Supporting Information

Nickel-Catalyzed Ligand Controlled Silylation and Reduction of Aryl Ammonium Salts

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I) General Experimental Details

All reagents were used as received unless otherwise noted. Solvents were purified under
nitrogen using a solvent purification system (Innovative Technology, Inc. Model # SPS400-3 and
PS-400-3). Et₃SiH (Sigma-Aldrich), BnMe₂SiH (Sigma-Aldrich), PhMe₂SiH (Sigma-Aldrich), and
(TMSO)MeSiH (TCI Chemicals) were passed through basic alumina and distilled before use
and stored under nitrogen. IPr*OMe (made from known procedure[1]), IMes·HCl (made from
known procedure[2]), other N-heterocyclic carbenes (Sigma-Aldrich), and NaO-t-Bu (Strem
Chemicals) were stored and weighed in an inert atmosphere glovebox.

Analytical thin layer chromatography (TLC) was performed on Kieselgel 60 F254 (250
µm silica gel) glass plates and compounds were visualized with UV light and p-anisaldehyde,
potassium permanganate or ceric ammonium molybdate stains. Flash column chromatography
was performed using Kieselgel 60 (230-400 mesh) silica gel. Eluent mixtures are reported as v:v
percentages of the minor constituent in the major constituent. All compounds purified by column
chromatography were sufficiently pure for use in further experiments unless otherwise indicated.

¹H NMR spectra were collected at 400 MHz on a Varian MR400, at 500 MHz on a Varian Inova
500 or Varian vnmrs 500, or at 700 MHz on a Varian vnmrs 700 instrument. The proton signal of
the residual, nondeuterated solvent (δ 7.26 for CHCl₃) was used as the internal reference for ¹H
NMR spectra. ¹³C NMR spectra were completely heterodecoupled and measured at 125 MHz or
175 MHz. Chloroform-d (δ 77.00) was used as an internal reference. High resolution mass spectra
were recorded on a VG 70-250-s spectrometer manufactured by Micromass Corp. (Manchester
UK) at the University of Michigan Mass Spectrometry Laboratory. GCMS analysis was carried
out on a HP 6980 Series GC system with HP-5MS column (30 m x 0.250 mm x 0.25 µm). GCFID
analysis was carried out on a HP 6980N Series GC system with a HP-5 column (30 m x 0.32 mm
x 0.25 µm).
II) General Procedures

**General procedure for nickel-catalyzed silylation of aryl ammonium salts:**

To an oven-dried 8 mL vial equipped with a Teflon-coated magnetic stir bar was added Ni(COD)$_2$ (2.8 mg, 0.01 mmol, 0.1 equiv), N,N'-Bis(2,6-bis(diphenylmethyl)-4-methoxyphenyl)imidazolium chloride (IPr*OMe·HCl) (9.8 mg, 0.01 mmol, 0.1 equiv), NaO-t-Bu (24 mg, 0.25 mmol, 2.5 equiv), and ammonium salt (0.1 mmol, 1 equiv) were combined under inert atmosphere and suspended in 0.5 mL of dioxane at rt. Silane (0.5 mmol, 5 equiv) was added and the vial was sealed with a Teflon cap before removing from the glovebox to heat to 40 °C overnight. Upon completion, the reaction mixture was quenched with 1 mL EtOAc and run through a silica gel plug with 5 mL EtOAc. The solvent was removed by rotary evaporation and the crude reaction mixture was purified by silica gel chromatography.

**Modified general procedure using air-tolerant nickel(0) catalyst:**

To an oven-dried 8 mL vial equipped with a Teflon-coated magnetic stir bar was added (1,3-Bis(2,6-bis(diphenylmethyl)-4-methoxyphenyl)imidazol-2-ylidene)bis(phenyl acrylate)nickel(0) (Ni(IPr*OMe)(phenyl acrylate)$_2$) (26 mg, 0.01 mmol, 0.1 equiv), NaO-t-Bu (48 mg, 0.50 mmol, 2.5 equiv), and ammonium salt 2a (68 mg, 0.2 mmol, 1 equiv) were combined under inert atmosphere and suspended in 1.0 mL of dioxane at rt. Triethylsilane (156 µL, 1.0 mmol, 5 equiv) was added and the vial was sealed with a Teflon cap before removing from the glovebox to heat to 40 °C overnight. Upon completion, the reaction mixture was quenched with 1 mL EtOAc and run through a silica gel plug with 5 mL EtOAc. Analysis of the crude reaction mixture by GCFID using tridecane as an internal standard showed 76% yield of aryl silane 2a and 13% yield of 3a. The solvent was removed by rotary evaporation and the crude reaction mixture was purified by flash chromatography (100% hexanes) to give 2a as a colorless oil in 67% yield (35.9 mg, 0.134 mmol).

**General procedure for nickel-catalyzed reduction of aryl ammonium salts:**

To an oven-dried 8 mL vial equipped with a Teflon-coated magnetic stir bar was added Ni(COD)$_2$ (2.8 mg, 0.01 mmol, 0.1 equiv), IMes-HCl (10 mol%), Et$_3$Si–H (5 equiv.), NaOtBu (2.5 equiv.) and DMF (0.2M), 40 °C, overnight.
To an oven-dried 8 mL vial equipped with a Teflon-coated magnetic stir bar was added Ni(COD)$_2$ (2.8 mg, 0.01 mmol, 0.1 equiv), 1,3-Bis(2,4,6-trimethylphenyl)imidazolium chloride (IMes·HCl) (3.4 mg, 0.01 mmol, 0.1 equiv), NaO-t-Bu (24 mg, 0.25 mmol, 2.5 equiv), and ammonium salt (0.1 mmol, 1 equiv) were combined under inert atmosphere and dissolved in 0.5 mL of DMF at rt. Triethylsilane (80 µL, 0.5 mmol, 5 equiv) was added and the vial was sealed with a Teflon cap before removing from the glovebox to heat to 40 ºC overnight. Upon completion, the reaction mixture was quenched with 1 mL EtOAc and run through a silica gel plug with 5 mL EtOAc. The solvent was removed by rotary evaporation and the crude reaction mixture was purified by silica gel chromatography.

**General procedures for reductive amination:**

\[
\begin{align*}
\text{R} & \quad \text{NH}_2 & \rightarrow & \quad \text{R} & \quad \text{NMe}_2 \\
\text{NaHB(OAc)$_3$} & \quad \text{formaldehyde}, \text{K$_2$CO$_3$} & \quad \text{AcOH} & \quad \text{CH}_3\text{CN} (0.25M), 0 \degree \text{C to r.t.} & \quad \text{overnight}
\end{align*}
\]

To an appropriately sized round-bottom flask equipped with a Teflon-coated magnetic stir bar under a nitrogen atmosphere were added aniline (1 equiv) and CH$_3$CN (0.25M). The flask was cooled to 0 ºC before adding formaldehyde solution (37%) (6 equiv) and K$_2$CO$_3$ (2 equiv). After 1 hour of stirring NaHB(OAc)$_3$ (3 equiv) was added followed by the slow addition of AcOH (11 equiv). The solution was warmed to room temperature after 30 min and stirred overnight. The reaction was quenched with H$_2$O and EtOAc. The solution was basified with sat. NaHCO$_3$ and extracted with 3xEtOAc. The organics were dried over brine, then Na$_2$SO$_4$ and concentrated before purifying by silica gel column chromatography.

**General procedures for Suzuki-Miura coupling:**

\[
\begin{align*}
\text{Br} & \quad \text{NMe}_2 & \rightarrow & \quad \text{Br} & \quad \text{NMe}_2 \\
\text{Boronic Acid} & \quad \text{K$_2$CO$_3$}, \text{Pd(OAc)$_2$} & \quad \text{acetylacetone} & \quad \text{H}_2\text{O}/\text{DMF} (1:1), 90 \degree \text{C} & \quad \text{overnight}
\end{align*}
\]

To an appropriately sized round-bottom flask equipped with a Teflon-coated magnetic stir bar and a reflux condenser was added 4-bromo-dimethylaniline (1.00 equiv), arylboronic acid (1.50 equiv), K$_2$CO$_3$ (2.00 equiv), Pd(OAc)$_2$ (0.01 equiv), and acetylacetone (0.02 equiv). The flask was backfilled with N$_2$ three times before adding H$_2$O (0.66M) and DMF (0.66M). The reaction was heated to 90 ºC overnight. The reaction was cooled and quenched with Et$_2$O and the organics were washed 1x H$_2$O, 2x brine. The organics were then dried over MgSO$_4$ and concentrated before purifying by silica gel column chromatography.$^{[3]}$

**General procedures for ammonium salt formation:**

\[
\begin{align*}
\text{R} & \quad \text{NMe}_2 & \rightarrow & \quad \text{R} & \quad \text{NMe}_3\text{I} \\
\text{MeI} & \quad \text{r.t.} & \quad \text{or} & \quad 40 \degree \text{C} & \quad \text{overnight}
\end{align*}
\]

To an appropriately sized vial equipped with a Teflon-coated magnetic stir bar and a reflux
condenser was added $N,N$-dimethylaniline (1.00 equiv) and MeI (10.00 equiv). The vial was sealed and stirred until a white precipitate formed. Electron deficient aniline typically required heating to 40 °C overnight while electron rich anilines reached full conversion in a few hours. The solid was then filtered washed copiously with Et₂O and rigorously dried on high vac for several hours. The trimethylammonium salts were used as is in subsequent chemistry. [4]
III) Starting Material Synthesis

![Chemical Structure](image)

\[ \text{N,N-dimethyl-[1,1'-biphenyl]-4-amine (2)} \]

The general procedure for Suzuki-Miura coupling was followed using 4-bromo-dimethylaniline (1.00 g, 5.00 mmol, 1.00 equiv), phenylboronic acid (914 mg, 7.5 mmol, 1.50 equiv), \( \text{K}_2\text{CO}_3 \) (1.38 g, 10.00 mmol, 2.00 equiv), Pd(OAc)\(_2\) (11 mg, 0.05 mmol, 0.01 equiv), acetylacetone (10 mg, 0.10 mmol, 0.02 equiv), \( \text{H}_2\text{O} \) (7.5 mL), and DMF (7.5 mL). Purification by flash chromatography (90:10 hexanes/EtOAc) gave the title compound as a white solid in 87% yield (690 mg, 3.49 mmol). The spectral data matches that previously reported in the literature.\(^3\)

\(^1\text{H NMR}\) (401 MHz, Chloroform-\(d\)) \( \delta \) 7.61 – 7.53 (m, 2H), 7.51 (d, \( J = 8.8 \) Hz, 2H), 7.39 (t, \( J = 7.6 \) Hz, 2H), 7.26 (m, 1H), 6.81 (d, \( J = 8.8 \) Hz, 2H), 3.00 (s, 6H).

\(^13\text{C NMR}\) (126 MHz, Chloroform-\(d\)) \( \delta \) 150.11, 141.36, 129.38, 128.77, 127.83, 126.42, 126.11, 112.90, 40.71.

\( \text{N,N-dimethyl-3',5'-bis(trifluoromethyl)-[1,1'-biphenyl]-4-amine (3)} \)

To an oven-dried 25-mL round-bottom flask containing a Teflon-coated magnetic stir bar were brought into a \( \text{N}_2 \) glovebox and Pd(PPh\(_3\))\(_4\) (34.7 mg, 0.03 mmol, 3 mol%) was added. The round bottom was sealed with a septa and removed from the glovebox. 4-bromo-\( \text{N,N-dimethylaniline} \) (200 mg, 1.00 mmol, 1.00 equiv) and 3,5-bis(trifluoromethyl)phenylboronic acid (257 mg, 1.00 mmol, 1.00 equiv) were added, followed by toluene (10 mL, 0.1M), EtOH (3 mL, 0.33M), and Sat. Na\(_2\text{CO}_3\) (5 mL). A reflux condensor was added and the reaction was heated to 80 \( ^\circ \)C overnight. The reaction was cooled to room temperature and quenched with \( \text{H}_2\text{O}\) (20 mL) and Et\(_2\)O (20 mL). The mixture was then extracted 2x20 mL Et\(_2\)O. The organic layers were washed with 50 mL brine, then dried over MgSO\(_4\). The organics were concentrate and purified by flash chromatography (100% to 95:5 hexanes/EtOAc) gave the title compound as a white solid in quantitative yield (333 mg, 1.00 mmol).\(^5\)

\(^1\text{H NMR}\) (400 MHz, Chloroform-\(d\)) \( \delta \) 7.97 (s, 2H), 7.74 (s, 1H), 7.63 – 7.47 (m, 2H), 6.90 – 6.74 (m, 2H), 3.04 (s, 6H).

\(^13\text{C NMR}\) (100 MHz, Chloroform-\(d\)) \( \delta \) 150.98, 143.38, 132.01 (q, \( J = 32.9 \) Hz), 127.96, 126.04, 123.74 (q, \( J = 273.6 \) Hz), 119.56 – 118.93 (m), 112.76, 40.45.

\(^19\text{F NMR}\) (376 MHz, Chloroform-\(d\)) \( \delta \) -62.91.
The general procedure for reductive amination was followed using p-toluidine (107 mg, 1.00 mmol, 1.00 equiv), NaHB(OAc)₃ (636 mg, 3.00 mmol, 3.00 equiv), formaldehyde solution (37%) (0.45 mL, 6.00 mmol, 6.00 equiv), K₂CO₃ (276 mg, 2.00 mmol, 2.00 equiv), AcOH (0.7 mL, 11.00 mmol, 11.00 equiv), CH₃CN (4 mL, 0.25M). Purification by flash chromatography (100% to 95:5 hexanes/EtOAc) gave the title compound as a colorless oil in 23% yield (31 mg, 0.23 mmol). The spectral data matches that previously reported in the literature. [6]

\[ \text{^{1}H NMR (500 MHz, Chloroform-d) } \delta 7.08 (d, J = 8.0 \text{ Hz, 2H}), 6.71 (d, J = 8.0 \text{ Hz, 2H}), 2.92 (s, 6H), 2.28 (s, 3H). \]

\[ \text{^{13}C NMR (126 MHz, Chloroform-d) } \delta 148.97, 129.71, 126.22, 113.34, 41.21, 20.39. \]

The general procedure for reductive amination was followed using 4-(tert-butyl)aniline (597 mg, 4.00 mmol, 1.00 equiv), NaHB(OAc)₃ (2.54 g, 12.00 mmol, 3.00 equiv), formaldehyde solution (37%) (1.05 mL, 14.00 mmol, 3.52 equiv), K₂CO₃ (1.11 g, 8.00 mmol, 2.00 equiv), AcOH (2 mL, 34.70 mmol, 8.70 equiv), CH₃CN (8 mL, 0.2M). Purification by flash chromatography (100% to 95:5 hexanes/EtOAc) gave the title compound as a colorless oil in quantitative yield (710 mg, 4.00 mmol). The spectral data matches that previously reported in the literature. [7]

\[ \text{^{1}H NMR (500 MHz, Chloroform-d) } \delta 7.34 – 7.26 (m, 2H), 6.81 – 6.71 (m, 2H), 2.93 (s, 6H), 1.31 (s, 9H). \]

\[ \text{^{13}C NMR (126 MHz, Chloroform-d) } \delta 148.71, 139.51, 125.98, 112.76, 40.99, 33.89, 31.67. \]

The general procedure for reductive amination was followed using 4-aminobenzotrifluoride (1.40 mL, 11.18 mmol, 1.00 equiv), NaHB(OAc)₃ (7.00 g, 34.54 mmol, 3.0 equiv), formaldehyde solution (37%) (4.99 mL, 67.08 mmol, 6.00 equiv), K₂CO₃ (3 g, 22.36 mmol, 2.00 equiv), AcOH (5 mL, 79.99 mmol, 7.09 equiv), CH₃CN (56 mL, 0.2M). Purification by flash chromatography (95:5 hexanes/EtOAc) gave the title compound as a white solid in 36% yield (751 mg, 4.02 mmol). The spectral data matches that previously reported in the literature. [8]

\[ \text{^{1}H NMR (500 MHz, Chloroform-d) } \delta 7.08 (d, J = 8.0 \text{ Hz, 2H}), 6.71 (d, J = 8.0 \text{ Hz, 2H}), 2.92 (s, 6H), 2.28 (s, 3H). \]

\[ \text{^{13}C NMR (126 MHz, Chloroform-d) } \delta 148.97, 129.71, 126.22, 113.34, 41.21, 20.39. \]
The general procedure for reductive amination was followed using p-anisidine (493mg, 4.00 mmol, 1.00 equiv), NaHB(OAc)$_3$ (2.54 g, 12.00 mmol, 3.00 equiv), formaldehyde solution (37%) (1.05 mL, 14.00 mmol, 3.52 equiv), K$_2$CO$_3$ (1.11 g, 8.00 mmol, 2.00 equiv), AcOH (2 mL, 34.70 mmol, 8.70 equiv), CH$_3$CN (8 mL, 0.2M). Purification by flash chromatography (90:10 hexanes/EtOAc) gave the title compound as a light yellow solid in 99% yield (600 mg, 3.97 mmol). The spectral data matches that previously reported in the literature.[9]

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 7.45 (d, $J = 8.4$ Hz, 2H), 6.70 (d, $J = 8.4$ Hz, 2H), 3.01 (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta$ 152.45, 126.44 (q, $J = 3.8$ Hz), 117.59 (q, $J = 32.6$ Hz), 111.28, 40.19.

$^{19}$F NMR (471 MHz, Chloroform-$d$) $\delta$ -60.86.

