

Dichlorination of olefins with NCS/Ph₃P

Yasumasa Kamada, Yuta Kitamura, Tetsuaki Tanaka and Takehiko Yoshimitsu*

Graduate School of Pharmaceutical Sciences, Osaka University, 1-6 Yamadaoka, Suita,

Osaka 565-0871, Japan

yoshimit@phs.osaka-u.ac.jp

Supporting Information

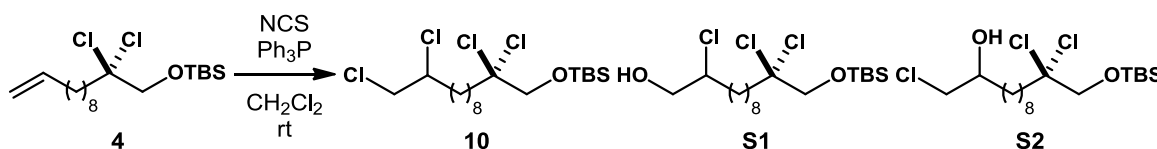
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General. Melting points are uncorrected. All reagents were used as received from commercial suppliers unless otherwise noted. ^1H NMR spectra (400 or 300 MHz) and ^{13}C NMR spectra (125 or 100 or 75 MHz) were measured in the specified solvents. Chemical shifts are reported in ppm relative to the internal solvent signal [chloroform-*d*: 7.26 ppm (^1H NMR), 77.0 ppm (^{13}C NMR)]. FT-IR spectra were recorded for samples loaded as neat films on NaCl plates. Mass spectra were obtained according to the specified technique. Analytical thin layer chromatography (TLC) was performed using Kieselgel 60 F₂₅₄. Compounds were visualized with UV light and stained with anisaldehyde solution or phosphomolybdic acid solution.

Dichlorination of olefins with a 2:1 mixture of NCS/Ph₃P (Table 1):

Table 1, entry 1

***tert*-Butyldimethyl((2,2,11,12-tetrachlorododecyl)oxy)silane (10), 12-((*tert*-Butyldimethylsilyl)oxy)-2,11,11-trichlorododecan-1-ol (S1), and 12-((*tert*-Butyldimethylsilyl)oxy)-1,11,11-trichlorododecan-2-ol (S2)**

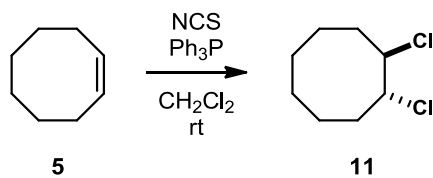


To a solution of olefin **4** (70.7 mg, 0.20 mmol) in CH_2Cl_2 (2 mL) were added Ph_3P (78.7 mg, 0.30 mmol) and NCS (80.1 mg, 0.60 mmol). After being stirred for 1 h at room temperature, the mixture was treated with sat. NaHCO_3 and poured into a separatory funnel where it was extracted with CH_2Cl_2 . The phases were separated and the organic phase was washed with brine, dried over MgSO_4 , filtered, and concentrated. The residue was purified by flash silica gel column chromatography (*n*-hexane to EtOAc/*n*-hexane 1:3) to yield tetrachloride **10** (76.5 mg, 89%) as a colorless oil. Further elution gave separable regioisomeric chlorohydrins **S1** (3.2 mg, 4%) and **S2** (2.4 mg, 3%), both as colorless oils. **Tetrachloride 10**: IR (neat) ν 2930, 2857, 1119, 839, 779 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 4.04 (m, 1H), 3.92 (s, 2H), 3.76 (dd, 1H, $J = 11.4, 5.0$ Hz), 3.65 (dd, 1H, $J = 11.4, 7.3$ Hz), 2.21-2.14 (m, 2H), 1.99 (m, 1H), 1.72 (m, 1H), 1.64-1.50 (m, 3H), 1.48-1.20 (m, 9H) 0.91 (s, 9H), 0.11 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 93.4, 72.1, 61.2, 48.2, 43.4, 35.0, 29.22, 29.20, 28.97, 28.89, 25.8, 25.7 (3C), 24.7, 18.2, -5.4 (2C);

