Synthesis of Optically Pure Aryl Silyl Carbinols and Their Use as Chiral Auxiliaries in Oxacarbenium Ion Reactions

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General Experimental Details. Unless otherwise noted, all air and moisture-sensitive reactions were carried out in flame-dried or oven-dried glassware using magnetic stirring under a positive pressure of argon. Unless specifically stated, all reagents were commercially obtained and where appropriate, purified prior to use. Flash column chromatography was performed using 230–400 mesh silica gel. The reaction solvents tetrahydrofuran (THF), methylene chloride (CH_2Cl_2), diethyl ether (Et_2O) and toluene (PhMe) were dried by filtration through alumina according to the method described by Grubbs.[1] Benzene was distilled from CaH_2 at atmospheric pressure under nitrogen. Concentrations *c* associated with optical rotations are reported in g/100 mL. ^{1}H

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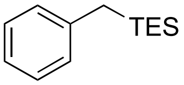
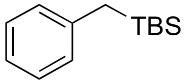
[1] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics,* **1997,** 1571.

NMR spectra were obtained at 400 or 500 MHz while ^{13}C spectra were obtained at 125 MHz, recorded in ppm, and referenced to residual solvent. Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), integration and coupling constant(s) in Hertz (Hz). Multiplets (m) are reported over the range (ppm) at which they appear at the indicated field strength.

General procedure for preparation of arylsilanes: Mg powder (40–80 mesh, 1.1 equiv) was washed three times with Et_2O, dried *in vacuo*, and then stirred vigorously for 24 h prior to the addition of sufficient THF to make a 0.8 M solution of aryl halide. The suspension was cooled to 0 °C and the aryl halide (1.0 equiv) was added as a single portion. After 1 h the mixture was allowed to warm to ambient temperature and was maintained for l h. The mixture was then heated to reflux and the indicated chlorosilane (1.4 equiv) was added dropwise. After 12 h, the mixture was cooled to 0 °C and the reaction was quenched with saturated aqueous NH_4Cl. The mixture was allowed to warm to ambient temperature, concentrated *in vacuo*, then taken up in Et_2O and washed three times with brine. The combined aqueous phases were extracted twice with Et_2O and the combined organic layers were dried over $MgSO_4$ then concentrated *in vacuo*. Purification by flash chromatography afforded the title compounds.



Benzyltriethylsilane (8a).[2] The general procedure above was applied to 4.8 mL (42 mmol) of benzyl chloride and 9.9 mL (59 mmol) of TESCl. Flash chromatography (2% Et_2O/petroleum ether) afforded 6.90 g (80%) of **8a** as a slightly yellow oil: IR (neat) 3050, 2953, 1493, 1013, 769 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.21 (t, J = 7.6, 2H), 7.08–7.02 (m, 3H), 2.11 (s, 2H), 0.93, (t, J = 7.9, 9H), 0.52 (q, J = 7.9, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.6, 128.1, 128.1, 123.7, 21.6, 7.3, 3.0; HRMS (CI/NH_3) m / z calcd for $C_{13}H_{22}Si$ $[M]^+$ 206.1491, found 206.1488.



Benzyl-*tert*-butyldimethylsilane (8b).[3] The general procedure above was applied to 5.6 mL (48 mmol) of benzyl chloride and 9.49 g (63.0 mmol) of TBSCl. Flash chromatography (5% CH_2Cl_2/petroleum ether) afforded 9.11 g (91%) of **8b** as a colorless oil: IR (neat) 3025, 2928, 1493, 1429, 830 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.23–7.20 (m, 2H), 7.09–7.06 (m, 1H), 7.03–7.01 (m, 2H), 2.10 (s, 2H), 0.92 (s, 9H), –0.10 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.9, 128.5, 128.3, 124.0, 26.8, 22.8, 17.0, –6.4; HRMS (CI/NH_3) m / z calcd for $C_{13}H_{22}Si$ $[M]^+$ 206.1491, found 206.1493.

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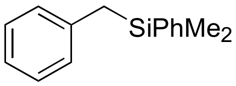
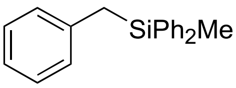
[2] Gilman, H.; Ingham, R. K.; Smith, A. G. *J. Org. Chem.* **1953,** *18,* 1743.

[3] Arnauld, T.; Barrett, A. G. M.; Hopkins, B. T. *Tetrahedron Lett.* **2002,** *43,* 1081.