4-methoxy-$N,N$-dimethylaniline (9)

The general procedure for reductive amination was followed using 4-phenoxyaniline (741mg, 4.00 mmol, 1.00 equiv), NaHB(OAc)$_3$ (2.54 g, 12.00 mmol, 3.00 equiv), formaldehyde solution (37%) (1.05 mL, 14.00 mmol, 3.52 equiv), K$_2$CO$_3$ (1.11 g, 8.00 mmol, 2.00 equiv), AcOH (2 mL, 34.70 mmol, 8.70 equiv), CH$_3$CN (8 mL, 0.2M). Purification by flash chromatography (95:5 hexanes/EtOAc) gave the title compound as a clear oil in 94% yield (600 mg, 3.75 mmol). The spectral data matches that previously reported in the literature.[10]

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 6.86 (d, $J = 9.2$ Hz, 2H), 6.80 – 6.74 (m, 2H), 3.78 (s, 3H), 2.88 (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta$ 159.23, 147.80, 147.43, 129.62, 122.05, 121.06, 117.28, 114.08, 41.95.

$N,N$-dimethyl-4-phenoxyaniline (10)

The general procedure for reductive amination was followed using 4-phenoxyaniline (741mg, 4.00 mmol, 1.00 equiv), NaHB(OAc)$_3$ (2.54 g, 12.00 mmol, 3.00 equiv), formaldehyde solution (37%) (1.05 mL, 14.00 mmol, 3.52 equiv), K$_2$CO$_3$ (1.11 g, 8.00 mmol, 2.00 equiv), AcOH (2 mL, 34.70 mmol, 8.70 equiv), CH$_3$CN (8 mL, 0.2M). Purification by flash chromatography (95:5 hexanes/EtOAc) gave the title compound as a clear oil in 94% yield (600 mg, 3.75 mmol). The spectral data matches that previously reported in the literature.[10]

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 7.28 (d, $J = 7.5$ Hz, 1H), 7.03 – 6.99 (m, 1H), 6.96 (d, $J = 9.0$ Hz, 2H), 6.95 – 6.91 (m, 2H), 6.74 (d, $J = 9.0$ Hz, 2H), 2.94 (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta$ 159.23, 147.80, 147.43, 129.62, 122.05, 121.06, 117.28, 114.08, 41.36.

(4-(dimethylamino)phenyl)methanol (11')
To an oven-dried 10-mL round-bottom flask containing a Teflon-coated magnetic stir bar under a nitrogen atmosphere was added 4-dimethylaminobenzaldehyde (149 mg, 1.00 mmol, 1.00 equiv) and THF (2.5 mL, 0.25M). The flask was cooled to 0 ºC and LiAlH₄ (38 mg, 1.00 mmol, 1.00 equiv) was added. The reaction was stirred for 4 hours at 0 ºC before quenching with MeOH (2 mL) and H₂O (2 mL). The reaction was diluted with 10 mL H₂O and extracted 3x10 mL Et₂O. The organic layers were dried with 20 mL brine and then MgSO₄ before concentrating.

Purification by flash chromatography (90:10 hexanes/EtOAc) gave the title compound as a clear oil in 95% yield (144 mg, 0.952 mmol). The spectral data matches that previously reported in the literature. [1]

**1H NMR** (400 MHz, Chloroform- d) δ 7.25 (d, J = 8.3 Hz, 2H), 6.84 – 6.62 (m, 2H), 4.57 (s, 2H), 2.96 (s, 6H).

**13C NMR** (100 MHz, Chloroform- d) δ 150.51, 129.02, 128.77, 112.76, 65.51, 40.79.

4-((tert-butyldimethylsilyl)oxy)methyl)-N,N-dimethylaniline (11)

To an oven-dried 25-mL round-bottom flask containing a Teflon-coated magnetic stir bar under a nitrogen atmosphere were added 11' (1.00 g, 6.61 mmol, 1.00 equiv) and DCM (6.60 mL, 1M). The solution was cooled to 0 ºC before adding TBSCI (1.00 g, 6.61 mmol, 1.00 equiv) and imidazole (900 mg, 13.22 mmol, 2.00 equiv). The reaction was then warmed to room temperature and stirred for 15 min. The reaction was quenched with sat. NaHCO₃ and extracted 3x30 mL hexanes. The organics were dried 1x30 mL brine and Na₂SO₄ before concentrating. The title compound was obtained in yield as a clear oil in 94% yield (1.65 g, 6.23 mmol) pure by NMR.

**1H NMR** (401 MHz, Chloroform- d) δ 7.19 (d, J = 8.6 Hz, 2H), 6.72 (d, J = 8.7 Hz, 2H), 4.64 (s, 2H), 2.93 (s, 6H), 0.93 (s, 9H), 0.08 (s, 6H).

**13C NMR** (126 MHz, Chloroform- d) δ 150.07, 129.66, 127.66, 112.76, 65.15, 40.95, 26.17, 25.80, -4.97.

**HRMS (ESI) (m/z):** [M+H] calculated for C₁₅H₂₇NOSi, 266.1940, found, 266.1945.

4'-(dimethylamino)-[1,1'-biphenyl]-4-ol (12')

The general procedure for Suzuki-Miura coupling was followed using 4-bromo-dimethylaniline (200 mg, 1.00 mmol, 1.00 equiv), 4-hydroxyphenylboronic acid (207mg, 1.5 mmol, 1.50 equiv), K₂CO₃ (275 mg, 2.00 mmol, 2.00 equiv), Pd(OAc)₂ (2.2 mg, 0.01 mmol, 0.01 equiv), acetylacetone (2 mg, 0.02 mmol, 0.02 equiv), H₂O (2 mL), and DMF (2 mL). Purification by flash chromatography (70:30 hexanes/EtOAc) gave the title compound as a white solid in 95% yield (203 mg, 0.952 mmol). The spectral data matches that previously reported in the
literature.[12]

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 9.74 (br), 7.52 – 7.34 (m, 4H), 6.95 – 6.72 (m, 4H), 2.97 (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta$ 154.30, 149.76, 134.27, 129.54, 127.69, 127.44, 115.68, 113.33, 40.95.

HRMS (EI) (m/z): [M] calculated for C$_{20}$H$_{29}$NOSi, 328.2091, found, 328.2096.

To an oven-dried 25-mL round-bottom flask containing a Teflon-coated magnetic stir bar under a nitrogen atmosphere were added 12' (670 mg, 3.14 mmol, 1.00 equiv) and DCM (6.28 mL, 0.5M). The solution was cooled to 0 ºC before adding TBSCl (473 mg, 3.14 mmol, 1.00 equiv) and imidazole (428 mg, 6.28 mmol, 2.00 equiv). The reaction was then warmed to room temperature and stirred for 15 min. The reaction was quenched with sat. NaHCO$_3$ and extracted 3x30 mL hexanes. The organics were dried 1x30 mL brine and Na$_2$SO$_4$ before concentrating. The title compound was obtained in yield as an off-white crystalline solid in 76% yield (780 mg, 2.39 mmol) pure by NMR.

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 7.45 (d, $J$ = 8.7 Hz, 2H), 7.41 (d, $J$ = 8.6 Hz, 2H), 6.87 (d, $J$ = 8.5 Hz, 2H), 6.80 (d, $J$ = 8.3 Hz, 2H), 2.98 (s, 6H), 1.01 (s, 9H), 0.23 (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta$ 154.40, 149.73, 134.57, 129.41, 127.45, 127.34, 120.34, 113.04, 40.83, 25.88, 18.39, -4.22.

To an oven-dried 25-mL round-bottom flask containing a Teflon-coated magnetic stir bar were brought into a N$_2$ glovebox and Pd$_2$(dba)$_3$ (11.4 mg, 0.0125 mmol, 0.5 mol%), P(tert-Bu)$_3$ (5.1 mg, 0.05 mmol, 1 mol%), and NaO-t-Bu (250 mg, 2.50 mmol, 1.00 equiv) were added. The round bottom was sealed with a septa and removed from the glovebox. Toluene (5 mL, 0.5M) and morpholine (0.27 mL, 3.12 mmol, 1.25 equiv) were added, followed by 3-bromo-$N,N$-dimethylaniline (500 mg, 2.50 mmol, 1.00 equiv). The reaction was stirred at room temperature overnight. The reaction was quenched with 20 mL H$_2$O and extracted 3x30 mL Et$_2$O. The organics were washed with 60 mL brine and dried over MgSO$_4$ before concentrating. Purification by flash chromatography (90:10 to 1:1 hexanes/EtOAc) gave the title compound as a yellowish
powder in 62% yield (320 mg, 1.55 mmol). The spectral data matches that previously reported in the literature.\textsuperscript{[13]}

\textbf{\textsuperscript{1}H NMR} (500 MHz, Chloroform-d) \(\delta\) 6.90 (d, \(J = 8.9\) Hz, 2H), 6.76 (d, \(J = 9.0\) Hz, 2H), 3.89 – 3.84 (m, 4H), 3.08 – 3.01 (m, 4H), 2.88 (s, 6H).

\textbf{\textsuperscript{13}C NMR} (126 MHz, Chloroform-d) \(\delta\) 151.98, 138.24, 120.93, 115.53, 66.59, 58.13, 47.97.

\includegraphics{images/14.png}

\textit{N,N-dimethyl-3-morpholinoaniline (14)}

To an oven-dried 25-mL round-bottom flask containing a Teflon-coated magnetic stir bar were brought into a \(\text{N}_2\) glovebox and \(\text{Pd}_2(\text{dba})_3\) (22.9 mg, 0.025 mmol, 0.5 mol%), \(\text{P(tert-Bu)}_3\) (10.1 mg, 0.05 mmol, 1 mol%), and \(\text{NaO-\text{t-Bu}}\) (481 mg, 5.00 mmol, 1.00 equiv) were added. The round bottom was sealed with a septa and removed from the glovebox. Toluene (10 mL, 0.5M) and morpholine (0.54 mL, 6.25 mmol, 1.25 equiv) were added, followed by 3-bromo-\(N,N\)-dimethylaniline (1.00 g, 5.00 mmol, 1.00 equiv). The reaction was stirred at room temperature overnight. The reaction was quenched with 20 mL \(\text{H}_2\text{O}\) and extracted 3x30 mL \(\text{Et}_2\text{O}\). The organics were washed with 60 mL brine and dried over \(\text{MgSO}_4\) before concentrating. Purification by flash chromatography (70:30 hexanes/\(\text{EtOAc}\)) gave the title compound as a yellowish oil in 35% yield (360 mg, 1.80 mmol). The spectral data matches that previously reported in the literature.\textsuperscript{[13]}

\textbf{\textsuperscript{1}H NMR} (500 MHz, Chloroform-d) \(\delta\) 7.15 (t, \(J = 8.1\) Hz, 1H), 6.34 (dd, \(J = 8.2, 2.1\) Hz, 2H), 6.28 (s, 1H), 3.86 (t, \(J = 4.7\) Hz, 4H), 3.16 (t, \(J = 4.7\) Hz, 4H), 2.94 (s, 6H).

\textbf{\textsuperscript{13}C NMR} (126 MHz, Chloroform-d) \(\delta\) 152.66, 151.83, 129.76, 105.63, 105.11, 100.89, 67.21, 50.00, 40.90.

\includegraphics{images/15.png}

\textit{N,N-dimethyl-4-(1-propyl-1H-pyrazol-4-yl)aniline (15)}

The general procedure for Suzuki-Miura coupling was followed using 4-bromo-dimethylaniline (400 mg, 2.00 mmol, 1.00 equiv), 1-propylpyrazole-4-boronic acid (462mg, 3.00 mmol, 1.50 equiv), \(\text{K}_2\text{CO}_3\) (553 mg, 4.00 mmol, 2.00 equiv), \(\text{Pd(OAc)}_2\) (4.5 mg, 0.02 mmol, 0.01 equiv),
acetylace tone (4 mg, 0.04 mmol, 0.02 equiv), H₂O (7 mL), and DMF (7 mL). Purification by flash chromatography (80:20 hexanes/EtOAc) gave the title compound as a white solid in 76% yield (350 mg, 1.52 mmol).

**¹H NMR** (500 MHz, Chloroform-\(d\)) \(\delta\): 7.69 (d, \(J = 0.8\) Hz, 1H), 7.52 (d, \(J = 0.8\) Hz, 1H), 7.36 (d, \(J = 8.8\) Hz, 2H), 6.75 (d, \(J = 8.8\) Hz, 2H), 4.09 (t, \(J = 7.1\) Hz, 2H), 2.96 (s, 6H), 1.92 (q, \(J = 7.3\) Hz, 2H), 0.95 (t, \(J = 7.4\) Hz, 3H).

**¹³C NMR** (126 MHz, Chloroform-\(d\)) \(\delta\): 149.45, 136.17, 126.49, 125.09, 123.07, 121.47, 113.18, 54.08, 40.86, 23.93, 11.34.

**HRMS** (ESI) (m/z): [M+H] calculated for C\(_{14}\)H\(_{19}\)N\(_3\), 230.1657, found, 230.1649.

1**6**

\(N,N,2,5\)-tetramethylaniline (16)

The general procedure for reductive amination was followed using 2,5-dimethylaniline (0.5 mL, 4.06 mmol, 1.00 equiv), NaHB(OAc)\(_3\) (2.59 g, 12.20 mmol, 3.00 equiv), formaldehyde solution (37%) (1.05 mL, 14.00 mmol, 3.52 equiv), K\(_2\)CO\(_3\) (1.12 g, 8.12 mmol, 2.00 equiv), AcOH (2 mL, 34.70 mmol, 8.70 equiv), CH\(_3\)CN (8 mL, 0.2M). Aqueous workup gave the title compound as a clear oil, pure by NMR, in 76% yield (450 mg, 3.09 mmol). The spectral data matches that previously reported in the literature.\(^{14}\)

**¹H NMR** (500 MHz, Chloroform-\(d\)) \(\delta\): 7.04 (d, \(J = 7.5\) Hz, 1H), 6.84 (s, 1H), 6.77 (d, \(J = 7.6\) Hz, 1H), 2.69 (s, 6H), 2.31 (s, 3H), 2.28 (s, 3H).

**¹³C NMR** (126 MHz, Chloroform-\(d\)) \(\delta\): 153.46, 136.07, 131.12, 128.97, 123.33, 119.26, 44.39, 21.36, 18.10.

1**7’**

1-(4-(dimethylamino)phenyl)cyclohexan-1-ol (17’)

To an oven-dried 10–mL round-bottom flask containing a Teflon-coated magnetic stir bar were added freshly ground magnesium metal (64 mg, 2.62 mmol, 1.05 equiv) and 4-bromodimethylaniline (500 mg, 2.50 mmol, 1.00 equiv). THF (4 mL) was added along with a small crystal of I\(_2\) (to activate the magnesium) and the mixture was stirred until nearly all of the magnesium was consumed. The mixture was cooled in a salt/ice bath for 10 minutes before adding cyclohexanone (0.23 mL, 2.25 mmol, 0.90 equiv) dropwise. The reaction was then stirred
for 1 hour before warming to room temperature overnight. The solution was poured into a sat.
NH₄Cl solution and extracted 3x20 mL DCM. The organics were dried over Na₂SO₄ and
concentrated. Purification by flash chromatography (90:10 to 80:20 hexanes/EtOAc) gave the title
compound as a white solid in 45% yield (224 mg, 1.02 mmol). The spectral data matches that
previously reported in the literature.¹⁵

¹H NMR (500 MHz, Chloroform-d) δ 7.42 (dd, J = 8.9, 2.2 Hz, 2H), 6.78 (dd, J = 8.9, 2.2 Hz,
2H), 2.98 (s, 6H), 1.93 – 1.72 (m, 8H), 1.64 (dd, J = 11.1, 4.7 Hz, 2H), 1.40 – 1.26 (m, 1H).
¹³C NMR (126 MHz, Chloroform-d) δ 149.36, 137.50, 125.46, 112.41, 72.48, 40.66, 38.80,
25.66, 22.38.

¹H NMR (400 MHz, Chloroform-d) δ 7.30 (d, J = 8.4 Hz, 2H), 6.71 (d, J = 8.4 Hz, 2H), 6.01 (s,
1H), 2.94 (s, 6H), 2.39 (q, J = 5.2 Hz, 2H), 2.19 (dq, J = 6.4, 3.2 Hz, 2H), 1.77 (q, J = 5.9 Hz,
2H), 1.66 (q, J = 5.9 Hz, 2H).
¹³C NMR (100 MHz, Chloroform-d) δ 149.64, 136.12, 131.33, 125.67, 121.70, 112.63, 40.87,
27.48, 26.01, 23.36, 22.50.

A modified general procedure for reductive amination was followed using 3,4-(dimethylenoxy)aniline (2 g, 14.06 mmol, 1.00 equiv), NaH₃BCN (917 mg, 14.06 mmol, 1.00 equiv), formaldehyde solution (37%) (3.60 mL, 45.2 mmol, 3.10 equiv), ZnCl₂ (1 g, 7.30 mmol,
0.50 equiv), MeOH (70 mL, 0.2M). Aqueous workup gave the title compound as a clear oil, pure
by NMR, in 14% yield (340 mg, 1.97 mmol). The spectral data matches that previously reported
in the literature.¹⁶
The general procedure for Suzuki-Miura coupling was followed using 4-bromo-dimethylaniline (400 mg, 2.00 mmol, 1.00 equiv), 2,4-difluoroophenylboronic acid (472 mg, 3.00 mmol, 1.50 equiv), K$_2$CO$_3$ (553 mg, 4.00 mmol, 2.00 equiv), Pd(OAc)$_2$ (4.5 mg, 0.02 mmol, 0.01 equiv), acetylacetone (4 mg, 0.04 mmol, 0.02 equiv), H$_2$O (7 mL), and DMF (7 mL). Purification by flash chromatography (95:5 to 90:10 hexanes/EtOAc) gave the title compound as an off-white solid in quantitative yield.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.42 – 7.38 (m, 2H), 7.36 (dd, $J = 8.9$, 6.6 Hz, 1H), 6.89 (dddd, $J = 13.3$, 11.3, 8.5, 2.7 Hz, 2H), 6.82 – 6.76 (m, 2H), 3.00 (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta$ 162.63, 162.54, 150.14, 130.90 (q, $J = 5.3$ Hz) 129.70 (d, $J = 3.2$ Hz), 122.88, 112.45, 111.43 (dd, $J = 3.6$ Hz), 104.43 (d, $J = 25.4$ Hz), 104.22 (d, $J = 25.3$ Hz), 40.62.

