Electronic Supplementary Information

Enhanced sol-gel polymerization of organoallylsilanes by solvent effect

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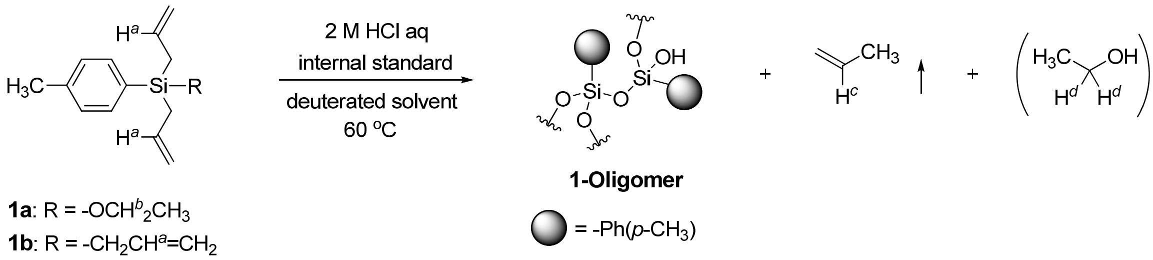
Contents

1. Observation of sol-gel polymerization behaviors of 1a and 1b by ^{1}H NMR spectroscopy



Scheme S1 Acid-catalyzed sol-gel polymerization of **1a** and **1b**. The protons H^{a}, H^{b}, H^{c} and H^{d} were monitored by ^{1}H NMR spectroscopy.

Conversion of the allyl groups in the organoallylsilane precursors **1a** and **1b** during the reactions was monitored by ^{1}H NMR spectroscopy. The measurements were carried out for their sol-solutions containing internal standards (1,4-dichlorobenzene: DCB or naphthalene: Nap). Figs. S1-S6 show the ^{1}H NMR spectra of **1a** or **1b** in various deutrated solvents at 0 min, 10 min and 4 h after the addition of HCl. In the figures, the letters (*a*, *b*, *c*, and *d*) indicate the signals corresponding to the protons shown in Scheme 1.

For **1a**, the signals corresponding to the proton *b* completely disappeared along with the appearance of the signals corresponding to the proton *d* within 10 min for all the solvents (Figs. S1-S5), which indicates that the ethoxy group in **1a** is immediately converted to ethanol regardless of the nature of solvents. In contrast, the nature of solvents strongly affected the deallylation rate of **1a**. After 4 h, intensities of the signals corresponding to the proton *a* decreased by 100% for MeCN (Fig. S1), 76% for acetone (Fig. S2) and less than 30% for MeOH, THF, and DMSO (Figs. S3-S5). Weak signals at the similar positions after 4 h for MeCN were identified as the proton *c* of propene dissolved in the solvents.

MeCN was also effective for deallylation of **1b** and the signals corresponding to the proton *a* completely disappeared within 4 h (Fig. S6a). Meanwhile, 80% of the allyl groups remained after 4 h for acetone (Fig. S6b).

