Supporting Information

Efficient Synthesis of \(\alpha\)-Tertiary \(\alpha\)-Silylamines from Aryl Sulfonylimidates via One-Pot, Sequential C–Si/C–C Bond Formations

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1. General experimental information

All reactions were carried out under an argon atmosphere in flame-dried glassware with magnetic stirring. THF and Et₂O were freshly distilled from sodium/benzophenone. CH₂Cl₂ was distilled from CaH₂. Other solvents and commercial reagents were used without additional purification. Purification of the reaction products was carried out by flash column chromatography using 200–300 mesh silica gel. Visualization on TLC (analytical thin layer chromatography) was achieved by the use of UV light (254 nm) and treatment with phosphomolybdic acid or anisaldehyde stain followed by heating. Unless otherwise noted, yields refer to chromatographically and spectroscopically pure compounds. High-resolution mass spectra (HRMS) were recorded using electron spray ionization (ESI). Proton and carbon magnetic resonance spectra (¹H NMR and ¹³C NMR) were recorded on a 400 MHz (¹HNMR at 400 MHz and ¹³CNMR at 100 MHz) spectrometer with solvent resonance as the internal standard (¹HNMR: CDCl₃ at 7.26 ppm, C₆D₆ at 7.16 ppm; ¹³C NMR: CDCl₃ at 77.23 ppm, C₆D₆ at 128.06 ppm). NMR data are represented as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant in Hertz (Hz), integration. Melting points were reported uncorrected.
2. General procedure for the preparation of aryl tosylimidates

2.1 Method A:¹

\[
\begin{align*}
\text{R} & \quad \text{O} \quad \text{O} \\
& \quad \text{TsNH}_2 \quad 150 \, ^\circ\text{C}, 12 \, \text{h} \\
& \quad \text{OMe}
\end{align*}
\]

\[
\text{R} = \text{H, Cl}
\]

**Scheme S1.** General procedure for the preparation of aryl tosylimidates: Method A

A round-bottomed flask was charged with \( p\)-Toluenesulfonamide (1.0 equiv) and orthoester (1.2 equiv). The reaction mixture was stirred at 150 °C for 12 h. The crude oil was purified by column chromatography (\( n\)-hexane:EtOAc:CH\(_2\)Cl\(_2\) = 20:1:0.3 to 10:1:0.3, gradient elution) to give the aryl tosylimidate.

2.2 Method B:²⁻³

\[
\begin{align*}
\text{CN} & \quad \text{MeOH, HCl(gas)} \quad \text{DCM, rt} \\
& \quad \text{R=Me, MeO, F}
\end{align*}
\]

**Scheme S2.** General procedure for the preparation of aryl tosylimidates: Method B

A three-neck flask was equipped with a gas inlet tube and a gas outlet tube, and it was charged with nitrile (1.0 equiv), MeOH (1.2 equiv), and DCM (10 mL). HCl gas (excess, prepared with concentrated sulfuric acid and NaCl, dried with concentrated sulfuric acid) was bubbled into the solution for 3 h with stir while a temperature of 15–25 °C was maintained. Then the reaction mixture was stirred at room temperature for another 6 h before 40 mL of Et\(_2\)O was added. After the mixture was stirred for 3 h at room temperature, the solid (methyl zimidate hydrochloride) was filtered, washed with Et\(_2\)O, and vacuum-dried. The solid (1.0 equiv, 10 mmol, without further

purification) was stirred in CH₂Cl₂ (30 mL) at room temperature and Et₃N (2.5 equiv) was added dropwise to the reaction mixture. After it was stirred at room temperature for 0.5 h, TsCl (2.0 equiv) and DMAP (4-dimethylaminopyridine, 1.0 equiv) were added in sequence. The reaction mixture was stirred for 3 d. The reaction mixture was diluted with CH₂Cl₂, and washed with a 1.0 M solution of HCl, aqueous sodium bicarbonate, and brine. The organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated. The crude product was purified by column chromatography (n-hexane:EtOAc:CH₂Cl₂ = 20:1:0.3 to 7:1:0.3, gradient elution) to give the aryl tosylimidate.

2.3 Method C:⁴ ⁵

\[
\begin{align*}
\text{R'} \text{Cl} & \xrightarrow{TsNH₂, 150 °C} \text{R'} \text{N-Ts} \\
\text{R'} \text{N-Ts} & \xrightarrow{\text{reflux}, \text{POCl₃}, \text{POCl₃}} \text{NTs} \\
\text{NTs} & \xrightarrow{\text{NaOMe, } 0 °C, 0.5 h} \text{OMe}
\end{align*}
\]

Scheme S3. General procedure for the preparation of aryl tosylimidates: Method C

A mixture of p-Toluenesulfonamide (1.0 equiv) and acyl chloride (1.1–1.5 equiv) was stirred at 150 °C for 1–2 h. The crude product was recrystallized from ethanol to give a white solid N-tosylamide. N-tosylamide (1.0 equiv) and PCl₅ (1.05 equiv) was dissolved in POCl₃ (20 equiv), and the reaction mixture was refluxed for 0.5–1 h. The solvent was removed in vacuo, and the crude product was recrystallized from diethyl ether to give a white solid N-tosylimidoyl chloride. A solution of sodium methoxide (5.0 equiv) in MeOH was slowly added dropwise to N-tosylimidoyl chloride (1.0 equiv) in THF at 0 °C. The solution was stirred at 0 °C for 0.5 h. The crude product was purified by column chromatography (n-hexane/EtOAc/CH₂Cl₂, gradient elution) to give the aryl tosylimidate.

3. Characterization data of aryl tosylimidates (1a–1h)

(1a): Method A was followed with TsNH₂ (1.71 g, 10 mmol) and Trimethyl

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⁵ Barcock, R. A.; Chadwick, D. J.; Storr, R. C.; Fuller, L. S.; Young, J. H. Tetrahedron 1994, 50, 4149.
orthobenzoate (2.65 g, 15 mmol). Purification by column chromatography afforded 2.73 g (94%) of 1a as a white solid. The pure 1a was recrystallized from EtOAc/n-hexane to afford a colorless needles: mp 125–126 °C (lit.\(^6\) mp 123–124 °C); \(R_f = 0.29\) (n-hexane:EtOAc = 5:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.86 (d, \(J = 7.1\) Hz, 2H), 7.81 (d, \(J = 8.0\) Hz, 2H), 7.57 (t, \(J = 7.5\) Hz, 1H), 7.46 (t, \(J = 7.7\) Hz, 2H), 7.27 (d, \(J = 8.0\) Hz, 2H), 3.89 (s, 3H), 2.42 (s, 3H).

\[\text{(1b): According to the Method B, p-Tolunitrile (3.6 g, 30 mmol) was used and afforded methyl 4-methylbenzimidate hydrochloride (crude product, 4.8 g, 86%) as a white solid. Methyl 4-methylbenzimidate hydrochloride (1.86 g, approx. 10 mmol) in 30 mL CH\(_2\)Cl\(_2\), Et\(_3\)N (3.5 mL, 25 mmol), TsCl (3.82 g, 20 mmol), and DMAP (1.22 g, 10 mmol) were used and the reaction mixture was refluxed for 3 d. It was purified by column chromatography to afford 1b (1.74 g, 58%) as a white solid. The pure 1b was recrystallized from EtOAc/n-hexane to afford a colorless needles: mp 98–99 °C; \(R_f = 0.33\) (n-hexane:EtOAc = 5:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.83 (d, \(J = 8.7\) Hz, 2H), 7.81 (d, \(J = 8.7\) Hz, 2H), 7.27 (d, \(J = 8.7\) Hz, 4H), 3.87 (s, 3H), 2.42 (s, 6H); 

\[^{13}\text{C NMR (100 MHz, CDCl}_3\text{)} \delta\) 170.2, 143.6, 143.1, 139.9, 129.8, 129.4, 129.0, 128.4, 126.8, 56.2, 21.9, 21.7; HRMS: (ESI) calculated for C\(_{16}\)H\(_{18}\)NO\(_3\)S ([M+H\(^+\)]: 304.1007, found: 304.0994.}

\[\text{(1c): According to the Method B, 4-Methoxybenzonitrile (4.0 g, 30 mmol) was used and afforded methyl 4-methoxybenzimidate hydrochloride (crude product, 4.8 g, 79%) as a white solid. Methyl 4-methoxybenzimidate hydrochloride (1.86 g, approx. 10 mmol) in 30 mL CH\(_2\)Cl\(_2\), Et\(_3\)N (3.5 mL, 25 mmol), TsCl (3.82 g, 20 mmol), and DMAP (1.22 g, 10 mmol) were used and the reaction mixture was stirred at room temperature for 3 d. It was purified by column chromatography to afford 1c (0.99 g, 31%) as a white solid. The pure 1c was recrystallized from EtOAc/n-hexane to afford a colorless needles: mp 119–120 °C; \(R_f = 0.21\) (n-hexane:EtOAc = 5:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.97 (d, \(J = 9.0\) Hz, 2H), 7.85 (d, \(J = 8.3\) Hz, 2H), 7.28 (d, \(J = 8.0\) Hz, 2H), 6.96 (d, \(J = 9.0\) Hz, 2H), 3.87 (s, 3H), 3.85 (s, 3H), 2.42 (s, 3H);}

13C NMR (100 MHz, CDCl3) δ 169.4, 163.5, 143.0, 140.1, 132.4, 129.4, 126.7, 123.1, 113.7, 56.1, 55.7, 21.7; HRMS: (ESI) calculated for C16H18NO4S ([M+H]+): 320.0957, found: 320.0895.

