Supporting Information

for

Efficient gold(I)/silver(I)-cocatalyzed cascade intermolecular N-Michael addition/intramolecular hydroalkylation of unactivated alkenes with α-ketones

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**Experimental section**

**General methods.** Reagents were obtained commercially and used without further purification unless indicated otherwise. All anhydrous solvents used in the reactions were dried and freshly distilled. All manipulations with air-sensitive reagents were carried out under a dry argon atmosphere. The catalysts Au(PPh$_3$)$_2$Cl [1], (Cy)$_2$(2',4',6'-triisopropyl-o-biphenyl)PAuCl [1,2], (t-Bu)$_2$(o-diphenyl)PAuCl [1,2] and IPrAuCl [3] were prepared following literature procedures. 2-Methylene-3,4-dihyronaphthalen-1(2H)-one was prepared according to the literature procedure [4]. α,β-Unsaturated ketones were prepared following the literature procedure [5]. Substituted allylic amines were prepared following the literature procedure [6]. NMR spectra were recorded on Bruker AM300/400 spectrometers at 300/400 MHz for $^1$H NMR and 75/100 MHz for $^{13}$C NMR in CDCl$_3$ with TMS as an internal standard. The chemical shifts are expressed in ppm and coupling constants are given in Hz. Data for $^1$H NMR are recorded as follows: Chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constant (Hz), integration. Data for $^{13}$C NMR are reported in terms of chemical shift (δ, ppm). Mass spectra were obtained on a HP5989A spectrometer (EI), an IonSpec 4.7 Tesla FTMS spectrometer (MALDI), or a Bruker
Daltonics FTMS-7 spectrometer (ESI). IR spectra were recorded as KBr discs, on a Bio-Rad FTS-185 spectrometer; frequencies are given in reciprocal centimeters (cm⁻¹) and only selected absorbance is reported.

**General procedure for gold/silver-cocatalyzed one-pot tandem intermolecular N-Michael addition/intramolecular hydroalkylation**

A mixture of (t-Bu)₂(o-diphenyl)PAuCl (6.7 mg, 0.0125 mmol), AgClO₄ (7.8 mg, 0.0375 mmol) (Warning! The perchlorate salt is potentially explosive and should be handled with great caution.), α,β-unsaturated ketone (0.25 mmol) and substituted allylic amine (0.375 mmol, 1.5 equiv) in toluene (0.5 mL) was stirred at 90 °C under Ar atmosphere for 20 h. Upon completion, the solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (eluent: EtOAc/petroleum ether = 1:12-1:6) to give the desired products.

**trans-4-Methyl-1-tosylpyrrolidin-3-yl)(phenyl)methanone (3a)**

trans/cis: 4.1:1. Major diastereomer could be separated on a silica gel column, and the relative configuration of 3a was determined with reference to 1-(trans-4-methyl-1-tosylpyrrolidin-3-yl)ethanone [7].

White solid. ¹H NMR(300 MHz, CDCl₃): δ 7.86 (d, J = 7.3 Hz, 2H), 7.72 (d, J = 8.2 Hz, 2H), 7.60 (t, J = 7.3 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.34 (d, J = 7.3 Hz, 2H), 3.79 (t, J = 8.2 Hz, 1H), 3.55 (q, J = 8.0 Hz, 1H), 3.47 (dd, J = 7.2, 9.0 Hz, 1H), 3.29 (t, J = 9.0 Hz, 1H), 3.05 (t, J = 7.6 Hz, 1H), 2.56-2.46 (m, 1H), 2.44 (s, 3H), 1.04 (d, J = 6.7 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 198.1, 143.6, 136.2, 133.7, 133.4, 129.7,
128.8, 128.3, 127.6, 54.2, 50.8, 36.5, 21.6, 17.4. IR (FILM): $\nu_{\text{max}}$ 3286, 2956, 2924, 1712, 1679, 1597, 1448, 1341, 1223, 1161, 1093, 1041, 815 cm$^{-1}$. MS (ESI) $m/z$: 366 (M+Na$^+$), 344 (M+H$^+$). HRMS (ESI): calcd. for C$_{19}$H$_{22}$NO$_3$S$^+$ (M+H$^+$): 344.13149, found: 344.13189.

(4-Methoxyphenyl)(trans-4-methyl-1-tosylpyrrolidin-3-yl)methanone (3b)

$trans/cis$: 1.0: 1. One of the diastereomers could be separated on a silica gel column, and the relative configuration of 3b was determined with reference to 3a.

