

## Supplementary Information

The starting materials for the syntheses were purchased from Aldrich and used without further purification. **10** was synthesized using a literature procedure.<sup>1</sup> The solvents were dried by standard methods.<sup>2</sup> The reactions were conducted using the Schlenk technique and the moisture sensitive chemicals were handled in a glove box.

<sup>1</sup>H, <sup>13</sup>C and <sup>29</sup>Si NMR spectra were recorded with a Varian INOVA 400 spectrometer operating at 400.2 MHz for <sup>1</sup>H, 100.4 MHz for <sup>13</sup>C and 79.6 MHz for <sup>29</sup>Si. The chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) for <sup>1</sup>H and <sup>13</sup>C with the solvent resonances as the internal standard. <sup>29</sup>Si chemical shifts are reported in ppm with TMS in benzene as external standard. Mass spectra were obtained from the Analytical Service Laboratory in the Department of Chemistry at Northwestern University. The elemental analyses were provided by Prevalere Life Sciences, Inc. (Whitesboro, NY).

Preparation of **1**: A solution of chlorodimethylsilane (0.95 g, 10 mmol) in diethyl ether (40 mL) was added through a syringe at a rate of 15 mL/h to an ice-cooled solution of diphenylsilanediol (6.5 g, 30 mmol) and pyridine (0.95 g, 12mmol) in THF/diethyl ether (1:2, 60 mL). The mixture was stirred at room temperature for another 4 h. The solvent was then evaporated under vacuum, and 80 mL of pentane was added. The solid containing diphenylsilanediol and pyridine hydrochloride was filtered off. The residue obtained by vacuum evaporation of the filtrate was purified by chromatography (silica gel, diethyl ether/ hexane 1:6) to obtain a colorless liquid product at 86% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 7.67 (d, 4H, Ph), 7.45-7.38 (m, 6H, Ph), 4.90 (sept, 1H, SiH), 2.67 (s, br, 1H, SiOH), 0.26 (d, 6H, Me<sub>2</sub>Si). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ): 135.2, 134.4, 130.4, 128.1, 0.94. <sup>29</sup>Si NMR (CDCl<sub>3</sub>, δ): -3.19, -36.50. MS (EI, *m/z*, %): 274 (M<sup>+</sup>, 10), 259 (M<sup>+</sup>-Me, 45), 196 (M<sup>+</sup>-Ph-H, 70), 181 (M<sup>+</sup>-Ph-Me-H, 100). Anal. Calc. for C<sub>14</sub>H<sub>18</sub>Si<sub>2</sub>O<sub>2</sub> (274.2): C, 61.28; H, 6.57%. Found: C, 60.97; H, 6.27%.

Compounds **2** and **4** were synthesized by catalyzed oxidation of their corresponding organo-H-siloxane. The method to prepare **10** has been described in literature.<sup>1</sup>

**2**: Yield: 92%. Colorless solid. Mp. 109-111 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 7.64 (d, 4H, Ph), 7.42 (t, 2H, Ph), 7.36 (t, 4H, Ph), 0.15 (s, 6H, Me<sub>2</sub>Si). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ): 135.1, 134.4, 130.5, 128.1, 0.57. <sup>29</sup>Si NMR (CDCl<sub>3</sub>, δ): -7.70, -37.25. MS (EI, *m/z*, %): 290 (M<sup>+</sup>, 8), 275 (M<sup>+</sup>-Me, 45), 213 (M<sup>+</sup>-Ph, 32), 197 (M<sup>+</sup>-Ph-OH+H<sup>+</sup>, 100).

**4**: Yield: 98%. Colorless liquid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 7.62 (d, 4H, Ph), 7.42 (t, 2H, Ph), 7.36 (t, 4H, Ph), 2.70 (s, Br, 2H, SiOH), 0.16 (s, 6H, Me<sub>2</sub>Si), 0.12 (s, 6H, Me<sub>2</sub>Si), 0.07 (s, 6H, Me<sub>2</sub>Si). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ): 136.0, 134.3, 130.1, 127.9, 1.18, 0.56, 0.42. <sup>29</sup>Si NMR (CDCl<sub>3</sub>, δ): -9.10, -10.28, -18.90, -47.67ppm. MS (EI, *m/z*, %): 405 (M<sup>+</sup>-2OH+H<sup>+</sup>, 11), 327 (M<sup>+</sup>-Ph-2OH, 29), 267 (M<sup>+</sup>-2Ph-OH, 100).

