Cationic Gold(I)-Catalyzed Enantioselective Hydroalkylation of Unactivated Alkenes: Influence of the Chloride Scavenger on the Stereoselectivity

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Supporting Information

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General information

Unless otherwise stated, commercially available reagents were used as received without further purification. \((R)\)-DTBM-SEGPHOS was purchased from Aldrich. \(\text{Cu(OTf)}_2\) was purchased from Alfa Aesar. JohnPhosAuCl was either purchased from Strem Chemicals or prepared from \(\text{Me}_2\text{S} \cdot \text{AuCl}\) (Aldrich) and JohnPhos (Aldrich).\(^1\) Compounds A\(_1\), \(^2\) A\(_1\)'\(^2\), A\(_2\), \(^3\) B\(_1\), \(^4\) B\(_2\), \(^5\) C\(_1\), \(^6\) C\(_2\), \(^7\) D, \(^8\) E, \(^9\) G, \(^10\) H, \(^11\) I, \(^12\) and K\(^13\) have been previously described. Complexes F\(^12,14\) and J\(^15\) are new but structurally close to other previously reported gold catalyst. Bis-oxazoline and Salen copper complexes were either generated in situ from \(\text{Cu(OTf)}_2\) and L\(_1\)-L\(_5\), or isolated prior to use in the catalytic reaction in the case of L\(_1\)Cu(SbF\(_6\))\(_2\).\(^16\) Toluene was distilled over calcium hydride. Tetrahydrofuran (THF) was distilled over sodium. Dioxane and MeNO\(_2\) were used without purification. Products were purified by flash column chromatography on 40-63 \(\mu\)m silica gel. Analytical thin-layer chromatography (TLC) was performed on TLC silica gel plates (0.25 mm) precoated with a fluorescent indicator. Visualization was made with ultraviolet light and/or \(p\)-anisaldehyde stain.

NMR spectra were recorded on AM250, AV300, AV360, DRX400 MHz Bruker spectrometers. Chemical shifts are given in ppm. The spectra were calibrated to the residual \(^1\)H and \(^13\)C signals of the solvent. Data are represented as follows: chemical shift \(\delta\) (ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant \(J\) (Hz) and integration. High-resolution mass spectra were obtained by electrospray ionization on a TOF instrument (MicrOTOFq Bruker spectrometer).

Compounds 1a, 1b, 2a, 2a′, and 2b were already described.\(^17\)
Preparation of the gold complex J

(3aS,8aS)-2,2-Dimethyl-4,4,8,8-tetraphenyl-6-(p-tolyloxy)tetrahydro-[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphepine-(AuCl) (J)\(^{15}\)

To a solution of Me\(_2\)S•AuCl (1 equiv) in CH\(_2\)Cl\(_2\) (0.315 M) was added a solution of (−)TAD-P-cresol\(^{18}\) in CH\(_2\)Cl\(_2\) (0.0315 M). The mixture was stirred for 1.5 h at room temperature and then evaporated under reduced pressure to give the gold complex as a white solid, which was used without purification. \(^1\)H NMR (360 MHz / CDCl\(_3\)): δ 7.60–7.51 (m, 4H), 7.49–7.28 (m, 16H), 7.02 (d, J = 8.6 Hz, 2H), 6.65 (d, J = 8.6 Hz, 2H), 5.48 (d, J = 8.0 Hz, 1H), 5.42 (d, J = 8.0 Hz, 1H), 2.29 (s, 3H), 0.68 (s, 3H), 0.63 (s, 3H); \(^3\)P NMR (101 MHz / CDCl\(_3\)): 105.9; \(^{13}\)C NMR (90 MHz / CDCl\(_3\)): 147.4, 143.1, 142.7, 139.22, 139.16, 138.9, 138.8, 135.5, 130.3, 129.1, 128.9, 128.8, 128.6, 128.3, 128.0, 127.6, 127.5, 127.24, 127.20, 120.4, 120.3, 114.8, 92.6, 92.4, 89.3, 89.2, 80.51, 80.45, 79.21, 79.20, 29.7, 26.5, 26.4, 20.7.

Preparation of the substrates

N-Benzyl-2-oxo-N-(prop-2-en-1-yl)cyclopentane-1-carboxamide (1b)

According a published procedure,\(^{17}\) a solution of N-benzylprop-2-en-1-amine (2.9 g, 20.00 mmol, 1 equiv), ethyl 2-oxocyclopentane carboxylate (4.5 g, 28.80 mmol, 1.44 equiv) and DMAP (0.3 equiv) in toluene (15 mL) was refluxed for 22 h. The solvent was then removed under reduced pressure and the residue was purified by flash chromatography on silica gel (cyclohexane/EtOAc: 5:1) to give the desired product (3.5 g, 68%) and as mixture of tautomers and rotamers. \(^1\)H NMR (360 MHz / CDCl\(_3\)): δ 7.34–7.13 (m, 5H), 5.80–5.68 (m, 1H), 5.18–5.09 (m, 2H), 4.96 (t, J=20.4 Hz, 1H), 4.44–4.17 (m, 2H), 3.77–3.56 (m, 1H), 3.44–3.36 (m, 1H), 2.56–2.44 (m, 1H), 2.31–2.23 (m, 2H), 2.20–2.04 (m, 2H), 1.86–1.70 (m, 1H); \(^{13}\)C NMR (90 MHz / CDCl\(_3\)): 2 rotamers δ 214.6 (2 C), 169.5 (C), 169.3 (C), 137.1 (C), 136.8 (C), 133.0 (CH), 132.4 (CH), 128.9 (CH), 128.6 (2 CH), 127.7 (2 CH), 127.5 (CH), 127.2 (2 CH), 126.2 (2 CH), 117.1 (CH\(_2\)), 116.6 (CH\(_2\)), 52.1 (CH), 52.0 (CH), 50.2 (CH\(_2\)), 49.2 (CH\(_2\)), 48.6 (CH\(_2\)), 48.3 (CH\(_2\)), 38.6 (2 CH\(_2\)), 27.6 (CH\(_2\)), 27.5 (CH\(_2\)), 21.0 (2 CH\(_2\)); HRMS (ESI): m/z calcd. for C\(_{16}\)H\(_{19}\)NO\(_2\)Na (M + Na\(^+\)) 280.1308, found 280.1296.

