SUPPORTING INFORMATION

Pinacol-Derived Chlorohydrosilane in Metal Free Reductive Amination for the Preparation of Tertiary Alkylphenolmethyl Amines

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1. General considerations
All synthesis were carried out in oven-dried glassware under inert atmosphere. Anhydrous dichloromethane was obtained using PureSolv Micro multi-unit purification system. Acetonitrile was left standing over 3 Å molecular sieves and used without further drying. Triethylamine, and pyridine were purified and dried before use. All other reagents were purchased from Sigma Aldrich or TCI and used without further purification. Reactions were monitored through thin-layer chromatography (TLC) with commercial silica gel plates (Merck silica gel, 60 F254). Visualization of the developed plates was performed under UV lights at 254 nm and by staining with cerium ammonium molybdate. Flash column chromatography was performed on silica gel 60 (40-63 μm) as stationary phase. NMR spectra were recorded with Varian Mercury 300MHz or JEOL ECZR 500 instruments using CDCl₃ as solvent. Chemical shifts (δ) are reported in ppm referenced to the CDCl₃ residual peak (δ 7.26) or TMS peak (δ 0.00) for ¹H NMR and to CDCl₃ (δ 77.16) for ¹³C NMR. The following abbreviations were used to describe peak splitting patterns: s = singlet, d = doublet, t = triplet, m = multiplet. Coupling constants, J, were reported in Hertz (Hz). High-resolution mass spectra were recorded on a Waters ESI-TOF MS spectrometer.

2. Optimization of Reaction Conditions
   (I) Optimization of reaction conditions with 2'-hydroxyacetophenone and indoline [a]

\[
\begin{align*}
\text{2'-hydroxyacetophenone} & \quad \text{+ indoline} \\
\text{CH}_2\text{Cl}_2 & \quad \text{40 °C (24 h)} \\
\text{MeCN} & \quad \text{80 °C (18 h)} \\
\text{Toluene} & \quad \text{100 °C (16 h)} \\
\text{(CH}_2\text{Cl)}_2 & \quad \text{84 °C (18 h)} \\
\end{align*}
\]

| Solvent  | Reflux conditions | Yield (%) |
|----------|------------------|-----------|
| CH₂Cl₂   | 40 °C (24 h)     | 64        |
| MeCN     | 80 °C (18 h)     | 67        |
| Toluene  | 100 °C (16 h)    | 23        |
| (CH₂Cl)₂ | 84 °C (18 h)     | 43        |

\[
\begin{align*}
\text{2'-hydroxyacetophenone} & \quad \text{+ indoline} \\
\text{1. 3 Å MS, MeCN, Reflux, 18 h} \\
\text{2. PCS (1.2 equiv), DMPU (20 mol %)}  \\
\text{rt, 1 h then TBAF} \\
\end{align*}
\]

Variation of the amount of Indoline

| Indoline equiv | Conditions          | Yield (%) |
|----------------|---------------------|-----------|
| 2              | DMPU (0.2 equiv), PCS   | 84        |
| 1              | DMPU (0.2 equiv), PCS   | 61        |
| 2              | No DMPU, Only PCS     | 80        |
| 1              | No DMPU, Only PCS     | 42        |
| 1.2            | No DMPU, Only PCS     | 63        |
| Amount of DMPU (equiv) | Yield (%) |
|------------------------|-----------|
| 0.2                    | 61        |
| 0.4                    | 50        |
| 0.6                    | 72        |
| 0.8                    | 76        |
| 1                      | 62        |

[a] Reactions were carried out on 0.54 mmol scale in solvent (2 mL) under inert atmosphere. Isolated yields are reported.

(II) Optimization of reaction conditions with 2’-hydroxyacetophenone and Morpholine [a]

![Reaction diagram]

| DMAP equiv | Rxn conditions                      | Yield (%) |
|------------|-------------------------------------|-----------|
| 0.2        | 1. Re reflux (overnight)             | n.d [b]   |
|            | 2. rt (20 min)                       |           |
| 0.5        | 1. Re reflux (overnight)             | 51        |
|            | 2. rt (20 min)                       |           |
| 0.8        | 1. Re reflux (36 h)                  | 63        |
|            | 2. rt (20 min)                       |           |
| 0.8        | 1. Re reflux (36 h)                  | 64        |
|            | 2. 0 °C (20 min)                     |           |
| 1.0        | 1. Re reflux (overnight)             | 61        |
|            | 2. rt (20 min)                       |           |
| 1.2        | 1. Re reflux (36 or 24 h)            | 73        |
|            | 2. rt (20 min)                       |           |

[a] Reactions were carried out on 0.54 mmol scale in solvent (2 mL) under inert atmosphere. Isolated yields are reported.

[b] no product detected
3. General procedure for synthesis of aminoalkylphenols

\[
\begin{array}{c}
\text{R}^1 \quad \text{R}^2 \\
\text{R}^3 \quad \text{R}^4
\end{array}
\]

1. 3 Å MS, MeCN, reflux, 24 h
2. PCS (1.2 equiv), Pyridine (1.2 equiv), rt, 20 min
then TBAF

A mixture of 2'-hydroxyacetophenone (0.54 mmol), secondary amine (0.54 mmol) and molecular sieves (3 Å, 250 mg) in acetonitrile (1 mL) in a round bottom flask equipped with a condenser was refluxed under argon. The mixture was then cooled to rt and pyridine (52 µL, 0.65 mmol) added in one portion followed by dropwise addition of a solution of PCS (118 mg, 0.65 mmol) in acetonitrile (1 mL) via a syringe pump over 5 min. The resulting mixture was stirred for 20 min, treated with a solution of TBAF in 1 M THF (0.75 mL, 0.75 mmol) and stirred for additional 10 min. The mixture was quenched with saturated NH₄Cl (15 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layer was dried over MgSO₄, filtered out and solvent removed under vacuum. Residue was then purified by flash column chromatography.

4. Procedure for one – mmol scale synthesis of product 2

\[
\begin{array}{c}
\text{R}^1 \\
\text{R}^2
\end{array}
\]

1. 3 Å MS, MeCN, reflux, 24 h
2. PCS (1.2 equiv), Pyridine (1.2 equiv), rt 20 min
then TBAF

A mixture of 2'-hydroxyacetophenone (136 mg, 1 mmol), morpholine (86 µL, 1 mmol) and molecular sieves (3 Å, 550 mg) in acetonitrile (2 mL) in a round bottom flask equipped with a condenser was refluxed under argon. The mixture was then cooled to rt and pyridine (96.7 µL, 0.65 mmol) added in one portion followed by dropwise addition of a solution of PCS (216.8 mg, 1.2 mmol) in acetonitrile (2 mL) via a syringe pump over 5 min. The resulting mixture was stirred for 20 min, treated with a solution of TBAF in 1 M THF (1.4 mL, 1.38 mmol) and stirred for additional 10 min. The mixture was quenched with saturated NH₄Cl (15 mL) and extracted with EtOAc (3 × 20 mL). The combined organic layer was dried over MgSO₄, filtered out and solvent removed under vacuum. Residue was then purified by flash column chromatography on silica (Hexane/EtOAc = 8:2, 0.3% triethylamine) to give 2 as a colourless oil in 82% yield (170 mg, 0.82 mmol).