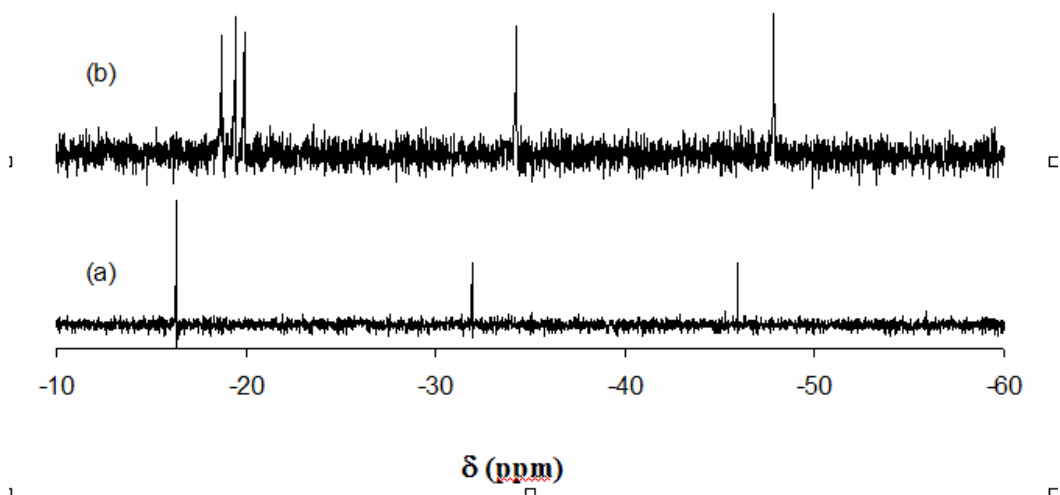
Preparation of **3**: To an ice-cooled solution of **2** (0.014 mol, 4.0 g) in 120 mL of diethyl ether, a mixture of Me<sub>2</sub>SiHCl (3.9 g, 0.041 mol) and pyridine (3.2 g, 0.041 mol)

in 60 mL of diethyl ether was added via a syringe. A colorless precipitate was formed immediately, and the mixture was stirred at room temperature for 4 h. The solvent, excess  $\text{Me}_2\text{SiHCl}$  and pyridine were evaporated under vacuum. Pentane (100 mL) was added to the residue, and the solid was filtered off. The desired organo-H-siloxane product **3** was obtained in high purity from the filtrate after the solvent was evaporated under reduced pressure. Yield 88%. Colorless liquid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 7.61 (d, 4H, Ph), 7.43-7.34 (m, 6H, Ph), 4.86 (sept, 1 H, SiH), 4.68 (sept, 1H, SiH), 0.22 (d, 6H,  $\text{Me}_2\text{SiH}$ ), 0.13 (d, 6H,  $\text{Me}_2\text{SiH}$ ), 0.10 (s, 6H,  $\text{Me}_2\text{Si}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 136.1, 134.4, 130.1, 127.9, 1.14, 0.93, 0.80.  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): -4.08, -6.26, -18.33, -46.53. MS (EI,  $m/z$ , %): 406 ( $\text{M}^+$ , 14), 391 ( $\text{M}^+$ -Me, 14), 327 ( $\text{M}^+$ -Ph-2H, 56), 269 ( $\text{M}^+$ -SiMe<sub>2</sub>H-H-Ph, 68), 135 (100). Anal. Calc. for  $\text{C}_{18}\text{H}_{30}\text{Si}_4\text{O}_3$  (406.3): C, 53.16; H, 7.38%. Found: C, 53.07; H, 7.46%.

General procedure for the syntheses of **5** and **11**: 50 mL of 2.74 mmol of the corresponding siloxanediol (1.2 g of **4** and 1.0 g of **10**) in diethyl ether and 50 mL of one equivalent of dichloromethylphenylsilane mixed with 6.6 mmol (0.52 g) of pyridine in diethyl ether were added simultaneously to a Schlenk flask containing 300 mL of diethyl ether under nitrogen at room temperature over a period of 5 h with vigorous stirring. Afterwards, the resulting mixture was stirred for 16 h. The solvent was removed by vacuum evaporation, and the crude product was extracted with 80 mL of pentane. The pentane was evaporated and the residue was purified by column chromatography (silica gel, diethyl ether/hexane 1:6). All the products are colorless liquid. Their  $^{29}\text{Si}$  NMR spectra are shown in Figure S1.

