Direct Chlorination of Alcohols with Chlorodimethylsilane Catalyzed by a Gallium Trichloride/Tartrate System under Neutral Conditions

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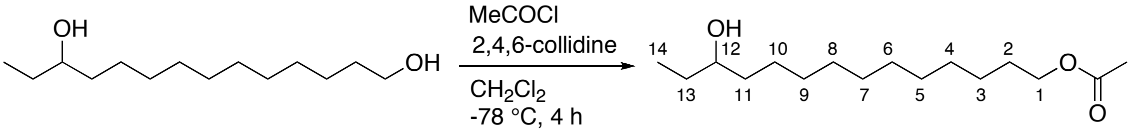
Supporting Information

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 400, 100, and 78.7 MHz spectrometer, respectively, with TMS as internal standard. Mass spectra were recorded on a JEOL JMS-DS303. All reactions were carried out under nitrogen. 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.

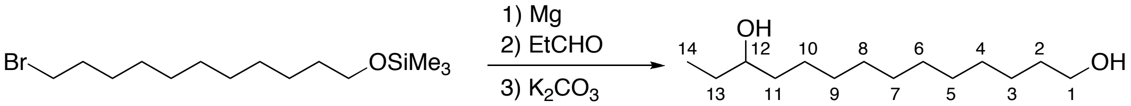
Materials. Dichloromethane, dehydrated (stabilized with 2-methyl-2-butene) was used without purification. All regents in Table 1 ($HSiMe_2Cl$ **2**, **4a-e**, $GaCl_3$, $GaBr_3$, GaI_3, $Ga(OTf)_3$, $InCl_3$, $AlCl_3$, $ZnCl_2$, $TiCl_4$, and $BiCl_3$) and alcohols **1a**-**f**, **1j**, **1m**, **1n** were commercially available. The alcohols **1k**[1] and **1l**[2] were prepared by known method. The alcohols **1g-i** and silylether **9** were prepared as shown below.

12-Hydroxytetradecyl acetate (1g)



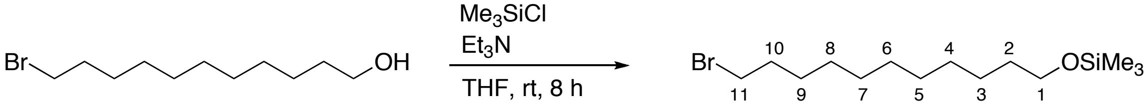
To a solution of tetradecane-1,12-diol (10 mmol) in CH_2Cl_2 (20 mL) were added 2,4,6-collidine (20 mmol) and acetyl chloride (13 mmol) at -78 °C.[3] The reaction mixture was stirred for 4 h at -78 °C. The mixture was quenched by HCl aq (1M, 10 mL) and extracted with CH_2Cl_2 (20 x 3 mL). The collected organic layers were washed with $NaHCO_3$ aq (20 x 2 mL) and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by column chromatography (hexane/EtOAc, 80:20). Further purification was employed by recrystalization to give 12-hydroxytetradecyl acetate as a white solid (5.76 mmol, 58 %). mp: 35 °C; IR: (KBr) 3352 (OH), 1732 (C=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 4.05 (t, J = 6.8 Hz, 2H, 1-H_2), 3.52 (brs, 1H, 12-H), 2.05 (s, 3H, CH_3CO), 1.63-1.27 (m, 23H, 2-H_2, 3-H_2, 4-H_2, 5-H_2, 6-H_2, 7-H_2, 8-H_2 9-H_2, 10-H_2, 11-H_2, 13-H_2 and OH), 0.94 (t, J = 7.6 Hz, 3H, 14-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 171.3 (C, CO), 73.3 (CH, C-12), 64.6 (CH_2, C-1), 36.9 (CH_2), 30.1 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 29.2 (CH_2), 36.9 (CH_2), 28.6 (CH_2), 25.9 (CH_2), 25.6 (CH_2), 21.0 (CH_3, *C*H_3CO), 9.9 (CH_3, C-14); MS: (CI, 200 eV) *m*/*z* 273 (M^+ + 1, 19), 255 (M^+ + 1 - H_2O, 100), 195 (M^+ + 1 - H_2O - CH_3COOH, 48); HRMS: (CI, 200 eV) calcd for $C_{16}H_{33}O_3$ 273.2429 found *m*/*z* 273.2425 (M^+ + 1). Anal. Calcd for $C_{16}H_{32}O_3$: C, 70.54; H, 11.84. Found: C, 70.48; H, 11.61.