MS m/z 437 (M+H)⁺, 73 (100%); HRMS (FAB) calcd for C₁₈H₃₇O³⁵Cl₄Si (MH⁺) 437.1368, found: 437.1328. **Chlorohydrin S1:** IR (neat) ν 3404, 2928, 2857, 1119, 839, 779 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 4.04 (m, 1H), 3.92 (s, 2H), 3.79 (m, 1H), 3.66 (m, 1H), 2.22-2.13 (m, 2H), 1.80-1.64 (m, 2H), 1.64-1.50 (m, 3H), 1.45-1.28 (m, 9H), 0.91 (s, 9H), 0.11 (s, 6H); ¹³CNMR (75 MHz, CDCl₃) δ 93.5, 72.1, 67.0, 65.4, 43.5, 34.2, 29.23, 29.19, 29.02, 28.97, 26.3, 25.7 (3C), 24.7, 18.2, -5.4 (2C); MS m/z : 421 (M+H)⁺, 73 (100%); HRMS (FAB) calcd for C₁₈H₃₇O₂³⁵Cl₂³⁷ClSi (M+H)⁺ 421.1677, found 421.1681. **Chlorohydrin S2:** IR (neat) ν 3447, 2926, 2855, 1260, 1119, 839 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.92 (s, 2H), 3.80 (m, 1H), 3.65 (dd, 1H, $J = 11.0, 3.1$ Hz), 3.48 (dd, 1H, $J = 11.0, 7.2$ Hz), 2.22-2.08 (m, 2H), 1.64-1.42 (m, 5H), 1.38-1.28 (m, 9H), 0.91 (s, 9H), 0.11 (s, 6H); ¹³CNMR (75 MHz, CDCl₃) δ 93.5, 72.1, 71.4, 50.6, 43.5, 34.2, 29.4, 29.30, 29.26, 29.0, 25.7 (3C), 25.5, 24.7, 18.2, -5.4 (2C); MS m/z : 441 (M+Na)⁺, 73 (100%); HRMS (FAB) calcd for C₁₈H₃₇O₂³⁵Cl₂³⁷ClSiNa (M+Na)⁺ 441.1526, found: 441.1535.

Table 1, entry 2

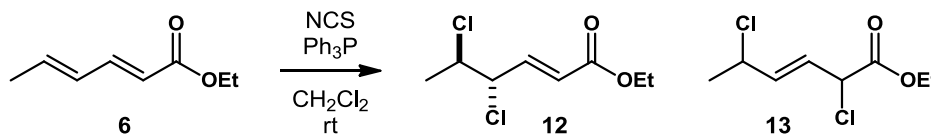
(1*R,2*R**)-1,2-Dichlorocyclooctane (11)**



The title compound was prepared according to the general procedure described for entry 1 using olefin **5** (26.0 μ L, 0.20 mmol), Ph₃P (78.7 mg, 0.30 mmol), and NCS (80.1 mg, 0.60 mmol). (Reaction time: 1 h) Purification by flash silica gel column chromatography (*n*-hexane) gave dichloride **11** (33.8 mg, 93%) as a colorless oil. The ¹H NMR spectrum of compound **11** is in good agreement with that reported.¹ **Dichloride 11:** IR (neat) ν 2926, 2857, 1462, 733 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 4.32-4.24 (m, 2H), 2.34-2.22 (m, 2H), 2.10-1.96 (m, 2H), 1.92-1.80 (m, 2H), 1.77-1.64 (m, 2H), 1.63-1.50 (m, 2H), 1.48-1.35 (m, 2H); ¹³CNMR (100 MHz, CDCl₃) δ 68.4, 33.6, 25.7, 25.4.

Table 1, entry 3

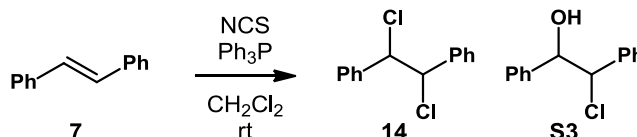
(4*S,5*R**,*E*)-Ethyl 4,5-dichlorohex-2-enoate (**12**) and (*E*)-Ethyl 2,5-dichlorohex-3-enoate (**13**)**



