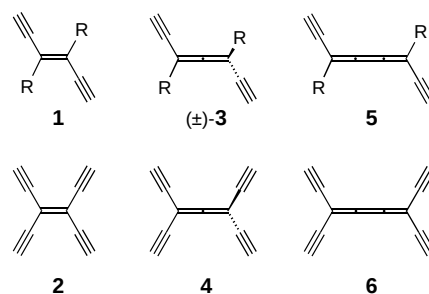


- ment with the presence of methyldiene tantalum species. Determination of the exact structure of these surface complexes is underway.
- [6] The reaction of ^{13}C -monolabeled ethane on **1+2** gave the partially scrambled metathesis products of ethane along with unlabeled NpH and partially labeled NpMe (35% ^{13}C incorporated). This shows that at least 70% of this compound arises from cross-metathesis. The excess of unlabeled compound probably arises from rearrangement of **1+2**. Heating **1+2** under Ar at 150 °C for 15 h gives 0.25 equiv of NpH and 0.01 equiv of NpMe.
- [7] While the addition of a C–C bond to a M=C bond has never been observed before in organometallic chemistry, there are examples of additions of C–H bonds: L. R. Chamberlain, I. P. Rothwell, J. C. Huffman, *J. Am. Chem. Soc.* **1986**, *108*, 1502; H. van der Heijden, B. Hessen, *Chem. Commun.* **1995**, 145.
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- [9] This is an upper limit, since neopentane can also be formed by direct α -H abstraction of a neighboring ligand without involving an intermolecular C–H bond. For the reference experiment under Ar, see ref. [6].
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1,3-Diethynylallenes: New Modules for Three-Dimensional Acetylenic Scaffolding**

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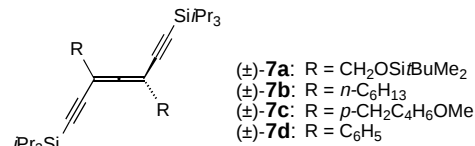
Oxidative coupling^[1] of multiply ethynylated building blocks has facilitated the assembly of well-defined molecular architecture that displays unusual electronic and optical properties.^[2] In particular, derivatives of (*E*)-1,2-diethynylethene (**1**, (*E*)-DEE, (*E*)-hex-3-ene-1,5-diyne) and tetraethynylethene (**2**, TEE, 3,4-diethynylhex-3-ene-1,5-diyne) have provided a unique class of π -conjugated precursors for the modular construction of one- and two-dimensional carbon-rich scaffolds (Scheme 1).^[3] They have provided access to monodisperse, linearly π -conjugated polytriacyetylene (PTA) oligomers that extend up to 18 nm in length,^[4] to perethynylated expanded radialenes that feature all-carbon cores (C_{30} to C_{60}), which undergo facile electrochemical reduction and



Scheme 1. Diethynyl- and tetraethynyl[n]cumulenes ($n = 1–3$) as carbon-rich modules for acetylenic scaffolding.

display low-energy electronic absorption bands with remarkably high molar extinction coefficients,^[5] and to photochromic molecules for photochemical switching without competing thermal isomerization pathways.^[6] Expansion of the central olefinic fragment in DEEs and TEEs leads to the di- and tetraethynylated allenes ($\pm$)-**3** and **4**, and butatrienes **5** and **6** (Scheme 1). Whereas silylated derivatives of peralkynylated butatriene **6** have been reported,^[7] 1,3-diethynyl- and tetraethynylallenes have remained elusive, despite intensive efforts aimed at their preparation.^[8] The major problems encountered in previous attempts to synthesize these novel building blocks for three-dimensional acetylenic scaffolding were their high tendency for rearrangement and facile [2+2] cycloaddition, which occurred readily even at room temperature or below.^[9]

Herein we describe the synthesis of the first 1,3-diethynylallenes ($\pm$)-**7a–d**. As a result of the inherent 90° twist of the

