Indium-Catalyzed Direct Chlorination of Alcohols Using Chlorodimethylsilane-Benzil as a Selective and Mild System

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Supporting Information

General. IR spectra were recorded as thin films or as solids in KBr pellets on a HORIBA FT-720 spectrophotometer. ^{1}H, ^{13}C and ^{29}Si NMR spectra were obtained with a 270, 67.9 and 53.6 MHz spectrometer, respectively, with TMS as internal standard. Mass spectra were recorded on a JEOL JMS-DS303 spectrometer. GLC analyses were performed on a Shimadzu GC-14A with FID using a 15 m × 3 mm capillary column packed with TC-WAX, TC-5, or TC-1701 (0.25 μm). Column chromatography was performed on silica gel (MERK C60). Bulb-to-bulb distillation (Kugelrohr) was accomplished in a Sibata GTO-250RS at the oven temperature and pressure indicated. Yields were determined by GLC or ^{1}H NMR using internal standards.

Materials. Dichloromethane, dehydrated (stabilized with 2-methyl-2-butene) was used without purification. 1,2-Dichloroethane was distilled after the removal of H_2O by CaH_2. All additives in Chart 1, $HSiMe_2Cl$, $HSiPh_2Cl$, $InCl_3$, $AlCl_3$, $Sc(OTf)_3$, alcohols **1a**-**n**, **1p**, **1r**, and **13** were commercially available. The alcohol **1q** was prepared by known method.[1] The alcohols **1o** and **10** were prepared as shown below.

Ethyl *p*-(hydroxymethyl)benzoate (1o). *p*-(Hydroxymethyl)benzoic acid (7.0 mmol) and H_2SO_4 (3 mL) was added to a stirred solution in EtOH (30 mL) at reflux. After stirring for 8 h, aqueous $NaHCO_3$ was added to the reaction mixture. The mixture was extracted with ethyl acetate. The organic layer was washed with water and dried over $MgSO_4$. The volatiles were evaporated and the residue was purified by chromatography (ethyl acetate) on silica gel to give the product (0.79 g, 60%). bp: 140 ℃ / 0.1 mmHg; IR: (neat) 3448 (OH), 1716 (C=O) cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) 8.00 (d, J = 8.3 Hz, 2H, *o*), 7.40 (d, J = 8.3 Hz, 2H, *m*), 4.74 (s, 2H, CH_2OH), 4.36 (q, J = 7.1 Hz, 2H, CH_3CH_2), 2.47 (brs, 1H, OH), 1.39 (t, J = 7.1 Hz, 3H, CH_3); ^{13}C NMR (67.9 MHz, $CDCl_3$) 166.47 (C=O), 145.87 (*p*), 129.66 (*o*), 129.42 (*i*), 126.31 (*m*), 64.55 (CH_2OH), 60.98

(CH_2), 14.31 (CH_3); MS: (EI, 70 eV) *m/z* 180 (M^+, 22), 135 (M^+ - EtO, 100); HRMS: (EI, 70 eV) calcd for $C_{10}H_{12}O_3$ 180.0786 found *m/z* 180.0775 (M^+). Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found C, 66.11; H, 6.76.

15-Methylhexadecan-1,15-diol (10).[2] Methyllithium (87.5 mmol) was added to a stirred solution of oxacyclohexadecan-2-one (35.0 mmol) in dry THF (60 mL) at -78 ºC. The reaction mixture was stirred at -78 ºC for 0.5 h and was allowed to warm to room temperature over 6 h. Acetic acid (87.5 mmol) was added to the reacion mixture and the white precipitate was formed. After stirring for 12 h, the precipitate was filtered off and the filtrate was washed with water, extracted with diethylether and then dried over $MgSO_4$. The volatiles were evaporated to give the crude product as a yellow viscous liquid. purification by recrystalization (9:1 hexane/ EtOAc) gave the pure product as a white solid (3.1 g, 36%). mp: 62 ºC; IR: (KBr) 3367 (OH) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) 3.63 (t, J = 6.7 Hz, 2H, 1-H_2), 1.59 (brs, 2H, 1-OH and 15-OH, D_2O-exchangeable), 1.56 (tt, J = 6.7, 6.7 Hz, 2H, 2-H_2), 1.47-1.44 (m, 2H, 14-H_2), 1.34-1.32 (m, 4H, 3, 13-H_2), 1.34-1.26 (m, 18H, 4, 5, 6, 7, 8, 9, 10, 11 and 12-H_2), 1.20 (s, 6H, 16-H_3, 15-CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) 71.06 (s, C-15), 62.98 (t, C-1), 43.99 (t, C-14), 32.80 (t, C-2), 30.19 (C-12), Some signals appear between 29.70-29.50 ppm as a broad peak, 29.43 (C-4), 29.20 (C-16, 15-CH_3), 25.75 (C-3), 24.37 (C-13); MS: (CI, 70 eV) *m/z* 273 (M^+ + 1, 3), 255 (M^+ + 1 - H_2O, 100); HRMS: (CI, 70 eV) calcd for $C_{17}H_{37}O_2$ 273.2794 found *m/z* 273.2789 (M^+ + 1). Anal. Calcd for $C_{17}H_{36}O_2$: C, 74.94; H, 13.32. Found: C, 74.80; H, 13.08.

General procedure for chlorination of alcohols (Tables 1 and 2). To a mixture of $InCl_3$ (0.1 mmol), benzil (2.0 mmol) and alcohol **1** (2.0 mmol) in dichloromethane (or dichloroethane in the reaction at 80 ºC) (4.0 mL) was added chlorodimethylsilane ($HSiMe_2Cl$) (2.2 mmol) under nitrogen. The reaction mixture was stirred under the reaction conditions noted in the text. The resulting mixture was poured into aqueous $NaHCO_3$ (50 mL) and extracted with EtOAc (50 mL). The organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The procedures of further purification for new compounds are shown in the Product data section.

Reaction of 1a using various 1,2-dicarbonyl additives (Chart 1). All reactions were carried out using additives described in Chart 1 instead of bezil under the same reaction conditions of the general procedure.

Reaction of chlorosilyl ether 5 under an $InCl_3$/benzil system (ref. 7). To a mixture of $InCl_3$ (0.1 mmol) and benzil (2.0 mmol) in dichloromethane (4.0 mL) was added chlorosilyl ether **5** (2.0 mmol). The reaction mixture was stirred at room temperature for 7 h. The resulting mixture was

poured into aqueous $NaHCO_3$ (50 mL) and extracted with EtOAc (50 mL). The organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The formation of the chloride **3a** (82% yield) was confirmed by ^1H NMR.

