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Mild Metal-free 1,2-Dichlorination of Alkyne by NCS-PPh₃-H₂O System

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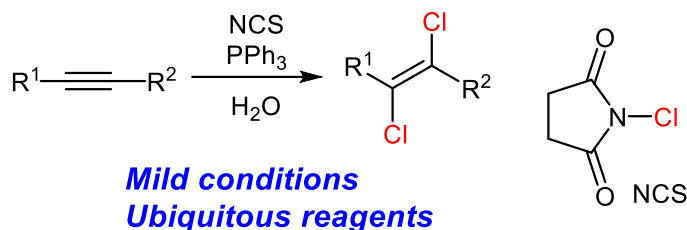
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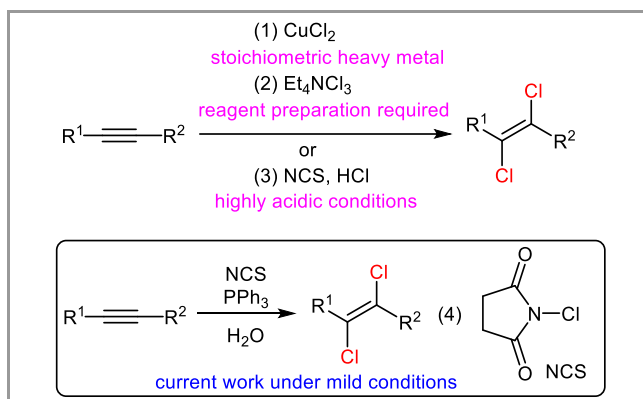


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Abstract: Facile dichlorination reaction of alkynes to give 1,2-dichloroalkenes are described. Previous studies for the synthesis of the 1,2-dichloroalkenes from the corresponding alkyne require stoichiometric amount of copper salt, preparation of the reagent from hazardous compounds such as molecular chlorine and highly acidic conditions. In this paper, only ubiquitous reagents, NCS-PPh₃-H₂O, are used to prepare the 1,2-dichloroalkenes from the alkyne under mild conditions. Various functional groups such as esters, ethers or carbamates were tolerated under these reaction conditions.

Key words: Dichloroalkene, Chlorination, Internal alkyne, Terminal alkyne, NCS

Haloalkenes are highly important molecules not only for final products such as natural products¹, functionalized materials² and pharmaceuticals³ but also for building blocks toward cross-coupling reaction⁴ and functional group transformation⁵. Extensive efforts have been made for the preparation of homo⁶(dibromo or diiodo)- or hetero-1,2-dihaloalkene⁷ to achieve ubiquitous combination of reagent and operation. On the other hand, although 1,2-dichloroalkene shows unique reactivity,⁸ preparation of reagent from commercially available compounds or hazardous reagents is still required for the synthesis of the 1,2-dichloroalkenes. For examples, the previous reports of the 1,2-dichloroalkene from the corresponding alkyne are shown in Scheme 1; (1) more than stoichiometric amount of CuCl₂⁹ is necessary, generating large amounts of heavy metal waste, (2) Et₄NCl₃,¹⁰ a mild and useful reagent, must be prepared by the user from Et₄NCl and hazardous molecular chlorine, and (3) combination of NCS and aqueous HCl,¹¹ a strong acidic condition, are employed. These conditions still make the dichlorination of alkyne to be hesitated for synthetic chemists due to generation of huge waste of heavy metal, use of hazardous chlorine or functional group tolerance.



Scheme 1 Previous synthesis of 1,2-dichloroalkenes from alkyne, and current work

We have conducted synthetic studies on chlorosulfolipids (CSLs), which are highly chlorinated natural products.¹² Unique synthetic methodologies of dichlorination to 1,2-dichloroalkane from alkene¹³ or epoxide¹⁴ have been developed through the synthesis of CSLs. Among them, we envisioned Yoshimitsu's conditions, which involve converting an alkene to the corresponding 1,2-dichloroalkane with 3.0 equivalent of NCS and 1.5 equivalent of PPh₃ in CH₂Cl₂ at room temperature.¹⁵ These conditions are mild and require only ubiquitous reagents. Thus, we have planned the application of these conditions toward the synthesis of a 1,2-dichloroalkene. Herein, we describe effective syntheses of the 1,2-dichloroalkene under mild conditions from alkyne having various functional groups.

