Silylium Ion-Promoted Reduction of Imines with Hydrosilanes

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1 General Information
All reactions were performed in flame-dried glassware using an MBraun glove box (O₂ < 0.5 ppm, H₂O < 0.5 ppm) or conventional Schlenk techniques under a static pressure of argon or nitrogen. Liquids and solutions were transferred with syringes. Tetrahydrofuran (THF) was dried over potassium. 1,2-F₂C₆H₄ (purchased from ABCR) and 1,2-Cl₂C₆H₄ (purchased from Sigma-Aldrich) were dried over CaH₂ prior to use and stored over molecular sieves in a glove box. Technical grade solvents for extraction or chromatography (dichloromethane, cyclohexane, tert-butyl methyl ether and ethyl acetate) were distilled prior to use. CDCl₃ and C₆D₆ (purchased from Eurisotop) were used without further purification and stored over molecular sieves. Ferrocene was purchased from Alfa Aesar and used without further purifications. Lithium aluminium deuteride was purchased from Sigma-Aldrich. Triethylsilane was purchased from Sigma-Aldrich and dried over CaH₂ prior to use. [Ph₃C]+[B(C₆F₅)₄]⁻ (3),[S1] tert-butylferrocentylmethylsilane (2)[S2] and tert-butylchloromethylsilane[S2] were prepared according to reported procedures. All imines were prepared according to reported procedures (4a–4f,[S3] 4f,[S4] 6f,[S3] 9f,[S5] 10f–13f,[S6] 14f,[S7] 15f,[S8] 16f[S7]) and dried under vacuum prior to use. Analytical thin layer chromatography (TLC) was performed on silica gel 60 F254 glass plates by Merck. Flash column chromatography was performed on silica gel 60 (40–63 μm, 230–400 mesh, ASTM) by Merck using the indicated solvents. ¹H, ¹³C and ²⁹Si NMR spectra were recorded in CDCl₃ or C₆D₆ on Bruker AV300 and Bruker AV400 instruments (Westfälische Wilhelms-Universität Münster) and Bruker AV400 and AV500 instruments (Technische Universität Berlin). Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard (CHCl₃: δ = 7.26 ppm for ¹H NMR and CDCl₃: δ = 77.2 ppm for ¹³C NMR; C₆D₆: δ = 7.16 ppm for ¹H NMR and C₆D₆: δ = 128.1 ppm for ¹³C NMR). Data are reported as follows: chemical shift, multiplicity (br s = broad singlet, s = singlet, d = doublet, t = triplet, m = multiplet, mc = centrosymmetric multiplet), coupling constants (Hz) and integration. Gas liquid chromatography (GLC) was performed either on a Shimadzu GC-17A gas chromatograph or on an Agilent Technologies 7820A gas chromatograph both equipped with a FS-SE-54 capillary column (30 m × 0.32 mm, 0.25 μm film thickness) by CS-Chromatographie Service using the following program: N₂ carrier gas, injection temperature 240°C, detector temperature 300°C, flow rate: 1.74 mL/min; temperature program: start temperature 40°C, heating rate 10°C/min, end temperature 280°C for 10 min. Infrared (IR) spectra were recorded on a Varian 3100 FT-IR spectrometer (Westfälische Wilhelms-Universität Münster) and an Agilent Technologies Cary 630 FT-IR spectrometer (Technische Universität Berlin), both
equipped with an ATR unit and are reported in wavenumbers (cm⁻¹). Melting points (mp) were determined with a Stuart Scientific SMP20 melting point apparatus and are not corrected. Mass spectrometry (MS) was obtained from the Analytical Facilities at the Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster and at the Institut für Chemie, Technische Universität Berlin.
2 General Procedure for the Silylium Ion-Promoted Reduction of Imines

In a glove box, a flame-dried 10 mL Schlenk tube equipped with a magnetic stir bar is charged with [Ph₃C][B(C₆F₅)₄]– (3, 9.20 mg, 9.97 μmol, 5.00 mol%). 1,2-F₂C₆H₄ or 1,2-Cl₂C₆H₄ (0.0010–0.030 M) is added inside the glove box or after transferring the Schlenk tube to a fume cupboard, connected to an argon/nitrogen-vacuum manifold. After silane addition (2 or 8, 0.033–0.052 mmol, 0.18–0.26 equiv), the resulting solution is stirred for 10 min. A solution of the imine (0.167–0.200 mmol, 1.00 equiv) in 1,2-F₂C₆H₄ or 1,2-Cl₂C₆H₄ (0.050–0.40M) and a solution of silane 2 or 8 (0.167–0.200 mmol, 1.00 equiv) in 1,2-F₂C₆H₄ or 1,2-Cl₂C₆H₄ (0.29–0.40M) are added subsequently and the reaction mixture is stirred at room temperature for the indicated time (cf. Tables 1 and 2, and Scheme 2). After addition of water (5 mL), the phases are separated, the aqueous phase is extracted with tert-butyl methyl ether or dichloromethane (3 × 5 mL) and the combined organic phases are dried over Na₂SO₄. After evaporation of solvents under reduced pressure, the resulting residue is purified by flash column chromatography on silica gel using cyclohexane/tert-butyl methyl ether or cyclohexane/ethyl acetate/triethylamine mixtures affording analytically pure amines.
3 Experimental Details for the Silylium Ion-Promoted Reduction of Imines 4d–4f, 9f–16f, and 6f

3.1 N-Benzyl-1,1-diphenylmethaneamine (5d)

Prepared from [Ph₃C][B(C₆F₅)₄]⁻ (3, 9.20 mg, 9.97 µmol, 5.00 mol%), tert-butyl-ferrocenylmethylsilane (2, 69.2 mg, 0.242 mmol, 1.21 equiv) and imine 4d (54.2 mg, 0.200 mmol, 1.00 equiv) in 1,2-F₂C₆H₄ (1.7 mL) according to the general procedure; purification by flash column chromatography on silica gel using cyclohexane:tert-butyl methyl ether (20:1) as eluent afforded the analytically pure product 5d (21.6 mg, 40%) as a yellow oil. 