Benzyldimethylphenylsilane (8c).[4] The general procedure above was applied to 4.6 mL (40 mmol) of benzyl chloride and 10.5 mL (51.7 mmol) of $SiPhMe_2Cl$. Flash chromatography (5% CH_2Cl_2/hexanes) afforded **8c** as a colorless oil, which contained an unidentified impurity. The product was used in impure form: ^1H NMR (400 MHz, $CDCl_3$) δ 7.49–7.47 (m, 2H), 7.39–7.34 (m, 3H), 7.20 (t, *J* = 8.0, 2H), 7.08 (t, *J* = 7.3, 1H), 6.95 (d, *J* = 7.6, 2H) 2.32 (s, 2H), 0.26 (s, 6H).



Benzyldiphenylmethylsilane (8d).[4] The general procedure above was applied to 1.2 mL (10 mmol) of benzyl chloride and 2.5 mL (11 mmol) of $SiPh_2MeCl$. Flash chromatography (10% CH_2Cl_2/hexanes) afforded 9.11 g (91%) of **8d** as a white solid: mp = 67–68 °C; IR (neat) 3051, 2955, 1598, 1426, 1108, 774 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.48–7.46 (m, 4H), 7.41–7.33 (m, 6H), 7.14–7.12 (m, 2H), 7.07–7.04 (m, 1H), 6.88 (d, *J* = 7.0, 2H), 2.63 (s, 2H), 0.48 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.1, 136.6, 134.9, 129.5, 128.9, 128.3, 128.0, 124.5, 24.6, –4.6; HRMS (CI/NH_3) *m / z* calcd for $C_{20}H_{20}Si$ $[M]^+$ 288.1334, found 288.1334.

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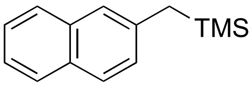
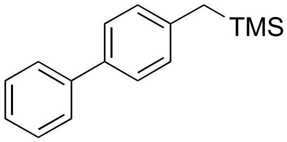
[4] Brook, A.G.; Quigley, M. A.; Peddle, G. J. D.; Schwartz, N. V.; Warner, C. M. *J. Am. Chem. Soc.* **1960,** *82,* 5102.



2-Naphthyltrimethylsilane (8e).[5] Mg (0.85 g, 35 mmol) was prepared as described in the general procedure. THF (21 mL) was added and the mixture cooled to 0 °C. TMSCl (5.7 mL, 44. mmol) was added as a single portion and the mixture was maintained for 15 min. 2-Naphthylbromide (7.00 g, 31.7 mmol) was dissolved in THF (56 mL) and added dropwise *via* syringe pump. The mixture was maintained for 5 h, and then it was allowed to warm to ambient temperature and maintained for 12 h. The mixture was then cooled to 0 °C and the reaction was quenched and worked up as described in the general procedure. Flash chromatography (2% Et_2O/petroleum ether) afforded 6.10 g (90%) of **8e** as a white solid: mp = 56–58 °C; IR (neat) 3050, 2953, 1246, 848, 769 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3, 1H), 7.72 (t, *J* = 9.0, 2H), 7.44–7.41 (m , 2H), 7.39–7.36 (m, 1H), 7.17 (dd, *J* = 8.3, 1.72, 1H), 2.26 (s, 2H), 0.03 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.7, 134.3, 131.4, 128.4, 128.0, 127.9, 127.4, 126.2, 125.6, 124.8, 27.8, –1.4; HRMS (EI/isobutane) *m / z* calcd for $C_{14}H_{18}Si$ $[M]^+$ 214.1178, found 214.1185.



4-Phenylbenzyltrimethylsilane (8f).[6] Mg (6.35 g, 261 mmol) was prepared as described in the general procedure. THF (31 mL) was added and the mixture was cooled to 0 °C. TMSCl (9.5 mL, 73 mmol) was added as a single portion and the mixture was maintained for 15 min. 4-Phenylbenzylbromide (12.91 g, 52.25 mmol) was dissolved in THF (100

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[5] Bock, H.; Alt, H; Seidl, H. *J. Am. Chem. Soc.* **1969,** *91,* 355.

