Exhaustive Chemoselective Reduction of Nitriles by Catalytic Hydrosilylation Involving Cooperative Si–H Bond Activation

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1 General Information

All reactions were performed in flame-dried glassware using a MBraun glove box or conventional Schlenk techniques under a static pressure of nitrogen unless otherwise stated. Liquids and solutions were transferred with syringes and cannulas. CH$_2$Cl$_2$ was dried and purified following standard procedures. Technical grade solvents for extraction, crystallization, and chromatography (cyclohexane, tert-butyl methyl ether, and Et$_2$O) were distilled prior to use. Mesitylene was dried over CaH$_2$ and distilled prior to use. Catalysts [3a–c]$^+$$[^{1,1'}$biphenyl]-4-carbonitrile, 2-(trifluoromethyl)benzonitrile, 3-(trifluoromethyl)benzonitrile, 4-(trifluoromethyl)benzonitrile, 2-methoxybenzonitrile, 3-methoxybenzonitrile, 4-methoxybenzonitrile, 2-hydroxybenzonitrile, 3-hydroxybenzonitrile, 4-hydroxybenzonitrile, 4-(dimethylamino)benzonitrile, 2-chlorobenzonitrile, 3-chlorobenzonitrile, 4-chlorobenzonitrile, 2-bromobenzonitrile, 3-bromobenzonitrile, 4-bromobenzonitrile, acetonitrile, hex-5-enenitrile, 2-phenylacetonitrile, and furan-2-carbonitrile were purchased from commercial suppliers and used without further purification. 2-((tert-Butyldiphenylsilyloxy)benzonitrile, 3-((tert-butyldiphenylsilyloxy)benzonitrile, and 4-((tert-butyldiphenylsilyloxy)benzonitrile were prepared according to a modified reported procedure.$^{[S2]}$ Analytical thin layer chromatography (TLC) was performed on silica gel 60 F254 aluminium sheets by Merck. Flash column chromatography was performed on silica gel 60 (40–63 µm, 230–400 mesh, ASTM) by Merck using the indicated solvents. $^1$H NMR, $^{13}$C NMR, and $^{29}$Si NMR spectra were recorded in CDCl$_3$, CD$_2$Cl$_2$ or DMSO-$d_6$ on Bruker AV500 or Bruker AV400 instruments. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard (CHCl$_3$: $\delta = 7.26$ ppm for $^1$H NMR and CDCl$_3$: $\delta = 77.16$ ppm for $^{13}$C NMR, CDHCl$_2$: $\delta = 5.32$ for $^1$H NMR and CD$_2$Cl$_2$: $\delta = 53.84$ ppm for $^{13}$C NMR, (CD$_3$)($CD_2$H)SO: $\delta = 2.50$ ppm for $^1$H NMR and (CD$_3$)$_2$SO: $\delta = 39.52$ ppm for $^{13}$C NMR).$^{[S3]}$ NMR data are reported as follows: chemical shift, multiplicity (s = singlet, s$_b$ = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet, mc = centrosymmetric multiplet), coupling constants (Hz) and integration. $^{29}$Si DEPT NMR spectra were measured with an optimized coupling constant of 7.0 Hz for the $^3$J$_{H, \text{Si}}$ coupling. The peak intensities in the $^{29}$Si DEPT NMR spectra cannot be correlated to the amount of compound. Gas liquid chromatography (GLC) was performed on an Agilent Technologies 7820A gas chromatograph 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: N$_2$ 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. Mass spectra (MS) were obtained from the Analytical Facility at the Institut für Chemie, Technische Universität Berlin.
2 Experimental Details

2.1 General Procedures (GPs)

2.1.1 General Procedure for the TBDPS-Protection of Hydroxybenzonitriles (GP1)
According to a modified procedure reported by Maruoka,\textsuperscript{[S2]} TBDPSCl (1.1 equiv) is added dropwise to a stirring solution of the indicated hydroxybenzonitrile (1.0 equiv) and imidazole (2.0 equiv) in CH$_2$Cl$_2$ (20 mL), and the resulting mixture is maintained at room temperature for 3 d. Saturated aqueous NH$_4$Cl solution (20 mL) is added, and the resulting suspension is extracted with Et$_2$O (3 × 30 mL). The combined organic extracts are washed with H$_2$O (20 mL), brine (40 mL), dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The residue is purified by flash column chromatography on silica gel using the indicated cyclohexane/tert-butyl methyl ether mixtures. The procedure affords the protected hydroxybenzonitriles as white solids.

2.1.2 General Procedure for Nitrile-to-Amine Reduction Catalyzed by [3a]$^+$$^-$[BAr$_F^4$] (GP2)
In a glove box, a flame-dried GLC vial equipped with a magnetic stir bar is charged with [3a]$^+$$^-$[BAr$_F^4$] (1.0 mol%) and Me$_2$PhSiH (2a) (2.1 or 5.0 equiv). The indicated nitrile is added either in the glove box (for solid starting materials) or by micro syringe outside the glove box, and the resulting reaction mixture is maintained at room temperature for the indicated time. The reaction is quenched by the addition of a mixture of cyclohexane and tert-butyl methyl ether (90:10) containing 4% Et$_3$N (0.5 mL), and the resulting solution is filtered through a pad of Celite® coated by a small layer of silica gel with a solution of cyclohexane and tert-butyl methyl ether (90:10) containing 4% Et$_3$N (3–4 mL) as eluent. Solvents are removed under reduced pressure, and the residue is dissolved in Et$_2$O (1 mL) followed by addition of HCl (2M in Et$_2$O, 1.0 mL, 2.0 mmol, 10 equiv). The resulting suspension is stirred for 1 h and filtered, affording the amines as hydrochloride salts as white to yellow solids.

2.1.3 General Procedure for Nitrile-to-Imine Reduction Catalyzed by [3a]$^+$$^-$[BAr$_F^4$] (GP3)
In a glove box, a flame-dried GLC vial equipped with a magnetic stir bar is charged with [3a]$^+$$^-$[BAr$_F^4$] (1.0 mol%), Et$_3$SiH (2b) (2.0 equiv) and mesitylene (10 μL, 8.7 mg, 0.20 mmol, internal standard). The indicated nitrile is added either in the glove box (for solid starting materials) or by micro syringe outside the glove box, and the resulting reaction mixture is maintained at room temperature for 18 h. The mixture is then dissolved in CD$_2$Cl$_2$ (0.6 mL) and transferred into a NMR tube. $^1$H NMR spectroscopy is used to determine the yield with reference to mesitylene.
2.2. TBDPS-Protection of Hydroxybenzonitriles

2.2.1 2-(tert-Butyldiphenylsilyloxy)benzonitrile (4m)

Prepared from 2-hydroxybenzonitrile (500 mg, 4.20 mmol, 1.00 equiv), imidazole (572 mg, 8.39 mmol, 2.00 equiv) and TBDPSCl (1.27 g, 1.20 mL, 4.62 mmol, 1.10 equiv) according to GP1. After stirring for 3 d at room temperature and workup, the crude product was purified by flash column chromatography on silica gel using cyclohexane/tert-butyl methyl ether (10:1). This afforded analytical pure product 4m (388 mg, 26%) as a white solid. 