(1d): According to the Method B, 4-fluorobenzonitrile (4.84 g, 40 mmol) was used and afforded methyl 4-fluorobenzimidate hydrochloride (crude product, 6.9 g, 91%) as a white solid. Methyl 4-fluorobenzimidate hydrochloride (1.90 g, approx. 10 mmol) in 30 mL CH2Cl2, Et3N (3.5 mL, 25 mmol), TsCl (3.82 g, 20 mmol), and DMAP (1.22 g, 10 mmol) were used and the reaction mixture was refluxed for 3 d. It was purified by column chromatography to afford 1d (0.69 g, 22%) as a white solid. The pure 1d was recrystallized from EtOAc/n-hexane to afford a colorless needles: mp 105–106 °C; Rf = 0.30 (n-hexane:EtOAc = 5:1); 1H NMR (400 MHz, CDCl3) δ 7.94 (dd, J = 8.7, 5.3 Hz, 2H), 7.82 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 8.2 Hz, 2H), 7.15 (t, J = 8.6 Hz, 2H), 3.88 (s, 3H), 2.42 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 168.9, 165.5 (d, JCF = 254.4 Hz), 143.3, 139.6, 132.4 (d, JCF = 9.2 Hz), 129.5, 127.4 (d, JCF = 3.3 Hz), 126.8, 115.6 (d, JCF = 22.1 Hz), 56.4, 21.8; HRMS: (ESI) calculated for C15H15FNO3S ([M+H]+): 308.0757, found: 308.0751.

(1e): Method A was followed with TsNH2 (0.52 g, 3.0 mmol) and trimethyl 4-chloroorthobenzoate (0.81 g, 3.75 mmol). Purification by column chromatography afforded 0.75 g (77%) of 1e as a white solid. The pure 1e was recrystallized from EtOAc/n-hexane to afford a colorless needles: mp 117–118 °C; Rf = 0.32 (n-hexane:EtOAc = 5:1); 1H NMR (400 MHz, CDCl3) δ 7.84 (d, J = 8.6 Hz, 2H), 7.82 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 3.88 (s, 3H), 2.42 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 169.0, 143.4, 139.5, 139.2, 131.1, 129.7, 129.5, 128.7, 126.8, 56.4, 21.8; HRMS: (ESI) calculated for C15H15ClNO3S ([M+H]+): 324.0461, found: 324.0455.

(1f): Method C was followed with TsNH2 (1.20 g, 7 mmol) and 1-naphthoyl chloride (1.56 g, 8 mmol). The reaction mixture was stirred for 2 h at 150 °C. Then PCl5 (1.62 g, 7.8 mmol) and POCl3 (5 mL) was added to the reaction mixture of the previous step (without
further purification). The reaction was refluxed for 1 h and the solvent was removed in vacuo. The crude product was recrystallized from diethyl ether to give a white solid \(N\)-tosyl-1-naphthimidoyl chloride (1.42 g, total yield 59%). A solution of sodium methoxide (0.54 g, 10 mmol) in MeOH was slowly added dropwise to \(N\)-tosyl-1-naphthimidoyl chloride (1.42 g, 4.1 mmol) in THF at 0 °C. The solution was stirred at 0 °C for 0.5 h. The crude product was purified by column chromatography (n-hexane:EtOAc:CH\(_2\)Cl\(_2\) = 10:1:0.3 to 5:1:0.3, gradient elution) to give the aryl tosylimidate \(1f\) (1.39 g, 99%). The pure \(1f\) was recrystallized from EtOAc/n-hexane to afford a colorless crystals: mp 122−123 °C; \(R_f\) = 0.20 (n-hexane:EtOAc = 5:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.92 (d, \(J = 8.0\) Hz, 1H), 7.79 (d, \(J = 8.1\) Hz, 1H), 7.61 (dd, \(J = 7.1, 0.9\) Hz, 1H), 7.54 – 7.48 (m, 1H), 7.46 (dd, \(J = 7.6, 3.5\) Hz, 1H), 7.44 – 7.42 (m, 1H), 7.42 – 7.38 (m, 3H), 6.92 (d, \(J = 8.0\) Hz, 2H), 4.09 (s, 3H), 2.22 (s, 3H). \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 171.9, 143.1, 137.6, 133.1, 131.1, 129.5, 129.4, 129.0, 128.5, 127.3, 127.2, 126.9, 126.5, 124.70, 124.65, 56.4, 21.5; HRMS: (ESI) calculated for C\(_{19}\)H\(_{18}\)NO\(_3\)S ([M+H\(^+\)]: 340.1007, found: 340.1008.

(1g): Method C was followed with TsNH\(_2\) (3.42 g, 20 mmol) and 2-Furoyl chloride (3.92 g, 30 mmol). The reaction mixture was stirred for 2 h at 150 °C. Then PCl\(_5\) (4.58 g, 22 mmol) and POCl\(_3\) (15 mL) was added to the reaction mixture of the previous step (without further purification). The reaction was refluxed for 1 h and the solvent was removed in vacuo. The crude product was purified by column chromatography (n-hexane:EtOAc:CH\(_2\)Cl\(_2\) = 10:1:0.3 to 5:1:0.3, gradient elution) to give a white solid \(N\)-tosylfuran-2-carbimidoyl chloride (1.47 g, total yield 26%). A solution of sodium methoxide (0.54 g, 10 mmol) in MeOH was slowly added dropwise to \(N\)-tosylfuran-2-carbimidoyl chloride (1.42 g, 5 mmol) in THF at 0 °C. The solution was stirred at 0 °C for 0.5 h. The crude product was purified by column chromatography (n-hexane:EtOAc:CH\(_2\)Cl\(_2\) = 10:1:0.3 to 5:1:0.3, gradient elution) to give the aryl tosylimidate \(1g\) (1.32 g, 95%). The pure \(1g\) was recrystallized from EtOAc/n-hexane to afford a pale yellow crystals: mp 117−118 °C; \(R_f\) = 0.23 (n-hexane:EtOAc = 5:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.94 – 7.84 (m, 3H), 7.69 (d, \(J = 0.7\) Hz, 1H), 7.31 (d, \(J = 8.0\) Hz, 2H), 6.61 (d, \(J = 1.7\) Hz, 1H), 3.85 (s, 3H), 2.43 (s, 3H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 157.2, 147.6, 143.1, 142.8, 140.3, 129.3, 126.7, 123.4, 112.9, 55.5, 21.7; HRMS: (ESI) calculated for C\(_{13}\)H\(_{14}\)NO\(_4\)S ([M+H\(^+\)]: 280.0644, found:
Method C was followed with TsNH₂ (5.13 g, 30 mmol) and 2-thenoyl chloride (5.13 g, 35 mmol). The reaction mixture was stirred for 1 h at 130 °C. The crude product was recrystallized from ethanol to give a white solid N-tosylthiophene-2-carboxamide (6.4 g, 76%). N-tosylthiophene-2-carboxamide (2.81 g, 10 mmol) and PCl₅ (2.29 g, 11 mmol) was dissolved in POCl₃ (15 mL), and the reaction mixture was refluxed for 1 h. The solvent was removed in vacuo. The crude product was recrystallized from diethyl ether to give a white solid N-tosylthiophene-2-carbimidoyl chloride (1.48 g, 51%). A solution of sodium methoxide (1.08 g, 20 mmol) in MeOH was slowly added dropwise to N-tosylfuran-2-carbimidoyl chloride (1.20 g, 4 mmol) in THF at 0 °C. The solution was stirred at 0 °C for 0.5 h. The crude product was purified by column chromatography (n-hexane:EtOAc:CH₂Cl₂ = 20:1:0.3 to 10:1:0.3, gradient elution) to give a white solid 1h (1.13g, 96%). The pure 1h was recrystallized from EtOAc/n-hexane to afford a colorless crystals: mp 71−72 °C; Rₚ = 0.28 (n-hexane:EtOAc = 5:1); ¹H NMR (400 MHz, CDCl₃) δ 8.65 (dd, J = 4.0, 1.1 Hz, 1H), 7.90 (d, J = 8.3 Hz, 2H), 7.66 (dd, J = 5.0, 1.1 Hz, 1H), 7.31 (d, J = 8.1 Hz, 2H), 7.21 (dd, J = 5.0, 4.1 Hz, 1H), 3.83 (s, 3H), 2.44 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 161.5, 143.2, 140.0, 138.0, 134.0, 130.8, 129.5, 128.7, 126.6, 55.9, 21.8; HRMS: (ESI) calculated for C₁₃H₁₄NO₃S₂ ([M+H]+): 296.0415, found: 296.0418.

