19 (d, ^3J(H,H) = 8.1 Hz, 2H, Ar-H), 7.13 (d, ^3J(H,H) = 6.5 Hz, 2H, Ar-H), 5.38 (s, 1H, 4-H), 4.53-4.49 (m, 1H, 2-H/5-H), 4.47-4.44 (m, 1H, 2-H/5-H), 4.27 (d, ^2J(H,H) = 12.1 Hz, 1H, CH_2Ph), 4.07 (d, ^2J(H,H) = 12.1 Hz, 1H, CH_2Ph), 4.01 (dd, ^2J(H,H) = 10.5 Hz, ^3J(H,H) = 2.8 Hz, 1H, 2-CH_2), 3.54 (dd, ^2J(H,H) = 10.5 Hz, ^3J(H,H) = 1.7 Hz, 1H, 2-CH_2), 2.75-2.65 (m, 1H, 5-CH), 2.35 (s, 3H, Ar-CH_3), 1.66 (s, 3H, 3-CH_3), 0.90 (d, ^3J(H,H) = 6.9 Hz, 3H, CH(CH_3)$_2$), 0.63 (d, ^3J(H,H) = 6.9 Hz, 3H, CH(CH_3)$_2$).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.6, 139.3, 138.2 (3x, Ar-C), 136.5 (x, C-3), 129.3, 128.3, 127.6, 127.5, 126.8 (5+, Ar-C), 120.9 (+, C-4), 72.8 (–, *C*H_2Ph), 72.6 (–, 2-CH_2), 70.4 (+, C-5), 67.3 (+, C-2), 30.7 (+, 5-CH), 21.5 (+, Ar-*C*H_3), 19.6 (+, 3-CH_3), 15.2, 13.8 (2+, CH(*C*H_3)$_2$).



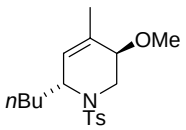
6-Butyl-4-methyl-3,6-dihydro-2*H*-pyran-3-yl acetate (**6a**)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.62 (s, 1H, 5-H), 5.21-5.16 (m, 1H, 3-H), 4.11-4.05 (m, 1H, 6-H), 4.03 (dd, ^2J(H,H) = 11.8 Hz, ^3J(H,H) = 4.5 Hz, 1H, 2-H), 3.53 (dd, ^2J(H,H) = 11.8 Hz, ^3J(H,H) = 5.7 Hz, 1H, 2-H), 2.09 (s, 3H, $COCH_3$), 1.70 (s, 3H, 4-CH_3), 1.58-12.7 (m, 6H, Bu-CH_2), 0.91-0.85 (m, 3H, Bu-CH_3).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.1 (x, *C*OCH_3), 130.5 (x, C-4), 129.7 (+, C-5), 73.7 (+, C-3), 67.9 (+, C-6), 64.8 (–, C-2), 33.7 (–, Bu-CH_2), 27.7 (–, Bu-CH_2), 22.8 (–, Bu-CH_2), 21.2 (+, CO*C*H_3), 19.3 (+, 4-CH_3), 14.2 (+, Bu-CH_3).



6-Benzyl-4-methyl-3,6-dihydro-2*H*-pyran-3-yl acetate (**6b**)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34-7.18 (m, 5-H, Ar-H), 5.62 (s, 1H, 4-H), 5.24-5.18 (m, 1H, 2-H), 4.39-4.32 (m, 1H, 6-H), 4.10 (dd, ^2J(H,H) = 11.8 Hz, ^3J(H,H) = 4.5 Hz, 1H, 2-H), 3.58 (dd, ^2J(H,H) = 11.8 Hz, ^3J(H,H) = 5.8 Hz, 1H, 2-H), 2.91 (dd, ^2J(H,H) = 13.6 Hz, ^3J(H,H) = 7.7 Hz, 1H, 6-CH_2), 2.74 (dd, ^2J(H,H) = 13.6 Hz, ^3J(H,H) = 6.5 Hz, 1H, 6-CH_2), 2.09 (s, 3H, $COCH_3$), 1.71 (s, 3H, 4-CH_3).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.0 (x, *C*OCH_3), 138.0 (x, Ar-C), 131.2 (x, C-4), 129.4, 128.6, 128.5 (3+, Ar-C), 126.5 (+, C-5), 74.7 (+, C-3/C-6), 67.7 (+, C-3/C-6), 64.9 (–, C-2), 40.5 (–, 6-CH_2), 21.1 (+, CO*C*H_3), 19.4 (+, 4-CH_3)
IR (KBr): ν (cm^{-1}) = 3062 (w, C-H), 3028 (w, C-H), 2972 (w, C-H), 2921 (w, C-H), 2859 (w, C-H), 1736 (s, C=O), 1369 (m), 1236 (s), 1030 (s).
HRMS (CI) calcd for $[M+H]^+$ $C_{15}H_{19}O_3^+$ 247.1329, obsd 247.1335.



2-Butyl-5-methoxy-4-methyl-1-tosyl-1,2,5,6-tetrahydropyridine (**8**)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76*/7.70 (d, ^3J(H,H) = 8.3 Hz, 2H, Ar-H), 7.27/7.23* (d, ^3J(H,H) = 8.3 Hz, 2H, Ar-H), 5.58-5.53*/5.45-5.42 (m, 1H, 3-H), 4.21-4.18/4.15-4.03* (m, 2H, 2-H + 6-H), 3.34-3.19 (m, 4H, 5-H + OCH_3), 3.10*/2.91 (dd, ^2J(H,H) = 14.8 Hz, ^3J(H,H) = 2.2 Hz, 1H, 6-H), 2.42/2.40* (s, 3H, Ar-CH_3), 1.73*/1.68 (s, 3H, 4-CH_3), 1.61-1.55 (m, 2H, Bu-CH_2), 1.41-1.23 (m, 4H, Bu-CH_2), 0.91-0.84 (m, 3H, Bu-CH_3).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.3/142.9*, 138.3/138.1* (2x, Ar-C), 134.8/131.9* (x, C-4), 129.7/129.2*, 127.8*/127.1 (2+, Ar-C), 126.0*/125.3 (+, C-3), 75.2*/73.3 (+, C-5), 57.7/56.7* (+, C-2), 53.9/53.5* (+, OCH_3), 42.2/41.0* (–, C-6), 34.0/33.6*, 28.5/28.1*, 22.8*/22.7 (3–, Bu-CH_2), 21.6 (+, Ar-CH_3), 21.2*/18.8 (+, 4-CH_3), 14.1 (+, Bu-CH_3).
IR (KBr): ν (cm^{-1}) = 3294 (w, C-H), 3027 (s, C-H), 2930 (s, C-H), 2823 (s, C-H), 1915 (m), 1738 (m), 1598 (s), 1494 (s), 1453 (s), 1383 (s).
HRMS (FAB) calcd for $[M-H]^+$ $C_{18}H_{26}NO_3S^+$ 336.1633, obsd 336.1626.