Supporting Information
for
**“Palladium-catalyzed Silylations of Hydrosilanes with Aryl
Halides Using Bulky Alkyl Phosphine”**

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Supporting Information

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Experimental procedure for the large scale preparation of 5. To a solution of Pd(*t*-Bu₃P)₂ (0.10 g, 0.2 mmol) and K₃PO₄ (12.7 g, 60 mmol) in dry and degassed NMP (40 mL), trialkylsilane (3.8 mL, 24 mmol) and 4-iodo-*N,N*-dimethylaniline (4.94 g, 20 mmol) were added under a nitrogen atmosphere. After stirring for 5 h at room temperature, the reaction mixture was quenched with water, extracted with CH₂Cl₂ three times, and dried over Na₂SO₄. The solvent was evaporated under reduced pressure, and column chromatography on silica gel (Eluent: hexane/EtOAc = 10/1) afforded the spectroscopically pure silylated product. The analytical pure sample **5** was obtained by distillation as colorless oil (3.45 g 73%).

(4-methoxyphenyl)triethylsilane (1).^{1,2} Eluent for chromatography: hexane/EtOAc = 20/1. Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.43–7.40 (m, 2H), 6.92–6.89 (m, 2H), 3.80 (s, 3H), 0.96 (t, 3H, *J* = 7.4 Hz), 0.78 (q, 2H, *J* = 7.4 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 160.2 (C_q), 135.6 (CH), 130.5 (CH), 21.4 (CH), 7.5 (CH₃), 3.4 (CH₂); EI-MS *m/z* 222 (M⁺).

(4-methoxyphenyl)triphenylsilane (2).^{1,3-5} Eluent for chromatography: hexane/EtOAc = 20/1. Colorless solid. ¹H NMR (500 MHz, CDCl₃) δ 7.53 (dd, *J* = 8.1, 1.5 Hz, 6H), 7.49 (d, *J* = 8.6 Hz, 2H), 7.44–7.35 (m, 9H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 160.9 (C_q), 137.9 (CH), 136.4 (CH), 134.7 (C_q), 129.5 (CH), 127.8 (CH), 124.9 (C_q), 113.7 (CH), 55.0 (CH₃); EI-MS *m/z* 366 (M⁺).

(4-methoxyphenyl)dimethylphenylsilane (3).^{1,6} Eluent for chromatography: hexane. Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.52–7.50 (m, 2H), 7.45 (d, *J* = 8.6 Hz, 2H), 7.36–7.32 (m, 3H), 6.91 (d, *J* = 8.6 Hz, 2H), 3.81 (s, 3H), 0.96 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 160.5 (C_q), 138.6 (C_q), 135.6 (CH₂), 134.1 (CH₂), 129.2 (CH₂), 129.0 (C_q), 127.7 (CH₂), 113.6 (CH₂), 54.9 (CH₃), -2.2 (CH₃); EI-MS *m/z* 242 (M⁺).

(4-(*N,N*-dimethylaminophenyl))triethylsilane (6). Eluent for chromatography: hexane/EtOAc = 10/1. Colorless oil. Bp. ca. 180 °C/1 mmHg (glass tube oven temperature). ¹H NMR (500 MHz, CDCl₃) δ 7.36 (d, *J* = 8.8 Hz, 2H), 6.73 (d, *J* = 8.6 Hz, 1H), 2.95 (s, 6H), 0.96 (t, 9H, *J* = 7.8 Hz), 0.75 (q, 6H, *J* = 7.8 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 150.8 (C_q), 135.3 (CH₂), 122.4 (C_q), 111.9 (CH), 40.2 (CH₃), 7.5 (CH₃), 3.7 (CH₂); EI-MS *m/z* 235 (M⁺). Anal. Calcd for C₁₄H₂₅NSi: C, 71.42; H, 10.70; N, 5.95. Found: C, 71.29; H, 10.71; N, 5.78.