Tetradecane-1,12-diol



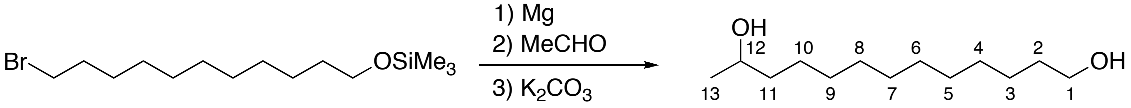
To a solution of Grignard reagent in THF (20 mL), which was synthesized from Mg (30 mmol) and 11-bromo-1-trimethylsilyloxyundecane (20 mmol) was added propionaldehyde (20 mmol) in THF (5 mL) dropwise at 0 °C. The reaction mixture was stirred for 20 h at rt. The mixture was cooled to 0 °C, then quenched by HCl (1N, 50 mL) and extracted with ether (50 x 3 mL). The collected organic layers were dried over $MgSO_4$. The solvent was evaporated and added MeOH (60 mL). To a soluion was added K_2CO_3 in some portions at 0 °C. The reaction mixture was stirred for 2.5 h at rt. The mixture was cooled to 0 °C, then quenched by H_2O (50 mL) and extracted with ether (50 x 3 mL). The collected organic layers were dried over $MgSO_4$. The solvent was evaporated and purified by the residue was purified by column chromatography (hexane/EtOAc, 50:50). Further purification was employed by recrystalization to give tetradecane-1,12-diol as a white solid (6.21 mmol, 31 %). mp: 51-53 °C; IR: (KBr) 3340 (OH) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 3.64 (t, $J = 6.5$ Hz, 2H, 1-H_2), 3.52 (m, 1H, 12-H), 1.60-1.20 (m, 24H, 2-H_2, 3-H_2, 4-H_2, 5-H_2, 6-H_2, 7-H_2, 8-H_2, 9-H_2, 10-H_2, 11-H_2, 13-H_2 and two OHs), 0.94 (t, $J = 7.6$ Hz, 3H, 14-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 73.3 (CH, C-12), 63.0 (CH_2, C-1), 36.9 (CH_2), 32.8 (CH_2, C-2), 30.1 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 25.7 (CH_2), 25.6 (CH_2), 9.9 (CH_3, C-14); MS: (CI, 200 eV) *m*/*z* 231 (M^+ + 1, 8.0), 213 (M^+ + 1 - H_2O, 100); HRMS: (CI, 200 eV) calcd for $C_{14}H_{31}O_2$ 231.2324 found *m*/*z* 231.2325 (M^+ + 1). Anal. Calcd for $C_{14}H_{30}O_2$: C, 72.99; H, 13.12. Found: C, 72.76; H, 13.03.

11-Bromo-1-trimethylsiloxyundecane



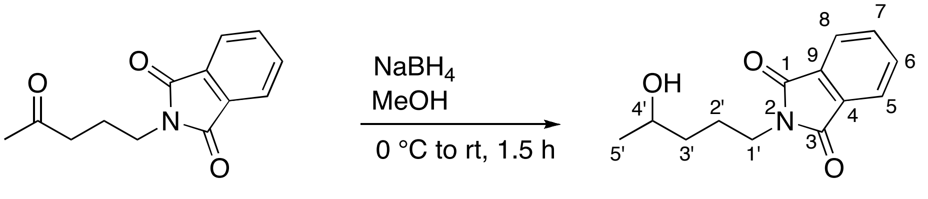
To a solution of 11-bromo-1-undecanol (80 mmol) in THF (100 mL) were added TMSCl (120 mmol) and Et_3N (120 mmol). The reaction mixture was stirred for 8 h at rt. Evaporation of solvents and removal of the resultant salt by filtration to gave a crude mixture. The resultant mixture was distilled to give the pure product as a colorless liquid (22.6 g, 88%). bp: 94 °C/ 0.05 mmHg; IR: (KBr) 2927, 1250, 1099 (Si-O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 3.57 (t, $J = 6.8$ Hz, 2H, 1-H_2), 3.41 (t, $J = 6.9$ Hz, 2H, 11-H_2), 1.85 (tt, $J = 6.9, 6.9$ Hz, 2H, 10-H_2), 1.59-1.47 (m, 2H, 9-H_2), 1.47-1.36 (m, 2H, 2-H_2), 1.36-1.19 (m, 12H, 3-H_2, 4-H_2, 5-H_2, 6-H_2, 7-H_2 and 8-H_2), 0.11 (s, 9H, $SiMe_3$); ^{13}C NMR: (100 MHz, $CDCl_3$) 62.7 (CH_2, C-1), 34.1 (CH_2, C-11), 32.8 (CH_2, C-9 or C-10), 32.7 (CH_2, C-10 or C-9), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.4 (CH_2), 28.7 (CH_2), 28.2 (CH_2), 25.8 (CH_2), -0.5 (CH_3, $SiMe_3$); MS: (CI, 200 eV) *m*/*z* 325 (M^+ + 3, 100), 323 (M^+ + 1, 99.8); HRMS: (CI, 200 eV) calcd for $C_{14}H_{32}BrOSi$ 325.1385 found *m*/*z* 325.1390 (M^+ + 3) and calcd for $C_{14}H_{32}BrOSi$ 323.1406 found *m*/*z* 323.1387 (M^+ + 1). Anal. Calcd for $C_{14}H_{31}BrOSi$: C, 52.00; H, 9.66. Found: C, 52.08; H, 9.61.