The title compounds were prepared according to the general procedure described for entry 1 using olefin **6** (28.0 mg, 0.20 mmol), Ph₃P (78.7 mg, 0.30 mmol), and NCS (80.1 mg, 0.60 mmol). (Reaction time: 5 min) Purification by flash silica gel column chromatography (toluene/*n*-hexane 1:3) gave dichloride **13** (8.9 mg, 21%) as a pale yellow oil. Further elution gave regioisomeric dichloride **12** (32.0 mg, 76%) as a pale yellow oil. The ¹H NMR spectra of these compounds are in good agreement with those reported.² **Dichloride 12**: IR (neat) ν 2984, 2930, 1724, 1661, 1370, 1317, 1271, 1227, 1177, 1040, 974, 656 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 6.91 (dd, 1H, *J* = 15.6, 8.2 Hz), 6.10 (d, 1H, *J* = 15.6 Hz), 4.49 (dd, 1H, *J* = 8.2, 7.3 Hz), 4.23 (q, 2H, *J* = 7.3 Hz), 4.15 (dq, 1H, *J* = 7.3, 6.4 Hz), 1.63 (d, 3H, *J* = 6.4 Hz), 1.31 (t, 3H, *J* = 7.3 Hz); ¹³CNMR (100 MHz, CDCl₃) δ 165.3, 142.1, 125.3, 63.7, 60.9, 58.8, 21.9, 14.2. **Regioisomeric dichloride 13**: IR (neat) ν 2928, 1744, 1443, 1371, 1267, 1177, 1018, 964, 677 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 6.00 (dd, 1H, *J* = 15.1, 6.9 Hz), 5.93 (dd, 1H, *J* = 15.1, 7.3 Hz), 4.77 (d, 1H, *J* = 7.3 Hz), 4.55 (dq, 1H, *J* = 6.9, 6.4 Hz), 4.26 (q, 2H, *J* = 6.9 Hz), 1.62 (d, 3H, *J* = 6.9 Hz), 1.32 (t, 3H, *J* = 6.9 Hz) ¹³CNMR (100 MHz, CDCl₃) δ 171.9, 137.5, 125.6, 62.5, 56.5, 55.8, 24.7, 14.0.

Table 1, entry 4

1,2-Dichloro-1,2-diphenylethane (14**) and 2-Chloro-1,2-diphenylethanol (**S3**)**

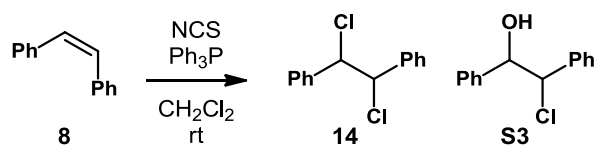


The title compounds were prepared according to the general procedure described for entry 1 using olefin **7** (36.1 mg, 0.20 mmol), Ph₃P (78.7 mg, 0.30 mmol), and NCS (80.1 mg, 0.60 mmol). (Reaction time: 15 min) Purification by flash silica gel column

chromatography (toluene/*n*-hexane 1:3) gave dichloride **14** (38.5 mg, 77%) as a colorless amorphous solid. Further elution gave chlorohydrin **S3** (7.6mg, 7%) as a colorless amorphous solid. The ¹H NMR spectra of these compounds were in good agreement with those reported.³ **Dichloride 14** (1:1 diastereomeric mixture): IR (neat) ν 1454, 909, 733, 704, 675 cm^{-1} ; ¹H NMR (400 MHz, CDCl₃) δ 7.47-7.36 (m, 5H), 7.24-7.13 (m, 5H), 5.25 (s, 1H), 5.23 (s, 1H); ¹³CNMR (100 MHz, CDCl₃) δ 138.3, 137.2, 129.0, 128.6, 128.5, 128.13, 128.08, 128.01, 67.7, 65.7. **Chlorohydrin S3** (1:1 diastereomeric mixture): IR (neat) ν 3420, 1454, 1053, 725, 696 cm^{-1} ; ¹H NMR (400 MHz, CDCl₃) δ 7.30-6.99 (m, 10H), 5.02 (d, 0.5H, *J* = 6.5 Hz), 4.94 (d, 0.5H, *J* = 6.5 Hz), 4.93 (d, 0.5H, *J* = 8.3 Hz), 4.88 (d, 0.5H, *J* = 8.3 Hz), 2.98 (brs, 0.5H), 2.29 (brs, 0.5H); ¹³CNMR (100 MHz, CDCl₃) δ 139.4, 138.6, 137.6, 137.2, 128.7, 128.5, 128.43, 128.38, 128.34, 128.31, 128.2, 128.1, 127.9, 127.1, 126.9, 78.8, 78.2, 70.7, 66.9.

