Supporting Information

Diorganotelluride-Catalyzed Oxidation of Silanes to Silanols under Atmospheric Oxygen

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Experimental

General. Melting points were determined using a Yamato MP-21 melting point apparatus in open capillaries and are uncorrected. ¹H, ¹³C, ²⁹Si, and ¹²⁵Te nuclear magnetic resonance (NMR) spectra were measured on a Varian Mercury plus 400 spectrometer at 400, 100, 80, and 126 MHz, respectively. All chemical shifts are reported as δ values (ppm) relative to residual chloroform (δ_H 7.26), the central peak of deuteriochloroform (δ_C 77.0), tetramethylsilane (δ_{Si} 0.0), and dimethyl telluride (δ_{Te} 0) unless otherwise noted; and J values are expressed in Hz. For ¹²⁵Te NMR, Mes₂Te (δ_{Te} 275)¹ or Tip₂TeO (δ_{Te} 1314)^{2a} was used as a secondary external standard. Mass spectra were obtained with a JEOL JMS-AX-500 spectrometer. Infrared spectra were measured with a JASCO IR Report-100 spectrometer.

Flash column chromatography was performed on a KANTO CHEMICAL Silica gel 60 N (spherical, neutral) 40–50 μ m. For analytical purposes, thin layer chromatography (TLC) was performed using Merck Silica gel 60 F₂₅₄ pre-coated aluminum sheets (Merck 5554) which were observed under ultraviolet irradiation. GC measurements were performed on a Shimadzu GC-18A gas chromatograph using a 50 m × 0.25 mm methyl silicone capillary column (Quadrex).

All reagents and solvents were of commercial grade and used according to supplier instructions unless otherwise mentioned.

Materials.

Tellurides. Diphenyl telluride, bis(4-methoxyphenyl) telluride (An₂Te), and bis(2,4,6-trimethylphenyl) telluride (Mes₂Te) were prepared following the procedure described previously.^{2b}

For example, to a solution of MesMgBr, prepared from magnesium (1.34 g, 55.1 mmol) and MesBr (10.0 g, 50.2 mmol) in THF (50 ml), was added tellurium powder (6.48 g, 50.8 mmol) under an argon atmosphere. After it was refluxed for 1 h, the mixture was cooled to room temperature, diluted with benzene (65 ml), and poured into a mixture of crushed ice and concentrated HCl. After being stirred overnight, the organic phase was separated, washed with water and brine, dried over magnesium sulfate, and concentrated under reduced pressure. The crude product was washed with EtOH (30 ml) to give 73% yield of MesTeTeMes (9.05 g, 18.3 mmol) as a dark red solid, mp 124–127 °C (lit,³ 125–127 °C). The obtained ditelluride was dissolved in toluene (30 ml) and the solution was refluxed overnight in the presence of copper powder (4.67

¹ Laur, P. H.; Saberi-Niaki, S. M.; Scheiter, M.; Hu, C.; Englert, U.; Wang, Y.; Fleischhauer, J. *Phosphorus, Sulfur, Silicon, Rel. Elm.* **2005**, *180*, 1035–1044.

² (a) Oba, M.; Endo, M.; Nishiyama, K.; Ouchi, A.; Ando, W. *Chem. Commun.* 2004, 1672–1673;
(b) Oba, M.; Okada, Y.; Nishiyama, K.; Ando, W. *Org. Lett.* 2009, *11*, 1879–1881.

³ Akiba, M.; Lakshmikantham, M. V.; Jen, K.-Y.; Cava, M. P. J. Org. Chem. **1984**, 49, 4819–4821.

g, 73.5 mmol). After removal of insoluble materials by filtration, the solution was concentrated under reduced pressure to give pure Mes₂Te^{3,4} (6.43 g, 17.6 mmol, 70%) as a pale yellow solid, mp 122–124.5 °C (lit,⁴ 124–126 °C). ¹H NMR (CDCl₃) δ 2.24 (s, 6H), 2.34(s, 12H), 6.86 (s, 4H). ¹³C NMR (CDCl₃) δ 20.8, 28.1, 119.0 (d satellite, ¹*J*_{C-Te} = 295 Hz), 127.7, 137.7, 144.1. ¹²⁵Te NMR (CDCl₃) δ 275. MS (EI) *m/z* 368 (M⁺).