5. Procedure for control experiments

Reductive amination with Ph₂SiHCl

\[
\begin{array}{c}
\text{Me} \\
\text{N}
\end{array}
\]

1, 66%

A mixture of acetophenone (63 µL, 0.54 mmol), indoline (61 µL 0.54 mmol) and molecular sieves (3 Å, 250 mg) in acetonitrile (1 mL) in a round bottom flask equipped with a condenser was refluxed under argon. The mixture was then cooled to rt and pyridine (52 µL, 0.65 mmol) added in one portion. This was followed by dropwise addition of a solution of chlorodiphenylsilane (142 mg, 0.65 mmol) in acetonitrile (1 mL) via a syringe pump over 5 min. The resulting mixture was stirred for 2 h, treated with
a solution of TBAF in 1 M THF (0.75 mL, 0.75 mmol) and stirred for additional 10 min. The mixture was quenched with saturated NH$_4$Cl (15 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layer was dried over MgSO$_4$, filtered out and solvent removed under vacuum. Residue was then purified by flash column chromatography on silica (Hexane/EtOAc = 9:1, 0.3% triethylamine) to give 1 as a brown solid in 66% yield (85 mg, 0.355 mmol).

**Phenol Control Experiments**

A mixture of the ketone (0.54 mmol), indoline (61 µL 0.54 mmol) and molecular sieves (3 Å, 250 mg) in acetonitrile (1 mL) in a round bottom flask equipped with a condenser was refluxed under argon. The mixture was then cooled to rt and pyridine (52 µL, 0.65 mmol) added in one portion. This was followed by dropwise addition of a solution of PCS (118 mg, 0.65 mmol) in acetonitrile (1 mL) via a syringe pump over 5 min. The resulting mixture was stirred overnight at rt. Monitoring of the reaction mixture by TLC indicated the absence of the desired tertiary amine even after treatment with TBAF in 1 M THF (0.75 mL, 0.75 mmol) and aqueous work up with saturated NH$_4$Cl.

A mixture of acetophenone (63 µL, 0.54 mmol), indoline (61 µL 0.54 mmol) and molecular sieves (3 Å, 250 mg) in acetonitrile (1 mL) in a round bottom flask equipped with a condenser was refluxed under argon. The mixture was then cooled to rt and phenol (51 mg, 0.54 mmol) and pyridine (52 µL, 0.65 mmol) added in one portion. This was followed by dropwise addition of a solution of PCS (118 mg, 0.65 mmol) in acetonitrile (1 mL) via a syringe pump over 5 min. The resulting mixture was stirred for 20 min, treated with a solution of TBAF in 1 M THF (0.75 mL, 0.75 mmol) and stirred for additional 10 min. The mixture was quenched with saturated NH$_4$Cl (15 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layer was dried over MgSO$_4$, filtered out and solvent removed under vacuum. Residue was then purified by flash column chromatography on silica (Hexane/EtOAc = 9:1, 0.3% triethylamine) to give 27 as a yellow oil in 65% yield (78.5 mg, 0.35 mmol).
6. Product characterization data

2-(1-{indolin-1-yl}ethyl)phenol (1): Following the general procedure, 2’-hydroxyacetophenone (74 mg, 0.54 mmol), indoline (0.54 mmol, 61 µL) and PCS (118 mg, 0.65 mmol) in the presence of pyridine (52 µL, 0.65 mmol). The product was purified by flash chromatography on silica (Hexane/EtOAc = 9:1, 0.3% triethylamine) to give 1 as a brown solid in 78% yield (101 mg, 0.42 mmol). ¹H NMR (CDCl₃, 300 MHz) δ = 9.62 (br.s., 1H), 7.16-7.32 (m, 3H), 7.10 (t, J=8.2 Hz, 1H), 6.83-6.99 (m, 3H), 6.68 (d, J=7.6 Hz, 1H), 4.80 (d, J=7.0 Hz, 1H), 3.26-3.37 (m, 1H), 3.10-3.24 (m, 1H), 3.00 (d, J=5.9 Hz, 2H), 1.52 (d, J=7.0 Hz, 3H). ¹³C NMR (CDCl₃, 75 MHz): δ = 157.0, 149.5, 132.5, 129.0, 127.4, 126.4, 126.6, 124.8, 120.9, 119.8, 116.4, 111.5, 55.1, 48.7, 28.4, 12.6. HRMS (ESI) m/z calcd for C₁₆H₁₇NO⁺ [M + H]⁺ 240.1383, found 240.1390.

2-(1-{morpholinoethyl}phenol (2): This compound was synthesized from 2’-hydroxyacetophenone (74 mg, 0.54 mmol), morpholine (0.54 mmol, 47 µL) and PCS (118 mg, 0.65 mmol) in the presence of pyridine (52 µL, 0.65 mmol). The product was purified by flash chromatography on silica (Hexane/EtOAc = 8:2, 0.3% triethylamine) to give 2 as a colourless oil in 83% yield (93 mg, 0.45 mmol). ¹H NMR (CDCl₃, 300 MHz): δ = 11.10 (br. s., 1H), 7.10-7.20 (m, 1H), 6.98 (dd, J=2.3, 1.2 Hz, 1H), 6.80 (t, J=7.6 Hz, 2H), 3.75 (d, J=4.1 Hz, 4H), 3.57 (q, J=6.4 Hz, 1H), 2.40-2.80 (m, 4H), 1.41 (d, J=7.0 Hz, 3H). ¹³C NMR (CDCl₃, 75 MHz): δ = 156.5, 128.5, 127.9, 126.7, 119.4, 116.5, 67.0, 64.8, 16.5. HRMS (ESI) m/z calcd for C₁₂H₁₇NO₂⁺ [M + H]⁺ 208.1332, found 208.1343.

2-(1-{diallylamino}ethyl)phenol (3): Following the general procedure with 30 h of reflux; 2’-hydroxyacetophenone (74 mg, 0.54 mmol), diallylamine (0.54 mmol, 67 µL) and PCS (118 mg, 0.65 mmol) in the presence of pyridine (52 µL, 0.65 mmol). The product was purified by flash chromatography on silica (Hexane/EtOAc = 9:1, 0.3% triethylamine) to give 3 as a yellow oil in 51% yield (60 mg, 0.276 mmol). ¹H NMR (CDCl₃, 300 MHz): δ = 11.49 (br. s., 1H), 7.09-7.24 (m, 1H), 7.01 (d, J=7.0 Hz, 1H), 6.71-6.90 (m, 2H), 5.73-5.99 (m, 2H), 5.23 (d, J=1.2 Hz, 2H), 5.19 (dd, J=4.7, 1.2 Hz, 2H), 4.16 (q, J=7.0 Hz, 1H), 3.30 (dd, J=20.5, 6.4 Hz, 2H), 3.11 (dd, J=14.1, 7.6 Hz, 2H), 1.40 (d, J=6.4 Hz, 3H). ¹³C NMR (CDCl₃, 75 MHz): δ = 157.8, 134.0, 128.5, 127.2, 126.9, 119.0, 116.4, 58.0, 51.9, 12.7. HRMS (ESI) m/z calcd for C₁₄H₁₉NO⁺ [M + H]⁺ 218.1539, found 218.1542.
2-(1-(3,4-dihydroquinolin-1(2H)-yl)ethyl)phenol (4): This compound was synthesized from 2'-hydroxyacetophenone (74 mg, 0.54 mmol), 1,2,3,4-tetrahydroquinoline (0.54 mmol, 68 µL) and PCS (118 mg, 0.65 mmol) in the presence of pyridine (52 µL, 0.65 mmol). The product was purified by flash chromatography on silica (Hexane/EtOAc = 9:1, 3% triethylamine) to give 4 as a colourless oil in 51% yield (70 mg, 0.276 mmol). 

\[ \text{\textsuperscript{1}H NMR (CDCl}_3, 500 \text{ MHz}): \delta = 9.05 (s, 1H), 7.18-7.29 (m, 2H), 7.04-7.18 (m, 3H), 6.78-6.97 (m, 3H), 5.27 (q, \text{J} = 6.9 \text{ Hz}, 1H), 2.69-3.01 (m, 4H), 1.80-2.02 (m, 2H), 1.50 (d, \text{J} = 6.9 \text{ Hz}, 3H). \]

\[ \text{\textsuperscript{13}C NMR (CDCl}_3, 126 \text{ MHz}): \delta = 157.1, 130.3, 129.0, 127.1, 126.0, 119.9, 116.9, 116.3, 115.3, 54.5, 42.6, 28.0, 22.5, 11.6. \]

HRMS (ESI) m/z calcd for C\textsubscript{17}H\textsubscript{19}NO\textsuperscript{+} [M + H] \textsuperscript{+} 254.1539, found 254.1541.

