Supporting Information

Iron-Catalyzed Protodehalogenation of Alkyl and Aryl Halides Using Hydrosilanes

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1. GENERAL INFORMATION

1.1 Analysis and purification:
Reactions were monitored by single Quadrupole GC/MS-Agilent which has a silica capillary column (Cat. No. 19091S-433UI, HP-5MSUI, with dimensions 30 m X 0.25 mm) and thin layer chromatography (Merck, Cat. No. 1.05554.0007, aluminium sheets with TLC Silica gel 60 F<sub>254</sub> coating). TLC analysis was done using shortwave UV-254 nm or I<sub>2</sub> as visualizing agents or the stain made out of phosphomolybdic acid, then heating as the developer. NMR spectra were recorded using 700 and 500 MHz Bruker avance spectrometer, with TMS as internal standard and <sup>1</sup>H and <sup>13</sup>C spectra were reported in δ (ppm) with respect to a reference. CDCl<sub>3</sub> from sigma Aldrich (Cat. No. 151823, 99.8 atom % D) was used for NMR analysis. 1,3,5-trimethoxybenzene from Alfa Aesar (Cat. No. A13981, 99%), was used as an internal standard to calculate the NMR yield. GC yield was taken by first calibrating the authentic sample (May it be the isolated one or the commercial one) with an internal standard and then analysing the yield using the calibrated values to find the relative yield of the product to that of the internal standard. IR Spectra were recorded on FT-IR Alpha E (Bruker) spectrometer. Solid and liquid compounds were measured by neat condition. The wave numbers are given in cm<sup>-1</sup>. Q-Exactive benchtop HRMS was used for the high resolution analysis. Celite 545 (purchased from Merck) was used for filtration. The column chromatography was performed using Silica Gel 230-400 mesh from FINAR (CASR: 63231-67-4). Kugelrohr apparatus was used for distillation of the reaction crude using ice as the coolant.

1.1.1 Solvents:
Tetrahydrofuran (THF), purchased from Spectrochem (anhydrous grade) was distilled over Sodium wire. Dichloromethane (DCM/CH<sub>2</sub>Cl<sub>2</sub>), purchased from Merck was stirred in CaH<sub>2</sub> for 2 h, refluxed and then distilled. Acetonitrile (CH<sub>3</sub>CN), purchased from Spectrochem (HPLC grade), was passed through an activated alumina column. All the dry solvents were degassed for a minimum of 20 min. using nitrogen balloon and stored over 4Å molecular sieves.

1.1.2 Chemicals:
Iron (III) chloride, (FeCl$_3$, Cat. No. 12357, CAS 7705-08-0, 98%), Iron (II) chloride (FeCl$_2$, Cat. No. 35701, 99.5%), Phenylsilane (PhSiH$_3$, Cat. No. A17901, 97%) and Sodium methoxide (NaOMe, Cat. No. L05673, 98%) were purchased from Alfa Aesar.

Table S1: Results of deviations from the optimized condition

<table>
<thead>
<tr>
<th>Entry</th>
<th>Deviations from the optimized conditions</th>
<th>Time (h)</th>
<th>Conversion of SM (%)</th>
<th>Yield * (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1$^b$</td>
<td>10 mol% FeCl$_2$, 1.8 eq. NaO'Bu without PhSiH$_3$</td>
<td>15</td>
<td>55</td>
<td>24</td>
</tr>
<tr>
<td>2</td>
<td>10 mol% FeCl$_2$, 0.3 eq. EtMgBr without PhSiH$_3$</td>
<td>15</td>
<td>63</td>
<td>25</td>
</tr>
<tr>
<td>3$^b$</td>
<td>10 mol% FeCl$_2$, 1.8 eq. NaO'Bu, 0.3 eq. B$_2$Pin$_2$ without PhSiH$_3$</td>
<td>15</td>
<td>72</td>
<td>21</td>
</tr>
<tr>
<td>4</td>
<td>10 mol% FeCl$_2$, 1.8 eq. NaO'Bu, 0.2 eq. HBPin without PhSiH$_3$</td>
<td>15</td>
<td>64</td>
<td>15</td>
</tr>
<tr>
<td>5$^b$</td>
<td>10 mol% FeCl$_2$, 1.8 eq. NaO'Bu, 1.5 eq. Si$_2$Me$_6$</td>
<td>15</td>
<td>2</td>
<td>ND</td>
</tr>
<tr>
<td>6</td>
<td>2 eq. of MeOH as additive</td>
<td>15</td>
<td>100</td>
<td>19</td>
</tr>
<tr>
<td>7</td>
<td>TBAF instead of NaOMe</td>
<td>15</td>
<td>70</td>
<td>ND</td>
</tr>
<tr>
<td>8</td>
<td>K$_3$PO$_4$ instead of NaOMe</td>
<td>15</td>
<td>10</td>
<td>ND</td>
</tr>
<tr>
<td>9</td>
<td>H$_2$O instead of THF</td>
<td>15</td>
<td>0</td>
<td>ND</td>
</tr>
<tr>
<td>10</td>
<td>20 mol% FeCl$_3$, 2 eq. PhSiH$_3$, 2 eq. NaOMe</td>
<td>15</td>
<td>100</td>
<td>95</td>
</tr>
<tr>
<td>11$^b$</td>
<td>t-BuOH instead of PhSiH$_3$</td>
<td>32</td>
<td>10</td>
<td>ND</td>
</tr>
<tr>
<td>12$^b$</td>
<td>Me$_2$PhSiH instead of PhSiH$_3$</td>
<td>15</td>
<td>32</td>
<td>ND</td>
</tr>
<tr>
<td>13</td>
<td>PhSiH instead of PhSiH$_3$</td>
<td>15</td>
<td>22</td>
<td>5</td>
</tr>
<tr>
<td>14</td>
<td>10 mol% FeCl$_2$, 1.8 eq. NaO'Bu</td>
<td>15</td>
<td>100</td>
<td>59</td>
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<tr>
<td>15</td>
<td>10 mol% Fe(acac)$_3$, 1.8 eq. NaO'Bu</td>
<td>15</td>
<td>70</td>
<td>62</td>
</tr>
<tr>
<td>16</td>
<td>1.8 eq. NaO'Bu instead of NaOMe, 1.5 eq. PhSiH$_3$</td>
<td>32</td>
<td>94</td>
<td>82</td>
</tr>
<tr>
<td>17$^b$</td>
<td>1.8 eq. KO'Bu instead of NaOMe, 1.5 eq. PhSiH$_3$</td>
<td>16</td>
<td>95</td>
<td>53</td>
</tr>
<tr>
<td>18</td>
<td>2 eq. PhSiH$_3$, 2 eq. NaOMe</td>
<td>15</td>
<td>98</td>
<td>83</td>
</tr>
<tr>
<td>19</td>
<td>1.8 eq. CsF instead of NaOMe</td>
<td>32</td>
<td>47</td>
<td>&lt;5%</td>
</tr>
<tr>
<td>20</td>
<td>1.8 eq. KOMe instead of NaOMe</td>
<td>15</td>
<td>5</td>
<td>&lt;5%</td>
</tr>
<tr>
<td>21</td>
<td>3 eq. K$_2$CO$_3$ instead of NaOMe, EtOH instead of THF</td>
<td>13</td>
<td>13</td>
<td>ND</td>
</tr>
<tr>
<td>22</td>
<td>3 eq. Lutidine instead of NaOMe</td>
<td>12</td>
<td>12</td>
<td>ND</td>
</tr>
<tr>
<td>23</td>
<td>Without FeCl$_3$</td>
<td>4</td>
<td>13</td>
<td>7</td>
</tr>
<tr>
<td>24</td>
<td>Without NaOMe</td>
<td>12</td>
<td>0</td>
<td>ND</td>
</tr>
<tr>
<td>25</td>
<td>Without PhSiH$_3$</td>
<td>12</td>
<td>5</td>
<td>ND</td>
</tr>
<tr>
<td>26$^b$</td>
<td>CH$_3$CN as solvent</td>
<td>15</td>
<td>98</td>
<td>31</td>
</tr>
<tr>
<td>27</td>
<td>Et$_2$O as solvent</td>
<td>18</td>
<td>97</td>
<td>92</td>
</tr>
</tbody>
</table>

