### **Electronic Supplementary Information**

### Alkylfluorenyl substituted N-Heterocyclic Carbenes in Copper(I) catalysed Hydrosilylation of Aldehydes and Ketones

Matthieu Teci,<sup>a</sup> Nicolas Lentz,<sup>a</sup> Eric Brenner,<sup>\*a</sup> Dominique Matt,<sup>\*a</sup> and Loïc Toupet<sup>b</sup>

<sup>&</sup>lt;sup>a</sup>Laboratoire de Chimie Inorganique Moléculaire et Catalyse, Université de Strasbourg, Institut de Chimie de Strasbourg, UMR 7177 CNRS, 1, rue Blaise-Pascal, 67008 Strasbourg cedex, France. E-mail : eric.brenner @unistra.fr or dmatt@unistra.fr

<sup>&</sup>lt;sup>b</sup>Groupe Matière Condensée et Matériaux, UMR 6626, Université de Rennes 1, Campus de Beaulieu, 35042, Rennes cedex, France

### Content

- General procedure for the hydrosilylation of acetophenone catalysed by 3 mol% of complexes 2b-d and [IPrCuCl] using Et<sub>3</sub>SiH (influence of the base and the solvent) as shown in Table 1

- General procedure for the hydrosilylation of ketones catalysed by 3 mol% of complex 2d using Et<sub>3</sub>SiH as shown in Table 2

- General procedure for the hydrosilylation of acetophenone catalysed by 0.25 mol% of complexes 2a-c and [IPrCuCl] using Et<sub>3</sub>SiH (influence of the base and the solvent) as shown in Table 3

- General procedure for the hydrosilylation of ketones catalysed by 0.25 mol% of complex 2d as shown in Table 4

- General procedure for the hydrosilylation of benzaldehyde catalysed by 0.25 mol% of complex 2d using Et<sub>3</sub>SiH (influence of the base and the solvent) as shown in Table 5

- General procedure for the hydrosilylation of benzaldehyde derivatives catalysed by 0.25 mol% of complex 2c as shown in Table 6

- List of hydrosilylation compounds produced in this study and NMR spectra (<sup>1</sup>H NMR, 300.1 MHz; <sup>13</sup>C NMR, 75.5 MHz) thereof. For unreported silylation compounds, full characterizing data are provided

- References

### General procedure for the hydrosilylation of acetophenone catalysed by 3 mol% of complexes 2b-d and [IPrCuCl] using Et<sub>3</sub>SiH (influence of the base and the solvent) as shown in Table 1

In a Schlenk tube under nitrogen were introduced the copper complex ( $6.0 \cdot 10^{-3}$  mmol) and *t*-BuOK ( $2.7 \cdot 10^{-4}$  g; 0.24 mmol) or *t*-BuONa ( $2.3 \cdot 10^{-4}$  mg; 0.24 mmol) followed by THF or toluene (2 mL). The mixture was stirred at room temperature for 10 min. Triethylsilane (6 mmol) was then added and the mixture stirred at room temperature for a futher 10 min. After this period of activation, acetophenone (2 mmol) was added and the reaction mixture was stirred at room temperature for 3 h. The mixture was filtered through a short pad of Celite using CH<sub>2</sub>Cl<sub>2</sub>. The solvent was removed under reduced pressure and the residue analysed by <sup>1</sup>H NMR.

## General procedure for the hydrosilylation of ketones catalysed by 3 mol% of complex 2d using Et<sub>3</sub>SiH as shown in Table 2

In a Schlenk tube under nitrogen were introduced the **2d** ( $3.3 \cdot 10^{-4}$  g; 0.06 mmol) and *t*-BuOK ( $2.7 \cdot 10^{-4}$  g; 0.24 mmol) or *t*BuONa ( $2.3 \cdot 10^{-4}$  g; 0.24 mmol) followed by THF or toluene (2 mL). The mixture was stirred at room temperature for 10 min. Triethylsilane (6 mmol) was then added and the mixture stirred at room temperature for 10 min. After this activation period, the ketone (2 mmol) was added and the reaction mixture was stirred at room temperature for 3 h. The mixture was filtered through a short pad of Celite using CH<sub>2</sub>Cl<sub>2</sub> as solvent. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (SiO<sub>2</sub>; AcOEt–petroleum ether) to afford the hydrosilylated products as colourless oils.