N- Allyl-N-benzyl-1-oxo-1,2,3,4-tetrahydroxynaphthalene-2-carboxamide (1c)

S3
According a published procedure, the reaction was performed with methyl 1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (1.57 g, 7.69 mmol) to afford 1c (1.54 g, 63%) as an orange oil and as mixture of tautomers and rotamers. \(^{1}\text{H} \text{NMR (250 MHz / CDCl}_3\): \(\delta\) 8.06–8.00 (m, 1H), 7.51–7.19 (m, 8H), 5.86–5.75 (m, 1H), 5.40–5.15 (m, 2H), 4.81–4.04 (m, 3H), 3.83–3.72 (m, 2H), 3.09–2.88 (m, 2H), 2.68–2.58 (m, 1H), 2.30–2.18 (m, 1H); \(^{13}\text{C NMR (63 MHz / CDCl}_3\):} 2 rotamers \(\delta\) 194.6 (2 C), 170.7 (C), 170.5 (C), 144.1 (2 C), 137.2 (C), 136.9 (C), 133.8 (2 CH), 133.3 (2 CH), 132.4 (C), 132.0 (C), 128.9 (2 CH), 128.8 (2 CH), 128.6 (2 CH), 127.8 (2 CH), 127.5 (2 CH), 127.2 (2 CH), 126.7 (2 CH), 126.2 (2 CH), 117.2 (CH\(_2\)), 116.4 (CH\(_2\)), 51.8 (2 CH), 50.3 (CH\(_2\)), 49.2 (CH\(_2\)), 48.5 (CH\(_2\)), 48.2 (CH\(_2\)), 28.4 (CH\(_2\)), 28.2 (CH\(_2\)), 26.7 (CH\(_2\)), 26.6 (CH\(_2\)); \text{HRMS (ESI):} m/z calcd. for C\(_{21}\)H\(_{21}\)NO\(_2\)Na (M + Na\(^+\)) 342.1465, found 342.1458.

\(\text{N-Allyl-N benzyl-2-methyl-3-oxobutanamide (1d)}\)

According a published procedure, the reaction was performed with methyl 2-methyl-3-oxobutanoate (1.121 g, 8.62 mmol) to afford 1d (813 mg, 38%) as a yellow oil and as mixture of tautomers and rotamers. \(^{1}\text{H NMR (360 MHz / CDCl}_3\):} 2 rotamers \(\delta\) 7.37–7.15 (m, 10H), 5.79–5.69 (m, 2H), 5.19–5.14 (m, 4H), 4.76–4.43 (m, 2H), 4.47–4.43 (m, 2H), 4.19–3.57 (m, 6H), 2.16 (s, 3H), 2.12 (s, 3H), 1.38 (d, \(J = 7\) Hz, 3H), 1.34 (d, \(J = 7\) Hz, 3H); \(^{13}\text{C NMR (90 MHz / CDCl}_3\):} 2 rotamers \(\delta\) 204.8 (C), 204.7 (C), 170.9 (C), 170.8 (C), 137.1 (C), 136.4 (C), 132.6 (CH), 132.3 (CH), 128.9 (2 CH), 128.5 (2 CH), 128.0 (2 CH), 127.7 (2 CH), 127.4 (CH), 126.2 (CH), 117.6 (CH\(_2\)), 117.0 (CH\(_2\)), 51.4 (CH), 51.3 (CH), 50.3 (CH\(_2\)), 49.2 (CH\(_2\)), 48.4 (CH\(_2\)), 48.3 (CH\(_2\)), 27.2 (2 CH\(_3\)), 13.9 (2 CH\(_3\)); \text{HRMS (ESI):} m/z calcd. for C\(_{15}\)H\(_{20}\)NO\(_2\) (M + H\(^+\)) 246.1489, found 246.1492.