(a) determined by GC analysis using dodecane as an internal standard (b) elimination observed, values in parentheses are isolated yield, ND = not detected
Table S2. Influence of the varying amounts of phenyl silane and sodium methoxide in the optimized reaction condition

![Reaction Scheme](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>NaOMe (eq.)</th>
<th>PhSiH₃ (eq.)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>5 h</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.3</td>
<td>3</td>
<td>12.2</td>
</tr>
<tr>
<td>3</td>
<td>1.2</td>
<td>3</td>
<td>38.4</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>3</td>
<td>99.2</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>1.2</td>
<td>53</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>2</td>
<td>55</td>
</tr>
<tr>
<td>8</td>
<td>2</td>
<td>2</td>
<td>82</td>
</tr>
</tbody>
</table>

(a) determined by GC analysis using dodecane as an internal standard

Fig. S1: Amount of NaOMe vs. yield  
Fig. S2: Amount of PhSiH₃ vs. yield

Increase in the concentration of NaOMe in the reaction mixture led to the increase in the yield of the protodehalogenated product. Also, increase in the amount of PhSiH₃ led to the increase in the yield.

Table S3: Scope of other alkyl/aryl halides

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Temp. (°C)</th>
<th>Time (h)</th>
<th>Yield (%)</th>
</tr>
</thead>
</table>

1°, 2°, or 3° alkyl halides
X = Br, Cl, I
1.1.3 General procedure for the Iron-Catalysed Protodehalogenation of Alkyl and Aryl Halides Using Hydrosilanes:

A flame dried Schlenk tube was evacuated and refilled with nitrogen. The Schlenk tube was taken inside the glove box and was charged with iron (III) chloride (5 mol%, 0.0302 mmol, 5 mg) and NaOMe (3 eq., 1.81 mmol, 100 mg). It was then removed from the glove box and was connected to the Schlenk line. Half of the required solvent (1.5 mL, fig. S3) was added into it (total conc. of the reaction is 0.2 M). Addition of Phenylsilane (3 eq., 1.81 mmol, and 231 µL) into the reaction tube gave a dark grey/black coloured solution from light yellow solution which indicates the formation of active catalyst (fig. S4). After few minutes of stirring, the substrate was added followed by the addition of remaining solvent (1.5 mL). Note: Phenylsilane must be added in the end as mentioned above, we noticed a spark when mixing phenylsilane and NaOMe alone in the absence of FeCl₃ and alkyl halides that may due to the formation of SiH₄, details are in page S16. The reaction was typically monitored using GC/MS or TLC. After the reaction was complete, the mixture was filtered through a celite plug using Et₂O/CH₂Cl₂/THF (based on the volatility and polarity of the material) to remove metal salts and the filtrate was concentrated under vacuum. The crude was taken for further purification step.

Fig. S3: Before the addition of silane  Fig. S4: After the addition of silane
2. SCOPE OF HALIDES

4-\textit{n}-butylanisole (1a-1c)

4-\textit{n}-butylanisole was obtained as a colourless oil from 4-(\textit{p}-methoxy)phenyl-2-bromobutane (0.604 mmol, 147 mg, 5 h) by following the general procedure. The crude was distilled slowly using Kugelrohr apparatus and the desired product was obtained at 100 °C with 4 mbar pressure in 92% yield (91 mg). Increasing the temperature leads to the distillation of diphenylsilane (by-product, at around 120 °C). 4-\textit{n}-butylanisole from 4-(\textit{p}-methoxy)phenyl-2-chlorobutane and 4-(\textit{p}-methoxy)phenyl-2-iodobutane gave 63% and 92% yield respectively. \textbf{FT-IR} (neat) \(\nu\): 2998, 2955, 2928, 2859, 1612, 1510, 1461, 1298, 1241, 1177, 1036, 825, 698, 556 cm\(^{-1}\). \textbf{\textsuperscript{1}H NMR} (500 MHz, CDCl\(_3\)) \(\delta\) 7.12 (d, \(J = 8.5\) Hz, 2H), 6.83 (d, \(J = 8.6\) Hz, 2H), 3.79 (s, 4H), 2.66 (m, 2H), 1.80 – 1.68 (m, 2H), 1.46 – 1.43(m, 1H), 1.22 (d, \(J = 6.2\) Hz, 3H). \textbf{\textsuperscript{13}C NMR} (126 MHz, CDCl\(_3\)) \(\delta\) 157.8, 134.1, 129.3, 113.8, 67.5, 55.3, 41.1, 31.2, 23.6. \textbf{MS} (m/z): 164.1 (C\(_{11}\)H\(_{16}\)O\(^{+}\)).

Dodecane (1d-1e)

Dodecane was obtained from 1-bromododecane (1d, 0.604 mmol, 152 mg, 10 h), 1-chlorododecane (1e, 0.604, 124 mg, 75 °C, 19 h) in 90% and 95% GC yield respectively. \textbf{MS} (m/z): 170.2 (C\(_{12}\)H\(_{26}\)\(^{+}\)).

