Supporting Information

Enantioselective Synthesis of Chiral Acylsilanes by Copper/HZNU-Phos-Catalyzed Asymmetric Conjugate Addition of Diethyzinc to $\alpha,\beta$-Unsaturated Acylsilanes

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Table of Contents

1. General Information..............................................................................................................2

2. General Procedure for the preparation of $\alpha,\beta$-unsaturated acylsilanes..................2

3. General Procedure for Cu(II)/($S,R$)-HZNU-Phos-catalyzed enantioselective Cu-catalyzed conjugate addition........................................................................................................3

4. Characterization data of 3.................................................................................................4

Figure S1-S5. Calculated and Experimental CD spectrum.................................................14

Table S1. The reaction results of copper-catalyzed asymmetric conjugate addition of other organometallic reagents to $\alpha,\beta$-unsaturated acylsilane 1a........................................16

5. 1H, 13C, 19F and 29Si NMR Spectra...............................................................................17

6. HPLC Spectra......................................................................................................................48
1. General Information.

All reactions were performed in flame- or oven-dried glassware under inert of argon or N\textsubscript{2} and conjugate additions were carried out using standard Schlenk techniques. Unless specifically stated, all reagents were commercially available and purified prior to use. For example, all the aldehydes were recrystallized or distilled prior to use. Dichloromethane and toluene were freshly distilled from CaH\textsubscript{2}, and THF was freshly distilled from sodium prior to use. Ether (Et\textsubscript{2}O) and 1,4-dioxane were dried and distilled from sodium and benzophenone. Alcohol solvents were dried and distilled from magnesium. Except \(\alpha,\beta\)-unsaturated acylsilanes, other reagents and solvents were commercially available and used directly without purification. Reactions were monitored by thin layer chromatography (TLC) using silica gel plates. Flash column chromatography was performed over silica (300 - 400 mesh). \(^1\)H, \(^13\)C, \(^19\)F and \(^29\)Si NMR spectra were recorded on a Bruker 400 MHz or 500 MHz spectrometer in CDCl\textsubscript{3}. Multiplicities were given as: s (singlet); d (doublet); \(dd\) (doublets of doublet); t (triplet); q (quartet); or m (multiplets). High resolution mass spectra (HRMS) of the products were obtained on a Bruker Daltonics micro TOF-spectrometer. HPLC was carried out with Agilent 1260 infinity using a chiralpak AD-H column, a chiralpak OJ-H column or a chiralcel IC column.

2. General Procedure for the preparation of \(\alpha,\beta\)-unsaturated acylsilanes

General experimental details for the synthesis of \(\alpha,\beta\)-unsaturated acylsilanes are the same as those previously reported.\cite{1} To a round-bottomed flask equipped with a stir bar and charged with \(n\)-Bu\textsubscript{4}N•ReO\textsubscript{4} (0.05 eq.), \(\rho\)-TsOH•H\textsubscript{2}O (0.05 eq.) was added a 0.2 M solution of propargyl alcohol (1.00 eq) in DCM. After overnight stirring at ambient temperature the reaction was diluted with water and the aqueous phase separated. The organic phase was washed with brine, dried with anhydrous MgSO\textsubscript{4}, and concentrated in vacuo.
The crude product was purified by flash column chromatography, eluting with
the indicated solvent mixture to afford the desired product. For example,
when the propargyl alcohol 1a (0.69 mmol, 1.0 eq.) was converted into
\( \alpha,\beta \)-unsaturated acyl silane 2a, the product was obtained with 72% yield as an
red oil after purification by flash column chromatography (EA/PE=1/20).