\(\text{N-Allyl-N benzyl-2-ethyl-3-oxobutanamide (1e)}\)

To a solution of \(\text{N-allyl-N benzyl-3-oxobutanamide}^{17}\) (500 mg, 2.16 mmol, 1 equiv) in dry DMF (8 mL) at 0 °C was added K\(_2\)CO\(_3\) (1.804 g, 13.05 mmol, 6 equiv). The mixture was stirred for 20 min and iodoethane (677 \(\mu\)L, 8.47 mmol, 3.9 equiv) was then added dropwise. The mixture was stirred at room temperature for 16 h. Water was then added at 0 °C and the mixture was extracted with EtOAc. The combined organic phases were washed with brine, dried over MgSO\(_4\) and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel (cyclohexane/EtOAc: 5/1) to give 1e in 89% yield (500 mg) as an orange oil and as mixture of tautomers and rotamers. \(^{1}\text{H NMR (360 MHz / CDCl}_3\):} 2 rotamers \(\delta\) 7.35–7.14 (m, 10H), 5.76–5.68 (m, 2H), 5.24–5.06 (m, 4H), 4.85–4.69 (m, 2H), 4.42–4.35 (m, 2H), 4.30–3.96 (m, 2H), 3.78–3.72 (m, 2H), 3.48–3.44 (m, 2H), 2.14 (d, \(J = 9.6\) Hz, 6H), 2.20–1.97 (m, 2H), 1.94–1.86 (m, 2H), 0.90 (dt, \(J = 21.8, 7.3\) Hz, 6H); \(^{13}\text{C NMR (90 MHz / CDCl}_3\):} 2 rotamers \(\delta\) 205.3 (2C), 169.6 (C), 169.4 (C), 137.4 (C), 136.6
(C), 132.7 (CH), 132.6 (CH), 129.0 (CH), 128.7 (2 CH), 128.2 (2 CH), 127.8 (CH), 127.6 (2 CH), 126.5 (2 CH), 117.8 (CH₂), 117.2 (CH₂), 60.1 (CH), 60.0 (CH), 50.2 (CH₂), 49.2 (CH₂), 48.8 (CH₂), 48.6 (CH₂), 27.0 (2 CH₃), 23.0 (2 CH₃), 12.3 (2 CH₃); HRMS (ESI): m/z calcd. for C₁₆H₂₁NO₂Na (M + Na)⁺ 282.1465, found 282.1465

*N-Allyl-N,2-dibenzyl-3-oxobutanamide (1f)*

This compound was prepared according to the procedure described for 1e with N-allyl-N-benzyl-3-oxobutanamide (0.5 g, 2.16 mmol, 1 equiv) and benzylbromide (1.0 mL, 8.64 mmol, 4 equiv). The crude product was purified by flash chromatography on silica gel (cyclohexane/EtOAc: 5/1) to afford 1f in 86% yield (600 mg) as a colorless oil and as mixture of tautomers and rotamers. ¹H NMR (360 MHz / CDCl₃): 2 rotamers δ 7.36–6.83 (m, 20H), 5.75–5.42 (m, 4H), 4.69–4.06 (m, 4H), 3.89–3.69 (m, 4H), 3.53 (dd, J = 17.7, 4.9 Hz, 1H), 3.36–3.27 (m, 2H), 3.21–3.09 (m, 2H), 2.18 (d, J = 20.7 Hz, 6H); ¹³C NMR (90 MHz / CDCl₃): 2 rotamers δ 204.0 (2C), 169.3 (C), 169.0 (C), 138.6 (C), 138.5 (C), 137.1 (C), 136.4 (C), 129.2 (4 CH), 129.0 (2 CH), 128.7 (6 CH), 128.3 (2 CH), 127.7 (CH), 127.6 (CH), 126.8 (2 CH), 126.5 (2 CH), 118.0 (CH₂), 117.3 (CH₂), 60.0 (CH), 59.7 (CH), 50.2 (CH₂), 49.3 (CH₂), 48.9 (CH₂), 48.9 (CH₂), 35.6 (2 CH₂), 27.7 (CH₃), 27.6 (CH₃); MS (CI): m/z calcd. for C₂₁H₂₄NO₂ (M + H)⁺ 322.18, found 322.2.

*N-Allyl-N-benzyl-2-methyl-3-oxopentanamide (1g)*

This compound was prepared according to the procedure described for 1e with N-allyl-N-benzyl-3-oxopentanamide (1.0 g, 4.08 mmol, 1 equiv) and iodomethane (1.0 mL, 16.31 mmol, 4 equiv). The crude product was purified by flash chromatography on silica gel (cyclohexane/EtOAc: 5/1) to afford 1g in 94% yield (1.0 g) as a yellow oil and as mixture of tautomers and rotamers. ¹H NMR (250 MHz / CDCl₃): δ 7.39–7.23 (m, 5H), 5.82–5.67 (m, 1H), 5.26–5.08 (m, 2H), 4.79–4.40 (m, 2H), 4.21–3.73 (m, 2H), 3.69–3.59 (m, 1H), 2.63–2.39 (m, 2H), 1.38 (dd, J = 9.8, 6.9 Hz, 3H), 1.02 (dd, J = 14.2, 7.3 Hz, 3H); ¹³C NMR (90 MHz / CDCl₃): 2 rotamers δ 207.6 (2C), 171.2 (C), 171.1 (C), 137.3 (C), 136.6 (C), 132.8 (CH), 132.6 (CH), 129.1 (CH), 128.7 (2 CH), 128.2 (2 CH), 127.9 (CH), 127.6 (2 CH), 126.4 (2 CH), 117.8 (CH₂), 117.2 (CH₂), 51.0 (CH₂), 50.9 (CH₂), 50.5 (CH), 49.4 (CH), 48.7 (CH₂), 48.5 (CH₂), 33.0 (2 CH₂), 14.1 (2 CH₃), 7.8 (2 CH₃); HRMS (ESI): m/z calcd. for C₁₆H₂₁NO₂Na (M + Na)⁺ 282.1465, found 282.1463.
Procedures for enantioselective hydroalkylation of ene-β-ketoamides