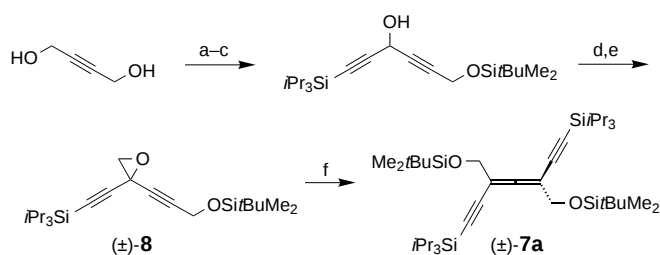


allene moiety, alkyne deprotection and oxidative acetylenic coupling of these compounds in enantiomerically pure form promises access to a fascinating new class of three-dimensional helical oligomers and polymers.^[10] Optically active helical polymers^[11] are attracting increasing interest as materials that exhibit circularly polarized electroluminescence^[12] or as dopants for cholesteric liquid-crystalline phases.^[13]

Palladium-catalyzed cross-coupling reactions have proven valuable in the preparation of alkynylallenes from substrates that bear propargylic leaving groups such as halides, epoxides, acetates, and carbonates.^[14] Given an appropriate regiochemical bias, application of these conditions to bispropargylic precursors should yield the corresponding 1,3-diethynylallenes. Thus, target compound ($\pm$)-**7a** was obtained from bispropargylic epoxide precursor ($\pm$)-**8**^[15] (prepared in five steps from but-2-yne-1,4-diol, Scheme 2) and $i\text{Pr}_3\text{SiC}\equiv\text{CH}$ under standard palladium-catalyzed cross-coupling conditions ($[\text{Pd}(\text{PPh}_3)_4]$, CuI , HNiPr_2 , CH_2Cl_2). In situ protection of the primary alcohol that results from epoxide ring opening as the Si^tBuMe_2 ether gave 1,3-diethynylallene ($\pm$)-**7a** (Table 1)

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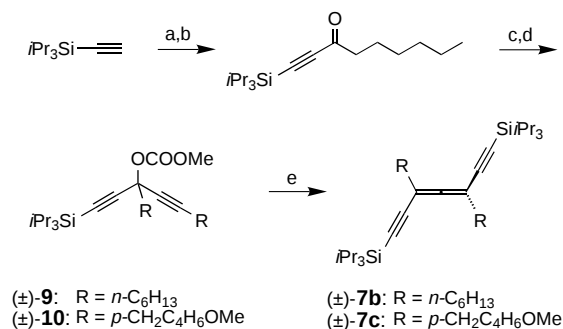
[**] We thank the ETH Research Council and the Fonds der Chemischen Industrie for their support of this work.



Scheme 2. Synthesis of 1,3-diethynylallene (±)-7a by means of epoxide ring opening. Reagents and conditions: a) NaH, *t*BuMe₂SiCl, 0 °C → RT, 65 %; b) MnO₂, Et₂O, RT; c) *n*BuLi, *i*Pr₃SiC≡CH, THF, −78 °C → RT, 34 % (over two steps); d) MnO₂, Et₂O, RT, 77 %; e) MeLi · LiBr, CH₂I₂, THF, −78 °C → RT, 79 %; f) [Pd(PPh₃)₄], CuI, HN*i*Pr₂, CH₂Cl₂, RT; then *t*BuMe₂SiCl, imidazole, DMAP, RT, 52 %. DMAP = 4-(dimethylamino)-pyridine.

as a colorless solid in 52 % yield from (±)-8. Gratifyingly, the difference in steric bulk of the two alkyne substituents (Si*i*Pr₃ vs. CH₂OSi*t*BuMe₂) in (±)-8 had induced the desired regioselectivity in the cross-coupling reaction.^[16]

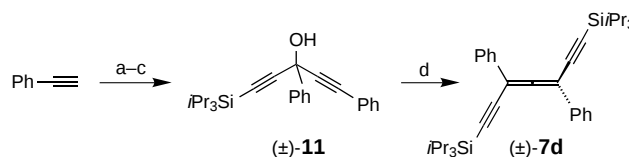
The structural limitations imposed by the epoxide opening were circumvented through the use of carbonate as the propargylic leaving group. Under the same cross-coupling conditions used above, bispropargylic precursor (±)-9 (prepared in four steps from *i*Pr₃SiC≡CH, Scheme 3) provided the



