Supporting Information for

Bifunctional squamide-catalyzed asymmetric synthesis of chiral α-mercaptosilanes

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I: General Information

Commercially available materials were purchased from Alfa Aesar and Sigma-Aldrich. THF was distilled over sodium. Other solvents were dried over 4Å molecular sieve prior use. Proton nuclear magnetic resonance (\(^1\)H NMR) spectra were recorded on a Bruker (400 MHz) spectrometer. Chemical shifts were recorded in parts per million (ppm, \(\delta\)) relative to tetramethylsilane (\(\delta\) 0.00) or chloroform (\(\delta\) = 7.26, singlet). \(^1\)H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), triplet of doublets (dt), triplet of triplets (tt), multiplets (m), and etc. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). Carbon nuclear magnetic resonance (\(^13\)C NMR) spectra were recorded on a Bruker (400 MHz) (100 MHz) spectrometer. High resolution mass spectral analysis (HRMS) was performed on a Waters Q–TOF Permier Spectrometer. The determination of enantiomeric excess was performed via chiral HPLC analysis using Shimadzu LC-20AD HPLC workstation. X-ray crystallography analysis was performed on Bruker X8 APEX X-ray diffractionmeter. Optical rotations were measured using a 1 mL cell with a 1 dm path length on a Jasco P-1030 polarimeter and are reported as follows: [\(\alpha\)]\textsubscript{D}\textsuperscript{c} (c is in gm per 100 mL solvent). Analytical thin-layer chromatography (TLC) was carried out on Merck 60 F254 pre-coated silica gel plate (0.2 mm thickness).
II. General procedure

a) Synthesis of β-silylated enones 1

β-silyl enones 1a–1q were synthesized according to the literature.[1-5]

b) General procedure for the reactions of 1 with 2 to synthesize products 3 (3a as an example)

\[
\text{Ph} = 
\text{TMS} + \text{Me} \quad \xrightarrow{\text{cat.A (0.5 mol%)}} \quad \text{Me} \quad \xrightarrow{\text{Toluene, -30°C, 4h}} \quad \text{Ph} \quad \text{TMS}
\]

To a dried 10 mL Schlenk tube equipped with a tiny magnetic stir bar was added 1a (0.1 mmol, 20.4 mg), 2a (0.11 mmol, 13.6 mg) and Cat.A (0.0005 mmol, 0.3 mg). To this mixture was added dry Toluene (3.0 mL), then the reaction mixture was stirred at -30°C for 4 hours. The reaction mixture was purified by flash column chromatography (silica gel, Petroleum ether/EtOAc, 20:1, v/v) to afford product 3a (0.095 mmol, 31.2 mg) as a colorless oil in 95% yield and 92% ee.

c) General procedure for the reactions of 4 from 3b

\[
\text{MeO} = \text{TMS} \quad \xrightarrow{\text{mCPBA (4 eq.)}} \quad \text{MeO} \quad \xrightarrow{\text{DCM, -40°C}} \quad \text{MeO} \quad \text{TMS}
\]

To a dried 10 mL Schlenk tube equipped with a tiny magnetic stir bar was added 3b (0.1 mmol, 35.8 mg) and CH₂Cl₂ (1 mL). The reaction mixture was cooled to -40 °C and added m-CPBA (0.4 mmol, 69.0 mg, 4.0 equiv). The was stirred at -40°C overnight. The reaction mixture was purified by flash column chromatography (silica gel, Petroleum ether/EtOAc, 10:1, v/v) to afford the product 4 (0.095 mmol, 37.1 mg) in 95% yield and 92% ee.
d) Stereochemistry determination 4 via X-ray crystallographic analysis

Product 4 was crystallized as a colorless crystal via vaporization of a hexane/Dichloromethane solution, and its absolute configuration was determined by x-ray structure analysis. CCDC 2044606 (DOI: 10.5517/ccdc.csd.cc26ml1h) contains the supplementary crystallographic data that can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
III. Characterizations of products, reference

Structures of known compounds were confirmed by NMR spectral comparison with literature datas. The compound not reported before, $^1$H NMR and $^{13}$C NMR characterization and the corresponding spectra are provided.

