Supporting Information

Zirconium Hydroaminoalkylation. An Alternative Disconnection for the Catalytic Synthesis of α-Arylated Primary Amines

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1.1 Solvents and general experimental conditions

All air and moisture sensitive reactions were performed using a MBraun LABmaster glovebox filled with a N₂ atmosphere. All pieces of glassware, Teflon coated magnetic stirring bars and canulas were dried for at least overnight in a 180 °C oven before being transferred into the glovebox or used in the Schlenk line. Ether was passed over activated alumina columns into Teflon sealed Straus flasks and stored therein until use. d₆-Benzene was dried over molecular sieves 3Å, degassed, and stored in Teflon sealed Schlenk flasks prior to use. N-silylation of the amines was conducted with the use of the Schlenk line. The hydroaminoalkylation reaction was conducted on NMR tube scale and performed in J-Young NMR tubes (8” x 5 mm) sealed with screw-type Teflon caps. N-N-Dimethylformamide (DMF) was dried over 4Å molecular sieves.

1.2 Materials

Zr(NMe₂)₄ (Sigma-Aldrich) was used as received. All amines and alkenes were purchased from commercial sources (Sigma-Aldrich, Oakwood, Combi-blocks), dried over CaH₂ and distilled before use. n-Buli 1.6 M in hexanes was purchased from Sigma-Aldrich. TMSCl was purchased from Sigma-Aldrich, dried over CaH₂, distilled and stored in Teflon sealed Straus flasks. Sulfuryl diimidazole (SDI) was prepared following a previously reported procedure. Screw caps and PTFE/Silicon septa were purchased from Chemglass Life Sciences LLC. BD Intramedic™ (I.D. 1.57mm, O.D. 2.08mm) polyethylene tubing was used for the reactions. For the manipulation of the 1,1-dihydrofluoroalkylating reagent (2,2,2-trifluoroethyl fluorosulfate), caution is advised. However, this reagent is less reactive than its other derivatives, such as trifluoroethyl triflate or methyl fluorosulfonate.

1.3 Instrumentation

NMR spectra were recorded as dilute solutions in deuterated chloroform or benzene or methanol on a Bruker 400 MHz spectrometer at room temperature at the Faculty of Pharmaceutical Sciences and the Department of Chemistry at UBC. ¹H chemical shift data are reported in units δ relative to the residual protic solvent where δ (CDCl₃) = 7.26 ppm, δ (C₆D₆) = 7.16 ppm and δ (CD₃OD) = 3.31 ppm, while ¹³C chemical shift data are given in units δ relative to the solvent where δ (CDCl₃) = 77.23 ppm, δ (C₆D₆) = 128.39 ppm and (CD₃OD) = 49.17 ppm. NMR yields were determined by ¹⁹F NMR using a relaxation delay (or recycle delay) of 40 seconds to ensure complete relaxation of all fluorine nuclei. α,α,α-Trifluorotoluene (PhCF₃) was used as an internal standard. High-resolution mass spectra were measured by the mass spectrometry and microanalysis service at the Department of Chemistry, University of British Columbia. Mass spectra were recorded on a Kratos MS-50 spectrometer using an electron impact (70 eV) source or a Bruker Esquire LC spectrometer using electrospray ionization source with the fragment signals being reported in mass to charge number (m/z).

The synthesis, characterization and NMR spectra of the products are presented below. For the mixture of products obtained from the alkene scope in Table 2, the clearly diagnostic peaks are indicated in colors red (linear), blue (major diastereomer) and black (minor diastereomer). Overlapping peaks are indicated in
purple. For products 4a-4c and 9a-9c, we present the GC-MS spectra which corroborate the \(^1\)H NMR regio- and diastereoselectivity ratios.

1.4 Synthesis and characterization of compounds

1.4.1 General procedure for the hydroaminoalkylation reaction – alkene scope

To a solution of \(\text{Zr(NMe}_2\text{)}_4\) (0.1 equiv, 0.05 mmol, 13.37 mg) in 200-300 \(\mu\)L \(\text{C}_6\text{D}_6\), the \(N\)-trimethylsilylbenzylamine (1 equiv, 0.50 mmol, 89.67 mg) was added followed by the addition of the alkene 1-9 (Table 2) (1.8 equiv, 0.90 mmol). The solution was then transferred quantitatively into a J-Young tube via an additional 200-300 \(\mu\)L \(\text{C}_6\text{D}_6\) and placed in an oil bath at 145 °C. The reaction times for each product are presented below. Upon the reaction completion, the J-Young seal was broken and DCM and MeOH were added to the existing solution. The quenched solution was then passed through a pipet with a Celite™ plug and 2-3 droplets of NaOH 3M were added to the filtrate. The solvents were evaporated and ether was added to the residue. The amine was extracted in the form of its hydrochloric salt (4x10 mL) with HCl 1M and the combined aqueous layers were basified with NaOH 3M. The amine was back-extracted with ether (3x20 mL). The ethereal layers were dried over anhydrous Na\(_2\)SO\(_4\) and evaporated to afford the product as a single or mixture of regioisomers.

**Linear: 1,5-diphenylpentan-1-amine (1a)**

**Branched: 2-methyl-1,4-diphenylbutan-1-amine (1b and 1c)**

Catalyst Loading (0.1 equiv, 0.05 mmol, 13.37 mg); Alkene 1 (1.8 equiv, 0.90 mmol, 119 mg); Reaction time: 48 h. Physical state: Yellow oil. \(^1\)H NMR RR (linear:branched 1:3). \(^1\)H NMR DR (1b:1c 3:1). Yield (93 mg, 78%). Clearly separated diagnostic peaks of the linear regioisomer 1a: \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 3.88\) (t, \(J = 6.7\) Hz, 0.4 H, \(\text{CHNH}_2\), integration relative to the benzylic peak at 3.83 ppm); Clearly separated diagnostic peaks of the major branched diastereomer 1b: \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 0.99\) (d, \(J = 6.4\) Hz, 3 H, \(\text{CH}_2\text{CH}\)), 3.83 (d, \(J = 6.7\) Hz, 1 H, \(\text{CHNH}_2\)); Clearly separated diagnostic peaks of the minor branched diastereomer 1c: \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 0.86\) (d, \(J = 6.8\) Hz, 1 H, \(\text{CH}_2\text{CH}\), integration relative to the aliphatic peak at 0.99 ppm), 1.89-1.98 (m, 1 H, \(\text{CH}_3\text{CH}\)), 3.76 (d, \(J = 6.7\) Hz, 0.3 H, \(\text{CHNH}_2\), integration relative to the benzylic peak at 3.83
Overlapping peaks of 1a, 1b and 1c: 1H NMR (400 MHz, CDCl$_3$): $\delta$ = 1.24-1.45 (m, overlap of 1a, 1b and 1c, CH$_3$ (1a), CH$_2$CH$_2$Ph (1b and 1c)), 1.60-1.81 (m, overlap of 1a, 1b and 1c, CH$_2$ (1a), CH$_2$CH$_2$Ph (1b and 1c), CH$_3$CH (1b and 1c)), 2.49-2.61 (m, overlap of 1a, 1b and 1c, CH$_2$ (1a), CH$_2$Ph (1b and 1c), CH$_2$CH$_2$Ph (1b)), 2.66-2.79 (m, overlap of 1b and 1c, CH$_2$Ph (1b and 1c)), 7.10-7.20 (m, overlap of 1a, 1b and 1c, ArH), 7.24-7.34 (m, overlap of 1a, 1b and 1c, ArH). Clearly separated diagnostic peaks of the linear regioisomer 1a: 13C NMR (100 MHz, CDCl$_3$): $\delta$ = 26.5, 31.7, 36.0, 39.7 (CH$_2$CH$_2$), 56.4 (CHNH$_2$), 142.8 (CCH$_2$), 146.9 (CCHNH$_2$); Clearly separated diagnostic peaks of the major branched diastereomer 1b: 13C NMR (100 MHz, CDCl$_3$): $\delta$ = 15.2 (CH$_3$CH), 33.7 (CH$_2$CH$_2$Ph), 35.6 (CH$_2$CH$_2$Ph), 40.0 (CH$_3$CH), 60.6 (CHNH$_2$), 142.7 (CCH$_2$), 145.6 (CCHNH$_2$); Clearly separated diagnostic peaks of the minor branched diastereomer 1c: 13C NMR (100 MHz, CDCl$_3$): $\delta$ = 16.4 (CH$_3$CH), 33.6 (CH$_2$CH$_2$Ph), 34.9 (CH$_2$CH$_2$Ph), 40.2 (CH$_3$CH), 61.2 (CHNH$_2$), 142.9 (CCH$_2$), 145.3 (CCHNH$_2$); Aromatic peaks (all three products): 13C NMR (100 MHz, CDCl$_3$): $\delta$ = 125.8, 125.9, 126.5, 126.9, 127.0, 127.1 (2xArC), 127.3, 128.4 (3xArC), 128.5 (2xArC), 128.6 (2xArC). HRMS (HESI) $m/z$ calcd for C$_{17}$H$_{21}$NH$^+$ [M + H$^+$], 240.1752: Found 240.1753.