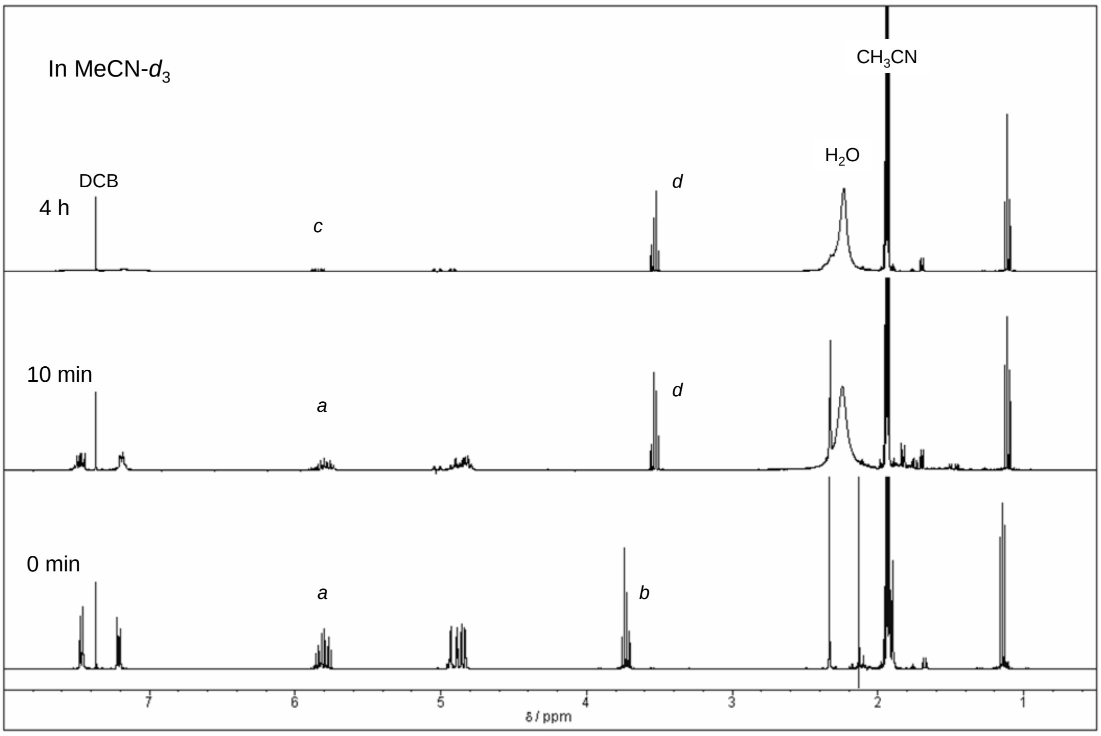


Fig. S1 ^{1}H NMR spectra of the sol-solution of **1a** in MeCN-d_3 at 0 min, 10 min and 4 h after the addition of HCl.

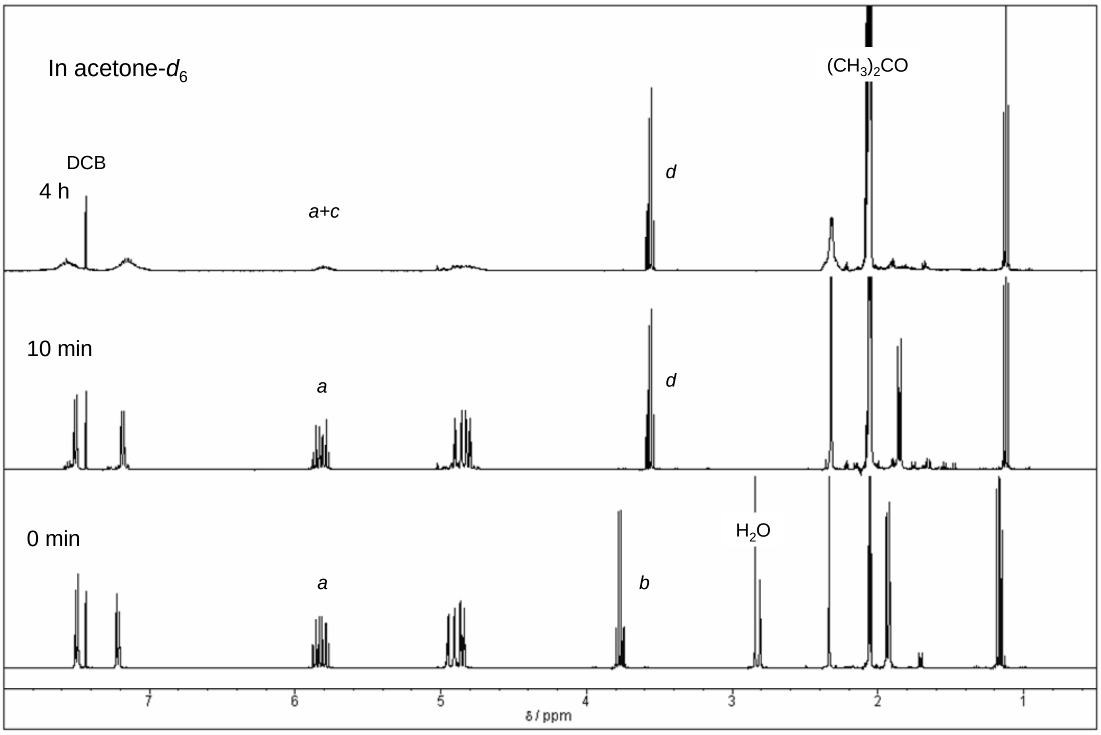


Fig. S2 ^{1}H NMR spectra of the sol-solution of **1a** in acetone-d_6 at 0 min, 10 min and 4 h after the addition of HCl.