Rᵣ = 0.56 (cyclohexane:ethylacetate = 6:1). GLC (SE-54): tᵣ = 21.4 min. IR (ATR): ν = 3061 (w), 3025 (w), 2927 (w), 1600 (w), 1452 (s), 1340 (w), 1302 (w), 1280 (w), 1155 (w), 1071 (m), 1028 (m), 1002 (w), 972 (w), 912 (w), 840 (w), 762 (m), 743 (s), 737 (m), 694 (s) cm⁻¹. HRMS (ESI) calculated for C₂₀H₁₉N [(M+H)⁺]: 274.1590; Found: 274.1591. \(^1\)H NMR (400 MHz, CDCl₃): δ = 1.73 (br s, 1H), 3.67 (s, 2H), 4.79 (s, 1H), 7.11–7.18 (m, 3H), 7.19–7.25 (m, 8H), 7.35–7.37 (m, 4H) ppm. \(^1\)C NMR (100 MHz, CDCl₃): δ = 52.0, 66.6, 127.1, 127.2, 127.5, 128.3, 128.5, 128.6, 140.6, 144.1 ppm.
3.2  \textit{N-Benzylaniline (5e)}

\[
\begin{align*}
\text{HN} & \quad \text{C}_9\text{H}_7\text{N} \\
\text{5e} & \quad M = 183.25 \text{ g/mol}
\end{align*}
\]

Prepared from [\text{Ph}_3\text{C}]^+\text{[B(C_6\text{F}_5)_4]}^- (3, 9.20 mg, 9.97 \mu\text{mol}, 5.00 \text{ mol%}), \textit{tert}-\text{butyl-ferrocenylmethylsilane (2, 69.2 mg, 0.242 mmol, 1.21 equiv)} and imine 4e (36.2 mg, 0.200 mmol, 1.00 equiv) in 1,2-\text{F}_2\text{C}_6\text{H}_4 (2.0 mL) according to the general procedure; purification by flash column chromatography on silica gel using cyclohexane: \textit{tert}-\text{butyl methyl ether (20:1)} as eluent afforded the analytically pure product 5e (30.9 mg, 84\%) as a yellow oil.

\( R_f = 0.60 \) (cyclohexane: ethylacetate = 6:1). \textsc{GlC} (SE-54): \( t_R = 15.8 \text{ min} \). \textsc{Ir} (ATR): \( \tilde{\nu} = 3419 \) (m), 1601 (s), 1511 (s), 1492 (s), 1450 (m), 1441 (w), 1432 (w), 1329 (m), 1302 (w), 1280 (m), 1176 (m), 1151 (w), 1118 (w), 1105 (w), 1079 (w), 1027 (w), 985 (m), 854 (w), 799 (w), 744 (m), 736 (s), 696 (m), 688 (s) cm\textsuperscript{-1}. \textsc{Hrms} (ESI) calculated for C\textsubscript{13}H\textsubscript{13}N \((\text{M+H})^+\): 184.1121; Found: 184.1121. \textsc{Anal. Calcld} for C\textsubscript{13}H\textsubscript{13}N: C, 85.21; H, 7.15; N, 7.64; Found: C, 85.02; H, 7.19; N, 7.40. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \( \delta = 4.07 \) (br s, 1H), 4.35 (s, 2H), 6.66 (m, 2H), 6.74 (tt, \( ^3J = 7.4 \text{ Hz}, ^4J = 1.0 \text{ Hz}, 1H), 7.20 (m, 2H), 7.30 (m, 1H), 7.35–7.41 (m, 4H) ppm. \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \( \delta = 48.5, 113.0, 117.7, 127.4, 127.6, 128.8, 129.4, 139.5, 148.3 \text{ ppm.} \)
3.3 4-Methyl-N-(benzyl)phenylsulfonamide (5f)

A) Prepared from [Ph₃C][B(C₆F₅)₄]⁻ (3, 9.20 mg, 9.97 µmol, 5.00 mol%), tert-butylferrocenylmethylsilane (2, 69.2 mg, 0.242 mmol, 1.21 equiv) and imine 4f (51.9 mg, 0.200 mmol, 1.00 equiv) in 1,2-Cl₂C₆H₄ (2.0 mL) according to the general procedure; purification by flash column chromatography on silica gel using cyclohexane:ethyl acetate:triethylamine (24:4:1) as eluent afforded the analytically pure product 5f (47.0 mg, 90%) as a white solid.

B) Prepared from [Ph₃C][B(C₆F₅)₄]⁻ (3, 9.20 mg, 9.97 µmol, 5.00 mol%), triethylsilane (8, 28.0 mg, 0.241 mmol, 1.20 equiv) and imine 4f (51.9 mg, 0.200 mmol, 1.00 equiv) in 1,2-Cl₂C₆H₄ (2.0 mL) according to the general procedure; purification by flash column chromatography on silica gel using cyclohexane:ethyl acetate:triethylamine (24:4:1) as eluent afforded the analytically pure product 5f (50.0 mg, 96%) as a white solid.