# General procedure for the hydrosilylation of acetophenone catalysed by 0.25 mol% of complexes 2b-d and [IPrCuCl] using Et<sub>3</sub>SiH (influence of the base and the solvent) as shown in Table 3

In a Schlenk tube under nitrogen were introduced the complex  $(5.0 \cdot 10^{-3} \text{ mmol})$  and *t*-BuOK  $(1.1 \cdot 10^{-3} \text{ g}; 1.0 \cdot 10^{-2} \text{ mmol})$  or *t*-BuONa  $(1 \cdot 10^{-3} \text{ g}; 1.0 \cdot 10^{-2} \text{ mmol})$  followed by THF or toluene (2 mL). The mixture was stirred at room temperature for 10 min. Triethylsilane (6 mmol) was then added and the mixture stirred at room temperature for a further 10 min. After the activation period, acetophenone (2 mmol) was added and the reaction mixture was stirred at 65°C for 24 h. The mixture was filtered through a short pad of Celite using CH<sub>2</sub>Cl<sub>2</sub>. The solvent was removed under reduced pressure and the residue analysed by <sup>1</sup>H NMR.

# General procedure for the hydrosilylation of ketones catalysed by 0.25 mol% of complex 2d as shown in Table 4

In a Schlenk tube under nitrogen were introduced the **2d** ( $2.8 \cdot 10^{-3}$  g;  $5.0 \cdot 10^{-3}$  mmol) and *t*-BuOK ( $1.1 \cdot 10^{-3}$  g;  $1.0 \cdot 10^{-2}$  mmol) followed by THF (2 mL). The mixture was stirred at room temperature for 10 min. Triethylsilane (6 mmol) was then added and the mixture stirred at room temperature for 10 min. After this period of activation, the ketone (2 mmol) was added and the reaction mixture was stirred at 65°C for 24 h. The mixture was cooled to room temperature and filtered through a short pad of Celite using CH<sub>2</sub>Cl<sub>2</sub> as solvent. The mixture was filtered through a short pad of Celite using CH<sub>2</sub>Cl<sub>2</sub>. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (SiO<sub>2</sub>; AcOEt–petroleum ether) to afford the hydrosilylated products as colourless oils.

### General procedure for the hydrosilylation of benzaldehyde catalysed by 0.25 mol% of complex 2d using Et<sub>3</sub>SiH (influence of the base and the solvent) as shown in Table 5

In a Schlenk tube under nitrogen were introduced the **2d** ( $2.8 \cdot 10^{-3}$  g;  $5.0 \cdot 10^{-3}$  mmol) and *t*BuOK ( $1.1 \cdot 10^{-3}$  g;  $1.0 \cdot 10^{-2}$  mmol) or *t*BuONa ( $1 \cdot 10^{-3}$  g;  $1.0 \cdot 10^{-2}$  mmol) followed by THF or toluene (2 mL). The mixture was stirred at room temperature for 10 min. Triethylsilane (6 mmol) was then added and the mixture stirred at room temperature for 10 min. After this period of activation, benzaldehyde (2 mmol) was added and the reaction mixture was stirred at room temperature for 2 h. The mixture was filtered through a short pad of Celite using CH<sub>2</sub>Cl<sub>2</sub> as solvent. The solvent was removed under reduced pressure and the residue analysed by <sup>1</sup>H NMR.