Tridecane-1,12-diol (1h)



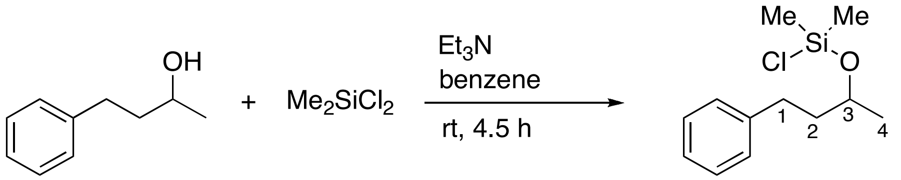
To a solution of Grignard reagent in THF (40 mL), which was synthesized from Mg (60 mmol) and 11-bromo-1-trimethylsilyloxyundecane (40 mmol) was added acetaldehyde (40 mmol) in THF (10 mL) dropwise at 0 °C. The reaction mixture was stirred for 1.5 h at rt. The mixture was cooled to 0 °C, then quenched by HCl (1N, 50 mL) and extracted with ether (100 x 3 mL). The collected organic layers were dried over $MgSO_4$. The solvent was evaporated and added MeOH (120 mL). To a soluion was added K_2CO_3 in some portions at 0 °C. The reaction mixture was stirred for 4 h at rt. The mixture was cooled to 0 °C, then quenched by H_2O (100 mL) and extracted with ether (70 x 3 mL). The collected organic layers were dried over $MgSO_4$. The solvent was evaporated and purified by the residue was purified by recrystalization to give tridecane-1,12-diol as a white solid (28.7 mmol, 72 %). mp: 49-50 °C; IR: (KBr) 3309 (OH) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 3.79 (m, 1H, 12-H), 3.64 (t, *J* = 6.5 Hz, 2H, 1-H_2), 1.64-1.22 (m, 24H, 2-H_2, 3-H_2, 4-H_2, 5-H_2, 6-H_2, 7-H_2, 8-H_2, 9-H_2, 10-H_2, 11-H_2, and two OHs), 1.18 (d, *J* = 6.4 Hz, 3H, 13-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 68.2 (CH, C-12), 63.1 (CH_2, C-1), 39.3 (CH_2), 32.8 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 25.8 (CH_2), 25.7 (CH_2), 23.5 (CH_3, C-13), some signals are obscured by similar chemical shifts.; MS: (CI, 200 eV) *m*/*z* 217 (M^+ + 1, 14), 199 (M^+ + 1 - H_2O, 100); HRMS: (CI, 200 eV) calcd for $C_{13}H_{29}O_2$ 217.2167 found *m*/*z* 217.2175 (M^+ + 1). Anal. Calcd for $C_{13}H_{28}O_2$: C, 72.17; H, 13.04. Found: C, 71.95; H, 12.74.

2-(4-Hydroxypentyl)-isoindole-1,3-dione (1i)



To a solution of crude 2-(4-oxo-pentyl)-isoindole-1,3-dione (ca.11 mmol) in MeOH (25 mL) was added $NaBH_4$ (5.5 mmol) in two portions at 0 °C. The reaction mixture was stirred for 1.5 h at rt. The mixture was cooled to 0 °C, then quenched by HCl aq (1M, 10 mL) and extracted with ether (20 x 3 mL). The collected organic layers were washed with $NaHCO_3$ aq (20 x 2 mL) and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by flash column chromatography (hexane/EtOAc, 50:50). Further purification was employed by distillation under reduced pressure to give the pure product as a pale yellow liquid (5.10 mmol, 58 %). bp: 185 °C / 0.4 mmHg; IR: (neat) 3444, 1774, 1709 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.83 (dd, *J* = 5.4, 3.0 Hz, 2H, 5-H and 8-H), 7.72 (dd, *J* = 5.4, 3.0 Hz, 2H, 6-H and 7-H), 3.85 (tq, *J* = 6.7, 6.7 Hz, 2H, 4'-H), 3.71 (t, 2H, 1'-H_2), 2.46 (s, 1H, OH), 1.85-1.70 (m, 2H, 3'-H_2), 1.50 (m, 2H, 2'-H_2), 1.19 (d, *J* = 6.7, 3H, 5'-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 168.4 (s, C-1 and C-3), 133.8 (d, C-6 and C-7), 131.9 (s, C-4 and C-9), 123.0 (d, C-5 and C-8), 67.2 (d, C-4'), 37.7 (d, C-1'), 35.9 (d, C-2'), 24.8 (t, C-3'), 23.3 (q, C-5'); MS: (EI, 70 eV) *m/z* 233 (M^+, 2.8), 173 (32), 161 (39), 160 (M^+ - $CH_2CH_2CHOHCH_3$, 100), 149 (51), 85 (23); HRMS: (EI, 70 eV) calcd for $C_{13}H_{15}NO_3$ 233.1052 found *m/z* 233.1048 (M^+). Anal. Calcd for $C_{13}H_{15}NO_3$: C, 66.94; H, 6.48; N, 6.00. Found: C, 66.71; H, 6.35; N, 5.95.