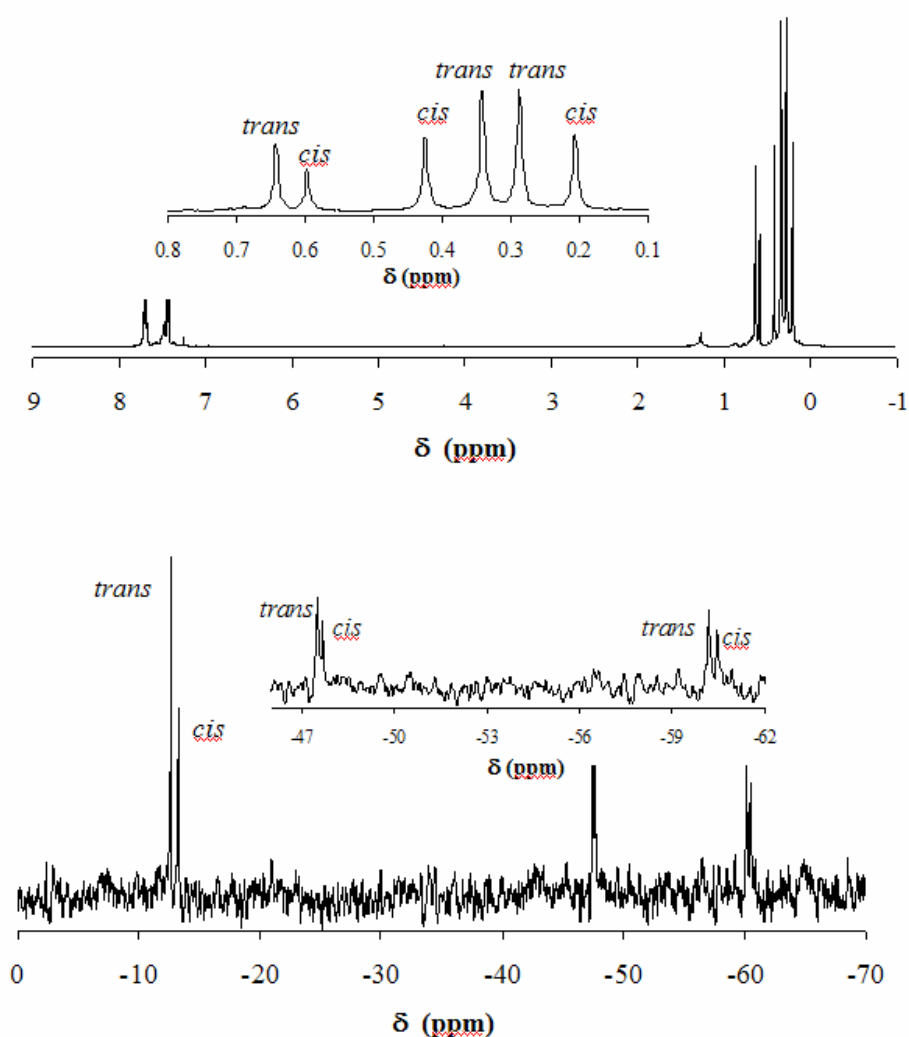
**5**: Yield: 74%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 7.65 (d, 2H, Ph), 7.57 (t, 4H, Ph), 7.42-7.29 (m, 9H, Ph), 0.28 (s, 3H, MeSi), 0.18 (s, 3H,  $\text{Me}_2\text{Si}$ ), 0.14 (s, 3H,  $\text{Me}_2\text{Si}$ ), 0.11 (s, 3H,  $\text{Me}_2\text{Si}$ ), 0.08 (s, 3H,  $\text{Me}_2\text{Si}$ ), 0.07 (s, 3H,  $\text{Me}_2\text{Si}$ ), 0.01 (s, 3H,  $\text{Me}_2\text{Si}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 136.3, 136.2, 134.4, 134.3, 133.4, 130.0, 129.9, 129.8, 127.9, 127.8, 1.19, 1.12, 1.00, -0.07.  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): -18.73, -19.43, -19.92, -34.26, -47.85. MS (CI, gas  $\text{CH}_4$ ,  $m/z$ , %): 541 ( $\text{M}^+$ -Me, 76), (479 ( $\text{M}^+$ -Ph, 100), 405 ( $\text{M}^+$ -SiPhMeO-Me, 10). Anal. Calc. for  $\text{C}_{25}\text{H}_{36}\text{Si}_5\text{O}_5$  (556.4): C, 53.92; H, 6.47%. Found: C, 53.23; H, 6.16%.