2-(1-(ethyl(phenyl)amino)ethyl)phenol (5): This compound was synthesized from 2'-hydroxyacetophenone (74 mg, 0.54 mmol), ethylaniline (0.54 mmol, 68 µL) and PCS (118 mg, 0.65 mmol) in the presence of pyridine (52 µL, 0.65 mmol). The product was purified by flash chromatography on silica (Hexane/EtOAc = 9.6:0.4, 0.3% triethylamine) to give 5 as a pale yellow oil in 59% yield (77 mg, 0.32 mmol).

\[ \text{\textsuperscript{1}H NMR (CDCl}_3, 500 \text{ MHz}): \delta = 11.01 (br. s., 1H), 7.31-7.46 (m, 2H), 7.13-7.30 (m, 4H), 7.05-7.11 (m, 1H), 6.78-6.99 (m, 2H), 4.56 (q, \text{J} = 6.9 \text{ Hz}, 1H), 3.04-3.28 (m, 1H), 2.82-2.98 (m, 1H), 1.25 (d, \text{J} = 6.9 \text{ Hz}, 3H), 0.96 (t, \text{J} = 6.9 \text{ Hz}, 3H). \]

\[ \text{\textsuperscript{13}C NMR (CDCl}_3, 126 \text{ MHz}): \delta = 157.3, 147.0, 129.3, 128.7, 127.6, 127.3, 124.8, 124.4, 119.5, 116.7, 63.2, 44.3, 16.5, 13.1. \]

HRMS (ESI) m/z calcd for C\textsubscript{16}H\textsubscript{19}NO\textsuperscript{+} [M + H] \textsuperscript{+} 242.1539, found 242.1534.

2-(1-(dibenzylamino)ethyl)phenol (6): This compound was synthesized from 2'-hydroxyacetophenone (74 mg, 0.54 mmol), dibenzylamine (0.65 mmol, 125 µL) and PCS (118 mg, 0.65 mmol) in the presence of pyridine (52 µL, 0.65 mmol). The product was purified by flash chromatography on silica (Hexane/EtOAc = 9:1, 0.3% triethylamine) to give 6 as a pale yellow solid in 18% yield (31 mg, 0.097 mmol).

\[ \text{\textsuperscript{1}H NMR (CDCl}_3, 500 \text{ MHz}): \delta = 11.30 (br. s., 1H), 7.24-7.36 (m, 10H), 7.16 (t, \text{J} = 7.7 \text{ Hz}, 1H), 7.11 (d, \text{J} = 7.4 \text{ Hz}, 1H), 6.78-6.88 (m, 2H), 4.20 (q, \text{J} = 6.9 \text{ Hz}, 1H), 3.80 (d, \text{J} = 13.2 \text{ Hz}, 2H), 3.46 (d, \text{J} = 13.2 \text{ Hz}, 2H), 1.52 (d, \text{J} = 6.9 \text{ Hz}, 3H). \]

\[ \text{\textsuperscript{13}C NMR (CDCl}_3, 126 \text{ MHz}): \delta = 157.2, 137.1, 129.3, 128.4, 127.3, 126.8, 126.4, 118.9, 116.1, 55.0, 53.1, 9.2. \]

2-(1-(indolin-1-yl)ethyl)-4-methylphenol (7): This compound was synthesized from 2'-hydroxy-5'-methylacetophenone (81 mg, 0.54 mmol), indoline (0.54 mmol, 61 µL) and PCS (118 mg, 0.65 mmol) in the presence of pyridine (52 µL, 0.65 mmol). The product was purified by flash chromatography on silica (Hexane/EtOAc = 9:1, 0.3% triethylamine) to give 7 as a brown crystalline solid in 69% yield (94 mg, 0.37 mmol).

\[ \text{\textsuperscript{1}H NMR (CDCl}_3, 500 \text{ MHz}): \delta = 9.36 (s, 1H), 6.97-7.21 (m, 4H), 6.77-6.91 (m, 2H), 6.67 (d, \text{J} = 8.2 \text{ Hz}, 1H), 4.75 (q, \text{J} = 6.4 \text{ Hz}, 1H), 3.25-3.39 (m, 1H), 3.08-3.21 (m, 1H), 2.89-3.03 (m, 2H), 2.34 (s, 3H), 1.50 (d, \text{J} = 7.0 \text{ Hz}, 3H). \]

\[ \text{\textsuperscript{13}C NMR (CDCl}_3, 75 \text{ MHz}): \delta = 154.5, 149.7, 132.2, 129.3, 128.7, 127.4, 127.1, 126.2, 124.8, 120.7, 116.1, 111.5, 55.1, 48.7, 28.4, 20.8, 12.7. \]

HRMS (ESI) m/z calcd for C\textsubscript{17}H\textsubscript{19}NO\textsuperscript{+} [M + H] \textsuperscript{+} 254.1541, found 254.1555.

S7
5-bromo-2-(1-(indolin-1-yl)ethyl)phenol (8): This compound was synthesized from 4'-Bromo-2'-hydroxyacetophenone (116 mg, 0.54 mmol), indoline (0.54 mmol, 61 µL) and PCS (118 mg, 0.65 mmol) in the presence of pyridine (52 µL, 0.65 mmol). The product was purified by flash chromatography on silica (Hexane/EtOAc = 9:1, 0.3% triethylamine) to give 8 as a brown solid in 79% yield (136 mg, 0.427 mmol). \[^1\text{H} \text{NMR (CDCl}_3, 300 \text{ MHz)}: \delta = 9.10-10.55 \text{ (br. s., 1H), 7.18 (d, J=7.0 Hz, 1H), 7.00-7.14 (m, 4H), 6.88 (t, J=7.6 Hz, 1H), 6.65 (d, J=8.2 Hz, 1H), 4.71 (q, J=6.4 Hz, 1H), 3.23-3.36 (m, 1H), 3.07-3.21 (m, 1H), 2.90-3.03 (m, 2H), 1.48 (d, J=7.0 Hz, 3H). \]^1^C \text{NMR (CDCl}_3, 75 \text{ MHz)}: \delta = 157.9, 149.2, 132.2, 127.8, 127.4, 125.6, 124.9, 122.8, 122.1, 121.2, 119.7, 111.6, 55.1, 48.7, 28.4, 12.7. HRMS (ESI) m/z calcd for C\text{\textsubscript{16}}H\text{\textsubscript{15}}BrNO\textsuperscript{+} [M + H] \textsuperscript{+} 318.0488, found 318.0492.