Reference

3. General Procedure for Cu(II)/(S,R)-HZNU-Phos-catalyzed
enantioselective Cu-catalyzed conjugate addition of
\( \alpha,\beta \)-unsaturated acylsilanes

\[
\begin{align*}
\text{Cu(OTf)}_2 & \quad (2.0 \text{ mol\%}) \\
\text{(S,R)-HZNU-Phos} & \quad (3.2 \text{ mol\%}) \\
\text{Et}_2\text{Zn} (3 \text{ eq.}) & \quad \text{Et}_2\text{O, -20°C} \\
\end{align*}
\]

A flame-dried Schlenk tube was charged with Cu(OTf)\(_2\) (3.6 mg, 0.01 mmol,
2.0 mol\%) and (S,R)-HZNU-Phos (10.0 mg, 0.016 mmol, 3.2 mol\%) under an
\( \text{N}_2 \) atmosphere, and the mixture was dissolved in dry Et\(_2\)O (3.0 mL). The
solution was stirred at room temperature for 30 min and then cooled to -20°C.
Diethylzinc (3.0 mmol, 3.0 mL of 1 M toluene solution, 6 eq.) was added
dropwise to the above solution. Then \( \alpha,\beta \)-unsaturated acylsilane (0.5
mmol) was added to the clear yellow solution at once. The mixture was stirred
at -20°C for 9-12 h before quenched with aqueous saturated NH\(_4\)Cl (aq.). The
layers were separated and the aqueous layer was extracted with ethyl acetate
(5 mL \( \times \) 2). The combined organic layers were dried over anhydrous Na\(_2\)SO\(_4\)
and concentrated under reduced pressure. The residue was purified by
column chromatography on silica gel to give the addition product. The
enantiomeric excess of the product was determined by chiral HPLC.
4. Characterization data of 3

(E)-3-phenyl-1-(trimethylsilyl)prop-2-en-1-one (α,β-unsaturated acyl silane 2a), has been reported in ref. [1].

(E)-3-(p-tolyl)-1-(trimethylsilyl)prop-2-en-1-one (2b)

Purification by flash column chromatography (EA/PE = 1/20) yielded the product (65%) as an red oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.29 (dd, J = 12.4, 6.1 Hz, 3H), 7.04 (d, J = 8.0 Hz, 2H), 6.71 (d, J = 16.4 Hz, 1H), 2.21 (s, 3H), 0.17 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 236.9, 144.3, 142.1, 133.4, 131.8, 130.9, 129.5, 22.7, -0.74. $^{29}$Si NMR (99 MHz, CDCl$_3$) δ -8.70 (s). HRMS Calculated for [M+H]$^+$: C$_{13}$H$_{19}$OSi: 219.1200; Found: 219.1209

(E)-3-(4-ethylphenyl)-1-(trimethylsilyl)prop-2-en-1-one (2c)

Purification by flash column chromatography (EA/PE = 1/20) yielded the product (70%) as an red oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.38-7.23 (m, 3H), 7.08 (d, J = 7.8 Hz, 2H), 6.73 (d, J = 16.4 Hz, 1H), 2.52 (q, J = 7.5 Hz, 2H), 1.10 (t, J = 7.6 Hz, 4H), 0.18 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 238.1, 149.3, 145.1, 134.4, 132.6, 130.5, 130.3, 30.8, 17.3, -0.0... $^{29}$Si NMR (99 MHz, CDCl$_3$) δ -8.48 (s). HRMS Calculated for: C$_{14}$H$_{21}$OSi [M+H]$^+$: 233.1356; Found: 233.1366
(E)-3-(4-chlorophenyl)-1-(trimethylsilyl)prop-2-en-1-one (2d)

Purification by flash column chromatography (EA/PE = 1/20) yielded the product (80%) as an red oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.30 (d, $J = 8.4$ Hz, 2H), 7.18 (d, $J = 8.6$ Hz, 3H), 6.69 (d, $J = 16.4$ Hz, 1H), 0.14 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 238.1, 143.0, 133.4, 131.5, 131.3, -0.0. $^{29}$Si NMR (99 MHz, CDCl$_3$) $\delta$ -7.86 (s). HRMS Calculated for: C$_{12}$H$_{14}$OSi[M+Na]$^+$: 295.0083; Found: 295.0093