HRMS (EI, 70 eV) calculated for C_{19}H_{14}OSi [M–C_{4}H_{9}]: 300.0845; found: 300.0839. ^1H NMR (500 MHz, CDCl3): δ 1.09 (s, 9H), 6.41 (m, 1H), 6.83 (ddd, J = 8.0 Hz, J = 7.6 Hz, J = 1.0 Hz, 1H), 7.04 (ddd, J = 8.5 Hz, J = 7.5 Hz, J = 1.8 Hz, 1H), 7.30–7.35 (m, 4H), 7.36–7.41 (m, 2H), 7.47 (ddd, J = 7.7 Hz, J = 1.8 Hz, J = 0.3 Hz, 1H), 7.63–7.68 (m, 4H) ppm. ^13C{^1H} NMR (126 MHz, CDCl3): δ 19.7 (s), 26.5 (s, 3C), 104.9 (s), 117.1 (s), 119.7 (s), 121.3 (s), 128.2 (s, 4C), 130.5 (s, 2C), 131.7 (s, 2C), 133.6 (s), 133.8 (s), 135.6 (s, 4C), 158.0 (s) ppm.

2.2.2 3-(tert-Butyldiphenylsilyloxy)benzonitrile (4n)

Prepared from 3-hydroxybenzonitrile (500 mg, 4.20 mmol, 1.00 equiv), imidazole (572 mg, 8.39 mmol, 2.00 equiv) and TBDPSCl (1.27 g, 1.20 mL, 4.62 mmol, 1.10 equiv) according to GP1. After stirring for 3 d at room temperature and workup, the crude product was purified by flash column chromatography on silica gel using cyclohexane/tert-butyl methyl ether (10:1). This afforded analytical pure product 4n (1.27 g, 85%) as a white solid.
2.2.3 4-(tert-Butyldiphenylsilyloxy)benzonitrile (4o)

Prepared from 4-hydroxybenzonitrile (2.00 g, 16.8 mmol, 1.00 equiv), imidazole (2.29 g, 33.6 mmol, 2.00 equiv) and TBDPSCl (5.08 g, 4.79 mL, 18.5 mmol, 1.10 equiv) according to GP1. After stirring for 3 d at room temperature and workup, the crude product was purified by recrystallization from cyclohexane/tert-butyl methyl ether. This afforded analytical pure product 4o (4.46 g, 74%) as a white solid.

**HRMS** (El, 70 eV) calculated for C_{23}H_{23}NOSi [M]^+: 357.1543; found: 357.1537. **^1H NMR** (500 MHz, CDCl_3): δ 1.11 (s, 9H), 6.80 (m c, 2H), 7.36–7.42 (m, 6H), 7.43–7.48 (m, 2H), 7.68 (m c, 4H) ppm. **^13C{^1H} NMR** (126 MHz, CDCl_3): δ 19.6 (s), 26.5 (s, 3C), 104.7 (s), 119.3 (s), 120.8 (s, 2C), 127.7 (s), 128.2 (s, 4C), 130.5 (s, 2C), 131.9 (s), 133.9 (s, 2C), 135.5 (s, 4C), 159.6 (s) ppm. The analytical and spectroscopic data are in accordance with those reported.[S5]

2.3 Nitrile-to-Amine Reduction Catalyzed by [3a]^+\[BArF_4]^−

2.3.1 Phenylmethanamine Hydrochloride (6a·HCl)

Prepared from benzonitrile (4a, 21 mg, 21 μL, 0.20 mmol, 1.0 equiv) and Me_2PhSiH (2a, 57 mg, 65 μL, 0.42 mmol, 2.1 equiv) using [3a]^+\[BArF_4]^− (2.9 mg, 2.0 μmol, 1.0 mol%) according to GP2. After stirring for 18 h at room temperature and workup, the crude product was dissolved in Et_2O (1.0 mL)
and HCl (2.0M in Et₂O, 1.0 mL, 10 equiv) was added. The resulting suspension is stirred for 1 h and filtered, affording analytical pure product 6a·HCl (28.5 mg, 99%) as a white solid.

**HRMS (ESI)** calculated for C₇H₁₀N [M–Cl]⁺: 108.0813; found: 108.0806. **¹H NMR** (500 MHz, DMSO-d₆): δ 4.00 (q, J = 5.8 Hz, 2H), 7.35–7.43 (m, 3H), 7.48–7.53 (m, 2H), 8.51 (s, 3H) ppm. **¹³C{¹H} NMR** (126 MHz, DMSO-d₆): δ 42.1 (s), 128.4 (s), 128.5 (s, 2C), 128.9 (s, 2C), 134.1 (s) ppm. The analytical and spectroscopic data are in accordance with those reported.[S4]

### 2.3.2 o-Tolylmethanamine Hydrochloride (6b·HCl)

![6b·HCl](image)

Prepared from 2-methylbenzonitrile (4b, 24 mg, 24 μL, 0.20 mmol, 1.0 equiv) and Me₂PhSiH (2a, 58 mg, 65 μL, 0.42 mmol, 2.1 equiv) using [3a][BARF₄]⁻ (2.9 mg, 2.0 μmol, 1.0 mol%) according to GP2. After stirring for 18 h at room temperature and workup, the crude product was dissolved in Et₂O (1.0 mL) and HCl (2.0M in Et₂O, 1.0 mL, 10 equiv) was added. The resulting suspension is stirred for 1 h and filtered, affording analytical pure product 6b·HCl (23 mg, 73%) as a white solid.

**HRMS (ESI)** calculated for C₈H₁₂N [M–Cl]⁺: 122.0970; found: 122.0962. **¹H NMR** (500 MHz, DMSO-d₆): δ 2.35 (s, 3H), 3.99 (s, 2H), 7.20–7.30 (m, 3H), 7.40–7.46 (m, 1H), 8.53 (s, 3H) ppm. **¹³C{¹H} NMR** (126 MHz, DMSO-d₆): δ 18.8 (s), 39.4 (s), 126.0 (s), 128.4 (s), 129.2 (s), 130.3 (s), 132.3 (s), 136.6 (s) ppm. The analytical and spectroscopic data are in accordance with those reported.[S4]

### 2.3.3 m-Tolylmethanamine Hydrochloride (6c·HCl)

![6c·HCl](image)

Prepared from 3-methylbenzonitrile (4c, 24 mg, 24 μL, 0.20 mmol, 1.0 equiv) and Me₂PhSiH (2a, 58 mg, 65 μL, 0.42 mmol, 2.1 equiv) using [3a][BARF₄]⁻ (2.9 mg, 2.0 μmol, 1.0 mol%) according to GP2. After stirring for 18 h at room temperature and workup, the crude product was dissolved in Et₂O (1.0 mL) and HCl (2.0M in Et₂O, 1.0 mL, 10 equiv) was added. The resulting suspension is stirred for 1 h and filtered, affording analytical pure product 6c·HCl (27 mg, 85%) as a white solid.
HRMS (ESI) calculated for C₈H₁₂N [M−Cl]⁺: 122.0970; found: 122.0962. ¹H NMR (500 MHz, DMSO-d₆): δ 2.31 (s, 3H), 3.95 (s, 2H), 7.15–7.21 (m, 1H), 7.26–7.34 (m, 3H), 8.54 (s, 3H) ppm. ¹³C{¹H} NMR (126 MHz, DMSO-d₆): δ 20.9 (s), 42.1 (s), 125.9 (s), 128.5 (s), 128.9 (s), 129.5 (s), 134.0 (s), 137.7 (s) ppm. The analytical and spectroscopic data are in accordance with those reported. ¹³C{¹H}