White solid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.84 (d, $J = 8.4$ Hz, 2H), 7.71 (d, $J = 7.5$ Hz, 2H), 7.33 (d, $J = 7.5$ Hz, 2H), 6.93 (d, $J = 8.4$ Hz, 2H), 3.87 (s, 3H), 3.75 (t, $J = 8.7$ Hz, 1H), 3.54-3.43 (m, 2H), 3.27 (t, $J = 9.0$ Hz, 1H), 3.04 (t, $J = 8.7$ Hz, 1H), 2.54-2.44 (m, 1H), 2.44 (s, 3H), 1.01 (d, $J = 6.9$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 196.4, 163.9, 143.6, 133.4, 130.7, 129.7, 129.2, 127.5, 113.9, 55.5, 54.2, 51.6, 51.0, 36.6, 21.5, 17.3; MS (ESI) $m/z$: 396 (M+Na$^+$); HRMS (ESI): calcd. for C$_{20}$H$_{23}$NNaO$_4$S$^+$ (M+Na$^+$): 396.12400, found: 396.12381.

(cis-4-Methyl-1-tosylpyrrolidin-3-yl)(4-nitrophenyl)methanone (3c)

$trans/cis$: 1.7: 1. One of the diastereomers could be separated on a silica gel column, and the relative configuration of 3c was determined with reference to 3a.

Pale yellow solid.$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.32 (d, $J = 8.4$ Hz, 2H), 8.04 (d, $J = 8.4$ Hz, 2H), 7.77 (d, $J = 7.8$ Hz, 2H), 7.37 (d, $J = 7.8$ Hz, 2H), 4.07-3.99 (m, 1H),
3.75-3.58 (m, 3H), 3.08 (dd, J = 9.6, 3.6 Hz, 1H), 2.76-2.72 (m, 1H), 2.47 (s, 3H), 0.57 (d, J = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 196.9, 150.9, 144.1, 141.1, 133.8, 128.0, 124.5, 55.4, 49.9, 47.9, 36.6, 21.9, 14.9; IR (FILM): $\nu_{\text{max}}$ 3108, 2967, 2925, 1688, 1602, 1526, 1493, 1407, 1346, 1221, 1164, 1093, 1032, 985 cm$^{-1}$; MS (ESI) m/z: 411(M+Na$^+$); HRMS (ESI): calcd. for C$_{19}$H$_{20}$N$_2$NaO$_5$S$^+$ (M+Na$^+$): 411.10102, found: 411.09913.

**1-(trans-4-Methyl-1-tosylpyrrolidin-3-yl)propan-1-one (3d)**

trans/cis: 5.5:1. Major diastereomer could be separated on a silica gel column, and the relative configuration of 3d was determined with reference to 3a.

White solid. $^1$H NMR (300 MHz, CDCl$_3$): δ 7.71 (d, J = 8.1Hz, 2H), 7.34 (d, J = 8.1Hz, 2H), 3.60 (dd, J = 9.6, 8.4Hz, 1H), 3.41 (dd, J = 9.6, 7.5Hz, 1H), 3.24 (dd, J = 9.9, 8.4Hz, 1H), 2.90 (dd, J = 9.6, 8.1Hz, 1H), 2.69 (dd, J = 16.5, 8.1Hz, 1H), 2.45 (s, 3H), 2.45-2.23 (m, 3H), 1.04-0.99 (m, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 209.1, 143.7, 133.3, 129.7, 127.6, 56.7, 54.3, 49.9, 36.3, 36.1, 21.5, 17.5, 7.5; IR (FILM): $\nu_{\text{max}}$ 2972, 2937, 2877, 1713, 1598, 1459, 1379, 1343, 1162, 1093 cm$^{-1}$; MS (ESI) m/z: 318 (M+Na$^+$), 296 (M+H$^+$); HRMS (ESI): calcd. for C$_{15}$H$_{21}$NNaO$_5$S$^+$ (M+Na$^+$): 318.11344, found: 318.11249.
1-(trans-4-Methyl-1-(4-nitrophenylsulfonyl)pyrrolidin-3-yl)propan-1-one (3e)

*trans/cis*: 5.3:1. Major diastereomer could be separated on a silica gel column, and the relative configuration of 3e was determined with reference to 3a.

Pale yellow solid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.38 (d, $J = 8.7$Hz, 2H), 8.00 (d, $J = 8.7$Hz, 2H), 3.60 (dd, $J = 9.9$, 1.8Hz, 1H), 3.38-3.31 (m, 2H), 2.99 (dd, $J = 9.6$, 7.2Hz, 1H), 2.77 (dd, $J = 15.0$, 7.5Hz, 1H), 2.46-2.39 (m, 2H), 2.38-2.28 (m, 1H), 1.05 (d, $J = 6.6$Hz, 3H), 0.99 (t, $J = 7.2$Hz, 3H): $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 209.2, 150.4, 142.9, 128.9, 124.7, 56.6, 54.5, 49.8, 36.9, 36.4, 17.9, 7.8; MS (EI) $m/z$: 326 (M$^+$, 1), 140 (100), 122 (13), 113 (48), 108 (12), 85 (15), 84 (60), 82(41); HRMS (EI): calcd. for C$_{12}$H$_{13}$N$_2$O$_5$S$^+$ (M$^+$): 297.0545, found: 297.0542.