Other diaryl tellurides were similarly prepared and the physical and spectral data are as follows.

An₂Te.⁴ Yield 63%, colorless viscous oil. ¹H NMR (CDCl₃) δ 3.78 (s, 6H), 6.76 (d, J = 9 Hz, 4H), 7.63 (d, J = 9 Hz, 4H). ¹³C NMR (CDCl₃) δ 54.9, 104.2 (d satellite, ¹ $J_{C-Te} = 279$ Hz), 155.2, 139.5, 159.4. ¹²⁵Te NMR (CDCl₃) δ 667. MS (EI) *m/z* 344 (M⁺).

Ph₂Te.^{3,4} Yield 96%, pale yellow oil. ¹H NMR (CDCl₃) δ 7.24 (m, 2H), 7.31 (m, 6H), 7.73 (d, J = 7 Hz, 4H). ¹³C NMR (CDCl₃) δ 114.6 (d satellite, ¹ $J_{C-Te} = 276$ Hz), 127.8, 129.4, 137.9. ¹²⁵Te NMR (CDCl₃) δ 707. MS (EI) m/z 284 (M⁺).

Mes₂TeO. According to the literature method,⁵ a solution of Mes₂Te (918 mg, 2.51 mmol) and *N*-chlorosuccinimide (401 mg, 3.00 mmol) in MeOH-CH₂Cl₂ (350 ml, 1:1) was stirred at room temperature for 15 min. Then, the solution was added saturated aqueous NaHCO₃ (100 ml) and the stirring was continued for an additional 15 min. The reaction mixture was diluted with water (100 ml) and the organic phase was separated, washed with water, dried over MgSO₄, and concentrated under reduced pressure. Recrystallization of the crude products from ethyl acetate gave Mes₂TeO³ (853 mg, 2.23 mmol, 89%) as a colorless solid, mp 180–182 °C (lit,³ 179–180 °C). ¹H NMR (CDCl₃) δ 2.26 (s, 6H), 2.54 (s, 12H), 6.84 (s, 4H). ¹³C NMR (CDCl₃) δ 21.2, 21.6, 130.7, 131.1 (d, satellite, ¹*J*_{C-Te} = 350 Hz), 141.1, 143.0. ¹²⁵Te NMR (CDCl₃, Tip₂TeO) δ 1308.

Silanes. Ph₃SiH, Ph₂MeSiH, PhMe₂SiH, and Et₃SiH are commercial products. (*R*)-(+)-Me(α-Np)PhSiH was prepared in 67% yield by LiAlH₄-reduction of the corresponding (-)-menthoxysilane following the procedure described by Sommer and co-workers.⁶ ¹H NMR (CDCl₃) δ 0.76 (d, *J* = 4 Hz, 3H), 5.36 (q, *J* = 4 Hz, 1H), 7.32–7.40 (m, 3H), 7.42–7.50 (m, 3H), 7.58 (d, *J* = 8 Hz, 2H), 7.74 (d, *J* = 7 Hz, 1H), 7.87 (d, *J* = 8 Hz, 1H), 7.92 (d, *J* = 8 Hz, 1H), 8.06 (d, *J* = 8 Hz, 1H). ¹³C NMR (CDCl₃) δ -4.5, 125.2, 125.6, 126.1, 128.0, 128.0, 128.9, 129.5, 130.5, 133.2, 133.3, 134.9, 135.2, 135.4, 137.1. ²⁹Si NMR (CDCl₃) δ -20.0. EI-MS (70 eV) *m/z* 248 (M⁺). IR (KBr, cm⁻¹) 2120 (Si-H). [α]_D²⁶+32.3 (*c* 3.99, cyclohexane) (lit, ⁶ [α]_D +33.7 (*c* 4.00, cyclohexane)).