[6] Hayashi, T.; Katsuro, Y,; Okamoto, Y.; Kumada, M. *Tetrahedron Lett.* **1981,** *22,* 4449.

mL) and added dropwise *via* addition funnel. The mixture was maintained for 10 h, and then it was allowed to warm to ambient temperature and maintained for 12 h. The mixture was then cooled to 0 °C and the reaction was quenched and worked up as described in the general procedure. Flash chromatography (8% CH_2Cl_2/hexanes) followed by recrystallization from MeOH afforded 5.97 g (48%) of **8f** as a white solid: mp = 46–47 °C; IR (KBr) 3030, 2955, 1406, 1247, 851, cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60–7.58 (m, 2H), 7.47–7.46 (m, 2H), 7.44–7.41 (m, 2H), 7.32–7.30 (m, 1H), 7.07 (d, *J* = 8.0, 2H), 2.13 (s, 2H), 0.03 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.4, 140.0, 136.9, 128.9, 128.6, 127.0, 127.0, 126.9, 27.0, –1.6; HRMS (CI/NH_3) *m / z* calcd for $C_{16}H_{20}Si$ $[M]^+$ 240.1334, found 240.1335.

General procedure for preparation of α,α-dibromoarylsilanes: The general procedure established by Brook was followed.[7] To a 0.2 M solution of arylsilane **8** (1.0 equiv) in benzene, was added NBS (2.1 equiv) and AIBN (0.05 equiv). The mixture was heated to reflux and maintained for 24 h. The mixture was then allowed to cool to ambient temperature, filtered through a plug of glass wool and concentrated *in vacuo*. The resulting residue was taken up in CH_2Cl_2 and washed once with saturated aqueous $Na_2S_2O_3$ then three times with brine. The combined aqueous phases were extracted twice with CH_2Cl_2 and the combined organic layers were dried over $MgSO_4$ then concentrated *in vacuo*. Purification by flash chromatography afforded the title compounds.

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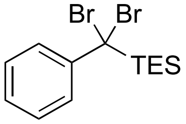
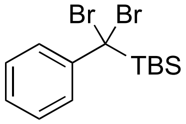
[7] Brook, A. G. *J. Am. Chem. Soc.* **1957,** *79,* 4373.



α,α-Dibromobenzyltriethylsilane (9a).[8] The general procedure above was applied to 10.2 g (49.4 mmol) of **8a** and 17.6 g (98.8 mmol) of NBS with the following changes: carbon tetrachloride was used instead of benzene and benzoyl peroxide was substituted for AIBN. Flash chromatography (2% Et_2O/petroleum ether) of a small amount of the resulting residue afforded 0.14 g of **9a** as a yellow oil. The remainder was used without purification: IR (neat) 3060, 2956, 1460, 1008, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.78–7.74 (m, 2H), 7.34–7.30 (m, 2H), 7.26–7.22 (m, 1H), 0.97 (t, $J = 7.8$, 9H), 0.84 (q, $J = 7.8$, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.5, 128.6, 127.9, 127.7, 66.8, 7.7, 3.6; HRMS (CI/NH_3) m/z calcd for $C_{13}H_{20}Br_2Si$ $[M]^+$ 361.9701, found 361.9689.



α,α-Dibromobenzyl-*tert*-butyldimethylsilane (9b). The general procedure above was applied to 1.10 g (5.33 mmol) of **8b** and 1.99 g (11.2 mmol) of NBS. Flash chromatography (5% CH_2Cl_2/petroleum ether) of a small amount of the resulting residue afforded 0.17 g of **9b** as an orange oil. The remainder was used without purification: IR (neat) 3055, 2933, 1468, 1254, 836 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.84–7.83 (m, 1H), 7.82–7.81 (m, 1H), 7.35–7.30 (m, 2H), 7.25–7.23 (m, 1H), 0.75 (s, 9H), 0.41 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.0, 128.9, 128.1, 128.1, 66.9, 28.1, 19.9, –4.3; HRMS (EI/isobutane) m/z calcd for $C_{12}H_{17}Br_2Si$ $[M – CH_3]^+$ 346.9470, found 346.9471.

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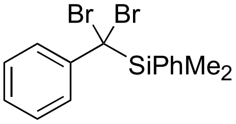
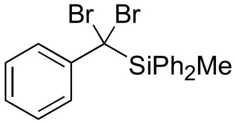
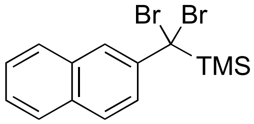
[8] Ando, W.; Sekiguchi, A. *J. Organomet. Chem.* **1977,** *133,* 219.