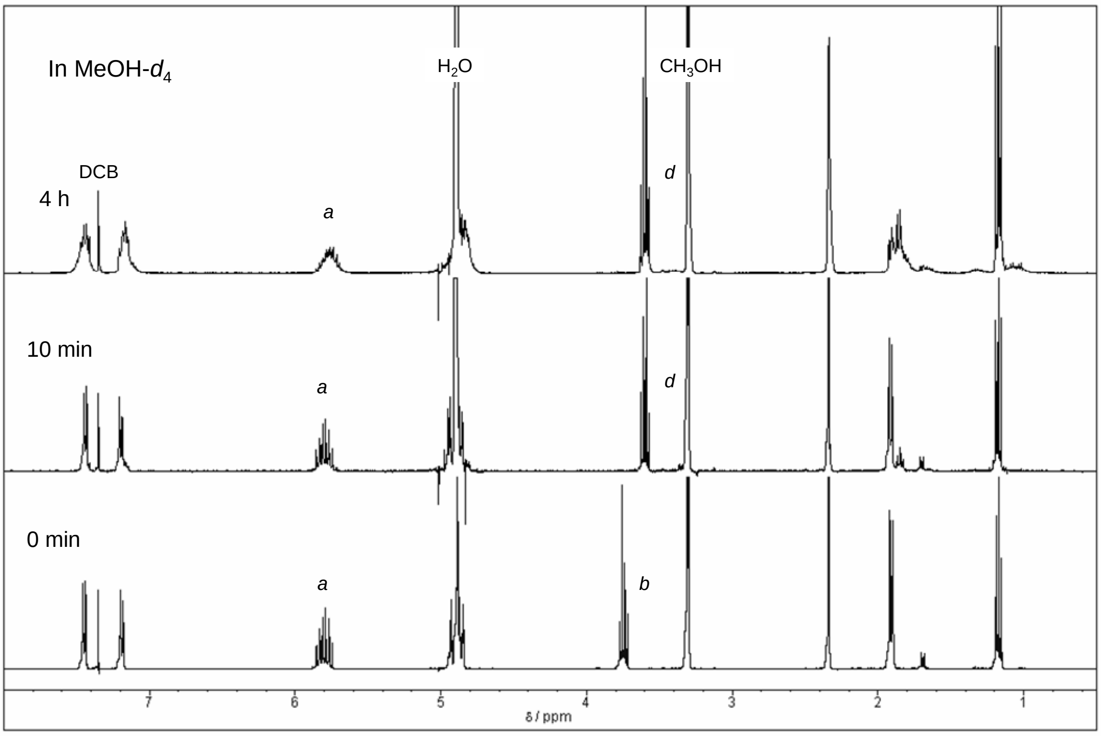


Fig. S3 [1]H NMR spectra of the sol-solution of **1a** in MeOH-d_4 at 0 min, 10 min and 4 h after the addition of HCl.