Enantioselective hydroalkylation of ene-β-ketoamide 1a using an achiral gold complex and a chiral copper complex (Table S1)

In air, a 10 mL oven-dried tube equipped with a Teflon-coated magnetic stir bar was charged with copper (II) triflate (3.6 mg, 0.010 mmol, 0.1 equiv), ligand L1-L5 (0.010 mmol, 0.1 equiv) and toluene (0.5 mL) and the mixture was stirred at room temperature for 5 min. (JohnPhos)AuCl (10 mol% of gold) and substrate 1a (27.3 mg, 0.10 mmol, 1 equiv) in toluene (0.5 mL) were added and the tube was sealed with a plastic stopper. The reaction tube was immersed and stirred in a preheated oil bath at 110 °C (external temperature) for 24 h. Then the reaction mixture was filtered through a pad of silica gel, rinsed with diethyl ether and evaporated to afford the crude product. Conversion and diastereoselectivity were determined by $^1$H NMR analysis and enantioselectivity was analyzed by SFC.

Solvent and gold catalyst screening in the enantioselective hydroalkylation of ene-β-ketoamide 1a (Table 2). A 10 mL oven-dried tube equipped with a Teflon-coated magnetic stir bar was charged with gold complex (10 mol% of gold), silver (I) triflate (2.6 mg, 0.010 mmol, 0.1 equiv) and solvent (0.5 mL) and the mixture was stirred at room temperature for 1 min. Substrate 1a (27.3 mg, 0.10 mmol, 1 equiv) in solvent (0.5 mL) was added and the tube was sealed with a plastic stopper. The reaction tube was covered by aluminum foil, immersed and stirred in a preheated oil bath at indicated temperature for 24 h. Then, the reaction mixture was filtered through a short pad of silica gel, rinsed with diethyl ether, and evaporated to afford the crude product, which was analyzed by SFC.

Screening of activators in the enantioselective hydroalkylation of ene-β-ketoamide 1a (Table 1, Table 2 entry 9, and Table 3). A 10 mL oven-dried tube equipped with a Teflon-coated magnetic stir bar was charged with C1 (8.2 mg, 0.0050 mmol, 0.05 equiv), Lewis acid (x mol%) and toluene (0.5 mL) and the mixture was stirred at room temperature for 1 min. Substrate 1a (27.3 mg, 0.10 mmol, 1 equiv) in toluene (0.5 mL) was added and the tube was sealed with a plastic stopper. The reaction tube covered by aluminum foil, immersed and stirred in a preheated oil bath at indicated temperature. Then, the reaction mixture was filtered through a short pad of silica gel, rinsed with diethyl ether and evaporated to afford the crude product, which was analyzed by SFC.

Procedure for Table 4. The above procedure was used with AgOTf (2.6 mg, 0.010 mmol) and substrate 1b-g (0.1 mmol).
Additional experiments not described in the manuscript

The unexpected activity of copper in the reaction of 1a encouraged us to briefly examine the case of chiral ligands located at copper instead of gold (Table S1). With the inactive achiral monogold precatalyst (JohnPhos)AuCl, a preliminary control experiment showed that addition of Cu(OTf)₂ eventually provided the desired product in a 75/25 ratio (entry 1). Addition of bis-oxazoline or Salen ligands L₁-5 resulted in low enantioinductions (entries 2–6). Interestingly, the teamwork between gold and copper in this transformation was revealed when using Cu/L₂ without gold (entry 7), leading to 2a’ as major product instead of 2a with Au/Cu/L₂ (entry 3). Besides, the enantioselectivity was greatly lowered in the absence of gold. Finally, in contrast with L₁/Cu(OTf)₂, the use of L₁Cu(SbF₆)₂ in the Au/Cu-catalyzed reaction led to a racemic mixture (entry 8), emphasizing a strong counterion effect in this chemistry.

Table S1 Enantioselective hydroalkylation of ene-β-ketoamide 1a using an achiral gold complex and a chiral copper complex

<table>
<thead>
<tr>
<th>Entry</th>
<th>[Au]</th>
<th>L</th>
<th>Conv (%)</th>
<th>dr</th>
<th>ee (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(JohnPhos)AuCl</td>
<td>none</td>
<td>100</td>
<td>75/25</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>(JohnPhos)AuCl</td>
<td>L₁</td>
<td>100</td>
<td>68/32</td>
<td>15/3</td>
</tr>
<tr>
<td>3</td>
<td>(JohnPhos)AuCl</td>
<td>L₂</td>
<td>100</td>
<td>66/34</td>
<td>38/5</td>
</tr>
<tr>
<td>4</td>
<td>(JohnPhos)AuCl</td>
<td>L₃</td>
<td>89</td>
<td>67/33</td>
<td>24/2</td>
</tr>
<tr>
<td>5</td>
<td>(JohnPhos)AuCl</td>
<td>L₄</td>
<td>100</td>
<td>41/59</td>
<td>5/7</td>
</tr>
<tr>
<td>6</td>
<td>(JohnPhos)AuCl</td>
<td>L₅</td>
<td>100</td>
<td>50/50</td>
<td>0/8</td>
</tr>
<tr>
<td>7</td>
<td>none</td>
<td>L₂</td>
<td>100</td>
<td>36/64</td>
<td>3/0</td>
</tr>
<tr>
<td>8</td>
<td>(JohnPhos)AuCl</td>
<td>L₁Cu(SbF₆)</td>
<td>94</td>
<td>n.d.</td>
<td>0/0</td>
</tr>
</tbody>
</table>
Having shown the existence of a partnership between gold and copper, we next checked whether a matched pair of chiral complexes could be formed (Table S2). This was not the case with A and L1 (entries 1 and 2). On the other hand, A1’ and L1 formed a mismatched pair (entries 3 and 4).