2,4-dibromo-6-(1-(indolin-1-yl)ethyl)phenol (9): This compound was synthesized from 3',5'-Dibromo-2'-hydroxyacetophenone (159 mg, 0.54 mmol), indoline (0.54 mmol, 61 µL) and PCS (118 mg, 0.65 mmol) in the presence of pyridine (52 µL, 0.65 mmol). The product was purified by flash chromatography on silica (Hexane/EtOAc = 9:1, 0.3% triethylamine) to give 9 as a brown solid in 78% yield (168 mg, 0.42 mmol). \[^1\text{H} \text{NMR (CDCl}_3, 300 \text{ MHz)}: \delta = 10.15-11.32 \text{ (br. s., 1H), 7.53-7.72 (m, 1H), 6.99-7.31 (m, 3H), 6.80-6.96 (m, 1H), 6.48-6.68 (m, 1H), 4.68 (q, J=6.6 Hz, 1H), 3.27-3.40 (m, 1H), 3.10-3.24 (m, 1H), 2.92-3.04 (m, 2H), 1.48 (d, J=7.0 Hz, 3H). \]^1^C \text{NMR (CDCl}_3, 75 \text{ MHz)}: \delta = 153.0, 148.7, 134.3, 132.1, 129.6, 128.7, 127.5, 125.0, 121.7, 111.8, 111.5, 111.4, 55.8, 49.0, 28.4, 13.1. HRMS (ESI) m/z calcd for C\text{\textsubscript{16}}H\text{\textsubscript{15}}Br\text{\textsubscript{2}}NO\textsuperscript{+} [M + H] \textsuperscript{+} 395.9593, found 395.9586.

5-fluoro-2-(1-(indolin-1-yl)ethyl)phenol (10): This compound was synthesized from 4'-Fluoro-2'-hydroxyacetophenone (83 mg, 0.54 mmol), indoline (0.54 mmol, 61 µL) and PCS (118 mg, 0.65 mmol) in the presence of pyridine (52 µL, 0.65 mmol). The product was purified by flash chromatography on silica (Hexane/EtOAc = 9:1, 0.3% triethylamine) to give 10 as a dark brown solid in 75% yield (104 mg, 0.394 mmol). \[^1\text{H} \text{NMR (CDCl}_3, 300 \text{ MHz)}: \delta = 9.97 \text{ (br. s., 1H), 7.01-7.23 (m, 3H), 6.88 (t, J=7.6 Hz, 1H), 6.52-6.75 (m, 3H), 4.76 (q, J=7.0 Hz, 1H), 3.22-3.34 (m, 1H), 3.06-3.22 (m, 1H), 2.87-3.04 (m, 2H), 1.49 (d, J=7.0 Hz, 3H). \]^1^C \text{NMR (CDCl}_3, 75 \text{ MHz)}: \delta = 165.0, 161.7, 158.4, 149.2, 132.3, 127.4, 124.9, 122.3, 121.1, 111.6, 106.3, 103.8, 54.7, 48.5, 28.4, 12.6. HRMS (ESI) m/z calcd for C\text{\textsubscript{16}}H\text{\textsubscript{14}}FNO\textsuperscript{+} [M + H] \textsuperscript{+} 258.1289, found 258.1292.

2-(1-(indolin-1-yl)ethyl)-5-methoxyphenol (11): This compound was synthesized from 2'-Hydroxy-4'-methoxycacetophenone (90 mg, 0.54 mmol), indoline (0.54 mmol, 61 µL) and PCS (118 mg, 0.65 mmol) in the presence of pyridine (52 µL, 0.65 mmol). The product was purified by flash chromatography on silica (Hexane/EtOAc = 9:1, 0.3% triethylamine) to give 11 as a colourless solid in 60% yield (88 mg, 0.326 mmol). \[^1\text{H} \text{NMR (CDCl}_3, 300 \text{ MHz)}: \delta = 8.61-10.55 \text{ (br. s., 1H), 7.00-7.21 (m, 3H), 6.85 (t, J=8.8 Hz, 1H), 6.67 (d, J=7.6 Hz, 1H), 6.43-6.51 (m, 2H), 4.75 (q, J=7.0 Hz, 1H), 3.79 (s, 3H), 3.22-3.36 (m, 1H), 3.07-3.20 (m, 1H), 2.89-3.02 (m, 2H), 1.46 (d, J=6.4 Hz, 3H). \]^1^C \text{NMR (CDCl}_3, 75 \text{ MHz)}: \delta = 161.1, 157.5, 132.3, 127.2, 124.8, 120.8, 118.7, 111.6, 105.6, 101.9, 55.3, 54.5, 48.4, 28.4, 12.4. HRMS (ESI) m/z calcd for C\text{\textsubscript{17}}H\text{\textsubscript{15}}NO\textsubscript{2}\textsuperscript{+} [M + H] \textsuperscript{+} 270.1489, found 270.1610.
4-chloro-2-(1-indolin-1-yl)ethyl)-5-methylphenol (12): This compound was synthesized from 5'-Chloro-2'-hydroxy-4'-methylacetophenone (100 mg, 0.54 mmol), indoline (0.54 mmol, 61 µL) and PCS (118 mg, 0.65 mmol) in the presence of pyridine (52 µL, 0.65 mmol). The product was purified by flash chromatography on silica (Hexane/EtOAc = 9:1, 0.3% triethylamine) to give 12 as a pale brown solid in 79% yield (123 mg, 0.427 mmol). HRMS (ESI) m/z calcd for C_{18}H_{14}ClINOS [M + H]^+ 319.0854, found 319.0844.

4-chloro-2-(1-indolin-1-yl)ethyl)-6-nitrophenol (13): This compound was synthesized from 5'-Chloro-2'-hydroxy-3'-nitroacetophenone (116 mg, 0.54 mmol), indoline (0.54 mmol, 61 µL) and PCS (118 mg, 0.65 mmol) in the presence of pyridine (52 µL, 0.65 mmol). The product was purified by flash chromatography on silica (Hexane/EtOAc = 9:1, 0.3% triethylamine) to give 13 as a reddish brown solid in 27% yield (47 mg, 0.147 mmol). HRMS (ESI) m/z calcd for C_{18}H_{14}ClINO [M + H]^+ 319.0844, found 319.0854.

2-(1-indolin-1-yl)ethyl)-4-methyl-6-nitrophenol (14): This compound was synthesized from 2'-Hydroxy-5'-methyl-3'-nitroacetophenone (105 mg, 0.54 mmol), indoline (0.54 mmol, 61 µL) and PCS (118 mg, 0.65 mmol) in the presence of pyridine (52 µL, 0.65 mmol). The product was purified by flash chromatography on silica (Hexane/EtOAc = 9:1, 0.3% triethylamine) to give 14 as a brown solid in 63% yield (102 mg, 0.34 mmol). HRMS (ESI) m/z calcd for C_{18}H_{14}INO [M + H]^+ 319.1390, found 319.1387.