Adamantane (1f-1g)

Adamantane was obtained as a colourless solid from 1-bromoadamantane (1f, 0.747 mmol, 160.8 mg), and 1-chloroadamantane (1g, 0.369 mmol, 63.1 mg) in 78% and 89% yield respectively, by following the general procedure. The crude was distilled to give the product at 300 mbar and 50 °C. \textbf{FT-IR} (neat) \(\nu\): 2893, 2845, 2662, 1448, 1352, 1263, 1099, 1028, 802 cm\(^{-1}\). \textbf{\textsuperscript{1}H NMR} (700 MHz, CDCl\(_3\)) \(\delta\) 1.87 (s, 4H), 1.75 (s, 12H). \textbf{\textsuperscript{13}C NMR} (126 MHz, CDCl\(_3\)) \(\delta\) 37.8, 28.4. \textbf{MS} (m/z): 136.0 (C\(_{10}\)H\(_{16}\)\(^{+}\)).

Hexadecane (1h)

S6
Hexadecane was obtained as a colourless oil from 1-bromohexadecane (0.363 mmol, 113 mg, 3 h) by following the general procedure. The crude was distilled and the product was obtained as first fraction at 110 °C and 2 mbar pressure in 94% yield. FT-IR (neat) ν: 2957, 2921, 2853, 1463, 1260, 1096, 1019, 803, 726 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 1.26 (s, 28H), 0.89 (t, J = 6.9 Hz, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 31.9, 29.7, 29.7, 29.4, 22.7, 14.1. MS (m/z): 226.3 (C₁₆H₃₄)⁺.

Decane (1i-1k, 1n)

Decane was obtained from 1,10-dibromodecane (1i, 0.604 mmol, 187 mg, 2 h), 1-bromodecane (1j, 0.242 mmol, 54.5 mg, 4 h), 1-chlorodecane (1k, 0.242 mmol, 43.6 mg, 100 °C, 17 h), 1-iododecane (1n, 0.604 mmol, 165 mg, 2 h), in 61%, 80%, 62%, 89% of GC yield respectively. MS (m/z): 142.2 (C₁₀H₂₂)⁺.

Triphenylmethane (1l)

Triphenylmethane was obtained as a colourless solid from bromotriphenylmethane (0.363 mmol, 120 mg, 4 h) by following the general procedure. The crude was purified using column chromatography (has an Rf value of 0.6 in 98:2 of PET ether : Ethyl acetate) to give 60 mg of product in 54% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.29 (t, J = 7.5 Hz, 6H), 7.22 (d, J = 7.2 Hz, 3H), 7.12 (d, J = 7.5 Hz, 6H), 5.56 (s, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 143.9, 129.5, 128.3, 126.3, 56.9. MS (m/z): 244.1 (C₁₉H₁₆)⁺.

Cholest-5-ene (1m)

Cholest-5-ene was obtained as a colourless solid from Cholesteryl iodide (0.483 mmol, 240 mg, 2 h) by following the general procedure. The crude was purified using column chromatography (Rf = 0.8 in 100% PET ether) in 86% yield. FT-IR (neat) ν: 2927, 2854, 1727, 1461, 1375, 1266, 1121, 1024, 987, 959, 832, 801, 734, 635, 555 cm⁻¹. ¹H NMR
(500 MHz, CDCl$_3$) $\delta$ 5.27 (dd, $J = 5.0$, 2.3 Hz, 1H), 2.28 – 2.19 (m, 1H), 2.04 – 1.91 (m, 3H), 1.87 – 1.78 (m, 2H), 1.76 – 1.70 (m, 1H), 1.62 – 1.30 (m, 12H), 1.26 (s, 2H), 1.19 – 1.03 (m, 7H), 1.00 (s, 6H), 0.92 (d, $J = 6.5$ Hz, 3H), 0.87 (dd, $J = 6.7$, 2.3 Hz, 6H), 0.68 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 119.0, 56.9, 56.2, 50.6, 42.3, 39.9, 39.9, 39.5, 36.2, 35.8, 32.9, 31.9, 28.3, 28.1, 28.0, 24.3, 23.9, 22.8, 22.6, 20.8, 19.5, 18.7, 11.9. HRMS (ESI, m/z): Calculated for C$_{27}$H$_{46}$ (M+H)$^+$ 371.3672, found 371.3664.

1-undecanol (1o)

1-undecanol was obtained as a colorless liquid from 11-bromoundecan-1-ol (0.967 mmol, 243 mg, 1 h) by following the general procedure. The crude was distilled (110 °C, 4.7 mbar) to give pure product in 72% yield. FT-IR (neat) $\nu$: 3341, 2922, 2855, 1461, 1378, 1056, 722 cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 3.63 (d, $J = 6.3$ Hz, 2H), 1.58 (d, $J = 4.1$ Hz, 4H), 1.27 (d, $J = 11.8$ Hz, 13H), 0.88 (s, 3H), 0.07 (s, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 62.1, 31.8, 30.9, 28.6, 28.4, 28.3, 24.7, 21.7, 13.1. MS (m/z): 171.1 (C$_{11}$H$_{24}$O)$^+$.

4-methylbenzylalcohol (1p)

4-methylbenzylalcohol was obtained as white needles from methyl 4-(bromomethyl)benzoate (0.967 mmol, 221 mg) by following the general procedure. The product was purified by distillation (60 °C, 4.7 mbar) which gave the pure product in 63% yield. FT-IR (neat) $\nu$: 3360, 3277, 2971, 2916, 1514, 1444, 1344, 1015, 802, 628 cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.19 (d, $J = 7.9$ Hz, 2H), 7.10 (d, $J = 7.8$ Hz, 2H), 4.58 (d, $J = 3.6$ Hz, 2H), 2.28 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 137.9, 137.4, 129.3, 127.1, 65.3, 21.2. MS (m/z): 122.1 (C$_8$H$_{10}$O)$^+$.

Naphthalene (4a- 4b)

Naphthalene was obtained as a colourless solid from 1-bromonaphthalene (4a, 0.363 mmol, 0 °C, 30 min.) and 1-chloronaphthalene (4b, 0.363 mmol, ambient temperature, 12 h) in 40% and 71% yield respectively. FT-IR (neat) $\nu$: 3047, 1586, 1498, 1383, 1265, 1118, 957, 767 cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.90 (dd, $J = 6.2$, 1.3 Hz, 2H), 7.88 (d, $J = 7.9$, 2H), 7.81 (d, $J = 7.8$, 2H), 7.58 (d, $J = 3.5$, 2H), 2.19 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 138.0, 137.7, 129.4, 128.3, 127.1, 64.0, 22.2. MS (m/z): 171.1 (C$_{11}$H$_{24}$O)$^+$.
3.3 Hz, 4H), 7.53 (dd, \( J = 6.2, 3.2 \) Hz, 4H). ¹³C NMR (126 MHz, CDCl₃) \( \delta \) 133.5, 133.5, 128.0, 127.9, 125.9, 125.9. MS (m/z): 128.0 (C₁₀H₆)⁺.