4. Preparation of silyl-lithium Reagent

4.1 Preparation of dimethylphenylsilyllithium (LiSiMe₂Ph)⁷

Lithium wire (0.50 g, 70 mmol) was stirred rapidly for 15 min in hexane (20 mL) under argon. The hexane was removed and the lithium suspended in THF (15 mL). The mixture was stirred rapidly with chlorodimethylphenylsilane (3.0 mL, 18 mmol) and some splinters of glass at 0 °C for 6 h to give a deep red solution (approx. 1.0 M). The solution was stored at −18 °C.

4.2 Preparation of diphenylmethylsilyllithium (LiSiMePh₂)⁸

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Hexane-washed lithium wire (0.050 g, 7 mmol) was suspended in dry THF (1.2 mL) under argon. The mixture was stirred rapidly with chlorodiphenylmethylsilane (0.21 mL, 1.0 mmol) and some splinters of glass at room temperature for 4 h to give a deep black-red solution (approx. 0.8 M). The solution was used within several hours.

5. Procedure for the preparation of compound 4

Scheme S4. Procedure for the preparation of compound 4

(4): 1a (115.7 mg, 0.4 mmol) was dissolved in 2.0 mL THF and added to a flame-dried schlenk flask equipped with a magnetic stirring bar under argon. The solution was cooled to −78 °C. Dimethylphenylsilyllithium (approx. 1.0 M solution in THF, 0.48 mL, 0.48 mmol) was added dropwise to the solution via syringe. The reaction mixture was stirred for 1 h at −78 °C. Then it was quenched at −78 °C by the addition of 3.0 mL of saturated aqueous sodium bicarbonate. The resulting heterogeneous mixture was allowed to warm to room temperature and then stirred for 15 minutes. The reaction mixture was diluted with 40 mL EtOAc. The layers were separated, and the aqueous layer was extracted with EtOAc (2×5 mL). The organic extracts were washed with brine (2×15 mL), dried over anhydrous Na₂SO₄, filtered, and concentrated in vacuo to afford a white solid (crude product). The solid was recrystallized from n-hexane/CH₂Cl₂ to afford the product 4 (153.5 mg, 90%) as a white solid: mp 115−116 °C; R_f = 0.29 (n-hexane:EtOAc = 6:1); ^1H NMR (400 MHz, CDCl₃) δ 7.50 (d, J = 8.4, 2H), 7.39−7.31 (m, 3H), 7.25 (t, J = 6.6, 2H), 7.21−7.13 (m, 5H), 7.08−7.02 (m, 2H), 5.31 (s, 1H), 2.71 (s, 3H), 2.41 (s, 3H), 0.50 (s, 3H), 0.27 (s, 3H); ^13C NMR (101 MHz, CDCl₃) δ 143.3, 139.4, 139.2, 136.7, 135.3, 129.4, 129.3, 127.9, 127.5, 127.4, 127.19, 127.16, 90.7, 49.1, 21.8, −3.7, −4.2; HRMS: (ESI) calculated for C₂₃H₂₇NNaO₃SSi ([M+Na]^+): 448.1379, found: 448.1376.

6. Procedure for the preparation of compound 5
Scheme S5. Procedure for the preparation of compound 5

(5): 1a (86.8 mg, 0.3 mmol) was dissolved in 1.5 mL THF and added to a flame-dried schlenk flask equipped with a magnetic stirring bar under argon. The solution was cooled to anhydrous –78 °C. Dimethylphenylsilyllithium (appro. 1.0 M solution in THF, 0.36 mL, 0.36 mmol) was added dropwise to the solution via syringe. The reaction mixture was stirred for 1h at –78 °C. Then it was quenched at –78 °C by the addition of 3.0 mL of 6.0 M solution of HCl. The resulting heterogeneous mixture was allowed to warm to room temperature (a lot of white solid will be separated out, 1 mL THF and 1 mL CH2Cl2 should be added to dissolve it.) and then stirred rapidly for an additional 1.5 h. The reaction mixture was diluted with 30 mL EtOAc. The layers were separated, and the aqueous layer was extracted with EtOAc (2×5 mL). The organic extracts were washed with saturated aqueous sodium bicarbonate (15 mL) and brine (15 mL), dried over anhydrous Na2SO4, filtered, and concentrated in vacuo. The residue was purified by column chromatography (n-hexane:Et2O = 100:1) yielding pure product 5 (61.3 mg, 85%) as a yellow solid: mp 55–56 °C; Rf = 0.61 (n-hexane:EtOAc = 6:1); 1H NMR (400 MHz, CDCl3) δ 7.78 – 7.73 (m, 2H), 7.63 – 7.57 (m, 2H), 7.47 (t, J = 7.2 Hz, 1H), 7.42 – 7.34 (m, 5H), 0.63 (s, 6H). The 1H NMR spectrum of this compound matched the reported spectral data.9

7. Procedure for the preparation of compound 7

Scheme S6. Procedure for the preparation of compound 7

(7): 1a (144.7 mg, 0.5 mmol) was dissolved in 2.5 mL THF and added to a flame-dried schlenk flask equipped with a magnetic stirring bar under argon. The solution was

cooled to –78 °C. Dimethylphenylsilyllithium (approx. 1.0 M solution in THF, 0.6 mL, 0.6 mmol) was added dropwise to the solution via syringe. The reaction mixture was stirred for 1 h at –78 °C. Then it was quenched at –78 °C by the addition of 4.0 mL of 1.0 M solution of HCl. The resulting heterogeneous mixture was allowed to warm to room temperature (a lot of white solid will be separated out, 1 mL THF and 1 mL CH₂Cl₂ should be added to dissolve it.) and then stirred rapidly for an additional 2 h. The reaction mixture was diluted with 30 mL EtOAc. The layers were separated, and the aqueous layer was extracted with EtOAc (2×5 mL). The organic extracts were washed with saturated aqueous sodium bicarbonate (15 mL) and brine (15 mL), dried over anhydrous Na₂SO₄, filtered, and concentrated in vacuo. The residue was purified by column chromatography (n-hexane:EtOAc:CH₂Cl₂ = 100:1:0.3 to 20:1:0.3, gradient elution) yielding product 7 (134.6 mg, 68% yield) as a white solid and product 5 (24.5 mg, 20% yield). The product 7 could be recrystallized from Et₂O/n-pentane to afford a white solid. The analytic data of 7: mp 92−93 °C; R₉ = 0.36 (n-hexane:EtOAc = 6:1); ¹H NMR (400 MHz, CD₆D₆) δ 7.95 (d, J = 7.2 Hz, 2H), 7.59 – 7.20 (m, 4H), 7.10 (d, J = 7.2 Hz, 3H), 6.94 (s, 3H), 6.72 (d, J = 7.1 Hz, 2H), 1.83 (s, 3H), 0.33 (s, 6H); ¹³C NMR (100 MHz, CD₆D₆) δ 202.5, 143.1, 139.5, 134.6, 130.2, 129.50, 129.46, 128.39, 128.36, 128.1, 128.0, 127.9, 126.1, 21.2, –3.8; HRMS: (ESI) calculated for C₂₂H₂₄NO₂SSi ([M+H]⁺): 394.1297, found: 394.1292.