$^{19}$F NMR (471 MHz, Chloroform-$d$) $\delta$ -113.56 (p, $J = 7.6$ Hz), -114.04 (q, $J = 9.0$ Hz).

HRMS (ESI) (m/z): [M+H] calculated for C$_{14}$H$_{13}$F$_2$N, 234.1094, found, 234.1090.
IV) Supplemental Tables

**Table S1**: Ligand screening for the optimization of the silylation of 1a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ligand</th>
<th>Yield 2a (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Yield 3a (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PPh&lt;sub&gt;3&lt;/sub&gt;</td>
<td>&lt;1</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>PCy&lt;sub&gt;3&lt;/sub&gt;</td>
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<td>&lt;1</td>
</tr>
<tr>
<td>3</td>
<td>ICy⋅HCl</td>
<td>&lt;1</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>IMes⋅HCl</td>
<td>&lt;1</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>IPr⋅HCl</td>
<td>14</td>
<td>7</td>
</tr>
<tr>
<td>6</td>
<td>IPr&lt;sup&gt;Me&lt;/sup&gt;⋅HCl</td>
<td>21</td>
<td>5</td>
</tr>
<tr>
<td>7</td>
<td>IPr&lt;sup&gt;Cl&lt;/sup&gt;⋅HCl</td>
<td>12</td>
<td>8</td>
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<tr>
<td>8</td>
<td>IPr&lt;sup&gt;OMe&lt;/sup&gt;⋅HCl</td>
<td>89</td>
<td>11</td>
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<tr>
<td>9</td>
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<td>&lt;1&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>10</td>
<td>none</td>
<td>10</td>
<td>90</td>
</tr>
</tbody>
</table>

Following the general procedure for silylation of ammonium salts, reaction were run for 6 hours, and quenched. <sup>a</sup> Yield determined by GCFID of the crude reaction mixture using tridecane as an internal standard. <sup>b</sup> Used DMF instead of dioxane.

**Table S2**: Solvent screening for the optimization of the silylation of 1a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Yield 2a (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Yield 3a (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MeOH</td>
<td>&lt;1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CN</td>
<td>&lt;1</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>DME</td>
<td>&lt;1</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>toluene</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>5</td>
<td>Et&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>6</td>
<td>THF</td>
<td>65</td>
<td>37</td>
</tr>
<tr>
<td>7</td>
<td>dioxane</td>
<td>89</td>
<td>11</td>
</tr>
</tbody>
</table>

Following the general procedure for silylation of ammonium salts, reaction were run for 6 hours, and quenched. <sup>a</sup> Yield determined by GCFID of the crude reaction mixture using tridecane as an internal standard.
Following the general procedure for silylation of ammonium salts, reactions were run for 6 hours, and quenched. a Yield determined by GCFID of the crude reaction mixture using tridecane as an internal standard. b 1 equiv base used.

### Table S3: Base screening for the optimization of the silylation of 1a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base</th>
<th>Yield 2a (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Yield 3a (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>none</td>
<td>&lt;1</td>
<td>&lt;1</td>
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<tr>
<td>2</td>
<td>NaOMe</td>
<td>24</td>
<td>&lt;1</td>
</tr>
<tr>
<td>3</td>
<td>LiO-t-Bu</td>
<td>41</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>KO-t-Bu</td>
<td>48</td>
<td>7</td>
</tr>
<tr>
<td>5</td>
<td>NaO-t-Bu</td>
<td>89</td>
<td>11</td>
</tr>
<tr>
<td>6&lt;sup&gt;b&lt;/sup&gt;</td>
<td>NaO-t-Bu</td>
<td>72</td>
<td>13</td>
</tr>
<tr>
<td>7</td>
<td>Cs₂CO₃</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>8</td>
<td>Et₃N</td>
<td>48</td>
<td>7</td>
</tr>
<tr>
<td>9</td>
<td>pyridine</td>
<td>55</td>
<td>12</td>
</tr>
</tbody>
</table>

### Table S4: Ligand screening for the optimization of the reduction of 8

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ligand</th>
<th>Yield 4a (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>none</td>
<td>15</td>
</tr>
<tr>
<td>2&lt;sup&gt;b&lt;/sup&gt;</td>
<td>PPh₃</td>
<td>45</td>
</tr>
<tr>
<td>3&lt;sup&gt;b&lt;/sup&gt;</td>
<td>PCy₃</td>
<td>31</td>
</tr>
<tr>
<td>4</td>
<td>IMes·HCl</td>
<td>56</td>
</tr>
<tr>
<td>5</td>
<td>SIMes·HCl</td>
<td>47</td>
</tr>
<tr>
<td>6</td>
<td>IAd·HCl</td>
<td>46</td>
</tr>
<tr>
<td>8</td>
<td>IPr*OMe·HCl</td>
<td>49</td>
</tr>
</tbody>
</table>
Following the general procedure for silylation of ammonium salts, reaction were run for 12 hours, and quenched. Superscript a yield determined by GCFID of the crude reaction mixture using tridecane as an internal standard. Superscript b Reaction run for 6 hours.

**Table S5: Solvent screening for the optimization of the reduction of 8**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Yield 4a (%)^a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>dioxane</td>
<td>29</td>
</tr>
<tr>
<td>2</td>
<td>THF</td>
<td>27</td>
</tr>
<tr>
<td>3</td>
<td>DMF</td>
<td>56</td>
</tr>
<tr>
<td>4^a</td>
<td>DMF</td>
<td>58</td>
</tr>
<tr>
<td>5^c</td>
<td>DMF</td>
<td>51</td>
</tr>
<tr>
<td>6^d</td>
<td>DMF</td>
<td>60</td>
</tr>
</tbody>
</table>

Following the general procedure for silylation of ammonium salts, reaction were run for 12 hours, and quenched. Superscript a yield determined by GCFID of the crude reaction mixture using tridecane as an internal standard. Superscript b Reaction run at 80 ºC. Superscript c Reaction run at 40 ºC. Superscript d Reaction run at room temperature (21 ºC).

**Table S6: Reductant screening for the optimization of the reduction of 8**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reductant</th>
<th>Yield 4a (%)^a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Et₂SiH₂</td>
<td>54</td>
</tr>
<tr>
<td>2</td>
<td>Et₂SiH</td>
<td>56</td>
</tr>
<tr>
<td>3</td>
<td>Ph₂SiH</td>
<td>48</td>
</tr>
<tr>
<td>4</td>
<td>i-Pr₂SiH</td>
<td>24</td>
</tr>
<tr>
<td>5</td>
<td>Me(OTMS)₂SiH</td>
<td>18</td>
</tr>
<tr>
<td>6</td>
<td>Ti(i-OPr)₄</td>
<td>42</td>
</tr>
</tbody>
</table>

Following the general procedure for silylation of ammonium salts, reaction were run for 12 hours, and quenched. Superscript a yield determined by GCFID of the crude reaction mixture using tridecane as an internal standard.
V) Calibration Curves

Solutions containing a constant concentration of an internal standard (tridecane (0.164 M) and varying concentrations of the desired product (0.05, 0.10, 0.15 and 0.20 M) were prepared in ethyl acetate. Each was analyzed by GC-FID and the response factor (F) calculated by solving equation S1 for the area of product to give equation S2, where the response factor (F) is the slope. Yields of crude reactions mixtures, containing a known amount of internal standard, were then determined by solving Equation S1 for the concentration of the product to give Equation S3 and filling in the known data from a crude reaction.

\[
\frac{(\text{Area of Product})}{(\text{Concentration of Product})} = F \times \frac{(\text{Area of Standard})}{(\text{Concentration of Standard})}
\]

(Equation S1)

\[
\text{Area of Product} = F \times \left( \frac{(\text{Area of Standard} \times (\text{Concentration of Product})}{(\text{Concentration of Standard})} \right)
\]

(Equation S2)

\[
\text{Concentration of Product} = \frac{(\text{Concentration of Standard} \times \text{Area of Product})}{(F \times (\text{Area of Standard}))}
\]

(Equation S3)

Calibration curve for [1,1'-biphenyl]-4-yltriethylsilane (Compound 2a):

\[
y = 1.6459x - 2 \times 10^8
\]

\[
R^2 = 0.99938
\]

Figure 1: Plot of 2a area versus (std area x [2a]) / [std] fitted to \( y = mx + b \) where \( m = 1.6459 \) and \( b = -2 \times 10^8 \) with a \( R^2 \) of 0.9994.

<table>
<thead>
<tr>
<th>mmol 2a</th>
<th>mmol tridecane</th>
<th>Area IS</th>
<th>Area Pdt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.048420739</td>
<td>0.16403</td>
<td>7535226346</td>
<td>3329460100</td>
</tr>
<tr>
<td>0.08715733</td>
<td>0.16403</td>
<td>6961574030</td>
<td>5961048038</td>
</tr>
<tr>
<td>0.143027414</td>
<td>0.16403</td>
<td>6242681983</td>
<td>8751150218</td>
</tr>
<tr>
<td>0.192938021</td>
<td>0.16403</td>
<td>6254367926</td>
<td>11816631504</td>
</tr>
</tbody>
</table>
Calibration curve for [1,1'-biphenyl]-4-yl(benzyl)dimethylsilane (2b):

**Figure S2:** Plot of 2b area versus (std area x [2b]) / [std] fitted to $y = mx + b$ where $m = 0.5795$ and $b = -1 \times 10^8$ with a $R^2$ of 0.99674.

<table>
<thead>
<tr>
<th>mmol 2b</th>
<th>mmol tridecane</th>
<th>Area IS</th>
<th>Area Pdt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.91768E-06</td>
<td>0.164026904</td>
<td>3947284982</td>
<td>419876796</td>
</tr>
<tr>
<td>0.049919006</td>
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<td>3315120257</td>
<td>1789461089</td>
</tr>
<tr>
<td>0.102152137</td>
<td>0.164026904</td>
<td>3575670979</td>
<td>3999385208</td>
</tr>
<tr>
<td>0.150418196</td>
<td>0.164026904</td>
<td>3564399649</td>
<td>6087760854</td>
</tr>
<tr>
<td>0.199345433</td>
<td>0.164026904</td>
<td>3665141539</td>
<td>7872337807</td>
</tr>
</tbody>
</table>
Calibration curve for biphenyl (3a):

**Figure S3:** Plot of analyte area versus (std area x [3a]) / [std] fitted to $y = mx + b$ where $m = 0.951$ and $b = 4 \times 10^7$ with a $R^2$ of 0.9998.

<table>
<thead>
<tr>
<th>mmol 3a</th>
<th>mmol tridecane</th>
<th>Area IS</th>
<th>Area Pdt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0509</td>
<td>0.16403</td>
<td>5647778523</td>
<td>1707314294</td>
</tr>
<tr>
<td>0.0966</td>
<td>0.16403</td>
<td>6596748815</td>
<td>3699921557</td>
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<tr>
<td>0.1582</td>
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<td>6622184645</td>
<td>6149186696</td>
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<tr>
<td>0.192</td>
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<td>6176751384</td>
<td>6891778392</td>
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<tr>
<td>0.0509</td>
<td>0.16403</td>
<td>5647778523</td>
<td>1707314294</td>
</tr>
</tbody>
</table>

Calibration curve for diphenyl ether (4a):

**Figure S4:** Plot of 4a area versus (std area x [4a]) / [std] fitted to $y = mx + b$ where $m = 1.5018$ and $b = 0$ with a $R^2$ of 0.99963.
<table>
<thead>
<tr>
<th>mmol 4a</th>
<th>mmol tridecane</th>
<th>Area IS</th>
<th>Area Pdt.</th>
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</thead>
<tbody>
<tr>
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</tr>
<tr>
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<td>3522436673</td>
<td>1891415126</td>
</tr>
<tr>
<td>0.202398676</td>
<td>0.164026904</td>
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<td>3112052070</td>
</tr>
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<td>0.270229584</td>
<td>0.164026904</td>
<td>320105098</td>
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</tr>
<tr>
<td>0.336966444</td>
<td>0.164026904</td>
<td>3504987328</td>
<td>4783168130</td>
</tr>
</tbody>
</table>

Calibration curve for trifluorotolunene (19b):

![Calibration curve graph](image)

**Figure S5:** Plot of $19b$ area versus (std area x $[19b]$) / [std] fitted to $y = mx + b$ where $m = 2.2662$ and $b = 0$ with a $R^2$ of 0.97223.

<table>
<thead>
<tr>
<th>mmol 19b</th>
<th>mmol tridecane</th>
<th>Area IS</th>
<th>Area Pdt.</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.16403</td>
<td>4492524320</td>
<td>574994724</td>
</tr>
<tr>
<td>0.100061597</td>
<td>0.16403</td>
<td>3927418367</td>
<td>1032274349</td>
</tr>
<tr>
<td>0.150092396</td>
<td>0.16403</td>
<td>4914023783</td>
<td>1990945854</td>
</tr>
<tr>
<td>0.200123195</td>
<td>0.16403</td>
<td>3902305473</td>
<td>1878381691</td>
</tr>
<tr>
<td>0.250153994</td>
<td>0.16403</td>
<td>4893566950</td>
<td>3494602386</td>
</tr>
</tbody>
</table>
Calibration curve for anisole (19c):

\[ y = 2.1214x \]
\[ R^2 = 0.99673 \]

**Figure S6:** Plot of 19c area versus (std area x [19c])/[std] fitted to \( y = mx + b \) where \( m = 2.1214 \) and \( b = 0 \) with a \( R^2 \) of 0.99673.

<table>
<thead>
<tr>
<th>mmol 19c</th>
<th>mmol tridecane</th>
<th>Area IS</th>
<th>Area Pdt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0501862</td>
<td>0.164026904</td>
<td>400010473</td>
<td>527950383</td>
</tr>
<tr>
<td>0.101301774</td>
<td>0.164026904</td>
<td>3537739243</td>
<td>960449091</td>
</tr>
<tr>
<td>0.151487974</td>
<td>0.164026904</td>
<td>3236629289</td>
<td>1427195136</td>
</tr>
<tr>
<td>0.201674174</td>
<td>0.164026904</td>
<td>3602495138</td>
<td>1828214896</td>
</tr>
<tr>
<td>0.252789749</td>
<td>0.164026904</td>
<td>3975653755</td>
<td>2912617178</td>
</tr>
</tbody>
</table>

Calibration curve for naphthalene (19e):

\[ y = 0.9816x - 6.9783 \]
\[ R^2 = 0.95217 \]

**Figure S7:** Plot of 19e area versus (std area x [19e])/[std] fitted to \( y = mx + b \) where \( m = 0.9816 \) and \( b = -6.9783 \) with a \( R^2 \) of 0.95217.
### Calibration curve for t-butylbenzene (19f):

Figure S8: Plot of 19f area versus (std area x [19f]) / [std] fitted to $y = mx + b$ where $m = 1.3793$ and $b = 0$ with a $R^2$ of 0.99639.

<table>
<thead>
<tr>
<th>mmol 19e</th>
<th>mmol tridecane</th>
<th>Area IS</th>
<th>Area Pdt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.049153468</td>
<td>0.16403</td>
<td>5560584759</td>
<td>1352944750</td>
</tr>
<tr>
<td>0.103768433</td>
<td>0.16403</td>
<td>7185032978</td>
<td>3353404616</td>
</tr>
<tr>
<td>0.154482328</td>
<td>0.16403</td>
<td>6904005775</td>
<td>4614671198</td>
</tr>
<tr>
<td>0.201295155</td>
<td>0.16403</td>
<td>6790282011</td>
<td>6296395603</td>
</tr>
</tbody>
</table>

### Table S1: Calibration curve data for t-butylbenzene (19f):

<table>
<thead>
<tr>
<th>mmol 19f</th>
<th>mmol tridecane</th>
<th>Area IS</th>
<th>Area Pdt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.049738489</td>
<td>0.16403</td>
<td>2518295474</td>
<td>574090525</td>
</tr>
<tr>
<td>0.100122932</td>
<td>0.16403</td>
<td>3255077022</td>
<td>1477595029</td>
</tr>
<tr>
<td>0.149861422</td>
<td>0.16403</td>
<td>3930989531</td>
<td>2559730260</td>
</tr>
<tr>
<td>0.200245865</td>
<td>0.16403</td>
<td>3546712147</td>
<td>3032026099</td>
</tr>
<tr>
<td>0.249984354</td>
<td>0.16403</td>
<td>3479578042</td>
<td>3925217274</td>
</tr>
</tbody>
</table>
Calibration curve for \( p \)-xylene (19g)

**Figure S9:** Plot of 19g area versus (std area x [19g])/[std] fitted to \( y = mx + b \) where \( m = 2.2235 \) and \( b = 0 \) with a \( R^2 \) of 0.98064.

<table>
<thead>
<tr>
<th>mmol 19g</th>
<th>mmol tridecane</th>
<th>Area IS</th>
<th>Area Pdt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.067830908</td>
<td>0.164026904</td>
<td>3288937475</td>
<td>545232412</td>
</tr>
<tr>
<td>0.134567768</td>
<td>0.164026904</td>
<td>3669199995</td>
<td>1145416244</td>
</tr>
<tr>
<td>0.202398676</td>
<td>0.164026904</td>
<td>3546770818</td>
<td>1870406001</td>
</tr>
<tr>
<td>0.270229584</td>
<td>0.164026904</td>
<td>3601846681</td>
<td>2352337673</td>
</tr>
<tr>
<td>0.336966444</td>
<td>0.164026904</td>
<td>2666629964</td>
<td>2562696982</td>
</tr>
</tbody>
</table>
Calibration curve for pyridine (19i):

Figure S10: Plot of 19i area versus (std area x [19i]) / [std] fitted to $y = mx + b$ where $m = 29.763$ and $b = -2 \times 10^9$ with a $R^2$ of 0.96197.