Table 1, entry 5

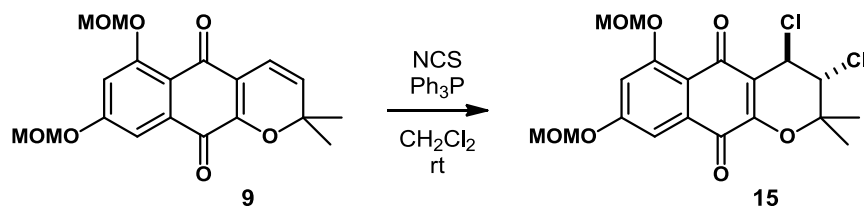
1,2-Dichloro-1,2-diphenylethane (**14**) and 2-Chloro-1,2-diphenylethanol (**S3**)



The title compounds were prepared according to the general procedure described for entry 1 using olefin **8** (36.1 mg, 0.20 mmol), Ph₃P (78.7 mg, 0.30 mmol), and NCS (80.1 mg, 0.60 mmol). (Reaction time: 15 min) Purification by flash silica gel column chromatography (toluene/*n*-hexane 1:3) gave dichloride **14** (40.7 mg, 81%) as a colorless amorphous solid. Further elution gave chlorohydrin **S3** (6.6 mg, 6%) as a colorless amorphous solid. The spectra of these products were identical with those obtained above.

Table 1, entry 6

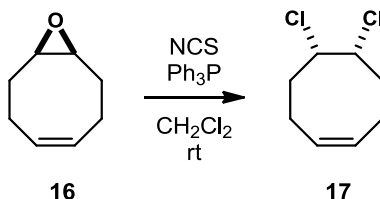
(3*R**,4*R**)-3,4-Dichloro-6,8-bis(methoxymethoxy)-2,2-dimethyl-3,4-dihydro-2*H*-benzo[*g*]chromene-5,10-dione (**15**)



The title compound was prepared according to the general procedure described for entry 1 using olefin **9** (36.0 mg, 0.10 mmol), Ph₃P (39.3 mg, 0.15 mmol), and NCS (40.1 mg, 0.30 mmol). (Reaction time: 5 min) Purification by flash silica gel column chromatography (EtOAc/*n*-hexane 1:3) gave dichloride **15** (41.2 mg, 96%) as a yellow oil. **Dichloride 15**: IR (neat) ν 2926, 1736, 1593, 1152 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.48 (d, 1H, *J* = 2.4 Hz), 7.16 (d, 1H, *J* = 2.4 Hz), 5.33, (s, 2H), 5.30 (d, 1H, *J* = 3.2 Hz), 5.28 (s, 2H), 4.37 (d, 1H, *J* = 3.2 Hz), 3.55 (s, 3H), 3.49 (s, 3H), 1.70 (s, 3H), 1.64 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 180.14, 178.96., 161.58, 159.30, 151.71, 134.36, 117.61, 115.22, 110.35, 108.08, 95.29, 94.19, 80.03, 63.61, 56.72, 56.58, 51.04, 26.33, 25.72; MS *m/z*: 430 (M⁺); HRMS (EI) calcd for C₁₉H₂₀O₇Cl₂ (M⁺): 430.0586, found: 430.0580.

Dichlorination of epoxy cyclooctene 16 with a 2:1 or 1:1 mixture of NCS/Ph₃P (Scheme 3): With a 1:1 combination of NCS/Ph₃P:

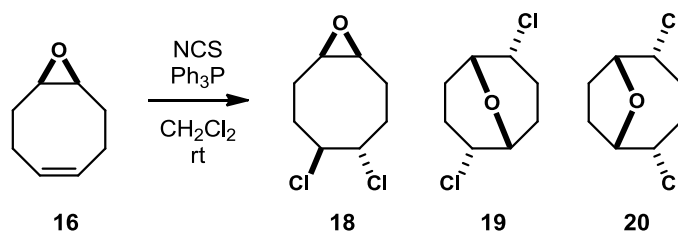
(5*R,6*S**,*Z*)-5,6-Dichlorocyclooct-1-ene (17)**



The title compound was prepared according to the general procedure described for Table 1 using epoxy olefin **16** (24.8 mg, 0.20 mmol), Ph₃P (157.3 mg, 0.60 mmol), and NCS (80.1 mg, 0.60 mmol). (Reaction time: 2.5 h) Purification by flash silica gel column chromatography (*n*-hexane) gave dichloride **17** (34.0 mg, 95%) as a colorless oil. The ¹H NMR spectrum of this compound was in good agreement with that reported.⁴ **Dichloride 17**: IR (neat) ν 2939, 750 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.80-5.65 (m, 2H), 4.65-4.45 (m, 2H), 2.67-2.63 (m, 2H), 2.36-2.27 (m, 2H), 2.11-1.97 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 128.47, 56.28, 27.80, 23.35.