Scheme 3. Synthesis of 1,3-diethynylallenes (±)-7b and (±)-7c from bispropargylic carbonates. Reagents and conditions: a) *n*BuLi, CH₃(CH₂)₅CHO, THF, −78 °C → RT, 79 %; b) (COCl)₂, Me₂SO, Et₃N, CH₂Cl₂, −78 °C, 94 %; c) *n*BuLi, 1-octyne, THF, −78 °C → RT, 66 %; d) *n*BuLi, MeOCOC(OMe), THF, −78 °C → RT, 71 %; e) [Pd(PPh₃)₄], CuI, HN*i*Pr₂, CH₂Cl₂, RT, 94 % ((±)-7b), 57 % ((±)-7c). Carbonate (±)-10 was prepared analogously to (±)-9.

dihexyl-substituted 1,3-diethynylallene (±)-7b (Table 1) in 94 % yield, with complete conversion observed after only 30 min at room temperature. The preparation of the di(4-methoxybenzyl)-substituted allene (±)-7c (Table 1) from (±)-10 proceeded analogously, but the cross-coupling provided the target in only 57 % yield, possibly as a result of the acidity of the benzylic protons. Unlike the more sterically encumbered derivative (±)-7a, compounds (±)-7b and (±)-7c were susceptible to thermal dimerization, presumably through a stepwise radical mechanism.^[17] The half-life of neat (±)-7b was in the order of one day at room temperature, and this process was not entirely suppressed by storage at low temperature, although dilute solutions showed minimal dimerization over the course of several months.

The synthesis of cross-conjugated 1,3-diethynyl-1,3-diphenylallene (±)-7d (Table 1) was hampered by the instability of the desired propargylic carbonate precursor, even in solution at low temperature. Similarly, other acylated derivatives could not be isolated in pure form. Ultimately, access to the desired allene was achieved in a one-pot procedure through the intermediate formation of the benzoate from tertiary alcohol (±)-11, followed by direct application of the cross-coupling conditions (Scheme 4). This allene proved especially susceptible to thermal dimerization, which proceeded within minutes for the neat compound at room temperature, and therefore it could only be handled and characterized in solution.



Scheme 4. Synthesis of cross-conjugated allene (±)-7d via the bispropargylic benzoate, prepared in situ. Reagents and conditions: a) *n*BuLi, PhCHO, THF, −78 °C → RT; b) MnO₂, Et₂O, RT, 99 % (over two steps); c) *n*BuLi, *i*Pr₃SiC≡CH, THF, −78 °C → RT, 96 %; d) *n*BuLi, PhCOCl; then [Pd(PPh₃)₄], CuI, HN*i*Pr₂, THF, reflux, 38 %.

Allene (±)-7a is solid and stable at room temperature, which allowed unambiguous structural determination by X-ray crystallography.^[18] The unit cell contains two molecules each of the *P* and *M* enantiomers. The ORTEP representation (Figure 1A) shows that although there is significant thermal and orientational disorder in the silyl protecting groups, the structure of the diethynylallene backbone is well defined, with all bond lengths and angles within the expected ranges. The view down the allene axis (Figure 1B) clearly shows the orthogonal disposition of the C≡CSi*i*Pr₃ and CH₂OSi*t*BuMe₂ substituents.

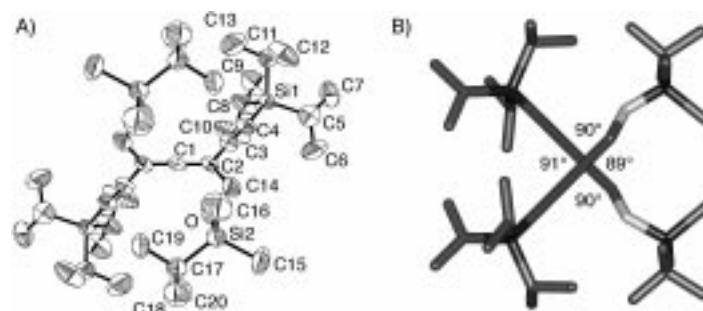


Figure 1. A) ORTEP representation of (±)-7a with vibrational ellipsoids at the 30 % probability level. Bond lengths [Å] and angles [°] for the diethynylallene backbone: C1–C2 1.297(6), C2–C3 1.433(7), C3–C4 1.205(6), C2–C1–C2' 177.7(7), C1–C2–C3 121.7(5), C2–C3–C4 176.6(6), C3–C4–Si1 175.8(5), C1–C2–C14 123.1(4), C3–C2–C14 115.2(5). B) Stick representation of (±)-7a showing the orthogonal orientation of the allene substituents.