Linear: 1-phenylnonan-1-amine (2a)

Catalyst Loading (0.1 equiv, 0.05 mmol, 13.37 mg); Alkene 2 (1.8 equiv, 0.90 mmol, 101 mg); Reaction time: 72 h. Physical state: Yellow oil. 1H NMR RR (linear: branched 1:2). 1H NMR DR (2b:2c 3:1). Yield (60 mg, 55%). Clearly separated diagnostic peaks of the linear regioisomer 2a: 1H NMR (400 MHz, CDCl$_3$): $\delta$ = 3.86 (t, $J$ = 7.0 Hz, 0.6 H, CHNH$_2$, integration relative to the benzylic peak at 3.78 ppm); Clearly separated diagnostic peaks of the major branched diastereomer 2b: 1H NMR (400 MHz, CDCl$_3$): $\delta$ = 3.78 (d, $J$ = 6.2 Hz, 1 H, CHNH$_2$); Clearly separated diagnostic peaks of the minor branched diastereomer 2c: 1H NMR (400 MHz, CDCl$_3$): $\delta$ = 0.74 (d, $J$ = 7.1 Hz, 1 H, CH$_3$CH, integration relative to the benzylic peak at 3.78 ppm), 3.69 (d, $J$ = 7.4 Hz, 0.4 H, CHNH$_2$, integration relative to the benzylic peak at 3.78 ppm); Overlapping peaks of 2a, 2b and 2c: 1H NMR (400 MHz, CDCl$_3$): $\delta$ = 0.84-0.89 (m, overlap of 2a, 2b and 2c, CH$_2$CH$_2$ (2a, 2b and 2c), CH$_2$CH (2b)), 1.00-1.33 (m, overlap of 2a, 2b and 2c, CH$_2$ (2a, 2b and 2c)), 1.62-1.72 (m, overlap of 2a, 2b and 2c, CHCH$_2$ (2a), CHCH$_3$ (2b and 2c)), 7.22-7.25 (m, overlap of 2a, 2b and 2c, ArH), 7.28-7.33 (m, overlapping peaks of 2a, 2b and 2c, ArH). Clearly separated diagnostic peaks of the linear regioisomer 2a: 13C NMR (100 MHz, CDCl$_3$): $\delta$ = 14.3 (CH$_3$CH), 22.9 (CH$_2$), 26.8 (CH$_3$), 29.5 (2xCH$_2$), 33.0 (CH$_2$), 34.0 (CH$_2$), 39.9 (CH$_2$CHNH$_2$), 56.5 (CHNH$_2$), 147.1 (CCHNH$_2$); Clearly separated diagnostic peaks of the major branched diastereomer 2b: 13C NMR (100 MHz, CDCl$_3$): $\delta$ = 14.3 (CH$_3$CH), 22.8 (CH$_2$), 27.4 (CH$_3$), 22.4 (CH$_3$), 29.7 (CH$_3$), 32.1 (CH$_3$), 40.5 (CH$_3$CH), 60.6 (CHNH$_2$), 145.9 (CCHNH$_2$); Clearly separated diagnostic peaks of the minor branched diastereomer 2c: 13C NMR (100 MHz, CDCl$_3$): $\delta$ = 16.5 (CH$_3$CH), 22.9 (CH$_2$), 27.2 (CH$_2$), 29.7 (CH$_3$), 29.9 (CH$_2$), 32.1 (CH$_3$), 40.5 (CH$_3$CH), 61.4 (CHNH$_2$), 145.6 (CCHNH$_2$); Aromatic peaks (all three products): 13C NMR (100 MHz, CDCl$_3$): $\delta$ = 126.5, 126.8, 126.9, 127.0, 127.1, 127.3, 128.3, 128.6. HRMS (HESI) $m/z$ calcd for C$_{18}$H$_{23}$NH$^+$ [M + H$^+$], 220.2065: Found 220.2057.

Linear: 1,4-diphenylbutan-1-amine (3a)

Branching: 2-methyl-1,3-diphenylpropan-1-amine (3b and 3c)
Catalyst Loading (0.1 equiv, 0.05 mmol, 13.37 mg); Alkene 3 (1.8 equiv, 0.90 mmol, 106 mg); Reaction time: 72 h. Physical state: Yellow oil. \(^1\)H NMR RR (linear:branched 1:2). \(^1\)H NMR DR (3b:3c 3:1). Yield (92 mg, 82%).