With a 2:1 combination of NCS/Ph₃P:

(1R*,4S*,5S*,8S*)-4,5-Dichloro-9-oxabicyclo[6.1.0]nonane (18), (1S*,5S*)-1,5-Dichloro-9-oxabicyclo[3.3.1]nonane (19) and (1R*,2R*,5S*,6S*)-2,5-Dichloro-9-oxabicyclo[4.2.1]nonane (20)



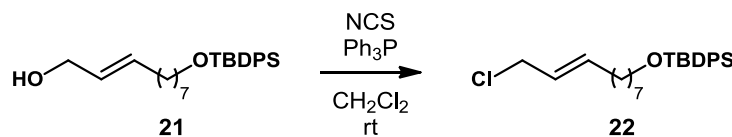
The title compounds were prepared according to the general procedure described for Table 1 using epoxy olefin **16** (24.8 mg, 0.20 mmol), Ph₃P (78.7 mg, 0.30 mmol), and NCS (80.1 mg, 0.60 mmol). (Reaction time: 5 min) Purification by flash silica gel column chromatography (EtOAc/*n*-hexane 1:15) gave dichloride **18** (16.1 mg, 41%) as a colorless amorphous solid, a mixture of **19** (2.7 mg, 7%) and **20** (13.0 mg, 33%) as a colorless amorphous solid. The mixture of **19** and **20** was further subjected to flash column chromatography eluted with Et₂O/*n*-hexane (1:20) to afford sufficiently pure materials. The ¹³C NMR spectrum of compound **20** was identical to that reported.⁵

Dichloride 18: IR (neat) ν 2932, 1476, 1236, 1028, 934, 916, 847, 789, 721, 621 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 4.65-4.54 (m, 2H), 3.15 (m, 1H), 3.06 (m, 1H), 2.59-2.47 (m, 2H), 2.26-1.96 (m, 4H), 1.72-1.59 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 61.4, 60.4, 55.9, 54.9, 30.5, 28.5, 24.0, 22.4. **Dichloride 19:** IR (neat) ν 2926, 1738, 1485, 1123, 1044, 899, 870, 820 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 4.33-4.27 (m, 2H), 3.93-3.90 (dd, 2H, *J* = 6.0, 5.5 Hz), 2.35 (dt, 2H, *J* = 14.2, 3.7 Hz), 2.22-2.12 (m, 4H), 2.07-1.94 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 69.5, 57.6, 30.2, 24.0. **Dichloride 20:** IR (neat) ν 2953, 2934, 1479, 1061, 932, 910, 793, 656 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 4.62-4.51 (m, 2H), 4.29-4.19 (m, 2H), 2.40-2.29 (m, 2H), 2.18-1.96 (m, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 81.6, 60.4, 30.8, 26.2.

Dichlorination of allylic alcohol 21 with NCS/Ph₃P in either 2:1 or 1:1 stoichiometry (Scheme 4):

With a 1:1 combination of NCS/Ph₃P:

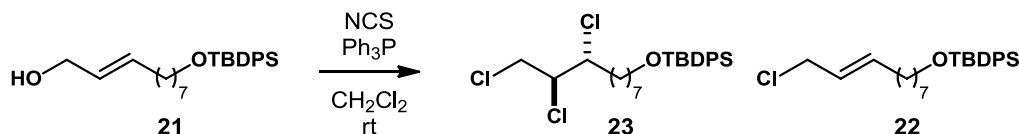
(E)-tert-Butyl((10-chlorodec-8-en-1-yl)oxy)diphenylsilane (22)