<table>
<thead>
<tr>
<th>mmol 19i</th>
<th>mmol tridecane</th>
<th>Area IS</th>
<th>Area Pdt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.062134632</td>
<td>0.164026904</td>
<td>4233992225</td>
<td>66403740</td>
</tr>
<tr>
<td>0.31067316</td>
<td>0.164026904</td>
<td>4031783804</td>
<td>371135414</td>
</tr>
<tr>
<td>0.62134632</td>
<td>0.164026904</td>
<td>4249091608</td>
<td>623374155</td>
</tr>
<tr>
<td>0.93201948</td>
<td>0.164026904</td>
<td>3760306370</td>
<td>710497433</td>
</tr>
</tbody>
</table>
VI) Silylation Substrates

[1,1'-biphenyl]-4-yltriethylsilane (2a)

The general procedure for silylation was followed using \( N,N,N \)-trimethylanilinium iodide 2 (73 mg, 0.215 mmol) and triethylsilane (160 \( \mu \)L, 1 mmol). Purification by flash chromatography (100% hexanes) gave the title compound as a colorless oil in 86% yield (50 mg, 0.186 mmol). The spectral data matches that previously reported in the literature.\(^{[17]}\)

\(^1\)H NMR (401 MHz, Chloroform-\( d \)) \( \delta \) 7.62 (m, 6H), 7.59 (d, \( J = 1.5 \) Hz, 2H), 7.45 (dd, \( J = 8.3, 6.9 \) Hz, 1H), 7.40 – 7.30 (m, 1H), 1.01 (t, \( J = 7.8 \) Hz, 9H), 0.84 (q, \( J = 7.3 \) Hz, 6H).

\(^13\)C NMR (126 MHz, Chloroform-\( d \)) \( \delta \) 141.56, 141.33, 136.38, 134.83, 128.88, 127.41, 127.27, 126.52, 7.60, 3.57.

[1,1'-biphenyl]-4-yl(benzyl)dimethylsilane (2b)

The general procedure for silylation was followed using \( N,N,N \)-trimethylanilinium iodide 2 (66 mg, 0.194 mmol) and dimethylnbenzylsilane (160 \( \mu \)L, 1 mmol). Purification by flash chromatography (100% hexanes to 98:2 hex/EtOAc) gave the title compound as a white solid in 85% yield (50 mg, 0.165 mmol). The spectral data matches that previously reported in the literature.\(^{[17]}\)

\(^1\)H NMR (400 MHz, Chloroform-\( d \)) \( \delta \) 7.68-7.57 (m, 4H), 7.54 (d, \( J = 8.0 \) Hz, 2H), 7.46 (dd, \( J = 8.3, 6.8 \) Hz, 2H), 7.4-7.33 (m, 1H), 7.20 (t, \( J = 7.5 \) Hz, 2H), 7.13-7.02 (m, 2H), 6.98 (d, \( J = 7.3 \) Hz, 2H), 2.35 (s, 2H), 0.29 (s, 6H).

\(^13\)C NMR (100 MHz, Chloroform-\( d \)) \( \delta \) 141.92, 141.18, 139.76, 137.37, 134.36, 128.92, 128.28, 128.13, 127.54, 127.29, 126.58, 124.25, 26.35, -3.24.

[1,1'-biphenyl]-4-yldimethyl(phenyl)silane (2c)

The general procedure for silylation was followed using \( N,N,N \)-trimethylanilinium iodide 2 (73 mg, 0.215 mmol), 30 mg of 4Å molecular sieves powder, IPr*OMe free carbene (9.4 mg, 0.1 equiv, 0.01 mmol), and dimethylphenylsilane (156 \( \mu \)L, 1 mmol). Purification by flash
chromatography (100% hexanes) gave the title compound in an inseparable mixture with phenyldimethylsilane as a colorless oil. 65% yield (41 mg, 0.14 mmol) by NMR analysis. The spectral data matches that previously reported in the literature.[18]

1H NMR (500MHz, Chloroform-d) δ 7.65-7.53 (m, 8H), 7.45 (t, J= 7.7 Hz, 2H), 7.41-7.32 (m, 4H), 0.60 (s, 6H).

13C NMR (126 MHz, Chloroform-d) δ 142.01, 141.20, 138.30, 137.13, 134.81, 134.33, 129.29, 128.90, 127.99, 127.53, 127.31, 126.70, 32.22, -2.19.

The general procedure for silylation was followed using N,N,N-trimethylanilinium iodide 5 (45.7 mg, 0.100 mmol) and triethylsilane (80 µL, 1 mmol). Yield determined by NMR of the crude reaction mixture using fluoroform as an internal standard (98%). The spectral data matches that previously reported in the literature.[19]

1H NMR (500MHz, Chloroform-d) δ 8.02 (d, J=1.6Hz, 2H), 7.85 (s, 1H), 7.63 (d, J=8.1Hz, 2H), 7.5 (d, J=8.1Hz, 2H), 0.99 (t, J= 7.8 Hz, 9H), 0.84 (q, J=7.8 Hz, 6H).

13C NMR (176 MHz, Chloroform-d) δ 143.51, 138.79, 138.52, 132.23 (q, J= 33.3Hz), 127.35, 126.55, 123.55 (q, J= 272.8Hz), 121.04 (m), 7.52, 3.46.

The general procedure for silylation was followed using N,N,N-trimethylanilinium iodide 6 (54 mg, 0.195 mmol) and triethylsilane (160 µL, 1 mmol). Yield determined by NMR of the crude reaction mixture using CH2Br2 as an internal standard (90%). The spectral data matches that previously reported in the literature.[19]

1H NMR (400MHz, Chloroform-d) δ 7.39 (d, J= 7.9 Hz), 2H), 7.17 (d, J= 7.5 Hz, 2H), 2.35 (s, 3H), 0.96 (t, J= 7.7 Hz, 9H), 0.77 (q, J=7.6 Hz, 6H).

13C NMR (126 MHz, Chloroform-d) δ 138.62, 134.38, 133.38, 128.67, 7.58, 3.56.
The general procedure for silylation was followed using \( N,N,N \)-trimethylanilinium iodide (6) (57 mg, 0.206 mmol) and 1,1,3,5,5,5-heptamethyltrisiloxane (272 \( \mu \)L, 1 mmol). Yield determined by NMR of the crude reaction mixture using \( \text{CH}_2\text{Br}_2 \) as an internal standard (81%).

\[ ^1H \text{ NMR} (400\text{MHz}, \text{Chloroform-}d) \delta 7.44 (d, J = 7.8 \text{ Hz}, 2H), 7.17 (d, J = 7.5 \text{ Hz}, 2H), 2.35 (s, 3H), 0.25 (s, 3H), 0.10 (s, 18H). \]

\[ ^{13}C \text{ NMR} (100\text{MHz}, \text{Chloroform-}d) \delta 139.36, 135.17, 133.43, 128.54, 21.70, 2.03, 0.28. \]

HRMS (EI) (m/z): [M] calculated for \( \text{C}_{14}\text{H}_{28}\text{O}_2\text{Si}_3 \), 312.1397, found, 312.1409.

The general procedure for silylation was followed using \( N,N,N \)-trimethylanilinium iodide (6) (28 mg, 0.101 mmol) and dimethylbenzylsilane (80 \( \mu \)L, 0.5 mmol). Yield determined by NMR of the crude reaction mixture using \( \text{CH}_2\text{Br}_2 \) as an internal standard (79%).

\[ ^1H \text{ NMR} (400 \text{MHz}, \text{Chloroform-}d) \delta 7.38 (d, J = 7.6 \text{ Hz}, 2H), 7.19 (d, J = 7.3 \text{ Hz}, 4H), 7.08 (t, J = 7.3 \text{ Hz}, 1H), 7.03 – 6.91 (m, 2H), 2.38 (s, 3H), 2.31 (s, 2H), 0.24 (s, 5H). \]

\[ ^{13}C \text{ NMR} (126\text{MHz}, \text{Chloroform-}d) \delta 139.94, 139.03, 134.96, 133.89, 128.71, 128.45, 128.22, 124.16, 26.42, 21.62, -3.22. \]

HRMS (EI) (m/z): [M] calculated for \( \text{C}_{16}\text{H}_{20}\text{Si} \), 240.1334, found, 240.1343.

The general procedure for silylation was followed using \( N,N,N \)-trimethylanilinium iodide (6) (56 mg, 0.202 mmol) and dimethylphenylsilane (156 \( \mu \)L, 1 mmol). Yield determined by NMR of the crude reaction mixture using \( \text{CH}_2\text{Br}_2 \) as an internal standard (74%). The spectral data matches that previously reported in the literature.\[18\]
$^1$H NMR (400 MHz, Chloroform-\textit{d}) $\delta$ 7.54 (dt, $J = 4.7, 2.3$ Hz, 2H), 7.44 (d, $J = 7.5$ Hz, 2H), 7.42 – 7.31 (m, 3H), 7.20 (d, $J = 7.5$ Hz, 2H), 2.37 (s, 3H), 0.56 (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-\textit{d}) $\delta$ 134.38, 134.32, 134.30, 129.23, 129.15, 128.80, 127.94, 127.91, 21.62, -2.16.

$^1$H NMR (500 MHz, Chloroform-\textit{d}) $\delta$ 7.43 (d, $J = 8.2$ Hz, 2H), 7.37 (d, $J = 6.5$ Hz, 2H), 1.32 (s, 9H), 0.97 (t, $J = 7.8$ Hz, 9H), 0.78 (q, $J = 8.0$ Hz, 6H).

$^{13}$C NMR (126 MHz, Chloroform-\textit{d}) $\delta$ 151.64, 134.19, 133.97, 124.74, 34.74, 31.42, 7.63, 3.61.

The general procedure for silylation was followed using $N,N,N$-trimethylanilinium iodide $7$ (62 mg, 0.194 mmol) and triethylsilane (160 $\mu$L, 1 mmol). Purification by flash chromatography (100% hexanes) gave the title compound as a colorless oil in 76% yield (37 mg, 0.149 mmol). The spectral data matches that previously reported in the literature.$^{[17]}$

$^1$H NMR (500 MHz, Chloroform-\textit{d}) $\delta$ 7.50 (d, $J = 7.5$ Hz, 2H), 7.38 (d, $J = 7.6$ Hz, 2H), 1.33 (s, 9H), 0.26 (s, 3H), 0.12 (s, 18H).

$^{13}$C NMR (126 MHz, Chloroform-\textit{d}) $\delta$ 152.43, 135.16, 133.83, 133.27, 124.65, 34.82, 31.41, 2.04, 0.41.

The general procedure for silylation was followed using $N,N,N$-trimethylanilinium iodide $7$ (68 mg, 0.213 mmol) and 1,1,1,3,5,5,5-heptamethyltrisiloxane (272 $\mu$L, 1 mmol). Purification by flash chromatography (100% hexanes) gave the title compound as a colorless oil in 46% yield (34 mg, 0.096 mmol).

$^1$H NMR (500 MHz, Chloroform-\textit{d}) $\delta$ 7.50 (d, $J = 7.5$ Hz, 2H), 7.38 (d, $J = 7.6$ Hz, 2H), 1.33 (s, 9H), 0.26 (s, 3H), 0.12 (s, 18H).

$^{13}$C NMR (126 MHz, Chloroform-\textit{d}) $\delta$ 152.43, 135.16, 133.83, 133.27, 124.65, 34.82, 31.41, 2.04, 0.41.

S30
The general procedure for silylation was followed using \(N,N,N\)-trimethylanilinium iodide 7 (64 mg, 0.200 mmol) and dimethybenzylsilane (160 \(\mu\)L, 1 mmol). Purification by flash chromatography (100% hexanes) gave the title compound as a white solid in 41% yield (23 mg, 0.081 mmol).

\(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 7.42 (d, \(J = 8.0\) Hz, 2H), 7.38 (d, \(J = 8.1\) Hz, 2H), 7.19 (t, \(J = 7.5\) Hz, 2H), 7.07 (t, \(J = 7.3\) Hz, 1H), 6.97 (d, \(J = 7.0\) Hz, 2H), 2.30 (s, 2H), 1.33 (s, 9H), 0.22 (s, 6H).

\(^{13}\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 152.01, 140.01, 135.15, 133.73, 128.47, 128.24, 124.85, 124.16, 34.80, 31.40, 26.36, -3.23.

HRMS (EI) (m/z): [M] calculated for \(C_{19}H_{26}Si\), 282.1804, found, 282.1814.

The general procedure for silylation was followed using \(N,N,N\)-trimethylanilinium iodide 7 (67 mg, 0.210 mmol) and dimethyphenylsilane (156 \(\mu\)L, 1 mmol). Purification by flash chromatography (100% hexanes) gave the title compound as a white solid in 93% yield (53 mg, 0.198 mmol). The spectral data matches that previously reported in the literature.\(^{[18]}\)

\(^1\)H NMR (401 MHz, Chloroform-\(d\)) \(\delta\) 7.53 (ddd, \(J = 7.5, 4.9, 2.3\) Hz, 2H), 7.47 (d, \(J = 8.2\) Hz, 2H), 7.38 (d, \(J = 8.2\) Hz, 2H), 7.36 (dd, \(J = 4.7, 2.7\) Hz, 3H), 1.32 (s, 9H), 0.54 (s, 6H).

\(^{13}\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 152.15, 138.65, 134.76, 134.31, 134.20, 129.14, 127.90, 124.92, 34.79, 31.39, -2.18.

The general procedure for silylation was followed using \(N,N,N\)-trimethylanilinium iodide 8 (68 mg, 0.205 mmol) and triethylsilane (160 \(\mu\)L, 1 mmol). Yield determined by NMR of the crude reaction mixture using fluorobenzene as an internal standard (50%). The spectral data matches that previously reported in the literature.\(^{[20]}\)

\(^1\)H NMR (401 MHz, Chloroform-\(d\)) \(\delta\) 7.60 (d, \(J = 8.5\) Hz, 2H), 7.58 (d, \(J = 8.4\) Hz, 2H), 0.96 (t, \(J = 7.7\) Hz, 9H), 0.81 (q, \(J = 7.7\) Hz, 6H).

\(^{13}\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 155.84, 142.74, 134.56, 130.82 (q, \(J = 31.8\) Hz), 124.28 (q, \(J = 3.7\) Hz), 7.43, 3.32.

\(^{19}\)F NMR (377 MHz, Chloroform-\(d\)) \(\delta\) -62.91.
benzyldimethyl(4-(trifluoromethyl)phenyl)silane (8b)

The general procedure for silylation was followed using N,N,N-trimethylanilinium iodide 8 (66 mg, 0.199 mmol) and dimethybenzylsilane (63 µL, 0.4 mmol). Yield determined by NMR of the crude reaction mixture using fluorobenzene as an internal standard (52%). Purification by preparative TLC (100% hexanes) gave the title compound as a clear oil.

\(^1^H \text{ NMR} (500 \text{ MHz, Chloroform-}d) \delta 7.58 (d, J = 7.8 \text{ Hz, } 2\text{H}), 7.55 (d, J = 7.9 \text{ Hz, } 2\text{H}), 7.19 (t, J = 7.4 \text{ Hz, } 2\text{H}), 7.08 (t, J = 7.6 \text{ Hz, } 2\text{H}), 6.92 (d, J = 7.6 \text{ Hz, } 2\text{H}), 2.32 (s, 2\text{H}), 0.29 (s, 6\text{H}).

\(^{13}C \text{ NMR} (126 \text{ MHz, Chloroform-}d) \delta 143.57, 139.11, 134.14, 131.02, 128.41, 128.37, 124.48, 124.34 (q, J = 3.8 \text{ Hz}), 26.00, -3.42.

\(^{19}F \text{ NMR} (471 \text{ MHz, Chloroform-}d) \delta -62.92.

HRMS (EI) (m/z): [M] calculated for C\(_{16}\)H\(_{17}\)F\(_3\)Si, 294.1052, found, 294.1062.

dimethyl(phenyl)(4-(trifluoromethyl)phenyl)silane (8c)

The general procedure for silylation was followed using N,N,N-trimethylanilinium iodide 8 (65 mg, 0.196 mmol) and dimethyphenlsilane (62 µL, 0.4 mmol). Yield determined by NMR of the crude reaction mixture using fluorobenzene as an internal standard (47%). Purification by preparative TLC (100% hexanes) gave the title compound as a clear oil. The spectral data matches that previously reported in the literature.\(^{[18]}\)

\(^1^H \text{ NMR} (401 \text{ MHz, Chloroform-}d) \delta 7.64 (d, J = 7.9 \text{ Hz, } 1\text{H}), 7.59 (d, J = 7.9 \text{ Hz, } 1\text{H}), 7.55 – 7.48 (m, 1\text{H}), 7.45 – 7.33 (m, 1\text{H}), 0.59 (s, 3\text{H}).

\(^{13}C \text{ NMR} (126 \text{ MHz, Chloroform-}d) \delta 143.54, 137.21, 134.57, 134.26, 131.19 (d, J = 32.4 \text{ Hz}), 129.61, 128.14, 124.45 (q, J = 3.7 \text{ Hz}), -2.45.

\(^{19}F \text{ NMR} (471 \text{ MHz, Chloroform-}d) \delta -62.95.

triethyl(4-methoxyphenyl)silane (9a)

The general procedure for silylation was followed using N,N,N-trimethylanilinium iodide 9 (58 mg, 0.198 mmol) and triethylsilane (160 µL, 1 mmol). Yield determined by NMR of the crude...
reaction mixture using CH$_2$Br$_2$ as an internal standard (98%). The spectral data matches that previously reported in the literature.\[21]\]

$^1$H NMR (500MHz, Chloroform-d) $\delta$ 7.42 (d, $J$ = 8.6 Hz, 2H), 6.91(d, $J$ = 8.6 Hz, 2H), 3.81 (s, 3H), 0.96 (t, $J$ = 7.9 Hz, 9H), 0.76 (q, $J$ = 7.9 Hz, 6H).