1-Dodecyldimethylsilane was prepared by reduction of the corresponding chloride. To a suspension of $LiAlH_4$ (3.78 g, 99.6 mmol) in THF (100 ml) was added dropwise

⁴ Suzuki, H.; Nakamura, T. *Synthesis*, **1992**, 549–551; Suzuki, H.; Inoue, M. *Chem. Lett.* **1985**, 389–390.

⁵ Detty, M. R. J. Org. Chem. **1980**, 45, 274–279.

⁶ Sommer, L. H.; Frye, C. L.; Parker, G. A.; Michael, K. W. J. Am. Chem. Soc. 1964, 86, 3271–3276.

1-dodecyldimethylsilyl chloride (21.8 g, 82.9 mmol) under an argon atmosphere at room temperature and the mixture was stirred for an additional 1h. The reaction mixture was quenched by the addition of dilute HCl and extracted with ether. The organic layer was washed with water and brine, dried over MgSO₄, and filtered and the solvent was removed by rotary evaporation. Vacuum distillation of the residue afforded pure 1-dodecyldimethylsilane⁷ (17.0 g, 74.4 mmol, 90%) as a colorless liquid, bp 105 °C/2 mmHg (lit,⁷ 84 °C/0.8 mmHg). ¹H NMR (CDCl₃) δ 0.06 (d, *J* = 4 Hz, 6H), 0.57 (m, 2H), 0.88 (t, *J* = 8 Hz, 3H), 1.26 (m, 20H), 3.83 (sept, *J* = 4 Hz, 1H). ¹³C NMR (CDCl₃) δ -4.4, 14.1, 14.2, 22.7, 24.4, 29.4, 29.4, 29.6, 29.7, 29.7, 29.7, 31.7, 33.3. ²⁹Si NMR (CDCl₃) δ -13.1. EI-MS (70 eV) *m/z* 226 [(M - H₂)⁺]. IR (neat, cm⁻¹) 2110 (Si-H).

Aryldimethylsilanes were prepared using the procedure developed by Fujita and co-workers.^{8a} For example, to a suspension of Mg (1.82 g, 74.8 mmol) and a catalytic amount of I_2 in THF (40 ml) was added dropwise a solution of 1-bromo-4-(trifluoromethyl)benzene (9.38 68.0 ml, 15.3 g, mmol) and chlorodimethylsilane (7.4 ml, 6.44 g, 68.1 mmol) in THF (30 ml) at room temperature under an argon atmosphere. After being stirred overnight, the reaction mixture was quenched by the addition of saturated aqueous NH₄Cl and extracted with ether. The organic layer was washed with water and brine, dried over MgSO₄, and filtered and the solvent was removed by rotary evaporation. Vacuum distillation of the residue afforded pure (4-trifluoromethylphenyl)dimethylsilane^{8a} (5.59 g, 27.4 mmol, 40%) as a colorless liquid, bp 96–98 °C/10 mmHg (lit, ^{8b} 100 °C/10 mmHg). ¹H NMR (CDCl₃) δ 0.39 (d, J = 4 Hz, 6H), 4.48 (sept, J = 4 Hz, 1H), 7.62 (d, J = 8 Hz, 2H), 7.68 (d, J = 8 Hz, 2H). ¹³C NMR (CDCl₃) δ -4.1, 124.2 (q, J = 272 Hz), 124.4 (q, J = 4 Hz), 131.2 (q, J = 32 Hz), 134.3, 142.5. ²⁹Si NMR (CDCl₃) δ -16.4. EI-MS (70 eV) m/z 203 [(M - H)⁺]. IR (neat, cm⁻¹) 2140 (Si-H).

(4-Methoxyphenyl)dimethylsilane,^{8a} (4-chlorophenyl)dimethylsilane,⁹ and (2-thienyl)dimethylsilane¹⁰ were similarly prepared and the physical and spectral data are as follows.

(4-Methoxyphenyl)dimethylsilane.^{8a} Yield 48%, colorless liquid, bp 108–110 °C/31 mmHg (lit,^{8a} 120 °C (bath temp)/20 mmHg). ¹H NMR (CDCl₃) δ 0.32 (d, *J* = 4 Hz, 6H), 3.82 (s, 3H), 4.41 (sept, *J* = 4 Hz, 1H), 6.92 (d, *J* = 8 Hz, 2H), 7.47 (d, *J* = 8 Hz, 2H). ¹³C NMR (CDCl₃) δ -3.6, 55.0, 113.6, 128.2, 135.4, 160.5. ²⁹Si NMR (CDCl₃) δ -17.7. EI-MS (70 eV) *m/z* 166 (M⁺). IR (neat, cm⁻¹) 2120 (Si-H).