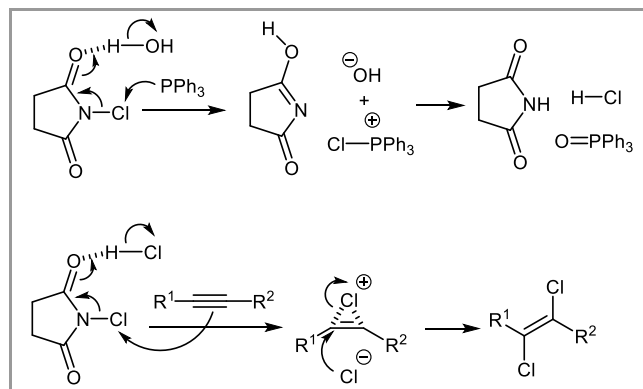
Reaction conditions were optimized with 0.50 mmol of model alkyne **1**, as shown in Table 1. Reaction solvents were first screened using 3.0 equivalent of NCS and 1.5 equivalent of PPh₃. Dichloromethane, used by Yoshimitsu, and THF gave dichloroolefin **2** in high yields (entries 1 and 2). Almost recovery of starting **1** was observed in toluene and acetonitrile (entries 3 and 4). It was **expected that addition** of water in this reaction increases the reaction efficiency because water enhances reactivity of NCS through hydrogen bond to carbonyl group and hydrolysis of phosphonium chloride into phosphine oxide to release HCl (Scheme 2). Furthermore, the generated HCl is expected to accelerate by coordination with the second

equivalent of NCS as Bronsted acid. According to the above consideration, addition of 1.5 equivalent of water in dichloromethane improved yield to 85% (entry 5).¹⁶ **In order to confirm effect of contaminated water in small scale reaction, 3.0 mmol of 1 was employed under same conditions as entries 1 and 5 although longer reaction time was required for the complete conversion. To our surprise, dramatic decrease of yield was observed when water was not added (entry 6). We believe this is because trace amount of water in CH₂Cl₂ induced the high yield. On the other hand, the result with 1.5 equivalent of water was parallel to that of reaction with 0.5 mmol of 1 (entry 7).**

Table 1 Optimization of dichlorination reaction^a

Entry	Solvent	H ₂ O (equiv.)	Time (h)	Yield (%) ^b
1	CH ₂ Cl ₂	0	1	77
2	THF	0	1	74
3	Toluene	0	1	NR
4	CH ₃ CN	0	1	2
5	CH ₂ Cl ₂	1.5	1	85
6 ^c	CH ₂ Cl ₂	0	2	53
7 ^c	CH ₂ Cl ₂	1.5	3	82

^a 0.50 mmol of **1** was used otherwise noted, ^b isolated yield, ^c 3.0 mmol of **1**,



Scheme 2 Proposed reaction mechanism

With optimized conditions in hand, various alkynes were converted to 1,2-dichloroalkenes as shown in Figure 1. Other substituents on hydroxy group such as benzyl ether and acetate at propargylic position were applied to afford the desired alkenes **3** and **4** in high yields, respectively. *N*-protected amino acid esters (alanine and phenylalanine) including NH functionality were also transformed to the target compounds **5–7** in the presence of carbamate group. Simple internal alkyne without functional group was also employed to provide **8**, when terminal alkynes were used, the current 1,2-dichlorination proceeded in moderate yields, giving **9** and **10** with benzyl or silyl ether. Alkynes directly attached aromatic rings were also good substrates for the current reaction to produce 1,2-dichloroalkenes **11–15** in 55–94% yield although longer reaction time (24 h) was required for the completion of the reaction. We believe this longer time is due to a conjugation between the aromatic ring and alkyne to reduce the reactivity of