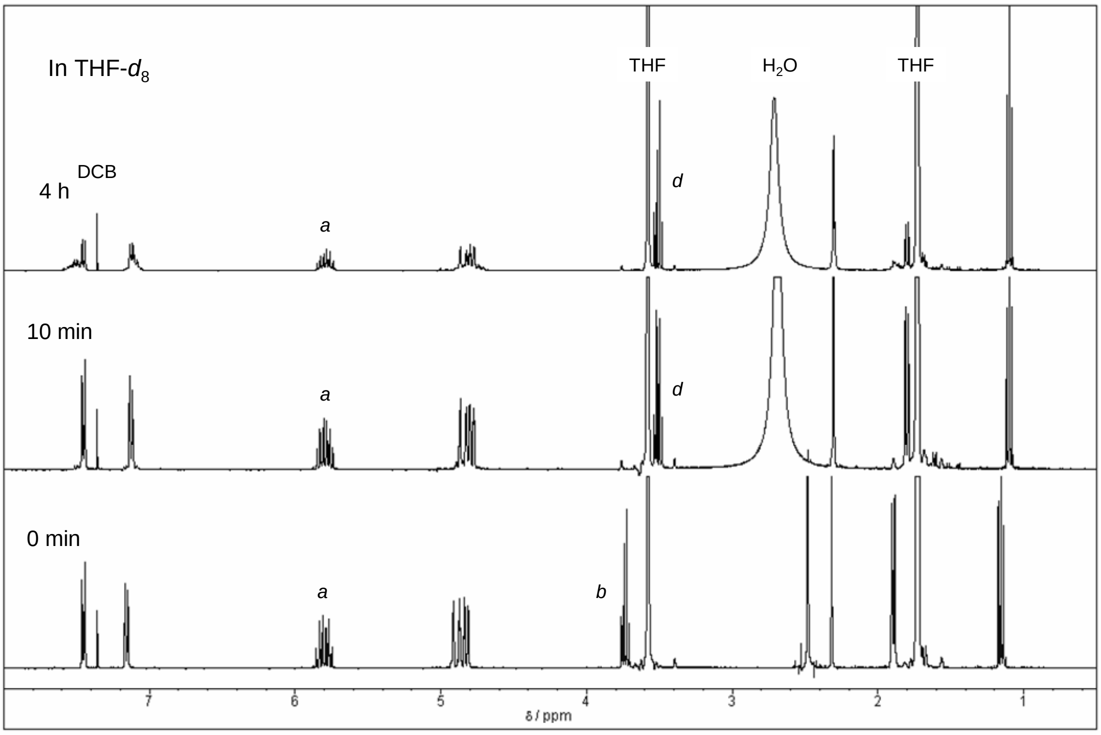


Fig. S4 [1]H NMR spectra of the sol-solution of **1a** in THF-d_8 at 0 min, 10 min and 4 h after the addition of HCl.

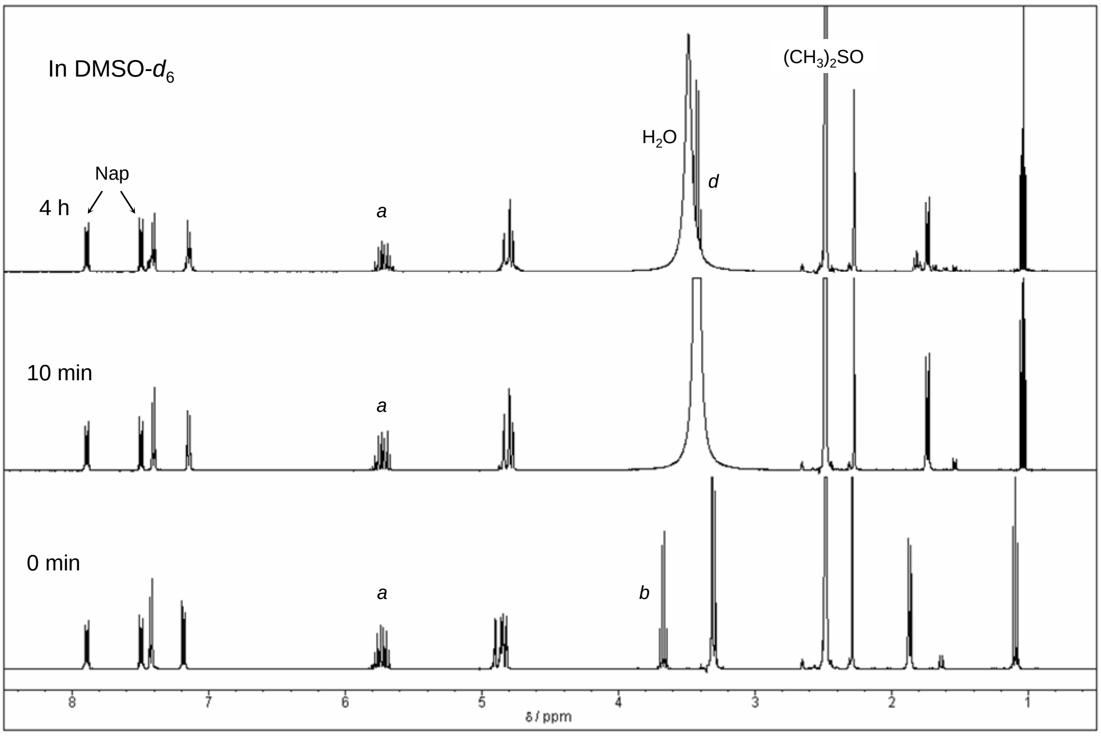


Fig. S5 [1]H NMR spectra of the sol-solution of **1a** in DMSO-d_6 at 0 min, 10 min and 4 h after the addition of HCl.