**tert-butylbenzene (4c)**

The *tert*-butyl benzene was obtained in 74% GC yield from 1-bromo-4-(*tert*-butyl) benzene (0.604 mmol, 133 mg, 1 h) by following the general procedure. MS (m/z): 134.1 (C₁₀H₁₄)⁺.

**Indole (4d)**

Indole was obtained as a colourless solid from 5-bromoindole (0.620 mmol, 118 mg) by following the general procedure with the exceptions that the reaction mixture was heated to 60 °C and 4 eq. silane was used. With 3 eq. of PhSiH₃ decrease in the yield was seen (probably due to the removal of acidic hydrogen by the *in-situ* generated hydride). The reaction crude was purified using column chromatography to give 40% of the desired product. ¹H NMR (500 MHz, CDCl₃) \( \delta \) 8.10 (s, 1H), 7.68 (dd, \( J = 8.0, 2.5 \) Hz, 1H), 7.41 (d, \( J = 8.1 \) Hz, 1H), 7.25 – 7.18 (m, 2H), 7.17 – 7.12 (m, 1H), 6.58 (d, \( J = 2.8 \) Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) \( \delta \) 135.8, 127.9, 124.1, 122.0, 120.8, 119.8, 111.0, 102.7. MS (m/z): 117.0 (C₈H₇N)⁺.

**Toluene (4e)**

Toluene was obtained in 74% GC yield from 4-chlorotoluene (0.242 mmol, 31.2 mg) at 100 °C. MS (m/z): 91.0 (C₇H₈)⁺.

**1,2,3-trimethoxybenzene (4f)**

1,2,3-trimethoxybenzene was obtained as a colourless solid from 5-bromo-1,2,3-trimethoxybenzene (0.604 mmol, 154 mg) in 2 h by following the general procedure. The crude was purified by distillation (130 °C with 130 mbar) to obtain the desired product in 61% (62.2 mg) yield. FT-IR (neat) ν: 3050, 2938, 2838, 1722, 1595, 1478, 1298, 1254, 1177, 1110, 1009, 778, 733, 696, 530 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) \( \delta \) 6.99 (t, \( J = 8.4 \) Hz, 1H), 6.58 (d, \( J = 8.4 \) Hz, 2H), 3.86 (d, \( J = 4.6 \) Hz,
9H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 153.5, 123.6, 105.3, 60.8, 56.1. MS (m/z): 168.1 (C$_9$H$_{12}$O$_3$)$^+$. 

Anisole (4g-4i)

Anisole was obtained in 66%, 78%, 46% of GC yield from 4-bromoanisole (4g, 0 °C, 1h), 4-chloroanisole (4h, 100 °C, 34 h) and 4-iodoanisole (4i, 0 °C, 0.5 h) respectively. MS (m/z): 108.0 (C$_7$H$_8$O)$^+$. 

1-Phenylethanol (4j)

1-phenylethanol was obtained as a colourless liquid in 50% yield from 4-bromoacetophenone in 1 h by following the general procedure. The product was purified by column chromatography (95:5, PET ether: Ethyl acetate). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.49 – 7.44 (m, 2H), 7.24 (d, $J$ = 5.9 Hz, 2H), 4.80 (s, 1H), 4.76 (d, $J$ = 6.5 Hz, 1H), 1.36 (dd, $J$ = 6.5, 3.5 Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 145.9, 128.5, 127.5, 125.4, 70.4, 25.2. MS (m/z): 122.1 (C$_8$H$_{10}$O)$^+$. 

4-phenylphenol (4l):

4-phenylphenol was obtained from 4′-bromo-(1,1′-biphenyl)-4-ol by following the general procedure in 33% yield. The crude mixture was purified using column chromatography. FT-IR (neat) v: 3384, 3033, 1598, 1502, 1479, 1370, 1239, 1194, 1112, 825, 749, 677 cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.54 (d, $J$ = 6.9 Hz, 2H), 7.48 (d, $J$ = 8.5 Hz, 2H), 7.42 (t, $J$ = 7.7 Hz, 2H), 7.34 – 7.28 (m, 1H), 6.91 (d, $J$ = 8.5 Hz, 2H), 5.02 (s, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 155.1, 140.7, 134.1, 128.7, 128.4, 126.7, 115.7. MS (m/z): 170.1 (C$_{12}$H$_{10}$O)$^+$. 
2.1 SIDE PRODUCTS:

Diphenylsilane:

Diphenylsilane was obtained as a by-product in all the reactions done by using the general procedure. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.64 – 7.60 (m, 4H), 7.46 – 7.37 (m, 6H), 4.95 (s, 2H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 135.7, 131.5, 129.9, 128.1. MS (m/z): 184.1 (C\(_{12}\)H\(_{12}\)Si\(^+\)).

5-(diphenylsilyl)-N, N-dimethylpyridin-2-amine:

5-(diphenylsilyl)-N,N-dimethylpyridin-2-amine was obtained as a colourless liquid (by-product) along with 2-N,N-dimethyl amino pyridine from 2-dimethylamino-5-bromopyridine (0.604 mg, 121 mg), by following the general procedure, in 24% isolated yield. This has an R\(_f\) of 0.6 in 100% PET ether. FT-IR (neat) \(\nu\): 3058, 3006, 2922, 2119, 1585, 1508, 1432, 1384, 1211, 1112, 1006, 798, 541 cm\(^{-1}\). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.30 (d, \(J = 1.8\) Hz, 1H), 7.59 (dt, \(J = 8.2, 2.4\) Hz, 5H), 7.44 – 7.35 (m, 7H), 6.53 (d, \(J = 8.5\) Hz, 1H), 5.44 (s, 1H), 3.11 (s, 6H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 155.1, 144.0, 135.7, 133.6, 129.7, 128.0, 112.4, 105.8, 37.9. \(^{13}\)C NMR DEPT - 135 (126 MHz, CDCl\(_3\)) \(\delta\) 155.18, 144.02, 135.71, 129.75, 128.05, 105.77. MS (m/z): 304.1 (C\(_{19}\)H\(_{20}\)N\(_2\)Si\(^+\)). HRMS (ESI, m/z): Calculated for C\(_{19}\)H\(_{20}\)N\(_2\)Si (M+H\(^+\)) 305.1469, Found: 305.1411.
3. MECHANISTIC STUDIES