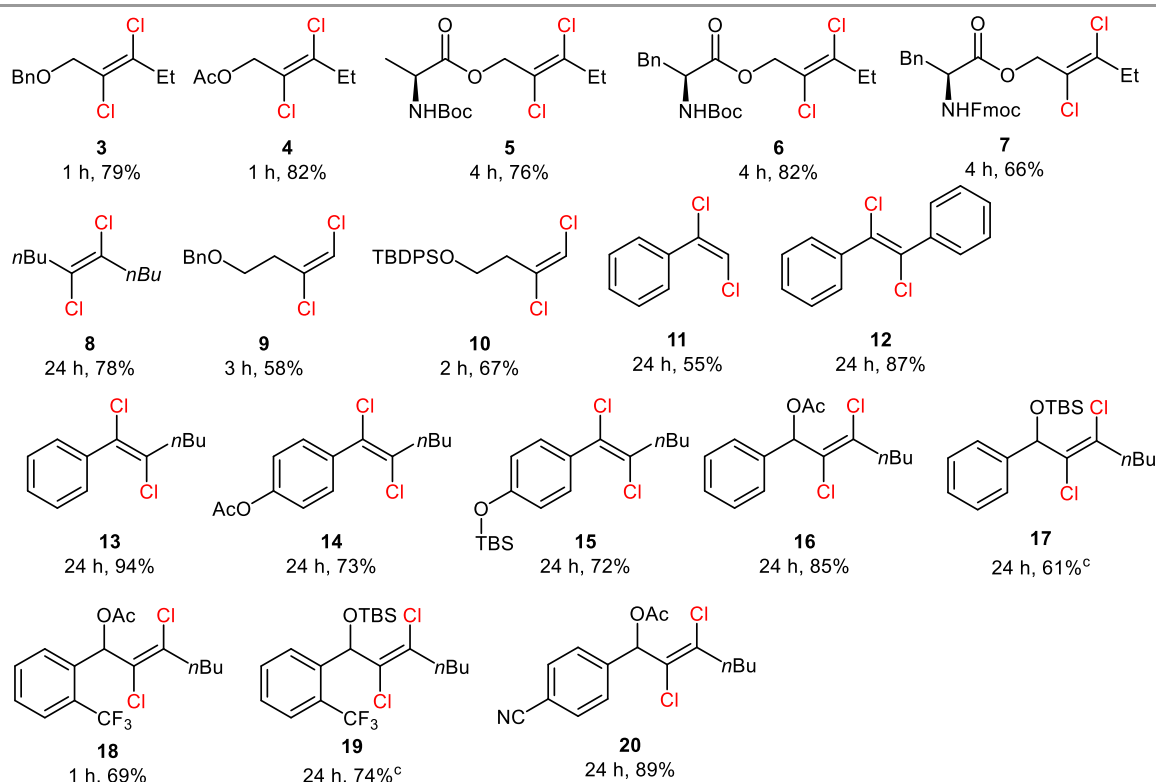


Figure 1^{a,b} Synthesis of 1,2-dichloroalkenes

^a isolated yield, ^b 0.50 mmol of alkyne is used, ^c one equivalent of *i*Pr₂NEt was added.

alkyne. Propargyl acetates or silyl ethers on benzylic position were converted to the corresponding products **16–20** in moderate yields. In these reactions for the synthesis of TBS ether **17** and **19**, complex mixtures were observed by the generation of HCl generated in reaction mixture, removing TBS ether to induce side reactions such as Appel reaction. However, addition of *i*Pr₂NEt could prevent the deprotection of TBS ether, proceeding the only dichlorination reaction.

In summary, we have described synthesis of 1,2-dichloroalkenes under mild reaction conditions with ubiquitous reagents, NCS, PPh₃ and water. It is noteworthy that water showed unique property for the activation of NCS through hydrogen bond. The present reaction showed high substrate scope because various functional groups such as esters, silyl ethers, benzyl ethers, aromatic rings and carbamate groups were employed to give the desired alkene in moderate to high yield. This convenient reaction encourages organic synthetic chemists to prepare 1,2-dichloroalkene. Currently, developments of new reactions with the resultant 1,2-dichloroalkenes are underway.

Procedures

General Methods. The IR spectra were recorded on a JASCO FTIR-4100 Type A spectrometer (JASCO corporation, Tokyo, Japan) using a NaCl cell. ESI-MS were obtained on a JEOL JMS-700TZ (JEOL Ltd., Tokyo, Japan) or BRUKER DALTONICS micro TOF-HS focus spectrometer (Bruker Japan Ltd., Yokohama, Japan). Optical rotations were recorded on a HORIBA SEPA-300 polarimeter (HORIBA Ltd., Kyoto, Japan). The ¹H NMR and ¹³C NMR spectra were recorded using a **JNM-ECZR 500 (500 MHz and 126 MHz)** spectrometer (JEOL Ltd., Tokyo, Japan). Chemical shifts were reported in ppm relative to CHCl₃ in CDCl₃ for ¹H NMR (δ = 7.26) and ¹³C NMR (δ = 77.0). Splitting patterns for ¹H NMR were designated as “s, d, t, q, m, dt, dd, and td”. These symbols indicate “singlet, doublet, triplet, quartet, multiplet, doublettriplet, doubletdoublet, and tripletdoublet” respectively. All commercially obtained reagents were employed as received. Analytical TLC was carried out using pre-coated silica gel plates (Wako TLC Silicagel 70F₂₅₄, FUJIFILM Wako Pure Chemical Corporation, Osaka, Japan). Wakogel 60N 63–212 μm was used for column chromatography.