2.3.4  p-Tolylmethanamine Hydrochloride (6d·HCl)

Prepared from 4-methylbenzonitrile (4d, 24 mg, 24 μL, 0.20 mmol, 1.0 equiv) and Me₂PhSiH (2a, 0.14 g, 0.15 mL, 1.0 mmol, 5.0 equiv) using [3a][BARF₄]⁻ (2.9 mg, 2.0 μmol, 1.0 mol%) according to GP2. After stirring for 18 h at room temperature and workup, the crude product was dissolved in Et₂O (1.0 mL) and HCl (2.0M in Et₂O, 1.0 mL, 10 equiv) was added. The resulting suspension is stirred for 1 h and filtered, affording analytical pure product 6d·HCl (31.4 mg, 99%) as a white solid. HRMS calculated for C₈H₁₂N [M−Cl]⁺: 122.0970; found: 122.0961. ¹H NMR (500 MHz, DMSO-d₆): δ 2.30 (s, 3H), 4.94 (q, J = 5.8 Hz, 2H), 7.21 (d, J = 7.6 Hz, 2H), 7.38 (d, J = 7.7 Hz, 2H), 8.47 (s, 3H) ppm. ¹³C{¹H} NMR (126 MHz, DMSO-d₆): δ 20.7 (s), 41.9 (s), 128.9 (s, 2C), 129.0 (s, 2C), 131.0 (s), 137.7 (s) ppm. The analytical and spectroscopic data are in accordance with those reported.

2.3.5  [1,1'-Biphenyl]-4-ylmethanamine Hydrochloride (6e·HCl)

Prepared from [1,1'-biphenyl]-4-carbonitrile (4e, 36 mg, 0.20 mmol, 1.0 equiv) and Me₂PhSiH (2a, 0.14 g, 0.15 mL, 1.0 mmol, 5.0 equiv) using [3a][BARF₄]⁻ (2.9 mg, 2.0 μmol, 1.0 mol%) according to GP2. After stirring for 18 h at room temperature and workup, the crude product was dissolved in Et₂O (1.0 mL) and HCl (2.0M in Et₂O, 1.0 mL, 10 equiv) was added. The resulting suspension is stirred for 1 h and filtered, affording analytical pure product 6e·HCl (44 mg, 99%) as a white solid. HRMS (ESI) calculated for C₁₃H₁₄N [M−Cl]⁺: 184.1126; found: 184.1119. ¹H NMR (500 MHz, DMSO-d₆): δ 4.05 (q, J = 5.5 Hz, 2H), 7.38 (m, 1H), 7.47 (m, 2H), 7.58–7.62 (m, 2H), 7.66–7.73 (m, 2H).
(m, 4H), 8.60 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, DMSO-d$_6$): δ 41.8 (s), 126.7 (s, 2C), 126.7 (s, 2C), 127.6 (s), 129.0 (s, 2C), 129.6 (s, 2C), 133.3 (s), 139.5 (s), 140.2 (s) ppm. The analytical and spectroscopic data are in accordance with those reported.\textsuperscript{[S4]}

### 2.3.6 (2-(Trifluoromethyl)phenyl)methanamine Hydrochloride (6f·HCl)

![Structure of 6f·HCl](image)

Prepared from 2-(trifluoromethyl)benzonitrile (4f, 34 mg, 27 μL, 0.20 mmol, 1.0 equiv) and Me$_2$PhSiH (2a, 58 mg, 65 μL, 0.42 mmol, 2.1 equiv) using [3a]$^+$$\text{[BArF}_4^-]$ (2.9 mg, 2.0 μmol, 1.0 mol%) according to GP2. After stirring for 18 h at room temperature and workup, the crude product was dissolved in Et$_2$O (1.0 mL) and HCl (2.0M in Et$_2$O, 1.0 mL, 10 equiv) was added. The resulting suspension is stirred for 1 h and filtered, affording analytical pure product 6f·HCl (8 mg, 19%) as a white solid.

HRMS the product couldn’t be detected by EI or ESI measurements $^1$H NMR (500 MHz, DMSO-d$_6$): δ 4.17 (s, 2H), 7.58–7.66 (m, 1H), 7.75–7.84 (m, 3H), 8.65 (s, 3H) ppm. Selected carbon signals: $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, DMSO-d$_6$): δ 38.6 (s), 126.1 (q, J = 5.8 Hz), 129.1 (s), 130.6 (s), 132.0 (s), 133.0 (s) ppm. The analytical and spectroscopic data are in accordance with those reported.\textsuperscript{[S7]}

### 2.3.7 (3-(Trifluoromethyl)phenyl)methanamine Hydrochloride (6g·HCl)

Prepared from 3-(trifluoromethyl)benzonitrile (4g, 34 mg, 0.20 mmol, 1.0 equiv) and Me$_2$PhSiH (2a, 0.14 g, 0.15 mL, 1.0 mmol, 5.0 equiv) using [3a]$^+$$\text{[BArF}_4^-]$ (2.9 mg, 2.0 μmol, 1.0 mol%) according to GP2. After stirring for 18 h at room temperature and workup, the crude product was dissolved in Et$_2$O (1.0 mL) and HCl (2.0M in Et$_2$O, 1.0 mL, 10 equiv) was added. The resulting suspension is stirred for 1 h and filtered, affording analytical pure product 6g·HCl (42 mg, 99%) as a white solid.

HRMS (ESI) calculated for C$_8$H$_9$F$_3$N [M–Cl]$^+$: 176.0687; found: 176.0681. $^1$H NMR (500 MHz, DMSO-d$_6$): δ 4.13 (q, J = 5.6 Hz, 2H), 7.65 (m, 1H), 7.73 (d, J = 7.8 Hz, 1H), 7.85 (d, J = 7.8 Hz,
1H), 7.95 (s, 1H), 8.69 (s, 3H) ppm. **\(^{13}\)C\{\(^1\)H\} NMR** (126 MHz, DMSO-\(d_6\)): \(\delta\) 41.5 (s), 124.1 (q, \(J = 272.3\) Hz), 125.0 (m), 125.8 (m), 129.1 (d, \(J = 31.1\) Hz), 129.5 (s), 133.3 (s), 135.5 (s) ppm.

### 2.3.8 (4-(Trifluoromethyl)phenyl)methanamine Hydrochloride (6h-HCl)

![Chemical Structure](image)

Prepared from 4-(trifluoromethyl)benzonitrile (4h, 34 mg, 0.20 mmol, 1.0 equiv) and Me\(_2\)PhSiH (2a, 0.14 g, 0.15 mL, 1.0 mmol, 5.0 equiv) using [3a]\(^+\)[BAr\(_F^4\)]\(^-\) (2.9 mg, 2.0 \(\mu\)mol, 1.0 mol\%) according to GP2. After stirring for 18 h at room temperature and workup, the crude product was dissolved in Et\(_2\)O (1.0 mL) and HCl (2.0M in Et\(_2\)O, 1.0 mL, 10 equiv) was added. The resulting suspension is stirred for 1 h and filtered, affording analytical pure product 6h-HCl (42 mg, 99%) as a white solid.