3.1 Treating the reaction mixture

3.1.1 With TEMPO:

\[
\begin{align*}
\text{O} & \quad \text{Br} \\
\text{O} & \quad \text{N} \\
1.5 \text{ eq.} & \quad \text{FeCl}_3 (5 \text{ mol%}) \text{ PhSiH}_3 (3 \text{ eq.}) \text{ THF, rt, 12 h}
\end{align*}
\]

\[
\begin{align*}
4-(\text{p-methoxy})\text{phenyl-2-bromobutane} (0.60 \text{ mmol, 147 mg}) \text{ was treated to the conditions as in the given procedure. TEMPO} (0.906 \text{ mmol, 142 mg}) \text{ was added additionally just before the addition of the substrate. When monitored using GC/MS, no new peak corresponding to TEMPO coupled substrate was seen. The reaction proceeded towards protodehalogenation to give 4-\text{n-butyranisole in 72% yield.}
\end{align*}
\]

3.1.2 With galvinoxyl:

\[
\begin{align*}
\text{O} & \quad \text{Br} \\
\text{O} & \quad \text{O} \\
1.1 \text{ eq.} & \quad \text{FeCl}_3 (5 \text{ mol%}) \text{ PhSiH}_3 (3 \text{ eq.}) \text{ THF, rt, 5 h}
\end{align*}
\]

\[
\begin{align*}
4-(\text{p-methoxy})\text{phenyl-2-bromobutane} (0.242 \text{ mmol, 58.8 mg}) \text{ was treated to the conditions as in the given procedure. Galvinoxyl} (0.266 \text{ mmol, 112 mg}) \text{ was added additionally just before the addition of the substrate. When monitored using GC/MS, no new peak corresponding to the galvinoxyl adduct of the substrate was seen. The reaction proceeded towards protodehalogenation to give 4-\text{n-butyranisole in 96% yield.}
\end{align*}
\]

3.1.3 With THF-\text{d}8:
5-bromo-1,2,3-trimethoxybenzene (0.483 mmol, 123 mg), was subjected to the reaction conditions as in the general procedure in THF-\textit{d8} instead of normal THF. The reaction was monitored using GC/MS. After the completion of the reaction, the mixture was passed through celite, concentrated and distilled (130 °C and 130 mbar) to obtain 45 mg (55% yield) of the product.

NMR studies has proven that the material obtained was non-deuterated which implies that solvent doesn’t act as the source of H-atom. $^{1}$$\text{H}$ NMR (500 MHz, CDCl$_3$) $\delta$ 6.99 (t, $J = 8.4$ Hz, 1H), 6.58 (d, $J = 8.4$ Hz, 2H), 3.86 (d, $J = 4.6$ Hz, 9H).

3.1.4 With PhSiD$_3$:

5-bromo-1,2,3-trimethoxybenzene (0.483 mmol, 123 mg), was subjected to the reaction conditions as in the general procedure with an exception that PhSiD$_3$ was taken. The reaction was monitored using GC/MS. After the completion of the reaction, the crude was purified using column chromatography. NMR shows 72% incorporation of the deuterium.

3.1.5 With 2-(2-bromoethoxy)benzaldehyde:

A carbonyl trap experiment was done using 2-(2-bromoethoxy)benzaldehyde as substrate. It also led to the uncyclized product. The crude was purified by column chromatography and was
further confirmed by NMR analysis. \(^1\text{H NMR}\) (500 MHz, CDCl\(_3\)) \(\delta\) 7.27 (s, 1H), 7.26 (s, 1H), 6.93 (d, \(J = 1.0\) Hz, 1H), 6.87 (d, \(J = 8.7\) Hz, 1H), 4.70 (s, 2H), 4.10 (d, \(J = 7.0\) Hz, 2H), 1.45 (s, 3H). \(^{13}\text{C NMR}\) (126 MHz, CDCl\(_3\)) \(\delta\) 156.7, 129.1, 128.9, 128.8, 120.6, 111.1, 63.5, 62.5, 14.9. \(\text{MS (m/z): 152.1 (C}_9\text{H}_{12}\text{O}_2^+}\).

### 3.1.6 Protodehalogenation of an iodoalkene, comparison with literature\(^3\):

**Scheme a:** Literature (0.387 mmol of substrate, 0.0387 mmol of FeCl\(_2\), 0.58 mmol of NaBH\(_4\), 1 mL CH\(_3\)CN)

**Scheme b:** Optimised reaction conditions (0.387 mmol of substrate, 0.0387 mmol of FeCl\(_3\), 1.16 mmol PhSiH\(_3\), 1.16 mmol NaOMe, 1 mL CH\(_3\)CN)

As reported by Ollivier et. al., protodehalogenation via cyclization is the reaction pathway for 2-(allyloxy)-3-bromotetrahydro-2H-pyran. This substrate with the optimized reaction conditions always gave a product with the same mass but a different retention time in GC/MS. Efforts to obtain exclusively the cyclized product didn’t go well, giving a mixture of products with the same mass, even with the usage of CH\(_3\)CN as solvent which promotes radical type reactions.

This information supports that the formation of cyclized product is not favoured with our reaction conditions thereby concluding that the reaction doesn’t undergo radical pathway.
3.1.6 Disproportionation of PhSiH$_3$

When PhSiH$_3$ was treated with NaOMe (1 eq.) in THF, we observed the formation of Ph$_2$SiH$_2$ (care must be taken as we noticed a spark when mixing phenylsilane and NaOMe alone in the absence of FeCl$_3$ and alkyl halides, the spark may due to the formation of flammable SiH$_4$, the spark was observed only in the initial stage of reaction but not during the course of reaction). GCMS analysis (shown below) indicates the PhSiH$_3$ converted into Ph$_2$SiH$_2$ in 1h and we also observed traces of PhSi(OMe)$_3$ (m/z: 198), Ph$_2$Si(OMe)$_2$ (m/z: 244), and Ph$_2$Si(OMe)OH (m/z: 230).
4. LARGE SCALE SYNTHESIS

4.1 Reaction of 4-(p-methoxy)phenyl-2-bromobutane with 1 mol% catalyst loading:

\[
\begin{align*}
\text{FeCl}_3 (1 \text{ mol\%}) & \quad \text{PhSiH}_3 (3 \text{ eq.}) \\
\text{NaOMe (3 eq.)} & \quad \text{THF, rt, 6 h}
\end{align*}
\]

4-(p-methoxy)phenyl-2-bromobutane (2.04 mmol, 500 mg) was subjected to the reaction conditions as in the general procedure with an exception that 1 mol% of FeCl$_3$ was taken. 4-bromoanisole was obtained by distillation in 90% isolated yield (91% GC yield).