(4-Chlorophenyl)dimethylsilane.⁹ Yield 42%, colorless liquid, bp 71 °C/10 mmHg. ¹H NMR (CDCl₃) δ 0.34 (d, J = 4 Hz, 6H), 4.41 (sept, J = 4 Hz, 1H), 7.34 (d, J = 8 Hz,

⁷ Itami, K.; Terakawa, K.; Yoshida, J.; Kajimoto, O. J. Am. Chem. Soc. 2003, 125, 6058–6059.

⁸ (a) Fujita, M.; Hiyama, T. J. Org. Chem. **1988**, 53, 5405–5415; (b) Andreev, A. A.; Konshin, V. V.; Komarov, N. V.; Rubin, M.; Brouwer, C.; Gevorgyan, V. Org. Lett. **2003**, 6, 421–424.

⁹ Hevesi, L.; Dehon, M.; Crutzen, R.; Lazarescu-Grigore, A. J. Org. Chem. 1997, 62, 2011–2017.

¹⁰ Hu, S.-S.; Weber, W. P. J. Organomet. Chem. **1989**, 369, 155–163.

2H), 7.46 (d, J = 8 Hz, 2H). ¹³C NMR (CDCl₃) δ -3.8, 128.1, 135.3, 135.3, 135.6. ²⁹Si NMR (CDCl₃) δ -16.8. EI-MS (70 eV) m/z 170 (M⁺). IR (neat, cm⁻¹) 2150 (Si-H).

(2-Thienyl)dimethylsilane.¹⁰ Yield 54%, colorless liquid, bp 39 °C/13 mmHg (lit,¹⁰ 74–75 °C/60 mmHg). ¹H NMR (CDCl₃) δ 0.40 (d, J = 4 Hz, 6H), 4.41 (sept, J = 4 Hz, 1H), 7.21 (dd, J = 4 and 5 Hz, 1H), 7.32 (d, J = 4 Hz, 1H), 7.63 (d, J = 5 Hz, 1H). ¹³C NMR (CDCl₃) δ -2.8, 128.2, 131.0, 135.1, 136.2. ²⁹Si NMR (CDCl₃) δ -23.3. EI-MS (70 eV) m/z 142 (M⁺). IR (neat, cm⁻¹) 2130 (Si-H).

General procedure for diorganotelluride-catalyzed oxidation of triorganosilanes. A 0.1 M solution (20 ml) of silane (2.00 mmol) containing diaryl telluride (10 mol %) in the presence of an appropriate photosensitizer $(1.00 \times 10^{-4} \text{ M})$ was irradiated under aerobic conditions (in an open flask with vigorous stirring) using a 500 W halogen lamp at a distance of 10–15 cm. An ice bath can be used to keep the reaction temperature between 10 and 20 °C, without which the temperature rose to 50–70 °C during irradiation. The progress of the reaction was monitored by ¹H NMR spectroscopy and the chemical yields were determined by integration of the ¹H NMR signals using *tert*-butylbenzene as an internal standard. After careful evaporation of the solvent, silanols were isolated by flash column chromatography on silica gel using a mixture of hexanes and ethyl acetate as an eluent. Identification of the products was carried out by comparison of ¹H, ¹³C, and ²⁹Si NMR, MS, and infrared spectra to literature data or to those of commercial products. Physical and spectral data for the isolated silanols are as follows.

(4-Trifluoromethylphenyl)dimethylsilanol.¹¹ Colorless viscous oil. ¹H NMR (CDCl₃) δ 0.43 (s, 6H), 1.96 (s, 1H), 7.63 (d, J = 8 Hz, 2H), 7.70 (d, J = 8 Hz, 2H). ¹³C NMR (CDCl₃) δ -0.1, 124.1 (q, J = 272 Hz), 124.3 (q, J = 4 Hz), 131.5 (q, J = 32 Hz), 133.3, 143.8. ²⁹Si NMR (CDCl₃) δ 7.4. EI-MS (70 eV) m/z 220 (M⁺). IR (neat, cm⁻¹) 3300 (OH).