2-(1-indolin-1-yl)ethyl)naphthalen-1-ol (15): This compound was synthesized from 2'-Hydroxy-1'-acetonaphthone (101 mg, 0.54 mmol), indoline (0.54 mmol, 61 µL) and PCS (118 mg, 0.65 mmol) in the presence of pyridine (52 µL, 0.65 mmol). The product was purified by flash chromatography on silica (Hexane/EtOAc = 9:1, 0.3% triethylamine) to give 15 as a brown solid in 50% yield (78 mg, 0.27 mmol). HRMS (ESI) m/z calcd for C_{18}H_{14}ClINO [M + H]^+ 299.1390, found 299.1388.
Hz, 1H), 6.70-6.94 (m, 2H), 6.28 (d, J=7.0 Hz, 1H), 5.02 (q, J=7.0 Hz, 1H), 3.83-4.02 (m, 1H), 2.93-3.33 (m, 3H), 1.71 (d, J=7.0 Hz, 3H). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta =$ 154.7, 151.6, 132.1, 131.0, 129.2, 127.5, 126.8, 124.4, 122.8, 121.8, 121.0, 119.7, 118.4, 112.4, 57.2, 53.0, 28.8, 19.2. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{19}\text{NO}^+ [\text{M} + \text{H}]^+$ 290.1539, found 290.1551.

2-(1-(indolin-1-yl)propyl)phenol (16): This compound was synthesized from 2'-Hydroxypropiophenone (81 mg, 0.54 mmol), indoline (0.54 mmol, 61 µL) and PCS (118 mg, 0.65 mmol) in the presence of pyridine (52 µL, 0.65 mmol). The product was purified by flash chromatography on silica (Hexane/EtOAc = 9:1, 0.3% triethylamine) to give 16 as a brown liquid in 60% yield (82 mg, 0.33 mmol). $^1$H NMR (CDCl$_3$, 300 MHz): $\delta =$ 9.09-9.50 (br. s., 1H), 7.12-7.34 (m, 3H), 7.04 (t, J=8.8 Hz, 1H), 6.80-6.98 (m, 3H), 6.59 (d, J=8.2 Hz, 1H), 4.32 (dd, J=9.7, 3.8 Hz, 1H), 3.39-3.59 (m, 1H), 3.07-3.25 (m, 1H), 2.90-3.02 (m, 2H), 1.89-2.19 (m, 2H), 1.00 (t, J=7.6 Hz, 3H). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta =$ 156.9, 150.7, 131.9, 128.7, 127.7, 127.4, 125.3, 124.7, 120.7, 119.6, 116.7, 111.5, 63.2, 50.2, 28.5, 22.5, 11.6. HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{19}\text{NO}^+ [\text{M} + \text{H}]^+$ 254.1539, found 254.1541.

2-(indolin-1-yl)(phenyl)methyl)phenol (17): This compound was synthesized from 2'-Hydroxybenzophenone (107 mg, 0.54 mmol), indoline (0.54 mmol, 61 µL) and PCS (118 mg, 0.65 mmol) in the presence of pyridine (52 µL, 0.65 mmol). The product was purified by flash chromatography on silica (Hexane/EtOAc = 9:1, 0.3% triethylamine) to give 17 as a brown solid in 54% yield (88 mg, 0.29 mmol). $^1$H NMR (CDCl$_3$, 300 MHz): $\delta =$ 9.85-10.43 (m, 1H), 7.44-7.58 (m, 2H), 7.10-7.43 (m, 5H), 6.80-7.08 (m, 5H), 6.51 (d, J=7.6 Hz, 1H), 5.34 (s, 1H), 3.01-3.30 (m, 2H), 2.87-3.00 (m, 2H). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta =$ 156.2, 151.1, 139.6, 132.2, 128.8, 128.5, 128.1, 127.4, 125.3, 124.7, 120.1, 117.0, 112.1, 110.0, 70.3, 53.5, 28.5. HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{19}\text{NO}^+ [\text{M} + \text{H}]^+$ 302.1539, found 302.1531.

2-(1-(indolin-1-yl)-3-phenylpropyl)phenol (18): This compound was synthesized from 2'-Hydroxy-3-phenylpropiophenone (122 mg, 0.54 mmol), indoline (0.54 mmol, 61 µL) and PCS (118 mg, 0.65 mmol) in the presence of pyridine (52 µL, 0.65 mmol). The product was purified by flash chromatography on silica (Hexane/EtOAc = 9:1, 0.3% triethylamine) to give 18 as a brown solid in 60% yield (107 mg, 0.325 mmol). $^1$H NMR (CDCl$_3$, 300 MHz): $\delta =$ 9.16 (br. s., 1H), 7.23-7.37 (m, 5H), 7.13-7.22 (m, 3H), 6.99 (q, J=7.6 Hz, 3H), 6.83 (t, J=7.0 Hz, 1H), 6.37 (d, J=7.6 Hz, 1H), 4.54 (dd, J=10.0, 2.9 Hz, 1H), 3.35-3.48 (m, 1H), 3.07-3.24 (m, 1H), 2.90-3.03 (m, 2H), 2.77-2.89 (m, 1H), 2.58-2.73 (m, 1H), 2.38-2.54 (m, 1H), 2.10-2.28 (m, 1H). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta =$ 157.0, 150.1, 141.3, 131.9, 128.8, 127.4, 126.2, 124.9, 120.7, 119.8, 116.9, 111.3, 59.6, 49.8, 33.1, 30.4, 28.5. HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{23}\text{NO}^+ [\text{M} + \text{H}]^+$ 330.1852, found 330.1859.
(E)-2-(1-morpholino-3-phenylallyl)phenol (19): Following the general procedure with 10 h of reflux, this compound was synthesized from 2'-Hydroxychalcone (121 mg, 0.54 mmol), morpholine (0.54 mmol, 47 µL) and PCS (118 mg, 0.65 mmol) in the presence of pyridine (52 µL, 0.65 mmol). The product was purified by flash chromatography on silica (Hexane/EtOAc = 9:1, 0.3% triethylamine) to give 19 as a colourless oil in 63% yield (101 mg, 0.34 mmol).

1H NMR (CDCl3, 300 MHz): δ = 10.84-11.36 (br. s., 1H), 7.10-7.51 (m, 6H), 7.03 (dd, J = 7.6, 1.8 Hz, 1H), 6.73-6.95 (m, 2H), 6.62 (d, J = 16.4 Hz, 1H), 6.27-6.45 (m, 1H), 4.06 (d, J = 9.4 Hz, 1H), 3.63-3.89 (m, 4H), 2.30-3.05 (m, 4H).

13C NMR (CDCl3, 75 MHz): δ = 156.4, 136.1, 134.0, 128.8, 128.1, 126.6, 126.1, 124.0, 119.8, 116.7, 74.1, 66.9, 51.2.

HRMS (ESI) m/z calcd for C13H19NO2+ [M + H]+ 222.1489, found 222.1499.

4-methyl-2-(1-morpholinoethyl)phenol (20): This compound was synthesized from 2'-hydroxy-5'-methylacetophenone (81 mg, 0.54 mmol), morpholine (0.54 mmol, 47 µL) and PCS (118 mg, 0.65 mmol) in the presence of pyridine (52 µL, 0.65 mmol). The product was purified by flash chromatography on silica (Hexane/EtOAc = 8:2, 0.3% triethylamine) to give 20 as a pink oil in 53% yield (63 mg, 0.28 mmol).

1H NMR (CDCl3, 300 MHz): δ = 10.27-11.26 (br. s., 1H), 6.94 (dd, J = 8.2, 1.8 Hz, 1H), 6.77 (d, J = 2.3 Hz, 1H), 6.70 (d, J = 8.2 Hz, 1H), 3.65-3.84 (m, J = 4.7 Hz, 4H), 3.50 (q, J = 6.8 Hz, 1H), 2.41-2.77 (m, 4H), 2.23 (s, 3H), 1.39 (d, J = 7.0 Hz, 3H).