**Clearly separated diagnostic peaks of the linear regiosomer 3a:** \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 1.63-1.75\) (m, 2 H, \(CH_2CH_2CH_2Ph\), integration relative to the aliphatic peak at 0.86 ppm), 2.61 (t, \(J = 7.4\) Hz, 1 H, \(CH_3Ph\), integration relative to the aliphatic peak at 0.86 ppm), 3.90 (t, \(J = 6.6\) Hz, 0.7 H, CHNH\(_2\), integration relative to the aliphatic peak at 0.86 ppm); **Clearly separated diagnostic peaks of the major branched diastereomer 3b:** \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 0.86\) (d, \(J = 6.8\) Hz, 3 H, \(CH_3\)), 2.72-2.76 (dd, \(J = 13.2\) Hz, \(J = 5.1\) Hz, 1 H, \(CH_2Ph\)); **Clearly separated diagnostic peaks of the minor branched diastereomer 3c:** \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 0.69\) (d, \(J = 6.8\) Hz, 1 H, \(CH_3Ch\), integration relative to the aliphatic peak at 0.86 ppm), 2.99-3.03 (dd, \(J = 13.2\) Hz, \(J = 5.1\) Hz, 0.3 H, \(CH_2Ph\), integration relative to the aliphatic peak at 0.86 ppm); **Overlapping peaks of 3a, 3b and 3c:** \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 2.01-2.08\) (m, overlap of 3b and 3c, \(CH_2CH\) (3b and 3c)), 2.24-2.31 (m, overlap of 3b and 3c, \(CH_3Ph\) (3b and 3c)), 3.83 (d, \(J = 6.2\) Hz, overlap of 3b and 3c, CHNH\(_2\) (3b and 3c)), 7.12-7.19 (m, overlap of 3a, 3b and 3c, ArH), 7.24-7.35 (m, overlap of 3a, 3b and 3c, ArH). **Clearly separated diagnostic peaks of the linear regiosomer 3a:** \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 28.6\) (CH\(_2CH_2CH_2Ph\)), 36.0 (CH\(_2CH_2Ph\)), 39.9 (CH\(_2CH_2Ph\)), 56.4 (CHNH\(_2\)), 141.3 (CH\(_3\)), 145.2 (CHCHNH\(_2\)); **Clearly separated diagnostic peaks of the major branched diastereomer 3b:** \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 14.7\) (CH\(_3CH\)), 40.5 (CH\(_2CH_2Ph\)), 42.8 (CH\(_3CH\)), 60.2 (CH\(_2CH\)), 141.4 (CH\(_3\)), 145.6 (CHCHNH\(_2\)); **Clearly separated diagnostic peaks of the minor branched diastereomer 3c:** \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 16.3\) (CH\(_3CH\)), 39.5 (CH\(_2CH_2Ph\)), 42.7 (CH\(_3CH\)), 61.2 (CHNH\(_2\)), 142.5 (CH\(_3\)), 146.7 (CHCHNH\(_2\)); **Aromatic peaks (all three products):** \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 25.9, 126.0, 126.5, 127.0, 127.1, 127.1, 127.3, 128.4, 128.6, 128.7, 129.2, 129.3, 129.4\). HRMS (HESI) m/z calcd for C\(_{16}H_{20}NH^+\) [M + H\(^+\)], 226.1596: Found 226.1593.

**Linear: 3-cyclohexyl-1-phenylpropan-1-amine (4a)**

Catalyst Loading (0.1 equiv, 0.05 mmol, 13.37 mg); Alkene 4 (1.8 equiv, 0.90 mmol, 99 mg); Reaction time: 72 h. Physical state: Yellow oil. \(^1\)H NMR RR (linear:branched 3:1). \(^1\)H NMR DR (4b:4c 3:1). Yield (72 mg, 66%). **Clearly separated diagnostic peaks of the linear regiosomer 4a:** \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 3.83\) (t, \(J = 6.9\) Hz, 1 H, CHNH\(_2\)); **Clearly separated diagnostic peaks of the major branched diastereomer 4b:** \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 3.97\) (d, \(J = 6.7\) Hz, 0.3 H, CHNH\(_2\), integration relative to the benzylic peak at 3.83 ppm); **Clearly separated diagnostic peaks of the minor branched diastereomer 4c:** \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 0.53\) (d, \(J = 7.1\) Hz, 0.2 H, CH\(_3\), integration relative to the benzylic peak at 3.83 ppm), 3.70 (d, \(J = 6.7\) Hz, 0.1 H, CHNH\(_2\), integration relative to the benzylic peak at 3.83 ppm); **Overlapping peaks of 4a, 4b and 4c:** \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 0.75-0.85\) (m, overlap of 4a and 4b, CH\(_2\) (4a), CH\(_3\) (4b)), 1.00-1.24 (m, overlap of 4a, 4b and 4c, CHcycc (4a), CH\(_2\) (4a, 4b and 4c)), 1.55-1.65 (m, overlap of 4a, 4b and 4c, CH\(_2\) (4a, 4b and 4c)), 7.15-7.23 (m, overlap of 4a, 4b and 4c, ArH), 7.24-7.30 (m, overlap of 4a, 4b and 4c, ArH). **Clearly separated diagnostic peaks of the linear
**regioisomer 4a:** $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 26.7, 29.9, 33.5, 33.6, 34.5, 37.2, 37.9 (CH$_2$CHCH$_3$), 38.3, 56.9 (CHNH$_3$), 147.0 (CCHNH$_3$); Clearly separated diagnostic peaks of the major branched diastereomer 4b: $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 11.0 (CH$_3$), 26.7, 26.9, 28.8, 32.1, 39.7, 45.9, 57.7 (CHNH$_3$), 146.6 (CCHNH$_3$); Clearly separated diagnostic peaks of the minor branched diastereomer 4c: $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 12.2 (CH$_3$), 32.7, 38.3, 45.6, 59.0 (CHNH$_3$), 146.4 (CCHNH$_3$); Aromatic peaks (all three products): $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 126.5, 126.7, 126.9, 127.0, 127.4, 128.4, 128.5, 128.6. HRMS (HESI) $m/z$ calcd for C$_{15}$H$_{22}$NH$^+$ [M + H$^+$], 218.1909: Found 218.1909.

**Linear: 1-phenyl-3-(o-tolyl)propan-1-amine (5a)**

**Branched: 1-phenyl-2-(o-tolyl)propan-1-amine (5b and 5c)**

Catalyst Loading (0.1 equiv, 0.05 mmol, 13.37 mg); Alkene 5 (1.8 equiv, 0.90 mmol, mg); Reaction time: 48 h. Physical state: Yellow oil. $^1$H NMR RR (linear:branched 17:1). $^1$H NMR DR (5b:5c 1:7). Yield (63 mg, 56%). The linear regioisomer 5a: $^1$H NMR (400 MHz, CD$_3$OD): $\delta$ = 1.85-2.04 (m, 2 H, CH$_2$CH), 2.16 (s, 3 H, ArCH$_3$), 2.36-2.44 (m, 1 H, CH$_2$Ar), 2.52-2.59 (m, 1 H, CH$_2$Ar), 3.85-3.89 (dd, $J$ = 8.1 Hz, $J$ = 6.0 Hz, 1 H, CHNH$_3$), 7.01-7.08 (m, 4 H, ArH), 7.24-7.29 (m, 1 H, ArH), 7.33-7.37 (m, 4 H, ArH); Clearly separated diagnostic peaks of the minor branched diastereomer 5b: $^1$H NMR (400 MHz, CD$_3$OD): $\delta$ = 1.12 (d, $J$ = 6.4 Hz, 3 H, CH$_3$CH), 4.07 (d, $J$ = 9.5 Hz, 1 H, CHNH$_3$); Clearly separated diagnostic peaks of the major branched diastereomer 5c: $^1$H NMR (400 MHz, CD$_3$OD): $\delta$ = 1.32 (d, $J$ = 7.1 Hz, 3 H, CH$_2$CH), 4.00 (dd, $J$ = 8.8 Hz, 1 H, CHNH$_3$). The linear regioisomer 5a: $^{13}$C NMR (100 MHz, CD$_3$OD): $\delta$ = 19.4 (ArCH$_3$), 31.4 (2xCH$_2$Ar), 40.8 (CH$_2$CH$_2$Ar), 57.5 (CHNH$_3$), 127.1 (ArC), 127.9 (ArC), 128.4 (ArC), 129.8 (ArC), 129.9 (ArC), 131.3 (ArC), 136.9 (ArC), 141.5 (ArC), 146.6 (CCHNH$_3$); Clearly separated diagnostic peaks of the major branched diastereomer 5c: $^{13}$C NMR (100 MHz, CD$_3$OD): $\delta$ = 18.3 (ArCH$_3$), 43.7 (CH$_2$CHAr), 62.6 (CHNH$_3$), 127.0 (2xArC), 127.8 (ArC), 128.2 (ArC), 129.0 (ArC), 131.2 (ArC), 136.7 (ArC), 144.4 (ArC), 145.5 (CCHNH$_3$). HRMS (HESI) $m/z$ calcd for C$_{15}$H$_{22}$NH$^+$ [M + H$^+$], 226.1596: Found 226.1598.