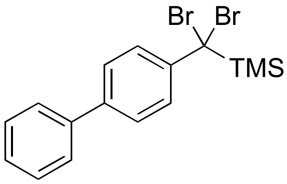
α,α-Dibromobenzyldimethylphenylsilane (9c).[4] The general procedure above was applied to 7.01 g (31.0 mmol) of impure **8c** and 11.6 g (65.0 mmol) of NBS. Flash chromatography (10% CH_2Cl_2/hexanes) followed by recrystallization from absolute ethanol afforded 6.51 g (55%) of **9c** as a white solid: mp = 87–88 °C; IR (KBr) 3055, 2962, 1440, 1248, 1116, 861 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.47–7.44 (m, 2H), 7.42–7.39 (m, 1H), 7.36–7.34 (m, 2H), 7.30–7.28 (m, 2H), 7.22–7.19 (m, 3H), 0.58 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.1, 135.7, 133.4, 130.3, 129.1, 127.9, 127.7, 127.5, 66.2, –3.8; HRMS (EI/isobutane) *m / z* calcd for $C_{15}H_{16}BrSi$ $[M - Br]^+$ 303.0210, found 303.0205.



α,α-Dibromobenzyldiphenylmethylsilane (9d).[4] The general procedure above was applied to 2.20 g (7.73 mmol) of **8d** and 2.85 g (16.0 mmol) of NBS. Flash chromatography (10% CH_2Cl_2/hexanes) afforded 3.11 g (91%) of **9d** as a white solid: mp = 95–96 °C; IR (KBr) 3069, 2995, 1428, 1106, 722 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.60–7.57 (m, 4H), 7.47–7.41 (m, 4H), 7.34–7.30 (m, 4H), 7.22–7.16 (m, 3H), 0.93 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.5, 136.4, 132.8, 130.3, 129.6, 128.2, 127.8, 127.7 63.7, –3.4; HRMS (EI/isobutane) *m / z* calcd for $C_{20}H_{19}BrSi$ $[M - Br + H]^+$ 366.0439, found 366.0440.



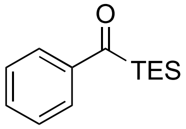
α,α-Dibromo-2-naphthyltrimethylsilane (9e).[5] The general procedure above was applied to 6.10 g (28.5 mmol) of **8e** and 10.6 g (59.7 mmol) of NBS. Flash chromatography (5% Et_2O/hexanes) of a small amount of the resulting residue afforded 0.23 g of **9e** as a white solid. The remainder was used without purification: mp = 89.5–90.5 °C; IR (KBr) 3055, 2960, 1251, 845 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 1.9, 1H), 7.89–7.78 (m, 4H), 7.54–7.50 (m, 2H), 0.28 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.4, 132.8, 132.7, 128.8, 127.7, 127.6, 127.6, 127.0, 126.9, 126.6, 67.7, –2.0; HRMS (EI/isobutane) *m / z* calcd for $C_{14}H_{16}Br_2Si$ $[M]^+$ 369.9388, found 369.9388.



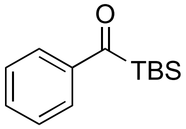
α,α-Dibromo-4-phenylbenzyltrimethylsilane (9f). The general procedure above was applied to 5.97 g (24.8 mmol) of **8f** and 9.29 g (52.2 mmol) of NBS. Flash chromatography (8% CH_2Cl_2/hexanes) of a small amount of the resulting residue afforded 0.19 g of **9f** as a white solid. The remainder was used without purification: mp = 128–130 °C; IR (KBr) 3029, 2961, 1482, 1400, 1248, 1007, 882, 845 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81–7.79 (m, 2H), 7.63–7.61 (m, 2H), 7.57–7.55 (m, 2H), 7.47–7.44 (m, 2H), 7.39–7.36 (m, 1H), 0.28 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ

141.0, 140.7, 140.2, 129.2, 129.1, 127.9, 127.3, 126.6, 67.3, –2.2; HRMS (CI/NH_3) *m / z* calcd for $C_{16}H_{18}Br_2Si$ $[M]^+$ 395.9544, found 395.9549.

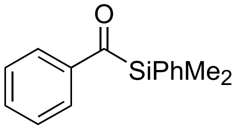
General procedure for preparation of aryl-acylsilanes: The general procedure established by Brook was followed.[7] The α,α-dibromoarylsilane **9** (1.0 equiv) was added to an aluminum foil-wrapped flask and dissolved in H_2O/acetone/EtOH (in a ratio of 1:2:3 by volume) to make a 0.1 M solution. AgOAc (2.0 equiv) was added and the mixture was maintained for 24 h. With protection from light, the mixture was filtered through a plug of glass wool, concentrated *in vacuo*, taken up in petroleum ether and washed three times with brine. The combined aqueous phases were extracted twice with petroleum ether and the combined organic layers were dried over $MgSO_4$ then concentrated *in vacuo*. Purification by flash chromatography afforded the title compounds.