8. The reaction of compound 4 and Grignard reagent (MeMgBr)

![Scheme S7](image)

Scheme S7. The reaction of compound 4 and Grignard reagent (MeMgBr)

Compound 4 (85.2 mg, 0.2 mmol) was dissolved in 2.0 mL THF and added to a flame-dried schlenk flask equipped with a magnetic stirring bar under argon. The solution was cooled to –78 °C. Methylmagnesium bromide (3.0 M solution in Et₂O, 0.2 mL, 0.6 mmol) was added dropwise, and the reaction mixture was allowed to warm slowly to –70 °C over 1 h. Then it was quenched at –70 °C by the addition of 3.0 mL of 1.0 M solution of HCl. The resulting heterogeneous mixture was allowed to warm to room temperature and then stirred for an additional 0.5 h. The reaction
mixture was diluted with 30 mL EtOAc. The layers were separated, and the aqueous layer was extracted with EtOAc (2×5 mL). The organic extracts were washed with saturated aqueous sodium bicarbonate (15 mL) and brine (15 mL), dried over anhydrous Na₂SO₄, filtered, and concentrated in vacuo. The residue was purified by column chromatography (n-hexane:EtOAc:CH₂Cl₂ = 50:1:0.3 to 20:1:0.3, gradient elution) yielding pure product 6j (73.7 mg, 90%).

9. The reaction of compound 7 and Grignard reagent (MeMgBr)

Scheme S8. The reaction of compound 7 and Grignard reagent (MeMgBr)

Compound 7 (78.7 mg, 0.2 mmol) was dissolved in 2.0 mL THF and added to a flame-dried schlenk flask equipped with a magnetic stirring bar under argon. The solution was cooled to −78 °C. Methylmagnesium bromide (3.0 M solution in Et₂O, 0.2 mL, 0.6 mmol) was added dropwise, and the reaction mixture was allowed to warm slowly to −70 °C over 1 h. Then it was quenched at −70 °C by the addition of 3 mL of 1.0 M solution of HCl. The resulting heterogeneous mixture was allowed to warm to room temperature and then stirred for an additional 0.5 h. The reaction mixture was diluted with 30 mL EtOAc. The layers were separated, and the aqueous layer was extracted with EtOAc (2×5 mL). The organic extracts were washed with saturated aqueous sodium bicarbonate (15 mL) and brine (15 mL), dried over anhydrous Na₂SO₄, filtered, and concentrated in vacuo. The residue was purified by column chromatography (n-hexane:EtOAc:CH₂Cl₂ = 50:1:0.3 to 20:1:0.3, gradient elution) yielding pure product 6j (77.7 mg, 95%).

10. General procedure for the synthesis of α,α-dibranched α-silylamines

Scheme S9. General procedure for the synthesis of α,α-dibranched α-Silylamines

Aryl tosylimidate (dissolved in THF, 1.0 equiv) was added to a flame-dried schlenk flask
equipped with a magnetic stirring bar under argon. The solution was cooled to –78 °C. Silyl lithium (1.2 equiv) was added dropwise to the solution via syringe. The reaction mixture was stirred for 1h at –78 °C. Grignard reagent (1.5 equiv) was added dropwise, and the reaction mixture was allowed to warm slowly to –45 °C over 2.5 h. Then it was quenched at –45 °C by the addition of 3 mL of 1.0 M solution of HCl. The resulting heterogeneous mixture was allowed to warm to room temperature and then stirred for an additional 1 h. The reaction mixture was diluted with 30 mL EtOAc. The layers were separated, and the aqueous layer was extracted with EtOAc (2×5 mL). The organic extracts were washed with saturated aqueous sodium bicarbonate (15 mL) and brine (15 mL), dried over anhydrous Na₂SO₄, filtered, and concentrated in vacuo. The residue was purified by column chromatography (n-hexane:EtOAc:CH₂Cl₂ = 50:1:0.3 to 20:1:0.3, gradient elution) yielding pure product.

11. The procedure for gram-scale preparation of 6a

1a (1.157 g, 4 mmol) was dissolved in 20 mL THF and added to a flame-dried schlenk flask equipped with a magnetic stirring bar under argon. The solution was cooled to –78 °C. Dimethylphenylsilyllithium (appro. 1.0 M in THF, 4.2 mL, 4.2 mmol) was added dropwise to the solution via syringe. The reaction mixture was stirred for 1 h at –78 °C. Allylmagnesium bromide (1.0 M solution in THF, 6.0 mL, 6.0 mmol) was added dropwise, and the reaction mixture was allowed to warm slowly to –45 °C over 2.5 h. Then it was quenched at –45 °C by the addition of 10 mL of 1.0 M solution of HCl. The resulting heterogeneous mixture was allowed to warm to room temperature and then stirred for an additional 1 h. The reaction mixture was diluted with 100 mL EtOAc. The layers were separated, and the aqueous layer was extracted with EtOAc (2×15 mL). The organic extracts were washed with saturated aqueous sodium bicarbonate (50 mL) and brine (50 mL), dried over anhydrous Na₂SO₄, filtered, and concentrated in vacuo. The residue was purified by column chromatography (n-hexane:EtOAc:CH₂Cl₂ = 50:1:0.3 to 20:1:0.3, gradient elution) yielding pure product 6a (1.649 g, 95%).

12. Characterization data of α-silylamines (6a–6r, 8, 9)
(6a): According to the general procedure for α-silylamines, 1a (86.8 mg, 0.3 mmol) dissolved in THF (1.5 mL), Dimethylphenylsilyllithium (appro. 1.0 M in THF, 0.36 mL, 0.36 mmol), and allylmagnesium bromide (1.0 M solution in THF, 0.45 mL, 0.45 mmol) were used and afforded the product 6a (116.6 mg, 89%) as a white solid: mp 150–151 °C; Rf = 0.36 (n-hexane:EtOAc = 6:1); 1H NMR (400 MHz, CDCl3) δ 7.48 (d, J = 8.3 Hz, 2H), 7.36 (t, J = 7.4 Hz, 1H), 7.26 (t, J = 7.4 Hz, 2H), 7.20 – 7.12 (m, 4H), 7.10 – 7.02 (m, 3H), 6.98 – 6.91 (m, 2H), 5.80 – 5.64 (m, 1H), 5.07 – 4.92 (m, 2H), 4.77 (s, 1H), 3.16 (dd, J = 15.3, 5.4 Hz, 1H), 2.89 (dd, J = 15.3, 3.0 Hz, 1H), 2.39 (s, 3H), 2.27 (s, 3H), 0.34 (s, 3H), 0.29 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 143.0, 141.3, 140.4, 135.4, 135.2, 134.1, 129.8, 129.4, 127.8, 127.6, 127.3, 127.2, 125.9, 119.1, 58.2, 38.9, 21.7, –3.7, –3.8; HRMS: (ESI) calculated for C25H29NNaO2SSi ([M+Na]+): 458.1586, found: 458.1589.

(6b): According to the general procedure for α-silylamines, 1b (91.0 mg, 0.3 mmol) dissolved in THF (1.5 mL), Dimethylphenylsilyllithium (appro. 1.0 M in THF, 0.36 mL, 0.36 mmol), and allylmagnesium bromide (1.0 M solution in THF, 0.45 mL, 0.45 mmol) were used and afforded the product 6b (122.5 mg, 91%) as a white solid: mp 116–117 °C; Rf = 0.40 (n-hexane:EtOAc = 6:1); 1H NMR (400 MHz, CDCl3) δ 7.46 (d, J = 8.3 Hz, 2H), 7.37 (t, J = 7.3 Hz, 1H), 7.27 (t, J = 7.4 Hz, 2H), 7.21 (dd, J = 8.1, 1.4 Hz, 2H), 7.14 (dd, J = 8.5, 0.5 Hz, 2H), 6.86 (q, J = 8.5 Hz, 4H), 5.78 – 5.61 (m, 1H), 5.04 – 4.89 (m, 2H), 4.75 (s, 1H), 3.13 (dd, J = 15.3, 5.4 Hz, 1H), 2.87 (dd, J = 15.3, 7.9 Hz, 1H), 2.39 (s, 3H), 2.27 (s, 3H), 0.34 (s, 3H), 0.29 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 142.9, 140.4, 138.2, 135.6, 135.4, 135.3, 134.2, 129.7, 129.4, 128.3, 127.7, 127.3, 127.2, 118.9, 57.9, 38.8, 21.7, 21.1, –3.70, –3.72; HRMS: (ESI) calculated for C26H31NNaO2SSi ([M+Na]+): 472.1742, found: 472.1746.