13C NMR (CDCl3, 75 MHz): δ = 154.0, 128.9, 128.5, 128.4, 126.5, 116.3, 67.0, 64.9, 50.3, 20.5, 16.7. HRMS (ESI) m/z calcd for C13H19NO2+ [M + H]+ 222.1489, found 2221499.

4-bromo-2-(1-(3,4-dihydroquinolin-1(2H)-yl)ethyl)phenol (21): This compound was synthesized from 4'-Bromo-2'-hydroxyacetophenone (116 mg, 0.54 mmol), 1,2,3,4-tetrahydroquinoline (0.54 mmol, 68 µL) and PCS (118 mg, 0.65 mmol) in the presence of pyridine (52 µL, 0.65 mmol). The product was purified by flash chromatography on silica (Hexane/EtOAc = 9:1, 0.3% triethylamine) to give 21 as a pink solid in 61% yield (83 mg, 0.33 mmol).

1H NMR (CDCl3, 300 MHz): δ = 9.31-9.49 (br. s., 1H), 6.98-7.21 (m, 5H), 6.86 (t, J = 8.2 Hz, 1H), 5.18 (q, J = 6.4 Hz, 1H), 2.64-3.05 (m, 4H), 1.78-2.08 (m, 2H), 1.48 (d, J = 7.0 Hz, 3H). 13C NMR (CDCl3, 75 MHz): δ = 158.3, 143.9, 130.2, 128.2, 127.2, 127.0, 125.1, 122.7, 122.2, 120.3, 119.5, 115.4, 110.0, 54.5, 42.7, 27.8, 22.3, 11.6. HRMS (ESI) m/z calcd for C17H18BrNO+ [M + H]+ 332.0645, found 332.0628.

2-(1-(ethyl(phenyl)amino)ethyl)-5-fluorophenol (22): This compound was synthesized from 4'-Fluoro-2'-hydroxyacetophenone (83 mg, 0.54 mmol), ethylaniline (0.54 mmol, 68 µL) and PCS (176 mg, 0.97 mmol) in the presence of pyridine (52 µL, 0.65 mmol). The resulting reaction mixture was treated with TBAF (1.1 mL, 1.12 mmol). The product was purified by flash chromatography on silica (Hexane/EtOAc = 9:1, 0.3% triethylamine) to give 22 as a colourless oil in 63% yield (88 mg, 0.34
**1H NMR (CDCl$_3$, 300 MHz):** $\delta = 10.42$-$11.77$ (br. s., 1H), 7.34-$7.43$ (m, 2H), 7.25 (s, 3H), 6.95-$7.07$ (m, 1H), 6.48-$6.66$ (m, 2H), 4.51 (q, $J=6.4$ Hz, 1H), 3.04-$3.35$ (m, 1H), 2.75-$2.99$ (m, 1H), 1.23 (d, $J=6.4$ Hz, 3H), 0.96 ppm (t, $J=7.0$ Hz, 3H).

**13C NMR (CDCl$_3$, 75 MHz):** $\delta = 164.8, 161.6, 158.7, 146.6, 129.2, 128.2, 124.7, 105.9, 103.8, 62.9, 43.6, 16.2, 12.9$. HRMS (ESI) m/z calcd for C$_{16}$H$_{18}$FNO$^+$ [M + H]$^+$ 260.1445, found 260.1452.

5-chloro-2-(1-(ethyl(phenyl)amino)ethyl)-4-methylphenol (23): This compound was synthesized from 5'-Chloro-2'-hydroxy-4'-methylacetophenone (100 mg, 0.54 mmol), ethylaniline (0.54 mmol, 68 µL) and PCS (176 mg, 0.97 mmol) in the presence of pyridine (52 µL, 0.65 mmol). The resulting reaction mixture was treated with TBAF (1.1 mL, 1.12 mmol). The product was purified by flash chromatography on silica (Hexane/EtOAc = 9:1, 0.3% triethylamine) to give 23 as a yellow oil in 58% yield (91 mg, 0.31 mmol).

**1H NMR (CDCl$_3$, 300 MHz):** $\delta = 10.80$-$11.01$ (br. s., 1H), 7.33-$7.42$ (m, 2H), 7.14-$7.27$ (m, 3H), 7.04 (s, 1H), 6.78 (s, 1H), 4.49 (q, $J=6.4$ Hz, 1H), 3.08-$3.23$ (m, 1H), 2.81-$2.95$ (m, 1H), 2.33 (s, 3H), 1.23 (d, $J=6.4$ Hz, 3H), 0.96 (t, $J=7.0$ Hz, 3H).

**13C NMR (CDCl$_3$, 75 MHz):** $\delta = 155.7, 146.6, 136.0, 129.2, 127.6, 126.3, 124.9, 124.2, 118.9, 62.6, 43.9, 19.8, 16.1, 12.9$. HRMS (ESI) m/z calcd for C$_{17}$H$_{20}$ClNO$^+$ [M + H]$^+$ 290.1306, found 290.1302.

2-(1-(3,4-dihydroquinolin-1(2H)-yl)ethyl)-5-fluorophenol (24): This compound was synthesized from 4'-Fluoro-2'-hydroxyacetophenone (83 mg, 0.54 mmol), 1,2,3,4-tetrahydroquinoline (0.54 mmol, 68 µL) and PCS (118 mg, 0.65 mmol) in the presence of pyridine (52 µL, 0.65 mmol). The product was purified by flash chromatography on silica (Hexane/EtOAc = 9:1, 0.3% triethylamine) to give 24 as a yellow crystalline solid in 76% yield (111 mg, 0.41 mmol).

**1H NMR (CDCl$_3$, 300 MHz):** $\delta = 9.45$ (br. s., 1H), 7.06-$7.24$ (m, 4H), 6.79-$6.95$ (m, 1H), 6.55-$6.71$ (m, 1H), 5.22 (q, $J=7.0$ Hz, 1H), 2.71-$3.07$ (m, 4H), 1.94 (d, $J=1.8$ Hz, 2H), 1.50 (d, $J=6.4$ Hz, 3H).

**13C NMR (CDCl$_3$, 75 MHz):** $\delta = 164.9, 161.5, 158.1, 143.7, 130.2, 127.7, 127.1, 121.9, 120.2, 115.4, 106.3, 103.8, 54.3, 42.5, 27.8, 22.4, 11.7$. HRMS (ESI) m/z calcd for C$_{17}$H$_{18}$FNO$^+$ [M + H]$^+$ 272.1454, found 272.1454.

5-bromo-2-(1-morpholinoethyl)phenol (25): This compound was synthesized from 4'-Bromo-2'-hydroxyacetophenone (116 mg, 0.54 mmol), morpholine (0.54 mmol, 47 µL) and PCS (118 mg, 0.65 mmol) in the presence of pyridine (52 µL, 0.65 mmol). The product was purified by flash chromatography on silica (Hexane/EtOAc = 8:2, 0.3% triethylamine) to give 25 as a pale yellow solid in 74% yield (115 mg, 0.40 mmol).

**1H NMR (CDCl$_3$, 300 MHz):** $\delta = 10.59$-$12.06$ (br. s., 1H), 6.96 (d, $J=1.8$ Hz, 1H), 6.87-$6.92$ (m, $J=2.3$ Hz, 1H), 6.81 (d, $J=8.2$ Hz, 1H), 3.63-$3.83$ (m, $J=4.7$ Hz, 4H), 3.56 (q, $J=6.4$ Hz, 1H), 2.40-$2.74$ (m, 4H), 1.37 (d, $J=7.0$ Hz, 3H).