$^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 160.30, 135.70, 128.28, 113.59, 55.11, 7.34, 3.65.

![9b](image)

3-(4-methoxyphenyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (9b)

The general procedure for silylation was followed using $N,N,N$-trimethylanilinium iodide 9 (29 mg, 0.096 mmol) and 1,1,1,3,5,5,5-heptamethyltrisiloxane (136 µL, 0.5 mmol). Yield determined by NMR of the crude reaction mixture using CH$_2$Br$_2$ as an internal standard (59%). The spectral data matches that previously reported in the literature.\[22]\]

$^1$H NMR (500 MHz, Chloroform-d) $\delta$ 7.48 (d, $J$ = 8.5 Hz, 2H), 6.90 (d, $J$ = 8.5 Hz, 2H), 3.82 (s, 3H), 0.25 (s, 3H), 0.10 (s, 18H).

$^{13}$C NMR (126 MHz, Chloroform-d) $\delta$ 160.79, 134.91, 129.96, 113.42, 55.13, 2.02, 0.33.

![9c](image)

benzyl(4-methoxyphenyl)dimethylsilane (9c)

The general procedure for silylation was followed using $N,N,N$-trimethylanilinium iodide 9 (58 mg, 0.198 mmol) and dimethyldimethoxysilane (160 µL, 1 mmol). Yield determined by NMR of the crude reaction mixture using CH$_2$Br$_2$ as an internal standard (98%).

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.42 – 7.33 (m, 2H), 7.23 – 7.14 (m, 2H), 7.12 – 7.04 (m, 1H), 7.00 – 6.88 (m, 3H), 3.83 (s, 3H), 2.29 (s, 2H), 0.24 (s, 6H).

$^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 160.57, 139.96, 135.29, 129.39, 128.44, 128.20, 124.14, 113.63, 55.16, 26.61, -3.12.

HRMS (ESI) (m/z): [M+Na] calculated for C$_{16}$H$_{20}$OSi, 279.1176, found, 279.1179.

![9d](image)

(4-methoxyphenyl)dimethyl(phenyl)silane (9d)
The general procedure for silylation was followed using \(N,N,N\)-trimethylanilinium iodide (9) (58 mg, 0.198 mmol) and dimethylphenylsilane (156 \(\mu\)L, 1 mmol). Yield determined by NMR of the crude reaction mixture using \(\text{CH}_2\text{Br}_2\) as an internal standard (92%). The spectral data matches that previously reported in the literature.\textsuperscript{[18]}

\(^1\text{H NMR}\) (500 MHz, Chloroform-\(d\)) \(\delta\) 7.58 – 7.51 (m, 2H), 7.48 (d, \(J = 8.0\) Hz, 2H), 7.37 (m, \(J = 5.8\) Hz, 3H), 6.94 (d, \(J = 8.0\) Hz, 2H), 3.83 (s, 3H), 0.56 (s, 6H).

\(^{13}\text{C NMR}\) (126 MHz, Chloroform-\(d\)) \(\delta\) 160.63, 138.82, 135.78, 134.27, 129.13, 127.91, 113.74, 55.16, -2.04.

\(\text{SiEt}_3\) \(\text{PhO}\)

**10a**

triethyl(4-phenoxyphenyl)silane (10a)

The general procedure for silylation was followed using \(N,N,N\)-trimethylanilinium iodide (10) (70 mg, 0.197 mmol) and triethylsilane (160 \(\mu\)L, 1 mmol). Purification by flash chromatography (100% hexanes) gave the title compound as a colorless oil in 89% yield (50 mg, 0.176 mmol).

\(^1\text{H NMR}\) (500 MHz, Chloroform-\(d\)) \(\delta\) 7.44 (d, \(J = 7.4\) Hz, 2H), 7.39 – 7.31 (m, 2H), 7.11 (t, \(J = 7.4\) Hz, 1H), 7.04 (d, \(J = 8.7\) Hz, 2H), 6.98 (d, \(J = 7.4\) Hz, 2H), 0.97 (t, \(J = 7.9\) Hz, 9H), 0.78 (q, \(J = 7.9\) Hz, 6H).

\(^{13}\text{C NMR}\) (126 MHz, Chloroform-\(d\)) \(\delta\) 158.24, 156.98, 135.85, 129.86, 123.53, 119.43, 119.02, 118.01, 7.56, 3.63.

HRMS (EI) (m/z): [M] calculated for \(\text{C}_{18}\text{H}_{24}\text{O} \text{Si}\), 284.1596, found, 284.1609.

\(\text{SiMe}_2\text{Bn}\) \(\text{PhO}\)

**10b**

benzyl(dimethyl(4-phenoxyphenyl)silane (10b)

The general procedure for silylation was followed using \(N,N,N\)-trimethylanilinium iodide (10) (73 mg, 0.206 mmol) and dimethybenzylsilane (64 \(\mu\)L, 0.4 mmol). Purification by flash chromatography (100% hexanes) gave the title compound as a white solid in 72% yield (47 mg, 0.148 mmol).

\(^1\text{H NMR}\) (500 MHz, Chloroform-\(d\)) \(\delta\) 7.42 (d, \(J = 7.2\) Hz, 2H), 7.37 (t, \(J = 8.1\) Hz, 2H), 7.20 (t, \(J = 6.6\) Hz, 29H), 7.15 (t, \(J = 7.9\) Hz, 1H), 7.09 (d, \(J = 6.9\) Hz, 1H), 7.05 (d, \(J = 7.8\) Hz, 2H), 7.00 (d, \(J = 6.6\) Hz, 2H), 6.96 (d, \(J = 7.1\) Hz, 2H), 2.31 (s, 0H), 0.27 (s, 1H).

\(^{13}\text{C NMR}\) (126 MHz, Chloroform-\(d\)) \(\delta\) 158.46, 156.95, 139.77, 135.46, 132.53, 129.90, 128.44, 128.24, 124.22, 123.59, 119.37, 118.10, 26.50, -3.16.

HRMS (ESI) (m/z): [M+Na] calculated for \(\text{C}_{21}\text{H}_{22}\text{OSi}\), 341.1332, found, 341.1338.
The general procedure for silylation was followed using N,N,N-trimethylanilinium iodide 10 (70 mg, 0.197 mmol), 30 mg of 4Å molecular sieves powder, IPr*OMe free carbene (9.4 mg, 0.1 equiv, 0.01 mmol), and dimethyldiphenylsilane (156 µL, 1 mmol). Purification by flash chromatography (100% hexanes) gave the title compound in an inseparable mixture with phenyldimethyldisilane as a colorless oil. 68% yield (41 mg, 0.1348 mmol) by NMR analysis.

\[ \text{1H NMR (401 MHz, Chloroform-}d) \delta 7.53 (\text{ddd, } J = 7.4, 5.1, 2.1 \text{ Hz, 3H}), 7.47 (\text{d, } J = 8.1 \text{ Hz, 2H}), 7.41 - 7.30 (\text{m, 5H}), 7.12 (\text{t, } J = 7.4 \text{ Hz, 1H}), 7.03 (\text{d, } J = 8.1 \text{ Hz, 2H}), 6.98 (\text{d, } J = 8.4 \text{ Hz, 2H}), 0.54 (\text{s, 6H}). \]

\[ \text{13C NMR (126 MHz, Chloroform-}d) \delta 158.60, 156.84, 138.44, 135.93, 134.27, 132.24, 129.89, 129.25, 127.97, 123.65, 119.49, 118.08, -2.09. \]

\[ \text{HRMS (EI) (m/z): [M] calculated for C}_{20}\text{H}_{20}\text{OSi, 304.1283, found, 304.1294.} \]

The general procedure for silylation was followed using N,N,N-trimethylanilinium iodide 11 (80 mg, 0.196 mmol), 30 mg of 4Å molecular sieves powder, IPr*OMe free carbene (18.8 mg, 0.1 equiv, 0.01 mmol), triethylsilane (160 µL, 1 mmol). Purification by flash chromatography (100% hexanes) gave the title compound as a yellow solid in 46% yield (31 mg, 0.091 mmol).

\[ \text{1H NMR (401 MHz, Chloroform-}d) \delta 7.46 (\text{d, } J = 7.6 \text{ Hz, 2H}), 7.31 (\text{d, } J = 7.5 \text{ Hz, 2H}), 4.74 (\text{s, 2H}), 0.96 (\text{t, } J = 7.8 \text{ Hz, 9H}), 0.95 (\text{s, 9H}), 0.78 (\text{q, } J = 7.8 \text{ Hz, 6H}), 0.10 (\text{s, 3H}). \]

\[ \text{13C NMR (100 MHz, Chloroform-}d) \delta 142.05, 135.80, 134.29, 125.46, 65.08, 26.13, 18.60, 7.56, 3.54, -5.11. \]

\[ \text{HRMS (ESI) (m/z): [M+Na] calculated for C}_{19}\text{H}_{36}\text{OSi}_2, 359.2197, \text{found, 359.2197.} \]
The general procedure for silylation was followed using \(N,N,N\)-trimethylanilinium iodide 11 (81 mg, 0.199 mmol), 30 mg of 4Å molecular sieves powder, IPr*OMe free carbene (9.4 mg, 0.1 equiv, 0.01 mmol), and dimethyphenylsilane (156 µL, 1 mmol). Purification by flash chromatography (100% hexanes) gave the title compound as an off white solid in 57% yield (40 mg, 0.113 mmol).

\[^{1}H\text{ NMR}\ (400\ \text{MHz, Chloroform-}d)\ \delta\ 7.51\ (dd, J = 3.0, 1.6\ \text{Hz, 2H}),\ 7.49\ (d, J = 8.6\ \text{Hz, 2H}),\ 7.34\ (m, 3\ \text{H}),\ 7.31\ (d, J = 7.7\ \text{Hz, 2H}),\ 4.74\ (s, 2\ \text{H}),\ 0.94\ (s, 9\ \text{H}),\ 0.54\ (s, 6\ \text{H}),\ 0.10\ (s, 6\ \text{H}).\]

\[^{13}C\text{ NMR}\ (126\ \text{MHz, Chloroform-}d)\ \delta\ 142.57,\ 138.54,\ 136.60,\ 134.31,\ 134.29,\ 129.18,\ 127.92,\ 125.57,\ 65.01,\ 26.12,\ 18.59, -2.18, -5.11.\]

\[^{1}H\text{ NMR}\ (400\ \text{MHz, Chloroform-}d)\ \delta\ 7.54\ (m, 4\ \text{H}),\ 7.48\ (d, J = 8.6\ \text{Hz, 2H}),\ 6.90\ (d, J = 8.6\ \text{Hz, 2H}),\ 1.00\ (s, 9),\ 0.82\ (q, J = 7.4\ \text{Hz, 6H}),\ 0.23\ (s, 6\ \text{H}).\]

\[^{13}C\text{ NMR}\ (100\ \text{MHz, Chloroform-}d)\ \delta\ 155.46,\ 141.23,\ 135.52,\ 134.78,\ 134.37,\ 128.19,\ 126.10,\ 120.47,\ 25.86,\ 18.40,\ 7.60,\ 3.59, -4.21.\]

\[^{1}H\text{ NMR}\ (400\ \text{MHz, Chloroform-}d)\ \delta\ 7.54\ (d, J = 7.7\ \text{Hz, 2H}),\ 7.52 – 7.44\ (m, 4\ \text{H}),\ 7.19\ (t, J = 7.5\ \text{Hz, 2H}),\ 7.07\ (t, J = 7.3\ \text{Hz, 1H}),\ 6.96\ (d, J = 7.6\ \text{Hz, 2H}),\ 6.91\ (d, J = 8.3\ \text{Hz, 2H}),\ 2.33\ (s, 2H),\ 1.01\ (s, 9H),\ 0.27\ (s, 6H),\ 0.23\ (s, 6H).\]

\[^{13}C\text{ NMR}\ (126\ \text{MHz, Chloroform-}d)\ \delta\ 155.57,\ 141.61,\ 139.83,\ 136.55,\ 134.32,\ 134.21,\ 128.48,\ 128.27,\ 128.23,\ 126.16,\ 124.22,\ 120.50,\ 26.40,\ 25.86, -3.22, -4.21.\]
**HRMS (ESI) (m/z):** [M+Na] calculated for C_{27}H_{36}O_{2}Si, 455.2197, found, 455.2200.

4-(4-(triethylsilyl)phenyl)morpholine (13a)

The general procedure for silylation was followed using N,N,N-trimethylanilinium iodide 13 (73 mg, 0.210 mmol) and triethylsilane (160 µL, 1 mmol). Purification by flash chromatography (95:5 hexanes/EtOAc) gave the title compound as a white solid in 86% yield (51 mg, 0.184 mmol).

\[ {^1}H \text{ NMR} \ (500 \text{ MHz, Chloroform-}d) \ \delta \ 7.41 \ (d, J = 8.4 \text{ Hz, 2H}), \ 6.91 \ (d, J = 8.6 \text{ Hz, 2H}), \ 3.86 \ (dd, J = 5.8, 3.9 \text{ Hz, 4H}), \ 3.20 \ (dd, J = 5.9, 3.8 \text{ Hz, 4H}), \ 0.97 \ (t, J = 7.8 \text{ Hz, 9H}), \ 0.77 \ (q, J = 7.6 \text{ Hz, 6H}). \]

\[ {^{13}}C \text{ NMR} \ (126 \text{ MHz, Chloroform-}d) \ \delta \ 151.55, \ 135.44, \ 127.01, \ 114.78, \ 67.08, \ 48.83, \ 7.59, \ 3.66. \]

**HRMS (ESI) (m/z):** [M+H] calculated for C_{16}H_{27}NO_{2}Si, 278.1940, found, 278.1936.

4-(4-(benzyldimethylsilyl)phenyl)morpholine (13b)

The general procedure for silylation was followed using N,N,N-trimethylanilinium iodide 13 (70 mg, 0.201 mmol) and dimethyldimethyloxysilane (160 µL, 1 mmol). Purification by flash chromatography (95:5 to 90:10 hexanes/EtOAc) gave the title compound as a white solid in 76% yield (47 mg, 0.151 mmol).

\[ {^1}H \text{ NMR} \ (500 \text{ MHz, Chloroform-}d) \ \delta \ 7.36 \ (d, J = 7.8 \text{ Hz, 2H}), \ 7.18 \ (t, J = 7.5 \text{ Hz, 2H}), \ 7.06 \ (t, J = 7.3 \text{ Hz, 1H}), \ 6.94 \ (d, J = 7.6 \text{ Hz, 2H}), \ 6.90 \ (d, J = 8.2 \text{ Hz, 2H}), \ 3.89 - 3.84 \ (m, 4H), \ 3.20 \ (t, J = 4.9 \text{ Hz, 4H}), \ 2.28 \ (s, 2H), \ 0.21 \ (s, 6H). \]

\[ {^{13}}C \text{ NMR} \ (126 \text{ MHz, Chloroform-}d) \ \delta \ 151.86, \ 140.08, \ 135.01, \ 128.46, \ 128.19, \ 128.08, \ 124.10, \ 114.80, \ 67.04, \ 48.85, \ 26.61, \ -3.15. \]

**HRMS (ESI) (m/z):** [M+H] calculated for C_{19}H_{25}NO_{2}Si, 312.1784, found, 312.1786.
4-(4-(dimethyl(phenyl)silyl)phenyl)morpholine (13c)

The general procedure for silylation was followed using N,N,N-trimethylanilinium iodide 13 (67 mg, 0.198 mmol) and dimethylphenylsilane (156 µL, 1 mmol). Purification by flash chromatography (95:5 hexanes/EtOAc) gave the title compound as a white solid in 78% yield (46 mg, 0.155 mmol).

\[ {^1}H\text{ NMR (500 MHz, Chloroform-}d\text{)} \delta 7.55 - 7.48 (m, 2H), 7.43 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 6.2 Hz, 3H), 6.90 (d, J = 8.0 Hz, 2H), 3.85 (t, J = 4.6 Hz, 4H), 3.19 (t, J = 4.7 Hz, 4H), 0.52 (s, 6H). \]

\[ {^{13}}C\text{ NMR (126 MHz, Chloroform-}d\text{)} \delta 151.89, 138.99, 135.49, 134.28, 129.06, 127.86, 127.66, 114.84, 67.02, 48.77, -2.07. \]

HRMS (ESI) (m/z): [M+Na] calculated for C\text{18}H\text{23}NOSi, 298.1622, found, 298.1628.

\[
\begin{align*}
\text{SiEt}_3 & \\
\text{N} & \\
\text{O} & \\
14a
\end{align*}
\]

4-(3-(triethylsilyl)phenyl)morpholine (14a)

The general procedure for silylation was followed using N,N,N-trimethylanilinium iodide 14 (70 mg, 0.201 mmol) and triethylsilane (160 µL, 1 mmol). Purification by flash chromatography (100% hexanes to 95:5 hexanes/EtOAc) gave the title compound as a white solid in 81% yield (45 mg, 0.162 mmol). The spectral data matches that previously reported in the literature.\[^{[17]}\]

\[ {^1}H\text{ NMR (401 MHz, Chloroform-}d\text{)} \delta 7.29 (d, J = 7.7 Hz, 1H), 7.06 (d, J = 2.6 Hz, 1H), 7.03 (dd, J = 7.2, 1.1 Hz, 1H), 6.91 (dd, J = 8.2, 2.6 Hz, 1H), 3.92 - 3.84 (m, 4H), 3.17 (dd, J = 5.8, 3.8 Hz, 4H), 0.97 (t, J = 7.7 Hz, 9H), 0.79 (q, J = 7.8 Hz, 6H). \]

\[ {^{13}}C\text{ NMR (100 MHz, Chloroform-}d\text{)} \delta 150.71, 138.52, 128.61, 126.25, 121.76, 116.37, 67.17, 49.73, 7.61, 3.55. \]

HRMS (ESI) (m/z): [M+H] calculated for C\text{18}H\text{23}NOSiO, 298.1627, found, 298.1628.

\[
\begin{align*}
\text{SiMe}_2\text{Bn} & \\
\text{N} & \\
\text{O} & \\
14b
\end{align*}
\]

4-(3-(benzyldimethylsilyl)phenyl)morpholine (14b)

The general procedure for silylation was followed using N,N,N-trimethylanilinium iodide 14 (69 mg, 0.198 mmol) and dimethybenzylsilane (160 µL, 1 mmol). Purification by flash
chromatography (95:5 hexanes/EtOAc) gave the title compound as a white solid in 85% yield (53 mg, 0.167 mmol).

\[ ^1H \text{NMR (400 MHz, Chloroform-} d \text{)} \delta 7.29 (d, J = 7.5 Hz, 1H), 7.23 - 7.13 (m, 2H), 7.06 (t, J = 7.2 Hz, 1H), 7.00 (d, J = 7.1 Hz, 1H), 6.98 - 6.88 (m, 4H), 3.90 - 3.82 (m, 4H), 3.16 - 3.10 (m, 4H), 2.29 (s, 2H), 0.24 (s, 6H). \]

\[ ^{13}C \text{NMR (100 MHz, Chloroform-} d \text{)} \delta 150.66, 139.88, 139.48, 128.73, 128.49, 128.24, 125.62, 121.32, 116.73, 67.13, 49.66, 26.38, -3.20. \]

HRMS (ESI) (m/z): [M+H] calculated for C\(_{19}\)H\(_{25}\)NOSi, 312.1784, found, 312.1791.