1-Phenyl-3-(chlorodimethylsiloxy)butane (9)



To a solution of 4-phenyl-2-butanol (9.0 g, 60 mmol) and triethylamine (10.6 g, 105 mmol) in benzene (30 mL) was slowly added a solution of Me_2SiCl_2 (13.5 g, 105 mmol) in benzene (60 mL) at room temperature for 30 min. The mixture was stirred at rt for 4 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 (2.4 g, 16%). bp: 54 °C / 0.03 mmHg; IR: (neat) 1261 cm^{-1}; ^1H NMR: (400 MHz, CD_2Cl_2) 7.26-7.13 (m, 5 H, aroma), 4.07 (tq, *J* = 6.1, 6.1 Hz, 1H, 2-H), 2.71 (ddd, *J* = 13.9, 10.9, 5.8 Hz, 1H, 1-H_A), 2.60 (ddd, *J* = 13.9, 10.3, 6.4 Hz, 1H, 1-H_B) 1.78 (m, 2H, 2-H_2), 1.23 (d, *J* = 6.1 Hz, 3H, 4-H_3), 0.45 (s, 3H, $SiMe_A$), 0.44 (s, 3H, $SiMe_B$); ^{13}C NMR: (100 MHz, CD_2Cl_2) 142.6 (s, *i*), 128.7 (d, *o* or *m*), 128.6 (d, *m* or *o*), 126.0 (d, *p*), 70.0 (d, C-3), 41.2 (t, C-2), 32.3 (t, C-1), 23.5 (q, C-4), 2.9 (q, $SiMe_A$), 2.6 (q, $SiMe_B$); MS: (CI, 200 eV) *m/z* 245 (M^+ + 3, 1.39), 243 (M^+ + 1, 3.32), 133 (M^+ +

1- $HOSiMe_2Cl$, 100); HRMS: (CI, 200 eV) calcd for $C_{12}H_{20}ClOSi$ 243.0972 found *m*/*z* 243.0964 ($M^+ + 1$).

Procedure for optimization of chlorination of alcohols (Table 1). According to the "General procedure for chlorination of alcohols catalyzed by $GaCl_3$/tartrate system (Table 2)" as shown below, the reactions were employed under the conditions noted in text.

General procedure for chlorination of alcohols catalyzed by $GaCl_3$/tartrate system (Table 2). To a solution of (+)-diethyl tartrate (0.1 mmol) in CH_2Cl_2 (1 mL) were added $GaCl_3$ in pentane (0.5 M, 0.1 mL, 0.05 mmol), alcohol **1** (1.0 mmol), and $HSiMe_2Cl$ **2** (1.3 mmol) under nitrogen. The reaction mixture was stirred under the conditions noted in text. H_2 gas generated for the first ca. 15 minutes. The mixture was quenched by addition of water (10 mL) and extracted with diethyl ether (10 x 3 mL). The collected 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.

General procedure for chlorination of alcohols catalyzed by $GaCl_3$ system (Table 3). To a solution of $GaCl_3$ (in pentane 0.5 M, 0.1 mL, 0.05 mmol) in CH_2Cl_2 (1 mL) were added alcohol **1** (1.0 mmol) and $HSiMe_2Cl$ **2** (1.3 mmol) under nitrogen. The reaction mixture was stirred under the conditions noted in text. The mixture was quenched by addition of water (10 mL) and extracted with diethyl ether (10 x 3 mL). The collected 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.

Mechanistic investigation. To a solution of (+)-diethyl tartrate (0.5 mmol) in CD_2Cl_2 (1 mL) were added $GaCl_3$ in pentane (0.5 M, 0.1 mL, 0.05 mmol) and $HSiMe_2Cl$ **2** (1.0 mmol) under nitrogen. The reaction mixture was stirred at rt for 15 min. H_2 gas generated for the first ca. 2 minutes. The mixture was observed by NMR spectroscopy and the formation of **5** was confirmed (Chart A1-3: ^{29}Si NMR of $HSiMe_2Cl$ is also shown for comparison.). To the mixture including **5** was added 1-octanol (1.0 mmol) and the mixture was stirred at rt for 6 h. The mixture was observed by NMR spectroscopy and the formation of chloro(octanoxy)silane **7** and diethyl tartrate **4a** was confirmed (Chart B1-3). The species **7** and **8** were assigned with the characteristic signals of the related compounds reported in the literature.[4] To a solution of $GaCl_3$ (in pentane 0.5 M, 0.1 mL, 0.05 mmol) in CH_2Cl_2 (1 mL) was added chlorosilyl ether **9** (1.0 mmol) under nitrogen. The reaction mixture was stirred at rt for 5 h. The mixture was quenched by water (10 mL) and extracted with diethyl ether (10 x 3 mL). The collected organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The formation of **3a** was observed by NMR (62% yield).