**4,4-dimethyl-1-phenylpentan-1-amine (6a)**

Catalyst Loading (0.1 equiv, 0.05 mmol, 13.37 mg); Alkene 6 (1.8 equiv, 0.90 mmol, 76 mg); Reaction time: 240 h. Physical state: Yellow oil. Yield (45 mg, 47%). $^1$H NMR (400 MHz, CD$_3$OD): $\delta$ = 0.85 (s, 9 H, C(CH$_3$)$_3$), 0.92-0.99 (m, 1 H, CH$_2$C(CH$_3$)$_3$), 1.19-1.26 (m, 1 H, CH$_2$C(CH$_3$)$_3$), 1.61-1.79 (m, 2 H, CH$_2$CH$_2$C(CH$_3$)$_3$), 3.73 (td, $J$ = 6.8 Hz, 1 H, CHNH$_3$), 7.22-7.25 (m, 1 H, ArH), 7.30-7.34 (m, 4 H, ArH). $^{13}$C NMR (100 MHz, CD$_3$OD): $\delta$ = 29.9 (CH$_3$), 31.0 (C(CH$_3$)$_3$), 35.2 (CH$_2$CH$_2$C(CH$_3$)$_3$), 41.9 (CH$_2$CH$_2$C(CH$_3$)$_3$), 58.3 (CHNH$_3$), 127.9 (2xArC), 128.3 (ArC$_4$), 129.7 (2xArC), 146.9 (CCHNH$_3$). HRMS (HESI) $m/z$ calcd for C$_{15}$H$_{22}$NH$^+$ [M + H$^+$], 192.1752: Found 192.1748.
1-phenyl-3-(trimethylsilyl)propan-1-amine (7a)

Catalyst Loading (0.1 equiv, 0.05 mmol, 13.37 mg); Alkene 7 (1.8 equiv, 0.90 mmol, 90 mg); Reaction time: 24 h. Physical state: Yellow oil. Yield (54 mg, 52%). 1H NMR (400 MHz, CDCl3): δ = -0.07 (s, 9 H, Si(CH3)3), 0.26-0.34 (m, 1 H, CH2Si), 0.48-0.56 (m, 1 H, CH3Si), 1.58-1.64 (m, 2 H, CH2CH2Si), 3.76 (t, J = 6.7 Hz, 1 H, CH2NH2), 7.21-7.30 (m, 5 H, ArH). 13C NMR (100 MHz, CDCl3): δ = -1.6 (CH3), 13.5 (CH2Si), 34.1 (CH2CH2Si), 59.2 (CHNH2), 126.7 (2xArC), 127.1 (ArC), 128.6 (2xArC), 146.6 (CCHNH2). HRMS (HESI) m/z calcd for C12H12NSiH+ [M + H]+, 208.1522; Found 208.1522.

3-(dimethyl(phenyl)silyl)-1-phenylpropan-1-amine (8a)

Catalyst Loading (0.1 equiv, 0.05 mmol, 13.37 mg); Alkene 8 (1.8 equiv, 0.90 mmol, 123 mg); Reaction time: 24 h. Physical state: Yellow oil. Yield (78 mg, 58%). 1H NMR (400 MHz, CDCl3): δ = 0.24 (s, 6 H, Si(CH3)2Ph), 0.55-0.63 (m, 1 H, CH2Si), 0.76-0.84 (m, 1 H, CH3Si), 1.63-1.68 (m, 2 H, CH2CH2Si). 3.79 (t, J = 6.8 Hz, 1 H, CH2NH2), 7.24-7.34 (m, 8 H, ArH), 7.45-7.47 (m, 2 H, ArH). 13C NMR (100 MHz, CDCl3): δ = -3.0 (CH3), -2.9 (CH3), 12.6 (CH2Si), 34.0 (CH2CH2Si), 59.1 (CHNH2), 126.7 (2xArC), 127.1 (ArC), 128.0 (2xArC), 128.6 (2xArC), 129.1 (ArC), 133.8 (2xArC), 139.3 (CpSi), 146.6 (CCHNH2). HRMS (HESI) m/z calcd for C17H17NSiH+ [M + H]+, 270.1678; Found 270.1678.

Linear: 1-phenyl-4-(trimethylsilyl)butan-1-amine (9a)

Branched: 2-methyl-1-phenyl-3-(trimethylsilyl)propan-1-amine (9b and 9c)

Catalyst Loading (0.1 equiv, 0.05 mmol, 13.37 mg); Alkene 9 (1.8 equiv, 0.90 mmol, 103 mg); Reaction time: 240 h. Physical state: Yellow oil. 1H NMR RR (linear:branched 1:7). 1H NMR DR (9b:9c 3:1). Yield (75 mg, 68%). Clearly separated diagnostic peaks of the linear regioisomer 9a: 1H NMR (400 MHz, CDCl3): δ = -0.05 (s, 1.5 H, Si(CH3)3, integration relative to the benzylic peak at 3.72 ppm), 0.48-0.52 (m, 0.4 H, CH3Si, integration relative to the benzylic peak at 3.83 ppm), 1.65-1.71 (m, 0.4 H, CH2CH2 integration relative to the benzylic peak at 3.83 ppm), 3.89 (t, J = 5.7 Hz, 0.2 H, CH2NH2, integration relative to the benzylic peak at 3.72 ppm); Clearly separated peaks of the major branched diastereomer 9b: 1H NMR (400 MHz, CDCl3): δ = -0.03 (s, 9 H, Si(CH3)3), 0.90 (d, J = 6.6 Hz, 3 H, CH3CH), 3.72 (d, J = 6.2 Hz, 1 H, CHNH2); Clearly separated diagnostic peaks of the minor branched diastereomer 9c: 1H NMR (400 MHz, CDCl3): δ = -0.02 (s, 2 H, Si(CH3)3, integration relative to the benzylic peak at 3.72 ppm), 0.82 (d, J = 6.6 Hz, 1 H, CH3CH, integration relative to the benzylic peak at 3.72 ppm), 3.64 (d, J = 6.2 Hz, 0.3 H, CH2NH2, integration relative to the benzylic peak at 3.72 ppm). Overlapping peaks of 9a, 9b and 9c: 1H NMR (400 MHz, CDCl3): δ = 0.26-0.36 (m, overlap of 9a, 9b and 9c, CH3Si), 0.60-0.64 (dd, J = 14.2 Hz, J = 3.2 Hz, overlap of 9b and 9c, CH3Si), 1.83-1.92 (m, overlap of 9b and 9c, CH2CH3), 7.20-7.25 (m, overlap of 9a, 9b and 9c, ArH), 7.27-7.34 (m, overlap of 9a, 9b and 9c, ArH). Clearly separated diagnostic peaks of the linear regioisomer 9a: 13C NMR (100 MHz, CDCl3): δ = -1.4 (Si(CH3)3), 16.8, 21.2, 43.8 (CH2CH3), 56.2 (CHNH2), 147.1 (CCHNH2); Clearly separated diagnostic peaks of the major branched diastereomer 9b: 13C NMR (100 MHz, CDCl3): δ = -0.5 (Si(CH3)3), 18.0 (CH3CH), 21.6 (CH3Si), 37.0 (CH2CH), 63.3 (CHNH2), 145.5 (CCHNH2); Clearly separated
diagnostic peaks of the minor branched diastereomer 9c: $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = -0.5 (Si(CH$_3$)$_3$), 19.7 (CH$_2$CH), 20.0 (CH$_2$Si), 37.4 (CH$_2$CH), 63.5 (CHNH$_2$), 145.6 (CCHNH$_2$); **Aromatic peaks (all three products):** $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 126.5, 126.9, 127.0, 127.3, 127.3, 128.3, 128.6. HRMS (HESI) m/z calcd for C$_{13}$H$_{23}$NSiH$^+$ [M + H$^+$], 222.1678: Found 222.1681.

