SUPPORTING INFORMATION

Mo(CO)6 Catalysed Chemoselective Hydrosilylation of α,β-Unsaturated Amides for the Formation of Allylamines

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Instrumentation

Characterizations were made by $^1$H and $^{13}$C NMR spectroscopy. NMR spectra were recorded at Bruker 400, 500 MHz ($^1$H) and 100, 125 MHz ($^{13}$C), and were referenced internally with CDCl$_3$ ($\delta$H 7.26, $\delta$C 77.16 ppm) (CD$_3$)$_2$SO ($\delta$H 2.50, $\delta$C 39.52 ppm). High temperature experiments were performed at Bruker 500 MHz ($^1$H) and 125 MHz ($^{13}$C). HRMS was performed on Bruker micrOTOF/ESI.

Material

Unless otherwise noted, materials were purchased from commercial suppliers and were used without purification. Mo(CO)$_6$, sublimed 99.9+% was purchased from Sigma-Aldrich and used as received. THF was purchased from Fischer Scientific, and dispersed from a solvent drying system.

General

The 1 mmol scale catalytic reduction of amides was performed in microwave tubes 2-5 mL from Biotage, with a Teflon-coated magnetic stirring bar. The tubes were fitted with a cap containing a septum and the reactions were run under nitrogen atmosphere.
**Substrate scope investigation**

**General procedure for catalytic reduction of amides.**

Amide (1.0 mmol) and Mo(CO)$_6$ (0.0132 g, 0.05 mmol) were added to an oven dried 10 mL microwave tube equipped with a magnetic stirring bar. To the sealed tube, dry THF (2 mL) and TMDS (0.265 mL, 1.5 mmol) were added and the reaction mixture was stirred at 65 °C for 24 h. The reaction was quenched with NaOH (Aq. 2M, 10 mL) and the stirring was continued at r.t for 8 h. The mixture was extracted with DCM (3 x 20 mL), dried with Na$_2$SO$_4$ and evaporated under reduced pressure. The crude products were purified by column chromatography.

**Evaluation of β,γ-unsaturated amide 7**

Amide 7 (1.0 mmol) and Mo(CO)$_6$ (0.0132 g, 0.05 mmol) were added to an oven dried 10 mL microwave tube equipped with a magnetic stirring bar. To the sealed tube, dry THF (2 mL) and TMDS (0.265 mL, 1.5 mmol) were added and the reaction mixture was stirred at 65 °C for 24 h. The solvent was evaporated and 1,3,5-trimethoxybenzene (0.056 g, 0.33 mmol) was added as internal standard. The mixture was dissolved in CDCl$_3$ (3 mL) where after the $^1$H NMR spectrum was immediately recorded.

**Synthesis of Naftifine (14)**

**Synthesis of N-(naphthalen-1-ylmethyl)cinnamamide (12)**

Dry THF (17 mL) was added to the carboxylic acid 10 (0.741 g, 5.0 mmol), activated molecular sieves 4Å (2.5 g) and zirconium(IV)chloride (0.118 g, 10 mol%) under nitrogen atmosphere and the mixture was heated under stirring to 100°C in a capped microwave vial. The amine 11 (0.943 g, 6.0 mmol) was added dropwise and the reaction was stirred at the same temperature for 24 h and then cooled to r.t. The mixture was filtered through a plug of silica (4 x 3.5 cm) with 150 mL of an EtOAc:Et$_3$N (200:1) eluent. The solvent was removed under reduced pressure affording analytically pure compound 12 (1.306 g, 91%).
Synthesis of N-methyl-N-(naphthalen-1-ylmethyl)cinnamamide (13)
In 25 mL round-bottom flask to a suspension of NaH (0.12 g, 5.0 mmol) in 10 mL of dry DMF 1 g (3.5 mmol) of amide (12) was added drop wise as a solution in 2 mL of DMF at 0 °C and the reaction mixture was stirred for 2 h. 0.36 mL (5.9 mmol) of methyl iodide was thereafter added drop wise and the temperature was raised to r.t and the mixture was left stirring for 10 h. The reaction was quenched with 2 mL of 95% ethanol followed by water (40 mL). The reaction was then extracted with EtOAc (3x40 mL). The combined organic layers were dried over Na₂SO₄ and the solvent was removed by rotary evaporation. Crude product was purified by column chromatography using pentane/ethyl acetate (4:1) as an eluent yielding 0.976 g (93 %) of the target compound (13).