Product data. The spectral data of **3r** was in an excellent agreement with the reported data.[3] The spectral data of **2a**, **3e**, **3g**, **3j-m**, **3p**,[4] and **14** were in an excellent agreement with those of commercially available products. Spectral data for the products, **3a-d**, **3f**, **3h**, **3n**, **3o**, **3q**, **11**, and **12** are shown below.

2-Chloro-1-phenylpropane (3a). According to the general procedure, this compound was prepared from $HSiMe_2Cl$, **1a**, benzil and $InCl_3$ in dichloromethane to give the product as a colorless liquid after chromatography (hexane). Further purification was performed by distillation under reduced pressure: bp: 50 °C / 0.1 mmHg; IR: (neat) 3027, 2973, 2927, 2865 (alkyl) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) 7.35-7.20 (m, 5H, aroma), 4.24 (qdd, J = 6.6, 7.1, 6.8 Hz, 1H, 2-H), 3.09 (dd, J = 13.9, 6.8 Hz, 1H, 1-H^A), 2.96 (dd, J = 13.9, 6.8 Hz, 1H, 1-H^B), 1.51 (d, J = 6.6 Hz, 3H, 3-H_3); ^1H NMR (270 MHz, CD_2Cl_2) 7.35-7.20 (m, 5H, aroma), 4.24 (qdd, J = 6.4, 7.1, 6.6 Hz, 1H, 2-H), 3.05 (dd, J = 13.9, 7.1 Hz, 1H, 1-H^A), 2.98 (dd, J = 13.9, 6.6 Hz, 1H, 1-H^B), 1.50 (d, J = 6.4 Hz, 3H, 3-H_3); ^{13}C NMR (67.9 MHz, $CDCl_3$) 137.90 (*i*), 129.28 (*m*), 128.35 (*o*), 126.74 (*p*), 58.52 (C-2), 46.69 (C-1), 24.69 (C-3); ^{13}C NMR (67.9 MHz, CD_2Cl_2) 138.18 (s, *i*), 129.35 (d, *m*), 128.32 (d, *o*), 126.70 (d, *p*), 58.99 (d, C-2), 46.57 (t, C-1), 24.70 (q, C-3); MS: (EI, 70 eV) *m/z* 156 (M^+ + 2, 5), 154 (M^+, 14), 91 (M^+ - CH_3CHCl, 100); HRMS: (EI, 70 eV) calcd for $C_9H_{11}Cl$ 154.0549 found *m/z* 154.0553 (M^+). Anal. Calcd for $C_9H_{11}Cl$: C, 69.90; H, 7.17; Cl, 22.93. Found: C, 69.61; H, 7.07; Cl, 22.66.

4-Chlorodecane (3b). According to the general procedure, this compound was prepared from $HSiMe_2Cl$, **1b**, benzil and $InCl_3$ in dichloromethane to give the product as a colorless liquid after distillation under reduced pressure. The obtained fraction includes some rearranged compounds. The main product was in an excellent agreement with the one prepared by known method.[5] To a solution of thionyl chloride (4.4 mmol) in DMF (5 mL) was slowly added 4-decanol (4.0 mmol) at 0 °C and the mixture was heated at 100 °C. After stirring for 1 h, H_2O was added to the reaction mixture. The mixture was extracted with diethyl ether. The organic layer was washed with water and dried over $MgSO_4$. The volatiles were evaporated and the residue was purified by chromatography (hexane) on silica gel to give the product. Futher purification was performed by distillation under reduced pressure to give the colorless liquid (0.224 g, 38%): bp: 110 °C / 30 mmHg; IR: (neat) 2954, 2938, 2870 (alkyl) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) 3.94 (tt, J = 6.6, 6.6 Hz, 1H, 4-H), 1.79-1.64 (m, 4H, 3-H_2, 5-H_2), 1.64-1.30 (m, 10H, 2, 6, 7, 8 and 9-H_2), 0.96 (t, J = 7.3 Hz, 3H, CH_3), 0.92 (t, J = 6.7 Hz, 3H, CH_3); ^{13}C NMR (67.9 MHz, $CDCl_3$) 64.05 (d, C-4),

40.06 (t), 38.57 (t), 31.75 (t), 28.89 (t), 26.49 (t), 22.63 (t), 19.75 (t) 14.11 (q), 13.65 (q); MS: (EI, 70 eV) *m/z* 140 (M^+ - HCl, 37), 111 (M^+ - HCl - C_2H_5, 48), 97 (M^+ - HCl - C_3H_7, 67), 55 (100); Anal. Calcd for $C_{10}H_{21}Cl$: C, 67.96; H, 11.98; Cl, 20.06. Found: C, 67.90; H, 11.68; Cl, 19.98.

Cyclododecychloride (3c). According to the general procedure, this compound was prepared from $HSiMe_2Cl$, **1c**, benzil and $InCl_3$ in dichloromethane to give the product as a colorless liquid after distillation under reduced pressure: bp 60 ℃/ 0.11 mmHg; ^1H NMR (270 MHz, $CDCl_3$) δ 4.12 (1H, 1-H), 1.94 (2H, 2,11-H^A), 1.78 (2H, 2,11-H^B), 1.60-1.22 (18H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 60.35 (C-1), 33.90, 23.89, 23.46, 22.03; MS (EI, 70 eV) 166 (M^+ - Cl, 41). Anal. Calcd for $C_{12}H_{23}Cl$: C, 70.91; H, 11.38; Cl, 17.48. Found: C, 71.08; H, 11.43; Cl, 17.55.

2-Chloroadamantane (3d). According to the general procedure, this compound was prepared from $HSiMe_2Cl$, **1d**, benzil and $InCl_3$ in dichloromethane to give the product as a white powder after recrystallization: mp 137 ℃; ^1H NMR (270 MHz, $CDCl_3$) δ 4.40 (s, 1H, 2-H), 2.27 (d, J = 12.70 Hz, 2H, 4,10-H^A), 2.08 (s, 2H, 1,3-H), 1.95 (d, J = 10.99 Hz, 4H, 8,9-H^B), 1.84 (d, J = 10.99 Hz, 2H, 5,7-H), 1.76 (s, 2H, 6-H), 1.57 (d, J = 9.77 Hz, 2H, 4,10-H^B); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 68.28 (C-2), 38.11 (C-8,9), 37.66 (C-6), 35.76 (C-1,3), 30.95 (C-4,10), 27.40 (C-7), 26.81 (C-5); IR (KBr) 810 cm^{-1} (C-Cl); MS (EI, 70 eV) 170 (M^+, 17), 134 (M^+ - Cl, 100); HRMS (EI, 70 eV) calcd for ($C_{10}H_{15}Cl$) 170.0862 (M^+) found for *m/z* 170.0849. Anal. Calcd for $C_{10}H_{25}Cl$: C, 70.37; H, 8.86; Cl, 20.77. Found: C, 70.23; H, 8.50; Cl, 20.86.