a) Characterizations of Products

**3a**

(S)-1-phenyl-3-(p-tolylthio)-3-(trimethylsilyl)propan-1-one (3a): colorless oil; $[\alpha]_D^{23}$ (c 0.372, CHCl$_3$) = +18.8; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 0.13 (s, 9H), 2.26 (s, 3H), 3.18 (dd, $J$ = 17.6, 4.4 Hz, 1H), 3.26-3.29 (m, 1H), 3.36-3.42 (m, 1H), 7.02 (d, $J$ = 8.0 Hz, 2H), 7.24 (d, $J$ = 8.0 Hz, 2H), 7.41 (t, $J$ = 7.6 Hz, 1H), 7.82-7.85 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = -2.2, 21.1, 28.2, 41.2, 128.1, 128.6, 129.8, 130.1, 132.9, 133.1, 136.2, 136.9, 199.2; HRMS(ESI) calcd for C$_{19}$H$_{24}$O$_2$Si (M+Na)$^+$: 351.1209, Found: 351.1204; 92% ee as determined by HPLC (Chiralcel AD, 95:5 hexanes/i-PrOH, 0.3 mL/min), $t_r$ (minor) = 14.8 min, $t_r$ (major) = 15.5 min.

**3b**

(S)-1-(4-methoxyphenyl)-3-(p-tolylthio)-3-(trimethylsilyl)propan-1-one(3b): colorless oil; $[\alpha]_D^{23}$ (c 0.198, CHCl$_3$) = +9.0; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 0.13 (s, 9H), 2.23 (s, 3H), 3.15 (dd, $J$ = 17.2, 4.4 Hz, 1H), 3.26-3.38 (m, 2H), 3.85 (s, 3H), 7.25 (dt, $J$ = 8.4, 2.0 Hz, 2H), 7.04 (m, 2H), 7.25 (m, 2H), 7.84 (dt, $J$ = 8.8, 2.8 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = -2.2, 21.1, 28.2, 40.7, 55.6, 113.7, 129.8, 129.9, 130.1, 130.4, 133.1, 136.1, 163.5, 197.7; HRMS(ESI) calcd for C$_{20}$H$_{26}$O$_2$Si (M+Na)$^+$: 381.1315, Found: 381.1325; 99% ee as determined by HPLC (Chiralcel ADH, 95:5 hexanes/i-PrOH, 0.3 mL/min), $t_r$ (minor) = 20.9 min, $t_r$ (major) = 23.3 min.
(S)-1-(p-tolyl)-3-(p-tolylthio)-3-(trimethylsilyl)propan-1-one (3c): colorless oil; [α]D <sup>23</sup> (c 0.448, CHCl<sub>3</sub>) = +18.2; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 0.14 (s, 9H), 2.27 (s, 3H), 3.17 (dd, J = 17.2, 4.0 Hz, 1H), 3.26-3.29 (m, 1H), 3.38 (dd, J = 17.6, 8.0 Hz, 1H), 7.03 (d, J = 8.0 Hz, 2H), 7.20-7.26 (m, 4H), 7.75 (d, J = 8.4 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = -2.2, 21.1, 21.7, 28.1, 41.0, 128.2, 129.3, 129.8, 130.0, 134.5, 136.1, 143.9, 198.8; HRMS(ESI) calcd for C<sub>20</sub>H<sub>26</sub>OSSi (M+Na)<sup>+</sup>: 365.1366, Found: 365.1366; 83% ee as determined by HPLC (Chiralcel ADH, 95:5 hexanes/i-PrOH, 0.3 mL/min), t<sub>r</sub> (minor) = 17.1 min, t<sub>r</sub> (major) = 18.4 min.