m.p. = 115°C (cyclohexane/ethyl acetate). Rᵣ = 0.16 (cyclohexane:ethyl acetate = 6:1). GLC (SE-54): tᵣ = 23.7 min. IR (ATR): ν = 3268 (m), 2916 (w), 2848 (w), 1599 (w), 1496 (w), 1453 (m), 1422 (m), 1320 (s), 1310 (s), 1288 (m), 1177 (m), 1159 (s), 1094 (m), 1082 (m), 1058 (m), 1029 (m), 874 (m), 813 (w), 804 (m), 795 (w), 741 (s), 700 (s), 660 (s), 641 (w), 628 (w), 601 (s) cm⁻¹. HRMS (ESI) calculated for C₁₄H₁₅NO₂SNa [(M+Na)+]: 284.0716; Found: 284.0712. Anal. Calcd for C₁₄H₁₅NO₂S: C, 64.34; H, 5.79; N, 5.36; Found: C, 64.29; H, 5.80; N, 5.16. ¹H NMR (400 MHz, CDCl₃): δ = 2.44 (s, 3H), 4.11 (d, 3J = 6.0 Hz, 2H), 4.82 (br t, 3J = 5.8 Hz, 1H), 7.18–7.21 (m, 2H), 7.24–7.28 (m, 3H), 7.30 (m, 2H), 7.76 (m, 2H). ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 21.7, 47.4, 127.3, 128.0, 128.0, 128.8, 129.9, 136.4, 137.0, 143.6 ppm.
3.4 4-Methyl-N-([1-^2^H]-benzyl)phenylsulfonamide (d₁-5f)

Prepared from [Ph₃C]^⁺[B(C₆F₅)₄]⁻ (3, 9.20 mg, 9.97 µmol, 5.00 mol%), [1-^2^H]-tert-butylferrocenylmethylsilane (d₁-2, 67.4 mg, 0.235 mmol, 1.17 equiv) and imine 4f (51.9 mg, 0.200 mmol, 1.00 equiv) in 1,2-Cl₂C₆H₄ (2.0 mL) according to the general procedure; purification by flash column chromatography on silica gel using cyclohexane:ethyl acetate:triethylamine (24:4:1) as eluent afforded the analytically pure product d₁-5f (47.4 mg, 90%, >98% deuteration grade determined by HRMS) as a white solid.

m.p. = 115°C (cyclohexane/ethyl acetate). Rₚ = 0.16 (cyclohexane:ethyl acetate = 6:1). GLC (SE-54): tᵣ = 23.6 min. IR (ATR): \( \tilde{\nu} = 3264 \) (s), 3031 (w), 2922 (m), 2890 (m), 2854 (w), 1595 (w), 1492 (w), 1404 (s), 1320 (s), 1156 (s), 1084 (s), 1056 (s), 957 (w), 894 (w), 845 (w), 808 (s), 726 (s) cm⁻¹. HRMS (ESI) calculated for C₁₄H₁₄DNO₂SNa [(M+Na)+]: 285.0778; Found: 285.0771. ^1^H NMR (400 MHz, CDCl₃): \( \delta = 2.44 \) (s, 3H), 4.10 (d, \(^3^J = 6.1\) Hz, 1H), 4.97 (d, \(^3^J = 5.9\) Hz, 1H), 7.19–7.21 (m, 2H), 7.25–7.28 (m, 3H), 7.30 (m, 2H), 7.76 (m, 2H) ppm. ^1^C NMR (100 MHz, CDCl₃): \( \delta = 21.6, 47.1 \) (t, \(^2^J_{C,D} = 21\) Hz), 127.3, 127.9, 128.0, 128.7, 129.8, 136.4, 137.1, 143.6 ppm.
3.5 Methyl-N-(4-bromobenzyl)phenylsulfonamide (17f)

\[
\text{C}_{14}H_{14}BrNO}_2S \quad M = 340.24 \text{ g mol}^{-1}
\]

A) Prepared from \([\text{Ph}_3\text{C}^+][\text{B(C}_6\text{F}_5)_4^-] \ (3, \ 9.20 \text{ mg, } 9.97 \mu\text{mol, 5.00 mol%}), \text{ tert-butyl-ferrocenylmethylsilane (2, 68.2 mg, 0.238 mmol, 1.19 equiv)} \) and imine 9f \ (67.6 mg, 0.200 mmol, 1.00 equiv) in 1,2-Cl\textsubscript{2}C\textsubscript{6}H\textsubscript{4} (2.0 mL) according to the general procedure; purification by flash column chromatography on silica gel using cyclohexane:ethyl acetate:triethylamine (24:4:1) as eluent afforded the analytically pure product 17f \ (41.5 mg, 61\%) as a white solid.

B) Prepared from \([\text{Ph}_3\text{C}^+][\text{B(C}_6\text{F}_5)_4^-] \ (3, \ 9.20 \text{ mg, } 9.97 \text{ mmol, 5.00 mol%}), \text{ triethylsilane (8, 28.0 mg, 0.241 mmol, 1.21 equiv)} \) and imine 9f \ (67.6 mg, 0.200 mmol, 1.00 equiv) in 1,2-Cl\textsubscript{2}C\textsubscript{6}H\textsubscript{4} (4.0 mL) according to the general procedure; purification by flash column chromatography on silica gel using cyclohexane:ethyl acetate:triethylamine (24:4:1) as eluent afforded the analytically pure product 17f \ (62.4 mg, 92\%) as a white solid.

\textbf{m.p.} = 117°C (cyclohexane/ethyl acetate). \( R_f = 0.16 \) (cyclohexane:ethyl acetate = 6:1). \textbf{GLC} (SE-54): \( t_R = 27.0 \text{ min.} \) \textbf{IR} (ATR): \( \tilde{v} = 3272 \text{ (s), } 3049 \text{ (w), } 2860 \text{ (w), } 1641 \text{ (w), } 1598 \text{ (m), } 1486 \text{ (m), } 1450 \text{ (s), } 1366 \text{ (w), } 1317 \text{ (s), } 1307 \text{ (s), } 1256 \text{ (m), } 1200 \text{ (w), } 1158 \text{ (s), } 1092 \text{ (m), } 1064 \text{ (s), } 1012 \text{ (s), } 877 \text{ (s), } 802 \text{ (s), } 723 \text{ (m), } 660 \text{ (m) cm}^{-1}. \)

\textbf{HRMS} (ESI) calculated for C\textsubscript{14}H\textsubscript{14}BrNO\textsubscript{2}SNa [(M+Na\textsuperscript{+}): 361.9821; Found: 361.9811.