2-Chloro-2,5-dimethylhexane (3f). According to the general procedure, this compound was prepared from $HSiMe_2Cl$, **1f**, benzil and $InCl_3$ in dichloromethane to give the product as a colorless liquid after chromatography (pentane). Further purification was performed by distillation under reduced pressure: bp: 50 ℃ / 30 mmHg; IR: (neat) 2954, 2870 (alkyl) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) 1.78-1.70 (m, 2H, 3-H_2), 1.65-1.46 (m, 1H, 5-H), 1.57 (s, 6H, 1-H_3, 2-CH_3), 1.42-1.31 (m, 2H, 4-H_2), 0.91 (d, J = 6.4 Hz, 6H, 6-H_3, 5-CH_3); ^{13}C NMR (67.9 MHz, $CDCl_3$) 71.25 (s, C-2), 44.00 (t, C-3), 34.15 (t, C-4), 32.47 (q, C-1, 2-Me), 28.27 (d, C-5), 22.66 (q, C-6, 5-Me); MS: (EI, 70 eV) *m/z* 135 (M^+ + 2 - Me, trace), 133 (M^+ - Me, trace), 112 (M^+ - HCl, 21), 77 (M^+ - C_5H_{11}, 42), 57 (M^+ - C_4H_8Cl, 100); Anal. Calcd for $C_8H_{17}Cl$: C, 64.63; H, 11.53; Cl, 23.85. Found: C, 64.52; H, 11.21; Cl, 23.73.

1-Chloroadamantane (3h). According to the general procedure, this compound was prepared from $HSiMe_2Cl$, **1h**, benzil and $InCl_3$ in dichloromethane to give the product as a white powder after recrystallization: ^1H NMR (270 MHz, $CDCl_3$) δ 2.11 (s, 9H, CH,CH_2), 1.69 (s, 6H, CH_2); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 69.01 (s, C-Cl), 47.96 (s, C-2), 36.75 (CH_2), 31.57 (CH_2); MS (EI, 70 eV) 172 (M^+ + 2, trace), 170 (M^+, 1), 135 (M^+ - Cl, 100); HRMS (EI, 70 eV) calcd for ($C_{10}H_{15}Cl$) 170.0862 (M^+) found for *m/z* 170.0854.

1-Chloro-1,2-diphenylpropane (3i).[6] According to the general procedure, this compound was prepared from $HSiMe_2Cl$, **1i**, benzil and $InCl_3$ in dichloromethane to give the product as a white solid after chromatography (hexane): Mixtures of diastereomers (A:B = ca. 1:1); ^1H NMR (600 MHz, $CDCl_3$) δ 7.33-7.02 (m, 10H x 2, Ar from A and B), 4.98 (d, J = 8.3 Hz, 1H, 1-H from A), 4.95 (d, J = 8.8 Hz, 1H, 1-H from B), 3.35 (qd, J = 7.1, 8.3 Hz, 1H, 2-H from B), 3.33 (qd, J = 6.9, 8.8 Hz, 1H, 2-H from A), 1.53 (d, J = 6.9 Hz, 3H, 3-H_3 from A) 1.15 (d, J = 7.1 Hz, 3H, 3-H_3 from B); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.27 (s, 2-Ar *ipso* from B), 142.67 (s, 2-Ar *ipso* from A), 140.63 (s, 1-Ar *ipso* from A), 140.24 (s, 1-Ar *ipso* from B), 128.37, 128.26, 128.23, 128.15, 128.02, 127.89, 127.87, 127.77, 127.68, 127.52, 126.88, 126.63, 69.64 (d, C-1 from A), 68.66 (d, C-1 from B), 48.47 (d, C-2 from B), 48.42 (d, C-2 from A), 19.43 (q, C-3 from B), 18.65 (q, C-3 from A); MS (EI, 70 eV) (RT: 12.53 min) 232 (M^+ + 2, 0.5), 230 (M^+, 1.3), 194 (M^+ - HCl, 8.8), 105 (100) and (RT: 12.94 min) 232 (M^+ + 2, 0.6), 230 (M^+, 1.9), 194 (M^+ - HCl, 5.6), 105 (100); HRMS (EI, 70 eV) calcd for ($C_{15}H_{15}Cl$) 230.0862 (M^+) found for *m/z* 230.0874 (RT: 12.53 min) and 230.0860 (RT: 12.94 min).

***p*-Nitrobenzyl chloride (3n).** According to the general procedure, this compound was prepared from $HSiMe_2Cl$, **1n**, benzil and $InCl_3$ in dichloromethane to give the product as a white solid after chromatography (ethyl acetate). Further purification was performed by recrystalization (9:1 hexane/ EtOAc): mp: 72 °C; IR: (KBr) 1535, 1350 (NO_2) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) 8.23 (d, J = 8.8 Hz, 2H, *m*), 7.57 (d, J = 8.8 Hz, 2H, *o*), 4.65 (s, 2H, CH_2Cl); ^{13}C NMR (67.9 MHz, $CDCl_3$) 147.78 (*p*), 144.23 (*i*), 129.23 (*o*), 123.88 (*m*), 44.49 (CH_2Cl); MS: (EI, 70 eV) *m/z* 173 (M^+ + 2, 20), 171 (M^+, 54), 136 (M^+ -Cl, 100), 127 (M^+ + 2 - NO_2, 12), 125 (M^+ - NO_2, 34); HRMS: (EI, 70 eV) calcd for $C_7H_6ClNO_2$ 171.0087 found *m/z* 171.0069 (M^+). Anal. Calcd for $C_7H_6ClNO_2$: C, 49.00; H, 3.52; Cl, 20.66; N, 8.16. Found: C, 48.76; H, 3.45; Cl, 20.37; N, 8.15.