**Table S2** Enantioselective hydroalkylation of ene-β-ketoamide 1a using a chiral gold and chiral copper complexes

<table>
<thead>
<tr>
<th>Entry</th>
<th>[Au]</th>
<th>L</th>
<th>Conv (%)</th>
<th>dr (%)</th>
<th>ee (%)(^ab)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A1</td>
<td>none</td>
<td>100</td>
<td>68/32</td>
<td>59/35</td>
</tr>
<tr>
<td>2</td>
<td>A1</td>
<td>L1</td>
<td>100</td>
<td>60/40</td>
<td>59/44</td>
</tr>
<tr>
<td>3</td>
<td>A1’</td>
<td>none</td>
<td>100</td>
<td>65/35</td>
<td>–57/-39</td>
</tr>
<tr>
<td>4</td>
<td>A1’</td>
<td>L1</td>
<td>100</td>
<td>38/62</td>
<td>–22/-27</td>
</tr>
</tbody>
</table>

\(^a\) Estimated by chiral SFC; diastereomeric ratios shown are 2a/2a’. \(^b\) Corresponding to 2a/2a’.

The use of complex A1 with various activators in summarized in Table S3 below. Again, the conversion reached with these activators in the absence of gold remained insignificant, except with Zn(OTf)\(_2\) (entry 1) and Ga(OTf)\(_3\) (entry 4). Looking at the diastereoselectivity, it is noteworthy that the nature of the major product varies as a function of the Lewis acid. Focusing on triflates, which allowed to reach high conversions, while In, Si, and Bi gave rise to 2a as major diastereomer (entries 6, 10, and 12 respectively), Zn and Ga favored the formation of 2a’ (entries 2 and 4). Although reasonable enantioselectivities were obtained with In(OTf)\(_3\), In(NTf)\(_2\), and Bi(OTf)\(_3\) (entries 6–8, 11, and 12), the results were less satisfying than with AgOTf or AgNTf\(_2\). Nevertheless, this study clearly shows that Lewis acids of different element series should be systematically tested during the optimization process of a stereoselective gold-catalyzed reaction.

**Table S3** Screening of other activators in the enantioselective hydroalkylation of ene-β-ketoamide 1a

<table>
<thead>
<tr>
<th>Entry</th>
<th>[LA]</th>
<th>T (°C)</th>
<th>Conv (%)</th>
<th>dr (%)</th>
<th>ee (%)(^abc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(^a)</td>
<td>Yb(OTf)(_3)</td>
<td>110</td>
<td>8</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>2(^a)</td>
<td>Zn(OTf)(_2)</td>
<td>110</td>
<td>100 (27)</td>
<td>36/64</td>
<td>8/11</td>
</tr>
<tr>
<td>3(^a)</td>
<td>Al(OTf)(_3)</td>
<td>110</td>
<td>30 (6)</td>
<td>40/60</td>
<td>50/39</td>
</tr>
<tr>
<td>4(^a)</td>
<td>Ga(OTf)(_3)</td>
<td>110</td>
<td>100 (19)</td>
<td>36/64</td>
<td>65/21</td>
</tr>
<tr>
<td>5(^a)</td>
<td>GaCl(_3)</td>
<td>110</td>
<td>trace</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

\(^a\) Estimated by chiral SFC; diastereomeric ratios shown are 2a/2a’. \(^b\) Corresponding to 2a/2a’.\(^c\)
Characterization of the products

1'-Benzy1-4'-methyl-3,4-dihydro-1\textit{H}-spiro[naphthalene-2,3'-pyrrolidine]-1,2'-dione (2c)

The general procedure was followed using \textit{N}-allyl-\textit{N}-benzyl-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxamide (1c). The crude product was purified flash chromatography on silica gel (cyclohexane/EtOAc: 9/1) to afford 2c (27 mg, 85%) as a yellow oil. The two diastereoisomers were separated by flash chromatography.