**General procedure for trimethylsilanamines**

\[
\begin{align*}
\text{R} & \quad \text{NH}_2 \quad \xrightarrow{1) \text{n-BuLi/ Et}_2\text{O}} \quad \text{R} \quad \text{NH} \quad \xrightarrow{2) (\text{CH}_3)_3\text{SiCl}} \quad \text{R} \\
\text{for } X = \text{CH}_2 \text{ conditions as shown} & \quad \text{For } X = \text{N, then } 1) \text{n-BuLi/ Et}_2\text{O at -78 }^\circ\text{C for 30 min; 2) (CH}_3)_3\text{SiCl at 0 }^\circ\text{C to rt, 48 h}
\end{align*}
\]

For X = CH$_2$ conditions as shown
For X = N, then 1) n-BuLi/ Et$_2$O at -78 °C for 30 min; 2) (CH$_3$)$_3$SiCl at 0 °C to rt, 48 h

The $N$-silylation of amines was adapted from the literature.$^3$ n-Buli 1.6 M in hexanes (1 equiv) was added to a solution of amine (1 equiv) in 50-80 mL (see below for each amine) of anhydrous Et$_2$O in a 250 mL Schlenk flask at 0 °C or -78 °C (see below for each amine) and left to stir at this temperature for 5-10 min. TMSCl (1 equiv) was added to the formed lithium-amide at 0 °C and then a white precipitate - corresponding to LiCl - started to form. The suspension was left to reach room temperature and stirred overnight or over two nights (see below for each amine). Then the amine was canula-filtered to another Schlenk flask. Ether was evaporated at 0 °C and the residue corresponding to the amine was canula-transferred to a 25 ml Schlenk flask containing CaH$_2$. After overnight stay over CaH$_2$, the amines were distilled and brought into the glove box where they were stored. Specific conditions for the $N$-silylation of the amines are presented below.

**N-**<sub>benzyl</sub>-1,1,1-<sub>trimethylsilanamine</sub><sup>3 (10)</sup>

Prepared according to the general procedure. Starting amine: 46.7 mmol, 5 g, 5 mL in approximately 50 mL of anhydrous Et$_2$O; n-BuLi 1.6 M in hexanes: 46.7 mmol, 29.2 mL; TMSCl: 46.7 mmol, 5.1 g, 6 mL; Lithiation temperature: 0 °C, $N$-silylation temperature 0 °C. Stirred overnight after the addition of TMSCl. Yield (5.6 g, 67%). Colorless liquid. NMR data match with the reported data.$^3$

**N-**(4-methoxybenzyl)-1,1,1-<sub>trimethylsilanamine</sub><sup>4 (11)</sup>

Prepared according to the general procedure. Starting amine: 29.1 mmol, 4 g, 3.8 mL in approximately 50 mL of anhydrous Et$_2$O; n-BuLi 1.6 M in hexanes: 29.1 mmol, 18.2 mL; TMSCl: 29.2 mmol, 3.2 g, 3.7 mL; Lithiation temperature: 0 °C, $N$-silylation temperature 0 °C. Stirred overnight after the addition of TMSCl. Yield (2.38 g, 39%). Colorless liquid. Colorless liquid. $^1$H NMR (400 MHz, C$_6$D$_6$): $\delta$ = 0.01 (s, 9 H, Si(CH$_3$)$_3$), 0.39 (broad s, 1 H, NH), 3.31 (s, 3 H, OCH$_3$), 3.70 (d, $J$ = 8.1 Hz, 2 H, CH$_2$), 6.76 (d, $J$ = 8.5 Hz, 2 H, ArH), 7.09 (d, $J$ = 8.8 Hz, 2 H, ArH). NMR data match with the reported data.$^4$

**N-**<sub>(4-fluorobenzyl)</sub>-1,1,1-<sub>trimethylsilanamine</sub><sup>5 (12)</sup>
Prepared according to the general procedure. Starting amine: 31.9 mmol, 4 g, 3.7 mL in approximately 50 mL of anhydrous Et₂O; n-BuLi 1.6 M in hexanes: 31.9 mmol, 19.9 mL; TMSCl: 31.9 mmol, 3.5 g, 4.1 mL; Lithiation temperature: 0 °C, N-silylation temperature 0 °C. Stirred overnight after the addition of TMSCl. Yield (2.45 g, 39%). Colorless liquid. ¹H NMR (400 MHz, C₆D₆): δ = 0.03 (s, 9 H, Si(CH₃)₃), 0.32 (broad s, 1 H, NH), 3.62 (d, J = 8.4 Hz, 2 H, CH₂), 6.86 (t, 3JHF = 8.6 Hz, 2 H, ArH₃), 7.09 (dd, 3JHF = 8.5 Hz, 4JHF = 5.6 Hz, 2 H, ArH₂). ¹³C NMR (100 MHz, C₆D₆): δ = 0.4 (q, J = 11.7 Hz, 3xCH₃), 45.7 (CH₃NHSi), 115.5 (d, JCF = 21.2 Hz, 2xArC₃), 129.0 (d, 3JCF = 8.1 Hz, 2xArC₂), 140.7 (d, 4JCF = 3.1 Hz, CCH₂NHSi), 162.5 (d, JCF = 243.2 Hz, CF). ¹⁹F NMR (376 MHz, C₆D₆): m/z: 213.

N-(4-chlorobenzyl)-1,1,1-trimethylsilanamine (13)

Prepared according to the general procedure. Starting amine: 28.2 mmol, 4 g, 3.4 mL in approximately 50 mL of anhydrous Et₂O; n-BuLi 1.6 M in hexanes: 28.2 mmol, 17.6 mL; TMSCl: 28.2 mmol, 3.1 g, 3.6 mL; Lithiation temperature: 0 °C, N-silylation temperature 0 °C. Stirred overnight after the addition of TMSCl. Yield (1.85 g, 31%). Colorless liquid. ¹H NMR (400 MHz, C₆D₆): δ = 0.01 (s, 9 H, Si(CH₃)₃), 0.30 (broad s, 1 H, NH), 3.58 (d, J = 8.1 Hz, 2 H, CH₂), 6.94 (d, J = 8.4 Hz, 2 H, ArH), 7.15 (d, J = 8.4 Hz, 2 H, ArH). ¹³C NMR (100 MHz, C₆D₆): δ = 0.5 (3xCH₃), 45.7(CH₃NHSi), 128.9 (ArC), 132.6 (CCH₂NHSi), 143.5 (ArC₆). MS (EI) m/z: 213.