4-(3-(dimethyl(phenyl)silyl)phenyl)morpholine (14c)

The general procedure for silylation was followed using \(N,N,N\)-trimethylanilinium iodide 14 (70 mg, 0.201 mmol) and dimethylphenylsilane (156 µL, 1 mmol). Purification by flash chromatography (95:5 hexanes/EtOAc) gave the title compound as a white solid in 70% yield (42 mg, 0.141 mmol).

\[ ^1H \text{NMR (400 MHz, Chloroform-} d \text{)} \delta 7.56 - 7.49 (m, 2H), 7.40 - 7.32 (m, 3H), 7.29 (d, J = 7.6 Hz, 1H), 7.11 - 7.02 (m, 2H), 6.97 - 6.88 (m, 1H), 3.89 - 3.81 (m, 4H), 3.17 - 3.10 (m, 4H), 0.54 (s, 6H). \]

\[ ^{13}C \text{NMR (100 MHz, Chloroform-} d \text{)} \delta 150.78, 139.21, 138.42, 134.32, 129.21, 128.83, 127.92, 126.19, 121.65, 116.69, 67.12, 49.59, -2.17. \]

1-propyl-4-(4-(triethylsilyl)phenyl)-1H-pyrazole (15a)

The general procedure for silylation was followed using \(N,N,N\)-trimethylanilinium iodide 15 (73 mg, 0.197 mmol) and triethylsilane (160 µL, 1 mmol). Purification by flash chromatography (90:10 hexanes/EtOAc) gave the title compound as a white solid in 81% yield (48 mg, 0.160 mmol).

\[ ^1H \text{NMR (500 MHz, Chloroform-} d \text{)} \delta 7.80 (s, 1H), 7.64 (s, 1H), 7.49 (d, J = 8.1 Hz, 2H), 7.47 (d, J = 8.1 Hz, 2H), 4.11 (t, J = 7.0 Hz, 2H), 1.93 (h, J = 7.2 Hz, 2H), 0.98 (t, J = 7.8 Hz, 9H), 0.94 \]
(t, J = 7.4 Hz, 3H), 0.80 (q, J = 7.9 Hz, 6H).

$^1$H NMR (500 MHz, Chloroform-CD$_2$) δ 7.80 (s, 1H), 7.65 (s, 1H), 7.54 (d, J = 7.8 Hz, 2H), 7.47 (d, J = 7.8 Hz, 2H), 4.11 (t, J = 7.1 Hz, 2H), 1.93 (h, J = 7.3 Hz, 2H), 0.95 (t, J = 7.4 Hz, 3H), 0.27 (s, 3H), 0.11 (s, 18H).


HRMS (ESI) (m/z): [M+H] calculated for C$_{19}$H$_{26}$N$_2$Si, 407.1944, found, 407.1938.
The general procedure for silylation was followed using $N,N,N$-trimethylanilinium iodide 15 (36 mg, 0.097 mmol) and dimethyphenylsilane (78 µL, 0.5 mmol). Purification by flash chromatography (90:10 hexanes/EtOAc) gave the title compound as a white solid in 72% yield (22 mg, 0.069 mmol).

$^1$H NMR (500 MHz, Chloroform-$d$) δ 7.79 (s, 1H), 7.64 (s, 1H), 7.57 – 7.49 (m, 4H), 7.49 – 7.45 (m, 2H), 7.40 – 7.33 (m, 3H), 4.11 (t, $J = 7.1$ Hz, 2H), 1.93 (q, $J = 7.3$ Hz, 2H), 0.95 (t, $J = 7.4$ Hz, 3H), 0.57 (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) δ 138.44, 136.78, 135.93, 134.90, 134.29, 133.62, 129.21, 128.96, 127.94, 126.20, 124.98, 54.20, 23.87, 11.29, -2.21.

HRMS (ESI) (m/z): [M+H] calculated for C$_{20}$H$_{24}$N$_2$Si, 321.1787, found, 321.1781.

(2,5-dimethylphenyl)triethylsilane (16a)

The general procedure for silylation was followed using $N,N,N$-trimethylanilinium iodide 16 (58 mg, 0.198 mmol) and triethylsilane (160 µL, 1 mmol). Yield determined by NMR of the crude reaction mixture using CH$_2$Br$_2$ as an internal standard (35%). The spectral data matches that previously reported in the literature.$^{[23]}$

$^1$H NMR (500MHz, Chloroform-$d$) δ 7.22 (s, 1H), 7.05 (q, $J = 7.8$ Hz, 2H), 2.39 (s, 3H), 2.31 (s, 3H), 0.95 (t, $J = 8$ Hz, 9H), 0.85 (q, $J = 7.9$ Hz, 6H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) δ 140.81, 136.30, 135.31, 133.83, 129.84, 129.78, 22.61, 21.30, 7.78, 4.16.
benzyl(2,5-dimethylphenyl)dimethylsilane (16b)

The general procedure for silylation was followed using \( \text{N,N,N-} \text{trimethylanilinium iodide} \) 16 (58 mg, 0.198 mmol) and dimethylbenzilsilane (160 \( \mu L \), 1 mmol). Yield determined by NMR of the crude reaction mixture using \( \text{CH}_2\text{Br}_2 \) as an internal standard (65%).

\( ^1\text{H NMR} \) (500MHz, Chloroform-\( d \)) \( \delta \) 7.22 (d, \( J = 1.8 \) Hz, 1H), 7.19 (t, \( J = 7.5 \) Hz, 2H), 7.08 (qd, \( J = 8.1 \), 7.5, 4.9 Hz, 3H), 7.00- 6.92 (m, 2H), 2.40 (s, 3H), 2.38 (s, 3H), 0.28 (s, 6H).

\( ^{13}\text{C NMR} \) (126 MHz, Chloroform-\( d \)) \( \delta \) 140.58, 140.11, 136.60, 135.57, 134.17, 130.20, 130.01, 128.48, 128.25, 124.21, 26.36, 22.84, 21.20, -1.95.

\( \text{HRMS (EI)} \) (m/z): [M] calculated for \( \text{C}_{17}\text{H}_{22}\text{Si} \), 254.1491, found, 254.1489.

(2,5-dimethylphenyl)dimethyl(phenyl)silane (16c)

The general procedure for silylation was followed using \( \text{N,N,N-} \text{trimethylanilinium iodide} \) 16 (58 mg, 0.198 mmol) and dimethylphenylsilane (156 \( \mu L \), 1 mmol). Yield determined by NMR of the crude reaction mixture using \( \text{CH}_2\text{Br}_2 \) as an internal standard (47%).

\( ^1\text{H NMR} \) (500MHz, Chloroform-\( d \)) \( \delta \) 7.56- 7.44 (m, 2H), 7.41 - 7.28 (m, 4H), 7.13 (dd, \( J = 7.7 \), 2.1 Hz, 1H), 7.05 (dd, \( J = 7.7 \), 2.0 Hz, 1H), 2.33 (s, 3H), 2.22 (s, 3H), 0.58 (s, 6H).

\( ^{13}\text{C NMR} \) (126 MHz, Chloroform-\( d \)) \( \delta \) 141.07, 139.24, 136.15, 134.42, 134.15, 134.15, 130.43, 129.99, 128.99, 127.93, 22.77, 21.24, -1.18.

\( \text{HRMS (EI)} \) (m/z): [M] calculated for \( \text{C}_{16}\text{H}_{20}\text{Si} \), 240.1334, found, 240.1344.

triethyl(2’,3’,4’,5’-tetrahydro-[1,1’-biphenyl]-4-yl)silane (17a)

The general procedure for silylation was followed using \( \text{N,N,N-} \text{trimethylanilinium iodide} \) 17 (137 mg, 0.399 mmol) and triethylsilane (192 \( \mu L \), 1.2 mmol). Reaction was run under a stream of nitrogen in order to prevent hydrogenation of the product. Purification by flash chromatography (100% hexanes) gave the title compound as a white solid in 45% yield (49 mg, 0.180 mmol) and the hydrogenated product in 10% yield (11mg, 0.040 mmol).
**17a:**

**1H NMR** (500 MHz, Chloroform-\(d\)) \(\delta \) 7.43 (d, \(J = 7.8 \) Hz, 2H), 7.37 (d, \(J = 7.7 \) Hz, 2H), 6.16 (tt, \(J = 3.9, 1.7 \) Hz, 1H), 2.42 (tq, \(J = 6.5, 2.3 \) Hz, 2H), 2.21 (dh, \(J = 6.1, 2.8 \) Hz, 2H), 1.81 – 1.73 (m, 2H), 1.70 – 1.62 (m, 2H), 0.96 (t, \(J = 7.8 \) Hz, 9H), 0.78 (q, \(J = 7.8 \) Hz, 6H).

**13C NMR** (100 MHz, Chloroform-\(d\)) \(\delta \) 142.94, 136.61, 135.42, 134.33, 125.04, 124.25, 27.36, 26.08, 23.23, 22.35, 7.58, 3.56.

**HRMS** (EI) (m/z): [M] calculated for C\(_{18}\)H\(_{30}\)Si, 274.2117, found, 274.2125.

**HRMS** (EI) (m/z): [M] calculated for C\(_{18}\)H\(_{30}\)Si, 274.2117, found, 274.2125.

**17a**: 

**1H NMR** (500 MHz, Chloroform-\(d\)) \(\delta \) 7.41 (d, \(J = 6.6 \) Hz, 2H), 7.19 (d, \(J = 6.9 \) Hz, 2H), 2.58 – 2.42 (m, 1H), 1.96 – 1.80 (m, 3H), 1.74 (d, \(J = 13.1 \) Hz, 1H), 1.41 (h, \(J = 12.4 \) Hz, 3H), 1.31 – 1.18 (m, 1H), 0.96 (t, \(J = 7.7 \) Hz, 9H), 0.77 (q, \(J = 8.0 \) Hz, 7H).

**13C NMR** (126 MHz, Chloroform-\(d\)) \(\delta \) 148.64, 134.37, 134.34, 126.37, 44.66, 34.48, 27.10, 26.36, 7.62, 3.62.

**HRMS** (EI) (m/z): [M] calculated for C\(_{21}\)H\(_{26}\)Si, 306.1804, found, 306.1811.

The general procedure for silylation was followed using \(N,N,N\)-trimethylanilinium iodide 17 (136 mg, 0.396 mmol) and dimethybenzylsilane (190 \(\mu\)L, 1.2 mmol). Reaction was run under a stream of nitrogen in order to prevent hydrogenation of the product. Purification by flash chromatography (100% hexanes to 98:2 hexanes/EtOAc) gave the title compound as a white solid in 59% yield (72 mg, 0.234 mmol).

**1H NMR** (400 MHz, Chloroform-\(d\)) \(\delta \) 7.40 (d, \(J = 8.2 \) Hz, 2H), 7.36 (d, \(J = 8.1 \) Hz, 2H), 7.18 (t, \(J = 7.5 \) Hz, 2H), 7.06 (t, \(J = 7.3 \) Hz, 1H), 6.94 (d, \(J = 7.3 \) Hz, 2H), 6.16 (tt, \(J = 4.1, 1.7 \) Hz, 1H), 2.42 (dq, \(J = 6.1, 3.8, 3.1 \) Hz, 2H), 2.30 (s, 2H), 2.22 (dq, \(J = 6.3, 3.5 \) Hz, 2H), 1.79 (ddt, \(J = 12.0, 8.6, 4.5 \) Hz, 1H), 1.71 – 1.62 (m, 2H), 0.23 (s, 6H).

**13C NMR** (100 MHz, Chloroform-\(d\)) \(\delta \) 143.40, 139.91, 136.60, 133.84, 128.46, 128.23, 125.30, 124.37, 124.17, 27.39, 26.39, 26.08, 23.20, 22.32, -3.24.

**HRMS** (EI) (m/z): [M] calculated for C\(_{21}\)H\(_{26}\)Si, 306.1804, found, 306.1811.

![Image of 17b](image-url)

**17b**

benzyldimethyl(2',3',4',5'-tetrahydro-[1,1'-biphenyl]-4-yl)silane (17b)

The general procedure for silylation was followed using \(N,N,N\)-trimethylanilinium iodide 17 (136 mg, 0.396 mmol) and dimethybenzylsilane (190 \(\mu\)L, 1.2 mmol). Reaction was run under a stream of nitrogen in order to prevent hydrogenation of the product. Purification by flash chromatography (100% hexanes to 98:2 hexanes/EtOAc) gave the title compound as a white solid in 59% yield (72 mg, 0.234 mmol).

**1H NMR** (400 MHz, Chloroform-\(d\)) \(\delta \) 7.40 (d, \(J = 8.2 \) Hz, 2H), 7.36 (d, \(J = 8.1 \) Hz, 2H), 7.18 (t, \(J = 7.5 \) Hz, 2H), 7.06 (t, \(J = 7.3 \) Hz, 1H), 6.94 (d, \(J = 7.3 \) Hz, 2H), 6.16 (tt, \(J = 4.1, 1.7 \) Hz, 1H), 2.42 (dq, \(J = 6.1, 3.8, 3.1 \) Hz, 2H), 2.30 (s, 2H), 2.22 (dq, \(J = 6.3, 3.5 \) Hz, 2H), 1.79 (ddt, \(J = 12.0, 8.6, 4.5 \) Hz, 1H), 1.71 – 1.62 (m, 2H), 0.23 (s, 6H).

**13C NMR** (100 MHz, Chloroform-\(d\)) \(\delta \) 143.40, 139.91, 136.60, 133.84, 128.46, 128.23, 125.30, 124.37, 124.17, 27.39, 26.39, 26.08, 23.20, 22.32, -3.24.

**HRMS** (EI) (m/z): [M] calculated for C\(_{21}\)H\(_{26}\)Si, 306.1804, found, 306.1811.

![Image of 17c and 17c'](image-url)

**17c**

result of reaction scheme: 17b + 17c

**17c**

dimethyl(phenyl)(2',3',4',5'-tetrahydro-[1,1'-biphenyl]-4-yl)silane (17c)

The general procedure for silylation was followed using \(N,N,N\)-trimethylanilinium iodide 17 (138 mg, 0.402 mmol) and dimethyphenylsilane (187 \(\mu\)L, 1.2 mmol). Reaction was run under a stream of nitrogen in order to prevent hydrogenation of the product. Purification by flash chromatography (100% hexanes to 98:2 hexanes/EtOAc) gave the title compound as a white solid in 59% yield (72 mg, 0.234 mmol).
chromatography (100% hexanes to 98:2 hexanes/EtOAc) gave the title compound as a white solid in 56% yield (65 mg, 0.222 mmol) and the hydrogenated product in 27% yield (32 mg, 0.109 mmol).

17c:

\[ \text{H NMR (500 MHz, Chloroform-}d) \delta 7.58 – 7.49 (m, 2H), 7.47 (d, J = 8.2 Hz, 2H), 7.36 (dt, J = 10.5, 3.6 Hz, 5H), 6.15 (tt, J = 5.7, 2.6 Hz, 1H), 2.41 (tq, J = 6.4, 2.1 Hz, 2H), 2.21 (dddd, J = 8.9, 6.6, 4.4, 2.5 Hz, 2H), 1.78 (ddt, J = 8.4, 6.1, 3.8 Hz, 2H), 1.70 – 1.61 (m, 2H), 0.54 (s, 6H). \]

13C NMR (126 MHz, Chloroform-\(d\)) \(\delta 143.48, 136.10, 134.31, 133.14, 129.39, 129.16, 127.91, 127.84, 125.34, 124.47, 27.38, 26.06, 23.19, 22.30, -2.19. \]

HRMS (EI) (m/z): [M] calculated for C\(_{20}\)H\(_{24}\)Si, 292.1647, found, 292.1646.