# General procedure for the hydrosilylation of benzaldehyde derivatives catalysed by 0.25 mol% of complex 2d as shown in Table 6

In a Schlenk tube under nitrogen were introduced the **2d** ( $2.8 \cdot 10^{-3}$  g;  $5.0 \cdot 10^{-3}$  mmol) and *t*BuONa ( $1 \cdot 10^{-3}$  g;  $1.0 \cdot 10^{-2}$  mmol) followed by THF (2 mL). The mixture was stirred at room temperature for 10 min. Triethylsilane (6 mmol) was then added and the mixture stirred at room temperature for 10 min. After this period of activation, the aldehyde (2 mmol) was added and the reaction mixture was stirred at room temperature for 2 h. The mixture was filtered through a short pad of Celite using CH<sub>2</sub>Cl<sub>2</sub> as solvent. The solvent was removed under reduced pressure and the residue analysed by <sup>1</sup>H NMR.

List of hydrosilylation compounds produced in this study and NMR spectra (<sup>1</sup>H NMR, 300.1 MHz; <sup>13</sup>C NMR, 75.5 MHz) thereof. For unreported silylation compounds, full characterizing data are provided.

Triethyl(octan-2-yloxy)silane (see main text: Table 2, entry 1 and Table 4, entry 1):



This compound was prepared as described in the general procedures. It was purified by flash chromatography (SiO<sub>2</sub>; neat petroleum ether) and obtained as colourless oil. Spectroscopic data were consistent with those described in the literature.<sup>[1, 2]</sup>

Triethyl(pentan-3-yloxy)silane (see main text: Table 2, entry 2 – Table 4, entry 2):

 $^{\circ}$ <sup>SiEt</sup><sub>3</sub> This compound was prepared as described in the general procedures. It was purified by flash chromatography (SiO<sub>2</sub>; neat petroleum ether) and obtained as colourless oil. Spectroscopic data were consistent with those described in the literature.<sup>[1]</sup>

(Bicyclo[2.2.1]heptan-2-yloxy)triethylsilane (see Table 2, entry 3 – Table 4, entry 3):

This compound was prepared as described in the general procedures. It was purified by flash chromatography (SiO<sub>2</sub>; neat petroleum ether) and obtained as colourless oil. The exo product could not be isolated purely, however, endo / exo ratios could be determine by comparison of the respective CHOSiEt<sub>3</sub> integrations. Spectroscopic data were consistent with those

described in the literature.<sup>[3]</sup>

Triethyl(2-methylcyclohexyloxy)silane (see main text: Table 2, entry 4 – Table 4, entry 4):

<sup>O-SiEt</sup><sup>3</sup> This compound (diastereomeric mixture) was prepared as described in the general procedures. It was purified by flash chromatography (SiO<sub>2</sub>; neat petroleum ether) and obtained as colourless oil. Spectroscopic data for the syn and anti products were consistent with those described in the literature.<sup>[4]</sup>

**Triethyl(((1***R***+***S***,2***S***,5***R***)-2-isopropyl-5-methylcyclohexyl)oxy)silane (see main text: Table 2, entry 5 – Table 4, entry 8):** 

This compound was prepared as described above. It was purified by flash chromatography (SiO<sub>2</sub>; neat petroleum ether) and obtained as colourless oil. The compound was obtained as a diastereomeric mixture of triethyl-(2(*S*)-isopropyl-5(*R*)-methylcyclohexyloxy)silane. The diastereomeric ratio (40:60) was determined by NMR. Spectroscopic data for both diatereomers were consistent with those described in the literature, but only the NMR spectra of the pure (1*R*,2*S*,5*R*) disatereomer is shown below.<sup>[5]</sup>

**Triethyl(1-phenylethoxy)silane** (see main text: Table 2, entry 6 – Table 4, entry 6):



This compound was prepared as described in the general procedures. It was purified by flash chromatography (SiO<sub>2</sub>; neat petroleum ether) and obtained as colourless oil. Spectroscopic were consistent with those described in the literature.<sup>[6]</sup>

(1-(4-chlorophenyl)ethoxy)triethylsilane (see main text: Table 2, entry 7 – Table 4, entry 7):