**11**: Yield: 92%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 7.65 (d, 2H, Ph), 7.56 (t, 4H, Ph), 7.42-7.29 (m, 9H, Ph), 0.30 (s, 3H, MeSiPh), 0.19 (s, 6H,  $\text{Me}_2\text{Si}$ ), 0.08 (s, 6H,  $\text{Me}_2\text{Si}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 137.5, 136.0, 135.9, 134.4, 134.3, 133.5, 130.2, 130.1, 129.9, 127.9, 127.8, 1.15, 0.95, -0.16.  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): -16.30, -31.93, -45.96 (2:1:1). MS (EI,  $m/z$ , %): 467 ( $\text{M}^+$ -Me, 27), 389 ( $\text{M}^+$ -Ph-Me-1, 100). Anal. Calc. for  $\text{C}_{23}\text{H}_{30}\text{Si}_4\text{O}_4$  (482.3): C, 57.22; H, 6.22%. Found: C, 57.68; H, 6.43%.



**Figure S1.**  $^{29}\text{Si}$  NMR spectra of the cyclic siloxane compounds **11** (a) and **5** (b) measured in  $\text{CDCl}_3$  at room temperature.

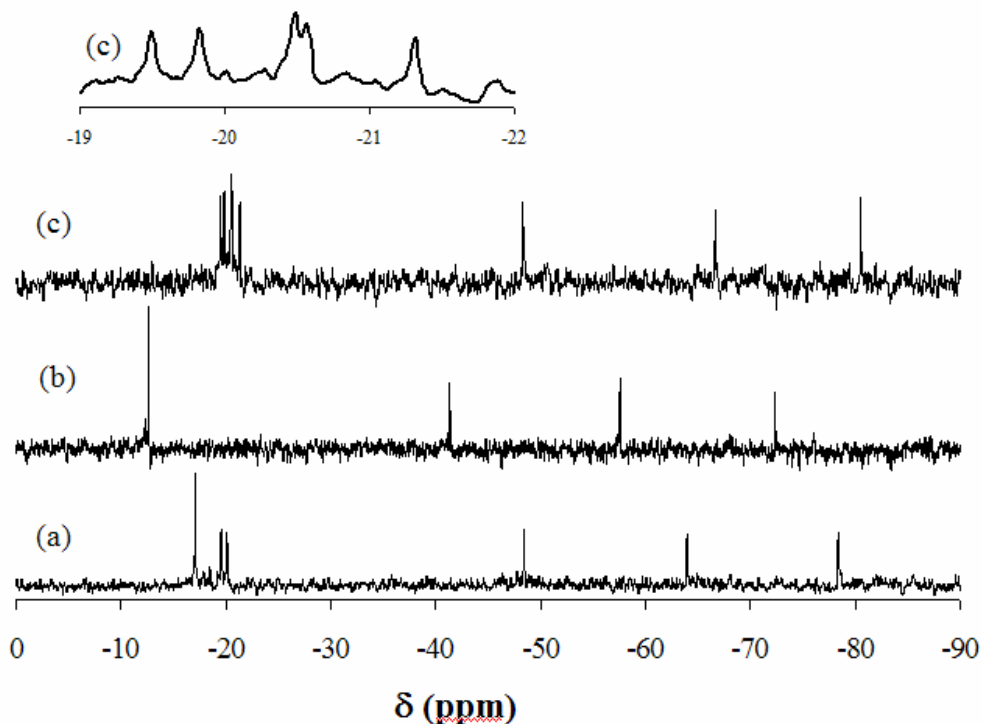
Preparation of **12**: To a solution of 1.2 g (2.5 mmol) of **11** in 2 mL of carbon tetrachloride (**CAUTION**: a probable carcinogen, for the safety information and safe handling, see [http://physchem.ox.ac.uk/MSDS/CA/carbon\\_tetrachloride.html](http://physchem.ox.ac.uk/MSDS/CA/carbon_tetrachloride.html)) 1.6 g (10 mmol) of bromine was added, and the solution was stirred at room temperature for 4 h. The volatile species were removed by vacuum evaporation, and the liquid residue was a mixture of *cis*-**12** (40%) and *trans*-**12** (60%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 7.68 (t, 2H, Ph), 7.48-7.40 (m, 3H, Ph), 0.64 (s, 1.8 H, MeSiBr for *trans*), 0.58 (s, 1.2H, MeSiBr for *cis*), 0.42 (s, 2.4H,  $\text{Me}_2\text{Si}$  for *cis*), 0.33 (s, 3.6H,  $\text{Me}_2\text{Si}$  for *trans*), 0.28 (s, 3.6H,  $\text{Me}_2\text{Si}$  for *trans*), 0.20 (s, 2.4H,  $\text{Me}_2\text{Si}$  for *cis*).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 135.2, 134.0, 133.6, 133.5, 131.4, 131.3, 128.3, 128.2, 4.57, 4.42, 0.61, 0.56.  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): -12.62, -47.48, -60.17(2:1:1, *trans*), -13.28, -47.67, -60.46 (2:1:1, *cis*). MS (EI,  $m/z$ , %): 473 ( $\text{M}^+$ -Me, 10), 393 (M-Me-Br, 100). Anal. Calc. for  $\text{C}_{11}\text{H}_{20}\text{Br}_2\text{Si}_4\text{O}_4$  (488.2): C, 27.04; H, 4.10%. Found: C, 27.18; H, 4.01%.  $^1\text{H}$  and  $^{29}\text{Si}$  NMR spectra of **12** are shown in Figure S2.



**Figure S2.**  $^1\text{H}$  and  $^{29}\text{Si}$  NMR spectra of **12** measured in  $\text{CDCl}_3$  at room temperature.

Preparation of **7**: To a solution of 1.0 g (1.8 mmol) of **5** in 4 mL of carbon tetrachloride 1.2 g (7.5 mmol) of bromine was added, and the solution was stirred at room temperature for 4 h. The volatile species were removed by vacuum evaporation at room temperature and then at 60 °C. The liquid residue, which contained **6**, was mixed with 0.54 g (6.8 mmol) of pyridine in 50 mL of diethyl ether. 1.0 g (2.7 mmol) of **1** was separately dissolved in 50 mL of diethyl ether. These two solutions were simultaneously added to a Schlenk flask containing 300 mL of diethyl ether under nitrogen at room temperature over a period of 5 h with vigorous stirring. The resulting mixture was then stirred for 16 h. The solvent was removed by vacuum evaporation, and the crude product was extracted with 80 mL of pentane. After removing the pentane and purification by column chromatography (silica gel, diethyl ether/hexane 1:6), a colorless liquid was obtained. Yield: 19% starting from **5**.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 7.65 (m, 4H, Ph), 7.57 (d, 2H, Ph), 7.42-7.35 (m, 9H, Ph), 0.16-0.08 (m, 30H,  $\text{Me}_2\text{Si}$ ), -0.03 (s, 3H, MeSi).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 136.3, 136.2, 135.1, 134.5, 134.4, 133.9, 129.9, 129.8, 127.8, 127.7, 1.27,

1.08, 1.03, 0.90, 0.72, -2.57.  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): -19.49, -19.83, -20.49, -20.56, -21.32, -48.33, -66.65, -80.52. MS (EI,  $m/z$ , %): 749( $\text{M}^+$ -Me, 12), 734( $\text{M}^+$ -2Me, 8), 661( $\text{M}^+$ -SiMe<sub>2</sub>-3Me, 100). Anal. Calc. for  $\text{C}_{29}\text{H}_{48}\text{Si}_8\text{O}_9$  (764.7): C, 45.51; H, 6.28%. Found: C, 45.22; H, 6.13%. The  $^{29}\text{Si}$  NMR spectra of **7**, **8** and **9** are shown in Figure S3.



**Figure S3.**  $^{29}\text{Si}$  NMR spectra of the bicyclosiloxane compounds **9** (a), **8** (b) and **7** (c) measured in  $\text{CDCl}_3$  at room temperature.

Preparation of **8** and **9**: 2.0 mmol (1.0 g) of **12** (mixture of *cis* and *trans* isomers) mixed with 6.6 mmol (0.52 g) of pyridine in 50 mL of diethyl ether and 3.2 mmol of siloxanediol (0.69 g of  $\text{Ph}_2\text{Si}(\text{OH})_2$  for **8** and 1.17 g of **10** for **9**) also in 50 mL of diethyl ether were added simultaneously to a Schlenk flask containing 300 mL of diethyl ether under nitrogen at room temperature over a period of 5 h with vigorous stirring. The resulting mixture was then stirred for 16 h. The solvent was removed by vacuum evaporation, and the crude product was extracted with 80 mL of pentane. The pentane was evaporated and the residue was purified by column chromatography (silica gel, diethyl ether/hexane 1:6).

**8**: Yield : 97% from *cis*-isomer. Colorless solid. Mp. 130-132 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 7.75 (d, 2H, Ph), 7.69 (d, 4H, Ph), 7.44-7.35 (m, 9H, Ph), 0.31 (s, 3 H, MeSi), 0.21 (s, 6H, Me<sub>2</sub>Si), -0.10 (s, 6H, Me<sub>2</sub>Si).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 135.0, 134.5, 134.4, 134.3, 130.8, 130.4, 128.0, 127.9, 0.90, 0.32, -4.1.  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): -12.65, -41.35, -57.57, -72.39 (2:1:1:1). MS (CI, gas  $\text{CH}_4$ ,  $m/z$ , %): 527 ( $\text{M}^+$ -Me, 45), 465 ( $\text{M}^+$ -Ph, 100). Anal. Calc. for  $\text{C}_{23}\text{H}_{30}\text{Si}_5\text{O}_6$  (542.3): C, 50.88; H, 5.53%. Found: C, 50.60; H, 5.45%.

**9**: Yield : 97% from *cis*-isomer. Colorless liquid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 7.60 (t, 6H, Ph), 7.40-7.33 (m, 9H, Ph), 0.13 (s, 12 H, Me<sub>2</sub>Si), 0.10 (s, 3H, MeSi), 0.09 (s, 6H,

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Me<sub>2</sub>Si), 0.05 (s, 6H, Me<sub>2</sub>Si). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ): 136.1, 134.5, 134.4, 134.3, 134.0, 130.1, 130.0, 127.9, 127.8, 1.10, 0.90, 0.69, -2.93. <sup>29</sup>Si NMR (CDCl<sub>3</sub>, δ): -17.09, -19.54, -20.12, -48.42, -63.94, -78.36 (2:1:1:1:1:1). MS (CI, gas CH<sub>4</sub>, *m/z*, %): 675 (M<sup>+</sup>-Me, 82), 613 (M<sup>+</sup>-Ph, 100), 525 (M<sup>+</sup>-Ph-SiMe<sub>2</sub>-2Me, 16), 463 (M<sup>+</sup>-2Ph-SiMe<sub>2</sub>-Me, 25). MS (CI, gas NH<sub>3</sub>, *m/z*, %): 708 (M<sup>+</sup>+NH<sub>4</sub><sup>+</sup>, 100), 675 (M<sup>+</sup>-Me, 18), 630 (M<sup>+</sup>-4Me, 30), 613 (M<sup>+</sup>-Ph, 85), 525 (M<sup>+</sup>-Ph-SiMe<sub>2</sub>-2Me, 5), 463 (M<sup>+</sup>-2Ph-SiMe<sub>2</sub>-Me, 4). Anal. Calc. for C<sub>27</sub>H<sub>42</sub>Si<sub>7</sub>O<sub>8</sub> (690.6): C, 46.92; H, 6.08%. Found: C, 46.51; H, 5.96%.

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<sup>1</sup> J. Beckmann, D. Dakternieks, A. Duthie, R. C. Foitzik, *Silicon Chem.* 2003, 2, 27.

<sup>2</sup> D. D. Perrin, W. L. F. Armarego, D. R. Perrin, *Purification of Laboratory Chemicals*, 2<sup>nd</sup> ed., Pergamon Press, Oxford, 1980.