\textbf{\textsuperscript{1}H NMR} (400 MHz, CDCl\textsubscript{3}): \( \delta = 2.43 \text{ (s, } 3\text{H), } 4.05 \text{ (d, } ^3J = 6.3 \text{ Hz, } 2\text{H), } 5.22 \text{ (t, } ^3J_1 = 6.2 \text{ Hz, } 1\text{H), } 7.06 \text{ (m, } 2\text{H), } 7.27 \text{ (m, } 2\text{H), } 7.35 \text{ (m, } 2\text{H), } 7.70 \text{ (m, } 2\text{H) ppm.} \)

\textbf{\textsuperscript{13}C NMR} (125 MHz, CDCl\textsubscript{3}): \( \delta = 21.7, \ 46.7, \ 121.8, \ 127.2, \ 129.7, \ 129.9, \ 131.8, \ 135.6, \ 136.9, \ 143.7 \text{ ppm.} \)
3.6 4-Methyl-N-(4-methylbenzyl)phenylsulfonamide (18f)

A) Prepared from [Ph₃C][B(C₆F₅)₄]⁻ (3, 9.20 mg, 9.97 µmol, 5.00 mol%), tert-butylferrocenylmethylsilane (2, 70.2 mg, 0.246 mmol, 1.23 equiv) and imine 10f (54.7 mg, 0.200 mmol, 1.00 equiv) in 1,2-Cl₂C₆H₄ (2.0 mL) according to the general procedure; purification by flash column chromatography on silica gel using cyclohexane:ethyl acetate:triethylamine (24:4:1) as eluent afforded the analytically pure product 18f (46.8 mg, 85%) as a white solid.

B) Prepared from [Ph₃C][B(C₆F₅)₄]⁻ (3, 9.20 mg, 9.97 µmol, 5.00 mol%), triethylsilane (8, 28.0 mg, 0.241 mmol, 1.21 equiv) and imine 10f (54.7 mg, 0.200 mmol, 1.00 equiv) in 1,2-Cl₂C₆H₄ (3.0 mL) according to the general procedure; purification by flash column chromatography on silica gel using cyclohexane:ethyl acetate:triethylamine (24:4:1) as eluent afforded the analytically pure product 18f (43.1 mg, 78%) as a white solid.

**m.p.** = 95°C (cyclohexane/ethyl acetate). R_f = 0.16 (cyclohexane/ethyl acetate = 6:1). **GLC** (SE-54): t_R = 24.7 min. **IR** (ATR): ν ~ 3270 (s), 3031 (m), 2919 (m), 2854 (m), 1597 (w), 1515 (w), 1424 (m), 1324 (s), 1309 (s), 1290 (m), 1200 (w), 1152 (s), 1092 (s), 1064 (s), 843 (s), 815 (s), 742 (m), 708 (m) cm⁻¹. **HRMS** (ESI) calculated for C₁₅H₁₇NO₂SNa [(M+Na)+]: 298.0872; Found: 298.0881. **¹H NMR** (400 MHz, CDCl₃): δ = 2.30 (s, 3H), 2.43 (s, 3H), 4.05 (d, 3_J = 6.1 Hz, 2H), 4.91 (t, 3_J = 6.0 Hz, 1H), 7.07 (m, 4H), 7.29 (m, 2H), 7.75 (m, 2H) ppm. **¹³C NMR** (125 MHz, CDCl₃): δ = 21.2, 21.6, 47.1, 127.3, 127.9, 129.4, 129.8, 133.4, 137.0, 137.7, 143.5 ppm.
3.7 4-Methyl-N-(2-methylbenzyl)phenylsulfonamide (19f)

\[
\begin{align*}
\text{19f} & \\
\text{C}_{16}H_{17}NO_2S \\
M = 275.37 \text{ g/mol}
\end{align*}
\]

**A)** Prepared from \([\text{Ph}_3\text{C}]^+\)[\(\text{B}(\text{C}_6\text{F}_5)_4\)]\(^-\) (3, 9.20 mg, 9.97 µmol, 5.00 mol%), tert-butyl-ferrocenylmethylsilane (2, 67.2 mg, 0.235 mmol, 1.17 equiv) and imine 11f (54.7 mg, 0.200 mmol, 1.00 equiv) in 1,2-Cl\(_2\)C\(_6\)H\(_4\) (2.0 mL) according to the general procedure; purification by flash column chromatography on silica gel using cyclohexane:ethyl acetate:triethylamine (24:4:1) as eluent afforded the analytically pure product 19f (32.4 mg, 59%) as a white solid.

**B)** Prepared from \([\text{Ph}_3\text{C}]^+\)[\(\text{B}(\text{C}_6\text{F}_5)_4\)]\(^-\) (3, 9.20 mg, 9.97 µmol, 5.00 mol%), triethylsilane (8, 28.0 mg, 0.241 mmol, 1.21 equiv) and imine 11f (54.7 mg, 0.200 mmol, 1.00 equiv) in 1,2-Cl\(_2\)C\(_6\)H\(_4\) (4.0 mL) according to the general procedure; purification by flash column chromatography on silica gel using cyclohexane:ethyl acetate:triethylamine (24:4:1) as eluent afforded the analytically pure product 19f (51.1 mg, 93%) as a white solid.