Synthesis of (E)-N-methyl-N-(naphthalen-1-ylmethyl)-3-phenylprop-2-en-1-amine (Naftifine) (14)
Amide 13 was reduced following general procedure for catalytic reduction of amides.
Compound characterization.

1-cinnamylpiperidine 2a

0.176 g, 87 % yield; \(^1^H\)NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.39 – 7.36\) (m, 2H), 7.32 – 7.28 (m, 2H), 7.24 – 7.19 (m, 1H), 6.50 (d, \(J = 15.8\) Hz, 1H), 6. 30 (dt, \(J_1 = 6.7\) Hz, \(J_2 = 15.8\) Hz, 1H), 3.12 (dd, \(J_1 = 1.2\) Hz, \(J_2 = 6.7\) Hz, 2H), 2.44 (bs, 4H), 1.65 – 1.57 (m, 4H), 1.49 – 1.40 (m, 2H); \(^1^C\)NMR (100 MHz, CDCl\(_3\)): \(\delta = 137.2, 132.8, 128.7, 127.5, 127.3, 126.4, 62.0, 54.7, 26.1, 24.5\); HRMS (ESI, m/z) calcd. for C\(_{14}\)H\(_{20}\)N [M + H]\(^+\) 202.1590, found 202.1585.

1-cinnamylpyrrolidine 2b

0.167 g, 89 % yield; \(^1^H\)NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.39 – 7.36\) (m, 2H), 7.33 – 7.28 (m, 2H), 7.24 – 7.19 (m, 1H), 6.53 (d, \(J = 15.9\) Hz, 1H), 6. 34 (dt, \(J_1 = 6.7\) Hz, \(J_2 = 15.9\) Hz, 1H), 3.26 (dd, \(J_1 = 1.3\) Hz, \(J_2 = 6.7\) Hz, 2H), 2.59 – 2.53 (m, 4H), 1.83 – 1.77 (m, 4H); \(^1^C\)NMR (100 MHz, CDCl\(_3\)): \(\delta = 137.3, 131.9, 128.7, 127.9, 127.5, 126.4, 58.6, 54.2, 23.6\); HRMS (ESI, m/z) calcd. for C\(_{13}\)H\(_{18}\)N [M + H]\(^+\) 188.1434, found 188.1433.

4-cinnamylmorpholine 2c

0.180 g, 89 % yield; \(^1^H\)NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.39 – 7.36\) (m, 2H), 7.34 – 7.28 (m, 2H), 7.26 – 7.21 (m, 1H), 6.54 (d, \(J = 15.9\) Hz, 1H), 6. 26 (dt, \(J_1 = 6.7\) Hz, \(J_2 = 15.9\) Hz, 1H), 3.77 – 3.72 (m, 4H), 3.16 (dd, 2H, \(J_1 = 1.32\) Hz, \(J_2 = 6.8\) Hz), 2.53 – 2.48 (m, 4H); \(^1^C\)NMR (100 MHz, CDCl\(_3\)): \(\delta = 136.9, 133.5, 128.7, 127.7, 126.5, 126.2, 67.1, 61.6, 53.8\); HRMS (ESI, m/z) calcd. for C\(_{13}\)H\(_{18}\)NO [M + H]\(^+\) 204.1383, found 204.1379.

\((E)\)-N,N-dimethyl-3-phenylprop-2-en-1-amine 2d

0.117 g, 73 % yield; \(^1^H\)NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.40 – 7.36\) (m, 2H), 7.33 – 7.28 (m, 2H), 7.25 – 7.20 (m, 1H), 6.52 (d, \(J = 15.7\) Hz, 1H), 6.27 (dt, \(J_1 = 6.6\) Hz, \(J_2 = 15.7\) Hz, 1H), 3.08 (dd, \(J_1 = 1.3\) Hz, \(J_2 = 6.7\) Hz, 2H), 2.28 (s, 6H); \(^1^C\)NMR (100 MHz, CDCl\(_3\)): \(\delta = 137.2, 132.6, 128.7, 127.6, 127.5, 126.4, 62.2, 45.4\); HRMS (ESI, m/z) calcd. for C\(_{11}\)H\(_{16}\)N [M + H]\(^+\) 162.1277, found 162.1276.
(E)-N,N-dibenzyl-3-phenylprop-2-en-1-amine 2e