$^1$H NMR (300 MHz / CDCl$_3$): Minor diastereoisomer $\delta$ 8.03 (d, $J$ = 7.8 Hz, 1H), 7.51–7.46 (m, 1H), 7.39–7.24 (m, 7H), 4.63 (d, $J$ = 14.9 Hz, 1H), 4.51 (d, $J$ = 14.9 Hz, 1H), 3.31–3.22 (m, 2H), 2.89–2.79 (m, 1H), 2.58–2.45 (m, 1H), 2.10 (dt, $J$ = 13.6, 4.9 Hz, 1H), 0.94 (d, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (63 MHz / CDCl$_3$): Minor diastereoisomer $\delta$ 196.1 (C), 173.1 (C), 144.4 (C), 136.6 (C), 133.8 (CH), 131.9 (C), 128.9 (3 CH), 128.4 (2 CH), 127.7 (2 CH), 126.8 (CH), 58.7 (C), 51.2 (CH$_2$), 47.0 (CH$_2$), 33.1 (CH), 25.7 (CH$_2$), 25.5 (CH$_2$), 14.7 (CH$_3$). $^1$H NMR (300 MHz / CDCl$_3$): Major diastereoisomer $\delta$ 8.04 (dd, $J$ = 7.7, 1.3 Hz, 1H), 7.46 (td, $J$ = 7.7, 1.3 Hz, 1H), 7.39–7.24 (m, 7H), 4.55 (d, $J$ = 14.9 Hz, 1H), 4.45 (d, $J$ = 14.9 Hz), 1H), 3.52–3.42 (m, 2H), 3.07 (dd, $J$ = 13.6, 6.9 Hz, 1H); 2.97 (ddd, $J$ = 16.9, 7.0, 5.1 Hz, 1H), 2.81 (dd, $J$ = 9.5, 6.1 Hz, 1H), 2.40–2.33 (m, 1H), 2.23–2.14 (m, 1H), 1.03 (d, $J$ = 7.0 Hz, 3H); $^{13}$C NMR (63 MHz / CDCl$_3$): Major diastereoisomer $\delta$ 196.5 (C), 174.6 (C), 143.8 (C), 136.5 (C), 133.9 (CH), 132.7 (C), 128.8 (3 CH), 128.2 (2 CH), 127.6 (2 CH), 127.0 (CH), 58.9 (C), 51.7 (CH$_2$), 47.0 (CH$_2$), 39.1 (CH), 32.0 (CH$_2$), 25.5 (CH$_2$), 14.7 (CH$_3$); HRMS (ESI): m/z calcd. for C$_{21}$H$_{21}$NO$_2$Na (M + Na)$^+$ 342.1465, found 342.1462.

3-Acetyl-1-benzyl-3,4-dimethylpyrrolidin-2-one (2d)

The general procedure was followed with \textit{N}-allyl-\textit{N}-benzyl-2-methyl-3-oxobutanamide (1d). The crude product was purified flash chromatography on silica gel (cyclohexane/EtOAc: 9/1) to afford 2d (15 mg, 60%) as a colorless oil. The two diastereoisomers were separated by flash chromatography. $^1$H NMR (360 MHz / CDCl$_3$): Minor diastereoisomer $\delta$ 7.33–7.26 (m, 3H), 7.21–7.18 (m, 2H), 4.43 (dd, $J$ = 14.5, 6.4 Hz, 2H), 3.30 (dd, $J$ = 6.8, 1.8 Hz, 1H), 2.83–2.71 (m, 2H), 2.31 (s, 3H), 1.24 (s, 3H), 0.91 (d, $J$ = 7 Hz, 3H);
$^{13}$C NMR (90 MHz / CDCl$_3$): Minor diastereoisomer δ 206.7 (C), 174.4 (C), 136.3 (C), 128.8 (2 CH), 128.1 (2 CH), 127.8 (CH), 60.7 (C), 50.9 (CH$_2$), 46.9 (CH$_2$), 32.8 (CH$_3$), 26.5 (CH), 14.0 (CH$_3$), 13.2 (CH$_3$); $^1$H NMR (360 MHz / CDCl$_3$): Major diastereoisomer δ 7.31–7.25 (m, 5H), 4.56 (d, $J=14.5$ Hz, 1H), 4.42 (d, $J=14.5$ Hz, 1H), 3.24 (t, $J=9.6$ Hz, 1H), 2.98 (t, $J=9.6$ Hz, 1H), 2.21–2.15 (m, 1H), 2.08 (s, 3H), 1.41 (s, 3H), 0.96 (d, $J=7$ Hz, 3H); $^{13}$C NMR (90 MHz / CDCl$_3$): Major diastereoisomer δ 207.1 (C), 174.7 (C), 136.0 (C), 128.7 (2 CH), 128.3 (2 CH), 127.7 (CH), 60.9 (C), 51.4 (CH$_2$), 47.0 (CH$_2$), 39.5 (CH$_3$), 29.3 (CH), 19.7 (CH$_3$), 13.1 (CH$_3$); HRMS (ESI): $m/z$ calcd. for C$_{15}$H$_{19}$NO$_2$Na (M + Na)$^+$ 268.1308, found 268.1311. The relative configuration of each diastereoisomer was determined by 1D selective NOE experiment (see pages S51 and S54).