Benzoyltriethylsilane (10a).[8] The general procedure above was applied to 7.16 g (19.7 mmol) of **9a** and 6.56 g (39.3 mmol) of AgOAc. Flash chromatography (5% Et_2O/hexanes) afforded 3.75 g (86% over 2 steps) of **10a** as a bright yellow oil: IR (neat) 3062, 2956, 1613, 1209, 737 861 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.82–7.80 (m, 2H), 7.54–7.52 (m, 1H), 7.49–7.46 (m, 2H), 1.02–0.99 (m, 9H), 0.94–0.89 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 236.3, 142.7, 132.8, 128.9, 127.3, 7.6, 3.9; HRMS (CI/NH_3) *m / z* calcd for $C_{13}H_{20}OSi$ $[M]^+$ 220.1283, found 220.1287.



Benzoyl-*tert*-butyldimethylsilane (10b).[9] The general procedure above was applied to 12.4 g (33.9 mmol) of **9b** and 11.32 g (67.82 mmol) of AgOAc. Flash chromatography (5% CH_2Cl_2/petroleum ether) afforded 7.07 g (95% over 2 steps) of **10b** as a bright yellow oil: IR (neat) 3060, 2931, 1612, 1467, 1208, 809 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.82–7.80 (m, 2H), 7.54–7.51 (m, 1H), 7.48–7.45 (m, 2H), 0.97 (s, 9H), 0.38 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 236.1, 143.0, 132.7, 128.8, 127.8, 27.0, 17.2, –4.5; HRMS (CI/NH_3) *m / z* calcd for $C_{13}H_{21}OSi$ $[M + H]^+$ 221.1361, found 221.1364.



Benzoyldimethylphenylsilane (10c).[4] The general procedure above was applied to 6.51 g (17.0 mmol) of **9c** and 5.66 g (33.9 mmol) of AgOAc. Flash chromatography (6% Et_2O/hexanes) afforded 3.72 g (91%) of **10c** as a bright yellow solid: mp = 55–56 °C; IR (KBr) 3065, 2950, 1604, 1446, 1211, 815 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.77–7.74 (m, 2H), 7.61–7.59 (m, 2H), 7.49–7.46 (m, 1H), 7.43–7.37 (m, 5H), 0.63 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 234.0, 141.5, 135.9, 134.2, 133.0, 130.0, 128.8, 128.5, 128.0, –2.7; HRMS (CI/NH_3) *m / z* calcd for $C_{15}H_{15}OSi$ $[M – H]^+$ 239.0892, found 239.0891.

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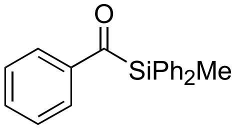
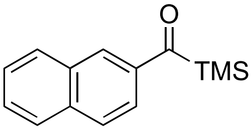
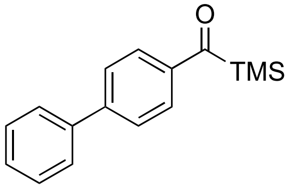
[9] Portella, C.; Dondy, B. *Tetrahedron Lett.* **1991,** *32,* 83.



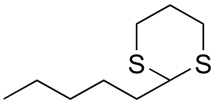
Benzoyldiphenylmethylsilane (10d).[4] The general procedure above was applied to 3.03 g (6.79 mmol) of **9d** and 2.50 g (15.0 mmol) of AgOAc. Flash chromatography (5% Et_2O/hexanes) afforded 1.68 g (84%) of **10d** as a bright yellow solid: mp = 34–35 °C; IR (KBr) 3063, 2955, 1607, 1429, 1212, 1113, 796, 734 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.80–7.78 (m, 2H), 7.63–7.61 (m, 4H), 7.50–7.43 (m, 3H), 7.41–7.35 (m, 6H), 0.90 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 232.2, 141.9, 135.3, 133.9, 133.1, 130.2, 128.7, 128.4, 128.4, –3.1; HRMS (CI/NH_3) *m / z* calcd for $C_{20}H_{18}OSi$ $[M]^+$ 302.1127, found 302.1113.



2-Naphthoyltrimethylsilane (10e).[5] The general procedure above was applied to 10.6 g (28.4 mmol) of **9e** and 9.49 g (56.9 mmol) of AgOAc. Flash chromatography (5% Et_2O/petroleum ether) afforded 5.52 g (85% over 2 steps) of **10e** as a bright yellow oil: IR (neat) 3059, 2961, 1603, 1250, 845 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.37 (s, 1 H), 7.99 (d, J = 7.9, 1H), 7.91–7.87 (m, 3H), 7.62–7.55 (m, 2H), 0.46 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 235.6, 139.0, 135.7, 132.9, 131.0, 129.8, 128.9, 128.6, 128.1, 126.9, 122.6, –0.9; HRMS (CI/NH_3) *m / z* calcd for $C_{14}H_{16}OSi$ $[M]^+$ 228.0970, found 228.0972.