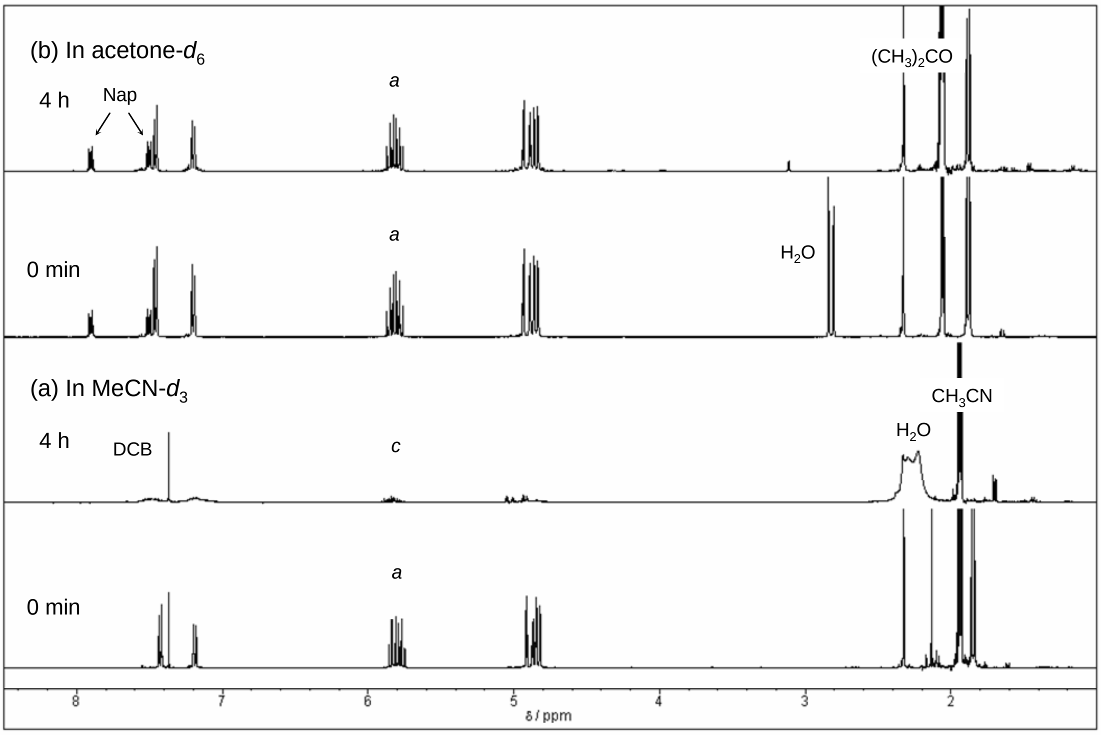
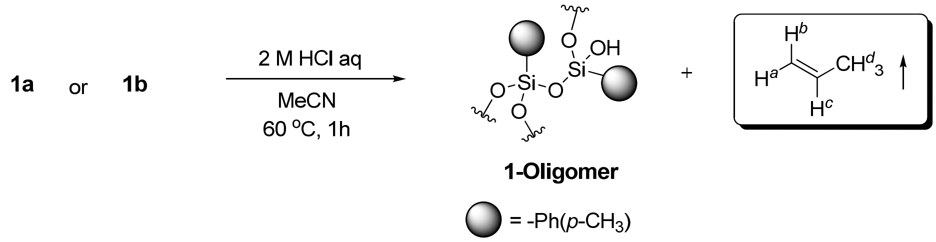


Fig. S6 [1]H NMR spectra of the sol-solutions of **1b** in (a) MeCN-d_3 and (b) acetone-d_6 at 0 min and 4 h after the addition of HCl.

2. Identification of the generated gas during sol-gel polymerization of 1a and 1b



Scheme S2 Generation of propene during acid-catalyzed sol-gel polymerization of **1a** and **1b**.

The generated gas during acid-catalyzed sol-gel polymerization of **1a** and **1b** was identified by ^{1}H NMR spectroscopy (Scheme S2). A 50 mL, one-necked, round-bottomed flask equipped with a magnetic stirring bar was sequentially charged with **1a** or **1b** (250 mg, 1.0 mmol) and MeCN (2.50 mL). After addition of a 2 M HCl aqueous solution (0.25 mL, 0.50 mmol), the flask was capped with a septum and stirred at 60 °C for 1 h (*Caution!: the increased inner pressure may blow out the septum*). The gas phase in the flask was collected with a syringe and passed through MeCN-d_3. The solution was immediately characterized by ^{1}H NMR spectroscopy (Fig. S1). The generated gas was identified as propene.[1]

^{1}H NMR (400 MHz, MeCN-d_3) δ 1.70 (ddd, J = 6.4 Hz, 1.7 Hz, 1.4 Hz, 3H), 4.93 (ddq, J = 10.1 Hz, 2.2 Hz, 1.4 Hz, 1H), 5.04 (ddq, J = 16.6 Hz, 2.2 Hz, 1.7 Hz, 1H), 5.85 (ddq, J = 16.6 Hz, 10.1 Hz, 6.4 Hz, 1H).