(S)-1-(4-bromophenyl)-3-(p-tolylthio)-3-(trimethylsilyl)propan-1-one (3d):
colorless oil; [α]D <sup>23</sup> (c 0.525, CHCl<sub>3</sub>) = +43.6; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 0.13 (s, 9H), 2.26 (s, 3H), 3.23 (m, 3H), 7.03 (d, J = 6.8 Hz, 2H), 7.23 (d, J = 6.8 Hz, 2H), 7.54 (m, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = -2.7, 18.2, 34.5, 38.7, 115.6, 115.8, 130.7, 130.8, 133.4, 133.5, 164.4, 166.9, 174.1, 198.3; HRMS(ESI) calcd for C<sub>19</sub>H<sub>23</sub>BrOSSi (M+Na)<sup>+</sup>: 429.0314, Found: 429.0315. HRMS(ESI) calcd for C<sub>19</sub>H<sub>23</sub>BrOSSi (M+Na)<sup>+</sup>: 431.0293, Found: 431.0289; 99% ee as determined by HPLC (Chiralcel AZH, 99:1 hexanes/i-PrOH, 0.2 mL/min), t<sub>r</sub> (major) = 13.5 min, t<sub>r</sub> (minor) = 15.2 min.

(S)-1-(4-fluorophenyl)-3-(p-tolylthio)-3-(trimethylsilyl)propan-1-one (3e):
colorless oil; [α]D <sup>23</sup> (c 0.825, CHCl<sub>3</sub>) = +88.5; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 0.13 (s, 9H), 2.26 (s, 3H), 3.13-3.60 (m, 3H), 7.01-7.08 (m, 4H), 7.23 (d, J = 8.0 Hz, 2H), 7.83-8.00 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = -2.3, 21.1, 28.4, 41.1, 115.6, 115.8, 129.8, 130.2, 130.7, 130.8, 132.8, 133.3, 133.4, 136.3, 164.50, 167.1, 197.7; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ = -105.64; HRMS(ESI) calcd for C<sub>19</sub>H<sub>23</sub>FNaOSSi...
(M+Na): 369.1115, Found: 369.1113; 99% ee as determined by HPLC (Chiralcel AZH, 95:5 hexanes/i-PrOH, 0.7 mL/min), tᵣ (major) = 65.2 min, tᵣ (minor) = 67.3 min.

(S)-1-(3-chlorophenyl)-3-(p-tolylthio)-3-(trimethylsilyl)propan-1-one (3f):
colorless oil; [α]D 23 (c 0.712, CHCl₃) = +36.0; ¹H NMR (400 MHz, CDCl₃) δ = 0.14 (s, 9H), 2.27 (s, 3H), 3.17 (dd, J = 16.8, 4.8 Hz, 1H), 3.22-3.25 (m, 1H), 3.32 (dd, J = 16.8, 6.8 Hz, 1H), 7.02 (d, J = 8 Hz, 2H), 7.22 (d, J = 8 Hz, 2H), 7.34 (t, J = 7.6 Hz, 1H), 7.48-7.50 (m, 1H), 7.69 (dt, J = 8.0, 1.6 Hz, 1H), 7.75 (t, J = 1.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ = -2.3, 21.1, 28.6, 41.4, 126.1, 128.2, 129.8, 129.9, 130.4, 132.7, 133.0, 134.9, 136.5, 198.1; HRMS(ESI) calcd for C₁₉H₂₃ClOSSi (M+Na)⁺: 385.0820, Found: 385.0818; HRMS(ESI) calcd for C₁₉H₂₃ClOSSi (M+Na)⁺: 387.0790, Found: 387.0791; 93% ee as determined by HPLC (Chiralcel IA, 98:2 hexanes/i-PrOH, 0.2 mL/min), tᵣ (minor) = 22.8 min, tᵣ (major) = 24.2 min.

(S)-1-(naphthalen-2-yl)-3-(p-tolylthio)-3-(trimethylsilyl)propan-1-one (3g):
colorless oil; [α]D 23 (c 0.656, CHCl₃) = +31.2; ¹H NMR (400 MHz, CDCl₃) δ = 0.17 (s, 9H), 2.25 (s, 3H), 3.31-3.37 (m, 2H), 3.49-3.56 (m, 1H), 7.03 (d, J = 8 Hz, 2H), 7.28 (d, J = 8 Hz, 2H), 7.53-7.58 (m, 2H), 7.83-7.85 (m, 2H), 8.32 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ = -2.2, 21.1, 28.6, 41.3, 123.9, 126.9, 127.9, 128.5, 128.6, 129.7, 129.7, 129.8, 130.2, 132.5, 132.9, 134.3, 135.6, 136.3, 199.2; HRMS(ESI) calcd for C₂₃H₂₆OSSi (M+H)⁺: 379.1546, Found: 379.1548; 95% ee as determined by HPLC (Chiralcel ADH, 99:1 hexanes/i-PrOH, 0.3 mL/min), tᵣ (minor) = 19.1 min, tᵣ (major) = 21.1 min.