\[
\begin{align*}
0.16 \text{g, 51 \% yield;} \quad & ^1\text{H-NMR (400 MHz, CDCl}_3\text{): } \delta = 7.42 - 7.19 \text{ (m, 15H), 6.54 (d, } J = 15.8 \text{ Hz, 1H), 6.31 (dt, } J_1 = 6.5 \\
& \text{Hz, } J_2 = 15.8 \text{ Hz, 1H), 3.64 (s, 4H), 3.23 (dd, } J_1 = 1.2 \text{ Hz, } J_2 = 6.5 \text{ Hz, 2H); } ^{13}\text{C-NMR (100 MHz, CDCl}_3\text{): } \delta = 139.8, \quad 137.4, \quad 132.6, \quad 128.9, \quad 128.7, \quad 128.4, \quad 127.9, \quad 127.4, \quad 127.0, \\
& \quad 126.4, \quad 58.1, \quad 55.9; \quad \text{HRMS (ESI, m/z) calcd. for C}_{23}\text{H}_{24}\text{N [M + H]}^+ \quad 314.1903, \quad \text{found 314.1911.}
\end{align*}
\]

(E)-N,N-dimethyl-4-(3-(piperidin-1-yl)prop-1-en-1-yl)aniline 4a

\[
\begin{align*}
0.210 \text{g, 82 \% yield;} \quad & ^1\text{H-NMR (400 MHz, CDCl}_3\text{): } \delta = 7.29 - 7.25 \text{ (m, 2H), 6.69 - 6.66 \text{ (m, 2H), 6.40 (d, } J = \\
& 15.7 \text{ Hz, 1H), 6.09 (dt, } J_1 = 7.0 \text{ Hz, } J_2 = 15.7 \text{ Hz, 1H), 3.09 (dd, } J_1 = 1.1 \text{ Hz, } J_2 = 7.0 \text{ Hz, 2H), 2.94 (s, 6H), 2.42 (bs, 4H), 1.64 - 1.56 \text{ (m, 4H), 1.48 - 1.42 \text{ (m, 2H); } ^{13}\text{C-NMR (100 MHz, CDCl}_3\text{): } \delta = 150.0, \quad 132.7, \quad 127.2, \\
& \quad 125.8, \quad 122.7, \quad 112.5, \quad 62.1, \quad 54.5, \quad 40.5, \quad 26.0, \quad 24.4; \quad \text{HRMS (ESI, m/z) calcd. for C}_{16}\text{H}_{24}\text{Na}_2 [M + 2Na]^2+ \quad 145.0862, \quad \text{found 145.0863.}
\end{align*}
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(E)-1-(3-(4-bromophenyl)allyl)piperidine 4b

\[
\begin{align*}
0.256 \text{g, 91 \% yield;} \quad & ^1\text{H-NMR (400 MHz, CDCl}_3\text{): } \delta = 7.41 - 7.37 \text{ (m, 2H), 7.22 - 7.19 \text{ (m, 2H), 6.40 (d, } J = \\
& 15.9 \text{ Hz, 1H), 6.27 (dt, } J_1 = 6.6 \text{ Hz, } J_2 = 15.8 \text{ Hz, 1H), 3.07 (dd, } J_1 = 1.0 \text{ Hz, } J_2 = 6.6 \text{ Hz,} \\
& \text{2H), 2.40 (bs, 4H), 1.63 - 1.55 \text{ (m, 4H), 1.45 - 1.41 \text{ (m, 2H); } ^{13}\text{C-NMR (100 MHz, CDCl}_3\text{): } \delta = 136.1, \quad 131.7, \quad 131.4, \quad 128.3, \quad 127.9, \quad 121.1, \quad 61.8, \quad 54.7, \quad 26.0, \quad 24.4; \quad \text{HRMS (ESI, m/z) calcd. for C}_{14}\text{H}_{19}\text{BrN [M + H]}^+: \quad 280.0695, \quad \text{found 280.0685.}
\end{align*}
\]