(6c): According to the general procedure for α-silylamines, 1c
(95.8 mg, 0.3 mmol) dissolved in THF (1.5 mL), Dimethylphenylsilyllithium (appro. 1.0 M in THF, 0.36 mL, 0.36mmol), and allylmagnesium bromide (1.0 M solution in THF, 0.45 mL, 0.45 mmol) were used and afforded the product 6c (122.8 mg, 88%) as a white solid: mp 117–118 °C; R_f = 0.25 (n-hexane:EtOAc = 6:1); ^1H NMR (400 MHz, CDCl_3) δ 7.46 (d, J = 8.3 Hz, 2H), 7.36 (t, J = 7.3 Hz, 1H), 7.27 (t, J = 7.4 Hz, 2H), 7.19 (dd, J = 8.1, 1.4 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 6.84 (d, J = 9.0 Hz, 2H), 6.59 (d, J = 9.0 Hz, 2H), 5.80 – 5.66 (m, 1H), 5.04 – 4.93 (m, 2H), 4.74 (s, 1H), 3.76 (s, 3H), 3.12 (dd, J = 15.2, 5.5 Hz, 1H), 2.86 (dd, J = 15.2, 7.9 Hz, 1H), 2.39 (s, 3H), 0.35 (s, 3H), 0.29 (s, 3H); 13C NMR (100 MHz, CDCl_3) δ 157.7, 142.9, 140.4, 135.6, 135.2, 134.1, 133.2, 129.8, 129.4, 128.5, 127.8, 127.2, 119.0, 112.9, 57.5, 55.4, 39.0, 21.7, −3.65, −3.71; HRMS: (ESI) calculated for C_{26}H_{31}NNaO_{3}SSi ([M+Na]^+): 488.1692, found: 488.1689.

(6d): According to the general procedure for α-silylamines, 1d (92.2 mg, 0.3 mmol) dissolved in THF (1.5 mL), Dimethylphenylsilyllithium (appro. 1.0 M in THF, 0.36 mL, 0.36 mmol), and allylmagnesium bromide (1.0 M solution in THF, 0.45 mL, 0.45 mmol) were used and afforded the product 6d (126.1 mg, 93%) as a white solid: mp 129–130 °C; R_f = 0.35 (n-hexane:EtOAc = 6:1); ^1H NMR (400 MHz, CDCl_3) δ 7.49 (d, J = 8.0 Hz, 2H), 7.38 (t, J = 7.1 Hz, 1H), 7.28 (t, J = 7.4 Hz, 2H), 7.17 (d, J = 7.4 Hz, 4H), 6.92 – 6.82 (m, 2H), 6.73 (t, J = 8.5 Hz, 2H), 5.86 – 5.67 (m, 1H), 5.04 (d, J = 13.2 Hz, 2H), 4.80 (s, 1H), 3.17 (dd, J = 15.3, 5.4 Hz, 1H), 2.89 (dd, J = 15.1, 7.9 Hz, 1H), 2.40 (s, 3H), 0.34 (s, 3H), 0.32 (s, 3H); 13C NMR (100 MHz, CDCl_3) δ 161.2 (d, J_{CF} = 245.2 Hz), 143.2, 140.4, 137.1 (d, J_{CF} = 3.1 Hz), 135.1, 135.0, 134.1, 130.0, 129.5, 128.9 (d, J_{CF} = 7.8 Hz), 127.9, 127.2, 119.2, 114.3 (d, J_{CF} = 21.2 Hz), 57.7, 39.3, 21.7, −3.9; HRMS: (ESI) calculated for C_{25}H_{28}FNNaO_{2}SSi ([M+Na]^+): 476.1492, found: 476.1496.

(6e): According to the general procedure for α-silylamines, 1e (97.1 mg, 0.3 mmol) dissolved in THF (1.5 mL), Dimethylphenylsilyllithium (appro. 1.0 M in THF, 0.36 mL, 0.36 mmol), and allylmagnesium bromide (1.0 M solution in THF, 0.45 mL, 0.45 mmol)
were used and afforded the product 6e (126.2 mg, 90%) as a white solid: mp 117–118 °C; Rf = 0.35 (n-hexane:EtOAc = 6:1); 1H NMR (400 MHz, CDCl3) δ 7.43 (d, J = 8.3 Hz, 2H), 7.34 (t, J = 7.4 Hz, 1H), 7.23 (d, J = 8.6 Hz, 2H), 7.16 – 7.09 (m, 4H), 6.96 (d, J = 8.8 Hz, 2H), 6.79 (d, J = 8.8 Hz, 2H), 5.80 – 5.64 (m, 1H), 4.99 (d, J = 13.6 Hz, 2H), 4.80 (s, 1H), 3.12 (dd, J = 15.3, 5.4 Hz, 1H), 2.83 (dd, J = 15.3, 8.0 Hz, 1H), 2.36 (s, 3H), 0.29 (s, 3H), 0.27 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 143.3, 140.3, 140.11, 135.1, 134.7, 134.1, 131.8, 130.1, 129.5, 128.7, 128.0, 127.6, 127.1, 119.2, 57.8, 39.2, 21.7, –3.9; HRMS: (ESI) calculated for C25H28ClNNaO2SSi ([M+Na]+): 492.1196, found: 492.1201.

(6f): According to the general procedure for α-silylamines, 1f (101.8 mg, 0.3 mmol) dissolved in THF (1.5 mL), Dimethylphenylsilyllithium (appro. 1.0 M in THF, 0.36 mL, 0.36 mmol), and allylmagnesium bromide (1.0 M solution in THF, 0.45 mL, 0.45 mmol) were used. But after allylmagnesium bromide was added dropwise, the reaction mixture was allowed to warm slowly to –60 °C over 1 h. The reaction was quenched at –60 °C by the addition of 3 mL of 1.0 M solution of HCl. Standard operation followed, purification by column chromatography (n-hexane:EtOAc:CH2Cl2 = 50:1:0.3 to 25:1:0.3, gradient elution) and afforded the product 6f (87.9 mg, 60%) as a white solid: mp 179–180 °C; Rf = 0.40 (n-hexane:EtOAc = 6:1); 1H NMR (400 MHz, CDCl3) δ 8.47 (d, J = 8.9 Hz, 1H), 7.73 (d, J = 8.2 Hz, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.37 – 7.27 (m, 5H), 7.26 – 7.17 (m, 4H), 7.15 – 7.06 (m, 2H), 6.95 (d, J = 8.0 Hz, 2H), 6.03 – 5.88 (m, 1H), 5.21 – 5.08 (m, 2H), 4.94 (s, 1H), 3.55 (dd, J = 15.0, 5.2 Hz, 1H), 3.13 (dd, J = 15.1, 7.6 Hz, 1H), 2.32 (s, 3H), 0.44 (s, 3H), 0.41 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 142.8, 138.9, 136.74, 136.67, 135.2, 134.7, 133.7, 131.8, 129.5, 129.0, 128.8, 128.5, 128.2, 127.7, 127.1, 126.4, 125.0, 124.7, 124.3, 120.1, 58.4, 41.5, 21.6, –0.2, –1.3; HRMS: (ESI) calculated for C29H31NNaO2SSi ([M+Na]+): 508.1742, found: 508.1741.

(6g): According to the general procedure for α-silylamines, 1g (83.8 mg, 0.3 mmol) dissolved in THF (1.5 mL), Dimethylphenylsilyllithium (appro. 1.0 M in THF, 0.36 mL,
0.36 mmol), and allylmagnesium bromide (1.0 M solution in THF, 0.45 mL, 0.45 mmol) were used and afforded the product 6g (69.0 mg, 54%) as a white solid: mp 141–142 °C; Rf = 0.34 (n-hexane:EtOAc = 6:1); 1H NMR (400 MHz, CDCl3) δ 7.48 – 7.28 (m, 7H), 7.08 (d, J = 8.1 Hz, 2H), 6.87 (s, 1H), 6.08 (s, 1H), 5.88 (s, 1H), 5.84 – 5.70 (m, 1H), 5.14 – 4.99 (m, 2H), 4.81 (s, 1H), 2.97 (dd, J = 36.7, 14.9, 6.8 Hz, 2H), 2.36 (s, 3H), 0.38 (s, 3H), 0.36 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 154.8, 142.5, 141.0, 139.3, 135.1, 135.0, 134.3, 131.0, 129.2, 128.0, 127.2, 118.8, 110.4, 107.5, 52.8, 38.8, 21.7, –3.4, –3.6; HRMS: (ESI) calculated for C23H27NNaO3SSi ([M+Na]+): 448.1379, found: 448.1380.