Ethyl *p*-(chloromethyl)benzoate (3o). According to the general procedure, this compound was prepared from $HSiMe_2Cl$, **1o**, benzil and $InCl_3$ in dichloromethane to give the product as a colorless liquid after chromatography (hexane:ethyl acetate = 99:1). Further purification was performed by distillation under reduced pressure: bp: 115 °C / 0.3 mmHg; IR: (neat) 1720 (C=O) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) 8.04 (d, J = 8.1 Hz, 2H, *o*), 7.47 (d, J = 8.1 Hz, 2H, *m*), 4.62 (s, 2H, CH_2Cl), 4.39 (q, J = 7.1 Hz, 2H, CH_3CH_2), 1.40 (t, J = 7.1 Hz, 3H, CH_3); ^{13}C NMR (67.9 MHz, $CDCl_3$) 166.01 (C=O), 142.02 (*p*), 130.39 (*i*), 129.91 (*o*), 128.38 (*m*), 61.10 (CH_2), 45.42 (CH_2Cl), 14.35 (CH_3); MS: (EI, 70 eV) *m/z* 200 (M^+ + 2, 6), 198 (M^+, 22), 155 (M^+ + 2 - EtO, 31), 153 (M^+ - EtO, 100); HRMS: (EI, 70 eV) calcd for $C_{10}H_{11}ClO_2$ 198.0448 found *m/z* 198.0444 (M^+). Anal. Calcd for $C_{10}H_{11}ClO_2$: C, 60.46; H, 5.58; Cl, 17.85. Found: C, 60.32; H, 5.60; Cl, 17.65.

Ethyl 2-chloro-2-phenylpropanoate (3q). According to the general procedure, this compound was prepared from $HSiMe_2Cl$, **1q**, benzil and $InCl_3$ in dichloromethane to give the product as a colorless liquid after distillation under reduced pressure: bp 80 ℃/ 0.11 mmHg; ^1H NMR (270 MHz, $CDCl_3$) δ 7.43-7.31 (m, 5H, aroma), 5.35 (dd, J = 5.81 Hz, 8.91 Hz, 1H, 3-H), 4.16 (q, J = 6.83 Hz, 2H, 1'-H), 3.17 (dd, J = 8.91 Hz, 15.66 Hz, 1H, 2-H^A), 3.02 (dd, J = 5.81 Hz, 15.66 Hz, 3H, 2-H^B), 1.23 (t, J = 6.83 Hz, 3H, 2'-H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 169.52 (s, C=O), 140.24 (s, *ipso*-Ph), 128.75 (d, Ph), 128.68 (d, Ph), 126.89 (d, Ph), 61.00 (t, C-1'), 58.08 (d, C-3), 44.87 (t, C-2), 14.08 (q, C-2'); IR (neat) 1740 cm^{-1} (C=O); MS (EI, 70 eV) 214 (M^+ + 2, 20), 212 (M^+, 57), 183 (M^+ - C_2H_5, 37), 167 (M^+ - OEt, 19), 91 (Bn, 11), 77 (Ph, 29); HRMS (EI, 70 eV) calcd for ($C_{11}H_{13}O_2Cl$) 212.0604 found for *m/z* 212.0613 (M^+).

Reaction of 1q with PCl_3. To a solution of alcohol **1q** (1.0 mmol) in dry dichloromethane (2 mL) was added PCl_3 (1.0 mmol) at rt for 1 h. Aqueous $NaHCO_3$ (15%, 10mL) was added to the reaction mixture. The mixture was extracted with ethyl acetate. The organic layer was washed with water and dried over $MgSO_4$. The volatiles were evaporated under reduced pressure, and the residue showed a complicated mixture by NMR mesurement.

Reaction of 1q with PCl_5. To a solution of alcohol **1q** (1.0 mmol) in dry CCl_4 (1 mL) was added PCl_5 (1.0 mmol) at 77 ℃ for 30 min. Aqueous $NaHCO_3$ (15%, 10mL) was added to the reaction mixture. The mixture was extracted with ethyl acetate. The organic layer was washed with water and dried over $MgSO_4$. The volatiles were evaporated under reduced pressure, and the residue showed the formation of **3q** (66%) and ethyl-3-phenyl-2-propenoate (5%) by NMR measurement.

Reaction of 1q with PPh_3/CCl_4. To a solution of alcohol **1q** (1.0 mmol) in dry CCl_4 (1 mL) was added PPh_3 (1.3 mmol) at 77 ℃ for 12 h. Aqueous $NaHCO_3$ (15%, 10mL) was added to the reaction mixture. The mixture was extracted with ethyl acetate. The organic layer was washed with water and dried over $MgSO_4$.The volatiles were evaporated under reduced pressure, and the residue showed the formation of **3q** (62%) and ethyl-3-phenyl-2-propenoate (8%) by NMR measurement.

Methanol mediated procedure for chlorination of alcohol 1r (Tables 2, entry 17). To a mixture of $InCl_3$ (0.1 mmol), benzil (2.0 mmol) and methanol (2.0 mmol) in dichloromethane (4.0 mL) was added $HSiMe_2Cl$ (2.2 mmol) under nitrogen. The reaction mixture was stirred for 1 h with generating quantitative H_2. The addition of the alcohol **1r** and the mixture was stirred for 0.1 h. The resulting mixture was poured into aquous $NaHCO_3$ (50 mL) and extracted with EtOAc (50 mL).

The organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The spectral data of **3r** was in an excellent agreement with the reported data.[3]

Selective Chlorination of Unsymmetrical Diol 10.

Me_2SiHCl/benzil/$InCl_3$ System; 15-Chloro-15-methylhexadecan-1-ol (11). To a mixture of $InCl_3$ (0.1 mmol), benzil (2.0 mmol) and alcohol **10** (2.0 mmol) in dichloromethane (4.0 mL) was added $HSiMe_2Cl$ (2.2 mmol) under nitrogen. The reaction mixture was stirred at room temperature for 12 h. The resulting mixture was poured into EtOAc (50 mL) and washed by aqueous $NaHCO_3$ (50 mL). The organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The volatiles were evaporated and the residue was purified by chromatography (ethyl acetate) on silica gel to give the product **11**. Futher purification was performed by distillation under reduced pressure to give the colorless liquid, which turned to a white solid after 1 h: bp: 150 °C / 0.1 mmHg; mp: 36 °C; IR: (KBr) 3367 (OH) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) 3.53 (t, J = 6.8 Hz, 2H, 1-H_2), 2.78 (brs, 1H, OH, D_2O-exchangeable), 1.67-1.63 (m, 2H, 14-H_2), 1.52-1.45 (m, 2H, 2-H_2), 1.49 (s, 6H, 16-H_3, 15-CH_3), 1.41-1.38 (m, 2H, 13-H_2), 1.24-1.20 (m, 20H, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12-H_2); ^{13}C NMR (150 MHz, $CDCl_3$) 71.06 (s, C-15), 62.61 (t, C-1), 45.98 (t, C-14), 32.57 (t, C-2), 32.27 (t, C-16), Some signals appear between 29.62-29.36 ppm as a broad peak, 25.66 (t, C-3), 24.99 (t, C-13); MS: (EI, 70 eV) *m/z* 254 (M^+ - HCl, 3), 236 (M^+ - HCl - H_2O, 6), 69 (100); HRMS: (CI, 70 eV) calcd for $C_{17}H_{35}O$ 255.2688 found *m/z* 255.2675 (M^+ + 1 - HCl). Anal. Calcd for $C_{17}H_{35}ClO$: C, 70.19; H, 12.13; Cl, 12.19. Found: C, 70.31; H, 11.98; Cl, 12.27.