**13C NMR (CDCl$_3$, 75 MHz):** $\delta = 157.7, 129.0, 125.7, 122.3, 121.8, 119.8, 66.8, 64.3, 50.3, 16.2$. HRMS (ESI) m/z calcd for C$_{12}$H$_{16}$BrNO$^+$ [M + H]$^+$ 286.0428, found 286.0437.
2-(1-morpholinopropyl)phenol (26): This compound was synthesized from 2'-Hydroxypropiophenone (81 mg, 0.54 mmol), morpholine (0.54 mmol, 47 µL) and PCS (118 mg, 0.65 mmol) in the presence of pyridine (52 µL, 0.65 mmol). The product was purified by flash chromatography on silica (Hexane/EtOAc = 9:1, 0.3% triethylamine) to give 26 as a colourless liquid in 75% yield (90 mg, 0.407 mmol).

1H NMR (CDCl₃, 300 MHz): δ = 10.66-11.13 (br. s., 1H), 7.08-7.21 (m, 1H), 6.91 (dd, J=9.4, 4.1 Hz, 1H), 2.44-2.83 (m, 4H), 1.81-2.02 (m, 1H), 1.63-1.81 (m, 1H), 0.75 (t, J=7.6 Hz, 3H).

13C NMR (CDCl₃, 75 MHz): δ = 156.5, 129.7, 128.5, 124.4, 118.8, 116.4, 72.0, 67.0, 51.4, 23.5, 10.6. HRMS (ESI) m/z calcd for C₁₃H₁₉NO₂⁺ [M + H]+ 222.1489, found 222.1496.

1-(1-phenylethyl)indoline (27): 1H NMR (CDCl₃, 500 MHz): δ = 7.40 (d, J=8.6 Hz, 2H), 7.32 (t, J=7.4 Hz, 2H), 7.22-7.28 (m, J=7.4 Hz, 1H), 7.05 (d, J=6.9 Hz, 1H), 6.98 (t, J=8.6 Hz, 1H), 6.59 (t, J=7.4 Hz, 1H), 4.71 (q, J=6.9 Hz, 1H), 3.17-3.57 (m, 2H), 2.94 (t, J=8.3 Hz, 2H), 1.52 (d, J=6.9 Hz, 3H).

13C NMR (CDCl₃, 126 MHz): δ = 151.1, 142.6, 129.8, 128.1, 126.8, 124.1, 116.6, 106.9, 54.2, 47.6, 27.9, 16.2

7. Computational Details
Calculations were performed using the GAUSSIAN 09 software package,[4] and the PBE0 functional, without symmetry constraints. That functional uses a hybrid generalized gradient approximation (GGA), including 25% Hartree-Fock exchange with DFT exchange-correlation, given by Perdew, Burke and Ernzerhof functional (PBE).[7] The optimized geometries were obtained with a standard 6-31G(d,p) basis set. Transition state optimizations were performed with the Synchronous Transit-Guided Quasi-Newton Method (STQN) developed by Schlegel et al.[9] following extensive searches of the Potential Energy Surface. Frequency calculations were performed to confirm the nature of the stationary points, yielding one imaginary frequency for the transition states and none for the minima. Each transition state was further confirmed by following its vibrational mode downhill on both sides and obtaining the minima presented on the energy profile. The electronic energies (Eₚₑ) obtained at the PBE0/6-31G(d,p) level of theory were converted to free energy at 298.15 K and 1 atm (G₀) by using zero point energy and thermal energy corrections based on structural and vibrational frequency data calculated at the same level.

Single point energy calculations were performed on the geometries obtained at the PBE0/6-31G(d,p) level using the M06-2X functional and a 6-311++G(d,p) basis set.[10] The M06-2X functional is a hybrid meta-GGA functional developed by Truhlar and Zhao,[11] and it was shown to perform very well for the kinetics of main group element systems, providing a good description of weak and long range interactions.[12] Solvent effects (MeCN) were accounted for in all calculations by means of the Polarisable Continuum Model (PCM) initially devised by Tomasi and coworkers[13] with radii and non-electrostatic terms of the SMD solvation model, developed by Truhlar et al.[14].

The free energy values presented (G₀) were derived from the electronic energy values obtained at the M06-2X/6-311++G(d,p)/PBE0/6-31G(d,p) level, including solvent effects (Eₛₑ), according to the following expression:

\[ G₀ = Eₛₑ + G₀ - Eₚₑ \]
Additional Energy profile

Fig S1. Free energy profile for the reductive amination reaction catalyzed by DMPU. The free energy values are relative to the separated reagents: trialkoxyhydrosilyliminium plus DMPU.

Using the same parameters as in the pyridine catalyzed reaction mechanism, the energy profile, which details the reaction mechanism involving DMPU as base catalyst, is depicted in Fig S1. The catalytic steps are no different from the pyridine-catalyzed mechanism with the first step being the coordination of the O-atom in the base catalyst, DMPU to the Si-atom through transition state TS_{FG} to give intermediate G. Similarly, rotation around the Si-phenol bond leads to a less stable conformer, G'.

In the next step, the hydride attack into the iminium C-atom proceeds through TS_{G'H} with energy barrier of only 6 kcal/mol, almost 3 times less than the energy required to overcome TS_{B'C} to give intermediate H. H' which is a less stable conformer of H begins the third step of the N-atom coordination to the Si-atom to form intermediate I. In the corresponding transition state, TS_{HI} is 3 kcal/mol less stable than H'.

The last step that involves liberation of the catalyst from I to J has the highest energy barrier, 26 kcal/mol in the entire reaction paths through the corresponding transition state TS_{IJ}. The Si-O_{DMPU} bond breaking in TS_{IJ} 1.01 Å longer than the distance in I with a remaining distance of 1.47 Å to reach its final value in the product J.
Figure S2. Free energy profile for the uncatalyzed reductive amination reaction. Free energy values [Kcal/mol] relative to the trialkoxyhydrosilyliminium (K).

The mechanism for the uncatalyzed reductive amination process is concerted with simultaneous hydride transfer and N coordination to Si through transition state TS_{KL} with a significant energy barrier of 41 kcal/mol. In the transition state, the Si–H bond is 1.4 Å shorter while the C–H bond is 0.52 Å longer than their respective final values in the product L. Also, the Si–N bond formation is only 0.45 Å longer than in L. The reaction is exergonic with free energy balance of -15 kcal/mol.
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9. NMR Spectra

2-(1-(indolin-1-y1)ethyl)phenol (1) $^1$H NMR (300 MHz, CDCl$_3$)

2-(1-(indolin-1-y1)ethyl)phenol (1) $^{13}$C NMR (75 MHz, CDCl$_3$)
2-(1-morpholinoethyl)phenol (2) $^1$H NMR (300 MHz, CDCl$_3$)

![NMR spectrum of 2-(1-morpholinoethyl)phenol (2)]

2-(1-morpholinoethyl)phenol (2) $^{13}$C NMR (75 MHz, CDCl$_3$)

![NMR spectrum of 2-(1-morpholinoethyl)phenol (2)]
2-(1-(diallylamino)ethyl)phenol (3) $^1$H NMR (300 MHz, CDCl$_3$)

2-(1-(diallylamino)ethyl)phenol (3) $^{13}$C NMR (75 MHz, CDCl$_3$)
2-(1-(3,4-dihydroquinolin-1(2H)-yl)ethyl)phenol (4) $^1$H NMR (500 MHz, CDCl$_3$)