(S)-1-(furan-2-yl)-3-(p-tolylthio)-3-(trimethylsilyl)propan-1-one (3h):
colorless oil; [α]D 23 (c 0.599, CHCl₃) = +37.0; ¹H NMR (400 MHz, CDCl₃) δ = 0.14 (s, 9H), 2.27 (s, 3H), 3.02-3.09 (m, 1H), 3.18-3.25 (m, 2H), 6.49 (q, J = 1.6 Hz, 1H),
7.03 (d, J = 7.6 Hz, 2H), 7.08 (dd, J = 3.6, 0.8 Hz, 1H), 7.23-7.26 (m, 2H), 7.53 (dd, J = 1.6, 0.8 Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ = -2.3, 21.1, 28.6, 40.8, 112.3, 117.2, 129.7, 130.4, 132.8, 136.3, 146.4, 152.7, 188.3; HRMS(ESI) calcd for C\(_{17}\)H\(_{22}\)O\(_2\)SSi (M+H): 319.1183, Found: 319.1186; 91\% ee as determined by HPLC (Chiralcel ADH, 95:5 hexanes/i-PrOH, 0.3 mL/min), \(t_r\) (minor) = 17.3 min, \(t_r\) (major) = 20.1 min.

(S)-1-(thiophen-2-yl)-3-(p-tollythio)-3-(trimethylsilyl)propan-1-one (3i): colorless oil; \([\alpha]_D^{23}\) (c 0.235, CHCl\(_3\)) = +11.8; \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ = 0.15 (s, 9H), 2.27 (s, 3H), 3.13 (dd, J = 16.4, 4.4 Hz, 1H), 3.21-3.32 (m, 2H), 7.03 (d, J = 7.6 Hz, 2H), 7.08 (dd, J = 4.8, 4.4 Hz, 1H), 7.24-7.27 (m, 2H), 7.60-7.61 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ = -2.3, 21.1, 28.8, 41.7, 128.1, 129.8, 130.3, 131.9, 132.7, 133.8, 136.3, 144.3, 192.0; HRMS(ESI) calcd for C\(_{17}\)H\(_{22}\)O\(_2\)SSi (M+Na): 357.1674, Found: 357.1679; 94\% ee as determined by HPLC (Chiralcel IA, 99:1 hexanes/i-PrOH, 0.2 mL/min), \(t_r\) (major) = 38.5 min, \(t_r\) (minor) = 41.4 min.

(S)-1-cyclohexyl-3-(p-tollythio)-3-(trimethylsilyl)propan-1-one (3j): colorless oil; \([\alpha]_D^{23}\) (c 0.674, CHCl\(_3\):CHCl\(_3\)) = +54.5; \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ = 0.09 (s, 9H), 1.12-1.32 (m, 6H), 1.59-1.75 (m, 5H), 2.28 (s, 3H), 2.69 (dd, J = 18.4, 4.2 Hz, 1H), 2.81 (dd, J = 18.4, 7.2 Hz, 1H), 3.05 (dd, J = 7.2, 5.2 Hz, 1H), 7.05 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ = -2.3, 21.1, 25.7, 25.8, 25.9, 26.0, 27.2, 28.5, 28.6, 43.2, 51.1, 129.7, 129.8, 129.9, 133.2, 136.0, 162.8; HRMS(ESI) calcd for C\(_{19}\)H\(_{10}\)OSSi (M+Na): 357.1679, Found: 357.1679; 83\% ee as determined by HPLC (Chiralcel IA, 95:5 hexanes/i-PrOH, 0.3 mL/min), \(t_r\) (minor) = 12.5 min, \(t_r\) (major) = 13.2 min.