\[\text{m.p.} = 120^\circ\text{C (cyclohexane/ethyl acetate)}. \quad R_f = 0.16 \text{ (cyclohexane:ethyl acetate} = 6:1). \quad \text{GLC (SE-54): } t_r = 24.4 \text{ min.} \quad \text{IR (ATR): } \tilde{\nu} = 3259 \text{ (s), 3021 (w), 2961 (w), 2921 (w), 2873 (w), 1595 (m), 1489 (m), 1422 (m), 1317 (s), 1152 (s), 1090 (s), 1033 (s), 947 (w), 878 (m), 837 (w), 806 (m), 745 (m), 702 (s) cm}^{-1}. \quad \text{HRMS (ESI) calculated for } \text{C}_{15}\text{H}_{17}\text{NO}_2\text{S} [(\text{M+H})^+]: 276.1053; \text{ Found: 276.1056.} \quad \text{^1H NMR (400 MHz, CDCl}_3): } \delta = 2.24 \text{ (s, 3H), 2.44 (s, 3H), 4.09 (d, } ^3\text{J} = 6.0 \text{ Hz, 2H), 4.60 (t, } ^3\text{J} = 5.9 \text{ Hz, 1H), 7.07–7.14 \text{ (m, 3H), 7.15–7.19 (m, 1H), 7.31 (m, 2H), 7.76 (m, 2H) ppm.} \quad \text{^13C NMR (125 MHz, CDCl}_3): } \delta = 18.9, 21.7, 45.5, 126.3, 127.3, 128.3, 129.0, 129.8, 130.7, 134.0, 136.8, 136.8, 143.6 \text{ ppm.} \]
3.8 4-Methyl-N-(naphthalen-1-ylmethyl)phenylsulfonamide (20f)

![Chemical Structure](image)

**A** Prepared from [Ph₃C][B(C₆F₅)₄] (3, 9.20 mg, 9.97 µmol, 5.00 mol%), tert-butylferrocenylmethylsilane (2, 69.2 mg, 0.242 mmol, 1.21 equiv) and imine 12f (61.9 mg, 0.200 mmol, 1.00 equiv) in 1,2-Cl₂C₆H₄ (2.0 mL) according to the general procedure; purification by flash column chromatography on silica gel using cyclohexane:ethyl acetate:triethylamine (24:4:1) as eluent afforded the analytically pure product 20f (58.2 mg, 93%) as a white solid.

**B** Prepared from [Ph₃C][B(C₆F₅)₄] (3, 9.20 mg, 9.97 µmol, 4.96 mol%), triethylsilane (8, 28.0 mg, 0.241 mmol, 1.20 equiv) and imine 12f (62.3 mg, 0.201 mmol, 1.00 equiv) in 1,2-Cl₂C₆H₄ (4.0 mL) according to the general procedure; purification by flash column chromatography on silica gel using cyclohexane:ethyl acetate:triethylamine (24:4:1) as eluent afforded the analytically pure product 20f (56.4 mg, 90%) as a white solid.

**m.p.** = 157°C (cyclohexane/ethyl acetate). **Rf** = 0.16 (cyclohexane:ethyl acetate = 6:1). **GLC** (SE-54): *t*ᵣ = 30.6 min. **IR** (ATR): *ν* ~ = 3328 (m), 3295 (m), 2925 (w), 1597 (m), 1510 (w), 1492 (w), 1418 (m), 1393 (m), 1340 (s), 1318 (m), 1230 (w), 1158 (s), 1120 (w), 1093 (m), 1035 (s), 968 (m), 919 (m), 902 (m), 859 (m), 804 (s), 780 (s), 742 (w), 714 (w), 668 (s) cm⁻¹. **HRMS** (ESI) calculated for C₂₈H₂₇NO₂SNa [(M+Na)+]: 334.0872; Found: 334.0870. **¹H NMR** (400 MHz, CDCl₃): δ = 2.44 (s, 3H), 4.45 (br s, 1H), 4.53 (s, 2H), 7.28–7.34 (m, 4H), 7.48 (m, 2H), 7.75–7.77 (m, 3H), 7.81–7.85 (m, 1H), 7.87–7.90 (m, 1H) ppm. **¹³C NMR** (100 MHz, CDCl₃): δ = 21.7, 45.6, 123.4, 125.3, 126.2, 126.8, 127.1, 127.4, 128.8, 129.2, 129.8, 131.3, 131.5, 133.9, 136.7, 143.7 ppm.
3.9 4-Methyl-N-(naphthalen-2-ylmethyl)phenylsulfonamide (21f)

A) Prepared from [Ph₃C][B(C₆F₅)₄]⁻ (3, 9.20 mg, 9.97 µmol, 5.00 mol%), tert-butyl-ferrocenylmethylsilane (2, 72.0 mg, 0.252 mmol, 1.26 equiv) and imine 13f (61.9 mg, 0.200 mmol, 1.00 equiv) in 1,2-Cl₂C₆H₄ (3.5 mL) according to the general procedure; purification by flash column chromatography on silica gel using cyclohexane:ethyl acetate:triethylamine (24:4:1) as eluent afforded the analytically pure product 21f (39.0 mg, 63%) as an off-white solid.

B) Prepared from [Ph₃C][B(C₆F₅)₄]⁻ (3, 9.20 mg, 9.97 µmol, 4.96 mol%), triethylsilane (8, 28.0 mg, 0.241 mmol, 1.20 equiv) and imine 13f (62.3 mg, 0.201 mmol, 1.00 equiv) in 1,2-Cl₂C₆H₄ (4.0 mL) according to the general procedure; purification by flash column chromatography on silica gel using cyclohexane:ethyl acetate:triethylamine (24:4:1) as eluent afforded the analytically pure product 21f (41.3 mg, 66%) as an off-white solid.