N-(3,5-difluorobenzyl)-1,1,1-trimethylsilanamine (14)

Prepared according to the general procedure. Starting amine: 32.8 mmol, 4.7 g, 3.9 mL in approximately 50 mL of anhydrous Et₂O; n-BuLi 1.6 M in hexanes: 32.8 mmol, 20.5 mL; TMSCl: 32.8 mmol, 3.6 g, 4.2 mL; Lithiation temperature: 0 °C, N-silylation temperature 0 °C. Stirred overnight after the addition of TMSCl. Yield (4.9 g, 70%). Colorless liquid. ¹H NMR (400 MHz, C₆D₆): δ = -0.04 (s, 9 H, Si(CH₃)₃), 0.20 (broad s, 1 H, NH), 3.45 (d, J = 8.2 Hz, 2 H, CH₂), 6.44-6.50 (d, 1 H, ArH₄), 6.67 (d, J = 6.5 Hz, 2 H, ArH₂). ¹³C NMR (100 MHz, C₆D₆): δ = 0.1 (q, JCSi = 12.6 Hz, 3xCH₃), 45.6 (CH₃NHSi), 102.1 (t, JCF = 25.6 Hz, ArC), 109.7-110.0 (dd, JCF = 18.6 Hz, JCF = 6.6 Hz, 2xArC), 149.9 (t, JCF = 7.9 Hz, ArC), 162.5-165.2 (dd, JCF = 247.1 Hz, JCF = 12.4 Hz, 2xArC). ¹⁹F NMR (376 MHz, C₆D₆): δ = -110.25. MS (EI) m/z: 215.

1,1,1-trimethyl-N-(pyridin-3-ylmethyl)silanamine (15)

Prepared according to the general procedure. Starting amine: 32.3 mmol, 3.5 g, 3.3 mL in approximately 80 mL of anhydrous Et₂O; n-BuLi 1.6 M in hexanes: 32.3 mmol, 20.2 mL; TMSCl: 32.2 mmol, 3.5 g, 4.1 mL; Lithiation temperature: -78 °C, N-silylation temperature 0 °C. Stirred over two nights after the addition of TMSCl. Yield (1.79 g, 34%). Colorless liquid. ¹H NMR (400 MHz, C₆D₆): δ = -0.01 (s, 9 H, Si(CH₃)₃), 0.32 (broad s, 1 H, NH), 3.55 (d, J = 8.2 Hz, 2 H, CH₂), 6.78-6.81 (dd, J = 7.7 Hz, J = 4.6 Hz, 1 H, ArH₄), 7.22-7.26 (d, 1 H, ArH₃), 8.50 (d, J = 4.5 Hz, ArH₂), 8.62 (d, J = 1.3 Hz, ArH₃). ¹³C NMR (100 MHz, C₆D₆): δ = 0.4 (3xCH₃), 43.9 (CH₃NHSi), 123.5 (ArC₆), 134.5 (ArC₆), 139.7 (CCH₂NHSi), 148.8 (ArC₂), 149.9 (ArC₆). MS (EI) m/z: 180.
1.4.2 General procedure for the hydroaminoalkylation reaction – amine scope

To a solution of Zr(NMe₂)₄ (0.1 or 0.2 equiv, 0.05 or 0.1 mmol, 13.37 or 26.74 mg) in 200-300 µL C₆D₆, the amine 10-15 (1 equiv, 0.50 mmol) was added followed by the addition of vinyltrimethylsilane (1.8 equiv, 0.90 mmol, 90.20 mg). The solution was then transferred quantitatively into a J-Young tube via an additional 200-300 µL C₆D₆ and placed in an oil bath at 145 °C for 24 h. Upon the reaction completion, the J-Young seal was broken and DCM and MeOH were added to the existing solution. The quenched solution was then passed through a pipet with a Celite™ plug and 2-3 droplets of NaOH 3M were added to the filtrate. The solvents were evaporated and ether was added to the residue. The amine was extracted in the form of its hydrochloric salt (4x10 mL) with HCl 1M and the combined aqueous layers were basified with NaOH 3M. The amine was back-extracted with ether (3x20 mL). The ethereal layers were dried over anhydrous Na₂SO₄ and evaporated to afford the product as a single regioisomer.

1-(4-methoxyphenyl)-3-(trimethylsilyl)propan-1-amine (16)

Starting amine employed: 11 (1 equiv, 0.50 mmol, 105 mg); Catalyst Loading (0.1 equiv, 0.05 mmol, 13.37 mg); Reaction time: 24 h. Physical state: Yellow oil. Yield (69%). ¹H NMR (400 MHz, CDCl₃): δ = -0.05 (s, 9 H, Si(CH₃)₃), 0.27-0.35 (m, 1 H, CH₂Si), 0.48-0.56 (m, 1 H, CH₂Si), 1.55-1.66 (m, 2 H, CH₂CH₂Si), 3.75 (t, J = 6.6 Hz, 1 H, CHNH₂), 3.80 (s, 3 H, OCH₃), 6.87 (d, J = 8.5 Hz, 2 H, ArH), 7.22 (d, J = 8.5 Hz, 2 H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ = -1.6 (q, J_CSi = 12.2 Hz, CH₃), 13.6 (CH₂Si), 34.2 (CH₂CH₂Si), 55.4 (OCH₃), 113.9 (ArC), 127.6 (ArC), 138.8 (ArC), 158.6 (COCH₃). HRMS (HESI) m/z calcd for C₁₃H₁₃NOSiH⁺ [M + H⁺], 238.1627; Found 238.1620.

1-(4-fluorophenyl)-3-(trimethylsilyl)propan-1-amine (17)

Starting amine employed: 12 (1 equiv, 0.50 mmol, 99 mg); Catalyst Loading (0.1 equiv, 0.05 mmol, 13.37 mg); Reaction time: 24 h. Physical state: Yellow oil. Yield (55%). ¹H NMR (400 MHz, CDCl₃): δ = -0.06 (s, 9 H, Si(CH₃)₃), 0.24-0.32 (m, 1 H, CH₂Si), 0.47-0.55 (m, 1 H, CH₂Si), 1.55-1.60 (m, 2 H, CH₂CH₂Si), 3.78 (t, J = 6.6 Hz, 1 H, CHNH₂), 7.00 (t, J = 8.7 Hz, 2 H, ArH₂, 5), 7.25 (t, J = 8.1 Hz, 2 H, ArH₂), 13C NMR (100 MHz, CDCl₃): δ = -1.6 (q, J_CSi = 12.1 Hz, CH₃), 13.5 (CH₂Si), 34.3 (CH₂CH₂Si), 58.5 (CHNH₂), 115.3 (d, J_CF = 21.6 Hz, 2xFerC₃), 128.1 (d, J_CF = 7.4 Hz, 2xFerC₂), 142.3 (d, J_CF = 3.3 Hz, CCHNH₂), 161.94 (d, J_CF = 245.5 Hz, ArC). ¹⁹F NMR (376 MHz, CDCl₃): -116.12. HRMS (HESI) m/z calcd for C₁₂H₂₀FNSiH⁺ [M + H⁺], 226.1427; Found 226.1424.
1-(4-chlorophenyl)-3-(trimethylsilyl)propan-1-amine (18)

Starting amine employed: 13 (1 equiv, 0.50 mmol, 107 mg); Catalyst Loading (0.1 equiv, 0.005 mmol, 13.37 mg); Reaction time: 24 h. Physical state: Yellow oil. Yield (41%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = -0.05\) (s, 9 H, Si(CH\(_3\))\(_3\)), 0.25-0.33 (m, 1 H, CH\(_2\)Si), 0.47-0.55 (m, 1 H, CH\(_2\)Si), 1.56-1.62 (m, 2 H, CH\(_2\)CH\(_2\)Si), 3.79 (t, J = 6.7 Hz, 1 H, CHNH\(_2\)), 7.24 (d, J = 8.6 Hz, 2 H, ArH), 7.30 (d, J = 8.6 Hz, 2 H, ArH). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = -1.6\) (q, J\(_{CF} = 12.1\) Hz, CH\(_3\)), 13.4 (CH\(_2\)Si), 34.2 (CH\(_2\)CH\(_2\)Si), 58.6 (CHNH\(_2\)), 128.1 (2xArC), 128.7 (2xArC), 132.6 (ArC\(_6\)), 145.0 (CCHNH\(_2\)). HRMS (HESI) \(m/z\) calcd for C\(_{13}\)H\(_{20}\)FNSiH\(^+\) [M + H\(^+\)], 242.1132; Found 242.1122.