<sup>SiEt</sup><sub>3</sub> This compound was prepared as described in the general procedures. It was purified by flash chromatography (SiO<sub>2</sub>; neat petroleum ether) and obtained as colourless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  7.26 (s, 4H, ArH), 4.83 (q, <sup>3</sup>*J* = 6.3 Hz, 4H, OCH), 3.75 (d, <sup>3</sup>*J* = 6.3 Hz, 3H, CH<sub>3</sub>), 0.91 (t, <sup>3</sup>*J* = <sup>3</sup>*J*' = 8.1 Hz, 9 H, CH<sub>2</sub>-CH<sub>3</sub>), 0.61-0.52 (m, 6H, CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  145.6 (arom. Cq), 132.5 (arom. Cq), 128.3 (arom. CH), 126.7 (arom. CH), 70.1 (OCH), 27.4 (CH<sub>3</sub>), 6.9 (CH<sub>2</sub>CH<sub>3</sub>), 4.9 (CH<sub>2</sub>CH<sub>3</sub>). Anal. Calcd for C<sub>14</sub>H<sub>23</sub>ClOSi (*M*<sub>r</sub> = 270.87) C, 62.08; H, 8.56; Found: C, 62.17; H, 8.35.

[1-(4-methoxyphenyl)ethoxy]triethylsilane (see main text: Table 2, entry 7 – Table 4, entry 7):



This compound was prepared as described in the general procedures. It was purified by flash chromatography (SiO<sub>2</sub>; AcOEt : petroleum ether (10 : 90)) and obtained as colourless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  7.29-7.27 (m, 2H, ArH),

6.89-6.86 (m, 2H, ArH), 4.85 (q,  ${}^{3}J$  = 6.4 Hz, 1H, C*H*), 3.82 (s, 3H, OCH<sub>3</sub>), 1.43 (d,  ${}^{3}J$  = 8.1 Hz, 9 H, CH<sub>2</sub>CH<sub>3</sub>), 0.63-0.53 (m, 6H, CH<sub>2</sub>CH<sub>3</sub>).  ${}^{13}C{}^{1}H$  NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  158.6 (arom. Cq), 139.3

(arom. Cq), 126.5 (arom. CH), 113.6 (arom. CH), 70.3 (CH), 55.3 (OCH<sub>3</sub>), 27.4 (CH<sub>3</sub>), 7.0 (CH<sub>2</sub>CH<sub>3</sub>), 5.0 (CH<sub>2</sub>CH<sub>3</sub>). Anal. Calcd for  $C_{15}H_{26}O_2Si$  ( $M_r = 266.46$ ) C, 67.62; H, 9.84 Found: C, 67.72; H, 9.96. **[1-(4-bromophenyl)ethoxy]triethylsilane** (see main text: Table 2, entry 8 – Table 4, entry 8):



This compound was prepared as described in the general procedures. It was purified by flash chromatography (SiO<sub>2</sub>; neat petroleum ether) and obtained as colourless oil. Spectroscopic data were consistent with those described in the literature.<sup>[7]</sup>

[1-(4-bromophenyl)ethoxy]triethylsilane (see main text: Table 2, entry 9 – Table 4, entry 9):

<sup>Br</sup>  $J^{\text{SiEt}_3}$  This compound was prepared as described in the general procedures. It was purified by flash chromatography (SiO<sub>2</sub>; AcOEt : petroleum ether (10 : 90)) and obtained as colourless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  7.64 (dd, <sup>3</sup>*J* = 7.3 Hz, <sup>3</sup>*J*<sup>2</sup> = 1.8 Hz, 1H, ArH), 7.47 (dd, <sup>3</sup>*J* = 7.8 Hz, <sup>3</sup>*J*<sup>2</sup> = 1.3 Hz, 1H, ArH), 7.36-7.28 (m, 1H, ArH), 7.09 (ddd, <sup>3</sup>*J* = 7.8 Hz, <sup>3</sup>*J*<sup>2</sup> = 7.3 Hz, <sup>4</sup>*J* = 1.8 Hz, 1H, ArH), 5.19 (q, <sup>3</sup>*J* = 6.2 Hz, 1H, CH), 1.40 (d, <sup>3</sup>*J* = 6.2 Hz, 3H, CH<sub>3</sub>), 0.92 (t, <sup>3</sup>*J* = 7.9 Hz, 9H, CH<sub>2</sub>CH<sub>3</sub>), 0.58 (m, AB part of ABX<sub>3</sub>, <sup>3</sup>*J* = 7.9 Hz, <sup>2</sup>*J* = 2.7 Hz, 9H, CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  146.1 (arom. Cq), 132.3 (arom. CH), 128.3 (arom. CH), 127.7 (arom. CH), 127.5 (arom. CH), 120.9 (arom. Cq), 69.7 (CH), 25.8 (CH<sub>3</sub>), 6.9 (CH<sub>2</sub>CH<sub>3</sub>), 4.9 (CH<sub>2</sub>CH<sub>3</sub>). Anal. Calcd for C<sub>14</sub>H<sub>23</sub>BrOSi (*M*<sub>r</sub> = 315.33) C, 53.33; H, 7.35. Found: C, 53.12; H 7.49,