(S)-4-(p-tollythio)-4-(trimethylsilyl)butan-2-one (3k): colorless oil; \([\alpha]_D^{23}\) (c 0.375, CHCl\(_3\)) = +35.2; \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ = 0.10 (s, 9H), 2.04 (s, 3H),
2.29 (s, 3H), 2.64-2.82 (m, 2H), 3.00-3.03 (m, 1H), 7.06 (d, J = 8.0 Hz, 1H), 7.23-7.25 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ = -2.5, 21.1, 27.9, 30.4, 46.0, 129.8, 130.2, 133.0, 136.3, 207.7; HRMS(ESI) calcd for C$_{14}$H$_{22}$OSSi (M+Na)$^+$: 289.1053, Found: 289.1047; 62% ee as determined by HPLC (Chiralcel ADH, 98:2 hexanes/i-PrOH, 0.5 mL/min), tr (minor) = 9.0 min, tr (major) = 10.3 min.

![Chemical Structure](image)

(S)-3-(dimethyl(phenyl)silyl)-1-phenyl-3-(p-tolylthio)propan-1-one (3l): colorless oil; [α]$_D$$^{23}$ (c 0.302, CHCl$_3$) = +10.4; $^1$H NMR (400 MHz, CDCl$_3$) δ = 0.44 (d, J = 1.6 Hz, 6H), 2.25 (s, 3H), 3.14 (dd, J = 17.6, 5.2 Hz, 1H), 3.30-3.37 (m, 1H), 3.43-3.46 (dd, J = 7.2, 5.2 Hz, 1H), 7.20-7.23 (m, 2H), 7.30-7.37 (m, 5H), 7.49 (tt, J = 7.2, 1.2 Hz, 1H), 7.57-7.60 (m, 2H), 7.70-7.71 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ = -4.0, -3.5, 21.1, 28.5, 41.3, 127.9, 128.0, 128.5, 129.6, 129.8, 130.5, 132.9, 133.0, 134.3, 136.4, 136.9, 199.0; HRMS(ESI) calcd for C$_{24}$H$_{26}$OSSi (M+Na)$^+$: 413.1366, Found: 413.1368; 83% ee as determined by HPLC (Chiralcel AD, 95:5 hexanes/i-PrOH, 0.3 mL/min), t$_r$ (major) = 18.3 min, t$_r$ (minor) = 21.0 min.

![Chemical Structure](image)

(S)-1-(4-bromophenyl)-3-(dimethyl(phenyl)silyl)-3-(p-tolylthio)propan-1-one (3m): colorless oil; [α]$_D$$^{23}$ (c 0.765, CHCl$_3$) = +61.7; $^1$H NMR (400 MHz, CDCl$_3$) δ = 0.37 (s, 6H), 2.18 (s, 3H), 3.03-3.09 (m, 1H), 3.27 (dd, J = 17.6, 7.2 Hz, 1H), 3.36-3.39 (m, 1H), 6.92 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 7.25-7.28 (m, 4H), 7.40-7.43 (m, 1H), 7.50-7.52 (m, 2H), 7.63 (d, J = 7.6 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ = -4.0, -3.5, 21.1, 28.3, 29.8, 41.2, 128.0, 128.0, 128.5, 128.6, 129.6, 129.8, 129.9, 130.4, 132.9, 133.0, 134.3, 136.4, 136.5, 136.9, 199.1; HRMS(ESI) calcd for C$_{24}$H$_{25}$BrOSSi (M+Na)$^+$: 491.0471, Found: 491.0472; HRMS(ESI) calcd for C$_{24}$H$_{25}$BrOSSi (M+Na)$^+$: 493.0450, Found: 493.0455; 86% ee as determined by HPLC (Chiralcel ADH, 95:5 hexanes/i-PrOH, 0.3 mL/min), t$_r$ (major) = 21.7 min, t$_r$ (minor) = 29.4 min.
(S)-3-(dimethyl(phenyl)silyl)-1-(4-fluorophenyl)-3-(p-tolylthio)propan-1-one (3n): colorless oil; \([\alpha]_D^{23}\) (c 0.375, CHCl\(_3\)) = +56.5; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 0.44\) (s, 6H), 2.25 (s, 3H), 3.08 (dd, \(J = 17.6, 5.6\) Hz, 1H), 3.24-3.30 (m, 1H), 3.41 (dd, \(J = 7.2, 5.6\) Hz, 1H), 6.99-7.03 (m, 4H), 7.20 (d, \(J = 8.0\) Hz, 2H), 7.30-7.34 (m, 3H), 7.56-7.58 (m, 2H), 7.68-7.72 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = -4.2, -3.5, 21.1, 28.6, 41.1, 115.4, 115.6, 127.9, 129.6, 129.8, 130.5, 130.6, 130.7, 134.3, 136.4, 136.5, 197.5; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta = -105.64\); HRMS(ESI) calcd for C\(_{24}\)H\(_{25}\)F\(_3\)O\(_2\)Si (M+Na): 431.1272, Found: 431.1270; 90\% ee as determined by HPLC (Chiralcel IA, 99:1 hexanes/i-PrOH, 0.2 mL/min), \(t_\mathrm{r}\) (minor) = 36.1 min, \(t_\mathrm{r}\) (major) = 52.2 min.