m.p. = 132°C (cyclohexane/ethyl acetate). Rf = 0.16 (cyclohexane:ethyl acetate = 6:1). GLC (SE-54): tR = 31.2 min. IR (ATR): ν = 3283 (s), 3051 (w), 2921 (w), 2852 (w), 1599 (m), 1507 (w), 1494 (w), 1449 (m), 1432 (m), 1397 (w), 1364 (w), 1323 (s), 1303 (s), 1153 (s), 1123 (w), 1093 (s), 1053 (s), 1020 (w), 954 (m), 885 (m), 862 (m), 842 (m), 826 (s), 810 (s), 772 (w), 752 (s), 729 (w), 661 (s) cm⁻¹. HRMS (ESI) calculated for C₁₈H₁₇NO₂SNa [(M+Na)+]: 334.0872; Found: 334.0861. ¹H NMR (400 MHz, CDCl₃): δ = 2.42 (s, 3H), 4.30 (d, ³J = 6.3 Hz, 2H), 4.68 (t, ³J = 6.0 Hz, 1H), 7.28–7.32 (m, 3H), 7.47 (m, 2H), 7.61 (br s, 1H), 7.72–7.81 (m, 5H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 21.6, 47.6, 125.8, 126.3, 126.5, 126.8, 127.3, 127.8, 127.9, 128.7, 129.8, 133.0, 133.3, 133.8, 137.1, 143.6 ppm.
3.10 4-Methyl-N-(cyclohexylmethyl)phenylsulfonamide (22f)

A) Prepared from [Ph₃C][B(C₆F₅)₄]⁻ (3, 9.20 mg, 9.97 µmol, 5.00 mol%), tert-butylferrocenylmethylsilane (2, 69.2 mg, 0.242 mmol, 1.21 equiv) and imine 14f (53.1 mg, 0.200 mmol, 1.00 equiv) in 1,2-Cl₂C₆H₄ (2.0 mL) according to the general procedure; purification by flash column chromatography on silica gel using cyclohexane:ethyl acetate:triethylamine (24:4:1) as eluent afforded the analytically pure product 22f (52.6 mg, 98%) as a white solid.

B) Prepared from [Ph₃C][B(C₆F₅)₄]⁻ (3, 9.20 mg, 9.97 µmol, 5.00 mol%), triethylsilane (8, 28.0 mg, 0.241 mmol, 1.21 equiv) and imine 14f (53.1 mg, 0.200 mmol, 1.00 equiv) in 1,2-Cl₂C₆H₄ (4.0 mL) according to the general procedure; purification by flash column chromatography on silica gel using cyclohexane:ethyl acetate:triethylamine (24:4:1) as eluent afforded the analytically pure product 22f (52.9 mg, 99%) as a white solid.

m.p. = 79–82°C (cyclohexane/ethyl acetate). Rᵣ = 0.24 (cyclohexane:ethyl acetate = 6:1). GLC (SE-54): tᵣ = 23.6 min. IR (ATR): ν = 3284 (s), 2922 (s), 2850 (s), 1599 (w), 1426 (s), 1149 (s), 1091 (s), 1063 (m), 964 (w), 898 (w), 879 (w), 834 (w), 814 (s), 666 (s) cm⁻¹. HRMS (ESI) calculated for C₁₄H₂₁NO₂SNa [(M+Na)⁺]: 290.1185; Found: 290.1183. ¹H NMR (400 MHz, CDCl₃): δ = 0.79–0.88 (m, 2H), 1.03–1.22 (m, 3H), 1.39 (m, 1H), 1.60–1.68 (m, 5H), 2.42 (s, 3H), 2.74 (dd, 3J = 6.6 Hz, 3J = 6.6 Hz, 2H), 4.64 (t, 3J = 6.4 Hz, 1H), 7.30 (m, 2H), 7.74 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 21.7, 25.9, 26.5, 30.8, 38.0, 49.6, 127.3, 129.9, 137.3, 143.5 ppm.
3.11 4-Methyl-N-(2,2-dimethylpropyl)phenylsulfonamide (23f)

A) Prepared from \([\text{Ph}_3\text{C}]^+\text{[B(C_6\text{F}_5)_4]}^-\) (3, 9.20 mg, 9.97 µmol, 5.00 mol%), tert-butylferrocenylmethylsilane (2, 67.2 mg, 0.235 mmol, 1.17 equiv) and imine 15f (47.9 mg, 0.200 mmol, 1.00 equiv) in 1,2-Cl_2C_6H_4 (2.0 mL) according to the general procedure; purification by flash column chromatography on silica gel using cyclohexane:ethyl acetate:triethylamine (24:4:1) as eluent afforded the analytically pure product 23f (45.9 mg, 95%) as a white solid.

B) Prepared from \([\text{Ph}_3\text{C}]^+\text{[B(C_6\text{F}_5)_4]}^-\) (3, 9.20 mg, 9.97 µmol, 5.00 mol%), triethylsilane (8, 28.0 mg, 0.241 mmol, 1.21 equiv) and imine 15f (47.9 mg, 0.200 mmol, 1.00 equiv) in 1,2-Cl_2C_6H_4 (3.0 mL) according to the general procedure; purification by flash column chromatography on silica gel using cyclohexane:ethyl acetate:triethylamine (24:4:1) as eluent afforded the analytically pure product 23f (46.5 mg, 96%) as a white solid.

m.p. = 110–111°C (cyclohexane/ethyl acetate). R_f = 0.24 (cyclohexane:ethyl acetate = 6:1). GLC (SE-54): t_R = 19.3 min. IR (ATR): \(\vec{\nu} = 3269\) (s), 2955 (m), 2866 (m), 1719 (w), 1598 (w), 1417 (m), 1364 (w), 1319 (s), 1257 (m), 1214 (w), 1157 (s), 1091 (m), 1062 (m), 1023 (m), 948 (w), 872 (w), 814 (m), 713 (m) cm\(^{-1}\). HRMS (ESI) calculated for C_{12}H_{19}NO_2SNa [(M+Na)^+]: 264.1029; Found: 264.1023. \(^1\text{H NMR}\) (400 MHz, CDCl_3): \(\delta = 0.87\) (s, 9H), 2.42 (s, 3H), 2.65 (d, \(^3\nu = 6.9\) Hz, 2H), 4.81 (br t, \(^3\nu = 6.8\) Hz, 1H), 7.30 (m, 2H), 7.75 (m, 2H) ppm. \(^{13}\text{C NMR}\) (125 MHz, CDCl_3): \(\delta = 21.6, 27.2, 31.5, 54.8, 127.2, 129.8, 137.3, 143.3\) ppm.
3.12 4-Methyl-N-(2-ethylbutyl)phenylsulfonamide (24f)