**HRMS** (ESI) calculated for C\(_8\)H\(_9\)F\(_3\)N [M–Cl]+: 176.0687; found: 176.0681.

**\(^1\)H NMR** (500 MHz, DMSO-\(d_6\)): \(\delta\) 4.12 (s, 2H), 7.75 (d, \(J = 8.5\) Hz, 2H), 7.79 (d, \(J = 8.5\) Hz, 2H), 8.71 (s, 3H) ppm.

**\(^{13}\)C\{\(^1\)H\} NMR** (126 MHz, DMSO-\(d_6\)): \(\delta\) 41.5 (s), 124.1 (q, \(J = 272.3\) Hz), 125.3 (q, \(J = 3.5\) Hz, 2C), 128.8 (q, \(J = 31.5\) Hz), 129.8 (s, 2C), 138.8 (s) ppm. The analytical and spectroscopic data are in accordance with those reported.[S4]

### 2.3.9 (4-(tert-Butyldiphenylsilyloxy)phenyl)methanamine Hydrochloride (6o-HCl)

![Chemical Structure](image)

Prepared from 4-(tert-butyldiphenylsilyloxy)benzonitrile (4o, 72 mg, 0.20 mmol, 1.0 equiv) and Me\(_2\)PhSiH (2a, 0.14 g, 0.15 mL, 1.0 mmol, 5.0 equiv) using [3a]\(^+\)[BAr\(_F^4\)]\(^-\) (2.9 mg, 2.0 \(\mu\)mol, 1.0 mol\%) according to GP2. After stirring for 18 h at 60 °C and workup, the crude product was dissolved in Et\(_2\)O (1.0 mL) and HCl (2.0M in Et\(_2\)O, 1.0 mL, 10 equiv) was added. The resulting suspension is stirred for 1 h and filtered, affording analytical pure product 6o-HCl (78 mg, 98%) as a white solid.

**HRMS** (EI, 70 eV) calculated for C\(_{23}\)H\(_{28}\)NOSi [M–Cl]+: 361.1856; found: 361.1854.

**\(^1\)H NMR** (500 MHz, DMSO-\(d_6\)): \(\delta\) 1.04 (s, 9H), 3.85 (q, \(J = 5.6\) Hz, 2H), 6.74 (d, \(J = 8.3\) Hz, 2H), 7.24–7.30 (m, 2H), 7.40–7.46 (m, 4H), 7.47–7.52 (m, 2H), 7.67 (m), 8.35 (s, 3H) ppm.

**\(^{13}\)C\{\(^1\)H\} NMR** (126 MHz, DMSO-\(d_6\)): \(\delta\) 41.5 (s), 124.1 (q, \(J = 272.3\) Hz), 125.3 (q, \(J = 3.5\) Hz, 2C), 128.8 (q, \(J = 31.5\) Hz), 129.8 (s, 2C), 138.8 (s) ppm.
MHZ, DMSO-d$_6$): $\delta$ 18.9 (s), 26.3 (s, 3C), 41.5 (s), 119.2 (s, 2C), 126.8 (s), 128.1 (s, 4C), 130.3 (s, 2C), 130.4 (s, 2C), 131.9 (s, 2C), 135.0 (s, 4C), 155.1 (s) ppm.

2.3.10 (2-Chlorophenyl)methanamine Hydrochloride (6p·HCl)

Prepared from 2-chlorobenzonitrile (4p, 28 mg, 0.20 mmol, 1.0 equiv) and Me$_2$PhSiH (2a, 0.14 g, 0.15 mL, 1.0 mmol, 5.0 equiv) using [3a][BAr$_{4}$F]$^-$ (2.9 mg, 2.0 $\mu$mol, 1.0 mol%) according to GP2. After stirring for 18 h at room temperature and workup, the crude product was dissolved in Et$_2$O (1.0 mL) and HCl (2.0M in Et$_2$O, 1.0 mL, 10 equiv) was added. The resulting suspension is stirred for 1 h and filtered, affording analytical pure product 6p·HCl (35 mg, 98%) as a white solid.

HRMS (ESI) calculated for C$_7$H$_9$ClN [M–Cl]$^+$: 142.0424; found: 142.0418. $^1$H NMR (500 MHz, DMSO-d$_6$): $\delta$ 4.11 (m, 2H), 7.38–7.45 (m, 2H), 7.49–7.57 (m, 1H), 7.64–7.72 (m, 1H), 8.79 (s, 3H) ppm. $^{13}$C($^1$H) NMR (126 MHz, DMSO-d$_6$): $\delta$ 39.3 (s), 127.4 (s), 129.4 (s), 130.2 (s), 130.7 (s), 131.6 (s), 132.8 (s) ppm. The analytical and spectroscopic data are in accordance with those reported.[S4]

2.3.11 (3-Chlorophenyl)methanamine Hydrochloride (6q·HCl)

Prepared from 3-chlorobenzonitrile (4q, 28 mg, 0.20 mmol, 1.0 equiv) and Me$_2$PhSiH (2a, 0.14 g, 0.15 mL, 1.0 mmol, 5.0 equiv) using [3a][BAr$_{4}$F]$^-$ (2.9 mg, 2.0 $\mu$mol, 1.0 mol%) according to GP2. After stirring for 18 h at room temperature and workup, the crude product was dissolved in Et$_2$O (1.0 mL) and HCl (2.0M in Et$_2$O, 1.0 mL, 10 equiv) was added. The resulting suspension is stirred for 1 h and filtered, affording analytical pure product 6q·HCl (36 mg, 99%) as a white solid.

HRMS (ESI) calculated for C$_7$H$_9$ClN [M–Cl]$^+$: 142.0424; found: 142.0416. $^1$H NMR (500 MHz, DMSO-d$_6$): $\delta$ 4.02 (m, 2H), 7.47 (m, 2H), 7.46–7.52 (m, 1H), 7.65 (m, 1H), 8.67 (s, 3H) ppm. $^{13}$C($^1$H) NMR (126 MHz, DMSO-d$_6$): $\delta$ 41.3 (s), 127.7 (s), 128.2 (s), 128.9 (s), 130.3 (s), 133.0 (s), 136.5 (s) ppm. The analytical and spectroscopic data are in accordance with those reported.[S4]
2.3.12 (4-Chlorophenyl)methanamine Hydrochloride (6r·HCl)

Prepared from 4-chlorobenzonitrile (4r, 28 mg, 0.20 mmol, 1.0 equiv) and Me₂PhSiH (2a, 0.14 g, 0.15 mL, 1.0 mmol, 5.0 equiv) using [3a][BAr^f]_4^– (2.9 mg, 2.0 μmol, 1.0 mol%) according to GP2. After stirring for 18 h at room temperature and workup, the crude product was dissolved in Et₂O (1.0 mL) and HCl (2.0M in Et₂O, 1.0 mL, 10 equiv) was added. The resulting suspension is stirred for 1 h and filtered, affording analytical pure product 6r·HCl (36 mg, 99%) as a white solid.