(4-Chlorophenyl)dimethylsilanol.¹² Colorless viscous oil. ¹H NMR (CDCl₃) δ 0.40 (s, 6H), 1.82 (s, 1H), 7.36 (d, J = 8 Hz, 2H), 7.52 (d, J = 8 Hz, 2H). ¹³C NMR (CDCl₃) δ -0.1, 128.1, 134.4, 135.9, 137.3. ²⁹Si NMR (CDCl₃) δ 7.5. EI-MS (70 eV) m/z 186 (M⁺). IR (neat, cm⁻¹) 3300 (OH).

(4-Methoxyphenyl)dimethylsilanol.¹¹ Colorless viscous oil. ¹H NMR (CDCl₃) δ 0.39 (s, 6H), 2.02 (s, 1H), 3.82 (s, 3H), 6.94 (d, *J* = 8 Hz, 2H), 7.53 (d, *J* = 8 Hz, 2H). ¹³C NMR (CDCl₃) δ 0.0, 55.0, 113.5, 130.2, 134.6, 160.7. ²⁹Si NMR (CDCl₃) δ 7.4. EI-MS (70 eV) *m*/*z* 182 (M⁺). IR (neat, cm⁻¹) 3300 (OH).

(2-Thienyl)dimethylsilanol.¹³ Colorless viscous oil. ¹H NMR (CDCl₃) δ 0.47 (s,

¹¹ Hirabayashi, K.; Kawashima, J.; Nishihara, Y.; Mori, A.; Hiyama, T. Org. Lett. 1999, 1, 299–301.

¹² Denmark, S. E.; Smith, R. C.; Chang, W. T.; Muhuhi, J. M. J. Am. Chem. Soc. 2009, 131,

^{3104-3118.}

¹³ Denmark, S. E.; Baird, J. D. Org. Lett. **2006**, *8*, 793–795.

6H), 2.13 (s, 1H), 7.21 (dd, J = 3 and 4 Hz, 1H), 7.37 (d, J = 3 Hz, 1H), 7.64 (d, J = 4 Hz, 1H). ¹³C NMR (CDCl₃) δ 0.8, 128.1, 131.0, 134.6, 138.5. ²⁹Si NMR (CDCl₃) δ 3.3. EI-MS (70 eV) m/z 158 (M⁺). IR (neat, cm⁻¹) 3280 (OH).

1-Dodecyldimethylsilanol.⁷ Colorless viscous oil. ¹H NMR (CDCl₃) δ 0.12 (s, 6H), 0.59 (m, 2H), 0.88 (t, J = 7 Hz, 3H), 1.24–1.36 (m, 20H), 1.60 (s, 1H). ¹³C NMR (CDCl₃) δ -0.3, 14.1, 16.5, 17.8, 22.7, 23.2, 29.4, 29.6, 29.7, 29.7, 29.7, 31.9, 33.5. ²⁹Si NMR (CDCl₃) δ 17.6. EI-MS (70 eV) m/z 230 (M⁺). IR (neat, cm⁻¹) 3280 (OH).

Triphenylsilanol.¹⁴ Colorless solid, mp 150-151 °C (lit,¹⁵ 148-150 °C). ¹H NMR (CDCl₃) δ 2.53 (brs, 1H), 7.36-7.46 (m, 9H), 7.63–7.65 (m, 6H). ¹³C NMR (CDCl₃) δ 127.9, 130.1, 135.0, 135.1. ²⁹Si NMR (CDCl₃) δ -12.6. EI-MS (70 eV) m/z 276 (M⁺). IR (KBr, cm⁻¹) 3300 (OH).