A) Prepared from [Ph₃C][B(C₆F₅)₄]⁻ (3, 9.20 mg, 9.97 µmol, 5.00 mol%), tert-butylferrocenylmethylsilane (2, 69.2 mg, 0.242 mmol, 1.21 equiv) and imine 16f (50.7 mg, 0.200 mmol, 1.00 equiv) in 1,2-Cl₂C₆H₄ (2.0 mL) according to the general procedure; purification by flash column chromatography on silica gel using cyclohexane:ethyl acetate:triethylamine (24:4:1) as eluent afforded the analytically pure product 24f (49.4 mg, 97%) as a yellow oil.

B) Prepared from [Ph₃C][B(C₆F₅)₄]⁻ (3, 9.20 mg, 9.97 µmol, 5.00 mol%), triethylsilane (8, 28.0 mg, 0.241 mmol, 1.21 equiv) and imine 16f (50.7 mg, 0.200 mmol, 1.00 equiv) in 1,2-Cl₂C₆H₄ (4.0 mL) according to the general procedure; purification by flash column chromatography on silica gel using cyclohexane:ethyl acetate:triethylamine (24:4:1) as eluent afforded the analytically pure product 24f (49.1 mg, 96%) as a yellow oil.

Rᵣ = 0.32 (cyclohexane:ethyl acetate = 6:1). GLC (SE-54): tᵣ = 21.1 min. IR (ATR): ν̃ = 3279 (s), 2960 (s), 2928 (s), 2874 (s), 1598 (w), 1459 (m), 1423 (m), 1320 (s), 1155 (s), 1092 (s), 962 (w), 917 (m), 856 (m), 812 (s) cm⁻¹. HRMS (ESI) calculated for C₁₃H₂₁NO₂S [(M+H)+]: 256.1366; Found: 256.1367. ¹H NMR (400 MHz, CDCl₃): δ = 0.78 (t, ³J = 7.3 Hz, 6H), 1.23–1.30 (m, 5H), 2.42 (s, 3H), 2.83 (dd, ³J = 6.0 Hz, ³J = 6.0 Hz, 2H), 4.74 (t, ³J = 6.4 Hz, 1H), 7.30 (m, 2H), 7.75 (m, 2H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 10.8, 21.6, 23.5, 40.8, 45.6, 127.2, 129.7, 137.1, 143.3 ppm.
3.13 4-Methyl-N-(1-phenylethyl)phenylsulfonamide (7f)

A) Prepared from [Ph₃C][B(C₆F₅)₄]⁻ (3, 7.70 mg, 8.35 µmol, 5.00 mol%), tert-butylferrocenylmethylsilane (2, 57.5 mg, 0.201 mmol, 1.20 equiv) and imine 6f (45.7 mg, 0.167 mmol, 1.00 equiv) in 1,2-Cl₂C₆H₄ (3.0 mL) according to the general procedure; purification by flash column chromatography on silica gel using cyclohexane:ethyl acetate:triethylamine (24:4:1) as eluent afforded the analytically pure product 7f (8.60 mg, 19%) as an orange oil.

B) Prepared from [Ph₃C][B(C₆F₅)₄]⁻ (3, 8.50 mg, 9.22 µmol, 4.98 mol%), triethylsilane (8, 25.8 mg, 0.222 mmol, 1.20 equiv) and imine 6f (50.5 mg, 0.185 mmol, 1.00 equiv) in 1,2-Cl₂C₆H₄ (4.0 mL) according to the general procedure; purification by flash column chromatography on silica gel using cyclohexane:ethyl acetate:triethylamine (24:4:1) as eluent afforded the analytically pure product 7f (38.6 mg, 76%) as an orange oil.

R_f = 0.21 (cyclohexane:ethyl acetate = 6:1). GLC (SE-54): t_R = 23.3 min. IR (ATR): ν = 3250 (m), 2924 (w), 2870 (w), 1729 (w), 1449 (m), 1321 (s), 1154 (s), 1081 (s), 1015 (m), 956 (m), 857 (m), 811 (s) cm⁻¹. HRMS (ESI) calculated for C₁₅H₁₇NO₂SNa [(M+Na)+]: 298.0872; Found: 298.0869. ¹H NMR (500 MHz, CDCl₃): δ = 1.42 (d, 𝐽 = 6.9 Hz, 3H), 2.38 (s, 3H), 4.60 (m, 1H), 4.86 (d, 𝐽 = 6.2 Hz, 1H), 7.06–7.14 (m, 2H), 7.14–7.23 (m, 5H), 7.62 (d, 𝐽 = 8.1 Hz, 2H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 21.6, 23.7, 53.7, 126.2, 127.2, 127.6, 128.7, 129.6, 137.8, 142.2, 143.3 ppm.
4 Synthesis of Deuterated Ferrocenylsilane $d_{1-2}$

Ferrocene (186 mg, 1.00 mmol, 1.00 equiv) and potassium tert-butoxide (11.2 mg, 0.100 mmol, 0.100 equiv) were dissolved in THF (10 mL) and cooled to –78°C. tert-Butyllithium (1.60M in pentane, 0.613 mL, 0.980 mmol, 0.980 equiv) was added dropwise and the reaction mixture was stirred at –78°C for 30 min, slowly warmed to room temperature and stirred for an additional 30 min. At –20°C, a solution of tert-butyldichloromethylsilane (172 mg, 1.01 mmol, 1.01 equiv) in THF (5 mL) was added via canula. The reaction mixture was stirred at room temperature for 2 days, added to a dispersion of lithium aluminium deuteride (76.0 mg, 2.00 mmol, 2.00 equiv) in THF (5 mL) and heated under reflux for 1 day. After the addition of water (5 mL) and aqueous HCl (2M, 5 mL), the phases were separated, and the aqueous phase was extracted with tert-butyl methyl ether (3 x 10 mL). The combined organic phases were washed with brine, dried over anhydrous Na$_2$SO$_4$ and the solvents were evaporated under reduced pressure. Purification of the crude product by flash column chromatography on silica gel using cyclohexane as eluent afforded the analytically pure deuterated silane $d_{1-2}$ (151 mg, 53%, >98% deuteration grade determined by HRMS).