6h: According to the general procedure for α-silylamines, 1h (88.6 mg, 0.3 mmol) dissolved in THF (1.5 mL), Dimethylphenylsilyllithium (appro. 1.0 M in THF, 0.36 mL, 0.36 mmol), and allylmagnesium bromide (1.0 M solution in THF, 0.45 mL, 0.45 mmol) were used and afforded the product 6h (46.5 mg, 35%) as a white solid: mp 151–152 °C; Rf = 0.35 (n-hexane:EtOAc = 6:1); 1H NMR (400 MHz, CDCl3) δ 7.49 (d, J = 8.1 Hz, 2H), 7.38 (d, J = 3.6 Hz, 1H), 7.34 – 7.21 (m, 4H), 7.13 (d, J = 7.8 Hz, 2H), 7.01 (d, J = 4.4 Hz, 1H), 6.66 (s, 1H), 6.25 (s, 1H), 5.86 – 5.70 (m, 1H), 5.15 – 5.00 (m, 2H), 4.83 (s, 1H), 3.20 (dd, J = 15.1, 5.5 Hz, 1H), 2.96 (dd, J = 14.9, 7.8 Hz, 1H), 2.38 (s, 3H), 0.41 (s, 6H); 13C NMR (100 MHz, CDCl3) δ 146.6, 143.0, 140.2, 135.2, 133.9, 130.0, 129.4, 127.9, 127.2, 126.4, 125.2, 123.2, 119.4, 56.4, 41.0, 21.7, –3.5, –3.6; HRMS: (ESI) calculated for C23H27NNaO2S2Si ([M+Na]+): 464.1150, found: 464.1150.

6i: According to the general procedure for α-silylamines, 1a (86.8 mg, 0.3 mmol) dissolved in THF (1.5 mL), Dimethylphenylsilyllithium (appro. 1.0 M in THF, 0.36 mL, 0.36 mmol), and vinylmagnesium bromide (freshly prepared, appro. 1.0 M solution in THF, 0.9 mL, 0.9 mmol) were used. But after vinylmagnesium bromide was added dropwise, the reaction mixture was allowed to warm slowly to –50 °C over 2 h. The reaction was quenched at –50 °C by the addition of 3 mL of 1.0 M solution of HCl. Standard operation followed, column chromatography afforded the title compound 6i (76.3 mg, 60%) as a white solid: mp 154–155 °C;
$R_f = 0.31$ ($\text{n-hexane:EtOAc = 6:1}$); $^1\text{H NMR (400 MHz, CDCl}_3\text{)} \delta 7.42\ (t, J = 7.4\ \text{Hz, 1H}),\ 7.37\ (d, J = 8.2\ \text{Hz, 2H}),\ 7.31\ (t, J = 7.5\ \text{Hz, 2H}),\ 7.23\ (d, J = 6.9\ \text{Hz, 2H}),\ 7.17 - 7.02\ (m, 7H),\ 6.15\ (dd, J = 17.3, 10.9\ \text{Hz, 1H}),\ 5.27\ (d, J = 13.5\ \text{Hz, 1H}),\ 5.24\ (d, J = 7.2\ \text{Hz, 1H}),\ 4.84\ (s, 1H),\ 2.38\ (s, 3H),\ 0.32\ (s, 3H),\ 0.21\ (s, 3H);\ ^{13}\text{C NMR (100 MHz, CDCl}_3\text{)} \delta 142.7,\ 140.9,\ 139.3,\ 135.7,\ 135.1,\ 133.8,\ 130.3,\ 129.1,\ 128.1,\ 127.8,\ 127.4,\ 127.1,\ 126.1,\ 116.4,\ 61.5,\ 21.7,\ -5.0;\ \text{HRMS: (ESI) calculated for C}_{24}\text{H}_{27}\text{NNaO}_2\text{SSi ([M+Na]+=): 444.1429, found: 444.1409.}$

(6j): According to the general procedure for $\alpha$-silylamines, 1a (86.8 mg, 0.3 mmol) dissolved in THF (1.5 mL), Dimethylphenylsilyllithium (approx. 1.0 M in THF, 0.36 mL, 0.36 mmol), and methylmagnesium bromide (3.0 M solution in Et$_2$O, 0.15 mL, 0.45 mmol) were used and afforded the product 6j (106.2 mg, 86%) as a white solid: mp 159–160 °C (lit. $^{10}$ mp 163 °C); $R_f = 0.31$ ($\text{n-hexane:EtOAc = 6:1}$); $^1\text{H NMR (400 MHz, CDCl}_3\text{)} \delta 7.44\ (t, J = 7.6\ \text{Hz, 3H}),\ 7.34\ (t, J = 7.5\ \text{Hz, 2H}),\ 7.24\ (d, J = 1.4\ \text{Hz, 1H}),\ 7.15 - 7.03\ (m, 5H),\ 6.95 - 6.89\ (m, 2H),\ 4.91\ (s, 1H),\ 2.34\ (s, 3H),\ 1.69\ (s, 3H),\ 0.29\ (s, 3H),\ 0.15\ (s, 3H).$ The $^1\text{H NMR spectrum of this compound matched the reported spectral data.}^{10}$

(6k): According to the general procedure for $\alpha$-silylamines, 1a (86.8 mg, 0.3 mmol) dissolved in THF (1.5 mL), Dimethylphenylsilyllithium (approx. 1.0 M in THF, 0.36 mL, 0.36 mmol), and ethylmagnesium bromide (3.0 M solution in Et$_2$O, 0.15 mL, 0.45 mmol) were used and afforded the product 6k (112.1 mg, 88%) as a white solid: mp 171–172 °C; $R_f = 0.38$ ($\text{n-hexane:EtOAc = 6:1}$); $^1\text{H NMR (400 MHz, CDCl}_3\text{)} \delta 7.53\ (d, J = 8.1\ \text{Hz, 2H}),\ 7.35\ (t, J = 7.2\ \text{Hz, 1H}),\ 7.25\ (t, J = 7.2\ \text{Hz, 2H}),\ 7.22 - 7.15\ (m, 4H),\ 7.13 - 7.04\ (m, 3H),\ 7.00 - 6.92\ (m, 2H),\ 4.72\ (s, 1H),\ 2.40\ (s, 3H),\ 2.30\ (dq, J = 14.4, 1H),\ 2.14\ (dq, J = 14.4, 7.1\ \text{Hz, 1H}),\ 0.74\ (t, J = 7.2\ \text{Hz, 3H}),\ 0.36\ (s, 3H),\ 0.30\ (s, 3H);\ ^{13}\text{C NMR (100 MHz, CDCl}_3\text{)} \delta 143.0,\ 141.6,\ 140.5,\ 136.1,\ 135.0,\ 129.6,\ 129.4,\ 127.8,\ 127.7,\ 127.2,\ 127.1,\ 125.8,\ 59.6,\ 26.7,\ 21.7,\ 8.7,\ -3.7,\ -4.1;\ \text{HRMS: (ESI) calculated for C}_{24}\text{H}_{29}\text{NNaO}_2\text{Si ([M+Na]+=): 446.1586, found: 446.1585.}$

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According to the general procedure for α-silylamines, 1a (86.8 mg, 0.3 mmol) dissolved in THF (1.5 mL), Dimethylphenylsilyllithium (approx. 1.0 M in THF, 0.36 mL, 0.36 mmol), and benzylmagnesium bromide (1.0 M solution in THF, 0.45 mL, 0.45 mmol) were used and afforded the product 6l (103.4 mg, 71%) as a white solid: mp 120−121 °C; R_f = 0.40 (n-hexane:EtOAc = 6:1); ¹H NMR (400 MHz, CDCl₃) δ 7.38 (d, J = 8.2 Hz, 2H), 7.32 (t, J = 7.3 Hz, 1H), 7.20 (t, J = 7.5 Hz, 2H), 7.16 − 6.94 (m, 12H), 6.97 (d, J = 6.8 Hz, 2H), 4.76 (s, 1H), 3.78 (d, J = 15.3 Hz, 1H), 3.43 (d, J = 15.3 Hz, 1H), 2.38 (s, 3H), 0.43 (s, 3H), 0.24 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 142.9, 141.1, 140.1, 136.69, 136.67, 135.4, 130.9, 129.4, 129.3, 128.3, 127.68, 127.64, 127.5, 127.0, 126.7, 126.2, 59.8, 39.8, 21.7, −3.27, −3.29; HRMS: (ESI) calculated for C₂₉H₃₁NNaO₂Si ([M+Na]⁺): 508.1742, found: 508.1732.