Bisalkynylation has a profound effect on the allenic ¹³C NMR resonances. In tetraalkylallenes, the resonance for the central allene carbon atom appears at around δ = 200, whereas in tetraphenylallene the signal is shifted downfield to

$\delta = 208$.^[19] In the 1,3-diethynylallenes, this resonance appears further downfield at $\delta = 215$ –217 in ($\pm$)-**7a–c** and at $\delta = 222.6$ in ($\pm$)-**7d**. The terminal allenic resonance in ($\pm$)-**7a–d** is located between $\delta = 99$ and 102, whereas the acetylenic signals appear between $\delta = 92$ and 97 (Table 1).

Table 1. Selected physical and spectroscopic data of 1,3-diethynylallenes.

($\pm$)- 7a : $R_f(\text{SiO}_2) = 0.45$ (hexane/ CH_2Cl_2 4:1); white solid; m.p. 56–57 °C; IR (film): $\tilde{\nu} = 2944, 2891, 2147, 1944, 1464, 1388, 1361, 1333, 1254, 1111, 994, 878, 833, 779, 667 \text{ cm}^{-1}$; ^1H NMR (300 MHz, CDCl_3): $\delta = 4.20$ (s, 4H), 1.07 (s, 42H), 0.89 (s, 18H), 0.08 (s, 12H); ^{13}C NMR (75 MHz, CDCl_3): $\delta = 214.9, 98.7, 95.9, 95.1, 64.1, 25.7, 18.5, 18.1, 11.2, -5.4, -5.5$; EI-MS: m/z : 688.4 [M^+]; elemental analysis calcd for $\text{C}_{39}\text{H}_{76}\text{O}_2\text{Si}_4$ (689.38) (%): C 67.95, H 11.11; found: C 67.85, H 11.13
($\pm$)- 7b : $R_f(\text{SiO}_2) = 0.60$ (hexane); colorless oil; IR (film): $\tilde{\nu} = 2927, 2851, 2133, 1933, 1464, 1380, 1154, 1072, 990, 883, 672 \text{ cm}^{-1}$; ^1H NMR (200 MHz, CDCl_3): $\delta = 2.15$ (t, $J = 7.1 \text{ Hz}$, 4H), 1.58–1.43 (m, 4H), 1.40–1.22 (m, 12H), 1.07 (s, 42H), 0.88 (t, $J = 6.6 \text{ Hz}$, 6H); ^{13}C NMR (50 MHz, CDCl_3): $\delta = 216.2, 101.7, 92.6, 91.8, 34.1, 31.6, 28.2, 27.4, 22.4, 18.5, 14.0, 11.2$; EI-MS: m/z : 568.6 [M^+]; elemental analysis calcd for $\text{C}_{37}\text{H}_{68}\text{Si}_2$ (569.12) (%): C 78.09, H 12.04; found: C 78.22, H 12.08
($\pm$)- 7c : $R_f(\text{SiO}_2) = 0.47$ (hexane/ EtOAc 10:1); colorless oil; IR (film): $\tilde{\nu} = 2943, 2851, 2133, 1939, 1611, 1512, 1464, 1303, 1248, 1174, 1039, 883, 815, 677 \text{ cm}^{-1}$; ^1H NMR (200 MHz, CDCl_3): $\delta = 7.00$ (d, $J = 8.7 \text{ Hz}$, 4H), 6.75 (d, $J = 8.7 \text{ Hz}$, 4H), 3.78 (s, 6H), 3.34 (s, 2H), 3.33 (s, 2H), 1.03 (s, 42H); ^{13}C NMR (75 MHz, CDCl_3): $\delta = 216.9, 158.4, 130.2, 130.0, 113.6, 101.0, 93.9, 93.2, 55.1, 39.8, 18.4, 11.1$; EI-MS: m/z : 640.3 [M^+]; HR-EI-MS calcd for $\text{C}_{41}\text{H}_{60}\text{O}_2\text{Si}_2$ [M^+]: 640.4132; found 640.4129
($\pm$)- 7d : $R_f(\text{SiO}_2) = 0.65$ (hexane/ CH_2Cl_2 10:1); yellow oil; IR (film): $\tilde{\nu} = 2944, 2862, 2144, 1944, 1492, 1462, 1062, 990, 882, 759, 676 \text{ cm}^{-1}$; ^1H NMR (300 MHz, CDCl_3): $\delta = 7.65$ –7.61 (m, 2H), 7.40–7.27 (m, 8H), 1.15 (s, 42H); ^{13}C NMR (75 MHz, CDCl_3): $\delta = 222.6, 132.7, 128.7, 128.2, 126.8, 98.7, 97.6, 97.3, 18.5, 11.2$. For the [2+2] dimer of ($\pm$)- 7d : EI-MS: m/z : 1104.7 [M^+]; elemental analysis calcd for $\text{C}_{74}\text{H}_{104}\text{Si}_4$ (1106.00) (%): C 80.36, H 9.48; found: C 80.17, H 9.34