4-Phenylbenzoyltrimethylsilane (10f). The general procedure above was applied to 9.89 g (24.8 mmol) of **9f** and 8.29 g (49.7 mmol) of AgOAc. Flash chromatography (5% Et_2O/hexanes) afforded 4.38 g (69% over 2 steps) of **10f** as a bright yellow solid: mp = 80–81 °C; IR (KBr) 3063, 2961, 1592, 1484, 1219, 1169, 844 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, J = 8.2, 2H), 7.71 (d, J = 8.2, 2H), 7.63 (d, J = 7.2, 2H), 7.48 (t, J = 7.7, 2H), 7.4o (t, J = 7.4, 1H), 0.42 (s, 9H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 235.2, 145.7, 140.7, 140.5, 129.5, 128.7, 128.5, 127.8, 127.8, –1.1; HRMS (CI/NH_3) *m / z* calcd for $C_{16}H_{18}OSi$ $[M]^+$ 254.1127, found 254.1121; Anal. Calcd for $C_{16}H_{18}OSi$: C, 75.54; H, 7.13. Found: C, 75.77; H, 7.36.



2-Pentyl-[1,3]-dithiane (14). The general procedure of Nishida was followed.[10] To a 4.0 M solution of hexanal (2.0 mL, 16 mmol) in CH_2Cl_2 was added 1,3-propanedithiol (1.9 mL, 18 mmol). The mixture was cooled to 0 °C and $BF_3{\cdot}OEt_2$ (1.0 mL, 8.2 mmol) was added dropwise. The mixture was allowed to warm to ambient temperature and was maintained for 26 h. The reaction was quenched by the addition of saturated aqueous $NaHCO_3$. The mixture was diluted with CH_2Cl_2 and washed twice with 0.1 M NaOH then three times with brine. The combined aqueous phases were extracted twice with

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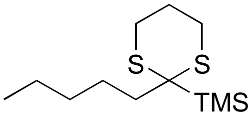
[10] Nishida, K.; Nakamura, D.; Yokota, K.; Sumiya, T.; Node, M.; Ueda, M.; Fuji, K. *Heterocycles,* **1997,** *44,* 393.

CH_2Cl_2 and the combined organic layers were dried over $MgSO_4$ then concentrated *in vacuo*. Flash chromatography (4% Et_2O/hexanes) afforded 3.0 g (96%) of **14a** as a colorless oil: IR (neat) 2930, 1422, 1275, 1182, 908 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.05 (t, *J* = 6.9, 1H), 2.91–2.80 (m, 4H), 2.15–2.09 (m, 1H), 1.90–1.82 (m, 1H), 1.76–1.72 (m, 2H), 1.51 (quintet, *J* = 7.6, 2H), 1.33–1.25 (m, 4H), 0.89 (t, *J* = 7.0, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 47.9, 35.6, 31.6, 30.7, 26.5, 26.3, 22.6, 14.2; HRMS (EI/isobutane) *m / z* calcd for $C_9H_{18}S_2$ $[M]^+$ 190.0850, found 190.0846.



Trimethyl-(2-pentyl-[1,3]-dithian-2-yl)-silane (14a). The general procedure of Corey was followed.[11] To a 1.0 M solution of **14** (0.72 g, 3.8 mmol) in THF at 0 °C was added dropwise *n*-BuLi (1.4 M in hexanes, 3.0 mL, 4.2 mmol). The mixture was maintained for 0.5 h then TMSCl (0.54 mL, 4.2 mmol) was added dropwise. The mixture was allowed to warm to ambient temperature and was maintained for 1.5 h. The mixture was cooled to 0 °C and the reaction was quenched by the addition of saturated aqueous NH_4Cl. The mixture was allowed to warm to ambient temperature, diluted with Et_2O, and washed three times with brine. The combined aqueous phases were extracted twice with Et_2O and the combined organic layers were dried over $MgSO_4$ then concentrated *in vacuo*. Flash chromatography (4% Et_2O/hexanes) afforded 0.92 g (92%) of **14a** as a colorless oil: IR (neat) 2934, 1421, 1249, 843 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.07–3.01 (m, 2H), 2.45 (ddd, *J* = 14.5, 4.5, 3.4, 2H), 2.21–2.18 (m, 2H), 2.07–2.02 (m, 1H), 1.94–1.85

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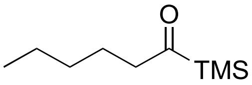
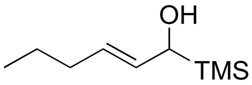
[11] Corey, E. J.; Seebach, D.; Freedman, R. *J. Am. Chem. Soc.* **1967,** *89,* 434.