According to the general procedure for α-silylamines, 1a (86.8 mg, 0.3 mmol) dissolved in THF (1.5 mL), Dimethylphenylsilyllithium (approx. 1.0 M in THF, 0.36 mL, 0.36 mmol), and phenylmagnesium bromide (3.0 M solution in Et₂O, 0.15 mL, 0.45 mmol) were used and afforded the product 6m (92.8 mg, 66%) as a white solid: mp 184−185 °C; R_f = 0.33 (n-hexane:EtOAc = 6:1); ¹H NMR (400 MHz, CDCl₃) δ 7.43 (dq, J = 8.0, 4.1 Hz, 1H), 7.36 (d, J = 4.4 Hz, 4H), 7.27 (t, J = 3.8, 3.0 Hz, 4H), 7.15 − 7.03 (m, 6H), 6.81 (q, J = 8.4 Hz, 4H), 5.21 (s, 1H), 2.29 (s, 3H), 0.25 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 141.9, 140.2, 140.1, 136.69, 136.72, 135.4, 130.9, 129.4, 129.3, 128.3, 127.68, 127.64, 127.5, 127.0, 126.7, 126.2, 92.8, 39.8, 21.7, −3.27, −3.29; HRMS: (ESI) calculated for C₂₈H₃₀NO₂Si ([M+H]⁺): 472.1767, found: 472.1762.

1a (86.8 mg, 0.3 mmol) was dissolved in 1.5 mL THF and added to a flame-dried schlenk flask equipped with a magnetic stirring bar under argon. The solution was cooled to −78 °C. Dimethylphenylsilyllithium (approx. 1.0 M in THF, 0.36 mL, 0.36 mmol) was added dropwise to the solution via syringe. The reaction mixture was stirred for 1h at −78 °C and
then was allowed to warm slowly to –55 °C. 4-fluorophenylmagnesium bromide (1.0 M solution in THF, 3.0 mL, 3.0 mmol) was added dropwise at –55 °C, and the reaction mixture was allowed to warm slowly to –22 °C over 3 h. Then it was quenched at –22 °C by the addition of 3 mL of 1.0M solution of HCl. The resulting heterogeneous mixture was allowed to warm to room temperature and then stirred for an additional 1 h. The reaction mixture was diluted with 30 mL EtOAc. The layers were separated, and the aqueous layer was extracted with EtOAc (2×5 mL). The organic extracts were washed with saturated aqueous sodium bicarbonate (15 mL) and brine (15 mL), dried over anhydrous Na2SO4, filtered, and concentrated in vacuo. The residue was purified by column chromatography (n-hexane:EtOAc:CH2Cl2 = 50:1:0.3 to 20:1:0.3, gradient elution) yielding pure product 6n (79.5 mg, 54%) as a white solid: mp 192−193 °C; Rf = 0.30 (n-hexane:EtOAc = 6:1); 1H NMR (400 MHz, CDCl3) δ 7.47 – 7.40 (m, 1H), 7.39 – 7.33 (m, 4H), 7.30 – 7.24 (m, 2H), 7.23 – 7.17 (m, 2H), 7.16 – 7.08 (m, 3H), 6.84 (q, J = 8.4 Hz, 4H), 6.71 (t, J = 8.6 Hz, 2H), 5.28 (s, 1H), 2.30 (s, 3H), 0.29 (s, 3H), 0.22 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 161.6 (d, JCF = 246.2 Hz), 142.1, 140.4, 140.0, 135.9 (d, JCF = 3.3 Hz), 135.3, 134.9, 131.6 (d, JCF = 7.9 Hz), 130.3, 129.1, 128.9, 128.5, 127.7, 126.6, 126.2, 114.2 (d, JCF = 21.2 Hz), 62.1, 21.5, –3.1, –3.4; HRMS: (ESI) calculated for C28H28FNNaO2SSi ([M+Na]+): 512.1492, found: 512.1497.

(60): 1a (86.8 mg, 0.3 mmol) was dissolved in 1.5 mL THF and added to a flame-dried schlenk flask equipped with a magnetic stirring bar under argon. The solution was cooled to –78 °C. Dimethylphenylsilyllithium (approx. 1.0 M in THF, 0.36 mL, 0.36 mmol) was added dropwise to the solution via syringe. The reaction mixture was stirred for 1 h at –78 °C and then was allowed to warm slowly to –58 °C. 4-methoxyphenylmagnesium bromide (1.0 M solution in THF, 3.0 mL, 3.0 mmol) was added dropwise at –58 °C, and the reaction mixture allowed to warm slowly to –25 °C over 4 h. Then it was quenched at –25 °C by the addition of 3 mL of 1.0 M solution of HCl. The resulting heterogeneous mixture was allowed to warm to room temperature and then stirred for an additional 1 h. The reaction mixture was diluted with 30 mL EtOAc. The layers were separated, and the aqueous layer was extracted with EtOAc (2×5 mL).
The organic extracts were washed with saturated aqueous sodium bicarbonate (15 mL) and brine (15 mL), dried over anhydrous Na₂SO₄, filtered, and concentrated in vacuo. The residue was purified by column chromatography (n-hexane:EtOAc:CH₂Cl₂ = 50:1:0.3 to 15:1:0.3, gradient elution) yielding pure product 6o (87.3 mg, 58%) as a white solid: mp 183−184 °C; Rᵢ = 0.22 (n-hexane:EtOAc = 6:1); ¹H NMR (400 MHz, CDCl₃) δ 7.46 – 7.40 (m, 1H), 7.39 – 7.33 (m, 4H), 7.31 – 7.27 (m, 2H), 7.17 – 7.09 (m, 5H), 6.87 – 6.76 (m, 4H), 6.52 (d, J = 9.2, 2H), 5.21 (s, 1H), 3.75 (s, 3H), 2.29 (s, 3H), 0.31 (s, 3H), 0.18 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 158.2, 141.7, 140.0, 135.7, 135.0, 131.9, 131.4, 130.1, 128.9, 128.7, 128.4, 127.5, 126.31, 126.27, 112.7, 62.0, 55.3, 21.6, –3.1, –3.4; HRMS: (ESI) calculated for C₂₉H₃₁NNaO₃SSi ([M+Na]⁺): 524.1692, found: 524.1690.

(6p): According to the general procedure for α-silylamines, 1a (86.8 mg, 0.3 mmol) dissolved in THF (1.5 mL), Dimethylphenylsilyllithium (appro. 1.0 M in THF, 0.36 mL, 0.36 mmol), and iospropylmagnesium bromide (2.0 M solution in THF, 0.23 mL, 0.46 mmol) were used and afforded the product 6p (70.6 mg, 54%) as a white solid and 6r (44.8 mg, 38%) as a white solid. The analytic data of 6p: mp 165−166 °C; Rᵢ = 0.41 (n-hexane:EtOAc = 6:1); ¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, J = 8.3 Hz, 2H), 7.39 – 7.33 (m, 1H), 7.32 – 7.26 (m, 6H), 7.22 – 7.06 (m, 5H), 4.47 (s, 1H), 2.73 – 2.62 (m, 1H), 2.45 (s, 3H), 1.05 (d, J = 6.8 Hz, 3H), 0.92 (d, J = 6.8 Hz, 3H), 0.29 (s, 3H), 0.24 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 142.9, 142.0, 140.8, 136.9, 135.4, 129.7, 129.6, 127.9, 127.8, 127.6, 126.6, 125.8, 66.2, 33.3, 21.8, 20.0, 18.8, –0.3, –2.5; HRMS: (ESI) calculated for C₂₅H₃₁NNaO₂SSi ([M+Na]⁺): 460.1742, found: 460.1742.

(6q): (1) According to the general procedure for α-silylamines, 1a (86.8 mg, 0.3 mmol) dissolved in THF (1.5 mL), Dimethylphenylsilyllithium (appro. 1.0 M in THF, 0.36 mL, 0.36 mmol), and cyclohexylmagnesium bromide (1.0 M solution in THF, 0.45 mL, 0.45 mmol) were used and afforded the product 6q (37.4 mg, 26%) as a white solid and 6r (67.9 mg, 57%) as a white solid.