General procedure for dichlorination of alkyne: To a solution of the alkyne (0.500 mmol, 1 equiv.) in CH₂Cl₂ (2.5 mL) were added H₂O (0.75 mmol, 1.5 equiv.), PPh₃ (0.750 mmol, 1.5 equiv.) and NCS (1.50 mmol, 3.0 equiv.) under Ar atmosphere at room temperature. The mixture was stirred for the indicated time, quenched with 20% Na₂S₂O₃ aqueous solution, extracted with EtOAc, dried over anhydrous Na₂SO₄, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography to give 1,2-dichloroalkene.

(*E*)-*tert*-butyl((2,3-dichloropent-2-en-1-yl)oxy)diphenylsilane (**2**)

Yield 85% (**166 mg, 0.426 mmol**); colorless oil.

IR (neat) 3071, 3049, 2959, 2932, 2857, 1958, 1888, 1826, 1733, 1636, 1589, 1487, 1472, 1460, 1428, 1390, 1375, 1361, 1267, 1187, 1158, 1112, 1085, 1052, 1007, 997, 928, 823, 795, 739, 724, 700, 652, 610 cm⁻¹.

¹H NMR (CDCl₃, 500 MHz) δ 1.06 (9H, s), 1.08 (3H, t, *J* = 7.4 Hz), 2.54 (2H, q, *J* = 7.4 Hz), 4.48 (2H, s), 7.36–7.43 (6H, m), 7.69 (4H, d, *J* = 6.6 Hz).

¹³C NMR (CDCl₃, 126 MHz) δ 11.3, 19.4, 26.8, 29.6, 64.0, 127.8, 129.8, 133.3, 135.7.

HRMS (ESI) *m/z*: [M + Na] + Calcd for C₂₁H₂₆Cl₂OSiNa 415.1022; Found 415.1055.

(*E*)-(((2,3-dichloropent-2-en-1-yl)oxy)methyl)benzene (**3**)

Yield 79% (**96.8 mg, 0.397 mmol**); colorless oil.

IR (neat) 3088, 3064, 3031, 2978, 2937, 2860, 2361, 1732, 1636, 1603, 1496, 1455, 1387, 1357, 1314, 1270, 1205, 1154, 1108, 1088, 1027, 925, 802, 734, 697 cm⁻¹.

¹H NMR (CDCl₃, 500 MHz) δ 1.14 (3H, t, *J* = 7.4 Hz), 2.62 (2H, q, *J* = 7.4 Hz), 4.38 (2H, s), 4.52 (2H, s), 7.28–7.37 (5H, m).

¹³C NMR (CDCl₃, 126 MHz) δ 11.4, 29.9, 69.8, 72.0, 125.7, 127.9, 128.0, 128.5, 136.0, 137.8.

HRMS (ESI) *m/z*: [M + Na] + Calcd for C₁₂H₁₄Cl₂ONa 267.0314; Found 267.0323.

(*E*)-2,3-dichloropent-2-en-1-yl acetate (**4**)

Yield 82% (**80.4 mg, 0.410 mmol**); colorless oil.

IR (neat) 2979, 2928, 2880, 2855, 2353, 1750, 1639, 1456, 1436, 1376, 1361, 1223, 1105, 1078, 1030, 967, 929, 835, 801, 730, 688, 629 cm⁻¹.

¹H NMR (CDCl₃, 500 MHz) δ 1.14 (3H, t, *J* = 7.4 Hz), 2.11 (3H, s), 2.61 (2H, q, *J* = 7.4 Hz), 4.92 (2H, s).

¹³C NMR (CDCl₃, 126 MHz) δ 11.3, 20.8, 29.8, 64.2, 123.0, 137.1, 170.5.

HRMS (ESI) *m/z*: [M – OAc] + Calcd for C₅H₇Cl₂ 136.9919; Found 136.9936.

(*E*)-2,3-dichloropent-2-en-1-yl (*tert*-butoxycarbonyl)-L-alaninate (**5**)

Yield 76% (**124 mg, 0.380 mmol**); colorless oil.

IR (neat) 3369, 2978, 2937, 1750, 1717, 1497, 1455, 1367, 1348, 1250, 1168, 1107, 1078, 1054, 1019, 859, 802, 729, 700 cm⁻¹.