(m, 1H), 1.52–1.46 (m, 2H), 1.38–1.32 (m, 4H), 0.92 (t, *J* = 7.1, 3H), 0.19 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 39.0, 37.5, 32.6, 27.6, 25.4, 23.6, 22.8, 14.3, –2.3; HRMS (CI/NH_3) *m / z* calcd for $C_{12}H_{26}S_2Si$ $[M]^+$ 262.1245, found 262.1249.



Hexanoyltrimethylsilane (15).[12] The general procedure of Portella was followed.[13] To a 0.03 M solution of dithiane **14b** (0.28 g, 1.1 mmol) in a 50:50 (v:v) mixture of CH_3CN and H_2O in an aluminum foil-wrapped flask was added $CaCO_3$ (1.2 g, 12 mmol). Methyliodide was added and the mixture was heated to 55 °C and was maintained for 16 h. The mixture was allowed to cool to ambient temperature, diluted with EtOAc, and filtered through celite. The aqueous phase was extracted twice with EtOAc and the combined organic layers were dried over $MgSO_4$ then concentrated *in vacuo*. Flash chromatography (5% Et_2O/petroleum ether) afforded0.12 g (68%) of **15** as a pale yellow oil: IR (neat) 2959, 1644, 1250, 846 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.59 (t, *J* = 7.4, 2H), 1.52 (quintet, *J* = 7.4, 2H), 1.33–1.20 (m, 4H), 0.88 (t, *J* = 7.2, 3H), 0.20 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 249.0, 48.7, 31.8, 22.8, 22.1, 14.2, –2.9; HRMS (EI/isobutane) *m / z* calcd for $C_9H_{20}OSi$ $[M]^+$ 172.1283, found 172.1281.



(±)-1-Hexenyl-1-(trimethylsilyl)methanol (25).[14] The general procedure of Danheiser[15] was followed. To a 0.75 M solution of (*E*)-2-hexen-1-ol (0.36 mL, 2.9 mmol) in THF at –78 °C was added *n*-BuLi (1.4 M in hexanes, 2.1 mL, 3.1 mmol) dropwise. The mixture

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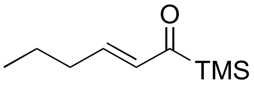
[12] Kang, J.; Lee, J. H.; Kim, K. S.; Jeong, J. U.; Pyun, C. *Tetrahedron Lett.* **1987,** *28,* 3261.
[13] Bouillon, J-P.; Portella, C. *Eur. J. Org. Chem.* **1999,** 1571.
[14] Kamimura, A.; Kaneko, Y.; Ohta, A.; Kakehi, A.; Matsuda, H.; Kanemasa, S. *Tetrahedron Lett.* **1999,** *40,* 4349.
[15] Danheiser, R. L.; Fink, D. M.; Okano, K.; Tsai, Y-M.; Szczepanski, S. W. *J. Org Chem.* **1985,** *50,* 5393.

was warmed to 0 °C and maintained for 15 min. The mixture was cooled to –78 °C and TMSCl (0.42 mL, 3.2 mmol) was added dropwise. The mixture was warmed to 0 °C and maintained for 15 min. The mixture was cooled to –78 °C and *t*-BuLi (1.7 M in pentane, 5.3 mL, 8.8 mmol) was added dropwise over a period of 10 min. The mixture was warmed to –30 °C and maintained for 6.0 h. The mixture was removed from the cold bath and the reaction was immediately quenched by the addition of saturated aqueous NH_4Cl. The mixture was allowed to warm to ambient temperature, diluted with Et_2O, and washed once with NH_4Cl then three times with brine. The combined aqueous phases were extracted twice with Et_2O and the combined organic layers were dried over $MgSO_4$ then concentrated *in vacuo*. Purification by flash chromatography (10% EtOAc/hexanes) afforded **25** (0.50 g, 98%) as a pale yellow oil: IR (neat) 3403, 3030, 2959, 1248, 968, 842 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.60 (dddd, *J* = 15.4, 6.6, 1.2, 1.2, 1H), 5.48 (dddd, *J* = 15.2, 6.8, 6.8, 1.5, 1H), 3.91 (dd, *J* = 6.6, 1.5, 1H), 2.03 (q, *J* = 7.1, 2H), 1.39 (sextet, *J* = 7.3, 2H), 1.28 (s, 1H), 0.90 (t, *J* = 7.4, 3H), 0.04 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 131.6, 127.8, 68.7, 34.8, 23.1, 13.8, –4.0; HRMS (EI/isobutane) *m / z* calcd for $C_8H_{17}OSi$ $[M - CH_3]^+$ 157.1049, found 157.1053.