Chart A1 (^{1}H NMR).

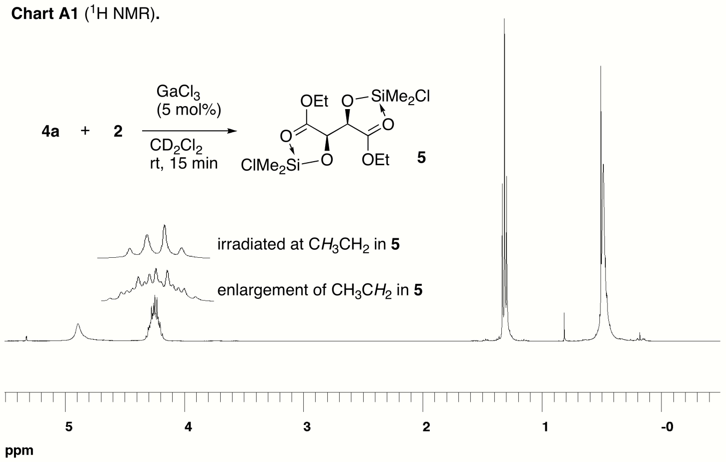


Chart A2 (^{13}C NMR).

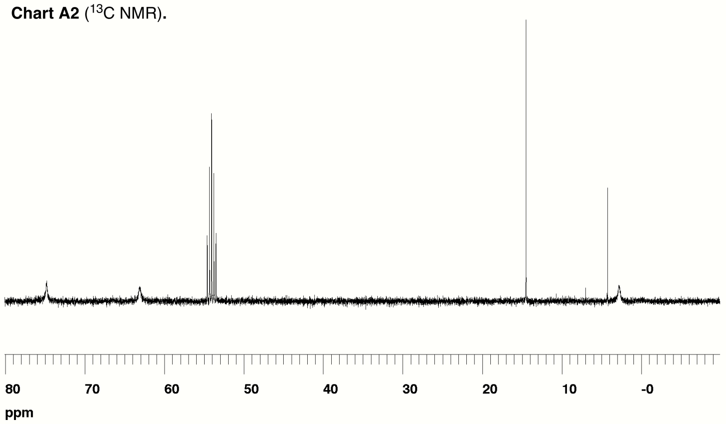
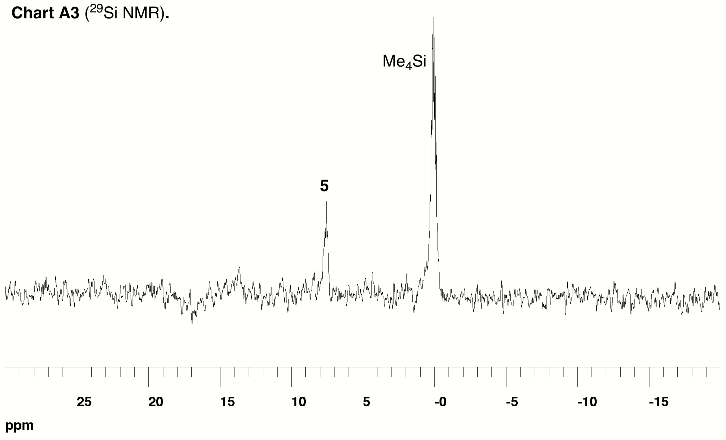


Chart A3 (^{29}Si NMR).



HSiMe$_2$Cl (^{29}Si NMR).

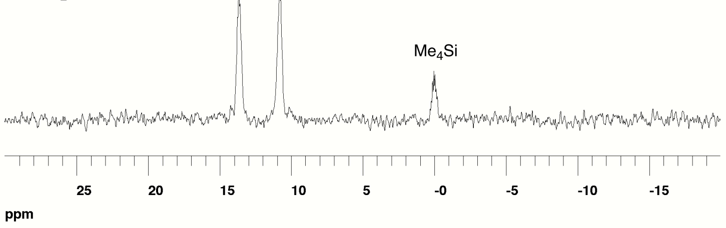


Chart B1 (^{1}H NMR).