Diphenylmethylsilanol.¹⁶ Colorless viscous oil. ¹H NMR (CDCl₃) δ 0.68 (s, 3H), 2.16 (s, 1H), 7.40 (m, 6H), 7.61 (d, J = 7 Hz, 4H). ¹³C NMR (CDCl₃) δ -1.3, 127.9, 129.8, 133.9, 137.0. ²⁹Si NMR (CDCl₃) δ -2.7. EI-MS (70 eV) m/z 214 (M⁺). IR (neat, cm⁻¹) 3280 (OH).

Dimethylphenylsilanol.¹⁴ Colorless viscous oil. ¹H NMR (CDCl₃) δ 0.40 (s, 6H), 3.10 (s, 1H), 7.38-7.43 (m, 3H), 7.59–7.62 (m, 2H). ¹³C NMR (CDCl₃) δ -0.1, 127.8, 129.5, 133.0, 139.1. ²⁹Si NMR (CDCl₃) δ 7.3. EI-MS (70 eV) *m/z* 152 (M⁺). IR (neat, cm⁻¹) 3280 (OH).

(*S*)-(+)-Methyl(α-naphthyl)phenylsilanol.⁶ Colorless viscous oil. ¹H NMR (CDCl₃) δ 0.83 (s, 3H), 2.31 (s, 1H), 7.34–7.50 (m, 6H), 7.64 (d, J = 7 Hz, 2H), 7.81 (d, J = 7 Hz, 1H), 7.87 (d, J = 7 Hz, 1H), 7.93 (d, J = 8 Hz, 1H), 8.12 (d, J = 8 Hz, 1H). ¹³C NMR (CDCl₃) δ -0.3, 124.9, 125.4, 125.9, 127.8, 128.4, 128.7, 129.6, 130.5, 133.2, 133.9, 134.6, 134.7, 136.6, 137.5. ²⁹Si NMR (CDCl₃) δ -1.6. EI-MS (70 eV) m/z 264 (M⁺). IR (neat, cm⁻¹) 3300 (OH). [α]_D²⁴ +18.2 (c 5.98, Et₂O) (lit, ⁶[α]_D +20.5 (c 6.66, Et₂O)).

Hammett plot for the reaction of substituted phenyldimethylsilanes with Mes₂TeO. The relative reaction rates of *para*-substituted phenyldimethylsilanes toward Mes₂TeO were determined via competition experiments by GC analysis. A pyridine solution (3 ml) containing two kinds of aryldimethylsilanes (total 2.25–6.00 mmol) was added to a 10 ml recovery flask and an initial molar ratio of aryldimethylsilanes was determined by GC analysis using decane (300–500 μ l) as an internal standard. To this solution was added Mes₂TeO (100–150 μ mol) and the mixture was stirred at room temperature for 30 min. The amounts of silanes consumed were determined by GC

¹⁴ Commercially available silanols.

¹⁵ Adam, W.; Mitchell, C. M.; Saha-Möller, C. R.; Weichold, O. J. Am. Chem. Soc. **1999**, *121*, 2097–2103.

¹⁶ Lycka, A.; Snobl, D.; Handlir, K.; Holecek, J.; Nadvornik, M. Collect. Czech. Chem. Commun. **1982**, 42, 603–612.

analysis. At least three runs were averaged for each competition. The relative rates calculated under these conditions and Hammett's σ_p -values¹⁷ are compiled in Table S-1.

(4-X-C ₆ H ₄)Me ₂ SiH + Ph Me ₂ SiH		Mes ₂ TeO		(4-	(4-X-C ₆ H ₄)Me ₂ SiOH + PhMe ₂ SiOH		
				in			
-	Х	$k_{\rm X}$	$k_{ m H}/k_{ m H}$	log(k	$k_{\rm X}/k_{\rm H})$	σ_p	
-	MeO	0.465	± 0.019	-0.333	± 0.018	-0.27	
	Н	1.000	± 0.000	0.000 =	± 0.000	0.00	
	Cl	3.61	± 0.18	0.557 =	± 0.022	0.23	
	CF ₃	21.2	± 1.0	1.33 =	± 0.02	0.54	

Table S-1. Relative reaction rates of substituted phenyldimethylsilanes toward Mes₂TeO

Kinetic isotope effect study of the oxidation of Ph₂MeSiH(D) with Mes₂TeO.