¹H NMR (CDCl₃, 500 MHz) δ 1.15 (3H, td, *J* = 7.4, 3.0 Hz), 1.40 (9H, s), 2.61 (2H, td, *J* = 7.3, 4.7 Hz), 3.08–3.17 (2H, m), 4.65 (1H, d, *J* = 5.7 Hz), 4.92–5.01 (3H, m).

¹³C NMR (CDCl₃, 126 MHz) δ 11.3, 28.4, 29.8, 38.2, 54.4, 65.0, 80.1, 127.1, 128.7, 129.5, 135.9, 155.1, 171.5.

HRMS (ESI) *m/z*: [M + H] + Calcd for C₁₃H₂₂Cl₂NO₄ 326.0920; Found 326.0927.

(*E*)-2,3-dichloropent-2-en-1-yl (*tert*-butoxycarbonyl)-L-phenylalaninate (**6**)

Yield 82% (**164 mg, 0.411 mmol**); colorless oil.

IR (neat) 3438, 3063, 3029, 2977, 2934, 1750, 1717, 1604, 1555, 1497, 1455, 1367, 1348, 1250, 1168, 1106, 1079, 1055, 1019, 928, 860, 801, 780, 728, 700 cm⁻¹.

¹H NMR (CDCl₃, 500 MHz) δ 1.15 (3H, t, *J* = 7.4 Hz), 1.40 (9H, s), 2.62 (2H, q, *J* = 7.4 Hz), 3.05–3.16 (2H, m), 4.65 (1H, d, *J* = 8.0 Hz), 4.93 (1H, d, *J* = 12.7 Hz), 4.94 (1H, brs), 4.99 (1H, dd, *J* = 12.7 Hz), 7.13–7.29 (5H, m).

¹³C NMR (CDCl₃, 126 MHz) δ 11.3, 14.1, 28.3, 28.4, 29.8, 65.0, 80.1, 122.5, 128.7, 129.0, 129.3, 129.6, 135.9, 137.8, 155.1, 171.5.

HRMS (ESI) *m/z*: [M – C₄H₈ + H] + Calcd for C₁₅H₁₈Cl₂NO₄ 346.0607; Found 346.0610.

(*E*)-2,3-dichloropent-2-en-1-yl (((9H-fluoren-9-yl)methoxy)carbonyl)-L-phenylalaninate (**7**)

Yield 66% (**173 mg, 0.331 mmol**); colorless oil.

IR (neat) 3333, 3064, 3029, 2977, 2938, 1725, 1513, 1447, 1413, 1343, 1248, 1181, 1077, 1051, 824, 772, 741, 700 cm⁻¹.

¹H NMR (CDCl₃, 500 MHz) δ 1.16 (3H, t, *J* = 7.4 Hz), 2.62 (2H, q, *J* = 7.4 Hz), 3.10–3.23 (2H, m), 4.17–4.23 (2H, m), 4.29–4.41 (1H, m), 4.48 (1H, dd, *J* = 9.9, 5.7 Hz), 4.73–4.78 (1H, m), 4.96 (1H, d, *J* = 12.6 Hz), 5.01 (1H, d, *J* = 12.6 Hz), 5.25 (1H, d, *J* = 7.9 Hz), 7.12–7.72 (13H, m).

¹³C NMR (CDCl₃, 126 MHz) δ 11.3, 29.8, 38.2, 47.2, 47.2, 54.8, 65.2, 66.7, 66.7, 120.1, 121.0, 122.3, 125.2, 125.2, 125.6, 127.3, 127.5, 128.0, 128.1, 128.8, 129.5, 132.8, 132.9, 135.5, 135.6, 138.0, 139.9, 140.4, 140.4, 143.4, 145.7, 155.5, 171.0.

HRMS (ESI) *m/z*: [M – Fmoc + 2H] + Calcd for C₁₄H₁₈Cl₂NO₂ 302.0709; Found 302.0727.

(*E*)-5,6-dichlorodec-5-ene (**8**)

Yield 78% (**70.3 mg, 0.390 mmol**); colorless oil.

IR (neat) 2969, 2935, 2876, 1747, 1455, 1380, 1102, 894, 791, 719, 676 cm^{-1} .

^1H NMR (CDCl_3 , 500 MHz) δ 0.92 (6H, t, J = 7.4 Hz), 1.54-1.61 (4H, m), 2.53 (4H, t, J = 7.4 Hz).

^{13}C NMR (CDCl_3 , 126 MHz) δ 13.1, 20.3, 37.7, 130.0.