3-Acetyl-1-benzyl-3-ethyl-4-methylpyrrolidin-2-one (2e)

The general procedure was followed with N-allyl-N-benzyl-2-ethyl-3-oxobutanamide (1e). The crude product was purified flash chromatography on silica gel (cyclohexane/EtOAc: 9/1) to afford 2e (16 mg, 60%) as a colorless oil and as a 78/22 mixture of diastereoisomers. $^1$H NMR (250 MHz / CDCl$_3$): Major diastereoisomer δ 7.35–7.24 (m, 5H), 4.52 (d, $J=4.7$ Hz, 2H), 3.29 (dd, $J=9.5$, 8.2 Hz, 1H), 2.94 (t, $J=9.1$ Hz, 1H), 2.44–2.35 (m, 1H), 2.11 (s, 3H), 2.08–1.97 (m, 1H), 1.86–1.78 (m, 1H), 0.97–0.91 (m, 6H); $^{13}$C NMR (63 MHz / CDCl$_3$): Major diastereoisomer δ 207.6 (C), 173.9 (C), 136.3 (C), 128.9 (2 CH), 128.5 (2 CH), 127.9 (CH), 65.4 (C), 51.6 (CH$_2$), 47.1 (CH$_2$), 34.0 (CH$_3$), 30.0 (CH), 25.2 (CH$_2$), 14.0 (CH$_3$), 9.0 (CH$_3$); HRMS (ESI): $m/z$ calcd. for C$_{16}$H$_{21}$NO$_2$Na (M + Na)$^+$ 282.1465, found 282.1459.

3-Acetyl-1,3-dibenzyl-4-methylpyrrolidin-2-one (2f)

The general procedure was followed with N-allyl-N$_2$-dibenzyl-3-oxobutanamide (1f). The crude product was purified flash chromatography on silica gel (cyclohexane/EtOAc: 9/1) to afford 2f (21 mg, 66%) as a colorless oil and as a 86/14 mixture of diastereoisomers. $^1$H NMR (250 MHz / CDCl$_3$): Mixture of two diastereoisomers δ 7.32–7.00 (m, 20H), 4.60–4.21 (m, 4H), 3.48–2.82 (m, 8H), 2.50–2.30 (m, 2H), 2.25 (s, 2H), 2.17 (s, 4H), 1.04 (d, $J=7$ Hz, 2H), 0.94 (d, $J=7$ Hz, 4H); $^{13}$C NMR (63 MHz / CDCl$_3$): Mixture of two diastereoisomers δ 206.4 (C), 205.8 (C), 173.4 (C), 172.2 (C), 136.9 (2 C), 136.1 (C), 135.8 (C), 130.9 (3 CH), 129.4 (CH), 128.8 (CH), 128.7 (3 CH), 128.4 (4 CH), 128.2 (CH), 128.1 (3 CH), 127.8 (CH), 127.7 (CH), 126.9 (CH), 126.7 (CH), 66.6 (C), 66.3 (C), 51.6 (CH$_2$), 51.4 (CH$_2$), 47.1 (CH$_2$), 46.8 (CH$_2$), 36.5 (CH$_2$), 34.7 (CH$_2$), 33.2 (CH$_3$), 32.2 (CH$_3$), 29.8 (CH), 27.0 (CH), 14.2 (CH$_3$), 13.3 (CH$_3$); HRMS (ESI): $m/z$ calcd. for C$_{21}$H$_{23}$NO$_2$Na (M + Na)$^+$ 344.1625, found 344.1625.

1-Benzyl-3,4-dimethyl-3-propionylpyrrolidin-2-one (2g)
The general procedure was followed with N-allyl-N-benzyl-2-methyl-3-oxopentanamide (1f). The crude product was purified flash chromatography on silica gel eluting with cyclohexane/EtOAC (100/0 to 90/10) to afford 2g (19 mg, 74%) as a colorless oil and as a 68/32 mixture of diastereoisomers. \( ^1H \text{ NMR} \) (250 MHz / CDCl\(_3\)): Mixture of two diastereoisomers \( \delta \) 7.37–7.18 (m, 10H), 4.60–4.43 (m, 4H), 3.31–3.21 (m, 2H), 2.99 (t, \( J=9.5 \) Hz, 1H), 2.80–2.52 (m, 4H), 2.47–2.17 (m, 3H), 1.44 (s, 3H), 1.26 (s, 3H), 1.00 (dt, \( J=18.3, 7 \) Hz, 6H), 0.94–0.89 (m, 6H); \( ^{13}C \text{ NMR} \) (63 MHz / CDCl\(_3\)): Mixture of two diastereoisomers \( \delta \) 209.6 (C), 209.4 (C), 175.1 (C), 174.6 (C), 136.3 (C), 136.2 (C), 128.9 (2 CH), 128.8 (2 CH), 128.4 (2 CH), 128.1 (2 CH), 127.8 (2 CH), 60.7 (C), 60.4 (C), 51.5 (CH\(_2\)), 51.0 (CH\(_2\)), 47.1 (CH\(_2\)), 46.9 (CH\(_2\)), 39.8 (CH), 34.7 (CH\(_2\)), 33.1 (CH), 31.7 (CH\(_2\)), 19.6 (CH\(_3\)), 14.0 (CH\(_3\)), 13.3 (CH\(_3\)), 13.2 (CH\(_3\)), 7.9 (CH\(_3\)), 7.1 (CH\(_3\)); HRMS (ESI): \( m/z \) calcd. for C\(_{16}\)H\(_{21}\)NO\(_2\)Na (M + Na)\(^+\) 282.1465, found 282.1464.
Chiral SFC and HPLC Traces:

\[
\text{1a} \xrightarrow{\text{JohnPhosAuCl (5 mol\%)}} \text{AgOTf (10 mol\%)} \xrightarrow{\text{toluene, 50 °C, 24h}} \text{2a/2a'}
\]

(Racemic reaction)