PPh_3/CCl_4 System; 16-Chloro-2-methylhexadecan-2-ol (12). To a solution of alcohol **10** (1.0 mmol) in dry CCl_4 (1 mL) was added PPh_3 (1.3 mmol) at 77 °C for 12 h. Aqueous $NaHCO_3$ (15%, 10mL) was added to the reaction mixture. The mixture was extracted with ethyl acetate. The organic layer was washed with water and dried over $MgSO_4$. The volatiles were evaporated and the residue was purified by distillation under reduced pressure to give the product **12** as a colorless liquid: bp: 160 °C / 0.1 mmHg; IR: (neat) 3371 (OH) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) 3.53 (t, J = 6.8 Hz, 2H, 16-H_2), 1.76 (tt, J = 7.4, 6.8 Hz, 2H, 15-H_2), 1.48-1.46 (brs, 1H, OH, D_2O-exchangeable), 1.47-1.45 (m, 2H, 3-H_2), 1.42 (tt, J = 7.4, 7.4 Hz, 2H, 14-H_2) 1.35-1.33 (m, 2H, 4-H_2), 1.29-1.25 (m, 18H, 5, 6, 7, 8, 9, 10, 11, 12 and 13-H_2), 1.20 (s, 6H, 1-H_3, 2-CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) 71.06 (s, C-2), 45.23 (t, C-16), 44.01 (t, C-14), 32.67 (t, C-15), 30.23 (C-5), Some signals appear between 29.64-29.49 ppm as a broad peak, 29.24 (C-1, 2-CH_3), 28.92 (C-13), 26.91 (t, C-14), 24.39 (t, C-4); MS: (EI, 70 eV) *m/z* 277 (M^+ + 2 - Me, 5), 275 (M^+ - Me, 14), 274 (M^+ + 2 - H_2O, 0.7), 272 (M^+ - H_2O, 2), 59 (100); HRMS: (EI, 70 eV) calcd for $C_{17}H_{33}Cl$

272.2271 found *m/z* 272.2289 (M^+ - H_2O). Anal. Calcd for $C_{17}H_{35}ClO$: C, 70.19; H, 12.13; Cl, 12.19; O, 5.50. Found: C, 69.93; H, 11.83; Cl, 11.95.

PCl_5 System. To a solution of alcohol **10** (1.0 mmol) in dry CCl_4 (1 mL) was added PCl_5 (0.5 mmol) at 77 °C for 12 h. Aqueous $NaHCO_3$ (15%, 10mL) was added to the reaction mixture. The mixture was extracted with ethyl acetate. The organic layer was washed with water and dried over $MgSO_4$. The volatiles were evaporated under reduced pressure, and the residue showed the formation of **12** (45%).

Competitive Chlorination between 1f and 13.

Me_2SiHCl/benzil/$InCl_3$ System. To a mixture of $InCl_3$ (0.1 mmol), benzil (2.0 mmol) and alcohols **1f** (2.0 mmol) and **13** (2.0 mmol) in dichloromethane (4.0 mL) was added $HSiMe_2Cl$ (2.2 mmol) under nitrogen. The reaction mixture was stirred at room temperature for 12 h. The resulting mixture was poured into diethyl ether and washed by aqueous $NaHCO_3$ (50 mL). The organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The volatiles were evaporated under reduced pressure, and the residue showed formation of **3f** (90%) and recovery of **13** (93%) by NMR measurement.

PPh_3/CCl_4 System. To a solution of alcohols **1f** (1.0 mmol) and **13** (1.0 mmol) in dry CCl_4 (1 mL) was added PPh_3 (1.3 mmol) at 77 °C for 1 h. Aqueous $NaHCO_3$ (15%, 10mL) was added to the reaction mixture. The mixture was extracted with diethyl ether. The organic layer was washed with water and dried over $MgSO_4$. The volatiles were evaporated under reduced pressure, and the residue showed the formation of **14** (85%) and recovery of **1f** (92%) by NMR measurement.

PCl_5 System. To a solution of alcohols **1f** (1.0 mmol) and **13** (1.0 mmol) in dry CCl_4 (1 mL) was added PCl_5 (0.5 mmol) at 77 °C for 30 min. Aqueous $NaHCO_3$ (15%, 10mL) was added to the reaction mixture. The mixture was extracted with diethyl ether. The organic layer was washed with water and dried over $MgSO_4$. The volatiles were evaporated under reduced pressure, and the residue showed the formation of **14** (73%) and **3f** (15%). The recovery of **1f** (ca. 80%) was observed.

Control Experiment (Scheme 1).

Uncatalyzed Reaction of 1a with $HSiMe_2Cl$. To a reaction mixture of alcohol **1a** (2 mmol) in dichloromethane (4 mL) was added $HSiMe_2Cl$ (2.2 mmol) at room temperature for 1 h. Removal of the volatiles gave a crude mixture. The formation of silyl ether **4** (ca. 30%) was

confirmed by ^{1}H NMR (CD_2Cl_2). The signals were in an excellent agreement with those of purely isolated authentic sample, that was prepared as follows (Chart A and Chart B).