(E)-4-(3-(piperidin-1-yl)prop-1-en-1-yl)phenol 4c

\[
\begin{align*}
0.196 \text{g, 90 \% yield;} \quad & ^1\text{H-NMR (400 MHz, CDCl}_3\text{): } \delta = 8.87 \text{ (bs, 1H), 7.11 - 7.04 \text{ (m, 2H), 6.75 - 6.64 \text{ (m, 2H), 6.39 (d, } J = 16.0 \text{ Hz, 1H), 5.98 (dt, } J_1 = 7.1 \text{ Hz, } J_2 = 15.9 \text{ Hz, 1H), 3.12 (d, } J_2 = 7.0 \text{ Hz, 2H), 2.57 (bs, 4H), 1.73 - 1.62 \text{ (m, 4H), 1.53 - 1.42 \text{ (m, 2H); } ^{13}\text{C-NMR (100 MHz, CDCl}_3\text{): } \delta = 157.0, \quad 134.3, \quad 128.3, \quad 127.9, \quad 122.0, \quad 116.4, \quad 61.7, \quad 54.4, \quad 25.2, \quad 24.1; \quad \text{HRMS (ESI, m/z) calcd. for C}_{14}\text{H}_{20}\text{NO [M + H]}^+: \quad 218.1539, \quad \text{found 218.1544.}
\end{align*}
\]
(E)-1-(3-(furan-2-yl)allyl)piperidine 4d

0.170 g, 89 % yield; \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.34 – 7.30\) (m, 1H), 6.37 – 6.28 (m, 2H), 6.26–6.16 (m, 2H), 3.09 – 3.06 (m, 2H), 2.41 (bs, 4H), 1.65 – 1.53 (m, 4H), 1.49 – 1.39 (m, 2H); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta = 152.9, 141.9, 126.2, 121.2, 111.3, 107.2, 61.7, 54.7, 26.1, 24.5\); HRMS (ESI, m/z) calcd. for C\(_{12}\)H\(_{18}\)NO [M + H]\(^+\) 192.1383, found 192.1375.

(E)-1-(3-(thiophen-2-yl)allyl)piperidine 4e

0.190 g, 92 % yield; \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.14 – 7.10\) (m, 1H), 6.97 – 6.88 (m, 2H), 6.13 (dt, 1H, \(J_1 = 6.9\) Hz, \(J_2 = 15.7\) Hz) 3.07 (dd, 2H, \(J_1 = 1.3\) Hz, \(J_2 = 6.9\) Hz), 2.42 (bs, 4H), 1.67–1.53 (m, 4H), 1.51 – 1.38 (m, 2H); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta = 142.5, 127.4, 127.3, 125.8, 125.2, 124.0, 61.7, 54.7, 26.1, 24.5\); HRMS (ESI, m/z) calcd. for C\(_{12}\)H\(_{18}\)NS [M + H]\(^+\) 208.1154, found 208.1158.

1-(2-methyl-3-phenylallyl)piperidine 6

0.191 g, 88 % yield; \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.40 – 7.19\) (m, 5H, minor and major), 6.52 (s, 1H, minor), 6.48 (s, 1H, major), 3.12 – 3.10 (m, 2H, minor), 3.04 – 3.01 (m, 2H, major), 2.42 (bs, 4H, major), 2.32 (bs, 4H, minor), 2.02 – 2.00 (m, 3H, minor), 1.98 – 1.96 (m, 3H, major), 1.69 – 1.56 (m, 4H, major and minor), 1.55 – 1.40 (m, 2H, major and minor); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta = 138.2, 136.5, 128.9, 128.1, 127.1, 126.2, 68.8, 54.7, 26.1, 24.6, 16.9\) (major); 138.2, 137.3, 129.2, 128.6, 127.9, 126.1, 59.8, 54.5, 26.1, 24.5, 23.2 (minor); HRMS (ESI, m/z) calcd. for C\(_{15}\)H\(_{22}\)N [M + H]\(^+\): 216.1747; found: 216.1737.

(E)-N-benzyl-3-phenylprop-2-en-1-amine 9

0.159 g, 71 % yield; \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.46 – 7.24\) (m, 10H), 6.59 (d, \(J = 15.9\) Hz, 1H), 6.38 (dt, \(J = 6.3\) Hz, 15.9 Hz, 1H), 3.90 (s, 2H), 3.49 (d, \(J = 5.5\) Hz, 2H), 2.66 (s, 1H); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta = 139.6, 137.0, 131.8, 128.5, 128.3, 127.8, 127.4, 127.1, 126.3, 53.0, 50.1\); HRMS (ESI, m/z) calcd. for C\(_{16}\)H\(_{18}\)N [M + H]\(^+\): 224.1434; found: 224.1444.
N-(naphthalen-1-ylmethyl)cinnamamide 12