The deuterium kinetic isotope effect (KIE) was determined using a conventional competitive technique. Approximately equal amounts of Ph₂MeSiH and Ph₂MeSiD (total 1 mmol) in pyridine- d_5 (1 ml) were incompletely oxidized with Mes₂TeO (0.6–0.8 mmol) at room temperature for 1 h. The initial proportion of Ph₂MeSiD (R_0), fractional conversion of silanes (F), and final proportion of the deuteride in the remaining silanes (R) were determined by ¹H NMR integration of the methyl proton signals. The KIE ($k_{\rm H}/k_{\rm D}$) was calculated from equation 1¹⁸ for a total of 4 reactions and the results are compiled in Table S-2.

KIE =
$$\frac{\ln(1-F)}{\ln[(1-F)R/R_0]}$$
 (eq. 1)

Run	Fractional	R/R_0	KIE
	conversion (F)		$(k_{ m H}/k_{ m D})$
1	0.52	1.076	1.112
2	0.70	1.095	1.081
3	0.73	1.113	1.089
4	0.83	1.126	1.072

Table S-2. Deuterium kinetic isotope effect for oxidation of $Ph_2MeSiH(D)$ with Mes_2TeO

¹⁷ Hansch, C.; Leo, A.; Taft, R. W. Chem. Rev. **1991**, *91*, 165–195.

¹⁸ (a) Bigeleisen, J.; Wolfsberg, M. Adv. Chem. Phys. **1958**, 1, 15–76; (b) Melander, L.; Saunders, W.

H., Jr. Reaction Rates of Isotopic Molecules; Wiley: New York, 1980; pp 95–102.



¹H NMR spectrum of (4-CF₃C₆H₄)Me₂SiOH



¹³C NMR spectrum of (4-CF₃C₆H₄)Me₂SiOH



²⁹Si NMR spectrum of (4-CF₃C₆H₄)Me₂SiOH



Infrared spectrum of (4-CF₃C₆H₄)Me₂SiOH



¹H NMR spectrum of (4-ClC₆H₄)Me₂SiOH



¹³C NMR spectrum of (4-ClC₆H₄)Me₂SiOH



²⁹Si NMR spectrum of (4-ClC₆H₄)Me₂SiOH



Infrared spectrum of (4-ClC₆H₄)Me₂SiOH



¹H NMR spectrum of (4-CH₃OC₆H₄)Me₂SiOH



¹³C NMR spectrum of (4-CH₃OC₆H₄)Me₂SiOH



²⁹Si NMR spectrum of (4-CH₃OC₆H₄)Me₂SiOH



Infrared spectrum of (4-CH₃OC₆H₄)Me₂SiOH





¹³C NMR spectrum of (2-thienyl)Me₂SiOH





Infrared spectrum of (2-thienyl)Me₂SiOH







¹³C NMR spectrum of (1-dodecyl)Me₂SiOH



²⁹Si NMR spectrum of (1-dodecyl)Me₂SiOH



Infrared spectrum of (1-dodecyl)Me₂SiOH

¹H NMR spectrum of Ph₃SiOH



¹³C NMR spectrum of Ph₃SiOH





Infrared spectrum of Ph₃SiOH





S32

шđđ 628.1-0 20 40 60 76.687 000.77 80 17.321 100 120 898.721 129.838 856.551 666.951 140

¹³C NMR spectrum of Ph₂MeSiOH



Infrared spectrum of Ph₂MeSiOH







S37



²⁹Si NMR spectrum of PhMe₂SiOH

Infrared spectrum of PhMe₂SiOH





 1 H NMR spectrum of Me(α -Np)PhSiOH

шđđ £22.0-20 40 60 **76.687** 000.77 80 T2E.77-100 724.937 125.372 125.860 127.800 120 128.403 128.746 129.632 875.0E1 140 133.220 268.551 672.457-734.732 136.648 160 202.752 180 200 220

¹³C NMR spectrum of Me(α-Np)PhSiOH



 ^{29}Si NMR spectrum of Me($\alpha\text{-Np})$ PhSiOH



Infrared spectrum of Me(α -Np)PhSiOH