(Caution: Addition of PhSiH$_3$ into Schlenk tube may generate SiH$_4$ & NaH in-situ which are pyrophoric in nature).

4.2 Reaction of 1-bromoadamantane with 1 mol% catalyst, 1.5 eq. PhSiH$_3$ and 1.7 eq. NaOMe:

\[
\begin{align*}
\text{Br} & \quad \text{FeCl}_3 (1 \text{ mol\%}) \\
\text{PhSiH}_3 (1.5 \text{ eq.}) & \quad \text{NaOMe (1.7 eq.)} \\
\text{THF, rt, 7 h} & \quad 95\%
\end{align*}
\]
1-bromoadamantane (4.6 mmol, 1 g) was subjected to the reaction conditions as in the general procedure with the exception that 1 mol% of FeCl₃, 1.5 eq. PhSiH₃ and 1.7 eq. of NaOMe was taken. Adamantane was obtained in 95% GC yield.

**4.3 Synthesis of hexadecane with 0.5 mol% of catalyst loading:**

\[
\begin{array}{c}
\text{H}_{14}\text{Br} \xrightarrow{\text{FeCl}_3 \ (0.5 \text{ mol\%)}} \text{H}_{14} \\
\xrightarrow{\text{PhSiH}_3 \ (3 \text{ eq.})} \xrightarrow{\text{NaOMe} \ (3 \text{ eq.})} \text{H}_{14} \\
\text{THF, rt, 3 h} \quad 89\%
\end{array}
\]

1-bromohexadecane (6.03 mmol, 1.86 mL) was subjected to the reaction conditions as in the general procedure with an exception that 0.5 mol% of FeCl₃ was taken. Hexadecane was distilled out from the crude after 3 h in 89% yield.

(Caution: Addition of PhSiH₃ into Schlenk tube may generate SiH₄ & NaH *insitu* which are pyrophoric in nature).
5. SYNTHESIS OF STARTING MATERIALS

5.1 Synthesis of 4-(p-methoxy)phenyl-2-halobutane:

A flame-dried two neck round bottomed flask equipped with a stir bar was fitted with a rubber septum and backfilled with N\textsubscript{2}. The ketone (58.7 mmol, 10 mL) and dry MeOH (25 mL) were taken into the flask, then kept in an ice bath. NaBH\textsubscript{4} (88 mmol, 3.33 g) was added portionwise at 0 °C to control the evolution of gas from the reaction flask. The ice bath was removed after the addition and allowed to stir at room temperature for 1.5 h. The reaction was quenched after the addition and allowed to stir at room temperature for 1.5 h. The reaction was quenched with saturated NaHCO\textsubscript{3} solution (25 mL) and diluted with 15 mL water to dissolve the precipitated materials, extracted three times with CH\textsubscript{2}Cl\textsubscript{2} (3 x 50 mL), dried with MgSO\textsubscript{4}, and rotor evaporated to yield 89% alcohol as a colourless oil. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) δ 7.12 (d, \(J = 8.5\) Hz, 2H), 6.83 (d, \(J = 8.6\) Hz, 2H), 3.79 (s, 4H), 2.73 – 2.58 (m, 2H), 1.80 – 1.68 (m, 2H), 1.44 (d, \(J = 4.3\) Hz, 1H), 1.22 (d, \(J = 6.2\) Hz, 3H). \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) δ 157.8, 134.1, 129.3, 113.8, 67.5, 55.3, 41.1, 31.2, 23.6.

For halogenation, a round bottomed flask was equipped with a stir bar and flame dried, then PPh\textsubscript{3} (1.05 eq.), imidazole (1.05 eq.) and halogenating agent (1.05 eq.) were added to the flask under N\textsubscript{2}. Dry CH\textsubscript{2}Cl\textsubscript{2} (0.2 M) was added and then flask was cooled to 0 °C using an ice bath and stirred for 10 min. At 0 °C alcohol (0.555 mmol), diluted 5:1 in CH\textsubscript{2}Cl\textsubscript{2}, was added drop by drop. After complete addition of the alcohol the reaction was left to stir overnight at room temperature. After the reaction was complete (confirm by TLC), the mixture was concentrated under reduced pressure and was diluted with 25% EtOAc in hexanes and filtered through silica plug. The filtrate was concentrated again in rotor evaporator and pure desired compound was isolated by column chromatography (98:2, PET ether: Ethyl acetate) to yield the alkyl halide.
4-(p-methoxy)phenyl-2-chlorobutane:

FT-IR (neat) v: 2934, 2837, 1612, 1510, 1452, 1242, 1177, 1035, 822, 609, 558 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 7.11 (d, J = 8.6 Hz, 2H), 6.83 (d, J = 8.6 Hz, 2H), 4.02 – 3.93 (m, 1H), 3.79 (s, 3H), 2.82 – 2.75 (m, 1H), 2.72 – 2.65 (m, 1H), 2.04 – 1.91 (m, 2H), 1.52 (d, J = 6.5 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 158.0, 133.1, 129.4, 113.9, 57.9, 55.3, 42.2, 32.0, 25.4. MS (m/z): 198.1(C₁₁H₁₅ClO⁺)

4-(p-methoxy)phenyl-2-bromobutane:

FT-IR (neat) v: 2926, 2835, 1611, 1510, 1451, 1297, 1241, 1176, 1035, 824, 749, 611, 527 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 7.11 (d, J = 8.6 Hz, 2H), 6.83 (d, J = 8.6 Hz, 2H), 4.02 – 3.93 (m, 1H), 3.79 (s, 3H), 2.84 – 2.64 (m, 2H), 2.04 – 1.91 (m, 2H), 1.52 (d, J = 6.5 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 158.0, 132.9, 129.4, 113.9, 55.3, 50.9, 42.9, 33.0, 26.5. MS (m/z): 242.1(C₁₁H₁₅BrO⁺)

4-(p-methoxy)phenyl-2-iodobutane:

FT-IR (neat) v: 2918, 2835, 1611, 1509, 1449, 1296, 1242, 1179, 1034, 822, 749, 705, 568 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 7.12 (d, J = 8.6 Hz, 2H), 6.84 (d, J = 8.6 Hz, 2H), 4.15 – 4.05 (m, 1H), 3.79 (s, 3H), 2.83 – 2.73 (m, 1H), 2.68 – 2.59 (m, 1H), 2.18 – 2.07 (m, 1H), 1.94 (d, J = 6.8 Hz, 3H), 1.88 – 1.80 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 158.0, 132.8, 129.4, 113.9, 55.3, 44.6, 34.9, 29.7, 29.0. MS (m/z): 290.1 (C₁₁H₁₅IO⁺)