1-Phenyl-2-dimethylsiloxypropane (4). To a mixture of ammonium chloride (0.07 g, 1.3 mmol) and 1-phenyl-2-propanol (5.54 g, 41 mmol) in a single neck round bottom flask was added 1,1,3,3-tetramethyldisilazane (5.12 g, 38 mmol). The mixture was stirred in room temperature for 20 h. Removal of the ammonia and unreacted disilazane by evaporation gave a crude mixture. The resultant mixture was distilled to give the product as a colorless liquid (3.21 g, 40%): bp: 75 °C / 0.1 mmHg; IR: (neat) 2114 (Si-H), 906 (Si-H) cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) 7.31-7.17 (m, 5H, aroma), 4.84 (sep, J = 2.9 Hz, 1H, Si-H satellite signals observed $^1J_{Si\text{-}H}$ = 200.9 Hz), 3.97 (qdd, J = 6.1, 7.1, 5.9 Hz, 1H, 2-H), 2.75 (dd, J = 13.2, 7.1 Hz, 1H, 1-H^A), 2.67 (dd, J = 13.2, 5.9 Hz, 1H, 1-H^B), 1.10 (d, J = 6.1 Hz, 3H, 3-H$_3$), 0.103 (d, J = 2.9 Hz, 3H, Si-CH$_3^A$), 0.014 (d, J = 2.9 Hz, 3H, Si-CH$_3^B$); ^{1}H NMR (270 MHz, CD_2Cl_2) 7.30-7.17 (m, 5H, aroma), 4.49 (sep, J = 2.9 Hz, 1H, Si-H, satellite signals observed $^1J_{Si\text{-}H}$ = 200.4 Hz), 3.98 (qdd, J = 6.1, 6.8, 5.6 Hz, 1H, 2-H), 2.75 (dd, J = 13.2, 6.8 Hz, 1H, 1-H^A), 2.67 (dd, J = 13.2, 5.6 Hz, 1H, 1-H^B), 1.17 (d, J = 6.1 Hz, 3H, 3-H$_3$), 0.092 (d, J = 2.9 Hz, 3H, Si-CH$_3^A$), 0.015 (d, J = 2.9 Hz, 3H, Si-CH$_3^B$); ^{13}C NMR (67.9 MHz, $CDCl_3$) 139.06 (*i*), 129.49 (*m*), 128.04 (*o*), 126.01 (*p*), 71.49 (C-2), 45.92 (C-1), 23.22 (C-3), -1.07 (Si-C^A), -1.36 (Si-C^B); MS: (EI, 70 eV) *m/z* 194 (M$^+$, 3), 103 (M$^+$ - PhCH$_2$, 100); ^{13}C NMR (67.9 MHz, CD_2Cl_2) 139.36 (s, *i*), 129.64 (d, *m*), 128.06 (d, *o*), 126.03 (d, *p*), 71.40 (d, C-2), 45.90 (t, C-1), 23.13 (q, C-3), -1.23 (q, Si-C^A), -1.48 (q, Si-C^B); HRMS: (EI, 70 eV) calcd for $C_{11}H_{18}OSi$ 194.1127 found *m/z* 194.1120 (M$^+$). Anal. Calcd for $C_{11}H_{18}OSi$: C, 67.98; H, 9.34. Found: C, 67.69; H, 9.27.

Catalyzed Reaction of 1a with $HSiMe_2Cl$. To a mixture of $InCl_3$ (0.025 mmol) and benzil (0.5 mmol) in CD_2Cl_2 (0.75 mL) in NMR tube was added the alcohol **1a** (0.5 mmol) and $HSiMe_2Cl$ (0.65 mmol). After 2 h, the signal corresponding to silyl ether **5** appeared. The signals were in an excellent agreement with those of purely isolated authentic sample, that was prepared as follows (Chart C and Chart D). Further stirring for 18 h, the signals of chloride **3** were observed (Chart E and Chart F).

1-Phenyl-2-(chlorodimethylsiloxy)propane (5). To a solution of 1-phenyl-2-propanol (8.2 g, 60 mmol) and triethylamine (9.1 g, 90 mmol) in benzene (35 mL) was slowly added a solution of Me_2SiCl_2 (11.6 g, 90 mmol) in benzene (65 mL) at ambient temperature for 1 h. The mixture was stirred at 60 °C for 3 h. Removal of the resultant salt by the centrifugal separation and evaporation of solvents gave a crude mixture. The resultant mixture was distilled to give the pure product as a colorless liquid (6.2 g, 45%): bp: 65 °C / 0.15 mmHg; IR: (neat) 3028, 2974, 2912 (alkyl) cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) 7.32-7.17 (m, 5H, aroma), 4.19 (qdd, J = 6.1, 7.3, 5.6 Hz, 1H, 2-H), 2.80 (d, J = 13.4, 7.3 Hz, 1H, 1-H^A), 2.71 (dd, J = 13.4, 5.6 Hz, 1H, 1-H^B), 1.25 (d, J

= 6.1 Hz, 3H, 3-H_3), 0.39 (s, 3H, Si-$CH_3{}^A$), 0.13 (s, 3H, Si-$CH_3{}^B$); ^{1}H NMR (270 MHz, CD_2Cl_2) 7.32-7.18 (m, 5H, aroma), 4.20 (qdd, *J* = 6.1, 7.1, 5.6 Hz, 1H, 2-H), 2.79 (d, *J* = 13.2, 7.1 Hz, 1H, 1-H^A), 2.72 (dd, *J* = 13.2, 5.6 Hz, 1H, 1-H^B), 1.24 (d, *J* = 6.1 Hz, 3H, 3-H_3), 0.39 (s, 3H, Si-$CH_3{}^A$), 0.15 (s, 3H, Si-$CH_3{}^B$); ^{13}C NMR (67.9 MHz, $CDCl_3$) 138.72 (*i*), 129.58 (*m*), 128.14 (*o*), 126.20 (*p*), 71.29 (C-2), 45.65 (C-1), 23.12 (C-3), 2.59 (Si-C^A), 1.82 (Si-C^B); ^{13}C NMR (67.9 MHz, CD_2Cl_2) 138.94 (s, *i*), 129.73 (d, *m*), 128.19 (d, *o*) 126.25 (d, *p*), 71.37 (d, C-2), 45.63 (t, C-1), 23.04 (q, C-3), 2.41 (Si-C^A), 1.64 (Si-C^B); MS: (EI, 70 eV) *m/z* 230 (M^+ + 2, 0.7), 228 ($M^{+\cdot}$ 2.0), 139 (M^+ + 2 - $PhCH_2$, 35), 137 (M^+ -$PhCH_2$, 100); HRMS: (EI, 70 eV) calcd for $C_{11}H_{17}ClOSi$ 228.0737 found *m/z* 228.0745 (M^+).