These first representative examples show how the overall stability of 1,3-diethynylallenes is affected by the electronic and steric properties of the substituents. The substantial stability of compound ($\pm$)-**7a** clearly demonstrates that bulky side chains prevent the approach of two allene units and are capable of mitigating the undesired thermal [2+2] cycloaddition to an appreciable extent. Since removal of the alkyne-protecting SiPr_3 groups from ($\pm$)-**7b** with Bu_4NF cleanly yields the corresponding bis-terminally deprotected diethynylallene (^1H NMR spectrum (CDCl_3): $\delta_{\text{C}\equiv\text{C}-\text{H}} = 2.94$), oxidative oligomerization of enantiomerically pure 1,3-diethynylallenes is expected to lead to the proposed helical oligomers with unusual chiroptical properties.

Experimental Section

($\pm$)-**7b**: $i\text{Pr}_3\text{SiC}\equiv\text{CH}$ (34 μL , 27 mg, 0.15 mmol) and HNiPr_2 (28 μL , 20 mg, 0.20 mmol) were added to ($\pm$)-**8** (46 mg, 0.10 mmol) in CH_2Cl_2 (1 mL) at room temperature. The solution was purged with Ar for several minutes, and $[\text{Pd}(\text{PPh}_3)_4]$ (5.8 mg, 5.0 μmol) and CuI (1.9 mg, 10 μmol) were added sequentially. After an additional minute of degassing, the solution was allowed to stir at room temperature for 30 min, at which point TLC showed complete conversion. The mixture was diluted with hexanes (5 mL) and filtered through celite. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on SiO_2 (hexane) to give ($\pm$)-**7b** (54 mg, 94 %) as a clear oil.

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- [18] X-ray crystal data of ($\pm$)-**7a** ($\text{C}_{39}\text{H}_{76}\text{O}_2\text{Si}_4$, $M_r = 689.36$): orthorhombic space group *Pbcn*, $Z = 4$, $D_c = 0.963 \text{ g cm}^{-3}$, $a = 14.767(5)$, $b = 11.746(4)$, $c = 27.420(13) \text{ Å}$, $V = 4756(3) \text{ Å}^3$, $\text{MoK}\alpha$ radiation, 2229 independent reflections, $2 < \theta < 20^\circ$. Single crystals were grown at 4°C from $\text{CH}_2\text{Cl}_2/\text{MeCN}$. The structure was calculated by direct methods (SHELXS-86) and refined by full-matrix least-squares methods (SHELXL-93). Final $R(F) = 0.0689$, $wR(F^2) = 0.1888$ for 199 variables and 2229 observed reflections with $I > 2\sigma(I)$. Crystallographic data (excluding structure factors) for the structures reported in this paper were deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-157566. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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Directed Intermolecular Carbomagnesation across Vinylsilanes: 2-PyMe₂Si Group as a Removable Directing Group**