(E)-3-(4-(trifluoromethyl)phenyl)-1-(trimethylsilyl)prop-2-en-1-one (2e)

purification by flash column chromatography (EA/PE=1/20) yielded the product (80%) as an red oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.45 (s, 5H), 7.23 (d, $J = 16.4$ Hz, 1H), 6.77 (dd, $J = 16.4$, 1.9 Hz, 1H), 0.14 (d, $J = 3.2$ Hz, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 238.5, 142.3, 140.7, 134.8, 130.6, 128.1 (q, $J = 3.8$ Hz), 0.0. $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -62.86. $^{29}$Si NMR (99 MHz, CDCl$_3$) $\delta$ -7.70. HRMS Calculated for C$_{13}$H$_{16}$F$_3$OSi [M+H]$^+$: 273.0917, found: 273.0927.

(E)-3-(4-bromophenyl)-1-(trimethylsilyl)prop-2-en-1-one (2f)

was Purification by flash column chromatography (EA/PE=1/20) yielded the product (75%) as an red oil $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.53 (d, $J = 8.5$ Hz, 2H), 7.41 (d, $J = 8.4$ Hz, 2H), 6.88 (d, $J = 16.4$ Hz, 1H), 1.26 (s, 1H), 0.32 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 238.2, 143.1, 136.0, 134.3, 133.5, 131.7, 126.8, 0.0. $^{29}$Si NMR (99 MHz, CDCl$_3$) $\delta$ -8.06 (s). HRMS Calculated for: C$_{12}$H$_{16}$FOSi[M+Na]$^+$: 285.0138; Found: 283.0148.
(E)-3-(2-fluorophenyl)-1-(trimethylsilyl)prop-2-en-1-one (2g)

Purification by flash column chromatography (EA/PE = 1/20) yielded the product (73%) as an red oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.47 – 7.34 (m, 2H), 7.14 (dd, $J = 13.9$, 7.0 Hz, 1H), 6.91 (dt, $J = 18.9$, 8.4 Hz, 2H), 6.68 (d, $J = 16.7$ Hz, 1H), 0.11 (s, 9H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 238.7, 164.7, 162.2, 137.4 (d, $J = 3.9$ Hz), 135.2 (d, $J = 4.5$ Hz), 133.9 (d, $J = 8.7$ Hz), 130.3 (d, $J = 2.7$ Hz), 126.7 (d, $J = 3.6$ Hz), 118.2 (d, $J = 22.0$ Hz), 0.0. $^{29}$Si NMR (99 MHz, CDCl$_3$) $\delta$ -7.98 (s). $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -115.26 (s). HRMS Calculated for: C$_{12}$H$_{16}$FOSi[M+H]$^+$: 223.0949; Found: 223.0958.

(E)-3-(2-chlorophenyl)-1-(trimethylsilyl)prop-2-en-1-one (2h)

Purification by flash column chromatography (EA/PE = 1/20) yielded the product (60%) as an red oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.73 (d, $J = 16.7$ Hz, 1H), 7.41 (dd, $J = 7.2$, 2.0 Hz, 1H), 7.18 (dd, $J = 7.6$, 1.6 Hz, 1H), 7.11 – 7.02 (m, 2H), 6.50 (d, $J = 16.7$ Hz, 1H), 0.14 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 238.5, 142.1, 137.0, 135.9, 134.9, 133.0, 131.9, 131.2, 129.0, 0.0. $^{29}$Si NMR (99 MHz, CDCl$_3$) $\delta$ -7.99 (s). HRMS Calculated for: C$_{12}$H$_{15}$ClO Si[M+Na]$^+$: 261.0473; Found: 261.0482.