HRMS (ESI) calculated for C₇H₉ClN [M–Cl]^+: 142.0424; found: 142.0418. ¹H NMR (500 MHz, DMSO-d₆): δ 4.00 (q, J = 5.4 Hz, 2H), 7.47 (d, J = 8.6 Hz, 2H), 7.55 (d, J = 8.6 Hz, 2H), 8.61 (s, 3H) ppm. ¹³C{¹H} NMR (126 MHz, DMSO-d₆): δ 41.3 (s), 128.4 (s, 2C), 131.0 (s, 2C), 133.1 (s), 133.1 (s) ppm. The analytical and spectroscopic data are in accordance with those reported.[S7]

2.3.13 (2-Bromophenyl)methanamine Hydrochloride (6s·HCl)

Prepared from 2-bromobenzonitrile (4s, 36 mg, 0.20 mmol, 1.0 equiv) and Me₂PhSiH (2a, 0.14 g, 0.15 mL, 1.0 mmol, 5.0 equiv) using [3a][BAr^f]_4^– (2.9 mg, 2.0 μmol, 1.0 mol%) according to GP2. After stirring for 18 h at room temperature and workup, the crude product was dissolved in Et₂O (1.0 mL) and HCl (2.0M in Et₂O, 1.0 mL, 10 equiv) was added. The resulting suspension is stirred for 1 h and filtered, affording analytical pure product 6s·HCl (44 mg, 99%) as a white solid.

HRMS (ESI) calculated for C₇H₉BrN [M–Cl]^+: 185.9918; found: 185.9914. ¹H NMR (500 MHz, DMSO-d₆): δ 4.10 (s, 2H), 7.33 (m, 1H), 7.46 (m, 1H), 7.63–7.72 (m, 2H), 8.77 (s, 3H) ppm. ¹³C{¹H} NMR (126 MHz, DMSO-d₆): δ 41.9 (s), 123.3 (s), 128.0 (s), 130.4 (s, 2C), 132.7 (s), 133.1 (s) ppm. The analytical and spectroscopic data are in accordance with those reported.[S8]
2.3.14 (3-Bromophenyl)methanamine Hydrochloride (6t·HCl)

\[
\text{NH}_2 \quad \text{HCl}
\]

\[
\text{C}_7\text{H}_9\text{BrClN}
\]

\[M = 222.51 \text{ g/mol}\]

Prepared from 3-bromobenzonitrile (4t, 37 mg, 0.20 mmol, 1.0 equiv) and Me₂PhSiH (2a, 0.14 g, 0.15 mL, 1.0 mmol, 5.0 equiv) using [3a][BAr₄]⁻ (2.9 mg, 2.0 μmol, 1.0 mol%) according to GP2. After stirring for 18 h at room temperature and workup, the crude product was dissolved in Et₂O (1.0 mL) and HCl (2.0M in Et₂O, 1.0 mL, 10 equiv) was added. The resulting suspension is stirred for 1 h and filtered, affording analytical pure product 6t·HCl (44 mg, 99%) as a white solid.


\[\text{^1H NMR (500 MHz, DMSO-}d_6\text{)}:\delta \text{4.01 (mc, 2H), 7.34–7.40 (m, 1H), 7.49–7.60 (m, 2H), 7.78 (s, 1H), 8.64 (sbr, 3H) ppm.}\]

\[\text{^13C\{^1H\} NMR (126 MHz, DMSO-}d_6\text{)}:\delta \text{41.4 (s), 121.6 (s), 128.1 (s), 130.6 (s), 131.2 (s), 131.7 (s), 136.8 (s) ppm.}\]

The analytical and spectroscopic data are in accordance with those reported.[S9]

2.3.15 (4-Bromophenyl)methanamine Hydrochloride (6u·HCl)

\[
\text{NH}_2 \quad \text{HCl}
\]

\[
\text{C}_7\text{H}_9\text{BrClN}
\]

\[M = 222.51 \text{ g/mol}\]

Prepared from 4-bromobenzonitrile (4u, 37 mg, 0.20 mmol, 1.0 equiv) and Me₂PhSiH (2a, 0.14 g, 0.15 mL, 1.0 mmol, 5.0 equiv) using [3a][BAr₄]⁻ (2.9 mg, 2.0 μmol, 1.0 mol%) according to GP2. After stirring for 18 h at room temperature and workup, the crude product was dissolved in Et₂O (1.0 mL) and HCl (2.0M in Et₂O, 1.0 mL, 10 equiv) was added. The resulting suspension is stirred for 1 h and filtered, affording analytical pure product 6u·HCl (44 mg, 99%) as a white solid.


\[\text{^1H NMR (500 MHz, DMSO-}d_6\text{)}:\delta \text{3.98 (mc, 2H), 7.45–7.50 (m, 2H), 7.59–7.63 (m, 2H), 8.63 (sbr, 3H) ppm.}\]

\[\text{^13C\{^1H\} NMR (126 MHz, DMSO-}d_6\text{)}:\delta \text{41.4 (s), 121.7 (s), 131.3 (s, 2C), 131.4 (s, 2C), 133.5 (s) ppm.}\]

The analytical and spectroscopic data are in accordance with those reported.[S4]
2.3.16 Ethanamine Hydrochloride (6v·HCl)

\[
\begin{align*}
\text{NH}_2 \cdot \text{HCl} \\
6v\cdot\text{HCl} \\
\text{C}_2\text{H}_5\text{ClN} \\
M = 81.54 \text{ g/mol}
\end{align*}
\]

Prepared from acetonitrile (4v, 17 mg, 21 μL, 0.40 mmol, 1.0 equiv) and Me₂PhSiH (2a, 0.12 g, 0.13 mL, 0.84 mmol, 2.1 equiv) using [3a][BArF₄]⁻ (5.7 mg, 4.0 μmol, 1.0 mol%) according to GP2. After stirring for 18 h at room temperature and workup, the crude product was dissolved in Et₂O (1.0 mL) and HCl (2.0M in Et₂O, 1.0 mL, 10 equiv) was added. The resulting suspension is stirred for 1 h and filtered, affording analytical pure product 6v·HCl (11 mg, 34%) as a white solid.

HRMS (EI, 70 eV) calculated for C₂H₈N [M–Cl]⁺: 66.0105; found: 66.0101. \(^1\)H NMR (500 MHz, DMSO-d₆): δ 1.16 (t, J = 7.5 Hz, 3H), 2.81 (qq, J = 7.3 Hz, J = 5.7 Hz, 2H), 8.50 (sbr, 3H) ppm.

\(^13\)C\(^{1}\)H NMR (126 MHz, DMSO-d₆): δ 11.5 (s), 33.0 (s) ppm.

2.3.17 Hex-5-en-1-amine Hydrochloride (6w·HCl)

\[
\begin{align*}
\text{NH}_2 \cdot \text{HCl} \\
6w\cdot\text{HCl} \\
\text{C}_6\text{H}_{14}\text{ClN} \\
M = 135.64 \text{ g/mol}
\end{align*}
\]

Prepared from hex-5-enenitrile (4w, 19 mg, 29 μL, 0.20 mmol, 1.0 equiv) and Me₂PhSiH (2a, 57 mg, 65 μL, 0.42 mmol, 2.1 equiv) using [3a][BArF₄]⁻ (2.9 mg, 2.0 μmol, 1.0 mol%) according to GP2. After stirring for 18 h at room temperature and workup, the crude product was dissolved in Et₂O (1.0 mL) and HCl (2.0M in Et₂O, 1.0 mL, 10 equiv) was added. The resulting suspension is stirred for 1 h and filtered, affording analytical pure product 6w·HCl (27 mg, 98%) as a white solid.