5.2 Synthesis of allyl-2-bromophenylether²:

\[
\begin{align*}
\text{ phenol} & \quad \text{allyl bromide} \\
\text{NaH (1.4 eq.)} & \quad \text{DMF, 0 °C} \\
\end{align*}
\]

To 2-bromophenol (11.3 mmol, 1.34 mL) in 25 mL DMF, NaH (1.4 eq., 15.9 mmol, 60% suspension) was added at 0 °C and stirred for 10 min., later allylbromide (1.5 eq.) was added dropwise to the reaction mixture. After 1 h, the reaction mixture was quenched with water and the crude was extracted using diethylether. Allyl-2-bromophenylether was isolated using column chromatography (95:5 of PET ether: Ethyl acetate) in 82% yield.
5.3 Synthesis of 2-(allyloxy)-3-iodotetrahydro-2H-pyran³:

\[
\text{\chem{\text{O}} \text{\chem{\text{O}}} \text{\chem{\text{I}}} \text{\chem{\text{NIS}}} (1.01 \text{ eq.}) \text{\chem{\text{CH}_2\text{Cl}_2}} (1.9 \text{ M}) \text{\chem{\text{CH}_2\text{Cl}_2}} (23 \text{ mL}) \text{ at -10 °C}}
\]

3,4-dihydro-2H-pyran (1 eq., 42.5 mmol, 3.62 g) was added dropwise to a mixture of N-iodosuccinimide (1.01 eq., 43.1 mmol, 10 g) and allyl alcohol (0.98 eq., 42 mmol, 2.49 g) in CH₂Cl₂ (23 mL) at -10 °C. The reaction mixture was allowed to warm to room temperature and was left to stir overnight. The reaction mixture was then diluted with CH₂Cl₂ and washed with saturated sodium thiosulfate (3 × 20 mL). The combined aqueous phase was extracted using CH₂Cl₂ and the combined organic layers was washed with brine, dried over Na₂SO₄ and was concentrated under reduced pressure. The pure product was obtained as a pale yellow liquid (10.147 g, 89.5%) by column chromatography. **FT-IR** (neat) ν: 3070, 2941, 2857, 1610, 1439, 1345, 1274, 1199, 1124, 1070, 1017, 928, 867, 694, 586 cm⁻¹. **¹H NMR** (500 MHz, CDCl₃) δ 5.93 (ddd, J = 16.2, 10.9, 5.3 Hz, 1H), 5.32 (dt, J = 17.2, 1.8 Hz, 1H), 5.24 – 5.14 (m, 1H), 4.67 (d, J = 5.4 Hz, 1H), 4.29 – 4.20 (m, 1H), 4.15 – 3.92 (m, 3H), 3.58 (td, J = 7.6, 3.7 Hz, 1H), 2.37 (dq, J = 11.5, 4.0 Hz, 1H), 2.07 – 1.96 (m, 1H), 1.76 (dq, J = 10.5, 3.4 Hz, 1H), 1.62 – 1.51 (m, 1H). **¹³C NMR** (126 MHz, CDCl₃) δ 133.9, 117.5, 101.6, 69.0, 63.5, 32.7, 29.2, 25.5. **MS (m/z)**: 268.1 (C₈H₁₅IO₂⁻)

5.4 Synthesis of 5-Bromo-N,N-dimethylpyridin-2-amine⁴:

\[
\text{\chem{\text{H}_2\text{N}} \text{\chem{\text{Br}}}} \text{\chem{\text{THF}}} (0.23 \text{ M}) \text{\chem{\text{NaH}}} (5.78 \text{ eq.}) \text{\chem{\text{MeI}}} (4.25 \text{ eq.}) \text{\text{0 °C}}
\]

NaH (1.96 g, 49.1 mmol) was added to a solution of 5-bromopyridin-2-amine in THF (36 mL) at 0 °C and stirred for 20 min. The methyl iodide (2.26 mL, 36.1 mmol) was added to the solution and stirred overnight. The reaction mixture was quenched with water (50 mL) and was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure. The compound was purified by flash column chromatography on silica gel (Ethyl acetate: PET ether, 0.75:10) to give the pure compound (1.6
g, 94%). **FT-IR** (neat) $\nu$: 2892, 2845, 2661, 1588, 1501, 1448, 1352, 1264, 1099, 965, 802 cm$^{-1}$.

$^1$$H$ NMR (500 MHz, CDCl$_3$) $\delta$ 8.16 (d, $J = 2.8$ Hz, 1H), 7.48 (dd, $J = 9.1, 2.7$ Hz, 1H), 6.40 (d, $J = 9.0$ Hz, 1H), 3.05 (s, 6H). $^{13}$$C$ NMR (126 MHz, CDCl$_3$) $\delta$ 157.8, 148.3, 139.3, 107.2, 106.0, 38.2, 30.9. **MS** (m/z): 200.0 (C$_7$H$_9$BrN$_2^+$).

### 5.5 Synthesis of Cholesteryl Iodide$^5$:

![Cholesteryl Iodide Synthesis](image)

To a solution of PPh$_3$ (1.68 eq., 1.62 g, 6.19 mmol) and imidazole (1.58 eq., 0.396 g, 5.82 mmol) in 5 mL CH$_2$Cl$_2$ at 0 °C, I$_2$ (1.58 eq., 1.48 g, 5.82 mmol) was added and stirred for 30 min. Cholesterol (1 eq., 1.5 g, 3.69 mmol) in 5 mL CH$_2$Cl$_2$ was added dropwise to the reaction mixture and was left for stirring at room temperature overnight. Completion of the reaction was confirmed through TLC and then water (15 mL) was added to the reaction mixture followed by workup with CH$_2$Cl$_2$ (3 X 15 mL). The crude mixture was obtained by combining organic extracts, drying over Na$_2$SO$_4$, followed by concentration. Pure product was isolated using column chromatography ($R_f$ = 0.8 in 100% PET ether) followed by recrystallization from acetone as colourless needles (83% yield). **FT-IR** (neat) $\nu$: 2939, 2868, 2360, 1667, 1530, 1461, 1374, 1179, 1122, 1027, 993, 958, 811, 671, 627, 586, 543 cm$^{-1}$. $^1$$H$ NMR (500 MHz, CDCl$_3$) $\delta$ 5.38 – 5.34 (m, 1H), 4.12 – 4.01 (m, 1H), 2.95 (td, $J = 13.2, 2.6$ Hz, 1H), 2.73 – 2.67 (m, 1H), 2.34 – 2.18 (m, 2H), 2.06 – 1.94 (m, 2H), 1.85 (dtd, $J = 13.5, 9.4, 6.0$ Hz, 1H), 1.75 (d, $J = 13.5$ Hz, 1H), 1.63 – 0.99 (m, 23H), 0.93 (d, $J = 6.6$ Hz, 3H), 0.89 (dd, $J = 6.6, 2.2$ Hz, 6H), 0.69 (s, 3H). $^{13}$$C$ NMR (126 MHz, CDCl$_3$) $\delta$ 121.7, 56.7, 56.2, 50.4, 46.4, 42.3, 41.9, 39.7, 39.5, 36.6, 36.5, 36.2, 35.8, 31.8, 31.7, 30.6, 28.2, 28.0, 24.3, 23.8, 22.8, 22.6, 20.8, 19.2, 18.7, 11.9. **HRMS** (ESI, m/z): Calculated for C$_{27}$H$_{45}$I (M+Na)$^+$ 519.2458, found 519.2345.