1.306 g, 91 % yield; \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.08 – 8.04 \text{ (m, 1H)}, 7.90 – 7.80 \text{ (m, 2H)}, 7.69 \text{ (d, } J = 15.6 \text{ Hz, 1H)}, 7.59 – 7.42 \text{ (m, 6H)}, 7.36 – 7.31 \text{ (m, 3H)}, 6.36 \text{ (d, } J = 15.6 \text{ Hz, 1H)}, 5.91 \text{ (bs, 1H)}, 5.03 – 5.00 \text{ (m, 2H)}; \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta = 165.6, 141.6, 134.9, 134.1, 133.6, 131.6, 129.9, 128.9, 128.9, 127.9, 127.1, 126.9, 126.2, 125.6, 123.7, 120.4, 42.2; \)HRMS (ESI, m/z) calcd. for C\(_{21}\)H\(_{19}\)NNaO [M + Na\(^+\)]: 324.1359; found: 324.1345.

N-methyl-N-(naphthalen-1-ylmethyl)cinnamamide 13

0.976 g, 93 % yield; \(^1\)H-NMR (500 MHz, (CD\(_3\))\(_2\)SO): \(\delta = 7.66 – 7.62 \text{ (m, 1H)}, 7.45 – 7.42 \text{ (m, 1H)}, 7.14 – 6.94 \text{ (m, 6H)}, 6.89 – 6.81 \text{ (m, 4H)}, 6.68 – 6.62 \text{ (m, 1H)}, 4.68 \text{ (s, 2H)}, 2.55 \text{ (s, 3H)}; \(^{13}\)C-NMR (125 MHz, (CD\(_3\))\(_2\)SO): \(\delta = 165.6, 140.9, 134.8, 133.1, 132.6, 130.7, 128.8, 128.1, 128.0, 127.3, 127.2, 125.7, 125.2, 124.8, 122.8, 118.5, 48.5, 33.8; \)HRMS (ESI, m/z) calcd. for C\(_{20}\)H\(_{17}\)NNaO [M + Na\(^+\)]: 310.1202; found: 310.1208.

(E)-N-methyl-N-(naphthalen-1-ylmethyl)-3-phenylprop-2-en-1-amine 14

0.263 g, 92 % yield; \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.40 – 8.36 \text{ (m, 1H)}, 7.93 – 7.88 \text{ (m, 1H)}, 7.87 – 7.81 \text{ (m, 1H)}, 7.63 – 7.51 \text{ (m, 3H)}, 7.50 – 7.44 \text{ (m, 3H)}, 7.41 – 7.35 \text{ (m, 2H)}, 7.32 – 7.26 \text{ (m, 1H)}, 6.65 \text{ (d, } J = 16.0 \text{ Hz, 1H)}, 6.45 \text{ (dt, } J = 6.6, 16.0 \text{ Hz, 1H}), 4.02 \text{ (s, 2H)}, 3.35 \text{ (dd, } J = 1.2, 6.6 \text{ Hz, 2H}), 2.35 \text{ (s, 3H)}; \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta = 137.3, 135.0, 134.0, 132.8, 132.6, 128.7, 128.6, 128.0, 127.7, 127.6, 127.5, 126.4, 126.0, 125.7, 125.2, 124.8, 60.5, 60.2, 42.6; \)HRMS (ESI, m/z) calcd. for C\(_{21}\)H\(_{22}\)N [M + H\(^+\)]: 288.1747; found: 288.1747.
Spectroscopic data.
CDCl₃
400 MHz

[Diagram of a 1H NMR spectrum with peak assignments at various ppm values.]

[Chemical structure of the compound with signals at ppm values.]
CDC$_3$

$400$ MHz
CDC13
100 MHz
CDCl₃
100 MHz

[Chemical structure image]
CDCl₃
100 MHz
CDCl₃
400 MHz

![NMR Spectrum](image)
CDCl₃
100 MHz

Br

1H NMR spectrum of an aromatic compound with a bromine substituent on the phenyl ring.
CDCl$_3$

100 MHz

N

O
CDCl₃
400 MHz

![NMR Spectrum Image]
CDC13
100 MHz
CDCl$_3$
400 MHz

silane

THF

silane

THF
CDCl₃
400 MHz

N

H

![NMR Spectrogram](image)
DMSO-d6, 125 MHz
95C d1=10
CDCl$_3$
400 MHz