(E)-3-(2-bromophenyl)-1-(trimethylsilyl)prop-2-en-1-one (2i)

Purification by flash column chromatography (EA/PE=1/20) yielded the product (65%) as an red oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.94 (d, $J = 16.6$ Hz, 1H), 7.70 – 7.60 (m, 2H), 7.39 – 7.23 (m, 2H), 6.70 (d, $J = 16.6$ Hz, 1H), 0.39 (s, 9H). $^{13}$C NMR (100 MHz,
CDCl$_3$ $\delta$ 238.1, 144.4, 136.1, 135.7, 134.7, 132.6, 129.1, 128.6, 127.1, -0.5.

$^{29}$Si NMR (99 MHz, CDCl$_3$) $\delta$ -7.75 (s). HRMS Calculated for: C$_{12}$H$_{16}$BrOSi[M+H]$^+$: 283.0148; Found: 283.0162

(2j) Purification by flash column chromatography (EA/PE = 1/20) yielded the product (80%) as a red oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.69 (d, $J$ = 16.6 Hz, 1H), 7.50 (dd, $J$ = 14.6, 7.9 Hz, 2H), 7.35 (t, $J$ = 7.6 Hz, 1H), 7.25 (t, $J$ = 7.5 Hz, 1H), 6.47 (d, $J$ = 16.5 Hz, 1H), 0.11 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 238.8, 141.9, 137.8, 135.9, 134.4, 131.9, 129.6, 128.3 (q, $J$ = 5.5 Hz), 127.7, 124.9, -0.0. $^{29}$Si NMR (99 MHz, CDCl$_3$) $\delta$ -7.41. $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -58.83. HRMS Calculated for C$_{13}$H$_{16}$F$_3$OSi [M+H]$^+$: 273.0917; found: 273.0927.

(2k) Purification by flash column chromatography (EA/PE = 1/20) yielded the product (50%) as a red oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.33 (s, 1H), 7.23 (d, $J$ = 7.0 Hz, 1H), 7.15 (dd, $J$ = 9.2, 7.2 Hz, 3H), 6.69 (d, $J$ = 16.4 Hz, 1H), 0.13 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 142.8, 139.0, 137.2, 134.0, 132.4, 130.1, 128.5, 0.0. $^{29}$Si NMR (99 MHz, CDCl$_3$) $\delta$ -7.85 (s) HRMS Calculated for: C$_{13}$H$_{16}$FOSi[M+Na]$^+$: 261.0482; Found: 261.0473.
(R)-3-phenyl-1-(trimethylsilyl)pentan-1-one (3a)

\[
\begin{align*}
&\text{\textsuperscript{1}H NMR (400 MHz, CDCl}_3\text{)} \delta 7.18 (\text{dd, J = 9.1, 5.8 Hz, 1H}), 7.11 - 7.04 (\text{m, 3H}), 3.03 (\text{ddd, J = 12.4, 9.1, 6.7 Hz, 1H}), 2.91 - 2.73 (\text{m, 2H}), 1.19 (\text{d, J = 11.1 Hz, 2H}), 0.67 (\text{t, J = 7.3 Hz, 3H}), 0.03 (\text{s, 9H}). \\
&\text{\textsuperscript{13}C NMR (100 MHz, CDCl}_3\text{)} \delta 177.3, 145.0, 128.3, 127.6, 126.1, 55.0, 41.2, 30.7, 29.3, 12.0, -3.3. \\
&\text{\textsuperscript{29}Si NMR (99 MHz, CDCl}_3\text{)} \delta -10.06 (\text{s}). \\
\end{align*}
\]

Enantiomeric excess was determined by HPLC with a Chiralpak OJ column (hexanes: 2-propanol = 99.5:0.5, 0.8 mL/min, 210 nm); \(t_R = 5.65\ \text{min}, \ t_R = 6.23\ \text{min}, \text{85\% ee.}\)