\(\begin{array}{c}
\text{(S)-3-(methyldiphenylsilyl)-1-phenyl-3-(p-tolylthio)propan-1-one (3o):} \\
\text{colorless oil; \([\alpha]_D^{23}\) (c 0.564, CHCl\(_3\)) = +20.0; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 0.72\) (s, 3H), 2.24 (s, 3H), 3.24 (dd, \(J = 17.6, 6.0\) Hz, 1H), 3.38-3.44 (m, 1H), 3.86 (t, \(J = 12.4, 6.4\) Hz, 1H), 6.96 (d, \(J = 8\) Hz, 2H), 7.20 (d, \(J = 8.0\) Hz, 2H), 7.30-7.39 (m, 8H), 7.45-7.49(m, 1H), 7.61-7.68 (m, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = -4.7, 21.1, 27.3, 41.6, 128.0, 128.0, 128.4, 129.7, 129.8, 130.8, 132.8, 132.9, 135.2, 135.2, 136.5, 136.9, 198.7; HRMS(ESI) calcd for C\(_{29}\)H\(_{28}\)OSSi (M+H): 453.1703, Found: 453.1700; 90\% ee as determined by HPLC (Chiralcel AD, 95:5 hexanes/i-PrOH, 0.3 mL/min), \(t_\mathrm{r}\) (major) = 22.6 min, \(t_\mathrm{r}\) (minor) = 33.5 min. 
\end{array}\)

\(\begin{array}{c}
\text{(S)-1-(4-bromophenyl)-3-(methyldiphenylsilyl)-3-(p-tolylthio)propan-1-one (3p):} \\
\text{colorless oil; \([\alpha]_D^{23}\) (c 0.220, CHCl\(_3\)) = +55.3; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 0.72\) (s, 3H), 2.24 (s, 3H), 3.24 (dd, \(J = 17.6, 6.0\) Hz, 1H), 3.38-3.44 (m, 1H), 3.86 (t, \(J = 12.4, 6.4\) Hz, 1H), 6.96 (d, \(J = 8\) Hz, 2H), 7.20 (d, \(J = 8.0\) Hz, 2H), 7.30-7.39 (m, 7H), 7.45-7.49(m, 1H), 7.61-7.68 (m, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = -4.7, 21.1, 27.3, 41.6, 127.9, 128.0, 128.4, 129.7, 129.8, 130.8, 132.8, 132.9, 135.2, 135.2, 135.2, 198.7; HRMS(ESI) calcd for C\(_{29}\)H\(_{28}\)OSSi (M+H): 453.1703, Found: 453.1700; 90\% ee as determined by HPLC (Chiralcel AD, 95:5 hexanes/i-PrOH, 0.3 mL/min), \(t_\mathrm{r}\) (major) = 22.6 min, \(t_\mathrm{r}\) (minor) = 33.5 min. 
\end{array}\)
136.5, 136.9, 198.7; HRMS(ESI) calcd for C_{29}H_{27}^{79}BrOSSi (M+Na)^+ : 553.0627, Found: 553.0625. HRMS(ESI) calcd for C_{29}H_{27}^{81}BrOSSi (M+Na)^+ : 555.0606, Found: 555.0605; 90% ee as determined by HPLC (Chiralcel AD, 95:5 hexanes/i-PrOH, 1.0 mL/min), t_r (major) = 8.1 min, t_r (minor) = 17.4 min.