(2) According to the general procedure for α-silylamines, 1a (86.8 mg, 0.3 mmol) dissolved in
THF (1.5 mL), Dimethylphenylsilyllithium (appro. 1.0 M in THF, 0.36 mL, 0.36 mmol), and cyclohexylmagnesium bromide (treated with 10 mmol% ZnCl₂ in advance: 1.0 mL 1.0 M cyclohexylmagnesium bromide in THF and 0.1 mL 1.0 M ZnCl₂ in Et₂O were stirred at room temperature for 1 h under argon before that was used, 0.5 mL, 0.45 mmol, 1.5 equiv) were used and afforded the product 6q (79.1 mg, 55%) and trace of 6r. The analytic data of 6q: mp 165–167 °C; Rᵥ = 0.44 (n-hexane:EtOAc = 6:1); ¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, J = 8.1 Hz, 2H), 7.40 – 7.34 (m, 1H), 7.33 – 7.26 (m, 5H), 7.21 – 7.05 (m, 5H), 4.47 (s, 1H), 2.45 (s, 3H), 2.23 (t, J = 8.8 Hz, 1H), 1.89 (d, J = 8.6 Hz, 1H), 1.78 – 1.66 (m, 3H), 1.61 (d, J = 12.5 Hz, 1H), 1.32 – 1.20 (m, 2H), 1.19 – 1.12 (m, 2H), 1.09 – 0.98 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 142.9, 141.5, 141.0, 137.0, 135.3, 129.7, 129.6, 127.9, 127.7, 127.6, 126.7, 125.7, 66.1, 44.6, 30.5, 28.3, 27.4, 27.1, 26.6, 21.7, −0.2, −2.6; HRMS: (ESI) calculated for C₂₈H₃₅NNaO₂SSi ([M+Na]⁺): 500.2055, found: 500.2051.

(6r): According to the general procedure for α-silylamines, 1a (86.8 mg, 0.3 mmol) dissolved in THF (1.5 mL), Dimethylphenylsilyllithium (appro. 1.0 M in THF, 0.36 mL, 0.36 mmol), and tert-butylmagnesium chloride (1.0 M solution in THF, 3.0 mL, 3.0 mmol) were used and afforded the product 6r (99.2 mg, 84%) as a white solid: Rᵥ = 0.27 (n-hexane:EtOAc = 6:1); ¹H NMR (400 MHz, CDCl₃) δ 7.45 – 7.38 (m, 1H), 7.38 – 7.26 (m, 6H), 7.05 – 6.98 (m, 3H), 6.96 (d, J = 7.9 Hz, 2H), 6.73 – 6.66 (m, 2H), 4.75 (d, J = 8.0 Hz, 1H), 4.11 (d, J = 8.0 Hz, 1H), 2.29 (s, 3H), 0.28 (s, 3H), 0.20 (s, 3H). The ¹H NMR spectrum of this compound matched the reported spectral data.¹⁰

(8): According to the general procedure for α-silylamines, 1a (86.8 mg, 0.3 mmol) dissolved in THF (1.5 mL), Diphenylmethylsilyllithium (appro. 0.8 M in THF, 0.45 mL, 0.36 mmol), and allylmagnesium bromide (1.0 M solution in THF, 0.45 mL, 0.45 mmol) were used. But after allylmagnesium bromide was added dropwise, the reaction mixture was allowed to warm slowly to −35 °C over 2 h. The reaction was quenched at −35 °C by the addition of 3 mL of 1.0 M solution of HCl. Standard operation followed column chromatography afforded the title
compound 8 (131.3 mg, 88%) as a white solid: mp 123−124 °C; Rf = 0.34 (n-hexane:EtOAc = 6:1);
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.47 (d, J = 7.0 Hz, 2H), 7.44−7.35 (m, 4H), 7.33−7.27 (m, 6H), 7.08 (t, J = 8.0 Hz, 3H), 7.02 (t, J = 7.5 Hz, 2H), 6.92 (d, J = 7.7 Hz, 2H), 5.84−5.70 (m, 1H), 5.03 (s, 1H), 4.94 (s, 1H), 4.90 (d, J = 4.3 Hz, 1H), 3.19 (ddd, J = 22.7, 15.4, 6.8 Hz, 2H), 2.37 (s, 3H), 0.62 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 142.9, 141.4, 140.3, 136.1, 135.8, 134.9, 133.8, 133.1, 130.1, 130.0, 129.3, 128.0, 127.8, 127.5, 127.2, 126.1, 118.7, 58.1, 39.8, 21.7, −4.4; HRMS: (ESI) calculated for C$_{30}$H$_{31}$NNaO$_2$Si ([M+Na]$^+$): 520.1742, found: 520.1735.

(9): According to the general procedure for α-silylamines, 1a (86.8 mg, 0.3 mmol) dissolved in THF (1.5 mL), phenyl lithium (1.9 M in n-butyl ether, 0.24 mL, 0.45 mmol), and allylmagnesium bromide (1.0 M solution in THF, 0.45 mL, 0.45 mmol) were used and afforded the product 9 (109.5 mg, 97%) as a white solid: mp 113−114 °C; Rf = 0.29 (n-hexane:EtOAc = 6:1); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.22−7.06 (m, 12H), 6.96 (d, J = 8.3 Hz, 2H), 5.46−5.35 (m, 1H), 5.34 (s, 1H), 5.26 (dd, J = 17.1, 2.0 Hz, 1H), 5.15 (dd, J = 9.9, 2.0 Hz, 1H), 3.31 (d, J = 6.9 Hz, 2H), 2.32 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 142.7, 142.4, 139.2, 133.0, 129.0, 128.2, 127.9, 127.3, 127.1, 121.2, 66.5, 45.2, 21.6; HRMS: (ESI) calculated for C$_{23}$H$_{23}$NNaO$_2$S ([M+Na]$^+$): 400.1347, found: 400.1344.
13. NMR Spectra of all new compounds

$^1$H NMR spectrum (CDCl$_3$, 400 MHz) of 1b

$^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of 1b
$^1$H NMR spectrum (CDCl$_3$, 400 MHz) of 1c

$^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of 1c
**1H NMR spectrum (CDCl₃, 400 MHz) of 1d**

**13C NMR spectrum (CDCl₃, 100 MHz) of 1d**
$^1$H NMR spectrum (CDCl$_3$, 400 MHz) of 1e

$^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of 1e
\(^1\)H NMR spectrum (CDCl\textsubscript{3}, 400 MHz) of \(1f\)

\(^{13}\)C NMR spectrum (CDCl\textsubscript{3}, 100 MHz) of \(1f\)
$^1$H NMR spectrum (CDCl$_3$, 400 MHz) of 1g

$^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of 1g
$^1$H NMR spectrum (CDCl$_3$, 400 MHz) of $1h$

$^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of $1h$
$^1$H NMR spectrum (CDCl$_3$, 400 MHz) of 4

$^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of 4
$^1$H NMR spectrum (CDCl$_3$, 400 MHz) of 6a

$^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of 6a
$^1$H NMR spectrum (CDCl$_3$, 400 MHz) of $6b$

$^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of $6b$

S33
\( ^1H \) NMR spectrum (CDCl\(_3\), 400 MHz) of 6c

\( ^{13}C \) NMR spectrum (CDCl\(_3\), 100 MHz) of 6c
$^1$H NMR spectrum (CDCl$_3$, 400 MHz) of 6d

$^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of 6d
$^1$H NMR spectrum (CDCl$_3$, 400 MHz) of 6e

$^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of 6e
$^1$H NMR spectrum (CDCl$_3$, 400 MHz) of 6f

$^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of 6f
$^1$H NMR spectrum (CDCl$_3$, 400 MHz) of 6g

$^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of 6g
$^1$H NMR spectrum (CDCl$_3$, 400 MHz) of 6h

$^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of 6h

S39
$^1$H NMR spectrum (CDCl$_3$, 400 MHz) of 6i

$^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of 6i
$^{1}$H NMR spectrum (CDCl$_3$, 400 MHz) of 6k

$^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of 6k
$^1$H NMR spectrum (CDCl$_3$, 400 MHz) of 6l

$^1$C NMR spectrum (CDCl$_3$, 100 MHz) of 6l
$^1$H NMR spectrum (CDCl$_3$, 400 MHz) of 6m

$^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of 6m
$^1$H NMR spectrum (CDCl$_3$, 400 MHz) of 6n

$^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of 6n
\(^1\)H NMR spectrum (CDCl\(_3\), 400 MHz) of 60

\(^{13}\)C NMR spectrum (CDCl\(_3\), 100 MHz) of 60
$^{1}$H NMR spectrum (CDCl$_3$, 400 MHz) of 6p

$^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of 6p
$^1$H NMR spectrum (CDCl$_3$, 400 MHz) of 6q

$^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of 6q
$^1$H NMR spectrum (C₆D₆, 400 MHz) of 7

$^{13}$C NMR spectrum (C₆D₆, 100 MHz) of 7
$^{1}$H NMR spectrum (CDCl$_3$, 400 MHz) of 8

$^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of 8
$^1$H NMR spectrum (CDCl$_3$, 400 MHz) of 9

$^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of 9