3-(p-tolyl)-1-(trimethylsilyl)pentan-1-one (3b)

\[
\begin{align*}
&\text{\textsuperscript{1}H NMR (400 MHz, CDCl}_3\text{)} \delta 6.95 (\text{q, J = 7.5 Hz, 4H}), 3.02 - 2.93 (\text{m, 1H}), 2.76 (\text{ddd, J = 24.0, 16.7, 6.9 Hz, 2H}), 2.18 (\text{s, 3H}), 1.53 - 1.33 (\text{m, 2H}), 0.63 (\text{t, J = 7.3 Hz, 3H}), -0.00 (\text{s, 9H}). \\
&\text{\textsuperscript{13}C NMR (100 MHz, CDCl}_3\text{)} \delta 246.8, 142.1, 129.7, 127.9, 127.1, 126.8, 53.8, 36.8, 28.2, 11.6, -3.3. \\
&\text{\textsuperscript{29}Si NMR (99 MHz, CDCl}_3\text{)} \delta -10.23 (\text{s}). \\
\end{align*}
\]

HRMS Calculated for: \(\text{C}_{15}\text{H}_{24}\text{OSi}[\text{M+Na}^+]^+ : 271.1489;\)

Found: 271.1498. Enantiomeric excess was determined by HPLC with a Chiralpak AD column (hexanes: 2-propanol = 99.5:0.5, 0.8 mL/min, 210 nm); \(t_R = 6.72\ \text{min}, \ t_R = 7.4\ \text{min}, \text{80\% ee.}\)

Purification by flash column chromatography (EA/PE=1/20) yielded the product (60\%) as an colorless oil \([\alpha]^{25}_D = 25 (c = 0.1, \ \text{CHCl}_3).\)
3-(4-ethylphenyl)-1-(trimethylsilyl)pentan-1-one (3c)

Purification by flash column chromatography (EA/PE = 1/20) yielded the product (60%) as an colorless oil. \([\alpha]_{D}^{25} = 15.42\) (c = 0.11, CHCl\(_3\)). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.97 (q, J = 8.1 Hz, 9H), 3.03-2.94 (m, 1H), 2.77 (ddd, J = 24.0, 16.6, 6.8 Hz, 1H), 2.49 (dd, J = 15.3, 7.6 Hz, 1H), 1.10 (t, J = 7.6 Hz, 1H), 0.64 (t, J = 7.3 Hz, 1H), 0.00 (s, 9H). \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 248.0, 142.3, 142.0, 127.9, 127.5, 55.2, 40.9, 29.4, 28.5, 15.6, 12.1, -3.3. \(^{29}\)Si NMR (99 MHz, CDCl\(_3\)) \(\delta\) -10.18 (s). HRMS Calculated for: C\(_{16}\)H\(_{26}\)OSi [M+Na]\(^+\): 285.1645; Found: 285.1655. Enantiomeric excess was determined by HPLC with a Chiralpak AD column (hexanes: 2-propanol = 99.8:0.2, 1 mL/min, 210 nm); \(t_R = 5.10 \text{ min}, t_S = 5.39 \text{ min}, 72\% \text{ ee}\).

(R)-3-(4-chlorophenyl)-1-(trimethylsilyl)pentan-1-one (3d)

\[\alpha\]_{D}^{25} = 11.94\) (c = 0.1, CHCl\(_3\)). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.10-6.99 (m, 3H), 6.91 (d, J = 7.4 Hz, 1H), 3.04-2.95 (m, 1H), 2.75 (ddd, J = 42.3, 17.0, 6.8 Hz,2H), 1.52-1.33 (m, 2H), 0.63 (t, J = 7.4 Hz, 3H), 0.00 (s, 9H). \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 247.1, 147.4, 134.3, 127.7, 126.4, 54.7, 41.0, 29.3, 12.1, -3.3. \(^{29}\)Si NMR (99 MHz, CDCl\(_3\)) \(\delta\) -7.89 (s). HRMS Calculated for: C\(_{14}\)H\(_{21}\)ClOSi [M+Na]\(^+\): 291.0952; Found: 291.0942. Enantiomeric excess was determined by HPLC with a Chiralpak IA column (hexanes: 2-propanol = 99.8:0.2, 1 mL/min, 210 nm); \(t_1 = 14.8 \text{ min}, t_2 =16.0 \text{ min, 66\% ee}\).
3-(4-(trifluoromethyl)phenyl)-1-(trimethylsilyl)pentan-1-one (3e)