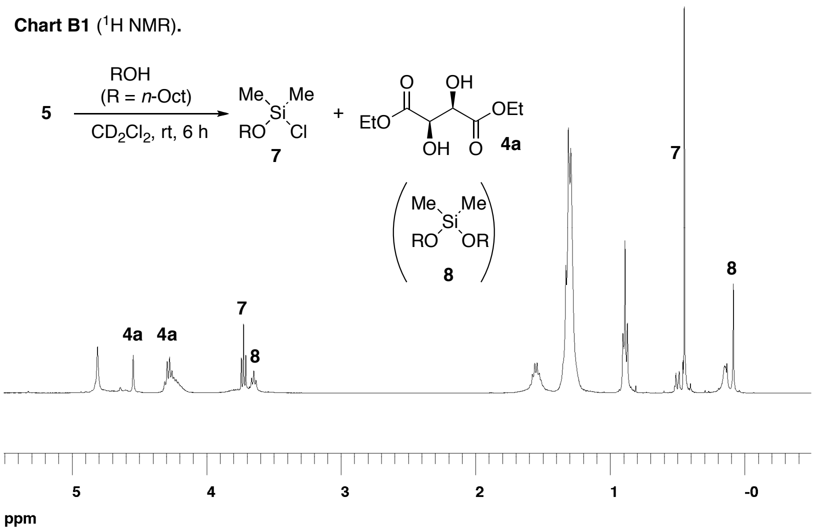


Chart B2 (^{13}C NMR).

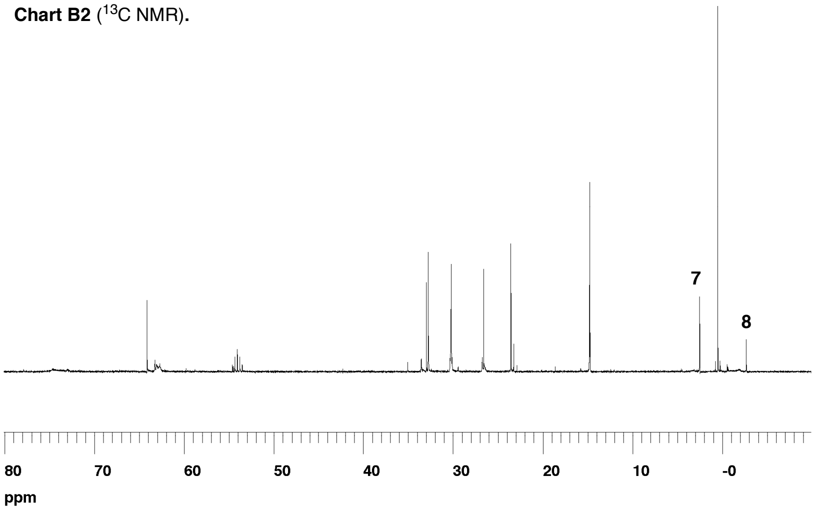
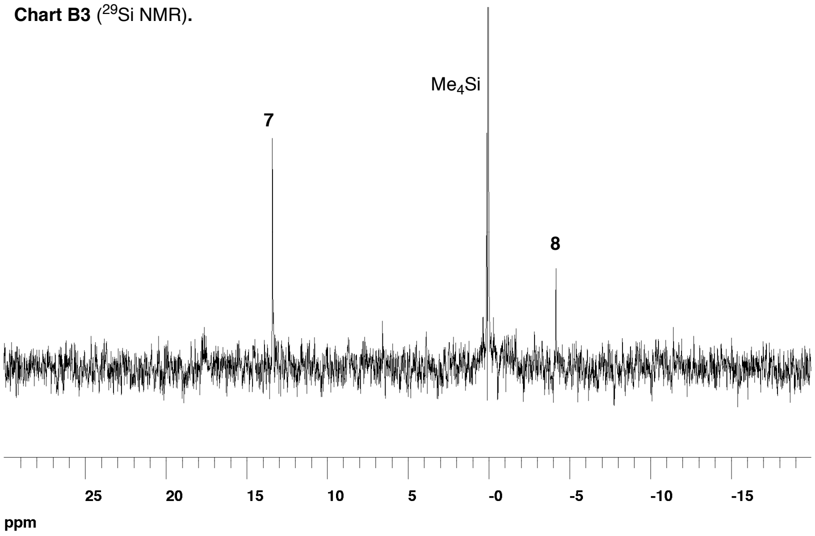
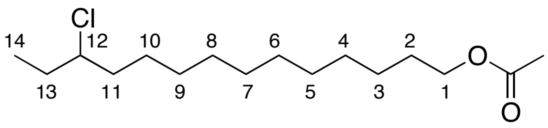


Chart B3 (^{29}Si NMR).