HRMS (ESI) calculated for C₆H₁₄N [M–Cl]⁺: 100.1126; found: 100.1120. \(^1\)H NMR (500 MHz, DMSO-d₆): δ 1.40 (m, 2H), 1.56 (m, 2H), 2.03 (m, 2H), 2.70–2.80 (m, 2H), 5.00 (m, 2H), 5.97 (ddt, J = 17.3 Hz, J = 10.3 Hz, J = 6.7 Hz, 1H), 8.01 (sbr, 3H) ppm. \(^13\)C\(^{1}\)H NMR (126 MHz, DMSO-d₆): δ 25.0 (s), 26.4 (s), 32.6 (s), 38.5 (s), 115.1 (s), 138.2 (s) ppm. The analytical and spectroscopic data are in accordance with those reported.[S10]

2.3.18 2-Phenylethan-1-amine Hydrochloride (6x·HCl)

\[
\begin{align*}
\text{NH}_2 \cdot \text{HCl} \\
6x\cdot\text{HCl} \\
\text{C}_8\text{H}_{12}\text{ClN} \\
M = 157.64 \text{ g/mol}
\end{align*}
\]

The analytical and spectroscopic data are in accordance with those reported.[S10]
Prepared from 2-phenylacetonitrile (4x, 24 mg, 24 μL, 0.20 mmol, 1.0 equiv) and Me₂PhSiH (2a, 59 mg, 68 μL, 0.43 mmol, 2.1 equiv) using [3a]⁺[Bar₄F]⁻ (2.9 mg, 2.0 μmol, 1.0 mol%) according to GP2. After stirring for 18 h at room temperature and workup, the crude product was dissolved in Et₂O (1.0 mL) and HCl (2.0M in Et₂O, 1.0 mL, 10 equiv) was added. The resulting suspension is stirred for 1 h and filtered, affording analytical pure product 6x·HCl (22 mg, 68%) as a white solid.

HRMS (ESI) calculated for C₈H₁₂N [M–Cl]⁺: 122.0970; found: 122.0962. ¹H NMR (500 MHz, DMSO-d₆): δ 2.87–2.94 (m, 2H), 2.96–3.05 (m, 2H), 7.22–7.28 (m, 3H), 7.30–7.37 (m, 2H), 8.18 (s br, 3H) ppm. ¹³C{¹H} NMR (126 MHz, DMSO-d₆): δ 32.9 (s), 39.8 (s), 126.7 (s), 128.6 (s, 2C), 128.6 (s, 2C), 137.4 (s) ppm. The analytical and spectroscopic data are in accordance with those reported.[S4]

2.3.19 Furan-2-ylmethanamine Hydrochloride (6y·HCl)

Prepared from furan-2-carbonitrile (4y, 19 mg, 18 μL, 0.20 mmol, 1.0 equiv) and Me₂PhSiH (2a, 57 mg, 65 μL, 0.42 mmol, 2.1 equiv) using [3a]⁺[Bar₄F]⁻ (2.9 mg, 2.0 μmol, 1.0 mol%) according to GP2. After stirring for 18 h at room temperature and workup, the crude product was dissolved in Et₂O (1.0 mL) and HCl (2.0M in Et₂O, 1.0 mL, 10 equiv) was added. The resulting suspension is stirred for 1 h and filtered, affording analytical pure product 6y·HCl (21 mg, 78%) as a white solid.

HRMS the product couldn’t be detected by EI or ESI measurements. ¹H NMR (500 MHz, DMSO-d₆): δ 4.06 (m, 2H), 6.48–5.51 (m, 1H), 6.54–6.56 (m, 1H), 7.73 (m, 1H), 8.50 (s br, 3H) ppm. ¹³C{¹H} NMR (126 MHz, DMSO-d₆): δ 34.9 (s), 110.2 (s), 110.9 (s), 143.6 (s), 147.6 (s) ppm. The analytical and spectroscopic data are in accordance with those reported.[S7]
2.4 Nitrile-to-Imine Reduction Catalyzed by [3a][BARF₄]⁻

2.4.1 1-Phenyl-N-(triethylsilyl)methanimine (5ab)

\[
\text{C}_{13}H_{25}NSi
\]
\[
M = 219.40 \text{ g/mol}
\]

Prepared from benzonitrile (4a, 21 mg, 21 μL, 0.20 mmol, 1.0 equiv) and Et₃SiH (2b, 47 mg, 64 μL, 0.40 mmol, 2.0 equiv) using [3a][BARF₄]⁻ (2.9 mg, 2.0 μmol, 1.0 mol%) according to GP3. ¹H NMR analysis showed the formation of 5ab (91%). ¹H NMR (500 MHz, CD₂Cl₂): δ 0.80 (m, 6H), 1.04 (m, 9H, overlaps with (CH₃CH₂)₃SiH), 7.44–7.49 (m, 3H), 7.80–7.85 (m, 2H), 9.08 (s, 1H) ppm. ¹³C(¹H) NMR (126 MHz, CD₂Cl₂): δ 4.1 (s, 3C), 7.2 (s, 3C), 128.7 (s), 129.0 (s, 2C), 131.6 (s, 2C), 139.7 (s), 169.1 (s) ppm. ²⁹Si DEPT NMR (99 MHz, CD₂Cl₂): δ 8.5 ppm. The analytical and spectroscopic data are in accordance with those reported.[S4]

2.4.2 N-(Triethylsilyl)-1-(4-(trifluoromethyl)phenyl)methanimine (5hb)

\[
\text{C}_{14}H_{25}F₃NSi
\]
\[
M = 287.40 \text{ g/mol}
\]

Prepared from 4-(trifluoromethyl)benzonitrile (4h, 34 mg, 0.20 mmol, 1.0 equiv) and Et₃SiH (2b, 47 mg, 64 μL, 0.40 mmol, 2.0 equiv) using [3a][BARF₄]⁻ (2.9 mg, 2.0 μmol, 1.0 mol%) according to GP3. ¹H NMR analysis showed the formation of 5ah (92%). ¹H NMR (500 MHz, CD₂Cl₂): δ 0.79 (m, 6H), 1.04 (m, 9H, overlaps with (CH₃CH₂)₃SiH), 7.44 (m, 2H), 7.77 (m, 2H), 9.04 (s, 1H) ppm. ¹³C(¹H) NMR (126 MHz, CD₂Cl₂): δ 4.1 (s, 3C), 7.3 (s, 3C), 125.2 (q, J = 272.6 Hz, 1C), 128.6 (q, J = 31.2 Hz, 1C), 129.3 (s, 2C), 130.0 (s, 2C), 137.6 (s), 167.5 (s) ppm. ²⁹Si DEPT NMR (99 MHz, CD₂Cl₂): δ 8.8 ppm.