References

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Chart A. Authentic sample **4** (CD_2Cl_2)

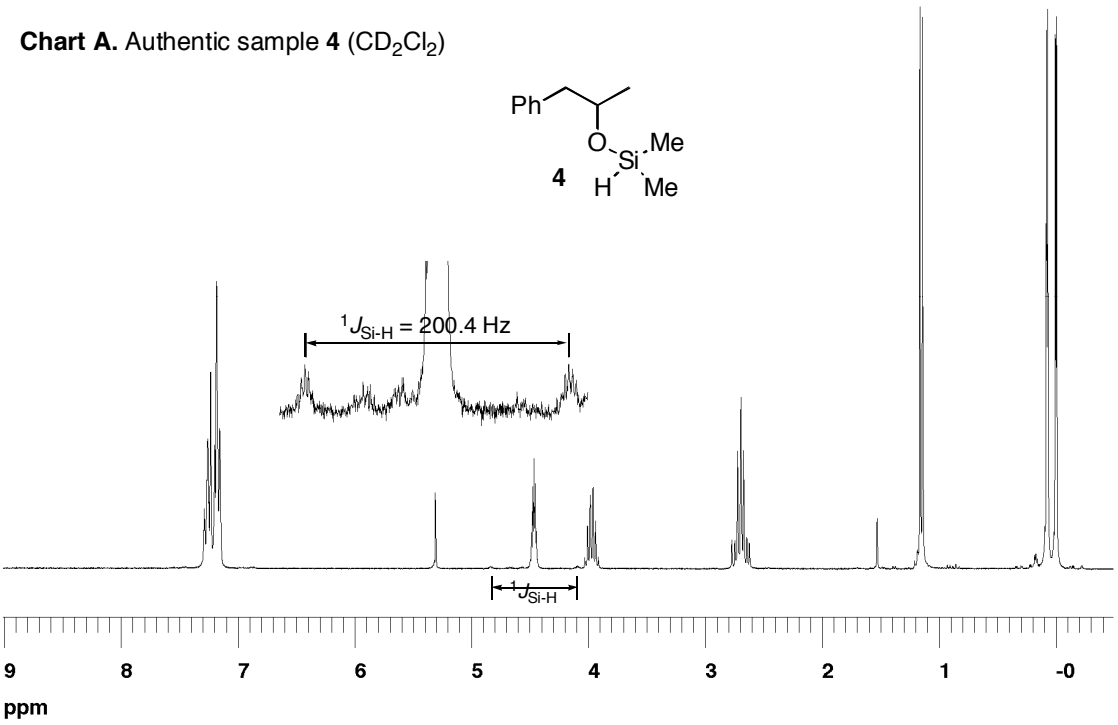

Chart B. Uncatalyzed reaction of **1a** with $HSiMe_2Cl$ (CD_2Cl_2)

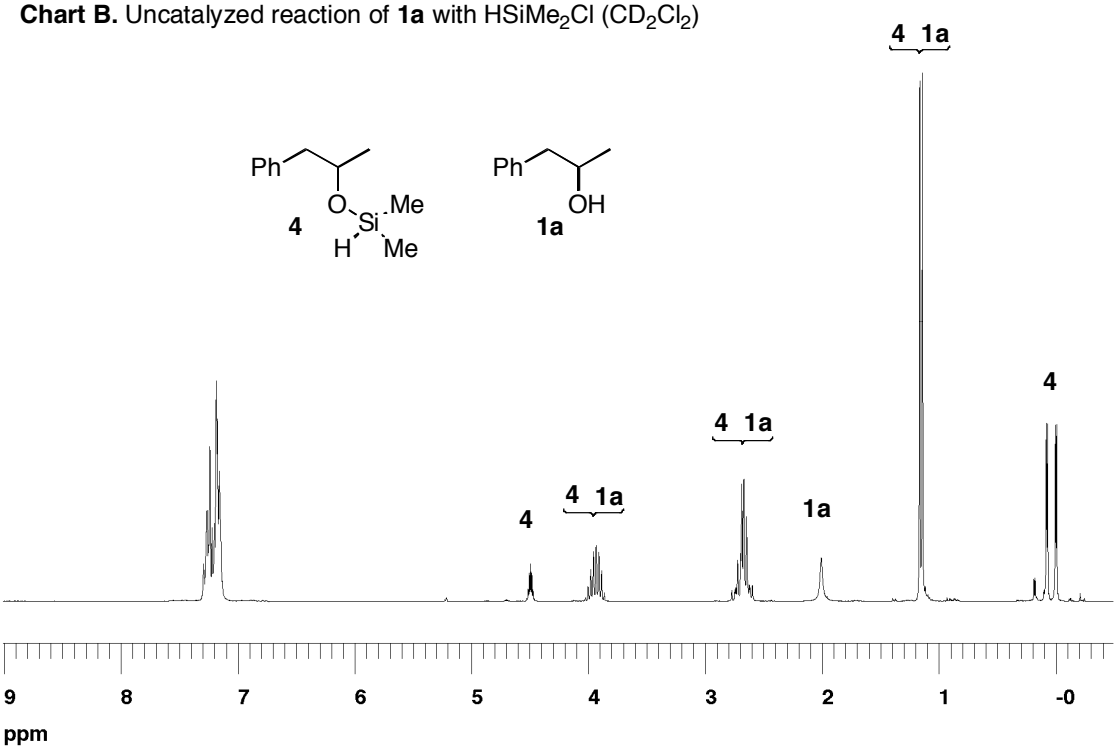

Chart C. Authentic sample **5** (CD_2Cl_2)