**2-(1-(triethylsilyloxy)ethyl)pyridine** (see main text: Table 2, entry 11 – Table 4, entry 11):



This compound was prepared as described in the general procedures. It was purified by flash chromatography (SiO<sub>2</sub>; AcOEt : petroleum ether (50 : 50)) and obtained as colourless oil. Spectroscopic were consistent with those described in the literature.<sup>[7]</sup>

Benzhydryloxytriethylsilane (see main text: Table 2, entry 12 – Table 4, entry 12):



This compound was prepared as described in the general procedures. It was purified by flash chromatography (SiO<sub>2</sub>; neat petroleum ether) and obtained as colourless oil. Spectroscopic data were consistent with those described in the literature.<sup>[7]</sup>

(dicyclohexylmethoxy)triethylsilane (see main text: Table 2, entry 13 – Table 4, entry 13):



This compound was prepared as described in the general procedures. It was purified by flash chromatography (SiO<sub>2</sub>; neat petroleum ether) and obtained as colourless oil. Spectroscopic data were consistent with those described in the literature.<sup>[7]</sup>

(2,2-dimethyl-1-phenylpropoxy)triethylsilane (see main text: Table 2, entry 14 – Table 4, entry 14):



This compound was prepared as described in the general procedures. It was purified by flash chromatography (SiO<sub>2</sub>; neat petroleum ether) and obtained as colourless oil. Spectroscopic data for were consistent with those described in the literature.<sup>[7]</sup>

Benzyl benzoate (see main text: Table 5, entry 5):



This compound was prepared as described in the general procedures. It was purified by flash chromatography (SiO<sub>2</sub>; neat petroleum ether) and obtained as colourless oil. Spectroscopic data for were consistent with those described in the

literature.[8]

Benzyloxytriethylsilane (see main text: Table 5, entry 1):



This compound was prepared as described in the general procedures. It was purified by flash chromatography (SiO<sub>2</sub>; neat petroleum ether) and obtained as colourless oil. Spectroscopic data for were consistent with those described in the literature.<sup>[6]</sup>

(4-chlorobenzyloxy)triethylsilane (see main text: Table 5, entry 2):



This compound was prepared as described in the general procedures. It was purified by flash chromatography (SiO<sub>2</sub>; AcOEt : petroleum ether (10 : 90)) and obtained as colourless oil. Spectroscopic data for were consistent with those described in the

literature.[9]

(2-bromobenzyloxy)triethylsilane (see main text: Table 5, entry 3)



This compound was prepared as described in the general procedures. It was purified by flash chromatography (SiO<sub>2</sub>; AcOEt : petroleum ether (10 : 90)) and obtained as colourless oil. Spectroscopic data for were consistent with those described in the

literature. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  7.64 (d, <sup>3</sup>*J* = 8.1 Hz, 1 H, ArH), 7.53 (d, <sup>3</sup>*J* = 7.9 Hz, 1H, ArH), 7.36 (t, <sup>3</sup>*J* = 8.1 Hz, 1H, ArH), 7.14 (t, <sup>3</sup>*J* = 7.9 Hz, 1H, ArH), 4.8 (s, 2H, CH<sub>2</sub>), 1.40 (d, <sup>3</sup>*J* = 6.2