(4-(*N,N*-dimethylaminophenyl))triphenylsilane (7).^{2,5,6-8} Eluent for chromatography: hexane/EtOAc = 10/1. Colorless solid. ¹H NMR (500 MHz, CDCl₃) δ 7.57 (dd, *J* = 8.1, 1.5 Hz, 6H), 7.42–7.33 (m, 11H), 6.73 (d, *J* = 8.8 Hz, 2H), 2.97 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 160.9 (C_q), 137.6 (CH), 136.4 (CH), 134.7 (C_q), 129.3 (CH), 127.9 (CH), 118.6 (C_q), 111.8 (CH), 40.1 (CH₃); EI-MS *m/z* 379 (M⁺).

(4-ethylphenyl)triethylsilane (8). Eluent for chromatography: hexane. Colorless oil. Bp. ca. 180 °C/1 mmHg (glass tube oven temperature). ¹H NMR (500 MHz, CDCl₃) δ 7.41 (d, *J* = 7.8 Hz, 2H), 7.19 (d, *J* = 7.1 Hz, 2H), 2.65 (q, *J* = 7.7 Hz, 2H), 1.25 (t, *J* = 7.6 Hz, 3H), 0.96 (t, 3H, *J* = 7.8 Hz), 0.78 (q, 2H, *J* = 7.9 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 144.7 (C_q), 134.3 (CH), 134.1 (C_q), 127.3 (CH), 28.8 (CH₂), 15.3 (CH₃), 7.4 (CH₃), 3.5 (CH₂); EI-MS *m/z* 220 (M⁺). Anal. Calcd for C₁₄H₂₄Si: C, 76.28; H, 10.97. Found: C, 76.17; H, 10.99.

(4-ethylphenyl)triphenylsilane (9). Eluent for chromatography: hexane. Colorless solid. Mp. 118.0–119.0 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.57 (dd, *J* = 8.1, 1.5 Hz, 6H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.44–7.35 (m, 9H), 7.22 (d, *J* = 8.1 Hz, 2H), 2.67 (q, *J* = 7.7 Hz, 2H), 1.25 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 145.8 (C_q), 136.5 (CH), 136.4 (CH), 134.5 (C_q), 130.8 (C_q), 129.5 (CH), 127.8 (CH), 127.5 (CH), 28.9 (CH₂), 15.3 (CH₃); EI-MS *m/z* 364 (M⁺). Anal. Calcd for C₂₆H₂₄Si: C, 85.66; H, 6.64. Found: C, 85.45; H, 6.83.

(3,5-dimethylphenyl)triethylsilane (10). Eluent for chromatography: hexane. Colorless oil. Bp. ca. 180 °C/1 mmHg (glass tube oven temperature). ¹H NMR (500 MHz, CDCl₃) δ 7.09 (s, 2H), 6.99 (s, 1H), 2.31 (s, 6H), 0.96 (t, 9H, *J* = 7.8 Hz), 0.77 (q, 6H, *J* = 7.9 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 137.2 (C_q), 136.8 (C_q), 131.9 (CH), 128.1 (C_q), 113.5 (CH), 54.9 (CH₃), 7.4 (CH₃), 3.5 (CH₂); EI-MS

m/z 220 (M^+). Anal. Calcd for $C_{14}H_{24}Si$: C, 76.28; H, 10.97. Found: C, 76.04; H, 10.95.

References

- (1) Bott, R. W.; Eaborn, C.; Jackson, P. M. *J. Organomet. Chem.* **1967**, 7, 79.
- (2) Gilman, H.; Benkeser, R. A.; Dunn, G. E. *J. Am. Chem. Soc.* **1950**, 72, 1689.
- (3) Eaborn, C.; Eidenschink, R.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1975**, 388.
- (4) Gilman, H. Brook, A. G.; Miller, L. S. *J. Am. Chem. Soc.* **1953**, 75, 4531.
- (5) Gilman, H. Marshall, F. J. *J. Am. Chem. Soc.* **1949**, 71, 2066.
- (6) van Walree, C. A.; Lauteslager, X. Y.; van Wageningen, A. M. A.; Zwikker, J. W.; Jenneskens, L. W. *J. Organomet. Chem.* **1995**, 496, 117.
- (6) Schiemenz, G. P. *Tetrahedron* **1971**, 27, 5723.
- (7) Gilman, H.; Plunkett, M. A.; Dunn, G. E. *J. Am. Chem. Soc.* **1951**, 73, 1686.
- (8) Sunthankar, S. V.; Gilman, H. *J. Org. Chem.* **1950**, 15, 1200.

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