(S)-1-phenyl-3-(p-tolthio)-3-(triethylsilyl)propan-1-one (3q): colorless oil; [α]_D^{23} (c 0.420, CHCl_3) = +45.3; \(^1^H\) NMR (400 MHz, CDCl_3) δ = 0.69 (q, J = 8.0 Hz, 6H), 1.01 (t, J = 8.0 Hz, 9H), 2.25 (s, 3H), 3.19-3.27 (m, 1H), 3.37-3.46 (m, 2H), 7.00 (d, J = 4.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.31-7.41 (m, 2H), 7.49-7.54 (m, 1H), 7.79-7.82 (m, 2H); \(^1^C\) NMR (100 MHz, CDCl_3) δ = 2.8, 7.7, 21.1, 25.6, 41.7, 128.1, 128.2, 128.6, 129.7, 130.1, 133.0, 133.1, 136.1, 136.9, 199.1; HRMS(ESI) calcd for C_{29}H_{31}OSSi^+ (M+H)^+ : 371.1859, Found: 371.1860. 96% ee as determined by HPLC (Chiralcel OJH, 99:1 hexanes/i-PrOH, 0.2 mL/min), t_r (major) = 32.4 min, t_r (minor) = 35.1 min.

(S)-3-((4-chlorophenyl)thio)-1-phenyl-3-(trimethylsilyl)propan-1-one (3r): colorless oil; [α]_D^{23} (c 0.764, CHCl_3) = +37.9; \(^1^H\) NMR (400 MHz, CDCl_3) δ = 0.13 (s, 9H), 3.16 (dd, J = 17.6, 7.6 Hz, 1H), 3.30 (dd, J = 7.2, 4.8 Hz, 1H), 3.41 (dd, J = 17.6, 7.6 Hz, 1H), 7.16 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H), 7.42 (t, J = 7.6 Hz, 2H), 7.52-7.56 (m, 1H), 7.84 (d, J = 7.6 Hz, 2H); \(^1^C\) NMR (100 MHz, CDCl_3) δ = -2.3, 27.8, 41.0, 128.1, 128.7, 129.1, 130.6, 132.0, 133.3, 135.4, 136.7, 199.0; HRMS(ESI) calcd for C_{18}H_{21}^{35}ClNaOSSi^+ (M+Na)^+ : 371.0663, Found: 371.0662. HRMS(ESI) calcd for C_{18}H_{21}^{37}ClNaOSSi^+ (M+Na)^+ : 373.0633, Found: 373.0628; 25% ee as determined by HPLC (Chiralcel AZH, 99:1 hexanes/i-PrOH, 0.2 mL/min), t_r (major) = 31.5 min, t_r (minor) = 35.3 min.

(S)-3-((4-methoxyphenyl)thio)-1-phenyl-3-(trimethylsilyl)propan-1-one (3s): colorless liquid; [α]_D^{23} (c 0.375, CHCl_3) = +56.1; \(^1^H\) NMR (400 MHz, CDCl_3) δ = 0.13 (s, 9H), 3.13-3.21 (m, 2H), 3.29-3.35 (m, 1H), 3.74 (s, 1H), 6.75 (d, J = 8.4 Hz, 2H).
(S)-3-((furan-2-ylmethyl)thio)-1-phenyl-3-(trimethylsilyl)propan-1-one (3t): colorless oil; [α]D$^2$ $^2$ (c 0.556, CHCl$_3$) = +41.1; $^1$H NMR (400 MHz, CDCl$_3$) δ = 0.18 (s, 9H), 2.62 (dd, $J$ = 6.8, 6.0 Hz, 1H), 3.26-3.28 (m, 2H), 3.65 (d, $J$ = 14.4 Hz, 1H), 3.81 (d, $J$ = 14.4 Hz, 1H), 6.15-7.23 (m, 2H), 7.28-7.29 (m, 1H), 7.45-7.49 (m, 2H), 7.55-7.59 (m, 1H), 7.94-7.96 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ = -2.7, 25.1, 30.4, 42.2, 108.0, 110.5, 128.2, 128.7, 133.2, 137.2, 142.1, 151.7, 199.7; HRMS(ESI) calcd for C$_{19}$H$_{22}$O$_2$SSi (M+H)$^+$: 345.1339, Found: 345.1340; 85% ee as determined by HPLC (Chiralcel IA, 99:1 hexanes/i-PrOH, 0.2 mL/min), $t_r$ (major) = 47.7 min, $t_r$ (minor) = 57.9 min.