Purification by flash column chromatography (EA/PE=1/20) yielded the product (60%) as an colorless oil. [α]$_D^{25}$ = 10.2 (c = 0.1, CHCl$_3$).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.40 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 3.08 (dd, J = 14.9, 6.4 Hz, 1H), 2.79 (dd, J = 15.7, 6.8 Hz, 2H), 1.55-1.37 (m, 2H), 0.63 (t, J = 7.3 Hz, 3H), 0.00 (s, 9H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 246.7, 149.3, 127.9, 125.3 (q, J = 3.8 Hz), 54.5, 40.8, 29.1, 11.9, -3.5.

$^{29}$Si NMR (99 MHz, CDCl$_3$) δ -7.89 (s).

HRMS Calculated for: C$_{15}$H$_{21}$F$_3$O$_2$Si[M+Na]$^+$: 325.1206; Found:325.1215. Enantiomeric excess was determined by HPLC with a Chiralpak AD column(hexanes: 2-propanol = 99.8:0.2, 1 mL/min, 210 nm); t$_1$ = 5.10 min, t$_2$ = 5.39 min, 52%ee.

(R)-3-(4-bromophenyl)-1-(trimethylsilyl)pentan-1-one (3f)

$[α]_D^{25}$ = 8.9 (c = 0.1, CHCl$_3$).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.30 (d, J = 8.4 Hz, 2H), 6.95 (d, J = 8.42Hz, 1H), 3.01 (ddd, J = 12.2, 9.4, 6.7 Hz, 1H), 2.78 (ddd, J = 37.6, 17.1, 6.8 Hz, 2H), 1.17 (s, 2H), 0.65 (t, J = 7.3 Hz, 3H), 0.03 (s, 9H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 247.1, 144.1, 131.4, 129.4, 119.7, 54.7, 40.0, 29.2, 11.9, -3.4.

$^{29}$Si NMR (99 MHz, CDCl$_3$) δ -9.83 (s). HRMS Calculated for: C$_{14}$H$_{21}$BrOSi[M+Na]$^+$: 337.0427; Found: 335.0437. Enantiomeric excess was determined by HPLC with a Chiralpak AD column(hexanes: 2-propanol = 99.8:0.2, 1 mL/min, 210 nm); t$_1$ = 12.97min, t$_2$ =14.16min, 73 %ee.
3-(2-fluorophenyl)-1-(trimethylsilyl)pentan-1-one (3g)

Purification by flash column chromatography (EA/PE = 1/20) yielded the product (35%) as a colorless oil \([\alpha]_{D}^{25} = 1.8\) (c = 0.05, CHCl₃).

\(^1\)H NMR (400 MHz, CDCl₃) \(\delta 7.01\) (dd, \(J = 10.5, 4.7\) Hz, 2H), 6.94 – 6.83 (m, 2H), 3.28 (dq, \(J = 9.0, 6.8\) Hz, 1H), 2.82 (ddd, \(J = 39.5, 17.0, 6.9\) Hz, 2H), 1.51-1.42 (m, 2H), 0.63 (t, \(J = 7.4\) Hz, 3H), 0.00 (s, 9H). \(^{13}\)C NMR (100 MHz, CDCl₃) \(\delta 246.1, 160.1\) (d, \(J = 244.9\) Hz), 130.4 (d, \(J = 14.2\) Hz), 128.3 (d, \(J = 5.5\) Hz), 126.5 (d, \(J = 8.4\) Hz), 123.0 (d, \(J = 3.4\) Hz), 114.5 (d, \(J = 23.0\) Hz), 52.5, 34.2, 27.1, 11.0, -4.4. \(^{29}\)Si NMR (99 MHz, CDCl₃) \(\delta -9.91\). \(^{19}\)F NMR (471 MHz, CDCl₃) \(\delta -117.49\) (s). HRMS Calculated for: C₁₅H₂₄O₂Si [M+Na]⁺: 275.1238; Found: 275.1247. Enantiomeric excess was determined by HPLC with a Chiralpak AD column(hexanes: 2-propanol = 99.8:0.2, 1 mL/min, 210 nm); \(t_1 = 4.74\) min, \(t_2 = 5.67\) min, 26% ee.