The title compound was prepared according to the general procedure described for Table 1 using alcohol **21** (82.1 mg, 0.20 mmol), Ph₃P (78.7 mg, 0.30 mmol), and NCS (40.1 mg, 0.30 mmol). (Reaction time: 5 min) Purification by flash silica gel column chromatography (*n*-hexane) gave chloride **22** (80.2 mg, 94%) as a colorless oil. **Allylic chloride 22**: IR (neat) ν 2930, 1111, 702 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.68-7.66 (m, 4H), 7.44-7.36 (m, 6H), 5.77 (dt, 1H, *J* = 14.8, 7.2 Hz), 5.61 (dt, 1H, 14.8, 6.8 Hz), 4.04 (d, 2H, 7.2 Hz), 3.66 (t, 2H, *J* = 6.4 Hz), 2.07-2.02 (m, 2H), 1.59-1.52 (m, 2H), 1.43-1.21 (m, 8H), 1.05 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 136.27, 135.56, 134.16, 129.47, 127.54, 125.82, 63.94, 45.55, 32.51, 32.02, 29.13, 29.05, 28.75, 26.86, 25.67, 19.21; MS *m/z*: 429 (M+H)⁺, 135 (100%); HRMS (FAB) calcd for C₂₆H₃₈OClSi⁺: 429.2380, found: 429.2366.

With a 2:1 combination of NCS/Ph₃P:

(E)-tert-Butyl((10-chlorodec-8-en-1-yl)oxy)diphenylsilane (22) and tert-Butyldiphenyl(((8R*,9S*)-8,9,10-trichlorodecyl)oxy)silane (23)



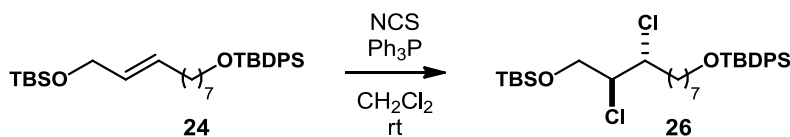
The title compounds were prepared according to the general procedure described for Table 1 using alcohol **21** (82.1 mg, 0.20 mmol), Ph₃P (78.7 mg, 0.30 mmol), and NCS (80.1 mg, 0.60 mmol). (Reaction time: 5 min) Purification by flash silica gel column chromatography (toluene/*n*-hexane 1:15) gave trichloride **23** (57.1 mg, 57%) and chloride **22** (20.9 mg, 24%), both as colorless oils. **Trichloride 23**: IR (neat) ν 2931, 2857, 1111, 702 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.70-7.68 (m, 4H), 7.46-7.38 (m, 6H), 4.21-4.19 (m, 2H), 4.06 (dd, 1H, *J* = 12.4, 4.0 Hz), 3.94 (dd, 1H, *J* = 12.4, 3.2 Hz), 3.68 (t, 2H, *J* = 6.4 Hz), 2.05 (m, 1H), 1.81 (m, 1H), 1.58 (m, 2H), 1.47-1.28 (m, 8H), 1.07 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 135.55, 134.12, 129.48, 127.55, 63.88, 63.53, 62.06, 47.00,

34.06, 32.45, 29.07, 28.85, 26.87, 25.62, 25.59, 19.20; MS m/z : 499 (M+H)⁺, 135 (100%); HRMS (FAB) calcd for C₂₆H₃₈OCl₃Si: 499.1758, found: 499.1729.

Dichlorination of olefins 24 and 25 with a 2:1 mixture of NCS/Ph₃P (Table 2):

Table 2, entry 1

(6*S,7*R**)-6,7-Dichloro-2,2,3,3,17,17-hexamethyl-16,16-diphenyl-4,15-dioxa-3,16-disilaoctadecane (26)**

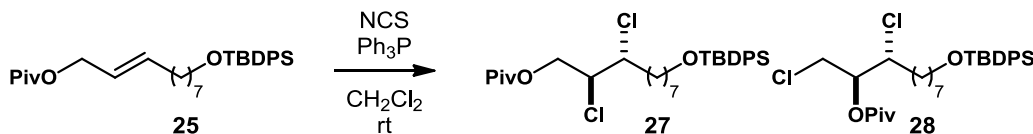


The title compound was prepared according to the general procedure described for Table 1 using olefin **24** (52.5 mg, 0.10 mmol), Ph₃P (39.3 mg, 0.15 mmol), and NCS (40.1 mg, 0.30 mmol). (Reaction time: 5 min) Purification by flash silica gel column chromatography (*n*-hexane) gave chloride **26** (45.9 mg, 77%) as a colorless oil.