Hz, 3H, CH<sub>3</sub>), 1.05 (t,  ${}^{3}J$  = 7.9 Hz, 9H, CH<sub>2</sub>CH<sub>3</sub>), 0.74 (q,  ${}^{3}J$  = 7.9 Hz, 9H, CH<sub>2</sub>CH<sub>3</sub>).  ${}^{13}C{}^{1}H$  NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  140.4 (arom. Cq), 132.1 (arom. CH), 128.3 (arom. CH), 127.7 (arom. CH), 127.4 (arom. CH), 121.2 (arom. Cq), 64.4 (CH<sub>2</sub>), 29.8 (CH<sub>3</sub>), 6.9 (CH<sub>2</sub>CH<sub>3</sub>), 4.7 (CH<sub>2</sub>CH<sub>3</sub>). Anal. Calcd for C<sub>13</sub>H<sub>21</sub>BrOSi ( $M_r$  = 301,30) C, 51.82; H, 7.03. Found: C, 51.56; H, 7.33.

#### (4-trifluoromethylbenzyloxy)triethylsilane (see main text: Table 5, entry 4):

<sup>SiEt<sub>3</sub></sup> This compound was prepared as described in the general procedures. It was purified by flash chromatography (SiO<sub>2</sub>; neat petroleum ether) and obtained as colourless oil. Spectroscopic data for were consistent with those described in the literature. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  7.59 (d, <sup>3</sup>*J* = 7.9 Hz, 2H, ArH), 7.45 (m, <sup>3</sup>*J* = 7.9 Hz, 2H, ArH), 4.79 (s, 2H, CH<sub>2</sub>), 0.99 (d, <sup>3</sup>*J* = 7.9 Hz, 9H, CH<sub>2</sub>CH<sub>3</sub>), 0.68 (q, <sup>3</sup>*J* = 7.9 Hz, 6H, CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  145.6 (arom. Cq), 129.3 (t, <sup>2</sup>*J* = 32.3 Hz, CF<sub>3</sub>), 126.2 (arom. CH), 125.3 (broad signal, arom. CH), 64.1 (CH<sub>2</sub>), 27.4 (CH<sub>3</sub>), 6.9 (CH<sub>2</sub>CH<sub>3</sub>), 4.6 (CH<sub>2</sub>CH<sub>3</sub>). Anal. Calcd for C<sub>14</sub>H<sub>21</sub>F<sub>3</sub>OSi (*M*<sub>r</sub> = 290,40) C, 57.90; H, 7.29. Found: C, 57.65; H, 7.36.

#### (4-methylbenzyloxy)triethylsilane (see main text: Table 5, entry 5):



This compound was prepared as described in the general procedures. It was purified by flash chromatography (SiO<sub>2</sub>; neat petroleum ether) and obtained as colourless oil. Spectroscopic data for were consistent with those described in the literature.<sup>[9]</sup>

(4-methoxybenzyloxy)triethylsilane (see main text: Table 5, entry 6):



This compound was prepared as described in the general procedures. It was purified by flash chromatography (SiO<sub>2</sub>; AcOEt : petroleum ether (10 : 90)) and obtained as colourless oil. Spectroscopic data for were consistent with those described in the literature.<sup>[9]</sup>

(2-methoxybenzyloxy)triethylsilane (see main text: Table 5, entry 7):



This compound was prepared as described in the general procedures. It was purified by flash chromatography (SiO<sub>2</sub>; AcOEt : petroleum ether (10 : 90)) and obtained as colourless oil. Spectroscopic data for were consistent with those described in the

literature.<sup>[10]</sup>



<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of the hydrosilylation products (CDCl<sub>3</sub>, 300 MHz, 75 MHz) Triethyl(octan-2-yloxy)silane (Table 2, entry 2 – Table 4, entry 2):