2-(1-(3,4-dihydroquinolin-1(2H)-yl)ethyl)phenol (4) $^{13}$C NMR (126 MHz, CDCl$_3$)
2-(1-ethyl(phenyl)amino)ethyl)phenol (5) $^1$H NMR (500 MHz, CDCl$_3$)

2-(1-ethyl(phenyl)amino)ethyl)phenol (5) $^{13}$C NMR (126 MHz, CDCl$_3$)

S21
2-(1-(dibenzylamino)ethyl)phenol (6) $^1$H NMR (500 MHz, CDCl$_3$)

2-(1-(dibenzylamino)ethyl)phenol (6) $^{13}$C NMR (126 MHz, CDCl$_3$)
2-(1-(indolin-1-yl)ethyl)-4-methylphenol (7) \( ^1 \text{H} \) NMR (300 MHz, CDCl\(_3\))

2-(1-(indolin-1-yl)ethyl)-4-methylphenol (7) \( ^{13} \text{C} \) NMR (75 MHz, CDCl\(_3\))
5-bromo-2-(1-(indolin-1-yl)ethyl)phenol (8) $^1$H NMR (300 MHz, CDCl$_3$)

5-bromo-2-(1-(indolin-1-yl)ethyl)phenol (8) $^{13}$C NMR (75 MHz, CDCl$_3$)
2,4-dibromo-6-(1-(indolin-1-yl)ethyl)phenol (9) $^1$H NMR (300 MHz, CDCl$_3$)

2,4-dibromo-6-(1-(indolin-1-yl)ethyl)phenol (9) $^{13}$C NMR (75MHz, CDCl$_3$)
5-fluoro-2-(1-(indolin-1-yl)ethyl)phenol (10) $^1$H NMR (300 MHz, CDCl$_3$)

5-fluoro-2-(1-(indolin-1-yl)ethyl)phenol (10) $^{13}$C NMR (75 MHz, CDCl$_3$)
2-(1-(indolin-1-yl)ethyl)-5-methoxyphenol (11) $^1$H NMR (300 MHz, CDCl$_3$)

2-(1-(indolin-1-yl)ethyl)-5-methoxyphenol (11) $^{13}$C NMR (75 MHz, CDCl$_3$)
4-chloro-2-(1-(indolin-1-yl)ethyl)-5-methylphenol (12) $^1$H NMR (300 MHz, CDCl$_3$)

4-chloro-2-(1-(indolin-1-yl)ethyl)-5-methylphenol (12) $^{13}$C NMR (75 MHz, CDCl$_3$)
4-chloro-2-(1-(indolin-1-yl)ethyl)-6-nitrophenol (13) $^1$H NMR (300 MHz, CDCl$_3$)

4-chloro-2-(1-(indolin-1-yl)ethyl)-6-nitrophenol (13) $^{13}$C NMR (75 MHz, CDCl$_3$)
2-(1-(indolin-1-yl)ethyl)-4-methyl-6-nitrophenol (14) $^1$H NMR (300 MHz, CDCl$_3$)

2-(1-(indolin-1-yl)ethyl)-4-methyl-6-nitrophenol (14) $^{13}$C NMR (75 MHz, CDCl$_3$)
2-(1-(indolin-1-yl)ethyl)naphthalen-1-ol (15) \( ^1H \) NMR (300 MHz, CDCl\(_3\))

2-(1-(indolin-1-yl)ethyl)naphthalen-1-ol (15) \( ^{13}C \) NMR (75 MHz, CDCl\(_3\))
2-(1-indolin-1-yl)propylphenol (16) $^1$H NMR (300 MHz, CDCl₃)

2-(1-indolin-1-yl)propylphenol (16) $^{13}$C NMR (75 MHz, CDCl₃)
2-(indolin-1-yl(phenyl)methyl)phenol (17) $^1$H NMR (300 MHz, CDCl$_3$)

2-(indolin-1-yl(phenyl)methyl)phenol (17) $^{13}$C NMR (75 MHz, CDCl$_3$)
2-(1-(indolin-1-yl)-3-phenylpropyl)phenol (18) $^1$H NMR (300 MHz, CDCl$_3$)

2-(1-(indolin-1-yl)-3-phenylpropyl)phenol (18) $^{13}$C NMR (75 MHz, CDCl$_3$)
(E)-2-(1-morpholino-3-phenylallyl)phenol (19) $^1$H NMR (300 MHz, CDCl$_3$)

(E)-2-(1-morpholino-3-phenylallyl)phenol (19) $^{13}$C NMR (75 MHz, CDCl$_3$)
4-methyl-2-(1-morpholinoethyl)phenol (20) $^1$H NMR (300 MHz, CDCl$_3$)

4-methyl-2-(1-morpholinoethyl)phenol (20) $^{13}$C NMR (75 MHz, CDCl$_3$)
4-bromo-2-(1-(3,4-dihydroquinolin-1(2H)-yl)ethyl)phenol (21) $^1$H NMR (300 MHz, CDCl$_3$)

$^1$C NMR (75 MHz, CDCl$_3$)
2-(1-ethyl(phenyl)amino)ethyl)-5-fluorophenol (22) \(^1\)H NMR (300 MHz, CDCl\(_3\))

2-(1-ethyl(phenyl)amino)ethyl)-5-fluorophenol (22) \(^{13}\)C NMR (75 MHz, CDCl\(_3\))
5-chloro-2-(1-(ethyl(phenyl)amino)ethyl)-4-methylphenol (23) $^1$H NMR (300 MHz, CDCl$_3$)

5-chloro-2-(1-(ethyl(phenyl)amino)ethyl)-4-methylphenol (23) $^{13}$C NMR (75 MHz, CDCl$_3$)
2-(1-(3,4-dihydroquinolin-1(2H)-yl)ethyl)-5-fluorophenol (24) $^1$H NMR (300 MHz, CDCl$_3$)

2-(1-(3,4-dihydroquinolin-1(2H)-yl)ethyl)-5-fluorophenol (24) $^{13}$C NMR (75 MHz, CDCl$_3$)
5-bromo-2-(1-morpholinoethyl)phenol (25) $^1$H NMR (300 MHz, CDCl$_3$)

5-bromo-2-(1-morpholinoethyl)phenol (25) $^{13}$C NMR (75 MHz, CDCl$_3$)
2-(1-morpholinopropyl)phenol (26) $^1$H NMR (300 MHz, CDCl$_3$)

![H NMR spectrum of 2-(1-morpholinopropyl)phenol (26)]

2-(1-morpholinopropyl)phenol (26) $^{13}$C NMR (75 MHz, CDCl$_3$)

![C NMR spectrum of 2-(1-morpholinopropyl)phenol (26)]
1-(1-phenylethyl)indoline (27) $^1$H NMR (500 MHz, CDCl$_3$)

1-(1-phenylethyl)indoline (27) $^{13}$C NMR (126 MHz, CDCl$_3$)
| H       | x     | y     | z     |
|---------|-------|-------|-------|
| H       | -1.537607 | -2.343131 | -2.441393 |
| H       | 1.815089  | 1.995299  | -1.730999 |
| H       | 1.220990  | 3.639993  | -1.462352 |
| H       | 0.264498  | 2.500705  | -2.462800 |
| H       | 1.218708  | 3.485299  | 0.918884  |
| H       | 2.042853  | 1.926855  | 0.652524  |
| H       | 0.620139  | 2.012351  | 1.726911  |