1-(trans-4-Methyl-1-(2,4,6-triisopropylphenylsulfonyl)pyrrolidin-3-yl)propan-1-one (3f)

*trans/cis*: 5.2:1. Major diastereomer could be separated on a silica gel column, and the relative configuration of 3f was determined with reference to 3a.

Pale yellow solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.15 (s, 2H), 4.21-4.15 (m, 2H), 3.63 (dd, $J = 7.2$, 6.3Hz, 1H), 3.41 (dd, $J = 6.9$, 5.4Hz, 1H), 3.31 (dd, $J = 7.5$, 6.3Hz, 1H), 2.97-2.78 (m, 3H), 2.51-2.44 (m, 3H), 1.27-1.22 (m, 18H), 1.09 (d, $J = 5.1$Hz,
3H), 1.04 (t, J = 5.4Hz, 3H); $^{13}$C NMR(100 MHz, CDCl$_3$): δ 209.6, 153.1, 151.2, 131.0, 123.8, 57.0, 53.2, 48.6, 36.7, 36.1, 34.1, 29.3, 24.8, 23.5, 17.3, 7.5; MS (EI) m/z: 407 (M$^+$, 1), 306 (14), 268 (18), 267 (100), 251 (32), 249 (9), 218 (24), 203 (14); HRMS (EI): calcd. for C$_{23}$H$_{37}$NO$_3$S$^+$ (M$^+$): 407.2494, found: 407.2487.

4'-Methyl-1'-tosyl-3,4-dihydro-1H-spiro[naphthalene-2,3'-pyrrolidin]-1-one (3g)

![3g](image)

trans/cis: 1.8: 1. One of diastereomers could be separated on a silica gel column.

White solid. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.86 (d, J = 7.2Hz, 1H), 7.72 (d, J = 8.1Hz, 2H), 7.49-7.44 (m, 1H), 7.35-7.26 (m, 3H), 7.21 (d, J = 7.8Hz, 2H), 3.83 (d, J = 9.9Hz, 1H), 3.67 (dd, J = 9.3, 7.2Hz, 1H), 3.27 (d, J = 10.5Hz, 1H), 3.13-3.02 (m, 2H), 2.94-2.85 (m, 1H), 2.46 (s, 3H), 2.39-2.32 (m, 1H), 2.25-2.17 (m, 1H), 2.08-1.99 (m, 1H), 0.71 (d, J = 6.9Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 197.7, 143.4, 142.6, 133.6, 133.3, 132.0, 129.6, 128.7, 127.62, 127.57, 126.8, 55.6, 54.8, 54.2, 39.9, 33.2, 25.8, 21.6, 14.1; MS(ESI) m/z: 392 (M+Na$^+$), 370 (M+H$^+$); HRMS (ESI): calcd. for C$_{21}$H$_{23}$NNaO$_3$S$^+$ (M+Na$^+$): 392.12909, found: 392.12958.

General procedure for control experiment

A mixture of AgClO$_4$ (20.7 mg, 0.1 mmol) (Warning! The perchlorate salt is potentially explosive and should be handled with great caution.), α,β-unsaturated ketone 1a (1.0 mmol) and substituted allylic amine 2a (1.5 mmol, 1.5 equiv) in toluene (2 mL) was stirred at 90 °C under Ar atmosphere for 3 h. Then, the solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (eluent: EtOAc/petroleum ether = 1:10) to give the desired product 4 in 85% yield (299 mg, 0.85 mmol).
$N$-Allyl-4-methyl-$N$-(3-oxo-3-phenylpropyl)benzenesulfonamide (4)

![Chemical Structure]

Colorless oil. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.93 (d, $J = 8.0$ Hz, 2H), 7.70 (d, $J = 8.3$ Hz, 2H), 7.58 (t, $J = 7.0$ Hz, 1H), 7.46 (t, $J = 7.2$ Hz, 2H), 7.28 (t, $J = 8.6$ Hz, 2H), 5.75-5.62 (m, 1H), 5.22-5.13 (m, 2H), 3.84 (d, $J = 6.6$ Hz, 2H), 3.48 (t, $J = 6.5$ Hz, 2H), 3.36 (t, $J = 7.2$ Hz, 2H), 2.44 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 198.3, 143.4, 136.3, 136.2, 133.3, 133.0, 129.7, 128.6, 127.9, 127.1, 119.3, 52.1, 43.1, 38.9, 21.5. IR(FILM): $\nu_{\text{max}}$ 3064, 2922, 1682, 1644, 1598, 1581, 1494, 1449, 1417, 1382, 1342, 1306, 1287, 1211, 1157, 1092, 1018, 986, 931, 876 cm$^{-1}$. MS(ESI) $m/z$: 366 (M+Na$^+$), 344 (M+H$^+$). HRMS(ESI): calcd. for C$_{19}$H$_{21}$NO$_3$SNa$^+$(M+Na$^+$): 366.1134, found: 366.1141. Anal. calcd. for C$_{19}$H$_{21}$O$_3$NS: C, 66.45; H, 6.16; N, 4.08, found: C, 66.45; H, 6.10; N, 4.05.
References