HRMS (EI) m/z : [M] + Calcd for $\text{C}_8\text{H}_{14}\text{Cl}_2$ 180.0467; Found 180.0468.

(*E*)-(((3,4-dichlorobut-3-en-1-yl)oxy)methyl)benzene (9)

Yield 58% (**66.9 mg, 0.291 mmol**); colorless oil.

IR (neat) 3086, 3065, 3030, 2862, 1949, 1870, 1811, 1719, 1603, 1495, 1477, 1454, 1420, 1362, 1308, 1266, 1204, 1105, 1028, 908, 808, 735, 697, 610 cm^{-1} .

^1H NMR (CDCl_3 , 500 MHz) δ 2.83-2.85 (2H, t, J = 6.7 Hz), 3.69 (2H, t, J = 6.7 Hz), 4.54 (2H, s), 6.23 (1H, s), 7.26-7.35 (5H, m).

^{13}C NMR (CDCl_3 , 126 MHz) δ 33.9, 66.3, 73.0, 115.6, 127.7, 127.7, 128.5, 133.1, 138.2.

HRMS (ESI) m/z : [M + Na] + Calcd for $\text{C}_{11}\text{H}_{12}\text{Cl}_2\text{ONa}$ 253.0157; Found 253.0164.

(*E*)-tert-butyl((3,4-dichlorobut-3-en-1-yl)oxy)diphenylsilane (10)

Yield 67% (**127 mg, 0.337 mmol**); colorless oil.

IR (neat) 3071, 3049, 2998, 2959, 2931, 2880, 2857, 2740, 1958, 1887, 1823, 1660, 1589, 1486, 1472, 1427, 1389, 1361, 1335, 1305, 1260, 1223, 1187, 1110, 1029, 1007, 998, 938, 918, 822, 809, 737, 700, 614 cm^{-1} .

^1H NMR (CDCl_3 , 500 MHz) δ 1.04 (9H, s), 2.77 (2H, t, J = 6.4 Hz), 3.85 (2H, t, J = 6.4 Hz), 6.23 (1H, s), 7.36-7.44 (6H, m), 7.67-7.68 (4H, m).

^{13}C NMR (CDCl_3 , 126 MHz) δ 19.3, 26.8, 36.7, 60.2, 115.6, 127.8, 129.8, 133.4, 133.6, 135.7.

HRMS (ESI) m/z : [M + Na] + Calcd for $\text{C}_{20}\text{H}_{24}\text{Cl}_2\text{OSiNa}$ 401.0866; Found 401.1052.

(*E*)-(1,2-dichlorovinyl)benzene (11)

Yield 55% (**47.3 mg, 0.275 mmol**); colorless oil.

The spectroscopic data were completely identical with those of the previous report.¹⁷

(*E*)-1,2-dichloro-1,2-diphenylethene (12)

Yield 87% (**107 mg, 0.435 mmol**); colorless oil.

The spectroscopic data were completely identical with those of the previous report.¹⁸

(*E*)-(1,2-dichlorohex-1-en-1-yl)benzene (13)

Yield 94% (**107 mg, 0.471 mmol**); colorless oil.

IR (neat) 3083, 3059, 3032, 3022, 2959, 2930, 2872, 2861, 2339, 1947, 1882, 1801, 1716, 1597, 1578, 1489, 1464, 1444, 1379, 1341, 1282, 1232, 1203, 1157, 1132, 1104, 1073, 1029, 1000, 967, 936, 917, 896, 861, 807, 742, 693, 641, 625, 605 cm^{-1} .

^1H NMR (CDCl_3 , 500 MHz) δ 0.97 (3H, t, J = 7.4 Hz), 1.40-1.45 (2H, m), 1.63-1.69 (2H, m), 2.72 (2H, t, J = 7.5 Hz), 7.30-7.44 (5H, m).

^{13}C NMR (CDCl_3 , 126 MHz) δ 14.0, 22.0, 29.1, 31.0, 36.4, 126.4, 128.2, 128.7, 129.3, 131.7, 137.6.

HRMS (EI) m/z : [M] + Calcd for $\text{C}_{12}\text{H}_{14}\text{Cl}_2$ 228.0467; Found 228.0470.

(*E*)-4-(1,2-dichlorohex-1-en-1-yl)phenyl acetate (14)

Yield 73% (**104 mg, 0.366 mmol**); colorless oil.

IR (neat) 2960, 2931, 2872, 1769, 1600, 1504, 1465, 1431, 1408, 1369, 1196, 1167, 1132, 1105, 1044, 1018, 945, 901, 844, 807, 750, 678 cm^{-1} .