Triethyl(pentan-3-yloxy)silane (Table 2, entry 2 – Table 4, entry 2):



(bicyclo[2.2.1]heptan-2-yloxy)triethylsilane Endo product(Table 2, entry 3 – Table 4, entry 3):



Triethyl(2-methylcyclohexyloxy)silane (*anti*-product) (Table 2, entry 4 – Table 4, entry 4):



Triethyl(2-methylcyclohexyloxy)silane (*syn*-product) (Table 2, entry 4 – Table 4, entry 4):



Triethyl((1R, 2S, 5R)-2-isopropyl-5methylcyclohexyloxy)silane (Table 2, entry 5 – Table 4, entry



Triethyl(1-phenylethoxy)silane (Table 2, entry 6 – Table 4, entry 6):



[1-(4-chlorophenyl)ethoxy]triethylsilane (Table 2, entry 7 – Table 4, entry 7):



[1-(4-methoxy)ethoxy]triethylsilane (Table 2, entry 8 – Table 4, entry 7):



[1-(4-bromophenyl)ethoxy]triethylsilane (Table 2, entry 8 – Table 4, entry 8):



[1-(2-bromophenyl)ethoxy]triethylsilane (Table 2, entry 9 – Table 4, entry 9):



[2-(1-(triethylsilyloxy)ethyl]pyridine (Table 2, entry 11 – Table 4, entry 11):



**Benzhydryloxytriethylsilane** (Table 2, entry 12 – Table 4, entry 12):



(dicyclohexylmethoxy)triethylsilane (Table 2, entry 13 – Table 4, entry 13):



(2,2-dimethyl-1-phenylpropoxy)triethylsilane (Table 2, entry 14 – Table 4, entry 14):

Benzylbenzoate (Table 5, entry 5):



Benzyloxytriethylsilane (Table 5, entry 1):



(4-chlorobenzyloxy)triethylsilane (Table 5, entry 2):



(2-bromobenzyloxy)triethylsilane (Table 5, entry 3):



(4-trifluoromethylbenzyloxy)triethylsilane (Table 5, entry 4):



(4-methylbenzyloxy)triethylsilane (Table 5, entry 5):

![](_page_30_Figure_1.jpeg)

![](_page_31_Figure_0.jpeg)

(4-methoxybenzyloxy)triethylsilane (Table 5, entry 6):

![](_page_32_Figure_0.jpeg)

![](_page_32_Figure_1.jpeg)

#### References

- [1] V. K. Dioumaev, R. M. Bullock, *Nature* **2003**, *424*, 530-532.
- [2] R. M. Denton, J. An, B. Adeniran, A. J. Blake, W. Lewis, A. M. Poulton, J. Org. Chem. 2011, 76, 6749-6767.
- [3] H. Kaur, F. K. Zinn, E. D. Stevens, S. P. Nolan, *Organometallics* **2004**, *23*, 1157-1160.
- [4] B. H. Lipshutz, C. C. Caires, P. Kuipers, W. Chrisman, Org. Lett. 2003, 5, 3085-3088.
- [5] L. D. Field, B. A. Messerle, M. Rehr, L. P. Soler, T. W. Hambley, *Organometallics* **2003**, *22*, 2387-2395.
- [6] E. A. Ison, E. R. Trivedi, R. A. Corbin, M. M. Abu-Omar, J. Am. Chem. Soc. 2005, 127, 15374-15375.
- [7] S. Diez-Gonzalez, H. Kaur, F. K. Zinn, E. D. Stevens, S. P. Nolan, J. Org. Chem. 2005, 70, 4784-4796.
- [8] L. Li, H. T. Sheng, F. Xu, Q. Shen, Chinese J. Chem. 2009, 27, 1127-1131.
- [9] S. Diez-Gonzalez, N. M. Scott, S. P. Nolan, Organometallics 2006, 25, 2355-2358.
- [10] Y. Do, J. Han, Y. H. Rhee, J. Park, Adv. Synth. Catal. 2011, 353, 3363-3366.