(R)-3-(2-chlorophenyl)-1-(trimethylsilyl)pentan-1-one (3h)

\(\alpha\) = 13 (c = 0.1, CHCl₃). \(^1\)H NMR (400 MHz, CDCl₃) \(\delta 7.29-6.98\) (m, 4H), 3.79 – 3.55 (m, 1H), 2.95-2.73 (m, 2H), 1.52 (s, 2H), 0.69 (t, \(J = 7.4\) Hz, 3H), 0.07 (s, 9H). \(^{13}\)C NMR (100 MHz, CDCl₃) \(\delta 246.8, 142.1, 134.2, 129.7, 128.0, 127.1, 126.8, 53.8, 36.8, 28.2, 11.6, -3.2\). \(^{29}\)Si NMR (99 MHz, CDCl₃) \(\delta -9.87\) (s). HRMS Calculated for: C₁₄H₂₁Cl₂O₂Si [M+H]⁺: 269.1133; Found: 269.1123. Enantiomeric excess was determined by HPLC
with a Chiralpak AD column (hexanes: 2-propanol = 99.8:0.2, 1 mL/min, 210 nm); $t_1 = 5.30$ min, $t_2 = 5.65$ min, 9% ee.

3-(2-bromophenyl)-1-(trimethylsilyl)pentan-1-one (3i)

Purification by flash column chromatography (EA/PE = 1/20) yielded the product (70%) as an colorless oil. $[\alpha]_{D}^{25} = 2.62$ (c = 0.12, CHCl$_3$).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36 (dd, $J$ = 8.0, 0.8 Hz, 1H), 7.12 – 6.97 (m, 1H), 6.85 (td, $J$ = 8.0, 1.6 Hz, 1H), 3.63 – 3.52 (m, 1H), 2.73 (qd, $J$ = 16.8, 6.9 Hz, 2H), 1.59 – 1.34 (m, 2H), 0.62 (t, $J$ = 7.4 Hz, 3H), -0.00 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 246.6, 143.8, 133.0, 127.9, 127.5, 127.5, 125.2, 55.0, 39.3, 28.4, 11.6, -3.3. $^{29}$Si NMR (99 MHz, CDCl$_3$) $\delta$ -9.96 (s). HRMS Calculated for: C$_{14}$H$_{21}$BrSi [M+Na]$^+$: 335.0437; Found: 337.0427. Enantiomeric excess was determined by HPLC with a Chiralpak IB column (hexanes: 2-propanol = 99.8:0.2, 1 mL/min, 210 nm); $t_1 = 5.43$ min, $t_2 = 5.68$ min, 34% ee.

3-(2-(trifluoromethyl)phenyl)-1-(trimethylsilyl)pentan-1-one (3j)