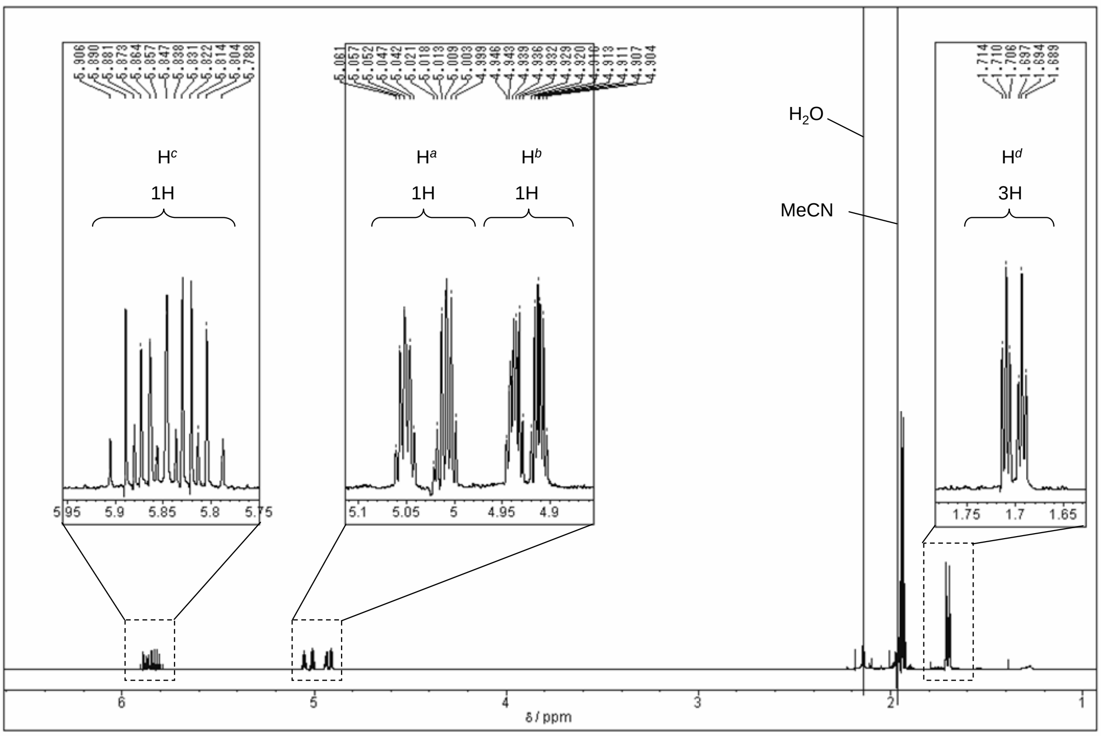


Fig. S7 ^{1}H NMR spectrum of the generated gas dissolved in MeCN-d_3.

3. Sol-gel polymerization of 1a in other organic solvents

We investigated the sol-gel polymerization behaviors of **1a** in other organic solvents to further confirm that SB rather than D_C or AN is the key factor of the reaction. *N*,*N*-dimethylformamide (DMF; SB: 0.614, D_C: 35.9, AN: 16.0) and a mixed solvent of 2,2,2-trifluoroethanol (TFE; SB: 0.107, D_C: 26.7, AN: 53.3)/THF (10:1) were newly selected and the sol-gel polymerization were carried out under 0.2 M HCl concentration for this purpose. The use of DMF did not form a solid organosilica film from the sol solution of **1a** even after stirring for 24 h. In contrast, the use of TFE/THF formed a solid organosilica film after stirring for only 1 h.

These experimental results and relationship between the SB and D_C or AN value were plotted, respectively (Fig. S8). As shown in Figs. S8a and S8b, the use of low SB solvents was found to be effective for the reaction regardless of D_C and AN values (MeCN vs DMF or THF, and TFE/THF vs MeCN). In addition, it should be noted that the use of high SB solvents is ineffective for the reaction regardless of D_C and AN values (DMF, MeOH and THF). These results clearly indicate that that SB is the key factor of the reaction rather than D_C or AN.