$R_f = 0.50$ (cyclohexane). GLC (SE-54): $t_R = 15.8$ min. IR (ATR): $\tilde{\nu} = 3097$ (w), 2926 (m), 2890 (w), 2854 (m), 2362 (w), 1533 (m), 1470 (m), 1422 (w), 1383 (w), 1361 (m), 1249 (m), 1164 (s), 1106 (s), 1034 (s), 1002 (m), 939 (w), 896 (w), 819 (s), 782 (s), 744 (w), 717 (s), 654 (w), 635 (s) cm$^{-1}$. HRMS (ESI) calculated for C$_{15}$H$_{21}$DFeSi $[M^{+}]$: 287.0898; Found: 287.0888. $^1$H NMR (300 MHz, C$_6$D$_6$): $\delta = 0.29$ (s, 3H), 0.98 (s, 9H), 3.96 (ddd, $^3J = 2.3$ Hz, $^4J = 1.2$ Hz, $^4J = 1.2$ Hz, 1H), 4.03 (s, 5H), 4.15 (ddd, $^3J = 2.3$ Hz, $^4J = 1.2$ Hz, $^4J = 1.2$ Hz, 1H), 4.18 (ddd, $^3J = 2.3$ Hz, $^3J = 2.3$ Hz, $^4J = 1.2$ Hz, 1H), 4.20 (ddd, $^3J = 2.3$ Hz, $^3J = 2.3$ Hz, $^4J = 1.2$ Hz, 1H) ppm. $^{13}$C NMR (75 MHz, C$_6$D$_6$): $\delta = -8.3$ (t, $^2J_{C,D} = 1.1$ Hz), 17.1 (t, $^2J_{C,D} = 1.0$ Hz), 27.0, 65.2, 68.8, 71.4, 71.8, 73.9, 74.8 ppm. $^{29}$Si DEPT NMR (60 MHz, C$_6$D$_6$): $\delta = -3.1$ (t, $^1J_{Si,D} = 28.9$ Hz) ppm.
5 References


6 NMR Spectra of Amines 5d–5f, d1-5f, 17f–24f, and 6f

6.1 N-Benzyl-1,1-diphenylmethaneamine (5d)

$^1$H NMR:

![NMR Spectrum of 5d](image)

$^{13}$C NMR:
6.2  *N*-Benzylandiline (5e)

$^1$H NMR:

![1H NMR spectrum](image)

$^{13}$C NMR:

![13C NMR spectrum](image)
6.3 4-Methyl-N-(benzyl)phenylsulfonamide (5f)

$^1$H NMR:

$^{13}$C NMR:
6.4 4-Methyl-\(N\)-(\([1-{}^2\text{H}\])\)-benzyl)phenylsulfonamide (\(d_{r-5f}\))

\(^1\text{H}\) NMR:

\[\text{Diagram of } ^1\text{H}\text{ NMR spectrum}\]

\(^{13}\text{C}\) NMR:

\[\text{Diagram of } ^{13}\text{C}\text{ NMR spectrum}\]
6.5 Methyl-N-(4-bromobenzyl)phenylsulfonamide (17f)

$^1$H NMR:

$^{13}$C NMR:
6.6  4-Methyl-N-(4-methylbenzyl)phenylsulfonamide (18f)

$^1$H NMR:

$^{13}$C NMR:
6.7  4-Methyl-N-(2-methylbenzyl)phenylsulfonamide (19f)

$^1$H NMR:

$^{13}$C NMR:
6.8 4-Methyl-N-(naphthalen-1-ylmethyl)phenylsulfonamide (20f)

$^1$H NMR:

![H NMR spectrum](image)

$^{13}$C NMR:

![C NMR spectrum](image)
6.9 4-Methyl-N-(naphthalen-2-ylmethyl)phenylsulfonamide (21f)

$^1$H NMR:

$^{13}$C NMR:
6.10 4-Methyl-N-(cyclohexylmethyl)phenylsulfonamide (22f)

$^1$H NMR:

\[ \text{HN} \]
\[ \text{S} \]
\[ \text{Me} \]

$^{13}$C NMR:

\[ \text{143.5} \]
\[ \text{137.3} \]
\[ \text{126.9} \]
\[ \text{127.3} \]
\[ \text{46.6} \]
\[ \text{30.8} \]
\[ \text{28.6} \]
\[ \text{217} \]
6.11 4-Methyl-N-(2,2-dimethylpropyl)phenylsulfonamide (23f)

$^1$H NMR:

\[
\text{HN}^\text{tBu}S^\text{Me}O
\]

$^{13}$C NMR:
6.12 4-Methyl-N-(2-ethylbutyl)phenylsulfonamide (24f)

$^1$H NMR:

$^{13}$C NMR:
6.13 4-Methyl-N-(1-phenylethyl)phenylsulfonamide (7f)

$^1$H NMR:

![1H NMR spectrum](image)

$^{13}$C NMR:

![13C NMR spectrum](image)
7  NMR Spectrum of Deuterated Ferrocenylsilane $d_{1-2}$

$^1$H NMR:

$^{13}$C NMR:
$^{29}\text{Si DEPT NMR}$: