

## Supplementary Experimental Details

### **Rapid and efficient entry to vinylsilanes from aldehydes via a novel metalation-Peterson sequence**

**James McNulty and Priyabrata Das**

**Department of Chemistry, McMaster University,  
Hamilton, Ontario, Canada, L8S 4M1**

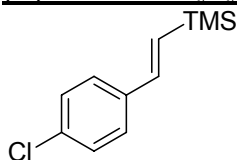
#### **General:**

Reactions were carried out under an Argon atmosphere in oven-dried glassware. All fine chemicals were obtained from Aldrich. THF was distilled from sodium metal with benzophenone indicator. Dichloromethane and ethyl acetate were distilled over calcium hydride.

CIMS were run on a Micromass Quattro Ultima spectrometer fitted with a direct injection probe (DIP) with ionization energy set at 70 eV and HRMS (CI) were performed with a Micromass Q-ToF Ultima spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker 500 or AV 700 spectrometer in  $\text{CDCl}_3$  with TMS as internal standard, chemical shifts ( $\delta$ ) are reported in ppm downfield of TMS and coupling constants ( $J$ ) are expressed in Hz. The (*E*) to (*Z*) ratios were determined from the relative integration of the  $^1\text{H}$ -NMR

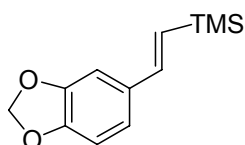
spectra for the olefinic protons in comparison to literature data. For new compounds, spectral data is reported for the major isomer.

**(E)-4-Chlorostyryl-trimethylsilane (Table 1, entry 1):**



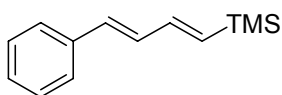
Into a flame-dried flask, containing a magnetic stirring bar, was weighed bis(trimethylsilyl)chloromethane (89.4 mg, 0.459 mmol) under argon and dry THF (0.918 mL) was added to make a 0.5 M solution. The flask was stirred for 15 min. at -78 °C whereupon sec-BuLi (426µL, 0.596 mmol, 1.4M stock, C<sub>6</sub>H<sub>12</sub>) was added slowly. After 40 mins, a 0.5 M solution (in THF) of 4-chlorobenzaldehyde (77.4 mg, 0.551 mmol) was added slowly to the reaction flask maintained at -78 °C. The flask was kept at -78 °C for 2 hrs and then slowly warmed to room temperature where it was stirred for a further 2 hr. The resulting mixture was concentrated to remove solvent. Water was added (5 mL) to the residue, and the resulting mixture was extracted with dichloromethane (3 x 15 mL). The combined organic layers were dried over MgSO<sub>4</sub>, filtered, and concentrated. Purification (silica gel column chromatography, eluted with 10% ethyl acetate in hexane) yielded the title compound, 87mg, (90%) as colorless viscous oil. The spectral data was identical to that reported.<sup>1</sup>

**(E)-4-(3',4'-Methylenedioxy)styryltrimethylsilane (Table 1, entry 2):**



Into a flame-dried flask, containing a magnetic stirring bar, was weighed bis(trimethylsilyl)chloromethane (89.4 mg, 0.459 mmol) under argon and dry THF (918 $\mu$ L) added to make a 0.5 M solution. The flask was stirred for 15 min. at -78 °C whereupon *s*-BuLi (426 $\mu$ L, 0.596 mmol, 1.4M stock, C<sub>6</sub>H<sub>12</sub>) was added slowly. After 40 mins, a 0.5 M solution (in THF) of piperonal (82.7 mg, 0.551 mmol) was added slowly to the reaction flask at -78°C. The flask was kept at -78 °C for 2 hrs and then slowly warmed to room temperature where it was stirred for a further 2 hr. Work-up and purification as before gave the title compound, 96mg, (95%) as off-white viscous oil. The spectral data was identical to that reported.<sup>2</sup>

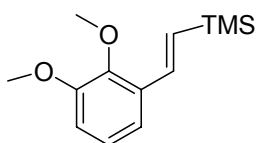
**(1E, 3E)-4-phenyl-1-trimethylsilyl-1,3-butadiene (Table 1, entry 3):**



Into a flame-dried flask, containing a magnetic stirring bar, was weighed bis(trimethylsilyl)chloromethane (89.4 mg, 0.459 mmol) under argon and dry THF (918 $\mu$ L) added to make a 0.5 M solution. The flask was stirred for 15 min. at -78 °C whereupon *sec*-BuLi (426 $\mu$ L, 0.596 mmol, 1.4M stock, C<sub>6</sub>H<sub>12</sub>) was added slowly. After 40 mins, a 0.5 M solution (in THF) of *trans*-cinnamaldehyde (69.5 $\mu$ L, 0.551 mmol) was added slowly to the reaction flask at -78°C. The flask was kept at -78 °C for 2 hrs and then slowly warmed to room temperature where it was stirred for a further 2 hr. The

resulting mixture was concentrated to remove solvent. Water was added (5 mL) to the residue, and the resulting mixture was extracted with dichloromethane (3 x 15 mL). Work-up and purification as before gave the title compound, 75.2 mg, (81%) as semisolid. The spectral data was identical to that reported.<sup>3</sup>

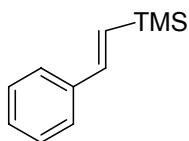
**(E)-2,3-Dimethoxystyryltrimethylsilane (Table 1, entry 4):**



Into a flame-dried flask, containing a magnetic stirring bar, was weighed bis(trimethylsilyl)chloromethane (89.4 mg, 0.459 mmol) under argon and dry THF (918 $\mu$ L) added to make a 0.5 M solution. The flask was stirred for 15 min. at -78 °C whereupon sec-BuLi (426 $\mu$ L, 0.596 mmol, 1.4M stock, C<sub>6</sub>H<sub>12</sub>) was added slowly. After 40 mins, a 0.5 M solution (in THF) of 2,3-dimethoxybenzaldehyde (91.6mg, 0.551 mmol) was added slowly to the reaction flask at -78°C. The flask was kept at -78 °C for 2 hrs and then slowly warmed to room temperature where it was stirred for a further 2 hr. The resulting mixture was concentrated to remove solvent. Work-up and purification as before gave the title compound, 97.6mg, (90%) as a semisolid.

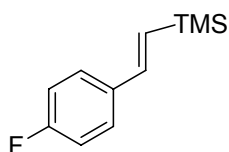
IR (neat): 3050, 2927, 1652, 1573, 1541, 1421, 1264, 1073, 1011, 865, 839, 745 cm<sup>-1</sup>.  
<sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  0.17 (s, 9H); 3.80 (s, 3H), 3.87 (s, 3H), 6.47 (d, J=19.4 Hz, 1H); 6.81 (d, J=9.4 Hz, 1H); 7.02 (t, J=8.01 Hz, 1H); 7.17 (d, J=9.4 Hz, 1H); 7.25 (d, J=19.4 Hz, 1H). <sup>13</sup>C-NMR (50 MHz, CDCl<sub>3</sub>):  $\delta$  -1.1; 55.9; 61.1; 111.7; 117.8; 124.0; 131.1; 132.7; 137.5; 146.5; 152.5. HRMS (M)<sup>+</sup> calcd. for C<sub>13</sub>H<sub>20</sub>O<sub>2</sub>Si: 236.1249, found: 236.1233.

**(E)-Styryltrimethylsilane (Table 1, entry 5):**



Into a flame-dried flask, containing a magnetic stirring bar, was weighed bis(trimethylsilyl)chloromethane (89.4 mg, 0.459 mmol) under argon and dry THF (918 $\mu$ L) added to make a 0.5 M solution. The flask was stirred for 15 min. at -78 °C whereupon sec-BuLi (426 $\mu$ L, 0.596 mmol, 1.4M stock, C<sub>6</sub>H<sub>12</sub>) was added slowly. After 40 mins, a 0.5 M solution (in THF) of benzaldehyde (56 $\mu$ L, 0.551 mmol) was added slowly to the reaction flask at -78°C. The flask was kept at -78 °C for 2 hrs and then slowly warmed to room temperature where it was stirred for a further 2 hr. The resulting mixture was concentrated to remove solvent. Work-up and purification as before yielded the title compound, 75.78mg, (80%) as colorless viscous oil. The spectral data was identical to that reported.<sup>4</sup>

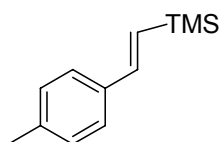
**(E)-4-Fluorostyryltrimethylsilane (Table 1, entry 6):**



Into a flame-dried flask, containing a magnetic stirring bar, was weighed bis(trimethylsilyl)chloromethane (89.4 mg, 0.459 mmol) under argon and dry THF (918 $\mu$ L) added to make a 0.5 M solution. The flask was stirred for 15 min. at -78 °C whereupon sec-BuLi (426 $\mu$ L, 0.596 mmol, 1.4M stock, C<sub>6</sub>H<sub>12</sub>) was added slowly. After 40 mins, a 0.5 M solution (in THF) of 4-fluorobenzaldehyde (59.1 $\mu$ L, 0.551 mmol) was

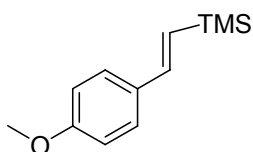
added slowly to the reaction flask at  $-78^{\circ}\text{C}$ . The flask was kept at  $-78^{\circ}\text{C}$  for 2 hrs and then slowly warmed to room temperature where it was stirred for a further 2 hr. The resulting mixture was concentrated to remove solvent. Work-up and purification as before yielded the title compound, 75.76mg, (85%) as viscous oil. The spectral data was identical to that reported.<sup>4</sup>

**(E)-4-Methylstyryltrimethylsilane (Table 1, entry 7):**



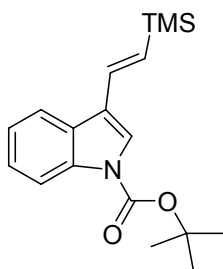
Into a flame-dried flask, containing a magnetic stirring bar, was weighed bis(trimethylsilyl)chloromethane (89.4 mg, 0.459 mmol) under argon and dry THF (918 $\mu\text{L}$ ) added to make a 0.5 M solution. The flask was stirred for 15 min. at  $-78^{\circ}\text{C}$  whereupon sec-BuLi (426 $\mu\text{L}$ , 0.596 mmol, 1.4M stock,  $\text{C}_6\text{H}_{12}$ ) was added slowly. After 40 mins, a 0.5 M solution (in THF) of 4-methylbenzaldehyde (65 $\mu\text{L}$ , 0.551 mmol) was added slowly to the reaction flask at  $-78^{\circ}\text{C}$ . The flask was kept at  $-78^{\circ}\text{C}$  for 2 hrs and then slowly warmed to room temperature where it was stirred for a further 2 hr. The resulting mixture was concentrated to remove solvent. Work-up and purification as before yielded the title compound, 75.96mg, (87%) as viscous oil. The spectral data was identical to that reported.<sup>4</sup>

**(E)-4-Methoxystyryltrimethylsilane (Table 1, entry 8):**



Into a flame-dried flask, containing a magnetic stirring bar, was weighed bis(trimethylsilyl)chloromethane (89.4 mg, 0.459 mmol) under argon and dry THF (918 $\mu$ L) added to make a 0.5 M solution. The flask was stirred for 15 min. at -78 °C whereupon sec-BuLi (426 $\mu$ L, 0.596 mmol, 1.4M stock, C<sub>6</sub>H<sub>12</sub>) was added slowly. After 40 mins, a 0.5 M solution (in THF) of 4-methoxybenzaldehyde (67 $\mu$ L, 0.551 mmol) was added slowly to the reaction flask at -78°C. The flask was kept at -78 °C for 2 hrs and then slowly warmed to room temperature where it was stirred for a further 2 hr. The resulting mixture was concentrated to remove solvent. Work-up and purification as before yielded the title compound, 88.03mg, (93%) as viscous oil. The spectral data was identical to that reported.<sup>2</sup>

**(E)-3-(2'-(trimethylsilyl)vinyl)-N-(tertbutoxycarbonyl)-indole (Table 1, entry 9):**

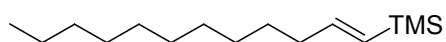


Into a flame-dried flask, containing a magnetic stirring bar, was weighed bis(trimethylsilyl)chloromethane (89.4 mg, 0.459 mmol) under argon and dry THF (918 $\mu$ L) added to make a 0.5 M solution. The flask was stirred for 15 min. at -78 °C

whereupon sec-BuLi (426 $\mu$ L, 0.596 mmol, 1.4M stock, C<sub>6</sub>H<sub>12</sub>) was added slowly. After 40 mins, a 0.5 M solution (in THF) of N-(*t*-butoxycarbonyl)indole-3-carboxaldehyde (119.7 mg, 0.551 mmol) was added slowly to the reaction flask at -78°C. The flask was kept at -78 °C for 2 hrs and then slowly warmed to room temperature where it was stirred for a further 2 hr. The resulting mixture was concentrated to remove solvent. Work-up as before yielded the title compound, 94.06mg, (65%) as yellow semisolid.

IR (neat): 3054, 2958, 2900, 1737, 1651, 1558, 1475, 1453, 1371, 1306, 1257, 1158, 1089, 1021, 983, 864, 841, 746 cm<sup>-1</sup>. <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  0.18 (s, 9H); 1.67 (s, 9H); 6.52 (d, J=19.3 Hz, 1H); 7.01 (d, J=19.3 Hz, 1H); 7.21-7.41 (m, 2H); 7.66 (s, 1H); 7.89 (d, J= 7.96 Hz, 1H); 8.18 (d, J= 7.96 Hz, 1H). <sup>13</sup>C-NMR (50 MHz, CDCl<sub>3</sub>):  $\delta$  - 1.12; 19.7; 84.5; 115.5; 120.2; 120.7; 123.1; 124.3; 124.8; 128.9; 130.2; 135.1; 136.3; 149.8. HRMS (M)<sup>+</sup> calcd. for C<sub>18</sub>H<sub>25</sub>NO<sub>2</sub>Si 315.1664, found: 315.1655.

**(E)-1-Dodecenyltrimethylsilane (Table 1, entry 10):**



Into a flame-dried flask, containing a magnetic stirring bar, was weighed bis(trimethylsilyl)chloromethane (89.4 mg, 0.459 mmol) under argon and dry THF (918 $\mu$ L) added to make a 0.5 M solution. The flask was stirred for 15 min. at -78 °C whereupon sec-BuLi (426 $\mu$ L, 0.596 mmol, 1.4M stock, C<sub>6</sub>H<sub>12</sub>) was added slowly. After 40 mins, a 0.5 M solution (in THF) of undecanal (113.7 $\mu$ L, 0.551 mmol) was added slowly to the reaction flask at -78°C. The flask was kept at -78 °C for 2 hrs and then slowly warmed to room temperature where it was stirred for a further 2 hr. The resulting mixture was concentrated to remove solvent. Work-up as before yielded the title



compound, 84.94mg, (77%) as colorless oil. The spectral data was identical to that reported.<sup>5</sup>

References:

1. T. Nakano, T. Miyamoto, T. Endoh, M. Shimotani, N. Ashida, T. Morioka and Y. Takahashi, *Applied Organometallic Chemistry*, 2004, **18**, 65.
2. N. Zhi-Jie, Y. Pin-Fan, N. P. K. Dennis, T. Yih-Ling and L. Tien-Yau, *J. Am. Chem. Soc.*, 1990, **112**, 9356.
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