1-(3,5-difluorophenyl)-3-(trimethylsilyl)propan-1-amine (19)

Starting amine employed: 14 (1 equiv, 0.50 mmol, 108 mg); Catalyst Loading (0.1 equiv, 0.005 mmol, 13.37 mg); Reaction time: 24 h. Physical state: Yellow oil. Yield (33%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = -0.04\) (s, 9 H, Si(CH\(_3\))\(_3\)), 0.22-0.36 (m, 1 H, CH\(_2\)Si), 0.48-0.56 (m, 1 H, CH\(_2\)Si), 1.55-1.61 (m, 2 H, CH\(_2\)CH\(_2\)Si), 3.80 (t, J = 6.7 Hz, 1 H, CHNH\(_2\)), 6.64-6.70 (tt, J = 8.9 Hz, J = 2.4 Hz, 1 H, ArH\(_6\)), 6.82-6.87 (dd, J = 7.6 Hz, J = 2.2 Hz, 2 H, ArH\(_6\)). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = -1.6\) (q, J\(_{CF} = 12.5\) Hz, CH\(_3\)), 13.2 (CH\(_2\)Si), 34.1 (CH\(_2\)CH\(_2\)Si), 58.6 (CHNH\(_2\)), 102.3 (t, J\(_{CF} = 25.5\) Hz, ArC\(_6\)), 109.3-109.6 (dd, J\(_{CF} = 18.5\) Hz, J\(_{CF} = 6.6\) Hz, 2xArC\(_2\)\(_6\)), 150.9 (t, J\(_{CF} = 8.2\) Hz, CCHNH\(_2\)), 163.2 (dd, J\(_{CF} = 247.7\) Hz, J\(_{CF} = 11.9\) Hz, 2xArC\(_2\)\(_6\)). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): -110.01. HRMS (HESI) \(m/z\) calcd for C\(_{13}\)H\(_{19}\)F\(_2\)NSiH\(^+\) [M + H\(^+\)], 244.1333: Found 234.1340.

1-(pyridin-3-yl)-3-(trimethylsilyl)propan-1-amine (20)

Starting amine employed: 15 (1 equiv, 0.50 mmol, 90 mg); Catalyst Loading (0.2 equiv, 0.1 mmol, 26.74 mg); Reaction time: 24 h. Physical state: Yellow oil. Yield (63%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = -0.05\) (s, 9 H, Si(CH\(_3\))\(_3\)), 0.26-0.34 (m, 1 H, CH\(_2\)Si), 0.49-0.57 (m, 1 H, CH\(_2\)Si), 1.56-1.66 (m, 2 H, CH\(_2\)CH\(_2\)Si), 3.85 (t, J = 6.7 Hz, 1 H, CHNH\(_2\)), 7.24-7.27 (dd, J = 7.2 Hz, J = 5.1 Hz, 1 H, ArH\(_3\)), 7.64-7.67 (dt, J = 7.8 Hz, J = 2.1 Hz, 1 H, ArH\(_4\)), 8.48-8.50 (dd, J = 4.7 Hz, J = 1.7 Hz, 1 H, ArH\(_6\)), 8.54 (d, J = 2.3 Hz, 1 H, ArH\(_6\)). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = -1.6\) (q, J\(_{CF} = 12.0\) Hz, CH\(_3\)), 13.3 (CH\(_2\)Si), 34.2 (CH\(_2\)CH\(_2\)Si), 56.8 (CHNH\(_2\)), 123.7 (ArC\(_6\)), 134.1 (ArC\(_6\)), 141.6 (CCHNH\(_2\)), 148.7 (ArC\(_6\)), 149.0 (ArC\(_2\)). HRMS (HESI) \(m/z\) calcd for C\(_{15}\)H\(_{19}\)N\(_2\)SiH\(^+\) [M + H\(^+\)], 209.1474: Found 209.1481.

1.4.3 Procedure for the trifluoroethylation reaction

1-phenyl-N-(2,2,2-trifluoroethyl)-3-(trimethylsilyl)propan-1-amine (21)

Two 20 mL vials equipped with magnetic stir-bars were capped with septum-fitted vial caps connected by a polyethylene tube. Vial A was charged with SDI (1.00 g, 5.05 mmol) and anhydrous KF (775 mg, 13.3 mmol), then the system was evacuated and filled with N\(_2\) three times. To vial B was added flame-dried silica (400 mg), DIPEA (1.30 mL, 7.47 mmol) and trifluoroethanol (0.125 mL, 1.75 mmol) in dry DMF (5.00 mL). The polyethylene tube in vial B was immersed into the solution and then to vial A was added TFA (2.00 mL). Vigorous bubbling of SO\(_2\)F\(_2\) and fuming were observed in vial B for a few
minutes and when the bubbling subsided, vial B was vented via a needle for 1-2 minutes (this triggered more bubbling of SO$_2$F$_2$ through the solution). The tube and needle were then removed and the mixture in vial B was allowed to stir for 20 min. The mixture was then degassed with nitrogen for 20 seconds. To vial B was then added the amine 7a (101 mg, 0.487 mmol) in a dry DMF (0.40 mL). The reaction mixture (vial B) was heated to 40˚C in an oil-bath and allowed to stir for 2 hours. Reaction mixture was allowed to cool and diluted 10-fold with water. The compound was extracted using pentane (4x10 mL) and the combined organic layers were dried over anhydrous Na$_2$SO$_4$. The solution was decanted and carefully concentrated in vacuo. The residual oil was loaded onto a basified column (5% Et$_3$N in ether then excessive washes with ether followed by pentane) and eluted with 0-8% ether in pentane. The solvent was carefully removed in vacuo to afford the title compound (79 mg, 0.27 mmol) as clear colorless oil. Yield (56%).