(S)-3-(cyclohexylthio)-1-phenyl-3-(trimethylsilyl)propan-1-one (3u): colorless oil; [α]D$^2$ $^3$ (c 0.343, CHCl$_3$) = +42.1; $^1$H NMR (400 MHz, CDCl$_3$) δ = 0.09 (s, 9H), 1.20-1.24 (m, 5H), 1.53-1.56 (m, 1H), 1.67-1.79 (m, 3H), 2.00-2.05 (m, 1H), 2.57-2.62 (m, 1H), 2.74 (t, $J$ = 6.4 Hz, 1H), 7.31 (dd, $J$ = 6.4 Hz, $J$ = 2.4 Hz, 2H), 7.45-7.49 (m, 2H), 7.55-7.59 (m, 1H), 7.96-7.98 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ = -2.5, 23.5, 25.9, 26.0, 26.3, 33.5, 33.9, 42.9, 44.6, 128.2, 128.7, 133.2, 137.3, 199.9; HRMS(ESI) calcd for C$_{18}$H$_{28}$O$_2$Si (M+Na)$^+$: 341.1002, Found: 341.1005; 25% ee as determined by HPLC (Chiralcel ADH, 99:1 hexanes/i-PrOH, 0.2 mL/min), $t_r$ (minor) = 41.4 min, $t_r$ (major) = 44.4 min.

(S)-1-(4-methoxyphenyl)-3-tosyl-3-(trimethylsilyl)propan-1-one (4): white solid; [α]D$^2$ $^3$ (c 1.025, CHCl$_3$) = +66.4; $^1$H NMR (400 MHz, CDCl$_3$) δ = 0.28 (s, 9H), 2.31 (s, 3H), 3.17 (dd, $J$ = 18.4, 6.0 Hz, 1H), 3.31 (dd, $J$ = 18.8, 5.2 Hz, 1H), 3.82 (dd, $J$ = 3.28

S12
6.0, 5.2 Hz, 1H), 3.85 (s, 3H), 6.85-6.89 (m, 2H), 7.17 (d, J = 7.6 Hz, 2H), 7.68-7.70 (m, 2H), 7.73-7.77 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = -1.0, 21.6, 34.8, 50.2, 55.6, 113.8, 128.1, 129.0, 129.7, 130.3, 137.5, 143.9, 163.9, 193.9\); HRMS(ESI) calcd for C\(_{20}\)H\(_{26}\)O\(_4\)Si (M+Na): 413.1213, Found: 413.1213; 92% ee as determined by HPLC (Chiralcel ODH, 98:2 hexanes/i-PrOH, 0.5 mL/min), \(t_r\) (major) = 59.2 min, \(t_r\) (minor) = 80.1 min.

b) References
IV: $^1$H, $^{13}$C, $^{19}$F NMR and HPLC dates of products

![Chemical structure](image)

$^1$H, $^{13}$C, $^{19}$F NMR spectra of product 3a

- $^1$H NMR spectrum showing chemical shifts from 0.14 to 7.86 ppm.
- $^{13}$C NMR spectrum showing chemical shifts from 126.3 to 208.0 ppm.
- $^{19}$F NMR spectrum showing chemical shifts from 51.0 to 51.5 ppm.

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