17c’:

\[ \text{H NMR (500 MHz, Chloroform-}d) \delta 7.53 (dd, J = 4.8, 2.5 Hz, 2H), 7.45 (d, J = 7.7 Hz, 2H), 7.40 – 7.32 (m, 5H), 7.20 (d, J = 7.5 Hz, 2H), 2.49 (dt, J = 11.6, 5.7 Hz, 1H), 1.93 – 1.79 (m, 4H), 1.74 (d, J = 13.1 Hz, 1H), 1.49 – 1.32 (m, 4H), 1.32 – 1.19 (m, 1H), 0.54 (s, 6H). \]

13C NMR (126 MHz, Chloroform-\(d\)) \(\delta 149.16, 134.38, 134.32, 129.23, 129.13, 127.94, 127.89, 126.55, 44.70, 34.45, 27.05, 26.32, -2.15. \]

HRMS (EI) (m/z): [M] calculated for C\(_{20}\)H\(_{26}\)Si, 294.1804, found, 294.1812.

18a

benzo[\(d\)][1,3]dioxol-5-ytriethylsilane (18a)

The general procedure for silylation was followed using N,N,N-trimethylanilinium iodide 18 (60 mg, 0.195 mmol) and triethylsilane (160 \(\mu\)L, 1 mmol). Purification by flash chromatography (100% hexanes) gave the title compound as a colorless oil in 68% yield (32 mg, 0.135 mmol). The spectral data matches that previously reported in the literature. \[^{[19]}\]  

\[ \text{H NMR (400 MHz, Chloroform-}d) \delta 6.96 (d, J = 7.6 Hz, 1H), 6.94 (s, 1H), 6.84 (d, J = 7.6 Hz, 1H), 5.93 (s, 2H), 0.95 (t, J = 7.8 Hz, 9H), 0.75 (q, J = 7.9 Hz, 6H). \]

13C NMR (100 MHz, Chloroform-\(d\)) \(\delta 148.26, 147.42, 130.44, 128.18, 113.57, 108.66, 100.55, 7.52, 3.66. \]

18b

benzo[\(d\)][1,3]dioxol-5-yl(benzyl)dimethylsilane (18b)

The general procedure for silylation was followed using N,N,N-trimethylanilinium iodide 18 (60 mg, 0.195 mmol) and dimethylbenzylsilane (160 \(\mu\)L, 1 mmol). Purification by flash chromatography (100% hexanes) gave the title compound as a colorless oil in 79% yield (42 mg, 0.155 mmol).
$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 7.19 (t, $J = 7.6$ Hz, 2H), 7.07 (t, $J = 7.3$ Hz, 1H), 6.97 – 6.90 (m, 4H), 6.90 (s, 1H), 6.84 (d, $J = 7.6$ Hz, 1H), 5.95 (s, 2H), 2.27 (s, 2H), 0.22 (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta$ 148.54, 147.45, 139.75, 128.42, 128.24, 127.86, 124.23, 113.19, 108.65, 100.67, 26.54, -3.08.

HRMS (EI) (m/z): [M] calculated for C$_{16}$H$_{18}$O$_2$Si, 270.1076, found, 270.1084.

18c
benzo[d][1,3]dioxol-5-yldimethyl(phenyl)silane (18c)

The general procedure for silylation was followed using $N,N,N$-trimethylanilinium iodide 18 (61 mg, 0.199 mmol) and dimethylphenylsilane (156 µL, 1 mmol). Purification by flash chromatography (100% hexanes) gave the title compound as a colorless oil in 60% yield (31 mg, 0.119 mmol).

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.56 – 7.47 (m, 2H), 7.40 – 7.31 (m, 3H), 7.01 (d, $J = 7.6$ Hz, 1H), 6.96 (s, 1H), 6.84 (d, $J = 7.6$ Hz, 1H), 5.93 (s, 2H), 0.53 (s, 6H).

$^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 148.63, 147.53, 138.45, 134.24, 131.36, 129.25, 128.39, 127.96, 113.65, 108.74, 100.69, -2.05.

HRMS (EI) (m/z): [M] calculated for C$_{15}$H$_{16}$O$_2$Si, 256.0920, found, 256.0921.
VII) Reduction Substrates

![19a](benzyloxy)(tert-butyl)dimethylsilane (19a)

The general procedure for reduction was followed using $N,N,N$-trimethylanilinium iodide 11 (41 mg, 0.101 mmol) and triethylsilane (80 µL, 0.5 mmol) in dioxane at 60 ºC. The crude reaction mixture was passed through a short silica gel plug with EtOAc and the solution was evaporated under reduced pressure. The yield was determined using CH$_2$Br$_2$ (7 µL) as an internal standard (68%) by $^1$H NMR. The spectral data matches that previously reported in the literature.$^{[24]}$

$^1$H NMR (401 MHz, Chloroform-$d$) δ 7.33 (d, $J = 4.4$ Hz, 5H), 4.75 (s, 2H), 1.24 (s, 9H), 0.10 (s, 6H).

![19b]( trifluorotoluene (19b)

The general procedure for reduction was followed using $N,N,N$-trimethylanilinium iodide 8 (33 mg, 0.100 mmol) and triethylsilane (80 µL, 0.5 mmol) in dioxane at 40 ºC. The crude reaction mixture was passed through a short silica gel plug with EtOAc. The yield was determined by GC-FID analysis using tridecane as an internal standard due to volatility of the product (67%).

![19c](anisole (19c)

The general procedure for reduction was followed using $N,N,N$-trimethylanilinium iodide 9 (29 mg, 0.989 mmol) and triethylsilane (80 µL, 0.5 mmol) in DMF at room temperature for 2 hours. The crude reaction mixture was passed through a short silica gel plug with EtOAc. The yield was determined by GC-FID analysis using tridecane as an internal standard due to volatility of the product (20%).
The general procedure for reduction was followed using \( N,N,N \)-trimethylanilinum iodide 10 (36 mg, 0.101 mmol) and triethylsilane (80 µL, 0.5 mmol) in DMF at room temperature for 2 hours. The crude reaction mixture was passed through a short silica gel plug with EtOAc. The yield was determined by GC-FID analysis using tridecane as an internal standard due to volatility of the product (60%).

The general procedure for reduction was followed using \( N,N,N \)-trimethylanilinum iodide 2 (36 mg, 0.100 mmol) and triethylsilane (80 µL, 0.5 mmol) in DMF at room temperature for overnight. The crude reaction mixture was passed through a short silica gel plug with EtOAc. The yield was determined by GC-FID analysis using tridecane as an internal standard due to volatility of the product (98%).

The general procedure for reduction was followed using \( N,N,N \)-trimethylanilinum iodide 13 (75 mg, 0.200 mmol) and triethylsilane (160 µL, 1 mmol) at room temperature. Purification by flash chromatography (100% hexanes/) gave the title compound as a white solid in 67% yield (25 mg, 0.134 mmol) with approximately 10% of an impurity that could not be separated by silica chromatography. The spectral data matches that previously reported in the literature.\(^{[25]}\)

\( ^1H \text{ NMR (400 MHz, Chloroform-d)} \) δ 7.51 (d, \( J = 7.9 \text{ Hz} \), 2H), 7.49 – 7.41 (m, 3H), 7.41 – 7.34 (m, 1H), 7.01 – 6.83 (m, 2H).

\( ^19F \text{ NMR (376 MHz, Chloroform-d)} \) δ -111.62 (p, \( J = 8.0 \text{ Hz} \)), -113.66 (q, \( J = 9.2 \text{ Hz} \)).
naphthalene (19e)

The general procedure for reduction was followed using N,N,N-trimethylanilinium iodide (63 mg, 0.201 mmol) and triethylsilane (160 µL, 1 mmol) in DMF at 40 ºC. The crude reaction mixture was passed through a short silica gel plug with EtOAc. The yield was determined by GC-FID analysis using tridecane as an internal standard due to volatility of the product (81%).

tert-butylbenzene (19f)

The general procedure for reduction was followed using N,N,N-trimethylanilinium iodide 7 (32 mg, 0.100 mmol) and triethylsilane (80 µL, 0.5 mmol) in dioxane at 40 ºC. The crude reaction mixture was passed through a short silica gel plug with EtOAc. The yield was determined by GC-FID analysis using tridecane as an internal standard due to volatility of the product (75%).

p-xylene (19g)

The general procedure for reduction was followed using N,N,N-trimethylanilinium iodide 16 (29 mg, 0.100 mmol) and triethylsilane (80 µL, 0.5 mmol) in dioxane at 60 ºC. The crude reaction mixture was passed through a short silica gel plug with EtOAc. The yield was determined by GC-FID analysis using tridecane as an internal standard due to volatility of the product (15%).
(1H-biphenyl)-4-yloxy)(tert-butyl)dimethylsilane (19h)

The general procedure for reduction was followed using N,N,N-trimethylanilinium iodide 12 (48 mg, 0.102 mmol) and triethylsilane (80 µL, 0.5 mmol) in dioxane at 40 °C. The crude reaction mixture was passed through a short silica gel plug with EtOAc and the solution was evaporated under reduced pressure. The yield was determined using CH₂Br₂ (7 µL) as an internal standard (80%) by ¹H NMR. The spectral data matches that previously reported in the literature.[¹⁷]

¹H NMR (500 MHz, Chloroform-d) δ 7.59 – 7.51 (m, 2H), 7.50 – 7.45 (m, 2H), 7.41 (t, J = 7.7 Hz, 2H), 7.35 – 7.27 (m, 1H), 6.91 (d, J = 8.6 Hz, 1H), 1.01 (s, 9H), 0.24 (s, 6H).

¹³C NMR (126 MHz, Chloroform-d) δ 155.42, 141.04, 134.43, 128.81, 128.22, 126.88, 126.78, 120.46, 25.86, 18.39, -4.22.

pyridine (19i)

The general procedure for reduction was followed using N,N,N-trimethylanilinium iodide (26 mg, 0.098 mmol) and triethylsilane (80 µL, 0.5 mmol) in dioxane at 90 °C. The crude reaction mixture was passed through a short silica gel plug with EtOAc. The yield was determined by GC-FID analysis using tridecane as an internal standard due to volatility of the product (37%).

4-phenyl-1-propyl-1H-pyrazole (19j)

The general procedure for reduction was followed using N,N,N-trimethylanilinium iodide 15 (77 mg, 0.207 mmol) and triethylsilane (160 µL, 1 mmol). Purification by flash chromatography (90:10% hexanes/EtOAc) gave the title compound as a white solid in 90% yield (35 mg, 0.189 mmol).

¹H NMR (500 MHz, Chloroform-d) δ 7.78 (s, 1H), 7.63 (s, 1H), 7.48 (d, J = 8.3 Hz, 2H), 7.43 – 7.30 (m, 2H), 7.25 – 7.16 (m, 1H), 4.11 (t, J = 7.1 Hz, 2H), 2.35 – 1.83 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H).
**13C NMR** (126 MHz, Chloroform-d) δ 136.71, 132.93, 128.97, 126.40, 126.07, 125.61, 122.89, 11.33.
**HRMS (ESI) (m/z):** [M+H] calculated for C_{12}H_{14}N_{2}, 187.1235, found, 187.1226.

![4-phenylmorpholine (19k)]

The general procedure for reduction was followed using N,N,N-trimethylanilinium iodide 13 (67 mg, 0.192 mmol) and triethylsilane (160 µL, 1 mmol) at 60 °C. Purification by flash chromatography (95:5% hexanes/EtOAc) gave the title compound as a white solid in 90% yield (20 mg, 0.150 mmol). The spectral data matches that previously reported in the literature.[26]

**1H NMR** (500 MHz, Chloroform-d) δ 7.29 (t, J = 7.8 Hz, 2H), 6.93 (d, J = 8.1 Hz, 2H), 6.89 (t, J = 7.3 Hz, 1H), 3.87 (t, J = 4.8 Hz, 4H), 3.17 (t, J = 4.8 Hz, 4H).

**13C NMR** (126 MHz, Chloroform-d) δ 151.42, 129.32, 120.18, 115.85, 67.09, 49.51.
To a suspension of AlCl$_3$ (520 mg, 3.92 mmol, 1.00 equiv) in DCM (12.5 mL) at 0 ºC was slowly added benzoyl chloride (0.46 mL, 3.92 mmol, 1.00 equiv). Dimethylaniline (0.52 mL, 4.12 mmol, 1.05 equiv) was then added dropwise and the reaction was stirred at 0 ºC for 4 hours before stirring at room temperature for 3 hours. Dilute reaction mixture with DCM and add ~15 mL H$_2$O. Wash organic layer 2x20 mL H$_2$O, 2x20 mL sat. NaHCO$_3$, 1x20 mL brine. Dry organic layer over Na$_2$SO$_4$ and concentrate. Purification by flash chromatography (90:10 hexanes/EtOAc) gave the title compound as a yellow solid in 43% yield (401 mg, 1.69 mmol) ($p$-/o- benzylation observed in ~2:1 ratio).[27]

$^1$H NMR (401 MHz, Chloroform-d) δ 7.80 (d, $J = 9.0$ Hz, 2H), 7.75 – 7.68 (m, 2H), 7.57 – 7.50 (m, 1H), 7.48 – 7.42 (m, 2H), 6.68 (d, $J = 9.0$ Hz, 2H), 3.08 (s, 6H).

$^{13}$C NMR (100 MHz, Chloroform-d) δ 195.26, 153.42, 139.44, 132.86, 131.22, 129.57, 128.12, 124.91, 110.67, 40.19.

HRMS (EI) (m/z): [M] calculated for C$_{17}$H$_{24}$O$_2$Si, 377.1759, found, 377.1764.

NaOH (1.02g, 25.5 mmol, 5 equiv) and hydrazine hydrate (1.25g, 25.5 mmol, 5 equiv) were added to a round bottom containing 20a (1.17g, 5.1 mmol, 1 equiv) in ethyleneglycol (30 mL). A reflux condenser was attached and the mixture was heated to 155 ºC overnight. The reaction mixture was cooled to room temperature and diluted with 50 mL EtOAc and 50 mL H$_2$O. The mixture was then extracted 2x50 mL EtOAc. The organic layers were dried over Na$_2$SO$_4$ and concentrated. Purification by flash chromatography (95:5 hexanes/EtOAc) gave the title compound as a clear oil in 80% yield (860 mg, 4.08 mmol).[27]

$^1$H NMR (500 MHz, Chloroform-d) δ 7.28 (d, $J = 8.0$ Hz, 2H), 7.20 – 7.15 (m, 3H), 7.07 (d, $J = 8.9$ Hz, 2H), 6.70 (d, $J = 8.8$ Hz, 2H), 3.90 (s, 2H), 2.91 (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 149.28, 153.42, 139.44, 132.86, 131.22, 129.57, 128.12, 124.91, 110.67, 40.19.

HRMS (EI) (m/z): [M] calculated for C$_{17}$H$_{36}$O$_2$Si, 377.1759, found, 377.1764.
4-benzyl-$N,N,N$-trimethylammoniumaniline iodide (21)

To a dry vial with a stirbar was added $20b$ (860 mg, 4.07 mmol, 1 equiv) and MeI (2.55 mL, 41.00 mmol, 10 equiv). The vial was sealed with a teflon cap and stirred until the reaction solidified (~5 hours). The contents were suspended in Et$_2$O and filtered, washing with 3x15 mL Et$_2$O to remove any unreacted starting material. The ammonium salt was dried on high vac for ~2 hours and used as is for subsequent reactions. The product was obtained as a white crystalline powder in 83% yield (1.2g, 2.80 mmol) and used without further purification.

benzyl(4-benzylphenyl)dimethylsilane (22)

The general procedure for silylation was followed using $N,N,N$-trimethylanilium iodide 21 (76 mg, 0.215 mmol) and benzylidimethylsilane (158 µL, 1 mmol). Purification by flash chromatography (100% hexanes) gave an inseparable mixture of the title compound in 66% yield (45 mg, 0.142 mmol) and 1,2-dibenzyl-1,1,2,2-tetramethyldisilane (12 mg, 0.040 mmol).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 7.39 (dd, $J = 8.1, 2.6$ Hz, 2H), 7.31 (td, $J = 7.7, 7.2, 2.3$ Hz, 2H), 7.20 (dq, $J = 14.3, 6.1$ Hz, 7H), 7.11 – 7.03 (m, 2H), 6.95 (dd, $J = 8.0, 2.7$ Hz, 2H), 4.00 (s, 2H), 2.30 (d, $J = 2.7$ Hz, 2H), 0.23 (d, $J = 2.8$ Hz, 6H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta$ 142.15, 141.07, 139.88, 135.93, 134.06, 129.11, 128.61, 128.50, 128.45, 128.23, 128.14, 126.24, 124.18, 124.04, 42.09, 32.20, 28.99, 26.37, 0.74, -3.25.

HRMS (El) (m/z): [M] calculated for C$_{22}$H$_{24}$Si, 316.1647, found, 316.1641.