$^1$H NMR (300 MHz, CDCl$_3$): δ = -0.06 (s, 9 H, Si(CH$_3$)$_3$), 0.24-0.34 (m, 1 H, CH$_2$Si), 0.45-0.56 (m, 1 H, CH$_2$Si), 1.57-1.72 (m, 3 H, CH$_2$CH$_2$Si), 2.98 (q, J = 9.5 Hz, 2 H, CH$_2$CF$_3$), 3.61 (t, J = 6.8 Hz, 1 H, CHNH$_2$), 7.24-7.28 (m, 3 H, ArH), 7.32-7.37 (m, 2 H, ArH). $^{13}$C NMR (75 MHz, CDCl$_3$): δ = -1.6 (CH$_3$), 13.3 (CH$_2$Si), 33.0 (CH$_2$CH$_2$Si), 48.4 (q, J = 31.0 Hz, CH$_2$CF$_3$), 65.4 (CHNH), 125.9 (q, J$_{CF}$ = 279.3 Hz, CF$_3$), 127.6 (3xArC), 128.7 (2xArC), 143.0 (CHNH$_2$). $^{19}$F NMR (282 MHz, CDCl$_3$): δ = -71.85 (t, J = 9.6 Hz). HRMS (HESI) m/z calcld for C$_{14}$H$_{22}$F$_3$NSiH$^+$ [M + H$^+$], 290.1552: Found 290.1553.

1.4.4 General procedure for amine trifluoroethylation using pre-formed trifluoroethyl fluorosulfate for NMR yields for amines 22-24

Two 4 mL vials equipped with magnetic stir-bars were capped with septum-fitted vial caps connected by a polyethylene tube. Vial A was charged with SDI (0.60 mmol) and anhydrous KF (1.6 mmol), then the system was evacuated and filled with N$_2$ three times. To vial B was added flame-dried silica (50 mg), DIPEA (0.91 mmol) and trifluoroethanol (0.21 mmol) in dry DMF (0.60 mL). The polyethylene tube in vial B was immersed into the solution and then to vial A was added TFA (0.50 mL). Vigorous bubbling of SO$_2$F$_2$ and fuming were observed in vial B for a few minutes and when the bubbling subsided, vial B was vented via a needle for 1-2 minutes (this triggered more bubbling of SO$_2$F$_2$ through the solution). The tube and needle were then removed and the mixture in vial B was allowed to stir for 20 min. The mixture was then degassed with nitrogen for 20 seconds. To vial B was then added the amine 17 or 19 or 20 (ca. 0.060 mmol) in a minimal volume of dry DMF. The reaction mixture was allowed to stir at 40˚C for 2 hours and then analyzed by quantitative $^{19}$F NMR spectroscopy using PhCF$_3$ as an internal standard.
1.4.5 $^1$H, $^{13}$C and $^{19}$F NMR Spectra

Linear: 1,5-diphenylpentan-1-amine (1a)
Branched: 2-methyl-1,4-diphenylbutan-1-amine (1b and 1c)

$^1$H NMR CDCl$_3$ 400MHz

$^{13}$C NMR CDCl$_3$ 100MHz
Linear: 1-phenylnonan-1-amine (2a)

Branched: 2-methyl-1-phenyloctan-1-amine (2b and 2c)

$^1$H NMR CDCl$_3$ 400MHz

$^{13}$C NMR CDCl$_3$ 100MHz
Linear: 1,4-diphenylbutan-1-amine (3a)

Branched: 2-methyl-1,3-diphenylpropan-1-amine (3b and 3c)

$^1$H NMR CDCl$_3$ 400MHz

$^{13}$C NMR CDCl$_3$ 100MHz
Linear: 3-cyclohexyl-1-phenylpropan-1-amine (4a)

Branched: 2-cyclohexyl-1-phenylpropan-1-amine (4b and 4c)

$^1$H NMR CDCl$_3$ 400MHz

$^{13}$C NMR CDCl$_3$ 100MHz
Linear: 1-phenyl-3-(o-tolyl)propan-1-amine (5a)

Branched: 1-phenyl-2-(o-tolyl)propan-1-amine (5b and 5c)

$^1$H NMR CD$_3$OD 400MHz

$^{13}$C NMR CD$_3$OD 100MHz
1,4-dimethyl-1-phenylpentan-1-amine (6a)

$^1$H NMR CD$_3$OD 400MHz

$^{13}$C NMR CD$_3$OD 100MHz
1-phenyl-3-(trimethylsilyl)propan-1-amine (7a)

$\text{H} NMR \text{CDCl}_3 400MHz$

$\text{C} NMR \text{CDCl}_3 100MHz$
3-(dimethyl(phenyl)silyl)-1-phenylpropan-1-amine (8a)

$^{1}$H NMR CDCl$_3$ 400MHz

$^{13}$C NMR CDCl$_3$ 100MHz
Linear: 1-phenyl-4-(trimethylsilyl)butan-1-amine (9a)

Branched: 2-methyl-1-phenyl-3-(trimethylsilyl)propan-1-amine (9b and 9c)

$^1$H NMR CDCl$_3$ 400MHz

$^{13}$C NMR CDCl$_3$ 100MHz
\( N\text{-}(4\text{-fluorobenzyl})\text{-}1,1,1\text{-trimethylsilanamine (12)} \)

\( ^1H\text{ NMR } C_6D_6\ 400MHz \)

\( ^{13}C\text{ NMR } C_6D_6\ 100MHz \)
$^{19}$F NMR $C_6D_6$ 376MHz
$N$-(4-chlorobenzyl)-1,1,1-trimethylsilanamine (13)

$^1$H NMR $C_6D_6$ 400MHz

$^{13}$C NMR $C_6D_6$ 100MHz
$N$-(3,5-difluorobenzyl)-1,1,1-trimethylsilanamine (14)

$^1$H NMR $\mathrm{C}_6\mathrm{D}_6$ 400MHz

$^{13}$C NMR $\mathrm{C}_6\mathrm{D}_6$ 100MHz
$^{19}\text{F NMR C}_6\text{D}_6 376\text{MHz}$
1,1,1-trimethyl-N-(pyridin-3-ylmethyl)silanamine (15)

$^1$H NMR C$_6$D$_6$ 400MHz

$^{13}$C NMR C$_6$D$_6$ 100MHz
1-(4-methoxyphenyl)-3-(trimethylsilyl)propan-1-amine (16)

$^1$H NMR CDCl$_3$ 400MHz

$^{13}$C NMR CDCl$_3$ 100MHz
$^{19}$F NMR CDCl$_3$ 376MHz
1-(4-chlorophenyl)-3-(trimethylsilyl)propan-1-amine (18)

$^1$H NMR CDCl$_3$ 400MHz

$^{13}$C NMR CDCl$_3$ 100MHz
1-(3,5-difluorophenyl)-3-(trimethylsilyl)propan-1-amine (19)

$^1$H NMR CDCl$_3$ 400MHz

$^{13}$C NMR CDCl$_3$ 100MHz
$^{19}$F NMR CDCl$_3$ 376MHz
1-((pyridin-3-yl)-3-((trimethylsilyl)propan-1-amine (20)

$\text{H NMR CDCl}_3$ 400MHz

$\text{C NMR CDCl}_3$ 100MHz
1-phenyl-N-(2,2,2-trifluoroethyl)-3-(trimethylsilyl)propan-1-amine (21)

$\text{H NMR CDCl}_3$ 300MHz

$\text{C NMR CDCl}_3$ 75MHz
$^{19}$F NMR CDCl$_3$ 282MHz
1.4.6 Representative GC-MS spectra for mixtures of products 4a-4c and 9a-9c
9a, 9b, 9c

Chemical structures:

- **9a**: H$_2$N$\text{-}\text{Si(CH}_3\text{)CH}_2\text{-H}
- **9b**: H$_2$N$\text{-}\text{Si(CH}_3\text{)CH}_2\text{-Ph}
- **9c**: H$_2$N$\text{-}\text{Si(CH}_3\text{)CH}_2\text{-Ph}

Graph shows counts (%) vs. acquisition time (min).
1.5 References