Purification by flash column chromatography (EA/PE = 1/20) yielded the product (40%) as an colorless oil $[\alpha]_{D}^{25} = -1.24$ (c = 0.06, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.45 (d, $J$ = 7.9 Hz, 1H), 7.32 (d, $J$ = 7.4 Hz, 1H), 7.22 (d, $J$ = 7.6 Hz, 1H), 7.11 (d, $J$ = 7.6 Hz, 1H), 3.48 (dd, $J$ = 8.8, 4.4 Hz, 2H), 2.68 (ddd, $J$ = 21.4, 16.9, 6.6 Hz, 2H), 0.56 (t, $J$ = 7.4 Hz, 3H), 0.00 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 244.4, 130.2, 126.0, 124.2 (dd, $J$ = 12.0,
6.2 Hz), 53.6, 34.0, 27.2, 10.1, -5.1. $^{19}$F NMR (471 MHz, CDCl$_3$) δ -58.45. $^{29}$Si NMR (99 MHz, CDCl$_3$) δ -9.64 (s). HRMS Calculated for: C$_{15}$H$_{21}$F$_3$OSi[M+Na]$^+$: 325.1206; Found: 325.1215. Enantiomeric excess was determined by HPLC with a Chiralpak Phenomenex column (hexanes: 2-propanol = 99.8:0.2, 1 mL/min, 210 nm); $t_R = 4.72$ min, $t_R = 5.66$ min, 27% ee.

3-(3-chlorophenyl)-1-(trimethylsilyl)pentan-1-one (3k)

3k

Purification by flash column chromatography (EA/PE = 1/20) yielded the product (98%) as an colorless oil. $[\alpha]_{D}^{25} = 21.86$ (c = 0.12, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.07 – 6.99 (m, 3H), 6.91 (dt, J = 7.4, 1.3 Hz, 1H), 3.04-2.95 (m, 1H), 2.81 (dd, J = 17.0, 6.7 Hz, 1H), 2.70 (dd, J = 17.0, 6.9 Hz, 1H), 1.53 – 1.35 (m, 2H), 0.62 (t, J = 7.4 Hz, 3H), 0.00 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 247.1, 147.5, 134.4, 129.8, 127.8, 126.5, 126.3, 54.8, 41.1, 29.4, 12.2, -3.2. $^{29}$Si NMR (99 MHz, CDCl$_3$) δ -9.85 (s). HRMS Calculated for:C$_{14}$H$_{21}$ClOSi [M+Na]$^+$: 291.0952; Found: 291.0942. 

Enantiomeric excess was determined by HPLC with a Chiralpak AD column (hexanes: 2-propanol = 99.8:0.2, 1 mL/min, 210 nm); $t_1 = 10.36$ min, $t_2 = 10.84$ min, 68% ee.
Figure S1. The experimental CD spectra of 4-Pheny-hexan-2-one (S-configuration).

Figure S2. The experimental CD spectra of product 3d.
**Figure S3.** Computed ECD spectra for compound (S)-3d in with the lowest-energy conformer calculated with TD DFT/CAM-B3LYP/6-31G(d,p)//CAM-B3LYP/6-31G(d,p) using PCM(CH₂Cl₂) model.

![Computed ECD spectra](image)

**Figure S4.** The optimized geometries of compound (S)-3d calculated at CAM-B3LYP/6-31G(d,p) using PCM model in dichloromethane.

The calculated ECD spectra were obtained from calculated excitation energies and rotational strengths as a sum of Gaussians functions centred at wavelength of each transition with bandwidth $\sigma=0.16$ eV using the SpecDis program.¹,² The final spectra were Boltzmann averaged ($T = 298$ K) weighted according to the population percentages of selected representative low-energy conformers based on the relative Gibbs free energies ($\Delta G$).

**Figure S5.** The experimental CD spectra of product 3b, 3e, 3h, 3c, 3k.

**Table S1.** The reaction results of copper-catalyzed asymmetric conjugate addition of other organometallic reagents to α,β-unsaturated acylsilane 1a.

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Note: <sup>a</sup> With Me₂Zn as a nucleophile. <sup>b</sup> With Ph₂Zn as a nucleophile. <sup>c</sup> With Et₃Al as a nucleophile. <sup>d</sup> nr is no reaction.
5. NMR Charts of Products (1H, 13C, 19F and 29Si NMR Spectra)
6. HPLC spectra of addition products.

![HPLC spectra](image)

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