2.4.3 1-(4-((tert-Butyldiphenylsilyloxy)phenyl)-N-(triethylsilyl)methanimine (5ob)

\[
\text{C}_{23}H_{29}OSi₂
\]
\[
M = 473.81 \text{ g/mol}
\]
Prepared from 4-(tert-butyldiphenylsilyloxy)benzonitrile (4o, 72 mg, 0.20 mmol, 1.0 equiv) and Et₃SiH (2b, 47 mg, 64 μL, 0.40 mmol, 2.0 equiv) using [3a][BARF₄]⁻ (2.9 mg, 2.0 μmol, 1.0 mol%) according to GP3. ¹H NMR analysis showed the formation of 5ob (90%). ¹H NMR (500 MHz, CD₂Cl₂): δ 0.77 (m c, 6H), 1.03 (m c, 9H, overlaps with (CH₃CH₂)₃SiH), 1.18 (s, 9H), 6.89 (m c, 2H), 7.42–7.46 (m, 4H), 7.47–7.51 (m, 2H), 7.61 (m c, 2H), 7.78–7.81 (m, 4H), 8.96 (s, 1H) ppm. ¹³C{¹H} NMR (126 MHz, CD₂Cl₂): δ 4.2 (s, 3C), 7.3 (s, 3C), 19.9 (s), 26.8 (s, 3C), 120.3 (s, 2C), 128.4 (s, 4C), 130.2 (s, 2C), 130.6 (s, 2C), 133.1 (s), 133.5 (s), 136.1 (s, 4C), 138.2 (s), 159.0 (s), 168.2 (s) ppm.

2.4.4 1-(4-Chlorophenyl)-N-(triethylsilyl)methanimine (5rb)

![Structure of 5rb](image)

Prepared from 4-chlorobenzonitrile (4r, 28 mg, 0.20 mmol, 1.0 equiv) and Et₃SiH (2b, 47 mg, 64 μL, 0.40 mmol, 2.0 equiv) using [3a][BARF₄]⁻ (2.9 mg, 2.0 μmol, 1.0 mol%) according to GP3. ¹H NMR analysis showed the formation of 5rb (99%). ¹H NMR (500 MHz, CD₂Cl₂): δ 0.80 (m c, 6H), 1.04 (m c, 9H, overlaps with (CH₃CH₂)₃SiH), 7.73 (d, 2H), 7.95 (s, 2H), 9.11 (s, 1H) ppm. ¹³C{¹H} NMR (126 MHz, CD₂Cl₂): δ 4.0 (s, 3C), 7.2 (s, 3C), 126.0 (m, 2C), 129.0 (s, 2C), 132.9 (m), 142.5 (s), 167.4 (s) ppm. ²⁹Si DEPT NMR (99 MHz, CD₂Cl₂): δ 9.3 ppm.

2.4.5 1-(4-Bromophenyl)-N-(triethylsilyl)methanimine (5ub)

![Structure of 5ub](image)

Prepared from 4-Bromobenzonitrile (4u, 37 mg, 0.20 mmol, 1.0 equiv) and Et₃SiH (2b, 47 mg, 64 μL, 0.40 mmol, 2.0 equiv) using [3a][BARF₄]⁻ (2.9 mg, 2.0 μmol, 1.0 mol%) according to GP3. ¹H NMR analysis showed the formation of 5ub (99%). ¹H NMR (500 MHz, CD₂Cl₂): δ 0.79 (m c, 6H), 1.04 (m c, 9H, overlaps with (CH₃CH₂)₃SiH), 7.60 (m c, 2H), 7.70 (m c, 2H), 9.01 (s, 1H) ppm. ¹³C{¹H} NMR (126 MHz, CD₂Cl₂): δ 4.1 (s, 3C), 7.2 (s, 3C), 126.1 (s), 130.2 (s, 2C), 132.2 (s, 2C), 138.6 (s), 167.6 (s) ppm. ²⁹Si DEPT NMR (99 MHz, CD₂Cl₂): δ 8.9 ppm. The analytical and spectroscopic data are in accordance with those reported.⁹⁴
3 NMR Spectra

Figure S1. $^1$H NMR (500 MHz, CDCl$_3$) of 2-(tert-Butyldiphenylsilyloxy)benzonitrile (4m).
Figure S2. $^{13}\text{C}^{('H)}\text{NMR}$ (126 MHz, CD$_2$Cl$_2$) of 2-(tert-Butyldiphenylsilyloxy)benzonitrile (4m).
Figure S3. $^1$H NMR (500 MHz, CDCl$_3$) of 3-(tert-Butyldiphenylsilyloxy)benzonitrile (4n).
Figure S4. $^{13}$C($^1$H)NMR (126 MHz, CDCl$_3$) of 3-(tert-Butyldiphenylsilyloxy)benzonitrile (4n).
Figure S5. $^1$H NMR (500 MHz, CDCl$_3$) of 4-(tert-Butyl)diphenylsilyl)benzonitrile (4o).
Figure S6. $^{13}$C($^1$H)NMR (126 MHz, CDCl$_3$) of 4-(tert-Butyldiphenylsilyloxy)benzonitrile (4o).
Figure S7. $^1$H NMR (500 MHz, DMSO-$d_6$) of Phenylmethanamine Hydrochloride (6a·HCl).
Figure S8. $^{13}$C($^1$H)NMR (126 MHz, DMSO-$d_6$) of Phenylmethanamine Hydrochloride (6a·HCl).
Figure S9. $^1$H NMR (500 MHz, DMSO-$d_6$) of o-Tolylmethanamine Hydrochloride (6b·HCl).
Figure S10. $^{13}$C$\{^1\text{H}\}$NMR (126 MHz, DMSO-$d_6$) of o-Tolylmethanamine Hydrochloride (6b·HCl).
Figure S11. $^1$H NMR (500 MHz, DMSO-$d_6$) of $p$-Tolylmethanamine Hydrochloride (6c·HCl).
Figure S12. $^{13}\text{C}^{(1}\text{H})\text{NMR}$ (126 MHz, DMSO-$d_6$) of $m$-Tolylmethanamine Hydrochloride (6c·HCl).
**Figure S13.** $^1$H NMR (500 MHz, DMSO-$d_6$) of $p$-Tolylmethanamine Hydrochloride (6d·HCl).
Figure S14. $^{13}$C{1H}NMR (126 MHz, DMSO-$d_6$) of p-Tolylmethanamine Hydrochloride (6d·HCl).
Figure S15. $^1$H NMR (500 MHz, DMSO-$d_6$) of [1,1'-Biphenyl]-4-ylmethanamine Hydrochloride (6e·HCl).
Figure S16. $^{13}$C{H}NMR (126 MHz, DMSO-$d_6$) of [1,1'-Biphenyl]-4-ylmethanamine Hydrochloride (6e·HCl).
Figure S17. $^1$H NMR (500 MHz, DMSO-$d_6$) of (2-(Trifluoromethyl)phenyl)methanamine Hydrochloride (6f·HCl).
Figure S18. $^{13}$C$^{[1H]}$NMR (126 MHz, DMSO-$d_6$) of (2-(Trifluoromethyl)phenyl)methanamine Hydrochloride (6f·HCl).
Figure S19. $^1$H NMR (500 MHz, DMSO-$d_6$) of (3-(Trifluoromethyl)phenyl)methanamine Hydrochloride (6g-HCl).
Figure S20. $^{13}$C{1H}NMR (126 MHz, DMSO-$d_6$) of (3-(Trifluoromethyl)phenyl)methanamine Hydrochloride (6g·HCl).
Figure S21. $^1$H NMR (500 MHz, DMSO-$d_6$) of (4-(Trifluoromethyl)phenyl)methanamine Hydrochloride ($6\text{h}\cdot\text{HCl}$).
Figure S22. $^{13}$C{${}^{1}H$}NMR (126 MHz, DMSO-$d_6$) of (4-(Trifluoromethyl)phenyl)methanamine Hydrochloride (6h·HCl).
Figure S23. $^1$H NMR (500 MHz, DMSO-$d_6$) of (4-(tert-Butyldiphenylsilyloxy)phenyl)methanamine Hydrochloride (6o·HCl).
Figure S24. $^{13}$C{$^{1}$H}NMR (126 MHz, DMSO-$_d_6$) of (4-(tert-Butyldiphenylsilyloxy)phenyl)methanamine Hydrochloride (6o·HCl).
Figure S25. $^1$H NMR (500 MHz, DMSO-$d_6$) of (2-Chlorophenyl)methanamine Hydrochloride (6p·HCl).
Figure S26. $^{13}\text{C}^{1\text{H}}\text{NMR}$ (126 MHz, DMSO-$d_6$) of (2-Chlorophenyl)methanamine Hydrochloride (6p•HCl).
Figure S27. $^{13}$C{¹H}DEPT NMR (126 MHz, DMSO-$d_6$) of (2-Chlorophenyl)methanamine Hydrochloride (6p·HCl).
Figure S28. $^1$H NMR (500 MHz, DMSO-$d_6$) of (3-Chlorophenyl)methanamine Hydrochloride (6q·HCl).
Figure S29. $^{13}\text{C}^{\text{1H}}\text{NMR}$ (126 MHz, DMSO-$d_6$) of (3-Chlorophenyl)methanamine Hydrochloride ($6q\cdot\text{HCl}$).
Figure S30. $^1$H NMR (500 MHz, DMSO-$d_6$) of (4-Chlorophenyl)methanamine Hydrochloride (6r·HCl).
Figure S31. $^{13}$C($^1$H)NMR (126 MHz, DMSO-$d_6$) of (4-Chlorophenyl)methanamine Hydrochloride ($6\cdot$HCl).