### 5.6 Synthesis of 4-Bromo-1-[(4-methylphenyl)sulfonyl]-piperidine$^6$:

...
N-tosyl-4-bromopiperidine was synthesized according to the literature protocol\(^6\). To a mixture of 4-bromopiperidine hydrobromide (0.718 mmol) and tosyl chloride (0.789 mmol) in CH\(_2\)Cl\(_2\) at 0 °C, triethylamine (1.58 mmol) was added dropwise and was left to stir overnight. Later, it was quenched with 2M HCl and was extracted using CH\(_2\)Cl\(_2\). The organic portion was then dried over MgSO\(_4\) and was concentrated. The crude was purified by column chromatography (80: 20 Ethyl acetate: PET ether) to give the compound as a white solid in 80% yield. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.65 (d, \(J = 8.0\) Hz, 2H), 7.34 (d, \(J = 7.9\) Hz, 2H), 4.27 – 4.21 (m, 1H), 3.23 – 3.06 (m, 4H), 2.45 (s, 3H), 2.23 – 2.14 (m, 2H), 2.10 – 2.01 (m, 2H).

5.7 Synthesis of Deuterated phenylsilane\(^7\):

\[
\begin{align*}
\text{PhCl}_3 & \xrightarrow{\text{LAD (2 eq.) Et}_2\text{O, reflux, 14 h}} \text{PhSiD}_3
\end{align*}
\]

A flame dried Schlenk round bottom flask, that was evacuated and refilled with nitrogen, was charged with LiAlD\(_4\) (2 eq., 7.15 mmol, 0.3 mg). Diethylether was added to it at 0 °C. Trichlorophenylsilane (3.57 mmol, 0.572 mL) was added dropwise. After the addition, the reaction mixture was brought to room temperature and refluxed for 20 h. The solvent was distilled out by fractional distillation and the product was distilled into a cold trap. NMR shows the presence of PhSiD\(_3\), which agrees with the reported literature, along with Et\(_2\)O. FT-IR (neat) \(\nu\): 3030, 2925, 2858, 1742, 1595, 1447, 1338, 1241, 1157, 1092, 1049, 925, 853, 807, 698, 647, 572, 545 cm\(^{-1}\). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.59 – 7.56 (m, 2H), 7.41 – 7.31 (m, 3H). \(^13\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 135.8, 129.8, 128.1. MS (m/z): 111.0 (C\(_6\)H\(_5\)D\(_3\)Si\(^+\)).

5.8 Synthesis of 2-(2-bromoethoxy)benzaldehyde\(^8\):
A flame dried two neck round bottomed flask equipped with a stir bar was fitted with a rubber septum and backfilled with N\textsubscript{2}. Salicylaldehyde (0.873 mL, 8.19 mmol) was taken and CH\textsubscript{3}CN (2 mL) was added. Then K\textsubscript{2}CO\textsubscript{3} (1.13 g, 8.19 mmol) was added into it. The solution was refluxed for 1 h, and then 1,2-dibromoethane (7.09 mL, 8.19 mmol) was added. Then the reaction mixture was refluxed for another 10 h under nitrogen. Later, the reaction mixture was cooled to room temperature, filtered through silica and was concentrated in vacuum. The resulting crude was purified by column chromatography to give a pure product with 80% yield. \textit{\textsuperscript{1}H NMR} (500 MHz, CDCl\textsubscript{3}) $\delta$ 7.85 (dd, $J$ = 7.7, 1.9 Hz, 1H), 7.54 (td, $J$ = 8.1, 7.5, 2.0 Hz, 1H), 7.06 (t, $J$ = 7.5 Hz, 1H), 6.95 (d, $J$ = 8.4 Hz, 1H), 4.41 (dd, $J$ = 6.9, 5.0 Hz, 2H), 3.70 (td, $J$ = 6.0, 1.8 Hz, 2H). \textit{\textsuperscript{13}C NMR} (126 MHz, CDCl\textsubscript{3}) $\delta$ 189.6, 160.4, 135.9, 128.5, 125.2, 121.5, 112.7, 68.3, 28.8. \textbf{MS} (m/z): 230.0 (C\textsubscript{9}H\textsubscript{9}BrO\textsubscript{2}\textsuperscript{+})

\textit{Competitive experiments \textsuperscript{1}}

Competitive experiments were conducted to determine the order of reactivity, in one-pot chlorodecane \textbf{1j}, bromide \textbf{1k} and iodide were subjected to the standard reaction condition, the complete consumption of iodides occurred within 20 minutes and the bromide took 24 h to get completely consumed, however, the chloride was intact even after 48 h.
6. REFERENCES


7. NMR SPECTRA

4-\textit{n}-butylanisole (1a-1c)
Adamantane (If-Ig)
Hexadecane (1h)
Triphenylmethane (II)
1-undecanol (1o)
4-methylbenzylalcohol (1p)
Naphthalene (4a-4b)
Indole (4d)
1,2,3-trimethoxybenzene (4f)
1-Phenylethanol (4j)
Diphenylsilane
5-(diphenylsilyl)-N, N-dimethylpyridin-2-amine
2-Ethoxybenzaldehyde
4-(4-methoxyphenyl)butan-2-ol
4-(P-methoxy)phenyl-2-chlorobutane
4-(P-methoxy)phenyl-2-bromobutane
4-(P-methoxy)phenyl-2-iodobutane
2-(allyloxy)-3-iodotetrahydro-2H-pyran
5-Bromo-N,N-dimethylpyridin-2-amine
Cholesteryl Iodide

Chemical structure of Cholesteryl Iodide with NMR spectrum showing peaks at different ppm values.
2-(2-bromoethoxy)benzaldehyde