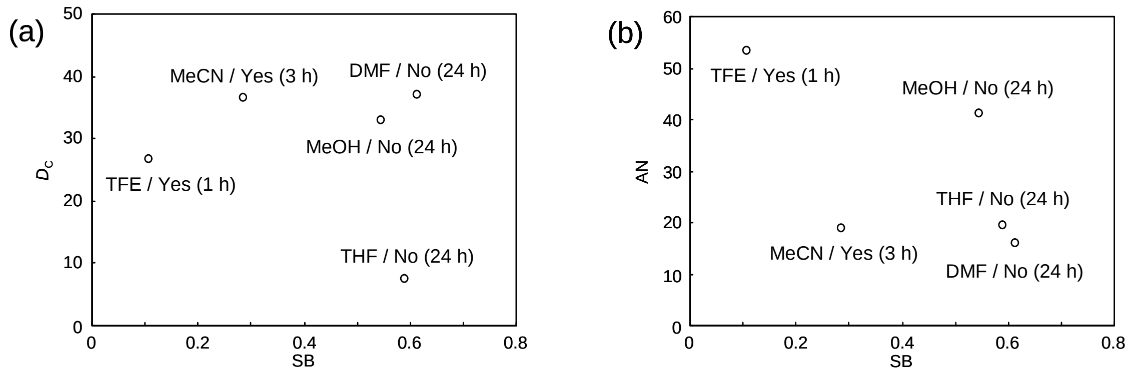


Fig. S8 Plots of (a) D_C and (b) AN vs. SB for DMF, TFE, MeCN, MeOH and THF. “Yes (X h)” and “No (X h)” denotes whether a solid organosilica film was formed or not from the sol solutions of **1a** using the corresponding solvents after stirring for X h.

4. Relationship between initial deallylation rate v_0 of 1a and other solvent parameters

The initial deallylation rate v_0 of **1a** was plotted against Gutmann's donor number (DN: an index of Lewis basicity)[2] and Dimroth-Reichardt's E_T^N value (an index of solvent polarity)[3] (Fig. S9) in addition to Catalán solvent basicity (SB), dielectric constant (D_C) and Gutmann's acceptor number (AN) (Fig. 4 in the main text). Apparent correlation was observed for v_0 vs DN, but not for v_0 vs E_T^N value.

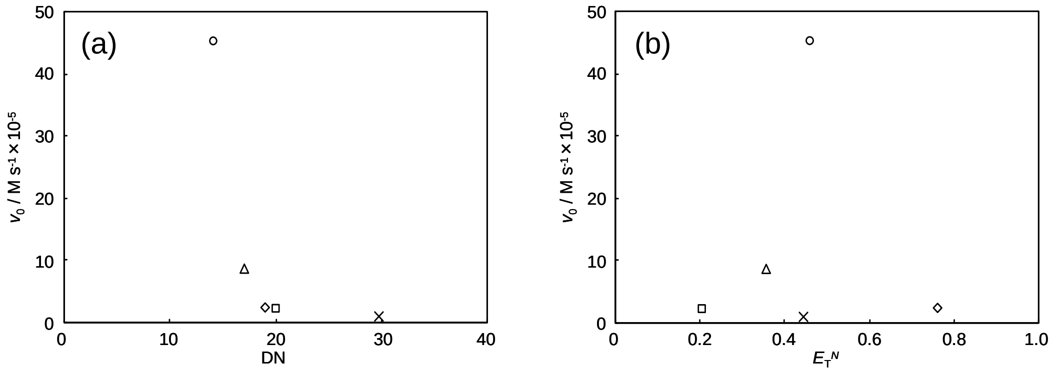


Fig. S9 Relationships between the initial deallylation rate (v_0) of **1a** and (a) Gutmann's donor number (DN) or (b) Dimroth-Reichardt's E_T^N value. Solvents were labelled as follows: MeCN (○); acetone (Δ); MeOH (◇); THF (□); and DMSO (×).

5. References

(1) G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176.

(2) V. Gutmann, *Coord. Chem. Rev.* **1976**, *19*, 225.

(3) C. Reichardt, *Chem. Rev.*, **1994**, *94*, 2319.