^1H NMR (CDCl_3 , 500 MHz) δ 0.97 (3H, t, J = 7.4 Hz), 1.40-1.44 (2H, m), 1.62-1.68 (2H, m), 2.29 (3H, s), 2.70-2.73 (2H, m), 7.07-7.10 (2H, m), 7.44-7.47 (2H, m).

^{13}C NMR (CDCl_3 , 126 MHz) δ 14.0, 21.2, 22.0, 29.1, 36.5, 121.3, 125.6, 130.6, 132.1, 135.0, 150.7, 169.2.

HRMS (ESI) m/z : [M + Na] + Calcd for $\text{C}_{14}\text{H}_{16}\text{Cl}_2\text{O}_2\text{Na}$ 309.0420; Found 309.0467.

(*E*)-tert-butyl(4-(1,2-dichlorohex-1-en-1-yl)phenoxy)dimethylsilane (15)

Yield 72% (**129 mg, 0.360 mmol**); colorless oil.

IR (neat) 3039, 2958, 2930, 2896, 2859, 2712, 2545, 2358, 1891, 1602, 1573, 1507, 1471, 1463, 1434, 1409, 1390, 1379, 1362, 1267, 1204, 1170, 1132, 1104, 1006, 915, 839, 823, 805, 781, 754, 721, 707, 669, 645, 616 cm^{-1} .

^1H NMR (CDCl_3 , 500 MHz) δ 0.2 (6H, s), 0.96 (3H, t, J = 7.5 Hz), 0.97 (9H, s), 1.40-1.45 (2H, m), 1.61-1.67 (2H, m), 2.70 (2H, t, J = 7.5 Hz), 6.78-6.81 (2H, m), 7.30-7.33 (2H, m).

^{13}C NMR (CDCl_3 , 126 MHz) δ -4.3, 14.0, 18.3, 22.0, 25.7, 29.1, 36.6, 119.5, 126.5, 130.4, 130.7, 131.0, 155.9.

HRMS (APCI) m/z : [M + H] + Calcd for $\text{C}_{18}\text{H}_{28}\text{Cl}_2\text{OSi}$ 359.1359; Found 359.1320.

(*E*)-2,3-dichloro-1-phenylhept-2-en-1-yl acetate (16)

Yield 85% (**127 mg, 0.426 mmol**); colorless oil.

IR (neat) 3064, 3032, 2960, 2931, 2872, 1750, 1632, 1604, 1586, 1495, 1453, 1433, 1371, 1226, 1158, 1080, 1024, 978, 939, 844, 806, 748, 700 cm^{-1} .

^1H NMR (CDCl_3 , 500 MHz) δ 0.90 (3H, t, J = 7.4 Hz), 1.28-1.35 (2H, m), 1.53-1.60 (2H, m), 2.19 (3H, s), 2.55-2.61 (2H, m), 7.11 (1H, s), 7.31-7.43 (5H, m).

^{13}C NMR (CDCl_3 , 126 MHz) δ 13.9, 21.0, 21.9, 28.9, 35.8, 72.8, 126.2, 127.5, 128.5, 128.5, 134.1, 136.7, 169.6.

HRMS (ESI) m/z : [M - OAc] + Calcd for $\text{C}_{13}\text{H}_{15}\text{Cl}_2$ 241.0545; Found 241.0539.

(*E*)-tert-butyl((2,3-dichloro-1-phenylhept-2-en-1-yl)oxy)dimethylsilane (17)

Yield 61% (**109 mg, 0.307 mmol**); colorless oil.

IR (neat) 3088, 3063, 3029, 2957, 2930, 2895, 2857, 2739, 2710, 1945, 1880, 1804, 1754, 1627, 1602, 1493, 1470, 1462, 1451, 1406, 1389, 1361, 1253, 1194, 1175, 1150, 1114, 1103, 1069, 1027, 1005, 962, 938, 915, 864, 852, 836, 805, 779, 741, 723, 698, 673, 640 cm^{-1} .

^1H NMR (CDCl_3 , 500 MHz) δ 0.11 (6H, s), 0.91 (3H, t, J = 7.5 Hz), 0.95 (9H, s), 1.31-1.35 (2H, m), 1.54-1.59 (2H, m), 2.50-2.64 (2H, m), 6.22 (1H, s), 7.24-7.27 (1H, m), 7.32 (2H, t, J = 6.7 Hz), 7.42 (2H, d, J = 6.9 Hz).