![NMR Spectrum Image]
Figure S32. $^1$H NMR (500 MHz, DMSO-$d_6$) of (2-Bromophenyl)methanamine Hydrochloride (6s·HCl).
Figure S33. $^{13}$C($^1$H)NMR (126 MHz, DMSO-$d_6$) of (2-Bromophenyl)methanamine Hydrochloride (6s·HCl).
Figure S34. $^1$H NMR (500 MHz, DMSO-$d_6$) of (3-Bromophenyl)methanamine Hydrochloride (6t·HCl).
Figure S35. $^{13}$C{H}NMR (126 MHz, DMSO-$d_6$) of (3-Bromophenyl)methanamine Hydrochloride (6t·HCl).
Figure S36. $^1$H NMR (500 MHz, DMSO-$d_6$) of (4-Bromophenyl)methanamine Hydrochloride (6u·HCl).
Figure S37. $^{13}$C($^1$H)NMR (126 MHz, DMSO-$d_6$) of (4-Bromophenyl)methanamine Hydrochloride ($6\text{u}$-HCl).
Figure S38. $^1$H NMR (500 MHz, DMSO-$d_6$) of Ethanamine Hydrochloride (6v·HCl).
Figure S39. $^{13}$C$^{[1]H}_1$NMR (126 MHz, DMSO-$d_6$) of Ethanamine Hydrochloride (6v·HCl).
Figure S40. $^1$H NMR (500 MHz, DMSO-$d_6$) of Hex-5-en-1-amine Hydrochloride (6w·HCl).
Figure S41. $^{13}\text{C}^{1\text{H}}\text{NMR}$ (126 MHz, DMSO-$d_6$) of Hex-5-en-1-amine Hydrochloride ($6w\cdot\text{HCl}$).
Figure S42. $^1$H NMR (500 MHz, DMSO-$d_6$) of 2-Phenylethan-1-amine Hydrochloride (6x-HCl).
Figure S43. $^{13}$C–${}^1$H}NMR (126 MHz, DMSO-$d_6$) of 2-Phenylethan-1-amine Hydrochloride (6·HCl).
Figure S44. $^{13}$C{$^1$H}DEPT NMR (126 MHz, DMSO-$d_6$) of 2-Phenylethan-1-amine Hydrochloride (6x·HCl).
Figure S45. $^1$H NMR (500 MHz, DMSO-$d_6$) of Furan-2-ylmethanamine Hydrochloride ($6y$-HCl).
**Figure S46.** $^{13}\text{C}\{^1\text{H}\}\text{NMR}$ (126 MHz, DMSO-$d_6$) of Furan-2-ylmethanamine Hydrochloride (6y·HCl).
Figure S47. $^1$H NMR (500 MHz, CD$_2$Cl$_2$) of 1-Phenyl-N-(triethylsilyl)methanimine (5ab).
Figure S48. $^{13}$C$\{^1H\}$NMR (126 MHz, CD$_2$Cl$_2$) of 1-Phenyl-N-(triethylsilyl)methanimine (5ab).
Figure S49. $^{29}\text{Si}$ NMR (99 MHz, CD$_2$Cl$_2$) of 1-Phenyl-$N$-(triethylsilyl)methanimine (5ab).
Figure S50. $^1$H NMR (500 MHz, CD$_2$Cl$_2$) of $N$-(Triethylsilyl)-1-(4-(trifluoromethyl)phenyl)methanimine (5hb).
Figure S51. $^{13}\text{C}^{[1\text{H}]}\text{NMR}$ (126 MHz, CD$_2$Cl$_2$) of N-(Triethylsilyl)-1-(4-(trifluoromethyl)phenyl)methanimine (5hb).
Figure S52. $^{29}$Si NMR (99 MHz, CD$_2$Cl$_2$) of $N$-(Triethylsilyl)-1-(4-(trifluoromethyl)phenyl)methanimine (5hb).
Figure S53. $^1$H NMR (500 MHz, CD$_2$Cl$_2$) of 1-(4-(tert-Butyldiphenylsilyl)oxy)phenyl)-N-(triethylsilyl)methanimine (5ob).
Figure S54. $^{13}$C\textsuperscript{1H}NMR (126 MHz, CD$_2$Cl$_2$) of 1-(4-((tert-Butyldiphenylsilyl)oxy)phenyl)-N-(triethylsilyl)methanimine (5ob).
Figure S55. $^1$H NMR (500 MHz, CD$_2$Cl$_2$) of 1-(4-Chlorophenyl)-N-(triethylsilyl)methanimine (5rb).
Figure S56. $^{13}$C$\{^1\text{H}\}$NMR (126 MHz, CD$_2$Cl$_2$) of 1-(4-Chlorophenyl)-N-(triethylsilyl)methanimine (5rb).
Figure S57. $^{29}$Si NMR (99 MHz, CD$_2$Cl$_2$) of 1-(4-Chlorophenyl)-N-(triethylsilyl) methanimine (5rb).
Figure S58. $^1$H NMR (500 MHz, CD$_2$Cl$_2$) of 1-(4-Bromophenyl)-N-(triethylsilyl)methanimine (5ub).
Figure S59. $^{13}$C($^1$H)NMR (126 MHz, CD$_2$Cl$_2$) of 1-(4-Bromophenyl)-$N$-(triethylsilyl)methanimine (5ub).
Figure S60. $^{29}$Si NMR (99 MHz, CD$_2$Cl$_2$) of 1-(4-Bromophenyl)-N-(triethylsilyl)methanimine (5ub).
4 References