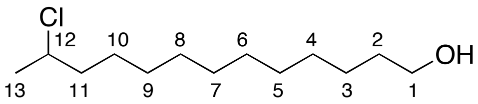
Product data. The spectral data of **3a**,[5] **3b**,[6] **3d**,[7] **3e**,[7] and **3k**[1] were in an excellent agreement with the reported data. The spectral data of **3c**, **3f**, **3m**, and **3n** were in an excellent agreement with those of commercially available products. Spectral data for the products, **3g**-**i**, **3j**, and **3l** are shown below.

12-Chlorotetradecyl acetate (3g)



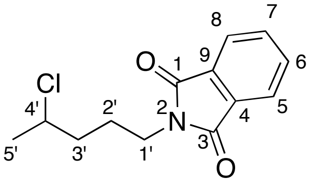
According to the general procedure, this compound was prepared from $HSiMe_2Cl$, **1g**, $GaCl_3$, and (+)-diethyl tartrate in dichloromethane to give the product as a colorless liquid after chromatography (hexane/EtOAc, 97:3). Further purification was performed by distillation under reduced pressure. Some rearrangement products were included: bp: 165 °C / 0.4 mmHg; IR: (neat) 2927 (C-H), 1743 (C=O), 1242 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 4.05 (t, J = 6.8 Hz, 2H, 1-H_2), 3.85 (m, 1H, 12-H), 2.05 (s, 3H, $COCH_3$), 1.03 (t, J = 7.4 Hz, 3H, 14-H_3) Other signals were not identified due to the overlap with those of rearrangement by-products; ^{13}C NMR: (100 MHz, $CDCl_3$) 171.3 (C, CO), 65.9 (CH, C-12), 64.5 (CH_2, C-1), 31.5 (CH_2, C-13), 10.9 (CH_3, C-14) Other signals were not identified due to the overlap with those of rearrangement by-products; MS: (CI, 200 eV) m/z 293 (M^+ + 3, 31), 291 (M^+ + 1, 100), 255 (M^+ + 1 - HCl, 65), 195 (M^+ + 1 - HCl - CH_3COOH, 47); HRMS: (CI, 200 eV) calcd for $C_{16}H_{32}ClO_2$ 291.2091 found m/z 291.2086 (M^+ + 1). Anal. Calcd for $C_{16}H_{31}ClO_2$: C, 66.07; H, 10.74. Found: C, 66.36; H, 10.59.

12-Chloro-1-tridecanol (3h)



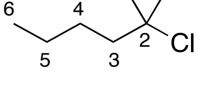
According to the general procedure, this compound was prepared from $HSiMe_2Cl$, **1h**, $GaCl_3$, and (+)-diethyl tartrate in dichloromethane to give the product as a colorless liquid after chromatography (hexane/EtOAc, 90:10). Further purification was performed by distillation under reduced pressure and GPC. Some rearrangement products were included: bp: 175 °C / 0.5 mmHg; IR: (neat) 3309 (OH) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 4.02 (tq, J = 6.6, 6.6 Hz, 1H, 12-H), 1.50 (d, *J* = 6.6 Hz, 3H, 13-H_3) Other signals were not identified due to the overlap with those of rearrangement by-products; ^{13}C NMR: (100 MHz, $CDCl_3$) 63.1 (CH_2, C-1), 59.0 (CH, C-12), 40.4 (CH_2, C-11), 25.7 (CH_3, C-13) Other signals were not identified due to the overlap with those of rearrangement by-products; MS: (CI, 200 eV) *m/z* 237 (M^+ + 3, 3.47), 235 (M^+ + 1, 12.3), 217 (M^+ + 1 – H_2O, 41.0), 199 (M^+ + 1 - HCl, 100), 181 (M^+ + 1 – HCl – H_2O, 22.1), 125 (24.0), 111 (26.6), 97 (21.1); HRMS: (CI, 200 eV) calcd for $C_{13}H_{28}ClO$ 235.1829 found *m/z* 235.1822 (M^+ + 1). Anal. Calcd for $C_{13}H_{27}ClO$: C, 66.50; H, 11.59. Found: C, 66.42; H, 11.44.

2-(4-Chloropentyl)isoindole-1,3-dione (3i)