^{13}C NMR (CDCl_3 , 126 MHz) δ -5.0, -4.8, 13.9, 18.3, 22.0, 25.9, 28.7, 35.7, 71.6, 125.6, 127.5, 128.1, 130.6, 133.3, 141.2.

HRMS (ESI) m/z : [M - OTBS] + Calcd for $\text{C}_{13}\text{H}_{15}\text{Cl}_2$ 241.0545; Found 241.0567.

(*E*)-2,3-dichloro-1-(2-(trifluoromethyl)phenyl)hept-2-en-1-yl acetate (18)

Yield 69% (**128 mg, 0.346 mmol**); colorless oil.

IR (neat) 3480, 3073, 2961, 2935, 2874, 2298, 2235, 1947, 1749, 1651, 1608, 1588, 1496, 1455, 1431, 1371, 1352, 1314, 1269, 1224, 1164, 1147, 1127, 1060, 1038, 1016, 958, 921, 855, 838, 769, 751, 670, 647, 626 cm^{-1} .

^1H NMR (CDCl_3 , 500 MHz) δ 0.88 (3H, td, J = 7.3, 2.8 Hz), 1.34-1.39 (2H, m), 1.46-1.51 (2H, m), 2.07 (3H, s), 2.23 (2H, td, J = 7.0, 2.8 Hz), 6.70 (1H, t, J = 2.8 Hz), 7.45 (1H, t, J = 7.7 Hz), 7.59-7.66 (2H, m), 7.95 (1H, d, J = 7.3 Hz).

^{13}C NMR (CDCl_3 , 126 MHz) δ 13.7, 18.6, 21.1, 22.0, 30.4, 62.4, 62.4, 76.4, 89.0, 126.1, 126.1, 128.9, 130.0, 132.3, 136.1, 169.4.

(*E*)-tert-butyl((2,3-dichloro-1-(2-(trifluoromethyl)phenyl)hept-2-en-1-yl)oxy)dimethylsilane (19)

Yield 74% (**163 mg, 0.372 mmol**); colorless oil.

IR (neat) 2958, 2932, 2898, 2858, 2282, 2225, 1941, 1835, 1722, 1650, 1608, 1587, 1490, 1471, 1462, 1455, 1432, 1406, 1389, 1379, 1362, 1314, 1259, 1162, 1125, 1070, 1053, 1034, 1005, 957, 939, 843, 778, 766, 726, 672, 660, 627 cm^{-1} .

¹H NMR (CDCl₃, 500 MHz) δ 0.07 (3H, s), 0.16 (3H, s), 0.86 (3H, t, *J* = 7.2 Hz), 0.88 (9H, s), 1.32–1.38 (2H, m), 1.41–1.46 (2H, m), 2.15 (2H, td, *J* = 7.0, 2.0 Hz), 5.75 (1H, t, *J* = 1.8 Hz), 7.35 (1H, t, *J* = 7.7 Hz), 7.56 (2H, t, *J* = 7.8 Hz), 7.93 (1H, d, *J* = 7.7 Hz).

¹³C NMR (CDCl₃, 126 MHz) δ –5.0, –4.6, 13.6, 18.3, 18.5, 21.9, 25.8, 30.6, 60.9, 81.0, 86.5, 125.3, 127.5, 128.8, 132.3.

(E)-2,3-dichloro-1-(4-cyanophenyl)hept-2-en-1-yl acetate (20)

Yield 89% (**144 mg**, **0.445 mmol**); colorless oil.

IR (neat) 2960, 2932, 2872, 2230, 1753, 1611, 1506, 1465, 1433, 1410, 1371, 1223, 1085, 1030, 1020, 984, 927, 860, 830, 806, 745, 678 cm^{–1}.

¹H NMR (CDCl₃, 500 MHz) δ 1.90 (3H, t, *J* = 7.4 Hz), 1.27–1.35 (2H, m), 1.53–1.60 (2H, m), 2.53–2.63 (2H, m), 7.14 (1H, s), 7.52 (2H, d, *J* = 8.0 Hz), 7.66 (2H, dd, *J* = 6.7, 1.8 Hz).

¹³C NMR (CDCl₃, 126 MHz) δ 13.9, 20.9, 21.8, 28.8, 35.8, 72.1, 112.4, 118.6, 126.9, 132.4, 135.4, 141.9.

HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₁₆H₁₇Cl₂NO₂Na 348.0529; Found 348.0529.

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Supporting Information

YES (this text will be updated with links prior to publication)

Primary Data

NO.

Conflict of Interest

The authors declare no conflict of interest.

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