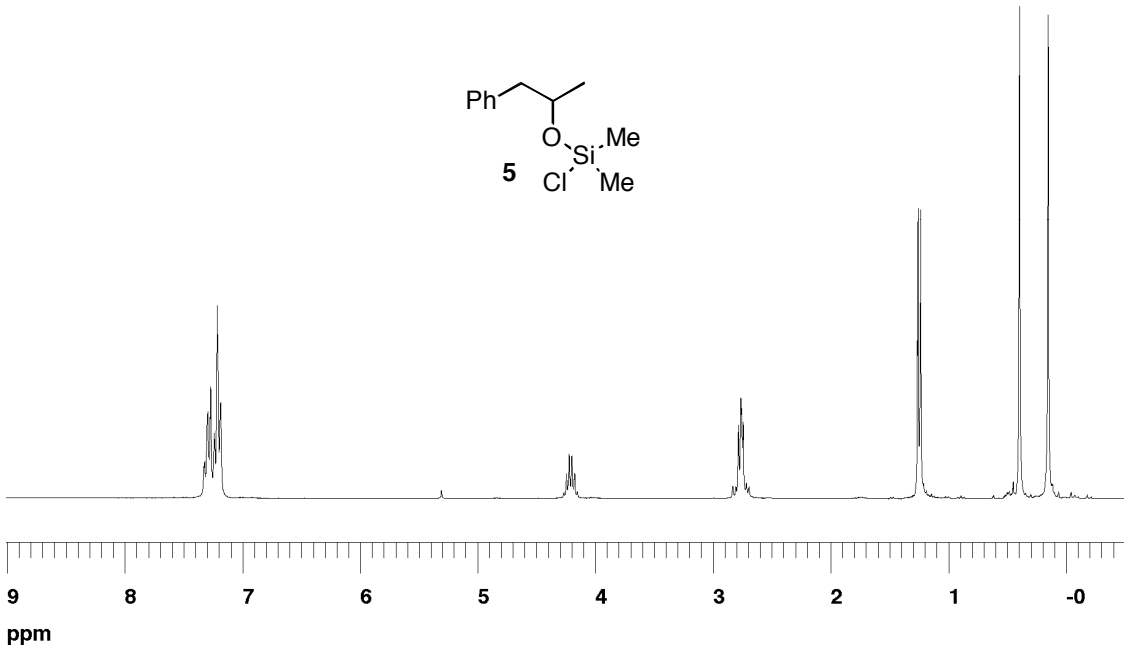

Chart D. Catalyzed reaction of **1a** with $HSiMe_2Cl$ after 2 h (CD_2Cl_2)

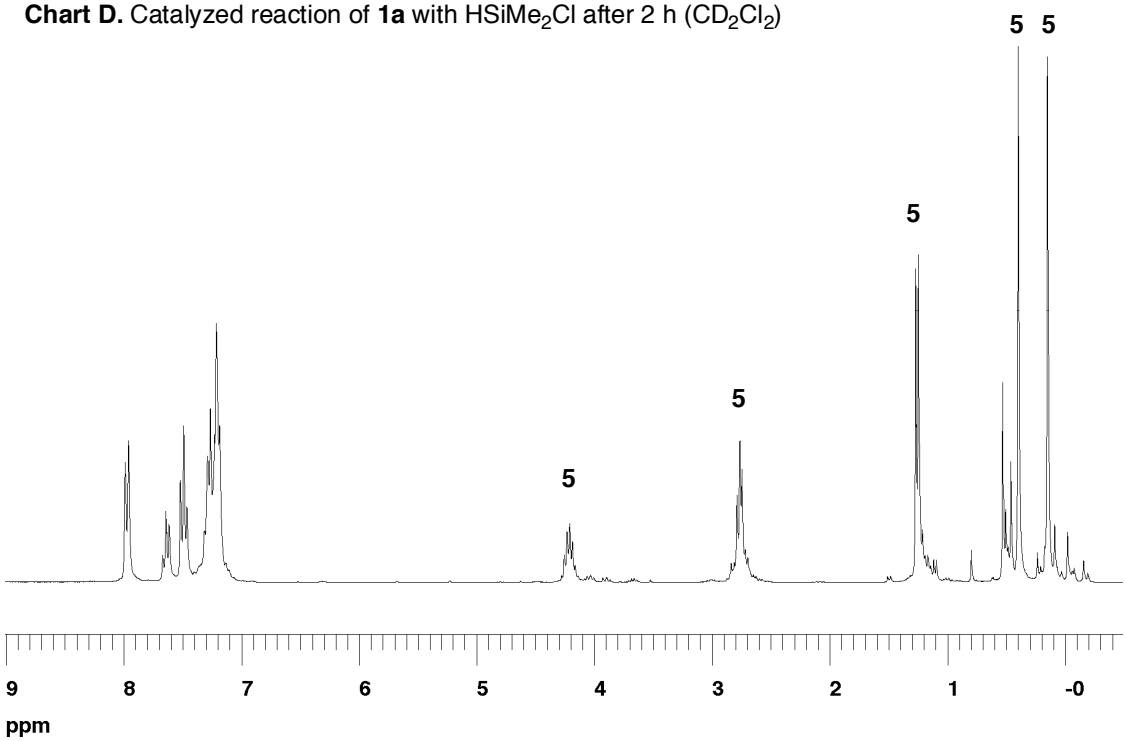

Chart E. Authentic sample **3a** (CD_2Cl_2)

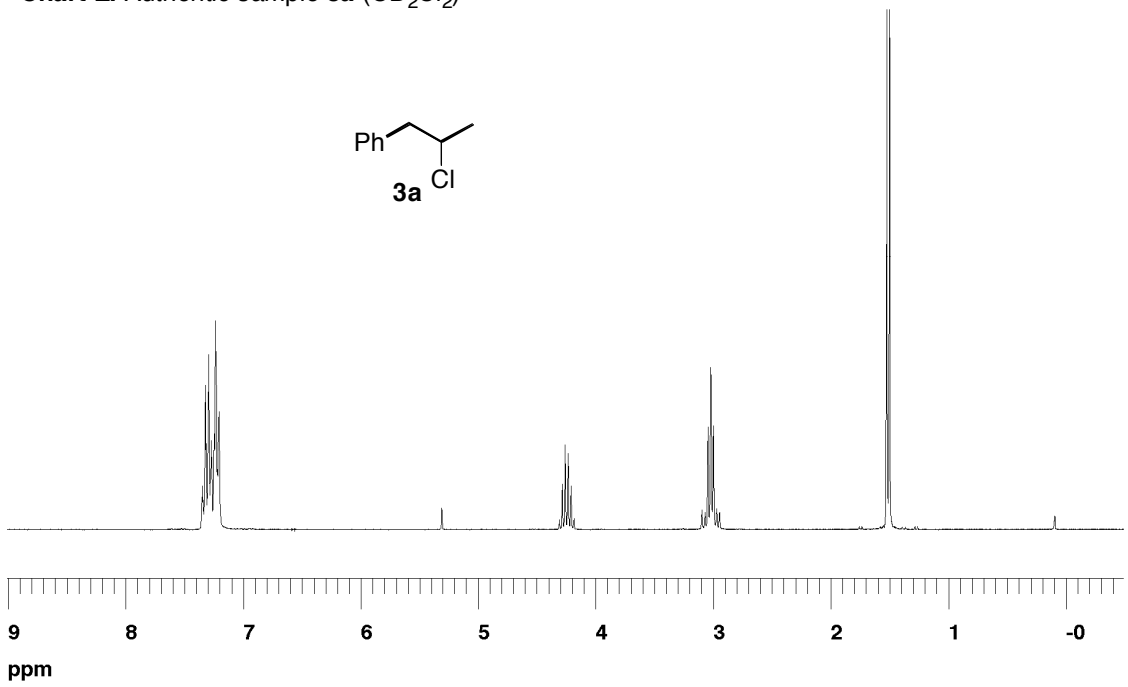

Chart F. Catalyzed reaction of **1a** with $HSiMe_2Cl$ after 20 h (CD_2Cl_2)