1-(((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl)oxy)-4-nitrobenzene (23a)
A solution of (−)-menthol (3.4g, 21.7 mmol, 2.0 equiv) in DMF (4 mL) was added dropwise to a flame dried 20 mL scintillation vial equipped with a stir bar containing a solution of NaH (60% dispersion in mineral oil) (120mg, 30 mmol, 3.0 equiv) in DMF (1 mL) at 0 °C. After 30min the vial was allowed to warm to room temperature. 4-fluoro-nitrobenzene (1.06 mL, 10 mmol, 1.0 equiv) was added slowly and the vial was sealed with a Teflon cap and headed to 90 °C for 48 hours. The solution was then cooled to room temperature, transferred to a separatory funnel, and diluted with 30 mL diethyl ether. The organics were then washed 2x50 mL 5M NaOH solution and 1x50 mL brine. The organic layer was dried with sodium sulfate before concentrating. The product can be obtained via Kugelrohr distillation at 0.5 bar at 80 ºC through the removal of unreacted 4-fluoro-nitrobenzene and excess menthol. The product was obtained as a yellow crystalline solid. The discoloration was removed through Purification by flash chromatography (90:10 hexanes/EtOAc) to give the title compound as a white crystalline solid in 30% yield (1.72 g, 6.2 mmol).

\[ ^1H \text{NMR (401 MHz, Chloroform-}d) \delta 8.18 (d, J = 8.9 Hz, 2H), 6.93 (d, J = 9.0 Hz, 2H), 4.16 (td, J = 10.6, 4.2 Hz, 1H), 2.20 – 2.04 (m, 2H), 1.85 – 1.69 (m, 2H), 1.63 – 1.46 (m, 2H), 1.18 – 1.01 (m, 3H), 0.93 (t, J = 7.5 Hz, 6H), 0.75 (d, J = 6.9 Hz, 3H). \]

\[ ^13C \text{NMR (176 MHz, Chloroform-}d) \delta 163.85, 141.13, 126.22, 115.13, 78.53, 47.96, 40.00, 34.43, 31.54, 26.38, 23.90, 22.19, 20.74, 16.77. \]

HRMS (ESI) (m/z): [M+Na] calculated for C_{16}H_{23}NO_3, 300.1570, found, 300.1580.

To a round bottom equipped with a stir bar was added 23a (400 mg, 1.44 mmol) and palladium on carbon (10%) (40 mg, 2.5 mol%). The flask was backfilled three times with nitrogen before adding methanol (15 mL) and EtOAc (2 mL). The flask was then backfilled three times with H_2 before attaching a H_2 balloon. The reaction was left to stir at room temperature overnight. The contents of the flask were then filtered through Celite with EtOAc. The filtrate was concentrated to give the title compound as a reddish solid in 97% yield (344 mg, 1.39 mmol).

\[ ^1H \text{NMR (700 MHz, Chloroform-}d) \delta 6.75 (d, J = 8.6 Hz, 2H), 6.63 (d, J = 8.7 Hz, 1H), 3.82 (td, J = 10.5, 4.2 Hz, 1H), 3.42 (s, 2H), 2.28 (pd, J = 7.0, 2.7 Hz, 1H), 2.11 (ddd, J = 12.6, 3.8, 1.9 Hz, 1H), 1.69 (dt, J = 14.3, 3.7 Hz, 2H), 1.45 (ddt, J = 13.3, 10.4, 3.2 Hz, 1H), 1.39 (tdq, J = 12.6, 6.6, 3.3 Hz, 1H), 1.10 – 1.02 (m, 1H), 1.01 – 0.94 (m, 1H), 0.92 (dd, J = 24.6, 6.8 Hz, 7H), 0.80 (d, J = 6.9 Hz, 3H). \]

\[ ^13C \text{NMR (176 MHz, Chloroform-}d) \delta 151.50, 140.24, 118.09, 116.51, 79.17, 48.34, 40.73, 34.70, 31.60, 26.03, 23.70, 22.32, 21.02, 16.58. \]

4-(((1\text{R},2\text{R},5\text{R})-2\text{-isopropyl-5-methylcyclohexyl})\text{oxy})-N,N\text{-dimethylaniline (23c)}

To a round bottom equipped with a stir bar was dissolved 23b (344 mg, 1.39 mmol, 1.0 equiv) in acetonitrile (5 mL). K$_2$CO$_3$ (384 mg, 2.78 mmol, 2.0 equiv) and an aqueous formaldehyde solution (37\%) (0.62 mL, 8.34 mmol, 6.0 equiv) were added and the reaction was stirred for 30 min. The reaction was then cooled in an ice bath for 5 min before adding sodium triacetoxyborohydride (883 mg, 4.17 mmol, 3.0 equiv) in 200 mg portions over 5 min. Acetic acid (1 mL) was slowly added and the reaction was warmed and allowed to stir at room temperature overnight. Quench the reaction with 15mL H$_2$O and 15 mL EtOAc. Basify with sat. NaHCO$_3$ and extract 3x25 mL EtOAc. Wash organic layers with 1x25 mL brine and dry over sodium sulfate before concentrating. The product was obtained as a light brown crystalline solid in 88\% yield (336 mg, 1.21 mmol) with no need for further purification.$^{[28]}$

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 6.84 (d, $J = 9.0$ Hz, 2H), 6.72 (d, $J = 8.9$ Hz, 2H), 3.85 (td, $J = 10.5$, 4.2 Hz, 1H), 2.87 (s, 6H), 2.29 (pd, $J = 7.1$, 2.7 Hz, 1H), 2.12 (d, $J = 12.4$ Hz, 1H), 1.70 (dt, $J = 14.6$, 3.8 Hz, 2H), 1.55 – 1.33 (m, 3H), 1.07 (td, $J = 13.2$, 9.6 Hz, 2H), 0.98 (m, 1H), 0.92 (dd, $J = 15.7$, 6.7 Hz, 6H), 0.80 (d, $J = 6.9$ Hz, 3H).

$^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 150.57, 145.97, 117.81, 114.88, 79.02, 48.34, 41.91, 40.76, 34.73, 31.61, 26.06, 23.74, 22.34, 21.04, 16.62.

HRMS (ESI) (m/z): [M+H] calculated for C$_{18}$H$_{29}$NO, 276.2327, found, 276.2323.

4-(((1\text{R},2\text{R},5\text{R})-2\text{-isopropyl-5-methylcyclohexyl})\text{oxy})-N,N,N\text{-trimethylammoniumaniline iodide (21)}
To a dry vial with a stirbar was added 23c (336 mg, 1.21 mmol, 1 equiv) and MeI (0.75 mL, 12.10 mmol, 10 equiv). The vial was sealed with a teflon cap and stirred until the reaction solidified (~5 hours). The contents were suspended in Et$_2$O and filtered, washing with 3x10 mL Et$_2$O to remove any unreacted starting material. The ammonium salt was dried on high vac for ~2 hours and used as is for subsequent reactions. The product was obtained as a white powder in 83% yield (419 mg, 1.00 mmol) and used without further purification.

The general procedure for silylation was followed using N,N,N-trimethylanilinium iodide 24 (87 mg, 0.208 mmol) and triethylsilane (160 µL, 1 mmol). Purification by flash chromatography (100% hexanes) gave the title compound as a clear oil in 58% yield (40 mg, 0.121 mmol).

$^1$H NMR (500 MHz, Chloroform-d) δ 7.38 (d, $J = 8.1$ Hz, 1H), 6.89 (d, $J = 8.4$ Hz, 1H), 4.06 (td, $J = 10.5$, 4.3 Hz, 1H), 2.20 (ddt, $J = 16.5$, 12.8, 3.7 Hz, 1H), 1.72 (dd, $J = 11.8$, 3.1 Hz, 1H), 1.60 – 1.38 (m, 1H), 1.10 (qd, $J = 12.6$, 2.9 Hz, 1H), 1.05 – 0.87 (m, 12H), 0.84 – 0.71 (m, 7H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 159.10, 135.73, 127.87, 115.28, 77.04, 48.18, 40.46, 34.70, 31.58, 26.17, 23.87, 22.30, 20.96, 16.76, 7.61, 3.71.

HRMS (EI) (m/z): [M] calculated for C$_{22}$H$_{38}$OSi, 346.2692, found, 346.2682.

1-(allyloxy)-4-nitrobenzene (26a)

To a solution of 26 (1g, 7.19 mmol, 1.00 equiv) in DMF (3 mL, 2.4M) was added K$_2$CO$_3$ (1g, 7.19 mmol, 1.00 equiv). Allylbromide (0.68 mL, 7.90 mmol, 1.10 equiv) was added and a reflux condenser was added before heating to 60 °C overnight. Upon cooling to room temperature, 20 mL H$_2$O and 20 mL Et$_2$O were added and the reaction mixture was extracted 2x20 mL Et$_2$O. The combined organics were then washed 2x20 mL 1M NaOH, 1x20 mL brine, and dried over MgSO$_4$ before concentrating. The product was obtained via Kugelrohr distillation to give a yellow oil that was carried on to the next step without further purification. [29]
**1H NMR** (401 MHz, Chloroform-d) δ 8.20 (d, *J* = 9.3 Hz, 1H), 6.97 (d, *J* = 9.2 Hz, 1H), 6.04 (ddt, *J* = 17.4, 10.6, 5.3 Hz, 1H), 5.44 (dt, *J* = 17.3, 1.5 Hz, 1H), 5.35 (dt, *J* = 10.6, 1.4 Hz, 1H), 4.64 (dt, *J* = 5.4, 1.6 Hz, 2H).

**13C NMR** (100 MHz, Chloroform-d) δ 163.71, 141.73, 132.01, 126.03, 118.82, 114.84, 69.54.

2-allyl-4-nitrophenol (26b)

Crude 26a (~1.3g) and an equal weight of diphenylether were added to a round bottom equipped with a reflux condenser. The mixture was heated to 210 ºC for 36 hours. The reaction was cooled to room temperature and diluted with 30 mL Et₂O. The organics were extracted 3x30 mL 6M NaOH. The combined aqueous layers were acidified with conc. HCl. The acidic aqueous solution was then extracted 3X30 mL Et₂O. The ether layers were combined and dried over MgSO₄. The product can be recrystallized. Product was obtained as a yellow crystalline solid in 46% over two steps (593 mg, 3.31 mmol).

**1H NMR** (500 MHz, Chloroform-d) δ 8.06 (m, 2H), 6.89 (d, *J* = 8.7 Hz, 1H), 6.01 (ddt, *J* = 16.8, 10.4, 6.6 Hz, 1H), 5.88 (br, 1H), 5.30 – 5.16 (m, 2H), 3.47 (d, *J* = 6.4 Hz, 2H).

**13C NMR** (126 MHz, Chloroform-d) δ 159.90, 141.77, 134.72, 126.60, 126.54, 124.44, 118.19, 116.01, 34.79.

2-allyl-1-methoxy-4-nitrobenzene (27)

In a dry round bottom, 26b (1.00 g, 5.58 mmol, 1 equiv) was dissolved in DMF (10 mL). K₂CO₃ (1.77g, 12.84 mmol, 2.3 equiv) was added followed by MeI (0.80 mL, 12.84 mmol, 2.3 equiv). The mixture was stirred at room temperature overnight. The reaction was quenched with 50 ml Et₂O and 50 ml H₂O. The organics were washed 2x40 mL 1M NaOH, then 1x40 mL brine followed by drying of the organics over MgSO₄. The product was obtained as pure a yellow oil in 97% yield (1.05 g, 5.41 mmol) with no need for further purification.
**1H NMR** (500 MHz, Chloroform-\(d\)) \(\delta\) 8.14 (dd, \(J = 9.0, 2.8\) Hz, 1H), 8.05 (d, \(J = 2.8\) Hz, 1H), 6.90 (d, \(J = 9.0\) Hz, 1H), 5.96 (ddt, \(J = 16.9, 10.1, 6.7\) Hz, 1H), 5.21 – 5.03 (m, 2H), 3.94 (s, 3H), 3.41 (d, \(J = 6.6\) Hz, 2H).

**13C NMR** (176 MHz, Chloroform-\(d\)) \(\delta\) 162.41, 141.44, 135.16, 130.04, 125.44, 124.16, 117.14, 109.80, 56.23, 34.07.

**HRMS** (ESI) (m/z): [M+H] calculated for C_{10}H_{15}NO, 194.0812, found, 194.0811.

![](image1.png)

To a round bottom equipped with a stir bar was added 27 (1.05 g, 5.43 mmol) and palladium on carbon (10%) (144 mg, 2.5 mol%). The flask was backfilled three times with nitrogen before adding methanol (50 mL). The flask was then backfilled three times with H\(_2\) before attaching a H\(_2\) balloon. The reaction was left to stir at room temperature overnight. The contents of the flask were then filtered through Celite with DCM. The filtrate was concentrated to give the title compound in quantitative yield as an off-white crystalline solid.

**1H NMR** (400 MHz, Chloroform-\(d\)) \(\delta\) 6.68 (d, \(J = 8.3\) Hz, 1H), 6.57 – 6.47 (m, 2H), 3.75 (s, 3H), 3.37 (s, 2H), 2.55 – 2.47 (m, 3H), 1.58 (h, \(J = 7.3\) Hz, 3H), 0.95 (t, \(J = 7.3\) Hz, 3H).

**HRMS** (ESI) (m/z): [M+H] calculated for C_{10}H_{15}NO, 166.1226, found, 166.1225.

![](image2.png)

4-methoxy-3-propylaniline (27a)

4-methoxy-\(N,N\)-dimethyl-3-propylaniline (27b)

To a round bottom equipped with a stir bar was dissolved 27a (897 mg, 5.43 mmol, 1.0 equiv) in acetonitrile (25 mL). K\(_2\)CO\(_3\) (1.5 g, 10.86 mmol, 2.0 equiv) and an aqueous formaldehyde solution (37%) (2.42 mL, 32.58 mmol, 6.0 equiv) were added and the reaction was stirred for 30 min. The reaction was then cooled in an ice bath for 5 min before adding sodium triacetoxyborohydride (3.45 mg, 16.29 mmol, 3.0 equiv) in 500 mg portions over 5 min. Acetic
acid (2.5 mL) was slowly added and the reaction was warmed and allowed to stir at room temperature overnight. Quench the reaction with 50 mL H₂O and 50 mL EtOAc. Basify with sat. NaHCO₃ and extract 3x50 mL EtOAc. Wash organic layers with 1x25 mL brine and dry over sodium sulfate before concentrating. The product was obtained as a crystalline solid in 83% yield (876 mg, 4.51 mmol) with no need for further purification.

\[ \text{1H NMR} \quad (400 \text{ MHz, Chloroform-d}) \delta 6.78 (d, J = 8.8 \text{ Hz}, 1\text{H}), 6.66 (d, J = 3.2 \text{ Hz}, 1\text{H}), 6.60 (dd, J = 8.8, 3.1 \text{ Hz}, 1\text{H}), 3.77 (s, 3\text{H}), 2.86 (s, 6\text{H}), 2.57 (dd, J = 8.8, 6.7 \text{ Hz}, 2\text{H}), 1.62 (h, J = 7.4 \text{ Hz}, 2\text{H}), 0.97 (t, J = 7.3 \text{ Hz}, 3\text{H}). \]

\[ \text{13C NMR} \quad (100 \text{ MHz, Chloroform-d}) \delta 150.36, 145.66, 132.02, 116.69, 111.85, 111.83, 56.24, 42.06, 32.93, 23.49, 14.33. \]

\[ \text{HRMS (ESI) (m/z): [M+H] calculated for C}_{12}\text{H}_{19}\text{NO, 194.1545, found, 194.1536.} \]

4-methoxy-3-propyl-N,N,N-trimethylammoniumaniline iodide (28)

To a dry vial with a stirbar was added 27b (860 mg, 4.53 mmol, 1 equiv) and MeI (2.82 mL, 45.30 mmol, 10 equiv). The vial was sealed with a teflon cap and stirred until the reaction solidified (~5 hours). The contents were suspended in Et₂O and filtered, washing with 3x15 mL Et₂O to remove any unreacted starting material. The ammonium salt was dried on high vac for ~2 hours and used as is for subsequent reactions. The product was obtained as a white crystalline powder in 88% yield (1.33g, 3.99 mmol) and used without further purification.

triethyl(4-methoxy-3-propylphenyl)silane (29)

The general procedure for silylation was followed using N,N,N-trimethylanilium iodide 28 (67 mg, 0.200 mmol) and triethylsilane (160 µL, 1 mmol). Purification by flash chromatography (100% hexanes) gave the title compound as a clear oil in 77% yield (41 mg, 0.154 mmol).

\[ \text{1H NMR} \quad (401 \text{ MHz, Chloroform-d}) \delta 7.30 (dd, J = 8.0, 1.6 \text{ Hz}, 1\text{H}), 7.22 (d, J = 1.7 \text{ Hz}, 1\text{H}), 6.85 (d, J = 8.1 \text{ Hz}, 1\text{H}), 3.82 (s, 3\text{H}), 2.75 – 2.36 (m, 2\text{H}), 1.61 (q, J = 7.5 \text{ Hz}, 2\text{H}), 1.11 – 0.87 (m, 9\text{H}), 0.76 (q, J = 7.9 \text{ Hz}, 3\text{H}). \]

\[ \text{13C NMR} \quad (126 \text{ MHz, Chloroform-d}) \delta 158.31, 136.02, 133.28, 130.39, 127.70, 109.84, 55.18, 32.60, 23.20, 14.27, 7.63, 3.72. \]

\[ \text{HRMS (ESI) (m/z): [M+Na] calculated for C}_{16}\text{H}_{28}\text{OSi, 287.1802, found, 287.1802.} \]
To a 50 mL round bottom was added Ni(COD)$_2$ (45 mg, 0.16 mmol, 0.05 equiv), N,N'-Bis(2,6-bis(diphenylmethyl)-4-methoxyphenyl)imidazolium chloride (IPr*OMe.HCl) (160 mg, 0.16 mmol, 0.05 equiv), NaO-t-Bu (787 mg, 8.17 mmol, 2.5 equiv), and 9 (3.27 mmol, 1 equiv) were combined under inert atmosphere and suspended in 15 mL of dioxane at rt. Silane (2.61 mL, 16.35 mmol, 5 equiv) was added and the vial was sealed with a Teflon cap before removing from the glovebox to heat to 40 °C overnight. Upon completion, the reaction mixture was filtered through Celite with DCM, the solvent was removed by rotary evaporation, and the crude reaction mixture was purified by silica gel chromatography (100% hexanes to 95:5 hexanes/ EtOAc) to give the title compound as a clear oil in 78% yield (569 mg, 2.55 mmol).
X) NMR Spectra

![NMR Spectra Image]

MeSiMe(OTMS)$_2$
Me
SiMe₂Bn

6c
SiEt₃

PhO

10a
SiMe(OTMS)$_2$
16b
SiMe$_2$Bn
XI) References