Dichloride 26: IR (neat) ν 2930, 1111, 837, 700 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.68-7.66 (m, 4H), 7.44-7.36 (m, 6H), 4.22 (m, 1H), 4.08-3.98 (m, 2H), 3.89 (dd, 1H, J = 10.8, 5.2 Hz), 3.65 (t, 2H, J = 6.4 Hz), 1.96 (m, 1H), 1.78 (m, 1H), 1.59-1.52 (m, 2H), 1.41-1.20 (m, 8H), 1.05 (s, 9H), 0.91 (s, 9H), 0.09 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 135.57, 134.13, 129.47, 127.55, 65.33, 64.62, 63.90, 62.09, 33.77, 32.49, 29.17, 28.98, 26.86, 25.86, 25.78, 25.66, 19.21, 18.27, -5.46; MS m/z : 595 (M+H)⁺, 73 (100%); HRMS (FAB) calcd for C₃₂H₅₃O₂Cl₂Si₂: 595.2961, found: 595.2958.

Table 2, entry 2

(2*S,3*R**)-10-((*tert*-Butyldiphenylsilyl)oxy)-2,3-dichlorodecyl pivalate (27) and (2*R**,3*R**)-10-((*tert*-Butyldiphenylsilyl)oxy)-1,3-dichlorodecan-2-yl pivalate (28)**



The title compounds were prepared according to the general procedure described for Table 1 using olefin **25** (99.0 mg, 0.20 mmol), Ph₃P (78.7 mg, 0.30 mmol), and NCS (80.1 mg, 0.60 mmol). (Reaction time: 5 min) Purification by flash silica gel column chromatography (toluene/*n*-hexane 1:4) gave dichlorides **27** (76.0 mg, 66%), and **28**

(14.0 mg, 12%), both as colorless oils. **Dichloride 27**: IR (neat) ν 2932, 1738, 1150, 1111, 702 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.69-7.67 (m, 4H), 7.45-7.37 (m, 6H), 4.53 (dd, 1H, $J = 12.0, 3.6$ Hz), 4.41 (dd, 1H, $J = 12.0, 6.0$ Hz), 4.18 (m, 1H), 4.08 (dt, 1H, $J = 7.2, 3.2$ Hz), 3.66 (t, 2H, $J = 6.4$ Hz), 2.04 (m, 1H), 1.83 (m, 1H), 1.58-1.53 (m, 2H), 1.44-1.20 (m, 8H), 1.24 (s, 9H), 1.06 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 177.90, 135.55, 134.10, 129.48, 127.55, 65.15, 63.88, 62.18, 61.62, 38.90, 34.64, 32.46, 29.11, 28.88, 27.10, 27.01, 26.85, 25.64, 19.20; MS m/z : 587 ($\text{M}+\text{Na}$) $^+$, 57 (100%); HRMS (FAB) calcd for $\text{C}_{31}\text{H}_{46}\text{O}_3\text{Cl}_2\text{SiNa}$ ($\text{M}+\text{Na}$) $^+$: 587.2491, found: 587.2482. **Dichloride 28**: IR (neat) ν 2932, 1736, 1142, 1111, 702 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.67-7.66 (m, 4H), 7.44-7.36 (m, 6H), 5.07 (m, 1H), 4.14 (m, 1H), 3.90 (dd, 1H, $J = 12.0, 5.2$ Hz), 3.79 (dd, 1H, $J = 12.0, 3.2$ Hz), 3.65 (t, 2H, $J = 6.4$ Hz), 1.79 (m, 1H), 1.65 (m, 1H), 1.59-1.52 (m, 2H), 1.42-1.21 (m, 8H), 1.24 (s, 9H), 1.05 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 177.31, 135.56, 134.12, 129.49, 127.56, 74.21, 63.89, 60.25, 43.36, 39.01, 33.53, 32.48, 29.11, 28.95, 27.02, 26.86, 25.84, 25.64, 19.21; MS m/z : 587 ($\text{M}+\text{Na}$) $^+$, 57 (100%); HRMS (FAB) calcd for $\text{C}_{31}\text{H}_{46}\text{O}_3\text{Cl}_2\text{SiNa}$ ($\text{M}+\text{Na}$) $^+$: 587.2491, found: 587.2467.

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