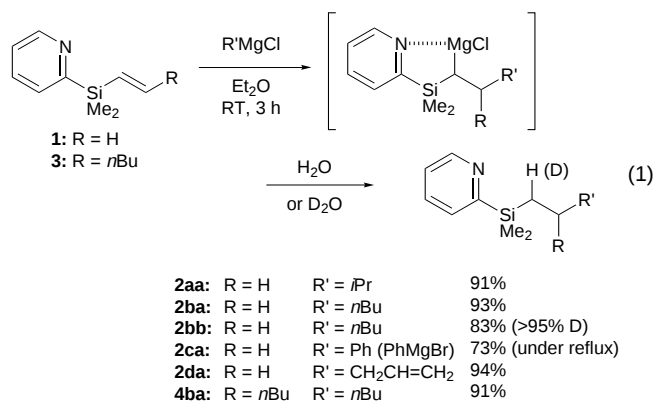
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The addition of organolithium reagents to vinylsilanes is one of the most powerful methods for the generation of synthetically useful α -silyl carbanions.^[1] Although Grignard reagents are viable alternatives for this addition reaction,^[2] serious limitations are associated with the carbomagnesation methodology: 1) Activating groups on silicon (e.g., chloro, alkoxy, and amino groups) are needed for the addition (no reaction with trialkyl(vinyl)silanes); 2) substitutions at the silicon atom are often observed as unavoidable side reactions when these activating groups are used; and 3) primary alkyl Grignard reagents are not applicable in the reaction.^[3, 4] These drawbacks profoundly diminish the synthetic usefulness of this otherwise attractive methodology.

Recently, we initiated a program to develop highly efficient hydro- and carbometalation reactions by utilizing the 2-pyr-

idyldimethylsilyl (2-PyMe₂Si) group as a removable directing group (intramolecular ligand).^[5–8] For example, highly efficient carbopalladation of vinylsilanes can be achieved with 2-PyMe₂Si group as a removable directing group.^[6] In ongoing efforts to exploit the utility of this removable directing group in carbometalation, we investigated directed intermolecular carbomagnesation across pyridyl-substituted vinylsilanes.

2-Pyridyldimethylvinylsilane (**1**) was treated with *i*PrMgCl in Et₂O, and the mixture was stirred for 3 h at room temperature. The reaction gave the corresponding α -silyl organomagnesium compound, and **2aa** was isolated after aqueous workup in 91 % yield [Eq. (1)].^[9] Much milder



reaction conditions and much shorter reaction times compared to the previous reported reactions with vinylsilanes clearly indicate the enhanced reactivity of **1**.^[2] We assume that this carbomagnesation was facilitated by the complex-induced proximity effect (CIPE).^[10] The reaction presumably involves a pre-equilibrium complex of **1** and RMgX, and this makes the subsequent carbomagnesation step intramolecular in nature. The importance of this pre-equilibrium complex was further supported by the observation of dramatic solvent effects: weakly coordinating solvents such as Et₂O favor this reaction, whereas strongly coordinating solvents such as THF disfavor it. These results may be attributed to inhibition of the formation of the pre-equilibrium complex by the coordinating solvent.^[11] In addition to this kinetic preference, we assume that stabilization of the generated α -silyl organomagnesium compound by intramolecular coordination of the pyridyl group is also responsible for the efficiency of this carbomagnesation process.^[8a]

Next we investigated the addition of a primary alkyl Grignard reagent, and found that *n*BuMgCl also adds to **1** at room temperature [Eq. (1)]. To our knowledge, this is the first example of the efficient addition of a primary alkyl Grignard reagent to a vinylsilane. In addition to secondary and primary alkyl Grignard reagents, PhMgBr^[12] and CH₂=CHCH₂MgCl also added across **1** [Eq. (1)]. The addition of CH₂=CHCH₂MgCl was complete within 1 h even at 0°C (90%). Moreover, the addition to β -substituted vinylsilane **3**, which represents a more difficult class of substrate, also took place [Eq. (1)]. Quantitative incorporation of deuterium in the position α to silicon occurred on quenching

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