Thar Investigator SFC Results

FWZ gradient method-35C: Co-solvent from 3% to 10% during the first 10 min, then keep 10%
\[
\text{R}^\text{2}-\text{DTBM-SEGPHOS} \cdot \text{(AuCl)}_2 (5 \text{ mol\%}) \rightarrow \text{AgOTf (10 mol\%)} \rightarrow \text{toluene, 110°C, 24h}
\]

(Ref: Table 2, entry 1)

**Thar Investigator SFC Results**

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**Single Absorbance (215nm) Plot**

FWZ gradient method: Co-solvent from 3% to 10% during the first 10 min, then keep 10%
(R)-DTBM-SEGPHOS-AuCl (5 mol%) → 2a + 2f

**General Info**

**Log Info**

- Log Date: 12/17/2012 11:31:33 AM
- Report Date: 12/17/2012
- File Name: Fwz-269_12-17-2012_1.txt

**Injection Info**

- Injection Date Time Stamp: 12/17/2012 11:31:33 AM
- Injection Volume: 50
- Co-Solvent: MeOH
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- Total Flow: 4
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- Wavelength: 0

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FWZ gradient method: Co-solvent from 3% to 10% during the first 10 min, then keep 10%
(Ref: Table 2, entry 9)

FWZ gradient method: Co-solvent from 3% to 10% during the first 10 min, then keep 10%

**Waters**

**Thar Investigator SFC Results**

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**Single Absorbance (210nm) Plot**

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RT 7.18: RT 7.87: A: 96.8658; A: 1.2776; Peak 2
RT 8.53: A: 2942.236; Peak 4
RT 9.08: A: 286.0476; A: 4.7815; Peak 4
FWZ gradient method: Co-solvent from 3% to 10% during the first 10 min, then keep 10%

(Ref: Table 3, entry 7)
FWZ gradient method: Co-solvent from 3% to 10% during the first 10 min, then keep 10%
Analyse : Fwz-151 B 2 - UV Gauche

Fwz-151 B 2 - UV Gauche

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**SOMME**

|     | 1471,62 | 100,00 |

Informations sur l'échantillon

Nom : Fwz-151 B
N° Flacon : 0
Quantité : 0,000000 mg
Dilution : 1
Informations :

OJ-H Hex/EtOH 95/5, 1.0 ml/min, 210nm, 20°C

Volume d'injection : 5,00 µl
Diviseur : 1
(Ref: Table 4, entry 1)

Analyse : Fwz-692 A-2 - UV Gauche

Résultats d'intégration

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Informations sur l'échantillon

Nom : Fwz-692 A-2
Type d'échantillon : Echantillon
N° Flacon : 0
Quantité : 0,000000 mg
Dilution : 1
Informations : O-JH hex/EtOH 95/5; 1 ml/min, 210nm, 10°C

Volume d'injection : 5,00 µl
Diviseur : 1
FWZ gradient method: Co-solvent from 3% to 10% during the first 10 min, then keep 10%
FWZ gradient method: Co-solvent from 3% to 10% during the first 10 min, then keep 10%
JohnPhosAuCl (5 mol%)  
AgOTf (10 mol%)  
toluene, 110 °C, 24h  

(Racemic reaction)  

Analyse : MP0616 Racemic-2 - UV Gauche  

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SOMME          | 1446.82  | 100.00  |

Informations sur l’échantillon  
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Quantité   | 0,000000 mg  
Dilution   | 1  
Informations :  
AU-Hex/tBuOH : 9/10; 1.0 ml/min, 210nm, 20°C  

Volume d’injection | 5,00 µl  
Diviseur | 1
(R)-DTBM-MeOBIPHEP-(AuCl)$_2$ (5 mol%) + AgOTf (10 mol%) → toluene, 110°C, 24h

(Ref: Table 4, entry 5)

Analyse : Fwz-691 C-5 - UV Gauche

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SOMME 1008,80 100,00

Informations sur l'échantillon
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N° Flacon : 0
Quantité : 0,00000 mg
Dilution : 1
Informations : AD-H hex/EtOH 90/10; 1,0 ml/min, 210nm, 20°C

Volume d'injection : 5,00 µl
Diviseur : 1
JohnPhosAuCl (5 mol%)  
AgOTf (10 mol%)  

toluene, 110 °C, 24h  

(Racemic reaction)
(R)-DTBM-MeOBIPHEP-(AuCl)$_2$ (5 mol%)  
AgOTf (10 mol%) 
toluene, 110°C, 24h 

(Ref: Table 4, entry 7)
Racemique réaction

Analyse : Fwz-592 A - UV Gauche

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SOMME | 1505.69 | 100.00

Informations sur l’échantillon

Nom | Fwz-592 A  
N° Flacon | 0  
Quantité | 0,000000 mg  
Dilution | 1  
Informations :
  - AU-H Hex/1%OH 90/10: 1.0 ml/min, 210nm, 20°C
  - Volume d'injection: 5,00 µl
  - Diviseur: 1
(Ref: Table 4, entry 9)
FWZ gradient method 1: Co-solvent from 1% to 10% during the first 20 min, then keep 10%
FWZ gradient method 1: Co-solvent from 1% to 10% during the first 20 min, then keep 10%
Spectra ($^1$H, $^{31}$P, $^{13}$C NMR)
Major diastereoisomer

2c
Major diastereoisomer

2c
Minor diastereoisomer

2c
Major diastereoisomer

2d
Major diastereoisomer

2d
2d Minor diastereoisomer
References