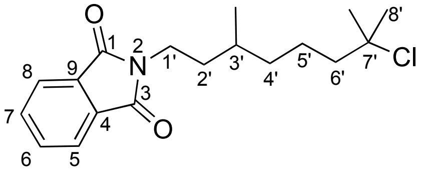
According to the general procedure, this compound was prepared from $HSiMe_2Cl$, **1i**, $GaCl_3$, and (+)-diethyl tartrate in dichloromethane to give the product as a colorless liquid after chromatography (hexane/EtOAc, 80:20). Further purification was performed by distillation under reduced pressure: bp: 175 °C / 1.0 mmHg; IR: (neat) 1774, 1712 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.85 (dd, *J* = 5.4, 3.2 Hz, 2H, 5-H and 8-H), 7.73 (dd, *J* = 5.4, 3.2 Hz, 2H, 6-H and 7-H), 4.08 (tq, *J* = 6.8, 6.8 Hz, 1H, 4'-H), 3.72 (t, *J* = 6.8 Hz, 2H, 1'-H_2), 1.92 (m, 1H, 3'-H^A), 1.87-1.72 (m, 3H, 3'-H^B and 2'-H_2), 1.50 (d, *J* = 6.8 Hz, 3H, 5'-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 168.4 (s, C-1 and C-3), 134.0 (d, C-6 and C-7), 132.0 (s, C-4 and C-9), 123.2 (d, C-5 and C-8), 57.9 (d, C-7'), 37.3 (d, C-1'), 37.3 (d, C-3'), 25.9 (t, C-2'), 25.4 (q, C-5'); MS: (EI, 70 eV) *m/z* 253 (M^++2, 0.82), 251 (M^+, 2.5), 160 (M^+ - $CH_2CH_2CHClCH_3$, 100); HRMS: (EI, 70 eV) calcd for $C_{13}H_{14}ClNO_2$ 251.0709 found *m/z* 251.0713 (M^+). Anal. Calcd for $C_{13}H_{14}ClNO_2$: C, 62.03; H, 5.61; N, 5.56. Found: C, 61.74; H, 5.49; N, 5.60.

2-Chloro-2-methylhexane (3j)



According to the general procedure, this compound was prepared from $HSiMe_2Cl$, **1j**, and $GaCl_3$, in dichloromethane to give the product as a colorless liquid after chromatography (hexane/EtOAc, 90:10). Further purification was performed by distillation under reduced pressure: bp: 58 °C / 50 mmHg; IR: (neat) 2962, 1466 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 1.74 (m, 2H, 3-H_2), 1.57 (s, 3H, 1-H_3 or 2-Me), 1.57 (s, 3H, 2-Me or 1-H_3), 1.46 (m, 2H, 4-H_2), 1.33 (tq, *J* = 7.4, 7.4 Hz, 2H, 5-H_2), 0.93 (t, *J* = 7.4 Hz, 3H, 6-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 71.3 (s, C-2), 45.8 (t, C-3), 32.4 (q, C-1 and 2-Me), 27.3 (t, C-4), 22.8 (t, C-5), 14.0 (q, C-6); MS: (EI, 70 eV) *m/z* 121 (M^+ + 2 - CH_3, 0.75), 119 (M^+ - CH_3, 2.2), 99 (M^+ - Cl, 17), 77 ($C(CH_3)_2Cl$, 65), 56 (100), 41 (55); HRMS: (EI, 70 eV) calcd for $C_6H_{12}Cl$ 119.0628 found *m/z* 119.0630 (M^+ - CH_3). Anal. Calcd for $C_7H_{15}Cl$: C, 62.44; H, 11.23. Found: C, 62.59; H, 11.05.

2-(7-Chloro-3,7-dimethyloctyl)isoindole-1,3-dione (3l)



According to the general procedure, this compound was prepared from $HSiMe_2Cl$, **1h**, and $GaCl_3$ in dichloromethane to give the product as a solid after recrystallization (hexane/ether): mp: 88-90 °C; IR: (KBr) 1770, 1712 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.84 (dd, *J* = 5.6, 3.2 Hz, 2H, 5-H and 8-H), 7.71 (dd, *J* = 5.6, 3.2 Hz, 2H, 6-H and 7-H), 3.71 (m, 2H, 1'-H_2), 1.70 (m, 3H), 1.56 (s, 6H, 8'-H_3 and 7'-Me), 1.59-1.21 (m, 5H), 1.21 (m, 1H), 0.99 (d, *J* = 6.3 Hz, 3H, 3'-Me); ^{13}C NMR: (100 MHz, $CDCl_3$) 168.4 (C, C-1 and C-3), 133.8 (CH, C-6 and C-7), 132.2 (C, C-4 and C-9), 123.1 (CH, C-5 and C-8), 71.2 (C, C-7'), 46.2 (CH_2), 36.7 (CH_2), 36.2 (CH_2), 35.5 (CH_2), 32.4 (CH_3, 7'-Me), 32.4 (CH_3, C-8'), 30.6 (CH, C-3'), 22.3 (CH_2), 19.3 (CH_3, 3'-Me); MS: (EI, 70 eV) *m/z* 323 (M^+ + 2, 2.41), 321 (M^+, 6.94), 200 (23.0), 161 (47.2), 160 ($PhthNCH_2$, 100), 148 (28.2); HRMS: (EI, 70 eV) calcd for $C_{18}H_{24}ClNO_2$ 321.1496 found *m/z* 321.1502 (M^+). Anal. Calcd for $C_{18}H_{24}ClNO_2$: C, 67.17; H, 7.52; N, 4.35. Found: C, 67.15; H, 7.38; N, 4.47.

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