Hexenoyltrimethylsilane (17).[16] The general oxidation procedure described by Narasaka was used.[17] A 0.5 M solution of *n*-propylmagnesium bromide (3.3 mmol) in THF was prepared and cooled to 0 °C. To the mixture was added a 0.5 M solution of **25**

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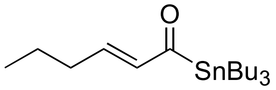
[16] Minami, N.; Abe, T.; Kuwajima, I. *J. Organomet. Chem.* **1978,** *145,* C1–C3.
[17] Narasaka, K.; Morikawa, A.; Saigo, K.; Mokaiyama, T. *Bull. Chem. Soc. Jpn.* **1977,** *50,* 2773.

(0.40 g, 2.3 mmol) in THF dropwise and the mixture was maintained for 15 min. A 0.3 M solution of azodicarbonyldipiperidine (0.82 g, 3.2 mmol) in THF was added dropwise and the mixture was maintained for 1 h. The reaction was then quenched by the addition of brine. The mixture was allowed to warm to ambient temperature, diluted with Et_2O, and washed twice with 1 N HCl, once with saturated $NaHCO_3$, and twice with brine. The organic layer was dried over $MgSO_4$ then concentrated *in vacuo*. Flash chromatography (3–10% Et_2O/pentane) afforded 0.34 g (86%) of **17** as a bright yellow oil: IR (neat) 3030, 2960, 1591, 1250, 847 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.76 (td, *J* = 16.2, 6.9, 1H), 6.21 (td, *J* = 16.2, 1.5, 1H), 2.23 (dq, *J* = 7.2, 1.5, 2H), 1.52 (sextet, *J* = 7.4, 2H), 0.95 (t, *J* = 7.4, 3H) 0.25 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 237.0, 149.0, 136.8, 35.0, 21.6, 13.9, –1.7; HRMS (EI/isobutane) *m / z* calcd for $C_9H_{18}OSi$ $[M]^+$ 170.1127, found 170.1124.



Hexenoyltributylstannane (18). The general procedure of Marshall was followed.[18] To a 0.5 M solution of lithium diisopropylamide (2.8 mmol) in THF at 0 °C was added tributyltin hydride (0.79 mL, 2.8 mmol) dropwise and the mixture was maintained for 15 min. The mixture was cooled to –78 °C and a 1.0 M solution of *trans*-2-hexenal (0.30 mL, 2.6 mmol) in THF was added dropwise and the mixture was maintained for 10 min. Azodicarbonyldipiperidine (0.72 g, 2.8 mmol) was added as a solid and the mixture was warmed to 0 °C and was maintained for 1 h. The reaction was quenched by the addition of saturated aqueous NH_4Cl. The mixture was allowed to warm to ambient temperature,

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[18] (a) Marshall, J. A.; Welmaker, G. S.; Gung, B. W. *J. Am. Chem. Soc.* **1991,** *113,* 647. (b) Marshall, J. A.; Hinkle, K. W. *J. Org. Chem.* **1995,** *60,* 1920.

diluted with Et_2O, and washed once with 3% HCl, twice with saturated $NaHCO_3$, and twice with brine. The combined organic layers were dried over $MgSO_4$ then concentrated *in vacuo*. Flash chromatography (1–3% Et_2O/pentane) afforded 0.67 g (ca. 67%) of **18** as a bright yellow/orange oil: IR (neat) 2958, 2928, 1603, cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.58 (ddd, *J* = 15.7, 6.9, 6.9, 1H), 6.10 (dt, *J* = 15.7, 1.4, 1H), 2.31 (dddd, *J* = 7.2, 7.2, 7.2, 1.4, 2H), 1.57–0.87 (m, 32H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 246.0, 155.5, 140.8, 34.9, 29.3, 28.1, 27.5, 21.8, 13.9, 11.4.